Supplementary Information

Selective binding of oxalate by a tris-ureido calix[6]tube in a protic environment

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1. NMR spectra of new compounds

1.1. Calixarene 2

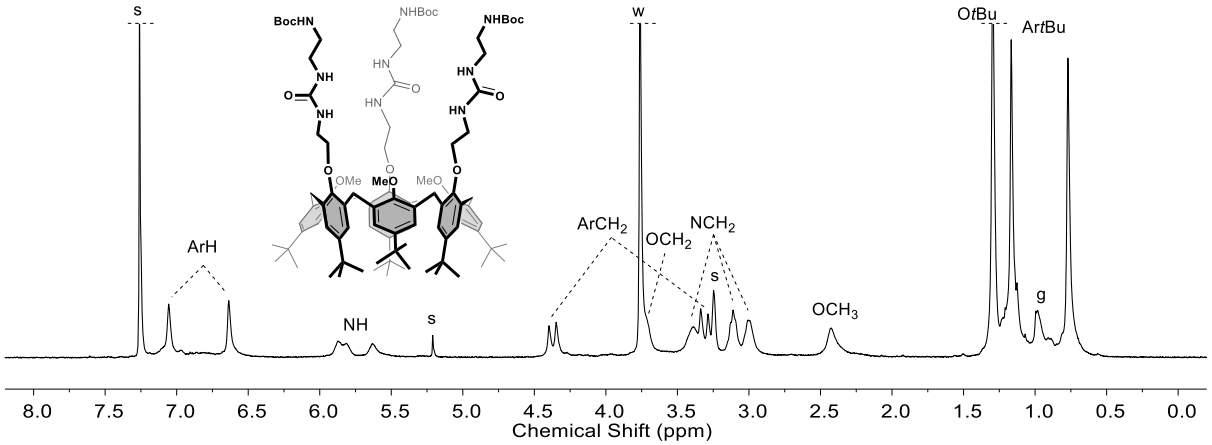

Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3/CD_3OD$, 10:1, 298 K) of calixarene **2**. s: solvent; w: water; g: grease.

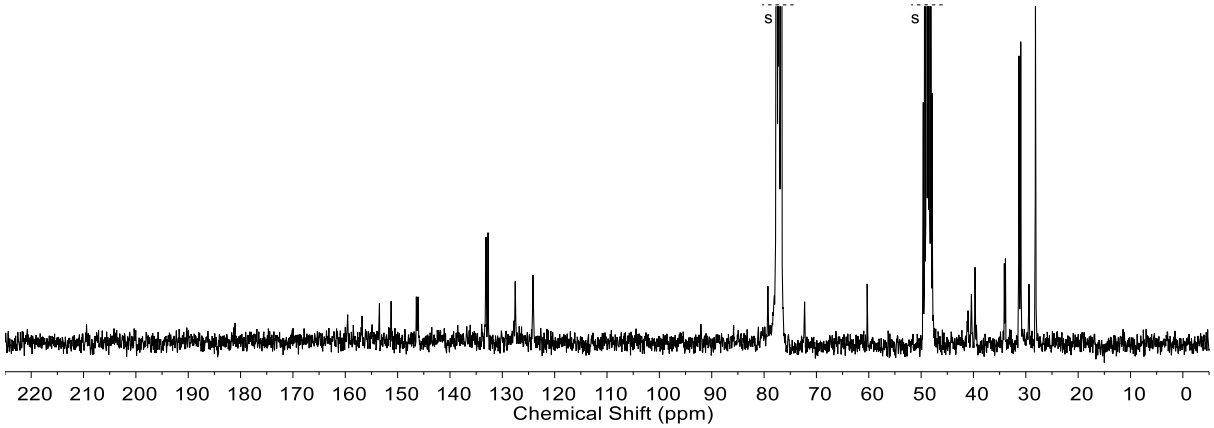

Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3/CD_3OD$, 5:1, 298 K) of calixarene **2**. s: solvent.

