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Communication

# Direct oxidation of the $C_{sp3}$–H bonds of N-heterocyclic compounds to give the corresponding ketones using a reusable heterogeneous $MnO_x$-N@C catalyst

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ABSTRACT

Novel reusable $MnO_x$-N@C catalyst has been developed for the direct oxidation of N-heterocycles under solvent-free conditions using TBHP as benign oxidant to give the corresponding N-heterocyclic ketones. The catalytic system exhibited a broad substrate scope and excellent regioselectivity, as well as being amenable to gram-scale synthesis. This $MnO_x$-N@C catalyst also showed good reusability and was successfully recycled six times without any significant loss of activity.



The direct oxidation of the $C_{sp3}$–H bonds is one of the most important and effective transformations in organic chemistry for the formation of ketones, which are useful intermediates in the synthesis of pharmaceuticals, agrochemicals and natural products [1–10]. N-Heterocycles are ubiquitous in natural products and pharmaceutical compounds, which exhibit a broad range of biological and medicinally relevant activities. Furthermore, a large number of pharmaceutical compounds have been derived from N-heterocyclic ketones, such as arpromidine, pheniramine, chlorpheniramine, triprolidine and doxylamine [11]. Traditionally, N-heterocyclic ketones have been synthesized using stoichiometric quantities of hazardous oxidant, resulting in the production of large amounts of unwanted byproducts [12–14]. During the last few decades, there have been numerous improvements in the methods available for the oxidation of N-heterocycles to give the corresponding N-heterocyclic ketones using transition metal catalysts [11,15–23]. However, the coordination of N-heterocyclic compounds to transition metals can result in the deactivation of the catalyst and poor chemoselectivity, and the purification of the resulting products can be complicated by difficulties associated with the removal of the metal residues. To address these issues, several researchers have focused on the development of non-metal catalysts during the last decade to affect these oxidative transformations [24,25]. Several activators have also been developed to improve the reactivity of aliphatic methylene groups, such as ethyl chloroacetate [22] and Brønsted acids [25].

Although many strategies have been developed for the oxidation of N-heterocycles to give the corresponding N-heterocy-

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clic ketones, most catalysts reported to date for these oxidative transformations are homogeneous. These catalysts are therefore difficult to recycle and often require high reaction temperatures, which has further limited their scope and application. The development of economically and environmentally friendly alternatives to these existing procedures is therefore strongly desired. Heterogeneous catalysts are preferred to homogenous systems because they can be readily recovered and reused. In 2012, Akhlaghinia et al. [26] reported the oxidation of 2-benzylpyridine to 2-benzoylpyridine using ceria nanoparticles as a catalyst. Unfortunately, this reaction used $KBrO_3$ as an oxidant, which is highly toxic, making it harmful to human health and the environment. This catalyst system also required the use of an organic solvent, making it environmentally unfriendly. Herein, we reported the development of a novel, reusable $MnO_x$-N@C catalyst for the direct oxidative transformations of $C_{sp3}$–H bonds to ketones using TBHP as an oxidant. Notably, this $MnO_x$-N@C catalyst is inexpensive with several notably advantages over existing systems, including a low loading, good functional group tolerance, high selectivity and good reusability. Most notably, this new $MnO_x$-N@C catalyst can be used under solvent-free conditions at lower reaction temperatures (Fig. 1).

