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Double Functionalization of 2-Amino-2′-hydroxy-1,1′-biaryls: Synthesis of 4-Nitro-dibenzofurans and Benzofuro-indoles

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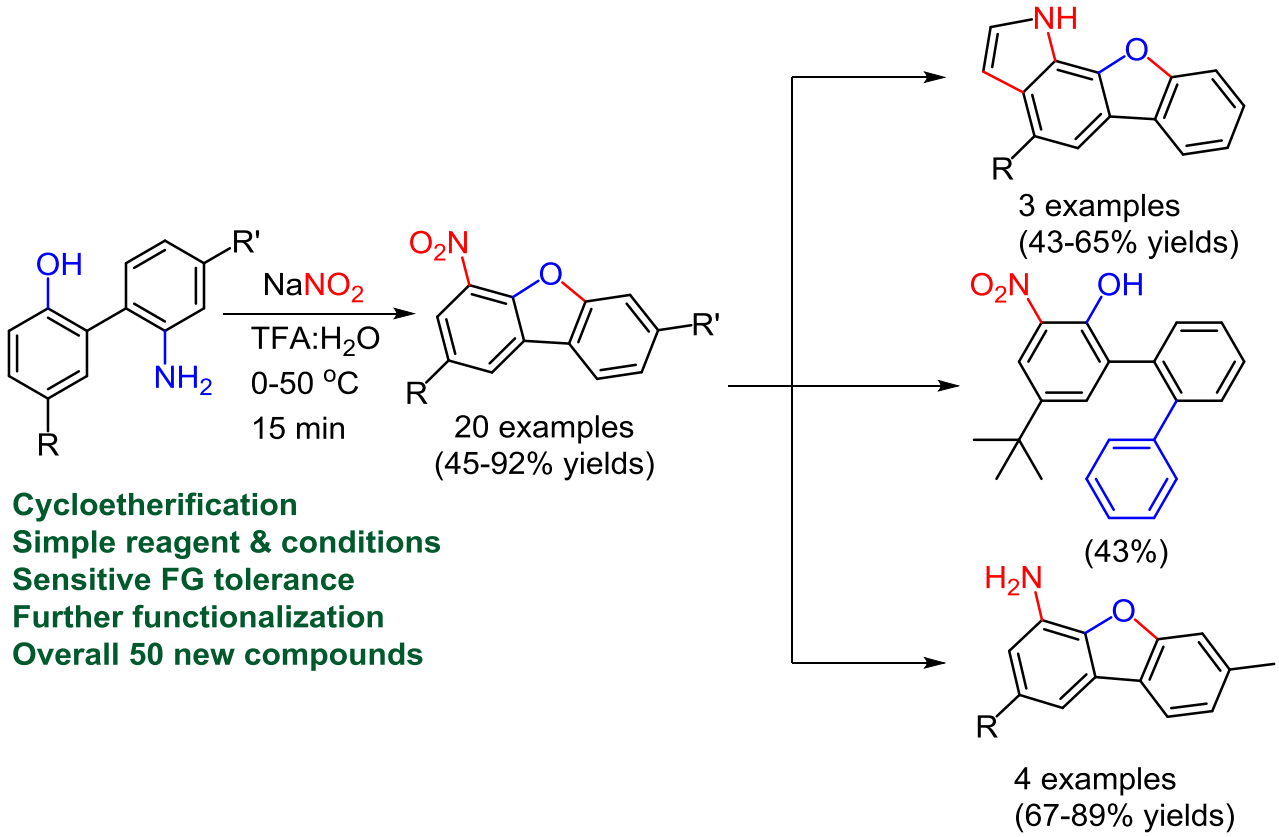

ABSTRACT: Several substituted 2'-amino-biphenyl-2-ols were synthesized. The mild and TM-free double functionalization; nitration and cycloetherification (see Scheme) of 2'-amino-biphenyl-2-ols have been achieved for the synthesis of functionalized 4-nitro-dibenzofurans utilizing $NaNO_2$ in TFA and water. Interestingly, nitration of phenol ring was observed along

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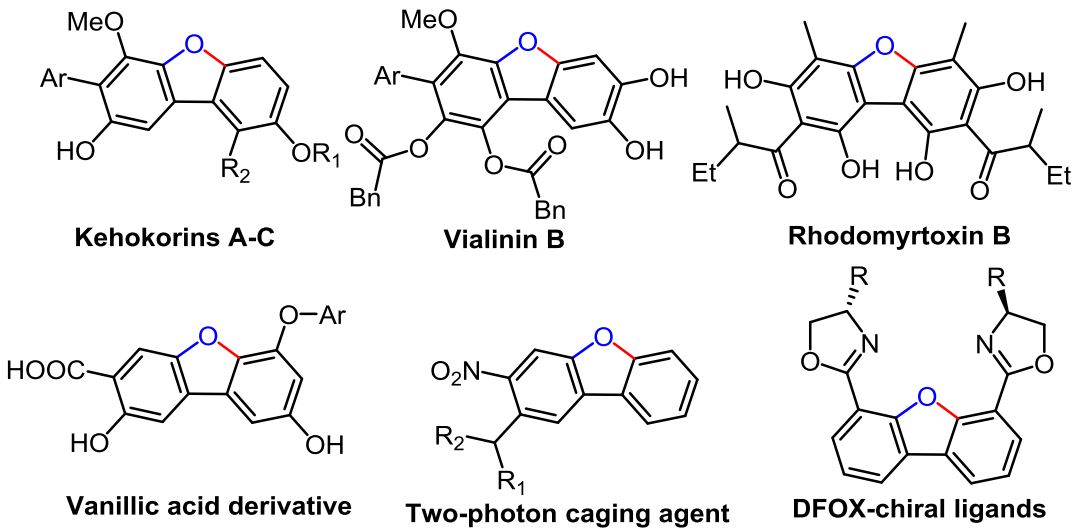
with the dibenzofuran ring formation in one pot. Position of nitro group in several dibenzofurans is also established by X-ray crystal structure studies. Further functionalization of the obtained 4-nitro-dibenzofurans has been carried into 3-nitro-terphenyl-2-ol, novel benzofuro-indoles, and amino-dibenzofurans. The mechanistic understanding on double functionalization of 2'-amino-biphenyl-2-ols suggests that reaction proceeds by a combination of nitration of phenol ring followed by Sandmeyer reaction for dibenzofuran ring formation.

Introduction

The development of new, mild and efficient methods for the synthesis of heterocycles is a separate area of research in organic synthesis. Heterocycles, particularly dibenzofuran scaffold present in natural products; kehokorins A-C, rhodomyrtoxin B, vialinin B, vanillic acid possess cytotoxic, anti-inflammatory, antibacterial and inhibitor of TNF-α production activities (Figure 1).[1] Also dibenzofurans served as the ligands in catalysis, precursors in natural product synthesis, two photon caging group, and used in material science due to their optical and electronic properties.[2]

Figure 1. **Biologically active dibenzofurans**



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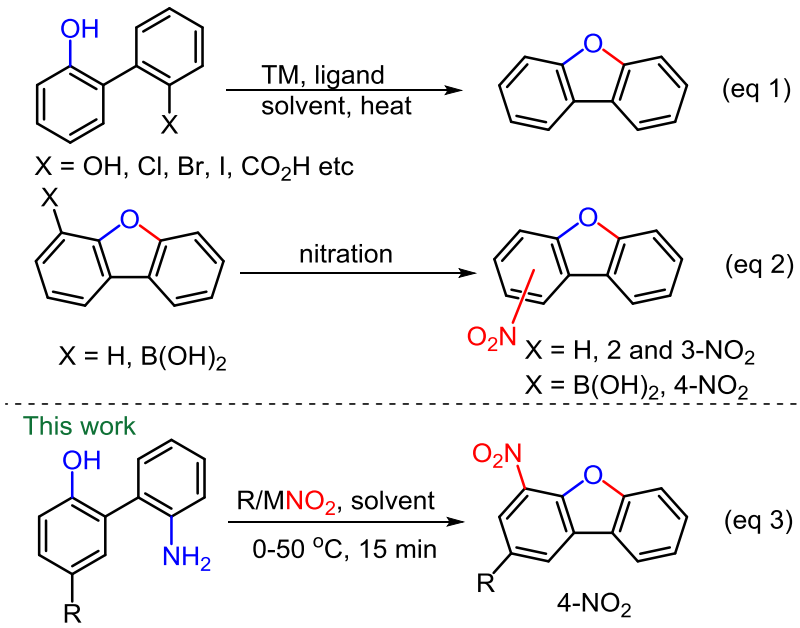
Various methods have been reported for the synthesis of substituted dibenzofurans (Scheme 1, eq 1).[3-10] Most of the methods depend on transition metal-catalysts, particularly; Pd used in C-H arylation of 1-halo-2-phenoxybenzene, oxidative C-O cyclization of 2-arylphenol, dehydrogenative cyclization of biphenyl ether, and decarbonylative intramolecular C-H arylation of 2-aryloxybenzoic acids.[3-6,8]

Scheme 1. Synthesis and nitration of dibenzofurans



TM-free approaches such as flash vacuum pyrolysis, super acid Nafion-catalyzed ring closure of 2,2'-dihydroxybiphenyls, and use of NaH in HMPT for the conversion of 2-nitrobiphenyl into dibenzofurans have also been studied.[9] Apart from the only one example of dibenzofuran reported by Kürti et al. using sodium nitrite reagent for the cyclization of 2'-amino-3'-bromo-[1,1'-biphenyl]-2-ol at 70 °C,[10] there is no report which uses mild conditions and could tolerate sensitive functional groups which are essential for post-modifications.

