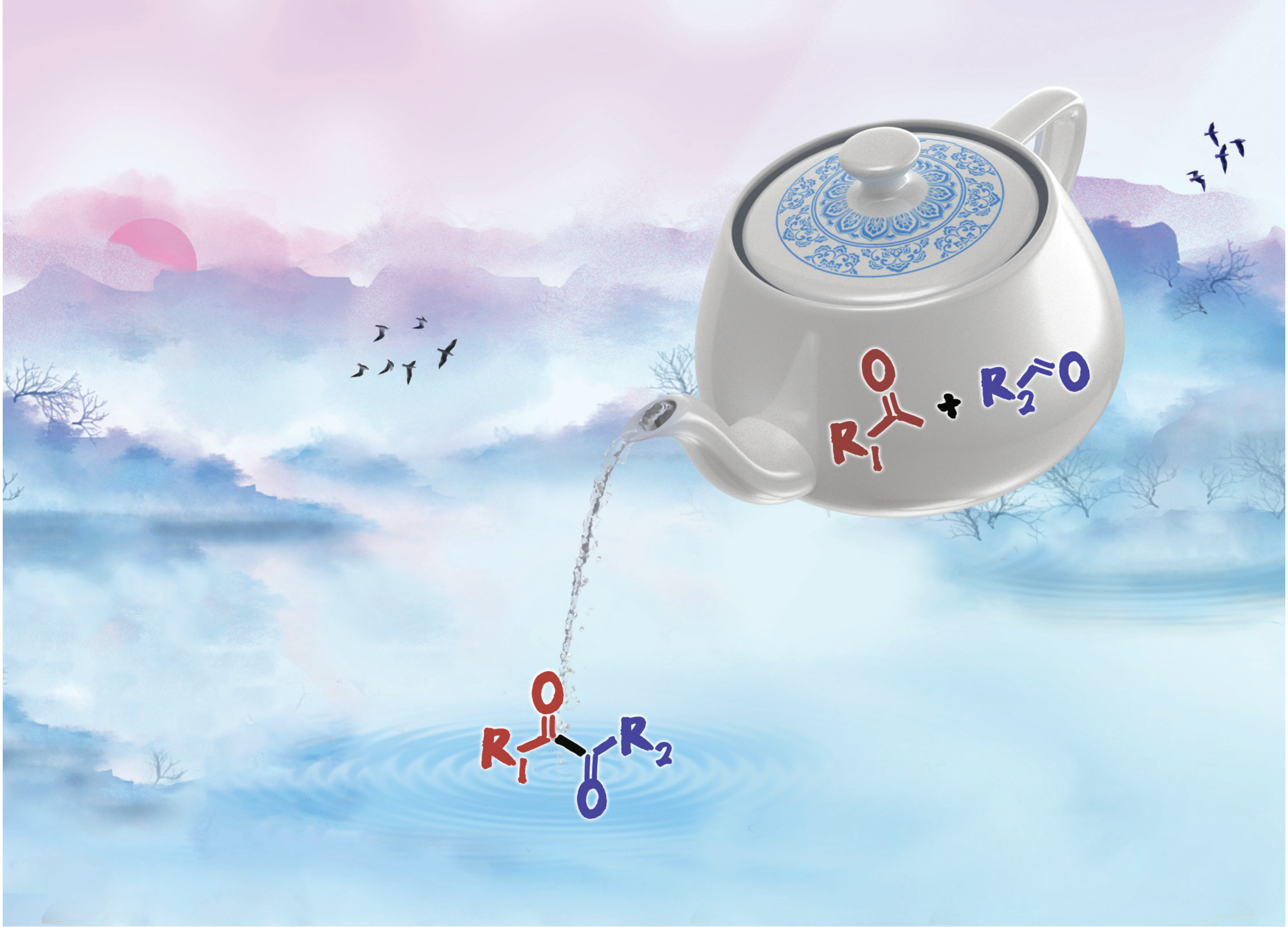

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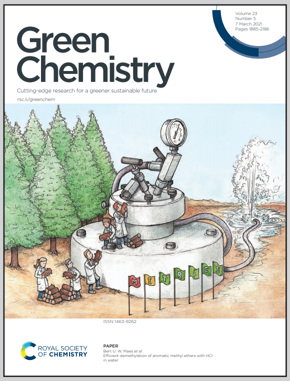

