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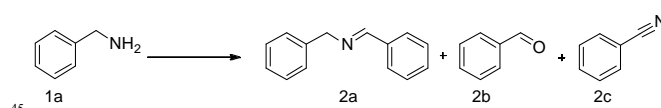
ARTICLE TYPE

Tert-Butyl Hydroperoxide (TBHP)-Mediated Oxidative Self-Coupling of Amines to Imines over α -MnO₂ CatalystZhe Zhang,^{a,b} Feng Wang,^{a,*} Min Wang,^a Shutao Xu,^a Haijun Chen,^{a,b} Chaofeng Zhang,^{a,b} Jie Xu^{a,*}

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We here demonstrate a simple, efficient and eco-friendly protocol for the direct synthesis of imines from amines via a facile α -MnO₂ catalyzed-procedure at rt. Up to 13 benzylic, heterocyclic, and normal aliphatic imines were synthesized with the 95-99% selectivity at the 82-99% conversion.

Table 1. Oxidative transformation of **1a** to **2a**.^[a]

Entry	Catalyst	Solvent	Conv. [%] ^[b]	Select. [%] ^[b]		
				2a	2b	2c
1 ^[c]	α -MnO ₂	MeCN	>99	74	1	25
2 ^[d]	α -MnO ₂	MeCN	0	-	-	-
3	α -MnO ₂	MeCN	>99	95	3	2
4 ^[e]	-	MeCN	28	90	2	8
5 ^[f]	α -MnO ₂	MeCN	0	-	-	-
6 ^[g]	α -MnO ₂	MeCN	98	98	1	1
7	α -MnO ₂	THF	90	98	1	1
8	α -MnO ₂	CH ₂ Cl ₂	70	94	3	3
9	α -MnO ₂	PhCl	52	94	2	4
10	α -MnO ₂	DMF	50	89	4	7
11 ^[h]	α -MnO ₂	DMF	59	90	2	8
12 ^[i]	α -MnO ₂	H ₂ O	>99	70	11	19
13	OMS-2	MeCN	>99	71	9	20
14	β -MnO ₂	MeCN	36	98	1	1
15	δ -MnO ₂	MeCN	73	97	2	1
16	Mn ₂ O ₃	MeCN	47	95	2	3
17	Mn ₃ O ₄	MeCN	27	93	3	4
18	Fe ₂ O ₃	MeCN	25	90	3	7
19	V ₂ O ₅	MeCN	30	90	3	7
20	CuO	MeCN	41	95	2	3
21	Co ₃ O ₄	MeCN	20	90	3	7
22	MoO ₃	MeCN	31	89	4	7

[a] Reaction conditions: catalyst (0.05 mol), **1a** (0.5 mmol), TBHP (1.0 mmol), solvent (2 mL), 17-25 °C, open air, 4 h. [b] As determined by GC-MS using dodecane as an internal standard. [c] Under 0.3 MPa O₂ and 100 °C. [d] With 1 mmol H₂O₂. [e] Without catalyst. [f] In open air without TBHP. [g] In Ar gas. [h] 12 h. [i] 1 h.

Imine is a significant class of compounds due to their versatile applications as synthetic intermediates.^[1] Among the existing methods for imine syntheses, the oxidative self-coupling of amines to imines has attracted more attentions. Relatively high yields have been achieved using homogeneous catalysts, such as Cu/TEMPO,^[2] Cu/ABNO,^[3] and TBHPQ^[4], and heterogeneous catalysts, such as precious metal catalysts (Pt^[5], Ru^[6], Pd,^[7] Au,^[8] Ir^[9]), vanadium oxides,^[10] Cu-Ce-O,^[11] Fe/MOF,^[12] GO,^[13] and photocatalysts.^[14] However, all of the above methodologies either require complicated catalyst preparation and reaction setup, involve cumbersome work-up or show limited compatibility for the inactivated amines, such as the normal aliphatic amine and benzyl amines substituted by electron-withdrawing groups. Moreover, the use of harsh reaction conditions usually causes side reactions such as hydrolysis and oxidation to aldehydes and nitriles. Therefore it is desirable to develop an efficient catalytic system working under mild conditions, preferably at room temperature, easily separable and reusable, and suitable for various amines.

