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Supplementary Information

Hydrogenolysis of 2-Tosyloxy-1,3-propanediol into 1,3-Propanediol over Raney Ni Catalyst

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The details of 2-tosyloxy-1,3-propanediol (TPD) synthesis

Preparation of 5-hydroxyl-2-phenyl-1,3-dioxane (HPD)

Glycerol (100.0 g, 1.09 mol), benzaldehyde (120.0 g, 1.13 mol), p-toluenesulfonic acid catalyst (1 g), and 1:1 petroleum ether-benzene mixture (100 mL) were refluxed in a flask equipped with a water separator at 80 °C. After 4 h, the reaction was completed, as evidenced by no more water being formed in the water separator. The reaction mixture was cooled, treated with 0.5 M NaOH solution (2 × 100 mL), dried over anhydrous K_2CO_3 (1 g), and finally filtrated. HPD, which formed in the reaction was crystallized at –10 °C and then filtrated from the reaction mixture. The crude HPD was recrystallized in toluene- petroleum ether mixture (1:1) to give pure HPD as large, white, prismatic needles; 48.8 g (25% yield). In our procedure, to take advantage of the acid-catalysed equilibrium between HMPD and HPD (ring transformation) in the acetalization reaction,1 the filtered liquid (mother liquor), which contained the undesired 4-hydroxymethy-2-phenyl-1, 3-dioxolane (HMPD) and unrecovered HPD was recycled for another acetalization batch. The reaction with the mother liquor plus supplemented glycerol (11.0 g, 0.119 mol) and benzaldehyde (13.0 g, 0.122 mol) was carried out in next experiment. After recrystallization, 21.0 g of HPD were obtained (98% yield). The chemical structure of HPD was confirmed by ^{1}H and ^{13}C NMR (nuclear magnetic resonance, Bruker AVANCE III 500 MHz, Switzerland) spectra and FTIR (transform infrared spectroscopy, Nicolet 6700, USA) (Figures S1, S2 and S3). Elemental analysis (Vario MACRO CUBE, Germany) Calc. for $C_{10}H_{12}O_3$ (%): C, 65.65; H, 6.71. Found (%): C, 65.49; H, 6.68.

Preparation of 2-pheny-5-tosyl-1,3-dioxane (PTD)

HPD (20.0 g, 0.111 mol), TsCl (24.0 g, 0.126 mol) and 400 mL of cold dry pyridine were added in a glass flask. The reaction mixture was stirred at 5 °C for 12 h. The product PTD was precipitated by adding 2.4 L cold water and then recrystallized in methanol, affording the PTD as large, colorless, prismatic needles (34.5 g, 93% yield). The chemical structure of PTD was confirmed by ^{1}H and ^{13}C NMR spectra and FTIR spectra (Figures S4, S5 and S6) Elemental analysis of PTD (%): C, 60.28; H, 5.60; S, 9.81% (Calc. for $C_{17}H_{18}O_5S$ (%): C,61.06; H, 5,43; S, 9.59).

Preparation of 2-tosyloxy-1,3-propanediol (TPD)

PTD (20.0 g, 0.060 mol), TsOH (2.0 g, 0.0116 mol) and 200 mL of methanol were added in a glass flask. The reaction mixture was stirred at 40 °C for 1 h. The benzaldehyde formed in the reaction was extracted by *n*-hexane. After carefully neutralized with NaOH, the solvent methanol was recycled by rotating evaporation below 40 °C, giving the TPD as colorless viscous oil (14.4 g, 98% yield). The chemical structure of TPD was confirmed by ^{1}H and ^{13}C NMR spectra and and FTIR spectra (Figures S7, S8 and S9). The hydrogenolysis product 1,3-PD was confirmed by 1H NMR and MS spectrum (Figures S10 and S14). Elemental analysis of TPD (%): C, 48.67; H, 5.79; S, 12.97%. (Calc. for $C_{10}H_{14}O_5S$ (%): C,48.77; H, 5,73; S, 13.02)..

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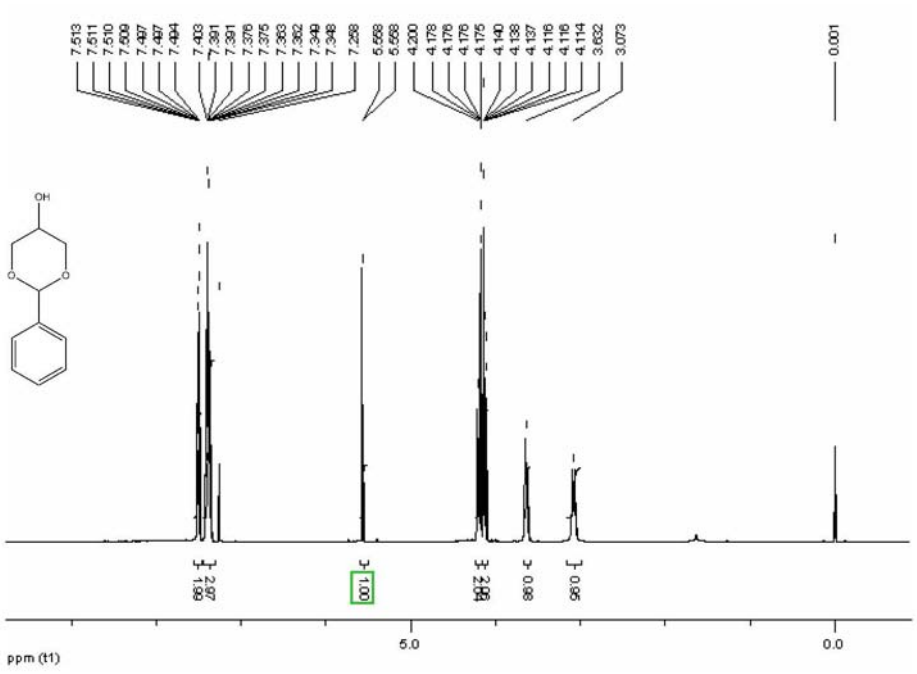


Figure S1. The ^{1}H NMR (500 MHz, CDCl3) spectrum of HPD.

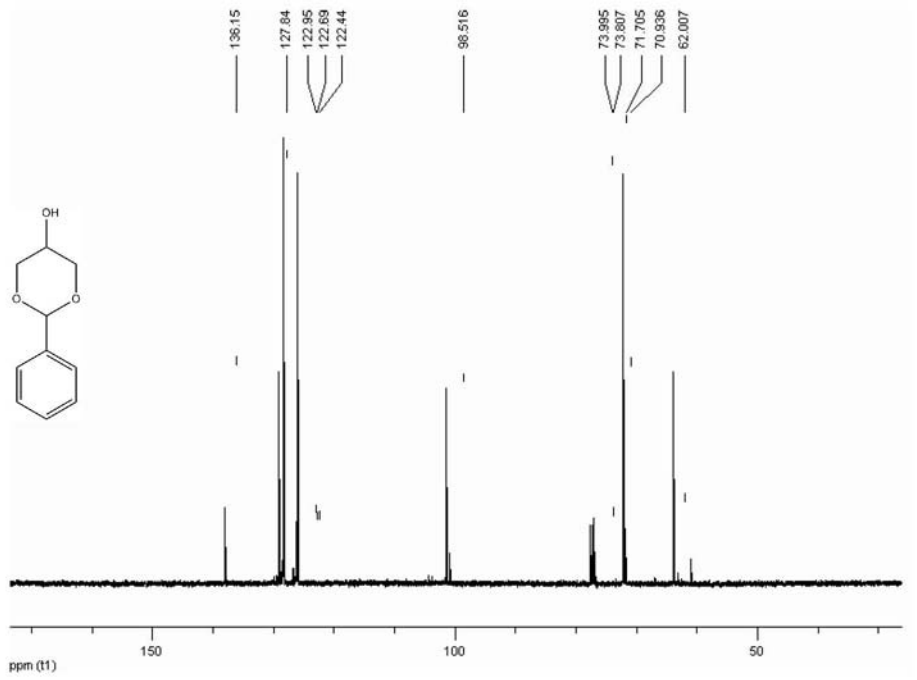


Figure S2. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of HPD.

