Supporting Information

An Allosteric Heteroditopic Receptor for Neutral Guests and Contact Ion Pairs with a Remarkable Selectivity for Ammonium Fluoride Salts

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SI1. ^{1}H NMR (298K, 300MHz) spectrum of **4** in $CDCl_3$

SI2. ^{1}H NMR (298K, 300MHz) spectrum of **4** in $CD_3CN/CDCl_3$ (1:2)

SI3. Variable temperature ^{1}H NMR (300MHz) study of **2** in $CDCl_3$

SI4. ^{1}H NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$

SI5. ^{1}H NMR (298K, 300MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)

SI6. ^{1}H NMR (298K, 600MHz) spectrum of **2** in $CD_3OD/CDCl_3$ (3:2)

SI7. ^{13}C NMR (298K, 75MHz) spectrum of **2** in $CDCl_3$

SI8. HSQC NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$

SI9. COSY NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$

SI10. ^{13}C NMR (298K, 100MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)

SI11. HSQC NMR (298K, 600MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)

SI12. HSQC NMR (298K, 600MHz) spectrum of **2** in $CD_3OD/CDCl_3$ (3:2)

SI13. ^{1}H NMR (298K, 300MHz) spectrum of **2.H**$^{+}$ in $CDCl_3$

SI14. ^{1}H NMR (298K, 300MHz) spectrum of **2⊃Mimi** in $CDCl_3$

SI15. ^{1}H NMR (298K, 300MHz) spectrum of **2** with Imi (2.5 equiv.) in $CD_3OD/CDCl_3$ (3:2)

SI16. ^{1}H NMR (298K, 300MHz) titration curve of **2** with fluoride anion in $CDCl_3$

SI17. Competitive ESI-MS binding studies of **2** with TBA^+ salts of F^-, Cl^-, Br^-, AcO^- and NO_3^- in $CHCl_3$

SI18. Low temperature ^{1}H NMR (243K, 600MHz) spectrum of **2** with TBA^+F^- (9 equiv.) in $CDCl_3$

SI19. Acid-triggered release of fluoride anion in $CDCl_3$

SI20. ^{1}H NMR (298K, 400MHz) spectrum of **2** with TBA^+F^- (10 equiv.) and TMA^+Pic^- (10 equiv.) in $CDCl_3$

SI21. ^{1}H NMR (298K, 300MHz) spectrum of **2** with TBA^+F^- (1 equiv.) and $HexNH_3^+Pic^-$ (1 equiv.) in $CDCl_3$

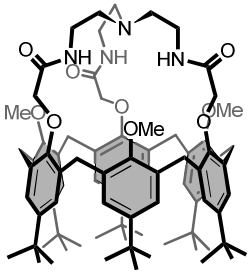
SI22. Guest region of the COSY NMR (298K, 300MHz) spectrum of **2⊃HexNH$_3^+$F$^-$** in $CDCl_3$

SI23. Acid-triggered release of $PrNH_3^+F^-$ in $CDCl_3$

SI24. Low temperature ^{1}H NMR (243K, 600MHz) spectrum of **2** with TBA^+F^- (5 equiv.) and $PrNH_3^+Pic^-$ (5 equiv.) in $CDCl_3$.

SI25. Guest region of the low temperature COSY NMR (243K, 600MHz) spectrum of **2** with TBA^+F^- (5 equiv.) and $PrNH_3^+Pic^-$ (5 equiv.) in $CDCl_3$.

SI1. ^{1}H NMR (298K, 300MHz) spectrum of **4** in $CDCl_3$



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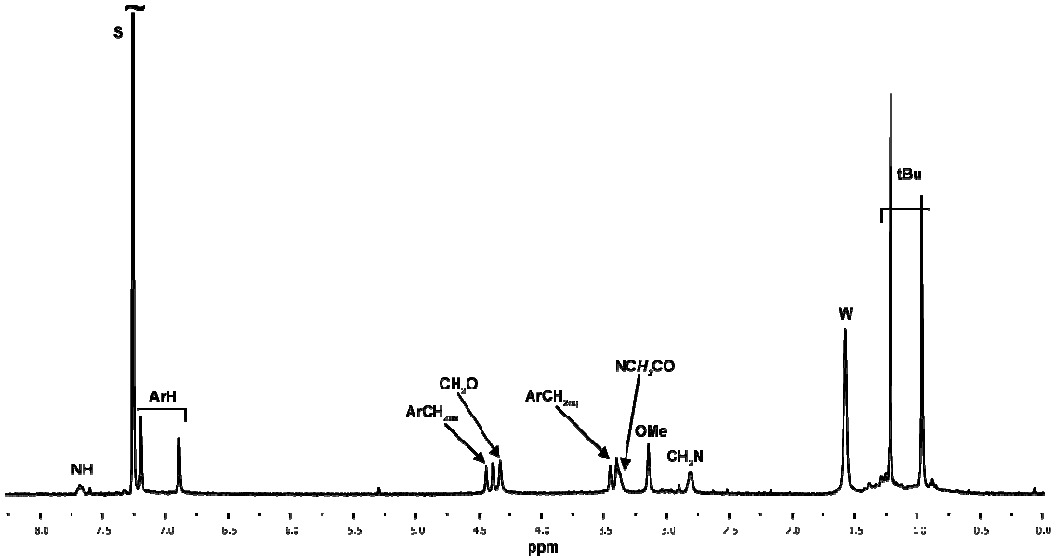
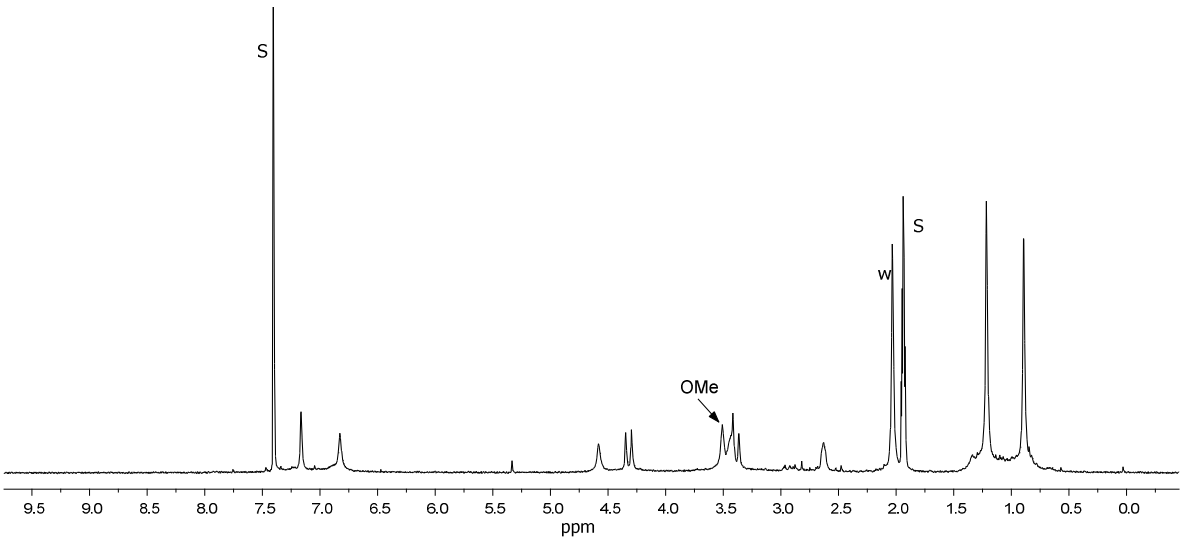


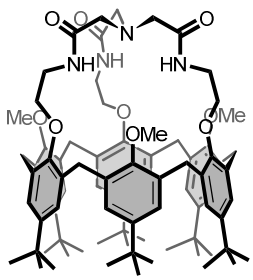
S: solvent; W: water.

SI2. ^{1}H NMR (298K, 300MHz) spectrum of **4** in $CD_3CN/CDCl_3$ (1:2)

