

Supporting Information

Ag⁺ Assisted Hydrosilylation – Complementary Behavior of Rh and Ir Catalysts (Reversal of Enantioselectivity)

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Table of Contents

p. S2:	General experimental methods
p. S2:	General procedure for the hydrosilylation of prochiral ketones
p. S2:	1-Phenylethanol
p. S3:	1-(4-Bromophenyl)ethanol
p. S3:	1-(4-Methoxyphenyl)ethanol
p. S3:	4-Phenyl-2-butanol
p. S3:	2-Octanol
p. S4:	¹ H NMR spectrum of 1-phenylethanol
p. S4:	¹³ C NMR spectrum of 1-phenylethanol
p. S5:	¹ H NMR spectrum of 1-(4-bromophenyl)ethanol
p. S5:	¹³ C NMR spectrum of 1-(4-bromophenyl)ethanol
p. S6:	¹ H NMR spectrum of 1-(4-methoxyphenyl)ethanol
p. S6:	¹³ C NMR spectrum of 1-(4-methoxyphenyl)ethanol
p. S7:	¹ H NMR spectrum of 4-phenyl-2-butanol
p. S7:	¹³ C NMR spectrum of 4-phenyl-2-butanol
p. S8:	¹ H NMR spectrum of 2-octanol
p. S8:	¹³ C NMR spectrum of 2-octanol
p. S9:	References

General Experimental Methods. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Tetrahydrofuran was taken from a Glass-contour solvent dispensing system. Flash chromatography was performed using silica gel 60H. ¹H NMR spectra were recorded at 500 or 400 MHz, ¹³C NMR spectra at 125 or 100 MHz, and ³¹P NMR spectra at 202 MHz. Acetophenone was purified by distillation. All other commercially available compounds were used without further purifications. Compounds **1-4** were synthesized according to our previously published procedures.¹ Compound **5** was synthesised in a way similar to that used for compounds **1-4** and was in that way obtained having identical spectroscopic properties to those published previously.²

General procedure for the hydrosilylation of prochiral ketones. Ligand (0.020 mmol, 2.0 mol %), [M(cod)Cl]₂ (0.0050 mmol, 1.0 mol % M) and if suitable AgBF₄ (3.89 mg, 0.020 mmol, 2.0 mol %) were suspended in THF (1 mL) and stirred for 1 h at rt. Ketone (1.0 mmol) was added. Diphenylsilane (223 μL, 1.2 mmol, 1.2 equiv.) was added dropwise and the mixture was stirred at the reported reaction temperature for the appropriate time. Samples were taken and analyzed by ¹H NMR to determine the conversion and the yield of silyl enol ether, which upon hydrolysis is converted back to starting material. MeOH (1 mL) and a catalytic amount of TsOH were added and the mixture was stirred at rt for 16 h. Et₂O (4 mL) was added and the mixture was filtered through a silica pad. A sample was taken for chiral GC or HPLC analysis. The solution was concentrated and the product purified by flash chromatography on silica gel (eluent: ether/pentane 1/6) to yield the secondary alcohol as a colorless oil.

1-Phenylethanol. The yield of silyl enol ether was in all cases below 15% and normally below 5%. Enantiomeric excesses were determined by GC analysis using a chiral column [Chiraldex, G-TA (gamma cyclodextrin trifluoroacetyl), 30 m x 0.25 mm, 90 °C, t_R (S) = 10.6 min, t_R (R) = 11.5 min]. Absolute configurations were assigned by comparing the sign of optical rotation with literature data.³

