

Rh^{III} and Ir^{III} complexes bearing *NNO*-heteroscorpionates and their application in catalytic transfer hydrogenation

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SUPPORTING INFORMATION

1. Material and methods
2. General Procedure for obtaining complex **1**
3. NMR and IR spectra for complex **1**
4. General Procedure for obtaining complex **2**
5. NMR and IR spectra for complex **2**
6. General procedure for catalytic transfer hydrogenation.
7. NMR spectra for the products of reduction catalytic transfer hydrogenation.

1. Material and methods

Commercially available reagents and solvents were used as received. The ligand [2,2-bis(3,5-dimethylpyrazol-1-yl)1-*p*-tolylethanol] was obtained according to literature procedures.¹ All manipulations related to the synthesis of complexes **1** and **2** were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. Infrared spectra were recorded on a GX Perkin Elmer FT-IR system using film technique. X-ray diffraction analyses were collected in an Agilent Gemini diffractometer using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures were solved using direct methods, using SHELX 2014 and refined by full matrix least squares against F².¹ All non-hydrogen atoms were refined anisotropically. The position of the hydrogen atoms was kept fixed with common isotropic displacement parameters.

Synthesis of complex 1.

Rhodium (III) chloride hydrate (0.227 mmol) and the ligand [2,2-bis(3,5-dimethylpyrazol-1-yl)1-*p*-tolylethanol] (0.227 mmol) were charged in a Schlenk flask and methanol was added (5 mL). The reaction mixture was placed in an oil bath at 80°C and stirred for 3 h. The mixture was cooled down to room temperature and stirred for 10 h. After removal of the solvent under reduced pressure, the crude material is washed thoroughly with pentane. Recrystallization from dichloromethane affords the respective metal complexes in analytical purity as orange crystalline solids.

¹H NMR (400 MHz, DMSO-*d*₆, 25 °C): δ (ppm) 7.42 (d, 2H, CH_{Ph}), 7.14 (d, 2H, CH_{Ph}), 6.66 (s, 1H, CH_{Pz}), 6.26 (s, 1H, CH_{Pz}), 5.98 (s, 1H, CH), 5.80 (s, 1H, CH_q), 2.78 (s, 3H, CH_{3Ph}), 2.76 (s, 3H, CH_{3Pz}), 2.74 (s, 3H, CH_{3Pz}), 2.31 (s, 3H, CH_{3Pz}), 1.89 (s, 3H, CH_{3Pz}). **¹³C{¹H} NMR (101 MHz, DMSO-*d*₆, 25 °C):** δ (ppm) 157.1 (C-15, 16), 143.6 (C-11, 12), 143 (C-13), 138.8 (C-14), 129.1 (C-10), 126.3 (C-9), 109.2 (C-3), 108.5 (C-2), 75.5 (C-5), 69.8 (C-4), 20.3 (C-1), 14.3 (C-7), 14.2 (C-6), 9.5 (C-8). **IR ν (cm⁻¹):** 3440 (OH), 2920 (CH₃Pz), 1638 (C=C), 1566 (N=C), 1060 (CH-OH), 811 (CH_{Ph}).

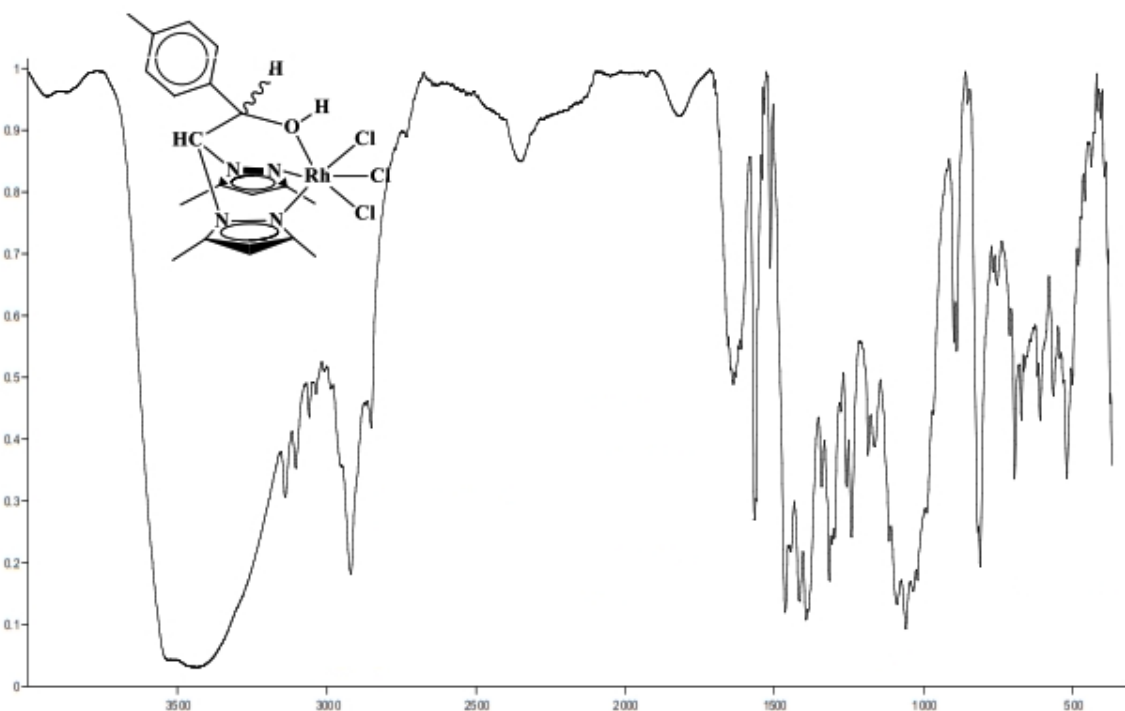


Figure S-1. Infrared spectrum for complex 1 in KBr.

