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Room Temperature Palladium-Catalyzed Decarboxylative Acyl/Aroylation using $[Fe(III)(EDTA)(\eta^2\text{-}O_2)]^{3-}$ as Oxidant at Biological pH

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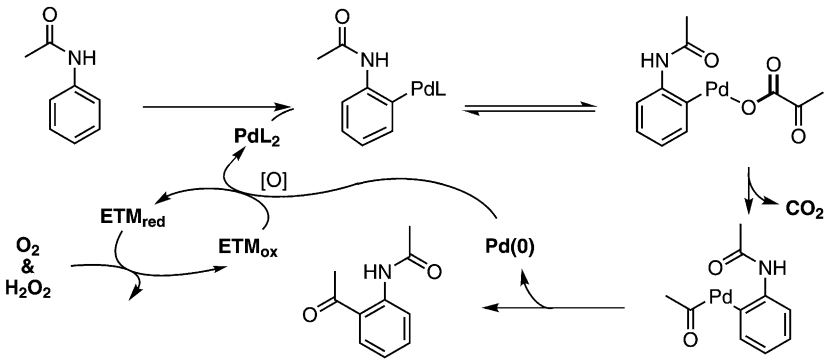
Abstract: The purple-coloured iron peroxo complex $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$ as a novel reagent system for Pd-catalyzed decarboxylative *ortho*-acylation of acetanilides with α-oxocarboxylic acids at room temperature in aqueous media has been realized. This reaction provides an effective access to *ortho*-acylacetanilides under mild conditions.

Keywords: carboxylic acids; cross-coupling decarboxylation; electron-transfer mediators; enamides; re-oxidation

Over the past three decades, the tenacious efforts of synthetic chemists to develop efficient methods for transition metal-catalyzed cross-coupling reactions have revolutionized the synthesis of unsymmetrical diaryl ketone and diaryl compounds.[1,2] Some of these methods involving in particular the palladium-catalyzed cross-coupling reactions between aryl halides and aryl organometallics are widely used in modern academic and industrial laboratories, and have led to core structures in medicinal chemistry and material sciences. Traditional cross-coupling methods require pre-activated coupling partners, such as expensive and/or moisture-sensitive organometallic reagents, and frequently produce unwanted, often toxic, stoichiometric side-products.[1] Therefore, attempts have been made to develop more atom economical, milder and greener protocols.[2i,3] Although many well-designed studies have demonstrated that high selectivity can be achieved in such direct arylation reactions by tuning directing groups, electronic effects, and steric factors, significant room for improvement still remains.[3]

Enamides and their derivatives are intrinsically useful intermediates[4] and have been successfully used as a coupling partner in the palladium catalyzed C–H bond activation reaction.[5] However, methods for direct olefin functionalization of enamides typically rely on the use of organometallic reagents,[4a,b] acrylates,[4c] or arenes,[4e] and catalytic decarboxylative–dehydrogenative couplings of carboxylic acids with enamides have thus become an innovative area to been investigated. Herein, we report a versatile palladium-catalyzed decarboxylative acylation of cyclic enamides with α-oxocarboxylic acid to access diaryl ketones and that it is equally efficient with aromatic acids to access diaryls *via* alkenyl C–H bond activation under mild conditions. The role of oxidants in the palladium-catalyzed cross-coupling is in the regeneration of the catalyst which is directly proportional to the turnover number.[6] The direct oxidation of the catalyst by molecular oxygen or hydrogen peroxide is often kinetically unfavoured.[7]

The use of coupled catalytic systems with electron-transfer mediators (ETMs, Scheme 1)[6d,e] usually facilitates these procedures by transporting the electrons from the catalyst to the oxidant along a low-energy pathway, thereby increasing the efficiency of the oxidation and thus complementing the direct oxidation reactions.[8]As a result of the similarities with biological systems, there are reports regarding electron-transfer mediators (ETMs) during the reoxidation of palladium and evidence for metal-catalyzed oxidation in biological systems.[9] The extensively recognized, purple-coloured iron peroxo complex $[Fe(II)EDTA\text{-}(\eta^2\text{-}O_2)]^{3-}$ has been shown to catalyze the oxidation of organic substrates[10] and the decomposition of H_2O_2.[11,12] Furthermore, it acts as a mimic for superoxide dismutase.[13]



Scheme 1. Schematic representation of the most plausible mechanism.

