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Pd-Catalysed Isocyanide Assisted Reductive Cyclization of 1-(2-Hydroxyphenyl)-Propargyl Alcohols for 2-Alkyl/Benzyl Benzofurans and their Useful Oxidative Derivatization

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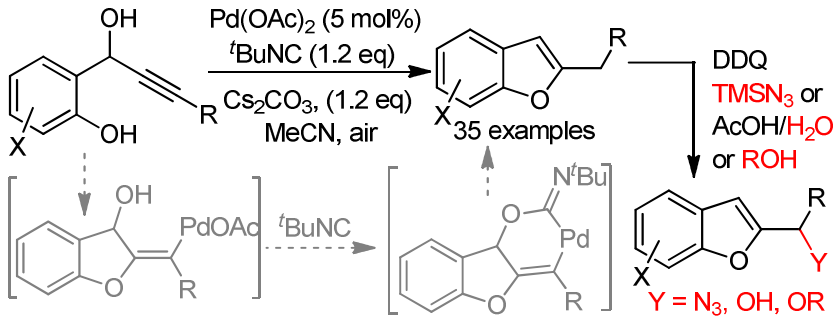


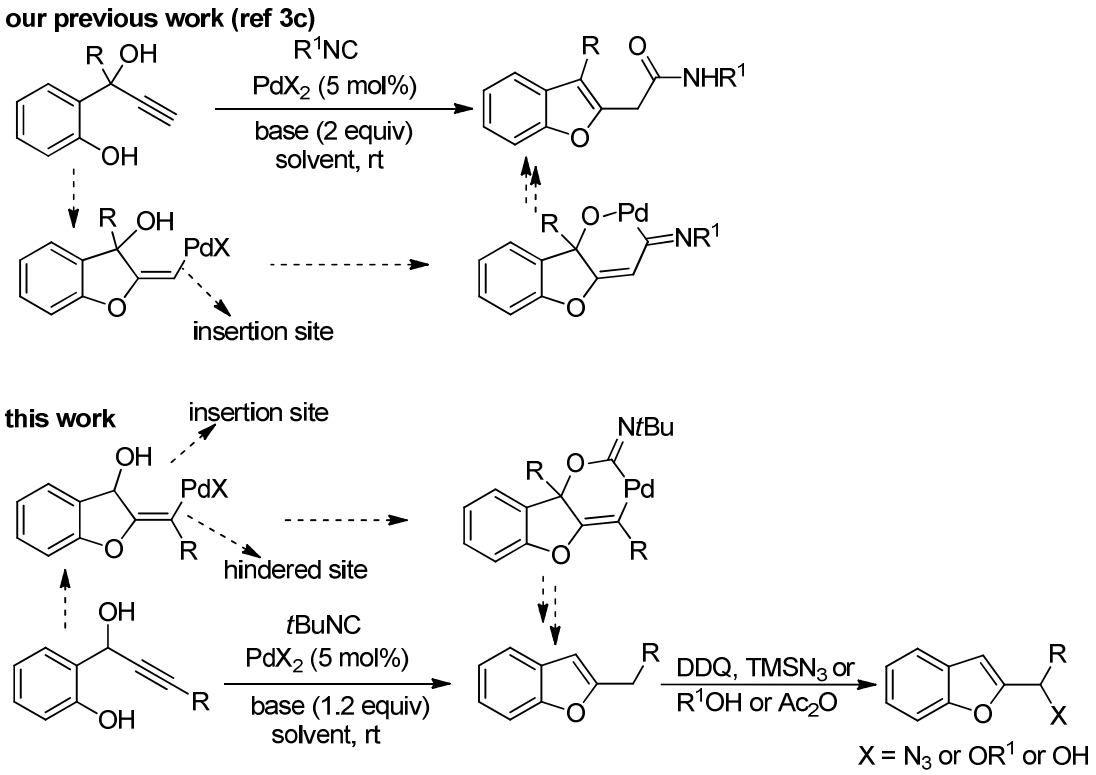
ABSTRACT: An unusual Pd-catalyzed isocyanide assisted *5-exo-dig* reductive cyclization of 1-(2-hydroxyphenyl)-propargyl alcohols is achieved for 2-alkyl/benzyl benzofurans. The reaction features a high substrate scope, insensitivity to air and excellent product yielding. Further, a direct metal free C-H functionalization (azidation, alkoxylation and hydroxylation) and selective oxidative cleavage of thus synthesized 2-benzylfurans is described for azido-, alkoxy-, hydroxyl-, amide- and tetrazolyl adducts.

INTRODUCTION

Electrophilic cyclization of alkynes with nucleophile tether is an increasingly versatile strategy for the synthesis of large variety of hetero- and carbocycles.[1] Among structurally

diverse substrates used in the strategy, the propargyl alcohols or their derivatives with nucleophile tether are very frequently used precursors which offer interesting post-cyclization transformations viz. elimination, migration, oxidation, etc.[1] On the other hand, the concept of isocyanide insertion between carbon-palladium bond has paved a useful pathway for the construction of variety of otherwise difficult C-C bonds.[2] As part of our on-going program of uncovering the new activities of activated alkynes,[3] we recently reported a tandem oxy-palladation/isocyanide insertion strategy for the conversion of hydroxyphenyl terminal propargyl alcohols to benzofuranyl acetamides (Scheme 1).[3c] Subsequently, we discovered a rare isocyanide assisted reductive cyclization of hydroxyphenyl internal propargyl alcohols to 2-alkyl/benzyl benzofurans,[4] the privileged scaffolds found in numerous biologically and medicinally active molecules.[5] Unlike in most cases reported,[3] we found the insertion of isocyanide between oxygen-palladium bond in preference to carbon-palladium perhaps due to

Scheme 1. Benzofurans *via* cyclization of hydroxyphenyl propargyl alcohols.

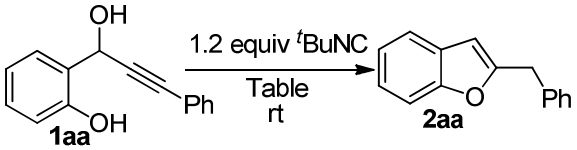


steric constraints. The 2-alkyl/benzyl-3-unsubstituted benzofurans we synthesized here are identified as excellent precursors for diverse selective functionalizations at both benzylic and C-3 positions via selective metal free C-H activations and benzofuranyl methyl-phenyl bond cleavage.

RESULTS AND DISCUSSION

We initiated our studies with the optimization of the conversion of **1aa** to **2aa** as shown in Table 1. A screen of several Pd(II)-catalysts along with Na_2CO_3 as base in acetonitrile revealed that $Pd(OAc)_2$ as the best choice. However, no reaction occurred in the absence of Pd-catalyst. Change of base to Cs_2CO_3 cleanly furnished the product in 85% yield. Organic bases like TEA, DIPEA and DBU were found to be poor promoters. Solvents other than acetonitrile were not suitable for the transformation.

Table 1. Optimization studies.[a]

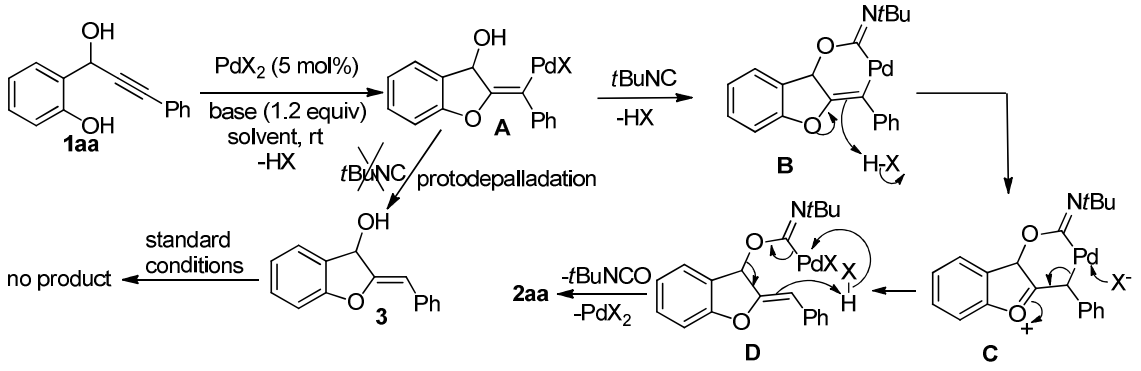


entry	catalyst	base	solvent	yield(%)[b]
1	$PdCl_2$	Na_2CO_3	CH_3CN	28
2	PdI_2	Na_2CO_3	CH_3CN	15
3	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	CH_3CN	21
4	$Pd(OAc)_2$	Na_2CO_3	CH_3CN	60
5	$Pd(OAc)_2$	K_2CO_3	CH_3CN	68
6	$Pd(OAc)_2$	Cs_2CO_3	CH_3CN	85
7	--	Cs_2CO_3	CH_3CN	--
8	$Pd(OAc)_2$	TEA	CH_3CN	10
9	$Pd(OAc)_2$	DIPEA	CH_3CN	15
10	$Pd(OAc)_2$	DBU	CH_3CN	--
11	$Pd(OAc)_2$	Cs_2CO_3	DMSO	30
12	$Pd(OAc)_2$	Cs_2CO_3	1,4-dioxane	25
13	$Pd(OAc)_2$	Cs_2CO_3	DCE	40
14	$Pd(OAc)_2$	Cs_2CO_3	Toluene	35

[a]Reaction conditions: *t*-BuNC (1.2 mmol), **1a** (1.0 mmol), base (1.2 mmol), cat (0.05 mmol), solvent (4 mL), open air. [b]Isolated yield.