The results of our previous work showed that 2,3-cyclopentenopyridine may be oxidized to 6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one using $Mn(OTf)_2$ as a catalyst [23]. However, this particular catalyst system was difficult recycle and expensive, thereby limiting its potential for industrial applications. Furthermore, this oxidation reaction required a large excess of TBHP (5 equiv.). To address these issues, we developed a new $MnO_x$-N@C catalyst, which is highly reusable and requires a much smaller amount of TBHP (3 equiv.). We chose $Mn(NO_3)_2$ as the metal source because nitryl is a good electron-withdrawing anion, just like trifluoromethanesulfonate, and $Mn(NO_3)_2$ is commercially inexpensive. The $MnO_x$-N@C catalysts were prepared by the complexation of $Mn(NO_3)_2$ with 1,10-phenanthroline, followed by pyrolysis at a high temperature (400–900 °C) for 2 h under an atmosphere of nitrogen (Scheme 1). First, the pyrolysis characteristics of complex **A** from $Mn(NO_3)_2$ and 1,10-phenanthroline were studied under an atmosphere of nitrogen by thermogravimetric analysis (Fig. 2). The result of this analysis showed that the weight of the complex remained stable for temperatures in the range of 400–600 °C. Furthermore, the carbonization of the complex occurred in this temperature range. However, the mass of the complex rapidly decreased by 53.99% when the temperature reached 365 °C. This change was attributed to the decomposition of the complex with the loss of 1,10-phenanthroline, which

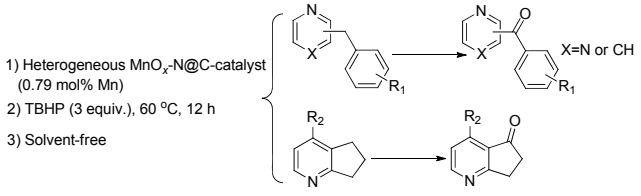
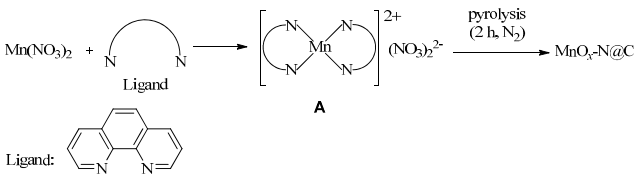



**Fig. 1.** Direct oxidation of the $C_{sp3}$–H bonds of N-heterocyclic systems using a reusable heterogeneous $MnO_x$-N@C catalyst.




**Scheme 1.** Preparation of the $MnO_x$-N@C catalysts.

would have evaporation (the boiling point of 1,10-phenanthroline is 365 °C at 1 atm). The carbide gradually decomposed at temperatures over 600 °C. Taken together, the results of this analysis revealed that 600 °C was the most appropriate temperature for the preparation of the $MnO_x$-N@C catalyst.

A 50 mL round-bottom flask (RBF) was charged with $Mn(NO_3)_2$ (2.3 g, 6.4 mmol, 50% in water), 1,10-phenanthroline (2.3 g, 12.8 mmol) and EtOH (40 mL). The flask was then sealed, and the mixture was stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and filtered through a pad of Celite. The filter cake was subsequently collected and dried at 120 °C for 2 h to give complex **A** in 93% yield.

Complex **A** (3.3 g) was subsequently pyrolyzed at 500 °C under an atmosphere of nitrogen for 2 h to give the $MnO_x$-N@C-catalyst (pyrolysis at 500 °C) in 32% yield.

Several other $MnO_x$-N@C-catalysts (pyrolyzed at 400, 600, 700, 800 and 900 °C) were also prepared according to this general oxidation procedure.

A 15-mL RBF was charged with substrate (0.5 mmol), $MnO_x$-N@C catalyst (1 mg, pyrolysis at 600 °C) and TBHP (1.5 mmol, 65% in $H_2O$). The flask was then sealed, and the mixture was heated at 60 °C for 12 h. The reaction was cooled to room temperature and diluted with ethyl acetate (4 mL), before being centrifuged at 10000 r/min for 1 min to separate the catalyst. The supernatant was removed and the catalyst was washed with ethyl acetate (5 × 4 mL). The supernatant was subsequently combined the ethyl acetate wash solutions and evaporated to dryness to give a residue, which was purified by flash column chromatography over silica gel (ethyl acetate/*n*-hexane = 1:10, v/v).

