A New, Expeditious Entry to the Benzophenanthrofuran Framework by a Pd-Catalyzed *C*- and *O*-Arylation/PIFA-Mediated Oxidative Coupling Sequence

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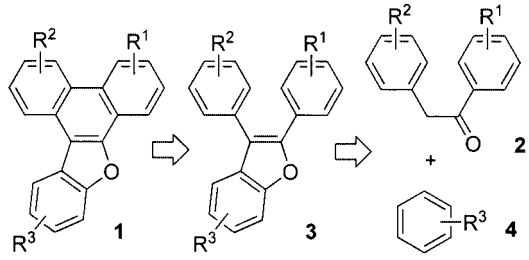
The synthesis of a series of 2,3-diarylbenzo[*b*]furans starting from 1,2-diarylethanones and 1,2-dibromoarenes proceeds by means of both homogeneous and polymer-anchored palladium catalysts. This tandem process can be effectively halted at the *C*-arylation step, thus providing key *o*-bromoarylated deoxybenzoin intermediates in good yields. The efficient oxidative coupling leading to benzo[*b*]phenanthro[9,10-*d*]furans is carried out using the safer hypervalent iodine reagent PIFA.

Introduction

The remarkable biological significance of 2,3-diarylbenzo[*b*]furans is clearly exemplified by the resveratrol-derived natural oligomers anigopreissin A and amurensins L and M inter alia,[1] and the pharmacological use of some other derivatives bearing the same framework.[2] Consequently, several synthetic approaches to such interesting systems, classified according to the number of bonds formed in the construction of the heterocycle, have been designed so far.[3,4] Among the protocols based on the sequential formation of two bonds of the furan moiety,[4] the palladium-catalysed coupling reaction between deoxybenzoins and dibromoarenes, first reported by Miura et al.,[5] is an elegant example of a tandem *C*-arylation/*O*-arylation reaction, although, in our opinion, it is still underexploited.

Phenanthro[9,10] heterocycles are also a target skeleton in the field of molecular materials. Apart from their use as large planar building blocks in supramolecular chemistry,[6] their unique photophysical properties make them suitable for a range of industrial and biological applications, including molecular tweezers for explosives, superradiant laser dyes,[7] chemical sensors,[8] pH-induced luminescent switches for energy conversion and information storage,[9] anisotropic liquid crystals in birefringent films,[10] photochromic dyes and sensitizers[11] or electroluminescent layers in light-emitting devices,[12] inter alia.[13]

Encouraged by the above illustrated interest in both diarylbenzofurans and phenanthroheterocycles, we envisaged a synthetic pathway to benzo[*b*]phenanthro[9,10-*d*]furans **1** starting from 1,2-diarylethanones **2**. Besides their availability, the choice of such starting materials was made considering our recently developed procedure for the access to deoxybenzoins, which is a more environmentally friendly protocol based on a palladium-catalysed monoarylation of acetophenones performed by polymer-anchored catalysts.[14] This paper describes the most noteworthy results obtained towards the completion of such a synthetic task.



Results and Discussion

Tandem *C*-Arylation/*O*-Arylation

Keeping in mind the pioneering work of Miura et al.,[5] we initially carried out several assays in order to optimise

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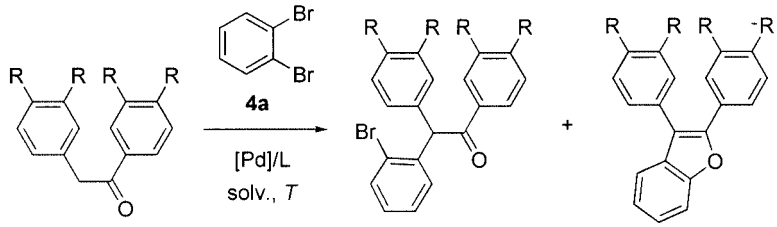
Table 1. Selected palladium-catalysed coupling assays with ketones **2a**,**b** and dibromobenzene **4a**.



R = H **2a**
R = OMe **2b**

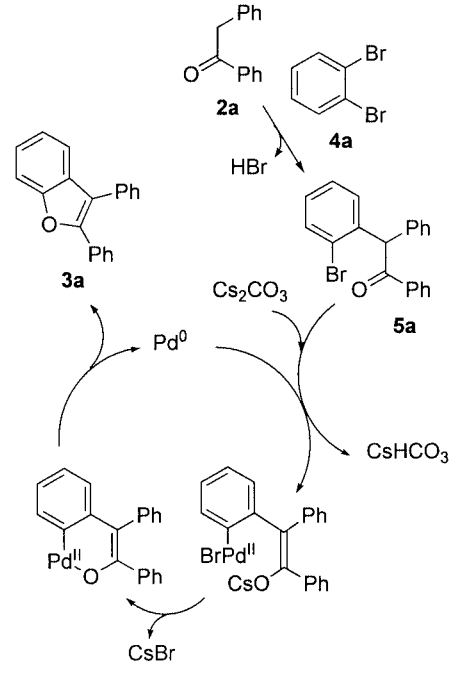
R = H **5a**
R = OMe **5b**

R = H **3a**
R = OMe **3b**

Entry	Reaction conditions	Product (yield [%])[a]
1	**2a**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 160 °C, 4 h[b][c]	**3a** (62), **2a** (5)
2	**2a**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, K_2CO_3, *o*-xylene, 160 °C, 24 h[b][c]	**3a** (42), **5a** (37)
3	**2b**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 160 °C, 4 h[b][c]	**3b** (57), **2b** (9)
4	**2b**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, K_2CO_3, *o*-xylene, 160 °C, 24 h[b][c]	**3b** (33), **5b** (36)
5	**2a**, 2 mol-% $Pd(OAc)_2$, 8 mol-% PPh_3, Cs_2CO_3, DMF, 150 °C, 6 h[b][c]	**3a** (38), **5a** (5), **2a** (3)
6	**2a**, 2 mol-% $Pd(OAc)_2$, 8 mol-% PPh_3, Cs_2CO_3, DMF, 170 °C, 6 h[b][c]	**3a** (16)
7	**2a**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, DMF, 150 °C, 6 h[b][c]	**3a** (21), **5a** (2)
8	**2a**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, DMF, 135 °C, 6 h[b][c]	–[d]
9	**2a**, 1 mol-% $Pd(OAc)_2$, 4 mol-% PPh_3, Cs_2CO_3, DMF, 150 °C, 16 h[c][e]	**3a** (32), **5a** (5), **2a** (8)
10	**2a**, 5 mol-% $Pd(OCOCF_3)_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 165 °C, 1.5 h[c][e]	**3a** (53)
11	**2a**, 0.5 mol-% $Pd(PPh_3)_4$, Cs_2CO_3, *o*-xylene, 165 °C, 6 h[b][c]	**3a** (3), **5a** (82), **2a** (3)
12	**2b**, 0.5 mol-% $Pd(PPh_3)_4$, Cs_2CO_3, *o*-xylene, 165 °C, 6 h[b][c]	**5b** (87), **2b** (5)
13	**2a**, 0.5 mol-% $Pd(PPh_3)_4$, Cs_2CO_3, DMF, 150 °C,1,5 h[c][e]	**3a** (5), **5a** (8)
14	**2a**, 5 mol-% $PdCl_2$, 20 mol-% PPh_3, K_2CO_3, DMF, 130 °C, 6 h[b][f]	**2a** (96)
15	**2a**, 5 mol-% $PdCl_2$, 20 mol-% PPh_3, K_2CO_3, DMF, 150 °C, 2 h[b][f]	–[d]
16	**2a**, 5 mol-% $PdCl_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 165 °C, 1.5 h[c][e]	**3a** (14), **2a** (4)
17	**2a**, 1 mol-% $Pd(OAc)_2$, 4 mol-% PPh_3, K_2CO_3, *o*-xylene, 150 °C, 8 h[b][c]	**5a** (92), **3a** (3)
18	**2b**, 1 mol-% $Pd(OAc)_2$, 4 mol-% PPh_3, K_2CO_3, *o*-xylene, 150 °C, 8 h[b][c]	**5b** (95), **2b** (1)
19	**2a**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 165 °C, 1.5 h[c][e]	**3a** (91)
20	**2b**, 5 mol-% $Pd(OAc)_2$, 20 mol-% PPh_3, Cs_2CO_3, *o*-xylene, 165 °C, 1.5 h[c][e]	**3b** (84)

[a] GC-MS ratios of detected products measured on the basis of the starting amount of deoxybenzoins **2a**,**b**. Propiophenone was used as the internal standard. The rest of the reaction crude contained complex mixtures of unidentified products. [b] 1.2 Equiv. of 1,2-dibromobenzene **4a** was used. [c] 2.5 Equiv. of base was used. [d] Complex mixtures of products. [e] 1.5 Equiv. of 1,2-dibromobenzene **4a** was used. [f] 3.0 Equiv. of base was used.

