Structural and kinetic investigations of alkali-mediated pseudorotaxanes

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Supplementary Information
Figure S1: Parts of $^1$H NMR of A·I complexes (CDCl₃/MeOD 98:2, 220K)

9-5.5ppm

A:1 1:1

9-5.5ppm

A:1 2:1

9-5.5ppm

A:1:LiBr
2:1:10

9-5.5ppm

A:1:LiOTf
2:1:10

9-5.5ppm

A:1:LiI
2:1:10

9-5.5ppm

A:1:LiI:NaI
2:1:10:10

9-5.5ppm

A:1:NaI
2:1:10
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

<table>
<thead>
<tr>
<th></th>
<th>Free A:H$_5$</th>
<th>Free A:H$_4$</th>
<th>H$_4$:H$_5$</th>
<th>Free 1:H$_1$</th>
<th>Me$_1$:Me$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A cr1 1:1</td>
<td>3.3</td>
<td>3.8</td>
<td>7.0</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
<td>-</td>
</tr>
<tr>
<td>A cr1 2:1</td>
<td>0.15</td>
<td>7.7</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A cr1 LiBr 2:1:10</td>
<td>0.13</td>
<td>0.14</td>
<td>0.12</td>
<td>7</td>
<td>0.32</td>
</tr>
<tr>
<td>A cr1 Litri$f$late 2:1:10</td>
<td>0.16</td>
<td>6</td>
<td>0.10</td>
<td>7.0</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td></td>
<td></td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>A cr1 LiI 2:1:10</td>
<td>0.12</td>
<td>0.11</td>
<td>3</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>3.5</td>
<td>3.9</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>A cr1 LiI NaI 2:1:10:10</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A cr1 NaI 2:1:10</td>
<td>0.25</td>
<td>0.25 (3.4 H$_2$:H$_1$)</td>
<td>2.9</td>
<td>2.2 (0.54 Me$_2$:Me$_1$)</td>
<td></td>
</tr>
</tbody>
</table>

Rate constant $k$ in s$^{-1}$, irradiated resonances first, **adjusted** for unequal populations

<table>
<thead>
<tr>
<th></th>
<th>Free A:H$_5$</th>
<th>Free A:H$_4$</th>
<th>H$_4$:H$_5$</th>
<th>Free 1:H$_1$</th>
<th>Me$_1$:Me$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:1 1:1</td>
<td>3.3</td>
<td>3.8</td>
<td>7.0</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
<td>-</td>
</tr>
<tr>
<td>A:1 2:1</td>
<td>0.39</td>
<td>7.7</td>
<td>0.37</td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>A:1 LiBr 2:1:10</td>
<td>0.31</td>
<td>7</td>
<td>0.32</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>A:1 Li triflate 2:1:10</td>
<td>0.44</td>
<td>7.0</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A:1 LiI 2:1:10</td>
<td>0.32</td>
<td>3.5</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A:1 LiI NaI 2:1:10:10</td>
<td></td>
<td></td>
<td></td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>A:1 NaI 2:1:10</td>
<td>1.5</td>
<td>1.5 (3.4 H$_2$:H$_1$)</td>
<td>2.9</td>
<td>2.2 (0.54 Me$_2$:Me$_1$)</td>
<td></td>
</tr>
</tbody>
</table>
Table S2: Chemical shift differences for bound acceptor A protons at 220K, all in CDCl₃/MeOD 98:2. For labelling see Figure 1.

<table>
<thead>
<tr>
<th>A:1:(salt) complex</th>
<th>Δ ppm H₄-H₅</th>
<th>Δ ppm free A-H₄</th>
<th>Δ ppm free A-H₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:1 = 1.0:1.0</td>
<td>0.12</td>
<td>0.46</td>
<td>0.58</td>
</tr>
<tr>
<td>A:1 = 2.2:1.0</td>
<td>0.11</td>
<td>0.49</td>
<td>0.60</td>
</tr>
<tr>
<td>A:1:LiBr = 2.2:1.0:10</td>
<td>0.12</td>
<td>0.49</td>
<td>0.61</td>
</tr>
<tr>
<td>A:1:LiOTf = 2.1:1.0:10</td>
<td>0.12</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>A:1:LiI = 2.1:1.0:10</td>
<td>0.14</td>
<td>0.47</td>
<td>0.61</td>
</tr>
<tr>
<td>A:1:NaI = 2.6:1.0:10</td>
<td>0.26</td>
<td>0.44</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table S3: Summary of activation barriers for decomplexation of A:1:(salt) complexes in CDCl₃/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.

