

Supporting Information for:

**Organoruthenium Complexes Containing
Phosphinodicarboxamide Ligands**

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Table of Contents

General Procedures.....	3
Crystallographic Methods	4
DOSY NMR Spectroscopic Studies	8
DFT Methodologies.....	9
Further Observations and Comments	9
References	10
Selected NMR spectra.....	11
Geometry optimised structures	25
Geometry optimised coordinates for 6a'.....	27
Geometry optimised coordinates for 6b'.....	28
Geometry optimised coordinates for 7a'.....	30
Geometry optimised coordinates for 7b'.....	32

General Procedures

All products described were treated with rigorous exclusion of air and water using standard air-sensitive-handling techniques which included bench-top operations (Schlenk line) and glove-box techniques. Standard laboratory solvents were dried *via* reflux over calcium hydride (CH_2Cl_2) or directly collected from the in house dry-solvent towers (dispensing system) and kept in an ampoule over activated molecular sieves. C_6D_6 was dried over potassium, CDCl_3 was dried over calcium hydride, sealed in an ampoule at 80 °C for 4 days, before vacuum-transferring it to an ampoule containing a potassium mirror (C_6D_6) and subsequently stored in the glove-box prior to use, while dry/degassed CD_2Cl_2 (0.03% v/v TMS) and CD_3CN were purchased from Sigma-Aldrich and directly stored in the glove-box over molecular sieves / K_2CO_3 (residual H^+ in CD_2Cl_2 , promotes the formation of intractable mixtures of products upon coordination). NMR samples were prepared using glove-box techniques and contained in Young's tap modified borosilicate glass NMR tubes. All NMR data was collected on Bruker DPX300, DPX400, AV400, AV(III)400 or AV(III)400HD spectrometers. Chemical shifts are quoted in ppm relative to TMS (^1H , $^{13}\text{C}\{^1\text{H}\}$) and 85% H_3PO_4 (^{31}P). DOSY NMR (Convection compensated) experiments were carried out using the PFGSE (Pulsed-Field Gradient Spin-Echo) NMR Diffusion methods and analysed with the software implemented by Bruker on an AV(III)400HD NMR spectrometer. The variation of the intensity (integral) of one selected signal in the ^1H NMR spectrum (I) is related to the strength of the gradient (G) by the following equation: $\text{Ln}(I/I_0) = -\gamma^2\delta^2G^2(\Delta-\delta/3)D$, where γ = gyromagnetic ratio of the proton, δ = length of the gradient pulse, G = gradient strength, Δ = delay between the midpoints of the gradients, and D = diffusion coefficient. 31 spectra were recorded, varying G ; (Diffusion time = 200 ms, gradient (sinusoidal) = 2 ms, datafit = monoexponential). These values provided a considerable reduction of the intensity of the signal, but remained strong enough to be integrated. The data were analysed with the Bruker's software, which provided directly the diffusion coefficient (D). The quality of the data was tested by representation $\text{Ln}(I)$ versus G^2 , which gave an excellent fit to a straight line in all the cases. Hydrodynamic radii (r_H) were calculated from the Stokes–Einstein equation: $r_H = (kT)/(6\pi\eta D)$ (where T is absolute temperature, k is the Boltzmann constant, η is the solvent viscosity and D is the coefficient of diffusion). Averaged molecular radii were estimated from the calculated molecular volume defined as the volume inside a contour of 0.001 electrons/Bohr³.

Anhydrous $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ was purchased from Sigma-Aldrich, and dried under vacuum overnight and stored in the glovebox prior to use. Carbon monoxide (CP Grade N3.0, minimum purity of 99.9%) was obtained from BOC and used as received. Phosphinocarboxamides (PCAs) [**L-1-L-3**] and phosphinodicarboxamides (PDCAs) [**L-4-L-5**], were prepared according to reported procedures.¹

Safety warnings: Carbon monoxide is an extremely flammable and toxic gas, good ventilation within a fumehood should be procured when running a Schlenk line with this gas as source, away from open flames and with a carbon monoxide detector operating at all times.

Elemental microanalyses were performed by Elemental Microanalysis Ltd., using Dumas combustion method (CHN); samples were prepared from freshly synthesised, crystalline material.

Air-sensitive mass spectrometry samples were prepared under an argon atmosphere by placing the sample inside glass capillaries. The spectra for the complexes described were recorded by the EPSRC National Mass Spectrometry Facility at Swansea University. Non air-sensitive samples were prepared by careful dilution of the sample in methanol and run through the departmental service at the School of Chemistry, University of Nottingham using a Bruker MicroToF (ESI⁺/ESI⁻). Infrared spectroscopy samples were recorded (ATR) using a Bruker ALPHA FTIR spectrometer over a frequency range of 4000-400 cm⁻¹.

Crystallographic Methods

Crystals suitable for single-crystal X-ray diffraction for **1-5** were grown from concentrated toluene (layered with hexane) or C₆D₆ extracts at room temperature, respectively. Under a flow of N₂, crystals suitable for single crystal X-Ray diffraction were quickly removed from the crystallisation vessel and covered with "fomblin" (YR-1800 perfluoropolyether oil). A suitable crystal was then mounted on a polymer-tipped MicroMountTM and cooled rapidly to 120K in a stream of cold N₂ using an Oxford Cryosystems open flow cryostat.² Single crystal X-ray diffraction data were collected either using an Agilent SuperNova diffractometer (Atlas CCD area detector), an Agilent SuperNovaII diffractometer (Atlas S2 CCD area detector), an Agilent SuperNovaII diffractometer (Titan S2 CCD area detector) or a Rigaku XtaLab Pro MM007 diffractometer (Pilatus 200K detector). All samples were collected with mirror monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$, with ω scans. Absorption corrections were applied using an analytical numerical method (CrysAlis Pro).³ All non-H atoms were located using direct methods⁴ and difference Fourier syntheses. In the case of the structures of **1**, **3** and **5**, the hydrogen atoms bound to N1 were restrained to 0.88(2) \AA . Unless otherwise specified, hydrogen atoms were placed and refined using a geometric riding model. All fully occupied non-H atoms were refined with anisotropic displacement parameters. The determination for **4** has solvent accessible voids in the crystal lattice, however no unaccounted residual density is present that could be attributed to partially occupied positions. Having said this, there are two disordered toluene molecules in the asymmetric unit. One of these sits across a centre of symmetry, and is half occupied. The other is disordered over two positions. The occupancy of these were refined competitively, converging to a ratio of 0.58:0.42. Chemically equivalent 1,2- and 1,3- distances of the toluenes were restrained to be approximately equal. The toluene across the centre of symmetry could not be sensibly modelled with anisotropic thermal parameters, so was refined isotropically. Similarly, restraints were applied to the thermal parameters of toluene carbon atoms. Following modelling and refinement of the fully occupied organic components in the structure, a residual electron density of 1.7 e \AA^{-3} could be observed flanking Ru1 and mirroring the plane generated by the *p*-cymene moiety. In the case of the structure of **5**, a similar Qpeak (proximal to the R1-P1 bond) with a value of 1.1 e \AA^{-3} is present. For both aforementioned structures, these observations are attributed to electron density surrounding the transition metal. Crystal structures were solved and refined using the Olex2 software package.⁵ Programs used include CrysAlisPro⁶ (control of Supernova, data integration and absorption correction), SHELXL⁷ (structure refinement), SHELXS⁸ (structure solution), SHELXT⁹ (structure solution), OLEX2^{5a} (molecular graphics). CIF files were checked using checkCIF.¹⁰

Crystal data for [Ru(*p*-cym){Ph₂PC(=O)N(H)^{*i*}Pr}Cl₂] (1):

C₃₂H₃₈Cl₂NOPRu (*M* = 655.57 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 10.6269(9) Å, *b* = 12.5033(13) Å, *c* = 12.5086(9) Å, *α* = 88.346(7)°, *β* = 89.950(6)°, *γ* = 66.060(9)°, *V* = 1518.3(2) Å³, *Z* = 2, *T* = 120(2) K, *μ*(CuKα) = 6.486 mm⁻¹, *D*_{calc} = 1.434 g/cm³, 10786 reflections measured (7.07° ≤ 2θ ≤ 147.608°), 5905 unique (*R*_{int} = 0.0274, *R*_{sigma} = 0.0369) which were used in all calculations. The final *R*₁ was 0.0248 (*I* > 2σ(*I*)) and *wR*₂ was 0.0634 (all data).

Crystal data for [Ru(*p*-cym){Ph₂PC(=O)N(H)Ph}Cl₂] (2):

C₂₉H₃₀Cl₂NOPRu (*M* = 611.48 g/mol): monoclinic, space group *P*2₁/*n* (no. 14), *a* = 11.40808(12) Å, *b* = 12.68260(10) Å, *c* = 18.88149(19) Å, *β* = 106.7865(11)°, *V* = 2615.44(5) Å³, *Z* = 4, *T* = 120(2) K, *μ*(CuKα) = 7.488 mm⁻¹, *D*_{calc} = 1.553 g/cm³, 25745 reflections measured (8.16° ≤ 2θ ≤ 154.218°), 5403 unique (*R*_{int} = 0.0348, *R*_{sigma} = 0.0164) which were used in all calculations. The final *R*₁ was 0.0321 (*I* > 2σ(*I*)) and *wR*₂ was 0.0895 (all data).

Crystal data for [Ru(*p*-cym){Ph₂PC(=O)N(H)*p*-tol}Cl₂] (3):

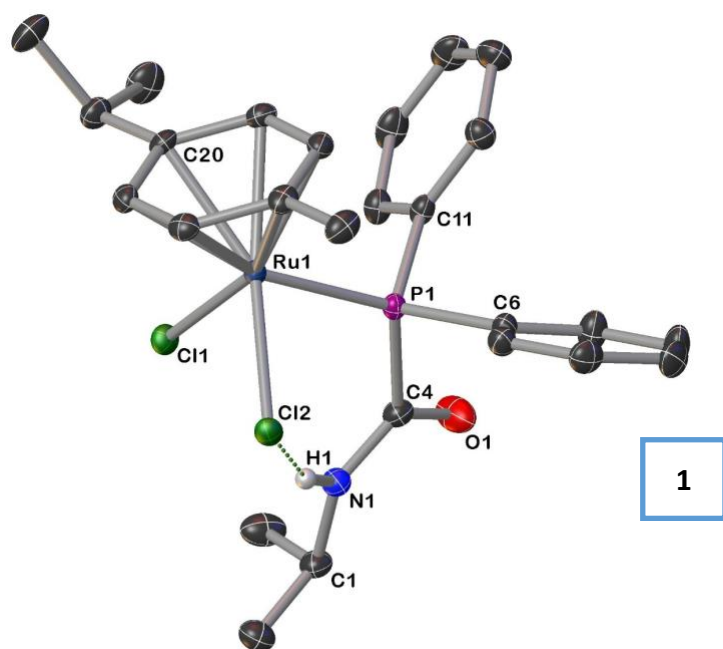
C₃₀H₃₂Cl₂NOPRu (*M* = 625.50 g/mol): monoclinic, space group *P*2₁/*n* (no. 14), *a* = 9.83232(16) Å, *b* = 16.1381(2) Å, *c* = 17.4667(2) Å, *β* = 102.2783(14)°, *V* = 2708.14(7) Å³, *Z* = 4, *T* = 120(2) K, *μ*(CuKα) = 7.246 mm⁻¹, *D*_{calc} = 1.534 g/cm³, 20656 reflections measured (7.54° ≤ 2θ ≤ 147.554°), 5362 unique (*R*_{int} = 0.0289, *R*_{sigma} = 0.0216) which were used in all calculations. The final *R*₁ was 0.0204 (*I* > 2σ(*I*)) and *wR*₂ was 0.0510 (all data).

Crystal data for [Ru(*p*-cym){Ph₂PC(=O)N(Ph)C(=O)N(H)Ph}Cl₂] (4):

C_{46.5}H₄₇Cl₂N₂O₂PRu (*M* = 868.80 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 10.3423(2) Å, *b* = 13.3792(3) Å, *c* = 15.2168(3) Å, *α* = 103.818(2)°, *β* = 90.321(2)°, *γ* = 100.687(2)°, *V* = 2006.42(7) Å³, *Z* = 2, *T* = 120(2) K, *μ*(CuKα) = 5.086 mm⁻¹, *D*_{calc} = 1.438 g/cm³, 23223 reflections measured (6.934° ≤ 2θ ≤ 147.79°), 7894 unique (*R*_{int} = 0.0288, *R*_{sigma} = 0.0269) which were used in all calculations. The final *R*₁ was 0.0382 (*I* > 2σ(*I*)) and *wR*₂ was 0.0962 (all data).

Crystal data for [Ru(*p*-cym){Ph₂PC(=O)N(*p*-tol)C(=O)N(H)*p*-tol}Cl₂] (5):

C₄₅H₄₇Cl₂N₂O₂PRu (*M* = 850.78 g/mol): monoclinic, space group *P*2₁/*c* (no. 14), *a* = 13.7569(4) Å, *b* = 11.3299(3) Å, *c* = 25.8146(10) Å, *β* = 96.096(3)°, *V* = 4000.8(2) Å³, *Z* = 4, *T* = 120(2) K, *μ*(CuKα) = 5.088 mm⁻¹, *D*_{calc} = 1.412 g/cm³, 18329 reflections measured (6.462° ≤ 2θ ≤ 147.096°), 7855 unique (*R*_{int} = 0.0422, *R*_{sigma} = 0.0457) which were used in all calculations. The final *R*₁ was 0.0516 (*I* > 2σ(*I*)) and *wR*₂ was 0.1219 (all data).

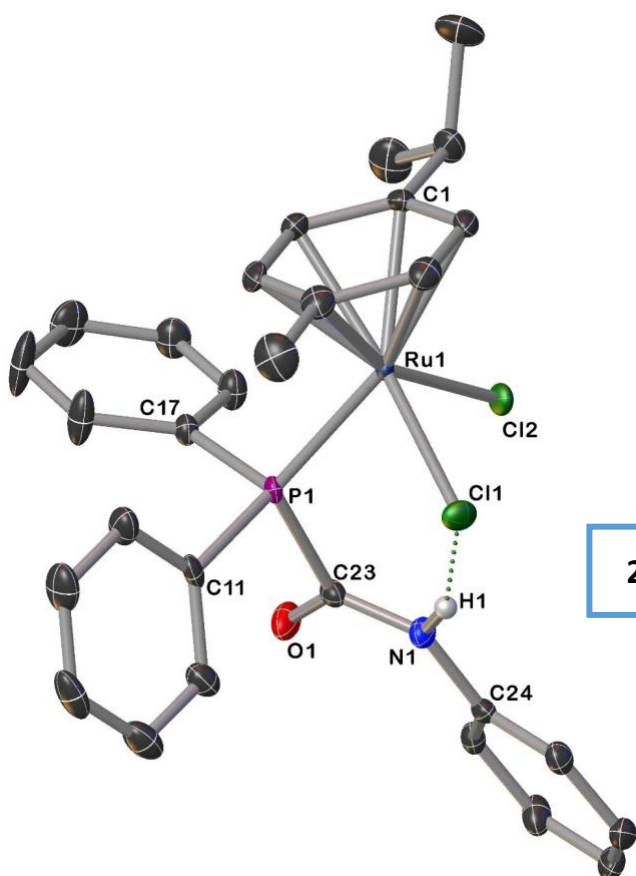


1

$C(20)_{\text{centroid}}-\text{Ru}(1)$ 1.7010(8); $\text{Ru}(1)-\text{Cl}(1)$ 2.4115(5);
 $\text{Ru}(1)-\text{Cl}(2)$ 2.4183(5); $\text{Ru}(1)-\text{P}(1)$ 2.3476(5); $\text{P}(1)-$
 $\text{C}(11)$ 1.8137(19); $\text{P}(1)-\text{C}(6)$ 1.8214(19); $\text{P}(1)-\text{C}(4)$
 1.902(2); $\text{C}(4)-\text{O}(1)$ 1.217(3); $\text{C}(4)-\text{N}(1)$ 1.328(3);
 $\text{N}(1)-\text{C}(1)$ 1.468(3)

$\text{Cl}(1)-\text{Ru}(1)-\text{Cl}(2)$ 88.442(17); $\text{Cl}(1)-\text{Ru}(1)-\text{P}(1)$
 87.354(17); $\text{Cl}(2)-\text{Ru}(1)-\text{P}(1)$ 86.958(18); $\text{Ru}(1)-$
 $\text{P}(1)-\text{C}(11)$ 110.96(6); $\text{Ru}(1)-\text{P}(1)-\text{C}(6)$ 117.60(7);
 $\text{Ru}(1)-\text{P}(1)-\text{C}(4)$ 120.52(6); $\text{N}(1)-\text{C}(4)-\text{P}(1)$
 114.12(14); $\text{N}(1)-\text{C}(4)-\text{O}(1)$ 126.14(19)

Figure S1. Molecular structure for **1** with displacement ellipsoids set at the 50% probability level. Crystallisation solvent and hydrogen atoms with the exception of H1, have been omitted for clarity.