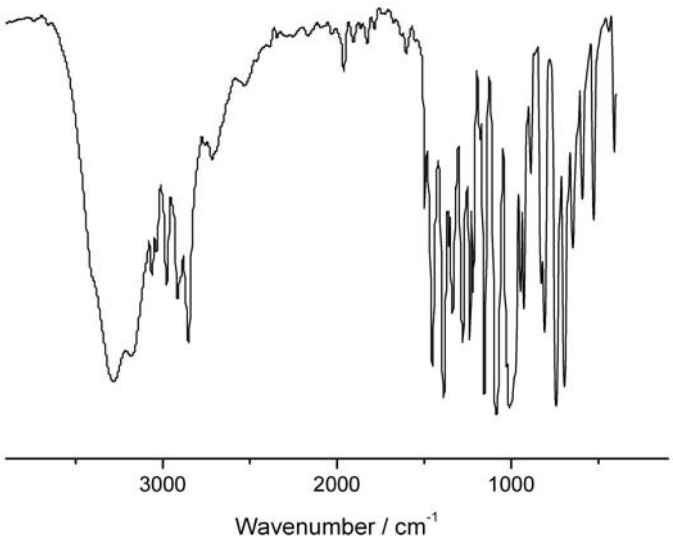


Figure S3. The FTIR spectra of HPD.

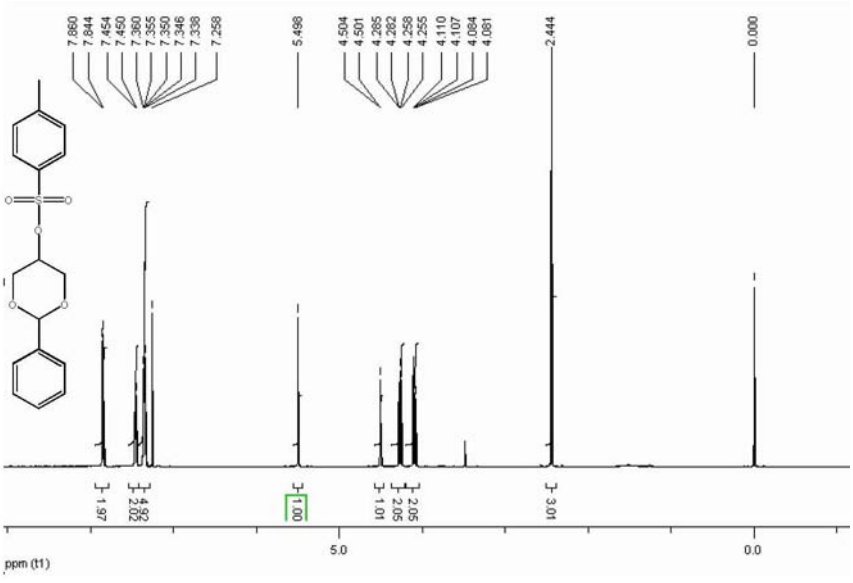


Figure S4. The ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PTD.

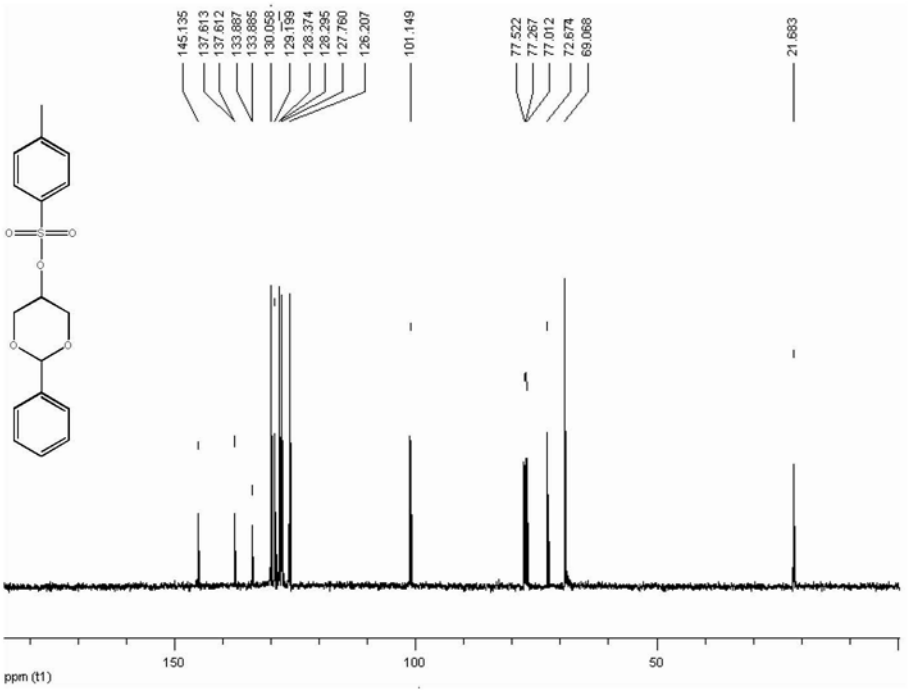


Figure S5. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of PTD.

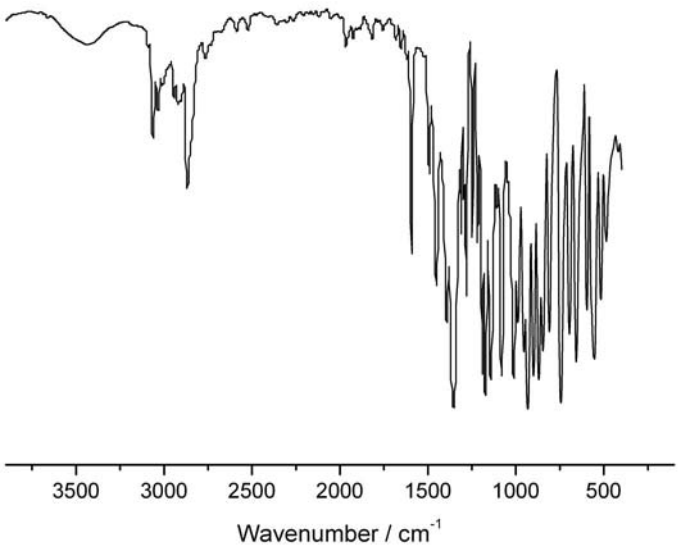


Figure S6. The FTIR spectra of PTD.

