Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Carbamate complexation by urea-based receptors: studies in solution and the solid state

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Supplementary Information

General Remarks: ^{1}H NMR (300MHz) spectra were determined on a Bruker AV300 spectrometer. Chemical shifts are reported in parts per million (ppm) calibrated to the solvent peak set.

Formation of receptor:guest complexes: A 0.01M solution of each receptor was prepared in DMSO-d_6, and the ^{1}H NMR spectrum acquired.

Subsequently either,

- **a)** 1,3-diaminopropane, (1eq, 0.01M, 0.73 mg/mL, 0.8 μL/mL),
- **b)** n-butylamine, (2eq, 0.02M, 1.46 mg/mL, 2.0 μL/mL),
- **c)** 1,3-diaminopropane, (1eq, 0.01M, 0.73 mg/mL, 0.8 μL/mL) and 18-crown-6, (1eq, 0.01M, 2.64mg/mL),
- **d)** n-butylamine, (2eq, 0.02M, 1.46mg/mL, 2.0μL/mL) and 18-crown-6, (1eq, 0.01M, 2.64mg/mL), or,
- **e)** 1,4,5,6-tetrahydropyrimidine, (1eq, 0.01M, 0.84mg/mL).

were added to the solution of receptor.

Carbon dioxide was bubbled through each solution for 3 minutes. After this time, a second ^{1}H NMR spectrum was acquired. The chemical shift change for each urea NH proton was calculated accordingly. This process was repeated three times for each receptor in each case a-e.

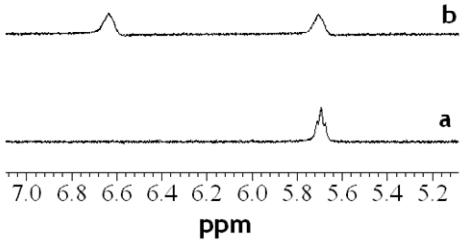

Fig. S1 Representative ^{1}H NMR spectra of a) Receptor **1**, b) Receptor **1** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

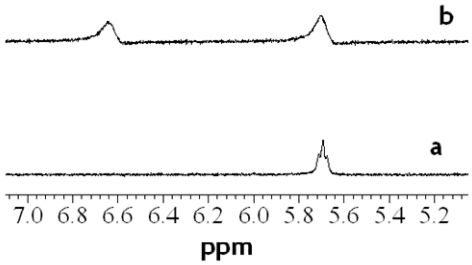

Fig. S2 Representative ^{1}H NMR spectra of a) Receptor **1**, b) Receptor **1** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

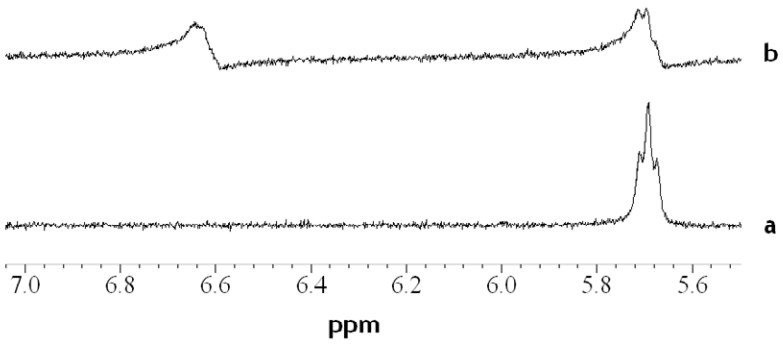

Fig. S3 Representative ^{1}H NMR spectra of a) Receptor **1**, b) Receptor **1** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

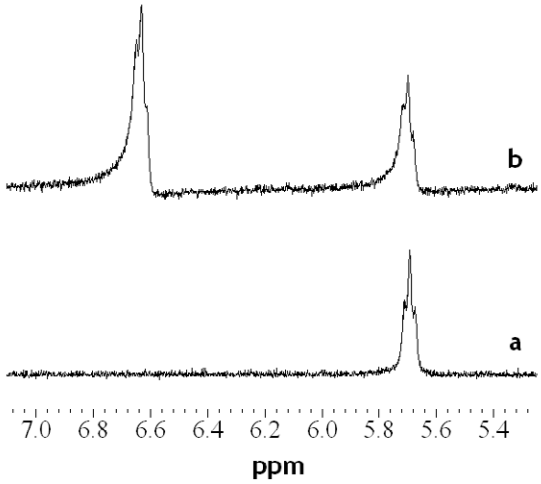

Fig. S4 Representative ^{1}H NMR spectra of a) Receptor **1**, b) Receptor **1** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

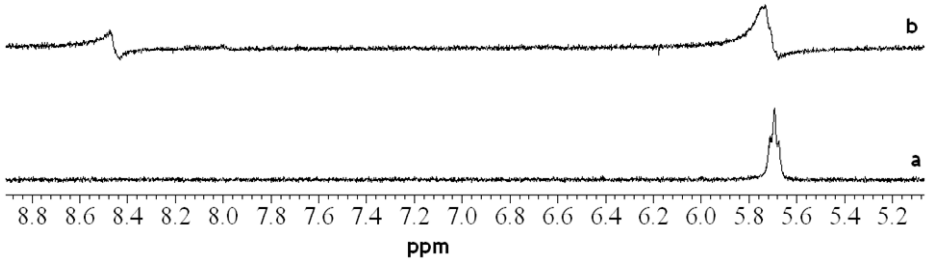

Fig. S5 Proton NMR spectra of a) Receptor **1**, b) Receptor **1** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

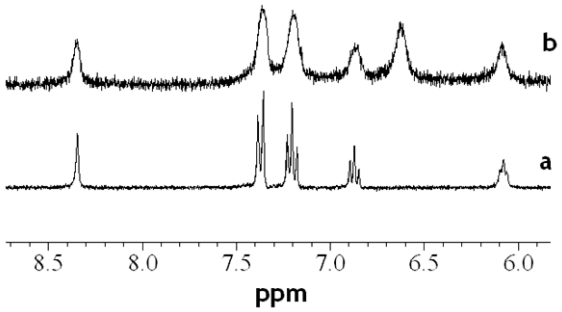

Fig. S6 Representative ^{1}H NMR spectra of a) Receptor **2**, b) Receptor **2** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

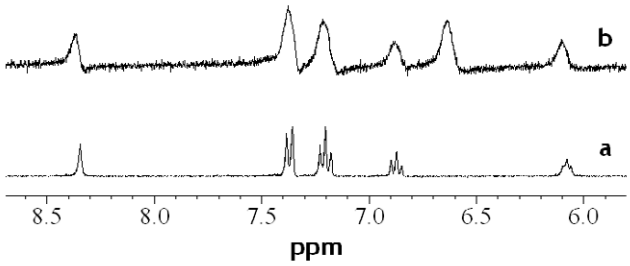

Fig. S7 Representative ^{1}H NMR spectra of a) Receptor **2**, b) Receptor **2** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

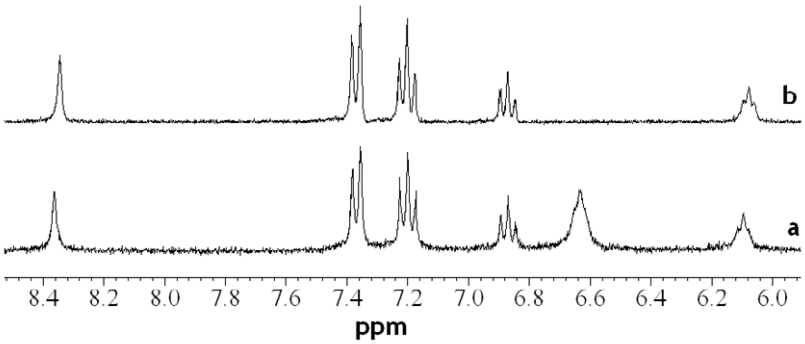

Fig. S8 Representative ^{1}H NMR spectra of a) Receptor **2**, b) Receptor **2** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

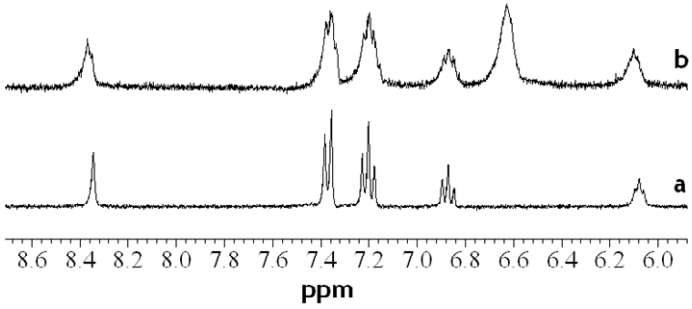

Fig. S9 Representative ^{1}H NMR spectra of a) Receptor **2**, b) Receptor **2** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

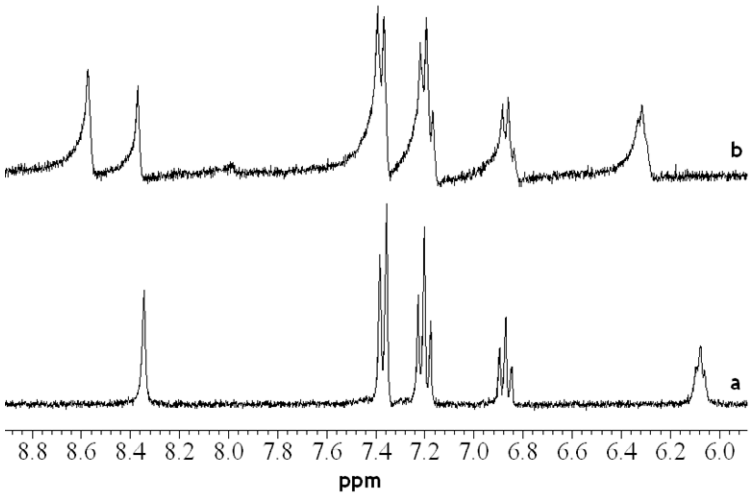

Fig. S10 Proton NMR spectra of a) Receptor **2**, b) Receptor **2** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

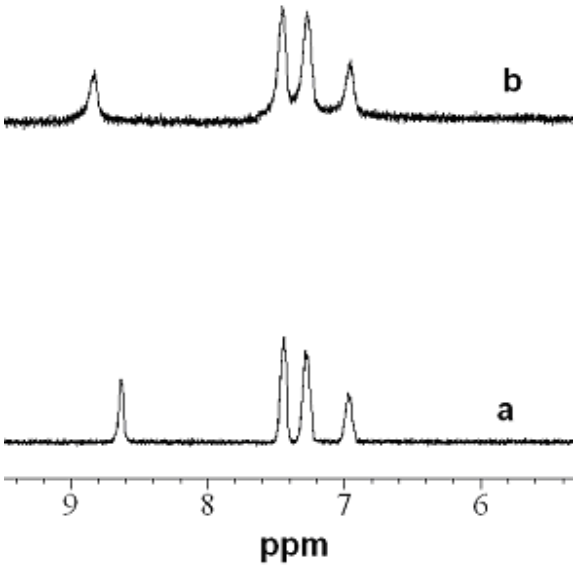

Fig. S11 Representative ^{1}H NMR spectra of a) Receptor **3**, b) Receptor **3** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

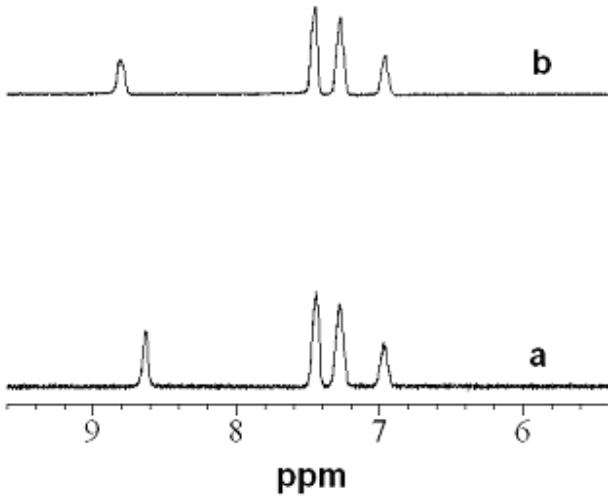

Fig. S12 Representative ^{1}H NMR spectra of a) Receptor **3**, b) Receptor **3** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

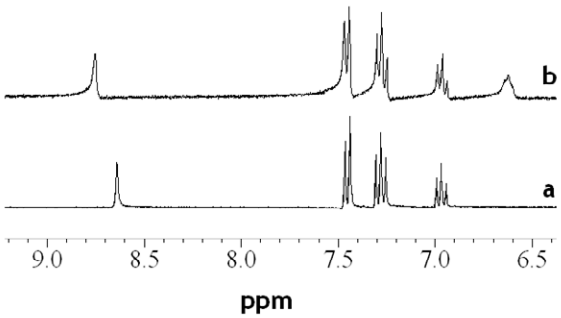

Fig. S13 Representative ^{1}H NMR spectra of a) Receptor **3**, b) Receptor **3** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

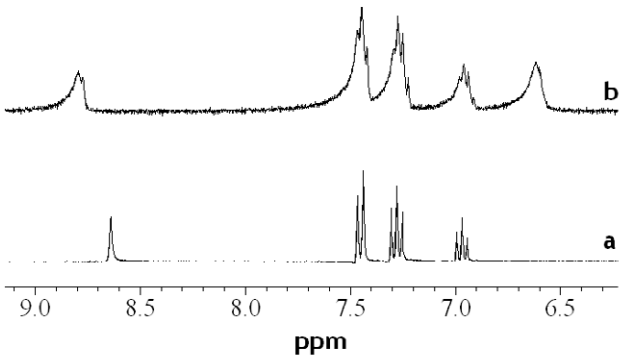

Fig. S14 Representative ^{1}H NMR spectra of a) Receptor **3**, b) Receptor **3** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

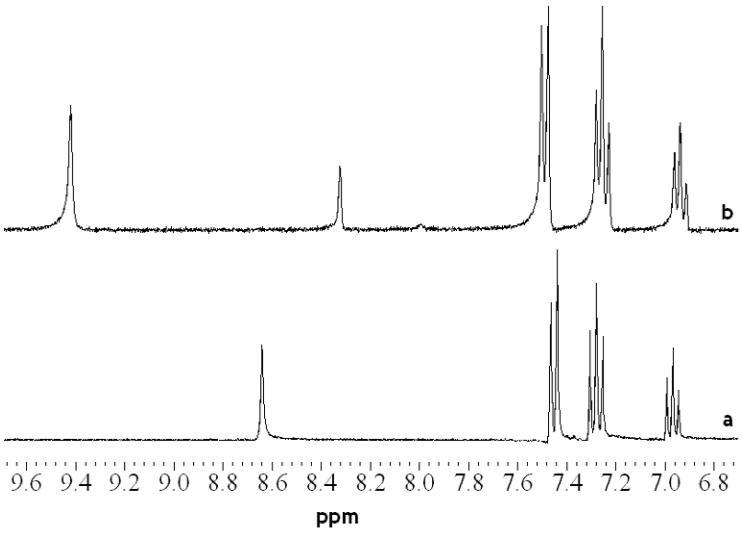

Fig. S15 Proton NMR spectra of a) Receptor **3**, b) Receptor **3** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

