Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

3-Hydroxyflavones vs. 3-Hydroxyquinolinones: Structure-Activity Relationships and Stability Studies on Ru^{II}(arene) Anticancer Complexes with Biologically Active Ligands

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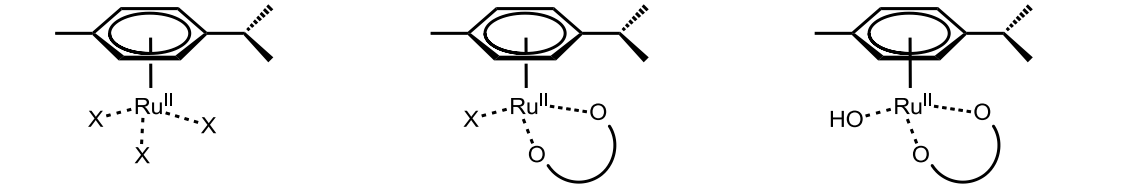
1.1. Solution equilibria: General formulae and definitions of formation equilibria



M = $[Ru^{II}(cym)X_3]^{n+}$
n = -1 - +2; X = Cl^-, H_2O or DMSO

ML = $[Ru^{II}(cym)(L)X]^{n+}$
n = 0 - +1; X = Cl^-, H_2O or DMSO

MLH_{-1} = $[Ru^{II}(cym)(L)OH]$

Figure S1. General formulae of the ruthenium(II)-η^6-*p*-cymene complexes

Definition of the stability constants of the metal complexes and equilibria

General formula:

M = $[Ru^{II}(cym)X_3]^{n+}$; **L** = deprotonated form of the ligand (L^-); **H** = H^+ (charges were omitted for simplicity).

$\beta(M_pL_qH_r) = [M_pL_qH_r]/[M]^p[L]^q[H]^r$ $\qquad pM + qL + rH \rightleftharpoons M_pL_qH_r$

Constant:	Equilibrium:
β(**ML** or **$[Ru^{II}(cym)(L)X]$**) = [ML]/[M][L]	$M + L \rightleftharpoons ML$
β(**MLH_{-1}** or **$[Ru^{II}(cym)(L)OH]$**) = $[MLH_{-1}]/[M][L][H]^{-1}$	$M + L - H \rightleftharpoons MLH_{-1}$
β(**M_2H_{-2}** or **$[(Ru^{II}(cym))_2(OH)_2]$**) = $[M_2H_{-2}]/[M]^2[H]^{-2}$	$2\,M - 2\,H \rightleftharpoons M_2H_{-2}$
β(**M_2H_{-3}** or **$[(Ru^{II}(cym))_2(OH)_3]$**) = $[M_2H_{-3}]/[M]^2[H]^{-3}$	$2\,M - 3\,H \rightleftharpoons M_2H_{-3}$