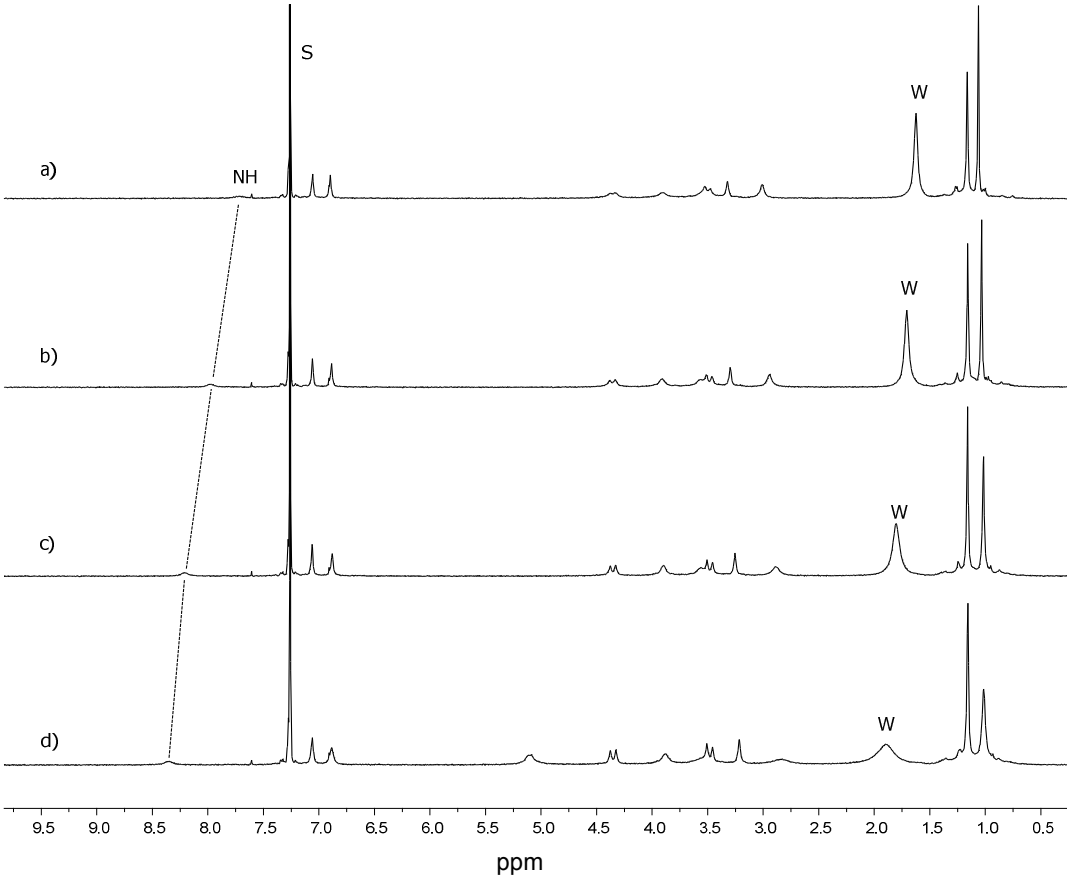


S: solvent; W: water.

SI3. Variable temperature ^{1}H NMR (300MHz) study of **2** in $CDCl_3$

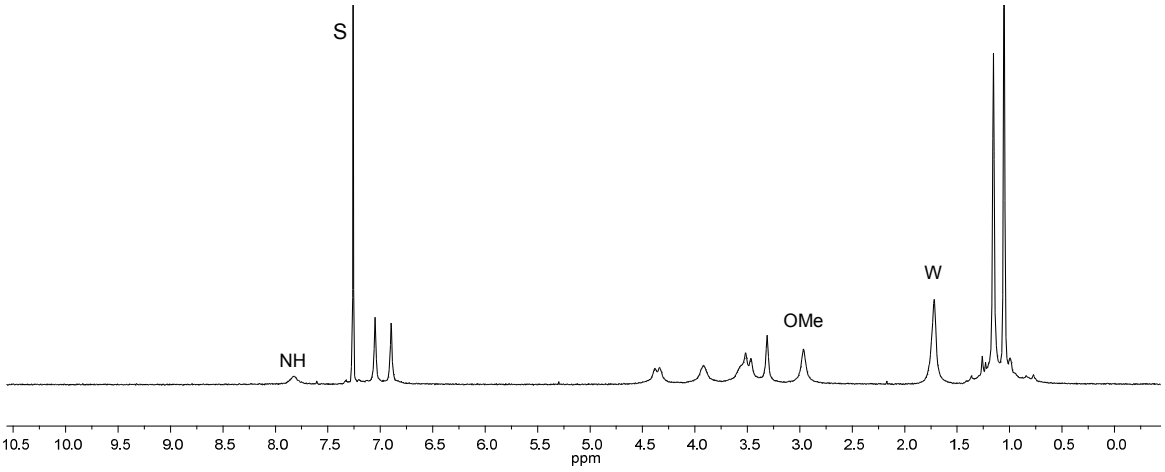


2



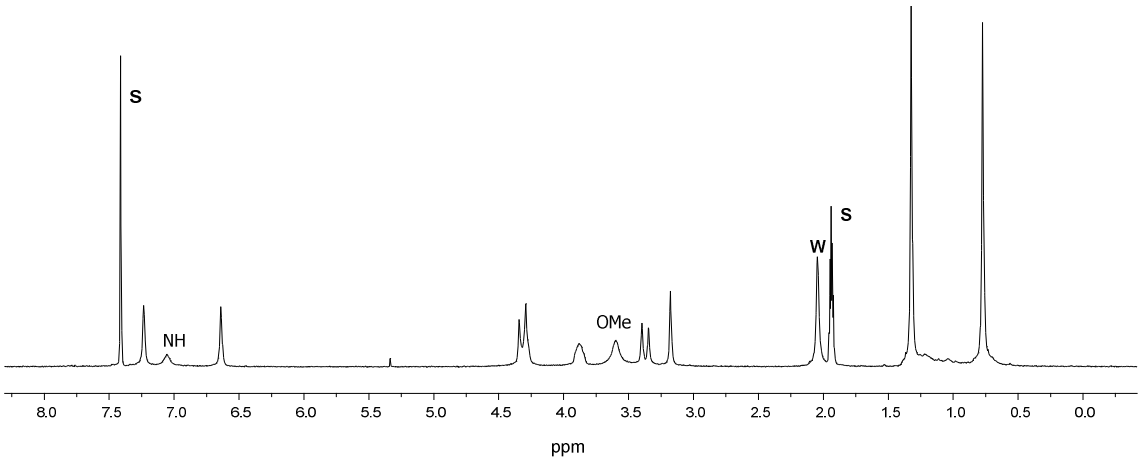
a) 308K; b) 293K; c) 278K and d) 263K. S: Solvent; W: water.

SI4. ^{1}H NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$



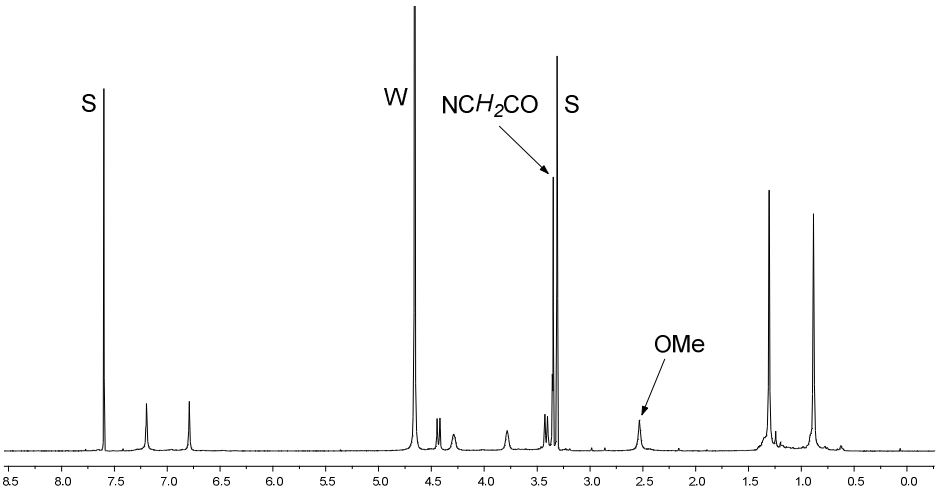
S: solvent; W: water.

SI5. ^{1}H NMR (298K, 300MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)



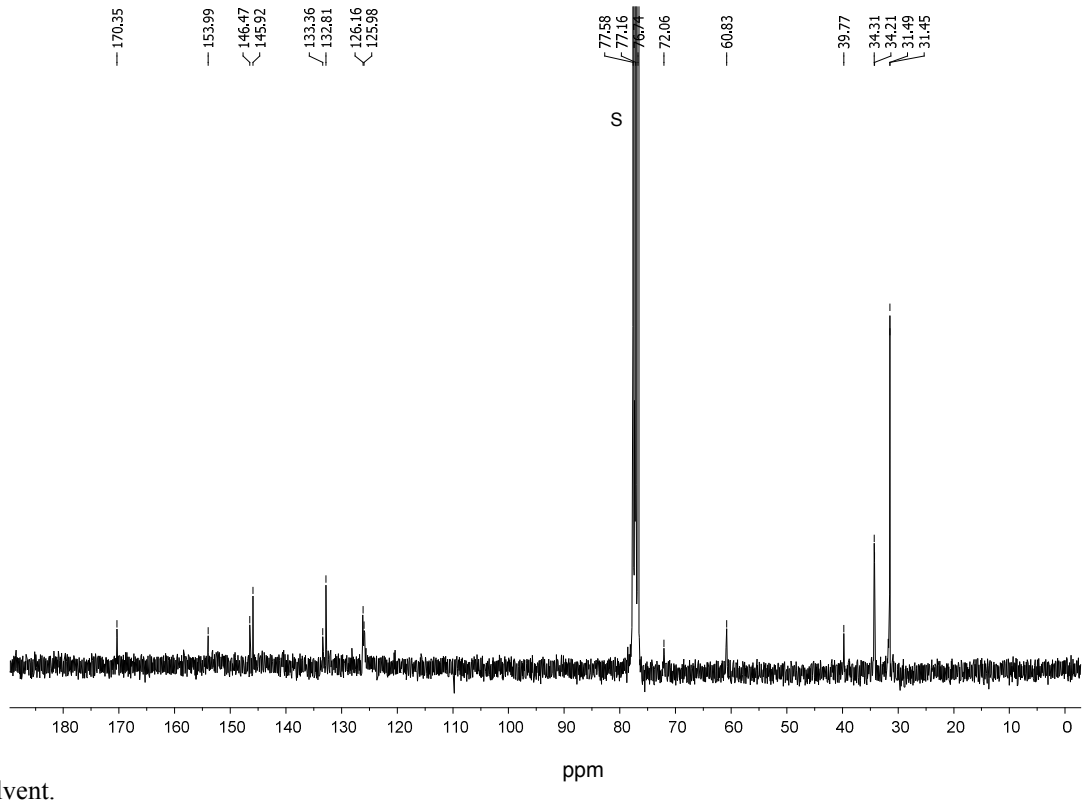
S: solvent; W: water.

