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Helicenes

Diversified Synthesis of Furans by Coupling between Enols/1,3-Dicarbonyl Compounds and Nitroolefins: Direct Access to Dioxa[5]helicenes

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Abstract: A versatile method for the diversified synthesis of furans and arenofurans has been developed that proceeds through K_2CO_3-promoted cyclization between enols/1,3-dicarbonyl compounds and nitroolefins at reflux in EtOH. This facile method has been successfully employed in the synthesis of benzotrifuran derivatives, which are useful hole-transporting materials. This procedure also provides direct access to dioxa[5]helicenes. This reaction offers a broad substrate scope, uses an inexpensive base and environmentally benign solvent, and is operationally simple.

Introduction

Polysubstituted furan derivatives are an important class of heterocycles and are widely found in nature.[1] These compounds serve as useful building blocks for various biologically active molecules, functional materials, and agrochemicals, as well as useful intermediates in organic synthesis.[2]

The substituted furan ring is also a key scaffold in various pharmaceutical drugs (Figure 1).[3]

Owing to their broad range of activities, several methods have been developed for the synthesis of furan derivatives. The important classical approaches are the Paal–Knorr[4a,b] and Feist–Benary syntheses,[4c,d] which have been established for the assembly of polysubstituted furans from dicarbonyl compounds. Prefunctionalized acyclic ketone derivatives, such as α-aryloxyketones,[5a] *o*-alkoxyketones,[5b,c] cyclopropenyl ketones,[5d] allenyl ketones,[5e] and β-acyloxy acetylenic ketones,[5f] have also been employed as key starting materials for the construction of this scaffold. However, these functionalized precursors are generally synthesized through specialized procedures that involve multi-step procedures. Transition-metal-catalyzed synthetic strategies that involve inter-/intramolecular coupling reactions have also been very effective for the synthesis of furan derivatives.[6] Arenofurans are another important class of heterocycles and many strategies have been developed for their synthesis. Most of the reported methods have involved transition metals as the catalyst and phenol or its derivatives as the starting material.[7] However, practical and general methods for the synthesis of these derivatives remain limited. Therefore, the development of new strategies for the synthesis of furan derivatives that use basic chemicals as starting materials and offer higher efficiencies and substrate scope, operational simplicity, and economic practicability is highly desirable.

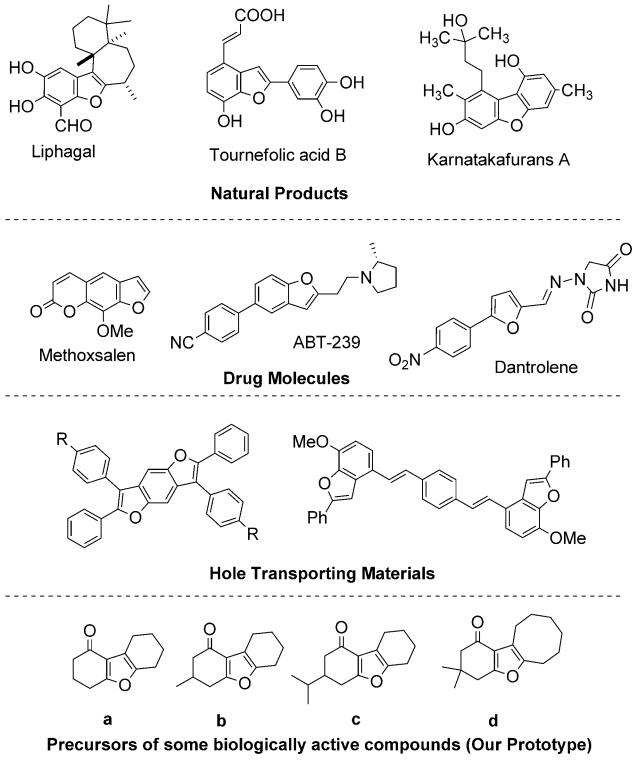

Figure 1. Important furan-containing molecules.

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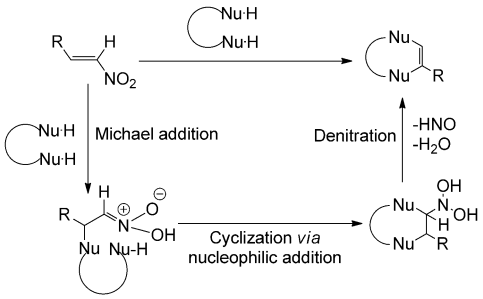
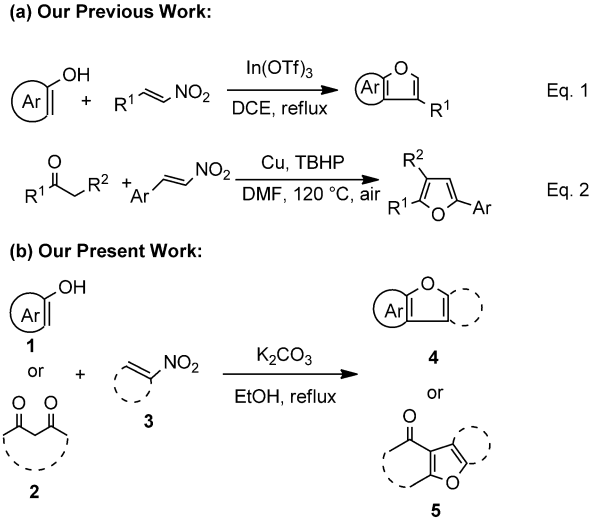
Conjugated nitroalkenes are efficient Michael acceptors, owing to the high electrophilicity of the double bond. These compounds are also used as versatile substrates in various organic transformations.[8] In addition, nitroalkenes are capable of binucleophilic addition to form various heterocycles and carbocycles in a cascade fashion through Michael addition/cyclization/denitration (Scheme 1).[9]

In this context, Chen and co-workers and Namboothiri and co-workers independently explored reactive nitroallylic acetates (the Morita-Baylis–Hillman acetates of nitroalkenes) for the synthesis of furan derivatives.[10] Recently, we developed several methods for the synthesis of various biologically important scaffolds, such as furan,[9a,11] imidazole,[12a] and imidazopyridine,[9b,12b] by using undecorated, readily accessible nitroalkenes and exploring their bielectrophilicity properties. Our previous work[9a] (Eq. (1), Scheme 2a) on the indium-triflate-catalyzed synthesis of arenofurans from readily accessible nitroalkenes and phenol/naphthols prompted us to look for an environmentally benign strategy. Furthermore, we have developed a regioselective synthesis of multisubstituted furans from simple alkyl ketones and nitroolefins (Eq. (2), Scheme 2a).[11] Herein, we report an efficient and general method for the synthesis of substituted furans through the coupling of 1,3-dicarbonyl compounds/enols with nitroolefins at reflux in dry EtOH with K_2CO_3 as a base (Scheme 2b).



Scheme 1. Mode of binucleophilic addition to nitroalkenes.

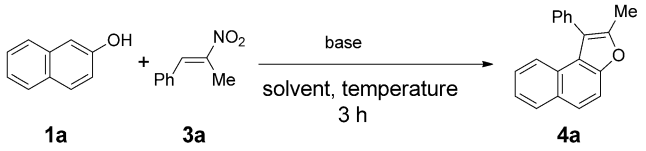


Scheme 2. Synthesis of substituted furan derivatives.

Results and Discussion

We commenced our study by taking β-naphthol (**1a**) and β-methyl-β-nitrostyrene (**3a**) as model substrates in the presence of K_2CO_3 (1 equiv) as a base in dry EtOH for 3 h under refluxing conditions (Table 1, entry 1). To our delight, the desired naphthofuran derivative (**4a**) was obtained in 95% yield and no further improvement was noted on increasing the reaction time. Encouraged by this result, we proceeded to optimize the reaction conditions, as summarized in Table 1. No significant decrease in yield was observed on lowering the amount of base to 50 mol% (Table 1, entry 2), whereas only 72% yield was obtained when 40 mol% K_2CO_3 was used (Table 1, entry 3). However, other bases, such as DABCO (1,4-diazabicyclo[2.2.2]octane), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Cs_2CO_3, NaOH, and KOH, were not as effective as K_2CO_3 for this reaction (Table 1, entries 4–8). Various solvents were also screened and dry EtOH (Table 1, entry 2) was found to be the best solvent among the common solvents, such as MeOH, DMF, DMSO, acetone, MeCN, and THF (Table 1, entries 9–14). It is notable that dry EtOH afforded a higher yield than rectified spirit (95% EtOH; Table 1, entry 15). Water was not a good solvent for this reaction (Table 1, entry 16); however, the reaction did not proceed in the absence of base (Table 1, entry 17). Thus, optimum reaction conditions were obtained by using β-naphthol (**1a**,

