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Synthesis of Fused Dibenzofuran Derivatives via Palladium-catalyzed Domino C-C Bond formation and Iron-catalyzed Cycloisomerization/Aromatization

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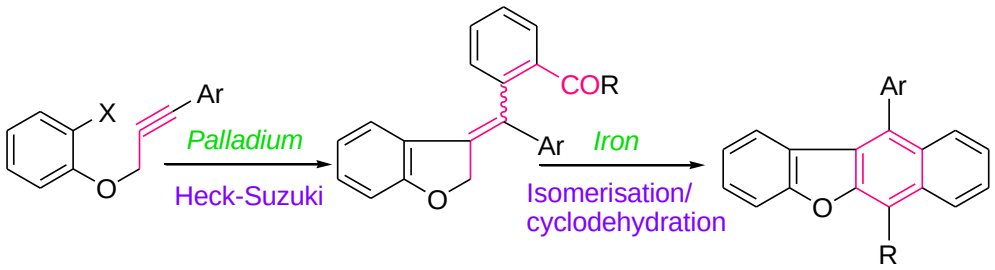


Abstract: A range of tetracyclic dibenzofuran derivatives bearing varieties of functional group were readily synthesized via a two stage domino strategy starting from propargyl ethers of 2-halo phenol derivatives. The first stage in the strategy involves a Pd(0)-catalyzed domino intramolecular carbopalladation/Suzuki coupling *via* 5-*exo*-*dig* cyclization onto alkyne leading to 3-Methylene-2,3-dihydrobenzofuran derivatives. In the second stage of the domino strategy, an iron(III)-catalyzed cycloisomerization and aromatization reaction produces tetracyclic benzofuran derivatives. This two-steps sequence provides an efficient access to diversely substituted polycyclic dibenzofuran derivatives in high yields with an atom-efficient and ecological manner. Moreover, this strategy has also successfully been used for the synthesis of naturally occurring tetracyclic dibenzofuran, *β*-Brazan.

Introduction:

Polycyclic oxygen heterocycles constitute an important class of fused heterocycles found in numerous natural products and have shown interesting biological properties. In particular, dibenzofuran derivatives are an important class of heterocyclic compounds that have attracted much interest over the years because of their occurrence in many natural products,[1] material science[2] and

pharmaceutically active compounds that exhibit anticancer, antibacterial, antiallergy, antimalarial, and anti-inflammatory activities.[3] Due to their broad range of biological activity and interesting pharmaceutical properties many synthetic routes have been developed to access dibenzofuran derivatives.[4] On the other hand, dibenzofuran embedded in tetracyclic structures are also found in many biologically active natural products and pharmaceutically active agents (**Fig 1**). For examples, tetracyclic *β*-Brazan **1a**, was isolated from the bark of the plant Caesalpiniaechinata Lamarck Brazilwood.[5a] It has also been reported that the related tetracyclic dibenzofuran derivatives are found to exhibit selective PTPase inhibitors that function as oral antidiabetic agents.[5b] Compound **1a** and its derivatives are also found to oxidized benzo[*b*]naphtha [2,3-*d*] furan-6,11-dione **1b**, which exhibits promising anticancer and anticoccidial W5599A activity.[5c-d] The tetracyclic structure balsaminone **A** (**1c**) is isolated from the pericarp of fruit of Impatiens balsamina**L**, this compound has significant antipruritic activity.[5e] Similarly, benzofurobenzofuran derivative **1d** exhibits strong potent antitubercular and antimycobacterial activity.[5f] Notably, benzofuroindole framework **1e** is highly efficient in the treatment of sexual hormone disorders, degenerative brain diseases and antitumor activity.[5g-h] Moreover, benzofuro[2,3-*b*]quinolinederivatives **1f** and benzofuro[2,3-*b*]pyridine **1g** have been reported as antituberculosis agent and CDK1, CDK5/p25 and GSK-3b inhibitor, respectively.[5i]

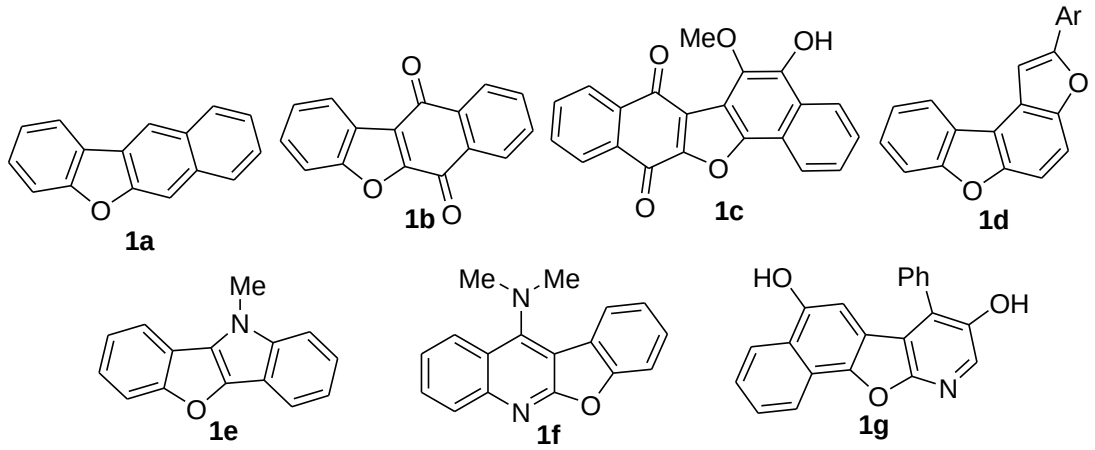


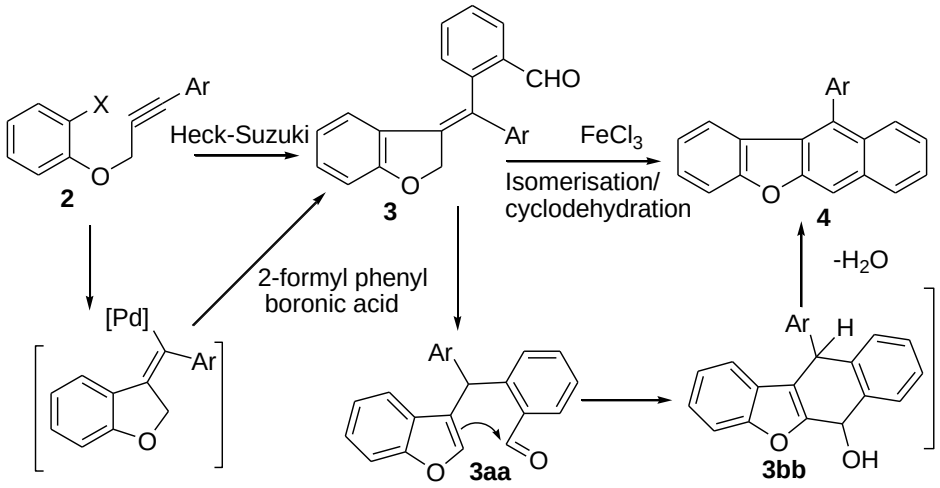
Figure 1. Fused-dibenzofuran derivatives in natural and medicinal compounds.

However, literature search revealed that a few methods has been developed for the synthesis of tetracyclic dibenzofuran derivatives.[4j,5b,6] Moreover, the described protocols are subjected to some

limitations, such as non-availability of starting materials, lack of generality, multistep operation, harsh reaction conditions, low chemical yields, unsatisfactory scope and efficiency. Owing to their important biological activities, a reliable synthetic method for this class of compounds in efficient and atom-economical manners are strongly required to further accesses in the area of drug discovery and development for new materials.

In recent years, transition metal-catalyzed domino process that allows the construction of complex molecules starting from simple substrates in a few steps represents a significant challenge for the synthesis of polycyclic molecules. In this context, palladium-catalyzed domino reactions are proved to be extremely powerful tools for the construction of polycyclic compounds.[7] In continuation of our investigation to the synthesis of polycyclic heterocycles,[8] recently, we have disclosed palladium-catalyzed domino carbopaladation/Suzuki reactions and iron(III)-mediated cycloisomerization/aromatization reaction for the simple synthesis of fused carbazole, C-3 substituted indoles and benzofuran derivatives.[9] This strategy was found to be very efficient, atom economical and environmentally friendly. Encouraged by these results, herein, we wish to report a simple, convenient and highly efficient two stage domino approach for the synthesis of diverse tetracyclic dibenzofuran derivatives starting from propargyl ethers of *o*-halo-phenol derivatives as the starting materials. Our strategy is depicted in Scheme 1. The first stage of this domino strategy involves intramolecular carbopalladation/Suzuki coupling of **2** to produce 3-methylene-2,3-dihydrobenzofuran derivative **3**. The reaction proceeds through an intramolecular *syn*-carbopalladation onto alkyne via a 5-*exo*-dig process produces a σ-alkylpalladium(II) intermediate, and subsequent intermolecular Suzuki coupling with 2-formyl phenylboronic acid derivatives gave the bicyclic product **3** in a stereoselective manner. In the second stage of this domino strategy, the compound **3** undergoes Lewis acid mediated isomerisation to **3aa**, followed by cyclization and aromatization reactions to generate tetracyclic dibenzofuran **4**. Significantly, the present method furnished wide range of functionalized tetracyclic benzofuran derivatives in excellent regioselective manner.

