

Supporting Information

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

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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, ^{13}C NMR spectra at 125 or 100 MHz, and ^{31}P 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 %), $[\text{M}(\text{cod})\text{Cl}]_2$ (0.0050 mmol, 1.0 mol % M) and if suitable AgBF_4 (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

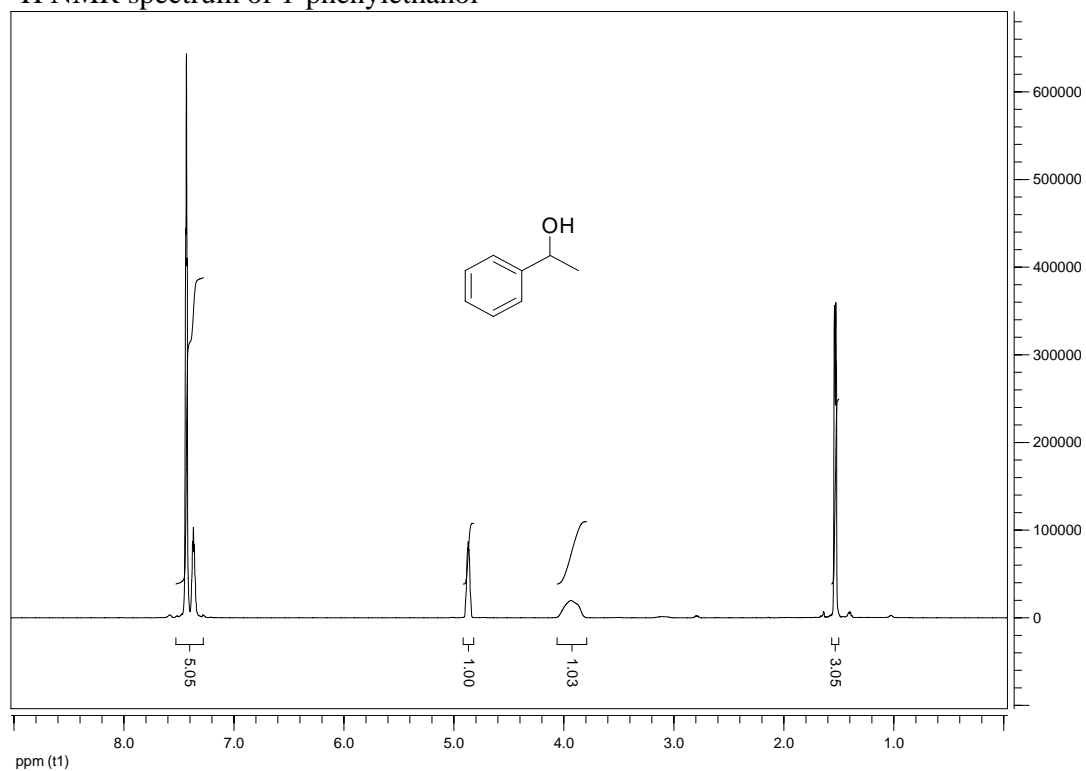
1-(4-Bromophenyl)ethanol. The ketone was added from the start and was present during the catalyst formation. The yield of silyl enol ether was in all cases below 6%. Enantiomeric excesses were determined using a chiral OD-H (0.46 cm Ø × 25 cm) HPLC column (eluent: degassed 2-propanol/hexane 10/90), flow 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

