Dual Cobalt and Photoredox Catalysis Enabled Redox-Neutral Annulation of 2-Propynolphenols

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Abstract: A hydroxyl-assisted, organophotoredox/ cobalt dual catalyzed annulation of 2-propynolphenols to form 2-hydroxymethyl-benzo[*b*]furans was developed by employing 1,2,3,5-tetrakis(carbazol-9yl)-4,6-dicyanobenzene (4CzIPN) as photosensitizer and $CoCl_2(PPh_3)_2/5,5'$ -dimethyl-2,2'-bipyridine as cobalt catalytic precursor. Various substrates and functional groups were tolerated. The practical applications of this reaction were further demonstrated by enlarged gram-scale and various derivations for complex heterocycles. Primary mechanistic studies suggested the involvement of cobalt-hydride mediated hydrogen atom transfer (HAT) process.

Keywords: Photoredox catalysis; cobalt; hydrogen atom transfer (HAT); redox-neutral; 2-propynolphenols

The first-row transition-metal hydrides (L_nM –H) mediated hydrogen atom transfer (HAT) reaction has recently attracted significant attentions in organic synthesis.^[1] A key step in these reactions is chemoselective generation of a radical/metal cage. The radical could either escape from the cage and thus be captured by radicalophiles^[2] or recombine with metal to form the cage-collapsed organometallics complex which would undergo transmetalation with other metals and thus introducing new functionalities.^[3] Catalysts based on cobalt are among the most studied systems for these types of transformations and proved extremely versatile (Scheme 1a, I and II).^[2a–I] Recently, Shigehisa,^[4] Pronin,^[5] and Zhu^[6] suggested that the radical or collapsed alkylcobalt(III) intermediate could be further transformed into a carbocation or alkylcobalt(IV) species via single electron oxidation process in the presence of *N*-fluorocollidinium salt or excited photocatalyst, and which can be captured by nucleophiles (Scheme 1a, III). By applying these strategies, a variety of carbon-carbon or carbon-heteroatom bonds have been constructed.^[11] Despite these great advances, the current HAT catalysis limits their substrates on alkenes. Alkynes, however, are rarely reported to achieve hydrofunctionalization via HAT strategies.^[7]

Catalytic cyclization of *o*-alkynylphenol is the most straightforward and atom-economic method to construct benzo[*b*]furan,^[8] which is widely existed in biologically active molecules.^[9] The traditional synthetic strategy is electrophilic activation of carboncarbon triple bonds by Lewis acidic metals (e.g. Ir, Rh, Pd, Au, Ag, Cu, Zn, In and others), followed by a nucleophilic attack on alkyne to realize the cyclization. It is of note that cobalt-based catalyst is rarely used to achieve such annulation.

Merging photoredox catalysis with transition-metal catalysis has been identified as vital ways to achieve novel and unique transformations under mild conditions.^[10] Recently, we developed an visible-light-promoted iridium/cobalt dual catalytic system for efficient construction 2,3-dihydrobenzofurans from 2-propynolphenols via tandem semi-hydrogenation and intramolecular cyclization processes (Scheme 1b).^[11] A low-valent cobalt catalyzed phenolic O–H activation or a further hydrogenation of (Z)-alkene followed by phenolic oxygen substitution on cobalt center is supposed to contribute to the cyclization. Based on this

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Scheme 1. Cobalt-hydride mediated HAT catalysis and photoredox/cobalt catalyzed cyclization of 2-propynolphenols.

work, we wondered if benzo[b]furan could be directly formed from o-alkynylphenol via photoredox/cobalt dual catalysis with an avoided semi-hydrogenation process. As an update of our previous work, we herein would like to report the successful realization of this goal by employing an organophotoredox/cobalt dual catalytic system with 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as photosensitizer (Scheme 1c). More importantly, primary mechanism studies suggest the reaction involves a novel cobalthydride mediated HAT pathway, which is highly different from our previous work. It is worth noting that this photoredox/Co dual catalytic system obviates the using of stoichiometric strong oxidants such as Nfluorocollidinium salt and high reducing silane reagent, which are generally indispensable for most metalhydride mediated HAT system.

