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Graphical Abstract

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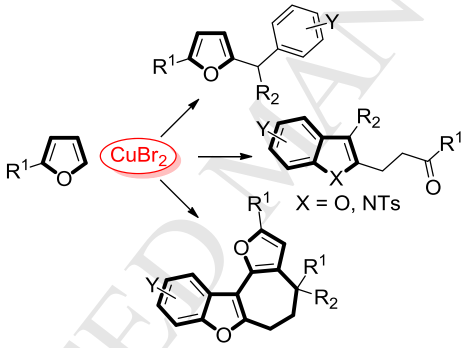

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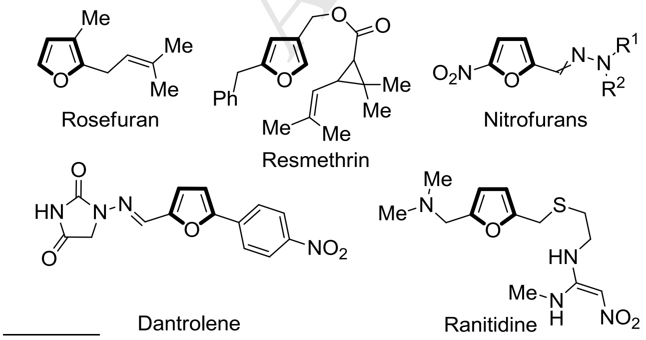
ABSTRACT

A $CuBr_2$-catalyzed alkylation of furans with a broad scope of benzyl alcohols and benzaldehydes is reported. Reaction proceeds efficiently under mild reaction conditions requiring no inert atmosphere or other precautions. Moreover, it is shown that $CuBr_2$ catalyzes domino reactions of furans with benzyl alcohols or benzaldehydes bearing a nucleophilic moiety in the *ortho*-position. These protocols offer a practical approach to densely substituted heterocyclic motifs from easily available furans.

1. Introduction

Furan and its derivatives are fundamental building blocks in organic and medicinal chemistry.[1] A multitude of natural products, synthetic bioactive molecules and approved drugs contain a mono or polysubstituted furan core (Figure 1). For example, rosefuran is the major constituent of the essential oil of *Perilla frutescens* and is used as a pheromone of the acarid mite *Caloglyphus sp.*[2] Resmethrin is a second-generation pyrethroid insecticide with many uses and low mammalian toxicity.[3] Nitrofurans form a wide group of antibacterial and antiprotozoal drugs (Macrobid®, Furoxone®, Lampit®, etc.).[4]

Figure 1. Several examples of useful furans.



Dantrolene (Dantrium®) is a postsynaptic muscle relaxant being used for the treatment and prevention of malignant hyperthermia.[5] Ranitidine (Zantac®) is a medication that decreases stomach acid production and is commonly used for the treatment of peptic ulcer disease.[6]

Today, most furans used in medicine and various areas of industry are available via functionalization of biomass-derived furans and their simple processed products. Amongst the plethora of modern protocols for functionalization of aromatic and heteroaromatic compounds, the prime position is occupied by the Friedel-Crafts reaction.[7] This process is one of the most universal, powerful, effective, and practical methods for the synthesis of complex structures – that being the main goal of organic chemists in industry and academia. Since the first announcement of the Friedel-Crafts reaction 140 years ago,[8] multiple modifications and variations of this reaction have been reported.[9] However, the Friedel-Crafts alkylation of furan derivatives often faces challenges as the use of strong and easily hydrolyzed Lewis acids usually results in significant polymerization providing low yields of desired products. To overcome these disadvantages, a large variety of Brønsted and Lewis acids as well as ion exchange resins and ionic liquids were screened.[10-18] Some of these protocols allow for minimizing side polymerization processes, however they have a number of other limitations such as: incomplete conversion of starting materials

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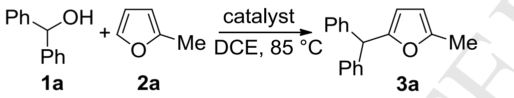
and, as a result, a moderate yield of target products; use of the excess of Brønsted or Lewis acids; need for specific, expensive or environmentally hazardous catalysts; harsh reaction conditions; a limited scope of application. Therefore, the development of an efficient and environment-friendly method for the Friedel-Crafts alkylation of a broad variety of furans based on the use of cheap and easily available catalysts is still very important. Herein, we report an efficient method for the $CuBr_2$-catalyzed alkylation of furans as well as domino reactions including this alkylation as the first key step.

2. Results/Discussion

The reaction of benzhydrol **1a** and 2-methylfuran (**2a**) was selected as a model process for the optimization of reaction conditions. We initially screened some commercially available transition metal sulfates as catalysts (15 mol %) in DCE at 85 °C. Amongst the tested catalysts, copper(II) sulfate pentahydrate was found to be the most efficacious (Table 1, entries 1-6). It provides a full conversion of the starting benzhydrol **1a** affording the desired product **3a** in 86% yield. Trace amounts of benzhydryl ether were also detected in the reaction mixture. Based on the obtained results, we decided to study the catalytic activity of other copper compounds and found that copper(II) acetate and nitrate as well as various Cu(I) sources were inefficient in this reaction (Table 1, entries 7-13). In reactions catalyzed by $CuCl_2$ and $Cu(OTf)_2$, the yields of the desired product **3a** were 58% and 78%, respectively. The formation of benzhydryl ether as a side product was also detected in these processes (Table 1, entries 14,15). The best yield of **3a** was achieved when we used $CuBr_2$ as a catalyst (Table 1, entry 16). In this case, we observed a full conversion of the initial benzhydrol **1a** within 3 hours with the formation of the target benzylfuran **3a** in quantitative yield.

Table 1. Screening of reaction conditions.[a]

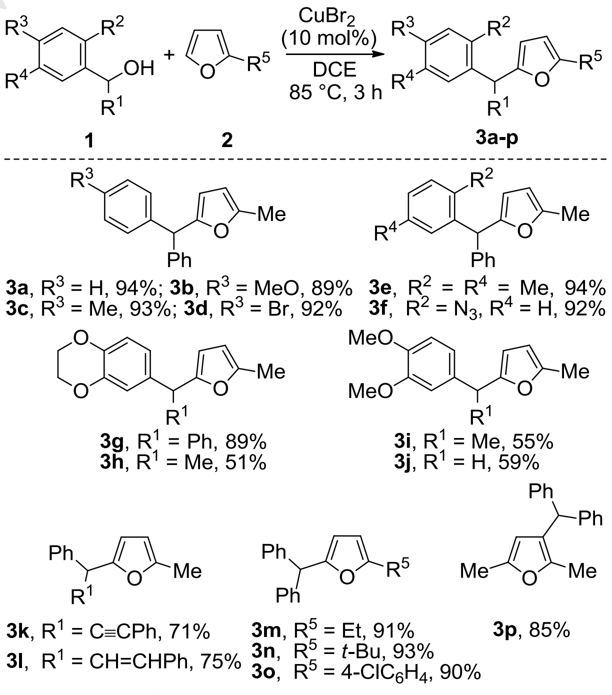


Entry	Catalyst (mol%)	Yield of **3a**, %[b]
1	$CuSO_4 \cdot 5H_2O$ (15)	86[c]
2	$CoSO_4 \cdot 7H_2O$ (15)	53[d]
3	$NiSO_4 \cdot 7H_2O$ (15)	62[d]
4	$FeSO_4 \cdot 7H_2O$ (15)	31[c]
5	$ZnSO_4 \cdot 7H_2O$ (15)	traces[c]
6	$MnSO_4 \cdot 5H_2O$ (15)	traces[c]
7	Cu_2O (15)	N/R
8	CuCl (15)	N/R
9	CuBr (15)	N/R
10	CuI (15)	N/R
11	CuO (15)	N/R
12	$Cu(OAc)_2 \cdot H_2O$ (15)	N/R
13	$Cu(NO)_3 \cdot 3H_2O$ (15)	12[c]
14	$CuCl_2 \cdot 2H_2O$ (15)	58[d]
15	$Cu(OTf)_2$ (15)	78[c]
16	$CuBr_2$ (15)	99
17	**$CuBr_2$ (10)**	**99 (94[e])**
18	$CuBr_2$ (5%)	87[f]
19	$CuBr_2$ (1%)	76[g]
20	HBr (10%)	42

[a] All reactions were performed on a 0.15 mmol scale of benzhydrol **1a** with 2-methylfuran (**2a**) (2.5 eq.). [b] The yield was determined by NMR with an internal standard. [c] Traces of benzhydryl ether was detected. [d] Yield of benzhydryl ether was 5-10%. [e] The reaction was performed at 1.5 mmol scale. Isolated yield. [f] Reaction time was 5 h. [g] Reaction time was 13 h.

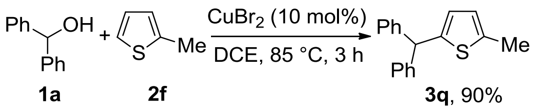
Next, we explored the scope and limitations of the $CuBr_2$-catalyzed alkylation under the optimized reaction conditions. As shown in Scheme 1, a series of benzhydrols **1b-g**, which contain diverse functionalities on the aromatic ring such as halogen, alkyl, alkoxy and azido groups, reacted smoothly with 2-methylfuran (**2a**) affording alkylated furans **3b-g** in excellent yields. Nevertheless, (4-nitrophenyl)(phenyl)methanol was found to be unreactive under these reaction conditions – presumably due to low stability of the 4-nitrobenzhydryl cation that prevents its formation from the corresponding benzhydryl alcohol. The replacement of an aromatic group at the α-position by an alkyl substituent significantly influenced the yield of desired products. Thus, we found that benzyl alcohols **1h-j** bearing strong electron donating groups could be utilized in this process, providing desired benzylfurans **3h-j** in reasonable yields. Conversely, benzyl and α-methylbenzyl alcohols did not yield the target benzylfurans. We believe that these unsuccessful results can also be explained by the inability of these alcohols to produce stabilized benzyl cations. We also studied the reactivity of 1,3-diphenylprop-2-yn-1-ol (**1k**) and (*E*)-1,3-diphenylprop-2-en-1-ol (**1l**) under the same reaction conditions. We found that these substrates produced the target benzylfurans **3k,l** in good yields. Finally, we found that a substituent at the C(2) atom in the starting furan has no a significant impact on the efficiency of alkylation and the corresponding benzylfurans **3m-o** were isolated in excellent yields. It is noteworthy that 2,5-dimethylfuran was successfully involved in the $CuBr_2$-catalyzed alkylation with benzhydrol **1a**. Benzylfuran **3p**, which is the product of the furan ring alkylation at the unsubstituted C(3) atom, was obtained in this reaction in high yield.

Scheme 1. Scope of the $CuBr_2$-catalyzed alkylation of furans **2** with benzyl alcohols **1**.



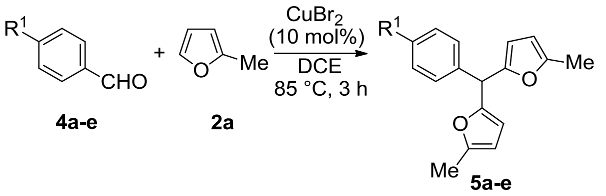
Moreover, under the same reaction conditions, 2-methylthiophene (**2e**) was successfully alkylated affording 2-(diphenylmethyl)-5-methylthiophene (**3q**) in 90% yield (Scheme 2).

