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Cobalt(III)-Catalyzed Construction of Benzofurans, Benzofuranones and One-Pot Orthogonal C−H Functionalizations to Access Polysubstituted Benzofurans

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Abstract: Benzofuran and benzofuranone derivatives have been synthesized through exclusive 5-*exo-dig* intramolecular hydroarylation using the amide-directed, cost-effective, high-valent Cp*Co^{III}-catalytic system. Challenging one-pot, orthogonal C−H functionalizations using two different electrophiles are also reported to afford polysubstituted benzofurans. Several valuable functional group interconversions along with removal of the amide directing group provide a route to access several diversely functionalized benzofurans. The mechanistic study suggests a reversible cobaltation step is operative here.

Keywords: benzofuran • benzofuranone • cobalt • intramolecular • orthogonal C−H activation

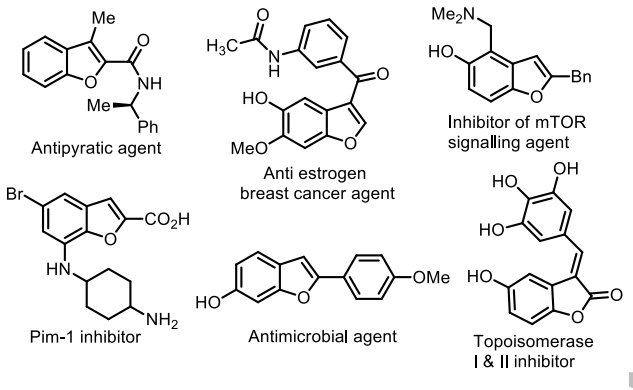
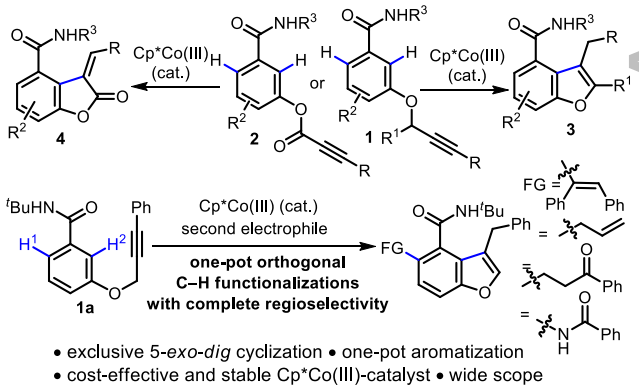


Figure 1. Bioactive benzofuran and benzofuranone derivatives.

Benzofuran and benzofuranone are privileged heterocycle motifs present in many natural products, biologically active compounds, pharmaceuticals and drugs (Figure 1).[1,2] They are also a key component found in organic materials possessing hole-transferring[3a] and photosensitizing properties.[3b] Owing to their diverse applications, the synthesis of this heterocyclic-backbone always lures chemists' attention. As a result, several synthetically feasible strategies have been developed for the construction of the benzofuran core such as transition metal-catalyzed annulation of alkynyl-substituted phenols,[4] direct functionalization of phenols with alkynes and other substrates,[5,6] or one-pot cross-coupling and subsequent annulation of *ortho*-halo phenols with alkynes.[7] Though a number of synthetic routes have been reported, the development of conceptually different synthetic strategies enabling synthesis of diversely substituted benzofurans are still in great demand. In this context, transition metal-catalyzed, directed intramolecular C−H bond functionalization approach can be very much effective. Additionally, a directing group-promoted, one-pot, orthogonal C−H functionalizations can lead to the rapid access to polysubstituted benzofuran derivatives.

However, intramolecular C−H activation is not always sterically facile. The possibility of an intermolecular reaction renders the reaction profile more complicated. Furthermore, in one-pot, two-fold, orthogonal C−H functionalizations, due to electronic-, steric- or coordinating-effect of mono-functionalized product, the situation becomes more challenging along with the selectivity issue.[8] Generally, directing group and catalytic systems are too specific to an electrophile for selective bond formation, which indicates another difficulty in two-fold orthogonal C−H functionalization.



