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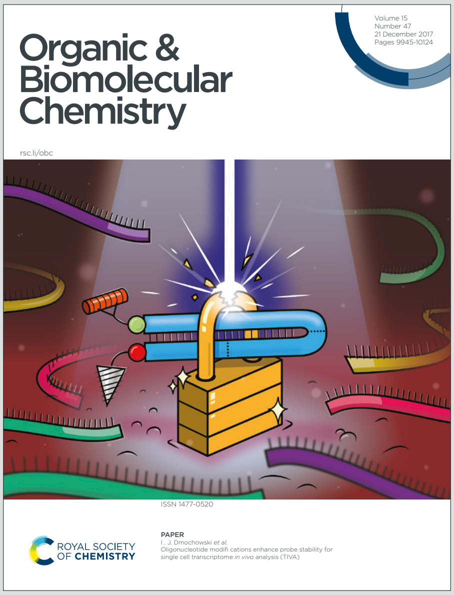

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ARTICLE

Nitrate Promoted Mild and Versatile Pd-catalysed C(sp^2)-H Oxidation with Carboxylic Acids

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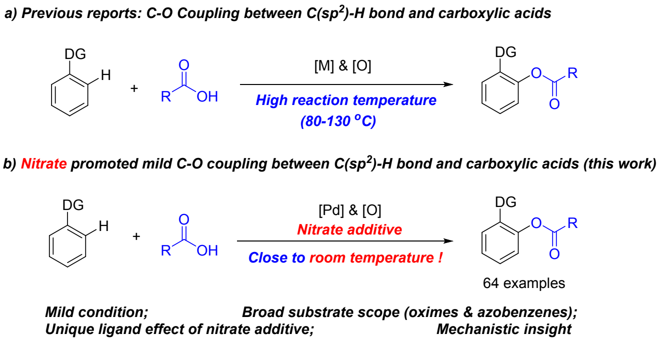
A nitrate-promoted Pd-catalysed mild cross-dehydrogenative C(sp^2)-H bond oxidation of oximes or azobenzenes with diverse carboxylic acids has been developed. In contrast to the previous catalytic systems, this protocol features mild conditions (close to room temperature for most cases) and broad substrate scope (up to 65 examples), thus constituting a versatile method to prepare diverse O-aryl esters directly. Moreover, the superiority of nitrate additive in this mild transformation was further determined by the experimental and computational evidence.

Introduction

O-aryl esters are widely found in medicinal chemistry.[1] A variety of synthetic routes have been disclosed to access O-aryl esters. Among the possible approaches, the direct formation of O-aryl esters from carboxylic acid with unactivated aromatics represents one of the most atom-efficiency ways. Indeed, various catalytic systems using different transition-metals (Rh, Ru, Pd, Cu, Co, *etc.*) have been developed for the rapid synthesis of O-aryl esters (Scheme 1a).[2,3,4] However, despite the extensive studies, the intermolecular CDC (cross-dehydrogenative-coupling) between carboxylic acid and aromatic C-H bond usually requires high reaction temperature (80-130 °C). In this regard, a mild and versatile method is still attractive and highly demanded for the sake of broad functional group tolerance.

Given the high BDE (bond dissociation energies) of inert C-H bonds, catalytic C-H bond functionalization usually requires harsh reaction conditions. Consequently, such transformations that proceed under mild conditions (*e.g.* ambient temperature) would be highly attractive for the organic synthesis.[4] Electrophilic cationic palladium catalysts that *in-situ* generated from palladium pre-catalyst and anionic additive exhibits enhanced reactivity and enables C(sp^2)-H bond activation at room temperature. Several additives *e.g.* CF_3COOH, HBF_4, TsOH, were widely used as effective promoters in the previous reports.[5] Besides the acid additives, our group also found that a unique nitrate additive could significantly accelerate the C(sp^2)-H bond fluorination of diverse substrates under mild conditions.[6] In particular, nitrate-promoted C(sp^2)-H bond fluorination of oximes and amides even took place at room temperature.[6b,6d] A cationic $[Pd(NO_3)]^+$ species was proposed to lower the activation barrier for aromatic C-H bond metalation. Moreover, a detailed mechanism has revealed that the poor nucleophilic nitrate additive could also serve as an anionic ligand, which enables the selective C-F bond reductive elimination.[7,8] In light of our previous work, we envisaged that a selective C(sp^2)-H bond acyloxylation with simple carboxylic acids in the presence of nitrate additive might render the transformation under mild conditions. Herein, we report the preliminary results of this study (Scheme 1b).