<table>
<thead>
<tr>
<th>A:1:(salt) complex</th>
<th>T in K</th>
<th>k (H_bound-H_free)* s⁻¹</th>
<th>ΔG^‡ / kcal mol⁻¹</th>
<th>k (H_bound-H_bound) s⁻¹</th>
<th>Ratio of k (H_bound-H_bound) to k (H_bound-H_free)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:1 = 1.0:1.0</td>
<td>220</td>
<td>3.6</td>
<td>12.2</td>
<td>7.0</td>
<td>2</td>
</tr>
<tr>
<td>A:1 = 2.2:1.0</td>
<td>220</td>
<td>0.37</td>
<td>13.2</td>
<td>7.7</td>
<td>20</td>
</tr>
<tr>
<td>A:1:LiBr = 2.2:1.0:10</td>
<td>220</td>
<td>0.32</td>
<td>13.2</td>
<td>7</td>
<td>22</td>
</tr>
<tr>
<td>A:1:Li triflate = 2.1:1.0:10</td>
<td>220</td>
<td>0.44</td>
<td>13.1</td>
<td>7.0</td>
<td>16</td>
</tr>
<tr>
<td>A:1:LiI = 2.1:1.0:10</td>
<td>220</td>
<td>0.32</td>
<td>13.2</td>
<td>3.5</td>
<td>11</td>
</tr>
<tr>
<td>A:1 LiI NaI 2:1:10:10</td>
<td>220</td>
<td>0.43</td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A:1:NaI = 2.6:1.0:10</td>
<td>220</td>
<td>1.7</td>
<td>12.5</td>
<td>2.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*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 CDCl₃/MeOD 98:2 at 220K. For labelling see Figures 1 and 2.

<table>
<thead>
<tr>
<th>Chemical shifts in ppm (CDCl₃ at 7.25ppm)</th>
<th>Integration ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free A</td>
<td>H₄</td>
</tr>
<tr>
<td>-------</td>
<td>----</td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1:LiI = 1:1</td>
<td>8.69 s</td>
</tr>
<tr>
<td>A:1 = 1.0:1.0</td>
<td>8.70 s</td>
</tr>
<tr>
<td>A:1:LiBr = 2.2:1.0:10</td>
<td>8.71 s</td>
</tr>
<tr>
<td>A:1:LiOTf = 2.1:1.0:10</td>
<td>8.73 s</td>
</tr>
<tr>
<td>A:1:LiI = 2.1:1.0:10</td>
<td>8.71 s</td>
</tr>
<tr>
<td>A:1:NaI 2:1:10:10</td>
<td>8.74 s</td>
</tr>
<tr>
<td>A:1:NaI = 2.6:1.0:10</td>
<td>8.72 s</td>
</tr>
<tr>
<td>1 (bound) : 1 (free) = 2.4:1.0</td>
<td></td>
</tr>
</tbody>
</table>

Me¹ belongs to bound acceptor A, Me² 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$_2$Cl$_2$. 