Table 1. Optimization of the reaction conditions for the synthesis of naphthofuran.[a]



1a **3a** **4a**

Entry	Base [mol%]	Solvent	*T* [°C]	Yield [%][b]
1	K_2CO_3 (100)	EtOH	reflux (85)	95
2	K_2CO_3 (50)	EtOH	reflux (85)	94
3	K_2CO_3 (40)	EtOH	reflux (85)	72
4	DABCO (100)	EtOH	reflux (85)	60
5	DBU (100)	EtOH	reflux (85)	56
6	Cs_2CO_3(100)	EtOH	reflux (85)	72
7	NaOH (100)	EtOH	reflux (85)	65
8	KOH (100)	EtOH	reflux (85)	68
9	K_2CO_3 (50)	MeOH	reflux (70)	75
10	K_2CO_3 (50)	acetone	reflux (60)	62
11	K_2CO_3 (50)	DMSO	100	37
12	K_2CO_3 (50)	DMF	100	22
13	K_2CO_3 (50)	MeCN	reflux (90)	<10
14	K_2CO_3 (50)	THF	reflux (70)	<10
15	K_2CO_3 (50)	EtOH	reflux (85)	70[c]
16	K_2CO_3 (50)	water	100	50
17	–	EtOH	reflux (85)	n.r.

[a] Reaction conditions: compound **1a** (0.5 mmol), compound **3a** (0.5 mmol), solvent (1.5 mL), 3 h; [b] yield of the isolated product; [c] rectified spirit (95% EtOH). DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, n.r. = no reaction.

Table 2. Substrate scope for the synthesis of substituted furans from naphthol derivatives.[a]

Entry	Naphthol	Nitroolefin	Product	Yield [%]
1	**1a**	**3a** (R = H)	**4a**	94
2	**1a**	**3b** (R = 4-Me)	**4b**	92
3	**1a**	**3c** (R = 4-NO_2)	**4c**	90
4	**1a**	**3d** (R = 4-Cl)	**4d**	87
5	**1a**	**3e** (R = 4-Br)	**4e**	85
6	**1a**	**3f**	**4f**	83
7	**1a**	**3g**	**4g**	80
8	**1a**	**3h**	**4h**	72
9	**1a**	**3i**	**4i**	69
10	**1a**	**3j**	**4j**	86[b]
11	**1a**	**3k**	**4k**	90
12	**1b**	**3b** (R = 4-Me)	**4l**	75
13	**1b**	**3d** (R = 4-Cl)	**4m**	70
14	**1b**	**3l**	**4n**	72
15	**1a**	**3m**	**4o**	86, (84)[c]
16	**1a**	**3n**	**4p**	90
17	**1c**	**3b** (R = 4-Me)	**4q**	92[d]
18	**1c**	**3d** (R = 4-Cl)	**4r**	87[d]

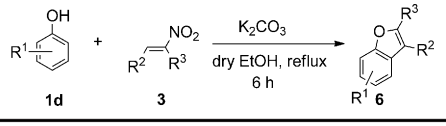
[a] Reaction conditions: compound **1** (0.5 mmol), compound **3** (0.5 mmol), K_2CO_3 (50 mol%), dry EtOH (1.5 mL), reflux, 3 h; yields are of the isolated products. [b] The reaction was performed for 6 h. [c] Reaction conditions: compound **1a** (20 mmol), compound **3m** (20 mmol), K_2CO_3 (50 mol%), dry EtOH (60 mL), reflux, 3 h. [d] The reaction was performed for 2.5 h.

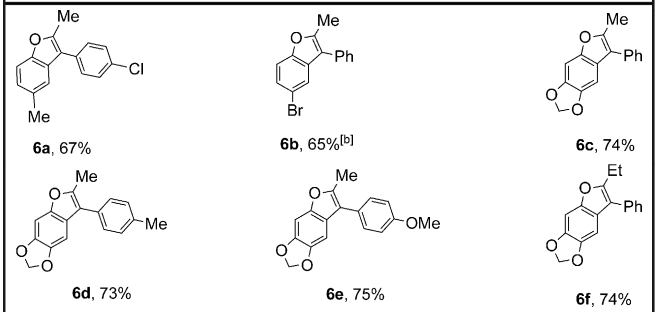
0.5 mmol) and β-methyl-β-nitrostyrene (**2a**, 0.5 mmol) in the presence of 50 mol% K_2CO_3 in dry EtOH (1.5 mL) at reflux for 3 h (Table 1, entry 2).

To explore the scope and limitations of this method, various nitroolefins were subjected to the reaction conditions (Table 2). Both β-methyl-β-nitrostyrenes and β-nitrostyrenes reacted well with naphthol and both electron-donating and electron-withdrawing substituents on the phenyl moiety of the nitroolefins reacted efficiently. Nitroolefins that contained electron-donating groups, such as –Me and –OMe groups, showed good efficiencies (**4b**, **4l**, **4o**, and **4n**). Nitrostyrene, which contained a strongly electron-withdrawing group (–NO_2) reacted very well, thereby affording the product in 90% yield (**4c**). Chloro- and bromo-substituted nitroolefins also smoothly afforded the corresponding products (**4d**, **4m**, and **4e**). The dioxole part of nitroolefin did not affect the reaction outcome (**4f**). A high yield was also obtained with a nitroolefin that contained a heteroaryl moiety (**4g**). Intriguingly, the unsaturated cinnamyl-substituted nitroolefin gave the desired product (**4h**) in good yield under the same reaction conditions. In addition, aliphatic nitroalkenes were also effective, thereby affording the desired products in good yields (**4i** and **4j**). β-Methyl-β-nitrostyrene and β-ethyl-β-nitrostyrene smoothly underwent the reaction (**4k**). It is notable that this procedure was also effective for α-naphthol (**1b**), which produced the corresponding naphthofuran derivatives (**4l**, **4m**, and **4n**). In addition, unsubstituted β-nitroolefin furnished the corresponding furan (**4o**) in good yield. The reaction also proceeded efficiently on a gram scale (20 mmol). 1-Naphthyl-substituted nitrostyrene, which contained polyaromatic rings, produced the corresponding naphthofuran (**4p**) in 90% yield. However, 2,7-dihydroxynaphthalene (**1c**) only afforded mono-furan derivatives, even when two equivalents of the nitroolefins (**4q** and **4r**) were added under the reaction conditions.

We continued our study by exploring the reactivity of phenol derivatives (**1d**) with various nitroolefins (**3**) under the reaction conditions (Table 3). Substituted phenols that contained –Me, –Br, or dioxole groups (sesamol) reacted smoothly with various nitroolefins and produced the corresponding benzofurans in good yields (**6a**–**6f**).

Table 3. Substrate scope for the synthesis of substituted furans from phenol derivatives.[a]





[a] Reaction conditions: compound **1d** (0.5 mmol), compound **3** (0.5 mmol), K_2CO_3 (50 mol%) in dry EtOH (1.5 mL), reflux, 6 h; yields are of the isolated products. [b] The reaction was performed for 9 h.

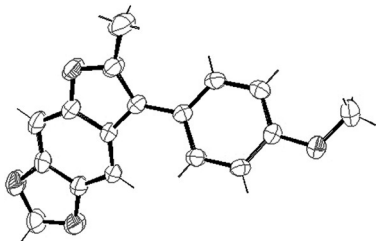


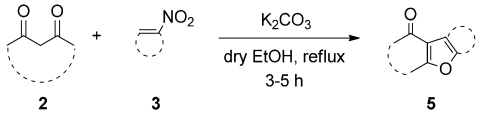
Figure 2. ORTEP of 7-(4-methoxyphenyl)-6-methyl-[1,3]dioxolo[4,5-*f*]benzofuran (**6e**); thermal ellipsoids are set at 30% probability.

X-ray crystallographic analysis was performed to confirm the structure of compound **6e** (Table 3), as shown in Figure 2.[13]

This method was also applicable to phloroglucinol, which reacted with three equivalents of the nitroolefins in one pot to afford the corresponding benzotrifurans (Scheme 3). These compounds are very useful hole-transporting materials (HTM) in multilayer organic light-emitting diodes (OLEDs).[3j,14]

This strategy was also extended to the synthesis of highly substituted furans from 1,3-dicarbonyl compounds (Scheme 4).

