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Copper Pincer Complexes as Advantageous Catalysts for the Heteroannulation of *ortho*-Halophenols and Alkynes

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Abstract: A new, non-symmetrical copper(II) pincer complex catalyzes much more efficiently the formation of benzofuran by the reaction between *ortho*-iodophenols and alkynes. The lowest catalyst loadings are realized for this reaction, and bromo- and chlorophenols are heteroannulated for the first time. Strong evidence for hydrophenoxylation and intramolecular halogen atom-transfer steps catalyzed by this remarkably active, recyclable homogeneous catalyst is provided.

Keywords: alkynes; copper; halophenols; heteroannulation; hydrophenoxylation

Introduction

The diversity of benzofuran scaffolds isolated from natural sources[1] as well as their biological relevance[2] have stimulated research into the development of more efficient approaches to the benzo[*b*]furan ring system. Over the last years, transition metal-catalyzed reactions have played a remarkable role in this area. Particularly, reactions catalyzed by palladium[3] and copper[4] or a mixture of both metals[5] have been employed due to the increased functional group tolerance, simplified procedures, and improved yields compared to classical approaches.[6]

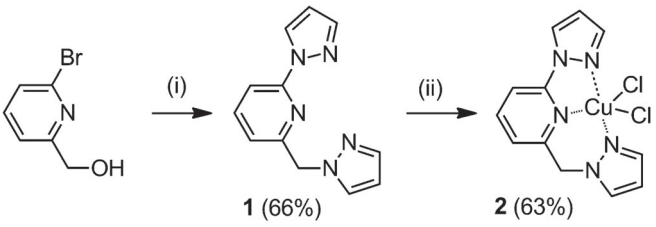
It is highly attractive to perform these reactions under palladium-free conditions due to its higher cost and relative toxicity. However, from a comparative view, in a broad number of cross-coupling reactions and related transformations that include those involved in the construction of the benzofuran core, copper catalysts usually require higher loadings than those of palladium. Therefore the former metal is considered as a source of much less efficient catalysts. In fact, most Cu-catalyzed coupling reactions are performed by using 5–20 mol% of the copper source.[7] This is particularly true for copper-catalyzed tandem reactions, such as the heteroannulation-type reaction of 2-iodophenols with arylacetylenes leading to benzofurans,[8] a field where an initial palladium-free Sonogashira-type coupling is assumed to occur.[8a–c,f–g,k]

Our idea was to synthesize a more efficient copper catalyst for the above transformation so that lower amounts could be employed (higher TON and TOF values) and residual toxicity associated to copper traces[9] would be further reduced. Moreover, a more active catalyst could in theory also mediate the reaction starting from 2-bromophenols, a copper-catalyzed transformation unexplored so far. With these aims in mind, we envisaged the synthesis and catalytic evaluation in this reaction of a new Cu(II) mononuclear pincer complex. The most remarkable results of the latter study are presented in this paper, including a new insight into the reaction mechanism that provides proof of an alternative mechanism based on copper-catalyzed initial hydrophenoxylation followed by an atom-transfer process.

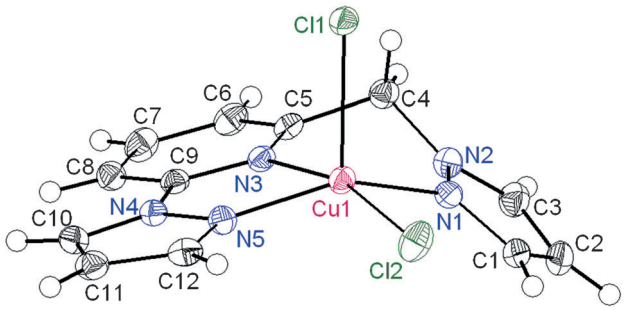
Results and Discussion

Synthesis of the Cu(II) Pincer Complex

As displayed in Scheme 1, the synthesis of the novel, non-symmetrical ligand **1** was performed in a high overall yield by a sequence of mesylation/nucleophilic substitution from commercially available (6-bromopyridin-2-yl)methanol. For an effective insertion of the copper ion, a KO-*t*-Bu/MeOH/CH_2Cl_2-mediated dearomatization–protonation process was required,[10b] since simple addition of $CuCl_2$ or other copper



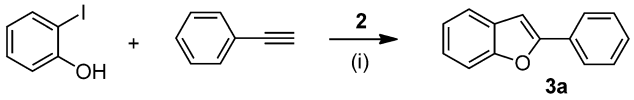
(i) 1. MsCl, Et_3N, THF, r.t.;
2. pyrazole, NaH, diglyme, 70 °C to 130 °C
(ii) $CuCl_2 \cdot 2\,H_2O$, KO-*t*-Bu, MeOH, CH_2Cl_2, r.t.



Scheme 1. Synthesis and molecular structure of copper pincer complex **2**.

sources provided negligible results. Full characterization of the resulting paramagnetic pentacoordinated Cu(II) complex **2** was achieved by X-ray diffractrometry, showing a pentacoordinated Cu in a distorted square based pyramidal structure (Scheme 1, monoclinic *P*21/*n* space group).[10a]

Table 1. Optimization of the reaction conditions leading to 2-arylbenzofuran **3a**.



Entry	[Cu] mol%	Conditions (i)[a]	Yield [%][b]
1	1.5	KOH, 1,4-dioxane, 120 °C, 48 h	–[c]
2	1.5	NaOH, THF, 100 °C, 48 h	–[c]
3	1.5	Et_3N, 1,4-dioxane, 130 °C, 48 h	–[c]
4	1.5	Et_3N, PhMe, 120 °C, 48 h	–[c]
5	1.5	DMAP, DCE, 120 °C, 48 h	–[c]
6	1.5	DBU, THF, 100 °C, 48 h	–[c]
7	1.5	DBU, MeCN, 90 °C, 48 h	–[c]
8	$7.5 \cdot 10^{-1}$	K_2CO_3, 1,4-dioxane, 120 °C, 48 h	16
9	$7.5 \cdot 10^{-1}$	K_2CO_3, H_2O, 120 °C, 48 h	–[c]
10	3.7	Cs_2CO_3, PEG-400, 130 °C, 30 h	18
11	1.9	Cs_2CO_3, H_2O, 130 °C, 24 h	<5
12	2.6	Cs_2CO_3, 1,4-dioxane, 130 °C, 48 h	>99
13	$1.5 \cdot 10^{-1}$	Cs_2CO_3, 1,4-dioxane, 130 °C, 48 h	>99
14[d]	$1.5 \cdot 10^{-1}$	Cs_2CO_3, 1,4-dioxane, 130 °C, 48 h	>99
15	$7.5 \cdot 10^{-2}$	Cs_2CO_3, 1,4-dioxane, 130 °C, 48 h	67
16	$3.7 \cdot 10^{-2}$	Cs_2CO_3, 1,4-dioxane, 130 °C, 48 h	43
17	$6 \cdot 10^{-1}$	Cs_2CO_3, 1,4-dioxane, 130 °C, 24 h	76
18	$1.5 \cdot 10^{-1}$	Cs_2CO_3, 1,4-dioxane, 100 °C, 48 h	58
19	$1.5 \cdot 10^{-1}$	Cs_2CO_3, 1,4-dioxane, 80 °C, 48 h	34
20[e]	$1.5 \cdot 10^{-1}$	Cs_2CO_3, 150 °C, MW, 30 min.	60

