Hydroxyl Assisted, Photoredox/Cobalt Co-catalyzed Semi-Hydrogenation and Tandem Cyclization of *o*-Alkynylphenols for Access to 2,3-Dihydrobenzofurans

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Abstract: Herein, a hydroxyl assisted, photoredox/cobalt co-catalyzed semi-hydrogenation and tandem cyclization of *o*-alkynylphenols is developed towards direct assembly of 2,3-dihydrobenzofurans. Moderate to good yields were obtained for a range of sterically and electronically diverse 2-propynolphenols under mild conditions. Mechanistic studies demonstrated the inevitable role of the alcoholic hydroxyl group with (Z)-alkene as the real intermediate. Finally, a key low-valent cobalt catalyzed intramolecular hydroetherification of alkene is proposed.

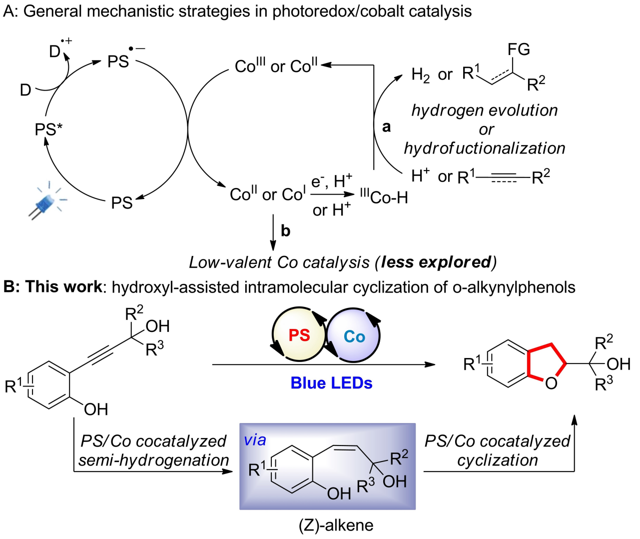
Keywords: cyclization; cobalt catalysis; photoredox catalysis; semi-hydrogenation; 2,3-dihydrobenzofuran

Cobalt, as a first-row transition metal, has gained particular attention in recent years, not only because of its earth-abundant and inexpensive advantages, but also because it offers possibilities of uncovering unique reactivity and selectivity.[1] As a consequence, various valuable cobalt catalytic systems have been developed.[2] Among them, the rational combination of photoredox catalysis with cobalt catalysis turned out to be a vital way to achieve novel and unique transformation since the oxidation state of cobalt could be feasible manipulated via single electron transfer (SET) process under mild conditions.[3]

As shown in scheme 1A, the active low-valent Co^I or cobalt hydride (Co–H) species could generate feasibly *in situ* by the reduction of high-valent cobalt precursors in the presence of electron donor reagent. Nowadays, extensive studies have been conducted in dehydrogenative reactions by using this strategy, in which Co–H reacted with proton to release hydrogen is the key procedure.[3a–c,4] On the other hand, Co–H mediated hydrocarbonation of alkenes represents another important reaction pattern in photoredox/cobalt dual catalysis (Scheme 1Aa). In this respect, Rovis,[5] Maji,[6] König,[7] Collins[8] and other groups[9] have made excellent contributions. However, after extensive literatures survey, it is surprising to discover that the photochemically generated low-valent cobalt complexes were rarely utilized in synthetic chemistry (Scheme 1Ab).[10] Considering that the feasible accessibility and unique reactivity of low-valent Co(I) complexes,[2a] exploration of new reaction patterns involving photoinduced low-valent cobalt species is of great significance and remains a big challenge.

Transition metal catalyzed intramolecular addition of oxygen-nucleophiles to C–C multiple bonds is a step- and atom-economic method for preparing oxygen-heterocycles. A range of transition metals (Pd, Pt, Rh, Ir, Cu, Au, Zn. et. al)[11] have been used to catalyze the transformation via protocols of either activation the C–C multiple bond or activation the O–H bond. However, cobalt is rarely reported for achieving this goal.[12]

Very recently, we disclosed a novel photoredox/cobalt co-catalyzed stereoselective transfer semi-hydrogenation of alkynes to Z-major alkenes.[13] Motivated by the results and envisaged catalytic potential of low-valent cobalt catalyst on O–H activation,[14] we wondered if photoredox/cobalt co-catalytic system could be used for the construction of 2,3-dihydrobenzofurans by using easily accessible *ortho*-alkynylphenols as the substrate via a sequential semi-hydro-



Scheme 1. Photoredox/cobalt mediated reactions. PS = photosensitizer. D = electron donor.

