SUPPLEMENTARY MATERIAL

Water vapour uptake and extrusion by a crystalline metallorganic solid based on half-sandwich Ru(II) building-blocks

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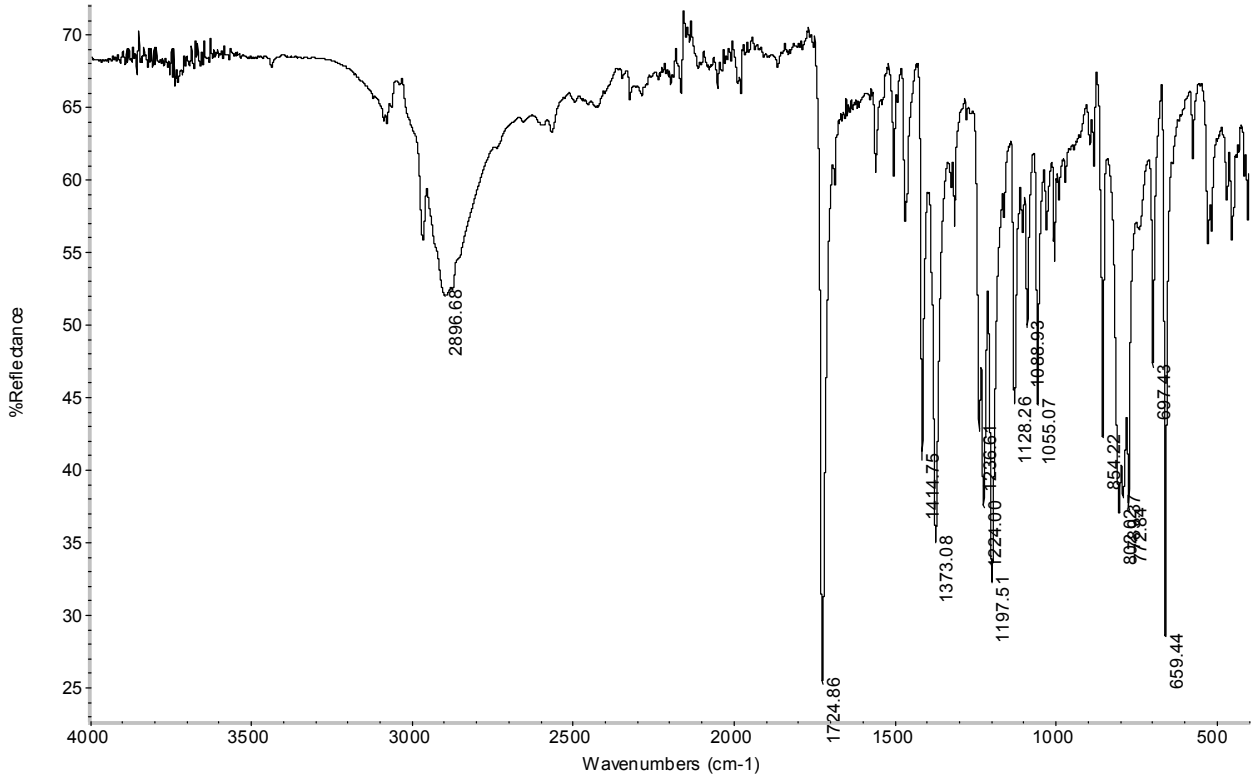


