SUPPORTING INFORMATION

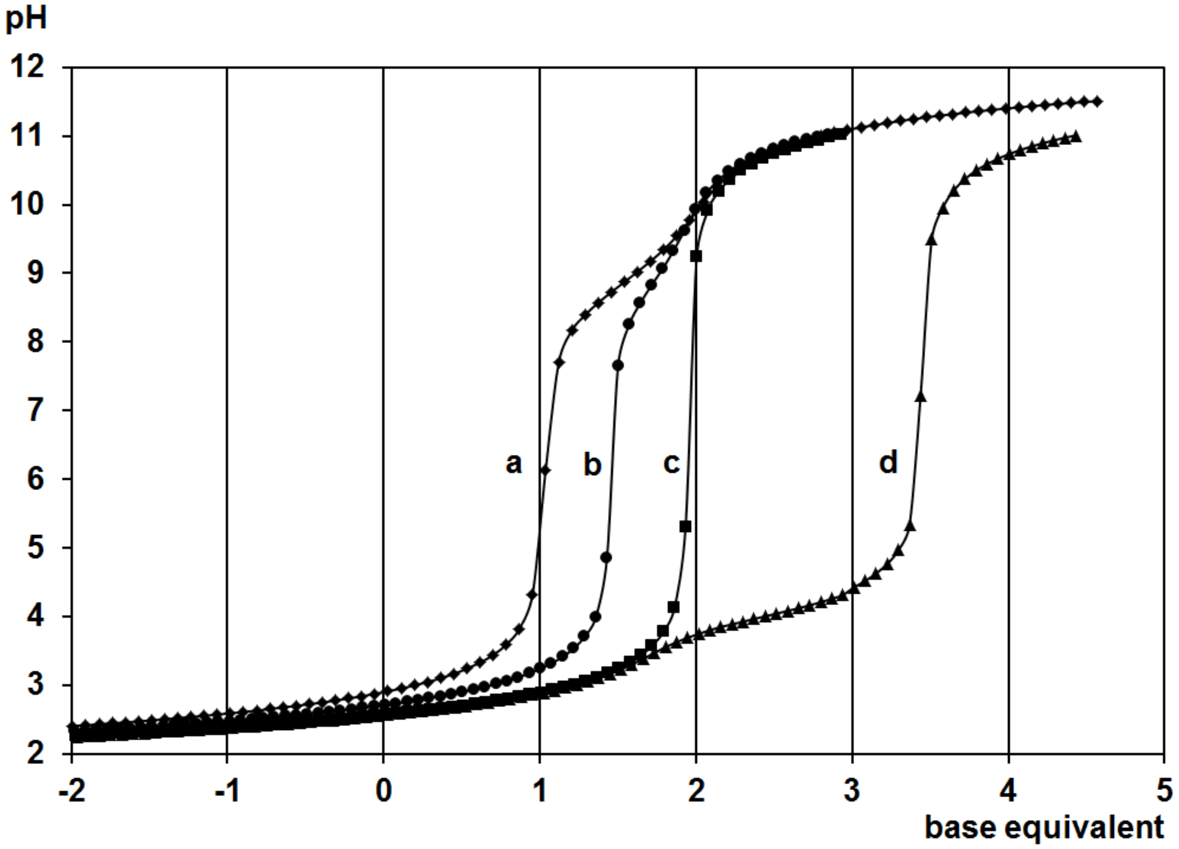
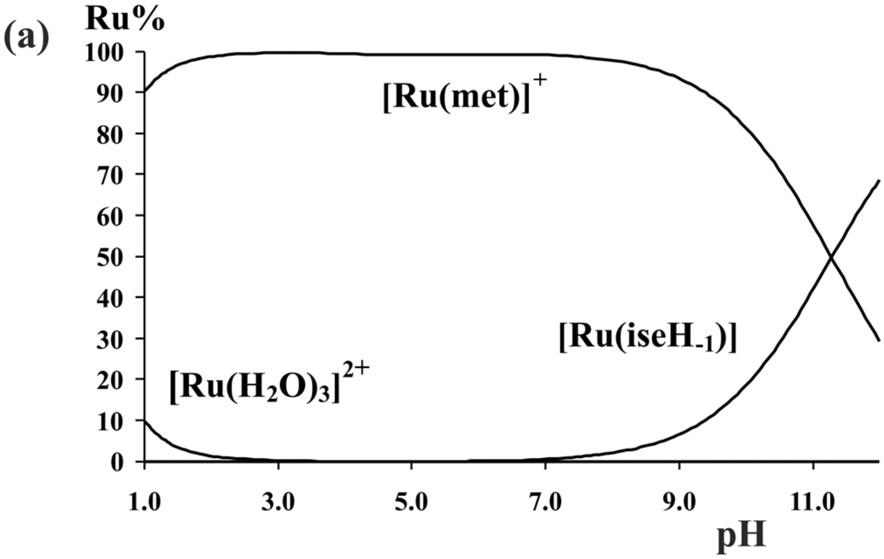