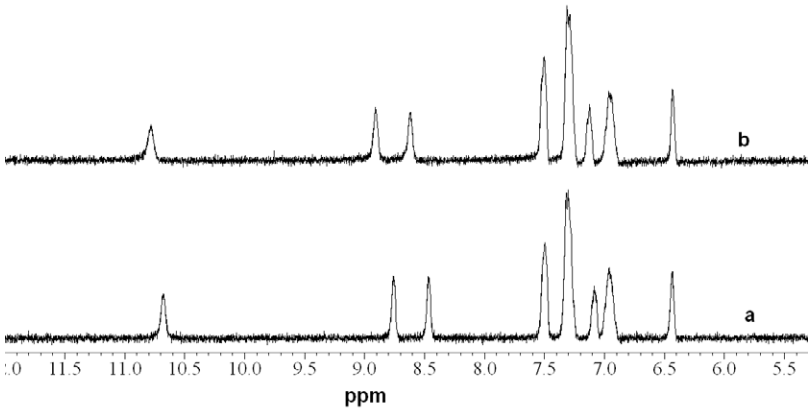

Fig. S16 Representative ^{1}H NMR spectra of a) Receptor **4**, b) Receptor **4** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

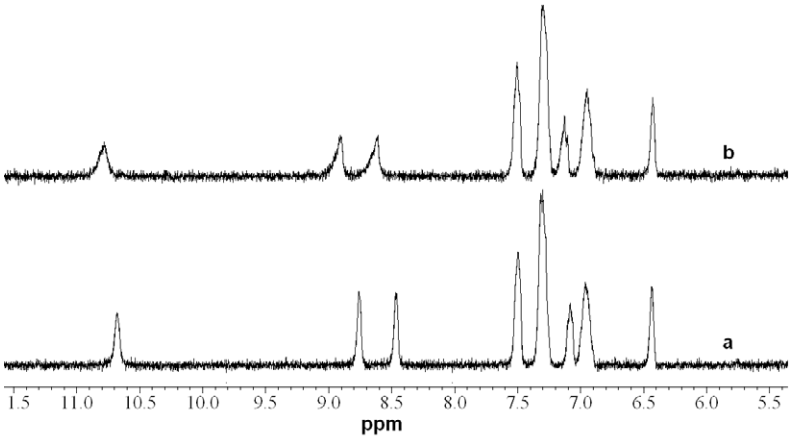

Fig. S17 Representative ^{1}H NMR spectra of a) Receptor **4**, b) Receptor **4** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

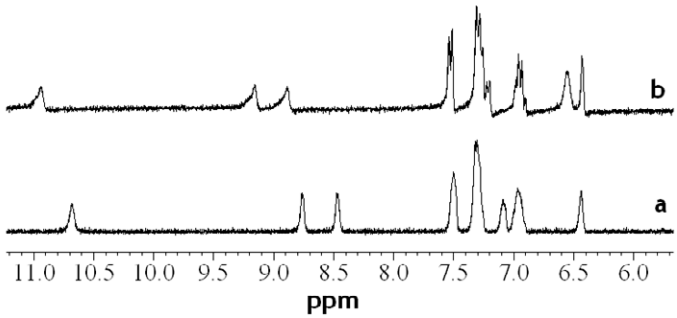

Fig. S18 Representative ^{1}H NMR spectra of a) Receptor **4**, b) Receptor **4** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

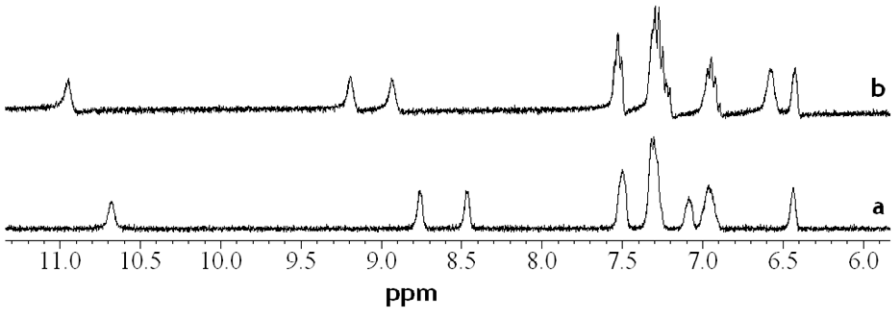

Fig. S19 Representative ^{1}H NMR spectra of a) Receptor **4**, b) Receptor **4** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

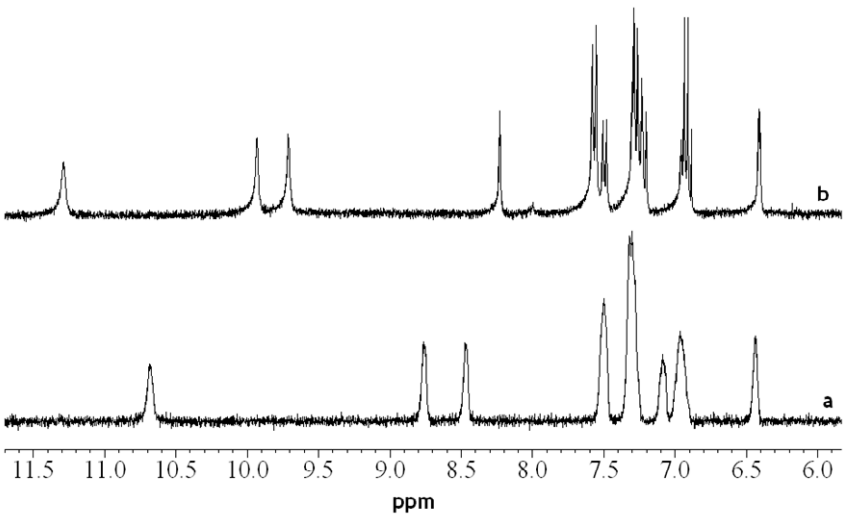

Fig. S20 Proton NMR spectra of a) Receptor **4**, b) Receptor **4** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

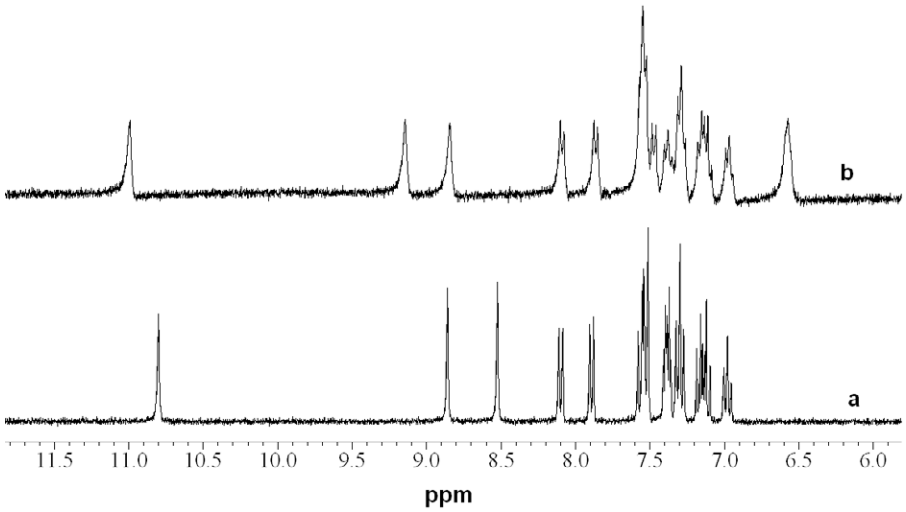

Fig. S21 Representative ^{1}H NMR spectra of a) Receptor **5**, b) Receptor **5** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

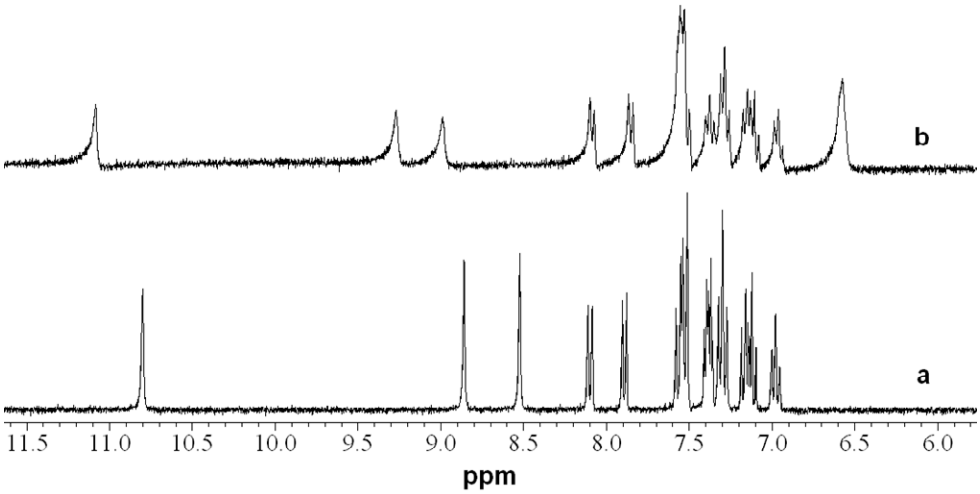

Fig. S22 Representative ^{1}H NMR spectra of a) Receptor **5**, b) Receptor **5** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

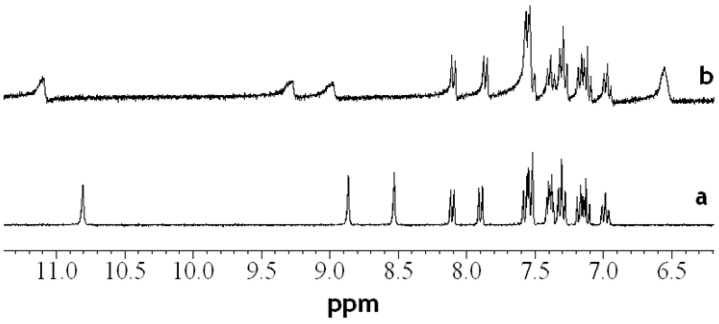

Fig. S23 Representative ^{1}H NMR spectra of a) Receptor **5**, b) Receptor **5** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

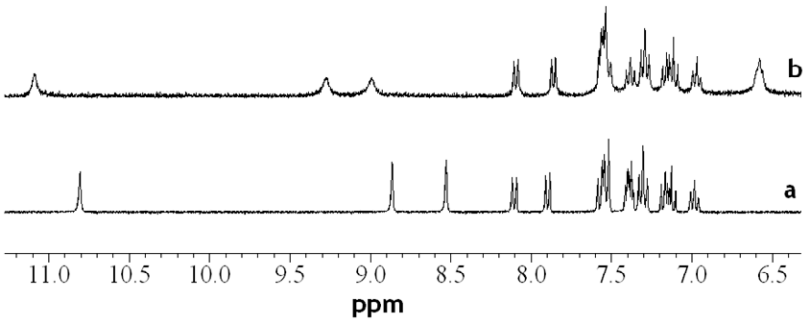

Fig. S24 Representative ^{1}H NMR spectra of a) Receptor **5**, b) Receptor **5** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

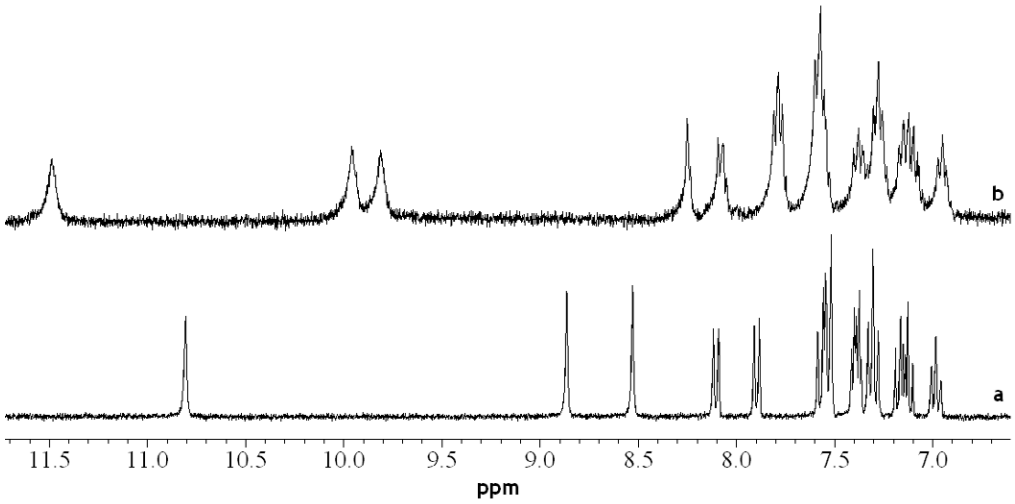

Fig. S25 Proton NMR spectra of a) Receptor **5**, b) Receptor **5** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

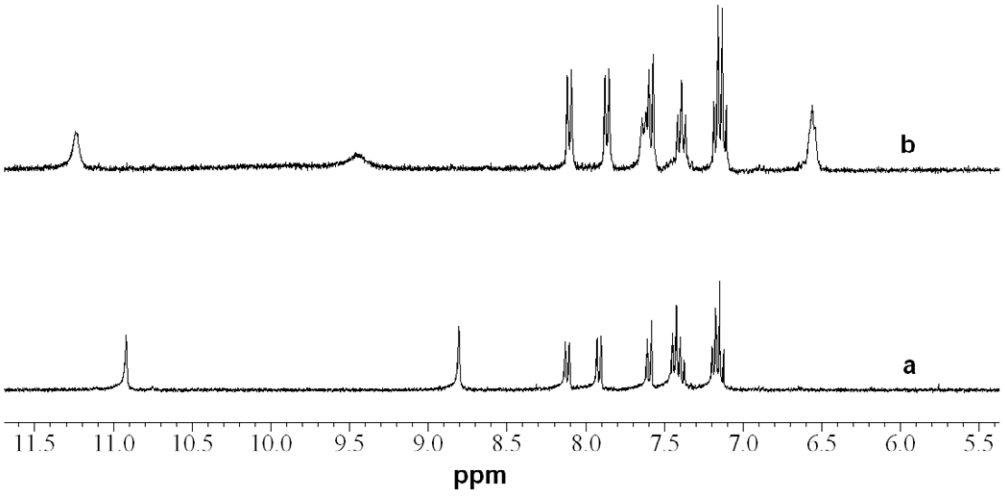

Fig. S26 Representative ^{1}H NMR spectra of a) Receptor **6**, b) Receptor **6** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