To our delight, when 1,3-dicarbonyl compounds were reacted with various nitroolefins, a diverse range of furan derivatives (**5**) were obtained in high yields (Table 4). Cyclic diketones, such as 5,5-dimethyl-1,3-cyclohexadione and 1,3-cyclohexadione, reacted smoothly with nitroolefins to furnish the desired furans. Nitroolefins containing –Me and –OMe group on the aryl ring gave the desired tetrasubstituted furan derivatives (**5b**, **5c**, **5l**, **5m**, and **5t**) in excellent yields. The chloro- and bromo-substituted nitrostyrene also reacted very well (**5f**, **5g**, **5o**, **5p**, **5u**, **5h**, **5i**, and **5q**). A notable advantage of this method is its efficiency for the synthesis of furan derivatives from both cyclic and acyclic 1,3-diketones. Acyclic diketones, such as acetylacetone and ethylacetoacetate, produced the desired products (**5s, 5t, 5u**, and **5v**) in good yields.



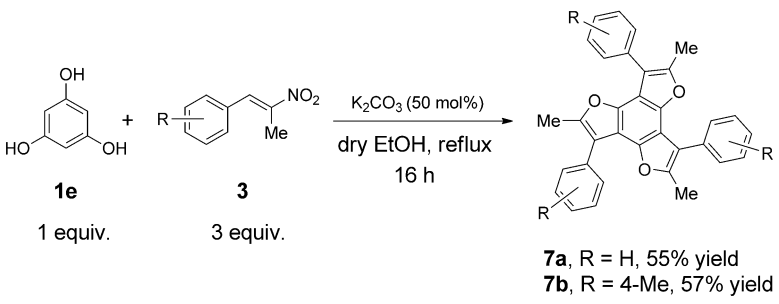
Scheme 4. Synthesis of substituted furans from 1,3-dicarbonyl compounds.

We were delighted to find that alicyclic nitroolefins **3s** and **3t** reacted well under the reaction conditions to produce large-sized-ring-fused substituted furan derivatives **5w** and **5x**, respectively, which could be further converted into biologically active compounds, such as dibenzofurans and 4-pyrone skeletons (Scheme 5).[3g]

The most-important achievement of this procedure is the one-pot synthesis of dioxa[5]helicenes in good yields. Helicenes have shown interesting biological activities, such as mutagenesis of bacterial cells,[15] high tumor-initiating activity,[15] chiral recognition[16] and selectivity for DNA binding and intercalation,[17] and enantioselectivity in telomerase inhibition.[18] Consequently, much attention has been devoted to the synthesis of helicenes over last few years.[19] To extend the scope of this method, 6-aryl-substituted dioxa[5]helicenes (**8a**–**8d**) were synthesized by the reaction of β-naphthol and 3-nitro-2*H*-chromenes under the reaction conditions (Scheme 6). Notably, this strategy uniquely allows the synthesis of this type of helicene derivatives from easily accessible starting materials in one pot.

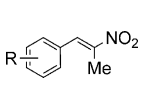
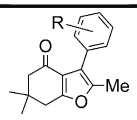
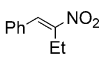
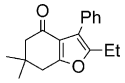
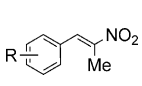
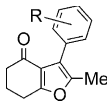
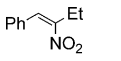
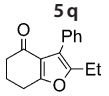
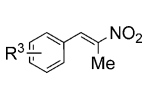
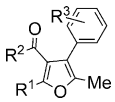
Next, we planned to prepare more functionalized arenofuran derivatives from the as-synthesized products (Scheme 7). The functionalization of synthesized naphthofurans (**4**) at the 2-position was performed by Pd-catalyzed arylation[20] to construct densely substituted furan derivatives. Substituted naphthofurans **10a** and **10b** were obtained in high yields. Furthermore, the aromatization of furan **5k** was achieved (to afford compounds **11a** and **11b**) by treatment with iodine in MeOH or EtOH under refluxing conditions.[21]

A plausible reaction mechanism is shown in Scheme 8 and is based on literature reports[10d,22] and our previous work.[9b] Initially, K_2CO_3-promoted

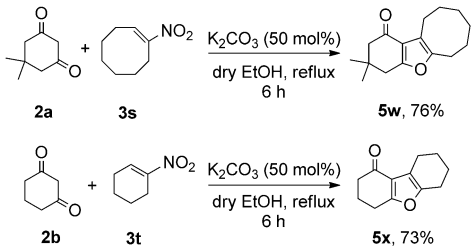


Scheme 3. Synthesis of hole-transporting materials.

Table 4. Substrate scope for the synthesis of substituted furans from 1,3-dicarbonyl compounds.[a]

Entry	1,3-Dicarbonyl compound	Nitroolefin	Product	Yield [%]
				
1	**2a**	**3a** (R = H)	**5a**	87
2	**2a**	**3b** (R = 4-Me)	**5b**	86
3	**2a**	**3o** (R = 4-OMe)	**5c**	85
4	**2a**	**3p** (R = 3-NO_2)	**5d**	86
5	**2a**	**3c** (R = 4-NO_2)	**5e**	87
6	**2a**	**3q** (R = 2-Cl)	**5f**	86
7	**2a**	**3d** (R = 4-Cl)	**5g**	89
8	**2a**	**3r** (R = 2-Br)	**5h**	87
9	**2a**	**3e** (R = 4-Br)	**5i**	90
10	**2a**	 **3k**	 **5j**	85
				
11	**2b**	**3a** (R = H)	**5k**	85
12	**2b**	**3b** (R = 4-Me)	**5l**	83
13	**2b**	**3o** (R = 4-OMe)	**5m**	81
14	**2b**	**3p** (R = 3-NO_2)	**5n**	78
15	**2b**	**3q** (R = 2-Cl)	**5o**	84
16	**2b**	**3d** (R = 4-Cl)	**5p**	86
17	**2b**	**3e** (R = 4-Br)	**5q**	88
18	**2b**	 **2l**	 **5r**	82
				
19[b]	**2c** (R^1, R^2 = Me)	**3a** (R^3 = H)	**5s**	82
20[b]	**2c**	**3b** (R^3 = 4-Me)	**5t**	83
21[b]	**2c**	**3d** (R^3 = 4-Cl)	**5u**	84
22[b]	**2d** (R^1 = Me, R^2 = OEt)	**3a** (R^3 = H)	**5v**	86

[a] Reaction conditions: compound **2** (0.5 mmol), compound **3** (0.5 mmol), K_2CO_3 (50 mol%), dry EtOH (1.5 mL), reflux, 5 h; yields are of the isolated products. [b] The reactions were performed for 3 h.



Scheme 5. Synthesis of precursors to biologically active compounds.

Michael addition of β-naphthol to nitroolefin **3a** occurs to form intermediate A. Next, intramolecular cyclization of intermediate A leads to the formation of cyclic intermediate B and, subsequently, the final product (**4a**) is formed by the elimination of water and HNO. In the case of dimedone (**2a**), the first step is the formation of Michael adduct D by the base-promoted addition of enol C to the nitroolefin (**3a**). Finally, the desired furan (**5a**) is formed through sequential intramolecular cyclization and denitration.

Conclusion

In summary, we have developed a versatile, one-pot, base-promoted synthesis of polysubstituted furans and arenofurans from the reaction between readily available phenols or 1,3-dicarbonyl compounds and nitroolefins at reflux in EtOH. This method has been applied to the synthesis of benzotrifuran derivatives, which are useful hole-transporting materials. The most-important achievement of this procedure is the direct synthesis of dioxa[5]helicenes in good yields. Furthermore, biologically significant large-sized-ring-fused substituted furans were also obtained by employing this simple strategy. The use of environmentally benign solvent and an inexpensive base, wide functional-group tolerance, general applicability, and operational simplicity are the key advantages of this method. These advantages render this environmentally benign procedure facile and suitable for creating a library of diversified furan derivatives in academia and in industry.

Experimental Section

Typical Procedure for the Synthesis of Naphthofurans 4

A mixture of the naphthol (**1**, 0.5 mmol) and the nitroolefin (**3**, 0.5 mmol) was stirred at reflux (80–85 °C) in dry EtOH (1.5 mL) in the presence of K_2CO_3 (35 mg, 50 mol%) until the reaction was complete (as determined by TLC). Then, the solvent was evaporated under reduced pressure and the crude residue was extracted with water/EtOAc (10 mL, 1:1). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on a short pad of silica gel (petroleum ether).

