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Visible-Light-Driven Alkyne Hydro-/Carbocarboxylation Using CO_2 via Iridium/Cobalt Dual Catalysis for Divergent Heterocycle Synthesis

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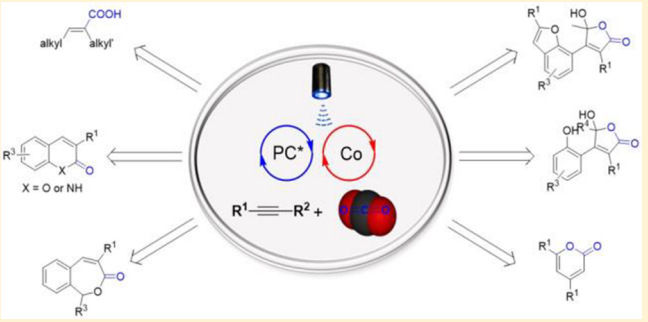
Supporting Information

ABSTRACT: We present herein the first visible-light-driven hydrocarboxylation as well as carbocarboxylation of alkynes using CO_2 via an iridium/cobalt dual catalysis. Such transformations provide access to various pharmaceutically important heterocycles in a one-pot procedure from readily available alkynes. Coumarins, 2-quinolones, and 2-benzoxepinones were directly accessed through a one-pot alkyne hydrocarboxylation/alkene isomerization/cyclization sequence in which the Ir photocatalyst serves a dual role to promote single-electron transfer in alkyne hydrocarboxylation and energy transfer in the subsequent alkene isomerization. Moreover, an unprecedented cobalt carboxylation/acyl migration cascade enables alkyne difunctionalization to introduce γ-hydroxybutenolides with high efficiency. We expect that this cascade strategy will inspire new perspectives for alkyne and alkene difunctionalization.



INTRODUCTION

Carbon dioxide is an attractive renewable C_1 feedstock due to its abundance, low cost, and nontoxicity. Utilization of CO_2 to replace toxic C_1 building blocks, such as phosgene, for fine chemical synthesis has received considerable momentum in the past decade.[1] One particularly intriguing transformation is the catalytic hydrocarboxylation of alkynes with CO_2 in which several catalytic systems have been developed for this transformation. However, the patterns of molecular scaffolds accessible by existing protocols are mainly limited to linear acrylic acids and 2-pyrones.[2] Moreover, stoichiometric amounts of metallic reagents such as Et_2Zn, silanes, Mn, or Zn powder are required as the reducing agents in hydrocarboxylation (Figure 1a). Thus, the introduction of catalytic activation modes that are environmentally benign and capable of achieving a higher degree of structural diversity are highly desirable.

Photocatalysis has witnessed dramatic developments over the past decade which have enabled previously inaccessible transformations.[3] However, a breakthrough for light-driven CO_2 fixation via C−C bond formation to deliver carboxylic acids and derivatives has not been achieved until very recently. In 2015, Murakami and co-workers reported the first example of direct carboxylation of benzylic C(sp^3)−H bonds using CO_2 under UV or sunlight irradiation.[4] In 2017, the Jamison group disclosed a straightforward synthesis of α-amino acid derivatives using amines and CO_2 as cheap feedstocks under UV light irradiation.[5] Very recently, several groups sequentially reported studies on visible-light-driven carboxylation of alkenes and organo halides,[6] without the usage of metallic reductants. However, to the best of our knowledge, light-promoted

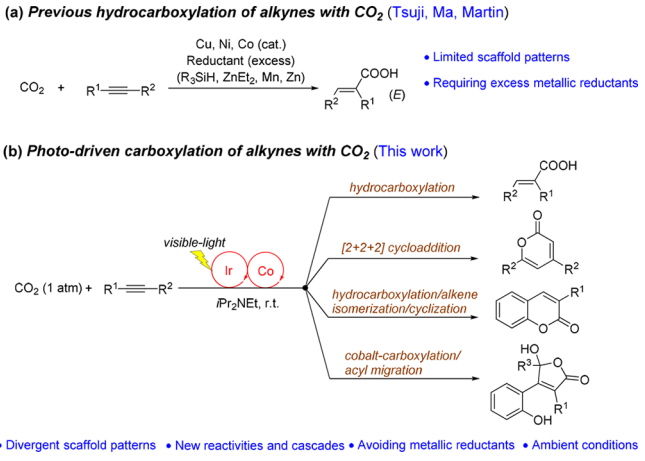


Figure 1. Transition-metal-catalyzed carboxylation of alkynes with CO_2.

