Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Acid-base modulation of a versatile heteroditopic calix[6]arene based receptor

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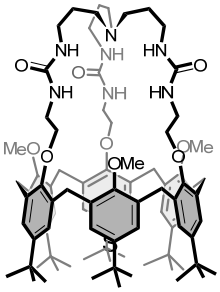
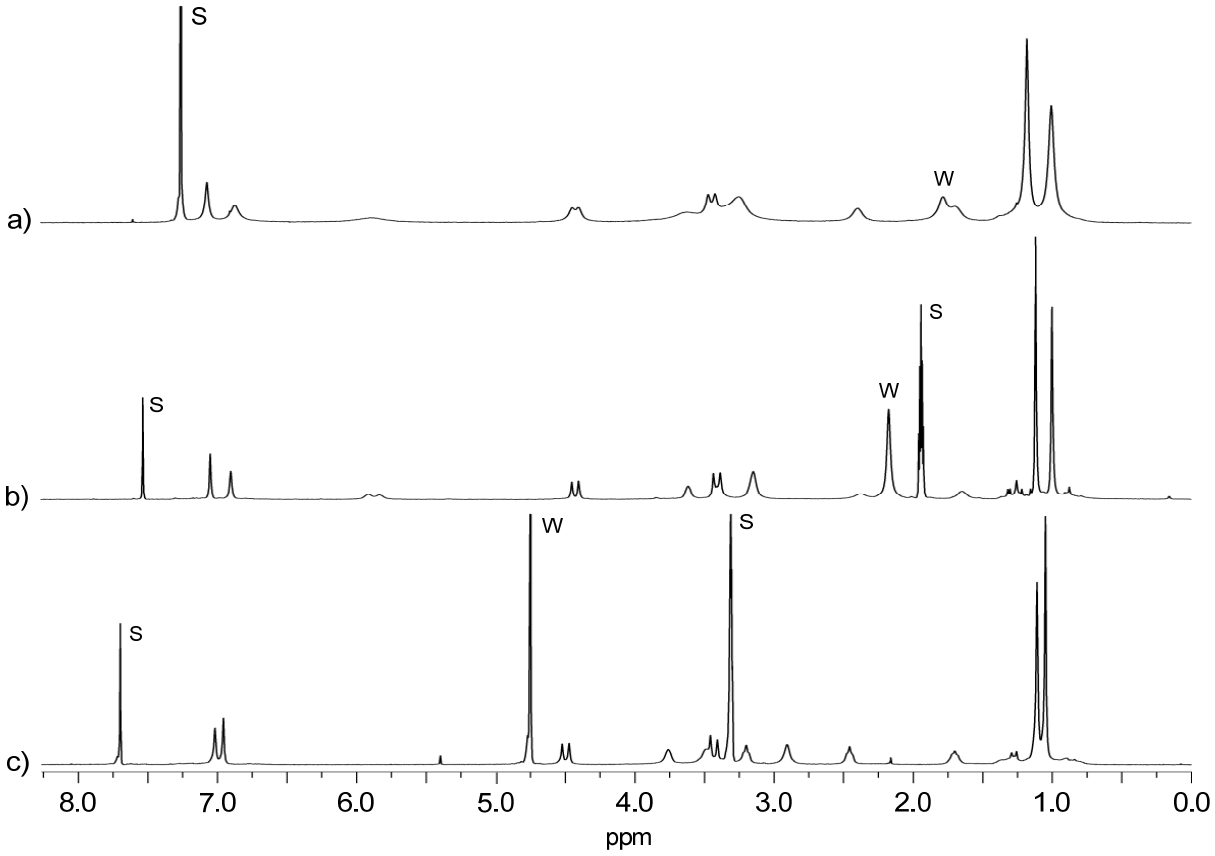
SI1. ^{1}H NMR (298K, 300MHz) spectra of **3** in $CDCl_3$, $CD_3CN/CDCl_3$ (7:3) and $CD_3OD/CDCl_3$ (7:3)

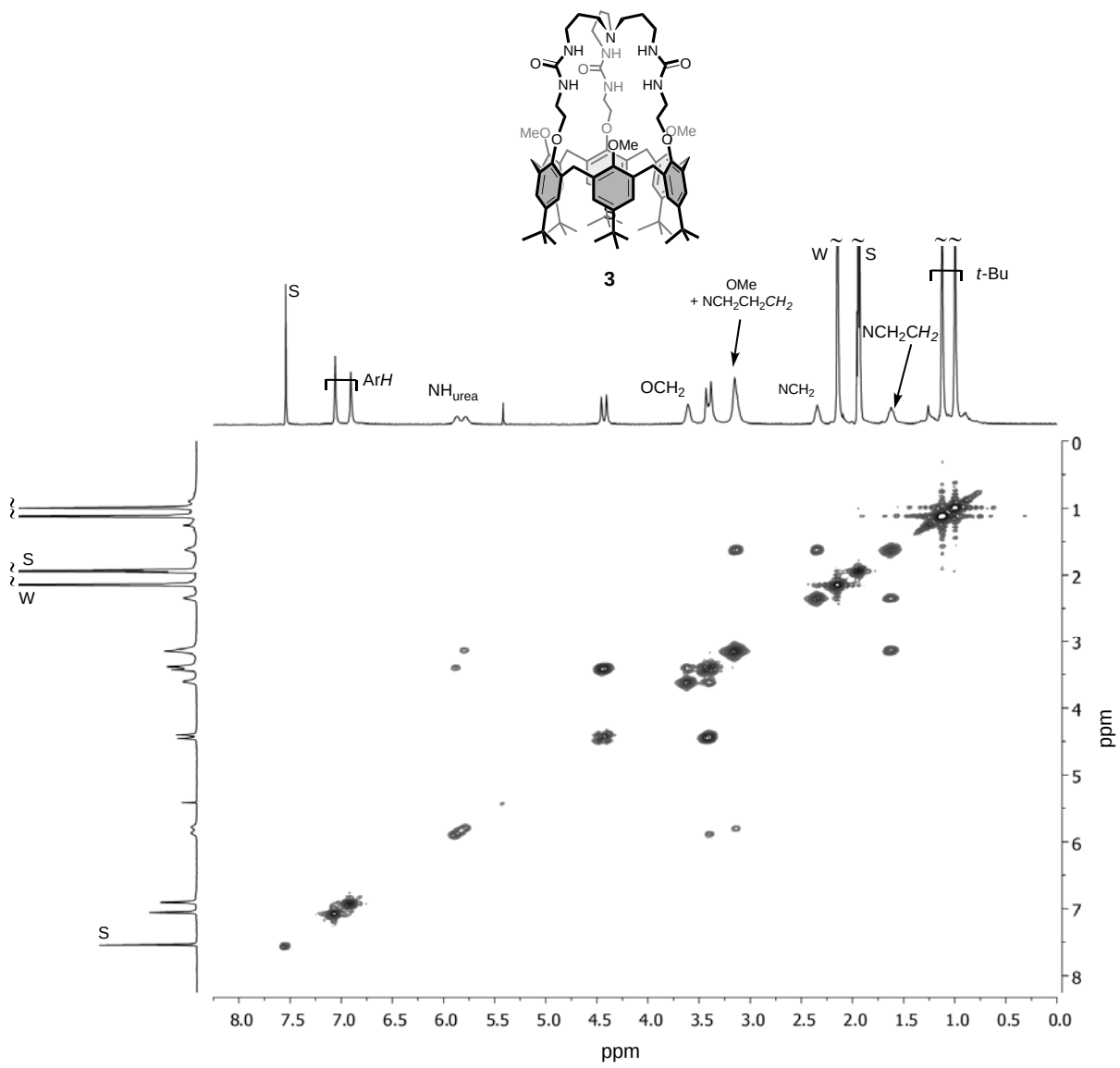


3



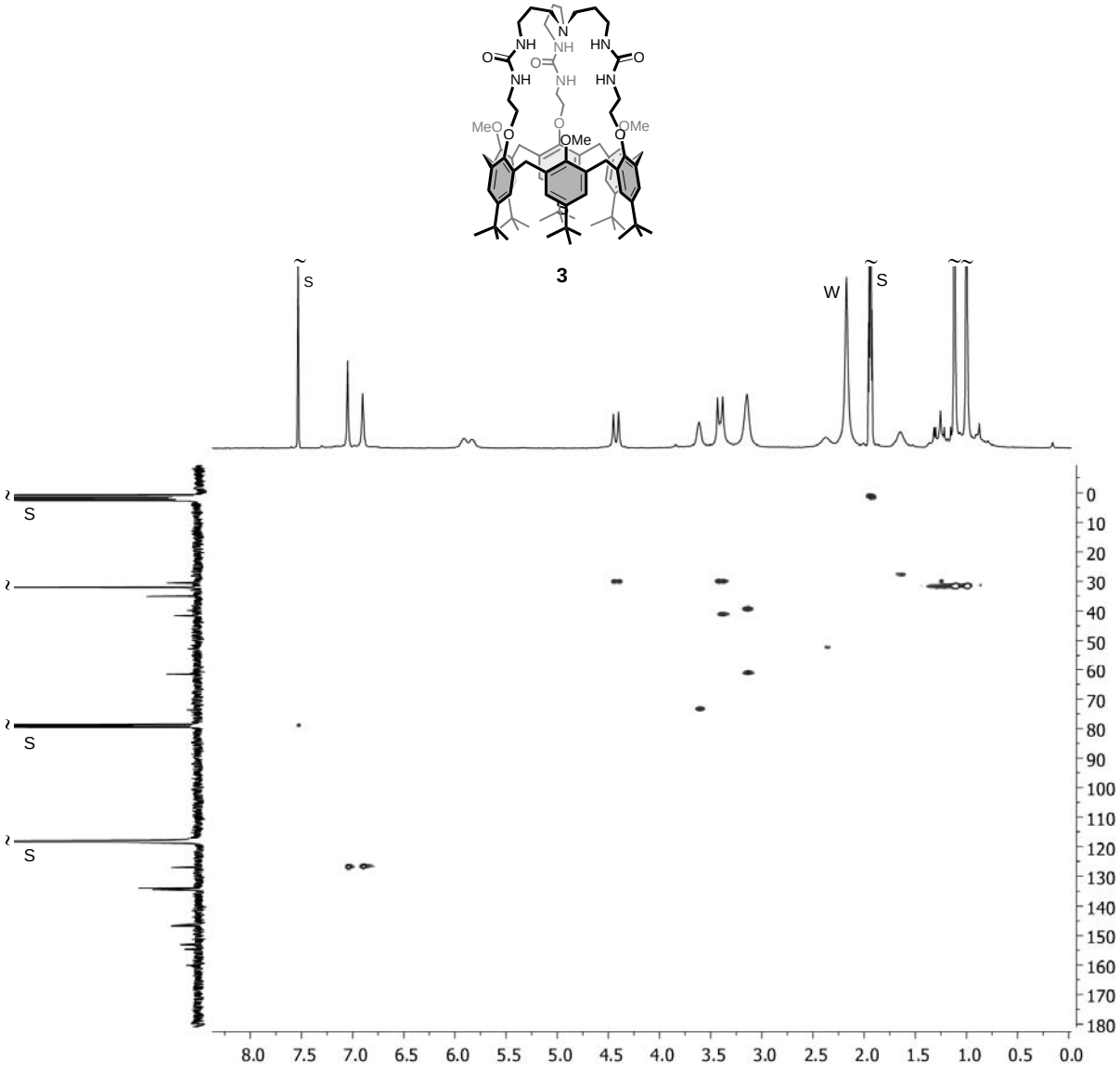
^{1}H NMR (298K, 300MHz) spectra of **3** in a) $CDCl_3$, b) $CD_3CN/CDCl_3$ (7:3) and c) $CD_3OD/CDCl_3$ (7:3). S: solvent; W: water.

