Supplementary Information

Di-platinum complexes containing thiolato-urea ligands: structural and anion binding studies

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1. ^{1}H NMR titration of metallo-receptors with different anions

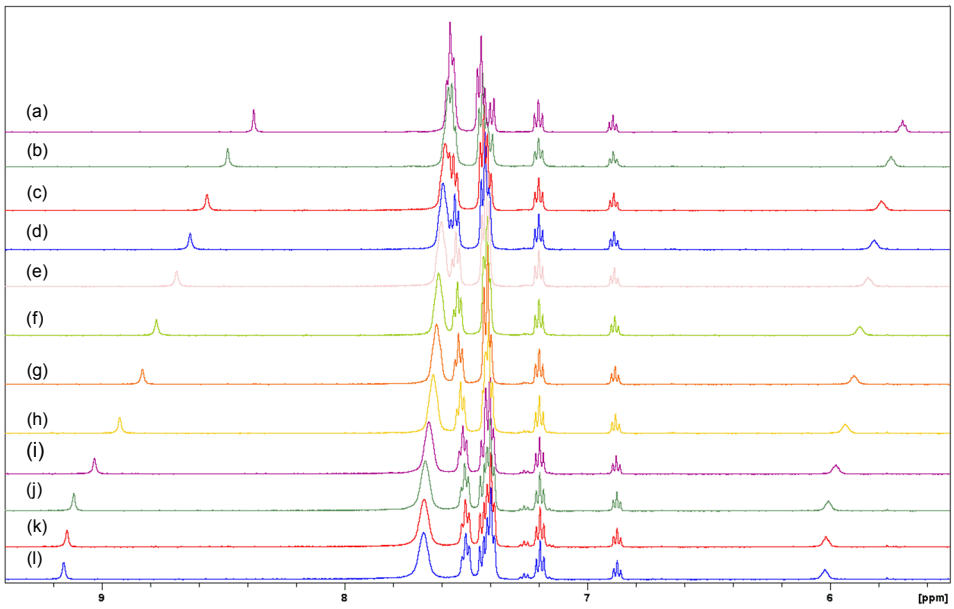


Figure S1. Partial ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **7** with *n*-$Bu_4N^+Cl^-$. The spectra were recorded after the addition of (a) 0.0, (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.3, (f) 1.8, (g) 2.4, (h) 3.5, (i) 5.4, (j) 7.9, (k) 10.0 and (l) 13.0 equivalents of Cl^-.

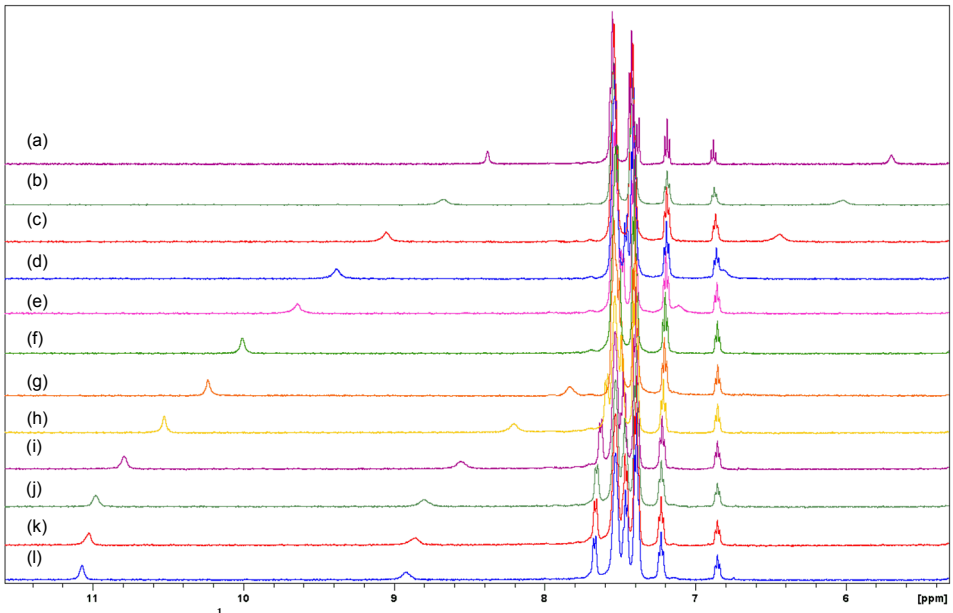


Figure S2. Partial ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **7** with *n*-$Bu_4N^+(CH_3COO^-)$. The spectra were recorded after the addition of (a) 0.0, (b) 0.3, (c) 0.6, (d) 0.9, (e) 1.2, (f) 1.8, (g) 2.3, (h) 3.4, (i) 5.2, (j) 7.7, (k) 9.6 and (l) 11.9 equivalents of CH_3COO^-.

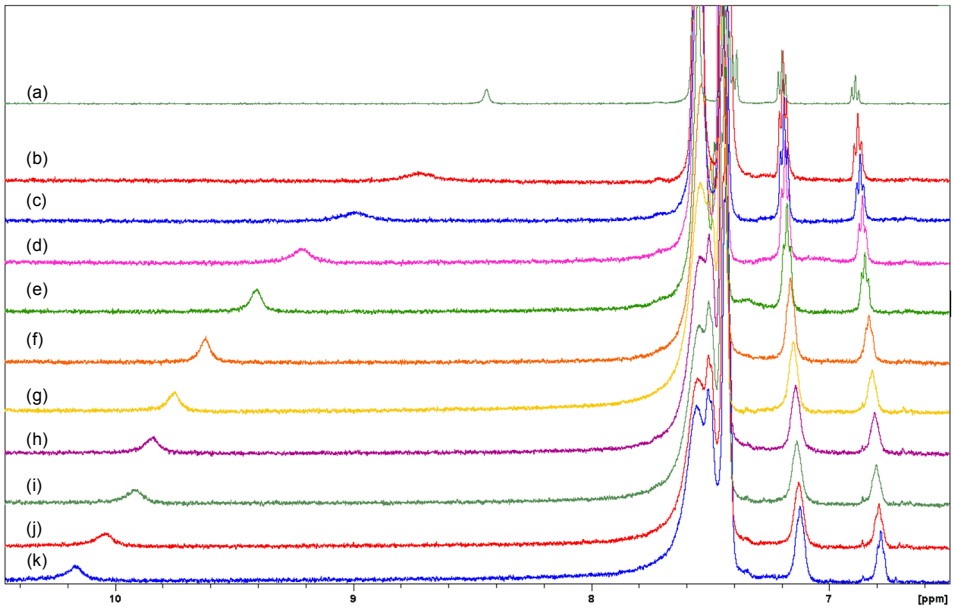


Figure S3. Partial ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **7** with *n*-$Bu_4N^+(H_2PO_4^-)$. The spectra were recorded after the addition of (a) 0.0, (b) 0.3, (c) 0.7 (d) 0.9, (e) 1.0, (f) 1.5, (g) 1.9, (h) 2.3, (i) 2.7, (j) 3.5 and (k) 4.9 equivalents of $H_2PO_4^-$.

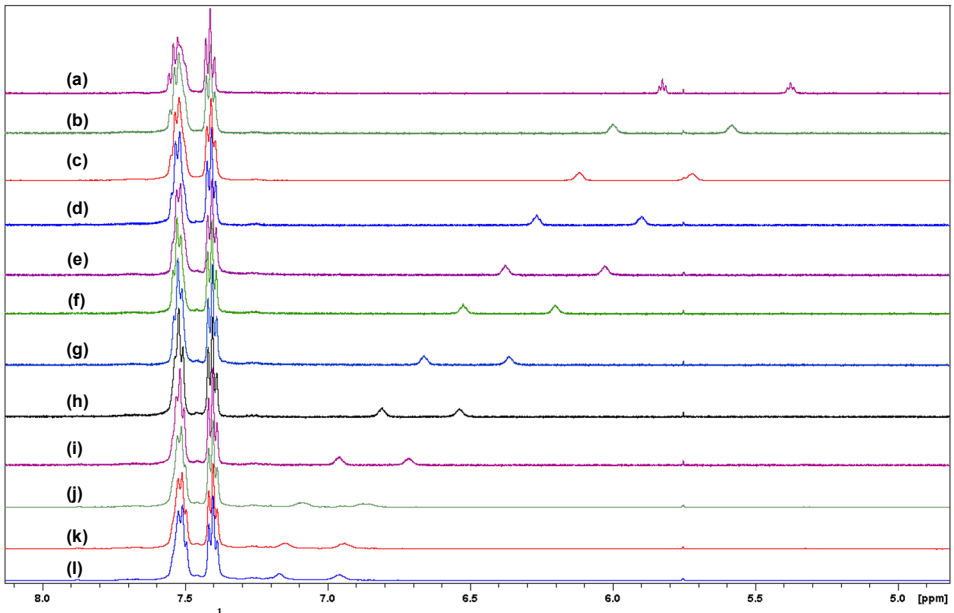


Figure S4. Partial ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **6** with *n*-$Bu_4N^+(CH_3COO^-)$. The spectra were recorded after the addition of (a) 0.0, (b) 0.4, (c) 0.7, (d) 1.0, (e) 1.4, (f) 2.0, (g) 2.8, (h) 4.0, (i) 5.9, (j) 8.6, (k) 10.6 and (l) 13.7 equivalents of CH_3COO^-.