Figure S1. Titration curves with S-methyl-L-cysteine for the H^+–ligand system (a) and the $[(\eta^6\text{-}p\text{-cym})Ru(H_2O)_3]^{2+}$–ligand systems at 1:2 (b), 1:1 (c) and 2:1 (d) ratios. Negative base equivalent refers to an excess of acid in the sample.

Figure S2. Dependence on pH of the ^{1}H NMR spectra of the $[(\eta^6\text{-}p\text{-cym})Ru(H_2O)_3]^{2+}$–met system at 1:1 ratio and at 298 K in D_2O (I = 0.20 M KNO_3, c_{Ru} = 15.3 mM).“Ru” stands for the $[(\eta^6\text{-}p\text{-cym})Ru]^{2+}$ entity.



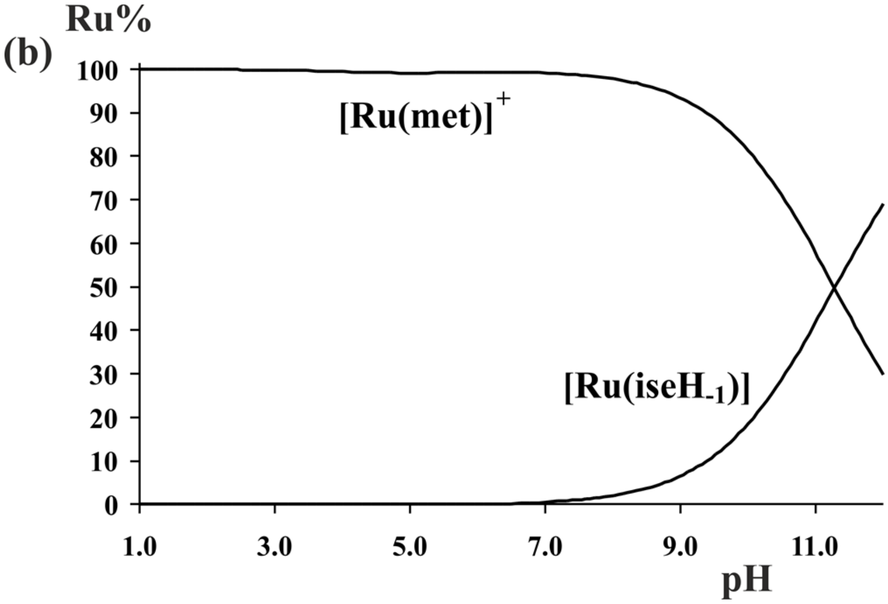


Figure S3. Percentage amount of ruthenium(II) in form of various methionato, citrato, isoserinato complexes as a function of pH in a hypothetical Ru–met–citr–ise system at 1:1:1:1 ratio using the previously determined logβ values[7,9] and the data in Table 2. c_{Ru} = 1 μM (a) and 10 mM (b); "Ru" refers to any form of $[(\eta^6\text{-}p\text{-cym})Ru]^{2+}$ entity.