Figure SI1 ATR-FTIR spectrum of **1α**

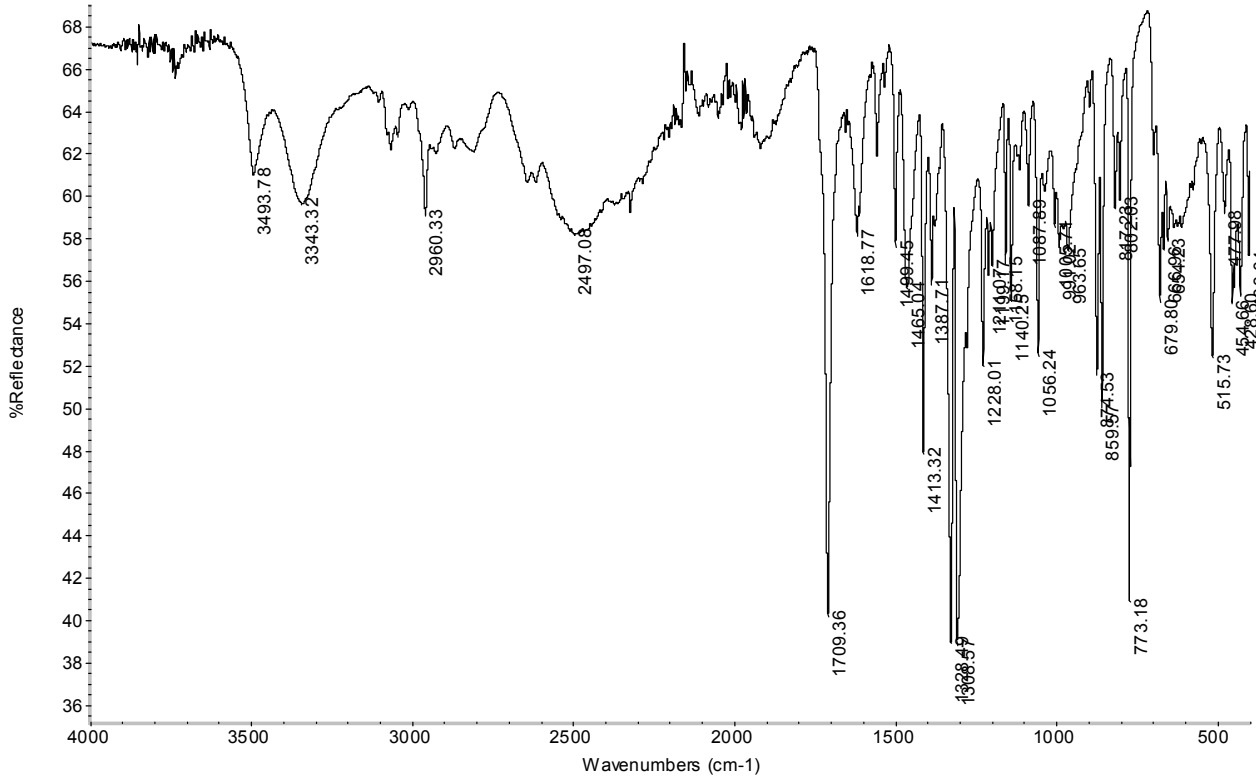


Figure SI2 ATR-FTIR spectrum of **wet**

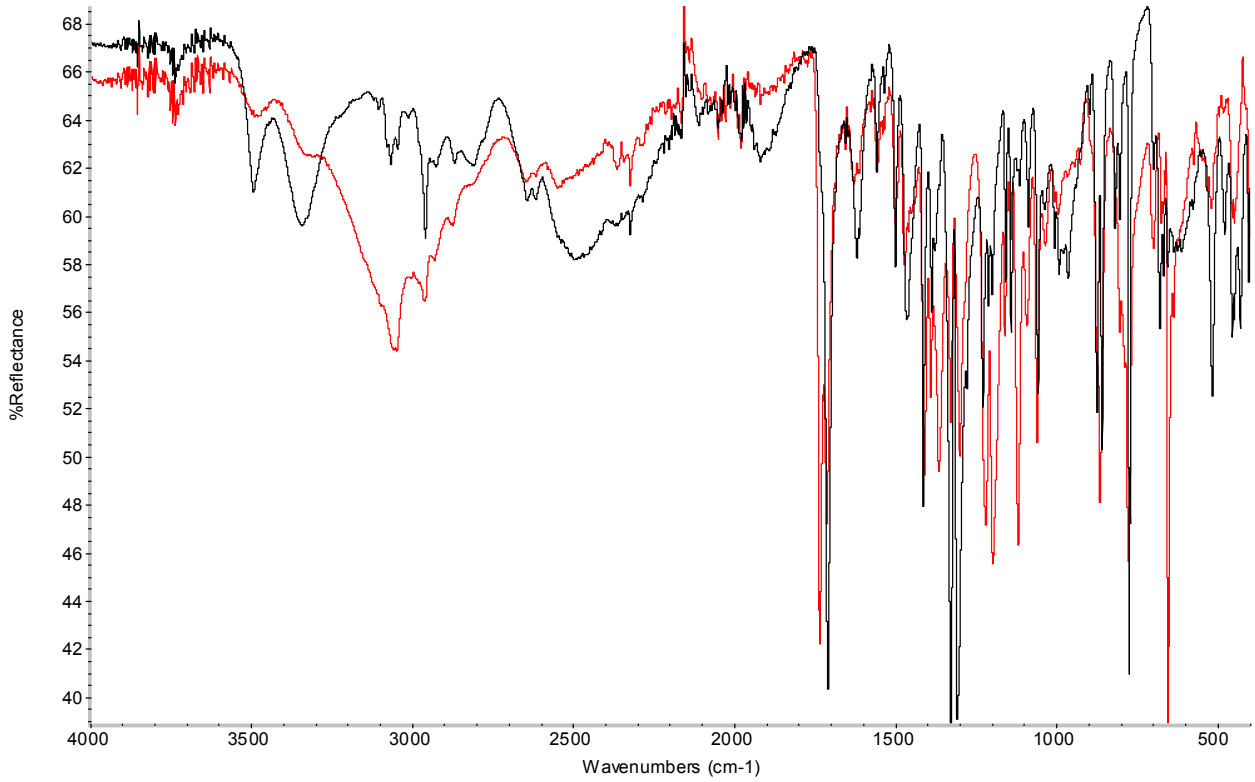