Scheme 2. The $CuBr_2$-catalyzed alkylation of 2-methylthiophene (**2f**) with alcohol **1a**.



The next part of our work was the investigation of the reaction between benzaldehydes and 2-alkylfurans. We found that under the reaction conditions, optimized for furan alkylation with benzyl alcohols, various benzaldehydes reacted smoothly with 2-methylfuran (**2a**) to form aryldifurylmethanes **5a-e** in high yields (Table 2). The substituents in the starting benzaldehydes had no significant effect on the yields of the desired products. It should also be noted that in contrast to (4-nitrophenyl)(phenyl)methanol, 4-nitrobenzaldehyde (**4d**) reacted efficiently with 2-methylfuran (**2a**) producing aryldifurylmethane **5d** in high yield. This difference in reactivity can be explained by better stabilization of the intermediate carbocation by the furyl moiety in comparison with the stabilization by phenyl.[20]

Table 2. Scope of the $CuBr_2$-catalyzed alkylation of 2-methylfuran (**2a**) with benzaldehydes **4**.[a]



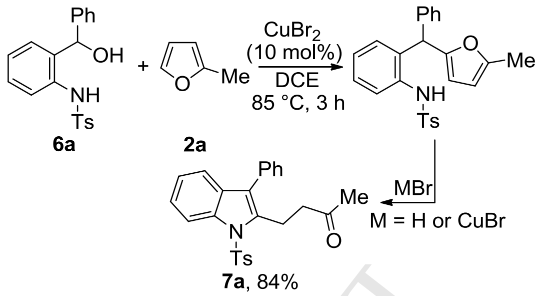
Entry	**4**,**5**	R^1	Yield of **5**, %[b]
1	**a**	H	79
2	**b**	Me	77
3	**c**	MeO	78
4	**d**	NO_2	85
5	**e**	CF_3	75

[a]All reactions were performed on a 1.5 mmol scale of benzaldehydes **4a-e** with 2-methylfuran (**2a**) (3 eq.). [b]Isolated yield.

To date, several Brønsted or Lewis acids (TSA,[11] TFA,[12] $HClO_4$,[13] $BF_3·OEt_2$,[14] $AuCl_3$,[15] I_2,[16] transition-metal triflates,[17] *etc.*[18]) have been utilized for the alkylation of furans with substituted benzyl alcohols or benzaldehydes. However, these methods are not overly general nor environmentally friendly given that specific starting materials must be used and some of these protocols require expensive Lewis acids or superstoichiometric amounts of Brønsted acids. In comparison, copper(II) bromide is widely used in modern organic synthesis,[21] but examples of $CuBr_2$-catalyzed Friedel-Crafts alkylation of aromatic or heteroaromatic compounds with alcohols or benzaldehydes are restricted by scarce examples.[22]

Earlier it was shown that benzylfurans containing various functional groups at the *ortho*-position of the aromatic core could be used as versatile building blocks for the synthesis of a wide range of promising heterocyclic motifs.[11,12,23] We therefore decided to explore the efficiency of copper(II) bromide as a catalyst for the transformation of 2-substituted benzhydrols into densely substituted heterocycles. This research was started with the investigation of the reaction between 2-(tosylamino)benzhydrol (**6a**) and 2-methylfuran (**2a**) under the reaction conditions used above for the reactions of furans with benzaldehydes and benzyl alcohols. This domino reaction proceeded via the key $CuBr_2$-catalyzed alkylation of 2-methylfuran (**2a**), subsequent Brønsted acid protonation (presumably by HBr, which is released after the first alkylation step) or Lewis acid activation ($CuBr_2$) of furan core, intramolecular nucleophilic attack of the *ortho*-amino group on the furanic C(2) atom followed by furan ring opening and indole ring aromatization. The desired indole **7a** was isolated with 84% yield (Scheme 3).

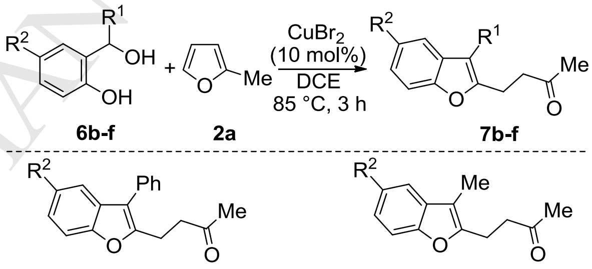
Scheme 3. The $CuBr_2$-catalyzed domino reaction of 2-methylfuran (**2a**) with alcohol **6a**.



7a, 84%

Encouraged by this result, we decided to extend the scope of this domino process by the involvement of a series of salicyl alcohols **6b-f** into the reaction with 2-methylfuran (**2a**). We found that the corresponding benzofurans **7b-f** were formed in high yields (Scheme 4). It is noteworthy that substituents at the phenolic core and at the α-position of the starting salicyl alcohol had no dramatic impact on the reaction efficiency. A slightly decreased yield of benzofuran **7e** is possibly related to the reduced nucleophilicity of the phenolic hydroxy group due to the electron-withdrawing effect of the chlorine substituent at the *para*-position.

Scheme 4. Scope of the $CuBr_2$-catalyzed domino reaction of 2-methylfuran (**2a**) with alcohols **6b-f**.



7b, R^1 = Ph, R^2 = H, 90%
7c, R^1 = Ph, R^2 = Me, 85%
7d, R^1 = Me, R^2 = Me, 87%
7e, R^1 = Me, R^2 = Cl, 75%
7f, R^1 = Me, R^2 = MeO, 86%

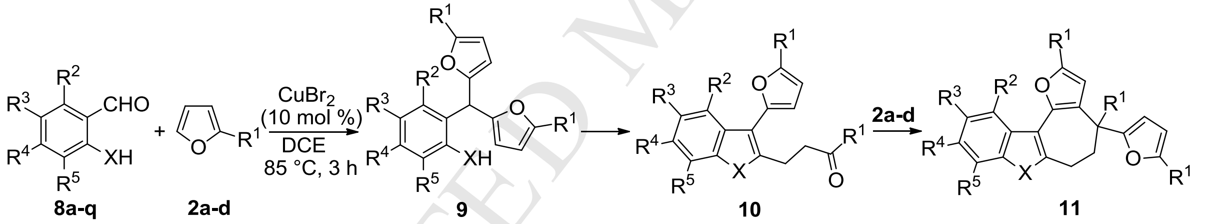
Finally, we studied the reactivity of benzaldehydes containing a nucleophilic moiety (OH, NHTs) at the *ortho*-position towards various furans. We found that the reaction of salicyl aldehyde **8a** with 2-methylfuran (**2a**) under the reaction conditions optimized for the furan alkylation led to a mixture of two products. The major product was substituted benzofuran **10a**, with the minor product being tetracyclic compound **11a** isolated in 11% yield. Butin *et al.* reported similar results in the reaction of **2a** with salicylaldehydes **8** induced by excess of $HClO_4$ in benzene under reflux, however tetracyclic products were isolated in trace amounts only.[24] It should be noted that three 2-methylfuran molecules per one benzaldehyde are required for the formation of this tetracyclic compound. Both the unusual stoichiometry and the complex structure of the products formed encouraged us to study this process in more detail and reoptimize reaction conditions, aiming to obtain compound **11a** in higher yield.

The variation of solvent, temperature, concentration, **2a**-to-**8a** ratio, catalyst loading, and order of reagents added revealed that the optimal reaction conditions were: a solution of substituted benzaldehyde **8** and 2-methylfuran (**2a**) (5 eq.) is heated at 85 °C in DCE containing $CuBr_2$ (10 mol%) for 3 h under an air atmosphere. Using these slightly modified conditions, yields of benzofuran **10a** and tetracyclic compound **11a** were 55% and 31%, respectively (Table 3, entry 1). With the optimal conditions in hand, we explored the scope and limitations of this domino reaction using a broad series of *ortho*-substituted benzaldehydes and a variety of furans.

We found that substitution at the C(5) atom of the furan core had a significant influence on the yields of the desired tetracyclic compounds. Thus, in the reaction of **8a** with 2-ethylfuran (**2b**) the corresponding product **11b** was obtained in only 15% yield. Meanwhile, benzofuran **10b** was isolated in 80% yield (Table 3, entry 2). In the reaction of **8a** with 2-*tert*-butylfuran (**2c**), we observed the exclusive formation of benzofuran **10c** obtained in nearly quantitative yield (Table 3, entry 3). These results are presumably explained by steric hindrance preventing the second alkylation and subsequent cyclization. When 2-(4-chlorophenyl)furan (**2d**) was used, aryldifurylmethane **9d** was the single isolated product (Table 3, entry 4). Possible reasons are the weak activating ability of $CuBr_2$ and/or the reversal of the regiochemistry of the electrophile (proton or Lewis acid) attack on the furan ring: for alkyl-substituted furans, the preferable path is protonation at the C(5) atom of the furan ring in compound **9**; for aryl-substituted furans, the corresponding attack at the C(2) atom produces a cation which is stabilized by the aromatic group and, as a result, not prone to the recyclization discussed.

Next, we studied the reaction of 2-methylfuran (**2a**) with a large series of salicylic aldehydes containing diverse substituents (halogen, alkyl, alkoxy, nitro groups) in the benzene ring. We found that aldehydes **8b-d**,**g**,**k-o** with neutral or electron donating substituent(s) produced mixtures composed of benzofurans **10** and tetracycles **11** (Table 3, entries 5-7, 10, 14-18). Conversely, the reaction of **2a** with aldehyde **8h** bearing a nitro group at the *ortho*-position to the nucleophilic moiety yielded exclusively 2-(2-hydroxybenzyl)furan **9k** (Table 3, entry 11). An intermediate position is occupied by aldehydes **8e**,**f**,**i**,**j** containing combinations of donating and withdrawing groups. In their reactions, 2-(2-hydroxybenzyl)furans **9** and benzofurans **10** were formed (Table 3, entry 8, 9, 12, 13). This led us to conclude that the reaction chemoselectivity is controlled by the electronic properties of the benzene moiety in the intermediate aryldifurylmethane **9**. Electron-donating substituents facilitate their recyclization into the corresponding benzofurans **10**. In comparison, acceptor moieties withdraw electron density from the nucleophilic hydroxyl group, thereby decreasing its ability to attack the activated furan ring. In the case of **9k** this effect is additionally strengthened by intramolecular OH···ON hydrogen bonding, and compound **9k** did not undergo the recyclization to benzofuran **10k**. Benzofuran **10m** was found to be formed together with aryldifurylmethane **9m** in the reaction of 2-methylfuran (**2a**) with 5-chloro-4-methyl-3-nitrosalicylaldehyde (**8j**). Two possible effects of the chlorine substituent could be responsible for this result. Firstly, due to its electron-withdrawing nature, the O–H bond in **9m** is less polarized than that in **9k**. This diminishes the ability of the proton to be involved in hydrogen bond formation. This repulsion increases the torsion angle between the benzene ring and the nitro group which decreases both its acceptor properties and its ability to form an intramolecular hydrogen bond. The importance of intramolecular hydrogen bonding in control of the reaction chemoselectivity is emphasized by the formation of aryldifurylmethane **9h** and benzofuran **10h** in ca. 1:1 ratio from the reaction of 5-nitrosalicylaldehyde (**8e**). Nevertheless, there is no simple self-consistent explanation of all obtained results. In addition to this, uncharacterized side processes would also have an impact on the yields of products formed.

