Organic & Biomolecular Chemistry

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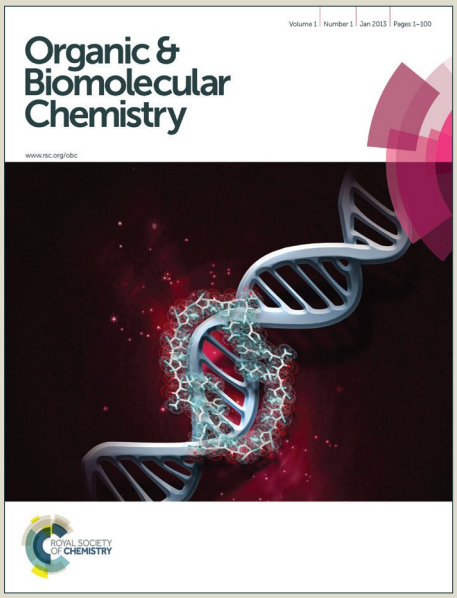

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View Article Online
DOI: 10.1039/C6OB00191B

Journal Name

ARTICLE

Synthesis of benzofuranyl and indolyl methyl azides by tandem silver-catalyzed cyclization and azidation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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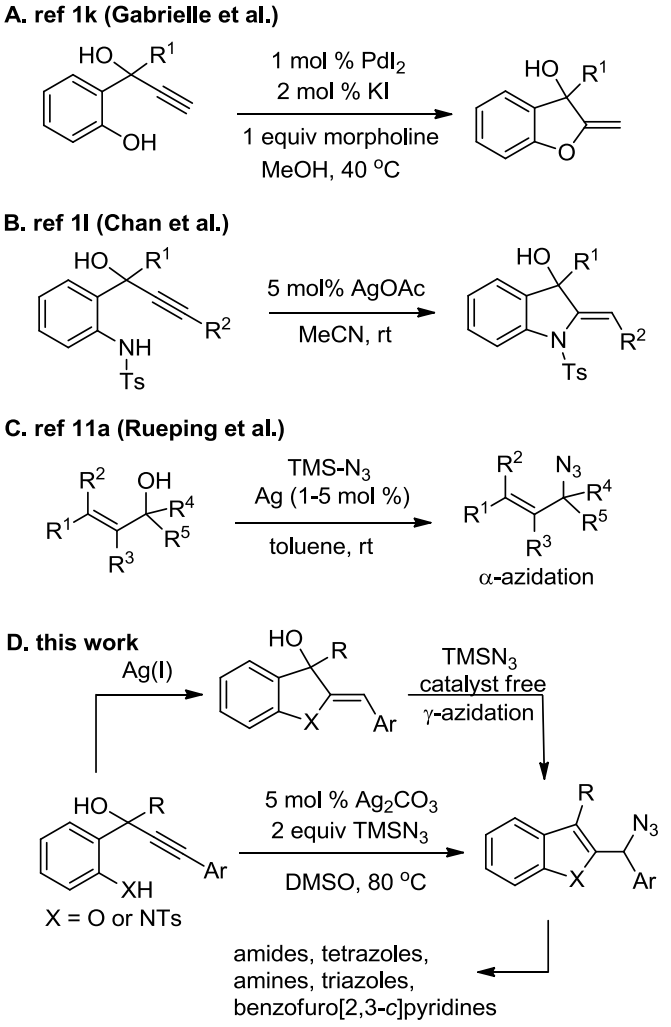
Ag(I)-catalyzed synthesis of 2-azidomethyl benzofurans/indoles from linear and readily available hydroxyl/amino-phenyl propargyl alcohols is described *via* a highly regioselective C-O and C-N bond formations. Control experiments reveal that the reaction involves the sequential Ag(I)-catalyzed *5-exo-dig* cyclization and a catalyst free γ-allylic azidation. The synthetic utility of this method has been demonstrated by using azidomethyl unit of the above synthesized heterocycles as base for variety of other functionalizations, like triazole-, tetrazole-, amide-, amine-, pyrido-derivatives.

Introduction

For practical considerations as well as green chemistry point of view, cascade/tandem reactions are ideal approaches in organic synthesis to build up intricate architectures. Electrophilic cyclization of functionalized alkynes forms an excellent platform for various tandem transformations, *viz*. couplings, isomerizations, rearrangements, etc.[1] A wide range of metal catalysts are identified as soft enough to activate the alkynes for the requisite cyclization. The incipient carbo/hetero metallated intermediate would undergo the said tandem reactions depending on their compatibility with the conditions employed. Although very attractive, this strategy is still underutilized because it needs a careful development of the reaction conditions as the independent reactions may have different requirements, and combining them as such is mostly not possible. Thus a careful study is required to set the appropriate conditions to execute such cascade transformations. As part of our on-going program of uncovering the new activities of activated functionalized alkynes,[2] we herein disclose a one pot tandem Ag(I)-catalyzed *5-exo-dig* oxy/amino cyclization and catalyst free γ-azidative allylic hydroxyl displacement for azidomethyl benzofurans/indoles (Scheme 1D). Azides are undoubtedly highly useful groups that serve as ready precursors for various N-containing functional groups like amines, imines, triazoles, tetrazoles and amides within a single-step transformation.[3] Additionally, azides have also achieved a significant position in medicinal chemistry, bio-conjugation and material science.[4]

Scheme 1. Synthesis of allyl alcohols and their azidation.



Depending on the site of the requirement, there are different strategies reported to introduce azide group in to the molecule. For

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Electronic Supplementary Information (ESI) available: See
DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C6OB00191B

example, donating group assisted azidation on C (SP^2)-H,[5] decarboxylative azidation on C(SP^3)-H,[6] direct Mn or Fe catalysed azidation on tertiary C(SP^3)-H,[7] etc. in addition to the conventional nucleophilic substitution approaches on C(SP^3)-X where X is halide.[8] Preactivation of hydroxyl group to tosylates, triflates, esters and silyl ethers also allow the azidation through substitution.[9] Direct substitution of hydroxyl group,[10] especially in catalytic conditions[11] would offer a straightforward, practical and site selective synthesis of C(SP^3)-azides. To date, a very few attempts are made in this direction.[11]

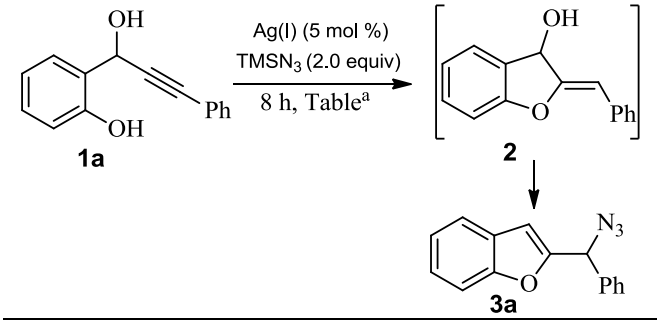
We herein report a catalyst free aromatization-driven γ-azidation of allylic alcohols prepared in situ from Ag(I)-catalyzed intramolecular oxy/amino- metallation of alkynes.[1k-l] This azidation at γ-position is in contrast to the silver catalysed α-azidative displacement reported by Rueping et al (Scheme 1C).[11a]

Results and Discussion

The optimization studies (Table 1) were initiated with the conversion of **1a**[1m] to **3a**. When a mixture of **1a**, 2 equiv of $TMSN_3$ and 5 mol % AgOAc in MeCN was stirred at rt, an unidentified mixture of products was obtained (entry 1). Addition of $TMSN_3$ after 2 h of the reaction (after cyclization) led to the isolation of the intermediate **2**[1m] (entry 2). Still, no intended product was detected. Raise of temperature to 80 °C did not bring any change in the course of the reaction (entry 3). No reaction took place in toluene at rt and the elevation of the temperature to 80 °C resulted in 40% of **2** (entries 4-5). Remarkably, switching of solvent to DMSO cleanly afforded the product in 80% yield at 80 °C (entry 6). Reaction at room temperature led only a slow conversion of the substrate to intermediate **2** (entry 7). However, no reaction was observed in the absence of the silver catalyst (entry 8). Pleasingly, change of catalyst to Ag_2CO_3 afforded the required product in increased yield of 86% (entry 10). Other Ag(I)-catalysts were found to be either ineffective or low productive (entries 11-15). Other metal catalysts like Pd(II) and Cu(II) could not promote the reaction (entries 16-17).