carboxylation of alkynes with CO_2 has not been developed so far. In contrast to conventional carboxylation of alkynes, we envisioned that photopromoted transformation may provide opportunities to access new structural diversity. For instance, the alkyne carboxylation products, especially aryl-substituted olefins, are prone to undergo *E*,*Z*-isomerization in the presence of a photocatalyst through a triplet−triplet energy transfer process.[7] As part of our ongoing efforts in developing visible-light-promoted transformations using inexpensive gaseous

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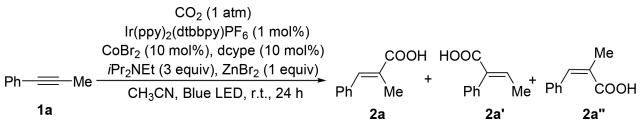
feedstocks,[8] we report herein the carboxylation of alkynes to directly access various types of compounds including biological important heterocycles using CO_2 as feedstocks through the synergistic combination of photoredox and cobalt catalysis (Figure 1b).

RESULTS AND DISCUSSION

Our study was initiated by employing 1-phenyl-1-propyne **1a** as the model substrate to investigate the hydrocarboxylation under 1 atm of CO_2 in the presence of a photocatalyst and a cobalt catalyst with blue LED irradiation.[2b,9] After extensive optimization (Table 1), we found that the combination of

Table 1. Optimization of Alkyne Hydrocarboxylation



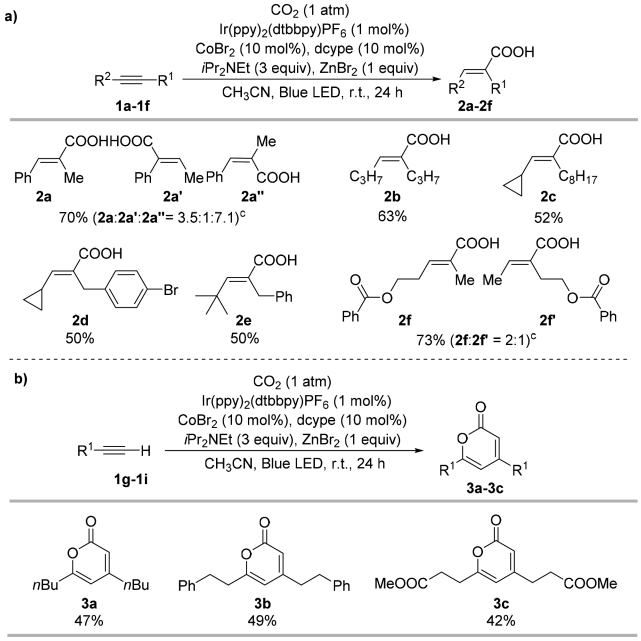
entry	deviation	yield (2a/2a′/2a″)[a] (%)
1	none	70 (3.3:1:6.7)
2	$CoCl_2$ instead of dcype	58 (2.5:1:6.1)
3	PCy_3 or dppe instead of dcype	<2
4	$Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	54 (4.4:1:5.4)
5	$MgBr_2$ instead of $ZnBr_2$	<10
6	iPr_2NEt 1.5 equiv instead of 3 equiv	41 (3.3:1:6)
7	DMF instead of MeCN	46 (5.2:1:5.2)
8	60 °C instead of rt	<10
9	without $ZnBr_2$	26 (9.5:1:2.5)
10	without $CoBr_2$ or dcype	no reaction
11	without $Ir(ppy)_2(dtbbpy)PF_6$	no reaction
12	without iPr_2NEt	no reaction
13	without light	no reaction

[a]Isolated combined yields. Isomer ratios were determined by analysis of ^1H NMR spectra of isolated products.

$Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %), $CoBr_2$ (10 mol %), dcype (10 mol %, bis(dicyclohexylphosphino)ethane), and $ZnBr_2$ (1 equiv) as the additive in the presence of iPr_2NEt (3 equiv) provided the best result, affording vinyl acids in 70% combined yield (**2a**/**2a′**/**2a″** = 3.3:1:6.7, entry 1). It is worth noting that the hydrocarboxylation proceeded with CO_2 insertion preferentially at the alkyl-substituted site. $CoCl_2$ catalyst was less effective than $CoBr_2$ (entry 2). The choice of phosphine ligand was crucial, as employing other ligands such as PCy_3 or 1,2-bis(diphenylphosphino)ethane (dppe) resulted in complete suppression of the reaction (entry 3). Using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ instead of $Ir(ppy)_2(dtbbpy)PF_6$ as the photocatalyst gave lower yield (entry 4). Only a trace amount of products was detected when $MgBr_2$ was used as the additive (entry 5). Hünig's base (3 equiv) was utilized in place of the metallic reductant, and a decrease in loading led to lower yield (entry 6). Switching the reaction solvent from MeCN to DMF delivered product **2** in decreased yield (entry 7). Hydrocarboxylation did not proceed well at 60 °C (entry 8). Reaction in the absence of $ZnBr_2$ yielded 26% of acid products with a significant amount of hydrogenated olefin byproducts (entry 9). No product was detected in the absence of $CoBr_2$, dcype, Ir photocatalyst, iPr_2NEt, or light, demonstrating the need for all of these components (entries 10–13). Despite our optimization efforts, only moderate *E*/*Z* selectivity was obtained with aryl-substituted alkynes.[10]

