Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Hydrolytic behaviour of mono-and dithiolato-bridged dinuclear arene ruthenium complexes and their interactions with biological ligands

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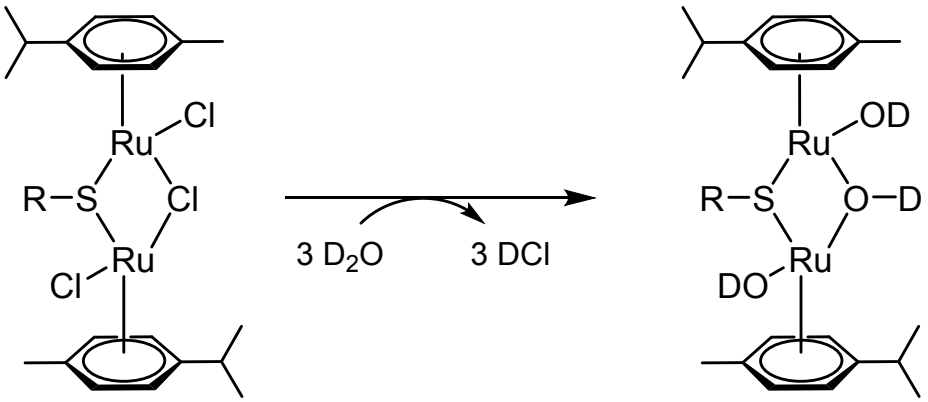
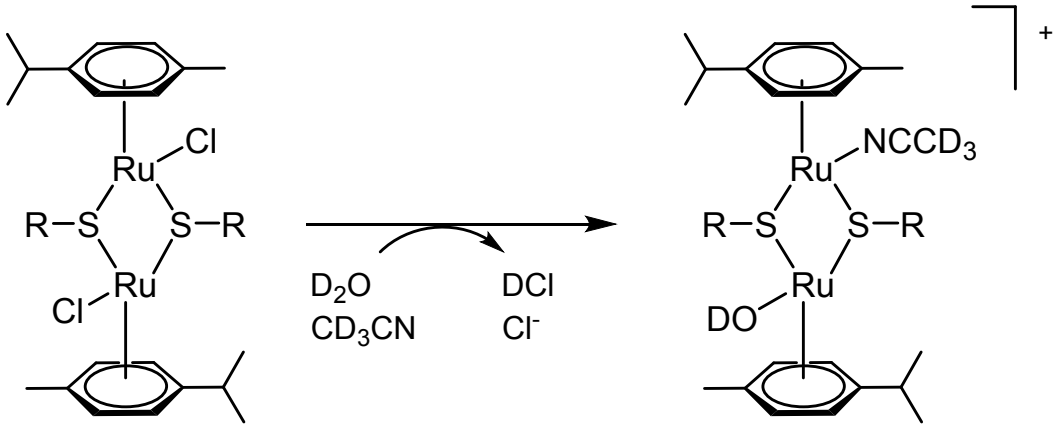


Scheme S1- Hydrolysis of the monothiolato complexes **1** and **2** in D_2O/acetone-d_6.



Scheme S2- Hydrolysis of the monothiolato complexes **3** and **4** in D_2O/CD_3CN.

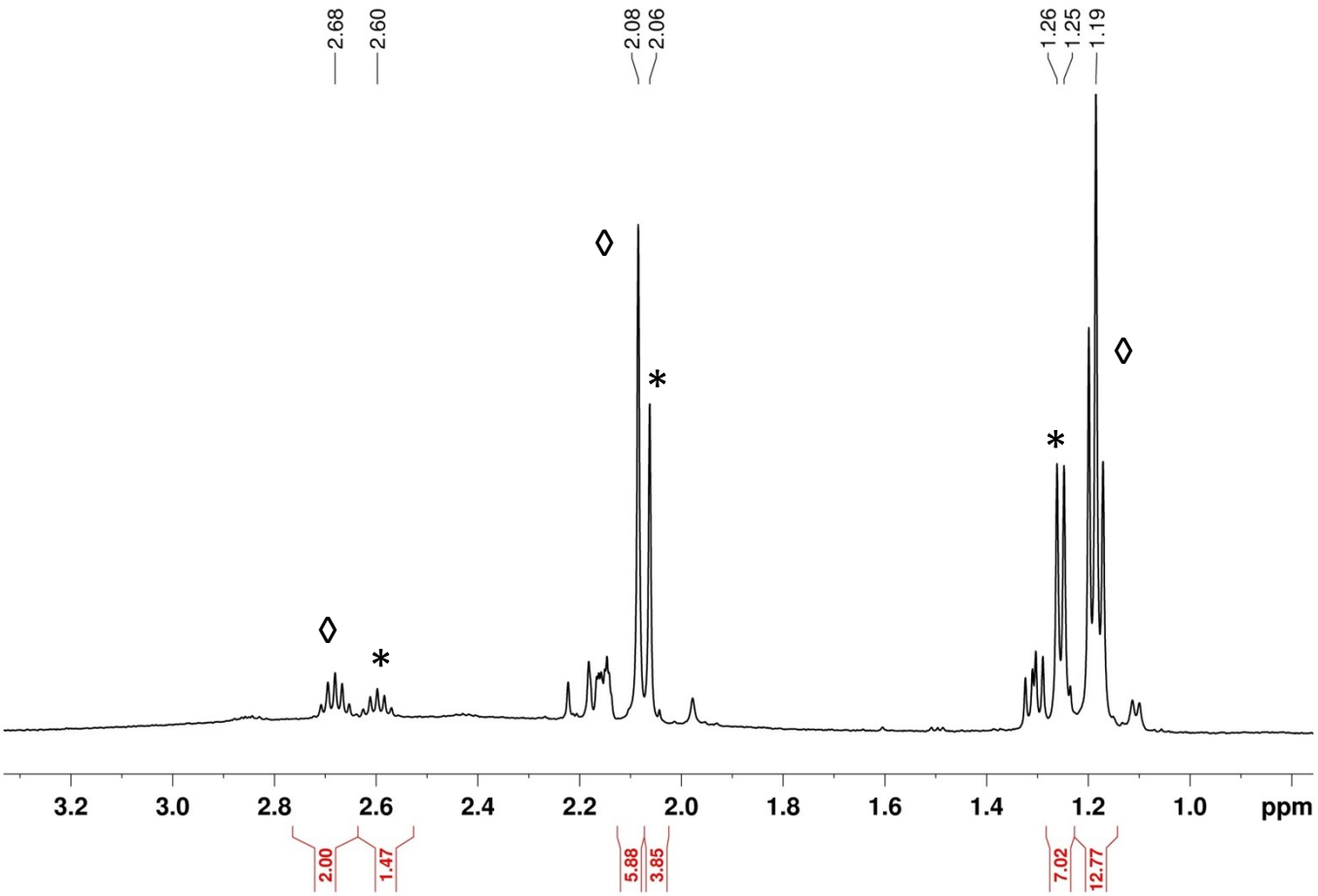


Fig. S1 – High field part of the ^{1}H NMR spectrum of $[(\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-S-m-9-B}_{10}\text{C}_2\text{H}_{11})]$ (**1**) dissolved in D_2O/acetone-d_6 (ratio 7 : 3) recorded 24 h after sample preparation, at 37 °C and at pD 7. The labels correspond to *p*-cymene ligands in different species present in solution. The species labeled * corresponds to complex **1**, and the species labeled ◊ is the fully hydrolysed complex $[(\eta^6\text{-p-MeC}_6\text{H}_4\text{-Pr}^i)_2\text{Ru}_2(\text{OD})_2(\mu\text{-OD})(\mu\text{-S-m-9-B}_{10}\text{C}_2\text{H}_{11})]$. A further characterisation of the minor species also present in the mixture was not attempted due to their very low concentration.

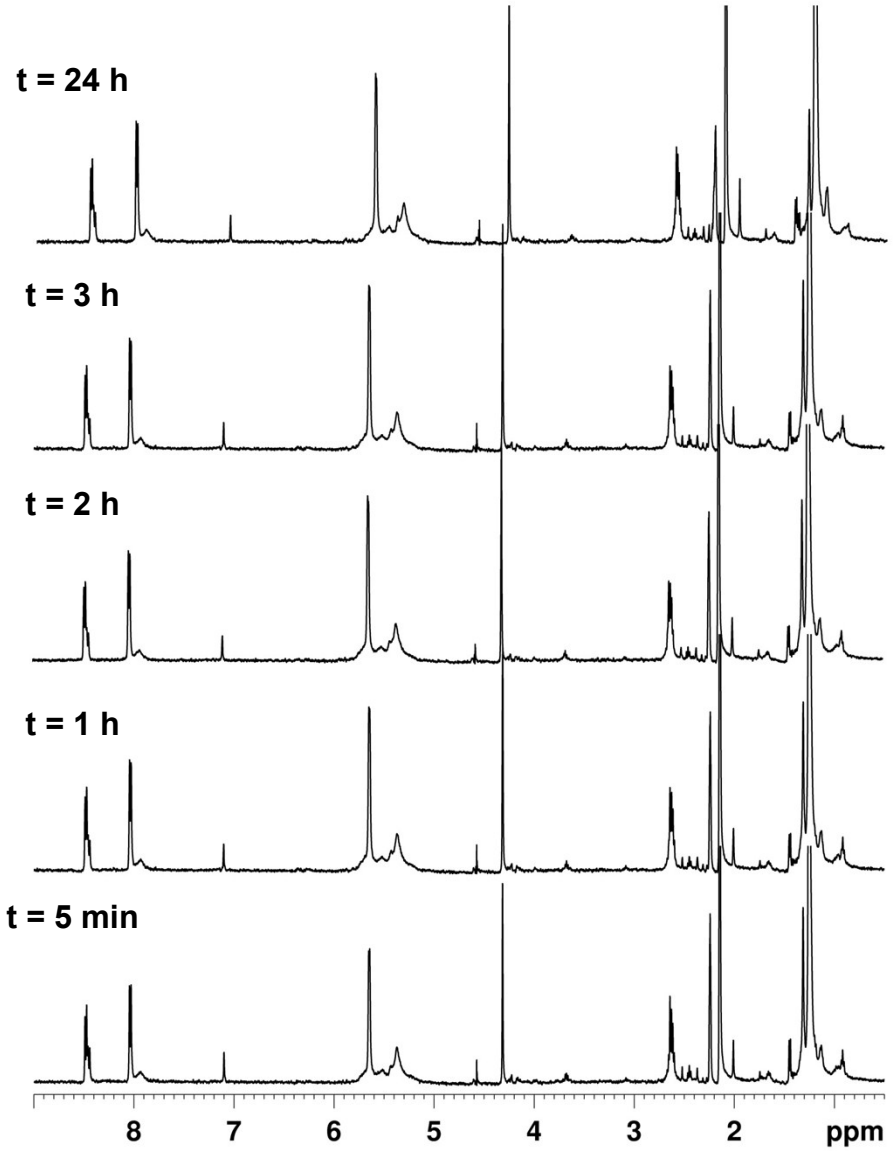


Fig. S2 - NMR time-courses for the reaction of thiolato complex **2** dissolved in an acetone-d_6/D_2O mixture (ratio 4 : 6) at pD 7 and 37 °C.

