Supporting information

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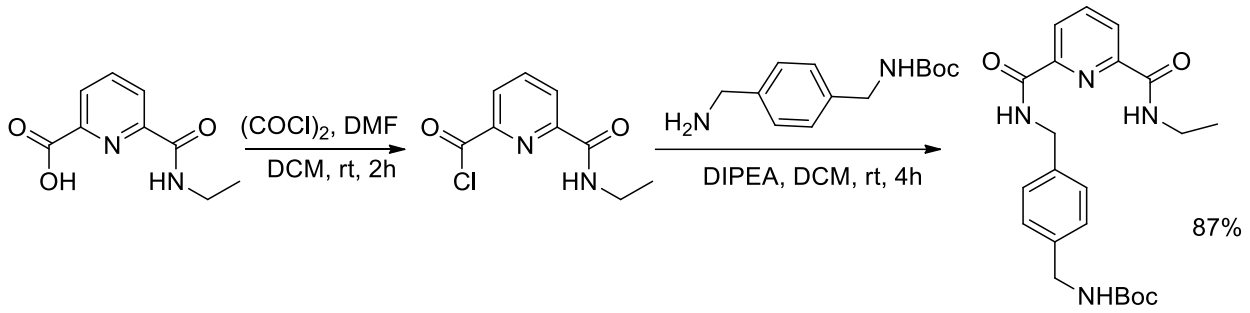
Synthesis of Receptors



Scheme S1. Synthesis of tert-butyl-4-((6-(ethylcarbamoyl)picolinamido)methyl)benzylcarbamate.

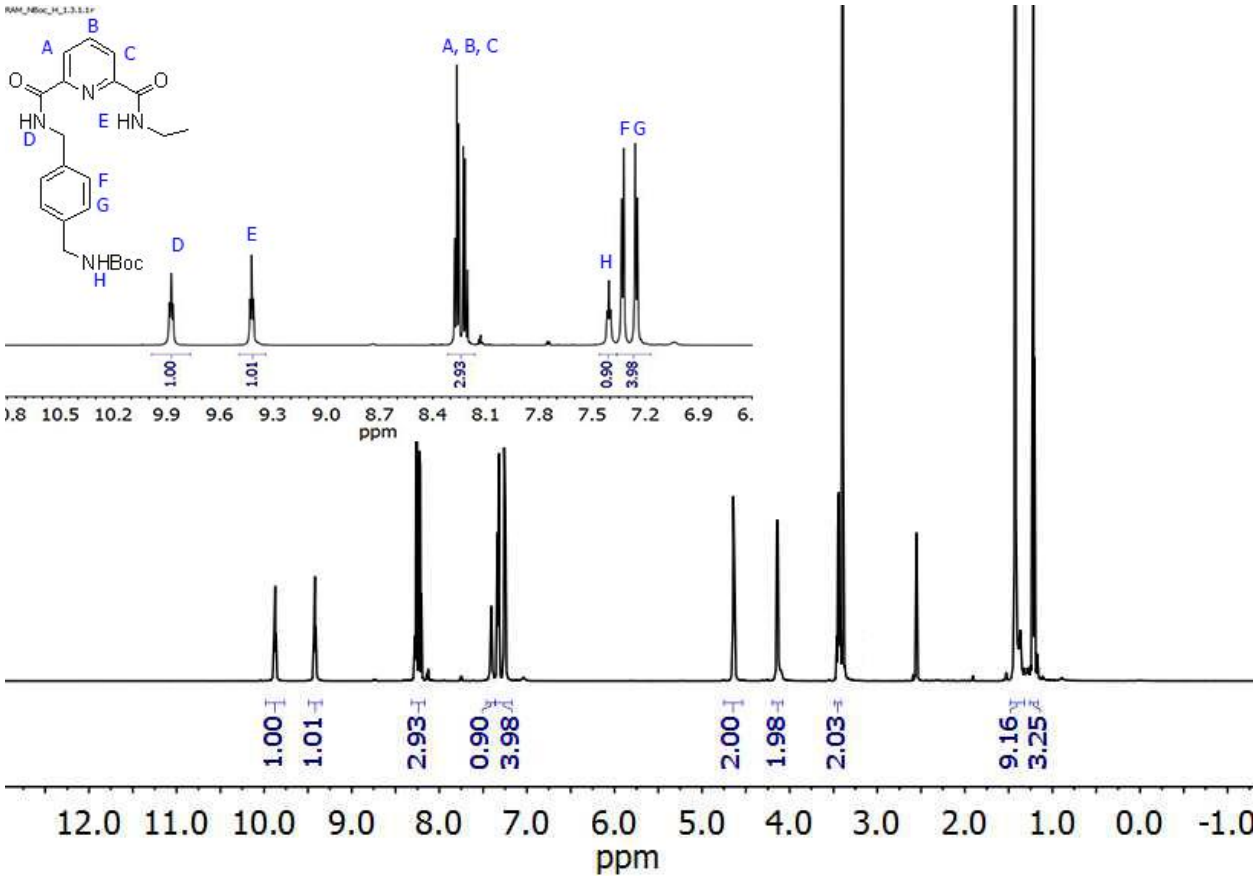


Figure S1. ^{1}H NMR spectrum of the Boc-protected compound **4.**

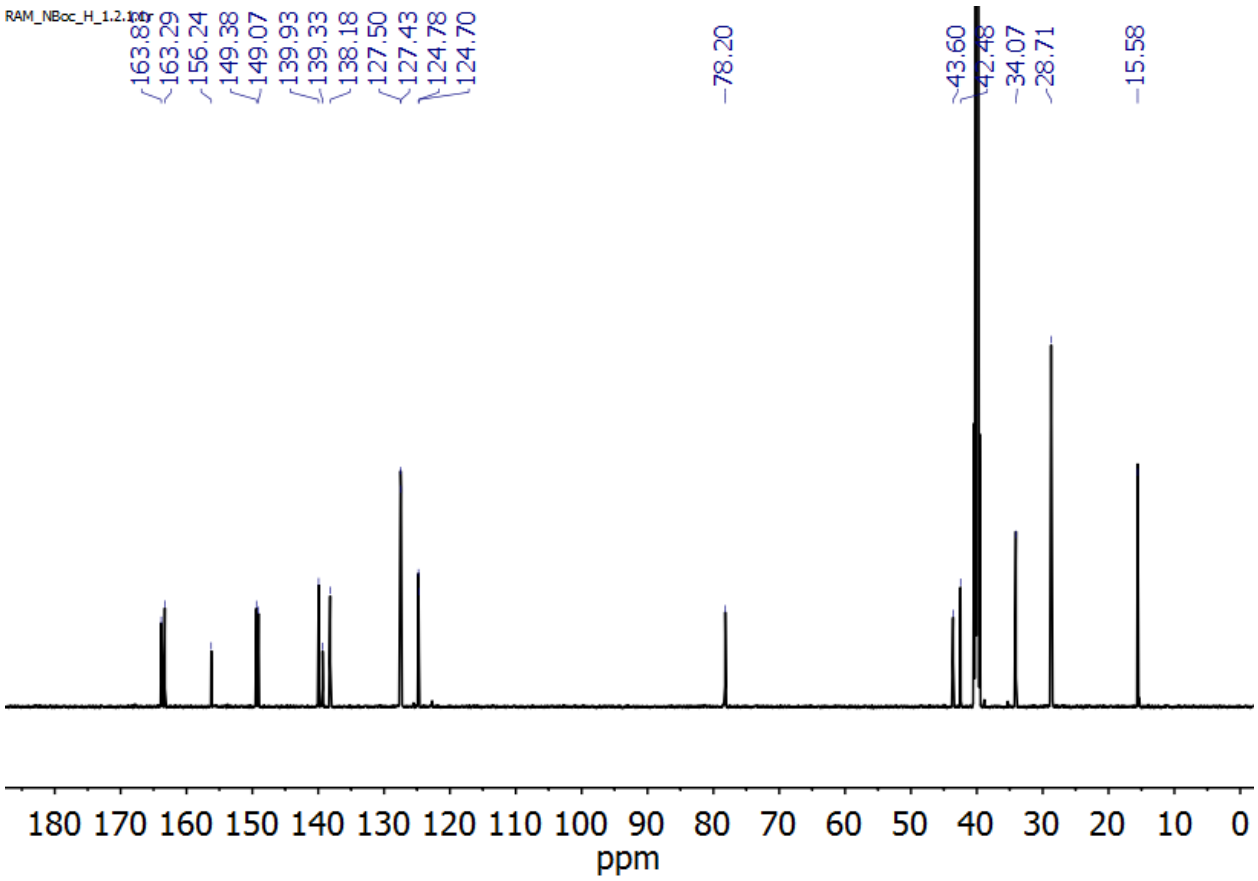
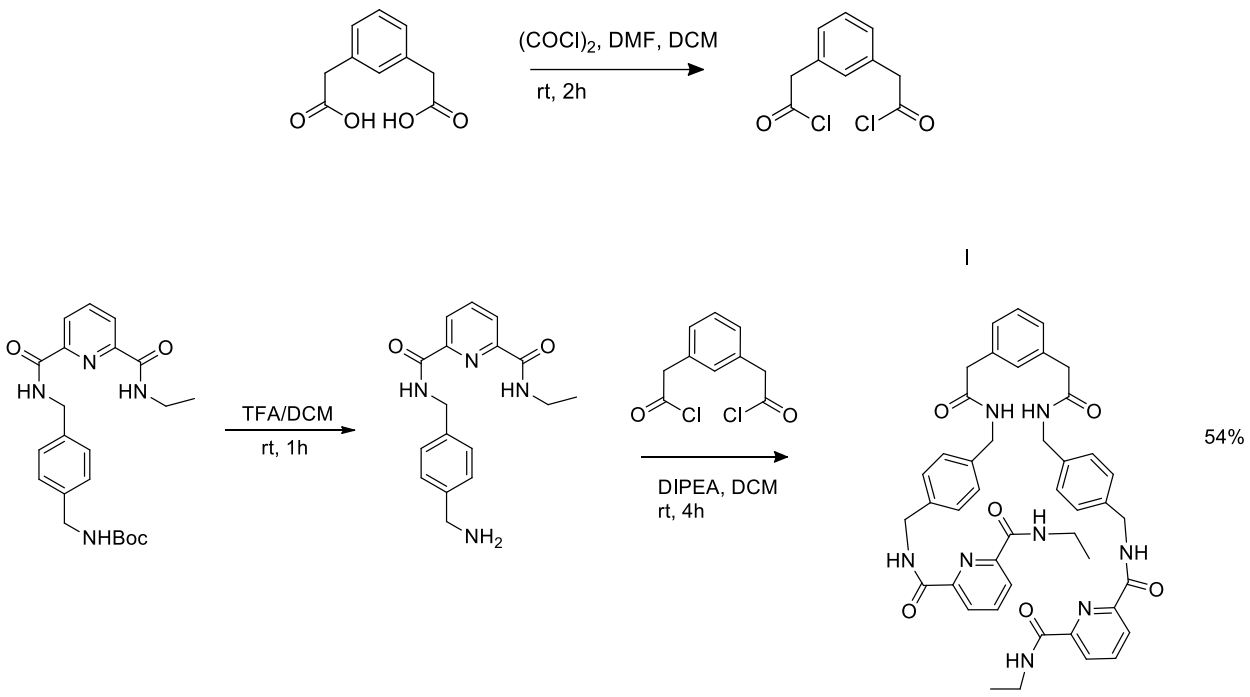