Table 3. Scope of the $CuBr_2$-catalyzed domino reaction of furans **2a-d** with benzaldehydes **8a-q**.[a]



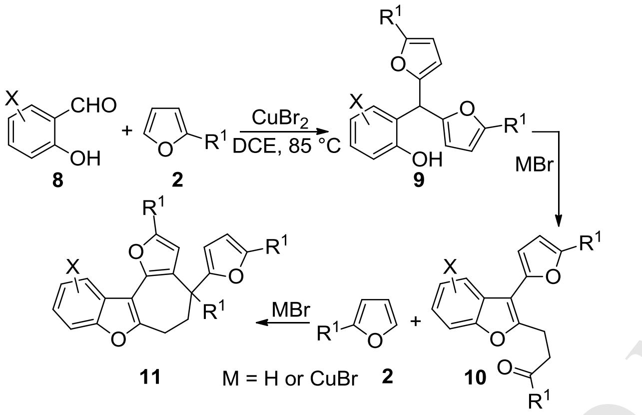
Entry	2	X	R^1	8	R^2	R^3	R^4	R^5	9-11	Yield, %[b] 9	10	11
1	**a**	O	Me	**a**	H	H	H	H	**a**	-	55	31
2	**b**	O	Et	**a**	H	H	H	H	**b**	-	80	15
3	**c**	O	*t*-Bu	**a**	H	H	H	H	**c**	-	95	-
4	**d**	O	4-ClC_6H_4	**a**	H	H	H	H	**d**	73	-	-
5	**a**	O	Me	**b**	OMe	H	H	OMe	**e**	-	34	40
6	**a**	O	Me	**c**	H	Me	H	H	**f**	-	30	52
7	**a**	O	Me	**d**	H	Cl	H	H	**g**	-	50	16
8	**a**	O	Me	**e**	H	NO_2	H	H	**h**	45	50	-
9	**a**	O	Me	**f**	H	Cl	H	OMe	**i**	33	53	-
10	**a**	O	Me	**g**	H	OMe	H	Me	**j**	-	43	40
11[c]	**a**	O	Me	**h**	H	Me	Me	NO_2	**k**	56	-	-
12[c]	**a**	O	Me	**i**	H	NO_2	Me	Me	**l**	-	40	-
13	**a**	O	Me	**j**	H	Cl	Me	NO_2	**m**	47	34	-
14[d]	**a**	O	Me	**k**	H	OMe	Me	OMe	**n**	-	-	43
15	**a**	O	Me	**l**	H	Me	Me	H	**o**	-	55	38
16	**a**	O	Me	**m**	H	H	Me	H	**p**	-	60	35
17	**a**	O	Me	**n**	H	H	Me	Me	**q**	-	31	32
18	**a**	O	Me	**o**	H	H	H	Cl	**r**	-	80	15
19[d]	**a**	NTs	Me	**p**	H	H	H	H	**s**	-	-	41
20[d]	**a**	NTs	Me	**q**	H	OCH_2CH_2O		H	**t**	-	-	40

[a] All reactions was performed on a 1.5 mmol scale of benzaldehyde **8** with 2-substituted furan **2** (5 eq.). [b] Isolated yield. [c] Incomplete conversion of the starting aldehydes was observed. [d] The formation of a complex mixture of products was observed.

We tested 2-tosylaminobenzaldehydes **8p**,**q** and found that the $CuBr_2$-catalyzed domino reaction leads to the formation of tetracyclic indole derivatives **11s**,**t** with moderate yields (Table 3, entries 19, 20).[25] The greater nucleophilicity of the amino group provides full conversion of **9** in these reactions; the moderate product yields are presumably related to the higher reactivity of **9** to various side processes.

The proposed reaction mechanism for the discussed $CuBr_2$-catalyzed reaction is given in Scheme 5. This includes two-fold Friedel-Crafts alkylation of furan **2** with salicylic aldehyde **8** to form (2-hydroxyphenyl)difurylmethane **9**. The subsequent acid-catalyzed (HBr or $CuBr_2$) rearrangement produces benzofuran **10** bearing a ketone moiety. Activated by $CuBr_2$, this ketone reacts with one more molecule of furan **2** affording a tertiary alcohol. Further intramolecular alkylation at the β-atom of the furan located at the C(3) atom of the benzofuran framework accomplishes the formation of tetracyclic compound **11**.

Scheme 5. Plausible mechanism of the $CuBr_2$-catalyzed domino reaction of furans **2** with salicylic aldehydes **8**.



3. Conclusion

In conclusion, we have developed an efficient and convenient $CuBr_2$-catalyzed protocol for the alkylation of furans with a broad scope of benzyl alcohols and benzaldehydes providing polyfuctionalized furans with high-to-excellent yields. Moreover, we applied this method for the realization of domino sequences (furan ring opening–heterocycle ring closure) affording promising densely substituted heterocyclic motifs. The mild reaction conditions, short reaction time, and compatibility with many functional groups make developed protocol a valid and alternative contribution to the known procedures for the alkylation of furans.

4. Experimental

4.1. General Information

NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets) and br (broadened). Mass spectra were obtained with a «Kratos MS-30» instrument using 70 eV electron impact ionization at 200 °C. Elemental analyses were performed with an Elementar Analysensysteme GmbH «Vario Macro CHN/CHNS». GC/MS analysis was performed on an «Agilent 7890B» interfaced to an «Agilent 5977A» mass selective detector. Melting points were determined with a «Stuart SMP 30», the values are uncorrected. Column chromatography was performed on silica gel Macherey Nagel (40-63 μm). Alcohols **1a-i, 1h-l**, **6d-f**, aldehydes **4a-e**, **8a-h**, **8j-o**, **8q**, furans **2a-d** were purchased from chemical suppliers and used as received. Substrates **1f**,[14b] **1g**,[26] **6a**,[19] **6b**,**c**,[27] **8p**[28] were synthesized according to known procedures. All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

4.2 General procedure for alkylation of substituted furans and thiophenes with benzyl alcohols

Copper(II) bromide (33.5 mg, 0.15 mmol) was added to a stirred solution of alcohol **1** (1.5 mmol) and 2-substituted furan **2** (3.75 mmol for 2-methylfuran **2a**; 1.5 mmol for 2-ethylfuran **2b**, 2-*tert*-butylfuran **2c**, 2-(4-chlorophenyl)furan **2d**, 2,5-dimethylfuran **2e** and 2-methylthiophene **2f**) in DCE (4 mL) in a 5 mL Wheaton V-vial, containing a stirring bar and Teflon pressure cap. The microreactor was placed into a preheated (85 °C) aluminum block and the resulting solution stirred for 3 h at this temperature. After completion of the reaction, the mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2) to afford the corresponding products.

*4.2.1. 2-(Diphenylmethyl)-5-methylfuran (**3a**)*[29]
Colorless oil; 350 mg, 94% yield; R_f = 0.55 (CH_2Cl_2/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 4H, H_{Ar}), 7.28–7.26 (m, 2H, H_{Ar}), 7.24–7.21 (m, 4H, H_{Ar}), 5.92 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.80 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.44 (s, 1H, CH), 2.29 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 151.6, 142.2 (2C), 128.9 (4C), 128.5 (4C), 126.7 (2C), 109.2, 106.1, 51.1, 13.8 ppm.

*4.2.2. 2-[(4-Methoxyphenyl)(phenyl)methyl]-5-methylfuran (**3b**)*[29]
Pale yellow solid; 371 mg, 89% yield; mp 80–81 °C (CH_2Cl_2/hexane); R_f = 0.25 (CH_2Cl_2/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 2H, H_{Ar}), 7.29–7.20 (m, 3H, H_{Ar}), 7.16–7.12 (m, 2H, H_{Ar}), 6.90–6.86 (m, 2H, H_{Ar}), 5.92 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.78 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.39 (s, 1H, CH), 3.83 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 155.3, 151.6, 142.6, 134.4, 129.9 (2C), 128.8 (2C), 128.5 (2C), 126.7, 113.9 (2C), 109.0, 106.0, 55.4, 50.3, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 100), 263 (50), 247 (33), 235 (72), 221 (61), 201 (73), 185 (32), 171 (68), 165 (31), 115 (30), 76 (40); Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.04; H, 6.29.

*4.2.3. 2-Methyl-5-[(4-methylphenyl)(phenyl)methyl]furan (**3c**)*
Colorless oil; 365 mg, 93% yield; R_f = 0.59 (CH_2Cl_2/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.41 (s, 1H, CH), 5.80–5.81 (m, 1H, H_{Ar}), 6.83–9.98 (m, 3H, H_{Ar}), 5.92–5.92 (m, 1H, H_{Ar}), 7.11–7.17 (m, 4H, H_{Ar}), 7.22–7.28 (m, 3H, H_{Ar}), 7.31–7.35 (m, 2H, H_{Ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 151.5, 142.5, 139.3, 136.3, 129.2 (2C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 126.7, 109.1, 106.0, 50.7, 21.2, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 100), 247 (49), 219 (54), 186 (23), 171 (55), 105 (25), 76 (32), 65 (36); Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.78; H, 6.87.

*4.2.4. 2-[(4-Bromophenyl)(phenyl)methyl]-5-methylfuran (**3d**)*[29]
White solid; 451 mg, 92% yield; mp 67–68 °C (CH_2Cl_2/hexane); lit 63–64 °C; R_f = 0.55 (CH_2Cl_2/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 2H, H_{Ar}), 7.36–7.26 (m, 3H, H_{Ar}), 7.20–7.17 (m, 2H, H_{Ar}), 7.11–7.07 (m, 2H, H_{Ar}), 5.92 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.79 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.39 (s, 1H, CH), 2.29 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ

= 154.3, 151.9, 141.6, 141.3, 131.6 (2C), 130.7 (2C), 128.8 (2C), 128.6 (2C), 127.0, 120.7, 109.4, 106.1, 50.5, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 328/326 (M^+, 100/100), 251/249 (55/52), 235 (28), 202 (81), 185 (22), 171 (73), 128 (42), 43 (18); Anal. Calcd for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62. Found: C, 66.22; H, 4.71.

4.2.5. 2-[(2,5-Dimethylphenyl)(phenyl)methyl]-5-methylfuran ***(3e)***

White solid; 389 mg, 94% yield; mp 79–80 °C (CH_2Cl_2/hexane); R_f = 0.50 (CH_2Cl_2/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 3H, H_{Ar}), 7.20–7.19 (m, 2H, H_{Ar}), 7.12–7.10 (m, 1H, H_{Ar}), 7.04–7.02 (m, 1H, H_{Ar}), 6.82 (br s, 1H, H_{Ar}), 5.93 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.71 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.59 (s, 1H, CH), 2.32 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.28 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 151.5, 141.7, 140.2, 135.4, 133.3, 130.5, 129.5, 129.1 (2C), 128.4 (2C), 127.5, 126.6, 109.5, 106.1, 47.7, 21.3, 19.3, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 276 (M^+, 100), 261 (37), 233 (82), 219 (35), 199 (44), 171 (42), 127 (27), 43 (20); Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.78; H, 7.49.