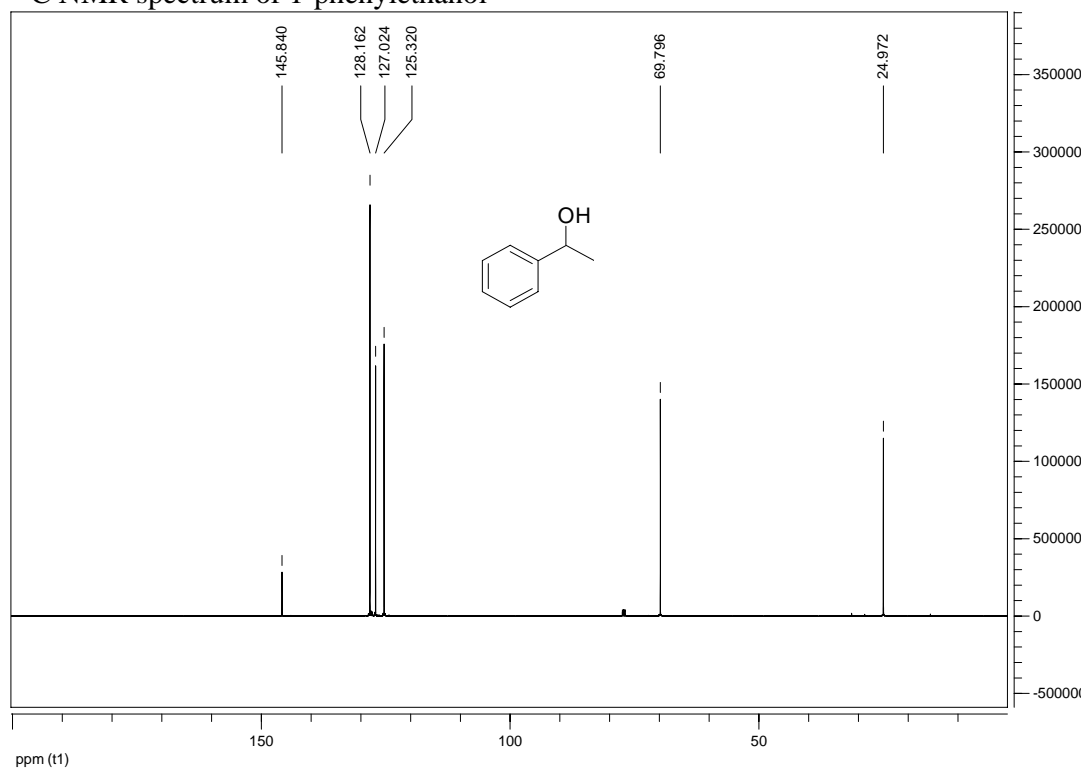
4-Phenyl-2-butanol. The yield of silyl enol ether was in all cases below 3%. Enantiomeric excesses were determined using a chiral OD-H (0.46 cm Ø × 25 cm) HPLC column (eluent: degassed 2-propanol/hexane 10/90), flow rate: 0.5 mL/min, UV detection at 220 nm, t_R (*R*) = 20.8 min, t_R (*S*) = 28.0 min.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