Figure S2. ^{13}C NMR spectrum of the Boc-protected compound **4.**



Scheme 2. Synthesis of Receptor **1.**

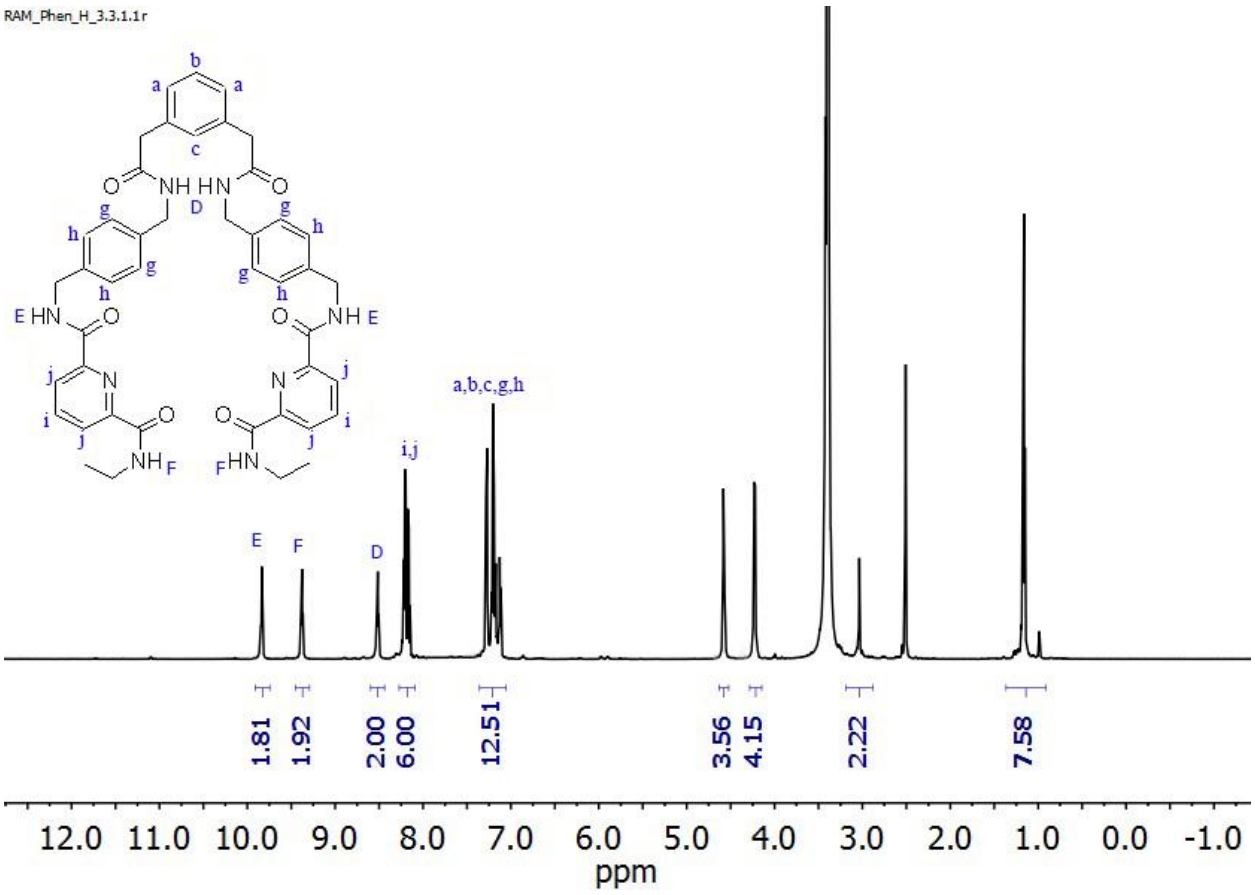


Figure S3. ^{1}H NMR spectrum of receptor **1.**

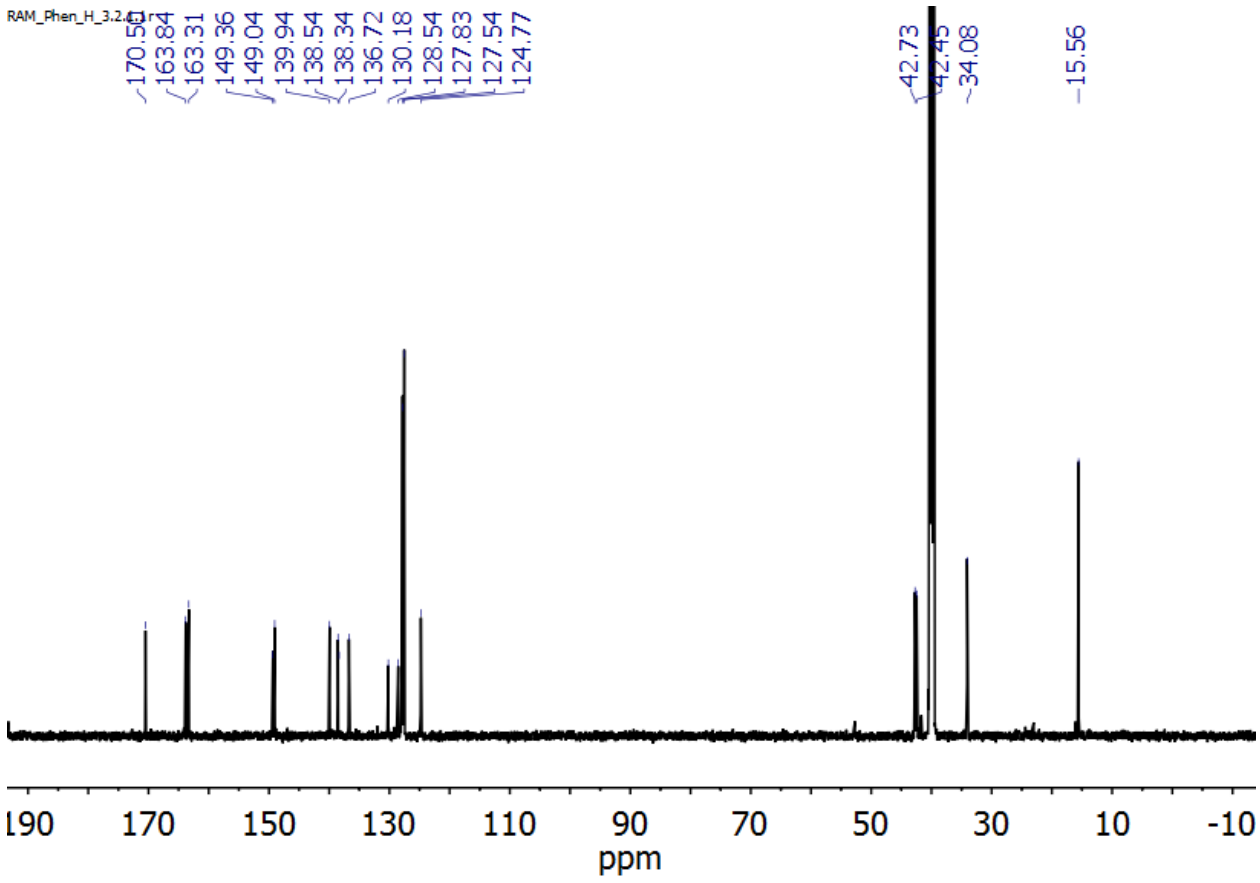
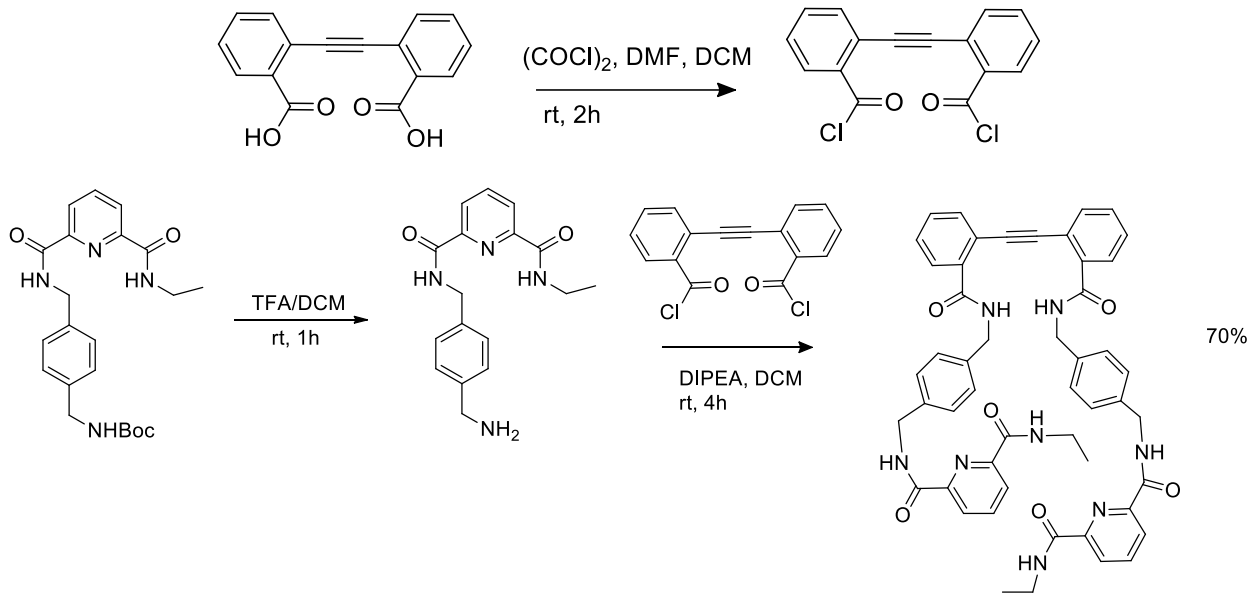