Although it was evident that there was no any reducing agent, which was essential for the reduction part of the reaction, other than isocyanide was used, a control experiment excluding *t*-BuNC was conducted to get insight in to the mechanism. The experiment yielded the simple *5-exo-dig* cyclization product **3**[4f] demonstrating that the isocyanide was necessary for reductive elimination of allylic hydroxyl group (Scheme 2). However, when **3** was subjected to the standard conditions, no reaction occurred but a slow decomposition. This indicates that the intermediate **A** with C-Pd bond intact was necessary to further proceed to the product *via* formation of oxapallada cycle **B** by the isocycanide insertion between palladium and oxygen. **B** then probably expelled *t*-BuNCO followed by PdX_2 to furnish final product **2aa** *via* **C** and **D** though addition elimination processes.

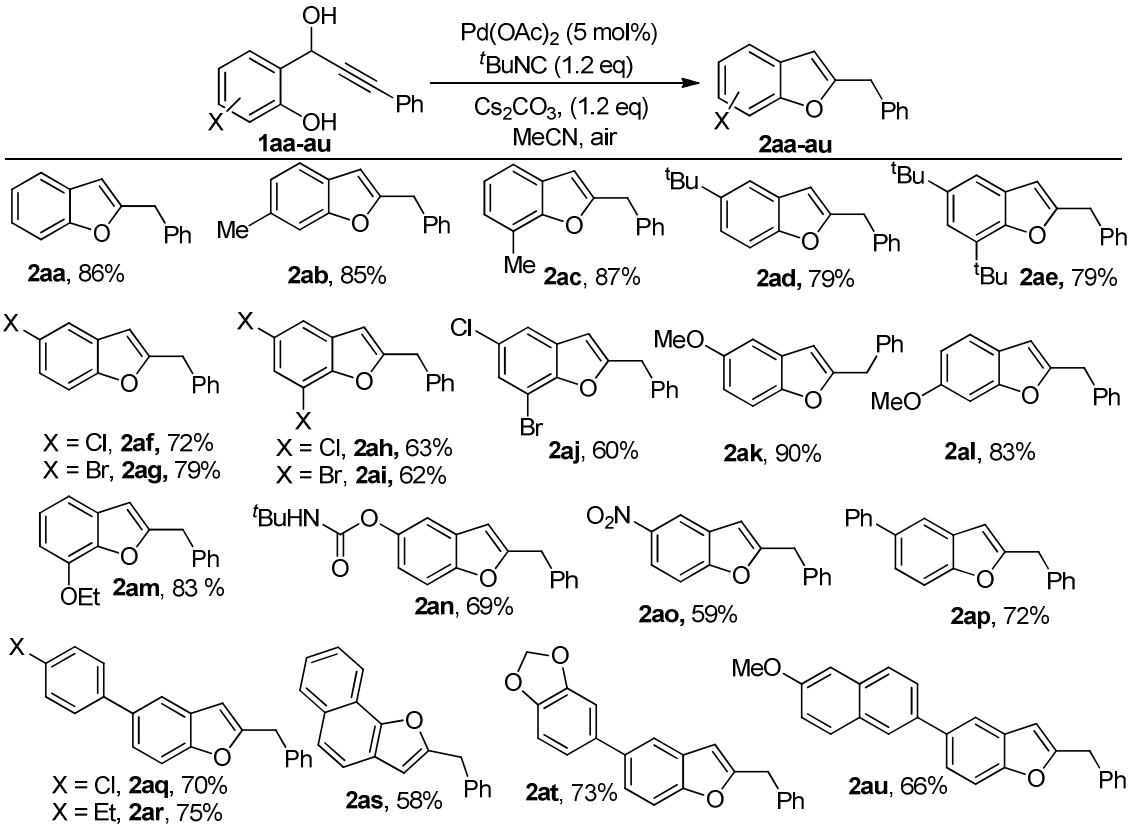
Scheme 2. Mechanistic evaluation.



With optimal reaction conditions in hand, we studied the scope of the tandem cyclization/reductive elimination of a variety of salicylaldehyde derived propargyl alcohols (Table 2). Substrates bearing alkyl groups (methyl or *t*-butyl) showed similar reactivity to **1aa** to produce **2ab-ad** in excellent yields (79-87%). Halo groups were found to be well compatible with the reaction as in case of the synthesis of **2af-aj** where mono halo precursors showed better reactivity than their dihalo counterparts. Irrespective of the position of alkoxy group (*ortho-, meta-* or *para-*), all the electron rich substrates **1ak-am** showed uniformly the

excellent reactivity (**2ak-am** in 83-90% yields). In case of substrate **1an**, the product was obtained with the concomitant transformation of unprotected hydroxyl group to carbamate (**2an**). This resulted *via* the phenoxyl addition to the isocyanate, the oxidized byproduct of isocyanide. This stands as a proof for the isocyanide assisted reductive elimination of the propargylic hydroxyl group. Next, electron deficient substrate **1ao** showed moderate reactivity to produce **2ao** in 59% yield. Finally, cyclization/reductive elimination cascade of substrates **1ap-au**, possessing aryl-substitution/fusion, occurred uneventfully affording products **2ap-au** in good to excellent yields.

Table 2. Reductive cyclization of hydroxyphenyl propargyl alcohols 1aa-au.[a]

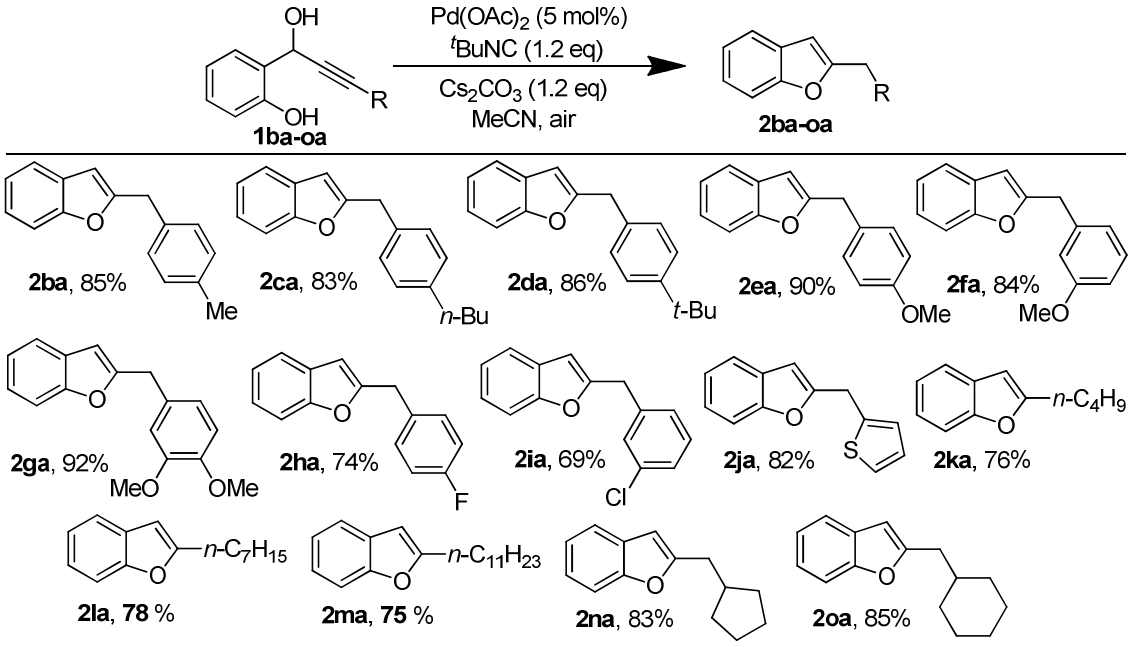


[a]Reaction conditions: *t*-BuNC (1.2 mmol), **1** (1.0 mmol), base (1.2 mmol), $Pd(OAc)_2$ (0.05 mmol), MeCN (4 mL), open air.

Next, substrate scope with respect to substitution on alkyne terminal was studied (Table 3). Aryl acetylene based substrates were initially screened. Thus, alkyl substituted aryl adducts **2ba-da** were obtained in excellent yields (83-86%). Electron rich precursors (**1ea-ga**) were relatively highly productive compared to halogenated substrates (**1ha-ia**). 2-thiophenyl substrate **1ja** also furnished the corresponding product **2ja** in 82% yield. Interestingly, alkyl acetylene based propargyl alcohols (**1ka-oa**) were found to be equally reactive (75-85%) in the cyclization/reductive elimination sequence.

Setting a limitation, the reaction was not applicable for 3°-propargyl alcohols (for the synthesis of 2,3-disubstituted benzofurans), perhaps due to steric hinderance from the both terminals of the reactive centre. Also, all the efforts to expand the reaction scope for the synthesis of indole- and benzothiophene-derivatives were failed to yield the desired products.

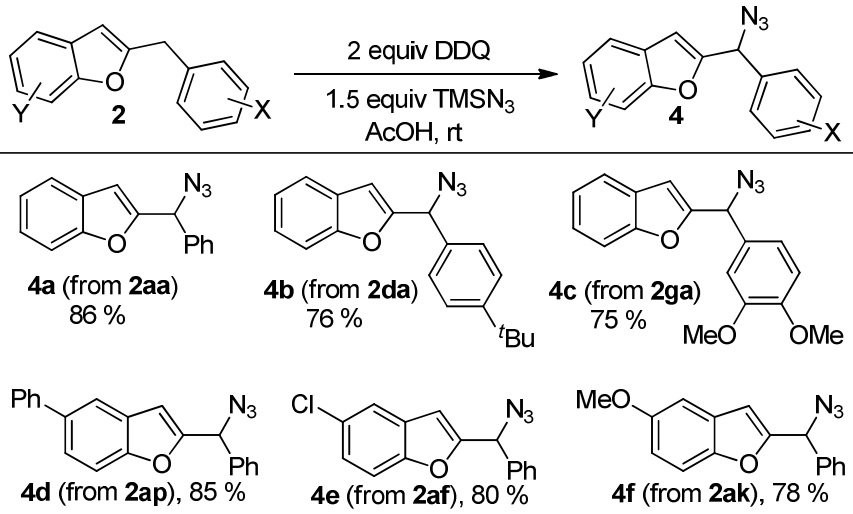
Table 3. Reductive cyclization of hydroxyphenyl propargyl alcohols 1ba-oa.[a]



[a]Reaction conditions: *t*-BuNC (1.2 mmol), **1** (1.0 mmol), base (1.2 mmol), $Pd(OAc)_2$ (0.05 mmol), MeCN (4 mL), open air.

