Supporting information

Supramolecular Protection with a Recyclable Molecular Container: an Efficient Strategy for the One-pot Selective Functionalization of Polyfunctional Substrates

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NMR studies of **Ox3** with 1,3-diaminopropane and picric acid

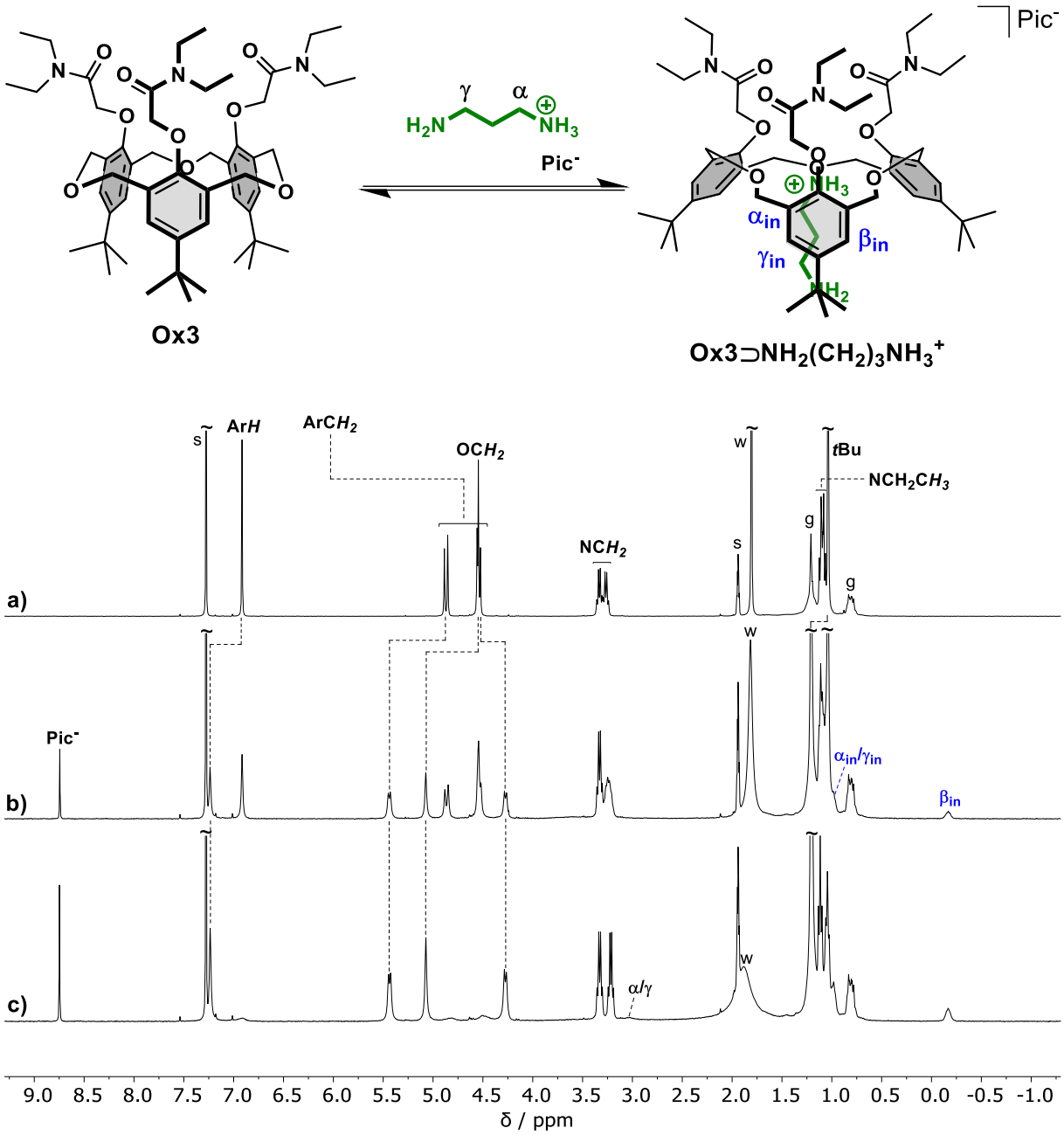


Figure S1. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.5 equiv. of 1,3-diaminopropane + 0.5 equiv. PicH (b) and **Ox3** + 1 equiv. of 1,3-diaminopropane + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease.

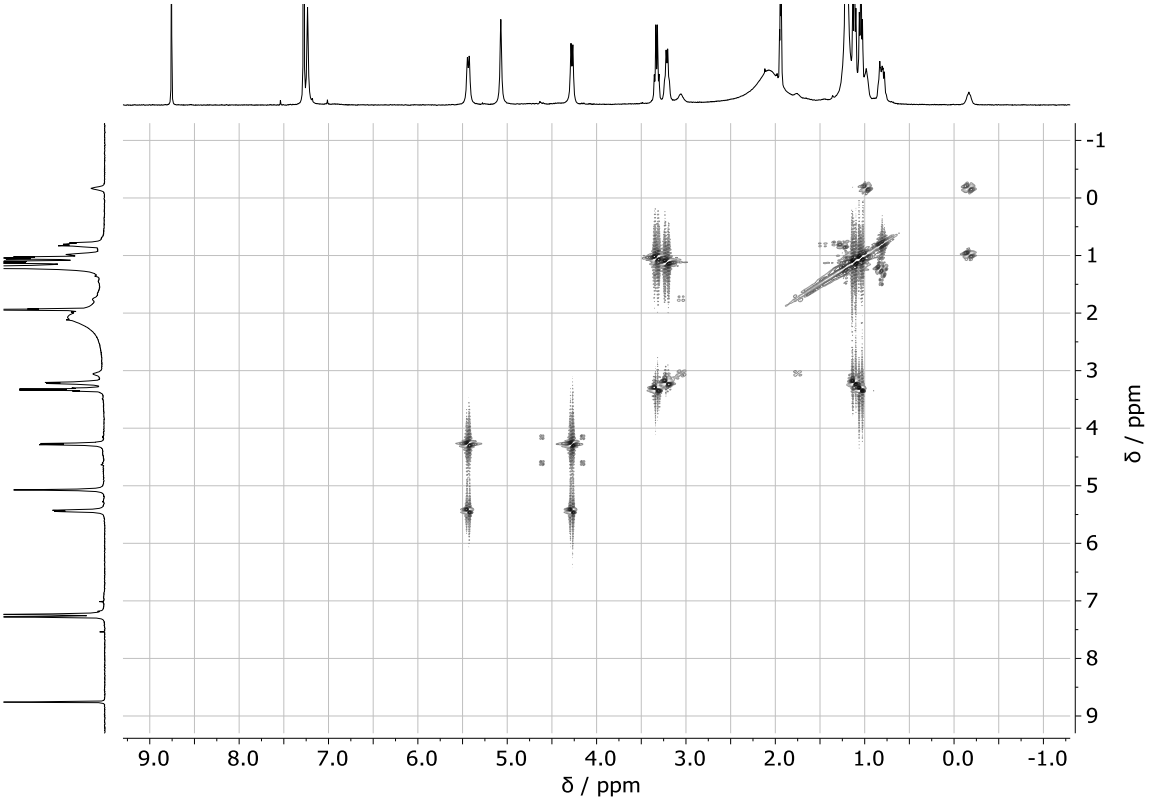


Figure S2. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.5 equiv. of 1,3-diaminopropane + 1.5 equiv. PicH.

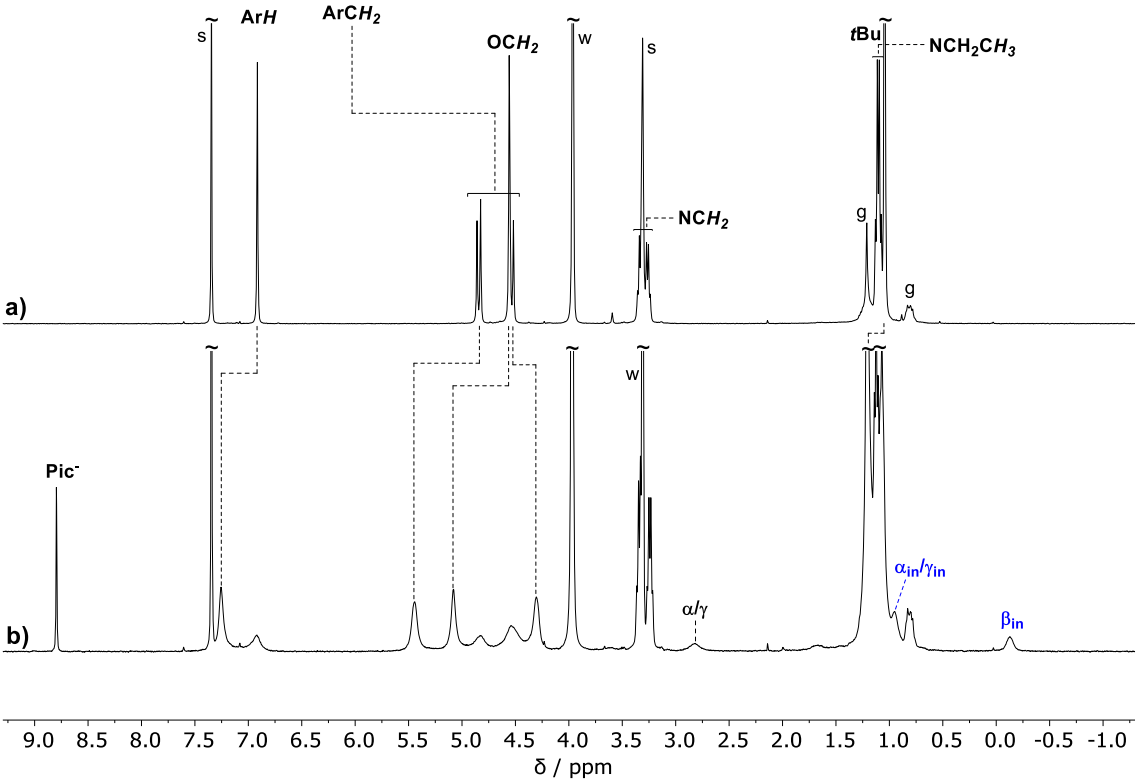


Figure S3. ^1H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a) and **Ox3** + 1 equiv. of 1,3-diaminopropane + 1 equiv. PicH (b). S: residual solvents; w: residual water; g: grease. Attribution of the signals of the complexed guest was done by comparison with the signals of the complexed guest in the NMR binding study performed in $CDCl_3/CD_3CN$ (9:1).

NMR studies of **Ox3** with putrescine (1,4-diaminobutane) and picric acid

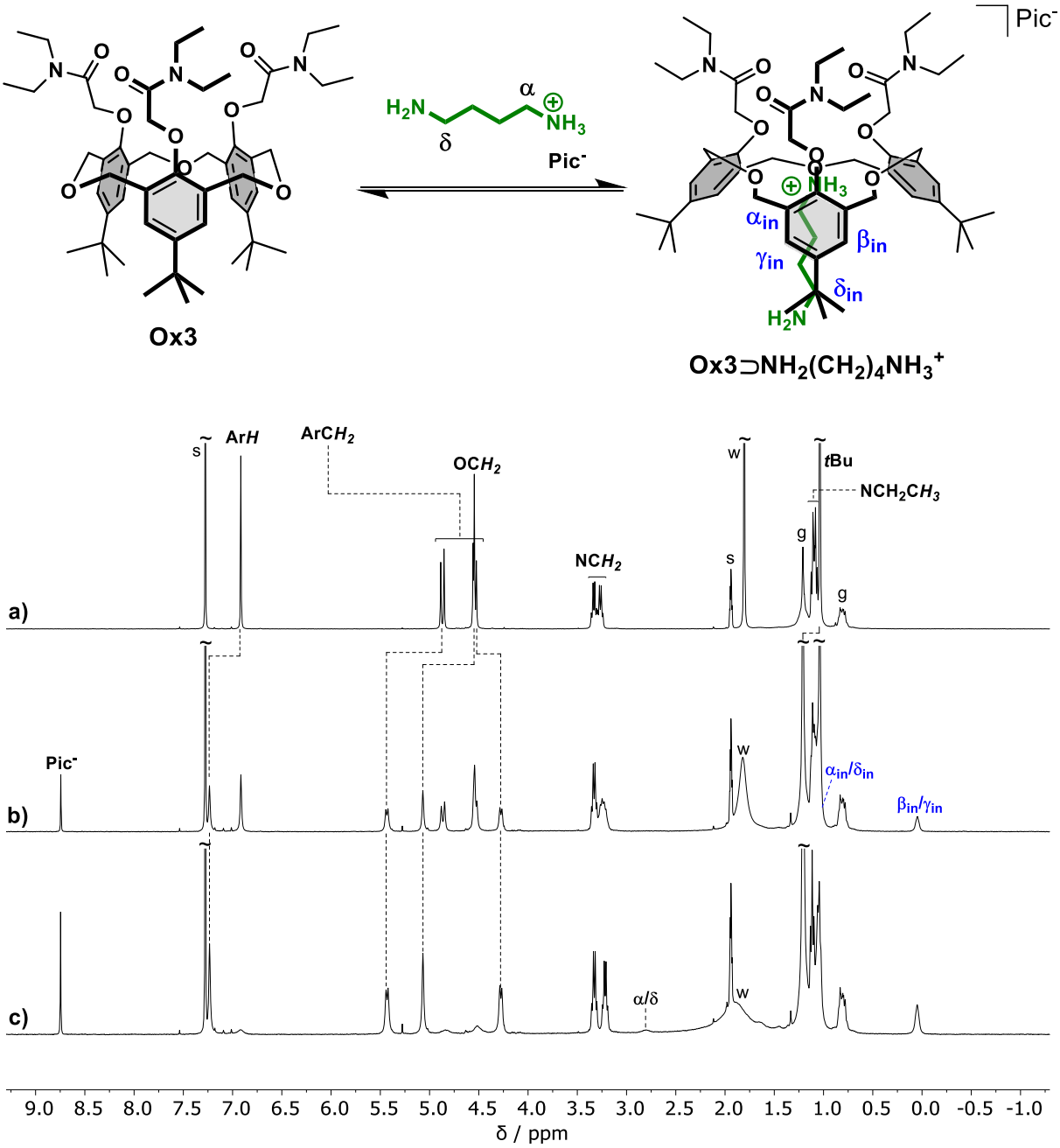


Figure S4. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.5 equiv. of putrescine + 0.5 equiv. PicH (b) and **Ox3** + 1 equiv. of putrescine + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease.

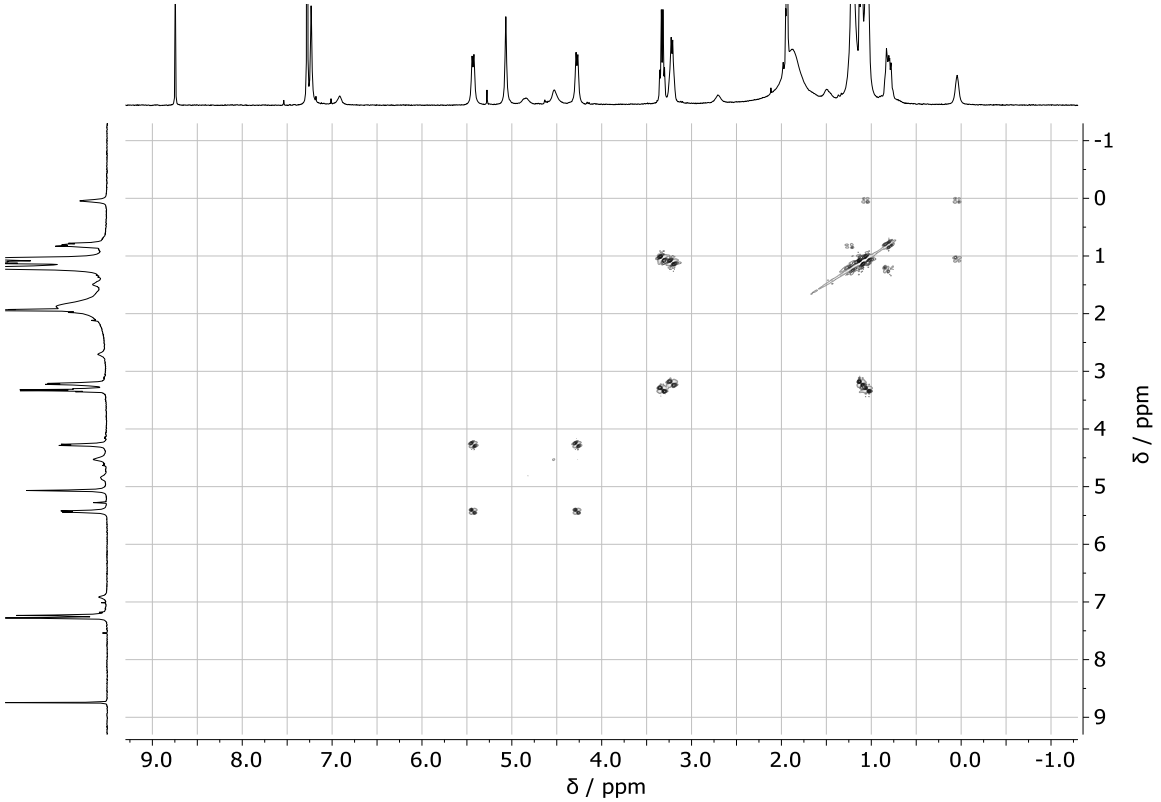


Figure S5. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.5 equiv. of putrescine + 1 equiv. PicH.

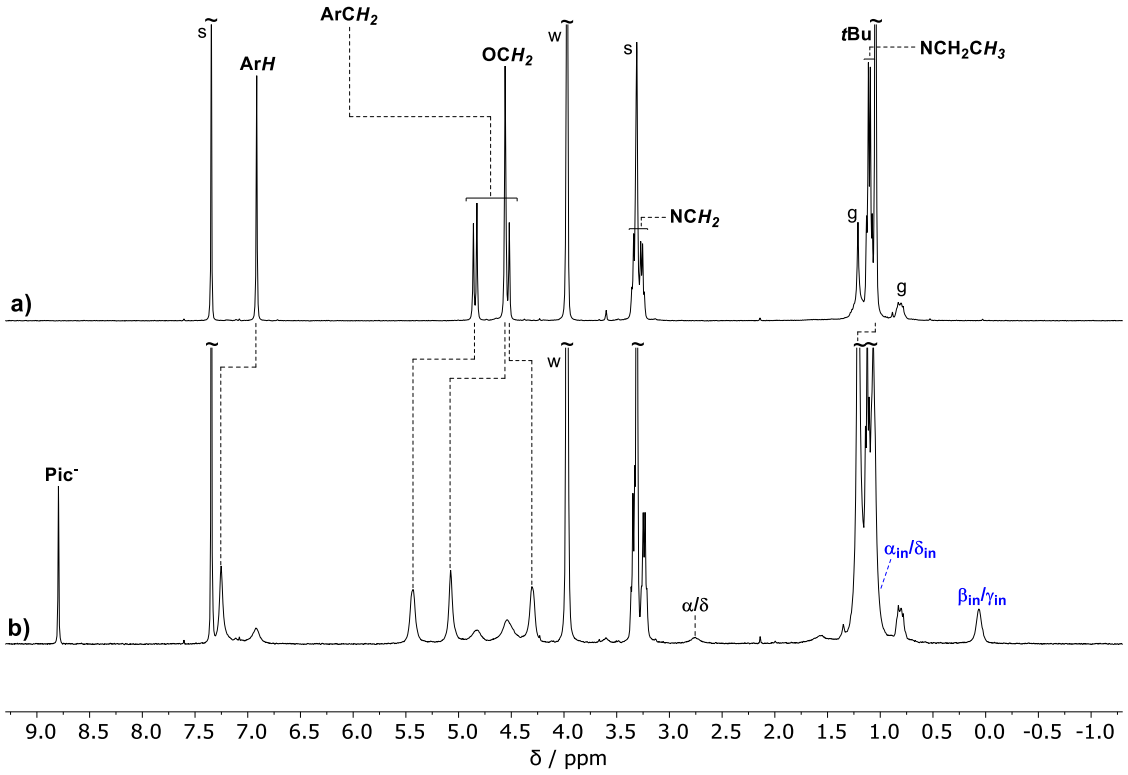


Figure S6. ^1H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a) and **Ox3** + 1 equiv. of putrescine + 1 equiv. PicH (b). S: residual solvents; w: residual water; g: grease. Attribution of the signals of the complexed guest was done by comparison with the signals of the complexed guest in the NMR binding study performed in $CDCl_3/CD_3CN$ (9:1).

NMR studies of **Ox3** with cadaverine (1,5-diaminopentane) and picric acid

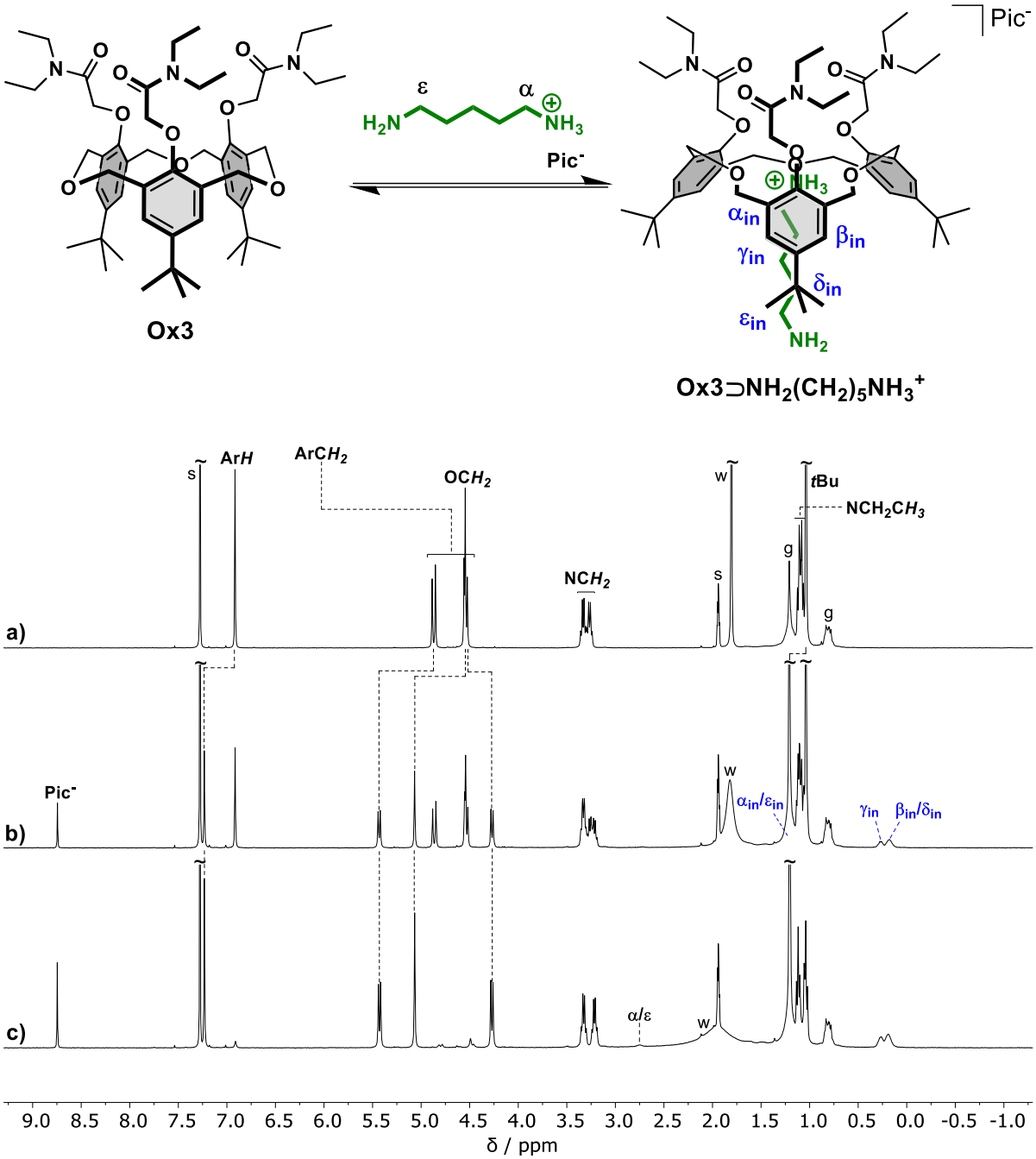


Figure S7. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.5 equiv. of cadaverine + 0.5 equiv. PicH (b) and **Ox3** + 1 equiv. of cadaverine + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease.