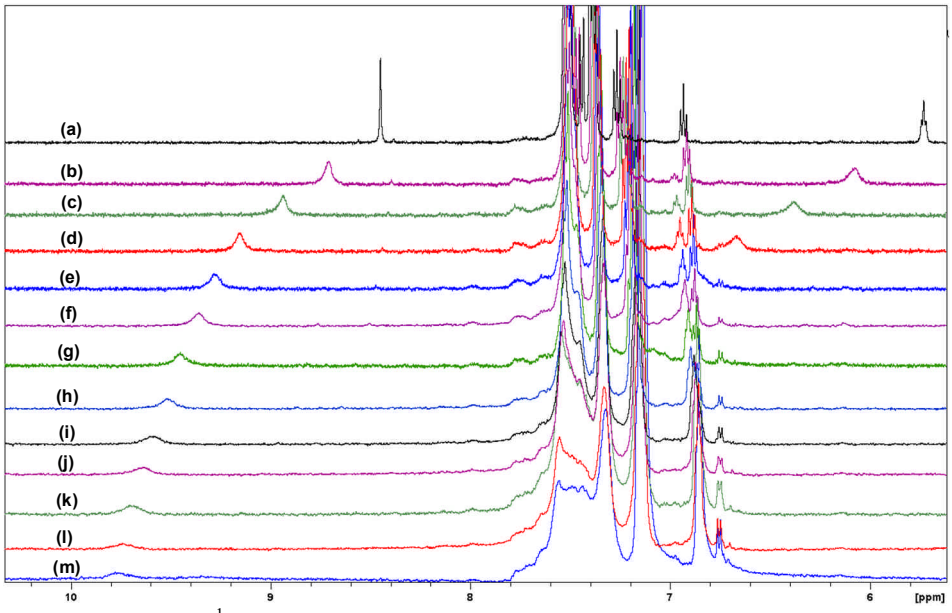


Figure S5. Partial ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **8** with *n*-$Bu_4N^+(P(=O)(OH)(OPh)O^-)$. The spectra were recorded after the addition of (a) 0.0, (b) 0.3, (c) 0.6, (d) 0.9, (e) 1.2, (f) 1.5, (g) 2.0, (h) 2.5, (i) 3.6, (j) 4.5, (k) 6.0, (l) 7.2 and (m) 9.3 equivalents of $[P(=O)(OH)(OPh)O]^-$.

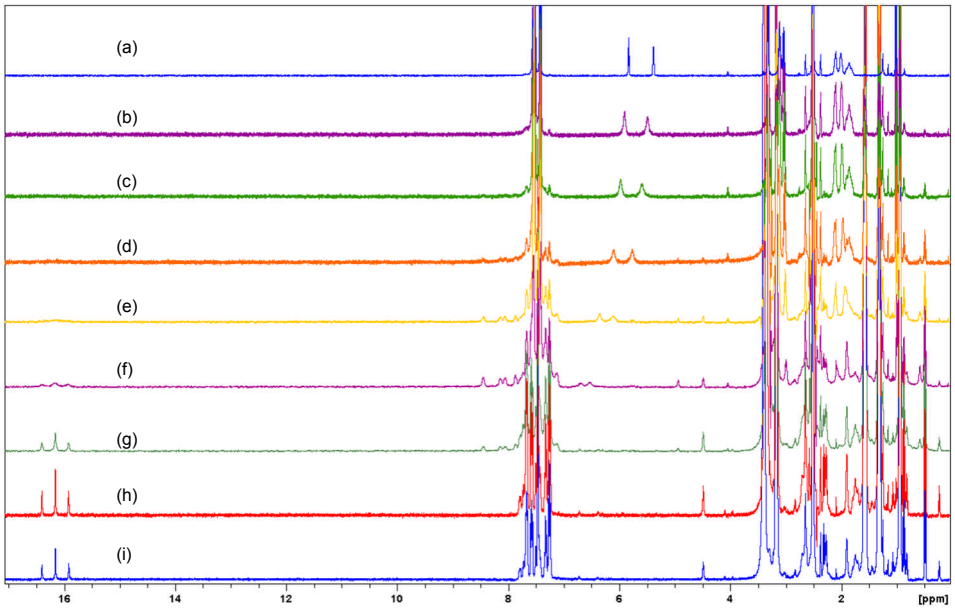
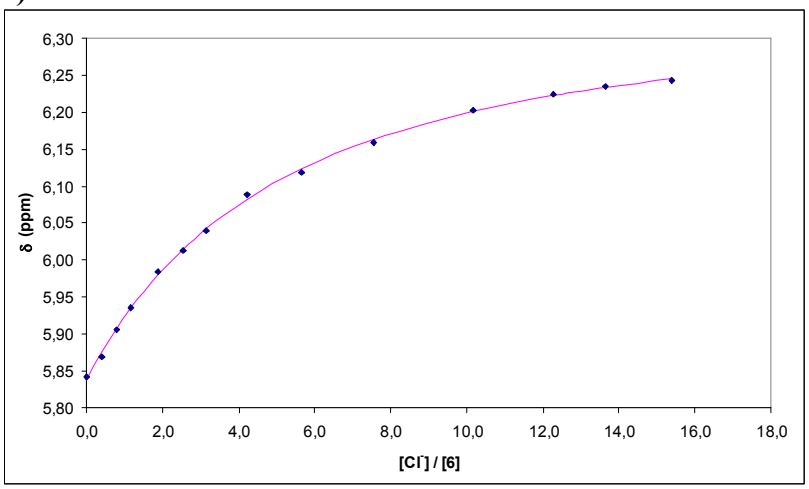


Figure S6. ^{1}H NMR spectra (500 MHz, DMSO-*d6*) for the titration of receptor **6** with *n*-$Bu_4N^+F^-$. The spectra were recorded after the addition of (a) 0.0, (b) 0.3, (c) 0.6, (d) 1.1, (e) 2.0, (f) 3.1 (g) 4.7, (h) 6.8 and (i) 10.7 equivalents of F^-.

^{1}H NMR titration curves of metallo-receptors with different anions

a)



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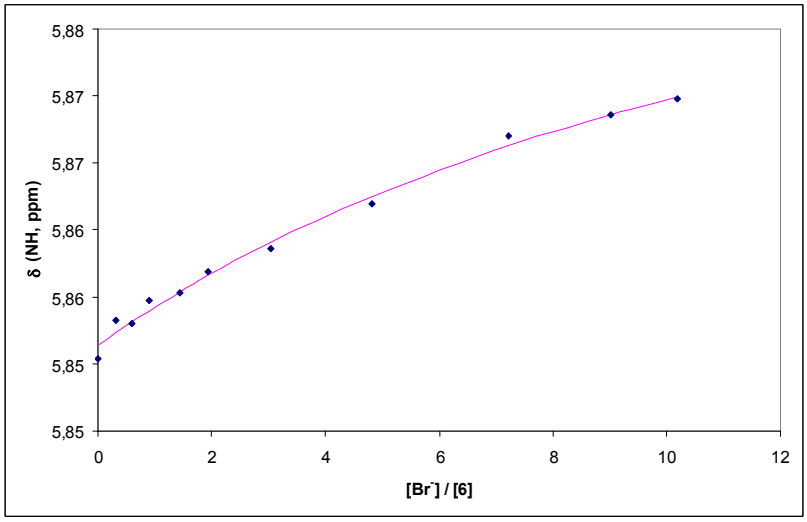