We next aimed at the derivatization of the 2-alkylbenzofurans as they seemed interesting with a nucleophilic C3 center and a benzylic system as radical/carbocation base. We first targeted the oxidative functionalization of benzylic position of **2**. We envisioned that DDQ can oxidize benzofuranyl benzylic position, and the resultant radical species/carbocation can be trapped by various nucleophiles. Thus, **2aa** was treated with 2 equivalents of DDQ in AcOH with $TMSN_3$ as azide source (nucleophile) to trap the incipient electrophile. As expected, azide adduct **4a** was cleanly obtained in 86% yield (Table 4). After thorough literature search, we found that there is no such precedent for direct metal free C-H azidation in the literature. Interestingly, even in case of metal catalysed direct C-H azidation, there are only two reports which appeared most recently, one of which was specific for tertiary C(sp^3)-H azidation via iodosobenzene assisted Fe(II)-catalysis[6a] and the other was non-specific with tertiary C(sp^3)-

Table 4. Metal free selective C(sp^3)-H azidation of 2.[a]



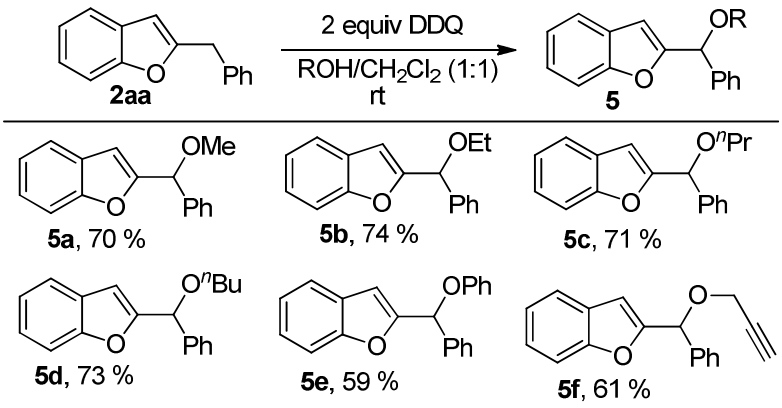
[a]Reaction conditions: **2** (1.0 mmol), $TMSN_3$ (1.5 mmol), DDQ (2 mmol), AcOH (4 mL), rt, 1-2 h.

H and benzylic C-H azidation via Mn(II)-catalysis.[6b] Having observed the dearth of literature on this useful transformation, we wanted to verify the generality of our new finding of DDQ assisted direct C-H azidation of 2-benzyl benzofurans. Pleasingly, various benzyl

benzofurans, irrespective of electronic nature of both benzyl- and benzofuran groups, could be directly azidated in good to excellent yields (75-86%).

We next turned to extend the method for direct C(sp^3)-H alkoxylation by substituting trapping agent $TMSN_3$ by an alcohol. When treated the **2aa** with 2 equivalents of DDQ in CH_2Cl_2/MeOH (1:1), the desired methoxy adduct **5a** was cleanly obtained in 70% yield (Table 5). Such a DDQ mediated alkoxylation was earlier reported by Bao et al[7] but it was specifically on aryl allyl benzenes. Surprisingly, there is no direct alkoxylation of diarylmethanes is pursued in the literature although a very few donating group assisted metal catalyzed methods are reported.[8] Hence, we decided to verify the generality of this direct alkoxylation of benzylbenzofurans. Similar to MeOH, other *n*-alknols like EtOH, *n*-PrOH and *n*-BuOH reacted smoothly (**5b-d** in 71-74%) whereas hindered alcohols *i*-PrOH and *t*-BuOH showed no reactivity. Notably, less nucleophilic phenol also smoothly reacted to give **5e** in 59% yield. Finally, propargyl alcohol was successfully used in this oxidative coupling to obtain **5f** in 61%.

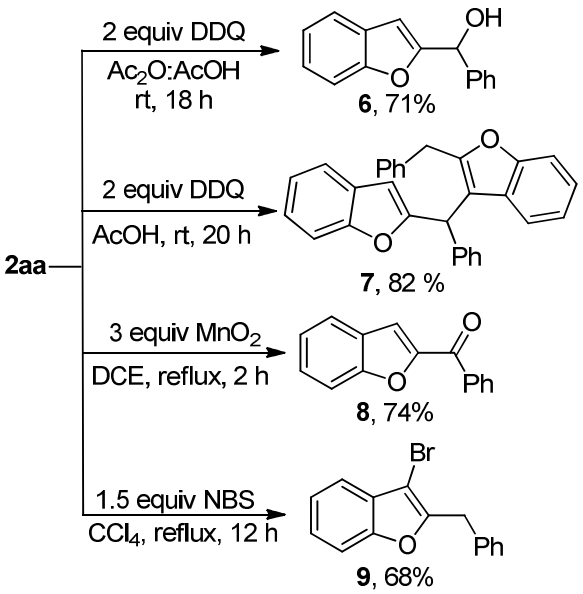
Table 5. Oxidative dehydrogenative coupling of alcohols with 2aa.[a]



[a]Reaction conditions: **2aa** (1.0 mmol), ROH/CH_2Cl_2 (1:1, 4 ml), DDQ (2 mmol), rt, 8-20 h.

Further, we treated **2aa** with Ac_2O/AcOH (1:1) to get acetoxy derivative in line with above oxidative couplings. But, it revealed the hydrolysed (deacylated) adduct **6** in 71% yield (Scheme 3). When treated with DDQ in AcOH in the absence of any trapping nucleophile, **2aa** underwent an oxidative dehydrogenative dimerization to afford **7** in 82% yield. It appears that electron rich C-3 of **2aa** acted as trapping nucleophile in the forcible conditions. When subjected to 3 equiv of MnO_2 in refluxing DCE, **2aa** produced the benzoyl benzofuran in 74% yield. Moving on to selective functionalization of C-3 of **2**, we treated **2aa** with NBS in refluxing CCl_4. 3-Bromo adduct **9** was isolated as a sole product in 68% yield.

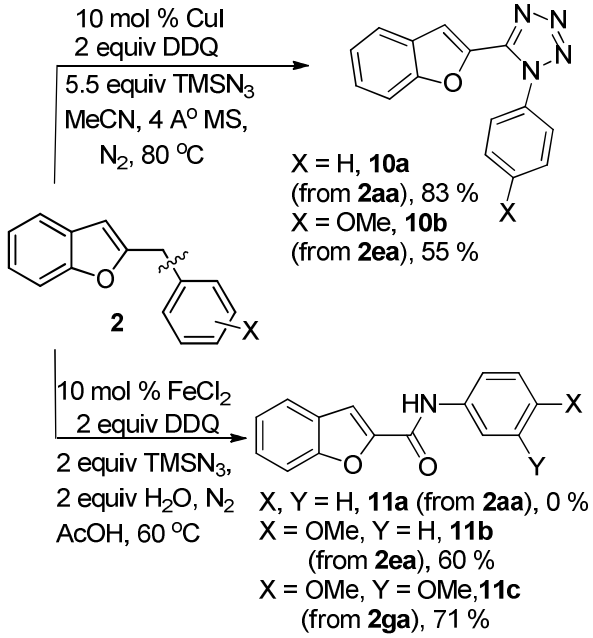
Scheme 3. Selective oxidative functionalizations of 2.



Finally, we attempted to uncover any difference in migratory aptitudes between phenyl and α-benzofuranyl groups of **2** in tandem oxidative cleavage/migration for the synthesis of tetrazole and amide adducts under known conditions.[9] The reports were only on symmetrical diaryl methanes, perhaps the unsymmetrical substrates were thought to yield mixture of adducts because of similar migratory aptitudes of both aryl groups. Pleasingly, when subjected to Cu(I)-catalyzed azidation-migration-triazolation cascade,[9a] **2aa** and **2ea** gave the

single regioisomers in 83% and 55% yields respectively, indicating that α-benzofuranyl group has relatively highly less migratory aptitude (Scheme 4). Similarly, Fe(II)-catalyzed DDQ-mediated amidative cleavage[9b] of **2ea** and **2ga** led to N-aryl benzofuranamides **11b-c** with complete selectivity whereas **2aa** underwent a mere oxidation probably *via* competitive hydrolysis of the imine intermediate.

Scheme 4. Derivatization of 2 via selective oxidative cleavages.



CONCLUSION

In summary, we demonstrated an efficient conversion of 1-(2-hydroxyphenyl) propargyl alcohols to 2-alkyl/benzyl benzofurans *via* Pd-catalyzed 5-*exo-dig* cyclization followed by a rare isocyanide assisted reductive elimination of allyl alcohol. The reaction, while providing a high substrate scope, neither required an inert atmosphere nor needed an elevated temperature. Further, a variety of useful transformations of the products is achieved via unassisted/direct C-H azidation/hydroxylation/alkoxylation and selective oxidatative cleavage of benzofuranylmethyl-phenyl bond.

