Supplementary Information

Structure and Dynamics of Binary and Ternary Lanthanide(III) and Actinide(III) - Tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] (TTA) Complexes. Part 2, The Structure and Dynamics of Binary and Ternary Complexes in the Y(III) – TTA – Tributylphosphate (TBP) System in Chloroform as Studied by NMR Spectroscopy and Quantum Chemical Methods.

Zoltán Szabó*[1], Valerie Vallet[2] and Ingmar Grenthe[1]

[1]Royal Institute of Technology (KTH), School of Chemistry S-100 44 Stockholm, Sweden

[2]Université des Sciences et Technologies de Lille 1, Laboratoire PhLAM, CNRS UMR 8523, CERLA, CNRS FR 2416, Bât P5, 59655 Villeneuve d'Ascq Cedex, France

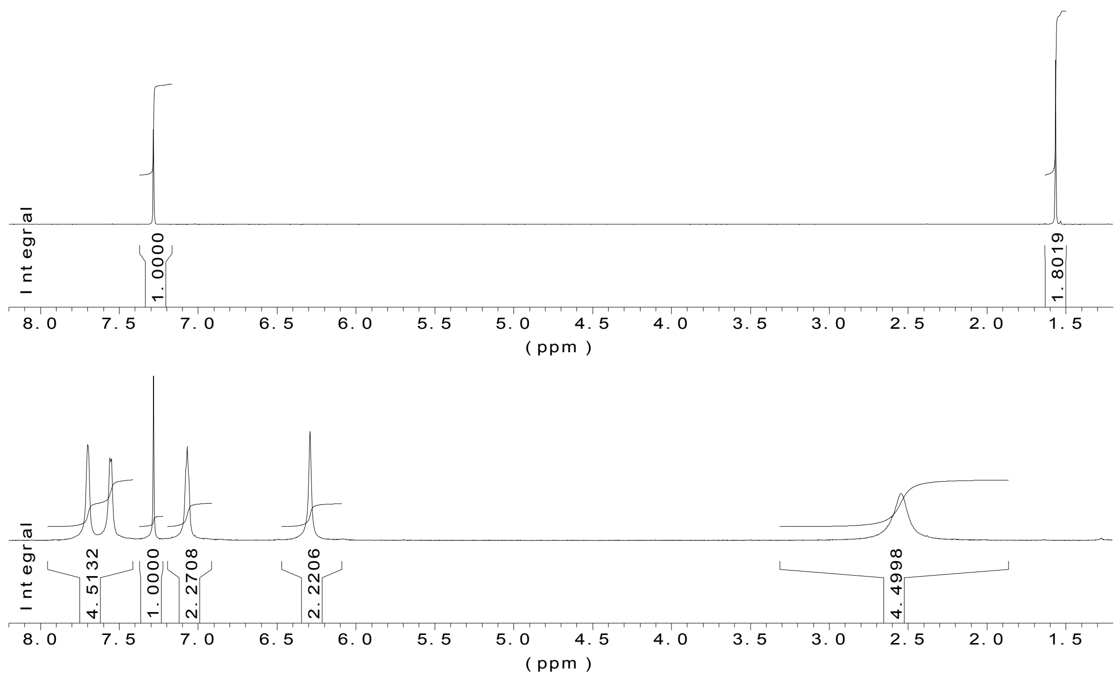


Figure S1 ^{1}H-NMR spectra of the binary Y(III)-TTA complex in $CDCl_3$ at 298 K (bottom) and the solvent $CDCl_3$ as reference for its water content (top).

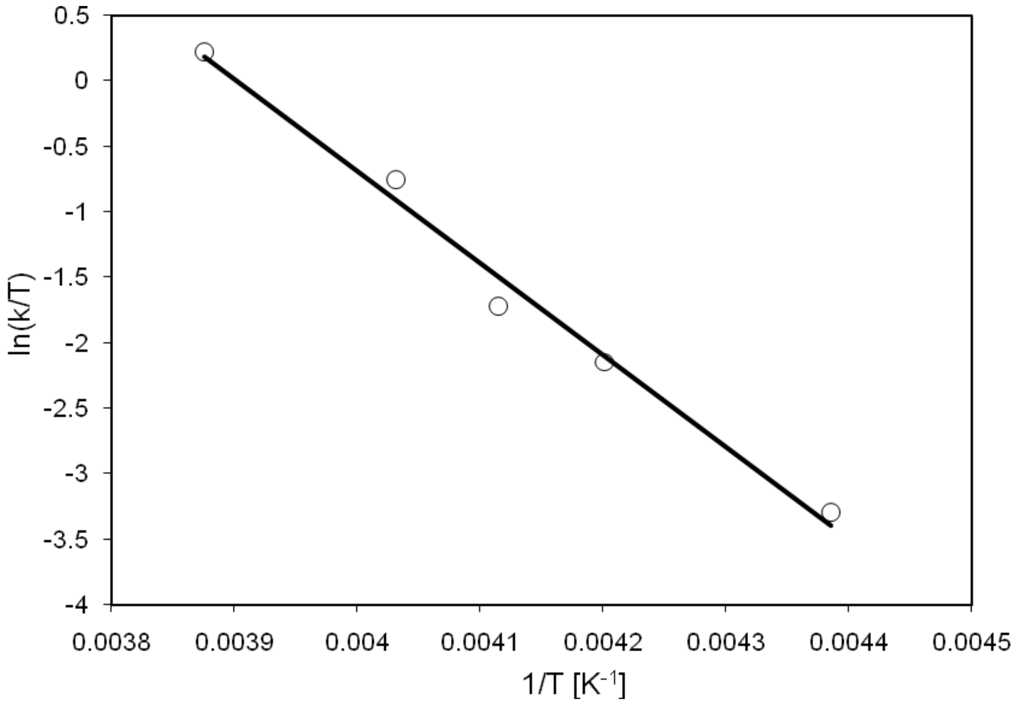


Figure S2 Eyring plot of the temperature dependence of the rate constant for the exchange between the coordinated TTA in $Y(TTA)_3(H_2O)_2$ based on the line shape analysis of the olefin proton signals measured in $CDCl_3$ between 228 and 258 K.

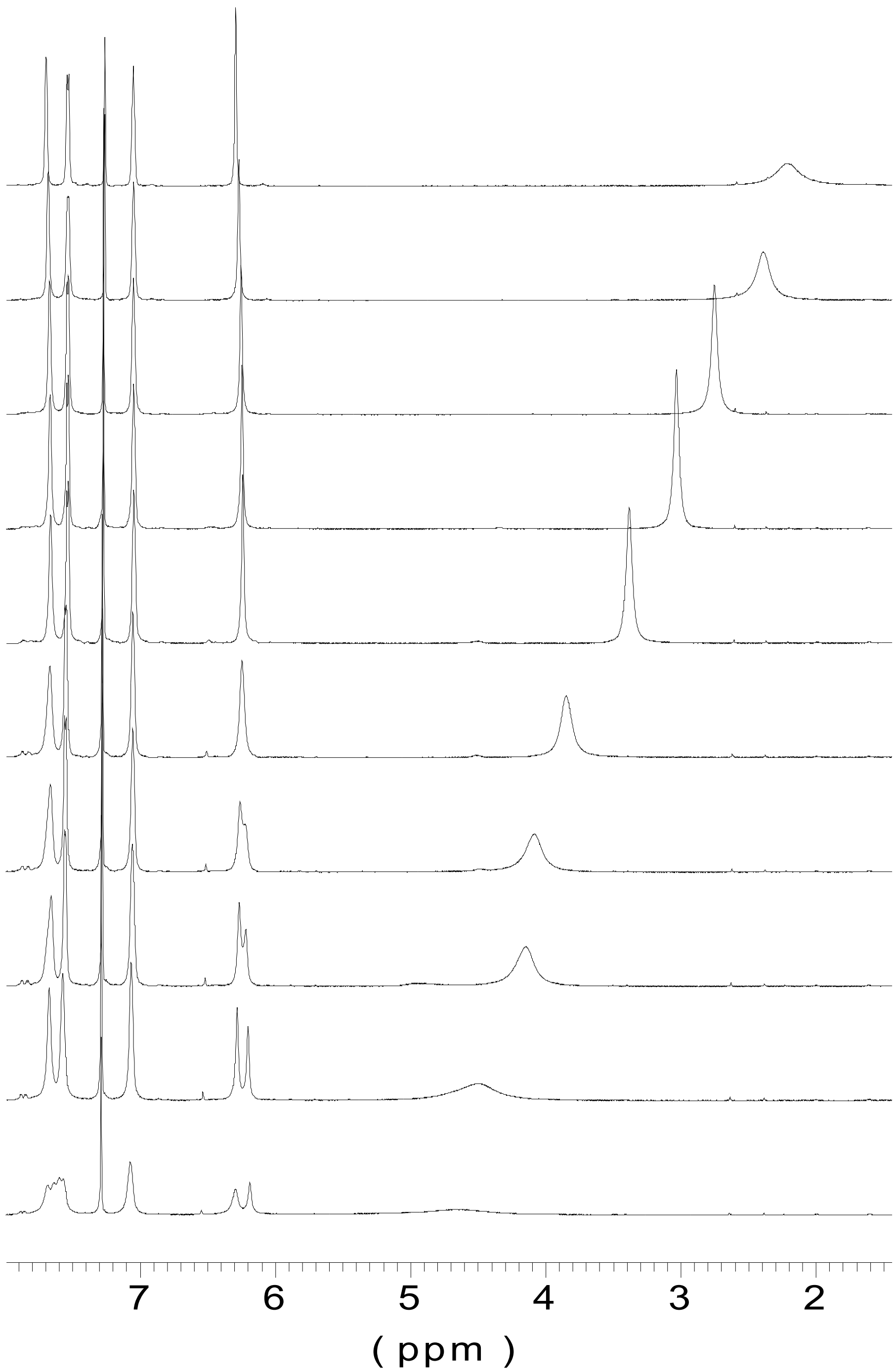


Figure S3 Temperature dependent ^{1}H-NMR spectra of $Y(TTA)_3(H_2O)_2$ recorded in $CDCl_3$ are showing only one exhange averaged water signal in the whole temperature range studied. The temperatures from below to top are 218, 228, 238, 243, 248, 258, 268, 278, 298 and 318 K.