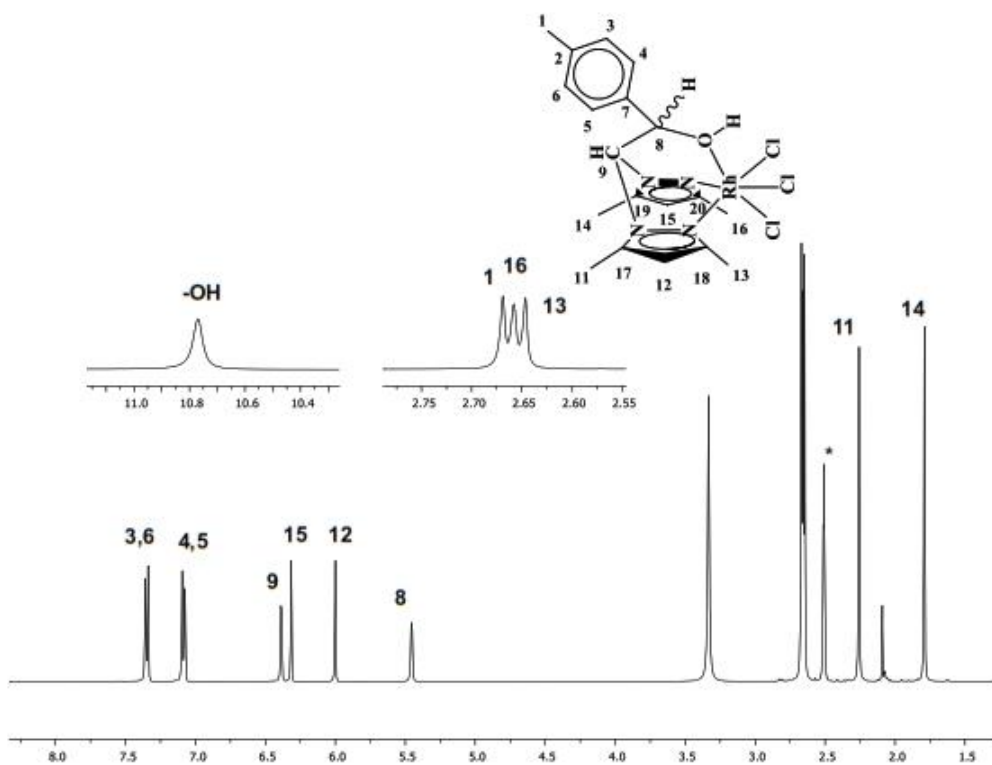


Figure S-2. ^1H NMR (400 MHz) spectrum for 1 in DMSO- d_6 .

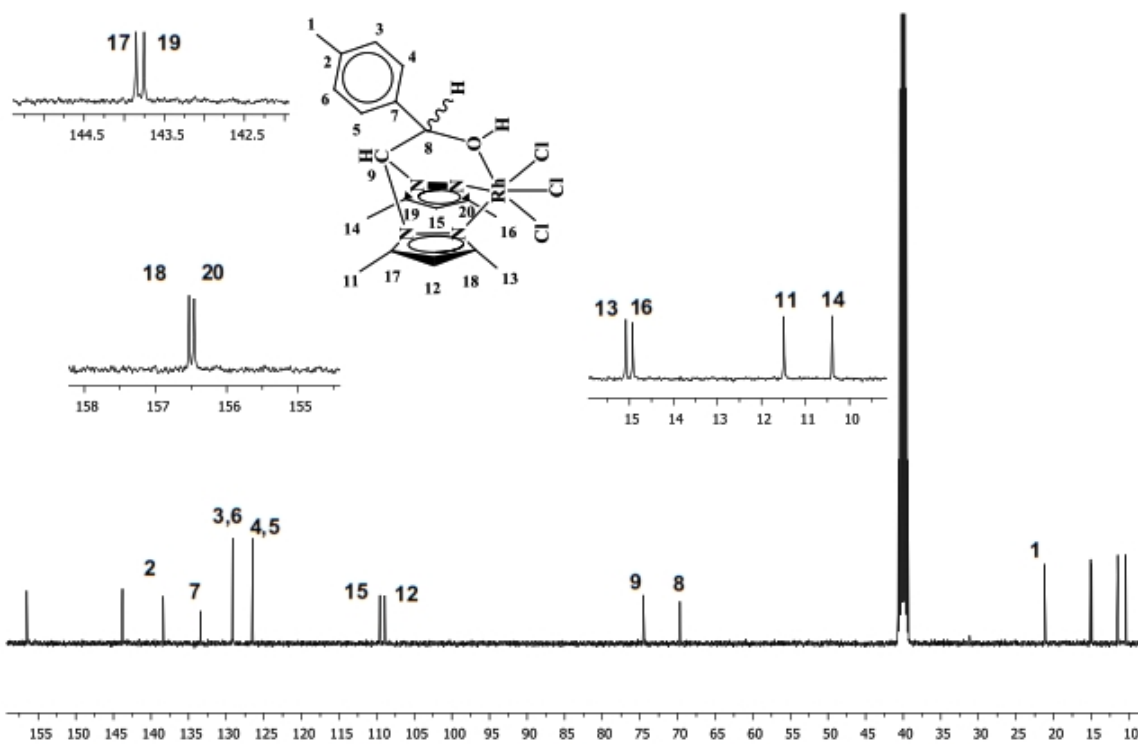


Figure S-3. ^{13}C NMR (100 MHz) spectrum for 1 in DMSO- d_6 .