4.2.6. 2-[(2-Azidophenyl)(phenyl)methyl]-5-methylfuran ***(3f)***[14b]

Yellow oil; 399 mg, 92% yield; R_f = 0.61 (ethyl acetate/petroleum ether = 1:6); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 4H, H_{Ar}), 7.18–7.16 (m, 3H, H_{Ar}), 7.12–7.10 (m, 2H, H_{Ar}), 5.90 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.75–5.72 (m, 2H, H_{Fur}+CH), 2.27 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 151.7, 141.4, 138.1, 133.6, 130.4, 128.9 (2C), 128.5 (2C), 128.2, 126.8, 124.9, 118.3, 109.5, 106.1, 45.0, 13.7 ppm.

4.2.7. 6-[(5-Methylfuran-2-yl)(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine ***(3g)***

Yellow oil; 408 mg, 89% yield; R_f = 0.35 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 2H, H_{Ar}), 7.28–7.22 (m, 3H, H_{Ar}), 6.85–6.83 (m, 1H, H_{Ar}), 6.75–6.70 (m, 2H, H_{Ar}), 5.92 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.81 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.33 (s, 1H, CH), 4.27 (m, 4H, $O(CH_2)_2O$), 2.30 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 151.6, 143.4, 142.4, 142.3, 135.6, 128.8 (2C), 128.5 (2C), 126.7, 121.9, 117.7, 117.2, 109.1, 106.1, 64.5, 64.4, 50.4, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 306 (M^+, 93), 263 (100), 229 (80), 191 (20), 171 (25), 77 (15), 43 (18); Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.34; H, 5.82.

4.2.8. 6-[1-(5-Methylfuran-2-yl)ethyl]-2,3-dihydro-1,4-benzodioxine ***(3h)***

Colorless oil; 187 mg, 51% yield; R_f = 0.65 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.79 (d, ^3J = 8.0 Hz, 1H, H_{Ar}), 6.74 (d, ^4J = 2.0 Hz, 1H, H_{Ar}), 6.70 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H, H_{Ar}), 5.90 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.85 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 4.23 (s, 4H, $O(CH_2)_2O$), 3.97 (q, ^3J = 7.5 Hz, 1H, CH), 2.24 (s, 3H, CH_3), 1.53 (d, ^3J = 7.5 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 150.9, 143.5, 142.2, 138.2, 120.4, 117.2, 116.2, 105.9, 105.6, 64.6, 64.5, 38.7, 20.9, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 244 (M^+, 42), 229 (100), 201 (14), 115 (9), 107 (12), 91 (8), 76 (14); Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.81; H, 6.57.

4.2.9. 2-[1-(3,4-Dimethoxyphenyl)ethyl]-5-methylfuran ***(3i)***

Yellow oil; 203 mg, 55% yield; R_f = 0.26 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.82–6.76 (m, 3H, H_{Ar}), 5.89 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.86 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 4.02 (q, ^3J = 7.5 Hz, 1H, CH), 3.86 (m, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3), 1.56 (d, ^3J = 7.5 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 150.9, 149.2, 147.9, 137.4, 119.4, 111.6, 111.2, 105.9, 105.6, 56.1, 56.0, 39.0, 20.9, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 246 (M^+, 55), 231 (100), 215 (19), 187 (35), 115 (15), 109 (22), 76 (14); Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.98; H, 7.33.

4.2.10. 2-(3,4-Dimethoxybenzyl)-5-methylfuran ***(3j)***

White solid; 205 mg, 59% yield; mp 39–40 °C (CH_2Cl_2/hexane); R_f = 0.45 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.82–6.77 (m, 3H, H_{Ar}), 5.90 (br s, 2H, H_{Fur}), 3.87–3.85 (m, 8H, 2 OCH_3 +CH_2), 2.25 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 151.0, 149.1, 147.8, 131.2, 120.8, 112.2, 111.4, 106.8, 106.1, 56.0, 55.9, 34.2, 13.6 ppm; MS (EI, 70 eV): *m/z* (%) = 232 (M^+, 100), 217 (22), 201 (38), 188 (26), 175 (55), 158 (37), 128 (18), 91 (23), 43 (40); Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.40; H, 6.92.

4.2.11. 2-(1,3-Diphenylprop-2-yn-1-yl)-5-methylfuran ***(3k)***[30]

Pale yellow oil; 290 mg, 71% yield; R_f = 0.48 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 4H, H_{Ar}), 7.40–7.36 (m, 2H, H_{Ar}), 7.34–7.30 (m, 4H, H_{Ar}), 6.16 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.92 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.24 (s, 1H, CH), 2.28 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 152.0, 139.4, 131.9 (2C), 128.7 (2C), 128.3 (2C), 128.2, 128.0 (2C), 127.4, 123.6, 107.5, 106.4, 88.0, 83.9, 38.1, 13.7 ppm.

4.2.12. 2-[(2E)-1,3-Diphenylprop-2-en-1-yl]-5-methylfuran ***(3l)***[31]

Pale yellow oil; 308 mg, 75% yield; R_f = 0.54 (ethyl acetate/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.24 (m, 10H, H_{Ar}), 6.63 (dd, ^3J = 7.5 Hz, ^3J = 16.0 Hz, 1H, CH), 6.46 (d, ^3J = 16.0 Hz, 1H, CH), 6.02 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.96 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 4.91 (d, ^3J = 7.5 Hz, 1H, CH), 2.32 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 151.5, 141.6, 137.3, 131.5, 130.3, 128.7 (2C), 128.6 (2C), 128.4 (2C), 127.5, 126.9, 126.5 (2C), 107.6, 106.1, 48.6, 13.7 ppm.

4.2.13. 2-(Diphenylmethyl)-5-ethylfuran ***(3m)***

Colorless oil; 358 mg, 91% yield; R_f = 0.61 (CH_2Cl_2/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.33 (m, 4H, H_{Ar}), 7.32–7.29 (m, 2H, H_{Ar}), 7.28–7.24 (m, 4H, H_{Ar}), 5.96 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.84 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.48 (s, 1H, CH), 2.68 (q, ^3J = 7.5 Hz, 2H, CH_2), 1.27 (t, ^3J = 7.5 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 154.8, 142.3 (2C), 128.9 (4C), 128.5 (4C), 126.7 (2C), 109.0, 104.4, 51.1, 21.5, 12.3 ppm; MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 100), 233 (31), 205 (62), 185 (82), 165 (24), 105 (36), 76 (73), 43 (15); Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.09; H, 7.16.

4.2.14. 2-tert-Butyl-5-(diphenylmethyl)furan ***(3n)***

White solid; 405 mg, 93% yield; mp 42–43 °C (CH_2Cl_2/hexane); R_f = 0.55 (CH_2Cl_2/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 4H, H_{Ar}), 7.29–7.24 (m, 2H, H_{Ar}), 7.22–7.20 (m, 4H, H_{Ar}), 5.91 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.78(d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.45 (s, 1H, CH), 1.29 (s, 9H, 3 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 154.4, 142.6 (2C), 128.9 (4C), 128.4 (4C), 126.6 (2C), 108.7, 102.2, 51.1, 32.7, 29.2 (3C) ppm; MS (EI, 70 eV): *m/z* (%) = 290 (M^+, 60), 275 (100), 233 (26), 105 (25), 91 (20), 76 (28), 43 (30); Anal. Calcd for $C_{21}H_{22}O$: C, 86.79; H, 7.79. Found: C, 86.85; H, 7.64.

4.2.15. 2-(4-Chlorophenyl)-5-(diphenylmethyl)furan ***(3o)***

White solid; 464 mg, 90% yield; mp 106–107 °C (CH_2Cl_2/hexane); R_f = 0.60 (CH_2Cl_2/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2H, H_{Ar}), 7.39–7.26 (m, 12H, H_{Ar}), 6.61 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.04 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.56 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 152.4, 141.9 (2C), 132.8, 129.6, 129.0 (4C), 128.9 (2C), 128.6 (4C), 126.9 (2C), 125.0 (2C), 110.8, 106.2, 51.2 ppm; MS (EI, 70 eV): *m/z* (%) = 346/344 (M^+, 34/100), 269/267 (27/80), 205 (75), 165 (44), 139 (33), 111 (41), 77 (30), 43 (15); Anal. Calcd for $C_{23}H_{17}ClO$: C, 80.11; H, 4.97. Found: C, 79.99; H, 5.12.

*4.2.16. 3-(Diphenylmethyl)-2,5-dimethylfuran (**3p**)*[32]

White solid; 334 mg, 85% yield; mp 64–65 °C (CH_2Cl_2/hexane); R_f = 0.55 (CH_2Cl_2/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 4H, H_{Ar}), 7.27–7.20 (m, 6H, H_{Ar}), 5.72 (s, 1H, H_{Fur}), 5.26 (s, 1H, CH), 2.24 (s, 3H, CH_3), 2.15 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 146.0, 144.3 (2C), 129.0 (4C), 128.4 (4C), 126.3 (2C), 122.0, 107.8, 47.6, 13.7, 11.9 ppm.

*4.2.17. 2-(Diphenylmethyl)-5-methylthiophene (**3q**)*[33]

Colorless oil; 356 mg, 90% yield; R_f = 0.64 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 10H, H_{Ar}), 6.63 (d, ^3J = 3.0 Hz, 1H, H_{Th}), 5.53 (d, ^3J = 3.0 Hz, 1H, H_{Th}), 5.66 (s, 1H, CH), 2.48 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 144.0 (2C), 139.2, 129.0 (4C), 128.5 (4C), 126.8 (2C), 126.3, 124.7, 52.4, 15.5 ppm.

*4.3 General procedure for the synthesis of aryldifurylmethanes **5***

Copper(II) bromide (33.5 mg, 0.15 mmol) was added to a stirred solution of aldehyde **4** (1.5 mmol) and 2-methylfuran **2a** (398 µL, 4.5 mmol) in DCE (4 mL) in a 5 mL Wheaton V-vial, containing a stirring bar and Teflon pressure cap. The microreactor was placed into a preheated (85 °C) aluminum block and the resulting solution stirred for 3 h at this temperature. After completion of the reaction the mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2) to afford the corresponding products.

*4.3.1. 2,2'-(Phenylmethanediyl)bis(5-methylfuran) (**5a**)*[34]

Pale yellow oil; 299 mg, 79% yield; R_f = 0.69 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 5H, H_{Ar}), 5.89 (s, 4H, H_{Fur}), 5.35 (s, 1H, CH), 2.26 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0 (2C), 150.5 (2C), 139.3, 127.5 (4C), 126.1, 107.3 (2C), 105.2 (2C), 44.4, 12.7 (2C) ppm.