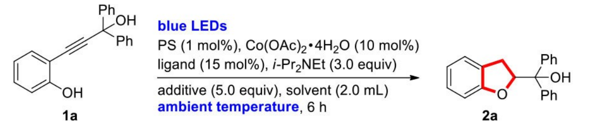
genation of alkynes and low-valent cobalt-mediated intramolecular cyclization processes. Importantly, the resulting 2,3-dihydrobenzofurans are ubiquitous structural motif in a wide range of biologically or pharmaceutically active compounds.[15] Moreover, to the best of our knowledge, directly accessing 2,3-dihydrobenzofurans from 2-alkynyl phenols remains unexplored.

Herein, we wish to report the first example of hydroxyl assisted, photoredox/cobalt cocatalyzed semi-hydrogenation and tandem intramolecular cyclizations in one-pot manipulation for direct construction of 2,3-dihydrobenzofurans from 2-propynolphenols. It's noteworthy that the inevitable role of the alcoholic hydroxyl as the assistant group is demonstrated. Additionally, an unusual low-valent cobalt catalyzed intramolecular hydroetherification of alkene is suggested.

As our continuous efforts on exploring the reactivity of 2-propynolphenol,[16] **1 a** was selected as model substrate for examining the aforenamed hypothesis. The initial investigation used Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ as photosensitizer, Co(OAc)$_2$·4H$_2$O as cobalt catalyst, 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbbpy) as ligand, *i*-Pr$_2$NEt as sacrificial reagent with blue LED irradiation, and several solvents were firstly evaluated (Table 1, entries 1-3). To our delight, the desired product **2 a** was observed in the solvent of CH$_3$CN, THF, and *n*-propanol. Among which, *n*-propanol delivered the best yield up to 65%. Other photosensitizer, such as Ir[ppy]$_2$(bpy)PF$_6$, Ir[ppy]$_2$(dtbbpy)PF$_6$, and 1, 2, 3, 5-tetrakis (carbazol-9-yl)-4, 6-dicyanobenzene (4CzlPN), displayed comparable yields of 50%, 56%, and 60%, respectively (entries 4-6). Then the effect of other ligands was investigated (entries 7–10). 2,2′-Bipyridine (bpy) induced higher efficiency. In order to accelerate the semi-hydrogenation process, proton additives, such as AcOH and H$_2$O, were examined. Fortunately, the relative weaker proton supplier of H$_2$O could further enhance the yield to 75% (entries 11 and 12). A further mixture solvent screening revealed that the mixture of n-propanol and THFcould improve the yield to 84% (entries 13 and 14). Finally, increasing the amounts of H$_2$O gave the highest isolated yield of 85% (entry 15). Control experiments proved that all the parameters, including photosensitizer, cobalt catalyst, organic amine sacrificial reagent, and visible-light irradiation were essential for successful transformation (entries 16–19).

Having established the optimized reaction conditions, the substrate scope for the cyclization was investigated (Table 2). Notably, the substrates with neutral or electron-deficient groups, such as hydrogen, fluoro, chloro, and ester, on the phenolic ring delivered the products in good to excellent yields (**2 a**–**2 d**, 68%–

Table 1. Screening of optimal reaction conditions.[a]