SI6. ^{1}H NMR (298K, 600MHz) spectrum of **2** in $CD_3OD/CDCl_3$ (3:2)



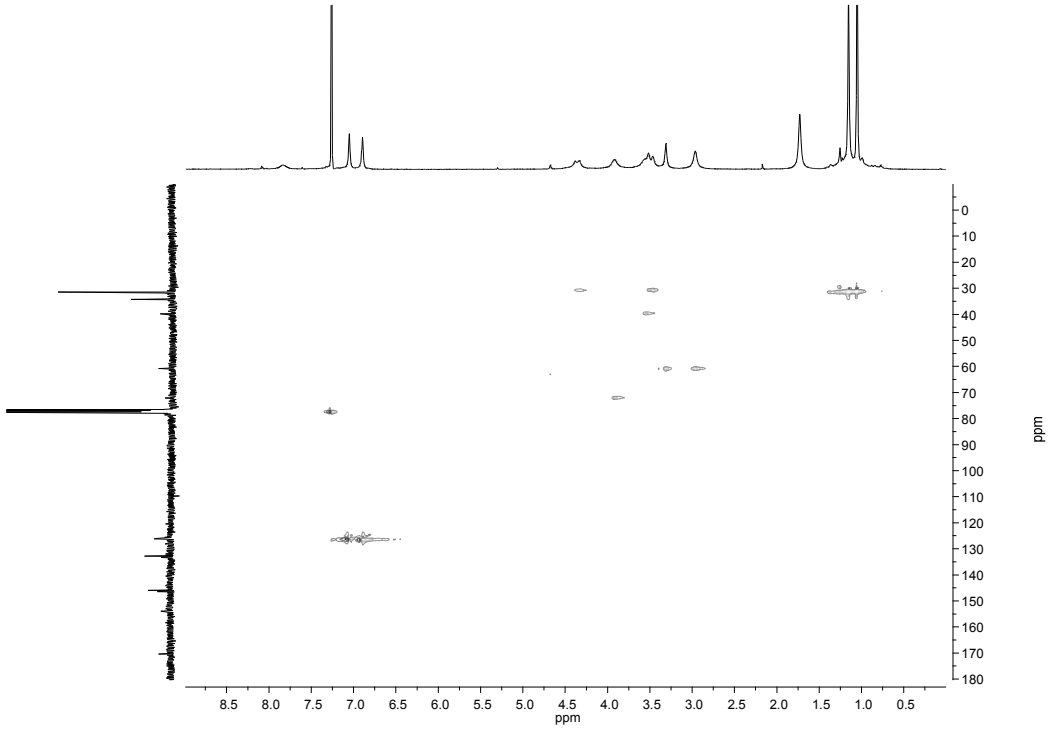
S: solvent; W: water.

SI7. ^{13}C NMR (298K, 75MHz) spectrum of **2** in $CDCl_3$

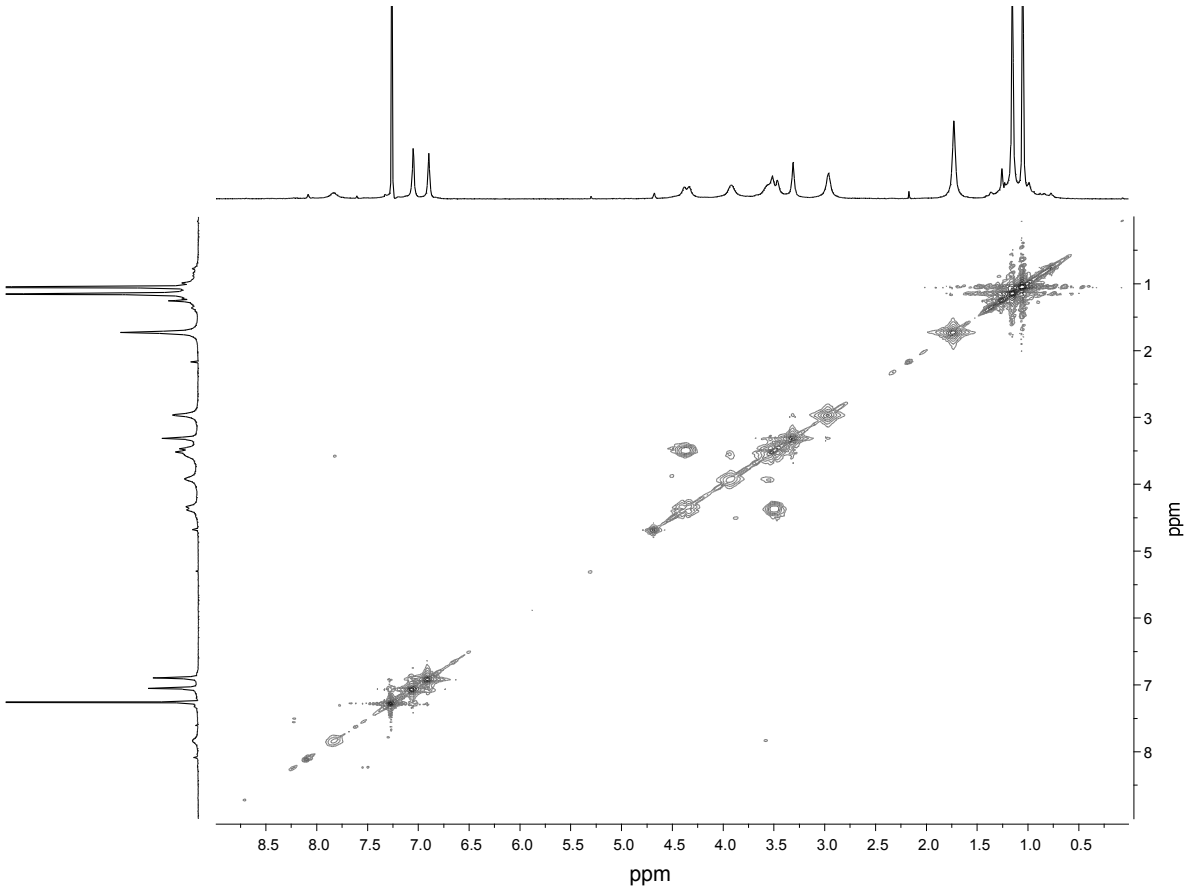


S: solvent.

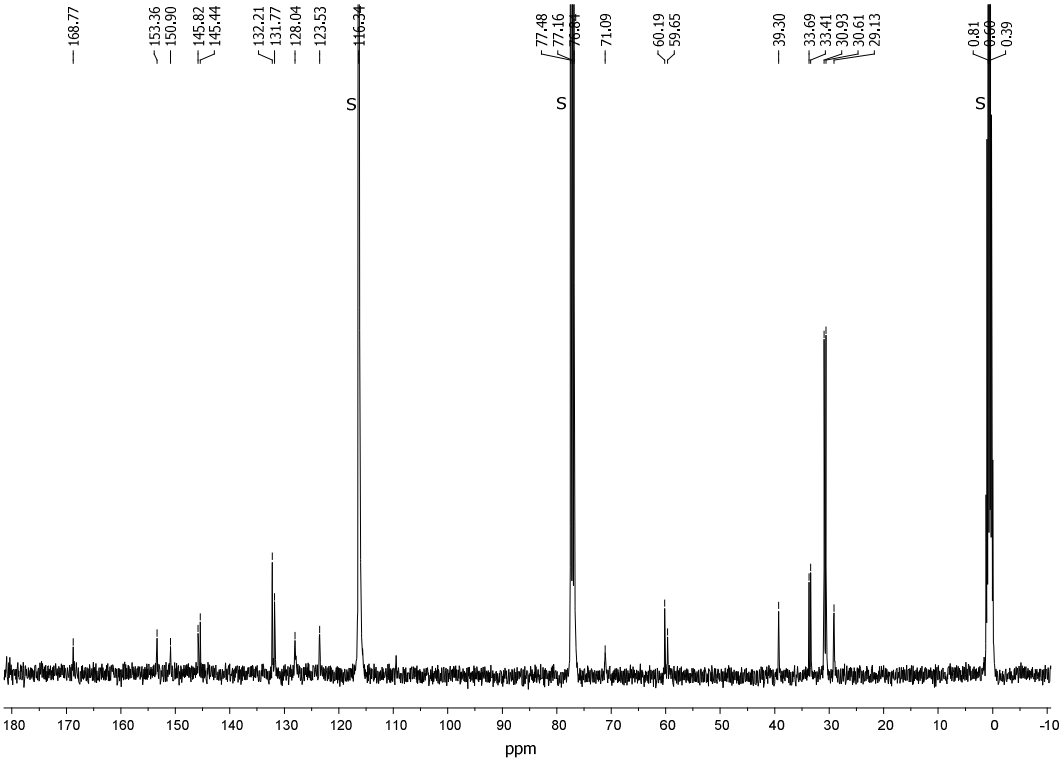
SI8. HSQC NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$