Complex A:2:LiI
Complex A:2:NaI

2D NOESY 220K

COSY 220K
A:2:Na triflate complex

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$_2$Cl$_2$, different temperatures)
Table S5: Chemical shift differences for bound acceptor A protons at different temperatures, all in CDCl₃/MeOD 98:2. For labelling see Figure 1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T in K</th>
<th>Δ ppm H₄-H₅</th>
<th>Δ ppm free A-H₄</th>
<th>Δ ppm free A-H₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2 LiCl 1:1:10</td>
<td>260</td>
<td>0.45</td>
<td>-0.08</td>
<td>0.37</td>
</tr>
<tr>
<td>A 2 LiCl 2:1:10</td>
<td>280</td>
<td>0.50</td>
<td>-0.13</td>
<td>0.37</td>
</tr>
<tr>
<td>A 2 LiBr 1:1:2</td>
<td>220</td>
<td>0.16</td>
<td>0.12</td>
<td>0.28</td>
</tr>
<tr>
<td>A 2 LiBr 1:1:10</td>
<td>220</td>
<td>0.17</td>
<td>0.12</td>
<td>0.29</td>
</tr>
<tr>
<td>A 2 LiBr 1:1:50</td>
<td>300</td>
<td>0.59</td>
<td>-0.24</td>
<td>0.35</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:10</td>
<td>230</td>
<td>0.22</td>
<td>0.06</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.36</td>
<td>-0.04</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.42</td>
<td>-0.10</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.50</td>
<td>-0.17</td>
<td>0.33</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:10 (5 µL D₂O added)</td>
<td>220</td>
<td>0.18</td>
<td>0.10</td>
<td>0.28</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:20</td>
<td>230</td>
<td>0.20</td>
<td>0.08</td>
<td>0.28</td>
</tr>
<tr>
<td>A 2 LiI 1:1:10</td>
<td>250</td>
<td>0.14</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.16</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.20</td>
<td>0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>A 2 LiI 2:1:10*</td>
<td>280</td>
<td>0.26</td>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.40</td>
<td>-0.09</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.38</td>
<td>-0.09</td>
<td>0.29</td>
</tr>
<tr>
<td>A 2 NaI 2:1:10*</td>
<td>220</td>
<td>0.41</td>
<td>0</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0.44</td>
<td>-0.06</td>
<td>0.38</td>
</tr>
<tr>
<td>A 2 NaOTf 2:1:10</td>
<td>220</td>
<td>0.17</td>
<td>0.31</td>
<td>0.48</td>
</tr>
<tr>
<td>A 2 LiOTf1:1:2</td>
<td>220</td>
<td>0.05</td>
<td>0.37</td>
<td>0.42</td>
</tr>
<tr>
<td>A 2 LiOTf 1:1:10</td>
<td>220</td>
<td>0.06</td>
<td>0.36</td>
<td>0.42</td>
</tr>
<tr>
<td>A 2 LiOTf1:1:20</td>
<td>220</td>
<td>0.06</td>
<td>0.36</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0.07</td>
<td>0.33</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.08</td>
<td>0.32</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.09</td>
<td>0.31</td>
<td>0.40</td>
</tr>
<tr>
<td>A 2 LiOTf 1:1:50*</td>
<td>300</td>
<td>0.13</td>
<td>(0.24)</td>
<td>(0.37)</td>
</tr>
<tr>
<td>A 2 LiOTf 2:1:10</td>
<td>220</td>
<td>0.06</td>
<td>0.36</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0.06</td>
<td>0.35</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.07</td>
<td>0.32</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Table S6: Chemical shift differences for bound acceptor A protons at different temperatures, all in CD$_2$Cl$_2$. For labelling see Figure 1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T in K</th>
<th>$\Delta$ ppm H$_4$-H$_5$</th>
<th>$\Delta$ ppm free A-H$_4$</th>
<th>$\Delta$ ppm free A-H$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2 LiBr 2:1:10</td>
<td>280</td>
<td>0.56</td>
<td>-0.23</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.62</td>
<td>-0.28</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>0.64</td>
<td>-0.30</td>
<td>0.34</td>
</tr>
<tr>
<td>A 2 LiI 2:1:10</td>
<td>280</td>
<td>0.56</td>
<td>-0.30</td>
<td>0.34</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:10</td>
<td>315</td>
<td>0.64</td>
<td>-0.30</td>
<td>0.34</td>
</tr>
<tr>
<td>A 2 LiNO$_3$ 2:1:10</td>
<td>280</td>
<td>0.08</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>A 2 NaI 2:1:10</td>
<td>200</td>
<td>0.52</td>
<td>-0.18</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>0.53</td>
<td>-0.22</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0.54</td>
<td>-0.21</td>
<td>0.33</td>
</tr>
<tr>
<td>A 2 Natriflate 2:1:10</td>
<td>240</td>
<td>0.06</td>
<td>0.33</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.05</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.04</td>
<td>0.34</td>
<td>0.38</td>
</tr>
<tr>
<td>A 2 Litriflate 2:1:10</td>
<td>280</td>
<td>0.14</td>
<td>0.23</td>
<td>0.37</td>
</tr>
</tbody>
</table>
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$_2$Cl$_2$, at different temperatures).