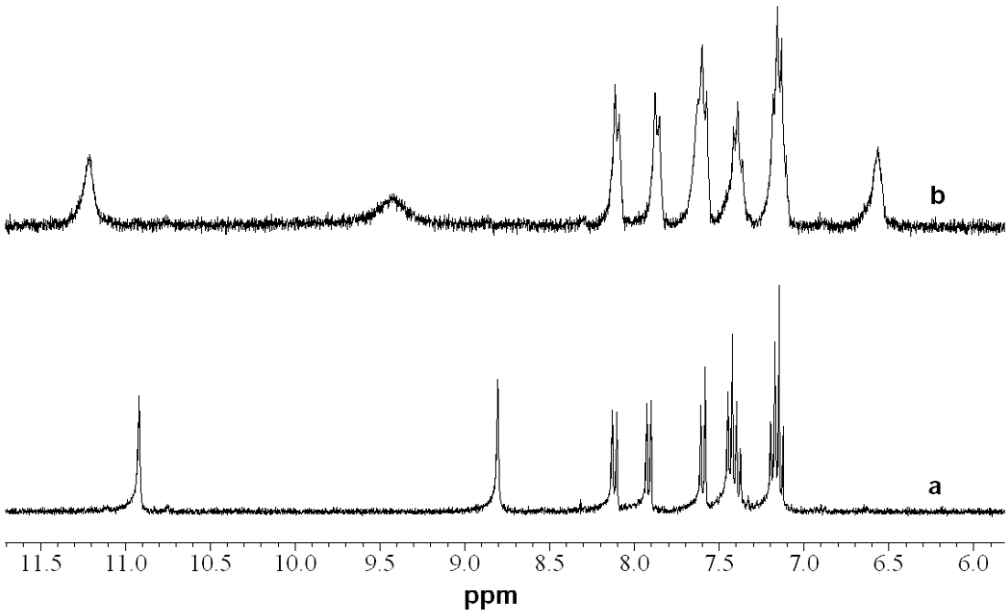

Fig. S27 Representative ^{1}H NMR spectra of a) Receptor **6**, b) Receptor **6** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

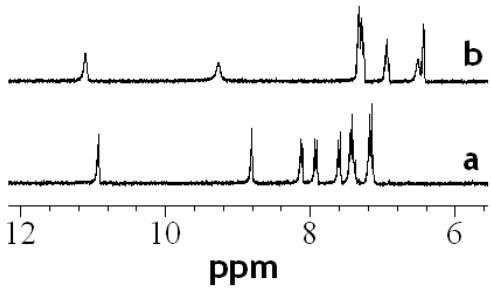

Fig. S28 Representative ^{1}H NMR spectra of a) Receptor **6**, b) Receptor **6** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

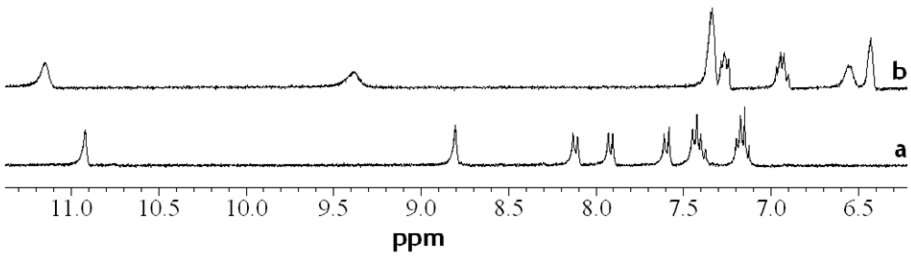

Fig. S29 Representative ^{1}H NMR spectra of a) Receptor **6**, b) Receptor **6** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

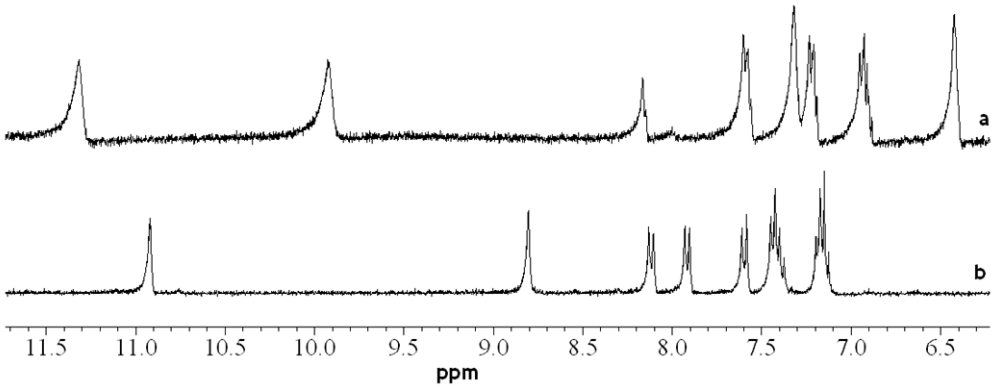

Fig. S30 Proton NMR spectra of a) Receptor **6**, b) Receptor **6** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

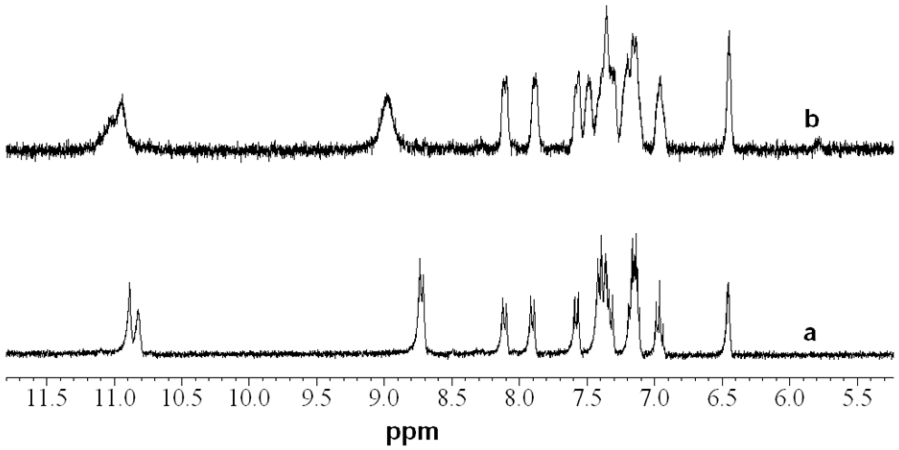

Fig. S31 Representative ^{1}H NMR spectra of a) Receptor **7**, b) Receptor **7** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

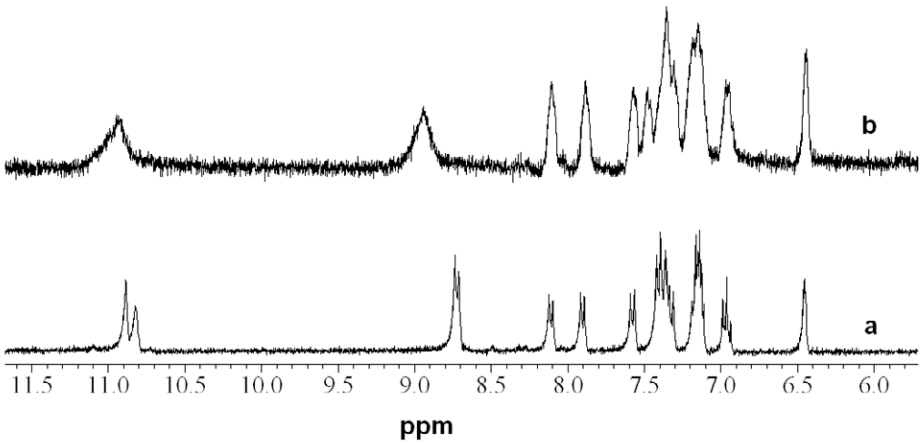

Fig. S32 Representative ^{1}H NMR spectra of a) Receptor **7**, b) Receptor **7** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

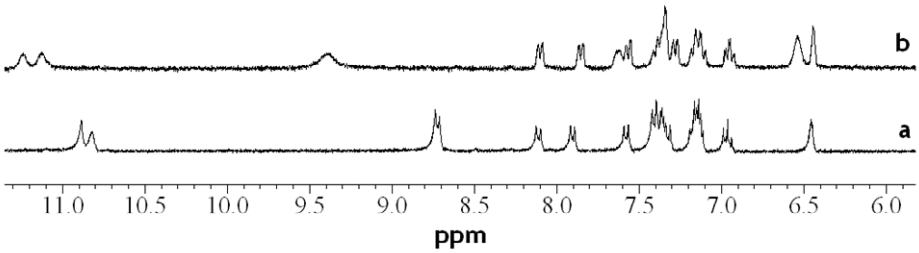

Fig. S33 Representative ^{1}H NMR spectra of a) Receptor **7**, b) Receptor **7** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

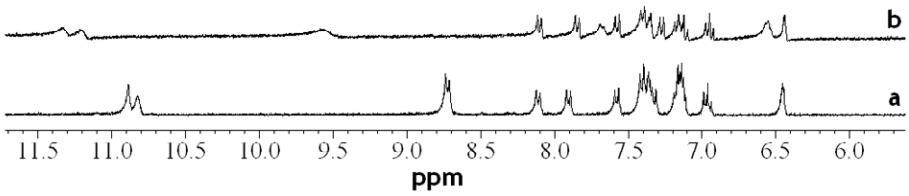

Fig. S34 Representative ^{1}H NMR spectra of a) Receptor **7**, b) Receptor **7** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

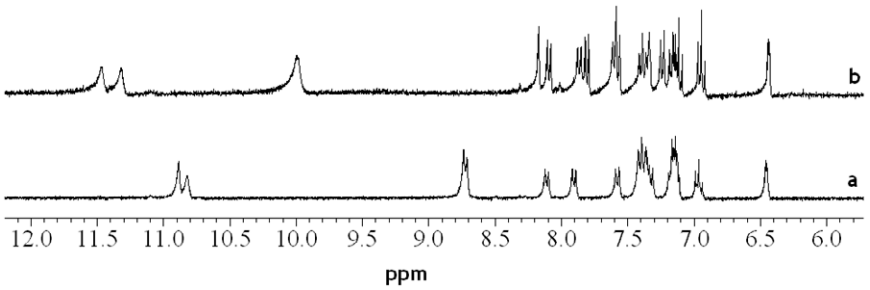

Fig. S35 Proton NMR spectra of a) Receptor **7**, b) Receptor **7** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

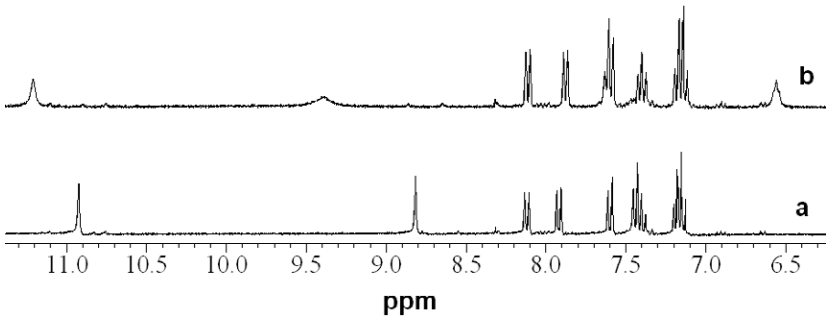

Fig. S36 Representative ^{1}H NMR spectra of a) Receptor **8**, b) Receptor **8** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

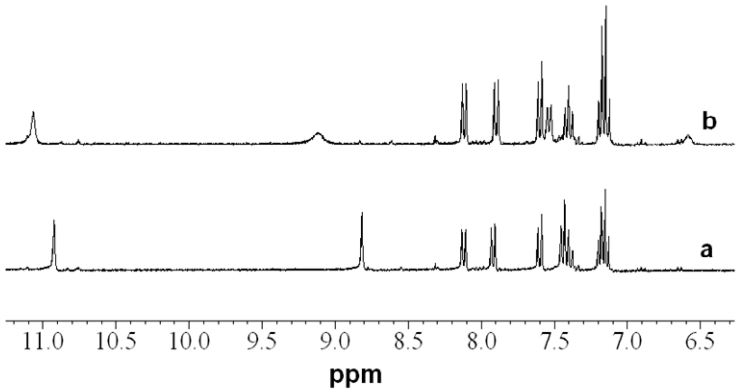

Fig. S37 Representative ^{1}H NMR spectra of a) Receptor **8**, b) Receptor **8** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

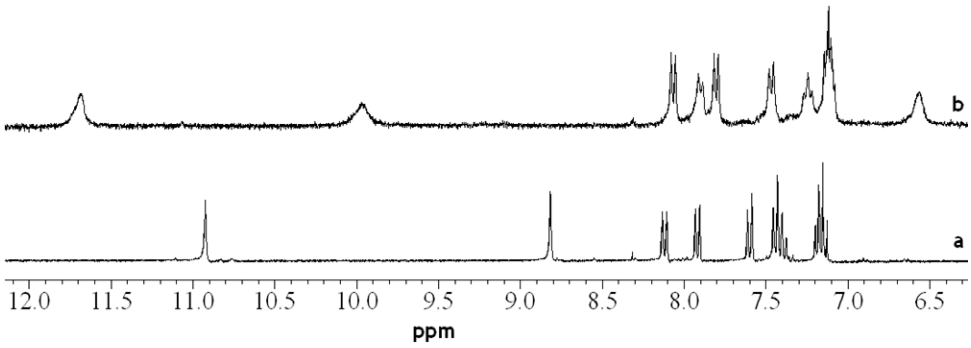

Fig. S38 Representative ^{1}H NMR spectra of a) Receptor **8**, b) Receptor **8** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