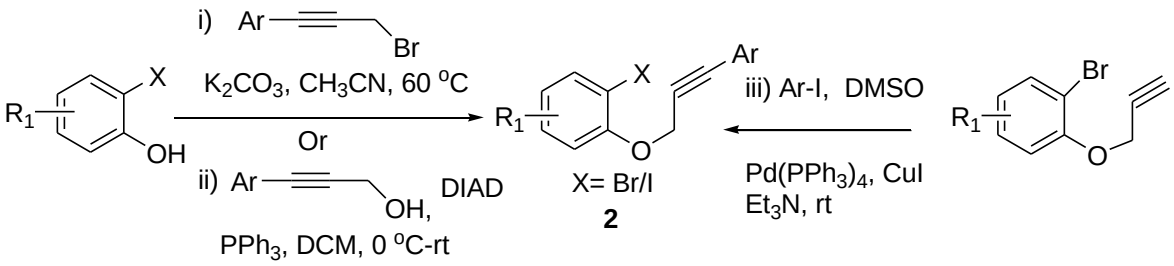
Scheme 1: The strategy of construction of substituted tetracyclic dibenzofuran system.



Results and Discussion

First, we prepared a series of 2-halo propargyl ethers derivatives **2** through two different routes (Scheme 2): a) reaction between 2-halo phenols and aryl propargyl bromide in the presence of K_2CO_3 in CH_3CN or Mitsunobu reaction of 2-halo phenols with propargyl alcohols; b) a selective Sonogashira cross-coupling of 1-bromo-(2-prop-2-ynyloxy)benzene derivatives with varieties of aryl iodides (Scheme 2). We have found both methods to be reliable and reproducible for reactions on both small and large scale in high yields.

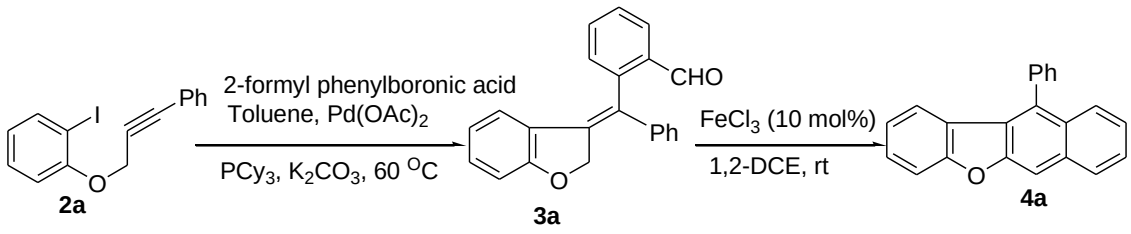
Scheme 2. Preparation of intermediate 1-halo-(2-prop-2-ynyloxy)benzenederivatives.



After having a series of 2-halopropargyl ethers, we investigated the synthesis of large array of tetracyclic dibenzofuran derivatives via our previously developed two steps method as described in scheme 3.[9] At first, we carry out the domino Heck−Suzuki coupling between **2a** and 2-formyl

phenylboronic acid to prepare the intermediate compound **3a** according to our previously developed method using 5 mol% of $Pd(OAc)_2$, 10 mol% of tricyclohexylphosphine (PCy_3) as ligand, and 2.5 M K_2CO_3 in combination with ethanol and toluene at 60 °C. Under these conditions, 3-Methylene-2,3-dihydrobenzofuran **3a** was obtained in 90% yield. In the next step, the compound **3a** was dissolved in 1,2-dichloroethane and was added $FeCl_3$ (10 mol%) at room temperature and it was observed that the final isomerisation/cylisation and aromatization process took place efficiently and afforded tetracyclic dibenzofuran **4a** in 95% yield within a short period of time at room temperature.

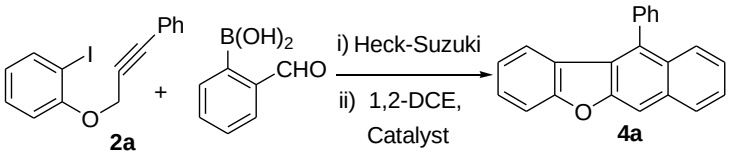
Scheme 3: Two steps preparation of tetracyclic dibenzofuran **4a**.



After that we intended to prepare a series of substrates **3b-3l** through Heck-Suzuki coupling with 2-formyl phenylboronic acid reactions under above said conditions. We noticed that in many cases a mixture of non separable isomers were isolated. To avoid the separation process, we decided to couple the above said two step domino strategies in one pot. Unfortunately, we observed that just after completion of Heck-Suzuki coupling when we added iron(III)-salt or any other Lewis and Brønsted acids directly to the reaction mixture no reaction took place. To our delight, we found that when the crude intermediate **3a** just after extraction with ethylacetate and removal of solvent, was subjected to second stage domino reactions without purification in the presence of anhydrous $FeCl_3$ (10 mol%), the final step domino reaction proceeded smoothly and gave the desired tetracyclic compound **4a** in 80% yield over two steps starting from **2a**. Switching to other Lewis- or Brønsted acids, such as $FeCl_3.6H_2O$, $FeBr_3$, $InCl_3$, AgOTf, $AlCl_3$, $ZnCl_2$, *p*-TsOH and TfOH to carry out this transformation under similar conditions were proved to be less efficient with respect to time, temperature and yields (Table 1). Various other solvents such as THF, toluene and acetonitrile were also studied, but did not give the better results. Thus, anhydrous $FeCl_3$ (10 mol%) in 1,2-

dichloroethane was set as the standard reaction conditions for the further study without isolating intermediate Heck-Suzuki products.

Table 1. Optimization of reaction conditions for cycloisomerization and aromatization process of **3a** to **4a**.[a]



2a **4a**

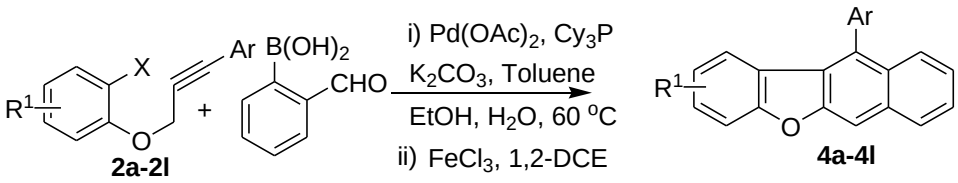
Entry	Catalysts	Temp (^oC)	Time (h)	Yield(%)
1	$FeCl_3$	rt	2	80
2	$FeCl_3,6H_2O$	60	1	70
3	$FeBr_3$	60	1	58
4	$InCl_3$	60	1.5	65
5	$In(OTf)_3$	60	4	62
6	AgOTf	60	2	70
7	p-TsOH	60	4	65
8	TfOH	60	1	72
9	$AlCl_3$	80	5	35[c]
10	$ZnCl_2$	80	6	20
11	CuCl	80	6	n.r

[a]Reaction conditions: i) Substrate **2a** (0.5 mmol), 2-formyl phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ (5 mol%), PCy_3(10 mol%), toluene (2 mL), EtOH (2 mL), aq. K_2CO_3 (2.5M, 2 mL); ii) catalyst (10 mol%),1,2-dichloroethane (3 mL). [c]2.5 equ. $AlCl_3$.

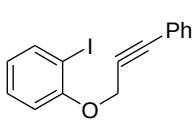
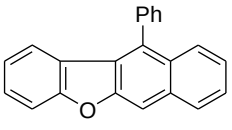
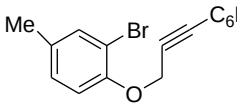
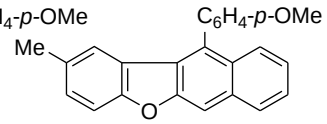
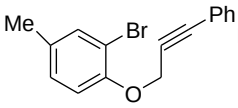
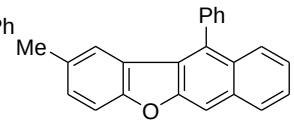
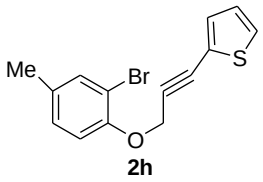
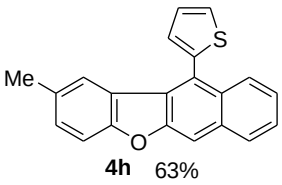
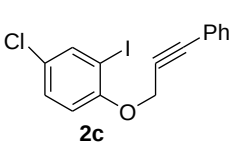
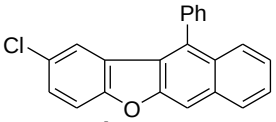
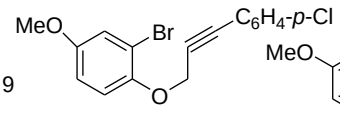
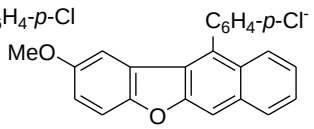
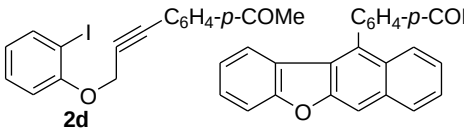
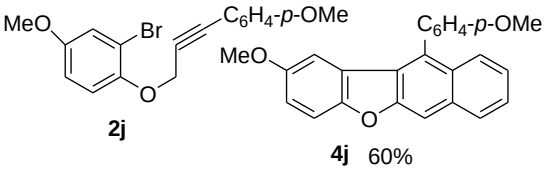
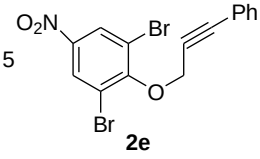
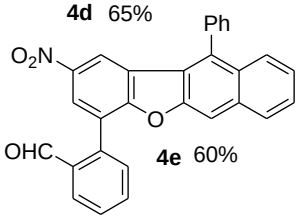
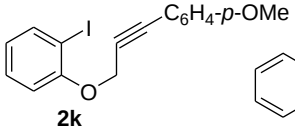
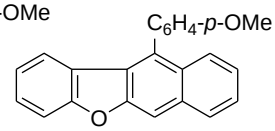
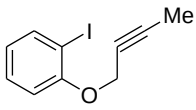
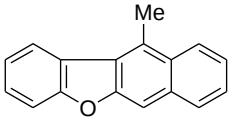
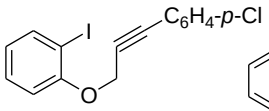
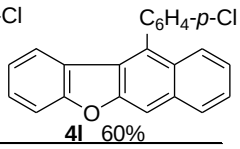
After developing the best reaction conditions using $FeCl_3$ in 1,2-dichloroethane, we decided to study the scope of this reaction on various substrates with different functional groups with crude Heck-Suzuki products. Both electron-donating such as –Me, –OMe (Scheme 4, entries **4b**, **4g**, **4h**, **4i** and **4j**) and withdrawing groups such as –Cl and $–NO_2$ were well tolerated (Scheme 4, entries **4c** and **4e**) and gave high yields of the desired tetracyclic ring in a two steps process. Interestingly, dibromo bearing aryl.ethers **2e**, when treated for domino Heck-Suzuki coupling reaction one of the halide