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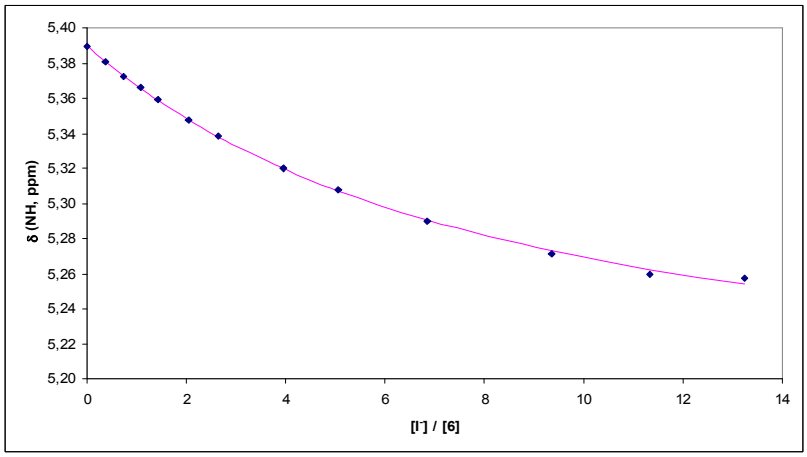
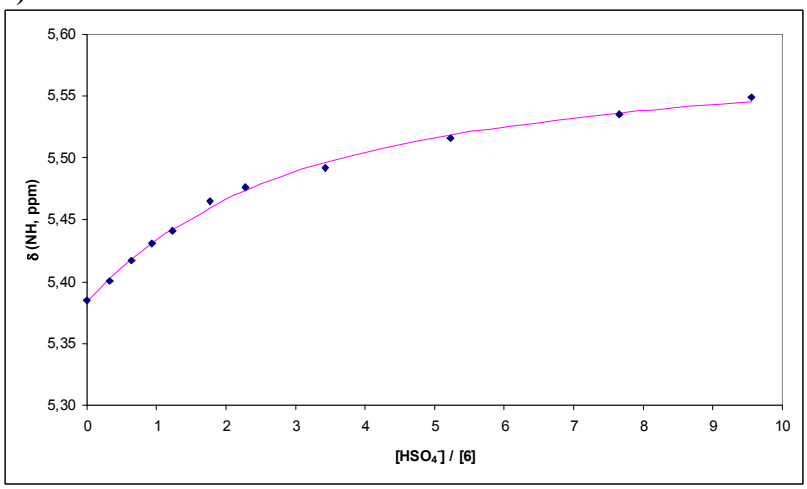


Figure S7. ^{1}H NMR titration curves for receptor **6** with a) Cl^-, b) Br^-, and c) I^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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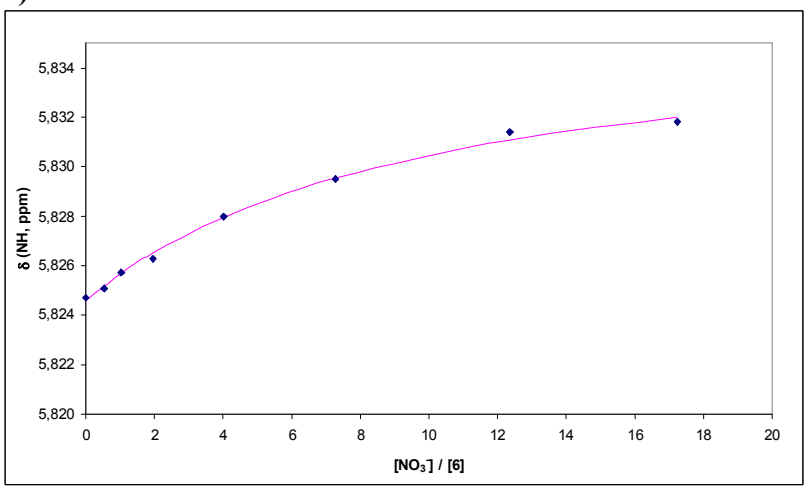

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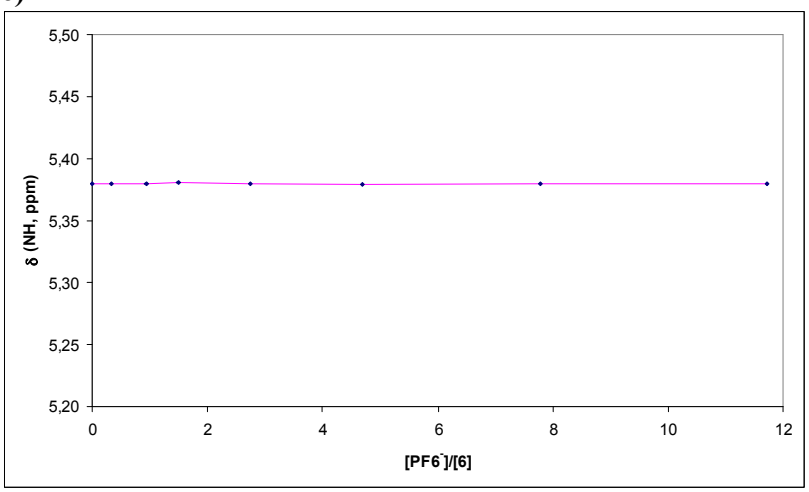
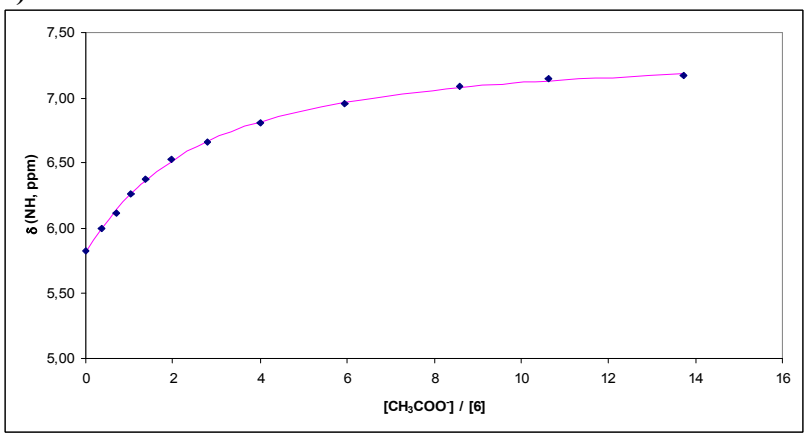


Figure S8. ^{1}H NMR titration curves for receptor **6** with a) HSO_4^-, b) NO_3^-, and c) PF_6^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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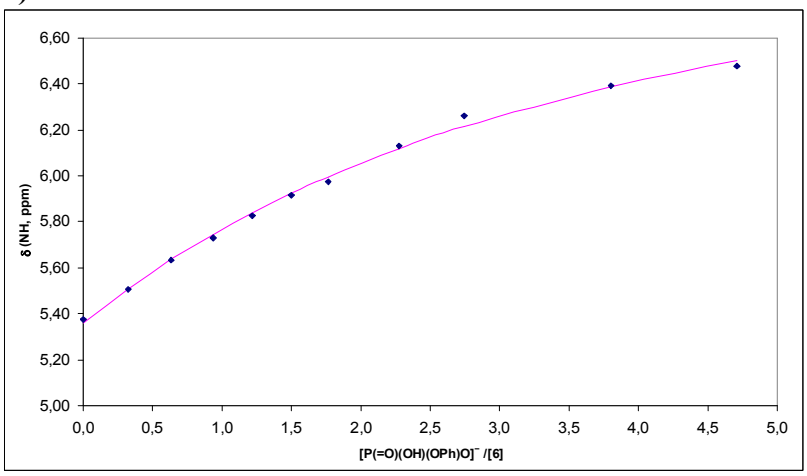


c)