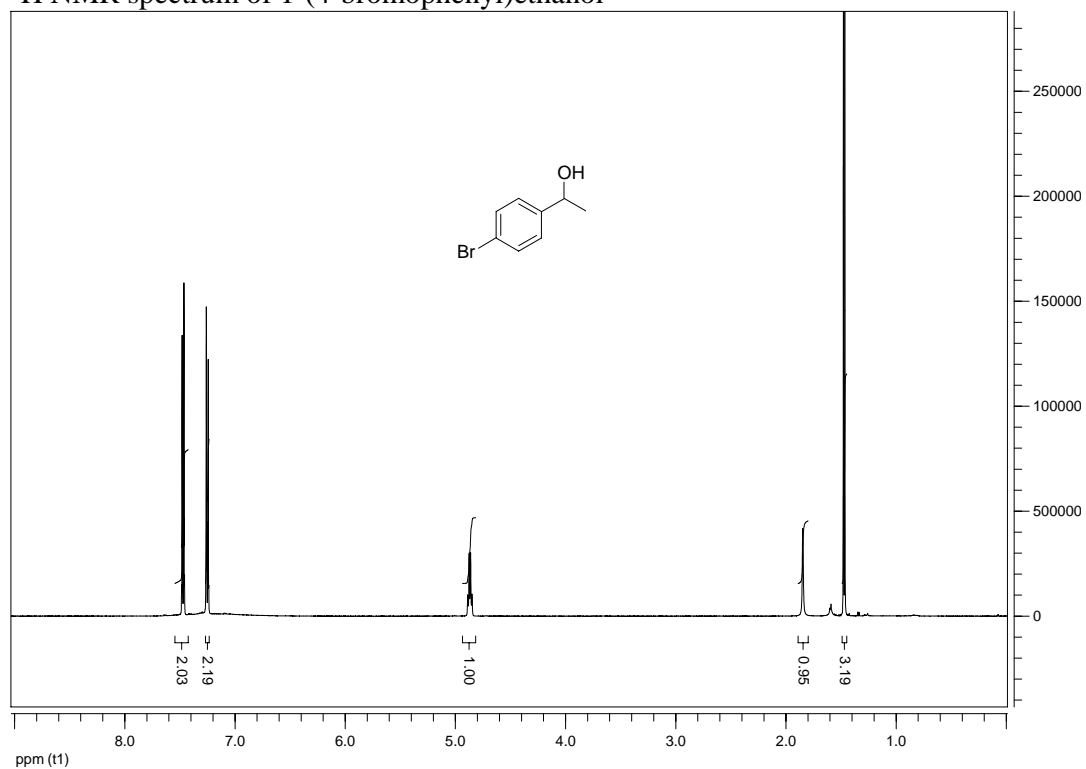
^1H NMR spectrum of 1-phenylethanol



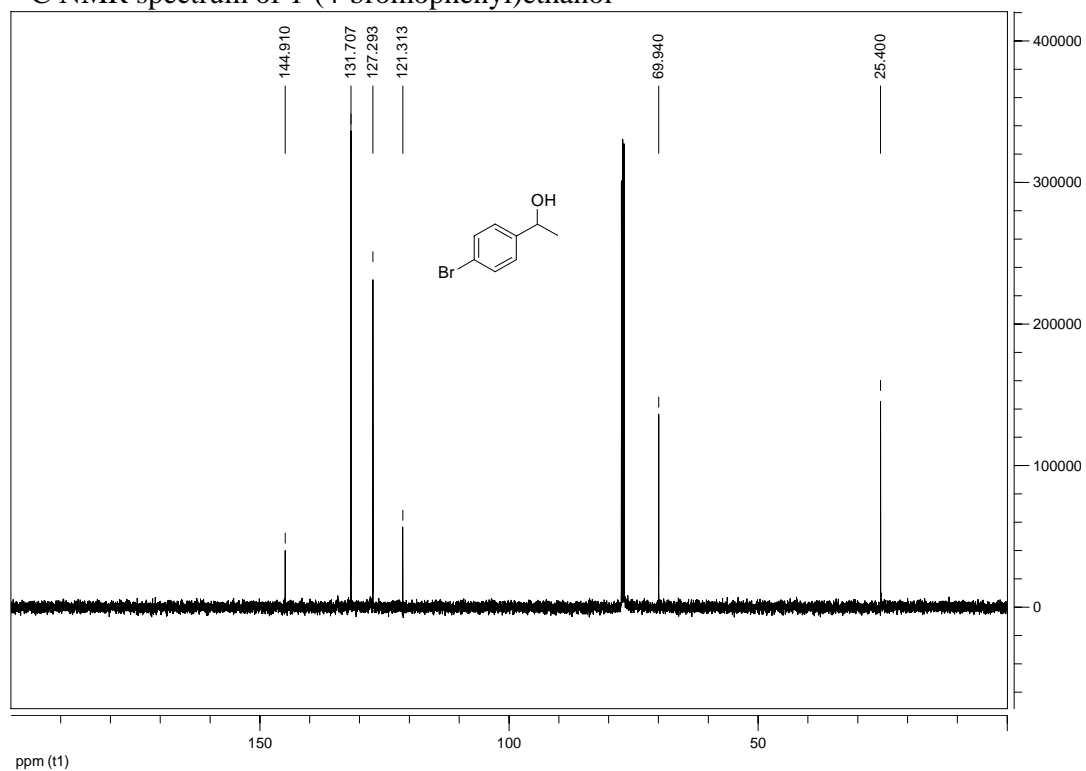