Manganese dioxide (MnO₂) is an oxidant in organic synthesis. N. Mizuno and co-workers have reported the oxidation of amines to amides with stoichiometric amount of MnO₂ (MnO₂:amine =2.3:1) at 130 °C.^[15] Imine (19%) as byproduct was detected over β -MnO₂. This provides a possibility of using MnO₂ as catalyst.

We herein report this endeavor on a MnO₂-TBHP catalytic system in the oxidative self-coupling of amines to imines. Up to 13 amines covering substituted benzylic amines, normal aliphatic amines, and O- and S-containing heterocyclic amines were high-selectively converted into the corresponding imines with excellent yields. To the best of our knowledge, this is the first example with satisfied imine yield, operational simplicity, and good tolerance with diverse amines.

We initiated the investigations with the benzyl amine (**1a**) conversion as a model reaction. A reaction under 0.3 MPa O₂ over α -MnO₂ (10% mol **1a**) at 100 °C afforded >99% conversion of **1a** and 74% of *N*-benzylidenebenzylamine (**2a**) with 1% benzaldehyde (**2b**) and 25% benzonitrile (**2c**) (Table 1, entry 1). Further optimization tests failed to realize both the conversion of **1a** and the selectivity of **2a** larger than >90%. We found the formation of **2b** and **2c** was thermally favourable and thus

decreasing reaction temperature could suppress the side reaction. But no reaction occurred when conducting the reaction with O₂ at rt. We then changed to H₂O₂ as oxidant. However, H₂O₂ (30% aq.) quickly decomposed over α -MnO₂ even at 0 °C and **1a** was not converted at all (entry 2). Unexpectedly, when 2.0 TBHP, 0.1 α -MnO₂ and 1.0 equivalent **1a** was stirred in a 2 mL acetonitrile at 20°C, the remarkably high conversion of **1a** (>99%) was obtained with 95% selectivity for **2a** (entry 3). The reaction was finished in 4 h in an open air without protection. The easy handling and high efficiency mark it as the best methodology for the self-coupling of amines to imines in open publications. The background reaction without catalyst was sluggish in 4 h (entry 4). The reaction without TBHP gave no product (entry 5). A reaction in Ar atmosphere proceeded comparably well (entry 6), indicating TBHP was the main oxidant. Notably only 2 equiv. of TBHP was used in this study, compared with 5-10 equivalent amount.^[10a, 16] A control test using the 4:1 mixture of **1a** to TBHP gave a 32% conversion of **1a**, indicating the 64% of TBHP utilization efficiency, much higher than literature value.^[17]

Solvent had great effect on the reaction. Acetonitrile was the best among the investigated solvents, such as tetrahydrofuran, dichloromethane, chlorobenzene, and dimethyl formamide (entries 7-10). Even if extending reaction time to 12 h, the reaction in dimethyl formamide only gave 59% of **2a** (entry 11). Particularly, when water was used as solvent, the conversion >99% was obtained but with 70% selectivity (entry 12).

Various oxidative oxide catalysts were compared with α -MnO₂. An octahedral molecular sieve (OMS-2), reported by S. L. Suib,^[18] was less selective (entry 13, 71% of **2a**) but much oxidative giving 20% of **2c**. Other manganese oxides, such as β -MnO₂, δ -MnO₂, Mn₂O₃ and Mn₃O₄, exhibited much less performance (Table 1, entries 14-17). Metal oxides such as Fe₂O₃, V₂O₅, CuO, Co₃O₄ and MoO₃ were inactive for the reaction (Table 1, entries 18-22).

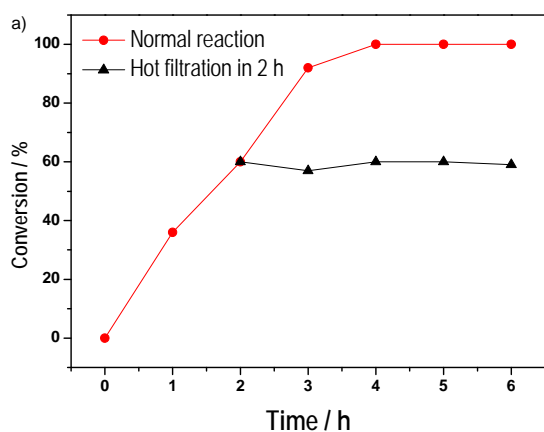


Fig. 1 Filtration test. Reaction conditions: 0.5 mmol benzylamine, 1 mmol TBHP, 2 mL MeCN, α -MnO₂ (10 mol%), r.t. The catalyst was filtrated at 2 h.

