Ruthenium(II) Complexes of Hemilabile Pincer Ligands: Synthesis and Catalysing the Transfer Hydrogenation of Ketones

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1. General Procedure

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk techniques under $N_{2(g)}$ atmosphere.

Unless otherwise stated, chemicals were purchased from Alfa AesarInc or Aldrich Chemical Company Inc, and used as received. Ruthenium(III) chloride hydrate was purchased from Precious Metals Online P/L and used without further purification. Bis-pyrazole ligand was synthesised according to our previous report.[1]

For the purposes of air sensitive manipulations and preparation of metal complexes, solvents were dispensed from a PuraSolv solvent purification system and stored under nitrogen or argon atmospheres in glass ampoules fitted with Youngs Teflon valves.

Bulk compressed gases of nitrogen (>99.5%) was obtained from Air Liquide.

1.1 NMR Spectroscopy

The ^{1}H NMR spectra were recorded on Bruker DPX300 (fitted with an Autosampler), DPX300, DMX400 and DMX600 spectrometers, operating at 300.2, 300.3, 399.9, 400.1 and 600.1 MHz (^{1}H) respectively. All spectra were recorded at 298 K unless stated otherwise and chemical shifts (δ) are quoted in ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ±0.05 Hz. ^{1}H NMR chemical shifts were referenced internally to residual solvent resonances. The following abbreviations are used to report the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Proton and carbon resonances were assigned using COSY (Correlation Spectroscopy), NOESY (Nuclear Overhauser Effect Spectroscopy), HSQC (^{1}H-^{13}C) (Heteronuclear Single Quantum Coherence), and HMBC (^{1}H-^{13}C) (Heteronuclear Multiple Bond Coherence) experiments. All NMR data was acquired and processed using TopSpin™ version 3.2 from Bruker NMR software.

2. NMR Spectra

2.1 Selected ^1H and ^{13}C NMR Spectra for Catalysts 2-6:

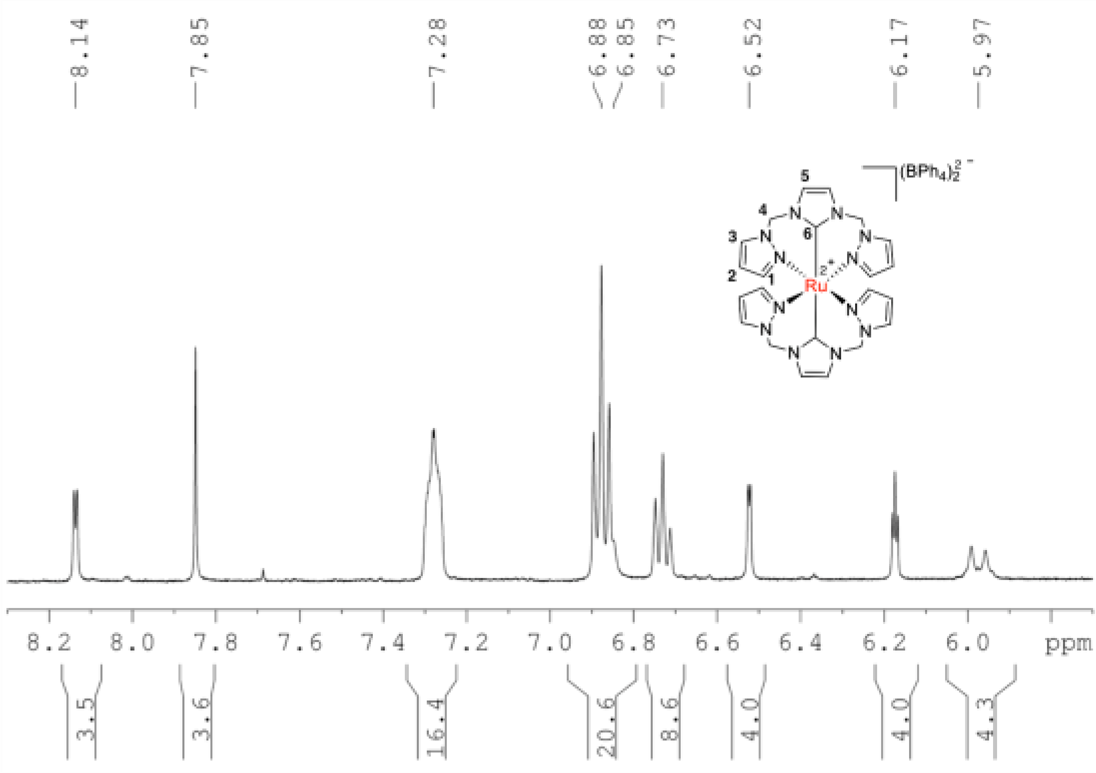


Figure 1. ^1H NMR (400 MHz, $(CD_3)_2CO$) spectrum of complex **2**.

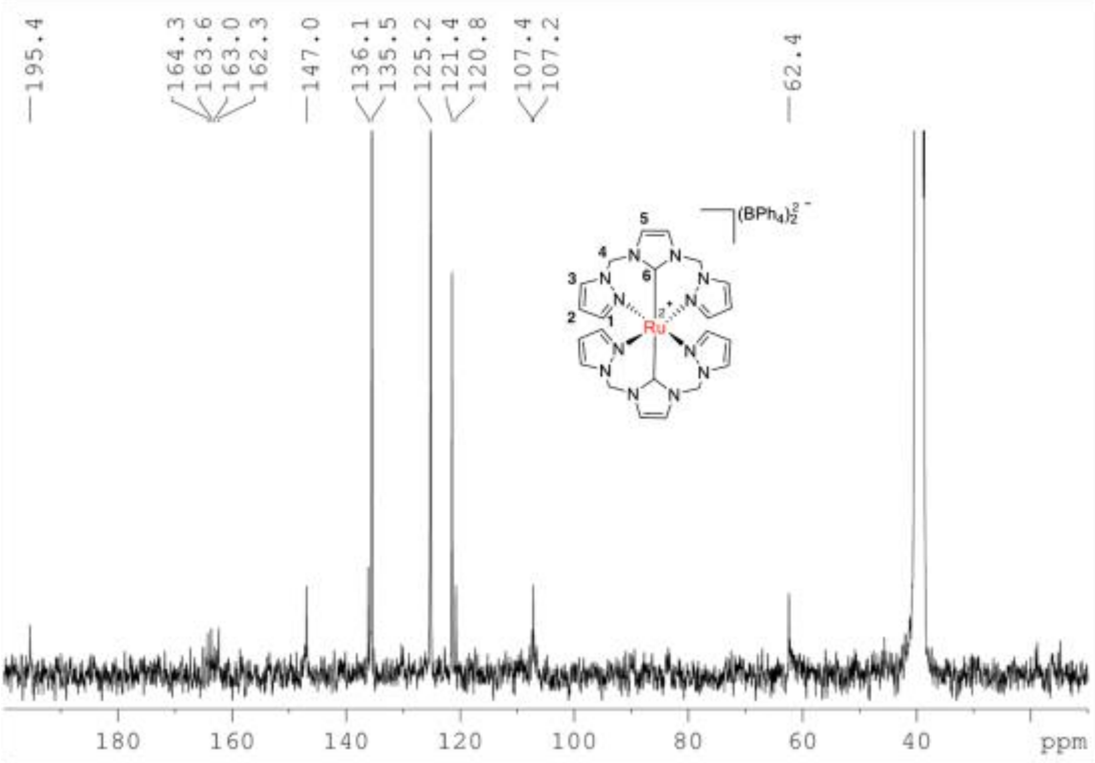


Figure 2. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) spectrum of complex **2**.

