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Rhodium(II)-Catalyzed Aryl C–H Carboxylation of 2-Pyridylphenols with CO_2

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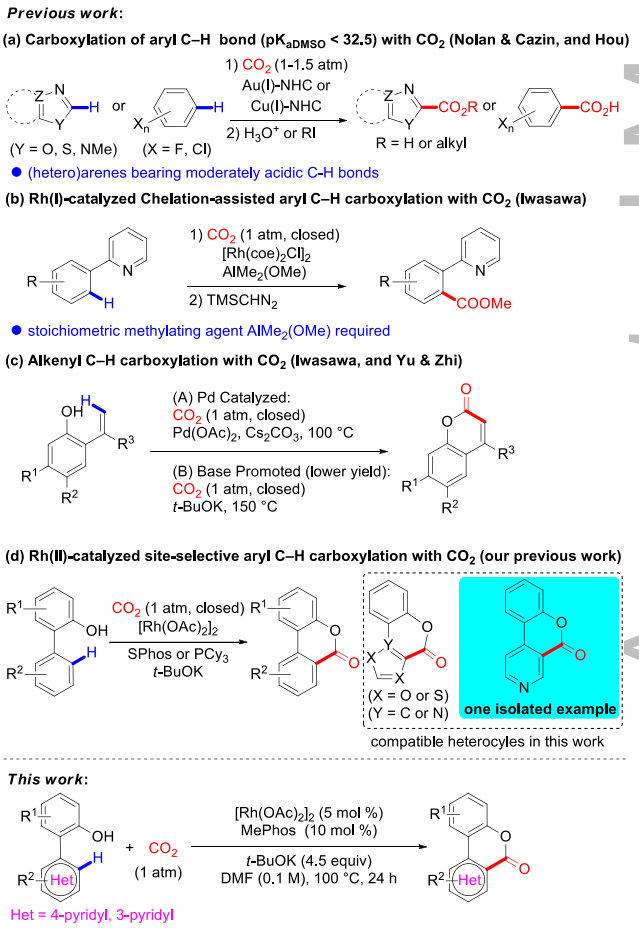
Abstract. A protocol for C–H carboxylation of electron-deficient 2-pyridylphenols with CO_2 through a Rh(II)-catalyzed C–H bond activation under redox-neutral conditions has been developed. A suitable phosphine ligand was crucial for this reaction. This method provided, in generally high yields, an access to a class of pyrido-coumari-ns that are key structural motifs in biologically important molecules. Facile product derivatizations were also exemplified.

Keywords: carbon dioxide fixation; carboxylation; C-H activation; rhodium; ligand promotion

Fine chemicals synthesis via fixation of carbon dioxide (CO_2), an abundant, renewable, low-cost, non-toxic and green C1 feedstock, is highly attractive.[1] This type of transformation is, however, often challenging as CO_2 is thermodynamically and kinetically stable. Therefore, direct carboxylation of aromatic compounds with CO_2 for the synthesis of (hetero)aromatic carboxylic acids or their derivatives through transition-metal-catalyzed C–H activation is very limited.[2] In 2010, the group of Nolan reported a breakthrough of carboxylation of moderately acidic sp^2 C–H bonds of arenes enabled by a gold complex [(NHC)AuOH] under basic conditions.[3] Shortly after, Hou and co-workers, as well as the Nolan and Cazin group independently reported a similar transformation but with Cu(I)-NHC complexes as the catalysts simultaneously (Scheme 1a).[4-5] Remarkably, the carboxylation of much less-acidic aryl C–H bond with CO_2 was achieved by Iwasawa and co-workers (Scheme 1b). The reaction proceeded *via* a Rh(I)/Rh(III) catalytic cycle, and a stoichiometric pyrophoric methylating reagent $AlMe_2OMe$ was the key for an efficient carboxylation.[6-7] Importantly, the same group demonstrated later that simple arenes could also be carboxylated with this method.[6b,c] Moreover, carboxylation of alkenyl C–H bonds, whose reactivity are different from aryl C–H bonds, was also realized by the Iwasawa group using a phenolic hydroxyl group as the chelating group with Pd(II) (Scheme 1c).[8a] This transformation was also achieved by Yu and Zhi under transition-metal-free conditions in lower yields, whose reaction conditions were better compatible with compounds containing an imidazo[1,2-a]pyridine scaffold (Scheme 1c).[8b]

Most recently, our group developed a site-selective and efficient carboxylation of 2-(hetero)arylphenols with CO_2 through a Rh(II)-catalyzed C–H bond activation under redox-neutral conditions, which



Scheme 1. Transition-metal-catalyzed carboxylation of aryl and alkenyl C–H bonds with CO_2.

