Supporting Information

Chiral Cryptates Derived from a Hexa-azamacrocycle.

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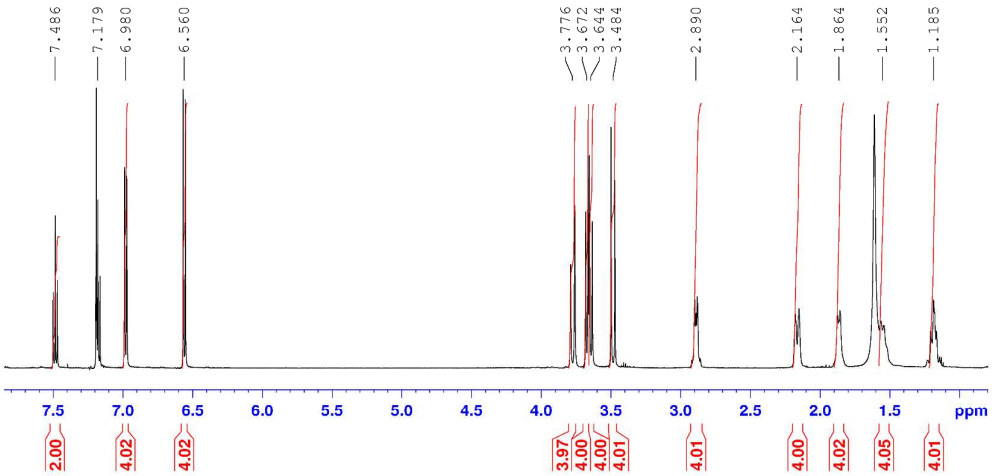

Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of [$Na^+ \subset$ ***R*-6**]Br.

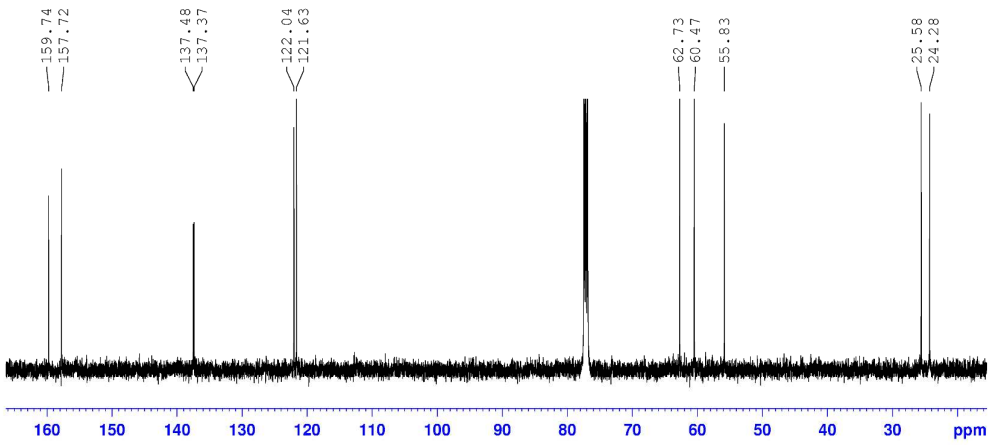

Figure S2. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of [$Na^+ \subset$ ***R*-6**]Br.

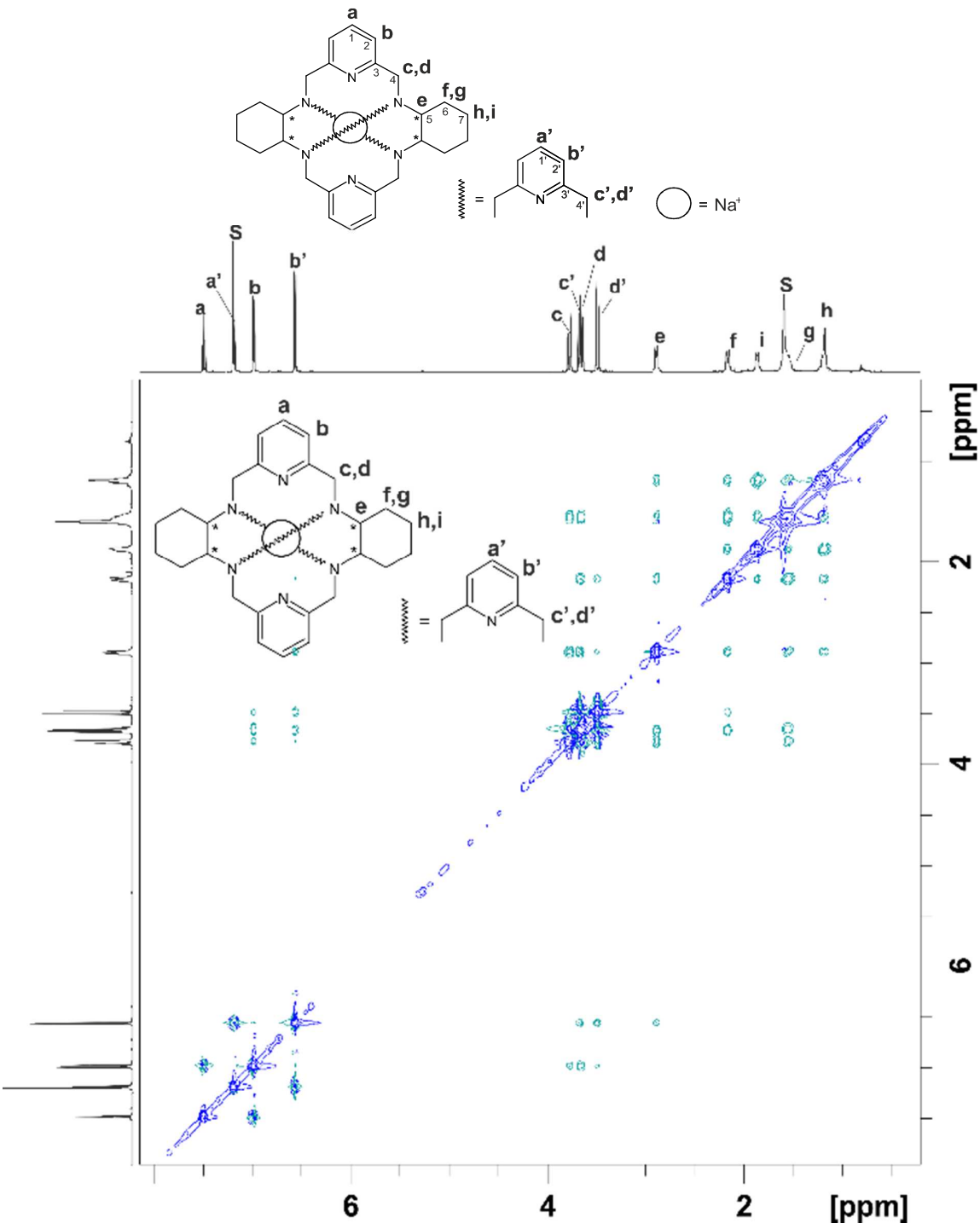

Figure S3. NOESY spectrum of [$Na^+ \subset$ *R*-**6**]Br ($CDCl_3$, 500 MHz, 298K).

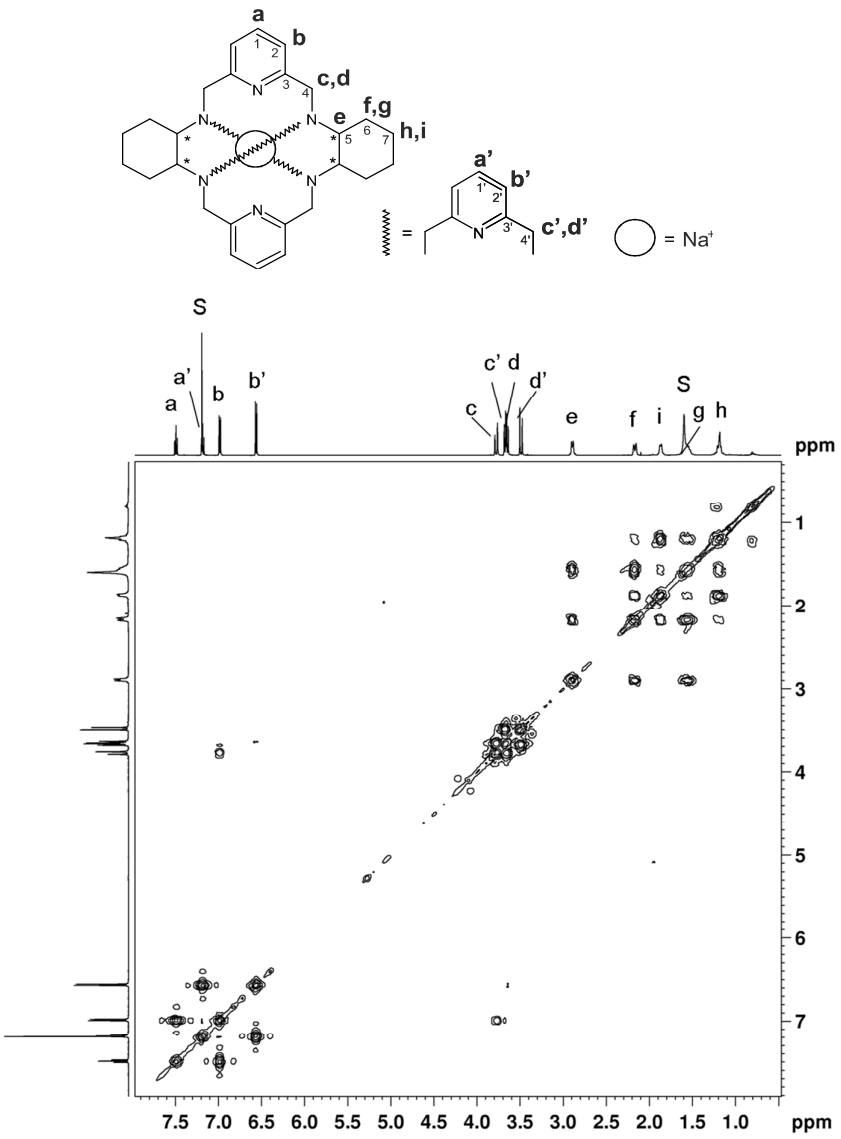

Figure S4. COSY spectrum ($CDCl_3$, 500 MHz, 298K) of [$Na^+ \subset$ *R*-**6**]Br.

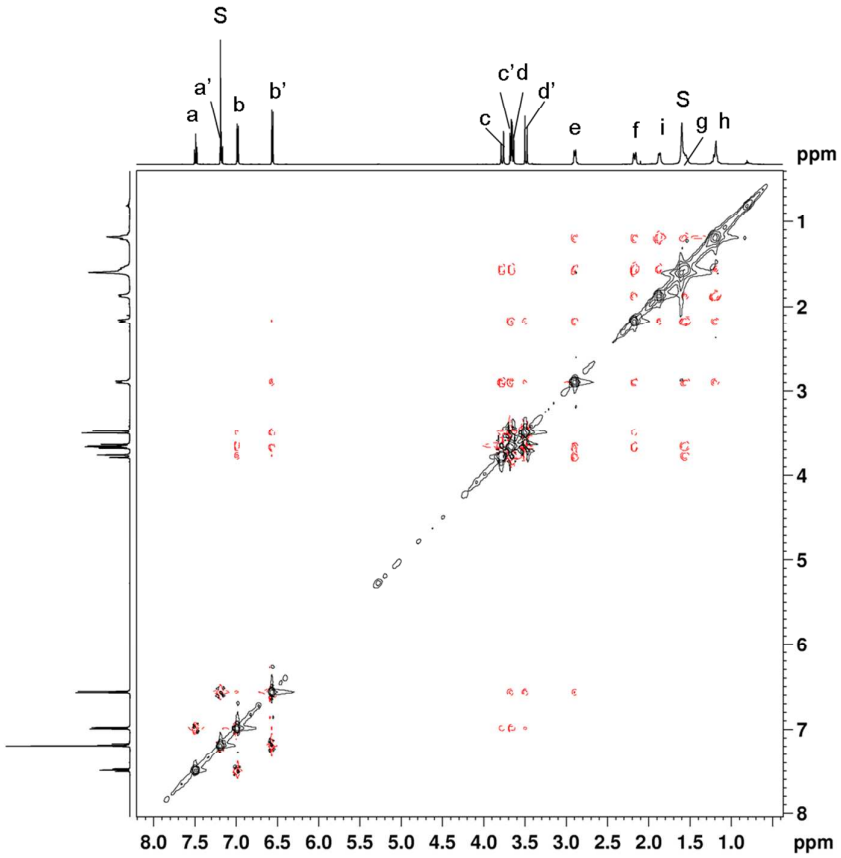

Figure S5. NOESY spectrum ($CDCl_3$, 500 MHz, 298K) of [$Na^+ \subset$ *R*-**6**]Br.

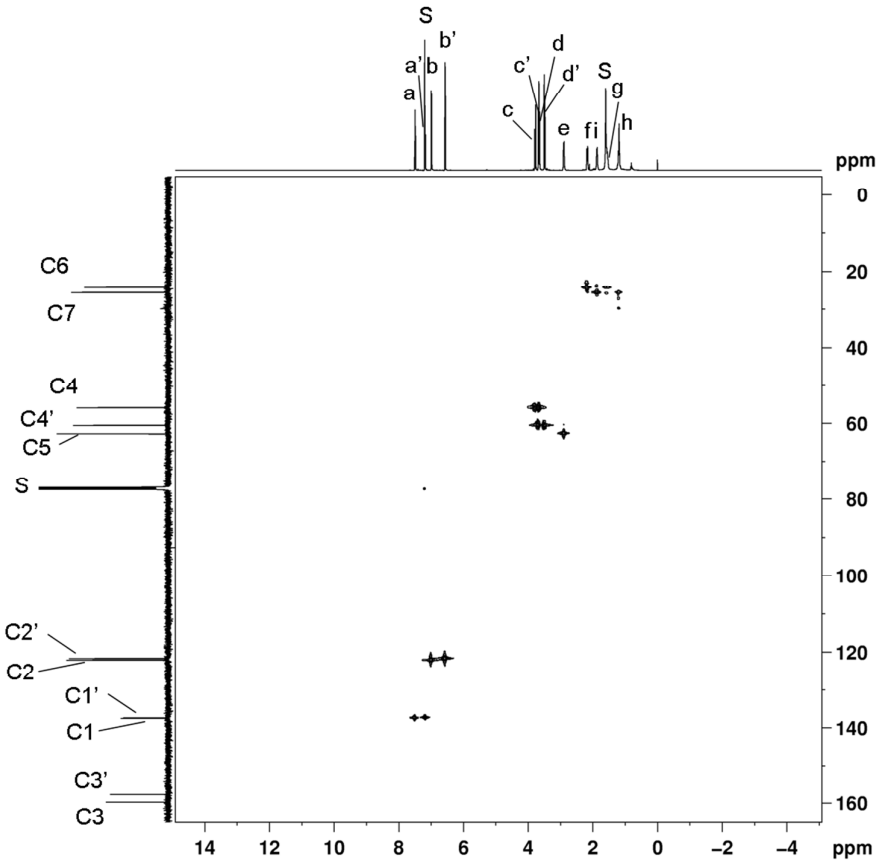

Figure S6. HMQC spectrum ($CDCl_3$, 500 MHz, 298K) of [$Na^+ \subset$ *R*-**6**]Br.

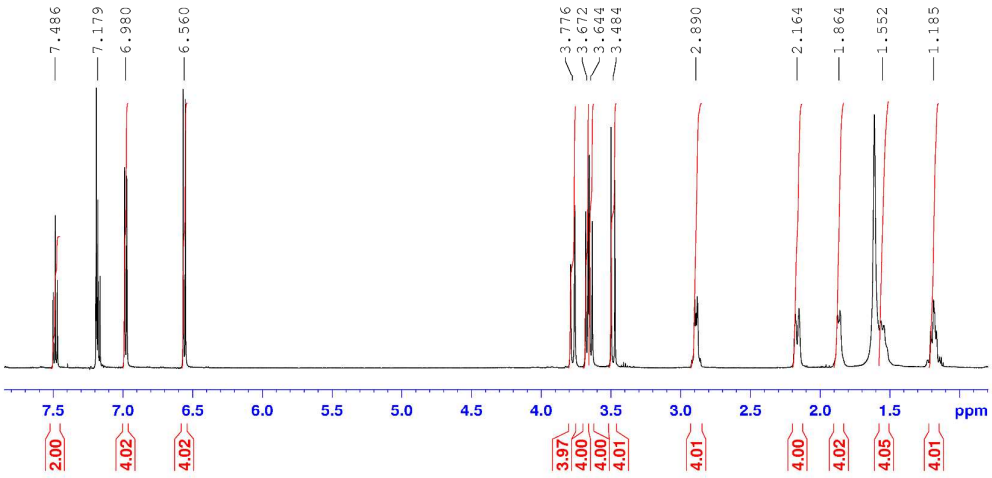

Figure S7. ^1H NMR spectrum (500 MHz, $CDCl_3$) of [$Na^+ \subset$ *S*-**6**]Br.

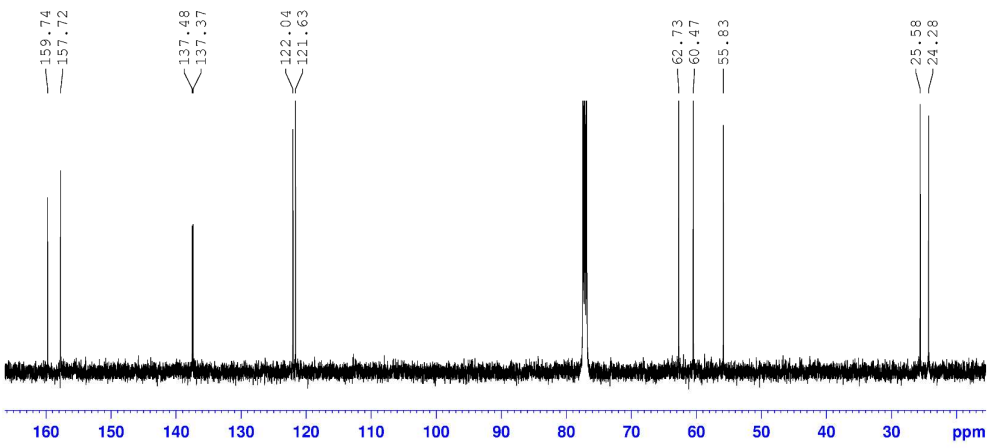

Figure S8. ^{13}C NMR HMQC spectrum (500 MHz, $CDCl_3$) of [$Na^+ \subset$ *S*-**6**]Br.

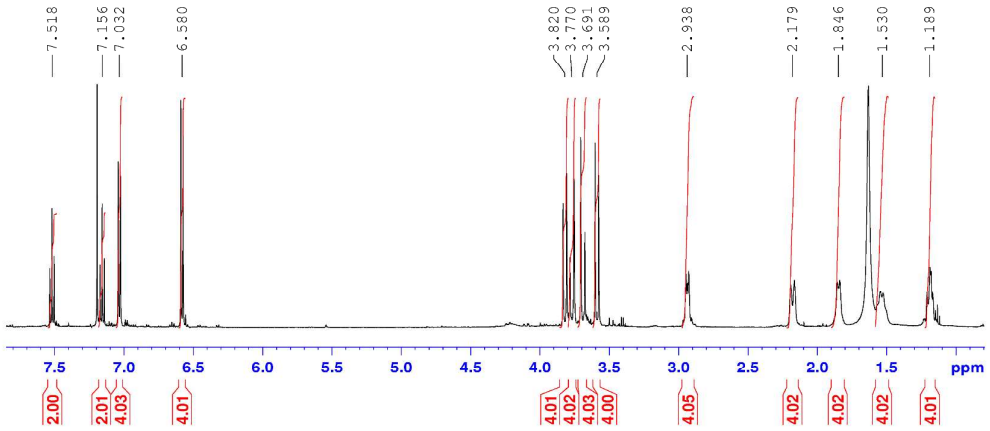

Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]Br.