entry	photosensitizer (PS)	ligand	additive	solvent	**2a**
1	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	dtbbpy	–	CH$_3$CN	30%
2	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	dtbbpy	–	THF	33%
3	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	dtbbpy	–	n-Propanol	65%
4	Ir[ppy]$_2$(bpy)PF$_6$	dtbbpy	–	n-Propanol	50%
5	Ir[ppy]$_2$(dtbbpy)PF$_6$	dtbbpy	–	n-Propanol	56%
6	4CZIPN	dtbbpy	–	n-Propanol	60%
7	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	o-Phen	–	n-Propanol	60%
8	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	–	n-Propanol	70%
9	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	Cy$_3$P	–	n-Propanol	50%
10	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	dppp	–	n-Propanol	none
11	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	AcOH	n-Propanol	28%
12	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol	75%
13	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol/CH$_3$CN (4/1)	72%
14	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol/THF (4/1)	84%
15[b]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol/THF (4/1)	90% (85%)[c]
16[b,d]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol/THF (4/1)	none
17[b,e]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	–	H$_2$O	n-Propanol/THF (4/1)	none
18[b]	–	bpy	H$_2$O	n-Propanol/THF (4/1)	none
19[b,f]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	bpy	H$_2$O	n-Propanol/THF (4/1)	none

[a] **1 a** (0.1 mmol), PS (1 mol%), Co(OAc)$_2$·4H$_2$O (10 mol%), Ligand (15 mol%), *i*-Pr$_2$NEt (3.0 equiv.), additive (5.0 equiv.), solvent (2.0 mL), irradiation with blue LEDs for 6 h, the reaction mixture was filtered by a small pad of silica gel after irradiation and ^{1}H NMR yield was reported using Cl$_2$CHCHCl$_2$ as an internal standard. dppp = 1,3-bis (diphenylphosphino) propane.

[b] H$_2$O = 10.0 equiv.

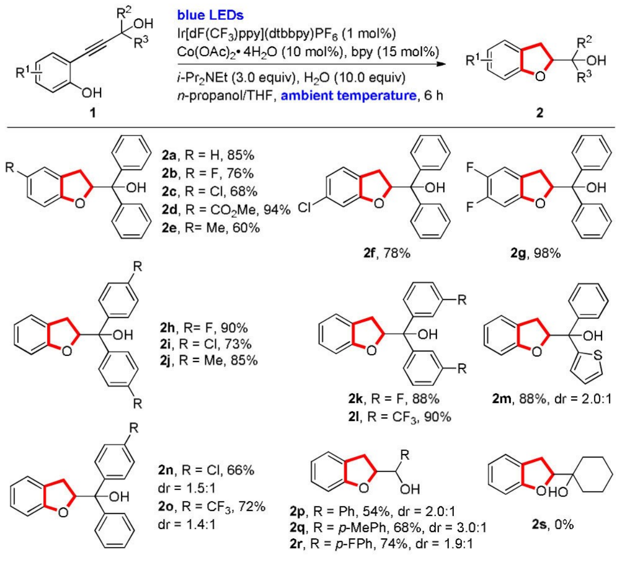
[c] isolated yield.

[d] no *i*-Pr$_2$NEt.

[e] no cobalt catalyst.

[f] in dark.

Table 2. Substrate scope.[a]



[a] Reaction condition: **1** (0.1 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (1 mol%), Co(OAc)$_2$·4H$_2$O (10 mol%), bpy (15 mol%), *i*-Pr$_2$NEt (3.0 equiv.), H$_2$O (10.0 equiv.), *n*-propanol/THF (*v:v* 4:1, 2.0 mL), irradiation with blue LEDs for 6 h, isolated yield was reported, d.r. ratio was determined by ^{1}H NMR analysis.

94%). In contrast, weak electron-donating group, such as methyl, slightly decreased the yield to 60% (**2e**). In the case of chloro on C5 position, the product **2f** was obtained in 78% yield. 3,4-difluoro substituted phenolic led to an excellent yield of 98% (**2g**). Next, the substituents on the diphenylmethanol were screened. Obviously, both electron- withdrawing and electron-donating groups on the symmetric diphenylmethanol could be well tolerated in the conditions, delivering the corresponding products in high yield (**2h**–**2l**, 73%–90%). Unsymmetric diphenylmethanols bearing electron withdrawing groups, such as fluoro and trifluromethyl, delivered the products **2n** and **2o** in 66% or 72% yields, respectively. It's obvious that the heterocycle of thienyl was also compatible to generate the corresponding product **2m** in 88% yield.