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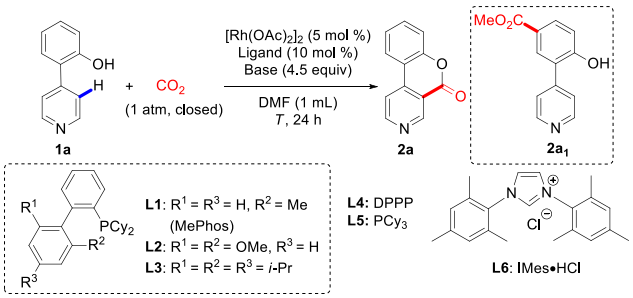
Table 1. Optimization of reaction conditions[a]



Entry	Ligand	Base	Temp (°C)	**2a** (%)
1	**L2**	*t*-BuOK	100	72
2	**L1**	***t*-BuOK**	**100**	**75 (74)**[b]
3	**L3**	*t*-BuOK	100	40
4	**L4**	*t*-BuOK	100	41
5	**L5**	*t*-BuOK	100	60
6[c]	**L6**	*t*-BuOK	150	75 (73)[b]
7	**L1**	*t*-BuOK	120	70
8	**L1**	*t*-BuOK	110	69
9	**L1**	*t*-BuOK	90	69
10	**L1**	*t*-BuOK	80	43
11[d]	**L1**	*t*-BuOK	100	23
12[e]	**L1**	*t*-BuOK	100	3
13[f]	**L1**	*t*-BuOK	100	1
14	-	*t*-BuOK	100	3
15[f]	-	*t*-BuOK	100	(**2a**$_1$, 52)[g]
16	**L1**	*t*-BuONa	100	73
17	**L1**	Cs_2CO_3	100	4
18[h]	**L1**	*t*-BuOK	100	15
19[i]	**L1**	*t*-BuOK	100	66
20[j]	**L1**	*t*-BuOK	100	0

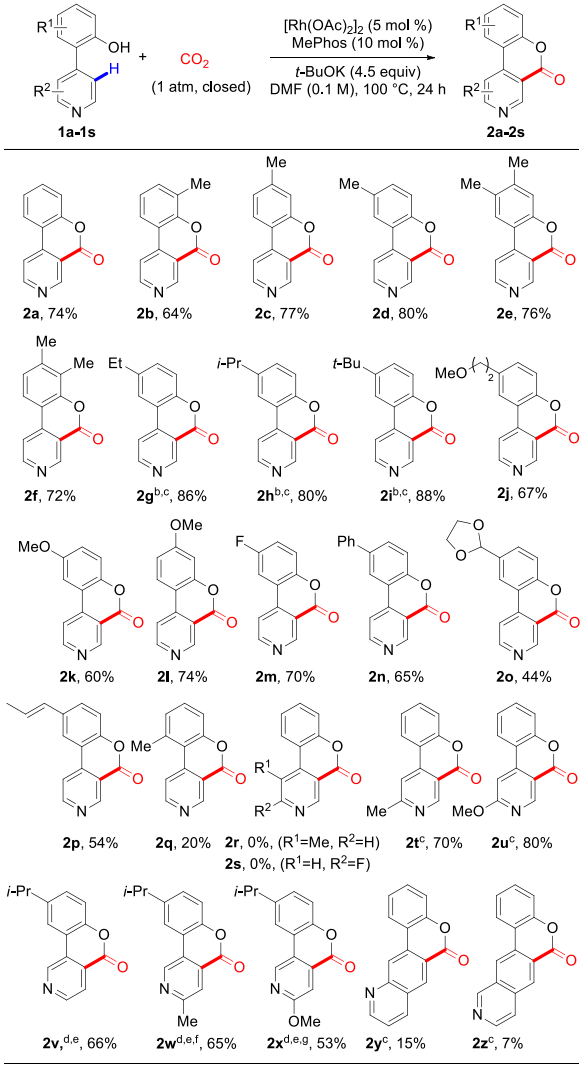
[a]Reaction conditions: **1a** (0.1 mmol), CO_2 (1 atm, closed), $[Rh(OAc)_2]_2$ (5 mol%), ligand (10 mol%), base (4.5 equiv), DMF (1 mL), 24 h. Yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard; **1a** and other side products including **2a$_1$** might exist for some reactions but they would be dissolved in the water phase during work-up and were not detected. [b]Isolated yield in parenthesis. [c]10 h. [d]DMA. [e]diglyme. [f]No $[Rh(OAc)_2]_2$. [g]Isolated yield of **2a$_1$** and 48% of **1a** was also found in the crude ^{1}H NMR; **2a$_1$** was obtained by treating the reaction with $SOCl_2$ in MeOH during reaction work-up, see SI for detailed procedure. [h]$[Rh(Cp^*)Cl_2]_2$ was used instead of $[Rh(OAc)_2]_2$. [i]$[Rh(OAc)_2]_2$ (2.5 mol%), **L1** (5 mol%), 48 h. [j]CO (1 atm, closed) was used instead of CO_2. DPPP: 1,3-bis(diphenylphosphino)propane; Cp*: pentamethylcyclopentadienyl.