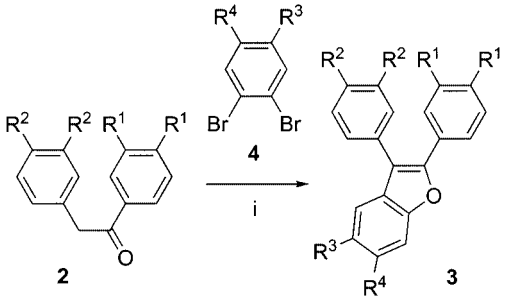
the generation of 2,3-diarylbenzofurans **3a**,**b** by means of a palladium-catalysed coupling of deoxybenzoins **2a**,**b** and dibromobenzene **4a**. To our surprise, the application of the above-mentioned bibliographic conditions[5] (entries 1–4 in Table 1) provided unexpected results, such as lower ratios of the target diarylbenzofurans **3** and the presence of remarkable amounts of triarylethanones **5a**,**b**. A brief mechanistic proposal based on previous work[5] is shown in Scheme 1. Accordingly, a more comprehensive study with a larger array of assays, summarised in Table 1, was performed. Not only were furan derivatives **3a**,**b** obtained in fair ratios (Table 1, entries 19 and 20), but the monoarylated intermediates **5a**,**b** were also efficiently prepared by a slight modification of the reaction conditions (Table 1, entries 17 and 18). Although our synthetic goal was not the latter, the easy preparation of such appealing building blocks[15] should not be underestimated. At this point, the noteworthy differences in terms of yield when performing only slight modifications in the reaction conditions (compare entries 1 and 19 in Table 1), and the great influence of the base employed, on the progress of the reaction (Table 1, entries 18 and 20) must be outlined. The optimised conditions for the preparation of furans **3a**,**b** were applied to a



Scheme 1.

range of diarylethanones **2** and dibromoarenes **4** to give the corresponding derivatives **3a**–**l** (Table 2).

Table 2. Diarylbenzofurans **3** prepared by homogeneous and heterogeneous catalysis.



i: Method A: $Pd(OAc)_2$, PPh_3, Cs_2CO_3, *o*-xylene, 165 °C, 1.5–4 h

Method B: FibreCat™ 1026, Cs_2CO_3, *o*-xylene, 165 °C, 8 h

Entry	R^1	R^2	R^3	R^4	**3** (yield [%])[a]
1	H	H	H	H	**3a** (87) *60*
2	OMe	OMe	H	H	**3b** (77) *74*
3	H	H	OMe	OMe	**3c** (65) *58*
4	OMe	H	H	H	**3d** (70) *69*
5	OMe	H	Me	Me	**3e** (87) *68*
6	OMe	H	F	F	**3f** (73) *71*
7	OMe	H	OMe	OMe	**3g** (79) *75*
8	OMe	H	OCH_2OOMe		**3h** (76) *70*
9	OMe	OMe	Me	Me	**3i** (78) *65*
10	OMe	OMe	F	F	**3j** (62) *68*
11	OMe	OMe	OMe	OMe	**3k** (81) *70*
12	OMe	OMe	OCH_2OOMe		**3l** (75) *68*

[a] Yield of pure crystalline compound (EtOAc). Yields of compounds obtained with method A are shown in parentheses and those with method B are given in italics.

The generality of the presented procedure relies on the fact that no substantial difference can be found when using electronically quite divergent dibromides **4**, since target derivatives **3** were obtained with good yields in all cases. With regard to deoxybenzoins, the choice of ketone precursors **2** was in our case heavily influenced by the next scheduled step of the synthetic sequence − the intramolecular coupling of the aryl rings attached to the C-2 and C-3 positions − as such oxidative ring-closure usually requires hydroxylated or alkoxylated coupling partners.[16]

Synthesis of Diarylbenzofurans by Means of Polymer-Anchored Palladium Catalysts

Nevertheless, before attempting the above-mentioned oxidative coupling we decided to explore the synthesis of benzofurans **3** using heterogeneous palladium catalysts, encouraged not only by the current tendency, based on sustainable chemistry principles, towards heterogeneous catalysis, but also by the scarcity of bibliographic examples featuring the use of heterogeneous catalysis in the preparation (non-related) of simple benzofurans[17] or in arylation reactions involving the formation of C–O bonds;[18] reports describing a sequence of synthetic transformations performed by the same heterogeneous palladium catalyst are even rarer.[19]

On the basis of the excellent results obtained when performing the arylation of ketone enolates by means of polymer-anchored catalysts FibreCat™,[14] we conceived that, as the first step of the tandem reactions leading to diarylbenzofurans **3** is again a palladium-catalysed arylation of deoxybenzoins,[20] the application of the latter polymer-supported catalyst[21] could constitute an interesting alternative to the homogeneous protocol. In consequence, different reaction conditions were assayed with ketone **2a**, dibromobenzene **4a** and commercially available FibreCat™ 1001, FibreCat™ 1007 and FibreCat™ 1026 catalysts[22] (Table 3). A brief comparison with another established heterogeneous system (Pd-C) was also made.

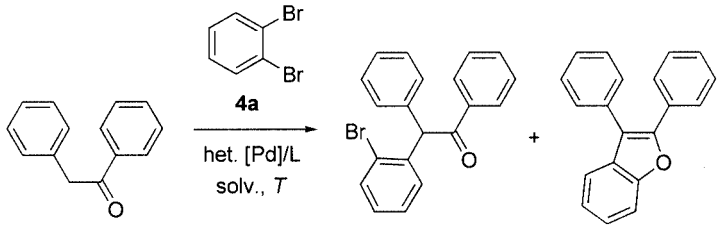
In a similar way to the monoarylation of deoxybenzoins,[14] the best yield of benzofuran **3a** was obtained when FibreCat™ 1026 was used. Such a result is a bit surprising because, unlike FibreCat™ 1001, which is clearly related to the homogeneous $Pd(OAc)_2/PPh_3$ system and is therefore the expected heterogeneous alternative, FibreCat™ 1026 features Cl^-, PPh_3 and CH_3CN ligands attached to palladium metal. Anyway, although slightly lower than under homogeneous conditions, the ratio attained was good enough to suggest application to the rest of the substrates **2** and **4**.

Precisely in the same way as in the above-mentioned monoarylation of deoxybenzoins, the results, although similar (see Table 2), were slightly inferior to the ones obtained by homogeneous catalysis. An explanation for such behaviour that can be shared by both transformations is that, unlike the homogeneous system, the sterically crowded catalytic centres attached to the polymer backbone of FibreCat™ 1026 are relatively hindered and cannot be efficiently reached by the common substrate, deoxybenzoins **2**. Nevertheless, weighed against the homogeneous reaction, the ease of work-up, catalyst separation and purification must be emphasised.

Regarding catalyst recycling, the relatively harsh conditions required, with temperatures above the thermal stability of the employed catalyst (ca. 120 °C) provoked its complete deactivation for further use.

Finally, the complete absence of aryl–phenyl exchange products generated by phenyl migration from the PPh_3 ligand, which is a side reaction observed in our previous research on arylation of ketones,[14,23a] suggests not only a high reactivity of both dibromoarenes **4** and intermediates **5** under these reaction conditions, but also that the formation of the heteroaromatic system **3** is energetically favoured in comparison with a hypothetical α-phenylated deoxybenzoin product.

Table 3. Selected coupling assays performed with heterogeneous palladium catalysts.