The oxidation of 2-benzylpyridine to give 2-benzoylpyridine (**2a**) was selected as a model reaction to study the catalytic activity of new $MnO_x$-N@C materials. It is noteworthy that all of

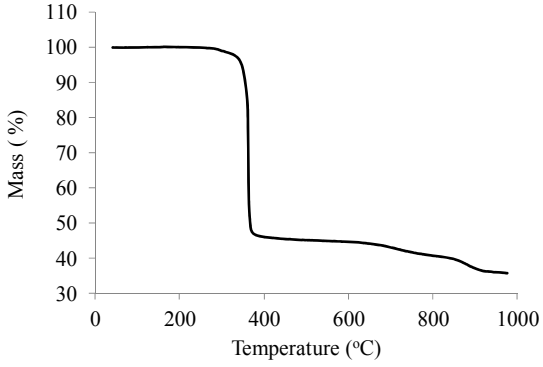
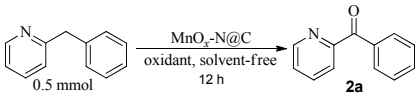



**Fig. 2.** The thermogravimetric analysis of the complex **A** from $Mn(NO_3)_2$ and 1,10-phenanthroline.

these experiments were conducted under solvent-free conditions. As expected, the $MnO_x$-N@C material (pyrolysis at 600 °C) showed the highest catalytic activity for the direct oxidation of 2-benzylpyridine, affording 2-benzoylpyridine in 82% yield (Table 1, entries 1–6). 2-Benzoylpyridine (**2a**) was obtained in 13% yield when the reaction was conducted in the absence of the catalyst (Table 1, entry 7). Furthermore, none of the desired 2-benzoylpyridine (**2a**) product was detected when $O_2$ or $H_2O_2$ was used as the oxidant (Table 1, entries 8 and 9). We also investigated different loadings of the $MnO_x$-N@C-catalyst (pyrolysis at 600 °C). The results revealed that the use of 1 mg of $MnO_x$-N@C catalyst (pyrolysis at 600 °C) gave 2-benzoylpyridine (**2a**) in 95% yield, indicating that the adsorption of 2-benzoylpyridine (**2a**) onto the $MnO_x$-N@C material may result in a lower yield (Table 1, entries 10–17). ICP experiments demonstrated that the percentage of Mn in the catalyst was 21.72%, representing a mole fraction of only 0.79 mol%. This result therefore indicated that the $MnO_x$-N@C catalyst (pyrolysis at 600 °C) has a very high catalytic activity. To the best of our knowledge, this study represents the first reported account of the use of a $MnO_x$-N@C catalyst for the efficient oxidation of an organic substrate under mild conditions. The reaction temperature and different amounts of TBHP were also studied (Table 1, entries 18–23), and the results revealed that the optimum reaction temperature and amount of TBHP were 60 °C and 3 equiv., respectively, producing 2-benzoylpyridine (**2a**) in 91% yield (Table 1, entry 21). Several attempts were made to reduce the reaction time, but resulted in much lower yield (Table 1, entry 24).