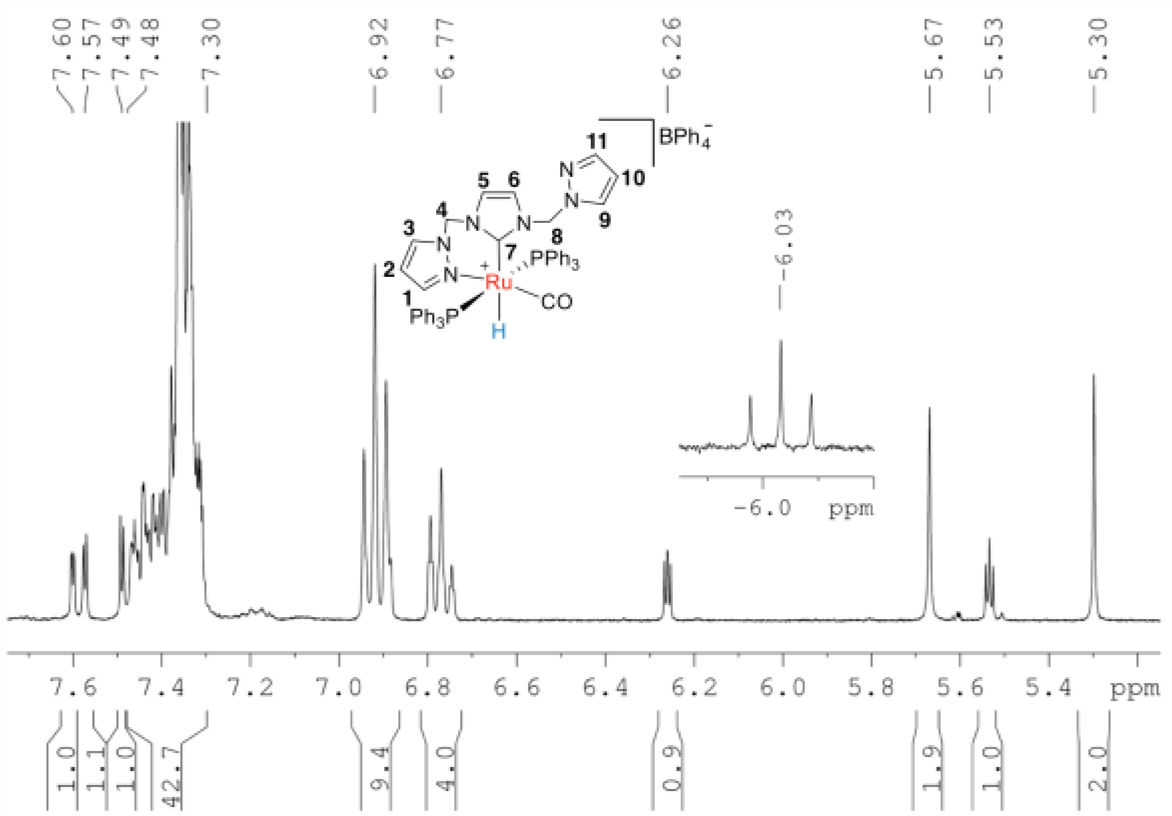


Figure 3. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) spectrum of complex **3**.

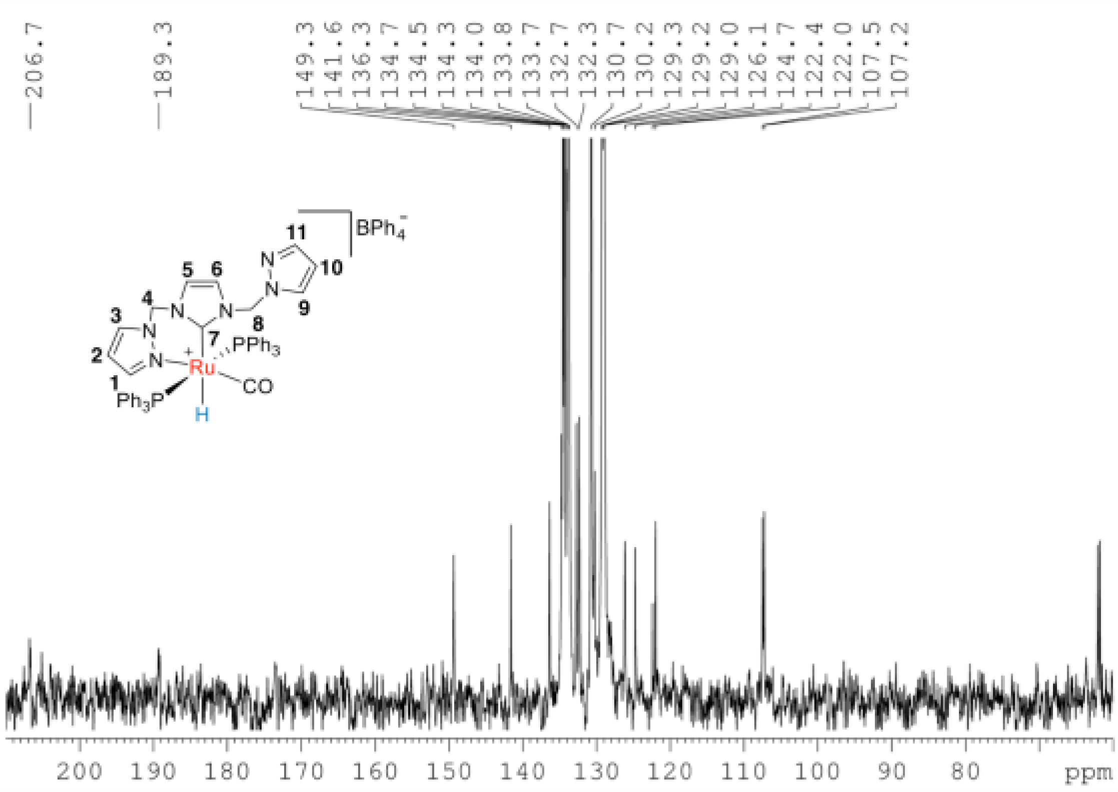


Figure 4. ^{13}C NMR (75 MHz, CD_2Cl_2) spectrum of complex **3**.