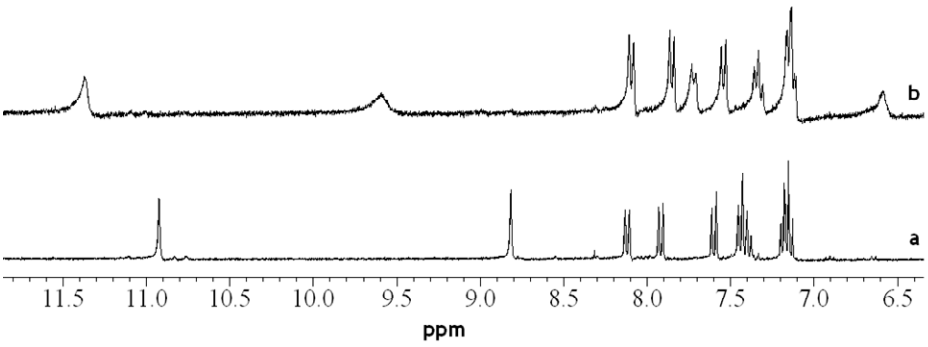

Fig. S39 Representative ^{1}H NMR spectra of a) Receptor **8**, b) Receptor **8** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

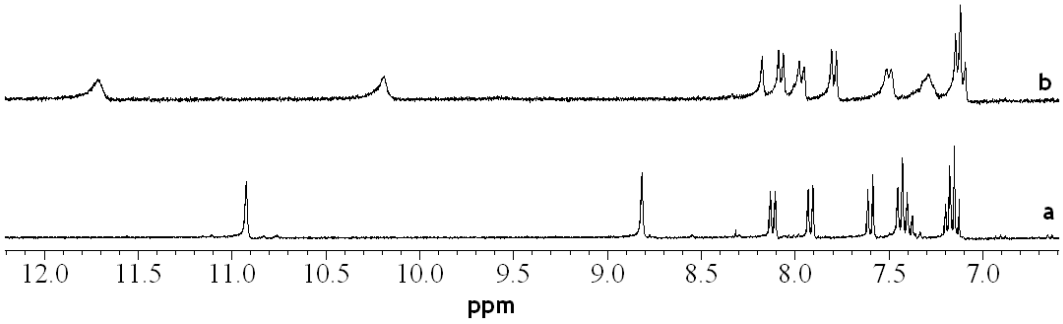

Fig. S40 Proton NMR spectra of a) Receptor **8**, b) Receptor **8** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

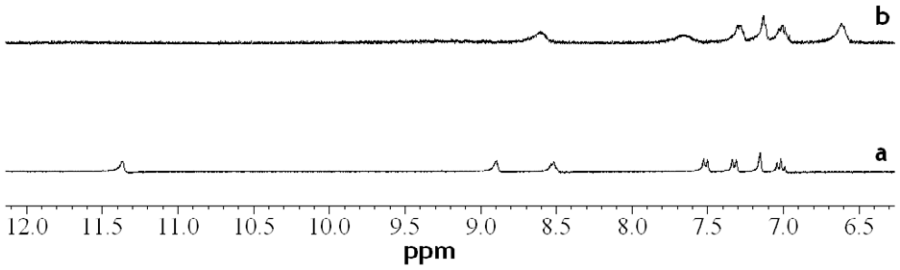

Fig. S41 Representative ^{1}H NMR spectra of a) Receptor **9**, b) Receptor **9** + 2eq. n-butylamine bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

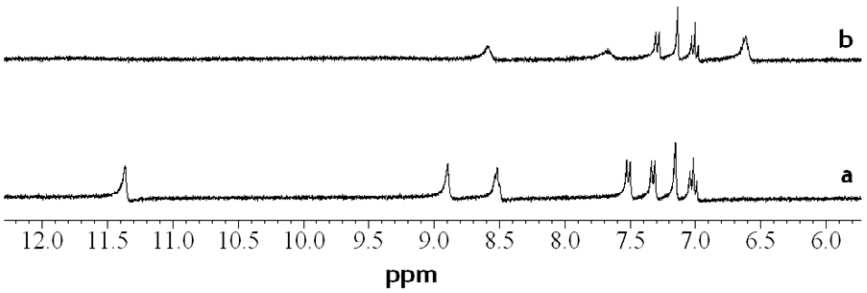

Fig. S42 Representative ^{1}H NMR spectra of a) Receptor **9**, b) Receptor **9** + 1eq. 1,3-diaminopropane bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

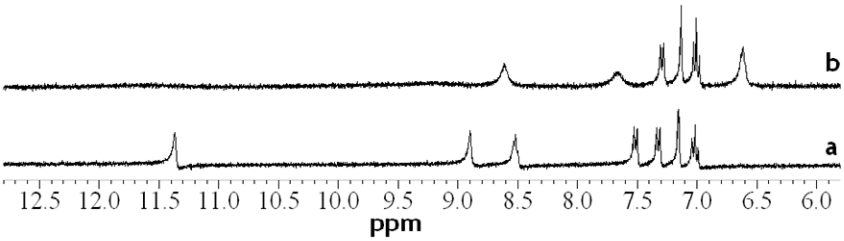

Fig. S43 Representative ^{1}H NMR spectra of a) Receptor **9**, b) Receptor **9** + 2eq. n-butylamine, and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes.
Spectra in DMSO-d_6.

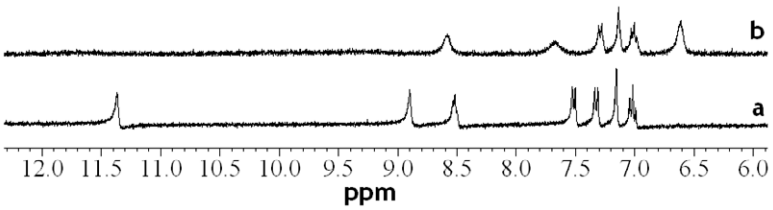

Fig. S44 Representative ^{1}H NMR spectra of a) Receptor **9**, b) Receptor **9** + 1eq. 1,3-diaminopropane and 1eq. 18-crown-6, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

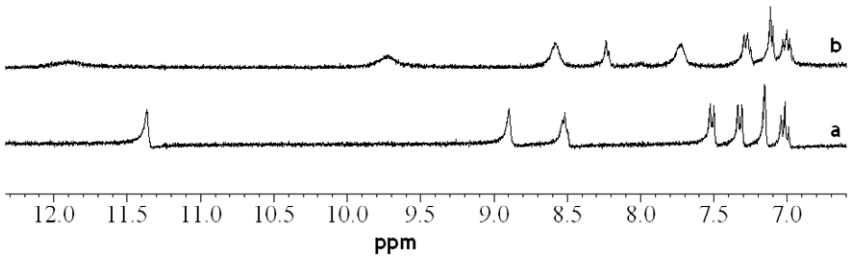

Fig. S45 Proton NMR spectra of a) Receptor **9**, b) Receptor **9** + 1eq. 1,4,5,6-tetrahydropyrimidine, bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

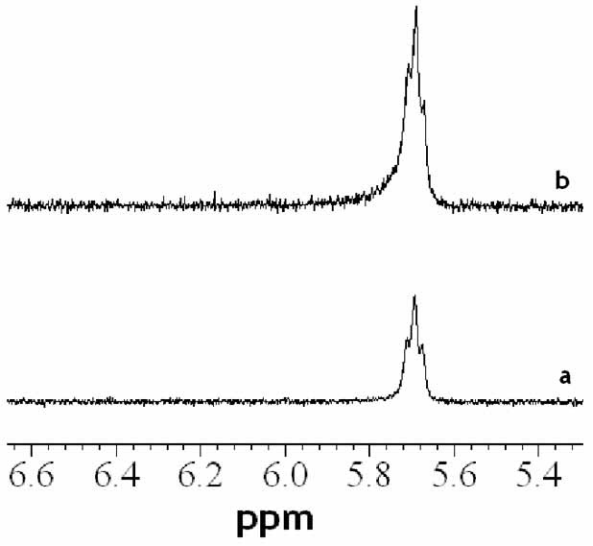

Fig. S46 Proton NMR spectra of a) Receptor **1**, b) Receptor **1** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

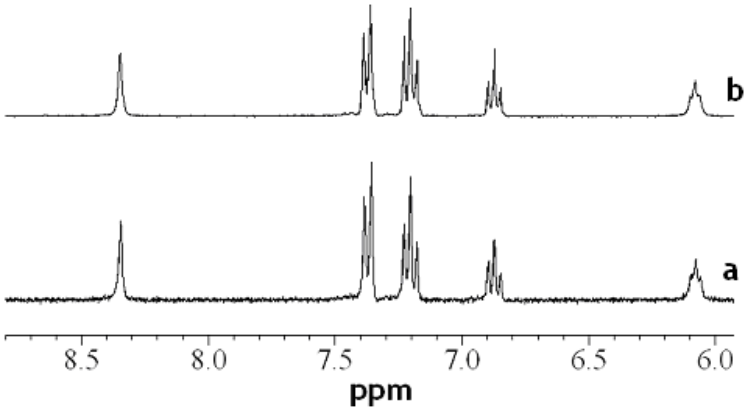

Fig. S47 Proton NMR spectra of a) Receptor **2**, b) Receptor **2** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

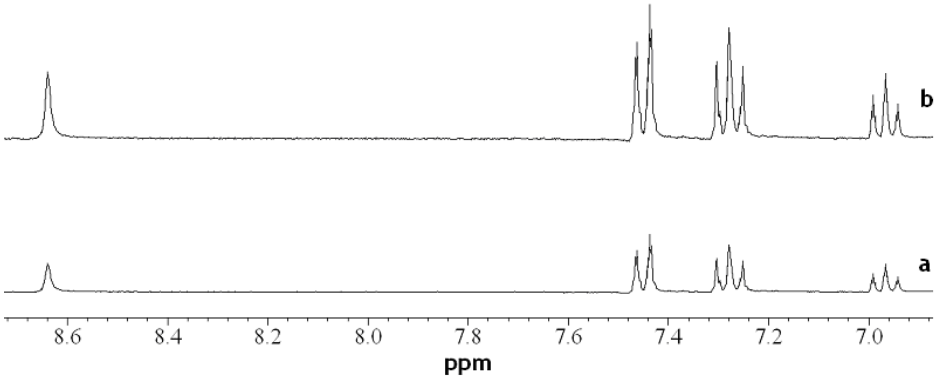

Fig. S48 Proton NMR spectra of a) Receptor **3**, b) Receptor **3** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

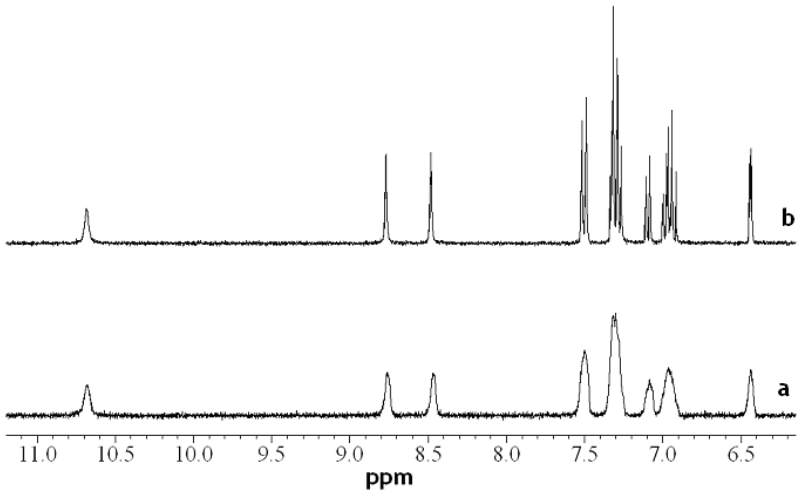

Fig. S49 Proton NMR spectra of a) Receptor **4**, b) Receptor **4** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

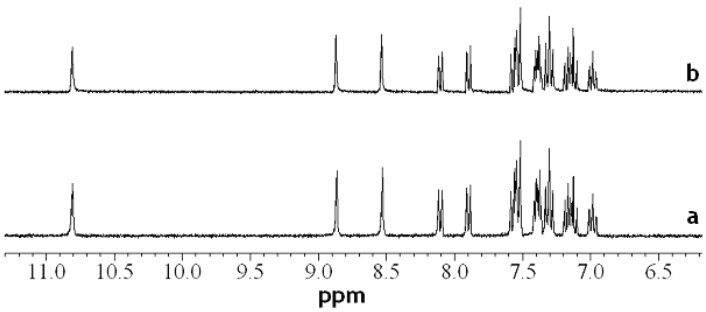

Fig. S50 Proton NMR spectra of a) Receptor **5**, b) Receptor **5** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

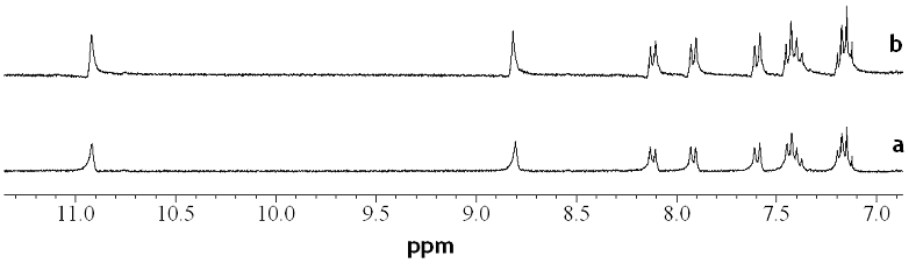

Fig. S51 Proton NMR spectra of a) Receptor **6**, b) Receptor **6** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

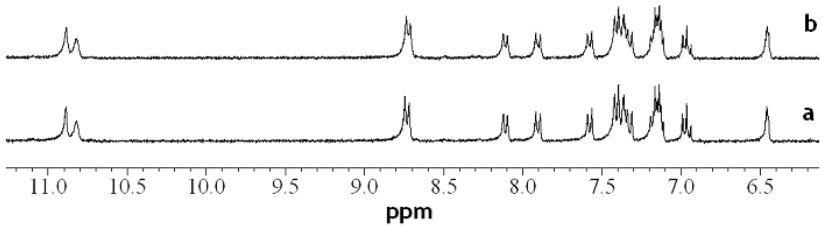

Fig. S52 Proton NMR spectra of a) Receptor **7**, b) Receptor **7** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

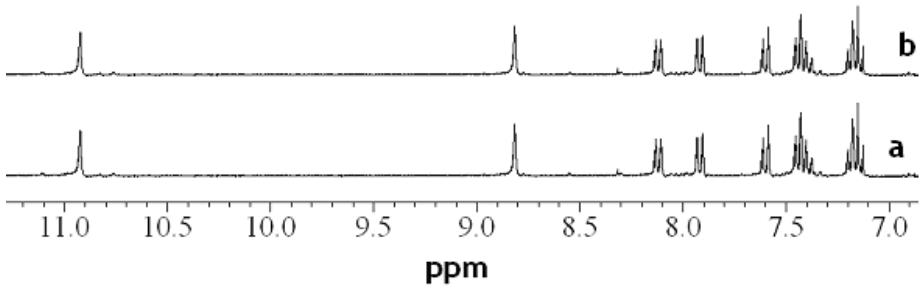

Fig. S53 Proton NMR spectra of a) Receptor **8**, b) Receptor **8** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

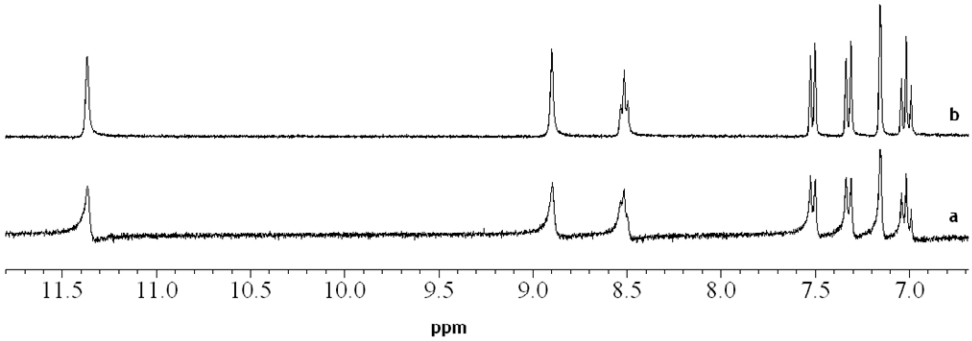

Fig. S54 Proton NMR spectra of a) Receptor **9**, b) Receptor **9** bubbled with CO_2 for 3 minutes. Spectra in DMSO-d_6.

