Supporting Information for

$[Cp^*Ru(CO)_2]_2$-Catalyzed Hydrodeoxygenation and Hydrocracking of Diols and Epoxides

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Experimental Procedure

General: Ruthenium powder (99.95%) was purchased from Strem chemicals. All other chemicals were purchased from Sigma Aldrich. $[Cp^*Ru(CO)_2]_2$ was prepared by literature method.[1] All other chemicals were purchased from Sigma Aldrich and used as received. Deoxydehydration reactions were performed in a 100 mL and 50 mL Parr steel autoclave (model 4792) fitted with glass liner.

Representative Procedure for $[Cp^*Ru(CO)_2]_2$-Catalyzed Hydrodeoxygenation and Hydrocracking of Diols and Epoxides

In a Parr steel autoclave, $[Cp^*Ru(CO)_2]_2$ (0.014 mmol) and diol/epoxide (0.14 mmol) and 5 μL dodecane (internal standard) were added to anhydrous benzene (6-10 mL). The autoclave was pressurized to desired pressure (60, 100, 300 psi) with molecular hydrogen and placed on a preheated oil bath to desired temperature (170º,

200℃). The aliquots of samples were withdrawn at desired intervals and analyzed by GC and GC-MS.

Analytical methods

Gas chromatography. Gas chromatography was performed with an HP GC system (model series II 5890) with capillary column β-dex (Supelco) an FID detector and with a thermal program of 40°C (5 min); 10°/min to 170°C. Product concentrations were calculated from GC calibration curves (lines) of alkene/dodecane weighed concentrations.

G.C.- M.S. GC-MS was performed on Agilent (GC model 7890, MS 5975C VL MSD with triple-axis detector) using a nonpolar Agilent column (model number 19091S-433). Various oven temperature programs were used depending upon the nature of products: i) 35°C (5 min); 10°C/min to 170°C; ii) 40°C, (5 min); 10°C/min to 170°C, and iii) 50°C (3 min); 10°C/min to 250°C then 5 min at 250°C.

Isolation of ethyl benzene: After completion of the reaction, the autoclave was allowed to cool at room temperature. The reaction mixture was purified by column chromatography using hexane as eluent. Since the product (Ethyl benzene, BP: 136 ^{o}C) cannot be identified by thin layer chromatography (TLC), all column fractions were subjected for GC analysis to find the product. We combined all the fractions containing product. The solvent was reduced partially under vacuum and the rest is left open at room temperature to minimize the hexane. The left over residue was used for NMR analysis and confirmed the presence of ethyl benzene.

Recovery of catalyst: We made an effort to recover Ru-species at the end of reaction. We choose our standard substrate, 1-phenyl-1.2-ethandiol, for the recovery of catalyst at the end of reaction. We isolated black solids at the end of 8h cycle and 24h cycle of reaction. Both materials were washed with acetone followed by diethyl ether and vacuum dried. The material did not show any catalytic activity when subjected to same reaction conditions. IR and ^{1}H-NMR of this substance is inconclusive.

Reference

1. King R.B.; Iqbal, M.Z.; King Jr., A.D. *J. Organomet. Chem.*, **1979**, 171, 53.

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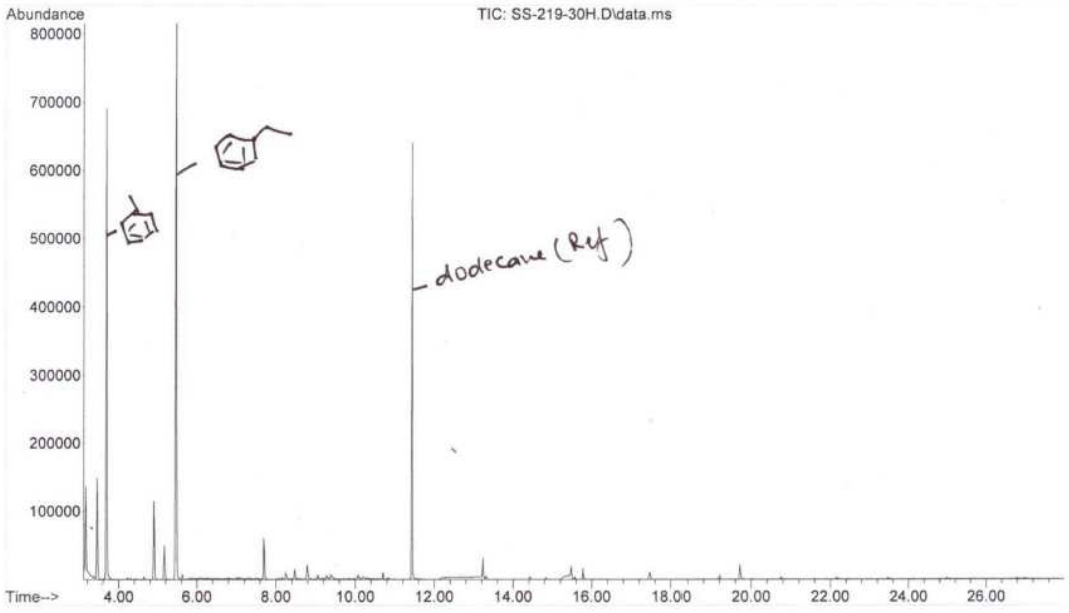