Scheme 1 C-O Bond coupling between C(sp^2)-H bond and carboxylic acids.

Results and discussion

At the outset of the project, acetophenone oxime **1a**[9] and benzoic acid **2a** were treated with Pd catalyst, NFSI (N-fluorobenzenesulfonimide), and stoichiometric KNO_3 in CH_3NO_2 under 30 °C (Table 1, entry 1). Gratefully, the desired O-aryl ester **3a** was obtained in a moderate yield (59%) and

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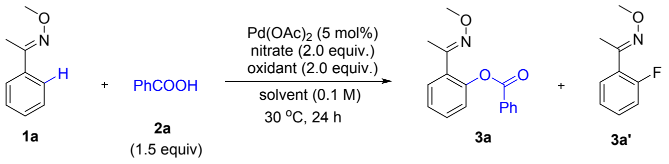
Table 1 Screening of the oxidation conditions[a]



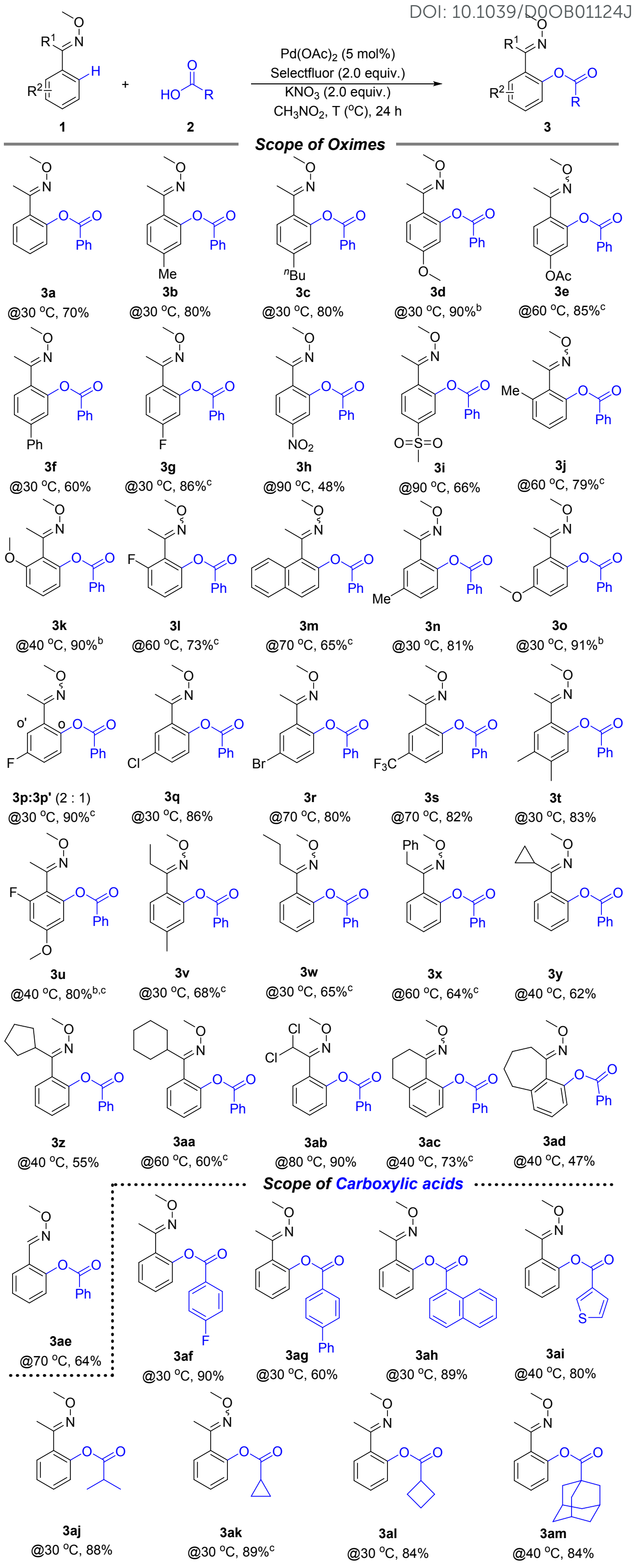
Entry	Oxidant	Solvent	Nitrate	Yield of 3a/3a' (%)
1	NFSI	CH_3NO_2	KNO_3	59/26
2	**Selectfluor**	**CH_3NO_2**	**KNO_3**	**74/8**
3	Selectfluor	CH_3NO_2	KNO_3	72/11[b]
4	O_2	CH_3NO_2	KNO_3	--/--
5	$Na_2S_2O_8$	CH_3NO_2	KNO_3	trace/--
6	$PhI(OAc)_2$	CH_3NO_2	KNO_3	--/--
7	$Cu(OAc)_2$	CH_3NO_2	KNO_3	--/--
8	BQ	CH_3NO_2	KNO_3	--/--
9	CAN	CH_3NO_2	KNO_3	65/--
10	Selectfluor	CH_3CN	KNO_3	44/--
11	Selectfluor	DCE	KNO_3	44/--
12	Selectfluor	$PhCH_3$	KNO_3	15/--
13	Selectfluor	EtOAc	KNO_3	--/--
14	Selectfluor	DMF	KNO_3	--/--
15	Selectfluor	THF	KNO_3	--/--
16	Selectfluor	CH_3NO_2	--	13/--
17	Selectfluor	CH_3NO_2	KNO_3	59/--[c]
18	Selectfluor	CH_3NO_2	$NaNO_3$	73/18
19	Selectfluor	CH_3NO_2	$AgNO_3$	73/16
20	Selectfluor	CH_3NO_2	$LiNO_3$	54/5
21	Selectfluor	CH_3NO_2	$Mg(NO_3)_2•6H_2O$	30/--