SI2. COSY (298K, 300 MHz) spectrum of **3** in $CD_3CN/CDCl_3$ (7:3)



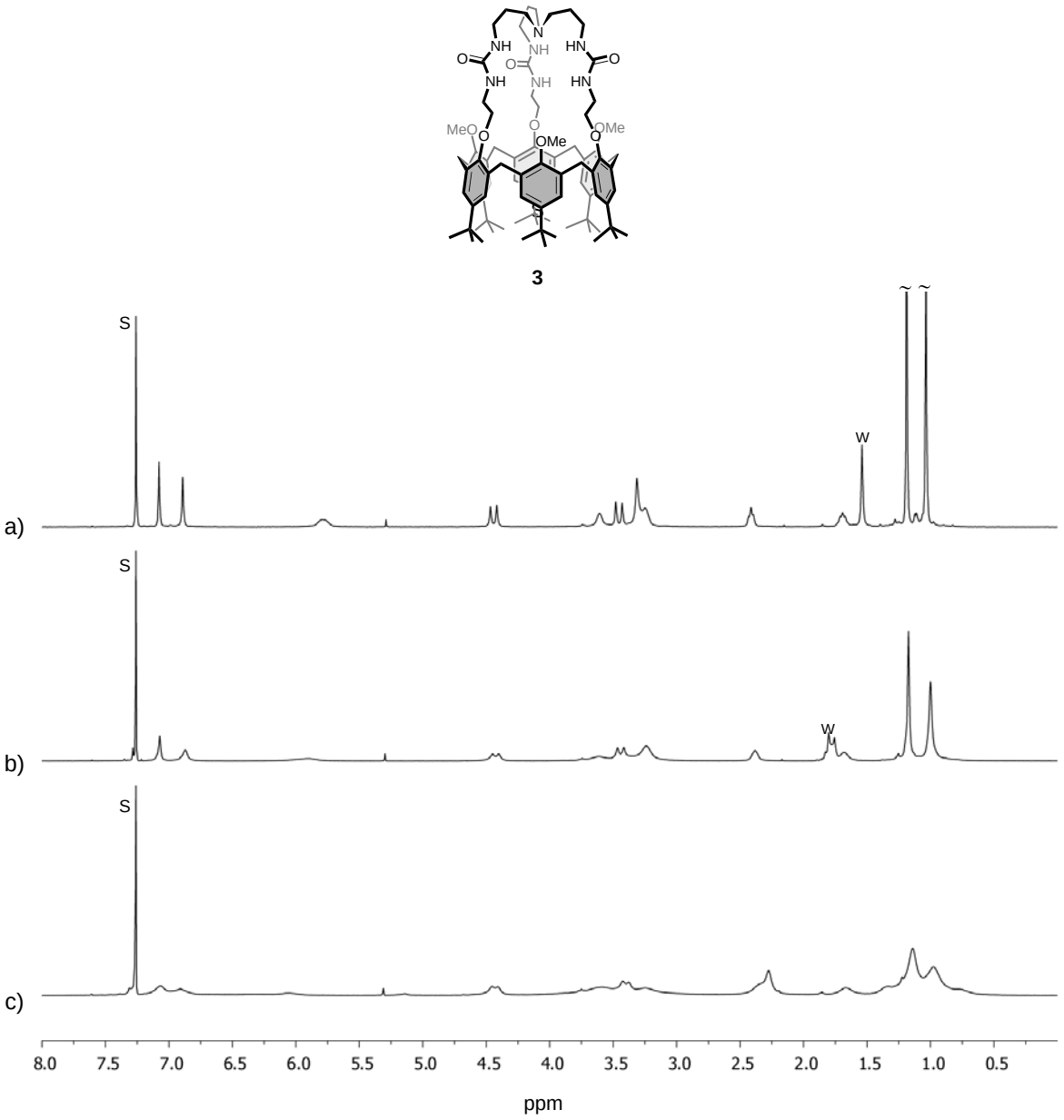
COSY (298 K, 300 MHz) spectrum of **3** in $CD_3CN/CDCl_3$ (7:3). S: solvent; W: water.

SI3. HSQC (298K, 300 MHz) spectrum of **3** in $CD_3CN/CDCl_3$ (7:3)



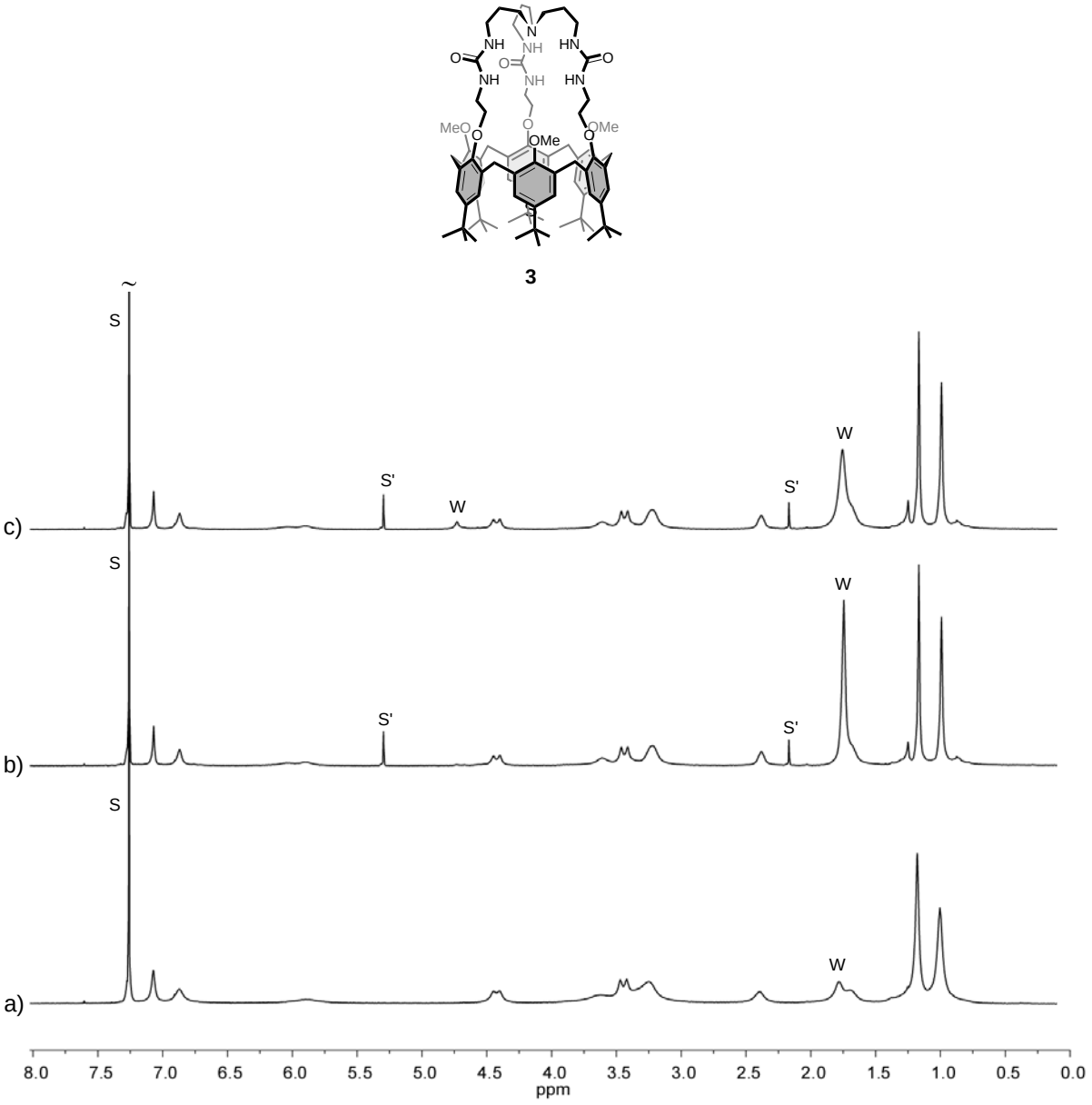
HSQC (298K, 300 MHz) spectrum of **3** in $CD_3CN/CDCl_3$ (7:3). S: solvent; W: water.

SI4. ^{1}H NMR (300 MHz) spectra of **3** in $CDCl_3$ at 328K, 298K and 258K



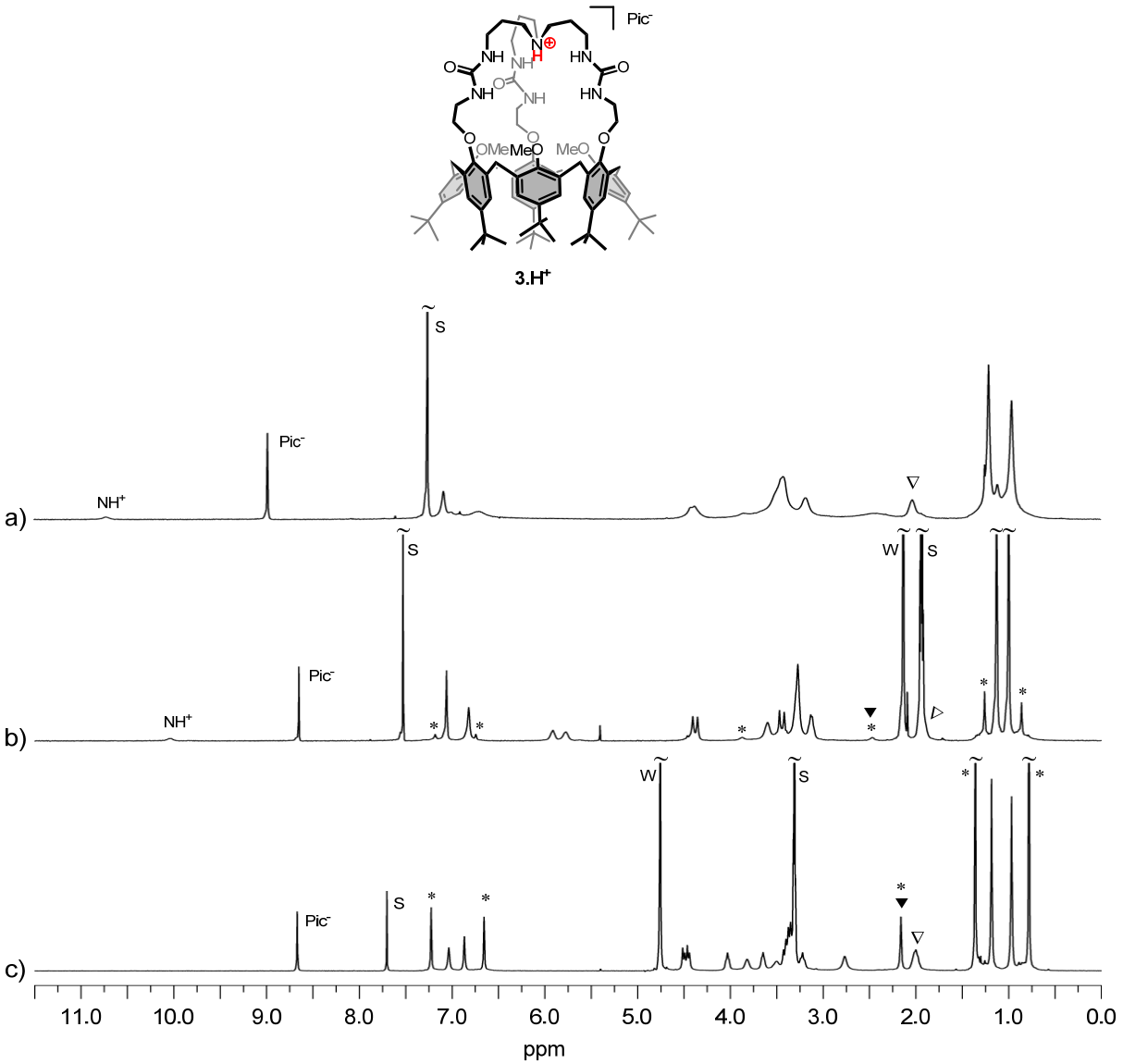
^{1}H NMR (300 MHz) spectra of **3** in $CDCl_3$ at a) 328K, b) 298K and c) 258K. S: solvent; W: water.

SI5. ^{1}H NMR (298K, 300 MHz) spectra of **3** in $CDCl_3$ with different amounts of water



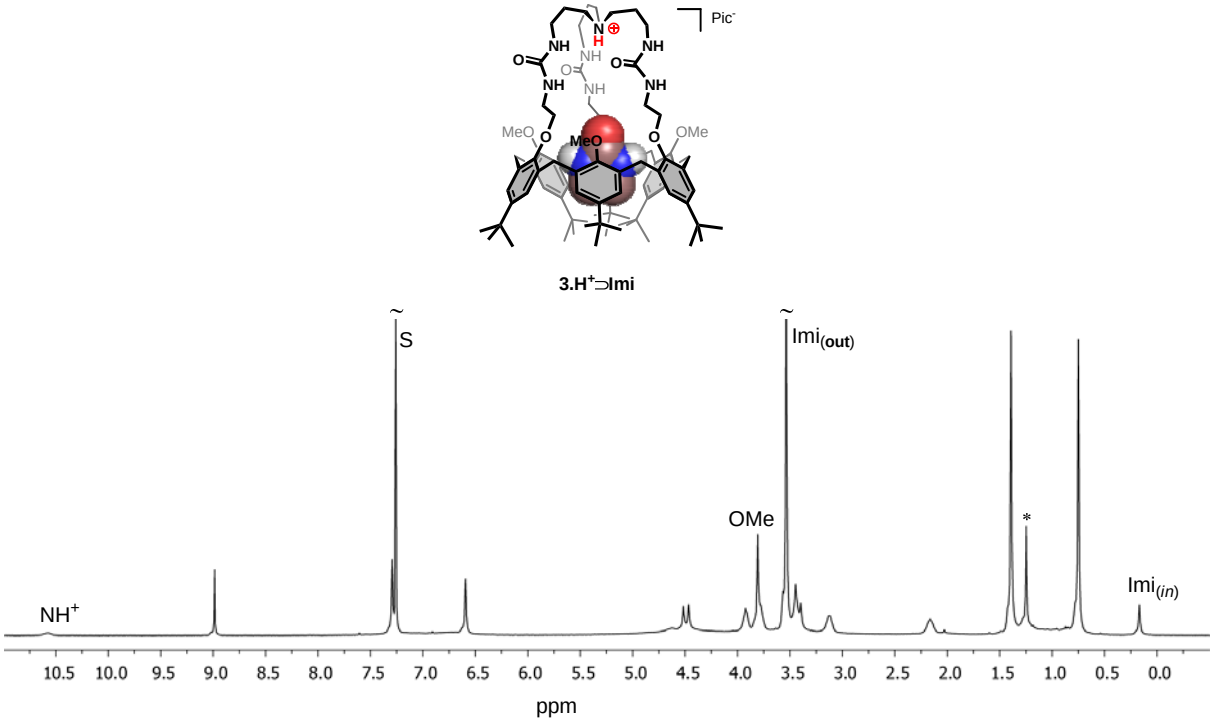
^{1}H NMR (298K, 300 MHz) spectra of **3** in $CDCl_3$ with a) 4 equiv. of H_2O, b) 26 equiv. of H_2O and c) saturated with H_2O. S: solvent; W: water, S': residual solvent.