Figure S4. ^{13}C NMR spectrum of receptor **1.**



Scheme S3. Synthesis of receptor **2.**

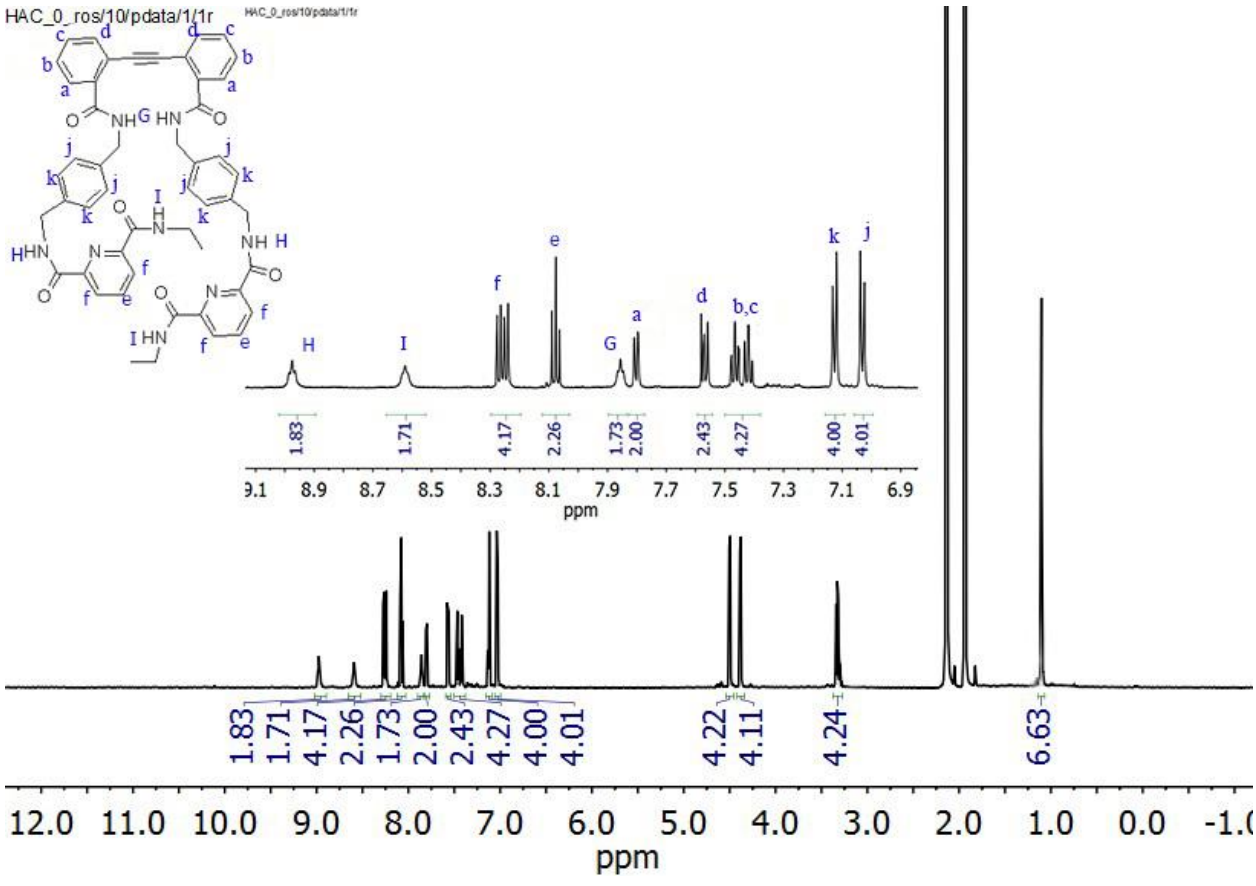


Figure S5. ^{1}H NMR spectrum of receptor **2.**

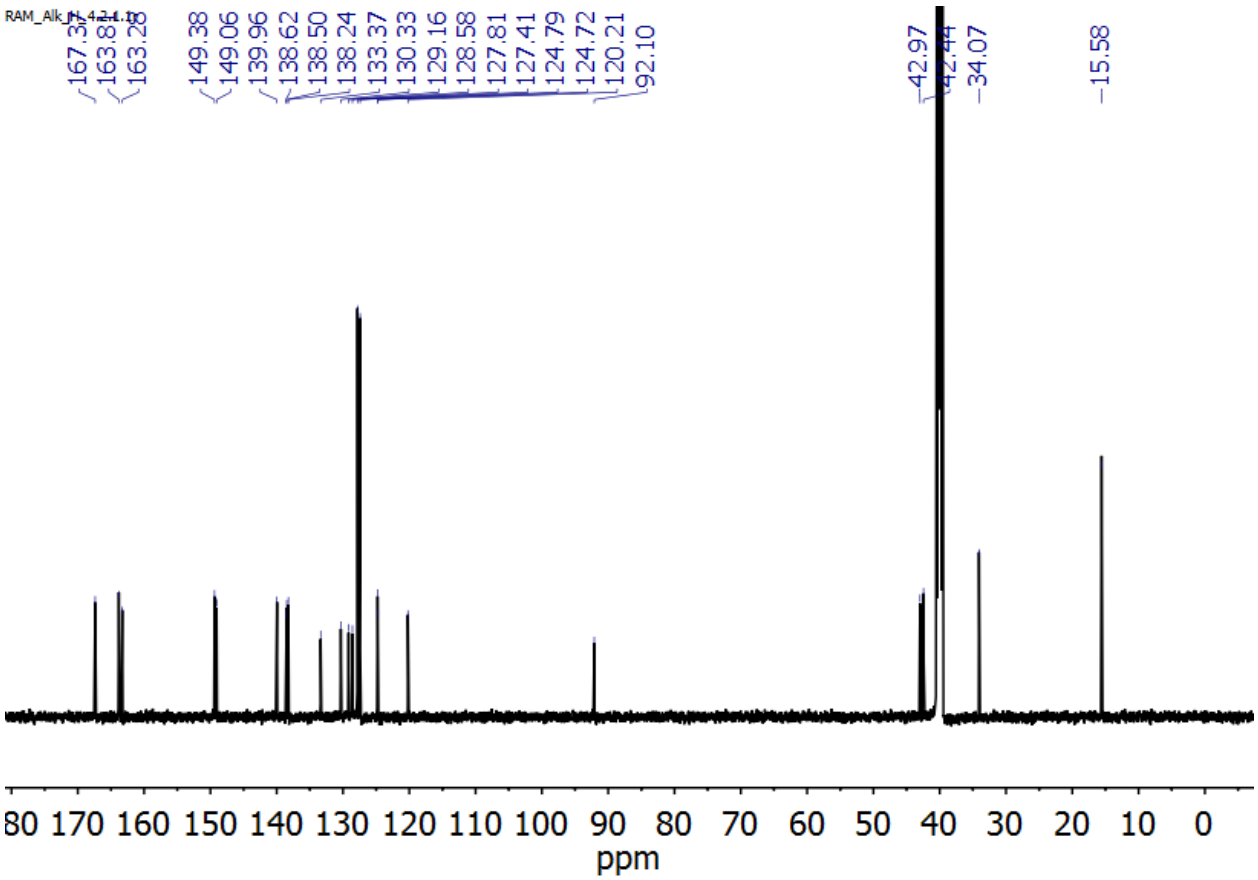
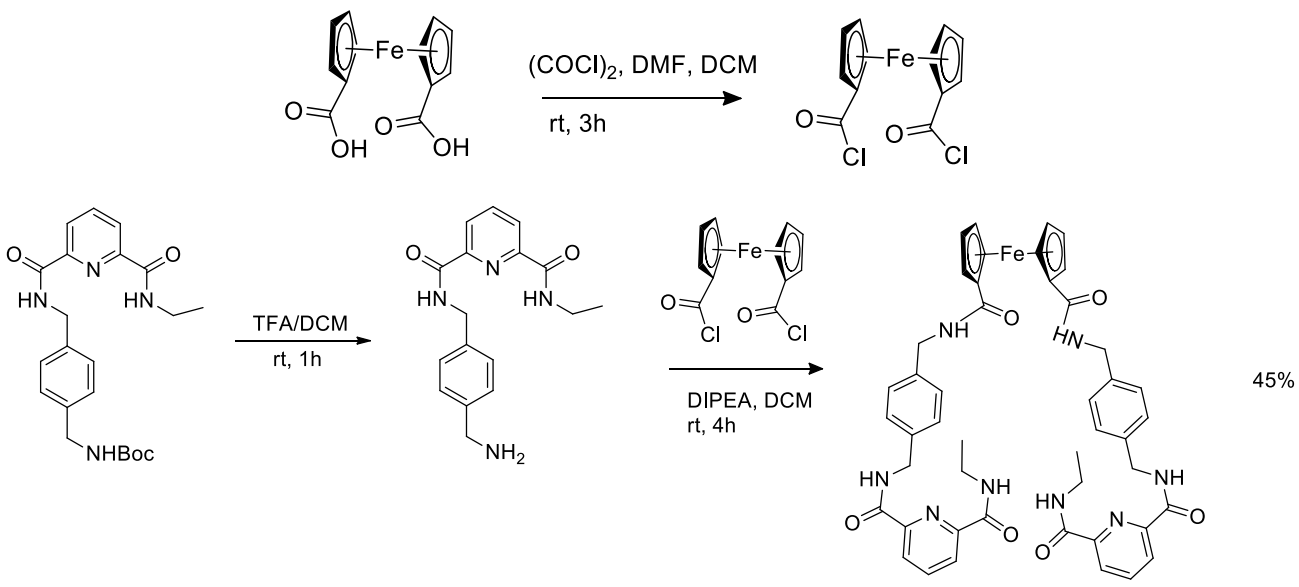