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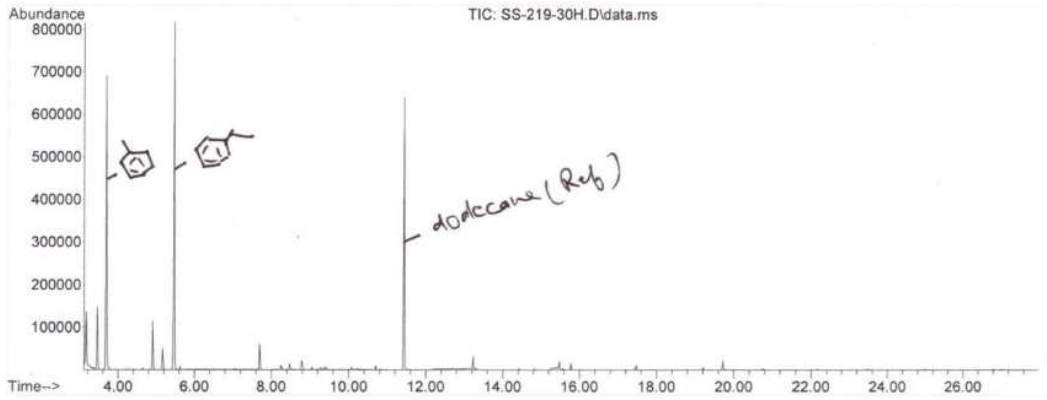

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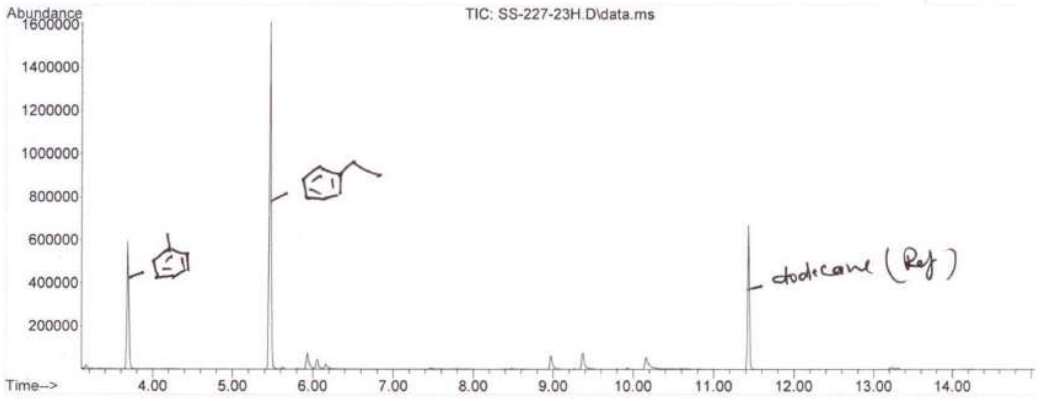