2-Methyl-1-phenylnaphtho[2,1-b]furan (4a)[9a]

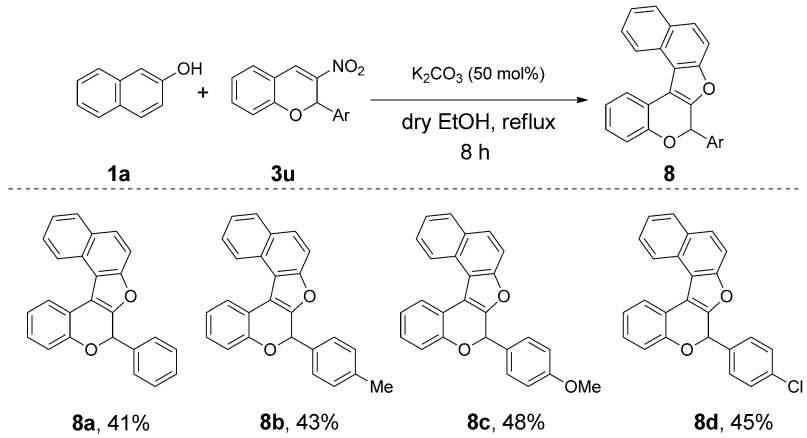
Colorless oil (121 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.56–7.49 (m, 2H), 7.39–7.36 (m, 4H), 7.34–7.32 (m, 1H), 7.27–7.22 (m, 1H), 7.17–7.13 (m, 1H), 2.29 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 134.3, 130.8, 130.6, 128.9, 128.7, 128.0, 127.6, 125.7, 124.6, 124.1, 123.3, 122.4, 119.1, 112.1, 12.4 ppm.

2-Methyl-1-p-tolylnaphtho[2,1-b]furan (4b)[9a]

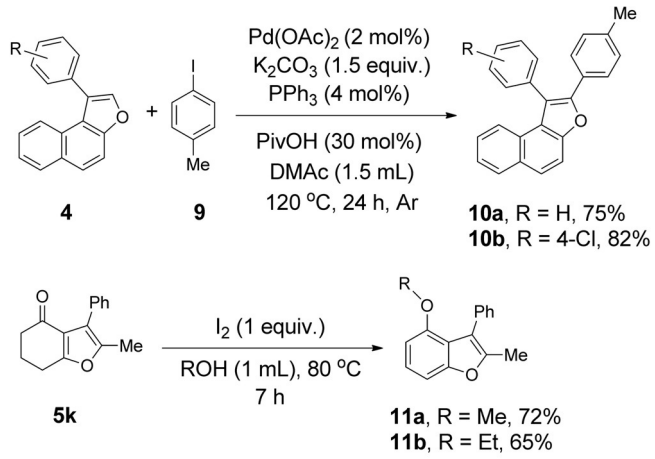
Colorless oil (125 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.80 (m, 2H), 7.59–7.58 (m, 2H), 7.34–7.29 (m, 3H), 7.25 (d, J = 8.4 Hz, 3H), 2.40 (s, 3H), 2.359 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 151.1, 137.1, 131.0, 130.7, 130.2, 129.2, 128.7, 127.9, 125.4, 124.38, 123.8, 123.1, 122.3, 118.8, 112.0, 21.2, 12.2 ppm.

2-Methyl-1-(4-nitrophenyl)naphtho[2,1-b]furan (4c)[9a]

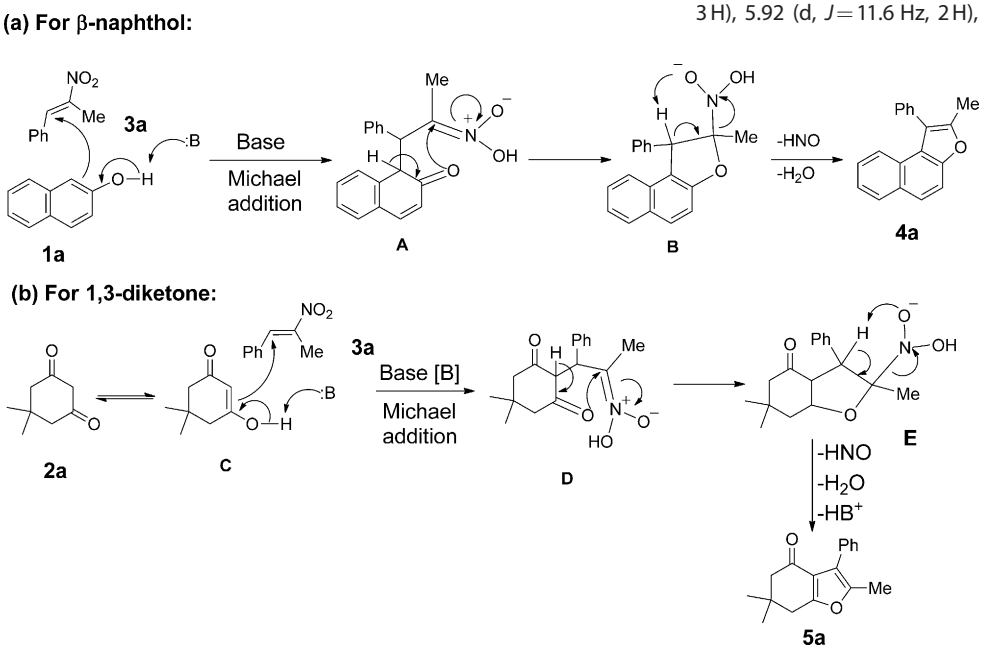
Colorless oil (136 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.62–7.52 (m, 5H), 7.32–7.28



Scheme 6. Synthesis of dioxa[5]helicenes.



Scheme 7. Synthesis of densely substituted arenofurans.



Scheme 8. Proposed reaction mechanism for the synthesis of furan derivatives.

(m, 1H), 7.23–7.19 (m, 1H), 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 151.5, 147.2, 141.5, 131.2, 130.8, 129.0, 127.3, 125.9, 125.2, 124.2, 123.8, 122.6, 121.3, 117.2, 112.0, 12.3 ppm.

1-(4-Chlorophenyl)-2-methylnaphtho[2,1-b]furan (4d)[9a]

Colorless oil (127 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.45(d, J = 8.8 Hz, 1H), 7.59 (d. J = 8.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.37–7.34 (m, 1H), 7.30–7.25 (m, 1H), 2.37 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 151.2, 133.5, 132.6, 131.7, 130.7, 128.8, 127.6, 125.72, 124.7, 124.0, 122.9, 121.9, 117.8, 112.0, 12.2 ppm.

1-(4-Bromophenyl)-2-methylnaphtho[2,1-b]furan (4e)[9a]

Colorless oil (143 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 3H), 7.49–7.46 (m, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.26–7.22 (m, 1H), 7.19 (d, J = 8.4 Hz, 1H), 2.28 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 151.2, 133.1, 132.1, 131.7, 130.6, 128.8, 127.6, 125.7, 124.7, 124.0, 122.9, 121.8, 121.6, 117.7, 112.0, 12.2 ppm; elemental analysis calcd (%) for $C_{19}H_{13}BrO$: C 67.67, H 3.89%; found: C 67.57, H 3.98%.

1-(Benzo[d][1,3]dioxol-5-yl)-2-methylnaphtho[2,1-b]furan (4f)[9a]

Colorless oil (125 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.73 (m, 2H), 7.55–7.48 (m, 2H), 7.28–7.19 (m, 2H), 6.84–6.80 (m, 3H), 5.92 (d, J = 11.6 Hz, 2H), 2.29 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 151.0, 147.7, 147.0, 130.6, 128.7, 127.7, 127.5, 125.6, 124.4, 123.9, 123.8, 123.1, 122.3, 118.5, 111.9, 110.8, 108.5, 101.1, 12.2 ppm; elemental analysis calcd (%) for $C_{20}H_{14}O_3$: C 79.46, H 4.67%; found: C 79.39, H 4.76%.

1-(Furan-2-yl)-2-methylnaphtho[2,1-b]furan (4g)[9a]

Light-brown oil (99 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.59–7.52 (m, 2H), 6.72–6.71 (m, 1H), 6.62–6.62 (m, 1H), 2.63 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 151.3, 146.8, 142.4, 130.7, 128.6, 127.4, 126.0, 124.9, 124.2, 123.5, 122.0, 111.8, 111.1, 110.1, 109.2, 12.7 ppm.

(E)-2-Methyl-1-styrylnaphtho[2,1-b]furan (4h)[9a]

Light-yellow oil (102 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48–7.46 (m, 2H), 7.41–7.38 (m, 2H), 7.35–7.29 (m, 4H), 7.23–7.21 (m, 1H), 6.71–6.67 (d, J = 16 Hz, 1H), 2.45 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 137.3, 133.2, 130.7, 130.4, 128.8, 128.7, 128.6, 128.2, 127.7, 127.5, 126.3, 126.0, 124.5, 124.0, 123.5, 122.0, 120.4, 116.5, 111.9, 13.1 ppm.