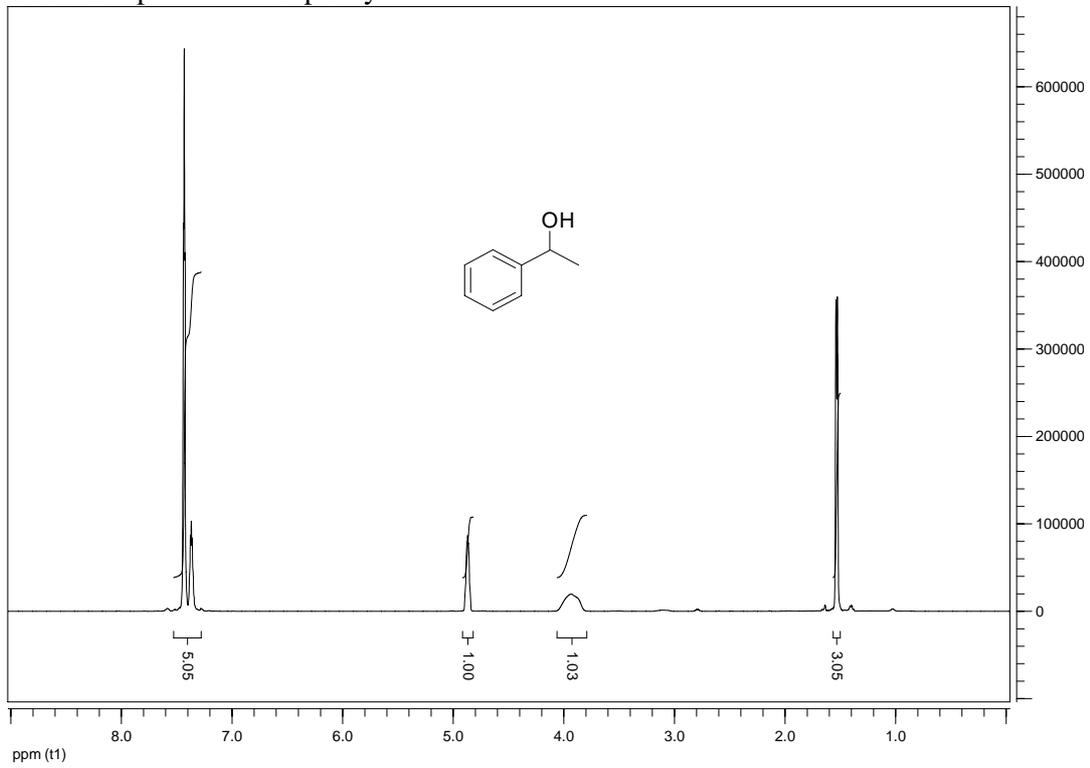
1-(4-Bromophenyl)ethanol. The ketone was added from the start and was present during the catalyst formation. The yield of silyl enol ether was in all cases below 6%. Enantiomeric excesses were determined using a chiral OD-H (0.46 cm Ø × 25 cm) HPLC column (eluent: degassed 2-propanol/hexane 10/90), flow rate: 0.5 mL/min, UV detection at 220 nm, t_R (*S*) = 18.3 min, t_R (*R*) = 19.5 min. Absolute configurations were assigned by comparing the sign of optical rotation with literature data.⁴

1-(4-Methoxyphenyl)ethanol. The ketone was added from the start and was present during the catalyst formation. The yield of silyl enol ether was in all cases below 4%. K₂CO₃ was used instead of TsOH as catalyst during the hydrolysis. Enantiomeric excesses were determined by a chiral OD-H (0.46 cm Ø × 25 cm) HPLC column (eluent: degassed 2-propanol/hexane 10/90), flow rate: 0.5 mL/min, UV detection at 220 nm, t_R (*R*) = 23.0 min, t_R (*S*) = 24.0 min. Absolute configurations were assigned by comparing the sign of optical rotation with literature data.⁵

