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Palladium-Catalyzed Decarboxylative *Ortho*-Ethoxycarbonylation of *O*-Methyl Ketoximes and 2-Arylpyridines with Potassium Oxalate Monoester

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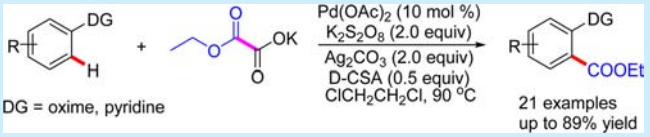
Supporting Information

ABSTRACT: A novel method for introducing an ester group via palladium-catalyzed ligand-directed C−H activation has been explored. The *ortho*-ethoxycarbonylation of *O*-methyl ketoximes proceeded smoothly with the nontoxic and easily handled reagent potassium oxalate monoester, affording the desired products in moderate to good yields. Furthermore, pyridine could also be employed as a directing group to obtain similar results in this transformation.



In recent decades, the transition-metal-catalyzed ligand-directed C−H bond activation has aroused extensive attention of a growing number of chemists because of its high efficiency and good functional group tolerance. Among these important reactions, a variety of nitrogen-containing functional groups such as pyridine,[1] quinoline,[2] imine,[3] and others[4] are widely utilized. *O*-Methyl ketoxime is undoubtedly one of the most popular directing groups due to its moderate coordination ability to transition metals. In particular, it is a removable functional group and easy to transform to other moieties.[5] In 2006, Sanford and co-workers reported the alkoxylation and acetoxylation of *O*-methyl ketoximes.[6] Then the Che group described the *ortho*-amidation of *O*-methyl ketoximes.[7] Many other functionalizations of *O*-methyl ketoximes including arylation,[1j,8] ethoxycarbonylation,[9] acylation,[10] nitration,[5b,11] cyanation,[12] and other transformations[13] were also demonstrated.

On the other hand, owing to the prevalence of the carbonyl group in organic molecules, comprehensive research has been conducted to introduce a carboxyl or ester group into aromatic compounds through ligand-directed C−H activation reactions during the past decade. Yu and other chemists reported the ligand-directed C−H carboxylation and esterification with CO and CO_2.[14] The Yu and You groups utilized the diethyl azodicarboxylate (DEAD) to realize the *ortho*-ethoxycarbonylation.[9,15] Many other research groups including the Kakiuchi,[16] Shi,[17] Tan,[18] and Wang[19] groups reported this important alkoxycarbonylation with different kinds of reagents. Although many protocols to realize the esterification by ligand-directed C−H activation strategy have been documented, there are still great challenges to develop a new method using a nontoxic and easily handled reagent to expand the scope of this important transformation. In 2009, Fu, Liu, and co-workers synthesized the aromatic esters via decarboxylative coupling reaction with the nontoxic and easily handled reagent potassium oxalate monoester and aryl halides.[20] After that, the Ge group utilized potassium phenyltrifluoroborate to react with potassium oxalate monoester or substituted oxalic acids to achieve an analogous reaction.[21] Nevertheless, the ethoxycarbonylation via C−H activation with potassium oxalate monoester has never been reported. As part of our continuing interest in C−H bond functionalizations,[22] herein we disclose the first example of the decarboxylative *ortho*-ethoxycarbonylation with potassium oxalate monoester via the palladium-catalyzed sp^2 C−H activation.

To explore the optimal reaction conditions of this *ortho*-ethoxycarbonylation, the coupling of *p*-methyl *O*-methyl ketoxime **1a** with potassium oxalate monoester **2** was chosen as the model reaction (Table 1). At first, $K_2S_2O_8$ and $ClCH_2CH_2Cl$ were employed as the oxidant and solvent, respectively. Only a trace amount of the desired product was observed (Table 1, entry 1). When 0.5 equiv of acidic additive such as *p*-toluenesulfonic acid (PTSA) or D-camphorsulfonic acid (D-CSA) was used in this reaction, product **3a** was obtained in 15−21% yield (Table 1, entries 2 and 3). Considering that silver salts had been utilized frequently in decarboxylative systems, different types of silver salts were examined in this reaction. In doing so, the yield of **3a** was dramatically increased to 73% when 2.0 equiv of AgOAc was added (Table 1, entry 4). Encouraged by this result, other silver salts such as Ag_2O and Ag_2CO_3 were also explored, but the yields were unsatisfactory (Table 1, entries 5 and 6). When other oxidants were used in this reaction, no better results were achieved (Table 1, entries 7−9). A yield of 75% was obtained when 0.5 equiv of D-CSA and 2.0 equiv of AgOAc were added together (Table 1, entry 10). Gratifyingly, when AgOAc was replaced by Ag_2CO_3, **3a** was produced in 83% yield (Table 1, entry 11). The yield was reduced sharply to 33% if the amount of $Pd(OAc)_2$ was decreased from 10 to 5 mol % (Table 1, entry 12). Product **3a** was isolated in 69%