*4.3.2. 2,2'-[(4-Methylphenyl)methanediyl]bis(5-methylfuran) (**5b**)*[34]

Pale yellow oil; 307 mg, 77% yield; R_f = 0.68 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.16 (m, 4H, H_{Ar}), 5.93 (s, 4H, H_{Fur}), 5.36 (s, 1H, CH), 2.38 (s, 3H, CH_3), 2.30 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2 (2C), 151.4 (2C), 137.2, 136.6, 129.2 (2C), 128.4 (2C), 108.1 (2C), 106.2 (2C), 44.9, 21.2, 13.7 (2C) ppm.

*4.3.3. 2,2'-[(4-Methoxyphenyl)methanediyl]bis(5-methylfuran) (**5c**)*[34]

Pale yellow oil; 330 mg, 78% yield; R_f = 0.68 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.19 (m, 2H, H_{Ar}), 6.89–6.87 (m, 2H, H_{Ar}), 5.91 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.88 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.32 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 2.27 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 153.3 (2C), 151.4 (2C), 132.3, 129.5 (2C), 113.9 (2C), 108.1 (2C), 106.2 (2C), 55.3, 44.5, 13.7 (2C) ppm.

*4.3.4. 2,2'-[(4-Nitrophenyl)methanediyl]bis(5-methylfuran) (**5d**)*[35]

Yellow oil; 379 mg, 85% yield; R_f = 0.65 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.16 (m, 2H, H_{Ar}), 7.44–7.41 (m, 2H, H_{Ar}), 5.96 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.92 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.45 (s, 1H, CH), 2.26 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2 (2C), 151.1 (2C), 147.6, 147.1, 129.4 (2C), 123.8 (2C), 108.9 (2C), 106.4 (2C), 44.9, 13.6 (2C) ppm.

*4.3.5. 2,2'-{[4-(Trifluoromethyl)phenyl]methanediyl}bis(5-methylfuran) (**5e**)*[35]

Yellow oil; 360 mg, 75% yield; R_f = 0.72 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, ^3J = 8.0 Hz, 2H, H_{Ar}), 7.45 (d, ^3J = 8.0 Hz, 2H, H_{Ar}), 6.00 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.97 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.48 (s, 1H, CH), 2.31 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0 (2C), 151.9 (2C), 144.4, 129.5 (q, ^2J = 32.5 Hz), 128.9 (2C), 125.5 (q, ^3J = 4.0 Hz, 2C), 124.5 (q, ^1J = 272.0 Hz), 108.7 (2C), 106.4 (2C), 45.2, 13.6 (2C) ppm.

*4.4 General procedure for the synthesis of compounds **7***

Copper(II) bromide (33.5 mg, 0.15 mmol) was added to a stirred solution of alcohol **6** (1.5 mmol) and 2-methylfuran **2a** (285 µL, 3.75 mmol) in DCE (4 mL) in a 5 mL Wheaton V-vial, containing a stirring bar and Teflon pressure cap. The microreactor was placed into a preheated (85 °C) aluminum block and the resulting solution stirred for 3 h at this temperature. After completion of the reaction, the mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2) to afford the corresponding products.

*4.4.1. 4-{1-[(4-Methylphenyl)sulfonyl]-3-phenyl-1H-indol-2-yl}butan-2-one (**7a**)*[19]

Pale yellow oil; 525 mg, 84% yield; R_f = 0.48 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.29–8.22 (m, 1H, H_{Ar}), 7.69–7.61 (m, 2H, H_{Ar}), 7.49–7.41 (m, 2H, H_{Ar}), 7.41–7.16 (m, 8H, H_{Ar}), 3.25 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.94 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.14 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.4, 145.0, 136.8, 136.4, 135.6, 132.8, 130.7, 130.0 (2C), 129.9 (2C), 128.9 (2C), 127.8, 126.5 (2C), 124.8, 124.6, 124.0, 119.6, 115.3, 44.8, 29.9, 21.7, 21.4 ppm.

*4.4.2. 4-(3-Phenyl-1-benzofuran-2-yl)butan-2-one (**7b**)*

Yellow oil; 356 mg, 90% yield; R_f = 0.64 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.48 (m, 6H, H_{Ar}), 7.43–7.39 (m, 1H, H_{Ar}), 7.33–7.24 (m, 2H, H_{Ar}), 3.20 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.95 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.19 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.9, 154.1, 153.1, 132.4, 129.1 (2C), 128.9 (2C), 128.8, 127.3, 123.9, 122.8, 119.7, 117.4, 110.9, 41.5, 29.9, 21.1 ppm; MS (EI, 70 eV): *m/z* (%) = 264 (M^+, 87), 207 (100), 194 (40), 178 (45), 115 (22), 105 (42), 91 (19); Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.40; H, 6.20.

*4.4.3. 4-(5-Methyl-3-phenyl-1-benzofuran-2-yl)butan-2-one (**7c**)*

Yellow oil; 354 mg, 85% yield; R_f = 0.78 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.49 (m, 4H, H_{Ar}), 7.40–7.32 (m, 3H, H_{Ar}), 7.10–7.08 (m, 1H, H_{Ar}), 3.15 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.91 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.16 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.0, 153.3, 152.6, 132.7, 132.4, 129.3 (2C), 129.1, 129.0 (2C), 127.3, 125.2, 119.6, 117.3, 110.5, 41.6, 29.9, 21.5, 21.3 ppm; MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 68), 235 (20), 221 (100), 207 (65), 178 (67), 165 (15), 115 (14), 76 (14); Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.88; H, 6.54.

*4.4.4. 4-(3,5-Dimethyl-1-benzofuran-2-yl)butan-2-one (**7d**)*

Yellow oil; 282 mg, 87% yield; R_f = 0.65 (ethyl acetate/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (br d, ^3J = 8.0 Hz, 1H, H_{Ar}), 7.22 (br s, 1H, H_{Ar}), 7.03 (br d, ^3J = 8.0 Hz, 1H, H_{Ar}), 3.01 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.86 (t, ^3J =

7.5 Hz, 2H, CH$_2$), 2.46 (s, 3H, CH$_3$), 2.17 (s, 6H, 2 CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.2, 152.6, 152.5, 131.6, 130.5, 124.6, 118.9, 110.1, 110.0, 41.6, 30.0, 21.4, 20.6, 7.9 ppm; MS (EI, 70 eV): m/z (%) = 216 (M$^+$, 59), 201 (15), 173 (38), 159 (100), 146 (24), 129 (23), 115 (40), 43 (20); Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.69; H, 7.56.

*4.4.5. 4-(5-Chloro-3-methyl-1-benzofuran-2-yl)butan-2-one (**7e**)*

Yellow oil; 266 mg, 75% yield; R$_f$ = 0.52 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (d, ^4J = 2.0 Hz, 1H, H$_{Ar}$), 7.25 (d, ^3J = 8.5 Hz, 1H, H$_{Ar}$), 7.15 (dd, ^3J = 8.5 Hz, ^4J= 2.0 Hz, 1H, H$_{Ar}$), 2.99 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.86 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.16 (s, 3H, CH$_3$), 2.14 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 206.8, 154.3, 152.4, 131.9, 127.9, 123.5, 118.7, 111.6, 110.2, 41.3, 30.0, 20.6, 7.8 ppm; MS (EI, 70 eV): m/z (%) = 238/236 (M$^+$, 20/65), 181/179 (35/100), 159 (25), 115 (18), 55 (30); Anal. Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54. Found: C, 65.70; H, 5.76.

*4.4.6. 4-(5-Methoxy-3-methyl-1-benzofuran-2-yl)butan-2-one (**7f**)*

Yellow oil; 299 mg, 86% yield; R$_f$ = 0.48 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.24 (d, ^3J = 9.0 Hz, 1H, H$_{Ar}$), 6.87 (d, ^4J = 2.5 Hz, 1H, H$_{Ar}$), 6.81 (dd, ^3J = 9.0 Hz, ^4J = 2.5 Hz, 1H, H$_{Ar}$), 3.85 (s, 3H, OCH$_3$), 2.98 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.86 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.16 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.3, 155.8, 153.5, 148.9, 131.0, 111.7, 111.0, 110.5, 102.0, 56.1, 41.6, 30.1, 20.7, 8.0 ppm; MS (EI, 70 eV): m/z (%) = 232 (M$^+$, 60), 175 (100), 159 (36), 132 (12), 91 (20), 55 (14), 43 (12); Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.29; H, 6.93.

*4.5. General procedure for the preparation of compounds **9-11***

Copper(II) bromide (33.5 mg, 0.15 mmol) was added to a stirred solution of benzaldehyde **8** (1.5 mmol) and 2-substituted furan **2** (7.5 mmol) in DCE (4 mL) in a 5 mL Wheaton V-vial, containing a stirring bar and Teflon pressure cap. The microreactor was placed into a preheated (85 °C) aluminum block and the resulting solution stirred for 3 h at this temperature. After completion of the reaction, the mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH$_2$Cl$_2$) to afford the corresponding products.

*4.5.1. 4-[3-(5-Methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10a**)*[24b]

Colorless oil; 221 mg, 55% yield; R$_f$ = 0.53 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.83–7.81 (m, 1H, H$_{Ar}$), 7.45–7.43 (m, 1H, H$_{Ar}$), 7.32–7.27 (m, 2H, H$_{Ar}$), 6.51 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 6.14 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 3.36 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.97 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.0, 154.1, 153.2, 151.4, 146.0, 126.9, 124.1, 123.0, 120.6, 111.0, 108.7, 107.8, 107.3, 41.5, 29.9, 22.4, 13.7 ppm.

*4.5.2. 2,4-Dimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2',3':3,4]cyclohepta[1,2-b][1]benzofuran (**11a**)*[24b]

Colorless oil; 154 mg, 31% yield; R$_f$ = 0.85 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.19–8.17 (m, 1H, H$_{Ar}$), 7.43–7.41 (m, 1H, H$_{Ar}$), 7.33–7.28 (m, 2H, H$_{Ar}$), 6.00 (s, 1H, H$_{Fur}$), 5.81 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 5.73 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 3.09 (ddd, ^2J = 18.0 Hz, ^3J = 2.5 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.84 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 2.49 (ddd, ^2J = 13.5 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.43 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 2.13 (ddd, ^2J = 13.5 Hz, ^3J = 2.5 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 1.68 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.4, 154.1, 153.5, 151.0, 149.7, 142.7, 126.6, 125.8, 123.8, 122.9, 121.6, 110.7, 109.2, 108.0, 107.1, 105.8, 38.9, 34.6, 27.4, 25.5, 13.8, 13.7 ppm.

*4.5.3. 1-[3-(5-Ethylfuran-2-yl)-1-benzofuran-2-yl]pentan-3-one (**10b**)*

Colorless oil; 355 mg, 80% yield; R$_f$ = 0.54 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81–7.79 (m, 1H, H$_{Ar}$), 7.43–7.40 (m, 1H, H$_{Ar}$), 7.28–7.25 (m, 2H, H$_{Ar}$), 6.50 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 6.13 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 3.34 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.92 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.75 (q, ^3J = 7.5 Hz, 2H, CH$_2$), 2.48 (q, ^3J = 7.5 Hz, 2H, CH$_2$), 1.32 (t, ^3J = 7.5 Hz, 3H, CH$_3$), 1.10 (t, ^3J = 7.5 Hz, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 209.8, 157.0, 154.2, 153.4, 145.9, 126.9, 124.1, 123.0, 120.6, 110.9, 108.7, 107.5, 105.7, 40.1, 36.1, 22.5, 21.6, 12.3, 8.0 ppm; MS (EI, 70 eV): m/z (%) = 296 (M$^+$, 60), 239 (46), 225 (100), 203 (31), 181 (71), 121 (51), 55 (55), 43 (29); Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.73; H, 6.88.