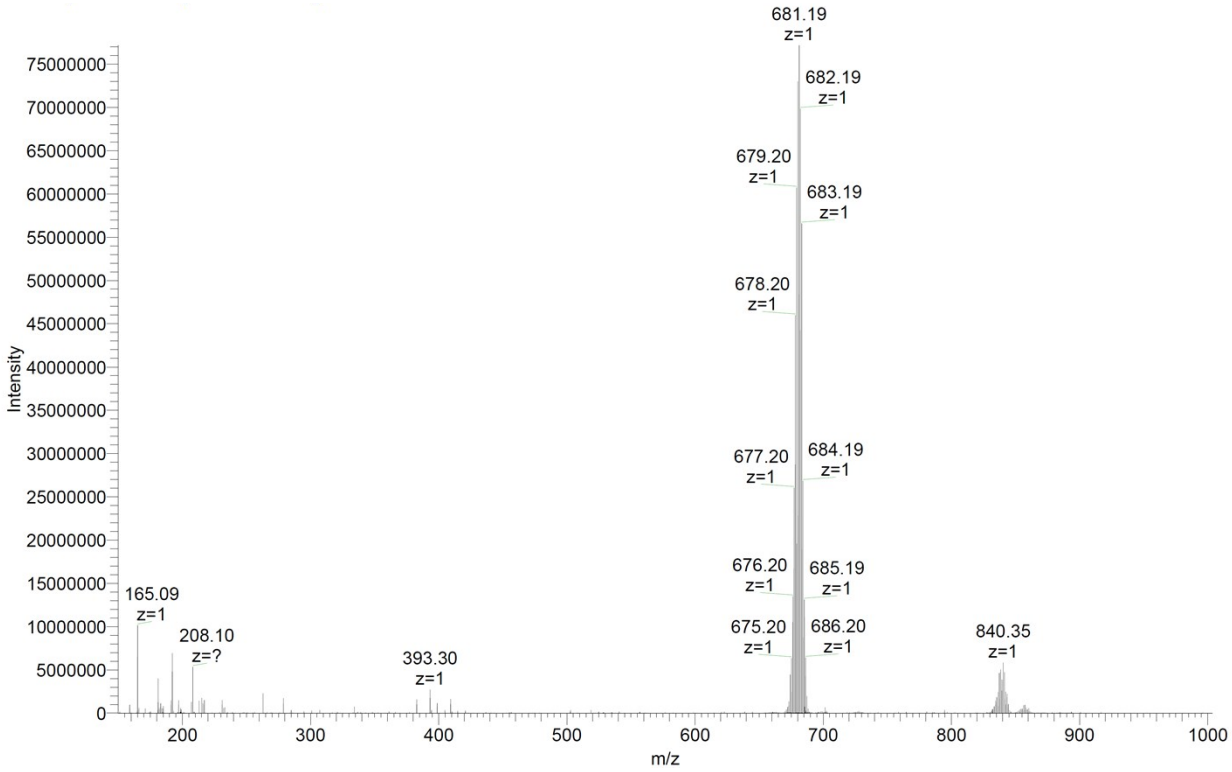


Fig. S3 – ESI-MS spectrum of **1** dissolved in an acetone-d_6/D_2O mixture (ratio 3:7) recorded at pH 7, 24 h after sample preparation. The ion peak centred at *m/z* 681.19 corresponds to the fully hydrolysed complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OH)_2(\mu\text{-}S\text{-}m\text{-}9\text{-}B_{10}C_2H_{11})]^+$.

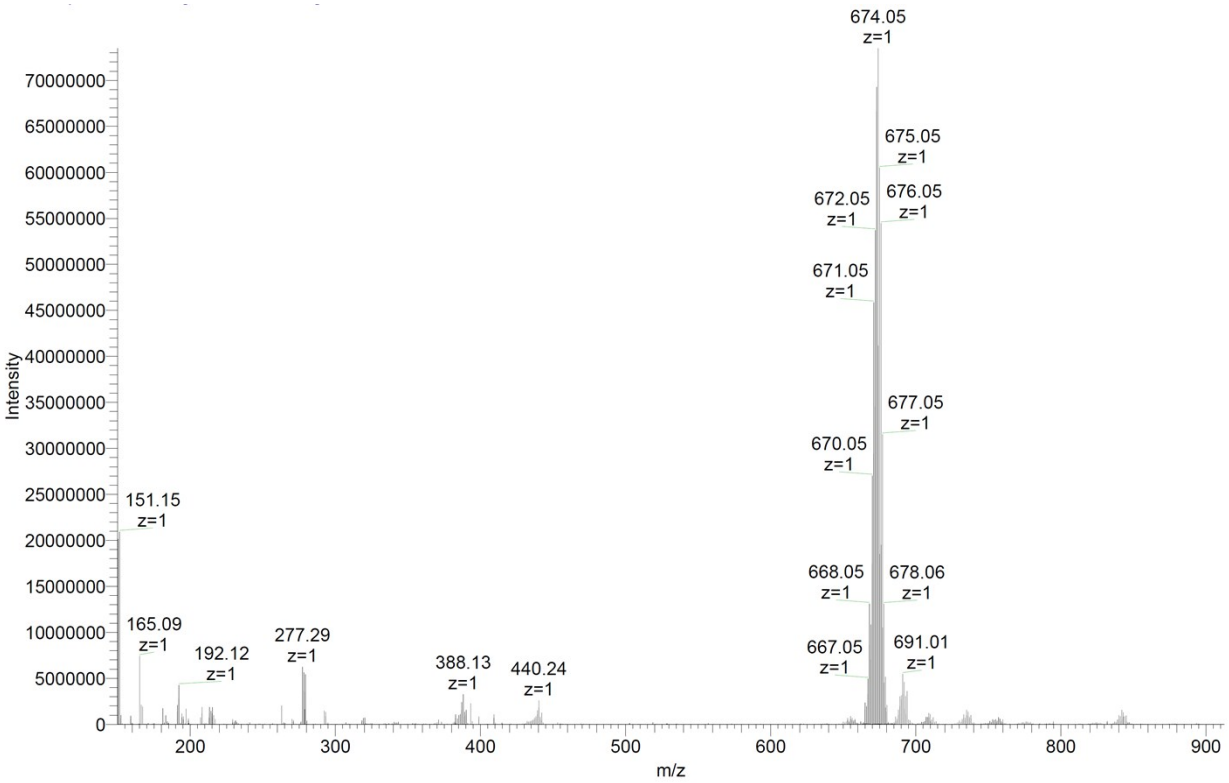


Fig. S4 – ESI-MS spectrum of **2** dissolved in an acetone-d_6/D_2O mixture (ratio 4:6) recorded at pH 7, 24 h after sample preparation. The ion peak centred at *m/z* 674.05 corresponds to the fully hydrolysed complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OH)_2(\mu\text{-}SCH_2\text{-}p\text{-}C_6H_4\text{-}NO_2)]^+$.

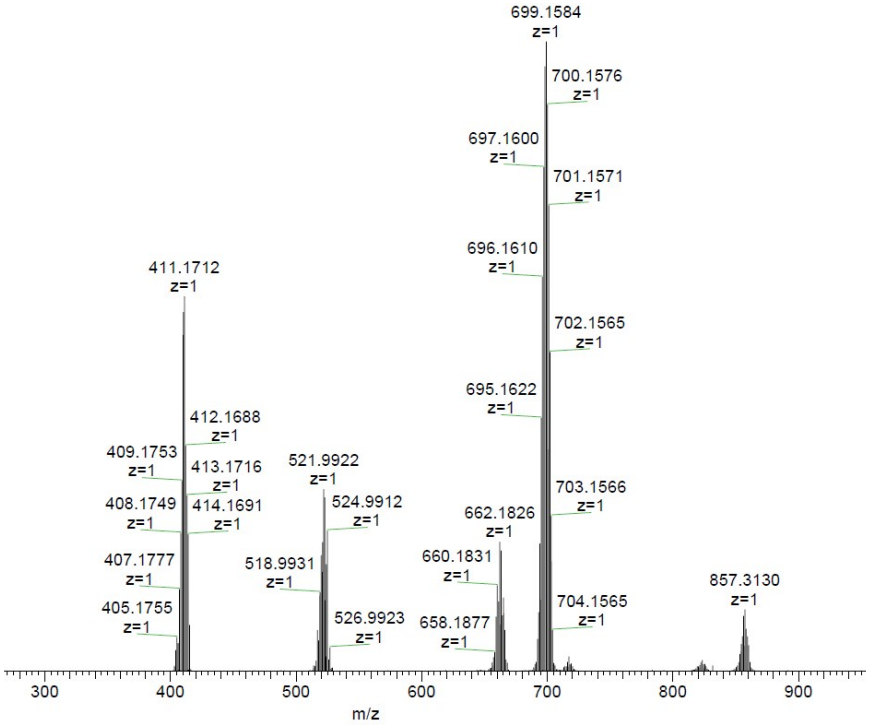


Fig. S5 – ESI-MS spectrum of **1** dissolved in an acetone-d_6/D_2O mixture (ratio 3:7) recorded at pH 4, 24 h after sample preparation.