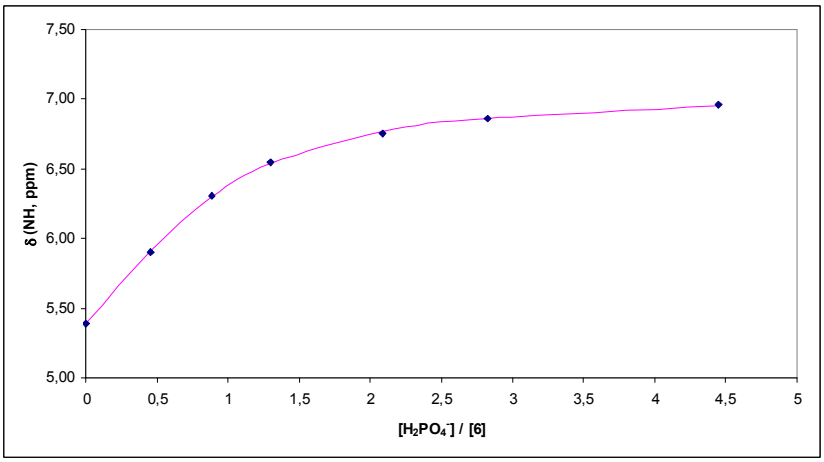
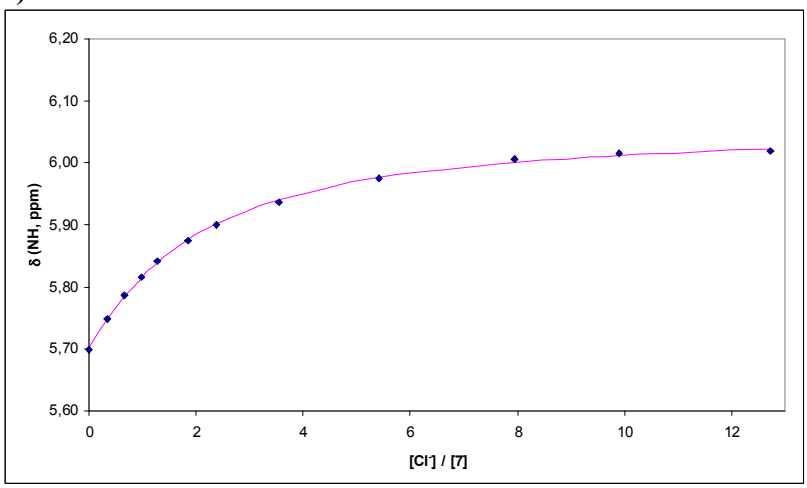


Figure S9. ^{1}H NMR titration curves for receptor **6** with a) CH_3COO^-, b) $[P(=O)(OH)(OPh)O]^-$ and c) $H_2PO_4^-$ in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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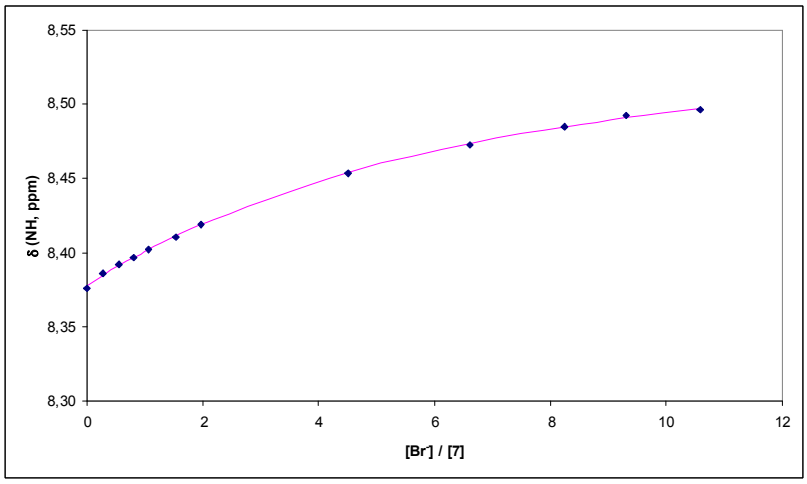


c)

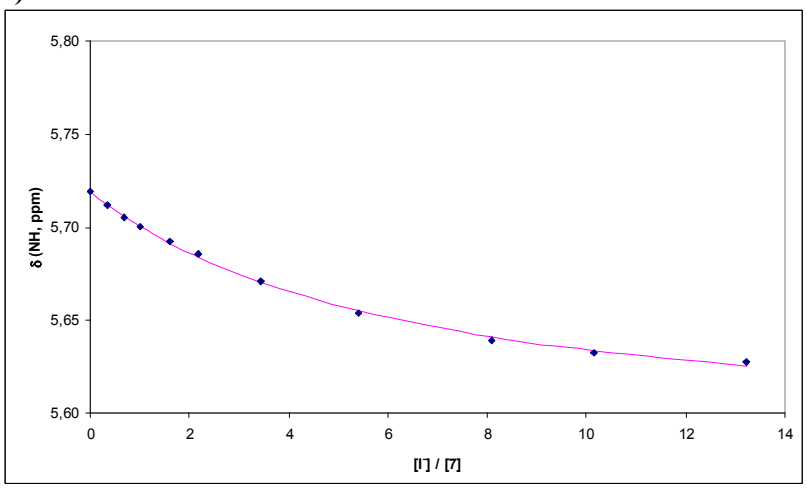
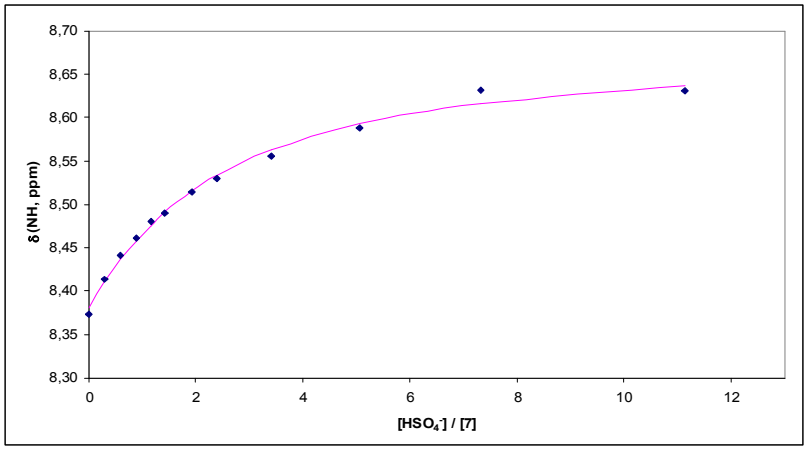


Figure S10. ^{1}H NMR titration curves for receptor **7** with a) Cl^-, b) Br^-, and c) I^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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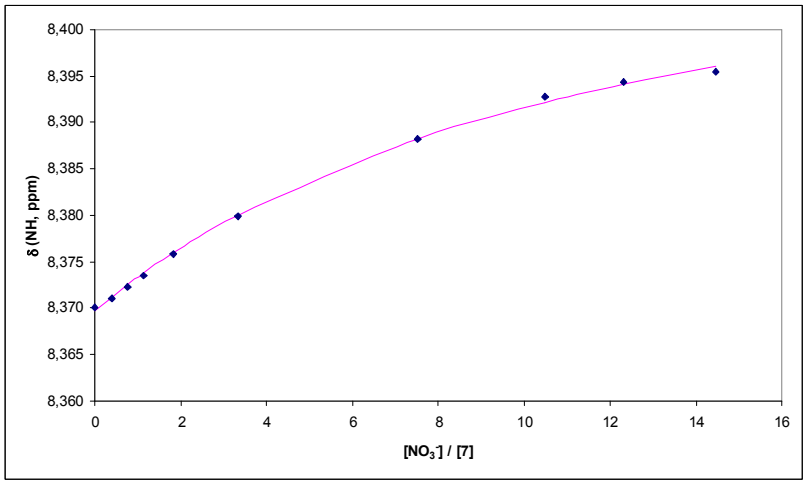