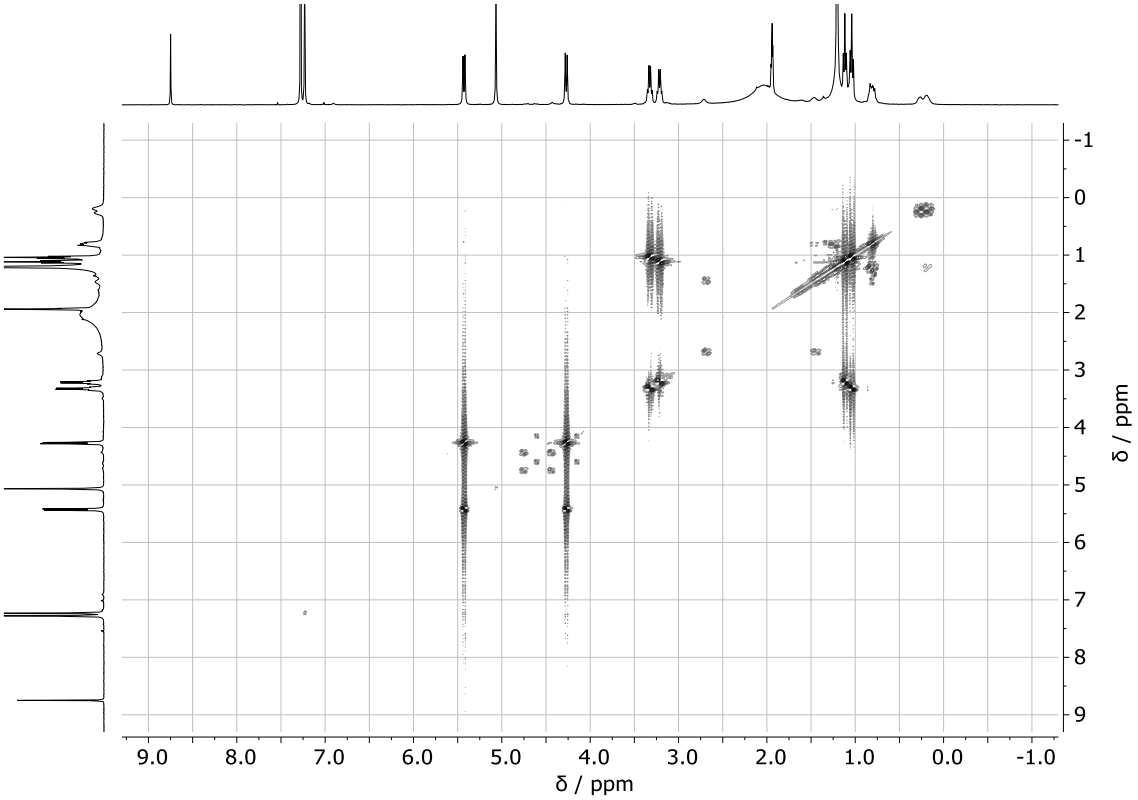


Figure S8. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.5 equiv. of cadaverine + 1.1 equiv. PicH.

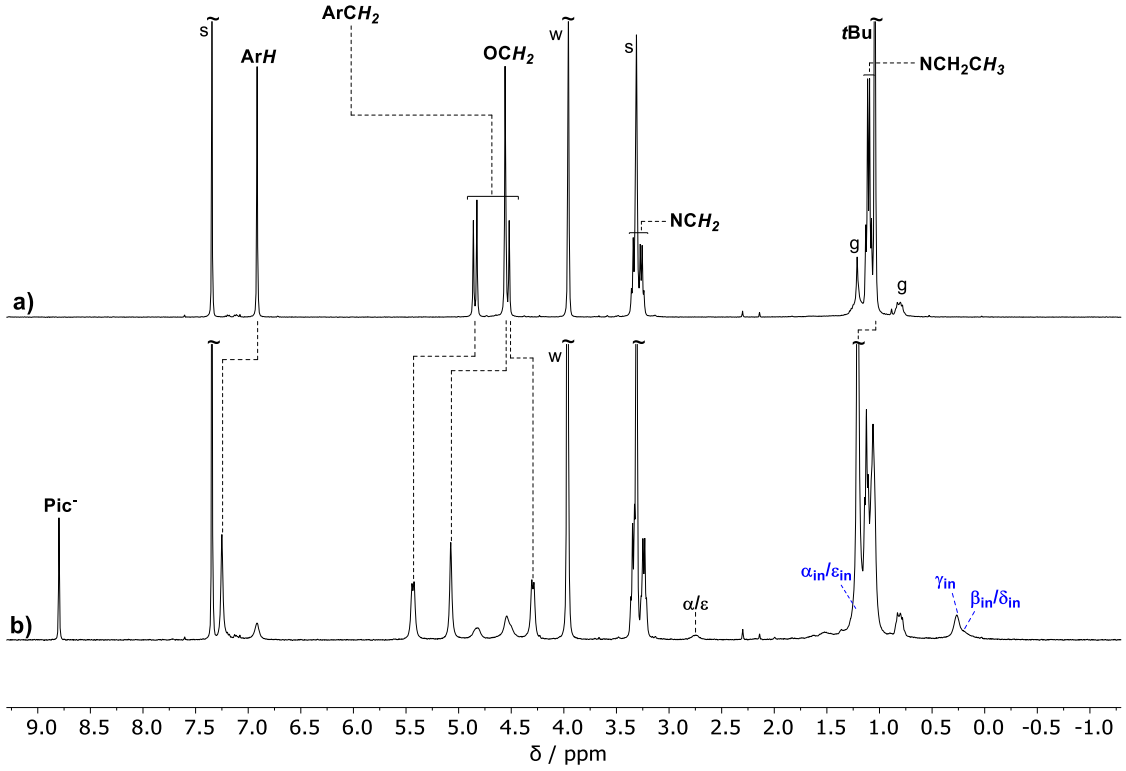


Figure S9. ^1H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a) and **Ox3** + 0.9 equiv. of cadaverine + 0.9 equiv. PicH (b). S: residual solvents; w: residual water; g: grease. Attribution of the signals of the complexed guest was done by comparison with the signals of the complexed guest in the NMR binding study performed in $CDCl_3/CD_3CN$ (9:1).

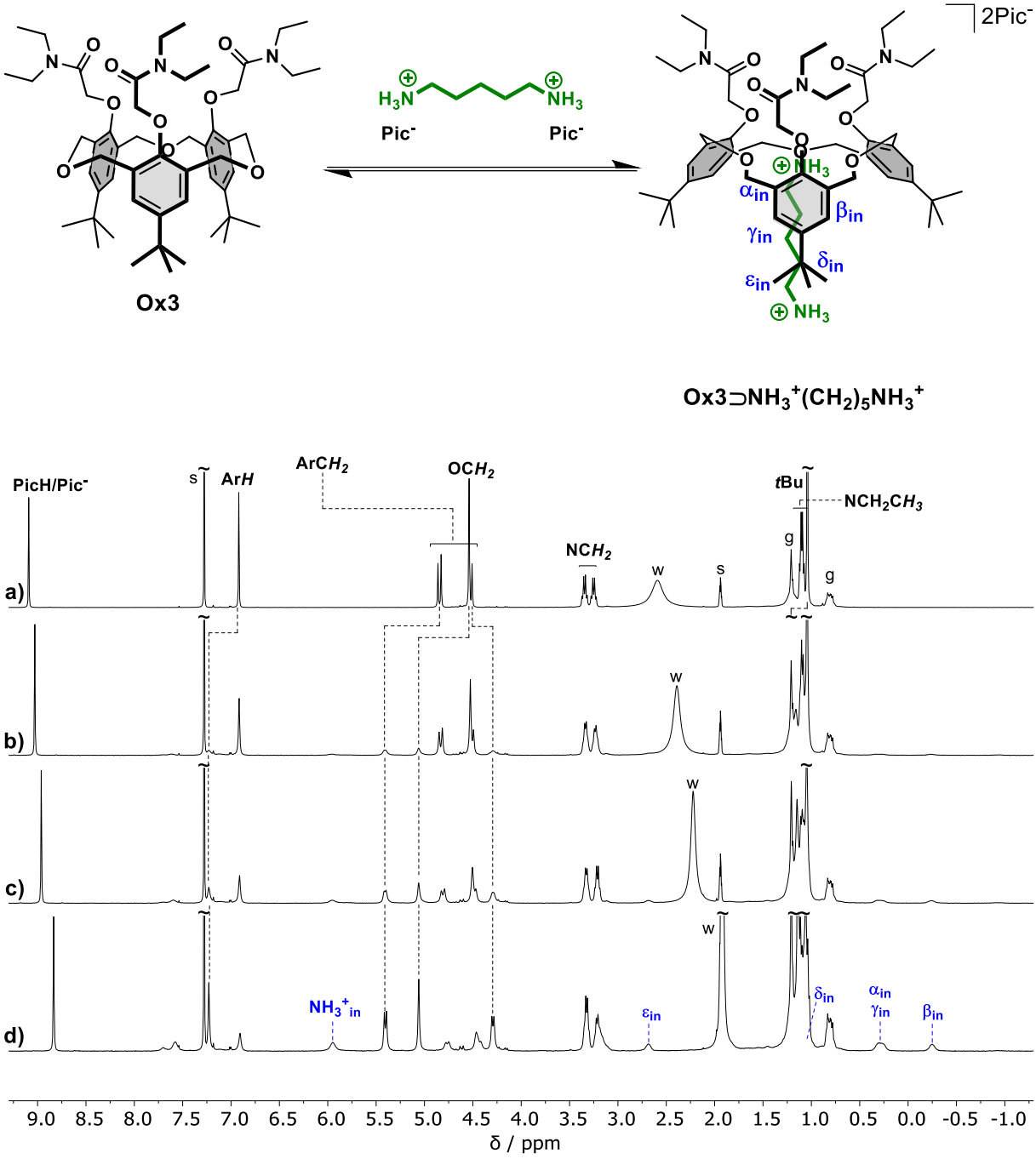


Figure S10. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 2.3 equiv. PicH (a); **Ox3** + 0.2 equiv. of cadaverine + 2.3 equiv. PicH (b); **Ox3** + 0.5 equiv. of cadaverine + 2.3 equiv. PicH (c) and **Ox3** + 0.8 equiv. of cadaverine + 2.3 equiv. PicH (d). S: residual solvents; w: residual water; g: grease.

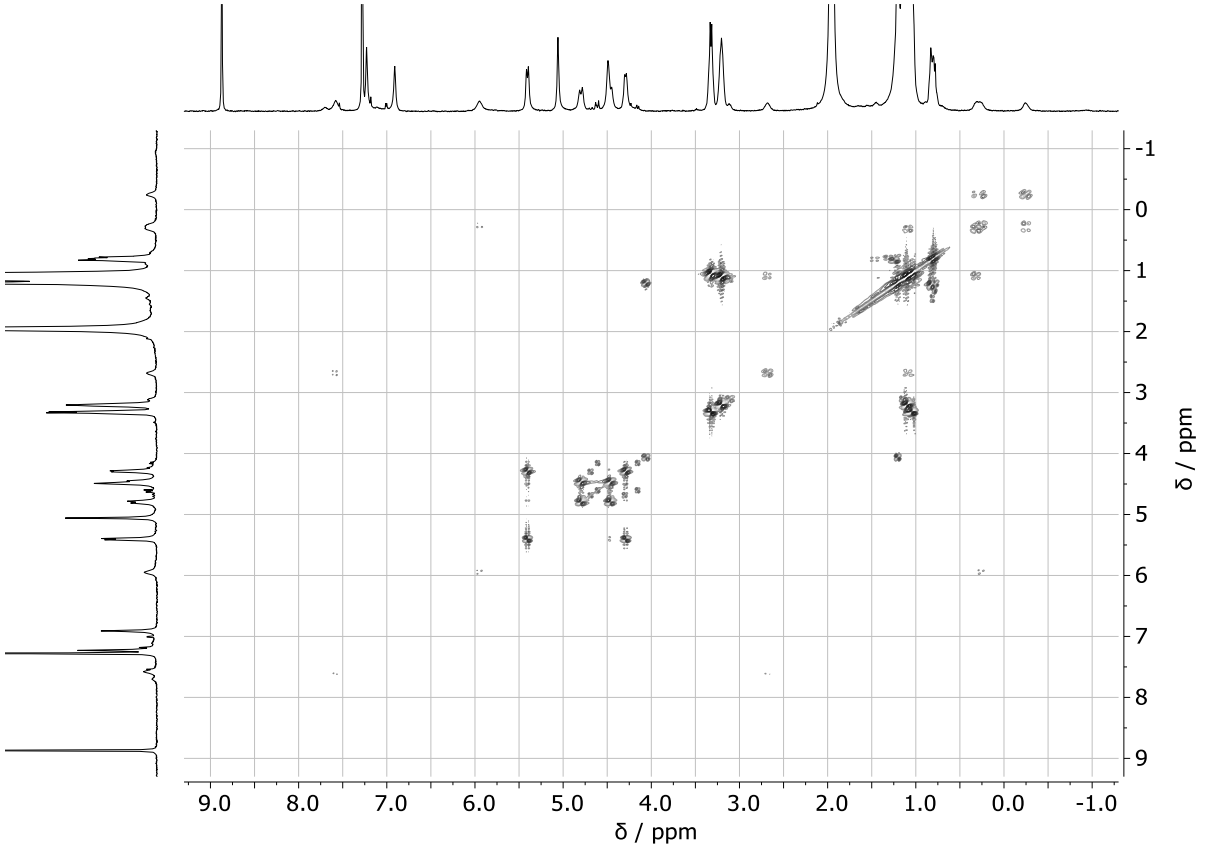


Figure S11. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.5 equiv. of cadaverine + 2.3 equiv. PicH.

NMR studies of **Ox3** with 1,6-diaminohexane and picric acid

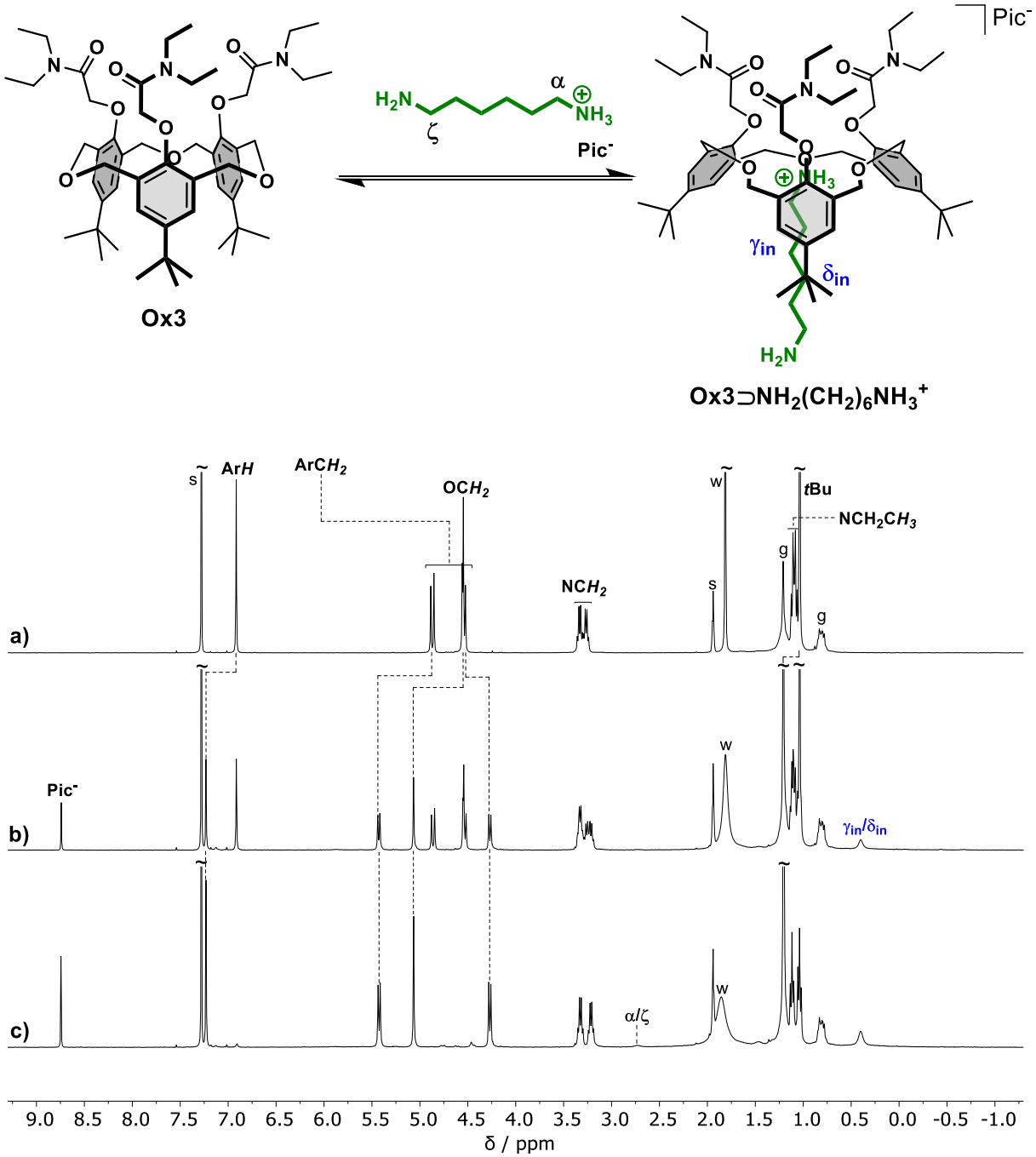


Figure S12. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.5 equiv. of 1,6-diaminohexane + 0.5 equiv. PicH (b) and **Ox3** + 1 equiv. of 1,6-diaminohexane + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease.

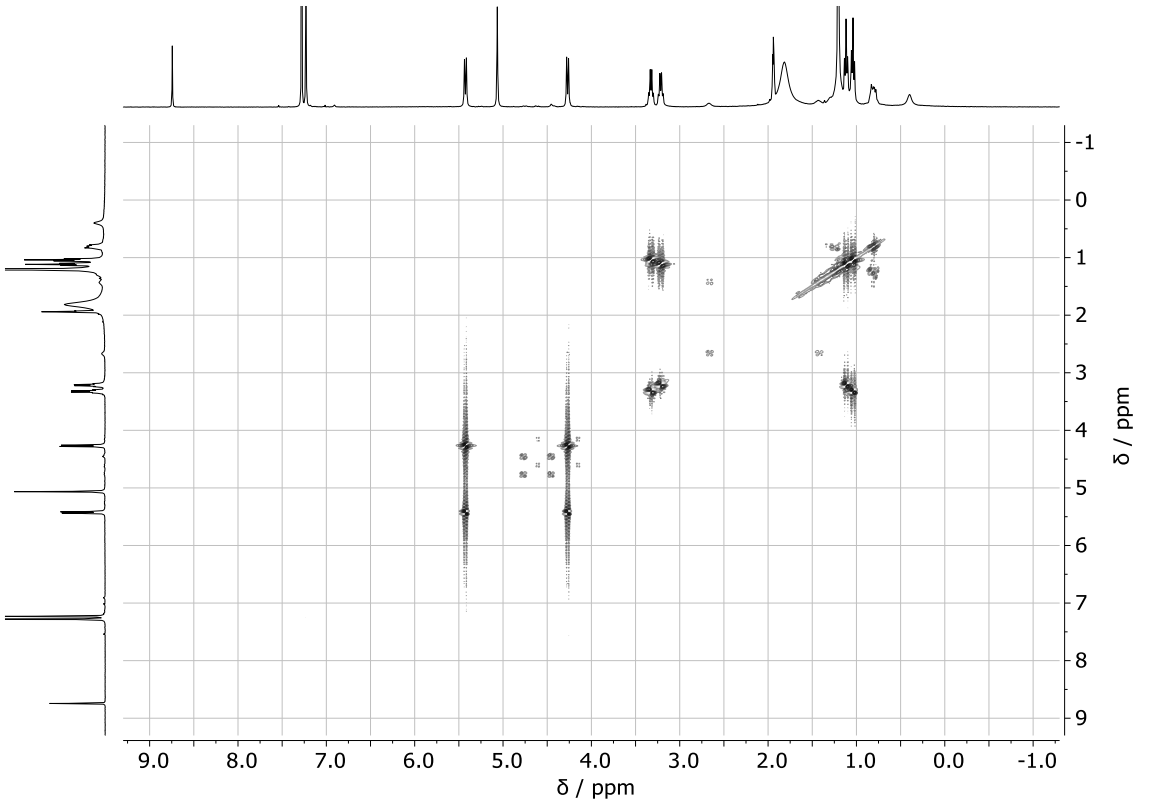


Figure S13. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.4 equiv. of 1,6-diaminohexane + 1 equiv. PicH.

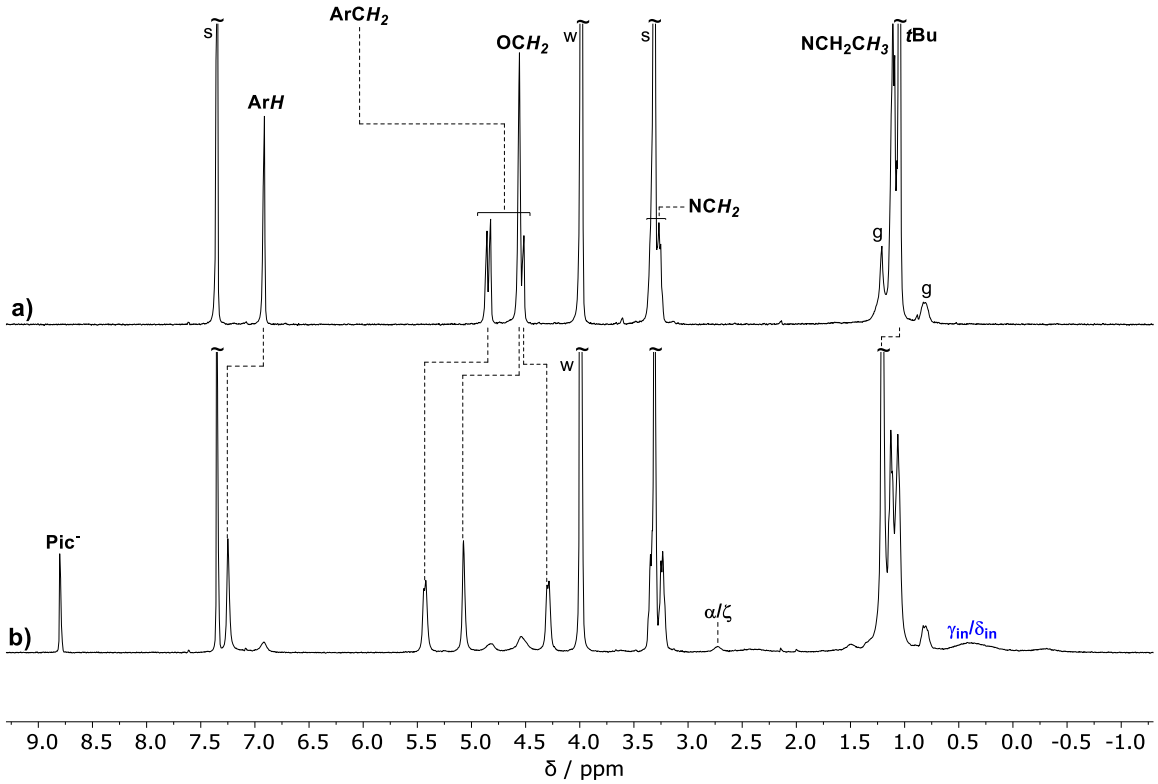


Figure S14. ^1H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a) and **Ox3** + 1 equiv. of 1,6-diaminohexane + 1 equiv. PicH (b). S: residual solvents; w: residual water; g: grease. Attribution of the signals of the complexed guest was done by comparison with the signals of the complexed guest in the NMR binding study performed in $CDCl_3/CD_3CN$ (9:1).

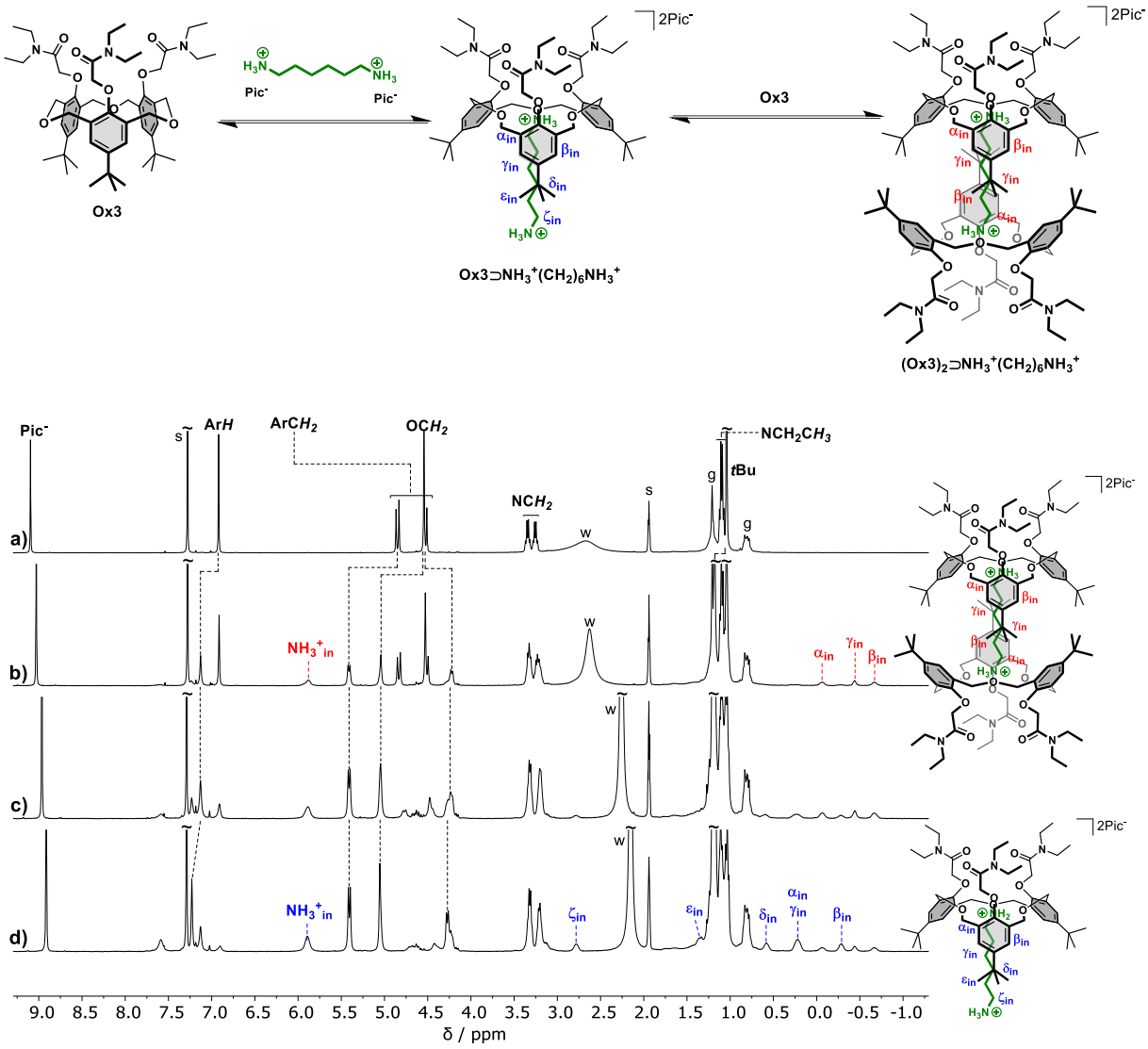


Figure S15. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 2.4 equiv. PicH (a); **Ox3** + 0.2 equiv. of 1,6-diaminohexane + 2.4 equiv. PicH (b); **Ox3** + 0.5 equiv. of 1,6-diaminohexane + 2.4 equiv. PicH (c) and **Ox3** + 0.9 equiv. of 1,6-diaminohexane + 2.4 equiv. PicH (d). S: residual solvents; w: residual water; g: grease. The ^{1}H NMR signals in red on spectrum (b) were attributed to the 2:1 complex between **Ox3** and the diammonium guest on the basis of the number of signals as well as of their chemical shift and integration.