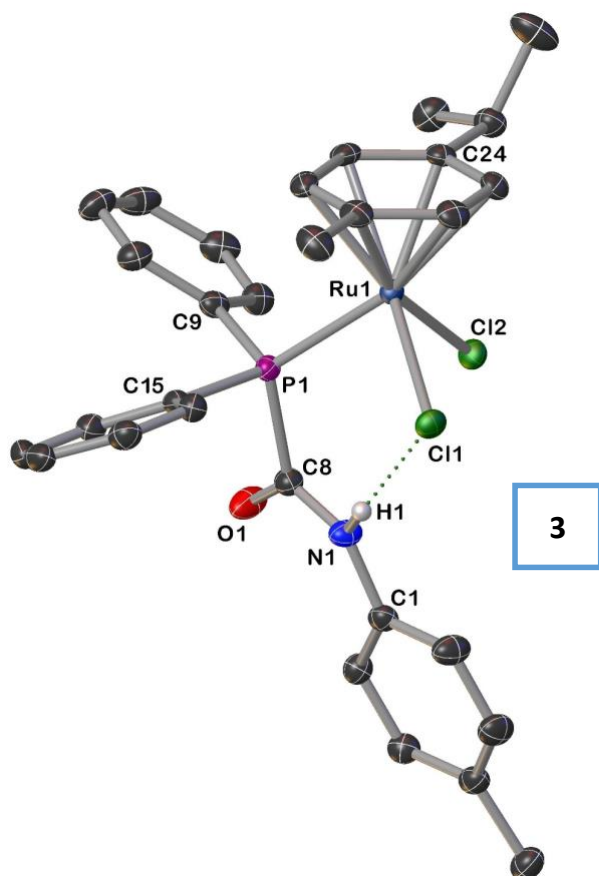


2

$C(1)_{\text{centroid}}-\text{Ru}(1)$ 1.7007(10); $\text{Ru}(1)-\text{Cl}(1)$ 2.4142(6);
 $\text{Ru}(1)-\text{Cl}(2)$ 2.4151(6); $\text{Ru}(1)-\text{P}(1)$ 2.3448(6); $\text{P}(1)-$
 $\text{C}(17)$ 1.819(2); $\text{P}(1)-\text{C}(11)$ 1.837(2); $\text{P}(1)-\text{C}(23)$
 1.901(2); $\text{C}(23)-\text{O}(1)$ 1.217(3); $\text{C}(23)-\text{N}(1)$ 1.344(3);
 $\text{N}(1)-\text{C}(24)$ 1.422(3)

$\text{Cl}(1)-\text{Ru}(1)-\text{Cl}(2)$ 88.95(2); $\text{Cl}(1)-\text{Ru}(1)-\text{P}(1)$
 85.17(2); $\text{Cl}(2)-\text{Ru}(1)-\text{P}(1)$ 86.87(2); $\text{Ru}(1)-\text{P}(1)-$
 $\text{C}(11)$ 118.55(8); $\text{Ru}(1)-\text{P}(1)-\text{C}(17)$ 111.89(8); $\text{Ru}(1)-$
 $\text{P}(1)-\text{C}(23)$ 118.02(7); $\text{N}(1)-\text{C}(23)-\text{P}(1)$ 114.45(17);
 $\text{N}(1)-\text{C}(23)-\text{O}(1)$ 126.4(2)

Figure S2. Molecular structure for **2** with displacement ellipsoids set at the 50% probability level. Hydrogen atoms with the exception of H1, have been omitted for clarity.

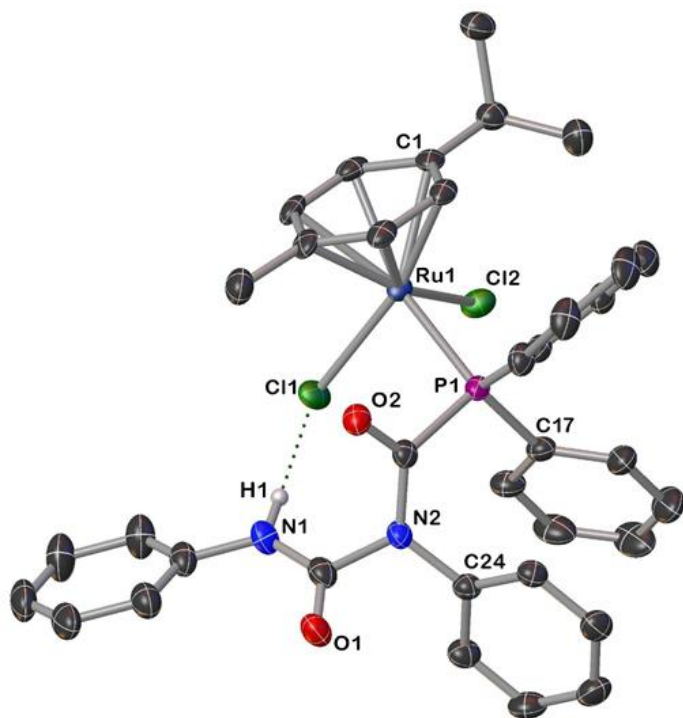


3

C(24)_{centroid}-Ru(1) 1.6989(7); Ru(1)-Cl(1) 2.4171(4); Ru(1)-Cl(2) 2.4078(4); Ru(1)-P(1) 2.3517(4); P(1)-C(15) 1.8262(17); P(1)-C(9) 1.8196(18); P(1)-C(8) 1.9066(18); C(8)-O(1) 1.217(2); C(8)-N(1) 1.338(2); N(1)-C(1) 1.413(2)

Cl(1)-Ru(1)-Cl(2) 89.156(14); Cl(1)-Ru(1)-P(1) 90.440(15); Cl(2)-Ru(1)-P(1) 83.286(15); Ru(1)-P(1)-C(9) 112.61(6); Ru(1)-P(1)-C(15) 117.59(6); Ru(1)-P(1)-C(8) 118.61(6); N(1)-C(8)-P(1) 111.80(12); N(1)-C(8)-O(1) 127.16(17)

Figure S3. Molecular structure for **3** with displacement ellipsoids set at the 50% probability level. Hydrogen atoms with the exception of H1, have been omitted for clarity.

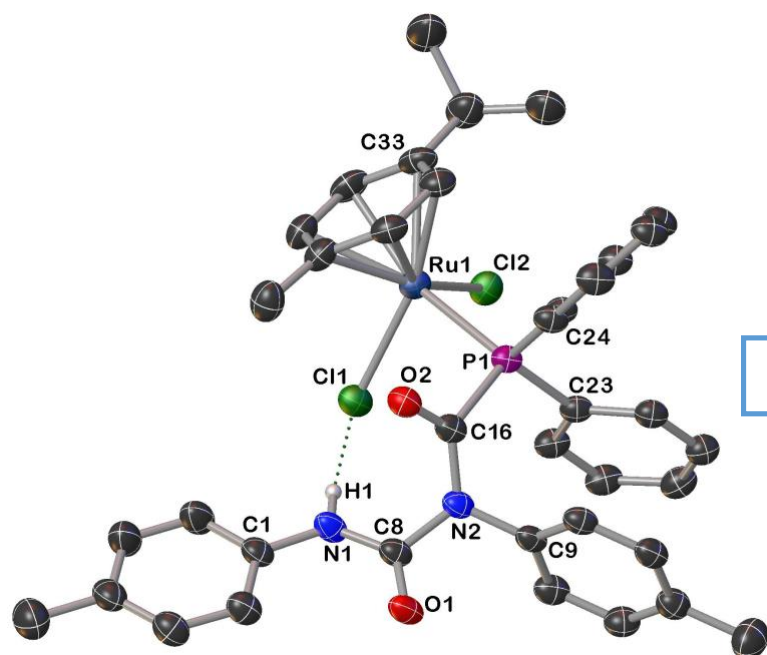


4

C(1)_{centroid}-Ru(1) 1.7010(11); Ru(1)-Cl(1) 2.4296(9); Ru(1)-Cl(2) 2.3941(7); Ru(1)-P(1) 2.3678(7); P(1)-C(11) 1.830(3); P(1)-C(17) 1.813(3); P(1)-C(23) 1.887(3); C(23)-O(1) 1.217(3); C(23)-N(1) 1.387(4); N(1)-C(30) 1.459(4); C(30)-O(2) 1.207(4); C(30)-N(2) 1.344(4); N(2)-C(31) 1.421(4)

Cl(1)-Ru(1)-Cl(2) 88.27(3); Cl(1)-Ru(1)-P(1) 89.33(2); Cl(2)-Ru(1)-P(1) 87.45(3); Ru(1)-P(1)-C(11) 112.44(9); Ru(1)-P(1)-C(17) 117.92(10); Ru(1)-P(1)-C(23) 105.81(8); N(1)-C(23)-P(1) 122.11(18); C(23)-N(1)-C(30) 117.4(2); O(1)-C(23)-P(1) 115.6(2); N(1)-C(23)-O(1) 121.8(3); N(1)-C(30)-N(2) 111.(3); C(30)-N(2)-C(31) 126.3(3)

Figure S4. Molecular structure for **4** with displacement ellipsoids set at the 50% probability level. Crystallisation solvent and hydrogen atoms with the exception of H2, have been omitted for clarity.



C(33)_{centroid}-Ru(1) 1.702(2); Ru(1)-Cl(1) 2.4302(11); Ru(1)-Cl(2) 2.3974(10); Ru(1)-P(1) 2.3635(10); P(1)-C(24) 1.826(4); P(1)-C(23) 1.829(4); P(1)-C(16) 1.898(4); C(16)-O(2) 1.208(5); C(16)-N(2) 1.385(5); N(2)-C(8) 1.450(6); C(8)-O(1) 1.213(5); C(8)-N(1) 1.346(6); N(1)-C(1) 1.418(6)

Cl(1)-Ru(1)-Cl(2) 88.76(4); Cl(1)-Ru(1)-P(1) 86.49(4); Cl(2)-Ru(1)-P(1) 89.70(4); Ru(1)-P(1)-C(24) 114.33(13); Ru(1)-P(1)-C(23) 120.11(13); Ru(1)-P(1)-C(16) 104.45(13); N(2)-C(16)-P(1) 120.2(3); C(16)-N(2)-C(8) 117.9(4); O(2)-C(16)-P(1) 115.7(3); N(2)-C(16)-O(2) 123.6(4); N(1)-C(8)-N(2) 112.4(4); C(8)-N(1)-C(1) 126.4(4)

5

Figure S5. Molecular structure for **5** with displacement ellipsoids set at the 50% probability level. Crystallisation solvent and hydrogen atoms with the exception of H1, have been omitted for clarity.

DOSY NMR Spectroscopic Studies

Table S1. Diffusion coefficient values obtained from DOSY NMR spectroscopy in CD₂Cl₂ (25 °C).

Substrate	Concentration (M)	Diffusion Coefficient (m ² /s)	Hydrodynamic Radius (m)
2	0.014	1.09x10 ⁻⁹	4.86x10 ⁻¹⁰
5	0.020	9.80x10 ⁻¹⁰	5.43x10 ⁻¹⁰
7	0.020	9.15x10 ⁻¹⁰	5.82x10 ⁻¹⁰

DFT Methodologies

Restricted geometry optimisations were performed for models of [**6a'**, **6b'**, **7a'** and **7b'**], using coordinates derived from the X-ray crystal structures of [**4** and **5**]. The models were geometry optimised without constraints and the energy minima were confirmed by frequency calculations, which showed the absence of imaginary frequencies. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2014.01.¹¹ The DFT geometry optimizations employed all-electron Slater type orbital (STO) triple- ζ -plus polarization basis sets (from the ZORA/TZP database of the ADF suite) for the Ru, Cl, P, C, N, O, and H atoms. Scalar relativistic approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation potential due to Vosko *et al.* was used in all of the calculations.¹² Gradient corrections were performed using the functionals of Becke and Perdew.¹³

Further Observations and Comments

In the context of the NMR characterisation of species **1-5** and **6a-7a**. We have made use of the term “bilaterally symmetrical” throughout the paper, in the context of the observed ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals arising from the *p*-cymene moiety. In cases in which a mirror plane bisects the *p*-cymene along the plane generated by the *iPr*---Me substituents. Examples of such behaviour can be observed in our NMR analyses, and when applicable, thoroughly labelled in all the pertinent spectra for clarity (please compare S8 vs. S17-S18).

Following synthesis and full characterisation of the species **1-5**. We carried out ligand stability tests of **4** and **5**, *via* exposure to $\text{CO}_{(\text{g})}$ atmosphere (please see S25); which provided evidence of the susceptibility of the phosphorous-bound ligand to be replaced. In turn, yielding [*p*-cymene} $\text{RuCl}_2(\text{CO})$] and the corresponding free PDCAs (**L-4** and **L-5**). This encouraged us to carry out analogous experiments with the six-membered chelate counterpart **6**. We were anticipating that the comparative strength between the ionic N-Ru bond, and the neutral P-Ru bond, summed to the introduction of the $\text{CO}_{(\text{g})}$ as ligand. Would in turn allow to selectively labilise the neutral P-Ru bond on the chelate, leaving the N-Ru bond intact, accessing carbonyl substituted species of the form $[\text{Ru}(p\text{-cym})\{\text{N-C(=O)N(R)C(=O)PPh}_2\}\text{Cl}(\text{CO})]$ [R = Ph or *p*-tol]. Unfortunately, the stability of the resulting six-membered chelate in **6** and **7**, proved greater than anticipated, limiting further studies.

In some cases, the NMR data presented derives from stoichiometric reactions carried out in Young's tap NMR tubes (*in situ* generated species). Unfortunately, and due to the inherently unstable nature of the PCA/PDCA ligands, towards air. Further purification of the resulting coordination compounds is limited to crystallisation in the glovebox. Despite this, adequate elemental analyses results were determined for **1-5**. With minimal deviation from the calculated values been attributed to spontaneous

decomposition in solution/solid-state, under anoxxygenous conditions. This was further evidenced by briefly heating samples at 40 °C, which proved susceptible to thermal degradation. While also been precedents in the literature for a family of closely related compounds (*p*-cymene)RuClL [L= (Pyridin-2-yl)NHC], that are hygroscopic and/or incorporate interstitial solvent molecules (please see *Organometallics* 2018, 37, 1575–1584). With the latter, also found in the XRD for some of our compounds (**1** and **5**). However, the possibility of the samples decomposing in transit, prior to the determination, cannot be ruled out.

It is possible that species such as **6** and **7** to be incorporating a stereogenic Ru centre, which in turn would make the aromatic CH and isopropyl Me groups, of the *p*-cymene ligand, diastereotopic. In fact, in some of our species observed in solution (**6b** and **7b**), this seems to be the case, with two different methyl peaks been observed for iPr (labelled as H1 and H1'). However, there are also two distinct CH peaks (labelled as H2 **6a** vs. **6b** and **7a** vs. **7b**), which clearly indicate two different species in solution. Also, integration of these peaks shows two distinctive species and supports our assignment (please see labelled signals for H1/H1' and H2 in S17 and S21). Further attempts to characterise these two species, and the likelihood of them interconverting in solution, was studied by variable temperature experiments, aiming towards 2D EXchange SpectroscopY (EXSY). However, we were limited to using CD₂Cl₂ due to instability and solubility of these compounds, and the resulting range of temperatures available with this solvent (268–298 K).