Scope of Photodriven Alkyne Hydrocarboxylation and [2 + 2 + 2] Cycloaddition. When the optimal hydrocarboxylation protocol was applied to bis-aliphatic substituted alkynes, *E*-acrylic acid products were obtained exclusively (Scheme 1a). Alkene *E*/*Z* isomerization was not

Scheme 1. Visible-Light-Driven Cobalt-Catalyzed Alkyne Hydrocarboxylation and [2 + 2 + 2] Cycloaddition with CO_2[a,b]



[a]Reaction conditions: alkyne **1** (0.2 mmol), CO_2 (1 atm), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %), $CoBr_2$ (10 mol %), dcype (10 mol %), $ZnBr_2$ (1 equiv), iPr_2NEt (3 equiv), and CH_3CN (1 mL) at ambient temperature under blue LED irradiation for 24 h. [b]Isolated yields. [c]Isomer ratios were determined by analysis of ^1H NMR spectra of the reaction mixtures.

detected for α,β-unsaturated acid products under visible-light irradiation. The symmetrical alkyne **1b** proceeded to give **2b** in 63% yield. A high degree of regioselectivity was achieved when the two alkyl substituents were sterically differentiated. Products **2c**–**e** were obtained as the sole regioisomer from **1c**–**e**, where CO_2 was inserted adjacent to the less sterically hindered substituent. It is worth noting that product **2d** bearing an aryl bromide moiety, which was not compatible with metal reductants, was smoothly produced under the photodriven conditions. However, in the absence of steric bias in the unsymmetrical alkyne starting materials **1f**, both regioisomers were produced. Notably, the Ir/Co dual catalysis protocol could be extended to aliphatic terminal alkynes to produce 2-pyrones (Scheme 1b, **3a**–**c**), which represents a rare example of 2-pyrone synthesis via intermolecular [2 + 2 + 2] cycloaddition between two alkynes and CO_2 at ambient pressure and temperature.[11] The reaction with phenylacetylene was also tested. However, less than 10% 2-pyrone product was obtained, with a significant amount of alkyne trimerization byproducts and starting materials left.

Development of One-Pot Aryl Alkyne Hydrocarboxylation/Alkene Isomerization/Cyclization. Our preliminary

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investigation suggested that it was difficult to achieve high E/Z selectivity for visible-light-mediated aryl alkyne hydrocarboxylation. Furthermore, encouraged by the formation of 2-pyrones from alkynes and CO_2, we turned our attention to heterocycle synthesis. We thus envisioned that the introduction of an ancillary substituent in proximity of the alkyne moiety should be able to direct the E/Z isomerization of the acrylic acid intermediate, in which the ring closure would drive the equilibrium to the Z-alkene (Figure 2).[12] In this manner, useful

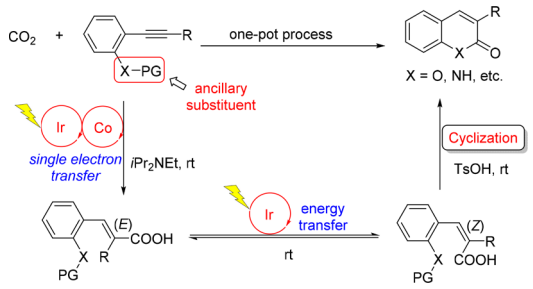
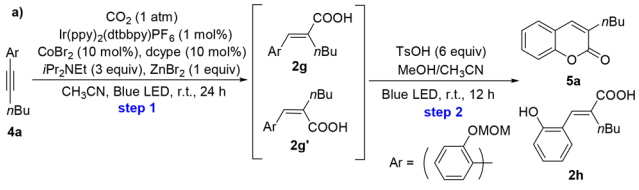


Figure 2. Proposed one-pot hydrocarboxylation/alkene isomerization/cyclization transformation.

heterocycles such as coumarins and 2-quinolones, which are important structural motifs in a myriad of pharmaceutical compounds that display significant biological properties (e.g., anticancer, antimicrobial, antiviral, and anti-inflammatory),[13] could be directly prepared from substituted alkynes and CO_2.