During our study on the transformation of 2'-aminobiphenyl-2-ol into dibenzofuran, nitration in phenol ring was also observed. Two steps in one pot reduce the waste and cost, avoid isolation of

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intermediates, and create new avenues for further transformations. Further, nitro group has wide scope in organic synthesis and chemical industry as there are various methods for derivatization of the nitro group such as conversion into indole, and carbazol and as leaving group in biaryl cross coupling.[11]

Nitro-dibenzofurans have been prepared by the electrophilic aromatic substitution in dibenzofurans utilizing nitrating agents which afforded a mixture of 2- and 3-NO_2 substituted dibenzofurans (eq 2).[12] Poor chemo and regioselectivity observed in the nitration of dibenzofurans. Keumi *et al*. has achieved regioselective 2- and 3-nitration in dibenzofuran.[12d] Nonetheless, synthesis of 4-NO_2 substituted dibenzofuran has not been reported till date by direct nitration and noticed to be difficult. Recently, pre-functionalized dibenzofuran-4-boronic acid has been used in the preparation of 4-nitrodibenzofurans.[13]

TM-free approach has attracted considerable interest for C-C and C-X (X = N, O, S, Se) bond formation and has been explored by us and others in recent time.[9e,14,15] Herein we report regioselective nitration and etherification of 2'-amino-biphenyl-2-ols for the synthesis of 4-nitro-dibenzofurans (eq 3). Further, synthesis of novel benzofuro-indoles, 3-nitro-terphenyl-2-ol, and amino-dibenzofurans has also been accomplished from synthesized nitrodibenzofurans.

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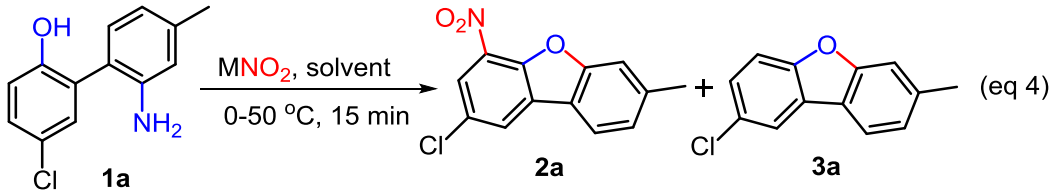
Results and Discussion

Table 1. Optimization of reaction conditions [a]



entry	MNO_2	solvent	yield **2a** [b]	**3a** [c]
1	$NaNO_2$	H_2O	ND	ND
2	$NaNO_2$	CF_3COOH	78	trace
3	**$NaNO_2$**	**CF_3COOH: H_2O**	**92**	**ND**
4	$NaNO_2$	CH_3COOH: H_2O	trace	53
5	$NaNO_2$	H_2SO_4: H_2O	10	54
6	**$NaNO_2$**	**HCl (35%)**	**trace**	**68**
7	$NaNO_3$	CF_3COOH: H_2O	ND	ND
8	$AgNO_2$	CF_3COOH: H_2O	77	trace
9	$^tBuNO_2$	CF_3COOH: H_2O	10	46
10[d]	$NaNO_2$	CF_3COOH: H_2O	40	ND

[a] Reaction were carried out using 1.0 mmol of 2'-amino-biphenyl-2-ol **1a**, 3 mmol of nitrite salt in TFA/H_2O (1.5 mL, 15:1 v/v). [b] ^1H NMR yield (mesitylene as internal standard).[c] Isolated yield. [d] Reaction was carried in presence of TEMPO (3 mmol). ND = Not detected

For the optimization, 2'-aminobiphenyl-2-ol **1a** was used as a model substrate in the presence of various nitrate salts in different acids (eq 4, Table 1). First various solvents were screened using readily available $NaNO_2$ salt to obtain high yield of 4-nitrodibenzofuran **2a**. As expected,

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reaction in water alone failed to provide **2a** (Table 1 entry 1). When reaction performed in neat TFA, **2a** was obtained in 78% yield (Table 1 entry 2). A 15:1 ratio (*v*/*v*) of TFA and water led to further improvement in the yield (92%) of the desired product **2a** (Table 1, entry 3). Water and other acids combinations were also screened, however, observed to be less effective (entries 4-6, Table 1). Combination of H_2SO_4: water or HCl (35%) yielded un-nitrated dibenzofuran as a major product (entries 5-6, Table 1). Next, various nitrite and nitrate salts, $^tBuNO_2$, $AgNO_2$ and $NaNO_3$ were studied in the nitro-cycloetherification reaction. Nonetheless, none of the nitrite found superior to the $NaNO_2$ (entries 7-9, Table 1).

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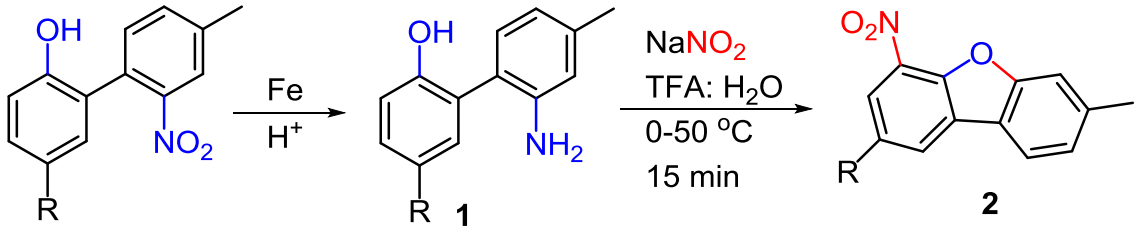
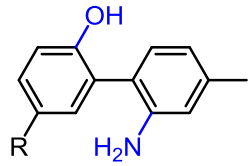
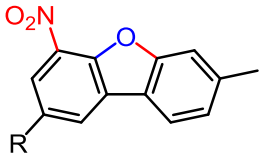
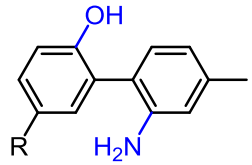
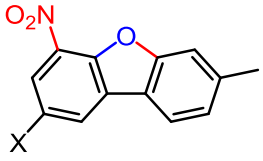
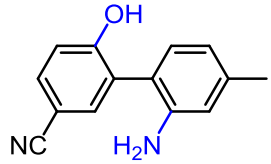
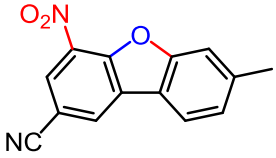
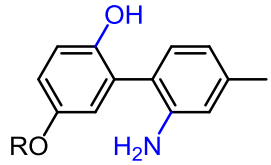
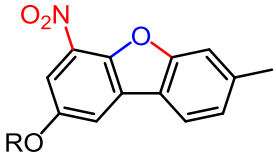
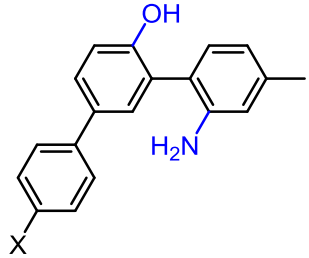
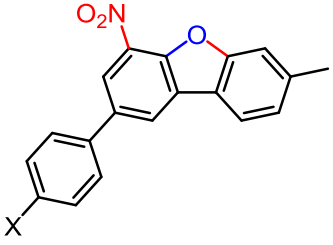
Table 2. Synthesis of 4-nitrodibenzofurans



entry	substrate [a]	4-nitrodibenzofuran[a]
		
1	**1b** R = H (84)	**2b** R = H (12), **2b'** (61)[b]
2	**1c** R = CH_3 (87)	**2c** R = CH_3 (74)
3	**1d** R = *tert*-Bu (86)	**2d** R = *tert*-Bu (77)
		
4	**1e** X = F (87)	**2e** X = F (74)
5	**1f** X = Br (89)	**2f** X = Br (72)
		
6	**1g** (79)	**2g** (49)
		
7	**1h** R = CH_3 (91)	**2h** R = CH_3 (79)
8	**1i** R = Benz (82)	**2i** R = Benz (56)
9	**1j** R = CF_3 (79)	**2j** R = CF_3 (79)
		
10	**1k** X = H (83)	**2k** X = H (65)
11	**1l** X = Br (67)	**2l** X = Br (56)

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[a] Isolated yield. Aminobiaryl-ols **1b-1l** were obtained by the reduction of respective nitrobiaryl-ols (see experimental section for details). [b] 2-Nitro-dibenzofuran was also isolated.

The scope of substrate was explored next under the optimized reaction conditions (Tables 2 and 3). 2'-Amino-biphenyl-2-ols **1a-1t** were obtained by the reduction of respective 2'-nitro-biphenyl-2-ols in 67-97% yields. Unsubstituted 2'-amino-biphenyl-2-ol **1b** afforded 4-nitrodibenzofuran **2b** as a minor regioisomer (12% yield) along with 2-nitrodibenzofuran **2b′** as major (61%) Table 2, entry 1. Next, electron donating methyl and *tert*-butyl **1c** and **1d** and withdrawing F, Br and CN **1e-1g** substrates were subjected for nitro-cycloetherification reaction. The outcome of the double functionalization reaction is unaffected by the electronic nature of the substituents as minor change in the yields (49-77%) of **2c-2g** was observed.

Similarly, substrates **1h-1j** with OCH_3, OCH_2Ph and OCF_3 functionalities afforded the corresponding 4-nitrodibenzofurans **2h-2j** in 79, 56 and 79% yields respectively (entries 7-9, Table 2). 4-Phenyl substituted phenol ring substrates **1k** and **1l** gave the corresponding product **2k** and **2l** with 65 and 56% yield, respectively. Functionalities such as CN, Cl, Br and OCF_3 are useful for further transformation, however, difficult to preserve under harsh reaction conditions. Here dibenzofurans **2a 2f**, **2g**, **2j**, and **2l** with Cl, Br, and CN functionalities along with a newly introduced nitro group have been obtained in one pot in good yields.

Next, the effect of substitution on the aniline ring was studied under optimized reaction condition (Table 3). 2'-Amino-biaryl-2-ols **1m-1o** with un-substituted aniline ring underwent double nitro and etherification reaction successfully lead to **2m-2o** in 69-79% yields (entries 1-3, Table 3).