To get insight in to the reaction mechanism, we isolated the intermediate **2**[1m] and treated with $TMSN_3$ in DMSO at 80 °C in the absence of the Ag(I)-catalyst (Scheme 2). Surprisingly, the conversion to the product **3a** was very clean (90% yield), suggesting that the catalyst was required only for the initial cyclization, and the dehydroxylative γ-azidation was driven by aromatization. With this exciting result in hand, we explored the scope and limitation of this tandem cyclization/azidation reaction. A number of hydroxyphenyl propargyl alcohols were initially applied under the optimal reaction conditions as shown in Table 2. Similar to **1a**, alkyl substitutedsubstrates afforded the products cleanly with the yields ranging from 62% to 90%. Interestingly, the closer the methyl group to hydroxyl the higher was the yield, suggesting that the efficiency of the reaction was dependent on the nucleophility of the hydroxyl group. Halogen groups (Br and Cl) could survive the reaction comfortably and gave the corresponding products in 45-56% yields. Electron rich methoxy substrate **3h** participated very well in the reaction (58%) whereas its electron deficient counterpart **3i** was found to be completely reluctant to initial cyclization and led to only the isolation of the starting

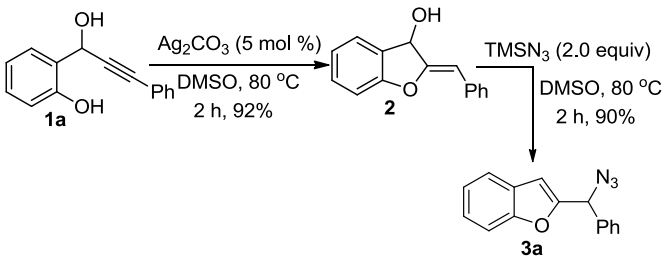
Table 1. Optimization studies



Entry	Catalyst	Solvent	temp	**2**[b]	**3a**[b]
1[c]	AgOAc	MeCN	rt	--[d]	--[d]
2	AgOAc	MeCN	rt	90%	--
3	AgOAc	MeCN	80 °C	93%	--
4	AgOAc	Toluene	rt	--[e]	--[e]
5	AgOAc	Toluene	80°C	40%	--
6	AgOAc	DMSO	80 °C	--	80%
7	AgOAc	DMSO	rt	30%	--
8	--	DMSO	80 °C	--[e]	--[e]
9	Ag_2CO_3	DMSO	rt	30%	--
10	**Ag_2CO_3**	**DMSO**	**80 °C**	**–**	**86%**
11	AgOTf	DMSO	80 °C	--	11%
12	AgF	DMSO	80 °C	--	40%
13	$AgSbF_6$	DMSO	80 °C	70%	--
14	$AgNO_3$	DMSO	80 °C	--	20%
15	$AgBF_4$	DMSO	80 °C	--	10%
16	$Pd(OAc)_2$	DMSO	80 °C	--	--
17	$Cu(OAc)_2$	DMSO	80 °C	--	--

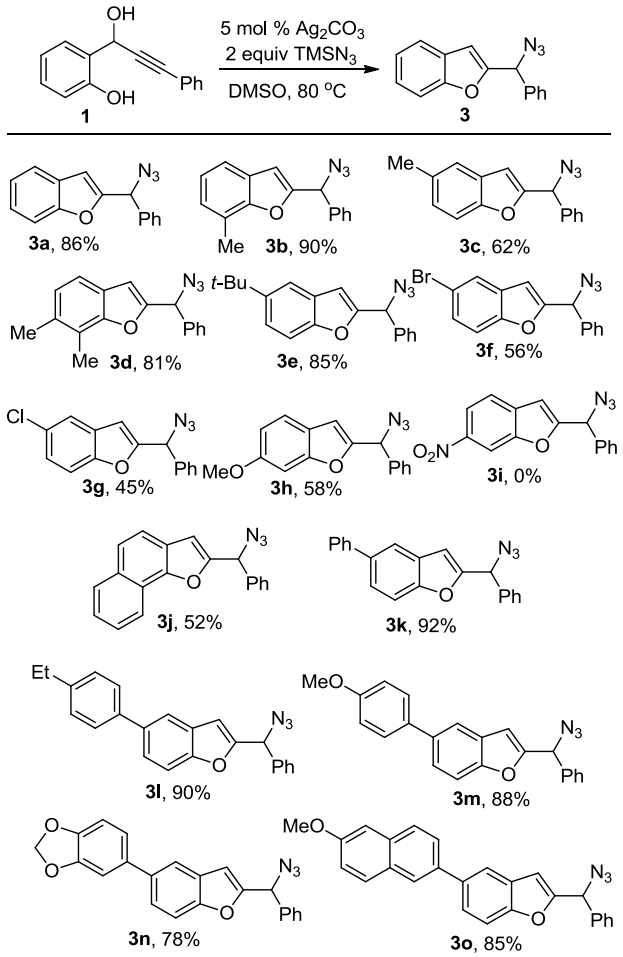
[a]Reaction conditions: a mixture of **1a** (1 mmol) and catalyst (0.05 equiv) in solvent (0.25 M) was stirred in open air at 80 °C and $TMSN_3$ (2.0 equiv) was added after 2 h. [b] Isolated yield. [c] $TMSN_3$ (2.0 equiv) was added at the beginning of the reaction. [d]A mixture of unidentified products. [e]Most of the starting material was recovered.

Scheme 2. Controlled experiment for the conversion of **1a** to **3a**



material. In fact, earlier reports on such cyclizations[1k-l] also did not include any nitro substituted substrates. Obviously, nucleophilic nature of phenoxyl group is substantially reduced by the highly electronegative nitro group and hence it cannot afford for nucleophilic attack required in cyclization. The substrates with embedded naphthalene ring moiety (**1j**) or with a pendant of electron-withdrawing and electron-donating containing phenyl ring on the aryl nucleus (**1k-o**) were found to proceed well, furnishing **3k-o** in 52-92% yields.

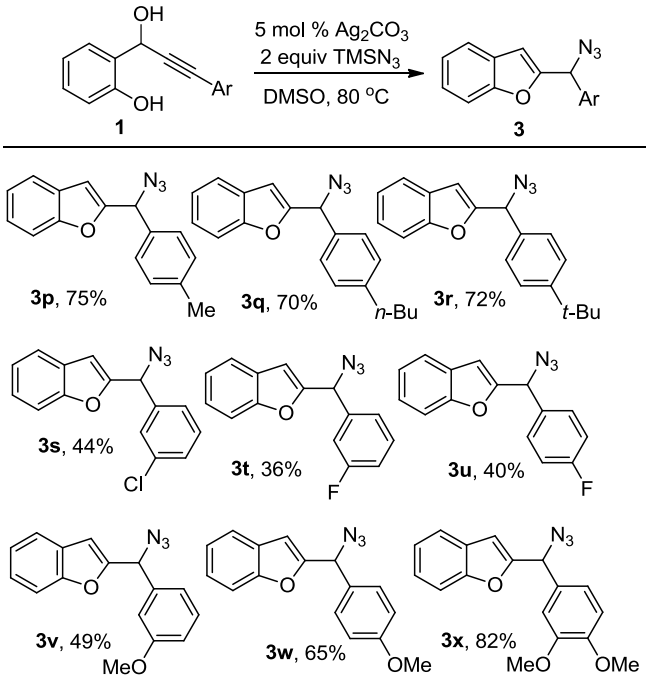
Table 2. Evaluation of substrate scope in tandem cyclization/azidation.



Reaction conditions: **1** (1.0 mmol), Ag_2CO_3 (0.05 mmol), DMSO (0.25 M), 80 °C, 2 h then $TMSN_3$ (2 mmol) 80 °C 6 h

Proceeding further, we tested the substrates with substitution variation on alkyne terminal of **1** (Table 3). Substrates with methyl-, *n*-butyl- and *t*-butyl-phenyl groups on alkyne (**1p-r**) participated well in the reaction to give corresponding products (**3p-r**) in excellent yields (70-75%). Halo substituents were found to slightly discourage the reaction to produce the corresponding products **3s-u** in moderate 36-44% yields. Next, position and number of methoxy groups on phenyl group were found to show clear influence on the outcome of the reaction, demonstrating that the electronic nature of the alkyne group is a crucial factor for the reaction. Thus **1v** with meta-methoxyphenyl group led to the product (**3v**) in moderate yield of 49% whereas para-methoxy- and dimethoxy phenyl compounds showed good to excellent reactivities (**3w** and **3x**, 65% and 82% respectively). Setting a limitation, the reaction worked for arylacetylene substrates only. The aliphatic alkyne based substrates simply gave cyclized intermediates **2** which further did not react with $TMSN_3$ even after the prolonged reaction times. This indicates that the extended conjugation from aryl groups facilitate the azidation at γ-position while assisting the olefinic bond isomerization (migration) to allylic position. We next aimed at the

Table 3. Substrate scope with respect to substitution on alkyne terminus.



Reaction conditions: **1** (1.0 mmol), Ag_2CO_3 (0.05 mmol), DMSO (0.25 M), 80 °C, 2 h then $TMSN_3$ (2 mmol) 80 °C 6 h

application of this tandem cyclization/γ-azidation to indole derivatives from readily available aminophenyl propargyl alcohols (Table 4).[1l] Initially, 2-amino acetophenone based propargyl alcohols were tested under the standard conditions. Pleasingly, unsubstituted- and, methyl-, butyl- and methoxy-phenyl acetylenic substrates **4a-d** underwent the reaction cleanly to afford the targeted adducts **5a-d** in 68-78% yields. Propiophenone based substrates reacted well under the standard conditions, but furnishd the corresponding adducts (**5e-f**) in moderate yields of 45-52%. Next, benzophenone derived materials were subjected to the title transformation to obtain diaryl adducts **5g-j** successfully in 45-75% yields. Halogen (Br and Cl) containing substrates showed poor reactivity and thus produced the corresponding products (**5k-l**) in moderate yields (36-40%). X-ray crystallographic analysis of **5b** unambiguously established its structure.[12]