EXPERIMENTAL SECTION

General Information: All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 400 or 500 MHz spectrometer for ^{1}H NMR, 50, 100 or 125 MHz for ^{13}C NMR spectroscopy. Chemical shifts are reported relative to the residual signals of tetramethylsilane in $CDCl_3$ or deuterated solvent $CDCl_3$ for ^{1}H and ^{13}C NMR spectroscopy. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). HRMS were recorded by using DART and Orbitrap mass spectrometers. Column chromatography was performed with silica gel (100–200 mesh) as the stationary phase. All reactions were monitored by using TLC. The purity and characterization of compounds were further established by using HRMS.

Starting materials 1 were prepared in one step following the literature procedures.[10]

General Procedure A for the Synthesis of 2-benzyl benzofurans (2aa-2oa) from 2-(1-hydroxy-3-phenylprop-2-yn-1-yl) phenols (1aa-1oa) taking Synthesis of 2aa as an example: To a stirred solution of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl) phenol **1aa** (224 mg, 1 mmol, 1 eq) in 4 mL of CH_3CN was added $Pd(OAc)_2$ (11.20 mg, 0.05 mmol, 0.05 eq), Cs_2CO_3 (390 mg, 1.2 mmol, 1.2 eq), *tert*-butyl isocyanide (99.6 mg, 1.2 mmol, 1.2 eq) at room temperature. The reaction mixture was stirred at room temperature until complete conversion of starting material monitored by TLC (4h for **2aa-2ae**, **2ak-2am**, 12h for **2af, 2ag, 2ao, 2ha-2ia,** 6h for **2ba-2ga, 2ja,** 10h for **2ap-2au**, **2an,** 15h for **2ka-2oa**, 18h for **2ah-2aj**). The reaction mixture was diluted with water (20ml) and extracted with EtOAc (2x20ml). The combined extracts were washed with brine (15 mL) and dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica

using hexane (2%-5% EtoAc/hexanes for **2ak-2am, 2ap-2au**, **2an, 2ba-2ga**) to get **2aa** (179 mg, 86 %) as yellow oil.

2-benzylbenzofuran[11a] (2aa): yellow oil; R_f = 0.80 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 7.34-7.24 (m, 4H), 7.24-7.14 (m, 3H), 6.37 (d, J = 0.8 Hz, 1H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.1, 137.3, 129.0, 128.9, 128.7, 126.8, 123.5, 122.6, 120.5, 111.0, 103.4, 35.0.

2-benzyl-6-methylbenzofuran (2ab): **2ab** (0.190 g) was obtained from **1ab** (0.238 g, 1 mmol) following general procedure A. Yield 85 %; colorless oil; R_f = 0.76 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 7.27-7.24 (m, 1H), 7.21 (d, J = 0.5 Hz, 1H), 7.03-6.97 (m, 1H), 6.32 (d, J = 0.9 Hz, 1H), 4.09 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.5, 137.5, 133.6, 129.0, 128.7, 126.8, 126.3, 123.9, 120.0, 111.3, 103.3, 35.1, 21.7; IR (neat) ν 2924, 1405, 1384, 1155, 668 cm^{-1}; HRMS (DART-TOF) calcd for $C_{16}H_{15}O[M + H]^+$ 223.1123, found 223.1129.

2-benzyl-7-methylbenzofuran (2ac): **2ac** (0.194 g) was obtained from **1ac** (0.238 g, 1 mmol) following general procedure A. Yield 87 %; colorless oil; R_f = 0.76 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 6H), 7.12 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 6.37 (s, 1H), 4.16 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 154.1, 137.5, 129.0, 128.6, 124.5, 122.6, 121.2, 117.9, 103.7, 35.1, 15.1; IR (neat) ν 3019, 1495, 1384, 1158, 954, 700 cm^{-1}; HRMS (DART-TOF) calcd for $C_{16}H_{15}O[M + H]^+$ 223.1123, found 223.1131.

2-benzyl-7-(*tert*-butyl)benzofuran (2ad): **2ad** (0.209 g) was obtained from **1ad** (0.280 g, 1 mmol) following general procedure A. Yield 79 %; Light yellow oil; R_f = 0.64 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.7 Hz, 1H), 7.41-7.36 (m, 2H), 7.36-7.27 (m, 5H), 6.41 (d, J = 0.9 Hz, 1H), 4.14 (s, 2H), 1.42 (s, 9H);^{13}C NMR (100 MHz,

$CDCl_3$) δ 157.9, 153.3, 145.6, 137.5, 128.9, 128.6,128.6, 126.8, 121.3, 116.8, 110.3, 103.6, 35.1, 34.7, 32.0; IR (neat) ν 3019, 1495, 1384, 1158, 954, 699 cm^{-1}; HRMS (DART-TOF) calcd for $C_{19}H_{21}O[M + H]^+$ 265.1592, found 265.1603.

2-benzyl-5,7-di-tert-butylbenzofuran (2ae): **2ae** (0.253 g) was obtained from **1ae** (0.336 g, 1 mmol) following general procedure A. Yield 79 %; colorless oil; R_f = 0.61 (SiO_2, Hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 7.27-7.20 (m, 1H), 7.18 (d, J = 1.9 Hz, 1H), 6.30 (s, 1H), 4.11 (s, 2H), 1.47 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 151.4, 145.3, 137.8, 133.6, 129.0, 128.6, 126.6, 118.1, 114.6, 103.2, 35.2, 34.9, 34.5, 32.0, 30.0; IR (neat) ν 2957, 1638, 1385, 1155, 1068, 668 cm^{-1}; HRMS (DART-TOF) calcd for $C_{23}H_{29}O[M + H]^+$ 321.2218, found 321.2230.

2-benzyl-5-chlorobenzofuran[11a] (2af): **2af** (0.175 g) was obtained from **1af** (0.258 g, 1 mmol) following general procedure A. Yield 72 %; yellow oil; R_f = 0.82 (SiO_2, Hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 1H), 7.37-7.27 (m, 6H), 7.16 (dd, J = 8.7, 2.1 Hz, 1H), 6.32 (d, J = 0.5 Hz, 1H), 4.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 153.5, 136.9, 130.3, 129.0, 128.8, 128.2, 127.0, 123.7, 120.1, 111.9, 103.1, 35.1.

2-benzyl-5-bromobenzofuran[11a] (2ag): **2ag** (0.225 g) was obtained from **1ag** (0.302 g, 1 mmol) following general procedure A. Yield 79 %; yellow gum; R_f = 0.82 (SiO_2, Hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 1.7 Hz, 1H), 7.37-7.27 (m, 7H), 6.32 (d, J = 0.8 Hz, 1H), 4.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.8, 136.9, 130.9, 129.0, 128.8, 127.0, 126.4, 123.2, 115.7, 112.4, 103.0, 35.0.

2-benzyl-5,7-dichlorobenzofuran (2ah): **2ah** (0.174 g) was obtained from **1ah** (0.292 g, 1 mmol) following general procedure A. Yield 63 %; yellow oil; R_f = 0.83 (SiO_2, Hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.25-7.17 (m, 5H), 7.14 (d, J = 1.9 Hz, 1H), 6.22 (s, 1H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 149.5, 136.4, 131.3, 129.1,

128.9, 128.4, 127.2, 123.7, 118.8, 116.9, 103.8, 35.0; IR (neat) ν 2926, 2400, 1445, 1384, 1156, 848,668 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{10}Cl_2O^{\cdot+}[M]^{\cdot+}$ 276.0109, found 276.0100.

2-benzyl-5,7-dibromobenzofuran (2ai): **2ai** (0.225 g) was obtained from **1ai** (0.380 g, 1 mmol) following general procedure A. Yield 62 %; light yellow oil; R_f = 0.83 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 2.6, 1.8 Hz, 2H), 7.38-7.27 (m, 5H), 6.31 (s, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.2, 136.4, 131.5, 129.1, 128.9, 127.2, 122.4, 115.8, 104.4, 103.8, 35.0; IR (neat) ν 3018, 2854, 1496, 1383, 1150, 847, 701, 499 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{10}Br_2O^{\cdot+}[M]^{\cdot+}$ 363.9093, found 363.9087.

2-benzyl-7-bromo-5-chlorobenzofuran (2aj): **2aj** (0.192 g) was obtained from **1aj** (0.336 g, 1 mmol) following general procedure A. Yield 60 %; light yellow oil; R_f = 0.83 (SiO_2, Hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 3H), 7.25-7.17 (m, 4H), 6.23 (s, 1H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.9, 136.4, 130.9, 129.1, 129.0, 128.9, 128.7, 127.2, 126.3, 119.4, 103.9, 35.0; IR (neat) ν 1622, 1405, 1219, 1155, 771 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{10}BrClO^{\cdot+}[M]^{\cdot+}$ 319.9604, found 319.9598.