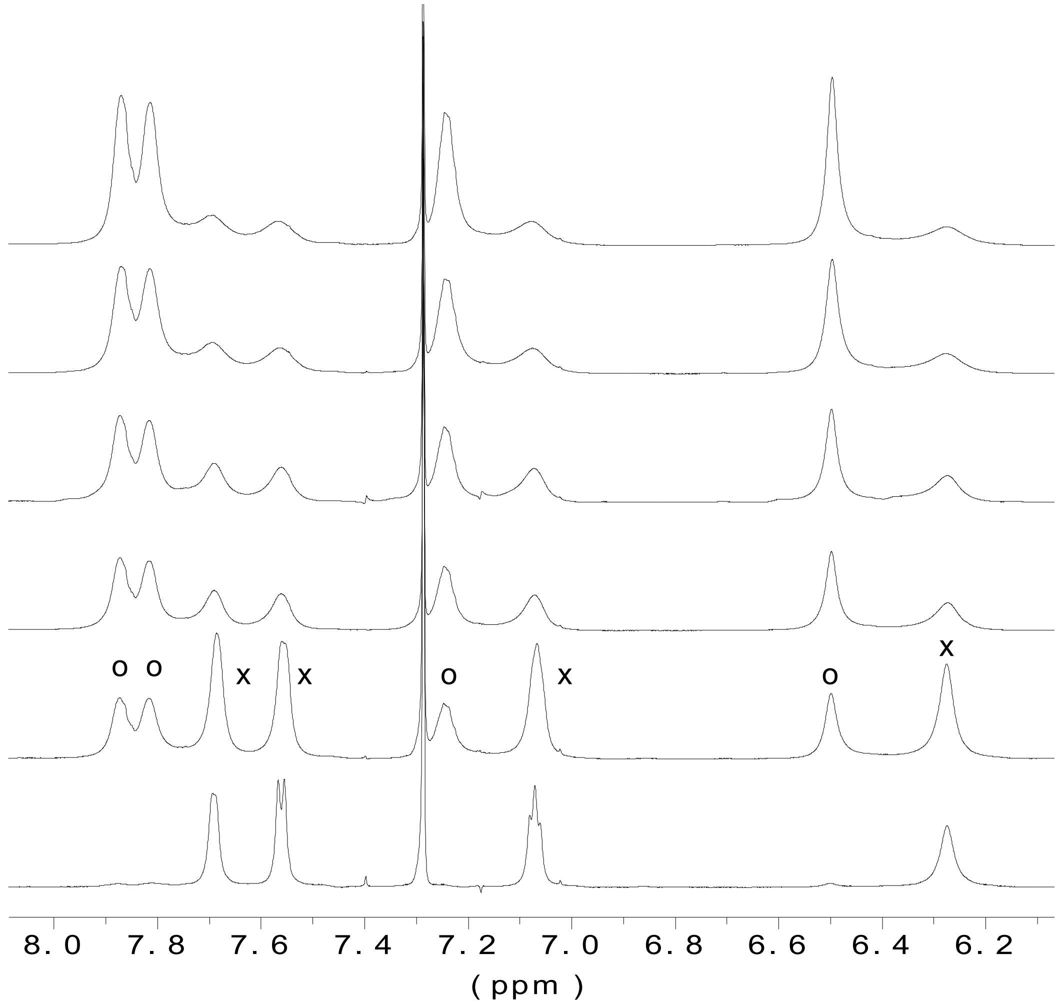


Figure S4 Partial ^{1}H-NMR spectra of the $Y(TTA)_3(H_2O)_2$ measured at various concentrations of free HTTA (260 K in $CDCl_3$). The free HTTA concentrations from bottom to top are 0, 18, 40.8, 52.1 75.0 and 100.3 mM. The $Y(TTA)_3(H_2O)_2$ concentration is 10.1 mM. o - Signals for free HTTA, x - signals for coordinated TTA ligands.

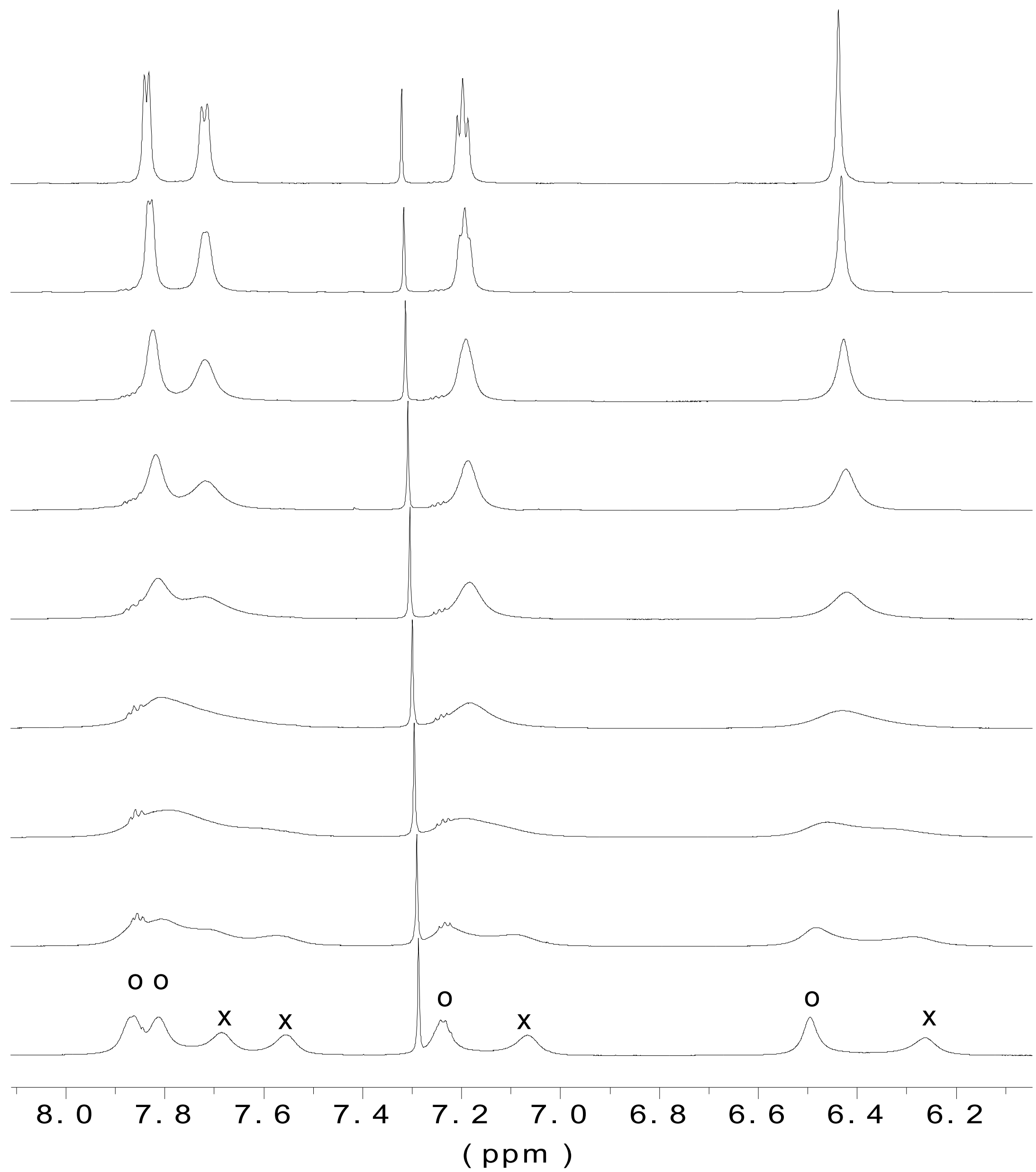


Figure S5 Temperature dependence of the ^{1}H-NMR signals of $Y(TTA)_3(H_2O)_2$ and free TTA in $CDCl_3$. The temperature from below to top are 260, 268, 273, 278, 283, 288, 293, 303 and 318 K. o - Signals for free HTTA, x - signals for coordinated TTA ligands.

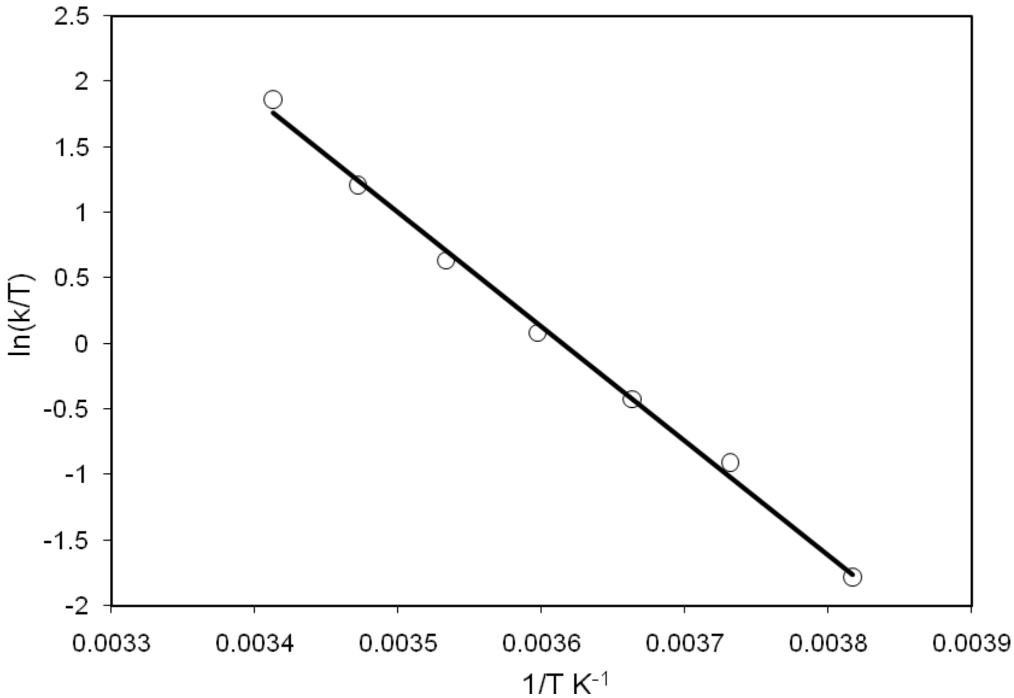


Figure S6 Eyring plot of the temperature dependence of the rate constant for the TTA exchange between $Y(TTA)_3(H_2O)_2$ and free HTTA based on the line shape analysis of the olefin proton signals measured in $CDCl_3$ between 262 and 293 K.

