SUPPORTING INFORMATION for
Selective Proton-Mediated Transport by Electrogenic K⁺-Binding Macrocycles

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Synthesis of compounds 1, r,s2, 3 :
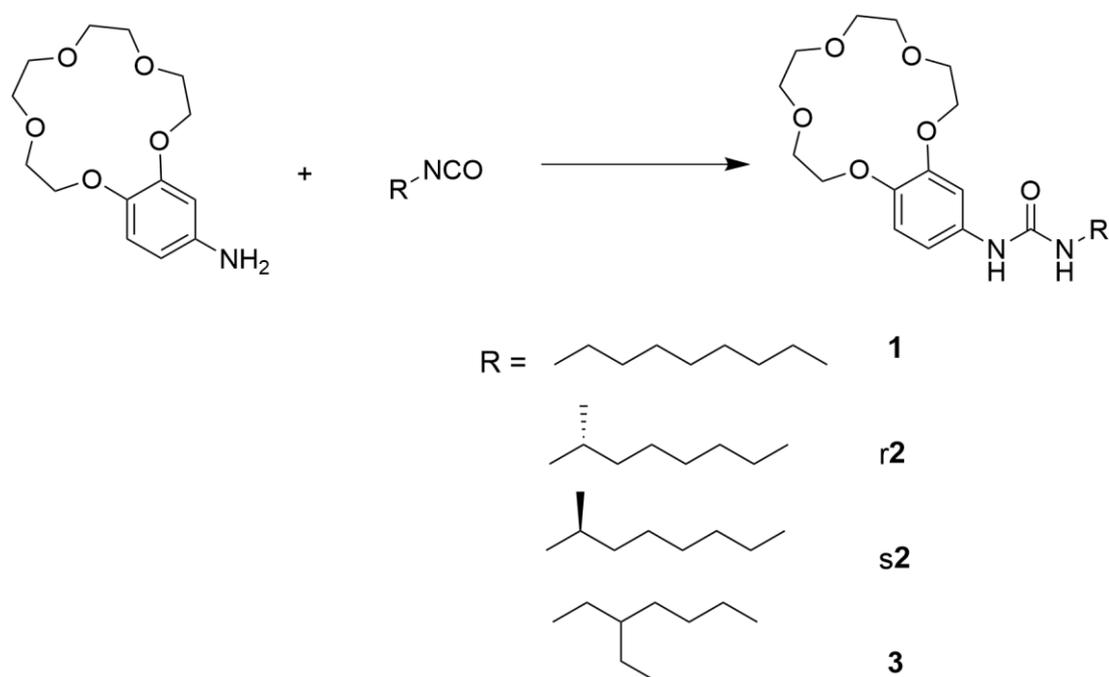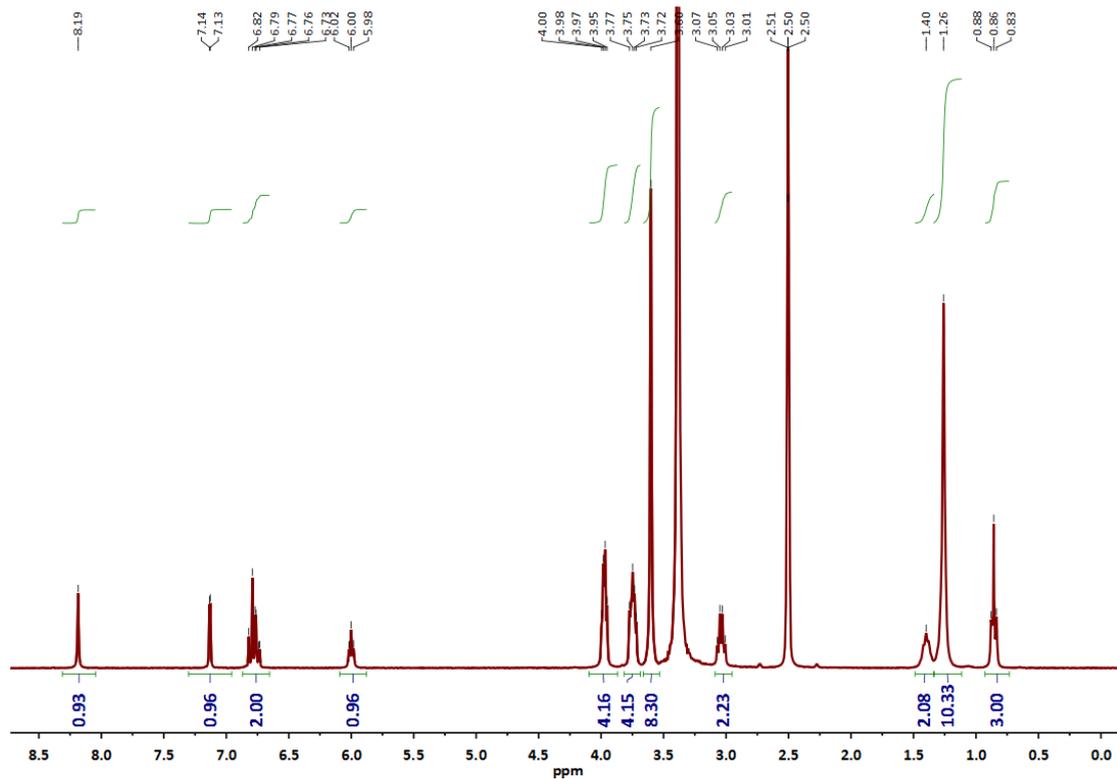

Scheme S1 Synthesis of compounds **1, r,s2, 3**

Figure S1. ^1H NMR spectrum of **1** (300 MHz, 298K, DMSO-d_6).