LiI 300K

LiI 280K

1D NOESY

LiBr 280K

1D NOESY

NaI 240K

1D NOESY

Na triflate 280K

1D NOESY

Li triflate 280K

1D NOESY
N.B. The irradiated frequency for the 1D NOESY spectra corresponds to the H₃ resonance. NOEs are seen at the H₆ and H₁₁ resonances, H₃ is not shown, see labelling in Figure 1.

**Figure S5**: Parts of ¹H COSY spectra (crown ether OCH₂ protons H₆ to H₁₄, 4.5 ppm-3.5 ppm) of A 2: salt = 2:1:10 complexes (CD₂Cl₂, different temperatures).

![LiI COSY 280K CD₂Cl₂](image1.png)

![LiBr COSY 280K CD₂Cl₂](image2.png)

![NaI COSY 220K CD₂Cl₂](image3.png)

![Li triflate COSY 280K CD₂Cl₂](image4.png)
Na triflate COSY 280K CD₂Cl₂

Li triflate COSY 280K CD₂Cl₂
Table S7: $^{13}$C NMR data (at room temperature) and $^1$H correlations for A:2:salt = 2:1:10 complexes in CD$_2$Cl$_2$ (salts: LiI and Na triflate). CD$_2$Cl$_2$ set to 55.0ppm. $^1$H and $^{13}$C labels are shown in Figure 1.

<table>
<thead>
<tr>
<th>LiI complex δ (ppm)</th>
<th>HMQC correlations</th>
<th>HMBC correlations</th>
<th>Na triflate complex δ (ppm)</th>
<th>HMQC correlations</th>
<th>Δppm (LiI-Na triflate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>163.91 C$_1$ H$_4$</td>
<td></td>
<td></td>
<td>163.66</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>162.49 C$_2$ H$_5$</td>
<td></td>
<td></td>
<td>162.56</td>
<td></td>
<td>-0.07</td>
</tr>
<tr>
<td>154.31 C$_6$ H$_6$</td>
<td>H$_1$&gt;&gt;H$_2$&gt;&gt;H$_3$</td>
<td></td>
<td>154.55</td>
<td></td>
<td>-0.24</td>
</tr>
<tr>
<td>132.93 C$_5$ H$_4$</td>
<td></td>
<td></td>
<td>131.21 Free A, C$_5$</td>
<td></td>
<td>Ca. 1.7</td>
</tr>
<tr>
<td>130.72 C$_6$ H$_5$</td>
<td></td>
<td></td>
<td>130.25 C$_6$</td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>128.49 C$<em>12$, C$</em>{10}$; H$_1$ H$_1$-H$_3$</td>
<td></td>
<td></td>
<td>128.65 C$_{10}$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>128.39</td>
<td></td>
<td></td>
<td>128.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>126.87 C$_3$, H$_4$</td>
<td></td>
<td></td>