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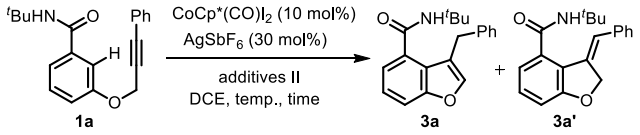
Scheme 1. Benzofuran and benzofuranone synthesis and one-pot, two-fold, orthogonal C−H functionalizations.

Intramolecular C−H bond functionalization often proves to be very advantageous for manufacturing heterocyclic motifs with fused ring system by stitching a molecular unit with desirable regioselectivity.[9] In this context, various research groups have reported the Rh, Ru, Ir, and Co-catalyzed, directed intramolecular hydroarylation of olefin-tethered arenes to synthesize several carbo and heterocycles.[10a-g] The Park and Glorius groups[11a,b] also described a Rh and Co-catalyzed intramolecular hydroarylation reaction of alkyne-tethered hydroxamic esters. Recently, the Shibata group demonstrated the C−H alkenylation on *N*-(pent-4-ynyl)indole using a low valent Rh- and Ir-catalyst.[11c] Herein, inspired by the recent development of high valent cobalt catalysis[12] which was pioneered by Kanai and Matsunaga *et al*. we report a novel approach to construct benzofuran and benzofuranone cores through cost-effective, high-valent, cobalt-catalyzed, amide-directed, intramolecular C−H activation. This method offers complete 5-*exo*-*dig* cyclization followed by aromatization in a one-pot fashion (Scheme 1). 5-Substituted benzofurans are also synthesized through one-pot, two-fold, unsymmetrical C−H functionalizations by employing a second electrophile.

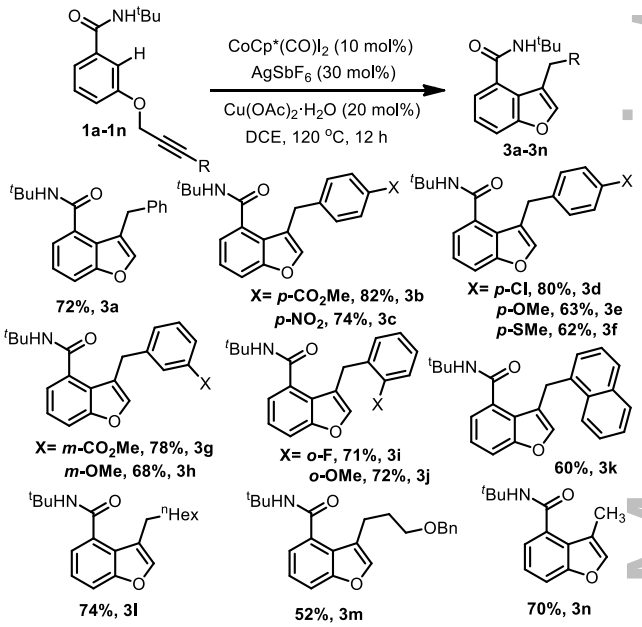
Table 1. Optimization of the reaction conditions.[a]



Entry	Additive II (mol%)	Temp [°C]	Time [h]	Yield [%][b] **3a**	**3a′**
1	$Cu(OAc)_2·H_2O$ (100)	100	6	4	57
2	$Cu(OAc)_2·H_2O$ (100)	120	6	8	60
3	none	120	6	28	36
4	none	120	12	32	28
5	$Cu(OAc)_2·H_2O$ (10)	120	12	58	12
6	$Cu(OAc)_2·H_2O$ (20)	120	12	72	4
7	$Cu(OAc)_2·H_2O$ (40)	120	12	8	63
8	NaOAc (20)	120	12	4	68
9	KOAc (20)	120	12	32	36
10	CsOAc (20)	120	12	28	35

[a]**1a** (0.2 mmol) and 2.5 mL DCE were used. [b]Isolated yields.