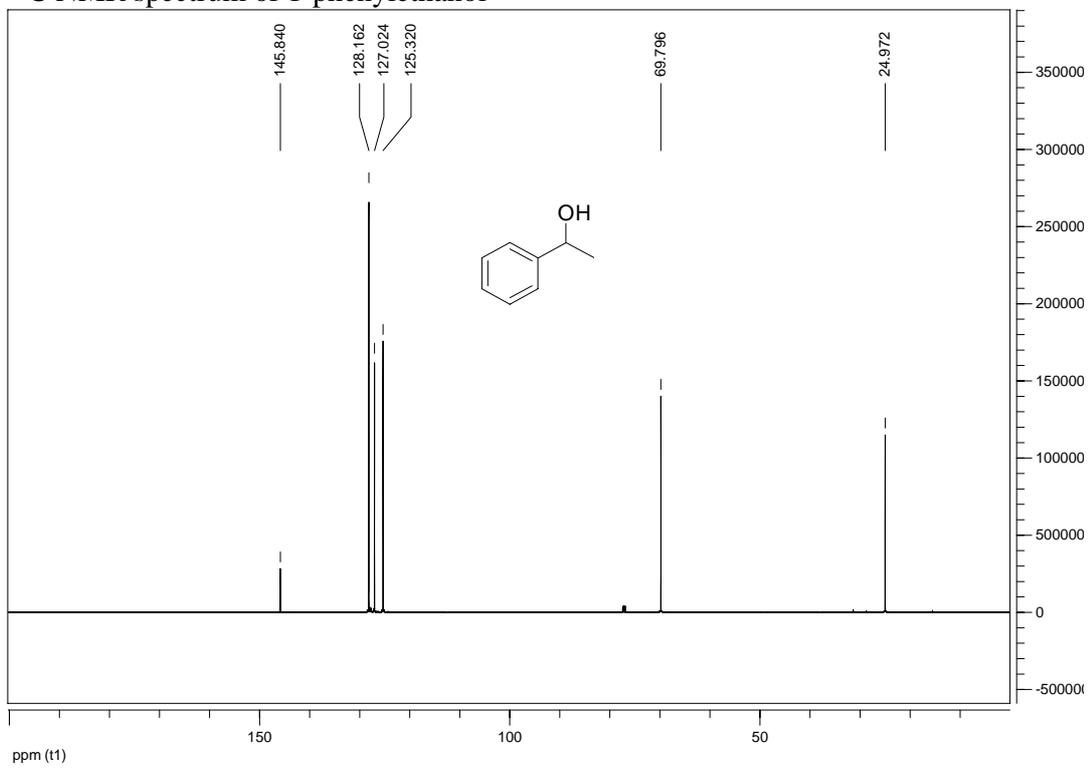
4-Phenyl-2-butanol. The yield of silyl enol ether was in all cases below 3%. Enantiomeric excesses were determined using a chiral OD-H (0.46 cm Ø × 25 cm) HPLC column (eluent: degassed 2-propanol/hexane 10/90), flow rate: 0.5 mL/min, UV detection at 220 nm, t_R (*R*) = 20.8 min, t_R (*S*) = 28.0 min. Absolute configurations were assigned by comparing the sign of optical rotation with literature data.⁵

2-Octanol. The yield of silyl enol ether was in all cases below 3%. Enantiomeric excesses were determined by GC analysis after acetylation using a chiral column [Chiraldex, G-TA (gamma cyclodextrin trifluoroacetyl), 30 m x 0.25 mm, 90 °C, t_R (*S*) = 12.7 min, t_R (*R*) = 13.9 min]. Absolute configurations were assigned by comparing the sign of optical rotation with literature data.³