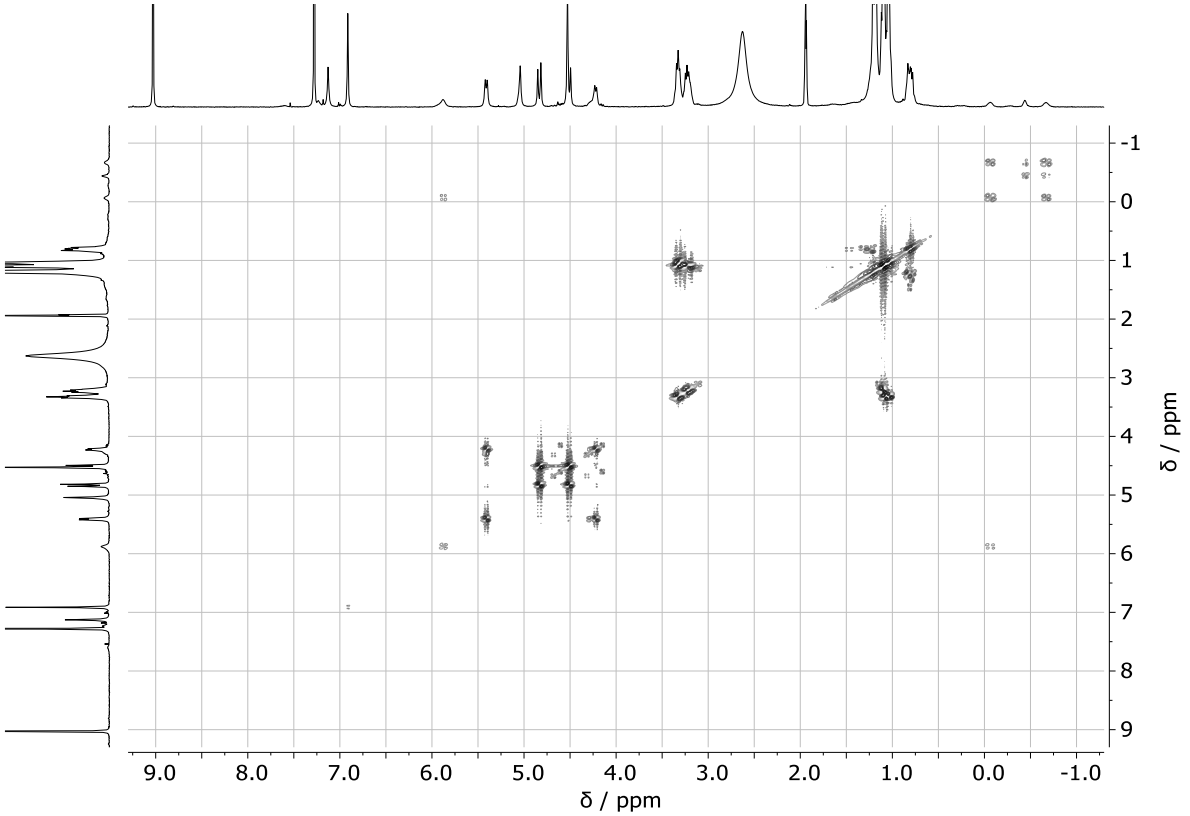


Figure S16. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.2 equiv. of 1,6-diaminohexane + 2.4 equiv. PicH.

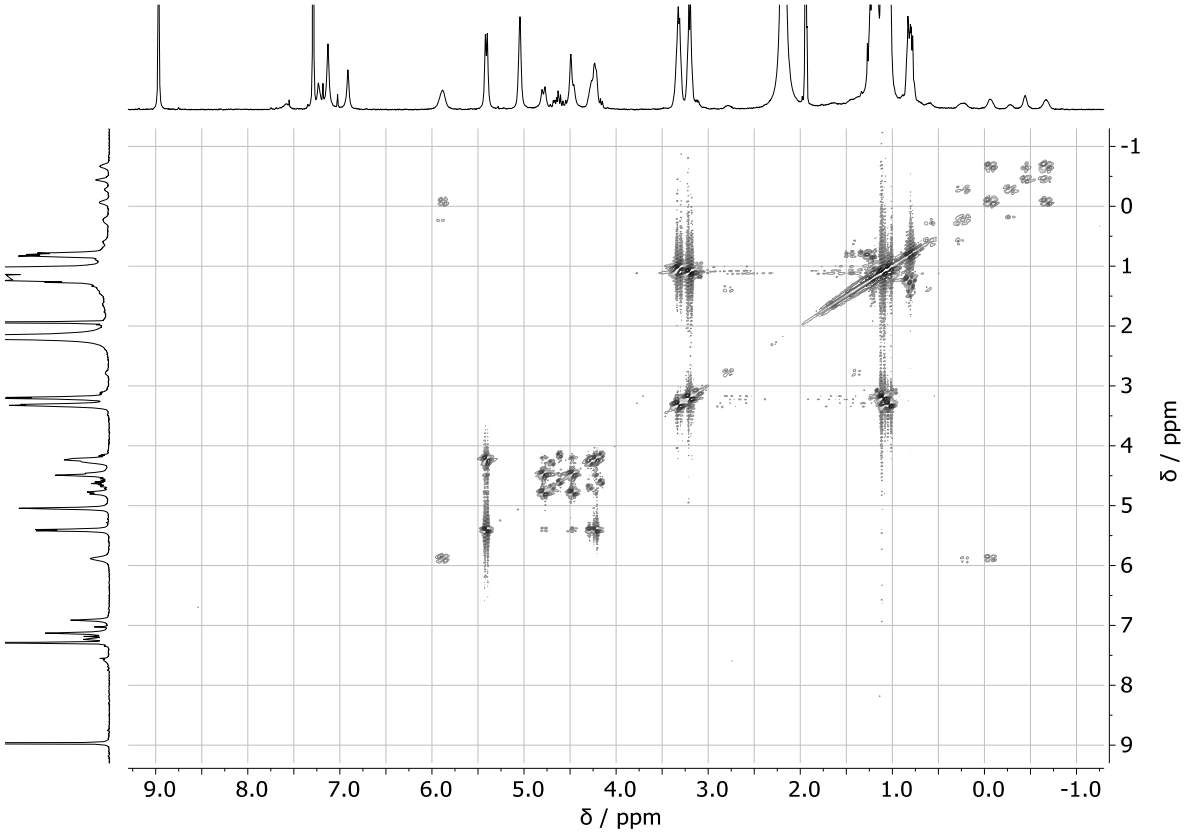
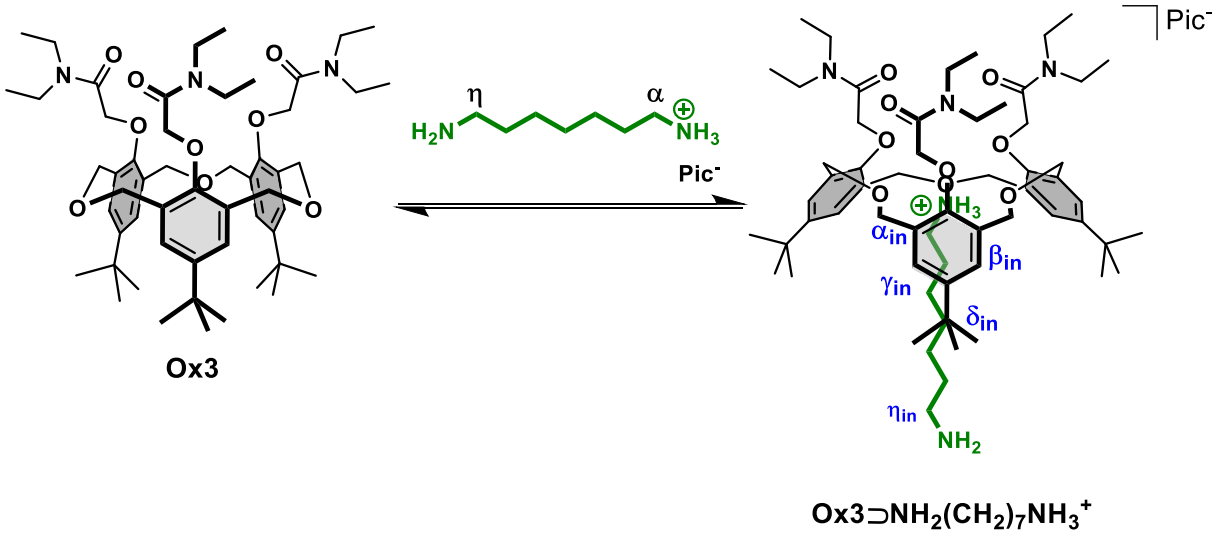


Figure S17. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.5 equiv. of 1,6-diaminohexane + 2.4 equiv. PicH.

NMR studies of **Ox3** with 1,7-diaminoheptane and picric acid



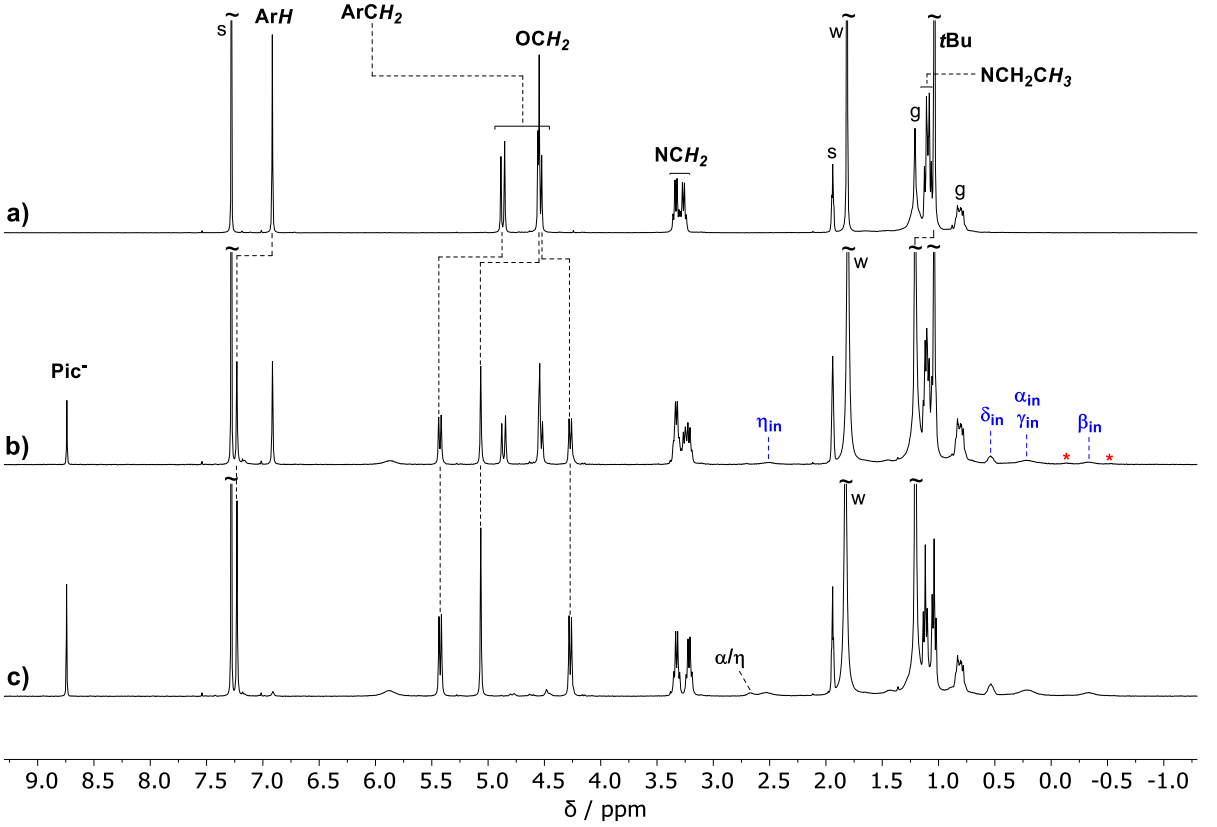


Figure S18. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.5 equiv. of 1,7-diaminoheptane + 0.5 equiv. PicH (b) and **Ox3** + 1 equiv. of 1,7-diaminoheptane + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease; *: traces of 2:1 complex. The attribution of the signals for the 2:1 complex was performed by comparison with the signals of the 2:1 complex evidenced in the titration with the diammonium form of the guest (see Figure S20). Attribution of the complexed guest (1:1 complex) were done by comparison with the signals of the 1:1 complex in the titration with the diammonium form of the guest (see Figure S20) as not all the signals could be attributed with the COSY spectrum (Figure S19) due to the broadness of some signals.

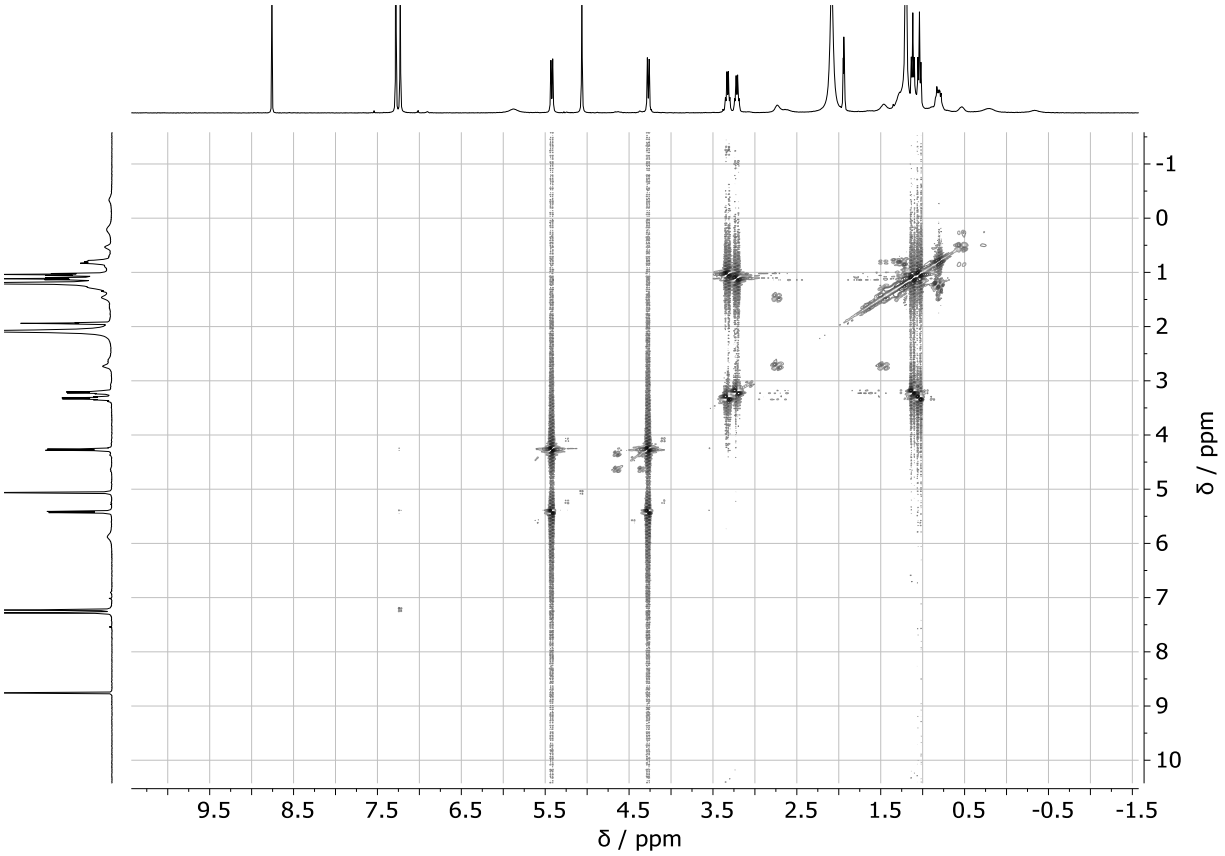


Figure S19. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.6 equiv. of 1,7-diaminoheptane + 1.6 equiv. PicH.

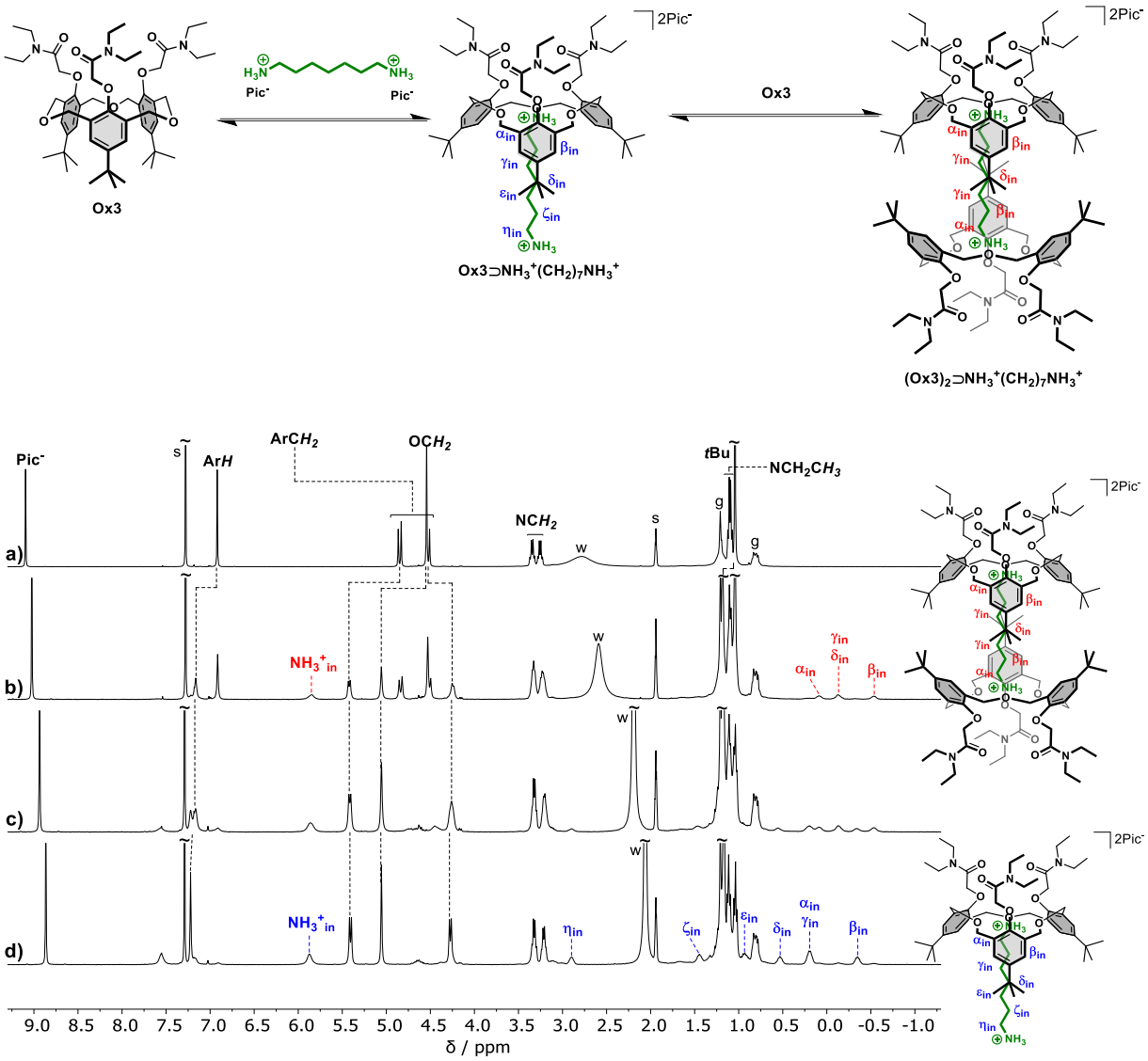


Figure S20. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 2.5 equiv. PicH (a); **Ox3** + 0.2 equiv. of 1,7-diaminoheptane + 2.5 equiv. PicH (b); **Ox3** + 0.5 equiv. of 1,7-diaminoheptane + 2.5 equiv. PicH (c) and **Ox3** + 1 equiv. of 1,7-diaminoheptane + 2.5 equiv. PicH (d). S: residual solvents; w: residual water; g: grease. The ^{1}H NMR signals in red on spectrum (b) were attributed to the 2:1 complex between **Ox3** and the diammonium guest on the basis of the number of signals as well as of their chemical shift and integration.

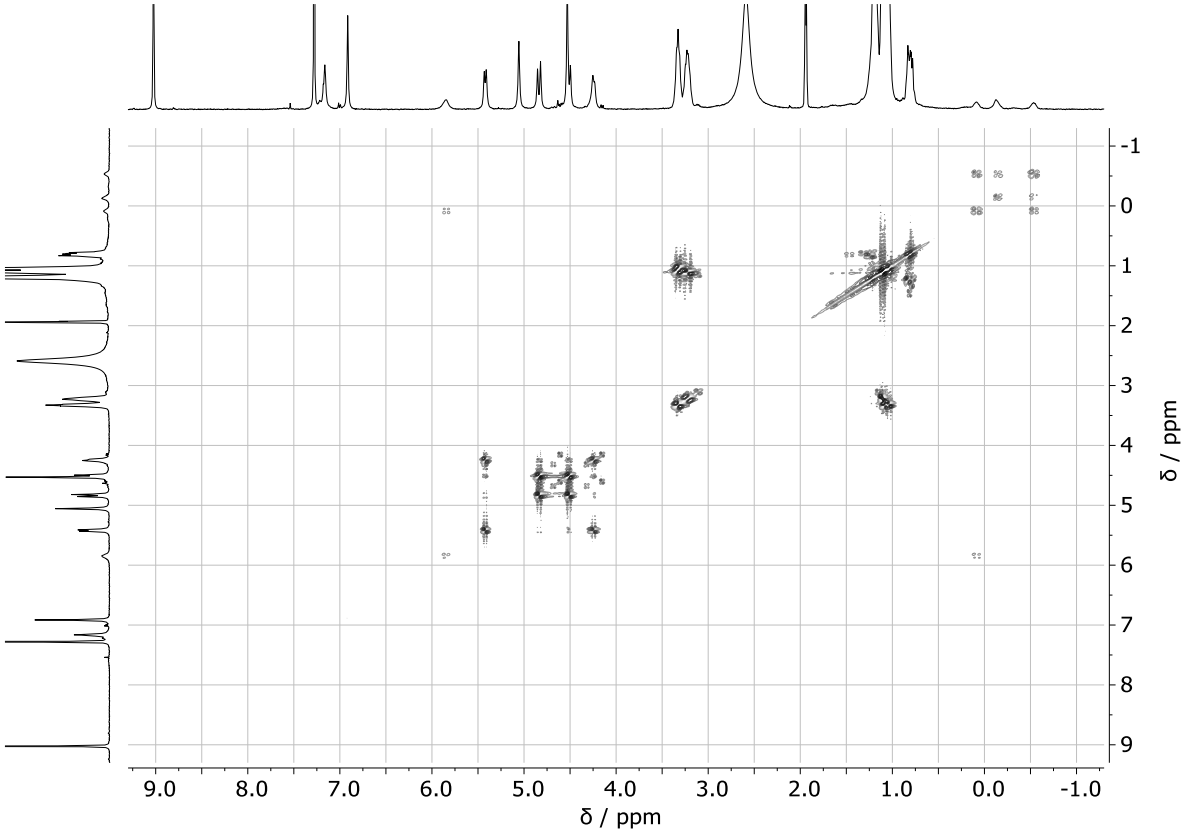


Figure S 21. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.2 equiv. of 1,7-diaminoheptane + 2.5 equiv. PicH.