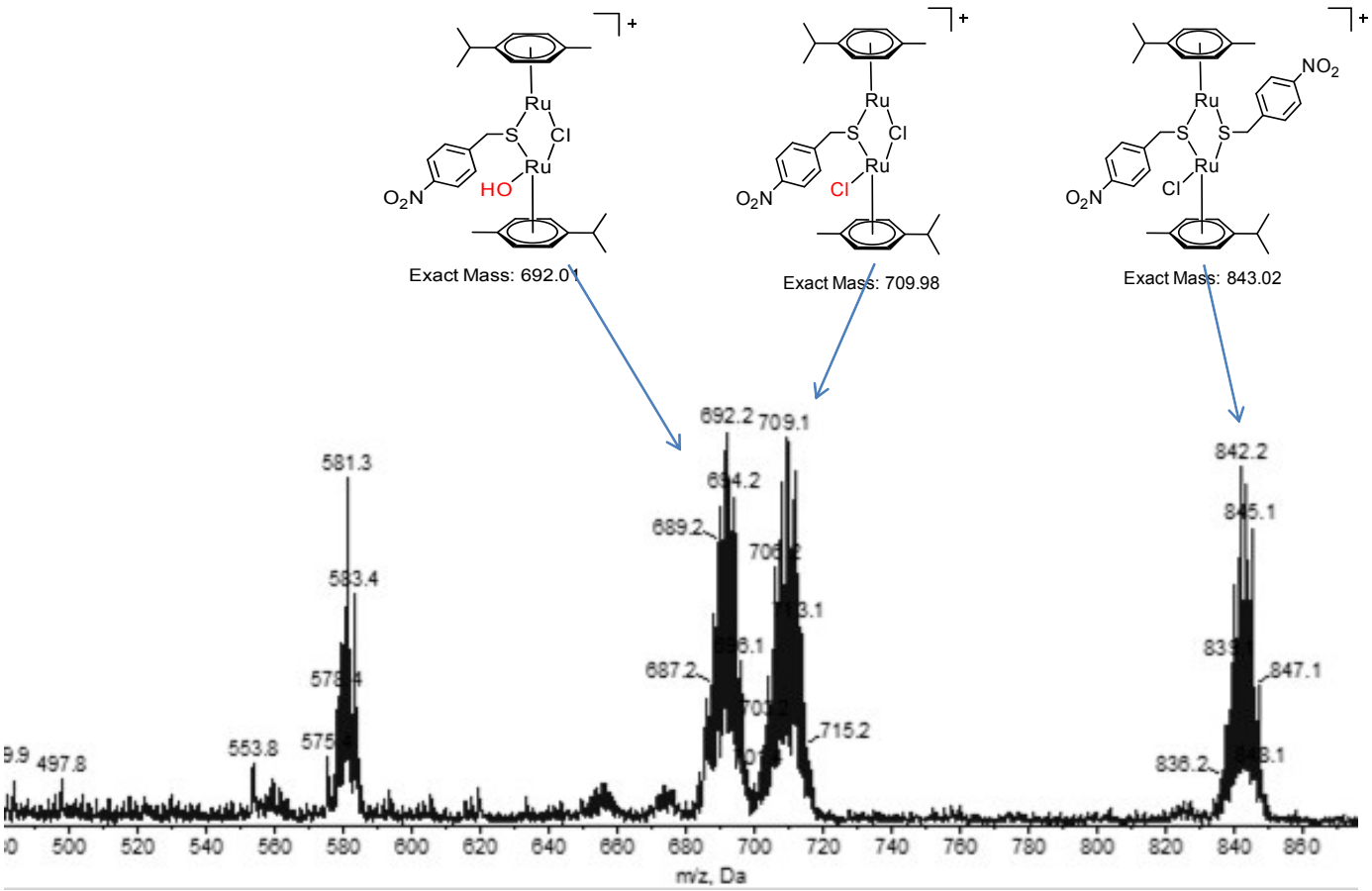


Fig. S6 – ESI-MS spectrum of **2** dissolved in an acetone-d_6/D_2O mixture (ratio 4:6) recorded at pH 4, 24 h after sample preparation. The structures of the suggested species are indicated on top of each peak.

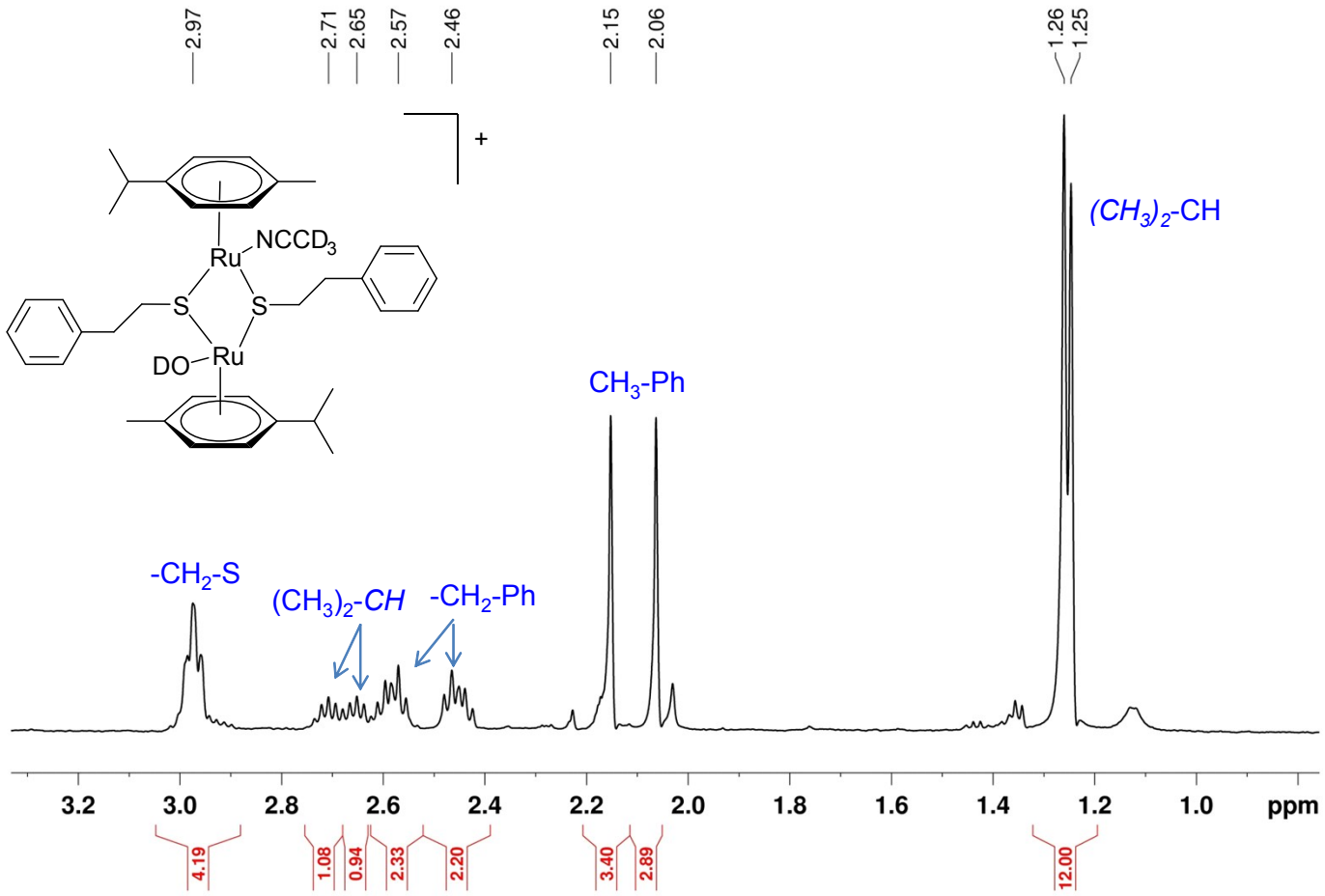


Fig. S7 – The *p*-cymene proton region of the ^{1}H NMR spectrum of $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(\mu\text{-}SC_2H_4Ph)_2Cl_2]$ (**3**) dissolved in D_2O/CD_3CN recorded 24 h after sample preparation, at 37 °C and at pD 7. The attribution of the different protons in the resulting hydroxo-acetonitrile cationic complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OD)(CD_3CN)(\mu\text{-}S\text{-}C_2H_4Ph)_2]^+$ is shown in the spectrum.

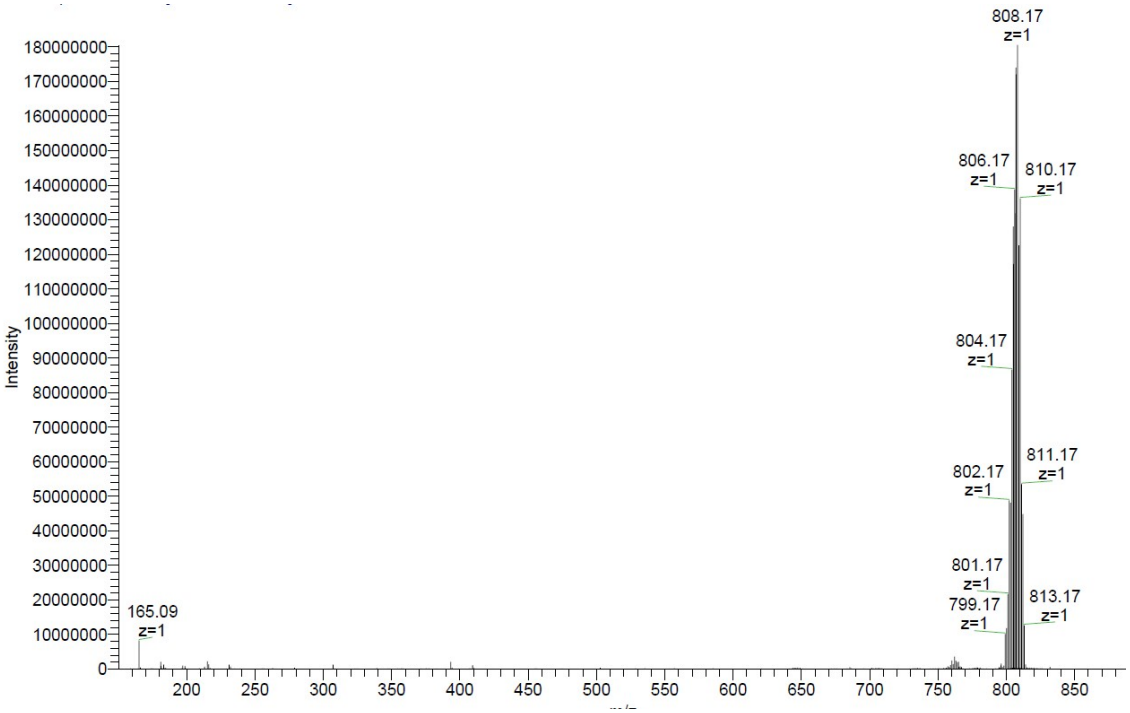


Fig. S8 - ESI-MS spectrum of **3** recorded 24 h after sample preparation at pH 7. The peak centred at *m/z* = 808.17 corresponds to the complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OH)(CH_3CN)(\mu\text{-}SCH_2CH_2\text{-}C_6H_5)_2]^+$.

