Microwave-Promoted Pd-Catalyzed Synthesis of Dibenzofurans from *Ortho*-Arylphenols

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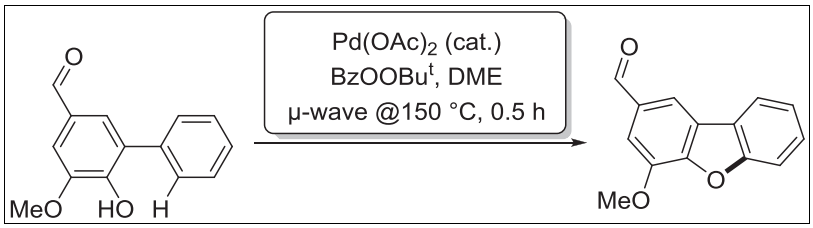

ortho-Aryl phenols, synthesized via protecting group free Suzuki–Miyaura coupling of *ortho*-halophenols and arene boronic acids, undergo a cyclization to dibenzofurans via oxidative C–H activation. The reaction proceeds under microwave irradiation in short reaction times using catalytic amounts of $Pd(OAc)_2$ without additional ligands.

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INTRODUCTION

Although dibenzofurans have received considerably less attention from the synthetic community than benzofurans [1], recent reviews discussing their role as natural products [2,3] or as environmental pollutants [4] suggest that their relevance as targets for organic synthesis has so far probably been underestimated. Bioactivities and biological sources of naturally occurring dibenzofurans are diverse and range from anticancer activity (e.g. kehokorin C, isolated from the slime mold *Trichia favoginea*) [5] via antibacterial activity against *Staphyllococcus aureus* (e.g. porric acid D, isolated from the marine fungus *Alternaria* sp.) [6] to activity as phytoalexins (e.g. eriobofuran, which is produced in apple shoots after infection with the fire blight bacterium) [7]. Polychlorinated dibenzodioxins and dibenzofurans are formed *inter alia* during municipal solid waste incineration [4]. They are highly toxic and can promote tumor growth, which has for instance been investigated for 2,3,4,7,8-pentachlorodibenzofuran (PCDF), one of the most toxic polychlorinated aromatic hydrocarbons (Fig. 1) [8].

Until today, variations of the classical Graebe–Ullmann cyclization [9] are often used for the synthesis of dibenzofurans. The method requires *ortho*-phenoxy arene diazonium salts, which undergo upon dediazonation a free radical cyclization to the desired dibenzofurans. In order to overcome limitations of the scope and to avoid undesired side reactions, such as hydrodediazonation, numerous attempts to find improved conditions have been undertaken over the decades, e.g. by using hydroquinone [10] or copper salts [11] as promoters. Photoredox catalysis [12], although highly successful for promoting many free radical transformations of the Pschorr type, has been of limited use in the case of dibenzofuran synthesis [13]. Electrochemical oxidative coupling of phenols has been found to furnish dibenzofurans; however, selectivities and isolated yields are not yet synthetically useful [14]. A viable free radical approach to dibenzofurans based on a Pschorr-type cyclization of *ortho*-borylated diphenylethers has recently been reported [15]. Many successful syntheses of dibenzofurans (**1**) are based on transition metal-catalyzed coupling reactions. These approaches can be roughly classified as outlined in Scheme 1.

Routes a and b start from diaryl ethers **2** or **3**, respectively. Route a employs diaryl ethers substituted with a leaving group (e.g. Br, I, OTos, N_2^+) *ortho* to the aryloxy substituent and Pd(0) catalysts. The dibenzofuran formation proceeds via oxidative addition of the C–X bond, intramolecular C–H activation, and reductive elimination [16–23]. Route b, which uses diarylethers **3** without *ortho*-leaving groups, was developed before route a, originally with stoichiometric or even overstoichiometric amounts of $Pd(OAc)_2$ as coupling reagent [24,25]. This approach relies on the high electrophilicity of Pd^{2+}, which reacts first in an intermolecular and then in an intramolecular carbopalladation and eventually undergoes reductive elimination to the dibenzofuran **1** and Pd(0). An attempt to make this synthesis catalytic in Pd was made shortly afterwards by using air as oxidant, but under the original conditions, numerous by-products were formed [26]. Later, improved protocols for Pd^{2+}-catalyzed aryl couplings using air as oxidant were described by Åkermark and coworkers, who identified $Sn(OAc)_2$ as efficient cocatalyst [27] and by Fagnou and coworkers, who found that pivalic acid is a better solvent for these reactions than the more

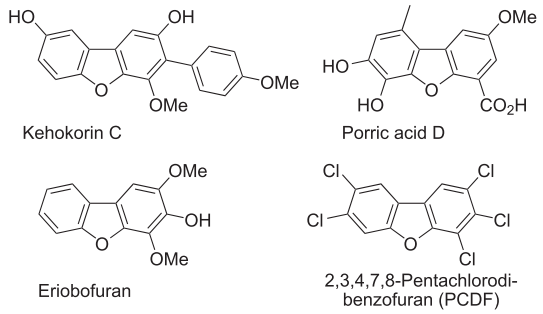
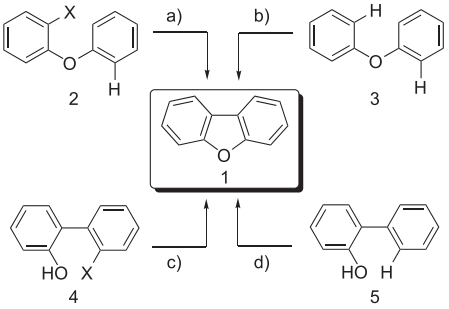


Figure 1. Structure of some bioactive dibenzofurans.

Scheme 1. Transition metal-catalyzed approaches to dibenzofurans.



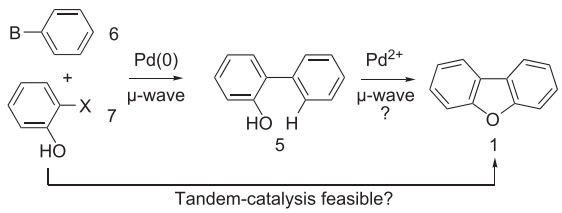
commonly used acetic acid [28]. In the course of a total synthesis, Koert and coworkers found that Fagnou's C–H activation conditions can be used for the synthesis of a polysubstituted dibenzofuran but that AgOAc is a better oxidant [29]. An interesting variant of route b has been developed by Larock and coworkers. Their approach to dibenzofurans is catalytic in Pd(0) and does not require any oxidants. It proceeds through a tandem carbopalladation of aryl iodides, subsequent vinyl-to-aryl migration of the Pd, intramolecular C–H activation, and eventually reductive elimination [30]. In routes c and d, biaryl compounds **4** and **5** are used as starting materials and the dibenzofuran formation is completed by an etherification. Biaryls **4**, substituted with a leaving group in the 2′ position, can undergo cyclization via a base-mediated S_{NAr} pathway [31], a copper mediated [32] or catalyzed [33] Ullmann-type reaction [34], or a Pd-catalyzed *O*-arylation. The latter method, developed by Buchwald and coworkers for the intermolecular synthesis of diaryl ethers [35] has later been expanded to the synthesis of dibenzofurans from biaryls **4** [36,37]. By far, the least explored way to dibenzofurans is represented by route d and relies on transition metal-catalyzed activation of C–H bonds with subsequent intramolecular etherification [38,39]. For example, Cu-catalyzed transformations of 2-hydroxybiaryls **5** to dibenzofurans **1** have been developed by Zhu and coworkers, who identified carboxylates [40], in particular pivalate, as rate accelerating agents and air as a suitable oxidant [41–43]. We are aware of only two publications describing a Pd-catalyzed synthesis of dibenzofurans via route d. Liu and coworkers reported that 2-hydroxybiaryls **5** undergo oxidative cycloetherification in the presence of air, using $Pd(OAc)_2$ in combination with an NHC ligand and mesitylcarboxylate as the catalyst system [44]. A substantial improvement was achieved by adding 4,5-diazafluoren-9-one, an ancillary ligand previously developed for the aerobic allylic oxidation [45]. Almost simultaneously, Wei and Yoshikai found that the same transformation can be achieved by using 5 or 10 mol% of $Pd(OAc)_2$ as a precatalyst, 3-nitropyridine as an ancillary ligand, and the unsymmetrical peroxide $BzOOBu^t$ as the oxidant [46]. A mixture of hexafluorobenzene and *N*,*N*′-dimethyl-imidazolinone was identified as the optimum solvent for this protocol.