SI6. ^{1}H NMR (298K, 300 MHz) spectra of **3.H$^+$** in $CDCl_3$, $CD_3CN/CDCl_3$ (7:3) and $CD_3OD/CDCl_3$ (7:3)



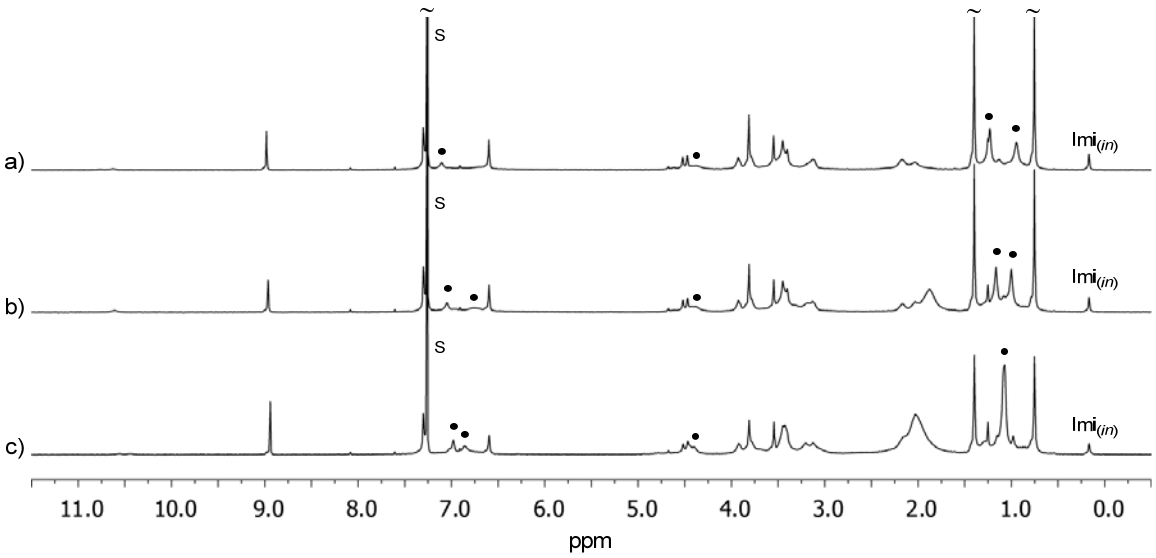
^{1}H NMR (298K, 300 MHz) spectra of **3.H$^+$** in a) $CDCl_3$, b) $CD_3CN/CDCl_3$ (7:3) and c) $CD_3OD/CDCl_3$ (7:3). S: solvent; W: water; *: C_{3v} symmetrical flattened cone conformation; ▼: $OMe_{(in)}$; ∇: $NH^+CH_2CH_2$

SI7. ^{1}H NMR (298K, 300 MHz) spectrum of **3.H^{+}⊃Imi** in $CDCl_3$



^{1}H NMR (298K, 300MHz) spectrum of **3** with PicH (1.6 eq) and Imi (8.5eq) in $CDCl_3$. S: solvent; W: water; *: residual grease.

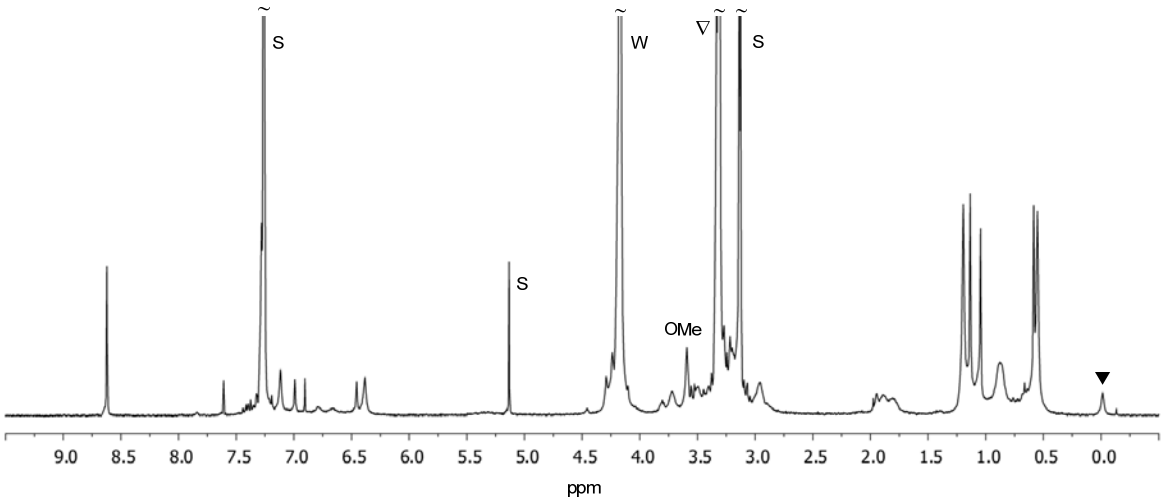
SI8. ^{1}H NMR (298K, 300 MHz) complexation studies of Imi in $CDCl_3$ in presence of water



^{1}H NMR (298K, 300MHz) spectra of **3.H$^+$** with Imi (1.6 equiv.) in $CDCl_3$ in the presence of a) 3 equiv.; b) 10 equiv.; c) 19 equiv.; S: solvent; W: water; ●: mixture of **3.H$^+$** and **3.H$^+$⊃nH_2O**.

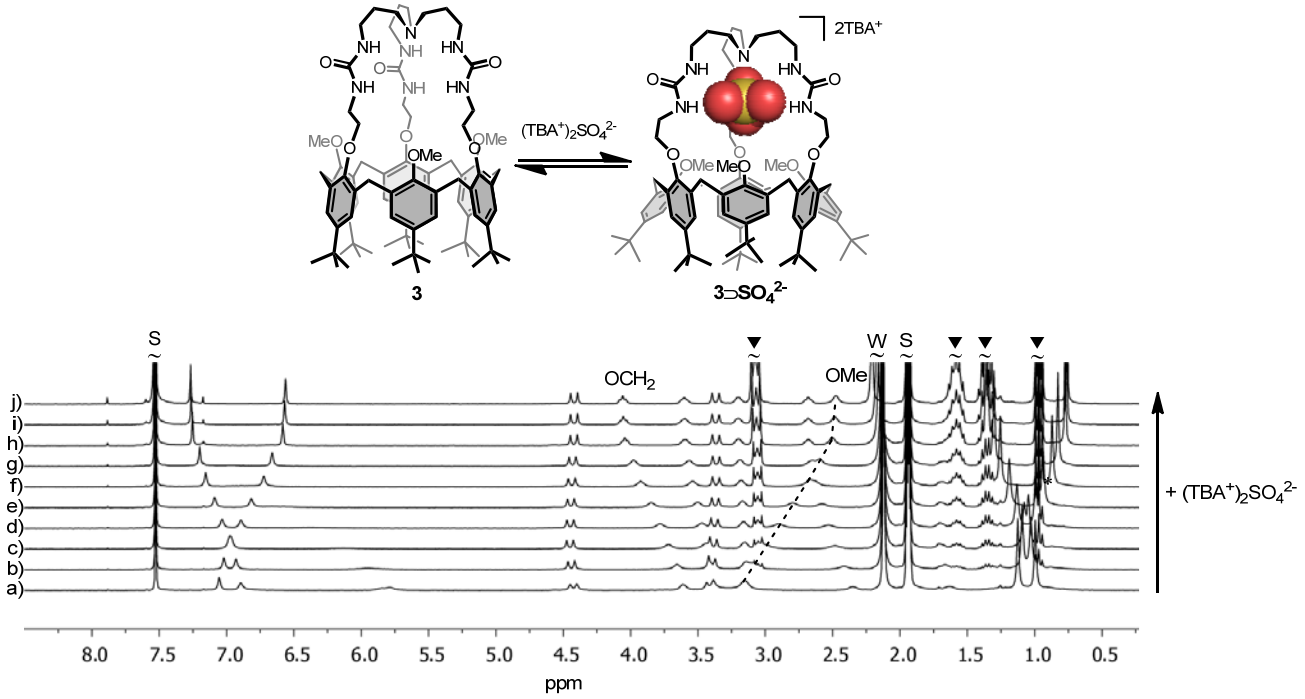
This NMR study clearly shows that **3.H$^+$** bounds water. Note that the chemical shifts of the NMR signals corresponding to the protonated calixarene species that do not include Imi (i.e.: ●) are modified upon the addition of water. This result can be rationalized by the fact that these signals correspond to a mixture of **3.H$^+$** and **3.H$^+$⊃nH_2O**, the exchange process between these two species being fast on the NMR time scale.

SI9. ^{1}H NMR (298K, 300 MHz) spectrum of **3.H**$^+$ with Imi in $CD_3OD/CDCl_3$ (1:2)



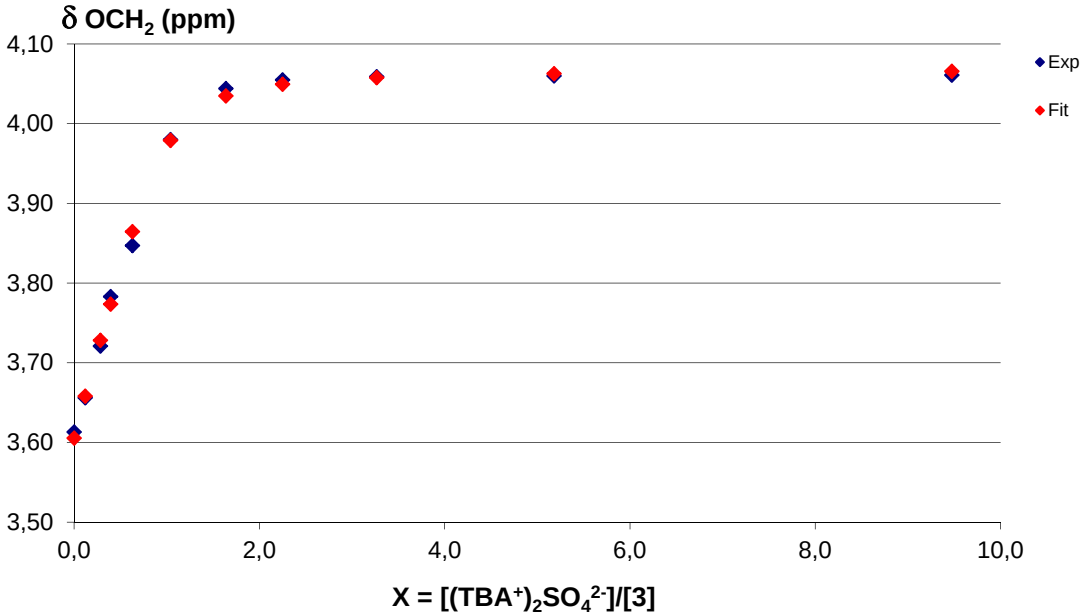
^{1}H NMR (298K, 300 MHz) spectrum of **3.H**$^+$ with Imi (38 equiv.) in $CD_3OD/CDCl_3$ (1:2). S: solvent; W: water; ▼: Imi in; ∇: Imi out.