SI9. COSY NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$

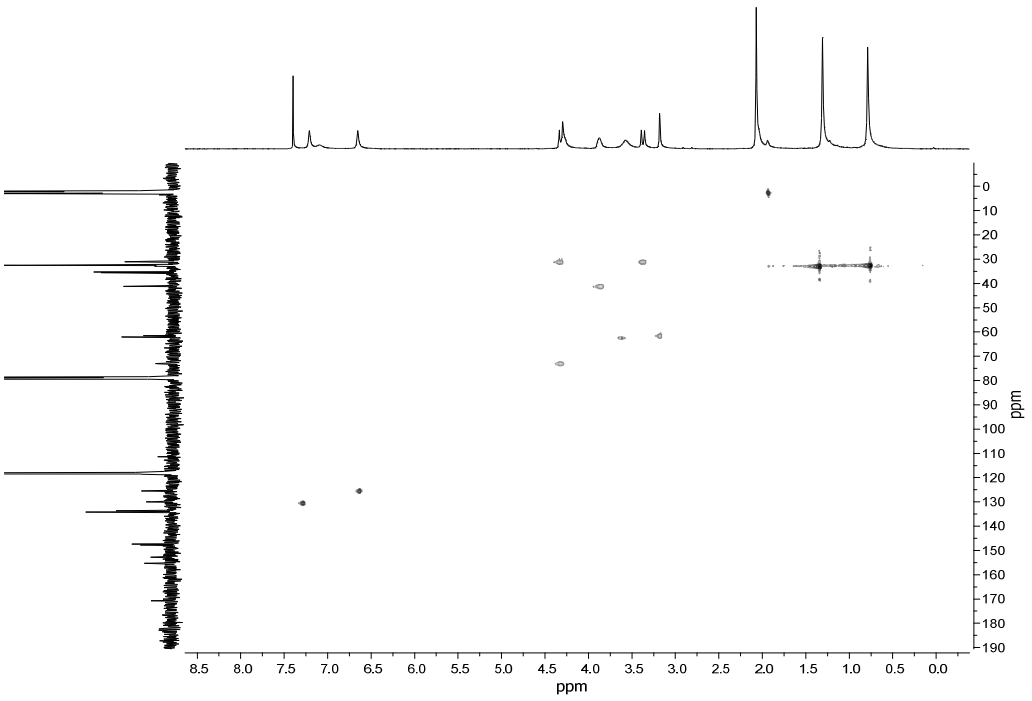


SI10. ^{13}C NMR (298K, 100MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)

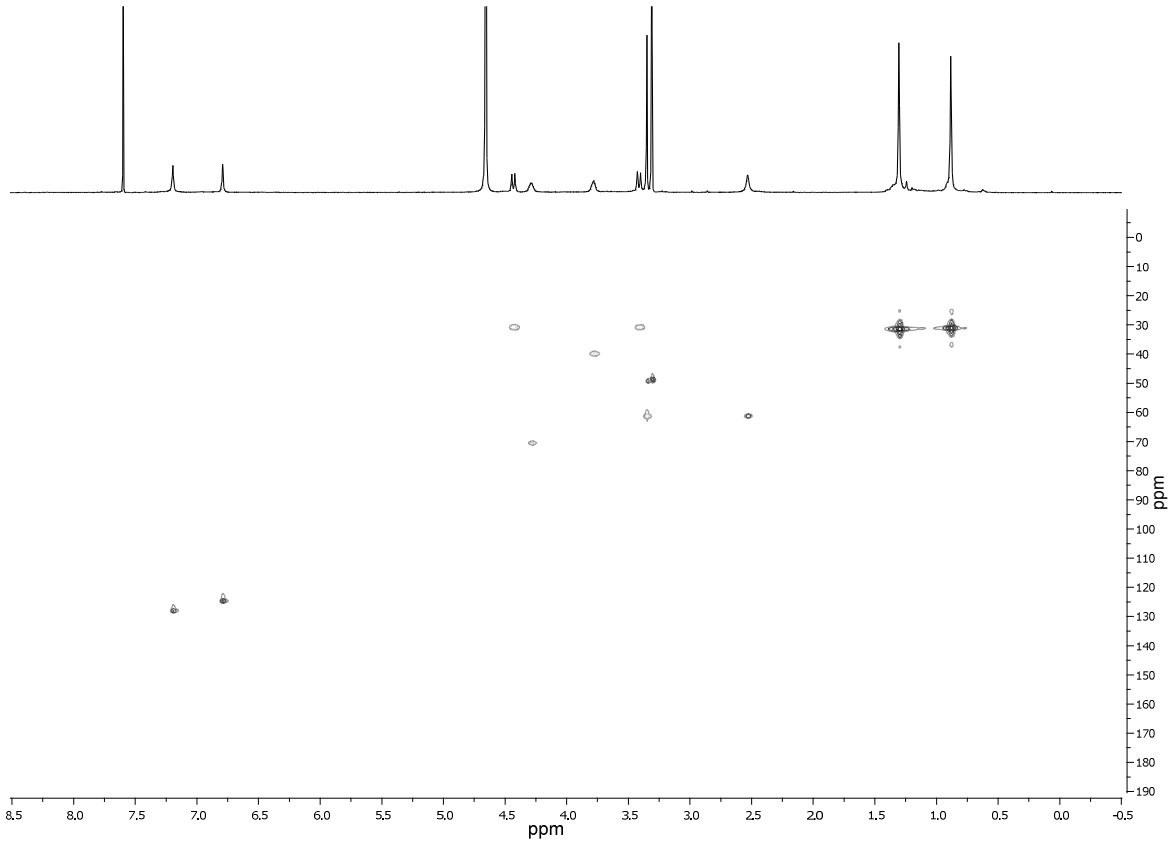


S: solvent.

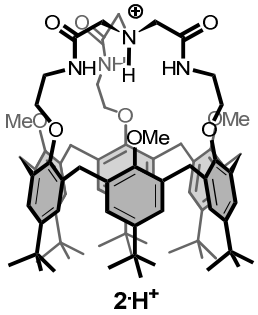
SI11. HSQC NMR (298K, 600MHz) spectrum of **2** in $CD_3CN/CDCl_3$ (1:2)

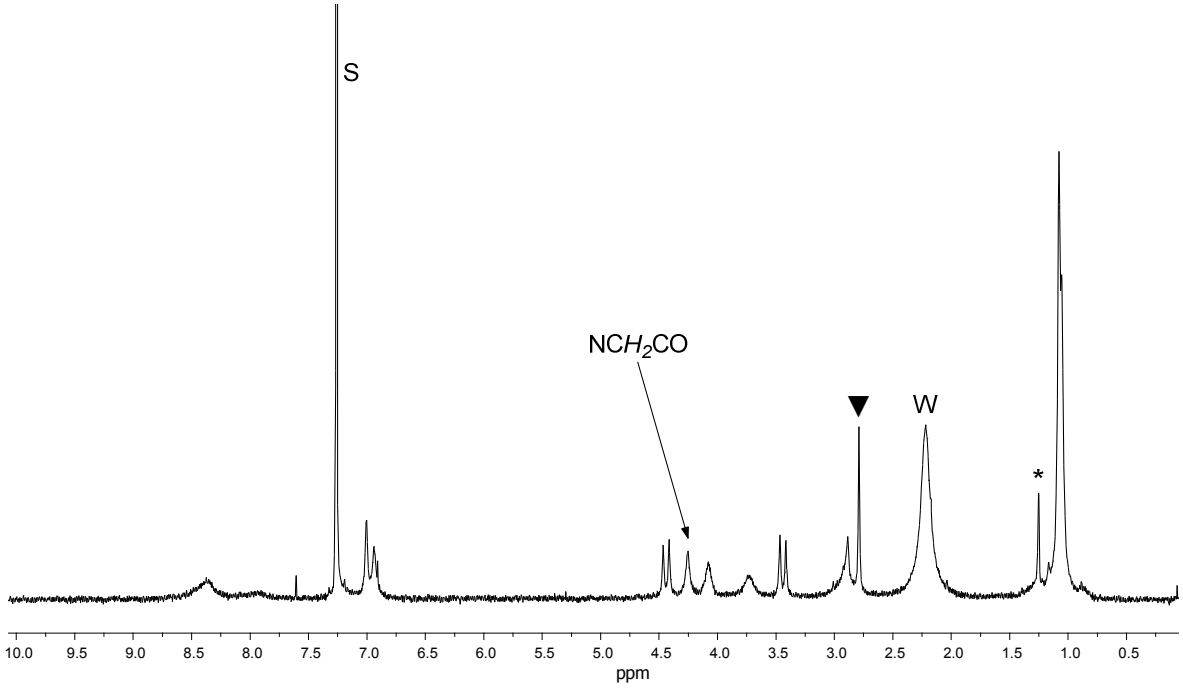


SI12. HSQC NMR (298K, 600MHz) spectrum of **2** in $CD_3OD/CDCl_3$ (3:2)