Synthesis of complex 2.

Iridium (III) chloride hydrate (0.227 mmol) and 2,2-dimethylpyrazolyl-1-*p*-tolyl-1-ethanol (0.227 mmol) were charged in a Schlenk flask in 5 mL of methanol. The reaction mixture was placed in an oil bath at 80°C and stirred for 3 h. The mixture was cooled down to room temperature and stirred for 10 h. After removal of the solvent under reduced pressure, the crude material is washed thoroughly with pentane. Recrystallization from dichloromethane affords the respective metal complexes in analytical purity as orange crystalline solids.

¹H NMR (400 MHz, Acetone-d₆, 25 °C): δ (ppm) 7.38 (d, 2H, CH_{Ph}), 7.10 (d, 2H, CH_{Ph}), 6.53 (s, 1H, CH_{Pz}), 6.19 (s, 1H, CH_{Pz}), 5.93 (s, 1H, CH), 5.91 (s, 1H, CH_q), 2.85 (s, 3H, CH_{3Ph}), 2.77 (s, 6H, CH_{3Pz}), 2.29 (s, 3H, CH_{3Pz}), 1.92 (s, 3H, CH_{3Pz}).

¹³C{¹H} NMR (101 MHz, Acetone-d₆, 25 °C): δ (ppm) 157.6 (C-15, 16), 143.4 (C-11, 12), 142.8 (C-13), 138.9 (C-14), 129.2 (C-10), 126.2 (C-9), 109.0 (C-3), 108.3 (C-2), 76.6 (C-5), 70.2 (C-4), 20.6 (C-1), 13.9 (C-7), 13.8 (C-6), 9.7 (C-8). **IR ν (cm⁻¹):** 3375 (OH), 2924 (CH_{3Pz}), 1684 (C=C), 1576 (N=C), 1054 (CH-OH), 816 (CH_{Ph}).

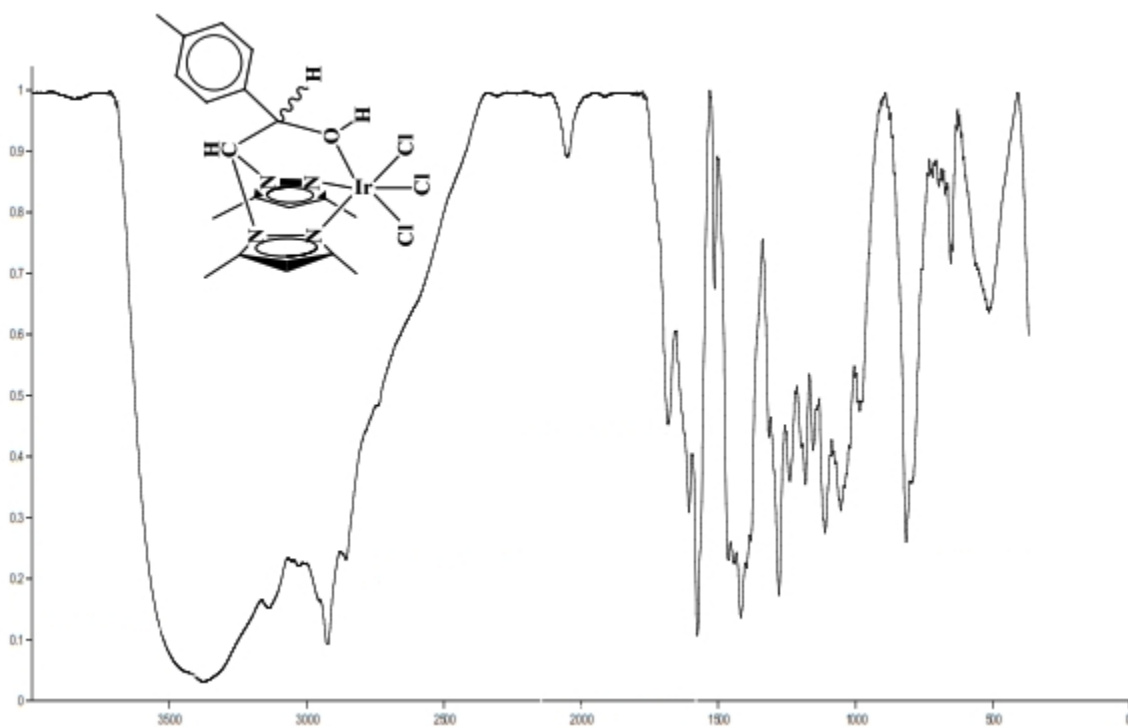


Figure S-4. Infrared spectrum for complex 2 in KBr.