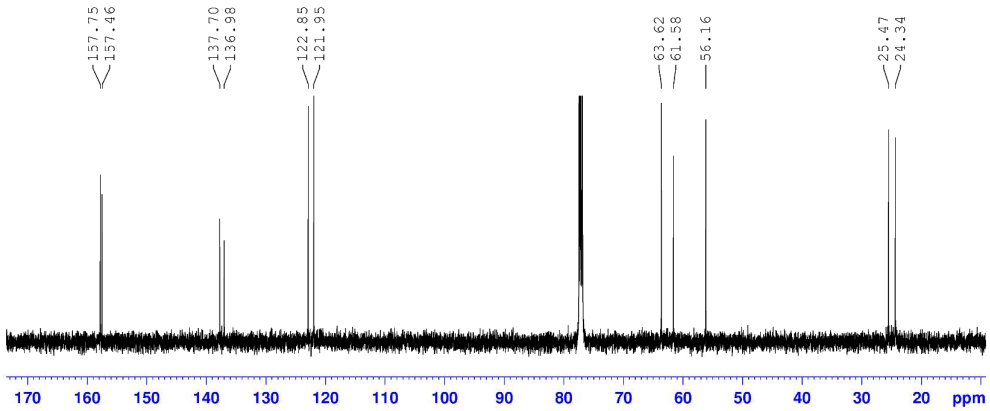

Figure S10. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]Br.

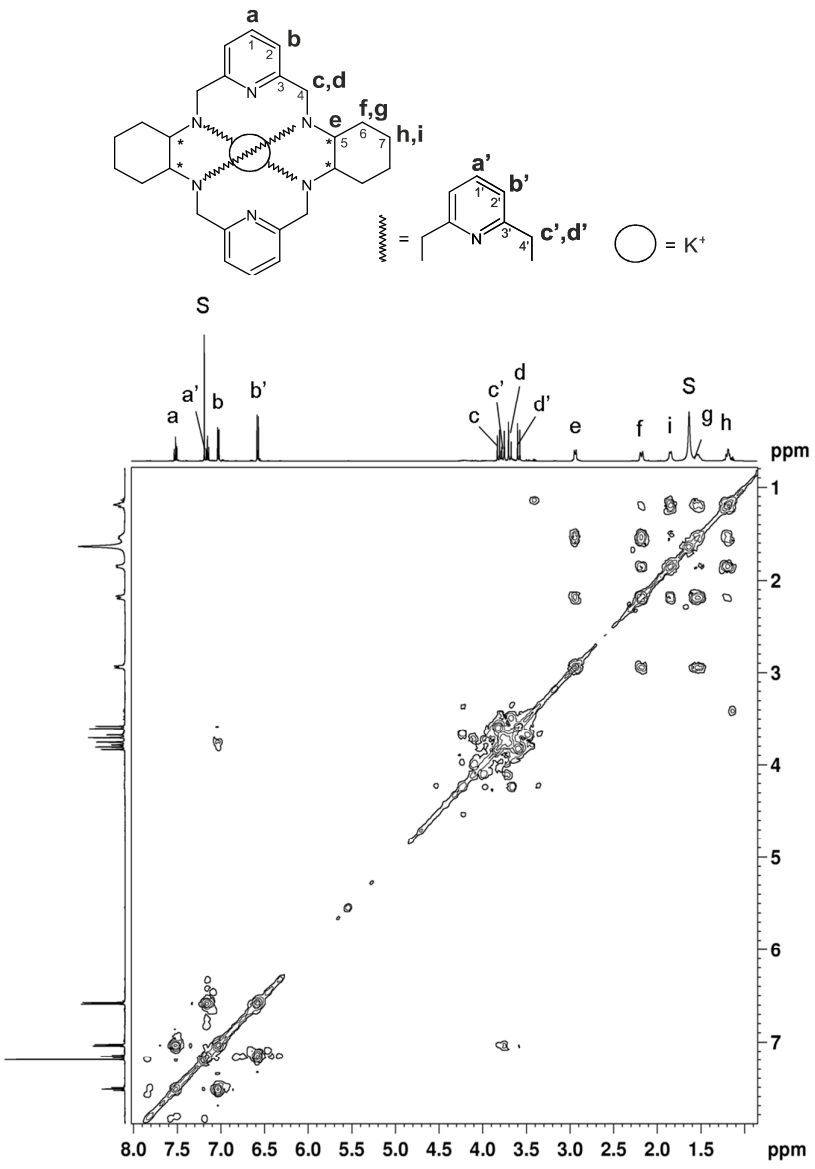

Figure S11. COSY spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]Br.

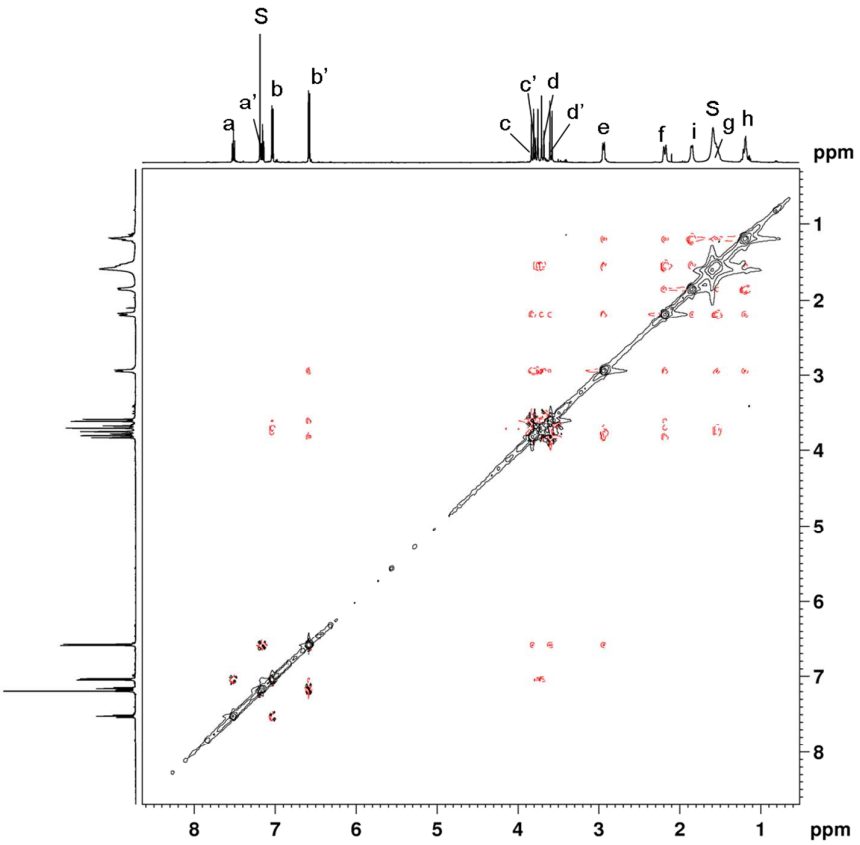

Figure S12. NOESY spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ ***R*-6**]Br.

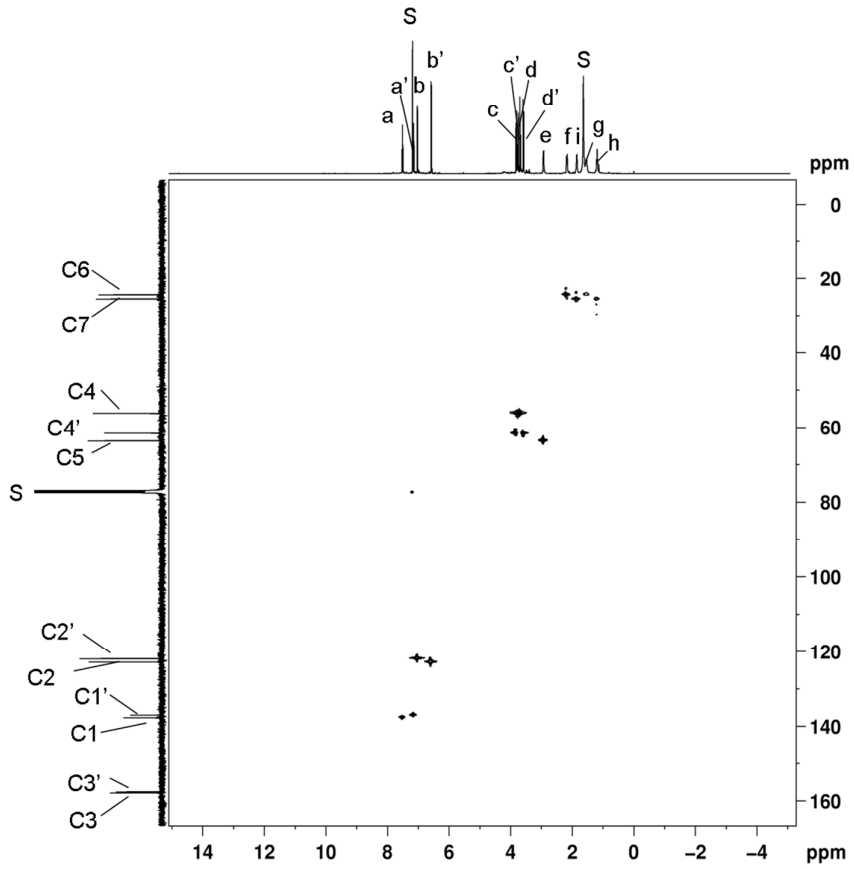

Figure S13. HMQC spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]Br.

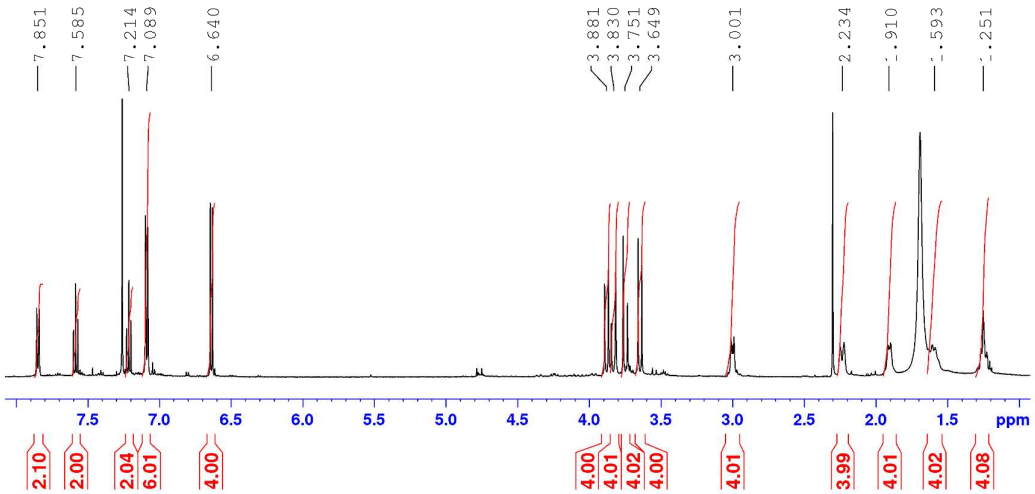

Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]OTs.

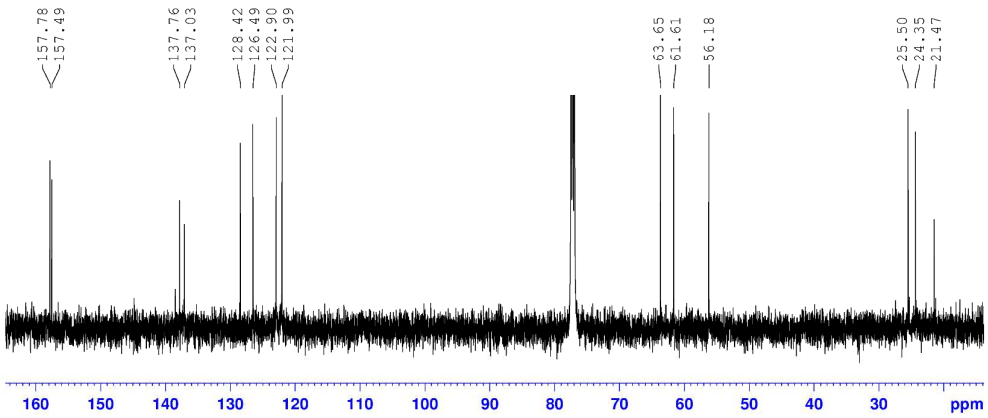

Figure S15. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of [$K^+\subset$ *R*-**6**]OTs.

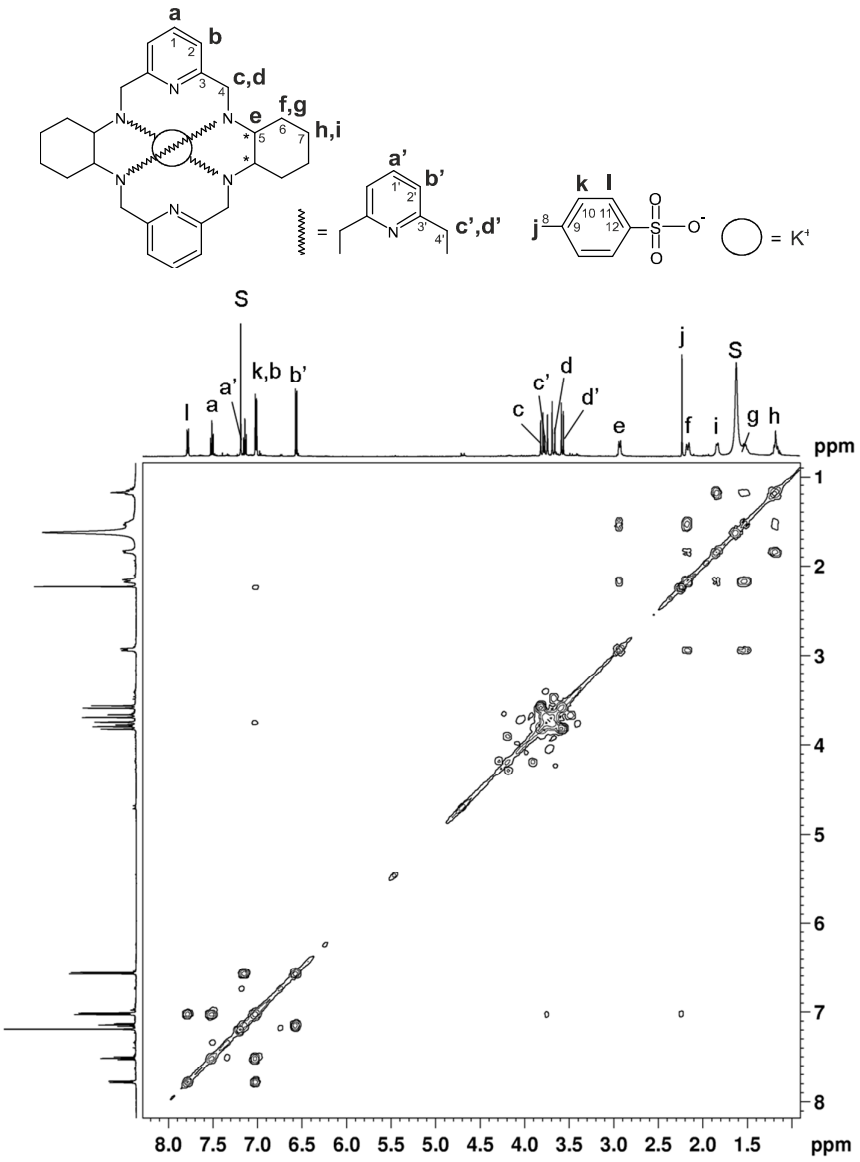

Figure S16. COSY spectrum (500 MHz, $CDCl_3$) of [$K^+\subset$ *R*-**6**]OTs.

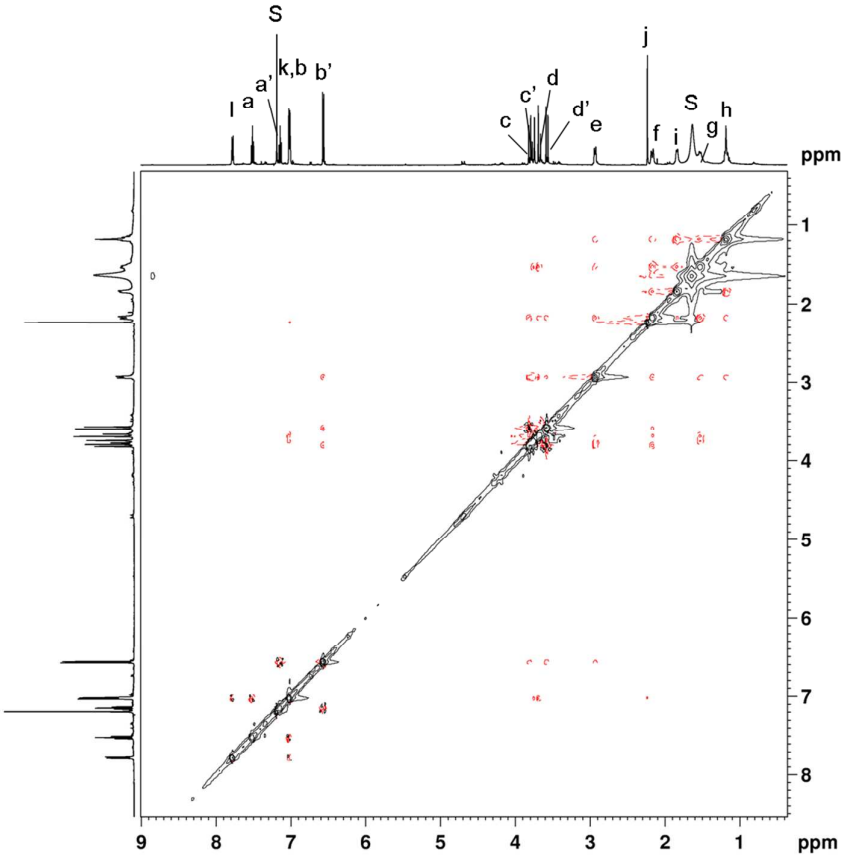

Figure S17. NOESY spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ ***R*-6**]OTs.

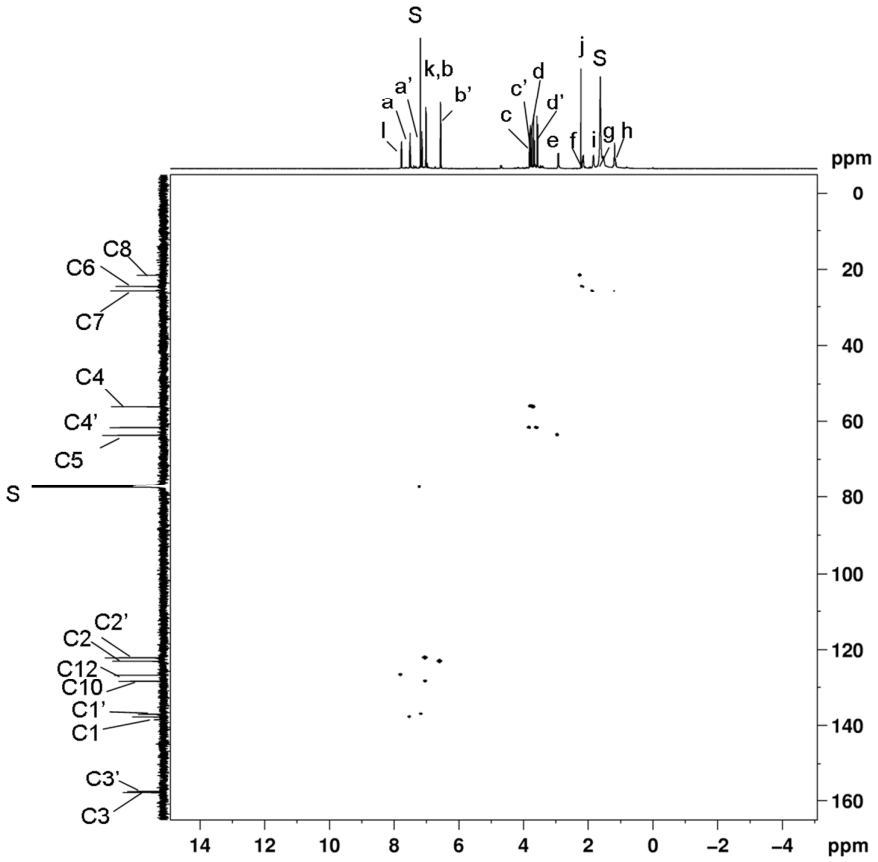

Figure S18. HMQC spectrum (500 MHz, $CDCl_3$) of [$K^+ \subset$ *R*-**6**]OTs.