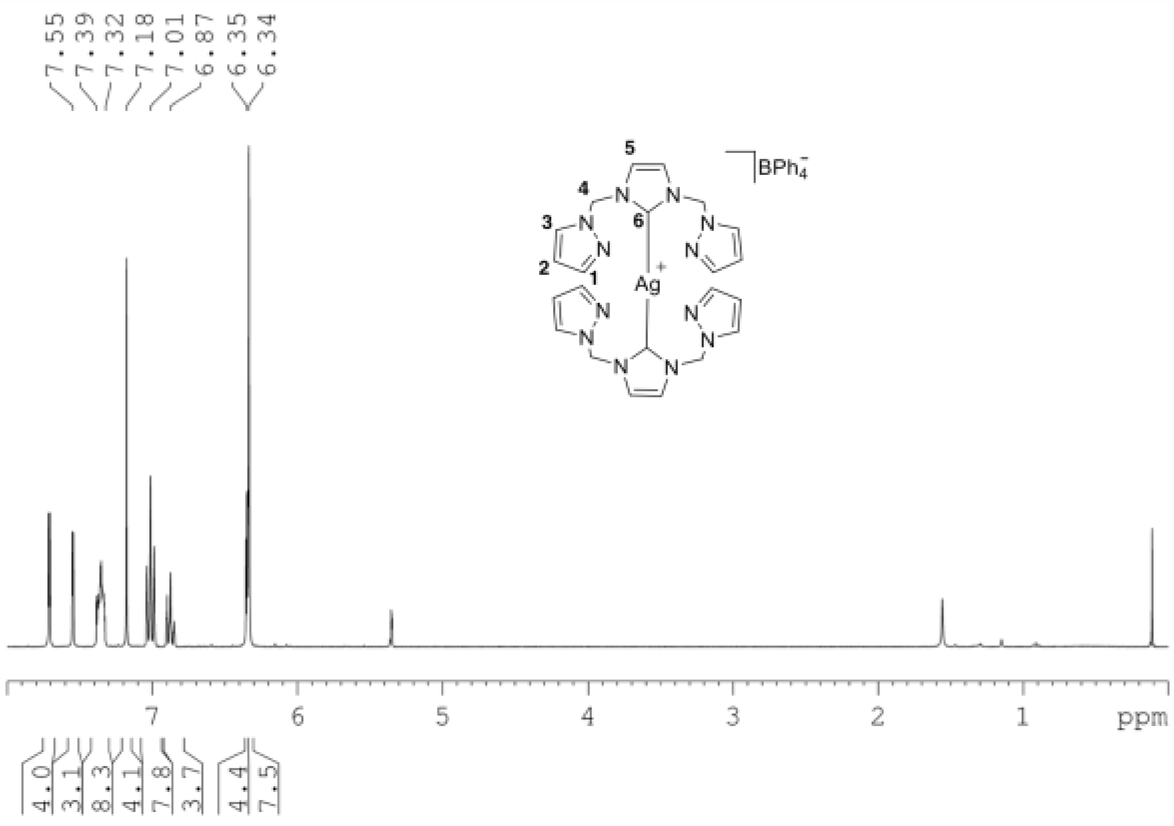


Figure 5.^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of complex **4**.

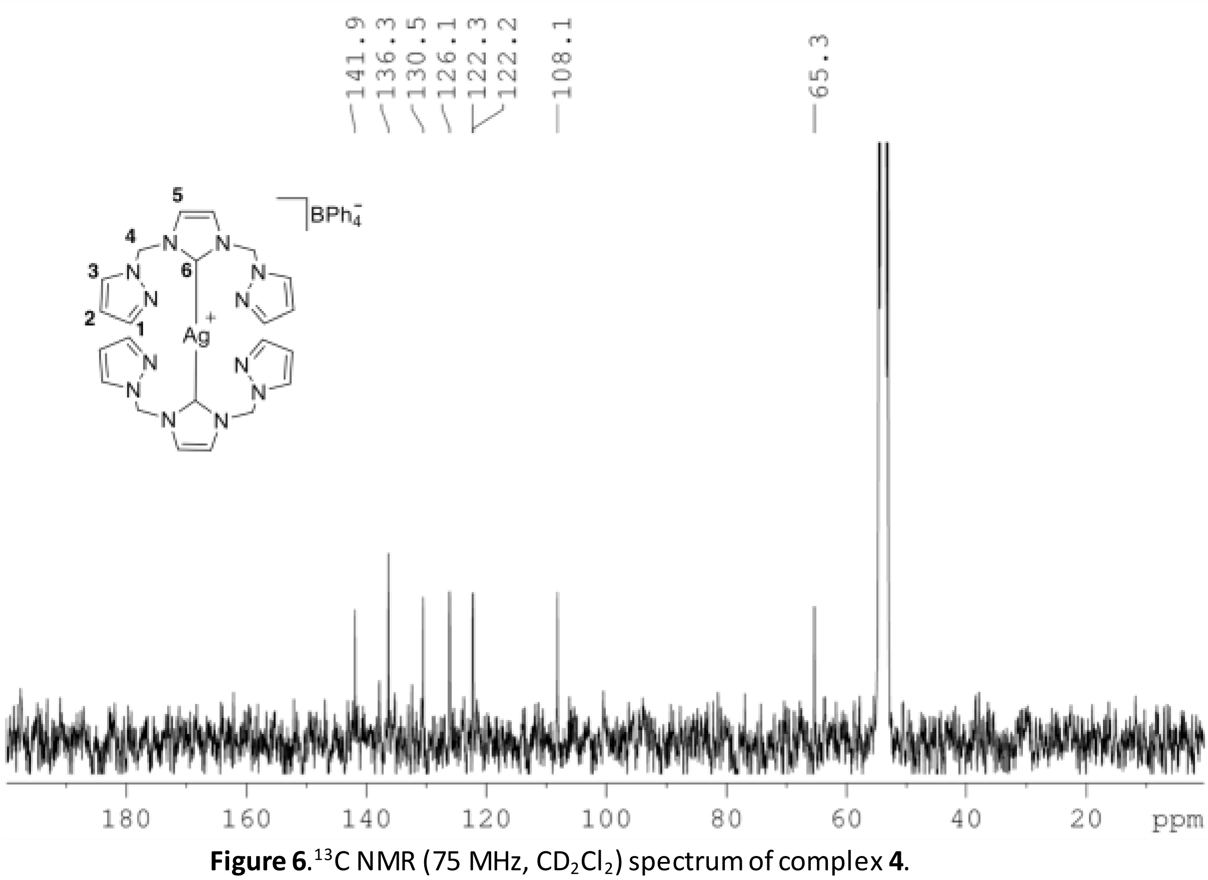


Figure 6.^{13}C NMR (75 MHz, CD_2Cl_2) spectrum of complex **4**.