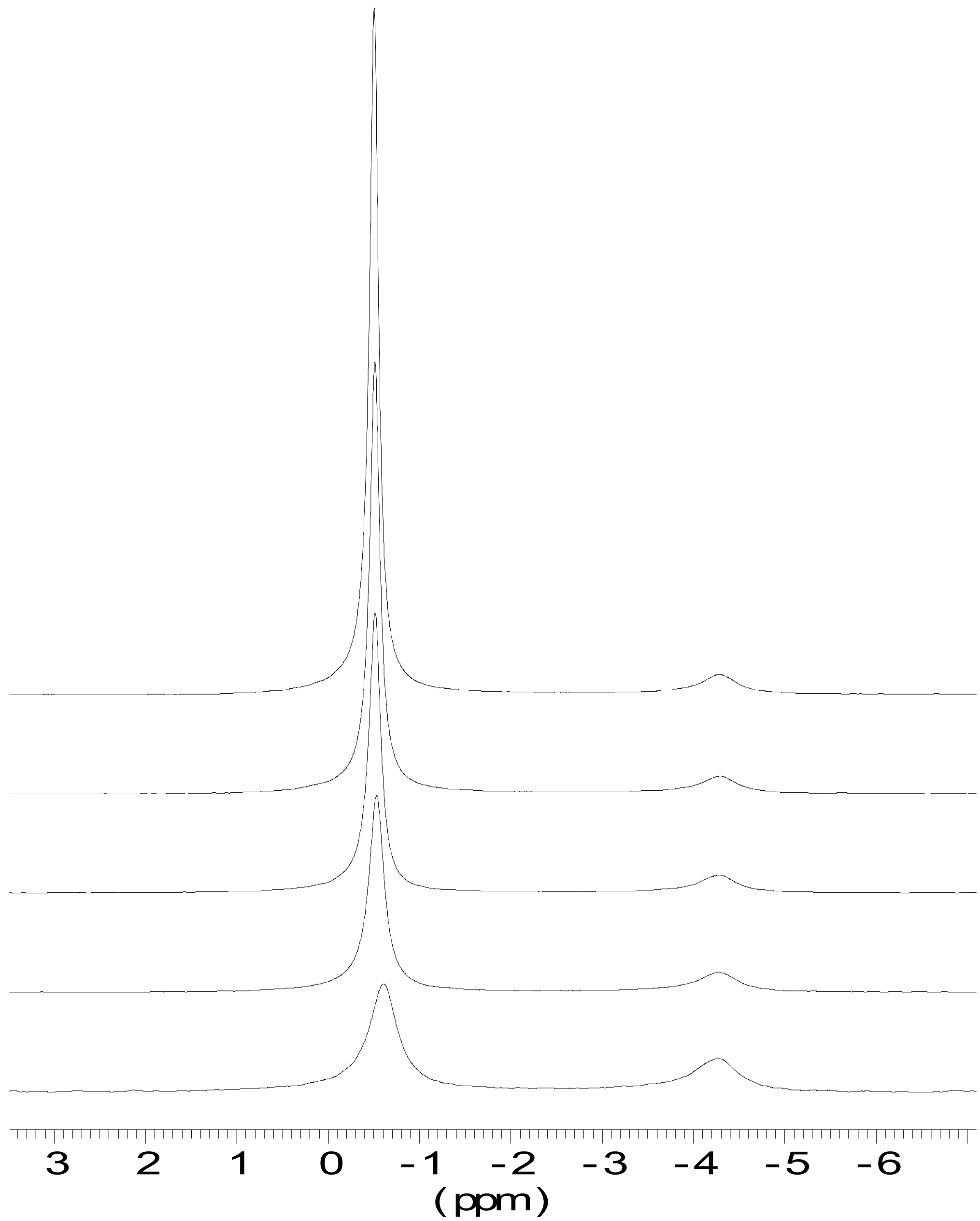


Figure S7 ^{31}P NMR signals for coordinated (-4.2 ppm) and free (-0.5 ppm) TBP in the ternary Y(III)-TTA-TBP system measured in $CDCl_3$ at 238 K. The $Y(TTA)_3(H_2O)_2$ concentration is 12 mM and the total TBP concentrations from bottom to top are 39.7, 71.5, 94.4, 127.0 and 182.1 mM

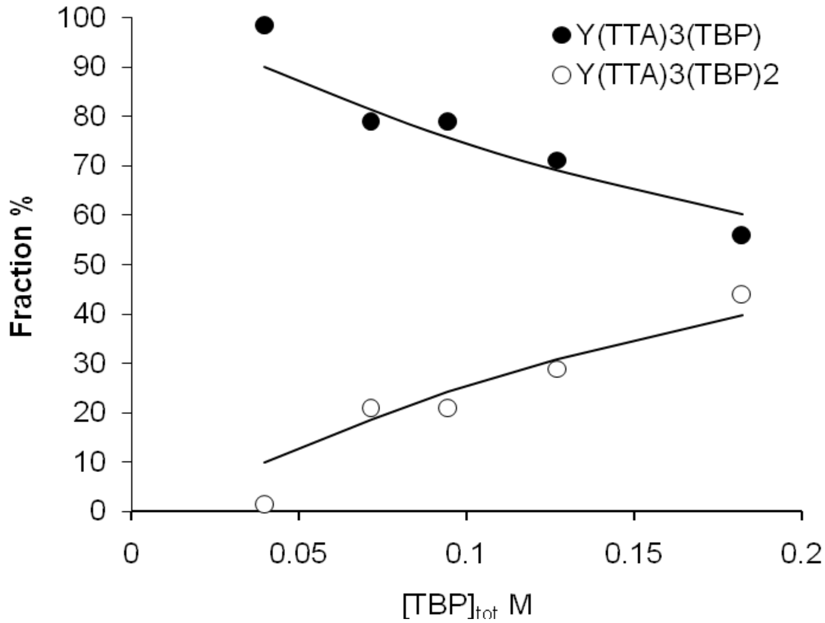


Figure S8 Y(III) equilibrium distribution diagrams as a function of the total TBP concentration for the ternary Y(III)-TTA-TBP system using the total $Y(TTA)_3(H_2O)_2$ concentration of 12 mM. The diagram is based on the ^{31}P NMR peak integrals of the spectra shown in Figure S7. The solid lines are generated using the equilibrium constant of 4 M^{-1}.

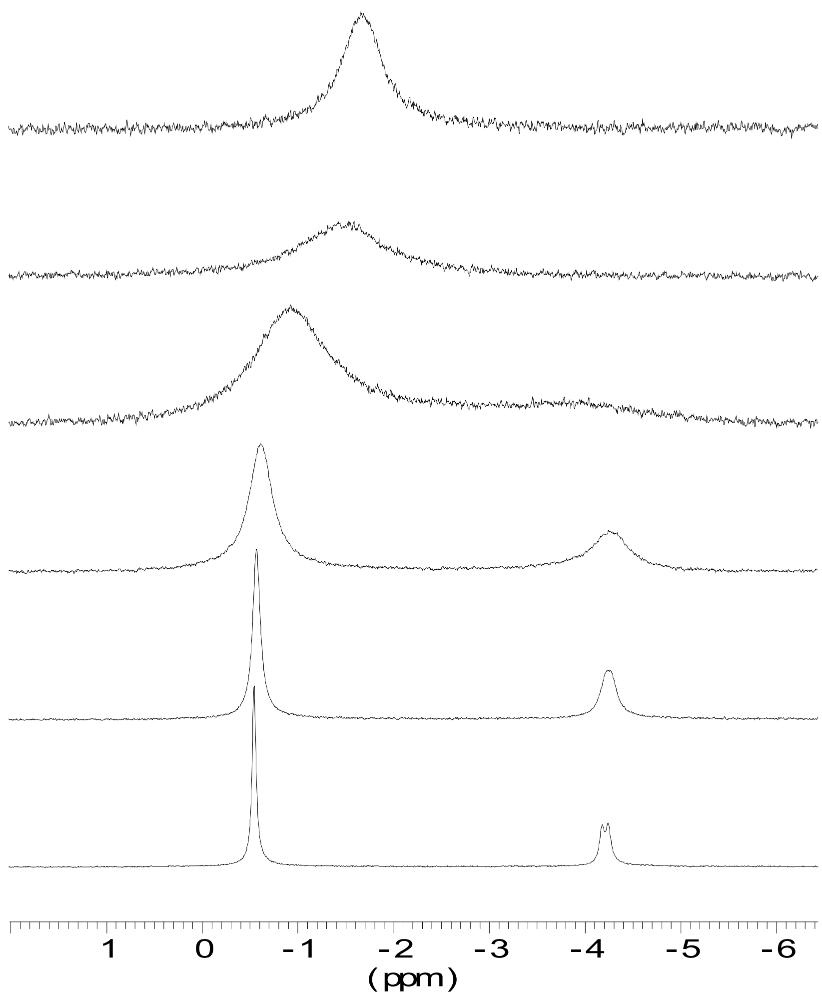


Figure S9 Temperature dependence of the ^{31}P NMR signals of free and coordinated TBP in $Y(TTA)_3TBP$ recorded in $CDCl_3$. The Y(III) concentration is 12 mM and the total TBP concentration is 39.7 mM. The temperatures from below to top are 218, 228, 238, 248, 258 and 268 K.