Figure SI3 ATR-FTIR spectrum of **wet** (black) after thermal treatment at 90°C under vacuum (red) (partial exposure to air moisture).

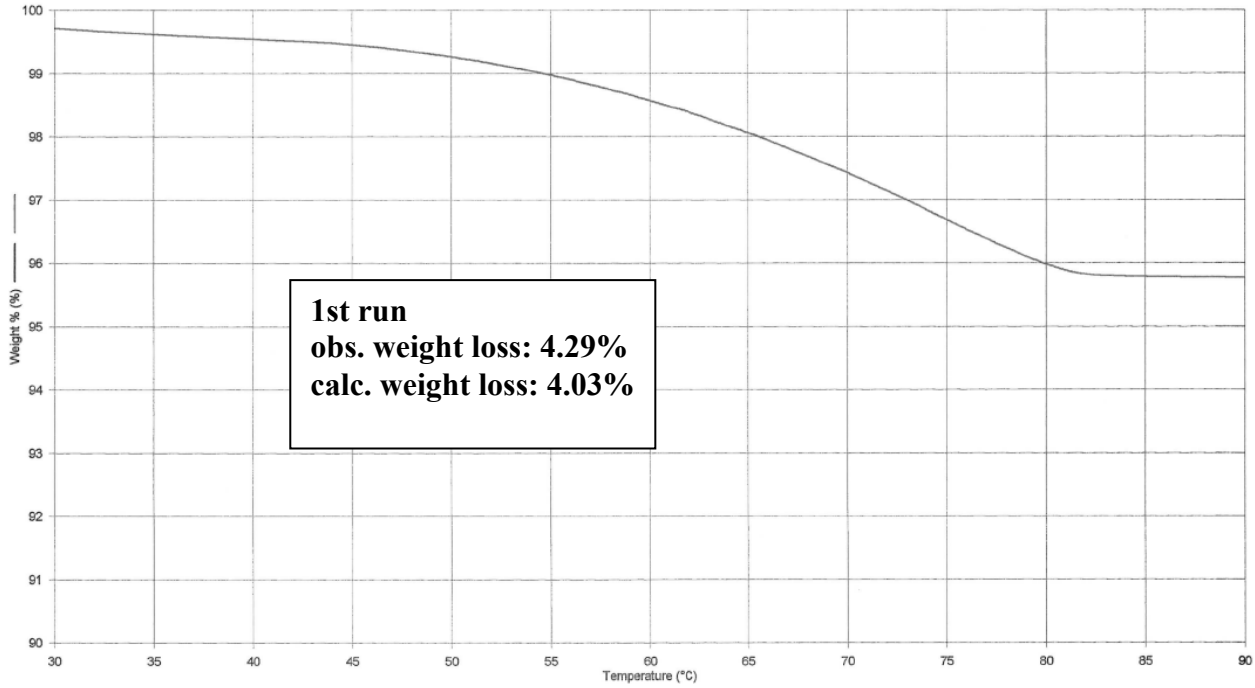


Figure SI4 TGA analysis of **wet** (1st run)