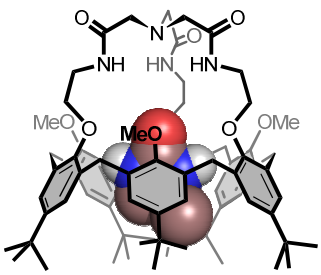
SI13. ^{1}H NMR (298K, 300MHz) spectrum of **2.H**$^+$ in $CDCl_3$



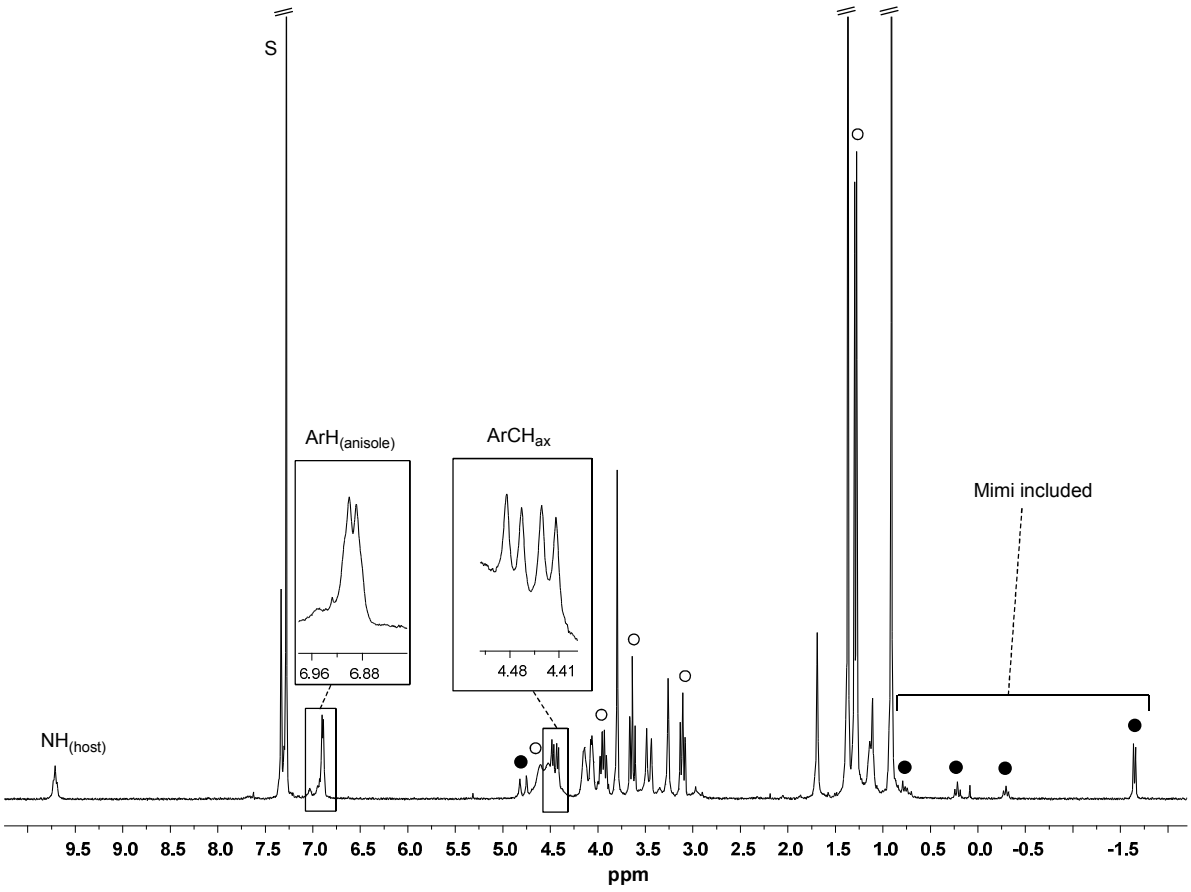


^{1}H NMR (298K, 300MHz) spectrum of **2** in $CDCl_3$ after addition of $MeSO_3H$ (2 equiv.); ▼: $MeSO_3^-$ + $MeSO_3H$; S: solvent; W: water; ***:** residual grease.

SI14. ^{1}H NMR (298K, 300MHz) spectrum of **2⊃Mimi** in $CDCl_3$

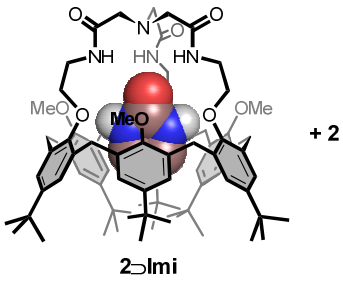


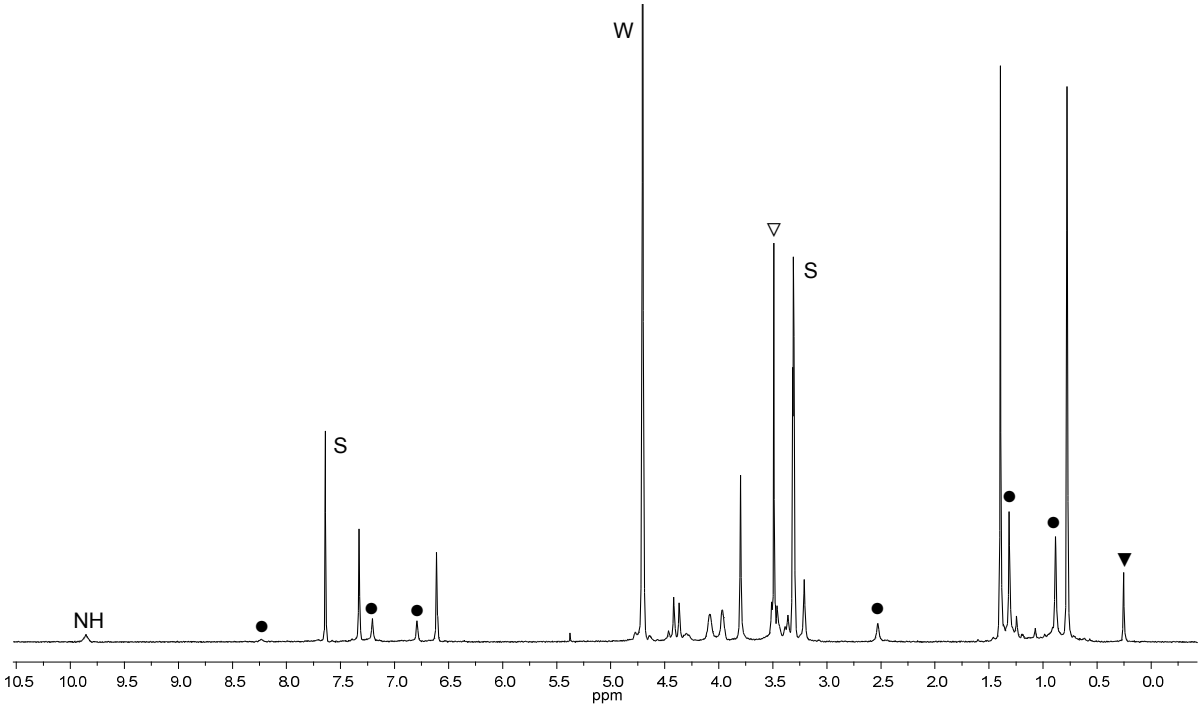
2⊃Mimi



○: free Mimi; ●: Mimi included. S: solvent; W: water.

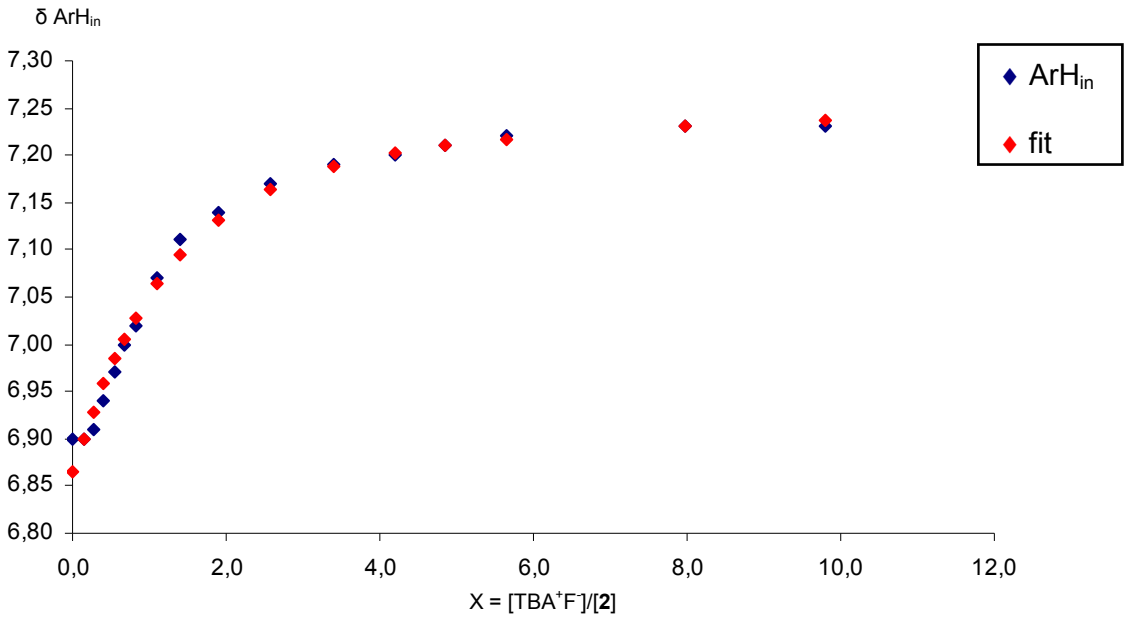
SI15. ^{1}H NMR (298K, 300MHz) spectrum of **2** with Imi (2.5 equiv.) in $CD_3OD/CDCl_3$ (3:2)