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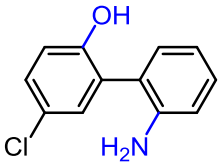
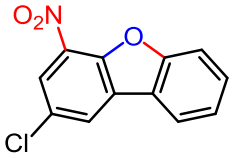
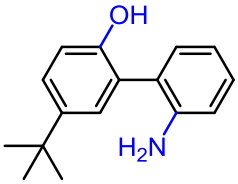
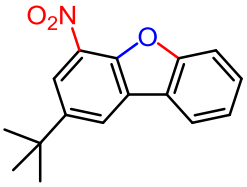
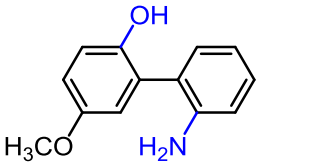
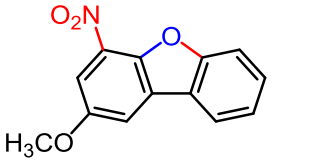
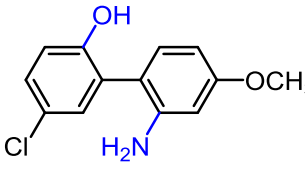
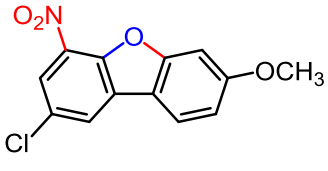
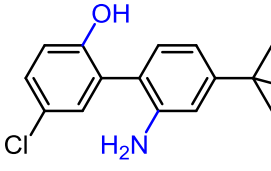
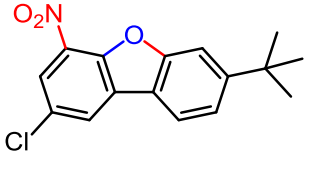
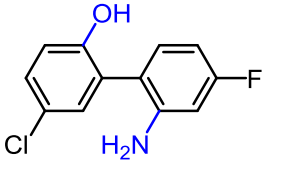
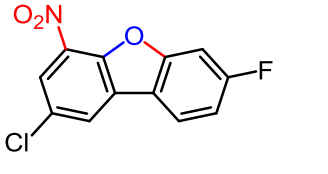
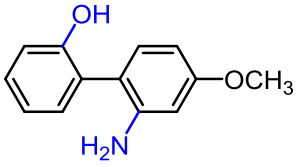
Table 3. Synthesis of 4-nitrodibenzofurans

entry	substrate	4-nitrodibenzofuran[a]
1	 **1m** (84)	 **2m** (69)
2	 **1n** (82)	 **2n** (76)
3	 **1o** (82)	 **2o** (79)
4	 **1p** (80)	 **2p** (69)
5	 **1q** (67)	 **2q** (62)
6	 **1r** (69)	 **2r** (68)
7	 **1s** (69)	**2s** (18), **2s'** (45)[b]

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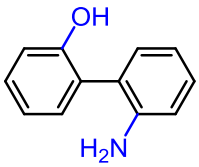
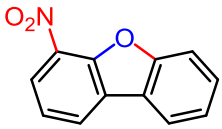
8	**1t** (69)		 **2t** (20), **2t'** (50)[b]

[a] Isolated yield, [b] 2-Nitro-dibenzofuran was also isolated

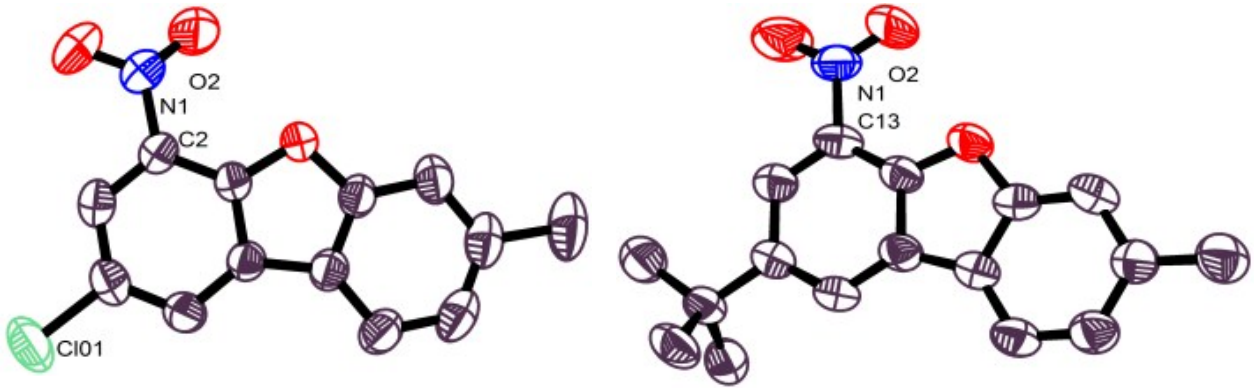


Figure 2. Crystal structures of 2a & 2d (for crystal structure studies of 1p, 2e, and 2o, see SI pages S118-S158)

Interestingly, nitration on the aniline ring was not observed despite the presence of electron withdrawing Cl or donating ^{t}Bu and OCH_3 substituent in the phenolic ring. Next, electron donating OCH_3 and ^{t}Bu and electron withdrawing F substituents in the aniline ring furnished the corresponding 4-nitrodibenzofurans **2p**, **2q**, and **2r** with 69, 62, and 68% yields, respectively (entries 4-6, Table 3). We also studied the nitration reaction of unsubstituted phenol ring of 2'-amino -[1,1'-biphenyl]-2-ols (entries 7, 8, Table 3). As noticed above (entry 1, Table 2), 2-nitro-dibenzofurans **2s'** and **2t'** were obtained as major product whereas 4-nitrodibenzofurans **2s** and **2t** were minor.

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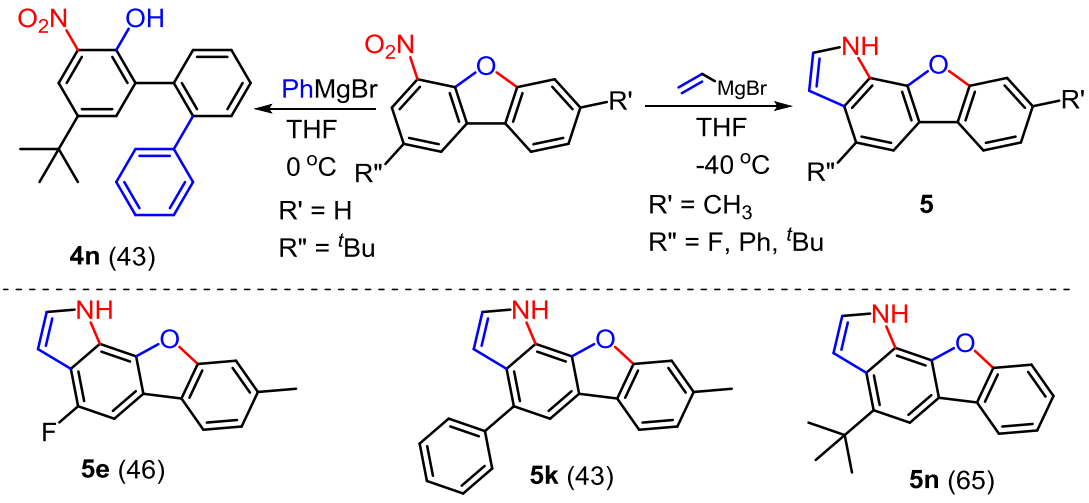
In several 4-nitrodibenzofurans **2a**, **2d**, **2e**, and **2o**, position of NO_2 group is also confirmed by X-ray single crystal study (Figure 2). Worthy to note that nitration occurred in a highly regioselective manner as it is unaffected by the electronic or steric nature of substituent in both of the aromatic rings in 2'-amino-biaryl-2-ol substrates **1a-1t**.

The feasibility of further transformation has been explored of synthesized 4-nitrodibenzofurans **2a**, **2d**, **2e**, **2k**, **2l**, and **2n** (Schemes 2 and 3). Reaction of **2n** with PhMgBr led to carbon-carbon bond formation by the cleavage of ether ring, which resulted novel terphenyl-2-ol **4n** in 43% yield. Next, 4-nitrodibenzofurans **2e**, **2k** and **2n** were converted into benzofuro-indoles. Heterocycles containing benzofuran and indole cores could be important in medicinal chemistry. For this transformation, nitrodibenzofurans were treated with 3 equiv. of vinyl magnesium bromide. This resulted in novel 1H-benzofuro[3,2-g]indoles **5e**, **5k** and **5n** in 43-65% yields (Scheme 2).

Scheme 2. Synthesis of terphenylol and benzofuro-indoles



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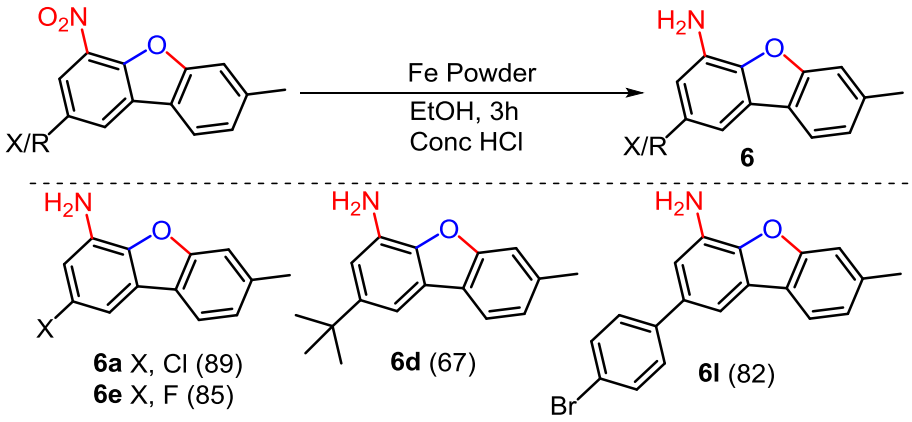
Next, nitro group in **2a**, **2d**, **2e**, and **2l** was selectively reduced into amine using Fe-powder in ethanol with a catalytic amount of HCl at 80 ^{o}C (Scheme 3).

Scheme 3. Reduction of the nitro group in dibenzofurans



Barry and co-workers have studied anti tuberculosis activity of aminodibenzofurans in which chloride *para* to ether linkage showed a positive effect on the activity.[16] Here, fluoro-, chloro-, and 4-bromo-phenylsubstituted aminodibenzofurans **6a**, **6d**, **6e** and **6l** were obtained in 82-89% yields.