*4.5.4. 2,4-Diethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2',3':3,4]cyclohepta[1,2-b][1]benzofuran (**11b**)*

Colorless oil; 84 mg, 15% yield; R$_f$ = 0.83 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.15–8.13 (m, 1H, H$_{Ar}$), 7.28–7.36 (m, 1H, H$_{Ar}$), 7.29–7.22 (m, 2H, H$_{Ar}$), 6.00 (s, 1H, H$_{Fur}$), 5.79 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 5.69 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 3.06 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 7.0 Hz, 1H, CH$_2$), 2.76 (q, ^3J = 7.5 Hz, 2H, CH$_2$), 2.62 (q, ^3J = 7.5 Hz, 2H, CH$_2$), 2.36 (ddd, ^2J = 14.0 Hz, ^3J = 3.0 Hz, ^3J = 7.0 Hz, 1H, CH$_2$), 2.29–2.16 (m, 3H, CH$_2$+CH$_2$), 2.06–1.97 (m, 1H, CH$_2$), 1.33 (t, ^3J = 7.5 Hz, 3H, CH$_3$), 1.21 (t, ^3J = 7.5 Hz, 3H, CH$_3$), 0.93 (t, ^3J = 7.5 Hz, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.4, 156.6, 155.3, 154.2, 153.8, 143.5, 126.7, 124.0, 123.8, 122.9, 121.7, 110.7, 109.3, 107.4, 106.7, 104.1, 43.0, 32.6, 30.9, 25.2, 21.7, 21.6, 12.4, 12.3, 8.9 ppm; MS (EI, 70 eV): m/z (%) = 374 (M$^+$, 63), 345 (100), 249 (38), 225 (11), 57 (29), 42 (44); Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 79.87; H, 7.15.

*4.5.5. 1-[3-(5-tert-Butylfuran-2-yl)-1-benzofuran-2-yl]-4,4-dimethylpentan-3-one (**10c**)*

Colorless oil; 502 mg, 95% yield; R$_f$ = 0.64 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.83–7.81 (m, 1H, H$_{Ar}$), 7.45–7.42 (m, 1H, H$_{Ar}$), 7.29–7.27 (m, 2H, H$_{Ar}$), 6.51 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 6.12 (d, ^3J = 3.0 Hz, 1H, H$_{Fur}$), 3.35 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 3.03 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 1.39 (s, 9H, 3 CH$_3$), 1.19 (s, 9H, 3 CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 214.1, 163.4, 154.2, 153.8, 145.8, 126.9, 124.0, 123.0, 120.6, 110.9, 108.7, 107.1, 103.6, 44.3, 34.9, 32.8, 29.3 (3C), 26.6 (3C), 22.8 ppm; MS (EI, 70 eV): m/z (%) = 352 (M$^+$, 100), 337 (26), 296 (14), 253 (13), 237 (58), 181 (10), 57 (30), 43 (34); Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.22; H, 8.09.

*4.5.6. 2-{bis[5-(4-Chlorophenyl)furan-2-yl]methyl}phenol (**9d**)*

Colorless oil; 505 mg, 73% yield; R$_f$ = 0.24 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.54 (d, ^3J = 8.0 Hz, 4H, H$_{Ar}$), 7.32 (d, ^3J = 8.0 Hz, 4H, H$_{Ar}$), 7.23–7.18 (m, 2H, H$_{Ar}$), 6.97–6.93 (m, 1H, H$_{Ar}$), 6.83–6.85 (m, 1H, H$_{Ar}$), 6.59 (d, ^3J = 3.0 Hz, 2H, H$_{Fur}$), 6.20 (d, ^3J = 3.0 Hz, 2H, H$_{Fur}$), 5.93 (br s, 1H, OH), 5.16 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.6 (2C), 153.4, 152.7 (2C), 133.0 (2C), 129.9 (2C), 129.5, 129.0 (4C), 128.9, 125.7, 125.0 (4C), 121.4, 116.4, 110.3 (2C), 106.4 (2C), 39.5 ppm; MS (EI, 70 eV): m/z (%) = 463/462/461/460 (M$^+$, 9/15/72/100), 284/282 (43/68), 247 (22), 139 (48), 45 (47); Anal. Calcd for $C_{27}H_{18}Cl_2O_3$: C, 70.29; H, 3.93. Found: C, 70.50; H, 4.17.

*4.5.7. 4-[4,7-Dimethoxy-3-(5-methylfuran-2-yl)-1-(benzofuran-2-yl)]butan-2-one (**10e**)*

Yellow oil; 167 mg, 34% yield; R_f = 0.55 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.68 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 6.68 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.55 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.06 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.96 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 3.29 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.92 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$), 2.17 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.2, 153.8, 151.4, 148.0, 145.1, 144.5, 140.1, 118.2, 111.2, 108.8, 107.2, 106.4, 104.1, 56.6, 56.2, 42.1, 29.9, 22.4, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 328 (M$^+$, 58), 271 (23), 225 (22), 189 (100), 149 (38), 55 (23), 43 (26); Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.42; H, 6.02.

*4.5.8. 8,11-Dimethoxy-2,4-dimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran (**11e**)*

Yellow oil; 235 mg, 40% yield; R_f = 0.79 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.70 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.66 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 5.97 (s, 1H, $\mathrm{H_{Fur}}$), 5.78 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 5.76 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.96 (s, 3H, OCH$_3$), 3.94 (s, 3H, OCH$_3$), 3.05 (ddd, ^2J = 17.5 Hz, ^3J = 2.5 Hz, ^3J = 8.0 Hz, 1H, CH$_2$), 2.86 (ddd, ^2J = 17.5 Hz, ^3J = 2.5 Hz, ^3J = 10.5 Hz, 1H, CH$_2$), 2.43 (ddd, ^2J = 13.5 Hz, ^3J = 2.5 Hz, ^3J = 8.0 Hz, 1H, CH$_2$), 2.37 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 2.05 (ddd, ^2J = 13.5 Hz, ^3J = 2.5 Hz, ^3J = 10.5 Hz, 1H, CH$_2$), 1.63 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.0, 154.6, 150.8, 149.4, 148.1, 144.6, 140.5, 140.3, 126.5, 118.3, 108.8, 107.1, 106.2, 106.1, 106.0, 105.8, 57.5, 56.5, 39.4, 35.8, 27.8, 25.2, 13.7 (2C) ppm; MS (EI, 70 eV): *m/z* (%) = 392 (M$^+$, 68), 349 (20), 295 (28), 189 (100), 95 (22), 59 (21), 42 (60); Anal. Calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.29; H, 6.35.

*4.5.9. 4-[5-Methyl-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10f**)*[24b]

Colorless oil; 127 mg, 30% yield; R_f = 0.58 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.58 (br s, 1H, $\mathrm{H_{Ar}}$), 7.30 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 7.09 (br d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.49 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 6.13 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.32 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.93 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 2.41 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.0, 153.3, 152.5, 151.3, 146.1, 132.4, 126.9, 125.2, 120.4, 110.4, 108.4, 107.7, 107.2, 41.4, 29.9, 22.4, 21.5, 13.7 ppm.

*4.5.10. 2,4,10-Trimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran (**11f**)*[24b]

Colorless oil; 270 mg, 52% yield; R_f = 0.85 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.95 (br s, 1H, $\mathrm{H_{Ar}}$), 7.28 (d, ^3J = 8.0 Hz, 1H, $\mathrm{H_{Ar}}$), 7.08 (br d, ^3J = 8.0 Hz, 1H, $\mathrm{H_{Ar}}$), 5.99 (s, 1H, $\mathrm{H_{Fur}}$), 5.80 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 5.72 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.06 (ddd, ^2J = 18.0 Hz, ^3J = 2.5 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.82 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 2.53 (s, 3H, CH$_3$), 2.48 (ddd, ^2J = 13.5 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.43 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 2.11 (ddd, ^2J = 13.5 Hz, ^3J = 2.5 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 1.67 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.6, 153.8, 152.6, 151.0, 149.6, 142.9, 132.3, 126.7, 125.6, 124.9, 121.5, 110.2, 109.0, 108.0, 107.1, 105.8, 39.0, 34.8, 27.4, 25.6, 21.6, 13.8, 13.7 ppm.

*4.5.11. 4-[5-Chloro-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10g**)*[36]

Yellow oil; 226 mg, 50% yield; R_f = 0.34 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.76 (d, ^4J = 2.0 Hz, 1H, $\mathrm{H_{Ar}}$), 7.31 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 7.22 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, $\mathrm{H_{Ar}}$), 6.45 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 6.11 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.29 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.93 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.40 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 206.7, 154.6, 152.5, 151.8, 145.2, 128.7, 128.3, 124.3, 120.4, 111.9, 108.5, 108.1, 107.4, 41.2, 29.9, 22.3, 13.7 ppm.

*4.5.12. 10-Chloro-2,4-dimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran (**11g**)*

Yellow oil; 88 mg, 16% yield; R_f = 0.79 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.11 (br s, 1H, $\mathrm{H_{Ar}}$), 7.29 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 7.21 (br d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 5.98 (s, 1H, $\mathrm{H_{Fur}}$), 5.80 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 5.70 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.08–3.01 (m, 1H, CH$_2$), 2.78–2.85 (m, 1H, CH$_2$), 2.44–2.49 (m, 1H, CH$_2$), 2.41 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 2.12–2.06 (m, 1H, CH$_2$), 1.66 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.3, 155.0, 152.6, 151.1, 150.1, 141.9, 128.4, 127.9, 126.2, 123.9, 121.3, 111.6, 108.1, 107.1, 105.8, 38.9, 34.6, 27.4, 25.6, 13.8, 13.7, 13.6 ppm; MS (EI, 70 eV): *m/z* (%) = 368/366 (M$^+$, 30/86), 353/351 (9/26), 271/269 (100/29), 189 (67), 42 (83); Anal. Calcd for $C_{22}H_{19}ClO_3$: C, 72.03; H, 5.22. Found: C, 72.18; H, 5.44.

*4.5.13. 2-[bis(5-Methylfuran-2-yl)methyl]-4-nitrophenol (**9h**)*[24b]

Colorless oil; 211 mg, 45% yield; R_f = 0.33 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.05 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz, 1H, $\mathrm{H_{Ar}}$), 8.02 (d, ^4J = 2.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.89 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 5.98 (d, ^3J = 3.0 Hz, 2H, $\mathrm{H_{Fur}}$), 5.91 (d, ^3J = 3.0 Hz, 2H, $\mathrm{H_{Fur}}$), 5.68 (s, 1H, CH), 5.29 (br s, 1H, OH), 2.25 (s, 6H, 2 CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.8, 152.3 (2C), 150.5 (2C), 141.6, 127.4, 126.3, 124.7, 116.5, 109.1 (2C), 106.5 (2C), 39.4, 13.6 (2C) ppm.