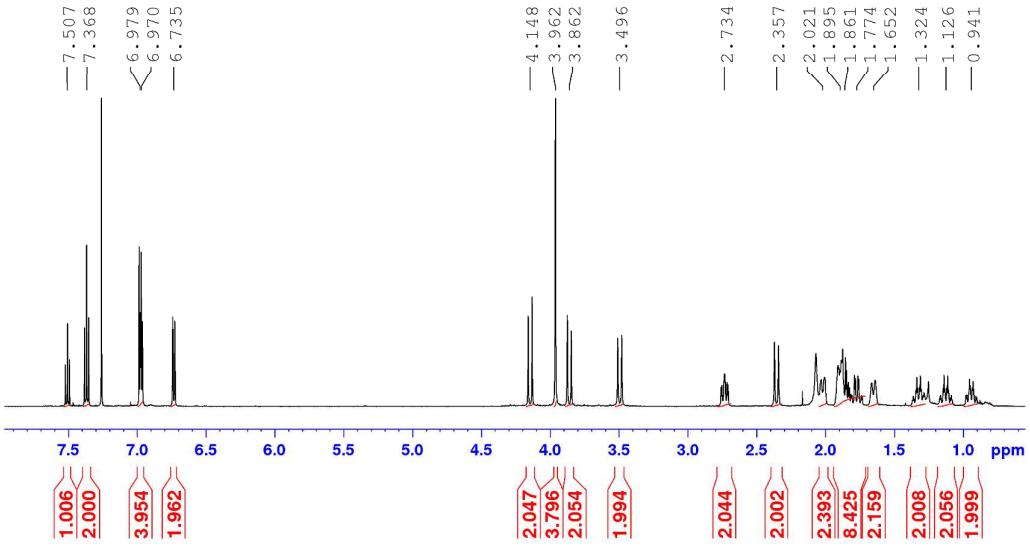

Figure S19. ^1H NMR spectrum (500 MHz, $CDCl_3$) of **5**.

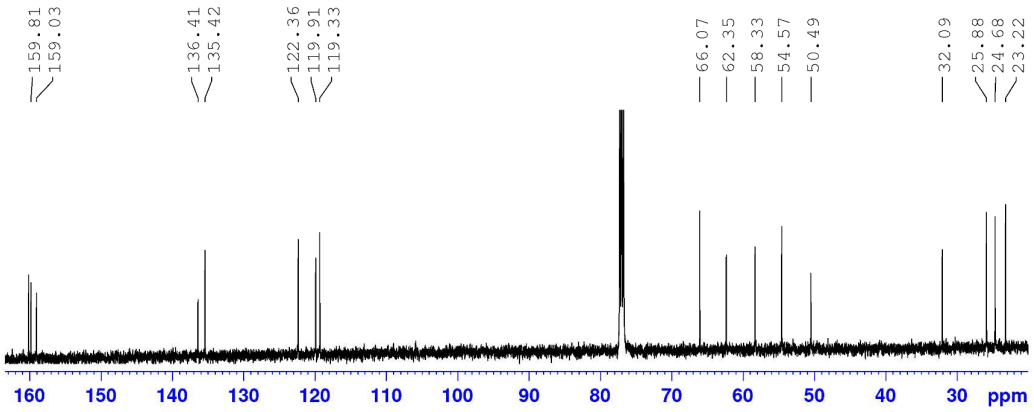

Figure S20. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of **5**.

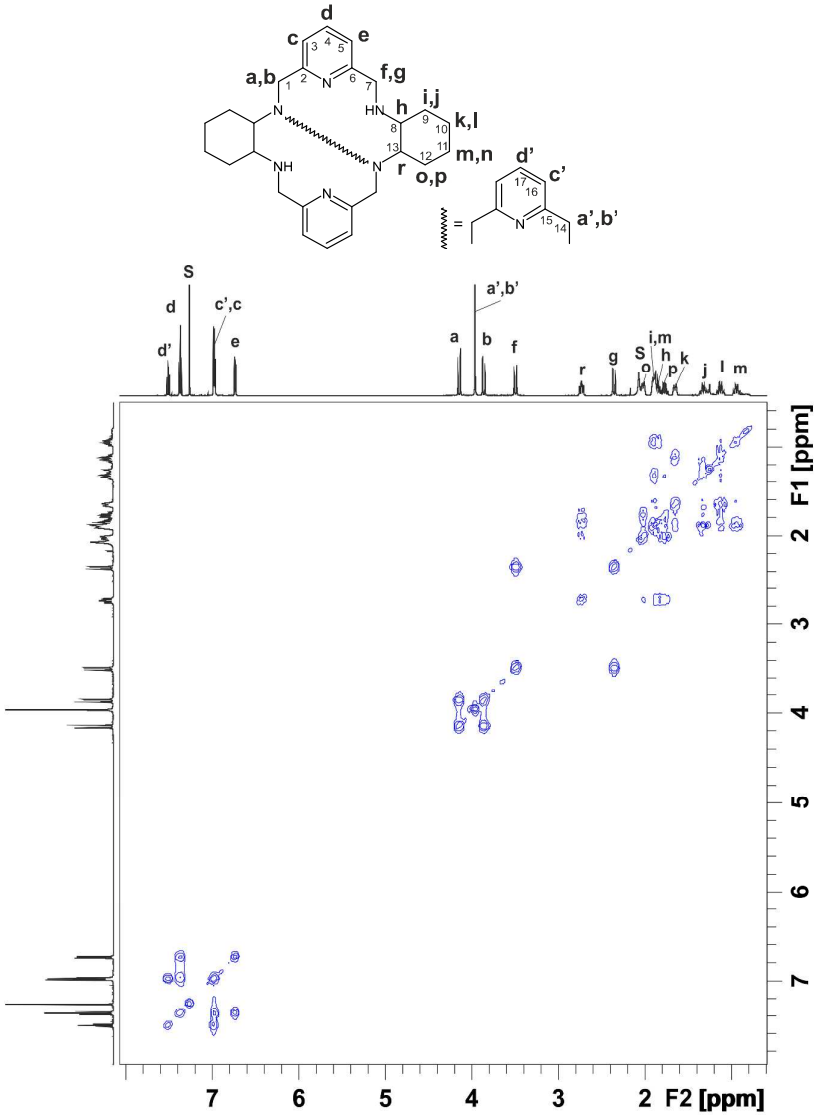

Figure S21. COSY spectrum (500 MHz, $CDCl_3$) of **5**.

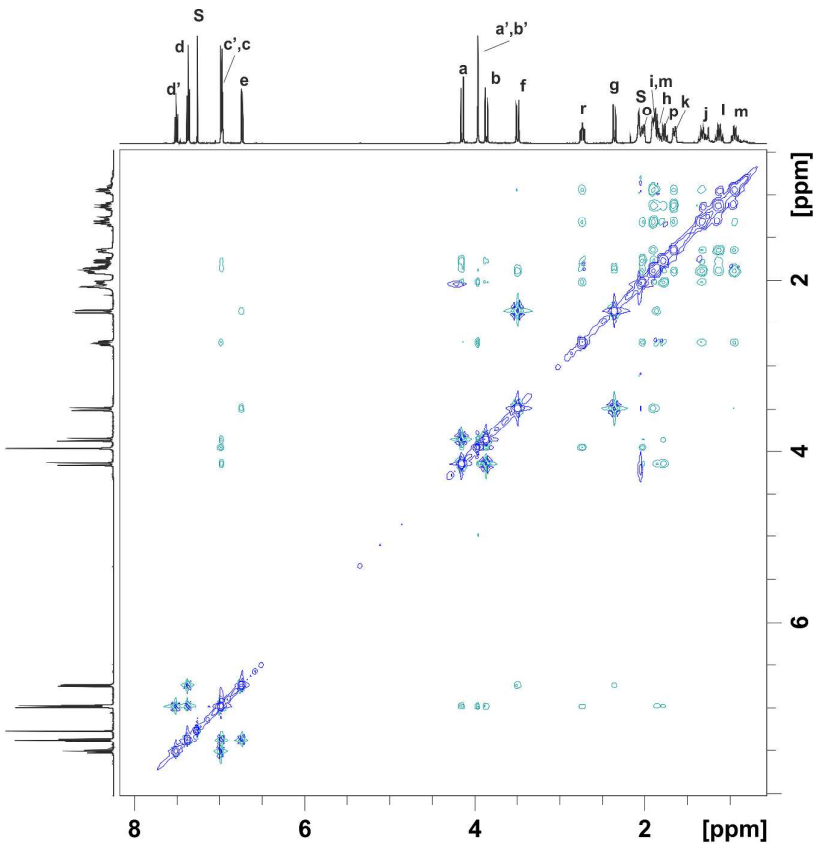

Figure S22. NOESY spectrum (500 MHz, $CDCl_3$) of **5**.

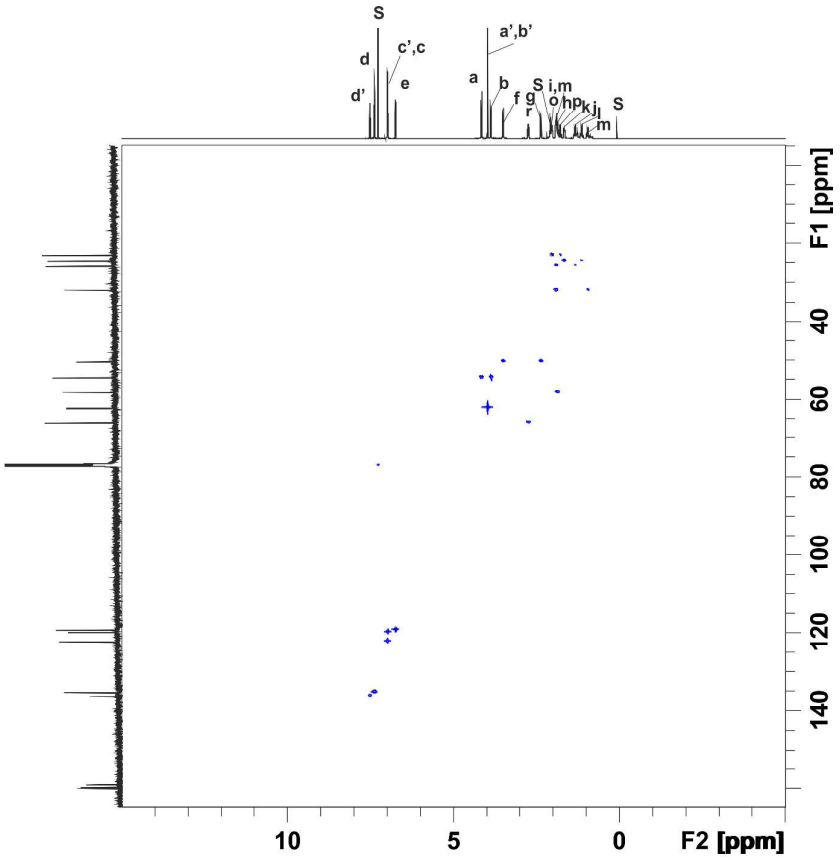

Figure S23. HMQC spectrum (500 MHz, $CDCl_3$) of **5**.

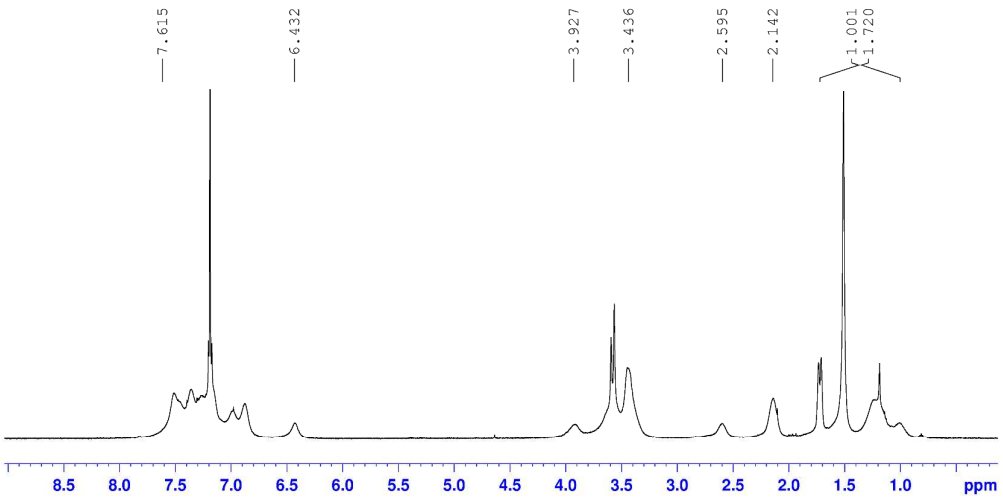

Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **8**.

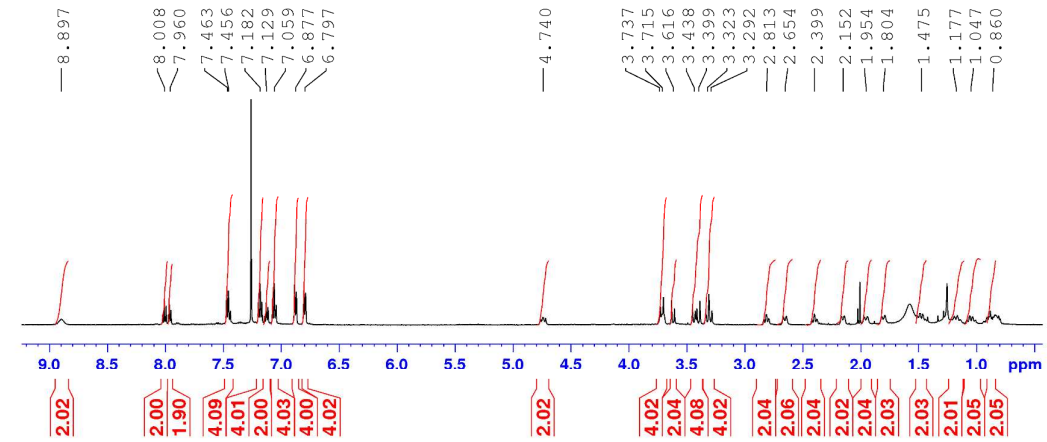

Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **8·2HClO$_4$**.

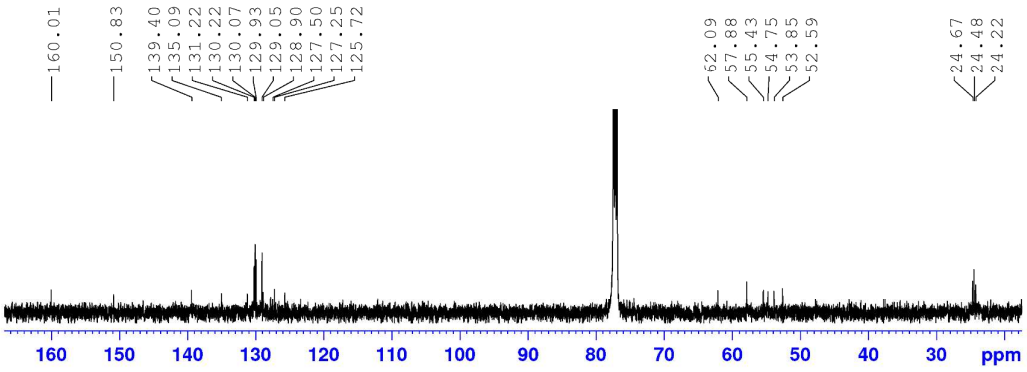

Figure S26. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of **8·2HClO$_4$**.

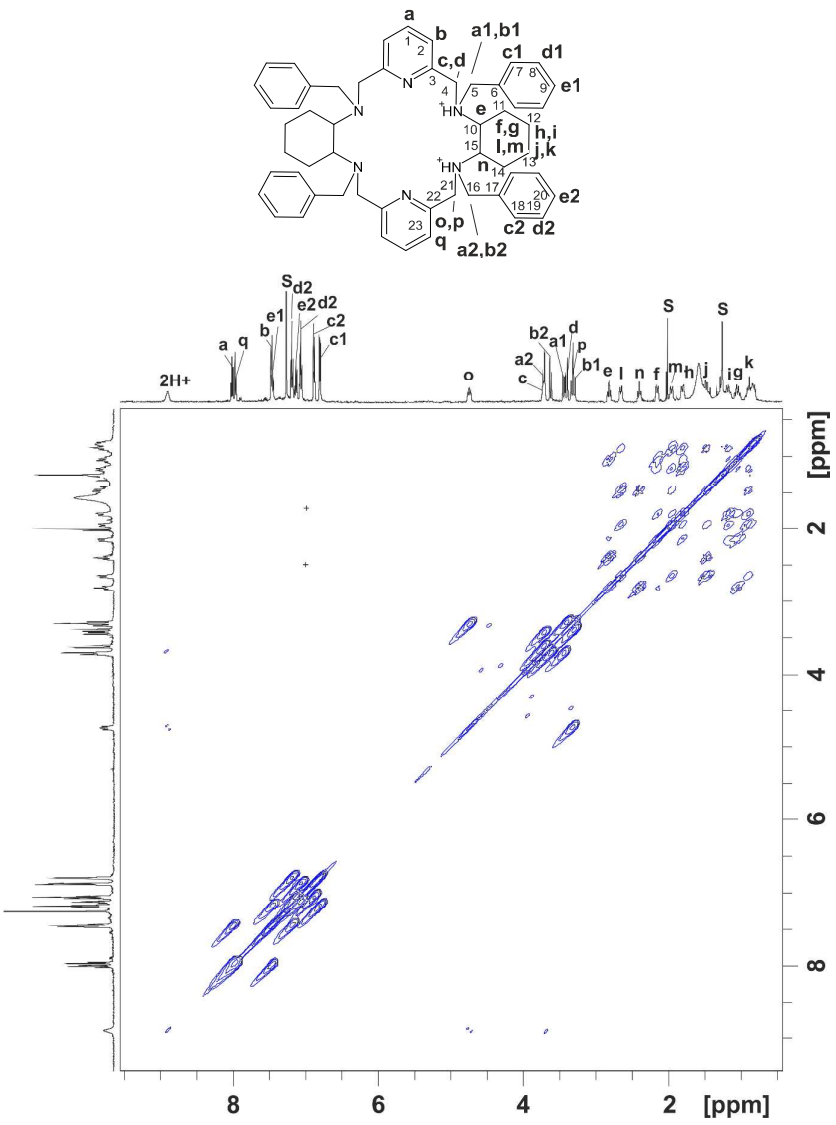

Figure S27. COSY spectrum ($CDCl_3$, 500 MHz, 298K) of **8·2HClO$_4$**.

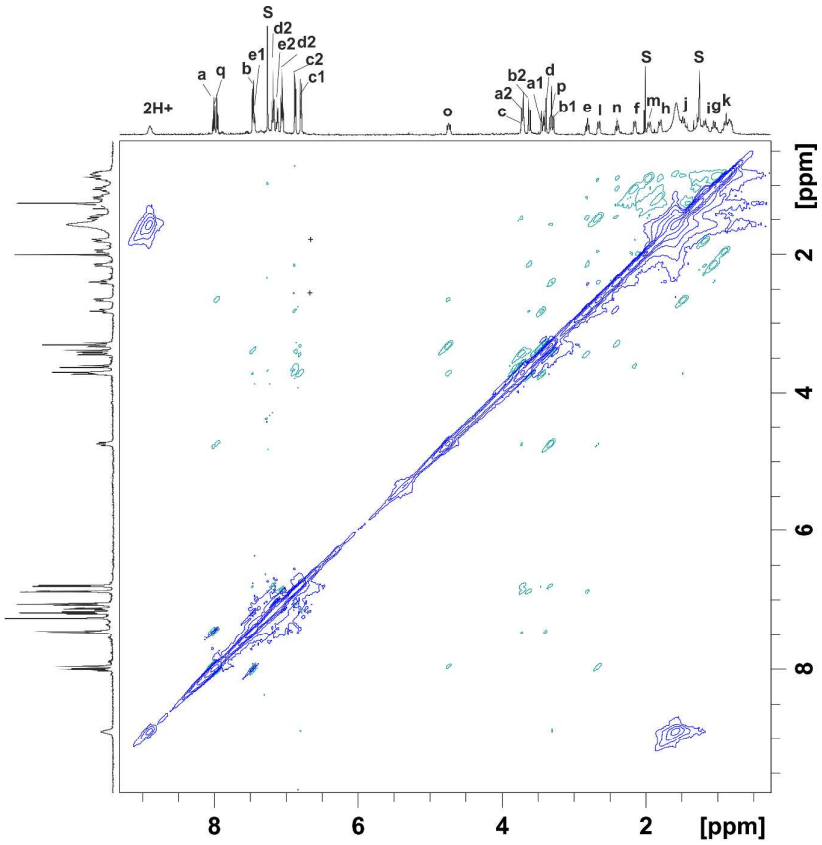

Figure S28. NOESY spectrum ($CDCl_3$, 500 MHz, 298K) of **8·2HClO$_4$**.