References

- [1] H. R. Sharpe, A. M. Geer, W. Lewis, A. J. Blake, D. L. Kays, *Angew. Chem. Int. Ed.*, **2017**, 56, 4845-4848.
- [2] J. Cosier, A. M. Glazer, *J. Appl. Crystallogr.* **1986**, 19, 105-107.
- [3] Agilent Technologies, 2013.
- [4] G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.
- [5] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339-341; b) O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schroder, *J. Appl. Crystallogr.* **2003**, 36, 1283-1284.
- [6] CrysAlisPRO Oxford Diffraction/Agilent Technologies UK Ltd Yarnton England.
- [7] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, 71, 3-8.
- [8] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, 64, 112-122.
- [9] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, 71, 3-8.
- [10] <http://checkcif.iucr.org>
- [11] a) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, **1998**, 99, 391-403. b) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.* **2001**, 22, 931-967.
- [12] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, **1980**, 58, 1200-1211.
- [13] a) A. D. Becke, *Phys. Rev. A*. **1988**, 38, 3098-3100. b) J. P. Perdew, *Phys. Rev. B*. **1986**, 33, 8822-8824.

Selected NMR spectra

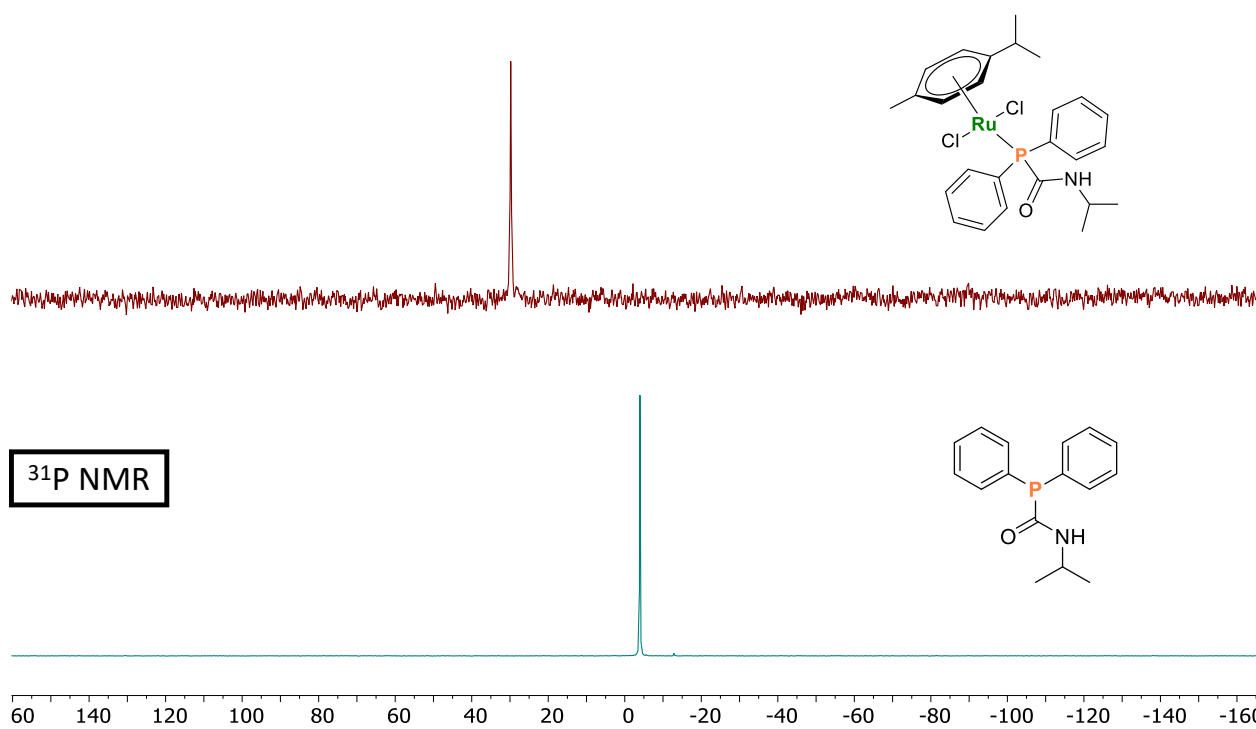
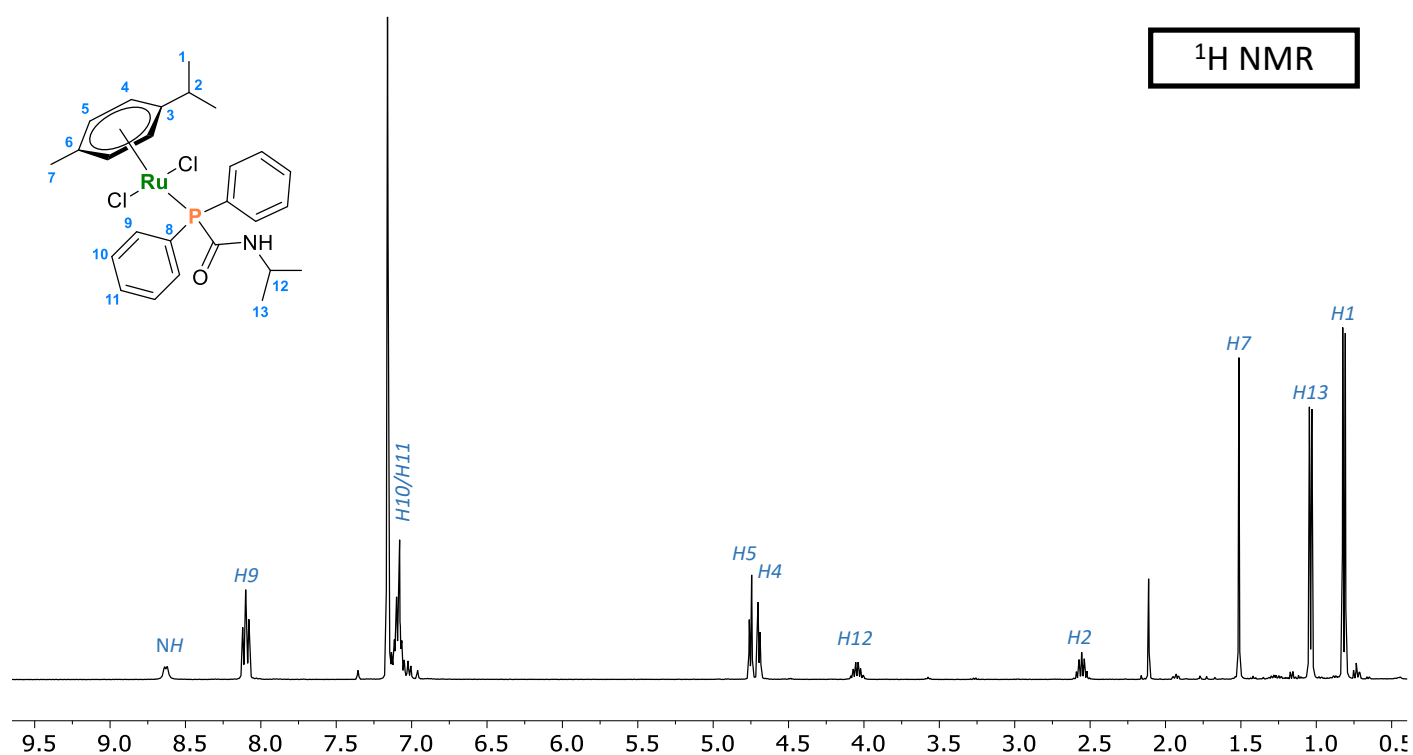


Figure S6. ^1H NMR spectrum of **1** and comparative ^{31}P NMR spectra of **1** and **L-1** in C_6D_6 .

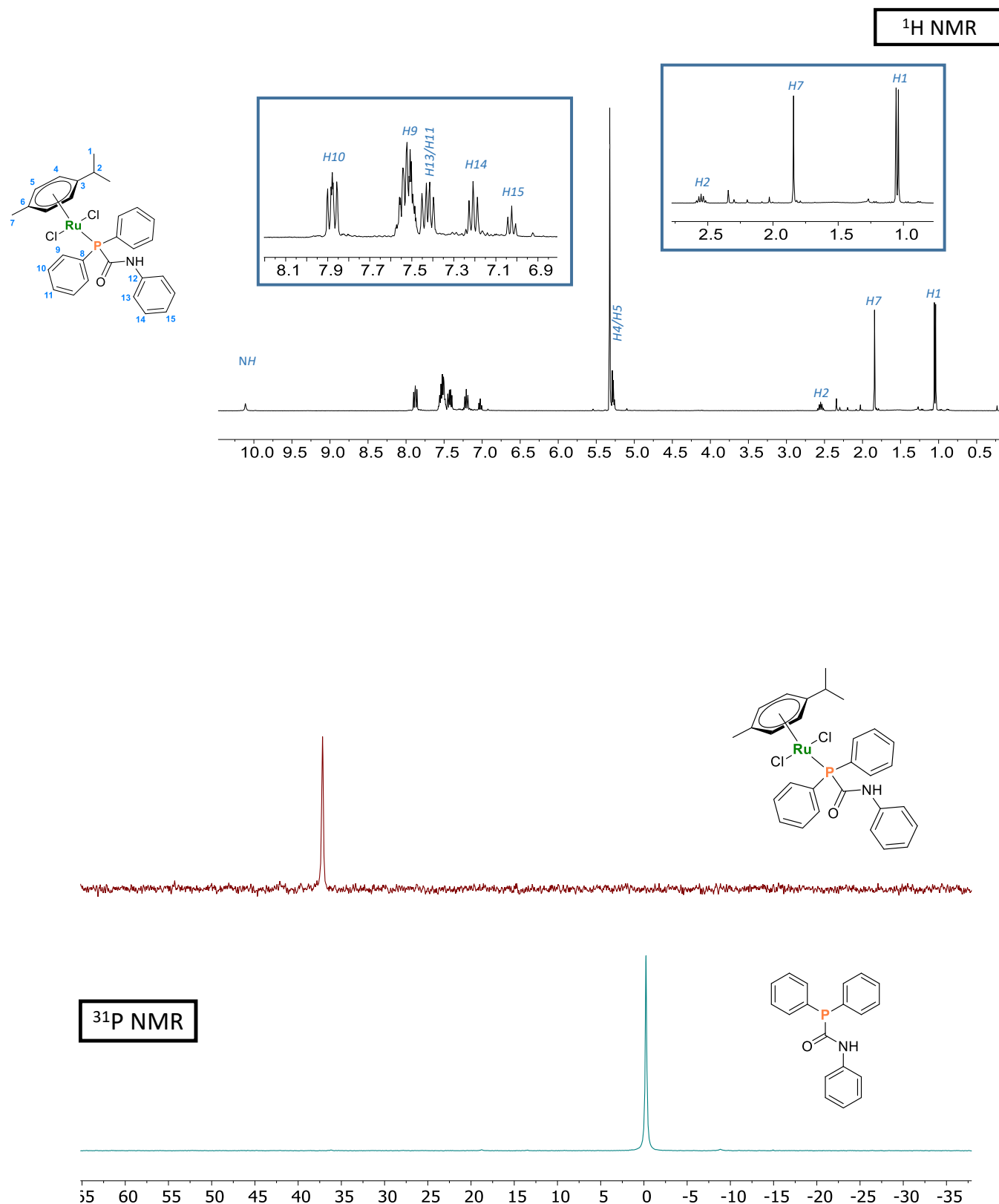


Figure S7. ^1H NMR spectrum of **2** and comparative ^{31}P NMR spectra of **2** and **L-2** in CD_2Cl_2 .

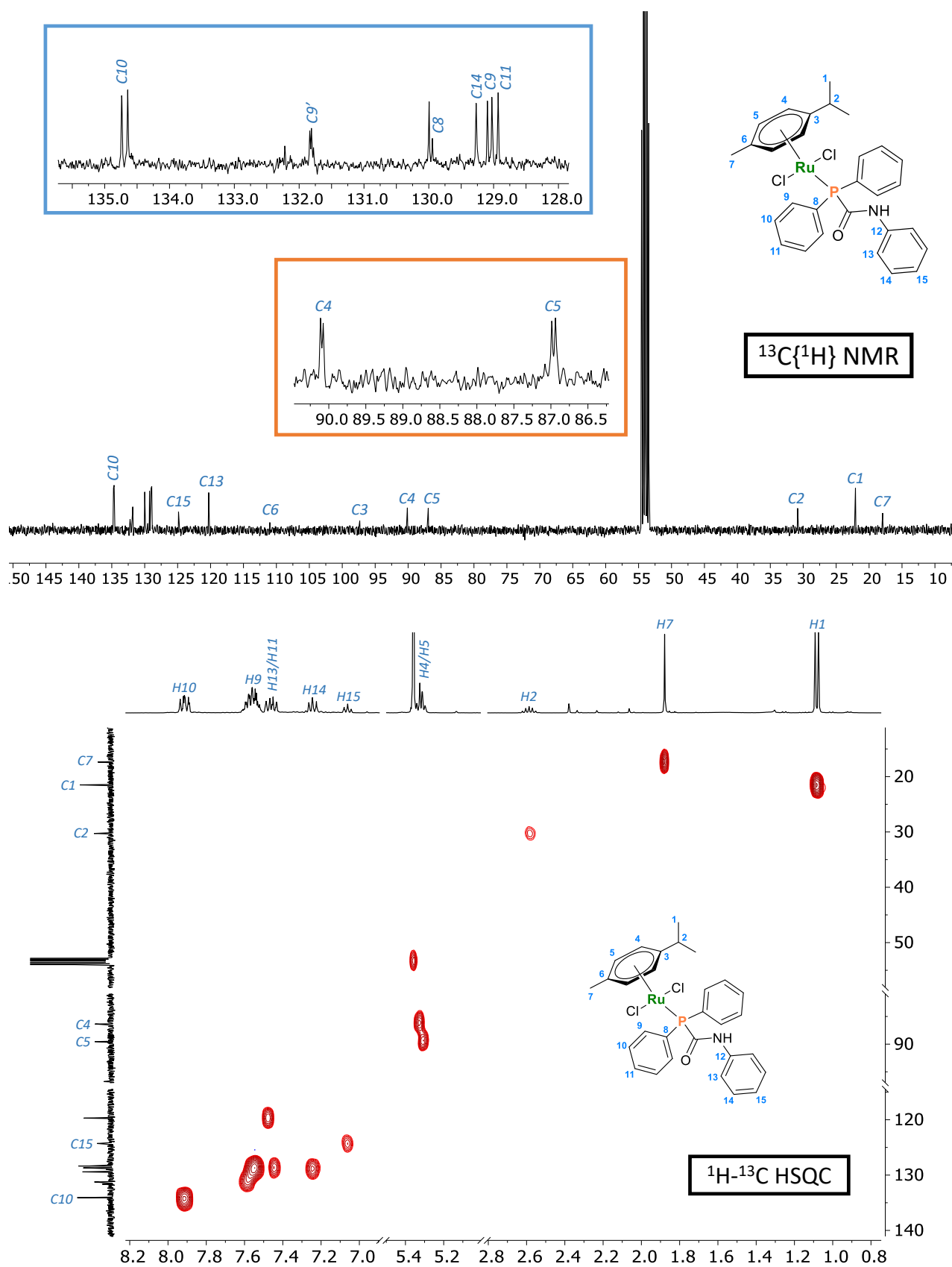


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR and $^1\text{H}-^{13}\text{C}$ HSQC NMR spectra of **2** in CD_2Cl_2 .