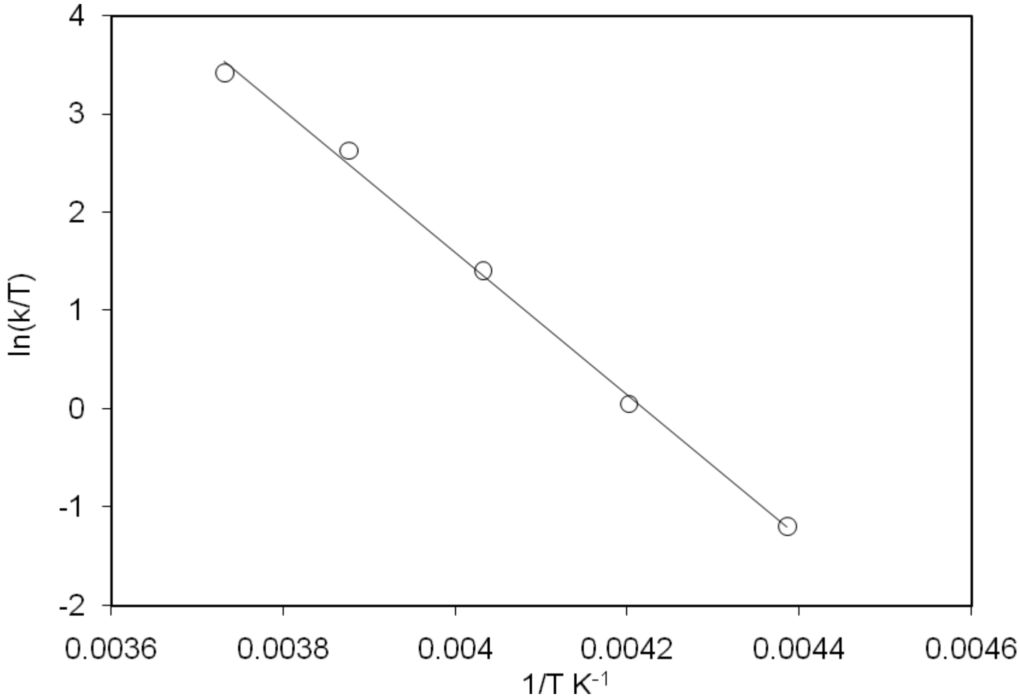


Figure S10 Eyring plot of the temperature dependence of the rate constant for the TBP exchange between $Y(TTA)_3TBP$ and free TBP based on the line shape analysis of the ^{31}P signals measured in $CDCl_3$ between 218 and 268 K.

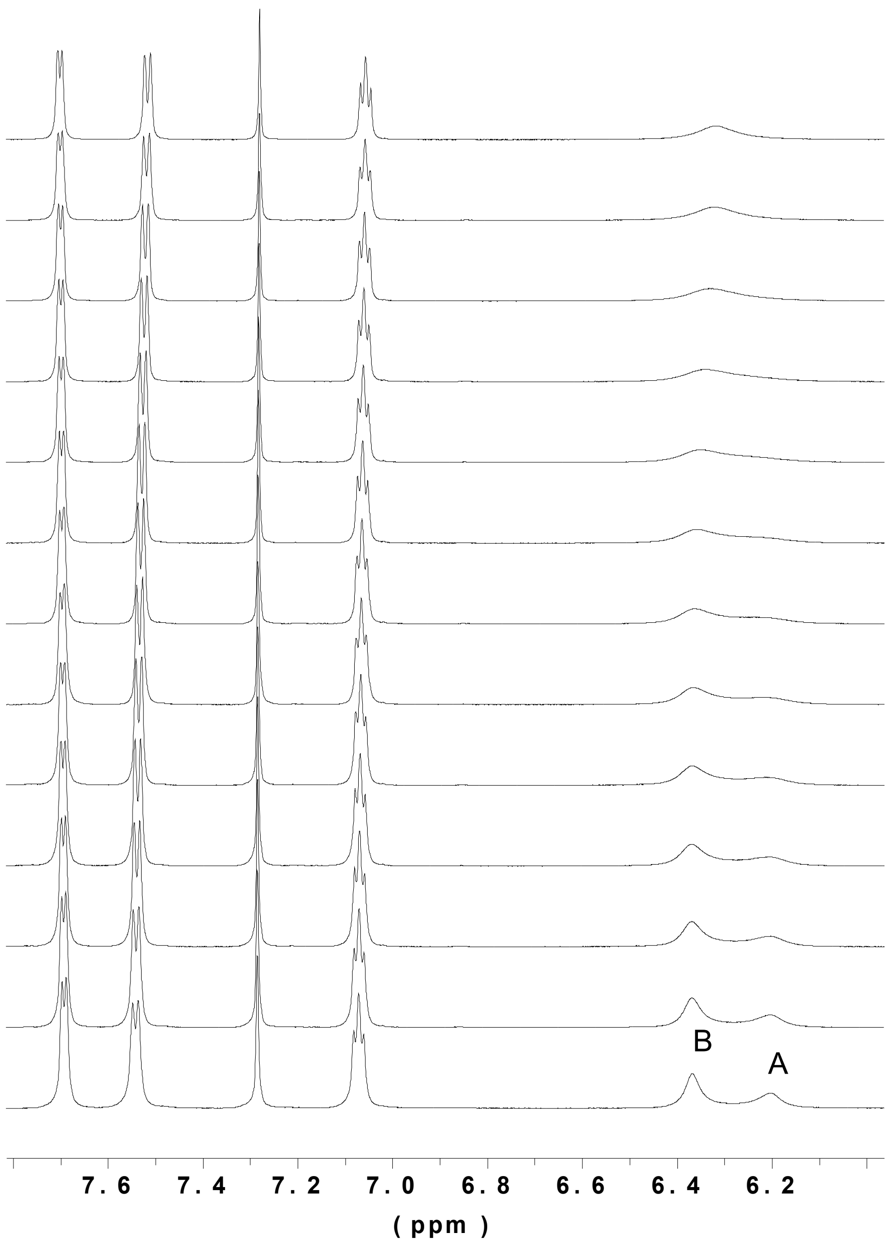


Figure S11 Temperature dependence of the TTA proton signals in $Y(TTA)_3TBP$ recorded in $CDCl_3$. The temperatures from below to top are 265, 270, 275, 280, 285, 290, 295, 300, 305, 310, 315, 320 and 325 K. “A” and “B” indicate the olefin signals for the two different isomers.

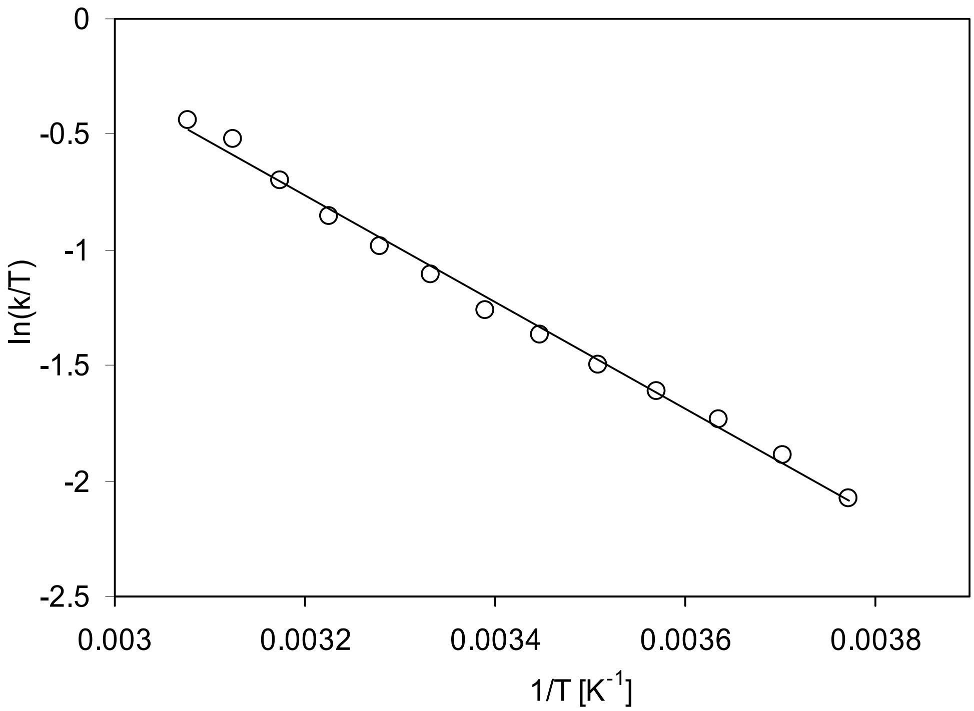


Figure S12 Eyring plot of the temperature dependence of the rate constant for the exchange between the coordinated TTA ligands in $Y(TTA)_3TBP$ based on the line shape analysis of the olefin proton signals measured in $CDCl_3$ between 265 and 325 K.