participated for Heck-Suzuki and other one underwent only Suzuki with 2-formyl boronic acids which subsequently transformed to the highly functionalized desired tetrcyclic product **4e** in 60% yield in two steps without affecting the other –CHO group. Alkyne unit bearing alkyl and aryl group also underwent smooth conversion to the desired product in high yields. Moreover, varieties of functional groups such as, -COMe, –OMe, and –Cl on aryl ring of alkyne were also survived for Heck-Suzuki coupling and subsequent $FeCl_3$-catalyzed cycloisomerization and dehydration reaction and gave good yields over two steps. It is noteworthy that 2-thiophenyl unit on alkyne terminus also underwent smooth Heck-Suzuki coupling and subsequent cyclization reactions to produce hybrid heterocycle **4h** (Scheme 4) in 63% yield.

Scheme 4. **Synthesis of varieties of teteracyclic dibenzofuran derivatives**.



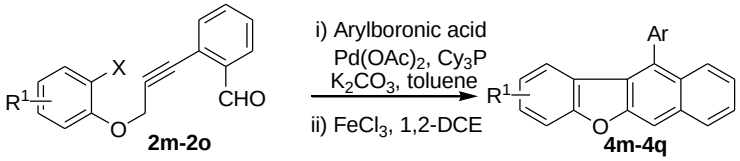
2a-2l **4a-4l**

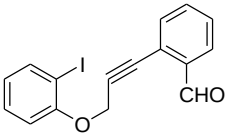
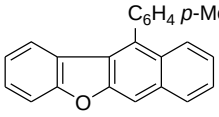
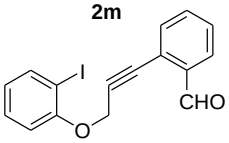
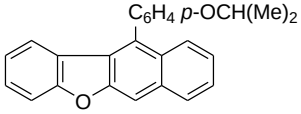
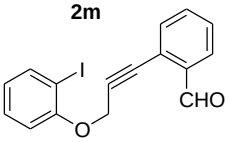
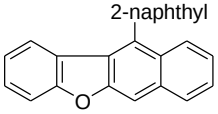
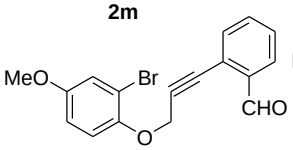
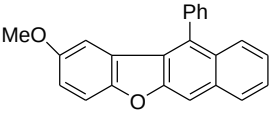
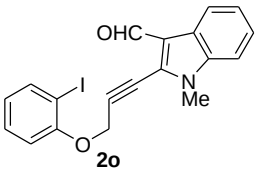
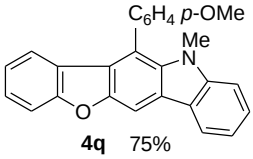
Entry	Substrate	Products	Entry	Substrate	Product
1	 **2a**	 **4a** 80%	7	 **2g**	 **4g** 70%
2	 **2b**	 **4b** 75%	8	 **2h**	 **4h** 63%
3	 **2c**	 **4c** 65%	9	 **2i**	 **4i** 65%
4	 **2d**	**4d** 65%	10	 **2j**	**4j** 60%
5	 **2e**	 **4e** 60%	11	 **2k**	 **4k** 85%
6	 **2f**	 **4f** 70%	12	 **2l**	 **4l** 60%

To demonstrate flexibility of this strategy, we also prepared a series of 2-halo propargylether of 2-formyl benzene **2m-2o** at the alkyne terminus (Table 2), so that any aryl boronic acid could be utilized for domino Heck-Suzuki coupling reactions instead of 2-formyl phenyl boronic acid. Gratifyingly, we observed that substrates **2m-2o** also underwent smoothly to the above said two steps domino strategies for the formation of tetracyclic dibenzofuran derivatives **4m-4q** in 60-75% yields in two steps (Table 2). For example, 2-naphthyl boronic acid underwent smooth conversion to produce naphthyl bearing tetracyclic dibenzofuran ring structure **4o** in 62% yield in overall two steps (Table 2, entry 3). Pleasantly, we also succeeded in synthesizing pentacyclic indole fused dibenzobenzofuran derivatives **4q** from the substrate **2o** via the above said two steps domino strategy in very good yields (Table 2, entry 5) at 60 °C. Both indole and dibenzofuran are present in many biologically active

natural products as well as pharmaceutically important substances; hence the hybrid structure **4q** would be very interesting pharmaceutical agent.

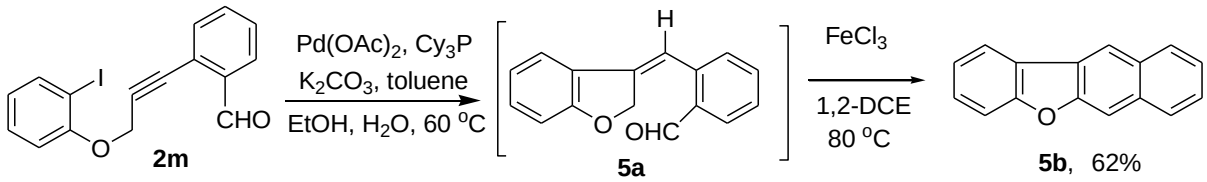
Table 2. Domino synthesis of polycyclic dibenzofuran with varities of aryl boronicacids.



Entry	Substrates	Products
1	 **2m**	 **4m** 60%
2	 **2m**	 **4n** 65%
3	 **2m**	 **4o** 62%
4	 **2n**	 **4p** 55%
5	 **2o**	 **4q** 75%

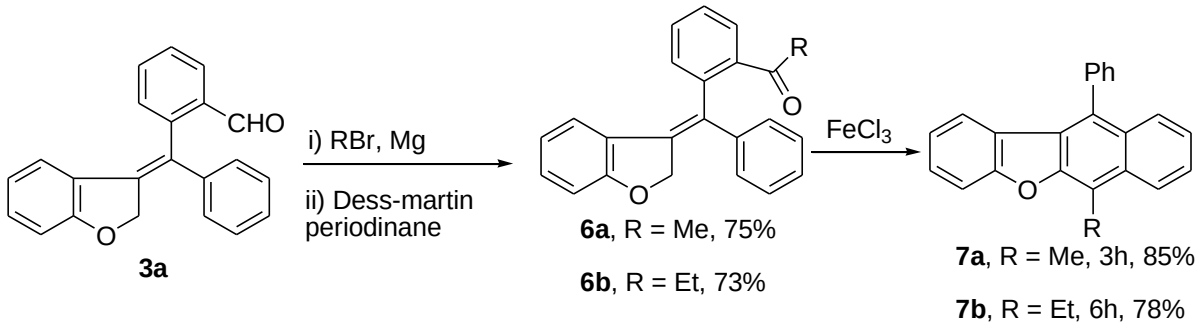
Next, we tried to synthesis the naturally occurring tetracyclic dibenzofuran, *β*-Brazan **5b**. The synthesis has been depicted in Scheme 5. When the substrate **2m** was subjected to carbopalladation and reduction, afforded the product **5a**.Then the crude product was treated with $FeCl_3$ (10 mol%), then the desired tetracyclic product **5b** was obtained in 62% yield in overall two steps. Our approach opens a novel route to the synthesis of natural product and its derivatives containing substituted tetracyclic dibenzofuran derivatives.

Scheme-5: Synthetic strategy for the synthesis of *β*-Brazan 5b.