[a] *Reaction conditions:* **2**, 2-iodophenol, 1.2 equiv. of phenylacetylene, 2.0 equiv. of base and solvent (4.4 mL per mmol of 2-iodophenol); unless otherwise noted.
[b] Isolated yield of chromatographically pure compound.
[c] Only starting material was observed by TLC.
[d] TEMPO (1.1 equiv.) was added.
[e] Microwave-assisted solvent-free reaction

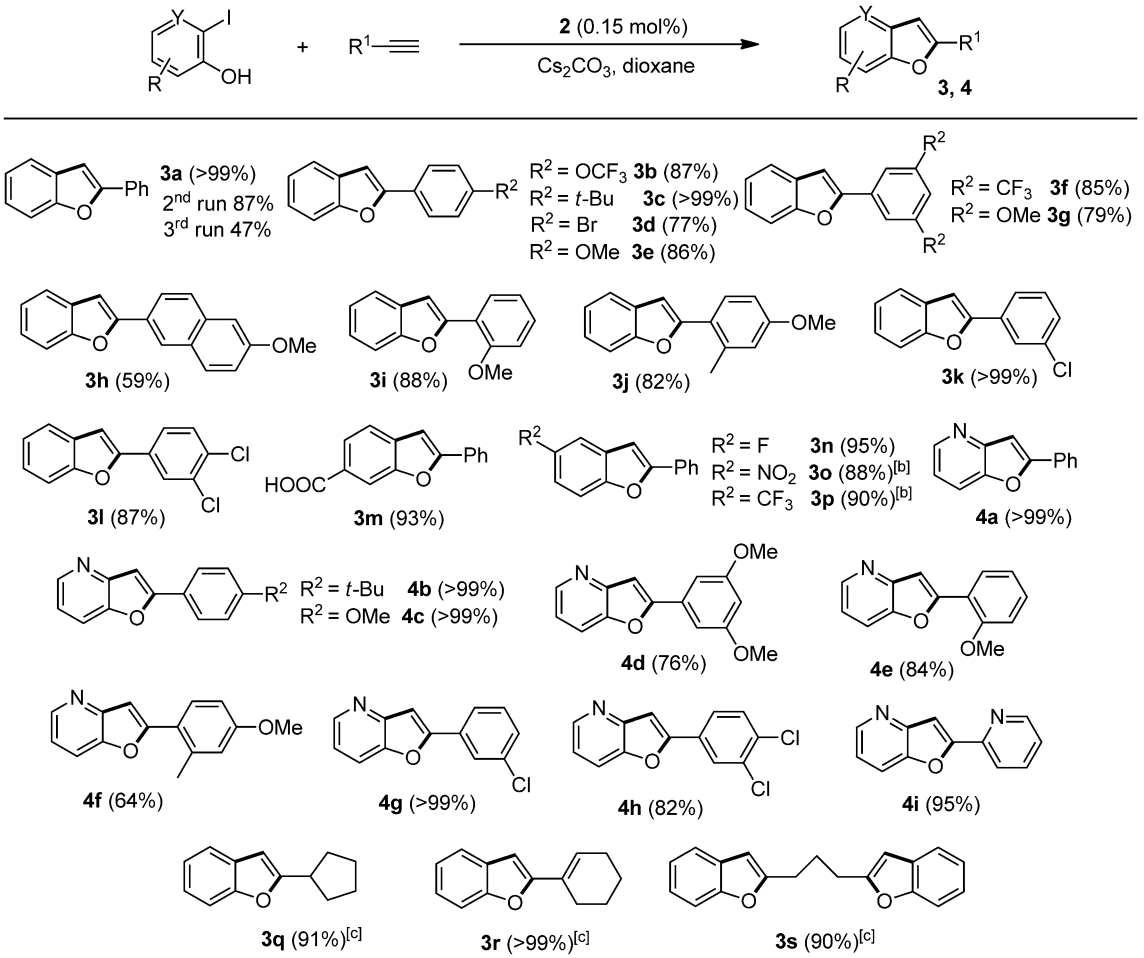
Reaction Development

A range of assays was then conducted to optimize the reaction conditions for the reaction between 2-iodophenol and phenylacetylene leading to benzofuran **3a** (Table 1). In addition to non-symmetrical complex **2**, the use of Cs_2CO_3/1,4-dioxane as the base/solvent system turned out to be critical for the reaction to progress. Quantitative yields were also obtained when the catalyst loading was reduced to $1.5 \cdot 10^{-1}$ mol%, thus reaching turnover numbers and frequencies (TON, TOF) of $6.7 \cdot 10^3$ and $1.4 \cdot 10^2\ h^{-1}$, respectively, the highest values so far. Moreover, no trace of diyne by-product from oxidative homocoupling was observed.[11] Lower amounts of **2** still promoted the reaction but with lower conversion rates. Finally, it should be pointed out that the reaction time can be dramatically shortened by microwave irradiation, although at the cost of lower yields.

The optimized reaction conditions were applied to an array of commercially available *o*-iodophenol and arylacetylene derivatives, providing the corresponding 2-arylbenzofurans **3** with the results displayed in Table 2. Good to excellent yields were obtained in all cases regardless of the electronic nature of both reagents and heteraromatic *ortho*-hydroxy iodides and alkynes were also successfully reacted under the same conditions to provide furo[3,2-*b*]pyridines **4**. 2-Alkyl- and 2-alkenylbenzofurans **3q** and **3r** were also regioselectively obtained by reaction with less reactive alkyl- and alkenylacetylenes, although a slightly higher loading of complex **2** was required. The same protocol proved also useful to generate bisbenzo[*b*]furan **3s** by a double heteroannulation from hepta-1,6-diyne.

The simple work-up procedure (addition of water and extraction with ethyl acetate) enabled an effective catalyst separation and recycling. This was verified in the formation of benzofuran **3a**. Even at such low amounts of complex **2**, it was possible to recycle it up to 3 times (Table 2). The infinitesimal content of copper traces ($<7.0 \cdot 10^{-5}$ mol, measured by ICP-MS) in the final products **3** accounts for an efficient catalyst separation aided by the low amount of the employed Cu complex. This fact cannot be ignored, con-

Table 2. NNN complex **2**-catalyzed heteroannulation of iodophenols and alkynes. Functional group tolerance.[a]



[a] *Reaction conditions:* 2-iodophenol (1 equiv.), alkyne (1.2 equiv.), **2** (0.15 mol%), Cs_2CO_3 (2 equiv.), 1,4-dioxane (4.4 mL/of iodophenol), 130 °C, 48 h. Isolated yield of chromatographically pure compound.
[b] 72 h.
[c] **2** (0.6 mol%).