Figure S6. ^{13}C NMR spectrum of receptor **2.**



Scheme S4. Synthesis of receptor **3.**

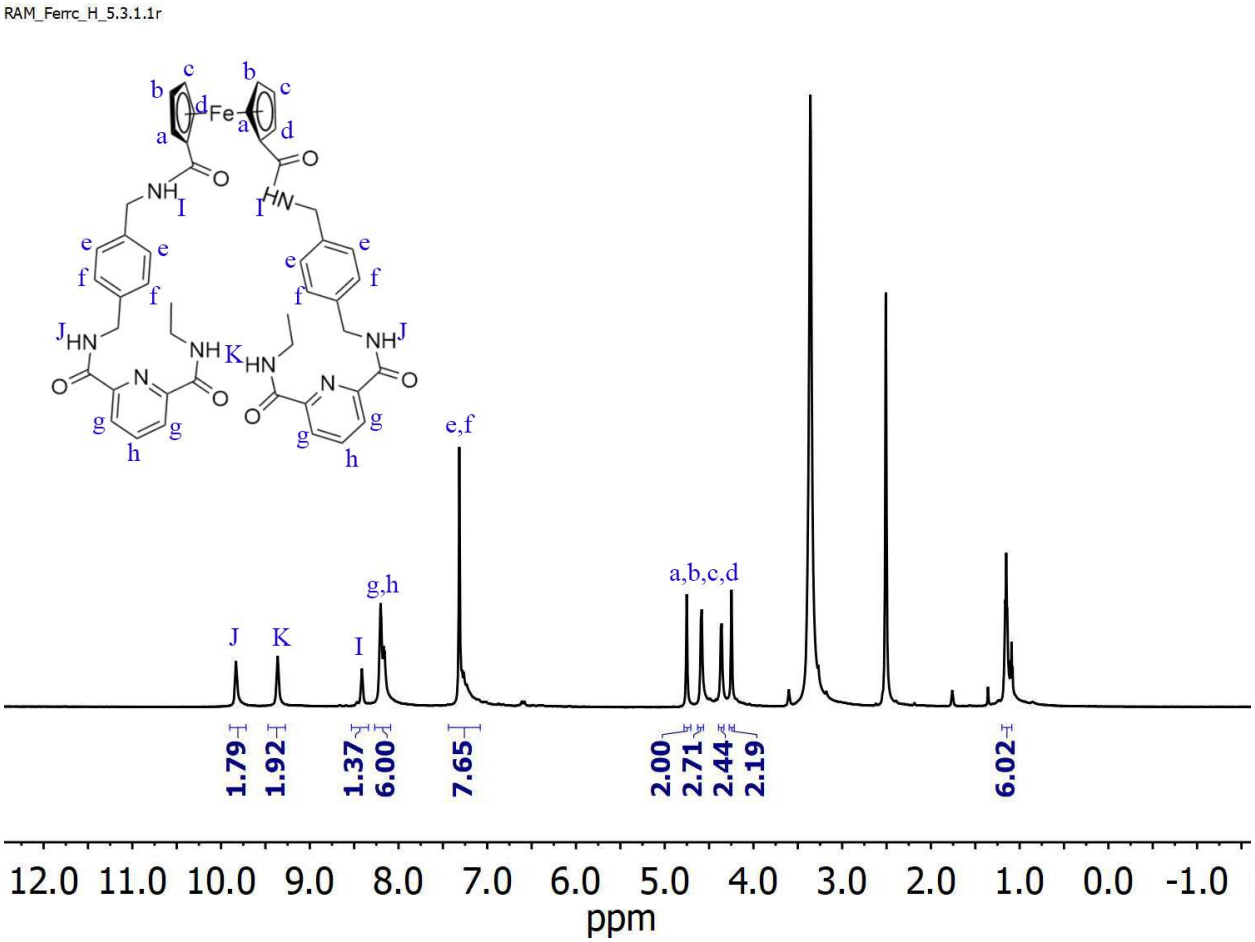


Figure S7. ^{13}C NMR spectrum of receptor **3.**

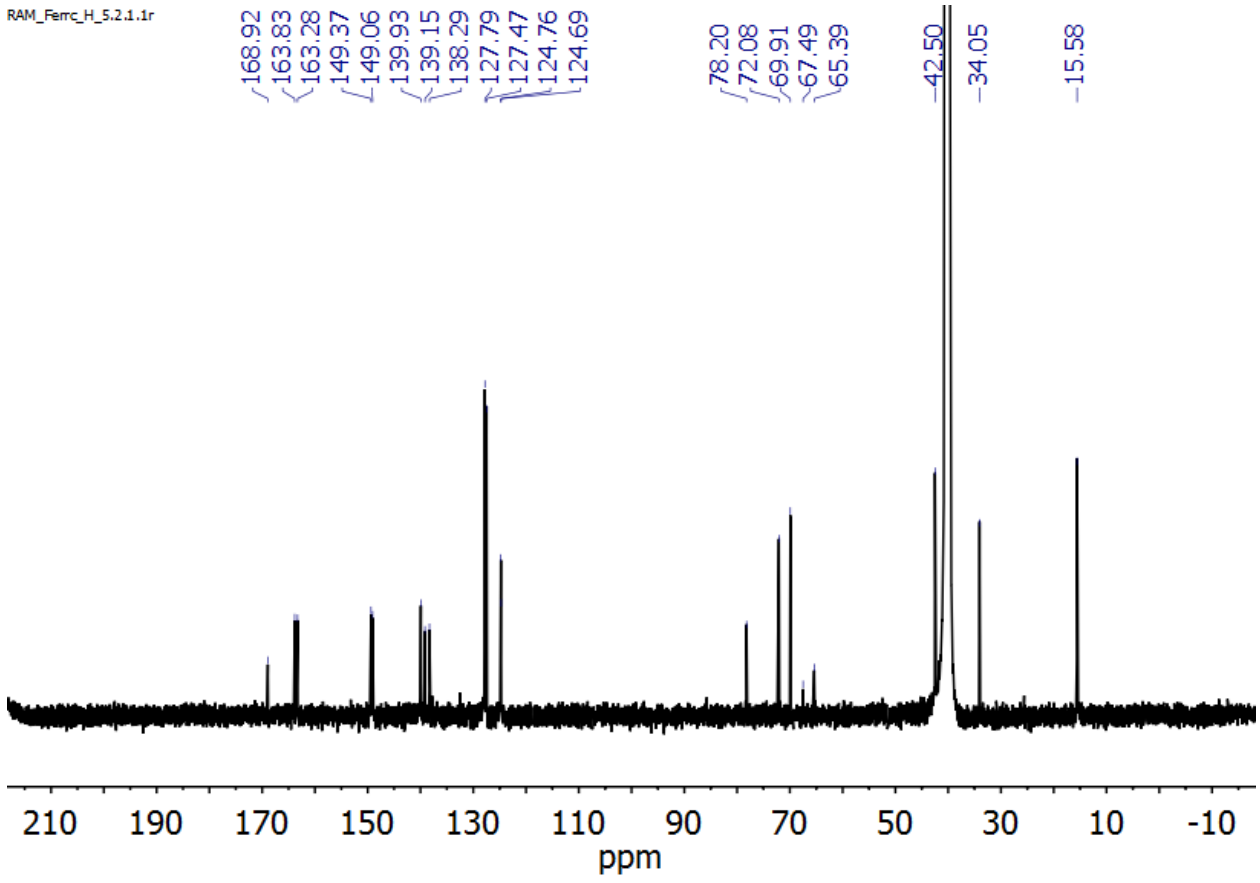


Figure S8. ^{13}C NMR spectrum of receptor **3.**

2D NMR spectra of receptor 2

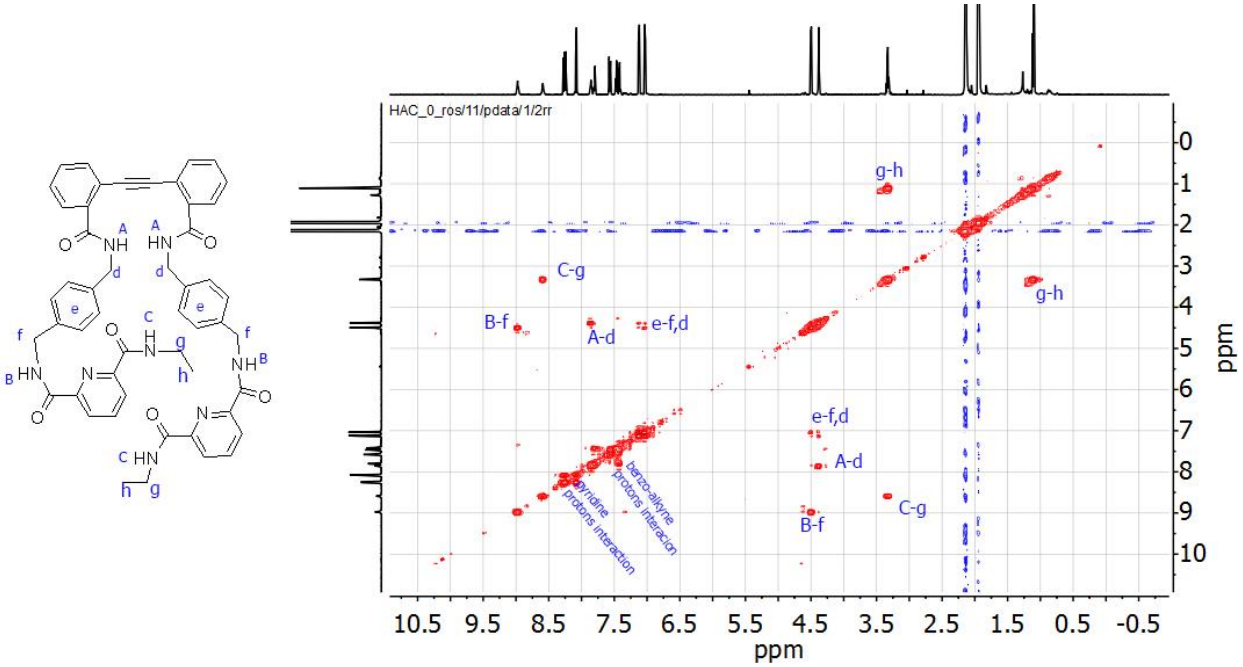


Figure S9. ^{1}H-^{1}H COSY spectrum of receptor **2.**

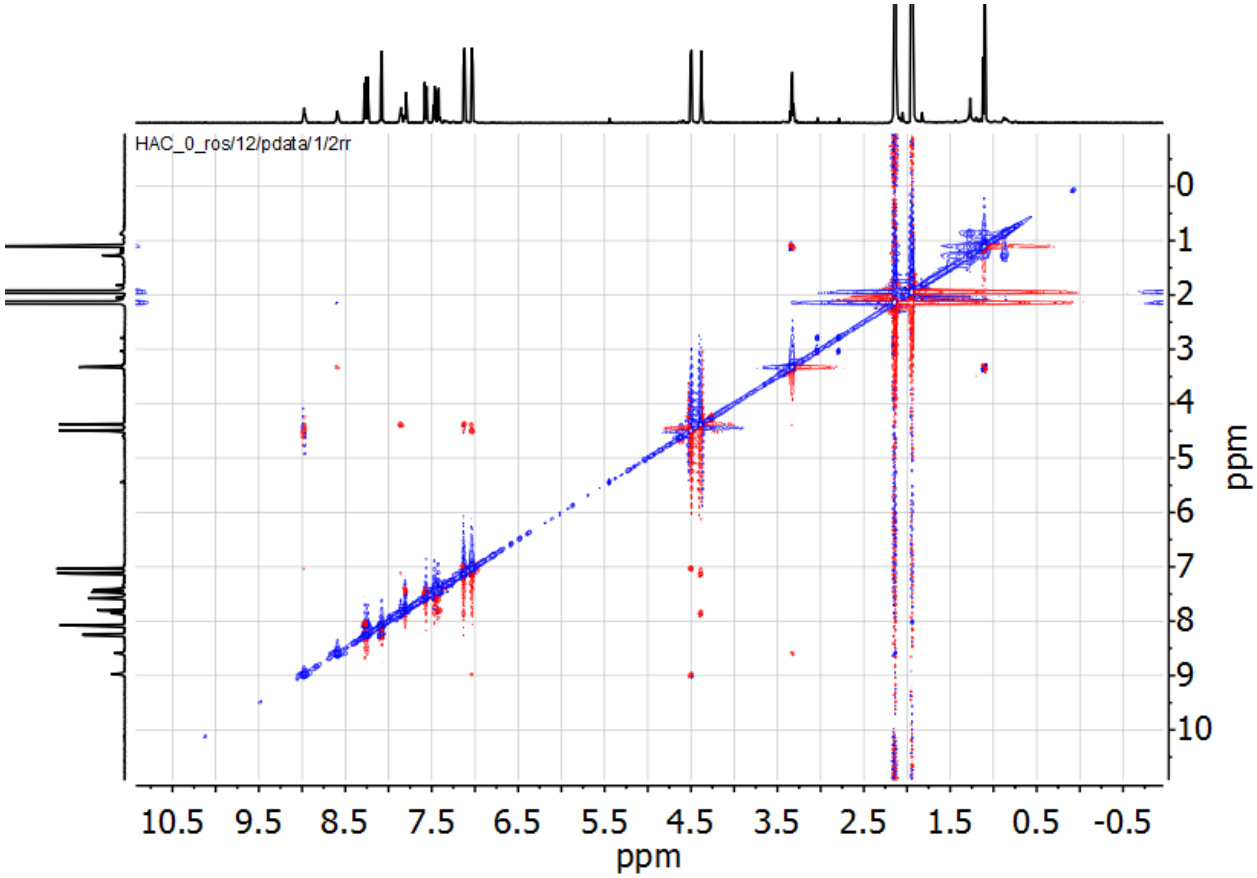
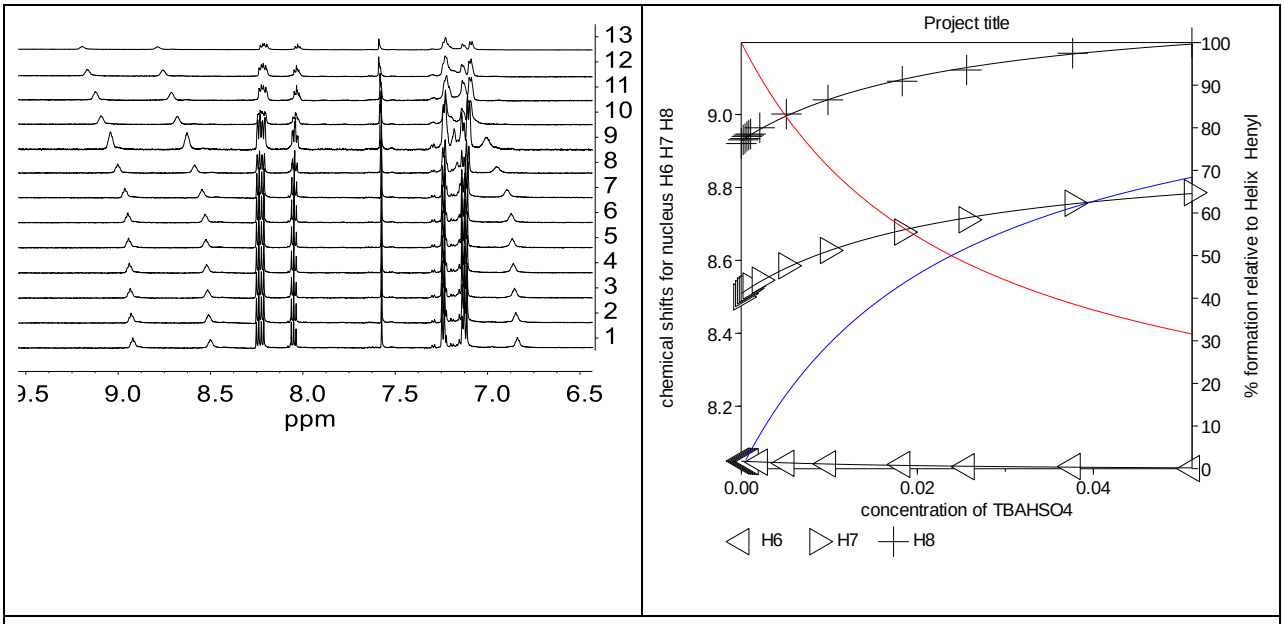