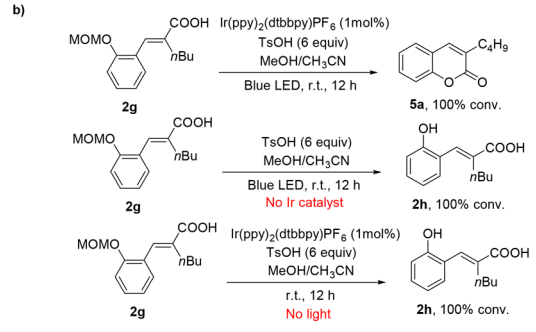
Our hypothesis was evaluated by employing phenyl alkyne **4a** with a methoxymethyl (MOM) protected hydroxyl group as the ancillary substituent. Hydrocarboxylation of **4a** under the optimized conditions gave vinyl acids **2g** and **2g′** in 28% and 47% isolated yields, respectively (Scheme 2a, entry 1). When

Scheme 2. Control Experiments of One-Pot Hydrocarboxylation/Alkene Isomerization/Cyclization[a]



entry	step	deviation	**2g** (%)[b]	**2g′** (%)[b]	**5a** (%)[b]
1	1	none	28	47	—
2	1	without $ZnBr_2$	21	7	—
3	1+2	none	—	—	73
4[c]	1+2	without light (the second step)	—	—	44

[a]Standard conditions: **4a** (0.2 mmol), CO_2 (1 atm), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%), $CoBr_2$ (10 mol%), dcype (10 mol%), $ZnBr_2$ (1 equiv), iPr_2NEt (3 equiv) and CH_3CN (1 mL) at ambient temperature under blue LED irradiation for 24 hours. Then added TsOH (6 equiv. in MeOH) at ambient temperature under blue LED irradiation for another 12 hours. [b]Isolated yields. [c]**2h** was isolated as by-product.



the reaction was conducted in the absence of $ZnBr_2$, the combined yield of acid products decreased to 28% (entry 2). Simple injection of TsOH methanol solution to the hydrocarboxylation reaction mixture followed by irradiation under blue LED for another 12 h produced the desired coumarin product **5a** in 73% isolated yield (entry 3). In the absence of light for the second step, **5a** was only obtained in 44% yield, together with 25% yield of MOM cleaved **2h** (entry 4). To further support that the E/Z isomerization was induced by light-driven Ir catalysis, conversion of presynthesized **2g** to **5a** was attempted (Scheme 2b). In the presence of both Ir photocatalyst and light, a full conversion to **5a** took place. In the absence of either Ir catalyst or light, in contrast, no cyclization but complete conversion of **2g** to **2h** was observed (Scheme 2b).

Scope of One-Pot Aryl Alkyne Hydrocarboxylation/Alkene Isomerization/Cyclization. Adopting the optimized one-pot sequential transformation protocol, the generality of this method was evaluated via a variety of aryl-substituted alkynes bearing a phenyl ether substituent (Scheme 3a). Replacing the protecting group from MOM to EOM (ethoxy methyl) did not affect the reactivity, providing **5a** in 71% yield. The sequential transformation proceeded well with various alkynes bearing different aliphatic substituents to deliver the corresponding coumarin products, such as methyl (**5b**), *n*-heptyl (**5c**), or even steric bulky ones like cyclopropyl (**5h**) or cyclohexyl (**5i**). Substrates bearing functional groups such as phenyl groups (**5d**), ethers (**5e**, **5f**), or esters (**5g**) were well tolerated. Furthermore, alkynes with electron-donating (**5j**, **5k**) or electron-withdrawing groups (**5l**–**n**) on MOM ether-containing aryl substituents furnished coumarin products in good yield. The bulky naphthyl alkyne afforded product **5o** in moderate yield. However, 1,2-diphenyl alkynes resulted in very low yield of the desired coumarin **5p**, with stilbene detected as the major side product. Moreover, this catalytic protocol was successfully applied to aryl alkynes with an *N*-Boc carbamate substituent. The corresponding 2-quinolones (**5q**–**t**) were produced in good yield for both electron-rich and electron-poor aryl-substituted alkynes.

Notably, the seven-membered ring 2-benzoxepinones (**7a**–**c**) could be selectively produced by changing phenyl ether substituted alkynes **4** to the benzyl ether substituted alkynes **6** (Scheme 3b), highlighting the utility of this catalytic method to access heterocycles with different ring sizes.