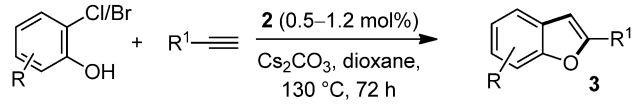
sidering the low, but not negligible toxicity of copper.[9]

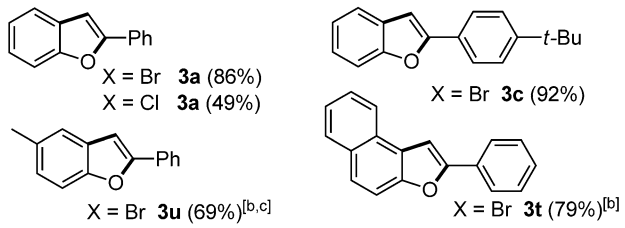
Encouraged by such unprecedented activity for a copper catalyst in this tandem reaction, we envisaged the use of *ortho*-bromophenols as starting materials. As shown in Table 3, good yields were obtained for benzofurans **3a**, **3c**, **3t** and **3u**, although at the price of a higher amount of catalyst **2**. Benzofuran **3a** was even obtained in a modest 49% yield from *ortho*-chlorophenol after a reaction time of 72 h. In addition to the relevance of the latter heteroannulations starting from much less active *ortho*-halophenols, already reported for Pd-catalyzed transformations[3r] but unprecedented in copper chemistry, significant data for a better understanding of the reaction mechanism were also gained, as explained below.

Mechanistic Studies

Indeed, two main mechanistic questions arise from these results. One deals with the real role of pincer complex **2**. The presence of any palladium co-catalyst was discarded by ICP-MS of the reaction mixture ($< 1.1 \cdot 10^{-4}$ mol%), and in order to clarify if **2** acts as a reservoir of copper nanoparticles, or if heterogeneous catalysts are involved in the reaction, an array of experiments including kinetic studies, Hg drop test, and quantitative poisoning assays was carried out. No sigmoidal shape was observed in the kinetic plot for the formation of benzofuran **3a** under the optimized conditions (Figure 1), and the addition of a drop of Hg to the reaction mixture exerted no inhibiting or poisoning effect either. Both results are in accordance with a homogeneous catalytic system.[12]

Table 3. Heteroannulation of 2-bromo- and 2-chlorophenols.[a]





[a] *Reaction conditions:* 2-halophenol (1 equiv.), alkyne (1.2 equiv.), **2** (0.5 mol%), Cs_2CO_3 (2 equiv.), 1,4-dioxane (4.4 mL mmol^{-1} of halophenol), 130 °C, 72 h. Isolated yield of chromatographically pure compound.
[b] **2** (0.8 mol%).
[c] 2,7-Dimethyldibenzo[*b,e*][1,4]dioxine was also detected as a by-product.

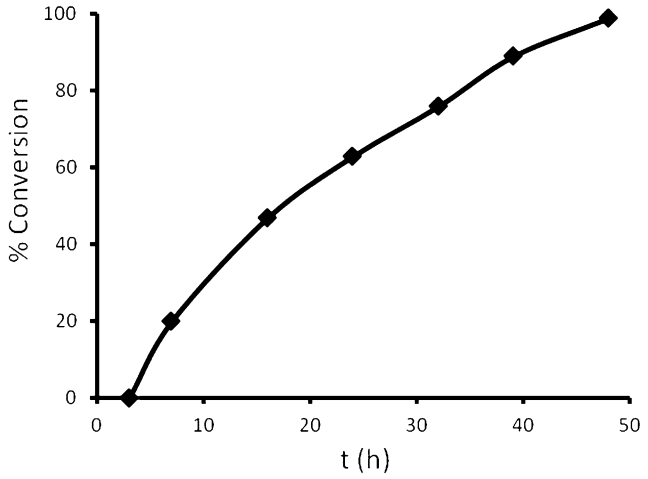
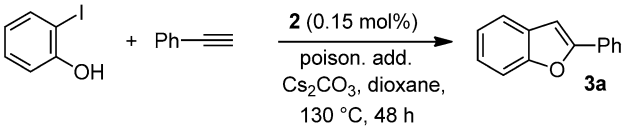


Figure 1. Conversion of 2-iodophenol as a function of time.

As shown in Table 4, the same trend (poor or no inhibition) was observed when adding substoichiometric amounts of commonly known poisons like CS_2 and PPh_3,[13] and a similar catalytic activity was observed in the presence of overstoichiometric amounts of pyridine and polyvinylpyridine (PVPy), another mechanistic experiment devised to distinguish between metal nanoparticles and homogeneous metal complexes.[14]

Once having elucidated the homogeneous nature of the employed catalyst, the second question was to clarify if the presented heteroannulation leading to benzofurans was based on an initial copper-catalyzed Sonogashira reaction (or catalytic Stephens–Castro reaction), as previously reported,[8a–c,f–g,k] or if other processes were really taking place.

Table 4. Summary of poisoning experiments.



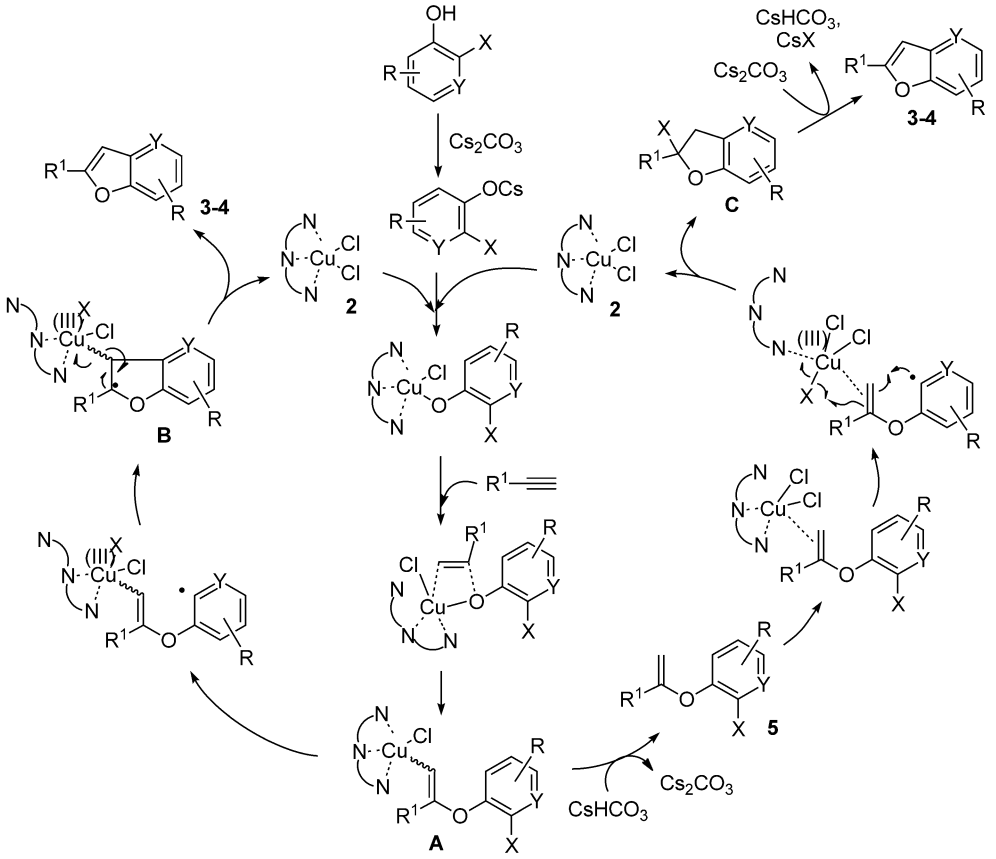
Entry	Poisoning additive	Conv. [%][a]
1	Hg (one drop)	>99
2	CS_2 (0.5 equiv. per metal atom)	73
3	CS_2 (2.0 equiv. per metal atom)	0
4	PPh_3 (0.03 equiv. per metal atom)	>99
5	PPh_3 (0. 3 equiv. per metal atom)	>99
6	PPh_3 (4.0 equiv. per metal atom)	0
7[b]	Py (150 equiv. per metal atom)	>99
8[c]	PVPy (300 equiv. per metal atom)	88

