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CO_2 = CO + [O]: recent advances in carbonylation of C–H bonds with CO_2

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Carbon dioxide (CO_2) is an ideal one-carbon source owing to its nontoxicity, abundance, availability, and recyclability. Although the thermodynamic stability and kinetic inertness of CO_2 bring its utilization challenges, many groups have achieved significant progress in the utilization of CO_2 to synthesize valuable carbonyl-containing compounds, which could be also generated *via* oxidative carbonylation of C–H bonds with CO. As CO_2 has a higher oxidation state than CO, it could be considered as a combination of CO and oxidant (CO_2 = CO + [O]), thus providing a safe, redox-neutral and economic strategy. In this Feature Article, we have summarized the recent advances in carbonylation of C–H bonds with CO_2 based on this concept. The plausible mechanisms of such reactions and future of this field are also discussed.

1. Introduction

CO_2 has been regarded as a promising C1 source for a long time as it is a nontoxic, abundant and recyclable building block providing various benefits in organic synthesis.[1] Although the utilization of CO_2 is restricted due to its thermodynamic stability and kinetic inertness, significant effort has been exerted toward the conversion of CO_2 into value-added chemicals.[2] Many kinds of organic transformations of CO_2 have been developed in the last few decades to generate a variety of valuable organic molecules, including important carbonyl-containing compounds.

As it is well known, carbonylation reaction is an important and useful method to synthesize carbonyl-containing compounds, which are widely found in natural products and pharmaceutical molecules.[3] Traditionally, phosgene is the main carbonylation reagent due to its high reactivity.[4] With the development of transition metal catalysis, the feedstock gas carbon monoxide (CO) has been extensively used as a replacement of phosgene in organic synthesis. Notably, the transition-metal-mediated and/or catalyzed oxidative carbonylation with CO *via* direct C–H bond functionalization[5] attracts more and more attention owing to the high efficiency and economy (Scheme 1A).[6] However, both highly toxic CO and stoichiometric oxidants, such as high-valence metal salts or O_2, are indispensable in such carbonylation reactions, which causes

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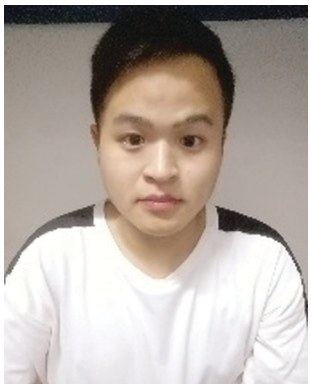

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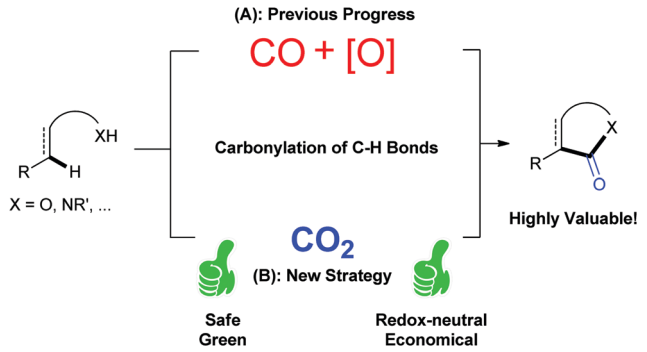

Scheme 1 CO_2 = CO + [O]: new strategy of carbonylation of C–H bonds with CO_2.

environmental impact, safety issues and high cost. Therefore, it is highly desirable to develop a novel carbonylation strategy avoiding the use of oxidants and toxic CO. Because the carbon in CO_2 shows a higher oxidation state than that in CO, CO_2 might act similarly to the combination of CO and oxidant, that is, CO_2 = CO + [O] (Scheme 1B).[2t] Following this concept, if we use CO_2 as the carbonylation source in carbonylation of C–H bonds, we could realize such transformations under redox-neutral conditions, and ideally, with "H_2O" (or carbonate in the presence of base) as the only byproduct, thus solving the problems remaining in the oxidative carbonylation reaction of C–H bonds with CO. Although it looks simple and fantastic, there are huge challenges to formally cleave the strong C═O bond, which is highly energy-demanding. In this Feature Article, we have summarized very recent advances in carbonylation of C–H bonds with CO_2, such as lactamization and lactonization, based on this concept. The plausible mechanisms of such reactions and future of this field are discussed. Another important strategy, *in situ* reduction of CO_2 to CO and the following carbonylation

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with CO,[6j,k] is different from the concept here and will be only briefly mentioned.

2. Lactamization of C–H bonds with CO_2

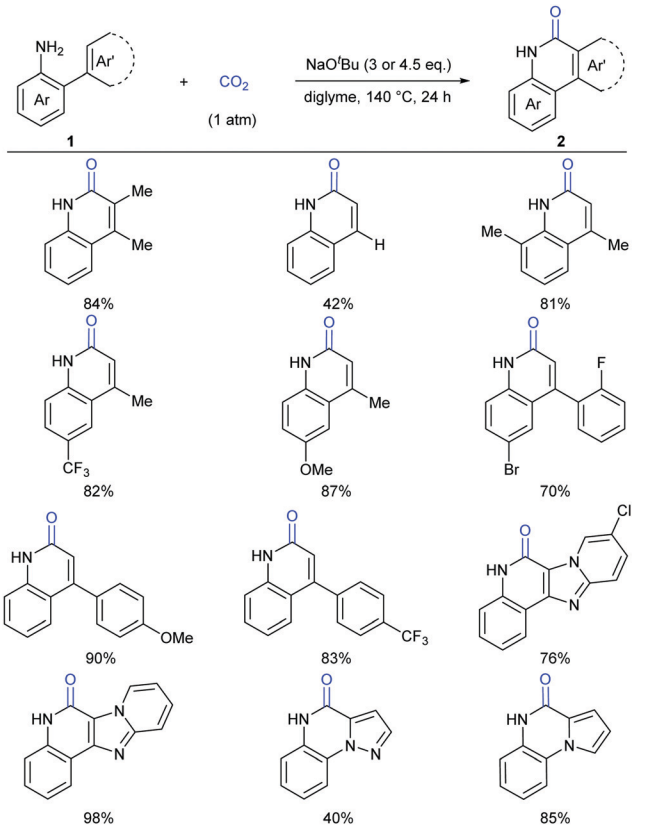
Lactam-containing heterocyclic compounds are common motifs in drugs and bioactive natural products, as well as important intermediates in organic synthesis (Scheme 2).[7] Recently, many groups, such as Alper, Zhu, Chuang, and Zhang groups, have developed nice and efficient methodologies to synthesize these compounds through transition-metal-catalyzed oxidative carbonylation of C–H bonds with CO.[8] However, the requirement of (sub)stoichiometric metal oxidants (Ag^+ or Cu^{2+} salts) represents a major limitation associated with the methods described above.

Different from previous strategies, our group reported the direct lactamization of C(sp^2)–H bonds in *o*-alkenyl- or *o*-heteroaryl-anilines with CO_2 in the presence of base (Scheme 3).[9] In these reactions, CO_2 serves as a carbonylation reagent to avoid the use of external chemical oxidants and toxic CO. These transition metal-free and redox-neutral reactions are simple to operate and user-friendly. By heating *o*-alkenyl- and *o*-heteroaryl-anilines with NaO^{t}Bu in diglyme under 1 atm of CO_2 at 140 °C for 24 hours, a series of important quinolinones and polyheterocyclic compounds were delivered in high efficiency, making it an attractive method for the pharmaceutical industry. We further showed the potential applications of this transformation toward some valuable intermediates and biologically active compounds, including an HBV inhibitor and a key intermediate to Tipifarnib.

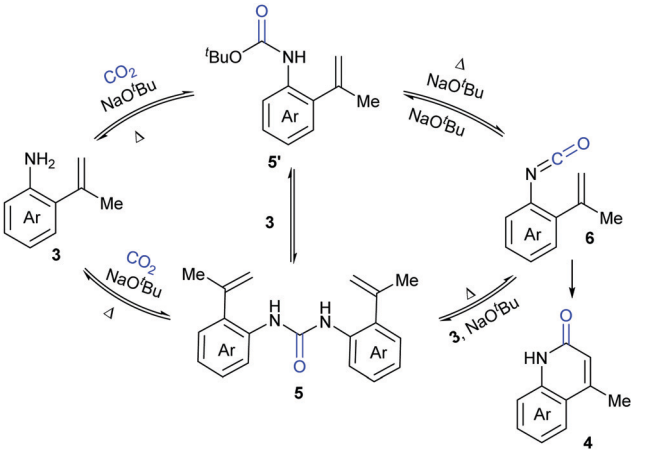
A series of control experiments were conducted to probe the mechanism of this process. First, NaO^{t}Bu-mediated nucleophilic attack of aniline **3** on CO_2 under the reaction conditions would generate intermediates **5** and **5′**, which could undergo elimination to give the key intermediate isocyanates **6**. The following cyclization reaction would efficiently afford the stable products **4** and/or the corresponding deprotonated versions, which might also be a driving force for this transformation (Scheme 4).