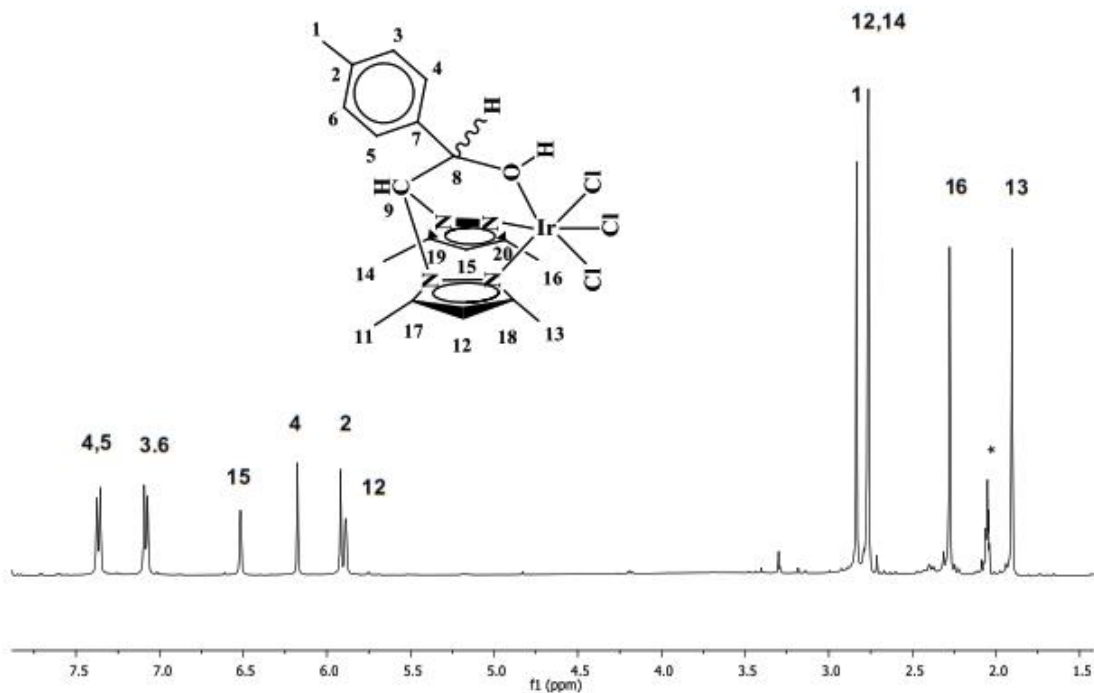


Figure S-5. ^1H NMR (400 MHz) spectrum for **2** in Acetone- d_6 .

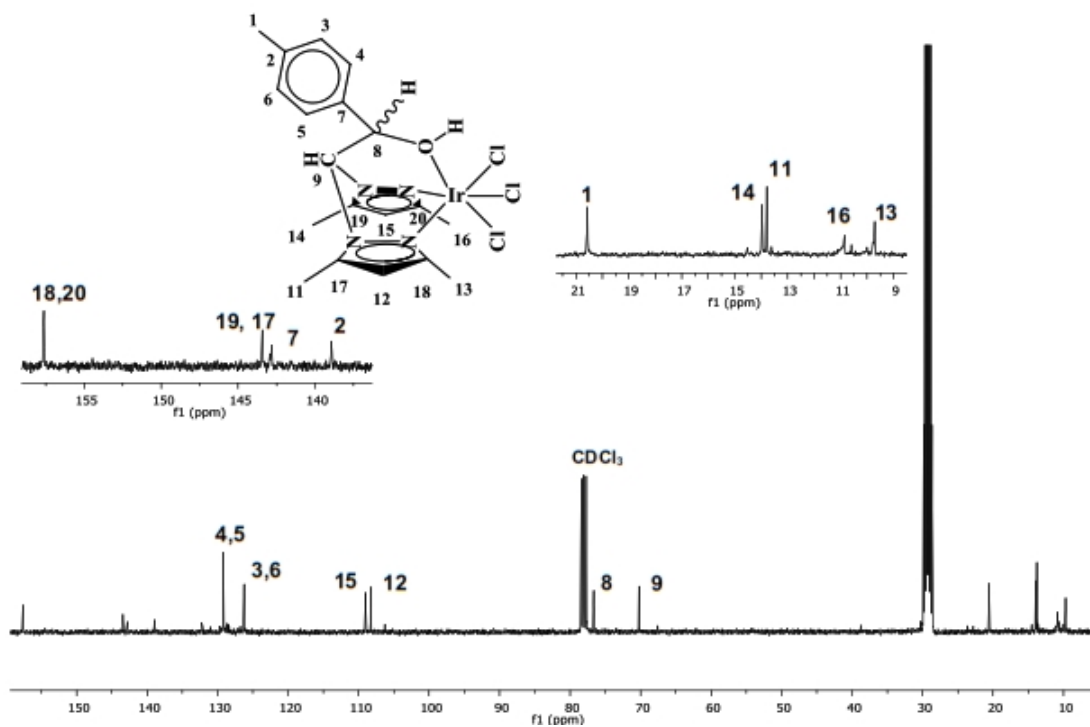
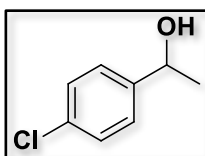


Figure S-6. ^{13}C NMR (100 MHz) spectrum for **2** in Acetone- d_6 - CDCl_3 .

General Procedure for Catalytic Transfer Hydrogenation.

A tube of reaction (meticulously cleaned with aqua regia to avoid the presence of metal impurities) was equipped with a bar magnetic and was charged with 1.0 mmol of the proper carbonyl derivative (ketone or Aldehyde), 50 % mol of t-BuOK, complex **1** or **2** (0.005 mol%) and 2-4 mL of dry propan-2-ol. The reaction tube was closed with a Teflon stopper and introduced in an oil bath heated at 80°C for 12 h. Once the reaction was completed the tube reaction was cooled a room temperature. The reaction mixture was filtered through a bed of celite and the solvent evaporated. The resulting crude was purified by chromatography column on silica gel and mixture of petroleum ether and ethyl acetate. The purified products were identified by ¹H NMR and they are consistent with literature data.²



NMR ^1H (400 MHz, δ ppm, CDCl_3) δ 7.30 (s, 4H, $\text{CH}_{\text{aromatic}}$), δ 4.87 (q, 1H, $^3J = 8\text{Hz}$, $\text{CH}_{\text{aliphatic}}$), δ 1.47 (d, 3H, $^3J = 8\text{Hz}$, CH_3). **NMR ^{13}C (101 MHz, δ ppm, CDCl_3)** δ 144.3 (C_{ipso}), δ 133.1 (C_{ipso}), δ 128.6 ($\text{CH}_{\text{aromatic}}$), δ 126.8 ($\text{CH}_{\text{aromatic}}$), δ 69.8 (CH-OH), δ 25.3 (CH_3).