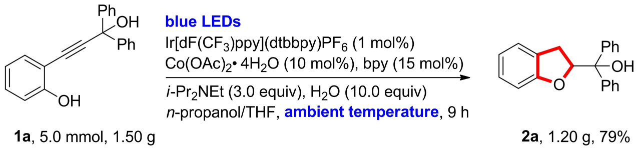
Moreover, monoarylmethanols were also applicable in the reaction. Various substituents, no matter electron-donating or electron-deficient groups on the phenyl ring, could be tolerated in the reaction, giving the corresponding products in moderate to good yields (**2p**–**2r**, 54%–74%). It should note that poor diastereoselectivities were obtained for unsymmetric diphenylmethanols or monoarylmethanols substrates (**2m**–**2r**). Compound **1s**, an example of typical dialkylmethanol, did not show any reaction efficiency, with the observation of semi-hydrogenated products of alkenes.

To demonstrate the potential synthetic application, a gram-scale reaction of **1a** was performed, which gave **2a** (1.20 g) in 79% yield (Scheme 2).

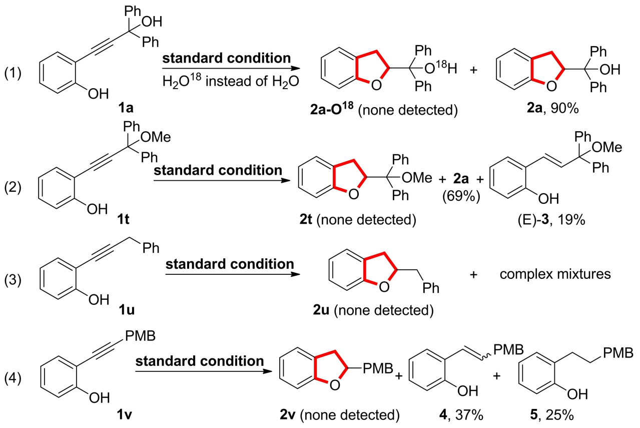
In order to shed light on the role of the hydroxyl group, several control experiments were conducted. Firstly, H_2O^{18} was employed under identical conditions, and no O^{18}-cooperated product was observed (Scheme 3, eq 1). This result proves that the hydroxyl group is intact during the reaction process. Secondely, the methyl protected substrate **1t** was conducted under standard conditions (Scheme 3, eq 2). Interestingly, instead of **2t**, but **2a** and (E)-**3** were isolated in 69% and 19% yields, respectively. Despite the mechanism remains obsucre, we speculate that a low-valent cobalt catalyzed demethoxylation of allyl ether (Tsuji-Trost type reaction) might involve in the reaction.[10c]

Further, hydroxyl-free compounds **1u** and **1v** were subjected to standard conditions, no desired cyclization products were detected (Scheme 3, eqs 3 and 4). Semi-hydrogenated product **4** and over-reduced product **5** were both detected in the case of **1v**. These observations suggest that the hydroxyl group plays a pivotal for the success of the transformation.

To gain more mechanistic insight, several other experiments were performed. Adding 2 equivalents of radical scavengers, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-di-tert-butyl-4-methylphenol (BHT), or 9,10-dihydroanthracene (DHA) to the model reactions, the reaction efficiency



Scheme 2. Gram-scale reaction.

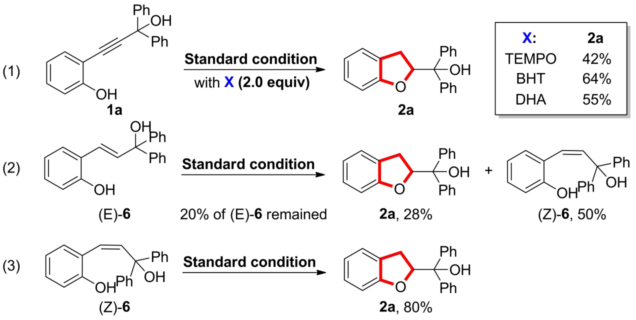


Scheme 3. Determination the role of alcoholic hydroxyl group. ^{1}H NMR yields using $Cl_2CHCHCl_2$ as an internal standard were reported. PMB = *para*-methoxylphenyl.

decreased slightly, indicating that free radicals may not involve in the reaction pathway (Scheme 4, eq 1). Moreover, monitoring of the reaction process showed the apparent generation and consumption of alkene intermediates ((Z)-**6** and (E)-**6**), demonstrating that the reaction proceeded via a sequential semi-hydrogenation/cyclization process (Figure 1, left).