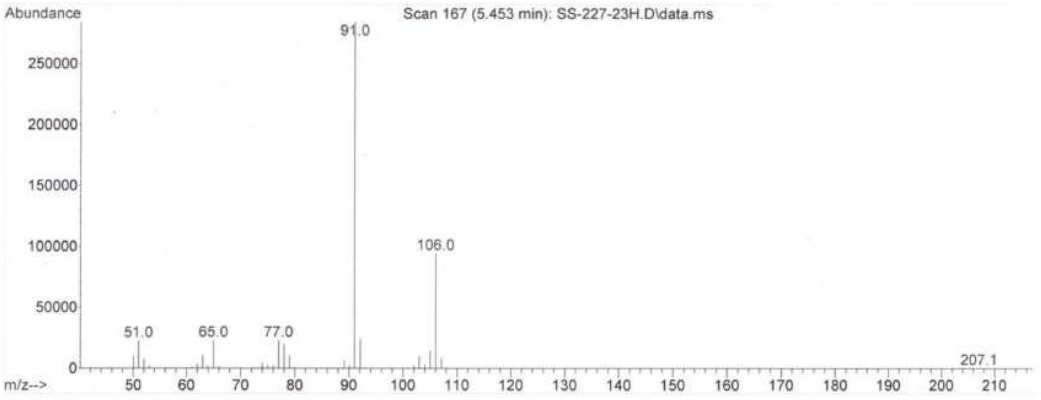

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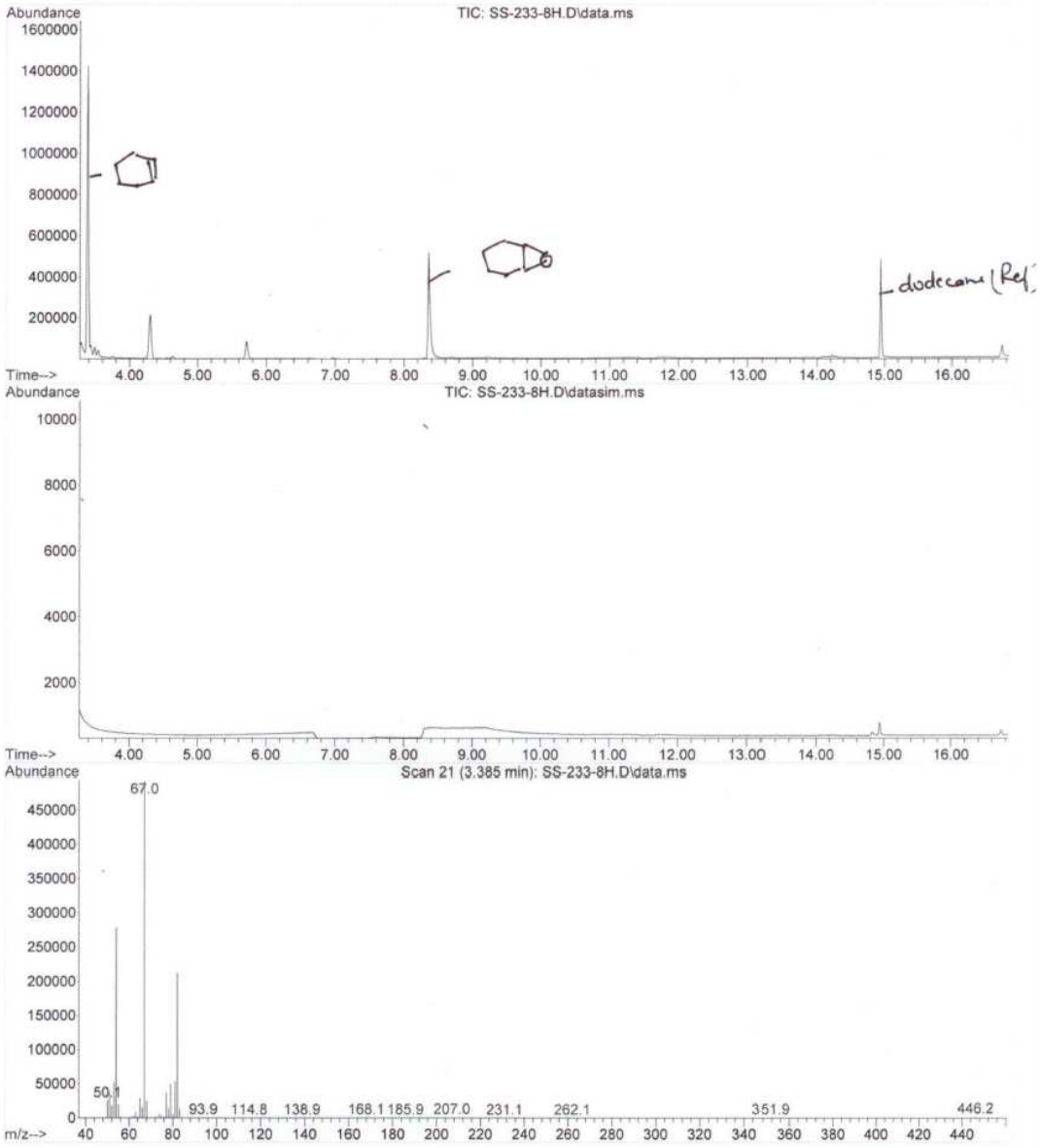

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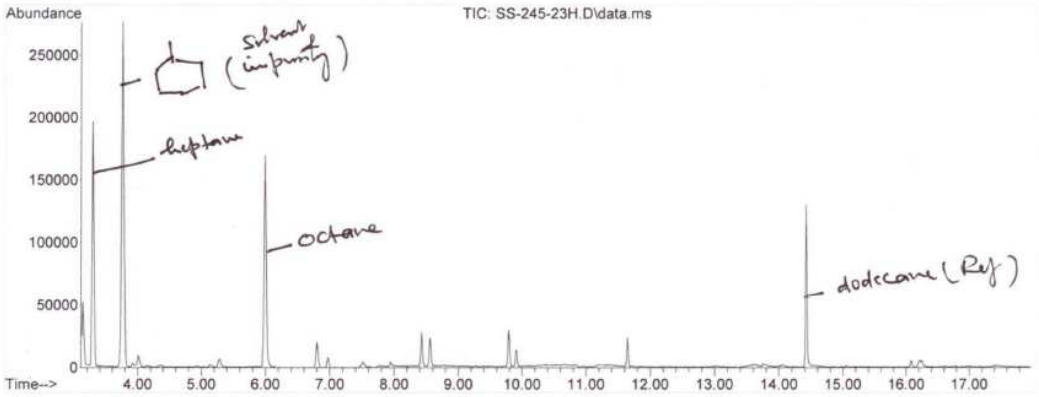