(*H_{-x} = deprotonation of a coordinated water molecule)*

1.2. Fluorescence spectra of ligand b and complex 2 in aqueous solution

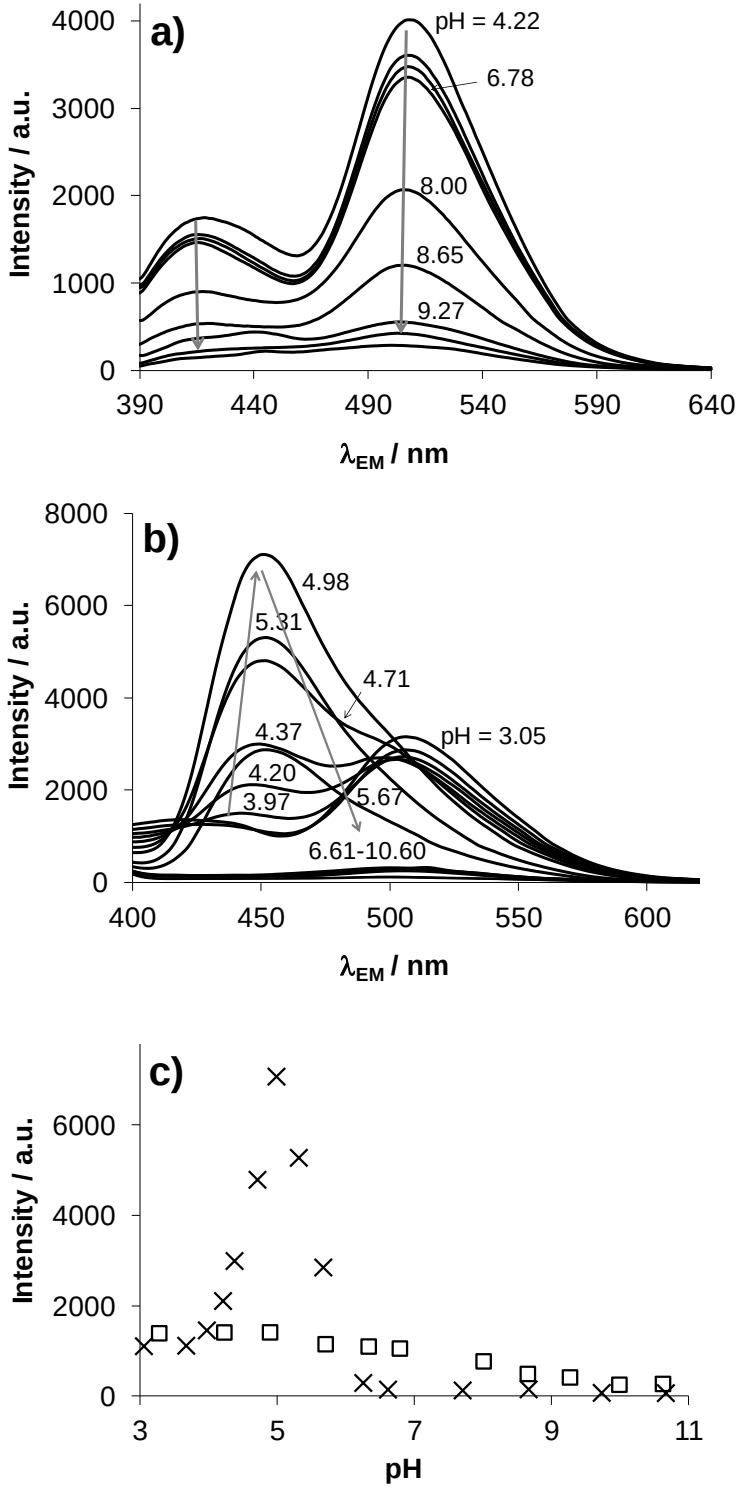


Figure S2. (a) pH-Dependent fluorescence emission spectra of ligand **b** (c = 1.5 × 10^{-5} M) and (b) of complex **2** (c = 1.5×10^{-5} M). (c) pH-dependent intensity changes at 448 nm of the ligand (□) and the complex (×){T = 25 °C; I = 0.20 M (KCl); λ_{EX} = 342 nm; PTM = 700 V; Slits: 10/10 nm, in H_2O}.

1.3. Measured and calculated UV-vis absorbance spectra and concentration distribution curves of the Ru^{II}(cym)/ligand b system