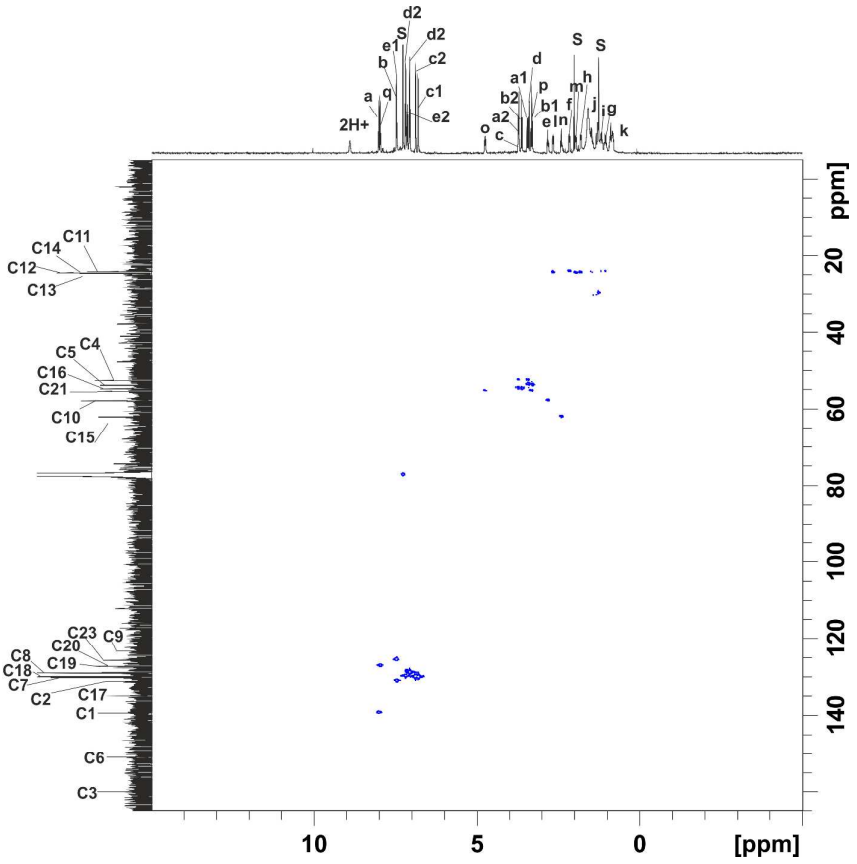

Figure S29. HMQC spectrum ($CDCl_3$, 500 MHz, 298K) of **8·2HClO$_4$**.

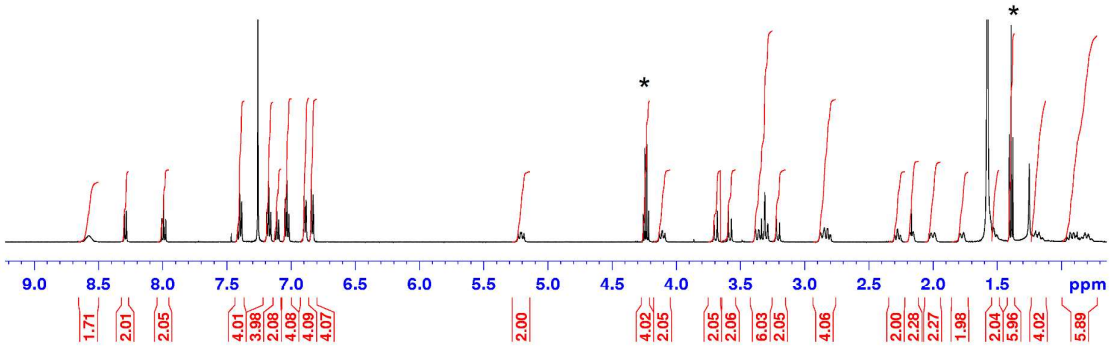

Figure S30. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298K) of **8·2H$_2$C$_2$H$_5$SO$_4$·2CH$_3$CN**.

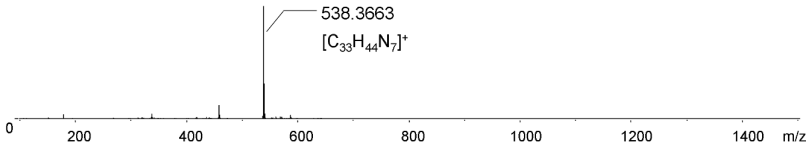

Figure S31. ESI-MS spectrum of *R*-**5**.

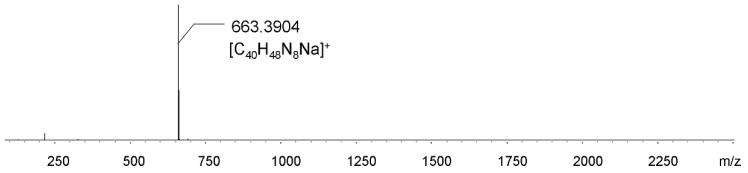

Figure S32. ESI-MS spectrum of [$Na^+\subset$ *R*-**6**]Br.

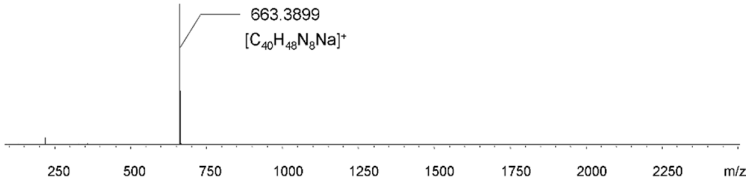

Figure S33. ESI-MS spectrum of [$Na^+\subset$ *S*-**6**]Br.

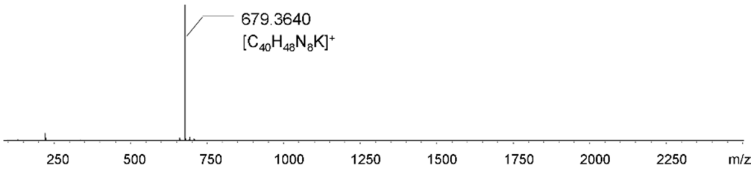

Figure S34. ESI-MS spectrum of [$K^+\subset$ *R*-**6**]Br.

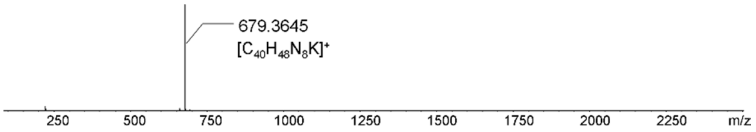

Figure S35. ESI-MS spectrum of [$K^+\subset$ *R*-**6**]OTs.

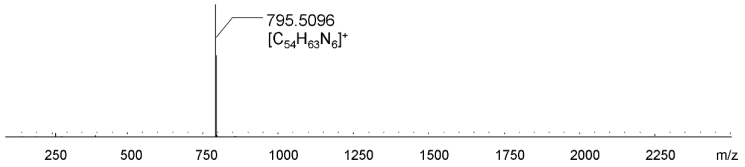

Figure S36. ESI-MS spectrum of **8**.

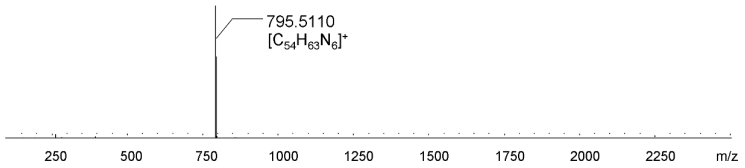

Figure S37. ESI-MS spectrum of **8**·**2HClO$_4$**.

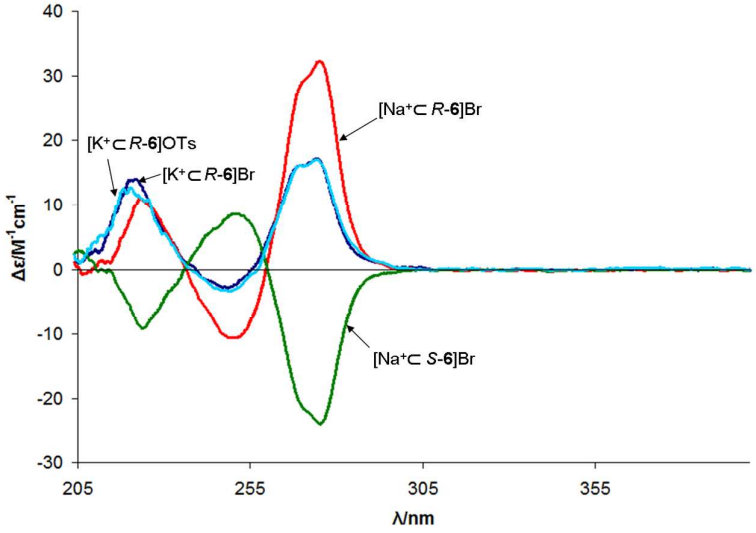

Figure S38. CD spectra of 0.25 mM solutions of the cryptates of **6** in acetonitrile.

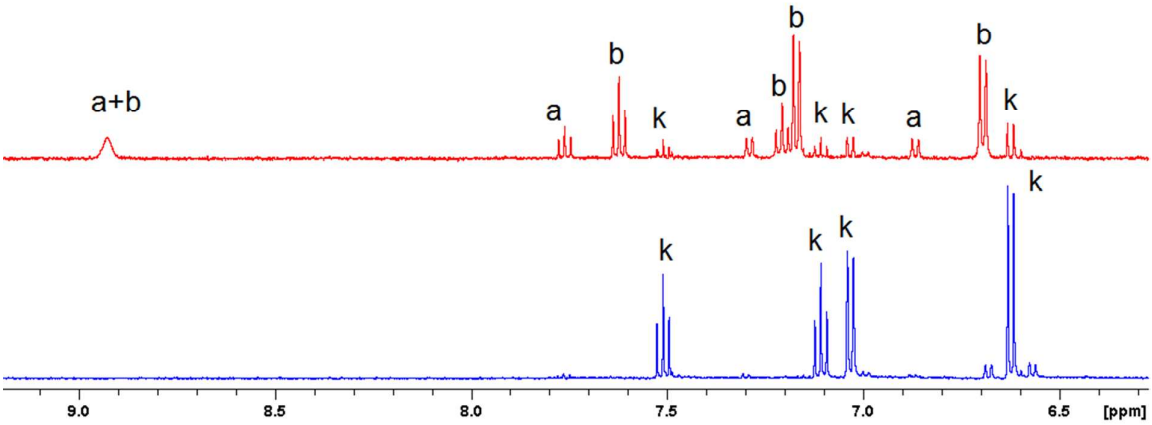

Figure S39. ^{1}H NMR spectrum (CD_3CN, 500 MHz, 298K) of [$K^+\subset$ ***R*-6**]Br before and after heating in water for 24 hours in a teflon vial. For the simplicity, only the aromatic part of the spectrum is shown (label **k** denotes the signals of [$K^+\subset$ ***R*-6**]Br, and **a, b** denotes the signals protonated cryptand forms).

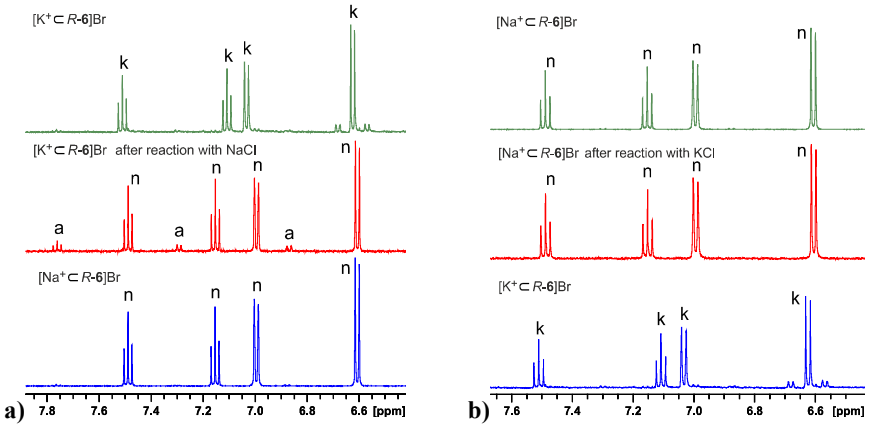

Figure S40. a) ^{1}H NMR spectrum (CD_3CN, 500 MHz, 298K) of [$K^+\subset$ ***R*-6**]Br before and after reaction with NaCl and spectrum of [$Na^+\subset$ ***R*-6**]Br for comparison, **b)** ^{1}H NMR spectrum (CD_3CN, 500 MHz, 298K) of [$Na^+\subset$ ***R*-6**]Br before and after reaction with KCl and spectrum of [$K^+\subset$ ***R*-6**]Br for comparison. For the simplicity, only the aromatic part of the spectrum is shown (label **k** denotes the signals of [$K^+\subset$ ***R*-6**]Br, **n** denotes the signals of [$Na^+\subset$ ***R*-6**]Br, and **a** denotes the signals of protonated cryptand form).

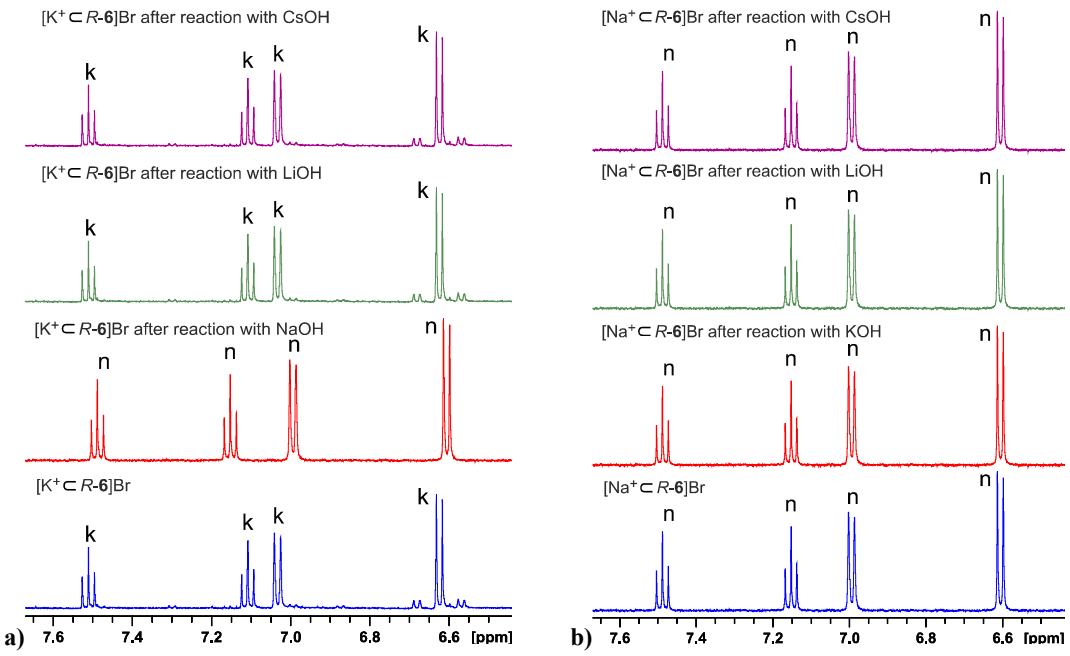

Figure S41. ^{1}H NMR spectrum (CD_3CN, 500 MHz, 298K) of the reaction of:

a) cryptand [$K^+\subset$ ***R*-6]**Br with potassium hydroxide, lithium hydroxide and cesium hydroxide.

b) cryptand [$Na^+\subset$ ***R*-6]**Br with potassium hydroxide, lithium hydroxide and cesium hydroxide For the simplicity, only the aromatic part of the spectrum is shown (label **k** denotes the signals of [$K^+\subset$ ***R*-6]**Br, **n** denotes the signals of [$Na^+\subset$ ***R*-6]**Br).

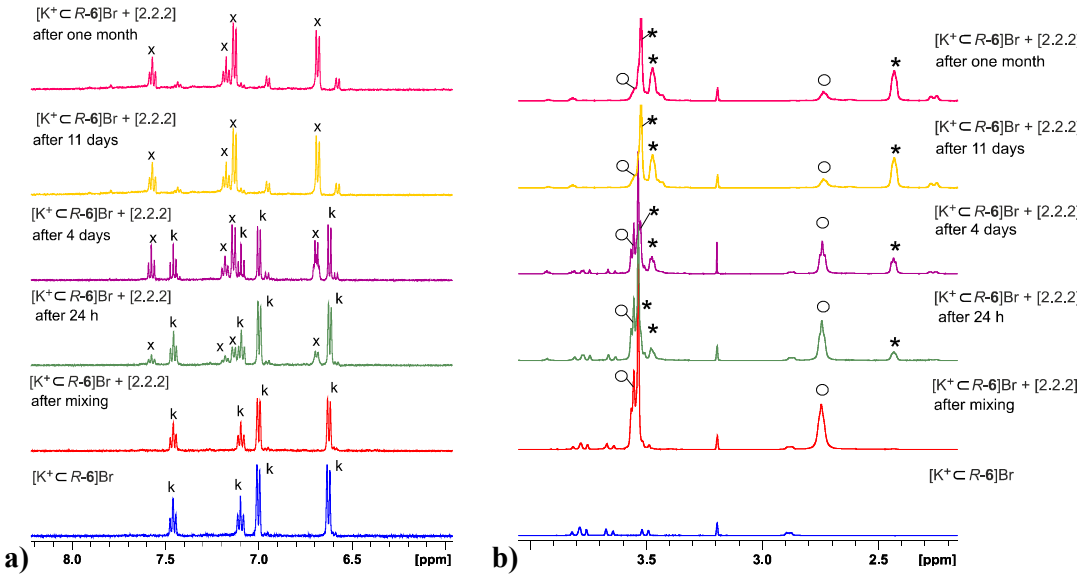

Figure S42. ^{1}H NMR spectrum (D_2O, 500 MHz, 298K) for competition reaction between [$K^+\subset$ ***R*-6**]Br cryptate and cryptand [2.2.2]; a**)** the aromatic fragment of the spectrum (label **k** denotes the signals of [$K^+\subset$ ***R*-6**]Br, label **x** - a new series of signals of demetallated form), b) the fragment showing the signals of the cryptand [2.2.2] (where ○ denotes the signals of free cryptand [2.2.2], and * denotes the signals of potassium cryptate $K^+\subset$ [2.2.2]).

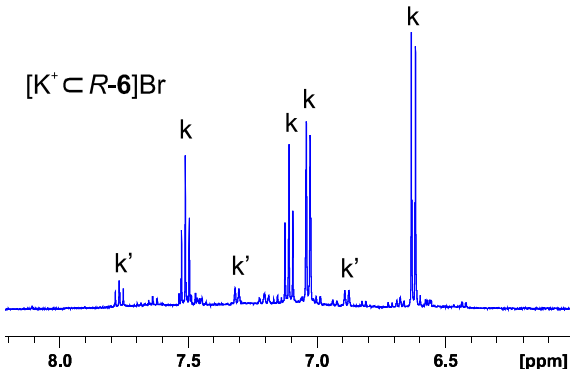

Figure S43. Aromatic region of the ^{1}H NMR spectrum (CD_3CN, 500 MHz, 298K) of a crude product [$K^+\subset$ ***R*-6**]Br, from which the crystals of perchlorate derivative of cryptand **7** were obtained after addition of perchloric acid. Labels **k** denote the signals of cryptand [$K^+\subset$ ***R*-6**]Br, labels **k'** denote signals of impurities, most likely those of the cryptand [$K^+\subset$ ***R*-7**]Br.

Details of X-ray crystal structure determination and crystallographic data

Crystals of $[Na^+\subset R\text{-}\mathbf{6}]Br{\cdot}2H_2O$, $[Na^+\subset S\text{-}\mathbf{6}]Br{\cdot}0.33MeOH{\cdot}0.5H_2O$, $[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.7MeOH{\cdot}0.9H_2O$, $[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.8MeOH{\cdot}0.7H_2O$ and $(R\text{-}\mathbf{7})(ClO_4)_4{\cdot}0.4H_2O$ were grown the vapor diffusion of diethyl ether to the methanol solution of the relevant compound. $(R\text{-}\mathbf{8})(EtOSO_3)_2{\cdot}2MeCN$ were grown the same method from the acetonitrile solution. X-ray quality crystals of $(R\text{-}\mathbf{5}){\cdot}4HCl{\cdot}7H_2O$ were obtained directly in the synthesis.

