Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information:

Ruthenium complexes with an N-heterocyclic carbene NNC-pincer ligand: preparation and catalytic properties

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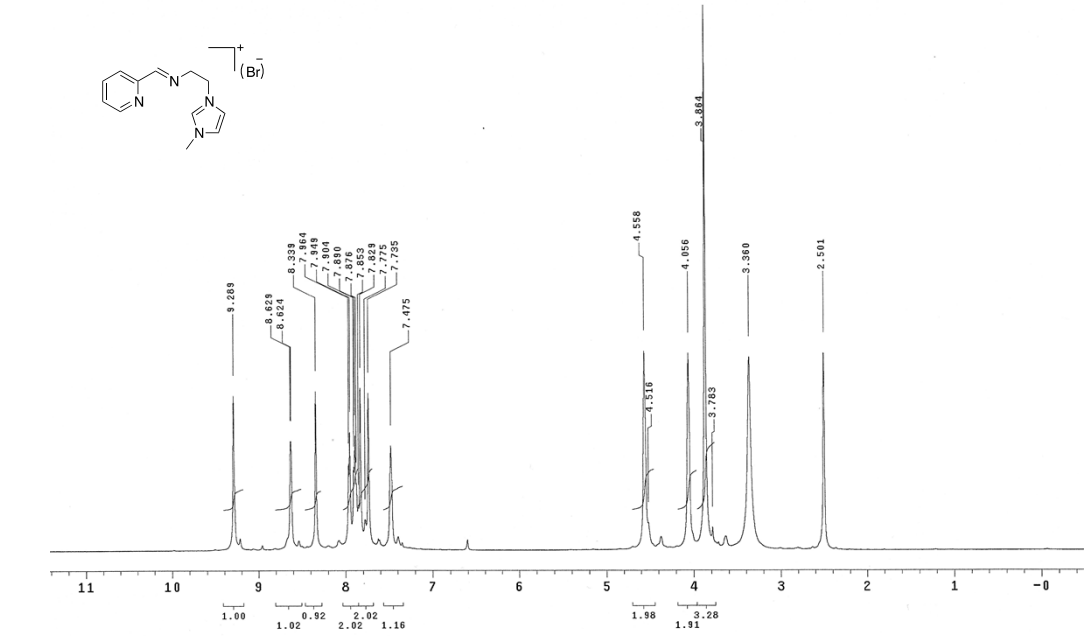
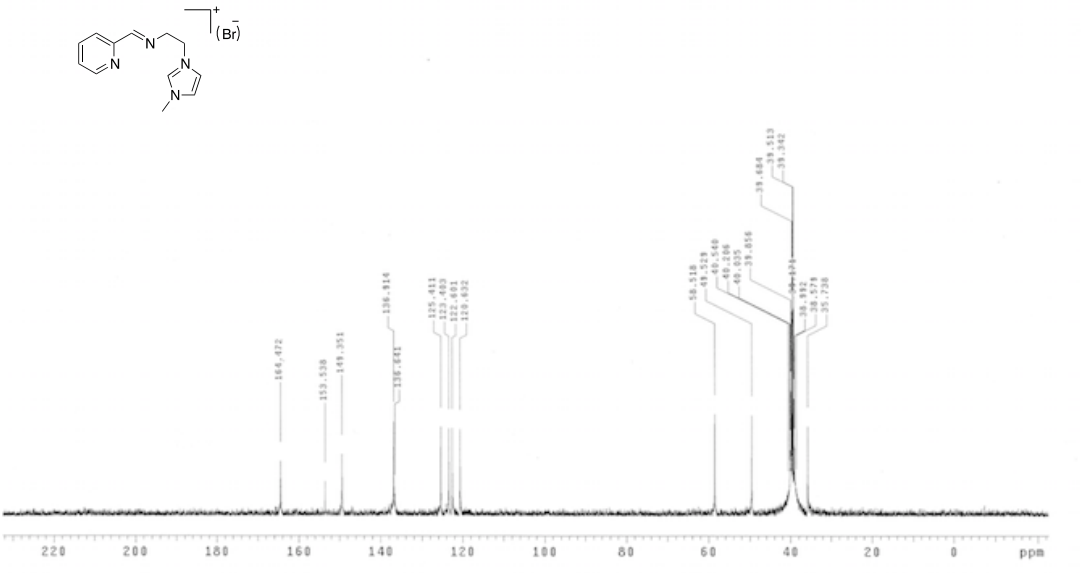
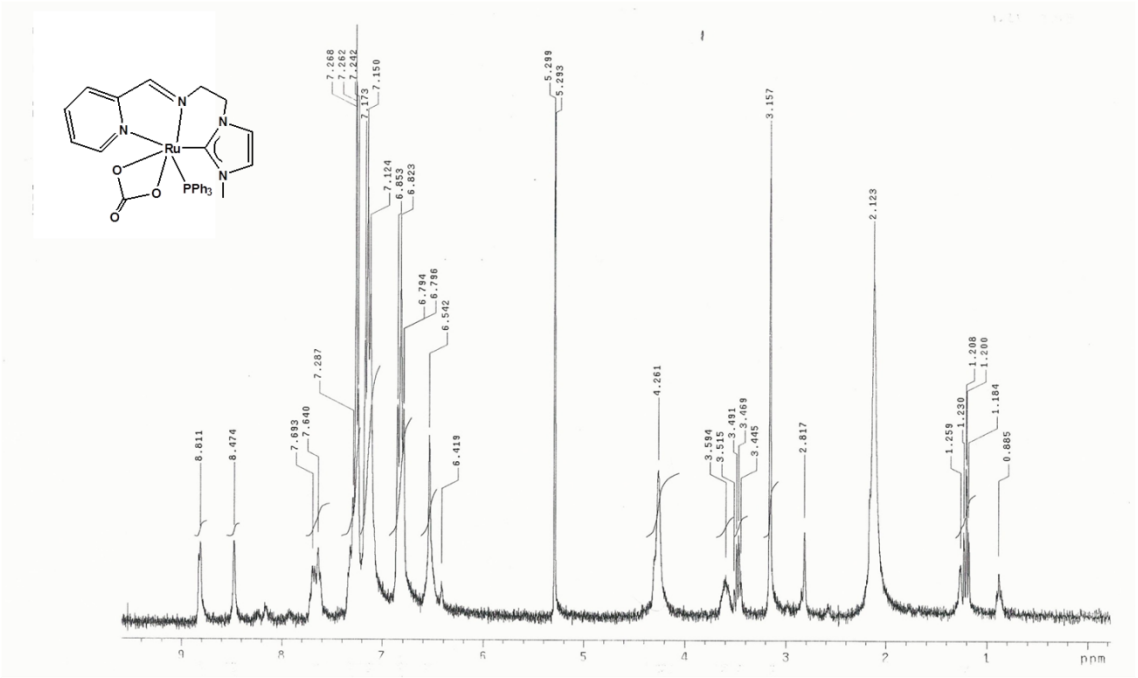
1. Spectra