2-benzyl-5-methoxybenzofuran[11a] (2ak): **2ak** (0.215 g) was obtained from **1ak** (0.254 g, 1 mmol) following general procedure A. Yield 90 %; brown gum; R_f = 0.62 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 6H), 6.94 (d, J = 2.5 Hz, 1H), 6.81 (dd, J = 8.8, 2.6 Hz, 1H), 6.31 (d, J = 0.8 Hz, 1H) 4.08 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 155.9, 150,1, 137.4, 129.5, 129.0, 128.7, 126.8, 111.9, 111.4, 103.6, 103.4, 56.0, 35.2;

2-benzyl-6-methoxybenzofuran[11a] (2al): **2al** (0.198 g) was obtained from **1al** (0.254 g, 1 mmol) following general procedure A. Yield 83 %; light brown gum; R_f = 0.62 (SiO_2, 2%

EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 6H), 7.00 (d, J = 2.0 Hz, 1H), 6.85 (dd, J = 8.5, 2.2 Hz, 1H), 6.33 (d, J = 0.9 Hz, 1H), 4.10 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.8, 156.0, 137.5, 128.9, 128.6, 126.8, 122.1, 120.5, 111.3, 103.1, 96.0, 55.8, 35.0;

2-benzyl-7-ethoxybenzofuran (2am): **2am** (0.210 g) was obtained from **1am** (0.268 g, 1 mmol) following general procedure A. Yield 83 %; light yellow gum; R_f = 0.59 (SiO_2, 2% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 5H), 7.15-7.04 (m, 2H), 6.77 (d, J = 7.2 Hz, 1H), 6.32 (s, 1H), 4.28 (q, J = 6.9 Hz, 2H), 4.16 (s, 2H), 1.53 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 144.4, 137.3, 130.7, 129.1, 128.6, 126.8, 123.2, 112.8, 107.1, 103.8, 64.5, 35.0, 15.0; IR (neat) ν 2400, 1385, 1155, 929, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{17}H_{17}O_2[M + H]^+$ 253.1229, found 253.1234.

2-benzylbenzofuran-5-yl *tert*-butylcarbamate (2an): **2an** (0.223 g) was obtained from **1an** (0.240 g, 1 mmol) following general procedure A. Yield 69 %; light yellow gum; R_f = 0.46 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 6H), 7.20 (d, J = 2.2 Hz, 1H), 6.94 (dd, J = 8.7, 2.3 Hz, 1H), 6.34 (s, 1H), 4.96 (bs, 1H), 4.09 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 152.4, 146.5, 137.2, 129.4, 128.9, 128.7, 126.9, 117.6, 113.4, 111.1, 103.8, 50.9, 35.1, 29.8; IR (KBr) ν 2926, 2400, 1740, 1384, 1162, 928 cm^{-1}; HRMS (DART-TOF) calcd for $C_{20}H_{22}NO_3[M + H]^+$ 324.1600, found 324.1609.

2-benzyl-5-nitrobenzofuran[11a] (2ao): **2ao** (0.150 g) was obtained from **1ao** (0.269 g, 1 mmol) following general procedure A. Yield 59 %; light yellow gum; R_f = 0.52 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 2.2 Hz, 1H), 8.15 (dd, J = 8.9, 2.3 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.39-7.24 (m, 5H), 6.50 (s, 1H), 4.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.9, 144.2, 136.2, 129.3, 129.0, 128.9, 127.3, 119.6, 117.0, 111.3, 104.2, 35.1;

2-benzyl-5-phenylbenzofuran (2ap): **2ap** (0.205 g) was obtained from **1ap** (0.300 g, 1 mmol) following general procedure A. Yield 72 %; white solid, mp 96-98 ^{o}C; R_f = 0.63 (SiO_2, Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70(s, 1H), 7.65-7.60 (m, 2H), 7.50-7.43 (m, 4H), 7.40-7.33 (m, 5H), 7.33-7.27 (m, 2H), 6.45 (s, 1H), 4.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO) δ 158.6, 154.7, 141.9, 137.2, 136.3, 129.4, 129.0, 128.8, 128.7, 127.5, 126.9, 126.8, 123.2, 119.1, 111.1, 103.7, 35.1; IR (KBr) ν 3019, 1406, 1385, 1155, 1068, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{21}H_{17}O[M + H]^+$ 285.1279, found 285.1289.

2-benzyl-5-(4-chlorophenyl)benzofuran (2aq): **2aq** (0.224 g) was obtained from **1aq** (0.334 g, 1 mmol) following general procedure A. Yield 70 %; light yellow solid, mp 99-101 ^{o}C; R_f = 0.65 (SiO_2, Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.55-7.49 (m, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.43-7.37 (m, 3H), 7.37-7.25 (m, 5H), 6.42 (s, 1H), 4.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 154.8, 140.4, 137.2, 135.1, 133.0, 129.5, 129.0, 128.9, 128.7, 128.7, 126.9, 123.0, 119.0, 111.2, 103.6, 35.1; IR (KBr) ν 3019, 1622, 1385, 1155, 669 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{21}H_{16}ClO[M + H]^+$ 319.0890, found 319.0883.

2-benzyl-5-(4-ethylphenyl)benzofuran (2ar): **2ar** (0.235 g) was obtained from **1ar** (0.328 g, 1 mmol) following general procedure A. Yield 75 %; white solid, mp 100-102 ^{o}C; R_f = 0.61 (SiO_2, Hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76(s, 1H), 7.55-7.50 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.31 (m, 4H), 7.30-7.25 (m, 3H), 6.42 (d, J = 0.5 Hz, 1H), 4.13 (s, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 154.6, 142.9, 139.3, 137.3, 136.3, 129.4, 129.0, 128.7, 128.3, 127.4, 126.9, 123.1, 118.9, 111.0, 103.7, 35.2, 28.6, 15.7; IR (KBr) ν 3019, 1621, 1406, 1155, 699 cm^{-1}; HRMS (DART-TOF) calcd for $C_{23}H_{21}O[M + H]^+$ 313.1592, found 313.1607.

2-benzylnaphtho[1,2-b]furan (2as): **2as** (0.150 g) was obtained from **1as** (0.274 g, 1 mmol) following general procedure A. Yield 58 %; Brown gum; R_f = 0.56 (SiO_2, Hexanes); ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.06-8.03 (m, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.59 (dd, J = 8.9, 0.7 Hz, 1H), 7.56-7.51 (m, 1H), 7.47-7.42 (m, 1H), 7.37-7.33 (m, 4H), 7.31-7.26 (m, 1H), 6.87 (d, J = 0.8 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 152.4, 137.5, 130.3, 129.0, 128.8, 127.6, 126.9, 126.1, 124.3, 124.3, 124.0, 123.5, 112.3, 102.6, 35.2; IR (neat) ν 2399, 1407, 1384, 1155, 928, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{19}H_{15}O[M + H]^+$ 259.1123, found 259.1127.

5-(2-benzylbenzofuran-5-yl)benzo[d][1,3]dioxole (2at): **2at** (0.240 g) was obtained from **1as** (0.344 g, 1 mmol) following general procedure A. Yield 73 %; Brown gum; R_f = 0.55 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 7.35-7.34 (m, 1H), 7.33-7.30 (m, 3H), 7.29-7.26 (m, 1H), 7.07-7.03 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 0.8 Hz, 1H), 5.99 (s, 2H) 4.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 154.5, 148.1, 146.8, 137.2, 136.3, 136.1, 129.4, 129.0, 128.7, 126.9, 123.0, 120.9, 118.8, 111.0, 108.6, 108.1, 103.6, 101.2, 35.1; IR (neat) ν 3019, 1621, 1505, 1405, 1384, 1155, 668 cm^{-1}; HRMS (DART-TOF) calcd for $C_{22}H_{17}O_3[M + H]^+$ 329.1178, found 329.1192.

2-benzyl-5-(6-methoxynaphthalen-2-yl)benzofuran (2au): **2au** (0.242 g) was obtained from **1au** (0.380 g, 1 mmol) following general procedure A. Yield 66 %; white solid mp 109-111 ^{o}C; R_f = 0.51 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 1.2 Hz, 1H), 7.82-7.70 (m, 4H), 7.58-7.46 (m, 2H), 7.37-7.31 (m, 4H), 7.29-7.26 (m, 1H), 7.19-7.14 (m, 2H), 6.44 (d, J = 0.7 Hz, 1H), 4.14 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 157.7, 154.7, 137.3, 137.1, 136.4, 133.6, 129.7, 129.5, 129.3, 129.0, 128.7, 127.3, 126.9, 126.6, 125.8, 123.3, 119.2, 119.1, 111.2, 105.7, 55.4, 35.2; IR (KBr) ν 3019, 2926, 1405, 1155, 1068, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{26}H_{21}O_2$ $[M + H]^+$ 365.1542, found 365.1557.

2-(4-methylbenzyl)benzofuran[11a] (2ba): **2ba** (0.189 g) was obtained from **1ba** (0.238 g, 1 mmol) following general procedure A. Yield 85 %; colorless gum; R_f = 0.76 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 1H), 7.43-7.40 (m, 1H), 7.20-7.17 (m, 4H), 7.10-7.13 (m, 2H), 6.37 (d, J = 0.9 Hz, 1H), 4.08 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 155.0, 136.4, 134.2, 129.4, 128.9, 123.4, 122.6, 120.5, 111.0, 103.3, 34.7, 21.2;

2-(4-butylbenzyl)benzofuran (2ca): **2ca** (0.220 g) was obtained from **1ca** (0.280 g, 1 mmol) following general procedure A. Yield 83 %; colorless oil; R_f = 0.72 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 1H), 7.48-7.42 (m, 1H), 7.29-7.14 (m, 6H), 6.40 (d, J = 0.8 Hz, 1H), 4.11 (s, 2H), 2.64 (q, J = 7.7 Hz, 2H), 1.69-1.59 (m, 2H), 1.45-1.35 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 155.1, 141.5, 134.5, 129.0, 128.8, 128.7, 123.4, 122.6, 120.5, 111.0, 103.3, 35.4, 34.7, 33.7, 22.5, 14.0; IR (neat) v 2958, 2858, 1513, 1384, 1159, 1070, 954, 668 cm^{-1}; HRMS (DART-TOF) calcd for $C_{19}H_{21}O[M + H]^+$ 265.1592, found 265.1604.