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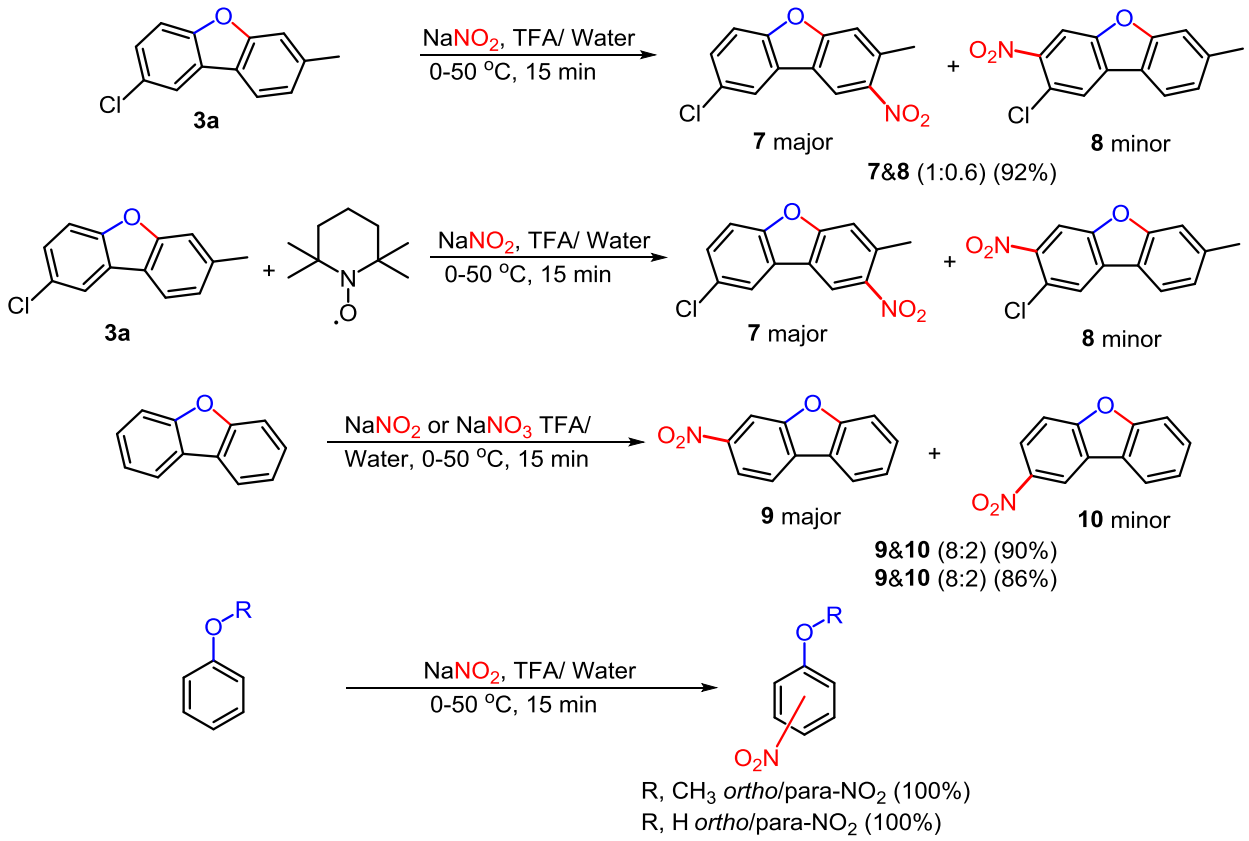
Mechanism

Scheme 4. Nitration in dibenzofuran, phenol, anisole and in the presence of TEMPO



For mechanistic understanding, dibenzofuran **3a** was subjected under the identical reaction conditions which provided a mixture of nitro-dibenzofurans **7** and **8** in 7:3 ratio (Scheme 4). Similarly, unsubstituted dibenzofuran gave a mixture of 3 and 2-nitro dibenzofurans **9** and **10** in 8:2 ratio. Phenol and anisol were then subjected for nitration. Indeed, phenol and anisol also converted into *ortho*/ *para*-nitrophenol and nitroanisol respectively. Next, addition of a radical quencher TEMPO to the reaction mixture provided nearly the same yields of nitrodibenzofurans **7** and **8** which preclude the possibility of radical pathway. Moreover, nitration in anisole could

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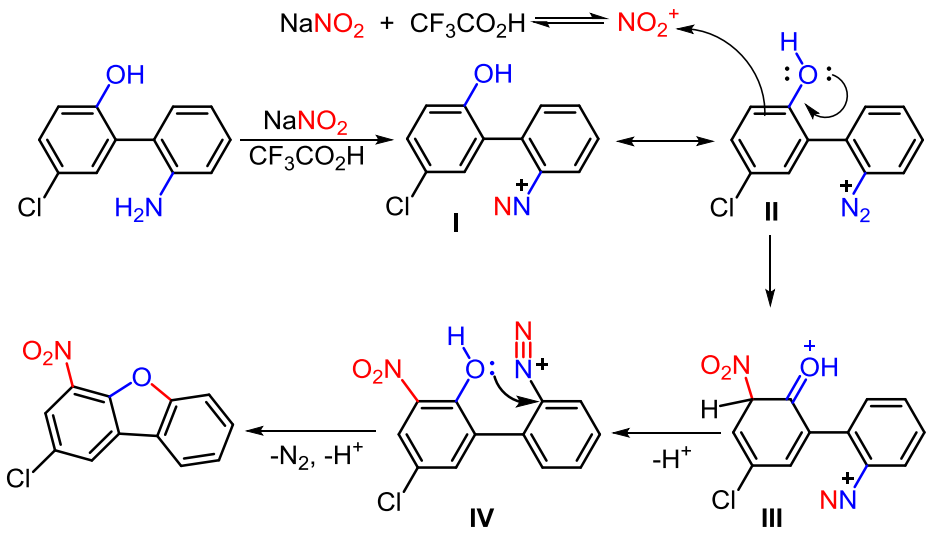
not be achieved if proceeds by radical pathway.[17] However, anisole provided quantitative nitrated anisole under optimized reaction conditions.

Because reactivity of positions in dibenzofuran is in the order of 3 >> 2 > 1 > 4, same as in the order of their electron density, towards electrophilic substitution of nitration.[12c-e] And also unsubstituted dibenzofuran gave 3-nitrodibenzofuran **9** as a major product under our conditions. Therefore, selective nitration of phenol ring over aniline ring may not be rationalized by electrophilic substitution in dibenzofuran.

Scheme 5. Proposed mechanism for double functionalization



The tentative mechanism is depicted in Scheme 5 and would involve a combination of nitration in phenol and Sandmeyer reaction for the formation of dibenzofuran ring. 2'-Amino-biphenyl-2-ol would transform into diazotonium salt **I** by the reaction with $NaNO_2$ in aqueous solution of CF_3CO_2H. Excess of $NaNO_2$ with CF_3CO_2H also generates NO_2^+. Attack of NO_2^+, *ortho* to –OH

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in **II** would lead to intermediate **III**. Deprotonation then give **IV**, nucleophilic attack at C-N_2^+, followed by N_2 and H^+ elimination would furnish 4-nitro-dibenzofuran.

Nitration noticed to be highly regioselective with regards to phenol ring and nitration in the aniline ring of 2'-amino-biphenyl-2-ols was not observed either at *ortho* (Tables 1 and 2) or *para* to NH_2 (entries 1-3, Table 2). This could be due to facile formation of diazonium salt over generation of NO_2^+. The N_2^+ shall make aniline ring electron deficient, disfavoring the electrophilic attack of NO_2^+.

Summary

To sum up, we have developed a nitration and cyclic-etherification reaction in 2'-amino-biphenyl-2-ols for the synthesis of 4-nitrodibenzofurans under TM-free reaction conditions in one pot. The nitration reaction noticed to be highly regioselective with regards to phenolic ring. Synthesized nitro-dibenzofuran further transformed into 3-nitro-terphenyl-2-ol, benzofuro-indoles, and amino-dibenzofurans, which demonstrates further utility of 4-nitrodibenzofurans. The developed methodology could be useful for the synthesis of highly substituted dibenzofurans. Since, reaction provides selective nitration of phenol ring over aniline under mild conditions. Further, efforts are being made to accomplish selective nitration in biaryls under TM-free mild reaction conditions.

General Experimental Details

All NMR experiments were carried out on 400 MHz and 700 MHz spectrometer and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$, (7.24 ppm for ^1H and 77.16 (± 0.06) ppm for ^{13}C, respectively), DMSO-d_6 (3.31 ppm for H_2O, 2.47 ppm for DMSO, 39.9 for carbon). High resolution mass analysis is performed on quadruple-time of flight (Q-TOF) mass spectrometer equipped with an ESI and APCI source (+ve/-ve). $NaNO_2$, DMSO,

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phenols, and potassium *tert*-butoxide (98% purity) used as purchased. Silica gel (100-200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using Merck silica gel (60 F_{254}) plates. Nitro-biaryl-ols substrates of **1a**–**1h**, **1k**-**1n**, **1p** and **3a** are known.[9e]

General Procedure for the Synthesis of Nitro-biaryl-ols (substrates for 1)[9e]

To a single neck flask, 4-chlorophenol (385 mg, 3.0 mmol) and 1-bromo-4-methyl-2-nitrobenzene (540 mg, 2.5 mmol) were added in DMSO (7 mL) and resulted reaction mixture was stirred for 5 min at room temperature under inert atmosphare. After this, KO^{t}Bu (673 mg, 6.0 mmol) was added portion wise. Progress of reaction was monitored by TLC. After completion of the reaction (5 h), the mixture was poured into 10 % aqueous solution of HCl, and extracted four times with 50 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4, and filtered. The solvent was removed under vacuo and the residue was purified by column chromatography (silica gel, eluent: hexane/ ethyl acetate). The product was obtained as yellow solid with 89.5% yield. Rest of the nitro-biaryl-ols were obtained by following the similar procedure.[9e]

5-(Benzyloxy)-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (substrate for 1i). R_f = 0.5 (ethyl acetate: hexane 1:9), viscous liquid, yield 0.52 g (62%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.44-7.39 (m, 4H), 7.38-7.32 (m, 2H), 7.28 (d, *J* = 7.9Hz, 1H), 6.83 (m, 2H), 7.73(d, *J* = 7.9Hz, 1H), 5.01 (s, 2H), 4.87 (brs, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 149.4, 146.7, 139.2, 137.0, 133.7, 132.4, 129.4, 128.6, 128.0, 127.6, 125.9, 124.6, 116.5, 116.4, 115.8, 70.8, 20.9. HRMS (ESI) *m/z* calcd for $C_{20}H_{17}NO_4$ [M] 335.1158, found 335.1165.