1-Isopropyl-2-methyl-naphtho[2,1-b]furan (4i)[9a]

Light-yellow oil (77 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.55–7.50 (m, 2H), 7.43–7.39 (m, 1H), 3.77–3.70 (m, 1H), 2.55 (s, 3H), 1.49 (d, J = 6.8 Hz, 3H), 1.44 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 148.8, 130.9, 129.2, 128.3, 125.7, 124.4, 123.7, 123.5, 122.4, 122.3, 112.1, 25.6, 22.4, 14.3 ppm.

8,9,10,11-Tetrahydronaphtho[2,1-b]benzofuran (4j)

Colorless oil (95 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.68–7.62 (m, 2H), 7.59–7.55 (m, 1H), 7.50–7.46 (m, 1H), 314–3.11 (m, 2H), 2.89–2.86 (m, 2H), 2.03–1.96 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 151.5, 130.6, 128.8, 128.5, 125.7, 123.9, 123.7, 123.6, 122.6, 114.4, 112.3, 23.8, 23.2, 23.2, 22.7 ppm; elemental analysis calcd (%) for $C_{16}H_{14}O$: C 86.45, H 6.35%; found: 86.59, H 6.47%.

2-Ethyl-1-phenyl-naphtho[2,1-b]furan (4k)[9a]

Light-yellow oil (122 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.60–7.56 (m, 2H), 7.45–7.34 (m, 5H), 7.27 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 2.65 (q, J = 7.6 Hz, 2H), 1.21 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 151.1, 134.1, 130.6, 130.5, 128.7, 128.5, 127.9, 127.5, 125.5, 124.4, 123.9, 123.1, 122.3, 118.1, 112.1, 19.9, 13.2 ppm.

2-Methyl-3-p-tolylnaphtho[1,2-b]furan (4l)

Colorless oil (102 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.54 (q, J = 8.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.36–7.33 (m, 3H), 7.20 (d, J = 7.6 Hz, 2H), 2.52 (s, 3H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 149.1, 136.6, 131.0, 129.9, 129.4, 128.8, 128.2, 126.1, 124.6, 124.0, 123.0, 121.1, 119.7, 118.3, 117.9, 21.2, 12.9 ppm; elemental analysis calcd (%) for $C_{20}H_{16}O$: C 88.20, H 5.92%; found: C 88.09, H 6.05%.

3-(4-Chloro-phenyl)-2-methylnaphtho[1,2-b]furan (4m)

Colorless oil (102 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.54–7.49 (m, 2H), 7.42–7.38 (m, 5H), 2.55 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 149.2, 132.8, 131.4, 131.1, 130.2, 129.0, 128.3, 126.3, 124.8, 123.6, 123.3, 121.1, 119.8, 117.9, 117.1, 12.9 ppm; elemental analysis calcd (%) for $C_{19}H_{13}ClO$: C 77.95, H 4.48%; found: C 77.83, H 4.59%.

2-Ethyl-3-(4-methoxyphenyl)-naphtho[1,2-b]furan (4n)

Colorless oil (108 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.55–7.54 (m, 2H), 7.51–7.47 (m, 1H), 7.39–7.35 (m, 3H), 6.96 (d, J = 9.2 Hz, 2H), 3.79 (s, 3H), 2.88 (q, J = 7.6 Hz, 2H), 1.33 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 155.1, 131.0, 130.1, 128.2, 126.0, 125.2, 124.6, 124.2, 122.9, 121.2, 119.8, 118.4, 116.9, 114.2, 55.3, 20.3, 13.3 ppm; elemental analysis calcd (%) for $C_{21}H18O_2$: C 83.42, H 6.00%; found: C 83.29, H 5.88%.

1-p-Tolyl-naphtho[2,1-b]furan (4o)[9a]

Colorless oil (111 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 1H), 7.55 (q, J = 8.8 Hz, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.35–7.31 (m, 2H), 7.30–7.24 (m, 3H), 7.17 (d, J = 8.4 Hz, 1H), 2.26 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 151.2, 135.3, 133.0, 132.5, 130.6, 129.8, 129.4, 128.6, 127.8, 126.9, 125.8, 124.5, 124.0, 122.7, 122.44, 116.1, 112.0, 12.4 ppm.

2-Methyl-1-(naphthalen-1-yl)naphtho[2,1-b]furan (4p)[9a]

Colorless oil (138 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.06 (m, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.86–7.81 (m, 3H), 7.74–7.00 (m, 2H), 7.61–7.58 (m, 1H), 7.44–7.38 (m, 2H), 7.36–7.33 (m, 1H), 7.17–7.13 (m, 1H), 2.46 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 151.3, 133.7, 132.9, 131.5, 130.6, 128.5, 128.4, 128.3, 128.2, 127.8, 126.3, 126.1, 126.0, 125.6, 125.6,124.5, 123.9, 123.4, 123.2, 116.5, 112.0, 12.3 ppm.

2-Methyl-1-p-tolylnaphtho[2,1-b]furan-8-ol (4q)

Yellow oil (132 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.20(d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 6.88 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 5.12 (Br, s, 1H), 2.35 (s, 3H), 2.30 ppm (s. 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 151.7, 150.7, 137.1, 130.6, 130.3, 129.3, 129.1, 126.9, 125.8, 124.3, 121.2, 118.6, 115.1, 109.7, 106.0, 21.3, 12.2 ppm; elemental analysis calcd (%) for $C_{20}H_{16}O_2$: C 83.31, H 5.59%; found: C 83.19, H 5.71%.

1-(4-Chlorophenyl)-2-methylnaphtho[2,1-b]furan-8-ol (4r)

Light-yellow oil (134 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.42–7.38 (m, 3H), 7.36–7.34 (m, 2H), 6.95–6.90 (m, 2H), 5.13 (Br, s, 1H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 151.8, 150.9, 133.5, 132.6, 131.8, 130.9, 130.8, 129.4, 128.9, 125.8, 124.7, 120.8, 117.6, 115.3, 109.7, 105.8, 12.2 ppm; elemental analysis calcd (%) for $C_{19}H_{13}ClO_2$: C 73.91, H 4.24%; found: C 74.09, H 4.38%.

Typical Procedure for the Synthesis of Benzofurans 6

A mixture of the phenol (**1d**, 0.5 mmol) and the nitroolefin (**3**, 0.5 mmol) was stirred at reflux (80–85 °C) in dry EtOH (1.5 mL) in the presence of K_2CO_3 (35 mg, 50 mol%) until the reaction was complete (as determined by TLC). Then, the solvent was evaporated and the crude residue was extracted with water/EtOAc (10 mL, 1:1). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on a short pad of silica gel (petroleum ether).

3-(4-Chlorophenyl)-2,5-dimethylbenzofuran (6a)

Colorless oil (86 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 4H), 7.31–7.28 (m, 2H), 7.05 (d, J = 6.8 Hz, 1H), 2.46 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 151.7, 132.9, 132.4, 131.7, 130.4, 129.1, 128.7, 125.1, 119.1, 115.9, 110.5, 21.6, 13.0 ppm; elemental analysis calcd (%) for $C_{16}H_{13}ClO$: C 74.85, H 5.10%; found: C 74.99, H 5.25%.

5-Bromo-2-methyl-3-phenylbenzofuran (6b)[9a]

White solid (93 mg, 65%); m.p. 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 2 Hz, 1H), 7.42–7.35 (m, 4H), 7.31–7.26 (m, 1H), 7.25–7.21 (m, 2H), 2.43 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 152.7, 132.0, 130.7 128.8, 108.8, 127.2, 126.3, 122.0, 116.6, 115.7, 112.1, 12.8 ppm.

6-Methyl-7-phenyl-[1,3]dioxolo[4,5-f]benzofuran (6c)

White solid (93 mg, 74%), m.p. 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.38 (m, 4H), 7.37–7.28 (m, 1H), 6.94 (s, 2H), 5.93 (s, 2H), 2.46 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 149.0, 145.5, 144.5, 133.0, 128.8, 127.0, 122.0, 1173, 101.2, 98.3, 93.3, 12.9 ppm; elemental analysis calcd (%) for $C_{16}H_{12}O_3$: C 76.18, H 4.79%; found: C 76.35, H 4.95%.

6-Methyl-7-p-tolylbenzofuro[5,6-d][1,3]dioxole (6d)

White solid (97 mg, 73%); m.p. 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.83 (s, 2H), 5.83 (s, 2H), 2.35 (s, 3H), 2.30 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 148.8, 145.2, 144.2, 136.5, 129.7, 129.4, 128.5, 122.0, 117.0, 101.0, 98.2, 93.1, 21.1, 12.7 ppm; elemental analysis calcd (%) for $C_{17}H_{14}O_3$: C 76.68, H 5.30%; found: C 76.52, H 5.49%.