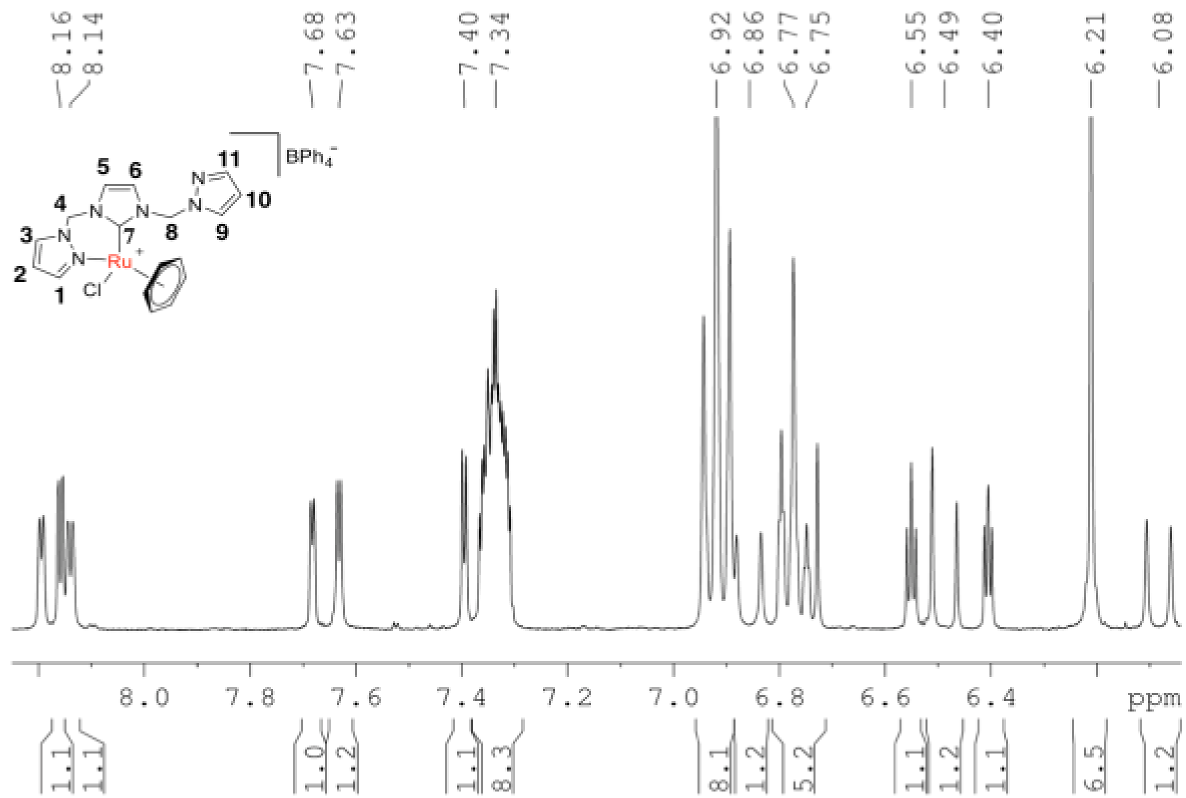


Figure 7. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) spectrum of complex **5**.

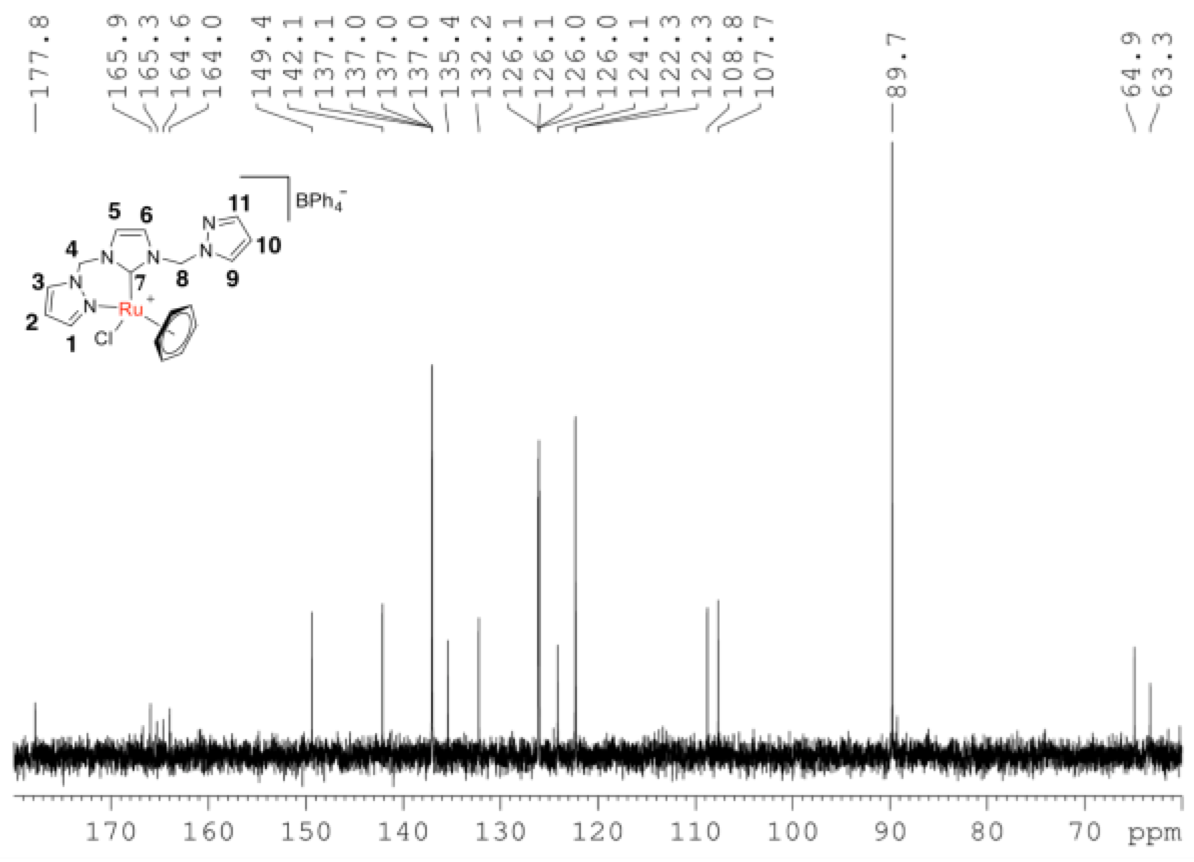


Figure 8. ^{13}C NMR (75 MHz, $(CD_3)_2CO$) spectrum of complex **5**.