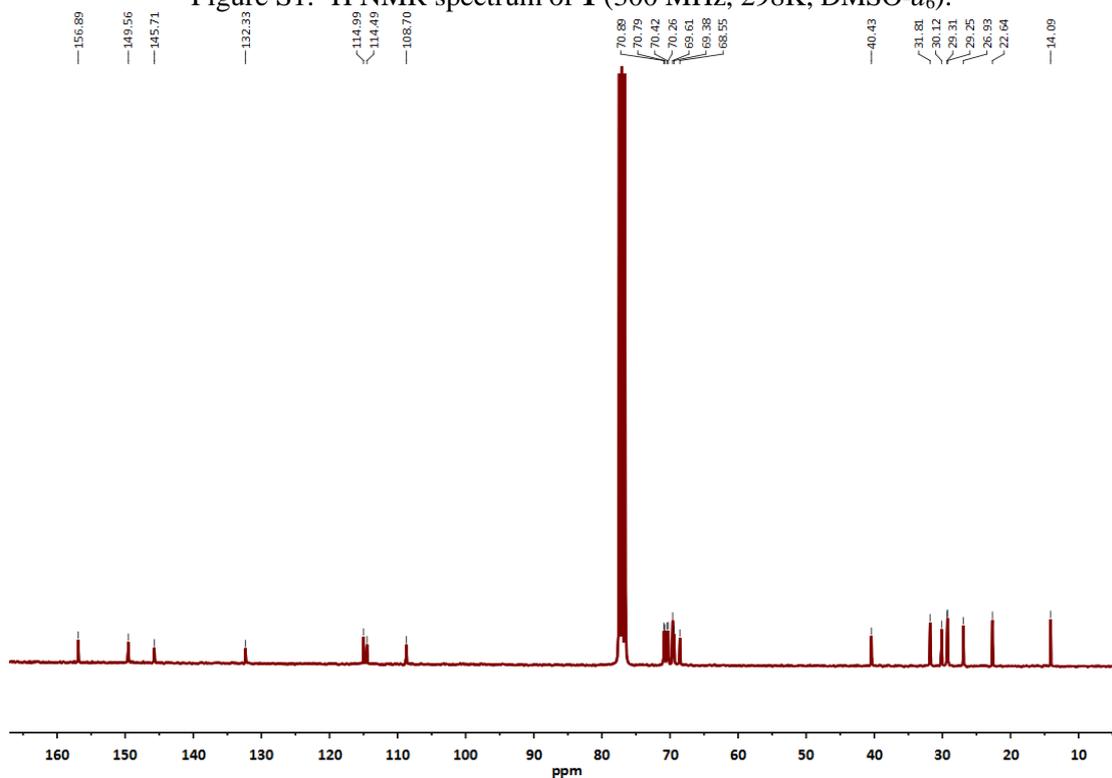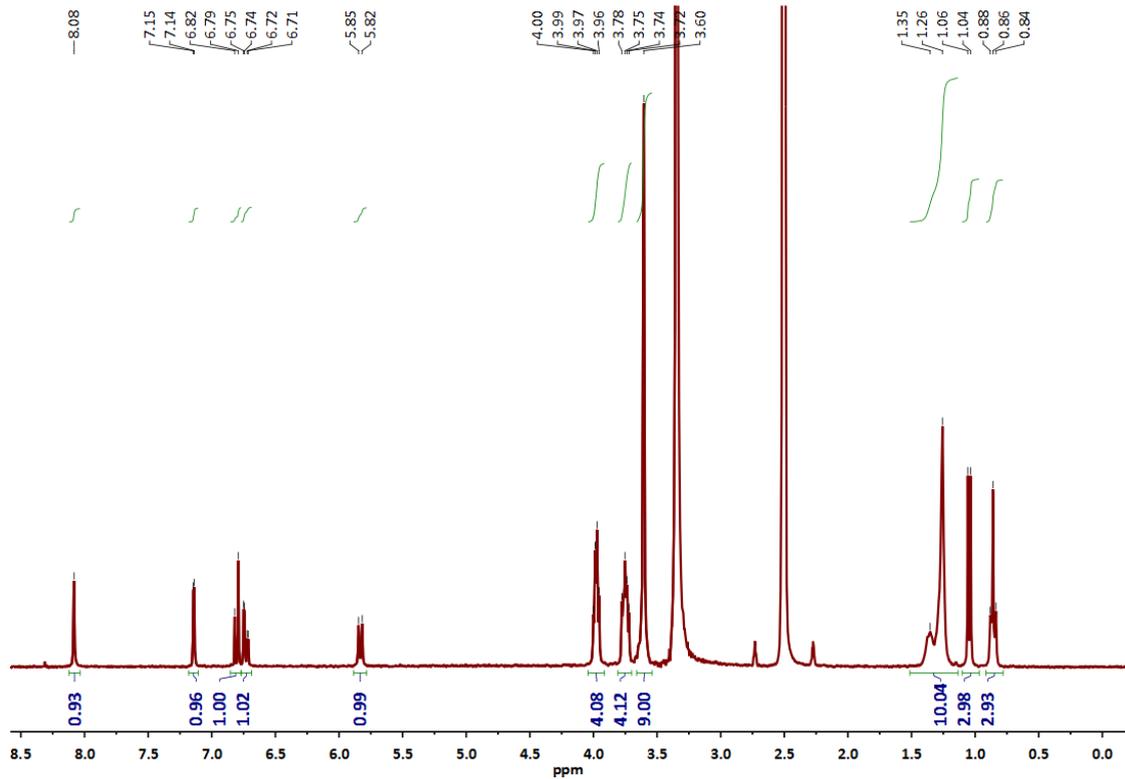Figure S2. ^{13}C NMR spectrum of **1** (75 MHz, 298K DMSO-d_6).

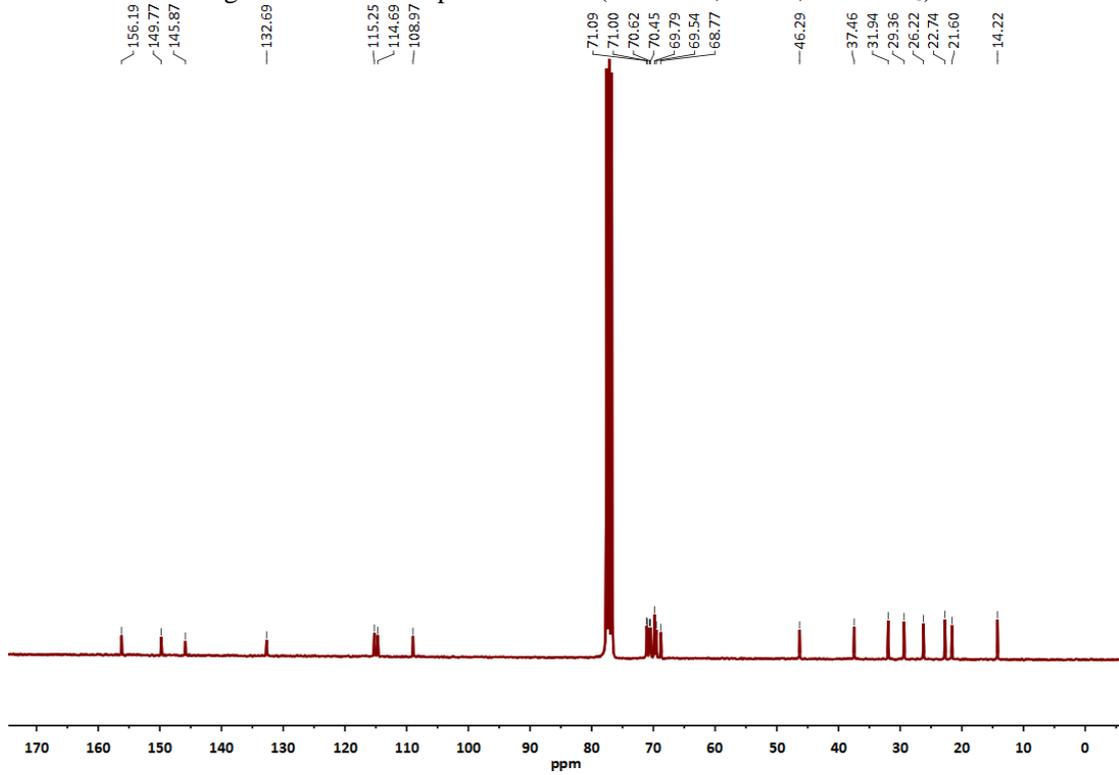Figure S3 ^{1}H NMR spectrum of r**2** (300 MHz, 298 K, DMSO-d_6).

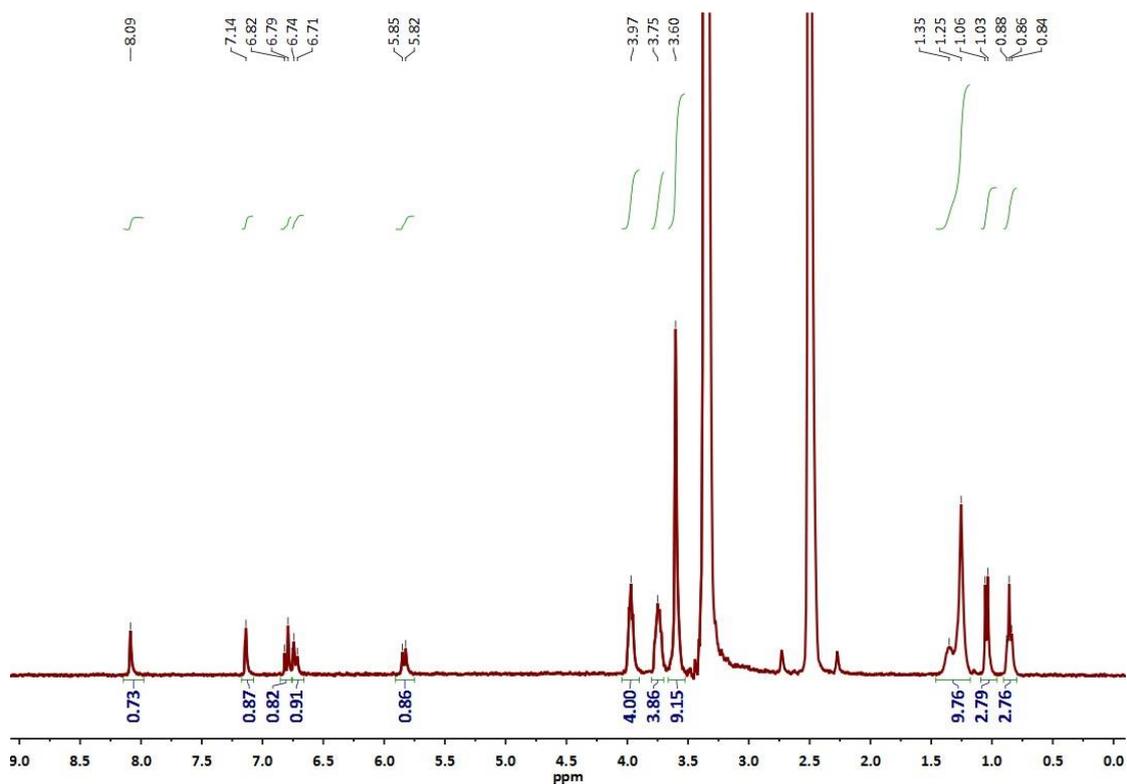Figure S4 ^{13}C NMR spectrum of r**2** (75 MHz, 298 K, CDCl$_3$).