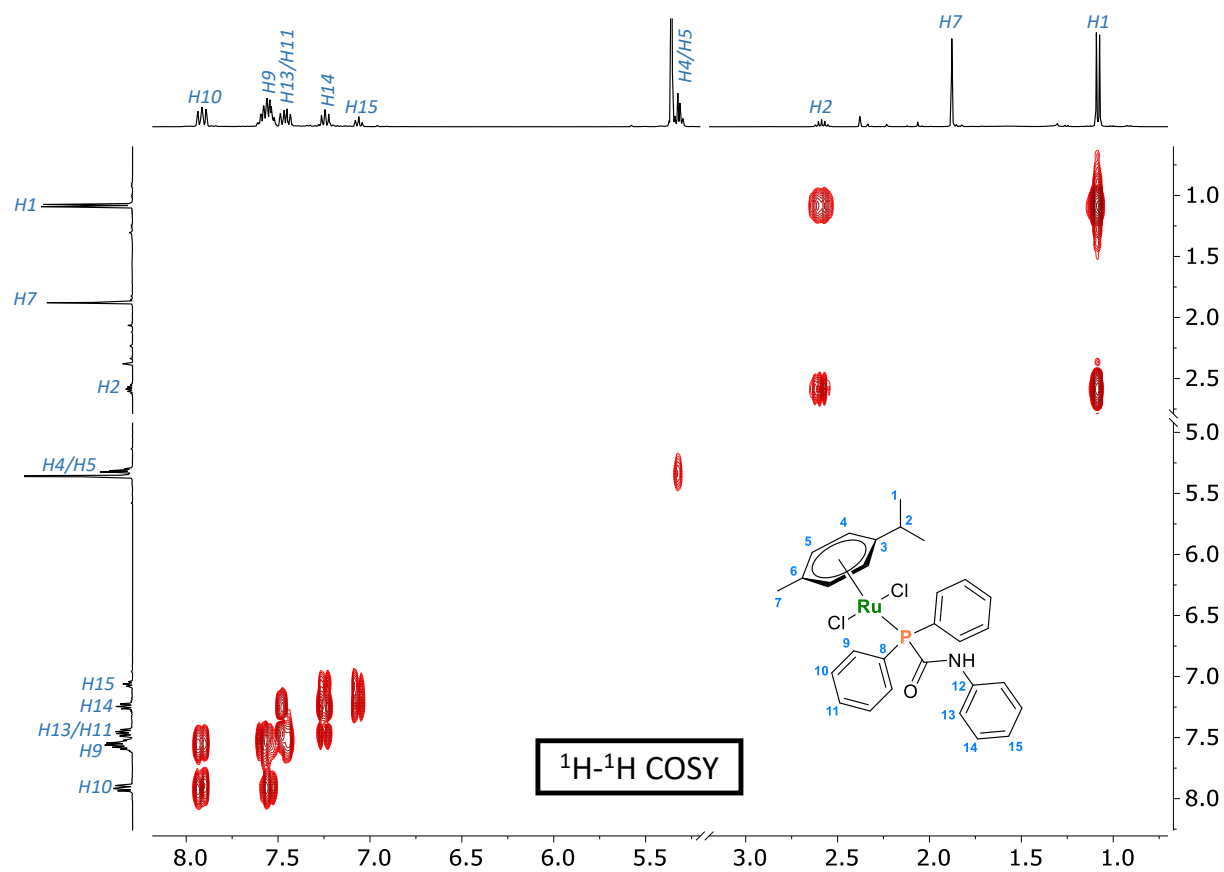


Figure S9. ^1H - ^1H COSY NMR spectrum of **2** in CD_2Cl_2 .

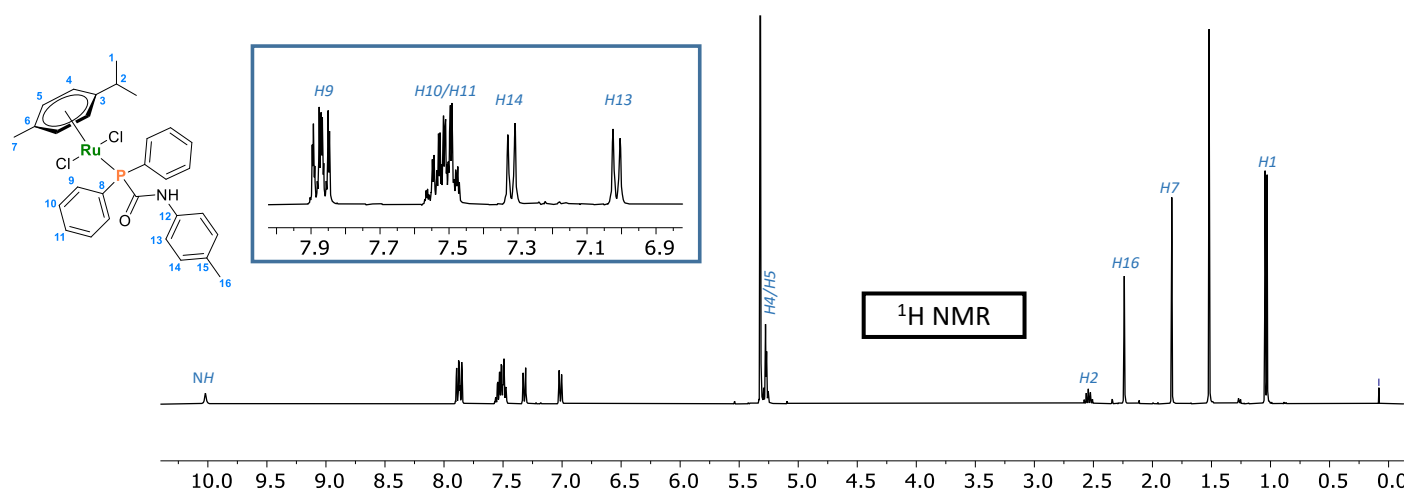


Figure S10. ^1H NMR spectrum of **3** in CD_2Cl_2 .

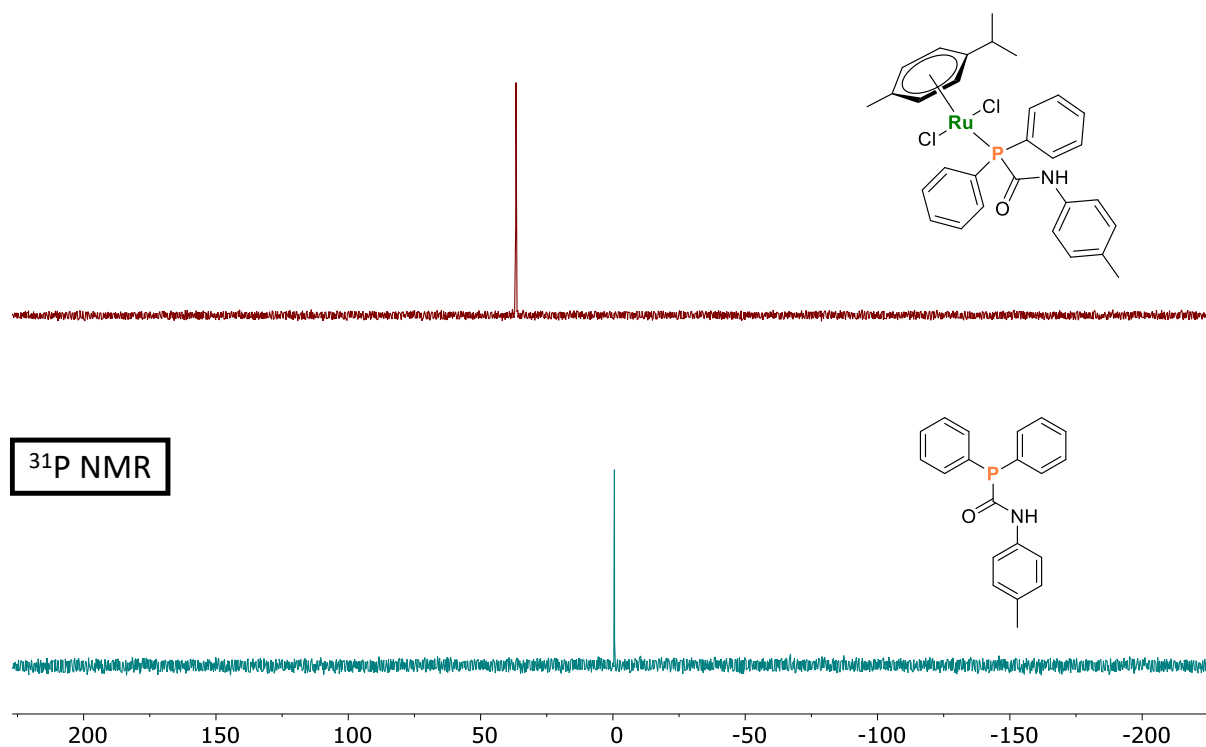


Figure S11. Comparative ^{31}P NMR spectra of **3** and free phosphine **L-3** (CD_2Cl_2).

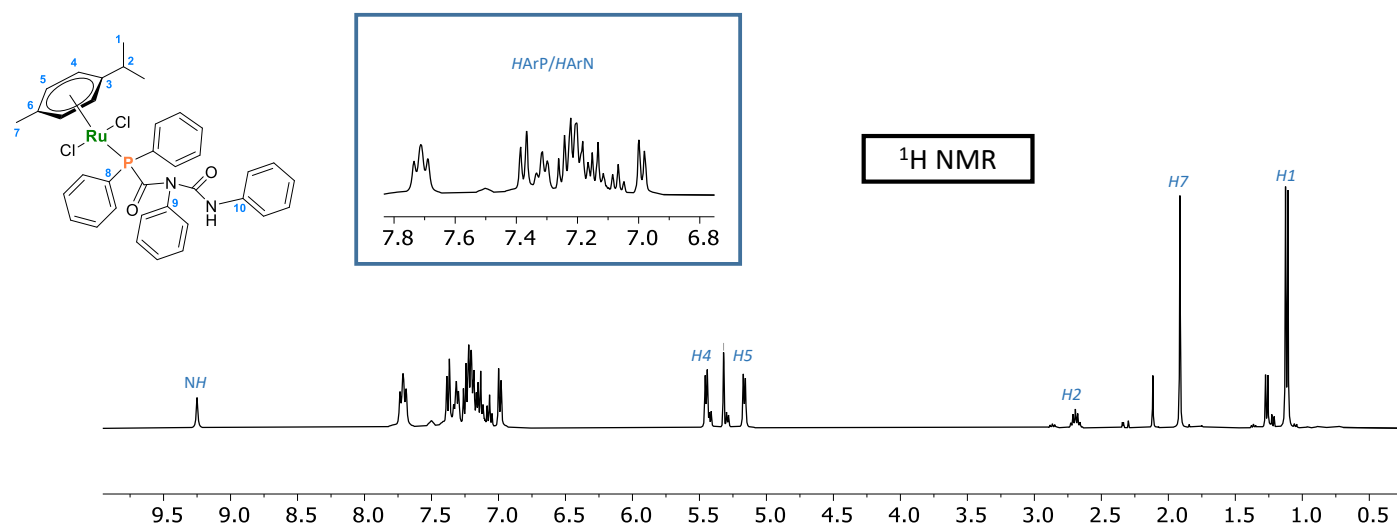


Figure S12. ^1H NMR spectrum of **4** in CD_2Cl_2 .

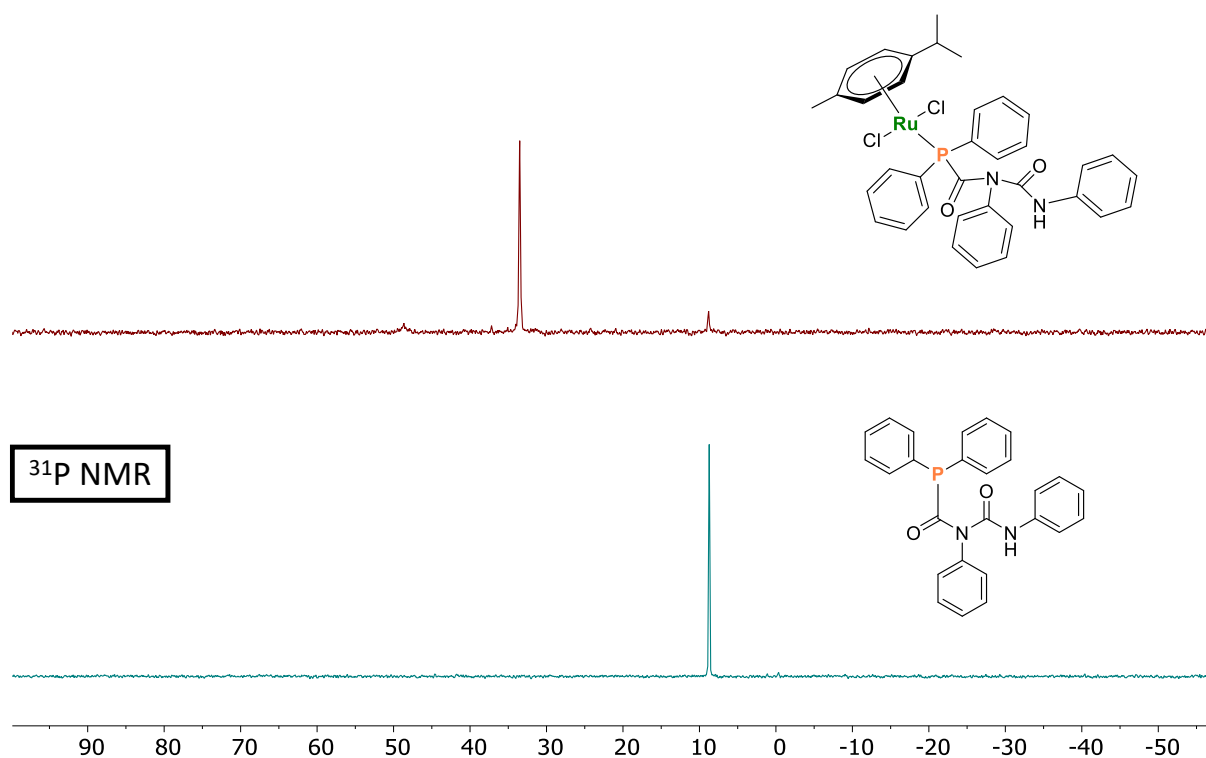


Figure S13. Comparative ^{31}P NMR spectra of **4** and free phosphine **L-4** (CD_2Cl_2).

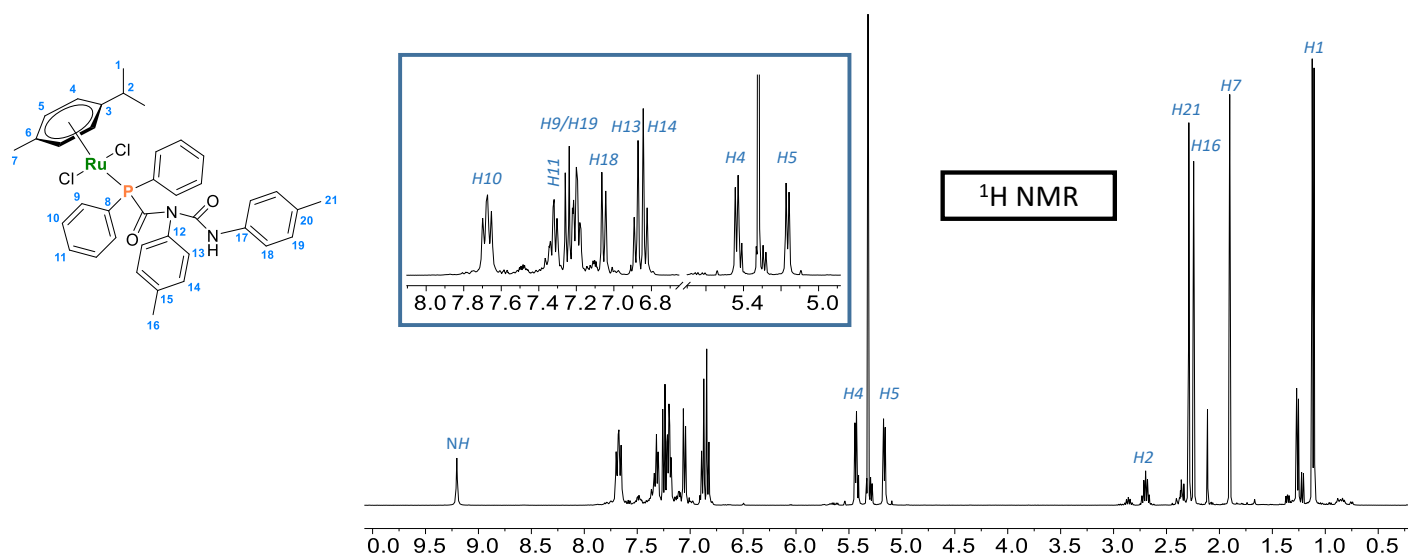


Figure S14. ^1H NMR spectrum of **5** in CD_2Cl_2 .

