Electronic Supplementary Information for Dalton Transactions

Structural and kinetic investigations of alkali-mediated pseudorotaxanes

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Supplementary Information

Figure S1: Parts of ^{1}H NMR of **A·1** complexes ($CDCl_3$/MeOD 98:2, 220K)

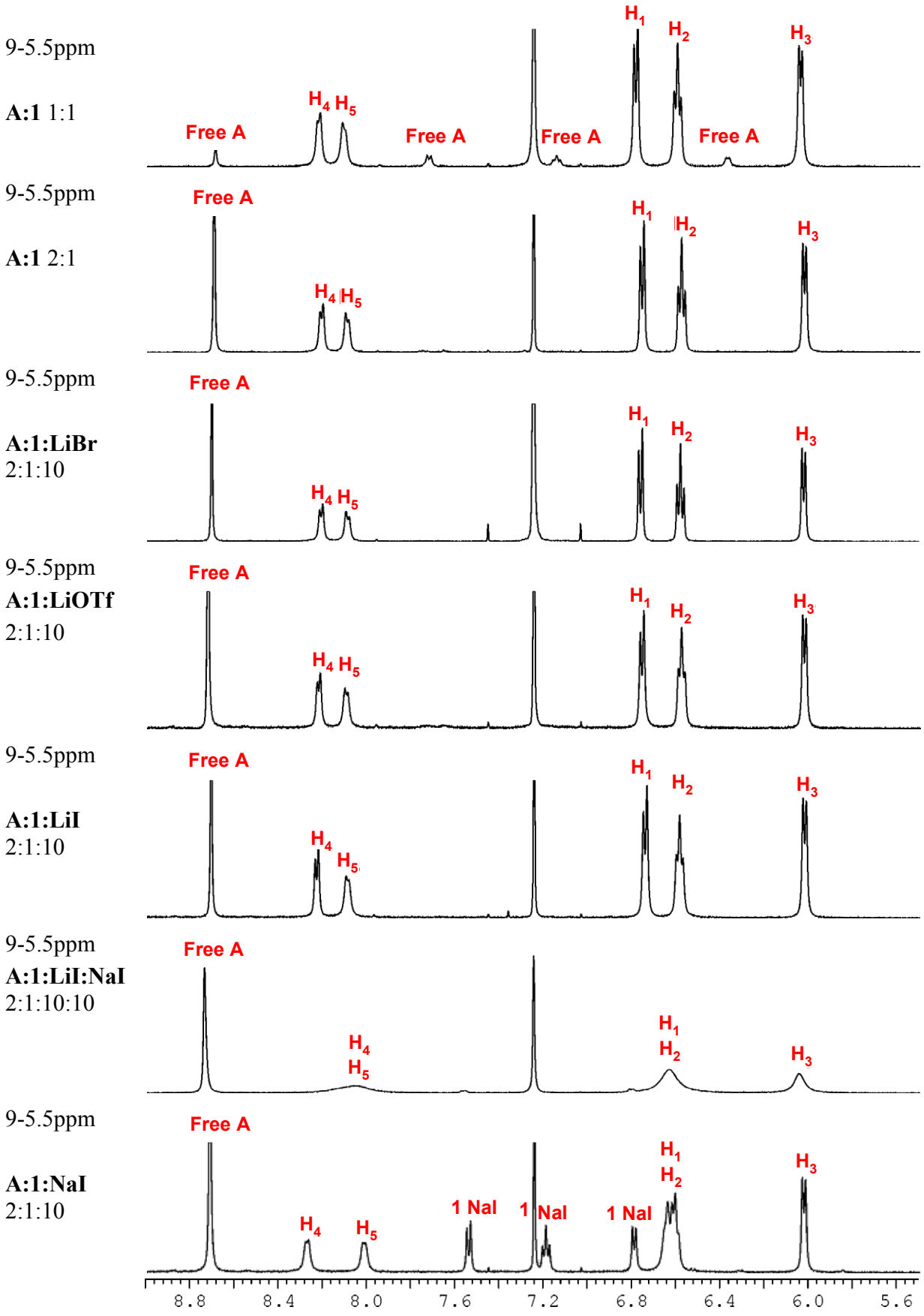


Table S1: Kinetic measurements for the system **A:1**

Rate constant k in s^{-1}, irradiated resonances first, not adjusted for unequal populations between exchanging resonances					
	Free **A**:H_5	Free **A**:H_4	H_4:H_5	Free **1**:H_1	Me_1:Me_2
A cr1 1:1	3.3	3.8	7.0	4.9	-
	-	-	-	5.1	-
A cr1 2:1	0.15		7.7		0.37
					0.47
A cr1 LiBr	0.13	0.14			
2:1:10	0.12		7		0.32
A cr1 Litriflate	0.16		6		
2:1:10	0.10		7.0		0.44
			4.8		0.48
A cr1 LiI 2:1:10	0.12	0.11	3		
	0.13		3.5		0.32
			3.9		0.35
A cr1 LiI NaI 2:1:10:10					0.43
A cr1 NaI 2:1:10					1.7
	0.25	0.25 (3.4 H_2:H_1)	2.9		2.2 (0.54 Me_2:Me_1)

Rate constant k in s^{-1}, irradiated resonances first, **adjusted** for unequal populations					
	Free **A**:H_5	Free **A**:H_4	H_4:H_5	Free **1**:H_1	Me_1:Me_2
A:1	3.3	3.8	7.0	4.9	-
1:1	-	-	-	5.1	-
A:1	**0.39**		7.7		0.37
2:1					0.47
A:1:LiBr	**0.31**		7		0.32
2:1:10					
A:1:Li triflate	**0.44**		7.0		0.44
2:1:10					
A:1:LiI	**0.32**		3.5		0.32
2:1:10					
A:1:LiI NaI					0.43
2:1:10:10					
A:1:NaI					1.7
2:1:10	**1.5**	**1.5** (3.4 H_2:H_1)	2.9		2.2 (0.54 Me_2:Me_1)

Table S2: Chemical shift differences for bound acceptor **A** protons at 220K, all in $CDCl_3$/MeOD 98:2. For labelling see *Figure 1*.

A:1:(salt) complex	**Δ ppm H_4-H_5**	**Δ ppm free A-H_4**	**Δ ppm free A-H_5**
A:1 = 1.0:1.0	0.12	0.46	0.58
A:1 = 2.2:1.0	0.11	0.49	0.60
A:1:LiBr = 2.2:1.0:10	0.12	0.49	0.61
A:1:LiOTf = 2.1:1.0:10	0.12	0.51	0.63
A:1:LiI = 2.1:1.0:10	0.14	0.47	0.61
A:1:NaI = 2.6:1.0:10	0.26	0.44	0.70

Table S3: Summary of activation barriers for decomplexation of **A·1·(salt)** complexes in $CDCl_3$/MeOD 98:2 obtained by 1D NOESY (EXSY) experiments at 220K at 500 MHz.[1] The rate constants were obtained by initial rate approximation; errors for rate constants are ± 20 %. H_{bound} represents any resonance in the complex, H_{free} represents any uncomplexed resonance.

A:1:(salt) complex	**T in K**	**k (H_{bound}-H_{free})* s^{-1}**	**$\Delta G^{\ddagger}$ / kcal mol^{-1}**	**k (H_{bound}-H_{bound}) s^{-1}**	**Ratio of k (H_{bound}-H_{bound}) to k (H_{bound}-H_{free})**
A:1 = 1.0:1.0	220	3.6	12.2	7.0	2
A:1 = 2.2:1.0	220	0.37	13.2	7.7	20
A:1:LiBr = 2.2:1.0:10	220	0.32	13.2	7	22
A:1:Li triflate = 2.1:1.0:10	220	0.44	13.1	7.0	16
A:1:LiI = 2.1:1.0:10	220	0.32	13.2	3.5	11
A:1 LiI NaI 2:1:10:10	220	0.43	13.1		
A:1:NaI = 2.6:1.0:10	220	1.7	12.5		
	220	2.2	12.4	2.9	1.3

*also k (H_{free}- H_{bound}). Rate constant were adjusted for unequal populations (corrected for NMR silent protons).

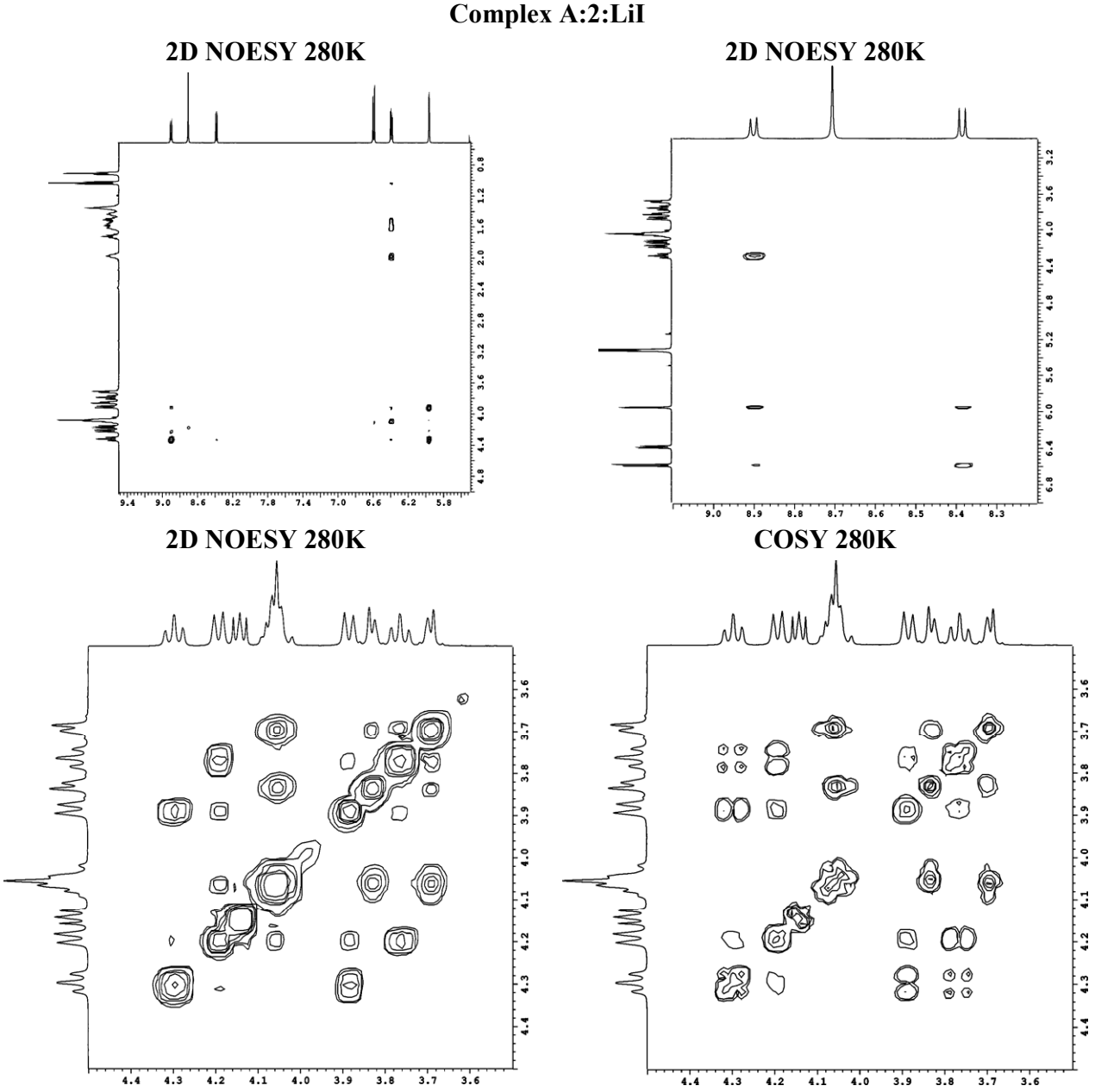
Table S4: Chemical shifts of **A·1** complexes, all in $CDCl_3$/MeOD 98:2 at 220K. For labelling see *Figures 1* and *2*.