We started the optimization of the reaction conditions by taking the substrate **1a** in the presence of 10 mol% Cp*Co(CO)I_2 as a catalyst and 30 mol% $AgSbF_6$ as a silver additive (Table 1). Initially, conducting the reaction by addition of 1.0 equiv of $Cu(OAc)_2·H_2O$ as a second additive in 1,2-dichloroethane (DCE) solvent at 100 °C provided the exocyclic product **3a′** as a major product in 57% yield (Table 1, entry 1). On increasing the temperature, the yield of **3a** increased slightly (entry 2). In the absence of second additive, the product **3a** formed preferentially (entries 3-4). The incorporation of 10 mol% $Cu(OAc)_2·H_2O$, largely improved the desired ratio, providing 58% of **3a** as the major product (entry 5). The best result was obtained in the presence of 20 mol% of $Cu(OAc)_2·H_2O$ (**3a**, 72%). Surprisingly, with 40 mol% $Cu(OAc)_2·H_2O$, the selectivity was completely reversed, yielding **3a′** as the major product (entry 6 vs 7). Though on changing counter cation from Na to K alters the selectivity but the complete selectivity towards **3a** was not obtained (entries 8-9). CsOAc was also not a suitable additive for this reaction (entry 10).

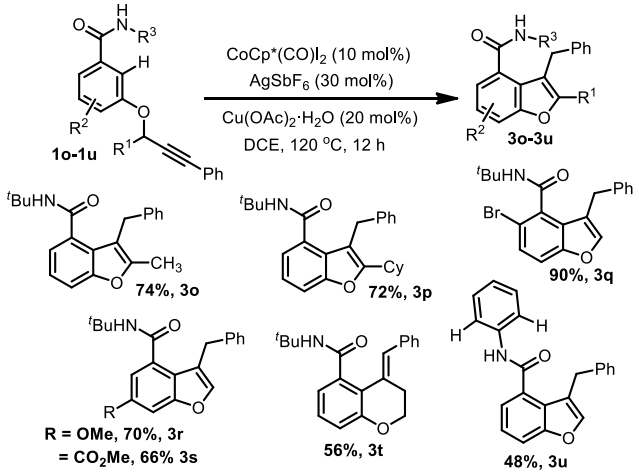


Scheme 2. Scope of 3-substituted benzofurans. **1a-1n** (0.2 mmol) and 2.5 mL DCE were used. All yields are isolated yields.

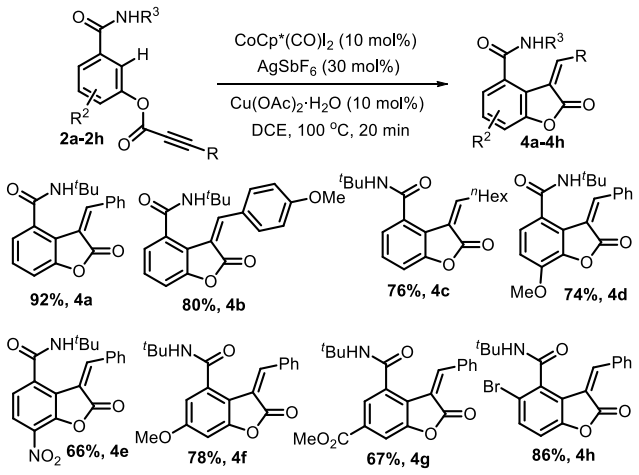
Having this optimized Co^{III}-catalytic system in hand (entry 6, Table 1), we examined the scope of this reaction by varying first the alkyne moiety (Scheme 2). Electron-withdrawing functional groups such as CO_2Me, NO_2, and Cl at the *para*-position of the phenyl ring are tolerated and furnished **3b-3d** in 74-82% yields. Alkynes bearing electron-donating substituents at the phenyl ring are also suitable substrates (**3e-3f**, 62-63%). Likewise, differently *meta*- and *ortho*-substituted phenyl rings attached to the alkyne also responded well under the reaction conditions to provide products **3g-3j** in 68-78% yields. Sterically demanding 1-naphthyl alkyne also proceeded in the reaction to provide **3k** in 60% yield. Gratifyingly, alkynes bearing *n*-hexyl and a benzyl-protected ether also afforded benzofurans **3l-3m** in 52-74% yields. Interestingly, *in situ* trimethylsilyl-deprotected product **3n** was isolated in 70% yield from the corresponding TMS-substituted alkyne substrate. However, our attempt to obtain **3n** by using

the corresponding terminal alkyne did not provide the desired product under the optimized conditions.

