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# Strategies for the lactamization/lactonization of 2-arylanilines/2-arylphenols using $CO_2$ as C1 source

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ABSTRACT

Phenanthridin-6(5*H*)-ones and 6*H*-benzo[*c*]chromen-6-ones are important tricyclic heterocycles found in several natural products and biologically active compounds. Besides classical synthetic methods, recently, many exciting advances in the synthesis of these classes of compounds have been reported. One of the most appealing strategies to obtain these heterocyclic motifs consists the direct lactamization/lactonization of 2-arylanilines/2-arylphenols using $CO_2$ as C1 source. In this review, recent advances involving the synthesis of phenanthridin-6(5*H*)-one and 6*H*-benzo[*c*]chromen-6-one derivatives through the lactamization and lactonization of 2-arylanilines and 2-arylphenols, respectively, with $CO_2$ are summarized. The review covers the period from April 2016 to June 2024.

## 1. Introduction

Carbon dioxide ($CO_2$) is an abundant, inexpensive, nontoxic, nonflammable, and renewable C1 resource [1-5] as well as a greenhouse gas responsible for global warming and climate change [6, 7]. Effective and efficient capture and utilization of $CO_2$ is becoming ever-increasingly important from the viewpoint of sustainability, and $CO_2$ fixation is a key molecular technology for realizing carbon-neutral societies [8]. The utilization of $CO_2$ as a C1-chemicals building block is a topic of high interest and nowadays heavily discussed and investigated. Over the years, a number of proficient reactions have been developed for the conversion of $CO_2$ into value-added chemicals such as carboxylic acids [9], carbamates [10], ureas [11], carbonates [12], ketones [13], aldehydes [14], alcohols [15], amides [16], and many more. Developing new synthetic approaches for benign $CO_2$ utilization is of current interest [17]. In this context, the synthesis of biologically important phenanthridin-6(5*H*)-ones [18-20] and 6*H*-benzo[*c*]chromen-6-ones [21-33] through the lactamization and lactonization of easily accessible 2-arylanilines and 2-arylphenols, respectively, with $CO_2$ has recently attracted considerable attention from the viewpoint of green and sustainable chemistry. However, to the best of our knowledge, a comprehensive review on this chemistry has not been reported in the literature till date. This mini-review is an attempt to summarize the data available from the literature about the synthesis of phenanthridin-6(5*H*)-one and 6*H*-benzo[*c*]chromen-6-one derivatives through the carboxylation of corresponding 2-arylanilines and 2-arylphenols, respectively, with $CO_2$ (Figure 1). Thus, the review is divided into three major sections. The first section will be focused on the lactamization of 2-arylanilines using

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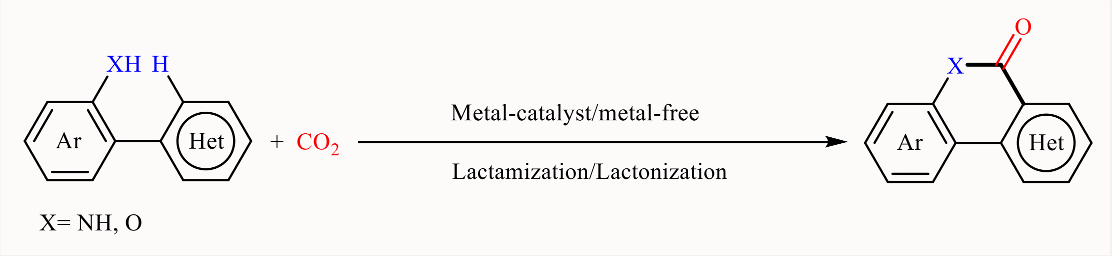
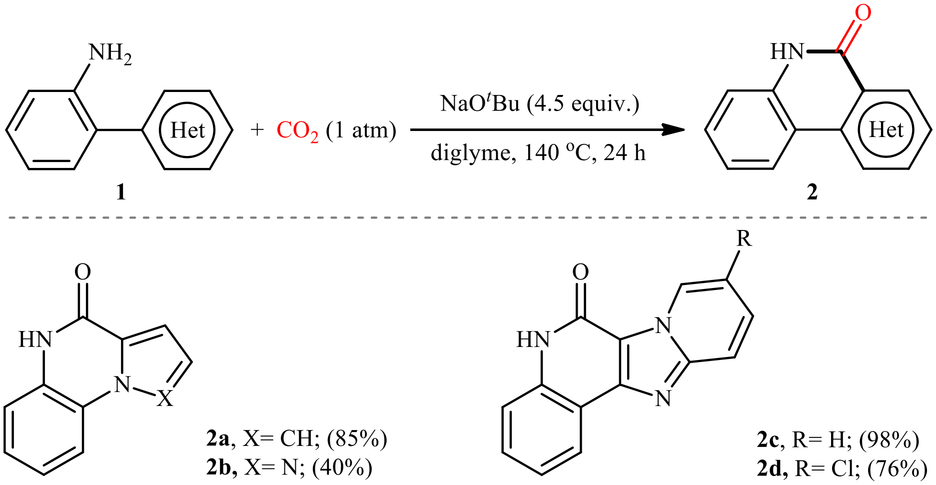


**Fig. 1.** Lactamization/lactonization of 2-arylanilines/2-arylphenols with $CO_2$.

$CO_2$. In the second section, methodologies for the lactonization of 2-arylphenols with $CO_2$ will be discussed. The mechanistic aspects of the reactions will be considered and discussed in detail.

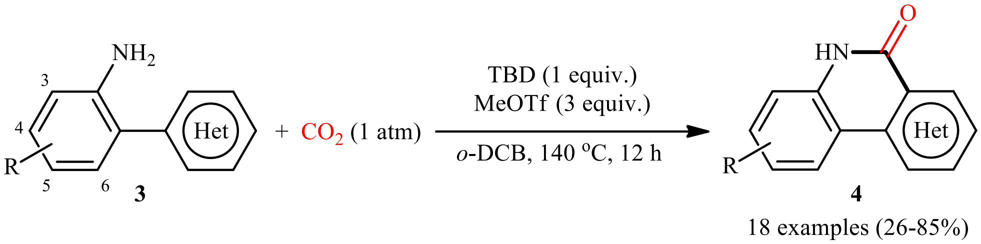
## 2. Lactamization of 2-(hetero)arylanilines

The first direct use of carbon dioxide in the lactamization of sp$^2$-hybridized carbon–hydrogen (C–H) bonds was described in 2016 by Yu and co-workers [34]. They showed that a series of 2-heteroarylanilines **1** underwent carbonylative cyclization by C-H activation using atmospheric $CO_2$ as the CO surrogate in the presence of excess amounts of sodium *tert*-butoxide as a base in diglyme at 140 °C. The corresponding polyheterocycles **2** containing a free (NH)-lactam motif were obtained in moderate to excellent yields, ranging from 40% to 98%. As shown in Scheme 1, anilines with various kinds of *ortho*-heteroarenes, including imidazo[1,2-*a*]pyridine, pyrazole, and pyrole were compatible substrates in this transformation. Notably, when 2-alkenylanilines were subjected to the same reaction conditions, the corresponding 2-quinolinones were formed in fair to high yields. According to the mechanism proposed by the author, this lactamization reaction proceeds a reactive isocyanate intermediate.