[a] Measured by ^{1}H NMR. Diethylene glycol dimethyl ether was used as internal standard.
[b] Py = pyridine.
[c] PVPy = polyvinylpyridine.

The key for the answer was the detection by TLC and EI-MS of small amounts (3–8%) of 1-halo-2-[(1-phenylvinyl)oxy]benzene **5** when the reaction was performed from *ortho*-chloro- and *ortho*-bromophenol. As depicted in the mechanistic proposal shown in Scheme 2, an intermolecular hydrophenoxylation step catalyzed by complex **2** would provide crucial intermediate **A**, which could then undergo an intramolecular halogen atom-transfer reaction. Aromatization of the so-formed alkoxyalkyl radical **B** would provide target products **3** and **4** and regenerate Cu(II) complex **2**. Alternatively, protonolysis of **A** would afford intermediate **5**. Then this alkene would react *via* atom-tranfer radical cyclization aided by **2** to give a 2-halogenated dihydrobenzofuran **C**, which upon elimination of HX would produce benzofurans **3** and **4**.

Alternatively, copper nanoparticles[15] stabilized by ligand **1** could be also responsible for the oxidative addition and reductive elimination steps required for a copper-catalyzed Heck-type cyclization[16] from intermediate **5**, but the above results in support of a homogenenous catalysis make it unlikely.

By our proposal depicted in Scheme 2, the difference in reactivity among *ortho*-iodo-, *ortho*-bromo and *ortho*-chlorophenols would come from the increasing homolytic bond dissociation energies that might hinder atom-transfer reaction processes. The intimate relationship between the catalyst framework and the radical center probably provokes the formation of caged radical species, which would account for the lack of inhibition observed when adding TEMPO and other radical traps to the reaction media.[17] Several examples have been reported for copper-catalyzed hydroalkoxylations[18] and also for copper-catalyzed intramolecular halogen atom-transfer reactions,[19] but as far as we know, this would be the first



Scheme 2. NNN Pincer **2**-catalyzed benzofuran formation. A tentative proposal.

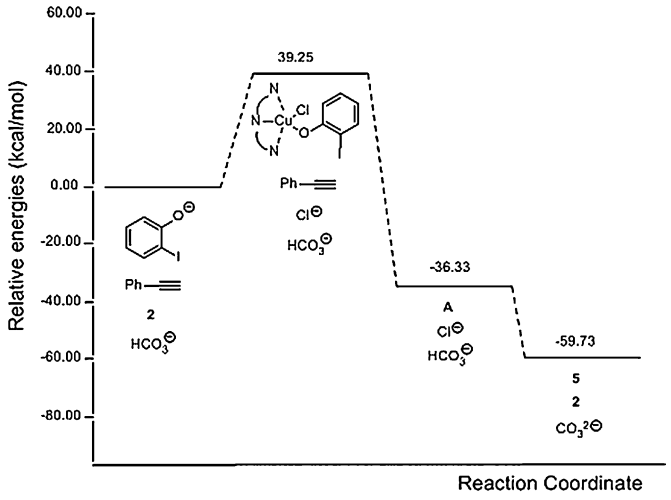
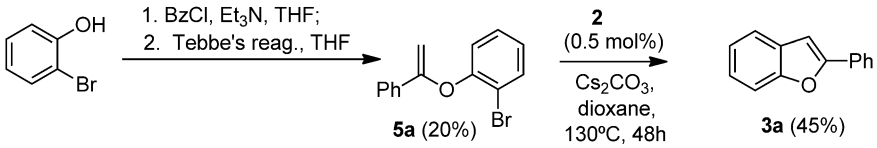


Figure 2. Energy profiles for the hydrophenoxylation reaction of phenylacetylene catalyzed by pincer complex **2**.

report which combines both processes. As displayed in Figure 2, the feasibility of our proposal was partially supported by comparison of the relative energies of the substrates and suggested intermediates for the hydrophenoxylation step by means of DFT calculations (B3LYP/6-31G*//3-21G).

To check this reaction and provide a more convincing proof in support of a mechanism based on a tandem hydrophenoxylation/atom-transfer radical cyclization catalyzed by Cu complex **2**, unstable alkene derivative **5a** (X = Br, Y = CH, R^1 = Ph) was prepared by a Tebbe methylenation of 2-bromophenyl benzoate,[20] and quickly reacted under our optimized heteroannulation conditions, providing benzofuran **3a** (Scheme 3).



Scheme 3. Synthesis of intermediate 1-halo-2-[(1-phenylvinyl)oxy]benzene (**5a**) and heteroannulation to provide **3a**.

Conclusions

To sum up, a new Cu(II) pincer complex allows the lowest (sub-mol%) catalytic loading in the heteroannulation of *ortho*-iodophenols and acetylenes to provide benzo[*b*]furan and furo[3,2-*b*]pyridine derivatives. The first examples of the copper-catalyzed formation of benzofurans from *ortho*-bromo- and *ortho*-chlorophenols are also reported. In addition, this outstanding NNN-type complex catalyst can be recycled several times. A series of mechanistic studies reveals the participation of homogeneous species, probably the pincer itself, as true catalysts, and a new, alternative pathway to explain the formation of benzofurans and furo[3,2-*b*]pyridines is also presented, featuring copper-catalyzed hydroalkoxylation and intramolecular atom-tranfer radical cyclization as the key steps.