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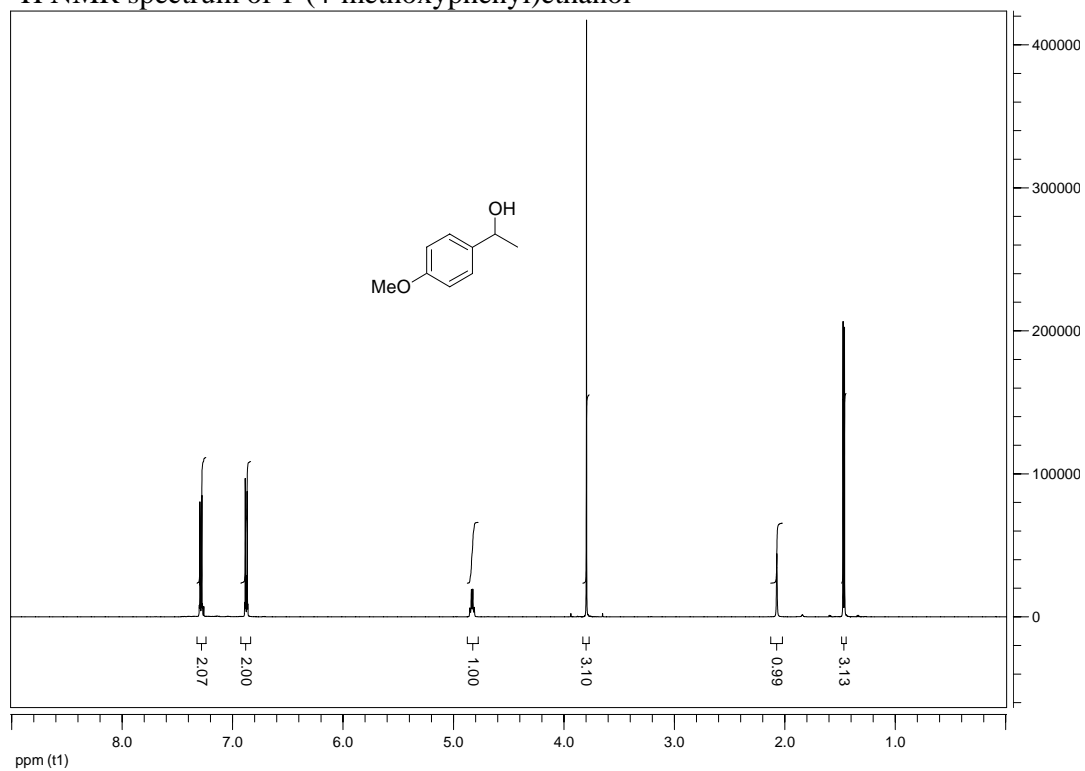
^1H NMR spectrum of 1-(4-bromophenyl)ethanol