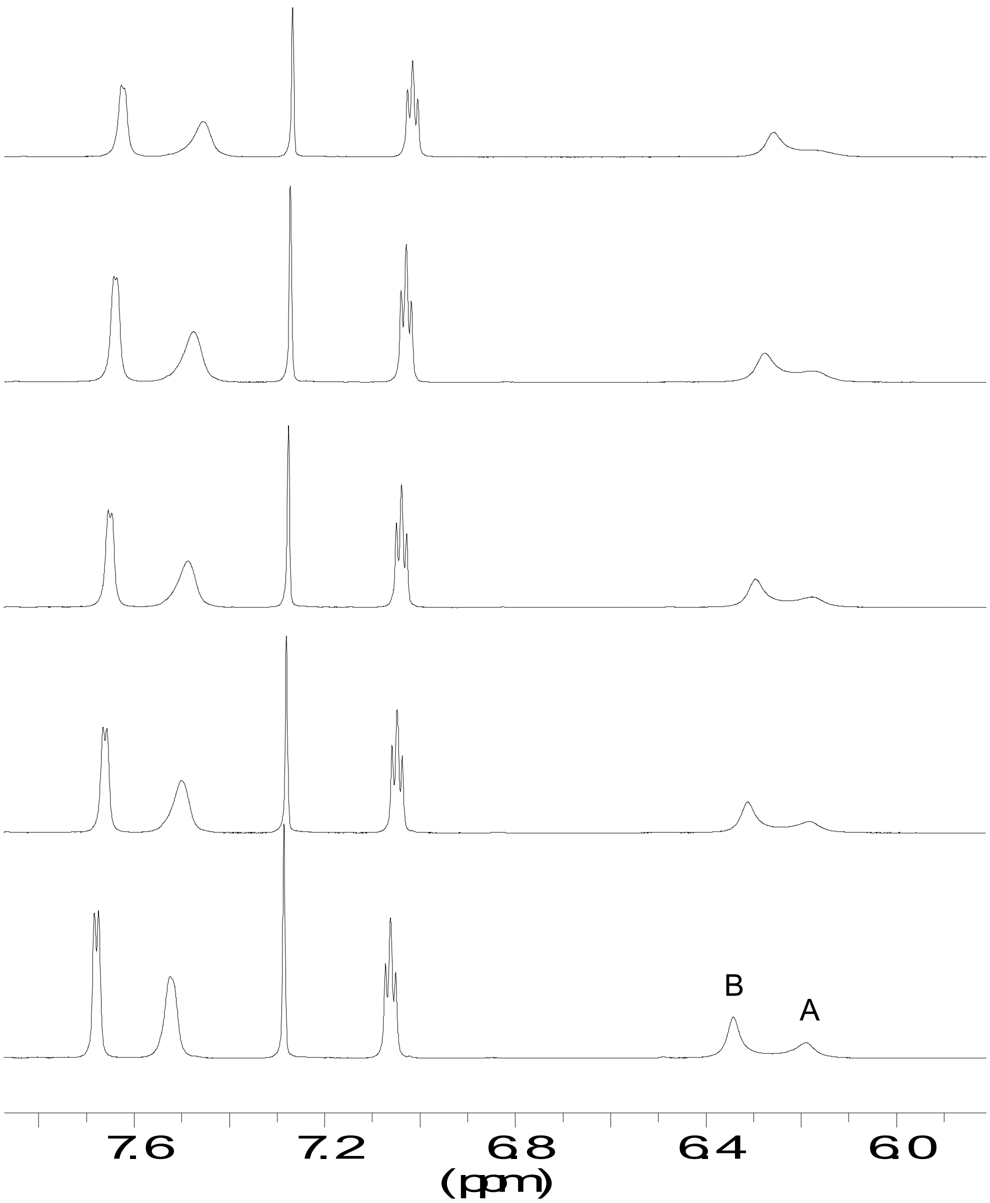


Figure S13 TBP concentration dependence of the TTA proton signals recorded in the ternary Y(III)-TTA-TBP system in $CDCl_3$ at 268 K. The Y(III) concentration is 12 mM and the total TBP concentrations from bottom to top are 39.7, 71.5, 94.4, 127.0 and 182.1 mM. “A” and “B” indicate the olefin signals for the two isomers.

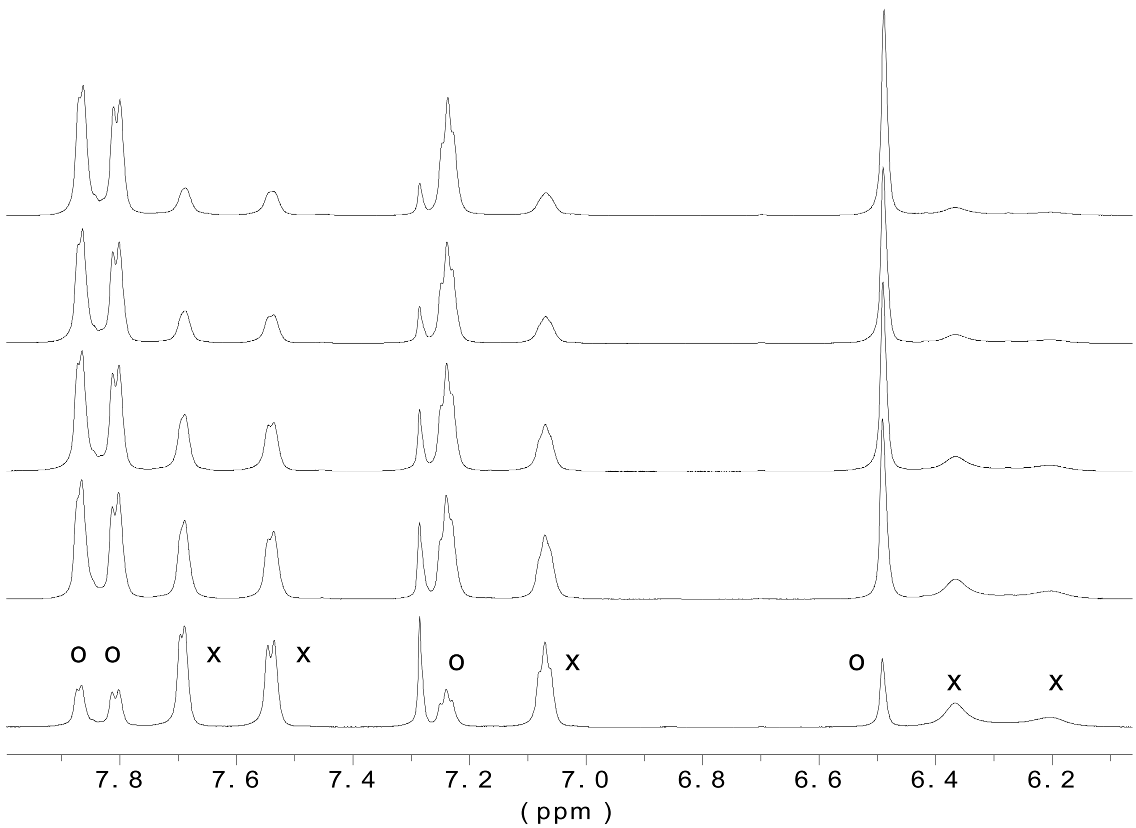


Figure S14 ^{1}H-NMR signals of $Y(TTA)_3TBP$ complex measured at various concentrations of free HTTA (268 K in $CDCl_3$). The free HTTA concentrations from bottom to top are 16.1, 51.4, 70.9, 108.4 and 132 mM. The $Y(TTA)_3TBP$ concentration is 12 mM, the total TBP concentration is 16.2 mM. o - Signals for free HTTA, x - signals for the complex.

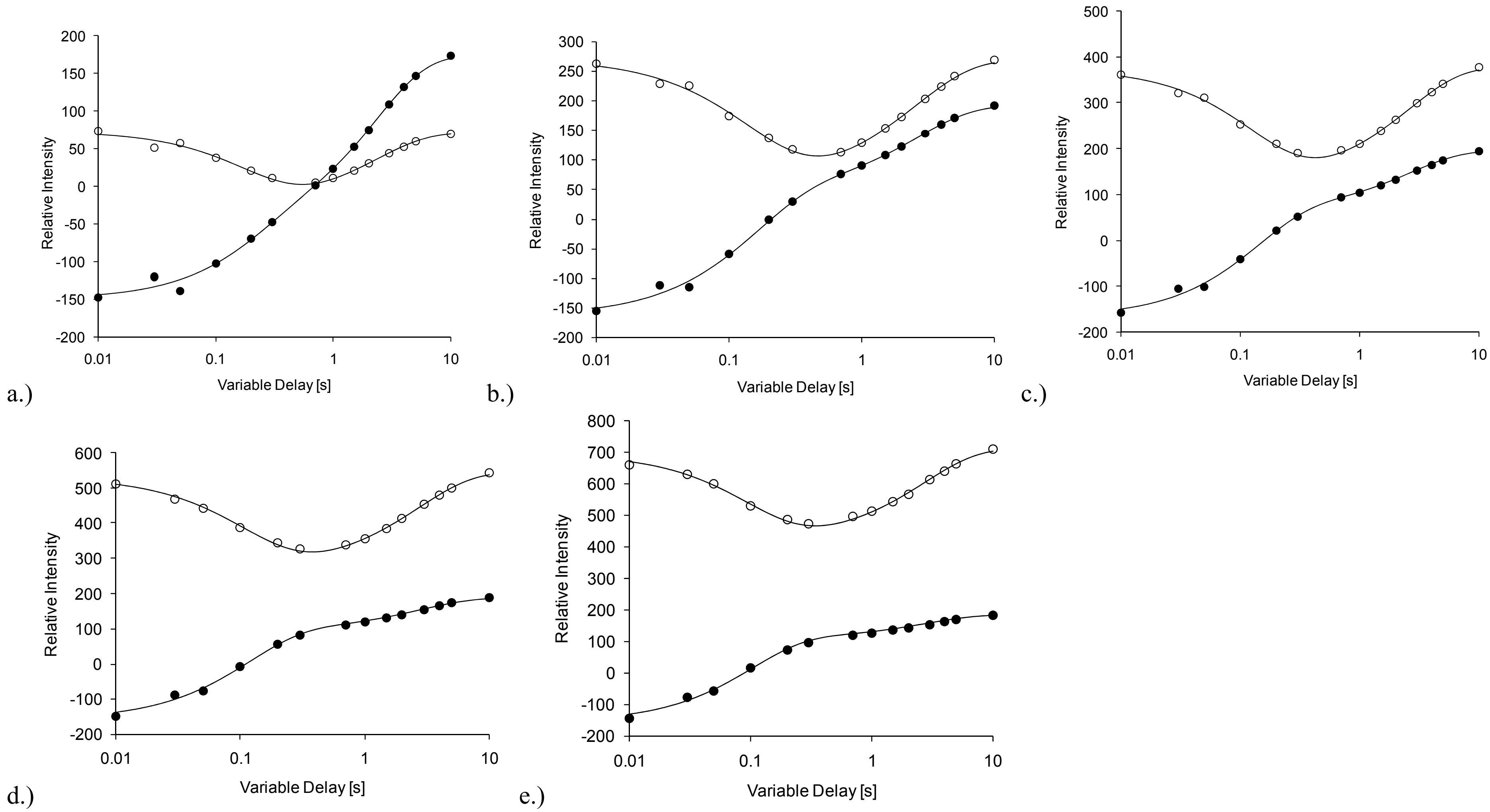


Figure S15 Plots of peak intensities against the variable delays from the ^{1}H NMR magnetization transfer experiments measured at different free HTTA concentrations to study the TTA exchange between $Y(TTA)_3TBP$ and free HTTA (at 268 K in $CDCl_3$). The solid lines are generated by a non-linear fitting procedure of the experimental data. The free HTTA concentrations are (a) 16.1, (b) 51.4, (c) 70.9, (d) 108.4 and (e) 132 mM. The $Y(TTA)_3TBP$ concentration is 12 mM, the total TBP concentration is 16.2 mM.