2a **5a** **3a**

Entry	Reaction conditions	Product (yield [%])[a]
1	5% Pd/C, Na_2CO_3, MeOH, 80 °C, 6 h[b]	**5a** (9), **2a** (79)
2	5% Pd/C, NaOH, NH_4HCO_2, 100 °C, H_20, 2 h[b]	**3a** (5), **5a** (16), **2a** (74)
3	5% Pd/C, Na_2CO_3, DMF, 150 °C, 1.5 h[b]	**3a** (17), **2a** (55)
4	2% FC 1007, K_2CO_3, *o*-xylene, 165 °C, 2 h[c]	**3a** (7), **5a** (22), **2a** (51)
5	5% FC 1007, K_2CO_3, *o*-xylene, 165 °C, 8 h[c]	**3a** (38), **5a** (24)
6	2% FC 1007, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[c]	**3a** (32), **5a** (21), **2a** (8)
7	5% FC 1007, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[c]	**3a** (47)
8	5% FC 1007, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[d]	**3a** (60), **2a** (2)
9	5% FC 1007, Cs_2CO_3, toluene, 130 °C, 8 h[d]	**3a** (4), **5a** (16), **2a** (45)
10	5% FC 1001, K_2CO_3, *o*-xylene, 165 °C, 8 h[d]	**3a** (3), **5a** (8), **2a** (74)
11	5% FC 1001, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[d]	**3a** (5), **5a** (4), **2a** (65)
12	5% FC 1001, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[c]	**3a** (8), **5a** (21), **2a** (46)
13	5% FC 1026, Cs_2CO_3, DMF, 150 °C, 8 h[c]	**3a** (27), **5a** (16), **2a** (2)
14	5% FC 1026, Cs_2CO_3, DMF, 165 °C, 8 h[c]	**3a** (18), **5a** (5)
15	5% FC 1026, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[d]	**3a** (43), **5a** (31)
16	5% FC 1026, Cs_2CO_3, *o*-xylene, 165 °C, 2 h[c]	**3a** (15), **5a** (3), **2a** (72)
17	5% FC 1026, Cs_2CO_3, *o*-xylene, 165 °C, 8 h[c]	**3a** (63)

[a] GC-MS ratios of detected products measured on the basis of the starting amount of deoxybenzoin **2a**. Propiophenone was used as the internal standard. The rest of the reaction crude contained complex mixtures of unidentified products. [b] 1.2 Equiv. of 1,2-dibromobenzene (**4a**), a 5% Pd/C mixture and 2.3 equiv. of base were used. [c] 1.6 Equiv. of 1,2-dibromobenzene (**4a**), 2.5 equiv. of base and the indicated FibreCatTM catalyst (FC) were used. The disclosed proportion of FC (%) refers to the relative amount of Pd metal from the FC catalyst. The average content of Pd in the employed FC samples is 3%. [d] 1.2 Equiv. of 1,2-dibromobenzene (**4a**) was used.

Intramolecular Oxidative Coupling

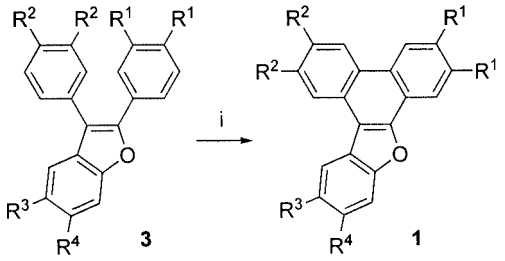
In spite of its longevity, oxidative coupling between two phenolic or alkoxylated arene partners[16,24] is still a good alternative to modern (Stille, Suzuki, Negishi) and old (Ullmann) metal-catalysed cross-coupling reactions since it avoids the use of halogenated/sulfonated substrates.[25] It is also favourably compared to photochemical approaches, as these often show limitations concerning substitution patterns in the substrates or regiochemistry of the process.[26] However, an important disadvantage of most oxidative coupling procedures is the need for heavy metal oxidants in stoichiometric amounts. Therefore, the use of peroxides and, above all, hypervalent iodine reagents has attracted much attention.[27]

In previous works we have proved the applicability of PIFA (phenyliodo(III) bis(trifluoroacetate), which is an environmentally safer reagent of low toxicity and ready biodegradability, to the synthesis of several phenanthro-fused heterocycles, such as isoxazoles, thiazoles, pyrazoles and pyrimidines.[28] In an attempt to extend the scope of the PIFA-mediated oxidative coupling methodology, the latter protocol was applied to diarylbenzofurans **3** (Table 4).

Depending on the electronic nature of the substrate employed, the reaction conditions were efficiently modulated. Hence, the coupling of furans **3b** and **3i**–**l** (Table 4, entries 2 and 9–12) was effected under milder conditions (method A) probably due to the activation of both arene rings to be coupled (R^1 = R^2 = OMe), and the absence of alkoxy groups in the aryl ring attached to the benzofuran C-2 position in substrates **3d**–**f** (R^1 = OMe; R^2 = H) conditioned the process to the use of more equivalents of the oxidizing agent PIFA/BF_3·OEt_2 and a higher temperature (Method B), a behaviour already reported in other PIFA-mediated reactions.[27d] The same hypothesis can be applied to explain the lack of reactivity of derivatives **3a** and **3c** (R^1 = R^2 = H) under both reaction conditions.

However, other factors must also be taken into account in order to understand the behaviour of furans **3g**,**h** (Table 4, entries 8 and 9). Although the aryl rings to be coupled are the same as in **3d**–**f**, the presence of electron-donating groups in the benzofuran moiety of **3g**,**h** is likely the cause of such dissimilar results. Our proposal is that, in the case of substrates **3g**,**h**, the corresponding intermediates **B** (Scheme 2) are highly stabilized by delocalisation of the charge within the electron-rich alkoxylated benzofuran sys-

Table 4. Benzo[*b*]phenanthro[9,10-*d*]furans **1** prepared by intramolecular oxidative coupling.



i: Method A: 1.1 equiv. PIFA, 1.2 equiv. $BF_3{\cdot}OEt_2$, CH_2Cl_2, –40 °C, 30 min

Method B: 1.5 equiv. PIFA, 3.0 equiv. $BF_3{\cdot}OEt_2$, CH_2Cl_2, –20 °C, 2.5 h

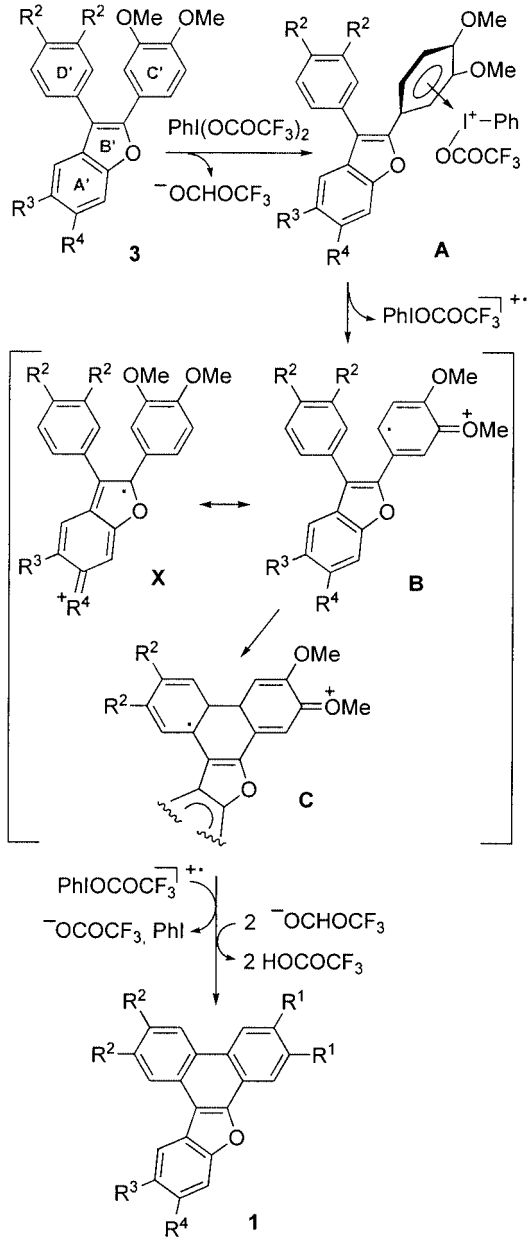
Entry	3	R^1	R^2	R^3	R^4	Method	1 (yield [%])[a]
1	**3a**	H	H	H	H	A, B	–[b]
2	**3b**	OMe	OMe	H	H	A	**1a** (80)
3	**3c**	H	H	OMe	OMe	A, B	–[b]
4	**3d**	OMe	H	H	H	A	**1b** (40)
5	**3d**	OMe	H	H	H	B	**1b** (79)
6	**3e**	OMe	H	Me	Me	B	**1c** (71)
7	**3f**	OMe	H	F	F	B	**1d** (85)
8	**3g**	OMe	H	OMe	OMe	A, B	–[b]
9	**3h**	OMe	H	OCH_2O		A, B	–[b]
10	**3i**	OMe	OMe	Me	Me	A	**1e** (84)
11	**3j**	OMe	OMe	F	F	A	**1f** (79)
12	**3k**	OMe	OMe	OMe	OMe	A	**1g** (73)
13	**3l**	OMe	OMe	OCH_2O		A	**1h** (83)