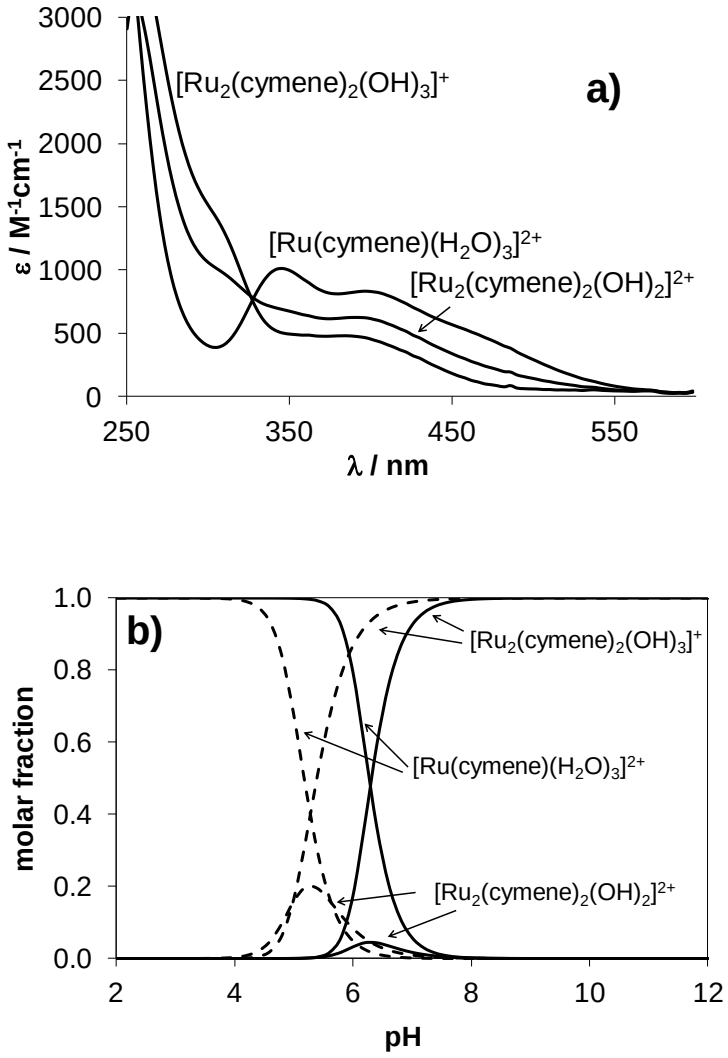


Figure S3. (a) Calculated individual UV-vis absorbance spectra of the species of $[Ru^{II}(cym)X_3]^{n+}$ divided by the number of Ru^{II} in each species in the DMSO/H_2O mixture; (b) Concentration distribution curves of the $[Ru^{II}(cym)X_3]^{n+}$ system at a wide range of pH values in the DMSO/H_2O mixture at c_{Ru} = 1.8 × 10^{-4} M and for comparison speciation in pure aqueous solution (dashed lines) {T = 25 °C; I = 0.20 M (KCl); 20% (w/w) DMSO/H_2O}.

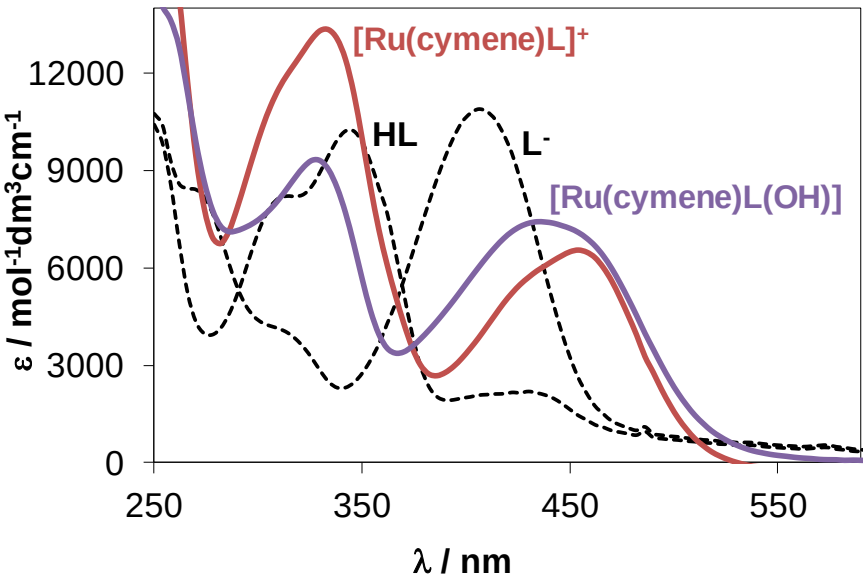


Figure S4. Calculated individual UV-vis absorbance spectra of the species formed in the Ru^{II}(cym)-ligand **b** system {T = 25 °C; I = 0.20 M (KCl); 20% (w/w) DMSO/H_2O}.