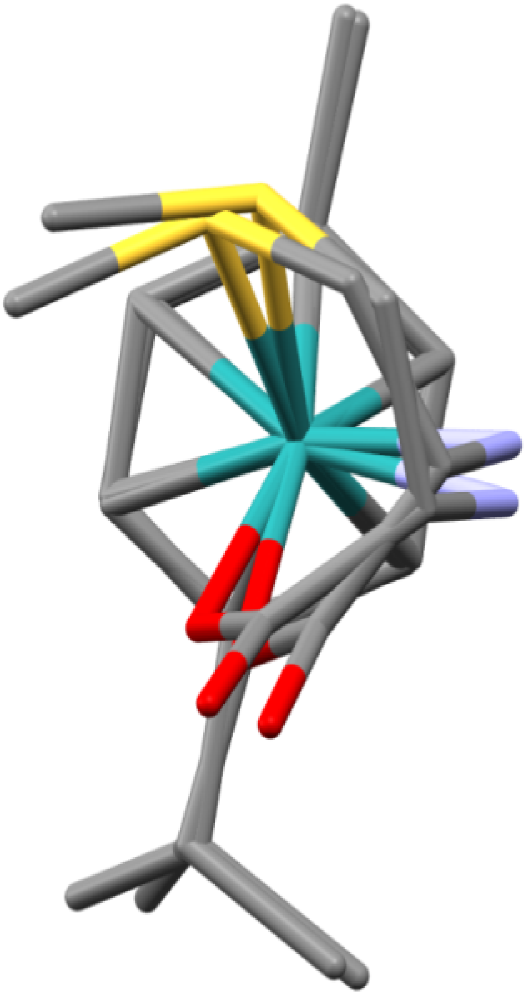


Figure S4. Superimposed molecular structures for the two conformers of the $R_{Ru}R_{\alpha C}S_S$ diastereomer of [(η^6-*p*-cym)Ru(mecys)]NO_3 (**10**).

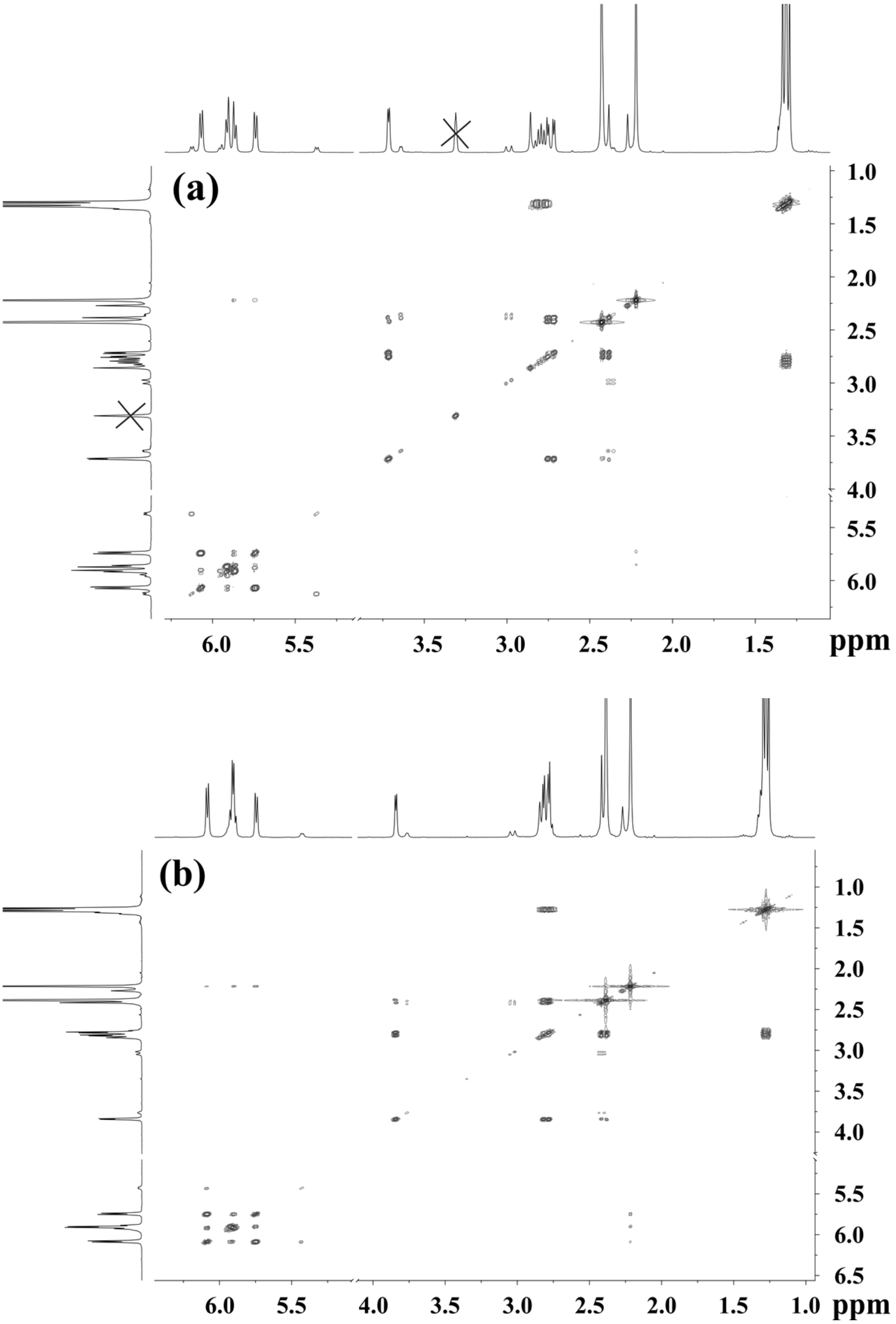


Figure S5. COSY spectra of [(η^6-*p*-cym)Ru(mecys)]CF_3SO_3 (**12**) in CD_3OD (a) and [(η^6-*p*-cym)Ru(mecys)]Cl (**1**) in D_2O (b).