Chemical shifts in ppm ($CDCl_3$ at 7.25ppm)										**Integration ratios**		
	Free A	**H_4**	**H_5**	**Free 1**			**H_1**	**H_2**	**H_3**	**Free A:(H_4+H_5)**	**Me^1:Me^{2*}**	**A:1**
1				7.74 d (8.0)	7.15 t (6.6)	6.36 d (6.7)				-	-	-
1:LiI = 1:1				7.74 d (8.4)	7.15 t (8.0)	6.38 d (7.6)				-	-	-
A:1 = 1.0:1.0	8.69 s	8.23 d (6.8 Hz)	8.11 d (6.7 Hz)	7.72 d (7.9 Hz)	7.15 t (7.8 Hz)	6.37 d (6.9 Hz)	6.78 d (8.2 Hz)	6.60 t (7.7 Hz)	6.04 d (7.3 Hz)	1.0:11.4	12.4:1.0	1.0:1.0
										1 (bound) : 1 (free) = 10.6:1.0		
A:1 = 2.2:1.0	8.70 s	8.21 d (6.6 Hz)	8.10 d (6.7 Hz)	No free 1			6.76 d (8.2 Hz)	6.58 t (7.6 Hz)	6.02 d (7.4 Hz)	1.2:1.0	1.0:1.1	2.2:1.0
A:1:LiBr = 2.2:1.0:10	8.71 s	8.22 d (6.8 Hz)	8.10 d (6.7 Hz)	No free 1			6.76 d (8.4 Hz)	6.59 t (7.9 Hz)	6.02 d (7.6 Hz)	1.2:1.0	1.0:1.1	2.2:1.0
A:1:LiOTf = 2.1:1.0:10	8.73 s	8.22 d (6.9 Hz)	8.10 d br	No free 1			6.76 d (8.0 Hz)	6.58 t (7.5 Hz)	6.02 d (7.3 Hz)	1.1:1.0	1.0:2.0	2.1:1.0
A:1:LiI = 2.1:1.0:10	8.71 s	8.24 d (7.2 Hz)	8.10 d (6.0 Hz)	No free 1			6.75 d (8.0 Hz)	6.59 t (7.5 Hz)	6.02 d (7.3 Hz)	1.1:1.0	1.0:1.0	2.1:1.0
A:1 LiI NaI 2:1:10:10	8.74 s	8.1 s (br)		7.57 d (br)		-	6.82 d br	6.6 s vbr	6.05 s br	-	1.0:1.6	-
A:1:NaI = 2.6:1.0:10	8.72 s	8.28 d (br)	8.02 d (br)	7.54 d (8.2 Hz)		7.20 t (7.9 Hz)	6.80 d (7.7 Hz)	6.61 (6.65-6.60) m	6.03 d (7.1 Hz)	3.0:1.0	1.0:2.8	2.6:1.0
										1 (bound) : 1 (free) = 2.4:1.0		

*Me^1 belongs to bound acceptor **A**, Me^2 to free **A**.

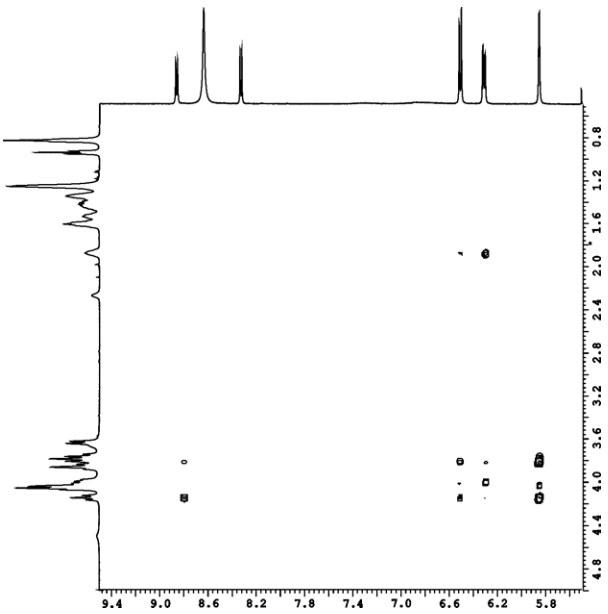
Complexes between acceptor molecule A and crown ether host 2

Figure S2: Parts of 2D NOESY and COSY experiments of **A:2:salt = 2:1:10** complexes in CD_2Cl_2.

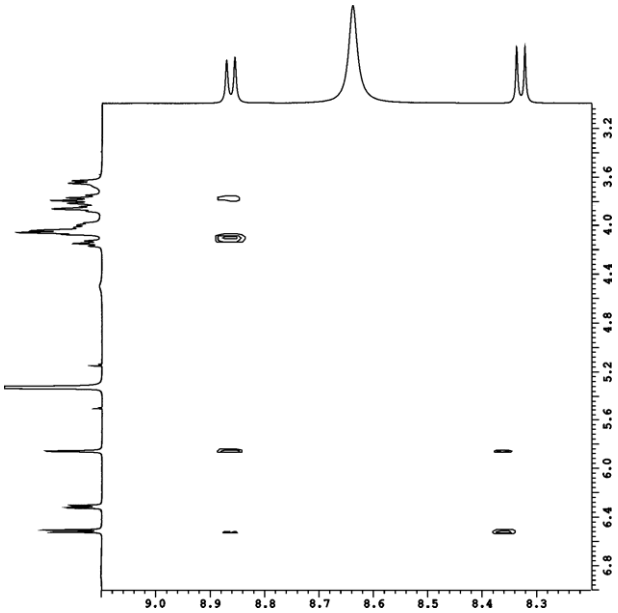


Complex **A:2:NaI**

2D NOESY 220K



2D NOESY 220K



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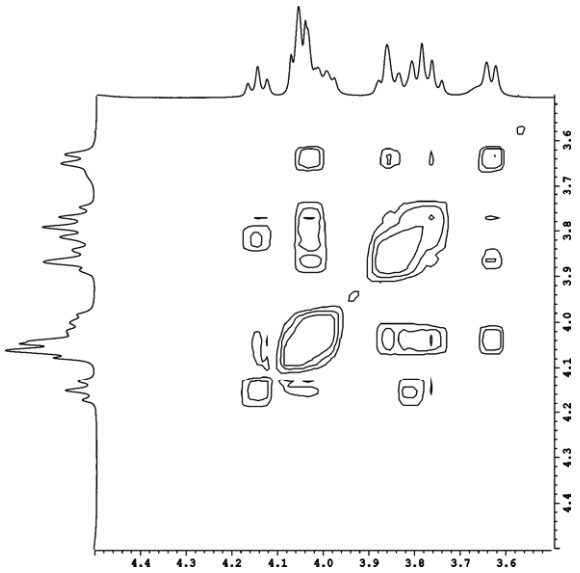
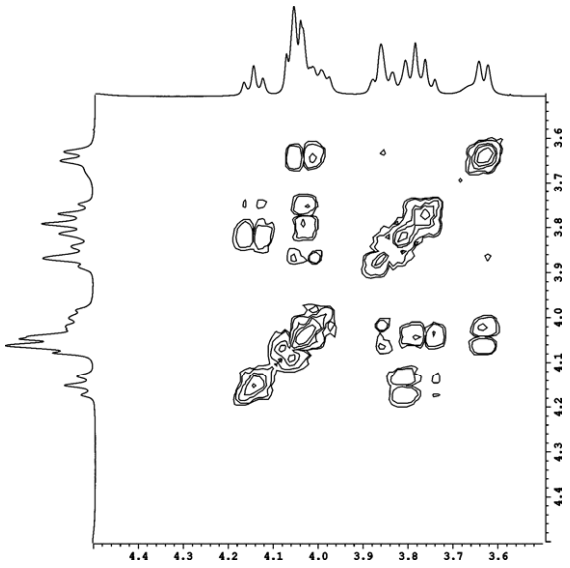
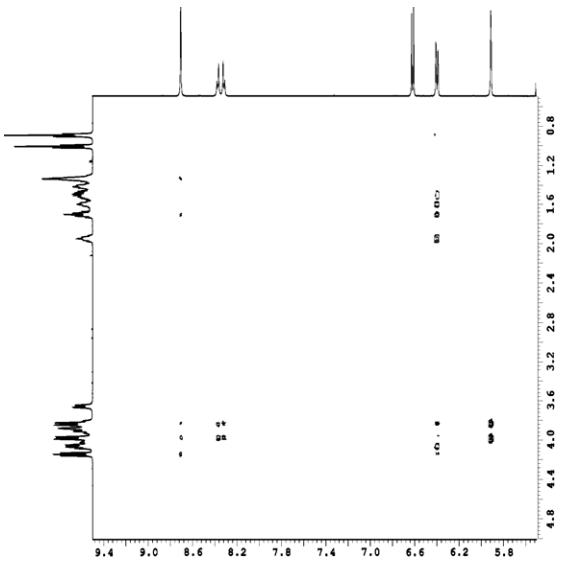


COSY 220K

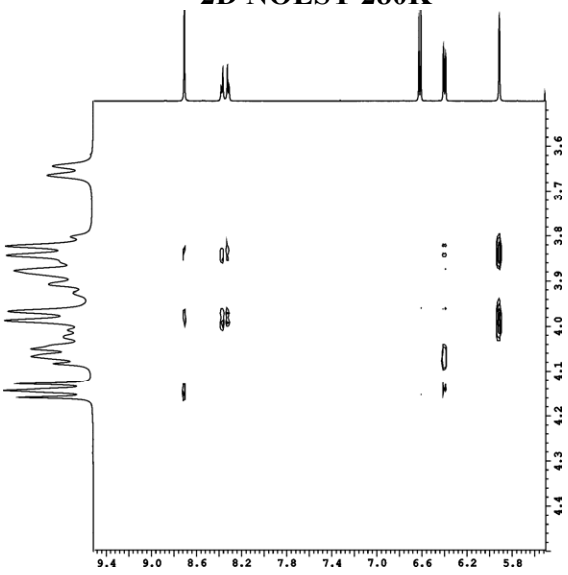


A:2:Na triflate complex

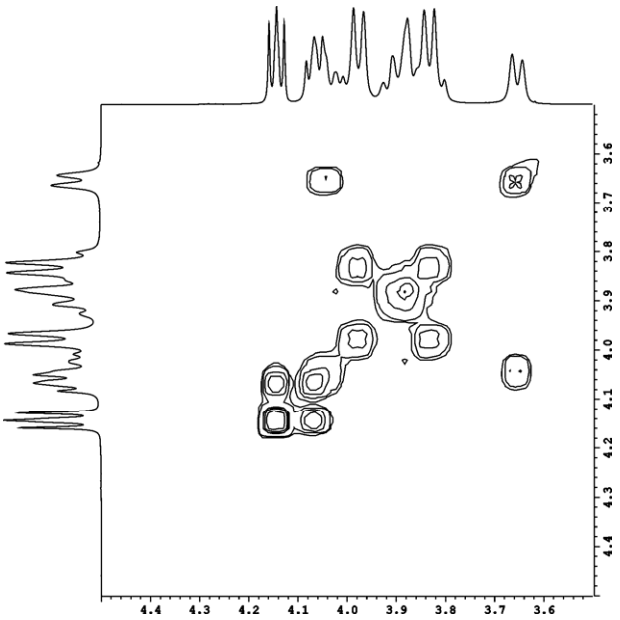
2D NOESY 280K



2D NOESY 280K



2D NOESY 280K



COSY 280K

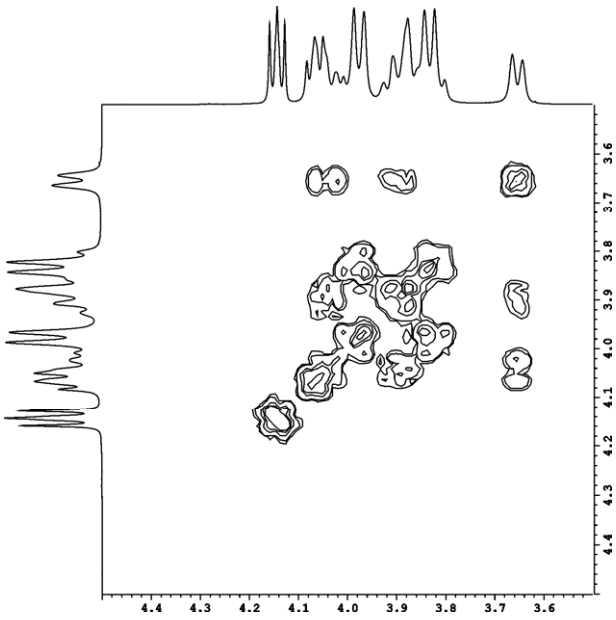


Figure S3: Selected regions of ^{1}H NMR spectra (aromatic protons H_1 to H_5, 9.2 ppm-5.5 ppm) of **A:2:salt = 2:1:10** complexes (CD_2Cl_2, different temperatures)