We became interested in oxidative cycloetherifications of 2-hydroxybiaryls **5** following our investigations into the protecting group-free synthesis of biphenols through Pd/C-catalyzed, microwave-promoted, and fluoride-accelerated Suzuki–Miyaura coupling reactions in water [47–49]. In the course of these investigations, we discovered that the 2-hydroxybiaryl substitution pattern **5**, required as the starting material for route d, is particularly good accessible using our aqueous-heterogeneous Suzuki–Miyaura coupling conditions. As both steps of the dibenzofuran synthesis depicted in Scheme 2 are Pd-catalyzed, we thought that a process that combines Suzuki–Miyaura coupling and oxidative cycloetherification to an assisted tandem catalysis might in principle be viable but that the reaction conditions of the individual steps had to be mutually adapted. As a first step, we investigated the compatibility of the oxidative cycloetherification protocol devised by Wei and Yoshikai [46] with the microwave conditions required for our Suzuki–Miyaura protocol [47].

RESULTS AND DISCUSSION

Adaptation of oxidative cyclization conditions for microwave irradiation. Wei and Yoshikai found that their oxidative cycloetherification requires $BzOOBu^t$ as an oxidant and that other peroxides, hydroperoxides, or other oxidants fail completely under the conditions tested by these authors [46]. For these reasons, we started our

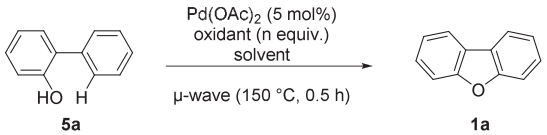
Scheme 2. Two-step Suzuki–Miyaura coupling/oxidative cycloetherification.



investigation into a microwave-promoted variant of this reaction by keeping the oxidant $BzOOBu^t$ and varying the solvent. As a test reaction, the conversion of 2-phenylphenol (**5a**) to dibenzofuran (**1a**) in the presence of a catalytic amount of $Pd(OAc)_2$ and two equivalents of $BzOOBu^t$ under microwave irradiation at 150°C was chosen (Table 1). The first solvent to be tested was water, because this solvent had previously been successfully used by us for the Suzuki–Miyaura coupling of 2-halophenols [47]. Under these conditions, **1a** was formed only in trace amounts, while the major part of the starting material was recovered unchanged (entry 1). With other undried protic (entries 2, 5) and aprotic (entries 3, 4) polar solvents, the same result was obtained. Only insubstantial conversion was observed in dry methanol (entry 6), and it was therefore concluded that protic solvents are generally not suitable for this transformation. While the yields in dry acetonitrile and dioxane (entries 7, 9) were only moderate, dry benzene (entry 8) and the ethereal solvents THF, methy-tert-butyl ether (MTBE), and dimethoxyethane (DME) (entries 10–12) resulted in synthetically useful yields. To avoid excessive pressure increase under

Table 1

Optimization of reaction conditions for Pd-catalyzed oxidative cyclization.



5a **1a**

Entry	Oxidant	*n* (equiv.)	Solvent	Dried?	Yield of **1a**
1	$BzOOBu^t$	2.0	Water	—	<5%[d]
2	$BzOOBu^t$	2.0	Ethylene glycol	No	<5%[d]
3	$BzOOBu^t$	2.0	DMSO	No	<5%[d]
4	$BzOOBu^t$	2.0	Pyridine	No	<5%[d]
5	$BzOOBu^t$	2.0	Polyethylene glycol	No	<5%[d]
6	$BzOOBu^t$	2.0	Methanol	Yes	<5%[d]
7	$BzOOBu^t$	2.0	Acetonitrile	Yes	20%
8	$BzOOBu^t$	2.0	Benzene	Yes	61%
9	$BzOOBu^t$	2.0	Dioxane	No	31%
10	$BzOOBu^t$	2.0	THF	Yes	60%
11	$BzOOBu^t$	2.0	MTBE	Yes	49%
12	$BzOOBu^t$	2.0	DME	Yes	58%
13	$BzOOBu^t$	2.0	DME	No	33%
14	$BzOOBu^t$	2.0	DME	Yes[a]	<5%
15	$BzOOBu^t$	2.0	DME	Yes[b]	56%
16	$BzOOBu^t$	2.0	DDME	Yes	49%
17	$BzOOBu^t$	2.0	DDME[c]	Yes	60%
18	None	—	DME	Yes	<5%
19	Ag_2CO_3	2.0	DME	Yes	<5%
20	IBX	2.0	DME	Yes	<5%
21	H_2O_2	2.0	DME	Yes	<5%
22	m-CPBA	2.0	DME	Yes	<5%
23	CumOOH	2.0	DME	Yes	<5%
24	Bu^tOOH	2.0	DME	Yes	<5%
25	CumOOCum	2.0	DME	Yes	<5%
26	Bu^tOOBu^t	2.0	DME	Yes	<5%
27	BzOOBz	2.0	DME	Yes	<5%[d]
28	$BzOOBu^t$	1.0	DME	Yes	24%
29	$BzOOBu^t$	3.0	DME	Yes	48%
30	$BzOOBu^t$	4.0	DME	Yes	54%
31[e]	$BzOOBu^t$	2.0	DME	Yes	45%
32[f]	$BzOOBu^t$	2.0	DME	Yes	<5%