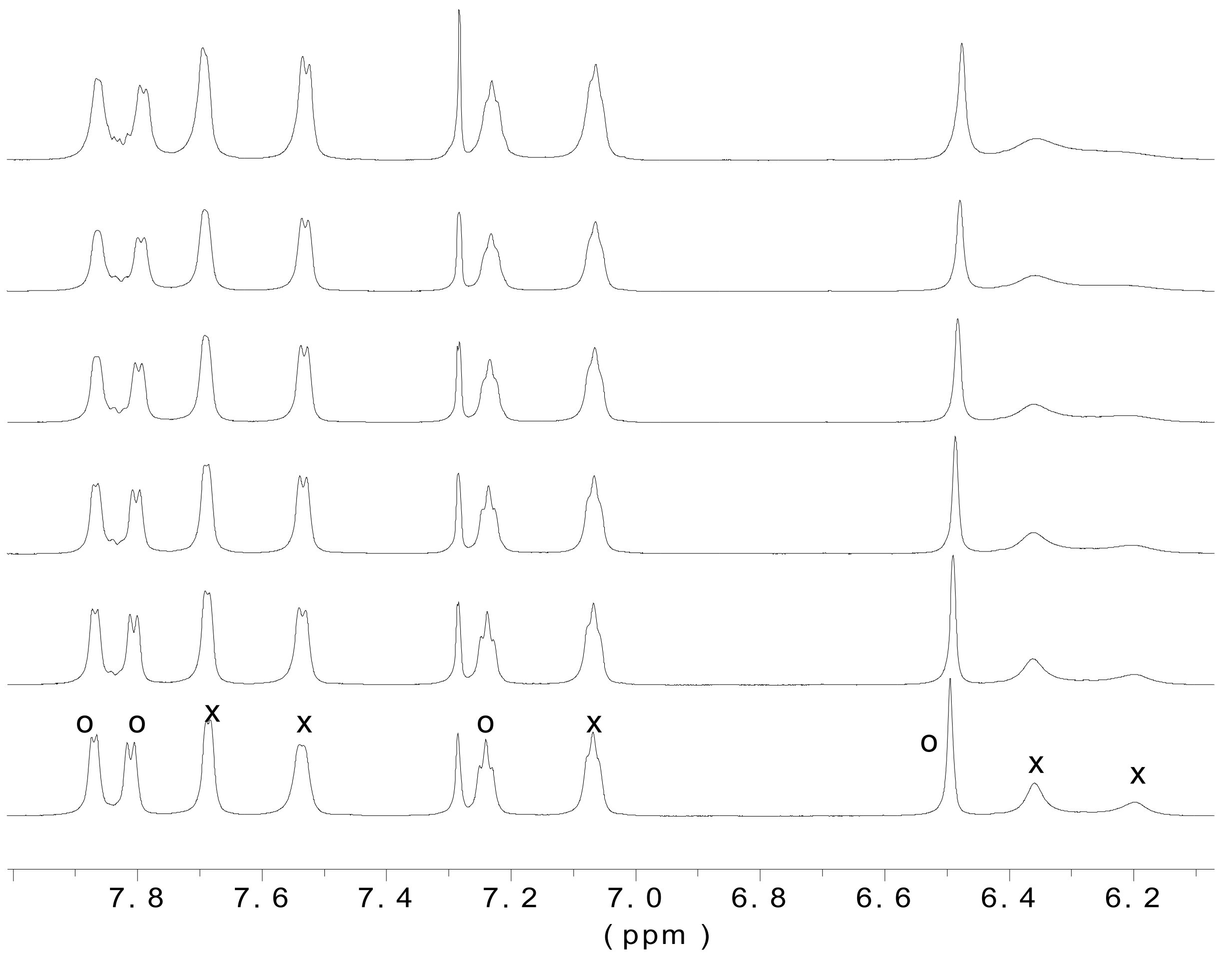
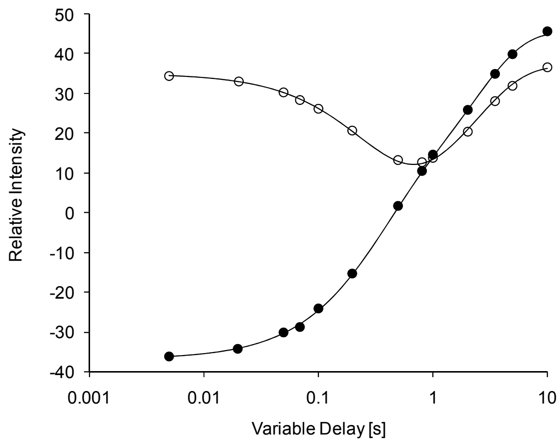


Figure S16 Temperature dependence of the ^1H NMR signals of $Y(TTA)_3TBP$ and free HTTA in $CDCl_3$. The temperature from below to top are 262, 268, 273, 278, 283 and 288 K. The $Y(TTA)_3TBP$ concentration is 16.2 mM, the free HTTA concentration is 41.3 mM and the total TBP concentration is 26.3 mM. o - Signals for free HTTA, x - signals for the complex.



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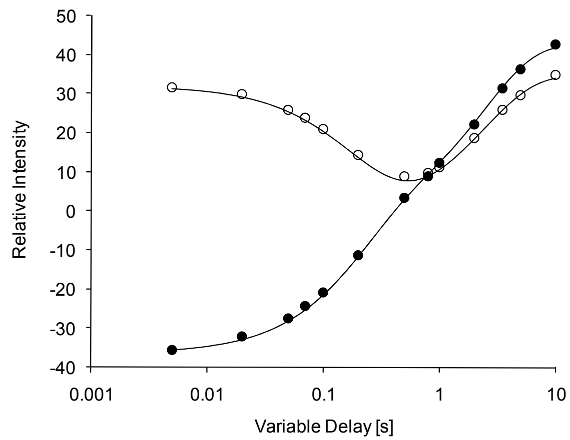
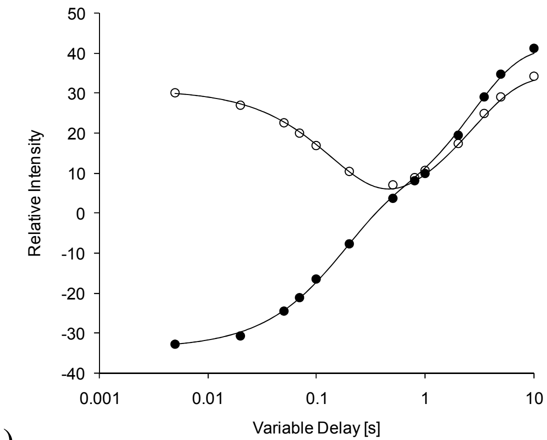
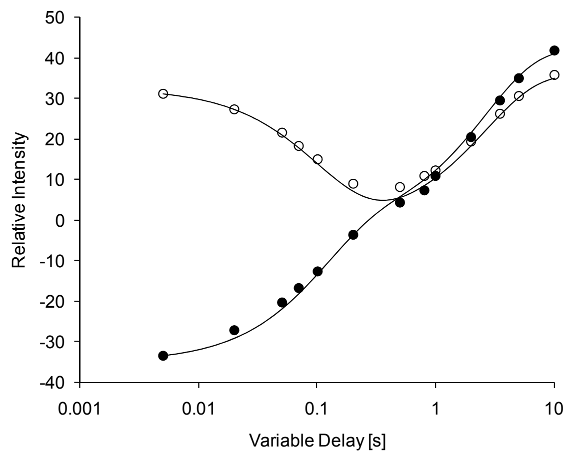


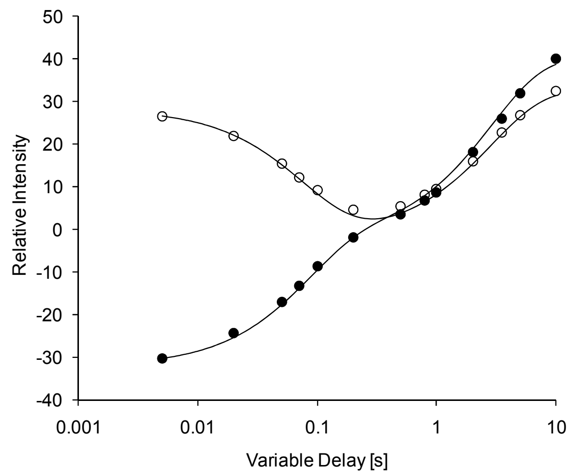
b.)



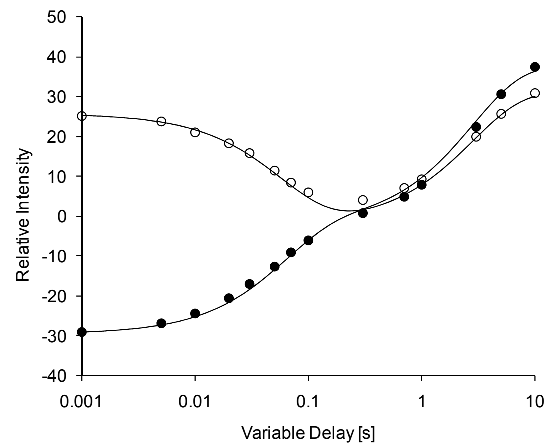
c.)



d.)



e.)



f.)