2-(4-(*tert*-butyl)benzyl)benzofuran (2da): **2da** (0.227 g) was obtained from **1da** (0.280 g, 1 mmol) following general procedure A. Yield 86 %; yellow oil; R_f = 0.64 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.41-7.35 (m, 2H), 7.31-7.16 (m, 4H), 6.41 (d, J = 0.8 Hz, 1H), 4.11 (s, 2H) 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 155.1, 149.7, 134.3, 129.0, 128.6, 125.6, 123.4, 122.6, 120.5, 111.0, 103.0, 34.6, 31.5, 29.8; IR (neat) v 2965, 1454, 1328, 1253, 1068, 668 cm^{-1}; HRMS (DART-TOF) calcd for $C_{19}H_{21}O[M + H]^+$ 265.1592, found 265.1603.

2-(4-methoxybenzyl)benzofuran[11a] (2ea): **2ea** (0.215 g) was obtained from **1ea** (0.254 g, 1 mmol) following general procedure A. Yield 90 %; brown gum; R_f = 0.54 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.37 (m, 2H), 7.32-7.11 (m, 4H), 6.89

(dd, J = 7.2, 0.7 Hz, 2H), 6.37 (d, J = 0.8 Hz, 1H), 4.07 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 158.4, 155.1, 130.0, 129.4, 128.9, 123.4, 122.6, 120.5, 114.1, 111.0, 103.2, 55.3, 34.2

2-(3-methoxybenzyl)benzofuran (2fa): **2fa** (0.200 g) was obtained from **1fa** (0.200 g, 1 mmol) following general procedure A. Yield 84 %; colorless gum; R_f = 0.53 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.43-7.39 (m, 1H), 7.27-7.14 (m, 3H), 6.92-6.88 (m, 1H), 6.88-6.84 (m, 1H), 6.81 (dd, J = 8.2, 2.1 Hz, 1H), 6.39 (d, J = 0.8 Hz, 1H), 4.09 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 157.7, 155.1, 138.9, 129.7, 128.9, 123.5, 122.6, 121.4, 120.5, 114.8, 112.2, 111.0, 103.5, 55.3, 35.1; IR (neat) ν 2927, 1489, 1455, 1155, 955, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{16}H_{15}O_2$[M + H]$^+$ 239.1072, found 239.1078.

2-(3,4-dimethoxybenzyl)benzofuran (2ga): **2ga** (0.247 g) was obtained from **1ga** (0.284 g, 1 mmol) following general procedure A. Yield 92 %; light yellow oil; R_f = 0.53 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 1H), 7.49-7.39 (m, 1H), 7.24-7.15 (m, 2H), 6.88-6.80 (m, 3H), 6.37 (d, J = 0.9 Hz, 1H), 4.06 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 155.0, 149.1, 148.0, 129.8, 128.9, 123.5, 122.6, 121.1, 120.5, 112.3, 111.4, 111.0, 103.0, 56.0, 55.9, 34.7; IR (neat) ν 2927, 1638, 1514, 1216, 1154, 1026, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{17}H_{17}O_3$[M + H]$^+$ 269.1178, found 269.1189.

2-(4-fluorobenzyl)benzofuran[11a] (2ha); **2ha** (0.168 g) was obtained from **1ha** (0.242 g, 1 mmol) following general procedure A. Yield 74 %; colorless oil; R_f = 0.77 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 1H), 7.44-7.39 (m, 1H), 7.29-7.24 (m, 2H), 7.23-7.16 (m, 2H), 7.05-6.98 (m, 2H), 6.37 (d, J = 0.8 Hz, 1H), 4.08 (s, 2H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 161.9 (d, J = 244 Hz), 157.6, 155.1, 133.0, 130.5 (d, J = 8 Hz), 128.8, 123.6, 122.7, 120.6, 115.5 (d, J = 21 Hz), 111.0, 103.5, 34.3;

2-(3-chlorobenzyl)benzofuran (2ia):[11a] **2ia** (0.167 g) was obtained from **1ia** (0.258 g, 1 mmol) following general procedure A. Yield 69 %; colorless oil; R_f = 0.81 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 1H), 7.44-7.40 (m, 1H), 7.30 (s, 1H), 7.27-7.18 (m, 5H), 6.42 (d, J = 0.8 Hz, 1H), 4.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.2, 139.4, 134.6, 129.9, 129.1, 128.8, 127.1, 123.8, 122.8, 120.6, 111.1, 103.8, 34.7.

2-(thiophen-2-ylmethyl)benzofuran (2ja): **2ja** (0.175 g) was obtained from **1ja** (0.230 g, 1 mmol) following general procedure A. Yield 82 %; Brown oil; R_f = 0.63 (SiO_2, Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 1H), 7.46-7.40 (m, 1H), 7.25-7.16 (m, 3H), 7.01-6.93 (m, 2H), 6.48 (d, J = 0.9 Hz, 1H), 4.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.0, 139.3, 128.8, 127.0, 126.1, 124.5, 123.7, 122.7, 120.7, 111.1, 103.4, 29.3; IR (neat) ν 2924, 1780, 1301, 1073, 952,850, 699 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{13}H_{11}OS[M + H]^+$ 215.0531, found 215.0525.

2-butylbenzofuran[11b] **(2ka)**; **2ka** (0.133 g) was obtained from **1ka** (0.190 g, 1 mmol) following general procedure A. Yield 76 %; light brown oil; R_f = 0.85 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 1H), 7.42-7.38 (m, 1H), 7.22-7.14 (m, 2H), 6.37 (d, J = 0.9 Hz, 1H), 2.77 (t, J = 7.5 Hz, 2H), 1.78-1.68 (m, 2H), 1.47-1.38 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.7, 129.1, 123.1, 122.4, 120.2, 110.8, 101.8, 29.9, 28.2, 22.4, 13.9;

2-heptylbenzofuran[11b] **(2la)**: **2la** (0.169 g) was obtained from **1la** (0.232 g, 1 mmol) following general procedure A. Yield 78 %; colorless oil, R_f = 0.84 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.43-7.39 (m, 1H), 7.22-7.14 (m, 2H), 6.37 (d, J = 0.8 Hz, 1H), 2.80-2.73 (m, 2H), 1.80-1.69 (m, 2H), 1.45-1.27 (m, 8H), 0.89 (t, J = 6.8 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.7, 129.1, 123.1, 122.4, 120.2, 110.8, 101.8, 31.9, 29.3, 29.1, 28.6, 27.8, 22.7, 14.2;

2-undecylbenzofuran (2ma): **2ma** (0.204 g) was obtained from **1ma** (0.288 g, 1 mmol) following general procedure A. Yield 75 %; Yellow oil; R_f = 0.81 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.45 (m, 1H), 7.43-7.38 (m, 1H), 7.22-7.14 (m, 2H), 6.37 (d, J = 0.8 Hz, 1H), 2.76 (t, J = 7.5 Hz, 2H), 1.81-1.67 (m, 2H), 1.41-1.20 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.7, 129.1, 123.1, 122.4, 120.2, 110.8, 101.8, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 28.6, 27.8, 22.8, 14.2; IR (neat) ν 2854, 2400, 1454, 1156, 1069, 669 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{19}H_{29}O[M + H]^+$ 273.2218, found 273.2209.

2-(cyclopentylmethyl)benzofuran[11c] (2na): **2na** (0.166 g) was obtained from **1na** (0.216 g, 1 mmol) following general procedure A. Yield 83 %; light yellow gum R_f = 0.72 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 1H), 7.43-7.38 (m, 1H), 7.23-7.14 (m, 2H), 6.37 (d, J = 0.8 Hz, 1H), 2.75 (d, J = 7.4 Hz, 2H), 2.39-2.23 (m, 1H), 1.87-1.78 (m, 2H), 1.69-1.61 (m, 2H), 1.60-1.53 (m, 2H), 1.31-1.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.7, 129.1, 123.1, 122.4, 120.2, 110.8, 102.3, 38.7, 34.6, 32.6, 25.2;

2-(cyclohexylmethyl)benzofuran (2oa): **2oa** (0.182 g) was obtained from **2oa** (0.230 g, 1 mmol) following general procedure A. Yield 85 %; Yellow gum; R_f = 0.82 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 1H), 7.44-7.38 (m, 1H), 7.23-7.14 (m, 2H), 6.37 (d, J = 0.6 Hz, 1H), 2.64 (d, J = 6.6 Hz, 2H), 1.82-1.63 (m, 4H), 1.31-1.10 (m, 4H), 1.08-0.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 154.8, 129.1, 123.1, 122.4, 120.2, 110.8, 102.9, 37.1, 36.4, 33.3, 26.5, 26.3; IR (neat) ν 2853, 1454, 1254, 1157, 948, 929, 669 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{19}O[M + H]^+$ 215.1436, found 215.1429.

(Z)-2-benzylidene-2,3-dihydrobenzofuran-3-ol[4f] (3): Yield 76 %; white solid, mp 109-110 ^{o}C; R_f = 0.47 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.41-7.32 (m, 3H), 7.28-7.21 (m, 1H), 7.13-7.05 (m, 2H), 6.01 (d, J = 1.1 Hz, 1H), 5.76 (d, J = 6.0 Hz, 1H), 2.19 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.1, 134.6, 130.7, 128.8, 128.5, 127.0, 126.9, 125.7, 123.0, 110.7, 106.1, 72.6.