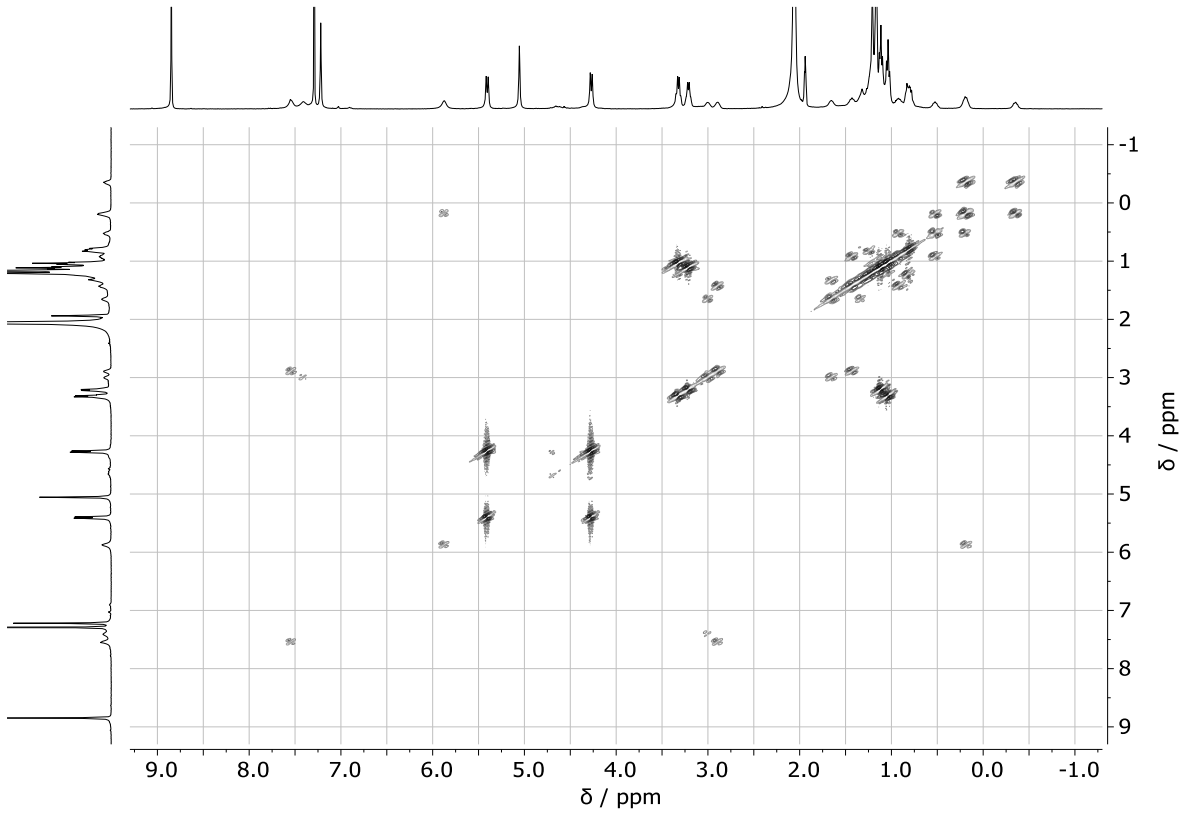


Figure S22. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.5 equiv. of 1,7-diaminoheptane + 4 equiv. PicH.

NMR studies of **Ox3** with 1,8-diaminooctane and picric acid

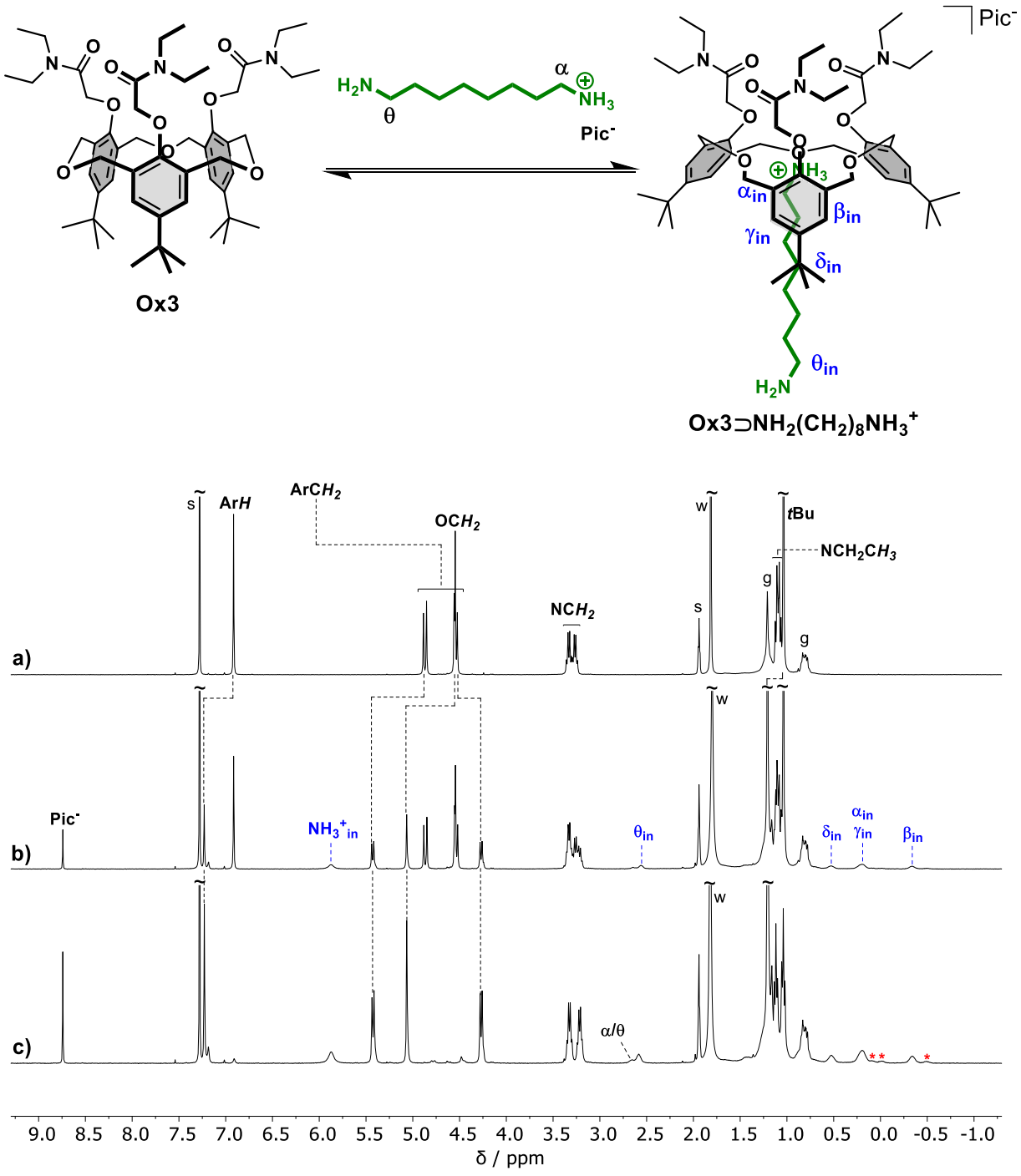


Figure S23. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); **Ox3** + 0.4 equiv. of 1,8-diaminooctane + 0.4 equiv. PicH (b) and **Ox3** + 1 equiv. of 1,8-diaminooctane + 1 equiv. PicH (c). S: residual solvents; w: residual water; g: grease; *: traces of 2:1 complex. The attribution of the signals for the 2:1 complex was performed by comparison with the signals of the 2:1 complex evidenced in the titration with the diammonium form of the guest (see Figure S25).

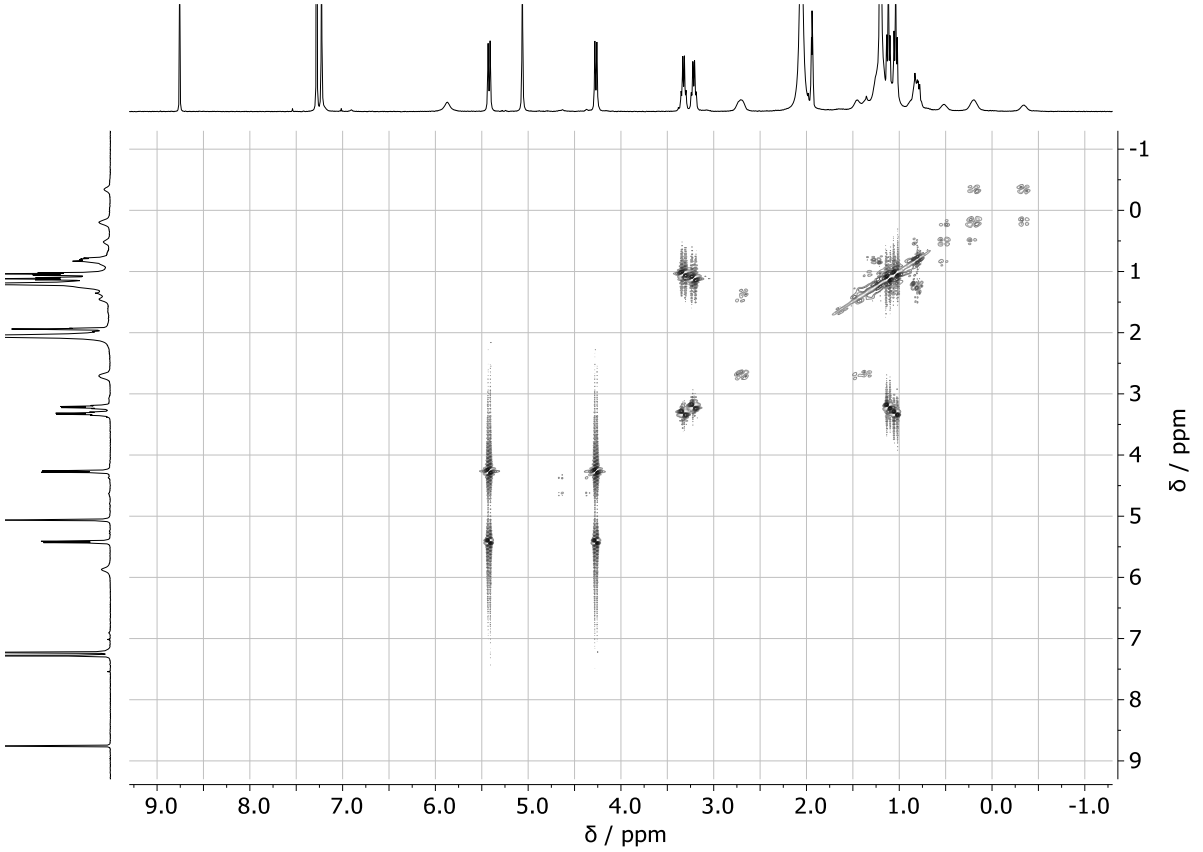


Figure S24. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 1.5 equiv. of 1,8-diaminooctane + 1.5 equiv. PicH.

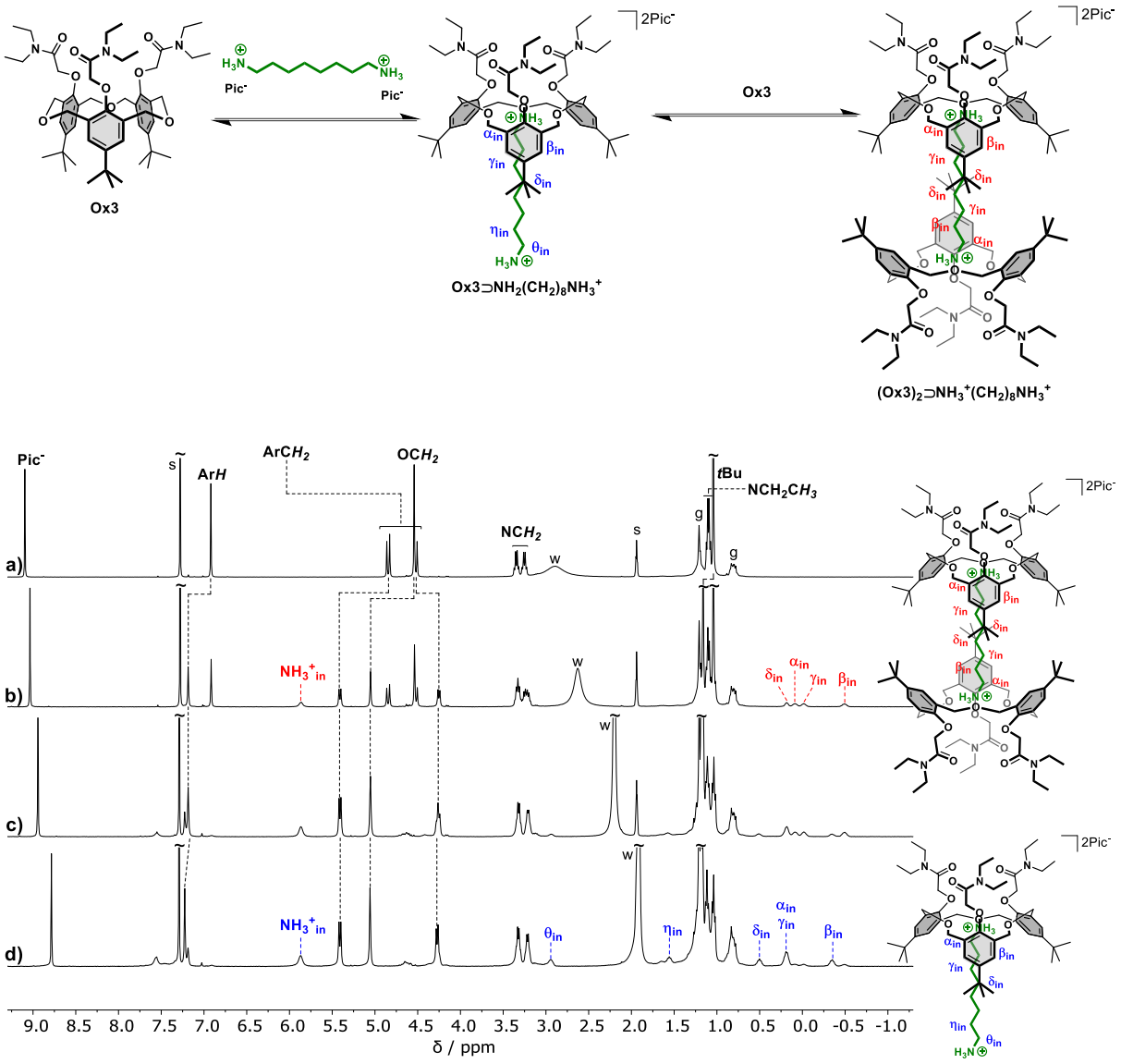


Figure S25. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 2.7 equiv. PicH (a); **Ox3** + 0.2 equiv. of 1,8-diaminooctane + 2.7 equiv. PicH (b); **Ox3** + 0.5 equiv. of 1,8-diaminooctane + 2.7 equiv. PicH (c) and **Ox3** + 1 equiv. of 1,8-diaminooctane + 2.7 equiv. PicH (d). S: residual solvents; w: residual water; g: grease. The ^{1}H NMR signals in red on spectrum (b) were attributed to the 2:1 complex between **Ox3** and the diammonium guest on the basis of the number of signals as well as of their chemical shift and integration.

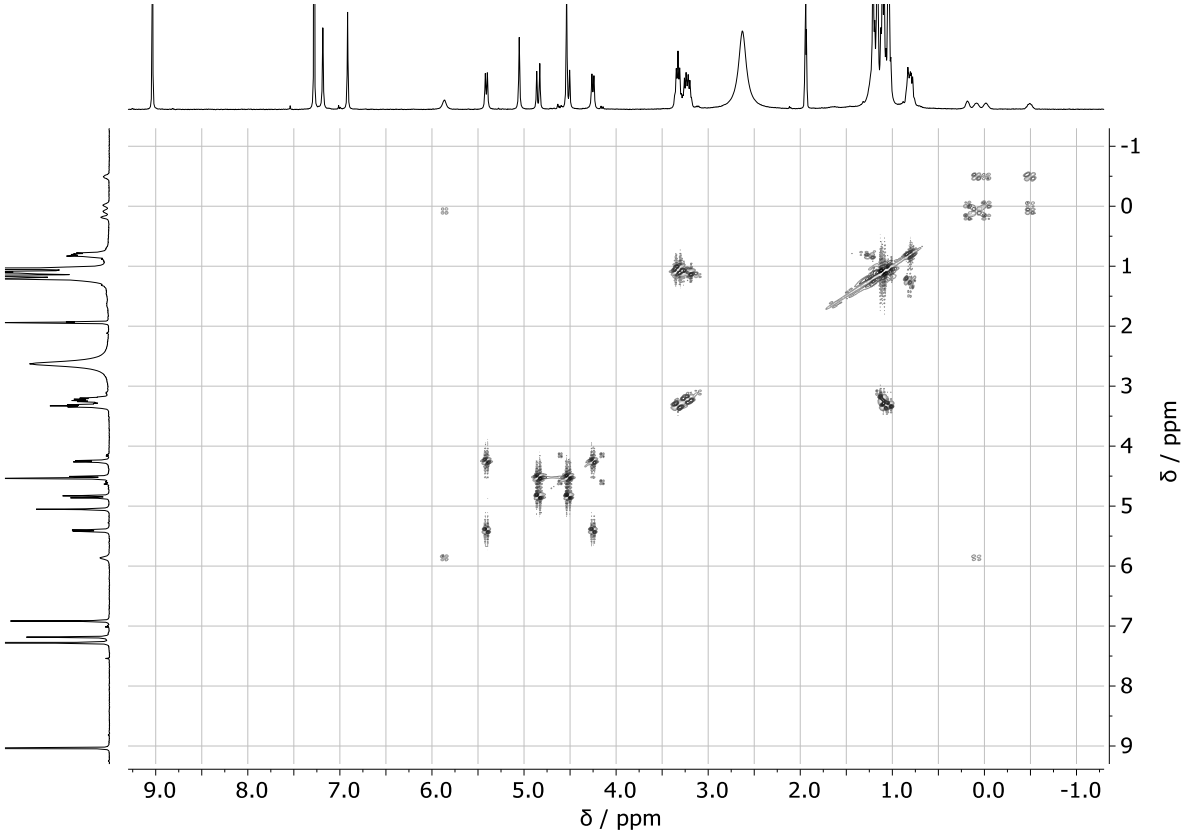


Figure S26. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.2 equiv. of 1,8-diaminooctane + 2.7 equiv. PicH.

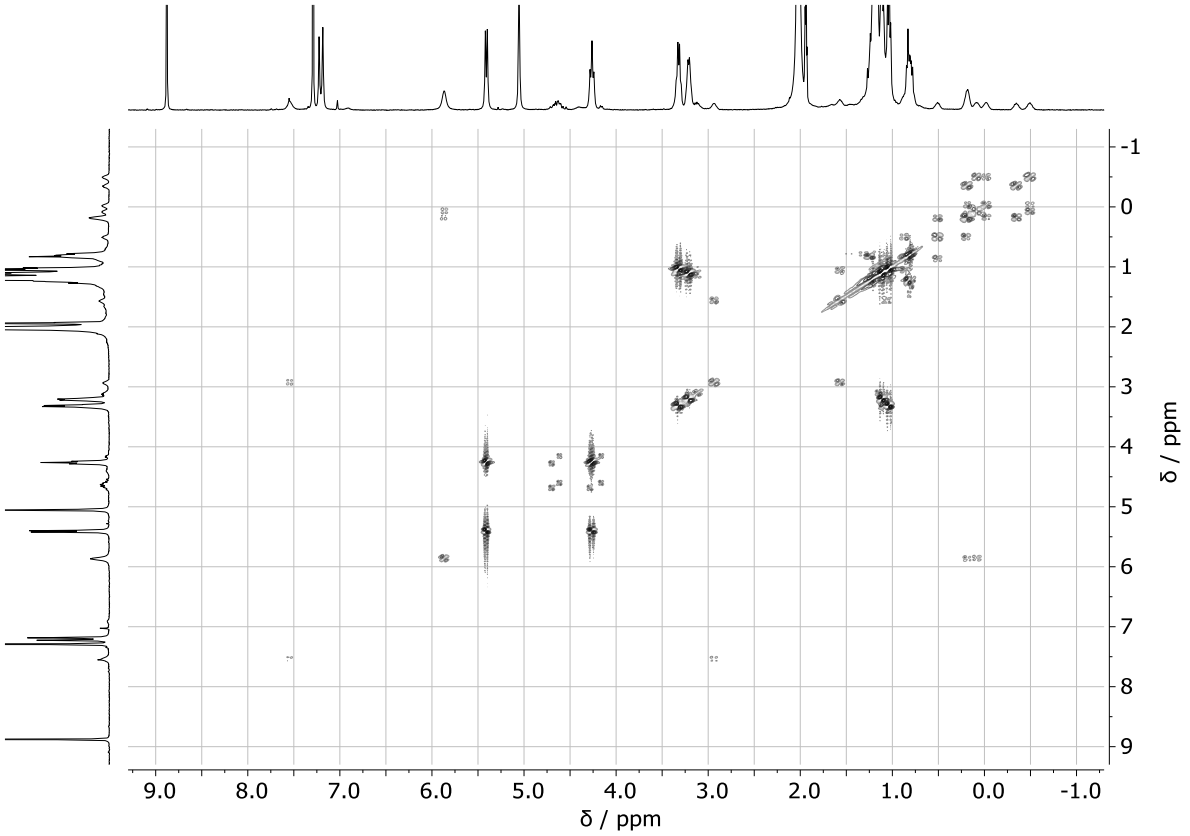


Figure S27. COSY spectrum (298 K, 400MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.8 equiv. of 1,8-diaminooctane + 2.5 equiv. PicH.

NMR studies of **Ox3** with 1,4-phenylene diamine and picric acid

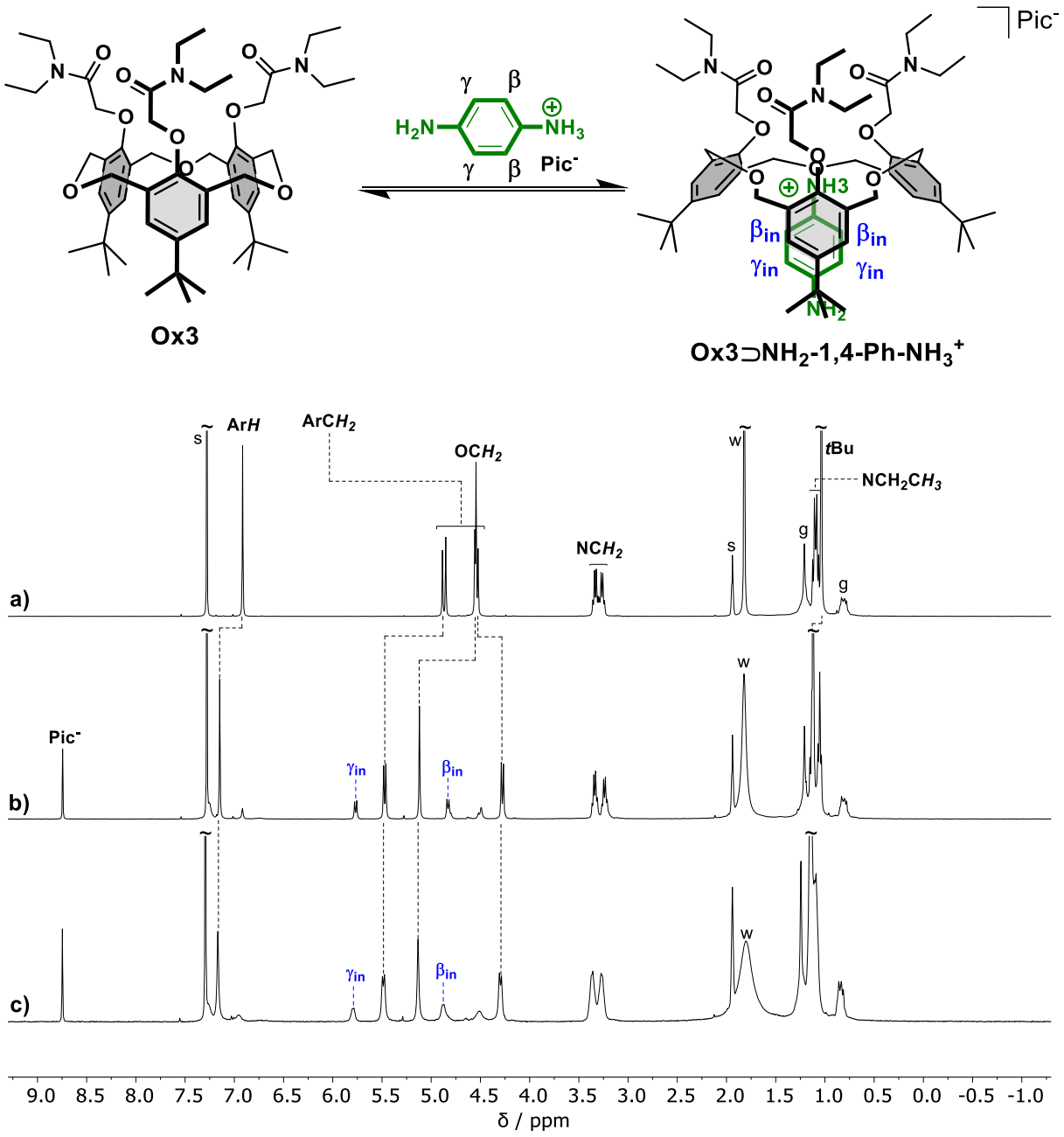


Figure S28. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) at 298 K (a); Ox3 + 0.9 equiv. of 1,4-phenylene diamine + 0.9 equiv. PicH at 298 K (b) and at 323 K (c). S: residual solvents; w: residual water; g: grease.

Monofunctionalization reactions of diamines

Monofunctionalization of cadaverine in the absence of **Ox3**

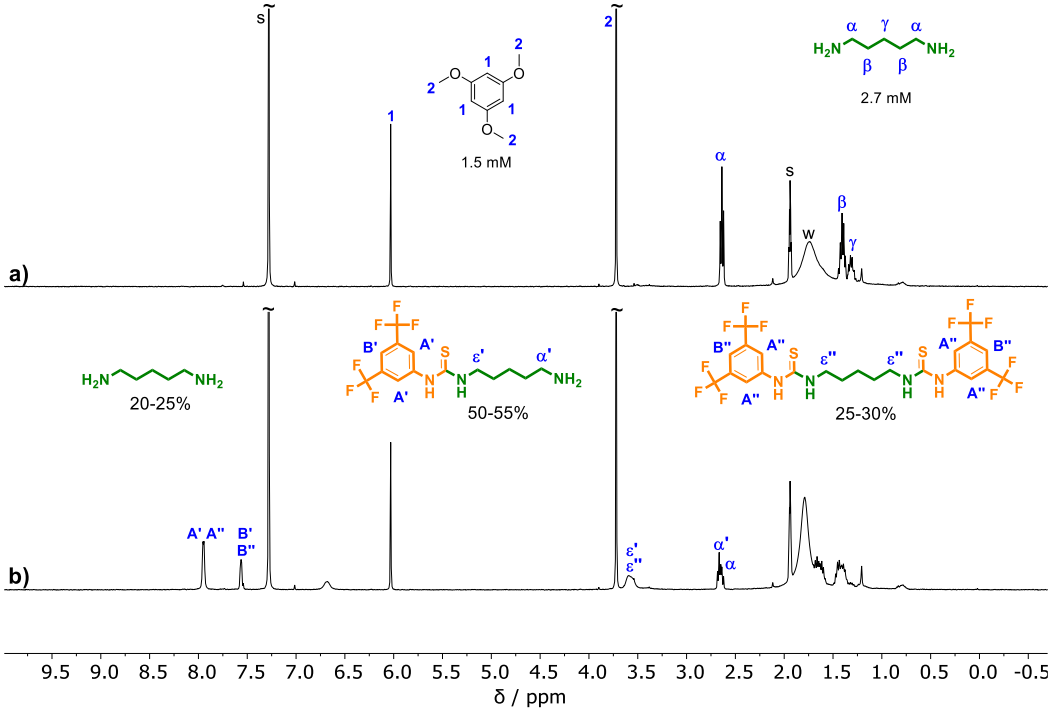


Figure S29. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of 1,3,5-trimethoxybenzene (internal standard, 1.5 mM) + cadaverine (2.7 mM) (a), after the addition 1 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 1 hour) (b). S: residual solvents; w: residual water.