**Table 1**
The oxidation of the $C_{sp3}$–H bonds of 2-benzylpyridine under various conditions.




| Entry | Pyrolysis (°C) | Dosage (mg) | Oxidant | Temperature (°C) | Yield [a] (%) |
|---|---|---|---|---|---|
| 1 | 400 | 25 | TBHP, 5 equiv. | 80 | 36 |
| 2 | 500 | 25 | TBHP, 5 equiv. | 80 | 68 |
| 3 | 600 | 25 | TBHP, 5 equiv. | 80 | 82 |
| 4 | 700 | 25 | TBHP, 5 equiv. | 80 | 81 |
| 5 | 800 | 25 | TBHP, 5 equiv. | 80 | 72 |
| 6 | 900 | 25 | TBHP, 5 equiv. | 80 | 76 |
| 7 | — | — | TBHP, 5 equiv. | 80 | 13 |
| 8 | 600 | 25 | $O_2$, 3 atm | 80 | Nr |
| 9 | 600 | 25 | $H_2O_2$, 5 equiv. | 80 | Nr |
| 10 | 600 | 35 | TBHP, 5 equiv. | 80 | 80 |
| 11 | 600 | 30 | TBHP, 5 equiv. | 80 | 81 |
| 12 | 600 | 20 | TBHP, 5 equiv. | 80 | 82 |
| 13 | 600 | 15 | TBHP, 5 equiv. | 80 | 82 |
| 14 | 600 | 10 | TBHP, 5 equiv. | 80 | 85 |
| 15 | 600 | 5 | TBHP, 5 equiv. | 80 | 86 |
| 16 | 600 | 3 | TBHP, 5 equiv. | 80 | 95 |
| 17 | 600 | 1 | TBHP, 5 equiv. | 80 | 95 |
| 18 | 600 | 1 | TBHP, 3 equiv. | 80 | 93 |
| 19 | 600 | 1 | TBHP, 2 equiv. | 80 | 89 |
| 20 | 600 | 1 | TBHP, 3 equiv. | 70 | 90 |
| 21 | 600 | 1 | TBHP, 3 equiv. | 60 | 91 |
| 22 | 600 | 1 | TBHP, 3 equiv. | 50 | 84 |
| 23 | 600 | 1 | TBHP, 3 equiv. | 40 | 59 |
| 24 [b] | 600 | 1 | TBHP, 3 equiv. | 60 | 77 |

[a] GC yield with biphenyl as the internal standard.
[b] Reaction time: 6 h.

The $MnO_x$-N@C material (pyrolysis at 600 °C) was initially characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The TEM images revealed that the $MnO_x$ particles were about 1.71–6.56 nm in size (Fig. 3(a) and (b)). The peaks in the N 1*s* spectrum at 398.3 and 399.7 eV were assigned to the N atoms in C–N and C=N bonds, respectively. The electron binding energy observed at 400.8 eV is characteristic of pyrrole-type nitrogen atoms, which can be formed following the carbonization of nitrogen-containing or-