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 *equiv.*), $Pd(OAc)_2$ (5 mol%), oxidant (2.0 *equiv.*), nitrate (2.0 *equiv.*), solvent (1.0 mL), 30 °C, ambient atmosphere, 24 h, GC-MS yield (unless otherwise noted). [b] Under N_2 atmosphere. [c] KNO_3 (0.2 *equiv.*).

fluorinated oxime **3a'** was also detected as a side-product (26%). Switching the oxidant from NFSI to another F^+ reagent Selectfluor enhanced the oxidation/fluorination selectivity under ambient atmosphere (**3a/3a'** = 74/8) (entries 2-3). Several other oxidants such as oxygen (entry 4), peroxides (entry 5), $PhI(OAc)_2$ (entry 6), copper salt (entry 7), and benzoquinone (entry 8) were inefficient in this transformation. Interestingly, inorganic oxidant CAN (Ceric ammonium nitrate), which contains nitrate anion, promoted the oxidation efficiently (entry 9). CH_3NO_2 performed the best among the solvents tested (entries 10-15). As anticipated, the oxidation reaction became sluggish in the absence of nitrate additive (entry 16). Catalytic amount of KNO_3 additive could dramatically improve the reaction efficiency (entry 17). Other nitrate additives were also investigated. $NaNO_3$ and $AgNO_3$ gave comparable results, albeit with lower selectivity (entries 18-19). $LiNO_3$ or $Mg(NO_3)_2•6H_2O$ could also serve as a promoter (entries 20-21). These results further demonstrate the crucial role of nitrate additive in this mild C-H bond oxidation.

With the optimized conditions in hand, the substrate scope of the oxidation was investigated. Diverse oximes were prepared and tested (Table 2). Generally, the reaction tolerated well with various substituents, *e.g.* alkyl (**3b**, **3c**, **3j**,

Table 2 C(sp^2)-H Oxidation of oximes with carboxylic acids[a]



[a] Reaction conditions: **1** (0.30 mmol), **2** (1.5 *equiv.*), $Pd(OAc)_2$ (5 mol%), Selectfluor (2.0 *equiv.*), KNO_3 (2.0 *equiv.*) in CH_3NO_2 (3.0 mL) under air at the indicated temperature for 24 h, isolated yield, unless otherwise noted. [b] DCE (3.0 mL). [c] The isolated product contains small amount of the Z-isomer as minor product (see ESI).