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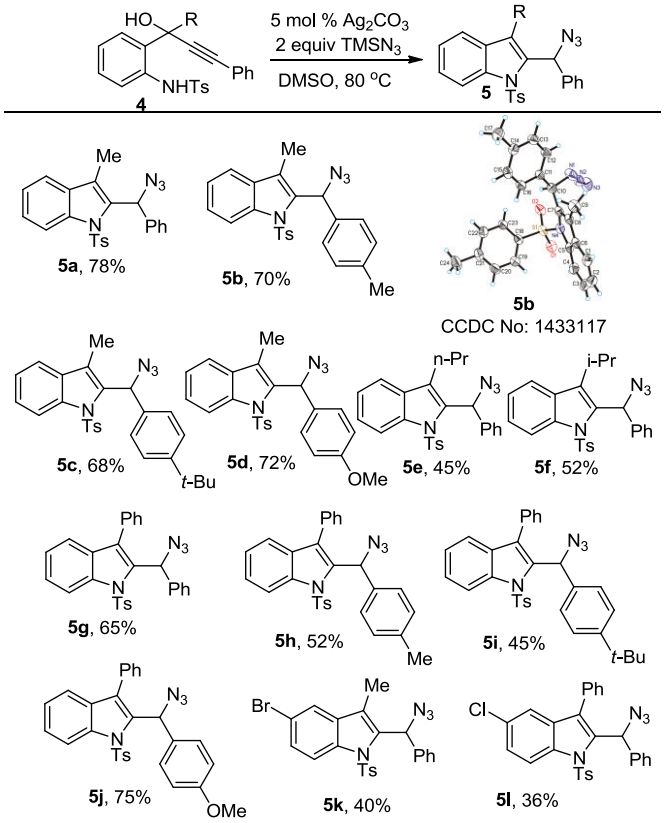
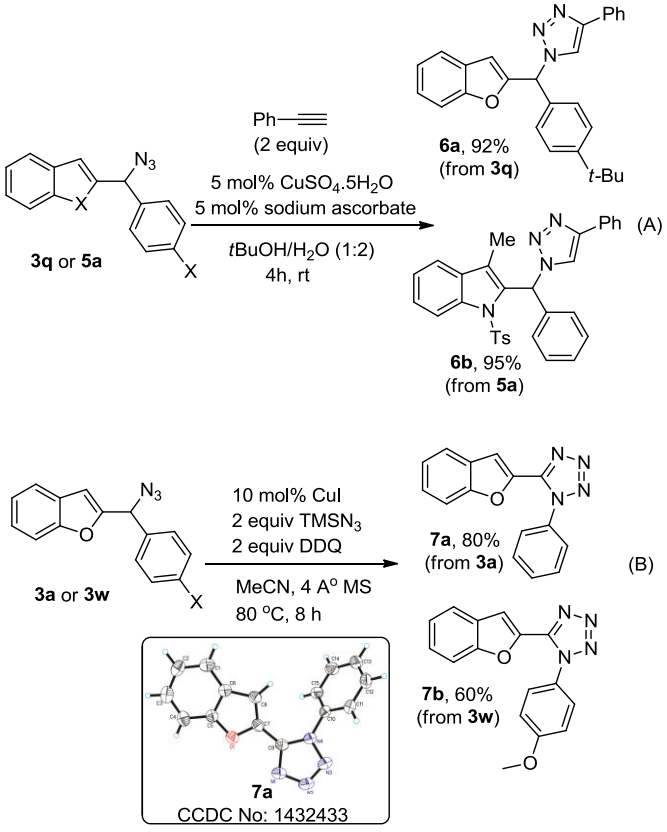
Table 4. Conversion of aminophenyl propargyl alcohols **4** to azidomethyl indoles **5**.



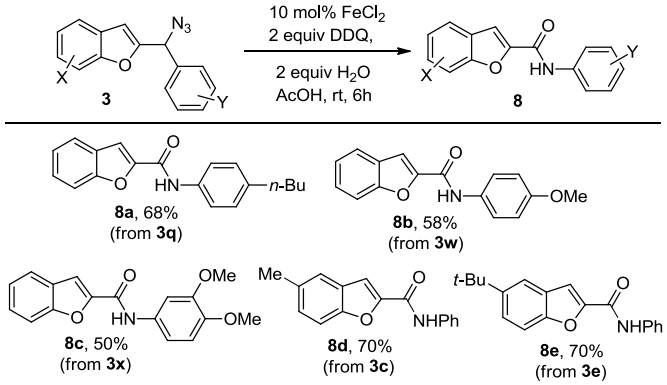
Reaction conditions: **4** (1.0 mmol), Ag_2CO_3 (0.05 mmol), DMSO (0.25 M), 80 °C, 2 h then $TMSN_3$ (2 mmol) 80 °C 6 h

Further, the synthetic utility of the above 2-azidomethyl benzoheteroles obtained via tandem cyclization/azidation reaction was examined. A substrate from each category was subjected to triazolation (click reaction) with phenyl acetylene to obtain **6a-b** in 92-95% yields (Scheme 3A). An oxidative cleavage for tetrazole formation using Jiao's conditions[13] surprisingly led to selective formation of regioisomers **7a-b**[12] *via* preferential migration of phenyl group over benzofuranyl group (Scheme 3B). Using this information, we immediately verified the fate of similar oxidative cleavage[14] for amide formation (Scheme 4). Pleasingly, when treated **3q** with 10 mol% $FeCl_2$ and equiv DDQ in aqueous acetic acid furnished a single regioisomer **8a** in 68% yield along with 12% of the ketone (2- benzoylfuran) via mere oxidation. Considering the significance of benzofuranamides in medicinal chemistry,[15] we examined the reaction for its generality. Similar to the phenyl migration in **3q** for **8a** synthesis, methoxy- and dimethoxy phenyl groups also migrated selectively as with the synthesis of **8b-c** in 50-58% yields. The reaction was smoother also with alkyl substitution on the benzofuran nucleus. Thus, **8d-e** were obtained in 70% yields.

Scheme 3. Synthesis of triazoles **6** and tetrazoles **7** from azidomethyl benzoheteroles.

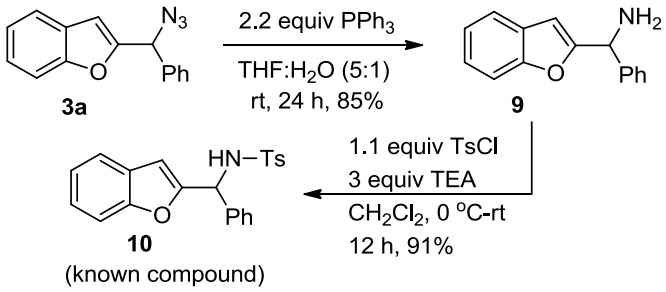


Scheme 4. Regioselective oxidative cleavage of **3** to **8**.



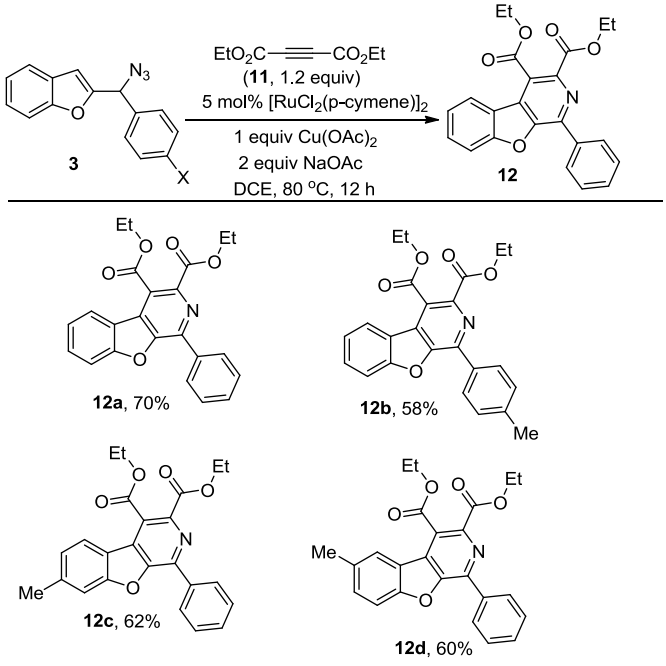
Afterward, continuing the various possible derivatizations of the adducts, azide group in **3a** was reduced to obtain corresponding amine **9** in 85% yield using 2.2 equiv PPh_3 in aqueous THF (Scheme 5). It was then tosylated to obtain known compound **10**[16] to unambiguously establish the structure of **3a**, as none of the compound in this category was reported in the literature.

Scheme 5. Structure establishement of **3a** via conversion to known compound **10**.



Finally, we attempted an oxidative [4+2] cycloaddition with alkyne diester **11** to obtain benzofuropyridine nucleus **12** (Scheme 6). The thought was aroused based on the knowledge that azides get oxidized to imines,[17] which in facilitating appropriate reaction conditions might undergo an in situ Diels-Alder reaction with asuitable dienophile. With the higher electron density, olefin group in benzofuran should join imine to form diene unit over the one in phenyl group. As expected, the reaction of **3a** with **11** with 5 mol% $[RuCl_2(p\text{-cymene})]_2$, 1 equiv $Cu(OAc)_2$ and 2 equiv of NaOAc in DCE at 80 °C cleanly furnished the cyclized adduct **12a** in 70% yield. Three more similar adducts were synthesized with methyl substitution either on core nucleus or the pendant phenyl ring.

Scheme 6. Oxidative [4+2] addition of **3** with alkyne diesters for benzofurano pyridines **11**.



In summary, an efficient synthetic route to 2-azidomethyl benzoheteroles based on tandem Ag(I)-catalyzed intramolecular cyclization and aromatization driven γ-azidation from readily available linear propargyl alcohols is reported. While it did not require exclusion of air or moisture, the reaction was applicable over a wide range of substrates. The synthetic utility of the reaction was demonstrated by the conversion of azidomethyl unit to various other useful functionalities via reduction, oxidation and cyclization reactions.