<td>126.72</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>125.75 C$_4$, H$_5$</td>
<td></td>
<td></td>
<td>125.47</td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>125.03 C$_7$, H$_4$, H$_5$</td>
<td></td>
<td></td>
<td>124.89</td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>118.46 C$_{11}$, H$_2$, H$_3$</td>
<td></td>
<td></td>
<td>118.59 C$_{11}$</td>
<td></td>
<td>-0.13</td>
</tr>
<tr>
<td>106.38 C$_9$, H$_3$, H$_1$&gt;&gt;H$_2$</td>
<td></td>
<td></td>
<td>106.01 C$_9$</td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td>71.34 C$_{14}$, H$<em>7$, H$</em>{13}$ H$_6$</td>
<td></td>
<td></td>
<td>71.41 C$_{14}$, H$<em>7$, H$</em>{13}$</td>
<td></td>
<td>-0.07</td>
</tr>
<tr>
<td>70.36 C$<em>{15}$, H$</em>{10}$, H$_{12}$</td>
<td></td>
<td></td>
<td>70.99 C$<em>{15}$, H$</em>{10}$, H$_{12}$</td>
<td></td>
<td>-0.63</td>
</tr>
<tr>
<td>69.86 C$_{16}$, H$<em>9$, H$</em>{14}$ H$_9$</td>
<td></td>
<td></td>
<td>70.57 C$_{16}$, H$<em>9$, H$</em>{14}$</td>
<td></td>
<td>-0.71</td>
</tr>
<tr>
<td>67.07 C$<em>{13}$, H$</em>{6}$, H$<em>{11}$ H$</em>{13}$</td>
<td></td>
<td></td>
<td>66.87 C$<em>{13}$, H$</em>{6}$, H$_{11}$</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>41.96 C$_{17}$, H$_8$</td>
<td></td>
<td></td>
<td>41.79 C$_{17}$, H$_8$</td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>32.36 C$_{20}$</td>
<td></td>
<td></td>
<td>32.43 C$_{20}$</td>
<td></td>
<td>-0.07</td>
</tr>
<tr>
<td>28.35 C$_{19}$</td>
<td></td>
<td></td>
<td>28.38 C$_{19}$</td>
<td></td>
<td>-0.03</td>
</tr>
<tr>
<td>28.16 C$_{18}$</td>
<td></td>
<td></td>
<td>28.18 C$_{18}$</td>
<td></td>
<td>-0.02</td>
</tr>
<tr>
<td>23.39 C$_{21}$</td>
<td></td>
<td></td>
<td>23.36 C$_{21}$</td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>14.54 C$_{22}$</td>
<td></td>
<td></td>
<td>14.57 C$_{22}$</td>
<td></td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Table S8: Complete $^1$H NMR data for A:2:LiI = 2:1:10 complex in CD$_2$Cl$_2$ at 300K. CD$_2$Cl$_2$ set to 5.32ppm. $^1$H labels are shown in Figure 1. Only resonances belonging to the complex are shown.

