1. Materials and Methods

1.1 Materials and analysis

Furfural (99%), 5-(Hydroxymethyl)furfural (HMF, 98%), vanillin (99%), anisaldehyde (99%), veratraldehyde (99%) were supplied by aladdin reagent co. ltd. 5-methylfurfural (5-MF, 99%), was obtained from J&K chemical co. ltd., Pt/C (5wt %), Pd/C (5wt %) and all the metal reductants or metal complex were purchased from Alfa Aesar. The other reagents, tetrahydrofuran (THF), NaOH (AR Grade) and NH₄Cl (AR Grade) were supplied by sinopharm chemical reagent co. ltd..

The reaction mixture was sampled, diluted 100 times in ethyl acetate and analyzed by GC-MS (Thermal Trace GC Ultra with a PolarisQ ion trap mass spectrometer) with either a TR-35MS or a TR-5MS capillary column (30m×0.25mm×0.25μm) and a shimazu GC equipped a AT-5 capillary column. Autosampler was used and split injection was performed at a split ratio of 50 using helium as carrier gas. Identification of compounds was carried out by comparison mass spectrum and retention time of pure chemical.

1.2 Preparation of solid acids

Preparation of NbOPO₄: In a typical synthesis of niobium phosphate, 2.0g Nb₂O₅ and 10.0g KOH were placed in a nickel crucible and then heated to 600°C for 2h to obtain a melted mixture. After cooled to room temperature, the melted mixture was dissolved in 50ml H₂O and the residues were filtered. Then, 3.0 mol/L H₃PO₄ were added dropwise to the above solution at a 1:2 Nb/ phosphate ratio with vigorously stirring, a white precipitate formed. Finally, the mixture was aged for 48h at room temperature. The precipitate obtained was washed with deionized water until pH 5 and dried at 120°C and calcined at 500°C for 3h. NbOPO₄ was obtained as white solid powder.

Preparation of TaOPO₄: The catalyst was prepared according to the literature.[1] 3g of Ta₂O₅·nH₂O was added to a 40 ml of 1 M H₃PO₄ solution and stirring at room temperature for 60 h. The mixture was aged at ambient condition for another 12 h. The precipitate was washed with deionized water until the pH was neutral and dried overnight at 65°C in dry chamber, followed by drying at 110°C in vacuum oven for 2 h and calcining in air at 300°C with slow heating rate for 3 h.

Preparation of WO₃: The catalyst was prepared according to the literature.[2] 1 g of poly(alkylene oxide) block copolymer was dissolved in 10 g of ethanol. To this solution, 0.01 mole of the respective anhydrous WCl₆ was added with vigorous stirring. The resulting sol solution was gelled in an open Petri dish at 60 °C in air for 15h. The as-made bulk sample was then calcined at 300-600 °C for 4-5 h to remove the block copolymer surfactant species.

2. Experiment section

2.1 General procedures for self-coupling reactions

In a typical general procedure, to a vigorously stirred suspension of aldehyde (2 mmol) in aqueous solution (3ml, 10wt % NaOH aq. or 0.1 mol/L NH₄Cl aq.) was added commercial metal powders (2mmol). Stirring was continued at room temperature till completion of the reaction (as monitored by TLC). After the reaction, the metal was in the form of metal hydroxide (M(OH)ₓ) which was a flocculus in the solution. The mixture was neutralized and extracted with EtOAc. The organic phase was washed with brine, dried with MgSO₄ and then concentrated in vacuo. The crude material was purified by column chromatography on silica gel.
2.2 GC-MS analysis of the self-coupling products

Fig S1 Representative chromatogram of dimerization reaction in Table 1, entry 15

2.3 General procedures for dehydration/hydrogenation reactions

The dehydration/hydrogenation of these dimer products were carried out in a Parr reactor (volume, 25ml). The catalyst (Pt/C or Pd/C 100mg, 5wt %; solid acids, 50mg), the dimer products (purified or crude, 200mg) and 10ml H₂O were added to the reactor. After purging the reactor with H₂, the reaction was carried out with 4 MPa H₂ (room temperature) at 573K for 3h at a stirring speed of 1000 rpm. After the reaction cooled to room temperature, ethyl acetate was used to extract the organic mixture three times. The organic layer was analyzed by GC and GC-MS. Internal standard (tridecane) was used to determine the amount of alkanes.