[a] Yield of pure crystallised compound (Et_2O). [b] Complex mixture containing unreacted starting material whatever the method used.

tem (**B** ↔ **X**), thus hindering the nucleophilic attack of the phenyl ring and allowing other side-reactions, such as the oxidation of the benzofuran moiety, a process that is already known.[29] In contrast, the absence of alkoxy groups in the benzofuran core of substrates **3d**–**f** meanss that a more reactive **B**, in which charge remains at the 3,4-dimethoxyphenyl ring (D′), readily undergoes attack of the adjacent phenyl nucleophile.

The above theoretical explanation was corroborated by the fact that no coupling was achieved with derivatives **3a**, **3c** and **3g**,**h** with a range of other oxidants.[30] The latter results, along with the good yields obtained in the rest of the cases, constitute a comparative proof of the potential of the chosen hypervalent iodine reagent.

Moreover, the presented coupling strategy is the only alternative to the currently existing photochemical approach to the benzo[*b*]phenanthro[9,10-*d*]furan nucleus,[31] an alternative protocol that is highly advantageous if the absence of specific instrumentation and the good overall yields are considered.



Scheme 2.

Conclusions

To sum up, a tandem *C*-/*O*-arylation conducted by homogeneous and polymer-anchored palladium catalysts has been applied to a series of 1,2-diarylethanones and 1,2-dibromoarenes to furnish the corresponding 2,3-diarylbenzofurans in a regioselective way. The latter intermediates can be oxidatively coupled in the presence of the iodine(III) reagent PIFA, thus avoiding the use of heavy metal oxidants or photochemical procedures and providing a new entry to the pentacyclic benzo[*b*]phenanthro[9,10-*d*]furan system.

Experimental Section

General Remarks: General experimental details have been reported previously.[32]

General Procedure for the Synthesis of 2,3-Diarylbenzofurans 3 by Homogeneous Catalysis: Dry, degassed *o*-xylene (2.5 mL) was added to an oven-dried reaction flask charged with $Pd(OAc)_2$ (0.02 mmol), Cs_2CO_3 (1.27 mmol), PPh_3 (0.10 mmol), ketone **2** (0.51 mmol) and dibromoarene **4** (0.76 mmol) under argon at room temperature. The resultant stirred suspension was heated to 165 °C for 1.5–4 h. After cooling, HCl (8 mL of a 1.4 M solution in water) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried with anhydrous sodium sulfate and the solvents evaporated in vacuo. The residue was purified by flash chromatography on silica gel with 10–40% EtOAc/hexane as eluent. This procedure gave compounds **3a**–**d**, **3g** and **3l**. The preparation of diarylbenzofurans **3e**,**f** and **3h**–**k** required the use of 0.56 mmol of dibromoarene **4**.

2,3-Diphenylbenzo[*b*]furan (3a): Yield: 87%. White powder, m.p. 122.5–123 °C (EtOAc) [ref.[5] 121 °C (EtOH)].

2,3-Bis(3,4-dimethoxyphenyl)benzo[*b*]furan (3b): Yield: 77%. Yellow powder, m.p. 148–150 °C (EtOAc). R_f = 0.59 (50% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.74 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 6.81 (d, J = 8.3 Hz, 1 H, ArH), 6.97–7.02 (m, 2 H, ArH), 7.08 (dd, J = 7.9, 1.6 Hz, 1 H, ArH), 7.20–7.44 (m, 4 H, 5-H, 6-H, ArH), 7.48 (d, J = 7.5 Hz, 1 H, 7-H), 7.54 (d, J = 7.9 Hz, 1 H, 4-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 55.4 (OCH_3), 55.6 (OCH_3), 109.4 (CH), 110.5 (C-7), 110.6 (CH), 111.2 (CH), 112.4 (CH), 115.7 (C-3), 119.4 (C-4), 119.5 (CH), 121.9 (CH), 122.6 (C-6), 123.1 (C), 124.0 (C-6), 125.1 (C), 130.2 (C-3a), 148.1 (*C*-OCH_3), 148.2 (*C*-OCH_3), 148.8 (*C*-OCH_3), 148.9 (*C*-OCH_3), 150.0 (C-2), 153.3 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1252 cm^{-1} (C–O), 1026 (C–O). EIMS: *m*/*z* (%) = 390 (100) [M$^+$], 375 (11). HRMS: calcd. for $C_{24}H_{22}O_5$ [M$^+$] 390.1467; found 390.1458. $C_{24}H_{22}O_5$ (390.43): calcd. C 73.83, H 5.68; found C 73.79, H 5.76.

5,6-Dimethoxy-2,3-diphenylbenzo[*b*]furan (3c):[33] Yield: 65%. White powder, m.p. 159–160 °C (EtOAc). R_f = 0.35 (20% Et_2O/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.88 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 6.90 (s, 1 H, 7-H), 7.13 (s, 1 H, ArH), 7.19 (s, 1 H, 4-H), 7.27–7.32 (m, 3 H, ArH), 7.42–7.51 (m, 4 H, ArH), 7.58–7.62 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 56.3 (OCH_3), 95.0 (C-7), 100.9 (C-4), 117.6 (C-3), 122.0 (C-3a), 126.3 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH), 128.9 (CH), 129.5 (CH), 130.8 (C), 133.0 (C), 146.6 (C-5, C-6), 148.2 (C-5, C-6, C-2), 148.5 (C-5, C-6, C-2), 149.5 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1261 cm^{-1} (C–O), 1027 (C–O). EIMS: *m*/*z* (%) = 330 (100) [M$^+$], 315 (11).

2-(3,4-Dimethoxyphenyl)-3-phenylbenzo[*b*]furan (3d): Yield: 70%. Yellow oil. R_f = 0.45 (20% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.82 (d, J = 8.7 Hz, 1 H, ArH), 7.14 (d, J = 1.8 Hz, 1 H, ArH), 7.19–7.35 (m, 3 H, 5-H, 6-H, ArH), 7.39–7.56 (m, 7 H, 4-H, 7-H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 55.8 (OCH_3), 109.8 (CH), 110.8 (CH), 110.9 (C-7), 116.2 (C-3), 119.6 (C-4, CH), 119.7 (C-4, CH), 122.8 (C-5), 123.3 (C), 124.2 (C-6), 127.5 (CH), 128.8 (CH), 129.8 (CH), 130.5 (C-3a), 133.0 (C), 148.5 (*C*-OCH_3), 149.1 (*C*-OCH_3), 150.5 (C-2), 153.7 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1251 cm^{-1} (C–O), 1025 (C–O). EIMS: *m*/*z* (%) = 330 (100) [M$^+$], 315 (13), 255 (12). HRMS: calcd. for $C_{22}H_{18}O_3$ [M$^+$] 330.1256; found 330.1244. $C_{22}H_{18}O_3$ (330.38): calcd. C 79.98, H 5.49; found C 79.91, H 5.52.