7-(4-Methoxyphenyl)-6-methyl-[1,3]dioxolo[4,5-f]benzofuran (6e)

White solid (105 mg, 75%); m.p. 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 5.80 (s, 2H), 3.71 (s, 3H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 150.0, 148.7, 145.2, 144.2, 129.7, 125.0, 122.0, 116.7, 114.1, 101.0, 98.1, 93.1, 55.1, 12.6 ppm; elemental analysis calcd (%) for $C_{17}H_{14}O_4$: C 72.33, H 5.00%; found: C 72.21, H 5.19%.

6-Ethyl-7-phenyl-[1,3]dioxolo[4,5-f]benzofuran (6f)

Colorless oil (98 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.34 (m, 4H), 7.29–7.25 (m, 1H), 6.89 (s, 1H), 6.85 (s, 1H), 5.88 (s, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.24 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 148.9, 145.4, 144.3, 132.8, 128.8, 128.7, 126.9, 121.9, 116.5, 101.1, 98.3, 93.2, 20.3, 13.0 ppm; elemental analysis calcd (%) for $C_{17}H_{14}O_3$: C 76.68, H 5.30%; found: C 76.40, H 5.48%.

Typical Procedure for the Synthesis of Benzotrifurans 7

A mixture of phloroglucinol (**1e**, 0.5 mmol) and the nitroolefin (**3**, 1.5 mmol) was stirred at reflux (80–85 °C) in dry EtOH (1.5 mL) in the presence of K_2CO_3 (35 mg, 50 mol%) until the reaction was complete (as determined by TLC). Then, the solvent was evaporated and the crude residue was extracted with water/EtOAc (10 mL, 1:1 v/v). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on a short pad of silica gel (petroleum ether).

2,5,8-Trimethyl-3,6,9-triphenylbenzo[1,2-b:3,4-b′:5,6-b″]trifuran (7a)

White solid (128 mg, 55%), mp > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.0 Hz, 6H), 7.43 (t, J = 7.6 Hz, 6H), 7.32 (t, J = 7.6 Hz, 3H), 2.44 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 144.2, 132.9, 129.7, 128.1, 126.8, 115.7, 109.8, 12.9 ppm; elemental analysis calcd (%) for $C_{33}H_{24}O_3$: C 84.59, H 5.16%; found: C 84.75, H 5.29%.

2,5,8-Trimethyl-3,6,9-tri-p-tolylbenzo[1,2-b:3,4-b′:5,6-b″]trifuran (7b)

White solid (145 mg, 57%), m.p. > 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.0 Hz, 6H), 7.34 (d, J = 8.0 Hz, 6H), 2.44 (s, 9H), 2.38 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 144.2, 136.4, 129.9, 129.6, 128.8, 115.5, 109.8, 21.3, 12.9 ppm; elemental analysis calcd (%) for $C_{36}H_{30}O_3$: C 84.68, H 5.92%; found: C 84.79, H 6.09%.

Typical Procedure for the Synthesis of Compounds 5

A mixture of 1,3-dicarbonyl compound (**2**, 0.5 mmol) and nitroolefin (**3**, 0.5 mmol) was stirred at reflux (80–85 °C) in dry EtOH (1.5 mL) in the presence of K_2CO_3 (35 mg, 50 mol%) until the reaction was complete (as determined by TLC). Then, the solvent was evaporated and the crude residue was extracted with water/EtOAc (10 mL, 1:1 v/v). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on a short pad of silica gel (petroleum ether/EtOAc, 20:1 v/v).

2,6,6-Trimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5a)

Yellow oil (110 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 4H), 7.30–7.28 (m, 1H), 2.74 (s, 2H), 2.37 (s, 2H), 2.31 (s, 3H), 1.15 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 165.0, 149.1, 131.7, 129.9, 127.9, 127.1, 119.1, 118.6, 53.1, 37.7, 35.0, 28.6, 12.1 ppm; elemental analysis calcd (%) for $C_{17}H_{18}O_2$: C 80.28, H 7.13%; found: C 80.05, H 7.39%.

2,6,6-Trimethyl-3-p-tolyl-6,7-dihydro-5H-benzofuran-4-one (5b)

Yellow oil (115 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.65 (s, 2H), 2.28 (s, 5H), 2.22 (s, 3H), 1.07 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.7, 148.7, 136.6, 129.6, 128.5, 118.9, 118.5, 53.0, 37.6, 34.8, 28.5, 21.2, 12.0 ppm; elemental analysis calcd (%) for $C_{18}H_{20}O_2$: C 80.56, H 7.51%; found: C 80.74, H 7.69%.

3-(4-Methoxyphenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5H)-one (5c)

Yellow oil (120 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.24 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 9.2 Hz, 2H,), 3.74 (s, 3H), 2.66 (s, 2H), 2.28 (s, 2H), 2.22 (s, 3H), 1.07 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 164.8, 158.5, 148.5, 130.8, 123.8, 118.5, 118.4, 113.3, 52.2, 52.9, 37.6, 34.8, 28.5, 12.0 ppm; elemental analysis calcd (%) for $C_{18}H_{20}O_3$: C 76.03, H 7.09%: Found: C 76.24, H 7.20%.

2,6,6-Trimethyl-3-(3-nitrophenyl)-6,7-dihydrobenzofuran-4(5H)-one (5d)

Yellow oil (128 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 8.09–8.06 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 2.69 (s, 2H), 2.31 (s, 2H), 2.27 (s, 3H), 1.08 ppm (d, J = 4.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 165.3, 149.9, 147.9, 136.0, 133.5, 128.6, 124.4, 121.9, 118.0, 117.2, 52.7, 37.4, 34.9, 28.4,

12.0 ppm; elemental analysis calcd (%) for $C_{17}H_{17}NO_4$: C 68.21, H 5.72; N, 4.68%; found: C 68.39, H 5.59; N, 4.81%.

2,6,6-Trimethyl-3-(4-nitrophenyl)-6,7-dihydrobenzofuran-4(5H)-one (5e)

Yellow oil (130 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 2.70 (s, 2H), 2.32 (s, 2H), 2.28 (s, 3H), 1.09 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 165.6, 150.3, 146.7, 138.8, 131.2, 130.5, 123.1, 122.9, 118.1, 117.6, 52.8, 37.5, 35.0, 28.5, 12.2 ppm; elemental analysis calcd (%) for $C_{17}H_{17}NO_4$: C 68.21, H 5.72; N, 4.68%; found: C 68.37, H 5.58; N, 4.83%.

3-(2-Chlorophenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5H)-one (5f)

White solid (124 mg, 86%); mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 1H), 7.21–7.18 (m, 3H), 2.68 (d, J = 4.8 Hz, 2H), 2.321–2.20 (m, 2H), 2.10 (s, 3H), 1.09 (s, 3H), 1.07 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 164.3, 149.8, 134.3, 131.8, 131.1, 129.3, 128.8, 126.2, 119.4, 116.0, 52.5, 37.5, 35.0, 28.5, 11.9 ppm; elemental analysis calcd (%) for $C_{17}H_{17}ClO_2$: C 70.71, H 5.93%; found: C 70.55, H 6.16%.

3-(4-Chlorophenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5H)-one (5g)

Yellow oil (128 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (s, 4H), 2.66 (s, 2H), 2.29 (s, 2H), 2.22 (s, 3H), 1.07 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 165.0, 149.1, 132.8, 131.0, 130.1, 128.0, 118.2, 118.0, 52.9, 37.5, 34.8, 28.4, 12.0 ppm; elemental analysis calcd (%) for $C_{17}H_{17}ClO_2$: C 70.71, H 5.93%; found: C 70.56, H 6.13%.

3-(2-Bromophenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5H)-one (5h)

Colorless oil (144 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.8 Hz, 1H), 7.31–7.29 (m, 1H), 7.25–7.23 (m, 1H), 7.21–7.18 (m, 1H), 2.75 (d, J = 4.4 Hz, 2H), 2.33 (d, J = 12.0 Hz, 2H), 2.16 (s, 3H), 1.17 (s, 3H), 1.15 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 164.2, 149.6, 133.2, 132.5, 131.7, 129.0, 126.9, 124.8, 119.4, 117.9, 52.4, 37.5, 35.0, 28.6, 28.4, 11.9 ppm; elemental analysis calcd (%) for $C_{17}H_{17}BrO_2$: C 61.28, H 5.14%; found: C 61.42, H 5.32%.