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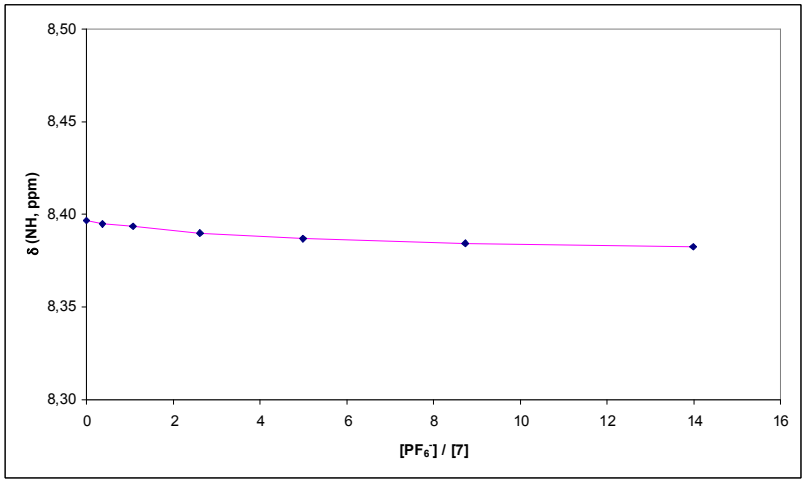
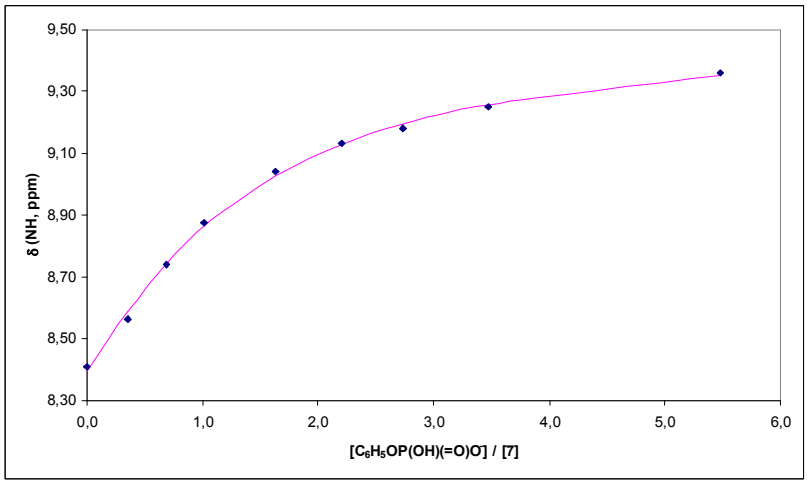


Figure S11. ^{1}H NMR titration curves for receptor **7** with a) HSO_4^-, b) NO_3^-, and c) PF_6^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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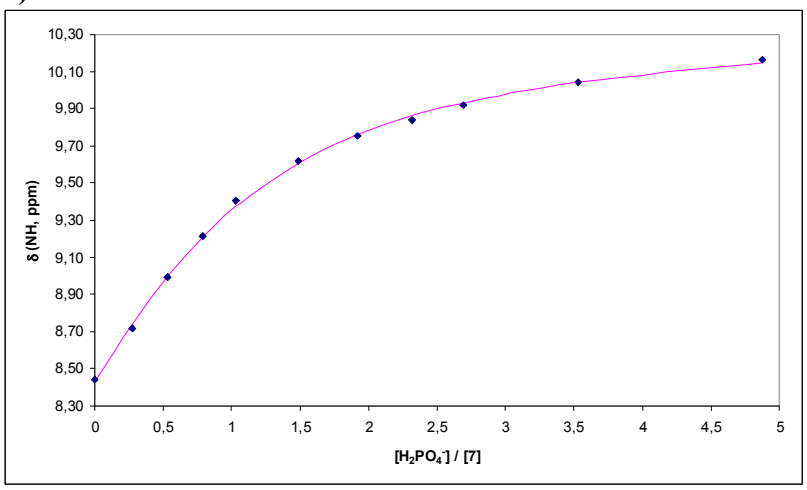


c)

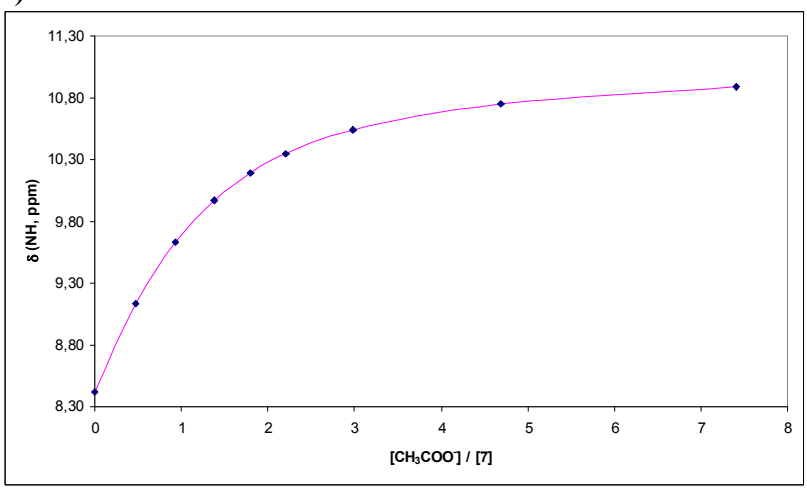
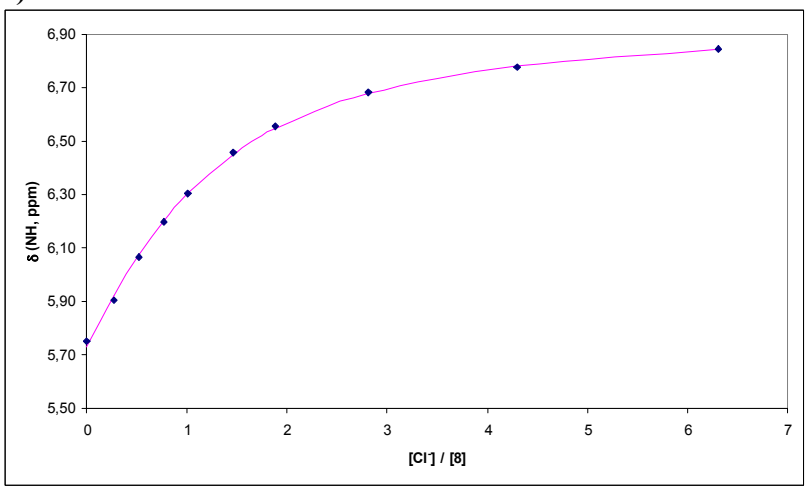


Figure S12. ^{1}H NMR titration curves for receptor **7** with a) $[P(=O)(OH)(OPh)O]^{-}$, b) $H_2PO_4^-$, and c) CH_3COO^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



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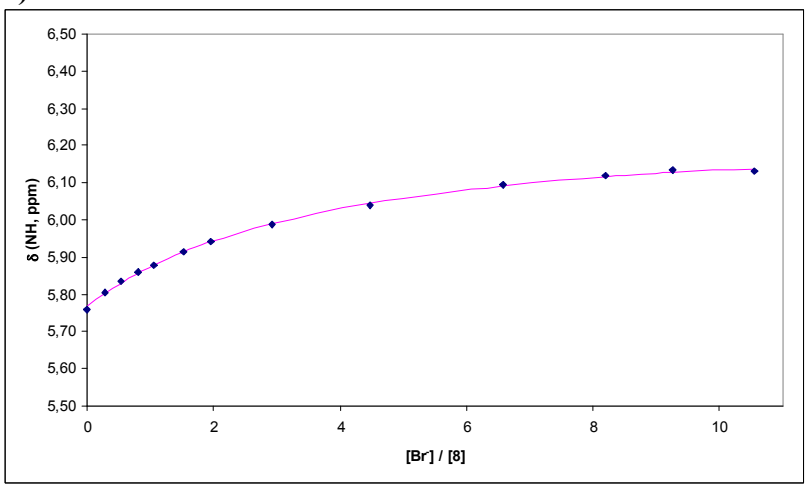


c)