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Cite this: *Green Chem.*, 2021, **23**, 1955

Received 4th November 2020,
Accepted 14th January 2021

DOI: 10.1039/d0gc03739g

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One-pot cascade synthesis of α-diketones from aldehydes and ketones in water by using a bifunctional iron nanocomposite catalyst†

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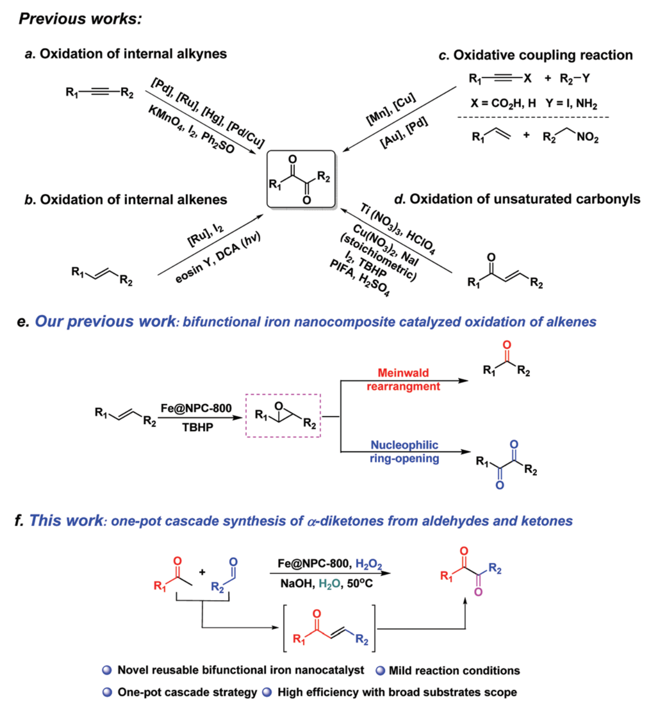
A new methodology for the synthesis of α-diketones was reported *via* a one-pot cascade process from aldehydes and ketones catalyzed by a bifunctional iron nanocomposite using H_2O_2 as a green oxidant in water. The one-pot strategy showed excellent catalytic stability, comprehensive suitability of substrates and important practical utility for directly synthesizing biologically active and medicinally valuable N-heterocycles *via* an intermittent process.

α-Diketones are vital skeletons in natural products.[1] As significant precursors, they are applied to synthesize anticonvulsant and antimicrobial drugs,[2] and other heterocyclic compounds such as quinoxaline, imidazole, and thiophene.[3] Moreover, they are also used as photoinitiators and corrosion inhibitors.[4] In view of their crucial usefulness, various methods have been developed for the preparation of α-diketones. Traditional methods, including the substitution of oxalyl chloride or α-keto acid chloride[5] and oxidation of α-halo, α-hydroxy ketones or their derivatives,[6] always need sophisticated and expensive substrates and harsh reaction conditions. Recently, the introduction of two oxygen atoms across unsaturated C–C bonds represents the most straightforward and high atom-economical approach for the synthesis of α-diketones. In this context, the oxidation strategies starting from various substrates have been reported, including the (i) oxidation of internal alkynes (Scheme 1a);[7] (ii) oxidation of internal alkenes (Scheme 1b);[8] (iii) oxidative coupling of terminal alkynes, alkynic acid or alkenes with aryl halide or other coupling partners (Scheme 1c);[9] and (iv) oxidation of α,β-unsaturated carbonyls (Scheme 1d).[10] Although these methods have been attractive in the synthesis aspect, they always employ high-cost, toxic and nonrecyclable noble metal catalysts such as Pd,[7a,b] Ru,[7c,d,8b,c] and Au,[7f,9c] stoichiometric Cu salts,[10a] virulent mercuric salts,[7e] or hazardous oxidants such as $KMnO_4$,[7h] I_2,[8c,d] Ph_2SO,[9c] $HClO_4$[10b] and PIFA.[10d,e] Even worse, these processes generally suffer from poor chemoselectivity and low tolerance of functional groups. Thus, it is greatly desirable to develop a facile, efficient, and highly selective approach to prepare α-diketones, ideally, using an inexpensive and robust heterogeneous catalyst with high activity, excellent selectivity, and broad substrate scope.