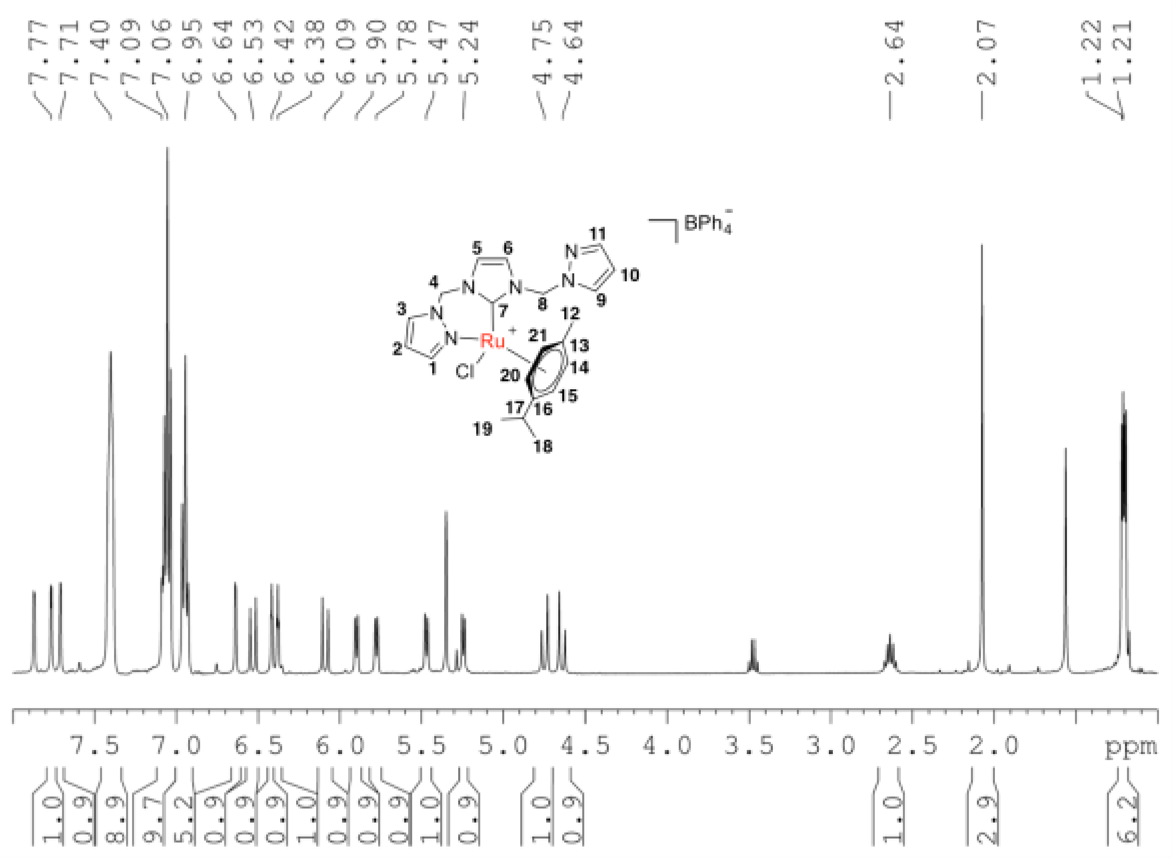


Figure 9. ^1H NMR (400 MHz, CD_2Cl_2) spectrum of complex **6b**.

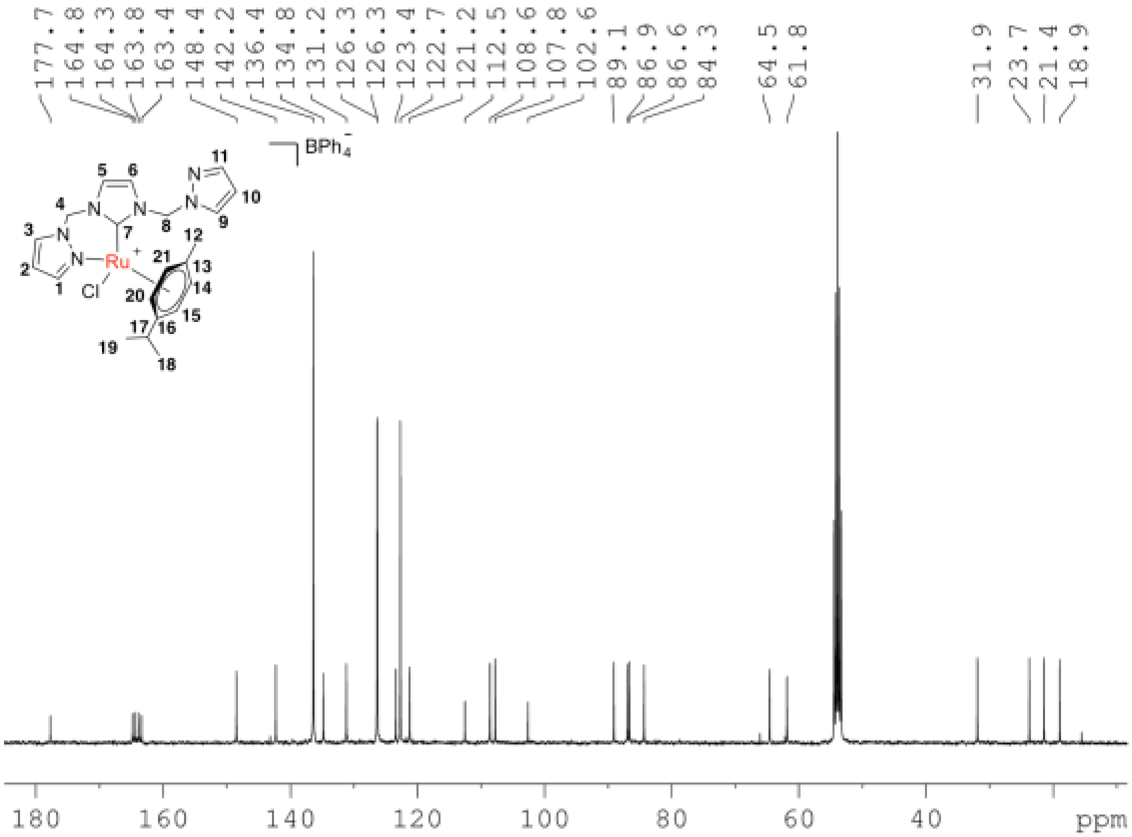


Figure 10. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **6b**.

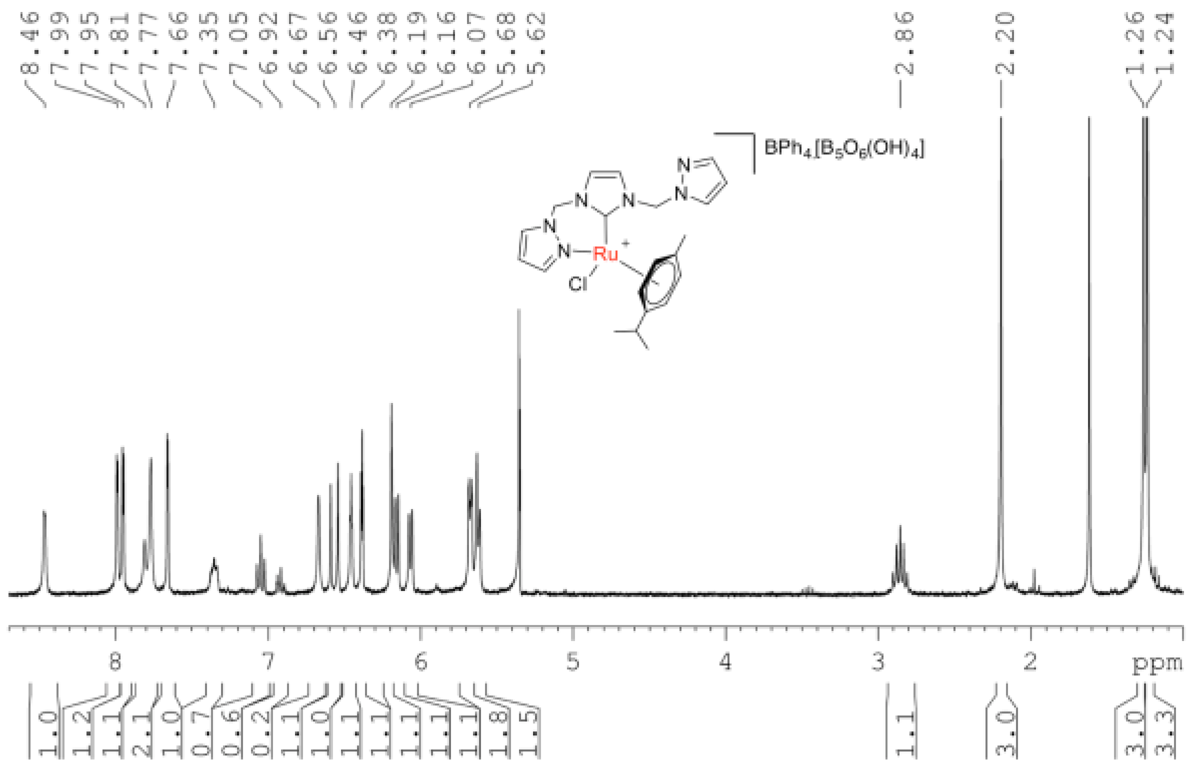


Figure 11. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of complex **6a**.