To achieve a more efficient protocol to access coumarins or 2-quinolones, the substrates without protecting group on the phenol or aniline were attempted (Scheme 3c). Alkyne **4u** bearing a free phenol did not incorporate CO_2 but led to the formation of benzofuran **8**. This transformation proceeded smoothly as well in the absence of CO_2. On the other hand, alkyne **4v** with a free aniline directly delivered 2-quinolone **5q** with good yield under the photo hydrocarboxylation conditions, representing a more step-economic protocol to access 2-quinolone compounds (Scheme 3c).

Development of Visible-Light-Driven Difunctionalization of Alkynes with CO_2 to Access γ-Hydroxybutenolides. Based on the formation of 2-pyrones from terminal aliphatic alkynes (Scheme 1b), we speculated that a five-membered cobaltacycle intermediate derived from the Co species, alkynes, and CO_2 might be involved under the optimal reaction conditions.[2b] To further expand the application of this aforementioned strategy, we postulated that the incorporation of an electrophilic substituent in the alkyne substrate may

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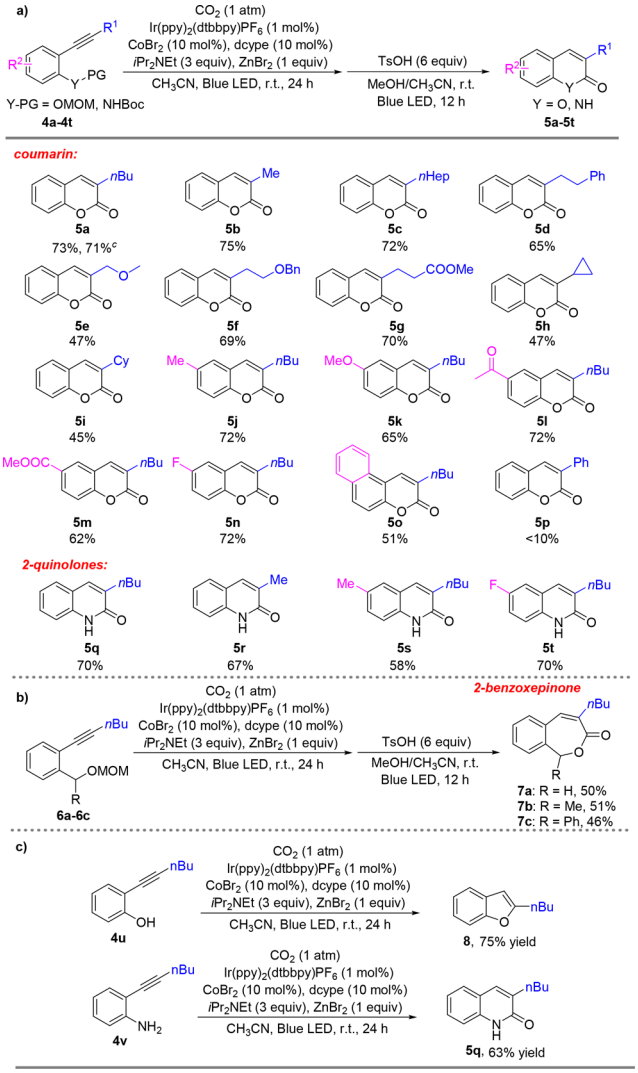
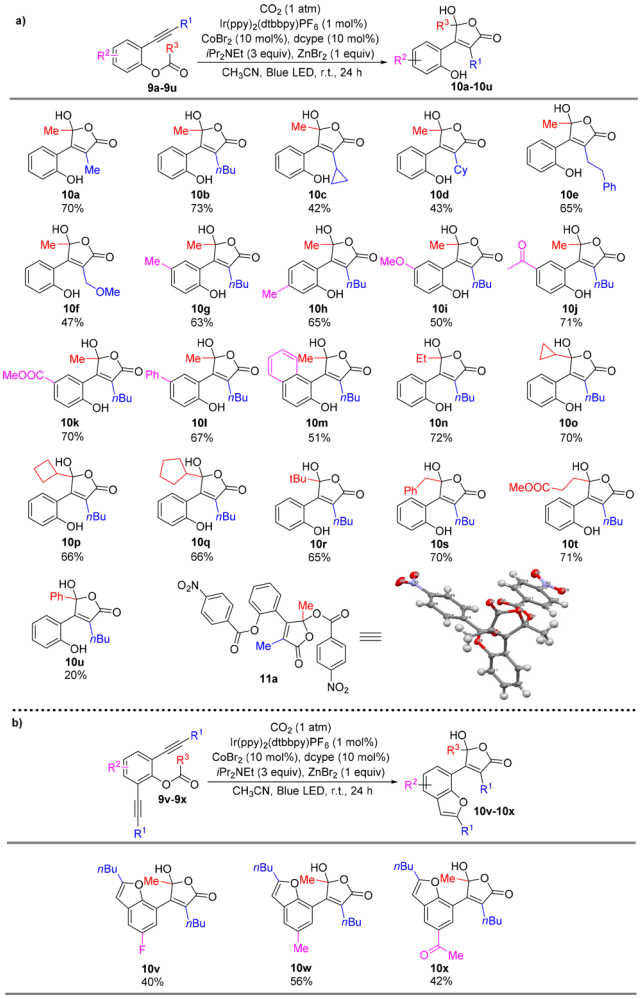
Scheme 3. Scope of the One-Pot Aryl Alkyne Hydrocarboxylation/Alkene Isomerization/Cyclization[a,b]