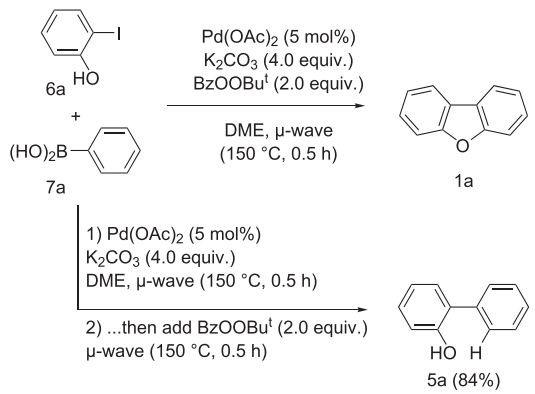
DDME, diethyleneglycoldimethylether; IBX, *ortho*-iodoxybenzoic acid; Cum, cumyl.
[a]Addition of water (20 vol%) as a cosolvent.
[b]Addition of molecular sieves (3 Å, 40 wt%) to the solvent.
[c]Reaction was run under conventional heating conditions (oil bath) and slow addition of the oxidant via syringe pump.
[d]Product observed in trace amounts by ^1H NMR.
[e]$Pd(OAc)_2$ (5 mol%), $BzOOBu^t$ (2.0 equiv.), **5a** in DME, 20°C, 3 h; then μ-wave, 150°C, 0.5 h.
[f]$BzOOBu^t$ (2.0 equiv.), **5a** in DME, μ-wave, 150°C, 0.5 h; then add $Pd(OAc)_2$ (5 mol%), μ-wave, 150°C, 0.5 h.

microwave conditions, we focused in further studies on the highest boiling of these solvents, DME. First, we checked whether the use of dry DME is really necessary but discovered that the isolated yield of dibenzofuran (**1a**) is significantly lower with undried and unpurified solvent (entry 13). When dried and purified DME was used together with water as a cosolvent, the reaction failed completely and unreacted **5a** was recovered (entry 14). On the other hand, addition of 3 Å molecular sieves to dried and purified DME did not lead to a notably improved yield (entry 15).

In an earlier, unrelated study on Ru-catalyzed allylic oxidation reactions with hydroperoxides as oxidants [50], we had discovered that yields and selectivities improve significantly if the oxidant is slowly added, preferably with a syringe pump. The required experimental setup cannot be combined routinely with a microwave apparatus. For these reasons, we investigated the effect of slow oxidant addition under conventional heating conditions in the similarly polar, but higher boiling solvent diethyleneglycoldimethylether (DDME) (entry 17). The isolated yield of **1a** was, however, very similar to the yield obtained in benzene, THF, or DME. For comparison, DDME was also used for the oxidative cyclization under microwave irradiation, with the full quantity of oxidant present from the beginning (entry 16). Under these conditions, a lower yield of **1a** was obtained than for DME (entry 12) or syringe pump addition of the oxidant (entry 17). In Wei and Yoshikai's pioneering study on the oxidative cyclization of 2-arylphenols, several oxidants were screened under their standard conditions, with the result that only $BzOOBu^t$ leads to a notable conversion to the desired dibenzofurans [46]. As our conditions are markedly different with respect to the solvent and the heating conditions, we repeated the oxidant screening. As expected, no conversion was observed in the absence of any oxidant (entry 18), and several other oxidants (entries 19–26) turned out to be equally ineffective, including two hydroperoxides (entries 23, 24) and two symmetrical peroxides (entries 25, 26). Trace amounts of **1a** were observed with BzOOBz, but the conversion was too low to allow isolation of the product (entry 27). Further investigations revealed that an amount of two equivalents of $BzOOBu^t$ (entry 12) is optimal, as both lower (entry 28) and higher (entries 29, 30) quantities result in decreased conversions and isolated yields. To gain additional insight into the stability of the oxidant under the oxidative cyclization conditions, two final experiments were performed. When $Pd(OAc)_2$, the oxidant, and **5a** were stirred at ambient temperature for 3 h, no conversion to the product was observed. Neither the starting material nor the oxidant decompose to a notable extent, and the Pd catalyst also appears to be unaffected by the presence of the oxidizing agent. If, after this time, the reaction mixture is irradiated in the microwave reactor, conversion to the dibenzofuran occurs, which could be isolated in 45% yield (entry 31). If the reaction mixture is subjected to microwave irradiation in the absence of the Pd catalyst, the oxidant decomposes quantitatively, but the starting material **5a** is not affected by the thermal peroxide decomposition. Upon addition of the Pd catalyst and renewed irradiation, no conversion to the product is observed, which indicates that the oxidant is indeed completely decomposed (entry 32).

Attempts toward a tandem Suzuki coupling-oxidative cyclization sequence. In an attempt to combine the biaryl synthesis and its oxidative cyclization to a tandem sequence, equimolar amounts of *ortho*-iodophenol (**6a**) and phenylboronic acid (**7a**) were subjected to microwave irradiation in DME in the presence of K_2CO_3 (the base required for the Suzuki coupling), the oxidant $BzOOBu^t$ (for the oxidative cyclization), and $Pd(OAc)_2$ as a precatalyst for both transformations. We could not detect the dibenzofuran from the crude reaction mixture but identified the Suzuki coupling product **5a**, which was formed along with other unidentified by-products in minor amounts. Obviously, the presence of the peroxide, which is supposed to oxidize a Pd(II) intermediate to a Pd(IV) intermediate during the oxidative cyclization, does not fully inhibit the cross-coupling step, which relies on the oscillation between Pd(0) and Pd(II) intermediates. However, it is evident that the peroxide interferes adversely with the Suzuki coupling, and we investigated for this reason a stepwise addition of the reagents required for the individual steps. *o*-Iodophenol (**6a**) and the boronic acid **7a** reacted upon microwave irradiation smoothly and selectively in the presence of K_2CO_3 as a base to the expected 2-phenylphenol (**5a**). The oxidant $BzOOBu^t$ was then added to the reaction mixture, and microwave irradiation was continued. However, no dibenzofuran could be detected in the reaction mixture. Instead, the Suzuki coupling product **5a** was isolated in high yield (Scheme 3).

Scheme 3. Attempted tandem Suzuki coupling-oxidative cyclization sequence.



These observations suggest that one of the reagents required for the Suzuki coupling, or one of the by-products, inhibit the oxidative cyclization step. To check this hypothesis, we repeated the oxidative cyclization of **5a** to **1a** under optimized conditions but in the presence of additives known to promote Suzuki couplings. Remarkably, the oxidative cyclization is nearly completely inhibited if K_2CO_3 is present; the standard base used for the microwave-promoted Suzuki coupling. With tetrabutylammonium fluoride (TBAF)-trihydrate, the dibenzofuran was detected only in trace amounts, but this might be attributed to the adverse effect of water rather than to the fluoride ion. KF, in contrast, does not completely inhibit the oxidative cyclization but leads to a decreased yield of 24%. If NaOAc was added to the mixture, virtually the same yield of **1a** was obtained as for additive-free conditions (Scheme 4).

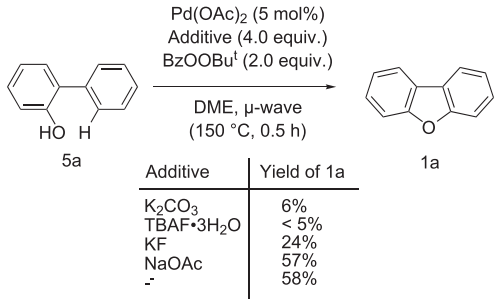
Unfortunately, NaOAc turned out to be ineffective to promote the Suzuki coupling under the conditions required for the envisaged tandem sequence. We tried to mend this problem by using potassium phenyltrifluoroborate as an alternative organoboron reagent [51,52], but to no avail. Neither with or without basic or nucleophilic rate accelerating additives did *ortho*-iodophenol (**6a**) react with K[F_3BPh] to the intermediate **5a**. Most likely, the reasons for this failure are the strictly anhydrous conditions, which are mandatory for the oxidative cyclization but disadvantageous for Suzuki couplings of organotrifluoroborates, because the formation of the actual reactive species, the boronic acid, through slow hydrolysis is not possible [53]. These rather disappointing results prompted us to pursue the development of a tandem Suzuki coupling-oxidative cyclization sequence not further.