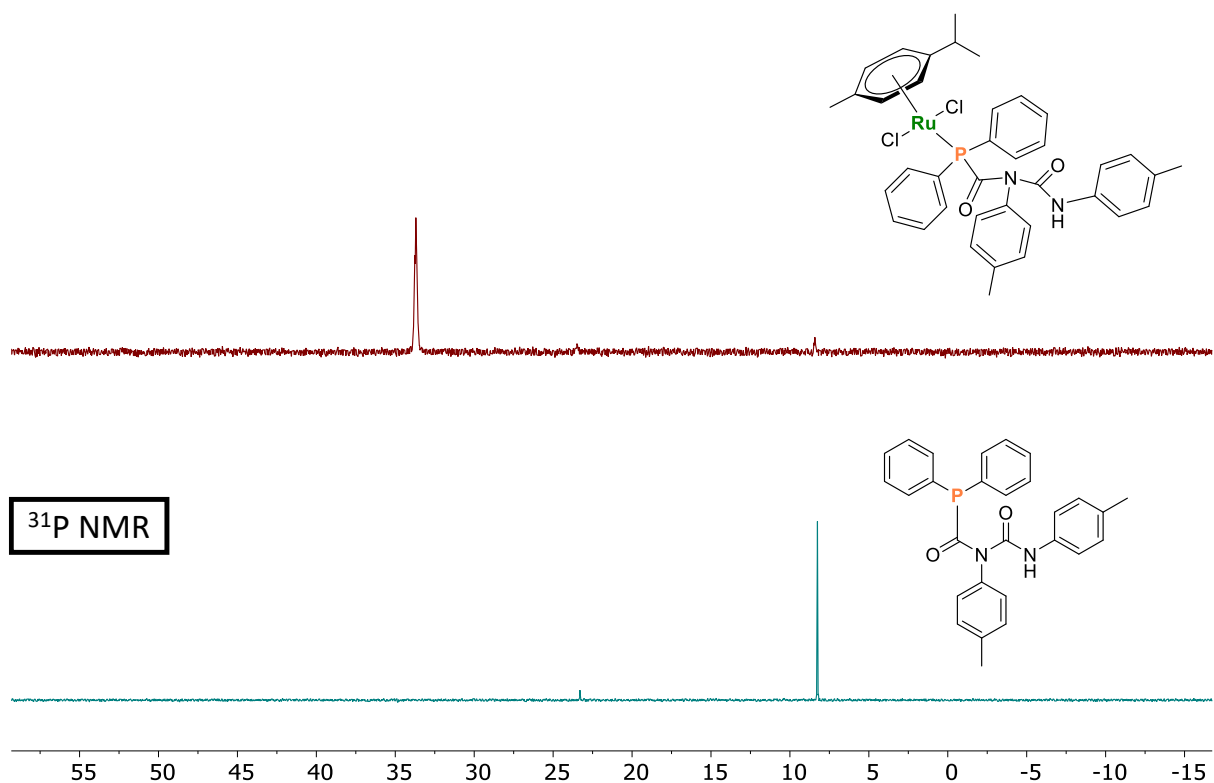


Figure S15. Comparative ^{31}P NMR spectra of **5** and free phosphine **L-5** (CD_2Cl_2).

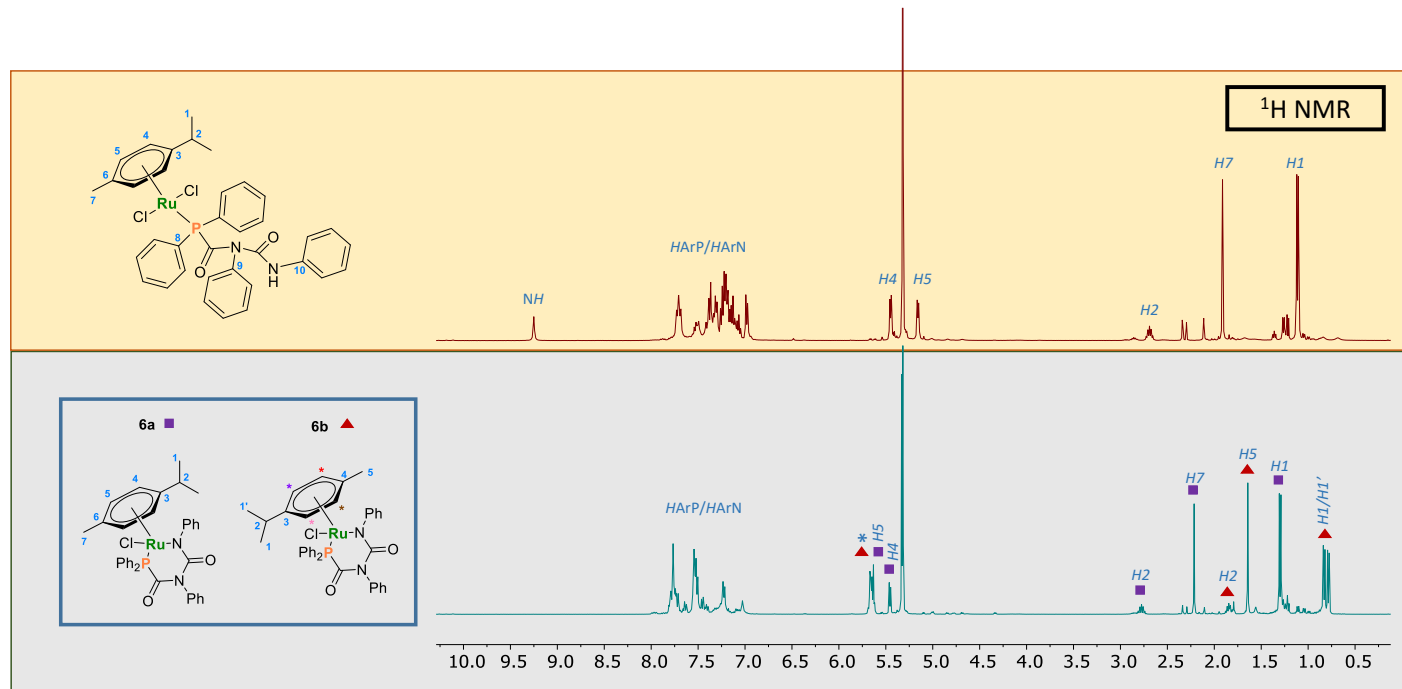


Figure S16. Comparative ^1H NMR spectra of **4** and cyclised products **6a** and **6b**; individual signals for the cyment moiety highlighted (CD_2Cl_2).

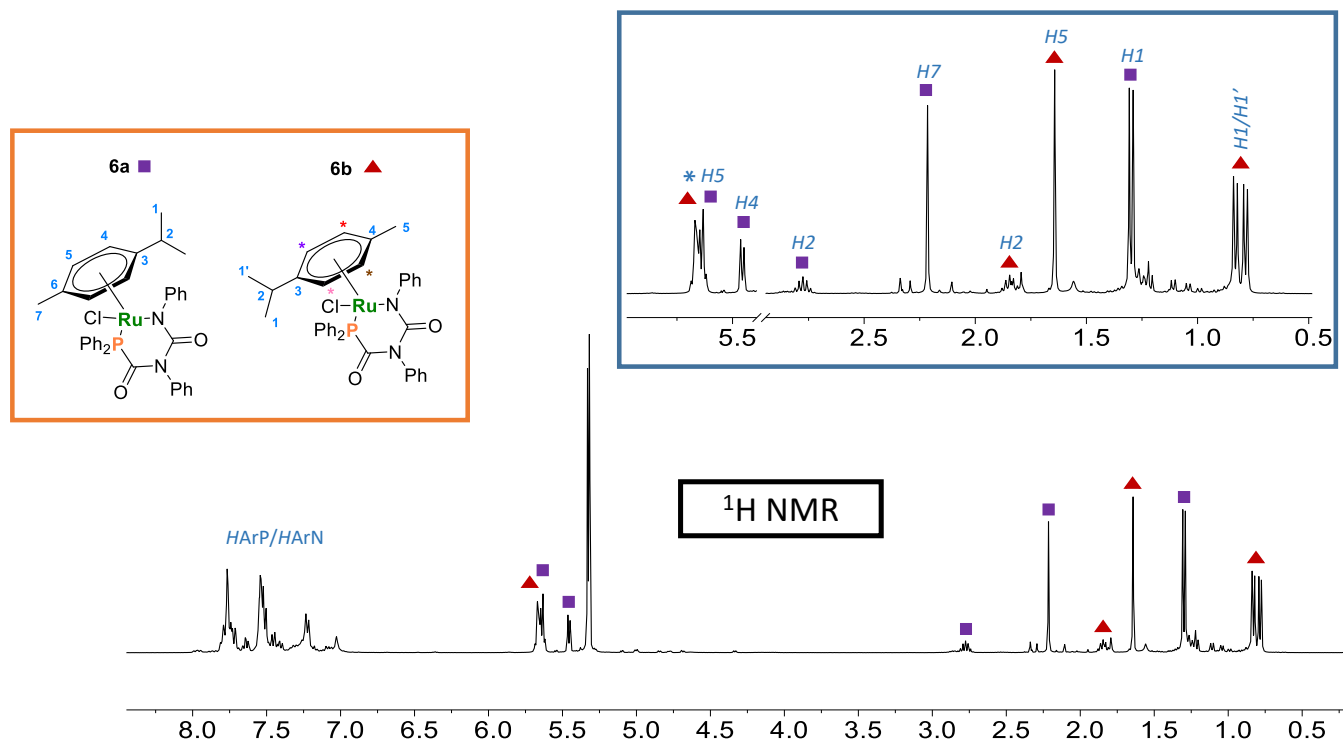


Figure S17. ^1H NMR spectrum of cyclised products **6a** and **6b** in CD_2Cl_2 ; individual signals for the p -cymene moiety highlighted.

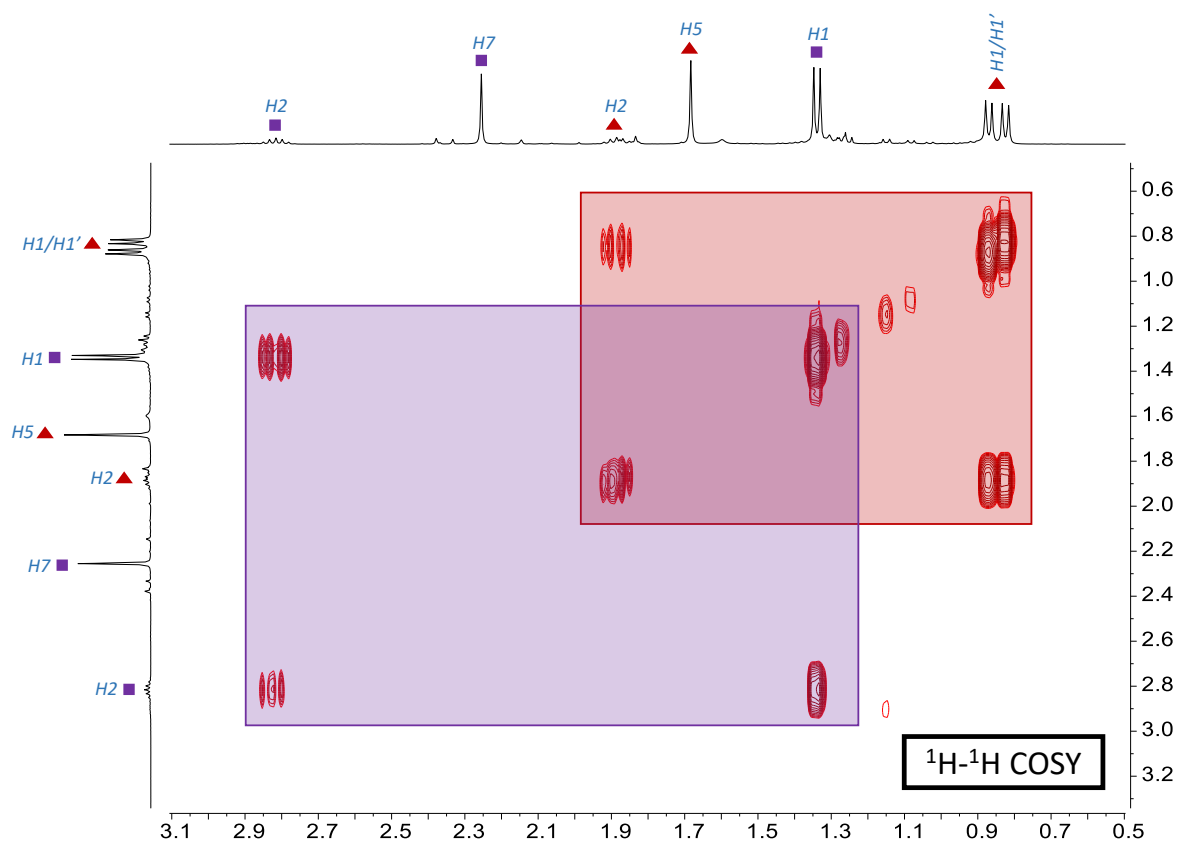


Figure S18. Selected region of the ^1H - ^1H COSY NMR spectrum of cyclised products **6a/6b** in CD_2Cl_2 (Distinctive p -cymene moieties highlighted).

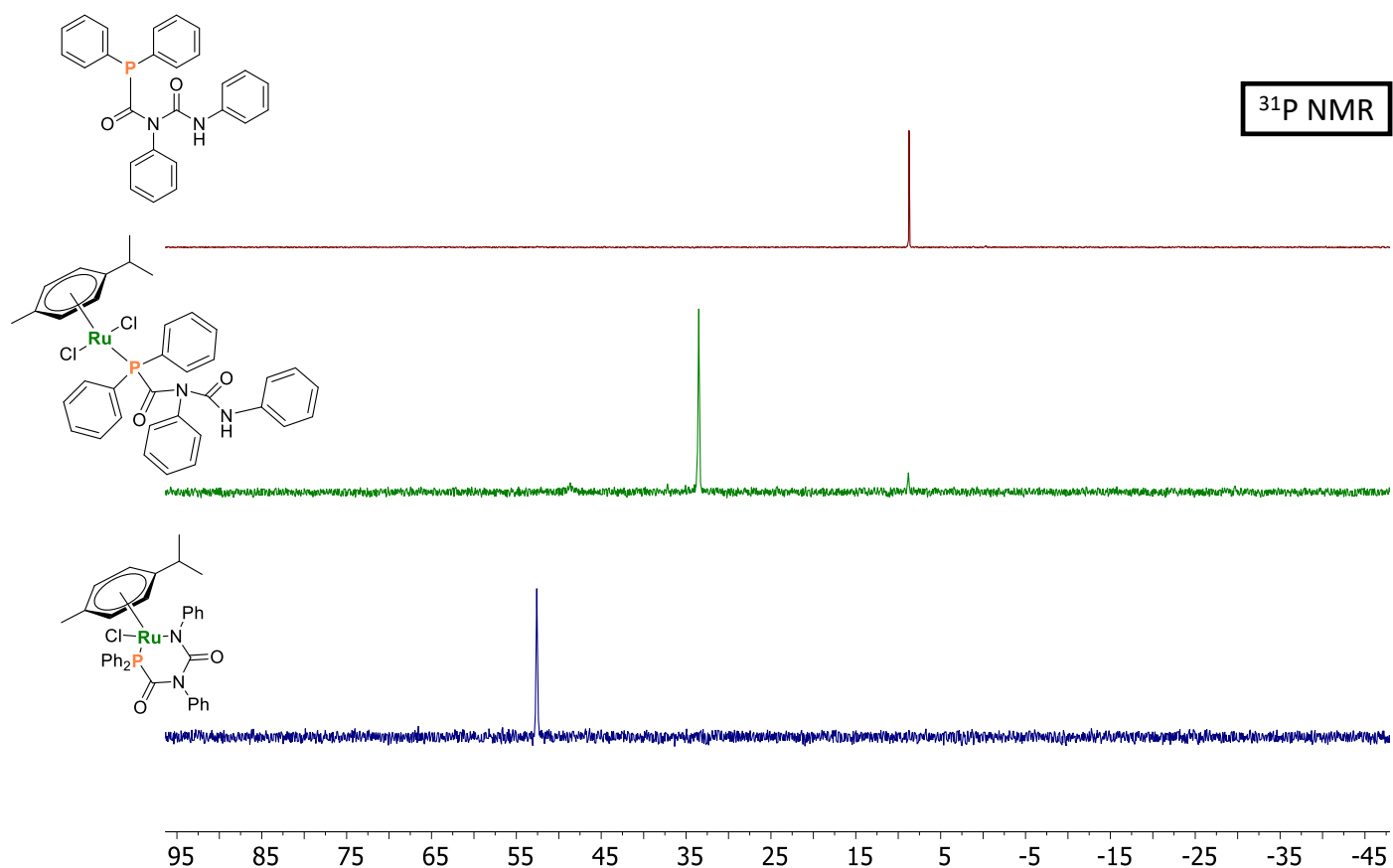


Figure S19. Comparative ^{31}P NMR spectra of the free phosphine **L-4** (*top*), **4** (*middle*) and the mixture of cyclised products **6** (*bottom*) (CD_2Cl_2).