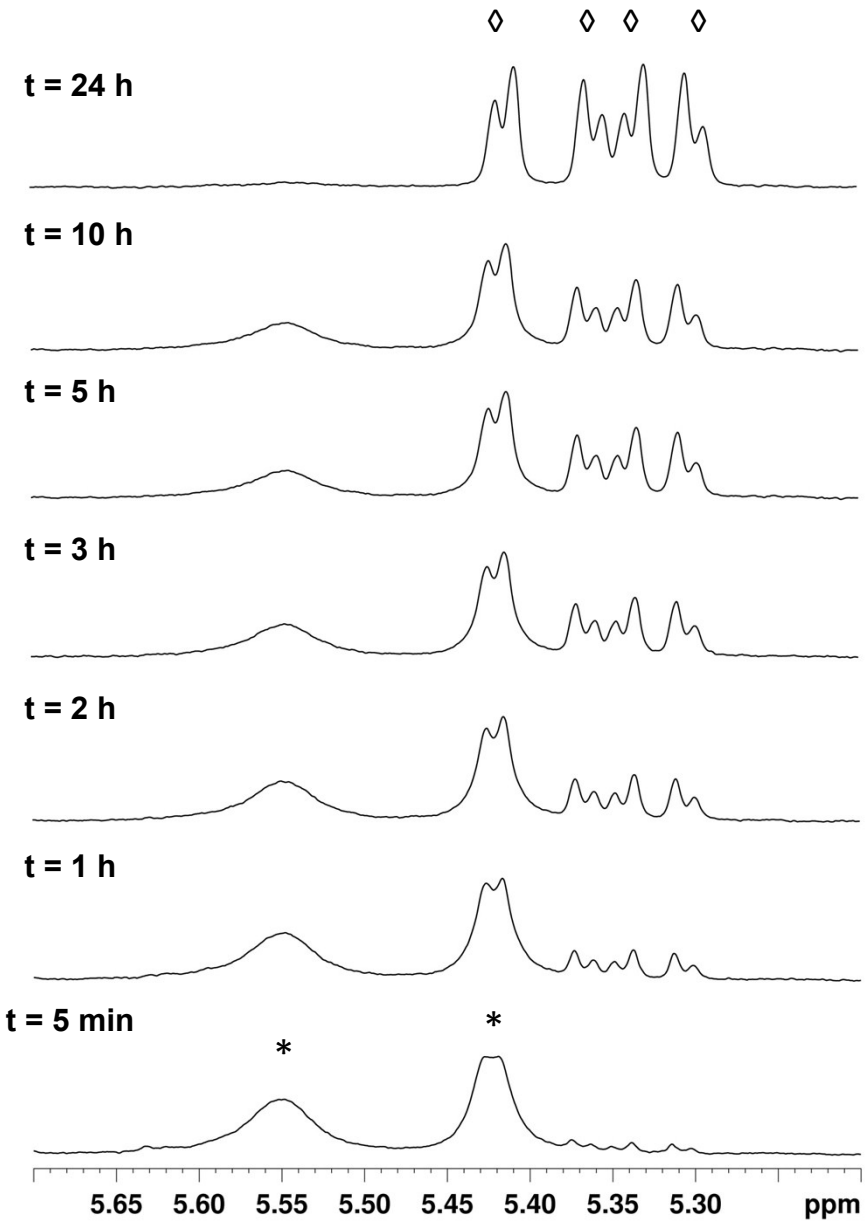


Fig. S9 - The *p*-cymene ring proton region of the ^{1}H NMR spectrum of **3** dissolved in a mixture D_2O/CD_3CN (ratio 7:3) at 37 °C at different times at pD 11. The labels correspond to *p*-cymene ligands in different species present in solution. The species labelled * corresponds to **3**, the species labelled ◊ is the hydroxo-acetonitrile complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OD)(CD_3CN)(\mu\text{-}SCH_2CH_2\text{-}C_6H_5)_2]^+$.

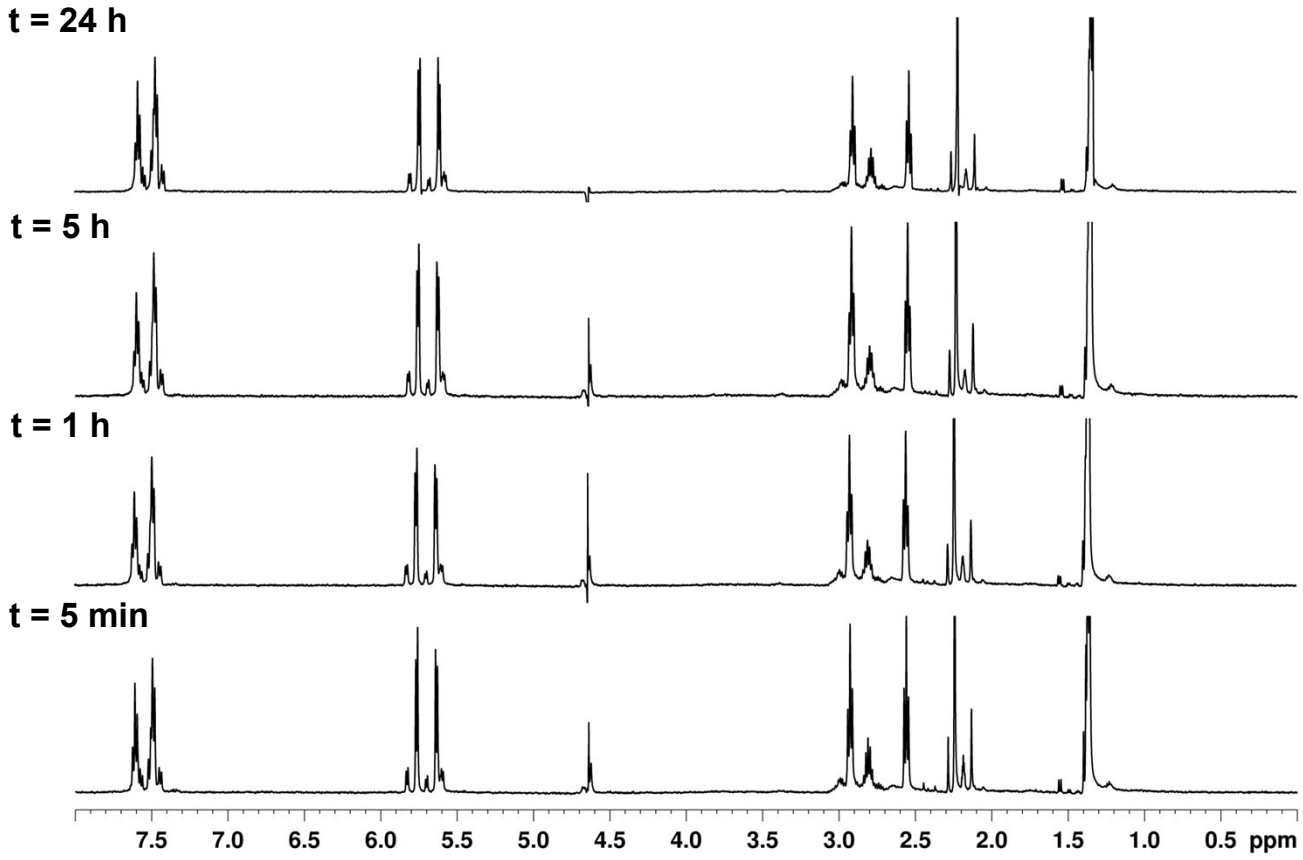


Fig. S10 - NMR time-courses for the reaction of thiolato complex **3** dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded at 37 °C and at pD 2.

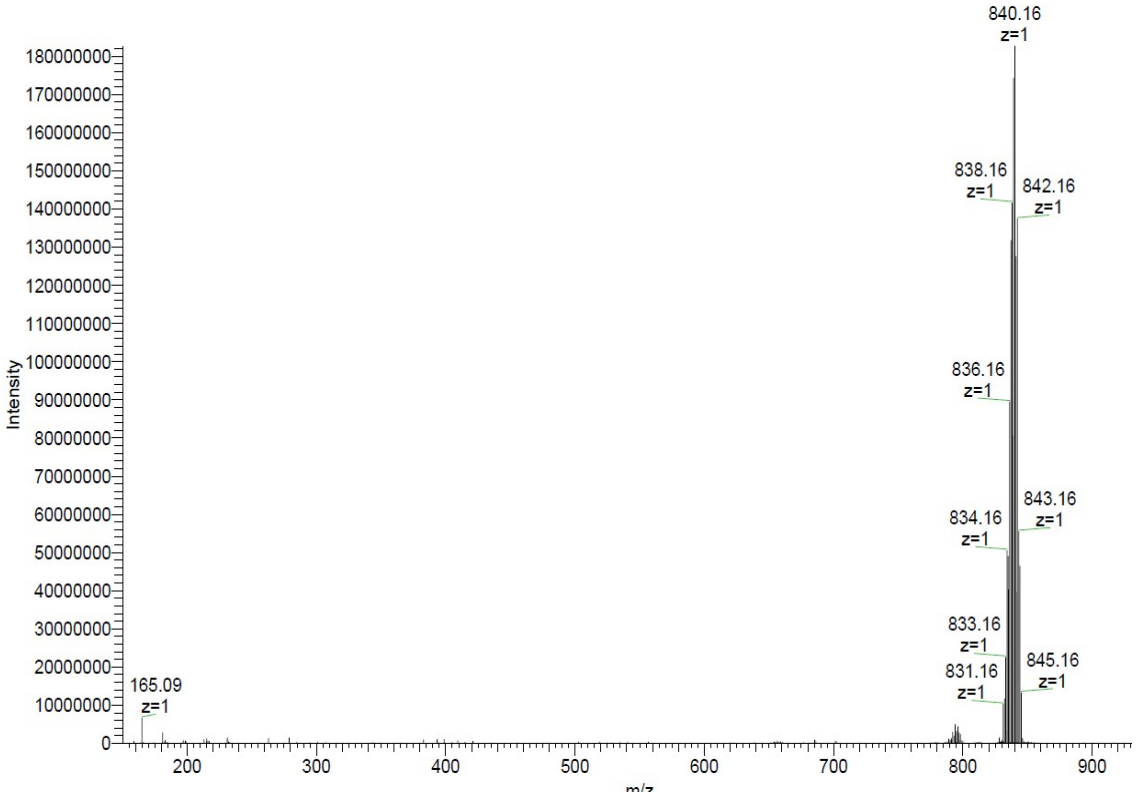


Fig. S11 - ESI-MS spectrum of **4** dissolved in H_2O/CH_3CN, recorded 24 h after sample preparation at pH 7. The group of peaks centred at *m/z* = 840.16 corresponds to the complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OH)(CH_3CN)(\mu\text{-}SCH_2\text{-}C_6H_4\text{-}p\text{-}OMe)_2]^+$.