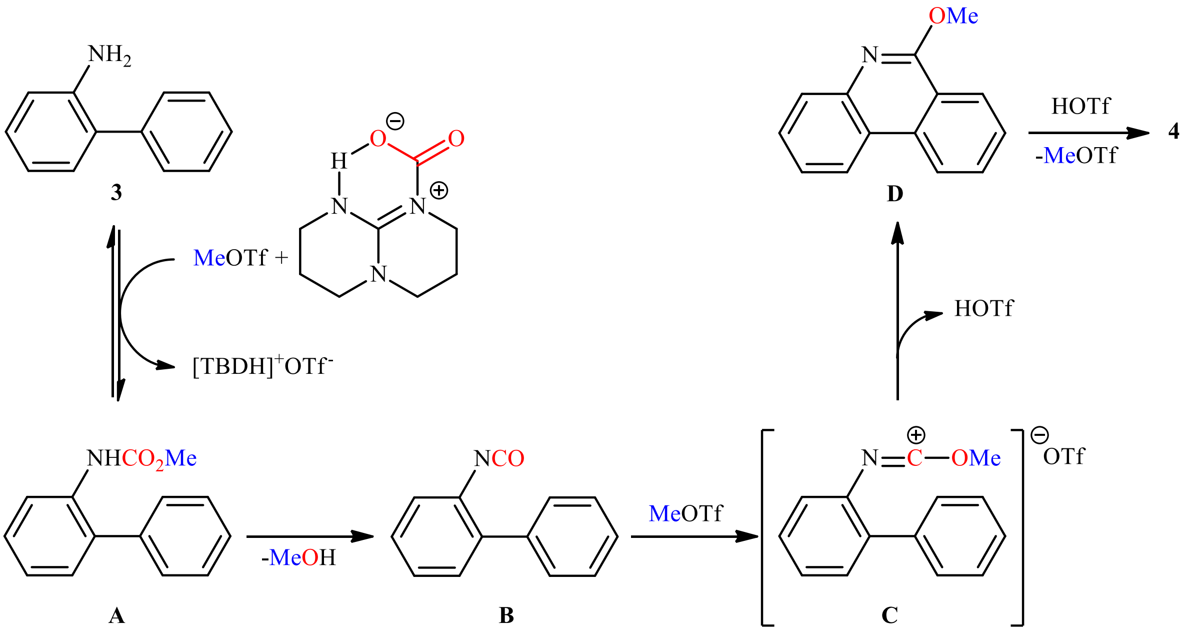
**Scheme 1.** Lactamization of 2-(hetero)arylanilines with $CO_2$, developed by Yu and co-workers.

Almost concurrently, Xi and co-workers reported the carbonylative cyclization of 2-(hetero)arylanilines **3** with $CO_2$ mediated by methyl trifluoromethanesulfonate (MeOTf) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) [35]. The reactions were carried out in *o*-DCB (1,2-dichlorobenzene) at 140 °C, tolerated various functionalized 2-arylanilines and 2-heteroarylanilines (such as pyridyl-, furanyl- and thienyl-substituted anilines), and provided the corresponding phenanthridinone derivatives **4** in relatively poor to high yields (Scheme 2). The electronic effect was obvious and generally substrates with electron-rich phenyl ring have gave higher yields than that of substrates with electron-poor phenyl rings. Notably, when a *meta*-substituted substrate (3'-methyl-[1,1'-biphenyl]-2-amine) was used, mixture of two possible isomers in 1:1 ratio were isolated. Unfortunately, 2-alkenylanilines failed to be transformed to the corresponding lactams in this reaction. Based on the mechanistic studies and previous reports, the authors proposed as possible pathway for this transformation (Scheme 3). First, 2-arylaniline **3** attacks of the TBD-$CO_2$ adduct to generate the methyl carbamate **A** with the aid of MeOTf. Subsequently, the carbamate **A** loses MeOH at high temperature to produce



R= H, 4-Me, 4-F, 4-Cl
(Het)Ar= Ph, 4-Ph-$C_6H_4$, 4-OMe-$C_6H_4$, 4-F-$C_6H_4$, 4-Cl-$C_6H_4$, 4-Br-$C_6H_4$, 3-Me-$C_6H_4$, 2-Me-$C_6H_4$, 2-OMe-$C_6H_4$, 3,5-(Me)$_2$-$C_6H_3$, 1-naphthyl, 2-benzofuryl, 2-benzothienyl, 2-pyrrolyl

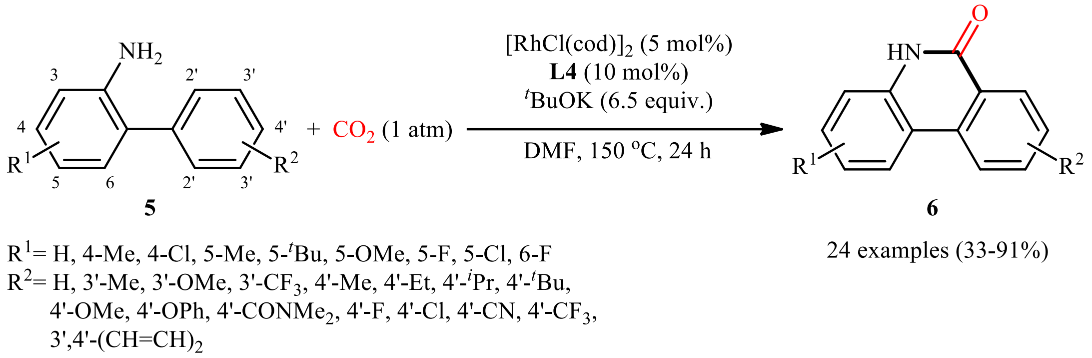
**Scheme 2.** Xi's synthesis of phenanthridin-6-ones **4**.