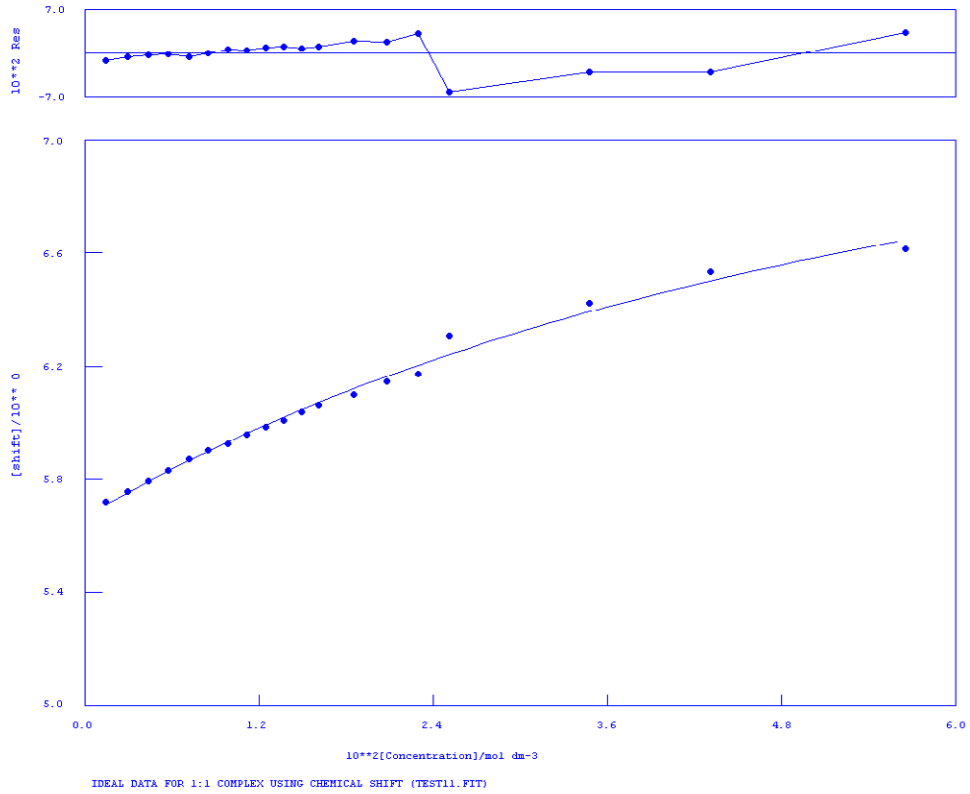

Fig. S55 Proton NMR titration of compound **1** vs TBAOBz in 0.5%H_2O:DMSO-d_6. (Ideal data for 1:1 complex). $K_a < 20M^{-1}$.

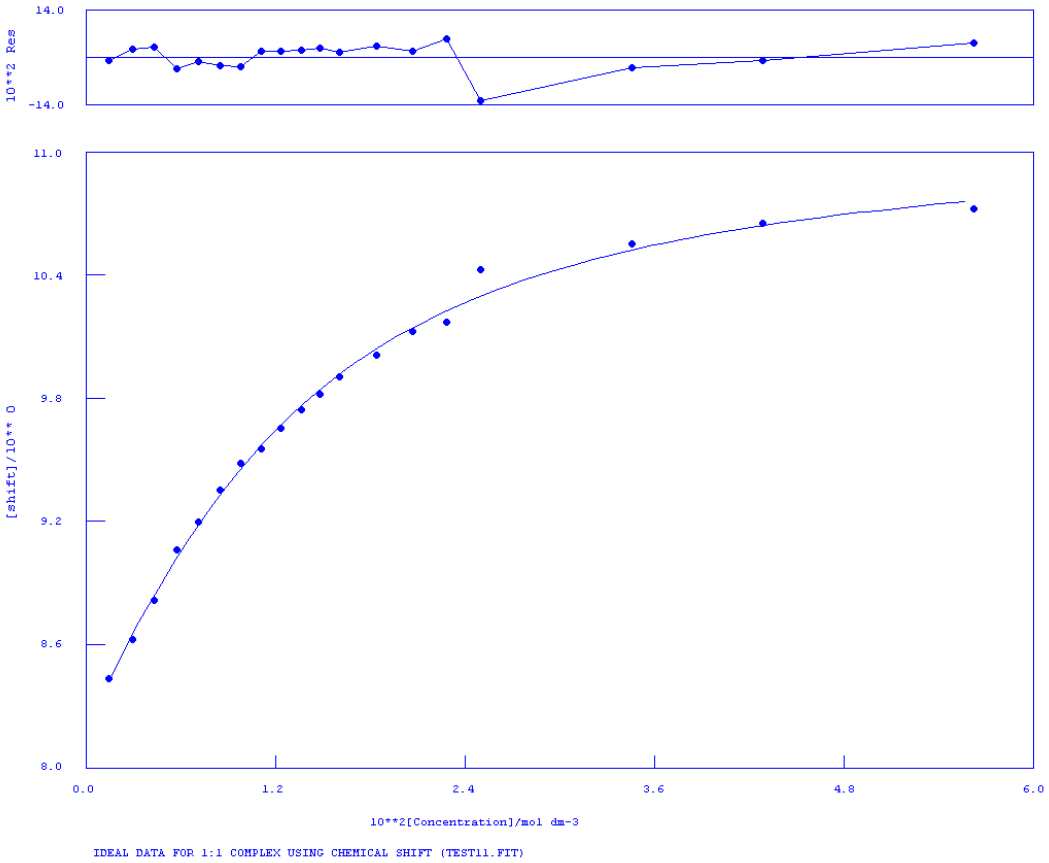

Fig. S56 Proton NMR titration of compound **2** vs TBAOBz in 0.5%H_2O:DMSO-d_6. (Ideal data for 1:1 complex). $K_a = 140M^{-1}$ (± 9%).

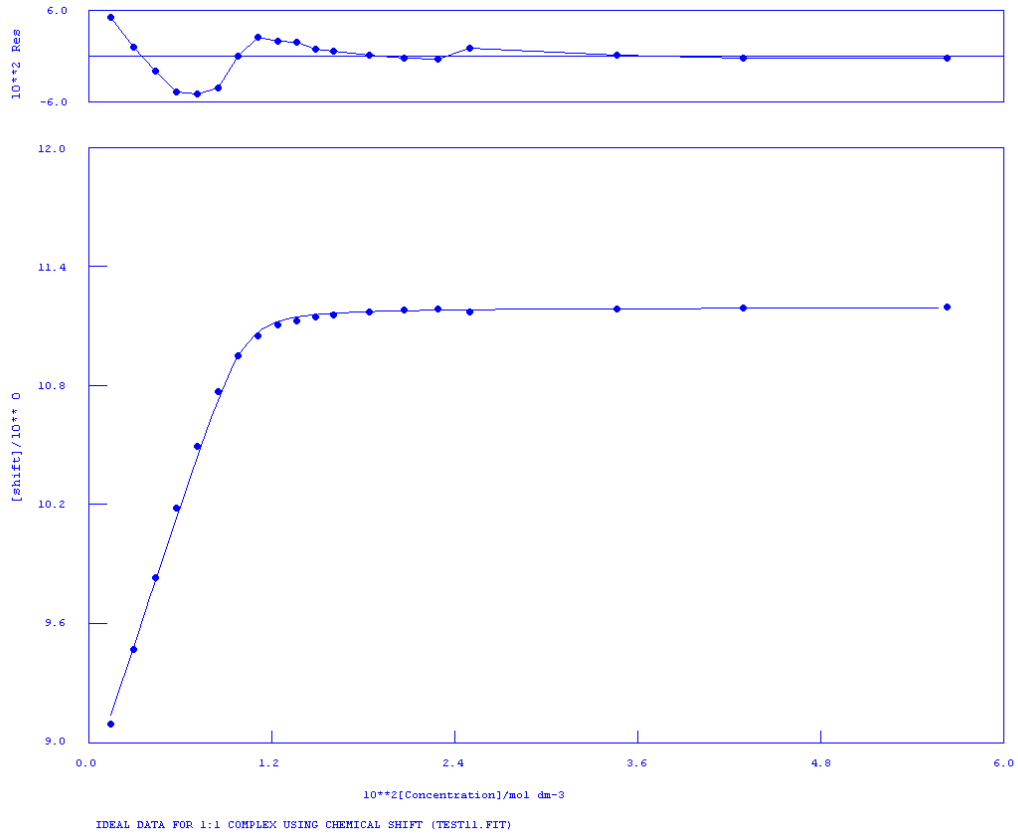

Fig. S57 Proton NMR titration of compound **4** vs TBAOBz in 0.5%H_2O:DMSO-d_6. (Ideal data for 1:1 complex). $K_a > 10{,}000M^{-1}$.

Table S1. Crystal data and structure refinement details.

Identification code	**2008sot1042**	
Empirical formula	$C_{87}H_{135}N_{16}O_{22.50}S_{0.50}$ $2(C_{27}H_{32}N_6O_3)$, $2(C_{12}H_{24}O_6)$, $2(C_4H_{10}N_2O_2)$, $0.5(C_2H_6OS)$	
Formula weight	1781.14	
Temperature	293(2) K	
Wavelength	0.68890 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.626(7) Å	α = 84.204(10)°
	b = 14.165(9) Å	β = 77.246(8)°
	c = 27.564(17) Å	γ = 72.121(9)°
Volume	4573(5) Å^3	
Z	2	
Density (calculated)	1.294 Mg / m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1914	
Crystal	Colourless block	
Crystal size	0.05 × 0.03 × 0.02 mm^3	
θ range for data collection	2.90 – 24.21°	
Index ranges	$-13 \le h \le 14$, $-14 \le k \le 16$, $-30 \le l \le 32$	
Reflections collected	34055	
Independent reflections	14794 [R_{int} = 0.0680]	
Completeness to θ = 24.21°	91.7 %	
Max. and min. transmission	0.9979 and 0.9948	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14794 / 0 / 1151	
Goodness-of-fit on F^2	1.052	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0649, $wR2$ = 0.1813	
R indices (all data)	$R1$ = 0.0854, $wR2$ = 0.1936	
Largest diff. peak and hole	0.283 and –0.484 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit*). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: Sheldrick, G. M. SADABS - Bruker Nonius area detector scaling and absorption correction - V2.10 S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model.

Table S2. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
O1	1760(2)	2700(2)	3245(1)	41(1)	1
O2	6919(2)	4379(2)	2280(1)	38(1)	1
O3	5950(2)	1405(2)	−52(1)	40(1)	1
N1	1216(2)	2676(2)	4084(1)	33(1)	1
N2	3377(2)	3623(2)	3276(1)	26(1)	1
N3	5104(2)	4325(2)	2574(1)	28(1)	1
N4	5872(2)	4127(2)	1752(1)	31(1)	1
N5	5894(2)	2940(2)	934(1)	29(1)	1
N6	4630(2)	1765(2)	651(1)	32(1)	1
C1	1467(3)	−563(3)	4454(1)	45(1)	1
C2	1435(3)	415(2)	4160(1)	40(1)	1
C3	441(3)	1263(2)	4393(1)	33(1)	1
C4	305(3)	2239(2)	4099(1)	35(1)	1
C5	1878(2)	2872(2)	3658(1)	28(1)	1
C6	2760(2)	3316(2)	3705(1)	27(1)	1
C7	3165(3)	3450(2)	4105(1)	29(1)	1
C8	4086(3)	3852(2)	3920(1)	27(1)	1
C9	4841(3)	4128(2)	4140(1)	34(1)	1
C10	5671(3)	4474(2)	3838(1)	36(1)	1
C11	5785(3)	4549(2)	3315(1)	33(1)	1
C12	5058(2)	4287(2)	3089(1)	27(1)	1
C13	4198(2)	3947(2)	3398(1)	26(1)	1
C14	6045(3)	4280(2)	2211(1)	28(1)	1
C15	6695(3)	4025(2)	1311(1)	30(1)	1
C16	7555(3)	4476(2)	1211(1)	32(1)	1
C17	8346(3)	4343(2)	760(1)	39(1)	1
C18	8301(3)	3779(3)	396(1)	40(1)	1
C19	7435(3)	3320(2)	480(1)	34(1)	1
C20	6646(2)	3455(2)	936(1)	30(1)	1
C21	7112(3)	2708(2)	203(1)	37(1)	1
C22	6179(3)	2485(2)	483(1)	31(1)	1
C23	5574(3)	1853(2)	343(1)	32(1)	1
C24	3988(3)	1161(2)	531(1)	38(1)	1
C25	3234(3)	1677(2)	163(1)	37(1)	1
C26	2365(3)	2645(2)	347(1)	42(1)	1
C27	1615(3)	3144(3)	−19(1)	53(1)	1
O4	8760(2)	6683(2)	4956(1)	37(1)	1
O5	8325(2)	11633(2)	2912(1)	36(1)	1
O6	13503(2)	7488(2)	1869(1)	40(1)	1
N7	10165(2)	6706(2)	4298(1)	30(1)	1
N8	9002(2)	8769(2)	4115(1)	27(1)	1
N9	9251(2)	10463(2)	3431(1)	30(1)	1
N10	10080(2)	10574(2)	2613(1)	29(1)	1
N11	11861(2)	9304(2)	1883(1)	26(1)	1
N12	14129(2)	7652(2)	1040(1)	34(1)	1
C28	13152(4)	6366(3)	4956(2)	61(1)	1
C29	12440(3)	6328(3)	4584(1)	44(1)	1
C30	11601(3)	5753(2)	4782(1)	34(1)	1
C31	10868(3)	5720(2)	4417(1)	32(1)	1
C32	9181(3)	7130(2)	4591(1)	29(1)	1
C33	8581(3)	8180(2)	4488(1)	29(1)	1
C34	7570(3)	8739(2)	4754(1)	33(1)	1