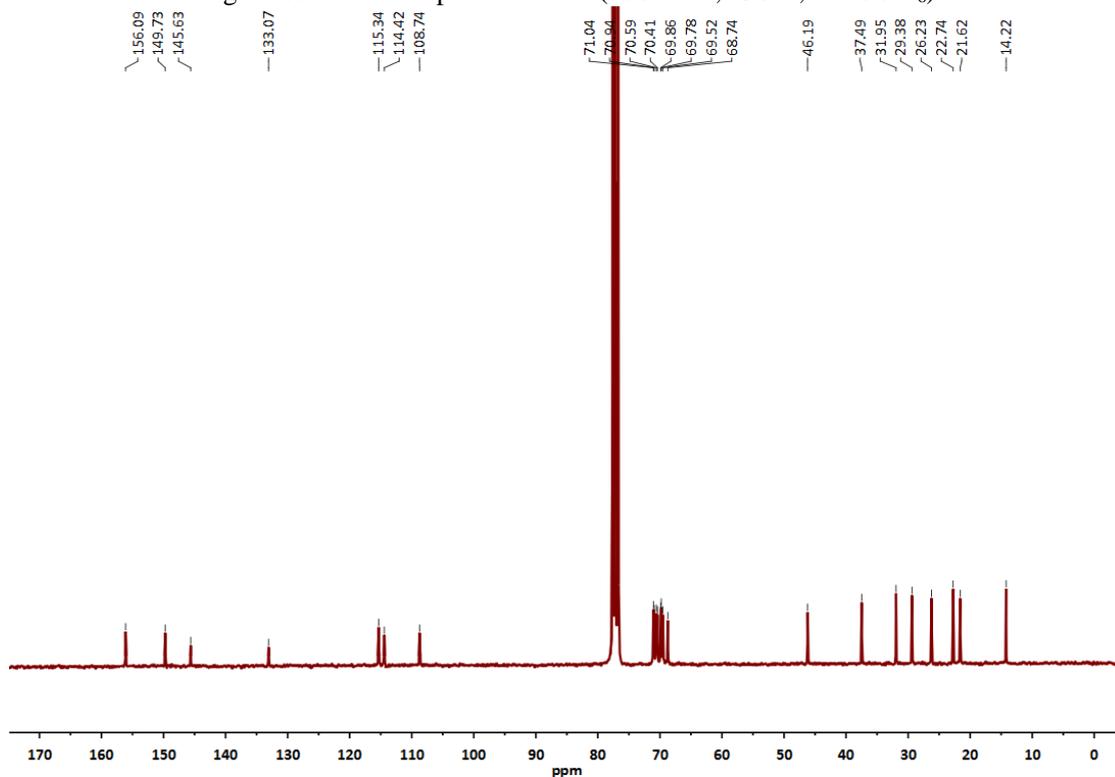Figure S5 ^{1}H NMR spectrum of s**2** (300 MHz, 298 K, DMSO-d_6).

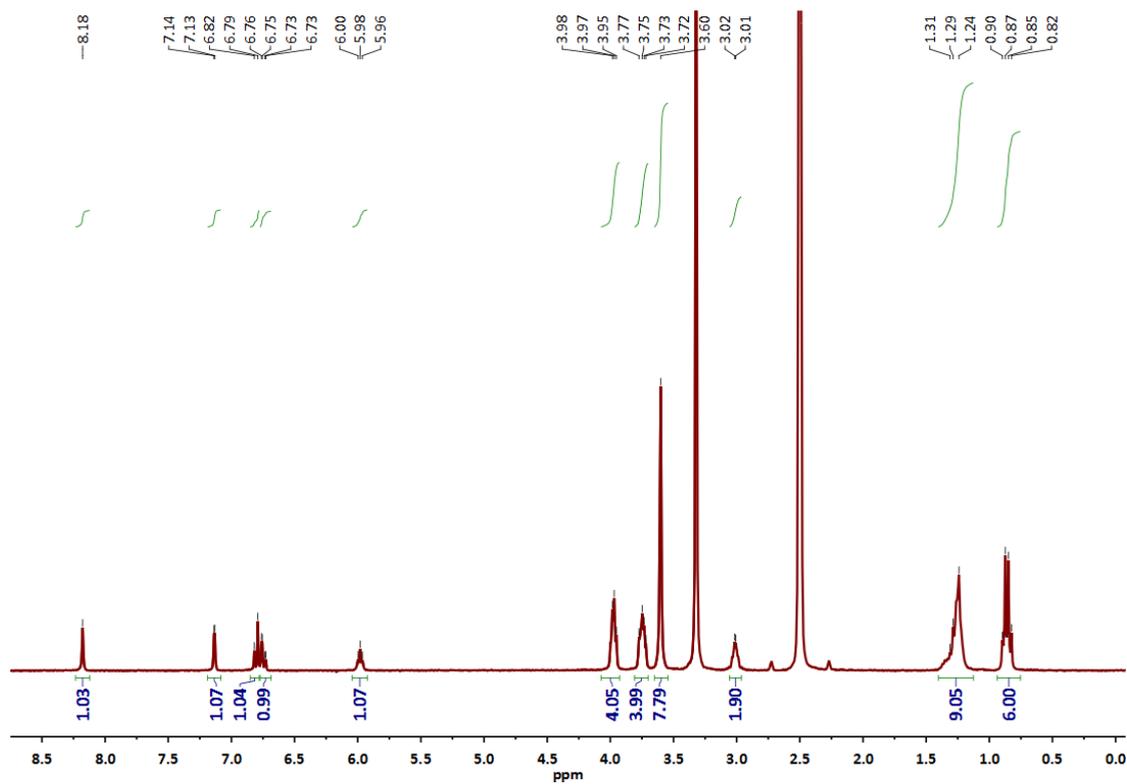Figure S6 ^{13}C NMR spectrum of s**2** (75 MHz, 298 K, CDCl$_3$).