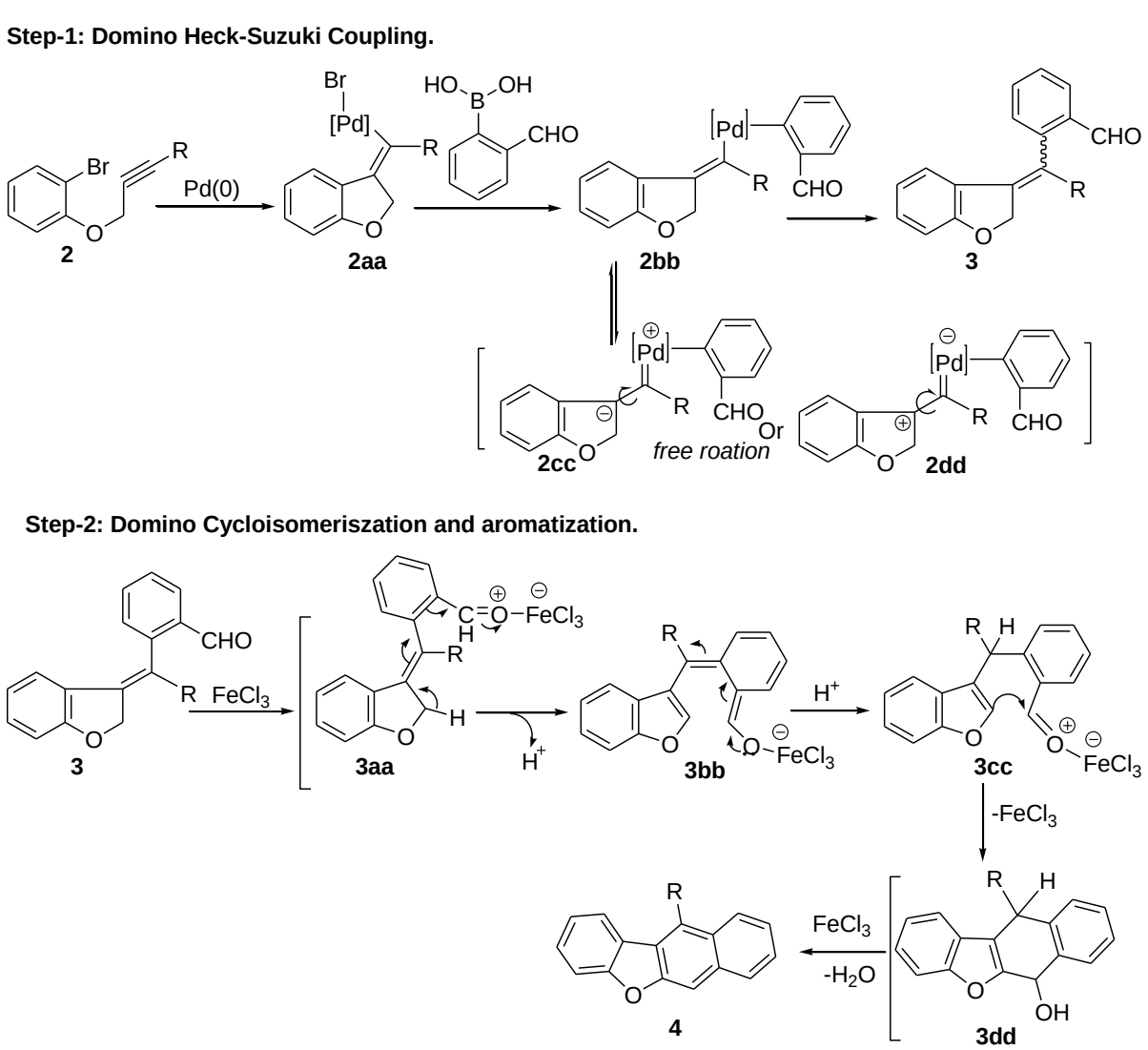


Finally, to make this strategy even more attractive, we also investigated $FeCl_3$-catalyzed cycloisomerization/aromatization of ketone **6a-6b**. The strategy is described in Scheme 6. The ketone functional group was introduced in the intermediate of Heck-Suzuki product **3a** by simple two steps reactions. First step involved reaction of alkyl Grignard reagents with **3a,** then the intermediate product without isolation was oxidized with Dess–Martin periodinane reagent to obtain **6a** (R = Me) in 75% yield and **6b** (R = Et) in 73% yield. Then when the substrates **6a-6b** were treated with $FeCl_3$ (10 mol%) in 1,2-dichloroethane at room temperature desired products **7a** and **7b** were obtained in 85% and 78% yields, respectively. Thus, this result adds another dimension to the versatility of this strategy.

Scheme 6: **Synthesis of tetracyclic dibenzofuran derivatives**.



Scheme 7: A Plausible mechanism for the domino synthesis of fused dibenzofuran.



Based on our previous experimental observations and following the literatures a plausible reaction pathway is delineated in Scheme 7. In Step-1, we propose a mechanism which involves oxidative addition of Pd(0)/PCy_3 with 2-halopropargyl ether 2 and followed by intramolecular *syn*-carbopalladation onto the carbon-carbon triple bond leading to generation of alkenylpalladium complex **2aa**. Next, transmetallation between **2aa** and aryl boronic acid in the presence of K_2CO_3 provides the intermediate **2bb,** which upon reductive elimination produces the product **3** with *syn*-configuration**,** and regenerates the catalyst for next catalytic cycles. Although the expected product in this sequence is the *syn*-**3** isomer, however, in many cases we have observed the formation of mixture of *syn*- and *anti*-isomers. Presumably, the isomerization of *syn*-adduct to *anti*-adduct in the carbopalladation step *via* the zwitterions intermediates **2cc** or **2dd**, and subsequent free rotation

around carbon-carbon sigma bond is the major reason for the formation of mixture isomers. This type of isomerization during carbopalladation of alkyne has also been reported in the literatures[10] and in our previous report.[9] For the step-II, a preliminary study shows that $FeCl_3$ did not initiate the isomerization/cyclization process of substrate **3** without bearing a 2-formyl group under the said reaction conditions and even heating at high temperature. Therefore, it was concluded that isomerization leading to the intermediate **3bb** must be driven by complexation of the carbonyl group of **3** with $FeCl_3$. Then, isomerization as shown in **3aa** and protonation of **3bb**, furnished the $FeCl_3$-bound intermediate **3cc**, which underwent intramolecular Fridel-Crafts alkylation and subsequent aromatization of **3dd** by dehydration of water afforded the tetracyclic dibenzofuran **3**, which is similar to the mechanism involved in Bradsher reaction.[11]

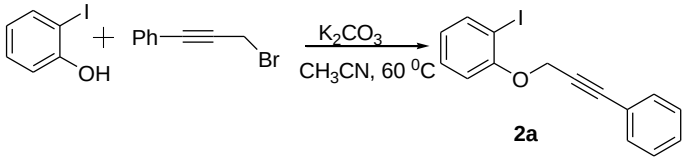
Conclusions

In summary, we have developed a simple and direct approach to access diverse range of synthetically and biologically important tetracyclic dibenzofuran derivatives by palladium-catalyzed domino carbopalladation/Suzuki coupling and subsequent iron(III)-catalyzed isomerization and cyclodehydration reaction. The strategy was found to be general and displays a wide substrate scope, good functional group tolerance, and provides moderate to high chemical yields. Moreover, this strategy has also been utilized for the synthesis of naturally occurring *β*-Brazan. So, the present method should have wide applications in organic and material chemistry.

Experimental Section :

General: ^1H NMR spectra were recorded with a (300, 400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, *δ*) and are referenced to $CDCl_3$ (*δ* = 7.26) as an internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded with a 300 (75 MHz), 400 (100 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts of $^{13}C\{^1H\}$ NMR are expressed in parts per million (ppm, *δ*) and are referenced to $CDCl_3$ (*δ* = 77.0 ppm) as an internal standard. HRMS measurement was done by ESI-TOF method.

Representative experimental procedure for the synthesis of propargylic ether (2a)



2a

To a solution of compound 2-iodo phenol (220 mg, 1 mmol) in dry acetonitrile (3 mL) was added phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol). The resulting mixture was heated at 60 °C for 2 h. After the completion of the reaction, the reaction mixture was extracted with dichloromethane. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated .The crude reaction product was purified by column chromatography using silica gel (60-120 mesh) eluting with petroleum ether to obtain the product **2a** as a colourless viscous liquid (300 mg, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.00 (s, 2H), 6.75 – 6.80 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.33 (s, 4H), 7.45 (s, 2H), 7.81 – 7.84 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.9, 83.5, 86.4, 87.7, 113.4, 122.2, 123.4, 128.3, 128.8, 129.4, 131.8, 139.7, 156.6 ppm. HRMS (ESI-TOF): cacld for $C_{15}H_{12}IO$ $[M+H]^+$ 334.9933; found 334.9930.

2-bromo-4-methyl-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (2b): Compound 4-methyl 2-bromo phenol (187 mg, 1 mmol) in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol) as described for the synthesis **2a** for 2 h to afford the product **2b** as a colourless viscous liquid (250mg, 0.83 mmol, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H), 4.96 (s, 2H), 7.03 – 7.07 (m, 2H), 7.27 – 7.33 (m, 3H), 7.39 (s, 1H), 7.41– 7.44 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 58.1, 83.6, 87.6, 112.4, 114.8, 122.3, 128.3, 128.8, 131.8, 132.6, 133.2, 132.6, 133.2, 133.9, 152.2 ppm. HRMS (ESI-TOF): cacld for $C_{16}H_{14}BrO$ $[M+H]^+$ 301.0228; found 301.0227.

4-chloro-2-iodo-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (2c): Compound 4-chloro 2-iodo phenol (255 mg, 1 mmol) in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol) as described for the synthesis **2a** for 2 h to afford the product **2c** as a white solid (295 mg, 0.80 mmol, 80%), m.p. 64 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.96 (s, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.33 (m, 4H), 7.39 – 7.44 (m, 2H), 7.77 (d, *J* = 1.9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 58.2, 82.9, 87.0, 88.1, 113.9, 121.9, 127.3, 128.4, 128.9, 129.1, 131.8, 138.8, 139.1, 155.5 ppm. HRMS (ESI-TOF): cacld for $C_{15}H_{11}ClIO$ $[M+H]^+$ 368.9543; found 368.9542.