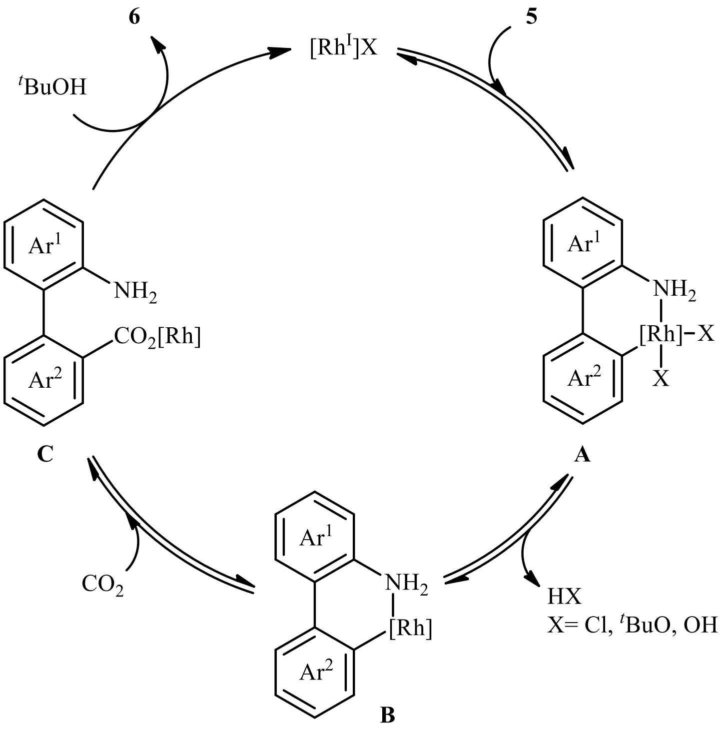
**Scheme 3.** Plausible reaction mechanism for the formation of phenanthridin-6-ones **4**.

isocynate **B** which after cyclization in the presence of MeOTf affords the 6-methoxyphenanthridine **D** *via* intermediate **C**. Finally, *in situ* acidification of the intermediate **D** leads to the formation of observed phenanthridinone **4**.

Three years later, metal-catalyzed version of this lactamization reaction was disclosed by Li and colleagues [36], who showed that various functionalized phenanthridinones **6** could efficiently be synthesized through the reaction of 2-arylaniline derivatives **5** with atmospheric $CO_2$ employing [RhCl(cod)]$_2$/tris[4-(trifluoromethyl)phenyl]phosphine (L4)/$^t$BuOK combination as a catalytic system (Scheme 4). Both electron-rich and electron-deficient substrates exhibited good reactivity for this $CO_2$ conversion reaction, which showed a significant improvement compared to the previous works. Besides 2-arylanilines, 2-various heteroarylanilines also could be applied as suitable substrates under the identical conditions. Unfortunately, applicability of 2-alkenylanilines as substrates was not investigated in this study. Moreover, the process is not viable for gram-scale due to the notable reduction in the yield (from 83% in the 0.2 mmol scale, to 71% in the 1.0 mmol scale). A possible reaction mechanism to explain this transformation is shown in Scheme 5. The reaction might start with reversible oxidative addition of 2-arylaniline **5** with a Rh$^I$ species to generate complex **A**, which after reductive elimination of HX deliver rhodacycle **B**. Next, reversible nucleophilic carboxylation of rhodacycle **B** with $CO_2$ affords rhodium carboxylate **C**. Finally, lactamization of **C** assisted by $^t$BuOK gives the observed product **6** and regenerates the Rh$^I$ catalyst.