Experimental Section

General Information: All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 400 MHz spectrometer for ^{1}H NMR, 100 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), triplet (t), quartet (q), multiplet (m). HRMS were recorded by using QTof mass spectrometer. Starting materials was prepared by literature procedure.[18] 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.

2.1. General Procedure for the Synthesis of 3 from 1 Using the Synthesis of 3a as an Example:

To a stirred solution of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl) phenol **1a** (112 mg, 0.5 mmol) in 2 mL of DMSO was added Ag_2CO_3 (6.8 mg, 0.025 mmol) and heated to 80 °C for 2h, Then added $TMSN_3$ (115 mg, 1 mmol) at the same temperature and stirred for 6h. The reaction mixture was cooled to rt then diluted with water (10 ml) and extracted with EtOAc (2x10 ml). The combined extracts were washed with brine (15 mL) and dried over Na_2SO_4. After removal of the solvent under reduced pressure crude material was purified by column chromatography (silica gel, using 2-5% EtoAc in hexanes) to get pure product **3a** (106 mg, 86%) as yellow oil.

2-(azido(phenyl)methyl)benzofuran (3a): 86% yield (106 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 1H); 7.47-7.38 (m, 6H); 7.31-7.26 (m, 1H); 7.24-7.20 (m, 1H); 6.60 (s, 1H); 5.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 155.0, 136.4, 129.0, 129.0, 127.8, 127.7, 124.8, 123.1, 121.4, 111.5, 105.6, 62.7; IR ν (cm^{-1}) 3393, 1637, 1069, 669; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{12}NO[M + H - N_2]^+$ 222.0919, found 222.0911.

2-(azido(phenyl)methyl)-7-methylbenzofuran (3b): 90% yield (118 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.38 (m, 6H); 7.16 (t, *J* = 7.3 Hz, 1H); 7.16 (d, *J* = 7.3 Hz, 1H); 6.58 (s, 1H); 5.82 (s, 1H); 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 154.5, 136.5, 128.9, 128.8, 127.7, 127.2,125.7, 123.2, 121.7, 118.7, 105.9, 62.6, 15.1; IR ν (cm^{-1}) 3400, 2101, 1644, 1069, 668; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO[M + H - N_2]^+$ 236.1075, found 236.1068.

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DOI: 10.1039/C6OB00191B

2-(azido(phenyl)methyl)-5-methylbenzofuran (3c): 62% yield (81 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (m, 6H); 7.27 (d, *J* = 0.6 Hz, 1H); 7.06-7.04 (m, 1H);6.54 (t, *J* = 0.8 Hz, 1H); 5.76 (s, 1H); 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 153.8, 136.4, 132.6, 128.9, 128.9, 127.9, 127.7, 126.0, 121.1, 111.0, 105.4, 62.7, 21.4; IR ν (cm^{-1}) 3423, 2101, 1639, 1070, 668; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO[M + H - N_2]^+$ 236.1075, found236.1068.

2-(azido(phenyl)methyl)-6,7-dimethylbenzofuran (3d): 81% yield (112 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.42 (m, 5H); 7.28 (d, *J* = 7.8 Hz, 2H); 7.07 (d, *J* = 7.8 Hz, 2H); 6.53 (s, 1H); 5.80 (s, 1H); 2.45 (s, 3H); 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 154.2, 136.6, 133.2, 128.8, 128.8, 127.7, 125.2, 125.1, 120.0, 117.8, 105.9, 62.7, 19.2, 11.8; IR ν (cm^{-1}) 3399, 2101, 1642, 1070, 669; HRMS (ESI-TOF) calcd for $C_{17}H_{16}NO[M + H - N_2]^+$ 250.1232, found 250.1231.

2-(azido(phenyl)methyl)-5-(tert-butyl)benzofuran (3e): 85% yield (129 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$)δ: 7.55 (s, 1H); 7.45-7.36 (m, 7H); 6.60 (s, 1H); 5.78 (s, 1H); 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 153.6, 146.3, 136.5, 128.9, 128.9, 127.7, 127.5, 122.8, 117.5, 110.8, 105.8, 62.7, 34.8, 31.9; IR ν (cm^{-1}) 3400, 3019, 1638, 1069, 669; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO[M + H - N_2]^+$ 278.1545, found 278.1537.

2-(azido(phenyl)methyl)-5-bromobenzofuran (3f): 56% yield (91 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 1.9 Hz, 1H); 7.44-7.30 (m, 7H); 6.55 (s, 1H); 5.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.4 154.1, 136.0, 129.8, 129.1, 129.1, 127.7, 127.7, 124.0, 116.2, 113.0, 105.0, 62.6; IR ν (cm^{-1}) 3400, 2103, 1644, 1069, 669; HRMS (ESI-TOF) calcd for $C_{15}H_{11}BrNO[M + H - N_2]^+$ 300.0024, found 300.0019.

2-(azido(phenyl)methyl)-5-chlorobenzofuran (3g): 45% yield (63 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz) δ: 7.50 (d, *J* = 2.0 Hz, 1H); 7.44-7.36 (m, 6H); 7.24 (dd, *J* = 8.6, 2.0 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, 129.1, 128.8, 127.7, 125.0, 120.9, 112.5, 105.1, 62.6; IR ν (cm^{-1}) 3400, 2103, 1644, 1068, 669; HRMS (ESI-TOF) calcd for $C_{15}H_{11}ClNO[M + H - N_2]^+$ 256.0529, found 256.0513.

2-(azido(phenyl)methyl)-6-methoxybenzofuran (3h): 58% yield (81 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz) δ: 7.48-7.40 (m, 6H); 7.03 (d, *J* = 2.0 Hz, 1H); 6.90 (dd, *J* = 8.5, 2.2 Hz, 1H); 6.54 (s, 1H); 5.77 (s, 1H); 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 156.4, 153.8, 136.5, 128.9, 128.8, 127.6, 121.4, 120.9, 112.3, 105.6, 96.0, 62.7, 55.7; IR ν (cm^{-1}) 3399, 2101, 1624, 1069, 669; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_2$ $[M + H - N_2]^+$ 252.1025, found 252.1017.

2-(azido(phenyl)methyl)naphtho[1,2-b]furan (3j): 52% yield (78mg); yellow semi solid; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.0 Hz, 1H); 7.93 (d, *J* = 8.0 Hz, 1H); 7.73 (d, *J* = 8.9 Hz, 1H); 7.62 (d, *J* = 8.9 Hz, 1H); 7.59-7.55 (m, 1H); 7.50-7.41 (m, 6H); 7.67 (s, 1H); 5.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 153.0, 136.5, 131.8, 130.4, 129.0, 129.0, 128.9, 127.7, 126.5, 125.8, 124.8, 123.4, 123.0, 112.4, 104.8, 62.8; IR ν (cm^{-1}) 3400, 2102, 1638, 1069, 669; HRMS (ESI-TOF) calcd for $C_{19}H_{14}NO[M + H - N_2]^+$ 272.1075, found 272.1065.

2-(azido(phenyl)methyl)-5-phenylbenzofuran (3k): 92% yield (149 mg); yellow solid; mp 85-87 ^{o}C; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (t, *J* = 1.1 Hz, 1H); 7.62-7.59 (m, 2H); 7.52 (d, *J* = 1.1 Hz, 2H); 7.48-7.41 (m, 7H); 7.36 (s, 1H); 6.66 (s, 1H); 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 155.0, 141.6, 136.9, 136.3, 129.0, 128.9, 128.3, 127.7, 127.5, 127.1, 124.5, 119.8, 111.6, 105.8, 62.7; IR ν (cm^{-1}) 3399, 2102, 1601, 1070, 669; HRMS (ESI-TOF) calcd for $C_{21}H_{16}NO[M +H - N_2]^+$ 298.1232, found 298.1231.

2-(azido(phenyl)methyl)-5-(4-ethylphenyl)benzofuran (3l): 90% yield (158 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73-7.72 (m, 1H); 7.55-751 (m, 4H); 7.47-7.40 (m, 5H); 7.30 (d, *J* = 8.3 Hz, 2H); 6.66 (s, 1H); 5.81 (s, 1H); 2.72 (q, *J* = 7.5 Hz, 2H); 1.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.5, 154.9, 143.2, 138.9, 136.9, 136.3, 129.0, 128.4, 128.3, 127.7, 127.4, 124.4, 119.6, 111.6, 105.8, 62.7, 28.6, 15.7; IR ν (cm^{-1}) 3400, 2102, 1638, 1069, 669; HRMS (ESI-TOF) calcd for $C_{23}H_{20}NO[M + H - N_2]^+$ 326.1545, found 326.1543.

2-(azido(phenyl)methyl)-5-(4-methoxyphenyl)benzofuran (3m):88% yield (156 mg); white solid; mp 78-80 ^{o}C; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (t, *J* = 0.9 Hz, 1H); 7.54 (d, *J* = 8.8 Hz, 2H); 7.49-7.41 (m, 7H); 7.00 (d, *J* = 8.8 Hz, 2H); 6.65 (s, 1H); 5.80 (s, 1H); 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 155.5, 154.7, 136.6, 136.3, 134.1, 129.0, 128.5, 128.3, 127.7, 124.2, 119.3, 114.3, 111.5, 105.8, 62.7, 55.4; IR (neat) ν 3400, 2102, 1639, 1069, 669; HRMS (ESI-TOF) calcd for $C_{22}H_{18}NO_2$ $[M + H - N_2]^+$ 328.1338, found 328.1333.