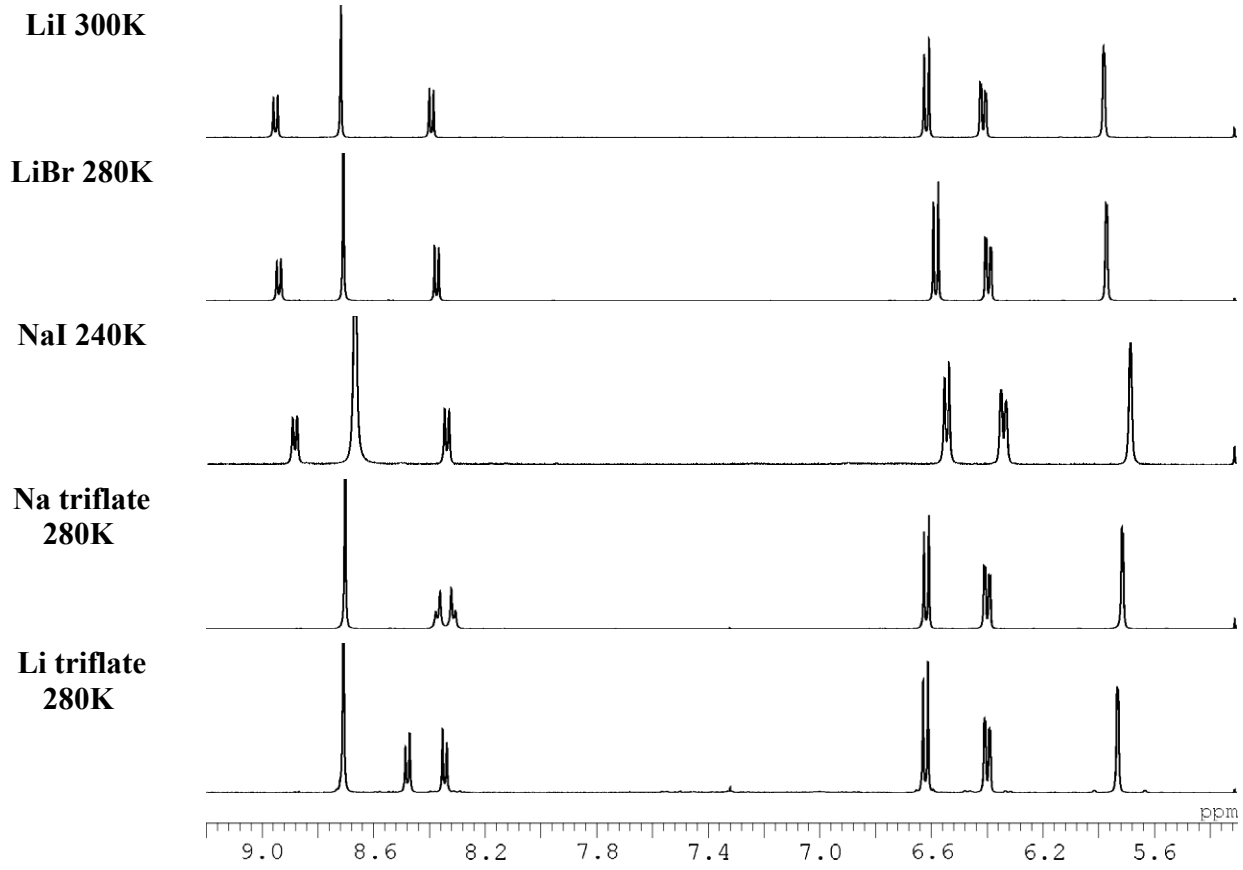


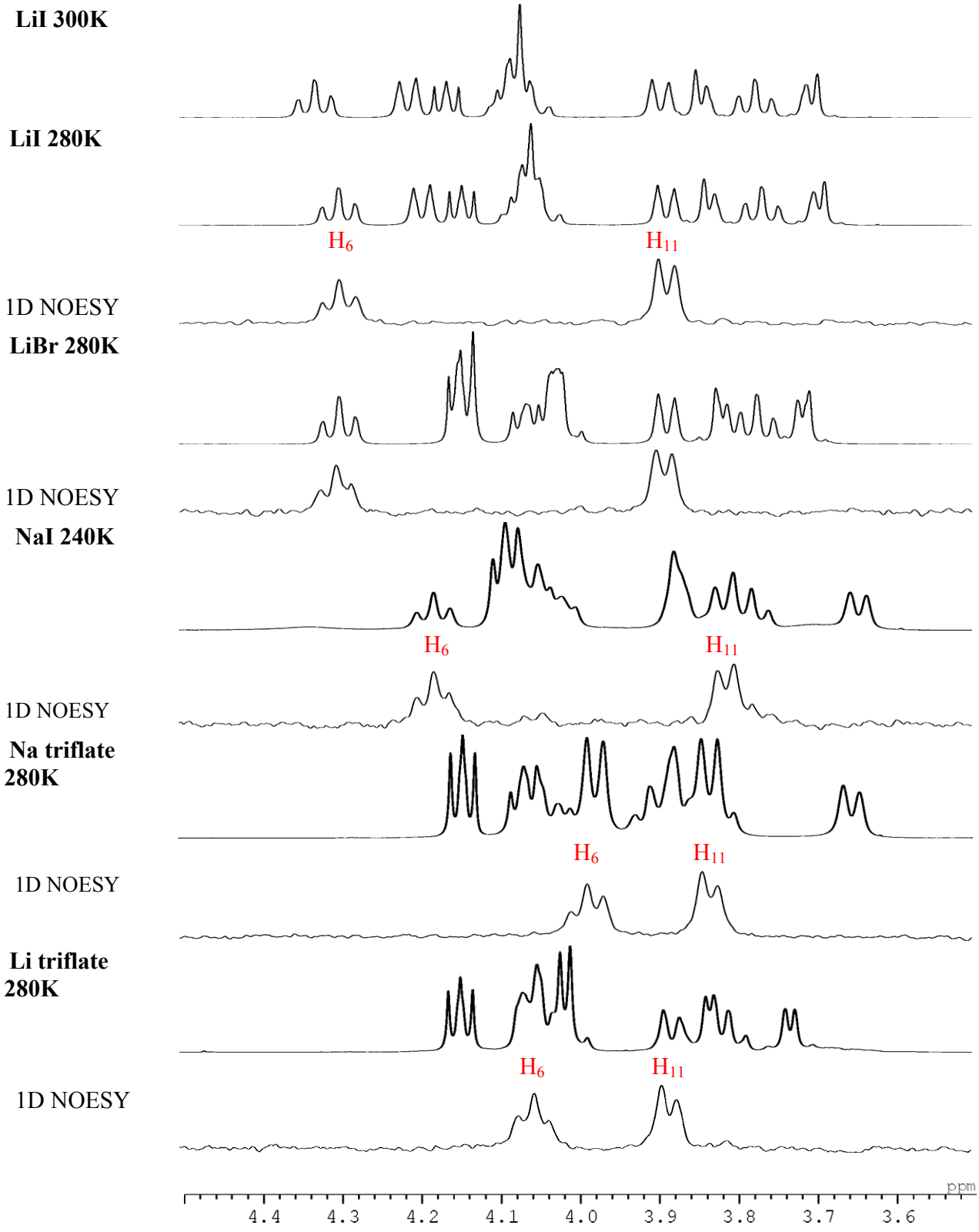
Table S5*:* Chemical shift differences for bound acceptor **A** protons at different temperatures, all in $CDCl_3$/MeOD 98:2. For labelling see *Figure 1*.

Complex	**T in K**	**Δ ppm H_4-H_5**	**Δ ppm free A-H_4**	**Δ ppm free A-H_5**
A 2 LiCl 1:1:10	260	0.45	-0.08	0.37
A 2LiCl 2:1:10	280	0.50	-0.13	0.37
A 2LiBr 1:1:2	220	0.16	0.12	0.28
A 2 LiBr 1:1:10	220	0.17	0.12	0.29
A 2 LiBr 1:1:50	300	0.59	-0.24	0.35
A 2 LiBr 2:1:10	230	0.22	0.06	0.28
	260	0.36	-0.04	0.32
	280	0.42	-0.10	0.32
	300	0.50	-0.17	0.33
A 2 LiBr 2:1:10 (5 µL D_2O added)	220	0.18	0.10	0.28
A 2 LiBr 2:1:20	230	0.20	0.08	0.28
A 2 LiI 1:1:10	250	0.14	0.10	0.24
	260	0.16	0.08	0.24
	280	0.20	0.04	0.24
A 2 LiI 2:1:10*	280	0.26	0	0.26
	300	0.40	-0.09	0.31
	310	0.38	-0.09	0.29
A 2NaI 2:1:10*	220	0.41	0	0.41
	240	0.44	-0.06	0.38
A 2 NaOTf 2:1:10	220	0.17	0.31	0.48
A 2 LiOTf1:1:2	220	0.05	0.37	0.42
A 2 LiOTf 1:1:10	220	0.06	0.36	0.42
A 2 LiOTf1:1:20	220	0.06	0.36	0.42
	240	0.07	0.33	0.40
	250	0.08	0.32	0.40
	260	0.09	0.31	0.40
A 2 LiOTf 1:1:50*	300	0.13	(0.24)	(0.37)
A 2 LiOTf 2:1:10	220	0.06	0.36	0.42
	230	0.06	0.35	0.41
	260	0.07	0.32	0.39

Table S6: Chemical shift differences for bound acceptor **A** protons at different temperatures, all in CD_2Cl_2. For labelling see *Figure 1*.

Complex	**T in K**	**Δ ppm H_4-H_5**	**Δ ppm free A-H_4**	**Δ ppm free A-H_5**
A 2 LiBr 2:1:10	280	0.56	-0.23	0.33
	300	0.62	-0.28	0.34
	315	0.64	-0.30	0.34
A 2 LiI 2:1:10	280	0.52	-0.19	0.33
	300	0.56	-0.23	0.33
A 2 $LiNO_3$ 2:1:10	260	0.08	0.28	0.36
A 2 NaI 2:1:10	200	0.52	-0.18	0.34
	220	0.53	-0.22	0.31
	240	0.54	-0.21	0.33
A 2 Natriflate 2:1:10	240	0.06	0.33	0.39
	280	0.05	0.33	0.38
	300	0.04	0.34	0.38
A 2 Litriflate 2:1:10	280	0.14	0.23	0.37

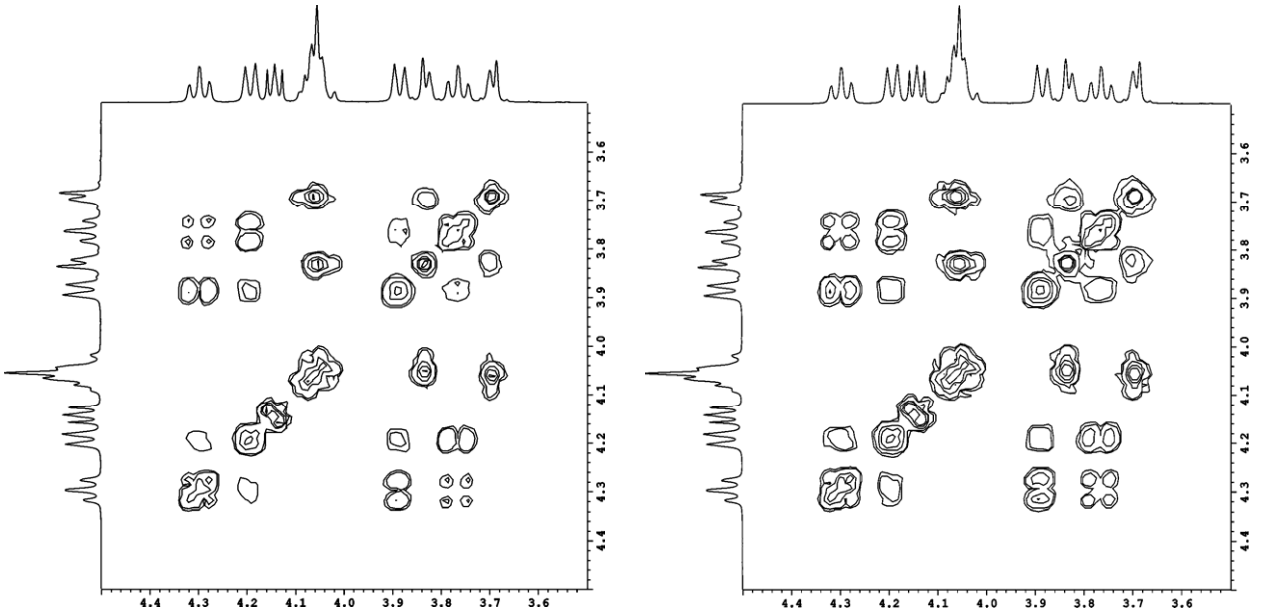
Figure S4: Parts of ^{1}H NMR and 1D NOESY spectra (crown ether OCH_2 protons H_6 to H_{14}, 4.5 ppm-3.5 ppm) of **A 2:salt = 2:1:10** complexes (in CD_2Cl_2, at different temperatures).



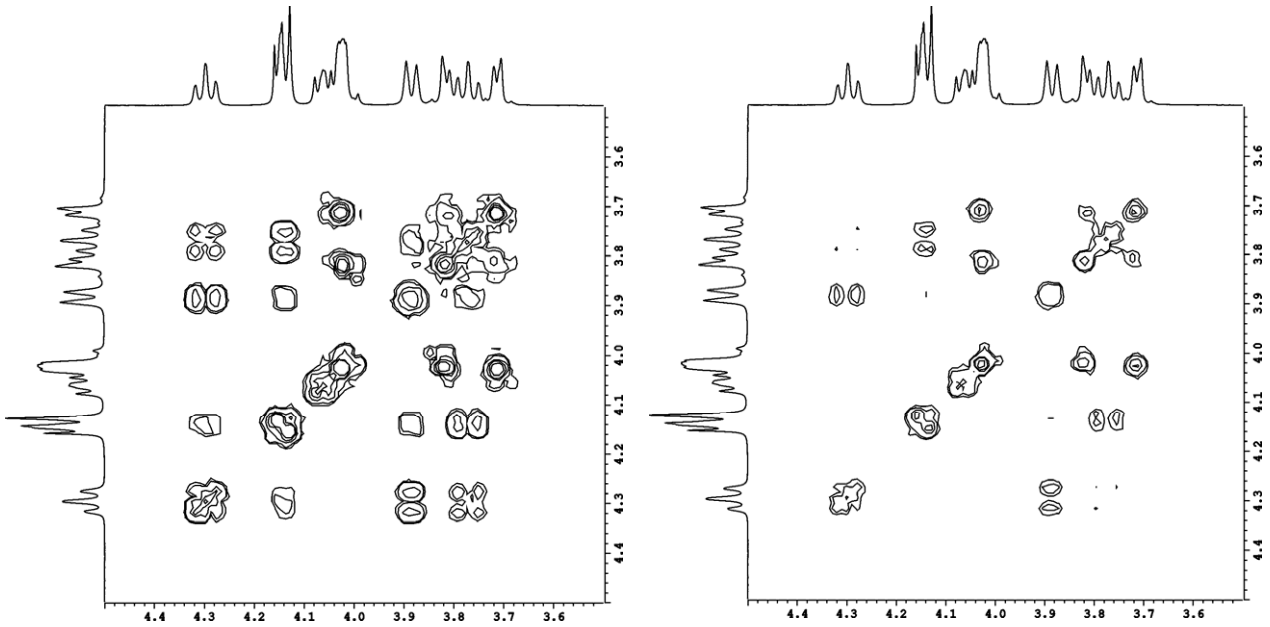
N.B. The irradiated frequency for the 1D NOESY spectra corresponds to the H_3 resonance. NOEs are seen at the H_6 and H_{11} resonances, H_3 is not shown, see labelling in *Figure 1*.