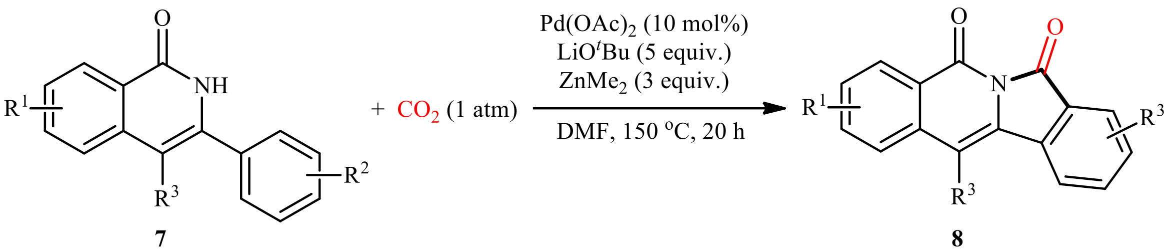


**Scheme 4.** Rh-catalyzed lactamization of 2-arylanilines **5** with atmospheric CO$_2$.



**Scheme 5.** Proposed mechanism for the reaction in Scheme 4.

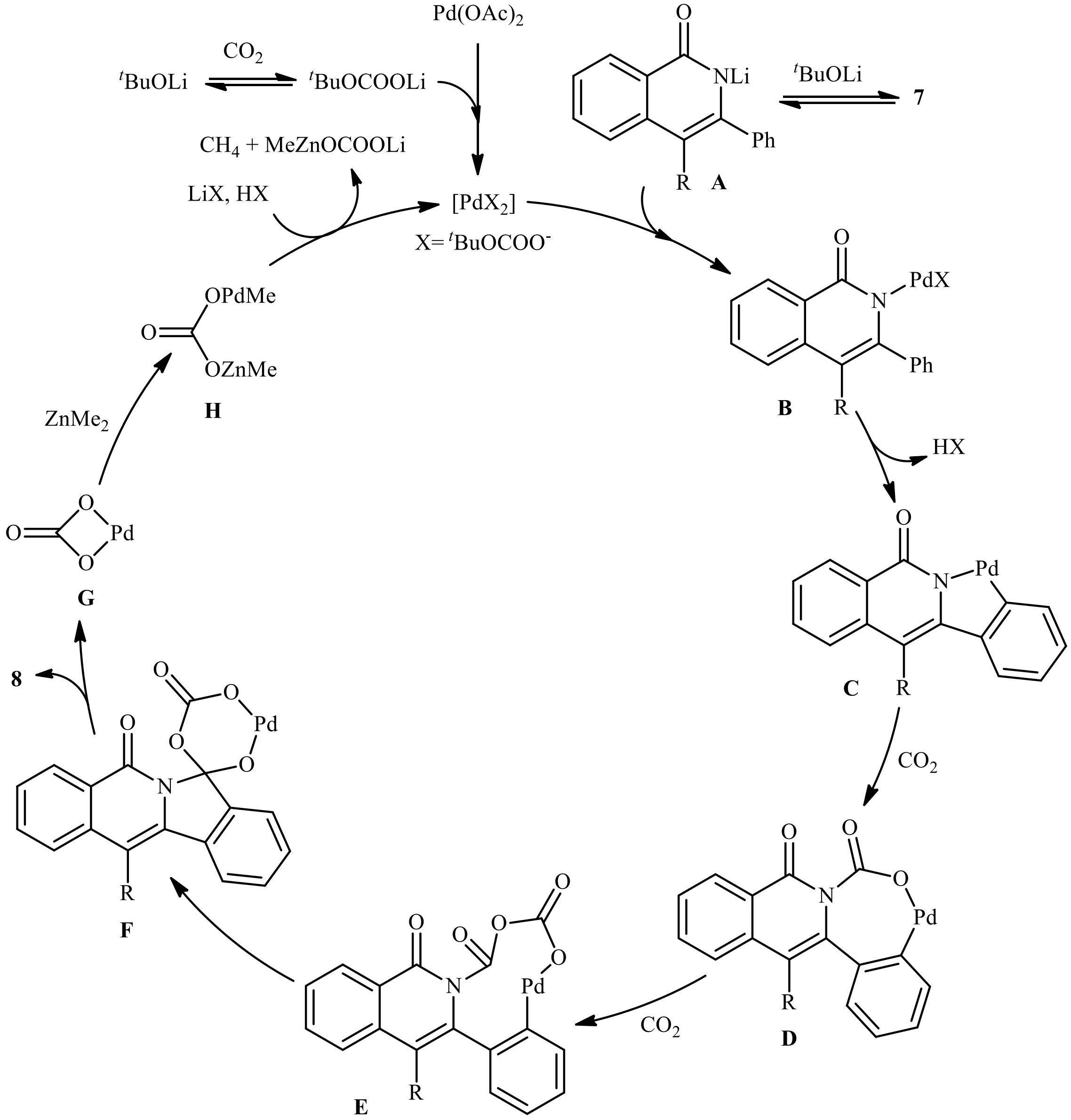
In the wake of the above reports, Wang and co-workers described an interesting Pd(II)-catalyzed C−H activation and cyclocarbonylation between isoquinolones **7** and CO$_2$ to synthesize isoindolo[2,1-*b*]isoquinoline-5,7-dione scaffolds **8** in moderate to high yields (Scheme 6) [37-38]. A wide panel of functional groups (*e.g.*, OMe, F, Cl, CN, CF$_3$, CO$_2$Me) were tolerated under the reaction conditions. However, isoquinolones bearing a nitro group at the C6-position or a methyl group at the *ortho* position of the 3-phenyl part, were unsuitable substrates under the optimal reaction, probably due to the strong electron-withdrawing property of the nitro group hampering the nucleophilic attack to CO$_2$ and the steric effect of the *ortho* substituent depressing C−H activation and cyclocarbonylation. Moreover, no corresponding product was detected when an isoquinolinone bearing a C(sp$^3$)-H reaction site was used as the substrate. According to the authors proposed mechanism (Scheme 7), Pd(OAc)$_2$ firstly undergoes ligand exchange with *in situ* generated hemicarbonate ion ($^t$BuOCOOLi) to give active catalytic complex hemicarbonate-Pd. At the same time, the proton exchange between solvated LiO$^t$Bu and isoquinolone **8** affords the intermediate **A**. Next, the counter anion exchange of starting active catalytic complex with intermediate **A** leads to the $^t$BuOCOOLi and palladium intermediate **B**. The later undergoes a concerted-metalation-deprotonation (CMD) process to produce the palladacycle intermediate **C** and $^t$BuOCOOH. Subsequently, insertion of CO$_2$ into the N−Pd bond and sequential CO$_2$ insertion into the O−Pd bond forms a seven-membered palladacycle intermediate **D**. Later, the



R$^1$= H, 6-Me, 6-Et, 6-$^t$Bu, 6-C$_7$H$_{15}$, 6-Ph, 6-OMe, 6-F, 6-Cl, 6-CN, 6-CO$_2$Me, 6-CF$_3$, 7-Me, 8-Cl, 5,7-(Me)$_2$, 6,7-(CH=CH)$_2$
R$^2$= H, 4-Me, 4-OMe, 4-CO$_2$Et, 4-F, 3-Me
R$^3$= H, Ph, 4-Me-C$_6$H$_4$, 4-OMe-C$_6$H$_4$, 4-F-C$_6$H$_4$, 4-CO$_2$Et-C$_6$H$_4$, 3-Me-C$_6$H$_4$

22 examples (41-81%)

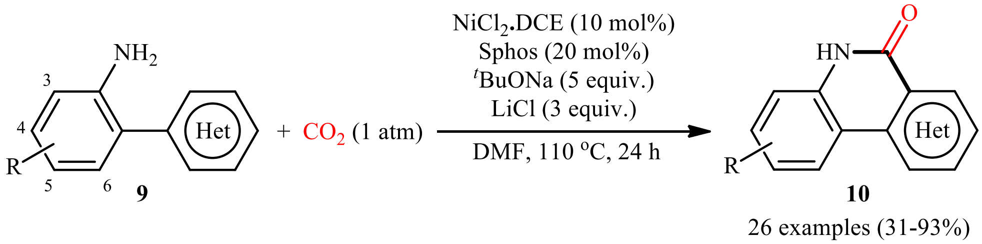
**Scheme 6.** Pd-catalyzed lactamization of isoquinolones **7** with CO$_2$.



**Scheme 7.** Mechanism that accounts for the formation of Isoindolo[2,1-*b*]isoquinoline-5,7-diones **2**.

second $CO_2$ insertion into the O−Pd bond affords a nine-membered palladacycle intermediate **E**, that after intramolecular nucleophilic addition results in spiroheterocyclic intermediate **F**. Next, decarbonization of intermediate **F** releases the final product **8** and carbonate palladium intermediate **G**. Afterwards, transmetalation between intermediate **G** and $ZnMe_2$ leads to the intermediate **H**, which after an acid-base exchange regenerates the active Pd(II) species.

Very recently, the same research group described that $NiCl_2 \cdot DME$ can also be used as an effective catalyst for the lactamization of $sp^2$-hybridized carbon–hydrogen (C–H) bonds with $CO_2$ [39]. 10 mol% of catalyst in combination with 20 mol% of Sphos, 5 equiv. $^t$BuONa and 3 equiv. LiCl has been utilized in the carbonylative cyclization of 2-(hetero)arylanilines **9** with $CO_2$ in DMF to give the corresponding phenanthridinones **10** in relatively poor to excellent yields, ranging from 31% to 93% (Scheme 8). The mechanism proposed for this transformation is similar to the one described in Scheme 1 for Rh-catalyzed lactamization reactions.