Very recently, we have developed a bifunctional iron nanocomposite catalyst containing two key iron species of $Fe–N_x$ and Fe phosphate as the oxidation and Lewis acid sites, which



Scheme 1 Strategies for the synthesis of α-diketones *via* the oxidation of unsaturated C–C bonds.

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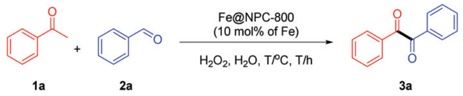
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0gc03739g

exhibited excellent reactivity and good tolerance of functional groups for oxidative cleavage of alkenes into ketones or their oxidation into α-diketones using TBHP as the oxidant in water under mild conditions (Scheme 1e).[11] Mechanistic studies reveal that one-carbon shorter ketones were produced *via* the formation of an epoxide as the key intermediate from the epoxidation of internal alkenes followed by subsequent Lewis acid-catalyzed Meinwald rearrangement. As such, we envision that the C=C double bond in α,β-unsaturated ketones could be oxidized into α-diketones *via* the formation of their corresponding epoxide catalyzed by the bifunctional iron nanocomposite under appropriate reaction conditions. It is well known that ketones and aldehydes could be converted into α,β-unsaturated ketones *via* aldol or the Claisen–Schmidt condensation in the presence of a base or an acid.[12] In our continuous contributions towards developing green and sustainable catalysts for organic transformations,[13] we herein expand the application of this bifunctional iron nanocomposite catalyst for the synthesis of α-diketones, and found that α-diketones could be efficiently synthesized *via* a one-pot cascade process from easily available aldehydes and ketones catalyzed by the bifunctional iron nanocomposite using H_2O_2 as the oxidant and water as a green solvent under mild conditions (Scheme 1f). A broad substrate scope of aldehydes and ketones with good functional group tolerance was converted into α-diketones in up to 90% yield. In addition, the iron nanocomposite can be easily recovered for successive use without obvious change in activity. To the best of our knowledge, this is the first example of an expedient and efficient synthesis of α-diketones from simple aldehydes and ketones in a cost-effective and sustainable manner.

Table 1 Optimization of reaction conditions[a]