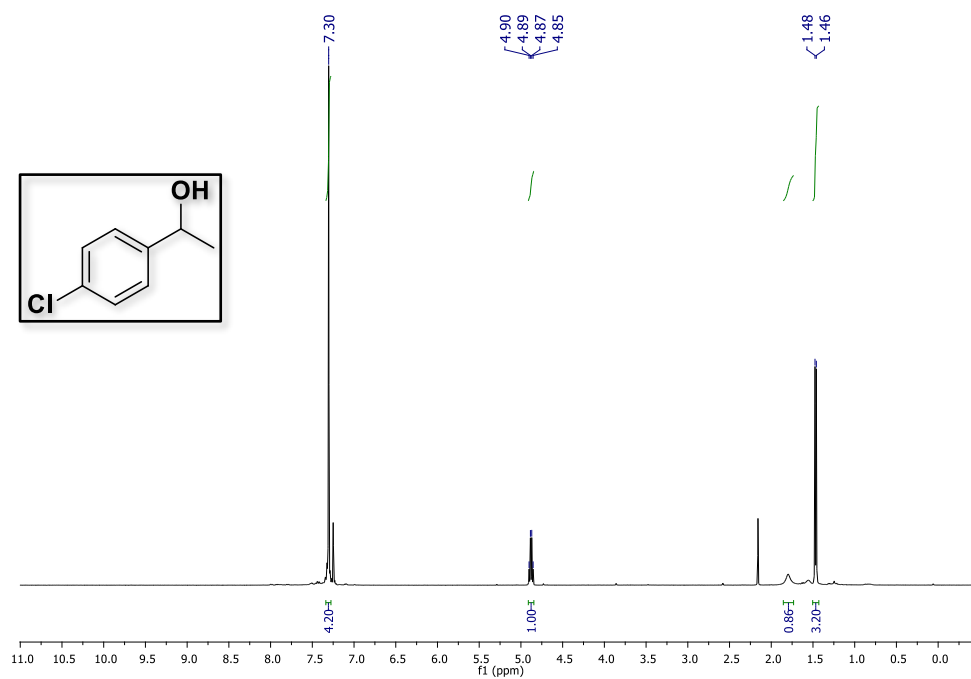


Figure S-7. ^1H NMR spectrum of 1-(4-chlorophenyl)ethanol in CDCl_3

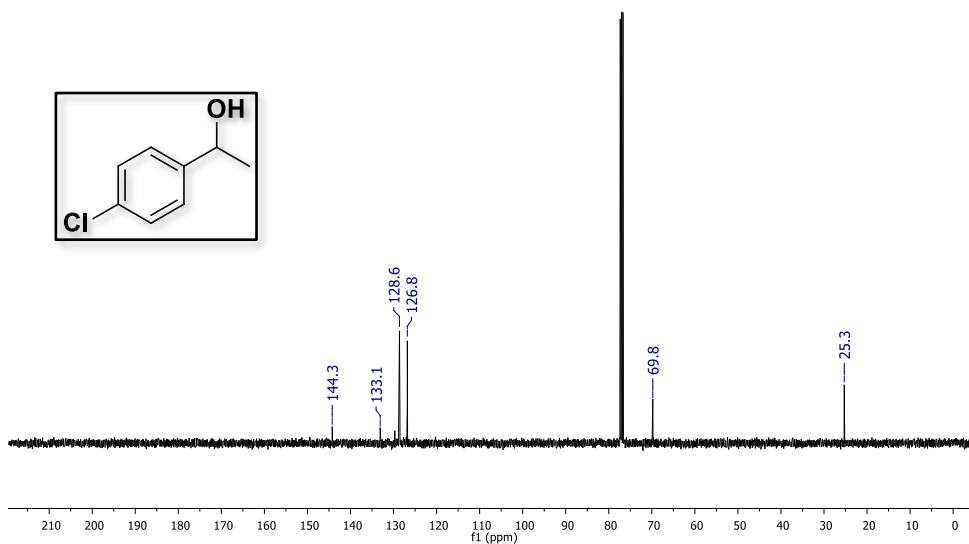
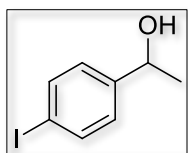


Figure S-8. ^{13}C NMR spectrum of 1-(4-chorophenyl)ethanol in CDCl_3



NMR ^1H (400 MHz, δ ppm, CDCl_3) δ 7.55 (d, 2H, $\text{CH}_{\text{aromatic}}$, $^3J = 8$ Hz,), δ 6.99 (d, 2H, $\text{CH}_{\text{aromatic}}$, $^3J = 8$ Hz), δ 4.73 (q, 1H, 4.70, $^3J = 8$ Hz, $\text{CH}_{\text{aliphatic}}$), δ 1.34 (d, 3H, CH_3). NMR ^{13}C (101 MHz, δ ppm, CDCl_3) δ 145.5 (*Cipso*), δ 137.5, ($\text{CH}_{\text{aromatic}}$), δ 127.4 ($\text{CH}_{\text{aromatic}}$), δ 92.7 (*Cipso*), δ 69.8 (CHOH), δ 25.2 (CH_3).