mainly focused on electron-neutral 2-phenylphenols and electron-rich substrates with a five-membered heterocycle (Scheme 1d).[9] And only an isolated example of 2-pyridylphenol was exemplified in this report. To further explore this strategy, we tried to developed better reaction conditions for more 2-pyridylphenols that possess an electron-deficient pyridyl group, which might be challenging due to the competing Kolbe-Schmitt type of reaction that could occur to the electron-rich phenolic ring (Scheme 1).

Herein, we report a ligand promoted, Rh(II)-catalyzed C–H carboxylation of 2-pyridylphenols through CO_2 fixation for the synthesis of a class of pyrido-coumarin derivatives, a motif found in biologically active compounds.[10-14]

To start our investigation, 2-(pyridin-4-yl)phenol **1a** was selected as the model substrate. Although **1a** has been proved to be able to afford the desired product **2a** as a single example in our previous report with ligand **L2** (Table 1 entry 1),[9] we attempted to find the optimal reaction conditions for this class of substrate by evaluating the ligands first. Gratifyingly, MePhos (**L1**) was proved to be the best new phosphine ligand after examining a series of mono- and di-phosphine ligands (see also Supporting Information (SI) for more reaction conditions

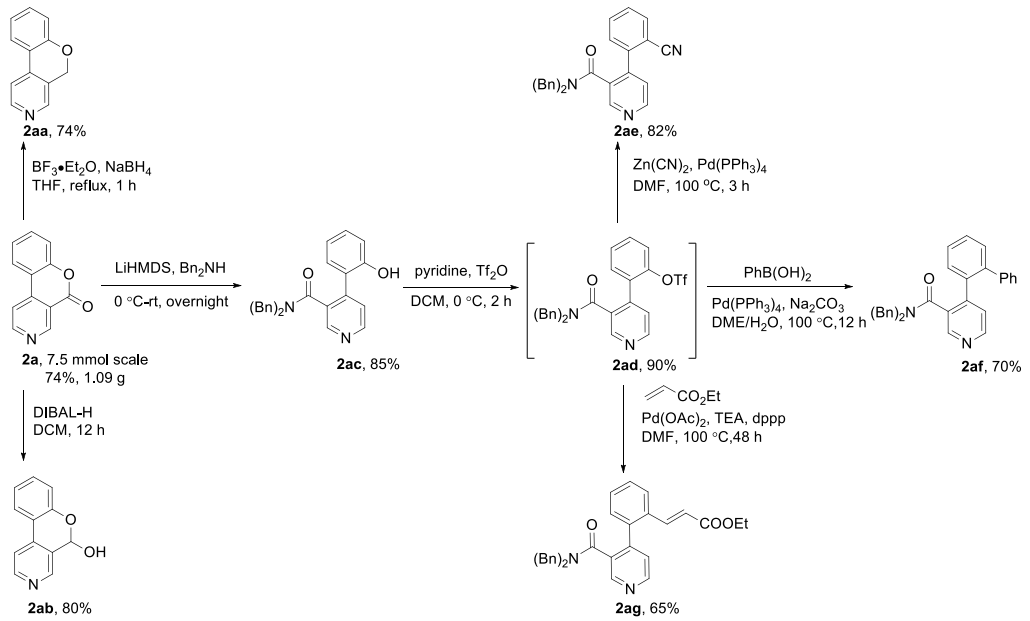
Table 2. Substrate scope[a]