Experimental Section

General Remarks

All reagents were purchased and used as received unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz for ^{1}H and 75.4 MHz for 13C) at 20 °C. Chemical shifts (d) are given in ppm downfield from Me_4Si and are referenced as internal standard to the residual solvent (unless indicated) $CDCl_3$ ($\delta = 7.26$ for ^{1}H and $\delta = 77.00$ for ^{13}C). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, Merck, 230–400 mesh ASTM). IR spectra were recorded on a Perkin–Elmer 1600 FT or JASCO FTIR-4100infrared spectrophotometer as KBr plates or as thin films, and only noteworthy absorptions are reported in cm^{-1}. Drying of organic extracts during work-up of reactions was performed over anhydrous Na_2SO_4. Evaporation of solvents was accomplished with a Büchi rotatory evaporator. MS and HR-MS were measured using a Waters GCT mass spectrometer. All theoretical calculations were performed using the Spartan software package. B3LYP density functional calculation of energy [the 6-31G* basis set was employed for the C, H, N, and O atoms, and LANL2DZ (LACVP*) for Cu] was preceded by Hartree–Fock 3-21G calculation of geometry. Single-crystal X-ray diffraction data were collected at room temperature on an Agilent SuperNova Cu automatic diffractometer equipped with an Atlas CCD detector. Lattice constants were obtained by using a standard program belonging to the software of the diffractometer, confirming at the same time the good quality of the single crystal. The Lorentz polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystal. The structures were solved by direct methods SHELXS97[21] and subsequent Fourier difference calculations.

Synthesis of NNN-Type Pincer Complex 2

(6-Bromopyridin-2-yl)methyl methanesulfonate:[22] To a stirred solution of (6-bromopyridin-2-yl)methanol (916 mg, 4.87 mmol), triethylamine (1.50 mL, 10.64 mmol) and methanesulfonyl chloride (1.0 mL, 12.92 mmol) were added dropwise at 0 °C under argon. The reaction mixture was stirred at room temperature for 15 min, then quenched with water (5 mL), and the aqueous phase was extracted with diethyl ether (2×15 mL). The combined organic layers were washed with NH_4Cl (5 mL), dried over anhydrous sodium sulfate and concentrated under vacuum to give a colorless oil. This crude product was used without further purification; yield: 1.29 g (99%). ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 7.57$ (t, $J =$ 7.8 Hz, 1H), 7.42–7.36 (m, 2H), 5.20 (s, 2H), 3.07 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 154.9$, 141.6, 139.6, 128.1, 121.2, 70.5, 38.1; IR (film): $\nu = 2937$, 1583, 1559, 1440, 1411, 1349, 1170, 1122, 951, 815 cm^{-1}; MS: *m/z* (%) = 266 (M^+,100); HR-MS: *m/z* = 265.9410, calcd. for $C_7H_9BrNO_3S$: 265.9408.

2-[(1*H*-Pyrazol-1-yl)methyl]-6-(1*H*-pyrazol-1-yl)pyridine (1): Pyrazole (661 mg, 9.71 mmol) in diglyme (10 mL) was added dropwise to a stirring solution of NaH (291.5 g, 12.14 mmol) in diglyme (10 mL) under argon. The mixture was stirred at 70 °C for 1.5 h, and then a solution of (6-bromopyridin-2-yl)methyl methanesulfonate (1.07 g, 4.05 mmol) in diglyme (10 mL) was added slowly. The mixture was stirred at 130 °C under argon for 24 h, and then allowed to cool. Addition of water to the reaction mixture afforded a creamy white precipitate, which was redissolved and extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated under vacuum to provide an oily residue which was purified by flash column chromatography over silica, using ethyl acetate/*n*-hexane (1:1) as eluent, affording ligand **1**[23] as a yellow oil; yield: 601.4 mg (66%). ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 8.49$ (d, $J = 2.5$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.68–7.63 (m, 2H), 7.55 (d, $J = 1.5$ Hz, 1H), 7.52 (d, $J =$ 2.1 Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.39 (t, $J = 1.7$ Hz, 1H), 6.29 (t, $J = 2.1$ Hz, 1H), 5.39 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 155.2$, 150.8, 141.9, 139.8, 139.5, 129.9, 126.8, 118.6, 111.0, 107.6, 106.0, 105.7, 56.8; IR (film): $\nu = 3005$, 1600, 1578, 1469, 1392, 1276, 1260, 749 cm^{-1}; MS: *m/z* (%) = 226 (M^+, 100); HR-MS: *m/z* = 226.1013, calcd. for $C_{12}H_{12}N_5$: 226.1014.

Dichloro{2-[(1*H*-pyrazol-1-yl-κ*N*^{2})methyl]-6-(1*H*-pyrazol-1-yl-κ*N*^{2})pyridine-κ*N*}copper(II) (2): A solution of ligand **1** (179 mg, 0.79 mmol) in CH_2Cl_2 (6.0 mL) was slowly added onto a solution of $CuCl_2{\cdot}2H_2O$ (135 mg, 0.79 mmol) in MeOH (6.0 mL) at room temperature under argon. This mixture was stirred for 5 min and then KO-*t*-Bu (89.0 mg, 0.79 mmol) was added. After stirring over 2 days, the precipitate (**2**) was collected and dried under vacuum; yield: 180 mg (63%). X-ray quality crystals of a solvate (**2**·MeOH) were obtained.

General Procedure for the Synthesis of Benzo[*b*]furans 3 and Furo[3,2-*b*]pyridines 4

Pincer complex **2** ($6.81{\cdot}10^{-4}$ mol) was added to a mixture of 2-iodophenol (0.45 mmol), alkyne (0.545 mmol), and Cs_2CO_3 (0.91 mmol) in anhydrous 1,4-dioxane (2 mL). This mixture was stirred in a screw-capped tube for 48 h at

130 °C under argon. After cooling, H_2O (5.0 mL) was added and the resulting aqueous suspension was extracted with ethyl acetate (3×15 mL). The organic layer was washed with H_2O (15 mL) and brine (2×15 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by flash chromatography, using ethyl acetate/hexane as eluent, to provide pure derivatives **3** and **4**.

2-Phenylbenzo[*b*]furan (3a):[24] Yield: 99%; white powder; mp 118–119 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.92 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 7.3 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 6.1 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.07 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.9, 154.9, 130.5, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3; IR (film): ν = 1868, 1843, 1556 cm^{-1}; MS: m/z (%) = 195 (M^+, 100), 166 (36); HR-MS: m/z = 195.0736, calcd. for $C_{14}H_{11}O$: 195.0732.

2-(4-Trifluoromethoxyphenyl)benzofuran (3b): Yield: 87%; white powder; mp 159–161 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.91 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.35–7.28 (m, 4H), 7.05 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.0, 154.5, 149.2, 129.2, 129.3, 129.0, 126.3, 124.7, 123.1, 121.5, 121.3, 121.1, 111.2, 101.9; IR (film): ν = 1500, 1451, 1256, 1207, 1157 cm^{-1}; MS: m/z (%) = 279 (M^+, 100), 278 (60); HR-MS: m/z = 279.0634, calcd. for $C_{15}H_{10}F_3O_2$: 279.0633.

2-(4-*tert*-Butylphenyl)benzofuran (3c):[25] Yield: >99%; white powder; mp 127–129 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.85 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.33–7.25 (m, 2H), 7.02 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 156.2, 154.9, 151.8, 129.4, 127.8, 125.7, 124.8, 124.0, 122.9, 120.8, 111.1, 100.7, 34.8, 31.3; MS: m/z (%) = 251 (M^+, 100), 250 (80); HR-MS: m/z = 251.1444, calcd. for $C_{18}H_{19}O$: 251.1436.