1.4. NMR studies on the stability of 12 in aqueous solution

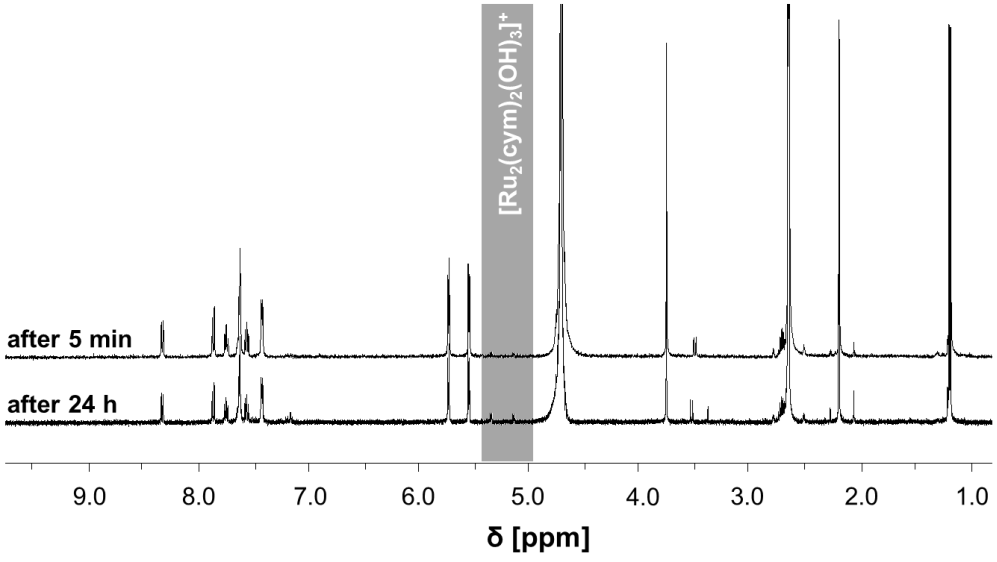


Figure S5. ^{1}H NMR spectra of **12** in 10% d_6-DMSO/D_2O after 5 min and 24 h.