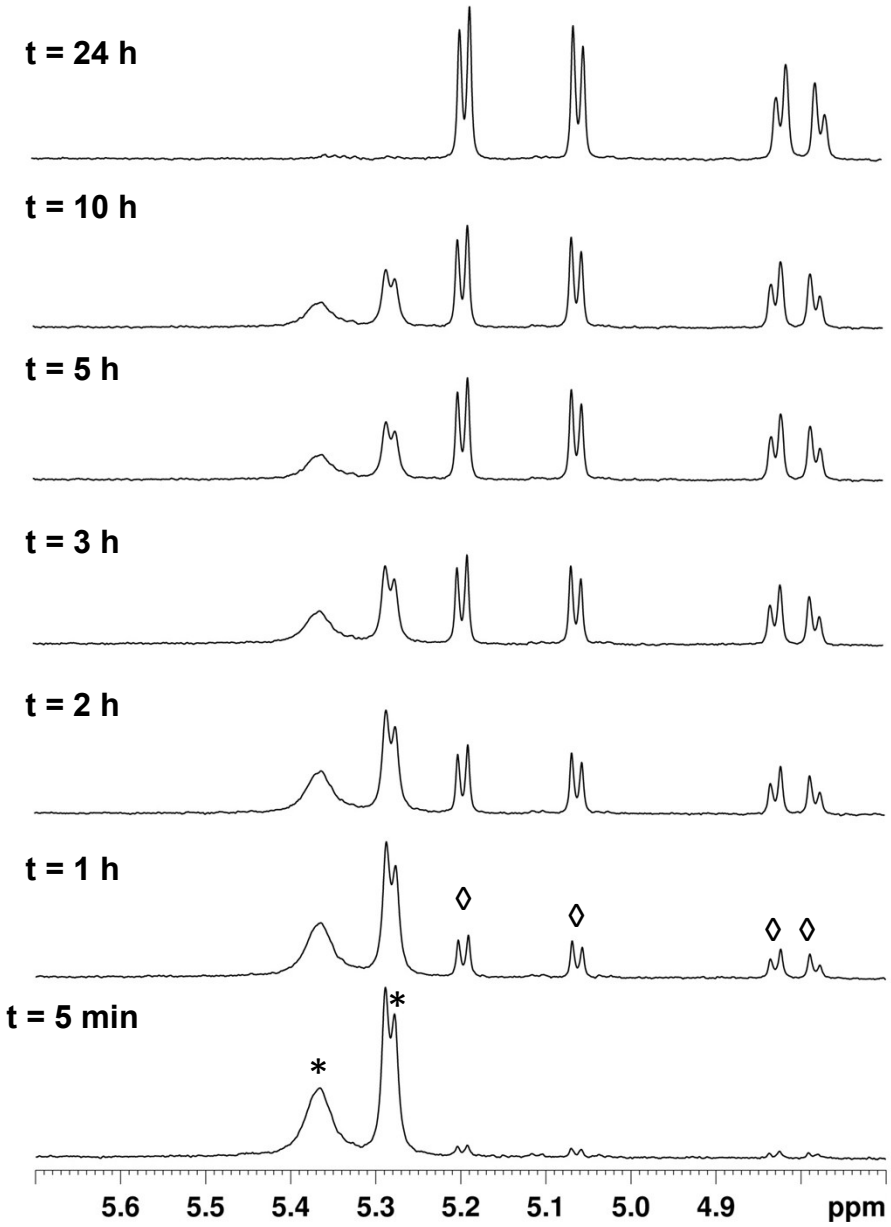


Fig. S12 - The *p*-cymene ring proton region of the ^{1}H NMR spectrum of **4** dissolved in a mixture D_2O/CD_3CN (ratio 7:3) at 37 °C at pD 11. The labels correspond to *p*-cymene ligands in different species present in solution. The species labelled * is the complex **4**, the species labelled ◊ is the hydroxo-acetonitrile complex complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(OD)(CD_3CN)(\mu\text{-}SCH_2\text{-}C_6H_4\text{-}p\text{-}OMe)_2]^+$.

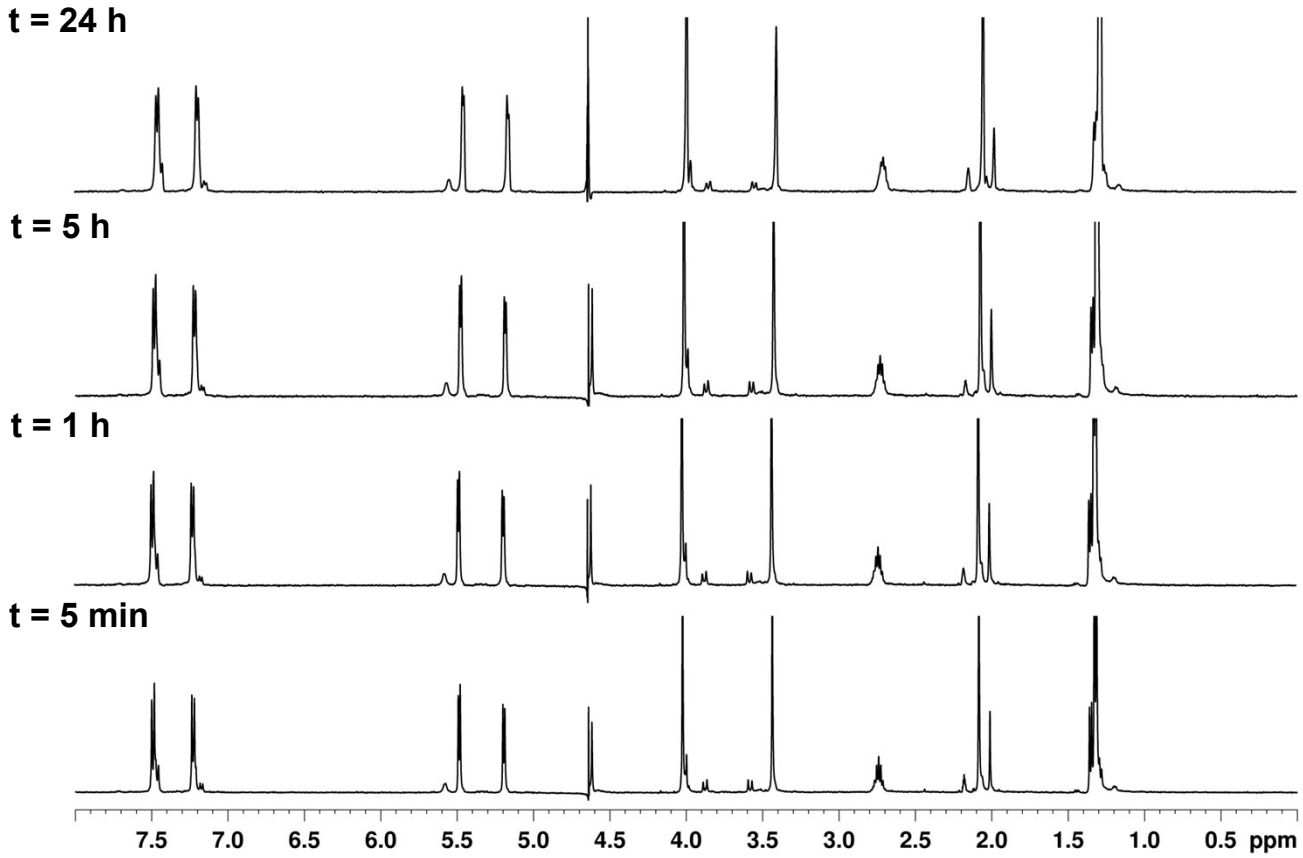


Fig. S13 - NMR time-courses for the reaction of thiolato complex **4** dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded at 37 °C and at pD 2.

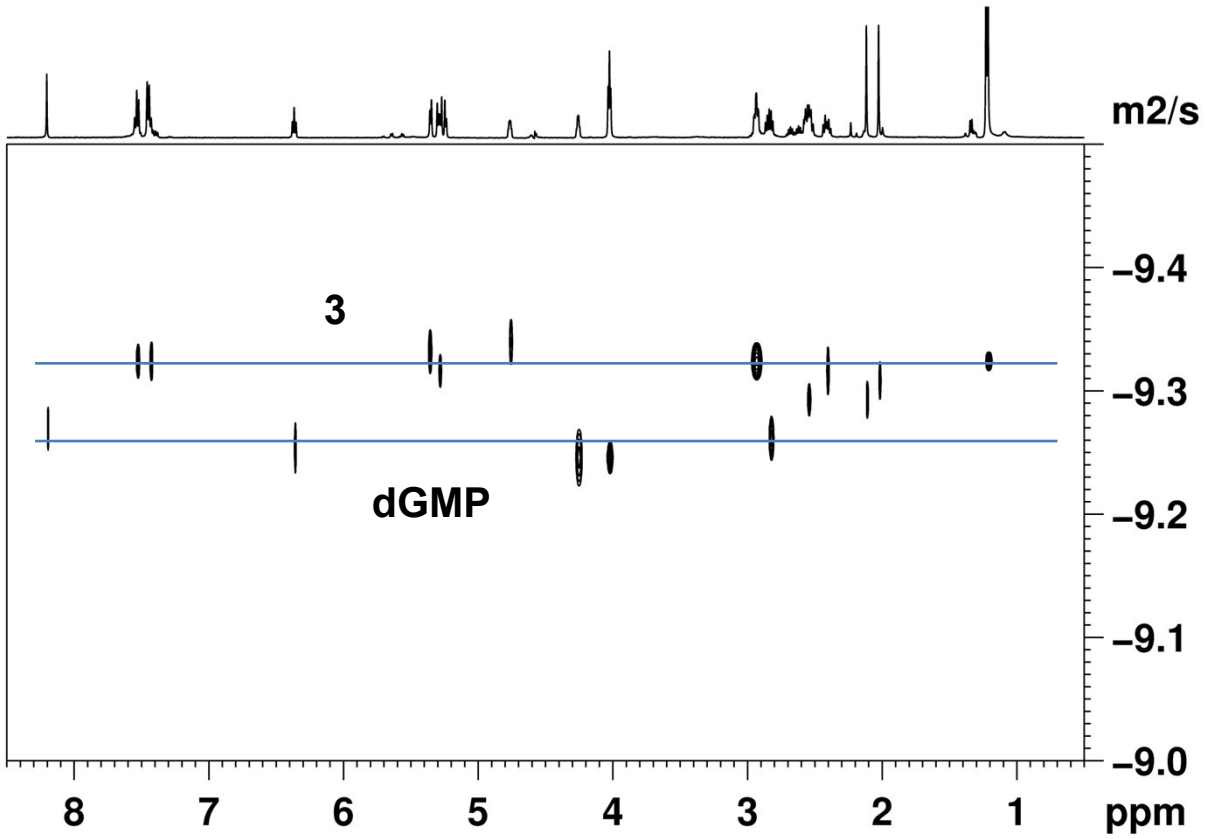
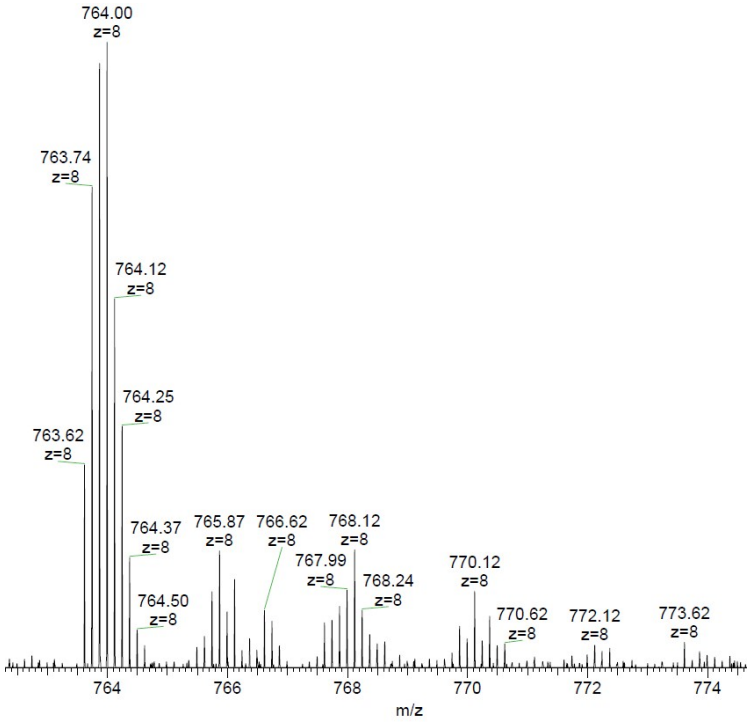


Fig. S14 - 2D-^{1}H DOSY spectrum of the mixture **3**:dGMP (ratio 1:3) dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded hydroxo-acetonitrile complex at 37 °C.