[a]Reaction conditions: **1** (0.1 mmol), CO_2 (1 atm, closed), $[Rh(OAc)_2]_2$ (5 mol%), MePhos (10 mol%), *t*-BuOK (4.5 equiv), DMF (1 mL), 100 °C, 24 h; isolated yield. Minor Kolbe-Schmitt type side product might be formed for some substrates. [b]$[Rh(OAc)_2]_2$ (2.5 mol%), MePhos (5 mol%), 100 °C. [c]48 h. [d]IMes·HCl (10 mol%), 150 °C, 24 h. [e]About 5% of isomer of carboxylation at the *ortho*-position of nitrogen atom was also detected but not isolated. [f]10 h. [g]100 °C, 72 h.

screening), leading to 74% of isolated yield of **2a** with 5 mol% $[Rh(OAc)_2]_2$ and 4.5 equiv of *t*-BuOK in DMF at 100 °C for 24 h under atmospheric pressure of CO_2 (Table 1, entries 2-5). *N*-heterocyclic carbene (NHC) ligands were also tested, and the IMes·HCl (**L6**) delivered a comparable yield of **2a** as MePhos in 10 h, but at a high temperature of 150 °C and lower yield would be obtained in a longer time (entry 6). After screening the reaction temperature carefully, it was revealed that 100 °C was still the best choice with MePhos as the ligand (entries 7-10). Notably, the choice of solvent was important in this reaction as other solvents such as DMA and diglyme led to much lower yield than DMF (entries 11 and 12). The reaction was almost shut down in the absence of a rhodium catalyst or the ligand (entries 13-15), and side product **2a₁** would be produced from the well-known Kolbe-Schmitt type of reaction under basic conditions (entry 15) by treating the reaction with $SOCl_2$ in MeOH during reaction work-up. Interestingly, the carboxylation at the *ortho*-position of phenolic hydroxyl group carboxylation was not observed, which might result from the use of potassium base, since the potassium cation could promote the formation of *para*-carboxylated products under basic conditions.[2a] However, by using the above work-up method only trace of (about 2%) **2a₁** was detected under the best reaction conditions in entry 2. The effect of base was also examined and *t*-BuOK was found to be the most suitable one (entries16 and 17). Moreover, other Rh-catalysts such as $[Rh(Cp^*)Cl_2]_2$ were also employed, but the reaction was almost inhibited (entry 18). In addition, good yield of **2a** could also be generated in 48 h when the loading of $[Rh(OAc)_2]_2$ was decreased to 2.5 mol% (entry 19). Finally, to test the carboxylic source,[11i] CO_2 was replaced with CO and not any desired product was obtained (entry 20). Since other solvents like *N*,*N*-dimethylacetamide could also lead to the desired prouct (see SI), it was concluded that DMF, which might decompose to generate CO and is the most likely carboxylic source except CO_2, was not likely the carboxylic source for this reaction.

With the optimized conditions in hand, we explored the scope of this reaction with substituted 2-(pyridin-4-yl)phenols and 2-(pyridin-3-yl)phenols, leading to a class of pyrido-coumarin derivatives in generally good to excellent yields (Scheme 2). Substrates with one or two methyl substituents on the phenolic ring reacted efficiently to give the desired products (**2b**-**2f**) in good yields, which also indicated that the number and the position of the methyl substituent on the aromatic ring exerted a small influence on the reaction. Since the substrates with substituents at the *para*-position of the hydroxyl of the phenolic ring was readily available, several *para*-substituted substrates with other alkyl substituents were also investigated and they were well tolerated (**2g**-**2j**). It is worth mentioning that products **2g**-**2i** could still be obtained in high yields with a lower loading of $[Rh(OAc)_2]_2$ (2.5 mol%), albeit in a longer reaction time. Subsequently, substrates bearing electron-donating methoxyl and electron-withdrawing groups such as fluoro and phenyl groups were also smoothly converted to the desired products (**2k**-**2n**). Notably, acetal **1o** was compatible with this reaction, albeit in a modest yield, enabling further elaborations at this position (**2o**). Interestingly, a carbon-carbon double bond transfer occurred when 4-allyl-2-(pyridin-4-yl)phenol **1p** was employed as the substrate, affording a propenyl product **2p**. However, a hindered methyl substitution on the phenol ring was not well tolerated (**2q**). Moreover, a hindered methyl substitution on the pyridin-4-yl ring could not be tolerated (**2r**). And a fluorine at the *ortho*-position of nitrogen atom led to no product with partial