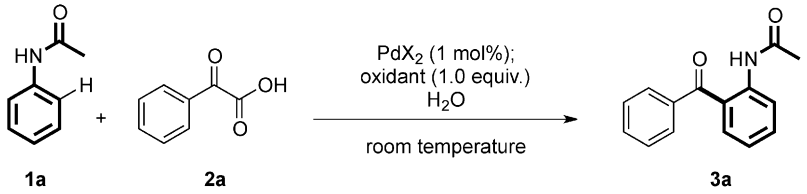
Our study commenced with the decarboxylative acylation of *N*-phenylacetamide**1a** with phenylglyoxylic acid **2** to the *N*-(2-benzoylphenyl)acetamide **3a** using Fe(III)-EDTA-H_2O_2 {or $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$} as the oxidant and $Pd(OAc)_2$ as the catalyst. Optimization of the reaction conditions demonstrated that the reaction was most productive using H_2O as solvent and 1.1 equiv. of $[FeIII(EDTA)(\eta^2\text{-}O_2)]^{3-}$ as oxidant, providing **3a** in 98% yield at room temperature within 0.5 h (entry 5, Table 1) and between a pH range of 7.2–7.8 (within the biological pH range). The exceptionally good yield anticipates the dual role of the iron peroxo complex as electron transfer-mediated oxidant and phase-transfer catalyst. Furthermore, the study showed that $Pd(TFA)_2$, $Pd(OTf)_2$ and $Pd(OAc)_2$ are efficient catalysts for this reaction at a minimum loading of 1.0 mol% while $PdCl_2$, $Pd(TPP)_2Cl_2$ and $Pd(OH)_2$ were inferior to the former three in the formation of **3a** (entries 17–19, Table 1). It was also noted that both the catalyst (1.0–2.0 mmol) and the oxidant (1.0–1.2 equiv.) were found to be stoichiometrically precise when Fe(III) complexes were used as the mediators (entries 4–6, 16–18 and 21–23, Table 1). The results obtained with $NH_4S_2O_8$, $K_2S_2O_8$ and TBHP indicated moderate oxidative properties in water due to the poor solubility of the substrates (**1a** and **2a**) in aqueous media.

In the initial trial, we were delighted that the desired product **3a** was obtained in 51% yield in the presence of the oxidant $NH_4S_2O_8$ (entry 1, Table 1) in water. A screening of oxidants showed that the best results wereobtained in the case of Fe(III) complexes {especially $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$} while $NH_4S_2O_8$, $K_2S_2O_8$, TBHP and H_2O_2 were only moderately effective in the formation of product (entries 1–4 and 12–15). The effectiveness of the oxidant was also examined and it was found that increasing the stoichiometry of $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$offered a better yield of the desired product with an optimal addition of 1.0–1.2 equiv. of catalyst $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$ which, in turn, provides the high atom economy during the reoxidation of the catalyst. Under the optimized reaction conditions [$Pd(OAc)_2$ 1–2 mol%, Fe(III)-EDTA 1.0 equiv.], a variety of substituted phenylglyoxylic acids and aryl/alkyl carboxylic acids were found to undergo efficient decarboxylative cross-coupling with cyclic enamides at room temperature to afford excellent yields of the products (Figure 1). Specifically, α-phenylglyoxylic acids with *ortho*- or *para*-substituted electron-donating or electron-withdrawing groups are all successfully engaged in this reaction (**3a**–**3i**). It is noteworthy that electronic properties do not affect the *ortho*-substituted phenylglyoxylic acids since both electron-donating and electron-withdrawing groups gave good yields (**3f–3h**). Satisfactorily, the β-naphthyloxoacetic acid also reacted smoothly to give the desired product **3i** in 97% yield. Applying 3-indoleglyoxylic acid and its 5-substituted derivatives resulted in the desired products in somewhat more moderate yields under the above conditions, however on employing 2.0 equivalents of $[Fe(III)EDTA(\eta^2\text{-}O_2)]^{3-}$ with 4 mol% of $Pd(TFA)_2$ promising yields were observed (**3j**–**3l**).