Scope and limitations of microwave-promoted oxidative cyclization of 2-arylphenols. Scope and limitations of the oxidative cyclization under the conditions optimized for microwave irradiation (refer to Table 1) were evaluated for a set of *ortho*-arylphenols **5**. Starting materials **5a**, **b** [47] and **5f–h** [48] are either commercially available or were synthesized via Pd/C-catalyzed Suzuki coupling under the aqueous protecting group-free conditions previously disclosed by us. Monoprotected 2,2′-biphenols **5c–e** were synthesized from **5b** through monoalkylation or monsilylation (Table 2).

The 2-phenyl phenols **5k**, **l** were obtained via heterogeneously catalyzed Suzuki coupling of iodoarenes **6k**, **l** with phenylboronic acid **7a** in aqueous media and under conventional heating conditions, following our previously published procedure. For the synthesis of **5k**, the standard additive K_2CO_3 was replaced by KF and the reaction was run in a water/ethanol mixture to improve the solubility of the reactants (Scheme 5) [48].

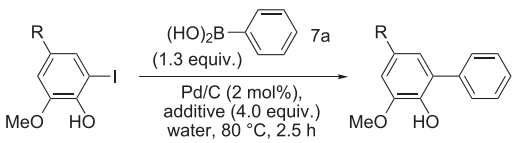
For the synthesis of **5i′, j, m,** and **n**, *ortho*-boronophenol (**7b**) was used as the coupling partner for aryl iodides **6i′**, **j**, **n** and aryl bromide **6 m**. The coupling of 2-bromonaphthalene (**6m**) required microwave irradiation at 150°C, while the aryl iodides reacted at 80°C under conventional heating conditions (Table 3) [48].

Scheme 4. Effect of additives on the oxidative cyclization sequence.



Additive	Yield of 1a
K_2CO_3	6%
TBAF•3H_2O	< 5%
KF	24%
NaOAc	57%
-	58%

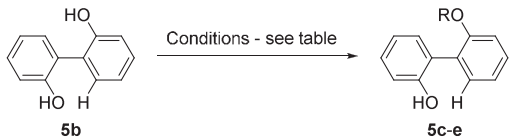
Scheme 5. Syntheses of **5k** and **5l**.



6k (R = CH=CHCO$_2$Et; additive: KF) 5k (87%)
6l (R = CHO; additive: K_2CO_3) 5l (97%)

Table 2

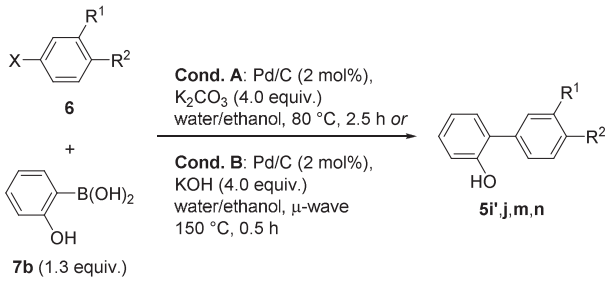
Synthesis of monoprotected 2,2′-biphenols.



Entry	Reaction conditions	R	Product	Yield
1	Allyl bromide (1.0 equiv.), K_2CO_3 (1.0 equiv.), DMF, 70°C 14 h	OAllyl	**5c**	95%
2	Benzyl bromide (1.0 equiv.), KOBu^t (1.0 equiv.), THF, 65°C, 14 h	OBn	**5d**	90%
3	TBSCl (1.0 equiv.), imidazol (1.1 equiv.), CH_2Cl_2, 20°C, 14 h	OTBS	**5e**	96%

Table 3

Synthesis of 2-arylphenols **5i′**, **j**, **m**, **n**.



Entry	6	X	R^1	R^2	Conditions	5	Yield
1	**6i′**	I	NO_2	H	A	**5i′**	96%
2	**6j**	I	H	NO_2	A	**5j**	88%
3	**6m**	Br	CH=CHCH=CH		B	**5m**	94%
4	**6n**	I	H	Me	A	**5n**	88%

2-Phenyl-4-nitrophenol (**5i**) was synthesized from 2-phenylphenol (**5a**) by regioselective nitration with nitric acid (Scheme 6).

The 2-arylphenols **5a–n** were next subjected to the oxidative cyclization conditions under microwave irradiation (Table 4). As Wei and Yoshikai reported a beneficial effect of 3-nitropyridine as an ancillary ligand, we repeated the oxidative cyclization of **5a** to **1a** in the presence of 5 mol % of this ligand. For this example, we could indeed observe a substantially higher yield of 80% (entry 2). Larger amounts of 3-nitropyridine (entry 3) or phosphine ligands (entries 4, 5) were detrimental. 2,2′-Biphenol (**5b**) and its monoalkylated derivatives **5c** and **5d** gave the corresponding dibenzofurans only in trace amounts (entries 6–8). While **5b** did not react under these conditions, presumably because of chelation of the Pd by both OH groups, **5c** and **5d** underwent extensive decomposition, which is probably initiated by allylic or benzylic oxidation of the O–CH_2 moiety. Only the tert-butyldimethylsilyl (TBS)-protected derivative **5e** could be cyclized to **1e** in a moderate yield (entries 9 and 10). Comparable yields of 25 and 22%, respectively, were obtained for the oxidative cyclization of the isomeric methyl ethers **5f** and **5h** (entries 11 and 14), whereas the yield of 4-methoxydibenzofuran (**1g**) from **5g** was considerably higher (entry 12). In this case, addition of 3-nitropyridine resulted only in a slightly increased yield (entry 13). We reason that the increased yield can be attributed to the location of the electron-donating substituent in *para*-position to the C–H activation site, which would enhance the nucleophilicity and faciliate electrophilic palladation. However, it is evident that other factors play a significant role, as the yield for all methoxysubstituted dibenzofurans is much lower than the yield obtained for the parent compound **1a**. As examples for electron-deficient 2-arylphenols, three nitrosubstituted derivatives were investigated (entries 15–17). Compounds **5i** and **5i′** react to the same 4-nitrodibenzofuran (**1i**). Starting from **5i**, with the electron-withdrawing substituent located *para* to the OH group, the isolated yield of **1i** is low (entry 15), but for the cyclization of **5i′** (with the nitro group *para* to the C–H activation site), a comparable yield could only be achieved by the addition of the ancillary ligand 3-nitropyridine (entry 16). Moving the electron-withdrawing group to the position *meta* to the C–H activation site results, as expected, in a higher but still moderate yield (entry 17). While Wei and Yoshikai do not report any examples for the oxidative cyclization of 2-arylphenols substituted with strongly electron-withdrawing substituents [46], Liu and coworkers observed high yields for some of these substrates, inter alia **5i′**, with their catalyst system [44]. These authors could also show that under their conditions (using a Pd-NHC catalyst, a carboxylate ancillary ligand, and air as an oxidant), an α,β-unsaturated ester moiety is tolerated. With the example of **5k,** we included such a derivative in our study but discovered that the standard conditions result in complete decomposition (entry 18). We reasoned that the C–C double bond is prone to oxidative cleavage and that a reduced amount of oxidant might be beneficial. With 1.0 equiv. of $BzOOBu^t$, we could indeed isolate the dibenzofuran **1k**, but conversion remained incomplete

Scheme 6. Synthesis of **5i** via regioselective nitration of **5a**.