This process was further demonstrated by the Li group.[10] Based on the DFT calculation, they speculated that the reaction went through three stages: (i) C–N bond construction to generate the intermediate carbamate species; (ii) deoxygenation of carbamate species to generate isocyanate species **6**; (iii) intramolecular cyclization and H migration to yield the final product **4**. The deoxygenation of the carbamate species in stage (ii) was the rate-determining step for the entire reaction and the base was very important in overcoming the energetic bottleneck in stages (i) and (iii).

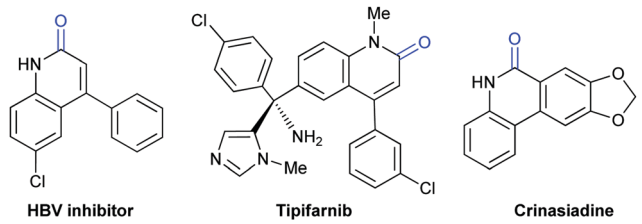
Although our system worked well for those anilines bearing electron-rich alkene or heteroarenes at the *ortho* position, it was not suitable for the unactivated *o*-phenylaniline derivatives, which might arise from the low electron density and nucleophilicity of the *o*-phenyl motif to attack the *in situ* generated isocyanate intermediate. Soon after the publication of our work,[9]



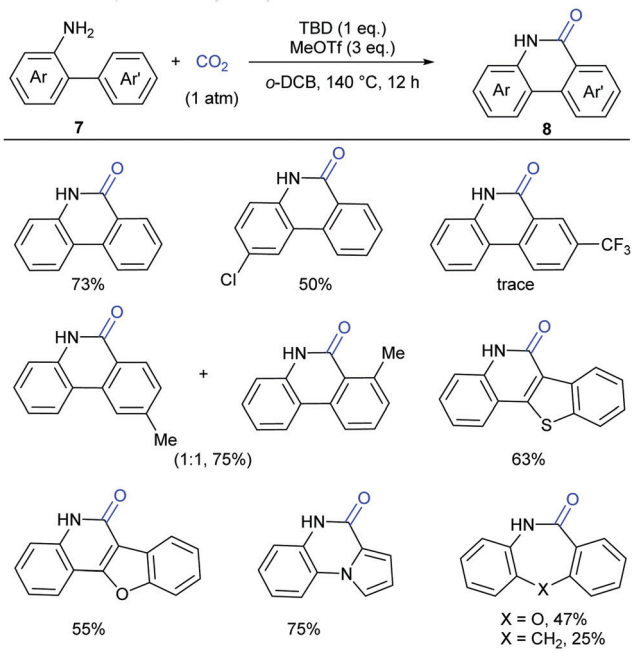
Scheme 3 Transition metal-free carbonylation of C(sp^2)–H bonds in *o*-alkenyl- and *o*-heteroaryl-anilines with CO_2 in the presence of NaO^{t}Bu.



Scheme 4 Possible mechanism for the lactamization reaction.



Scheme 2 Selected biologically active lactam-containing moieties.

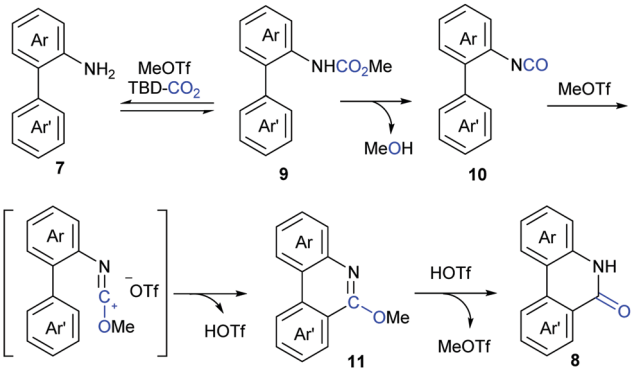


Scheme 5 Transition metal-free carbonylation of C(sp^2)–H bonds in *o*-(hetero)arylanilines with CO_2 in the presence of TBD and MeOTf. *o*-DCB = 1,2-dichlorobenzene.

Xi's group independently reported the carbonylation of (hetero)aryl C(sp^2)–H of *o*-arylanilines with CO_2 by utilizing the combination of methyl triflate (MeOTf) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Scheme 5).[11] Under such conditions, unactivated *o*-phenylaniline derivatives worked nicely. Importantly, high temperature and primary amines were also required for the success of this reaction. The reaction went well with electron-rich aromatic substrates to afford the desired products in high yields. In contrast, the electron-poor ones, such as a CF_3-substituted *o*-phenylaniline, only gave a trace amount of the desired products. When a *meta*-substituted substrate was applied, the regioselectivity of this transformation was difficult to control, providing a mixture of two isomers in 1 : 1 ratio. Notably, besides phenanthridinones, seven-membered lactams could also be obtained using this method, representing a significant advance in lactamization.

In lactamization by Xi's group, they isolated the methyl carbamate **9** and also observed the formation of isocyanate **10** in the reaction system. As shown in Scheme 6, with the aid of MeOTf, the substrate reacted with the adduct of TBD and CO_2 to afford methyl carbamate **9**, which underwent subsequent elimination of one molecule of MeOH at high temperature and converted to aryl isocyanate **10**. Then, methylation of **10** with MeOTf afforded a highly active species, such as the carbenium ion, which was attacked by the *o*-phenyl motif to generate 6-methoxyphenanthridine **11**. Finally, the desired product **8** was obtained *via* acidification.

In the above-mentioned two cases, the lactamization of C–H bonds with CO_2 requires the prepared *o*-alkenyl- or *o*-(hetero)-aryl-anilines as substrates. It has also been interesting whether the lactamization reaction could be realized in cascade reactions through generating such substrates *in situ* from simple

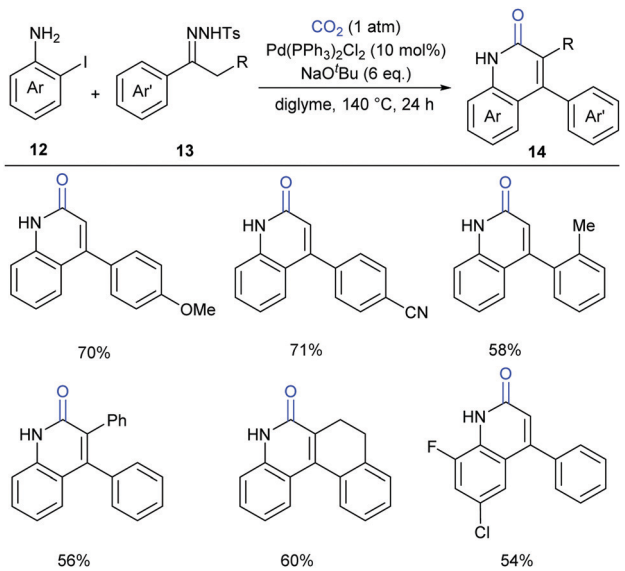


Scheme 6 Proposed mechanism by Xi's group.

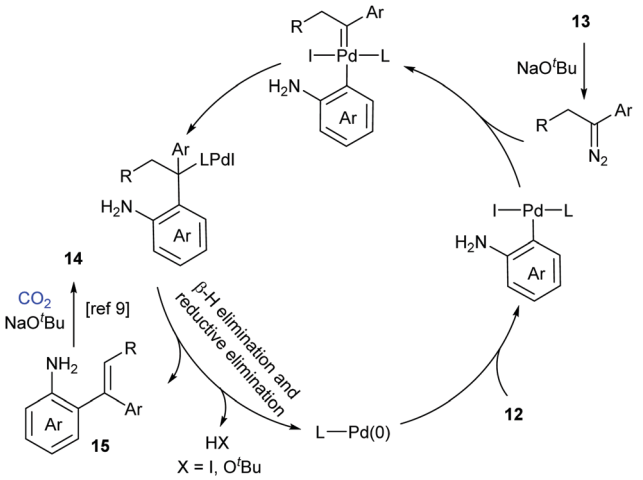
raw materials. Later in 2016, Cheng's group successfully developed a palladium-catalyzed three-component reaction with *N*-tosylhydrazones, 2-iodoanilines and atmospheric CO_2 to generate a series of 4-aryl-2-quinolinones (Scheme 7).[12] The procedure allowed the formation of four bonds in one pot synthesis, representing an efficient methodology for incorporation of CO_2 into heterocycles.