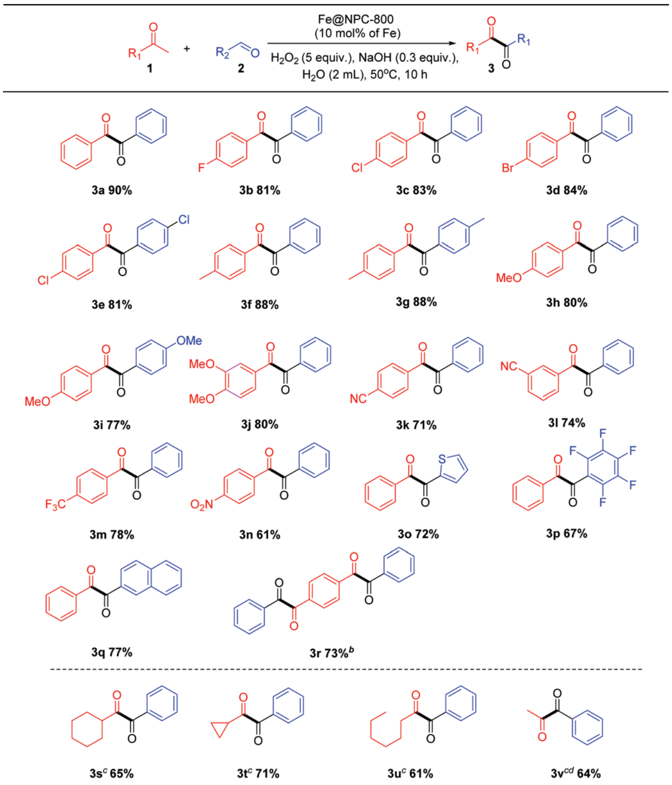
Entry	Additive	T/°C	t/h	Conv.(%)[b]	Yield[b] (%)
1	NaOH (0.5 equiv.)	110	12	100	98
2	NaOH (0.3 equiv.)	110	12	100	97
3	NaOH (0.1 equiv.)	110	12	84	51
4	NaOH (0.3 equiv.)	90	12	100	97
5	NaOH (0.3 equiv.)	70	12	100	97
6	NaOH (0.3 equiv.)	50	12	100	96
7	NaOH (0.3 equiv.)	RT	12	80	34
8	NaOH (0.3 equiv.)	50	10	100	96 (90)[c]
9	NaOH (0.3 equiv.)	50	8	100	89
10[d]	NaOH (0.3 equiv.)	50	10	100	57
11	$NaHCO_3$ (0.3 equiv.)	50	10	84	60
12	K_3PO_4 (0.3 equiv.)	50	10	67	47
13	TEA (0.3 equiv.)	50	10	81	15
14[e]	NaOH (0.3 equiv.)	50	10	97	0
15	—	50	10	10	1
16[f]	NaOH (0.3 equiv.)	50	10	98	3
17	NPC-800	50	10	90	0
18	Fe_2O_3	50	10	81	5
19	Fe_3O_4	50	10	83	3
20	$FeCl_3·6H_2O$	50	10	91	8

[a] Reaction conditions: acetophenone (0.2 mmol), benzaldehyde (0.22 mmol), Fe@NPC-800 (10 mol% of Fe), H_2O_2 30 wt% in water (5 equiv.), and H_2O (2 mL). [b] Determined by GC. [c] Isolated yields. [d] 3 eq. of H_2O_2. [e] Without Fe@NPC-800. [f] O_2 atmosphere.

The preparation and characterization of bifunctional iron nanocomposite catalyst have been reported in our previous study.[11] The catalyst Fe@NPC-800 (where NPC represents N,P co-doped carbon material and 800 represents the pyrolysis temperature at 800 °C) has two catalytically active sites of Fe–N_x and Fe phosphate as the oxidation and Lewis acid sites, which were simultaneously integrated into a hierarchical N,P-dual-doped porous carbon and showed the best catalytic performance for the oxidation of the internal alkenes. In this study, we continued to use Fe@NPC-800 as the catalyst to test the feasibility. We initiated our investigation by choosing the synthesis of benzil from benzaldehyde and acetophenone as a model reaction in the presence of 10 mol% of Fe@NPC-800, 0.5 equiv. NaOH, and 5 equiv. H_2O_2 at 110 °C in water (Table 1, entry 1). To our surprise, benzil was obtained with 100% conversion of acetophenone and 98% selectivity after 12 h. With this satisfactory result in hand, a set of parameters, including reaction temperatures, reaction times, the type and addition amount of bases, and the used amount of H_2O_2, was subsequently screened to achieve much milder conditions. Decreasing the addition amount of NaOH from 0.5 to 0.3 equiv. had a negligible impact on reactivity (Table 1, entry 2); however, lower conversion of acetophenone and poorer selectivity to benzil were achieved with 0.1 equiv. of NaOH (Table 1, entry 3). Lowering the reaction temperature to 50 °C led to the excellent maintenance of the outstanding activity and selectivity (Table 1, entry 6). The reaction did take place at room temperature, while a considerably lower activity and selectivity were obtained (Table 1, entry 7). We next conducted the reaction at 50 °C with shorter reaction times and found that 100% conversion of acetophenone with 90% isolated yield to benzil was afforded after 10 h (Table 1, entry 8), while the yields decreased slightly after further shortening the reaction time to 8 h (Table 1, entry 9). Other types of bases such as $NaHCO_3$, K_3PO_4, and triethylamine (TEA) were also investigated under otherwise identical conditions, giving relatively lower reactivity and selectivity to benzil (Table 1, entries 11–13). In addition, control experiments in the absence of either catalyst, or base, or in the presence of molecular oxygen as the oxidant, either gave low reactivity or condensation to α,β-unsaturated ketone as the major product (Table 1, entries 14–16), indicating the indispensability of the catalyst and base for the success of the cascade reaction. Control experiments employing NPC-800 without the introduction of iron or commercially available Fe_2O_3, Fe_3O_4, NPC-800, and $FeCl_3·6H_2O$ as catalysts show inferior reactivity for the generation of 1,2-diketone (Table 1, entries 17–20).