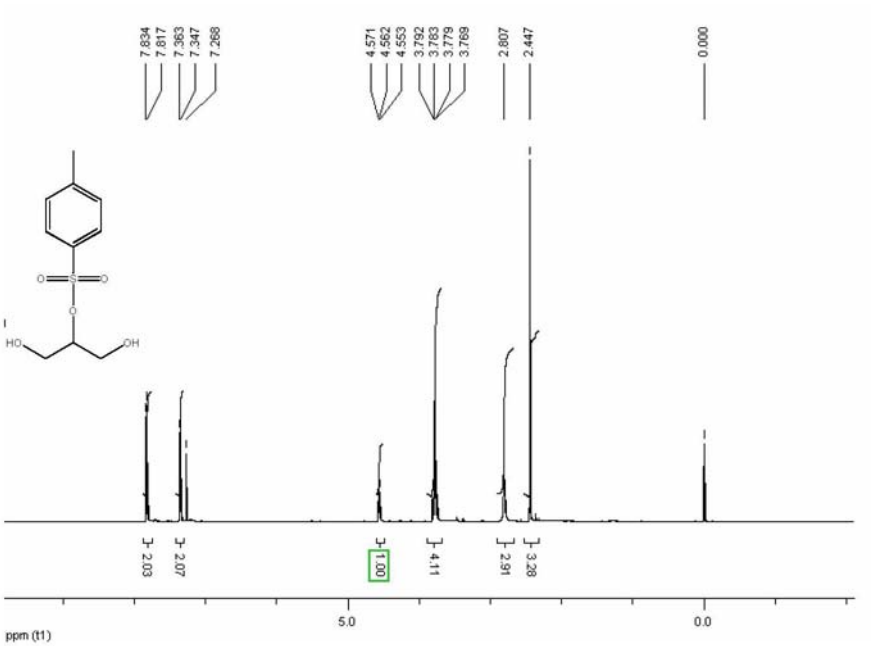


Figure S7. The ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of TPD.

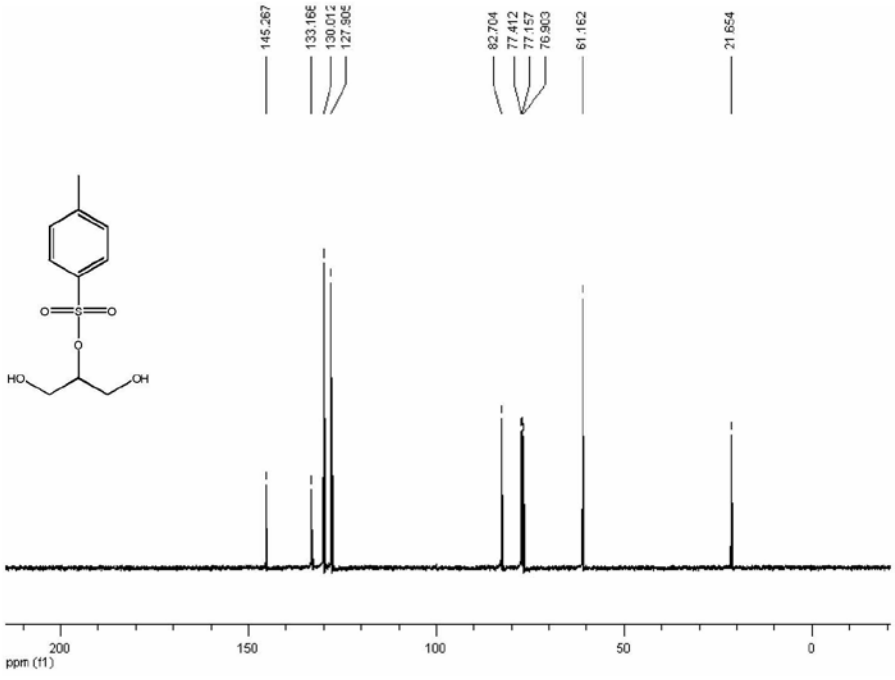


Figure S8. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of TPD.

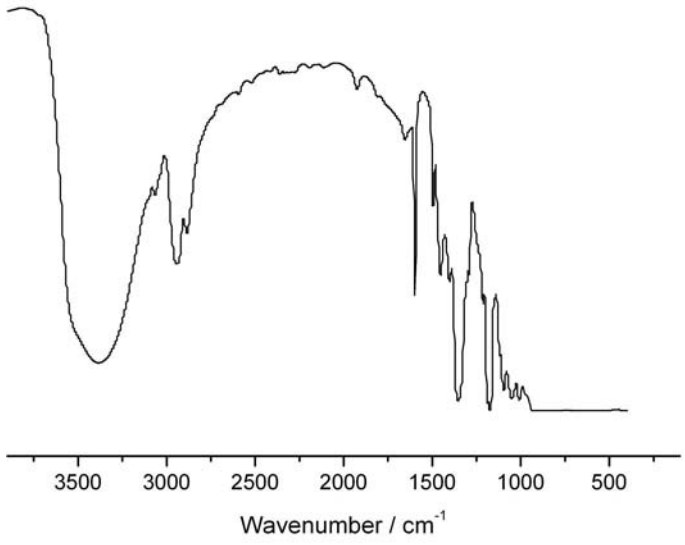


Figure S9. The FTIR spectra of TPD.

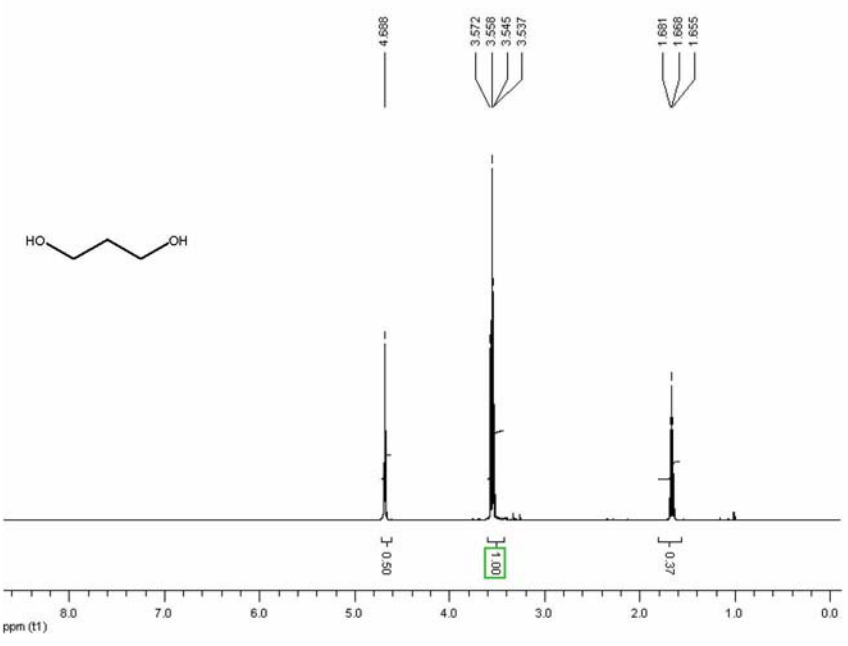


Figure S10. The ^{1}H NMR (500 MHz, D_2O) spectrum of 1,3-PD.