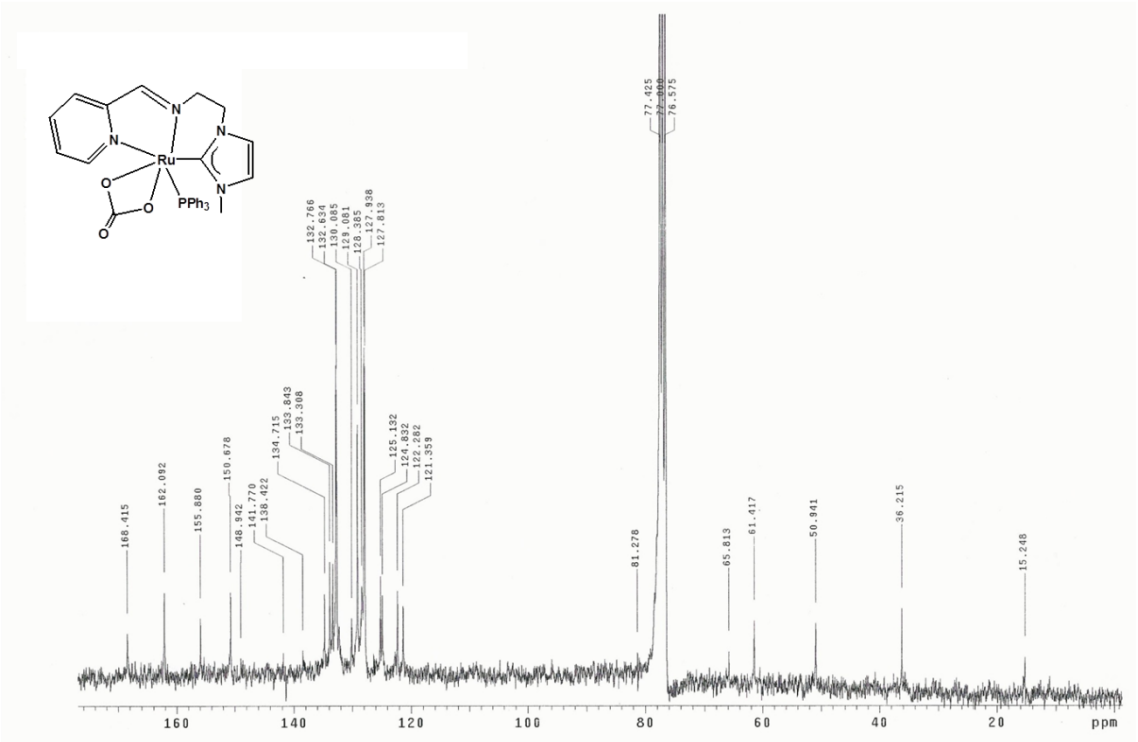
1.1. ^{1}H and ^{13}C NMR spectra of **1**