5-(2-(azido(phenyl)methyl)benzofuran-5-yl)benzo[d][1,3]dioxole (3n): 78% yield (143 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$)δ: 7.63 (d, *J* = 1.3 Hz, 1H); 7.48-7.39 (m, 7H); 7.07-7.03 (m, 2H); 6.89-6.87 (d, *J* = 7.9 Hz, 1H); 6.66 (S, 1H); 6.00 (s, 2H); 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 154.8, 148.2, 146.9, 136.7, 136.3, 136.0, 129.0, 128.3, 127.7, 124.3, 120.9, 119.5, 111.6, 108.6, 108.1, 105.7, 101.2, 62.7, 29.8; IR ν (cm^{-1}) 3399, 2102, 1638, 1069, 669; HRMS (ESI-TOF) calcd for $C_{22}H_{16}NO_3[M + H - N_2]^+$ 342.1130, found 342.1128

2-(azido(phenyl)methyl)-5-(6-methoxynaphthalen-2-yl)benzofuran (3o): 85% yield (172 mg); white solid; mp 87-89 ^{o}C; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 1.4

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DOI: 10.1039/C6OB00191B

Hz, 1H); 7.82-7.78 (m, 3H); 7.71 (dd, *J* = 8.5, 1.6 Hz, 1H); 7.62 (dd, *J* = 8.6, 1.8 Hz, 1H); 7.53 (d, *J* = 8.5 Hz, 1H); 7.48-7.40 (m, 5H); 7.20-7.17 (m, 2H); 6.67 (s, 1H); 5.81 (s, 1H); 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 155.6, 154.9, 136.9, 136.7, 136.3, 133.7, 129.7, 129.3, 129.0, 128.4, 127.7, 127.4, 126.5, 125.9, 124.6, 119.9, 119.3, 111.7, 105.8, 105.7, 62.7, 55.4; IR ν (cm^{-1}) 3399, 2102, 1632, 1069, 669; HRMS (ESI-TOF) calcd for $C_{26}H_{20}NO_2$ [M +H - N_2]$^+$ 378.1495, found 378.1489.

2-(azido(p-tolyl)methyl)benzofuran (3p): 75% yield (98 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 1H); 7.46 (dd, *J* = 8.0, 0.6 Hz, 1H); 7.33 (d, *J* = 8.1 Hz, 2H); 7.31-7.27 (m, 2H); 7.25-7.21 (m, 3H); 6.61 (t, *J* = 0.8 Hz, 1H); 5.75 (s, 1H); 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 155.2, 138.9, 133.3, 129.6, 127.8, 127.7, 124.7, 123.1, 121.3, 111.5, 105.4, 62.6, 21.3; IR ν (cm^{-1}) 3399, 2092, 1645, 1069, 747; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO$[M + H - N_2]$^+$ 236.1075, found 236.1068.

2-(azido(4-butylphenyl)methyl)benzofuran (3q): 70% yield (106 mg); yellow oil; R_f = 0.70 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.56 (m, 1H); 7.50 (d, *J* = 7.9 Hz, 1H); 7.38 (d, *J* = 8.1 Hz, 2H); 7.34-7.24 (m, 4H); 6.64 (s, 1H); 5.78 (s, 1H); 2.67 (t, *J* = 7.6 Hz, 2H); 1.69-1.62 (m, 2H); 1.46-1.37 (m, 2H); 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 155.2, 143.8, 133.5, 129.0, 127.8, 127.6, 124.7, 123.1, 121.3, 111.5, 105.4, 62.6, 35.4, 33.5, 22.4, 14.0; IR ν (cm^{-1}) 3399, 2101, 1638, 1069, 668 ; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO$[M + H - N_2]$^+$ 278.1545, found 278.1537.

2-(azido(4-(tert-butyl)phenyl)methyl)benzofuran (3r): Yield 72 % (109 mg);yellow gum; R_f = 0.70 (SiO_2, 10% 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 ν (cm^{-1}) 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-chlorophenyl)methyl)benzofuran (3s): 44% yield (62 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.55 (m, 1H); 7.48-7.45 (m, 2H); 7.38-7.29 (m, 4H); 7.26-7.24 (m, 1H); 6.64 (s, 1H); 5.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4, 154.1, 138.4, 134.9, 130.2, 129.1, 127.8, 127.6, 125.8, 125.0, 123.3, 121.5, 111.6, 105.9, 62.0; IR ν (cm^{-1}) 3400, 2103, 1644, 1069, 668; HRMS (ESI-TOF) calcd for $C_{15}H_{11}ClNO$[M + H - N_2]$^+$ 256.0529, found 256.0513.

2-(azido(3-fluorophenyl)methyl)benzofuran (3t): 36% yield (48 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.57 (m, 1H); 7.50 (dd, *J* = 8.0, 0.6 Hz, 1H); 7.42-7.37 (m, 1H); 7.35-7.31 (m, 1H); 7.29-7.20 (m, 3H); 7.13-7.08 (m, 1H); 6.66 (s, 1H); 5.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.8 (d, *J* = 247 Hz), 155.4, 154.2, 138.8 (d, *J* = 7 Hz), 130.5 (d, *J* = 8 Hz), 127.6, 125.0, 123.3, 123.2, 121.4, 115.9 (d, *J* = 21 Hz), 114.7 (d, *J* = 22 Hz), 111.5, 105.8, 62.0; IR ν (cm^{-1}) 3399, 2013, 1644, 1069, 669; HRMS (ESI-TOF) calcd for $C_{15}H_{11}FNO$[M + H - N_2]$^+$ 240.0825, found 240.0825.

2-(azido(4-fluorophenyl)methyl)benzofuran (3u): 40% yield (53 mg); yellow oil; R_f = 0.80 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 7.5, 0.6 Hz, 1H); 7.45-7.37 (m, 3H); 7.29-7.25 (m, 1H); 7.23-7.19 (m, 1H); 7.11-7.05 (m, 2H); 6.59 (s, 1H); 5.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.0 (d, *J* = 248 Hz), 155.4, 154.6, 132.2, 129.5 (d, *J* = 8 Hz), 127.7, 124.9, 123.2, 121.4, 116.0, 115.8 (d, *J* = 21 Hz), 105.6, 62.0; IR ν (cm^{-1}) 3399, 1643, 1069, 669; HRMS (ESI-TOF) calcd for $C_{15}H_{11}FNO$[M + H - N_2]$^+$ 240.0825, found 240.0825.

2-(azido(3-methoxyphenyl)methyl)benzofuran (3v): 49% yield (67 mg); yellow oil; R_f = 0.60 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.2 Hz, 1H); 7.45 (dd, *J* = 8.1, 0.5 Hz, 1H); 7.33 (t, *J* = 8.0 Hz, 1H); 7.30-7.26 (m, 1H); 7.23-7.20 (m, 1H); 7.01 (d, *J* = 7.6 Hz, 1H); 6.99 (t, *J* = 2.1 Hz, 1H); 6.93-6.91 (m, 1H); 6.61 (s, 1H); 5.75 (s, 1H); 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 155.4, 154.8, 137.8, 130.0, 127.8, 124.8, 123.1, 121.4, 120.0, 114.4, 113.4, 111.5, 105.6, 62.6, 55.4; IR ν (cm^{-1}) 3399, 3019, 1601, 1069, 669; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_2$ [M + H - N_2]$^+$ 252.1025, found252.1017.

2-(azido(4-methoxyphenyl)methyl)benzofuran (3w): 65% yield (90 mg); yellow oil; R_f = 0.60 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.52 (m, 1H); 7.45 (dd, *J* = 7.9, 0.6, 1H); 7.38-7.34 (m, 2H); 7.30-7.20 (m, 2H); 6.96-6.92 (m, 2H); 6.66 (s, 1H); 5.73 (s, 1H); 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 155.4, 155.3, 129.1, 128.4, 127.8, 124.7, 123.1, 121.3, 114.4, 111.5, 105.4, 62.3, 55.4; IR ν (cm^{-1}) 3400, 1639, 1329, 1068, 669; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_2$ [M + H - N_2]$^+$ 252.1025, found 252.1017.

2-(azido(3,4-dimethoxyphenyl)methyl)benzofuran (3x): 82% yield (127 mg); yellow oil; R_f = 0.40 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 1H); 7.46 (dd, *J* = 8.0, 0.5 Hz, 1H); 7.31-7.21 (m, 2H); 7.00-6.96 (m, 2H); 6.88 (d, *J* = 8.1 Hz, 1H); 6.62 (s, 1H); 5.74 (s, 1H); 3.89 (s, 3H); 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 155.1, 149.5, 149.4, 128.7, 127.7, 124.7, 123.1, 121.3, 120.3, 111.4, 111.1, 110.6, 105.3, 62.5, 56.0, 56.0; IR ν (cm^{-1}) 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)-3-methyl-1-tosyl-1H-indole (5a): 78% yield (162 mg); white solid; mp 136-138 °C; R_f = 0.70 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 7.9 Hz, 1H); 7.52 (d, *J* = 7.2 Hz, 2H); 7.46-7.37 (m, 3H); 7.32-7.27 (m, 5H); 7.13 (d, *J* = 7.2 Hz, 2H); 6.99 (s, 1H); 2.32 (s, 3H); 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 138.0, 136.7, 135.9, 133.0 , 131.2, 129.9, 128.6, 127.8, 127.0, 126.5, 125.7, 123.8, 121.4, 119.2, 115.6, 60.1, 21.6, 9.8; IR ν (cm^{-1}) 3399, 1643, 1068, 768; HRMS (ESI-TOF) calcd for $C_{23}H_{21}N_2O_2S$ [M + H - N_2]$^+$ 389.1324, found 389.1320.