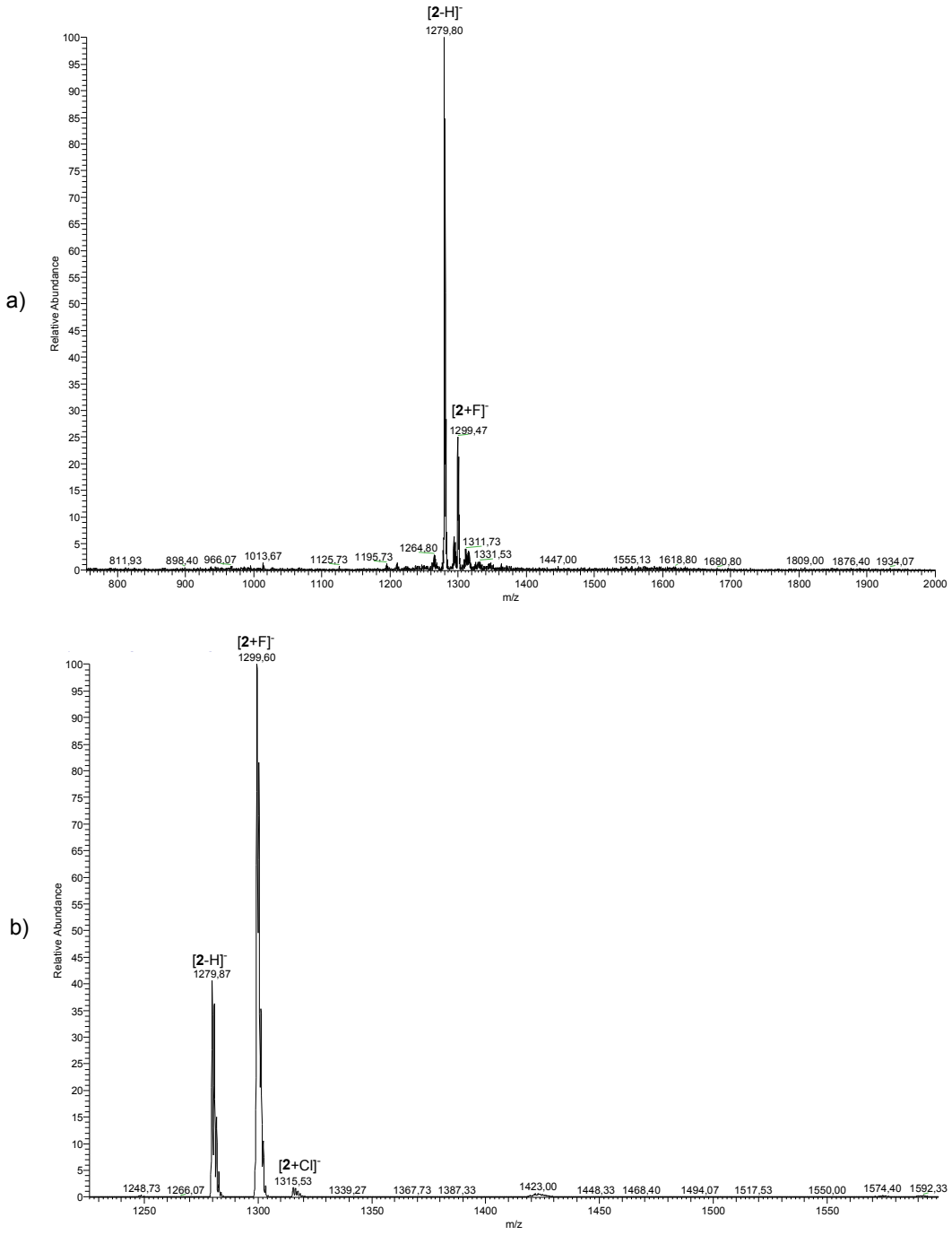


▽: free Imi; ▼: Imi included; ●: **2**. S: solvent; W: water.

SI16. ^{1}H NMR (298K, 300MHz) titration curve of **2** with fluoride anion in $CDCl_3$

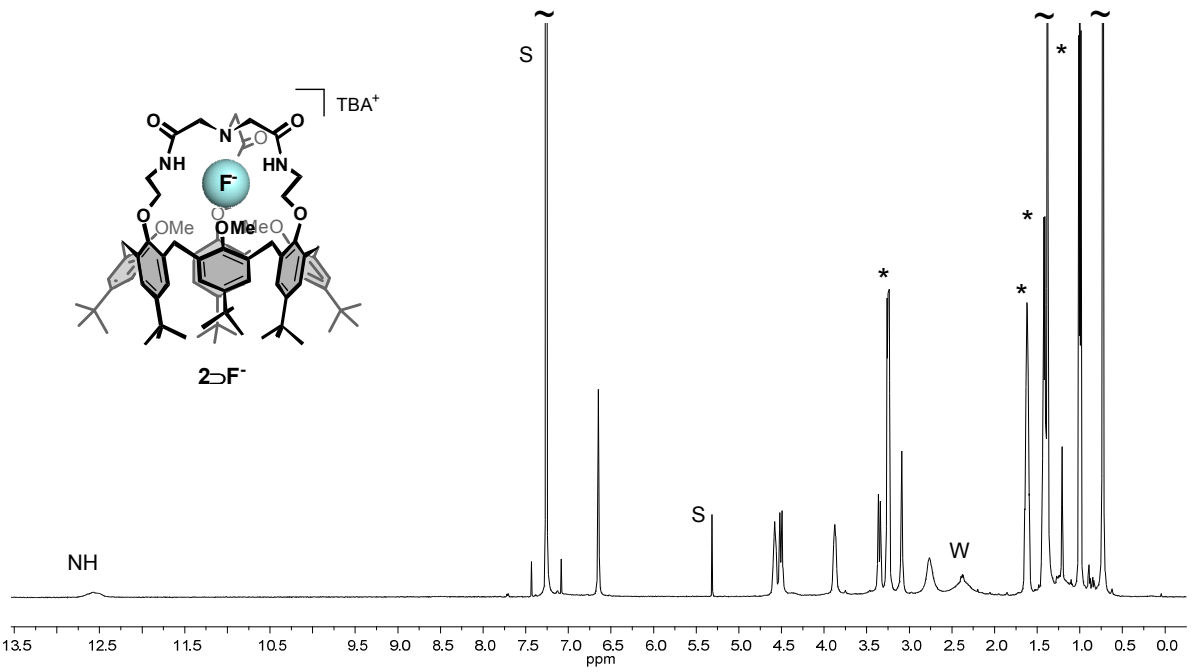


SI17. Competitive ESI-MS binding studies of **2** with TBA^+ salts of F^-, Cl^-, Br^-, AcO^- and NO_3^- in $CHCl_3$



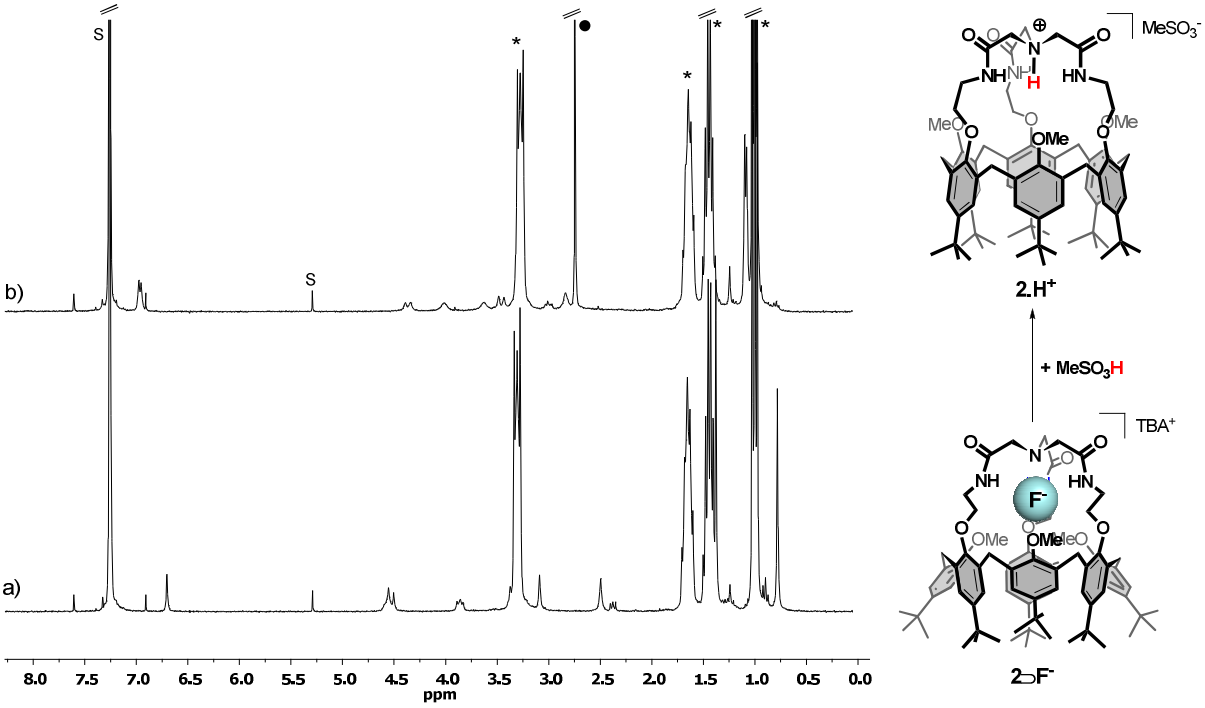
ESI-MS spectra in $CHCl_3$ of a) **2** in presence of an equimolar solution of TBA^+F^-, TBA^+Br^-, TBA^+AcO^- and $TBA^+NO_3^-$; b) **2** in presence of an equimolar solution of TBA^+F^- and TBA^+Cl^-.