[a]Reaction conditions: alkyne **4** or **6** (0.2 mmol), CO_2 (1 atm), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %), $CoBr_2$ (10 mol %), dcype (10 mol %), $ZnBr_2$ (1 equiv), iPr_2NEt (3 equiv), and CH_3CN (1 mL) at ambient temperature under blue LED irradiation for 24 h. Then added TsOH (6 equiv, in MeOH) at ambient temperature under blue LED irradiation for another 12 h. [b]Isolated yields. [c]Using EOM as the protection group. EOM = ethoxymethyl.

trigger a kinetically favored intramolecular addition of the cobaltacycle intermediate to realize alkyne difunctionalization. Various electrophilic substituents were therefore evaluated (Figure S1), and we were delighted to observe that γ-hydroxybutenolides could be synthesized using CO_2 with *ortho*-ester substituted aryl alkynes **9** under the photoredox/cobalt dual catalytic conditions, featuring an unprecedented intramolecular cobalt-carboxylation/acyl migration cascade reaction (Scheme 4).[14] γ-Hydroxybutenolides are important structural motifs widely found in natural products (e.g., ianthellidone G, manoalide, petrosaspongiolide M) and artificial pharmaceutical compounds (e.g., PD 156707), which exhibits important bioactivities such as anti-inflammatory, anticancer, and antimicrobial activities.[15] Rapid and effective synthesis of highly functionalized γ-hydroxybutenolides, especially from

Scheme 4. Photosynthesis of γ-Hydroxybutenolides from *Ortho*-Ester Substituted Aryl Alkynes and CO_2[a,b]



[a]Reaction conditions: alkyne **9** (0.2 mmol), CO_2 (1 atm), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol %), $CoBr_2$ (10 mol %), dcype (10 mol %), $ZnBr_2$ (1 equiv), iPr_2NEt (3 equiv), and CH_3CN (1 mL) at ambient temperature under blue LED irradiation for 24 h. [b]Isolated yields.

inexpensive feedstock CO_2, is of considerable importance for both synthetic and medicinal chemistry.[16]

The scope of the visible-light-driven γ-hydroxybutenolide synthesis was subsequently investigated. Various alkyl substituents on the alkyne such as methyl (**10a**), *n*-butyl (**10b**), cyclopropyl (**10c**), sterically demanding cyclohexyl (**10d**), phenylethyl (**10e**), and methoxymethyl (**10f**) were well tolerated to deliver γ-hydroxybutenolides in moderate to good yields. Importantly, only one regioisomer was generated in all cases. Reactions with phenyl acetates bearing either an electron-donating (**10g–i**) or an electron-withdrawn substituent (**10j–l**) proceeded effectively. Changing phenyl acetate to naphthyl acetate delivered γ-hydroxybutenolide **10m** in moderate yield. This CO_2-based synthetic method can be further expanded effectively to include various aliphatic substituted acyl groups with different steric effects (**10n–t**). However, benzoic ester was a poor candidate for this cascade transformation (**10u**). Notably, the use of 2,6-bisalkynyl phenyl acetates directly provided γ-hydroxybutenolides **10v–x** with a benzofuran moiety, in which one alkyne performed cobalt-

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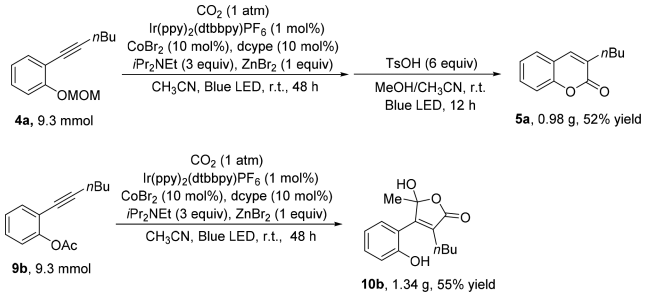
carboxylation/acyl migration cascade, while the other alkyne substituent underwent intramolecular cyclization with the in situ generated phenoxide to form the benzofuran substituent (Scheme 4b). The structural configuration of **10a** was clearly determined by X-ray diffraction using 4-nitrobenzoate derivative **11a**, and those of other products **10** were assigned by analogy.