We started to verify our hypothesis by using similar conditions in our previous work,^[11] that is, selecting **1** a as the model substrate, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as photocatalyst, 4,4'-di-tert-butyl-2,2'-bipyridine (L1) as ligand, and *i*-Pr₂NEt as radical sacrificial in *n*-propyl alcohol at room temperature (table 1, entry 1). Unfortunately, none of corresponding benzo[b] furan 2a was detected. Other cobalt catalysts were then explored (entries 2–3). To our great surprise, $CoCl_2(PPh_3)_2$ displayed reactivity on catalyzing the cyclization to afford 2a in 34% yield. The effects of bases were subsequently investigated (entries 4-6). Among them, DBU displayed a higher yield up to 44%. Solvent investigation revealed that EtOH is the best choice, delivering 2a in 56% yield (entries 7-9). Increasing the amount of base and solvent further elevated the vield up to 74% (entries 10, 11). The ligand screening showed that 5,5'-dimethyl-2,2'-bipyridine (L3) is the best choice (entries 12-15). Finally, 89% isolated yield was obtained by changing the iridium photosensitizer

 Table 1. Reaction optimization.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $		PhOH Ph Ph ii OH a 1a	ilue LEDs S (1 mol%), [Co] (10 gand (15 mol%), <i>i</i> -Pr dditive (20 mol%), so mbient temperature	mol%) ₂ NEt (3.0 eq olvent (2.0 m a, 6 h	iuiv)	\sum_{2a}^{P}	h OH h
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	entry ^[a]	photosensitizer (PS)	[Co]	ligand	additive	solvent	2a
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	Ir[dF(CF3)ppy]2(dtbbpy)PF6	Co(OAc)2•4H2O	L1	-	n-Propanol	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂	L1	-	n-Propanol	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₃	L1	-	n-Propanol	34%
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	Et ₃ N	n-Propanol	36%
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	K ₂ CO ₃	n-Propanol	28%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	DBU	n-Propanol	44%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	DBU	i-Propanol	52%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	DBU	EtOH	56%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	DBU	EtOAc	34%
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	10 ^[b,c]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CoCl ₂ (PPh ₃) ₂	L1	DBU	EtOH	70%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11 ^[c,d]	Ir[dF(CF3)ppy]2(dtbbpy)PF6	CoCl ₂ (PPh ₃) ₂	L1	DBU	EtOH	74%
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	12 ^[c,d]	${\sf Ir}[{\sf dF}({\sf CF}_3){\sf ppy}]_2({\sf dtbbpy}){\sf PF}_6$	CoCl ₂ (PPh ₃) ₂	L2	DBU	EtOH	76%
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	13 ^[c,d]	${\sf Ir}[{\sf dF}({\sf CF}_3){\sf ppy}]_2({\sf dtbbpy}){\sf PF}_6$	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	82%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14 ^[c,d]	$lr[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CoCl ₂ (PPh ₃) ₂	PPh_3	DBU	EtOH	0%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15 ^[c,d]	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	CoCl ₂ (PPh ₃) ₂	L4	DBU	EtOH	66%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16 ^[c,d,e]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	90% (89%) ^[f]
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	17 ^[c,e]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	-	EtOH	60%
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	18 ^[c,d,e,g]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	36%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19 ^[c,e,h]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	-	EtOH	22%
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20 ^[c,e,g,i]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	12%
$\begin{array}{cccccc} 22^{[c,d,e]} & 4C2IPN & - & - & DBU & EtOH & none \\ 23^{[c,d,e]]} & 4C2IPN & CoCl_2(PPh_3)_2 & L3 & DBU & EtOH & <5\% \\ \end{array}$	21 ^[c,d]	-	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	< 5%
$\begin{array}{c c} \underline{23^{[c:d,n]}} & \underline{4C2IPN} & \underline{CoCl_2(PPh_3)_2} & \underline{L3} & \underline{DBU} & \underline{EtOH} & <5\% \\ \hline \\ \hline \\ \underline{1-Bu} & & \\ \underline{1-Bu} & & \\ \hline \\ \underline{1-Bu} & & \\ \hline \\ \underline{1-Bu} & & \\ \hline \\ F_3C & & \\ \hline \\ F_3C & & \\ \hline \\ F_3C & & \\ \hline \\ \hline \\ F_3C & & \\ \hline \\ \hline$	22 ^[c,d,e]	4CzIPN	-	-	DBU	EtOH	none
$\begin{array}{c} F_{3}C & F \\ t - Bu & F_{3}C & F \\ t - Bu & F_{5}C & F \\ t - Bu & F_{5}C & F \\ \end{array}$	23 ^[c,d,e,j]	4CzIPN	CoCl ₂ (PPh ₃) ₂	L3	DBU	EtOH	< 5%
$F_{3}C$ \downarrow L_{1} $(K' = f-Bu, R'' = H)$ L_{4} L_{2} $(R^{1} = H, R^{2} = H)$	t-Bu			n N	R ¹	\mathbb{R}^2 \mathbb{R}^2 \mathbb{R}^2	
$Ir[dE(CE_{2})npv]_{2}dtbbpv(PE_{2})$ 4CzIPN 13 (P1 = H P2 = M_{2})	IrídE	F30 ~	4CzIPN	/	L2 (R ¹ =	= H, R ² = H)	,