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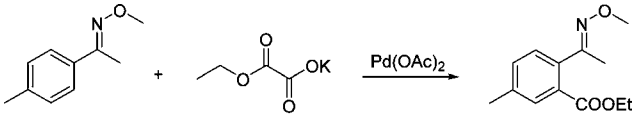
Table 1. Optimization of the Reaction Conditions[a]



1a 2 3a

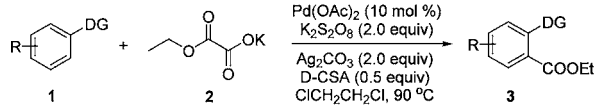
entry	oxidant	silver salt	additive	solvent	yield[b] (%)
1	$K_2S_2O_8$			$ClCH_2CH_2Cl$	trace
2	$K_2S_2O_8$		PTSA	$ClCH_2CH_2Cl$	15
3	$K_2S_2O_8$		D-CSA	$ClCH_2CH_2Cl$	21
4	$K_2S_2O_8$	AgOAc		$ClCH_2CH_2Cl$	73
5	$K_2S_2O_8$	Ag_2O		$ClCH_2CH_2Cl$	42
6	$K_2S_2O_8$	Ag_2CO_3		$ClCH_2CH_2Cl$	65
7	$Na_2S_2O_8$	AgOAc		$ClCH_2CH_2Cl$	44
8	$(NH_4)_2S_2O_8$	AgOAc		$ClCH_2CH_2Cl$	21
9	Oxone	AgOAc		$ClCH_2CH_2Cl$	11
10	$K_2S_2O_8$	AgOAc	D-CSA	$ClCH_2CH_2Cl$	75
11	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	83
12[c]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	33
13[d]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	69
14[e]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	50
15[f]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	41
16[g]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	75
17[h]	$K_2S_2O_8$	Ag_2CO_3	D-CSA	$ClCH_2CH_2Cl$	82
18	$K_2S_2O_8$	Ag_2CO_3	D-CSA	1,4-dioxane	trace
19	$K_2S_2O_8$	Ag_2CO_3	D-CSA	toluene	trace
20	$K_2S_2O_8$	Ag_2CO_3	D-CSA	DMSO	trace
21	$K_2S_2O_8$	Ag_2CO_3	D-CSA	HOAc	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (0.4 mmol), silver salt (0.4 mmol), additive (0.1 mmol), 80 °C, 16 h. [b]Isolated yield based on **1a**. [c]$Pd(OAc)_2$ (5 mol %). [d]Additive (0.05 mmol). [e]$K_2S_2O_8$ (0.2 mmol). [f]**2** (0.3 mmol). [g]Ag_2CO_3 (0.2 mmol). [h]**1a** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (1.0 mmol), Ag_2CO_3 (1.0 mmol), D-CSA (0.25 mmol), 90 °C, 12 h.