2.2 VT NMR Studies

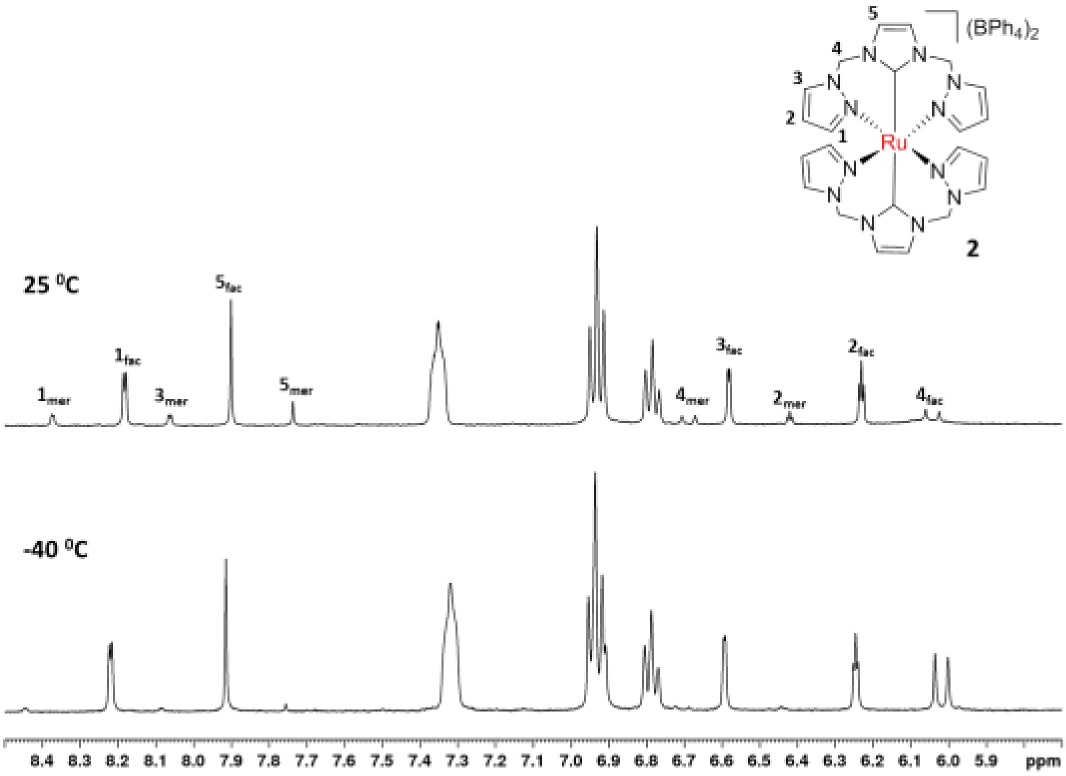


Figure 12. 1H NMR (400 MHz, $(CD_3)_2CO$) spectrum of complex **2** at -40 °C and 25 °C.

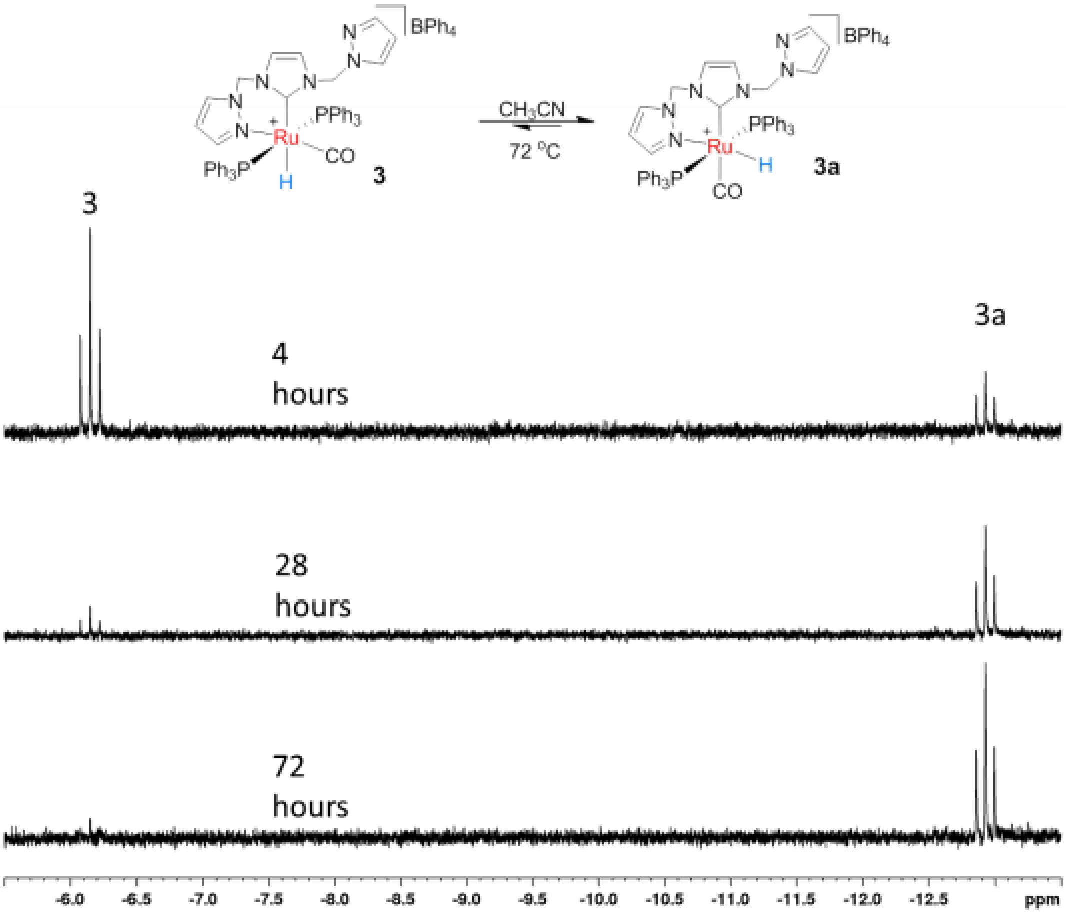


Figure 13. 1H NMR (400 MHz, (CD_3CN) spectra of the interconversion complex **3** into complex **3a** at 72 °C after 4 h, 28 h and 72 h.