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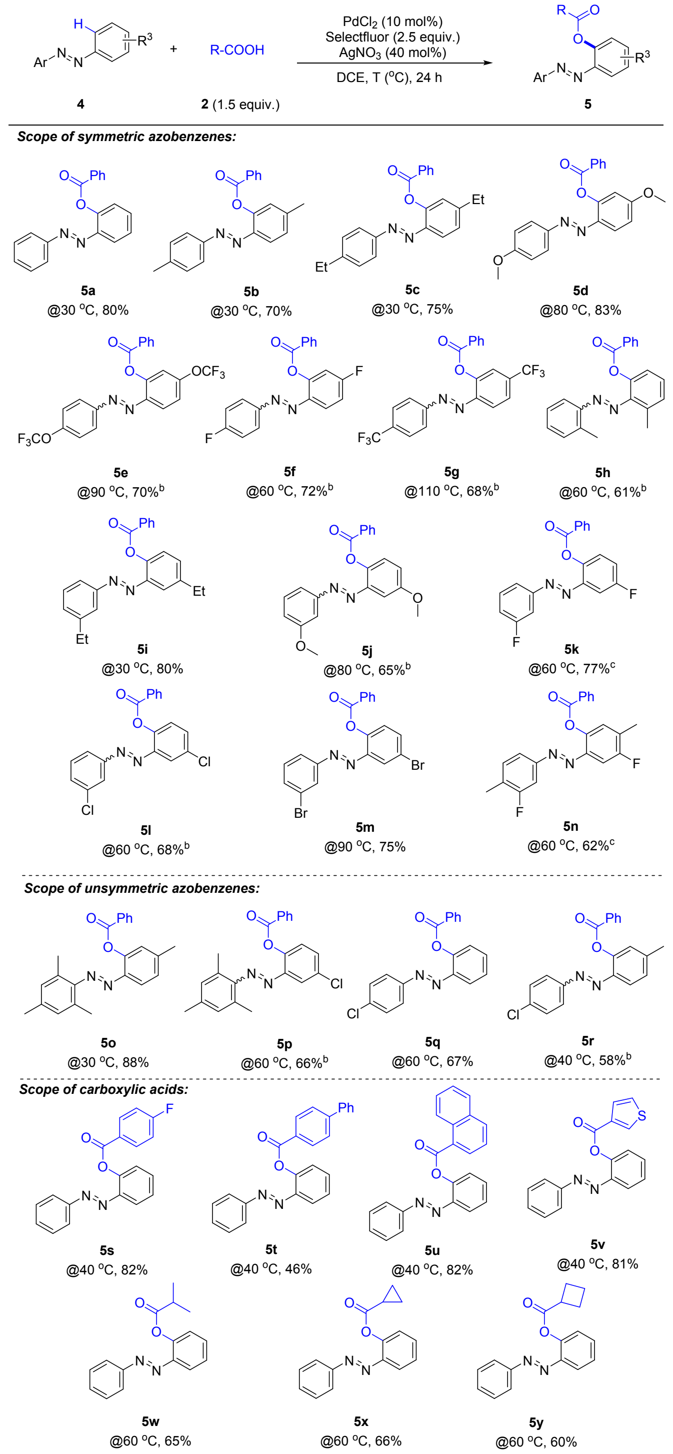
Table 3 C(sp^2)-H Oxidation of azobenzenes with carboxylic acids[a]



[a]Reaction conditions: **1** (0.30 mmol), **2** (1.5 *equiv.*), $PdCl_2$ (10 mol%), Selectfluor (2.5 *equiv.*), $AgNO_3$ (0.4 *equiv.*) in 1,2-dichloroethane (3.0 mL) under air at the indicated temperature for 24 h, isolated yield, unless otherwise noted. [b]The isolated product contains small amount of the Z-isomer as minor product (see ESI). [c]The isolated product contains small amount of unseparable regioisomer as minor product (see ESI).