Crystals of $[Na^+\subset S\text{-}\mathbf{6}]Br{\cdot}0.33MeOH{\cdot}0.5H_2O$ (monoclinic, space group $P2_1$, a = 11.978(4), b = 21.207(8), c = 21.485(6) Å, β = 97.68(3)°, V = 5409(3) Å^3, T = 100(2) K, Z = 6, Z' = 3) were multiple twins, giving diffraction pattern of very low quality. Therefore its full crystal structure is not presented here. The obtained model (Figure S43) revealed almost identical molecular structure as that observed in the cryptates of *R*-**6** (compare Figure 2 in the main text).

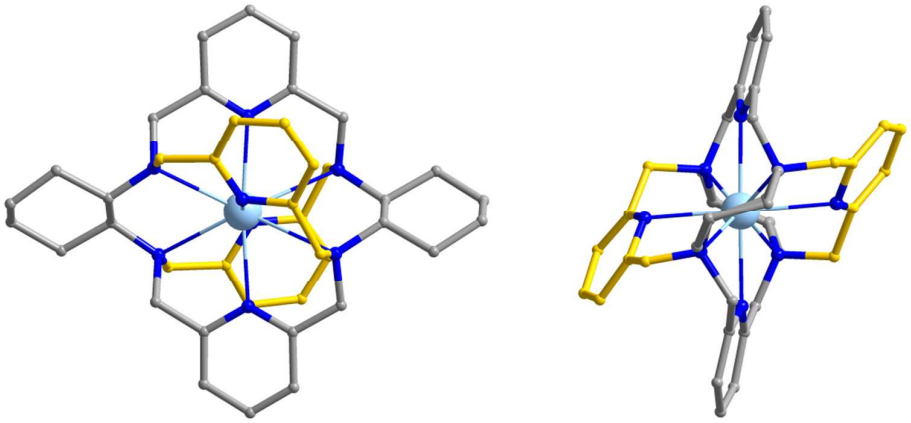

Figure S44. X-ray model of one of the independent cations in the crystal of $[Na^+\subset S\text{-}\mathbf{6}]Br{\cdot}0.33MeOH{\cdot}0.5H_2O$. Top (left) and side (right) views of the parent macrocyclic fragment (shown in grey).

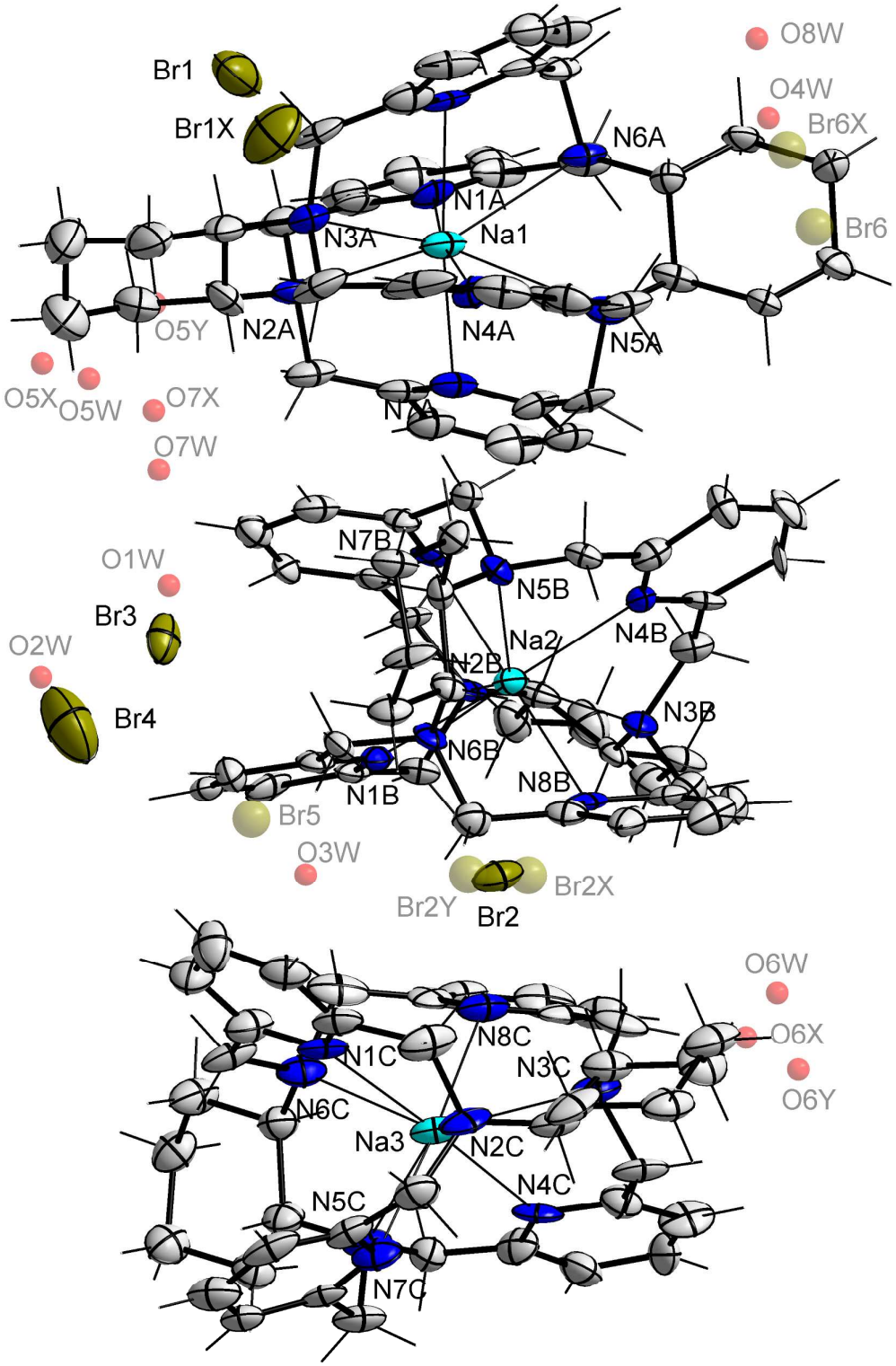

Figure S45. X-ray structure of [Na^+⊂*R*-**6**]Br·2H_2O, showing the partial atom-numbering scheme (for Na, Br, O and N atoms). Transparent spheres represent partially occupied atoms, which were refined isotropically. Displacement ellipsoids are shown at the 50% probability level.

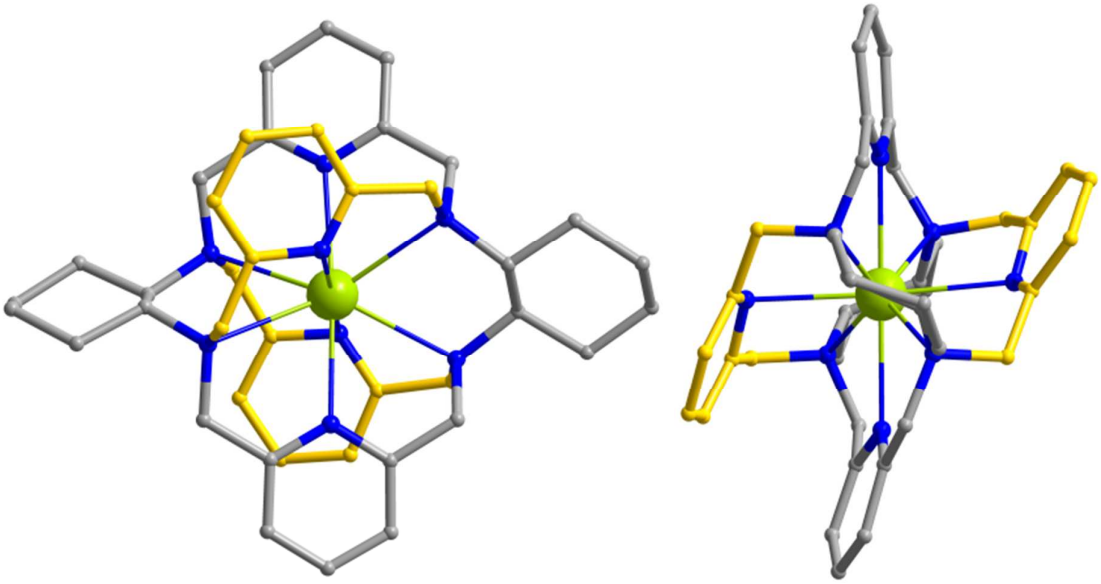

Figure S46. X-ray molecular structure of one of four independent cations $[K^+\subset R\text{-}6]^+$ of $[K^+\subset R\text{-}\mathbf{6}]Br\cdot 0.8MeOH\cdot 0.7H_2O$. The additional two pyridine fragments introduced to the macrocycle **1** are indicated in yellow. Top (left) and side (right) views of the parent macrocyclic fragment (shown in grey).

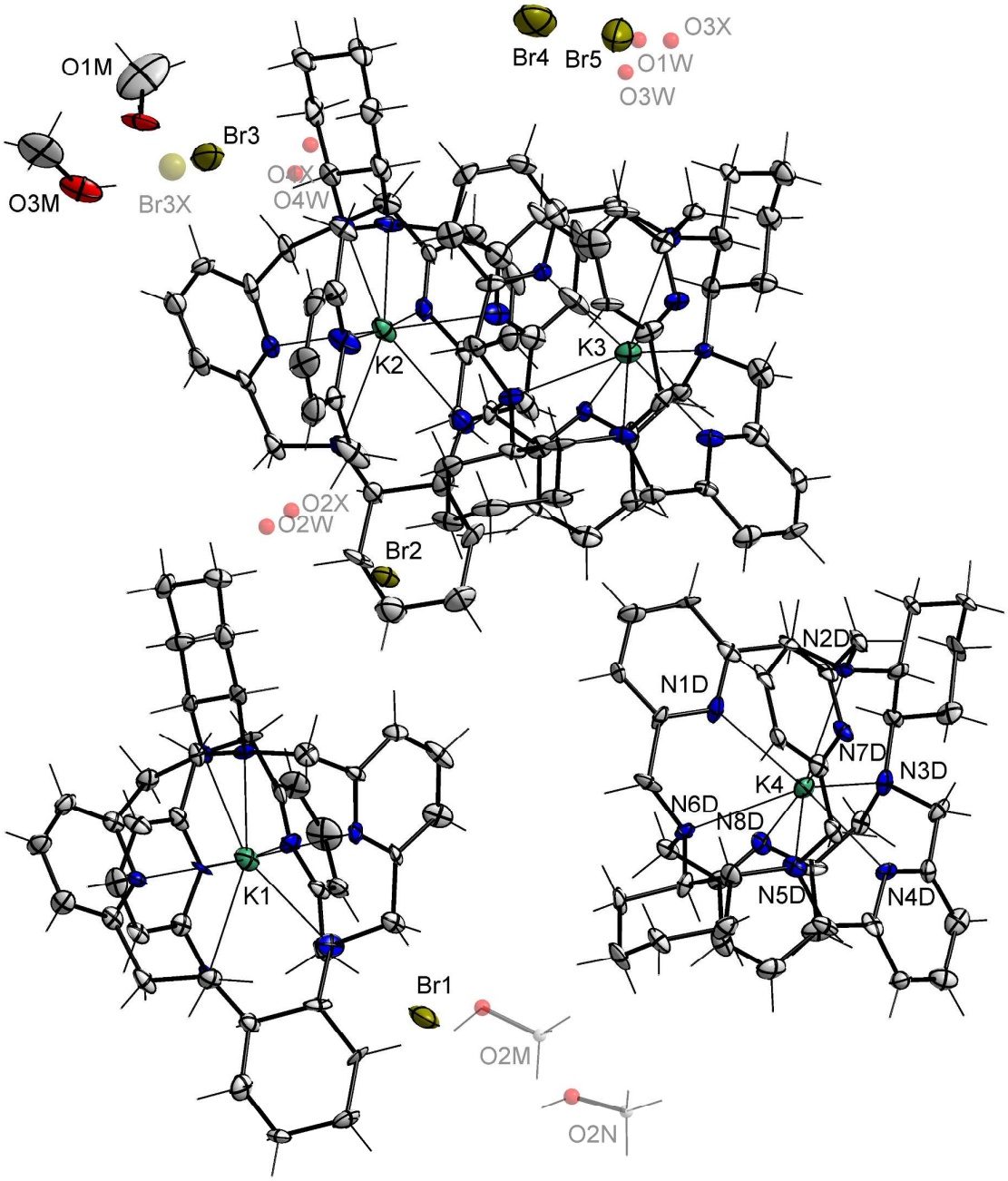

Figure S47. X-ray structure of $[K^{+}\subset R\text{-}\mathbf{6}]Br\cdot 0.7MeOH\cdot 0.9H_2O$, showing the partial atom-numbering scheme (for K, Br, O and selected N atoms). Transparent spheres (and bonds) represent partially occupied atoms, which were refined isotropically. Displacement ellipsoids are shown at the 50% probability level.

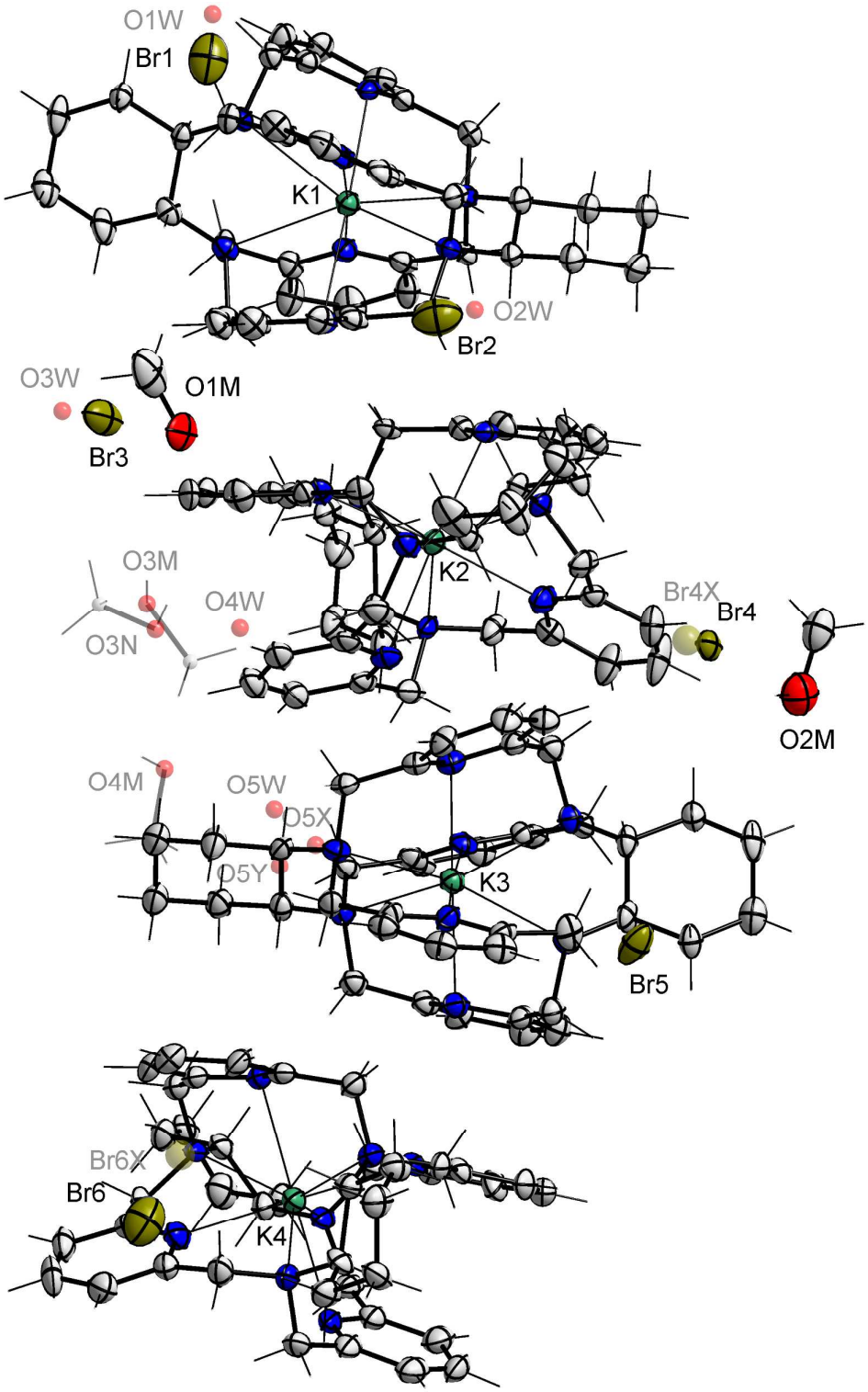

Figure S48. X-ray structure of $[K^{+}\subset R\text{-}\mathbf{6}]Br\cdot 0.8MeOH\cdot 0.7H_2O$, showing the partial atom-numbering scheme (for K, Br and O atoms). Transparent spheres (and bonds) represent partially occupied atoms, which were refined isotropically. Displacement ellipsoids are shown at the 50% probability level.

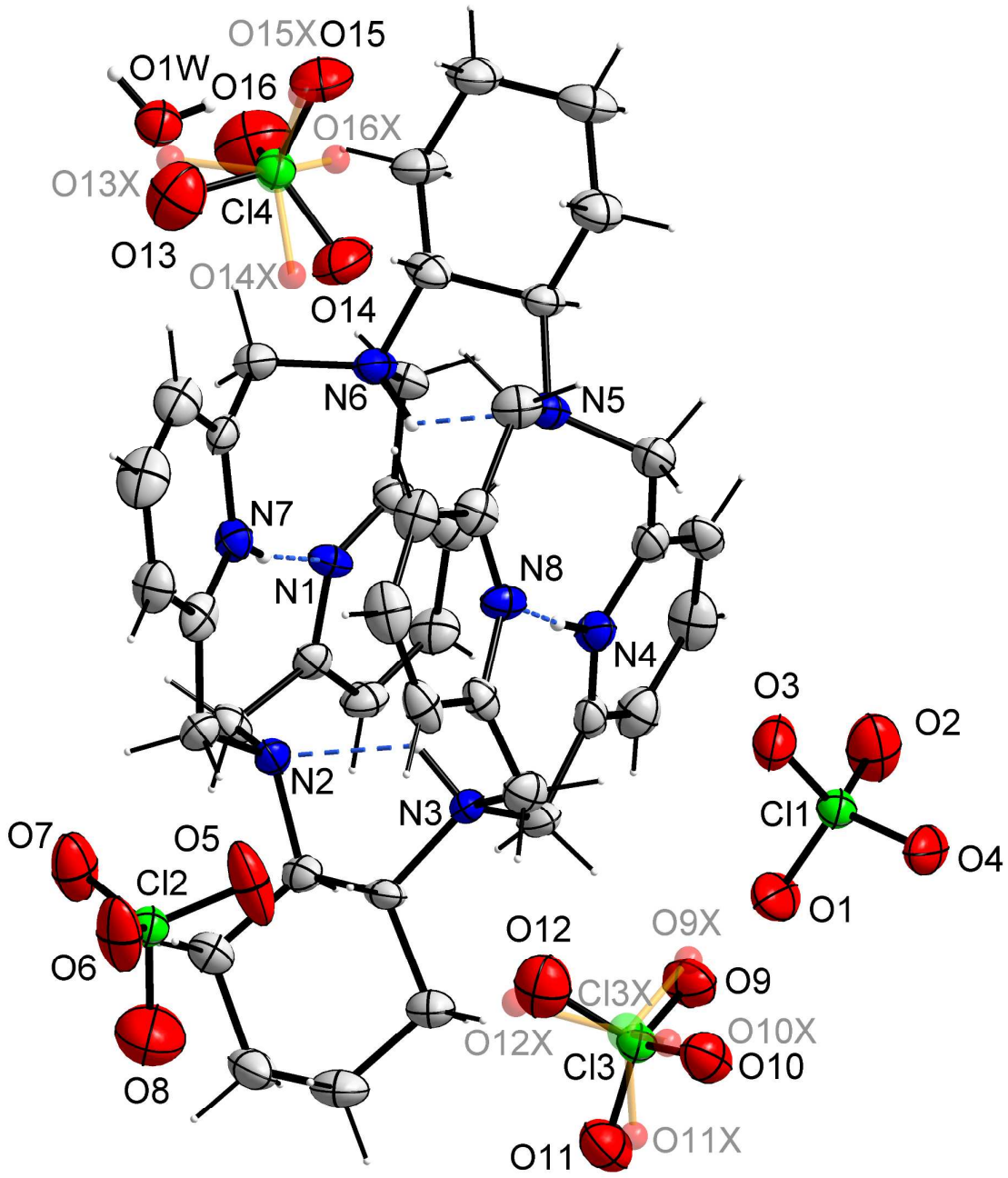

Figure S49. X-ray structure of (*R*-**7**)$(ClO_4)_4 \cdot 0.4H_2O$, showing the partial atom-numbering scheme (for Cl, O and N atoms), and symmetry independent intramolecular N–H···N hydrogen bonds (blue dashed lines). Transparent spheres (and bonds) represent positions of disordered perchlorate anions with lower occupancy factor (SOF < 0.5), which were refined isotropically. Displacement ellipsoids are shown at the 50% probability level.