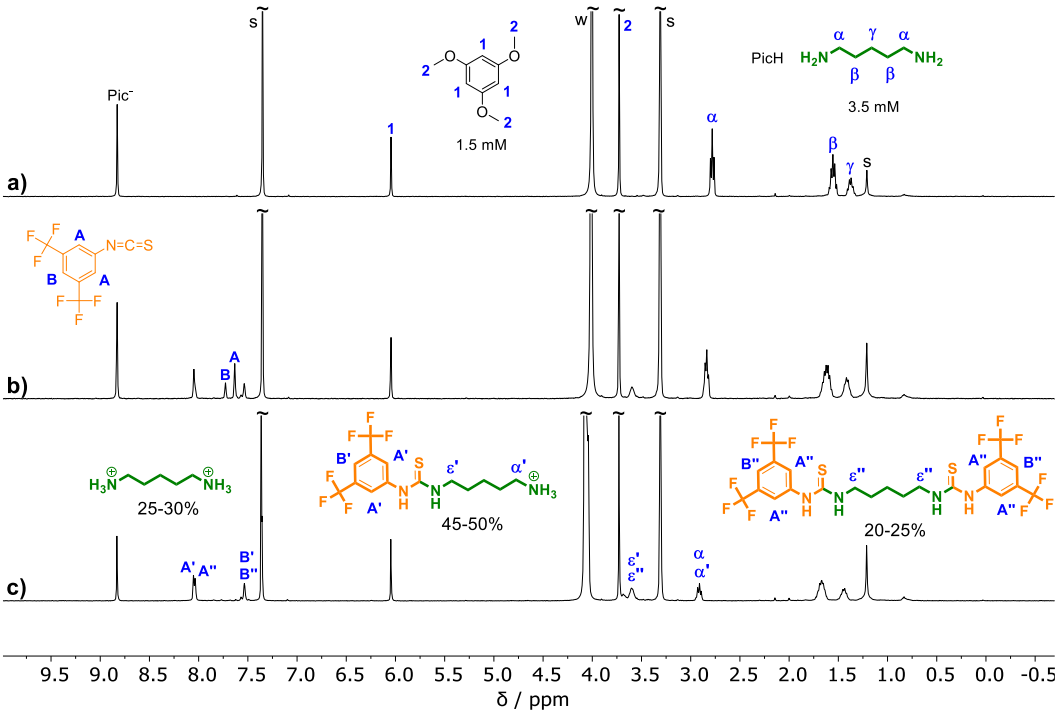


Figure S30. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of 1,3,5-trimethoxybenzene (internal standard, 1.5 mM) + cadaverine (3.5 mM) + 1 equiv. PicH (a); after the addition 1 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (b) and after 3 hours (c). S: residual solvents; w: residual water.

Monofunctionalization of putrescine (1,4-diaminobutane) in the presence of **Ox3**

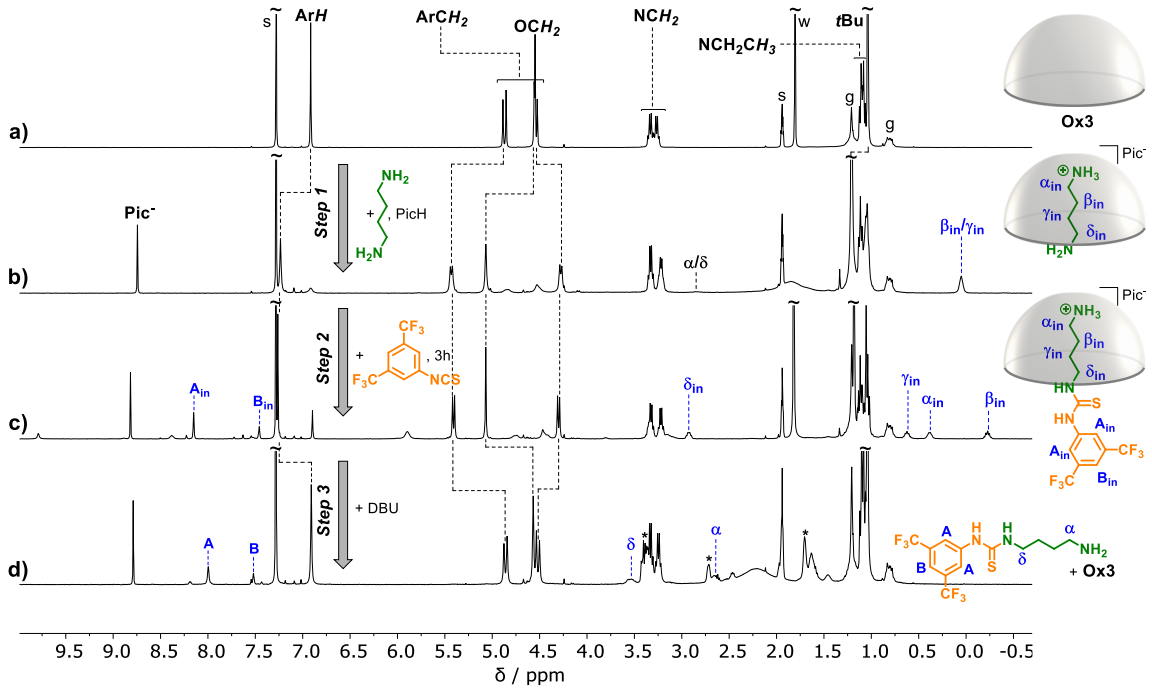


Figure S31. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of putrescine and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c) and 1.3 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

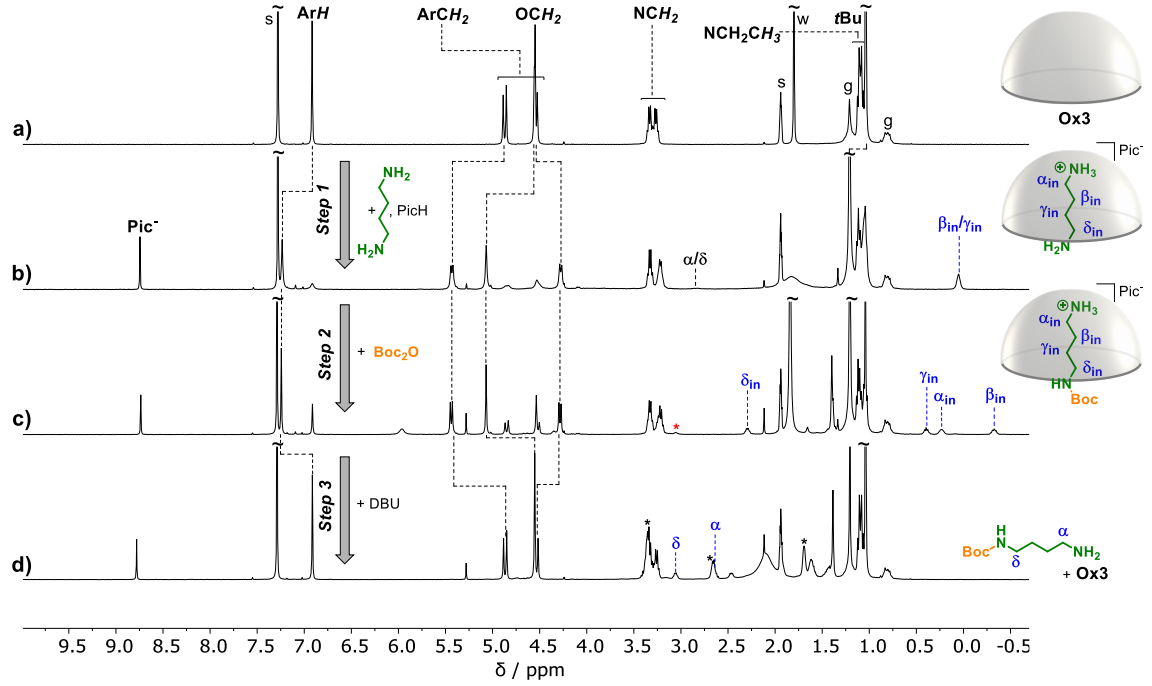


Figure S32. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of putrescine and 0.9 equiv. of PicH (b); 0.9 equiv. of di-*tert*-butyl dicarbonate (c) and 1.3 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$; *: traces of difunctionalized by-product. The very small ^{1}H signal was attributed to the difunctionalized product on the basis of its chemical shift.

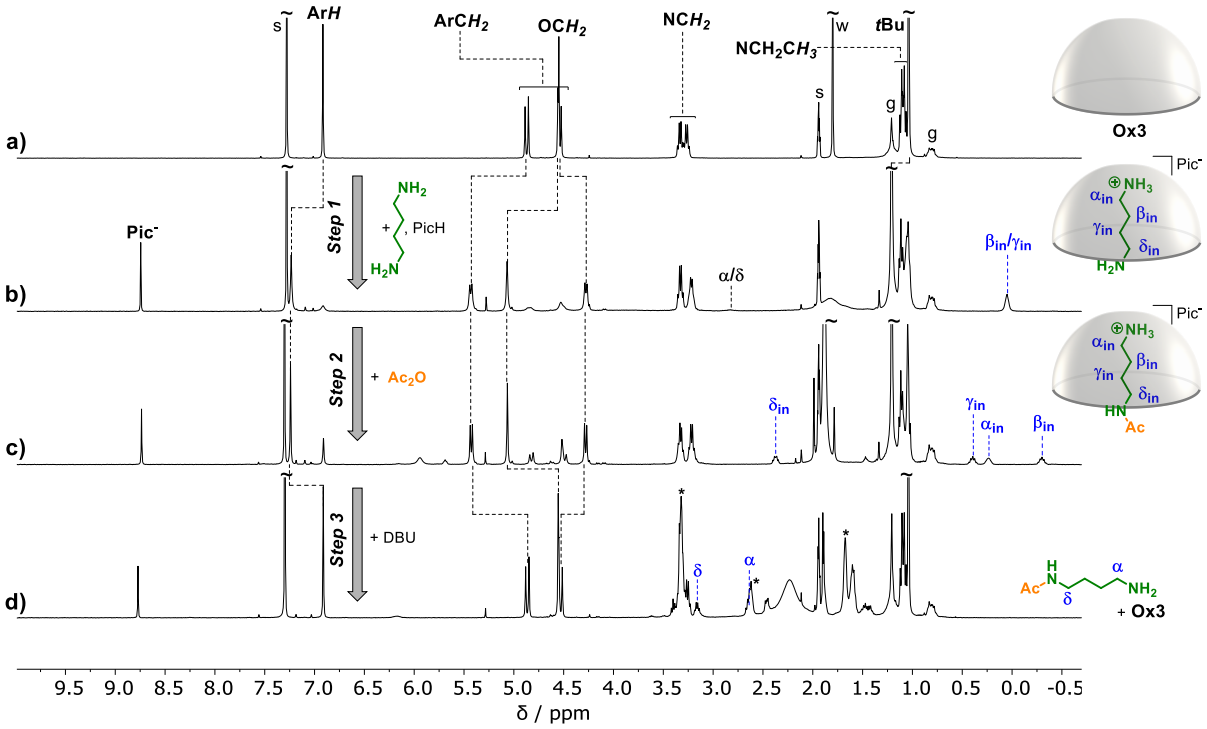


Figure S33. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of putrescine and 0.9 equiv. of PicH (b); 0.9 equiv. of acetic anhydride (c) and 1.8 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

Monofunctionalization of cadaverine (1,5-diaminopentane) in the presence of **Ox3**

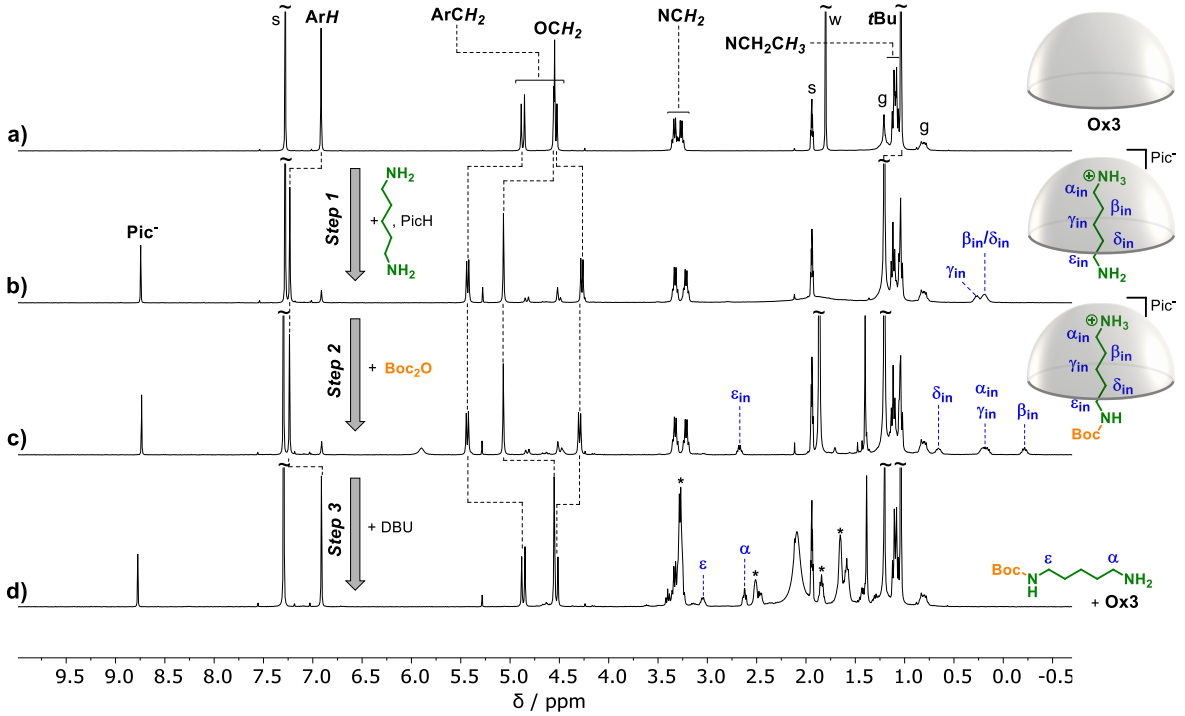


Figure S34. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of cadaverine and 0.9 equiv. of PicH (b); 0.9 equiv. of di-*tert*-butyl dicarbonate (c) and 2.0 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

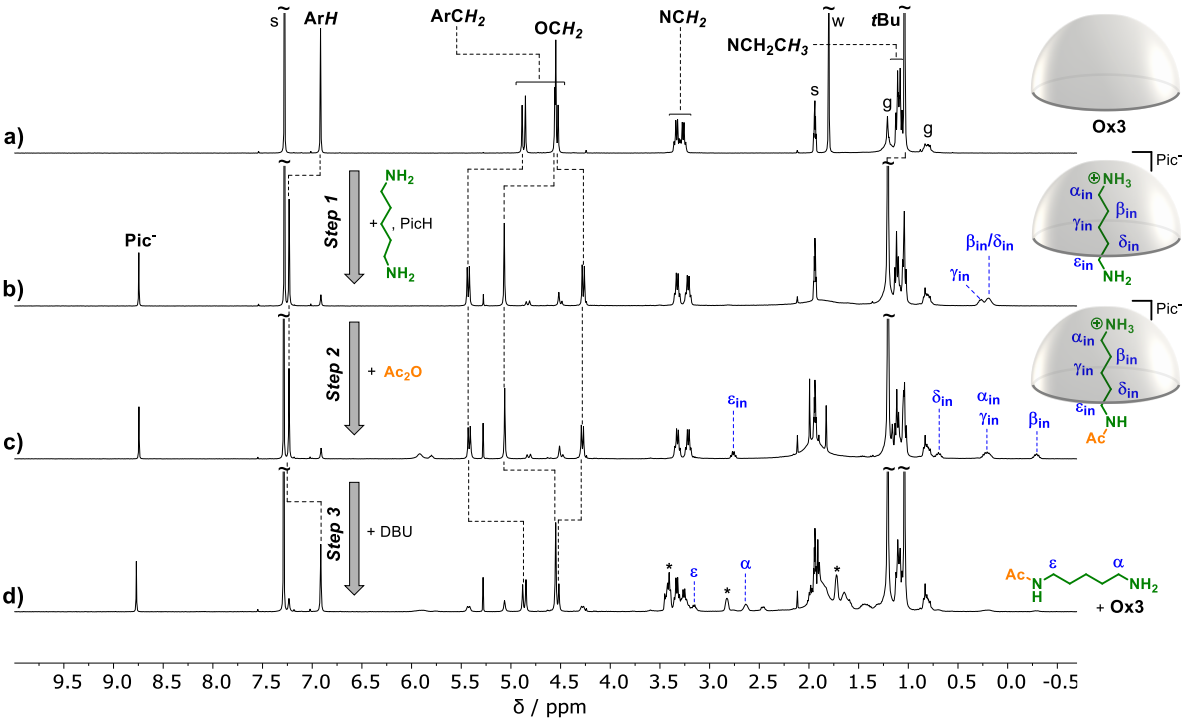


Figure S35. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of cadaverine and 0.9 equiv. of PicH (b); 0.9 equiv. of acetic anhydride (c) and 2.0 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

Monofunctionalization of 1,6-diaminohexane in the presence of **Ox3**

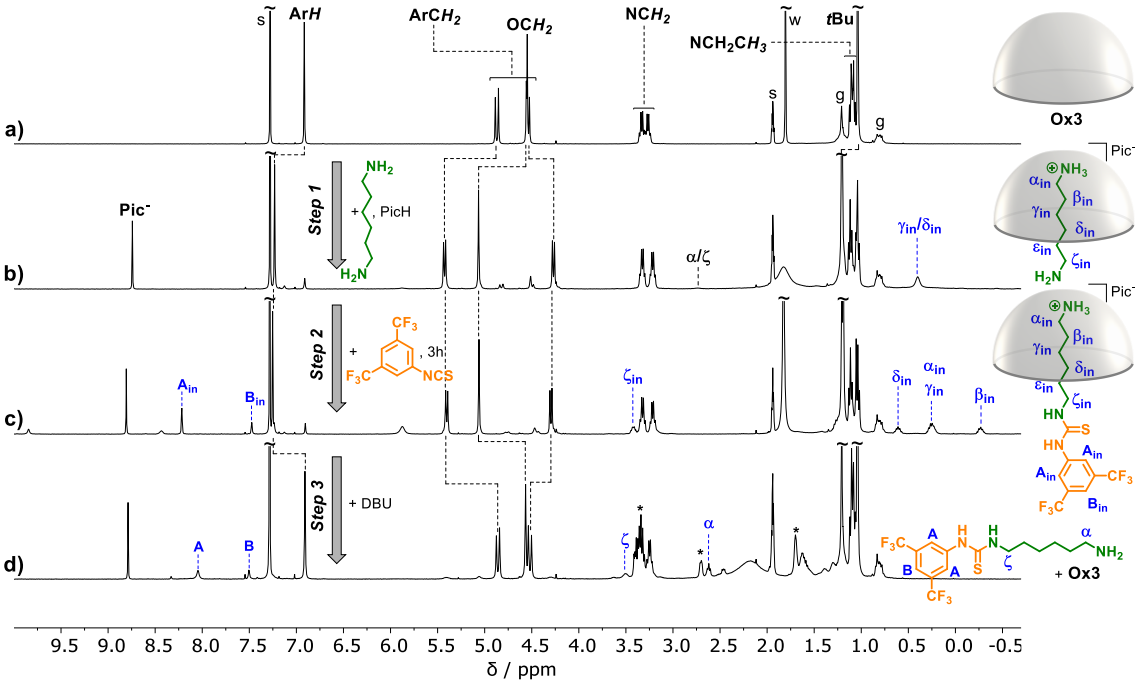


Figure S36. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,6-diaminohexane and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c) and 1.4 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

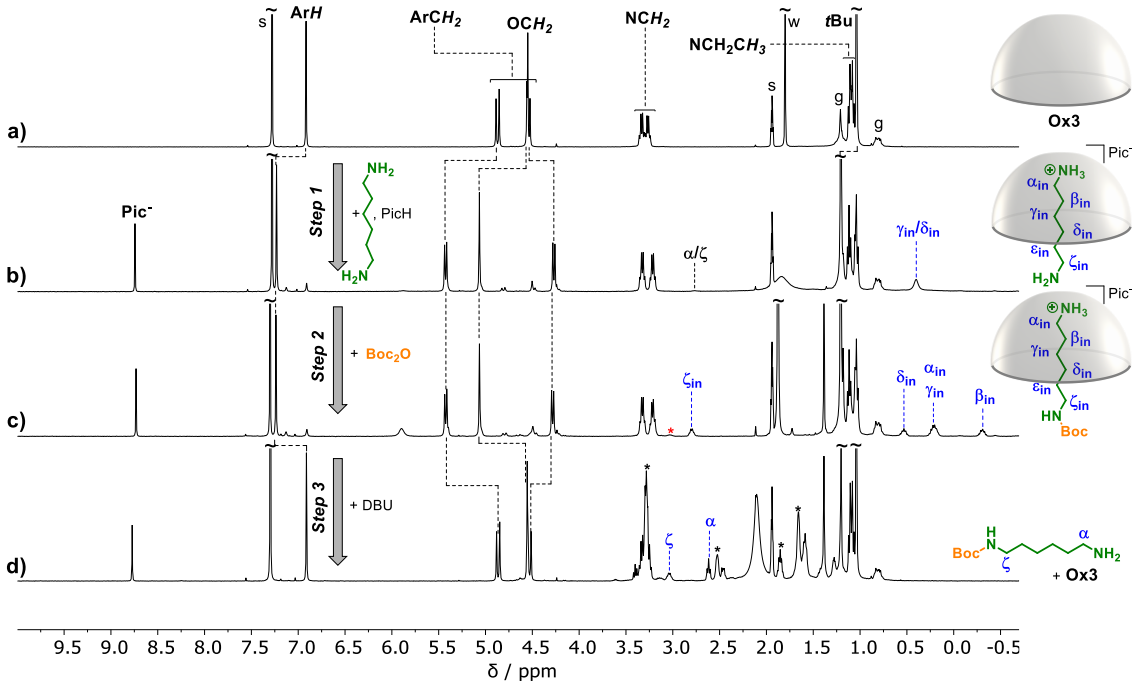


Figure S37. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,6-diaminohexane and 0.9 equiv. of PicH (b); 0.9 equiv. of di-*tert*-butyl dicarbonate (c) and 2.5 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$; *: traces of difunctionalized by-product. The very small ^{1}H signal was attributed to the difunctionalized product on the basis of its chemical shift.

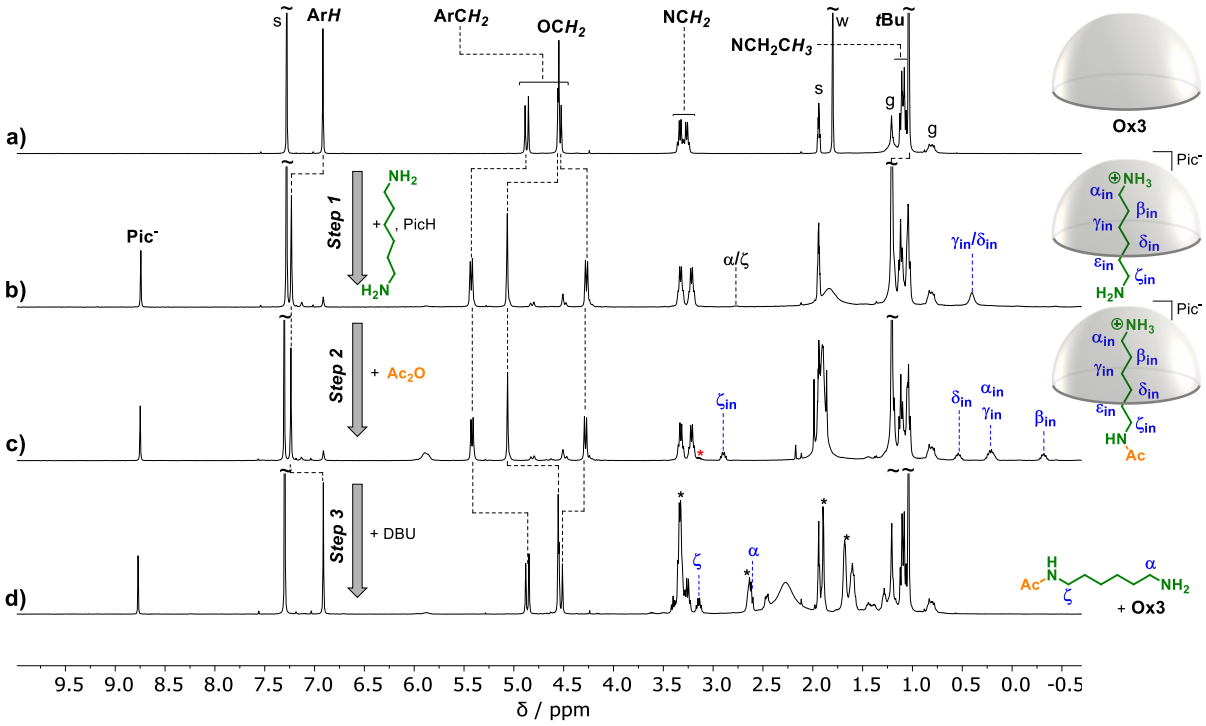


Figure S38. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,6-diaminohexane and 0.9 equiv. of PicH (b); 0.9 equiv. of acetic anhydride (c) and 2.0 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$; *: traces of difunctionalized by-product. The very small ^{1}H signal was attributed to the difunctionalized product on the basis of its chemical shift.