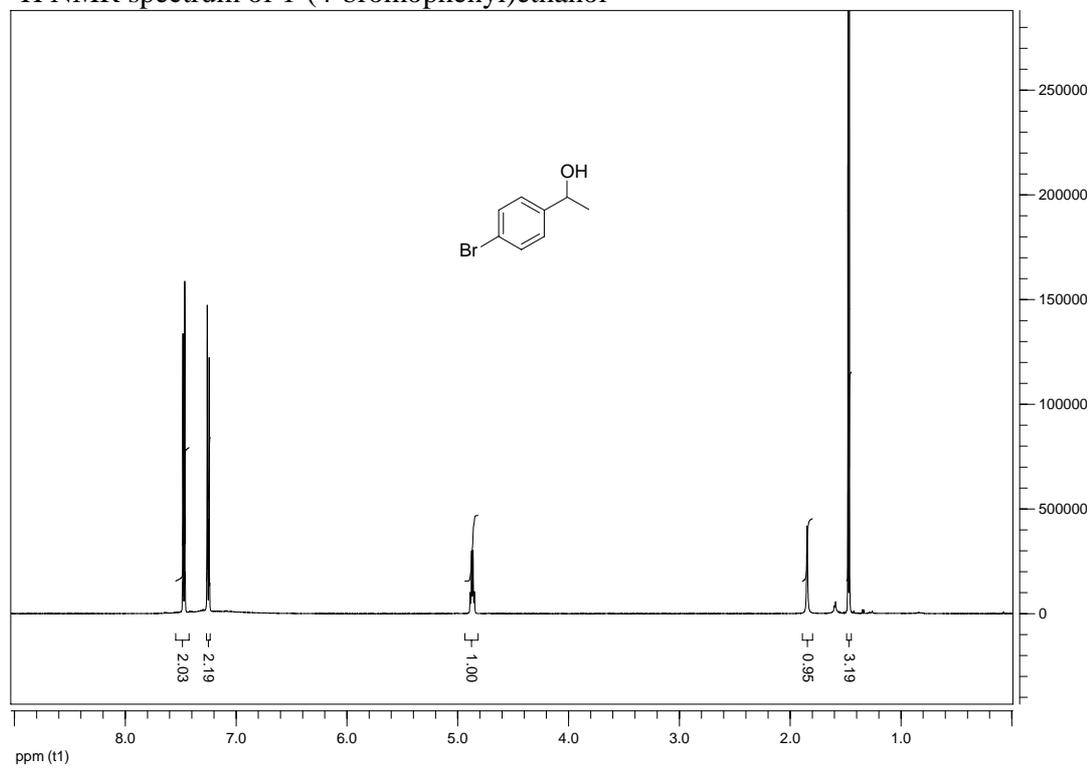
^1H NMR spectrum of 1-phenylethanol



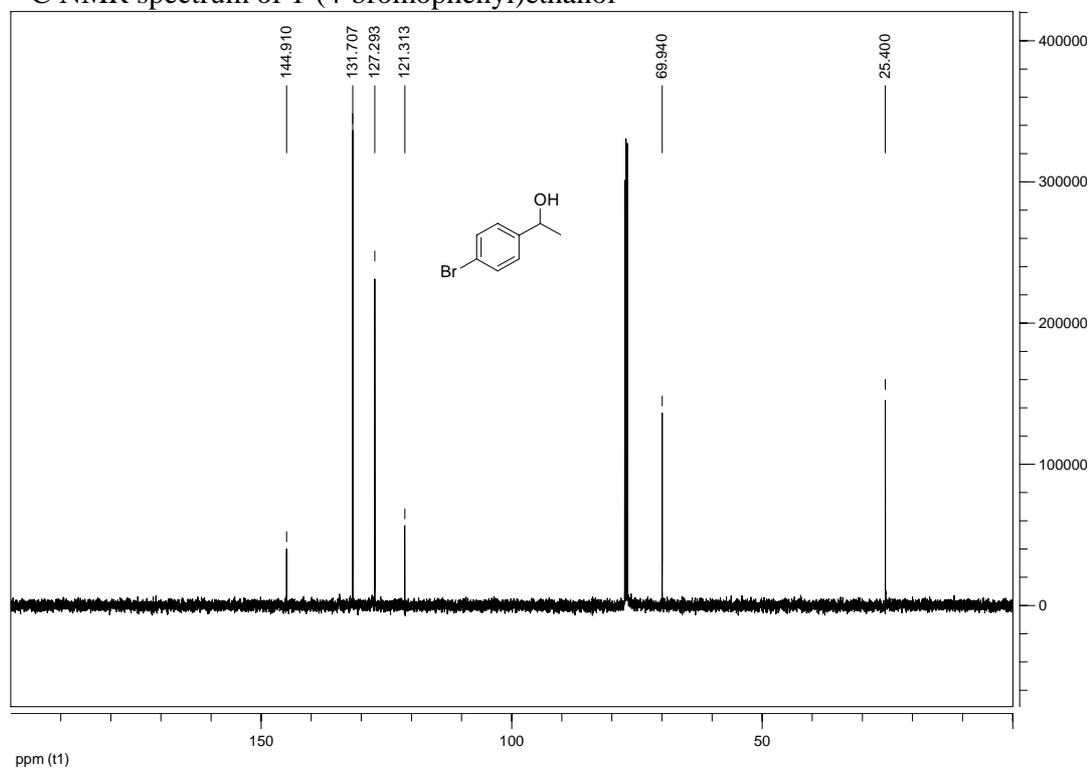