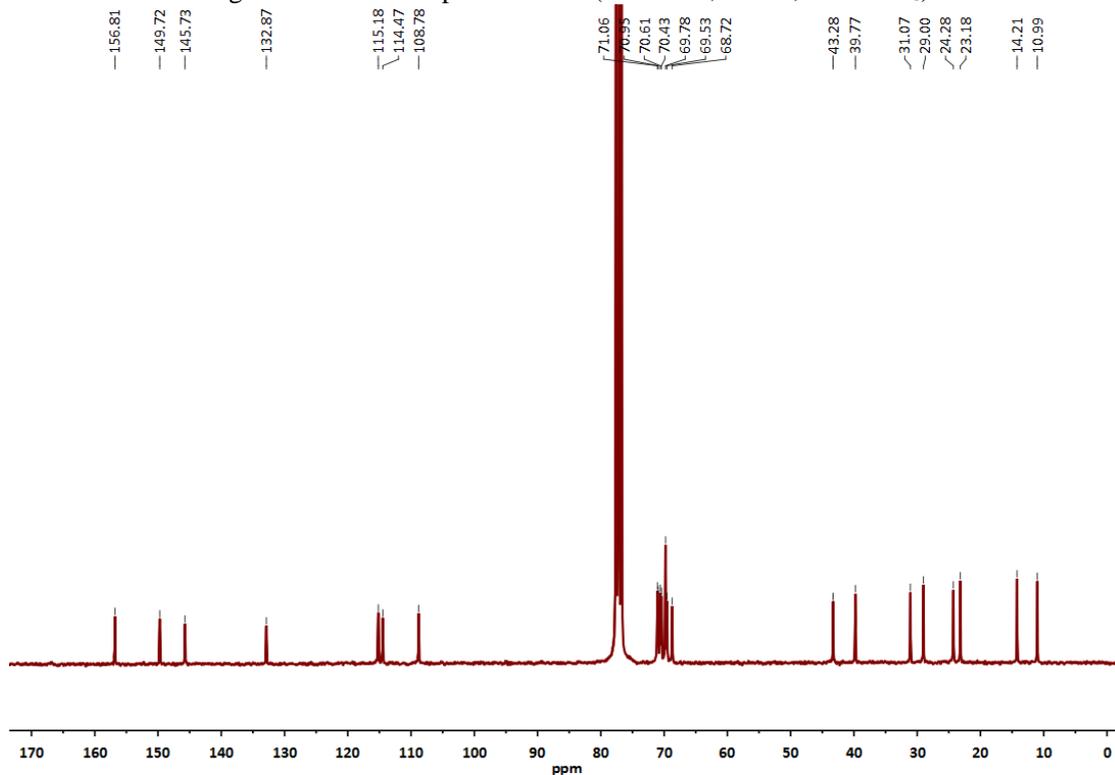Figure S7 ^{1}H NMR spectrum of **3** (300 MHz, 298 K, DMSO-d_6).

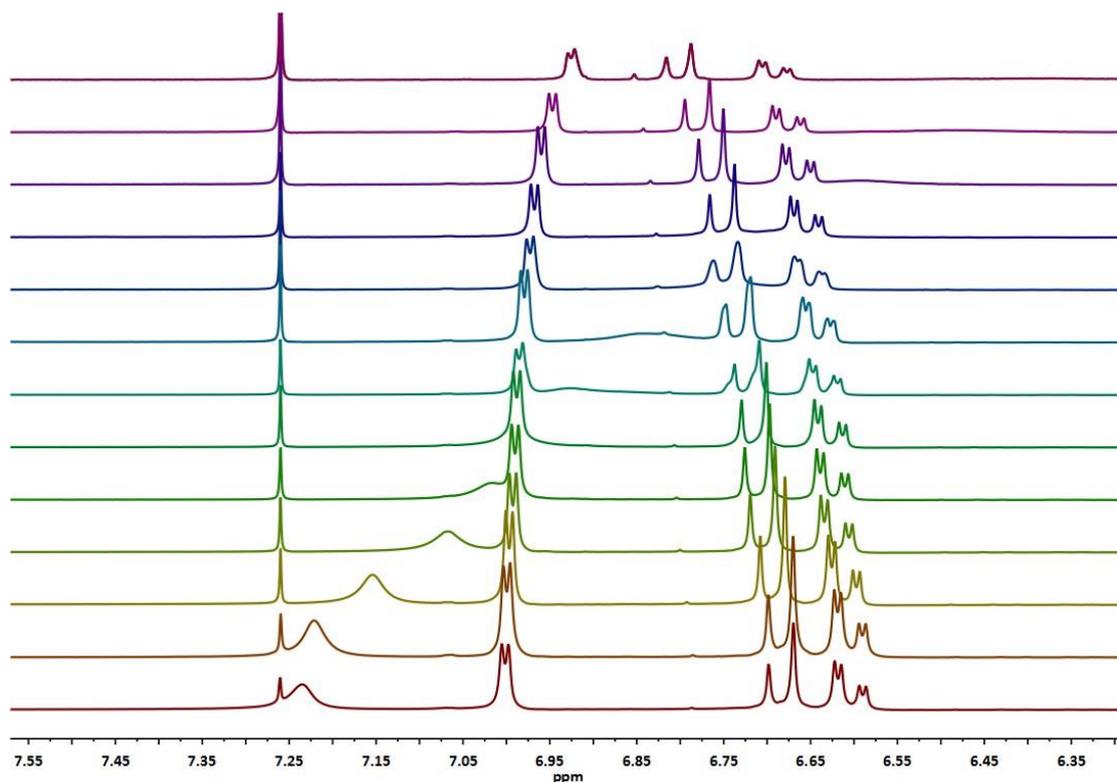Figure S8 ^{13}C NMR spectrum of **3** (75 MHz, 298 K, CDCl$_3$).

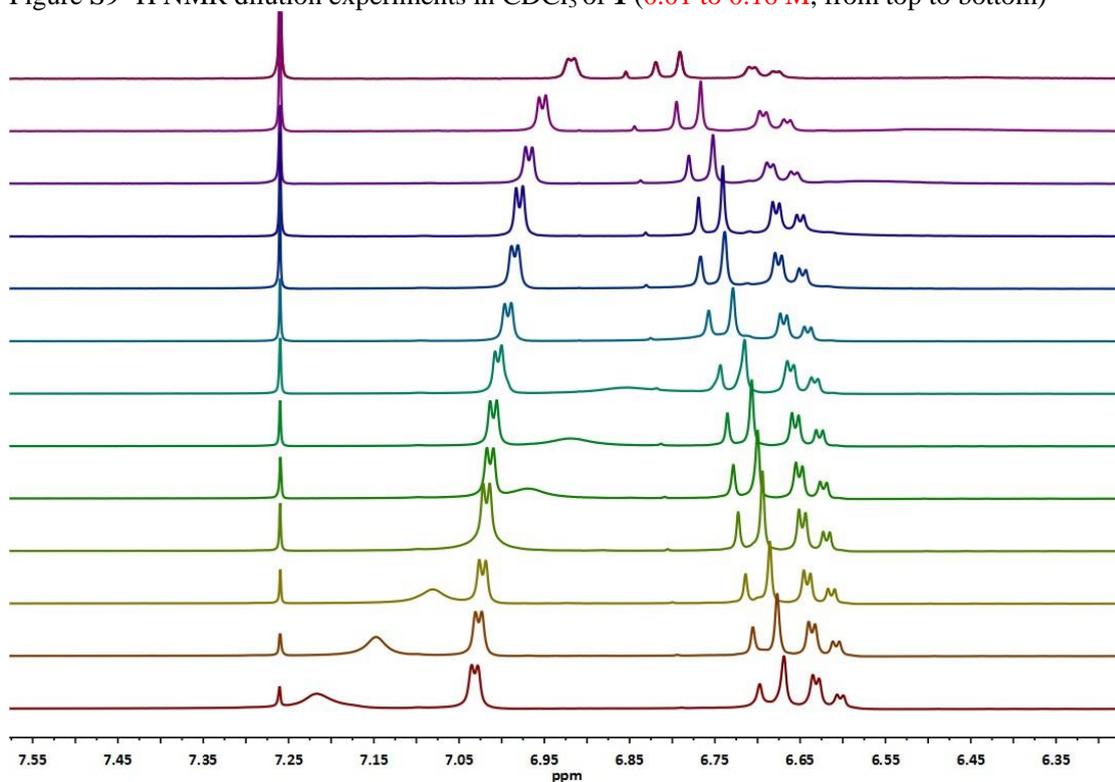Figure S9 ^{1}H NMR dilution experiments in CDCl$_3$ of **1** (0.01 to 0.16 M, from top to bottom)