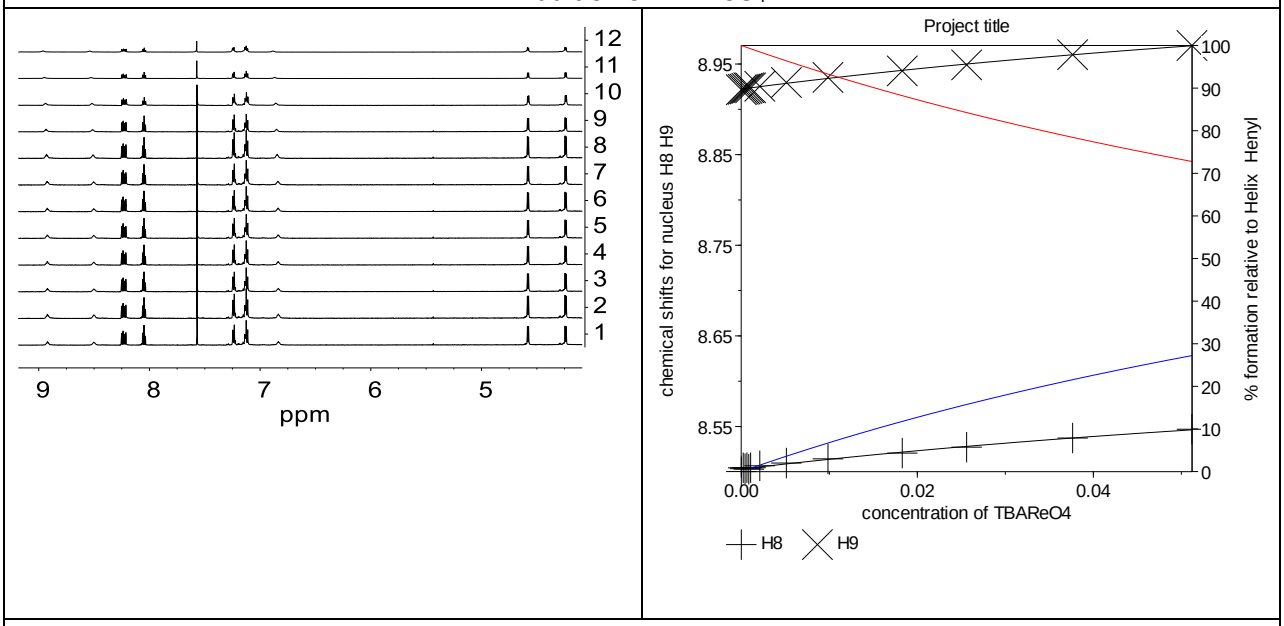
Figure S10. ^{1}H-^{1}H ROESY spectrum of receptor **2.**

NMR titrations

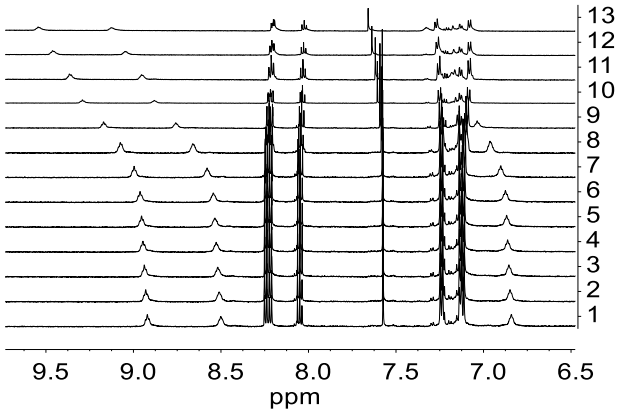
Table 1. Proton shifts observed during NMR titration experiments of Receptor **1** with anions in CH_3CN (8% $CHCl_3$) together with the fitting graphics of the aromatic and NH protons, which were exported from the HypNMR program.