Monofunctionalization of 1,8-diaminooctane in the presence of **Ox3**

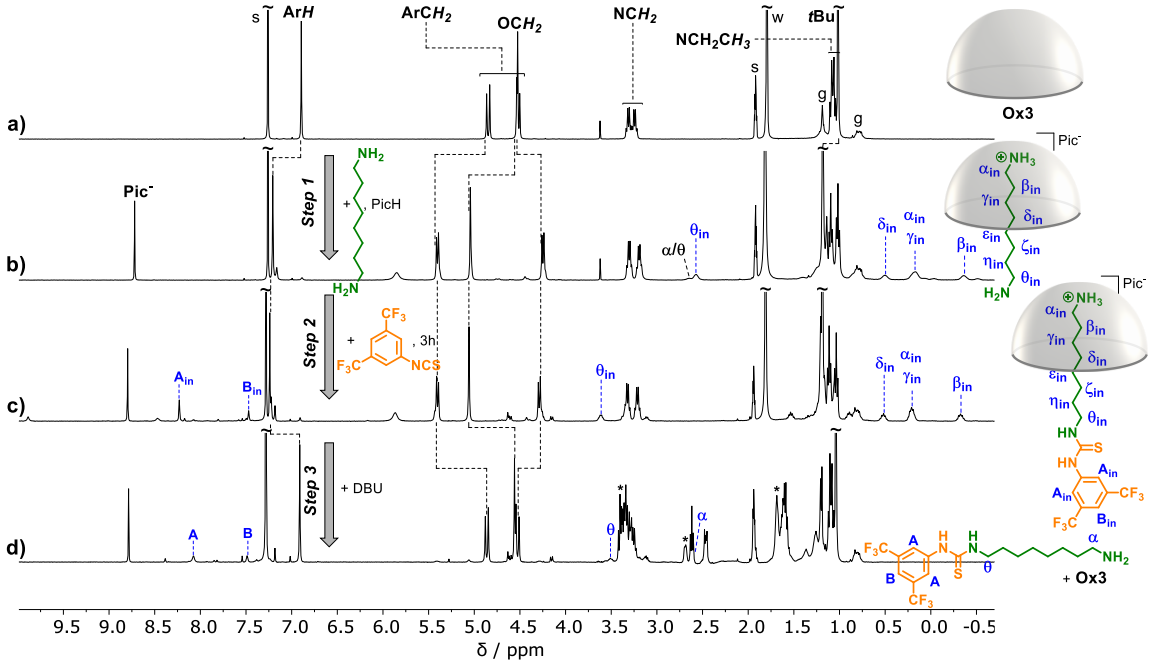


Figure S39. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,8-diaminooctane and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c) and 1.4 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

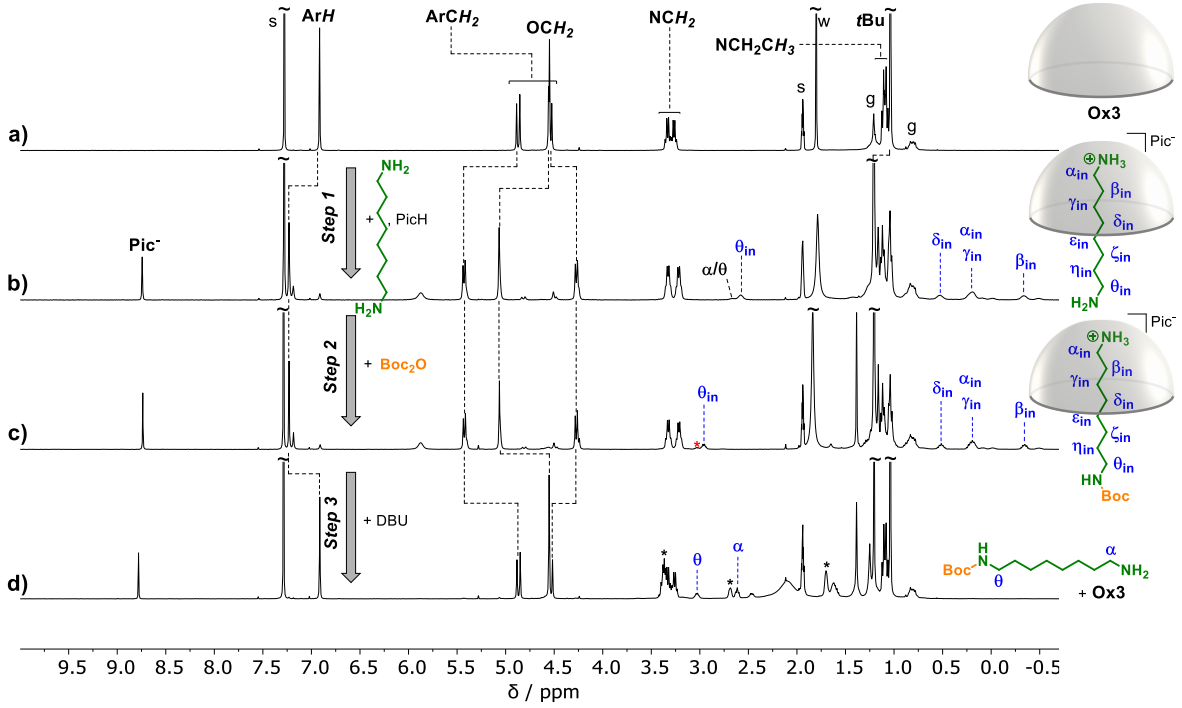


Figure S40. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,8-diaminooctane and 0.9 equiv. of PicH (b); 0.9 equiv. of di-*tert*-butyl dicarbonate (c) and 1.4 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$; *: traces of difunctionalized by-product. The very small ^{1}H signal was attributed to the difunctionalized product on the basis of its chemical shift.

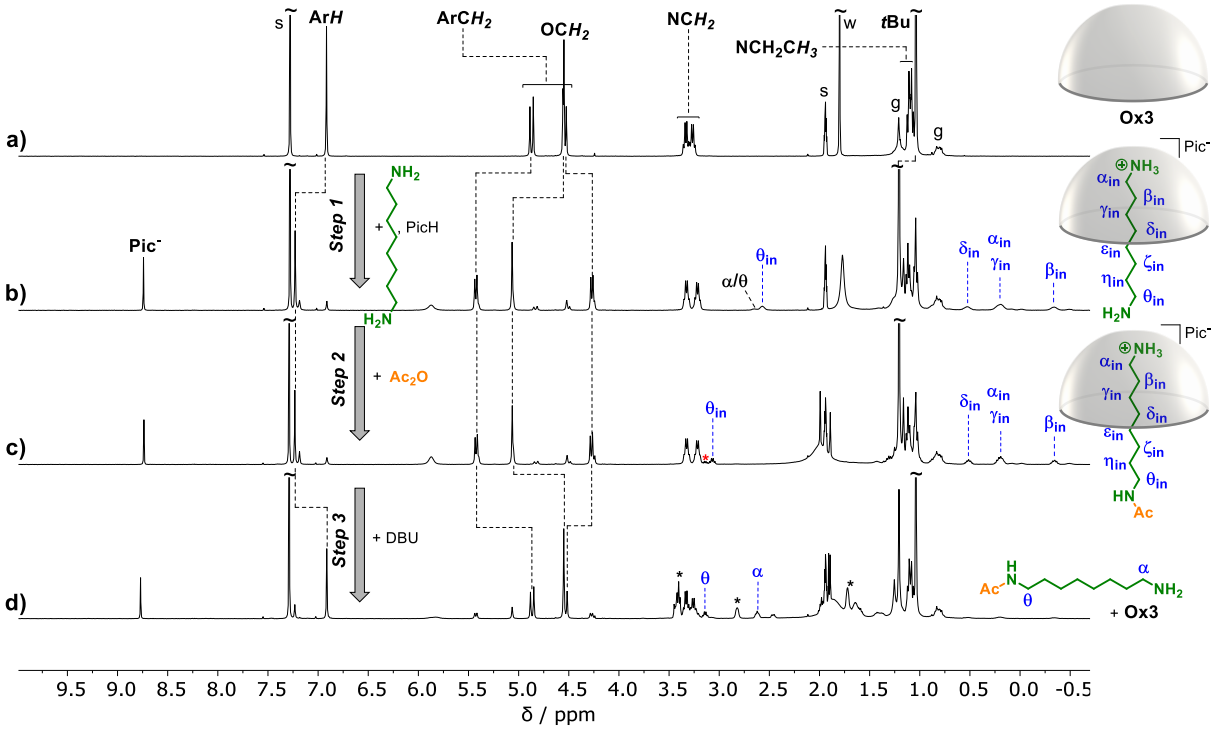


Figure S41. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,8-diaminooctane and 0.9 equiv. of PicH (b); 0.9 equiv. of acetic anhydride (c) and 1.8 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H^{+}; *: traces of difunctionalized by-product. The very small ^{1}H signal was attributed to the difunctionalized product on the basis of its chemical shift.

Monofunctionalization of 1,4-phenylene diamine in the presence of **Ox3**

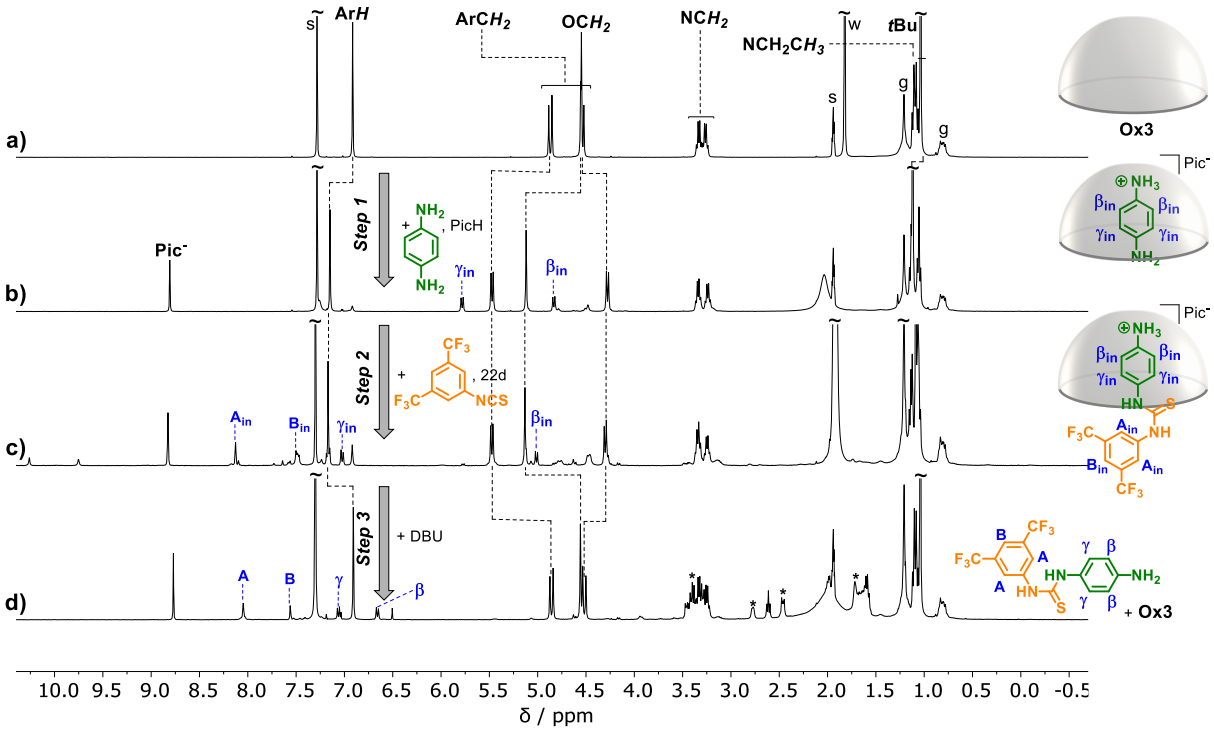
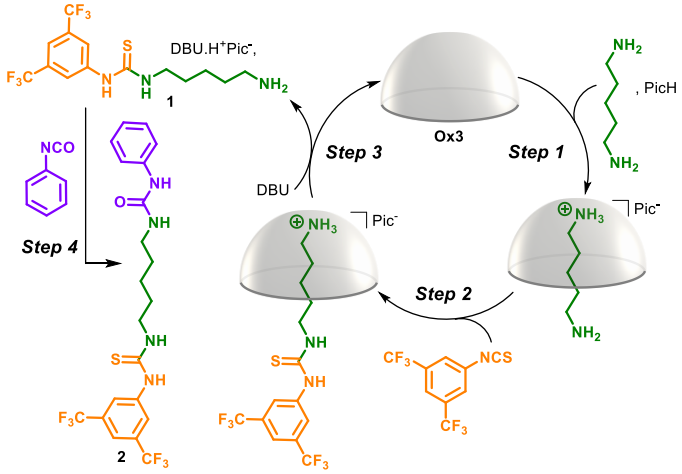


Figure S42. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of 1,4-phenylenediamine and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 22 days) (c) and 1.2 equiv. of DBU (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H^{+}.

One-pot cyclic processes

One-pot cyclic process for the accumulation of **2**



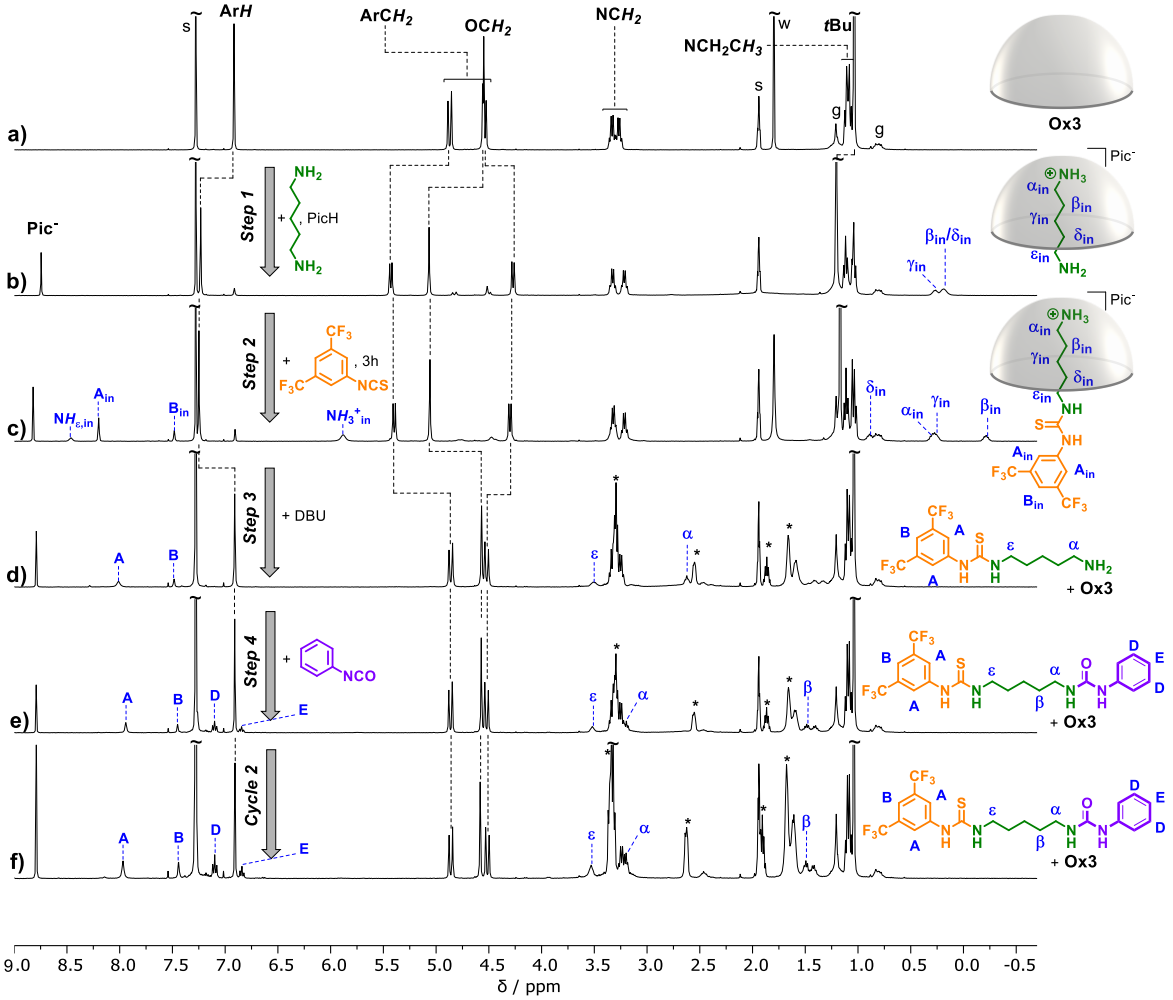


Figure S43. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of cadaverine and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c); 1.3 equiv. of DBU (d); 0.9 equiv. of phenyl isocyanate (e) and after a second cycle (with the successive additions of 0.9 equiv. of cadaverine, 1.3 equiv. of PicH, 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate, 2 equiv. of DBU and 0.9 equiv. of phenyl isocyanate) (f). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$.

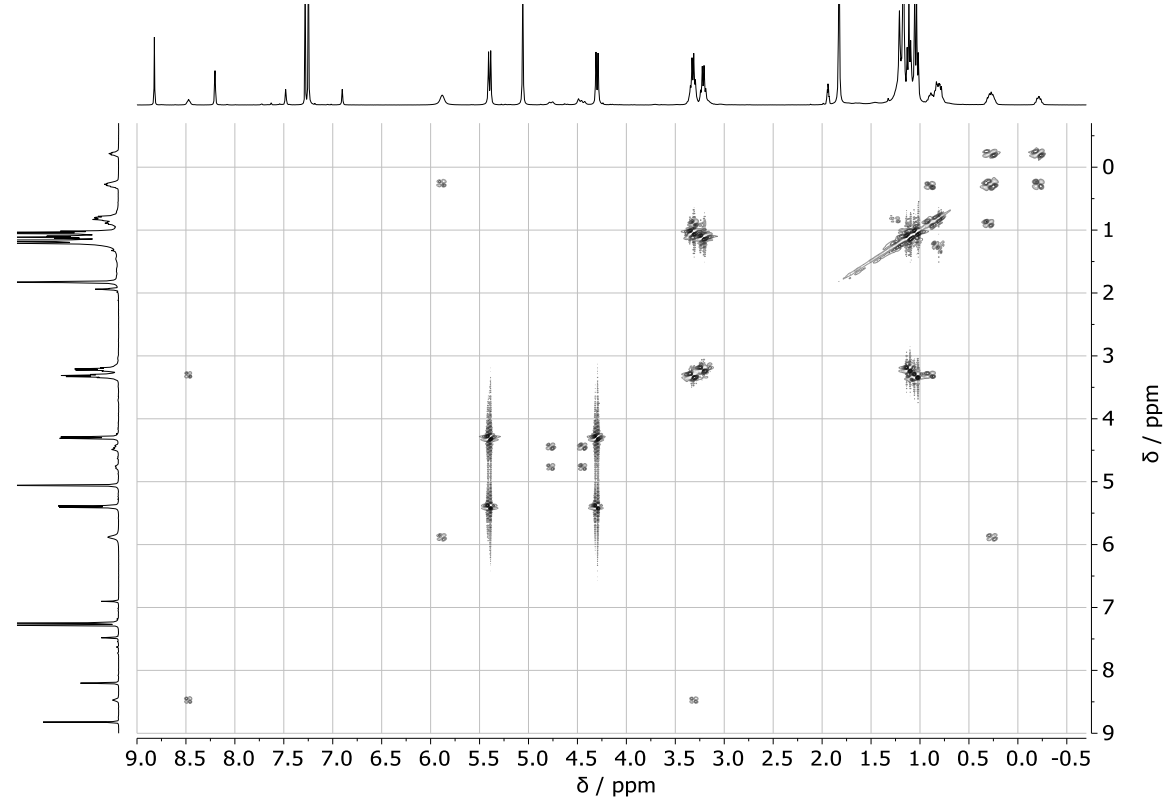


Figure S44. COSY spectrum (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.9 equiv. of cadaverine + 0.9 equiv. of PicH + 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (step 2).

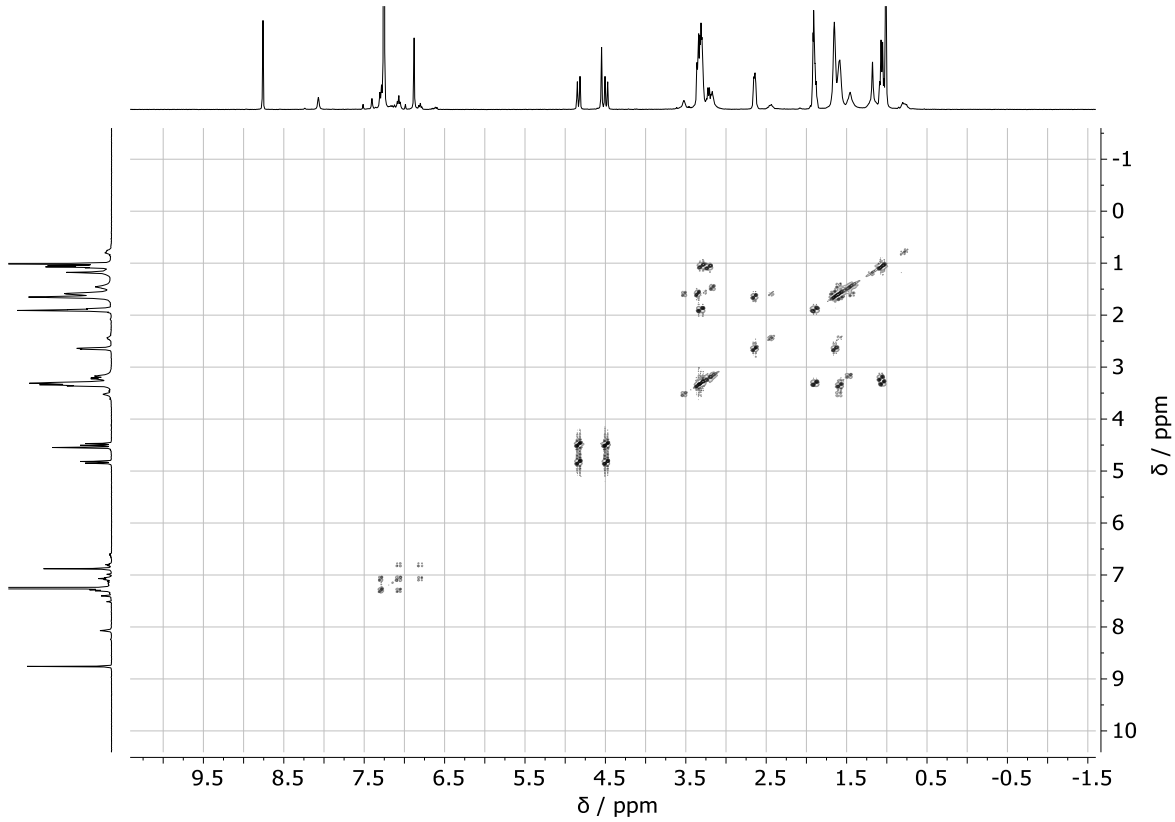


Figure S45. COSY spectrum (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.9 equiv. of cadaverine + 0.9 equiv. of PicH + 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) + 1.3 equiv. DBU + 0.9 equiv. of phenyl isocyanate (step 4).

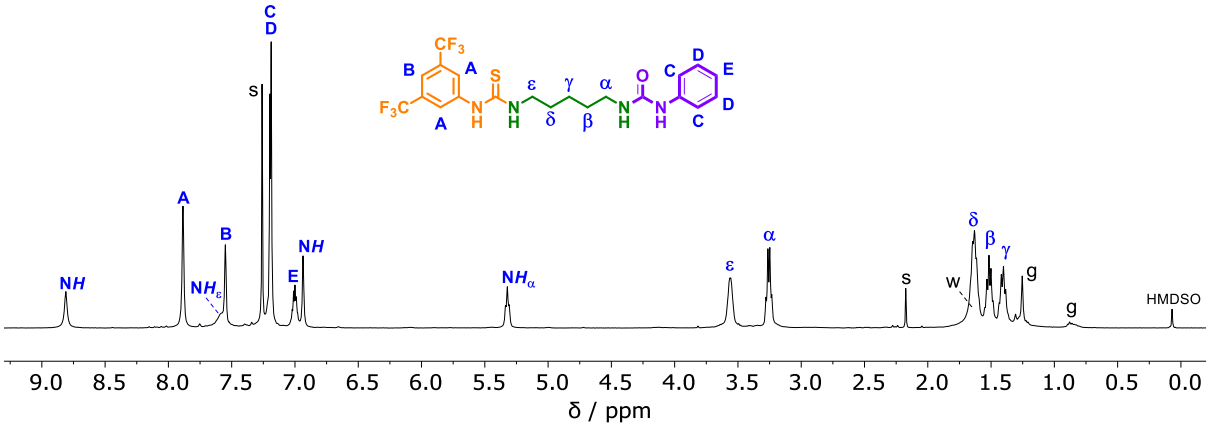


Figure S46. ^{1}H NMR spectrum (298 K, 400 MHz, $CDCl_3$) of isolated compound **2**.