General Procedure B for the Synthesis of 2-(azido(phenyl)methyl)benzofurans (4a-f) from 2-benzyl benzofurans (2aa, 2da, 2ga, 2ap, 2af, 2ak) taking Synthesis of 4a as an example: To a stirred solution of 2-benzyl benzofuran (208 mg, 1 mmol, 1 eq) in 4 mL of AcOH was added DDQ (454 mg, 2 mmol, 2 eq), $TMSN_3$(172.5 mg, 1.5 mmol, 1.5 eq) at room temperature. The reaction mixture was stirred at room temperature until complete conversion of starting material (2h for **4a, 4(d-f),** 1h for **4(b-c)**). The reaction mixture was neutralized with Na_2CO_3 (2 g), and evaporated under reduced pressure. The residue was diluted with water (20ml) and extracted with CH_2Cl_2 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 5% EtoAc/hexane to get **4a** (214 mg, 86 %) as yellow oil

2-(azido(phenyl)methyl)benzofuran (4a): R_f = 0.60 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.49 (m, 1H), 7.49-7.32 (m, 6H), 7.32-7.16 (m, 2H), 6.59 (s, 1H), 5.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 154.9, 136.3, 129.0, 127.8, 127.7, 124.8, 123.1, 121.3, 111.5, 105.6, 62.7; IR (neat) ν 3019, 2102, 1385, 1069, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{12}NO[M + H - N_2]^+$ 222.0919, found 222.0911.

2-(azido(4-(tert-butyl)phenyl)methyl)benzofuran (4b): **(4b)** (0.232 g) was obtained from **2da** (0.264 g, 1 mmol) following general procedure B. Yield 76 %; yellow gum; R_f = 0.5 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 1H), 7.52-7.43 (m, 3H), 7.43-7.35 (m, 2H), 7.35-7.20 (m, 2H), 6.64 (s, 1H), 5.78 (s, 1H), 1.36 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 155.1, 152.0, 133.3, 129.8, 127.9, 125.9, 124.7, 123.1, 121.3, 111.5, 105.5, 62.5, 34.8, 31.4; IR (neat) ν 1644,1217, 1069, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO[M + H - N_2]^+$ 278.1545, found 278.1535.

2-(azido(3,4-dimethoxyphenyl)methyl)benzofuran (4c): **(4c)** (0.231 g) was obtained from **2ga** (0.268 g, 1 mmol) following general procedure B. Yield 75 %; yellow oil; R_f = 0.45 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.52 (m, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.36-7.19 (m, 2H), 7.05-6.95 (m, 2H), 6.91 (d, J = 8.1 Hz, 1H), 6.63 (s, 1H), 5.76 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 155.1, 149.6, 149.4, 128.7, 127.8, 124.7, 123.1, 121.3, 120.3, 111.5, 111.2, 110.7, 105.3, 62.6, 56.0, 56.0; IR (neat) ν 3019, 2102, 1730, 1645, 1156, 669 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{16}NO_3[M + H - N_2]^+$ 282.1130, found 282.1134.

2-(azido(phenyl)methyl)-5-phenylbenzofuran (4d): **(4d)** (0.276 g) was obtained from **2ap** (0.284 g, 1 mmol) following general procedure B. Yield 85 %; white solid mp 97-99 ^{o}C; R_f = 0.5 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 1H), 7.64-7.58 (m, 2H), 7.55-7.50 (m, 2H), 7.50-7.32 (m, 8H), 6.67 (s, 1H), 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.0, 141.5, 136.9, 136.3, 129.0, 128.8, 128.3, 127.7, 127.5, 127.0, 124.5, 119.8, 111.6, 105.8, 62.7; IR (neat) ν 1644, 1385, 1218, 1070, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{16}NO[M + H - N_2]^+$ 298.1232, found 298.1231.

2-(azido(phenyl)methyl)-5-chlorobenzofuran (4e): **(4e)** (0.226 g) was obtained from **2af** (0.242 g, 1 mmol) following general procedure B. Yield 80 %; yellow oil; R_f = 0.6 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 1H), 7.46-7.40 (m, 5H), 7.39-7.33 (m, 1H), 7.24 (dd, J = 8.6, 2.1 Hz, 1H); 6.56 (s, 1H), 5.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.7, 136.0, 129.1, 129.1, 129.0, 128.7, 127.7, 125.0, 112.5, 105.1, 62.6; IR

(neat) *v* 1644, 1385, 1219, 1075, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{11}ClNO[M + H - N_2]^+$ 256.0529, found 256.0513.

2-(azido(phenyl)methyl)-5-methoxybenzofuran (4f): **(4f)** (0.218 g) was obtained from **2ak** (0.238 g, 1 mmol) following general procedure B. Yield 78 %; yellow oil; R_f = 0.6 (SiO_2, 10% EtOAc/Hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46-7.37 (m, 5H), 7.36-7.31 (m, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.54 (s, 1H), 5.75 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.7, 150.4, 136.4, 129.0, 128.9, 128.3, 127.7, 113.5, 112.0, 105.7, 103.8, 62.7, 56.0; IR (neat) *v* 3019, 2013, 1638, 1385, 1070, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_2[M + H - N_2]^+$ 252.1025, found 252.1017.

General Procedure C for the Synthesis of 2-alkoxy benzofurans (5a-f) from 2-benzyl benzofurans (2aa) taking Synthesis of 5a as an example:

To a stirred solution of **2aa** (208 mg, 1 mmol, 1 eq) in 4 mL of ROH: CH_2Cl_2 (1:1) was added DDQ (454 mg, 2 mmol, 2 eq), at room temperature. The reaction mixture was stirred at room temperature until complete conversion of starting material monitored by TLC. (8h for **5a-b**, 12h for **5c-d**, 20h for **5e-5f**). The reaction mixture was evaporated under reduced pressure. The residue was diluted with water (20ml) and extracted with CH_2Cl_2 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 2%-5% EtoAc/hexanes for **(5a-5f)** to get **5a** (167 mg, 70 %) as a yellow oil.

2-(methoxy(phenyl)methyl)benzofuran (5a): Yellow oil; R_f = 0.62 (SiO_2, 5% EtOAc/Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.43 (m, 4H), 7.42-7.32 (m, 3H), 7.27-7.16 (m, 2H), 6.50 (s, 1H), 5.40 (s, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.3, 138.6, 128.6, 128.4, 128.1, 127.4, 124.3, 122.8, 121.1, 111.5, 105.1, 79.6, 51.4; IR (neat) *v* 3019, 1638, 1385, 1154, 1069, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{15}H_{11}O[M - OCH_3]^+$ 207.0810 found 207.0805.

2-(ethoxy(phenyl)methyl)benzofuran (5b): **5b** (0.187 g) was obtained from **2aa** (208 g, 1 mmol) following general procedure C. Yield 74 %; colorless oil; R_f = 0.64 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 3H), 7.46-7.43 (m, 1H), 7.41-7.31 (m, 3H), 7.24-7.16 (m, 2H), 6.54 (t, J = 0.7 Hz, 1H), 5.52 (s, 1H), 3.71-3.58 (m, 2H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.3, 139.2, 128.6, 128.2, 128.1, 127.3, 124.2, 122.8, 121.1, 111.5, 104.8, 77.7, 65.1, 15.4; IR (neat) ν 2400, 1385, 1155, 928, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{15}H_{11}O[M - OC_2H_5]^+$ 207.0810 found 207.0806.

2-(phenyl(propoxy)methyl)benzofuran (5c): **5c** (0.189 g) was obtained from **2aa** (0.208 g, 1 mmol) following general procedure C. Yield 71 %; yellow gum; R_f = 0.68 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 3H), 7.47-7.44 (m, 1H), 7.41-7.32 (m, 3H), 7.27-7.17 (m, 2H), 6.56 (s, 1H), 5.51 (s, 1H), 3.60-3.68 (m, 2H), 1.76-1.66 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 155.3, 139.3, 128.5, 128.2, 127.3, 124.2, 122.7, 121.1, 111.5, 104.7, 77.8, 71.4, 23.1, 10.7; IR (neat) ν 1639, 1385, 1154, 1069, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{15}H_{11}O[M - OC_3H_7]^+$ 207.0810 found 207.0809.

2-(butoxy(phenyl)methyl)benzofuran (5d): **5d** (0.205 g) was obtained from **2aa** (0.208 g, 1 mmol) following general procedure C. Yield 73 %; colorless gum; R_f = 0.69 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.42 (m, 4H), 7.41-7.29 (m, 3H), 7.28-7.15 (m, 2H), 6.55 (s, 1H), 5.50 (s, 1H), 3.63-3.51 (m, 2H), 1.71-1.62 (m, 2H), 1.48-1.38 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 155.3, 139.3, 128.5, 128.2, 127.3, 124.2, 122.7, 121.1, 111.5, 104.7, 77.9, 69.6, 32.0, 19.5, 14.0; IR (neat) ν 3019, 1638, 1385, 1154, 1068, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{15}H_{11}O[M - OC_4H_9]^+$ 207.0810 found 207.0804.

2-(phenoxy(phenyl)methyl)benzofuran (5e): **5e** (0.177 g) was obtained from **2aa** (0.208 g, 1 mmol) following general procedure C. Yield 59 %; brown gum; R_f = 0.46 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.52-7.49 (m, 2H), 7.42-7.33 (m, 3H), 7.29-7.16 (m, 4H), 7.05-6.99 (m, 2H), 6.95 (t, J = 2.4 Hz, 1H), 6.58 (s, 1H), 6.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 156.3, 155.3, 138.2, 129.6, 128.8, 128.6, 128.1, 127.2, 124.5, 122.9, 121.7, 121.3, 116.3, 111.6, 105.4, 76.3; IR (neat) v 2924, 1638, 1216, 1154, 1068, 669 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{11}O[M - OC_6H_5]^+$ 207.0810 found 207.0806.