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4'-Methyl-2'-nitro-5-(trifluoromethoxy)-[1,1'-biphenyl]-2-ol (substrate for 1j) R_f = 0.5 (ethyl acetate: hexane 2:8), viscous liquid, yield 0.61 g (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.48 (d, *J* = 7.1Hz, 1H), 7.28 (d, *J* = 7.8HZ, 1H), 7.09 (d, *J* = 3.3Hz, 2H), 6.80-6.77 (m, 1H), 5.33 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 149.1, 142.8(q, *J* = 2.2), 139.9, 134.0, 132.3, 128.3, 126.3, 124.8, 122.8, 122.3, 121.8, 119.3, 116.4, 116.2, 20.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{10}F_3NO_4$ [M] + Na 336.0454, found 336.0452.

4-Bromo-4''-methyl-2''-nitro-[1,1':3',1''-terphenyl]-4'-ol (substrate for 1l) R_f = 0.4 (ethyl acetate: hexane 2:8), yellow solid, yield 0.56 g (59%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.51(m, 2H), 7.47(d, *J* = 7.8 Hz, 1H), 7.43-7.38 (m, 4H), 7.34(d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.30 (s, 1H), 2.47(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.4, 139.4, 139.3, 133.8, 133.2, 132.5, 131.8, 129.3, 128.4, 128.3, 128.1, 125.6, 124.7, 121.1, 116.2, 21.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{14}BrNO_3$ [M] + Na 406.0049, found 406.0060.

5-Methoxy-2'-nitro-[1,1'-biphenyl]-2-ol (substrate for 1o). R_f = 0.4 (ethyl acetate: hexane 1:9), yellow solid, yield 0.44 g (72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.64 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.82-6.74 (m, 3H), 4.91 (brs, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 149.6, 146.3, 132.9, 132.6, 132.5, 128.6, 125.9, 124.2, 116.6, 115.3, 114.9, 55.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_4$ [M] + Na 268.0580, found 268.0571.

4'-(tert-Butyl)-5-chloro-2'-nitro-[1,1'-biphenyl]-2-ol (substrate for 1q). R_f = 0.5 (ethyl acetate: hexane 1:9), yellow solid, yield 0.50 g (65%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.32 (d, 8.0 Hz, 1H), 7.21-7.18 (m, 2H), 6.77-6.75 (m, 1H), 5.31 (brs, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.3, 149.2, 132.2,

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130.3, 129.6, 129.3, 128.3, 126.8, 125.9, 121.4, 116.9, 35.0, 31.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}ClNO_3$ [M] -H 304.0711, found 304.0730.

5-Chloro-4'-fluoro-2'-nitro-[1,1'-biphenyl]-2-ol (substrate for 1r) R_f = 0.5 (ethyl acetate: hexane 1:9), yellow viscous liquid, yield 0.45 g (67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (td, *J* = 8.1, 1.5 Hz, 1H), 7.39 (dd, *J* = 6.5, 1.5 Hz, 2H), 7.22-7.20 (m, 2H), 6.75-6.72 (m, 1H), 5.24 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.4, 151.0, 134.1(d, *J* = 7.8 Hz), 129.6 (d, *J* = 11.1 Hz), 129.5, 127.6 (d, *J* = 4.1 Hz), 126.1, 125.9, 120.5, 120.3, 116.8, 116.7, 112.4, 112.1. HRMS (ESI) *m/z* calcd for $C_{12}H_7ClFNO_3$ [M] -H 266.0015, found 266.0044.

General Procedure for the reduction of $–NO_2$ into $–NH_2$

In a 25 mL round-bottom flask equipped with a stir bar, 5-chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (263 mg, 1.0 mmol) was added in 10 mL of ethanol/ water (4:1). After that, iron powder (280 mg, 5 mmol) and HCl (0.1 mL) was added. The reaction mixture was heated under reflux for 3 hours and then cooled to room temperature. Reaction mixture was diluted with ethyl acetate, filtered through celite, dried over sodium sulfate and the solvent removed *in vacuo*. The concentrated reaction mixture was purified by column chromatography (hexane/ethyl acetate, 90/10). Yield 209 mg (90%). Compounds **1b** to **1r** were obtained by following the same procedure.

2'-Amino-5-chloro-4'-methyl-[1,1'-biphenyl]-2-ol (**1a**). R_f = 0.4 (ethyl acetate: hexane 1:9), white solid, yield 209 mg (90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 7.10(d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.69 (s, 1H), 4.65 (brs, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 141.2, 139.5, 131.5, 130.5, 129.0, 127.8, 125.7,

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122.6, 122.4, 119.6, 118.3, 21.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}ClNO$ [M] + H 234.0680, found 234.0671.

2'-Amino-4'-methyl-[1,1'-biphenyl]-2-ol (1b). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 167 mg (84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-6.99 (m, 2H), 7.13 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.04-6.99 (m, 2H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.69 (s, 1H), 4,66 (brs, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 141.6, 139.0, 131.7, 131.1, 129.3, 126.1, 123.2, 121.9, 121.1, 118.0, 117.9, 21.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NO$ [M] + H 200.1070, found 200.1068.

2'-Amino-4',5-dimethyl-[1,1'-biphenyl]-2-ol (1c). R_f = 0.4 (ethyl acetate: hexane 1:9), white solid, yield 185 mg (87%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 3H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 4.50 (brs, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 141.6, 138.9, 131.6, 131.4, 130.2, 129.8, 125.8, 123.3, 121.8, 117.8, 117.7, 21.1, 20.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NO$ [M] + H 214.1226, found 214.1248.

2'-Amino-5-(tert-butyl)-4'-methyl-[1,1'-biphenyl]-2-ol (**1d**). R_f = 0.4 (ethyl acetate: hexane 1:9), white solid, brown viscous liquid, yield 220 mg (86%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* =8.4 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.69 (s, 1H), 4.31(brs, 2H), 2.33(s, 3H), 1.32(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 143.8, 141.7, 138.9, 131.7, 127.9, 126.2, 125.3, 123.8, 121.8, 117.8, 117.4, 34.2, 31.6, 21.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{21}NO$ [M] + H 256.1696, found 256.1686.

2'-Amino-5-fluoro-4'-methyl-[1,1'-biphenyl]-2-ol (**1e**). R_f = 0.4 (ethyl acetate: hexane 1:9), brown solid, yield 189 mg (87%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.8 Hz, 1H), 7.00-6.95 (m, 3H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 4.50 (brs, 2H), 2.33 (s, 3H); ^{13}C NMR (100

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MHz, $CDCl_3$) δ 158.4, 156.0, 149.8, 141.2, 131.5, 127.3(d, *J* = 7.7Hz), 122.3, 119.2(d, *J* = 8.3Hz), 118.3, 117.0, 116.7, 115.8, 115.5, 21.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}FNO$ [M] + H 218.0976, found 218.1002.

2'-Amino-5-bromo-4'-methyl-[1,1'-biphenyl]-2-ol (1f). R_f = 0.4 (ethyl acetate: hexane 1:9), brown solid, yield 250 mg (89%), ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.4 Hz, 1H), 7.36 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 4.45 (brs, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 141.2, 139.6, 133.4, 131.9, 131.6, 128.4, 122.5, 122.4, 120.0, 118.3, 112.9, 21.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}BrNO$ [M] + H 278.0175, found 278.0201.

2'-Amino-6-hydroxy-4'-methyl-[1,1'-biphenyl]-3-carbonitrile (1g). R_f = 0.5 (ethyl acetate: hexane 3:7), white solid, yield 177 mg (79%), ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.9 Hz, 1H), 7.54 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.08 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.74 (s, 1H), 4.13 (brs, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 140.8, 140.1, 135.5, 133.0, 131.7, 127.6, 123.0, 122.2, 119.4, 119.3, 118.9, 104.4, 21.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_2O$ [M] + H 225.1022, found 225.1004.

2'-Amino-5-methoxy-4'-methyl-[1,1'-biphenyl]-2-ol (1h). R_f = 0.4 (ethyl acetate: hexane 1.5:8.5), viscous liquid, yield 208 mg (91%), ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 8.6, 3.0 Hz, 1H), 6,83 (d, *J* = 3.0 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 3.78 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 147.6, 141.5, 139.1, 131.4, 126.8,123.4, 121.9, 118.8, 117.9, 115.7, 115.0, 55.8, 21.1.HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NO_2$ [M] + H 230.1176, found 230.1198.

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2'-Amino-5-(benzyloxy)-4'-methyl-[1,1'-biphenyl]-2-ol (1i). R_f = 0.4 (ethyl acetate: hexane 1:9), brown viscous liquid, yield 250 mg (82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.33-7.30 (m, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.95-6.94 (m, 2H), 6.92 (s, 1H), 6.79 (d, *J* = 7.2Hz, 1H), 6.68 (s, 1H), 5.04 (s, 2H), 4.28 (brs, 2H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 147.9, 141.5, 139.1, 137.3, 131.5, 128.6, 127.9, 127.6, 126.8, 123.4, 122.0, 118.9, 117.9, 116.9, 116.1, 70.7, 21.1. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_2$ [M] + H 306.1489, found 306.1511.

2'-Amino-4'-methyl-5-(trifluoromethoxy)-[1,1'-biphenyl]-2-ol (1j). R_f = 0.5 (ethyl acetate: hexane 2:8), white solid, yield 225 mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.10 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 3.83 (brs, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.8, 141.1(q), 139.7, 131.6, 127.3, 123.6, 122.5, 122.0, 121.9, 119.4, 119.1, 118.4, 21.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NO_2F_3$ [M] - H 282.0736, found 282.0762.

2''-Amino-4''-methyl-[1,1':3',1''-terphenyl]-4'-ol (1k). R_f = 0.4 (ethyl acetate: hexane 2:8), white solid, yield 225 mg (83%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.54-7.52 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.11-7.09 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 4.17 (brs, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 141.6, 140.7, 139.2, 134.2, 131.7, 129.8, 128.8, 128.5, 127.9, 126.8, 126.4, 123.3, 122.1, 118.4, 118.0, 21.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NO$ [M] + H 276.1383, found 276.1407.

2''-Amino-4-bromo-4''-methyl-[1,1':3',1''-terphenyl]-4'-ol (1l). R_f = 0.5 (ethyl acetate: hexane 2:8), white solid, yield 237 mg (67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.8, 1.8 Hz,

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2H), 7.49-7.47 (m, 2H), 7.43 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.10-7.08 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 3.86 (brs, 2H), 2.34(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 141.5, 139.7, 139.3, 132.9, 131.8, 131.7, 129.6, 128.3, 127.7, 126.6, 123.1, 122.2, 120.9, 118.6, 118.1, 21.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{16}BrNO$ [M] + H 354.0488, found 354.0510.