3-(4-Bromophenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5H)-one (5i)

Colorless oil (149 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.66 (s, 2H), 2.29 (s, 2H), 2.22 (s, 3H), 1.07 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 165.0, 149.1, 131.9, 131.3, 130.9, 130.5, 121.0, 118.1, 118.0, 52.8, 37.5, 34.9, 28.4, 12.0 ppm; elemental analysis calcd (%) for $C_{17}H_{17}BrO_2$: C 61.28, H 5.14%; found: C 61.40, H 5.35%.

2-Ethyl-6,6-dimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5j)

Pale yellow oil (114 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.28 (m, 4H), 7.23–7.21 (m, 1H), 2.68 (s, 2H), 2.58 (q, J = 7.6 Hz, 2H), 2.29 (s, 2H), 1.15 (t, J = 7.6 Hz, 3H), 1.08 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 164.9, 154.0, 131.6, 129.7, 127.7, 172.00, 118.3, 118.3, 52.9, 37.6, 34.8, 28.5, 19.4, 12.9 ppm; elemental analysis calcd (%) for $C_{18}H_{20}O_2$: C 80.56, H 7.51%; found: C 80.40, H 7.35%.

2-Methyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5k)

Colorless oil (96 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.28 (m, 4H), 7.24–7.20 (m, 1H) 2.79 (t, J = 6.0 Hz, 2H), 2.40 (t, J = 6.4 Hz, 2H), 2.22 (s, 3H), 2.11–2.05 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 165.7, 148.6, 131.6, 129.7, 127.7, 126.9, 119.5, 119.0, 38.5, 23.6, 22.4, 11.9 ppm; elemental analysis calcd (%) for $C_{15}H_{14}O_2$: C 79.62, H 6.24%; found: C 79.46, H 6.39%.

2-Methyl-3-p-tolyl-6,7-dihydro-5H-benzofuran-4-one (5l)

Light-yellow oil (99 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.89 (t, J = 6.4 Hz, 2H), 2.51 (dd, J_1 = 6.0 Hz, J_2 = 7.6 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 2.18 ppm (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 165.6, 148.3, 136.5, 129.5, 129.5, 128.5, 128.4, 119.6, 118.9, 38.5, 23.5, 22.3, 21.1, 11.8 ppm; elemental analysis calcd (%) for $C_{16}H_{16}O_2$: C 79.97, H 6.71%; found: C 80.14, H 6.86%.

3-(4-Methoxyphenyl)-2-methyl-6,7-dihydrobenzofuran-4(5H)-one (5m)

Colorless oil (103 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 2.78 (t, J = 6.4 Hz, 2H), 2.39 (t, J = 6.4 Hz, 2H), 2.21 (s, 3H), 2.08 ppm (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 165.6, 158.5, 148.2, 130.8, 123.9, 119.6, 118.6, 113.2, 55.1, 38.6, 23.6, 22.4, 11.8 ppm; elemental analysis calcd (%) for $C_{16}H_{16}O_3$: C 74.98, H 6.29%; found: C 75.21, H 6.38%.

2-Methyl-3-(3-nitrophenyl)-6,7-dihydrobenzofuran-4(5H)-one (5n)

Light-yellow oil (105 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.22 (m,1H), 8.16–8.14 (m, 1H), 7.77(d, J = 8.4 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 2.91 (t, J = 6.4 Hz, 2H), 2.51 (t, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.20 ppm (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2, 166.3, 149.6, 147.8, 136.0, 133.5, 128.6, 124.4, 121.9, 119.2, 117.3, 38.4, 23.5, 22.4, 11.9 ppm; elemental analysis calcd (%) for $C_{15}H_{13}NO_4$: C 66.41, H 4.83; N, 5.16%; found: C 66.30, H 4.98; N, 5.01%.

3-(2-Chlorophenyl)-2-methyl-6,7-dihydrobenzofuran-4(5H)-one (5o)

Yellow oil (109 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 1H), 7.27–7.23 (m, 3H), 2.90–2.86 (m, 2H), 2.47–2.42 (m, 2H), 2.17 ppm (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 165.2, 149.4, 134.1, 131.8, 131.0, 129.2, 128.7, 126.1, 120.5, 116.0, 38.1, 23.4, 22.4, 11.8 ppm; elemental analysis calcd (%) for $C_{15}H_{13}ClO_2$: C 69.10, H 5.03%; found: C 68.95, H 5.18%.

3-(4-Chlorophenyl)-2-methyl-6,7-dihydrobenzofuran-4(5H)-one (5p)

Yellow oil (112 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.22 (m, 4H), 2.80 (t, J = 6.4 Hz, 2H), 2.41 (t, J = 6.8 Hz, 2H), 2.21 (s, 3H), 2.03 ppm (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 165.9, 148.8, 132.9, 131.0, 130.2, 128.1, 128.0, 119.4, 118.1, 38.5, 23.6, 22.4, 11.9 ppm; elemental analysis calcd (%) for $C_{15}H_{13}ClO_2$: C 69.10, H 5.03%; found: C 68.93, H 5.20%.

3-(4-Bromophenyl)-2-methyl-6,7-dihydrobenzofuran-4(5H)-one (5q)

Yellow oil (134 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 2.78 (t, J = 6.4 Hz, 2H), 2.38 (t, J = 6.4 Hz, 2H), 2.19 (s, 3H), 2.07 ppm (p, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 166.0, 148.8, 131.4, 130.9, 130.6, 121.0, 119.4, 118.1, 38.5, 23.6, 22.4, 11.9 ppm. Anal. calcd. for $C_{15}H_{13}BrO_2$: C 59.04, H 4.29%; found: C 58.92, H 4.38%.

2-Ethyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5r)

Yellow oil (98 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 4H), 7.23–7.21 (m, 1H), 2.81 (t, J = 6.0 Hz, 2H), 2.56 (q, J = 7.6 Hz, 2H), 2.40 (t, J = 6.8 Hz, 2H), 2.09 (t, J = 6.4 Hz, 2H), 1.15 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 165.8, 153.8, 131.8, 129.8, 128.3, 127.8, 127.0, 126.1, 119.6, 118.5, 38.6, 23.7, 22.5, 19.4, 13.0 ppm; elemental analysis calcd (%) for $C_{16}H_{16}O_2$: C 79.97, H 6.71%; found: C 79.83, H 6.89%.

1-(2,5-Dimethyl-4-phenyl-furan-3-yl)-ethanone (5s)

Colorless oil (87 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.28 (m, 2H), 7.25 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.06 (s, 3H), 1.83 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 156.0, 146.8, 133.6, 129.7, 126.3, 127.2, 122.9, 120.7, 30.5, 14.1, 11.4 ppm; elemental analysis calcd (%) for $C_{14}H_{14}O_2$: C 78.48, H 6.59%; found: C 78.59, H 6.71%.

1-(2,5-Dimethyl-4-(p-tolyl)furan-3-yl)ethanone (5t)

Light-yellow oil (94 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H), 1.84 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 155.9, 146.7, 136.9, 130.5, 129.6, 129.0, 122.9, 120.6, 30.6, 21.1, 14.1, 11.4 ppm; elemental analysis calcd (%) for $C_{15}H_{16}O_2$: C 78.92, H 7.06%; found: C 78.78, H 7.19%.

1-(4-(4-Chlorophenyl)-2,5-dimethylfuran-3-yl)ethanone (5u)

Yellow oil (104 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H), 2.06 (s, 3H), 1.89 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 156.3, 147.1, 133.2, 132.1, 131.1, 128.5, 122.7, 119.6, 30.7, 14.2, 11.4 ppm; elemental analysis calcd (%) for $C_{14}H_{13}ClO_2$: C 67.61, H 5.27%; found: C 67.42, H 5.41%.

Ethyl-2,5-dimethyl-4-phenylfuran-3-carboxylate (5v)

Yellow oil (105 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.7.25,(m, 2H), 7.23–7.20 (m, 1H), 7.10–7.05 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 2.11 (s, 3H), 1.01 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 157.3, 147.0, 133.2, 129.9, 127.5, 126.7, 121.3, 113.5, 59.7, 14.0, 13.8, 11.7 ppm; elemental analysis calcd (%) for $C_{15}H_{16}O_3$: C 73.75, H 6.60%; found: C 73.92, H 6.79%.

3,3-Dimethyl-3,4,6,7,8,9,10,11-octahydrocycloocta[b]benzofuran-1(2H)-one (5w)

Colorless oil (93 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.74 (t, J = 6.4 Hz, 2H), 2.66 (t, J = 6.4 Hz, 2H), 2.58 (s, 2H), 2.21 (s, 2H), 1.66–1.29 (m, 4H), 1.44–1.35 (m, 4H), 1.04 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 164.0, 152.3, 119.3, 116.8, 52.8, 37.6, 35.2, 28.7, 27.9, 27.7, 25.8, 25.7, 25.7, 21.7 ppm; elemental analysis calcd (%) for $C_{16}H_{22}O_2$: C 78.01, H 9.00%; found: C 78.20, H 9.16%.