^{13}C NMR spectrum of 1-phenylethanol



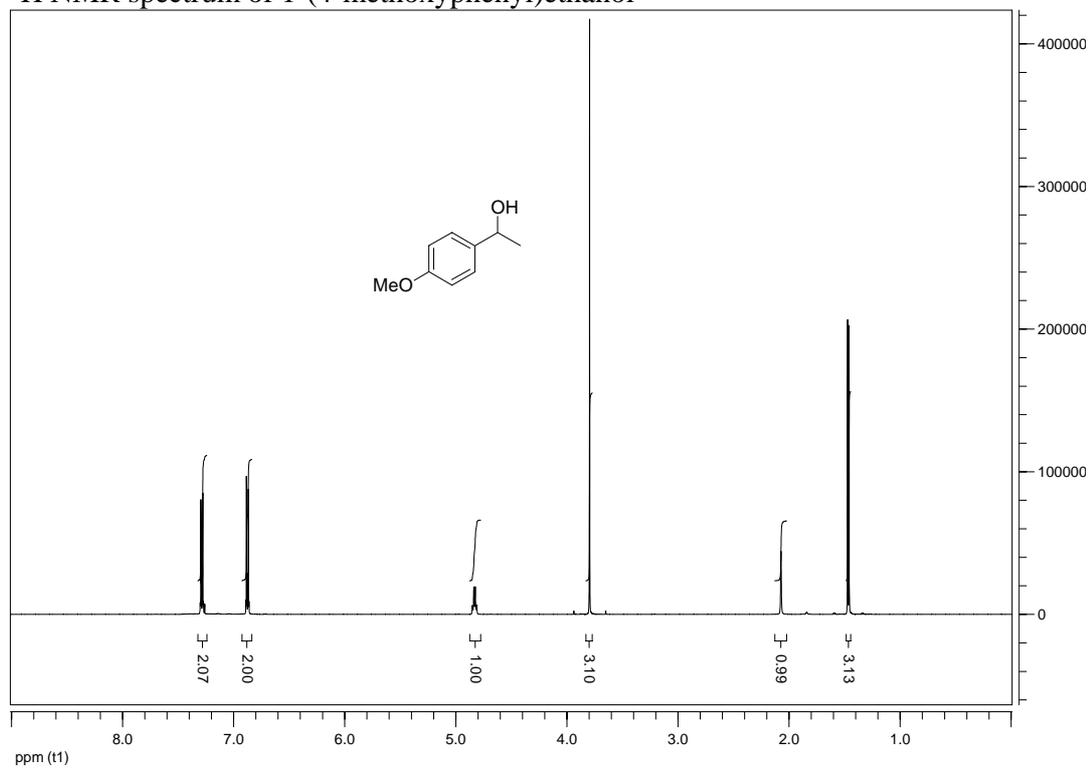
^1H NMR spectrum of 1-(4-bromophenyl)ethanol