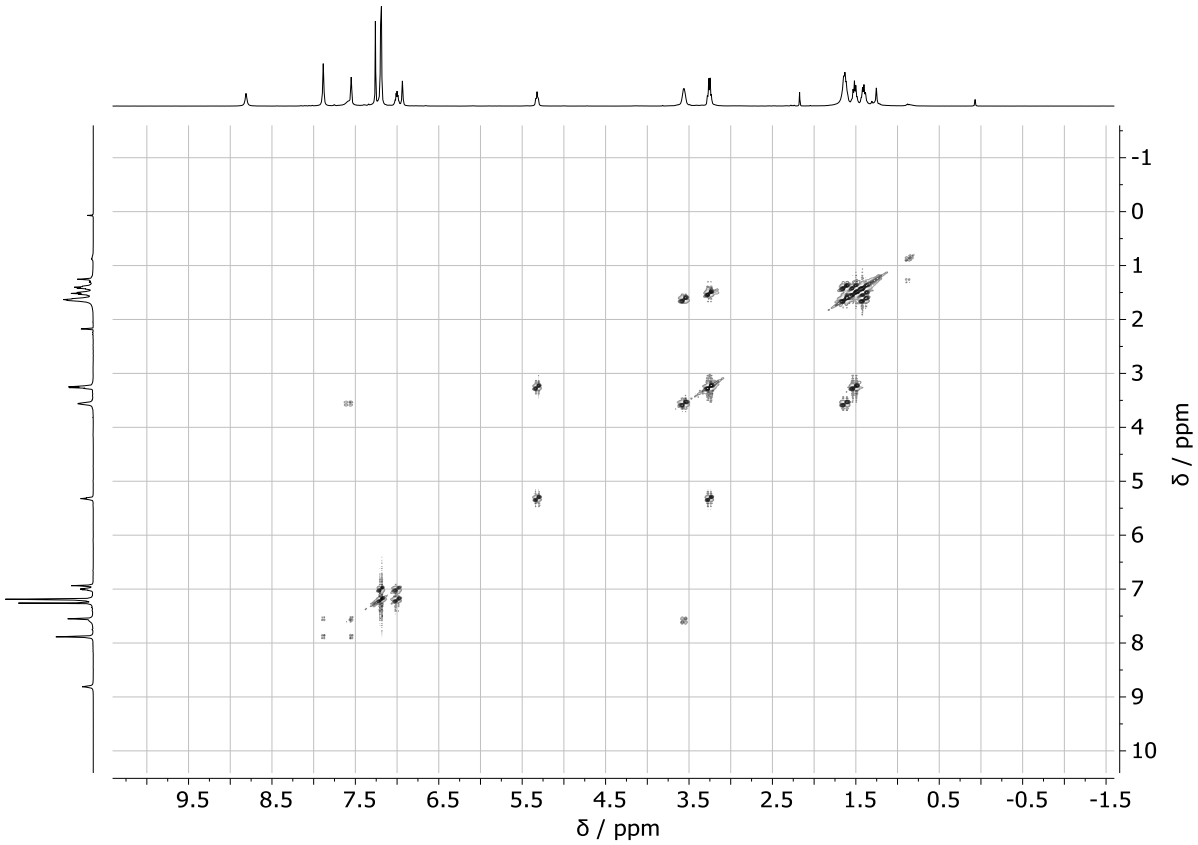


Figure S47. COSY spectrum (298 K, 400 MHz, $CDCl_3$) of isolated compound **2**.

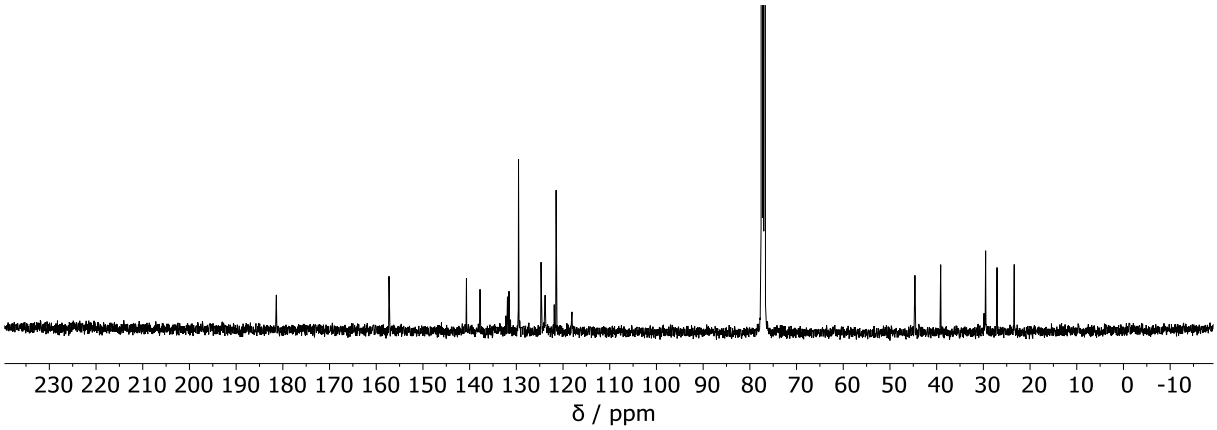


Figure 48. ^{13}C NMR spectrum (298 K, 100 MHz, $CDCl_3$) of isolated compound **2**.

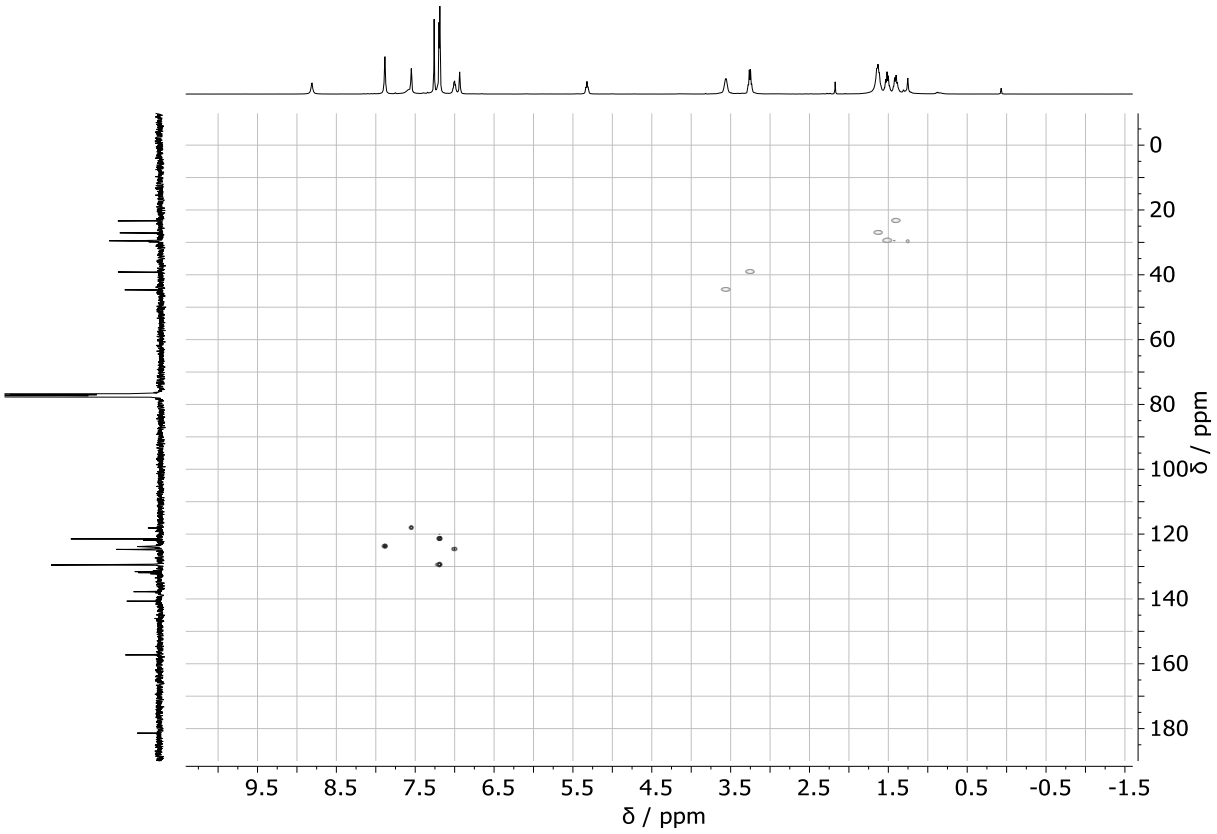


Figure S49. HSQC spectrum (298 K, 400 MHz, $CDCl_3$) of isolated compound **2**.

One-pot cyclic process for the accumulation of **3**

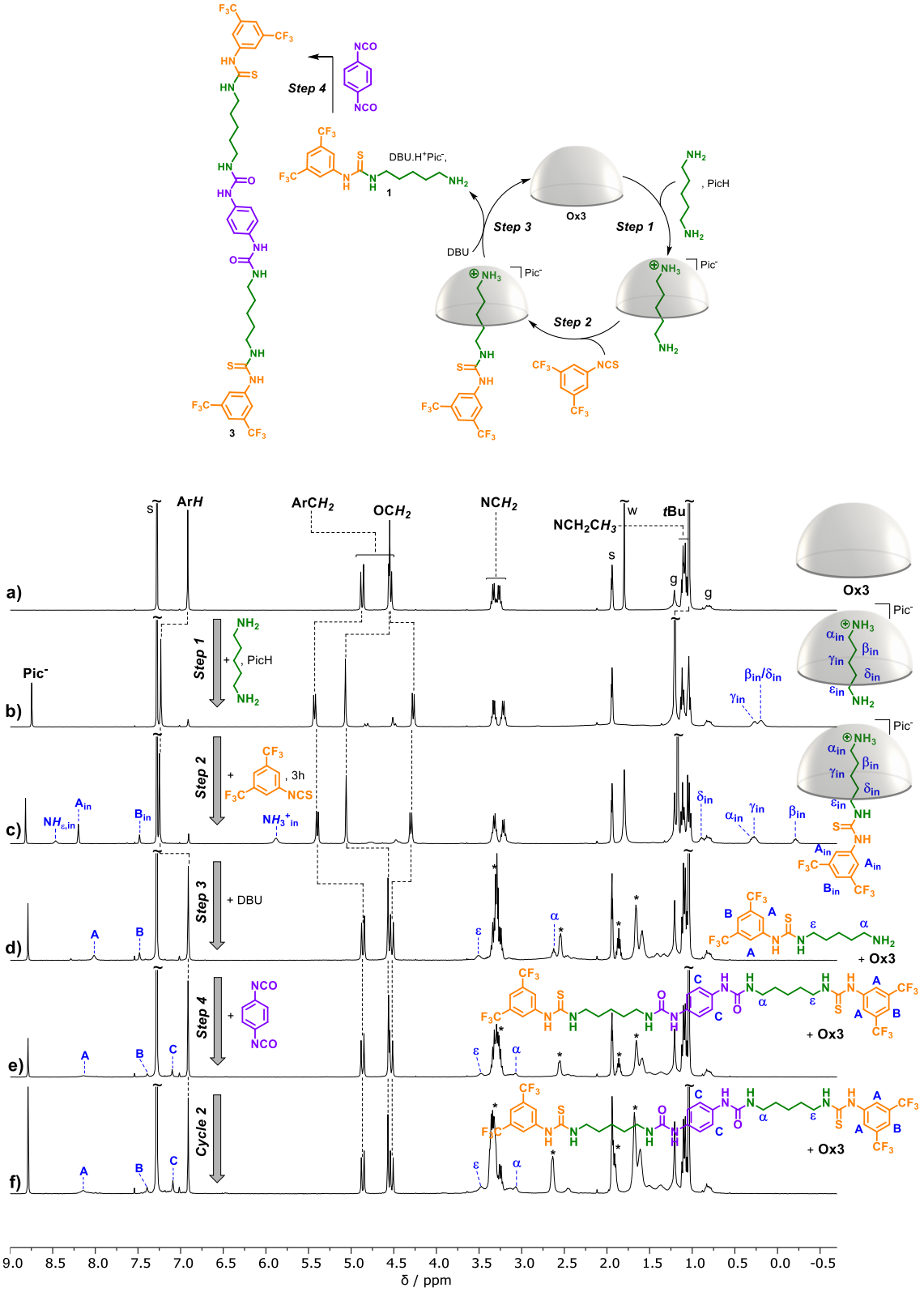


Figure S50. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1, cycle 1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of cadaverine and 0.9 equiv. of PicH (b); 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c); 1.3 equiv. of DBU (d); 0.45 equiv. of 1,4-phenylene diisocyanate (e) and after a second cycle (with the successive additions of 0.9 equiv. of cadaverine, 1.3 equiv. of PicH, 0.9 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate, 2 equiv. of DBU and 0.45 equiv. of 1,4-phenylene diisocyanate) (f). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H^{+}.

Reactions between different monoprotected substrates

Stability study of the amino-isocyanate intermediate

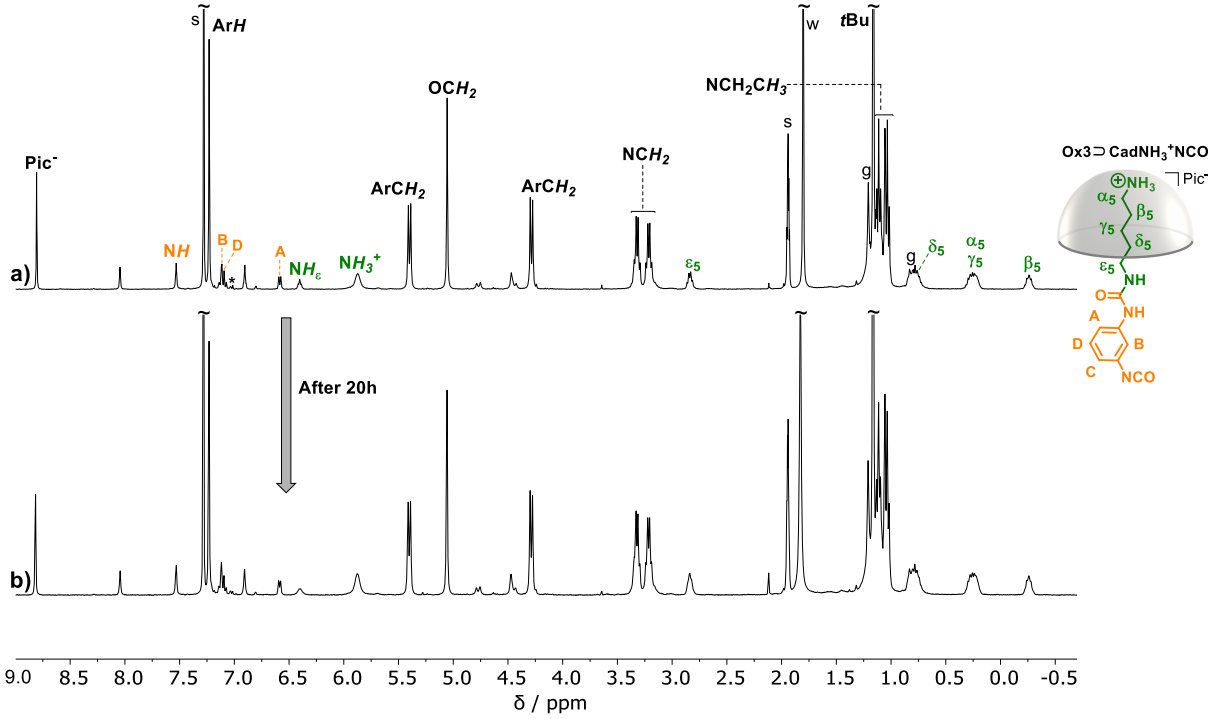


Figure S51. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.9 equiv. cadaverine + 0.9 equiv. PicH + 0.9 equiv. 1,3-phenylene diisocyanate (a) and after 20h (b). S: residual solvents; w: residual water; g: grease; *: traces of symmetrical diurea-diammonium by-product.

Characterization of compound **4**

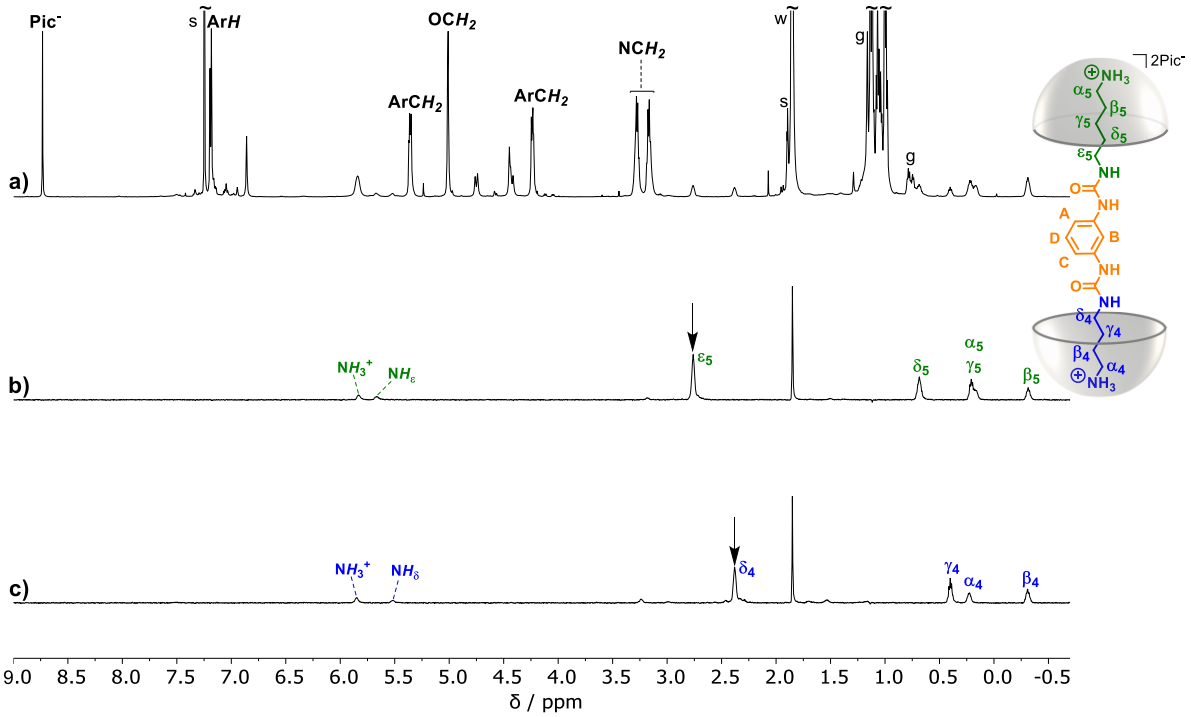


Figure S52. ^{1}H NMR spectrum (298 K, 600 MHz, $CDCl_3/CD_3CN$ 9:1) of protected diamino-diurea derivative **4.2H**$^{+}$ (a); 1D TOCSY spectra (298 K, τ = 120 ms) of protected diamino-diurea derivative **4.2H**$^{+}$ upon irradiation at 2.81 ppm (b) and at 2.43 ppm. S: residual solvents; w: residual water; g: grease.

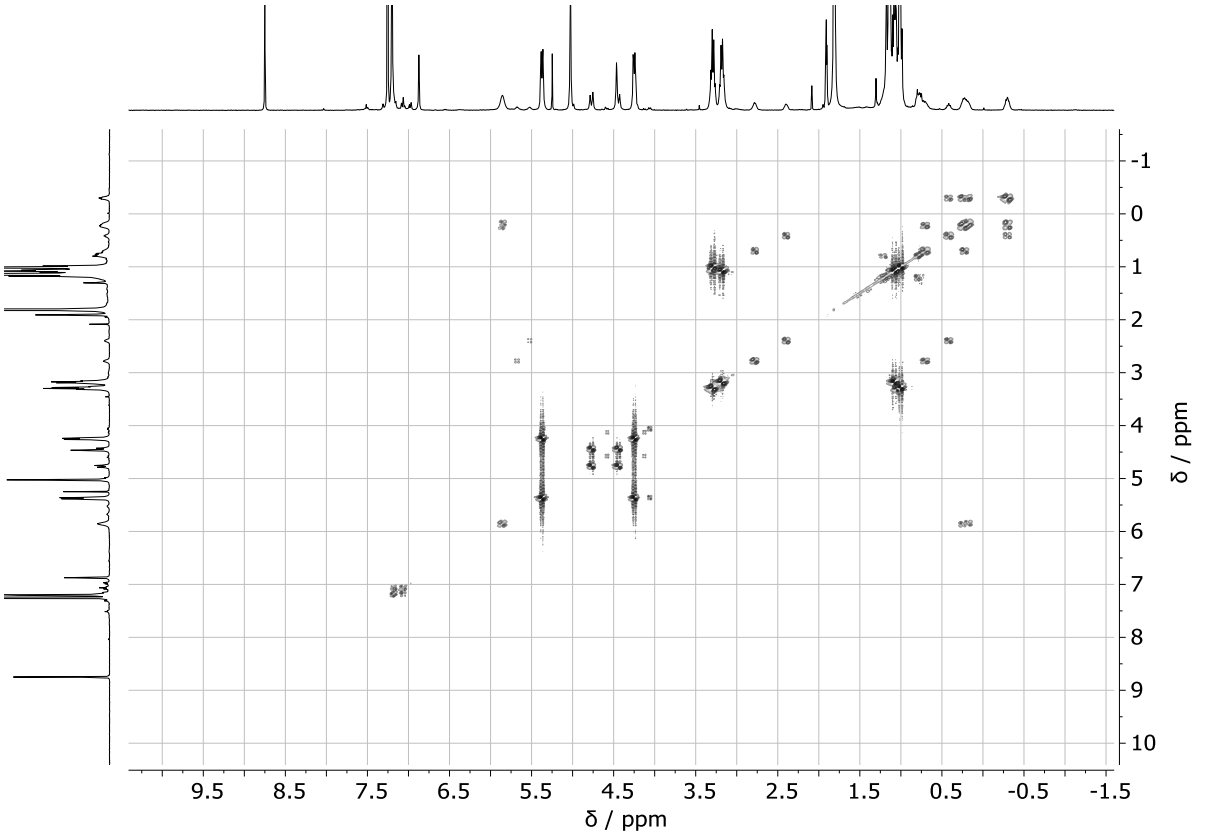


Figure S53. COSY NMR spectrum (298 K, 600 MHz, $CDCl_3/CD_3CN$ 9:1) of protected diamino-diurea derivative **4.2H**$^{+}$.

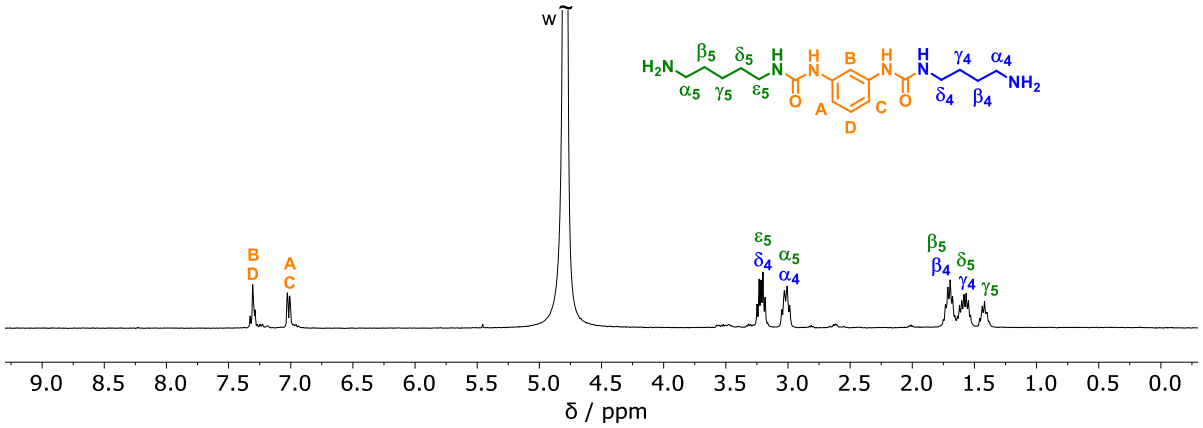


Figure S54. ^{1}H NMR spectrum (298 K, 400 MHz, D_2O) of the isolated diamino-diurea derivative **4**. w: residual water.