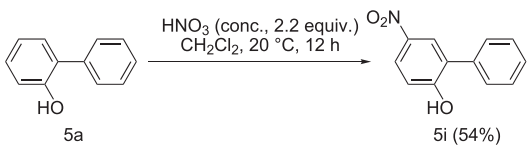
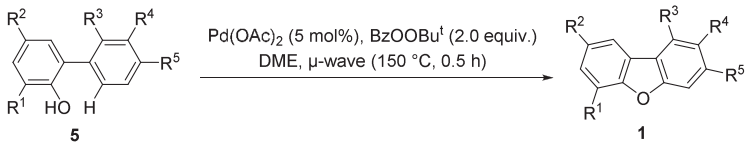


Table 4

Scope and limitations of microwave-promoted oxidative cyclization.[a]



Entry	5	R^1	R^2	R^3	R^4	R^5	$BzOOBu^t$ (equiv.)	1	Yield
1	**5a**	H	H	H	H	H	2.0	**1a**	58%
2[b]	**5a**	H	H	H	H	H	2.0	**1a**	80%
3[c]	**5a**	H	H	H	H	H	2.0	**1a**	43%
4[d]	**5a**	H	H	H	H	H	2.0	**1a**	10%
5[e]	**5a**	H	H	H	H	H	2.0	**1a**	20%
6	**5b**	H	H	OH	H	H	4.0	**1b**	<5%
7	**5c**	H	H	OAllyl	H	H	2.0	**1c**	<5%
8	**5d**	H	H	OBn	H	H	2.0	**1d**	<5%
9	**5e**	H	H	OTBS	H	H	2.0	**1e**	34%
10	**5e**	H	H	OTBS	H	H	4.0	**1e**	44%
11	**5f**	H	H	OMe	H	H	2.0	**1f**	25%
12	**5g**	H	H	H	OMe	H	2.0	**1g**	38%
13[b]	**5g**	H	H	H	OMe	H	2.0	**1g**	46%
14	**5h**	H	H	H	H	OMe	2.0	**1h**	22%
15	**5i**	H	NO_2	H	H	H	4.0	**1i**	22%
16[b]	**5in**	H	H	H	NO_2	H	2.0	**1i**	21%
17[b]	**5j**	H	H	H	H	NO_2	2.0	**1j**	33%
18	**5k**	OMe	$CH{=}CHCO_2Et$	H	H	H	2.0	**1k**	<5%
19	**5k**	OMe	$CH{=}CHCO_2Et$	H	H	H	1.0	**1k**	16%
20	**5l**	OMe	CHO	H	H	H	2.0	**1l**	62%
21[b]	**5l**	OMe	CHO	H	H	H	2.0	**1l**	69%
22[b,f]	**5m**	H	H	H	CH=CHCH=CH		2.0	**1m**	<60%
23[b]	**5n**	H	H	H	H	Me	2.0	**1n**	62%

[a]Optimized conditions as stated in Table 1, entry 12, unless otherwise stated.
[b]With addition of 3-nitropyridine (5 mol%).
[c]With addition of 3-nitropyridine (2.0 equiv.).
[d]With addition of PCy_3 (20 mol%).
[e]With addition of PPh_3 (20 mol%).
[f]Isolated together with numerous impurities.

and the isolated yield was very low (entry 19). The successful conversion of **5l** to **1l** illustrates that an oxidation-sensitive carbaldehyde group is tolerated under the oxidative cyclization conditions. In this case, addition of 3-nitropyridine leads only to a marginally improved yield (entries 20 and 21). A rather sluggish reaction was observed for the naphthalene derivative **5m** (entry 22): While the expected naphto[2,3-b]benzofuran (**1m**) is clearly the main product and could be identified via its spectroscopical data, the reaction mixture was contaminated with a substantial amount of by-products that could not be removed, even after repeated chromatography. A reason for the poor selectivity in this case might be partial oxidative degradation of the naphthalene moiety. In contrast, oxidation of alkyl side chains does not seem to be a significant problem under the oxidative cyclization conditions, as the tolylderivative **5n** was converted to 3-methyldibenzofuran (**1n**) in good selectivity and yield (entry 23).

CONCLUSION

In summary, we have investigated a tandem synthesis of dibenzofurans from haloarenes and boronic acids that proceeds via Suzuki coupling and oxidative cyclization. Our results show that the tandem concept has clear limitations, in particular if—as in the present case—solvent compatibility issues cannot be resolved. In the course of this investigation, we have identified alternative reaction conditions for the Pd-catalyzed oxidative cyclization of *ortho*-arylphenols that differ from previously reported conditions by using a less elaborate solvent and microwave irradiation to achieve reduced reaction times.

EXPERIMENTAL

General. ^1H NMR spectra were obtained at 300 MHz in $CDCl_3$ with $CHCl_3$ ($\delta = 7.26$ ppm) as an internal

standard or in methanol-d_4 with CHD_2OD (δ = 3.31 ppm) as an internal standard. Coupling constants (*J*) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ with $CHCl_3$ (δ = 77.0 ppm) as an internal standard or in methanol-d_4 with CD_3OD (δ = 49.2 ppm) as an internal standard. IR spectra were recorded as ATR-FTIR spectra. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m), or weak (w). Low- and high-resolution mass spectra were obtained by EI- or ESI-TOF. Microwave reactions were carried out in an Anton-Paar monowave-300 reactor at 150°C (monowave, maximum power 850 W, temperature control via IR sensor, vial volume: 20 mL). These starting materials were purchased or synthesized following literature procedures: **5a–5b** [47] and **5f–h** [48].

Syntheses and Analytical Data of *Ortho*-Arylphenols 5.

2'-(Allyloxy)-[1,1'-biphenyl]-2-ol (5c) [54]. To a solution of **5b** (1.86 g, 10.00 mmol) in dry and degassed DMF (20 mL) was added K_2CO_3 (1.38 g, 10.00 mmol). Allyl bromide (0.86 mL, 10.00 mmol) was added, and the mixture was stirred at 70°C for 14 h. Aqueous HCl (1 M, 25 mL) was added, and the mixture was extracted with MTBE. The combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was chromatographed to furnish **5c** (2.14 g, 9.47 mmol, 95%). Colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.56–7.41 (m, 4H), 7.28–7.10 (m, 4H), 6.69 (s, 1H), 6.07 (ddt, *J* = 17.1, 10.4, 5.1 Hz, 1H), 5.45 (ddd, *J* = 17.3, 2.7, 1.3 Hz, 1H), 5.35 (ddd, *J* = 11.0, 2.6, 1.3 Hz, 1H), 4.67 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 154.5, 153.7, 132.4, 132.2, 131.3, 129.1, 129.1, 127.7, 126.3, 122.3, 120.8, 118.0, 117.4, 113.4, 69.8; IR (ATR) cm^{-1}: 3392 (bw), 1574 (w), 1479 (m), 1441 (m), 1223 (m), 991 (m); HRMS (EI) calcd for $C_{15}H_{14}O_2$ [M^+] 226.0994, found 226.0991.