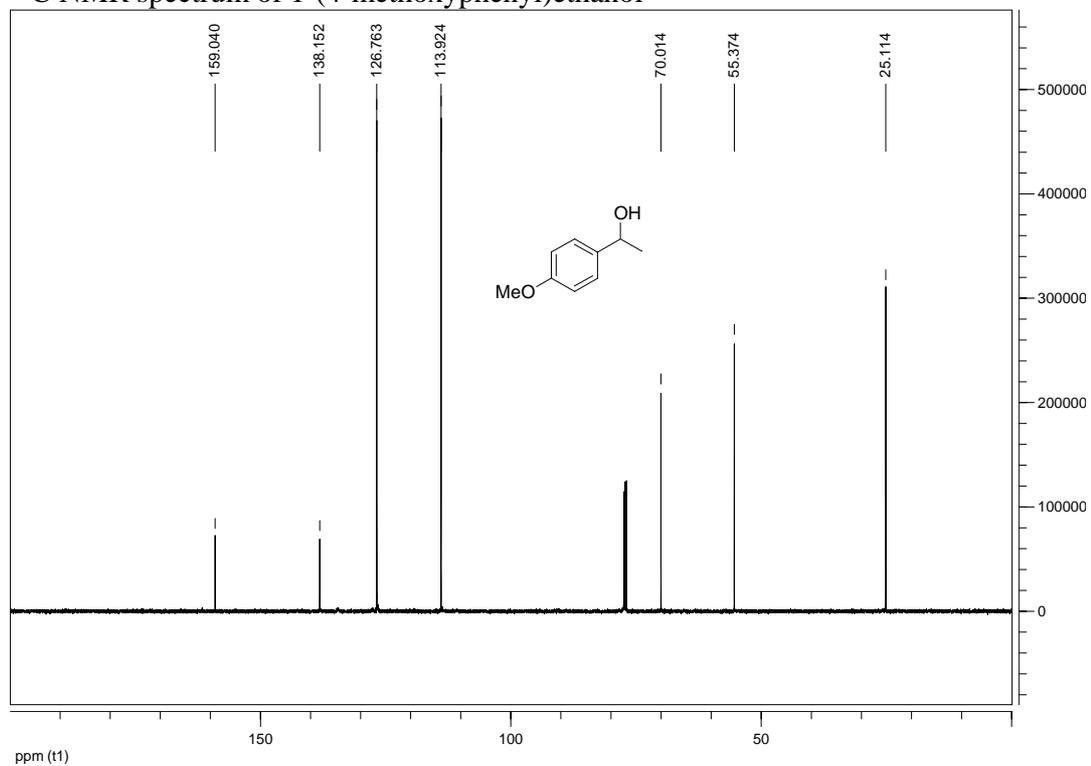
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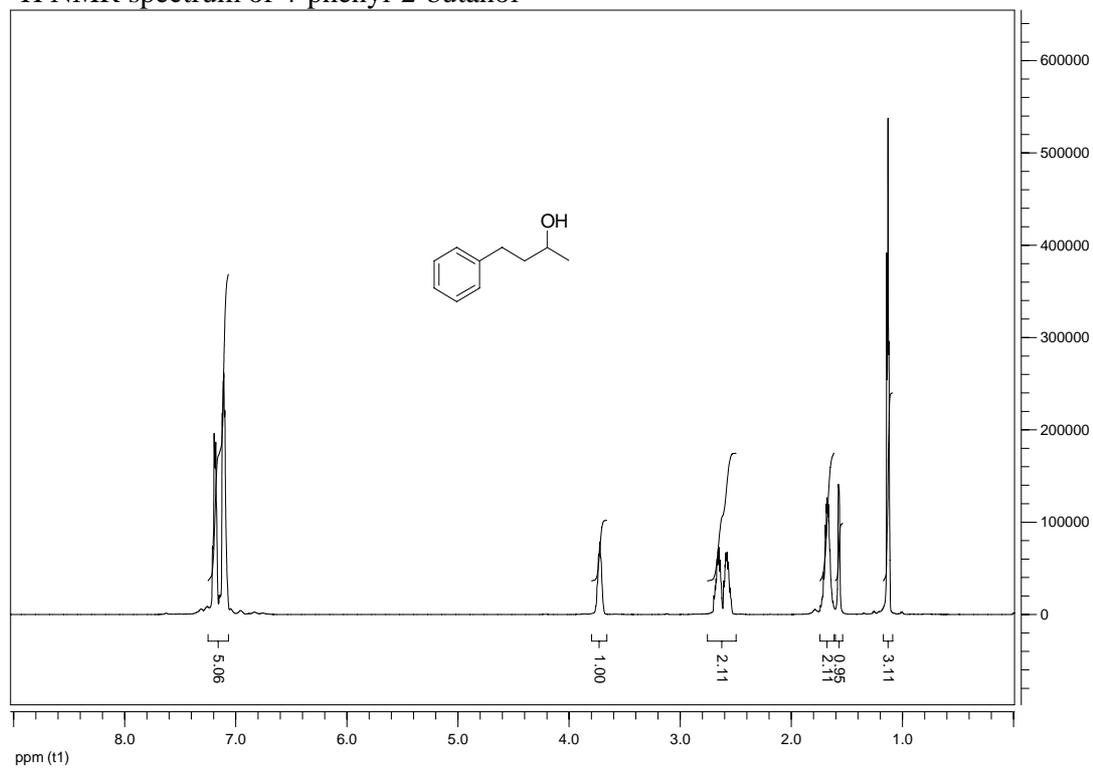
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