2-(3,4-Dimethoxyphenyl)-5,6-dimethyl-3-phenylbenzo[*b*]furan (3e): Yield: 87%. Yellow powder, m.p. 125–126 °C (EtOAc). R_f = 0.48 (20% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.82 (d, J = 8.3 Hz, 1 H, ArH), 7.11 (d, J = 1.9 Hz, 1 H, ArH), 7.22 (s, 1 H, 7-H), 7.26 (dd, J = 8.3, 1.9 Hz, 1 H, ArH), 7.33 (s, 1 H, 4-H), 7.38–7.54 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.9 (CH_3), 20.5 (CH_3), 55.4 (OCH_3), 55.7 (OCH_3), 109.7 (CH), 110.8 (CH), 111.3 (C-7), 115.9 (C-3), 119.4 (C-4), 119.7 (CH), 123.6 (C), 127.3 (CH), 128.2 (C-3a), 128.8 (CH), 129.8 (CH), 131.4 (C-5, C-6), 133.3 (C-5, C-6, C), 133.4 (C-5, C-6, C), 148.4 (*C*-OCH_3), 148.8 (*C*-OCH_3), 149.7 (C-2), 152.6 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1256 cm^{-1} (C–O), 1025 (C–O). EIMS: *m*/*z* (%) = 358 (100) [M$^+$], 343 (13). HRMS: calcd. for $C_{24}H_{22}O_3$ [M$^+$] 358.1569; found 358.1564. $C_{24}H_{22}O_3$ (358.43): calcd. C 80.42, H 6.19; found C 80.47, H 6.15.

2-(3,4-Dimethoxyphenyl)-5,6-difluoro-3-phenylbenzo[*b*]furan (3f): Yield: 73%. White powder, m.p. 108–109 °C (EtOAc). R_f = 0.33 (30% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.81 (d, J = 8.3 Hz, 1 H, ArH), 7.08 (d, J = 1.6 Hz, 1 H, ArH), 7.15–7.25 (m, 3 H, 7-H, ArH), 7.34 (dd, J = 9.5, 6.3 Hz, 1 H, 4-H), 7.40–7.48 (m, 4 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 55.8 (OCH_3), 100.1 [d, J(C,F) = 21.5 Hz, C-7), 106.5 (d, $J_{C,F}$ = 21.5 Hz, C-4), 109.6 (CH), 110.9 (CH), 116.0 (C-3), 119.6 (CH), 122.7 (C), 126.0 (d, $J_{C,F}$ = 6.8 Hz, C-3a), 127.9 (CH), 129.1 (CH), 129.6 (CH), 132.2 (C), 148.2 (dd, $J_{C,F}$ = 246.0, 14.4 Hz, C-5, C-6), 148.3 (*C*-OCH_3), 148.5 (*C*-OCH_3), 148.7 (dd, $J_{C,F}$ = 242.3, 16.2 Hz, C-5, C-6), 149.3 (C-2), 152.2 (d, $J_{C,F}$ = 5.3 Hz, C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1254 cm^{-1} (C–O), 1023 (C–O). EIMS: *m*/*z* (%) = 366 (100) [M$^+$], 351 (17), 295 (10), 291 (13). HRMS: calcd. for $C_{22}H_{16}F_2O_3$ [M$^+$] 366.1068; found 366.1066. $C_{22}H_{16}F_2O_3$ (366.36): calcd. C 72.13, H 4.40, F 10.37; found C 72.18, H 4.42, F 10.35.

2-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-3-phenylbenzo[*b*]furan (3g): Yield: 79%. Yellow powder, m.p. 133–134 °C (EtOAc). R_f = 0.79 (40% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.65 (s, 3 H, OCH_3), 3.86 (s, 6 H, OCH_3), 3.95 (s, 3 H, OCH_3), 6.79 (d, J = 8.7 Hz, 1 H, ArH), 6.86 (s, 1 H, 7-H), 7.05 (d, J = 1.9 Hz, 1 H, ArH), 7.11 (s, 1 H, 4-H), 7.21 (dd, J = 8.3, 1.9 Hz, 1 H, ArH), 7.35–7.53 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 55.7 (OCH_3), 56.2 (OCH_3), 56.3 (OCH_3), 94.9 (C-7), 100.7 (C-4), 109.3 (CH), 110.8 (CH), 116.3 (C-3), 118.9 (CH), 122.1 (C-3a), 123.6 (C), 127.4 (CH), 128.9 (CH), 129.7 (CH), 133.2 (C), 146.5 (C-5, C-6), 147.9 (C-5, C-6), 148.2 (C-2), 148.4 (*C*-OCH_3), 148.6 (*C*-OCH_3), 149.5 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1026 (C–O). EIMS: *m*/*z* (%) = 390 (100) [M$^+$], 375 (32), 319 (10). HRMS: calcd. for $C_{24}H_{22}O_5$ [M$^+$] 390.1467; found 390.1467. $C_{24}H_{22}O_5$ (390.43): calcd. C 73.83, H 5.68; found C 73.80, H 5.65.

2-(3,4-Dimethoxyphenyl)-5,6-methylenedioxy-3-phenylbenzo[*b*]furan (3h): Yield: 76%. Yellow powder, m.p. 156–157 °C (EtOAc). R_f = 0.42 (30% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 5.98 (s, 2 H, CH_2), 6.79 (d, J = 8.7 Hz, 1 H, ArH), 6.82 (s, 1 H, 7-H), 7. 04 (s, 1 H, 4-H), 7.05 (d, J = 1.9 Hz, 1 H, ArH), 7.19 (dd, J = 8.3, 1.9 Hz, 1 H, ArH), 7,35–7,48 (m, 5 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 55.6 (OCH_3), 93.1 (C-7), 98.1 (C-4), 101.1 (CH_2), 109.2 (CH), 110.7 (CH), 116.6 (C-3), 118.9 (CH), 123.4 (C-3a, C), 123.6 (C-3a, C), 127.4 (CH), 128.8 (CH), 129.6 (CH), 133.0 (C), 144.5 (C-5, C-6), 146.0 (C-5, C-6), 148.2 (C-2), 148.6 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.9 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1026 (C–O). EIMS: *m*/*z* (%) = 374 (100) [M$^+$], 359 (20). HRMS: calcd. for $C_{23}H_{18}O_5$ [M$^+$] 374.1154; found 374.1172. $C_{23}H_{18}O_5$ (374.39): calcd. C 73.79, H 4.85; found C 73.74, H 4.92.

2,3-Bis(3,4-dimethoxyphenyl)-5,6-dimethylbenzo[*b*]furan (3i): Yield: 78%. Yellow powder, m.p. 138.5–140 °C (EtOAc). R_f = 0.76 (40% EtOAc/hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.32 (s, 3 H,

CH_3), 2.39 (s, 3 H, CH_3), 3.73 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 6.81 (d, J = 8.3 Hz, 1 H, ArH), 6.97–7.00 (m, 2 H, ArH), 7.07 (dd, J = 8.3, 1.6 Hz, 1 H, ArH), 7.20–7.22 (m, 3 H, 7-H, ArH), 7.32 (s, 1 H, 4-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.8 (CH_3), 20.4 (CH_3), 55.5 (OCH_3), 55.6 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 109.4 (CH), 110.7 (CH), 111.3 (C-7), 112.6 (CH), 115.6 (C-3), 119.3 (C-4), 119.6 (CH), 122.0 (CH), 123.6 (C), 125.7 (C), 128.3 (C-3a), 131.3 (C-5, C-6), 133.3 (C-5, C-6), 148.2 (*C*-OCH_3), 148.4 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.0 (*C*-OCH_3), 149.4 (C-2), 152.4 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1259 cm^{-1} (C–O), 1026 (C–O). EIMS: *m*/*z* (%) = 418 (100) [M^+]. HRMS: calcd. for $C_{26}H_{26}O_5$ [M^+] 418.1780; found 418.1779. $C_{26}H_{26}O_5$ (418.48): calcd. C 74.62, H 6.26; found C 74.69, H 6.22.