Having identified the optimal conditions, we further explored the generality of this protocol for the synthesis of α-diketone compounds. A series of aldehydes and ketones was tested, as shown in Table 2. Halogen-substituted aromatic ketones (**1b–1e**) and aldehyde (**2e**) could be converted into the corresponding α-diketones (**3b–3e**) in more than 80% yields. The aromatic ketones bearing either electron-donating groups (–Me, –OMe) or electron-withdrawing groups (–CN, –NO_2, CF_3)

Table 2 Substrate scope of one-pot cascade synthesis of α-diketones[a]



[a] Reaction conditions: ketone (0.2 mmol), aldehyde (0.22 mmol), Fe@NPC-800 (10 mol% of Fe), H_2O_2 30 wt% in water (5 equiv.), H_2O (2 mL), and 10 h. Yields of isolated product are reported. [b] Benzaldehyde 0.44 mmol, Fe@NPC-800 (20 mol% of Fe), H_2O_2 30 wt% in water (10 equiv.), H_2O (2 mL), and 10 h. [c] 0.5 equiv. of NaOH, 90 °C, and 12 h. [d] 0.5 mL of acetone was used.

were smoothly transformed into α-diketones in 61–88% yields, while the corresponding products were obtained in relatively higher yields with electron-donating group-substituted substrates (**3f–3j**) than with the electron-withdrawing ones (**3k–3n**). Thiophene-2-carbaldehyde (**2o**) and 2-naphthaldehyde (**2q**) were suitable for the construction of the α-diketone framework in 72% and 77% yields, respectively. 2,3,4,5,6-Pentafluorobenzaldehyde (**2p**) also worked well to produce 1-(perfluorophenyl)-2-phenylethane-1,2-dione (**3p**) in 67% yield. 2,2′-(1,4-Phenylene)bis(1-phenylethane-1,2-dione) (**3r**) could be obtained from 1,4-diacetylbenzene (**1r**) containing two reaction sites in 73% yield using a twofold amount of benzaldehyde, catalyst, base and oxidant with the same reaction time. Moreover, the aliphatic ketones such as 1-cyclohexylethan-1-one (**1s**), 1-cyclopropylethan-1-one (**1t**), heptan-2-one (**1u**), and acetone (**1v**) were also converted into the corresponding α-diketones in 61–71% yields under slightly modified reaction conditions.

Subsequently, we investigated the recyclability of the Fe@NPC-800 catalyst for the benchmark reaction under the optimized conditions. The catalyst has been used six times consecutively with negligible changes in reactivity and selectivity, indicating its durable stability (Fig. 1).