Figure S10 ^{1}H NMR dilution experiments in CDCl$_3$ of **r2** (0.01 to 0.16 M, from top to bottom)
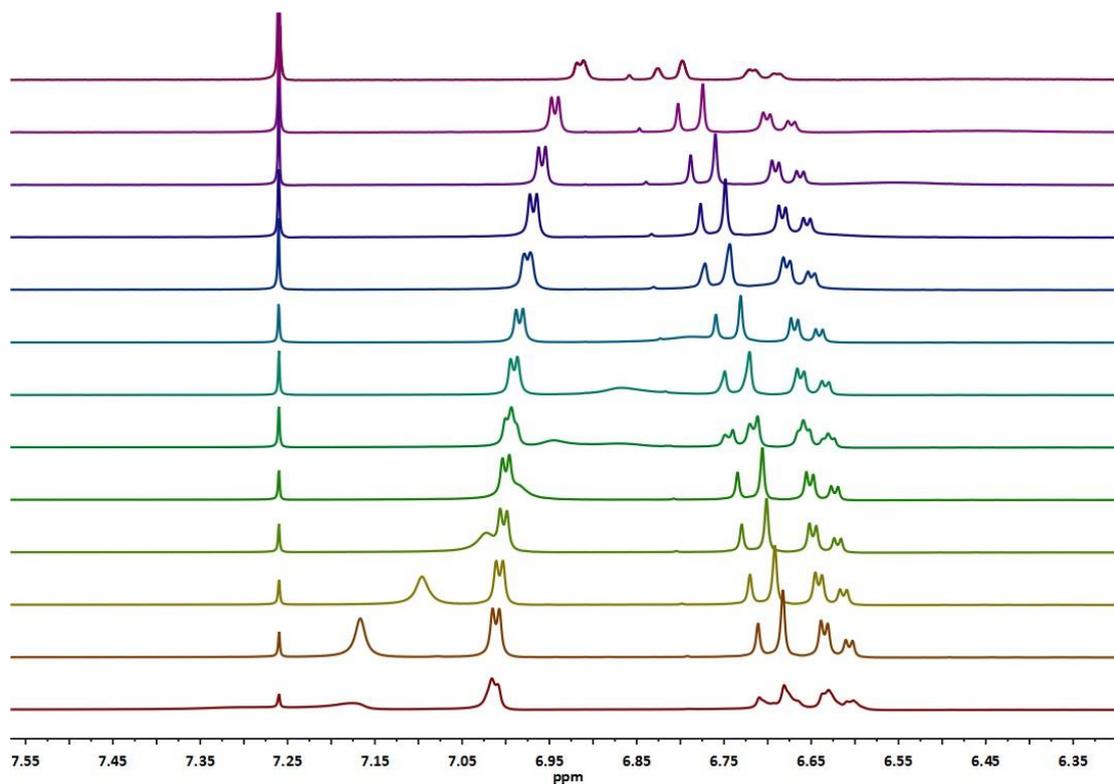
Figure S11 ^{1}H NMR dilution experiments in CDCl$_3$ of **3** (0.01 to 0.16 M, from top to bottom)
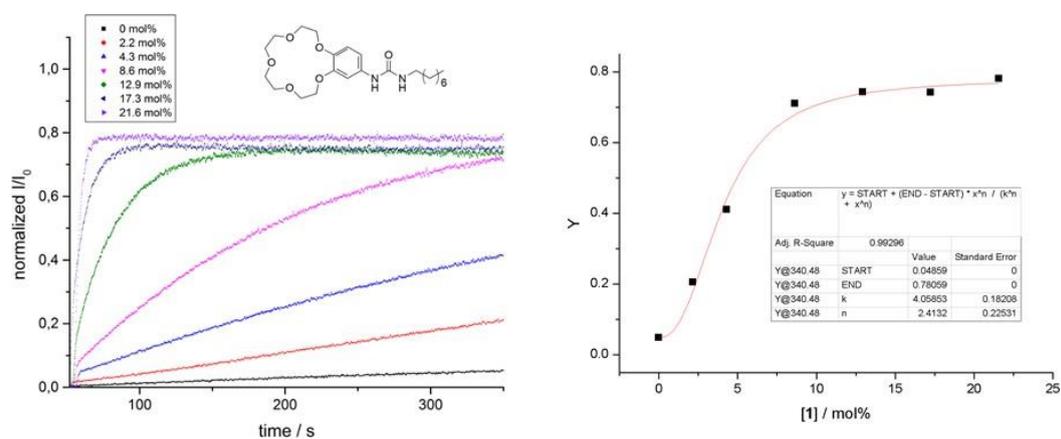
Hill plot analysis

Figure S12. Normalized I$_{460}$/I$_{403}$ for transporting K$^+$ across the bilayer membrane facilitated by different amount of **1** and hill plot analysis of K$^+$/H$^+$ antiport.

Figure S13. Normalized I_{460}/I_{403} for transporting Na$^+$ across the bilayer membrane facilitated by different amount of **1** and hill plot analysis of Na$^+$/H$^+$ antiport.

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Figure S14 Normalized I_{460}/I_{403} for transporting K$^+$ across the bilayer membrane facilitated by different amount of **1** coupled with FCCP (0.1 mol%) and hill plot analysis of K$^+$/H$^+$ antiport.

Figure S15 Normalized I_{460}/I_{403} for transporting Na$^+$ across the bilayer membrane facilitated by different amount of **1** coupled with FCCP (0.1 mol%) and hill plot analysis of Na$^+$/H$^+$ antiport.

Figure S16 Normalized I_{460}/I_{403} for transporting K$^+$ across the bilayer membrane facilitated by different amount of s**2** and Hill plot analysis of K$^+$/H$^+$ antiport.
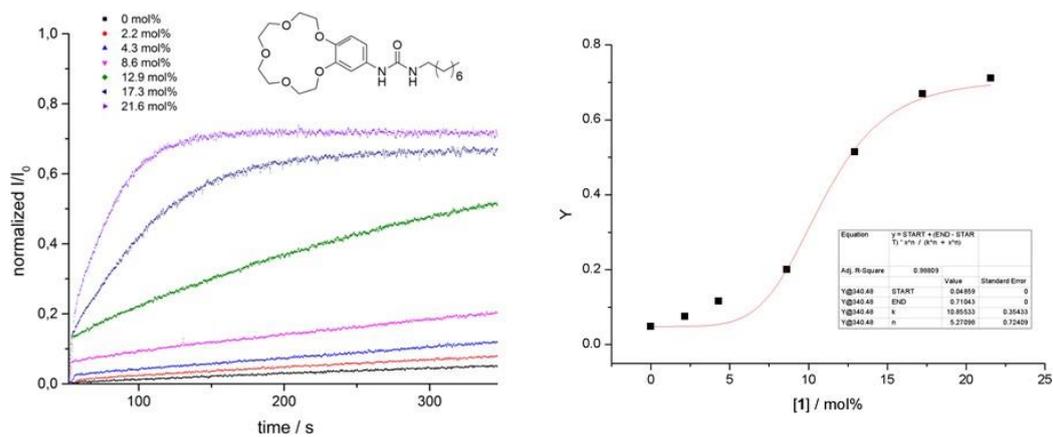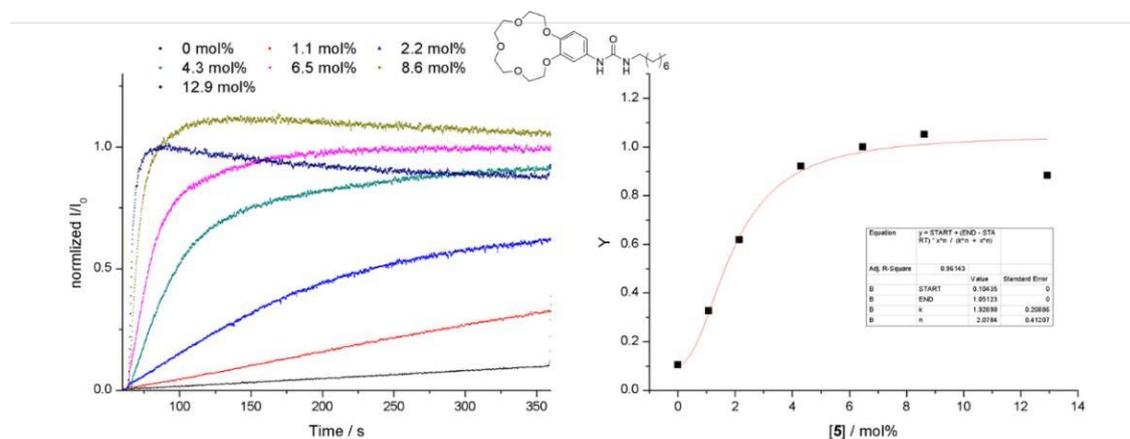
Figure S17 Normalized I_{460}/I_{403} for transporting Na^+ across the bilayer membrane facilitated by different amount of s**2** and hill plot analysis of Na^+/H^+ antiport.