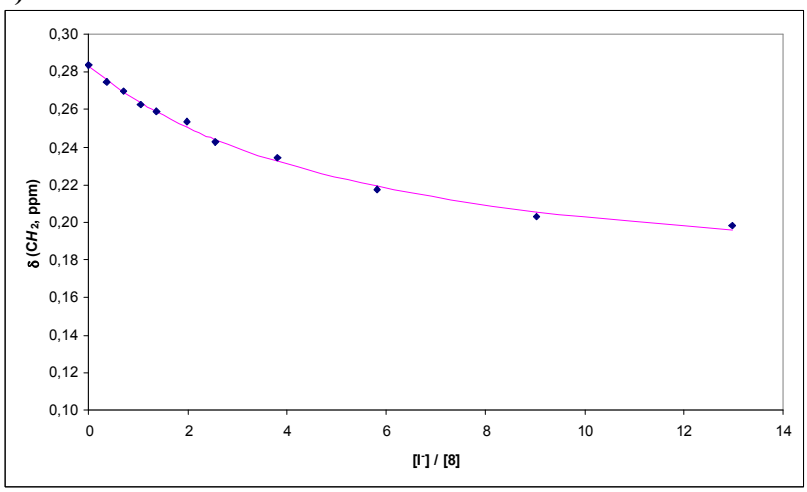
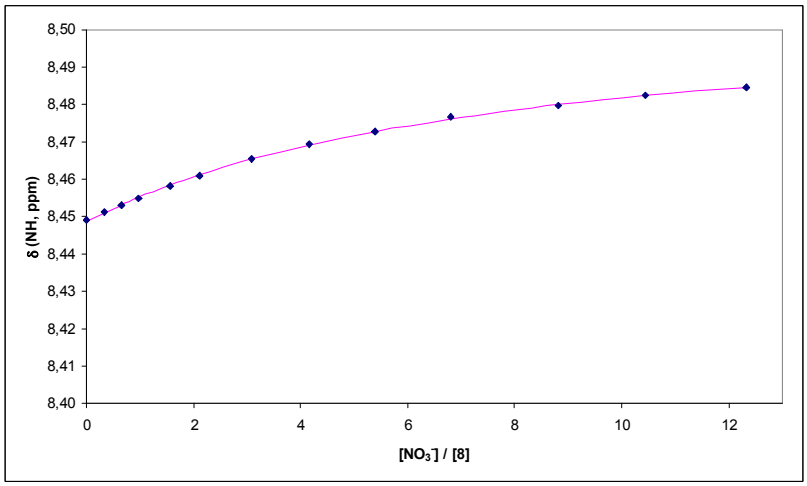
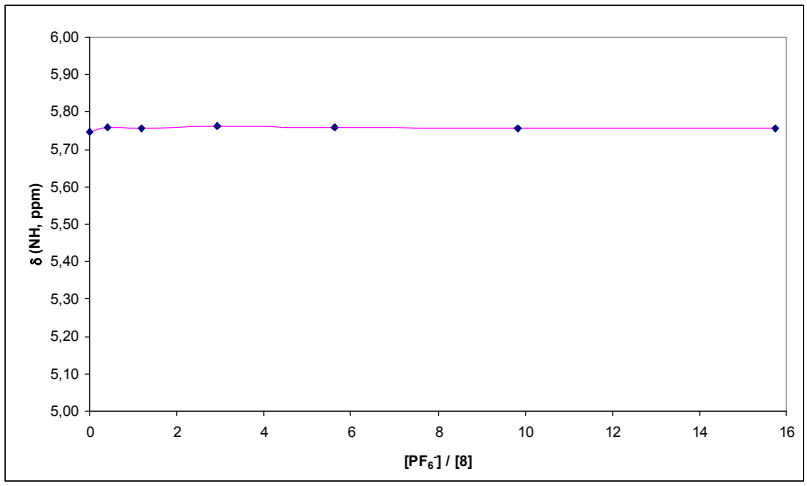


Figure S13. ^{1}H NMR titration curves for receptor **8** with a) Cl^-, b) Br^-, and c) I^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



b)



c)

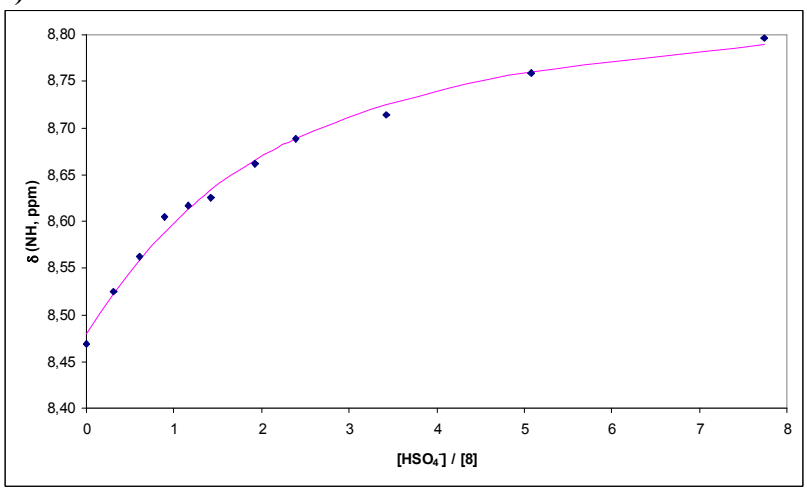
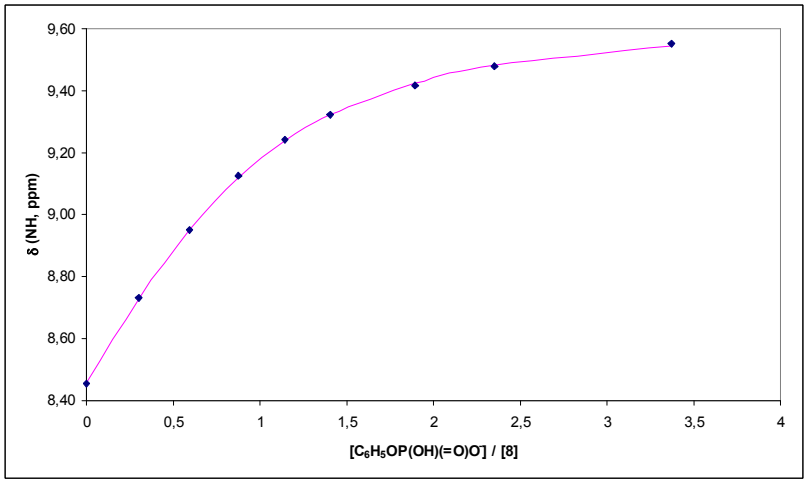
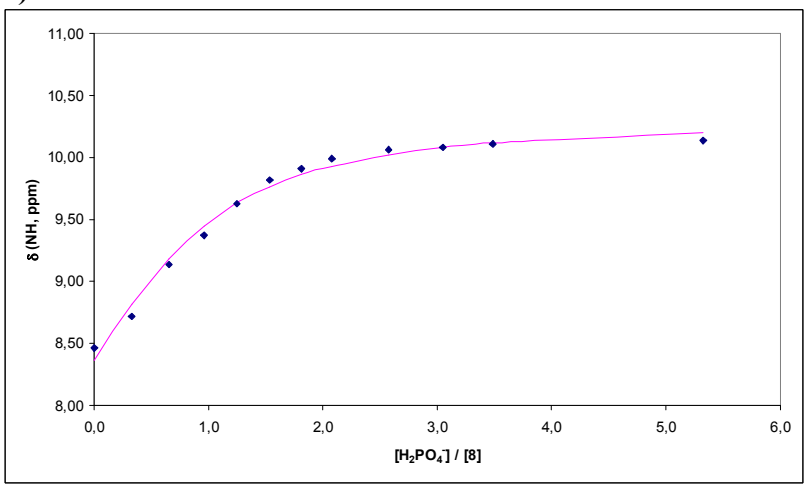


Figure S14. ^{1}H NMR titration curves for receptor **8** with a) NO_3^-, b) PF_6^- and c) HSO_4^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

a)



b)



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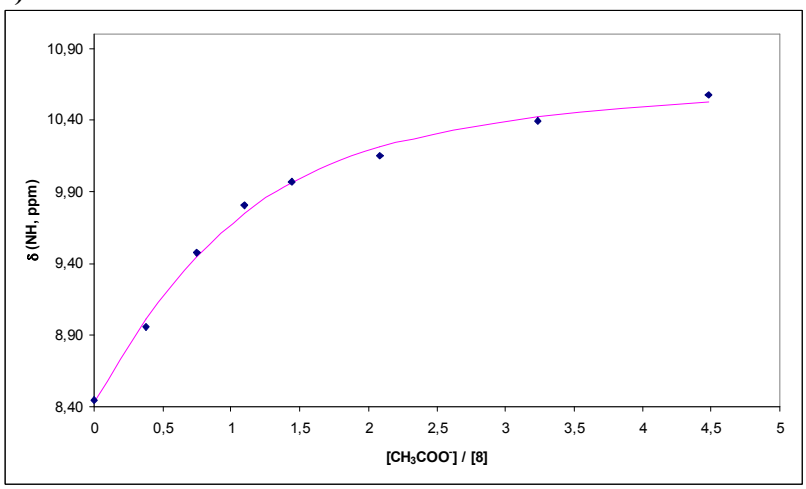

Figure S15. ^{1}H NMR titration curves for receptor **8** with a) $[P(=O)(OH)(OPh)O]^{-}$, b) $H_2PO_4^-$ and c) CH_3COO^- in DMSO-*d6*. Anions were added as their tetrabutylammonium salts.