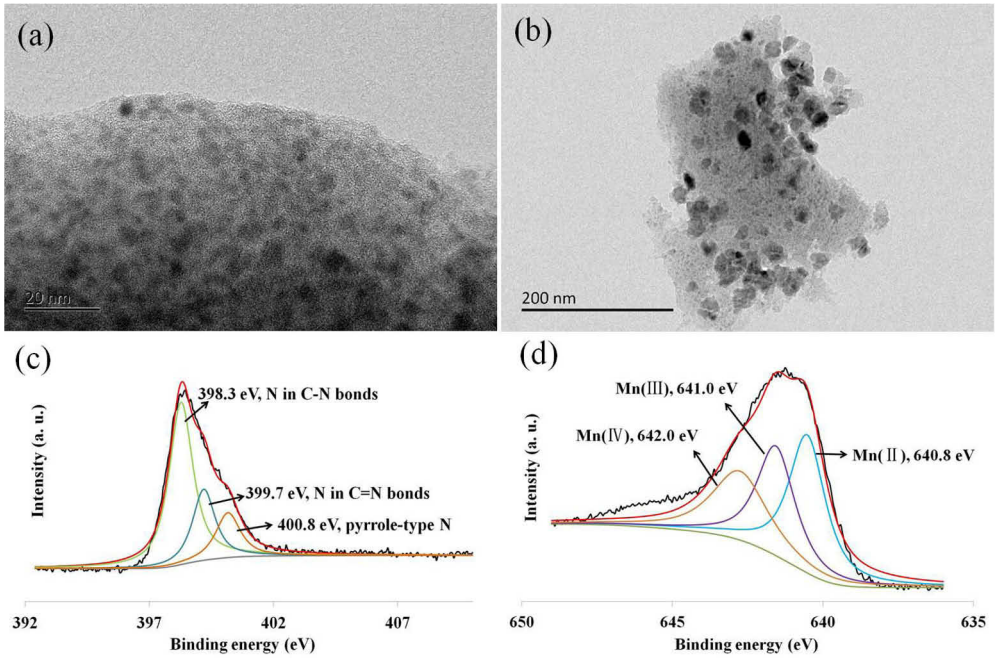
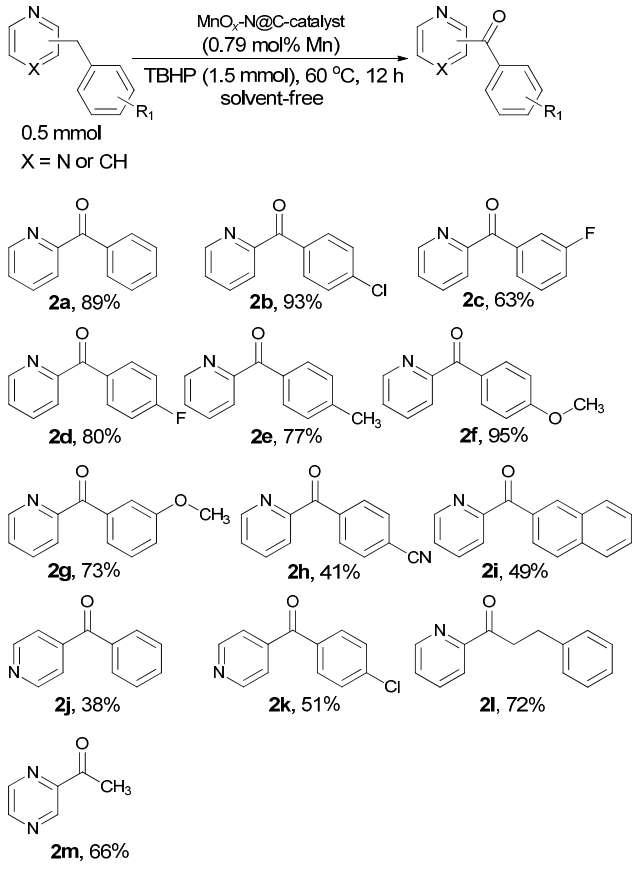


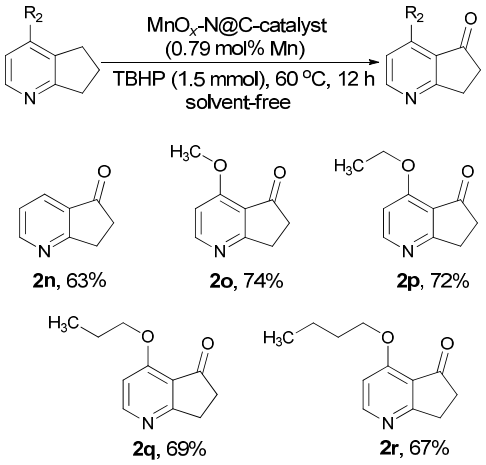

**Fig. 3.** TEM images (a, b) of the $MnO_x$-N@C catalyst (pyrolysis at 600 °C); N 1*s* (c) and Mn $2p_{3/2}$ (d) of the $MnO_x$-N@C catalyst (pyrolysis at 600 °C).




**Scheme 2.** $MnO_x$-N@C-catalyzed oxidation of substituted 2-benzylpyridines, 4-benzylpyridines and 2-ethylpyrazine. The isolated yields of **2a**–**2l** were obtained after column chromatography. The yield of **2m** was determined by $^1H$ NMR spectroscopy.

ganic materials (Fig. 3(c)) [27,28]. Based on the literature, the peaks in the Mn $2p_{3/2}$ spectrum at 640.8, 641.0 and 642.0 eV were assigned to Mn(II), Mn(III) and Mn(IV), respectively (Fig. 3(d)) [29,30].