The synthesis of 2-substituted benzofurans **3o**-**3p** were achieved in 72-74% yields by incorporating methyl and cyclohexyl substitutions at the appropriate position of the alkyne moiety (Scheme 3). We subsequently investigated the effect of different substitution on the aryl ring attached to the amide directing group. All the substitutions were well tolerated to produce **3q**-**3s** in good to excellent yields. On increasing the alkyne chain length, the *exo*-attack delivered a chroman moiety **3t** in 56% yield. In the case of amide **1u**, one out of the four possible C−H bonds reacted selectively to provide benzofuran derivative **3u** in 48% yield.

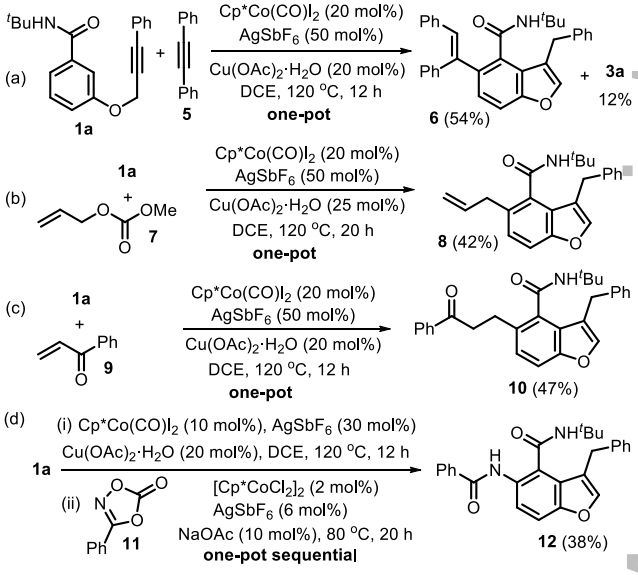


Scheme 3. Synthesis of polysubstituted benzofurans. **1o-1u** (0.2 mmol) and 2.5 mL DCE were used. All yields are isolated yields.



Scheme 4. Scope of benzofuranones. **2a-2h** (0.2 mmol) and 2.5 mL DCE were used. All yields are isolated yields.

Considering the immense importance of benzofuranones,[13] several benzofuranone derivatives were synthesized by extending our method (Scheme 4). This method afforded a rapid generation of benzofuranone derivatives within 20 minutes. Interestingly, in the absence of acetate source, the reaction provided similar results, albeit with longer reaction time (8 h). Aryl or alkyl-substituted alkynes are fully compatible and delivered benzofuranones **4a-4c** in good to excellent yields (76-92%). Subsequently, the incorporation of various functional groups such as methoxy, nitro, ester, and bromide on the aryl ring are well tolerated under the reaction conditions and furnished polysubstituted benzofuranone derivatives **4d-4h** in 66 to 86% yields. The geometry of the hydroarylated products **3a′**, **3t**, and **4a-4h** were assigned in analogy to our previous work.[14]



Scheme 5. One-pot, orthogonal, two-fold C−H functionalizations.

Although, single directing group promoted two-fold C−H activations are well documented, one-pot, orthogonal C−H functionalizations are scarce.[15] In our continuous efforts to develop one-pot sequential catalytic methods,[15a-b] herein amide-directed two-fold orthogonal C−H functionalizations are reported by employing two different electrophiles. The major challenge to execute this method is to get the desired regioselectivity in our product. In the presence of starting material **1a** and diphenyl acetylene **5**, one-pot unsymmetrical intra- and intermolecular hydroarylations were achieved, and C5-alkenylated benzofuran scaffold **6** was isolated in 54% yield (Scheme 5a).[14] The excellent regioselectivity of the reaction was supported by the fact that no intermolecular hydroarylated product at the 2-position of **1a** was detected. On introducing allylating agent **7** as a coupling partner, intramolecular hydroarylation and allylation occurred simultaneously to afford C5-allylated benzofuran **8** in 42% yield (Scheme 5b).[16a-c] In the presence of an *α,β*-unsaturated ketone **9**, product **10** is obtained in 47% yield via simultaneous intramolecular hydroarylation and C–H alkylation reactions (Scheme 5c).[16d] This one-pot orthogonal C−H