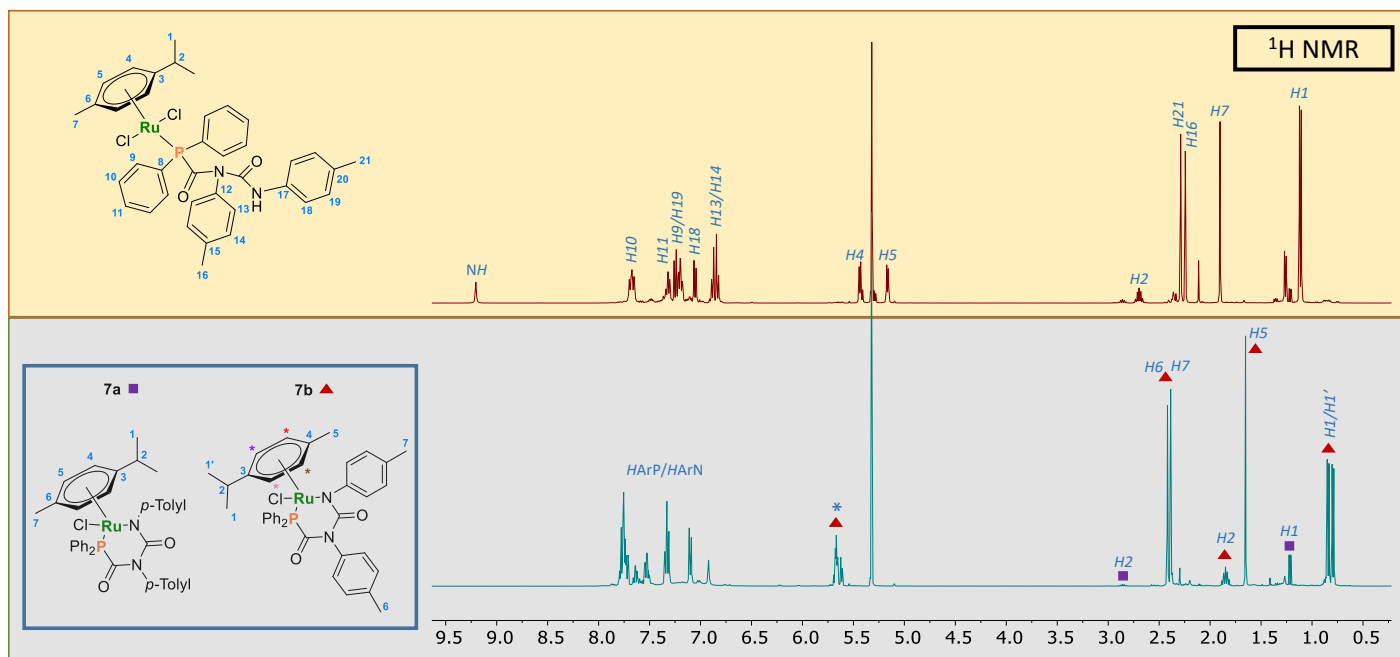


Figure S20. Comparative ^1H NMR spectra of **5** and cyclised products **7a** and **7b**; individual signals for the *p*-cymene moiety highlighted (CD_2Cl_2).

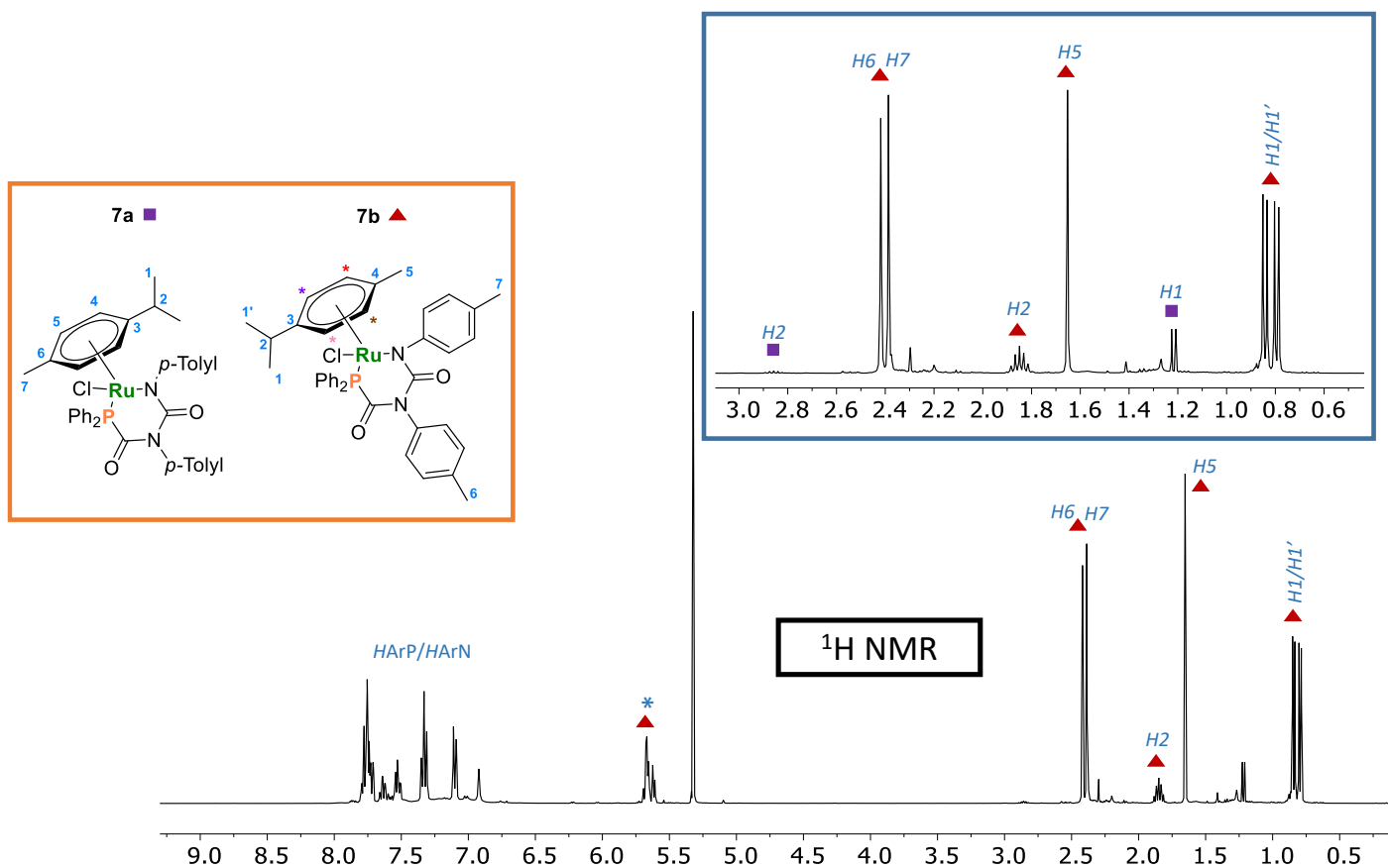


Figure S21. ^1H NMR spectrum of cyclised products **7a** and **7b** in CD_2Cl_2 ; individual signals for the *p*-cymene moiety highlighted.

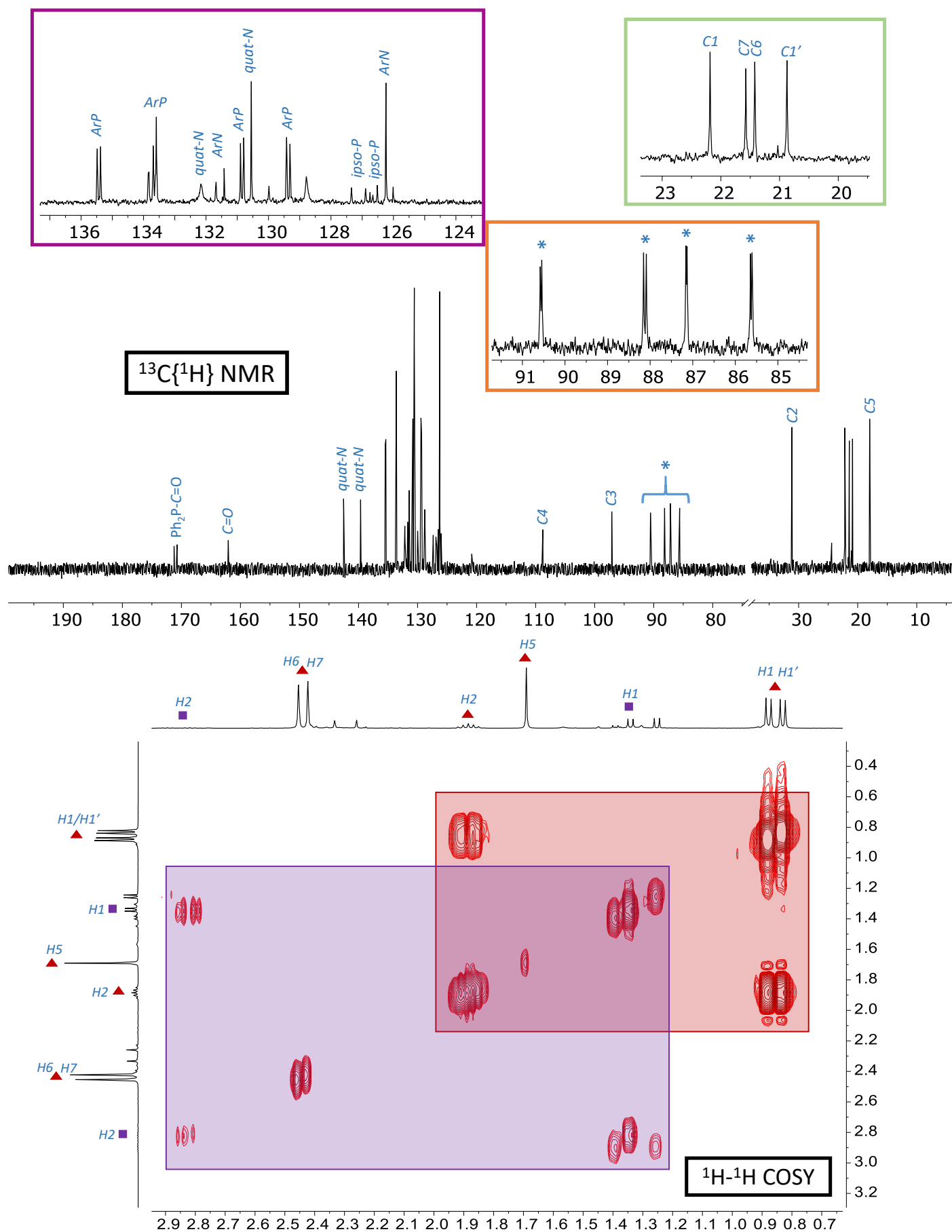


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and selected region of the $^1\text{H}\text{-}^1\text{H}$ COSY NMR spectra of cyclised products **7a/7b** in CD_2Cl_2 (Distinctive *p*-cymene moieties highlighted).

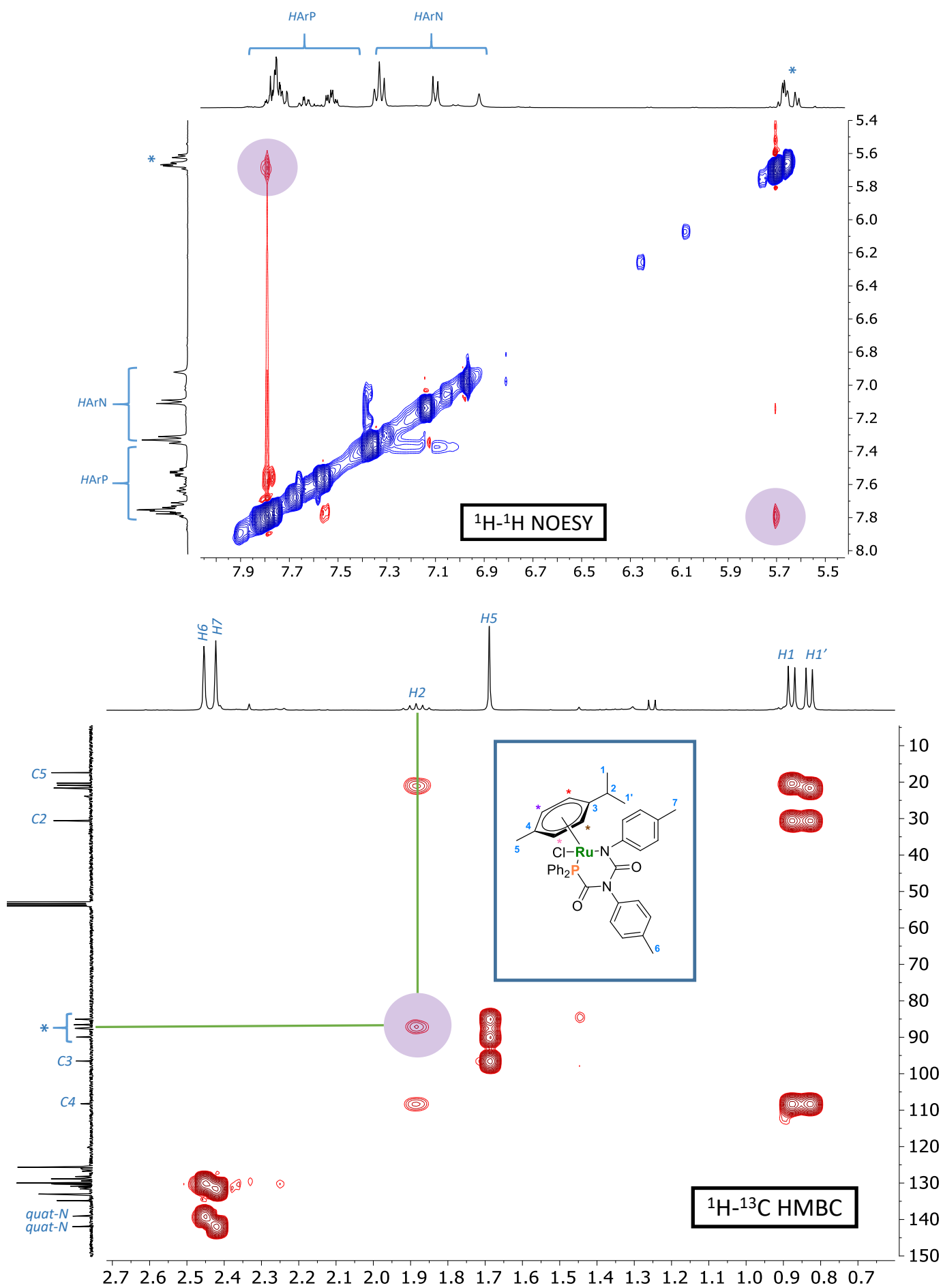


Figure S23. ^1H - ^1H NOESY NMR and ^1H - ^{13}C HMBC NMR spectra of cyclised product **7b** in CD_2Cl_2 .