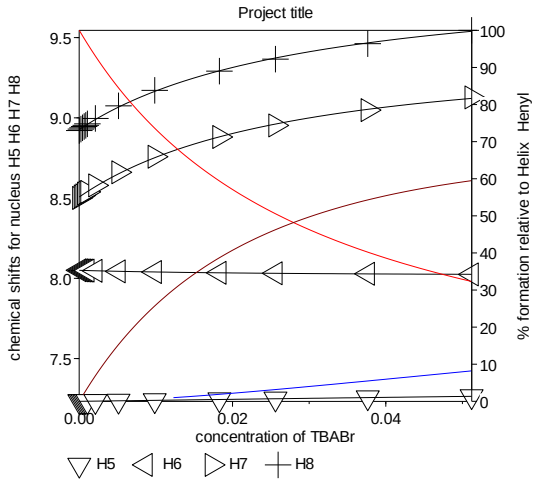


Addition of $TBAHSO_4$

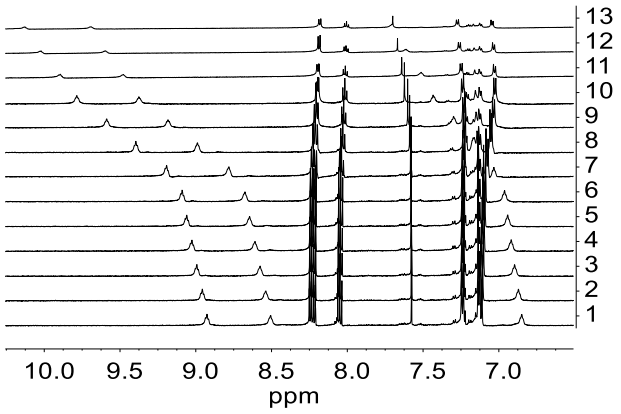


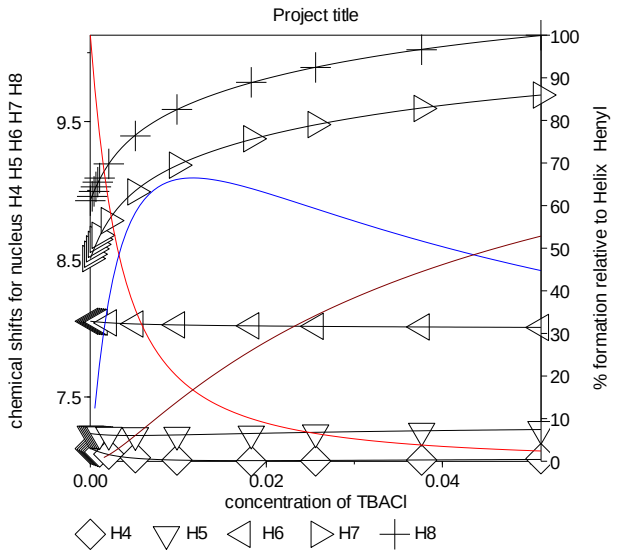
Addition of $TBAReO_4$



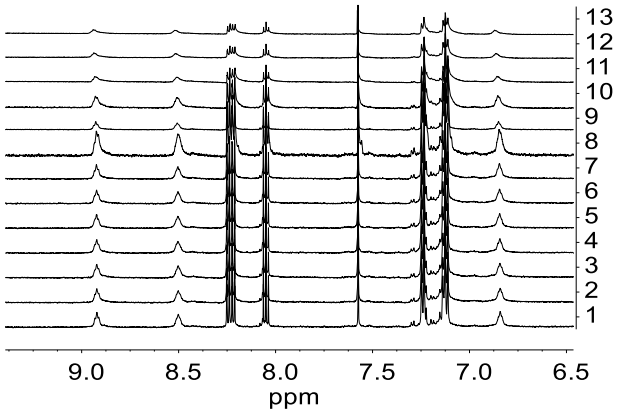


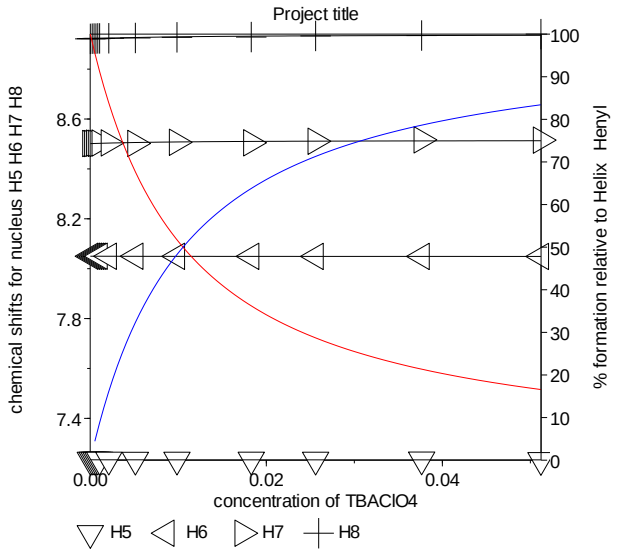
Addition of TBABr



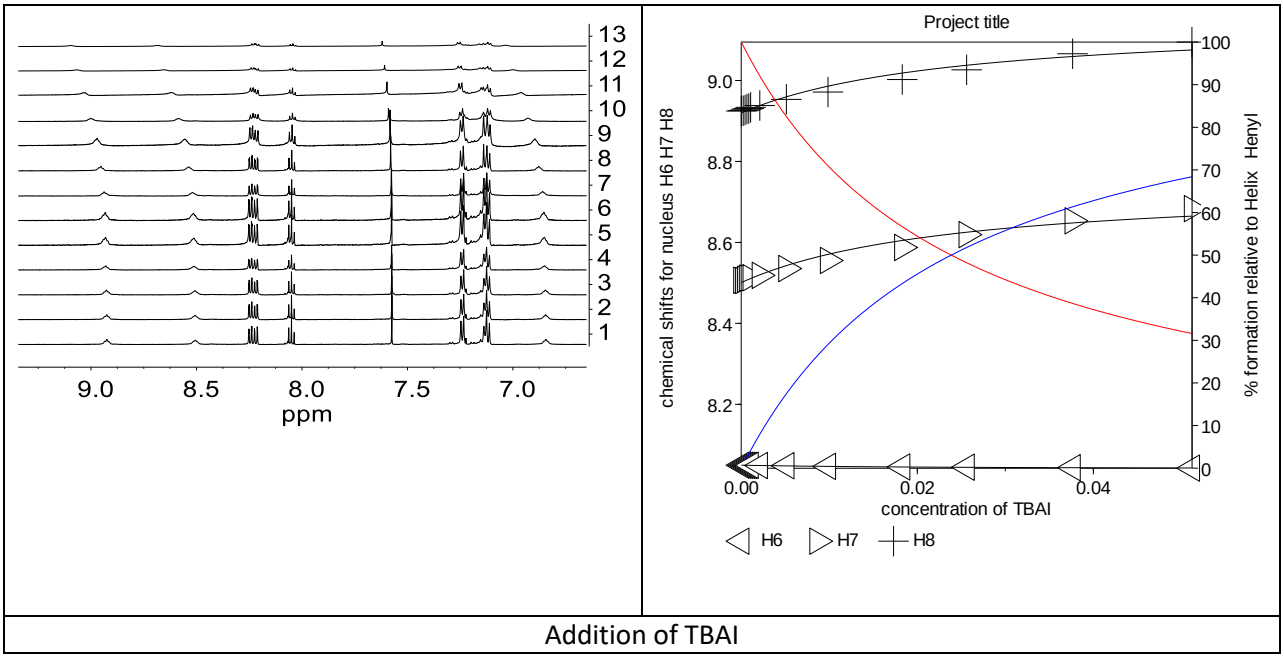


Addition of TBACl



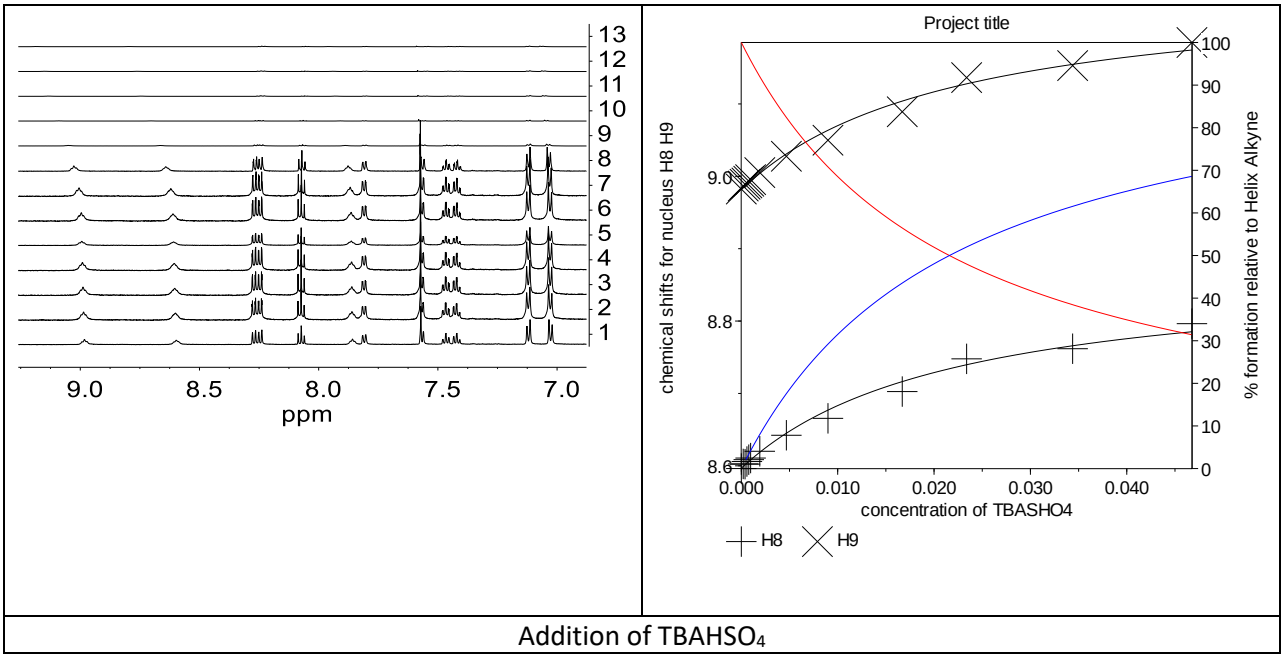


Addition of $TBAClO_4$

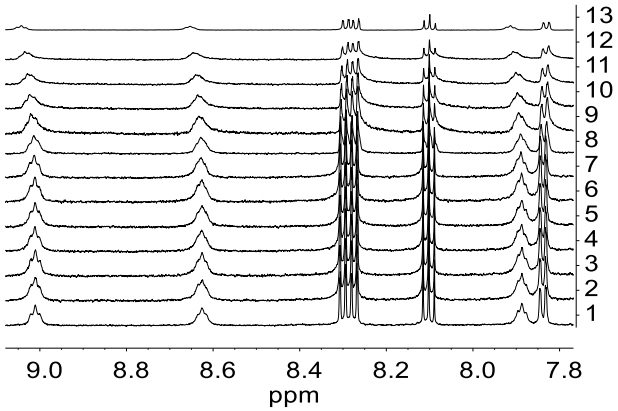


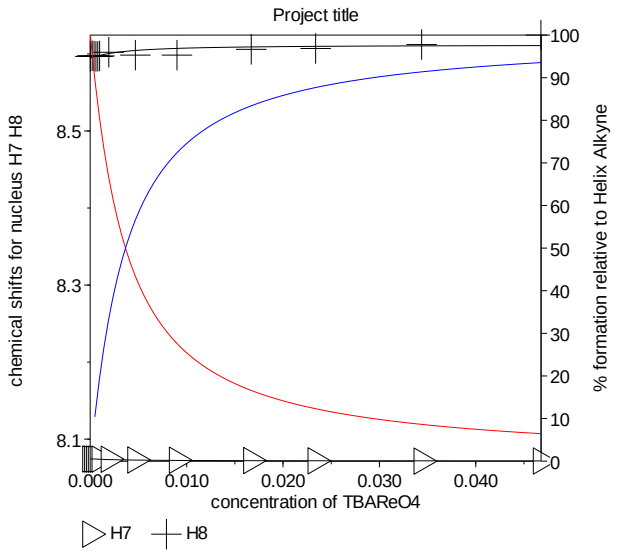
Addition of TBAI

Table 2. Proton shifts observed during NMR titration experiments of Receptor **2** with anions in CH_3CN (8% $CHCl_3$) together with the fitting graphics of the aromatic and NH protons, which were exported from the HypNMR program.

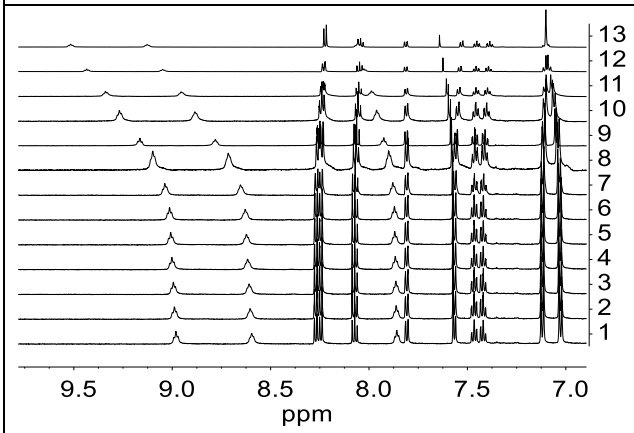


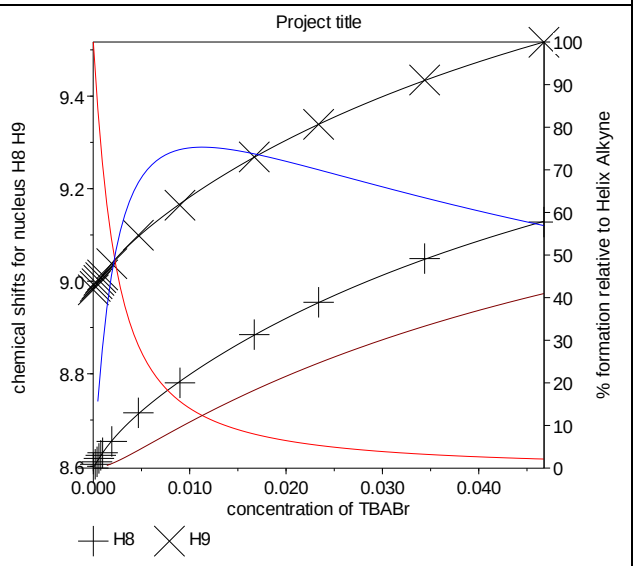
Addition of $TBAHSO_4$





Addition of $TBAReO_4$





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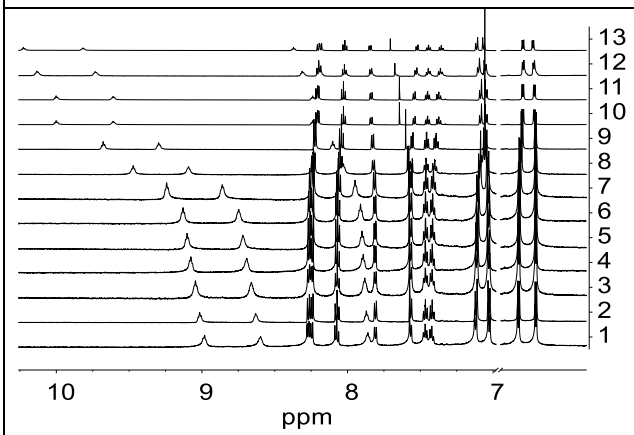
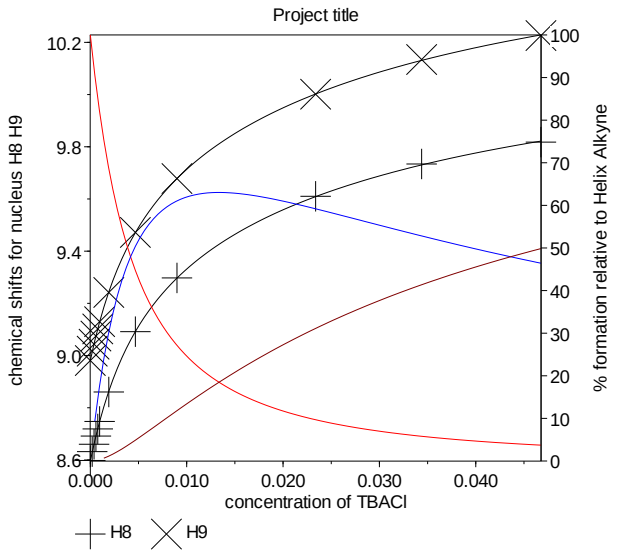