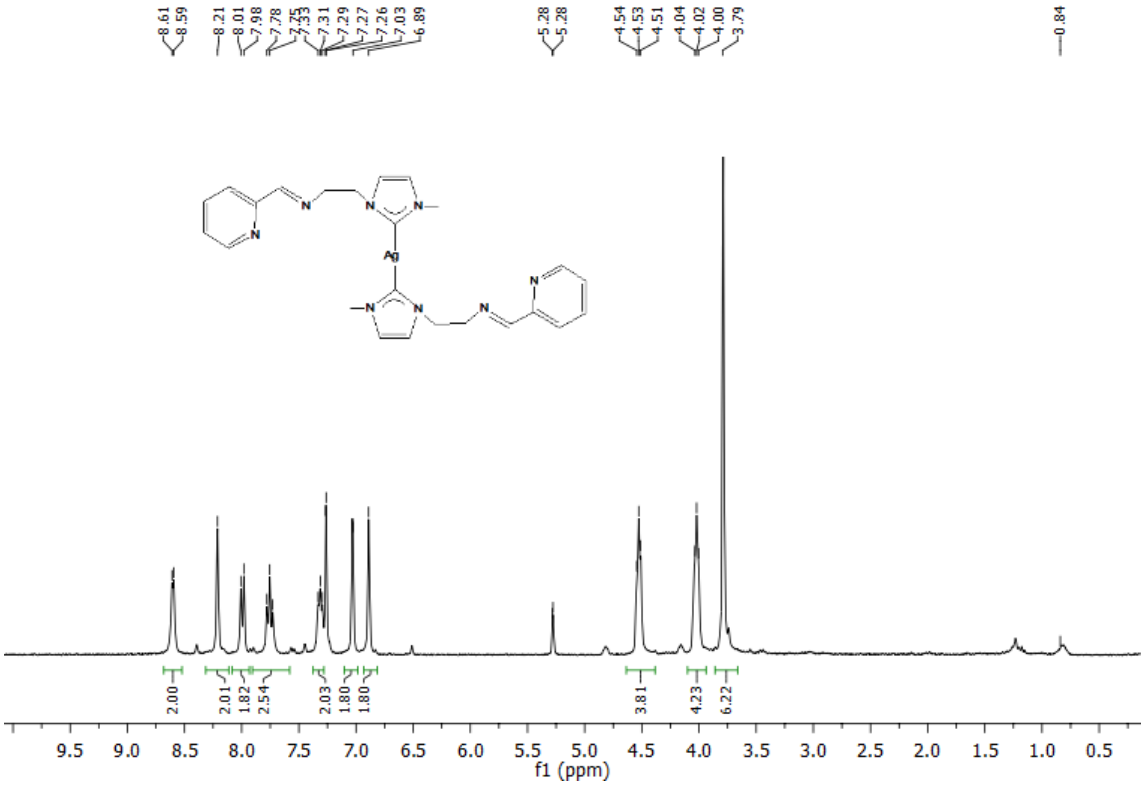


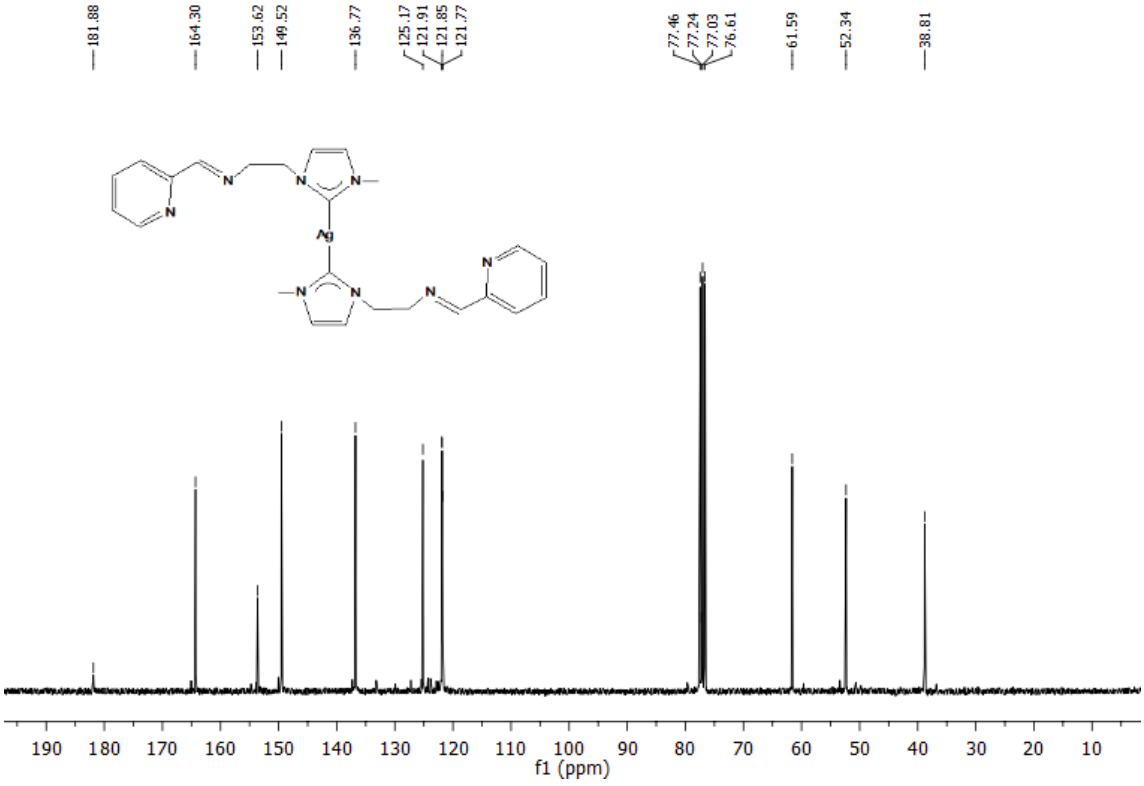
*1.2. ^{1}H and ^{13}C NMR spectra of **2***