2-(azido(p-tolyl)methyl)-3-methyl-1-tosyl-1H-indole (5b): 70% yield (150 mg); white solid; mp 116-118 °C; R_f = 0.70 (SiO_2, 10%

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DOI: 10.1039/C6OB00191B

EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.3 Hz, 1H); 7.54-7.52 (m, 2H); 7.49-7.47 (m, 1H); 7.41-7.39 (m, 1H);7.34-7.28 (m, 2H); 7.15-7.13 (m, 6H); 6.96 (s, 1H); 2.36 (s, 3H); 2.34 (s, 3H); 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 137.5, 136.6, 135.8, 134.9, 133.0, 131.2, 129.8, 129.2, 126.9, 126.4, 125.5, 123.7, 121.1, 119.1, 115.5, 60.0, 21.5, 21.1, 9.8; IR ν (cm^{-1}) 3399, 2099, 1638, 1069, 668; HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_2S$ $[M + H - N_2]^+$ 403.1480, found 403.1468.

2-(azido(4-(tert-butyl)phenyl)methyl)-3-methyl-1-tosyl-1H-indole (5c): 68% yield (160 mg); yellow gum; R_f = 0.70 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.4 Hz, 1H); 7.48-7.45 (m, 3H); 7.40-7.36 (m, 1H); 7.32-7.28 (m, 3H); 7.19 (d, *J* = 7.8 Hz, 2H); 7.08 (d, *J* = 8.3 Hz, 2H); 6.96 (s, 1H); 2.31 (s, 3H); 2.12 (s, 3H); 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.9, 144.9, 136.7, 135.9, 134.9, 133.1, 131.3, 129.8, 126.8, 126.5, 125.6, 125.5, 123.8, 121.2, 119.1, 115.6, 60.1, 34.6, 31.4, 21.6, 9.8; IR ν (cm^{-1}) 3399, 2100, 1639, 1069, 669; HRMS (ESI-TOF) calcd for $C_{27}H_{29}N_2O_2S$ $[M + H - N_2]^+$ 445.1950, found 445.1948.

2-(azido(4-methoxyphenyl)methyl)-3-methyl-1-tosyl-1H-indole (5d): 72% yield (160 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 8.3 Hz, 1H);7.48-7.46 (m, 3H); 7.37-7.36 (m, 1H); 7.31-7.29 (m, 1H); 7.16 (d, *J* = 8.5 Hz, 2H); 7.09 (d, *J* = 8.0 Hz, 2H); 6.91 (s, 1H); 6.82-6.80 (m, 2H); 3.79 (s, 3H); 2.31 (s, 3H); 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 145.0, 136.7, 135.9, 133.2, 131.3, 130.0, 129.9, 128.4, 126.5, 125.6, 123.8, 121.1, 119.1,115.6, 114.0, 60.0, 55.4, 21.6, 9.9; IR ν (cm^{-1}) 3399, 2099, 1609, 1089, 667; HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_3S$ $[M + H - N_2]^+$ 419.1429, found 419.1428.

2-(azido(phenyl)methyl)-3-propyl-1-tosyl-1H-indole (5e): 45% yield (100 mg); white solid; mp 82-84 °C; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.4 Hz, 2H); 7.58-7.55 (m, 1H); 7.40-7.35 (m, 1H); 7.29-7.25 (m, 7H); 7.15 (d, *J* = 7.9 Hz, 2H); 7.00 (s, 1H); 2.50-2.37 (m, 2H); 2.33 (s, 3H); 1.48-1.39 (m, 1H); 1.19-1.10 (m, 1H); 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 138.5, 137.0, 136.1, 132.9, 130.6, 129.9, 128.5, 127.7, 126.7, 126.5, 126.2, 125.5, 123.7, 119.7, 115.7, 59.9, 27.0, 22.7, 21.5, 14.4; IR ν (cm^{-1}) 3400, 2101, 1638, 1069, 668; HRMS (ESI-TOF) calcd for $C_{25}H_{25}N_2O_2S$ $[M + H - N_2]^+$ 417.1637, found 417.1629.

2-(azido(p-tolyl)methyl)-3-isopropyl-1-tosyl-1H-indole (5f): 52% yield (115 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.5 Hz, 1H); 7.69 (d, *J* = 7.7 Hz, 1H); 7.63-7.61 (m, 2H); 7.40-7.36 (m, 1H); 7.28-7.23 (m, 4H); 7.22-7.16 (m, 4H); 7.07 (s, 1H); 3.12-3.01 (m, 1H); 2.35 (s, 3H); 1.32 (d, *J* = 7.0 Hz, 3H); 0.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 138.7, 137.7, 136.2, 132.1, 130.9, 130.0, 128.6, 128.3, 127.5, 126.6, 126.4, 125.1, 123.2, 121.7, 115.9, 59.3, 26.3, 22.2, 21.6, 20.3; IR ν (cm^{-1}) 3400, 2100, 1597, 1069, 669; HRMS (ESI-TOF) calcd for $C_{25}H_{25}N_2O_2S$ $[M + H - N_2]^+$ 417.1637, found 417.1629.

2-(azido(phenyl)methyl)-3-phenyl-1-tosyl-1H-indole (5g): 65% yield (155 mg); white solid; mp 140-142 °C; R_f = 0.70 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.5 Hz, 1H); 7.68 (d, *J* = 8.3 Hz, 2H); 7.42-7.38 (m, 1H); 7.26-7.19 (m, 7H); 7.12-7.08 (m, 5H); 7.05-7.03 (m, 2H); 6.82 (s, 1H); 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 138.0, 136.4, 136.0, 133.5, 132.0, 130.6, 130.1, 129.9, 128.0, 127.9, 127.6, 127.5, 127.2, 126.6, 126.5, 125.9, 123.9, 120.4, 115.2, 60.2, 21.6; IR ν (cm^{-1}) 3399, 2100, 1637, 1069, 669; HRMS (ESI-TOF) calcd for $C_{28}H_{23}N_2O_2S$ $[M + H - N_2]^+$ 451.1480, found 451.1471.

2-(azido(p-tolyl)methyl)-3-phenyl-1-tosyl-1H-indole (5h): 52% yield (127 mg); white solid; mp 130-132 °C; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 8.5 Hz, 1H); 7.65 (d, *J* = 7.6 Hz, 2H); 7.42-7.38 (m, 1H); 7.28-7.25 (m, 3H); 7.23-7.21 (m, 2H); 7.18 (d, *J* = 8.0 Hz, 2H); 7.13-7.02 (m, 2H); 6.96-6.91 (m, 4H); 6.75 (s, 1H); 2.36 (s, 3H); 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 137.1, 136.6, 136.1, 135.1, 133.7, 132.3, 130.8, 130.2, 129.9, 128.8, 128.1, 127.7, 127.4, 126.7, 125.9, 124.0, 120.5, 115.3, 60.4, 21.7, 21.1; IR ν (cm^{-1}) 3399, 1642, 1068, 669; HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_2S$ $[M + H - N_2]^+$ 465.1637, found 465.1627.

2-(azido(4-(tert-butyl)phenyl)methyl)-3-phenyl-1-tosyl-1H-indole (5i): 45% yield (120 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.5 Hz, 1H); 7.67 (d, *J* = 8.2 Hz, 2H); 7.41-7.37 (m, 1H); 7.23-7.19 (m, 8H); 7.10-7.08 (m, 4H); 6.94 (d, *J* = 8.2 Hz, 2H); 6.81 (s, 1H); 2.36 (s, 3H); 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 145.1, 136.5, 136.1, 135.0, 134.0, 132.2, 130.9, 130.2, 129.9, 128.0, 127.6, 127.5, 126.7, 126.5, 125.9, 124.9, 124.0, 120.5, 115.3, 60.3, 34.5, 31.4, 21.7; IR ν (cm^{-1}) 3400, 2101, 1638, 1069, 668; HRMS (ESI-TOF) calcd for $C_{32}H_{30}NO_2S$ $[M - N_3]^+$ 492.1997, found 492.1998.

2-(azido(4-methoxyphenyl)methyl)-3-phenyl-1-tosyl-1H-indole (5j): 75% yield (190 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 8.4 Hz, 1H); 7.65 (d, *J* = 8.4 Hz, 2H); 7.42-7.37 (m, 1H); 7.29-7.27 (m, 3H); 7.23-7.18 (m,4H); 7.12 (d, *J* =3.6 Hz, 2H); 6.98 (d, *J* = 8.3 Hz, 2H); 6.76 (s, 1H); 6.65 (d, *J* = 8.8 Hz, 2H); 3.74 (s, 3H); 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 145.1, 136.5, 136.2, 133.9, 132.3, 130.9, 130.2, 129.9, 128.1, 127.7, 127.3, 126.7, 125.9, 124.0, 120.5, 115.3, 113.5, 60.2, 55.4, 21.7; IR ν (cm^{-1}) 3399, 3019, 2100, 1637, 1069, 668; HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_3S$ $[M + H - N_2]^+$ 481.1586, found 481.1574.

2-(azido(phenyl)methyl)-5-bromo-3-methyl-1-tosyl-1H-indole (5k): 40% yield (98 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (dd, *J* = 8.9, 0.3 Hz, 1H); 7.58-7.57 (m, 1H); 7.50-7.46 (m, 3H); 7.31-7.27 (m, 3H); 7.24-7.21 (m, 2H); 7.15-7.12 (m, 2H); 6.94 (s, 1H); 2.33 (s, 3H); 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.5, 137.7, 135.6, 135.4, 134.4, 133.0, 130.1, 128.7, 128.5, 128.0, 126.9, 126.5, 122.1, 120.5,

117.4, 117.1, 60.0, 21.7, 9.8; IR ν (cm^{-1}) 3400, 2101, 1597, 1068, 668; HRMS (ESI-TOF) calcd for $C_{23}H_{19}BrNO_2S$ [M - N_3]$^+$ 452.0320, found 452.0316.