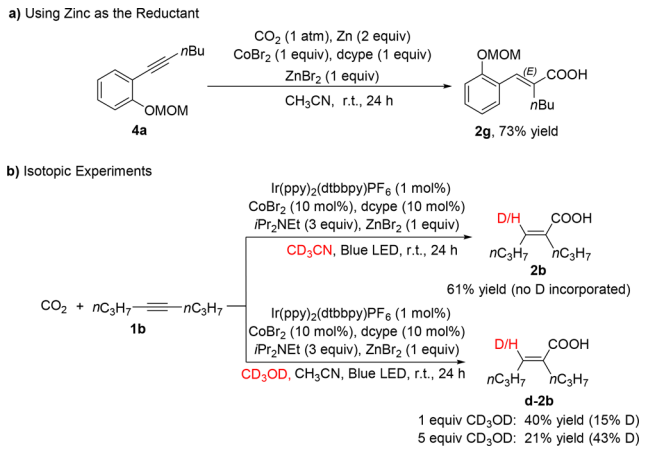
To further demonstrate the synthetic utility of this methodology, the synthesis of coumarins and γ-hydroxybutenolides were amenable to scale-up to gram quantities (Scheme 5). However, lower yield was observed compared to the small-scale reactions due to the incomplete conversion of starting materials.

Scheme 5. Gram-Scale Synthesis of Heterocycles



Mechanistic Study of Alkyne Hydrocarboxylation. The production of 2-pyrones with terminal aliphatic alkynes (Scheme 1b) suggested a five-membered cobaltacycle intermediate derived from the Co species, alkynes, and CO_2 in the presence of photoredox and cobalt catalysis.[2b] The five-membered cobaltacycle intermediate was further supported by using Zn powder as the reductant. Treatment of alkyne **4a** with stoichiometric amounts of $CoBr_2$ and dcype ligand with 2 equiv of Zn powder in the presence of CO_2, without any hydride or proton source, resulted in product **2g** in 73% yield, exhibiting the same regioselectivity as photoredox conditions (Scheme 6). Difunctionalization of alkynes was realized based on this hypothesized cobaltacycle intermediate by incorporating an intramolecular acyl migration. Moreover, no deuterium incorporation was observed in the product when the photo hydrocarboxylation was conducted in CD_3CN, indicating that

Scheme 6. Use of Zn Powder as the Reductant and Deuterium-Labeling Experiments



the hydrogen atom source should arise from iPr_2NEt.[17] In addition, cyclic voltammetry (CV) measurement was conducted with the complex of $CoBr_2$ and dcype, which demonstrated that the Co^{II} complex can be reduced to the Co^{I} complex at −0.75 V vs SCE in MeCN (Figure S3). The absolute role of $ZnBr_2$ is unclear at this stage and requires further investigation, even though it has been reported that the $ZnBr_2$ can stabilize a transient Co^{I} species in MeCN[18] and may facilitate the regeneration of Co catalyst from the carboxylatocobalt intermediate.

Tentative mechanistic pathways for alkyne hydrocarboxylation are proposed in light of all the experimental data (Scheme 7, left). Reductive quenching of visible-light-excited $Ir(ppy)_2(dtbbpy)PF_6$ by iPr_2NEt gives rise to an amine radical cation and a reduced Ir^{II} species, the latter ($E_{1/2}[Ir^{III}/Ir^{II}]$ = −1.51 V vs SCE in MeCN) is then oxidized by Co^{II} complex **A** ($E_{1/2}$ = −0.75 V vs SCE in MeCN) to regenerate Ir^{III}. The active Co^{I} species **B** generated in this step will react with CO_2 and alkyne substrates to produce the five-membered cobaltacycle intermediate **C**.[2b] Subsequent protonolysis of C−Co^{III} bond by cationic amine radicals will deliver the carboxylatocobalt intermediate **D**. The transient complex **D** may undergo photoredox-catalyzed reduction to regenerate Co^{I} species **B**, and $ZnBr_2$ may facilitate this step through transmetalation to furnish carboxylate **E**. Finally, the aryl substituted *E*-vinylcarboxylate **E** can undergo a reversible isomerization to its *Z*-isomer **F** through an Ir-mediated triplet−triplet energy transfer process under visible-light-irradiation,[10] following which an acid-mediated intramolecular cyclization delivers product **5**. As for terminal alkynes, insertion of another alkyne molecule into the five-membered cobaltacycle **C** will occur to give the seven-membered cobaltacycle **G**. Subsequent reductive elimination will afford 2-pyrone **3** and regenerate Co^{I} **B**. When *ortho*-ester substituted aryl alkyne **9** is applied as the substrate (Scheme 7, right), intramolecular addition of the in situ generated C−Co^{III} bond to the ester substituent furnishes the carbo-carboxylation intermediate **I**. The transient complex **I** may undergo photoredox-catalyzed reduction and transmetalation with $ZnBr_2$ to provide zinc complex **J** and regenerate Co^{I} species **B**. Tautomerization of **J** delivers the γ-keto acrylic zinc species **K**, which is followed by another tautomerization to accomplish the synthesis of γ-hydroxybutenolide **10**.

