

Supporting Information for:
**A green catalytic procedure for oxidation of pyridines catalyzed
by a lacunary polyoxometalate in water at room temperature**

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1. Experimental

1.1 Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

1.2 Preparation of catalyst $\Delta\text{-Na}_8\text{HPW}_9\text{O}_{34}\cdot 19\text{H}_2\text{O}$ [33]:

First 30 g of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ was dissolved in 37 ml of distilled water with stirring. Then 0.75 ml of 85 % H_3PO_4 , followed by 5.5 ml of glacial acetic acid was added to the stirring solution. After a few seconds, the solution became cloudy and after about 1 min a heavy white precipitate had formed. The solid was collected and first dried under aspiration for 24 h, and then the aspirated solid was left in air for 24 h. After that, the solid was dried at 140 °C for about 1.5 h. The yield of $\Delta\text{-Na}_8\text{HPW}_9\text{O}_{34}\cdot 19\text{H}_2\text{O}$ was about 80 %. IR spectrum (KBr, cm^{-1}): 1171, 1057, 994, 947, 896, 818, 742, 653, 624, 588, 507, 470, 417.

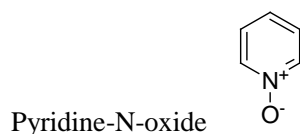
1.3 Characterization techniques

Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrometer. The catalysts were measured using 2–4 % (w/w) KBr pellets prepared by manual grinding. Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (Vario EL Cube). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 and Varian mercury 300 MHz spectrometer with TMS as an internal standard and CDCl_3 as solvent.

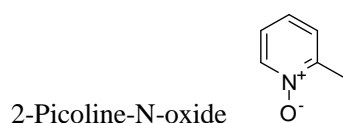
1.4 Catalytic reaction

Catalyst (0.03 mmol), H_2O (3 ml), substrate (4 mmol), and H_2O_2 (20 mmol, 30 % aq.) were charged in the reaction flask, which was firstly bathed in cold water (about 283 K). The mixture was then stirred at room temperature (about 298 K) for 16-24 h. The reaction was detected by TLC. After reaction, the system was concentrated by evaporation, and the catalyst precipitated from the mixture by after the addition of anhydrous ethyl alcohol. The recovered catalyst obtained by filtration was washed with anhydrous ethyl alcohol and diethyl ether, which was then used for the next oxidation after dried. The filtrate was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 , and the pure products were obtained by evaporation or column chromatography. The products were analyzed by ^1H NMR and ^{13}C NMR.

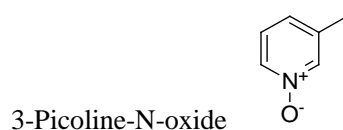
2. Characterization of oxidation products



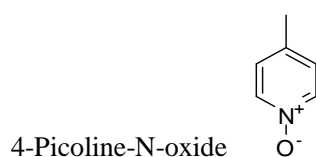
^1H NMR (CDCl_3 , 400 MHz) δ 7.97-7.96 (t, 2 H), 7.05-7.03 (m, 3 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 125.6 (2C), 125.8, 138.6 (2C).



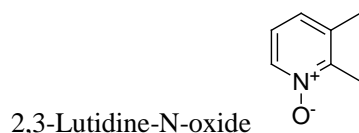
^1H NMR (CDCl_3 , 400 MHz) δ 8.18 (d, $J=6.4$ Hz, 1 H), 7.12-7.08 (t, 2 H), 7.04-7.00 (m, 1 H), 2.30 (s, 3 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 16.6, 123.0, 125.9, 126.8, 138.4, 148.0.



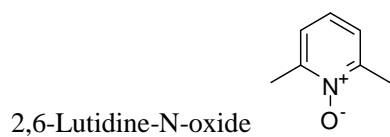
^1H NMR (CDCl_3 , 400 MHz) δ 8.05 (d, $J=9.6$ Hz, 2 H), 7.16-7.07 (m, 2 H), 2.28 (s, 3 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 18.2, 125.3, 127.3, 136.5, 136.8, 139.3.



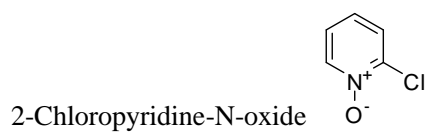
^1H NMR (CDCl_3 , 400 MHz) δ 8.10 (d, $J=6.8$ Hz, 2 H) 7.08 (d, $J=6.4$ Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 19.9, 126.4 (2C), 137.5, 138.3 (2C).



^1H NMR (CDCl_3 , 400 MHz) δ 8.09 (d, $J=4.8$ Hz, 1 H), 6.98-6.93 (m, 2 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 13.6, 19.4, 121.9, 127.0, 134.8, 137.0, 148.2.



^1H NMR (CDCl_3 , 400 MHz) δ 7.13 (d, $J=7.6$ Hz, 2 H), 7.08-7.05 (m, 1 H), 2.52 (s, 6 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 17.5, 17.6, 123.5, 125.3, 148.6.



^1H NMR (CDCl_3 , 400 MHz) δ 8.35 (s, 1 H), 7.53 (s, 1 H), 7.24 (s, 2 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 123.9, 126.2, 127.2, 140.8, 142.2.