SI10. ^{1}H NMR (298K, 300 MHz) spectra of titration of **3** with SO_4^{2-} in $CD_3CN/CDCl_3$ (7:3)

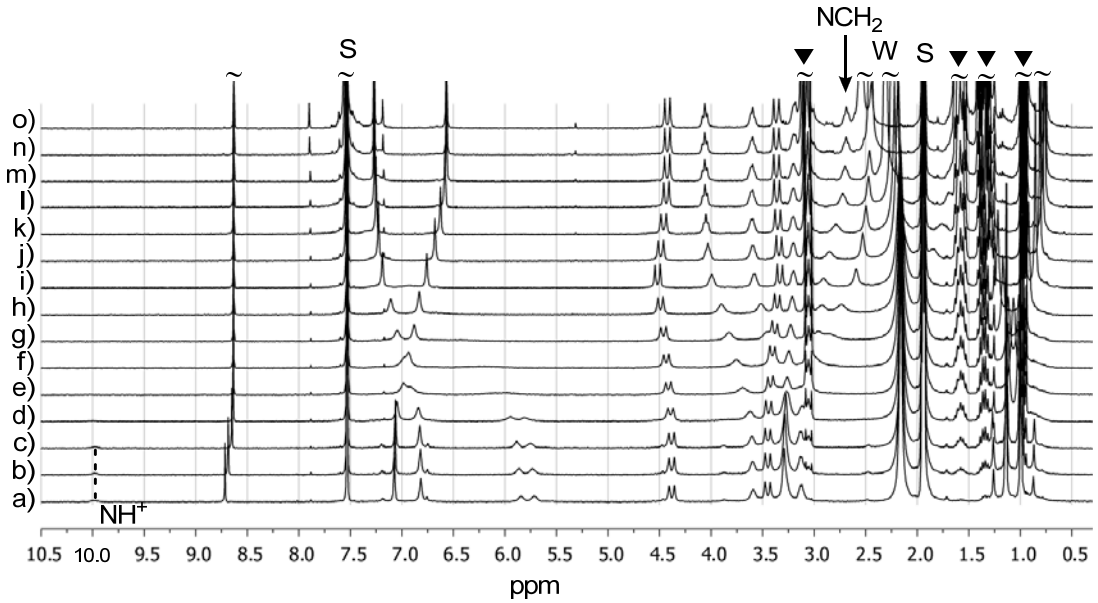


^{1}H NMR (298K, 300 MHz) spectra in $CD_3CN/CDCl_3$ (7:3) of a) **3** (1 mM) with b) 0.12 equiv.; c) 0.29 equiv.; d) 0.40 equiv.; e) 0.63 equiv.; f) 1.04 equiv.; g) 2.25 equiv.; h) 3.27 equiv.; i) 5.18 equiv.; j) 9.47 equiv. of $(TBA^+)_2SO_4^{2-}$. S: solvent; W: water; ▼: TBA^+.

SI11. ^{1}H NMR (298K, 300 MHz) titration curve of **3** with SO_4^{2-} in $CD_3CN/CDCl_3$ (7:3)

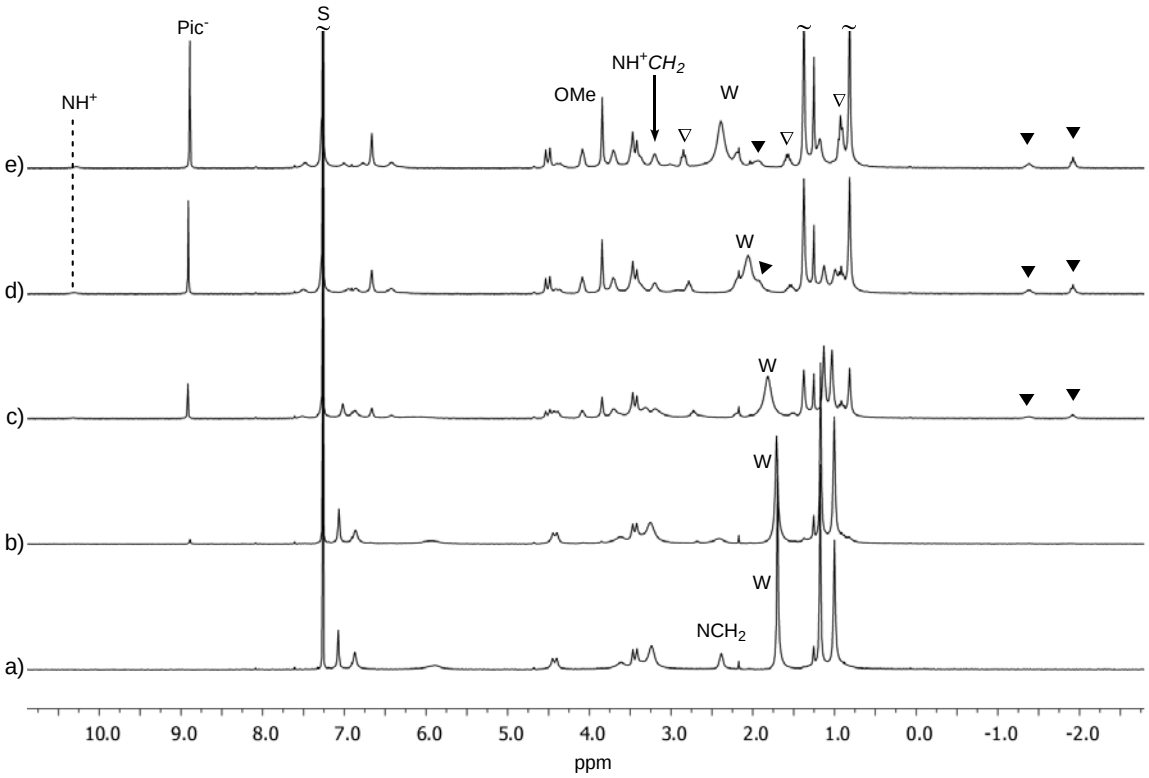


SI12. ^{1}H NMR (298K, 300 MHz) spectra of **3.H**$^+$ with SO_4^{2-} in $CD_3CN/CDCl_3$ (7:3)



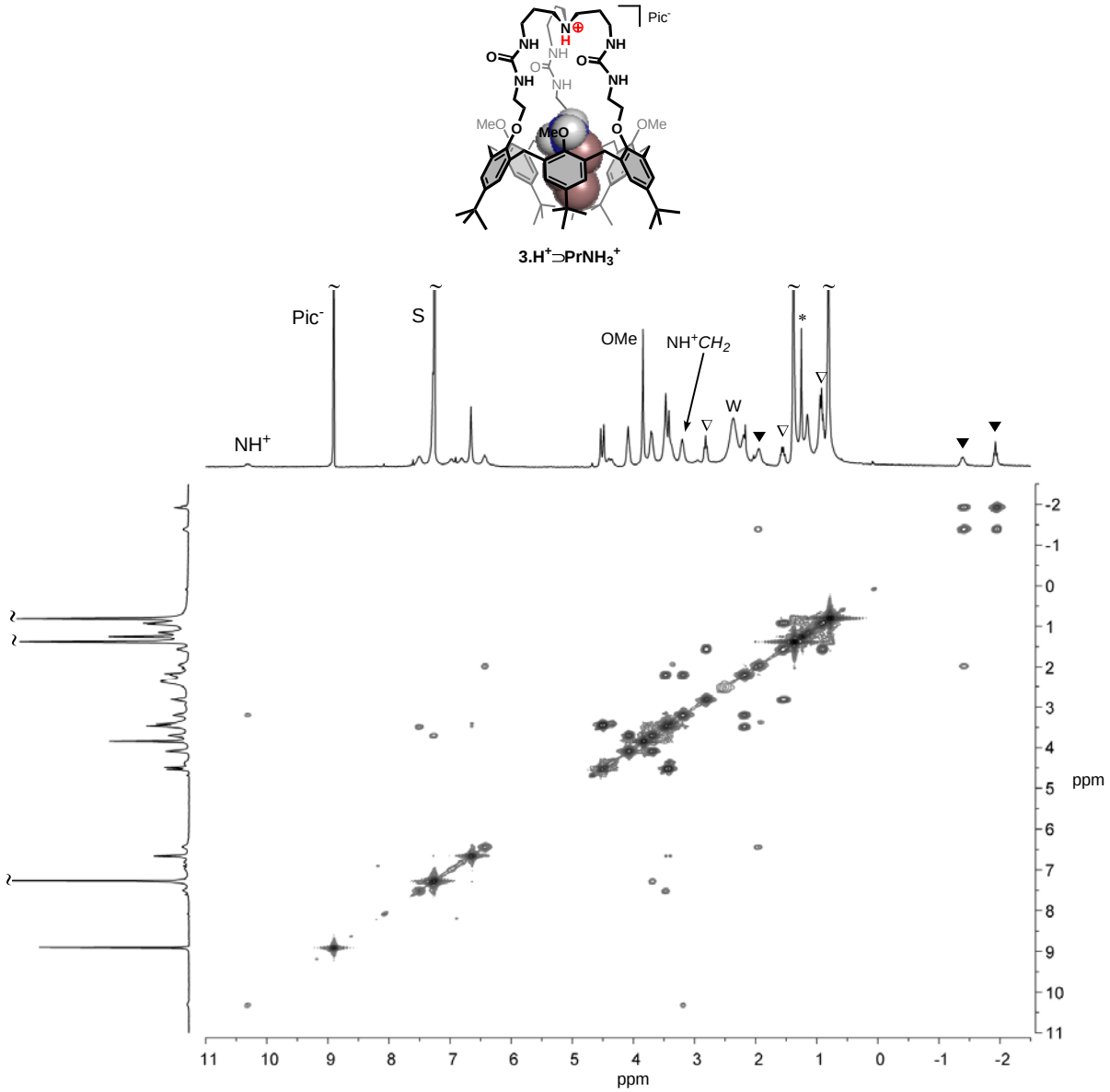
^{1}H NMR (298K, 300MHz) spectra in $CD_3CN/CDCl_3$ (7:3) of a) **3.H**$^+$ (1 mM) with b) 0.15 equiv.; c) 0.28 equiv.; d) 0.43 equiv.; e) 0.62 equiv.; f) 0.81 equiv.; g) 0.98 equiv.; h) 1.17 equiv.; i) 1.58 equiv.; j) 1.96 equiv.; k) 2.59 equiv.; l) 3.38 equiv.; m) 5.02 equiv.; n) 9.24 equiv.; o) 12.86 equiv. of $(TBA^+)_2SO_4^{2-}$. S: solvent; W: water.

SI13. ^{1}H NMR (298K, 300 MHz) spectra of **3** with $PrNH_3^+Pic^-$ in $CDCl_3$



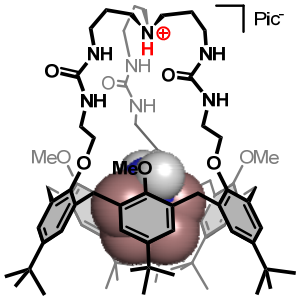
^{1}H NMR (298K, 300 MHz) spectra in $CDCl_3$ of a) **3** with b) 0.2 equiv.; c) 1.2 equiv.; d) 2.3 equiv.; e) 2.7 equiv. of $PrNH_3^+Pic^-$. S: solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out.

SI14. COSY (298K, 300 MHz) spectrum of **3.H$^+$⊃PrNH$_3^+$** in $CDCl_3$

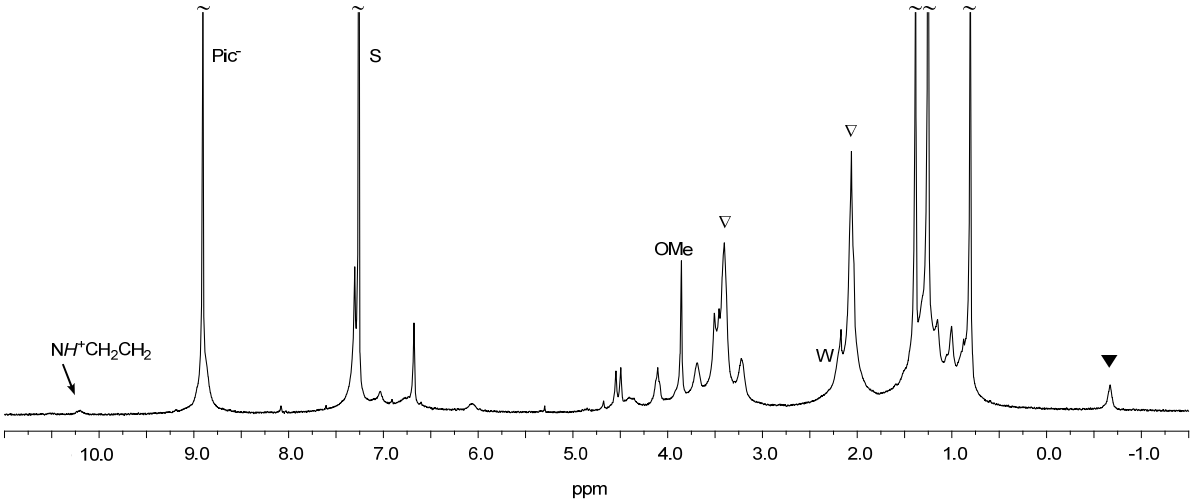


COSY (298K, 300 MHz) spectrum of **3** with $PrNH_3^+Pic^-$ (2.7 equiv.) in $CDCl_3$. S: solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; *: residual grease.