A possible reaction mechanism to explain the tandem carbene migratory insertion/lactamization pathway is shown in Scheme 8. The reaction might start with palladium-catalyzed coupling of aryl halides **12** and *N*-tosylhydrazones **13** to generate a vital intermediate, *o*-vinyl aniline **15**, which further undergoes a similar pathway with CO_2 as in our work to deliver the desired product **14**.[9] Meanwhile, the pathway generating *o*-iodoisocyanatobenzene prior to *o*-vinyl aniline **15** formation could not be excluded.

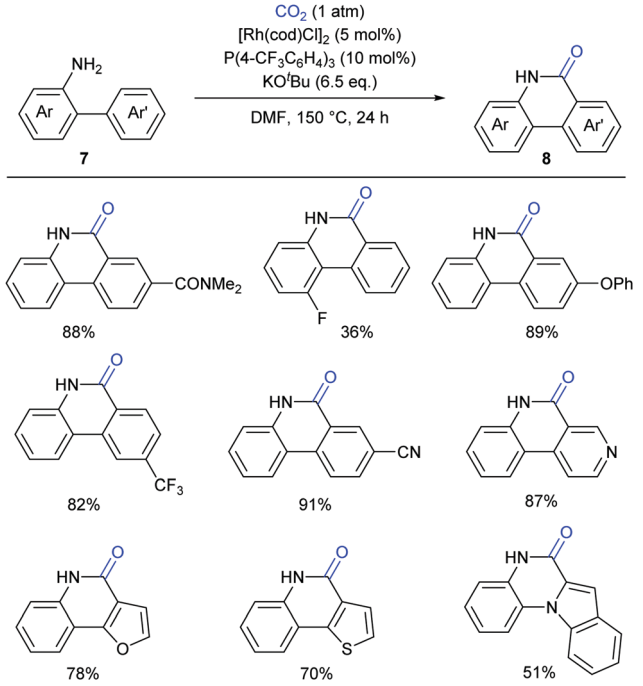
Although such transition-metal-free lactamization protocols are powerful and efficient, there are still limitations in electron-poor aryl substrates. Recently the Li group have reported a novel Rh(I)-catalyzed, amino-group-directed lactamization of aryl C(sp^2)–H bonds in *o*-(hetero)arylanilines with CO_2 in the presence of KO^{t}Bu (Scheme 9).[13] Based on the previous reports on Rh(I)-catalyzed C–H



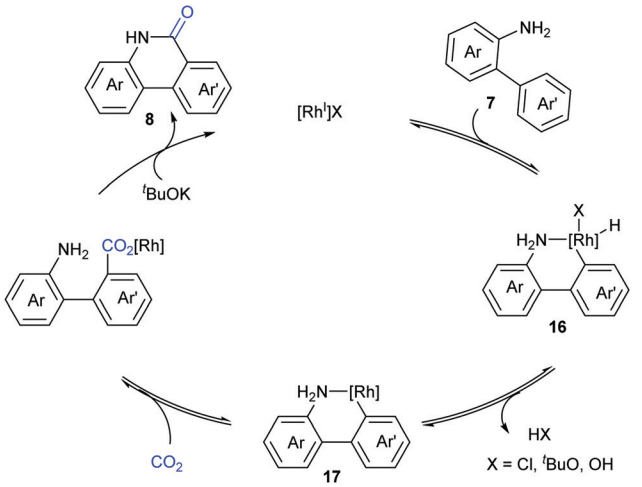
Scheme 7 Cascade lactamization by Cheng's group.



Scheme 8 The proposed mechanism by Chen's group.



Scheme 9 Rh-Catalyzed C–H lactamization of *o*-arylanilines with CO_2.



Scheme 10 The catalytic cycle of Rh(I)-catalyzed lactamization.

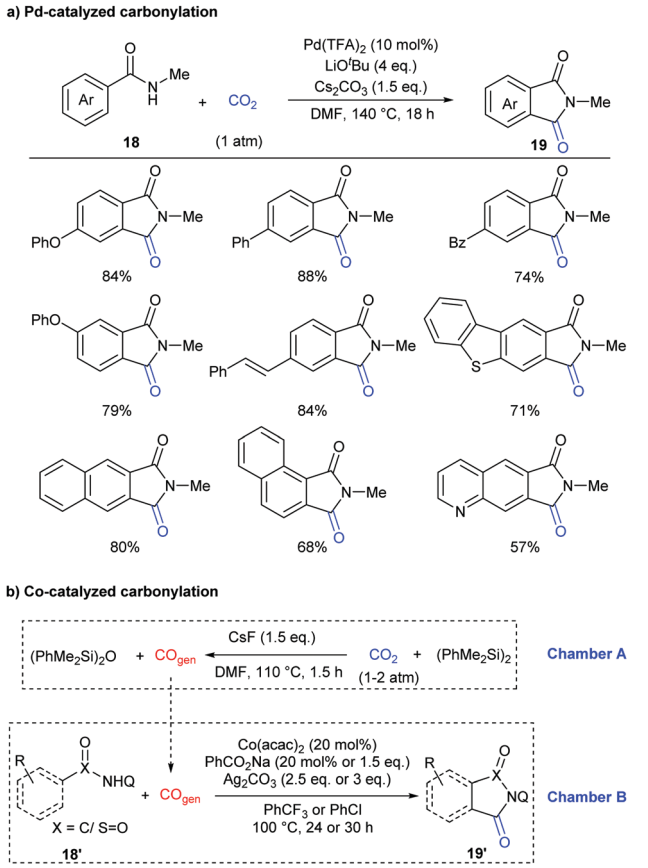
activation[5] and facile insertion of CO_2 into the rhodium–carbon bond,[14] the authors successfully realized such a Rh(I)-catalyzed carbonylation with generation of various functionalized phenanthridinones under redox-neutral conditions. Both electron-rich and electron-poor substrates showed good reactivity for this transformation, which showed a significant improvement compared to previous works.[9,11] Besides *o*-arylanilines, this reaction could be also extended to *o*-heteroarylanilines, such as pyridyl-, furanyl- and indolyl-substituted anilines, giving products with potential biological activity.

Based on the control experiments, a possible mechanism involving reversible oxidative addition of the aryl C–H bond to a Rh(I) species **16**, reductive elimination of HX, and reversible nucleophilic carboxylation with CO_2, followed by irreversible lactamization, was proposed by Li and co-workers (Scheme 10).

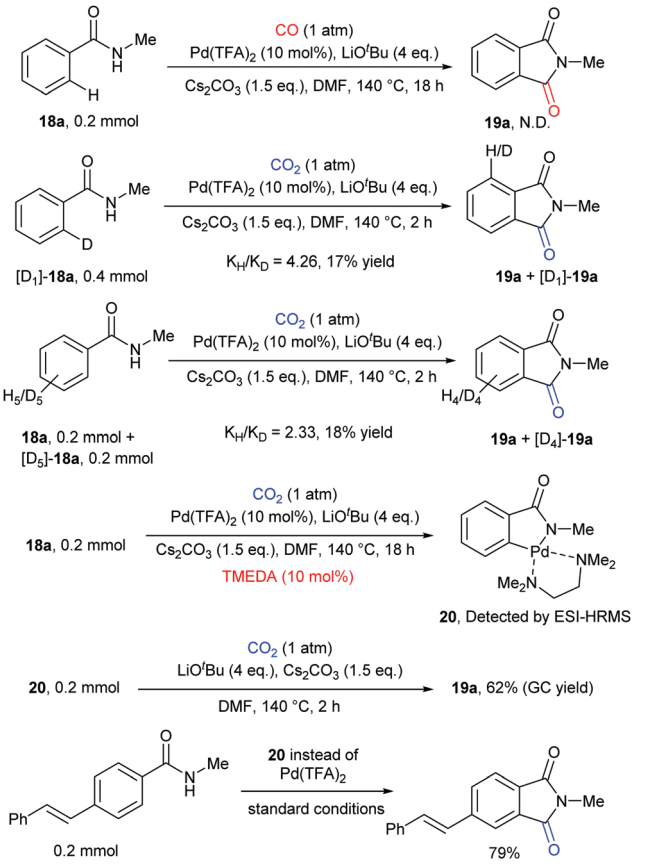
In addition to the construction of six-membered lactam-containing heterocyclic compounds, the core of five-membered phthalimides also attracts much attention.[15] Recently, this skeleton has usually been constructed through transition-metal-catalyzed carbonylation of C–H bonds with CO in the presence of oxidants or hydrogen acceptors.[16] In 2018, our group reported the first example of palladium-catalyzed carbonylation of unactivated aryl C–H bonds in benzamides with CO_2 to afford phthalimides under redox-neutral conditions (Scheme 11a).[17a] Due to the influence of steric hindrance and directing ability, the substituents on the nitrogen of the benzamides were crucial, only the methyl group featuring good reactivity. Both electron-donating groups and electron-withdrawing groups could be well tolerated in the standard conditions. It is worth mentioning that carbonylation of the C–H bond selectively occurred at the less hindered *ortho* position for the substrates with *meta* substituents.