C35	7352(3)	9718(2)	4546(1)	30(1)	1
C36	6490(3)	10609(2)	4657(1)	36(1)	1
C37	6571(3)	11439(2)	4367(1)	37(1)	1
C38	7477(3)	11417(2)	3963(1)	34(1)	1
C39	8336(3)	10554(2)	3840(1)	28(1)	1
C40	8272(2)	9709(2)	4144(1)	27(1)	1
C41	9151(3)	10952(2)	2973(1)	28(1)	1
C42	10179(2)	10808(2)	2097(1)	27(1)	1
C43	9487(3)	11599(2)	1882(1)	30(1)	1
C44	9665(3)	11764(2)	1362(1)	36(1)	1
C45	10529(3)	11146(2)	1049(1)	37(1)	1
C46	11255(3)	10324(2)	1254(1)	30(1)	1
C47	11071(3)	10162(2)	1777(1)	28(1)	1
C48	12197(3)	9518(2)	1056(1)	32(1)	1
C49	12538(3)	8910(2)	1445(1)	29(1)	1
C50	13427(2)	7959(2)	1469(1)	30(1)	1
C51	15025(3)	6714(2)	994(1)	35(1)	1
C52	14814(3)	5992(2)	686(1)	37(1)	1
C53	13835(3)	5595(2)	925(1)	41(1)	1
C54	13651(3)	4878(3)	602(1)	46(1)	1
O7	3519(2)	3727(2)	2221(1)	32(1)	1
O8	3932(2)	2871(2)	1530(1)	34(1)	1
N14	4973(2)	−357(2)	2488(1)	32(1)	1
C55	3443(2)	3051(2)	1974(1)	27(1)	1
N13	2771(2)	2484(2)	2211(1)	28(1)	1
C57	2637(2)	1661(2)	1989(1)	30(1)	1
C58	3659(3)	742(2)	1968(1)	29(1)	1
C59	3808(3)	313(2)	2483(1)	34(1)	1
O9	11643(2)	8884(1)	2900(1)	32(1)	1
O10	11036(2)	7943(2)	3537(1)	33(1)	1
N16	9736(2)	6091(2)	2485(1)	31(1)	1
C60	11570(2)	8055(2)	3102(1)	28(1)	1
N15	12132(2)	7235(2)	2831(1)	30(1)	1
C62	12200(2)	6236(2)	3017(1)	30(1)	1
C63	11127(3)	5961(2)	3020(1)	32(1)	1
C64	10937(3)	5965(2)	2500(1)	37(1)	1
O11	26(2)	5260(2)	1521(1)	39(1)	1
O12	−173(2)	4140(2)	2463(1)	40(1)	1
O13	−1594(2)	5147(2)	3304(1)	38(1)	1
O14	−1772(2)	7183(2)	3347(1)	35(1)	1
O15	−1356(2)	8241(2)	2433(1)	35(1)	1
O16	37(2)	7220(2)	1575(1)	41(1)	1
C65	630(3)	4241(2)	1594(1)	45(1)	1
C66	−63(3)	3757(2)	1988(1)	42(1)	1
C67	−812(3)	3671(2)	2846(1)	43(1)	1
C68	−962(3)	4130(2)	3326(1)	44(1)	1
C69	−1744(3)	5628(3)	3754(1)	40(1)	1
C70	−2430(3)	6677(3)	3705(1)	41(1)	1
C71	−2369(3)	8192(2)	3266(1)	36(1)	1
C72	−1604(3)	8667(2)	2905(1)	36(1)	1
C73	−547(3)	8609(2)	2087(1)	38(1)	1
C74	−433(3)	8274(2)	1582(1)	40(1)	1
C75	72(3)	6817(3)	1120(1)	48(1)	1
C76	669(3)	5740(3)	1147(1)	48(1)	1
O17	6752(2)	9054(2)	1554(1)	37(1)	1
O18	5818(2)	7662(2)	2129(1)	43(1)	1

O19	5067(2)	7802(2)	3189(1)	42(1)	1
O20	4636(2)	9667(2)	3553(1)	41(1)	1
O21	5809(2)	10932(2)	2977(1)	38(1)	1
O22	6321(2)	10895(2)	1915(1)	37(1)	1
C77	6608(3)	8242(3)	1341(1)	48(1)	1
C78	6734(3)	7406(2)	1720(1)	47(1)	1
C79	5737(3)	6850(2)	2466(2)	51(1)	1
C80	4783(3)	7193(3)	2891(1)	48(1)	1
C81	4179(3)	8166(3)	3603(1)	50(1)	1
C82	4534(3)	8835(3)	3873(1)	48(1)	1
C83	5026(3)	10340(3)	3770(1)	44(1)	1
C84	5013(3)	11221(3)	3430(1)	43(1)	1
C85	5893(3)	11776(2)	2659(1)	39(1)	1
C86	6729(3)	11450(2)	2194(1)	39(1)	1
C87	7091(3)	10598(2)	1459(1)	42(1)	1
C88	6723(3)	9894(2)	1220(1)	41(1)	1
C89	8914(4)	427(5)	141(2)	111(2)	1
S1	9952(2)	−435(2)	306(1)	54(1)	0.50
O23	9687(6)	−1331(4)	209(2)	79(2)	0.50

Table S3. Bond lengths [Å] and angles [°].

O1–C5	1.236(4)	N12–C50	1.334(4)
O2–C14	1.212(4)	N12–C51	1.452(4)
O3–C23	1.242(4)	C28–C29	1.519(5)
N1–C5	1.340(3)	C29–C30	1.506(4)
N1–C4	1.455(4)	C30–C31	1.522(4)
N2–C13	1.369(4)	C32–C33	1.478(4)
N2–C6	1.375(3)	C33–C34	1.370(4)
N3–C14	1.362(4)	C34–C35	1.415(4)
N3–C12	1.403(4)	C35–C36	1.399(4)
N4–C14	1.379(4)	C35–C40	1.416(4)
N4–C15	1.402(4)	C36–C37	1.370(4)
N5–C20	1.364(4)	C37–C38	1.404(4)
N5–C22	1.383(4)	C38–C39	1.376(4)
N6–C23	1.335(4)	C39–C40	1.402(4)
N6–C24	1.449(4)	C42–C43	1.366(4)
C1–C2	1.527(4)	C42–C47	1.405(4)
C2–C3	1.518(5)	C43–C44	1.407(4)
C3–C4	1.513(4)	C44–C45	1.361(4)
C5–C6	1.471(4)	C45–C46	1.398(4)
C6–C7	1.366(4)	C46–C47	1.417(4)
C7–C8	1.422(4)	C46–C48	1.421(4)
C8–C9	1.401(4)	C48–C49	1.369(4)
C8–C13	1.411(4)	C49–C50	1.471(4)
C9–C10	1.371(4)	C51–C52	1.511(5)
C10–C11	1.413(4)	C52–C53	1.507(5)
C11–C12	1.371(4)	C53–C54	1.517(5)
C12–C13	1.402(4)	O7–C55	1.266(3)
C15–C16	1.386(4)	O8–C55	1.258(3)
C15–C20	1.398(4)	N14–C59	1.488(4)
C16–C17	1.400(4)	C55–N13	1.362(3)
C17–C18	1.365(5)	N13–C57	1.440(4)
C18–C19	1.401(4)	C57–C58	1.522(4)
C19–C20	1.409(4)	C58–C59	1.514(4)
C19–C21	1.411(5)	O9–C60	1.268(3)
C21–C22	1.364(4)	O10–C60	1.260(3)
C22–C23	1.466(4)	N16–C64	1.481(4)
C24–C25	1.522(5)	C60–N15	1.359(4)
C25–C26	1.520(5)	N15–C62	1.438(4)
C26–C27	1.509(5)	C62–C63	1.518(4)
O4–C32	1.239(3)	C63–C64	1.505(4)
O5–C41	1.214(4)	O11–C76	1.419(4)
O6–C50	1.237(3)	O11–C65	1.428(4)
N7–C32	1.325(4)	O12–C67	1.420(4)
N7–C31	1.457(4)	O12–C66	1.430(4)
N8–C40	1.366(4)	O13–C68	1.420(4)
N8–C33	1.377(3)	O13–C69	1.423(4)
N9–C41	1.388(4)	O14–C71	1.418(4)
N9–C39	1.410(4)	O14–C70	1.427(4)
N10–C41	1.363(4)	O15–C73	1.421(4)
N10–C42	1.412(4)	O15–C72	1.421(4)
N11–C47	1.367(4)	O16–C75	1.416(4)
N11–C49	1.373(4)	O16–C74	1.428(4)

C65–C66	1.487(5)	O21–C84	1.425(4)
C67–C68	1.481(5)	O21–C85	1.427(4)
C69–C70	1.483(5)	O22–C87	1.421(4)
C71–C72	1.487(4)	O22–C86	1.421(4)
C73–C74	1.478(5)	C77–C78	1.493(5)
C75–C76	1.482(5)	C79–C80	1.480(5)
O17–C77	1.418(4)	C81–C82	1.485(5)
O17–C88	1.425(4)	C83–C84	1.480(5)
O18–C78	1.409(4)	C85–C86	1.481(5)
O18–C79	1.419(4)	C87–C88	1.483(5)
O19–C80	1.419(4)	C89–S1	1.608(6)
O19–C81	1.422(4)	S1–O23	1.471(6)
O20–C82	1.420(4)	S1–C89^{i}	1.672(6)
O20–C83	1.429(4)		

C5–N1–C4	122.9(3)	C20–C19–C21	105.9(3)
C13–N2–C6	108.7(2)	N5–C20–C15	128.9(3)
C14–N3–C12	125.9(3)	N5–C20–C19	108.6(3)
C14–N4–C15	124.6(3)	C15–C20–C19	122.5(3)
C20–N5–C22	108.4(2)	C22–C21–C19	108.4(3)
C23–N6–C24	121.2(3)	C21–C22–N5	108.7(3)
C3–C2–C1	111.6(3)	C21–C22–C23	126.8(3)
C2–C3–C4	114.5(2)	N5–C22–C23	124.5(2)
N1–C4–C3	113.7(3)	O3–C23–N6	121.4(3)
O1–C5–N1	122.6(3)	O3–C23–C22	120.0(3)
O1–C5–C6	121.0(2)	N6–C23–C22	118.7(3)
N1–C5–C6	116.3(3)	N6–C24–C25	113.1(3)
C7–C6–N2	109.5(3)	C24–C25–C26	113.5(3)
C7–C6–C5	132.3(2)	C27–C26–C25	113.0(3)
N2–C6–C5	118.0(3)	C32–N7–C31	121.4(2)
C6–C7–C8	107.2(2)	C40–N8–C33	108.8(2)
C9–C8–C13	119.2(3)	C41–N9–C39	123.7(3)
C9–C8–C7	134.2(3)	C41–N10–C42	125.9(3)
C13–C8–C7	106.6(3)	C47–N11–C49	109.0(2)
C10–C9–C8	118.4(3)	C50–N12–C51	123.2(3)
C9–C10–C11	121.8(3)	C30–C29–C28	112.9(3)
C12–C11–C10	121.1(3)	C29–C30–C31	113.6(2)
C11–C12–C13	117.2(3)	N7–C31–C30	111.9(2)
C11–C12–N3	125.5(3)	O4–C32–N7	122.2(3)
C13–C12–N3	117.3(3)	O4–C32–C33	118.9(3)
N2–C13–C12	129.8(3)	N7–C32–C33	118.8(2)
N2–C13–C8	107.9(2)	C34–C33–N8	109.0(3)
C12–C13–C8	122.3(3)	C34–C33–C32	126.9(3)
O2–C14–N3	124.4(3)	N8–C33–C32	124.1(3)
O2–C14–N4	124.0(3)	C33–C34–C35	107.8(3)
N3–C14–N4	111.6(3)	C36–C35–C34	134.7(3)
C16–C15–C20	116.6(3)	C36–C35–C40	119.0(3)
C16–C15–N4	124.4(3)	C34–C35–C40	106.2(3)
C20–C15–N4	119.0(3)	C37–C36–C35	118.3(3)
C15–C16–C17	121.2(3)	C36–C37–C38	122.2(3)
C18–C17–C16	122.0(3)	C39–C38–C37	121.3(3)
C17–C18–C19	118.5(3)	C38–C39–C40	116.7(3)
C18–C19–C20	119.2(3)	C38–C39–N9	124.7(3)
C18–C19–C21	134.9(3)	C40–C39–N9	118.6(3)