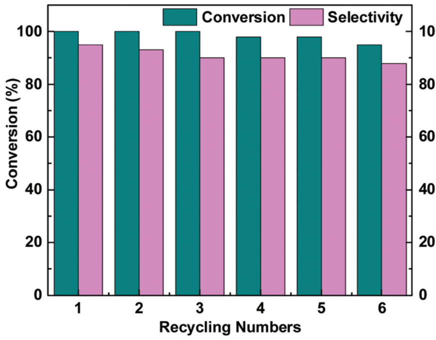
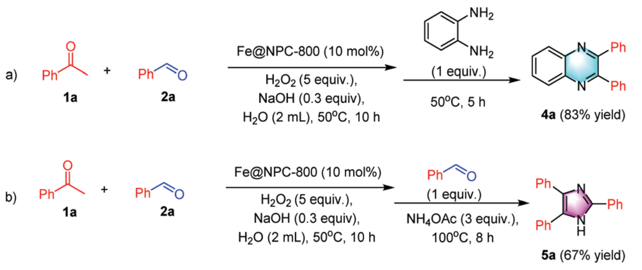


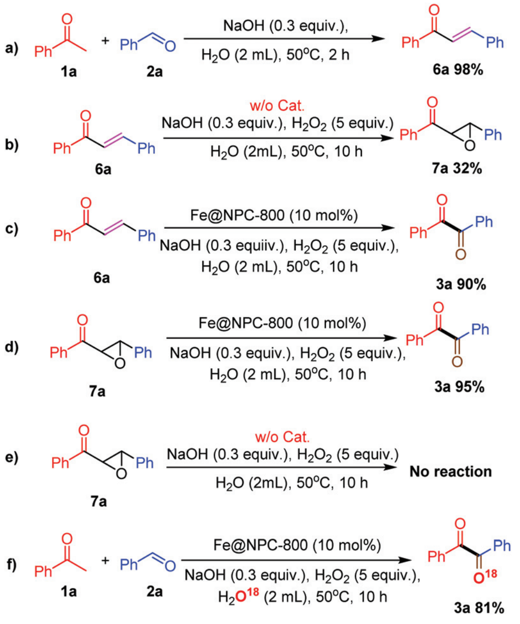
Fig. 1 Recycling performance of the Fe@NPC-800 catalyst.

α-Diketones as essential building blocks have been widely applied in the synthesis of biologically active N-heterocycles.[3] Therefore, to demonstrate the practical applicability of this one-pot cascade protocol, we attempted to directly synthesize quinoxaline and imidazole *via* an intermittent process without the separation and purification of intermediates (Scheme 2). After the formation of benzil under the optimized conditions was completed, benzene-1,2-diamine or benzyl aldehyde/NH_4OAc was directly added into the reaction mixture for sequential condensation cyclization. To our delight, 2,3-diphenylquinoxaline (**4a**) and 2,4,5-triphenyl-1*H*-imidazole (**5a**) were isolated in 83 and 67% yields, respectively. This provides an alternative and attractive synthetic method for the preparation of quinoxaline, imidazole or other important bioactive N-heterocyclic compounds, further highlighting the superiority of this novel bifunctional Fe nanocomposite and practical utility of this one-pot cascade strategy.

To gain an insight into the reaction pathway, a set of control experiments was carried out. In the absence of the Fe@NPC-800 catalyst, chalcone (**6a**) was obtained in 98% GC yield for the reaction of benzaldehyde and acetophenone with the assistance of 0.3 equiv. NaOH in H_2O at 50 °C within 2 h (Scheme 3, eqn. (a)). When **6a** was used as the starting material for the reaction in the absence of the Fe@PNC-800 catalyst under otherwise identical conditions, phenyl(3-phenyloxiran-2-yl)methanone (**7a**) was detected in 32% GC yield (Scheme 3, eqn (b)), which could be achieved *via* the nucleophilic attack of H_2O_2 on the C= bond mediated by the base.[15] In contrast, chalcone (**6a**) was smoothly converted into benzil in 90% yield