Negative mode



Positive mode

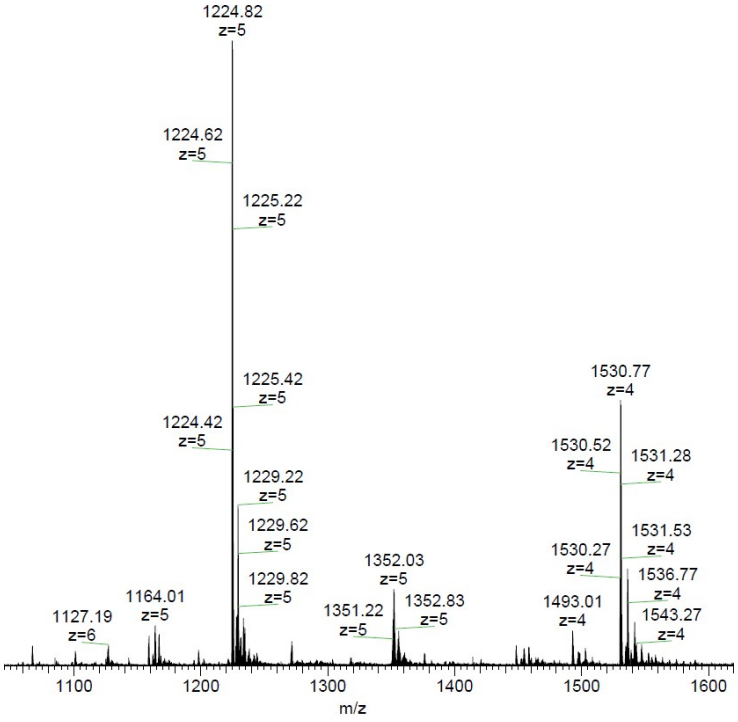


Fig. S15 - ESI-MS spectra of the mixture **2**: DNA 20-mer recorded in the negative and positive modes recorded 24 h after sample preparation.

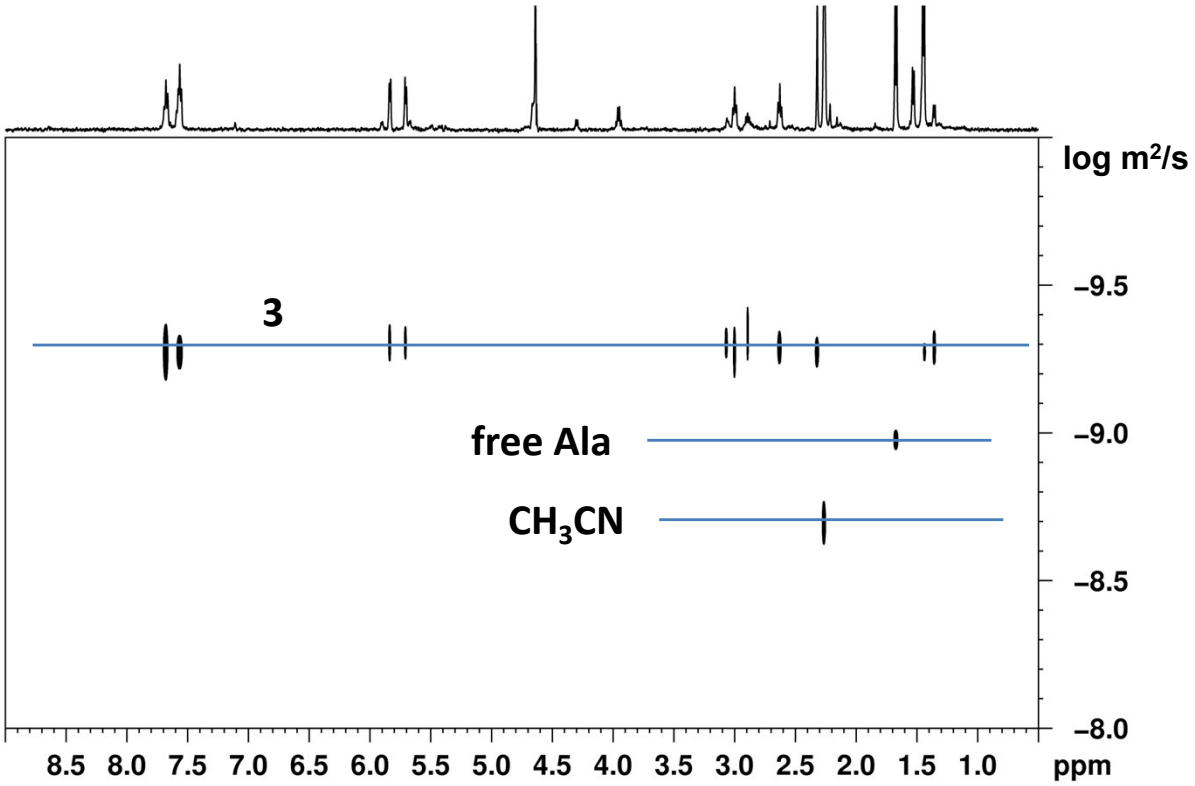


Fig. S16 - 2D-^{1}H DOSY spectrum of the mixture **3**:Ala (ratio 1:3) dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded 24 h after sample preparation at 37 °C.

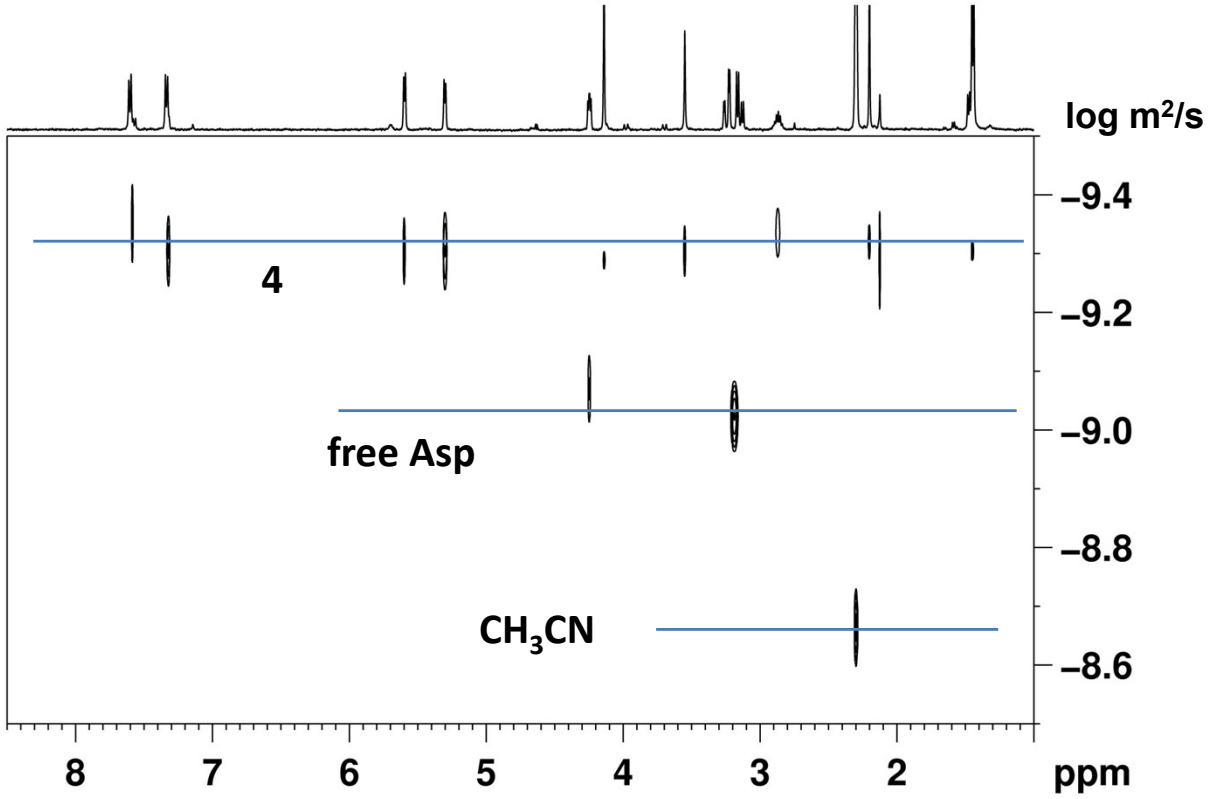


Fig. S17 - 2D-^{1}H DOSY spectrum of the mixture **4**:Asp (ratio 1:3) dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded 24 h after sample preparation at 37 °C.

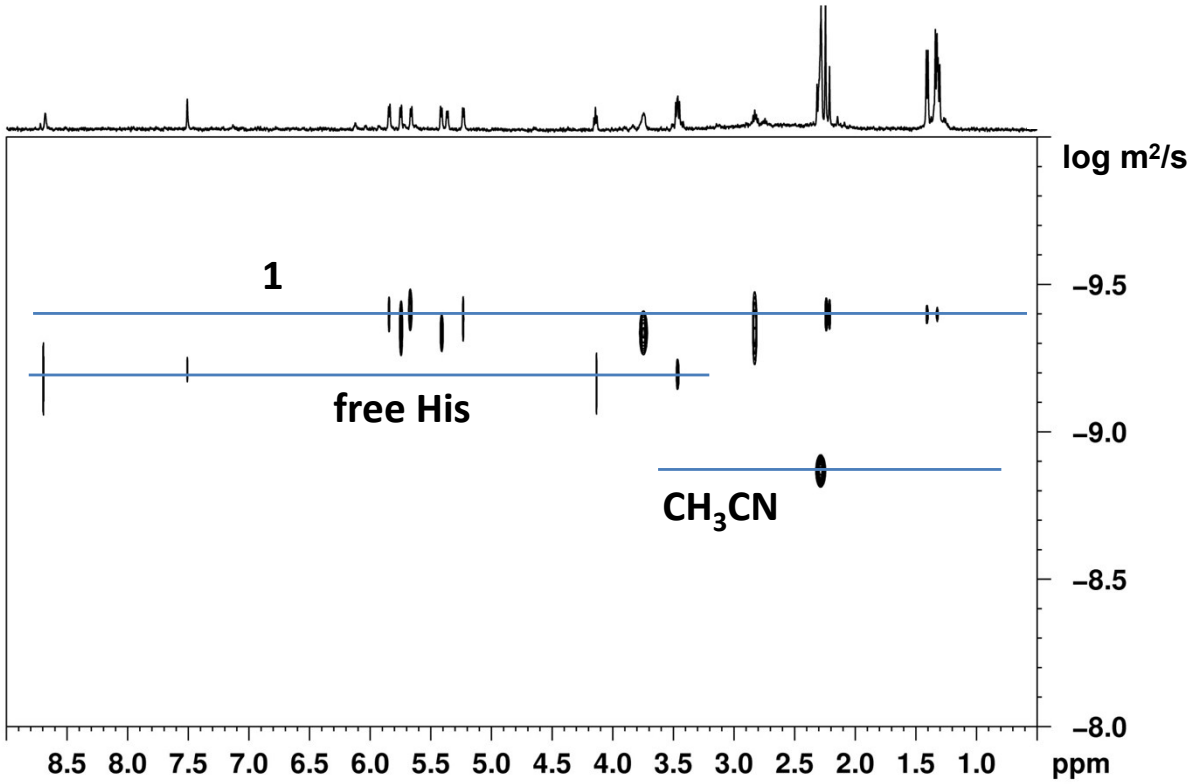


Fig. S18 - 2D-^{1}H DOSY spectrum of the mixture **1**:His (ratio 1:3) dissolved in a mixture D_2O/acetone-d_6 (ratio 6:4) recorded 24 h after sample preparation at 37 °C.