2-(3-Chlorophenyl)benzofuran (3k):[26] Yield: >99%; yellow oil; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.89 (s, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.42–7.27 (m, 5H), 7.08 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.0, 154.4, 134.9, 132.2, 130.1, 128.9, 128.4, 124.9, 124.8, 123.3, 123.0, 121.1, 111.3, 102.4; IR (film): ν = 1603, 1558, 1470, 1453 cm^{-1}; MS: m/z (%) = 230 (M+1, 33), 229 (M^+, 100), 228 (61), 193 (36); HR-MS: m/z = 229.0437, calcd. for $C_{14}H_{10}ClO$: 229.0420.

2-(4-Bromophenyl)benzofuran (3d):[24a] Yield: 77%; white powder; mp 150–154 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.75 (d, J = 8.6 Hz, 2H), 7.62–7.59 (m, 3H), 7.55 (d, J = 8.7 Hz, 1H), 7.33 (dt, J = 8.3, 1.2 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.05 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.9. 154.8, 132.0, 129.4, 129.1, 126.4, 124.6, 123.1, 122.5, 121.0, 111.2, 101.9; MS: m/z (%) = 275 (M+2, 65), 274 (M+1, 92), 273 (M^+, 68), 272 (M−1, 82), 194 (100); HR-MS: m/z = 272.9926, calcd. for $C_{14}H_{10}BrO$: 272.9915.

2-(2-Methoxyphenyl)benzofuran (3i):[27] Yield: 88%; yellow powder; mp 80–82 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.18 (d, J = 7. 7 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.46 (s, 1H), 7.41–7.26 (m, 3H), 7.16 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 156.6, 154.0, 152.3, 129.9, 129.3, 127.1, 124.2, 122.8, 121.1, 120.8, 119.4, 111.1, 110.9, 106.5, 55.5; IR (film): ν = 2939, 1492, 1446, 1282 cm^{-1}; MS: m/z (%) = 225 (M^+, 100), 224 (47); HR-MS: m/z = 225.0929, calcd. for $C_{15}H_{13}O_2$: 225.0916.

2-(4-Methoxyphenyl)benzofuran (3e):[28] Yield: 86%; white powder; mp 147–150 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.80 (d, J = 8.8 Hz, 2H), 7.57–7.49 (m, 2H), 7.29–7.19 (m, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.0, 156.1, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.4; IR (film): ν = 1505, 1298, 1251, 1023 cm^{-1}; MS: m/z (%) = 225 (M^+, 100), 224 (56); HR-MS: m/z = 225.0926, calcd. for $C_{15}H_{13}O_2$: 225.00916.

2-[3,5-Bis(trifluoromethyl)phenyl]benzofuran (3f):[29] Yield: 85%; brown powder; mp 147–150 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.27 (s, 2H), 7.83 (s, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.32–7.23 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.2, 152.5, 132.6, 132.5, 132.1, 128.5, 125.7, 125.0, 124.6, 123.6, 121.6, 121.5, 121.4, 111.5, 104.2; MS: m/z (%) = 359 (29), 332 (M^+1, 15), 331 (M^+, 98), 330 (M−1, 56), 311 (100); HR-MS: m/z = 331.0545, calcd. for $C_{16}H_9F_6O$: 331.0558.

2-(3,5-Dimethoxyphenyl)benzofuran (3g):[30] Yield: 79%; pale yellow powder; mp 48–51 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.61 (d, J = 7.1 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.33 (dt, J = 7.3, 1.3 Hz, 1H), 7.29–7.25 (m, 1H), 7.07 (d, J = 2.3 Hz, 2H), 7.04 (s, 1H), 6.52 (t, J = 2.3 Hz, 1H), 3.91 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 161.1, 155.7, 154.9, 132.3, 129.1, 124.4, 123.0, 121.0, 111.2, 103.1, 101.9, 101.1, 55.5; IR (film): ν = 2958, 2836, 1599, 1450, 1333 cm^{-1}; MS: m/z (%) = 255 (M^+, 100), 254 (36); HR-MS: m/z = 255.1034, calcd. for $C_{16}H_{15}O_3$: 255.1021.

2-(4-Methoxy-2-methylphenyl)benzofuran (3j): Yield: 82%; pale yellow powder; mp 129–133 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.82 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.33–7.26 (m, 2H), 6.90–6.88 (m, 2H), 6.83 (s, 1H), 3.89 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.7, 155.8, 154.2, 137.6, 129.7, 129.4, 123.8, 122.9, 122.7, 120.6, 116.6, 111.5, 110.9, 103.8, 55.3, 22.0; IR (film): ν = 2956, 2833, 1606, 1496, 1453, 1255 cm^{-1}; MS: m/z (%) = 239 (M^+, 100), 238 (60); HR-MS: m/z = 239.1096, calcd. for $C_{16}H_{15}O_2$: 239.1072.

2-(6-Methoxy-2-naphthyl)-1-benzofuran (3h):[31] Yield: 59%; pale yellow powder; mp 193–195 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.31 (s, 1H), 7.91–7.78 (m, 3H), 7.62–7.55 (m, 2H), 7.33–7.16 (m, 4H), 7.09 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.3, 156.3, 154.9, 134.6, 129.9, 129.4, 128.9, 127.3, 125.7, 124.1, 123.8, 123.4, 122.9, 120.8, 119.4, 111.1, 105.9, 101.1, 55.4 cm^{-1}; MS: m/z (%) = 275 (M^+, 100), 274 (66); HR-MS: m/z = 275.1090, calcd. for $C_{19}H_{15}O_2$: 275.1072.

2-Phenylfuro[3,2-*b*]pyridine (4a):[32] Yield: >99%; brown powder; mp 91–93 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.55 (d, J = 4.8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.24 (s, 1H), 7.22–7.19 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.7, 149.0, 148.0, 146.0, 129.7, 129.6, 128.9, 125.3, 118.8, 117.8, 102.4; MS: m/z (%) = 196 (M^+, 100); HR-MS: m/z = 196.0767, calcd. for $C_{13}H_{10}NO$: 196.0762.

2-Phenylbenzofuran-6-carboxyclic acid (3m): Yield: 93%; pale yellow powder; mp 189–192 °C; ^{1}H NMR (300 Hz, MeOD): δ = 8.17 (s, 1H), 7.95–7.92 (m, 3H), 7.66 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.27 (s, 1H); ^{13}C NMR (75.4 MHz, MeOH-d_4): δ = 169.6,

159.0, 154.3, 133.7, 129.7, 129.0, 128.6, 126.6, 124.9, 124.3, 120.3, 112.1, 101.1; MS; *m/z* (%) = 239 (M^+, 100), 238 (33); HR-MS: *m/z* = 239.0718, calcd. for $C_{15}H_{11}O_3$: 239.0708.

2-(3,4-Dichlorophenyl)benzofuran (3l): Yield: 87%; pale yellow powder; mp 153–155 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.98 (s, 1H), 7.77 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.56–7.53 (m, 2H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.29–7.28 (m, 1H), 7.07 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.5, 153.4, 133.2, 132.3, 130.8, 130.4, 128.8, 126.6, 125.0, 124.0, 123.3, 121.2, 111.3, 102.7; MS: *m/z* (%) = 265 (M+2, 65), 263 (M^+, 100), 262 (86), 227 (59); HR-MS: *m/z* = 263.0048, calcd. for $C_{14}H_9Cl_2O$: 263.0030.