Typical GC analysis of the TPD hydrogenolysis reaction

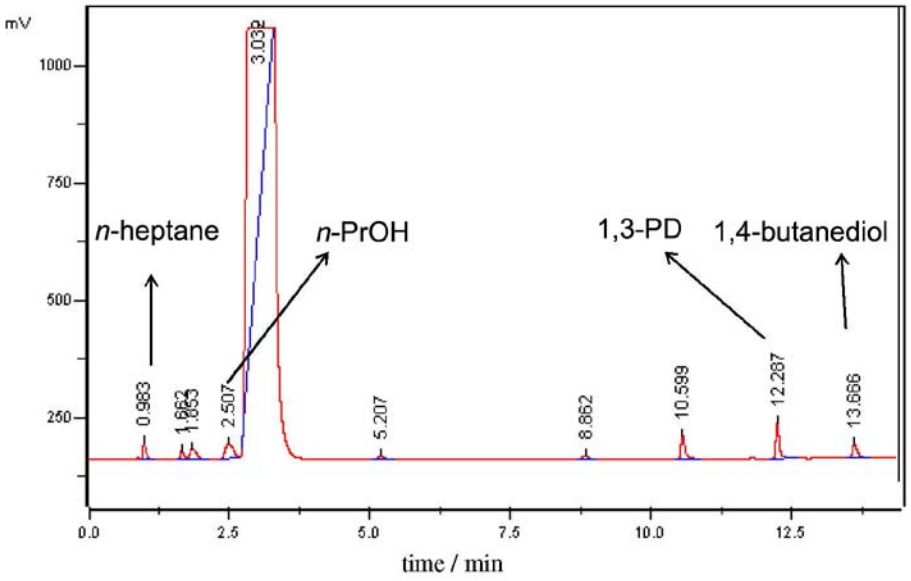


Figure S11. The standard GC spectrum of 1,3-PD and *n*-PrOH (the internal standards: *n*-heptane and 1,4-butanediol).

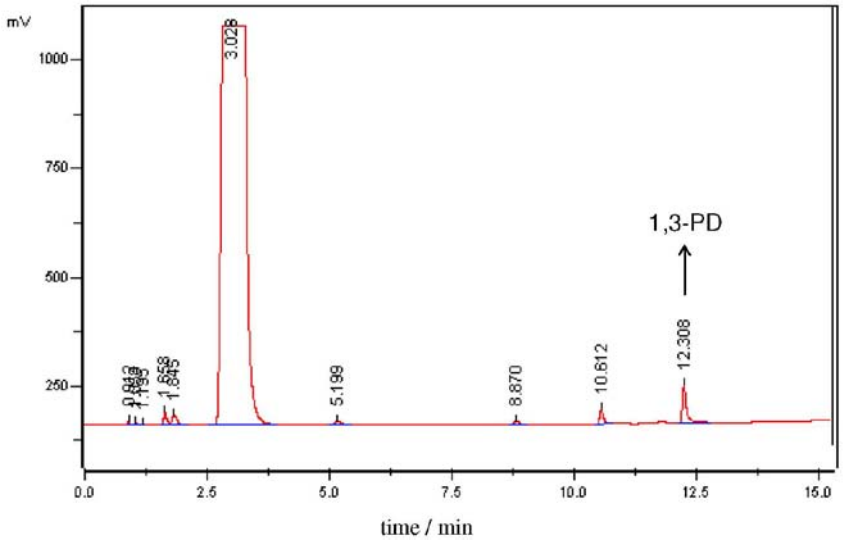


Figure S12. The GC spectrum of 1,3-PD hydrogenolysis (2 wt.% of 1,3-PD in dioxane, 140 °C, 0.8 g Raney Ni, 5 MPa H_2, 4 h).

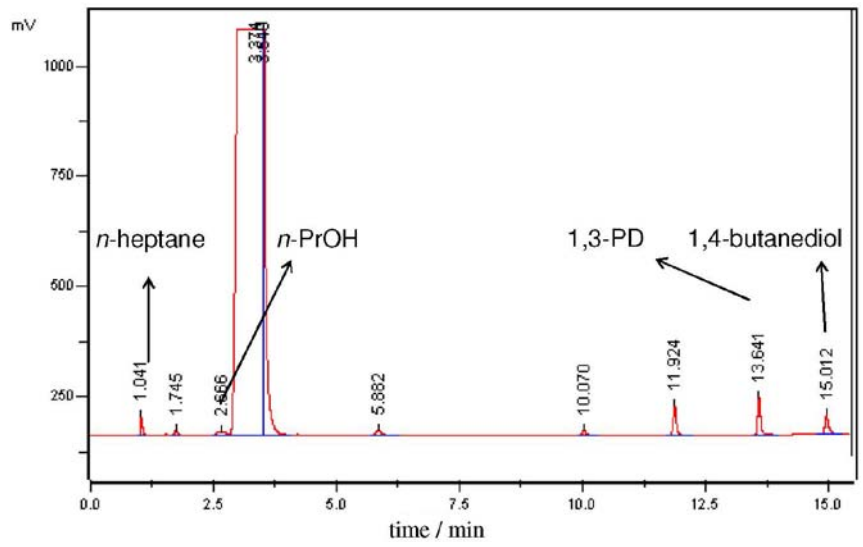


Figure S13. The GC spectrum of TPD hydrogenolysis (2 wt.% of TPD in dioxane, 140 °C, 0.8 g Raney Ni, 1 MPa H_2, 8 h).

The MS spectra of all products observed for TPD hydrogenolysis, including those from Scheme 4