Some control experiments were further conducted to shed light on the mechanism of the transformation (Scheme 12). We first excluded the possibility of the *in situ* generation of CO as the active carbonylation reagent and confirmed that the carbonyl group comes from CO_2 *via* ^{13}C-labeling experiments. The kinetic isotope effect (KIE) value indicated that the C–H activation step might be involved in the rate-determining step. We also postulated that the palladacycle species **20** might act as a vital intermediate in the reaction, as it was detected by ESI-HRMS when nitrogen ligands were employed to increase its stability. Notably, it also showed reactivity in both stoichiometric and catalytic version of such carbonylation.

Later, another strategy, *in situ* reduction of CO_2 to CO and the following carbonylation with CO, was also used to construct phthalimide skeletons by Sundararaju's group.[17b] A tandem reaction was realized in a two-chamber reactor for efficient fluoride-mediated generation of CO from CO_2 using disilane as a deoxygenating reagent and utilization of the *in situ*-produced CO for C–H carbonylation using cobalt catalysis (Scheme 11b). In addition to the C(sp^2)–H bond, the C(sp^3)–H bond was also compatible in the system.



Scheme 11 Transition-metal-catalyzed carbonylation of benzamides with CO_2.

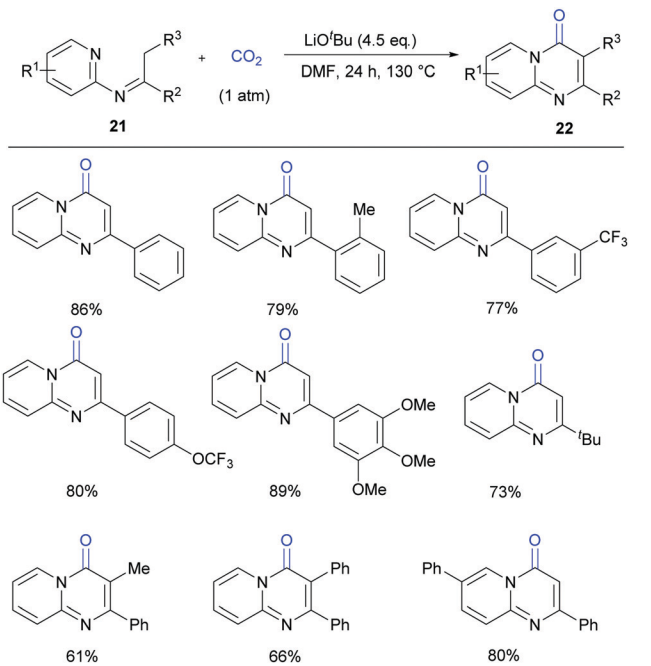


Scheme 12 Selected mechanistic studies for Pd-catalyzed carbonylation.

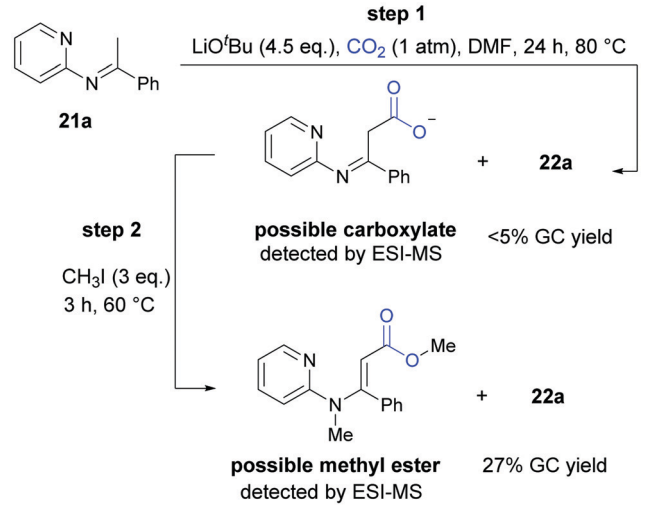
Compared to most of the research in this field which focused on the lactamization of C(sp^2)–H bonds, lactamization of C(sp^3)–H bonds with CO_2 is more challenging. Very recently, our group reported the lactamization of C(sp^3)–H bonds in pyridylamines with one atmosphere of CO_2 to synthesize important pyrimidinones (Scheme 13).[18a] Different from the previous report on Pd-catalyzed lactamization of ketoimines with CO and oxidant,[18b] these reactions take place under transition-metal-free and redox-neutral conditions with atmospheric CO_2 as the carbonyl source. The reactions can be performed on a gram scale, and the product can undergo derivatization easily. Moreover, some bio-active compounds can be quickly prepared by this method.

In the mechanistic studies, we found that **22a** was generated in very low yield at 80 °C and the carboxylative product could be detected obviously by ESI-MS. When the reaction was quenched by CH_3I, we detected the corresponding methyl ester by ESI-MS and the product **22a** in a higher yield, all of which indicated that both the carboxylate intermediate and the ester were important in cyclization reaction to generate the desired product (Scheme 14).

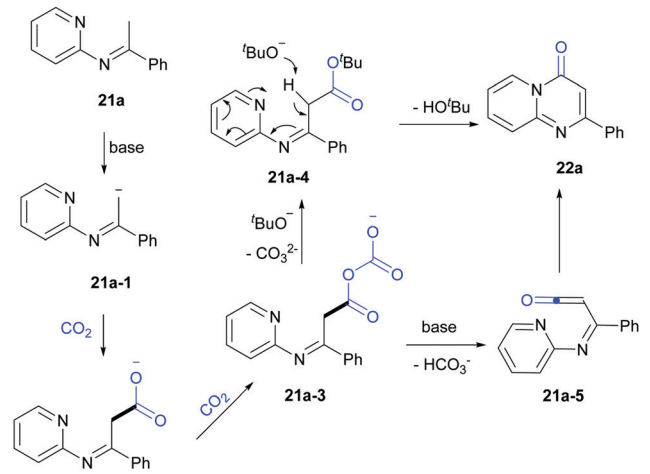
Based on the mechanistic studies and previous reports,[19] a possible pathway was proposed (Scheme 15). **21a-1** was formed in the presence of LiO^{t}Bu and further reacted with CO_2 to generate carboxylate intermediates **21a-2** and **21a-3**. Then **21a-3** might react with LiO^{t}Bu to generate **21a-4**, which transformed to **22a** in the presence of base. In addition, another pathway through **21a-5** might be also possible.



Scheme 13 Transition metal-free carbonylation of C(sp^3)–H bonds in pyridylamines with CO_2 in the presence of LiO^{t}Bu.



Scheme 14 Mechanistic studies for carbonylation of C(sp^3)–H bonds in pyridylamines with CO_2.