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2. **Job plots for metallo-receptors**

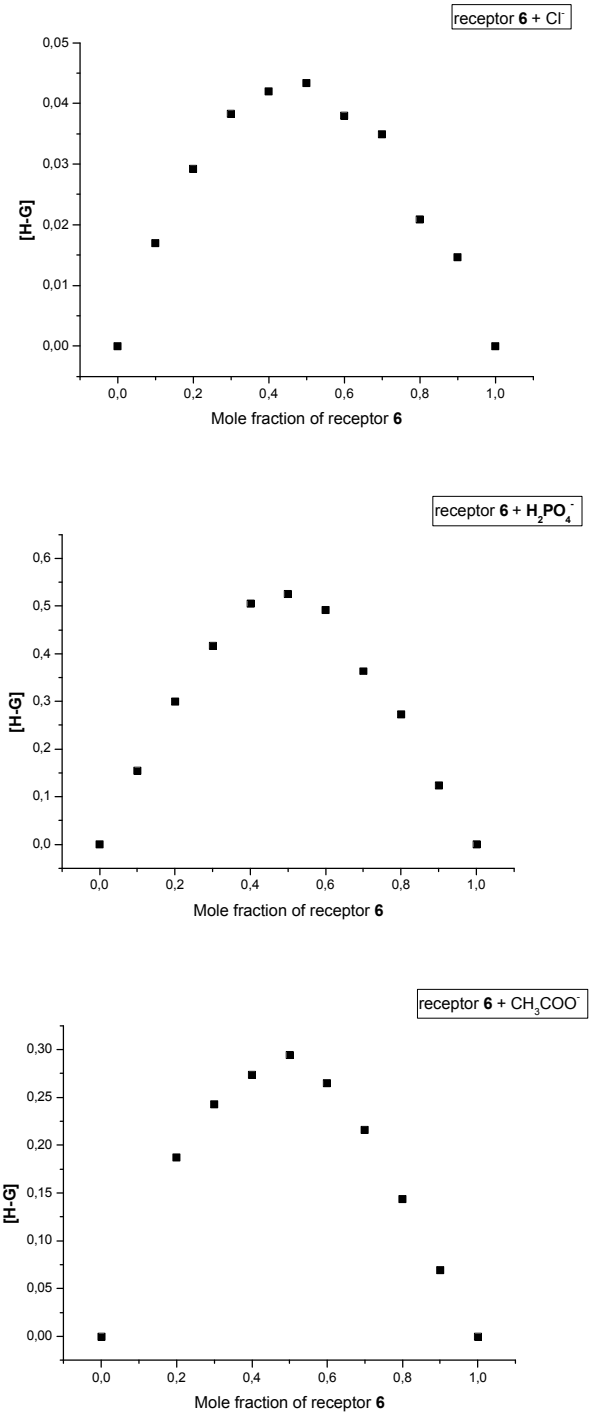

Figure S16. Job plot determined by ^{1}H NMR spectroscopy of the interaction between receptor **6** with different anions in DMSO-*d6*. The host-guest complex concentration was calculated as [H-G]=Δδ x (mole fraction of receptor **6**). The total concentration ([H]+[G]) was kept constant at 1.60 mM for Cl^- and $H_2PO_4^-$, and at 2.65 mM in the case of CH_3COO^-.

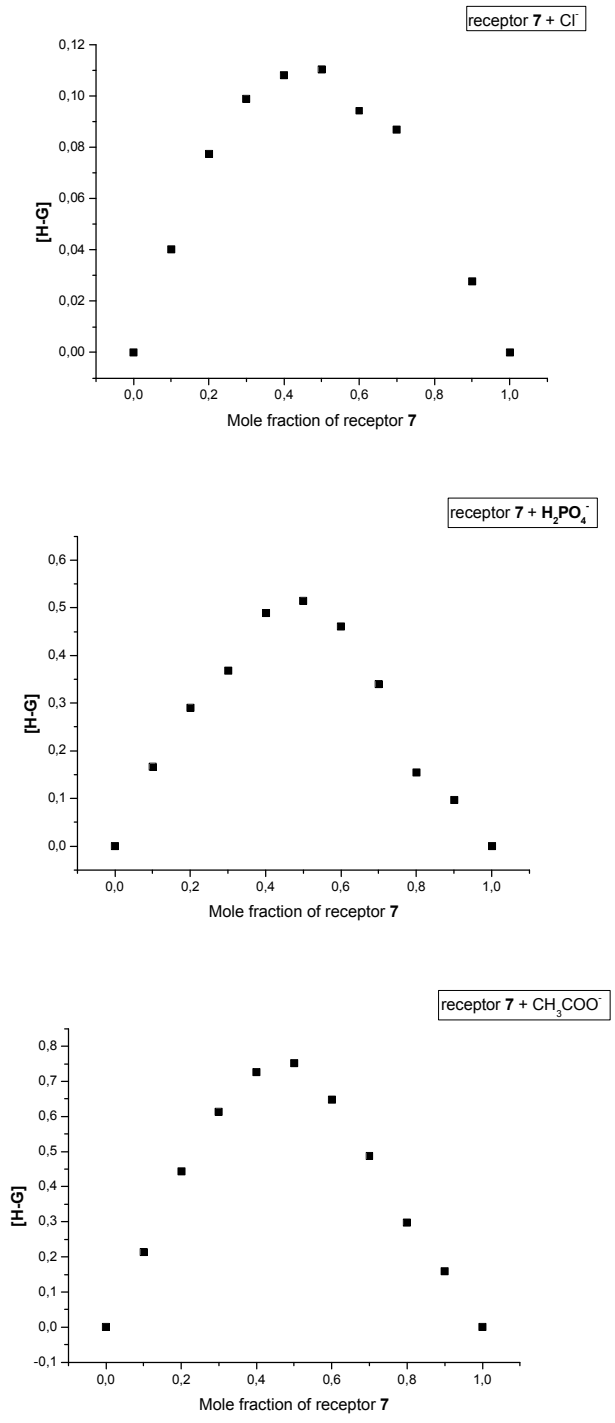

Figure S17. Job plot determined by ^{1}H NMR spectroscopy of the interaction between receptor **7** with different anions in DMSO-*d6*. The host-guest complex concentration was calculated as [H-G]=Δδ x (mole fraction of receptor **7**). The total concentration ([H]+[G]) was kept constant at 1.05 mM for Cl^- and $H_2PO_4^-$, and at 2.52 mM in the case of CH_3COO^-.