*4.5.14. 4-[3-(5-Methylfuran-2-yl)-5-nitro-1-benzofuran-2-yl]butan-2-one (**10h**)*[24b]

Colorless oil; 235 mg, 50% yield; R_f = 0.52 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.60 (br s, 1H, $\mathrm{H_{Ar}}$), 8.11 (br d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 7.40 (d, ^3J = 8.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.50 (br s, 1H, $\mathrm{H_{Fur}}$), 6.12 (br s, 1H, $\mathrm{H_{Fur}}$), 3.28 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.94 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.39 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 206.2, 156.7, 156.1, 152.2, 144.3, 144.1, 127.2, 119.8, 117.1, 111.1, 109.4, 108.8, 107.5, 40.6, 29.7, 22.1, 13.6 ppm.

*4.5.15. 2-[bis(5-Methylfuran-2-yl)methyl]-4-chloro-6-methoxyphenol (**9i**)*

Colorless oil; 164 mg, 33% yield; R_f = 0.20 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.78 (d, ^4J = 2.0 Hz, 1H, $\mathrm{H_{Ar}}$), 6.76 (d, ^4J = 2.0 Hz, 1H, $\mathrm{H_{Ar}}$), 5.91 (d, ^3J = 3.0 Hz, 2H, $\mathrm{H_{Fur}}$), 5.88 (d, ^3J = 3.0 Hz, 2H, $\mathrm{H_{Fur}}$), 5.78 (br s, 1H, OH), 5.71 (s, 1H, CH), 3.86 (s, 3H, OCH$_3$), 2.26 (s, 6H, 2 CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 151.9 (2C), 151.6 (2C), 147.0, 142.0, 127.1, 124.4, 121.4, 110.3, 108.4 (2C), 106.2 (2C), 56.4, 37.8, 13.7 (2C) ppm; MS (EI, 70 eV): *m/z* (%) = 334/332 (M$^+$, 17/44), 250 (100), 235 (63), 221 (28), 175 (45), 115 (18), 43 (33); Anal. Calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 65.17; H, 5.09.

*4.5.16. 4-[5-Chloro-7-methoxy-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10i**)*

Yellow oil; 264 mg, 53% yield; R_f = 0.51 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (d, ^4J = 1.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.77 (d, ^4J = 1.5 Hz, 1H, $\mathrm{H_{Ar}}$), 6.44 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 6.10 (d, ^3J = 3.0 Hz, 1H, $\mathrm{H_{Fur}}$), 3.98 (s, 3H, OCH$_3$), 3.29 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.94 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.38 (s, 3H, CH$_3$), 2.18 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 206.7, 154.4, 151.8, 145.2, 145.1, 142.0, 129.1, 128.9, 112.8, 108.9, 108.2, 107.6, 107.4, 56.4, 41.3, 29.9, 22.3, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 334/332 (M^+, 30/86), 289 (15), 277/275 (40/100), 247 (12), 169 (9), 55 (16), 42 (44); Anal. Calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 65.12; H, 5.35.

4.5.17. 4-[5-Methoxy-7-methyl-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10j**)

Yellow oil; 201 mg, 43% yield; R_f = 0.32 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (br s, 1H, H_{Ar}), 6.70 (br s, 1H, H_{Ar}), 6.43 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.11 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.85 (s, 3H, OCH_3), 3.31 (t, ^3J = 8.0 Hz, 2H, CH_2), 2.93 (t, ^3J = 8.0 Hz, 2H, CH_2), 2.47 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 156.3, 153.8, 151.3, 148.3, 146.2, 126.8, 121.8, 113.4, 109.0, 107.5, 107.2, 101.2, 56.1, 41.5, 29.9, 22.6, 15.2, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 312 (M^+, 57), 269 (13), 255 (100), 189 (10), 115 (15), 55 (13), 42 (28); Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.89; H, 6.52.

4.5.18. 10-Methoxy-2,4,8-trimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2',3':3,4]cyclohepta[1,2-b][1]benzofuran (**11j**)

Yellow oil; 225 mg, 40% yield; R_f = 0.63 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (br s, 1H, H_{Ar}), 6.69 (br s, 1H, H_{Ar}), 5.97 (s, 1H, H_{Fur}), 5.79 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.71 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.90 (s, 3H, OCH_3), 3.08–3.02 (m, 1H, CH_2), 2.85–2.78 (m, 1H, CH_2), 2.46 (s, 3H, CH_3), 2.47–2.43 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.13–2.06 (m, 1H, CH_2), 1.65 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 156.2, 154.2, 151.0, 149.5, 148.3, 142.9, 126.5, 125.5, 121.4, 113.0, 109.6, 108.0, 107.1, 105.8, 102.5, 56.2, 39.0, 34.8, 27.4, 25.7, 15.2, 13.8, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 376 (M^+, 100), 361 (36), 333 (18), 294 (19), 279 (75), 95 (15), 42 (46); Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.31; H, 6.33.

4.5.19. 6-[bis(5-Methylfuran-2-yl)methyl]-3,4-dimethyl-2-nitrophenol (**9k**)

Yellow oil; 286 mg, 56% yield; R_f = 0.50 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (br s, 1H, OH), 7.15 (s, 1H, H_{Ar}), 5.93 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.89 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.82 (s, 1H, CH), 2.38 (s, 3H, CH_3), 2.25 (s, 6H, 2 CH_3), 2.24 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 156.3, 153.8, 151.3, 148.3, 146.2, 126.8, 121.8, 113.4, 109.0, 107.5, 107.2, 101.2, 56.1, 41.5, 29.9, 22.6, 15.2, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 341 (M^+, 100), 324 (63), 281 (42), 251 (46), 244 (90), 175 (48), 165 (43), 97 (35), 43 (38); Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.52; H, 5.44; N, 4.04.

4.5.20. 4-[6,7-Dimethyl-3-(5-methylfuran-2-yl)-5-nitro-1-benzofuran-2-yl]butan-2-one (**10l**)

Yellow oil; 205 mg, 40% yield; R_f = 0.45 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H, H_{Ar}), 6.46 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.11 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.30 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.94 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.45 (s, 6H, 2 CH_3), 2.38 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.5, 154.7, 154.5, 152.0, 147.6, 144.7, 127.1, 123.8, 121.6, 114.7, 109.3, 108.4, 107.4, 41.0, 29.8, 22.3, 15.3, 13.7, 12.3 ppm; MS (EI, 70 eV): *m/z* (%) = 341 (M^+, 96), 284 (100), 238 (90), 189 (34), 165 (52), 152 (30), 42 (66); Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.67; H, 5.82; N, 4.27.

4.5.21. 6-[bis(5-Methylfuran-2-yl)methyl]-4-chloro-3-methyl-2-nitrophenol (**9m**)

Yellow oil; 255 mg, 47% yield; R_f = 0.38 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (br s, 1H, OH), 7.38 (s, 1H, H_{Ar}), 5.97 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.91 (d, ^3J = 3.0 Hz, 2H, H_{Fur}), 5.82 (s, 1H, CH), 2.56 (s, 3H, CH_3), 2.26 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2 (2C), 150.6 (2C), 149.9, 137.9, 135.3, 131.8, 129.3, 127.0, 109.0 (2C), 106.4 (2C), 37.9, 17.9, 13.7 (2C) ppm; MS (EI, 70 eV): *m/z* (%) = 363/361 (M^+, 34/100), 345/343 (19/60), 281/279 (31/90), 264 (70), 175 (51), 165 (28), 81 (50); Anal. Calcd for $C_{18}H_{16}ClNO_5$: C, 59.76; H, 4.46; N, 3.87. Found: C, 59.97; H, 4.76; N, 3.60.

4.5.22. 4-[5-Chloro-6-methyl-3-(5-methylfuran-2-yl)-7-nitro-1-benzofuran-2-yl]butan-2-one (**10m**)

Yellow oil; 184 mg, 34% yield; R_f = 0.41 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H, H_{Ar}), 6.48 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.13 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.29 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.94 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.54 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3, 155.6, 152.4, 144.1, 144.0, 136.1, 130.1, 128.0, 125.5, 124.1, 109.0, 108.7, 107.6, 40.6, 30.0, 22.1, 16.1, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 363/361 (M^+, 32/94), 302 (100), 271 (50), 229 (26), 189 (22), 58 (36), 42 (46); Anal. Calcd for $C_{18}H_{16}ClNO_5$: C, 59.76; H, 4.46; N, 3.87. Found: C, 59.58; H, 4.66; N, 3.67.

4.5.23. 10-Chloro-2,4,9-trimethyl-4-(5-methylfuran-2-yl)-8-nitro-5,6-dihydro-4H-furo[2',3':3,4]cyclohepta[1,2-b][1]benzofuran (**11n**)

Yellow oil; 262 mg, 43% yield; R_f = 0.69 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H, H_{Ar}), 5.97 (s, 1H, H_{Fur}), 5.79 (br s, 1H, H_{Fur}), 5.71 (br s, 1H, H_{Fur}), 4.10 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.09–3.02 (m, 1H, CH_2), 2.85–2.78 (m, 1H, CH_2), 2.48–2.43 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.12–2.06 (m, 1H, CH_2), 1.65 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 155.1, 153.2, 151.0, 149.5, 142.8, 140.8, 125.6, 125.5, 114.7, 109.6, 108.1, 107.1, 105.8, 97.2, 60.5, 56.4, 39.0, 34.8, 29.8, 27.4, 25.6, 13.8, 13.7, 9.1 ppm; MS (EI, 70 eV): *m/z* (%) = 406 (M^+, 100), 325 (17), 310 (26), 189 (17), 109 (11), 95 (15), 42 (25); Anal. Calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 73.63; H, 6.65.

4.5.24. 4-[5,6-Dimethyl-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one (**10o**)

Yellow oil; 244 mg, 55% yield; R_f = 0.40 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H, H_{Ar}), 7.20 (s, 1H, H_{Ar}), 6.47 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.11 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.30 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.91 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.37 (s, 6H, 2 CH_3), 2.19 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 153.1, 152.4, 151.2, 146.3, 133.1, 131.5, 124.7, 120.7, 111.5, 108.2, 107.5, 107.2, 41.6, 29.9, 22.4, 20.5, 20.1, 13.8 ppm; MS (EI, 70 eV): *m/z* (%) = 296 (M^+, 47), 239 (100), 188 (9), 175 (18), 55 (8), 42 (22); Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.81; H, 6.92.