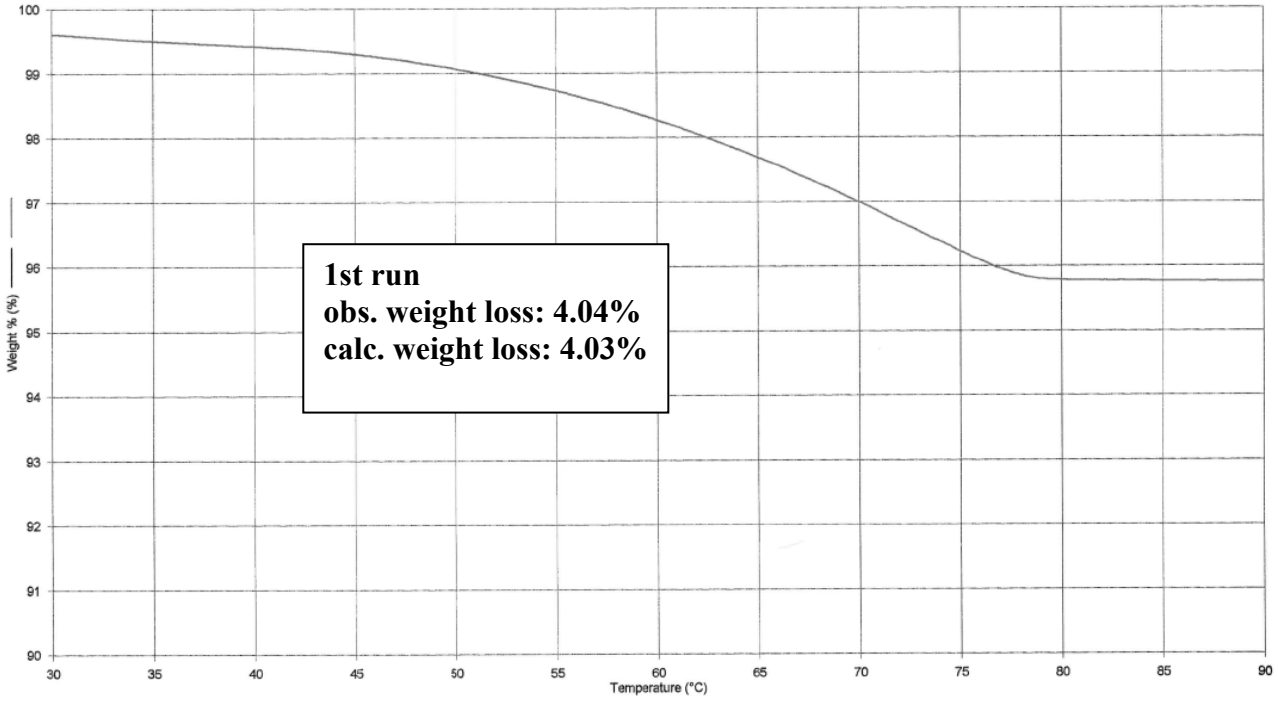


Figure SI5 TGA analysis of **wet** (2nd run); the sample of the 1st run has been cooled in air and subjected to a second TGA analysis