SI15. ^{1}H NMR (298K, 300 MHz) spectrum of **3.H$^+$⊃PyrNH$_2^+$** in $CDCl_3$

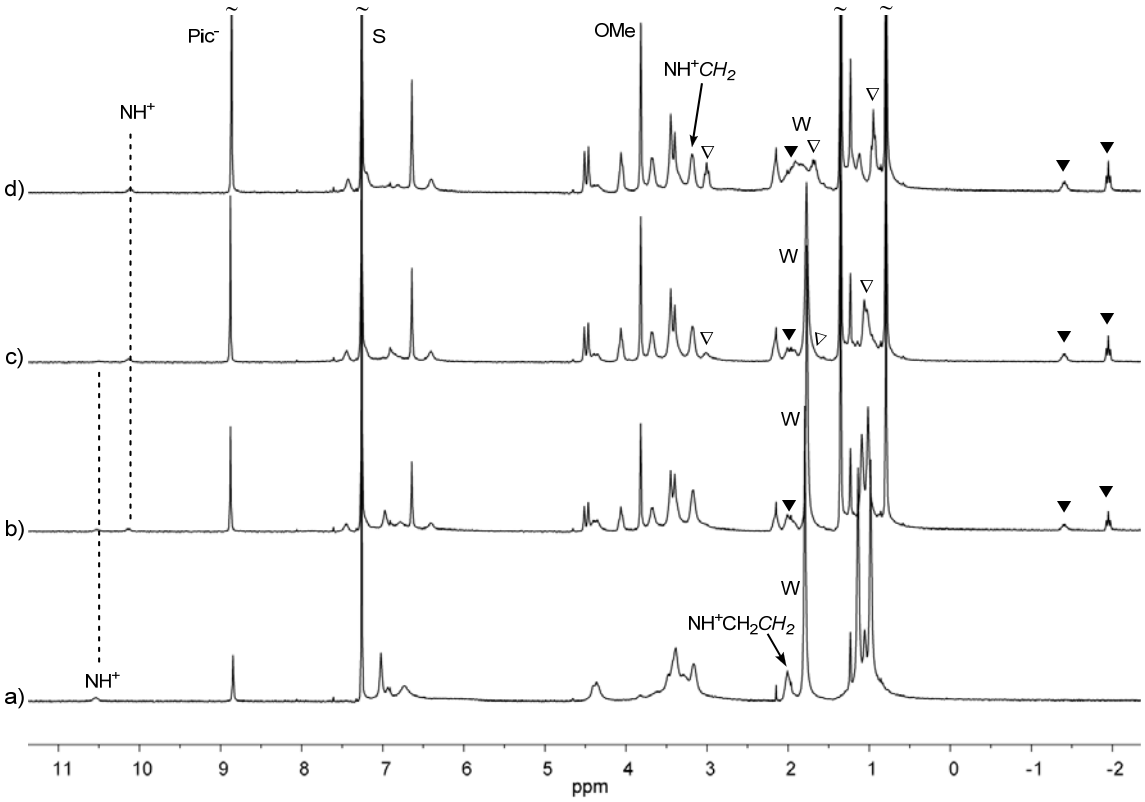


3.H$^+$⊃PyrNH$_2^+$



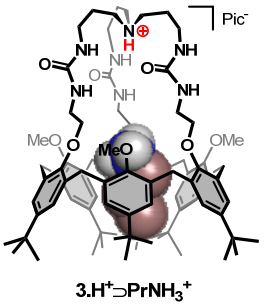
^{1}H NMR (298K, 300 MHz) spectrum of **3** with PicH (ca. 5 equiv.) and $PyrNH_2^+Pic^-$ (ca. 8 equiv.) in $CDCl_3$. S: Solvent; W: water; ▼: $PyrNH_2^+$ in; ∇: $PyrNH_2^+$ out.

SI16. ^{1}H NMR (298K, 300 MHz) spectra of **3.H**$^+$ with $PrNH_3^+Pic^-$ in $CDCl_3$

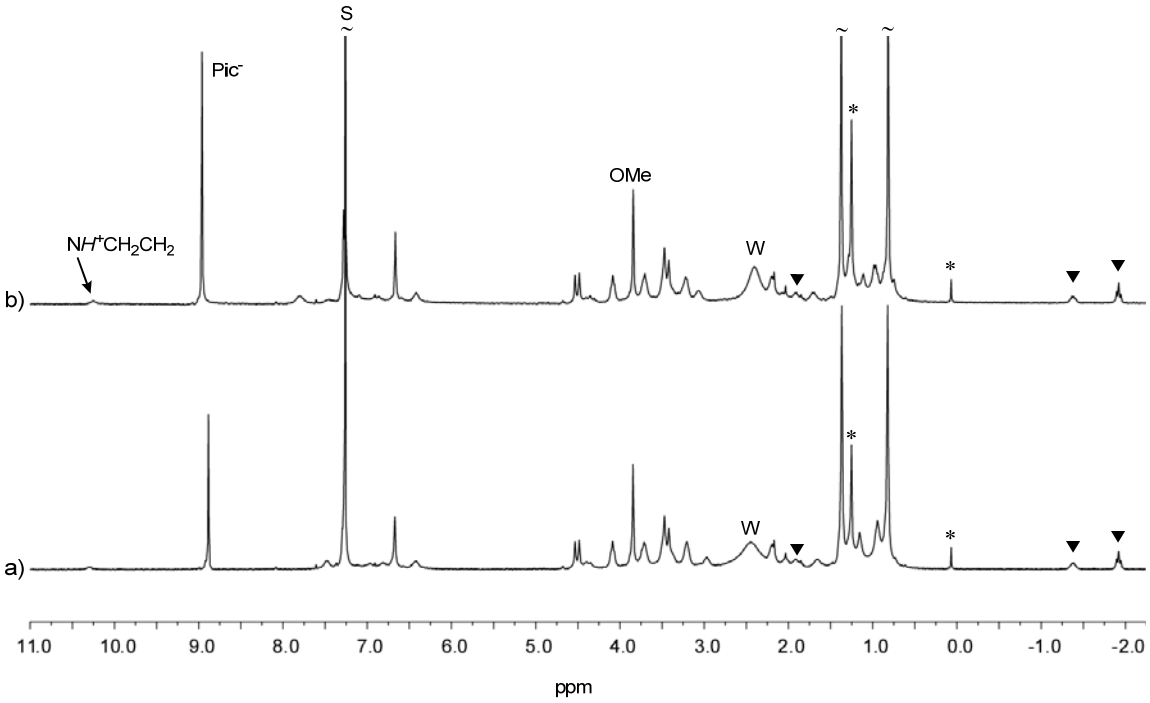


^{1}H NMR (298K, 300 MHz) spectra of **3** in $CDCl_3$ with a) PicH (1.2 equiv.); b) 0.4 equiv.; c) 1 equiv.; d) 2.2 equiv. of $PrNH_3^+$ Pic^-. S: solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out.

SI17. ^{1}H NMR (298K, 300 MHz) spectra of **3.H$^+$⊃PrNH$_3^+$** in $CDCl_3$ upon addition of PicH

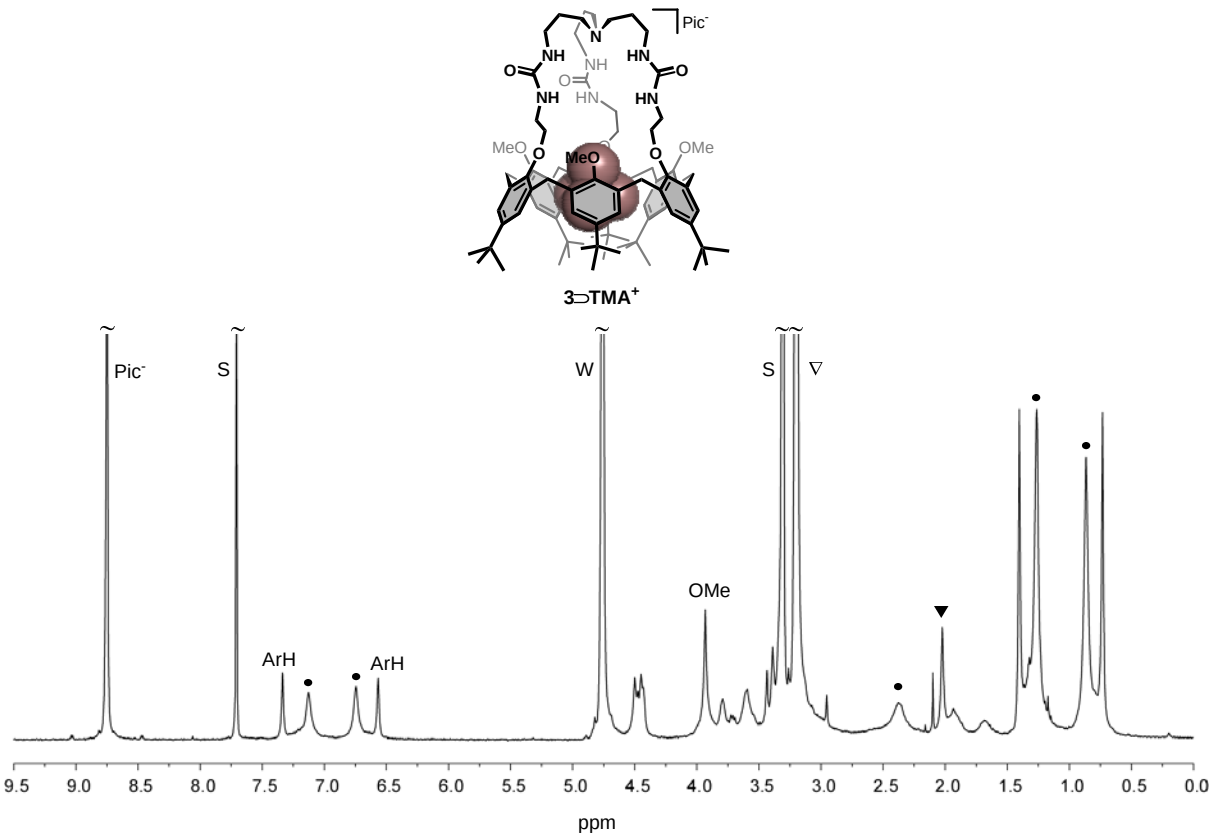


3.H$^+$⊃PrNH$_3^+$



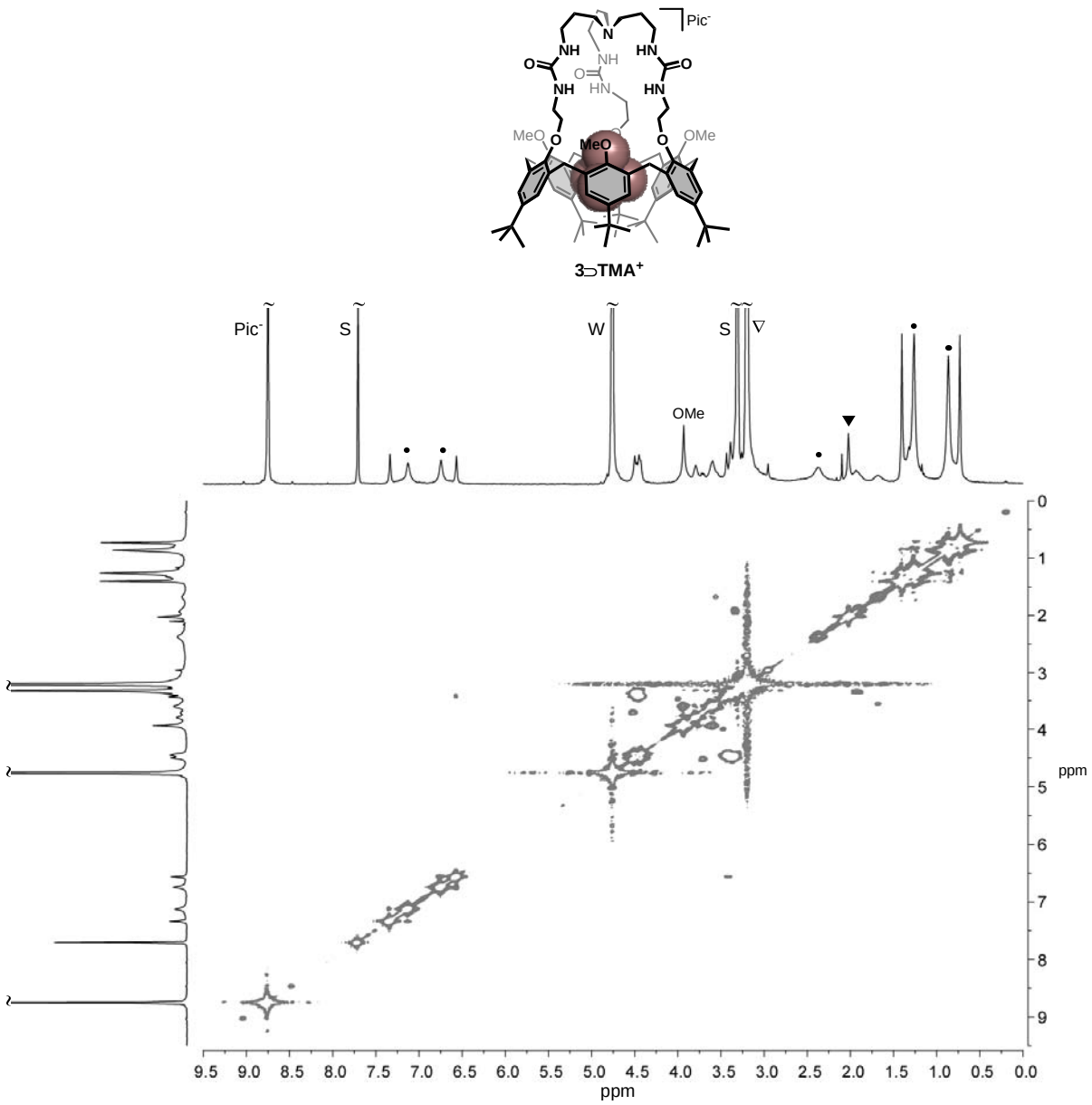
^{1}H NMR (298K, 300 MHz) spectra of a) **3.H$^+$⊃PrNH$_3^+$** in $CDCl_3$; b) after addition of PicH (1.9 equiv.). S: solvent; W: water; *: residual grease; ▼: $PrNH_3^+$ in.