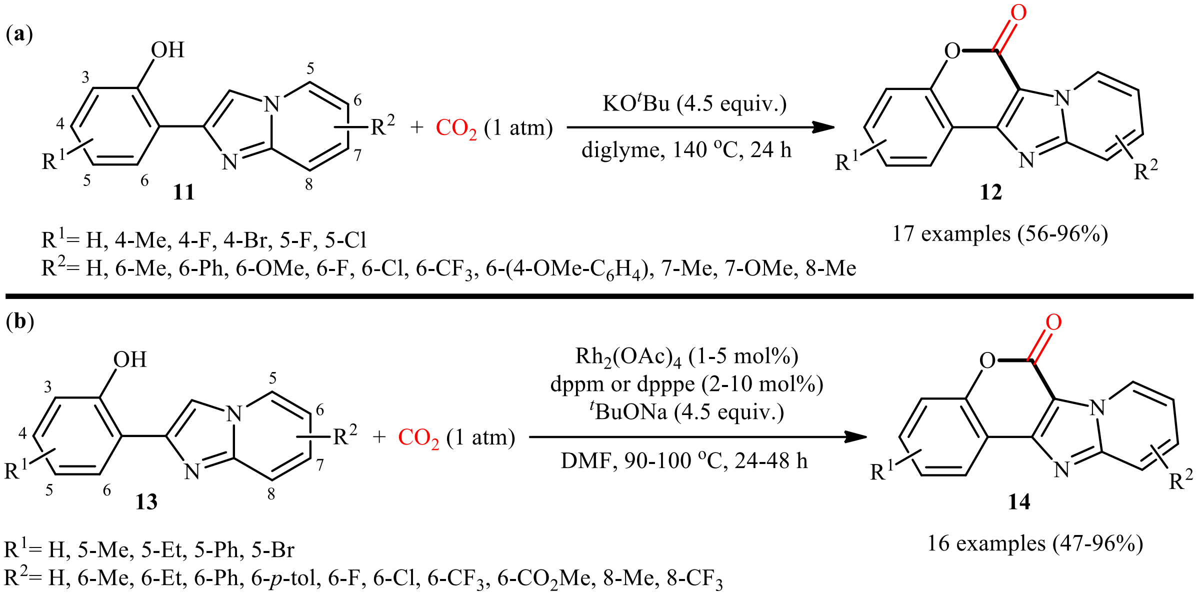


R= H, 4-Me, 4-OMe, 4-F, 4-Cl, 5-Me, 5-$^i$Pr, 5-OMe, 5-F, 5-Cl, 5-$CF_3$, 5-$CO_2Me$, 3,5-$(Me)_2$
(Het)Ar= Ph, 4-Me-$C_6H_4$, 4-$^t$Bu-$C_6H_4$, 4-OMe-$C_6H_4$, 4-OPh-$C_6H_4$, 4-F-$C_6H_4$, 4-Cl-$C_6H_4$, 4-$CF_3$-$C_6H_4$, 3-Me-$C_6H_4$, 3-Cl-$C_6H_4$, 2-Me-$C_6H_4$, 1-naphthyl, 2-thienyl, 2-furyl

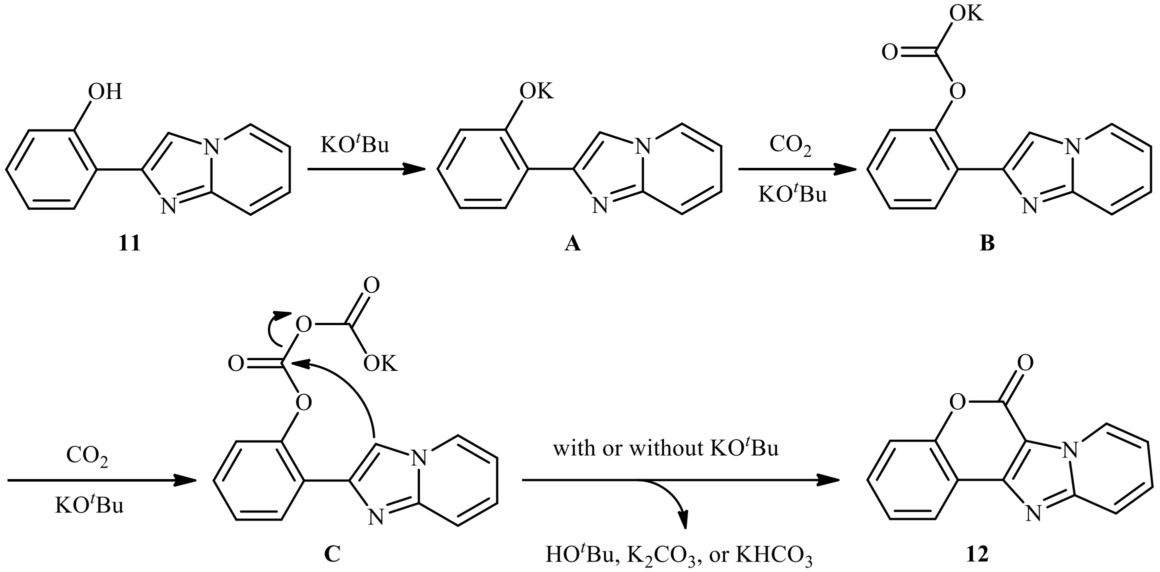
**Scheme 8.** Ni-catalyzed lactamization of 2-(hetero)arylanilines **9** with atmospheric $CO_2$, reported by Wang.