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>label</th>
<th>δ (ppm)</th>
<th>label</th>
<th>δ (ppm)</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.95 d (7.5 Hz)</td>
<td>H$_4$</td>
<td>4.33 t (10.1 Hz)</td>
<td>H$_6$</td>
<td>3.77 t (10.0 Hz)</td>
<td>H$_{13}$</td>
</tr>
<tr>
<td>8.39 d (7.5 Hz)</td>
<td>H$_5$</td>
<td>4.21 d (10.5 Hz)</td>
<td>H$_7$</td>
<td>3.70 m</td>
<td>H$_{14}$</td>
</tr>
<tr>
<td>6.61 d (8.8 Hz)</td>
<td>H$_1$</td>
<td>4.07 m</td>
<td>H$<em>8$-H$</em>{10}$</td>
<td>1.97 m</td>
<td>H$_{15}$</td>
</tr>
<tr>
<td>6.41 dd (8.8 Hz, 2.2 Hz)</td>
<td>H$_2$</td>
<td>3.89 d (10.5 Hz)</td>
<td>H$_{11}$</td>
<td>1.62-1.41 m</td>
<td>H$<em>{16}$-H$</em>{18}$</td>
</tr>
<tr>
<td>5.98 d (2.2 Hz)</td>
<td>H$_3$</td>
<td>3.84 m</td>
<td>H$_{12}$</td>
<td>1.02 t (7.2 Hz)</td>
<td>H$_{19}$</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T in K</th>
<th>k (H$<em>{\text{bound}}$- H$</em>{\text{free}}$)* in s$^{-1}$</th>
<th>$\Delta G^\ddagger$/ kcal mol$^{-1}$</th>
<th>k (H$<em>{\text{bound}}$- H$</em>{\text{bound}}$) in s$^{-1}$</th>
<th>Ratio of k (H$<em>{\text{bound}}$- H$</em>{\text{free}}$) to k (H$<em>{\text{bound}}$- H$</em>{\text{free}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2 LiBr 1:1:2</td>
<td>220</td>
<td>0.9-1.2</td>
<td>12.7</td>
<td>1.3, 1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>A 2 LiBr 1:1:10</td>
<td>220</td>
<td>4-9</td>
<td>12.0</td>
<td>4</td>
<td>0.5-1</td>
</tr>
<tr>
<td>A 2 LiBr 1:1:50</td>
<td>300</td>
<td>0.2</td>
<td>18.5</td>
<td>0.7-0.8</td>
<td>4</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:10</td>
<td>230</td>
<td>0.02</td>
<td>15.1</td>
<td>0.4-0.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.5-0.8</td>
<td>16.6</td>
<td>3.2-3.5</td>
<td>4-6</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2.4</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 LiBr 2:1:10 (5 μL D$_2$O added)</td>
<td>220</td>
<td>0.06-0.08</td>
<td>13.9</td>
<td>0.46</td>
<td>6</td>
</tr>
<tr>
<td>A 2 LiBr 2:1:20</td>
<td>230</td>
<td>0.02-0.06</td>
<td>14.8</td>
<td>0.3-0.5</td>
<td>15</td>
</tr>
<tr>
<td>A 2 LiCl 1:1:10</td>
<td>260</td>
<td>3.2</td>
<td>14.5</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>A 2 LiI 1:1:10</td>
<td>250</td>
<td></td>
<td>15.8</td>
<td>(0.28)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td></td>
<td></td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>1</td>
<td>16.3</td>
<td>2.9</td>
<td>3</td>
</tr>
<tr>
<td>A 2 LiI 2:1:10</td>
<td>300</td>
<td></td>
<td></td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.06</td>
<td>19.9</td>
<td>2.6-3.1</td>
<td>50</td>
</tr>
<tr>
<td>A 2 Li triflate 1:1:2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 Li triflate 1:1:2 (20 eqv MgSO$_4$ added)</td>
<td>220</td>
<td>5.4</td>
<td>12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 Li triflate 1:1:10</td>
<td>220</td>
<td>0.41</td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 Li triflate 2:1:10</td>
<td>230</td>
<td>0.15</td>
<td>14.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>1.8</td>
<td>14.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>6.8</td>
<td>14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 Li triflate 1:1:20</td>
<td>255</td>
<td>1.2-2</td>
<td>14.6</td>
<td>1.6-2</td>
<td>1</td>
</tr>
<tr>
<td>A 2 NaI 2:1:10</td>
<td>240</td>
<td>0.9-1.5</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 2 Na triflate 2:1:10</td>
<td>220</td>
<td>2.5</td>
<td>12.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When several resonances within one molecule were irradiated, the range of k is given. *also k (H$_{\text{free}}$- H$_{\text{bound}}$). Rate constant were adjusted for unequal populations (corrected for NMR silent
protons).\textsuperscript{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$_2$Cl$_2$ 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 %. $H_{\text{bound}}$ represents any resonance in the complex, $H_{\text{free}}$ represents any uncomplexed resonance.