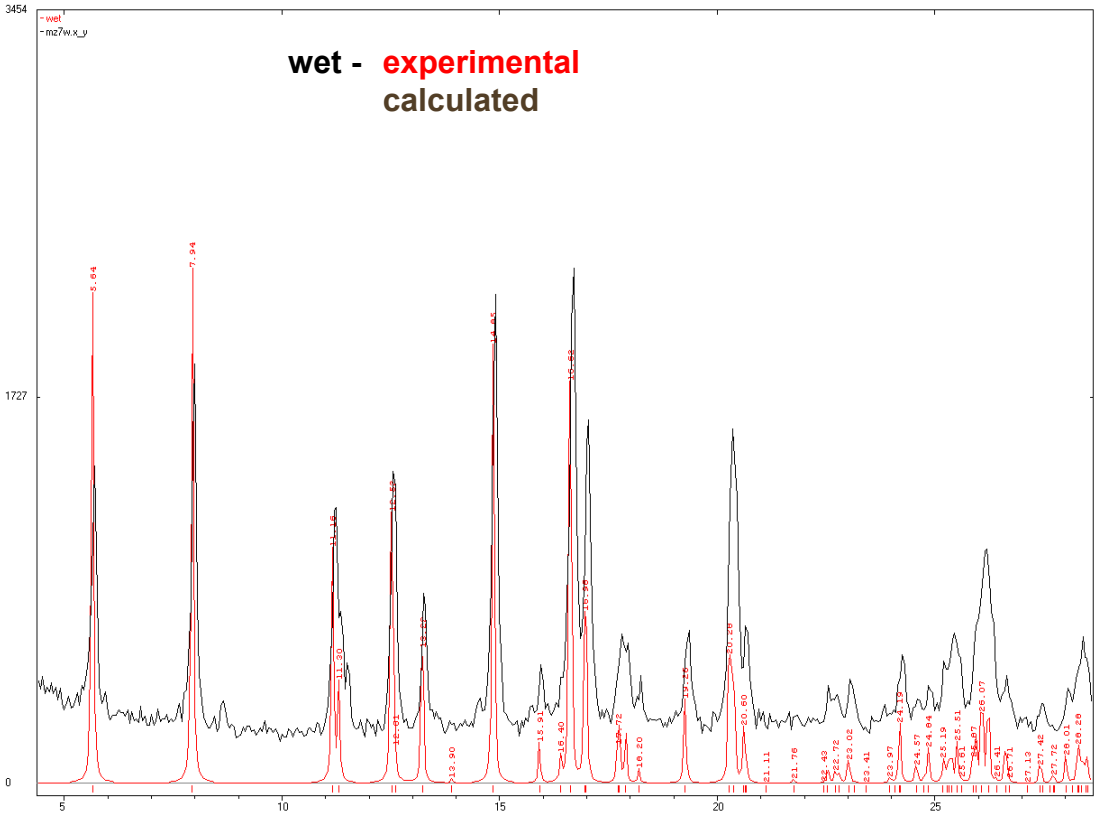


Figure SI6 Comparison of the XRPD spectra of **wet** calculated (red) and obtained after exposure of **1α** to water vapour (black).

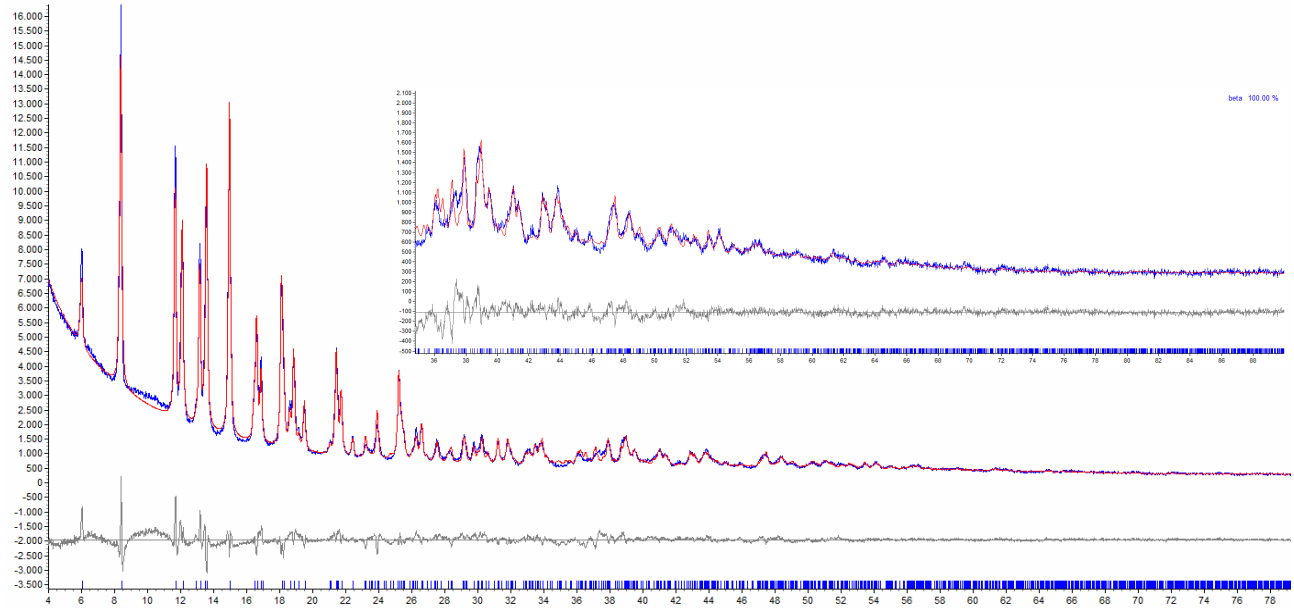


Figure SI7 Final Rietveld refinement for **1β** the high angle region has been magnified (4X) for clarity of the plot.