2.4 GC-MS analysis of the dehydration/hydrogenation products

Fig S2 Representative chromatogram of hydrodeoxygenation reaction in Table 2, entry 2.
Fig S3 Representative chromatogram of hydrodeoxygenation reaction in Table 2, entry 6.

Fig S4 Representative chromatogram of hydrodeoxygenation reaction in Table 2, entry 9

2.4 Pinacol rearrangement

Scheme S1. Pinacol rearrangement mechanism for the self-coupling product from vanillin.
3. Characterization Data

1,2-difuran-2-yl)ethane-1,2-diol: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.35\) (m, 1H), 7.32-7.31 (m, 1H), 6.31-6.30 (m, 1H), 6.26-6.23 (m, 2H), 6.20-6.19 (m, 1H), 4.98 (s, 1H), 4.94 (s, 1H), 3.56-3.14 (br, 2H). \(^{13}\)C-NMR (100MHz, CDCl\(_3\), \(\delta\) ppm): 152.8, 142.3, 110.3, 108.1, 70.1. HRMS (ESI) Calcd for \(\text{C}_{10}\text{H}_{16}\text{O}_2\), 194.0579; Found, 193.0507[M-H\(^+\)].

1,2-bis(5-methylfuran-2-yl)ethane-1,2-diol: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.17\) (d, \(J=3.1\)Hz, 1H), 6.08 (d, \(J=3.1\)Hz, 1H), 5.91-5.90 (m, 1H), 5.85-5.84 (m, 1H), 4.88 (s, 2H), 3.26 (s, 3H), 3.23 (s, 3H). \(^{13}\)C-NMR (100MHz, CDCl\(_3\), \(\delta\) ppm): 151.9, 151.0, 108.7, 106.1, 69.7, 13.5. HRMS (ESI) Calcd for \(\text{C}_{12}\text{H}_{18}\text{O}_2\), 222.0892; Found, 221.0815[M-H\(^+\)].

1,2-bis(4-methoxyphenyl)ethane-1,2-diol: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.21-7.19\) (d, \(J=8.7\)Hz, 1.46H), 7.05-7.03 (d, \(J=8.7\)Hz, 4H), 6.86-6.84 (d, \(J=8.7\)Hz, 1.44H), 6.77-6.75 (d, \(J=8.7\)Hz, 4H), 4.73 (s, 0.69H), 4.63 (s, 2H), 3.80 (s, 2.3H), 3.76 (s, 6H). \(^{13}\)C-NMR (100MHz, CDCl\(_3\), \(\delta\) ppm): 159.2, 130.1, 128.2, 113.5, 78.8, 55.2. HRMS (ESI) Calcd for \(\text{C}_{16}\text{H}_{18}\text{O}_2\), 274.1205; Found, 273.1127[M-H\(^+\)].

1,2-bis(3,4-dimethoxyphenyl)ethane-1,2-diol: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.69-6.67\) (m, 2H), 6.60-6.57 (m, 4H), 4.54 (s, 2H), 3.80 (s, 6H), 3.72 (s, 6H), 3.29 (br, 2H). \(^{13}\)C-NMR (100MHz, CDCl\(_3\), \(\delta\) ppm): 148.5, 132.6, 119.4, 110.6, 110.1, 78.9, 55.8. HRMS (ESI) Calcd for \(\text{C}_{18}\text{H}_{20}\text{O}_2\), 334.1416; Found, 333.1332[M-H\(^+\)].

2,2-bis(4-hydroxy-3-methoxyphenyl)acetaldehyde: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.87-9.86\) (d, \(J=2.8\) Hz,1H), 6.92 (d, \(J=8.1\) Hz, 2H), 6.73-6.68 (m, 4H), 5.62 (br, 2H), 4.74 (d, \(J=2.8\) Hz, 1H), 3.85 (s, 6H). \(^{13}\)C-NMR (100MHz, CDCl\(_3\), \(\delta\) ppm): 198.5, 146.9, 145.2, 128.1, 122.0, 114.7, 111.6, 63.2, 55.9. HRMS (ESI) Calcd for \(\text{C}_{16}\text{H}_{16}\text{O}_6\), 288.0998; Found, 289.1070[M+H\(^+\)].

References
4. $^1$H and $^{13}$C Spectrum
**1H NMR**

2,2'-bis(4-hydroxy-3-methoxyphenyl)acetaldheyde

**13C NMR**

2,2'-bis(4-hydroxy-3-methoxyphenyl)acetaldheyde