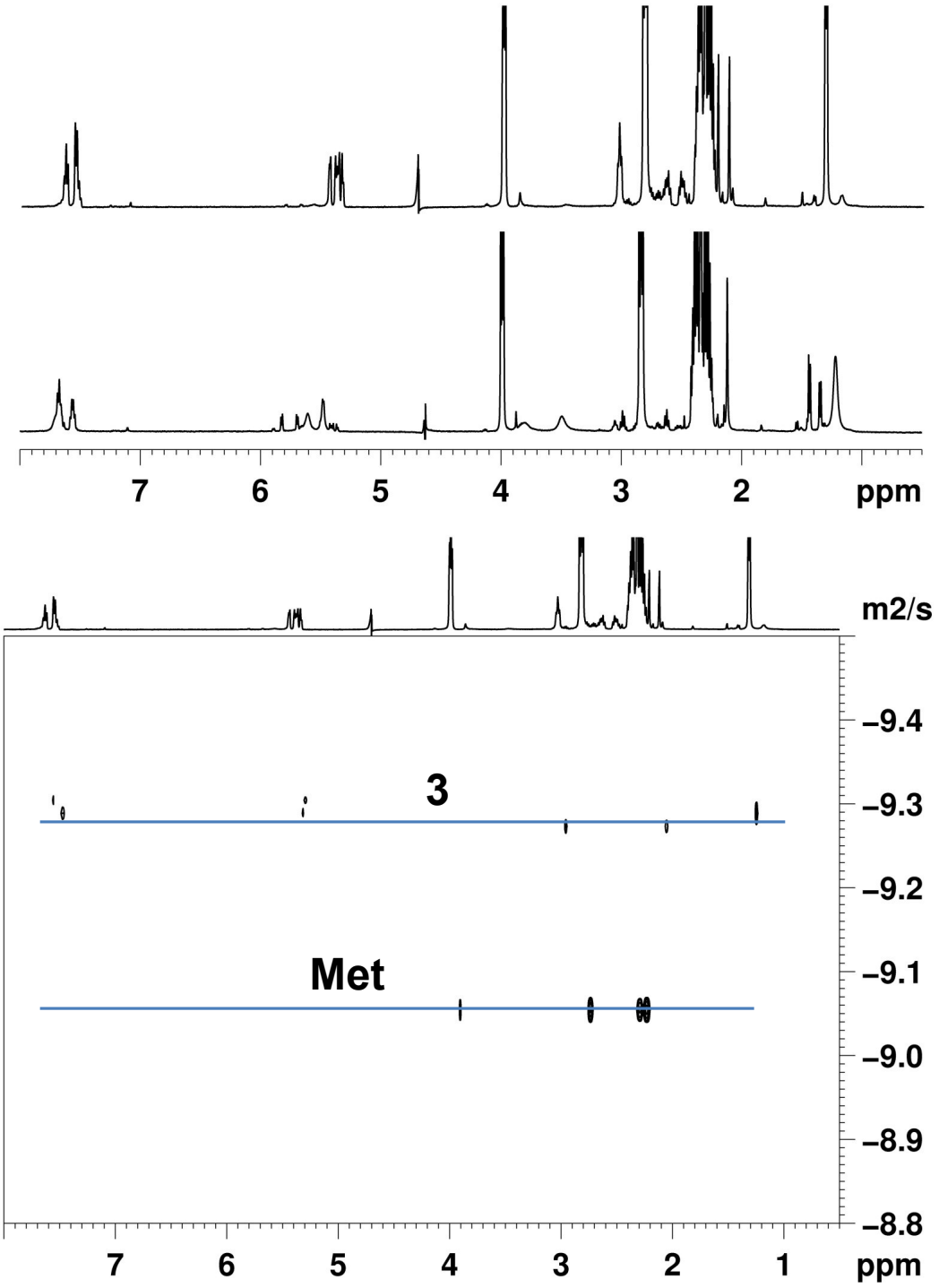


Fig. S19 - Top: 1D ^{1}H NMR spectrum of the mixture **3**:Met (ratio 1:4) dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded 24 h after sample preparation. Middle: 1D ^{1}H NMR spectrum recorded 10 min after sample preparation. Bottom: 2D-^{1}H DOSY spectrum recorded 48 h after sample preparation at 37 °C.

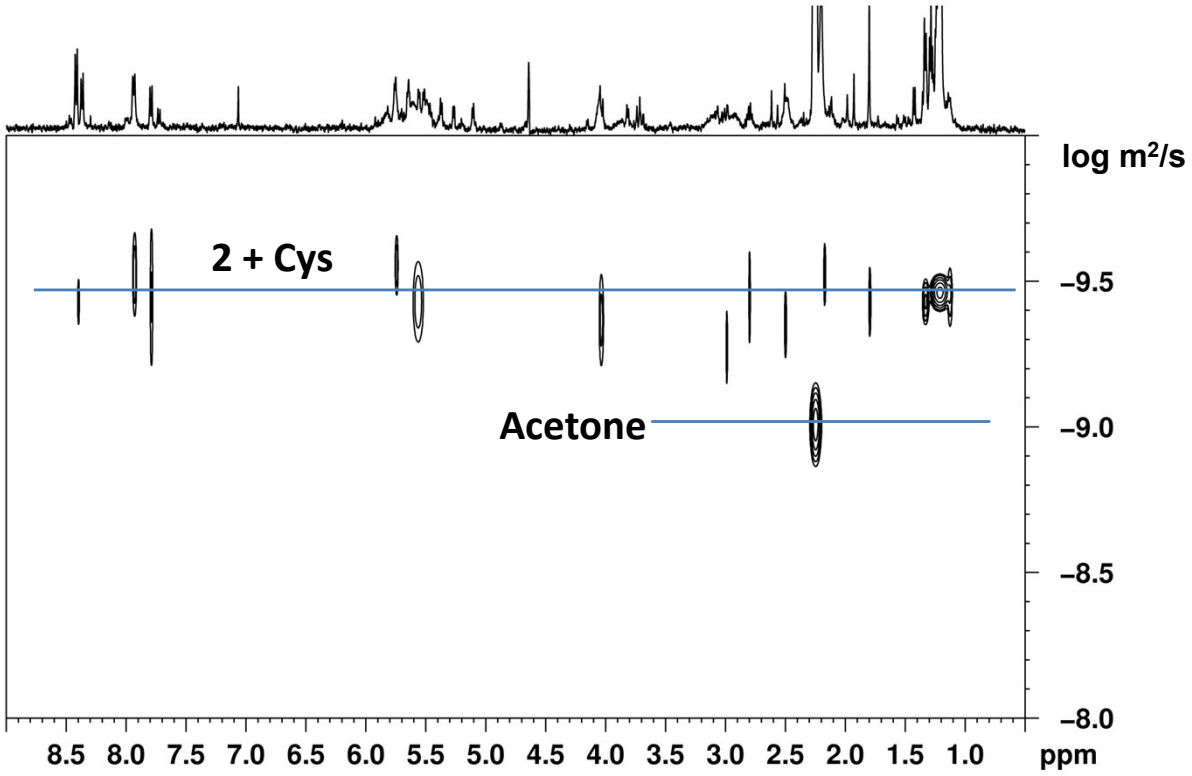


Fig. S20 - 2D-^{1}H DOSY spectrum of the mixture **1**:Cys (ratio 1:4) dissolved in a mixture D_2O/acetone-d_6 (ratio 6:4) recorded 24 h after sample preparation at 37 °C.

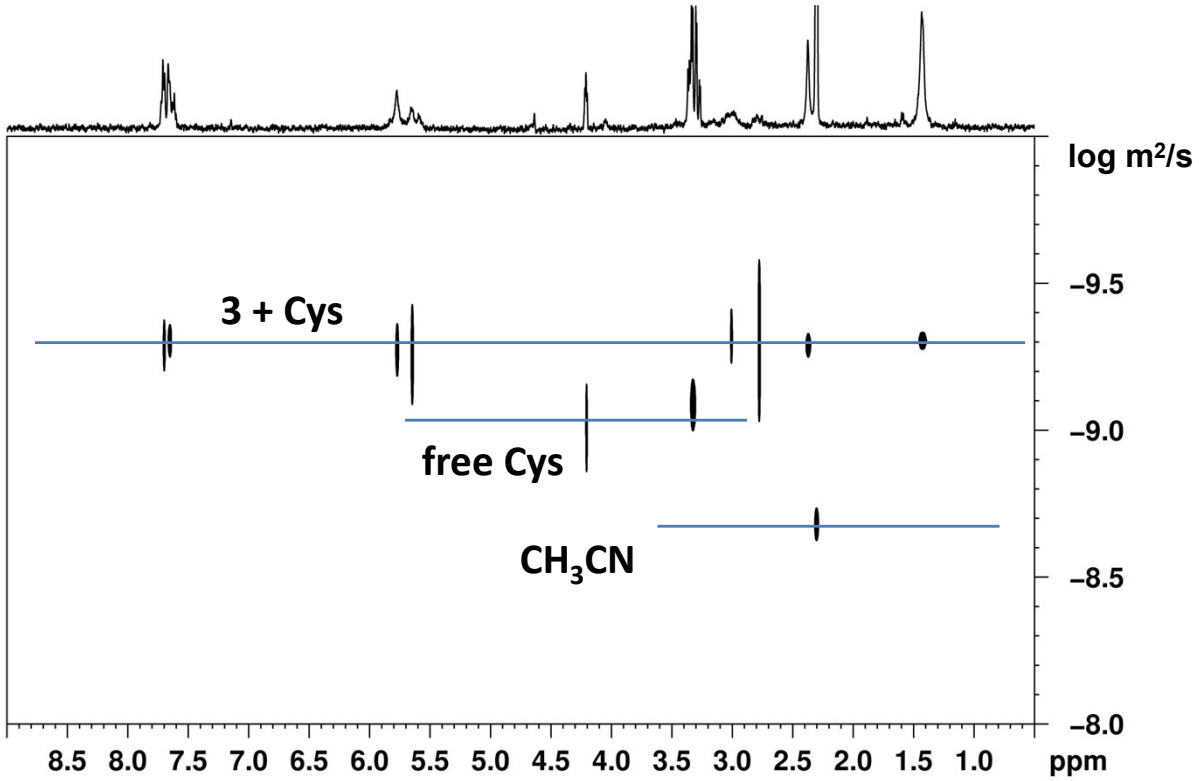


Fig. S21 - 2D-^{1}H DOSY spectrum of the mixture **3**:Cys (ratio 1:3) dissolved in a mixture D_2O/CD_3CN (ratio 7:3) recorded 24 h after sample preparation at 37 °C.