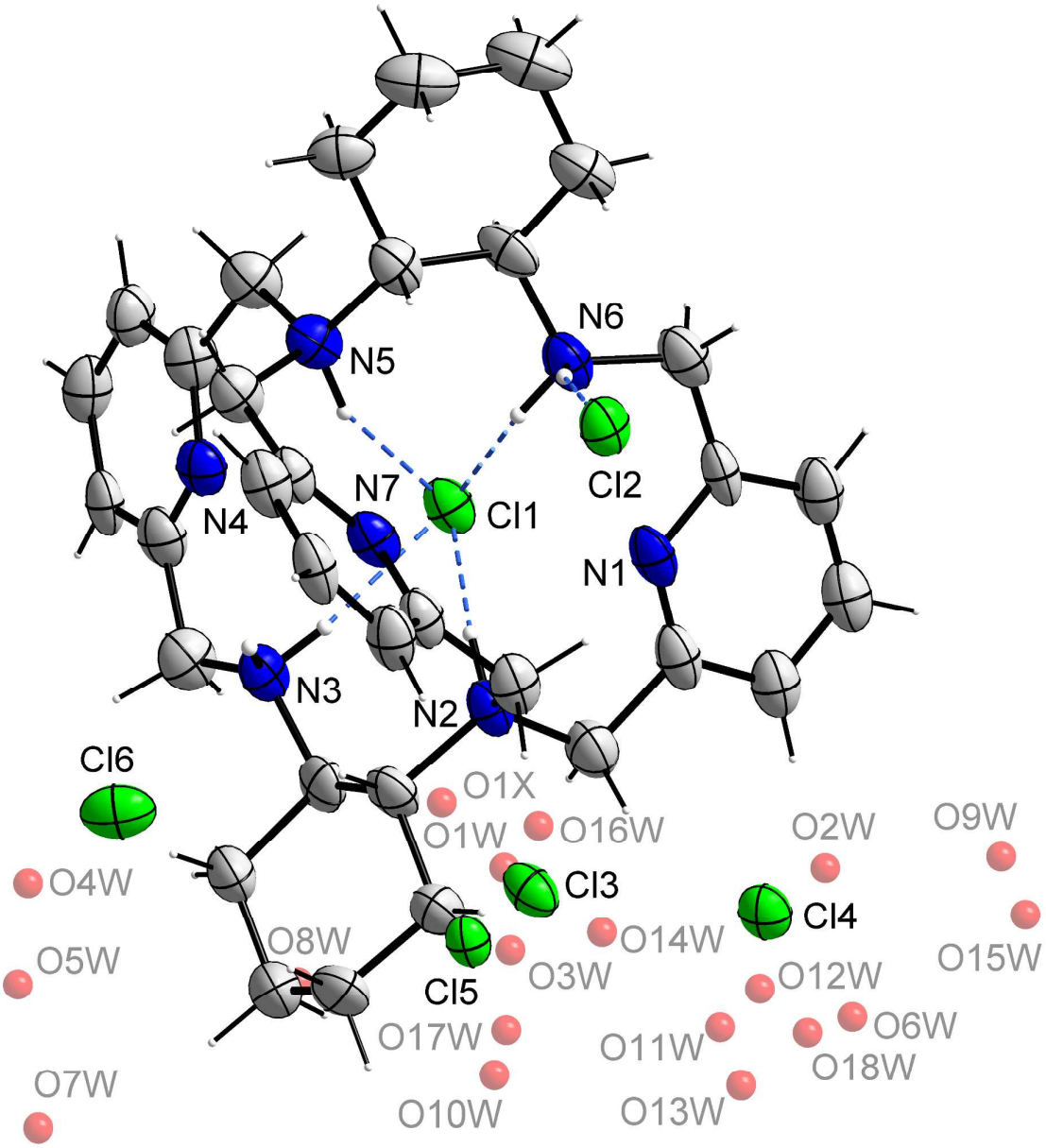

Figure S50. X-ray structure of (*R*-**5**)·4HCl·7H_2O, showing the partial atom-numbering scheme (for Cl, O and N atoms), and symmetry independent N–H···Cl hydrogen bonds (blue dashed lines). Transparent spheres represent partially occupied atoms, which were refined isotropically. Displacement ellipsoids are shown at the 50% probability level.

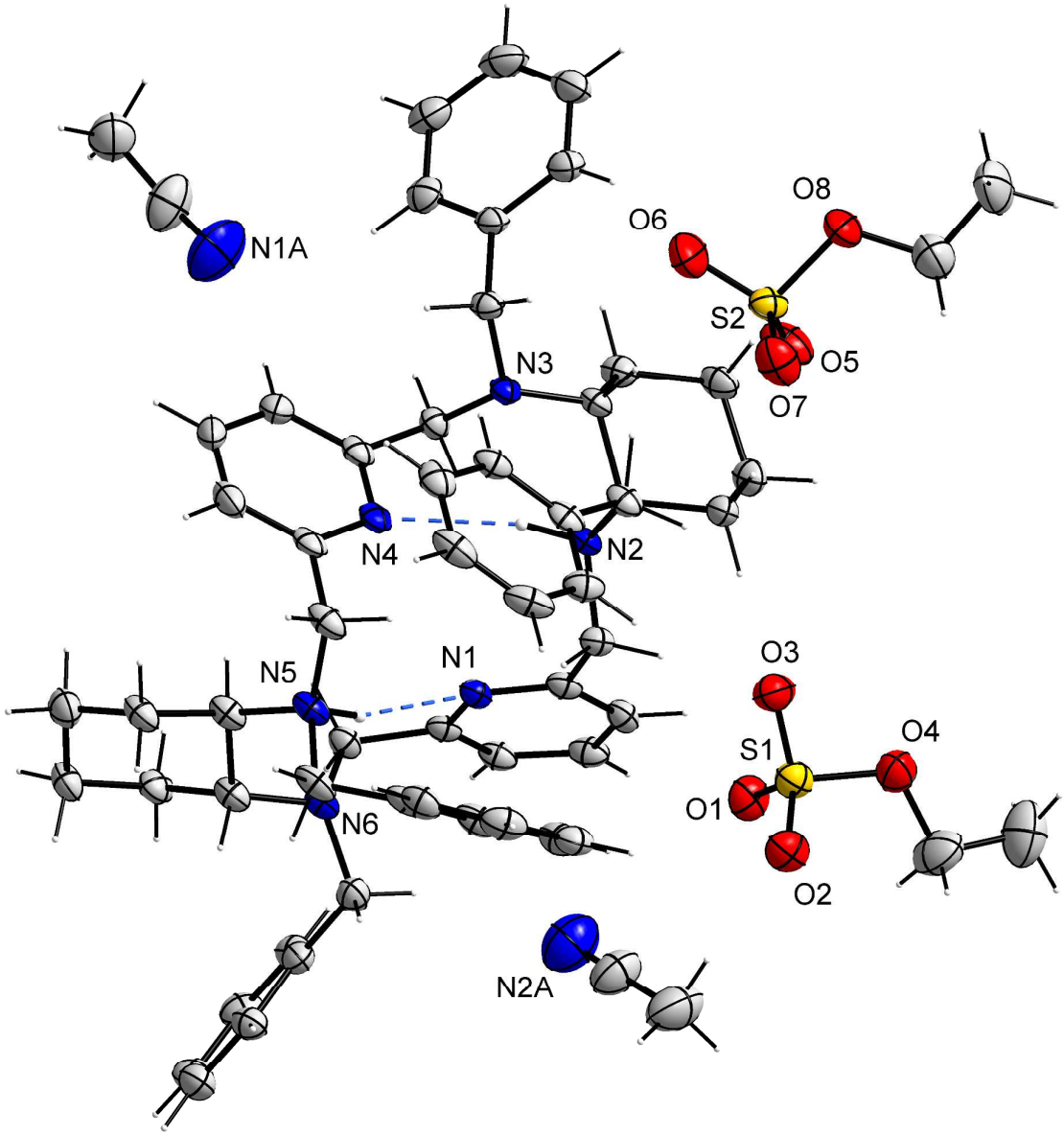

Figure S51. X-ray structure of (*R*-**8**)$(EtOSO_3)_2$·2MeCN, showing the partial atom-numbering scheme (for S, O and N atoms), and symmetry independent intramolecular N–H···N hydrogen bonds (blue dashed lines). Displacement ellipsoids are shown at the 50% probability level.

The crystallographic measurements for the remaining crystals were performed at 100(2)–120(2) K on a κ-geometry Kuma KM4-CCD, Agilent Technologies Xcalibur *R* or Oxford Diffraction Xcalirbur PX (ω scans) four-circle diffractometer with graphite-monochromatized Mo *K*α or Cu *K*α radiation (see details in Table S1). Data were corrected for Lorentz and polarization effects. Data collection, cell refinement, data reduction, and

analysis were carried out with *CrysAlis PRO*.[1] Analytical or empirical (multi-scan) absorption correction was applied to the data with the use of *CrysAlis PRO*.

Structures were solved by direct methods using the *SHELXT-2014*[2] program and refined on F^2 by a full-matrix least-squares technique using *SHELXL-2014*[2] with anisotropic thermal parameters for the ordered and fully occupied non-H atoms. Selected positions of the disordered positions of Br^-, Cl^- and ClO_4^- ions were also refined anisotropically (details are given below).

There are three or four crystallographically different molecules in $[Na^+\subset$*R*-**6**$]Br\cdot 2H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$ and $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$, all of them lying in general position. Most of the positions of Br^- ions in $[Na^+\subset$*R*-**6**$]Br\cdot 2H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$ and $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$, and Cl^- in (*R*-**5**)$Cl_4\cdot 7H_2O$ were found to be disordered (in two or three sites) or partially occupied, and were refined with site-occupancy factors (SOFs) of 0.523(5)/0.477(5), 0.89(2)/0.052(12)/0.053(17), 0.317(6), 0.328(9), 0.189(8), 0.084(5)/0.084(5) for Br1/Br1*X*, Br2/Br2*X*/Br2*Y*, Br3, Br4, Br5, Br6/Br6*X* in $[Na^+\subset$*R*-**6**$]Br\cdot 2H_2O$; 0.706(5)/0.154(6), 0.658(5), 0.481(5) for Br3/Br3*X*, Br4, Br5 in $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$; 0.571(5), 0.388(5), 0.556(4), 0.966(7)/0.034(7), 0.294(5)/0.191(6) for Br1, Br2, Br3, Br4/Br4*X*, Br6/Br6*X* in $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$ and 0.414(13), 0.578(10), 0.401(14), 0.607(9) for Cl3, Cl4, Cl5, Cl6 in (*R*-**5**)$Cl_4\cdot 7H_2O$. The sites with the SOF > 0.2 were refined anisotropically. Two from four ClO_4^- ions in (*R*-**7**)$(ClO_4)_4\cdot 0.4H_2O$ were found to be disordered over two sites each, and were refined with SOFs of 0.63(2)/0.37(2) and 0.589(6)/0.411(6), respectively, with anisotropic displacement parameters for the sites with the higher occupancy.

All water positions in $[Na^+\subset$*R*-**6**$]Br\cdot 2H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$, (*R*-**7**)$(ClO_4)_4\cdot 0.4H_2O$ and (*R*-**5**)$Cl_4\cdot 7H_2O$ are partially occupied and were refined isotropically with SOFs given in the CIF files (some of them being constrained to 0.5 or 0.25). Water H atoms were not found in difference Fourier maps (except for water molecule in (*R*-**7**)$(ClO_4)_4\cdot 0.4H_2O$). Similarly, most of the methanol molecules in $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$ and $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$ are disordered or partially occupied and were refined iso- or anisotropically with SOFs refined or constrained to 0.5. Disorder of some solvent molecules in $[Na^+\subset$*R*-**6**$]Br\cdot 2H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.7MeOH\cdot 0.9H_2O$, $[K^+\subset$*R*-**6**$]Br\cdot 0.8MeOH\cdot 0.7H_2O$ and (*R*-**5**)$Cl_4\cdot 7H_2O$, as well as H_2O molecule in (*R*-**7**)$(ClO_4)_4\cdot 0.4H_2O$, is correlated with the disorder of the $Br^-/Cl^-/ClO_4^-$ ions.

All H atoms in [Na^+⊂*R*-**6**]Br·2H_2O, [K^+⊂*R*-**6**]Br·0.7MeOH·0.9H_2O and [K^+⊂*R*-**6**]Br·0.8MeOH·0.7H_2O, and C-bound H atoms in (*R*-**7**)$(ClO_4)_4$·0.4H_2O, (*R*-**5**)Cl_4·7H_2O and (*R*-**8**)$(EtOSO_3)_2$·2MeCN were included from geometry and were refined using a riding model, with C–H = 0.95–1.00 Å, O–H = 0.84 Å, and with U_{iso}(H) = 1.2U_{eq}(C) for CH, CH_2, or U_{iso}(H) = 1.5U_{eq}(C) for CH_3 and OH. N-bound H atoms in (*R*-**7**)$(ClO_4)_4$·0.4H_2O, (*R*-**5**)Cl_4·7H_2O and (*R*-**8**)$(EtOSO_3)_2$·2MeCN, and water H atoms in (*R*-**7**)$(ClO_4)_4$·0.4H_2O were found in difference Fourier maps and were refined with N–H bond lengths restrained to 0.910(2) Å for NH_2, 0.880(2)–1.000(2) Å for NH, and water O–H restrained to 0.840(2) Å, and with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O), and were then constrained to ride on their parent atoms (AFIX 3 or AFIX 6 instructions in *SHELXL-2014*).

Some geometrical restraints (DFIX, SAME instructions in *SHELXL-2014*), anti-bumping restraints (BUMP), restraints on anisotropic displacement parameters (ISOR, SIMU), restraints on linear combinations of free variables (sum of the occupancies of a multi-component halogen ion and/or solvent molecule disorder; SUMP) were applied in the refinement procedures if appropriate.

Absolute configuration of all the crystals was determined based on the chemical information (known absolute configuration of the substrates) and confirmed by anomalous-dispersion effects in diffraction measurements.

The finally accepted formulas are [Na^+⊂*R*-**6**]Br·2H_2O, [K^+⊂*R*-**6**]Br·0.7MeOH·0.9H_2O, [K^+⊂*R*-**6**]Br·0.8MeOH·0.7H_2O, (*R*-**7**)$(ClO_4)_4$·0.4H_2O, (*R*-**5**)Cl_4·7H_2O and (*R*-**8**)$(EtOSO_3)_2$·2MeCN, but the amount of solvent molecules in the halogen salts should be treated as a rough approximation. Details of the refinement procedures are given in Table S1 and the crystallographic information files (CIFs) deposited at the Cambridge Crystallographic Data Centre (CCDC Nos. 1810812-1810817) and provided as Supporting information.

Table S1. Crystallographic data for the $[Na^+\subset R\text{-}\mathbf{6}]Br{\cdot}2H_2O$, $[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.7MeOH{\cdot}0.9H_2O$, $[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.8MeOH{\cdot}0.7H_2O$, $(R\text{-}\mathbf{7})(ClO_4)_4{\cdot}0.4H_2O$, $(R\text{-}\mathbf{5})Cl_4{\cdot}7H_2O$ and $(R\text{-}\mathbf{8})(EtOSO_3)_2{\cdot}2MeCN$ crystals.

	$[Na^+\subset R\text{-}\mathbf{6}]Br{\cdot}2H_2O$	$[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.7MeOH{\cdot}0.9H_2O$	$[K^+\subset R\text{-}\mathbf{6}]Br{\cdot}0.8MeOH{\cdot}0.7H_2O$	$(R\text{-}\mathbf{7})(ClO_4)_4{\cdot}0.4H_2O$	$(R\text{-}\mathbf{5})Cl_4{\cdot}7H_2O$	$(R\text{-}\mathbf{8})(EtOSO_3)_2{\cdot}2MeCN$
CCDC No.	1810812	1810813	1810814	1810815	1810816	1810817
Chemical formula	$(C_{40}H_{48}N_8Na)Br{\cdot}2H_2O$	$(C_{40}H_{48}KN_8)Br{\cdot}0.7MeOH{\cdot}0.9H_2O$	$(C_{40}H_{48}KN_8)Br{\cdot}0.8MeOH{\cdot}0.7H_2O$	$(C_{40}H_{52}N_8)(ClO_4)_4{\cdot}0.4H_2O$	$(C_{33}H_{47}N_7)Cl_4{\cdot}7H_2O$	$C_{54}H_{64}N_6{\cdot}2EtOSO_3{\cdot}2MeCN$
M_r	779.79	798.51	798.12	1049.90	809.68	1129.46
Crystal system, space group	Triclinic, $P1$	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Tetragonal, $P4_12_12$	Orthorhombic, $P2_12_12_1$
Temperature (K)	103(2)	100(2)	100(2)	120(2)	100(2)	100(2)
a, b, c (Å)	11.966(4), 13.517(5), 19.836(5)	12.092(4), 27.403(8), 23.358(9)	21.201(4), 26.732(6), 26.969(5)	11.232(2), 12.217(2), 33.308(8)	12.559(3), 12.559(3), 56.211(9)	16.703(3), 18.692(4), 18.760(4)
α, β, γ (°)	95.32(3), 104.25(3), 106.60(3)	90, 93.30(3), 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
V (Å^3)	2933.8(17)	7727(5)	15285(5)	4570.6(16)	8866(4)	5857(2)
Z	3	8	16	4	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.11	1.22	1.23	0.34	2.83	0.15
Crystal size (mm)	0.85 × 0.14 × 0.07	0.17 × 0.14 × 0.03	0.28 × 0.26 × 0.18	0.20 × 0.14 × 0.14	0.29 × 0.25 × 0.24	0.32 × 0.28 × 0.25
Diffractometer	Kuma, KM4-CCD	Agilent Technologies, Xcalibur R	Kuma, KM4-CCD	Agilent Technologies, Xcalibur R	Oxford Diffraction, Xcalibur PX	Kuma, KM4-CCD
Absorption correction	Analytical	Multi-scan	Multi-scan	Multi-scan	Analytical	Multi-scan
T_{min}, T_{max}	0.571, 0.953	0.987, 1.000	0.928, 1.000	0.981, 1.000	0.509, 0.594	0.927, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24498, 14241, 7128	31263, 20409, 12798	132959, 36660, 22160	12453, 9403, 6209	67941, 8044, 7715	70483, 13979, 9603
R_{int}	0.131	0.063	0.114	0.039	0.106	0.120
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.607	0.595	0.661	0.661	0.601	0.661
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.095, 0.264, 1.00	0.078, 0.159, 1.00	0.079, 0.221, 1.02	0.075, 0.167, 1.02	0.103, 0.282, 1.08	0.061, 0.142, 0.94
No. of reflections	14241	20409	36660	9403	8044	13979
No. of parameters	1455	1905	1925	662	499	725
No. of restraints	12	109	22	86	7	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.83, −0.58	0.96, −0.45	0.87, −0.96	0.43, −0.47	0.67, −0.49	0.55, −0.35
Absolute structure parameter	0.002(17)	0.021(6)	0.029(4)	−0.02(5)	0.084(8)	−0.09(5)

Computer programs: *CrysAlis PRO* (Agilent Technologies, 2012), *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT-2014* (Sheldrick, 2015), *SHELXL-2014*/7 (Sheldrick, 2015).

Detailed Discussion of Density Functional Theory modeling of the cryptand 6 and its cryptates with alkali metal ions

The binding energies reported in the main text were calculated by simple subtraction of electronic energy of the free ion and optimized free ligand **6** from the energy of the complex. Thus, the energies include structural relaxation, but do not include solvation effects (e.g. dehydration of the ions) or entropy considerations. When constructing a thermodynamic cycle to calculate enthalpy or free energy of binding, one would take into account hydration of **6** and the metal ion; the first quantity is obviously constant throughout the series of metals. Therefore, as a partial measure of taking into account variations in hydration energetics of the alkali metal ions, their experimental hydration enthalpies[3] were added to the calculated binding energies. The table below summarizes the computational results for binding energies, including the total DFT energies used to calculate the relative values.