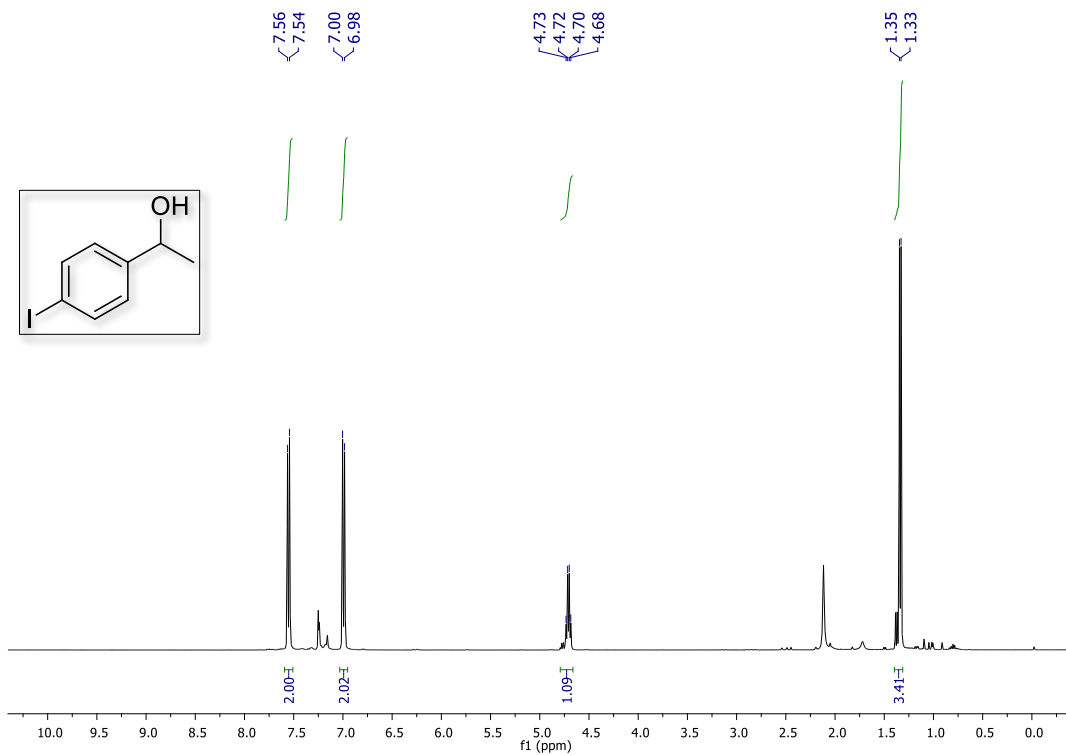


Figure S-9. ^{13}C NMR spectrum of 1-(4-iodophenyl)ethanol in CDCl_3

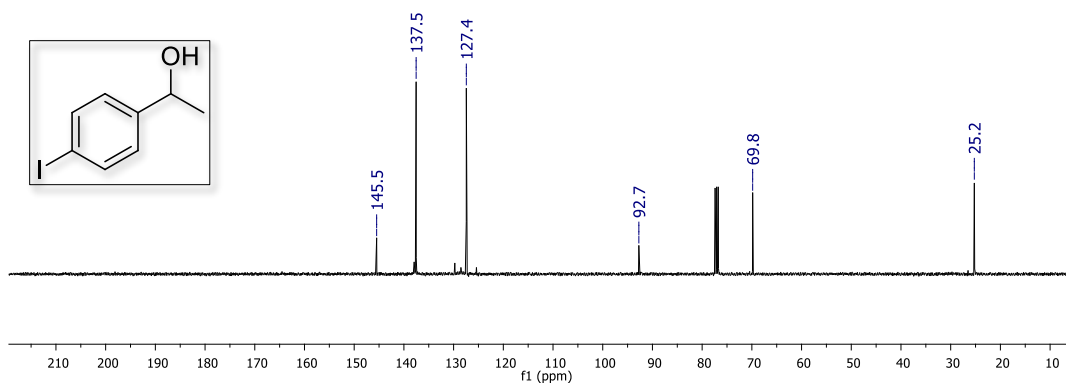
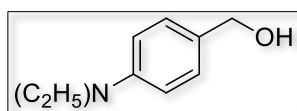


Figure S-10. ^{13}C NMR spectrum of 1-(4-iodophenyl)ethanol



NMR ^1H (400 MHz, δ ppm, CDCl_3). δ 7.21 (d, 2H, $^3J = 8\text{Hz}$, $\text{CH}_{\text{aromatic}}$), δ 6.66 (d, 2H, $^3J = 8\text{Hz}$, $\text{CH}_{\text{aromatic}}$), δ 4.54 (s, 2H, CH_2OH), δ 3.35 (q, 4H, $^3J = 8\text{Hz}$, CH_2N), δ 1.52 (s, 1H, OH), δ 1.16 (t, 6H, $3J = 8\text{Hz}$).

NMR ^{13}C (101 MHz, δ ppm, CDCl_3) δ 147.6 (C_{ipso}), δ 129 ($\text{CH}_{\text{aromatic}}$), δ 127.7 (C_{ipso}), δ 111.8 ($\text{CH}_{\text{aromatic}}$), δ 65.4 (CH_2OH), δ 65.4 (CH_2OH), δ 44.4, δ 65.4 ($\text{CH}_3\text{CH}_2\text{N}$), δ 12.6 ($\text{CH}_3\text{CH}_2\text{N}$).