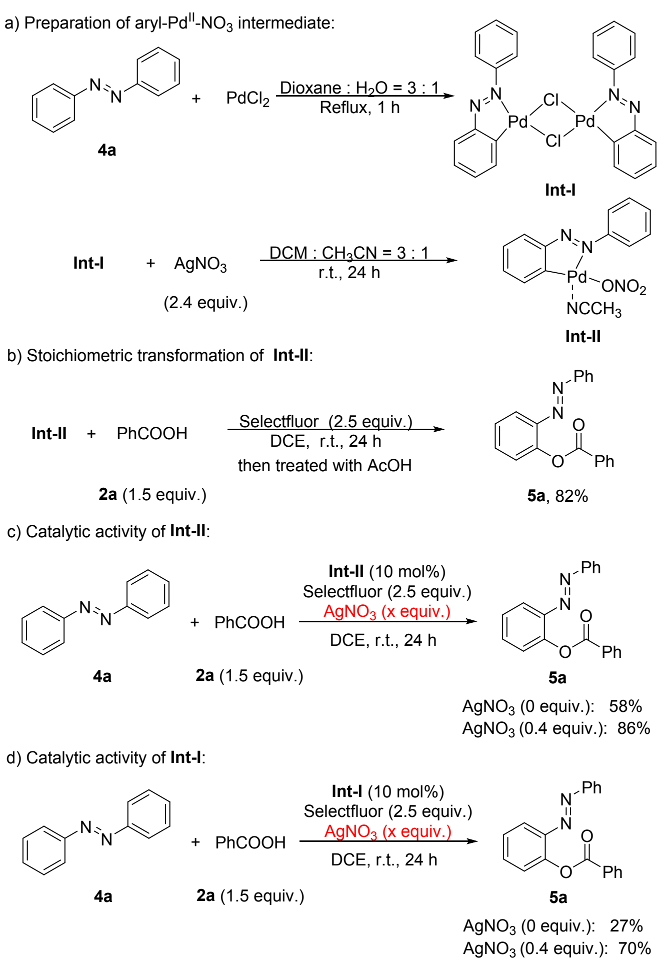
3n), alkoxyl (**3d**, **3k**, **3o**), ester (**3e**), aryl (**3f**), halo (**3g**, **3l**, **3q**, **3r**), nitro (**3h**), sulfonyl (**3i**), and trifluoromethyl (**3s**) functional groups. Disubstituted acetophenone oximes also underwent C-H bond oxidation efficiently to give poly-substituted products (**3t, 3u**) in good yield. To be noted, the oxidation took place close to room temperature in most cases. The substrates bearing strong electron-withdrawing functional groups (NO_2, CH_3SO_2, CF_3) required elevated reaction temperatures to reach comparable yields. Sterically demanding *ortho*-substituted oximes needed higher reaction temperature (**3j**-**3m**). For the *meta*-substituted oximes, C-H bond oxidation took place at the less sterically hindered position (**3n**-**3t**). However, a mixture of regioisomers was detected in the case of *meta*-fluoro acetophenone oxime due to the small size of fluorine atom (**3p**:**3p'** = 2:1).

Aromatic carbonyl oximes other than acetophenone derived oximes were also investigated (**3v**-**3ae**). Strained cyclopropanyl is compatible with the oxidative condition (**3y**). The sensitive dichloromethyl group also survived the reaction condition (**3ab**). The reaction of cyclic ketone oximes bearing different ring size took place smoothly as well (**3ac**, **3ad**). Notably, benzaldehyde oxime was also accommodated to the C-H bond oxidation with benzoic acid in a decent yield (**3ae**).

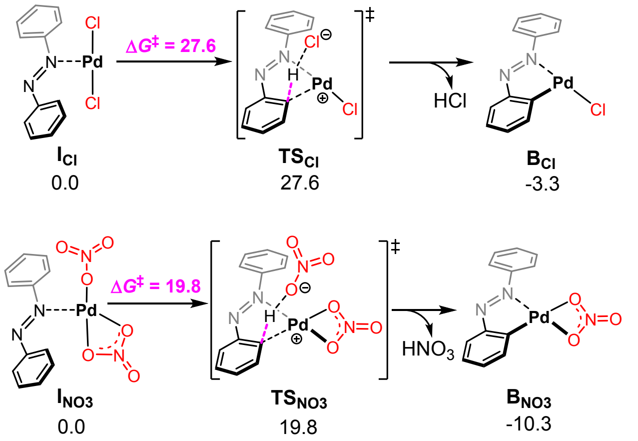
Next, different aromatic acids and aliphatic acids were tested. Substituted benzoic acids (**3af**, **3ag**), 1-naphthoic acid (**3ah**), and even 2-thiophenecarboxylic acid (**3ai**) underwent cross-dehydrogenative O-arylation with **1a** under mild conditions. Moreover, small isobutyric acid also worked well to give the corresponding O-aryl ester in high yield at 30 °C (**3aj**). Other aliphatic acids containing cyclopropanyl (**3ak**), cyclobutyl (**3al**), and adamantyl (**3am**) groups did not hamper the reaction efficiency.