Figure S17 Plots of peak intensities against the variable delays from the ^{1}H NMR magnetization transfer experiments measured at different temperatures to determine the activation parameters for the TTA exchange between $Y(TTA)_3TBP$ and free HTTA in $CDCl_3$. The temperature from a.) to f.) top are 262, 268, 273, 278, 283 and 288 K. The solid lines are generated by a non-linear fitting procedure of the experimental data. The $Y(TTA)_3TBP$ concentration is 16.2 mM, the free HTTA concentration is 41.3 mM and the total TBP concentration is 26.3 mM.

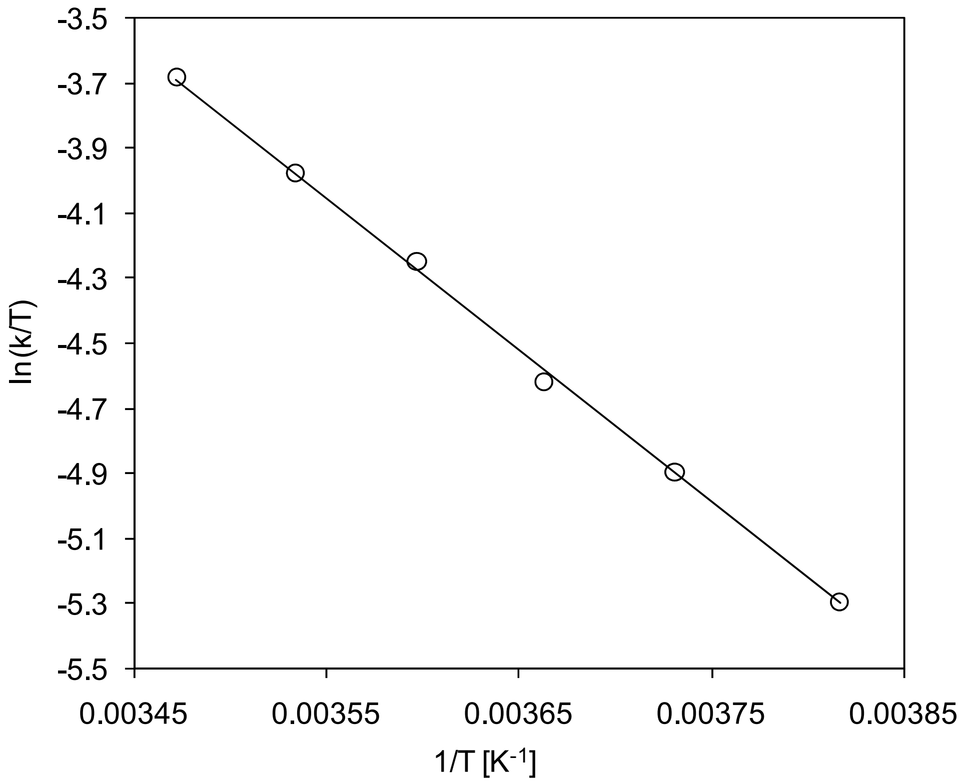


Figure S18 Eyring plot of the temperature dependence of the rate constant for the TTA exchange between $Y(TTA)_3(TBP)$ and free HTTA based on the ^1H NMR magnetization transfer experiments measured in $CDCl_3$ between 262 and 288 K.

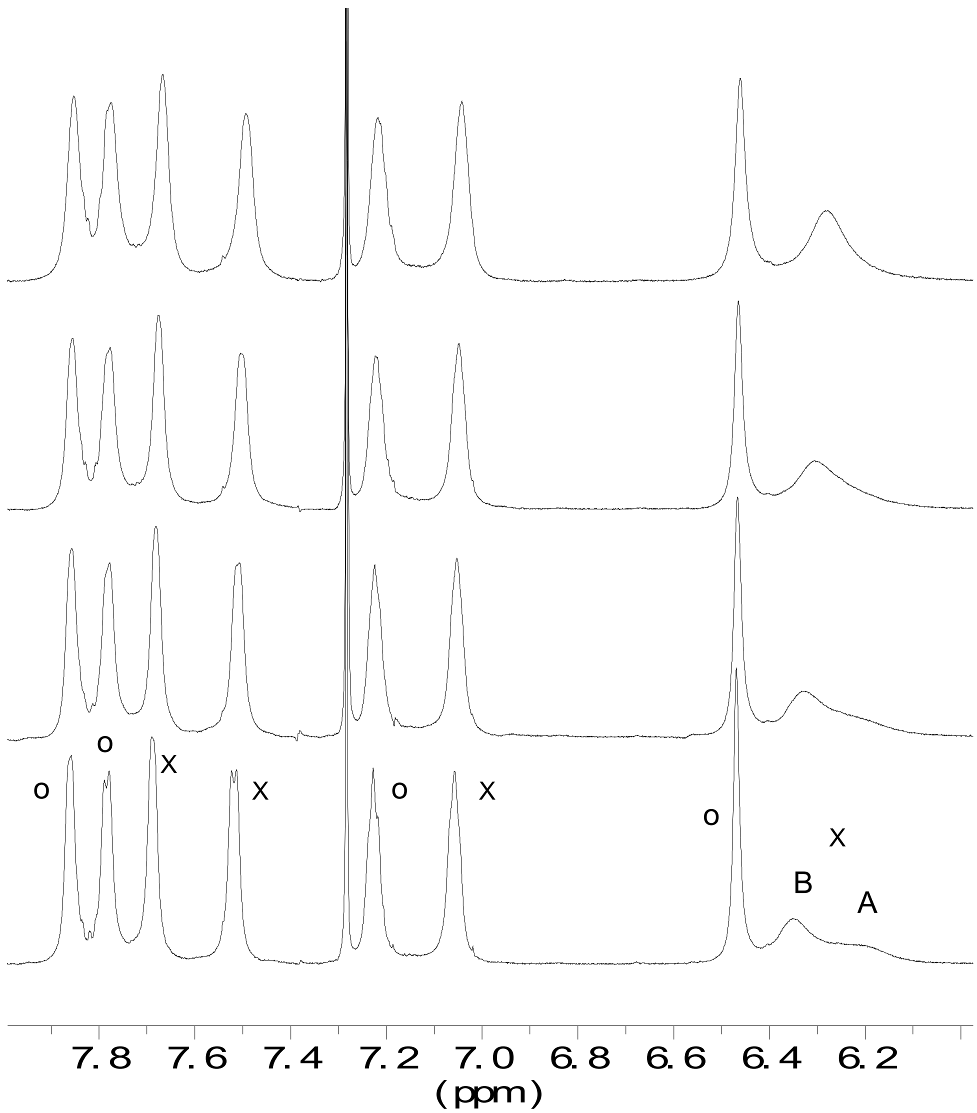


Figure S19 TBP concentration dependence of the TTA proton signals recorded in the ternary Y(III)-TTA-TBP system in the presence of free HTTA ($CDCl_3$, 298K). The Y(III) concentration is 10.7 mM, the free HTTA concentration is 30.8 mM and the total TBP concentrations from bottom to top are 41.3, 60.1, 85.5 and 122.2 mM. “A” and “B” indicate the olefin signals for the two isomers.
o - Signals for free HTTA, x - signals for coordinated TTA.

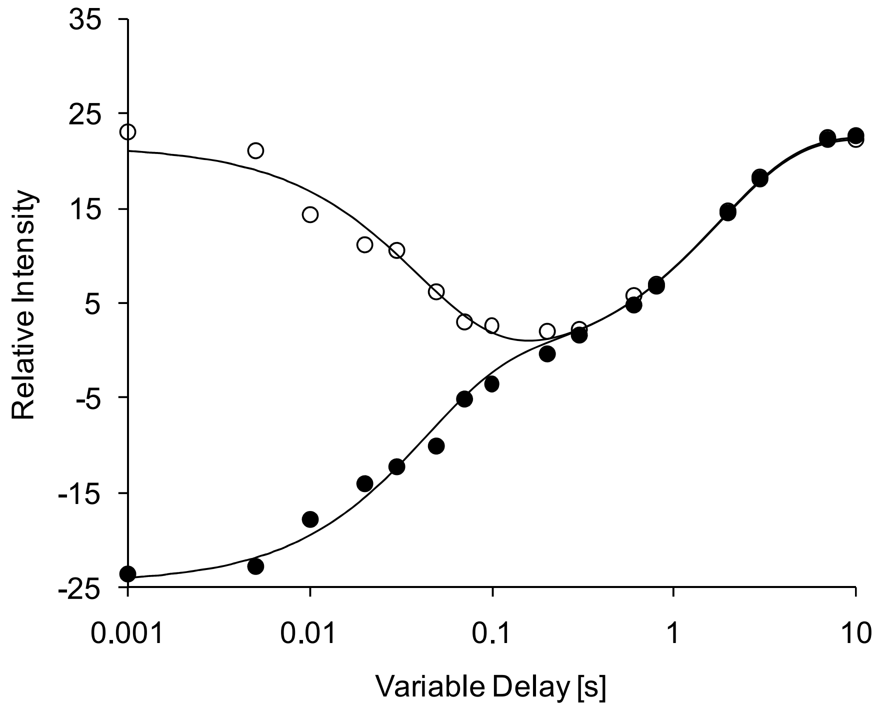


Figure S20 Plots of peak intensities against the variable delays from the ^{1}H NMR magnetization transfer experiment measured at high TBP concentration to study the effect of $Y(TTA)_3TBP_2$ on the the intermolecular TTA exchange (at 268 K in $CDCl_3$). The Y(III) concentration is 13.7 mM, the free HTTA concentration is 46.8 mM and the total TBP concentration is 197.5 mM.