## 3. Lactonization of 2-(hetero)arylanilines

Drawing inspiration from Iwasawa's work on the synthesis of coumarin derivatives through Pd-catalyzed carboxylation of alkenyl C−H bonds of corresponding 2-alkenylphenols with $CO_2$ [40], in 2017, the Yu-Zhi group have reported an elegant catalyst-free, hydroxyl-group-directed lactonization of aryl C($sp^2$)–H bonds in 2-(imidazo[1,2-*a*]pyridin-2-yl)phenols **11** with $CO_2$ (1 atm) under basic conditions to generate coumarin–imidazo[1,2-*a*]pyridine hybrids **12** with good to almost quantitative yields (Scheme 9a) [41]. Concerning the substrate scope, this novel $CO_2$-fixation reaction had relatively little dependence on the steric- and electronic-factors of substrates. Therefore, various 2-(imidazo[1,2-*a*]pyridin-2-yl)phenols with either electron-donating or electron-withdrawing substituents at different positions of the phenol group or at the imidazo[1,2-*α*]pyridine scaffold were efficiently reacted under the conditions employed [KO$^t$Bu (4.5 equiv.), diglyme, 140 °C, 24 h]. Noteworthy, the authors demonstrated the scalability of this reaction since 6*H*-chromeno[4',3':4,5]imidazo[1,2-*a*]pyridin-6-one could be obtained in 1.44 g scale in high yield of 87%. Although the precise mechanism of this reaction was not clear, a tentative mechanism was proposed as shown in Scheme 10. Initially, the phenol **11** undergoes deprotonation in the presence of strong base KO$^t$Bu to form phenoxide intermediate **A**. Subsequently, this intermediate attacks $CO_2$ or the *in situ* generated KOCOO$^t$Bu to afford carbonate intermediate **B**, which further reacts with $CO_2$ or KOCOO$^t$Bu to give the intermediate **C**. Finally, intramolecular nucleophilic attack and deprotonation with assistance from the base takes place to deliver the desired product **12** along with HO$^t$Bu/$K_2CO_3$ or $KHCO_3$ as byproducts. Shortly afterwards, Li and co-workers improved the efficiency of this transformation in the term of reaction temperature by using $Rh_2(OAc)_4$/dppm or dpppe/$^t$BuONa combination as the catalytic system and DMF as the solvent [42]. Various 2-(imidazo[1,2-*a*]pyridin-2-yl)phenols **13** bearing different functional groups were used to establish the general applicability of the method (Scheme 1b). Both electron-donating and electron-deficient functionality on the phenol ring or at the imidazo[1,2-*α*]pyridine scaffold were tolerated by this protocol.

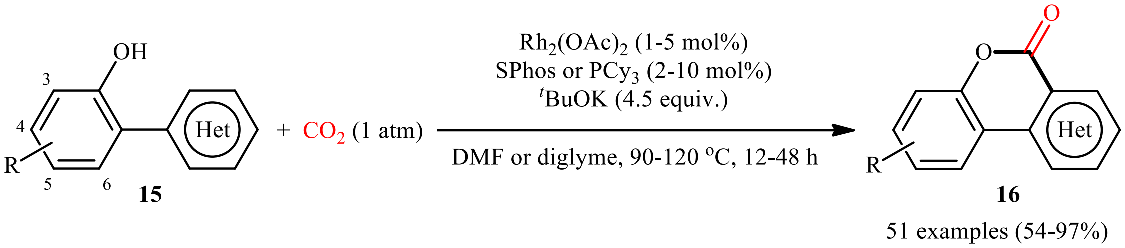


**Scheme 9.** (a) Yu-Zhi's synthesis of 6*H*-chromeno[4',3':4,5]imidazo[1,2-*a*]pyridin-6-ones **12**; (b) Li's synthesis of 6*H*-chromeno[4',3':4,5]imidazo[1,2-*a*]pyridin-6-ones **14**.



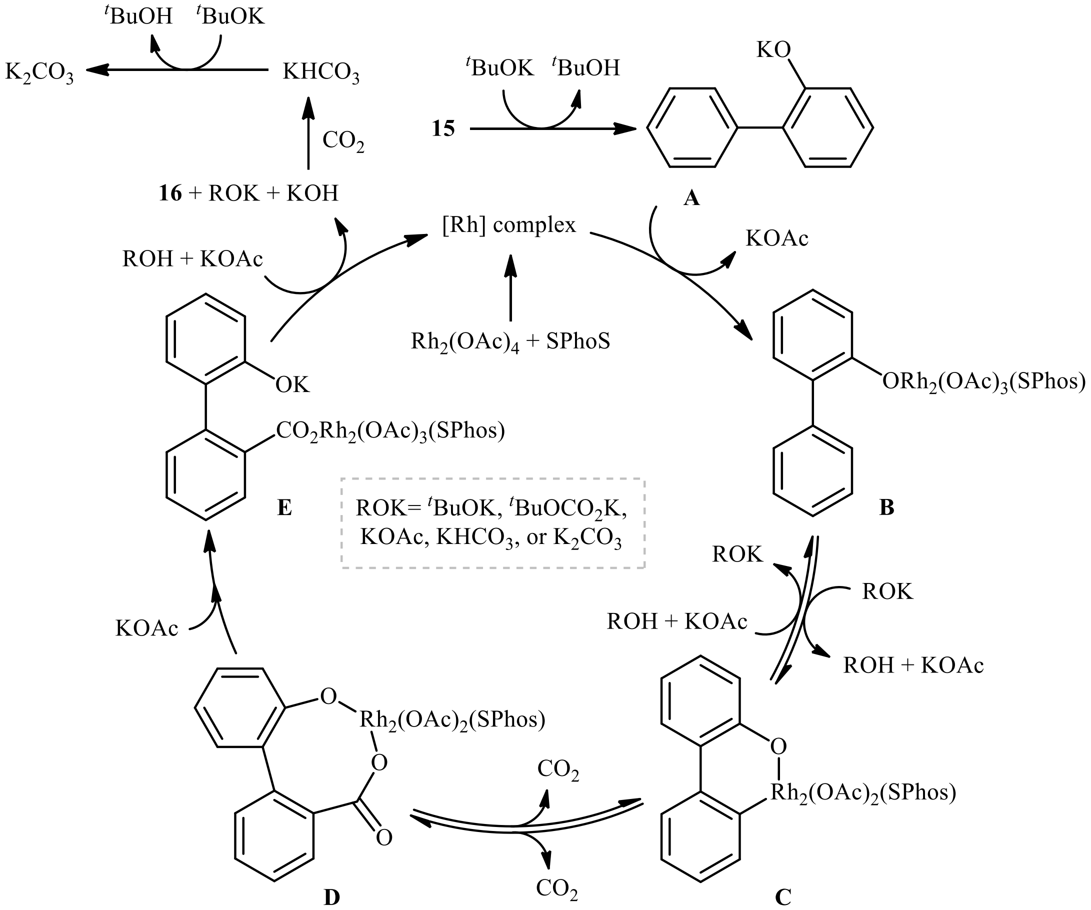
**Scheme 10.** Mechanistic proposal for the reaction in Scheme 9a.