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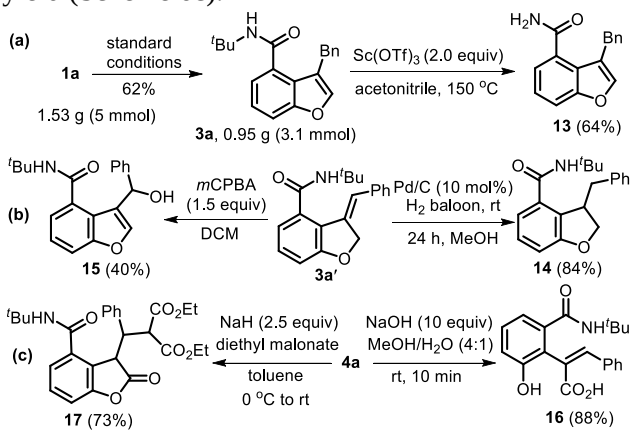
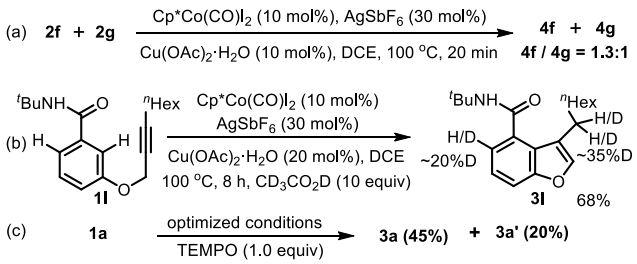
functionalizations strategy was also applied to the intramolecular hydroarylation and C−H amidation reaction to furnish C5-aminated benzofuran **12** in 38% yield (Scheme 5d).[12i] Here the amidation reaction was conducted after completing the intramolecular-hydroarylation reaction in a one-pot sequential fashion as the amidating agent **11** couldn't survive for sufficient time under the reaction conditions in the presence of $Cu(OAc)_2$ at 120 °C. Our attempt to conduct both reactions together resulted in a complex reaction mixture.

To examine the potential utility and practicality of our method, a gram scale synthesis of benzofuran derivative **3a** was performed. Under the standard conditions, 0.95 g of **3a** was successfully synthesized from 1.53 g of starting material (Scheme 6a). Simple amide **13** is synthesized by deprotection of the tertiary amide of **3a** using scandium triflate as a Lewis acid catalyst,[17a] which lays a platform for accessing several 4-substituted benzofuran derivatives. Dihydrobenzofurans are very important structural motif found in many biologically active and pharmaceutically important molecules such as ramelteon, lithospermic acid etc.[10a,17b] In the presence of palladium-charcoal and hydrogen, dihydrobenzofuran derivative **14** was readily synthesized from **3a′** (Scheme 6b). On treatment of **3a′** with *meta*-chloroperbenzoic acid, benzofuryl alcohol **15** was prepared, which can be used as a dienophile for [4+3] cycloaddition to afford fused 5,7,6-tricyclic skeleton present in the various natural products.[17c] The synthesis of benzene derivatives bearing several unique substituents are of immense importance and is a challenging synthetic task.[18a] Simple hydrolysis of compound **5a** provided *α,β*-unsaturated carboxylic acid **16**, a potent structural analogue for various biologically active molecules.[18b] This also provides a route to synthesize polysubstituted benzene derivatives having unique substitution pattern. Compound **4a** is also a very effective Michael acceptor and reacted with sodium diethyl malonate to produce **17** in 73% yield (Scheme 6c).

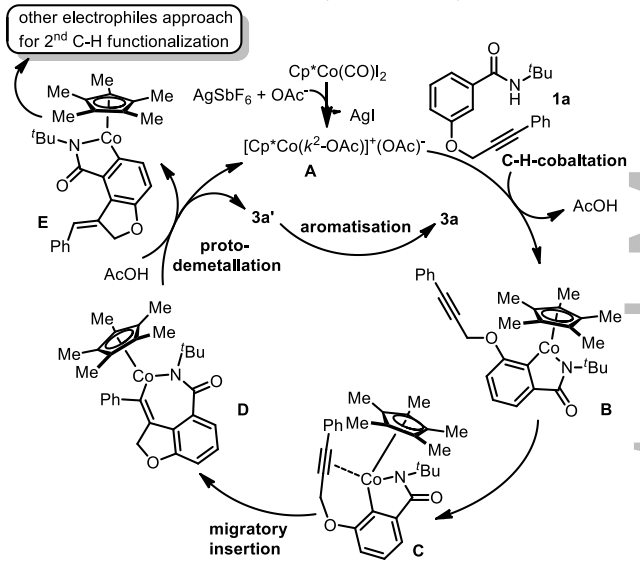


Scheme 6. Gram scale synthesis of **3a** and application of the hydroarylated products.