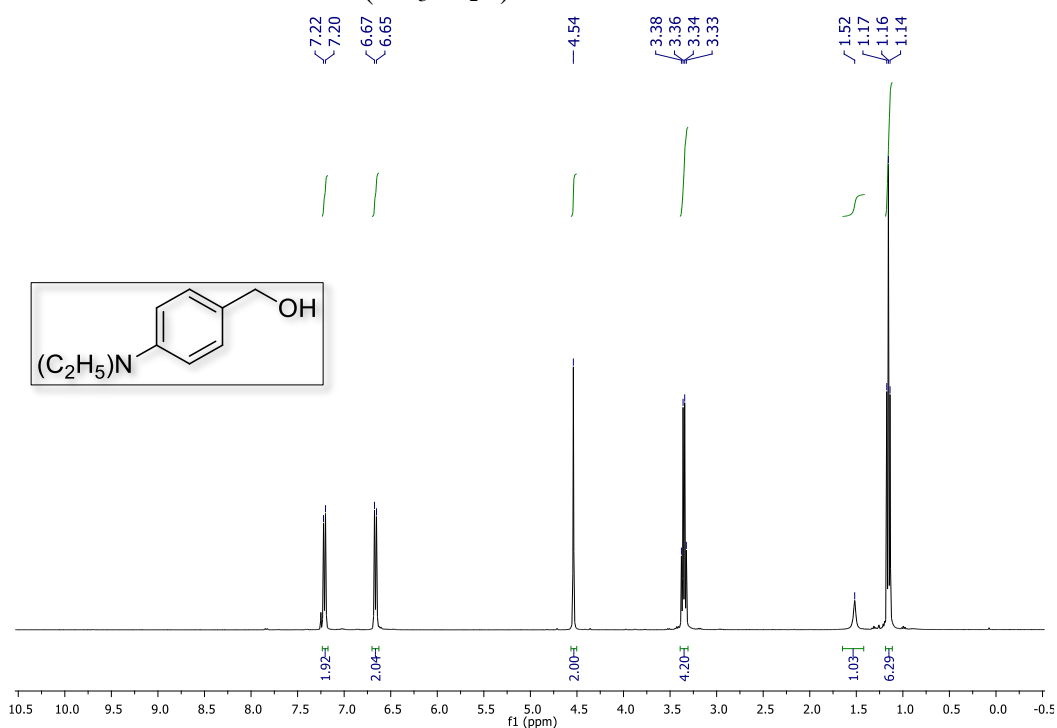


Figure S-11. ^1H NMR spectrum of 1-(4-(diethylamino)phenyl)methanol in CDCl_3

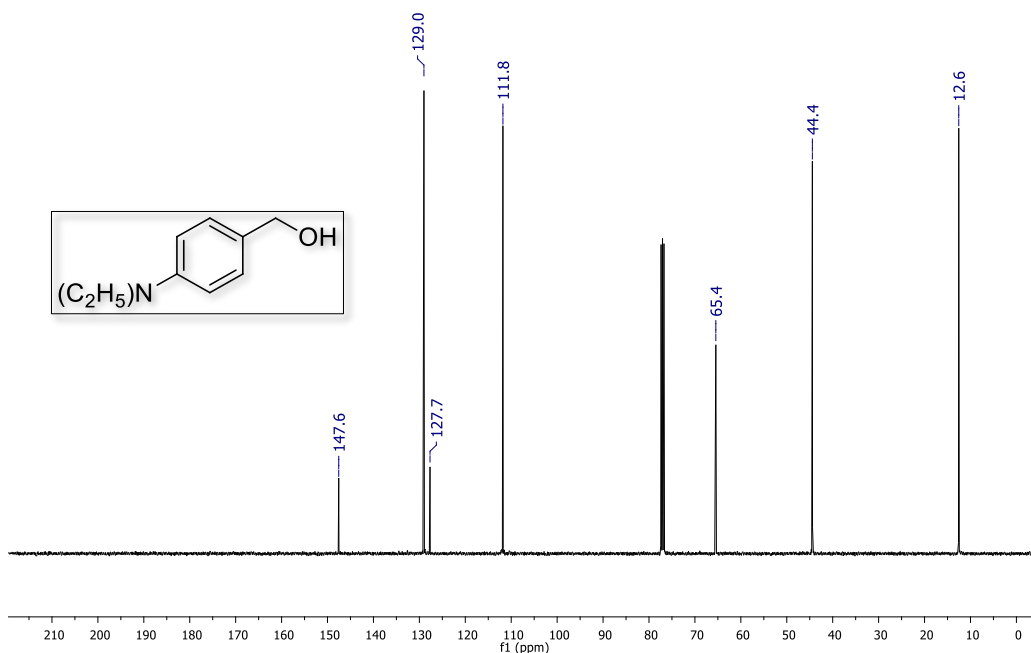
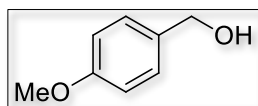


Figure S-12. ^1H NMR spectrum of 1-(4-(diethylamino)phenyl)ethanol in CDCl_3



NMR ^1H (400 MHz, δ ppm, CDCl_3). δ 7.18 (d, 2H, $3J = 8\text{Hz}$, $\text{CH}_{\text{aromatic}}$), δ 6.79 (d, 2H, $^3J = 8\text{Hz}$, $\text{CH}_{\text{aromatic}}$), δ 4.49 (s, 2H, CH_2OH), δ 3.71 (s, 3H, OMe) δ 1.99 (br s, 1H). **NMR ^{13}C (101 MHz, δ ppm, CDCl_3).** δ 159.2 (C_{ipso}), δ 133.2 (C_{ipso}), δ 128.7 ($\text{CH}_{\text{aromatic}}$), δ 113.9 ($\text{CH}_{\text{aromatic}}$), δ 64.9 (CH_2OH), δ 55.3 (OMe).