1.5. ^{1}H NMR spectroscopy studies on the interaction of 12' with 5'-GMP

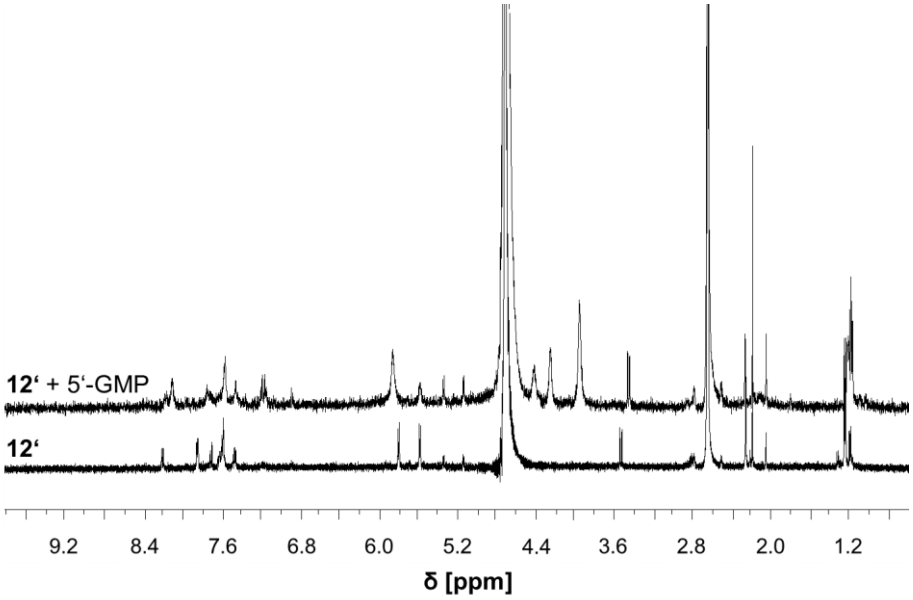


Figure S6. ^{1}H NMR spectra of **12'** and **12'** incubated with an excess of 5'-GMP in 10% d_6-DMSO/D_2O. The reaction of **12'** with 5'-GMP is indicated by the upfield shift of the *N*7 atom of 5'-GMP from approximately δ = 8.1 (free 5'-GMP) to 7.6 ppm (bound 5'-GMP) after addition of 5'-GMP in excess.

1.6. Reactions of 1', 12' and 13' with amino acids

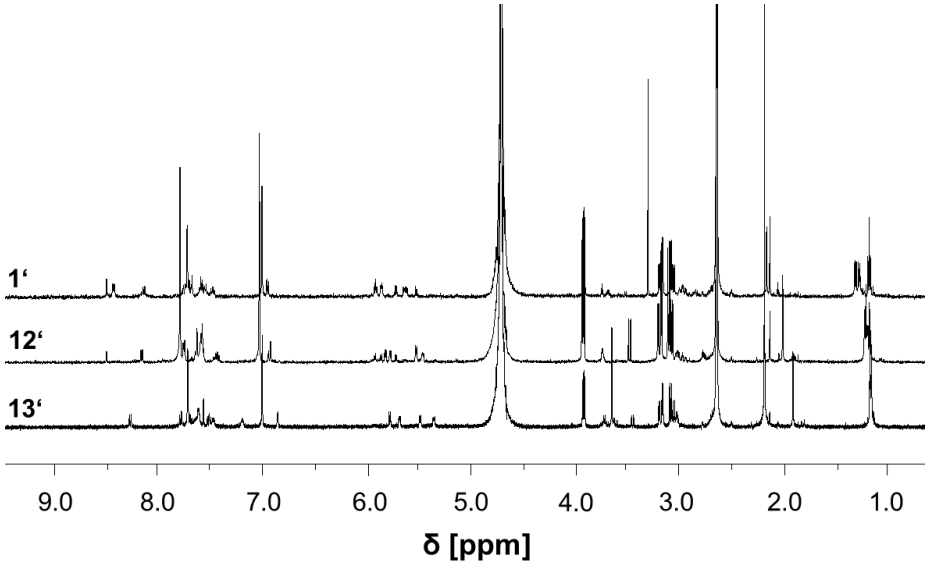


Figure S7. ^{1}H NMR spectra of the reactions of **1', 12'**and **13'** with an equimolar amount of L-histidine after 5 min.

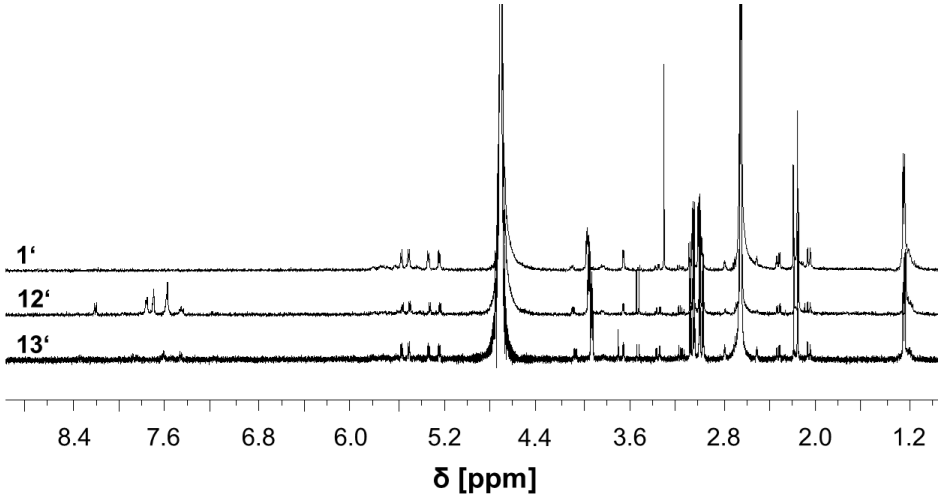


Figure S8. ^{1}H NMR spectra of the reactions of **1', 12'**and **13'** with an equimolar amount of L-cysteine after 5 min.