Scheme 7. Mechanistic study.

On performing the competition experiment using electronically different benzamides tethered alkyne **2f** and **2g** revealed that electron-rich benzamides are preferentially converted to **4g** with almost a 1.3:1 ratio, which indicated a base-assisted intermolecular electrophilic substitution reaction (BIES) type mechanism (Scheme 7a).[19] Incorporation of deuterium in the presence of CD_3CO_2D at the C5-position of benzofuran suggests the reversible cobalt incorporation at the *ortho*-position (Scheme 7b). As the presence of TEMPO did not inhibit the formation of the product, thus excluding the involvement of any stable radical intermediate (Scheme 7c).



Scheme 8. Proposed mechanism.

On the basis of the above observations and the previous literature precedents,[14] a plausible mechanism is proposed (Scheme 8). Initially, treatment of a cobalt catalyst with $AgSbF_6$ and $Cu(OAc)_2{\cdot}H_2O$ led to the formation of reactive cobalt(III)-species **A**, which upon reaction with **1a** affords the cyclic cobalt species **B** through acetate assisted directed C−H functionalization. Subsequently, the cobalt in the complex **B** experiences chelation from the alkyne present in the molecule and generates an intermediate **C**. Subsequent migratory insertion of intermediate **C**, delivers a seven-membered metallocycle **D**, which upon protonolysis regenerates the active catalyst **A** along with the product **3a´**. Aromatisation of **3a´**

furnishes **3a** which can undergo a second C−H functionalization. In another possibility, in presence of the second electrophile, the intermediate **E** proceeds for the second C−H functionalization. Compared to the intermolecular C−H functionalization, intramolecular funtionalization was much faster, and we observed that aromatization of **3a′** to furnish **3a** required longer reaction time.

In summary, we have developed a novel strategy for the synthesis of benzofuran and benzofuranone derivatives through high-valent Co(III)-catalyzed directed C−H bond functionalization. The reaction exhibits broad scope as differently substituted benzofurans and benzofuranones were synthesized. The single directing group promoted, one-pot, sequential, two-fold orthogonal C−H functionalization have also been demonstrated. This efficient method can easily be scaled up to grams, and is very much pragmatic for the preparation of various synthetically valuable intermediates.

Experimental Section

Procedure for benzofuran synthesis: *N*-(*tert*-Butyl)-3-((3-phenylprop-2-yn-1-yl)oxy)benzamide **1** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw-capped sealed tube and 2.5 mL of 1,2-dichloroethane was added. Then catalyst $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (8.0 mg, 0.04 mmol, 20.0 mol%) and $AgSbF_6$ (20.6 mg, 0.06 mmol, 30.0 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 12 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to obtain products **3-4**.

Procedure for benzofuranone synthesis: 3-(*tert*-Butylcarbamoyl)phenyl 3-phenylpropiolate **2** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw-capped sealed tube and 2.5 mL of 1,2-dichloroethane was added. Then catalyst $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (4.0 mg, 0.02 mmol, 10.0 mol%) and $AgSbF_6$ (20.6 mg, 0.06 mmol, 30.0 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 100 °C for 20 min. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to obtain pure products **5**.

Procedure for one-pot, orthogonal, two-fold C−H functionalizations:

(*E*)-3-Benzyl-*N*-(*tert*-butyl)-5-(1,2 diphenylvinyl)benzofuran-4-carboxamide (**6**): *N*-(*tert*-butyl)-3-((3-phenylprop-2-yn-1-yl)oxy)benzamide **1a** (61.4 mg, 0.2 mmol, 1.0 equiv) and diphenyl acetylene **5** (46.3 mg, 1.3 equiv) were taken in a 12.0 mL screw-capped sealed tube and 2.5 mL of 1,2-dichloroethane was added to the mixture. Then catalyst $Cp^*Co(CO)I_2$ (19 mg, 0.04 mmol, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (8.0 mg, 0.04 mmol, 20 mol%) and $AgSbF_6$ (34.3 mg, 0.1 mmol, 50.0 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 12 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to afford **6** as a major product (52.2 mg, 54%) along with **3a** (7.2 mg, 12%) as a minor product.