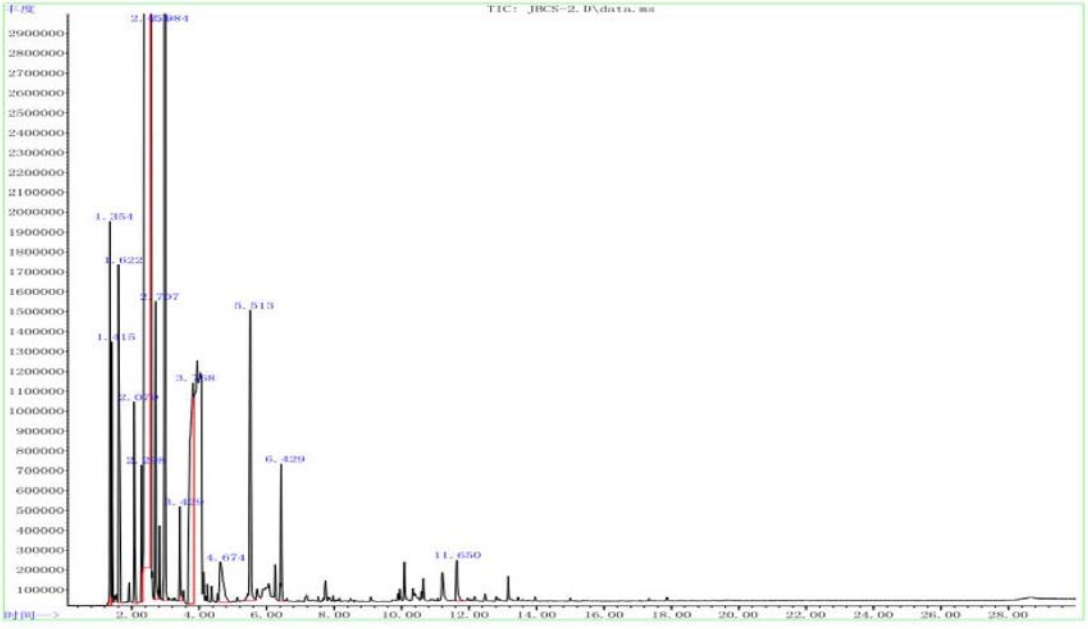
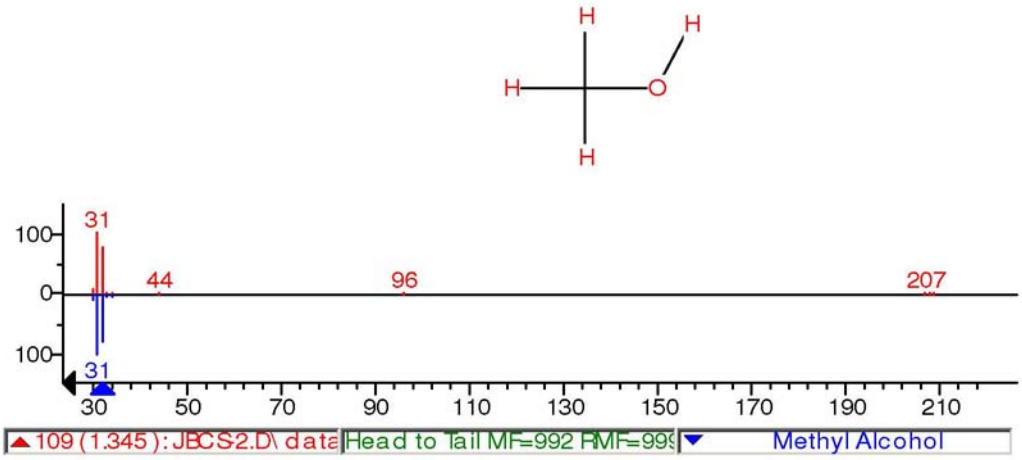
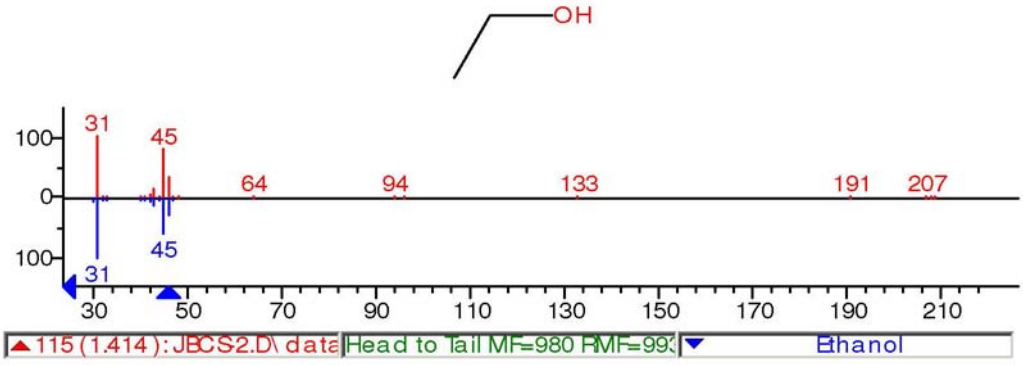


Figure S14. TIC and MS spectrum of TPD hydrogenolysis (140 °C, 20 wt.% TPD concentration, 40 wt.% Raney Ni of TPD, 1 MPa H_2, 8 h).

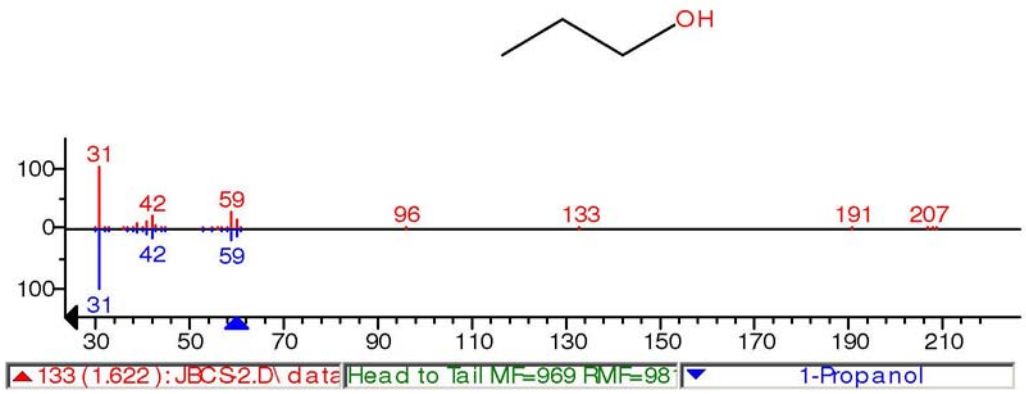
t_R = 1.345 (derived from the TPD prepararion)