2-(4-*tert*-Butylphenyl)furo[3,2-*b*]pyridine (4b): Yield: >99%; pale yellow powder; mp 135–137 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.51 (d, *J* = 4.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.20–7.16 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.9, 152.9, 149.2, 147.9, 145.9, 126.9, 125.9, 125.1, 118.5, 117.6, 101.8, 34.9, 31.2; MS: *m/z* (%) = 252 (M^+, 100), 251 (54); HR-MS: *m/z* = 252.1325, calcd. for $C_{17}H_{18}NO$: 252.1320.

2-(3-Chlorophenyl)furo[3,2-*b*]pyridine (4g): Yield: >99%; pale yellow powder; mp 130–132 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.55 (bs, 1H), 7.88 (s, 1H), 7.78–7.75 (m, 2H), 7.43–7.35 (m, 2H), 7.26–7.20 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.9, 148.7, 146.4, 135.0, 131.4, 130.2, 129.4, 125.2, 123.3, 119.2, 117.9, 103.5; MS: *m/z* (%) = 230 (M^+, 100), 167 (50); HR-MS: *m/z* = 230.0308, calcd. for $C_{13}H_9ClNO$: 230.0310.

2-(4-Methoxyphenyl)furo[3,2-*b*]pyridine (4c): Yield: >99%; yellow powder; mp 154–156 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.53 (bs, 1H), 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.39 (dt, *J* = 7.6, 1.5 Hz, 2H), 7.22–7.17 (m, 1H), 7.12–7.03 (m, 2H), 4.02 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.7, 159.8, 149.4, 145.8, 126.8, 122.5, 117.3, 114.3, 100.8, 55.4 cm; MS: *m/z* (%) = 226 (M^+, 100), 211 (93), 182 (53); HR-MS: *m/z* = 226.0821, calcd. for $C_{14}H_{12}NO_2$: 226.0810.

2-(3,5-Dimethoxyphenyl)furo[3,2-*b*]pyridine (4d): Yield: 76%; pale yellow powder; mp 57–60 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.53 (d, *J* = 4.0 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.22–7.18 (m, 2H), 7.05 (d, *J* = 2.2 Hz, 2H), 6.52 (7, *J* = 2.1 Hz, 1H), 3.88 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 161.2, 159.4, 148.9, 147.9, 146.1, 131.4, 118.9, 117.8, 103.4, 102.9, 101.9, 55.5 cm^{-1}; MS: *m/z* (%) = 256 (M^+, 100); HR-MS: *m/z* = 256.0883, calcd. for $C_{15}H_{14}NO_3$: 256.0895.

2-(4-Methoxy-2-methylphenyl)furo[3,2-*b*]pyridine (4f): Yield: 64%; pale yellow powder; mp 139–141 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.51 (d, *J* = 4.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.21–7.18 (m, 1H), 7.01 (s, 1H), 6.89–6.85 (m, 2H), 3.86 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.3, 159.6, 149.3, 147.2, 145.7, 138.2, 129.7, 122.0, 118.4, 117.4, 116.8, 111.6, 104.9, 55.3, 22.1; MS: *m/z* (%) = 240 (M^+, 100), 225 (42); HR-MS: *m/z* = 240.1005, calcd. for $C_{15}H_{14}NO_2$: 240.1001.

2-(3,4-Dichlorophenyl)furo[3,2-*b*]pyridine (4h): Yield: 82%; white powder; mp 160–164 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.57 (bs, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.71 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.26–7.20 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.0, 148.6, 146.5, 133.5, 133.4, 131.0, 129.7, 126.9, 124.4, 119.5, 118.0, 103.8; MS: *m/z* (%) = 266 (M+2, 61), 264 (M^+, 100); HR-MS; *m/z* = 263.9933, calcd. for $C_{13}H_8Cl_2NO$: 263.9930.

2-(Pyridin-2-yl)furo[3,2-b]pyridine (4i): Yield: 95%; brown powder; mp 102–104 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.37 (d, *J* = 4.7 Hz, 1H), 8.22 (d, *J* = 4.7 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.49–7.43 (m, 2H), 7.26 (s, 1H), 6.97–6.88 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.4, 150.1, 148.5, 146.6, 136.9, 123.7, 120.2, 119.6, 118.3, 105.7; MS: *m/z* (%) = 197 (M^+, 100); HR-MS: *m/z* = 197.0642, calcd. for $C_{12}H_9N_2O$: 197.0640.

2-(2-Methoxyphenyl)furo[3,2-*b*]pyridine (4e): Yield: 84%; brown powder; mp 95–97 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.53 (bs, 1H), 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.39 (dt, *J* = 7.6, 1.5 Hz, 2H), 7.22–7.17 (m, 1H), 7.12–7.03 (m, 2H), 4.02 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.0, 155.9, 149.6, 145.7, 130.3, 126.9, 120.7, 118.6, 117.3, 111.2, 107.3, 55.5; MS: *m/z* (%) = 226 (M^+, 100), 197 (45), 183 (53); HR-MS: *m/z* = 226.0810, calcd. for $C_{14}H_{12}NO_2$: 226.0803.

5-Fluoro-2-phenylbenzofuran (3n):[33] Yield; 95%, pale yellow powder; mp 133–135 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.86 (d, *J* = 7.4 Hz, 2H), 7.49–7.25 (m, 5H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.05–6.98 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.9, 157.8, 157.7, 151.1, 130.1, 128.9, 128.8, 125.0, 112.0, 111.8, 111.7, 106.5, 106.2, 101.4; IR (film): ν = 2927, 1749, 1683, 1652 cm^{-1}; MS: *m/z* (%) = 213 ($[M+H]^+$, 60), 212 (M^+, 100); HR-MS: *m/z* = 213.0715, calcd. for $[C_{14}H_{10}FO]^+$ $[M+H]^+$: 213.0716.

5-Nitro-2-phenylbenzofuran (3o):[3f] Yield: 88%; yellow powder; mp 148–153 °C (Lit.[34] 152–153 °C); ^{1}H NMR (300 Hz, $CDCl_3$): δ = 8.51 (d, *J* = 1.9 Hz, 1H), 8.23 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.55–7.32 (m, 4H), 7.13 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.3, 157.6, 132.5, 129.7, 129.2, 129.0, 128.4, 125.3, 120.1, 117.3, 111.4, 101.6; IR (film): ν = 2926, 1615, 1596 cm^{-1}; MS: *m/z* (%) = 240 ($[M+H]^+$, 100), 239 (M^+ 60); HR-MS: *m/z* = 240.0658, calcd. for $[C_{14}H_{10}NO_3]^+$: 240.0661.