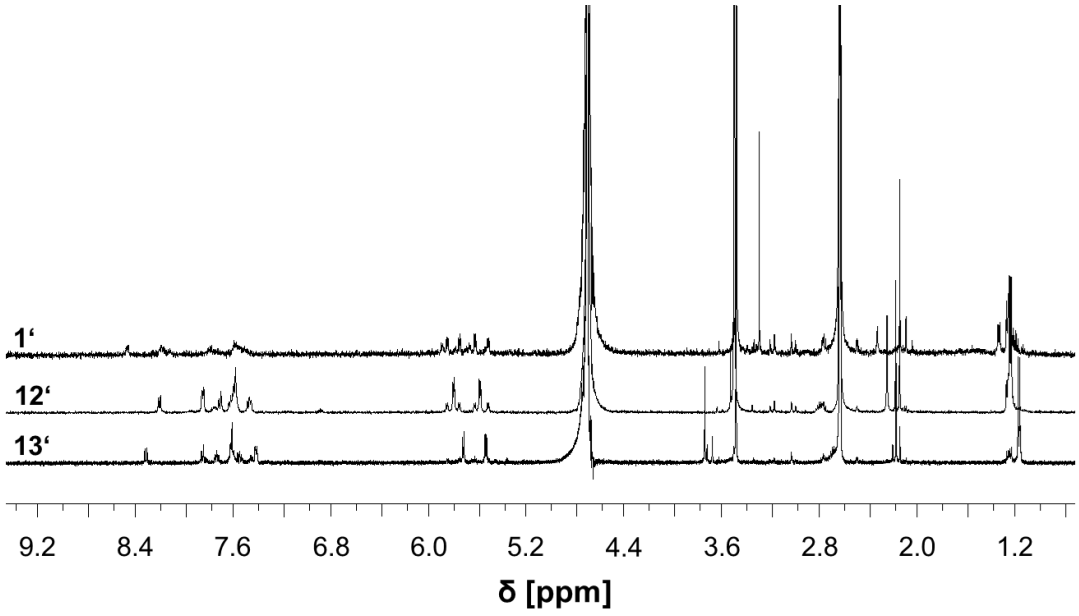


Figure S9. ^{1}H NMR spectra of the reactions of **1', 12'** and **13'** with an equimolar amount of glycine after 5 min.