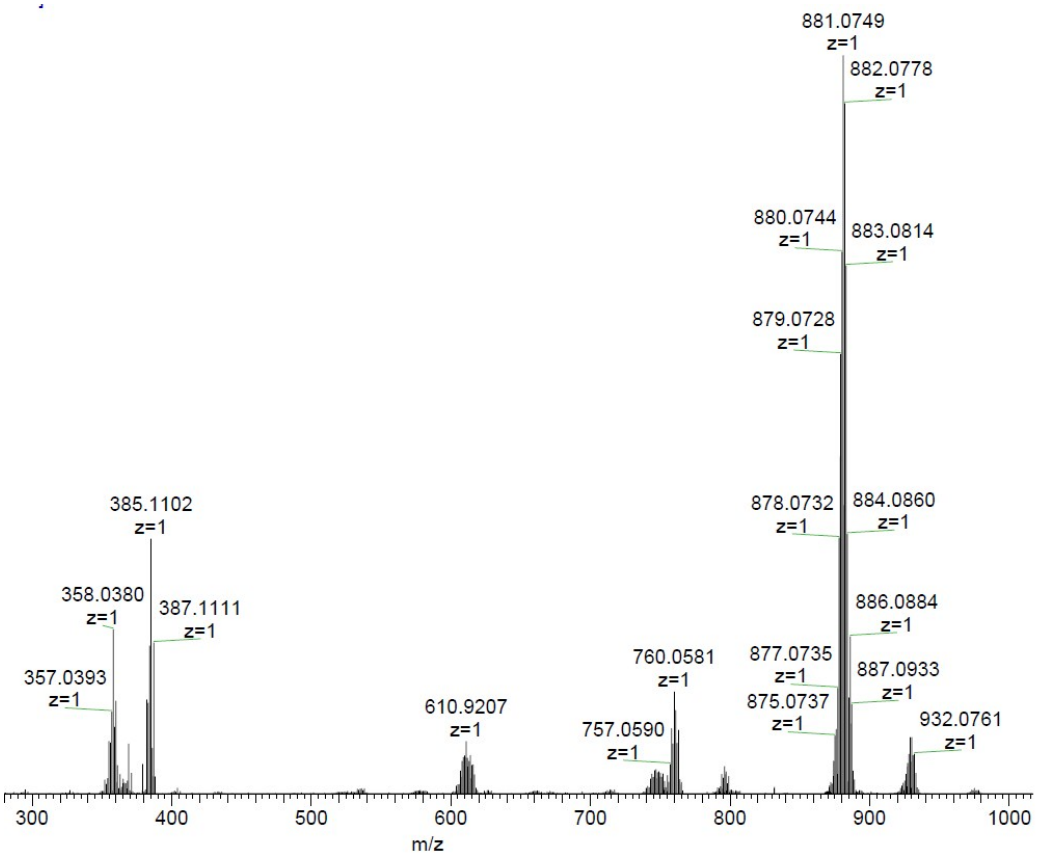


Fig. S22 - ESI-MS spectrum of the mixture **2:**Cys recorded in the negative mode recorded 24 h after sample preparation. The peak centred at *m/z* = 881.07 corresponds to the complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(\mu\text{-}SCH_2CH(NH_2)COOH)_2(\mu\text{-}SCH_2\text{-}p\text{-}C_6H_4\text{-}NO_2)]^+$.

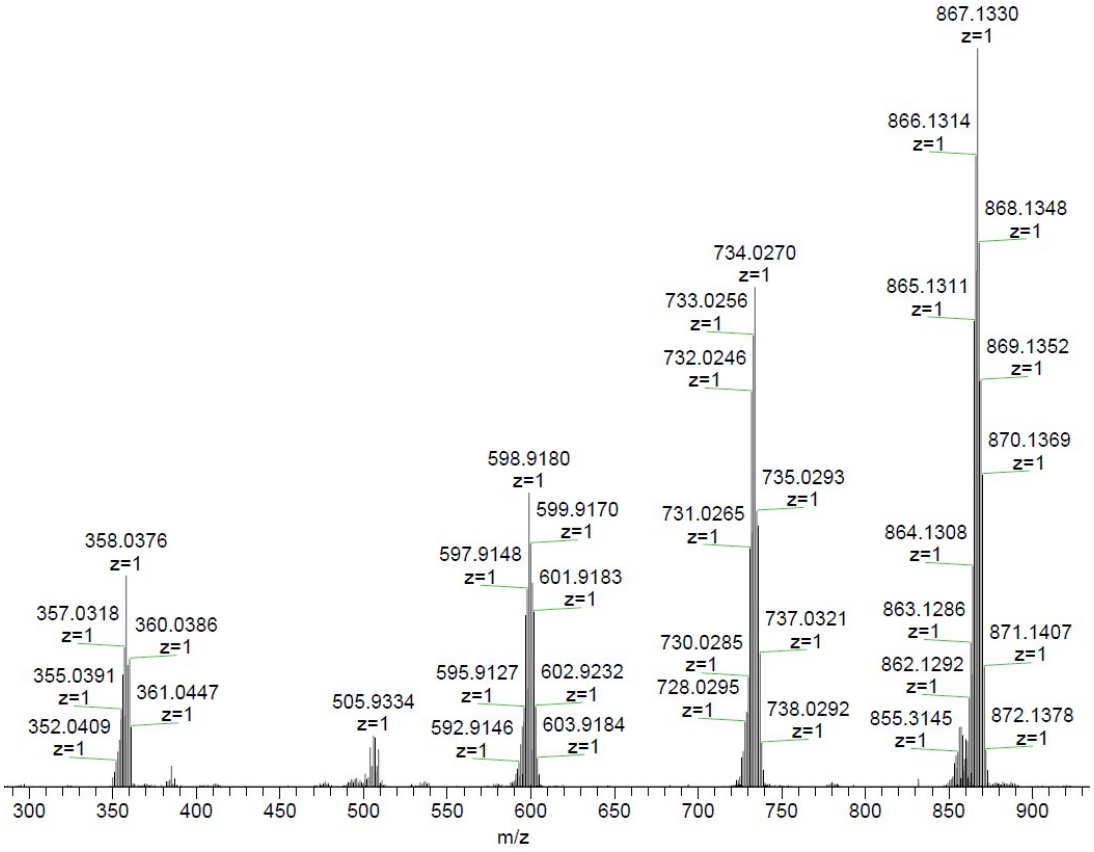


Fig. S23 - ESI-MS spectra of the mixture of **3:**Cys recorded in the negative mode recorded 24 h after sample preparation. The peak centred at *m/z* = 867.13 corresponds to the complex $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(\mu\text{-}SCH_2CH(NH_2)COOH)(\mu\text{-}SCH_2CH_2\text{-}C_6H_5)_2]^+$.

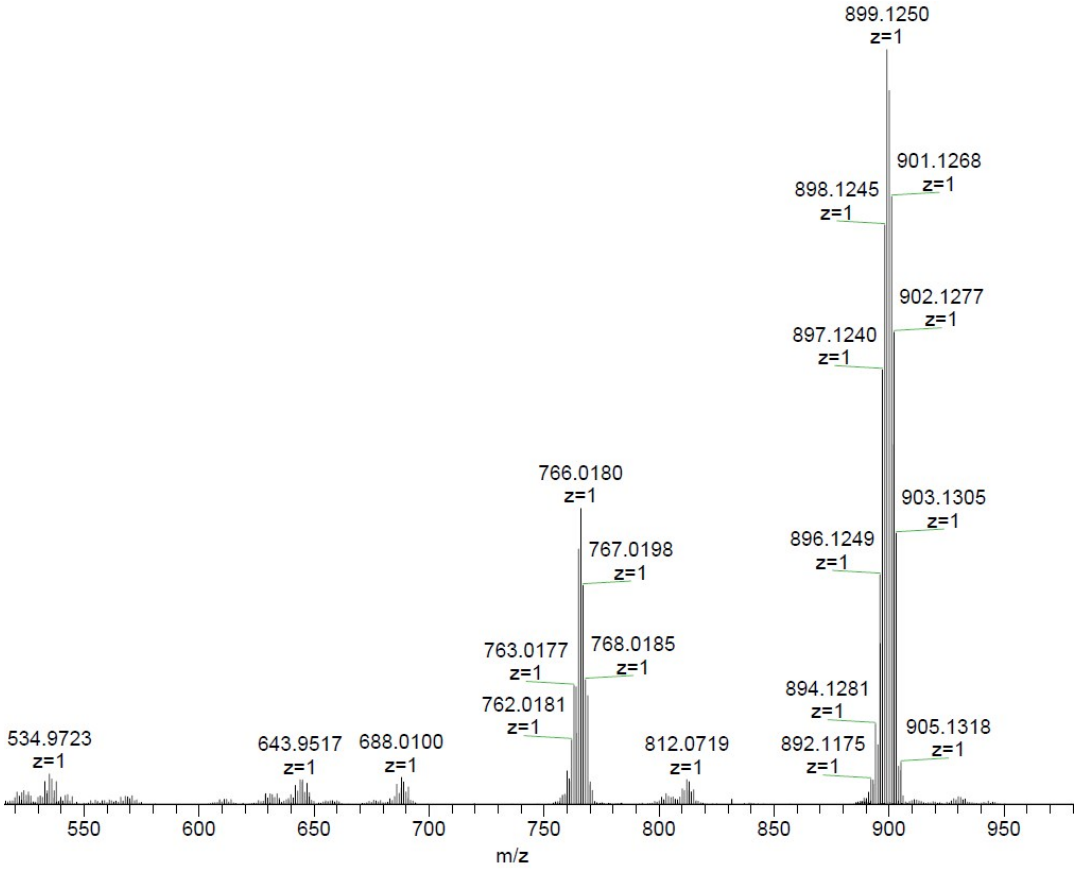


Fig. S24 - ESI-MS spectra of the mixture of **4:**Cys recorded in the negative mode recorded 24 h after sample preparation. The peak centred at *m/z* = 899.13 corresponds to the complex $[(\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu\text{-SCH}_2\text{CH(NH}_2\text{)COOH})(\mu\text{-SCH}_2\text{-C}_6\text{H}_4\text{-p-OMe})_2]^+$.