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Transition-Metal-Free Lactonization of sp^2 C–H Bonds with CO_2

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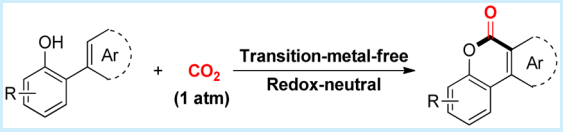
Supporting Information

ABSTRACT: The transition-metal-free lactonization of heteroaryl and alkenyl C–H bonds with carbon dioxide is reported to synthesize important coumarin derivatives in moderate to excellent yields. These redox-neutral reactions feature a broad substrate scope, good functional group tolerance, facile scalability, and easy product derivatization.



Transformations of carbon dioxide (CO_2) to high-value-added chemicals have received much attention because CO_2 is a nontoxic, abundant, and recyclable C1 building block.[1] CO_2 may represent a more user-friendly carbonyl source than the hazardous and toxic carbon monoxide (CO)[2] and phosgene,[3] which have been widely used in the laboratory and industry. However, the oxidative carbonylation reaction involving CO and oxidants is still one of the most developed and widely used methods to approach the important carbonyl-containing heterocycles.[4] Considering its higher oxidation state than CO, CO_2 could act as the combination of CO and oxidants in redox-neutral carbonylation reactions to generate carbonyl-containing heterocycles.

Due to high atom- and step-economy, direct C–H functionalization with CO_2 shows great power and efficiency in carboxylation[5] and heterocycle formation.[6−9] In 2013, the Iwasawa and Takaya group developed an unprecedented palladium-catalyzed carboxylation of alkenyl C–H bonds of 2-alkenylphenols with CO_2 to afford the corresponding coumarins via a lactonization process (Scheme 1A).[6] Our group[7a] and Xi's group[8] independently realized the transition-metal-free lactamization of sp^2 C–H bonds in 2-alkenylanilines and 2-(hetero)arylanilines with CO_2 (Scheme 1B). Very recently, Zhang and Lu's group also developed a novel transformation of 1-propenyl ketones to α-pyrones via CO_2 utilization (Scheme 1C).[9] However, hydroxyl group directed lactonization of aryl C–H bonds, especially heteroaryl C–H bonds, with CO_2 has not been reported yet.[10] As a continuation of our interest in construction of heterocycles with CO_2,[7a,b] herein, we report a challenging transition-metal-free and redox-neutral lactonization of heteroaryl and alkenyl C–H bonds with CO_2 (Scheme 1D).[11]

The compounds containing an imidazo[1,2-*a*]pyridine (IP) scaffold, such as necopidem, saripidem, and zolpidem, have attracted much attention due to their biological activities.[12] We wonder if we can directly functionalize the C–H bonds in imidazo[1,2-*a*]pyridines to obtain a class of hybrid structures of coumarin derivatives through lactonization with CO_2.[13] As shown in Table 1, we tested the reaction of 2-(imidazo[1,2-*a*]pyridin-2-yl)phenol (**1a**) with CO_2 as a model reaction. Inspired by our previous work on lactamization reactions (Scheme 1B),[7a] we first screened different solvents (entries 1–4) with KO^{t}Bu as the base and found diglyme to perform much better than others. The reason might be that diglyme has a similar structure to the crown ether, which can enhance the basicity and make the in situ generated potassium salts, including phenoxide and carbonate, more stable and soluble in the reaction conditions.[14] Furthermore, many kinds of bases (entries 4–11) were tested, and KO^{t}Bu was found to be the

Scheme 1. Lactonization/Lactamization of C–H Bond with CO_2

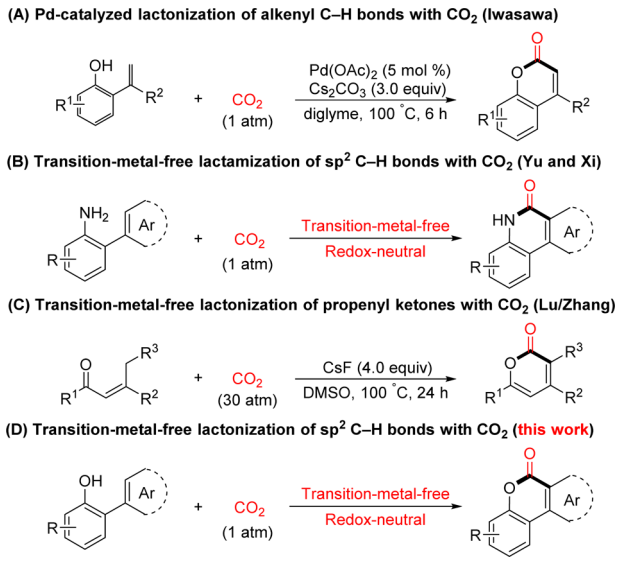


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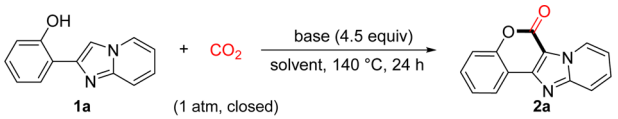
Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	yield (%)[b]	entry	base	solvent	yield (%)[b]
1	KO^{t}Bu	DMSO	38	9	Cs_2CO_3	diglyme	19
2	KO^{t}Bu	THF	18	10	K_3PO_4	diglyme	18
3	KO^{t}Bu	DMF	79	11	DBU	diglyme	0
4	**KO^{t}Bu**	**diglyme**	**93 (90)**	12[c]	KO^{t}Bu	diglyme	78
5	NaO^{t}Bu	diglyme	87	13[d]	KO^{t}Bu	diglyme	43
6	LiO^{t}Bu	diglyme	3	14[e]	KO^{t}Bu	diglyme	59
7	$Mg(O^tBu)_2$	diglyme	0	15[f]	KO^{t}Bu	diglyme	0
8	K_2CO_3	diglyme	0	16[g]	Cs_2CO_3	diglyme	36

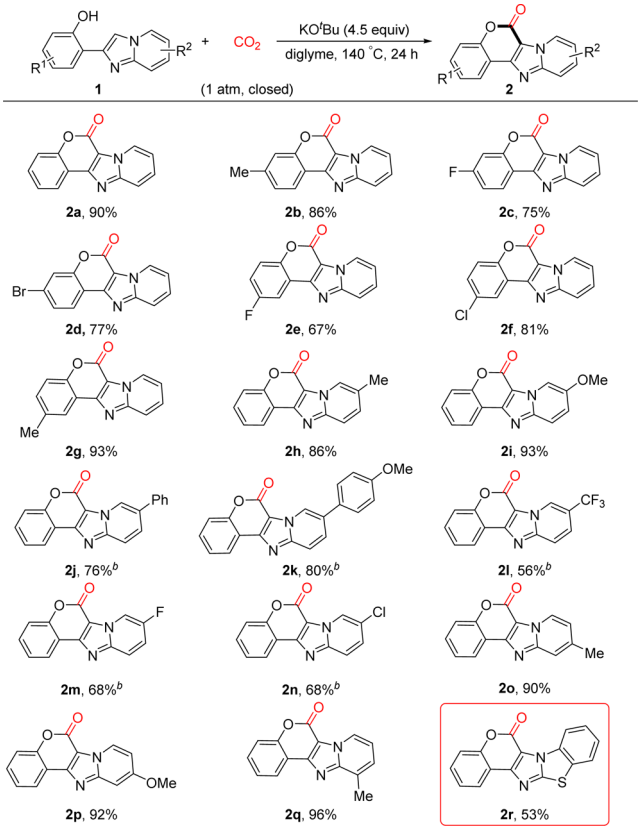
[a]Reaction conditions: **1a** (0.2 mmol), base (4.5 equiv), 1 atm of CO_2, 2 mL of solvent, 24 h, 140 °C. [b]GC yields are given with dodecane as an internal standard and the isolated yields are given in parentheses. [c]6 h. [d]1 h. [e]KO^{t}Bu (3.0 equiv). [f]KO^{t}Bu (1.0 equiv). [g]Cs_2CO_3 (3.0 equiv), $Pd(OAc)_2$ (10 mol %).

best choice. Moderate to good yields were obtained even if the reaction time was shortened to 6 or 1 h (entries 12 and 13). When a lower amount of KO^{t}Bu was used, the yield of **2a** was decreased dramatically (entries 14 and 15), which indicated the high importance of base in this transformation. Although palladium catalyst could promote the reaction in the presence of Cs_2CO_3 as the base, the efficiency was still not good enough at this stage (entry 16).[6]

With the optimized reaction conditions in hand, we investigated the substrate scope of this transformation (Scheme 2). First, we set out to investigate the scope of the substrates bearing substituents on the phenol ring (**1b**–**g**). As shown in Scheme 2, different substituents at the meta (**1b**–**d**) and para position (**1e**–**g**) of the phenol ring did not affect the reaction. Several kinds of carbon–halo bonds (**1c**–**f**) were well-tolerated under the current reaction conditions, thus providing great opportunity for further functionalization.[15] Furthermore, we investigated the effect of substitutions on the imidazo[1,2-*a*]pyridine scaffold (**1h**–**q**). We found that a variety of substrates with different substitutions on the IP scaffold also gave the desired products in good to excellent yields. Notably, many kinds of functional groups, such as methoxyl (**1i**, **1k**, **1p**), trifluoromethyl (**1l**), and carbon–halo bonds (**1m**, **1n**), did not inhibit the reaction. The substrates (**1i**, **1o**–**q**) with electron-donating groups gave the corresponding products in higher yields than those (**1l**, **1m**) with electron-withdrawing groups, which might arise from higher electron density at the nucleophilic site of the substrate. Besides the imidazo[1,2-*a*]pyridine motif, 2-(benzo[*d*]imidazo[2,1-*b*]thiazol-2-yl)-phenol (**1r**) could also be applied in this reaction to give **2r** in 53% yield.

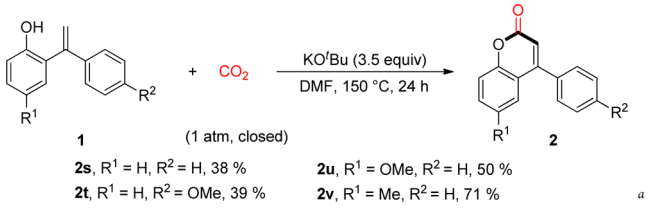
Furthermore, we were pleased to find that 2-alkenylphenols could also be suitable for this transformation (Scheme 3).[16] With slightly modified reaction conditions, **2s** was obtained in 38% yield, along with byproducts from carboxylation at the ortho and para position of phenol ring.[17] To our delight, the substrates (**1u**, **1v**) with substituents on the para position of the phenol ring could generate the corresponding products **2u** and **2v** in moderate to good yields.

Scheme 2. Lactonization of 2-(Imidazo[1,2-*a*]pyridin-2-yl)phenols with CO_2[a]



[a]Reaction conditions: **1** (0.2 mmol), KO^{t}Bu (4.5 equiv), 1 atm of CO_2, 2 mL of diglyme, 24 h, 140 °C. Isolated yields. [b]48 h.

Scheme 3. Lactonization of 2-(1-Arylvinyl)phenols with CO_2[a]



[a]Reaction conditions: **1** (0.2 mmol), KO^{t}Bu (3.5 equiv), 1 atm of CO_2, 2 mL of DMF, 24 h, 150 °C. Isolated yields are shown.

After developing the methodology, we further demonstrated its utility. First, the reaction of **1a** could be scaled up to gram quantity with 87% yield (Scheme 4A). Moreover, the product **2a** could be easily transformed to 2-(3-(2-hydroxypropan-2-yl)imidazo[1,2-*a*]pyridin-2-yl)phenol (**3**), 2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridine-3-carboxylic acid (**4**), and 2-(3-(hydroxymethyl)imidazo[1,2-*a*]pyridin-2-yl)phenol (**5**) in the presence of nucleophiles or a reductant (Scheme 4B; see the SI for details), all of which demonstrate that this transformation can be useful in organic synthesis.

Concerning the mechanism, there are two possible pathways for **1a** to react with CO_2 to generate **2a** (Scheme 5) because both the phenoxide and imidazole motif are electron-rich and nucleophilic. To gain insight into the reaction mechanism, a series of experiments were conducted.

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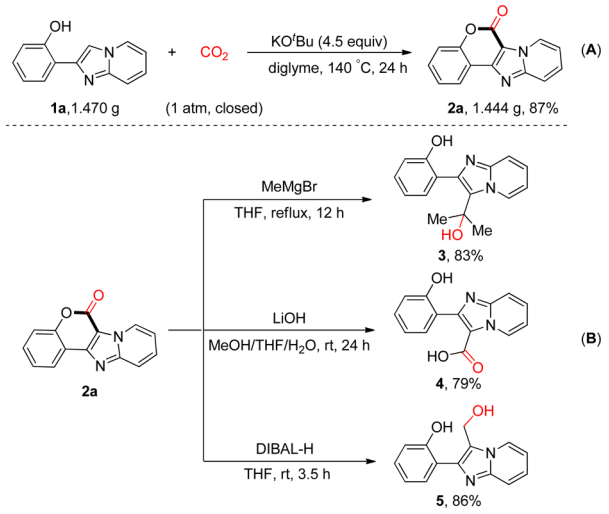
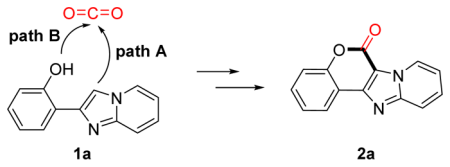
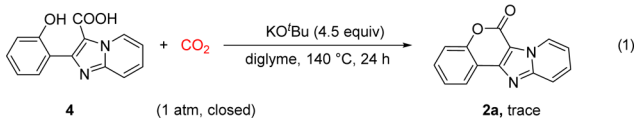
Scheme 4. Large-Scale Reaction and Synthetic Applications