1.7. The reactions of 12' with amino acids

1.7.1 Reaction of 12' with an equimolar amount of L-methionine

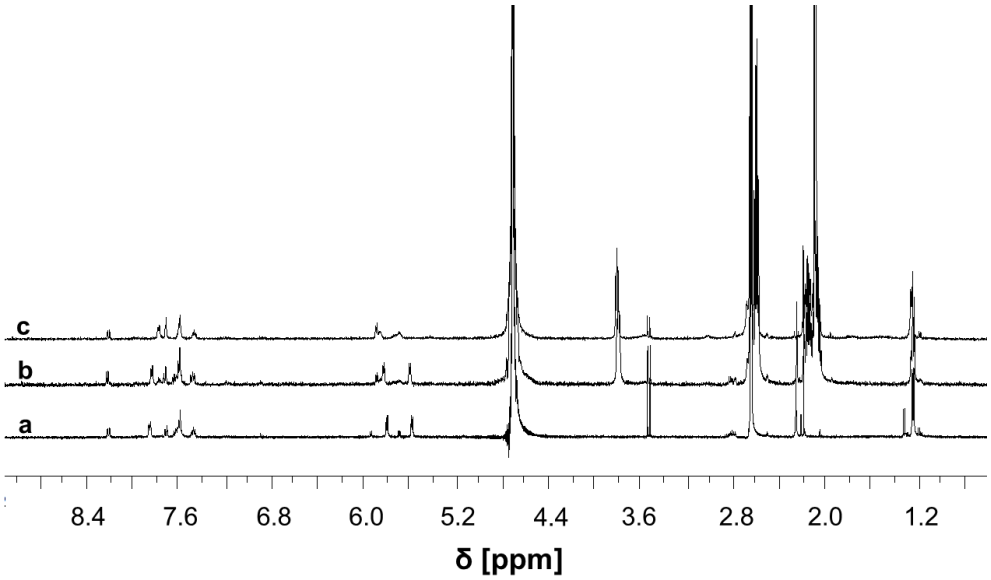


Figure S10. ^{1}H NMR spectra of a) **12'**, b) **12'** + 1 eq L-methionine after 5 min and c) after 24 h.

1.7.2 Reaction of 12' with an equimolar amount of L-histidine

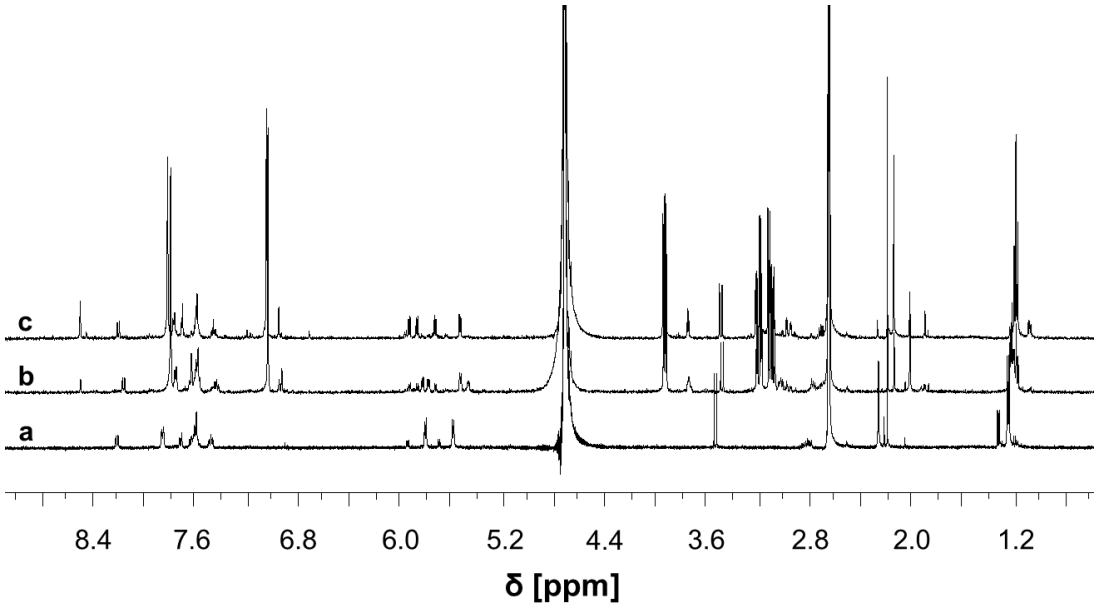


Figure S11. ^{1}H NMR spectra of a) **12'**, b) **12'** + 1 eq L-histidine after 5 min and c) after 24 h.