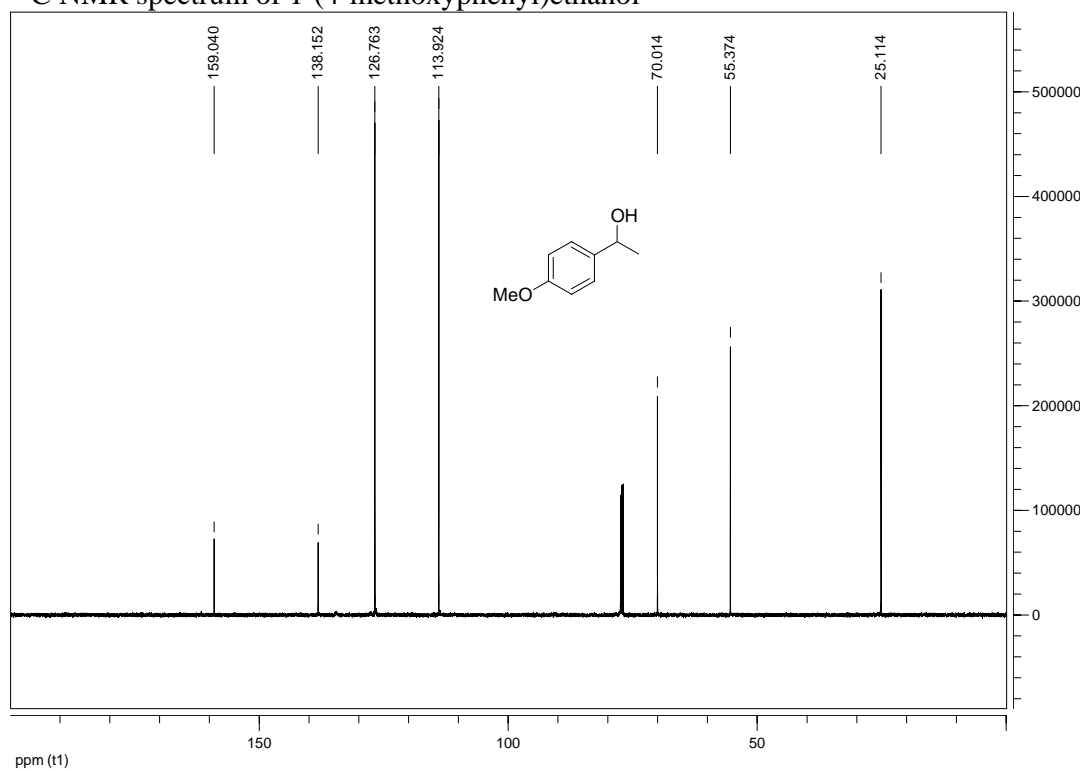
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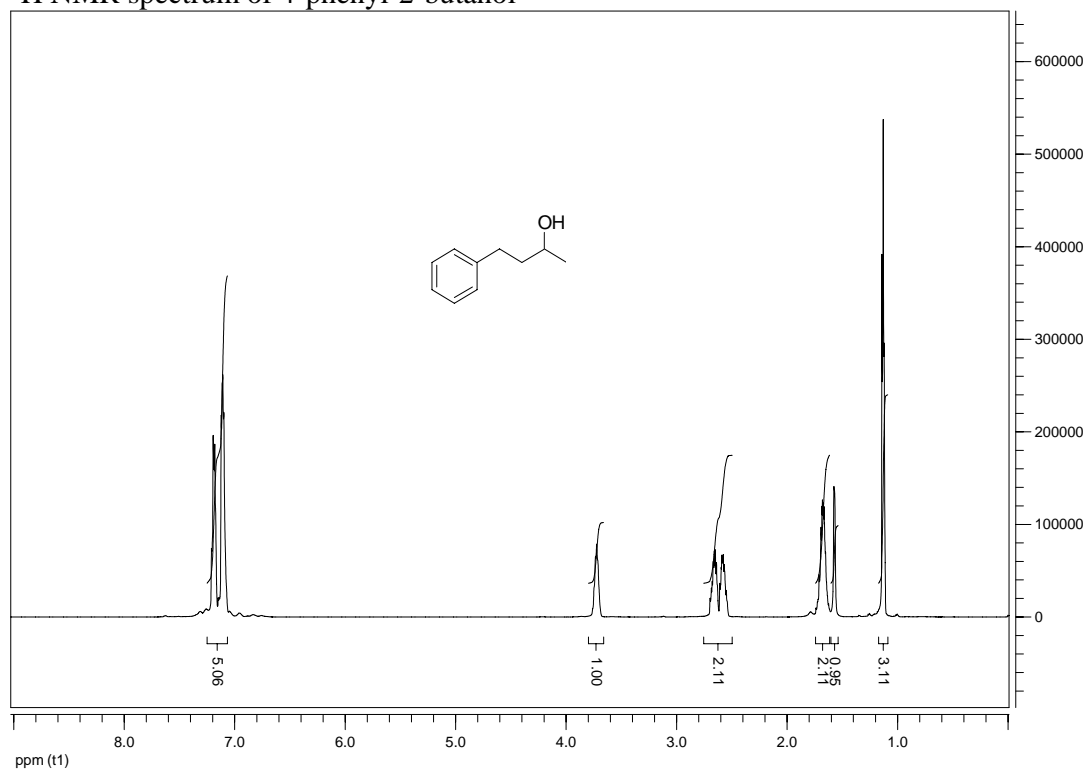