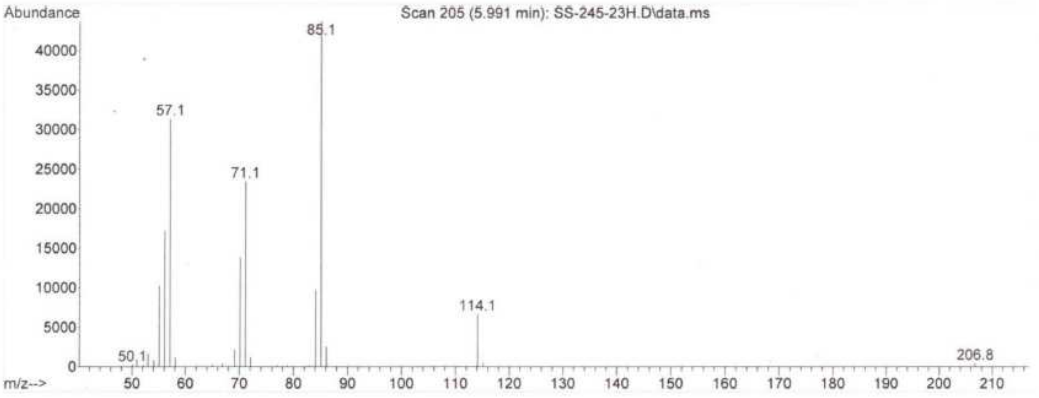

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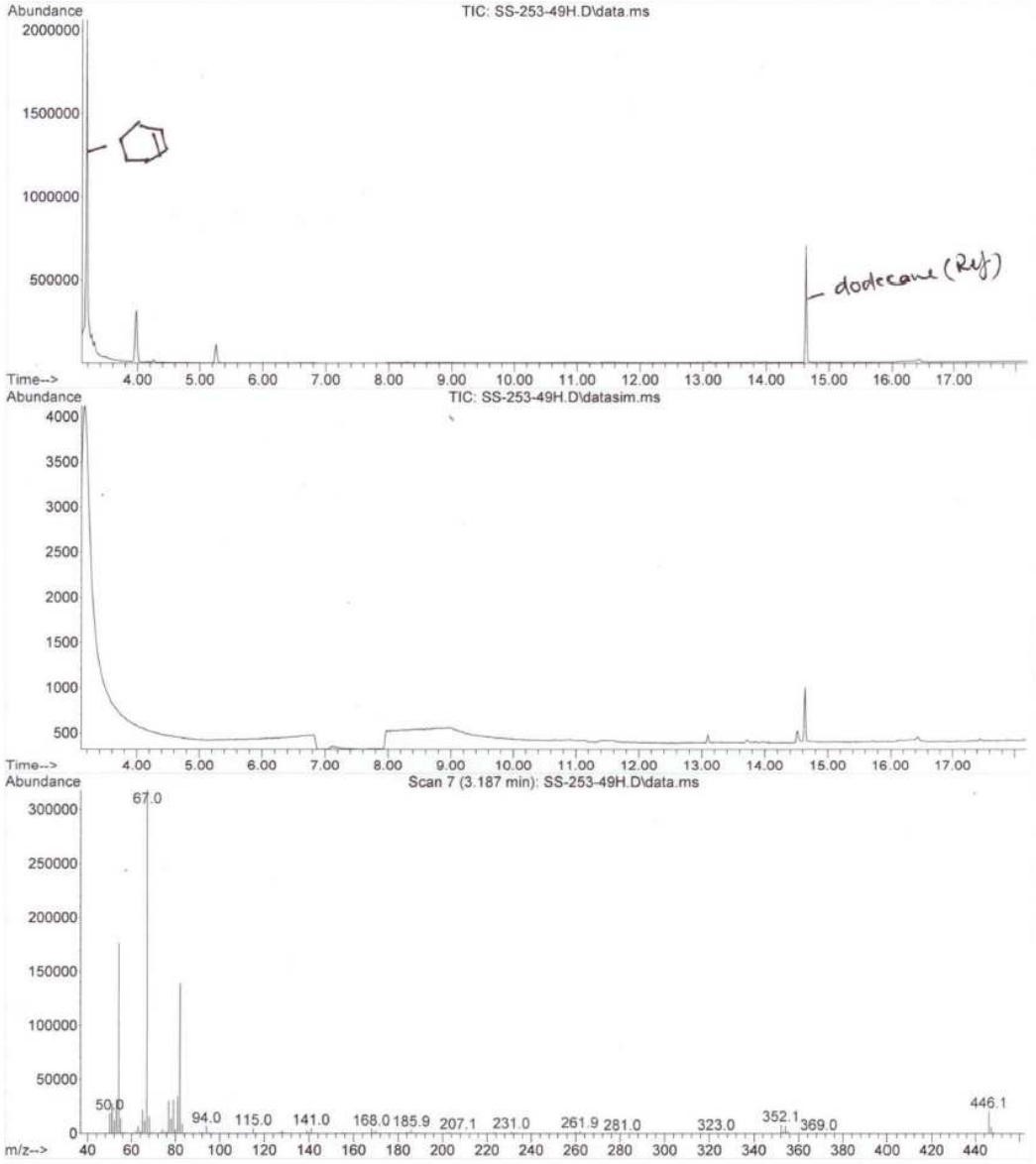