N8–C40–C39	129.4(3)	O14–C71–C72	108.9(2)
N8–C40–C35	108.1(2)	O15–C72–C71	109.4(3)
C39–C40–C35	122.5(3)	O15–C73–C74	110.4(3)
O5–C41–N10	125.3(3)	O16–C74–C73	109.3(3)
O5–C41–N9	122.8(3)	O16–C75–C76	107.6(3)
N10–C41–N9	111.9(3)	O11–C76–C75	110.1(3)
C43–C42–C47	117.2(3)	C77–O17–C88	113.2(3)
C43–C42–N10	126.0(3)	C78–O18–C79	113.1(3)
C47–C42–N10	116.8(3)	C80–O19–C81	112.4(3)
C42–C43–C44	121.4(3)	C82–O20–C83	112.8(3)
C45–C44–C43	122.0(3)	C84–O21–C85	111.0(2)
C44–C45–C46	118.6(3)	C87–O22–C86	111.5(2)
C45–C46–C47	119.2(3)	O17–C77–C78	107.0(3)
C45–C46–C48	134.9(3)	O18–C78–C77	108.8(3)
C47–C46–C48	105.9(3)	O18–C79–C80	109.5(3)
N11–C47–C42	130.1(3)	O19–C80–C79	109.5(3)
N11–C47–C46	108.2(2)	O19–C81–C82	108.1(3)
C42–C47–C46	121.7(3)	O20–C82–C81	108.1(3)
C49–C48–C46	107.9(3)	O20–C83–C84	109.0(3)
C48–C49–N11	109.1(3)	O21–C84–C83	109.6(3)
C48–C49–C50	132.4(3)	O21–C85–C86	109.6(2)
N11–C49–C50	118.4(2)	O22–C86–C85	110.2(3)
O6–C50–N12	123.1(3)	O22–C87–C88	109.4(3)
O6–C50–C49	120.7(3)	O17–C88–C87	106.7(3)
N12–C50–C49	116.2(2)	O23–S1–C89	101.4(4)
N12–C51–C52	112.5(3)	O23–S1–C89^{i}	103.1(4)
C53–C52–C51	114.7(3)	C89–S1–C89^{i}	105.3(2)
C52–C53–C54	112.8(3)		
O8–C55–O7	124.9(3)		
O8–C55–N13	117.9(3)		
O7–C55–N13	117.1(2)		
C55–N13–C57	123.7(2)		
N13–C57–C58	113.0(2)		
C59–C58–C57	111.8(2)		
N14–C59–C58	112.6(2)		
O10–C60–O9	124.5(3)		
O10–C60–N15	118.3(2)		
O9–C60–N15	117.1(2)		
C60–N15–C62	124.1(2)		
N15–C62–C63	112.7(2)		
C64–C63–C62	111.1(2)		
N16–C64–C63	112.8(2)		
C76–O11–C65	111.6(3)		
C67–O12–C66	111.2(2)		
C68–O13–C69	112.3(2)		
C71–O14–C70	112.7(2)		
C73–O15–C72	111.5(2)		
C75–O16–C74	113.5(2)		
O11–C65–C66	110.4(3)		
O12–C66–C65	110.3(3)		
O12–C67–C68	109.3(3)		
O13–C68–C67	110.0(3)		
O13–C69–C70	109.0(3)		
O14–C70–C69	108.5(3)		

Symmetry transformations used to generate equivalent atoms:
(i) −x+2,−y,−z

Table S4. Anisotropic displacement parameters [Å^2× 10^3]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	36(1)	67(2)	24(1)	−8(1)	1(1)	−23(1)
O2	30(1)	52(1)	35(1)	1(1)	−6(1)	−16(1)
O3	42(1)	46(1)	24(1)	−4(1)	1(1)	−9(1)
N1	32(2)	41(1)	26(1)	0(1)	−3(1)	−15(1)
N2	24(1)	30(1)	23(1)	−1(1)	−3(1)	−5(1)
N3	20(1)	34(1)	31(1)	2(1)	−8(1)	−8(1)
N4	23(2)	40(1)	29(1)	−1(1)	−2(1)	−9(1)
N5	26(2)	36(1)	22(1)	2(1)	−2(1)	−8(1)
N6	36(2)	40(1)	21(1)	−3(1)	−3(1)	−13(1)
C1	42(2)	45(2)	52(2)	6(2)	−8(2)	−21(2)
C2	36(2)	50(2)	36(2)	4(1)	−4(2)	−21(2)
C3	26(2)	48(2)	28(2)	3(1)	−6(1)	−18(2)
C4	26(2)	49(2)	33(2)	−4(1)	−3(1)	−15(2)
C5	21(2)	30(2)	28(2)	−1(1)	−1(1)	−3(1)
C6	22(2)	24(1)	28(2)	0(1)	1(1)	−2(1)
C7	32(2)	30(2)	21(1)	0(1)	−1(1)	−6(1)
C8	26(2)	25(1)	28(2)	−4(1)	−6(1)	−3(1)
C9	35(2)	35(2)	32(2)	−2(1)	−9(1)	−8(2)
C10	34(2)	39(2)	40(2)	−2(1)	−12(2)	−13(2)
C11	31(2)	37(2)	32(2)	1(1)	−5(1)	−12(1)
C12	28(2)	25(1)	29(2)	0(1)	−5(1)	−8(1)
C13	23(2)	24(1)	30(2)	−3(1)	−5(1)	−3(1)
C14	24(2)	26(2)	30(2)	2(1)	−3(1)	−6(1)
C15	27(2)	30(2)	28(2)	5(1)	−4(1)	−2(1)
C16	28(2)	32(2)	35(2)	10(1)	−9(1)	−9(1)
C17	30(2)	48(2)	39(2)	13(1)	−4(1)	−17(2)
C18	31(2)	57(2)	31(2)	11(1)	−3(1)	−16(2)
C19	28(2)	44(2)	26(2)	9(1)	−6(1)	−10(2)
C20	23(2)	34(2)	27(2)	6(1)	−4(1)	−5(1)
C21	33(2)	51(2)	22(2)	1(1)	−2(1)	−9(2)
C22	31(2)	36(2)	22(1)	3(1)	−5(1)	−6(1)
C23	32(2)	37(2)	20(1)	3(1)	−4(1)	−4(1)
C24	48(2)	40(2)	27(2)	−3(1)	−4(1)	−16(2)
C25	40(2)	45(2)	29(2)	−5(1)	−2(1)	−17(2)
C26	40(2)	46(2)	41(2)	−9(1)	−7(2)	−14(2)
C27	40(2)	60(2)	56(2)	−5(2)	−7(2)	−12(2)
O4	41(1)	40(1)	26(1)	3(1)	2(1)	−15(1)
O5	33(1)	34(1)	34(1)	2(1)	−5(1)	−4(1)
O6	36(1)	48(1)	27(1)	5(1)	−2(1)	−5(1)
N7	33(2)	32(1)	22(1)	3(1)	−2(1)	−8(1)
N8	26(1)	31(1)	21(1)	−3(1)	−3(1)	−6(1)
N9	24(2)	33(1)	31(1)	1(1)	−6(1)	−6(1)
N10	25(2)	31(1)	31(1)	1(1)	−6(1)	−7(1)
N11	28(2)	30(1)	22(1)	1(1)	−4(1)	−12(1)
N12	31(2)	38(1)	26(1)	0(1)	−2(1)	−7(1)
C28	59(3)	65(3)	66(3)	−10(2)	−27(2)	−17(2)
C29	44(2)	42(2)	47(2)	0(2)	−17(2)	−11(2)
C30	42(2)	31(2)	24(2)	3(1)	−9(1)	−2(1)
C31	38(2)	29(2)	27(2)	2(1)	−5(1)	−9(1)
C32	33(2)	36(2)	21(1)	1(1)	−5(1)	−14(1)
C33	30(2)	35(2)	22(1)	−4(1)	−2(1)	−11(1)

C34	30(2)	40(2)	25(2)	−1(1)	−3(1)	−9(1)
C35	28(2)	38(2)	24(2)	−7(1)	−4(1)	−7(1)
C36	29(2)	47(2)	25(2)	−7(1)	−1(1)	−3(2)
C37	34(2)	40(2)	31(2)	−14(1)	−4(1)	−1(2)
C38	43(2)	30(2)	29(2)	−4(1)	−11(1)	−9(2)
C39	33(2)	30(2)	22(1)	−8(1)	−3(1)	−9(1)
C40	27(2)	29(2)	25(1)	−8(1)	−7(1)	−4(1)
C41	29(2)	29(2)	31(2)	−4(1)	−7(1)	−14(2)
C42	28(2)	29(2)	30(2)	2(1)	−6(1)	−16(1)
C43	31(2)	27(2)	34(2)	0(1)	−5(1)	−14(1)
C44	38(2)	31(2)	36(2)	6(1)	−7(2)	−11(1)
C45	42(2)	41(2)	29(2)	6(1)	−8(1)	−19(2)
C46	35(2)	30(2)	27(2)	2(1)	−5(1)	−16(1)
C47	26(2)	31(2)	29(2)	2(1)	−5(1)	−13(1)
C48	34(2)	36(2)	29(2)	0(1)	−4(1)	−16(1)
C49	27(2)	37(2)	24(1)	0(1)	−2(1)	−15(1)
C50	22(2)	40(2)	26(2)	1(1)	−2(1)	−11(1)
C51	26(2)	43(2)	31(2)	−2(1)	−3(1)	−4(1)
C52	34(2)	39(2)	30(2)	−2(1)	−5(1)	2(2)
C53	40(2)	37(2)	41(2)	−5(1)	−7(2)	−4(2)
C54	45(2)	39(2)	47(2)	−6(2)	−13(2)	0(2)
O7	32(1)	35(1)	31(1)	−3(1)	−6(1)	−14(1)
O8	33(1)	45(1)	25(1)	−2(1)	2(1)	−16(1)
N14	34(2)	32(1)	31(1)	0(1)	−10(1)	−7(1)
C55	23(2)	33(2)	24(2)	1(1)	−6(1)	−7(1)
N13	29(2)	34(1)	21(1)	−4(1)	2(1)	−13(1)
C57	24(2)	35(2)	29(2)	−1(1)	−5(1)	−9(1)
C58	31(2)	35(2)	23(1)	1(1)	−7(1)	−13(1)
C59	29(2)	36(2)	34(2)	2(1)	−6(1)	−9(1)
O9	37(1)	30(1)	27(1)	1(1)	−6(1)	−9(1)
O10	30(1)	38(1)	24(1)	1(1)	−1(1)	−6(1)
N16	39(2)	29(1)	30(1)	−1(1)	−10(1)	−13(1)
C60	22(2)	34(2)	29(2)	2(1)	−8(1)	−9(1)
N15	29(2)	33(1)	24(1)	−2(1)	1(1)	−8(1)
C62	26(2)	31(2)	31(2)	0(1)	−5(1)	−5(1)
C63	34(2)	30(2)	30(2)	3(1)	−6(1)	−10(1)
C64	26(2)	44(2)	39(2)	−7(1)	−7(1)	−6(2)
O11	38(1)	38(1)	38(1)	−7(1)	−6(1)	−6(1)
O12	42(1)	35(1)	50(1)	2(1)	−16(1)	−17(1)
O13	40(1)	37(1)	42(1)	8(1)	−16(1)	−13(1)
O14	29(1)	36(1)	40(1)	0(1)	−4(1)	−10(1)
O15	35(1)	34(1)	40(1)	−3(1)	−6(1)	−16(1)
O16	46(2)	39(1)	36(1)	4(1)	−8(1)	−9(1)
C65	40(2)	40(2)	52(2)	−15(2)	−14(2)	−2(2)
C66	43(2)	29(2)	58(2)	−11(1)	−20(2)	−6(2)
C67	40(2)	28(2)	64(2)	10(2)	−18(2)	−14(2)
C68	37(2)	38(2)	59(2)	17(2)	−21(2)	−13(2)
C69	38(2)	55(2)	31(2)	7(1)	−10(1)	−22(2)
C70	34(2)	56(2)	35(2)	−3(1)	−5(2)	−19(2)
C71	29(2)	33(2)	43(2)	−13(1)	−8(1)	−2(1)
C72	36(2)	29(2)	45(2)	−6(1)	−14(2)	−6(1)
C73	37(2)	33(2)	50(2)	4(1)	−11(2)	−17(2)
C74	38(2)	32(2)	48(2)	10(1)	−9(2)	−10(2)
C75	55(2)	52(2)	32(2)	0(2)	−3(2)	−13(2)
C76	48(2)	57(2)	34(2)	−6(2)	1(2)	−15(2)
O17	43(1)	39(1)	29(1)	−1(1)	−9(1)	−11(1)

O18	43(2)	32(1)	55(1)	–2(1)	–12(1)	–11(1)
O19	31(1)	46(1)	50(1)	8(1)	–10(1)	–16(1)
O20	41(1)	47(1)	33(1)	0(1)	–9(1)	–8(1)
O21	37(1)	33(1)	43(1)	–9(1)	–9(1)	–4(1)
O22	30(1)	38(1)	42(1)	0(1)	–6(1)	–10(1)
C77	49(2)	48(2)	47(2)	–16(2)	–13(2)	–9(2)
C78	53(2)	34(2)	53(2)	–16(2)	–11(2)	–7(2)
C79	60(3)	32(2)	68(2)	1(2)	–21(2)	–17(2)
C80	53(2)	40(2)	65(2)	12(2)	–25(2)	–29(2)
C81	33(2)	66(2)	48(2)	16(2)	–5(2)	–20(2)
C82	38(2)	65(2)	35(2)	9(2)	–5(2)	–14(2)
C83	42(2)	50(2)	36(2)	–15(2)	–9(2)	–1(2)
C84	40(2)	44(2)	42(2)	–14(2)	–12(2)	0(2)
C85	35(2)	28(2)	56(2)	–9(1)	–13(2)	–6(1)
C86	32(2)	27(2)	58(2)	5(1)	–12(2)	–10(1)
C87	39(2)	41(2)	38(2)	8(1)	–1(2)	–9(2)
C88	39(2)	45(2)	34(2)	5(1)	–9(2)	–4(2)
C89	63(4)	141(6)	105(4)	–23(4)	5(3)	–6(4)
S1	69(1)	52(1)	43(1)	5(1)	–14(1)	–21(1)
O23	132(6)	61(4)	59(4)	9(3)	–26(4)	–52(4)

Table S5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H1	1335	2814	4360	39	1
H2	3267	3612	2980	32	1
H3	4482	4382	2479	34	1
H4	5213	4093	1735	37	1
H5	5337	2905	1172	35	1
H6	4399	2071	927	38	1
H1A	1586	−511	4781	68	1
H1B	2076	−1089	4286	68	1
H1C	759	−703	4480	68	1
H2A	2138	570	4147	48	1
H2B	1376	344	3821	48	1
H3A	536	1357	4723	40	1
H3B	−251	1076	4431	40	1
H4A	270	2136	3761	42	1
H4B	−411	2705	4245	42	1
H7	2889	3305	4437	35	1
H9	4780	4078	4484	41	1
H10	6172	4664	3981	43	1
H11	6363	4780	3121	40	1
H16	7608	4874	1447	38	1
H17	8920	4647	707	47	1
H18	8832	3701	98	48	1
H21	7474	2494	−116	44	1
H24A	3518	990	835	46	1
H24B	4513	549	391	46	1
H25A	2838	1232	96	44	1
H25B	3710	1811	−148	44	1
H26A	1893	2513	659	50	1
H26B	2760	3094	410	50	1
H27A	2076	3284	−328	79	1
H27B	1091	3753	114	79	1
H27C	1200	2713	−75	79	1
H7A	10392	7019	4031	36	1
H8	9623	8577	3899	32	1
H9A	9909	10084	3467	36	1
H10A	10658	10156	2707	35	1
H11A	11924	9051	2176	32	1
H12	14047	8027	777	40	1
H28A	12668	6720	5241	91	1
H28B	13705	6700	4803	91	1
H28C	13531	5703	5058	91	1
H29A	12031	7000	4494	52	1
H29B	12941	6025	4284	52	1
H30A	11110	6051	5085	41	1
H30B	12012	5079	4867	41	1
H31A	11355	5422	4113	39	1
H31B	10384	5306	4560	39	1
H34	7110	8515	5024	39	1
H36	5879	10637	4921	43	1
H37	6006	12036	4440	44	1
H38	7497	11997	3776	40	1
H43	8885	12038	2083	36	1
H44	9178	12312	1229	43	1
H45	10634	11268	707	44	1