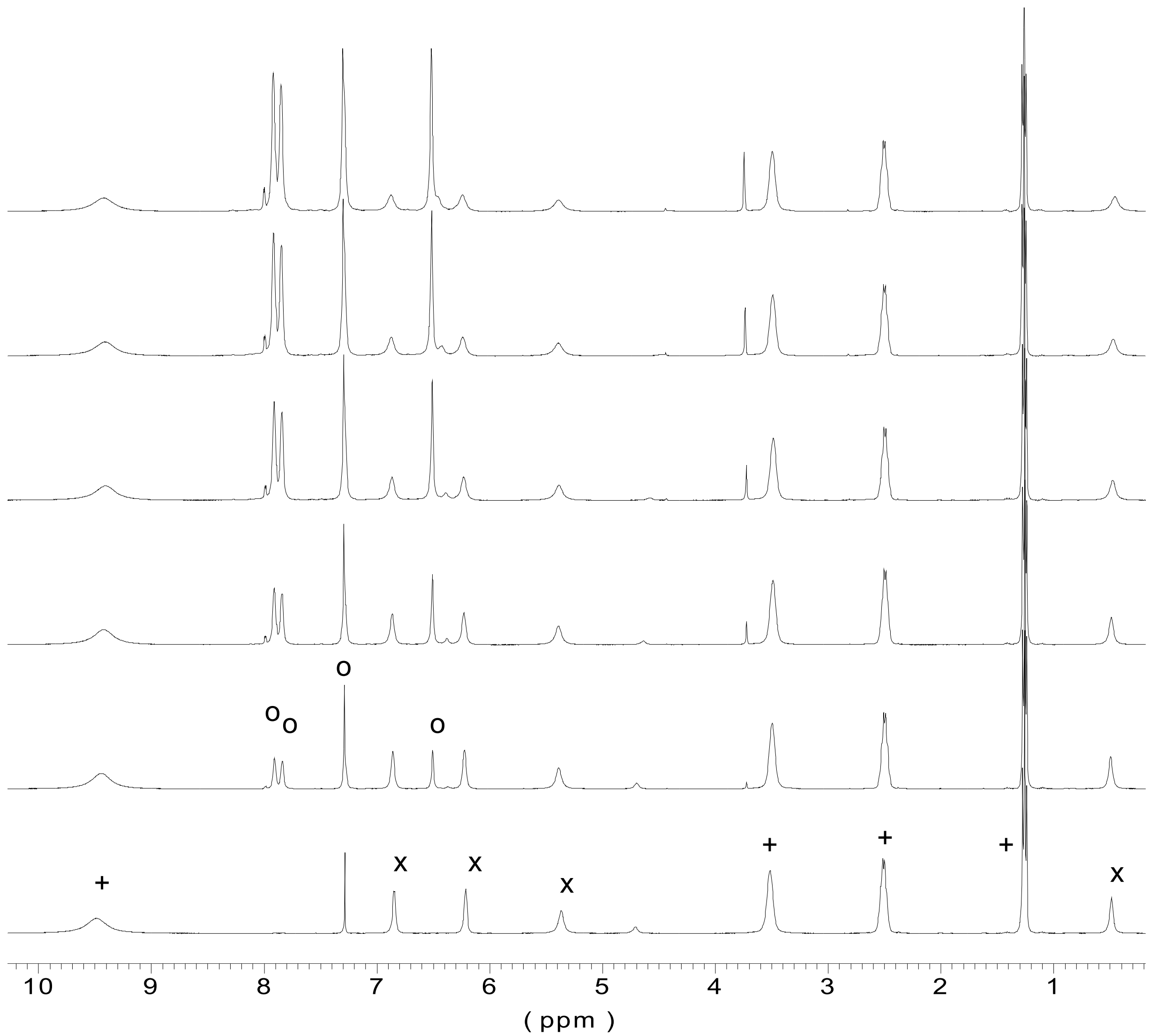
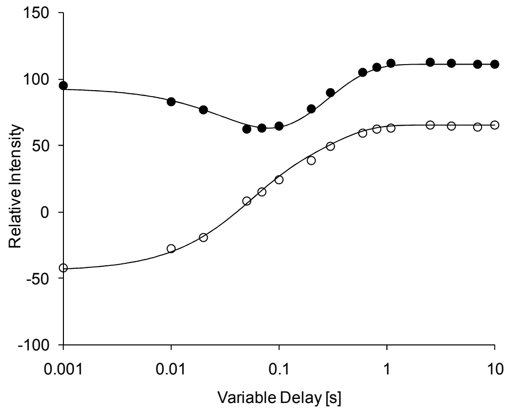


Figure S21 ^{1}H-NMR spectra measured in the Eu (III)-TTA-TBP system at various concentrations of free HTTA (268 K in $CDCl_3$). The free HTTA concentrations from bottom to top are 0, 34.8, 69.1, 130.7, 180.1 and 191.7 mM. The Eu(III) concentration is 19.3 mM, the total TBP concentration is 24.8 mM. o - Signals for free HTTA, x - signals for the Eu(III)-complex and + - signals for TBP.



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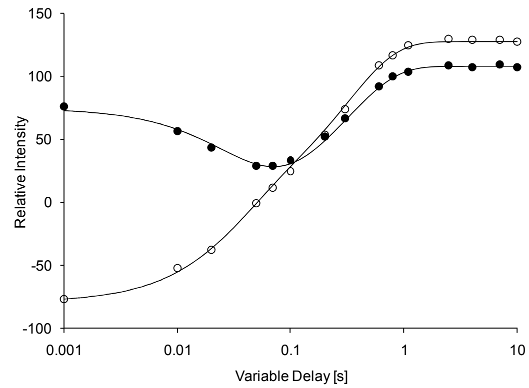
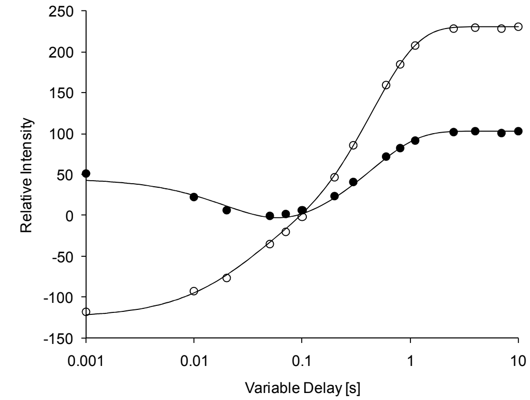
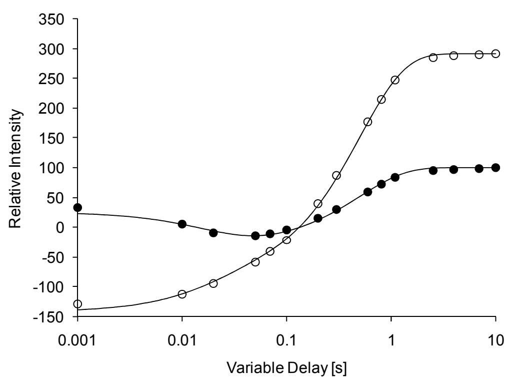


b.



c.



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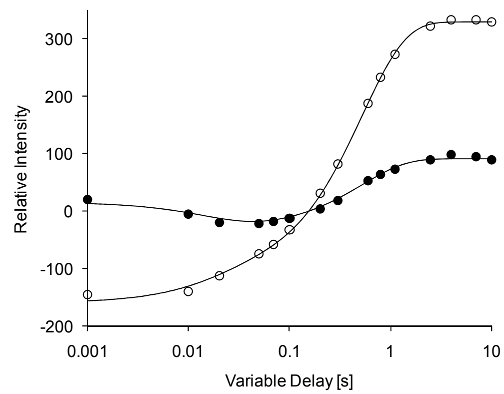

e.

Figure S22 Plots of peak intensities against the variable delays from the ^{1}H NMR magnetization transfer experiments measured at different free HTTA concentrations to study the TTA exchange between $Eu(TTA)_3TBP$ and free HTTA (at 268 K in $CDCl_3$). The solid lines are generated by a non-linear fitting procedure of the experimental data. The free HTTA concentrations are (a) 34.8, (b) 69.1, (c) 130.7, (d) 180.1 and (e) 191.7 mM. The $Eu(TTA)_3TBP$ concentration is 19.3 mM, the total TBP concentration is 24.8 mM.

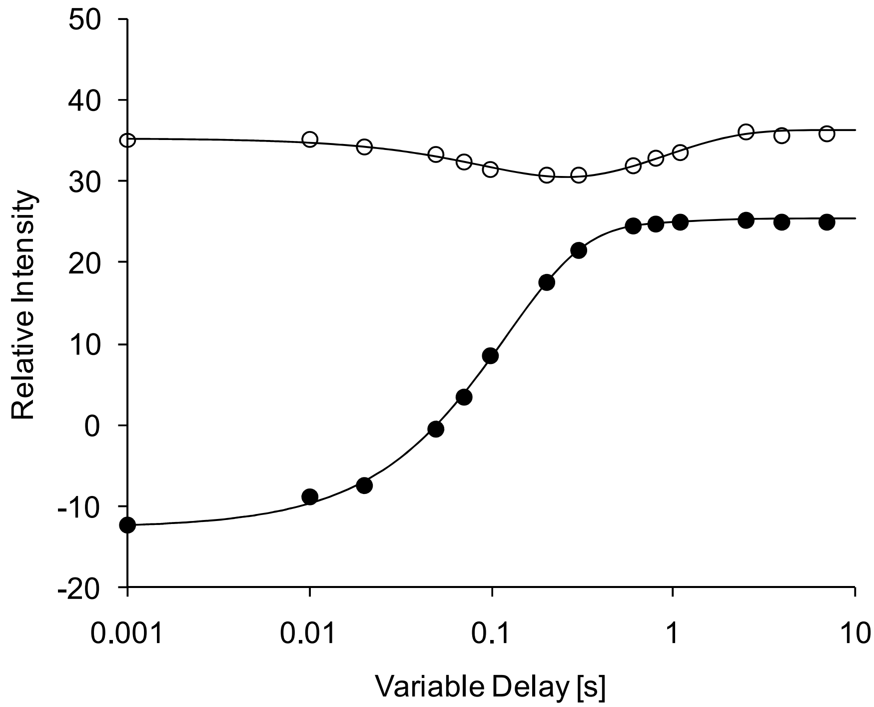

Figure S23 Plots of peak intensities against the variable delays from the ^1H NMR magnetization transfer experiment measured at high TBP concentration to study its effect on the intermolecular TTA exchange (at 268 K in $CDCl_3$). The Eu(III) concentration is 16.5 mM, the free HTTA concentrations is 72.9 mM and the total TBP concentration is 157.2 mM.