In 2018, the innovative group of Li reported an exciting ligand-enabled redox-neutral rhodium(II) catalyzed site-selective carboxylation of 2-(hetero)arylphenols under atmospheric pressure of CO$_2$ [43]. The reactions were run in the presence of only 1-5 mol% of Rh$_2$(OAc)$_2$ as a catalyst, 2-10 mol% of SPhos or PCy$_3$ as a ligand and 4.5 equiv. of KO$^t$Bu as in DMF or diglyme at 90-120 °C, tolerated various functionalized 2-arylanilines and 2-heteroarylanilines, such as pyridyl-, furanyl- and indolyl-substituted anilines **15**, and generally provided the desired hybrid structures of coumarin derivatives **16** in moderate to excellent yields (Scheme 11). Notably, phosphine ligands were extremely important for enhancing the reactivity of the rhodium catalyst, selectively on the less nucleophilic phenyl group, and avoiding the well-known Kolbe–Schmitt type reaction. According to the assumed mechanistic pathway, this Rh-catalyzed lactonization reaction proceeds through the following key steps (Scheme 12): (i) initial formation of intermediate **A** *via* the basification of 2-(hetero)arylphenol **15** with KO$^t$Bu; (ii) coordination of intermediate **A** with *in situ* generated [Rh]-complex to form the complex **B**; (iii) chelation-assisted aryl C–H bond activation of **B** *via* a proton abstraction process with the assistance of an external base ROK (such as KO$^t$Bu) to afford the metallacycle **C**; (iv) nucleophilic carboxylation of **C** with $CO_2$ to give eight-membered rhodacycle **D**; (v) ligand exchange of unstable complex **D** with KOAc to yield intermediate **E**; and (vi) protonolysis of **E** to produce the desired product **16** along with regeneration of active Rh-complex.



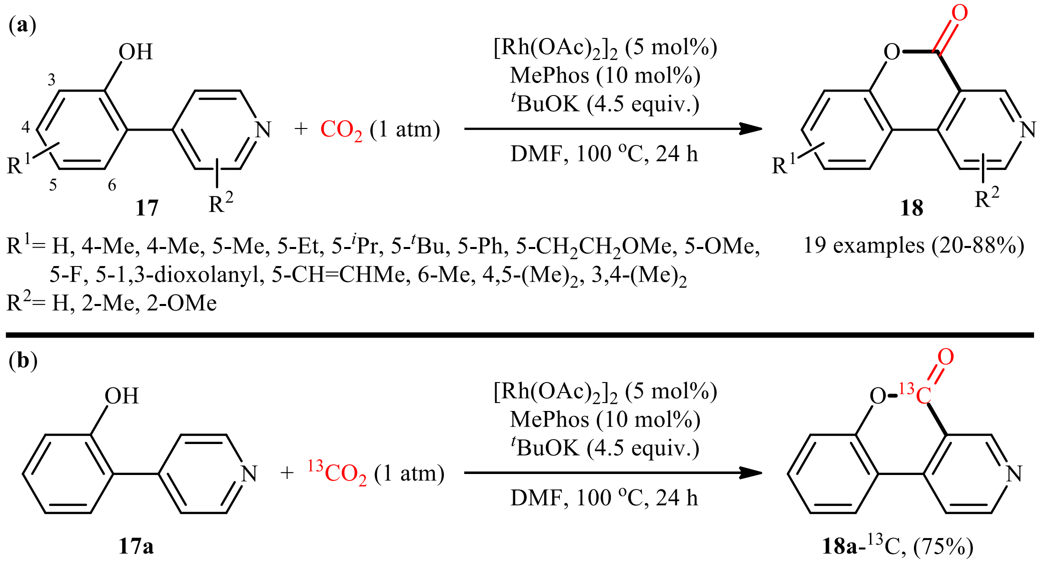
R= H, 6-Me, 5-Me, 5-OMe, 5-F, 5-Cl, 5-Ph, 5-Me, 4-OMe, 4-F, 4-$CF_3$, 4-CN, 5,6-$(CH{=}CH)_2$
(Het)Ar= Ph, 3-Me-$C_6H_4$, 3-OMe-$C_6H_4$, 3-$CF_3$-$C_6H_4$, 4-Me-$C_6H_4$, 4-$^t$Bu-$C_6H_4$, 4-Ph-$C_6H_4$, 4-OMe $C_6H_4$, 4-OPh-$C_6H_4$, 4-$NMe_2$-$C_6H_4$, 4-F-$C_6H_4$, 4-$CF_3$-$C_6H_4$, 4-$CONMe_2$-$C_6H_4$, 4-$CO_2Me$-$C_6H_4$, 3,4-$(Me)_2$-$C_6H_3$, 2-naphthyl, 2-furyl, 2-(5-Me)-furyl, 2-benzofuryl, 1-pyrrolyl, 2-thienyl, 3-thienyl, 4-pyridyl

**Scheme 11.** Rh-catalyzed Lactonization of 2-(hetero)arylanilines **15** with atmospheric $CO_2$, developed by Li.



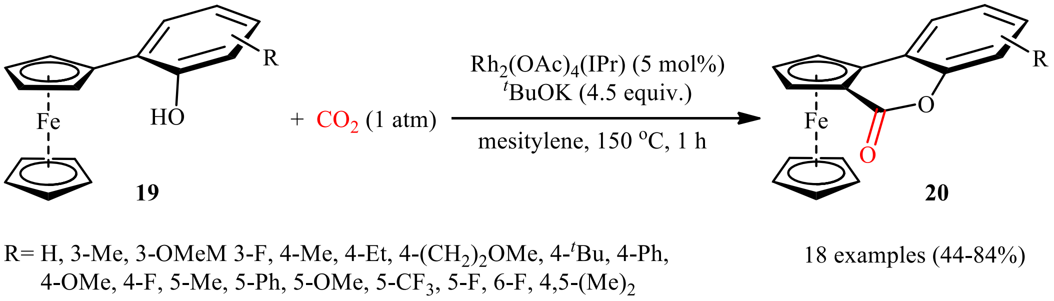
**Scheme 12.** Mechanistic proposal for the formation of 6*H*-benzo[*c*]chromen-6-one derivatives **16**.