2-Phenyl-5-(trifluoromethyl)benzofuran (3p): Yield: 90%; white powder; mp 115–120 °C; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 77.89–7.87 (m, 3H), 7.61–7.26 (m, 5H), 7.05 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.8, 156.1, 129.7, 129.3, 129.2, 128.9, 125.9, 125.1, 121.3, 121.2, 118.5, 118.4, 111.5, 101.2; IR (film): ν = 1635, 1451, 1256 cm^{-1}; MS: *m/z* (%) = 263 ($[M+H]^+$, 60), 262 (M^+, 100), 243 (50); HR-MS: *m/z* = 263.0672, calcd. for $[C_{15}H_{10}F_3O]^+$ $[M+H]^+$: 263.0684.

2-Cyclopentylbenzofuran (3q): Yield: 91%; colorless oil; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.49 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.26–7.16 (m, 3H), 6.39 (s, 1H), 3.24 (q, *J* = 7.3 Hz, 1H), 2.15–2.07 (m, 2H), 1.83–1.69 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.2, 154.6, 128.9, 123.0, 122.3, 120.1, 110.7, 100.3, 39.0, 31.7, 25.3; IR (film): ν = 2958, 2870, 1662, 1454, 1253 cm^{-1}; MS: *m/z* (%) = 187 (M^+, 100), 186 (60); HR-MS: *m/z* = 187.1121, calcd. for $C1_3H_{15}O$: 187.1123.

2-(Cyclohex-1-en-1-yl)benzofuran (3r): Yield: >99%; brown oil; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.28–7.17 (m, 2H), 6.65 (bs, 1H), 6.52 (s, 1H), 2.42 (bs, 2H), 2.30 (bs, 2H), 1.86–1.68 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.5, 154.5, 129.2, 127.2, 126.1, 123.8, 122.5, 120.6, 110.8, 100.1, 25.5, 25.0, 22.4, 22.2; MS: *m/z* (%) = 199 (M^+, 100), 198 (65); HR-MS: *m/z* = 199.1132, calcd. for $C_{14}H_{15}O$ 199.1123.

1,3-Di(benzofuran-2-yl)propane (3s):[8k] Yield: 90%; pale yellow oil; ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 7.49$ (d, $J = 8.7$ Hz, 2H), 7.43 (d, $J = 7.3$ Hz, 2H), 7.25–7.17 (m, 4H), 7.27–7.18 (m, 4H), 6.44 (s, 2H), 2.88 (d, $J = 7.4$, 4H); 2.22 (quin, $J = 14.9$, 7.4 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 158.5$, 154.7, 128.8, 123.2, 122.5, 120.3, 110.8, 102.4, 27.7, 25.7; IR (film): $\nu = 1600$, 1587, 1454 cm^{-1}; MS: m/z (%) = 277 (M^+, 30), 146 (14), 144 (100), 131 (33); HR-MS: $m/z = 277.1158$, calcd. for $C_{19}H_{17}O_2$: 277.1150.

2-Phenylnaphtho[2,1-*b*]furan (3t):[3f] Yield: 79%; white powder; mp 145–150 °C; ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 8.19$ (d, $J = 8.0$ Hz, 1H), 7.97–7.93 (m, 3H), 7.76–7.69 (m, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.54–7.46 (m, 4H), 7.37 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 155.4$, 152.4, 130.7, 130.5, 128.9, 128.8, 128.3, 127.6, 126.3, 125.2, 124.7, 124.6, 123.5, 112.3, 100.5; IR (film): $\nu = 2930$, 2845, 1630 cm^{-1}; MS: m/z (%) = 245 ($[M+H]^+$, 100); HR-MS: $m/z = 245.0893$, calcd. for $C_{18}H_{13}O^+$ $[M+H]^+$: 245.0888.

5-Methyl-2-phenylbenzofuran (3u):[35] Yield: 69%; white powder; mp 130–132 °C; ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 7.85$ (d, $J = 7.7$ Hz, 2H), 7.44 (t, $J = 8.2$ Hz, 2H), 7.39–7.34 (m, 3H), 7.09 (d, $J = 7.1$ Hz, 1H), 6.96 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 156.0$, 153.4, 132.5, 130.7, 129.3, 128.8, 128.5, 125.6, 124.9, 120.8, 110.7, 101.1, 21.4; IR (film): $\nu = 2959$, 2863, 1474, 1265 cm^{-1}; MS: m/z (%) = 209 ($[M+H]^+$, 100), 175.1 (30); HR-MS: $m/z = 209.0891$, calcd. for $C_{15}H_{13}O^+$ $[M+H]^+$: 209.0888.

Synthesis of 2-Bromophenyl Benzoate

To a stirred solution of 2-bromophenol (1.1 mL, 10.0 mmol) in dry THF (15 mL), triethylamine (1.50 mL, 20.8 mmol) and benzoyl chloride (1.50 mL, 12.9 mmol) were added dropwise at 0 °C under argon. The reaction mixture was stirred at room temperature for 15 min, then it was quenched with water (5 mL). The organic layer was separated and the aqueous phase was extracted twice with diethyl ether (2×15 mL). The combined organic extracts were washed with NH_4Cl (5 mL), dried over anhydrous sodium sulfate and concentrated under vacuum to give a colorless oil. This residue was purified by flash chromatography using ethyl acetate/hexane as eluent, to provide pure 2-bromophenyl benzoate as a colorless oil;[20b] yield: 2.89 g (>99%). ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 8.30$ (d, $J = 7.1$ Hz, 2H), 7.69–7.65 (m, 2H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.40 (dt, $J = 8.0$, 1.5 Hz, 1H), 7.33–7.30 (m, 1H), 7.18 (dt, $J = 7.6$, 1.7 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 164.3$, 148.5, 133.9, 133.5, 130.4, 129.0, 128.7, 128.6, 127.4, 124.0, 116.4; HR-MS: $m/z = 276.9792$, calcd. for $C_{13}H_{10}BrO_2$: 276.9786.

Synthesis of 1-Bromo-2-[1-phenylvinyl)oxy]benzene (5a)

To a stirred solution of 2-bromophenyl benzoate (823.1 mg, 2.99 mmol) in dry THF (10 mL), Tebbe's reagent, 0.5 M solution in toluene (10.8 mL, 5.39 mmol) was added dropwise at room temperature under argon. The reaction mixture was refluxed overnight, and after cooling, quenched with water (5 mL). The organic phase was separated and the aqueous layer extracted with ethyl acetate (2×15 mL). The combined organic phases were washed with NH_4Cl (5 mL), dried over anhydrous sodium sulfate and concentrated under vacuum to give a yellow oil, which was purified by flash chromatography using ethyl acetate/hexane as eluent, to provide pure 1-bromo-2-[1-phenylvinyl)oxy]benzene **5a** as a yellow oil; yield: 180.5 mg (20%). ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 7.75$–7.73 (m, 2H), 7.62 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.42–7.29 (m, 4H), 7.13 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.03 (dt, $J = 7.6$, 1.6 Hz, 1H), 5.02 (d, $J = 2.7$ Hz, 1H), 4.29 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 158.7$, 152.5, 134.7, 133.7, 129.0, 128.6, 128.4, 125.6, 125.4, 121.8, 115.4, 91.2; HR-MS: $m/z = 274.0012$, calcd. for $C_{14}H_{12}BrO$: 273.9993.

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