2,3-Bis(3,4-dimethoxyphenyl)-5,6-difluorobenzo[*b*]furan (3j): Yield: 62%. White powder, m.p. 120–122 °C (EtOAc). R_f = 0.64 (15% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 6.80 (d, J = 8.3 Hz, 1 H, ArH), 6.94–7.04 (m, 3 H, ArH), 7.16–7.26 (m, 3 H, 7-H, ArH), 7.35 (dd, J = 9.9, 6.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 55.8 (OCH_3), 55.9 (OCH_3), 100.1 (d, $J_{C,F}$ = 21.5 Hz, C-7), 106.4 (d, $J_{C,F}$ = 19.7 Hz, C-4), 109.5 (CH), 110.8 (CH), 111.6 (CH), 112.4 (CH), 115.9 (C-3), 119.6 (CH), 122.0 (CH), 122.8 (C), 124.4 (C), 126.1 (d, $J_{C,F}$ = 7.2 Hz, C-3a), 148.2 (dd, $J_{C,F}$ = 246.0, 16.2 Hz, C-5, C-6), 148.3 (*C*-OCH_3), 148.4 (*C*-OCH_3), 148.6 (*C*-OCH_3), 148.7 (dd, $J_{C,F}$ = 242.3, 14.4 Hz, C-5, C-6), 148.7 (*C*-OCH_3), 149.3 (C-2), 152.0 (d, $J_{C,F}$ = 3.6 Hz, C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1254 cm^{-1} (C–O), 1024 (C–O). EIMS: *m*/*z* (%) = 426 (100) [M^+]. HRMS: calcd. for $C_{24}H_{20}F_2O_5$ [M^+] 426.1279; found 426.1284. $C_{24}H_{20}F_2O_5$ (426.41): calcd. C 67.60, H 4.73, F 8.91; found C 67.52, H 4.76, F 8.95.

2,3-Bis(3,4-dimethoxyphenyl)-5,6-dimethoxybenzo[*b*]furan (3k): Yield: 81%. Orange powder, m.p. 144–145 °C (EtOAc). R_f = 0.61 (40% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.89 (s, 6 H, OCH_3), 6.73 (d, J = 8.3 Hz, 1 H, ArH), 6.83 (s, 1 H, 7-H), 6.95–6.97 (m, 2 H, ArH), 7.03 (dd, J = 8.3, 1.6 Hz, 1 H, ArH), 7,05 (s, 1 H, 4-H), 7.12–7.16 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 55.6 (OCH_3), 55.7 (OCH_3), 56.0 (OCH_3), 56.1 (OCH_3), 94.8 (C-7), 100.6 (C-4), 109.0 (CH), 110.6 (CH), 111.4 (CH), 112.5 (CH), 116.0 (C-3), 118.4 (CH), 121.8 (CH), 122.2 (C-3a), 123.5 (C), 125.4 (C), 146.4 (C-5, C-6), 147.8 (C-5, C-6), 148.0 (C-2, *C*–OCH_3), 148.1 (C-2, *C*–OCH_3), 148.2 (C-2, *C*–OCH_3), 148.4 (*C*-OCH_3), 148.9 (*C*-OCH_3), 149.1 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1020 (C–O). EIMS: *m*/*z* (%) = 450 (100) [M^+], 435 (24). HRMS: calcd. for $C_{26}H_{26}O_7$ 450.1679; found 450.1673. $C_{26}H_{26}O_7$ (450.48): calcd. C 69.32, H 5.82; found C 69.36, H 5.84.

2,3-Bis(3,4-dimethoxyphenyl)-5,6-(methylenedioxy)benzo[*b*]furan (3l): Yield: 75%. Orange powder, m.p. 161–162 °C (EtOAc). R_f = 0.53 (5% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.71 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 5.96 (s, 2 H, CH_2), 6.78 (d, J = 8.3 Hz, 1 H, ArH), 6.81 (s, 1 H, 7-H), 6.93–6.97 (m, 2 H, ArH), 7.01 (s, 1 H, 4-H), 7.02 (dd, J = 8.3, 1.6 Hz, 1 H, ArH), 7.13–7.19 (m, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 56.2 (OCH_3), 93.1 (C-7), 98.2 (C-4), 101.1 (CH_2), 109.1 (CH), 110.7 (CH), 111.4 (CH), 112.5 (CH), 116.4 (C-3), 118.9 (CH), 122.0 (CH), 123.5 (C-3a), 123.8 (C), 125.3 (C), 144.5 (C-5, C-6), 146.0 (C-5, C-6), 148.3 (*C*-OCH_3), 148.4 (*C*-OCH_3), 148.6 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.1 (C-2), 149.8 (C-7a) ppm. FTIR (neat): $\tilde{\nu}$ = 1259 cm^{-1} (C–O), 1023 (C–O). EIMS: *m*/*z* (%) = 434 (100) [M^+], 419 (19). HRMS: calcd. for $C_{25}H_{22}O_7$ 434.1366; found 434.1363. $C_{25}H_{22}O_7$ (434.44): calcd. C 69.12, H 5.10; found C 69.09, H 5.12.

General Procedure for the Synthesis of Intermediate *o*-Bromoarylated Deoxybenzoins 5: Dry, degassed *o*-xylene (2.5 mL) was added to an oven-dried reaction flask charged with $Pd(OAc)_2$ (0.005 mmol), K_2CO_3 (1.27 mmol), PPh_3 (0.02 mmol), ketone **2** (0.51 mmol) and dibromoarene **4** (0.61 mmol) under argon at room temperature. The resultant stirred suspension was heated to 150 °C for 8 h. After cooling, HCl (8 mL of a 1.4 M solution in water) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried with anhydrous sodium sulfate and the solvents evaporated in vacuo to give a residue, which was purified by flash chromatography on silica gel with 10–30% EtOAc/hexane as eluent.

2-(2-Bromophenyl)-1,2-diphenylethanone (5a): Yield: 84%. White powder, m.p. 99–100 °C (MeOH). R_f = 0.43 (10% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 6.56 (s, 1 H, CH), 7.12–7.17 (m, 2 H, ArH), 7.24 (dd, J = 6.7, 1.2 Hz, 1 H, ArH), 7.33–7.53 (m, 8 H, ArH), 7.65 (dd, J = 7.5, 1.6 Hz, 1 H, ArH), 8.01 (dd, J = 7.1, 1.6 Hz, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 58.8 (*C*H-C=O), 124.7 (CBr), 127.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.4 (CH), 130.9 (CH), 132.7 (CH), 132.9 (CH), 136.3 (C), 136.8 (C), 138.9 (C), 197.3 (C=O) ppm. FTIR (neat): $\tilde{\nu}$ = 1684 cm^{-1} (C=O). EIMS: *m*/*z* (%) = 105 (100). HRMS: calcd. for $C_{20}H_{15}BrO$ [M^+] 352.0286; found 352.0271. $C_{20}H_{15}BrO$ (351.24): calcd. C 68.39, H 4.30; found C 68.33, H 4.35.

2-(2-Bromophenyl)-1,2-bis(3,4-dimethoxyphenyl)ethanone (5b): Yield: 87%. Orange powder, m.p. 139–140 °C (MeOH). R_f = 0.44 (50% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.87 (s, 6 H, OCH_3), 6.34 (s, 1 H, CH), 6.80–6.83 (m, 4 H, ArH), 7.07–7.12 (m, 2 H, ArH), 7.20 (d, J = 7.1 Hz, 1 H, ArH), 7.55–7.58 (m, 2 H, ArH), 7.66 (dd, J = 8.3, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.7 (OCH_3), 55.8 (OCH_3), 55.9 (OCH_3), 58.1 (*C*H-C=O), 110.0 (CH), 110.8 (CH), 111.1 (CH), 112.3 (CH), 121.7 (CH), 123.4 (CH), 124.6 (CBr), 127.5 (CH), 128.6 (CH), 129.3 (C), 129.5 (C), 130.8 (CH), 132.7 (CH), 139.4 (C), 148.1 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.0 (*C*-OCH_3), 152.9 (*C*-OCH_3), 195.9 (C=O) ppm. FTIR (neat): $\tilde{\nu}$ = 1675 cm^{-1} (C=O), 1262 (C–O), 1024 (C–O). EIMS: *m*/*z* (%) = 472 (1) [M + 1], 470 (1) [M – 1], 165 (100). HRMS: calcd. for $C_{24}H_{23}BrO_5$ [M^+] 470.0729; found 470.0724. $C_{24}H_{23}BrO_5$ (471.34): calcd. C 61.16, H 4.92; found C 61.14, H 4.93.