Further to expand the scope of this direct acylation reaction, we next investigated the decarboxylative couplings of phenylglyoxylic acids (**2a**), α-oxocarboxylic acids and aromatic carboxylic acids with cyclic enamides, which were sucessfully accomplished to yield **4a–4i**. As shown in Figure 2, all of the 4-chromanone-derived enamides bearing electron-donating or electron-withdrawing groups on the phenyl ring afforded the desired products in moderate to good yields (**5a–5i**).

Furthermore, α-oxocarboxylic acids were also compatible in this reaction, giving good to excellent yields in the cross-coupling reaction, e.g., 2-[methoxy-(methyl)amino]-2-oxoacetic acid also gave excellent yields of products **4c** and **4e**, for the tetralone-derived enamide only a modest amount of product (**4i**) was observed. As shown in Figure 2, a variety of substituted phenylglyoxylic acids, including both those with electron-donating and those with electron-withdraw-

Table 1. Optimization of reaction conditions.[a]



1a 2a 3a

Entry	PdX_2	Oxidant	Time [h]	Yield [%][b]
1	$Pd(OAc)_2$	$NH_4S_2O_8$	16	51
2		$K_2S_2O_8$	12	34
3		TBHP	16	21
4		H_2O_2	4	10
5		Fe(III)-EDTA-H_2O_2	0.5	98
6		Hgb-H_2O_2	0.6	85
7		Fe(III)-Cit-H_2O_2	0.6	88
8		urea-H_2O_2	14	14
9		BzOOBz	12	22
10		air	24	trace
11		oxone	15	36
12	$Pd(TFA)_2$	$NH_4S_2O_8$	16	62
13		$K_2S_2O_8$	12	45
14		TBHP	16	18
15		H_2O_2	4	trace
16		Fe(III)-EDTA-H_2O_2	0.4	<98
17		Fe(III)-Cit-H_2O_2	0.4	91
18		Hgb-H_2O_2	0.5	94
19		urea-H_2O_2	12	14
20		oxone	15	36
21	$Pd(OTf)_2$	Fe(III)-EDTA-H_2O_2	0.4	91
22		Hgb-H_2O_2	0.4	<88
23		Fe(III)-Cit-H_2O_2	0.5	84
24	$Pd(TPP)_2Cl_2$	Fe(III)-EDTA-H_2O_2	4.5	19
25		Hgb-H_2O_2	3.4	14
26	$PdCl_2$	Fe(III)-EDTA-H_2O_2	0.4	74
27		Hgb-H_2O_2	0.4	55
28	$Pd(OH)_2/C$	Fe(III)EDTA-H_2O_2	2.0	26
29		Hgb-H_2O_2	2.5	19

[a] *Reaction conditions:* **1a** (1.0 mmol), **2a** (2.0 mmol), PdX_2 (0.01 mmol), oxidant (1.0—1.2 equiv.), water (60 mmol) for 10–30 min.
[b] Isolated yields in percentage.