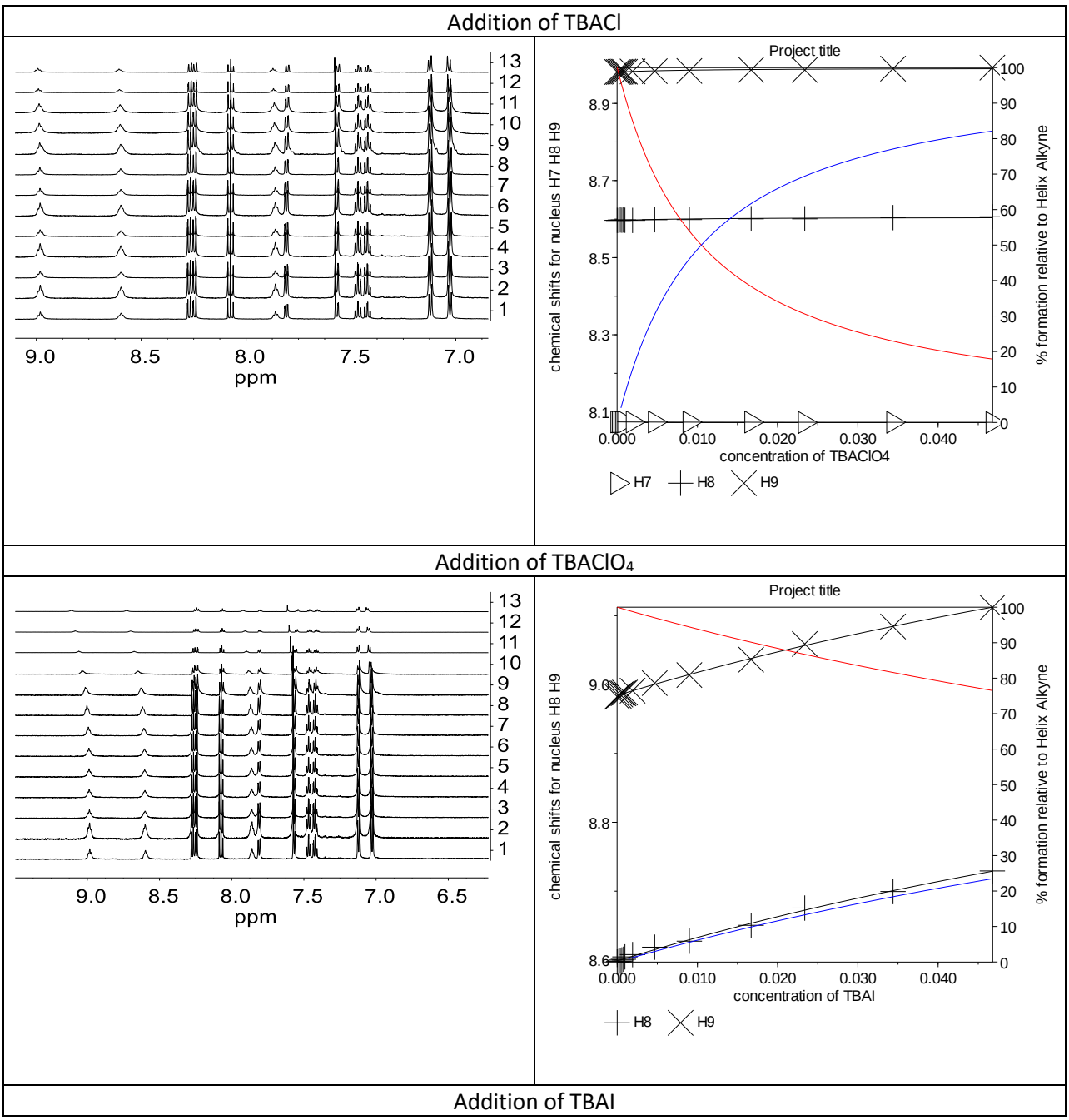
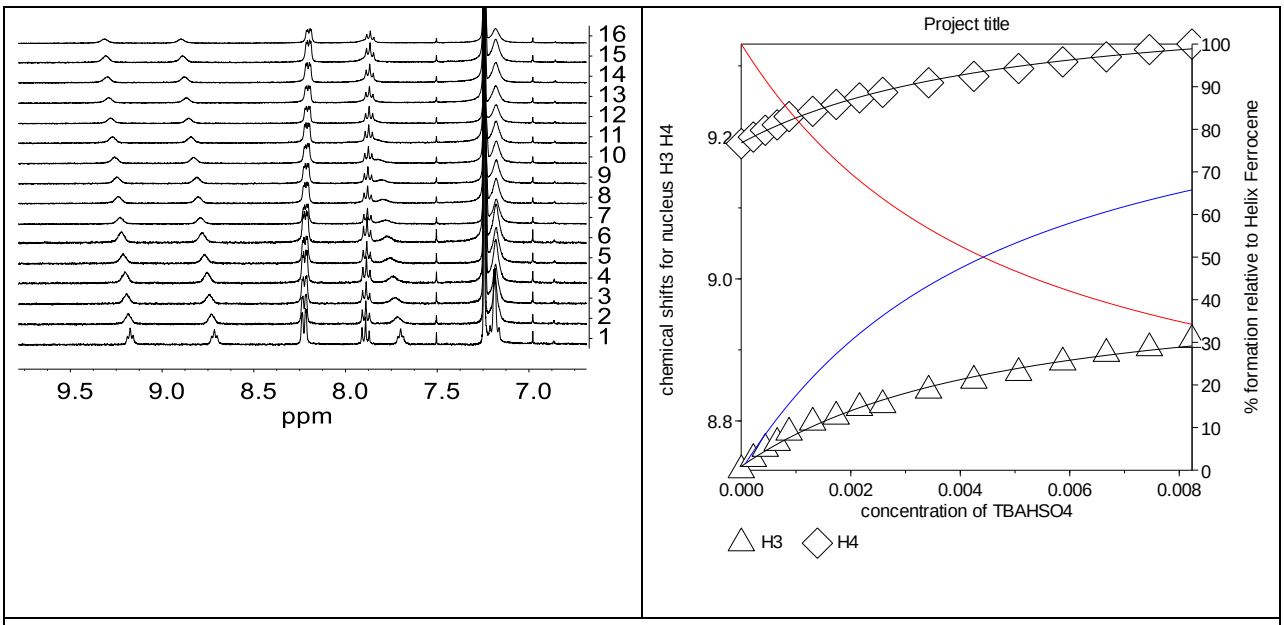
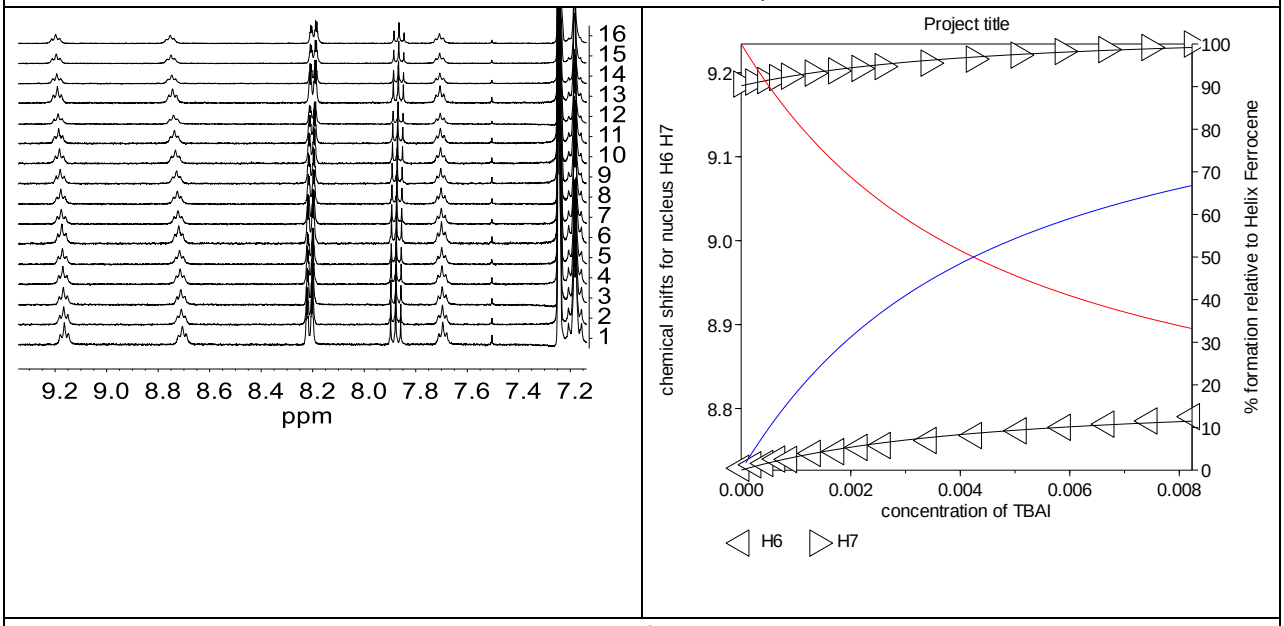


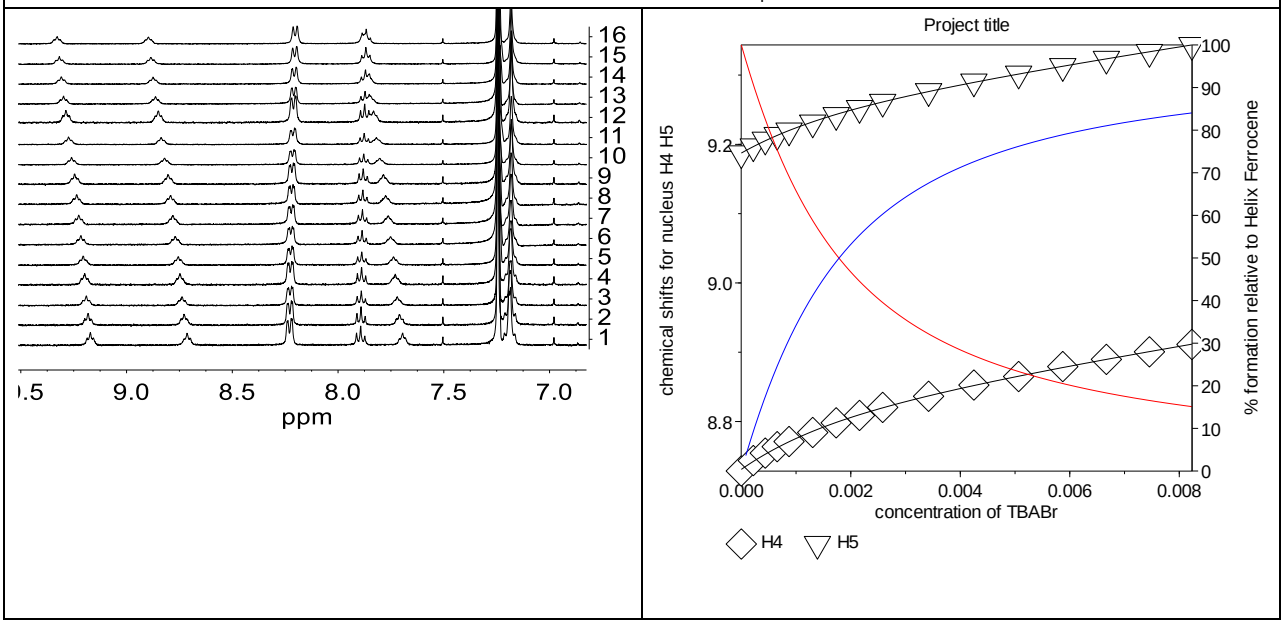
Table 3. Proton shifts observed during NMR titration experiments of Receptor **3** with anions in CH_3CN (8% $CHCl_3$) together with the fitting graphics of the aromatic and NH protons, which were exported from the HypNMR program.