SI18. Low temperature ^{1}H NMR (243K, 600MHz) spectrum of **2** with $TBA^{+}F^{-}$ (9 equiv.) in $CDCl_3$



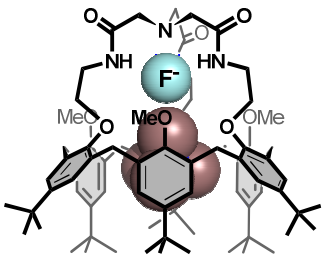
*: TBA^{+}; S: solvent; W: water.

SI19. Acid-triggered release of fluoride anion in $CDCl_3$

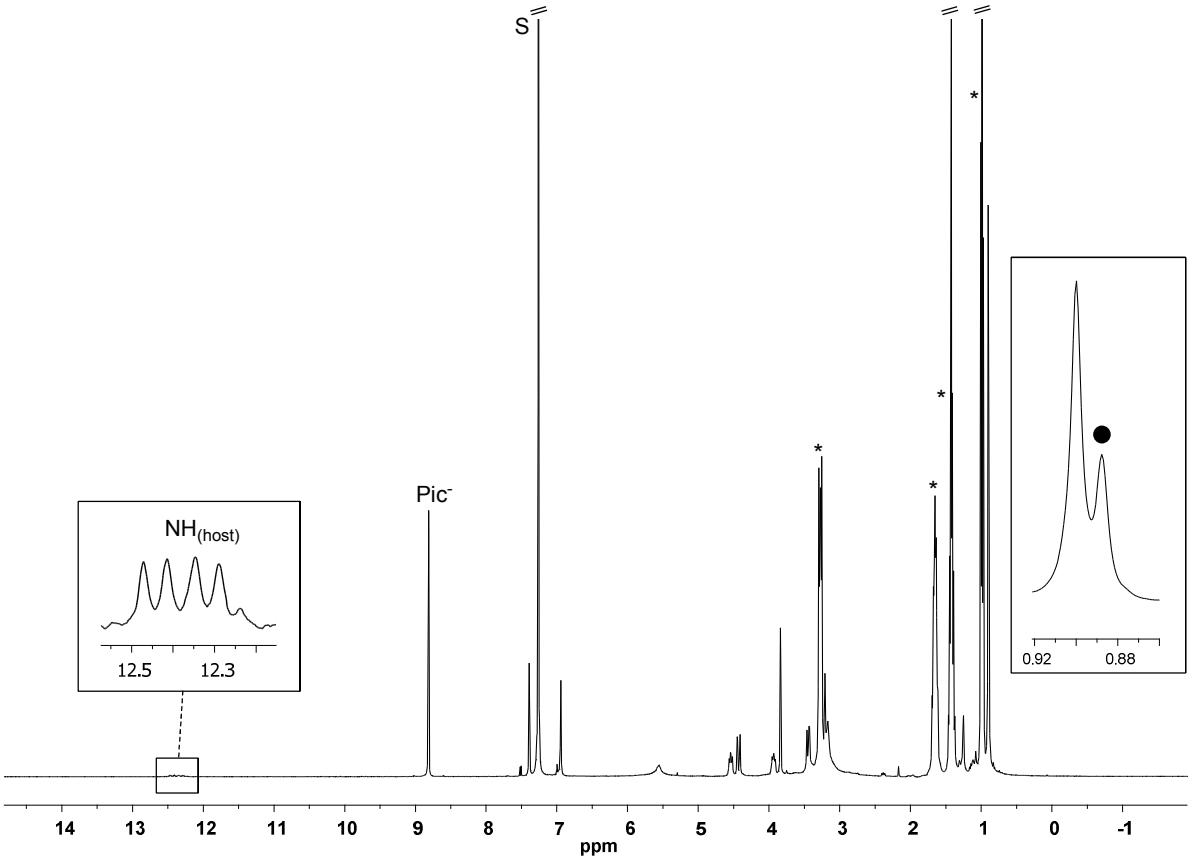


^{1}H NMR (298K, 300MHz) spectra of **2** in $CDCl_3$: a) with TBA^+F^- (20 equiv.); b) after addition of $MeSO_3H$ (15 equiv.); *: TBA^+; ●: $MeSO_3H$. S: solvent.

SI20. ^{1}H NMR (298K, 400MHz) spectrum of **2** with $TBA^{+}F^{-}$ (10 equiv.) and $TMA^{+}Pic^{-}$ (10 equiv.) in $CDCl_3$

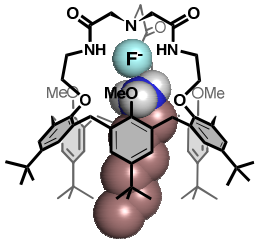


2⊃TMA^{+}F^{-}

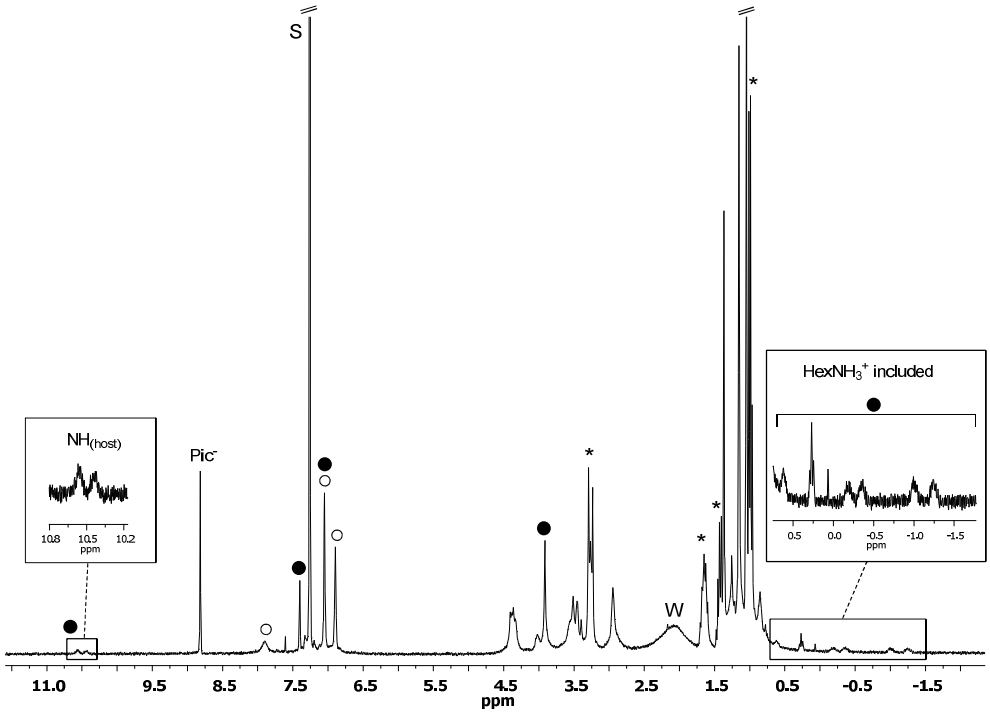


●: TMA^{+} included; *: TBA^{+}. S: solvent.