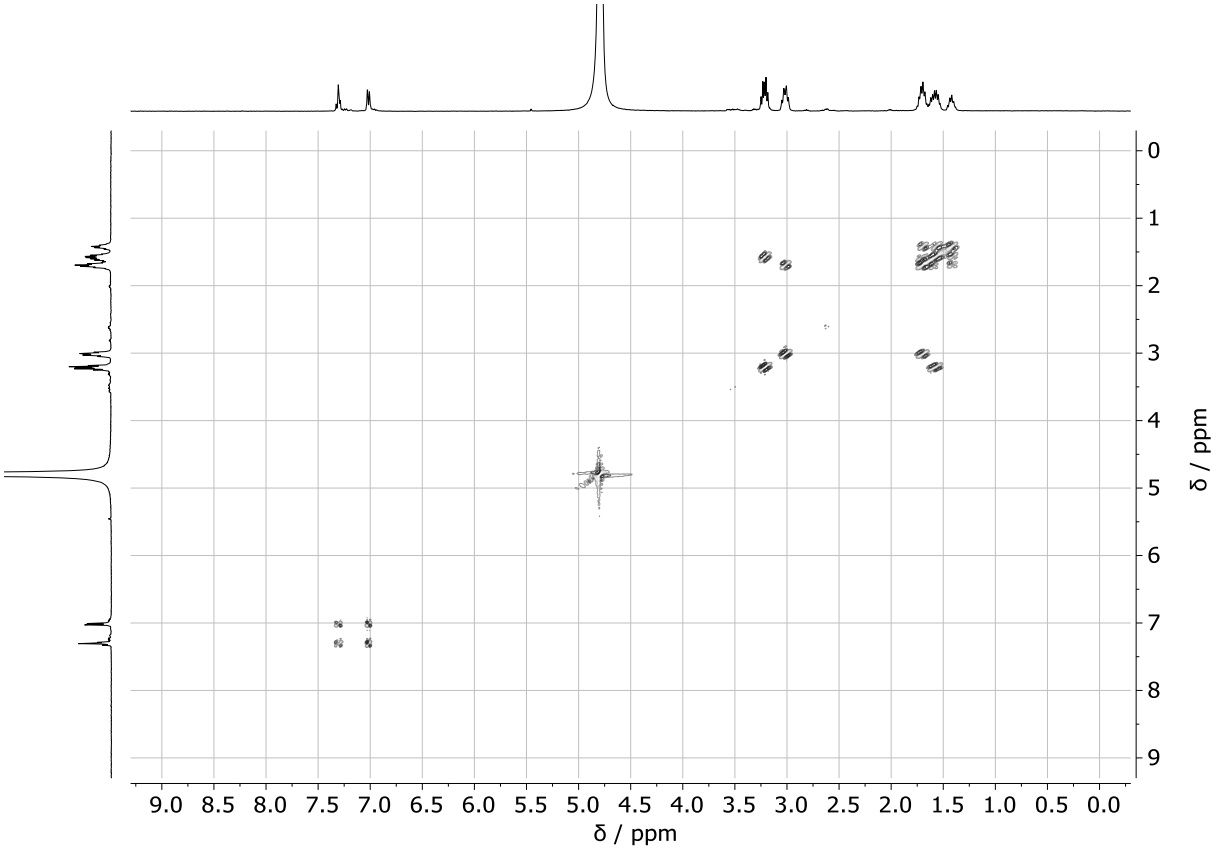


Figure S55. COSY NMR spectrum (298 K, 400 MHz, D_2O) of the isolated diamino-diurea derivative **4**.

Synthesis and characterization of compound **5**

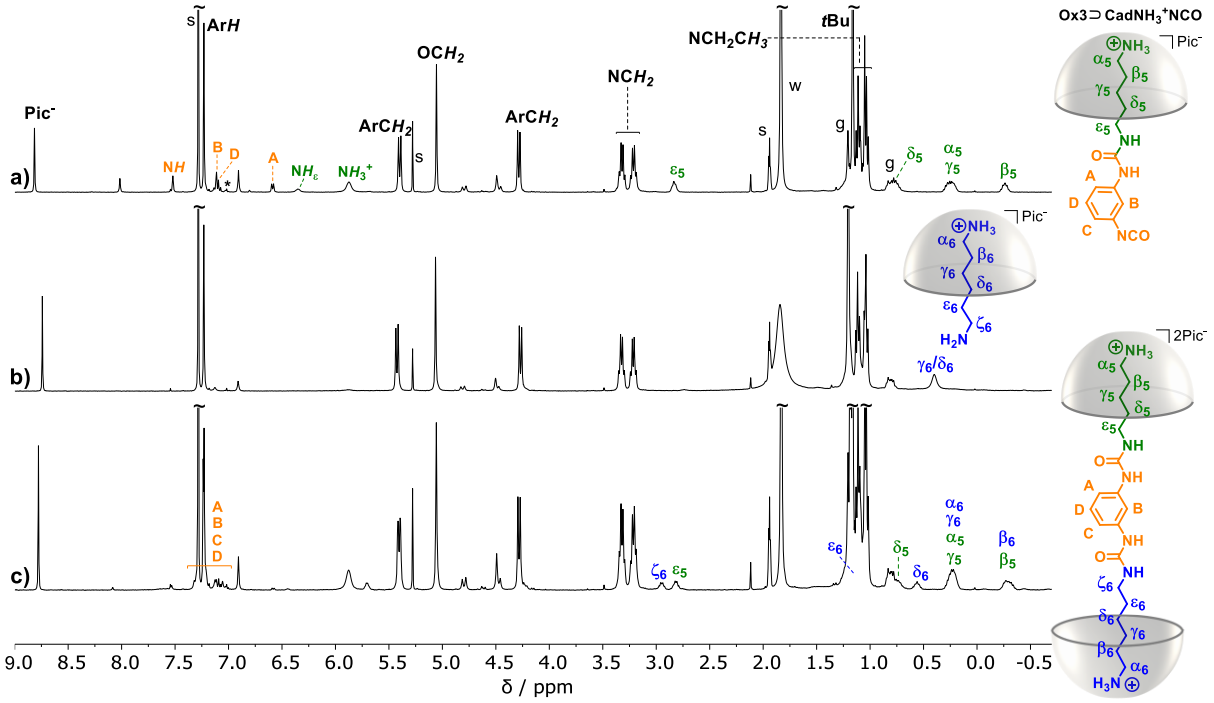


Figure S56. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) + 0.9 equiv. cadaverine + 0.9 equiv. PicH + 0.9 equiv. 1,3-phenylene diisocyanate (a); **Ox3** (3 mM) + 0.9 equiv. 1,6-diaminohexane + 0.9 equiv. PicH (b) and protected diamino-diurea derivative **5.2H**$^{+}$ (c). S: residual solvents; w: residual water; g: grease; *: traces of symmetrical diurea-diammonium by-product.

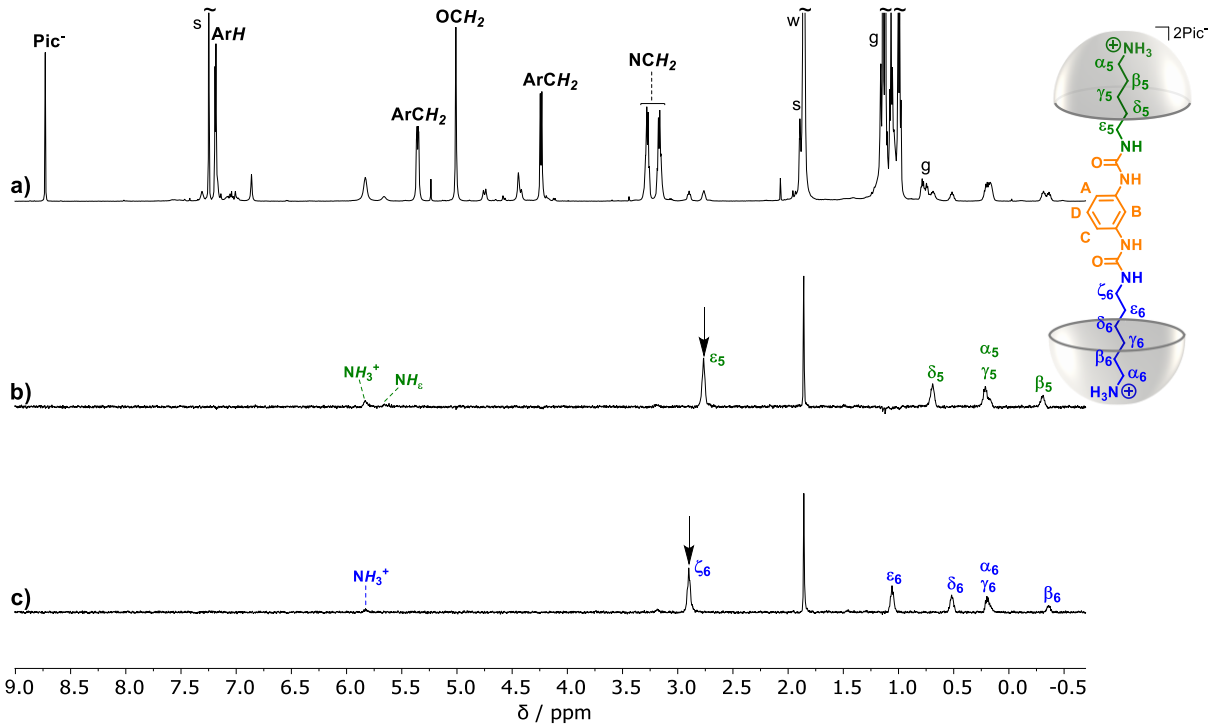


Figure S57. ^{1}H NMR spectrum (298 K, 600 MHz, $CDCl_3/CD_3CN$ 9:1) of protected diamino-diurea derivative **5.2H**$^{+}$ (a); 1D TOCSY spectra (298 K, τ = 120 ms) of protected diamino-diurea derivative **5.2H**$^{+}$ upon irradiation at 2.81 ppm (b) and at 2.94 ppm. S: residual solvents; w: residual water; g: grease.

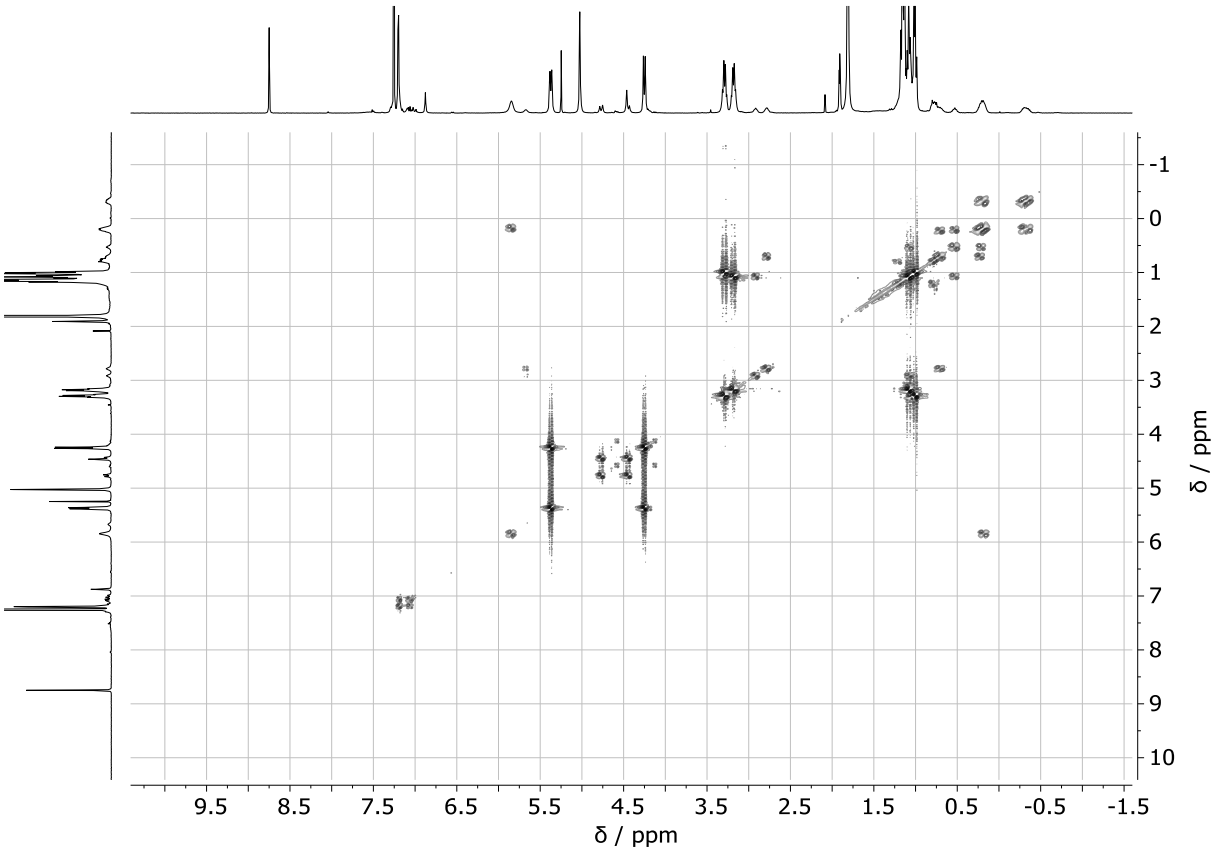


Figure S58. COSY NMR spectrum (298 K, 600 MHz, $CDCl_3/CD_3CN$ 9:1) of protected diamino-diurea derivative **5.2H**$^{+}$.

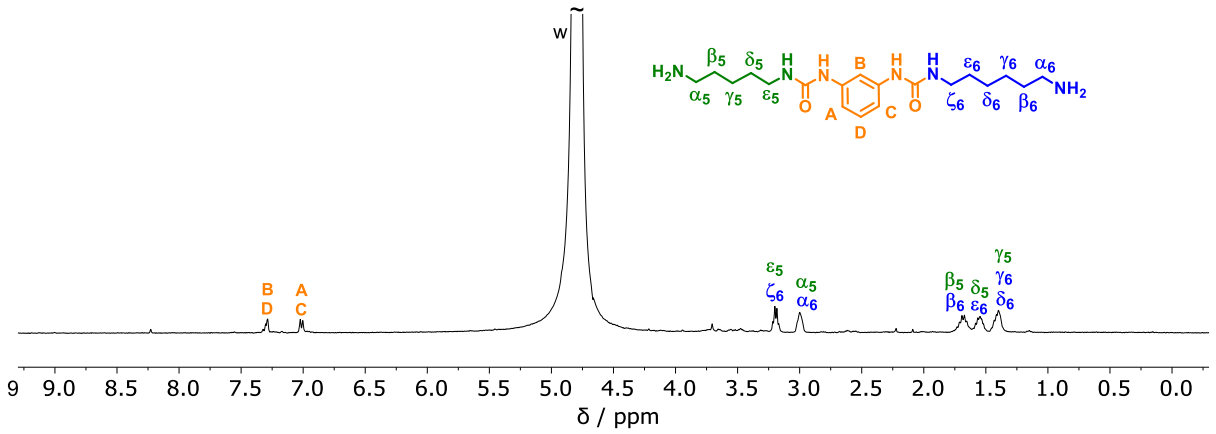


Figure S59. ^{1}H NMR spectrum (298 K, 400 MHz, D_2O) of the isolated diamino-diurea derivative **5**. w: residual water.

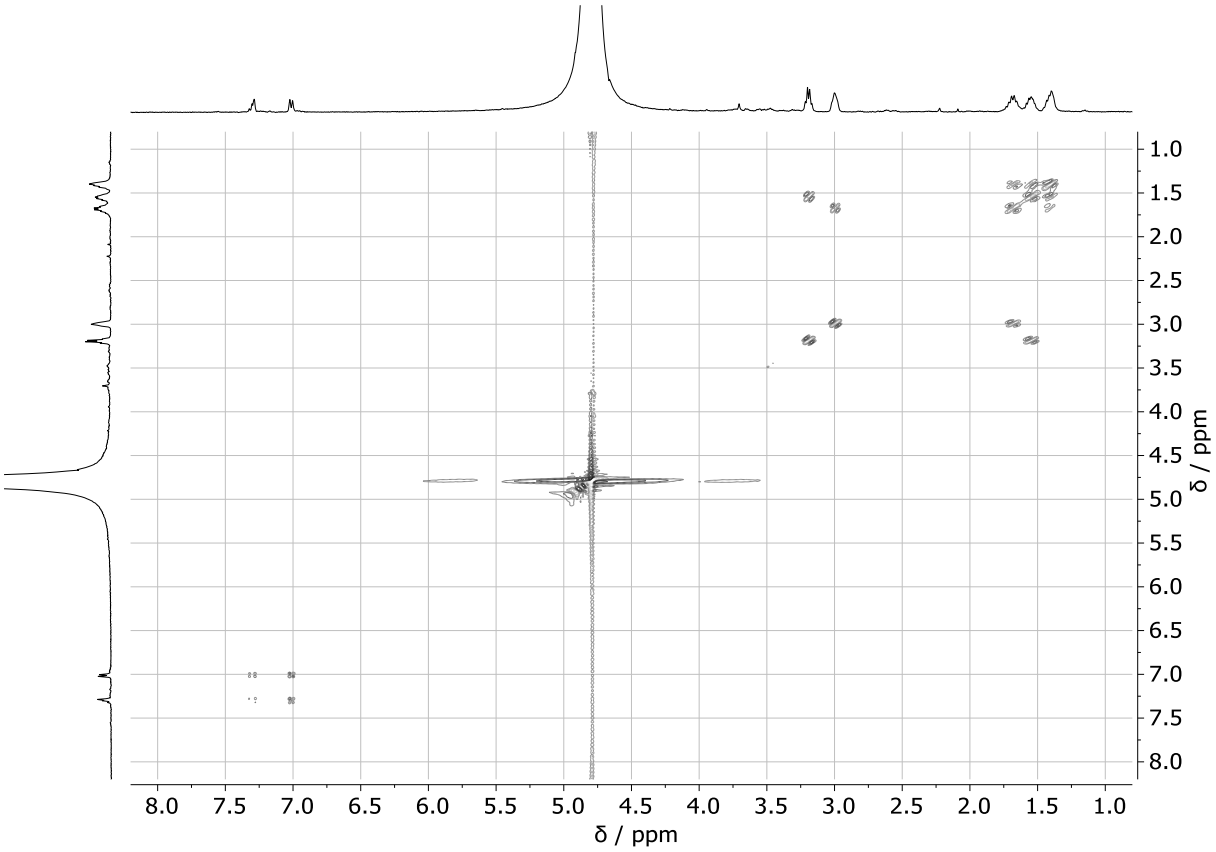


Figure S60. COSY NMR spectrum (298 K, 400 MHz, D_2O) of the isolated diamino-diurea derivative **5**.

Selective functionalization of polyamines

Monofunctionalization of a lysine derivative in the presence of **Ox3**

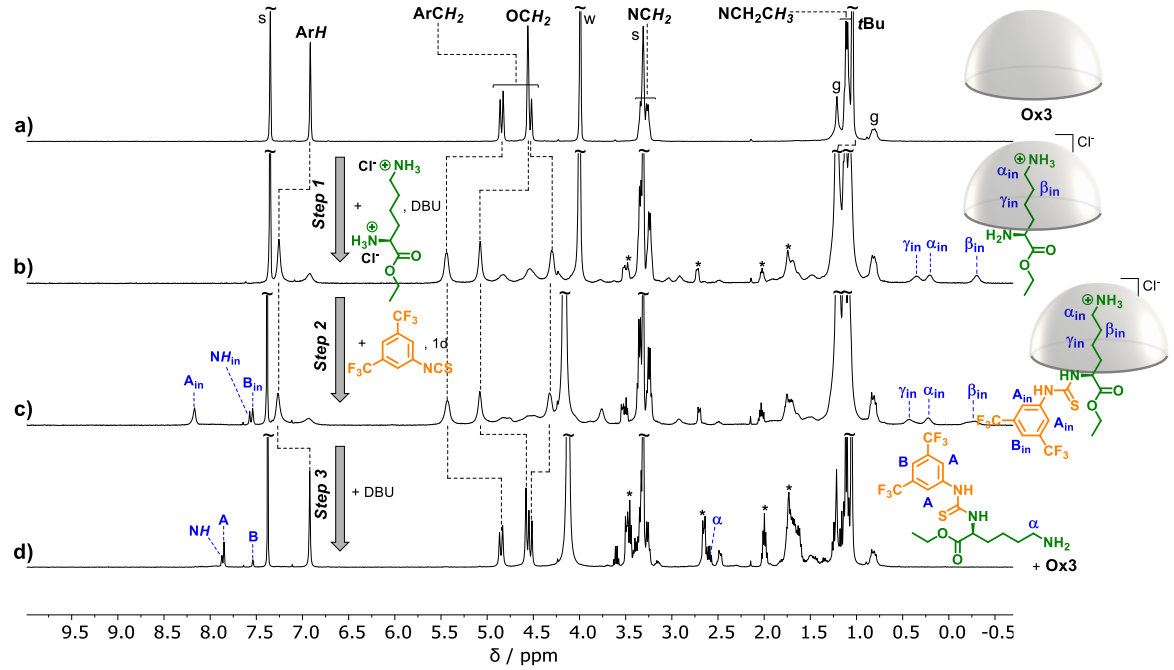


Figure S61. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a); after the successive addition of 0.8 equiv. of L-lysine ethyl ester dihydrochloride and 0.8 equiv. of DBU (b); 0.8 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 1 day) (c) and 2 equiv. of DBU (2.8 equiv. total) (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H^{+}.

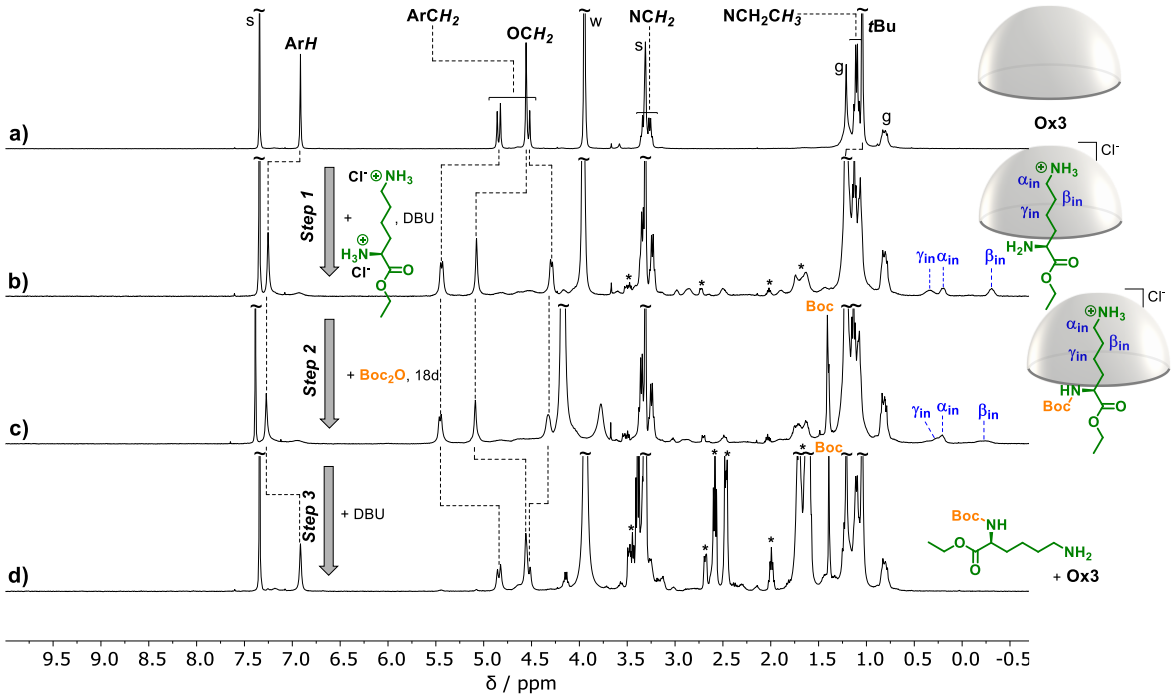


Figure S62. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3OD$ 4:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of L-lysine ethyl ester dihydrochloride and 0.9 equiv. of DBU (b); 0.9 equiv. of di-*tert*-butyl dicarbonate (after 18 days) (c) and 10 equiv. of DBU (10.9 equiv. total) (d). S: residual solvents; w: residual water; g: grease; *: DBU/DBU.H$^+$. In spectrum (d), deprotection of the monofunctionalized product is confirmed by the absence of signals in the high field region (around 0 ppm) and the recovery of the signals of the free **Ox3** receptor. Note that, except for the Boc signal, the signals of the free lysine-based product could not be attributed precisely as they are superimposed to other signals.

Difunctionalization of a triamine (tris(3-aminopropyl)amine) in the presence of **Ox3**

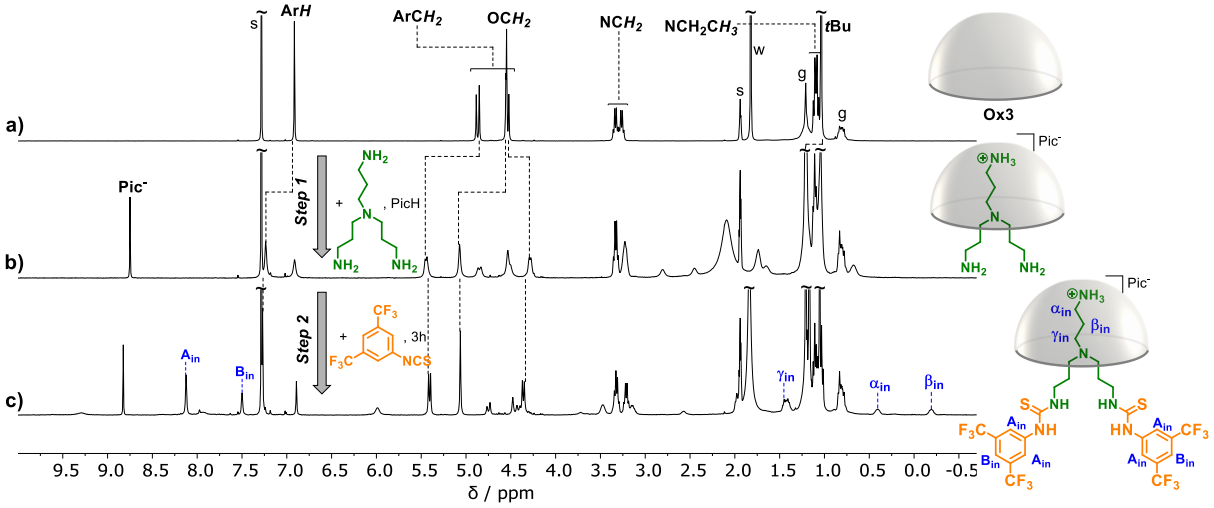


Figure S63. ^{1}H NMR spectra (298 K, 400 MHz, $CDCl_3/CD_3CN$ 9:1) of **Ox3** (3 mM) (a); after the successive addition of 0.9 equiv. of tris(3-aminopropyl)amine and 0.9 equiv. of PicH (b) and 1.8 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (after 3 hours) (c). S: residual solvents; w: residual water; g: grease. The deprotection (decomplexation) of the difunctionalized product was confirmed upon the addition of DBU by the absence of signals in the high field region (around 0 ppm) and the recovery of the signals of the free **Ox3** receptor. However, the free amino-dithiourea product was not observed probably because of the poor solubility of this highly polar compound in $CDCl_3/CD_3CN$ 9:1.