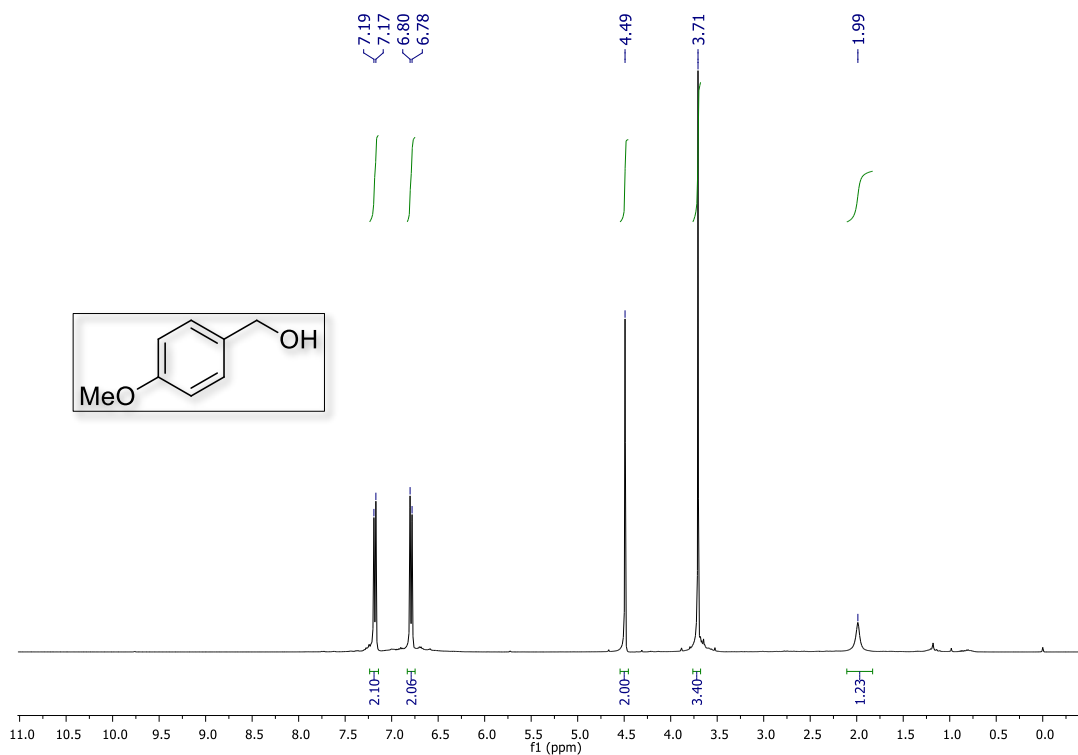


Figure S-13. ^1H NMR spectrum of (4-methoxyphenyl)methanol in CDCl_3

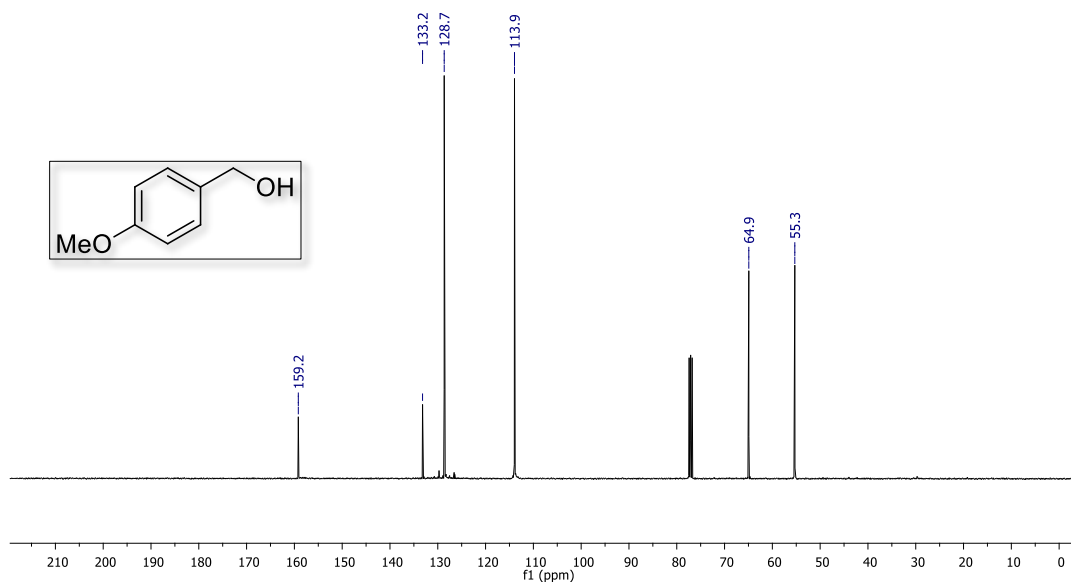


Figure S-14. ^{13}C NMR spectrum of (4-methoxyphenyl)ethanol in CDCl_3

Reference

- 1.- G. M. Sheldrick, SHELXS-2014, Program for Crystal Structure Solution and Refinement; Institut Für Anorganische Chemie, Göttingen, Germany, 2013.
- 2.- S. Julia, P. Sala, J. Del Mazo, M. Sancho, C. Ochoa, J. Elguero, J.-P. Fayet and M.-C. Vertut, *J. Heterocycl. Chem.* 1982, **19**, 1141–1145.