2'-Amino-5-chloro-[1,1'-biphenyl]-2-ol (1m). R_f = 0.4 (ethyl acetate: hexane 1:9), white solid, yield 184 mg (84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.23-7.21 (m, 2H), 7.00-6.95 (m, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.10 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 141.4, 131.7, 130.6, 129.4, 129.2, 127.8, 125.8, 125.4, 121.4, 119.7, 117.6. HRMS (ESI) *m/z* calcd for $C_{12}H_{10}ClNO$ [M] + H 220.0524, found 220.0546.

2'-Amino-5-(tert-butyl)-[1,1'-biphenyl]-2-ol (1n). R_f = 0.5 (ethyl acetate: hexane 2:8), white solid, yield 198 mg (82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.30-7.25 (m, 2H), 7.03-6.99 (m, 2H), 6.90 (dd, *J* = 7.8, 0.8 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 143.8, 141.9, 131.8, 128.8, 127.9, 126.6, 126.4, 125.4, 120.9, 117.5, 117.1, 34.2, 31.6. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NO$ [M] - H 240.1383, found 240.1400.

2'-Amino-5-methoxy-[1,1'-biphenyl]-2-ol (1o). R_f = 0.5 (ethyl acetate: hexane 2:8), white solid, yield 176 mg (82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 6.98-6.95 (m, 2H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.86-6.83 (m, 2H), 4.79 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.6, 141.8, 131.6, 129.0, 126.9, 126.3, 121.0, 118.9, 117.3, 115.7, 115.2, 55.8. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NO_2$ [M] + H 216.1019, found 216.1041.

2'-Amino-5-chloro-4'-methoxy-[1,1'-biphenyl]-2-ol (1p). R_f = 0.5 (ethyl acetate: hexane 2:8), white solid, yield 199 mg (80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 2H), 7.10 (d, *J* =

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8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.53 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.74 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 152.4, 143.0, 132.6, 130.6, 128.9, 127.4, 125.6, 119.2, 117.3, 106.8, 102.9, 55.3. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}ClNO_2$ [M] + H 250.0629, found 250.0659.

2'-Amino-4'-(tert-butyl)-5-chloro-[1,1'-biphenyl]-2-ol (1q). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 185 mg (67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.6 Hz, 1H), 7.23 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.89 (d, *J* = 1.8 Hz, 1H), 3.76 (brs, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.6, 140.8, 131.4, 130.5, 128.9, 127.8, 125.6, 122.9, 119.7, 118.9, 114.9, 34.6, 31.2. HRMS (ESI) *m/z* calcd for C16H18ClNO [M] - H 274.0993, found 274.1022.

2'-Amino-5-chloro-4'-fluoro-[1,1'-biphenyl]-2-ol (1r). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 163 mg (69%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 7.13 (m, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.65 (td, *J* = 8.4, 2.5 Hz, 1H), 6.57 (dd, *J* = 10.0, 2.5 Hz, 1H), 6.51 (brs, 1H), 3.83 (brs, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 162.4, 152.2, 143.8(d, *J* = 10.7 Hz), 133.1(d, *J* = 9.8 Hz), 130.6, 129.5, 126.4, 125.9, 119.6(d, *J* = 2.8 Hz), 119.1, 107.7, 107.5, 103.9, 103.6. HRMS (ESI) *m/z* calcd for $C_{12}H_9ClFNO$ [M] - H 236.0273, found 236.0298.

2'-Amino-4'-methoxy-[1,1'-biphenyl]-2-ol (1s). R_f = 0.4 (ethyl acetate: hexane 1:9), white solid, yield 150 mg (70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.12 (d, J = 8.5 Hz, 1H), 7.03-6.97 (m, 2H), 6.52 (dd, J = 8.5, 2.5 Hz, 1H), 6.40 (d, J = 2.5 Hz, 1H), 3.80 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 153.6, 143.4, 132.7, 131.2, 129.2, 125.6, 121.1, 117.9, 117.5, 106.3, 102.5, 55.3. HRMS (ESI) *m/z* calcd for $C_{13}H_3NO_2$ [M] - H 214.0868, found 214.0872

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2'-Amino-[1,1'-biphenyl]-2-ol (1t)[18]. R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 141 mg (76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.25-7.21 (m, 2H), 7.05-7.02 (m, 2H), 7.00-6.95 (m, 1H), 6.86 (d, J = 8.1 Hz, 1H), 4.65 (brs, 2H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 141.8, 131.8, 131.2, 129.5, 129.0, 126.1, 126.0, 121.2, 121.0, 118.1, 117.2.

General procedure for the synthesis of 4-nitro-dibenzofuran

In a 5 mL round-bottom flask equipped with a stir bar, $NaNO_2$ (104 mg, 1.5 mmol), **1a** (117 mg, 0.5 mmol) were added in 2 mL of CF_3COOH/H_2O (15:1) at 0 ^{o}C under nitrogen atmosphare. Then, reaction temperature was increased to 50 ^{o}C. Progress of reaction was monitored by TLC. After completion of the reaction (15 min.), the mixture was poured into water, and extracted four times with 15 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate) to afford the product **2a** with 92% yield.

2-Chloro-7-methyl-4-nitrodibenzo[b,d]furan (2a). R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), white solid, yield 120 mg (92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.4 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 2,54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 147.1, 140.8, 133.7, 129.8, 128.0, 126.1, 125.7, 122.0, 120.5, 118.9, 112.7, 22.1. HRMS (ESI) *m/z* calcd for $C_{13}H_8ClNO_3$ [M] + Na 284.0085, found 284.0089.

3-Methyl-6-nitrodibenzo[b,d]furan (2b). R_f = 0.6 (ethyl acetate: hexane 1:9), white solid, yield 14 mg (12%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.30 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.37 (s, 1H), 7.22 (d, *J* = 7.8Hz,

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1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.9, 143.7, 139.8, 125.2, 125.1, 122.4, 120.7, 120.4, 116.6, 112.4, 111.7, 22.0. HRMS (APCI) *m/z* calcd for $C_{13}H_9NO_3$ [M] - H 226.0499, found 226.0524.

7-Methyl-2-nitrodibenzo[b,d]furan (2b'). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 69 mg (61%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J*= 8.3, 0.8 Hz, 1H), 8.21 (dd, *J* =7.6, 0.8 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.57 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.29-7.27 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 148.6, 139.8, 134.1, 128.6, 126.5, 125.4, 122.5, 122.4, 120.3, 119.8, 112.7, 22.1. HRMS (APCI) *m/z* calcd for $C_{13}H_9NO_3$ [M] - H 226.0499, found 226.0524.

2,7-Dimethyl-4-nitrodibenzo[b,d]furan (2c). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 89 mg (74%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.47 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 2.54 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 147.0, 139.5, 133.4, 132.8, 128.4, 126.9, 125.2, 122.8, 120.2, 119.8, 112.6, 22.1, 21.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{11}NO_3$ [M] + H 242.0812, found 242.0805.

2-(*tert*-Butyl)-7-methyl-4-nitrodibenzo[b,d]furan (2d). R_f = 0.4 (hexane), white solid, yield 109 mg (77%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.51 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 2.54 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 146.9, 146.7, 139.5, 13.4, 128.2, 125.2, 123.5, 120.2, 120.1, 119.8, 112.7, 35.1, 31.6, 22.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NO_3$ [M] + Na 306.1101, found 306.1092.

2-Fluoro-7-methyl-4-nitrodibenzo[b,d]furan (2e). R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), white solid, yield 91 mg (74%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.8, 2.5 Hz, 1H),

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7.85 (dd, *J* = 7.3, 2.5 Hz, 1H), 7.78 (d, *J* =8.1 Hz, 1H), 7.250 (s, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 158.1, 156.1, 145.0, 140.8, 129.5(d, *J* =9.5 Hz), 125.5, 120.5, 119.4(d, *J* = 3.4 Hz), 113.4, 113.1, 112.8, 109.7, 109.5, 22.1. HRMS (ESI) *m/z* calcd for $C_{13}H_8FNO_3$ [M] 245.0483, found 245.0472.

2-Bromo-7-methyl-4-nitrodibenzo[b,d]furan (2f). R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), white solid, yield 110 mg (72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 1.49 (s, 1H), 7.24 (d, *J* =8.2 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 147.5, 140.8, 134.0, 130.3, 129.1, 125.8, 124.8, 120.5, 118.7, 114.7, 112.8, 22.1. HRMS (ESI) *m/z* calcd for $C_{13}H_8BrNO_3$ [M] + Na 327.9580, found 327.9568.

7-Methyl-4-nitrodibenzo[b,d]furan-2-carbonitrile (2g).. R_f = 0.5 (ethyl acetate: hexane 2:8), brown solid, yield 62 mg (49%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* =1.6Hz, 1H), 8.44 (d, *J* = 1.6Hz, 1H), 7.88 (d, *J* = 8.0HZ, 1H), 7.59 (s, 1H), 7.33 (d, *J* = 8.0Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) 158.1, 150.4, 141.9, 134.0, 130.0, 129.5, 126.5, 125.9, 120.8, 118.4, 117.1, 113.0, 106.9, 22.3. HRMS (APCI) *m/z* calcd for $C_{14}H_8N_2O_3$ [M] 252.0529, found 252.0553.

2-Methoxy-7-methyl-4-nitrodibenzo[b,d]furan (2h). R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), white solid, yield 101 mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.46 (s, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 3.94 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.1, 143.6, 139.9, 133.5, 129.1, 125.1, 120.3, 119.9, 112.7, 112.1, 107.8, 56.5, 22.1. HRMS (APCI) *m/z* calcd for $C_{14}H_{11}NO_4$ [M] + H 258.0761, found 258.0785.

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2-(Benzyloxy)-7-methyl-4-nitrodibenzo[b,d]furan (2i). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 93 mg (56%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.5 Hz, 1H), 7.78-7.75 (m, 2H), 7.47 (m, 3H), 7.41 (m, 2H), 7.35 (m 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.20 (s, 2H), 2.53(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.1, 143.8, 140.0, 135.9, 133.5, 129.2, 128.8, 128.4, 127.6, 125, 120.4, 119.9, 113.3, 112.7, 108.9, 71.4, 22.1. HRMS (APCI) *m/z* calcd for $C_{20}H_{15}NO_4$ [M] - H 332.0917, found 332.0945.