Addition of $TBAHSO_4$



Addition of $TBAReO_4$



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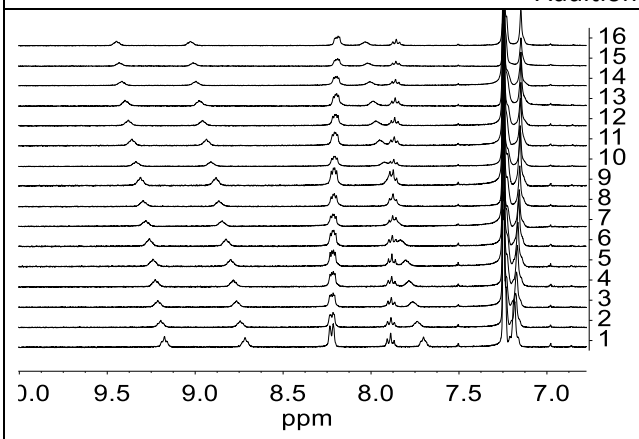
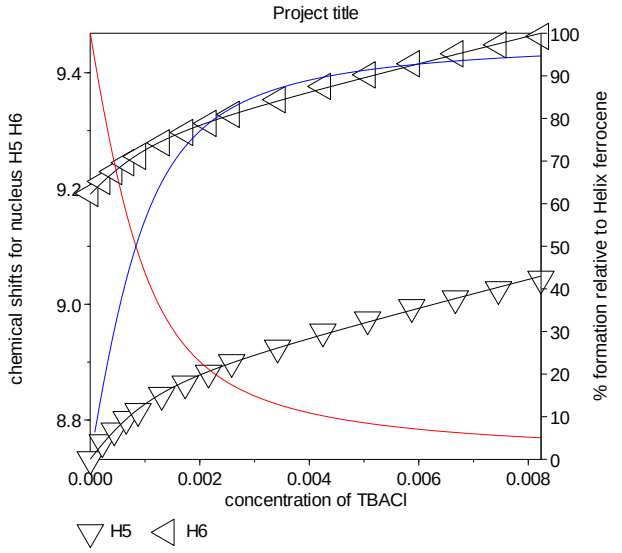
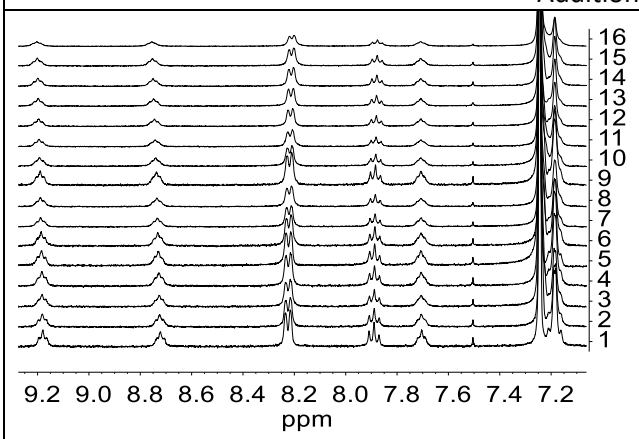
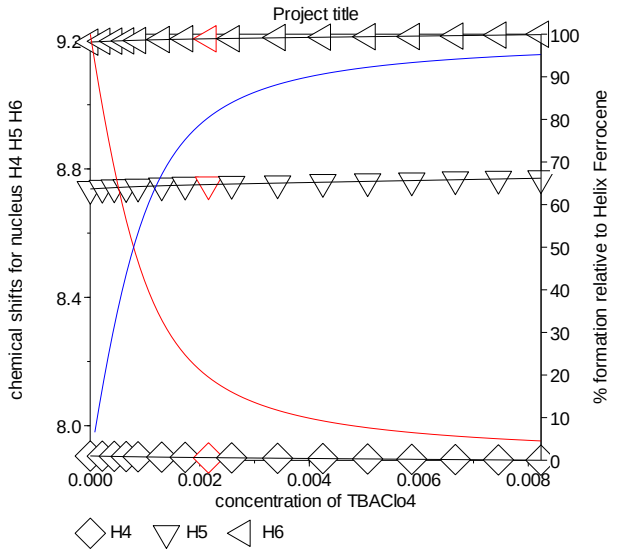


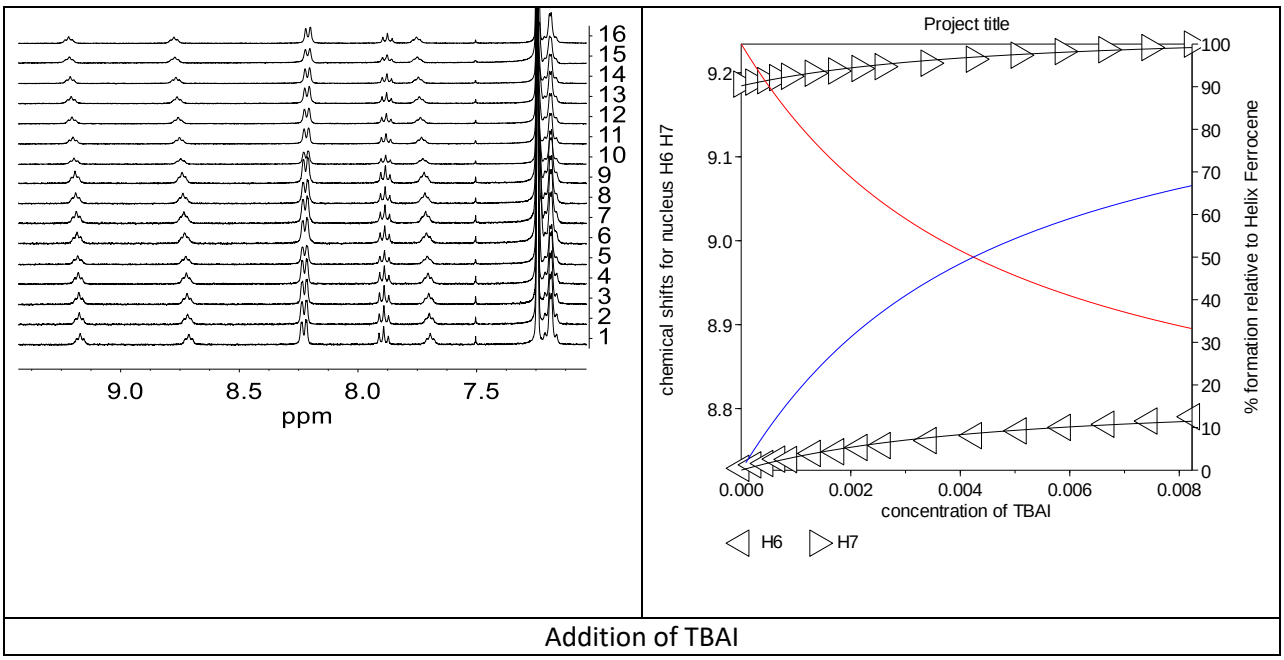


Addition of TBACl





Addition of $TBAClO_4$



Addition of TBAI

Dilution experiment.

The solutions of receptor **2** were prepared with different concentrations 10^{-4} to 10^{-6} M in CH_3CN solution containing 8% $CHCl_3$. The UV-Vis spectra were measured. As can be seen in **Figure S11**, the linear relationship was observed over this concentration range indicating the absence of self-aggregation.

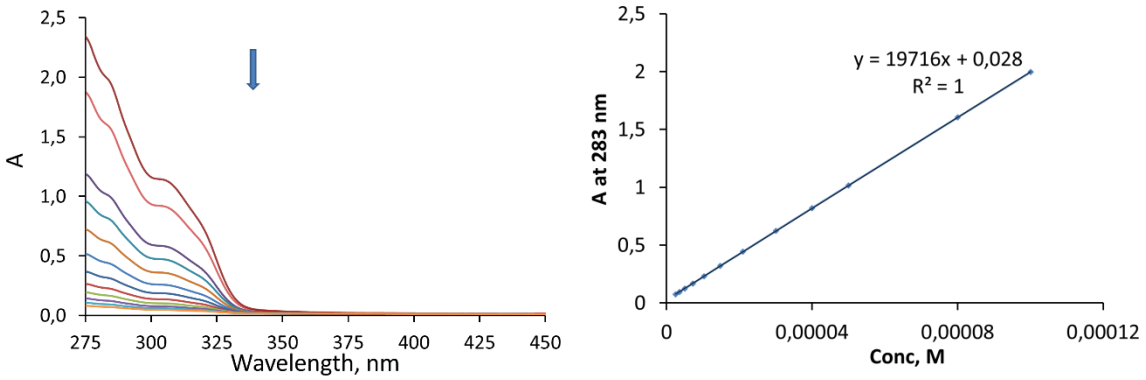


Figure S11. UV-Vis spectra of receptor 2 at different concentrations together with the linear fitting analysis.

UV-Vis titrations.

Stock solutions of receptors with concentrations of 10^{-5} M in a 50 mM acetate buffer (5% DMSO) were prepared for UV-Vis binding studies. The titrant (sodium salt, 0.01M) was sequentially added to a 2 mL sample of the host stock solution in the spectrometric cell and the changes in the spectral features were monitored. The total number of data points was 20-40, depending on the stoichiometry of complexation; for a presumed 1:1 complex 20 points were usually measured. The resulting data was imported in HypSpec program[4] and the data was fitted to obtain stability constants with anions. Concentration of receptors is 10^{-5} M.

Single crystal X-ray analysis

Colouress and plate-like single crystals of **2** suitable for diffraction analyses were grown from methanol. A suitable crystal of **2** with measures of 0.6 × 0.4 × 0.15 mm^3 was selected and mounted in Krytox® on an Rigaku-Oxford Gemini S diffractometer by choosing graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at T = 125 K. The structure was solved by Direct Methods implemented within SHELXS-2013 [1] using the WinGX software platform [2]. All C- and N-bonded hydrogen atoms were refined using a riding model; the positions of all O-bonded hydrogen atoms were taken from Difference Fourier Maps and were refined with respective constraints. The model was refined by full-matrix least-squares procedures on F^2 with SHELXL-2013 [1] until convergence. In the solid state the asymmetric unit of **2** comprises two crystallographically independent molecules of **2**, which interact with co-crystallized MeOH and H_2O molecules by means of hydrogen bond interaction. The overall formula of the single crystals of **2** used for crystallographic studies amounts to [(**2**)$_2$·3MeOH·5H_2O]. CCDC-2032743 contain the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A6*, 112–122.

[2] L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849–854.

DFT calculations

Molecular modeling calculations were performed using the DFT program "PRIRODA".[3] A PBE function that includes the electron density gradient was used. The TZ2p-atomic basis sets of grouped Gaussian functions were used to solve the Kohn—Sham equations. The criterion for convergence was a difference below 0.01 kcal/mol/Angstrom in energy between two sequential structures. Various stationary points on the potential energy surface (PES) were determined from analytical calculations of the second energy derivatives (Hessian matrixes).