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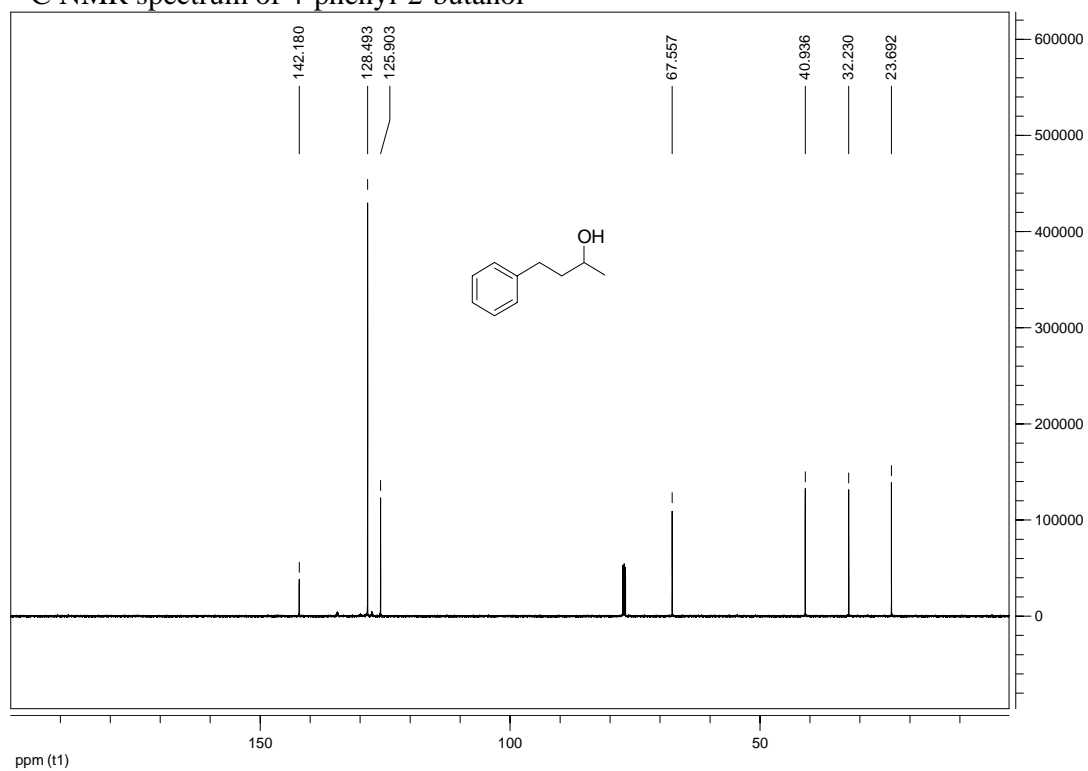
¹³C NMR spectrum of 1-(4-methoxyphenyl)ethanol