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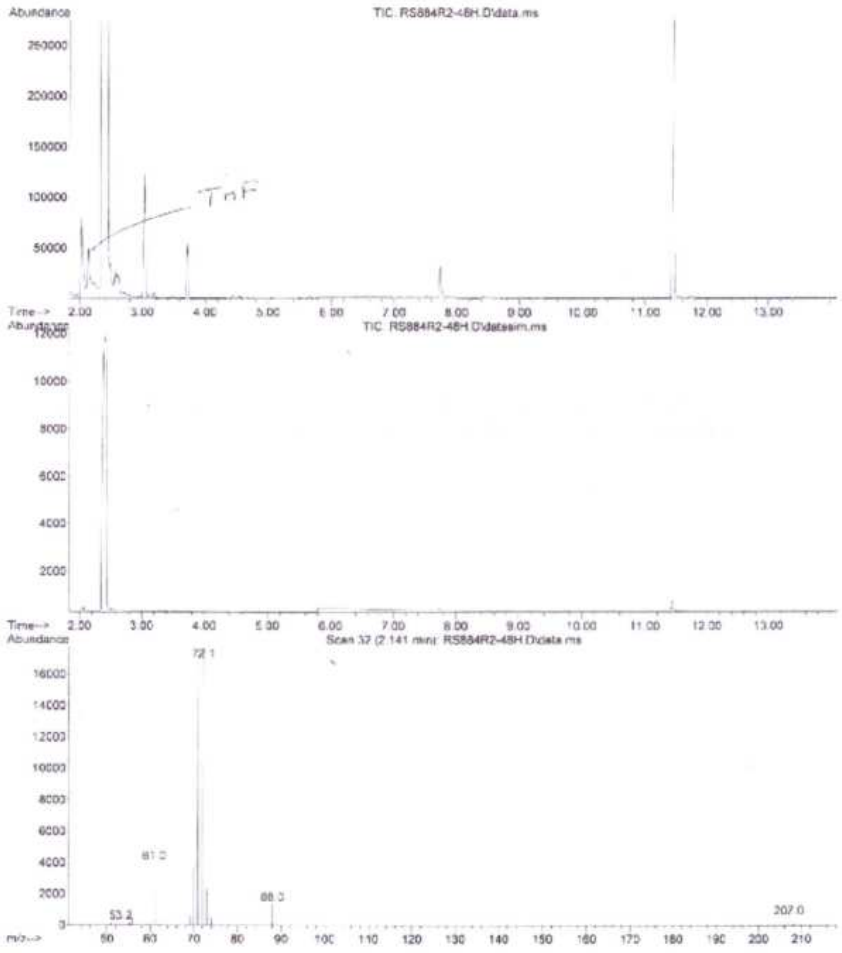

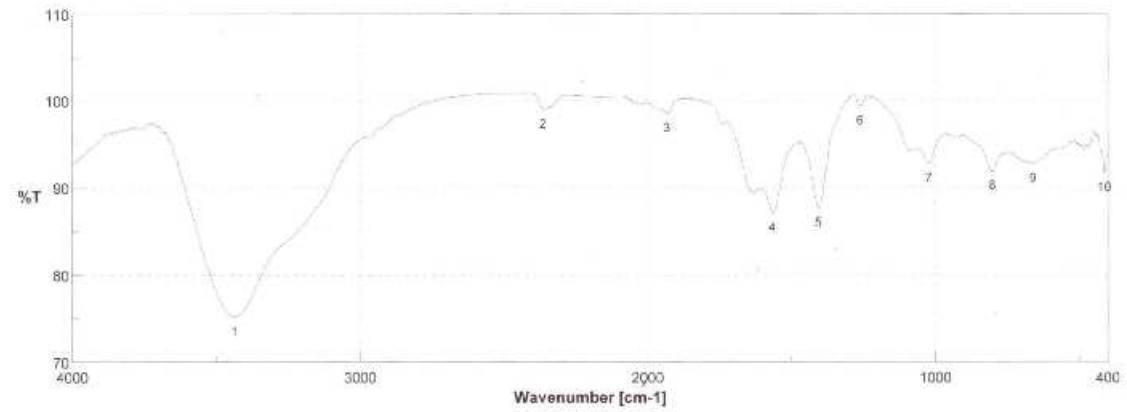

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Operator			
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Sample Name	Background		
Comment			