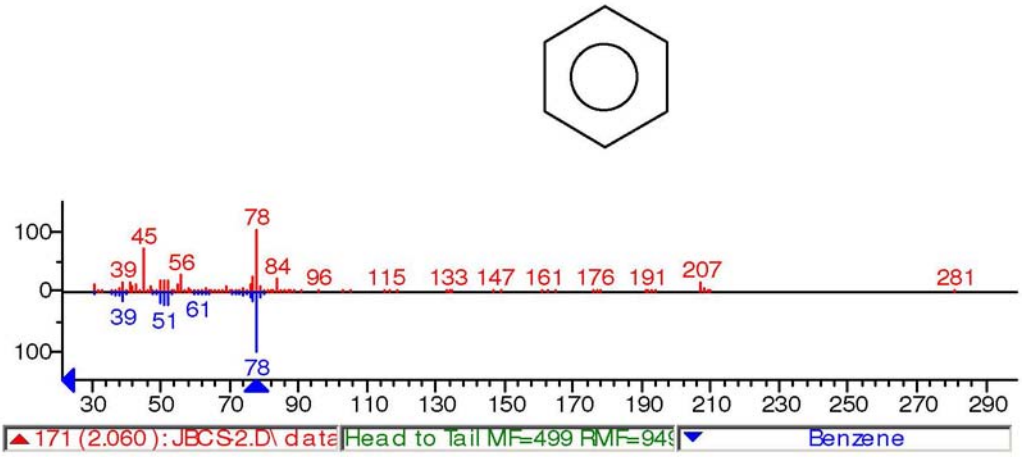
t_R = 1.415



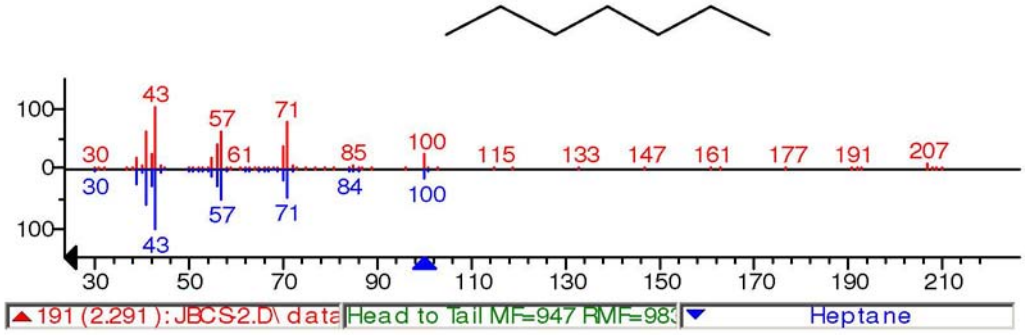
t_R = 1.622



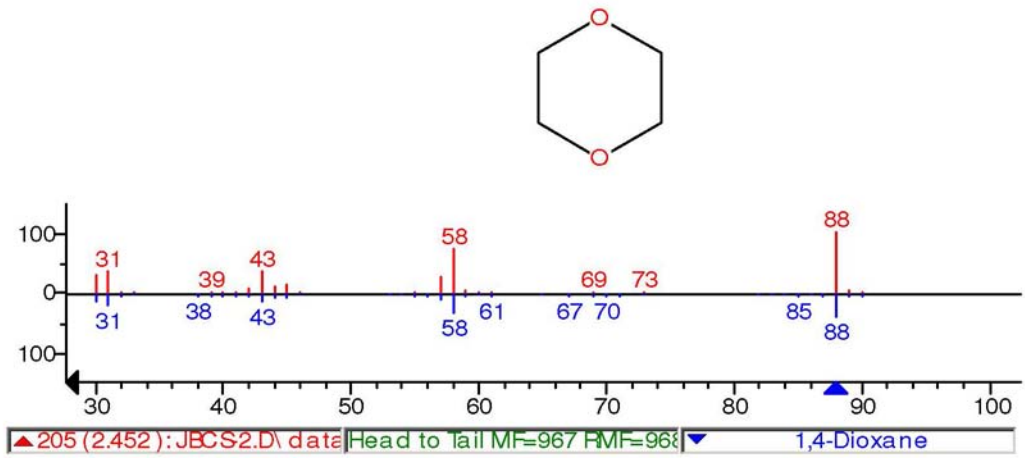
t_R = 2.079 (derived from the solvent)



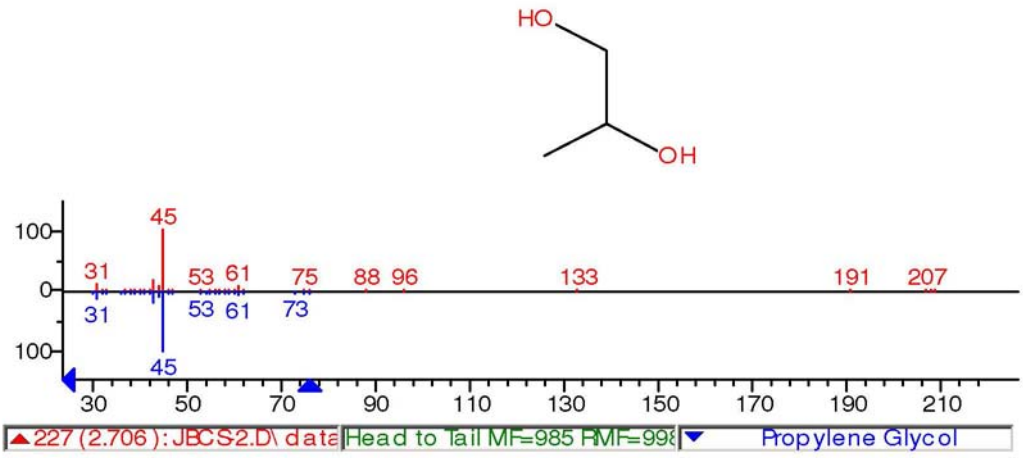
t_R = 2.985 (the internal standard substance)



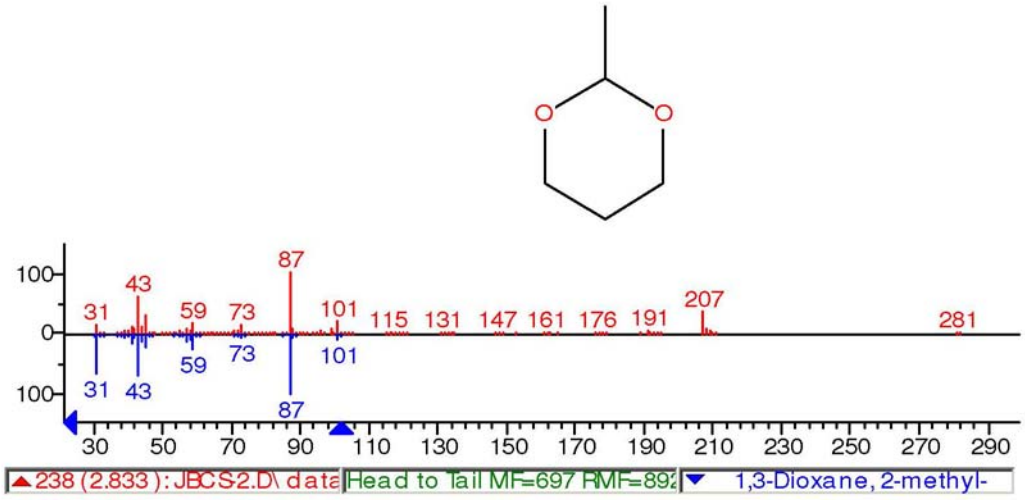
t_R = 2.451 (solvent)