Figure S5*:* Parts of ^{1}H COSY spectra (crown ether OCH_2 protons H_6 to H_{14}, 4.5 ppm-3.5 ppm) of A 2**:salt = 2:1:10** complexes (CD_2Cl_2, different temperatures).

LiI COSY 280K CD_2Cl_2

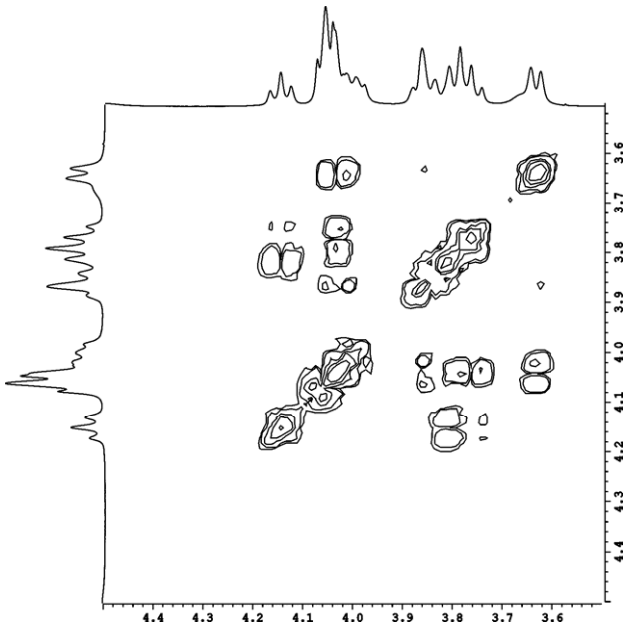


LiBr COSY 280K CD_2Cl_2

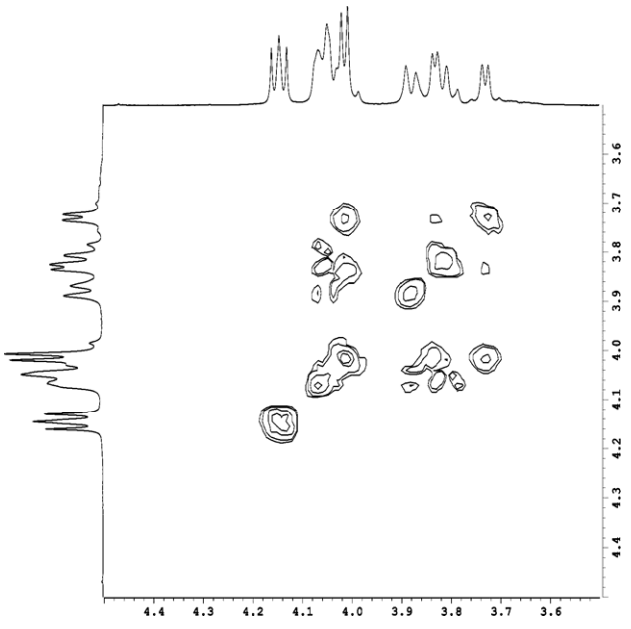


NaI COSY 220K CD_2Cl_2

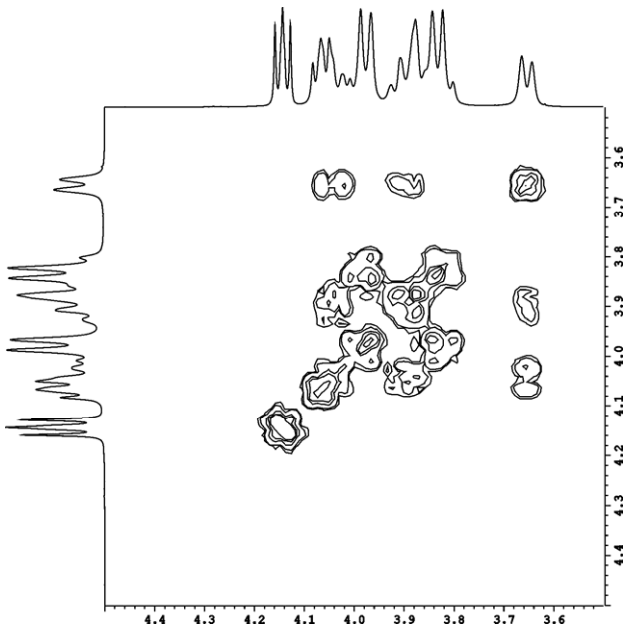
Li triflate COSY 280K CD_2Cl_2



Na triflate COSY 280K CD_2Cl_2



Li triflate COSY 280K CD_2Cl_2



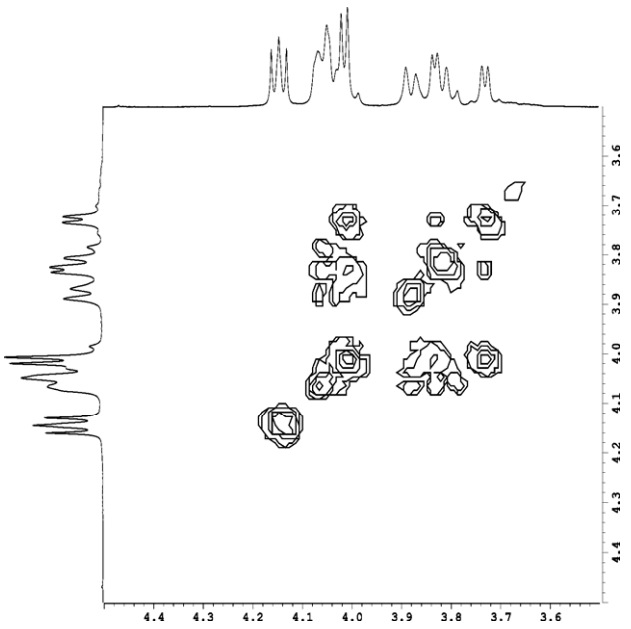


Table S7: ^{13}C NMR data (at room temperature) and ^{1}H correlations for **A:2:salt = 2:1:10** complexes in CD_2Cl_2 (salts: **LiI** and **Na triflate**). CD_2Cl_2 set to 55.0ppm. ^{1}H and ^{13}C labels are shown in *Figure 1*.

LiI complex δ (ppm)	**HMQC correlations**	**HMBC correlations**		**Na triflate complex δ (ppm)**	**HMQC correlations**		**Δppm (LiI-Na triflate)**
163.91	**C_1**	**H_4**		163.66			0.25
162.49	**C_2**	**H_5**		162.56			-0.07
154.31	**C_8**	**H_1>>H_3>H_2**		154.55			-0.24
132.93	**C_5**	**H_4**		131.21	**Free A, C_5**		Ca. 1.7
130.72	**C_6**	**H_5**		130.25	**C_6**		0.47
128.49	**C_{12}, C_{10}; H_1**	**H_1- H_3**		128.65	**C_{10}**		-
128.39				128.31			
126.87	**C_3,**	**H_4**		126.72			0.15
125.75	**C_4,**	**H_5**		125.47			0.28
125.03	**C_7,**	**H_4, H_5**		124.89			0.14
118.46	**C_{11}; H_2**	**H_3**		118.59	**C_{11}**		-0.13
106.38	**C_9, H_3**	**H_1>H_2**		106.01	**C_9**		0.37
71.34	**C_{14}, H_7, H_{13}**	**H_6**		71.41	**C_{14}, H_7, H_{13}**		-0.07
70.36	**C_{15}, H_{10}, H_{12}**	**H_{10}**		70.99	**C_{15}, H_{10}, H_{12}**		-0.63
69.86	**C_{16}, H_9, H_{14}**	**H_9**		70.57	**C_{16}, H_9, H_{14}**		-0.71
67.07	**C_{13}, H_6, H_{11}**	**H_{13}**		66.87	**C_{13}, H_6, H_{11}**		0.20
41.96	**C_{17}, H_8**			41.79	**C_{17}, H_8**		0.17
32.36	**C_{20}**			32.43	**C_{20}**		-0.07
28.35	**C_{19}**			28.38	**C_{19}**		-0.03
28.16	**C_{18}**			28.18	**C_{18}**		-0.02
23.39	**C_{21}**			23.36	**C_{21}**		0.03
14.54	**C_{22}**			14.57	**C_{22}**		-0.03

Table S8: Complete ^{1}H NMR data for **A:2:LiI = 2:1:10** complex in CD_2Cl_2 at 300K. CD_2Cl_2 set to 5.32ppm. ^{1}H labels are shown in *Figure 1*. Only resonances belonging to the complex are shown.

δ (ppm)	label		δ (ppm)	label		δ (ppm)	label
8.95 d (7.5 Hz)	H_4		4.33 t (10.1 Hz)	H_6		3.77 t (10.0 Hz)	H_{13}
8.39 d (7.5 Hz)	H_5		4.21 d (10.5 Hz)	H_7		3.70 m	H_{14}
6.61 d (8.8 Hz)	H_1		4.07 m	H_8-H_{10}		1.97 m	H_{15}
6.41 dd (8.8 Hz, 2.2 Hz)	H_2		3.89 d (10.5 Hz)	H_{11}		1.62-1.41 m	H_{16}-H_{18}
5.98 d (2.2 Hz)	H_3		3.84 m	H_{12}		1.02 t (7.2 Hz)	H_{19}

Table S9 Summary of activation barriers for decomplexation of **A:2:salt** complexes in $CDCl_3$/MeOD 98:2 obtained by 1D NOESY (EXSY) experiments at different temperatures at 500 MHz. The rate constants were obtained by initial rate approximation [1]; errors for rate constants are ± 20 %. H_{bound} represents any resonance in the complex, H_{free} represents any uncomplexed resonance.

Complex	**T in K**	**k (H_{bound}- H_{free})* in s^{-1}**	**$\Delta G^{\ddagger}$ / kcal mol^{-1}**	**k (H_{bound}- H_{bound}) in s^{-1}**	**Ratio of k (H_{bound}- H_{bound}) to k (H_{bound}- H_{free})**
A 2 LiBr 1:1:2	220	0.9-1.2	12.7	1.3, 1.7	1.5
A 2 LiBr 1:1:10	220	4-9	12.0	4	0.5-1
A 2 LiBr 1:1:50	300	0.2	18.5	0.7-0.8	4
A 2 LiBr 2:1:10	230	0.02	15.1	0.4-0.5	20
	280	0.5-0.8	16.6	3.2-3.5	4-6
	300	2.4	17.0		
A 2 LiBr 2:1:10 (5 µL D_2O added)	220	0.06-0.08	13.9	0.46	6
A 2 LiBr 2:1:20	230	0.02-0.06	14.8	0.3-0.5	15
A 2 LiCl 1:1:10	260	3.2	14.5	1.4	0.5
A 2LiCl 2:1:10	280	1.2-3.8	15.8	3.6-4.5	1-3
A 2 LiI 1:1:10	250			(0.28)	
	260			0.47	
	280	1	16.3	2.9	3
A 2LiI 2:1:10	300			0.43	
	310	0.06	19.9	2.6-3.1	50
A 2 Li triflate 1:1:2	220	4.3	12.1		
A 2 Li triflate 1:1:2 (20 eqv $MgSO_4$ added)	220	5.4	12.0		
A 2 Li triflate 1:1:10	220	0.41	13.1		
A 2 Li triflate 2:1:10	230	0.15	14.2		
	260	1.8	14.8		
	260	6.8	14.1		
A 2 Li triflate 1:1:20	255	1.2-2	14.6	1.6-2	1
A 2 NaI 2:1:10	240	0.9-1.5	13.8		
A 2 Na triflate 2:1:10	220	2.5	12.3		

When several resonances within one molecule were irradiated, the range of k is given. *also k (H_{free}- H_{bound}). Rate constant were adjusted for unequal populations (corrected for NMR silent

protons).[1] Pulse sequence used: selnogp.2: 1D NOESY using selective excitation with a shaped pulse; dipolar coupling may be due to NOE or chemical exchange.

Table S10: Summary of activation barriers for decomplexation of **A:2:salt** complexes in CD_2Cl_2 obtained by 1D NOESY (EXSY) experiments at different temperatures at 500 MHz. The rate constants were obtained by initial rate approximation [1]; errors for rate constants are ± 20 %. H_{bound} represents any resonance in the complex, H_{free} represents any uncomplexed resonance.