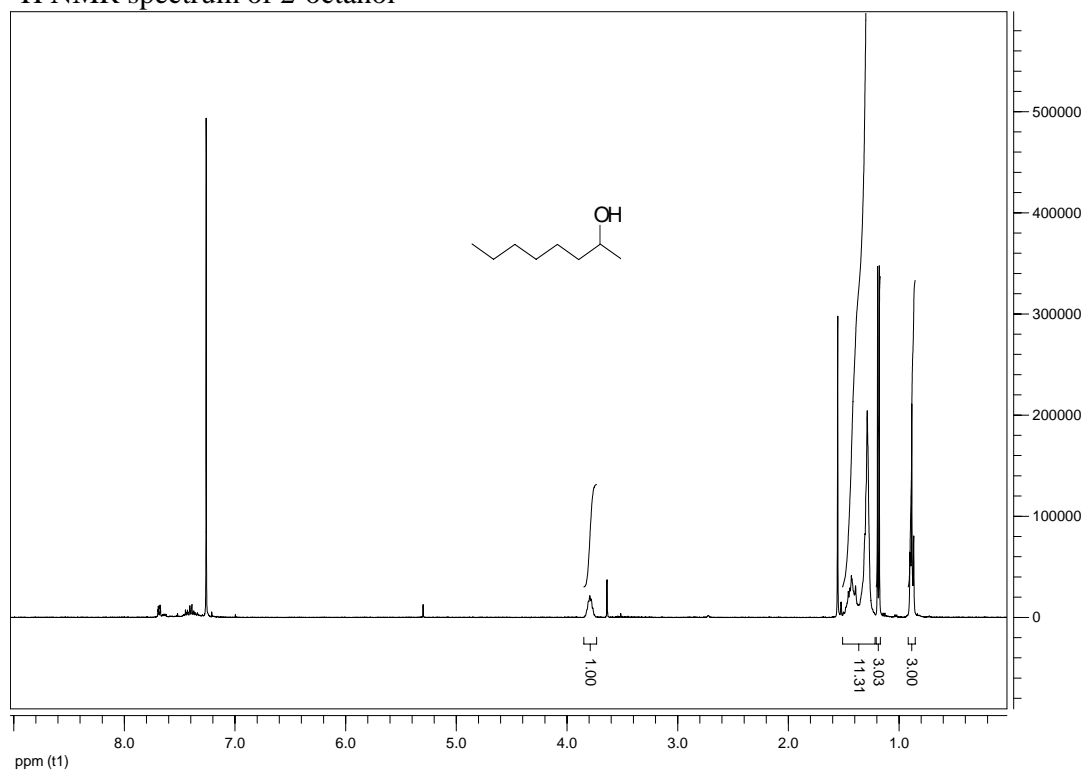
^1H NMR spectrum of 4-phenyl-2-butanol



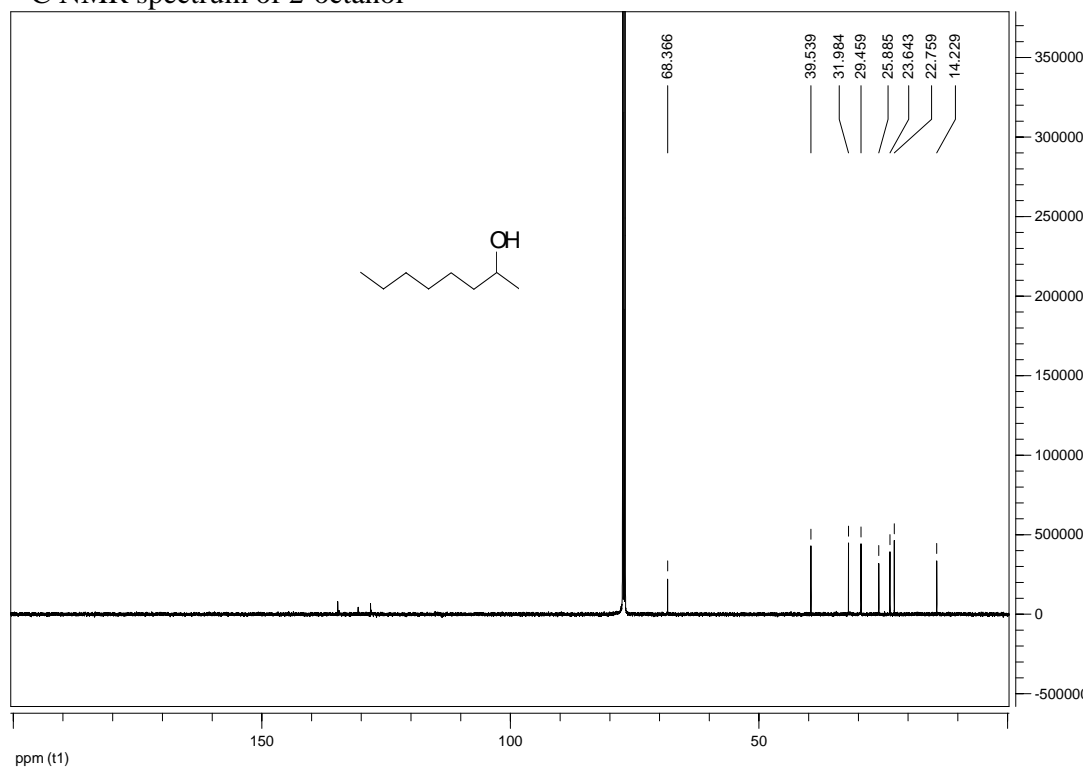
^{13}C NMR spectrum of 4-phenyl-2-butanol



^1H NMR spectrum of 2-octanol



^{13}C NMR spectrum of 2-octanol



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- (5) Tao, B.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 3892-3894.