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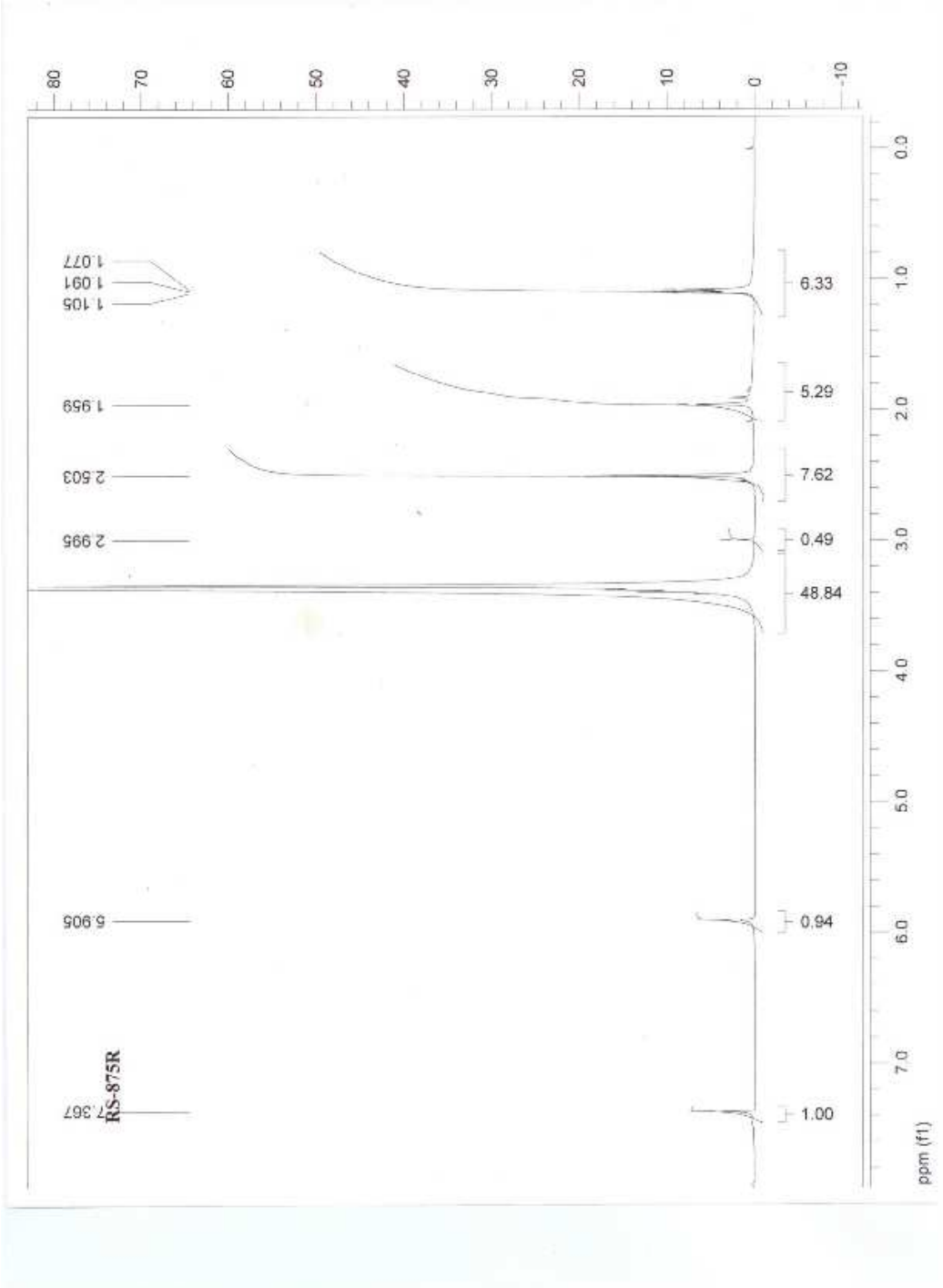
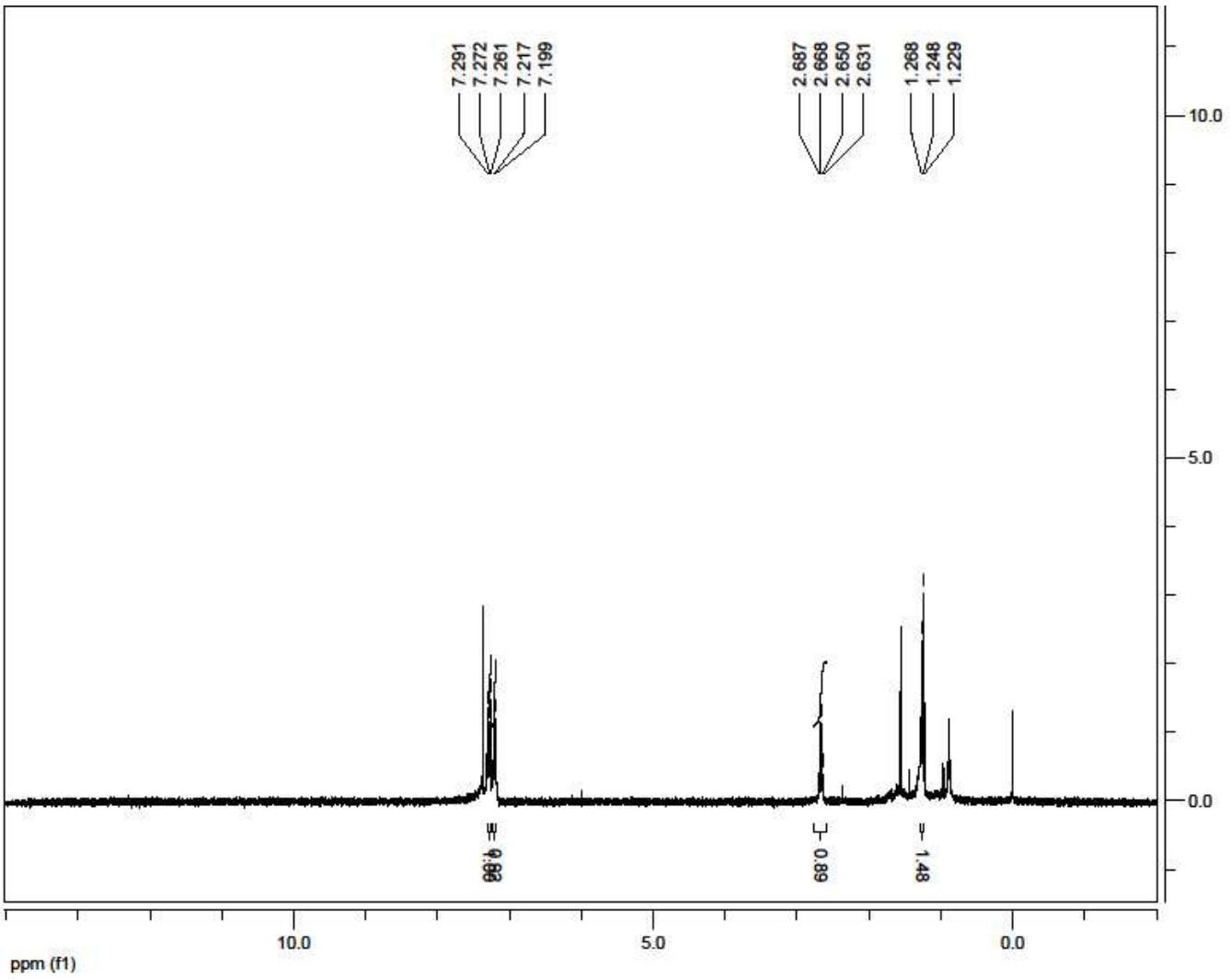
6	1262.18	99.3913	7	1023.05	92.7278	8	801.278	91.8862	9	660.5	92.7341	10	412.892	91.7039