Figure S18 Normalized I_{460}/I_{403} for transporting K^+ across the bilayer membrane facilitated by different amount of s**2** coupled with FCCP (0.1 mol%) and hill plot analysis of K^+/H^+ antiport.
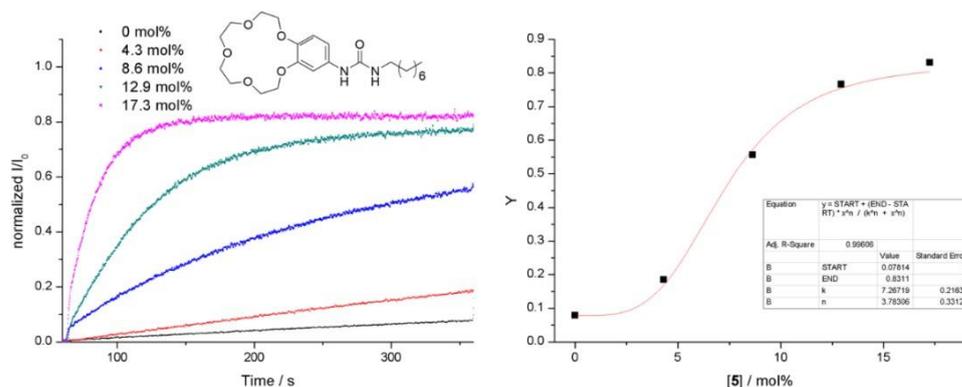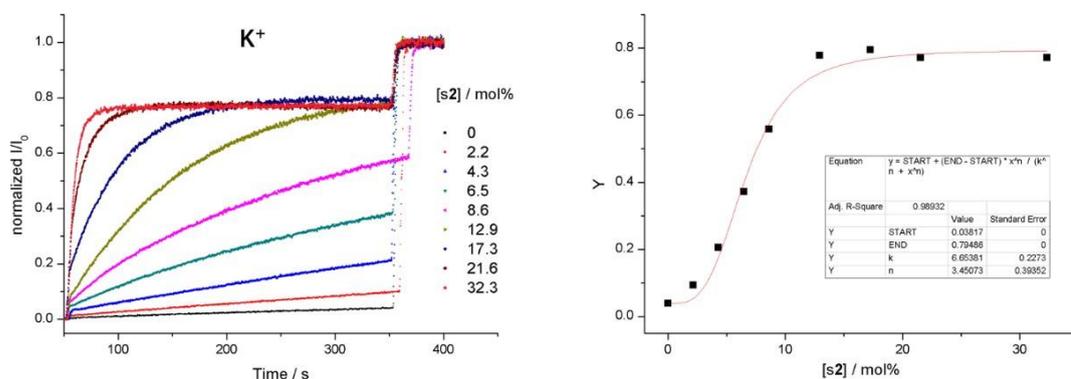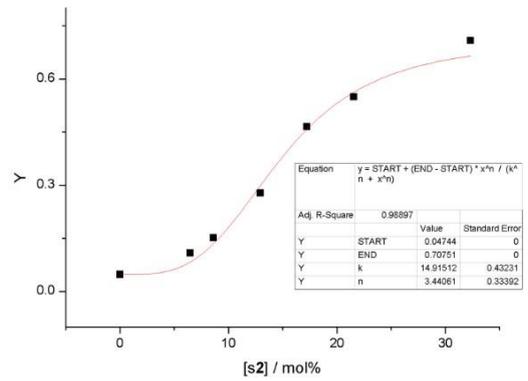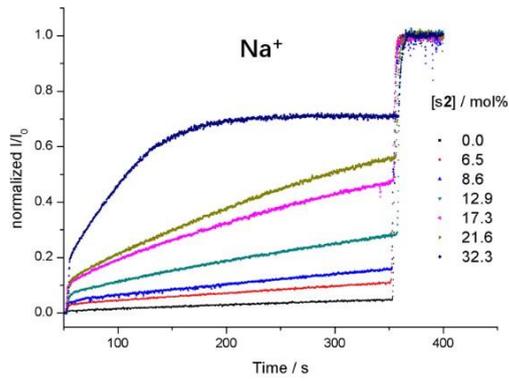

Figure S1 Normalized I_{460}/I_{403} for transporting Na^+ across the bilayer membrane facilitated by different amount of s**2** coupled with FCCP (0.1 mol%) and hill plot analysis of Na^+/H^+ antiport.

Figure S20 Normalized I_{460}/I_{403} for transporting K^+ across the bilayer membrane facilitated by different amount of r**2** coupled with FCCP (0.1 mol%) and hill plot analysis of K^+/H^+ antiport.