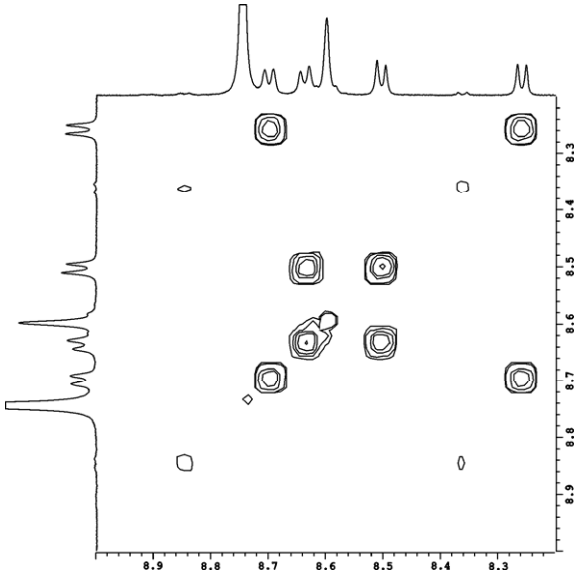
Complex	**T in K**	**k (H_{bound}-H_{free}) in s^{-1}**	**$\Delta G^{\ddagger}$ / kcal mol^{-1}**	**k (H_{bound}-H_{bound}) in s^{-1}**	**Ratio of k (H_{bound}-H_{bound}) to k (H_{bound}-H_{free})**
A 2 LiI 2:1:10	300	0.002	21.2		
A 2 NaI 2:1:10	240	0.90	14.0		
A 2 Na triflate 2:1:10	280	0.69	16.5		
A 2 Li triflate 2:1:10	280	0.51	16.7	1.1	2
A 2 LiBr 2:1:10	315	0.64	18.7	4.8	7.5
	260	0.12	16.2		
	300	0.17	18.6		

Table S11: Chemical shift differences for bound acceptor **II** protons in **II:cr3:salt 1:salt 2** complexes at different temperatures, all in $CDCl_3$/MeOD 98:2.

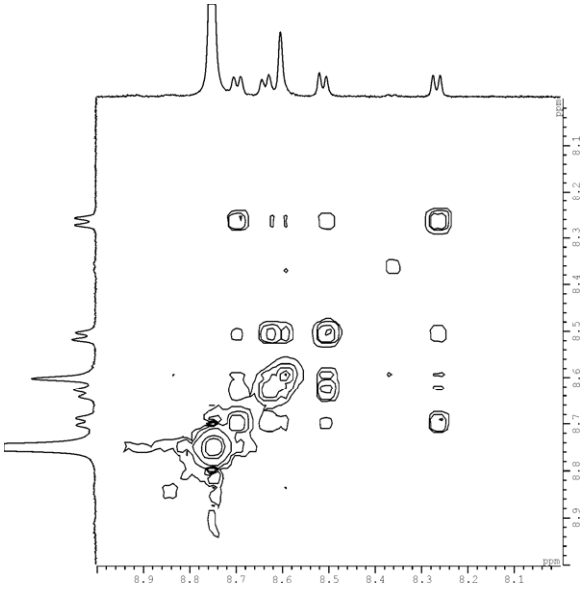
Complex	**T in K**	**Δ ppm H_4-H_5**	**Δ ppm free II-H_4**	**Δ ppm free II-H_5**
A 2 LiI Litriflate 2:1:5:5	220	0.10	0.24	0.34
A 2 LiI Litriflate 2:1:10:10	300	0.24	0.04	0.28
A 2 LiI NaI 2:1:5:5	220	0.45 0.13 0	0.04 0.11 0.15	0.49 0.24 0.15
A 2 LiI NaI 2:1:10:10	220	0.47 0.42 0.12 0	-0.08 0.06 0.12 0.16	0.39 0.48 0.24 0.16
A 2Litriflate NaI 2:1:5:5	220	0.10 0? 0.27	0.18 0.19 0.22	0.28 0.19 0.49

Figure S6: Parts of ^{1}H COSY and NOESY spectra of **A:2:LiI NaI** complexes ($CDCl_3$/MeOD 98:2, different temperatures).

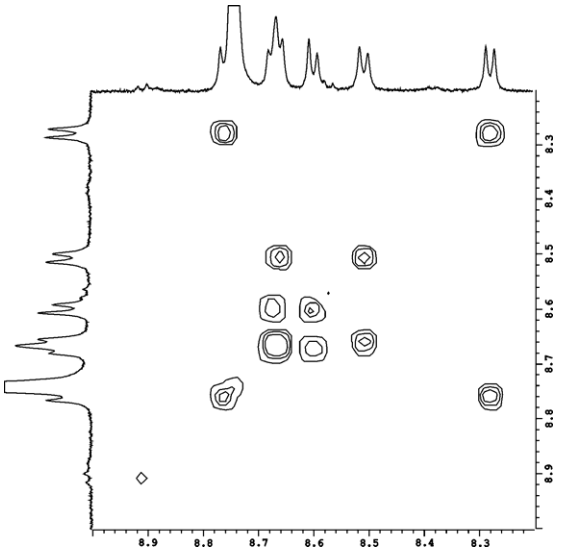
a) A:2:LiI:NaI = 2:1:5:5 COSY 220K



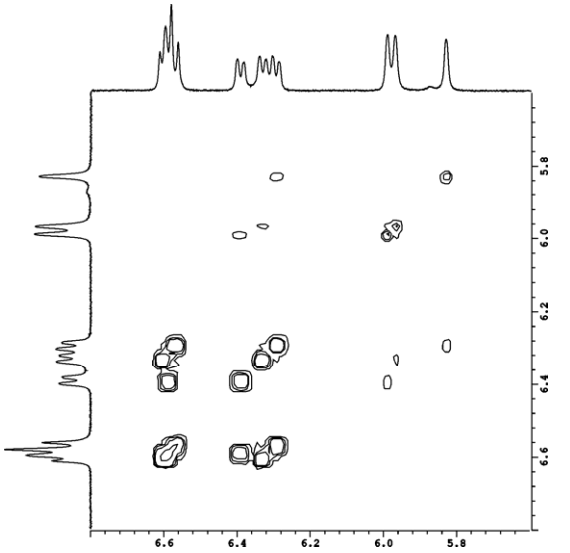
b) A:2:LiI:NaI = 2:1:5:5 NOESY 220K



c) A:2:LiI:NaI = 2:1:5:5 COSY 260K



A:2:LiI:NaI = 2:1:5:5 COSY 260K



d) A:2:LiI:NaI = 2:1:10:10 COSY 220K **A:2:LiI:NaI = 2:1:10:10 COSY 220K** cnoc1403

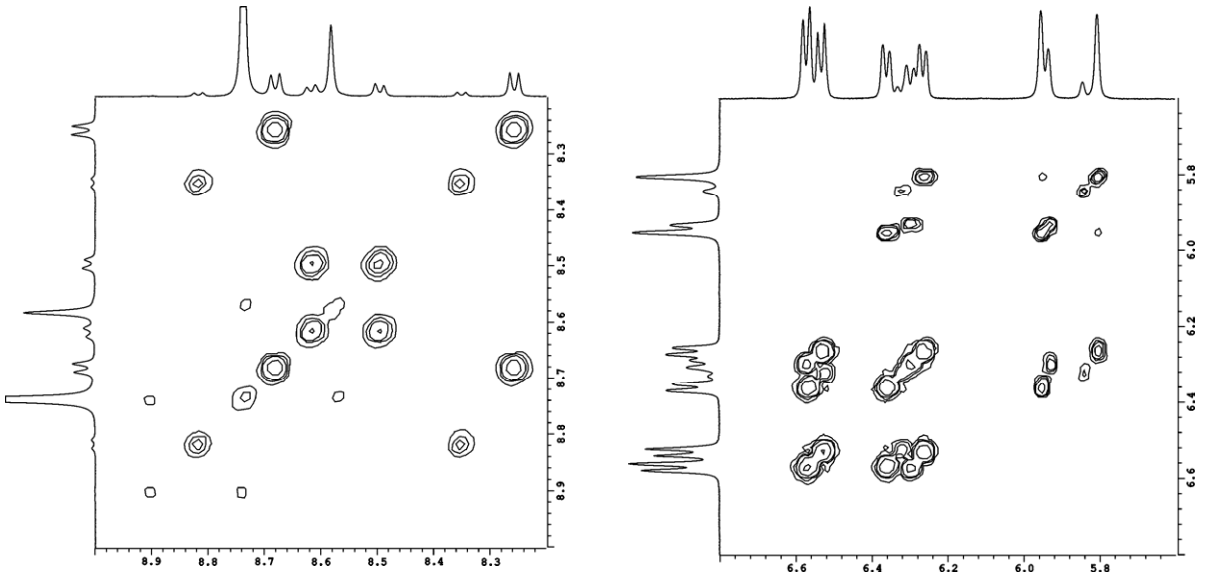


Figure S7: Parts of ^{1}H NMR and 1D NOESY spectra (aromatic acceptor **II** protons, 9-8.1 ppm) of **A:2:LiI:NaI = 2:1:5:5** complex in $CDCl_3$/MeOD 98:2 at different temperatures. The arrow marks the irradiated resonance. **Ex** means an above signal is due to exchange.

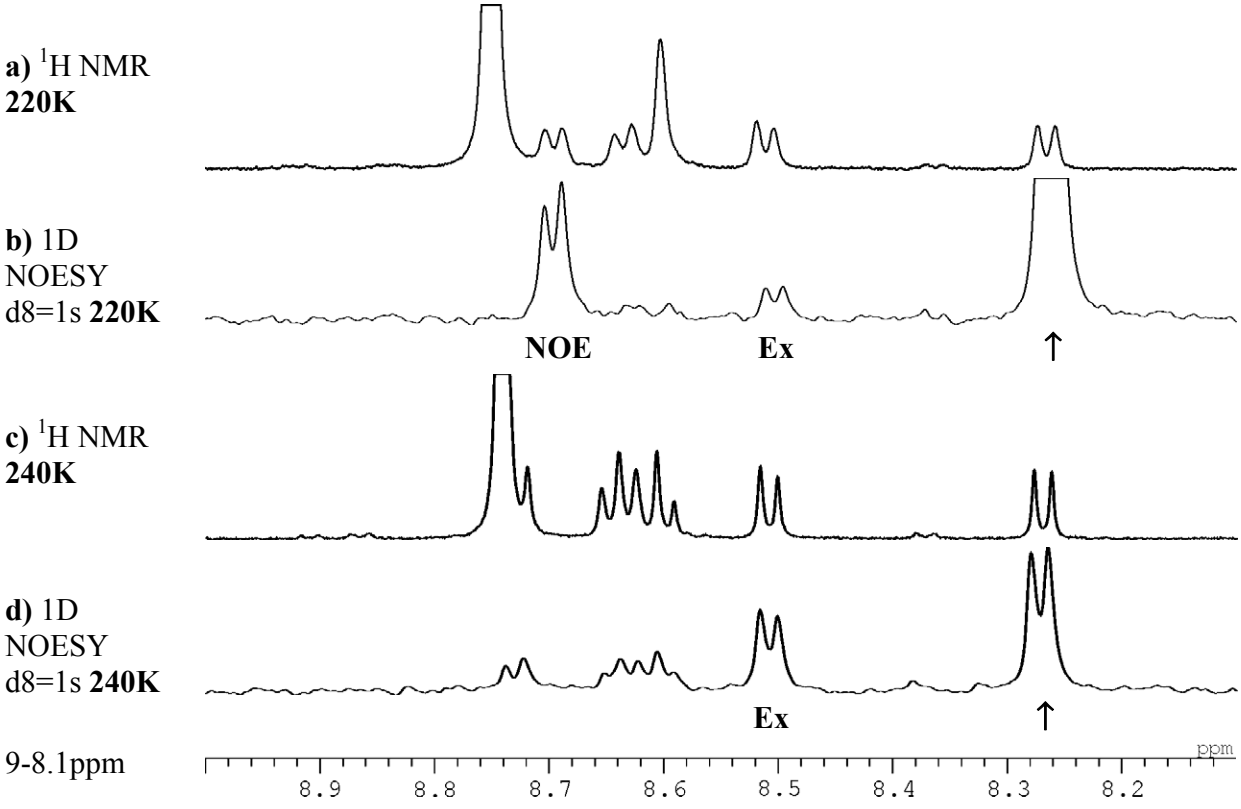


Figure S8: Parts of ^{1}H COSY spectrum of **A:2:Li triflate:NaI** complex (CD_2Cl_2, 260K).