To demonstrate the real intermediate, (E)-**6** and (Z)-**6** were isolated and used as the substrates, respectively. When (E)-**6** was conducted under standard condition, only 28% of product **2a** and 50% of (Z)-**6** were obtained with 20% of starting material remained (Scheme 4, eq 2). When we employed (Z)-**6** as the substrate, the reaction reached full conversion to generate a high yield of 80% for **2a** (Scheme 4, eq 3). Considering that (E)-alkene could be partially isomerized to (Z)-alkene via photoinduced energy transfer process,[13,17] it is reasonable to speculate that (Z)-**6** should be the actually active intermediate.

Besides, control experiments revealed that visible light, photosensitizer, cobalt complex, and *i*-Pr$_2$NEt were essential for the transformation of (Z)-**6** to **2a** (Table S2). To examine the impact of the light, this reaction was also monitored for **2a** with light on/off manipulation (Figure 1, right; Table S3). Continuous transformation after irradiation was noted, suggesting that visible light irradiation promotes the generation of active cobalt species which could further catalyze the cyclization in darkness. Since *i*-Pr$_2$NEt was usually used as the sacrificial reagent for reduction of high-valent cobalt precursors in photoredox/cobalt catalytic system, we deduced that a low-valent cobalt catalyst, such as Co^{I}, may be responsible for the final cyclization step.



Scheme 4. Control experiments. Yields were reported as ^{1}H NMR yields using Cl$_2$CHCHCl$_2$ as an internal standard.

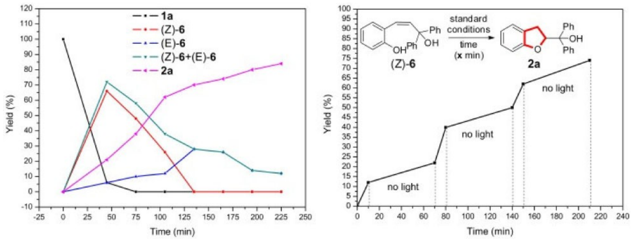
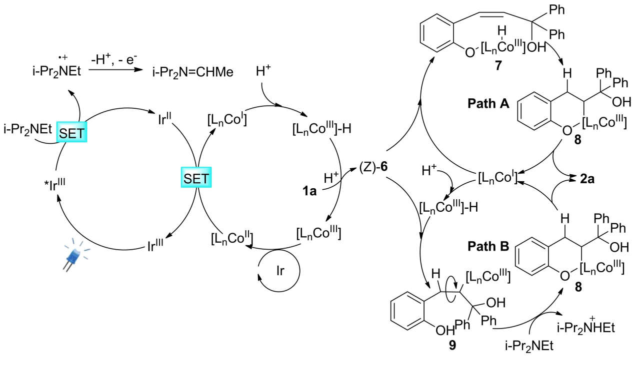


Figure 1. Yield/time diagram for preparation of **2a** (left) and light on/off experiments of (Z)-**6** based system (right).

Subsequently, emission-quenching experiments were conducted (Figure S5). As shown in Figure S5, the experiments revealed that both *i*-Pr$_2$NEt and Co(OAc)$_2$·bpy could quench the excited state of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$. However, the quenching rate of *i*-Pr$_2$NEt is much faster than the cobalt complex. In addition, substrate **1a** could not be an emission quencher of photosensitizer. These results suggest that single electron transfer (SET) of the exited photocatalyst *Ir^{III} dominantly occurs with *i*-Pr$_2$NEt.

In addition, the thermodynamic feasibility of the photoinduced electron transfer was analyzed by the oxidation-reduction potentials. The reduction potential E*III/II of *Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ and the ground state potential E$^{III/II}$ of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ were reported as +1.21 V vs. SCE and −1.37 V vs. SCE, respectively.[18] Meanwhile, the reduction potential E$^{II/I}$ of Co(OAc)$_2$·bpy and the oxidation potential of *i*-Pr$_2$NEt were determined to be −1.18 V vs. SCE and +0.75 V vs SCE, respectively (see SI). Obviously, *Ir^{III} could be easily reductive quenched by sacrificial agent *i*-Pr$_2$NEt to afford Ir^{II}, and Ir^{II} is capable of transferring electron to the high-valent cobalt complex Co(OAc)$_2$·bpy.