7-Methyl-4-nitro-2-(trifluoromethoxy)dibenzo[b,d]furan (2j). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 122 mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.2 Hz, 1H), 8.03 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.2, 146.8, 143.5(q, *J* = 2.3 Hz), 141.1, 133.5, 129.7, 125.8, 121.8, 120.6, 119.3, 119.2, 115.6, 112.9, 22.1. HRMS (APCI) *m/z* calcd for $C_{14}H_8F_3NO_4$ [M] 311.0400, found 311.0398.

7-Methyl-4-nitro-2-phenyldibenzo[b,d]furan (2k). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 98 mg (65%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.4 (d, *J* = 1.6 Hz, 1H), 8.32 (d, *J* =1.6 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 3H), 7.42 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.26-7.24 (m, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.0, 140.0, 138.9, 136.7, 134.0, 129.2, 129.1, 128.2, 127.3, 125.4, 124.7, 121.2, 120.4, 119.9, 112.8, 22.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{13}NO_3$ [M] + H 304.o968, found 304.0951.

2-(4-Bromophenyl)-7-methyl-4-nitrodibenzo[b,d]furan (2l). R_f = 0.5 (ethyl acetate: hexane 1:9), light yellow solid, yield 106 mg (56%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.5 Hz, 1H), 8.34 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 3H), 7.30 (d, *J* = 8.2 Hz, 1H), 2.59 (s, 3H), ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.8, 148.1,

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140.2, 137.9, 135.5, 134.0, 132.2, 129.3, 128.9, 125.6, 124.5, 122.6, 121.0, 120.4, 119.8, 112.8, 22.1. HRMS (APCI) *m/z* calcd for $C_{19}H_{12}BrNO_3$ [M] + H 382.0073, found 382.0064.

2-Chloro-4-nitrodibenzo[b,d]furan (2m). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 85 mg (69%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.59 (td, *J* = 8.4, 1.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 147.1, 134.0, 129.7(2C), 128.2, 126.3, 124.4, 122.7, 121.5, 121.1, 112.7. HRMS (ESI) *m/z* calcd for $C_{12}H_6ClNO_3$ [M] + H 248.0114, found 248.0117.

2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan (2n). R_f = 0.5 (hexane), white solid, yield 102 mg (76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.9 Hz, 1H), 8.24 (d, *J* = 1.9 Hz, 1H), 7.98(d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.53 (td, *J* = 8.3, 1.3 Hz, 1H), 7.41(td, *J* = 7.8, 1.3 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 146.9, 146.8, 133.5, 128.6, 128.1, 123.9, 123.8, 122.7, 120.7, 120.4, 112.5, 35.1, 31.6. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_3$ [M] + H 270.1125, found 270.1118.

2-Methoxy-4-nitrodibenzo[b,d]furan (2o). R_f = 0.5 (hexane), white solid, yield 96 mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.39 (t, 7.4 Hz, 1H), 3.96 (s, 3H), 1.24 (grease); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.2, 143.6, 133.6, 129.0, 128.9, 123.7, 122.5, 120.9, 112.5, 112.4, 108.6, 56.5. HRMS (ESI) *m/z* calcd for $C_{13}H_9NO_4$ [M] + H 244.0604, found 244.0589.

2-Chloro-7-methoxy-4-nitrodibenzo[b,d]furan (2p). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 96 mg (69%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* =

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2.1 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.1 Hz, 1H), 3,86 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.8, 159.0, 147.2, 133.6, 129.9, 128.3, 12.6, 121.5, 121.1, 114.4, 113.4, 96.8, 55.9. HRMS (APCI) *m/z* calcd for $C_{13}H_8ClNO_4$ [M] 277.0136, found 277.0165.

7-(tert-Butyl)-2-chloro-4-nitrodibenzo[b,d]furan (2q). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 94 mg (62%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 2.0, 1.0 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 1.4 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.4 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.9, 154.5, 147.3, 133.7, 129.8, 128.0, 126.2, 122.2, 122.1, 120.4, 118.7, 109.5, 35.6, 31.5. HRMS (ESI) *m/z* calcd for $C_{16}H_{14}ClNO_3$ [M] + H 304.0740, found 304.0756.

2-Chloro-7-fluoro-4-nitrodibenzo[b,d]furan (2r). R_f = 0.5 (ethyl acetate: hexane 1:9), white solid, yield 92 mg (68%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.92-7.88 (m, 1H), 7.45 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.21 (td, *J* = 8.9, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.3, 157.8(d, *J* = 13.6Hz), 147.6(d, *J* = 2.0Hz), 133.8, 129.0, 128.7, 126.2, 122.4, 121.9(d, *J* = 10.4Hz), 117.9(d, *J* = 2.2Hz), 113.0, 112.8, 100.9, 100.7. HRMS (APCI) *m/z* calcd for $C_{12}H_5ClFNO_3$ [M] 264.9937, found 264.9960.

3-Methoxy-6-nitrodibenzo[b,d]furan (2s). R_f = 0.45 (ethyl acetate: hexane 0.5:9.5), yellow solid, yield 22 mg (18%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.3, 1.0 Hz, 1H), 8.11 (dd, J = 8.3, 1.0 Hz, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 8.23 (d, J = 2.0 Hz, 1H), 7.01(dd, J = 8.6, 2.1 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 158.4, 148.7, 133.9, 128.6, 125.9, 122.7, 121.5, 121.2, 115.2, 112.9, 96.8, 55.9. HRMS (ESI) *m/z* calcd for $C_{13}H_9NO_4$ [M] + Na 266.0424, found 266.0423

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7-Methoxy-2-nitrodibenzo[b,d]furan (2s') [8b]**.** R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), yellow solid, yield 55 mg (45%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 2.3 HZ, 1H), 8.29 (dd, J = 8.9, 2.3 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 2.1 HZ, 1H), 7.01 (dd, J = 8.6, 2.1 HZ, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 159.3, 159.0, 143.9, 125.3, 121.7, 121.6, 116.0, 115.9, 112.4, 111.5, 96.8, 55.8.

4-Nitrodibenzo[b,d]furan (2t) [3e] R_f = 0.5 (ethyl acetate: hexane 0.5:9.5), yellow solid, yield 22 mg (20%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.3, 1.0 Hz, 1H), 8.23 (dd, J = 7.7, 1.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.56 (td, J = 7.4, 1.1 Hz, 1H), 7.44 (q, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 148.6, 134.1, 128.9, 128.4, 126.9, 124.1, 123.0, 122.7, 122.3, 120.9, 112.5.

2-Nitrodibenzo[b,d]furan (2t')[3e] R_f = 0.55 (ethyl acetate: hexane 0.5:9.5), white solid, yield 53 mg (50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 2.3 Hz, 1H), 8.38 (dd, J = 9.0, 2.3 HZ, 1H), 8.01 (d, J = 7.7 HZ, 1H), 7.64-7.61 (m, 2H), 7.56 (td, J = 8.3, 1.1 Hz, 1H), 7.43 (td, J = 8.3, 1.0 HZ, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 157.5, 143.9, 128.9, 125.0, 123.9, 123.1, 123.0, 121.3, 117.1, 112.3, 112.0.

4-(tert-Butyl)-3-nitro-[1,1':2',1''-terphenyl]-2-ol (4) from 2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan (1n). 2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan(108 mg, 0.4 mmol) was dissolved in THF (3 mL) and the solution cooled to 0 ^{o}C. Then phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 3.0 equiv) was added dropwise over 10 min, continue the reaction at 0 ^{o}C under nitrogen atmosphare. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3×15 mL), the combined organic layers

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were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane: ethyl acetate) to give the yellow solid with 43% yield. Rf: 0.5 (hexane: ethyl acetate 9:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.54 (q, *J* = 1.8 Hz, 2H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.43 (td, *J* = 8.3, 1.4 Hz, 1H), 7.35-7.30 (m, 3H), 7.19-7.17 (m, 2H), 6.99-6.96 (m, 1H), 6.13 (brs, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 146.9, 145.0, 142.8, 129.4, 127.7, 126.8, 125.1, 124.4, 122.7, 121.1, 120.7,117.6, 112.8, 111.67, 109.2, 35.1, 31.9. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}NO_3$ [M] - H 346.1438, found 346.1451.

Synthesis of 4-fluoro-8-methyl-1H-benzofuro[3,2-g]indole (5e) from 2-fluoro-7-methyl-4-nitrodibenzo[b,d]furan. 2-Fluoro-7-methyl-4-nitrodibenzo[b,d]furan (108 mg, 0.5 mmol) was dissolved in THF (5 mL) and the solution cooled to –40 ^{o}C. Then vinyl magnesium bromide (1.5 mL, 1M in THF, 3.0 equiv) was added dropwise over 15 min. After the addition was complete, the reaction mixture was stirred at –40 ^{o}C under nitrogen atmosphare. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3×15 mL), the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane: ethyl acetate) to give the brown solid with 46% yield. Rf: 0.4 (hexane: ethyl acetate 9:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.38 (s, 1H), 7.28-7.23 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.77 (t, *J* = 2.3 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.5, 153.7, 152.3, 138.5(d, *J* = 1.3Hz), 136.2, 124.1, 123.6, 123.1(d, *J* = 3.4Hz), 122.9, 122.8, 119.6, 118.1(d, *J* = 10.1Hz),117.9, 117.7, 111.9, 100.7, 96.5, 96.3, 21.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}FNO$ [M]-H 238.0663, found 238.0676.

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Synthesis of 8-methyl-4-phenyl-1H-benzofuro[3,2-g]indole (5k) from 7-methyl-4-nitro-2-phenyldibenzo[b,d]furan: 7-Methyl-4-nitro-2-phenyldibenzo[b,d]furan (122 mg, 0.4 mmol) was dissolved in THF (5 mL) and the solution cooled to –40 ^{o}C. Then vinyl magnesium bromide (1.2 mL, 1.0 M in THF, 3.0 equiv) was added dropwise over 15 min. After the addition was complete, the reaction mixture was stirred at –40 ^{o}C under nitrogen atmosphare. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3×15 mL), the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane: ethyl acetate) to give the viscous liquid with 43% yield. Rf: 0.4 (hexane: ethyl acetate 9:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.75 (m, 2H), 7.68 (s, 1H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.41-7.37 (m, 2H), 7.31(t, *J* = 2.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.84 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.2, 141.9, 141.4, 135.9, 130.2, 129.0, 128.5, 127.3, 126.8, 124.1, 124.0, 123.1, 121.5, 119.6, 118.7, 112.1, 111.8, 104.1, 21.9. HRMS (ESI) *m/z* calcd for $C_{21}H_{15}NO$ [M]-H 296.1070, found 296.1080.