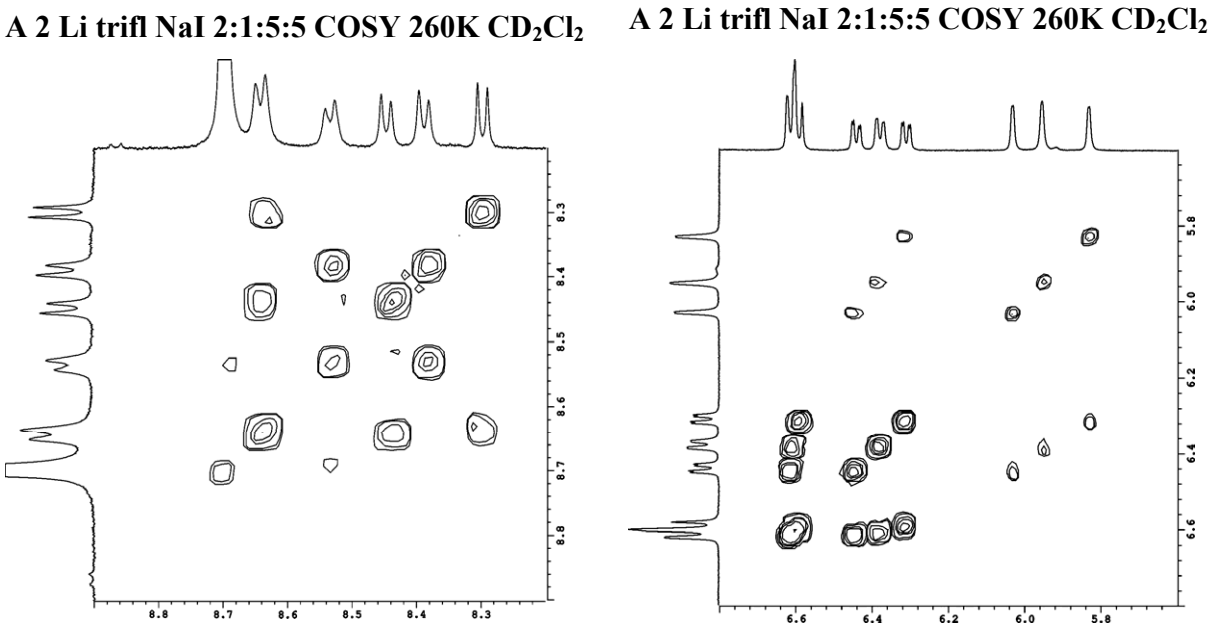
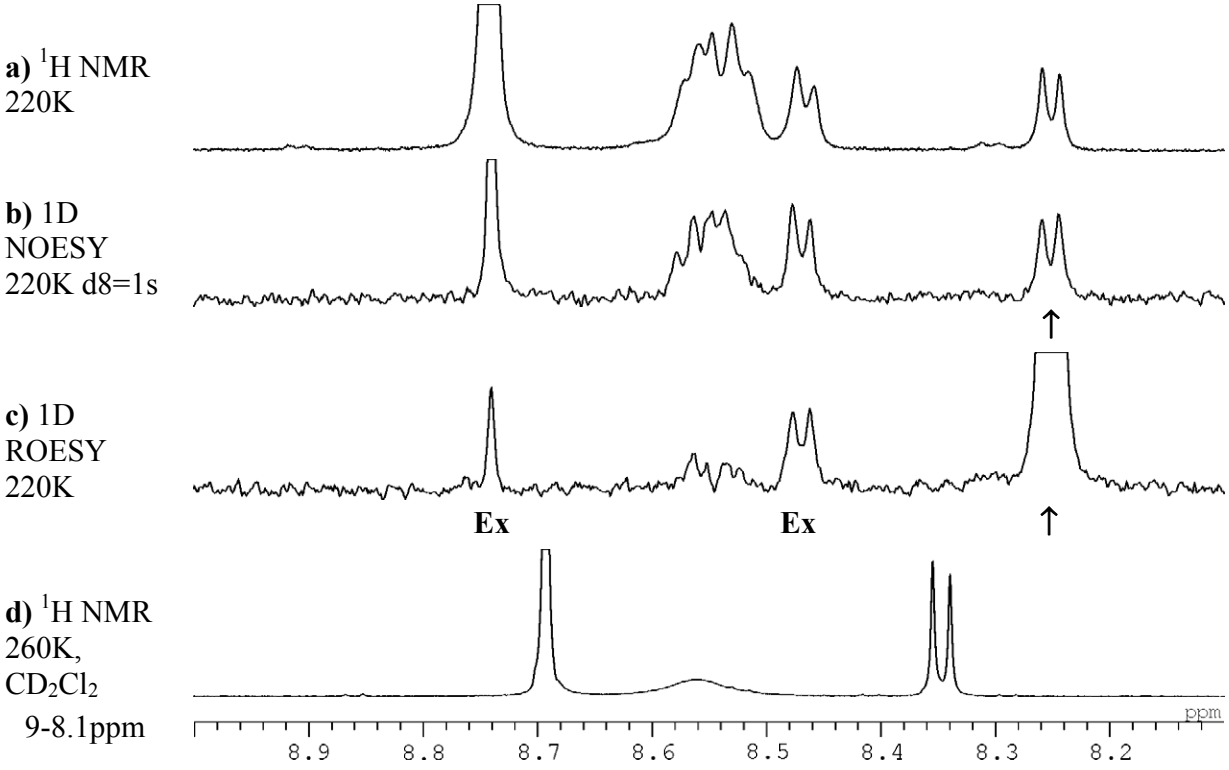


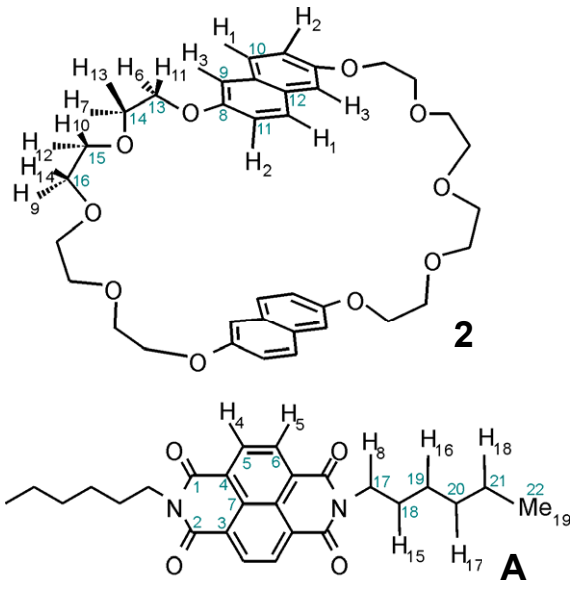
Figure S9: Parts of ^{1}H NMR and 1D NOESY spectra (aromatic acceptor **A** protons, 9-8.1 ppm) of **A:2:Li triflate:NaI = 2:1:5:5** complex in $CDCl_3$/MeOD 98:2. The arrow marks the irradiated resonance. **Ex** means an above signal is due to exchange. e) **A:2:LiBr:Na triflate = 2:1:5:5** complex in CD_2Cl_2.



Acceptor A and Crown 2 Complexes- a Summary of NMR Results

Figure S10: a) Labelling of protons and carbon atoms (blue) in **A·2·salt** complexes; b) spatial structure as seen from NOESY data.

a)



b)

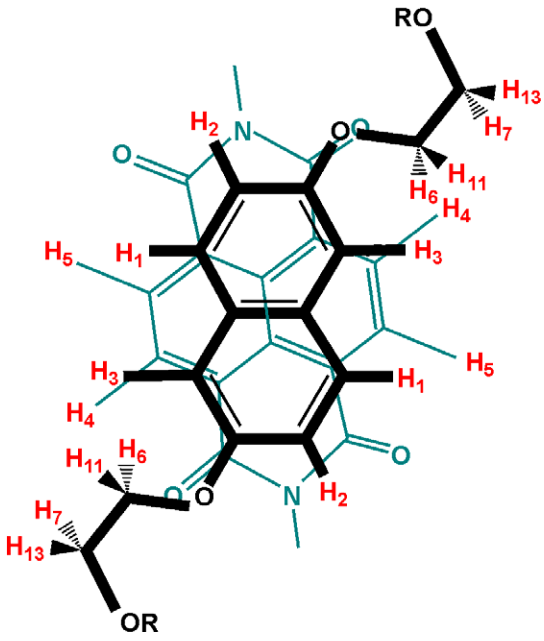


Table S12: Summary of key NOE correlations for **A:2:LiI = 2:1:10** complex (in CD_2Cl_2) when no decomplexation takes place. Labels refer to *Figure 1*.

From 2D NMR	from 1D NMR (in decreasing order)
H_4 is near crown ether protons, near H_3, then H_1, has no NOEs to H_2; H_5 has no NOE to crown ether protons, larger NOE to H_1 than H_3, no NOE to H_2; H_1 has no NOE to crown ether or NCH_2CH_2 protons; H_2 has NOEs to NCH_2CH_2 protons and only small ones to crown ether protons; H_3 has large NOEs to crown ether protons	H_4 to H_3 and H_6; H_5 to H_1 and H_3; H_1 to H_3 and H_5; H_2 to H_8 and H_{15}; H_3 to H_1, H_6, H_{11}, H_4 and H_5; H_6 to H_{11}, H_3 and H_4; H_{11} to H_6, H_3, H_7, H_{13}; H_{15} to H_8, H_2, H_{16}.

Comparison of ^1H chemical shifts of **A:2:salt** complexes:

The chemical shift differences for bound acceptor **A** protons (H_4, H_5) depend on:

a) Anion:

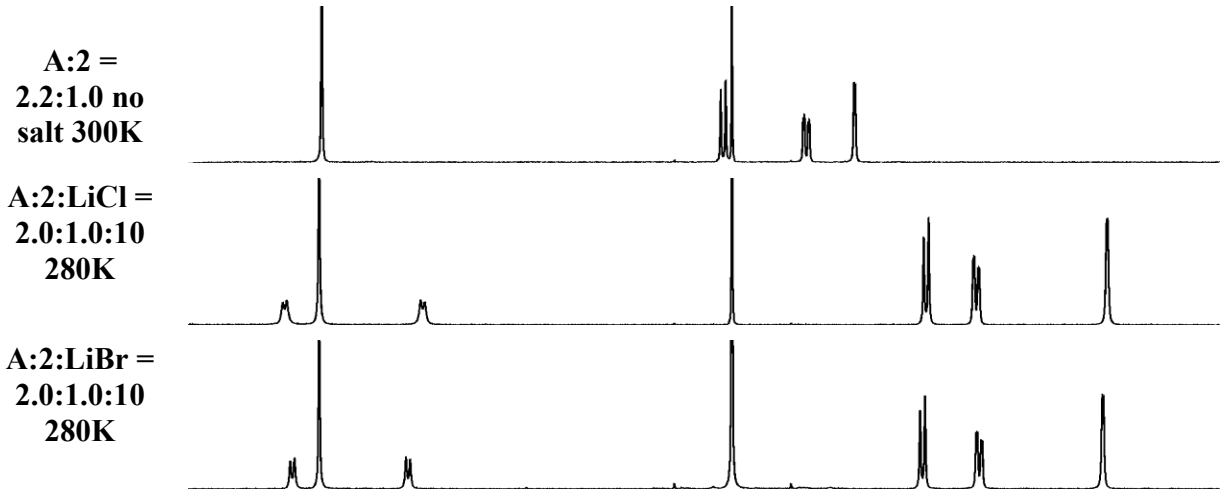
We used two kinds: halides (Cl^-, Br^-, and I^-) and oxygen containing anions (TfO^-, NO_3^-, ClO_4^-) oxyanions. The chemical shift difference for bound acceptor protons H_4 and H_5 are much larger for halide than for oxyanion complexes (*Figures 2 and 3* below and *Figure S2* in the supporting section). The chemical shift of the more downfield shifted bound acceptor proton H_4 is particularly affected by the nature of the anion (*Tables S1* and *S2* in the supporting section) There are only small differences for bound aromatic donor protons H_1-H_3, but large ones for H_6 and H_{11}, the O$\underline{CH_2}CH_2$ protons closest to naphthalene aromatic ring (see labelling in *Figure 1*). In halide complexes H_6 is closer to H_3 and has a larger chemical shift difference to its coupled H_{11} proton (*Table 2* and *Figure S3*).

b) Temperature:
Higher temperature **increases** the chemical shift differences between bound aromatic acceptor protons H_4 and H_5, particularly for halide complexes. H_4 is moving downfield with increasing temperature (*Figure 4* for difference between **LiBr** and **LiOTf** complexes). H_6 in **LiI** complexes is also moving downfield with higher temperature.

c) Cation:
The effect of the nature of the cation ($\mathbf{Na^+}$ or $\mathbf{Li^+}$) on chemical shifts is relatively small. Most changes are seen in the crown ether region ($\mathbf{Na^+}$ complexes are more spread upfield), but even there the nature of the anion is more important (*Figures S3 and S4*). The cation is important for the kinetic stability of the complex. $\mathbf{Li^+}$ complexes are generally more stable than $\mathbf{Na^+}$ complexes.

d) Solvent:
The solvent ($CDCl_3$/MeOD 98:2 or CD_2Cl_2) effect on chemical shifts is small. As for the cation there are differences in kinetic stability between the two solvent systems. Complexes in CD_2Cl_2 are kinetically more stable.