General Procedure for the Synthesis of 2,3-Diarylbenzofurans 3 in the Presence of Polymer-Anchored Palladium Catalysts: Dry, degassed *o*-xylene (1 mL) was added to an oven-dried reaction flask charged with FibreCat™ 1026 (0.01 mmol of Pd), Cs_2CO_3 (0.5 mmol), ketone **2** (0.2 mmol) and dibromoarene **4** (0.32 mmol) under argon at room temperature. The resultant stirred suspension was heated to 165 °C for 8 h. After cooling, the mixture was filtered, washed with CH_2Cl_2 and the filtrate was evaporated in vacuo to give a residue that was purified by flash chromatography on silica gel with 10–40% EtOAc/hexane as eluent. Compounds **3a**–**c**, **3e**, **3g**–**i** and **3k**,**l** were prepared by this procedure. However, the preparation of diarylbenzofurans **3d**, **3f** and **3j** required the use of 0.24 mmol of dibromoarene **4**.

General Procedure for the PIFA-Mediated Oxidative Coupling of Diarylbenzofurans 3. Synthesis of Benzo[*b*]phenanthro[9,10-*d*]furans (1). Method A: A solution of PIFA (0.11 mmol) in dry dichloromethane (1 mL) was added to a stirred solution of diarylbenzofuran **3** (0.1 mmol) in dry dichloromethane (1.5 mL) at –40 °C under argon. After addition of $BF_3{\cdot}Et_2O$ (0.12 mmol), the resulting blue

solution was stirred for 30 min at –40 °C and then quenched with Na_2CO_3 (3 mL of a 10% solution in water). The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), the combined organic extracts were dried with anhydrous sodium sulfate and the solvents were then evaporated in vacuo to give a residue which was purified by flash chromatography on silica gel with 30% EtOAc/hexane or 0–10% EtOAc/CH_2Cl_2 as eluent. Compounds **1a** and **1e**–**h** were prepared by this procedure.

2,3,6,7-Tetramethoxybenzo[*b*]phenanthro[9,10-*d*]furan (1a): Yield: 80%. Pink powder, m.p. 229–230 °C (Et_2O). R_f = 0.43 (5% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.09 (s, 3 H, OCH_3), 4.11 (s, 3 H, OCH_3), 4.13 (s, 3 H, OCH_3), 4.14 (s, 3 H, OCH_3), 7.44–7.50 (m, 2 H, ArH), 7.67–7.71 (m, 4 H, ArH), 7.76 (s, 1 H, ArH), 8.16 (ddd, J = 9.1, 8.7, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 55.8 (OCH_3), 55.9 (OCH_3), 101.2 (CH), 103.2 (CH), 103.6 (CH), 104.0 (CH), 111.4 (CH), 112.2 (C), 115.1 (C), 120.8 (CH), 121.2 (C), 121.9 (C), 122.8 (CH), 124.2 (C), 124.4 (CH), 125.5 (C), 147.0 (*C*-OCH_3), 148.5 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.0 (*C*-OCH_3), 149.7 (*C*-OCH_3), 155.2 (*C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1258 cm^{-1} (C–O), 1022 (C–O). EIMS: *m*/*z* (%) = 388 (100) [M^+], 373 (13), 314 (13), 194 (15). HRMS: calcd. for $C_{24}H_{20}O_5$ [M^+] 388.1311; found 388.1313. $C_{24}H_{20}O_5$ (388.41): calcd. C 74.21, H 5.19; found C 74.18, H 5.25.

2,3,6,7-Tetramethoxy-11,12-dimethylbenzo[*b*]phenanthro[9,10-*d*]furan (1e): Yield: 84%. White powder, m.p. 271–272 °C (Et_2O). R_f = 0.40 (10% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 6 H, CH_3), 4.05 (s, 3 H, OCH_3), 4.07(s, 3 H, OCH_3), 4.10 (s, 3 H, OCH_3), 4.11 (s, 3 H, OCH_3), 7.44 (s, 1 H, ArH), 7.55 (s, 1 H, ArH), 7.57 (s, 1 H, ArH), 7.59 (s, 1 H, ArH), 7.62 (s, 1 H, ArH), 7.32 (s, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.4 (CH_3), 20.6 (CH_3), 55.9 (OCH_3), 56.0 (OCH_3), 101.4 (CH), 103.7 (CH), 104.1 (CH), 104.6 (CH), 112.2 (CH), 112.6 (C), 115.8 (C), 121.2 (CH), 121.5 (C), 122.4 (C), 123.3 (C), 124.1 (C), 131.3 (CH), 133.9 (CH), 147.3 (*C*-OCH_3), 148.9 (*C*-OCH_3), 149.0 (*C*-OCH_3), 149.1 (*C*-OCH_3), 149.7 (*C*-OCH_3), 154.3 (*C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1255 cm^{-1} (C–O), 1022 (C–O). EIMS: *m*/*z* (%) = 416 (100) [M^+], 401 (30), 358 (16), 345 (11), 342 (21), 208 (10). HRMS: calcd. for $C_{26}H_{24}O_5$ [M^+] 416.1624; found 416.1618. $C_{26}H_{24}O_5$ (416.47): calcd. C 74.98, H 5.81; found C 74.95, H 5.83.

11,12-Difluoro-2,3,6,7-tetramethoxybenzo[*b*]phenanthro[9,10-*d*]furan (1f): Yield: 79%. Pink powder, m.p. >300 °C (Et_2O). R_f = 0.40 (5% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.13 (s, 9 H, OCH_3), 4.14 (s, 3 H, OCH_3), 7.49 (dd, J = 9.5, 5.9 Hz, 1 H, ArH), 7.58 (s, 1 H, ArH), 7.66 (s, 1 H, ArH), 7.77 (s, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.84 (dd, J = 10.3, 7.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 56.0 (OCH_3), 100.9 (d, $J_{C,F}$ = 21.5 Hz, CH), 101.4 (CH), 103.7 (CH), 103.8 (CH), 104.3 (CH), 107.9 (d, $J_{C,F}$ = 21.5 Hz, CH), 112.0 (C), 115.2 (C), 121.0 (d, $J_{C,F}$ = 10.8 Hz, C), 121.5 (C), 121.7 (C), 124.6 (C), 147.7 (dd, $J_{C,F}$ = 240.0, 14.4 Hz, CF), 147.8, 148.3 (dd, $J_{C,F}$ = 246.0, 16.2 Hz, CF), 149.2 (*C*-OCH_3), 149.4 (*C*-OCH_3), 149.7 (*C*-OCH_3), 149.7 (*C*-OCH_3), 150.4 (d, $J_{C,F}$ = 5.4 Hz, *C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1253 cm^{-1} (C–O), 1026 (C–O). EIMS: *m*/*z* (%) = 424 (100) [M^+], 409 (22), 381 (12), 366 (14), 353 (12), 350 (26). HRMS: calcd. for $C_{24}H_{18}F_2O_5$ [M^+] 424.1112; found 424.1109. $C_{24}H_{18}F_2O_5$ (424.39): calcd. C 67.92, H 4.28, F 8.95; found C 67.96, H 4.25, F 8.91.

2,3,6,7,11,12-Hexamethoxybenzo[*b*]phenanthro[9,10-*d*]furan (1g): Yield: 73%. Pink powder, m.p. 264–265 °C (Et_2O). R_f = 0.25 (15% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.03 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 4.15 (s, 9 H, OCH_3), 4.17 (s, 3 H, OCH_3), 7.31 (s, 1 H, ArH), 7.67 (s, 1 H, ArH), 7.73 (s, 1 H, ArH), 7.81 (s, 1 H, ArH), 7.84 (s, 1 H, ArH), 7.88 (s, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 55.9 (OCH_3), 56.2 (OCH_3), 56.7 (OCH_3), 95.6 (CH), 101.0 (CH), 103.3 (CH), 103.6 (CH), 104.0 (CH), 104.1 (CH), 112.9 (C), 115.6 (C), 117.1 (C), 121.4 (C), 121.8 (C), 123.4 (C), 145.9 (*C*-OCH_3), 147.1 (*C*-OCH_3), 148.1 (*C*-OCH_3), 148.7 (*C*-OCH_3), 148.7 (*C*-OCH_3), 149.5 (*C*-OCH_3), 150.3 (*C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1252 cm^{-1} (C–O), 1038 (C–O). EIMS: *m*/*z* (%) = 448 (100) [M^+], 433 (40), 374 (23). HRMS: calcd. for $C_{26}H_{24}O_7$ [M^+] 448.1522; found 448.1513. $C_{26}H_{24}O_7$ (448.46): calcd. C 69.63, H 5.39; found C 69.59, H 5.36.