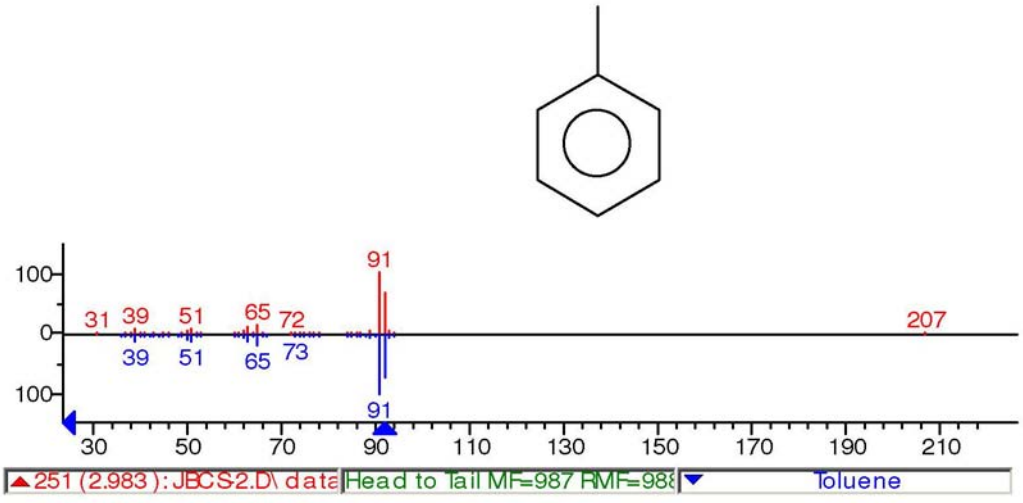
t_R = 2.707



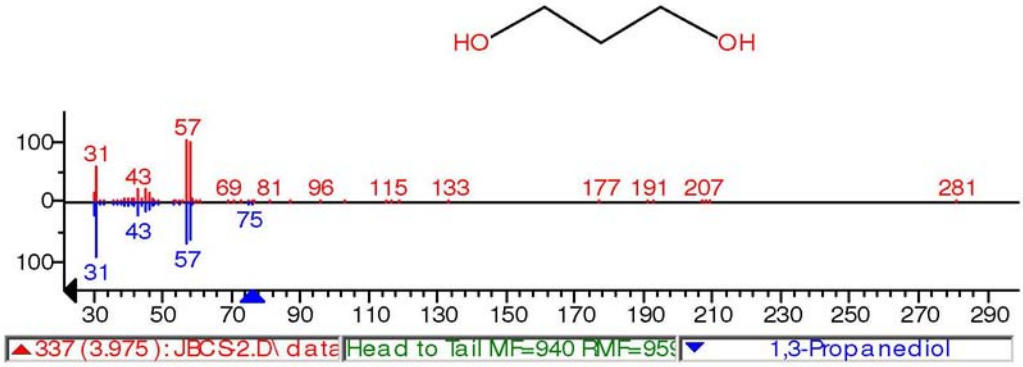
t_R = 2.833



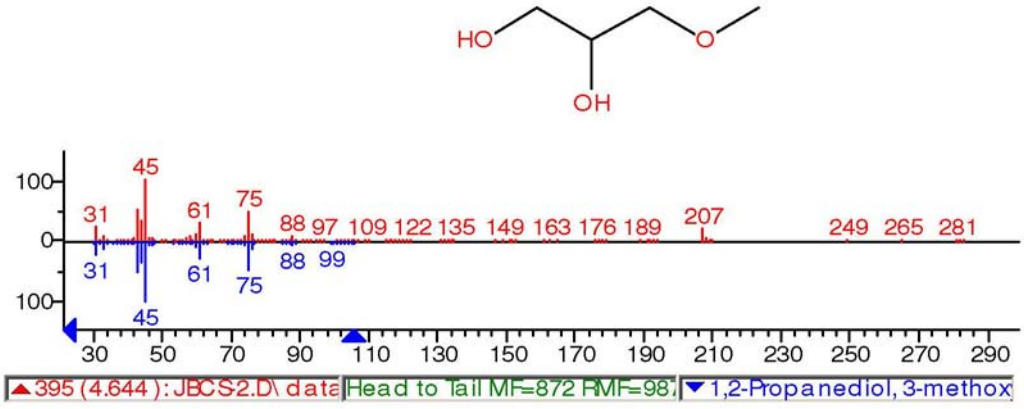
t_R = 2.984 (derived from the solvent)



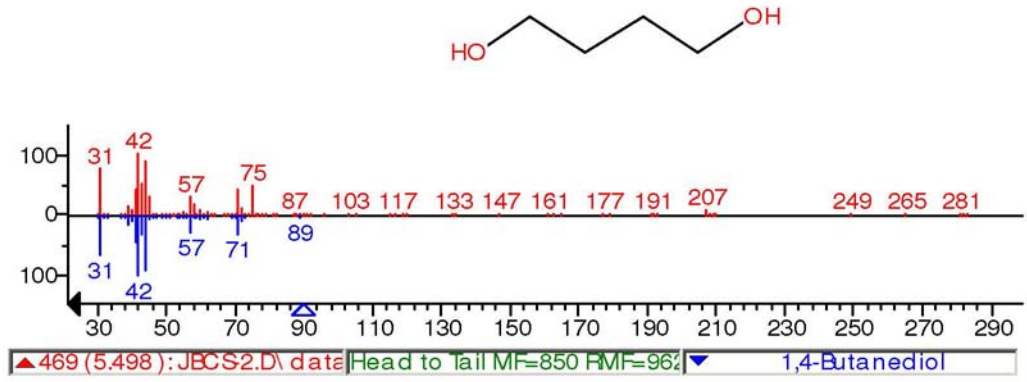
t_R = 3.768



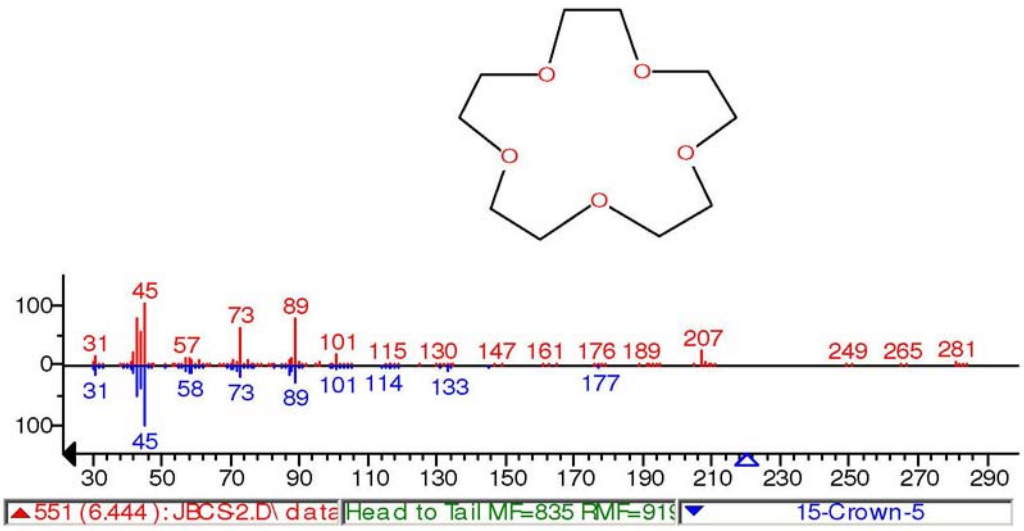
t_R = 4.764



t_R = 5.513 (the internal standard substance)



t_R = 6.429 (derived from the solvent)



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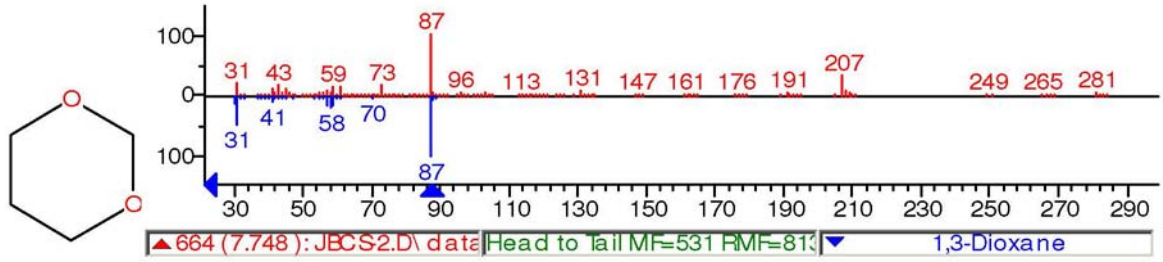

