

Supporting Information of

**A cascade synthesis of quinazolinones and quinazolines using α -MnO₂ catalyst
and *tert*-butyl hydroperoxide (TBHP) as oxidant**

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Reagents and Chemicals

β -MnO₂¹, δ -MnO₂², OMS-2³, Mn₃O₄⁴, Co₃O₄⁵, CeO₂⁶ were prepared according to the literature procedures. Fe₂O₃, CuO, Cu₂O, KMnO₄ and MnSO₄·H₂O were purchased from Tianjin Kermel. Solvents were obtained from Tianjin Kermel, and alcohols and amines substrates were purchased from J&K. TBHP (70% in water) was purchased from Sinopharm Chemical Reagent.

Catalyst preparation

The α -MnO₂ was prepared as the following.⁷ A 10 mL aqueous solution containing KMnO₄ (1 mmol) was mixed with 10 mL aqueous solution containing MnSO₄ (1.5 mmol), and then stirred continuously for 6 h. A dark-brown precipitate was formed, collected by centrifugation, washed repeatedly with deionized water, and dried overnight at 70 °C before use.

Heteroatom doping of α -MnO₂ was as the following⁸. Experiments were carried out by adding metal nitrate salts (the molar ratio of M/Mn²⁺=1:1) to the KMnO₄ and Mn²⁺ mixed solutions prior to mixing. Resultant materials were centrifuged, washed and dried in the same procedure with α -MnO₂.

Thermal annealing of α -MnO₂ followed the literature.¹ In general, α -MnO₂-150 denotes a sample prepared by heating α -MnO₂ at 150 °C for 2h in a following Ar (30 mL min⁻¹).

Oxidative cyclization of alcohols with α -aminobenzamides

A general procedure for the synthesis of quinazolinones was as the following. α -Aminobenzamides (0.5 mmol), α -MnO₂-150 catalyst (10 mol%), TBHP (2 mmol), alcohols (1.5 mmol), dodecane as internal standard and solvent (2 mL) were placed in a pressure vessel with a magnetic stir bar at 80 °C. The product was analyzed by GC using an Agilent 7890A instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion and yield was determined using internal standard method with dodecane. The selectivity was determined using area normalization method. After the reaction was complete, the used α -MnO₂ catalyst was separated by centrifugation, washed with ethanol and deionized water and dried at 70 °C prior to being recycled. Some catalyst powder was lost during separation. The reaction was thus scaled up in order to collect enough catalyst for recycling.

Rates of step reaction calculated

The calculation of rates of each step were as the following. Substrates in each step was 0.5 mmol in 2 mL solvent. The concentration of either substrate or intermediate was calculated by GC in initial 30 min reaction.

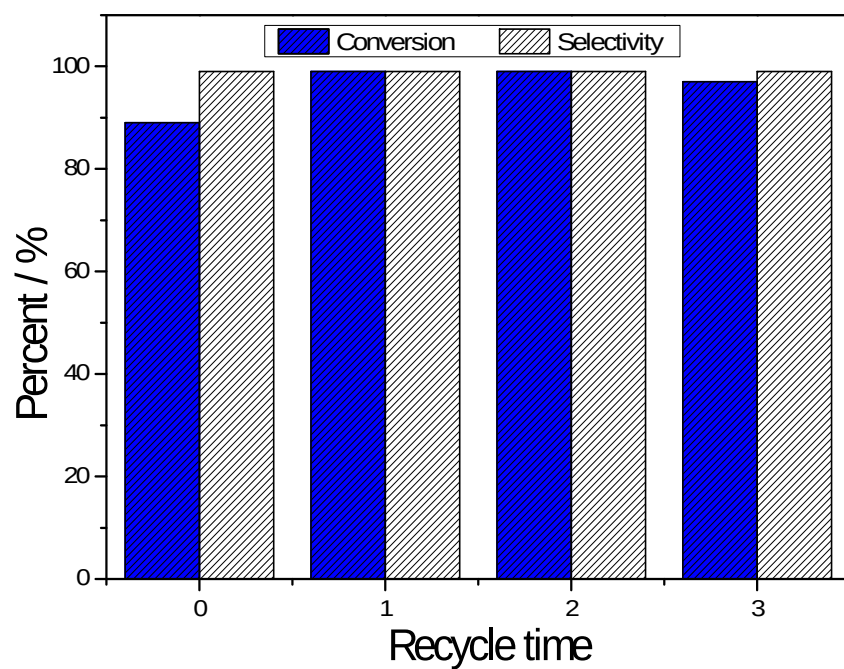


Figure S1. Cyclization of o-aminobenzamide and benzyl alcohol in methanol: recycling of the α -MnO₂-150 catalyst. Reaction conditions: 1.5 mmol benzyl alcohol, 0.5 mmol o-aminobenzamide, 2.0 mmol TBHP, 0.05 mmol catalyst, 80 °C, 16 h, 2 mL methanol.

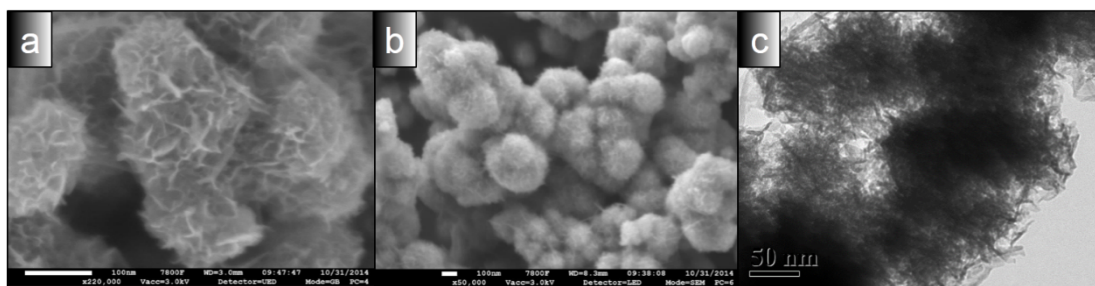
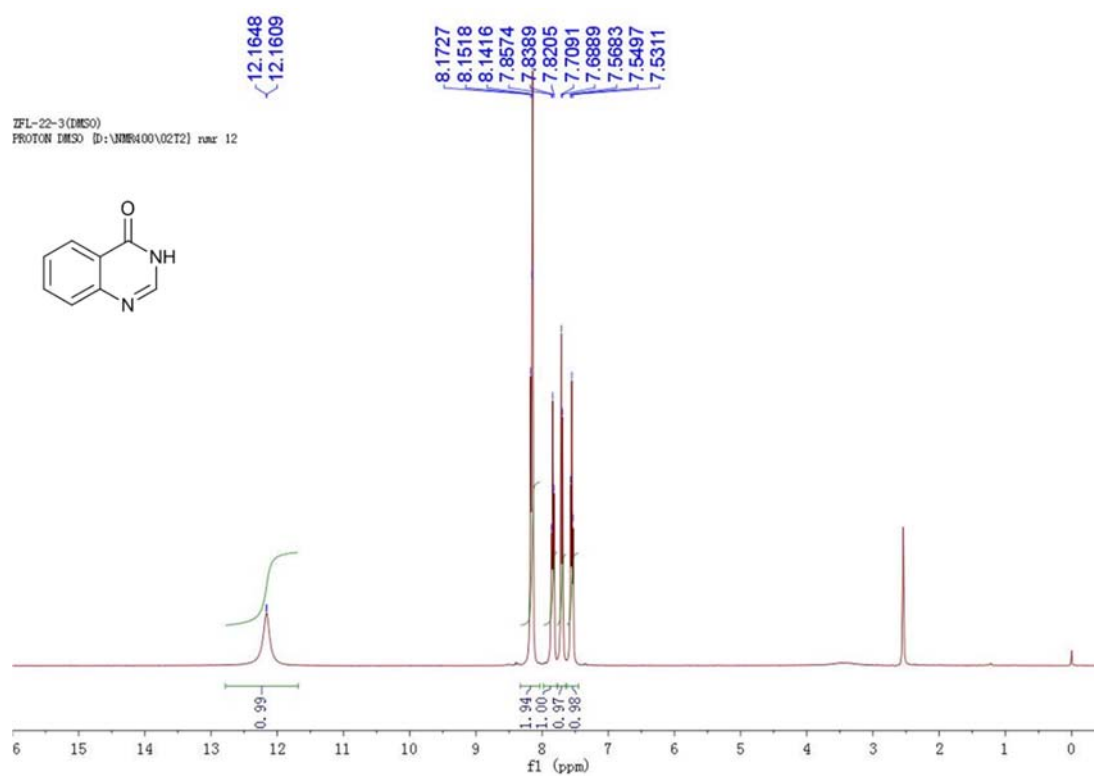
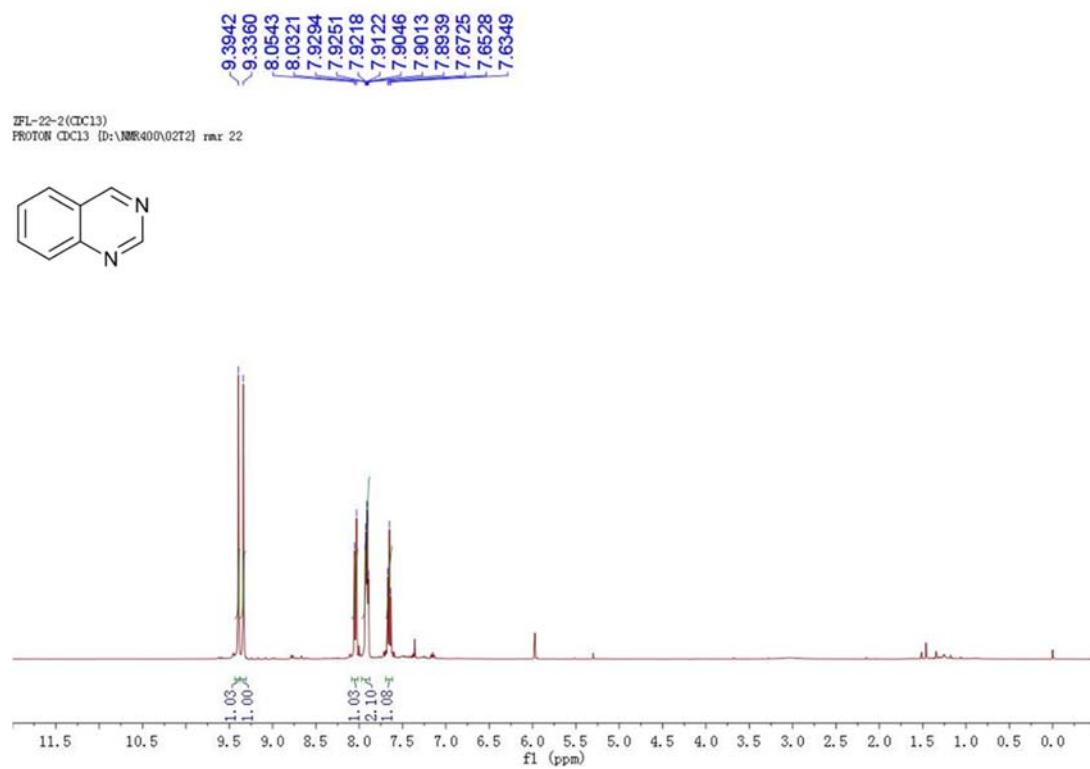


Figure S2. SEM and TEM images of α -MnO₂-150





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