Even though the hydrocarboxylation products could be generated without $ZnBr_2$, in the presence of $ZnBr_2$, we were unable to exclude the possibility of Co−Zn transmetalation of cobaltacycle **C** to form an alkenylzinc species, which can undergo subsequent protonation or intramolecular cyclization to achieve the same products (Figure S5).

CONCLUSION

In summary, we have disclosed the direct synthesis of various pharmaceutically important heterocycles, including 2-pyrones, coumarines, 2-quinolones, 2-benzoxepinones, and γ-hydroxybutenolides, from alkynes and CO_2 in a regio- and stereospecific fashion through the synergistic combination of photoredox and cobalt catalysis. In the one-pot synthesis of coumarins and 2-quinolones, the Ir photocatalyst plays a dual role to promote both the electron transfer in hydrocarboxylation and the triplet−triplet energy transfer in the subsequent alkene isomerization. Alkyne difunctionalization has also been realized through an unprecedented cobalt-carboxylation/acyl migration cascade to efficiently generate γ-hydroxybutenolides using CO_2. We expect that this carbometalation/rearrangement

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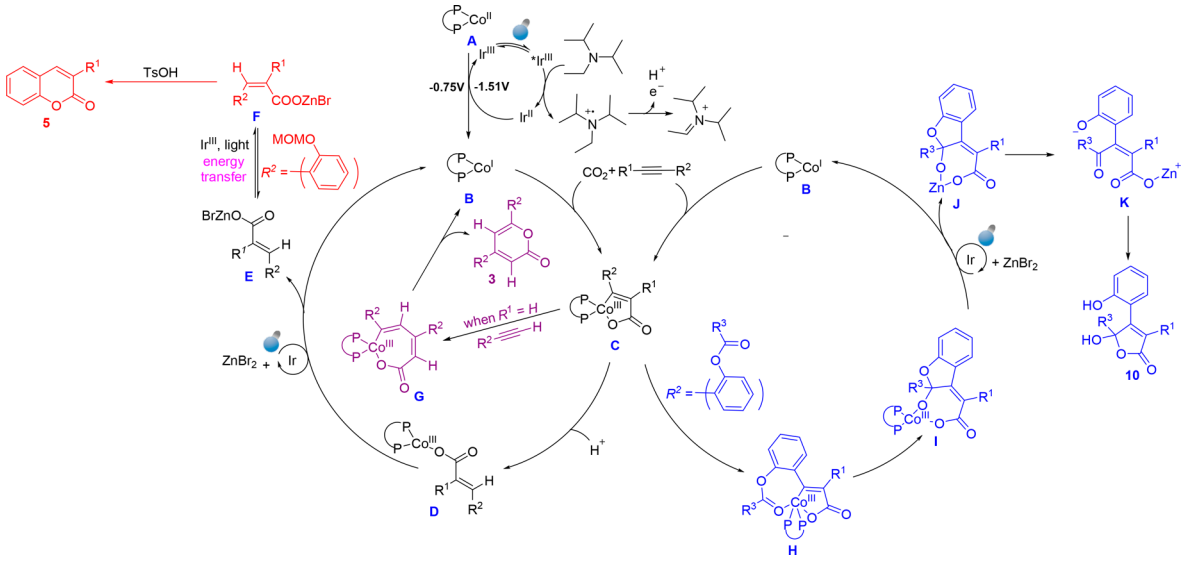
Scheme 7. Proposed Mechanism for Alkyne Carboxylation



cascade strategy promises to find wide applications with other types of metallacycles to enable difunctionalization of alkenes and alkynes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b01561.

General procedures, analytical data, and NMR spectra (PDF)

X-ray data for compound **11a** (CIF)

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Notes

The authors declare no competing financial interest.

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