The α -MnO₂ catalyst was separated by centrifugation and reused for at least three times (Figure S1). ICP analysis did not detect Mn species in the reaction mixture. The reaction stopped after the removal of MnO₂ from the reaction solution (Figure 1), indicating no dissolved species contributed to the catalysis and

the heterogeneous nature of the α -MnO₂ catalyst.

The search for new synthetic technologies has developed continuous process approach. Its main advantages are facile automation, reproducibility, safety, and process reliability, because constant reaction parameters can be assured.^[19] Up to now, no study has reported continuous synthesis of imines. This is a challenging task partly because it requires reaction rate to be fast enough to achieve high throughput. In this study, a column reactor (20 cm in length, 4 mm in diameter) packed with α -MnO₂ pellet (60-80 mesh) was employed for this purpose (Figure 2). Two acetonitrile solutions of TBHP and **1a** were fed into the reactor by two respective pumps. The reactor temperature was kept at 20 °C. The product mixture was collected at the other end of the reactor. After several optimization tests, we obtained >99% conversion of **1a** and average 93% selectivity for **2a**. The global space-time yield was 0.15 mol (mol cat)⁻¹ h⁻¹. Although we sacrificed *ca.* 1% selectivity compared with batch reactor, we were able to continuously run the reaction for more than 100 h without losing catalyst activity, showing a good promising industrial application.

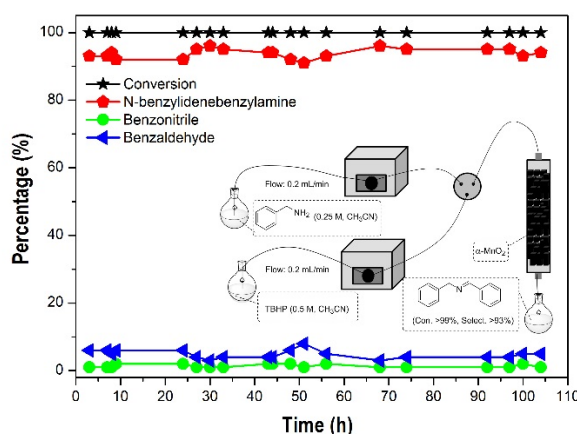
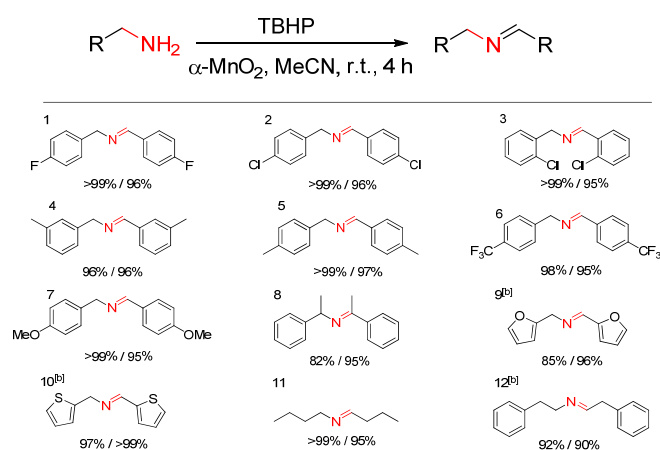


Fig. 2 A continuous synthesis setup and the catalytic result.

Table 2. Scope of the α -MnO₂ catalyzed conversion of amine to imine.^[a]



[a] Reaction conditions: 0.5 mmol amine, α -MnO₂ (10 mol%), 1 mmol TBHP, 2 mL MeCN, 17-25 °C, 4 h. The results were presented as conv. / select. Byproducts were aldehydes and nitriles. The conversion and selectivity were determined by GC-MS using dodecane as an internal standard. [b] 8 h.