RS 875R (Black solid)

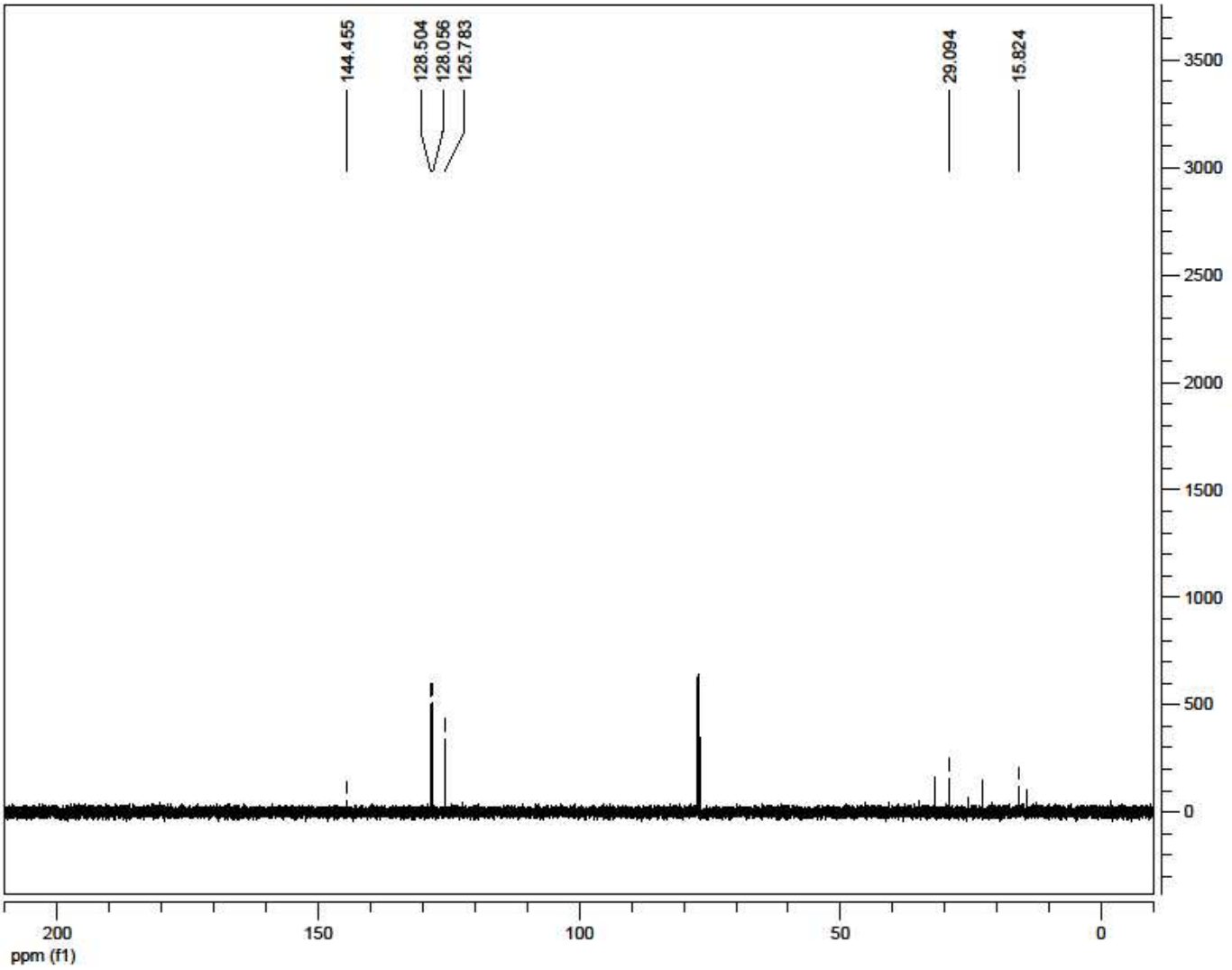
IR of solid (black) material recovered after reaction