Given that the $MnO_x$-N@C catalyst (pyrolysis at 600 °C) displayed the best activity for the direct oxidation of 2-benzylpyridine to 2-benzoylpyridine (**2a**), we evaluated the scope of this catalyst using a broad range of substrates. As shown in Scheme 2, a series of structurally diverse 2- and 4-benzylpyridines reacted smoothly in the presence of this catalyst system to give good to excellent yields of the corresponding ketones. As well as 2-benzylpyridine substrates bearing electron-donating groups, which improved the reactivity of the C–H bonds of these substituted systems (Scheme 2, **2e**–**2g**), we also investigated substrates bearing electron-withdrawing groups (e.g., halide and cyano groups, Scheme 2, **2b**–**2d**, **2h**). Substrates containing two chemically different benzylic positions were also tested, and reacted in a regioselective manner to give the corresponding ketones **2e** and **2l** as single products in good yields (Scheme 2). The selectivity of the $MnO_x$-N@C-catalyst (pyrolysis at 600 °C) was attributed to the nitrogen atom adjacent to the benzylic moiety directing the oxidation to this position by coordinating to the metal. The poorer reactivity of the 4-benzylpyridine substrates compared with the 2-benzylpyridine systems is also consistent




**Scheme 3.** $MnO_x$-N@C-catalyzed oxidation of 2,3-cyclopentenopyridine analogues. Isolated yield after column chromatography.

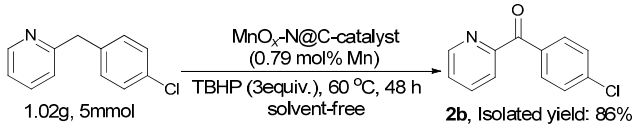
with this directing effect (Scheme 2, **2j**, **2k**). 2-Ethylpyrazine was also evaluated as a substrate and gave 2-acetylpyrazine (**2m**) obtained in good yield (Scheme 2). To the best of our knowledge, this work represents the first reported example of the direct oxidation of 2-ethylpyrazine to give 2-acetylpyrazine (**2m**) in good yield. For example, Wolt [31] only reported 1% yield for the same reaction, highlighting the effectiveness of our new catalyst.

6,7-Dihydro-5H-cyclopenta[b]pyridin-5-one (**2n**) is a very important and expensive intermediate in the synthesis of antipsychotics. With this in mind, we evaluated the direct oxidation of various 2,3-cyclopentenopyridine analogues using this new catalyst system. Pleasingly, we obtained the corresponding ketones in good yields (Scheme 3, **2n**–**2r**), thereby highlighting the economic potential of our new catalyst system.

To highlight the synthetic utility of our catalyst system, we conducted a gram-scale reaction using 2-(4-chlorobenzyl)pyridine as a test substrate. The desired ketone product **2b** was obtained in 86% isolated yield within 48 h (Scheme 4). This result therefore confirmed that our newly developed $MnO_x$-N@C catalyst (pyrolysis at 600 °C) is a highly active catalyst for the preparation of 2-(4-chlorobenzoyl)pyridine (**2b**) under solvent-free conditions.

Six consecutive oxidation experiments were conducted on one gram scale using 2-(4-chlorobenzyl)pyridine as a substrate to demonstrate the stability and reusability of the $MnO_x$-N@C catalyst (pyrolysis at 600 °C). Notably, this catalyst was successfully recycled up to six times without any significant loss of activity (Fig. 4).

Based on our previous studies [23,25] and pertinent literature [32], a possible mechanism was proposed (Scheme 5).