Figure S21 Normalized I_{460}/I_{403} for transporting Na^+ across the bilayer membrane facilitated by different amount of r**2** coupled with FCCP (0.1 mol%) and hill plot analysis of Na^+/H^+ antiport.
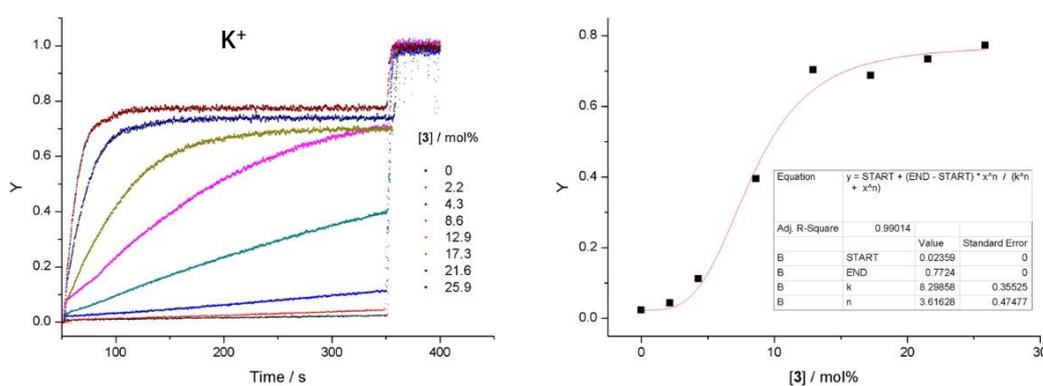
Figure S22 Normalized I_{460}/I_{403} for transporting K^+ across the bilayer membrane facilitated by different amount of **3** and hill plot analysis of K^+/H^+ antiport.
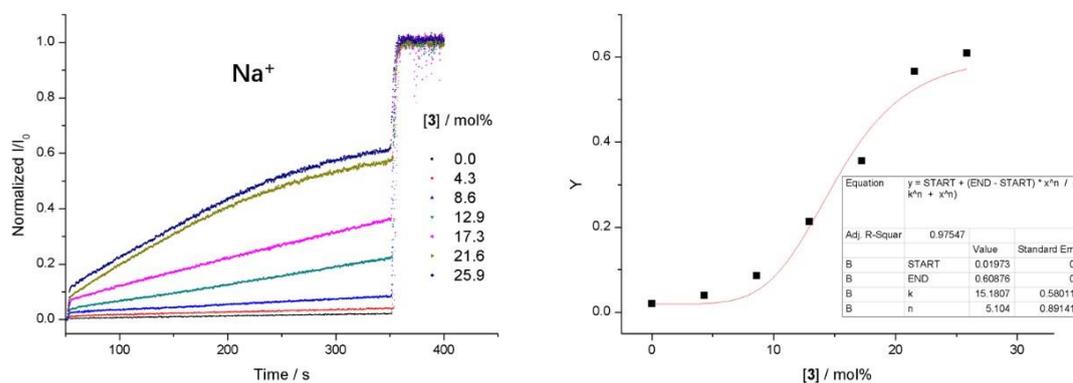
Figure S23 Normalized I_{460}/I_{403} for transporting Na^+ across the bilayer membrane facilitated by different amount of **3** and hill plot analysis of Na^+/H^+ antiport.
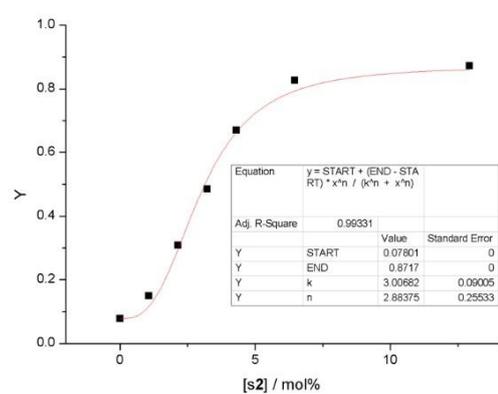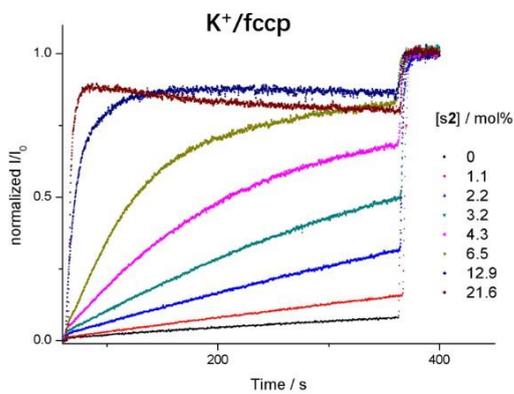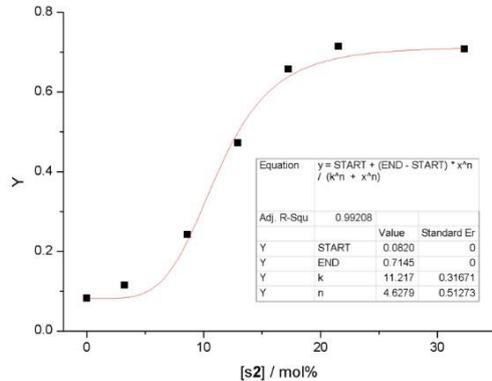
Figure S24 Normalized I_{460}/I_{403} for transporting K^+ across the bilayer membrane facilitated by different amount of **3** coupled with FCCP (0.1 mol%) and hill plot analysis of K^+/H^+ antiport.
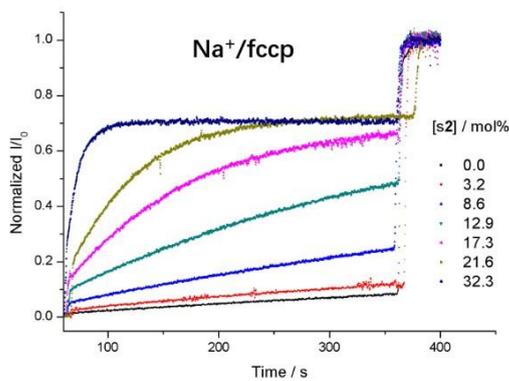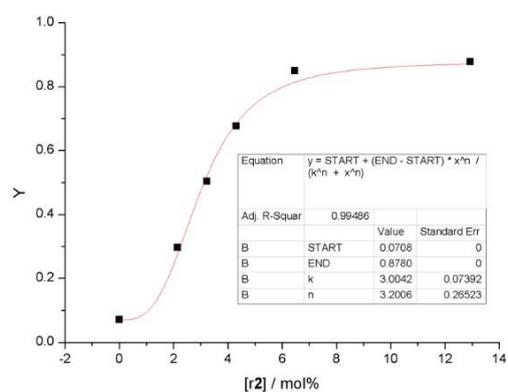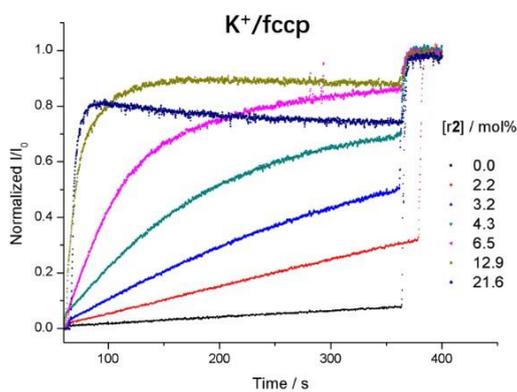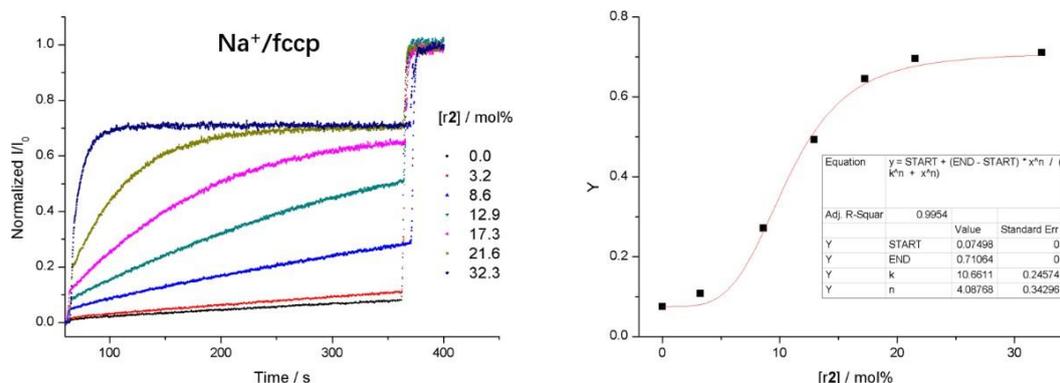