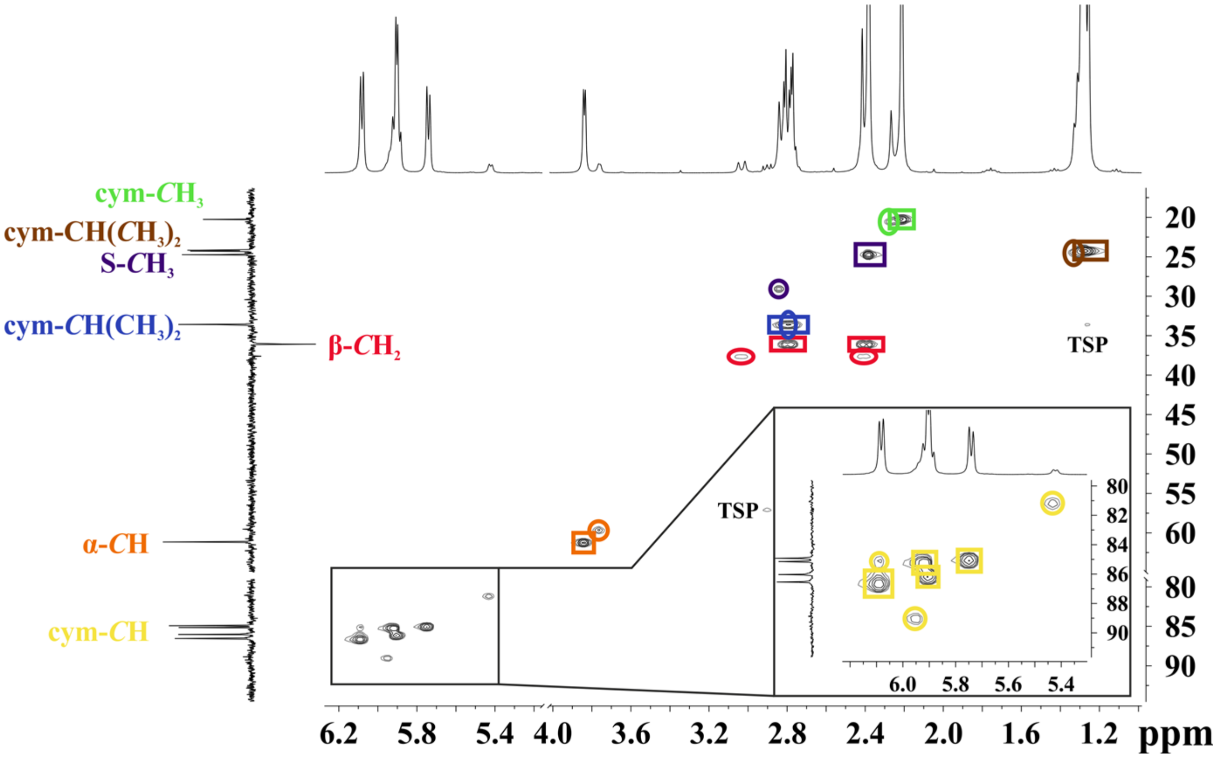
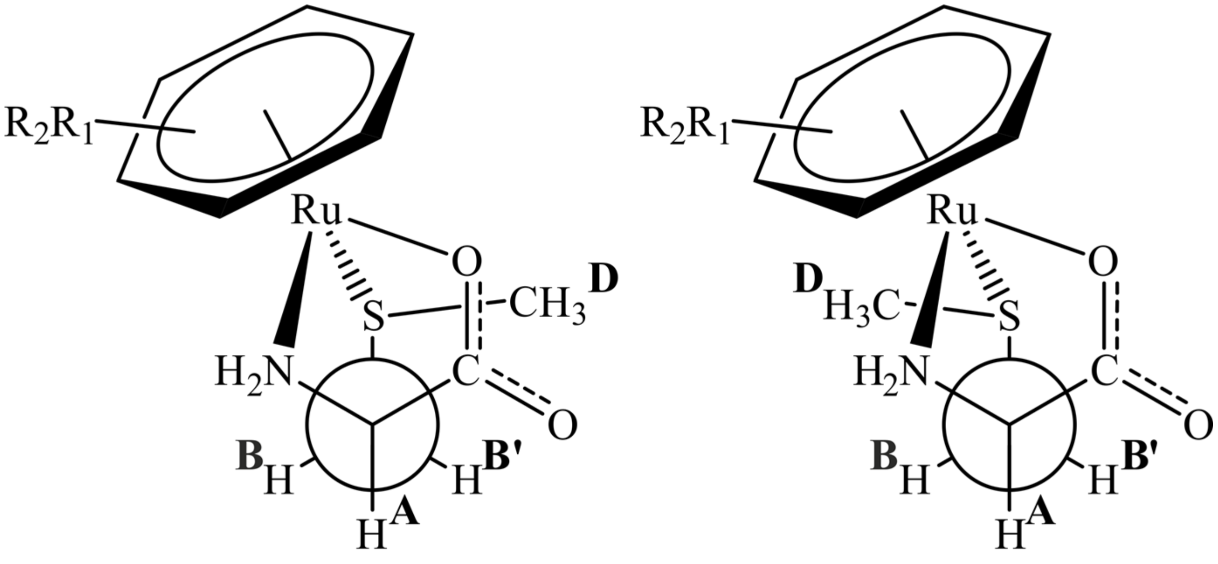