3,4,6,7,8,9-Hexahydrodibenzo[b,d]furan-1(2H)-one (5x)

Colorless oil (105 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.74 (t, J = 6.4 Hz, 2H), 2.58–2.54 (m, 2H), 2.48 (t, J = 6.4 Hz, 2H), 2.37 (t, J = 6.8 Hz, 2H), 2.09–2.03 (m, 2H), 1.77–1.71 (m, 2H), 1.66–1.61 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 165.7, 151.0, 120.5, 115.4, 38.2, 23.6, 22.9, 22.7, 22.7, 21.6 ppm; elemental analysis calcd (%) for $C_{12}H_{14}O_2$: C 75.76, H 7.42%; found: C 75.62, H 7.30%.

Typical Procedure for the Synthesis of Dioxa[5]helicenes 8

A mixture of 2-naphthol (**1a**, 0.5 mmol) and 3-nitro-2*H*-chromenes (**3u**, 0.5 mmol) was stirred at reflux (80–85 °C) in dry EtOH (1.5 mL) in the presence of K_2CO_3 (35 mg, 50 mol%) until the reaction was complete (as determined by TLC). Then, the solvent was evaporated and the crude residue was extracted with water/EtOAc (10 mL, 1:1 v/v). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on a short pad of silica gel (petroleum ether).

6-Phenyl-6H-naphtho[1′,2′:4,5]furo[2,3-c]chromene (8a)

Yellow oil (71 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.72–7.65 (m, 2H), 7.58–7.55 (m, 1H), 7.50–7.47 (m, 2H), 7.42–7.7.39 (m, 3H), 7.25–7.20 (m, 2H), 7.16–7.13 (m, 1H) 6.49 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 151.8, 151.7, 137.0, 131.2, 129.2, 129.0, 128.7, 128.0, 127.8, 127.6, 126.2, 126.1, 125.2, 124.9, 124.6, 122.5, 121.0, 119.3, 118.1, 113.2, 112.6, 75.8 ppm; elemental analysis calcd (%) for $C_{25}H_{16}O_2$: C 86.19, H 4.63%; found: C 86.02, H 4.78%.

6-(p-Tolyl)-6H-naphtho[1′,2′:4,5]furo[2,3-c]chromene (8b)

Gummy mass (77 mg, 43%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 9.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.14–7.09 (m, 4H), 7.02 (d, J = 9.2 Hz, 1H), 6.35 (s, 1H), 2.27 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 151.8, 139.0, 134.0, 131.2, 129.5, 129.4, 129.1, 128.0, 127.7, 127.7, 126.1, 126.1, 125.1,124.9, 124.6, 122.4, 121.1, 119.3, 118.1, 113.2, 112.6, 75.7, 21.2 ppm; elemental analysis calcd (%) for $C_{26}H_{18}O_2$: C 86.16, H 5.01%; found: C 86.01, H 5.15%.

6-(4-Methoxyphenyl)-6H-naphtho[1′,2′:4,5]furo[2,3-c]chromene (8c)

Gummy mass (90 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 9.2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.15–7.12 (m, 2H), 7.01 (d, J = 8.8 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.34 (s, 1H), 3.72 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 153.8, 151.8, 131.2, 129.2, 129.2, 129.0, 128.5, 127.7, 126.1, 125.1, 124.9, 124.6, 122.4, 121.1, 119.3, 118.8, 118.1, 114.1, 113.3, 112.6, 75.5, 55.2 ppm; elemental analysis calcd (%) for $C_{26}H_{18}O_3$: C 82.52, H 4.79%; found: C 82.38, H 4.92%.

6-(4-Chlorophenyl)-6H-naphtho[1′,2′:4,5]furo[2,3-c]chromene (8d)

Yellow solid (86 mg, 45%); m.p. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1HJ), 7.71 (d, J = 8.8 Hz, 1H), 7.57–7.48 (m, 2H), 7.48–7.44 (m, 1H), 7.31 (d, J = 8.8 Hz, 2H), 7.16–7.12 (m, 2H), 7.04–7.02 (m, 1H), 6.35 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 151.5, 151.1, 135.25, 134.9, 131.2, 129.2, 129.0, 128.9, 128.6, 128.0, 127.9, 126.4, 126.2, 125.2, 124.8, 124.7, 122.7, 120.9, 119.2, 118.1, 113.3, 112.5, 74.9 ppm; elemental analysis calcd (%) for $C_{25}H_{15}ClO_2$: C 78.43, H 3.95%; found: C 78.32, H 4.09%.

Typical Procedure for the Functionalization of Furans at the 2-Position

$Pd(OAc)_2$ (2 mol%), PPh_3 (4 mol%), K_2CO_3 (1.5 equiv), and PivOH (pivalic acid, 30 mol%) were placed in a sealed tube. Then, 4-iodotoluene (0.5 mmol) and furan (**4**, 0.5 mmol) were added, the tube was purged with argon, and DMAc (*N*,*N*-dimethylacetamide, 1.5 mL) was added. Then, the reaction mixture was stirred at 120 °C for 24 h. After cooling the reaction mixture to room temperature the solution was extracted with EtOAc. The organic layer was evaporated and the crude product was purified by column chromatography on silica gel (petroleum ether).

1-Phenyl-2-p-tolylnaphtho[2,1-b]furan (10a)

Gummy mass (125 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.4 Hz, 1H), 7.68–7.61 (m, 1H), 7.59–7.56 (m, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.48–7.44 (m, 1H), 7.41–7.39 (m, 1H), 7.36–7.33 (m, 1H), 7.28–7.26 (m, 6H), 7.26–7.24 (m, 1H), 7.17–7.15 (m, 1H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 141.6, 134.1, 130.7, 130.4, 129.8, 129.3, 128.7, 128.5, 127.8, 127.5, 126.7, 125.9, 125.5, 124.4, 123.9, 123.1, 122.2, 118.9, 112.0, 12.2 ppm; elemental analysis calcd (%) for $C_{25}H_{18}O$: C 89.79, H 5.43%; found: C 89.91, H 5.56%.

1-(4-Chlorophenyl)-2-p-tolylnaphtho[2,1-b]furan (10b)

Gummy mass (151 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 6.0 Hz, 2H), 7.46–7.43 (m, 4H), 7.39–7.37 (m, 2H), 7.33–7.30 (m, 3H), 7.21–7.18 (m, 2H), 7.00 (d, J = 6.8 Hz, 2H), 2.22 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 138.0, 132.0, 1308, 129.6, 129.6, 129.2, 129.0, 128.4, 127.9, 126.5, 126.2, 126.1, 126.0, 125.8, 124.2, 122.8 117.4, 112.1, 21.2 ppm; elemental analysis calcd (%) for $C_{25}H_{17}ClO$: C 81.41, H 4.65%; found: C 81.29, H 4.50%.

Typical Procedure for the Synthesis of Densely Substituted Benzofurans by Aromatization

The as-synthesized furan (**5k**, 0.5 mmol) was stirred in a solution of I_2 (1 equiv) in MeOH (1 mL) at 80 °C for a certain period of time (as determined by TLC analysis). Following completion of the reaction, the mixture was diluted with water/EtOAc (10 mL, 1:1 v/v). The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (petroleum ether) to afford the corresponding benzofuran (**11a**).

4-Methoxy-2-methyl-3-phenylbenzofuran (11a)

Colorless oil (85 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.38 (m, 2H), 7.35–7.31 (m, 2H), 7.27–7.25 (m, 1H), 7.12–7.08 (m, 1H), 7.02 (d, J = 8.8 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 3.66 (s, 3H), 2.35 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 153.9, 150.3, 133.2, 130.4, 129.8, 128.7, 127.4, 126.5, 124.0, 116.7, 104.0, 103.7, 55.3, 12.4 ppm; elemental analysis calcd (%) for $C_{16}H_{14}O_2$: C 80.65, H 5.92%; found: C 80.52, H 5.80%.

4-Ethoxy-2-methyl-3-phenylbenzofuran (11b)

Colorless oil (82 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.25–7.21 (m, 1H), 7.07 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 3.88 (q, J = 8.4 Hz, 2H), 2.35 (s, 3H), 1.10 ppm (t, J = 8.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 153.2, 150.2, 133.1, 130.6, 127.2, 126.5, 123.9, 117.9, 116.8, 104.8, 104.0, 64.0, 14.4, 12.4 ppm; elemental analysis calcd (%) for $C_{17}H_{16}O_2$: C 80.93, H 6.39%; found: C 80.80, H 6.52%.

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