Not long after this report, the authors extended the above lactonization to more challenging 2-pyridylphenols [44]. They showed that the treatment of electron-deficient 2-pyridylphenols **17** with atmospheric $CO_2$ in the presence of a slightly modified catalytic system afforded the corresponding pyrido-heterocycles **18** in poor to high yields (Scheme 13a). The results indicated that the substrates with either electron-donating or electron-withdrawing substituents at the *para*- and *meta*-positions of the hydroxyl of the phenolic ring were well tolerated by this reaction. However, a hindered methyl substitution on the phenol ring was not well tolerated. Next to 2-(pyridin-4-yl)phenols, also a series of 2-(pyridin-3-yl)phenols were also tested and gave the desired products, albeit a higher temperature or a longer reaction time was necessary. Unfortunately, quinoline and isoquinoline derivatives only led to very low yields of target products. The optimized condition was also successfully used to synthesize [$^{13}$C]-5*H*-chromeno[3,4-c]pyridin-5-one **18a'** in good radiochemical yield (RCY) from the corresponding 2-(pyridin-4-yl)phenol **17a** (Scheme 13b).

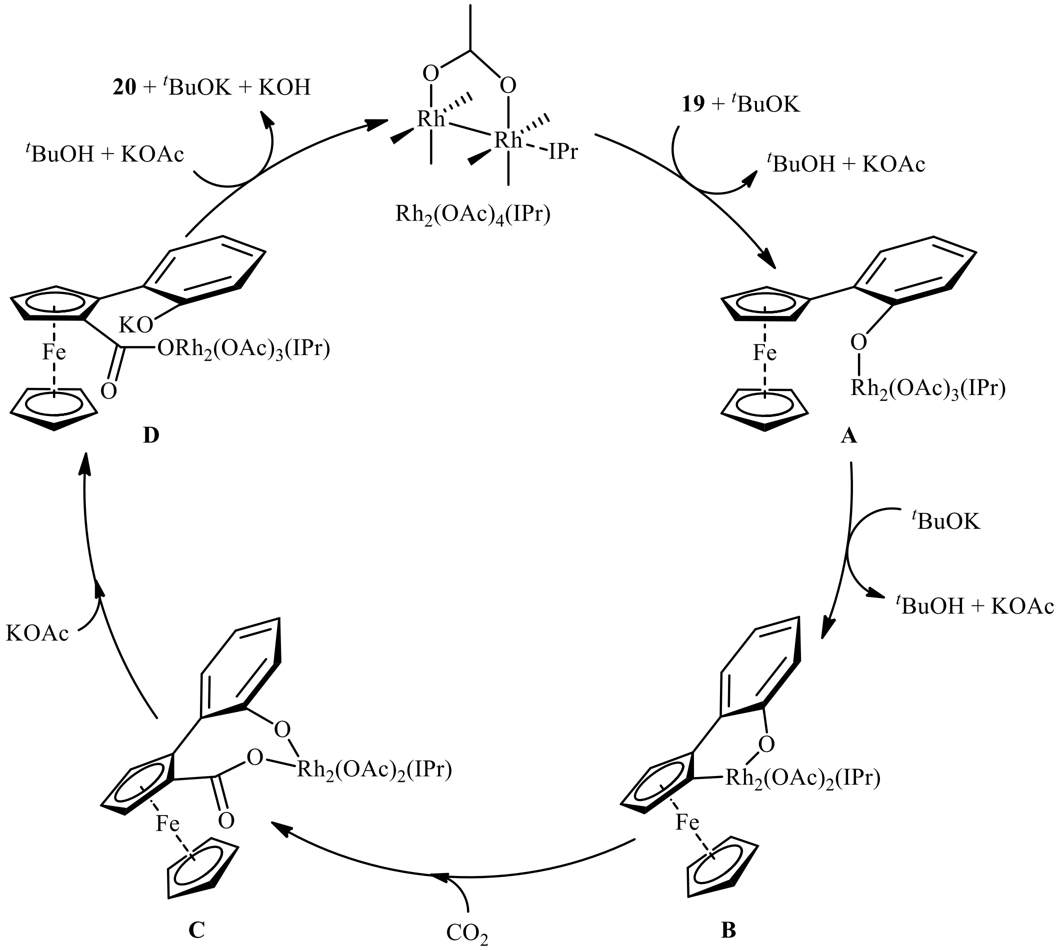


**Scheme 13.** (a) Rh-catalyzed Lactonization of 2-pyridylphenols **17** with atmospheric CO₂; (b) Rh-catalyzed Carboxylation of 2-pyridylphenol **17a** with [$^{13}$C]CO₂.

More recently, Li's group extended their methodology to carboxylation of inert sp$^2$ C–H bonds from the cyclopentadienyl (Cp) ring of ferrocene derivatives **19**, which provide an access to biologically important ferrocene-embedded lactones **20** [45]. By employing 2-ferrocenylphenol as the model substrate, the reaction variables such as metal precursor, ligand, and solvent were carefully investigated. The best conversion efficiency was obtained for the reaction performed in the presence of 5 mol% $Rh_2(OAc)_4$ as the metal precursor, 10 mol% IPr·HCl as the ligand and 4.5 equiv. KO$^t$Bu as the base in near refluxing mesitylene. Under the optimized condition, eighteen ferrocene derivatives **19** reacted well and afforded the corresponding ferrocene-embedded lactones **20** in modest to high yields (Scheme 14). Importantly, moderate enantioselectivites achieved with chiral NHC ligands, which can be regarded as the first example for asymmetric C–H carboxylation with CO₂. As shown in Scheme 15, the authors proposed mechanism for this reaction is analogous to the one they suggested for the lactonization of 2-arylanilines.



**Scheme 14.** Li's synthesis of ferrocene-embedded lactones **20**.



**Scheme 15.** Plausible mechanism for the formation of ferrocene-embedded lactones **20**.

## 4. Conclusion

Recent development of metal-catalyzed/-free lactamization and lactonization of 2-arylanilines and 2-arylphenols, respectively, utilizing $CO_2$ as C1 source to synthesize biologically valuable phenanthridin-6(5*H*)-one and 6*H*-benzo[*c*]chromen-6-one was summarized. As illustrated, this page of phenanthridin-6(5*H*)-one/6*H*-benzo[*c*]chromen-6-one synthesis offers several advantages such as high atom economy, broad substrate scope, scalability, and easily accessible starting materials. Interestingly, all reactions covered in this review were performed under atmospheric pressure of $CO_2$. The main drawback of the current protocols is the requirement for an elevated reaction temperature. Therefore, the development of new catalytic systems that allow these transformations under milder conditions would be highly desirable. Given the wide importance of phenanthridin-6(5*H*)-one and 6*H*-benzo[*c*]chromen-6-one derivatives in diverse fields and increasing interest in the usage of $CO_2$ as a sustainable source of carbon, we believe that this area will continue to attract the attention of synthetic chemists in the years to come. We hope that this review will stimulate further progress in this exciting field.

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