H48	12524	9422	720	38	1
H51A	15086	6418	1324	42	1
H51B	15742	6837	842	42	1
H52A	14672	6319	370	45	1
H52B	15498	5437	616	45	1
H53A	13147	6147	996	49	1
H53B	13976	5260	1240	49	1
H54A	13378	5233	317	69	1
H54B	13104	4569	790	69	1
H54C	14357	4379	493	69	1
H14A	5077	−911	2334	49	1
H14B	5058	−507	2801	49	1
H14C	5481	−54	2331	49	1
H13	2407	2626	2510	33	1
H57A	2514	1858	1654	36	1
H57B	1969	1498	2179	36	1
H58A	3564	244	1778	34	1
H58B	4339	913	1798	34	1
H59A	3647	852	2705	40	1
H59B	3263	−54	2609	40	1
H16A	9524	5584	2650	47	1
H16B	9663	6110	2170	47	1
H16C	9299	6656	2626	47	1
H15	12469	7317	2530	36	1
H62A	12338	6164	3353	36	1
H62B	12839	5779	2812	36	1
H63A	11188	5307	3176	38	1
H63B	10481	6431	3214	38	1
H64A	11175	6500	2304	44	1
H64B	11407	5345	2349	44	1
H65A	1339	4194	1690	53	1
H65B	807	3900	1285	53	1
H66A	−810	3877	1913	51	1
H66B	297	3046	1995	51	1
H67A	−418	2968	2869	51	1
H67B	−1548	3746	2770	51	1
H68A	−1357	3786	3592	53	1
H68B	−224	4070	3397	53	1
H69A	−1011	5598	3819	48	1
H69B	−2129	5295	4029	48	1
H70A	−3123	6710	3598	49	1
H70B	−2634	6989	4023	49	1
H71A	−2616	8532	3577	43	1
H71B	−3036	8236	3134	43	1
H72A	−1968	9375	2877	44	1
H72B	−906	8567	3022	44	1
H73A	183	8373	2186	46	1
H73B	−787	9328	2085	46	1
H74A	−1171	8467	1491	49	1
H74B	59	8584	1343	49	1
H75A	474	7137	844	58	1
H75B	−692	6922	1069	58	1
H76A	778	5455	828	57	1
H76B	1411	5641	1223	57	1
H77A	7178	8053	1040	57	1
H77B	5863	8419	1258	57	1
H78A	6737	6807	1577	56	1
H78B	7446	7281	1829	56	1
H79A	6441	6573	2586	62	1

H79B	5613	6335	2298	62	1
H80A	4104	7565	2769	58	1
H80B	4630	6625	3089	58	1
H81A	4038	7618	3821	60	1
H81B	3484	8526	3489	60	1
H82A	3973	9051	4174	57	1
H82B	5256	8488	3966	57	1
H83A	5791	10018	3823	53	1
H83B	4537	10542	4089	53	1
H84A	4258	11517	3360	52	1
H84B	5209	11711	3586	52	1
H85A	6130	12224	2826	47	1
H85B	5157	12129	2581	47	1
H86A	6861	12025	1997	47	1
H86B	7446	11044	2274	47	1
H87A	7850	10283	1521	50	1
H87B	7110	11176	1239	50	1
H88A	5960	10199	1160	50	1
H88B	7230	9696	904	50	1
H89A	8946	389	–208	166	1
H89B	8969	1063	204	166	1
H89C	8208	346	327	166	1

Table S6. Hydrogen bonds [Å and °].

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
N13–H13···O1	0.86	2.01	2.860(3)	168.7
N15–H15···O6	0.86	2.03	2.885(3)	170.1
N2–H2···O7	0.86	2.04	2.866(4)	159.8
N3–H3···O7	0.86	2.01	2.782(3)	148.2
N4–H4···O7	0.86	2.43	3.163(3)	143.5
N5–H5···O8	0.86	1.84	2.677(3)	163.2
N6–H6···O8	0.86	1.98	2.840(3)	174.7
N7–H7A···O10	0.86	2.01	2.846(3)	164.7
N8–H8···O10	0.86	1.84	2.688(3)	167.5
N9–H9A···O9	0.86	2.62	3.291(3)	135.6
N10–H10A···O9	0.86	1.95	2.767(3)	158.7
N11–H11A···O9	0.86	1.95	2.775(3)	160.6
N1–H1···O4^{ii}	0.86	2.05	2.893(4)	167.1
N12–H12···O3^{iii}	0.86	2.08	2.916(4)	165.4
N14–H14A···O18^{iv}	0.89	2.03	2.872(4)	157.6
N14–H14B···O20^{iv}	0.89	2.04	2.875(4)	154.9
N14–H14B···O19^{iv}	0.89	2.52	3.073(4)	120.9
N14–H14C···O22^{iv}	0.89	2.07	2.940(3)	166.1
N14–H14C···O17^{iv}	0.89	2.56	3.016(3)	112.7
N16–H16A···O12^{v}	0.89	2.06	2.738(4)	132.1
N16–H16A···O13^{v}	0.89	2.19	2.966(3)	144.8
N16–H16B···O11^{v}	0.89	2.14	2.919(4)	145.2
N16–H16B···O16^{v}	0.89	2.23	2.852(3)	126.5
N16–H16C···O15^{v}	0.89	2.20	2.935(4)	140.1
N16–H16C···O14^{v}	0.89	2.20	2.932(3)	139.6

Symmetry transformations used to generate equivalent atoms:
(i) –x+2,–y,–z (ii) –x+1,–y+1,–z+1 (iii) –x+2,–y+1,–z
(iv) x,y–1,z (v) x+1,y,z

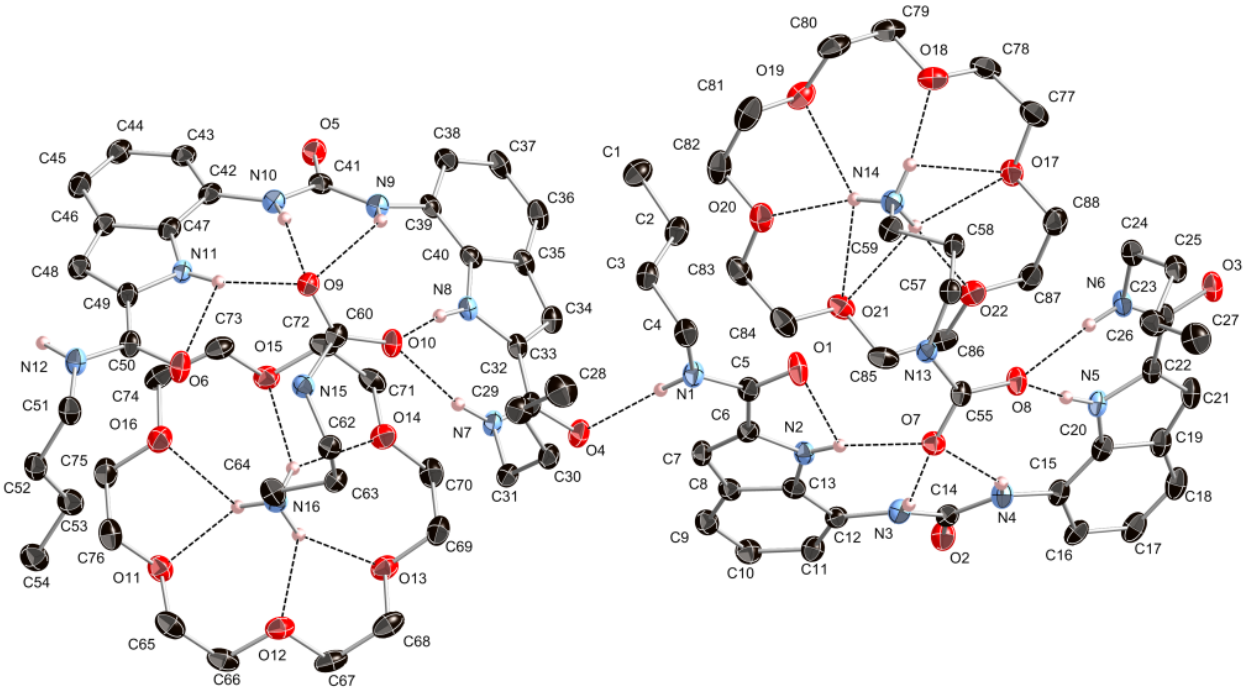

Figure S58 ORTEP view of the structure (thermal ellipsoids at the 30% probability level)

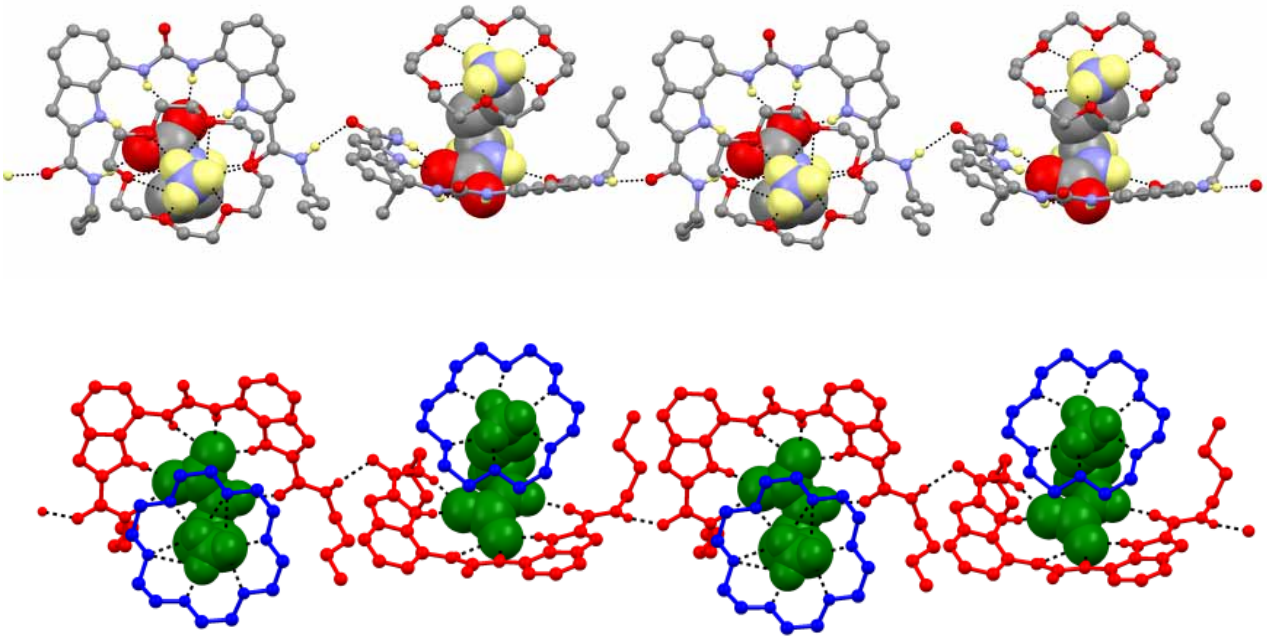

Figure S59 Views of the hydrogen bonding interactions between complexes in the solid state. The AAAC salt is shown in a spacefilling representation.

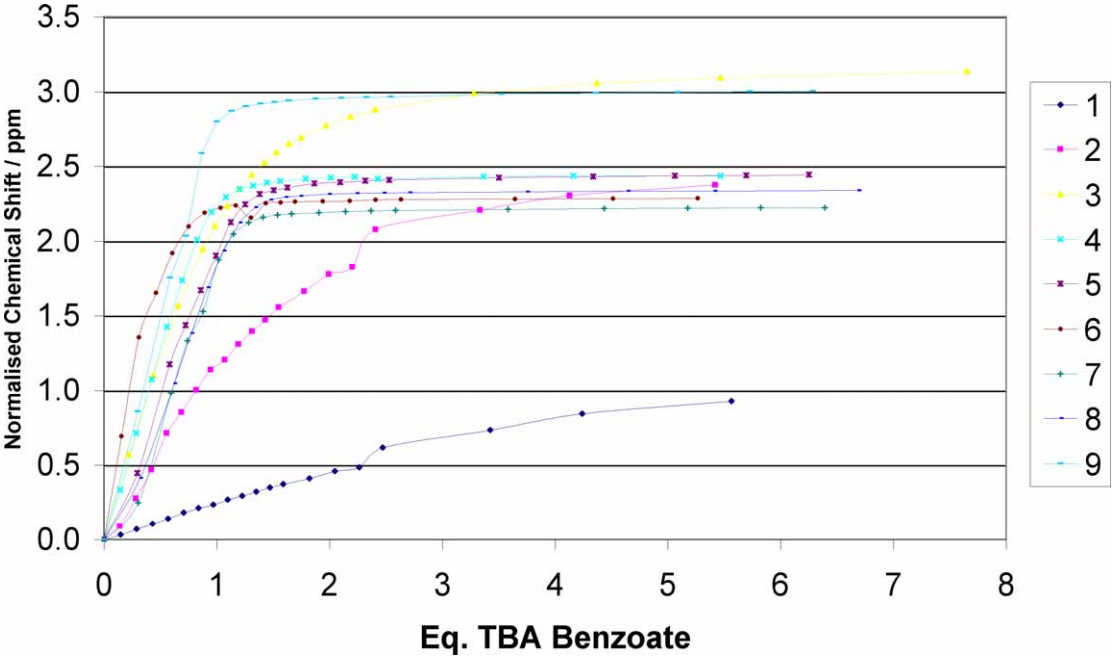

Figure S60 NMR titrations with TBA benzoate in DMSO-d_6/0.5% water.

Table S7: correlation between chemical shift of urea NH protons in the presence of one equivalent of benzoate *vs.* stability constant.

Receptor	K_a/M^{-1}	Δδ/ppm
1 Butyl-Hexyl	17	0.25
2 Butyl-Phenyl	140	1.20
3 Phenyl-Phenyl	674	2.10
Average shift for low affinity group		**1.2**
5 Phenyl-Carbazoyl	3400	1.85
7 Indole-Carbazoyl	5880	1.70
8 Carbazoyl-Carbazoyl	5670	1.70
Average shift for mid-affinity group		**1.75**
6 Indole-indole	10000	2.22
4 Phenyl-Indole	13000	2.25
9 Butyl appended bisindole	23000	2.70
Average shift for high affinity group		**2.4**