A broad scope of imines were converted using the methodology (Table 2). Regardless of the presence of electron-donating or electron-withdrawing groups, benzylamines were converted to the corresponding imines with >85% conversion and >90% selectivity (entries 1-7). 1-Phenylethylamine was relatively inert to be oxidized (82% conversion) (entry 8), which could be due to the steric hindrance effect. Heterocyclic amines and normal aliphatic amines were usually difficult to be converted.^[14a, 20] In this study, furan-2-ylmethanamine (entry 9) and thiophen-2-ylmethanamine (entry 10), bearing proximal oxygen and sulphur atom, were converted at 85% and 97% conversion with 96% and >99% selectivity, respectively. Moreover, we achieved high imine yields for n-butyl amine (95%) and 2-phenylethan-1-amine (83%), respectively (entries 11-12).

To gain insights into the mechanism details, several kinetic experiments were conducted using in situ ATR-IR. Experimental results indicated that the reaction was a pseudo-first-order with respect to **1a** (Figure S2). The apparent activation energy, E_a , was determined from the Arrhenius plot in the temperature range of 30-70 °C (Figure 3a). The least-square fit analysis yielded an E_a value of 62.8 kJ mol⁻¹. A linear relationship between $\log(k_x/k_H)$ and Brown-Okamoto constant σ^+ (Figure 3b and Figure S3) was established for the substituted benzylamines ($X = p\text{-Cl}, p\text{-H}, p\text{-Me}$ and $p\text{-OMe}$). The slope of the linear plot gave a ρ value close to zero, suggesting no electronic perturbation in the C α -H or N-H activation step.^[21]

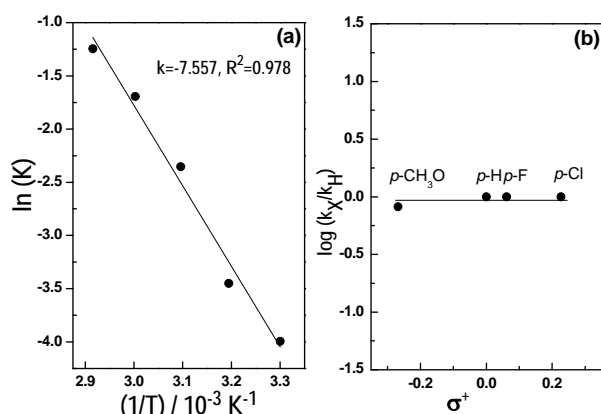


Fig. 3 (a) Arrhenius plot for the oxidation of benzylamine. (b) Hammett plot for the self-coupling of the substituted benzylamines over $\alpha\text{-MnO}_2$ using TBHP at rt. σ^+ is the Brown-Okamoto constant.^[21]

We added 2 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) as a radical scavenger or butylated hydroxytoluene (BHT) as a radical initiator to a reaction of **1a**. As a result, the reaction was not either inhibited or accelerated (Scheme S1), indicating a non-radical process. This was reinforced by in-situ ATR-IR test which did not observe induction period (Figure S4). This is different to the usual role as radical initiator played by TBHP.^[10a, 17]

To further investigate the reaction route, several control experiments were performed. First, reaction of **1a** at rt over $\alpha\text{-MnO}_2$ without TBHP gave no product in 4 h. The continuation of the reaction by adding TBHP reached 96% conversion and 95% selectivity of **2a** (equ 1). This result can not be explained by the general Mars-van-Krevelen mechanism over MnO_2 , with the

organic reactant being oxidized by lattice oxide ions of MnO_2 at elevated temperature. In our reaction, three facts that (i) MnO_2 alone could not oxidize amine under current condition, (ii) TBHP alone did oxidize amine but with low activity, and (iii) the complete oxidation of amine was achieved in the presence of both MnO_2 and TBHP, may infer that the formation of TBHP- MnO_2 adduct is responsible for the catalysis. We postulate that some surface defect sites or Mn-OH groups, instead of redox property of MnO_2 , play a key role at rt.