**Scheme 4.** Gram-scale reaction with the $MnO_x$-N@C-catalyst (pyrolysis at 600 °C).

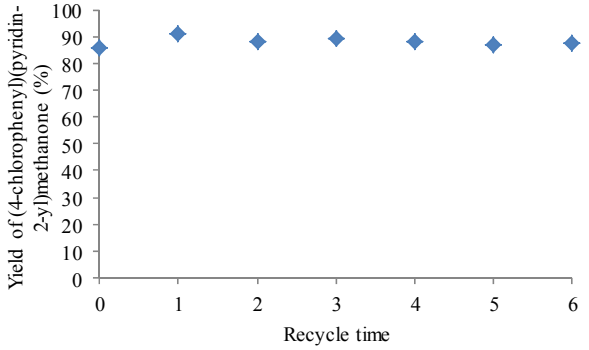
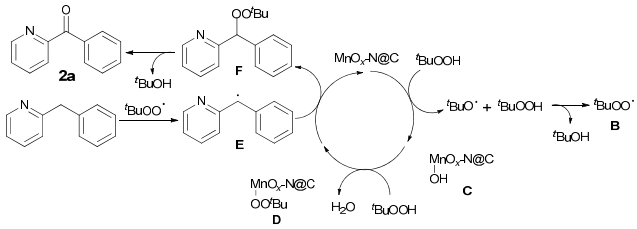



**Fig. 4.** Recycling of the $MnO_x$-N@C catalyst (pyrolysis at 600 °C) for oxidation experiments of 2-(4-chlorobenzyl)pyridine. Reaction conditions: 2-(4-chlorobenzyl)pyridine (5 mmol), TBHP (15 mmol) and catalyst (10 mg, 0.79 mol % Mn) at 60 °C for 48 h. Isolated yield after column chromatography.

First, the decomposition of *t*-BuOOH would produce *t*-BuO· and ·OH radicals, which would react with the $MnO_x$-N@C catalyst to give HO-$MnO_x$-N@C (species **C**). Species **C** would subsequently react with *t*-BuOOH to give the corresponding peroxy-complex **D**. The *t*-BuO· radical generated by the decomposition of *t*-BuOOH would capture a H· radical from *t*-BuOOH to give radical **B**, which would selectively abstract a hydrogen atom from the H-heterocyclic substrate to produce radical **E**. Peroxy-complex **D** would then react with radical **E** to give intermediate **F**, which would decompose to give compound **2a**. The XPS results revealed that the $MnO_x$-N@C catalyst contained Mn in multiple valence states. With this in mind, we concluded that Mn(II) transferred a *t*-BuOO· radical to the carbon-centered radical **E** via manganese peroxide **D**.

In summary, we have reported for the first time the development of a stable, inexpensive and reusable $MnO_x$-N@C catalyst for the direct oxidation of N-heterocycles under solvent-free conditions using TBHP as benign oxidant to give the corresponding N-heterocyclic ketones. This $MnO_x$-N@C catalyst exhibited a wide substrate scope and excellent regioselectivity, as well as being amenable to gram-scale synthesis.




**Scheme 5.** Proposed mechanism for this oxidation reaction.

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## Graphical Abstract

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**Direct oxidation of the $C_{sp3}$–H bonds of N-heterocyclic compounds to give the corresponding ketones using a reusable heterogeneous $MnO_x$-N@C catalyst**

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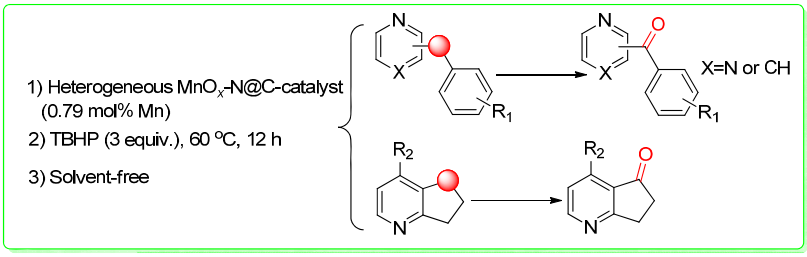


A novel reusable $MnO_x$-N@C catalyst has been developed for the direct oxidation of N-heterocycles under solvent-free conditions using TBHP as a benign oxidant to give the corresponding N-heterocyclic ketones. This catalytic system exhibited broad substrate scope and excellent regioselectivity, as well as being amenable gram-scale synthesis. Notably, this $MnO_x$-N@C catalyst was successfully recycled six times without any significant loss of activity.

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