1.7.3 Reaction of 12’ with an equimolar amount of glycine

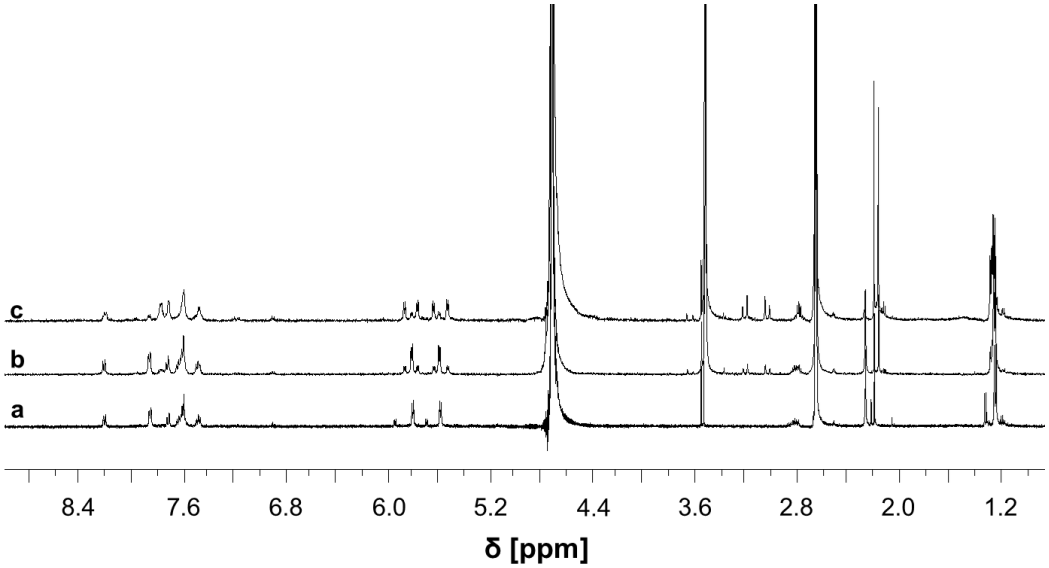


Figure S12. ^{1}H NMR spectra of a) **12’**, b) **12’** + 1 eq glycine after 5 min and c) after 24 h.

1.7.4 Reaction of 12’ with an equimolar amount of L-cysteine

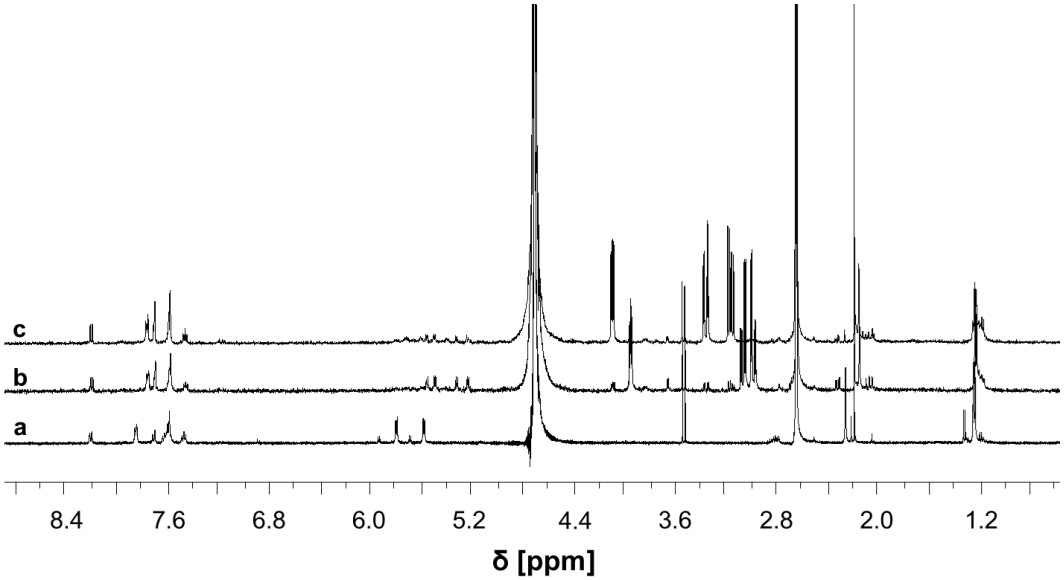


Figure S12. ^{1}H NMR spectra of a) **12’**, b) **12’** + 1 eq L-cysteine after 5 min and c) after 24 h.