Figure S6. HSQC spectrum of [(η^6-*p*-cym)Ru(mecys)]Cl (**1**) in D_2O. The peaks belonging to the major diastereomer are in squares, while the minor's in circles.



$R_{Ru}R_{\alpha C}S_{S}$ $R_{Ru}R_{\alpha C}R_{S}$

Figure S7. Newmann projection of the two diastrereomers of [(η^6-*p*-cym)Ru(mecys)]$^+$.

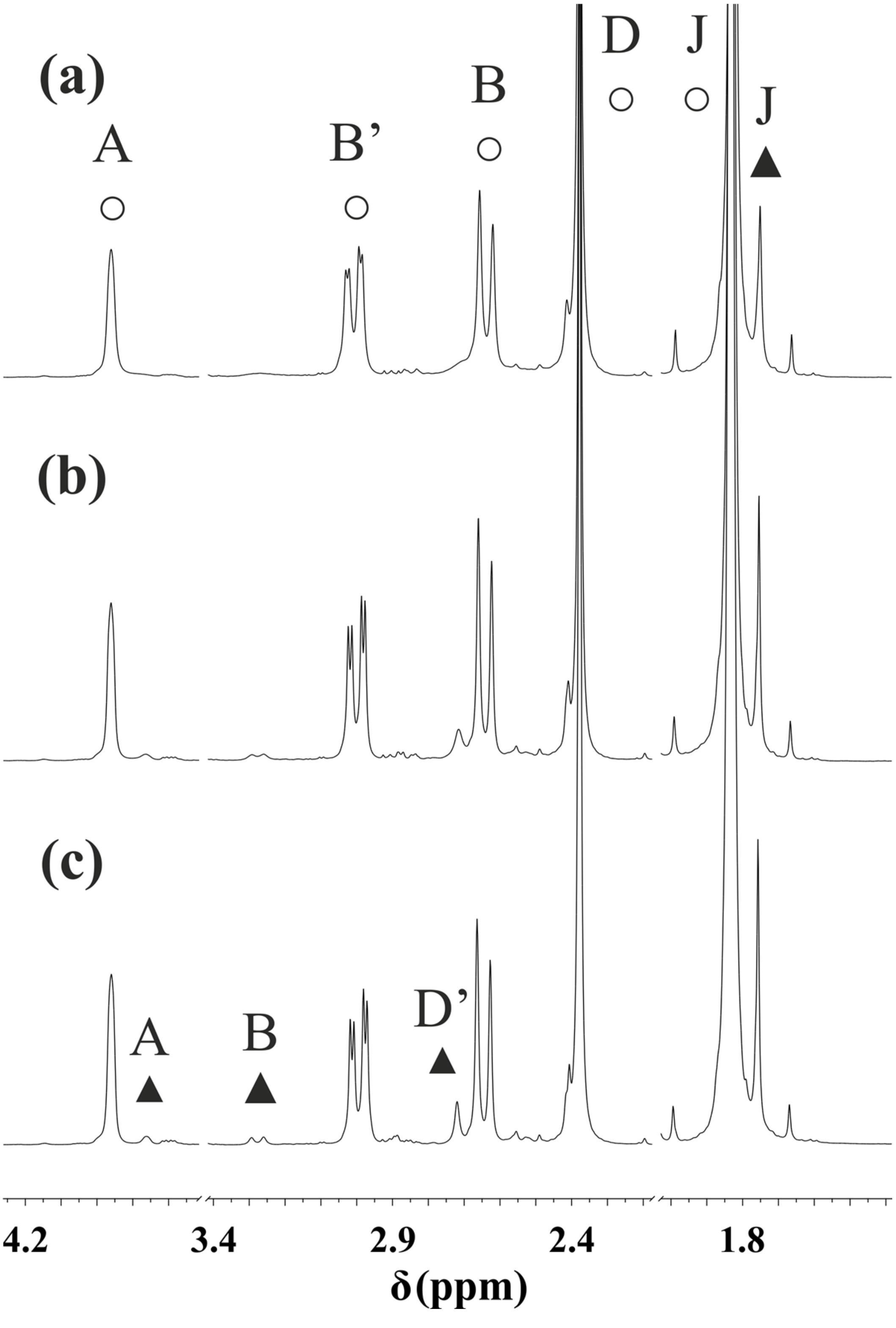


Figure S8. Dependence on temperature of the ^{1}H NMR spectra of [(η^5-Cp*)Rh(mecys)]Cl (**6**) in D_2O at 298 K (a), at 283 K (b) and at 273 K (c) together with the notation of the hydrogens according to Scheme 1. Resonances of the major diastereomer are marked with ○, while those of the minor one with ▲.