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

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.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T in K</th>
<th>$\Delta$ ppm H$_4$-H$_5$</th>
<th>$\Delta$ ppm free II-H$_4$</th>
<th>$\Delta$ ppm free II-H$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2 LiI Litriolate 2:1:5:5</td>
<td>220</td>
<td>0.10</td>
<td>0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>A 2 LiI Litriolate 2:1:10:10</td>
<td>300</td>
<td>0.24</td>
<td>0.04</td>
<td>0.28</td>
</tr>
<tr>
<td>A 2 LiI NaI 2:1:5:5</td>
<td>220</td>
<td>0.13</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>A 2 LiI NaI 2:1:10:10</td>
<td>300</td>
<td>0.12</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>A 2 LiI Litriolate NaI 2:1:5:5</td>
<td>220</td>
<td>0.47</td>
<td>-0.08</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>0.06</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>0.12</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.16</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>A 2 Litriolate NaI 2:1:5:5</td>
<td>220</td>
<td>0.10</td>
<td>0.18</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>0?</td>
<td>0.19</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>0.22</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>
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
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$_2$Cl$_2$, 260K).

A 2 Li trifl NaI 2:1:5:5 COSY 260K CD$_2$Cl$_2$

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$_2$Cl$_2$.

a) $^1$H NMR
220K

b) 1D NOESY
220K d8=1s

E

Ex

↑

c) 1D ROESY
220K

Ex

↑

d) $^1$H NMR
260K, CD$_2$Cl$_2$
9-8.1 ppm
Accepter 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.

Table S12: Summary of key NOE correlations for A:2:LiI = 2:1:10 complex (in CD₂Cl₂) when no decomplexation takes place. Labels refer to Figure 1.

<table>
<thead>
<tr>
<th>From 2D NMR</th>
<th>from 1D NMR (in decreasing order)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₄ is near crown ether protons, near H₃, then H₁, has no NOEs to H₂; H₅ has no NOE to crown ether protons, larger NOE to H₁ than H₃, no NOE to H₂; H₃ has no NOE to crown ether or NCH₂CH₂ protons; H₂ has NOEs to NCH₂CH₂ protons and only small ones to crown ether protons</td>
<td>H₄ to H₃ and H₆; H₅ to H₁ and H₃; H₁ to H₃ and H₅; H₂ to H₈ and H₁₅; H₃ to H₁, H₆, H₁₁, H₄ and H₅; H₆ to H₁₁, H₃ and H₄; H₁₁ to H₆, H₃, H₇, H₁₃; H₁₅ to H₈, H₂, H₁₆.</td>
</tr>
</tbody>
</table>

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

The chemical shift differences for bound acceptor A protons (H₄, H₅) 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 \(\text{OCH}_2\text{CH}_2\) 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 (Na\(^+\) or Li\(^+\)) on chemical shifts is relatively small. Most changes are seen in the crown ether region (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. Li\(^+\) complexes are generally more stable than Na\(^+\) complexes.

d) **Solvent:**
The solvent (CDCl\(_3\)/MeOD 98:2 or CD\(_2\)Cl\(_2\)) effect on chemical shifts is small. As for the cation there are differences in kinetic stability between the two solvent systems. Complexes in CD\(_2\)Cl\(_2\) 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 \(A:2:\text{salt} = \geq 2:1:10\) 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
Figure S12: Summary of chemical shifts for bound acceptor A protons H₄ and H₅ and aromatic crown ether protons H₁ to H₃: a) A:2: salt 2:1:10 complexes in CDCl₃/MeOD 98:2, b) A:2: salt 2:1:10 complexes in CD₂Cl₂.

Table S13:
1D NOESY irradiation of H₃ yields NOE to adjacent ArOCH₂ protons H₆ and H₁₁ (Figure S3). COSY data confirmed geminal coupling between H₆ and H₁₁. Labelling corresponds to Figure 1.

<table>
<thead>
<tr>
<th>A:2:salt = ≥2:1:10 complex (CD₂Cl₂)</th>
<th>T in K</th>
<th>H₆ (ppm)</th>
<th>H₁₁ (ppm)</th>
<th>Δppm H₆-H₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>280K</td>
<td>4.30</td>
<td>3.89</td>
<td>0.41</td>
</tr>
<tr>
<td>LiBr</td>
<td>280K</td>
<td>4.30</td>
<td>3.89</td>
<td>0.41</td>
</tr>
<tr>
<td>NaI</td>
<td>240K</td>
<td>4.18</td>
<td>3.81</td>
<td>0.37</td>
</tr>
<tr>
<td>NaOTf</td>
<td>280K</td>
<td>3.99</td>
<td>3.83</td>
<td>0.16</td>
</tr>
<tr>
<td>LiOTf</td>
<td>280K</td>
<td>4.05</td>
<td>3.88</td>
<td>0.17</td>
</tr>
</tbody>
</table>
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 H1 to H5 are shown, b) LiBr complexes only, protons H4 and H5 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 H4 and H5, the directly linked $^{13}$C atoms (C5, C6, labels refer to Figure 1) also differ: the halide complex shows a $\Delta$ ppm of 2.2 ppm between C5 and C6, 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 C17 to C22 belonging to the alkyl tail of bound acceptor A are hardly changed. In contrast, the inner crown ether carbons C15 and C16 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 H4 and H5