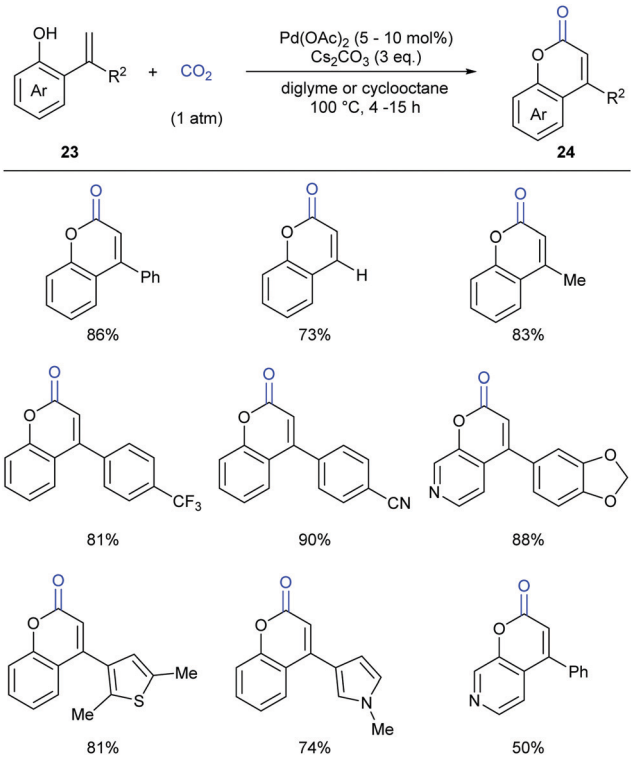


Scheme 15 Proposed mechanism for carbonylation of C(sp^3)–H bonds in pyridylamines with CO_2.

3. Lactonization of C–H bonds with CO_2

As another important class of carbonyl compounds, lactone-containing compounds are also prevalent in nature and a key structural motif in many bioactive molecules.[20] Among the diverse ways to synthesize such structures, it is of great significance to realize carbonylation of C–H bonds. However, the carbonylation reagents are mainly restricted to highly toxic CO.[3] Considering the advantages of CO_2, it is highly important to develop such reactions with CO_2 as the carbonyl source.

In 2013, the Iwasawa group pioneered in this field and developed the first palladium-catalyzed lactonization of alkenyl C–H bonds in *o*-alkenylphenols **23** with CO_2 to afford a variety of coumarins **24** with good yields (Scheme 16).[21] The use of Pd-catalyst was vital for the reaction and Cs_2CO_3 was important for the high efficiency. Many functional groups, such as

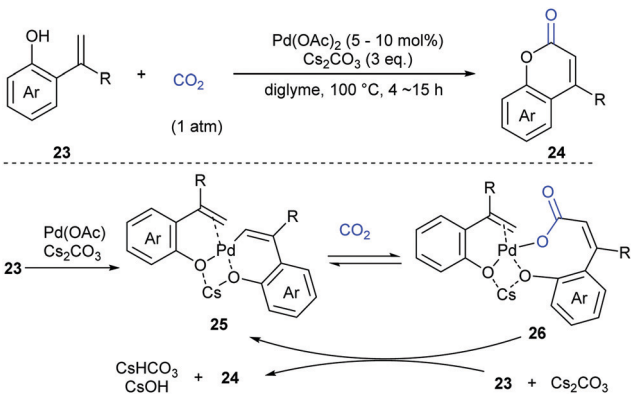


Scheme 16 Pd-Catalyzed carbonylation of cyclization of *o*-alkenylphenols with CO_2.

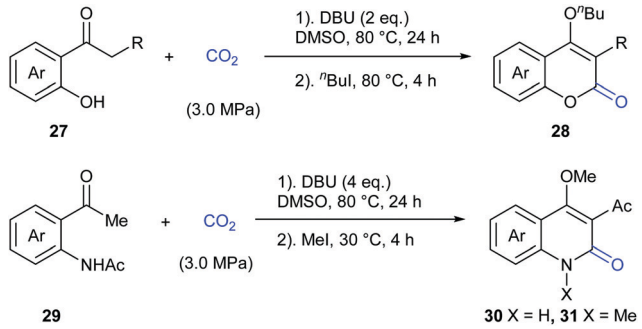
trifluoromethyl, methoxyl and cyano groups, as well as many heterocycles, such as thiophene, pyrrole and pyridine, could be well tolerated under the reaction conditions.

Extensive studies were performed to reveal the mechanism (Scheme 17). A six-membered palladacycle **25**, the key intermediate generated *via* C–H bond cleavage, was isolated and characterized by means of single-crystal X-ray diffraction. Then, the nucleophilic addition of **25** to CO_2 gave a palladium carboxylate intermediate, which further reacted with another molecule of *o*-alkenylphenol **23** and Cs_2CO_3 to give the desired coumarin product **24** and regenerate the intermediate **25**.

In 2015, the Zhang and Lu group reported a novel transition metal-free carbonylation of C(sp^3)–H bonds in *o*-hydroxyacetophenones and *o*-aminoacetophenones with CO_2 in the presence of



Scheme 17 Proposed mechanism for Pd-catalyzed carbonylation reaction.

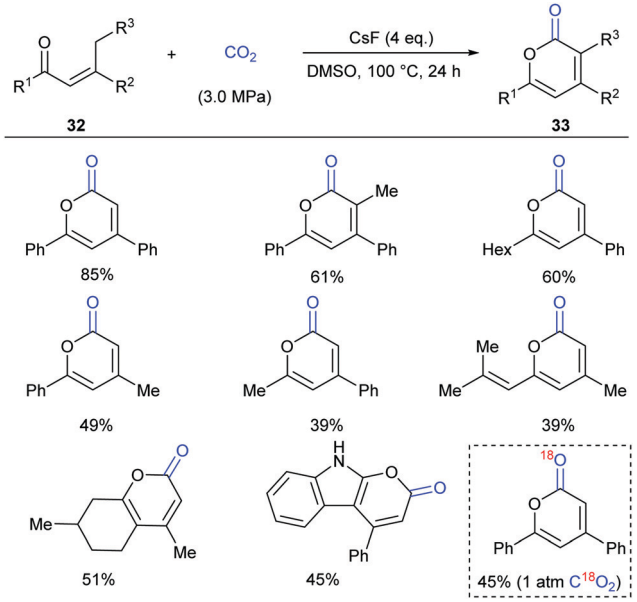


Scheme 18 DBU-mediated carbonylation reaction.

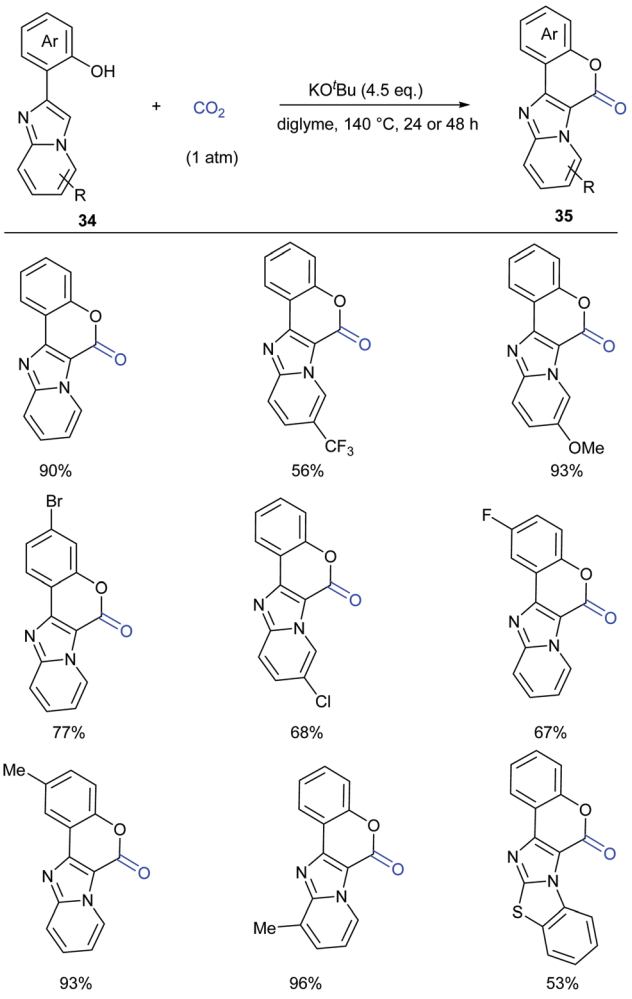
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base (Scheme 18).[22] The driving force for this transformation mainly relied on the cyclization of the *in situ* formed β-ketoester with tethered oxygen and nitrogen nucleophiles to form stable heterocycles.

Inspired by the results, in 2016 the same group continuously developed a CsF-promoted carboxylative cyclization of propenyl ketones with CO_2 to synthesize α-pyrones (Scheme 19).[23] A low concentration of the substrate and a high pressure of CO_2 are vital for high conversion and selectivity of the reaction. To exclude the possibility of a trace amount of palladium impurity in base functioning as a catalyst, $Pd(OAc)_2$ was added into the system and decreased reactivity was observed, implying a transition-metal free environment for the reaction conditions. When $C^{18}O_2$ was utilized in this reaction, the product was obtained with only one ^{18}O atom, which clearly demonstrated that the carbonyl was from CO_2 in this transformation.

Considering the important biological activity of imidazo[1,2-*a*]pyridine skeleton-containing compounds, we envisioned whether a series of hybrid structures of coumarin derivatives could be obtained *via* carbonylation of C–H bonds in imidazo[1,2-*a*]pyridines with CO_2. In 2017, our group successfully



Scheme 19 CsF-mediated carbonylation reaction.

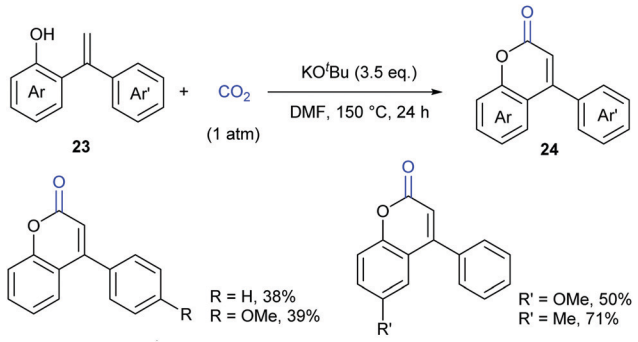


Scheme 20 Lactonization of *o*-(imidazole[1,2-α]pyridine-2-yl)phenols with CO_2.

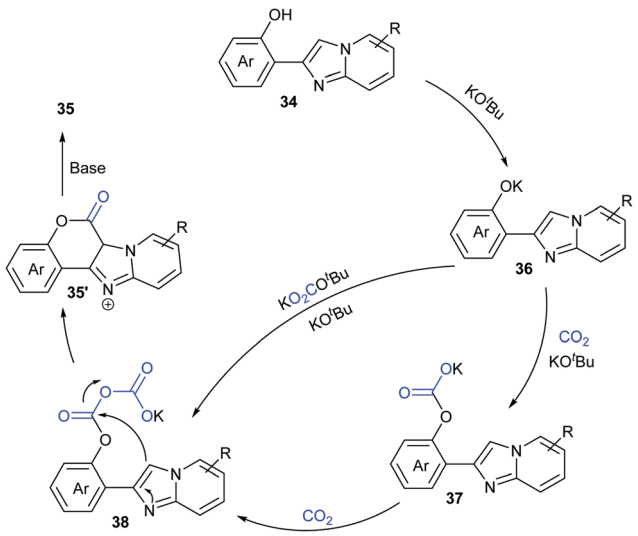
developed the KO^{t}Bu-promoted lactonization of *o*-heteroaryl- and *o*-alkenyl phenols with CO_2 to generate coumarin derivatives with good to excellent yields (Scheme 20).[24] This transformation featured a broad substrate scope and good functional group tolerance. In addition to *o*-(imidazole[1,2-α]pyridine-2-yl)phenols, *o*-(benzo[*d*]imidazo[2,1-*b*]thiazol-2-yl)-phenol and *o*-alkenylphenols could also undergo a similar lactonization reaction with high efficiency (Scheme 21).

Based on the control experiments, we proposed a possible mechanism (Scheme 22). Deprotonation of compounds **34** with KO^{t}Bu formed phenolic potassium **36**, which could react with CO_2 or with the *in situ* generated adduct of CO_2 and KO^{t}Bu (*e.g.* $KOCO_2{}^tBu$) to afford the carbonate intermediate **37**. Then, a similar process took place further to give the intermediate **38**. Intramolecular nucleophilic attack with the assistance of base afforded the desired coumarin product **35**.

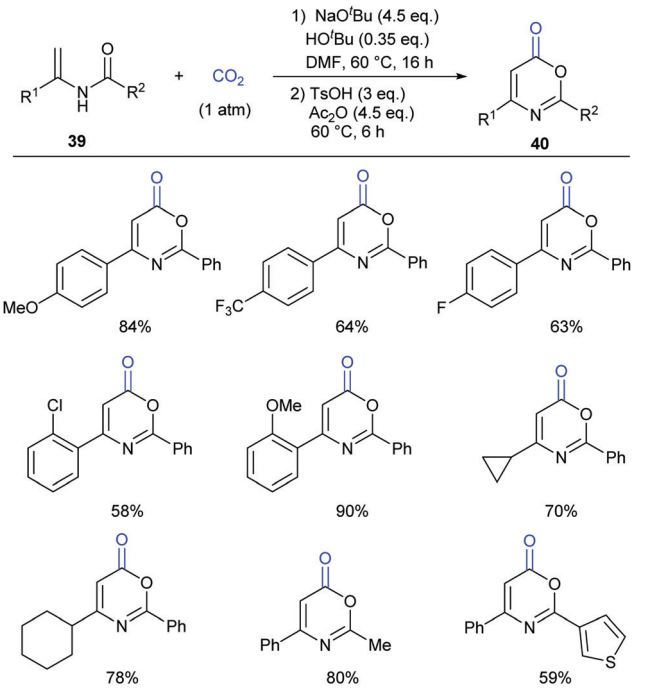
Different from our previous works,[9,24] we wondered whether the carbonylation initiated *via* the nucleophilic attack from the electron-rich carbon sites instead of heteroatom sites (such as nitrogen in aniline and oxygen in phenol) was feasible. Therefore, we turned our attention to electron-rich enamides, which should



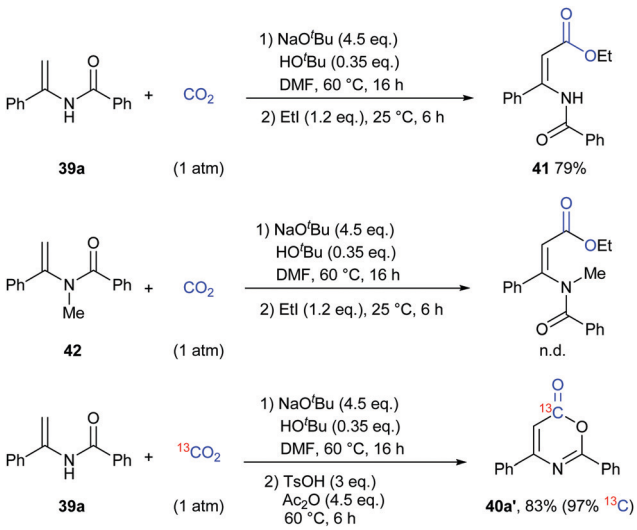
Scheme 21 KO^{t}Bu-promoted lactonization of *o*-alkenylphenols with CO_2.



Scheme 22 The plausible mechanism for KO^{t}Bu-promoted lactonization of *o*-(hetero)aryl/alkenyl phenols with CO_2.



Scheme 23 NaO^{t}Bu-promoted carboxylation cyclization of enamides with CO_2.

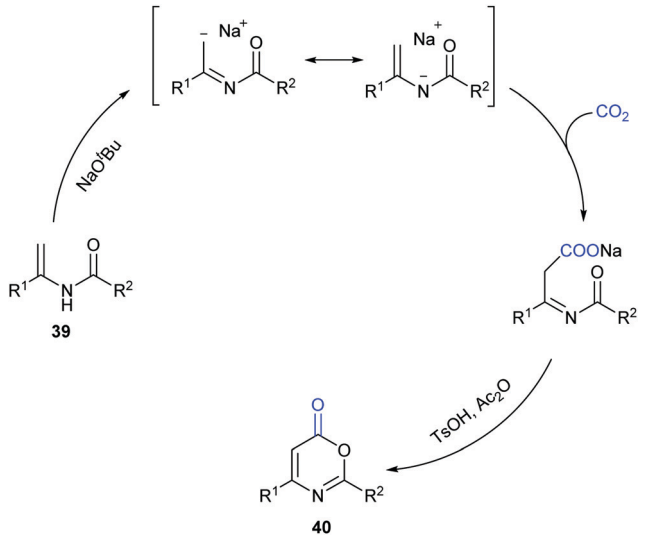


Scheme 24 Mechanistic studies for the carbonylation of enamides with CO_2.

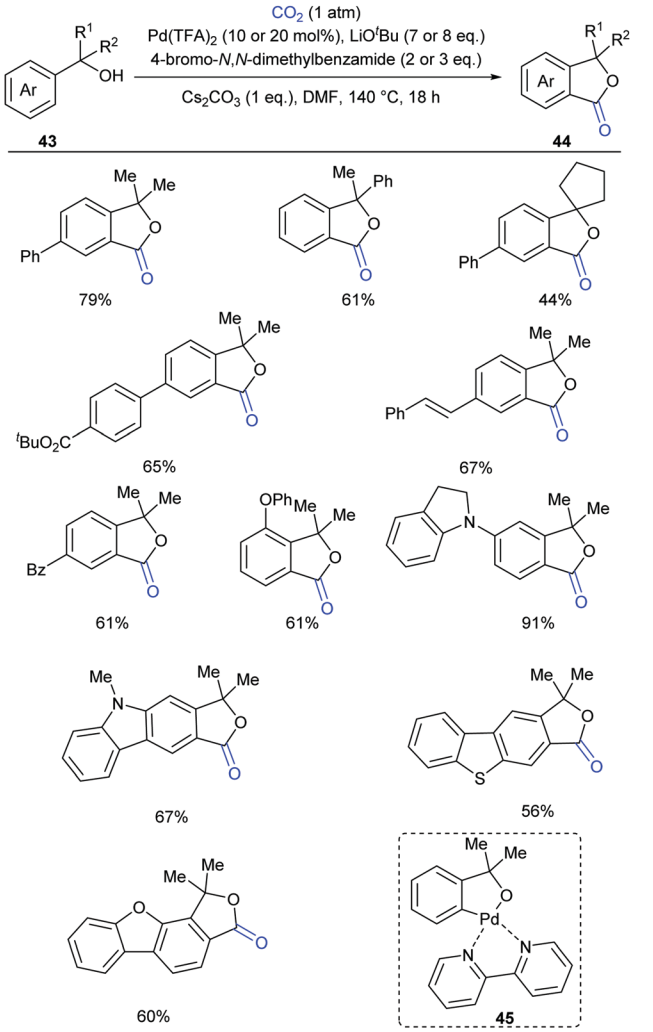
show higher nucleophilicity in the presence of a strong base. If the carboxylation of C(sp^2)–H bonds in enamides with CO_2 and the following cyclization happened in sequence, we might be able to construct important oxazinone motifs.[25] Indeed, based on this hypothesis, we succeeded in the synthesis of 1,3-oxazin-6-ones in one pot with two steps (Scheme 23).[26] Although we did realize the carboxylation of C(sp^2)–H bonds in enamides with CO_2 in the presence of NaO^{t}Bu, the intermediates did not undergo condensation under the basic reaction conditions. Therefore, additional acid and anhydride were vital to promote the condensation to afford the desired products. Notably, such products could be transformed to important pyrimidines and pyridines through decarboxylation [4+2] cycloaddition.

To gain more insight into this transformation, some mechanistic studies were conducted (Scheme 24). First, the corresponding ester **41** could be obtained by adding iodoethane (EtI) into the system, which could confirm the process of nucleophilic attack of electron-rich carbon in enamides on CO_2. Then, when the *N*-methyl substituted enamide **42** was used, this transformation could not occur, which indicated that the interconversion of enamides and imines was important for the reaction under the basic conditions. Moreover, we also ran this reaction with $^{13}CO_2$ and obtained the ^{13}C-labeled coumarin in high yield, demonstrating that the carbonyl was derived from CO_2.

On the basis of the results, we proposed a possible pathway as shown in Scheme 25. Deprotonation of enamides by NaO^{t}Bu occurred to generate the enamide anions, which could react with CO_2 to form carboxylates. Then, the desired product could be achieved by acidification and cyclization in the presence of acid and anhydride.



Scheme 25 The plausible mechanism of the carbonylation of enamides with CO_2.



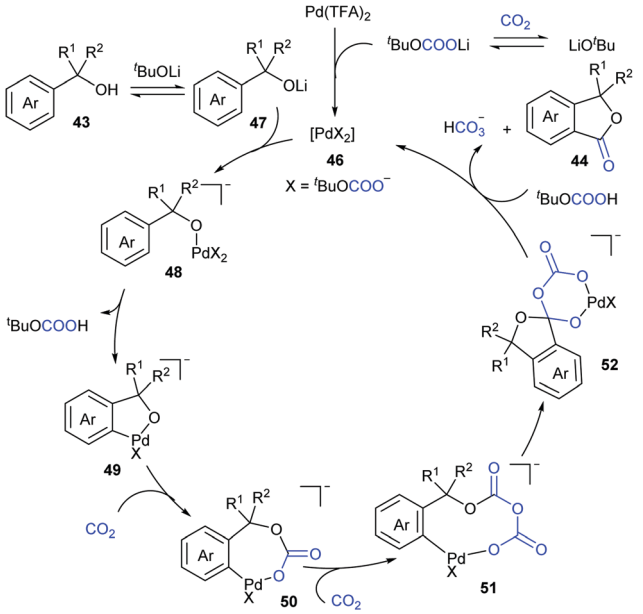
Scheme 26 Pd-Catalyzed carbonylation of tertiary benzylic alcohols with CO_2.

Compared to the C(sp^2)–H bonds in alkenes and electron-rich heteroarenes, the carbonylation of unactivated aryl C–H bonds with CO_2 is more difficult due to the lower reactivity and less nucleophilicity. In 2018, our group reported the first palladium-catalyzed carbonylation of the unactivated aryl C–H bond with CO_2 to construct phthalides (Scheme 26)[27] using tertiary benzylic alcohols as directing groups, which exhibit week coordination to transition metals and might undergo several side reactions, including β-H elimination and C–C bond cleavage. We used a strong base to deprotonate the benzyl alcohol, thus enhancing the coordinative ability of oxygen. However, under such basic conditions, the palladium(II) catalyst was prone to be reduced to inactive palladium black. After an extensive survey of mild oxidants, aryl bromides stood out for maintaining palladium(II) catalyst activity without interfering with the reaction. The selectivity issue arising from the side reactions of tertiary benzylic alcohols was suppressed by lactonization to form the desired products, although the primary and secondary alcohols mainly underwent oxidation *via* Pd-catalyzed β-H elimination. This reaction was not hampered by *ortho* substitution and C–H lactonization selectively occurred at the less hindered *ortho* position for *meta* substituted substrates. Heterocycles were also tolerated. When ^{13}C-labeled CO_2 and an ^{18}O-labeled substrate were used, we could confirm that the carbonyl group was from CO_2 and the alcohol oxygen atom was fully incorporated into the product. Based on the mechanistic experiments, we postulated that the five-membered palladacycle species **45** was a plausible intermediate, which could be detected by ESI-HRMS using bipyridine as the ligand.

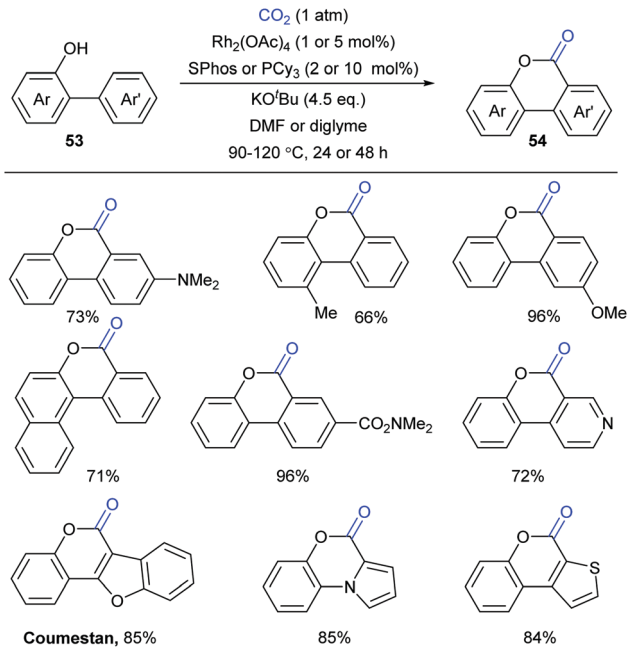
Based on the density functional theoretical (DFT) calculations and the experimental results, we proposed a possible mechanism (Scheme 27). The active catalytic complex **46** could be generated *in situ* from Pd(TFA)$_2$ in the presence of LiO^{t}Bu and CO_2, followed by a counter anion exchange with lithium alcoholate intermediate **47** to afford alcoholate–Pd intermediate **48**. Subsequent C–H bond cleavage generated the five-membered palladacycle intermediate **49**, followed by two sequential nucleophilic attack on CO_2 to afford intermediate **51**. Intramolecular attack then leads to complex **52**, which further underwent decarbonization and ligand exchange to deliver the desired product **44** and regenerate the catalyst **46**. In this catalytic cycle, CO_2 has been proven to promote this reaction by decreasing the ring strain in the intramolecular nucleophilic addition and enhancing the leaving ability and provide a novel pathway *via* decarbonization for C–O bond cleavage.

At the same time, the Li group independently displayed an elegant Rh-catalyzed lactonization of *o*-(hetero)arylphenols with CO_2 (Scheme 28).[14d] The utilization of an electron-rich phosphine ligand, 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos), greatly enhanced the reactivity and avoided the undesired Kolbe-Schmitt type reaction. KO^{t}Bu could trap CO_2 and increase the concentration of CO_2 in the solution. Steric hindrance was tolerated in the phenolic part but not in the phenyl part. This transformation occurred at the less hindered *ortho* position for *meta*-substituted substrates with unique selectivity.

A plausible reaction mechanism was proposed as shown in Scheme 29. The intermediate **55** was formed *in situ* by coordination

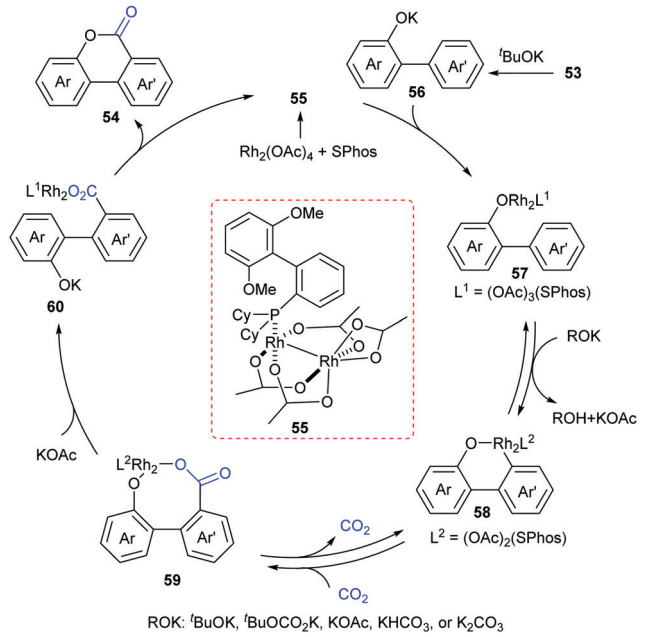


Scheme 27 Possible reaction mechanism for carbonylation of tertiary benzylic alcohols with CO_2.

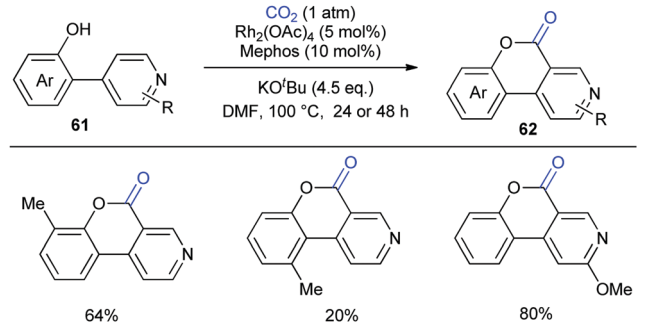


Scheme 28 Rh-Catalyzed lactonization of *o*-(hetero)arylphenols with CO_2.

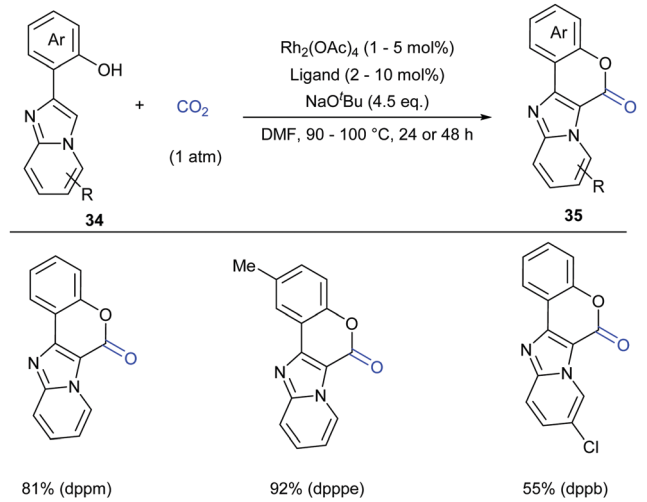
of the Rh-catalyst. Then, it coordinated with **56** generated from deprotonation of **53** by KO^{t}Bu to afford intermediate **57**. With the assistance of an external base, the rhodacycle **58** was generated through the reversible aryl C–H bond activation of **57** *via* a proton abstraction process, followed by nucleophilic attack on CO_2 to achieve the eight-membered complex **59**. Subsequently, ligand exchange and rapid lactonization delivered the desired product **54** and regenerated the complex **55**. It was noteworthy that the shift of the carboxylation–decarboxylation equilibrium to the



Scheme 29 The catalytic cycle of Rh-catalyzed lactonization reaction.



Scheme 30 Rh-Catalyzed C–H carbonylation of 2-pyridylphenols with CO_2. Mephos = 2-(dicyclohexylphosphino)-2′-methylbiphenyl.



Scheme 31 Rh-Catalyzed carbonylation of *o*-(imidazo[1,2-*a*]pyridine-2-yl)phenols with CO_2. dppm = bis(diphenylphosphino)methane, dpppe = 1,5-bis(diphenylphosphino)pentane, dppb = 1,4-bis(diphenylphosphino)butane.

carboxylation intermediate **59** could be determined by the ligand exchange and lactonization process. This process should be fast and irreversible under the reaction conditions.

Although the Li group have developed an efficient Rh-catalyzed lactonization method, there is only an isolated example of *o*-pyridylphenol in this work.[14d] To extend this strategy, this group further reported Rh-catalyzed C–H carboxylation cyclization of more challenging electron-deficient 2-pyridylphenols with CO_2 by tuning ligands (Scheme 30).[14e] A class of pyrido-coumarin derivatives has been synthesized. Apart from this, the group continuously expanded the catalytic system to *o*-(imidazo[1,2-*a*]pyridine-2-yl)phenols through ligand changes, and provided an access to coumarin derivatives based on the structure of imidazo[1,2-*a*]pyridine (Scheme 31).[14f]

4. Conclusions

Carbonylation of C–H bonds with CO_2 has emerged as an alternative to the traditional oxidative carbonylation in constructing carbonyl-containing heterocycles under redox-neutral conditions. As a carbonylation reagent, CO_2 has displayed great superiority over CO used in oxidative carbonylation, which usually poses safety, cost, and environmental issues. The main pathway for the redox-neutral carbonylation with CO_2 refers to the successive nucleophilic attack on CO_2 with the substrate possessing two nucleophilic sites. In many cases, a carbonate might be generated as a byproduct in the presence of base, facilitating the challenging C=O bond cleavage. Although promising, there are still many important challenges in the carbonylation with CO_2. For example, high temperature and high loading of a strong base are always required in the process. It would be more favorable to realize CO_2 transformation under milder and more environmentally benign conditions. Then, the current catalytic system is mainly focused on noble metal catalysis, and the turnover number/efficiency is still unsatisfactory. It is urgent to develop more efficient and inexpensive transition metal catalytic systems. Moreover, the type of C–H activation is essentially confined to C(sp^2)–H bonds and the relatively acidic C(sp^3)–H bonds; the more inert C(sp^3)–H bonds are less explored. Furthermore, the asymmetric C–H carbonylation should be further developed with suitable chiral ligands for highly enantioselective control. Last but not least, the application of this concept in the generation of ketones *via* double C–H carbonylation will be also highly attractive in organic synthesis. Taken together, we believe that the concept of CO_2 as the combination of CO and oxidant (CO_2 = CO + [O]) will continue to show its special advantages and invoke more and more attention in both laboratory and industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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