SI18. ^{1}H NMR (298K, 300 MHz) spectra of **3⊃TMA**$^+$ in $CD_3OD/CDCl_3$ (7:3)



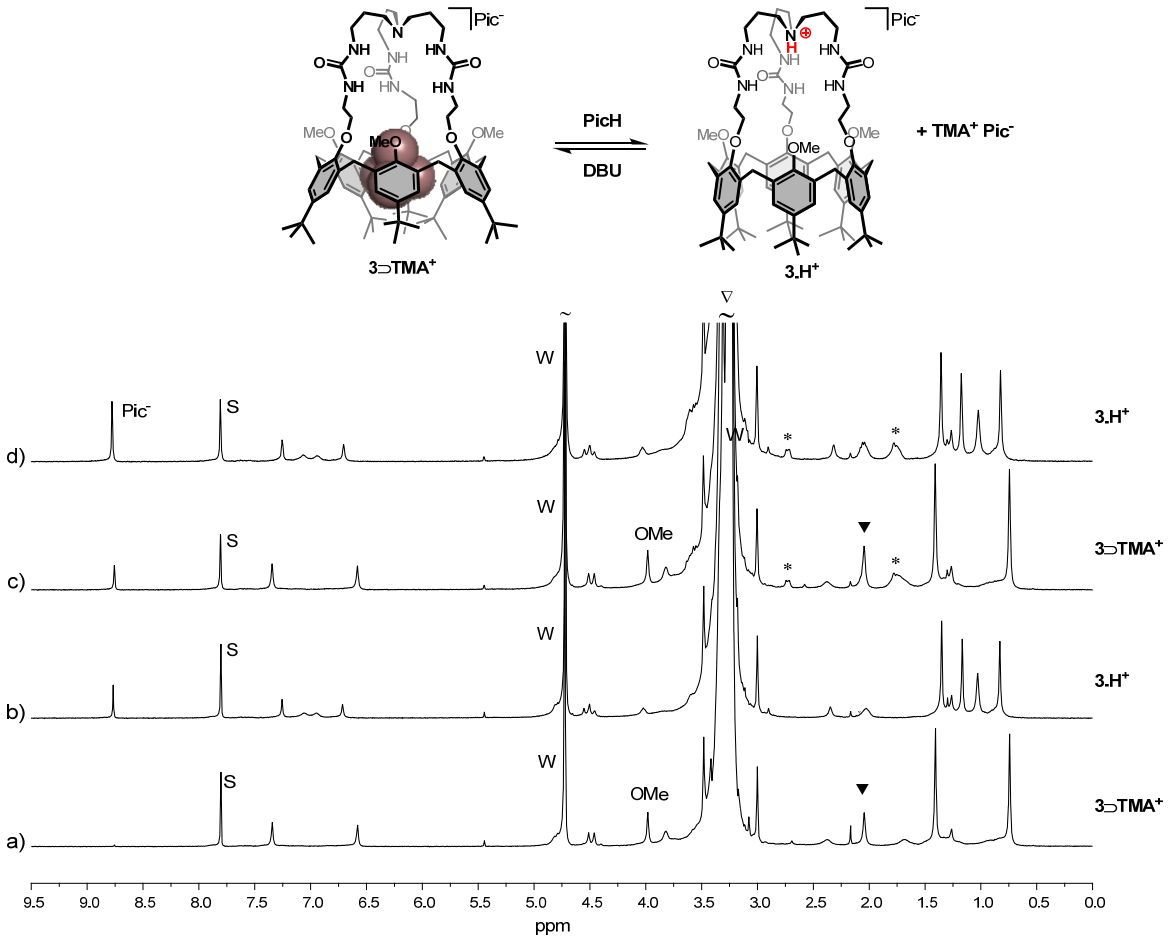
^{1}H NMR (298K, 300 MHz) spectra of **3** with TMA^+Pic^- (7.8 equiv.) in $CD_3OD/CDCl_3$ (7:3). S: solvent; W: water; ▼TMA^+ in; ∇: TMA^+ out; ●: **3**.

SI19. COSY (298K, 300 MHz) spectrum of **3**⊃**TMA**$^+$ in $CD_3OD/CDCl_3$ (7:3)



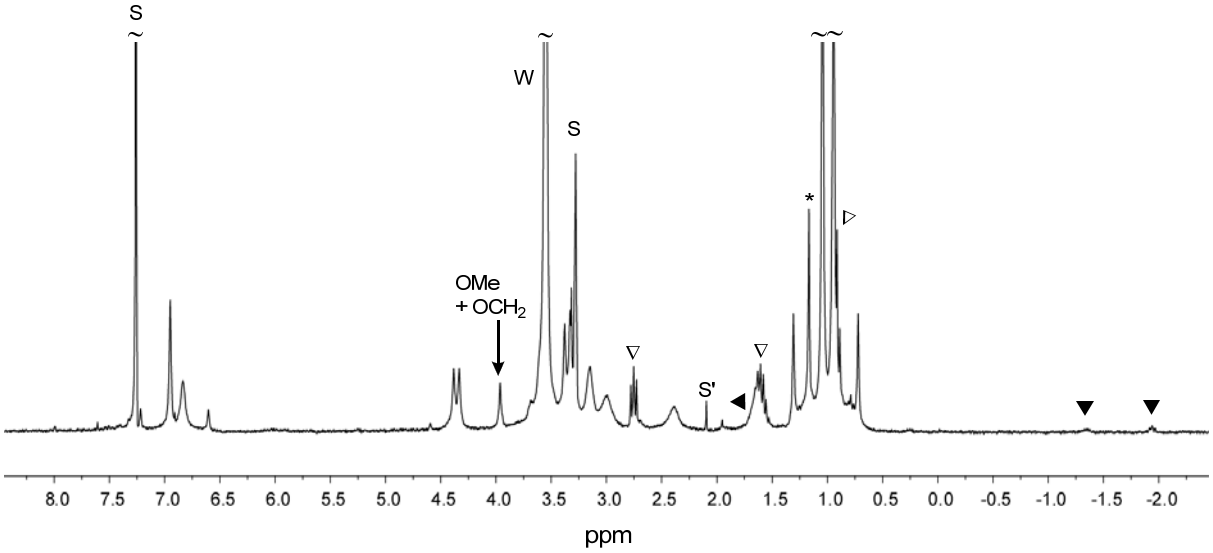
COSY (298K, 300 MHz) spectrum of **3** with TMA^+Pic^- in $CD_3OD/CDCl_3$ (7:3). S: solvent; W: water; ▼TMA^+ in; ∇: TMA^+ out; ●: **3**.

SI20. Interconversion between **3⊃TMA$^+$** and **3.H$^+$** in $CD_3OD/CDCl_3$ (7:3) monitored by ^1H NMR



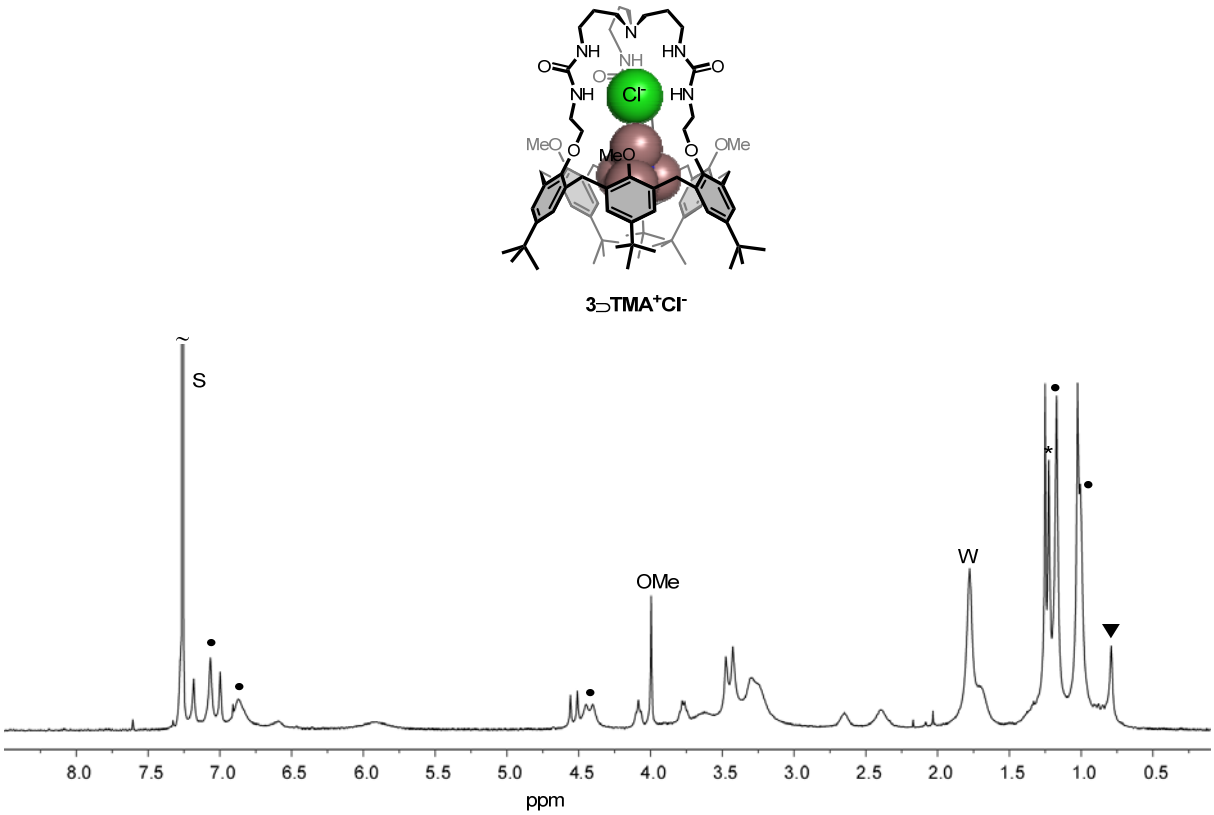
^1H NMR (298K, 300 MHz) spectra of **3** in $CD_3OD/CDCl_3$ (7:3) with a) TMA^+Cl^- (ca. 200 equiv.); b) after addition of PicH (1.5 equiv.); c) after addition of DBU (1.5 equiv.); d) after addition of PicH (3.5 equiv.). S: solvent; W: water; *: DBU; ▼: TMA^+ in; ∇: TMA^+ out.

SI21. ^{1}H NMR (298K, 300 MHz) spectrum of **3** with $PrNH_3^+Cl^-$ in $CD_3OD/CDCl_3$ (1:9)



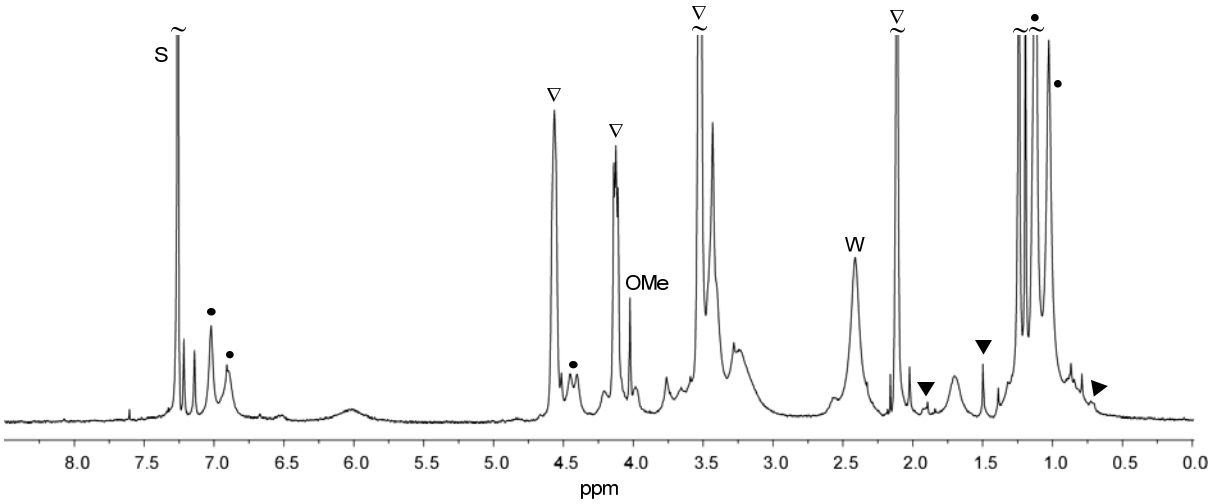
^{1}H NMR (298K, 300 MHz) spectrum of **3** with $PrNH_3^+Cl^-$ (1.3 equiv.) in $CD_3OD/CDCl_3$ (1:9). S: solvent; S': residual acetone; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; *: residual grease.