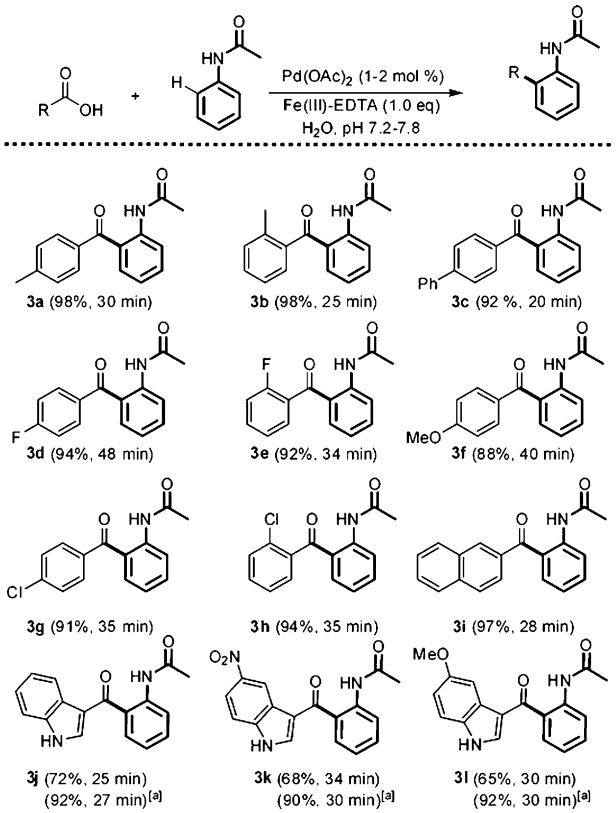
ing groups were compatible under the optimal reactionconditions. The coupling of 4-chromanone with 3-carboxyquinol-4-ones gave a good yield of **5i**. The results on the compatibility of substituted acetanilide are presented in Figure 2.

The formation of **6aa, 6ab** and **6b** under the optimized reaction condition was also well done using benzthiazole, benzoxazole, benzimidazole and *N*-acetylbenzimidazole, respectively. In the case of *N*-pivolylindole we obtained selectively the 3-substituted product (**6d**) in 87% yield whereas with *N*-acetyl- and *N*-benzoylindoles mixtures of 2- and 3-substituted products (**6e**, **6f** and **6g**, **6h**) were obtained.

In summary, we have succeeded in showing that aromatic and keto carboxylic acids that can act as the acyl sources in the oxidative coupling with the C–H bonds of different electronic systems. This efficient Pd-catalyzed *ortho*-acylation/aroylation process proceeds under mild reaction conditions. We believe this synthetic approach using $[Fe(III)(EDTA)(\eta^2\text{-}O_2)]^{3-}$ as an oxidant generated *in situ* by reacting Fe(III)EDTA with H_2O_2 at pH 7.2–7.8 will be useful for generating versatile *ortho*-acetamidodiaryls and diaryl ketones under mild and environmentally benign reaction conditions

Experimental Section

All solutions were prepared with deionized water. Unless otherwise noted, reactions were magnetically stirred and monitored by thin layer chromatography. Solutions of



[a] The reaction was carried out using $Pd(TFA)_2$ (2.0 equiv.) and $[Fe(III)EDTA(\eta^2\text{-}O_2)]_3$ (4 mol%) at room temperature in H_2O).

Figure 1. Scope of aryl keto carboxylic acids in palladium-catalyzed *ortho*-acylation of acetanilide.

$[Fe(III)(EDTA)H_2O]^-$ were prepared from solid Na[Fe(III)(EDTA)] (Fluka Acros). In all solutions, an equimolar quantity of $Na_2[H_2(EDTA)]$ (Aldrich) was present to prevent the precipitation of iron hydroxide at higher pH values.

General Procedure for the Cross-Coupling Reactions

To a solution of 33% H_2O_2 (10 mL), Fe(III)EDTA (0.1 mol) was added then followed by addition of 0.01 N NaOH (3.0 mL) which as a result forms a purple-coloured complex which was not isolated. The obtained purple-coloured solution was diluted to 100 mL to prepare the stock solution which was stored under low light and cooled atmosphere and was used as such.

To the 5 mL stock solution of purple-coloured Fe(III)EDTA solution 50 mg of **1a** (0.3 mmol) and 45 mg of **2a** (0.3 mmol) were added followed by the addition of $Pd(OAc)_2$ (0.7 mg, 1 mol%) and the mixture was vigourously stirred at room temperature for 30 min (as per TLC) (NB: during the completion of the reaction the mixture gets homogenized and the purple tinge disappears). After completion the reaction mixture was extracted with EtOAc (3× 5 mL), dried over anhydrous Na_2SO_4 and evaporated to obtain the crude product which was purified through column chromatography(silica gel 200–240 mesh) using