2'-(Benzyloxy)-[1,1'-biphenyl]-2-ol (5d) [55]. To a solution of **5b** (186 mg, 1.00 mmol) in dry and degassed THF (20 mL) was added $KOBu^t$ (112 mg, 1.00 mmol). Benzyl bromide (0.12 mL, 1.00 mmol) was added, and the mixture was stirred at 65°C for 14 h. The solvent was removed *in vacuo*, and the residue was mixed with aqueous HCl (1 M, 10 mL). The mixture was extracted three times with MTBE; the combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was purified by chromatography on silica using hexane-MTBE mixtures as eluent to give **5d** (248 mg, 0.90 mmol, 90%). Colorless solid, mp 96–99°C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.42–7.35 (m, 2H), 7.35–7.27 (m, 7H), 7.18–7.09 (m, 2H), 7.07–7.00 (m, 2H), 6.33 (s, 1H), 5.13 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 155.0, 153.8, 136.2, 132.7, 131.4, 129.4, 129.4, 128.7, 128.3, 128.2, 127.4, 126.4, 122.9, 121.1, 117.6, 114.6, 72.0; IR (ATR) cm^{-1}: 3393 (bw), 1579 (w), 1440 (s), 1222 (s), 1126 (m); HRMS (EI) calcd for $C_{19}H_{16}O_2$ [M^+] 276.1150, found 276.1146. *Anal.* Calcd for $C_{19}H_{16}O_2$ (276.33): C, 82.6; H, 5.8. Found: C, 82.2; H, 6.0.

2'-((tert-Butyldimethylsilyl)oxy)-[1,1'-biphenyl]-2-ol (5e). To a solution of **5b** (3.72 g, 20.00 mmol) and imidazol (1.50 g, 22.00 mmol) in dry and degassed CH_2Cl_2 (100 mL) was added TBSCl (3.01 g, 20.00 mmol), and the mixture was stirred at ambient temperature for 14 h. The reaction mixture was washed with a saturated aqueous solution of NH_4Cl (30 mL); the aqueous layer was separated and extracted with MTBE. The combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica using hexane-MTBE mixtures as eluent to yield **5e** (5.96 g, 19.84 mmol, 96%). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.40–7.32 (m, 2H), 7.29–7.26 (m, 1H), 7.15 (td, *J* = 7.5, 1.2 Hz, 1H), 7.08–6.98 (m, 3H), 6.53 (s, 1H), 0.87 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 153.9, 151.8, 132.5, 131.2, 130.4, 129.3, 129.1, 127.1, 123.2, 121.1, 120.8, 117.9, 25.6, 18.1, −4.6; IR (ATR) cm^{-1}: 3406 (bw), 1497 (m), 1478 (m), 1223 (m), 834 (s); HRMS (EI) calcd for $C_{18}H_{24}O_2Si$ [M^+] 300.1546, found 300.1524. *Anal*. Calcd for $C_{18}H_{24}O_2Si$ (300.47): C, 72.0; H, 8.1. Found: C, 71.5; H, 7.8.

5-Nitro-[1,1'-biphenyl]-2-ol (5i) [41]. To a solution of **5a** (1.70 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was added a solution of aqueous nitric acid (68 wt%, 1.00 mL, 22.0 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at ambient temperature for 12 h, diluted with brine (20 mL), and then extracted with ethyl acetate. The combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was chromatographed on silica using hexane-MTBE mixtures as eluent to give **5i** (1.17 g, 5.4 mmol, 54%). Yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.21–8.15 (m, 2H), 7.60–7.43 (m, 5H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 158.3, 141.9, 134.8, 129.9, 129.2, 129.1, 128.8, 126.4, 125.3, 116.5; IR (ATR) cm^{-1}: 3372 (bw), 1587 (w), 1498 (m), 1337 (s), 1286 (s); HRMS (EI) calcd for $C_{12}H_9O_3N$ [M^+] 215.0577, found 215.0579. *Anal*. Calcd for $C_{12}H_9O_3N$ (215.21): C, 67.0; H, 4.2; N, 6.5. Found C, 66.9; H, 4.1; N, 6.6.

3'-Nitro-[1,1'-biphenyl]-2-ol (5i') [56]. To a suspension of **6i′** (747 mg, 3.00 mmol), **7b** (558 mg, 3.90 mmol), and K_2CO_3 (1.66 g, 12.00 mmol) in water (12 mL) and ethanol (6 mL) was added Pd/C (10 wt%, 60 mg, 2 mol%). The mixture was heated to 80°C for 2.5 h, then cooled to ambient temperature, and quenched by addition of aqueous HCl (1 M, 10 mL). It was extracted with MTBE (three times 50 mL); the combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was purified by chromatography on silica using hexane-MTBE mixtures as eluent to furnish **5i′** (622 mg, 2.89 mmol, 96%). Yellow

solid, mp 99–100°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.43 (t, J = 1.9 Hz, 1H), 8.21 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.89 (ddd, J = 7.7, 1.6, 1.1 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.40–7.24 (m, 2H), 7.05 (td, J = 7.5, 1.1 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 5.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 152.5, 148.6, 139.6, 135.5, 130.7, 130.1, 129.6, 126.2, 124.4, 122.3, 121.7, 116.5; IR (ATR) cm^{-1}: 3448 (bw), 1522 (s), 1347 (s), 749 (m), 727 (m); HRMS (EI) calcd for $C_{12}H_9O_3N$ [M^+] 215.0577, found 215.0574.

4′-Nitro-[1,1′-biphenyl]-2-ol (5j) [57]. Following the procedure stated in the preceding texts for **5i′**, **6j** (747 mg, 3.00 mmol) and **7b** (558 mg, 3.90 mmol) were coupled to give **5j** (570 mg, 2.65 mmol, 88%). Yellow solid, mp 119–120°C; ^{1}H NMR (300 MHz, methanol-d_4): δ (ppm) = 8.24 (d, J = 9.0 Hz, 2H), 7.81 (d, J = 9.0 Hz, 2H), 7.32 (dd, J = 7.9, 1.7 Hz, 1H), 7.22 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 6.98–6.88 (m, 2H); ^{13}C NMR (75 MHz, methanol-d_4): δ (ppm) = 155.9, 147.8, 147.4, 131.5, 131.3, 131.0, 127.5, 124.0, 121.1, 117.3; IR (ATR) cm^{-1}: 3448 (bw), 1597 (m), 1509 (m), 1452 (m), 1341 (s); HRMS (EI) calcd for $C_{12}H_9O_3N$ [M^+] 215.0577, found 215.0567.