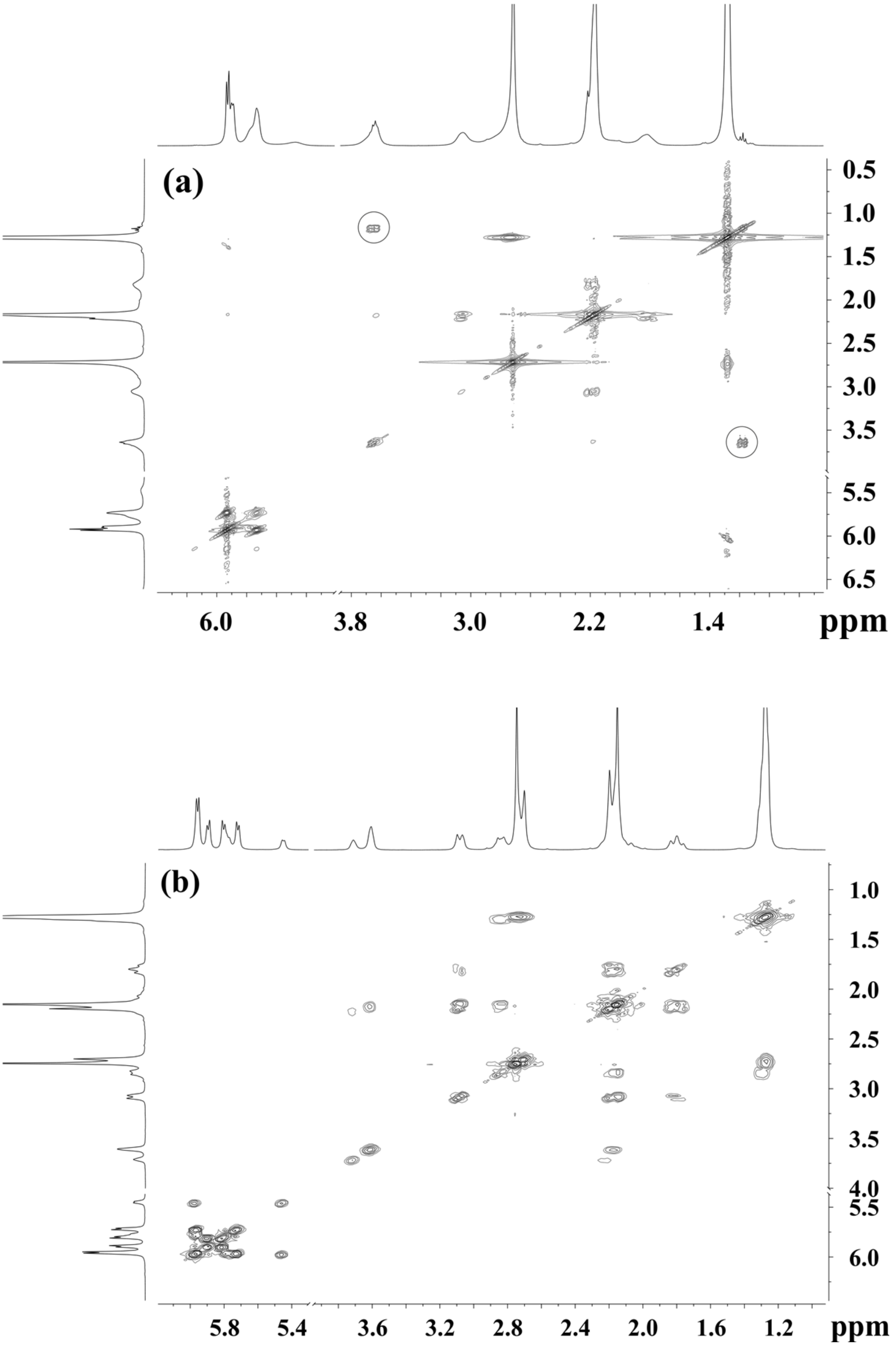


Figure S9. COSY spectra of [(η^6-*p*-cym)Ru(DL-met)]NO$_3$ (**11**) in D$_2$O at 298K (a) and [(η^6-*p*-cym)Ru(L-met)]Cl (**4**) in D$_2$O at 273K (b). Marked cross peaks originate from ethanol.