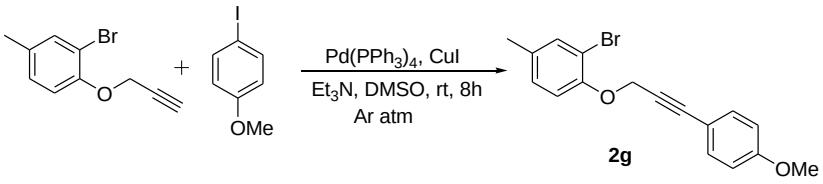
1-(4-(3-(2-iodophenoxy)prop-1-yn-1-yl)phenyl)ethanone (2d): Compound 2-iodo phenol (220 mg, 1 mmol) in dry acetonitrile was treated with 4-acetyl phenyl propargyl bromide (260 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol) as described for the synthesis **2a** for 2 h to afford the product **2d** as a

colourless viscous liquid (320 mg, 0.85 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.58 (s, 3H), 5.00 (s, 2H), 6.77 – 6.79 (m, 1H), 7.07 (dd, *J* = 1.2 Hz, 8.2 Hz, 1H), 7.30 – 7.34 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.80 (dd, *J* = 1.6 Hz, 7.8 Hz, 1H), 7.88 (dd, *J* = 1.7 Hz, 6.8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.6, 57.8, 86.7, 86.8, 113.3, 126.9, 128.2, 129.4, 131.9, 136.7, 139.8, 156.5, 197.2 ppm. HRMS (ESI-TOF): cacld for $C_{17}H_{14}IO_2$ $[M+H]^+$ 377.0038; found 377.0036.

1,3-dibromo-5-nitro-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (2e): Compound 4-nitro 2,6- dibromo phenol (295 mg, 1 mmol)in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol) as described for the synthesis **2a** for 2 h to afford the product **2e** as a yellow solid (37mg, 0.80 mmol, 80%), m.p. 98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.15 (s, 2H), 7.27 – 7.40 (m, 5H), 8.43 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 61.9, 82.2, 89.1, 119.4, 121.7, 127.6, 128.1, 128.3, 128.4, 128.9, 131.6, 144.5, 157.7 ppm. HRMS (ESI-TOF): cacld for $C_{15}H_{10}Br_2NO_3$ $[M+H]^+$ 409.9027; found 409.9028.

1-(but-2-yn-1-yloxy)-2-iodobenzene (2f): Compound 2-iodo phenol (220 mg, 1 mmol) in dry acetonitrile was treated with methyl propargyl bromide (163 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol) as described for the synthesis of **2a** for 2 h to afford the product **2f** as a colourless viscous liquid (244 mg, 0.85 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (t, *J* = 2.3 Hz, 3H), 4.71 (q, *J* = 2.2 Hz, 2H), 6.70 – 6.76 (m, 1H), 6.99 (dd, *J* = 1.1 Hz, 8.2 Hz, 1H), 7.27–7.33 (m, 1H), 7.77 (dd, *J* = 1.5 Hz, 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ3.8, 57.6, 73.7, 84.3, 86.7, 113.1, 123.1, 124.5, 129.4, 139.6, 156.6 ppm. HRMS (ESI-TOF):cacld for $C_{10}H_{10}IO$ $[M+H]^+$ 272.9776; found 272.9775.

Representative experimental procedure for the synthesis of propargylic ether (2g):



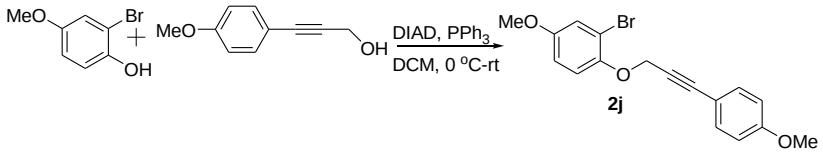
To a solution of 2-bromo-4-methyl-1-(prop-2-yn-1-yloxy)benzene (225 mg, 1.0 mmol), *p*-anisole (257 mg, 1.1 mmol) and triethyl amine (202 mg, 2.0 mmol) in DMSO (5 mL) were added CuI (4 mg, 0.02 equiv) and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv) successively. The resulting mixture was stirred at room temperature for 8 h under argon atmosphere. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine

solution, dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 98:2 (v/v) to afford the product **2g** as a light yellow viscous liquid (300 mg, 0.9 mmol, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H),3.80 (s, 3H), 4.94 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.05 – 7.09 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 55.3, 58.2, 82.3, 87.6, 112.3, 113.9, 114.3, 114.7, 128.8, 133.3, 133.9, 152.2, 159.9 ppm. HRMS (ESI-TOF): cacld for $C_{17}H_{16}BrO_2$ $[M+H]^+$ 331.0334; found 331.0331.

2-(3-(2-bromo-4-methylphenoxy)prop-1-yn-1-yl)thiophene (2h): Compound 2-bromo-4-methyl-1-(prop-2-yn-1-yloxy)benzene (225 mg, 1.0 mmol) in DMSO was treated with 2-iodo thiophene (230 mg, 1.1 mmol), triethyl amine (202 mg, 2.0 mmol), CuI (4 mg, 0.02 equiv) and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv) as described for the synthesis of **2g** to afford the **2h** as a light yellow viscous liquid (280 mg, 0.91 mmol, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H), 4.96 (s, 2H), 6.95 – 6.99 (m, 1H), 7.02 (s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.25 – 7.27 (m, 1H), 7.38 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 58.1, 80.9, 87.6, 112.4, 114.8,122.1, 126.9, 127.7, 128.8, 132.7, 132.8, 133.9, 152.1 ppm. HRMS (ESI-TOF):cacld for $C_{14}H_{12}BrOS$ $[M+H]^+$ 306.9792; found 306.9790.

2-bromo-1-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-4-methoxybenzene (2i): Compound 2-bromo-4-methoxy-1-(prop-2-yn-1-yloxy)benzene (241 mg, 1.0 mmol) in DMSO was treated with 1-chloro-4-iodobenzene (262 mg, 1.1 mmol) triethyl amine (202 mg, 2.0 mmol), CuI (4 mg, 0.02 equiv) and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv) as described for the synthesis of **2g** to afford the **2i** as a light yellow viscous liquid (330 mg, 0.94 mmol, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.78 (s, 3H), 4.93 (s, 2H), 6.85 (dd, *J* = 2.9 Hz, 8.9 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 2.9 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.8, 58.9, 84.8, 86.4, 113.6, 116.8, 118.9, 120.7, 128.7, 133.0, 134.8, 137.7, 148.5, 155.1 ppm. HRMS (ESI-TOF): cacld for $C_{16}H_{13}BrClO_2$ $[M+H]^+$ 350.9787; found 350.9785.

Representative experimental procedure for the synthesis of propargylic ether (2j):



2j

To an ice cooled solution of 4-methoxy-2-bromo phenol (203 mg, 1.0 mmol), p-methoxy phenyl propargyl alcohol (195 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane was added a solution of di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) in dichoromethane under argon atmosphere. Then the reaction was continued at room temperature for 28 h. After the completion of the reaction (monitored by TLC) the reaction mixture was extracted with dichloromethane, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction product was purified by column chromatography using silica gel (60-120 mesh) eluting with pet ether to afford the product **2j** as a colourless viscous liquid (300 mg, 0.8 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.76 (s, 3H), 3.80 (s, 3H), 4.91 (s, 2H), 6.81 – 6.84 (m, 3H), 7.09 – 7.13 (m, 2H), 7.34 – 7.40 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.2, 55.8, 59.0, 82.4, 87.6, 113.5, 113.7, 113.9, 114.3, 116.7, 118.8, 133.3, 148.6, 154.9, 159.9 ppm. HRMS (ESI-TOF): cacld for $C_{17}H_{16}BrO_3$ $[M+H]^+$ 347.0283; found 347.0282.

1-iodo-2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene (2k): Compound 2-iodo phenol (220 mg, 1.0 mmol), *p*-methoxy phenyl propargyl alcohol (194 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane was treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) as described for the synthesis of **2j** for 28 h to afford the product **2k** as a colourless viscous liquid (290 mg, 0.8 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.78 (s, 3H), 4.97 (s, 2H), 6.75 (dt, *J* = 1.2 Hz, 7.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.08 – 7.11 (m, 1H), 7.30 – 7.40 (m, 3H), 7.80 (dd, *J* = 1.5 Hz, 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3, 58.0, 82.2, 86.8, 87.7, 113.4, 113.9, 114.2, 123.3, 129.4, 133.4, 139.7, 156.7, 159.9 ppm. HRMS (ESI-TOF): cacld for $C_{16}H_{14}IO_2$ $[M+H]^+$ 365.0038; found 365.0035.

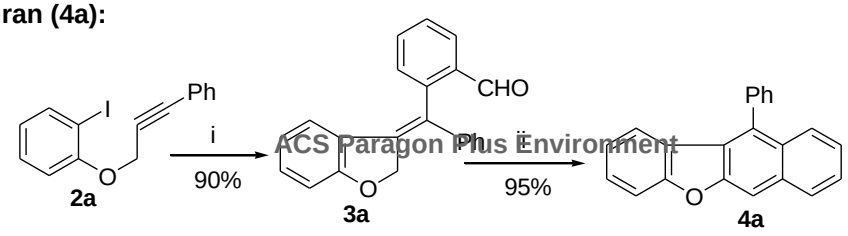
1-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-2-iodobenzene (2l): Compound 2-iodo phenol (220 mg, 1.0 mmol), *p*-chloro phenyl propargyl alcohol (200 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry DCM was treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) as described for the synthesis of **2j** for 24 h to afford the product **2l** as a colourless viscous liquid (276 mg, 0.75 mmol, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.97 (s, 2H), 6.76 (dt, *J* = 1.3 Hz, 7.5 Hz, 1H), 7.06 (dd, *J* = 1.2 Hz, 8.2 Hz, 1H), 7.28 – 7.31 (m, 2H), 7.34 – 7.37 (m, 3H), 7.81 (dd, *J* = 1.5 Hz, 7.8 Hz, 1H) ppm.^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.8, 84.5, 86.6, 113.4, 120.7, 123.5, 128.7, 129.4, 133.1, 134.9, 139.7, 156.6 ppm. HRMS (ESI-TOF): cacld for $C_{15}H_{11}ClIO$ $[M+H]^+$ 368.9543; found 368.9541.