***Ethyl-(E)*-3-(6-hydroxy-5-methoxy-[1,1′-biphenyl]-3-yl)acrylate (5k).** Following the procedure stated in the preceding texts for **5i**, **6k** (1.67 g, 5.0 mmol) and **7a** (732 mg, 6.50 mmol) were coupled to give **5k** (1.30 g, 4.36 mmol, 87%). Colorless solid, mp 111°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.66 (d, J = 15.9 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.36 (tm, J = 7.3 Hz, 1H), 7.18 (d, J = 1.8 Hz, 1H), 7.04 (d, J = 1.9 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 6.11 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.4, 147.2, 145.1, 144.8, 137.0, 129.2, 128.5, 128.0, 127.7, 126.7, 124.4, 116.1, 108.3, 60.5, 56.4, 14.5; IR (ATR) cm^{-1}: 1698 (m), 1633 (m), 1417 (m), 1263 (m), 1158 (s); HRMS (EI) calcd for $C_{18}H_{18}O_4$ [M^+] 298.1205, found 298.1208.

6-Hydroxy-5-methoxy-[1,1′-biphenyl]-3-carbaldehyde (5l) [58]. Following the procedure stated in the preceding texts for **5i′**, **6l** (1.39 g, 5.0 mmol) and **7a** (0.73 g, 6.5 mmol) were coupled to give **5l** (1.10 g, 4.8 mmol, 97%). The reaction was run in water instead of the water-ethanol mixture used for the synthesis of **5i′**. Colorless solid, mp 109–110°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.88 (s, 1H), 7.65–7.60 (m, 2H), 7.52 (d, J = 1.7 Hz, 1H), 7.50–7.33 (m, 4H), 6.45 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 191.1, 148.8, 147.6, 136.4, 129.5, 129.2, 128.8, 128.6, 127.9, 127.8, 107.6, 56.6; IR (ATR) cm^{-1}: 3356 (bw), 1679 (m), 1591 (m), 1423 (m), 1311 (s); HRMS (EI) calcd for $C_{14}H_{12}O_3$ [M^+] 228.0786, found 228.0780.

2-(Naphthalene-2-yl)phenol (5m) [59]. In a vessel suited for microwave irradiation was placed a suspension of **6m** (414 mg, 2.00 mmol), **7b** (359 mg, 2.60 mmol), and KOH (448 mg, 8.00 mmol) in water (12 mL) and ethanol (6 mL). Pd/C (10 wt%, 40 mg, 2 mol%) was added, and the mixture was irradiated in a dedicated microwave reactor at 150°C for 0.5 h, then cooled to ambient temperature, and quenched by addition of aqueous HCl (1 M, 10 mL). It was extracted with MTBE (three times 50 mL); the combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was purified by chromatography on silica using hexane-MTBE mixtures as eluent to furnish **5m** (412 mg, 1.87 mmol, 94%). Colorless solid, mp 92–95°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.05–7.95 (m, 2H), 7.95–7.88 (m, 2H), 7.65–7.48 (m, 3H), 7.43–7.30 (m, 2H), 7.11–7.01 (m, 2H), 5.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 152.7, 134.6, 133.7, 132.8, 130.6, 129.4, 129.3, 128.2, 128.0, 127.9, 127.9, 127.3, 126.8, 126.6, 121.1, 116.0; IR (ATR) cm^{-1}: 3532 (bw), 1489 (w), 1450 (w), 1279 (w), 752 (s); HRMS (EI) calcd for $C_{16}H_{12}O$ [M^+] 220.0883, found 220.0883.

4′-Methyl-[1,1′-biphenyl]-2-ol (5n) [60]. Following the procedure stated in the preceding texts for **5i′**, **6n** (436 mg, 2.00 mmol) and **7b** (359 mg, 2.60 mmol) were coupled to give **5n** (323 mg, 1.76 mmol, 88%). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.37 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.26–7.19 (m, 2H), 7.03–6.96 (m, 2H), 5.25 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 152.6, 137.9, 134.1, 130.3, 130.1, 129.1, 129.1, 128.2, 120.9, 115.8, 21.4; IR (ATR) cm^{-1}: 3535 (bw), 1481 (m), 1448 (m), 1780 (m), 750 (s); HRMS (EI) calcd for $C_{13}H_{12}O$ [M^+] 184.0883, found 184.0891.

Syntheses and Analytical Data of Dibenzofurans 1.

General procedure for the microwave-promoted synthesis of dibenzofurans 1 via oxidative cyclization. The appropriate *ortho*-arylphenol **5** (1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 5 mol%), $BzOOBu^t$ (372 μL, 2.00 mmol), and 3-nitropyridine (*optional*—refer to Table 2, 7.7 mg, 5 mol%) were dissolved in dry and degassed dimethoxyethane (5 mL) in a vessel suited for microwave irradiation. The vessel was sealed, placed in a dedicated microwave reactor, and irradiated at 150°C for 0.5 h. After cooling the reaction mixture to ambient temperature, ethyl acetate was added (20 mL) and the solution was washed with a saturated aqueous solution of Na_2CO_3 (10 mL). The organic layer was separated, dried with $MgSO_4$, filtered, and evaporated. The residue was purified by chromatography on silica using hexane-MTBE mixtures of increasing polarity as eluent.

Dibenzo[b,d]furan (1a) [61]. Obtained from **5a** (170 mg, 1.00 mmol). Yield of **1a** without added 3-nitropyridine: 97 mg (0.58 mmol, 58%); yield of **1a** with added 3-nitropyridine: 135 mg (0.80 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00 (d, J = 7.6 Hz, 2H),

7.63 (d, J = 8.2 Hz, 2H), 7.51 (td, J = 7.9, 1.0 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.3, 127.2, 124.3, 122.8, 120.7, 111.8; IR (ATR) cm^{-1}: 3046 (w), 1596 (w), 1444 (s), 1189 (m), 719 (s); HRMS (EI) calcd for $C_{12}H_8O$ [M^+] 168.0575, found 168.0565.

tert-Butyl(dibenzo[b,d]furan-1-yloxy)dimethylsilane (1e). Obtained from **5e** (300 mg, 1.00 mmol). Yield of **1e** without addition of 3-nitropyridine: 132 mg, 0.44 mmol, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.23 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.48 (td, J = 7.6, 0.9 Hz, 1H), 7.41 (t, J = 6.7 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 1.19 (s, 9H), 0.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.9, 155.7, 151.8, 127.6, 126.3, 123.8, 122.8, 122.7, 116.3, 112.4, 111.2, 104.8, 26.1, 18.6, −3.8; IR (ATR) cm^{-1}: 2930 (w), 1597 (m), 1448 (s), 1235 (m), 1053 (s).

tert-Butyl(dibenzo[1-methoxydibenzo[b,d]furan (1f) [46]. Obtained from **5f** (100 mg, 0.50 mmol). Yield of **1f** without added 3-nitropyridine: 25 mg (0.25 mmol, 25%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.46 (tm, J = 7.5 Hz, 1H), 7.41 (td, J = 8.2, 1.0 Hz, 1H), 7.37 (tm, J = 7.4 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.5, 156.0, 155.6, 128.0, 126.3, 123.7, 123.0, 122.9, 113.7, 111.1, 104.5, 103.9, 55.8.