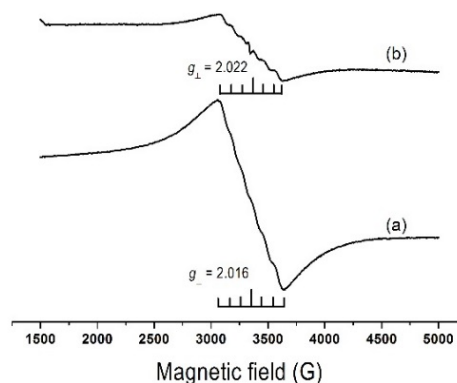


Fig. 4 ESR spectra of (a) $\alpha\text{-MnO}_2$ and (b) a combination of $\alpha\text{-MnO}_2$ + TBHP at room temperature.

This conclusion is supported by ESR characterization (Figure 4). The $\alpha\text{-MnO}_2$ is featured with wide line (a) with g_{\perp} value of 2.016, which is larger than 1.94 of the fully oxidized $\alpha\text{-MnO}_2$.^[22] Combining with the appearance of six visible and weak hyperfine structure lines in line (a), we may postulate the existence of exchange pair of $\text{Mn}^{3+}\text{-Mn}^{4+}$ in $\alpha\text{-MnO}_2$.^[22-23] Upon adding TBHP into MnO_2 , six clear symmetrical hyperfine structure lines with g_{\perp} value of 2.022 are superimposed on the line (a). The increase in g_{\perp} value and decrease in signal intensity suggest that the addition of TBHP may increase the concentration of Mn^{3+} ions, stabilized by forming a TBHP- MnO_2 adduct.

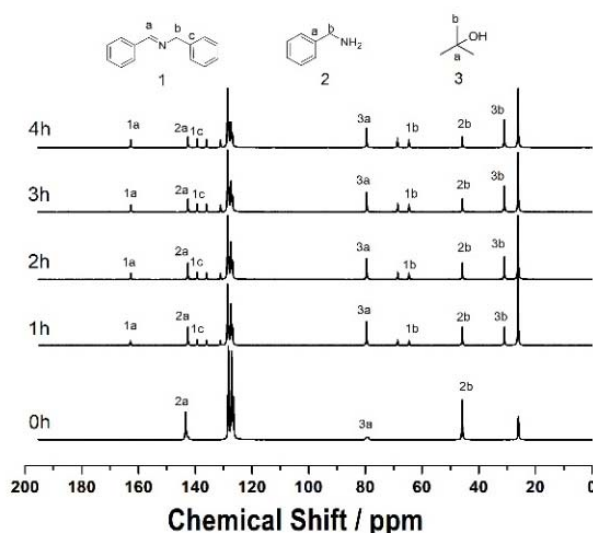
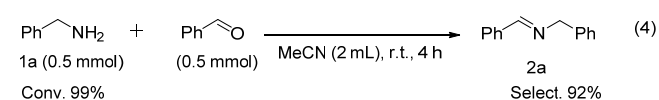
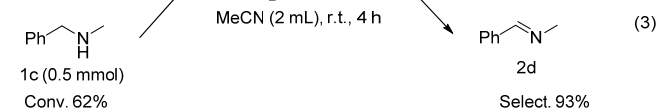
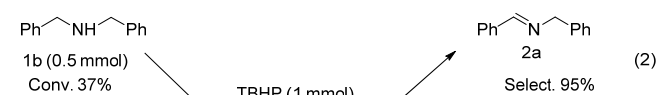
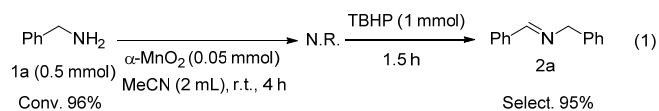


Fig. 5 Oxidation of benzylamine without solvents. Reaction conditions: 2.5 mmol substrate, 2.5 mmol TBHP, 0.25 mmol $\alpha\text{-MnO}_2$, reaction temperature 20 °C



Conclusions

In summary, we have demonstrated a simple, efficient and eco-friendly protocol for the direct synthesis of imines from amines *via* a facile $\alpha\text{-MnO}_2$ catalyzed-procedure at rt. The catalysis was truly heterogeneous and $\alpha\text{-MnO}_2$ could be reused without an appreciable loss of its high catalytic performance. A continuous synthesis approach proved the catalyst long-life stability in more than 100 h. The clean and mild synthetic procedure described herein is expected to contribute to its utilization for the development of new products and processes.