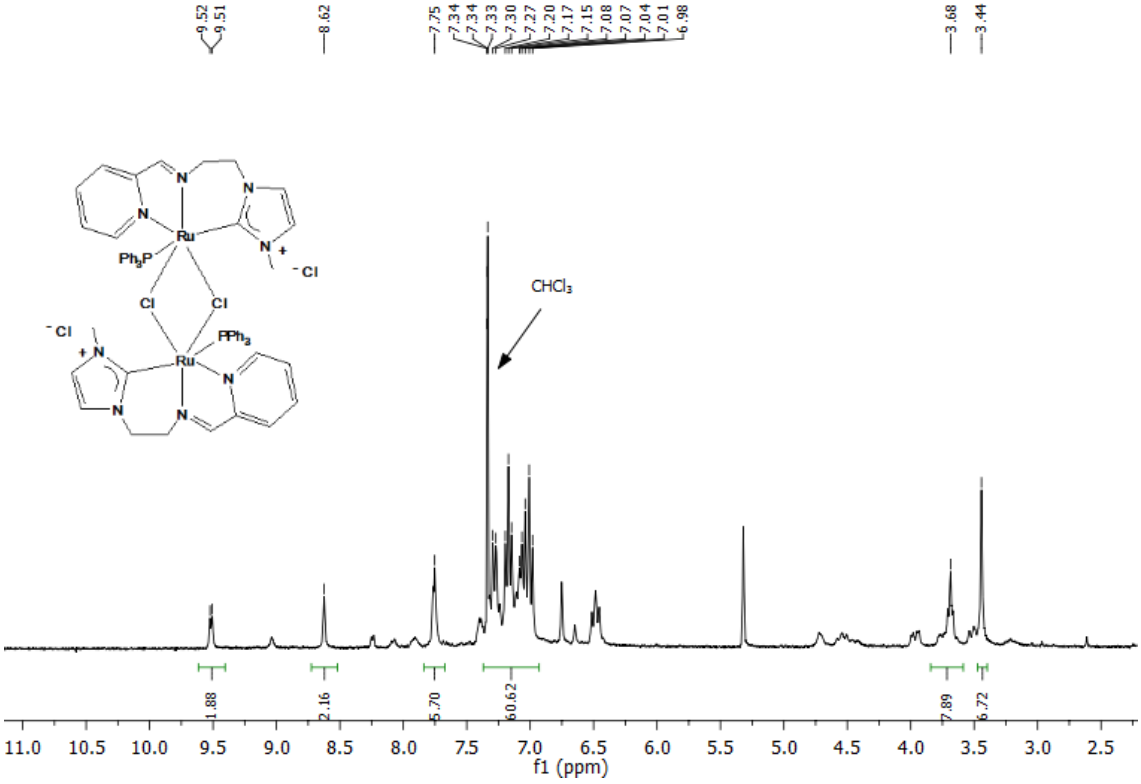


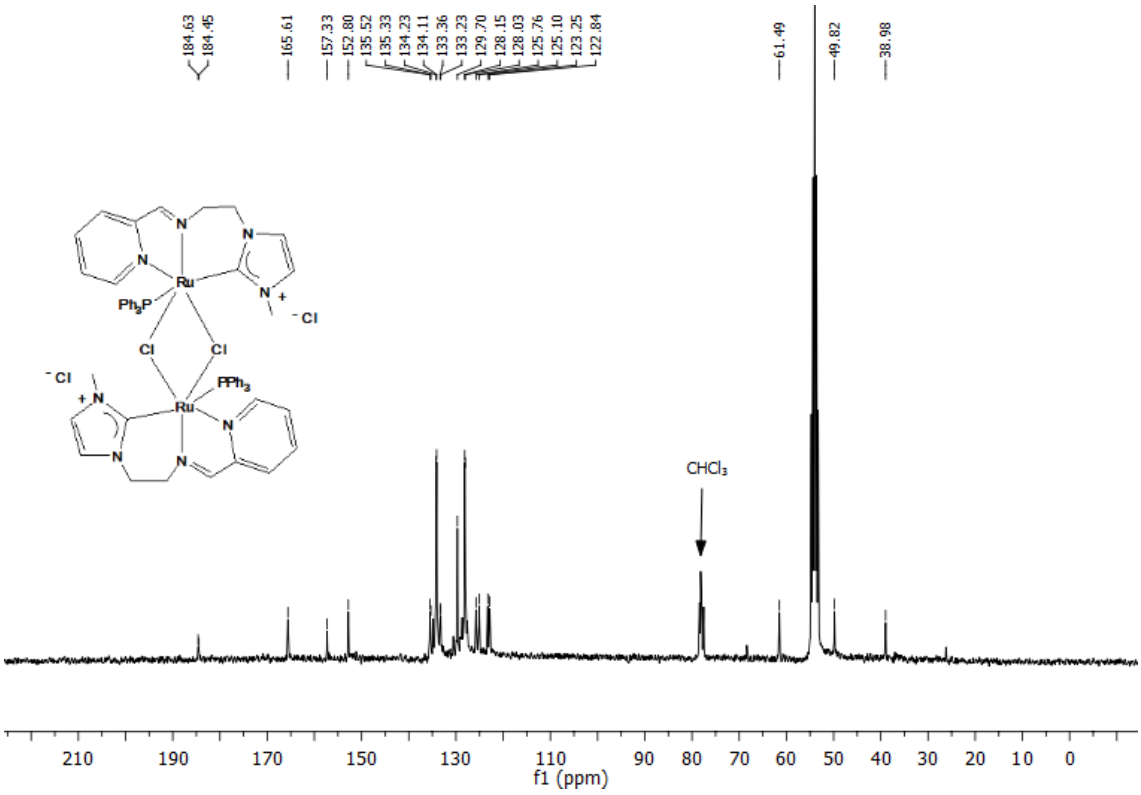
1.3. ^{1}H and ^{13}C NMR spectra of **3**