3. Selected Catalysis Data

3.1. GC-MS analysis example (acetophenone)

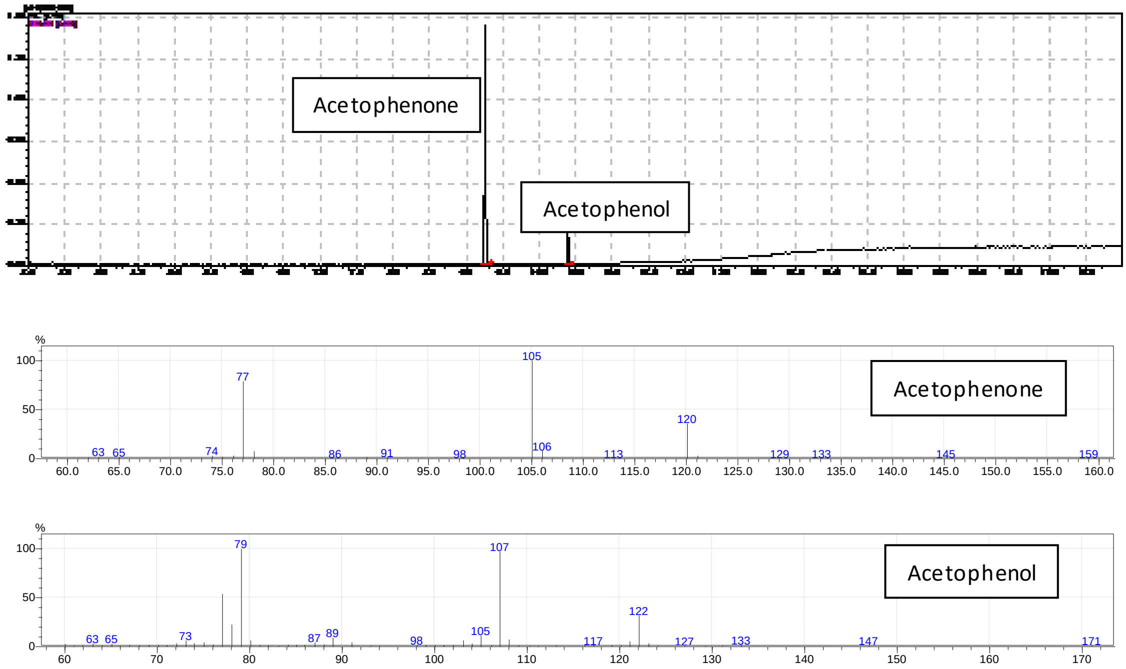


Figure 14. Gas chromatography (GC) trace of reaction mixture and mass spectra of eluted traces from GC.

9.256	9.205	9.330	TIC	17649740	88.68	14427118	88.82	1.22	MI
10.393	10.350	10.465	TIC	2254086	11.32	1816788	11.18	1.24	MI

Table 1. Retention times and peak height/areas of GC trace.

Compound	**RT(retention time)**	**Peak Height %**	**Peak Area %**
Acetophenone	**9.26**	**88.68**	**88.82**
Acetophenol	**10.39**	**11.32**	**11.18**

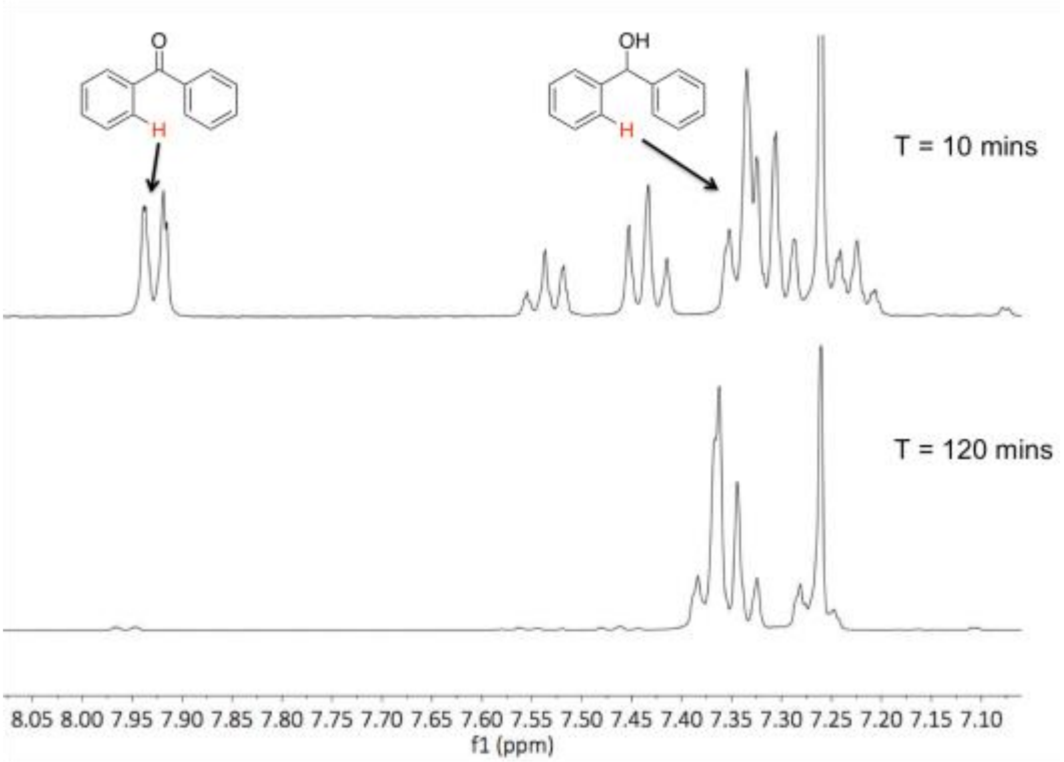


Figure 15. Stacked ^1H NMR (400 MHz, $CDCl_3$) spectra of the transfer hydrogenation reaction of benzophenone using catalyst **6b** at 10 minutes and 120 minute time points.

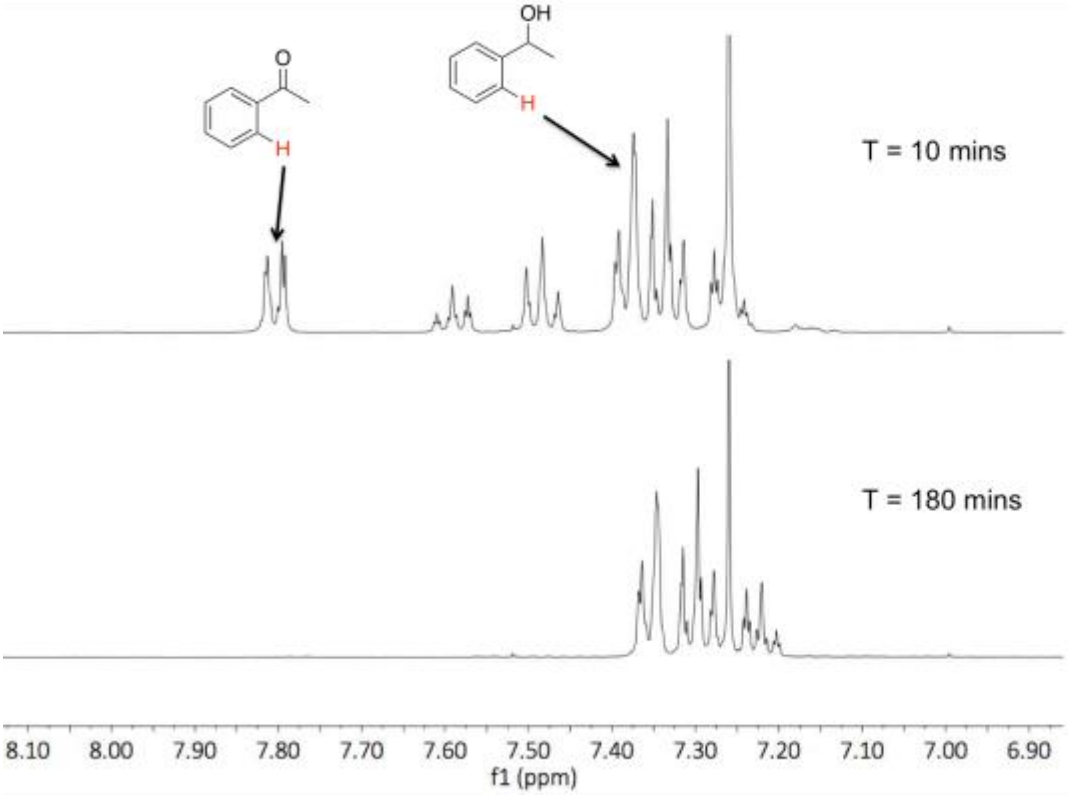
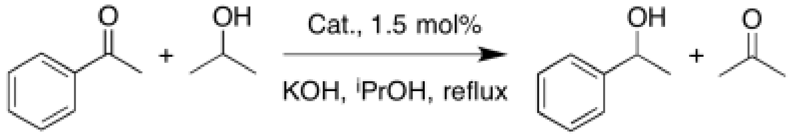