To further examine the application prospects of this Pd-nitrate catalysis in the mild aromatic C-H bond oxidation with carboxylic acids, diverse azobenzenes were also investigated (Table 3).[10] To our delight, the desired product **5a** was obtained in high yield under mild reaction condition (see SI).[11] Similar to the C-H bond oxidation of oximes, diverse functional groups (alkyl, alkoxyl, CF_3O, CF_3, F, Cl, Br) tethered at different positions of azobenzenes were well tolerated (**5a**-**5n**). Notably, the reaction temperatures were below 80 °C in most cases. The C-H bond oxidation of unsymmetrical azobenzenes bearing 2,6-diblocked mesityl group also took place smoothly (**5o**, **5p**). For the unsymmetrical azobenzenes bearing electronically biased aryl groups, C-H oxidation selectively took place at the more electron-rich aromatic side (**5q, 5r**). Again, the O-arylation of different aromatic acids and aliphatic acids with azobenzene **4a** proceeded smoothly under mild conditions (**5s**-**5y**).

To gain further information of the nitrate-promoted C(sp^2)-H bond oxidation protocol, several mechanistic experiments were carried out (Scheme 2). Firstly, a key aryl-Pd-NO_3 intermediate (**Int-II**) was prepared from **Int-I** in high yield according to the previous reports (Scheme 2, a).[7,8c,12] Treating the **Int-II** and **2a** with 2.5 equivalents of Selectfluor at room temperature for 24 hours gave the desired oxidation product **5a** in 82% yield (Scheme 2, b). Furthermore, using **Int-II** as the sole catalyst in the absence of nitrate additive could promote the C-H bond oxidation to afford **5a** in 58% yield. The yield of



Scheme 2 Mechanistic experiments.



Scheme 3 Computed C–H activation of **4a** catalyzed by PdCl$_2$ and Pd(NO$_3$)$_2$, respectively, calculated at the level of M06/6-311+G(d,p)-SDD(Pd) (DCE, SMD)//B3LYP/6-31G(d)-SDD(Pd). See Supporting Information for computational details.

the desired product was further improved with the extra addition of a catalytic amount of nitrate (Scheme 2, c). In sharp contrast, using **Int-I** as the catalyst was less efficient in the absence of nitrate additive (Scheme 2, d). In addition, a lack of induction period was observed in the kinetic experiment that using **Int-II** as the catalyst, indicating that the nitrate-containing palladacycle complex should be involved in the catalytic cycle (see SI, Figure S1). These stoichiometric and catalytic reactions demostrated a significant accelerating effect of nitrate additive in the present mild C(sp^2)-H bond oxidation.

To have a better understanding of the role of the nitrate additive, we performed the density functional theory (DFT) calculations on this reaction. Firstly, the C–H activation of **4a** by Pd catalysts in combination with Cl$^-$ or NO$_3^-$ anions was comparatively investigated and the most favorable pathways for each case were shown Scheme 3 (see also SI, Figures S3 and S4 for more details). Indeed, the C–H activation via **TS$_{Cl}$** has to overcome an energy barrier of 27.6 kcal mol^{-1} in the PdCl$_2$-catalyzed reaction (Scheme 3). In contrast, when nitrate was added into the reaction system, the computational result clearly suggested that the energy barrier of the C–H activation via **TS$_{NO3}$** was significantly reduced to 19.8 kcal mol^{-1}, indicating that the nitrate could promote the reaction to take place under mild conditions by facilitating the C-H bond cleavage.[13]