 ^[a] 1a (0.1 mmol), PS (1 mol%), [Co] (10 mol%), Ligand (15 mol%), *i*-Pr₂NEt (3.0 equiv.), additive (20 mol%), 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 ¹H NMR yield was reported using Cl₂CHCHCl₂ as an internal standard.

- $^{[b]}$ DBU = 1.2 equiv.
- $^{[c]}EtOH = 4.0 mL.$
- $^{[d]}$ DBU = 2.0 equiv.
- ^[e] 4CzIPN = 2 mol%.
- ^[f] isolate yield.
- ^[g] no *i*-Pr₂NEt.
- ^[h] *i*-Pr₂NEt = 5.0 equiv.
- ^[i] DBU = 5.0 equiv.
- ^[j] in dark. PS = photosensitizer.

to organic dye, 4CzIPN ($E^{PC^*/PC^-} = +1.43 \text{ V}$ vs SCE),^[12] and increasing the amount of photosensitizer to 2 mol% (entry 16). In absence of *i*-Pr₂NEt ($E_{ox} = +$ 0.75 V vs SCE, see SI) or DBU ($E_{ox} = +1.28 \text{ V}$ vs SCE)^[13] decreased the yield to 36% and 60% respectively (entries 17–18). From redox-potential analysis, DBU is capable of transferring electron to excited photosensitizer (4CzIPN*), so it may not only

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play the role of base but also partially serve as an electron donor reagent. Adding 5 equivalents of *i*- Pr_2NEt or DBU to the system decreased the yield to 22% and 12%, respectively (entries 19–20). The control experiments revealed that visible-light, photosensitizer, cobalt complexes were all essential for the successful transformation (entries 21–23).

With the optimized conditions in hand, the substrate scope of this transformation was then investigated (Table 2). First, the propargylic alcohols bearing various substituents on the phenolic ring were studied. Notably, both electron-deficient groups, such as fluorine, chlorine, bromine and ester, and electron-donating group, such as methyl were compatible to afford the products in excellent yields (**2 b**–**2 g**, 78–88%). The substrate bearing two fluorine atoms on the C4 and C5 positions of phenolic ring gave the product **2 h** in 73% yield.

Next, the influence of the substituents on the diphenylmethanol was investigated. Obviously, propargylic alcohols with electron-donating group on the *para*-position of phenyls (21, 92%) delivered higher yield than electron-withdrawing groups (2i-2k, 72–85%), illustrating that the electronic effect on the yield. Strong electron-withdrawing groups, such as fluorine and trifluoromethyl, on *meta*-position of the phenyls afforded the products 2 m in 86% yield and 2 n in 83% yield, respectively. Interestingly, replacement of one fluorine atom by methoxyl group afforded 20 in a

Table	2.	Substrate s	cope. ^[a]
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^[a] Reaction condition: 1 (0.1 mmol), 4CzIPN (2 mol%), CoCl₂ (Ph₃P)₂ (10 mol%), L3 (15 mol%), *i*-Pr₂NEt (3.0 equiv.), DBU (2.0 equiv.), EtOH (4.0 mL), irradiation with blue LEDs for 6 h, isolated yield was reported.

decreased yield of 55%. Other unsymmetric diphenylmethanols with electron-deficient groups on *para*position of phenyls generated the products in good yields (2p-2q, 75–78%). Ortho-fluoronated substrate 1r delivered the corresponding product 2r in 67% yield. In addition, the phenylnaphthalenyl methanol resulted in good reaction efficiency (2s, 89%). It's obvious that the heterocycle of thienyl was also compatible under the conditions to provide the corresponding product 2t in 78% yield. Tertiary propargylic alcohols with arylalkyl methanol or dialkyl methanols also reacted well under the standard conditions to give the corresponding products in excellent yields (2u-2w, 80–94%).