Figure S11: Parts of ^{1}H NMR spectra (aromatic protons H_1 to H_5, 9.2 ppm-5.5 ppm) of **A:2:salt = ≥2:1:10** complexes ($CDCl_3$/MeOD 98:2, different temperatures)



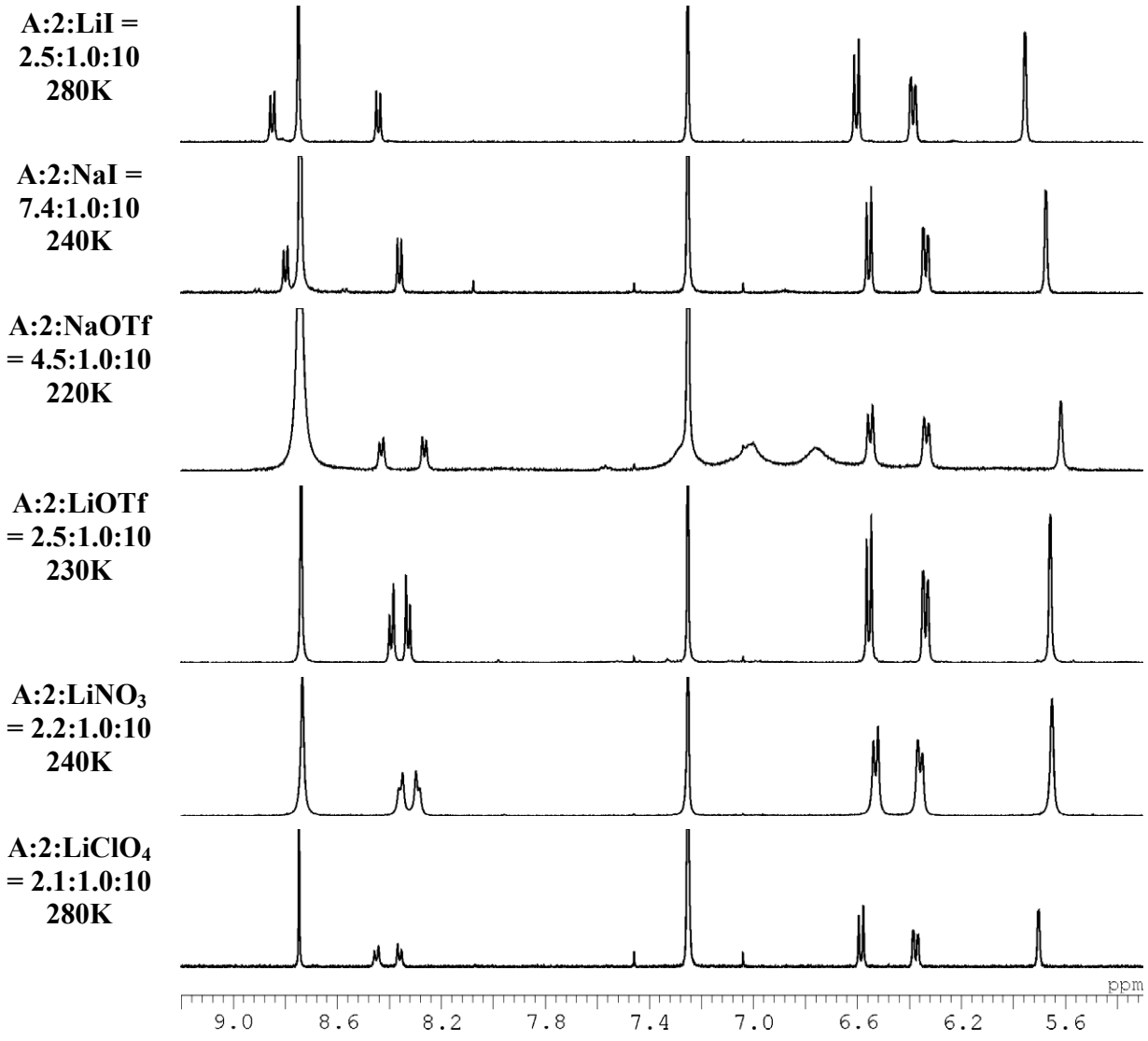

A:2:LiI = 2.5:1.0:10 280K
A:2:NaI = 7.4:1.0:10 240K
A:2:NaOTf = 4.5:1.0:10 220K
A:2:LiOTf = 2.5:1.0:10 230K
A:2:LiNO3 = 2.2:1.0:10 240K
A:2:LiClO4 = 2.1:1.0:10 280K
ppm
9.0
8.6
8.2
7.8
7.4
7.0
6.6
6.2
5.6

Figure S12: Summary of chemical shifts for bound acceptor **A** protons H_4 and H_5 and aromatic crown ether protons H_1 to H_3: a) A:2: salt 2:1:10 complexes in $CDCl_3$/MeOD 98:2, b) A:2: salt 2:1:10 complexes in CD_2Cl_2.

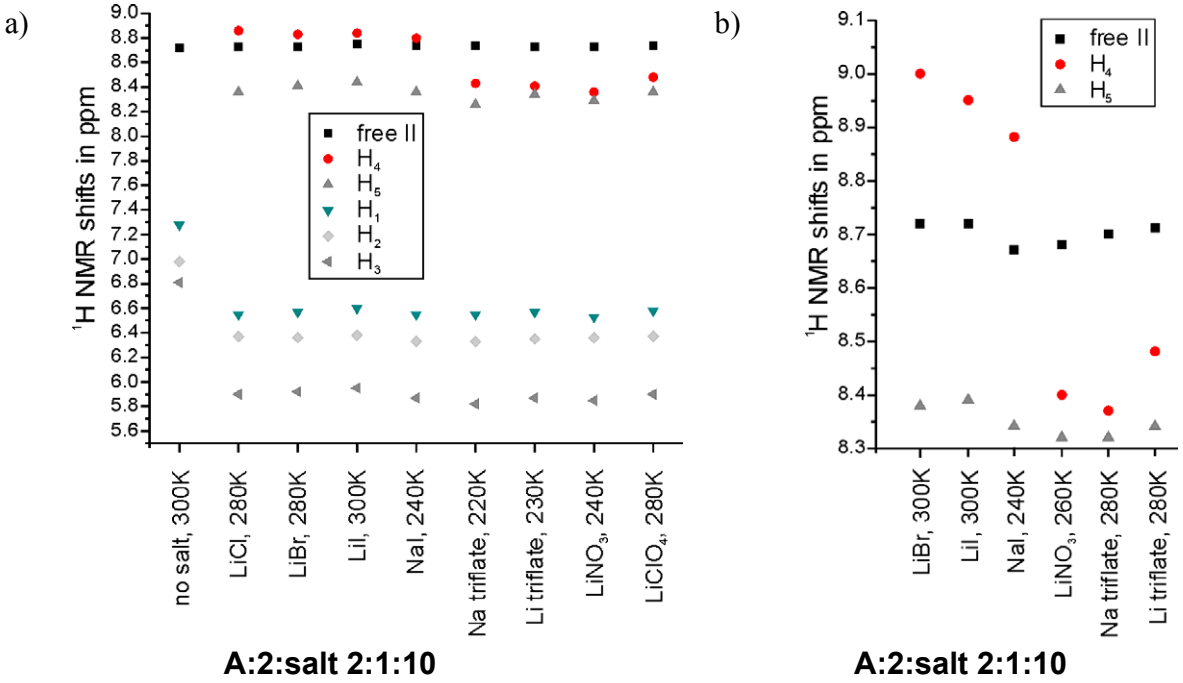
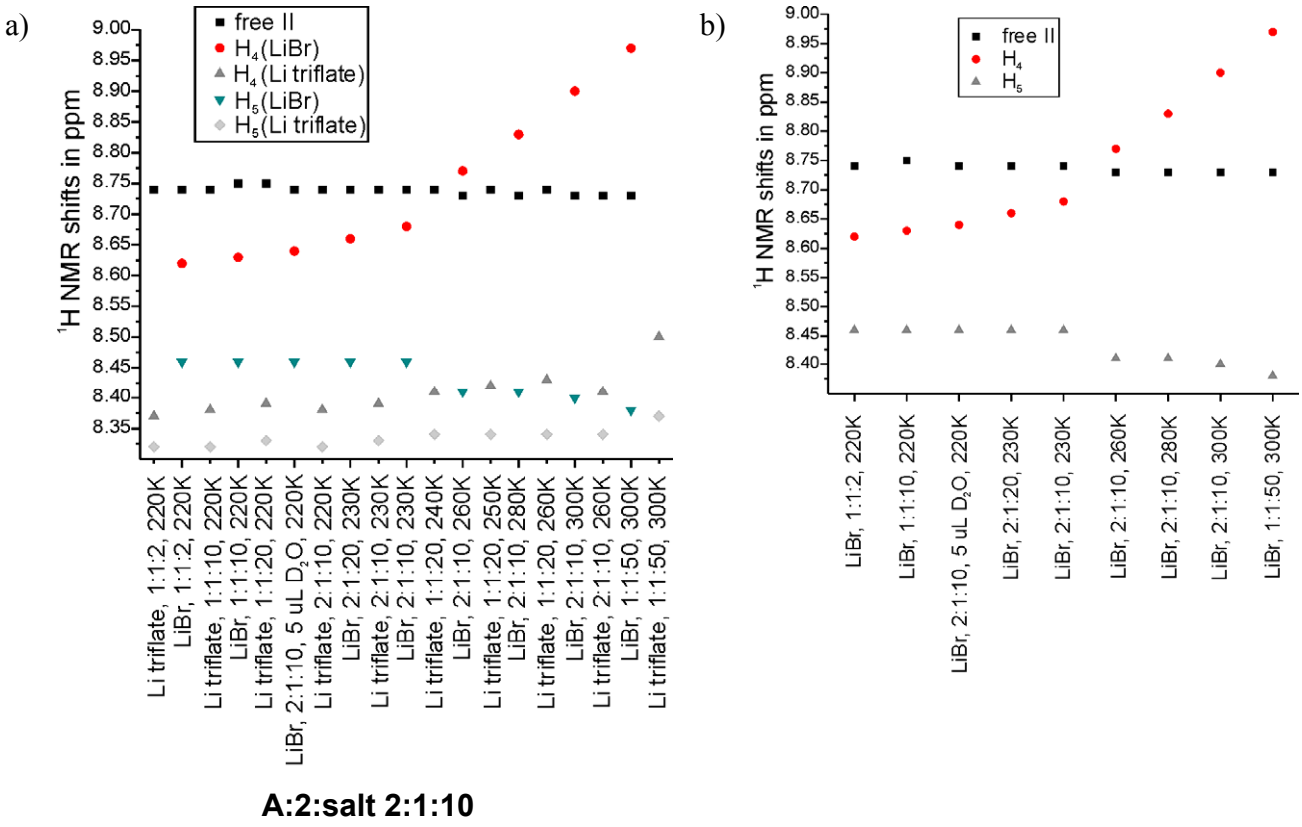


Table S13:
1D NOESY irradiation of H_3 yields NOE to adjacent $ArOCH_2$ protons H_6 and H_{11} (*Figure S3*). COSY data confirmed geminal coupling between H_6 and H_{11}. Labelling corresponds to Figure 1.

A:2:salt = ≥2:1:10 complex (CD_2Cl_2)	**T in K**	**H_6 (ppm)**	**H_{11} (ppm)**	**Δppm H_6-H_{11}**
LiI	280K	4.30	3.89	0.41
LiBr	280K	4.30	3.89	0.41
NaI	240K	4.18	3.81	0.37
NaOTf	280K	3.99	3.83	0.16
LiOTf	280K	4.05	3.88	0.17

Figure S13: Effect of temperature on chemical shift for **LiBr** and **LiOTf** complexes. Temperature increases from left to right on the x-axis. a) **LiBr** and **LiOTf** complexes. Protons H_1 to H_5 are shown, b) **LiBr** complexes only, protons H_4 and H_5 are shown.



Comparison of ^{13}C chemical shifts of A:2: :salt complexes: LiI and NaOTf

Mirroring the chemical shift differences for bound acceptor **A** protons H_4 and H_5, the directly linked ^{13}C atoms (C_5, C_6, labels refer to *Figure 1*) also differ: the halide complex shows a Δ ppm of 2.2 ppm between C_5 and C_6, compared with 1.0 ppm for the triflate complex. Many aromatic resonances of the **LiI** complex are shifted downfield by ca. 0.2 ppm. Carbon atoms C_{17} to C_{22} belonging to the alkyl tail of bound acceptor **A** are hardly changed. In contrast, the inner crown ether carbons C_{15} and C_{16} of the NaOTf complex are moved downfield by 0.6 ppm and 0.7 ppm. This may be due to the effect of Na^+ versus Li^+ binding, or alternatively caused by the involvement of triflate anion (see *Table 3*)

Table S14:

Aromatic bound acceptor **A** carbon atoms linked to H_4 and H_5

LiI	HMQC	HMBC		**NaOTf**	HMQC		Δppm (LiI-NaOTf)
δ (ppm)	correlations			δ (ppm)	correlations		
132.93	C_5	H_4		131.21	Free A, C_5		Ca. 1.7
130.72	C_6	H_5		130.25	C_6		0.47

OCH_2CH_2O crown ether carbon atoms

LiI	HMQC	HMBC		**NaOTf**	HMQC		Δppm (LiI-NaOTf)
δ (ppm)	correlations			δ (ppm)	correlations		
71.34	C_{14}, H_7, H_{13}	H_6		71.41	C_{14}, H_7, H_{13}		-0.07
70.36	C_{15}, H_{10}, H_{12}	H_{10}		70.99	C_{15}, H_{10}, H_{12}		-0.63
69.86	C_{16}, H_9, H_{14}	H_9		70.57	C_{16}, H_9, H_{14}		-0.71
67.07	C_{13}, H_6, H_{11}	H_{13}		66.87	C_{13}, H_6, H_{11}		0.20

Switching of pseudorotaxanes: preparation of acceptor A mixed crown complexes.

Table S15: Distribution of acceptor **A** aromatic resonances H_4 and H_5 among different species (**A:1:(salt)** and **A:2:salt**), see *Figure S1*. The numbers were obtained by integration.