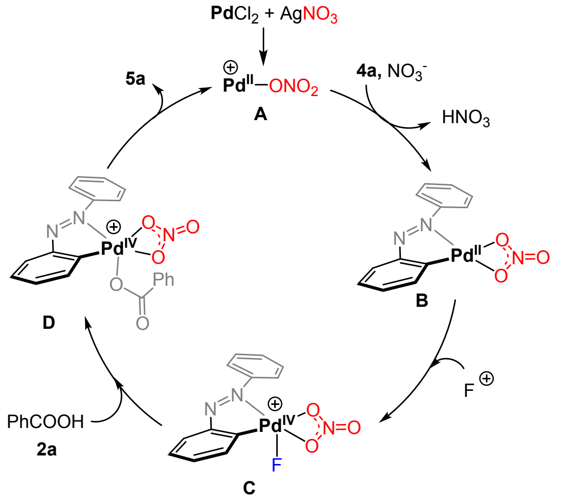


Figure 1 Possible reaction mechanism.

Based on the above experimental and computational results, as well as the previous literatures,[14] a possible mechanism is shown in Figure 1. The cationic Pd-NO$_3$ species **A** was *in-situ* generated from Pd precatalyst and nitrate additive. A chelation-assisted electrophilic C(sp^2)-H bond palladation of substrate **4a** with **A** occurs subsequently, followed by an oxidative addition with F$^+$ reagent to give the high-valent Pd^{IV} intermediate **C**. Given the poor nucleophilicity of fluoro anion and nitrate anion, the C-F bond formation or C-ONO$_2$ bond formation is disfavored under mild conditions.[15] In contrast, a nucleophilic ligand exchange of **C** with the carboxylic acid **2a** takes place to give intermediate **D**, which undergoes a selective C-O bond reductive elimination subsequently to provide the desired product **5a** and regenerate cationic Pd-NO$_3$ species **A** for the next catalytic cycle.

Conclusions

In conclusion, a nitrate-promoted mild C(sp^2)-H oxidation of diverse oximes or azobenzenes with diverse aromatic and aliphatic acids was developed for the first time. A variety of desired O-aryl esters were obtained in high yield under mild conditions (close to the ambient temperature for most cases). More importantly, the unique effect of nitrate additives was established by detailed studies on the well-defined aryl-Pd(II)-NO_3 intermediate. DFT studies also demostrated that nitrate additive could significantly lower the energy barrier of the C–H bond cleavage. The procotol not only provides a mild synthetic method towards useful O-aryl esters, but also shows new insight into the powerful Pd-nitrate catalysis in C-H bond activation. Utilizing this Pd-nitrate catalytic platform for the selective reductive elimination of other challenging chemical bonds is ongoing in our laboratory.

Conflicts of interest

The authors declare no competing financial interests.

Experimental Section

Typical procedure for the mild C(sp^2)-H oxidation of **1** with carboxylic acids **2**: In a 10 mL test tube equipped with a stir bar, oxime **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (0.015 mmol), Selectfluor (0.6 mmol), KNO_3 (0.6 mmol) and CH_3NO_2 (3.0 mL) were added successively. Then the tube was sealed and stirred at the indicated temperature for 24 h. Upon completion, the mixture was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford the desired products **3**.

Typical procedure for the mild C(sp^2)-H oxidation of **4** with carboxylic acids **2**: In a 10 mL test tube equipped with a stir bar, azobenzene **4** (0.3 mmol), **2** (0.45 mmol), $PdCl_2$ (0.03 mmol), Selectfluor (0.75 mmol), $AgNO_3$ (0.12 mmol) and 1,2-dichloroethane (3.0 mL) were added successively. Then the tube was sealed and stirred at the indicated temperature for 24 h. Upon completion, the mixture was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford the desired products **5**.

Acknowledgements

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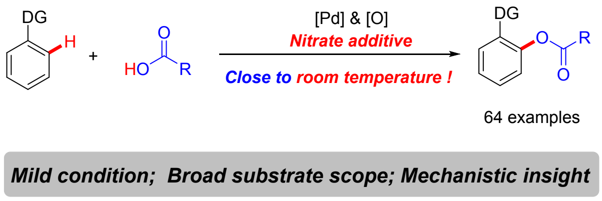

A nitrate-promoted Pd-catalysed cross-dehydrogenative C(sp^2)-H oxidation of oximes or azobenzenes with diverse aromatic and aliphatic acids was developed, allowing the versatile formation of O-aryl esters under mild reaction conditions.