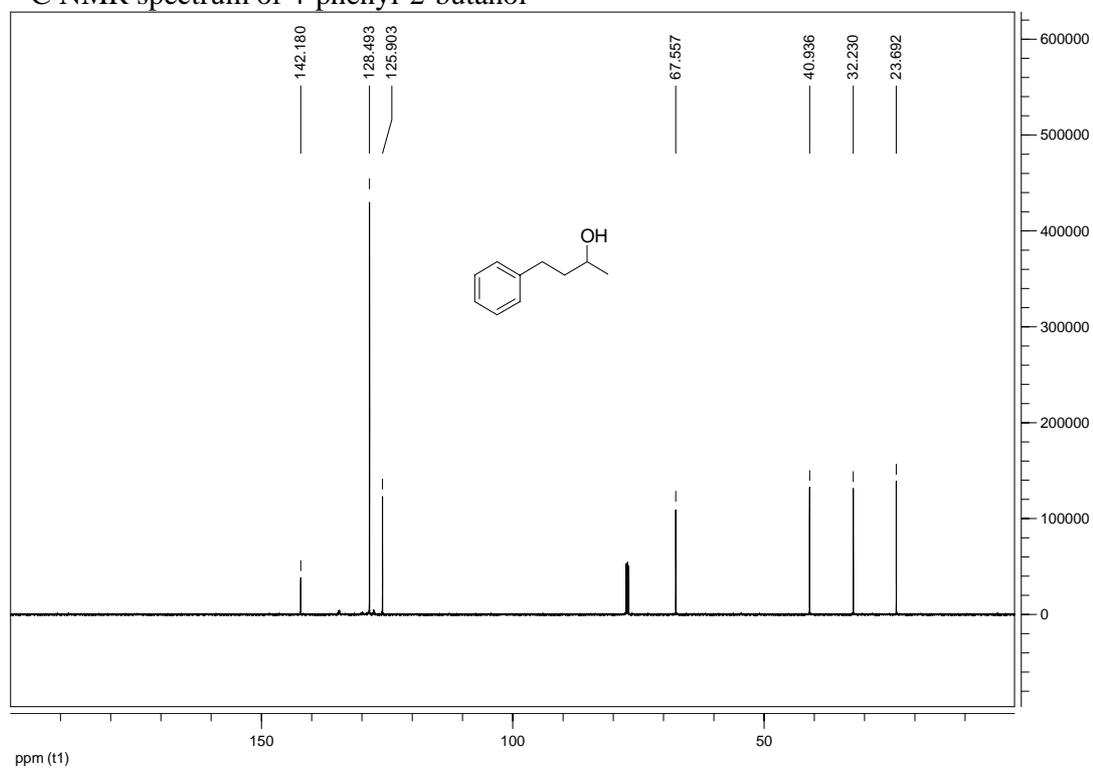
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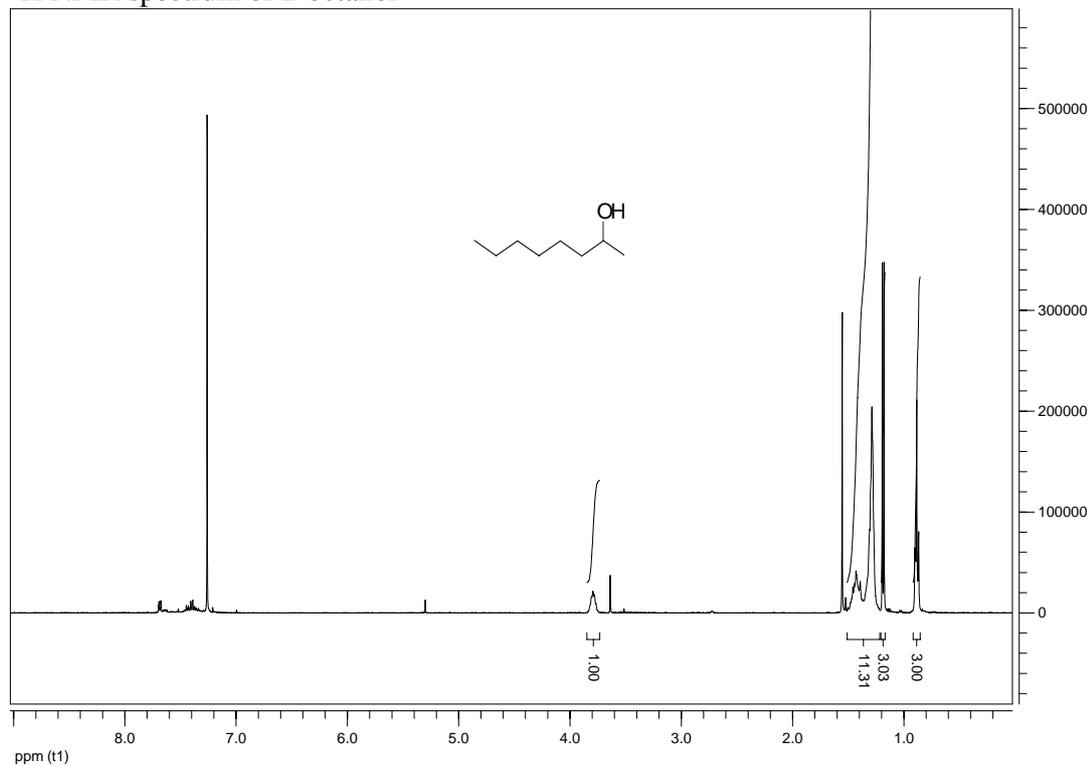
¹H NMR spectrum of 4-phenyl-2-butanol