Figure S25 Normalized I_{460}/I_{403} for transporting Na^+ across the bilayer membrane facilitated by different amount of **3** coupled with FCCP (0.1 mol%) and hill plot analysis of Na^+/H^+ antiport.
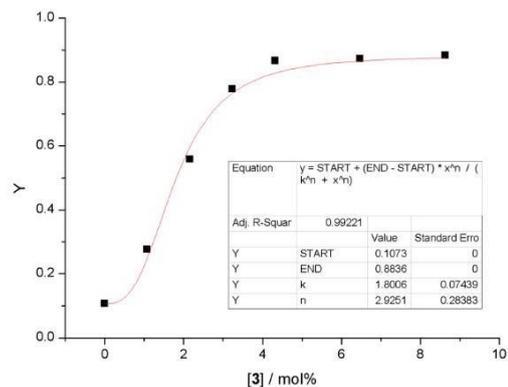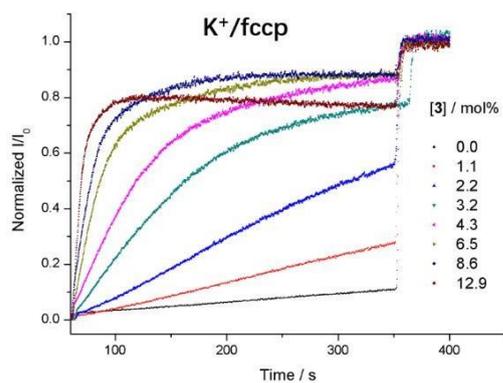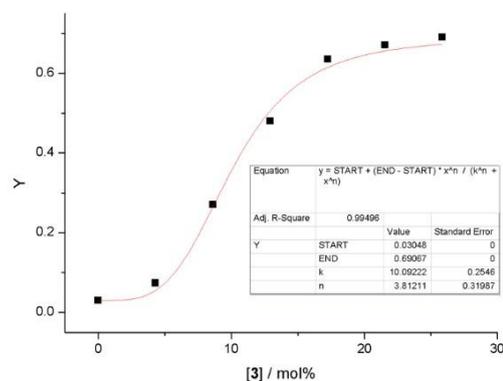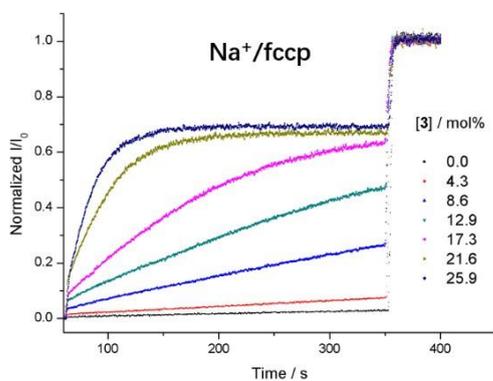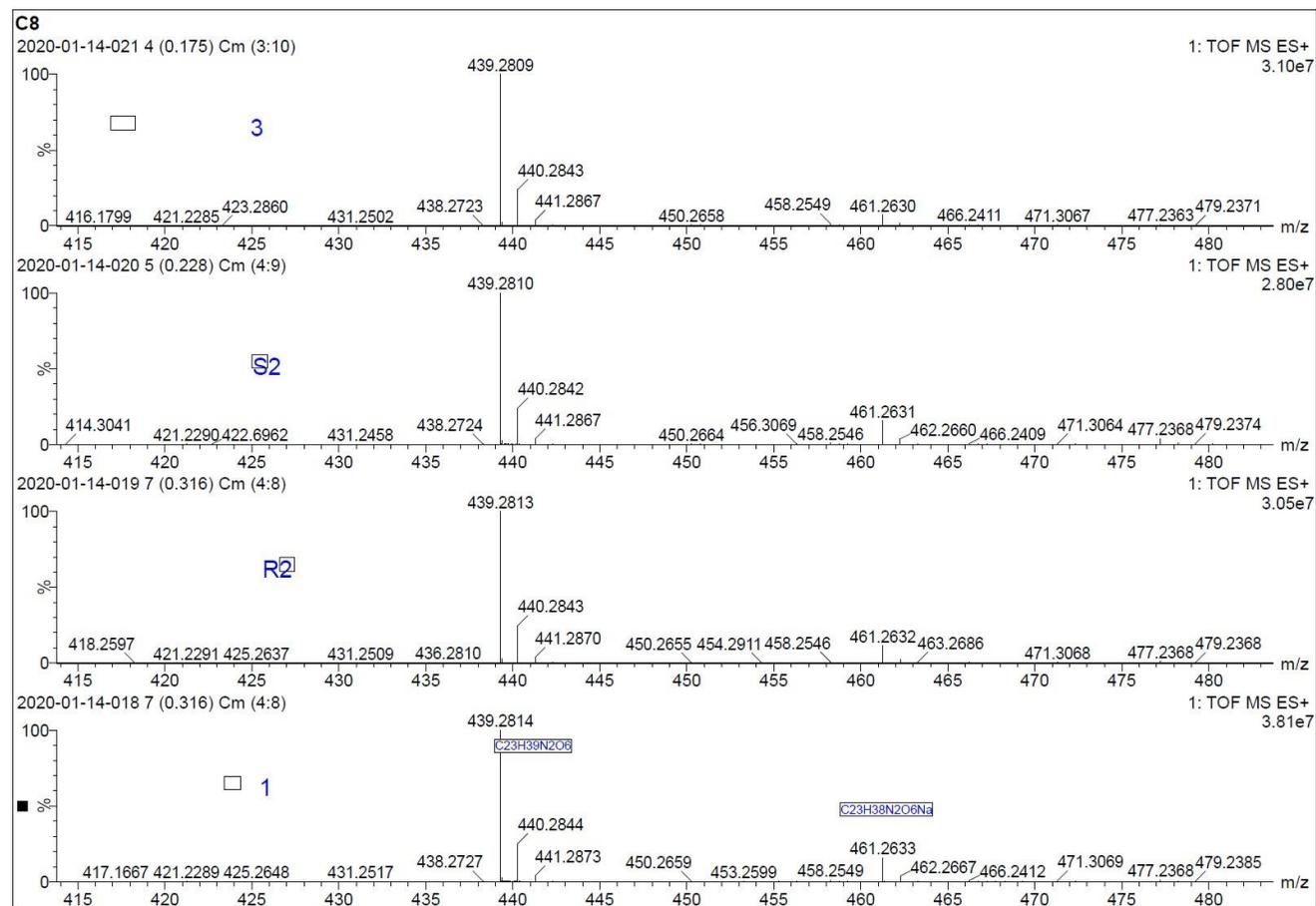
Figure S26. HR-MS spectra of compounds **1, r2, s2, 3**

Table S1 Pseudo first-order rate constants k (s^{-1}) for the transport of K$^+$/H$^+$ through LUVs at different concentrations of the compounds to lipid without or with proton transporter FCCP.

conc./ mol%	k for K$^+$						
	Without FCCP			With FCCP			
	1	s2	3	1	s2	r2	3
2.2	0.002	0.001	0.0004	0.0107	0.0031	0.003	0.0058
4.3	0.0042	0.0026	0.0013	0.0397	0.0097	0.0101	0.0291
6.5	/^{a}	0.0051	/	0.0847	0.0211	0.0339	0.0762
8.6	0.0097	0.0099	0.0073	0.2007	/	/	0.089
12.9	0.0338	0.0165	0.0096	0.402	0.2003	0.1818	0.2586
17.3	0.0569	0.027	0.0326	/	/	/	/
21.6	0.0789	0.0795	0.0537	/	0.5476	0.4586	/
25.9	/	/	0.0899	/	/	/	/
32.3	/	0.1639	/	/	/	/	/

The initial rate for the blank has already been subtracted from all the rates. a: There was no experiment at this condition.

Table S2 Pseudo first-order rate constants k (s^{-1}) for the transport of Na$^+$/H$^+$ through LUVs at different concentrations of the compounds to lipid without or with proton transporter FCCP. The initial rate for the blank has already been subtracted from all the rates.

conc./ mol%	k for Na$^+$						
	Without FCCP			With FCCP			
	1	s2	3	1	s2	r2	3
2.2	0.0003	/	/	/	/	/	/
4.3	0.0006	/	0.0001	0.001	/	/	0.0007
6.5	/	0.0006		/	/	/	/
8.6	0.0013	0.0012	0.0006	0.0043	0.0019	0.0022	0.0039
12.9	0.0051	0.0025	0.0027	0.0174	0.0044	0.006	0.0053
17.3	0.0163	0.0043	0.004	0.0185	0.0095	0.0098	0.0081
21.6	0.0264	0.0056	0.0082	/	0.021	0.0254	0.0341
25.9	/	/	0.0063	/	/	/	0.0448
32.3	/	0.0166	/	/	0.3367	0.3346	/