SI22. ^{1}H NMR (298K, 300 MHz) spectrum of **3** in $CDCl_3$ saturated with TMA^+Cl^-



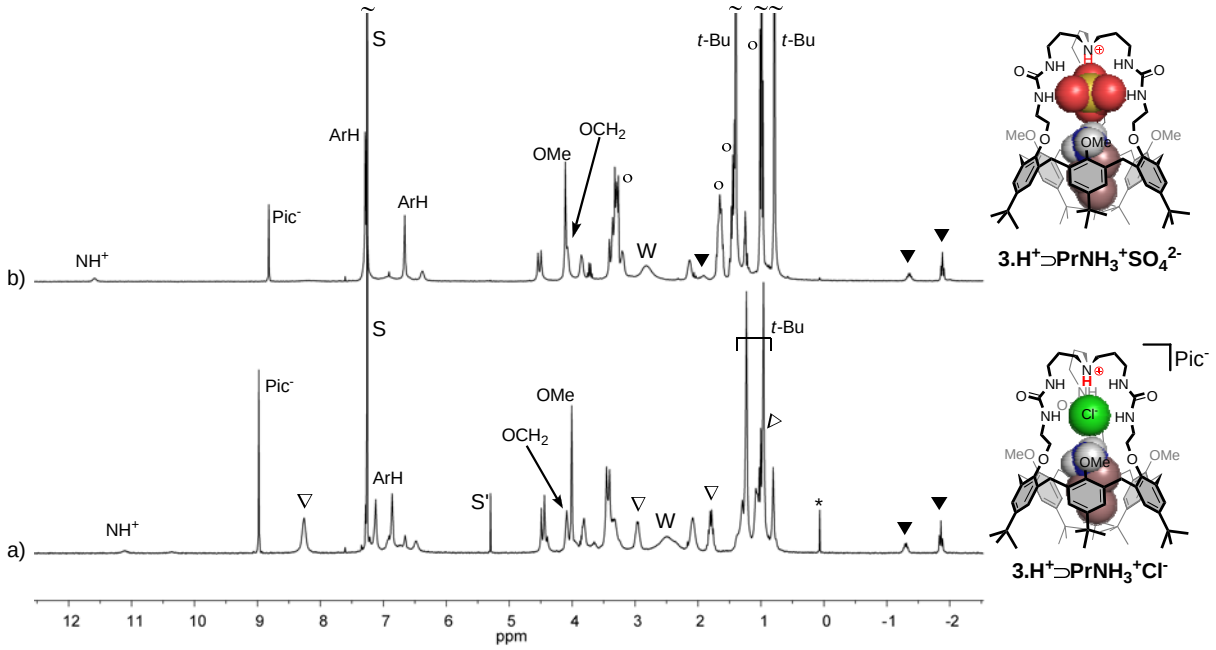
^{1}H NMR (298K, 300 MHz) spectrum of **3** in $CDCl_3$ saturated with TMA^+Cl^-. S: solvent; W: water; ▼: TMA^+ in; ●: **3**; *: residual grease.

SI23. ^{1}H NMR (298K, 300 MHz) spectrum of **3** with $Ach^{+}Cl^{-}$ in $CDCl_3$



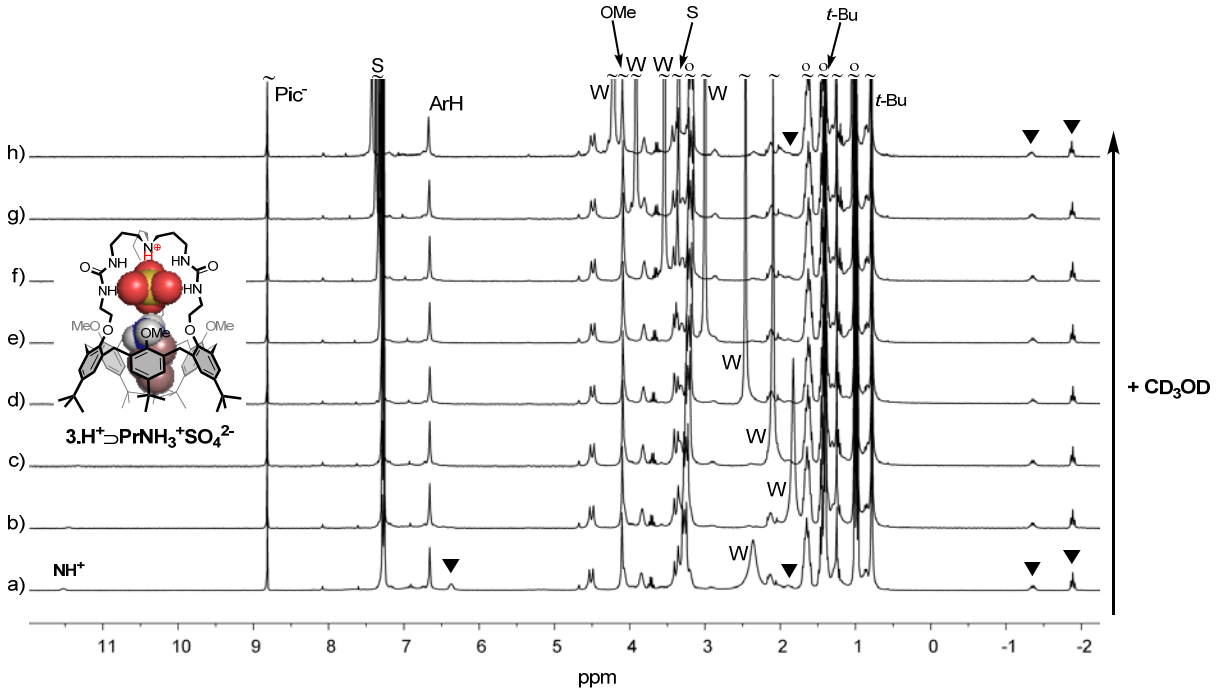
^{1}H NMR (298K, 300 MHz) spectrum of **3** with $Ach^{+}Cl^{-}$ (10.6 equiv.) in $CDCl_3$. S: solvent; W: water; ▼: $Ach^{+}Cl^{-}$ in; ∇: $Ach^{+}Cl^{-}$ out; ●: **3**.

SI24. ^{1}H NMR (298K, 300 MHz) spectra of **3.H$^+$⊃PrNH$_3^+$SO$_4^{2-}$** and **3.H$^+$⊃PrNH$_3^+$Cl$^-$** in $CDCl_3$



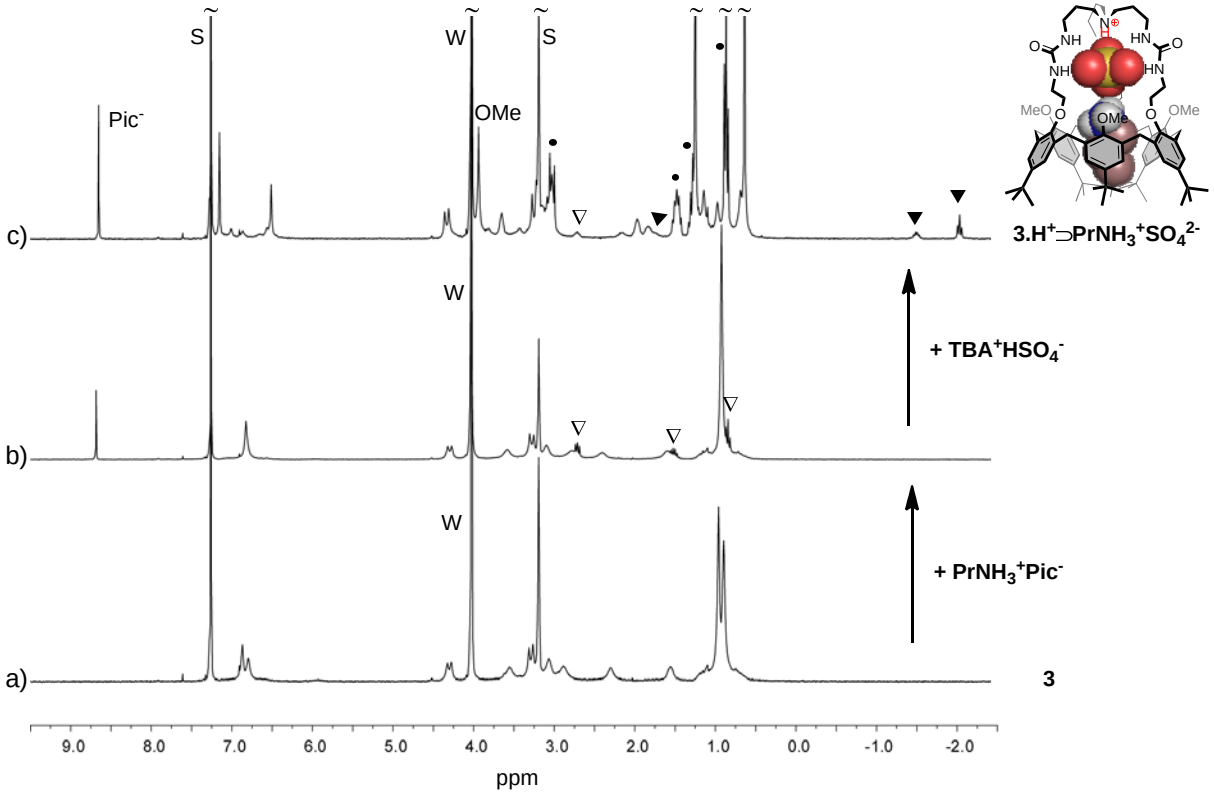
^{1}H NMR (298K, 300 MHz) spectra of a) **3** with PicH (3 equiv.) and $PrNH_3^+Cl^-$ (2.8 equiv.) and b) **3** with PicH (1 equiv.) and $TBA^+PrNH_3^+$ SO_4^{2-} (2 equiv.) in $CDCl_3$. S: solvent; S': dichloromethane; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; o: TBA^+; *: residual grease.

SI25. ^{1}H NMR (298K, 300 MHz) spectra of **3.H$^+$⊃PrNH$_3^+$SO$_4^{2-}$** in $CDCl_3$ upon addition of CD_3OD



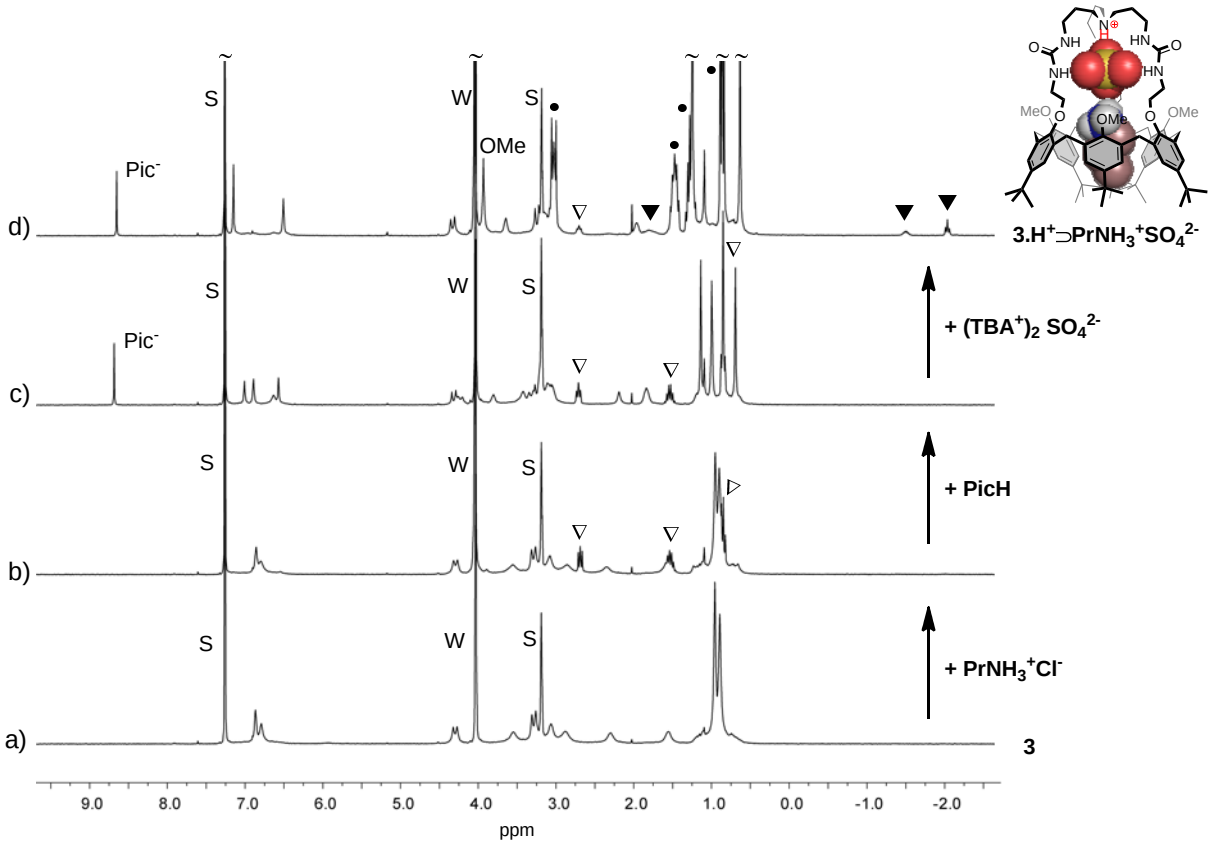
^{1}H NMR (298K, 300 MHz) spectra of a) **3** with PicH (1.3 equiv.) and TBA$^+$PrNH$_3^+$SO$_4^{2-}$ (2.4 equiv.) in $CDCl_3$; b) 5µL; c) 15µL; d) 25µL; e) 45 µL; f) 85 µL; g) 145 µL; h) 245 µL of CD_3OD. S: solvent; W: water; ▼: PrNH$_3^+$ in; o: TBA$^+$.