2-(3-(2-iodophenoxy)prop-1-yn-1-yl)benzaldehyde (2m): Compound 2-iodo phenol (220 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)benzaldehyde (192 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry DCM was treated with *di*-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) as described for the synthesis of **2j** for 20 h to afford the product **2m** as a dark yellow viscous liquid (280 mg, 0.77 mmol, 77%).^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.04 (s, 2H), 6.77 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 9.1 Hz, 1H), 7.31 – 7.37 (m, 1H), 7.41 – 7.46 (m, 1H), 7.53 (d, J = 3.7 Hz, 2H), 7.80 (dd, J = 1.4 Hz, 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 10.4 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.7, 83.5, 86.9, 90.5, 113.4, 123.7, 125.4, 127.3, 129.2, 129.4, 133.5, 133.7, 136.3, 139.9, 156.4, 191.2 ppm. HRMS (ESI-TOF): cacld for $C_{16}H_{12}IO_2$ $[M+H]^+$ 362.9882; found 362.9883.

2-(3-(2-bromo-4-methoxyphenoxy)prop-1-yn-1-yl)benzaldehyde (2n): Compound 4-methoxy 2-bromo phenol (203 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)benzaldehyde (192 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane was treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol)as described for the synthesis of **2j** for 24 h to afford the product **2n** as a dark yellow viscous liquid (275 mg, 0.79 mmol, 79%).^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.79 (s, 3H), 5.02 (s, 2H), 6.86 (dd, J = 2.9 Hz, 8.9 Hz, 1H), 7.11 (d, J = 8.9 Hz, 1H), 7.17 (d, J = 2.9 Hz, 1H), 7.44 – 7.51 (m, 1H), 7.55 – 7.57 (m, 2H), 7.92 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.9, 58.9, 83.3, 90.9, 113.7, 116.9, 119.0, 125.5, 127.3, 128.3, 128.5, 129.1, 133.5, 133.7, 136.2, 148.3, 155.3, 191.3 ppm. HRMS (ESI-TOF): cacld for $C_{17}H_{13}BrNaO_3$ $[M+Na]^+$ 366.9946; found 366.9945.

2-(3-(2-iodophenoxy)prop-1-yn-1-yl)-1-methyl-1H-indole-3-carbaldehyde (2o): Compound 2-iodo phenol (220 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)-1-methyl-1H-indole-3-carbaldehyde (255 mg, 1.2 mmol), PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane was treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) as described for the synthesis of **2j** for 24 h to afford the product **2o** as a dark yellow viscous liquid (290 mg, 0.70 mmol, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.76 (s, 3H), 5.14 (s, 2H), 6.80 (dt, J =1.3 Hz, 7.6 Hz, 1H), 7.07 (dd, J = 1.3 Hz, 8.2 Hz, 1H), 7.30 – 7.39 (m, 4H), 7.82 (dd, J = 1.5 Hz, 7.8, 1H,), 8.27 – 8.30 (m, 1H), 10.0 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 57.6, 86.9, 95.4, 109.8, 113.4, 120.6, 122.2, 123.4, 123.6, 124.2, 125.3, 129.8, 130.2, 137.4, 139.9, 156.1, 184.9 ppm. HRMS (ESI-TOF): cacld for $C_{19}H_{15}INO_2$ $[M+H]^+$ 416.0147; found 416.0144.

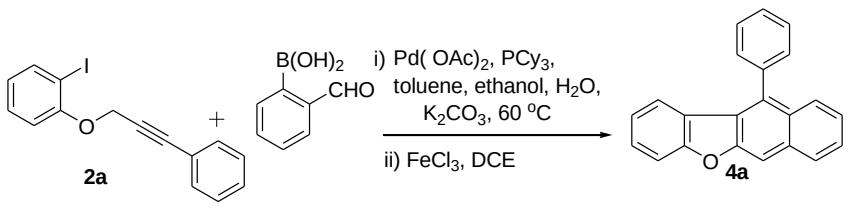
Representative experimental procedurefor the two step synthesis of 11-phenylnaphtho[2,3-*b*]benzofuran (4a):



Synthesis of (3a):[9a] To a solution of **2a** (167 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL) were added aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) successively. The resulting solution was stirred at 60 °C under argon atmosphere for 1 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated. After the completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography using silica gel (60-120 mesh), eluting with pet ether/EtOAc to afford the product **3a** as a light green solid (140 mg, 0.45 mmol, 90%), m.p. 189 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 5.35–5.49 (m, 2H), 5.89 (d, J = 7.8 Hz, 1H), 6.53 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz,1H), 7.07 – 7.12 (m, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.28 – 7.39 (m, 4H), 7.57 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 10.16 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.8, 75.3, 110.7, 120.7, 124.2, 125.3, 127.6, 127.8, 127.9, 128.4, 128.7, 128.8, 129.0, 130.6, 131.3, 133.7, 134.3, 135.2, 137.1, 141.1, 144.8, 164.3, 192.0 ppm. HRMS (ESI-TOF): cacld for $C_{22}H_{17}O_2$ $[M+H]^+$ 313.1229; found 313.1228.

Synthesis of (4a)[9a]**:** To a solution of compound **3a** (94 mg, 0.3 mmol) in 1,2-dichloethane was added anhydrous $FeCl_3$ (5 mg, 0.03 mmol) under argon atmosphere at room temperature for 2 h to afford **4a** as a white solid (84 mg, 0.28 mmol, 95%), m.p. 102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.93 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.37 (m, 2H), 7.51–7.56 (m, 4H), 7.61–7.67 (m, 3H), 7.78 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.4, 111.2, 122.4, 122.8, 123.5, 124.0, 124.2, 125.7, 126.2, 127.8, 128.0, 128.1, 128.9, 129.3, 130.0, 133.1, 134.2, 137.8, 154.2, 157.7 ppm. HRMS: cacld for $C_{22}H_{15}O$ [M+H]+ 295.1123; found 295.1122. 154.1, 157.8, 197.9 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{17}O_2$ $[M+H]^+$ 295.1123; found 295.1121.

Representative experimental procedure for the synthesis of 11-phenylnaphtho[2,3-*b*]benzofuran 4a without isolation of (3a):



To a solution of **2a** (167 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL) were added 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol) successively. The resulting solution was stirred at 60 °C under argon atmosphere for 1 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was dissolved in 1,2dichloroethane (3 mL) and $FeCl_3$ (8 mg, 10 mol%) was added to it. The reaction was continued at rt for 2 h under argon atmosphere. After the completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography using silica gel (60-120 mesh), eluting with pet ether/EtOAc 98:2 (v/v) to afford the product **4a** as a white solid (117 mg, 0.4 mmol, 80%).

2-methyl-11-phenylnaphtho[2,3-*b*]benzofuran (4b): Compound **2b** (151 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h to afford **4b** as a off white solid (115 mg, 0.37 mmol, 75%), m.p. 98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.27 (s, 3H), 6.68 (s, 1H), 7.21 – 7.26 (m, 1H), 7.36 – 7.44 (m, 2H), 7.50 – 7.55 (m, 3H), 7.63 (d, *J* = 6.5 Hz, 3H), 7.76 (d, *J* = 8.5 Hz, 1H) 7.93 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H) ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ21.4, 106.4, 110.9, 123.1, 123.7, 124.1, 125.8, 126.4, 127.9, 128.1, 129.0, 129.1, 129.4, 130.1, 131.9, 134.2, 137.9, 154.6, 156.1 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{17}O$ $[M+H]^+$ 309.1279; found 309.1276.

2-chloro-11-phenylnaphtho[2,3-*b*]benzofuran (4c): Compound **2c** (184 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1 h to afford **4c** as a off white solid (107 mg, 0.32 mmol, 65%), m.p. 145 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 6.81 (d, *J* = 2.1 Hz, 1H), 7.34 –7.56 (m, 6H), 7.63 – 7.66 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.94 (s,

1H), 8.01 (d, *J* = 8.3 Hz, 1H) ppm.^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 106.6, 112.2, 122.6, 124.5, 125.6, 126.4, 127.8, 127.9, 128.5, 129.1, 129.8, 133.4, 134.8, 154.5, 156.0 ppm. HRMS (ESI-TOF): cacld for $C_{22}H_{14}ClO$ $[M+H]^+$ 329.0733; found 329.0732.

1-(4-(naphtho[2,3-*b*]benzofuran-11-yl)phenyl)ethanone (4d): Compound **2d** (188 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h to afford **4d** as a off white solid (108 mg, 0.32 mmol, 65%), m.p. 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.77 (s, 3H), 6.89 (d, *J* = 7.6Hz, 1H), 7.04 – 7.09 (m, 1H), 7.37 – 7.46 (m, 2H), 7.52 – 7.68 (m, 2H), 7.63 – 7.68 (m, 3H), 8.01 (t, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 26.8, 107.0, 111.4, 122.6, 122.7, 123.3, 123.6, 124.6, 125.8, 125.9, 128.0, 128.4, 128.8, 128.9, 130.1, 132.7, 133.1, 136.9, 143.0, 154.1, 157.8, 197.9 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{17}O_2$ $[M+H]^+$ 337.1229; found 337.1228.