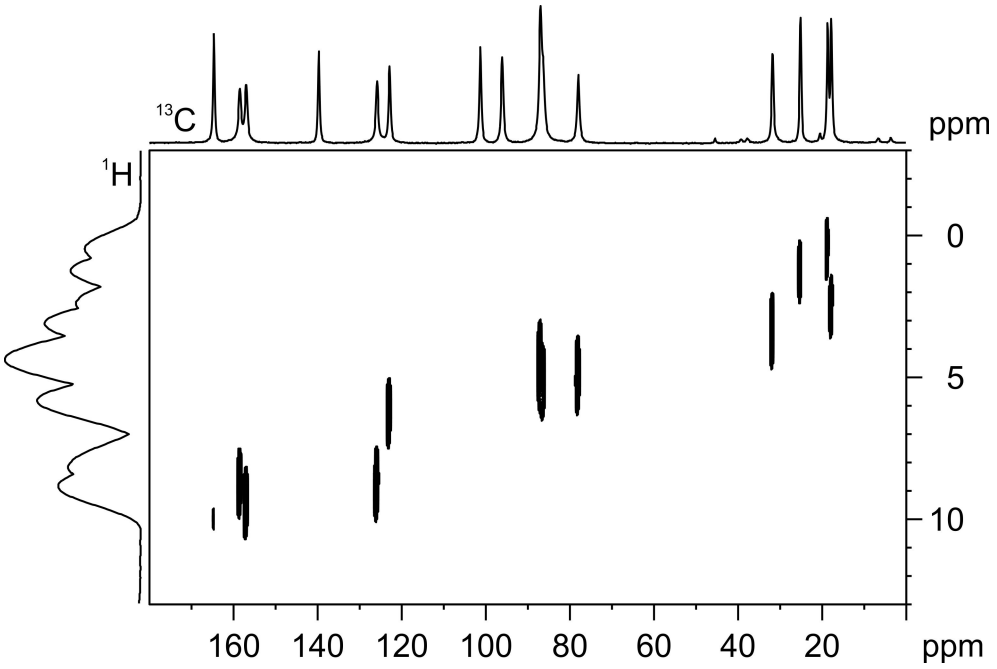


Figure SI8. ^{1}H–^{13}C FSLG-HETCOR spectrum of **1α** recorded with a spinning speed of 12 kHz and a contact time of 100 μs.

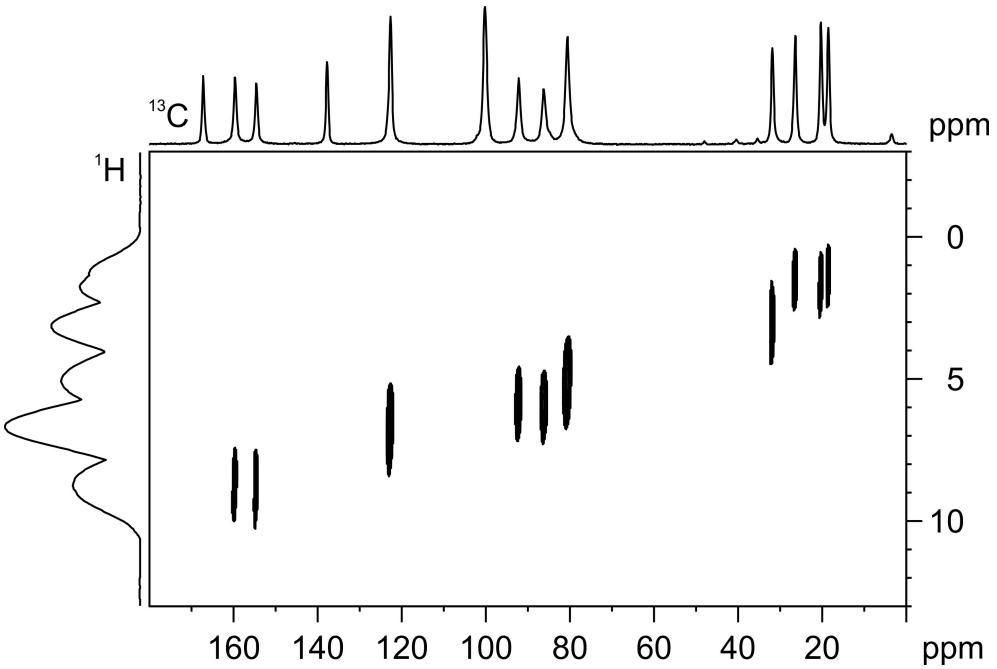


Figure SI9. ^{1}H–^{13}C FSLG-HETCOR spectrum of **wet** recorded with a spinning speed of 12 kHz and a contact time of 100 μs.