Scheme 2. Synthetic elaborations of carboxylated product **2a**.

decomposition of the substrate (**2s**). Pleasingly, reactions of substrates with a methyl or methoxyl group at the *ortho*-position of nitrogen atom on the pyridin-4-yl ring could afford good yields of desired products (**2t** and **2u**). Subsequently, 2-(pyridin-3-yl)phenols were examined and the desired products could be obtained with high regio-selectivity using IMes·HCl as the ligand (**2v-2x**), although a higher temperature (**2v** and **2w**) or a longer reaction time (**2x**) was necessary. Unfortunately, quinoline and isoquinoline derivatives only led to very low yields of desired products (**2y** and **2z**).

The utility of this methodology was demonstrated by further elaboration of the pyrido-coumarin product **2a** (Scheme 3). Firstly, the C–H carboxylation reaction of **1a** could be easily scaled up to a 7.5 mmol scale with the model substrate **1a**, affording **2a** (1.09 g) in 74% yield. Treatment of **2a** with $BF_3{\cdot}Et_2O/NaBH_4$ or DIBAL-H gave the corresponding reduced product **2aa** and **2ab** in 74% and 80% yields, respectively. Furthermore, triflate **2ad** was produced in 90% yield from **2ac**, which was prepared from **2a** with LiHMDS and Bn_2NH, by triflation of the hydroxyl group. Triflate **2ad** was then transformed to a range of synthetically useful substances with well-established coupling reactions such as cyanation (**2ae**), arylation (**2af**) and alkenylation (**2ag**) in good yields, demonstrating the versatility of the synthetic elaborations of this method.

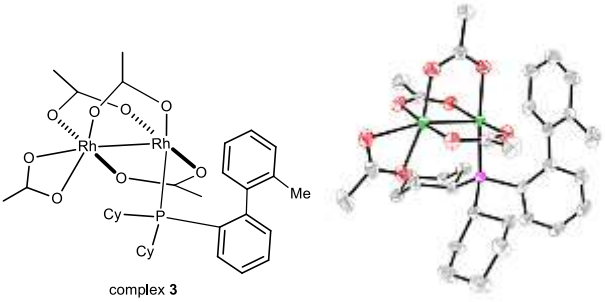
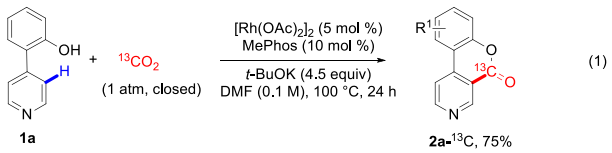


Figure 1. Ortep drawing of the asymmetric unit the crystal structure of complex **3** at 30% probability level.[15]

To gain more insights into the reaction mechanism, we obtained the potential active catalyst Rh(II) complex **3** (Fig. 1), whose structure was characterized by X-ray crystallography. Similar yield of desired product **2a** could be produced with 5 mol% of complex **3** with another 5 mol% of the ligand MePhos (**L1**), which implied that a total of 10 mol% of the ligand was required in this reaction (see SI). $^{13}CO_2$ was also utilized to confirm the carboxylic source [Eq. (1)], and the ^{13}C NMR as well as the high-resolution mass spectrometry clearly indicated that CO_2 was the carboxylic source (see SI).[11i] Based on the above investigations as well as our previous study,[8] the proposed tentative catalytic cycle is depicted in Fig. 2. First, deprotonation of **1a** with *t*-BuOK would generate the salt **1a'**, which would coordinate with complex **A** that is formed in