Scheme 5. Possible Pathways for the Reaction

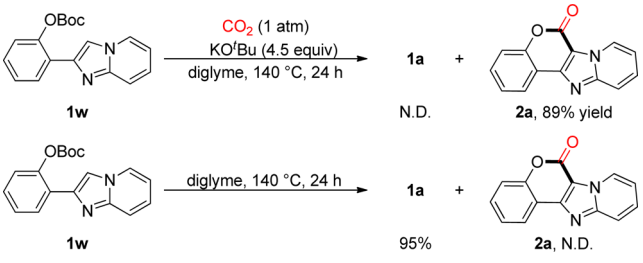


At first, we wondered whether compound **4** is one key intermediate that can transfer to the product **2a** through the lactonization reaction (Scheme 5, path A). However, only a trace of the target product **2a** was detected under the standard conditions (eq 1), which indicated that path A might be unfavored.



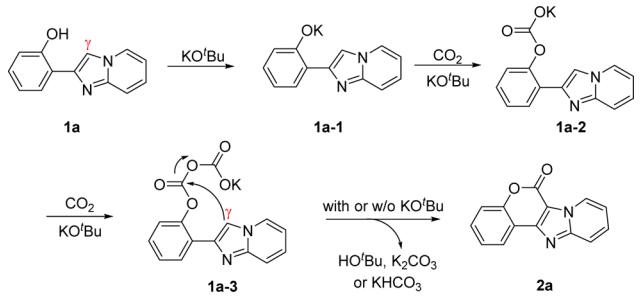
On the basis of the the above results, nucleophilic attack from oxygen in phenols may be a possible path for the reaction (Scheme 5, path B). On the basis of our previous work,[7a] the Boc-protected substrate **1w** was considered as possible intermediate and tested in this transformation (Scheme 6). Although **1w** could give the product **2a** under the standard conditions in 89% yield, we could not detect the **1w** formation in the reaction of **1a** anytime. Moreover, when **1w** was applied as the starting material in the reaction conditions without CO_2, **2a** was not detected, and only the free phenol **1a** was obtained. These results excluded the possibility of **1w** as intermediate and indicated that **1w** underwent decomposition at high temperature to generate **1a**, which further reacted with CO_2 to give other intermediates and the final product **2a**.

Scheme 6. Mechanistic Studies with 1w



At this stage, we speculated the phenoxide played an important role in CO_2 fixation and activating the γ-position, which is highly electron-rich and nucleophilic. Based on the above results and previous reports,[7,18] we proposed a preliminary reaction mechanism for this reaction (Scheme 7).

Scheme 7. Proposed Mechanism



Compound **1a** undergoes deprotonation in the presence of strong base KO^{t}Bu to form **1a-1**, which can generate **1a-2** through reaction with CO_2 or the in situ generated adduct of CO_2 with KO^{t}Bu (e.g., KOCOO^{t}Bu). Next, **1a-2** further reacts with CO_2 or the adduct of CO_2 to give the intermediate **1a-3**.[18] Intramolecular nucleophilic attack and deprotonation with assistance from the base might produce the desired product **2a** along with HO^{t}Bu/K_2CO_3 or $KHCO_3$ as byproducts. Further mechanistic studies are in progress in our laboratory.

In conclusion, we have developed a novel lactonization of heteroaryl and alkenyl C−H bonds with CO_2 to synthesize important coumarin derivatives under transition-metal-free and redox-neutral conditions. A variety of coumarin derivatives are generated in moderate to excellent yields. These reactions feature a broad substrate scope, good functional group tolerance, facile scalability, and easy product derivatization. Given the importance of coumarin derivatives, this user- and eco-friendly synthetic strategy is expected to find wide application in the pharmaceutical industry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03601.

Experimental procedures and characterization of all products (PDF)

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Notes

The authors declare no competing financial interest.

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(11) Lactonization of phenols with CO_2 is difficult, with the following challenges: (a) competitive background reactions of direct ortho and/or para carboxylation, well-known as the "Kolbe−Schmitt reaction"; (b) competitive hydrolysis of the lactones under basic reaction conditions; (c) challenging *O*-carboxylation than *N*-carboxylaiton; (d) compatibility of carboxylation and condensation under the same system.

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