2-(2-nitro-11-phenylnaphtho[2,3-*b*]benzofuran-4-yl)benzaldehyde (4e): Compound **2e** (206 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (186 mg, 1.25 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 4 h at 60 °C to afford **4e** as a light yellow solid (133 mg, 0.30 mmol, 60%), m.p. 246 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.46 (dt, *J* = 0.8 Hz, 6.8 Hz, 1H), 7.52 – 7.60 (m, 4H), 7.69 – 7.75 (m, 4H), 7.79 – 7.84 (m, 3H), 7.93 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.15 – 8.18 (m, 1H), 8.37 (d, *J* = 2.4 Hz, 1H), 9.95 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 107.6, 118.5, 121.8, 122.9, 124.5, 125.3, 126.6, 126.9, 128.1, 129.0, 129.3, 129.5, 129.6, 129.7, 131.5, 133.8, 134.1, 134.2, 135.9, 136.4, 136.9, 143.8, 154.6, 158.3, 190.7 ppm. HRMS (ESI-TOF): cacld for $C_{29}H_{18}NO_4$ $[M+H]^+$ 444.1236; found 444.1233.

11-methylnaphtho[2,3-*b*]benzofuran (4f): Compound **2f** (136 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the

synthesis of **4a** for 8 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2 dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at room tempetature to afford **4f** as a white solid (81 mg, 0.35 mmol, 70%), m.p. 107 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.12 (s, 3H), 7.35 – 7.41 (m, 1H), 7.48 – 7.59 (m, 4H), 7.77 (s, 1H), 7.94 – 7.97 (m, 1H), 8.19 – 8.25 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 104.9, 111.3, 122.6, 123.3, 123.6, 123.9, 124.0, 124.1, 124.8, 125.6, 127.6, 128.4, 129.2, 129.5, 133.2, 154.3, 157.5 ppm. HRMS (ESI-TOF): cacld for $C_{17}H_{13}O$ $[M+H]^+$ 233.0966; found 233.0965.

11-(4-methoxyphenyl)-2-methylnaphtho[2,3-*b*]benzofuran (4g): Compound **2g** (165 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at 60 °C to afford **4g** as a white solid (118 mg, 0.35 mmol, 70%), m.p. 135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3H), 3.99 (s, 3H), 6.81 (s, 1H), 7.16 – 7.21 (m, 2H), 7.25 (d, J = 4.9 Hz, 1H), 7.35 – 7.45 (m, 4H), 7.49 (m, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.91 (s, 1H), 7.99 (d, J= 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 55.5, 106.2, 110.7, 114.3, 122.9, 123.8, 124.0, 124.1, 125.6, 126.3, 127.8, 128.9, 129.9, 131.2, 131.8, 133.1, 154.6, 156.0, 159.5 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{18}NaO_2$ $[M+Na]^+$ 361.1204; found 361.1205.

2-methyl-11-(thiophen-2-yl)naphtho[2,3-*b*]benzofuran (4h): Compound **2h** (154 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1.5 h at room temperature to afford **4h** as a colourless viscous liquid (99 mg, 0.31 mmol, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.35 (s, 3H), 7.03 (s, 1H), 7.23 (t, J = 8.6 Hz, 1H), 7.39 – 7.44 (m, 1H), 7.46 – 7.51 (m, 3H), 7.56 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.96 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 8.41 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 111.3, 118.8, 120.9, 122.2, 122.6, 123.9, 124.9, 125.3, 126.2, 127.6, 128.7, 129.6, 131.5, 132.5, 138.4, 140.7, 144.2, 153.9 ppm. HRMS (ESI-TOF): cacld for $C_{21}H_{15}OS$ $[M+H]^+$ 315.0844; found 315.0843.

11-(4-chlorophenyl)-2-methoxynaphtho[2,3-*b*]benzofuran (4i): Compound **2i** (175 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 8 h at 60 °C to afford **4i** as a white solid (116 mg, 0.32 mmol, 65%),m.p. 85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.68 (s, 3H), 6.44 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 2.5 Hz, 8.9 Hz, 1H), 7.39 – 7.49 (m, 4H), 7.53 – 7.58 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.6, 106.5, 106.8, 111.7, 115.5, 123.8, 124.2, 124.4, 125.8, 127.9, 128.9, 129.1, 131.7, 132.5, 133.1, 134.3, 136.1, 152.4, 154.8, 155.4 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{16}ClO_2$ $[M+H]^+$ 359.0839 ; found 359.0840.

2-methoxy-11-(4-methoxyphenyl)naphtho[2,3-*b*]benzofuran (4j): Compound **2j** (174 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 3 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1 h at 60 °C to afford **4j** as a white solid (106 mg, 0.30 mmol, 60%), m.p. 104 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.64 (s, 3H), 3.96 (s, 3H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 2.6 Hz, 8.8 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.45 (m, 4H), 7.49 – 7.54 (m, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.6, 106.2, 106.7, 106.7, 111.4, 114.2, 115.2, 124.0, 124.1, 125.6, 126.2, 127.8, 129.4, 129.7, 131.3, 133.2, 133.9, 152.3, 154.9, 155.2, 159.5 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{19}O_3$ $[M+H]^+$ 355.1334; found 355.1331.

11-(4-methoxyphenyl)naphtho[2,3-*b*]benzofuran (4k): Compound **2k** (182 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 1 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at room temperature to afford **4k** as a white solid (138 mg, 0.43 mmol, 85%), m.p. 128 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.99 (s, 3H), 7.01 (d, *J* = 7.7 Hz, 1H), 7.08 (m, 1H), 7.17 (d, *J* = 8.5 Hz,

2H), 7.36 – 7.45 (m, 4H), 7.50 – 7.55 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 55.4, 106.2, 111.2, 114.3, 122.4, 122.9, 123.8, 124.2, 125.7, 125.7, 126.3, 127.8, 127.9, 129.7, 129.9, 1312.2, 133.2, 134.0, 154.2, 157.7, 159.5 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{16}NaO_2$ $[M+Na]^+$ 347.1048; found 347.1049.

11-(4-chlorophenyl)naphtho[2,3-*b*]benzofuran (4l): Compound **2l** (184 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at room temperature to afford **4l** as a white solid (98 mg, 0.30 mmol, 60%), m.p. 190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 6.97 (d, *J* = 7.8 Hz, 1H), 7.08 – 7.13 (m, 1H), 7.37 – 7.47 (m, 4H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 106.8, 111.4, 122.5, 122.7, 123.6, 123.7, 124.5, 125.8, 127.9, 128.3, 129.1, 129.3, 131.5, 132.6, 133.1, 134.2, 136.2, 154.1, 157.7 ppm. HRMS (ESI-TOF): cacld for $C_{22}H_{14}ClO$ $[M+H]^+$ 329.0733; found 329.0734.

11-(p-tolyl)naphtho[2,3-*b*]benzofuran (4m): Compound **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1 h at 60 °C to afford **4m** as a white solid (92 mg, 0.30 mmol, 60%), m.p. 144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.57 (s, 3H), 6.98 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.46 (m, 6H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 21.5, 106.2, 11.2, 122.4, 122.9, 123.6, 124.1, 124.2, 125.7, 126.4, 127.8, 127.9, 1 29.5, 129.6, 129.9, 133.2, 134.4, 134.7, 137.8, 154.2, 157.7 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{17}O$ $[M+H]^+$ 309.1279; found 309.1280.

11-(4-isopropoxyphenyl)naphtho[2,3-*b*]benzofuran (4n): Compound **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the

Suzuki step for the synthesis of **4a** for 1.5 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1 h at room temperature to afford **4n** as a white solid (115 mg, 0.32 mmol, 65%), m.p. 116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.48 (d, J = 6.0 Hz, 6H), 4.71 – 4.77 (m, 1H), 7.05 – 7.09 (m, 2H), 7.14 (d, J = 8.6 Hz, 2H), 7.39 – 7.44 (m, 4H), 7.49 – 7.55 (m, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.93 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ22.2, 70.1, 106.2, 111.2, 111.6, 116.2, 121.3, 122.4, 123.8, 124.1, 124.2, 125.7, 126.4, 127.8, 127.9, 128.4, 129.6, 129.7, 131.2, 133.2, 134.2, 154.2, 157.7, 157.8 ppm. HRMS (ESI-TOF): cacld for $C_{25}H_{21}O_2$ $[M+H]^+$ 353.1542; found 353.1540.

11-(naphthalen-2-yl)naphtho[2,3-*b*]benzofuran (4o): Compound **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 1.5 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at room temperature to afford **4o** as a white solid (107 mg, 0.31 mmol, 62%), m.p. 140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (d, J = 7.7 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 7.38 – 7.43 (m,2H), 7.53 – 7.57 (m, 2H), 7.61 – 7.67 (m, 3H), 7.81 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 8.01 – 8.07 (m, 4H), 8.13 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.6, 111.3, 122.5, 122.9, 123.7, 124.0, 124.3, 125.8, 126.3, 127.9, 128.0, 128.1, 128.2, 128.7, 129.1, 129.5, 133.1, 133.2, 133.7, 134.0, 135.3, 154.3, 157.8 ppm. HRMS (ESI-TOF): cacld for $C_{26}H_{17}O$ $[M+H]^+$ 345.1279; found 345.1276.