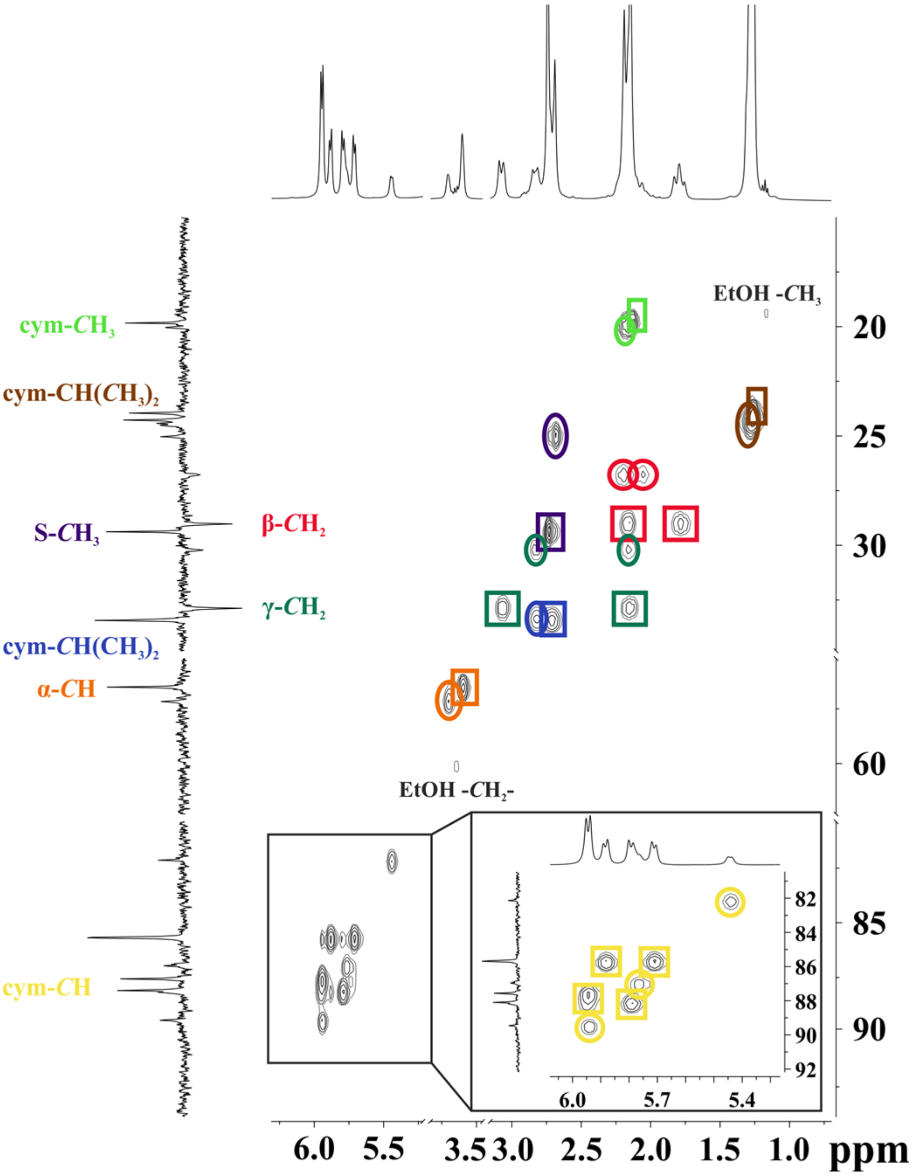


Figure S10. HSQC spectrum of [(η^6-*p*-cym)Ru(DL-met)]NO_3 (**11**) in D_2O at 273 K. The peaks belonging to the major diastereomer are in squares, while the minors in circles.