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Notes and references

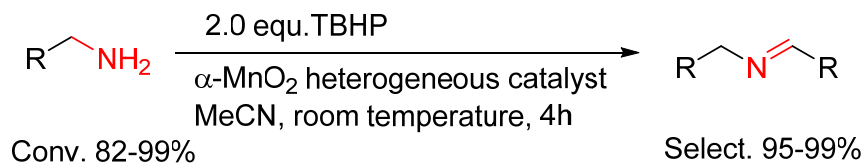
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Previous studies proposed benzaldimine as an intermediate in the dehydrogenation of benzyl amine.^[20] Hermans and co-workers did not detect it in GC-FID/MS and thought it was instable in reaction or analysis.^[24] Jones and co-workers recently proposed the same intermediate but still did not have experimental proof.^[11] At first we wondered that benzaldimine could not survive from high reaction and analyses temperature or probably the sampling method. Because our reaction can be conducted at rt, we tried to monitor the reaction by in situ NMR technique, a strong tool to detect intermediate. Likely, we did not detect benzaldimine from beginning to end (Figure 5). However, dibenzylamine and N-methyl-1-phenylmethanamine majorly generated the corresponding benzaldimines as detected by GC (equ. 2 and 3), suggesting benzaldimine to be the intermediate. This observation allowed us to conclude that benzaldimine was not generated as free molecule during reaction. Because benzaldimine has stronger basicity than benzyl amine and benzaldehyde,^[25] it may exist as the adsorbed species on catalyst surface in an activated state after the oxidative dehydrogenation reaction. The reaction was accelerated after adding a certain amount of water (Figure S5), indicating very possibly one of the steps involved the hydrolysis of the adsorbed benzaldimine. Similar to Hermans and Jones's discoveries, we also found benzaldehyde was easily condensed with **1a** to **2a** without catalyst (conv. 99%, select. 96%) (equ 4), suggesting a noncatalytic route to **2a** after the benzaldehyde was formed.

Further investigations into the identity of active sites are currently underway, and preliminary analyses combining the catalytic data, control tests and characterization results may suggest a tentative reaction mechanism including the five key steps: (i) the catalyst was activated by TBHP and a surface peroxide species (Mn-TBHP adduct) was formed; (ii) the substrate **1a** were oxidatively dehydrogenated to the activated benzaldimine and heterolytic cleavage of TBHP to *tert*-butyl alcohol via a concerted mechanism, which is the rate-determining step in the whole reaction; (iii) the adsorbed benzaldimine was quickly hydrolyzed to benzaldehyde with the release of NH₃, detected by MS (Figure S6); (iv) benzaldehyde was non-catalytically condensed with another **1a** to generate imines, and (v) the catalyst was generated by TBHP for next catalytic cycle.

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- 30 [25] The quantity of proton affinity (PA) determines basicity, which is related affinity to catalyst surface. Experimental data of PA values are referenced from literatures (Borislav Kovacevic, Joel F. Liebman and Zvonimir B. Maksic, *J. Chem. Soc., Perkin Trans.* **2002**, 2, 1544-1548; E.P. Hunter, S.G. Lias, *J. Phys. Chem. Ref. Data*, **1998**, *27*, 413-656). These data showed PA (benzalimine, 220 kcal mol⁻¹) > PA (benzyl amine, 218 kcal mol⁻¹) > PA (benzaldehyde, 199 kcal mol⁻¹).
- 35

Graphical Abstract



suitability for 13 aromatic and aliphatic amines
R = substituted benzene, furan, thiophene, alkane, etc.

A methodology for the direct synthesis of imines from amines via a facile $\alpha\text{-MnO}_2$ catalyzed-procedure at room temperature with TBHP as oxidant was described, which is simple, efficient and eco-friendly. The catalysis is suitability for 13 aromatic and aliphatic amines, and it is heterogeneous, recyclable and reusable.