Table S2. Total energies (in atomic units) and binding energies (in kcal/mol) for cryptates $H_3O^+ \subset$ **6** and $M^+ \subset$ **6** calculated at the B3LYP-D3/def2-TZVP level.

Complex	**Total energy [a.u.]**	**Binding energy [kcal/mol]**	**Binding energy corrected by hydration enthalpy of M^+ [kcal/mol]**
$H_3O^+ \subset$ **6**	-2067.576162624	-119.0	
$Li^+ \subset$ **6**	-1998.190485109	-141.8	-17.8
$Na^+ \subset$ **6**	-2152.942229505	-127.2	-29.4
$K^+ \subset$ **6**	-2590.514937304	-87.3	-10.3
$Rb^+ \subset$ **6**	-2014.691739751	-59.4	+10.7
$Cs^+ \subset$ **6**	-2010.695852954	-22.2	+40.9
Chemical species	**Total energy [a.u.]**	**Chemical species**	**Total energy [a.u.]**
6	-1990.685902116	K^+	-599.6899915692
H_3O^+	-76.7006406386	Rb^+	-23.91124507124
Li^+	-7.278559562746	Cs^+	-19.97457725669
Na^+	-162.053673962		

The uncorrected binding energies indicate that there is monotonic loss of binding affinity with increased metal ion size. Tentative comparison with the binding energy for H_3O^+ shows that at least Rb^+ and Cs^+ shall not be efficiently cryptated by **6**. However, complexation of the ions by **6** requires their loss of hydration shell. When experimental hydration energies (which also monotonically decrease with the alkali metal ions size) are subtracted from the binding energies, this simple model shows that Li^+, Na^+ and K^+ can be indeed efficiently complexed, while rubidium and especially cesium shall not occupy the internal cavity of **6**.

Another aspect of the complexation of the alkali metal ions by **6** is the inclination of the added pyridine rings with respect to the prototypic macrocyclic ring of the parent compound **1**. This inclination is rather pronounced for Li^+ and increases with growing ion size, so that for Cs^+ the rings are already oriented rather in parallel (interestingly, not perpendicular) to the prototypic macrocyclic plane of **1** – see the Figure S52 below. Differences in metal complexation mode are also visible in the metal – nitrogen atom distances, summarized in Table S3.

Table S3. Minimal and maximal metal – nitrogen atom distances in the $M^+\subset$ **6** cryptates. Results of B3LYP-D3/def2-TZVP calculations. Contacts with pyridine and aliphatic nitrogen atoms are shown separately.

Complex	**Metal – aliphatic nitrogen distances [Å]**		**Metal – pyridine nitrogen distances [Å]**	
	Minimum	**Maximum**	**Minimum**	**Maximum**
$Li^+\subset$ **6**	2.513	3.096	2.280	2.539
$Na^+\subset$ **6**	2.709	2.883	2.459	2.526
$K^+\subset$ **6**	2.789	2.841	2.635	2.651
$Rb^+\subset$ **6**	2.825	2.868	2.704	2.745
$Cs^+\subset$ **6**	2.866	2.907	2.787	2.840

The structures of the complexes exhibit a curious phenomenon: both aliphatic and pyridinic nitrogen atoms form two types of contacts with the metal, a shorter and a longer one. Effectively

this makes the symmetry of the complex close to the C_2 point group, as found also in the experiment. However, this asymmetry is minimized in the case of potassium ion, which is located closest to the geometric center of the ligand. Thus, K^+ can be said to provide best fit for the cavity of **6**. Li^+, and to a lesser degree Na^+, are "too small" and leave some free space inside, while cesium is too large and distorts the ligand cage. This "entropic" consideration, combined with the discussion on energy above, nominates Na^+ and K^+ as the ions with maximal affinity for **6** in the alkaline metal series.

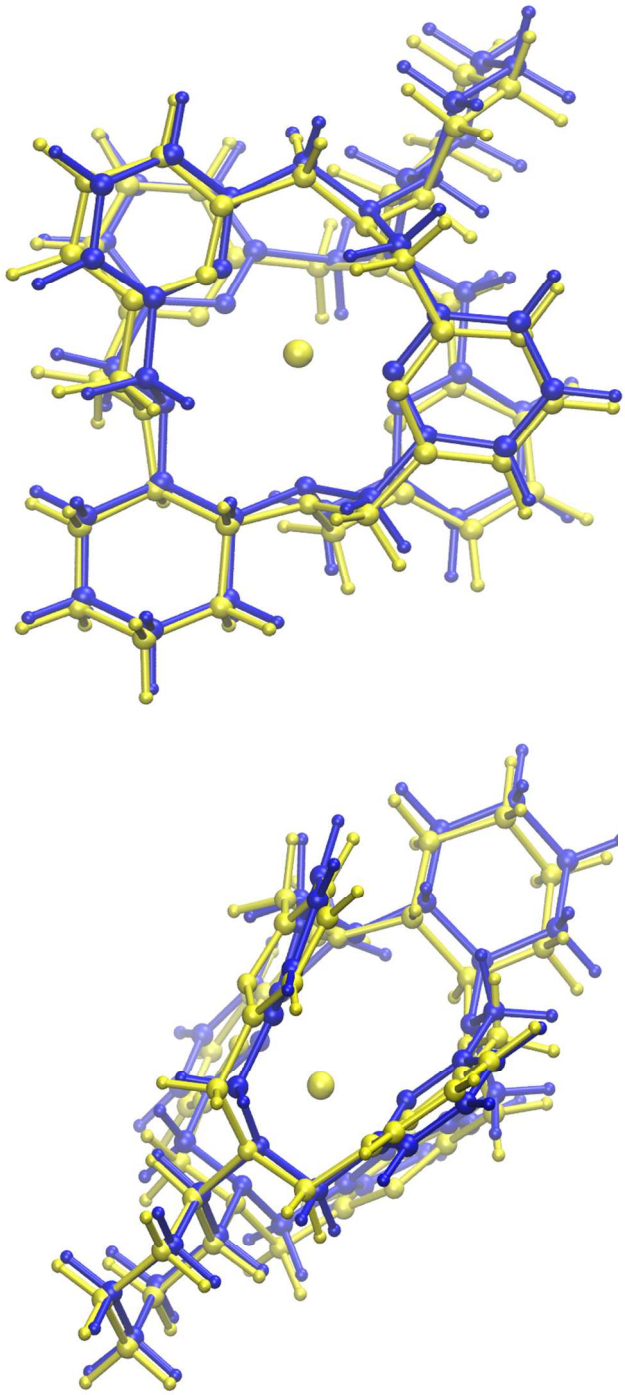

Figure S52. Top and side views of the structures of $Li^+\subset$**6** (blue) and $Cs^+\subset$**6** (yellow) optimized at the B3LYP-D3/def2-TZVP level, superimposed so that the metal positions coincide.

CARTESIAN COORDINATES OF THE STUDIED SYSTEMS OPTIMIZED AT THE B3LYP/def2-TZVP/D3 LEVEL OF THEORY

The structures are minima; no imaginary frequencies were found.

Data for **6**, empty cryptand

```
96
 Energy =   -1990.6859021160
 N     5.0374472   17.8091693   15.3272243
 N     7.0341629   16.6839404   13.2081518
 N     5.6664421   17.7080384   10.8872779
 N     3.0872021   15.9927173   11.2153845
 N     1.7683948   15.3942386   13.6103482
 N     2.2560269   17.8701452   15.1365050
 N     4.9254953   14.7503677   13.9283757
 N     3.5633462   19.0956206   12.4338953
 C     4.3775728   17.7605633   16.4720198
 C     5.0308753   17.7313351   17.7105299
 H     4.4580260   17.6989870   18.6300236
 C     6.4133993   17.7557226   17.7321917
 H     6.9510039   17.7369551   18.6726431
 C     7.1023678   17.8056142   16.5245578
 H     8.1844240   17.8279173   16.5014570
 C     6.3728028   17.8239504   15.3396702
 C     7.0546343   17.9129088   13.9992235
 H     6.5197887   18.6768225   13.4330044
 H     8.0823223   18.2678605   14.1780297
 C     7.7431028   16.7970130   11.9336396
 H     7.6224336   15.8304583   11.4348701
 C     9.2657845   17.0305521   12.0733823
 H     9.4462176   17.9739284   12.5968155
 H     9.6866760   16.2391333   12.7000562
 C     9.9804975   17.0798112   10.7232539
 H    11.0502883   17.2555548   10.8676622
 H     9.8870408   16.1088619   10.2223781
 C     9.3693557   18.1638698    9.8363670
 H     9.8633520   18.1898346    8.8609553
 H     9.5356260   19.1443428   10.2983373
 C     7.8693231   17.9264313    9.6628935
 H     7.7273493   16.9865584    9.1216449
 H     7.4261728   18.7133875    9.0458881
 C     7.1160888   17.8686674   11.0124300
 H     7.2704837   18.8387513   11.4943304
 C     5.2697312   16.4448952   10.2691637
 H     5.6187162   15.6387237   10.9161643
 H     5.7271873   16.3137077    9.2754268
 C     3.7847673   16.2466202   10.1047514
 C     3.1891195   16.2820165    8.8474611
 H     3.7841169   16.4830342    7.9657079
 C     1.8197658   16.0573356    8.7499719
 H     1.3246432   16.0804798    7.7865747
 C     1.1031990   15.8036939    9.9046949
 H     0.0361100   15.6171150    9.8706128
 C     1.7847346   15.7808197   11.1281646
 C     0.9954609   15.5059872   12.3949032
 H     0.2956683   16.3379864   12.5030569
 H     0.3676619   14.6156232   12.2006006
 C     1.0324901   15.7286443   14.8361926
 H     1.6384205   15.3661024   15.6677783
 C    -0.3366351   15.0172649   14.9340913
```

H	-0.9246257	15.2312784	14.0375218
H	-0.1716365	13.9360544	14.9409779
C	-1.1678479	15.4475057	16.1403455
H	-0.6535927	15.1789663	17.0710237
H	-2.1235279	14.9157267	16.1456018
C	-1.3846124	16.9591771	16.1021825
H	-1.9206445	17.2248439	15.1830689
H	-2.0121184	17.2852948	16.9364653
C	-0.0355755	17.6722377	16.1521551
H	0.4230117	17.4397745	17.1170855
H	-0.1676767	18.7577923	16.1296059
C	0.9249813	17.2648335	15.0116199
H	0.4971338	17.6502065	14.0852019
C	2.8603957	17.7360921	16.4420421
H	2.5626965	16.7745360	16.8668557
H	2.5067610	18.4991151	17.1613485
C	7.2639601	15.4425098	13.9246872
H	8.0988079	15.5021300	14.6428001
H	7.5481110	14.6870984	13.1874559
C	6.0340129	14.9133413	14.6504455
C	6.0943001	14.5918870	16.0057511
H	7.0094698	14.7466020	16.5613190
C	4.9583460	14.0986904	16.6275634
H	4.9734676	13.8388495	17.6791928
C	3.7998856	13.9552088	15.8787117
H	2.8961017	13.5621637	16.3276197
C	3.8178040	14.3075251	14.5267525
C	2.5714640	14.1727139	13.6749122
H	2.9029493	13.9415004	12.6655280
H	1.9771065	13.3141333	14.0357414
C	4.9586165	18.8959968	10.4433158
H	4.8307771	18.9414898	9.3487171
H	5.5673145	19.7616544	10.7168766
C	3.5979113	19.0843245	11.1012127
C	2.4539985	19.2642220	10.3246988
H	2.5199009	19.2399105	9.2452307
C	1.2360475	19.4467844	10.9599620
H	0.3294058	19.5904277	10.3845960
C	1.2007415	19.4320981	12.3461969
H	0.2694081	19.5847095	12.8772990
C	2.3898293	19.2382598	13.0538095
C	2.3922823	19.2120912	14.5695734
H	3.3515553	19.6109556	14.8900101
H	1.6065097	19.8927518	14.9438229

Data for $H_3O^+ \subset$ **6**

100

Energy = -2067.5761626240

O	4.1913257	16.9971051	13.1207764
H	3.6498279	17.1788923	13.9369564
H	5.1903804	16.8923314	13.2061065
H	3.7381978	16.5085023	12.3402174
N	5.1834479	17.8309487	15.4563144
N	6.8772031	16.6991620	13.3141465
N	5.5174092	17.8568409	10.8079443
N	3.0773565	16.0649081	11.0225367
N	1.8810182	15.3161772	13.5459709
N	2.4228834	17.9010437	15.0383920
N	4.9066763	14.5193736	13.9431671
N	3.5281409	19.4473990	12.4272976
C	4.4483584	17.8887560	16.5533315

C	5.0268215	17.9799546	17.8228297
H	4.4069061	18.0442341	18.7084647
C	6.4081760	17.9822029	17.9189283
H	6.8897391	18.0466495	18.8864662
C	7.1726455	17.8979705	16.7576167
H	8.2537938	17.8901528	16.8050759
C	6.5144477	17.8291487	15.5360565
C	7.2692577	17.7993841	14.2268155
H	7.0673480	18.7407367	13.7128382
H	8.3391408	17.7654122	14.4523158
C	7.5298125	16.8129798	11.9602483
H	7.2899804	15.8708624	11.4621542
C	9.0673813	16.8991168	12.0754812
H	9.3375436	17.7957054	12.6386796
H	9.4291210	16.0459490	12.6537238
C	9.7852731	16.9719685	10.7308466
H	10.8642476	17.0198584	10.8931950
H	9.5943659	16.0630981	10.1492928
C	9.2914778	18.1895609	9.9574472
H	9.7876774	18.2666028	8.9874761
H	9.5401126	19.1016551	10.5114869
C	7.7829966	18.0850473	9.7617376
H	7.5908448	17.2095182	9.1353449
H	7.4030743	18.9495468	9.2113481
C	6.9723002	17.9559130	11.0734154
H	7.1023500	18.8861471	11.6306397
C	5.1544545	16.7828846	9.8900155
H	5.7331182	15.8956133	10.1584960
H	5.4202253	17.0232595	8.8501620
C	3.7005172	16.3453448	9.8671041
C	3.0622418	16.1578966	8.6476508
H	3.5732692	16.3997180	7.7256572
C	1.7693594	15.6489649	8.6313935
H	1.2574625	15.4827772	7.6919791
C	1.1459427	15.3587311	9.8314715
H	0.1401232	14.9598729	9.8544587
C	1.8286479	15.6010019	11.0243439
C	1.0833445	15.4056035	12.3333018
H	0.4233248	16.2722440	12.4203345
H	0.4190762	14.5380940	12.1986133
C	1.1544999	15.7290242	14.7726731
H	1.7597884	15.3800802	15.6104439
C	-0.2261537	15.0430799	14.8907052
H	-0.8042333	15.2283920	13.9823256
H	-0.0757446	13.9620523	14.9424126
C	-1.0695578	15.5274442	16.0653637
H	-0.5768248	15.2922797	17.0156971
H	-2.0283621	15.0044164	16.0718717
C	-1.2673049	17.0356547	15.9530755
H	-1.7838575	17.2694636	15.0151418
H	-1.8994870	17.4109392	16.7607063
C	0.0914895	17.7280053	16.0033551
H	0.5208270	17.5174060	16.9850434
H	-0.0300680	18.8121218	15.9479269
C	1.0680556	17.2724422	14.8971262
H	0.6749185	17.6371841	13.9487499
C	2.9415249	17.8005140	16.4122236
H	2.6513833	16.8281659	16.8154161
H	2.4911598	18.5521413	17.0737797
C	7.1621612	15.3654748	13.9229861
H	8.0391930	15.4169048	14.5760872
H	7.4020997	14.6741771	13.1150868
C	5.9878540	14.7793035	14.6774001

C	6.0305431	14.5344522	16.0478463
H	6.9216857	14.7591516	16.6181269
C	4.9036302	14.0080279	16.6628288
H	4.9094884	13.7844557	17.7221307
C	3.7617770	13.7924004	15.9018148
H	2.8618154	13.3956251	16.3543442
C	3.7935086	14.0904562	14.5392674
C	2.5597383	14.0097189	13.6675117
H	2.8821741	13.7134452	12.6699833
H	1.8780938	13.2313267	14.0394020
C	4.9011244	19.1497902	10.4617811
H	4.8227042	19.2776906	9.3726418
H	5.5501226	19.9446338	10.8301893
C	3.5386866	19.3489762	11.0982382
C	2.3658625	19.3840535	10.3462070
H	2.4045347	19.3088301	9.2673753
C	1.1527744	19.5157828	11.0080079
H	0.2258685	19.5801362	10.4521112
C	1.1464126	19.5398642	12.3965072
H	0.2153913	19.6237533	12.9426738
C	2.3638742	19.4656568	13.0767096
C	2.4418033	19.3282242	14.5829161
H	3.3938742	19.7485166	14.8991486
H	1.6388695	19.8960677	15.0671989

Data for $Li^{+} \subset$ **6**

97

Energy = -1998.1904851090

Li	4.4562547	16.9442031	13.0568053
N	5.1304478	17.8229572	15.3412699
N	6.9519357	16.7573026	13.3018863
N	5.5609052	17.6096152	10.8998417
N	3.1217190	15.9972986	11.1367393
N	1.8236410	15.4245526	13.5875417
N	2.3104330	17.8580635	15.0934328
N	4.8346158	14.9216248	14.0396610
N	3.4546270	18.8993835	12.4196341
C	4.4142912	17.8646510	16.4613979
C	5.0042501	18.0135889	17.7210814
H	4.3821806	18.0532116	18.6065064
C	6.3786534	18.1084609	17.8145855
H	6.8628782	18.2161535	18.7768558
C	7.1264459	18.0699811	16.6432490
H	8.2052137	18.1472671	16.6691571
C	6.4633631	17.9351417	15.4313997
C	7.2334502	17.9308607	14.1398890
H	6.9600501	18.8279240	13.5804829
H	8.2985555	18.0109903	14.3856885
C	7.6554822	16.8043150	11.9950228
H	7.5036820	15.8189833	11.5473476
C	9.1787767	17.0172468	12.1144940
H	9.3780870	17.9652719	12.6201414
H	9.6003115	16.2304480	12.7456224
C	9.8826904	17.0579267	10.7593789
H	10.9533276	17.2184580	10.9032289
H	9.7754815	16.0935833	10.2502477
C	9.2784668	18.1614137	9.8939114
H	9.7678409	18.2024986	8.9184517
H	9.4461207	19.1338072	10.3704211
C	7.7816999	17.9165609	9.7125426
H	7.6629235	16.9773757	9.1666200
H	7.3340882	18.6983100	9.0931110

C	7.0200754	17.8381471	11.0515802
H	7.1133085	18.8161184	11.5301279
C	5.2539818	16.4372257	10.0693487
H	5.7456331	15.5658645	10.5069423
H	5.6357763	16.5488164	9.0479418
C	3.7815610	16.1457199	9.9789612
C	3.1653521	16.0240023	8.7413246
H	3.7355555	16.1618313	7.8323530
C	1.8099646	15.7184006	8.6955575
H	1.2981238	15.6134147	7.7473828
C	1.1341265	15.5454904	9.8870810
H	0.0812641	15.2929174	9.8981440
C	1.8258784	15.6995632	11.0931781
C	1.0405784	15.5427318	12.3751081
H	0.4050172	16.4277143	12.4585805
H	0.3521729	14.6946302	12.2288715
C	1.0608815	15.7391451	14.8126399
H	1.6547067	15.3530735	15.6451890
C	-0.3159135	15.0444760	14.8799382
H	-0.9012625	15.3017943	13.9937331
H	-0.1736018	13.9610539	14.8519162
C	-1.1367597	15.4512407	16.1018435
H	-0.6278739	15.1420666	17.0220948
H	-2.0998007	14.9359732	16.0890293
C	-1.3294145	16.9663404	16.1117824
H	-1.8737070	17.2710198	15.2104894
H	-1.9379714	17.2763722	16.9642214
C	0.0312009	17.6574085	16.1685856
H	0.4971666	17.3824726	17.1180840
H	-0.0861138	18.7441058	16.1856981
C	0.9608001	17.2658483	15.0004501
H	0.5150215	17.6714785	14.0885727
C	2.9106579	17.7214503	16.4044816
H	2.6802571	16.7245000	16.7881559
H	2.4919327	18.4274758	17.1397363
C	7.2000231	15.5061963	14.0241329
H	8.0191119	15.6019833	14.7476450
H	7.5231911	14.7532517	13.3009013
C	5.9855606	14.9218738	14.7190687
C	6.1117160	14.3215230	15.9693053
H	7.0525549	14.3673575	16.5016578
C	5.0157996	13.6694517	16.5114743
H	5.0794882	13.2000028	17.4850719
C	3.8413695	13.6102454	15.7728586
H	2.9774501	13.0740862	16.1434094
C	3.7871183	14.2468991	14.5363056
C	2.5530716	14.1615988	13.6675145
H	2.8856908	13.8988037	12.6640243
H	1.9182817	13.3355269	14.0220002
C	4.8547354	18.8045863	10.4283534
H	4.7231459	18.8041056	9.3390993
H	5.4710769	19.6774008	10.6578345
C	3.5146688	19.0531223	11.0932299
C	2.4347089	19.5203674	10.3485394
H	2.5119192	19.6038816	9.2725845
C	1.2690741	19.8725995	11.0101344
H	0.4089839	20.2313429	10.4588668
C	1.2328448	19.7783520	12.3950506
H	0.3562167	20.0847284	12.9507451
C	2.3478445	19.2886445	13.0693941
C	2.3805134	19.2234446	14.5794372
H	3.3279836	19.6569225	14.8975334
H	1.5822805	19.8629266	14.9856905