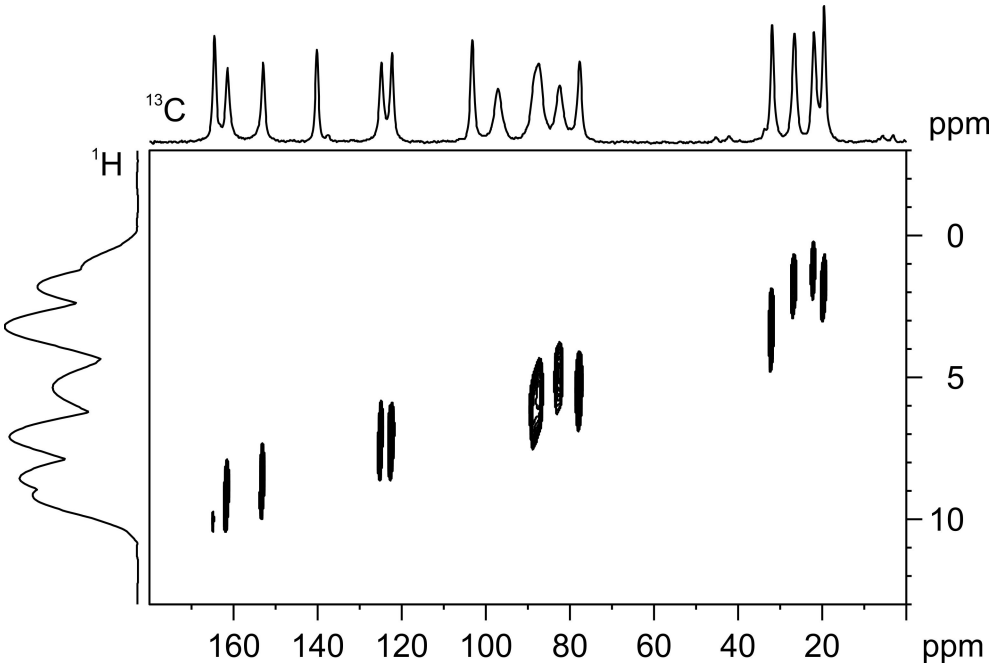


Figure SI10. ^{1}H–^{13}C FSLG-HETCOR spectrum of **1β** recorded with a spinning speed of 12 kHz and a contact time of 100 μs.

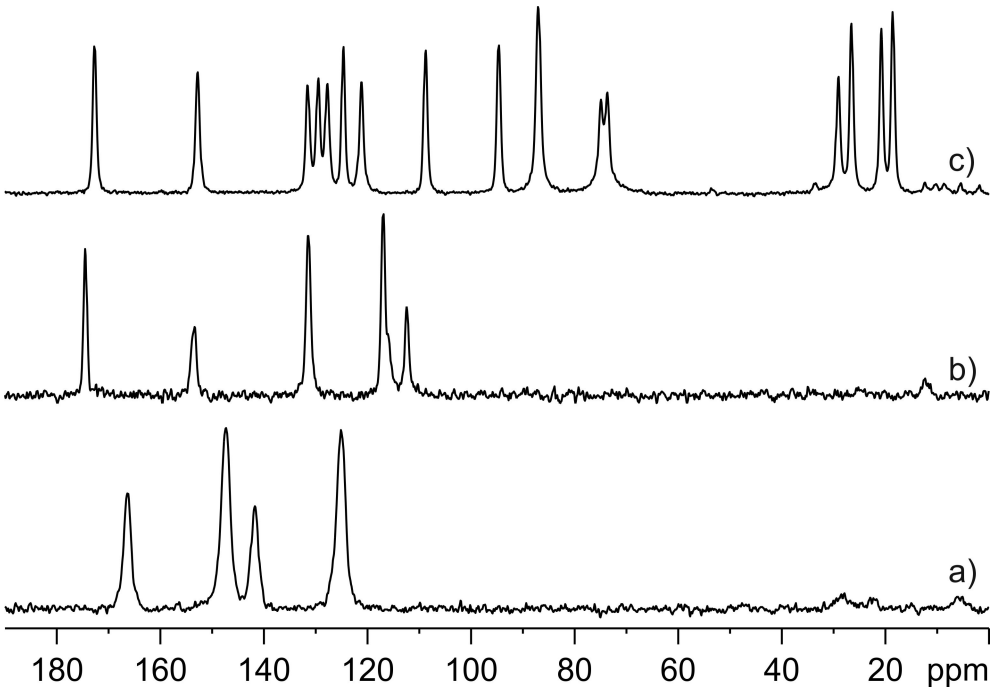


Figure SI11. ^{13}C CPMAS spectra of compounds INA (a), A4AB (b) and [(p-cymene)Ru(κN-A4AB)Cl_2] (c) recorded at 100.65 MHz with a spinning speed of 12 kHz.