situ, leading to complex **B**. C–H bond activation of **B** via a proton abstraction process with the assistance of an external base ROK (such as *t*-BuOK and *t*-$BuOCO_2K$) affords the metallacycle **C**. **C** can be transformed back to **B** by protonolysis reversibly. Nucleophilic carboxylation of **C** with CO_2 affords the rhodium carboxylate complex **D**. Nucleophilic carboxylation might be reversible and reproduce **C**. The eight-membered complex **D**, which might be unstable, can be converted to complex **E** by ligand exchange with KOAc. Another ligand exchange of rhodium carboxylate **E** with KOAc and subsequent protonolysis of the resulting carboxylate, followed by a lactonization, would generate the desired product **2a** and complex **A** as well. The lactonization should be fast and the stability of the lactonization product **2a** might be the key for the shift of the carboxylation−decarboxylation equilibrium to the product side. It should also be noted other catalytic cycles such as that involves other valent Rh species cannot be ruled out completely at present.

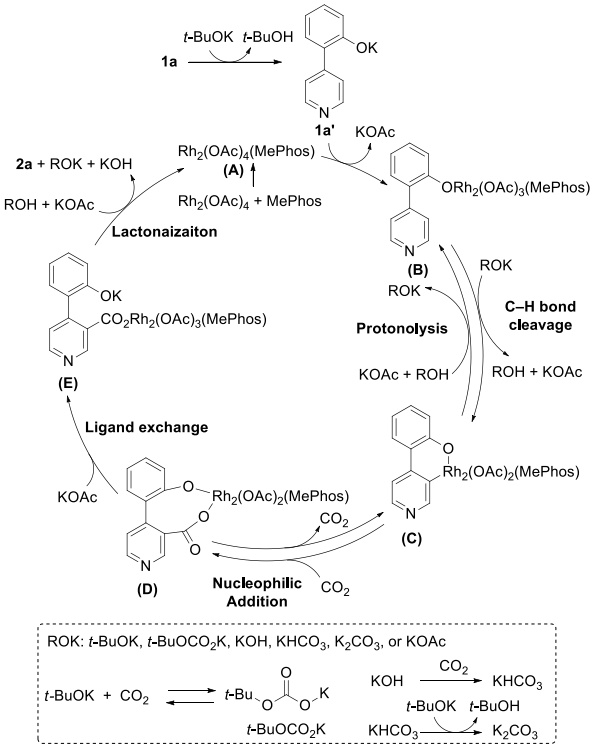


Figure 2. Tentative catalytic cycle.

In conclusion, we have developed an efficient Rh(II)-catalyzed C–H carboxylation of 2-pyridylphenols with CO_2 under redox-neutral

conditions. This novel method was compatible with challenging electron-deficient pyrido-heterocycles, leading to generally high yields of a series of pyrido-coumarins that are key structural motifs in biologically important molecules. Product derivatizations may also provide a short-cut to access to a new class of pyrido-heterocycles.

Experimental Section

General Procedure for Carboxylation of 2-Pyridylphenols 1 with CO_2: In a glove box, to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added **1** (0.1 mmol), $Rh_2(OAc)_4$ (2.5-5 mol %), ligand (5-10 mol %, MePhos or IMes·HCl) and *t*-BuOK (50 mg, 0.45 mmol) (Note: *t*-BuOK should be dry). After taken out of the glove box, the tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3). Then anhydrous solvent (1.0 mL) was added along the inside wall of the tube loaded with CO_2. Afterwards, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, × 3). The tube was capped and then placed into a preheated hotplate (100 or 150 °C). The reaction was stirred vigorously (Note: good stirring is important!) for 12-48 h and cooled to room temperature. The reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 10 mL of EtOAc. The filtrate was concentrated in vacuo, and purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/EtOAc (3/1) as the eluent to afford the desired product.

Acknowledgements

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[15] CCDC-1819284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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UPDATE

Rhodium(II)-Catalyzed Aryl C–H Carboxylation of 2-Pyridylphenols with CO_2

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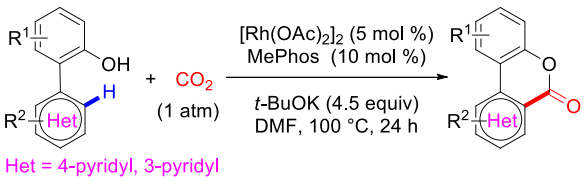

Het = 4-pyridyl, 3-pyridyl