1.4. ^{1}H and ^{13}C NMR spectra of **4**

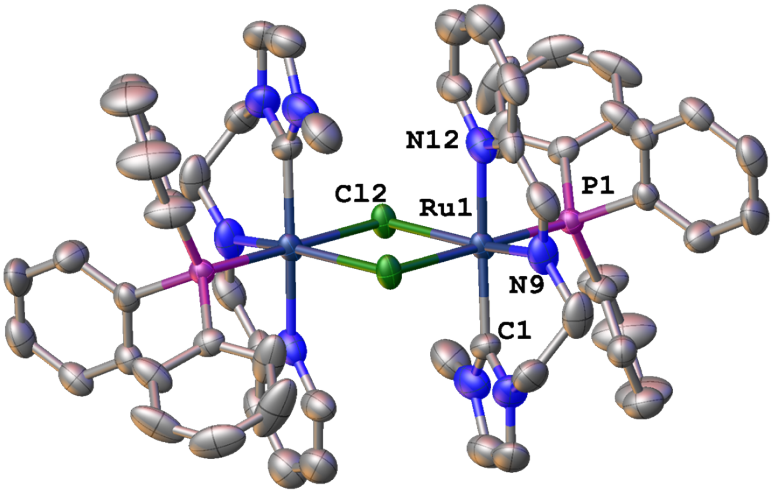




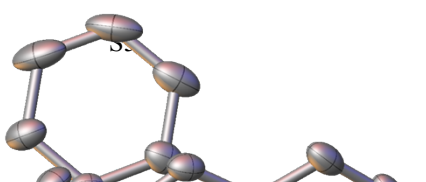
2. X-Ray Crystallography.

Single crystals of **2** and **4** suitable for X-ray crystallographyc analysis were obtained as described above. Diffraction data were collected on a Agilent SuperNova diffractometer equipped with an Altas CCD detector using Cu Kα radiation (λ = 1.54184 Å). Single mounted on a MicroMount polymer tip (MiteGen) in a random orientation. The crystals were kept at 293 K during data collection for **2** and at 290 K for **4**. The structures were solved by direct methods in SHELXS-97[4] and refined by the full-matrix method based on F^2 with the program SHELXL-97 using the OLEX software package.[1-2] Further crystallographic data may be found in the corresponding CIF files which were deposited at the Cambridge Crystallographic Data Centre CCDC, Cambridge, UK. The reference number for **2** and **4** were assigned as 1060997, 1060998 respectively.

*2.1 Crystal data, data collection and structure refinement details for **2** and **4**:*



Compound ***2***: $C_{70}H_{66}Cl_{34}N_8P_2Ru_2$ (M = 2488.68): monoclinic, space group $P2_1/a$, a = 13.2500(2)Å, b = 16.9695(3) Å, c = 23.3436(4) Å, α = 90°β = 103.9482(18)° γ = 90°, V = 5093.95(17) Å^3, Z = 2, T = 293(2) K, μ(CuKα) = 11.254 mm^{-1},$Dcalc$ = 1.623g/cm^3, 44887 reflections measured (7.38 ≤ 2Θ ≤ 131.968), 8883 unique (R_{int} = 0.0512, R_{sigma} = 0.0321), which were used in all calculations. The final R_1 was 0.0721 (I>=2u(I)) and wR_2 was 0.2154 (all data).



Compound **4**: $C_{32}H_{35}Cl_2N_4O_5PRu$ (M =758.58): monoclinic, space group $P2_1/c$, a = 18.2792(3)Å, b = 11.74106(11) Å, c = 17.1049(2)Å, V = 3259.49(9) Å^3, Z = 4, T = 199.95(10) K, μ(CuKα) = 1.54184 mm^{-1}, *Dcalc* = 1.546 g/mm^3, 27673 reflections measured (9.296 ≤ 2Θ ≤ 139.32), 6075 unique (R_{int} = 0.0499, R_{sigma} = 0.0291) which were used in all calculations. The final R_1 was 0.2354 (I > 2σ(I)) and wR_2 was 0.5147 (all data).

3. Catalytic studies: transfer hydrogenation.

3.1. General Procedure for the reduction of of ketones and aldehydes by transfer hydrogenation.

In a 50 mL high-pressure Schlenk tube, ketone (1 mmol), catalyst (0.5 mol %), Base (0.1 mmol) and *i*PrOH (3 mL) were placed. The mixture was stirred and heated to 85 ºC for 1h. The reaction yields were calculated by GC or ^{1}H NMR using Anisole as internal standard.

4. Bibliography

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.