SI26. ^{1}H NMR (298K, 300 MHz) spectra of **3** with $PrNH_3^+Pic^-$ and $TBA^+HSO_4^-$ in $CD_3OD/CDCl_3$ (1:3)



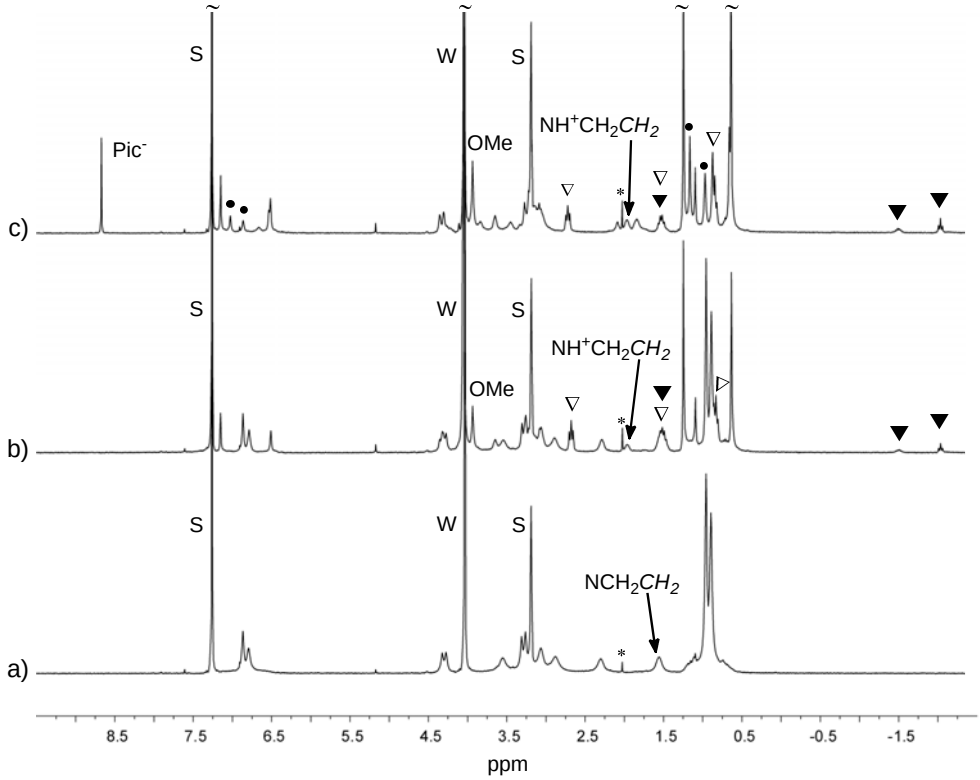
^{1}H NMR (298K, 300 MHz) spectra in $CD_3OD/CDCl_3$ (1:3) of a) **3**; b) after addition of $PrNH_3^+Pic^-$ (1.1 equiv.); c) after the subsequent addition of $TBA^+HSO_4^-$ (1.2 equiv.). S: solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; ●: TBA^+.

SI27. ^{1}H NMR (298K, 300 MHz) spectra of **3** with $PrNH_3^+Cl^-$, PicH and $(TBA^+)_2SO_4^{2-}$ in $CD_3OD/CDCl_3$



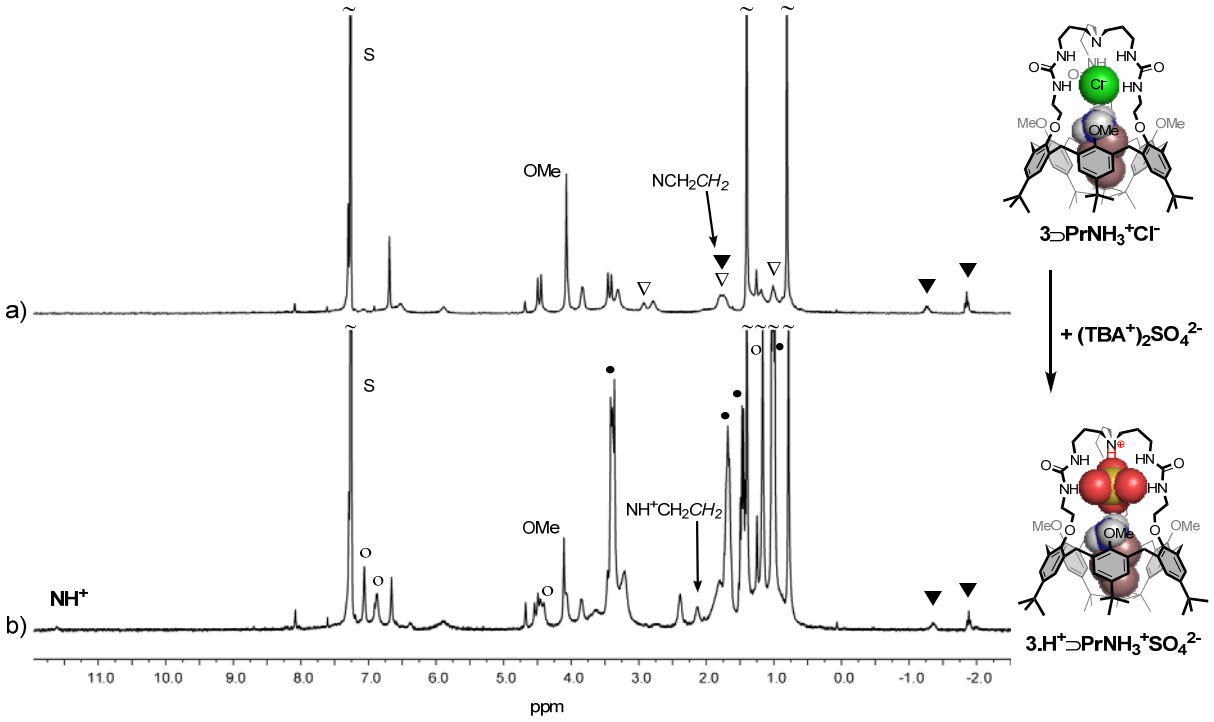
^{1}H NMR (298K, 300 MHz) spectra in $CD_3OD/CDCl_3$ (1:3) of a) **3**; b) after addition of $PrNH_3^+Cl^-$ (2 equiv.); c) after the subsequent addition of PicH (1 equiv.) and d) after the subsequent addition of $(TBA^+)_2SO_4^{2-}$ (2 equiv.). S: solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; ●: TBA^+.

SI28. ^{1}H NMR (298K, 300 MHz) spectra of **3** with $(PrNH_3^+)_2SO_4^{2-}$ and PicH in $CD_3OD/CDCl_3$ (1:3)



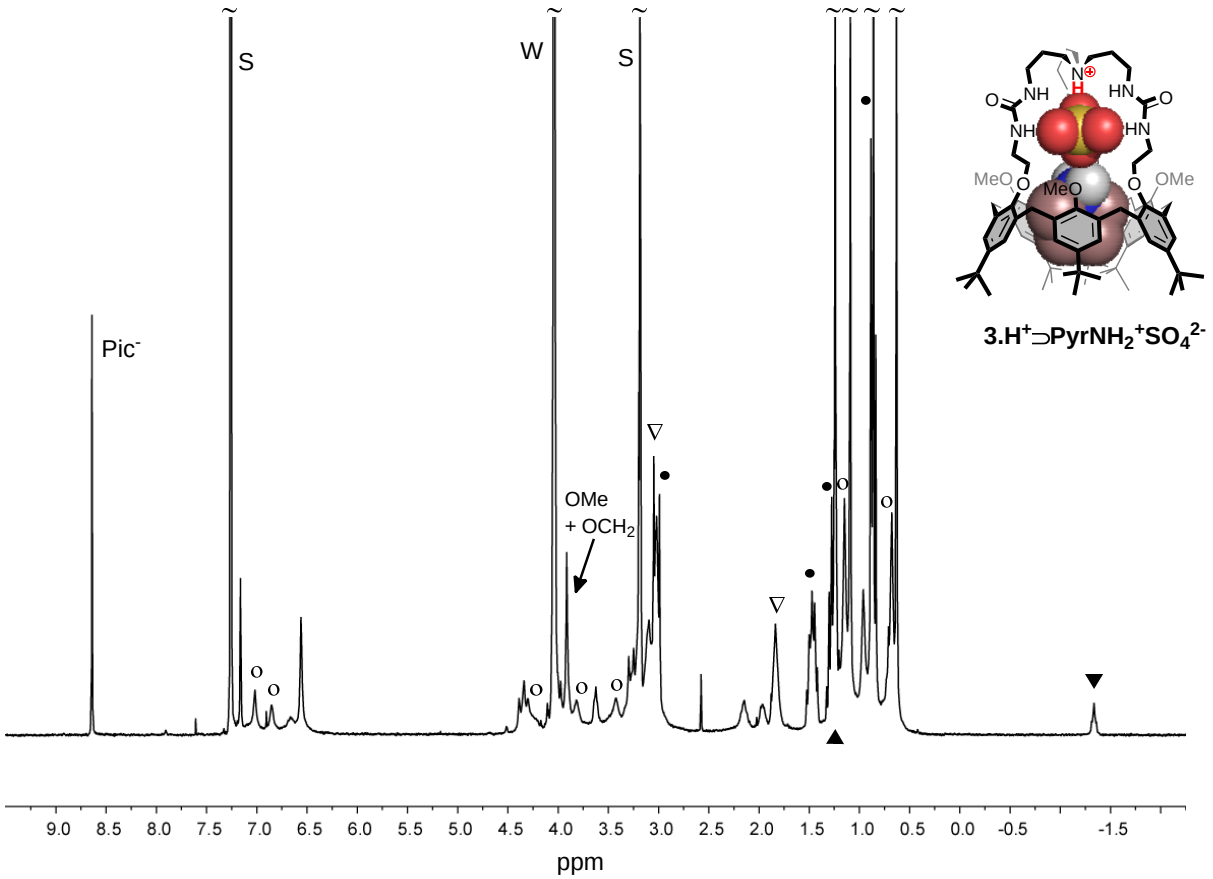
^{1}H NMR (298K, 300 MHz) spectra in $CD_3OD/CDCl_3$ (1:3) of a) **3**; b) after addition of $(PrNH_3^+)_2SO_4^{2-}$ (2.6 equiv.); c) after the subsequent addition of PicH (1.3 equiv.). S: Solvent; W: water; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; ●: **3.H**$^+$; *: residual acetone.

SI29. ^{1}H NMR (298K, 300 MHz) spectra of **3** with $PrNH_3^+Cl^-$ in $CDCl_3$ and after addition of $(TBA^+)_2SO_4^{2-}$



^{1}H NMR (298K, 300 MHz) spectra of **3** in $CDCl_3$ with a) $PrNH_3^+Cl^-$ (2 equiv.) and b) after addition of $(TBA^+)_2SO_4^{2-}$ (ca. 1.7 equiv.). S: solvent; ▼: $PrNH_3^+$ in; ∇: $PrNH_3^+$ out; o: **3.H$^+$**; ●: TBA^+.

SI30. ^{1}H NMR (298K, 300 MHz) spectrum of **3.H$^+$⊃PyrNH$_2$$^+SO_4$$^{2-}$** in $CD_3OD/CDCl_3$ (1:3)



^{1}H NMR (298K, 300 MHz) spectrum of **3** in $CD_3OD/CDCl_3$ (1:3) with $PyrNH_2^+Pic^-$ (1.2 equiv.) and $TBA^+HSO_4^-$ (1.2 equiv.). S: solvent; W: water; ▼: $PyrNH_2^+$ in; ∇: $PyrNH_2^+$ out; ●: TBA^+; o: **3.H$^+$**.