Figure 16. Stacked ^1H NMR spectrum (400 MHz, $CDCl_3$) of the transfer hydrogenation reaction of benzophenone using catalyst **6b** at 10 min and 180 min time points.

4. Isomerisation of Complex 3.

It is possible that the catalytic activity is affected by the relative position of the hydride and carbonyl co-ligands on the complex, which were found to interconvert upon heating the complex in solution *vida supra*. To test this hypothesis, complex **3a** was heated to 73 °C for 24 hours to produce the isomer **3b** with the hydrido group trans to the pyrazole. However, on testing **3b** as a catalyst for the transfer hydrogenation reaction, it achieved only 22% conversion of the substrate within four hours at 83 °C. This conversion was nearly identical to that of the *trans* isomer.



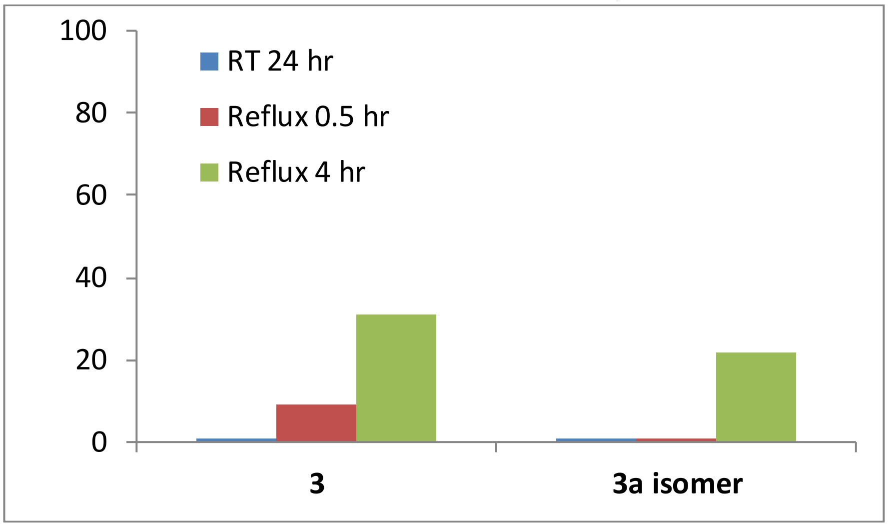


Figure 17. Catalysis results of catalyst **3** and its isomer **3a**.

5. Crystallographic Experimental Data Tables

	1	**2**	**3**	**4**	**5**	**6a**
Chemical formula	$C_{11}H_{13}N_6{\cdot}C_{24}H_{20}B$	$C_{11}H_{12}N_6Ru_{0.5}{\cdot}C_{24}H_{20}B$	$C_{48}H_{43}N_6OP_2Ru{\cdot}C_{24}H_{20}B$	$2(C_{22}H_{24}AgN_{12}){\cdot}C_{22}H_{23}AgN_{12}{\cdot}3(C_{24}H_{20}B)$	$C_{17}H_{18}ClN_6Ru{\cdot}3(C_{16}H_{18}ClN_7Ru){\cdot}4(C_{24}H_{20}B){\cdot}3(CH_4O)$	$C_{21}H_{26}ClN_6Ru{\cdot}B_5H_4O_{10}$
CCDC number	1481002	1480998	1480999	1480997	1481000	1481001
M (g mol^{-1})	548.48	598.01	1202.10	2649.82	3150.53	717.08
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Crystal Habit						
Temperature (K)	150	150	150	150	150	150
a (Å)	8.5977 (3)	9.6717 (8)	37.968 (2)	14.4586(6)	16.8274 (12)	11.3903 (4)
b (Å)	17.9211 (6)	15.4965 (13)	11.5676 (7),	19.1802(7)	18.3619 (15)	11.8757 (4)
c (Å)	19.1642 (7)	19.8638 (18)	28.5760 (18)	24.5632(10)	24.387 (2)	23.6462 (9)
α (°)	90	90	90	99.448(2)	74.808 (4)	90
β (°)	90	91.611 (5)	92.123 (3)	99.315(2)	89.916 (4)	101.366 (2)
γ (°)	90	90	90	106.299(2)	81.797 (4)	90
V (Å^3)	2952.82 (18)	2976.0 (4)	12542.0 (13)	6291.9 (4)	7192.5 (10)	3135.84 (19)
Z	4	4	8	2	2	4
Radiation type	Mo *Ka*	Mo *K*α	Mo *K*α	Mo *K*α	Mo *Ka*	Mo *K*α
μ (mm^{-1})	0.07	0.32	0.35	0.53	0.55	0.65
Crystal size (mm)	0.46 × 0.20 × 0.15	0.15 × 0.08 × 0.05	0.23 × 0.06 × 0.04	0.26 × 0.24 × 0.08	0.12 × 0.11 × 0.05	0.21 × 0.17 × 0.06
Tmin, Tmax	0.538, 0.746	0.636, 0.745	0.667, 0.746	0.692, 0.746	0.638, 0.746	0.660, 0.746
Refl. measured	14308	20709	27324	87774	112286	27698
Unique reflections	6260	5648	27320	21420	25301	6813
Obsd. Reflections [I > 2σ(I)]	5658	3092	11308	13558	16486	5717
Rint	0.051	0.111	0.0000	0.082	0.122	0.033
R[F^2> 2σ(F^2)]	0.042	0.055	0.068	0.047	0.091	0.034
wR(F^2)	0.105	0.133	0.172	0.117	0.240	0.094
S	1.04	1.00	0.88	1.00	1.03	1.06
Reflections used	6260	5648	27320	21420	25301	**3796**
Parameters	379	385	1524	1624	1861	413
Restraints	0	122	37	482	H-atom parameters constrained	6
Δρmax, Δρmin (e Å^{-3})	0.24,, -0.21	0.50, -0..91	1.36, -0.93	0.70, -0.70	4.71, -1.01	1.19, -0.77

6. References

1. Mancano, G., Page, M. J., Bhadbhade, M. & Messerle, B. A., *Inorg. Chem.* **53,** 10159–10170 (2014).