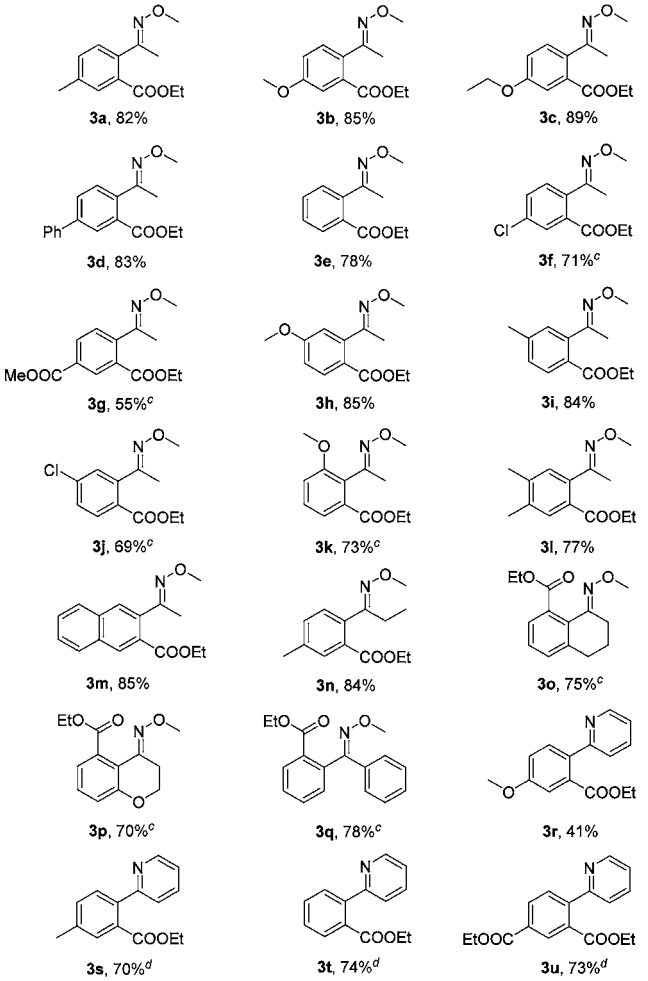
when the amount of D-CSA was reduced to 0.25 equiv (Table 1, entry 13). Decreasing the amount of oxidant or **2** provided worse results (Table 1, entries 14 and 15). Reducing the amount of Ag_2CO_3 to 1.0 equiv led to a slight decrease of product yield (Table 1, entry 16). Other solvents were also examined in this conversion, but no better result was achieved (Table 1, entries 18−21). When the amount of **1a** was amplified to 0.5 mmol, the temperature had to be raised to 90 °C to keep an 82% yield of product **3a** (Table 1, entry 17). Therefore, the optimized conditions for the palladium-catalyzed decarboxylative *ortho*-ethoxycarbonylation with potassium oxalate monoester were determined as follows: 10 mol % of $Pd(OAc)_2$ as the catalyst, 2.0 equiv of $K_2S_2O_8$ as the oxidant, 2.0 equiv of Ag_2CO_3 as the silver salt, 0.5 equiv of D-CSA as the additive, and 2.0 equiv of potassium oxalate monoester **2** as the partner of *O*-methyl ketoxime **1a**. The reaction performed best at 90 °C with $ClCH_2CH_2Cl$ as the solvent.

With the optimized conditions in hand, the substrate scope of *O*-methyl ketoximes **1** was examined with **2** in this reaction. As shown in Scheme 1, *O*-methyl ketoximes having both electron-rich and electron-deficient groups on the aryl ring could react with **2** to afford the ethoxycarbonylation products **3a**−**q** in moderate to good yields (55−89%). When the strong electron-donating groups OMe and OEt were substituted at the *para*-position, products **3b** and **3c** were obtained in good yields (85% and 89%) under our conditions. Similarly, *O*-methyl ketoximes

Scheme 1. Pd-Catalyzed Oxidative Ethoxycarboxylation of *O*-Methyl Oximes and 2-Arylpyridines[a,b]



1 2 3



[a]**1a** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (1.0 mmol), Ag_2CO_3 (1.0 mmol), D-CSA (0.25 mmol), 90 °C, 12 h. [b]Isolated yield based on **1a**. [c]The reaction was performed for 36 h. [d]The reaction was performed for 14 h.

with a phenyl group or no substituent groups at the *para*-position gave **3d** and **3e** in 83% and 78% yields. Electron-withdrawing groups such as chloro and ester groups located at the *para*-position were inferior in this transformation. When the time was prolonged to 36 h, the desired products **3f** and **3g** could be isolated in 71% and 55% yields. Notably, *meta*-substituted ketoximes exhibited good regioselectivities and efficiencies in the reaction to give products **3h**, **3i**, and **3j** in 85%, 84%, and 69% yields, respectively. Furthermore, the reaction could be applied to *ortho*-substituted and disubstituted *O*-methyl ketoximes, affording **3k** and **3l** in 73% and 77% yields. As anticipated, 2-naphthalenyl ketoxime **1m** gave the corresponding product **3m** at the less sterically hindered position in 85% yield. When **1n** was used to replace the structurally similar **1a**, **3n** was obtained in a yield (84%) close to that of **3a** (82%). Moreover, oximes with a bicyclic scaffold such as **1o** and **1p** could also undergo facile C−H

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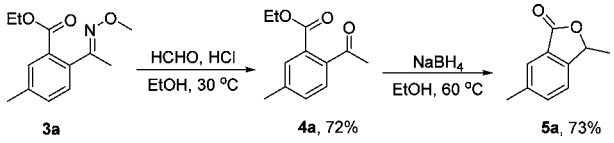
ortho-ethoxycarbonylation (75% and 70%). It is worth mentioning that in the case of **1q** with four *ortho*-C−H bonds only monoethoxycarbonylation took place to provide **3q** in 78% yield. In addition, pyridine derivatives were utilized to replace ketoximes, and products **3r**, **3s**, **3t**, and **3u** were obtained in 41−74% yields under the same conditions.