A: 1: 2:(salt) complex	free **A**	H_4+H_5 **A:1:(salt) complex**	H_4+H_5 **A:2:salt complex**	**1 (bound): 1 (free)**	**2 (bound): 2(free)**
a) A:1:2 = 1.0:1.0:0.6 no salt 220K	16%	84%	0	11.9:1.0	only **2 (free)**
b) A:1:2:Li triflate = 1.0:1.0:0.7:10 220K	0	42%	58%	1.0:1.0	14.5:1.0
c) A:1:3:LiI= 1.0:0.8:0.9:10 220K	0	16%	84%	1.0:4.4	9.9:1.0
d) A:1:2:LiI= 1.0:0.8:0.9:10 260K	0	9%	91%	only **1 (free)**	>16:1

Figure S14: Parts of ^{1}H NMR spectra (aromatic acceptor **A** protons, 8.9-7.8 ppm) of **A:1:2:salt** complexes in $CDCl_3$/MeOD 98:2 at different temperatures (see *Table 1*).

a) A:1:2 = 1.0:1.0:0.6 no salt 220K

b) A:1:2:Li triflate = 1.0:1.0:0.7:10 220K

c) A:1:2:LiI= 1.0:0.8:0.9:10 220K

d) A:1:2:LiI= 1.0:0.8:0.9:10 260K

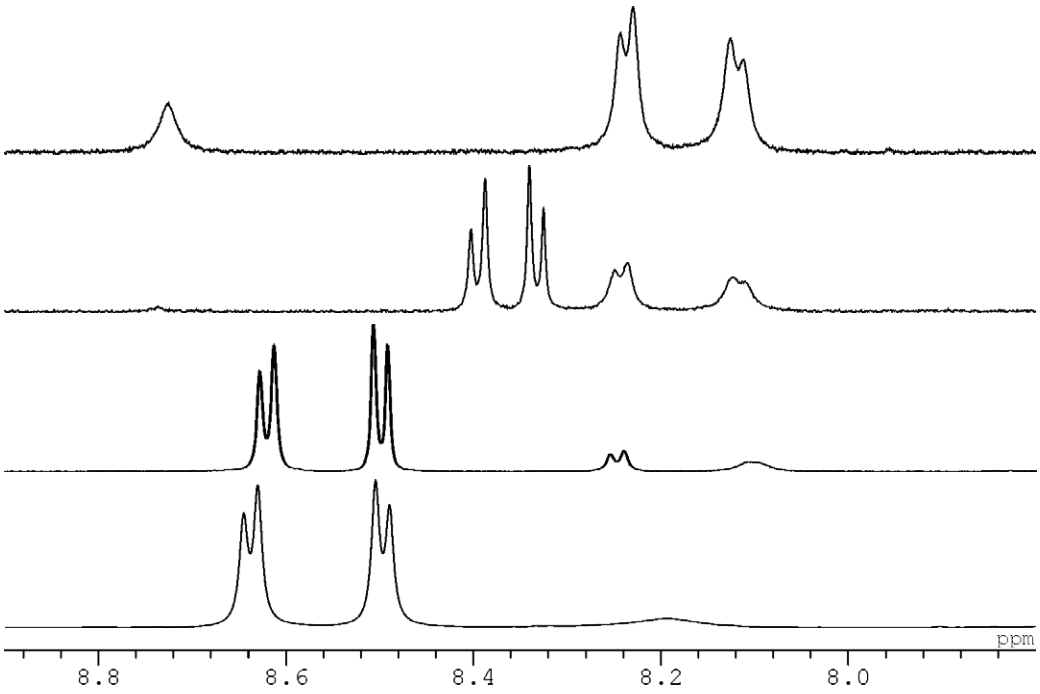
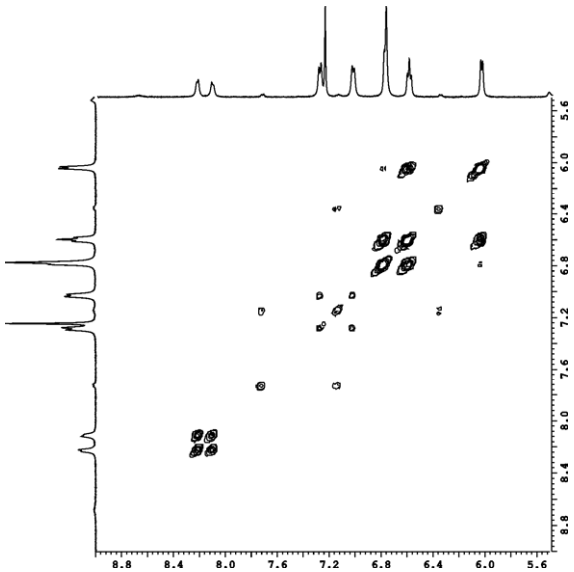


Figure S15: Parts of COSY spectra of **A:1:2:(salt)** complexes ($CDCl_3$:MeOD=98:2, 220K).

A:1:2 = 1.0:1.0:0.6 no salt COSY 220K



A:1:2:LiI= 1.0:0.8:0.9:10 COSY 220K

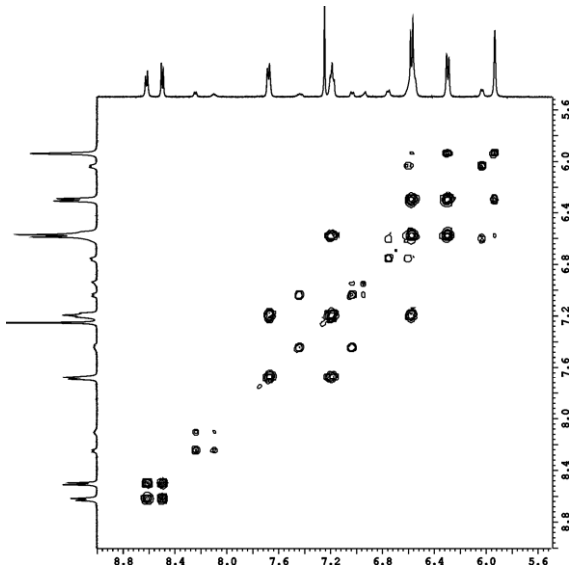
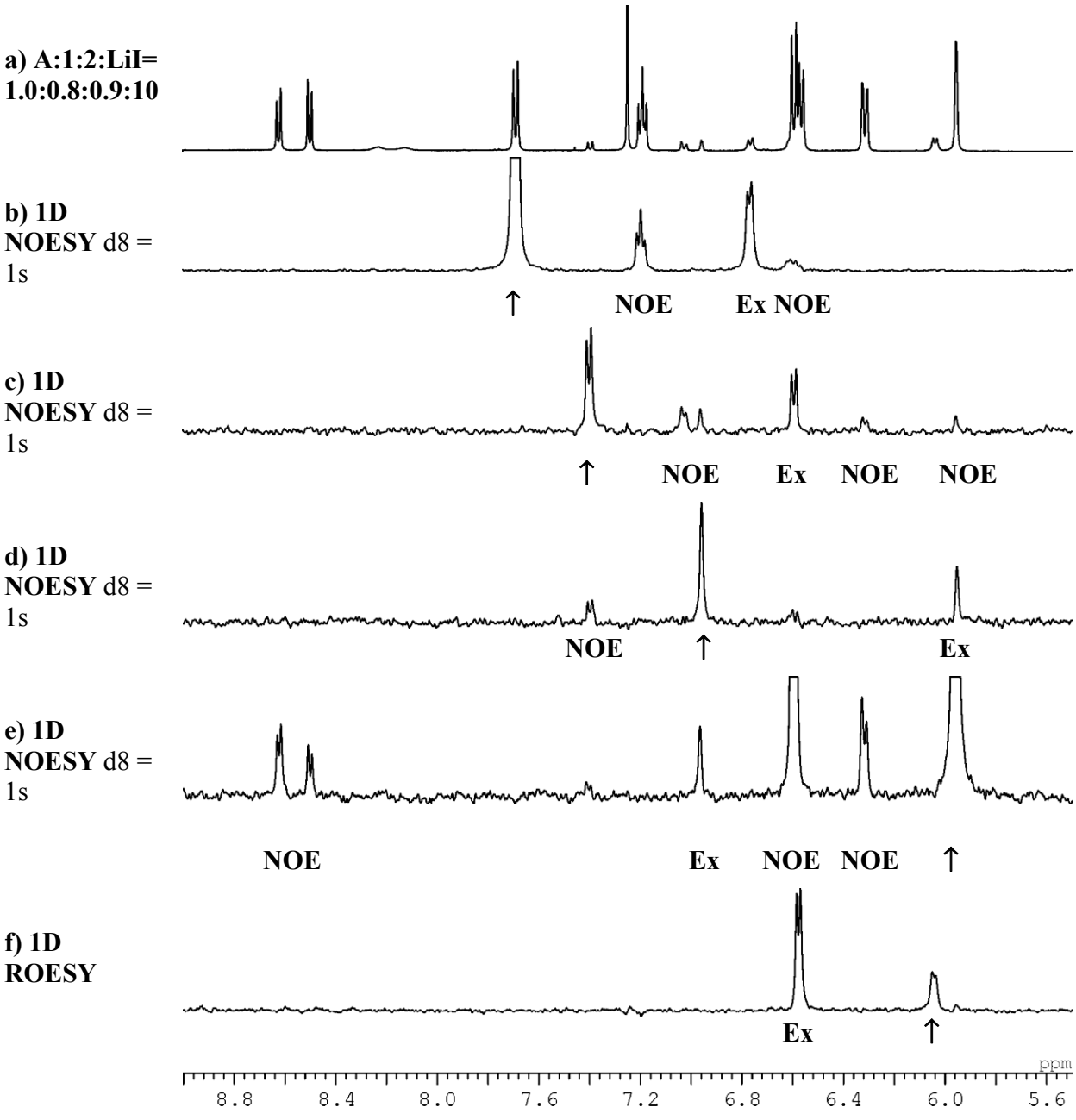


Figure S16. Parts of ^{1}H NMR, 1D NOESY and 1D ROESY spectra (aromatic acceptor **A** and crown ether protons, 9-5.5 ppm) of **A:1:2:LiI** complexes in $CDCl_3$:MeOD=98:2 at 240K. The arrow marks the irradiated resonance. **Ex** or **NOE** mean an above signal is due to exchange or NOE, respectively.



Comments on b) to f):
b) irradiation of H_1 resonance of free **host 1** shows exchange with H_1 resonance of bound **host 2** (**A:1** complex).

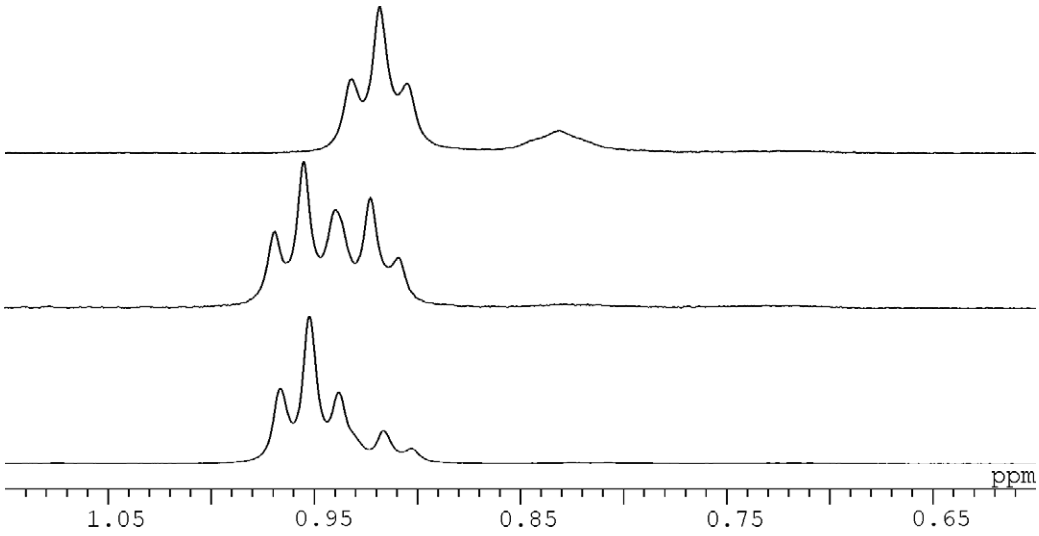
c) irradiation of H_1 resonance of free **host 2** (possibly **host 2:LiI** complex) shows exchange with H_1 resonance of bound crown 1 (**A:2:LiI** complex).
d) similar to c), irradiation of H_3 resonance of free **host 2**.
e) irradiation of H_3 resonance of bound **host 2** shows exchange with H_3 resonance of free **host 1**.
f) irradiation of H_3 resonance of bound **crown 1** shows exchange with H_3 resonance of free **host 1**.

Figure S17: Parts of ^{1}H NMR spectra (methyl protons of acceptor **A**, 1.1-0.6 ppm) of **A:1:2:salt** complexes in $CDCl_3$:MeOD=98:2 at 220K.

a) A:1:2 = 1.0:1.0:0.6 no salt

b) A:1:2:LiOTf = 1.0:1.0:0.7:10

c) A:1:2:LiI = 1.0:0.8:0.9:10



Comments on a) to c):
a) two species are visible;**A:1** complex (downfield) and free **A** (0.83 ppm);
b) new resonance downfield of the one for **A:1** corresponds to **A:2:LiOTf**;
c) reduced amount of **A:1** species

Reference:

1. Pulse sequence used: selnogp.2: 1D NOESY using selective excitation with a shaped pulse; dipolar coupling may be due to NOE or chemical exchange. K. Stott, J. Stonehouse, J. Keeler, T.-L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1995**,*117*, 4199. See also, C. Naumann, B. O. Patrick, J. C. Sherman, *Tetrahedron* **2002**, *58*, 787.