To further disclose the potential synthetic applications of the reaction, a series of derivatizations were conducted (Scheme 2). A gram-scale reaction of 1a was firstly performed under standard conditions, affording the product 2a (1.20 g) in 80% yield. Furthermore, 2-benzofuranmethanol has been identified as a versatile platform for further transformations. For example, the nucleophiles, such as diphenylphosphine oxide and indole, could be feasible installed at C3 position of the 2a to afford the products 4 and 6 under the catalysis of TfOH and TsOH·H₂O, respectively. In addition, a regioselective benzylic phosphinated product of 7 was obtained under the catalysis of TsOH·H₂O at a lower temperature of 15 °C. Considering the great importance of benzo[b]furan, indole, and phosphorous on pharmaceuticals' activity, these products provide foundation for further bioactive molecules' investigation.^[14]

To verify the role of alcoholic hydroxyl group in the substrate, several control experiments were conducted (Scheme 3a). Protecting the alcoholic hydroxyl group with methyl (1x) could not afford any desired product, but, interestingly, the demethoxyl product 2x'



Scheme 2. Gram-scale reaction and further transformations.

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Scheme 3. Control experiments.

was obtained in 29% yield with 58% of 1x recovery (eq. 1). Next, 2x was synthesized and tested under standard conditions to verify whether the demethoxylation occurred after ring closure (eq. 2). However, no demethoxylation was observed under the conditions, expelling the above-mentioned possibility. Unfortunately, the pathway of the demethoxylation remains obscure at this stage. Moreover, replacing the alcoholic hydroxyl group by methyl (1y) afforded the corresponding products only in trace amount (<5%yield, eq. 3). Since the reaction efficiency were greatly retarded when the alcoholic hydroxyl is protected or absent, we therefore deduced that the alcoholic hydroxyl group should play a significant role of chelation.

Mechanistic studies were conducted to gain more insights on the reaction. First, adding 2 equiv. of 2,2,6,6-tetramethyl-1-piperidineoxyl (TEMPO) to the standard reaction completely suppressed the transformation, suggesting that free radical might involve in the catalytic cycle. (Scheme 3b). Second, monitoring of the synthesis of 2a showed no apparent stable intermediates, but a byproduct of semi-hydrogenation of **1** a to alkene (Z)-8 was detected, suggesting that an active Co-H species, as well as a key alkenylcobalt intermediate should involve in the reaction (Figure 1a).



Next, the luminescent quenching experiments were conducted (Figure S7). 1a, $CoCl_2(PPh_3)_2$, and DBU, showed only slight quenching phenomena, but i-Pr₂NEt displayed an obvious quenching phenomenon. Meanwhile, cobalt complex CoCl₂(L3)₂, which formed in a 1:2 mixture of CoCl₂(PPh₃)₂ with L3 in EtOH and determined via HRMS (see Figure S1), showed a similar quenching rate with *i*-Pr₂NEt. These experiments suggest that single electron transfer (SET) of the exited photocatalyst 4CzIPN* dominantly occurs with i-Pr₂NEt or the cobalt complex. The thermodynamic feasibility of the photoinduced SET was analyzed by the oxidation-reduction potentials. The oxidation potential and reduction potential of 4CzIPN* were reported to be -1.18 V vs SCE and +1.43 V vs SCE, respectively.^[12] Obviously, the 4CzIPN* is capable of electrons abstracting *i*-Pr₂NEt from (E $^{i-Pr2Net/i-Pr2Neto+}$ = +0.75 V vs SCE, see Figure S8) or transferring electron to the cobalt complex $(E^{Co(II)})$ $^{Co(I)} = -1.05 \text{ V} \text{ vs SCE}$, see Figure S9).