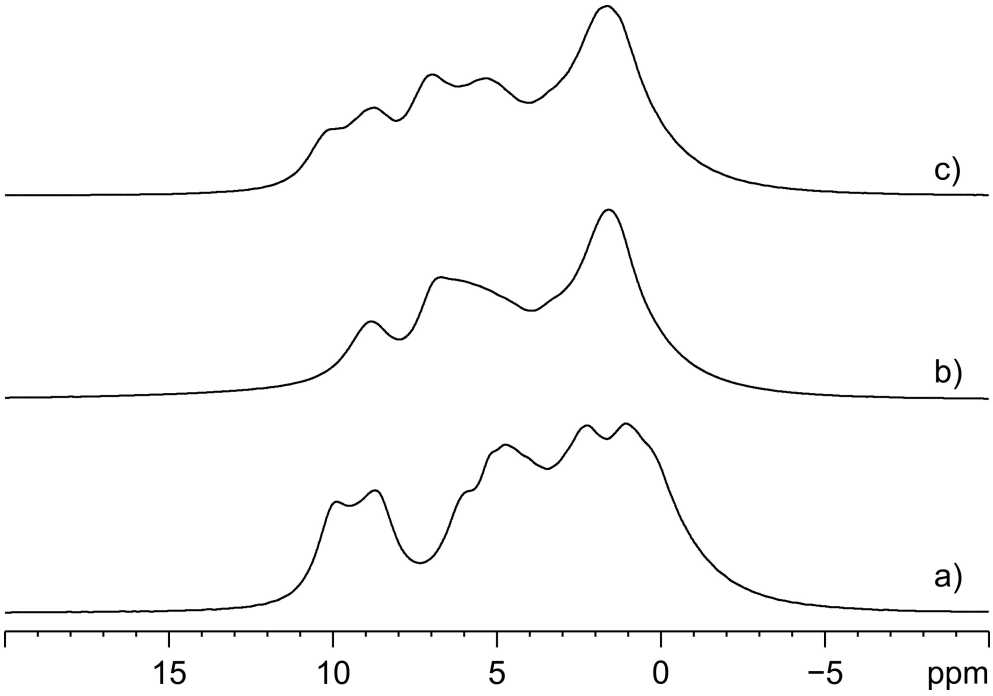
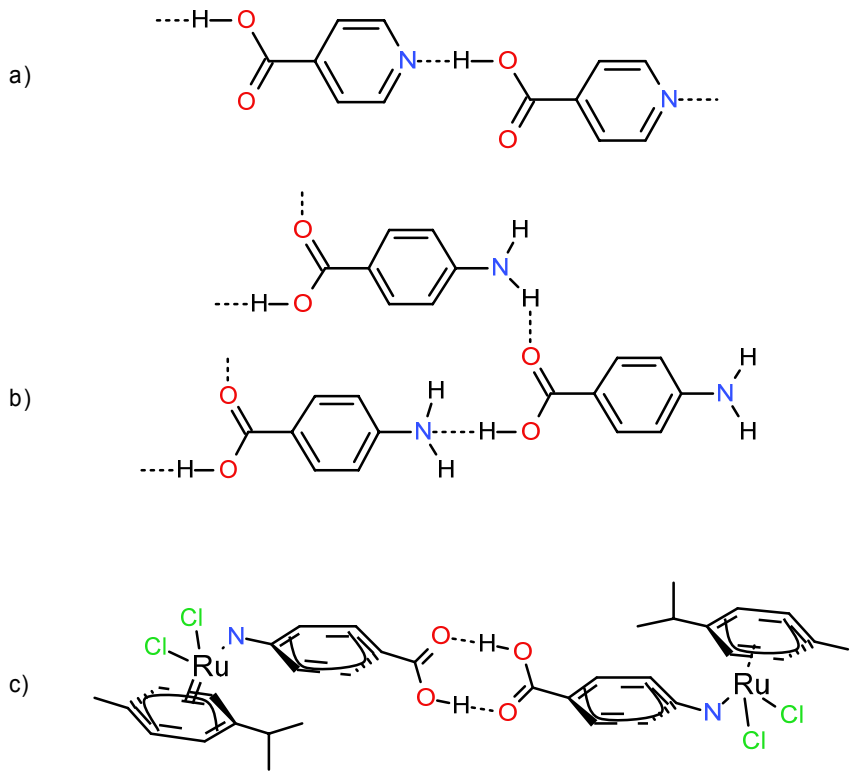


Figure SI12. ^{1}H MAS spectra of compounds **α** (a), **wet** (b) and **β** (c) recorded at 400.23 MHz with a spinning speed of 32 kHz.



Scheme SI1. Hydrogen bond arrangements in INA (a), A4AB (b) and [(p-cymene)Ru(κN-A4AB)Cl_2] (c).