2-Methoxydibenzo[b,d]furan (1g) [46]. Obtained from **5g** (100 mg, 0.50 mmol). Yield of **1g** without added 3-nitropyridine: 38 mg (0.19 mmol, 38%); yield of **1g** with added 3-nitropyridine: 46 mg (0.23 mmol, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.53–7.43 (m, 2H), 7.43 (d, J = 2.5 Hz, 1H), 7.33 (td, J = 7.6, 0.9 Hz, 1H), 7.06 (dd, J = 8.9, 2.7 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.1, 156.0, 151.1, 127.2, 124.8, 124.6, 122.5, 120.7, 115.3, 112.2, 111.9, 103.9, 56.2; IR (ATR) cm^{-1}: 1481 (s), 1437 (m), 1186 (s), 1167 (s), 1034 (m); HRMS (EI) calcd for $C_{13}H_{10}O_2$ [M^+] 198.0681, found 198.0689.

3-Methoxydibenzo[b,d]furan (1h) [46]. Obtained from **5h** (100 mg, 0.50 mmol). Yield of **1h** without added 3-nitropyridine: 22 mg (0.11 mmol, 22%). Colorless solid, mp 79–81°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.86 (dd, J = 7.3, 1.1 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.38 (td, J = 7.7, 1.5 Hz, 1H), 7.31 (td, J = 7.4, 1.1 Hz, 1H), 7.10 (d, J = 2.2 Hz, 1H), 6.95 (dd, J = 8.5, 2.2 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 160.1, 157.7, 156.5, 125.8, 124.6, 122.9, 121.1, 119.9, 117.5, 111.5, 111.1, 96.7, 55.9; IR (ATR) cm^{-1}: 2934 (w), 1605 (m), 1457 (s), 1277 (s), 1144 (s); HRMS (EI) calcd for $C_{13}H_{10}O_2$ [M^+] 198.0675, found 198.0680.

2-Nitrodibenzo[b,d]furan (1i) [41]. Obtained from **5i** (108 mg, 0.50 mmol). Yield of **1i** without added 3-nitropyridine: 22 mg (0.10 mmol, 21%). Obtained from **5i′** (108 mg, 0.50 mmol). Yield of **1i** with added 3-nitropyridine: 23 mg (0.11 mmol, 22%). Yellow solid, mp 143–146°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.85 (d, J = 2.4 Hz, 1H), 8.38 (dd, J = 9.0, 2.4 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.66–7.60 (m, 2H), 7.56 (tm, J = 7.5 Hz, 1H), 7.44 (tm, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 159.3, 157.6, 144.0, 129.1, 125.2, 124.1, 123.2, 123.1, 121.4, 117.2, 112.4, 112.1; IR (ATR) cm^{-1}: 2924 (w), 1522 (s), 1337 (s), 1182 (m), 893 (m); HRMS (EI) calcd for $C_{12}H_7O_3N$ [M^+] 213.0420, found 213.0418.

3-Nitrodibenzo[b,d]furan (1j) [62]. Obtained from **5j** (108 mg, 0.50 mmol). Yield of **1j** with added 3-nitropyridine: 35 mg (0.16 mmol, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.42 (d, J = 1.9 Hz, 1H), 8.26 (dd, J = 8.5, 2.0 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H), 8.01 (dm, J = 7.5 Hz, 1H), 7.64 (dm, J = 8.2 Hz, 1H), 7.59 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.43 (td, J = 7.2, 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 158.4, 155.2, 146.9, 130.3, 129.7, 123.9, 122.6, 121.9, 120.6, 118.6, 112.4, 108.1; IR (ATR) cm^{-1}: 1525 (s), 1458 (w), 1347 (s), 1196 (w), 821 (w); HRMS (EI) calcd for $C_{12}H_7O_3N$ [M^+] 213.0426, found 213.0432.

Ethyl-(E)-3-(4-methoxydibenzo[b,d]furan-2-yl)acrylate (1k). Obtained from **5k** (149 mg, 0.50 mmol) with a reduced amount of oxidant (1.0 equiv.). Yield of **1k** without added 3-nitropyridine: 24 mg (0.08 mmol, 16%). Colorless solid, mp 45–47°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.95 (d, J = 7.4 Hz, 1H), 7.83 (d, J = 15.9 Hz, 1H), 7.72 (d, J = 1.0 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.50 (td, J = 7.5, 1.4 Hz, 1H), 7.38 (td, J = 7.6, 1.0 Hz, 1H), 7.16 (d, J = 1.2 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.10 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.1, 156.7, 146.7, 145.9, 145.0, 130.6, 127.8, 126.2, 124.0, 123.4, 121.0, 117.6, 113.9, 112.3, 108.5, 60.6, 56.4, 14.5; IR (ATR) cm^{-1}: 2929 (w), 1705 (s), 1269 (m), 1146 (s), 748 (m); HRMS (EI) calcd for $C_{18}H_{16}O_4$ [M^+] 296.1049, found 296.1063.

4-Methoxydibenzo[b,d]furan-2-carbaldehyde (1l). Obtained from **5l** (114 mg, 0.50 mmol). Yield of **1l** without added 3-nitropyridine: 70 mg (0.31 mmol, 62%); yield of **1l** with added 3-nitropyridine: 78 mg (0.35 mmol, 69%). Colorless solid, mp 101–103°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.99 (s, 1H), 7.95 (d, J = 1.3 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.47 (ddd, J = 8.2, 7.5, 1.1 Hz, 1H), 7.45 (d, J = 1.3 Hz, 1H), 7.35 (td, J = 7.5, 0.9 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 191.2, 156.7, 148.9, 146.2, 133.0, 128.1, 125.8, 123.6, 123.6, 120.9, 117.9, 112.2, 107.6, 56.3; IR (ATR) cm^{-1}: 2936 (w), 1687 (s), 1585 (m), 1345 (m), 1134 (s);

HRMS (EI) calcd for $C_{14}H_{10}O_3$ [M^+] 226.0624, found 226.0630.

Naphtho[2,3-b]benzofuran (1m) [22]. Obtained from **5m** (110 mg, 0.50 mmol), contaminated with impurities. Yield of **1m** with added 3-nitropyridine: <60 mg (<0.30 mmol, <60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.41 (s, 1H), 8.09 (dm, J = 8.0 Hz, 1H), 8.06 (dm, J = 7.6 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.95 (s, 1H), 7.59–7.49 (m, 4H), 7.40 (td, J = 7.4, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.8, 155.0, 133.2, 130.3, 128.5, 128.0, 127.9, 125.9, 125.6, 124.4, 124.1, 122.9, 121.4, 119.3, 111.7, 107.1; IR (ATR) cm^{-1}: 3051 (w), 1463 (m), 1201 (m), 870 (m), 739 (s); HRMS (EI) calcd for $C_{16}H_{10}O$ [M^+] 218.0726, found 218.0720.

3-Methyldibenzo[b,d]furan (1n) [33]. Obtained from **5n** (92 mg, 0.50 mmol). Yield of **1n** with added 3-nitropyridine: 56 mg (0.31 mmol, 62%). Colorless solid, mp 56–59°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (dd, J = 7.6, 0.7 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.59 (dd, J = 8.2, 0.7 Hz, 1H), 7.45 (td, J = 7.3, 1.4 Hz, 1H), 7.41 (s, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.8, 156.3, 137.8, 126.6, 124.5, 124.1, 122.7, 121.8, 120.4, 120.3, 112.0, 111.7, 22.1; IR (ATR) cm^{-1}: 2921 (w), 1457 (m), 1206 (w), 1127 (w), 809 (m); HRMS (EI) calcd for $C_{13}H_{10}O$ [M^+] 182.0726, found 182.0731.

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