2-(azido(phenyl)methyl)-5-chloro-3-phenyl-1-tosyl-1H-indole (5l): 36% yield (92 mg); yellow gum; R_f = 0.50 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 8.9 Hz, 1H); 7.66 (d, *J* = 8.4 Hz, 2H); 7.37-7.34 (m, 1H); 7.28-7.22 (m, 5H); 7.16 (d, *J* = 2.0 Hz, 2H); 7.12-7.08 (m, 2H); 7.06-7.00 (m, 4H); 6.80 (s, 1H); 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.5, 137.8, 135.8, 135.1, 134.8, 132.1, 131.4, 130.1, 130.0, 128.3, 128.1, 128.0, 127.5, 126.8, 126.7, 126.6, 126.2, 120.0, 116.5, 60.2, 21.7; IR ν (cm^{-1}) 3399, 2100, 1638, 1072, 668; HRMS (ESI-TOF) calcd for $C_{28}H_{22}ClN_2O_2S$ [M + H - N_2]$^+$ 485.1091, found 485.1080.

General Procedure for the Synthesis of 6a & 6b from 3s & 5a. Using the Synthesis of 6a as an Example:

Azide**3s** (152 mg, 0.5 mmol) was dissolved in ^{t}BuOH/H_2O (1:2 v/v, 1.5 mL), were added $CuSO_4.5H_2O$ (6.2 mg, 0.025 mmol), sodium ascorbate (4.9 mg, 0.025 mmol), and phenylacetylene (102 mg, 1 mmol) at rt. The reaction mixture was stirred for 4 hours at the same temperature, then CH_2Cl_2 (10 mL) was added to the crude mixture and extracted with water. The water layers were extracted 2 times with CH_2Cl_2. The combined extracts were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (silica gel, using 10-15% EtoAc in hexanes) to get pure product **6a** (187 mg, 92%) as a yellow gum.

1-(benzofuran-2-yl(4-(tert-butyl)phenyl)methyl)-4-phenyl-1H-1,2,3-triazole (6a): 92% yield (187 mg); yellow gum; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.82 (m, 3H); 7.56 (d, *J* = 7.6 Hz, 1H); 7.48 (d, *J* = 8.2 Hz, 1H); 7.43-7.38 (m, 4H); 7.27-7.21 (m, 4H); 6.68 (s, 1H); 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.5, 152.9, 152.4, 148.0, 132.9, 130.6, 128.9, 128.3, 127.6, 127.3, 126.2, 125.9, 125.3, 123.4, 121.6, 119.5, 111.7, 107.7, 62.4, 34.8, 31.3; IR ν (cm^{-1}) 3400, 3019, 1643, 1068, 669; HRMS (ESI-TOF) calcd for $C_{27}H_{26}N_3O$ [M + H]$^+$ 408.2076, found 408.2074.

3-methyl-2-(phenyl(4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-1-tosyl-1H-indole (6b): 95% yield (246mg); yellow solid; mp 220-222 ^{o}C; R_f = 0.30 (SiO_2, 10% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.26 (m, 2H); 7.79 (d, *J* = 7.9 Hz, 2H); 7.63 (s, 1H); 7.47-7.40 (m, 4H); 7.35-7.30 (m, 5H); 7.19 (d, *J* = 8.1 Hz, 2H); 6.93-6.87 (m, 4H); 2.08 (s, 3H); 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 144.9, 138.1, 136.8, 135.2, 131.7, 131.1, 130.4, 129.6, 128.8, 128.2, 128.1, 126.5, 126.1, 125.9, 125.6, 123.9, 123.9, 120.8, 119.4, 115.7, 59.7, 21.2, 9.9; IR ν (cm^{-1}) 3400, 1643, 1384, 1071, 668; HRMS (ESI-TOF) calcd for $C_{31}H_{27}N_4O_2S$ [M + H]$^+$ 519.1855, found 519.1844.

General Procedure for the Synthesis of 7 from 3. Using the Synthesis of 7a as an Example:

To a stirred solution of 2-(azido(phenyl)methyl)benzofuran (124 mg, 0.5 mmol) in 2 mL of CH_3CN was added CuI (10mg, 0.05 mmol), DDQ (227 mg, 1.0 mmol), $TMSN_3$ (115 mg, 1.0 mmol), 4 ^{o}A MS (50 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 (8h). The reaction mixture was diluted with water (10ml) and extracted with EtOAc (2x10ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure the crude material was purified by column chromatography (silica gel, using 20% EtoAc in hexanes) to get pure product **7a** (104 mg, 80 %) as white solid.

5-(benzofuran-2-yl)-1-phenyl-1H-tetrazole (7a): 80% yield (104 mg); white solid; mp 150-152 ^{o}C; 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 ν (cm^{-1}) 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 (7b):60% yield (88 mg); yellow gum; R_f = 0.5 (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 ν (cm^{-1}) 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 for the Synthesis of 8 from 3. Using the Synthesis of 8a as an Example:

To a stirred solution of 2-(azido(4-butylphenyl)methyl)benzofuran (152 mg, 0.5 mmol,) in 2 mL of AcOH was added $FeCl_2$ (7 mg, 0.01 mmol), DDQ (227 mg, 1.0 mmol), $TMSN_3$ (115 mg, 1.0 mmol), H_2O (18 mg, 1.0 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at rt until complete conversion of starting material (6h). 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 (2x15ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, crude material was purified by column chromatography (silica gel, using 8-12% EtoAc in hexanes) to get pure product **8a** (100 mg, 68 %) as yellow gum.

N-(4-butylphenyl)benzofuran-2-carboxamide (8a): 68% yield (100mg); yellow gum; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (s, 1H); 7.73 (d, J = 7.9 Hz, 1H); 7.67-7.56 (m, 4H); 7.48 (t, *J* = 7.6 Hz, 1H); 7.35 (t, *J* = 7.6 Hz, 1H); 7.23 (d, *J* = 7.8 Hz, 2H); 2.63 (t, *J* = 7.2 Hz, 2H); 1.68-1.58 (m, 2H); 1.43-1.34 (m, 2H); 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 154.9, 148.8, 139.8, 134.9, 129.2, 127.9, 127.3, 124.0, 122.9, 120.2, 111.9, 111.4, 35.3, 33.8, 22.4, 14.1; IR ν (cm^{-1}) 3408, 1652, 1390, 1067, 759; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO_2$ [M + H]$^+$ 294.1494, found 294.1485.

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DOI: 10.1039/C6OB00191B

N-(4-methoxyphenyl)benzofuran-2-carboxamide (8b): 58% yield (77mg); white solid; mp 118-120 ^{o}C; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 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 ν (cm^{-1}) 3400, 1644, 1070, 772; 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 (8c): Yield 50% (74mg); light yellow gum; R_f = 0.40 (SiO_2,20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 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 ν (cm^{-1}) 3399, 1645, 1385, 104569, 669; HRMS (ESI-TOF) calcd for $C_{17}H_{16}NO_4$ $[M + H]^+$ 298.1079, found 298.1071

6-methyl-N-phenylbenzofuran-2-carboxamide (8d): 70% yield (88mg); yellow gum; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H); 7.74-7.71 (m, 2H); 7.59 (s, 1H); 7.54-7.50 (m, 1H); 7.42-7.37 (m, 2H); 7.27-7.21 (m, 2H); 7.20-7.16 (m, 1H); 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 154.2, 148.3, 137.3, 129.3, 128.2, 127.4, 124.9, 124.1, 122.2, 120.4, 120.3, 112.0, 15.3; IR ν (cm^{-1}) 3429, 1638, 1385, 1068, 769; HRMS (ESI-TOF) calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$ 252.1025, found 252.1024.

5-(tert-butyl)-N-phenylbenzofuran-2-carboxamide (8e): 70% yield (102mg); white solid; mp;134-136 ^{o}C; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.70 (m, 2H); 7.68 (dd, *J* = 1.9, 0.5 Hz, 1H); 7.56 (d, *J* = 0.9 Hz, 1H); 7.53 (dd, *J* = 8.9, 1.9 Hz, 1H); 7.49-7.46 (m, 1H); 7.41-7.37 (m, 2H); 7.19-7.14 (m, 1H); 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.8, 153.3, 148.7, 147.3, 137.4, 129.3, 127.6, 125.6, 124.8, 120.1, 118.9, 111.9, 111.2, 34.9, 31.8; IR ν (cm^{-1}) 3399, 3019, 1644, 1068, 669; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$ 294.1494, found 294.1485.