Based on the above results, plausible reaction pathways are proposed in Scheme 5. As consistent with our recently article,[13] the photosensitizer Ir^{III} is firstly exited to its excited state *Ir^{III} under visible light irradiation, which could abstract electron from sacrificial reagent *i*-Pr$_2$NEt to afford reductive photosensitizer Ir^{II} and radical cation of DIPEA. Proton and electron could be further released by the radical cation of DIPEA. Ir^{II} is capable of reducing Co^{II} to Co^{I}, which could capture a proton from the system to afford cobalt-hydride species (Co^{III}–H). Then, Co^{III}–H species could undergo a hydrometalation with alkyne to form an alkenyl-cobalt species, followed by a protonation process to release the semi-hydrogenated product (Z)-6



Scheme 5. Proposed mechanism.

and Co^{III} species. The Co^{III} would be reduced to Co^{II} by iridium catalysis and thus close the Co cycle. Subsequently, low-valent cobalt catalyzed cyclization of *ortho*-alkenylphenols affording 3,4-dihydrobenzofuran may occur (path A). Once (Z)-**6** is generated, Co^{I} can coordinate with the alkene and undergo oxidative addition to the phenolic hydroxyl group to generate Co ^{III} intermediate **7**, which could be directed and stabilized by the alcoholic hydroxyl group. This mechanism was proposed in the low-valent iridium (Ir ^{I}) catalyzed reactions of phenols and supported by the isolation of an Ir^{III}–H complex,[19] as well as proposed in Co catalyzed hydrogenation reaction using H_2O as the hydrogen source.[14] Due to the higher acidic of the phenolic hydroxyl group than alcoholic hydroxyl group, the oxidative addition is prone to react with the phenolic hydroxyl group.[19a,20] Subsequent migratory insertion in **7** would result in the formation of intermediate **8**. Finally, direct reductive elimination releases the product 3,4-dihydrobenzofuran **2 a** and regenerates the Co^{I} catalyst.

Alternatively (path B), a hydroxyl directed hydrometalation of (Z)-**6** with Co^{III}–H may occur to afford intermediate **9**, since (Z)-**6** possesses a less steric hindrance than (E)-**6**. Then, a bond rotation of **9** and subsequently interaction of phenolic hydroxyl group with cobalt center under basic condition would form the intermediate **8**. Finally, reductive elimination process occurs to produce **2 a** and Co^{I} species. The Co^{I} would further adopt a proton (H^{+}) to regenerate the Co ^{III}–H species.

In conclusion, we have developed an efficient and convenient dual catalytic system for the preparation of (2,3-dihydrobenzofuran-2-yl)methanol derivatives utilizing 2-propynolphenols as the substrate. The transformation occurred smoothly under blue LED irradiation at ambient temperature with excellent tolerance towards various functional groups and high yield was achieved for a gram-scale reaction. Obviously, the alcoholic hydroxyl group plays a vital role in the success of the reaction and (Z)-alkene was the real intermediate for the transformation. Further mechanism investigation and application of the photoredox/cobalt catalytic system are under investigation in our group.

Experimental Section

General Procedure for Synthesis of 2,3-Dihydrobenzofurans 2

To a Schlenk tube containing a stirring bar was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.001 mmol, 1 mol%), $Co(OAc)_2 \cdot 4H_2O$ (0.01 mmol, 10 mol%), 2,2′-bipyridine (0.015 mmol, 15 mol%), and 2-propynolphenol **1** (0.10 mmol, 1.0 equiv.). Then, *i*-Pr$_2$EtN (0.3 mmol, 3.0 equiv.), H_2O (1.0 mmol, 10.0 equiv.), and 2.0 mL anhydrous n-propanol/THF (4:1) were added to the reaction tube via syringe under Ar atmosphere. The reaction mixture was stirred for 6 h at Wattecs Parallel Light Reactor (Blue LED Light source, 10 W every position) at ambient temperature (the temperature range from 35 °C to 38 °C). Finally, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the compound **2**.

Acknowledgements

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