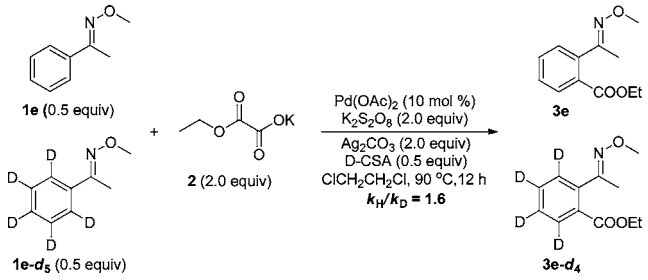
To demonstrate the synthetic utility of this reaction, we chose **3a** as a representative example to remove its directing group. In the event, **4a** could be isolated in 72% yield. Then, $NaBH_4$ was employed to reduce **4a** in EtOH, and lactone **5a** was obtained in 73% yield (Scheme 2).

Scheme 2. Removal of Directing Group



Further experiments were conducted to obtain insight into the reaction mechanism. The ethoxycarbonylation of **1e** under the optimized conditions gave only trace amounts of **3e** in the presence of 1.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). This result demonstrated that the reaction may involve a radical pathway. The intermolecular kinetic isotope effect (k_H/k_D) of **1e** to **1e**-d_5 for the C−H ethoxycarbonylation was determined to be 1.6 (Scheme 3), indicating that the C−H bond cleavage may not be the rate-limiting step.

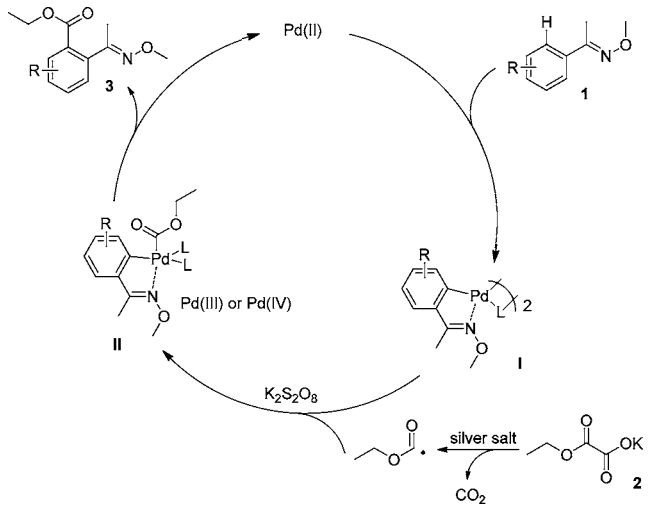
Scheme 3. Investigation on the Effect of Kinetic Isotope



On the basis of the observations described above, a possible reaction mechanism was proposed, which is shown in Scheme 4. At first, five-membered palladacycle **I** is formed via the *ortho*-palladation of **1** with Pd(II). Then, palladacycle **I** reacts with the ethoxyacyl radical generated from the decarboxylation of **2** with the aid of silver salt to provide intermediate **II** in the presence of $K_2S_2O_8$. Subsequently, product **3** is formed by reductive elimination, accompanied by the simultaneous release of a Pd(II) species to complete the catalytic cycle.

In summary, a novel and efficient approach for the Pd-catalyzed *ortho*-ethoxycarbonylation using potassium oxalate monoester via C−H bond activation has been developed. This new protocol extends the concept and scope of the recently popular ethoxycarboxylation. Different kinds of directing groups such as oxime and pyridine can be utilized in this transformation. In addition, this method also tolerates a wide range of functional groups. The ethoxycarbonylation products of *O*-methyl ketoximes can be further converted into ketoesters and lactones.

Scheme 4. Plausible Reaction Mechanism



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02422.

Detailed experimental procedures; ^1H NMR and ^{13}C NMR spectra of **3a**−**u**, **4a**, and **5a** (PDF)

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Notes

The authors declare no competing financial interest.

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