General Procedure for the Synthesis of 9 from 3:

Azide**3a** (124 mg, 0.5 mmol) was dissolved in a mixture of THF (1.5 mL) and H_2O (0.3 mL) and treated with PPh_3 (288 mg, 1.1 mmol). The reaction was stirred overnight at room temperature under nitrogen atmosphere and then the reaction mixture was concentrated by rotary evaporation. The residue was transferred into a separatory funnel with CH_2Cl_2 and extracted twice with HCl 1M (4.0 mL). The acid aqueous layer was washed 4 times with EtOAc (5.0 mL). The aqueous phase was then made basic (pH: 10-11) with NaOH 2M and extracted with DCM (5.0 mL). The last combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure crude material was purified by column chromatography (silica gel, using 10-12% EtoAc in hexanes) to get pure product **9** (95 mg, 85% yield) as a white solid

benzofuran-2-yl(phenyl)methanamine (9): 85% yield (95 mg); colourless oil; R_f = 0.40 (SiO_2, 30% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.49 (m, 1H); 7.48-7.35 (m, 5H); 7.34-7.29 (m, 1H); 7.26-7.17 (m, 2H); 6.52 (s, 1H); 5.30 (s, 1H); 1.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 155.1, 142.3, 128.8, 128.4, 127.9, 127.2, 123.9, 122.8, 120.9, 111.3, 102.8, 54.6; IR ν (cm^{-1}) 3670, 3398, 1638, 1068, 669; HRMS (ESI-TOF) calcd for $C_{15}H_{11}O$ $[M - NH_2]^+$207.0810, found 207.0811.

General Procedure for the Synthesis of 10 from 9:

To a stirred solution of benzofuran-2-yl(phenyl)methanamine (111 mg, 0.5 mmol) in 3 mL of CH_2Cl_2 was added TEA (151mg, 1.5 mmol). Reaction mixture was cooled to 0 ^{o}C then added TsCl (105 mg, 0.55 mmol), slowly reaction mixture was heated to room temperature and stirred until complete conversion of starting material monitored by TLC (12h). The reaction mixture was diluted with water (10ml) and extracted with EtOAc (2x10ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure crude material was purified by column chromatography (silica gel, using 6-8% EtoAc in hexanes) to get pure product **10** (171 mg, 91 %) as light yellow solid.

N-(benzofuran-2-yl(phenyl)methyl)-4-methylbenzenesulfonamide (10): 91% yield (171 mg); light yellow solid; mp 150-152 ^{o}C; R_f = 0.60 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.3 Hz, 1H); 7.41 (m, 1H); 7.26-7.13 (m, 8H); 7.00 (d, *J* = 7.9 Hz, 1H); 6.40 (s, 1H); 5.74 (d, *J* = 8.0 Hz, 1H); 5.39 (d, *J* = 8.0 Hz, 1H); 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 154.4, 143.4, 137.7, 137.1, 129.2, 128.8, 128.4, 127.8, 127.4, 127.2, 124.4, 123.0, 121.1, 111.2, 105.6, 55.9, 21.4; IR ν (cm^{-1}) 3399, 1643, 1385, 1068, 669; HRMS (ESI-TOF) calcd for $C_{22}H_{19}NNaO_3S$ $[M + Na]^+$ 400.0983, found 400.0993.

General Procedure for the Synthesis of 12 from 3. Using the Synthesis of 12a as an Example:

To a stirred solution of 2-(azido(phenyl)methyl)benzofuran (124 mg, 0.5 mmol,) in 2 mL of DCE was added $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 0.025 mmol), $Cu(OAc)_2$ (90 mg, 0.5 mmol), NaOAc (82 mg, 1.0 mmol), alkyne (170 mg, 0.6 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was heated to 80 ^{o}C and stirred until complete conversion of starting material (12h). The reaction mixture was cooled to room temperature and diluted with water (10ml) and extracted with EtOAc (2x10ml). The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure crude material was purified by column chromatography (silica gel, using 10-15% EtoAc in hexanes) to get pure product **12a** (135 mg, 70%) as yellow gum.

diethyl 4-phenyldibenzo[b,d]furan-1,2-dicarboxylate (12a): 70% yield (135 mg); yellow gum; R_f = 0.40 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53-8.49 (m, 2H); 8.21 (d, *J* = 8.0 Hz, 1H); 7.75 (d, *J* = 8.3 Hz, 1H); 7.71-7.66 (m, 1H); 7.62-7.57 (m, 2H); 7.55-7.50 (m, 1H); 7.49-7.44 (m, 1H); 4.60 (q, *J* = 7.2 Hz, 2H); 4.51 (q, *J* = 7.2 Hz, 2H); 1.48 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 165.8, 157.5, 150.9, 143.2, 141.6, 135.0, 131.0, 130.8, 130.4, 129.4, 128.9, 124.4, 124.3, 122.5, 121.0, 112.7, 62.5, 62.3, 14.4, 14.2; IR ν (cm^{-1}) 3398, 3019, 1719, 1632, 1066, 769, 669; HRMS (ESI-TOF) calcd for $C_{23}H_{20}NO_5[M + H]^+$ 390.1341, found 390.1331.

diethyl 4-(p-tolyl)dibenzo[b,d]furan-1,2-dicarboxylate (12b): 58% yield (116mg); white solid; mp 110-112 °C; R_f = 0.40 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, J = 8.2 Hz, 2H); 8.21 (d, *J* = 8.0 Hz, 1H); 7.73 (d, *J* = 8.4 Hz, 1H); 7.69-7.64 (m, 1H); 7.47-7.42 (m, 1H); 7.39 (d, *J* = 8.2 Hz, 2H); 4.59 (q, *J* = 7.2 Hz, 2H); 4.51 (q, *J* = 7.2 Hz, 2H); 2.46 (s, 3H); 1.47 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 165.9, 157.5, 150.7, 143.4, 141.6, 140.7, 132.3, 130.9, 130.7, 129.6, 129.3, 124.4, 124.2, 122.1, 121.1, 112.7, 62.4, 62.3, 21.7, 14.4, 14.2; IR ν (cm^{-1}) 3399, 1725, 1644, 1385, 1065, 769, 669; HRMS (ESI-TOF) calcd for $C_{24}H_{22}NO_5$ $[M + H]^+$ 404.1498, found 404.1488.

diethyl 7-methyl-4-phenyldibenzo[b,d]furan-1,2-dicarboxylate (12c): 62% yield (124mg); yellow gum; R_f = 0.40 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (m, 2H); 8.07 (d, *J* = 8.1 Hz, 1H); 7.61-7.49 (m, 4H); 7.28-7.26 (m, 1H); 4.58 (q, *J* = 7.2 Hz, 2H); 4.51 (q, *J* = 7.2 Hz, 2H); 2.58 (s, 3H); 1.49-1.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 165.8, 157.9, 150.7, 142.8, 142.2, 141.6, 134.9, 130.9, 130.1, 129.2, 128.7, 125.6, 123.8. 121.9, 118.3, 112.6, 62.2, 62.1, 22.2, 14.2, 14.1; IR ν (cm^{-1}) 3399, 3020, 1648, 1068, 669; HRMS (ESI-TOF) calcd for $C_{24}H_{22}NO_5$ $[M + H]^+$ 404.1498, found 404.1488.

Diethyl 8-methyl-4-phenyldibenzo[b,d]furan-1,2-dicarboxylate (12d): 60% yield (120mg); white solid; mp 104-106 °C; R_f = 0.40 (SiO_2, 20% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (m, 2H); 8.52-8.48 (m, 2H); 7.97-7.95 (m, 1H); 7.63-7.56 (m, 3H); 7.57-7.47 (m, 2H); 4.60 (q, *J* = 7.2 Hz, 2H); 4.51 (q, *J* = 7.2 Hz, 2H); 2.53 (s, 3H); 1.51-1.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 165.9, 155.9, 151.2, 143.1, 141.3, 135.1, 134.0, 132.3, 130.7, 130.3, 129.3, 128.8, 124.0, 122.6, 120.9, 112.2, 62.5, 62.3, 21.6, 14.4, 14.2; IR ν (cm^{-1}) 3399, 3019, 1643, 1068, 669; HRMS (ESI-TOF) calcd for $C_{24}H_{22}NO_5$ $[M + H]^+$ 404.1498, found 404.1488.

Acknowledgements

GRK and YKK thank CSIR for the fellowships. We thank SAIF division CSIR-CDRI for the analytical support and Dr. Tejender S. Thakur, Molecular and Structural Biology Division, CSIR-CDRI for supervising the X-ray data collection and structure determination of compounds 5b and 7a. We gratefully acknowledge the financial support by DST (SB/FT/CS-102/2012). CDRI Communication No: (will be inserted if accepted).

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DOI: 10.1039/C6OB00191B

Synthesis of benzofuranyl and indolyl methyl azides by tandem silver-catalyzed cyclization and azidation

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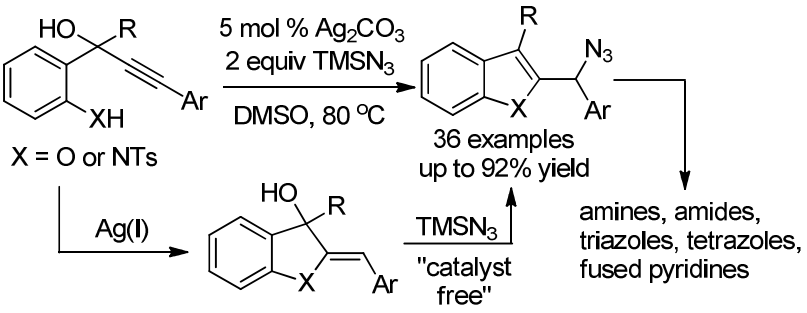

A tandem Ag-catalyzed 5-exo-dig cyclization and catalyst free γ-azidative allylic hydroxyl displacement for benzofuranyl/indolyl methyl azides from hydroxyl/amino-phenyl propargyl alcohols is presented. The synthetic utility is demonstrated by the conversion of azidomethyl unit to various functionalizations, like triazole-, tetrazole-, amide-, amine-, pyrido-derivatives.