Synthesis of 4-(tert-butyl)-1H-benzofuro[3,2-g]indole (5n) from 2-(*tert*-butyl)-4-nitrodibenzo[b,d]furan. 2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan (135 mg, 0.4 mmol) was dissolved in THF (5 mL) and the solution cooled to –40 ^{o}C. Then vinylmagnesium bromide (1.2 mL, 1.0 M in THF, 3.0 equiv) was added dropwise over 15 min. After the addition was complete, the reaction mixture was stirred at –40 ^{o}C under nitrogen atmosphare. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3×15 mL), the combined organic layers were washed with brine (10 mL) and dried over

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Na_2SO_4. The crude product was purified by column chromatography (hexane: ethyl acetate) to give the yellow solid with 65% yield. Rf: 0.4 (hexane: ethyl acetate 9:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (brs, 1H), 7.97-7.95 (m, 1H), 7.59-7.56 (m, 2H), 7.39-7.33 (m, 2H), 7.30 (t, *J* = 2.8Hz, 1H), 6.95 (t, *J* = 2.8Hz, 1H), 1.6 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 141.5, 138.8, 126.6, 126.1, 125.1, 122.7, 122.6, 121.9, 119.9, 117.5, 111.3, 108.1, 105.9, 35.8, 30.9. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO$ [M] - H 262.1226, found 262.1237.

2-Chloro-7-methyldibenzo[b,d]furan-4-amine (6a) from 2-chloro-7-methyl-4-nitrodibenzo[b,d]furan. 2-Chloro-7-methyl-4-nitrodibenzo[b,d]furan (131 mg, 0.5 mmol) was dissolved in ethanol/water mixture (3mL). After that iron powder (140 mg, 2.5 mmol,) and HCl (0.1 ml) was added. The reaction mixture was heated under reflux for 2.5 hours and then cooled to room temperature. Reaction mixture was diluted with ethyl acetate, passed through celite, combined filtrate washed with water and dried over sodium sulfate. The concentrated reaction mixture was purified by column chromatography (silica gel, hexane/ethyl acetate,) to give the white solid with yield 103mg, (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 1.9 Hz, 1H), 4.04 (brs, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 143.1, 138.1, 132.6, 128.6, 125.6, 124.2, 121.5, 120.5, 112.3, 112.0, 109.8, 21.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClNO$ [M] + H 232.0529, found 232.0542.

Synthesis of 2-fluoro-7-methyldibenzo[b,d]furan-4-amine (6e) from 2-fluoro-7-methyl-4-nitrodibenzo[b,d]furan. 2-Fluoro-7-methyl-4-nitrodibenzo[b,d]furan (108 mg, 0.5 mmol) was dissolved in ethanol/water mixture (3mL). After that iron powder (140 mg, 2.5 mmol,) and HCl (0.1 ml) was added. The reaction mixture was heated under reflux for 3 hours and then cooled to

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room temperature. Reaction mixture was diluted with ethyl acetate, passed through celite, combined filtrate washed with water and dried over sodium sulfate. The concentrated reaction mixture was purified by column chromatography (silica gel, hexane/ethyl acetate,) to give the white solid. Yield 91 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 7.8 Hz, 1H), 7.32 (s, 1H), 7.12 (d. *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.50 (dd, *J* = 10.6, 2.3 Hz, 1H), 3.99 (brs, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.6, 157.1, 140.9, 137.9, 132.6, 132.5, 124.8, 124.7, 124.0, 122.2 (d, J 4.4 Hz), 120.5, 112.0, 100.2, 100.0, 99.9, 95.8, 95.6, 21.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}FNO$ [M] + H 216.0819, found 216.0846.

Synthesis of 2-(*tert*-butyl)dibenzo[b,d]furan-4-amine (6d) from 2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan. 2-(*tert*-Butyl)-4-nitrodibenzo[b,d]furan (152 mg, 0.5 mmol) was dissolved in ethanol/water mixture (3mL). After that iron powder (140 mg, 2.5 mmol,) and HCl (0.1 ml) was added. The reaction mixture was heated under reflux for 3 hours and then cooled to room temperature. Reaction mixture was diluted with ethyl acetate, passed through celite, combined filtrate washed with water and dried over sodium sulfate. The concentrated reaction mixture was purified by column chromatography (silica gel, hexane/ethyl acetate,) to give the orange solid with yield 80 mg, (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.42-7.37 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 1.7 Hz, 1H), 3.98 (brs, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 147.0, 143.3, 130.9, 126.6, 125.2, 124.1, 122.5, 120.7, 111.6, 111.3, 107.0, 34.8, 31.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO$ [M] + H 240.1383, found 240.1405.

Synthesis of 2-(4-bromophenyl)dibenzo[b,d]furan-4-amine (6l) from 2-(4-bromophenyl)-7-methyl-4-nitrodibenzo[b,d]furan. 2-(4-Bromophenyl)-7-methyl-4-nitrodibenzo[b,d]furan (152

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mg, 0.4 mmol) was dissolved in ethanol/water mixture (3mL). After that iron powder (113 mg, 2.0 mmol,) and HCl (0.1 ml) was added. The reaction mixture was heated under reflux for 3 hours and then cooled to room temperature. Reaction mixture was diluted with ethyl acetate, passed through celite, combined filtrate washed with water and dried over sodium sulfate. The concentrated reaction mixture was purified by column chromatography (silica gel, hexane/ethyl acetate,) to give the white solid with yield 111 mg, (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.49-7.47 (m, 2H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.36 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 3.70 (bs, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 144.6, 140.8, 137.7, 136.0, 131.9, 131.7, 128.9, 125.3, 124.1, 122.2, 121.0, 120.4, 112.1, 111.7, 108.9, 22.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{14}BrNO$ [M] + H 352.0332, found 352.0352.

Nitration in 2-chloro-7-methyldibenzo[b,d]furan 3a

In a 5 mL round-bottom flask equipped with a stir bar, $NaNO_2$ (69 mg, 1.0 mmol), **3a** (86 mg, 0.4 mmol) were added in 1.5 mL of CF_3COOH/H_2O (15:1) at 0 ^{o}C. Then, reaction temperature was increased upto 50 ^{o}C. Progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was poured into water, and extracted four times with 15 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and recorded the crude reaction ^{1}H and ^{13}C NMR, and confirmed a mixture of two product 8-chloro-3-methyl-2-nitrodibenzo[b,d]furan and 2-chloro-7-methyl-3-nitrodibenzo[b,d]furan in 1:0.6 ratio.

Nitration of 2-chloro-7-methyldibenzo[b,d]furan 3a in the presence of TEMPO

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In a 5 mL round-bottom flask equipped with a stir bar, $NaNO_2$ (69 mg, 1.0 mmol), TEMPO (156mg, 1 mmol) and **3a** (86 mg, 0.4 mmol) were added in 1.5 mL of CF_3COOH/H_2O (15:1) at 0 ^oC. Then, reaction temperature was increased upto 50 ^oC under nitrogen atmosphare. Progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was poured into water, and extracted four times with 15 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and recorded the crude reaction ^1H NMR, and no effect was observed on the yield of corresponding product and ratio of regioisomer.

Nitration of dibenzo[b,d]furan under optimized condition

In a 5 mL round-bottom flask equipped with a stir bar, $NaNO_2$ (102 mg, 1.5 mmol), dibenzo[b,d]furan (84 mg, 0.5 mmol) were added in 1.5 mL of CF_3COOH/H_2O (15:1) at 0 ^oC. Then, reaction temperature was increased upto 50 ^oC under nitrogen atmosphare. Progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was poured into water, and extracted four times with 15 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and recorded the crude reaction ^1H and ^{13}C NMR, and confirmed a mixture of two product 3-nitrodibenzo[b,d]furan and 2-nitrodibenzo[b,d]furan in 8:2 ratio.

Nitration of dibenzo[b,d]furan under optimized condition using $NaNO_3$

In a 5 mL round-bottom flask equipped with a stir bar, $NaNO_2$ (127 mg, 1.5 mmol), dibenzo[b,d]furan (84 mg, 0.5 mmol) were added in 1.5 mL of CF_3COOH/H_2O (15:1) at 0 ^oC. Then, reaction temperature was increased upto 50 ^oC under nitrogen atmosphare. Progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was poured into

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water, and extracted four times with 15 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and recorded the crude reaction ^1H and ^{13}C NMR, and confirmed a mixture of two product 3-nitrodibenzo[b,d]furan and 2-nitrodibenzo[b,d]furan in 8:2 ratio.

Supporting Information

Spectra (^1H, ^{13}C NMR and HRMS), CIF files CCDC no. 1042915 (**1p**), 1042912 (**2a**), 1042911 (**2d**), 1042914 (**2e**), 1042913 (**2o**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Double Functionalization of 2-Amino-2′-hydroxy-1,1′-biaryls: Synthesis of 4-Nitro-dibenzofurans and Benzofuro-indoles

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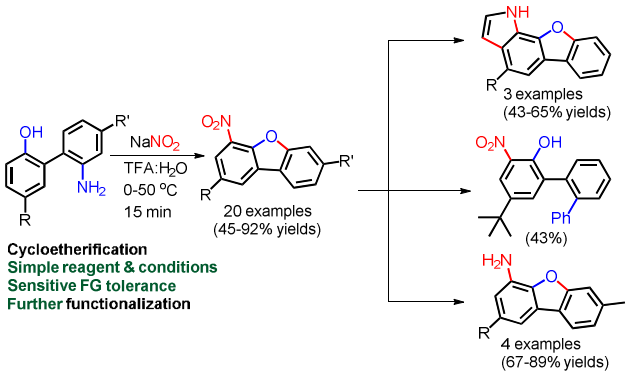

A TM-Free double functionalization of 2-Amino-2′-hydroxy-1,1′-biaryls (see Scheme above) has been presented for the synthesis of 4-nitro-dibenzofurans.