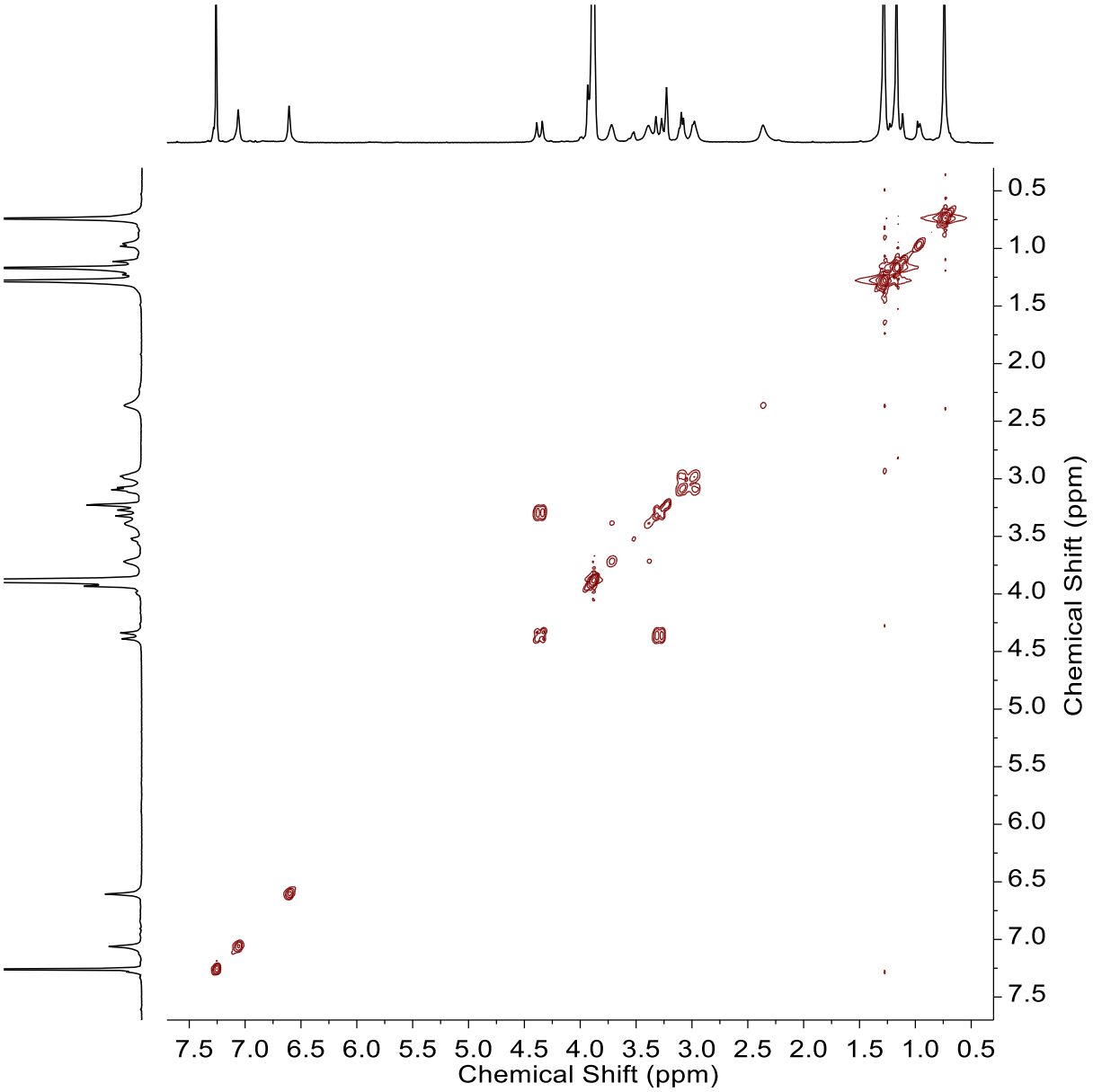

Figure S3. ^{1}H dqfCOSY NMR spectrum (300 MHz, $CDCl_3/CD_3OD$, 5:1, 298 K) of calixarene **2**.