SI21. ^{1}H NMR (298K, 300MHz) spectrum of **2** with TBA^+F^- (1 equiv.) and $HexNH_3^+Pic^-$ (1 equiv.) in $CDCl_3$

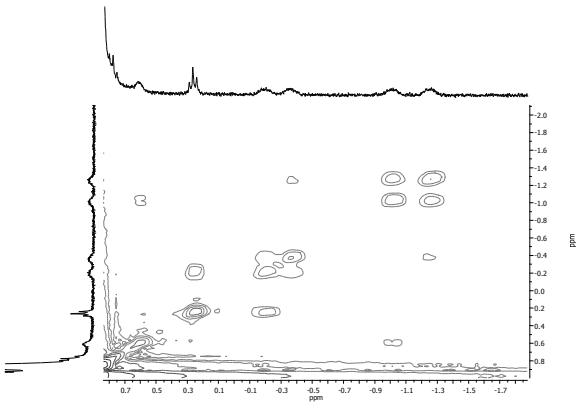


2⊃HexNH$_3^+$F$^-$

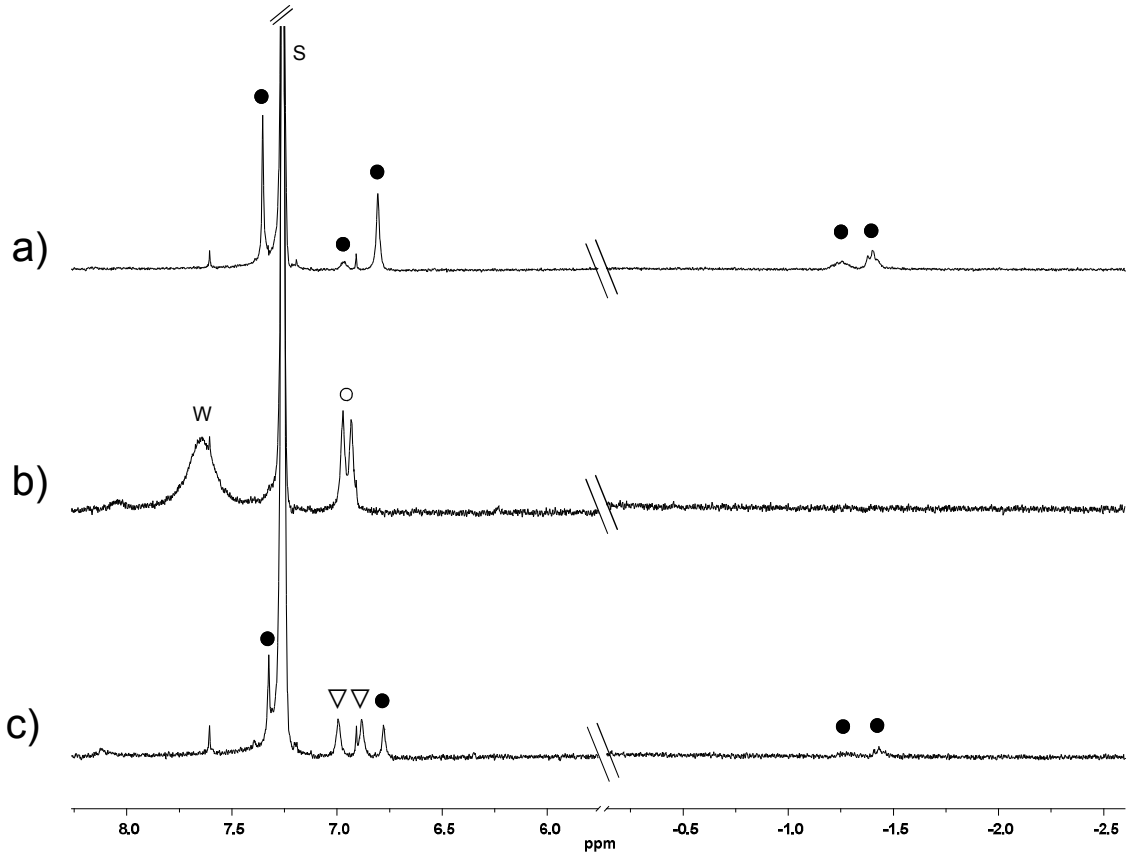


○: **2**; ●: **2⊃HexNH$_3^+$F$^-$**; *: TBA^+. S: solvent; W: water.

SI22. Guest region of the COSY NMR (298K, 300MHz) spectrum of **2⊃HexNH$_3^+$F$^-$** in $CDCl_3$

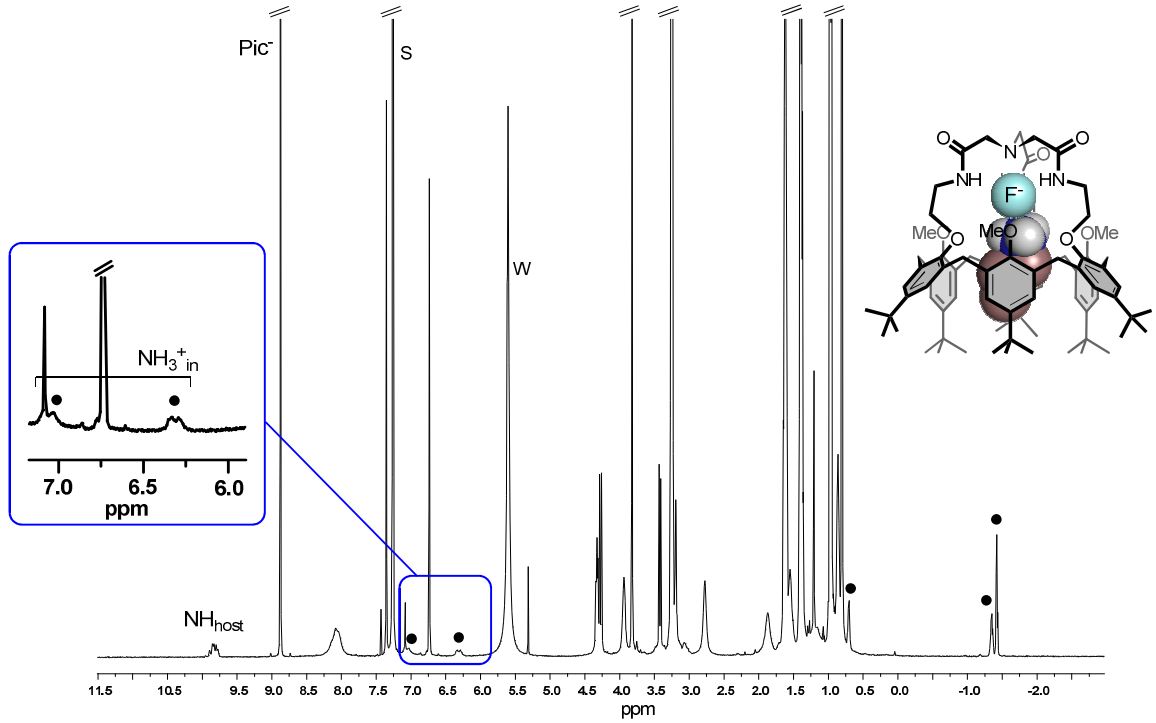


SI23. Acid-triggered release of $PrNH_3^+F^-$ in $CDCl_3$



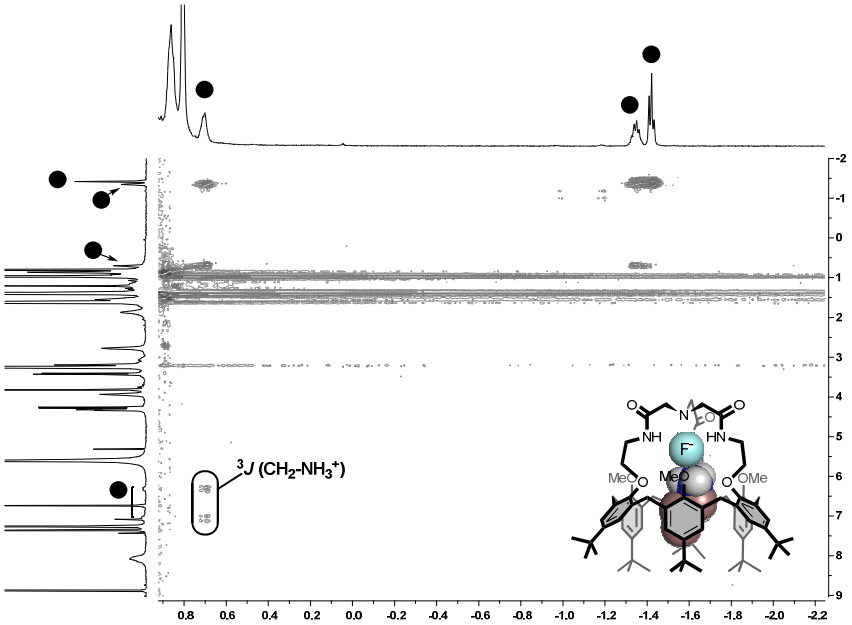
^{1}H NMR (298K, 300MHz) spectra of **2** in $CDCl_3$: a) with $PrNH_3^+F^-$ (6 equiv.); b) after addition of $MeSO_3H$ (24 equiv.); c) after addition of DBU (83 equiv.); ●: **2⊃PrNH$_3^+$F$^-$**; ○: **2.H$^+$**; ▽: **2** + **2.H$^+$**. S: solvent; W: protonated water.

SI24. Low temperature ^{1}H NMR (243K, 600MHz) spectrum of **2** with $TBA^{+}F^{-}$ (5 equiv.) and $PrNH_3^{+}Pic^{-}$ (5 equiv.) in $CDCl_3$.



●: **$PrNH_3^{+}$** included; S: solvent; W: water.

SI25. Guest region of the low temperature COSY NMR (243K, 600MHz) spectrum of **2** with $TBA^{+}F^{-}$ (5 equiv.) and $PrNH_3^{+}Pic^{-}$ (5 equiv.) in $CDCl_3$.



●: **$PrNH_3^{+}$** included.