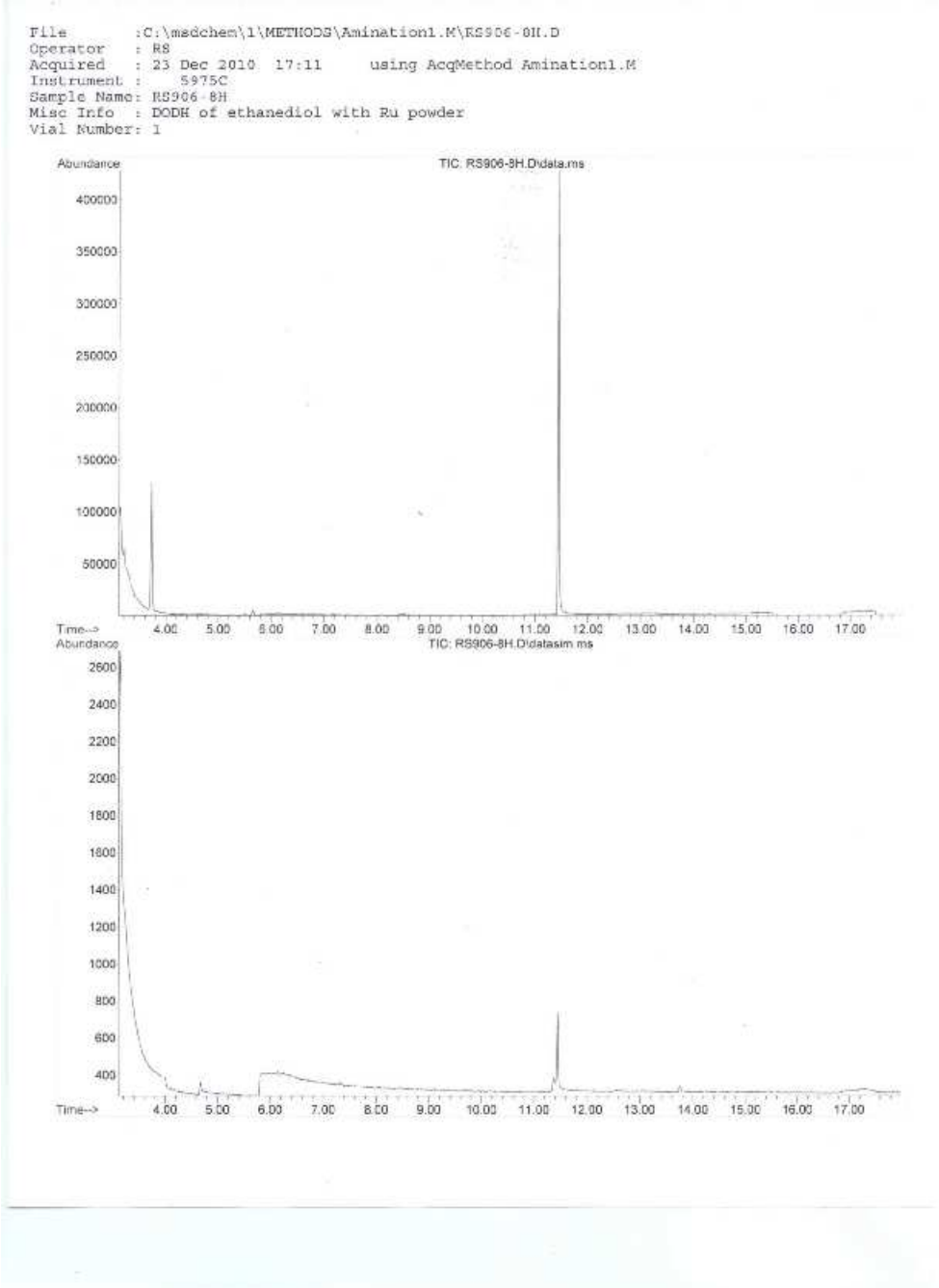
^{1}H-NMR of solid (black) material recovered after reaction



^{1}H-NMR of ethyl benzene



^{13}C-NMR of ethyl benzene



Catalytic DODH of 1-phenyl-1,2-ethanediol with ruthenium-powder