Based on the above results and literature reports.^[10d] a plausible reaction mechanism is proposed in Scheme 4. The photosensitizer 4CzIPN is initially irradiated by blue LEDs to its excited state 4CzIPN*. Then, two pathways might be involved in reduction of Co(II) to Co(I). In path a, 4CzlPN* is reductively quenched by *i*-Pr₂NEt to afford reductive photosensi-

4CzIPN*

4CzIPN



i-Pr₂NEt • e. - X-) i-Pr₂NEt i-Pr₂NEt [4CzIPN] +[4CzIPN] ColX L_nCo^{III}X L_nCo^{ll}X Co(III)-H ОН 4CzIPN L_nCo^{ll}X +e", +H* ∣`Ph · Ph OH (Z)-**8** L_nCo^{ll}X Ba [4CzIPN] 4CzIPN Ph L_nCo^{II}X

Figure 1. a) Yield/time diagram for preparation of 2 a (left) and b) light on/off experiments (right). Scheme 4. Plausible reaction mechanism.

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i-Pr₂NEt



tizer $[4CzIPN]^{\bullet-}$ $(E^{PC/PC\bullet-} = -1.24 \text{ V vs SCE})^{[12]}$ and radical cation of *i*-Pr₂NEt, and the former transfers one electron to Co(II) complex to produce the Co(I) species and regenerate 4CzIPN. Alternatively (path b), 4CzIPN* is oxidative quenched by Co(II) to afford Co(I) and the oxidative photosensitizer $[4CzIPN]^{\bullet+}$. $[4CzIPN]^{++}$ (E^{PC+/PC} = +1.49 V vs SCE)^[12] would subsequently abstract an electron from *i*-Pr₂NEt to regenerate 4CzIPN (path b). The generated Co(I) is quickly trapped by \overline{H}^+ to give Co(III)-H species.^[15] Subsequently, a Co(III)-H mediated HAT reaction might occur to form a radical cage consisting of radical species 9 and an Co(II) catalyst. Reacting with Co(III)-H or accepting an electron (e^{-}) and a proton (H^{+}) by 9 would afford the byproduct (Z)-8 and release a Co(II) species. Next, a substitution between phenolic hydroxyl group and cobalt center under basic condition might occur to form the intermediate 10, followed by a radical capture to afford Co(III) species 11. Considering the intersecting of photocatalysis with cobalt catalysis from light on/off experiments, as well as literature reports,^[10g] a single electron oxidation of **11** by 4CzIPN* might occure to give Co(IV) intermediate 12, which would undergo a reductive ellimination process to furnish 2 a and Co(II). Finally, to close both catalytic cycles, reduction of Co(II) by reductive photosensitizer [4CzIPN]^{•-} would regenerate the Co(I) catalyst and 4CzIPN. We reasoned that the alcoholic hydroxyl group should play a vital role of chelation to stabilize the intermediate or direct the selective addition of Co(III)-H to alkynes.

In conclusion, a catalytic system in combination of cobalt catalysis and an organic dye, 4CzIPN, promote a novel photochemical intramolecular cyclization process. Using the Co/4CzIPN catalytic system, 2-meth-anolbenzofurans are prepared in good to excellent yields from tertiary alkynlalcohols. The inevitable role of alcoholic hydroxyl group and its diverse functions for highly selective phosphorylation and indolation of 2-benzofuranylmethanols at benzylic or C3 position were demonstrated. Furthermore, the proposed hydrogen atom transfer mechanisms are supported by the detecting of semi-hydrogenated product (Z)-8, radical capture experiment and light on/off experiment. Further mechanism studies with synthetic exploration of this catalytic system are underway in our laboratory.

Experimental Section

General Procedure for the Synthesis of 2-hydroxymethylbenzo[b]furans 2

To a Schlenk tube containing a stirring bar was added 4CzIPN (0.002 mmol, 2 mol%), Co(PPh₃)₂Cl₂ (0.01 mmol, 10 mol%), 5,5'-dimethyl-2,2'-bipyridine (L3, 0.015 mmol, 15 mol%), and 2-propynolphenol 1 (0.10 mmol, 1.0 equiv.). Then, *i*-Pr₂EtN (0.3 mmol, 3.0 equiv.), DBU (0.2 mmol, 2.0 equiv.), and 4.0 mL

ethanol were added to the reaction tube via syringe under Ar atmosphere. The reaction mixture was stirred for 6 h at Wattcas Parallel Light Reactor System (Blue LED Light source, 10 W every position) at ambient temperature (the temperature range from 28 °C to 32 °C). Finally, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the compound **2**.

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Dual Cobalt and Photoredox Catalysis Enabled Redox-Neutral Annulation of 2-Propynolphenols

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