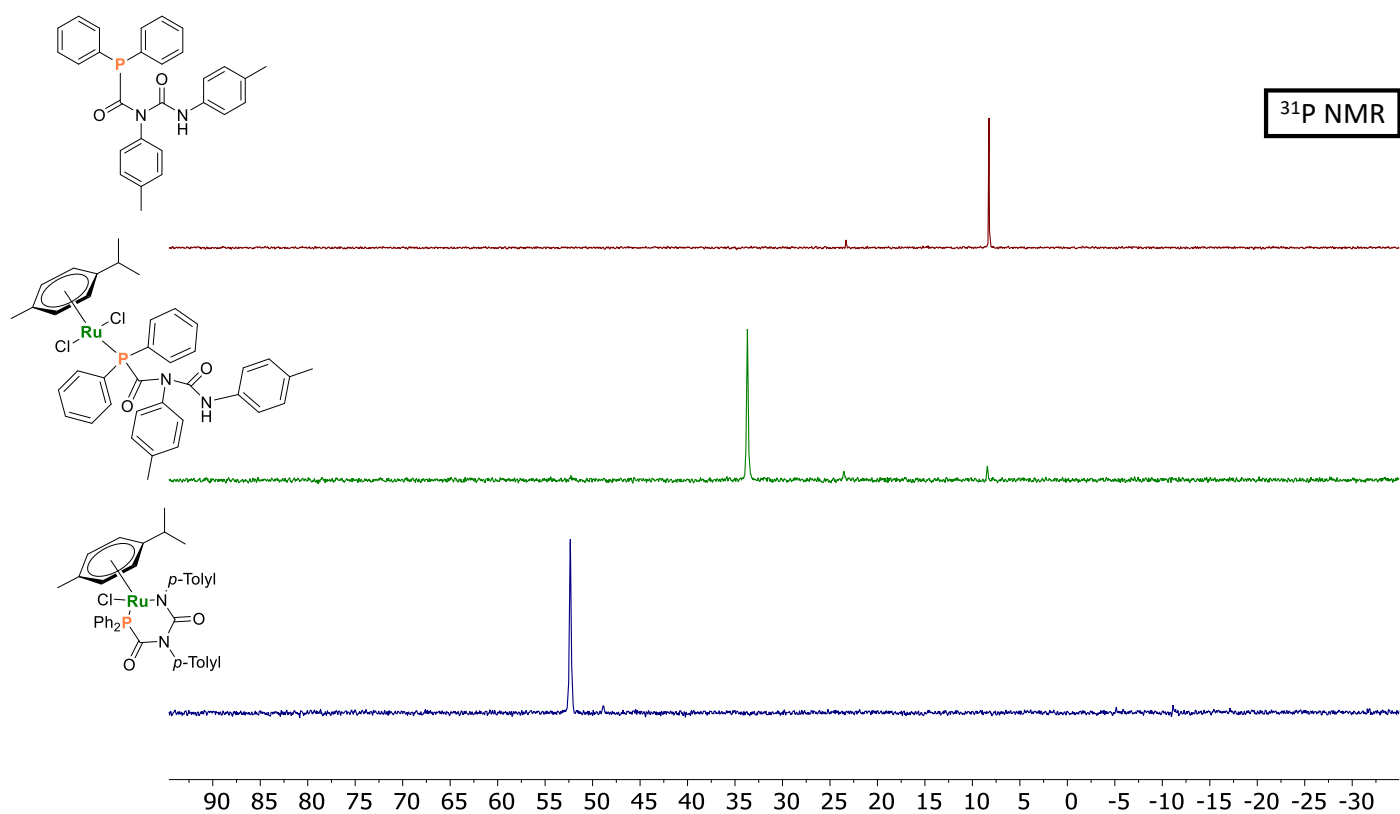


Figure S24. Comparative ^{31}P NMR spectra of the free phosphine **L-5** (*top*), **5** (*middle*) and the mixture of cyclised products **7** (*bottom*) in CD_2Cl_2 .

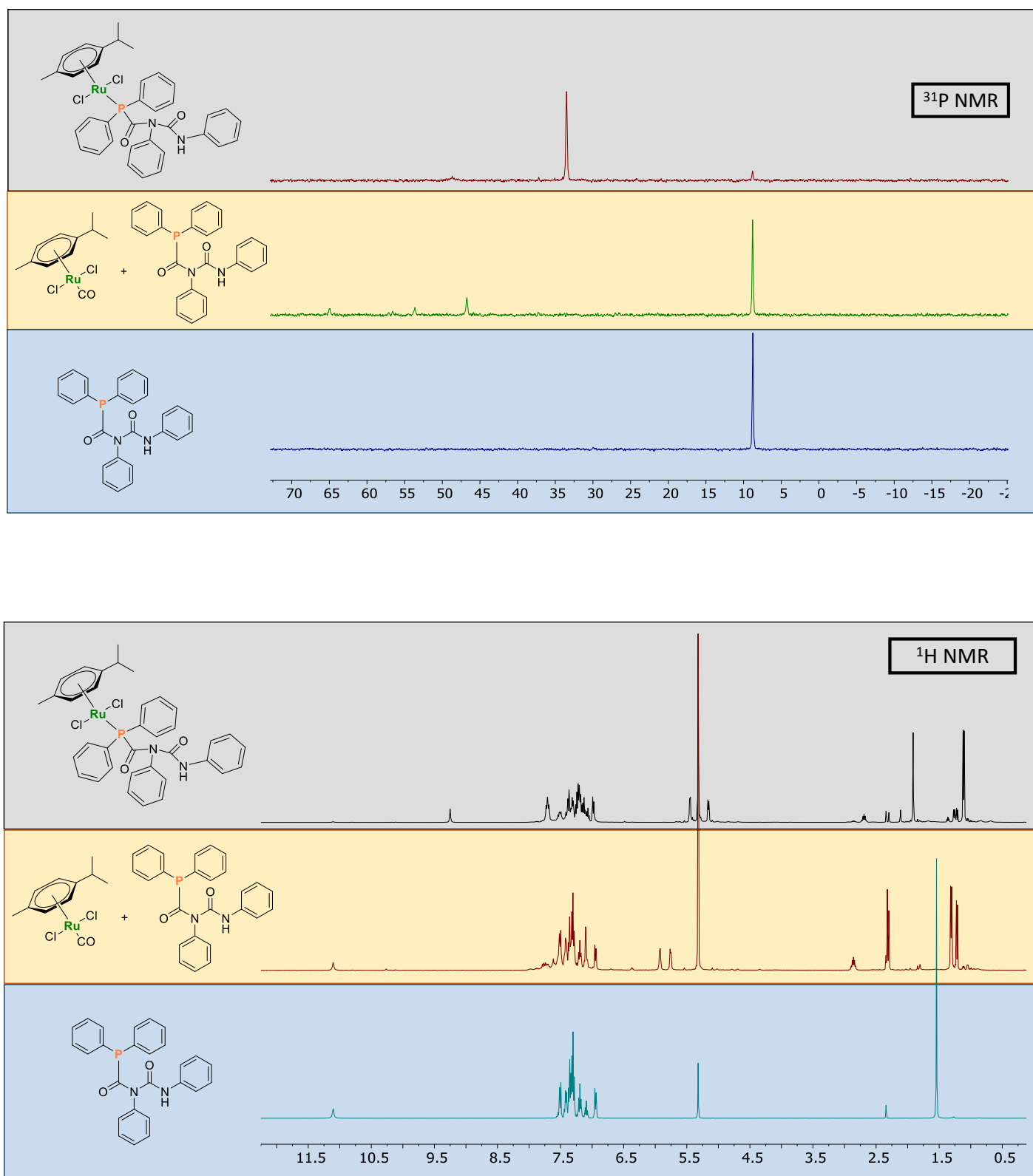


Figure S25. Comparative ¹H and ³¹P NMR spectra of **4**, after exposure to CO(g) and the corresponding free phosphine **L-4** (CD₂Cl₂).

Geometry optimised structures

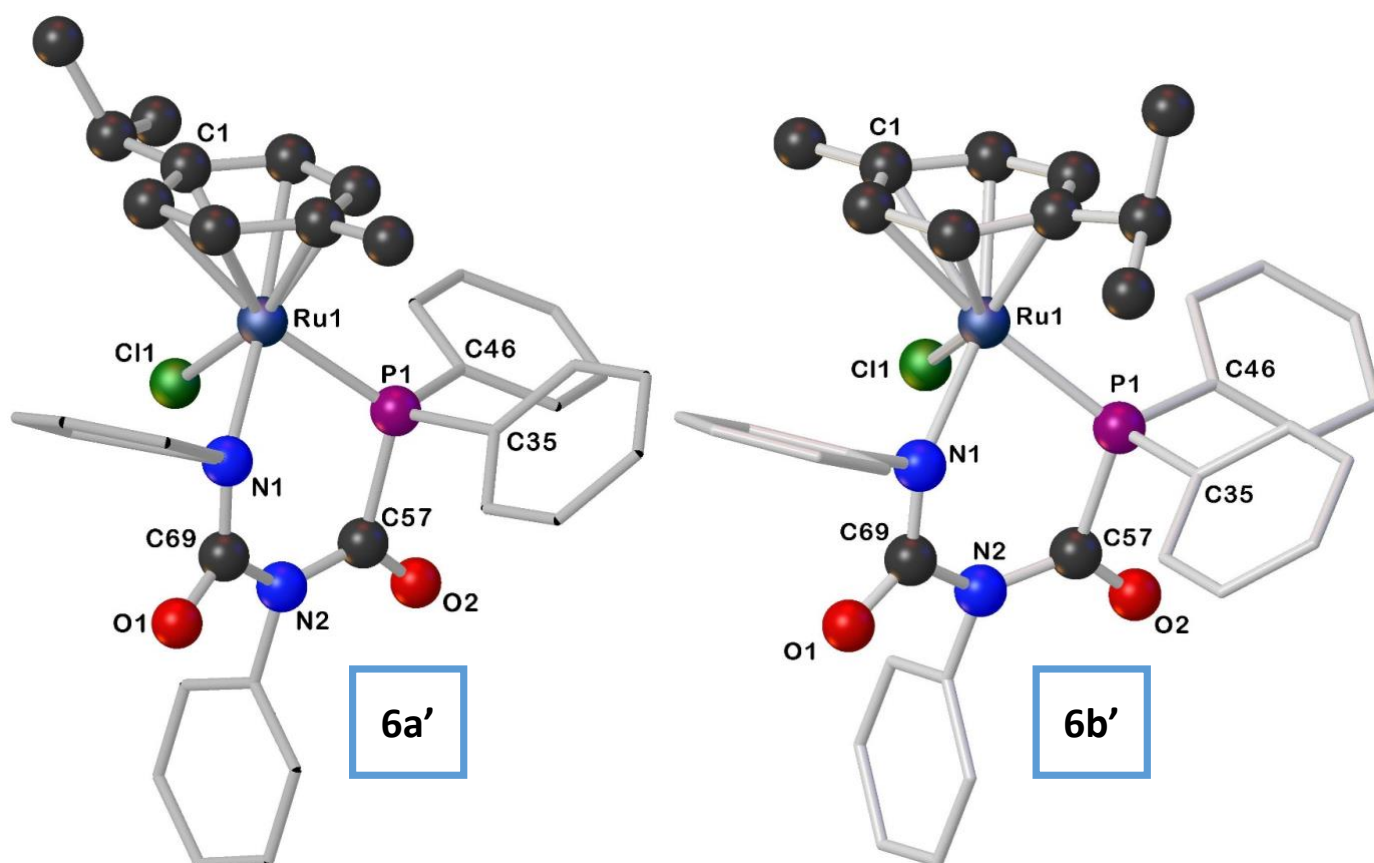


Figure S26. Illustrations for the geometry optimised structures for **6a'** and **6b'**.

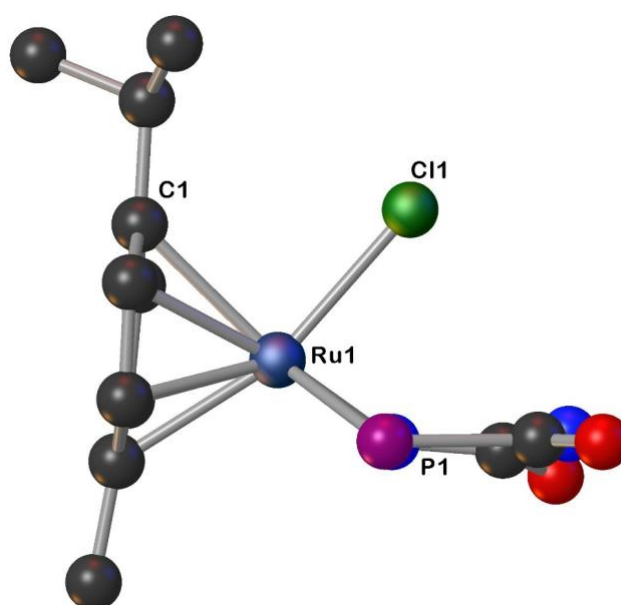


Figure S27. Side view of isomer **6a'**, depicting the ruthenium metal centre above the metallacycle ring. Flanking rings and hydrogen atoms have been omitted for clarity.

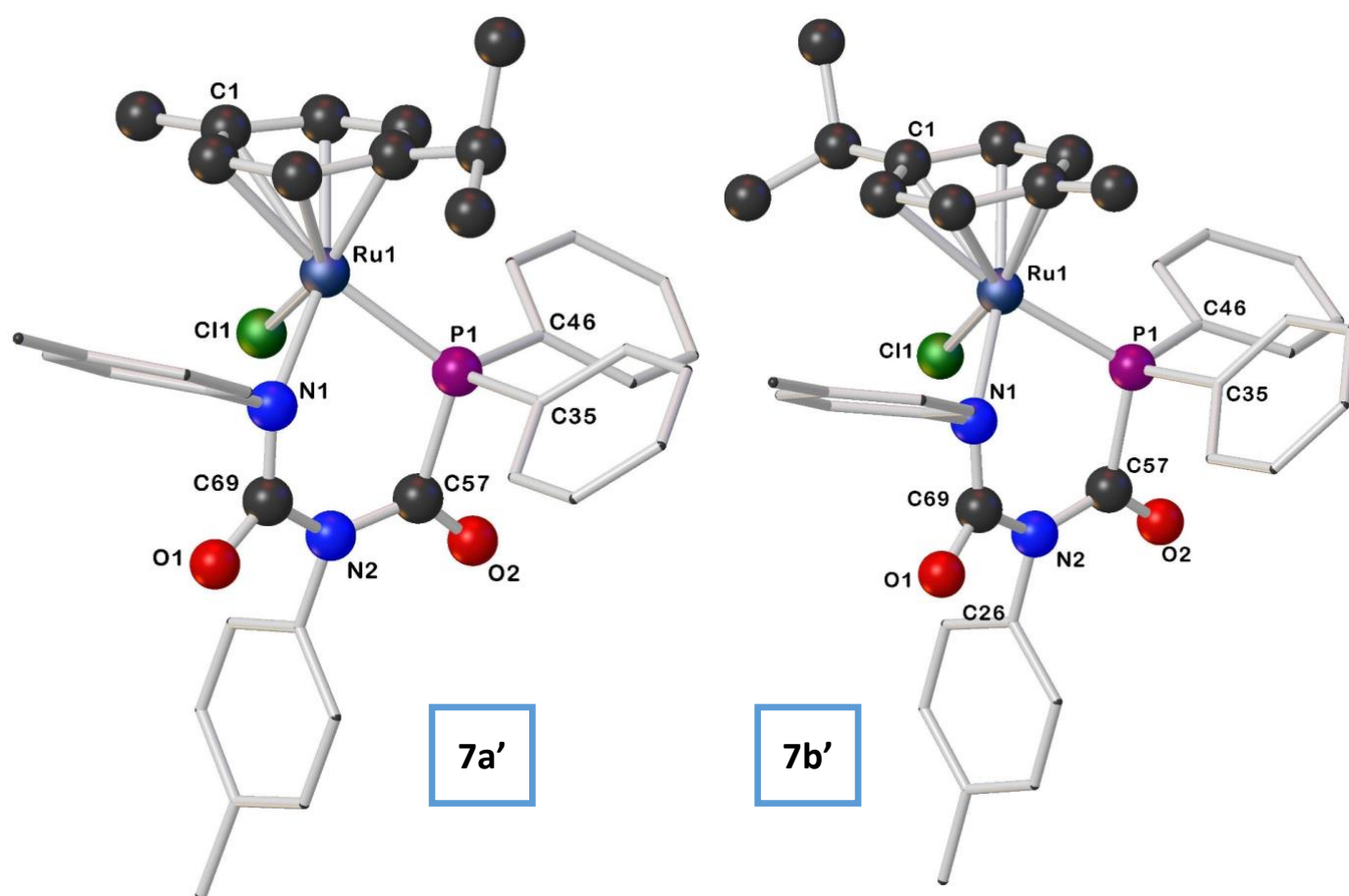


Figure S28. Illustrations for the geometry optimised structures for **7a'** and **7b'**.