5-Allyl-3-benzyl-*N*-(*tert*-butyl)benzofuran-4-carboxamide (**8**): *N*-(*tert*-butyl)-3-((3-phenylprop-2-yn-1-yl)oxy) benzamide **1a** (61.4 mg, 0.2 mmol, 1.0 equiv) and allyl carbonate **7** (46.4 mg, 2 equiv) were taken in a 12.0 mL screw-capped sealed tube and 2.5 mL of 1,2-dichloroethane was added to the mixture. Then catalyst $Cp^*Co(CO)I_2$ (19 mg, 0.04 mmol, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (10.0 mg, 0.05 mmol, 25 mol%) and $AgSbF_6$ (34.3 mg, 0.1 mmol, 50 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 12 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to give **8** as a white solid (29.3 mg, 42%).

3-Benzyl-*N*-(*tert*-butyl)-5-(3-oxo-3-phenylpropyl)benzofuran-4-carboxamide (**10**): *N*-(tert-butyl)-3-((3-phenylprop-2-yn-1-yl)oxy)benzamide **1a** (61.4 mg, 0.2 mmol, 1.0 equiv) and phenyl vinyl ketone **9** (52.8 mg, 2 equiv) were taken in a 12.0 mL screw-capped sealed tube and 2.5 mL of 1,2-dichloroethane was added to the mixture. Then catalyst $Cp^*Co(CO)I_2$ (19 mg, 0.04 mmol, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (8.0 mg, 0.04 mmol, 20 mol%) and $AgSbF_6$ (34.3 mg, 0.1 mmol, 50.0 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 12 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to afford **10** as a major product (40.8 mg, 47%).

5-Benzamido-3-benzyl-*N*-(*tert*-butyl)benzofuran-4-carboxamide (**12**): *N*-(*tert*-butyl)-3-((3-phenylprop-2-yn-1-yl)oxy)benzamide **1a** (30.7 mg, 0.1 mmol, 1.0 equiv) was taken in a 12.0 mL screw-capped sealed tube and 1.5 mL of 1,2-dichloroethane was added. Then catalyst $Cp^*Co(CO)I_2$ (4.8 mg, 0.01 mmol, 10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (4.0 mg, 0.02 mmol, 20 mol%) and $AgSbF_6$ (10.3 mg, 0.03 mmol, 30 mol%) were added successively to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 12 h. After that, 3-phenyl-1,4,2-dioxazol-5-one **11** (18 mg, 1.1 mmol, 1.1 equiv), $[Cp^*CoCl_2]_2$ (1.0 mg, 0.002 mmol, 2.0 mol%), sodium acetate (0.8 mg, 0.001 mmol, 10 mol%) were added to the mixture and allowed to stir at 80 °C for 15 h. After completion of the reaction, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethyl acetate as eluent to give **12** as a white solid (16.0 mg, 38%).

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FULL PAPER

Cobalt(III)-Catalyzed Construction of Benzofurans, Benzofuranones and One-Pot Orthogonal C–H Functionalizations to Access Polysubstituted Benzofurans

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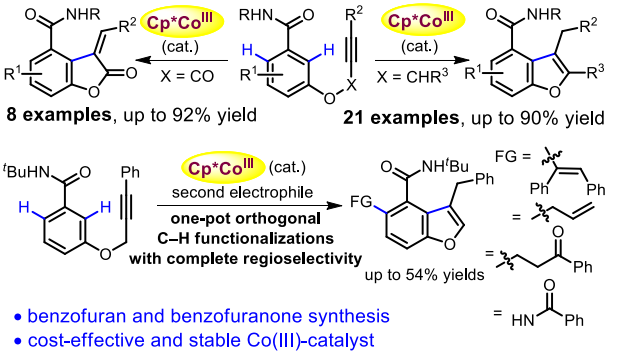

- benzofuran and benzofuranone synthesis
- cost-effective and stable Co(III)-catalyst
- exclusive 5-*exo-dig* cyclisation and aromatization • one- pot, two-fold orthogonal C–H functionalizations • amenable to gram scale