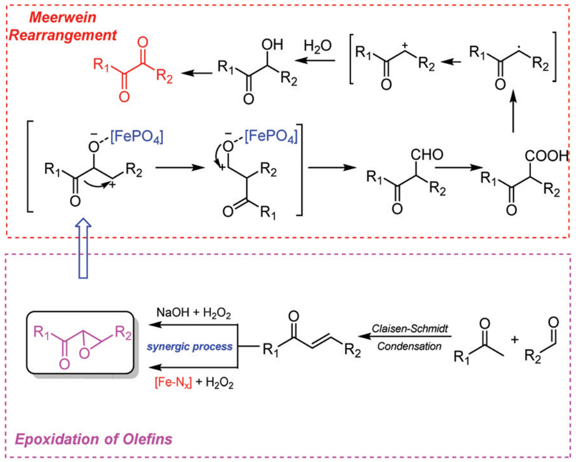
Scheme 2 Intermittent reaction for the synthesis of quinoxaline and imidazole.



Scheme 3 Control experiments for the one-pot synthesis of α-diketones.

under the optimized conditions (Scheme 3, eqn (c)), indicating the key role of the Fe@NPC-800 catalyst. According to our previous report,[11] phenyl(3-phenyloxiran-2-yl)methanone (**7a**) generated by the epoxidation of chalcone could be the key intermediate for benzil. Thus, phenyl(3-phenyloxiran-2-yl)methanone (**7a**) was subjected to the optimized conditions (Scheme 3, eqn (d)), and benzil was obtained in 95% GC yields in this case. However, phenyl(3-phenyloxiran-2-yl)methanone (**7a**) was kept intact in the absence of the Fe@PNC-800 catalyst under otherwise identical conditions (Scheme 3, eqn (e)), further verifying that the ring-opening of epoxide was catalyzed by Fe@NPC-800 rather than by NaOH. The O^{18}-labeling experiment was conducted using H_2O^{18} as the solvent, and a mono-O^{18}-incorporated product 1,2-diketones-O^{18} was obtained in 81% yield, suggesting that one of the oxygen atoms in 1,2-diketones originates from water (Scheme 3, eqn (f)).

Taking all control experiments into account, we proposed a plausible mechanism for the one-pot cascade synthesis of α-diketones as presented in Scheme 4. Initially, α,β-unsaturated ketones were formed by the condensation of ketones and aldehydes in the presence of a base. Subsequently, the generated unsaturated carbonyls were oxidized to an epoxide intermediate *via* the synergic processes of Fe–N_x site-catalyzed epoxidation[11,14] and the nucleophilic attack of H_2O_2 mediated by the base.[15] The epoxide intermediate could be converted into an α-carbonyl aldehyde in the presence of $FePO_4$ as a Lewis acid site *via* the Meinwald rearrangement.[11,16] Subsequently, α-carbonyl carboxylic acid was readily formed from the oxidation of α-carbonyl aldehyde under the standard reaction conditions, which underwent oxidative decarboxylation followed by the cascade oxidation process to obtain the α-diketones.



Scheme 4 Proposed mechanism for the one-pot synthesis of α-diketones.

Conclusions

In conclusion, we developed a new synthetic method for the synthesis of α-diketones from ketones and aldehydes catalysed by a bifunctional iron nanocomposite. A broad range of aldehydes and ketones could be efficiently converted into their corresponding α-diketones with good tolerance of functional groups using H_2O_2 as a green oxidant in water under mild conditions. In addition, the one-pot strategy was also applicable to the synthesis of quinoxaline and imidazole skeletons *via* an intermittent process. The catalyst could be readily recovered for successive recycling without an obvious decay of catalytic performance. This study not only represents a simple, efficient and environmentally friendly method for the synthesis of 1,2-diketones from simple aldehydes and ketones but also demonstrates an excellent example of the design and application of bifunctional catalysts for significant organic transformations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 22002178, 22078350), the Natural Science Foundation and Key Technology R&D Program of Shandong Province (ZR2020KB016, 2019GGX102075). Y. Y. also acknowledges the Royal Society (UK) for a Newton Advanced Fellowship (NAF/R2/180695), Open Projects of State Key Laboratory of Physical Chemistry of the Solid State Surface (Xiamen University) (No. 201808).

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