4.5.25. 2,4,9,10-Tetramethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2',3':3,4]cyclohepta[1,2-b][1]benzofuran (**11o**)

Yellow oil; 205 mg, 38% yield; R_f = 0.71 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H, H_{Ar}), 7.17 (s, 1H, H_{Ar}), 5.97 (s, 1H, H_{Fur}), 5.79 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.71 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.07–3.00 (m, 1H, CH_2), 2.84–2.76 (m, 1H, CH_2), 2.48–2.44 (m, 1H, CH_2), 2.42 (s, 6H, 2 CH_3), 2.38 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.13–2.07 (m, 1H, CH_2), 1.65 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 153.1, 152.9, 151.0, 149.5, 143.0, 132.6, 131.3, 125.5, 124.5, 121.7, 111.2, 108.9, 108.0, 107.0, 105.8, 39.0, 34.8, 27.3, 25.5, 20.5, 20.1, 13.9, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 360 (M^+, 100), 278 (37), 263 (82), 189 (56), 175

(19), 95 (43), 42 (27); Anal. Calcd for C$_{24}$H$_{24}$O$_3$: C, 79.97; H, 6.71. Found: C, 79.91; H, 6.77.

4.5.26. 4-[6-Methyl-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one ***(10p)***

Colorless oil; 254 mg, 60% yield; R_f = 0.47 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.66 (d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 7.23 (br s, 1H, H$_{\mathrm{Ar}}$), 7.09 (br d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 6.47 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 6.12 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.32 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.93 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.1, 154.5, 152.5, 151.3, 146.2, 134.3, 124.3, 120.1, 111.2, 108.4, 107.6, 107.2, 106.3, 41.5, 29.9, 22.4, 21.7, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 282 (M$^+$, 41), 239 (13), 225 (100), 175 (20), 135 (38), 108 (14), 78 (13), 57 (36), 43 (22); Anal. Calcd for C$_{18}$H$_{18}$O$_3$: C, 76.57; H, 6.43. Found: C, 76.58; H, 6.55.

4.5.27. 2,4,9-Trimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran ***(11p)***

Yellow oil; 182 mg, 35% yield; R_f = 0.81 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02 (d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 7.21 (br s, 1H, H$_{\mathrm{Ar}}$), 7.12 (br d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 5.98 (s, 1H, H$_{\mathrm{Fur}}$), 5.81 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 5.73 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.06 (ddd, ^2J = 18.0 Hz, ^3J = 2.5 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.83 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 10.5 Hz, 1H, CH$_2$), 2.49 (s, 3H, CH$_3$), 2.46 (ddd, ^2J = 13.5 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.41 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 2.11 (ddd, ^2J = 13.5 Hz, ^3J = 2.5 Hz, ^3J = 10.5 Hz, 1H, CH$_2$), 1.66 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.6, 154.6, 153.0, 151.0, 149.6, 142.9, 133.9, 125.7, 124.2, 124.1, 121.1, 111.0, 109.1, 108.0, 107.0, 105.8, 39.0, 34.8, 27.3, 25.5, 21.7, 13.8, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 346 (M$^+$, 100), 331 (17), 303 (17), 263 (22), 249 (88), 95 (10), 42 (51); Anal. Calcd for C$_{23}$H$_{22}$O$_3$: C, 79.74; H, 6.40. Found: C, 79.51; H, 6.31.

4.5.28. 4-[6,7-Dimethyl-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one ***(10q)***

Yellow oil; 138 mg, 31% yield; R_f = 0.48 (ethyl acetate/petroleum ether = 1:5); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.49 (d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 7.07 (d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 6.46 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 6.11 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.34 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.94 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$), 2.39 (s, 6H, 2 CH$_3$), 2.22 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.3, 153.6, 152.3, 151.2, 146.4, 132.5, 124.2, 119.5, 117.1, 108.8, 107.5, 107.2, 106.1, 41.7, 29.9, 22.5, 19.2, 13.7, 11.7 ppm; MS (EI, 70 eV): *m/z* (%) = 296 (M$^+$, 68), 253 (9), 239 (100), 211 (7), 58 (9), 42 (26); Anal. Calcd for C$_{19}$H$_{20}$O$_3$: C, 77.00; H, 6.80. Found: C, 77.11; H, 6.72.

4.5.29. 2,4,8,9-Tetramethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran ***(11q)***

Yellow oil; 173 mg, 32% yield; R_f = 0.83 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86 (d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 7.10 (d, ^3J = 8.0 Hz, 1H, H$_{\mathrm{Ar}}$), 5.97 (s, 1H, H$_{\mathrm{Fur}}$), 5.80 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 5.72 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.08 (ddd, ^2J = 18.0 Hz, ^3J = 2.5 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.84 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 2.47 (ddd, ^2J = 14.0 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.42 (s, 3H, CH$_3$), 2.41 (s, 6H, 2 CH$_3$), 2.28 (s, 3H, CH$_3$), 2.11 (ddd, ^2J = 14.0 Hz, ^3J = 2.5 Hz, ^3J = 11.0 Hz, 1H, CH$_2$), 1.66 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.6, 153.6, 152.8, 151.0, 149.5, 143.1, 132.1, 125.5, 124.9, 124.0, 119.2, 118.2, 109.5, 107.9, 107.0, 105.8, 38.9, 34.9, 27.3, 25.6, 19.2, 13.8, 13.7, 11.6 ppm; MS (EI, 70 eV): *m/z* (%) = 360 (M$^+$, 100), 345 (10), 287 (14), 277 (18), 263 (94), 95 (11), 42 (43); Anal. Calcd for C$_{24}$H$_{24}$O$_3$: C, 79.97; H, 6.71. Found: C, 79.75; H, 6.70.

4.5.30. 4-[7-Chloro-3-(5-methylfuran-2-yl)-1-benzofuran-2-yl]butan-2-one ***(10r)***

Colorless oil; 362 mg, 80% yield; R_f = 0.55 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.68 (d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 7.26 (d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 7.17 (t, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 6.47(d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 6.11 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.34 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.96 (t, ^3J = 7.5 Hz, 2H, CH$_2$), 2.39 (s, 3H, CH$_3$), 2.22 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 206.7, 154.0, 151.7, 149.8, 145.2, 128.5, 124.3, 123.9, 119.2, 116.5, 109.3, 108.2, 107.3, 41.1, 29.9, 22.3, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 304/302 (M$^+$, 30/95), 247/245 (30/100), 197 (25), 152 (25), 115 (17), 42 (74); Anal. Calcd for C$_{17}$H$_{15}$ClO$_3$: C, 67.44; H, 4.99. Found: C, 67.21; H, 5.09.

4.5.31. 8-Chloro-2,4-dimethyl-4-(5-methylfuran-2-yl)-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b][1]benzofuran ***(11r)***

Colorless oil; 82 mg, 15% yield; R_f = 0.82 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.04 (d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 7.25 (d, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 7.20 (t, ^3J = 7.5 Hz, 1H, H$_{\mathrm{Ar}}$), 5.97 (s, 1H, H$_{\mathrm{Fur}}$), 5.78 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 5.69 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.12 (ddd, ^2J = 18.0 Hz, ^3J = 2.5 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.86 (ddd, ^2J = 18.0 Hz, ^3J = 3.0 Hz, ^3J = 10.5 Hz, 1H, CH$_2$), 2.47 (ddd, ^2J = 14.0 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 2.39 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 2.10 (ddd, ^2J = 14.0 Hz, ^3J = 3.0 Hz, ^3J = 7.5 Hz, 1H, CH$_2$), 1.65 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.3, 154.4, 151.2, 150.1, 141.9, 128.2, 126.6, 124.0, 123.8, 120.3, 116.2, 110.1, 108.1, 107.1, 105.8, 39.0, 34.6, 29.8, 27.4, 25.5, 13.8, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 368/366 (M$^+$, 32/100), 351 (20), 284 (18), 269 (46), 95 (18), 57 (17), 42 (57); Anal. Calcd for C$_{22}$H$_{19}$ClO$_3$: C, 72.61; H, 5.22. Found: C, 72.81; H, 5.17.

4.5.32. 7-[(4-Methylphenyl)sulfonyl]-2,4-dimethyl-5,6-dihydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b]indole ***(11s)***

White solid; 298 mg, 41% yield; mp 158–159 °C (benzene/methanol); R_f = 0.83 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.32–8.25 (m, 2H, H$_{\mathrm{Ar}}$), 7.53 (d, ^3J = 8.0 Hz, 2H, H$_{\mathrm{Ar}}$), 7.33–7.31 (m, 2H, H$_{\mathrm{Ar}}$), 7.12 (d, ^3J = 8.0 Hz, 2H, H$_{\mathrm{Ar}}$), 6.02 (s, 1H, H$_{\mathrm{Fur}}$), 5.80 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 5.68 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 3.64–3.58 (m, 1H, CH$_2$), 3.00–2.93 (m, 1H, CH$_2$), 2.47–2.41 (m, 1H, CH$_2$), 2.39 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 2.02–1.96 (m, 1H, CH$_2$), 1.63 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.5, 151.0, 150.0, 144.6, 143.4, 137.0, 136.0, 135.9, 129.8 (2C), 128.0, 127.7, 126.4 (2C), 124.5, 124.1, 121.9, 115.2, 114.4, 108.3, 107.1, 105.7, 39.0, 36.5, 27.6, 24.7, 21.5, 13.8, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 485 (M$^+$, 49), 330 (100), 316 (26), 249 (27), 234 (15), 91 (31), 42 (68); Anal. Calcd for C$_{29}$H$_{27}$NO$_4$S: C, 71.73; H, 5.60; N, 2.88; S, 6.60. Found: C, 71.70; H, 5.70; N, 3.00; S, 6.81.

4.5.33. 9,10-Ethylenedioxy-7-[(4-methylphenyl)sulfonyl]-2,4-dimethyl-5,6,9,10-tetrahydro-4H-furo[2’,3’:3,4]cyclohepta[1,2-b]indole ***(11t)***

Colorless oil; 326 mg, 40% yield; R_f = 0.75 (ethyl acetate/petroleum ether = 1:3); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (s, 1H, H$_{\mathrm{Ar}}$), 7.73 (s, 1H, H$_{\mathrm{Ar}}$), 7.49 (d, ^3J = 8.0 Hz, 2H, H$_{\mathrm{Ar}}$), 7.12 (d, ^3J = 8.0 Hz, 2H, H$_{\mathrm{Ar}}$), 5.97 (s, 1H, H$_{\mathrm{Fur}}$), 5.78 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 5.63 (d, ^3J = 3.0 Hz, 1H, H$_{\mathrm{Fur}}$), 4.29 (s, 4H, 2 OCH$_2$), 3.55–3.49 (m, 1H, CH$_2$), ppm. 2.92–2.85 (m, 1H, CH$_2$), 2.42–2.36 (m, 1H, CH$_2$), 2.34 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 1.97–1.91 (m, 1H, CH$_2$), 1.59 (s, 3H, CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.5, 151.0, 149.9, 144.5, 143.4, 141.9, 141.5, 135.9, 135.2, 131.9, 129.7 (2C), 127.5, 126.4 (2C), 122.2, 114.2, 109.0, 108.2, 107.0, 105.7, 104.1, 64.6, 64.5, 39.0, 36.5, 27.5, 25.0, 21.6, 13.8, 13.7 ppm; MS (EI, 70 eV): *m/z* (%) = 543 (M^+, 42), 388 (100), 373 (42), 306 (15), 107 (10), 92 (20), 42 (32); Anal. Calcd for $C_{31}H_{29}NO_6S$: C, 68.49; H, 5.38; N, 2.58; S, 5.90. Found: C, 68.79; H, 5.52; N, 2.67; S, 6.01.

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