2-methoxy-11-phenylnaphtho[2,3-*b*]benzofuran (4p): Compound **2n** (172 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 2 h at room temperature to afford **4p** as a white solid (89 mg, 0.27 mmol, 55%), m.p. 96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.61 (s, 3H), 6.37 (d, J = 2.5, 1H), 7.01 (dd, J = 2.7 Hz, 8.9 Hz, 1H), 7.38– 7.46 (m, 2H), 7.52– 7.58 (m, 3H), 7.61– 7.69 (m, 3H), 7.80 (d, J = 8.5 Hz, 1H), 7.94 (s, 1H), 8.03 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.5, 106.3, 106.4, 111.5, 115.6, 124.2, 124.5, 125.7, 126.2,

127.8, 128.1, 128.9, 130.2, 133.2, 134.1, 137.7, 152.4, 154.9, 155.3 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{17}O_2$ $[M+H]^+$ 325.1229; found 325.1228.

2-methoxy-12-(4-methoxyphenyl)-11-methyl-11H-benzofuro[3,2-*b*]carbazole (4q): Compound **2o** (207 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 2 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 3 h at 60 °C to afford **4q** as an off white solid (153 mg, 0.38 mmol, 75%), m.p. 178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.39 (s, 3H), 3.98 (s, 3H), 6.79 (d, J = 7.7 Hz, 1H), 7.01 – 7.06 (m, 1H), 7.10 – 7.13 (m, 2H), 7.23 – 7.28 (m, 1H), 7.31 – 7.38 (m, 2H), 7.46 – 7.55 (m, 4H), 8.16 – 8.20 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.3, 55.4, 100.8, 108.6, 111.2, 114.0, 118.6, 118.7, 120.2, 121.9, 122.0, 122.6, 122.8, 123.8, 125.2, 126.2, 126.4, 129.4, 131.6, 135.6, 143.0, 150.4, 157.1, 159.6 ppm. HRMS (ESI-TOF): cacld for $C_{26}H_{20}NO_2$ $[M+H]^+$ 378.1494; found 378.1492.

naphtho[2,3-*b*]benzofuran (5b)[12]: Compound **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with aq. K_2CO_3 solution (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol) as described for the Suzuki step for the synthesis of **4a** for 1.5 h and then $FeCl_3$ (8 mg, 10 mol%) was added to the crude reaction mixture in 1,2-dichloroethane as described for the cyclization step for the synthesis of **4a** for 1 h at 80 °C to afford **5b** as a white solid (77 mg, 0.31 mmol, 62%), m.p. 205 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 – 7.40 (m, 1H), 7.46 – 7.59 (m, 4H), 7.92 (s, 1H), 7.97 (d, J = 7.83, 1H), 8.02 – 8.08 (m, 2H), 8.41 (s, 1H) ppm. HRMS (ESI-TOF): cacld for $C_{16}H_{11}O$ $[M+H]^+$ 219.0810; found 219.0808.

General representative procedure for the Synthesis of (*E*)-1-(2-(benzofuran-3(2H)-ylidene(phenyl)methyl)phenyl)ethanone (6a): Mg (18 mg, 0.75 mmol) was taken in a two necked round bottom flask and heated with a spirit lamp for 15 minutes. Then one granules of iodine was added to it and heated on an oil bath at 140 °C for 15 minutes and cooled to room temperature. Methyl iodide (106 mg, 0.75 mmol) in diethyl ether (5 mL) was added to the activated Mg and refluxed for 30 minutes and cooled to room temperature. Then compound **3a** (156 mg, 0.5 mmol) in diethyl ether (5 mL) was added and the reaction was continued at room temperature for 30 minutes. After the completion of the reaction (monitored by TLC) the reaction mixture was quenched with aq. NH_4Cl and

extracted with diethyl ether, dried over anhydrous Na_2SO_4 and concentrated. The crude alcohol was dissolved in dichloromethane (5 mL) and Dess–Martin periodinane (318 mg, 0.75 mmol) was added. The reaction was continued at room temperature for 30 minutes. After the completion of the reaction (monitored by TLC) the reaction mixture was extracted with dichloromethane, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was purified by column chromatography using silica gel (60-120 mesh) to afford the product **6a** as a green viscous liquid (122 mg, 0.37 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H), 5.33 (d, J = 14.8 Hz, 1H), 5.50 (d, J = 14.8 Hz, 1H), 6.56 – 6.61 (m, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.08 – 7.14 (m, 1H), 7.22 – 7.28(m, 3H), 7.33 – 7.41 (m, 4H), 7.50 – 7.62 (m, 2H), 7.82 (dd, J = 1.3 Hz, 7.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.0, 75.4, 110.4, 120.3, 124.1, 125.9, 127.3, 128.0, 128.2, 128.3, 129.4, 129.9, 131.6, 131.8, 132.3, 133.9, 139.4, 140.2, 140.9, 164.0, 200.6 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{19}O_2$ $[M+H]^+$ 327.1385; found 327.1386.

(*E*)-1-(2-(benzofuran-3(2H)-ylidene(phenyl)methyl)phenyl)propan-1-one (6b): Mg (18 mg, 0.75 mmol) was taken in a two necked round bottom flask and heated with a spirit lamp for 15 minutes. Then one granules of iodine was added to it and heated on an oil bath at 140 °C for 15 minutes and cooled to room temperature. Ethyl bromide (81 mg, 0.75 mmol) in THF (5 mL) was added to the activated Mg and stirred at room temperature until colour change of the reaction mixture took place. Then compound **3a** (156 mg, 0.5 mmol) in THF (5 mL) was added and the reaction was continued at room temperature for 30 minutes. After the completion of the reaction (monitored by TLC) the reaction mixture was quenched with aq. NH_4Cl and extracted with diethyl ether, dried over anhydrous Na_2SO_4 and concentrated. The crude alcohol was dissolved in DCM (5 mL) and Dess–Martin periodinane (318 mg, 0.75mmol) was added. The reaction was continued at room temperature for 30 minutes. After the completion of the reaction (monitored by TLC) the reaction mixture was extracted with DCM, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was purified by column chromatography using silica gel (60-120 mesh) to afford the product **6b** as a green viscous liquid (124 mg, 0.36 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.78 – 0.88 (m, 3H), 2.58 – 2.69 (m, 2H), 5.27 (d, J = 14.7 Hz, 1H), 5.45 (d, J = 14.7 Hz, 1H), 6.11 (d, J = 7.7Hz, 1H), 6.57 – 6.62 (m, 1H), 6.83 (d., J = 8.0 Hz, 1H), 7.05 – 7.11 (m, 1H), 7.18 – 7.40 (m, 5H), 7.48 – 7.55 (m, 3H), 7.71 (d, J = 7.3, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.10, 34.4, 110.4, 120.3, 124.2, 125.9, 127.3, 127.9, 128.3,

128.6, 128.8, 129.9, 131.6, 131.7, 133.9, 139.9, 141.0, 164.0, 204.1 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{21}O_2$ $[M+H]^+$ 341.1542; found 341.1543.

Representative experimental procedure for the synthesis of 6-methyl-11-phenylnaphtho[2,3-*b*]benzofuran (7a): To a solution of compound **6a** (98 mg, 0.3 mmol) in dry 1,2-dichloroethane (3 mL) was added anhydrous $FeCl_3$ (5 mg, 10 mol%) and the reaction was continued at room temperature for 3 h under argon atmosphere. After the completion of the reaction (monitored by TLC) the solvent was evaporated and the crude reaction mixture was purified by column chromatography using silica gel (60 -120 mesh) eluting with pet ether/EtOAc to obtain the product **7a** as a white solid (78 mg, 0.25 mmol, 85%), m.p. 176 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.97 (s, 3H), 6.90 (d, J = 7.4 Hz, 1H), 7.03 – 7.08 (m, 1H), 7.39 –7.44 (m, 2H), 7.49–7.55 (m, 2H), 7.56 – 7.64 (m, 5H), 7.79 (d, J = 8.5, 1H), 8.19 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.2 , 111.2, 113.7, 122.3, 122.8, 122.9, 13.6, 123.8, 124.6, 125.4, 126.8, 127.9, 128.0, 128.9, 129.4, 130.3, 131.8, 132.1, 138.1, 15.4, 157.6 ppm. HRMS (ESI-TOF): cacld for $C_{23}H_{17}O$ $[M+H]^+$ 309.1279; found 309.1277.

6-ethyl-11-phenylnaphtho[2,3-*b*]benzofuran (7b): Compound **6b** (102 mg, 0.3 mmol) in dry 1,2-dichloroethane was treated with $FeCl_3$ (5 mg, 10 mol%) at room temperature for 6h to obtain the product **7b** as a white solid (75 mg, 0.23 mmol, 78%), m.p. 96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.52 (t, J = 7.5 Hz, 3H), 3.54 (q, J = 7.5 Hz, 2H), 6.91 (d, J = 7.6 Hz, 1H), 7.04 – 7.09 (m, 1H), 7.38 – 7.45 (m, 2H), 7.51 – 7.54 (m, 2H), 7.57 – 7.68 (m, 5H), 7.82(d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.8, 19.1, 111.2, 120.2, 122.3, 122.8, 122.9, 123.5, 123.7, 124.6, 125.4, 127.0, 127.9, 128.0, 128.9, 129.7, 130.3, 131.2, 131.9, 138.2, 151.9, 157.6 ppm. HRMS (ESI-TOF): cacld for $C_{24}H_{19}O$ $[M+H]^+$ 323.1436; found 323.1435.

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Supporting Information availability statement:

^{1}H and ^{13}C NMR spectra of compounds **2a-2o**, **3a**, **4a-4q**, **6a-6b**, **7a-7b**, ^{1}H NMR spectra of **5b** and X-ray crystal structure of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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