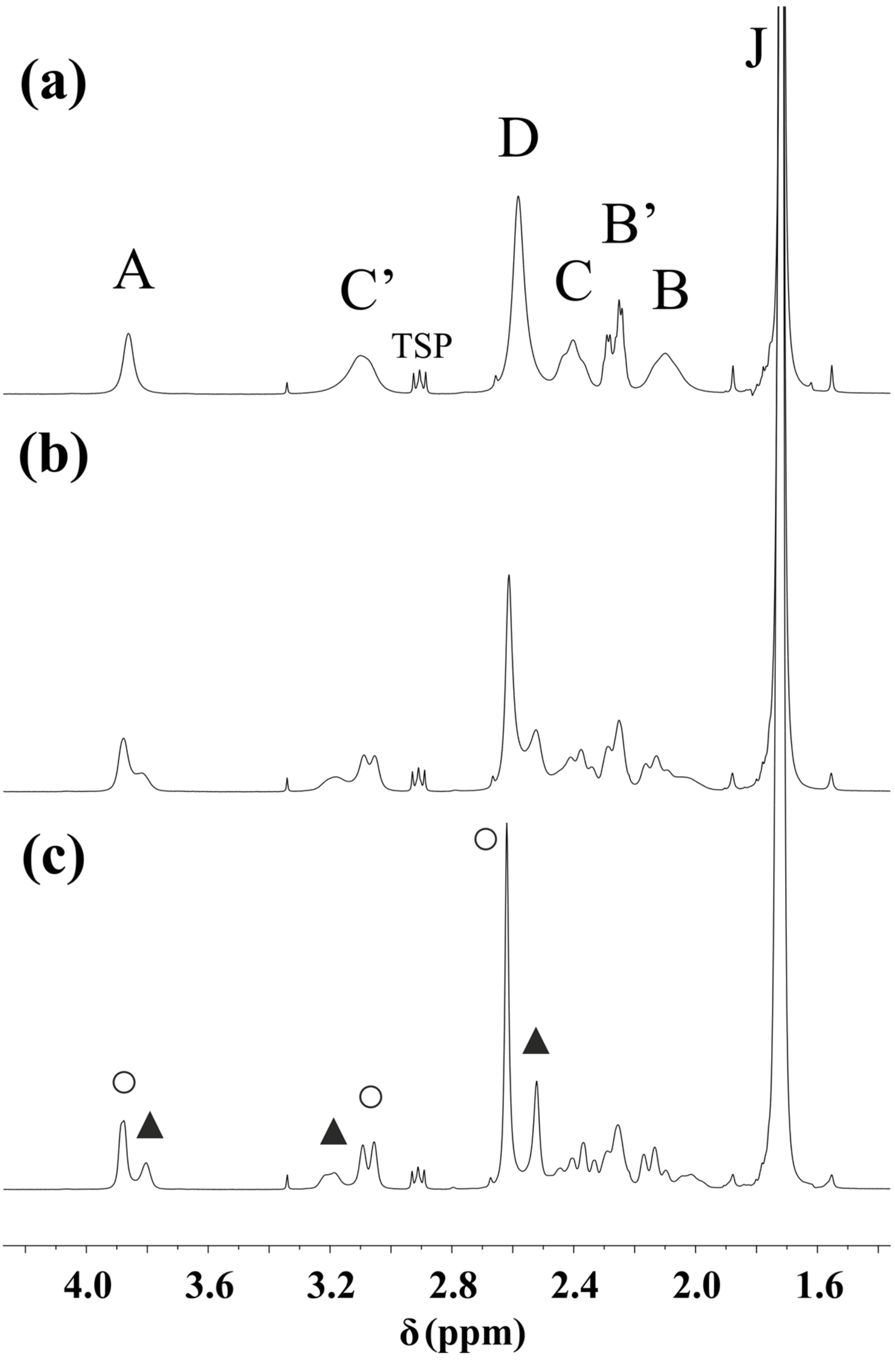


Figure S11. Dependence on temperature of the ^{1}H NMR spectra of [(η^5-Cp*)Rh(DL-met)]Cl (**7**) in D_2O at 298 K (a), at 283 K (b) and at 273 K (c) together with the notation of the hydrogens according to Scheme 1. Resonances of the major diastereomer are marked with ○, while those of the minor one with ▲.