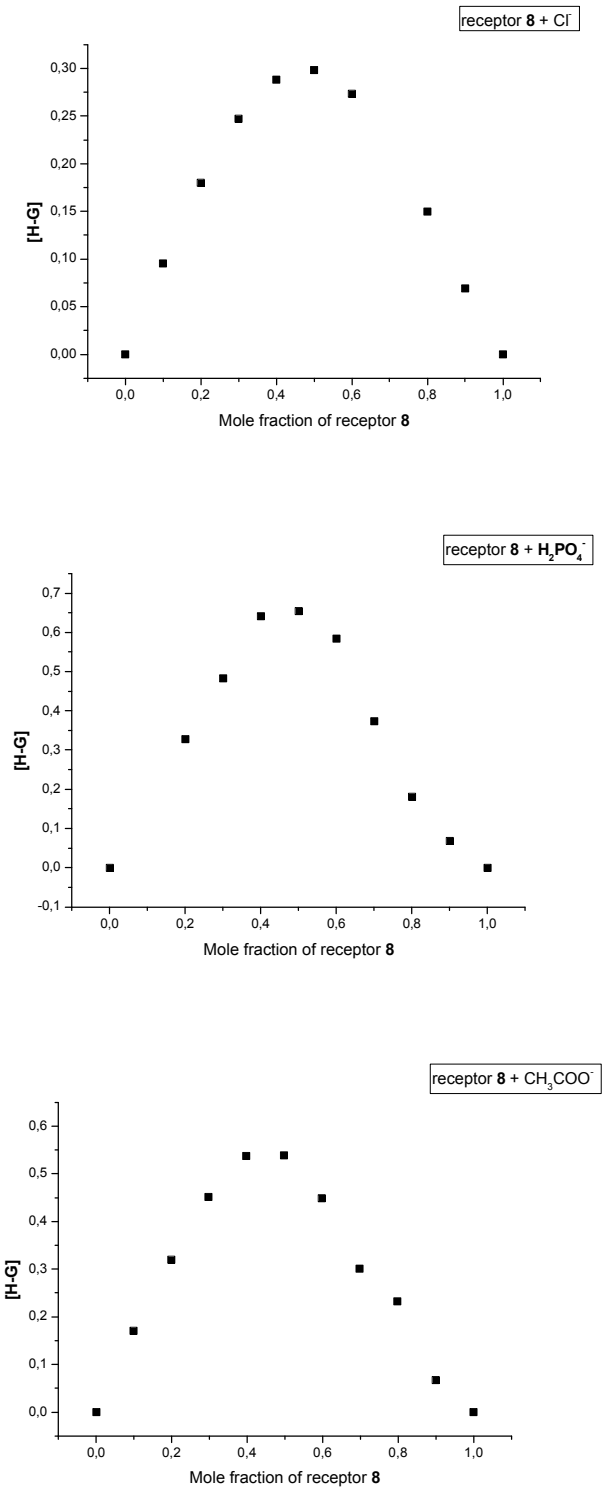

Figure S18. Job plot determined by ^{1}H NMR spectroscopy of the interaction between receptor **8** with different anions in DMSO-*d6*. The host-guest complex concentration was calculated as [H-G]=Δδ x (mole fraction of receptor **8**). The total concentration ([H]+[G]) was kept constant at 1.59 mM in the case of Cl^-, 1.00 mM in the case of $H_2PO_4^-$ and at 0.93 mM in the case of CH_3COO^-.

3. ^{1}H NMR titrations of interaction between methyl red and receptor 8

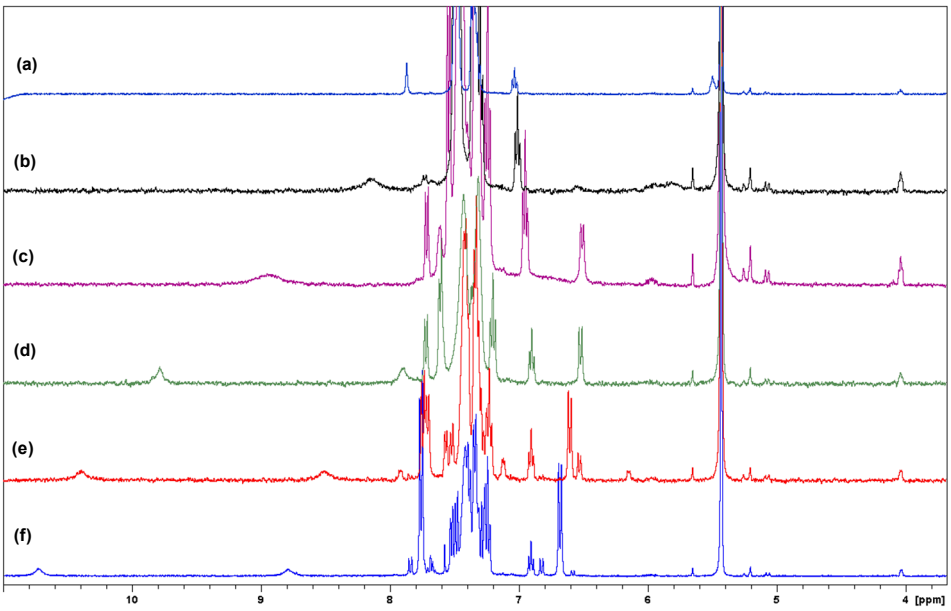

Figure S19. Partial ^{1}H NMR spectra (500 MHz, 75% CD_3CN- 25%CD_2Cl_2) for the titration of receptor **8** with tetrabutylammoniun methyl red. The spectra were recorded after the addition of (a) 0.0, (b) 0.2, (c) 0.5, (d) 1.1, (e) 2.0, (f) 4.0 equivalents of methyl red.

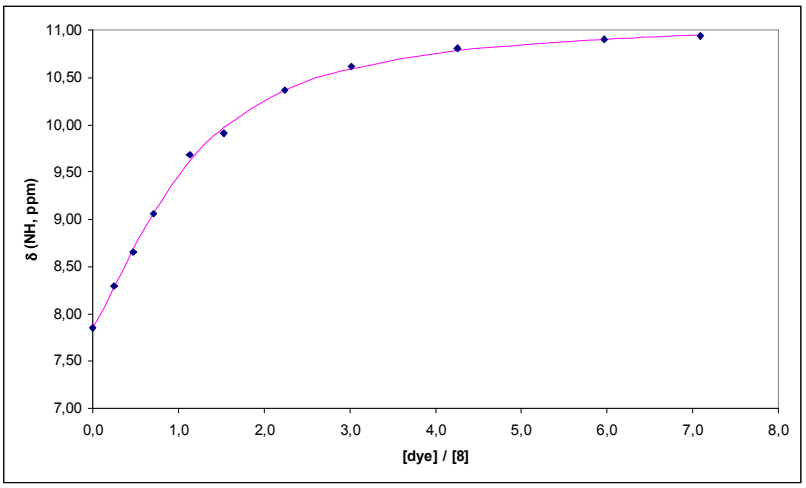

Figure S20. ^{1}H NMR titration curves for receptor **8** with tetrabutylammonium methyl red in 75% CD_3CN- 25%CD_2Cl_2.

4. UV/Vis titrations of interaction between dye and receptor 8

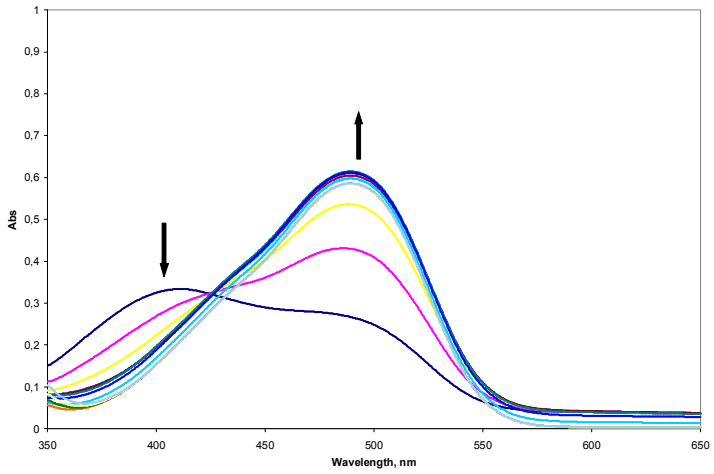

Figure S21. UV/Visible spectra of methyl red upon addition of increasing amounts of receptor **8** in 75% CH_3CN- 25%CH_2Cl_2.

5. Job plots for the interaction between metallo-receptor 8 and dye

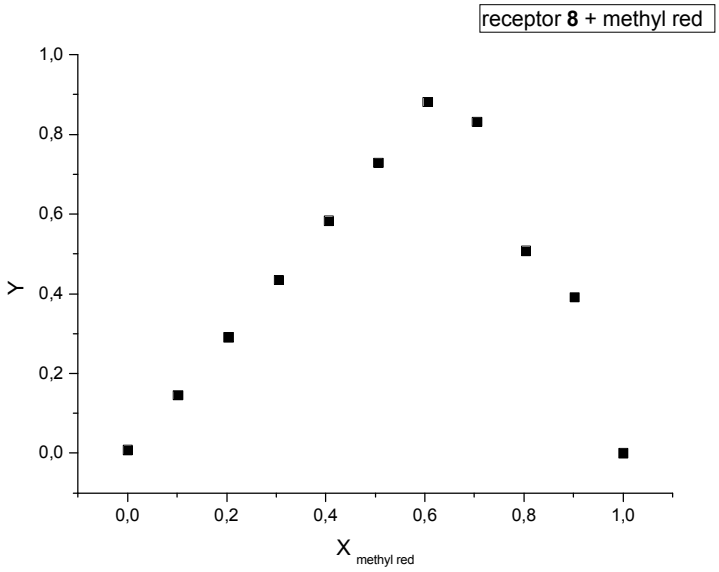

Figure S22. Job plot determined by visible spectroscopy of the interaction between receptor **8** with methyl red in CH_3CN 75%: CH_2Cl_2 25%. Y was calculated as $Y=A_{.494nm} - (A_{methyl\ red,\ 494nm})\ x\ (X_{methyl\ red})$. The total concentration = ([**8**]+[methyl red]) was kept constant at 50 μM.