2-(phenyl(prop-2-yn-1-yloxy)methyl)benzofuran (5f): **5f** (0.160 g) was obtained from **2aa** (0.208 g, 1 mmol) following general procedure C. Yield 61 %; colorless oil; R_f = 0.54 (SiO_2, 2% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 3H), 7.47-7.43 (m, 1H), 7.42-7.34 (m, 3H), 7.28-7.17 (m, 2H), 6.62 (s, 1H), 5.83 (s, 1H), 4.31-4.19 (m, 2H), 2.49 (t, J = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.4, 137.9, 128.7, 128.6, 128.0, 127.7, 124.5, 122.9, 121.2, 111.6, 105.7, 79.3, 75.9, 75.3, 56.2; IR (neat) v3019, 1639, 1385, 1154, 669 cm^{-1}; HRMS (DART-TOF) calcd for $C_{15}H_{11}O[M - OC_3H_3]^+$ 207.0810 found 207.0808.

Procedure for the Synthesis of benzofuran-2-yl(phenyl)methanol (6):[12] To a stirred solution of 2-benzyl benzofuran (208 mg, 1 mmol, 1 eq) in 3 mL of Ac_2OH: AcOH (1:1) was added DDQ (454 mg, 2 mmol, 2 eq), at room temperature. The reaction mixture was stirred at room temperature until complete conversion of starting material (18h). The reaction mixture was neutralized with Na_2CO_3 (2 g), and evaporated under reduced pressure. The residue was diluted with water (20ml) and extracted with CH_2Cl_2 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 5% EtoAc/hexane to get **6** (159 mg, 71 %) as yellow oil. R_f = 0.46 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 3H), 7.46-

7.34 (m, 4H), 7.28-7.17 (m, 2H), 6.53 (t, J = 0.8 Hz, 1H), 5.96 (s, 1H), 2.54 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.2, 140.4, 128.7, 128.5, 128.1, 126.9, 124.4, 122.9, 121.2, 111.4, 104.1, 70.8; IR (neat) ν 3400, 1638, 1385, 1217, 1154, 668 cm^{-1}.

Procedure for the Synthesis of 3-(benzofuran-2-yl(phenyl)methyl)-2-benzyl benzofuran (7): To a stirred solution of 2-benzyl benzofuran **(2aa)** (104 mg, 0.5 mmol, 0.5 eq) in 2 mL of AcOH was added DDQ (227 mg, 1 mmol, 2 eq), at room temperature. The reaction mixture was stirred at room temperature until complete conversion of starting material monitored by TLC (20h). The reaction mixture was neutralized with Na_2CO_3 (1 g), and evaporated under reduced pressure. The residue was diluted with water (10ml) and extracted with CH_2Cl_2 (2x10ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 5% EtoAc/hexane to get **7** (84 mg, 82%) as yellow gum. R_f = 0.62 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 1H), 7.41-7.36 (m, 2H), 7.31-7.24 (m, 5H), 7.23-7.13 (m, 9H), 7.07-7.02 (m, 1H), 6.36 (s, 1H), 5.79 (s, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 155.1, 154.4, 153.8, 139.8, 137.4, 128.7, 128.7, 128.6, 128.5, 127.3, 126.7, 123.9, 123.7, 122.8, 122.5, 120.8, 120.5, 115.1, 111.3, 111.1, 105.6, 41.7, 33.0; IR (neat) ν 3019, 1639, 1385, 1155, 1068, 668 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{30}H_{23}O_2$ $[M + H]^+$ 415.1698, found 415.1689.

General Procedure for the Synthesis benzofuran-2-yl(phenyl)methanone (8):[13] 2-benzyl benzofuran (104 mg, 0.5 mmol, 1 eq) in 2 mL DCE was added MnO_2 (130 mg, 1.5 mmol, 3 eq). The reaction mixture was stirred under reflux for 2h. The reaction mass was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (100–200 mesh) with 5 %EtOAc/Hexane as the eluent to give the pure product (83 mg, 74 %) as white solid. mp 90-92 ^{o}C; R_f = 0.51 (SiO_2, 5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.01 (m, 2H), 7.73 (d, J = 7.9 Hz, 1H),

7.68-7.60 (m, 2H), 7.57-7.46 (m, 4H), 7.37-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 156.1, 152.3, 137.3, 133.0, 129.5, 128.6, 128.5, 127.1, 124.1, 123.4, 116.6, 112.7.

Procedure for the Synthesis 2-benzyl-3-bromobenzofuran (9): To a stirred solution of 2-benzyl benzofuran **(2aa)** (208 mg, 1 mmol, 1 eq) in 5 mL of CCl_4 was added N-Bromo succinimide (266.8 mg, 1.5 mmol, 1.5 eq), at room temperature. The reaction mixture was stirred at 80 ^{o}C until complete conversion of starting material monitored by TLC (12h). The reaction mixture was diluted with water (20ml) and extracted with CH_2Cl_2 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 2% EtoAc/hexane to get **9** (194 mg, 68 %) as Brown oil. R_f = 0.68 (SiO_2, Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 1H), 7.44-7.37 (m, 1H), 7.36-7.22 (m, 7H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 153.8, 136.7, 128.8, 128.3, 126.9, 124.9, 123.3, 119.5, 111.4, 95.2, 33.0; IR (neat) ν 2926, 1405, 1216, 1155, 669 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{15}H_{11}BrO^{\cdot+}[M]^{\cdot+}$ 285.9988, found 285.9987.

General Procedure D for the Synthesis of 5-(benzofuran-2-yl)-1-phenyl-1H-tetrazoles (10a-10b) from (2aa,2ea) taking Synthesis of 10a as an example:

To a stirred solution of 2-benzyl benzofuran (208 mg, 1 mmol, 1 eq) in 4 mL of CH_3CN was added CuI (19mg, 0.1 mmol, 0.1 eq), DDQ (454 mg, 2 mmol, 2 eq), $TMSN_3$ (632 mg, 5.5 mmol, 5.5 eq), 4 ^{o}A MS (500 mg) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at 80 ^{o}C until complete conversion of starting material monitored by TLC (12h). The reaction mixture was diluted with water (20ml) and extracted with EtOAc (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 20% EtoAc/hexane to get **10a** (218 mg, 83 %) as brown gum.

5-(benzofuran-2-yl)-1-phenyl-1H-tetrazole (10a): R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.58 (m, 4H), 7.58-7.50 (m, 2H), 7.48-7.42 (m, 1H), 7.42-7.34 (m, 1H), 7.33-7.23 (m, 1H), 7.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 147.0, 140.3, 134.4, 131.1, 129.9, 127.2, 127.1, 125.9, 124.2, 122.4, 112.1, 111.4; IR (neat) ν 3019, 1645, 1069, 909, 669 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{11}N_4O[M + H]^+$ 263.0933, found 263.0934.

5-(benzofuran-2-yl)-1-(4-methoxyphenyl)-1H-tetrazole (10b): **(10b)** (0.160 g) was obtained from **2ea** (0.238 g, 1 mmol) following general procedure D. Yield 55 %; yellow gum; *Rf* = 0.46 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.5 Hz, 1H), 7.54-7.34 (m, 4H), 7.34-7.21 (m, 1H), 7.18-6.98 (m, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 155.6, 147.2, 140.2, 136.8, 127.4, 127.2, 127.1, 124.1, 122.3, 115.0, 112.1, 111.1, 55.8; IR (neat) ν 3019, 1644, 1385, 1069, 909, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{13}N_4O_2[M + H]^+$ 293.1039, found 293.1031.

General Procedure E for the Synthesis of N-phenylbenzofuran-2-carboxamides (11b-c) from (2ea, 2ga) taking 11b as an example:

To a stirred solution of 2-(4-methoxybenzyl)benzofuran (238 mg, 1 mmol, 1 eq) in 4 mL of AcOH was added $FeCl_2$ (12.5 mg, 0.1 mmol, 0.1 eq), DDQ (454 mg, 2 mmol, 2 eq), $TMSN_3$(230 mg, 2 mmol, 2 eq), H_2O (36 mg, 2 mmol, 2 eq) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at 60 ^{o}C until complete conversion of starting material (12). The reaction mixture was cooled to room temperature, neutralized with Na_2CO_3 (2 g), and evaporated under reduced pressure. The residue was diluted with water (20ml) and extracted with CH_2Cl_2 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified on silica using 8% EtoAc/hexane to get **11b** (160 mg, 60 %) as yellow solid.

N-(4-methoxyphenyl)benzofuran-2-carboxamide (11b): mp 118-120 ^{o}C R_f = 0.50 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (bs, 1H), 7.73-7.67 (m, 1H), 7.65-7.59 (m, 2H), 7.59-7.52 (m, 2H), 7.48-7.41 (m, 1H), 7.36-7.28 (m, 1H), 6.95-6.89 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.6, 154.9, 148.7, 130.4, 127.8, 127.2, 123.9, 122.9, 121.9, 114.4, 111.8, 111.2, 55.6; IR (neat) ν 3400, 1644, 1070, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_3[M + H]^+$ 268.0974, found 268.0968.

N-(3,4-dimethoxyphenyl)benzofuran-2-carboxamide (11c): **11c** (0.210 g) was obtained from **2ga** (0.268 g, 1 mmol) following general procedure E. Yield 71 %; light yellow gum; R_f = 0.40 (SiO_2,20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (bs, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.60-7.49 (m, 3H), 7.49-7.38 (m, 1H), 7.36-7.27 (m, 1H), 7.09 (dd, J = 8.6, 2.4 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.9, 149.3, 148.7, 146.4, 130.9, 127.8, 127.3, 124.0, 112.1, 111.9, 111.5, 111.3, 105.0, 56.2, 56.1; IR (neat) ν 3399, 1645, 1385, 104569, 669 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{16}NO_4[M + H]^+$ 298.1079, found 298.1071.

ASSOCIATED CONTENT

Spectroscopic data of all the products is available in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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