<table>
<thead>
<tr>
<th>LiI δ (ppm)</th>
<th>HMQC correlations</th>
<th>NaOTf δ (ppm)</th>
<th>HMQC correlations</th>
<th>Δppm (LiI-NaOTf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>132.93</td>
<td>C5</td>
<td>131.21</td>
<td>Free A, C5</td>
<td>Ca. 1.7</td>
</tr>
<tr>
<td>130.72</td>
<td>C6</td>
<td>130.25</td>
<td>C6</td>
<td>0.47</td>
</tr>
</tbody>
</table>

OCH2CH2O crown ether carbon atoms

<table>
<thead>
<tr>
<th>LiI δ (ppm)</th>
<th>HMQC correlations</th>
<th>NaOTf δ (ppm)</th>
<th>HMQC correlations</th>
<th>Δppm (LiI-NaOTf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.34</td>
<td>C14, H7, H13</td>
<td>71.41</td>
<td>C14, H7, H13</td>
<td>-0.07</td>
</tr>
<tr>
<td>70.36</td>
<td>C15, H10, H12</td>
<td>70.99</td>
<td>C15, H10, H12</td>
<td>-0.63</td>
</tr>
<tr>
<td>69.86</td>
<td>C16, H9, H14</td>
<td>70.57</td>
<td>C16, H9, H14</td>
<td>-0.71</td>
</tr>
<tr>
<td>67.07</td>
<td>C13, H6, H11</td>
<td>66.87</td>
<td>C13, H6, H11</td>
<td>0.20</td>
</tr>
</tbody>
</table>

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

Table S15: Distribution of acceptor A aromatic resonances H4 and H5 among different species (A:1:(salt) and A:2:salt), see Figure S1. The numbers were obtained by integration.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a) A:1:2 = 1.0:1.0:0.6 no salt 220K</td>
<td>16%</td>
<td>84%</td>
<td>0</td>
<td>11.9:1.0</td>
<td>only 2 (free)</td>
</tr>
<tr>
<td>b) A:1:2:Li triflate = 1.0:1.0:0.7:10 220K</td>
<td>0</td>
<td>42%</td>
<td>58%</td>
<td>1.0:1.0</td>
<td>14.5:1.0</td>
</tr>
<tr>
<td>c) A:1:3:LiI= 1.0:0.8:0.9:10 220K</td>
<td>0</td>
<td>16%</td>
<td>84%</td>
<td>1.0:4.4</td>
<td>9.9:1.0</td>
</tr>
<tr>
<td>d) A:1:2:LiI= 1.0:0.8:0.9:10 260K</td>
<td>0</td>
<td>9%</td>
<td>91%</td>
<td>only 1 (free)</td>
<td>&gt;16:1</td>
</tr>
</tbody>
</table>
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, 9.5-5.5 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.

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

b) 1D NOESY d8 = 1s

\[ \uparrow \text{NOE} \quad \text{Ex NOE} \]

c) 1D NOESY d8 = 1s

\[ \uparrow \text{NOE} \quad \text{Ex NOE NOE} \]

d) 1D NOESY d8 = 1s

\[ \uparrow \text{NOE} \quad \text{Ex} \]

e) 1D NOESY d8 = 1s

\[ \text{NOE} \quad \text{Ex} \quad \text{NOE NOE} \quad \uparrow \]

f) 1D ROESY

\[ \text{Ex} \quad \uparrow \]

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 H₁ resonance of free host 2 (possibly host 2:LiI complex) shows exchange with H₁ resonance of bound crown 1 (A:2:LiI complex).

d) similar to c), irradiation of H₃ resonance of free host 2.

e) irradiation of H₃ resonance of bound host 2 shows exchange with H₃ resonance of free host 1.

f) irradiation of H₃ resonance of bound crown 1 shows exchange with H₃ resonance of free host 1.

Figure S17: Parts of ¹H NMR spectra (methyl protons of acceptor A, 1.1-0.6 ppm) of A:1:2:salt complexes in CDCl₃: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: