

Electronic Supplementary Information

A green process for the oxidative lactonization of 1,2-benzenedimethanol by tungstic acid with aqueous H₂O₂

Quan-jing Zhu, Wei-Lin Dai,* and Kang-Nian Fan

*Department of chemistry & Shanghai key laboratory of molecular catalysis and innovative material,
Fudan University, Shanghai 200433, P. R. China.*

1. Materials.

1,2-Benzenedimethanol, 50% aqueous H₂O₂, *tert*-butanol, acetonitrile, *n*-butanol and iso-propanol were of analytical grade. Tungstic acid was obtained from Sinopharm Chemical Reagent Co., Ltd and of analytical grade. All of the materials were used as received.

2. Catalyst preparation.

The novel catalytic system was prepared by a simple method: the required amount of tungstic acid was added into aqueous H₂O₂ at 40 °C. After 0.5 h pre-reaction, the mixture was used as the catalytic system.

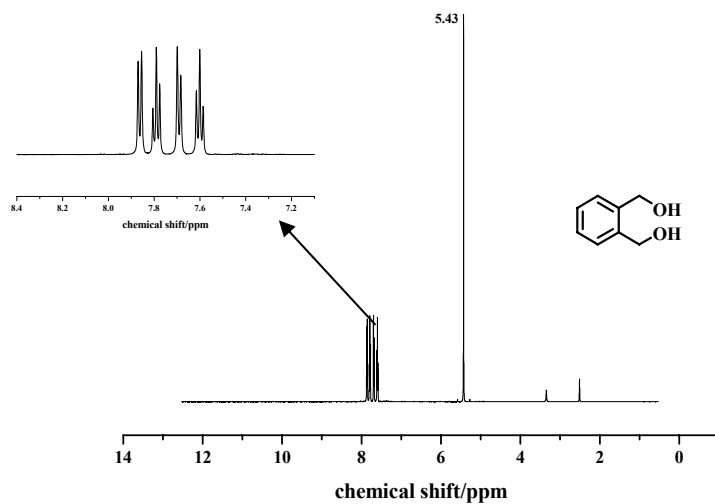
3. Procedure for the separation of phthalide under organic solvent-free condition

In a typical experiment, 0.0135 g of the WO₃·H₂O (0.054 mmol) and 0.67 ml of 50 wt% aqueous H₂O₂ (11.1 mmol) were introduced into the regular glass reactor at 40 °C with vigorous stirring. The reaction was started after the addition of 10 ml of water and 0.690 g of 1,2-benzenedimethanol (5 mmol) into the mixture and was kept for 24 h. Then, the reaction mixture was heated for 0.5 h at 90 °C after the reaction and the excessive H₂O₂ was decomposed. Thus, the catalyst WO₃·H₂O was easily recovered with hot filtration. The filtrate was cooled down and the product phthalide was separated out. Finally, the product was filtrated and dried at room temperature and 77.4% yield of phthalide was obtained. The melting point of the powder obtained by this route is 70.0 to 73.8 °C (Sinopharm Chemical Reagent Co., Ltd, 71.0 to 75.0 °C). The GC purity of the as-prepared phthalide was higher than 99.5%, which can be directly used in many fields.

4. Characterization of the product phthalide

The ¹H NMR Spectrum of the as-prepared phthalide was recorded on a DMX 500. The X-ray

powder diffraction (XRD) pattern of the as-prepared phthalide was recorded on a German Bruker D8 advance with Cu-K α radiation, operated at 40 kV and 40 mA.



Phthalide: ¹H NMR (DMSO) δ 7.85 (d, 1 H), 7.79 (t, 1H), 7.69 (d, 1H), 7.60 (t, 3H), 5.43 (s, 2H)

Figure S1. ¹H NMR of the powder obtained under organic solvent-free condition.

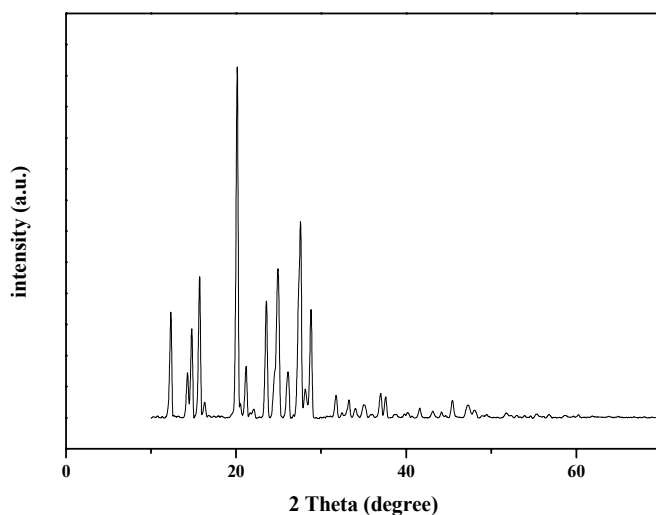


Figure S2. XRD pattern of the powder obtained under organic solvent-free condition.

The XRD pattern of the as-prepared phthalide matched well with that of the pure phthalide phase (PDF no.00-032-1841).