Geometry optimised coordinates for 6a'

Ru	1.66459135	6.11988229	2.74180261
Cl	3.54302003	6.49741122	4.25646446
C	0.08363036	2.58218396	2.66461630
P	0.35909660	7.05615155	4.37469351
O	0.46294987	7.09081510	7.07634153
O	1.41656334	2.89771277	5.66258181
N	1.22196307	5.09909923	6.22831957
N	1.27371912	4.35688340	3.89600596
H	-0.85922739	3.02852040	2.98293387
C	3.09257972	6.82601709	1.00220398
C	2.02744737	7.75010282	1.15656985
H	2.23452948	8.80010106	1.34793729
C	0.67676828	7.29222983	1.15087382
H	-0.12530415	8.01450348	1.30855656
C	0.33720357	5.93273942	0.85182958
C	1.42617807	5.03214762	0.70446240
H	1.21114040	3.97321593	0.56034034
C	2.77332911	5.45230395	0.77269777
H	3.57107662	4.71638474	0.68710232
C	4.55325355	7.24050140	1.00815250
H	5.07126537	6.51560038	1.65684832
C	5.11630700	7.10592728	-0.42456924
H	4.97792445	6.09453624	-0.82872616
H	6.19237627	7.32904128	-0.42556448
H	4.62217200	7.81360237	-1.10640219
C	4.82101558	8.64000445	1.56834391
H	4.36697227	9.42428243	0.94404950
H	5.90338130	8.82667514	1.58834002
H	4.44873027	8.72876519	2.59668310
C	-1.08304042	5.49609571	0.63943896
H	-1.37644991	5.67315822	-0.40822829
H	-1.77820693	6.05273405	1.28026603
H	-1.19890162	4.42484396	0.84350573
C	-1.45174065	6.76212738	4.18284123
C	-2.26255692	7.68283757	3.49541697
H	-1.84118115	8.62747693	3.14919054
C	-3.61569414	7.41174429	3.27716433
H	-4.23400075	8.14068594	2.75108060
C	-4.17643509	6.21765374	3.73888399
H	-5.23392303	6.00804064	3.57220698
C	-3.37723027	5.29654524	4.42175371
H	-3.80898517	4.36562844	4.79233985
C	-2.02420911	5.56376447	4.64199555
H	-1.41511925	4.83440564	5.17590512
C	0.49835035	8.85925782	4.70371706
C	-0.47411763	9.54098767	5.45607854
H	-1.35174167	9.01231559	5.82348326

C	-0.30842020	10.89523792	5.74922525
H	-1.06575975	11.41577765	6.33697555
C	0.82873511	11.57781402	5.30626508
H	0.95642155	12.63573644	5.54120489
C	1.80744190	10.89937183	4.57646197
H	2.70717000	11.42154985	4.24857176
C	1.64585793	9.54370119	4.27932041
H	2.42643513	8.99526829	3.75240482
C	0.70211508	6.36209830	6.12045832
C	1.61074643	4.68851314	7.57080818
C	2.92458356	4.91969981	7.97738094
H	3.62265639	5.38561153	7.28177107
C	3.31878856	4.54579693	9.26491396
H	4.34605180	4.72100771	9.58742132
C	2.40173212	3.94953164	10.13441153
H	2.71171452	3.65737610	11.13920997
C	1.08547998	3.72746293	9.71668465
H	0.36799380	3.25974386	10.39215018
C	0.68605029	4.09786199	8.43171911
H	-0.33372315	3.92142664	8.09151522
C	1.32998793	4.04754081	5.21749025
C	1.28549092	3.15740708	3.09588778
C	2.50098975	2.56487378	2.72370761
H	3.43063860	3.00046737	3.09159461
C	2.51143371	1.43484643	1.90479454
H	3.46272891	0.97794300	1.62602216
C	1.30915449	0.87548708	1.45470979
H	1.31937738	-0.00967980	0.81736330
C	0.09558442	1.44943970	1.84432220
H	-0.84734769	1.00860201	1.51583715

Geometry optimised coordinates for 6b'

Ru	1.57603423	5.89635135	2.73652462
Cl	3.42517089	6.51644187	4.20372521
C	0.01889774	2.38113994	2.87477297
P	0.26307591	6.87086694	4.34228409
O	0.56512094	7.11895188	7.01963156
O	1.51160845	2.84795044	5.85594641
N	1.31437473	5.08324877	6.27496059
N	1.26286727	4.18897419	4.00356407
H	-0.90977341	2.88398892	3.14679638
C	3.14785203	5.92043752	0.92623550
C	2.48593769	7.18523016	1.14046885
H	3.09041221	8.06929165	1.34049247
C	1.07960641	7.29630467	1.06181139

H	0.61387508	8.27518821	1.18260111
C	0.25289476	6.14078379	0.83890348
C	0.90980457	4.88993771	0.79589047
H	0.32547957	3.97505426	0.72220755
C	2.34330683	4.78723249	0.77241482
H	2.80003438	3.80131397	0.70188144
C	4.64273517	5.84331146	0.98218835
H	5.09074958	6.52169317	0.24114621
C	1.18678501	0.53590695	1.82183629
C	-0.00638159	1.18608788	2.14796369
H	1.16808550	-0.39897839	1.26015853
H	-0.96324435	0.75680313	1.84548650
C	2.40545600	1.08482378	2.23826393
H	3.34127920	0.57160321	2.00900442
H	3.37466488	2.70360272	3.30615948
C	2.43137331	2.27847808	2.96128324
C	-1.22570952	6.31543220	0.55743889
C	1.23690010	2.94286527	3.27733642
C	1.38637978	3.96254152	5.33765562
H	-1.58664675	7.12955947	1.20597861
C	-1.54320779	6.48560046	4.32373651
C	-2.46520660	7.35634304	3.71726524
H	-2.12634872	8.30685312	3.30419190
C	-3.82325549	7.03196986	3.67075845
H	-4.52727709	7.72319681	3.20486908
C	-4.27907422	5.83433265	4.22749756
H	-5.34075737	5.58489880	4.19705903
C	-3.36948228	4.96220236	4.83242092
H	-3.71756449	4.02932112	5.27809944
C	-2.01082465	5.28153464	4.87931641
H	-1.31617611	4.59087581	5.35679745
C	0.32375654	8.70064050	4.52782520
C	-0.59907452	9.37908036	5.34341075
H	-1.37648759	8.82538102	5.86670444
C	-0.51355378	10.76352353	5.49635525
H	-1.23299054	11.27988255	6.13341738
C	0.49471120	11.48313449	4.84794356
H	0.55841824	12.56567890	4.96995574
C	1.43014227	10.81085108	4.05806630
H	2.23430412	11.36409491	3.57065753
C	1.34918701	9.42447818	3.90294844
H	2.10424236	8.88995279	3.32793531
C	0.75679345	6.32332148	6.10764334
C	1.82243612	4.79577108	7.60883502
C	3.15355448	5.10602480	7.88652349
H	3.77262335	5.53992654	7.10104366
C	3.66465933	4.85301364	9.16190044
H	4.70628601	5.09089634	9.38292833
C	2.84555246	4.29845450	10.14889484
H	3.24619240	4.10113130	11.14424874
C	1.51104068	3.99600211	9.85955355

H	0.86978818	3.55988090	10.62675871
C	0.99484261	4.24555637	8.58704846
H	-0.04082212	4.00639135	8.34731802
C	-1.39233693	6.77674987	-0.90793021
C	-2.07865225	5.07644866	0.84078942
H	-1.83153606	4.24899813	0.15994367
H	-3.14032995	5.31478878	0.69353612
H	-1.94952307	4.72881212	1.87320725
H	4.99888816	4.82482645	0.78883967
H	4.98806213	6.15650959	1.98111379
H	-0.81854385	7.69037583	-1.11629308
H	-2.45072619	6.98184102	-1.12209210
H	-1.04900602	5.99544882	-1.60185748

Geometry optimised coordinates for 7a'

Ru	2.52821822	11.60552066	2.79354076
H	-0.65091377	9.96995533	-0.54103749
Cl	0.51799563	12.50273940	3.85262706
P	2.94864637	10.71686396	4.87256925
O	4.06943196	15.01611127	5.04950896
O	2.27658915	11.55711258	7.35270022
N	3.61866856	13.23520102	3.66765909
H	-0.14957112	11.31667356	-1.58861135
N	2.87528165	13.30960989	5.99209819
C	4.44620324	13.93348572	2.71690794
C	5.79959703	13.60990373	2.57295805
H	6.23281561	12.84363201	3.21726415
C	6.58777821	14.26224755	1.61908800
H	7.64349385	13.99692143	1.52374192
C	6.05268567	15.25782599	0.79042011
C	4.69496501	15.58377865	0.95401659
H	4.25373672	16.36866284	0.33483994
C	3.90397513	14.93776906	1.90269232
H	2.85658061	15.21168051	2.03388652
C	6.90761590	15.98419396	-0.21962129
H	6.40862947	16.05060481	-1.19744355
H	7.87303914	15.48116258	-0.36346856
H	7.11541294	17.01488662	0.10781063
C	3.55434299	13.91189869	4.84219406
C	2.47858581	14.25235588	7.02682713
C	1.22220420	14.84645689	6.93479871
H	0.57471822	14.59529311	6.09423118
C	0.81488547	15.75104357	7.91863039
H	-0.16952360	16.21752909	7.84127504
C	1.64526436	16.06787565	9.00158012

C	2.90410464	15.44805319	9.07466392
H	3.56964911	15.67825774	9.90960300
C	3.32260239	14.54710944	8.09769062
H	4.30406195	14.07760793	8.15926562
C	1.20737782	17.04708336	10.06407525
H	1.22093735	16.58366354	11.06215365
H	0.18994002	17.41267251	9.87496859
H	1.87783047	17.91904038	10.10200841
C	2.66229663	11.98518279	6.27121390
C	0.65123456	9.10389672	4.84740045
H	0.32787330	9.76407349	4.04303748
C	-0.18516639	8.08228950	5.30419716
H	-1.15359663	7.92263408	4.82765004
C	0.20886752	7.28013774	6.37773544
H	-0.44437263	6.48191677	6.73407890
C	1.43576582	7.51325122	7.00604848
H	1.73890982	6.90597538	7.86004788
C	2.27364927	8.53407365	6.55505750
H	3.21772592	8.72070541	7.06435720
C	1.89469426	9.32560327	5.45699793
C	4.67019298	10.13710114	5.19377139
C	5.03413263	8.80057905	4.94993373
H	4.27988703	8.08015149	4.63046438
C	6.35011320	8.37567110	5.14706664
H	6.61351535	7.33250698	4.96495791
C	7.32207186	9.27981172	5.58454574
H	8.34825138	8.94635072	5.74456018
C	6.97041422	10.61091853	5.82408357
H	7.72079523	11.32175484	6.17357997
C	5.65522550	11.03978297	5.62927993
H	5.39912346	12.08064275	5.82733005
C	3.90284105	10.41622028	1.35042537
C	3.66045816	11.69498088	0.79483448
H	4.51267251	12.33733929	0.57312156
C	2.35036434	12.17539613	0.50369482
H	2.23400419	13.17022608	0.08148029
C	1.21908293	11.39674586	0.83425747
C	1.43054809	10.12781159	1.45991926
H	0.57261623	9.52554510	1.75463862
C	2.74312211	9.66580638	1.74417746
H	2.87026930	8.69875687	2.23284408
C	5.29326124	9.86601568	1.47787256
H	6.03387419	10.67477312	1.50788013
H	5.52413083	9.22878509	0.60881900
H	5.40983057	9.25488825	2.38163597
C	-0.20090922	11.83856057	0.53954066
H	-0.79887158	11.54981384	1.41857118
C	-0.36435611	13.34962264	0.34695764
H	0.01004051	13.89737221	1.22115385
H	0.15571567	13.70631375	-0.55463981
H	-1.42882320	13.59186333	0.22513654

C	-0.72242048	11.05661331	-0.68640906
H	-1.77659812	11.30743364	-0.86898042

Geometry optimised coordinates for 7b'

Ru	2.77430556	11.36081923	2.73076179
C	0.35109195	12.06500956	0.26169715
Cl	0.73238653	12.25075959	3.72737961
P	3.20597728	10.57320404	4.84239118
O	4.15335950	14.93037345	4.83496440
O	2.50263362	11.49926651	7.28365442
N	3.79238233	13.07566619	3.52565022
H	0.57121305	12.97067292	-0.31585759
N	3.05366248	13.20931359	5.85432061
C	4.53975308	13.80809093	2.53267536
C	5.90521155	13.57370610	2.34525117
H	6.41031003	12.84708997	2.98249223
C	6.61978672	14.27041666	1.36490003
H	7.68697474	14.07295939	1.23819255
C	5.99617101	15.22596304	0.55207127
C	4.62674675	15.46673127	0.76088371
H	4.11731233	16.22224257	0.15750076
C	3.90859591	14.77290053	1.73328086
H	2.85099353	14.98206040	1.89954501
C	6.76791392	15.99590165	-0.49217434
H	6.26699758	15.96102073	-1.47103958
H	7.78236186	15.59492007	-0.61631653
H	6.85992829	17.05736745	-0.21474339
C	3.69540536	13.79369768	4.67448762
C	2.63974779	14.17855859	6.85824346
C	1.37779044	14.75642190	6.74017491
H	0.73891297	14.47399578	5.90299465
C	0.95254273	15.68276310	7.69544661
H	-0.03697721	16.13445367	7.59800924
C	1.77046183	16.03803615	8.77632930
C	3.03389455	15.43222391	8.87762253
H	3.68808480	15.68926091	9.71372625
C	3.47049739	14.50970021	7.92857794
H	4.45465387	14.04950459	8.01395399
C	1.31868825	17.05292109	9.79914671
H	1.48249412	16.68854214	10.82356152
H	0.25182402	17.28568583	9.68639197
H	1.87926238	17.99519496	9.69588017
C	2.87546374	11.89199195	6.18414577
C	0.99150872	8.84826503	4.81827981
H	0.68774135	9.42467443	3.94539021

C	0.17830844	7.82182302	5.30564200
H	-0.74873329	7.57326759	4.78683889
C	0.54331640	7.12809180	6.46168909
H	-0.09116988	6.32589895	6.84214342
C	1.71483198	7.47590716	7.14098417
H	1.99247734	6.95406320	8.05784058
C	2.52928908	8.50139954	6.65893000
H	3.42832585	8.77830153	7.20647826
C	2.18227256	9.18257895	5.47907752
C	4.93983886	10.06807376	5.22690155
C	5.33842932	8.72230859	5.14507260
H	4.60376673	7.94952692	4.91717579
C	6.66504764	8.35912460	5.38937779
H	6.95576478	7.30898489	5.33102921
C	7.61166196	9.33326480	5.71668445
H	8.64630165	9.04800871	5.91282233
C	7.22440167	10.67371519	5.80097349
H	7.95427585	11.44039421	6.06501969
C	5.89964137	11.04158159	5.55603966
H	5.61606458	12.09130590	5.62964367
C	3.99795564	9.88392266	1.40944709
C	4.05824091	11.17979937	0.84837309
H	5.02421907	11.65587983	0.69159471
C	2.87883408	11.87309053	0.41044536
H	2.98334339	12.85636253	-0.04543361
C	1.60579283	11.33937058	0.64106309
C	1.52225094	10.09137878	1.35706705
H	0.54095613	9.69200834	1.60985072
C	2.68796365	9.37137998	1.70648082
H	2.58922461	8.41065496	2.21365478
C	5.21475885	9.00039641	1.59860700
H	5.05029449	8.41072184	2.51490423
C	6.53452365	9.75870396	1.76231263
C	5.28742140	8.01232165	0.41317966
H	6.12060741	7.30988320	0.55588237
H	5.45286039	8.55054642	-0.53170363
H	4.36219120	7.42843427	0.31251879
H	-0.30379713	11.41336002	-0.33558328
H	-0.19563302	12.35101081	1.17521593
H	7.34733131	9.04918746	1.96678392
H	6.48608219	10.46826668	2.59737018
H	6.80364677	10.31070330	0.85034673