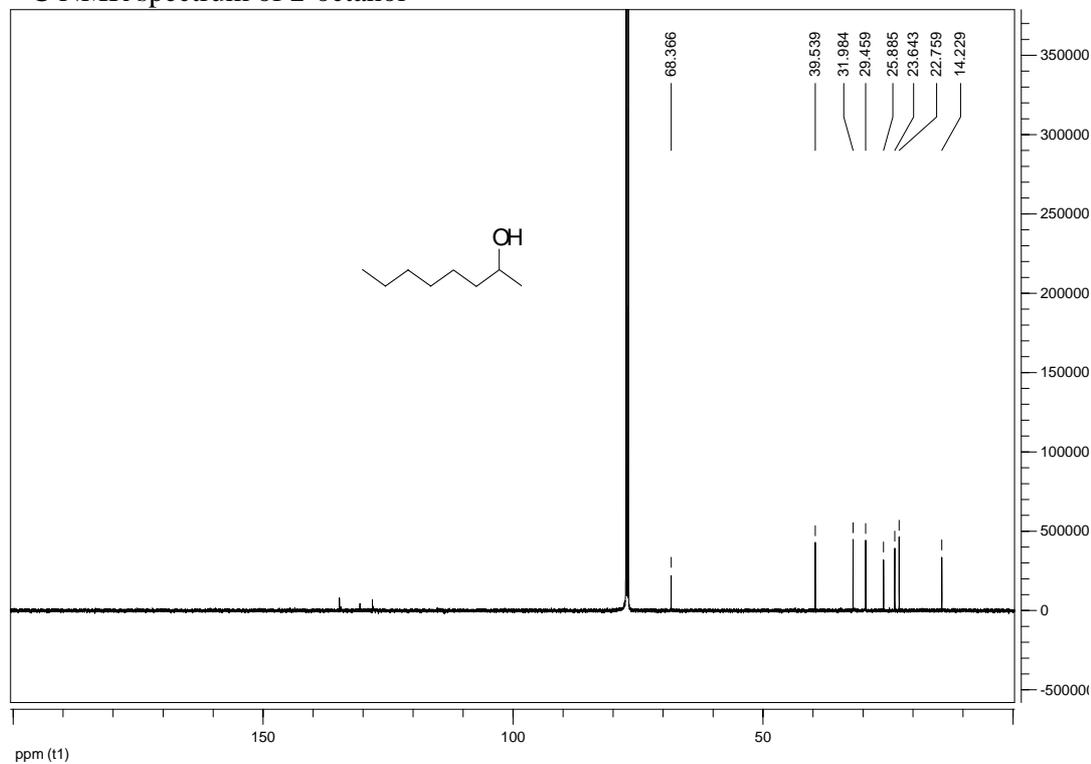
¹³C NMR spectrum of 4-phenyl-2-butanol



^1H NMR spectrum of 2-octanol



^{13}C NMR spectrum of 2-octanol



References

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