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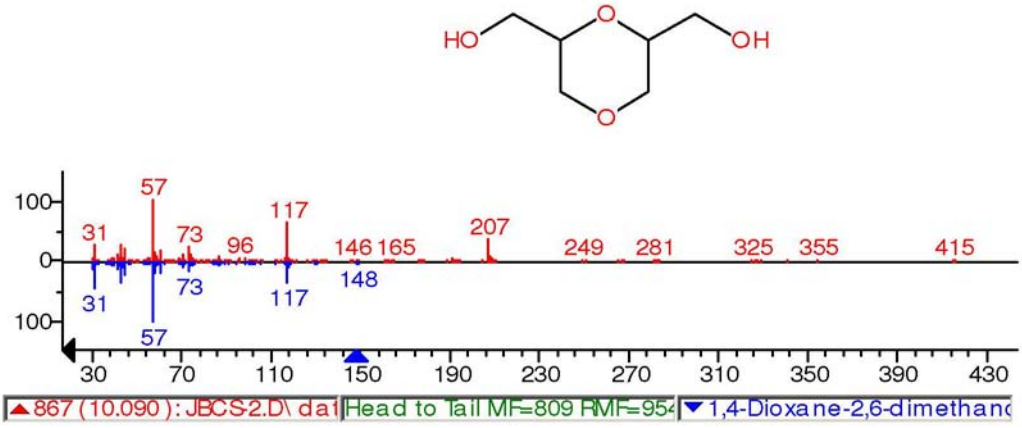

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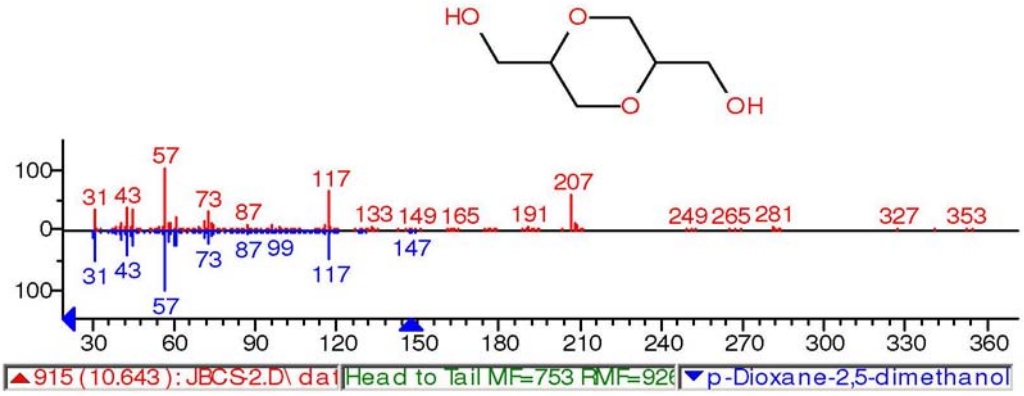

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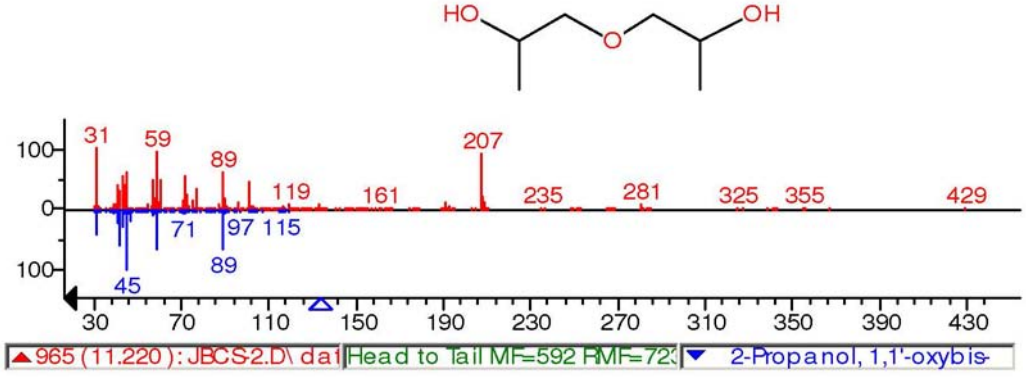

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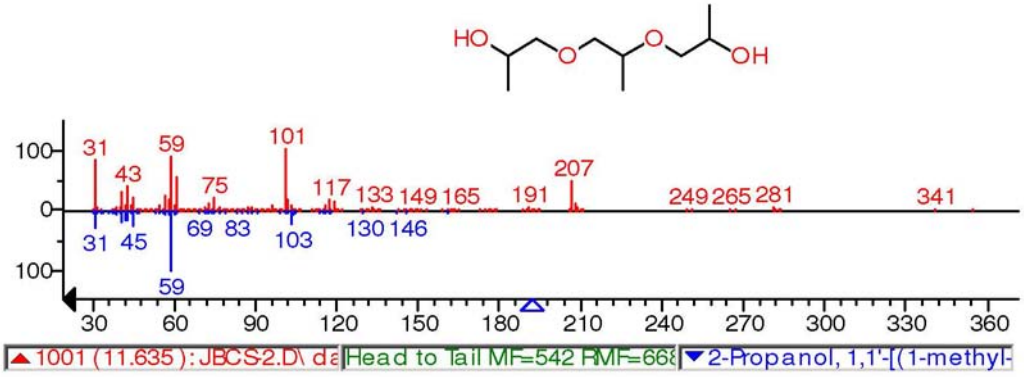
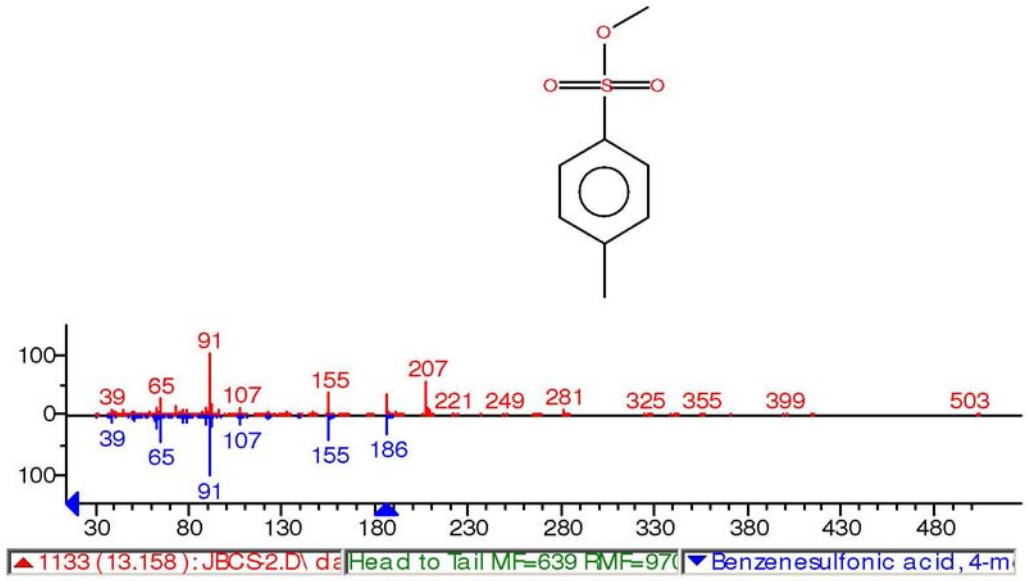


$t_R = 13.158$



References

1. Zheng, Z.; Luo, M.; Yu, J. E.; Wang, J. L.; Ji, J. B.; *Ind. Eng. Chem. Res.* **2012**, *51*, 3715.