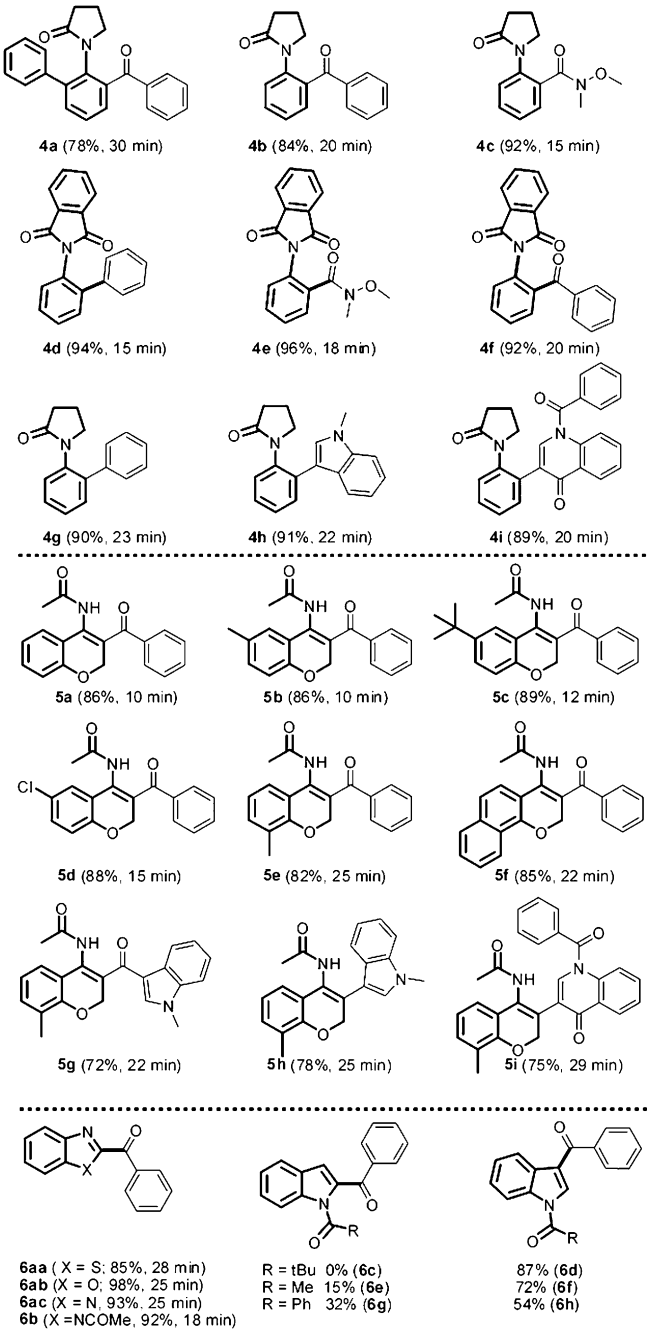


Figure 2. Results of decarboxylative cross-coupling reactions using electronically different enamides. *Reaction conditions:* carboxylic acid (1.0 mmol), **2a** (1.0 mmol), PdX_2 (0.01 mmol, 1 mol%), oxidant (as indicated, 1.0–1.2 equiv), water (60 mmol) for 10–30 min.

1%→5% ethyl acetate:hexane as eluent to obtain **3a**; yield: 70.2 mg (98%).

***N*-[2-(4-Methylbenzoyl)phenyl]acetamide (3a):** ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.67$ (d, $J = 8.1$ Hz, 1H), 7.76–7.58 (m, 5H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.12 (d, $J = 8.2$ Hz, 2H), 5.24 (Brs, 1H, NH + H_2O), 2.36 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (40 MHz, $CDCl_3$): $\delta = 201.61$, 169.12, 143.65, 143.41, 135.77, 134.95, 132.42, 130.22, 128.86, 128.49, 123.18,

122.60, 78.26, 24.56, 21.06; ESI-MS: $m/z = 254.4$ ($M+H^+$); HR-MS: $m/z = 253.1109$ [M^+], calculated for $C_{16}H_{15}NO_2$: 253.1103.

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