Data for $Na^+ \subset$ **6**

```
97
 Energy =   -2152.9422295050
Na    4.2741551   16.9300705   13.1624161
 N    5.1580668   17.7795959   15.3647791
 N    6.9659257   16.6536917   13.3087531
 N    5.5378209   17.7121471   10.8970386
 N    3.1067557   16.0375933   11.1076192
 N    1.8859877   15.3748266   13.5972437
 N    2.3278718   17.9189517   15.0394224
 N    4.8799873   14.7008363   14.0146385
 N    3.4523901   19.1246640   12.4178928
 C    4.4170821   17.9100909   16.4609318
 C    4.9840842   18.0924178   17.7259976
 H    4.3471953   18.2106232   18.5936702
 C    6.3603196   18.1114129   17.8473470
 H    6.8282925   18.2383368   18.8153599
 C    7.1326579   17.9716534   16.6999213
 H    8.2131763   17.9873090   16.7526885
 C    6.4934531   17.8222499   15.4763432
 C    7.3009358   17.7671096   14.2030316
 H    7.1221439   18.7016197   13.6667102
 H    8.3610148   17.7578074   14.4861249
 C    7.6215263   16.7675002   11.9774857
 H    7.4305822   15.8132601   11.4806080
 C    9.1541524   16.9303338   12.0796902
 H    9.3855837   17.8412139   12.6377965
 H    9.5581613   16.0971700   12.6605314
 C    9.8509475   17.0286196   10.7253205
 H   10.9274176   17.1436968   10.8700062
 H    9.7070835   16.1018722   10.1585423
 C    9.2767332   18.2029111    9.9384039
 H    9.7567142   18.2911463    8.9612801
 H    9.4794154   19.1372953   10.4738380
 C    7.7726565   18.0138063    9.7609486
 H    7.6211019   17.1134295    9.1599554
 H    7.3451374   18.8438831    9.1926550
 C    7.0039444   17.8758677   11.0936806
 H    7.1180791   18.8200836   11.6317274
 C    5.2068462   16.5965875   10.0038982
 H    5.7374149   15.7089028   10.3552129
 H    5.5416218   16.7841556    8.9758807
 C    3.7408302   16.2448208    9.9448338
 C    3.1114620   16.0885607    8.7169250
 H    3.6515146   16.2785616    7.7988983
 C    1.7848850   15.6738646    8.6913223
 H    1.2686503   15.5339328    7.7499982
 C    1.1415276   15.4367773    9.8910146
 H    0.1125724   15.1004413    9.9138051
 C    1.8370355   15.6439645   11.0860839
 C    1.0825291   15.4585719   12.3856311
 H    0.4172668   16.3202810   12.4736645
 H    0.4237387   14.5860374   12.2601880
 C    1.1262838   15.7431503   14.8170236
 H    1.7347802   15.4055831   15.6595084
 C   -0.2354494   15.0213615   14.9233545
 H   -0.8255511   15.2163066   14.0248115
 H   -0.0667200   13.9422233   14.9522096
 C   -1.0721955   15.4660209   16.1198604
 H   -0.5589703   15.2218697   17.0570815
 H   -2.0191499   14.9218154   16.1306582
```

C	-1.3073576	16.9720663	16.0452960
H	-1.8508408	17.2122040	15.1242871
H	-1.9312045	17.3126627	16.8746412
C	0.0342941	17.6990481	16.0767497
H	0.4951892	17.4866871	17.0442230
H	-0.1137230	18.7809200	16.0375652
C	0.9931058	17.2786902	14.9408055
H	0.5587465	17.6390048	14.0051493
C	2.9090507	17.8081131	16.3701519
H	2.6487001	16.8290196	16.7781437
H	2.4882461	18.5438834	17.0719960
C	7.2151787	15.3527612	13.9496327
H	8.0807705	15.3889639	14.6239876
H	7.4627945	14.6311916	13.1680818
C	6.0238573	14.7806442	14.6972257
C	6.1336239	14.3062872	16.0019677
H	7.0680574	14.3968988	16.5398286
C	5.0225294	13.7244032	16.5958827
H	5.0769512	13.3482902	17.6097686
C	3.8410948	13.6255249	15.8706661
H	2.9626062	13.1601108	16.2987253
C	3.8062680	14.1333528	14.5746409
C	2.5641511	14.0735126	13.7125112
H	2.8813525	13.7786100	12.7126407
H	1.8903136	13.2896129	14.0854319
C	4.8851841	18.9590949	10.4681011
H	4.8016013	19.0212761	9.3752029
H	5.5152067	19.7957211	10.7775795
C	3.5200509	19.2005397	11.0873189
C	2.4131465	19.5447870	10.3154995
H	2.4895521	19.5839717	9.2369104
C	1.2151459	19.8279849	10.9561945
H	0.3370026	20.0965558	10.3825107
C	1.1586631	19.7680162	12.3435394
H	0.2445667	20.0016428	12.8739924
C	2.3051041	19.4049223	13.0453412
C	2.3367012	19.3090722	14.5552127
H	3.2687592	19.7663988	14.8863956
H	1.5139740	19.8992051	14.9825724

Data for $K^+ \subset$ **6**

97

Energy = -2590.5149373040

K	4.2333165	16.9159589	13.1829909
N	5.2250271	17.8247092	15.4483146
N	6.9988007	16.6019720	13.3597518
N	5.5054318	17.7602746	10.8487920
N	3.0830393	15.9912745	11.0002331
N	1.9147574	15.3175122	13.5593309
N	2.3629714	17.9741704	15.0417013
N	4.9397893	14.4882479	13.9798846
N	3.4722991	19.3401731	12.4136036
C	4.4555373	17.9760107	16.5189808
C	5.0074741	18.1398596	17.7932941
H	4.3675702	18.2865762	18.6544559
C	6.3843669	18.0974173	17.9315412
H	6.8400659	18.2096934	18.9073196
C	7.1778227	17.9061496	16.8037653
H	8.2557535	17.8601967	16.8869062
C	6.5574913	17.7852612	15.5663874
C	7.3804275	17.6759551	14.2915159

H	7.2760232	18.6286150	13.7665842
H	8.4332807	17.5946423	14.5919955
C	7.5897371	16.7469332	11.9912414
H	7.3666669	15.8028683	11.4882105
C	9.1279236	16.8844336	12.0663661
H	9.3765454	17.7783311	12.6446467
H	9.5217074	16.0330255	12.6271750
C	9.8242177	17.0032621	10.7152184
H	10.9029256	17.0930407	10.8617030
H	9.6610781	16.0959462	10.1228337
C	9.2684297	18.2094355	9.9675590
H	9.7428625	18.3200880	8.9899173
H	9.4881390	19.1240784	10.5296720
C	7.7626710	18.0441369	9.7947781
H	7.5978865	17.1611947	9.1713529
H	7.3441437	18.8924266	9.2472615
C	6.9742907	17.8812181	11.1148726
H	7.0811283	18.8103196	11.6800996
C	5.1571707	16.6902433	9.8991345
H	5.7173739	15.7955757	10.1811291
H	5.4611306	16.9444092	8.8752887
C	3.6900560	16.2918999	9.8457655
C	3.0261082	16.1849109	8.6301083
H	3.5250827	16.4422091	7.7050424
C	1.7097708	15.7316524	8.6269167
H	1.1711901	15.6245606	7.6936971
C	1.0957122	15.4226895	9.8285561
H	0.0722303	15.0699200	9.8541611
C	1.8191018	15.5873157	11.0140047
C	1.1002414	15.3761684	12.3431178
H	0.4166498	16.2227618	12.4385475
H	0.4593519	14.4890770	12.2319115
C	1.1802536	15.7387636	14.7886045
H	1.8008616	15.4138288	15.6262290
C	-0.1808135	15.0172838	14.9200604
H	-0.7744893	15.1953832	14.0204227
H	-0.0045099	13.9399214	14.9612917
C	-1.0217614	15.4674750	16.1099276
H	-0.5067485	15.2436660	17.0512005
H	-1.9621520	14.9121161	16.1275200
C	-1.2709612	16.9683782	16.0091750
H	-1.8136781	17.1885481	15.0827554
H	-1.8987078	17.3196871	16.8311002
C	0.0658318	17.7019082	16.0332651
H	0.5232604	17.5052057	17.0056528
H	-0.0888932	18.7821372	15.9814232
C	1.0447444	17.2856729	14.9113961
H	0.6234102	17.6368702	13.9671142
C	2.9383365	17.8846880	16.3861953
H	2.6710178	16.9097397	16.8002744
H	2.5042671	18.6273221	17.0717203
C	7.2372603	15.2605046	13.9366444
H	8.1189377	15.2571139	14.5905161
H	7.4480969	14.5712979	13.1179257
C	6.0487977	14.6900619	14.6955126
C	6.1015863	14.3955261	16.0554755
H	7.0082011	14.5703770	16.6191224
C	4.9657174	13.8878257	16.6716271
H	4.9800056	13.6387254	17.7252403
C	3.8054931	13.7194532	15.9256115
H	2.9027117	13.3356675	16.3831986
C	3.8232285	14.0542722	14.5727438
C	2.5805681	14.0001170	13.7023889

H	2.8940085	13.6874464	12.7070351
H	1.8894704	13.2372786	14.0855143
C	4.8937641	19.0532549	10.4710164
H	4.8291980	19.1622773	9.3806994
H	5.5418161	19.8533021	10.8309168
C	3.5207396	19.2928927	11.0802421
C	2.3757090	19.4517694	10.3037807
H	2.4349500	19.4064954	9.2245593
C	1.1601665	19.6546162	10.9429763
H	0.2546577	19.7921737	10.3654298
C	1.1154953	19.6618021	12.3319099
H	0.1796275	19.8069003	12.8560396
C	2.3007111	19.4788825	13.0420575
C	2.3372547	19.3751195	14.5561339
H	3.2583549	19.8499925	14.8922272
H	1.4993236	19.9379965	14.9891237

Data for $Rb^{+} \subset$ **6**

97

Energy = -2014.6917397510

Rb	4.2390425	16.9192672	13.1784312
N	5.2477821	17.9124677	15.4827304
N	7.0379543	16.5975497	13.3909210
N	5.4987279	17.7708792	10.7979774
N	3.0845646	15.9070889	10.9528091
N	1.9242282	15.2685168	13.5608490
N	2.3581028	18.0254444	15.0389480
N	4.9865907	14.4085244	13.9965342
N	3.4687624	19.4281148	12.3738277
C	4.4588829	18.0005040	16.5439383
C	4.9959590	18.0408274	17.8353834
H	4.3498172	18.1402903	18.6989001
C	6.3686212	17.9364559	17.9858672
H	6.8117554	17.9595008	18.9736259
C	7.1756611	17.7853241	16.8600683
H	8.2477074	17.6758489	16.9594658
C	6.5738082	17.7801177	15.6081602
C	7.4072542	17.6736769	14.3310650
H	7.3053706	18.6254129	13.8042893
H	8.4580018	17.5930427	14.6398039
C	7.5932389	16.7523304	12.0032068
H	7.3743821	15.8023068	11.5095138
C	9.1308719	16.9074630	12.0686362
H	9.3682513	17.8111838	12.6368969
H	9.5309292	16.0678413	12.6426212
C	9.8324555	17.0141286	10.7200818
H	10.9097981	17.1136653	10.8706623
H	9.6785359	16.0983454	10.1383356
C	9.2697436	18.2062522	9.9571144
H	9.7422978	18.3077523	8.9775177
H	9.4828451	19.1297324	10.5072354
C	7.7659356	18.0269563	9.7881130
H	7.6063556	17.1335983	9.1777522
H	7.3416827	18.8636591	9.2273318
C	6.9660114	17.8785860	11.1037749
H	7.0650067	18.8131455	11.6615095
C	5.1386808	16.6947152	9.8539245
H	5.7041190	15.8030276	10.1342268
H	5.4332651	16.9476639	8.8267949
C	3.6645821	16.2921860	9.8093520
C	2.9584513	16.2829885	8.6132359

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 H    3.4287689   16.5963862    7.6903882
 C    1.6308648   15.8600473    8.6272945
 H    1.0604054   15.8280327    7.7074430
 C    1.0406359   15.4970132    9.8262235
 H    0.0044537   15.1837875    9.8612789
 C    1.8073338   15.5564263   10.9953464
 C    1.1121360   15.2972933   12.3389803
 H    0.3899875   16.1101945   12.4394970
 H    0.5103131   14.3832901   12.2243855
 C    1.2084188   15.7375793   14.7893888
 H    1.8422709   15.4381310   15.6263869
 C   -0.1444672   15.0058003   14.9524927
 H   -0.7402104   15.1439088   14.0470680
 H    0.0497580   13.9333601   15.0276397
 C   -0.9954851   15.4779157   16.1256543
 H   -0.4793908   15.2938412   17.0749468
 H   -1.9258510   14.9065341   16.1587550
 C   -1.2691835   16.9695510   15.9744549
 H   -1.8089497   17.1504831   15.0378144
 H   -1.9077938   17.3380770   16.7803671
 C    0.0557567   17.7230667   15.9839426
 H    0.5075358   17.5664017   16.9663026
 H   -0.1149338   18.7985683   15.8961113
 C    1.0592823   17.2959981   14.8871977
 H    0.6525067   17.6248334   13.9287515
 C    2.9324388   17.9642193   16.3879788
 H    2.6301440   17.0143462   16.8342484
 H    2.5184732   18.7426070   17.0463559
 C    7.2719642   15.2462728   13.9529972
 H    8.1543481   15.2364379   14.6059758
 H    7.4804639   14.5667800   13.1262129
 C    6.0835953   14.6667895   14.7148931
 C    6.1180146   14.4452109   16.0896014
 H    7.0141817   14.6576473   16.6564775
 C    4.9763823   13.9651765   16.7170873
 H    4.9791715   13.7693840   17.7819753
 C    3.8225709   13.7648088   15.9690420
 H    2.9125104   13.4137658   16.4385032
 C    3.8554830   14.0254449   14.5999353
 C    2.6068596   13.9581962   13.7312968
 H    2.9176381   13.6308282   12.7398882
 H    1.9208953   13.1986980   14.1301916
 C    4.8940118   19.0735822   10.4325670
 H    4.8278874   19.1878850    9.3428350
 H    5.5494589   19.8653050   10.7961536
 C    3.5175616   19.3216431   11.0425808
 C    2.3636359   19.4027081   10.2666541
 H    2.4203059   19.3171837    9.1900619
 C    1.1422240   19.5767816   10.9030451
 H    0.2308311   19.6581938   10.3241585
 C    1.0985807   19.6180122   12.2913601
 H    0.1563970   19.7288728   12.8126277
 C    2.2917650   19.5129756   13.0046039
 C    2.3232660   19.4203024   14.5239703
 H    3.2386082   19.9057993   14.8604665
 H    1.4779139   19.9813183   14.9449839
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Data for $Cs^+ \subset$ **6**

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Cs    4.2482426   16.9197661   13.1718935
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N	5.4905620	17.7768204	10.7352694
N	3.0908905	15.7813002	10.9070177
N	1.9430294	15.1947158	13.5773418
N	2.3405749	18.0977052	15.0224630
N	5.0462377	14.3338649	14.0336586
N	3.4572259	19.5084886	12.3128973
C	4.4438355	18.0300572	16.5579483
C	4.9497292	17.8980826	17.8565771
H	4.2867821	17.9209341	18.7129535
C	6.3137967	17.7258187	18.0229526
H	6.7323864	17.6281712	19.0168586
C	7.1412493	17.6413787	16.9045685
H	8.2017366	17.4559698	17.0155569
C	6.5729473	17.7885432	15.6458460
C	7.4230983	17.6891481	14.3709989
H	7.3113631	18.6329620	13.8331833
H	8.4716330	17.6260143	14.6912134
C	7.5994378	16.7601093	12.0221364
H	7.3951671	15.7997606	11.5425698
C	9.1345963	16.9483630	12.0791111
H	9.3505094	17.8708575	12.6259665
H	9.5465809	16.1322311	12.6779187
C	9.8450044	17.0304163	10.7343217
H	10.9193357	17.1513484	10.8909177
H	9.7102242	16.0969747	10.1764469
C	9.2681543	18.1918215	9.9376290
H	9.7390621	18.2720384	8.9552258
H	9.4674009	19.1336269	10.4611710
C	7.7678501	17.9862567	9.7741693
H	7.6190234	17.0723042	9.1916890
H	7.3341635	18.7994443	9.1867861
C	6.9551007	17.8697784	11.0861741
H	7.0480336	18.8158695	11.6249765
C	5.1171706	16.6786941	9.8148544
H	5.6858124	15.7942328	10.1092028
H	5.4036413	16.9139076	8.7811866
C	3.6348306	16.2784787	9.7869122
C	2.8743080	16.4106039	8.6322963
H	3.3130965	16.7953207	7.7208819
C	1.5292935	16.0478006	8.6753829
H	0.9164186	16.1278522	7.7862329
C	0.9712457	15.6206356	9.8687267
H	-0.0828022	15.3787238	9.9307961
C	1.7948764	15.5196073	10.9963361
C	1.1339285	15.1821769	12.3507412
H	0.3510686	15.9342649	12.4621133
H	0.6014779	14.2271926	12.2261057
C	1.2545679	15.7340889	14.7995858
H	1.9131477	15.4833144	15.6337633
C	-0.0784810	14.9790453	15.0213750
H	-0.6769113	15.0361926	14.1088843
H	0.1520925	13.9209263	15.1647375
C	-0.9500091	15.4934234	16.1599740
H	-0.4339422	15.3876039	17.1211306
H	-1.8602650	14.8930699	16.2250440
C	-1.2715405	16.9613354	15.9117442
H	-1.8038804	17.0650468	14.9591949
H	-1.9324726	17.3592152	16.6850939
C	0.0282241	17.7554859	15.8913716
H	0.4672205	17.6773996	16.8889431
H	-0.1752575	18.8171638	15.7338843

C	1.0748176	17.3074638	14.8425353
H	0.6948167	17.5946345	13.8598403
C	2.9109715	18.0767243	16.3764590
H	2.5537697	17.1727934	16.8730445
H	2.5344371	18.9105058	16.9881577
C	7.3217824	15.2401645	13.9851689
H	8.2009222	15.2345930	14.6426452
H	7.5414393	14.5697218	13.1541863
C	6.1363607	14.6379022	14.7473935
C	6.1639120	14.4605779	16.1293116
H	7.0555276	14.6955520	16.6936985
C	5.0215195	13.9986491	16.7685185
H	5.0215744	13.8382565	17.8392496
C	3.8683492	13.7781338	16.0248801
H	2.9543616	13.4525302	16.5051009
C	3.9069891	13.9839580	14.6468852
C	2.6485533	13.8976777	13.7857185
H	2.9538780	13.5481955	12.8001675
H	1.9720015	13.1428979	14.2089597
C	4.8930121	19.0860949	10.3735783
H	4.8213133	19.1952447	9.2836200
H	5.5603391	19.8714106	10.7287490
C	3.5140628	19.3576462	10.9846916
C	2.3587816	19.3958319	10.2064104
H	2.4184967	19.2881066	9.1323792
C	1.1316777	19.5527102	10.8359012
H	0.2206936	19.6008370	10.2527602
C	1.0818251	19.6123766	12.2234685
H	0.1342257	19.6976436	12.7398791
C	2.2748872	19.5597016	12.9421616
C	2.2921040	19.4809548	14.4673273
H	3.1967314	19.9836660	14.8074706
H	1.4342833	20.0381175	14.8677808

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