2,3,6,7-Tetramethoxy-11,12-(methylenedioxy)benzo[*b*]phenanthro[9,10-*d*]furan (1h): Yield: 83%. Beige powder, m.p. 260–261 °C (Et_2O). R_f = 0.45 (5% EtOAc/CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.14 (s, 6 H, OCH_3), 4.15 (s, 3 H, OCH_3), 4.16 (s, 3 H, OCH_3), 6.11 (s, 2 H, CH_2), 7.23 (s, 1 H, ArH), 7.60 (s, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.73 (s, 1 H, ArH), 7.82 (s, 1 H, ArH), 7.87 (s, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 56.0 (OCH_3), 94.1 (CH), 99.9 (CH_2), 101.2 (CH), 101.6 (CH), 103.8 (CH), 104.1 (CH), 104.4 (CH), 113.2 (C), 115.7 (C), 118.4 (C), 121.6 (C), 122.0 (C), 123.6 (C), 144.5 (*C*-OCH_2, *C*-OCH_3), 146.1 (*C*-OCH_2, *C*-OCH_3), 147.4 (*C*-OCH_2, *C*-OCH_3), 149.0 (*C*-OCH_2, *C*-OCH_3), 149.1 (*C*-OCH_2, *C*-OCH_3), 149.1 (*C*-OCH_2, *C*-OCH_3), 150.1 (*C*-OCH_2, *C*-OCH_3), 150.8 (*C*-OCH_2, *C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1030 (C–O). EIMS: *m*/*z* (%) = 432 (100) [M^+], 417 (21), 359 (12). HRMS. calcd. for $C_{25}H_{20}O_7$ [M^+] 432.1209; found 432.1206. $C_{25}H_{20}O_7$ (432.42): calcd. C 69.44, H 4.66; found C 69.49, H 4.61.

Method B: A solution of PIFA (0.15 mmol) in dry dichloromethane (1 mL) was added to a stirred solution of diarylbenzofuran **3** (0.1 mmol) in dry dichloromethane (1.5 mL) at –20 °C under argon. After addition of $BF_3{\cdot}Et_2O$ (0.3 mmol), the resulting blue solution was stirred for 2.5 h at –20 °C and then quenched with Na_2CO_3 (3 mL of 10% solution in water). The same work-up as described in method A provided a residue which was purified by flash chromatography on silica gel with 15% EtOAc/hexane as eluent. Compounds **1b**–**d** were prepared by this procedure.

6,7-Dimethoxybenzo[*b*]phenanthro[9,10-*d*]furan (1b): Yield: 79%. Orange powder, m.p. 176–177 °C (Et_2O). R_f = 0.21 (30% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.16 (s, 3 H, OCH_3), 4.17 (s, 3 H, OCH_3), 7.47 (d, J = 5.9 Hz, 1 H, ArH), 7.48 (d, J = 5.9 Hz, 1 H, ArH), 7.62–7.77 (m, 3 H, ArH), 7.84 (s, 1 H, ArH), 8.08 (s, 1 H, ArH), 8.37 (dd, J = 5.9, 2.7 Hz, 1 H, ArH), 8.64 (d, J = 7.9 Hz, 2 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 56.0 (OCH_3), 56.1 (OCH_3), 101.7 (CH), 104.3 (CH), 111.7 (CH), 113.6 (C), 116.7 (C), 121.5 (CH), 123.2 (CH), 123.3 (CH), 124.2 (CH), 124.6 (CH), 125.0 (CH), 125.3 (C), 125.8 (C), 126.5 (CH), 127.5 (C), 127.8 (C), 148.5 (*C*-OCH_3), 149.7 (*C*-OCH_3), 149.8 (*C*-OCH_3), 155.5 (*C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1028 (C–O). EIMS: *m*/*z* (%) = 328 (100) [M^+], 313 (24), 257 (40), 255 (19), 242 (23). HRMS: calcd. for $C_{22}H_{16}O_3$ [M^+] 328.1099; found 328.1087. $C_{22}H_{16}O_3$ (328.36): calcd. C 80.47, H 4.91; found C 80.52, H 4.93.

6,7-Dimethoxy-11,12-dimethylbenzo[*b*]phenanthro[9,10-*d*]furan (1c): Yield: 71%. White powder, m.p. 225–226 °C (Et_2O). R_f = 0.25 (30% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 4.15 (s, 3 H, OCH_3), 4.15 (s, 3 H, OCH_3), 7.51 (s, 1 H, ArH), 7.60–7.79 (m, 2 H, ArH), 7.80 (s, 1 H, ArH), 8.00 (s, 1 H, ArH), 8.10 (s, 1 H, ArH), 8.62 (d, J = 7.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.3 (CH_3), 20.5 (CH_3), 56.0 (OCH_3), 56.1 (OCH_3), 101.6 (CH), 104.3 (CH), 112.1 (CH), 112.2 (C), 116.9 (C), 121.8 (CH), 123.1 (CH), 123.5 (C), 124.2 (CH), 124.4 (CH), 124.8 (C), 126.2 (CH), 127.4 (C), 127.8 (C), 131.7 (CH), 134.1 (CH), 149.3 (*C*-OCH_3), 149.7 (*C*-OCH_3),

150.5 (*C*-OCH_3), 154.5 (*C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1255 cm^{-1} (C–O), 1022 (C–O). EIMS: *m*/*z* (%) = 356 (100) [M^+], 341 (26), 298 (23), 285 (23), 283 (11), 270 (15). HRMS: calcd. for $C_{24}H_{20}O_3$ [M^+] 356.1412; found 356.1410. $C_{24}H_{20}O_3$ (356.41): calcd. C 80.88, H 5.66; found C 80.84, H 5.69.

11,12-Difluoro-6,7-dimethoxybenzo[*b*]phenanthro[9,10-*d*]furan (1d): Yield: 85%. Orange powder, m.p. 230–230.5 °C (Et_2O); R_f 0.33 (50% EtOAc/hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 4.11 (s, 3 H, OCH_3), 4.12 (s, 3 H, OCH_3), 7.46 (dd, J = 9.5, 6.3 Hz, 1 H, ArH), 7.57–7.60 (m, 3 H, ArH), 7.93–8.00 (m, 2 H, ArH), 8.51 (d, J = 6.7 Hz, 1 H, ArH), 8.52 (d, J = 7.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 56.0 (OCH_3), 100.7 (d, $J_{C,F}$ = 21.6 Hz, CH), 101.2 (CH), 103.9 (CH), 108.3 (d, $J_{C,F}$ = 20.74 Hz, CH), 112.1 (C), 116.0 (C), 120.9 (d, $J_{C,F}$ = 5.4 Hz, C), 123.0 (CH), 123.3 (CH), 124.9 (CH), 125.0 (C), 126.4 (CH), 126.6 (C), 127.2 (C), 147.6 (dd, $J_{C,F}$ = 240.0, 14.4 Hz, CF), 148.6 (dd, $J_{C,F}$ = 246.0, 16.2 Hz, CF), 149.6 (*C*-OCH_3), 149.7 (*C*-OCH_3), 150.3 (*C*-OCH_3), 152.0 (d, $J_{C,F}$ = 3.6 Hz, *C*-OCH_3) ppm. FTIR (neat): $\tilde{\nu}$ = 1260 cm^{-1} (C–O), 1023 (C–O). EIMS: *m*/*z* (%) = 364 (100) [M^+], 349 (21), 293 (47), 291 (22), 278 (24). HRMS: calcd. for $C_{22}H_{14}F_2O_3$ [M^+] 364.0911; found 364.0909. $C_{22}H_{14}F_2O_3$ (364.34): calcd. C 72.52, H 3.87, F 10.43; found C 72.58, H 3.84, F 10.46.

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