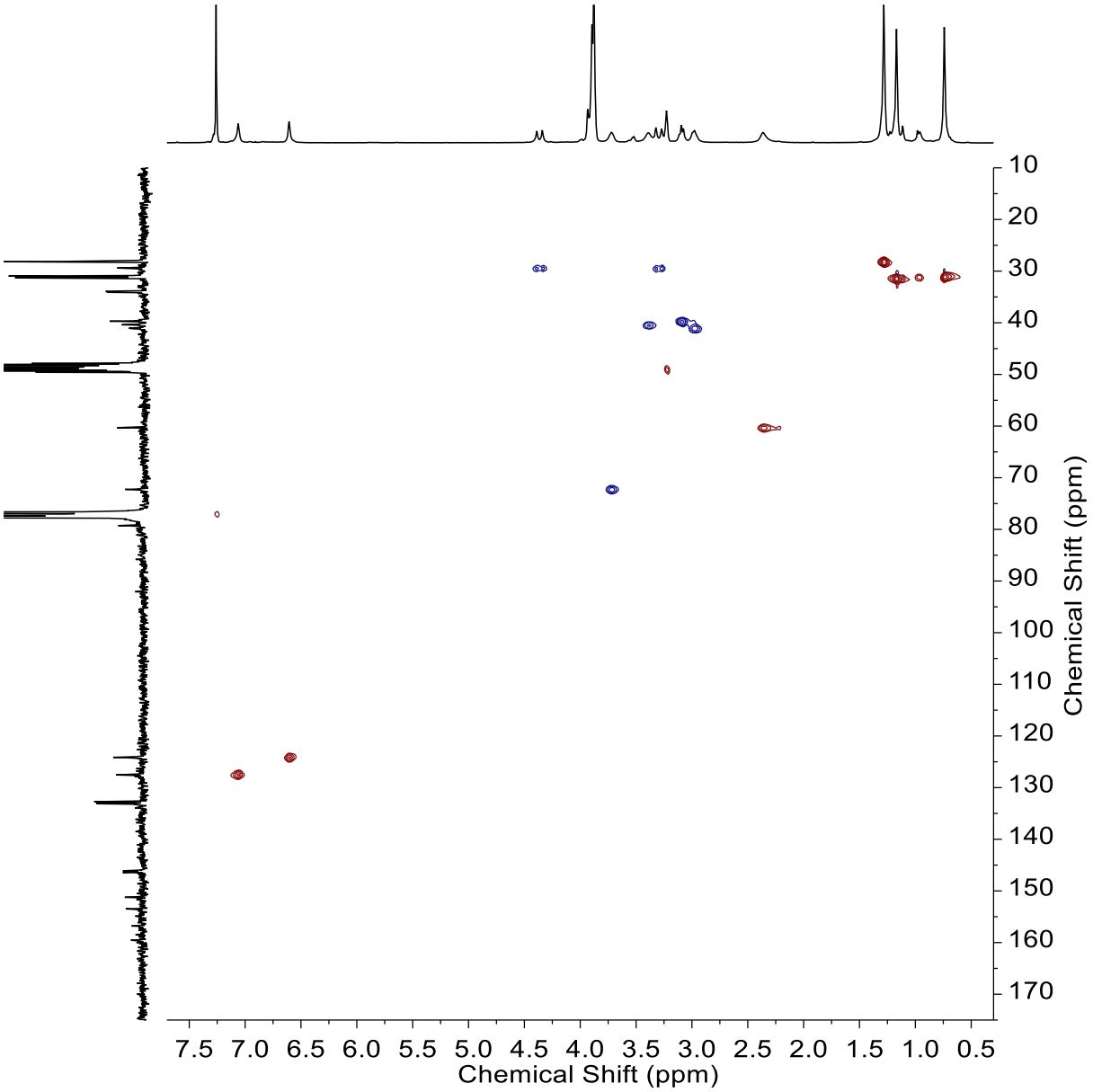

Figure S4. Edited ^{1}H-^{13}C HSQC NMR spectrum (7.0 Tesla, $CDCl_3/CD_3OD$, 5:1, 298 K) of calixarene **2**.

1.2. Calixarene 3

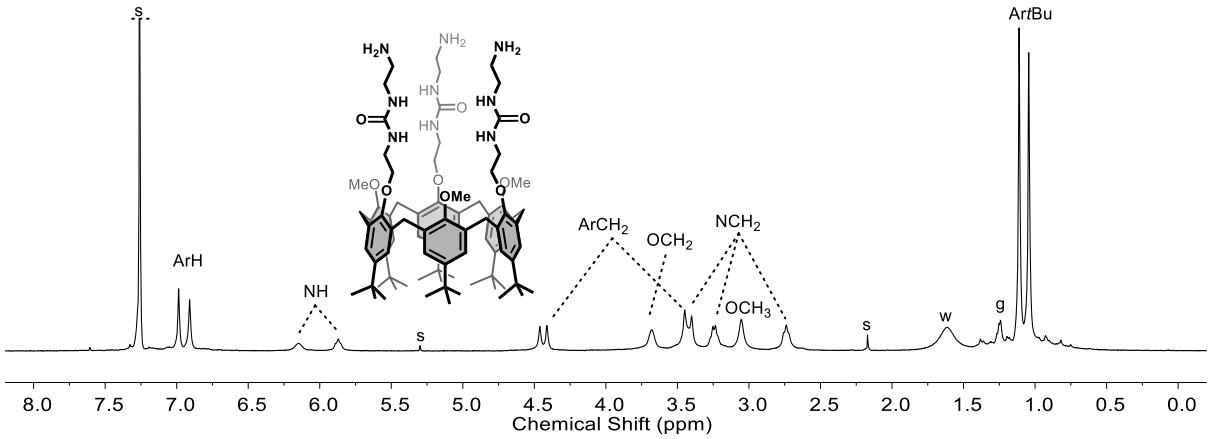

Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of calixarene **3**. s: solvent; w: water; g: grease.

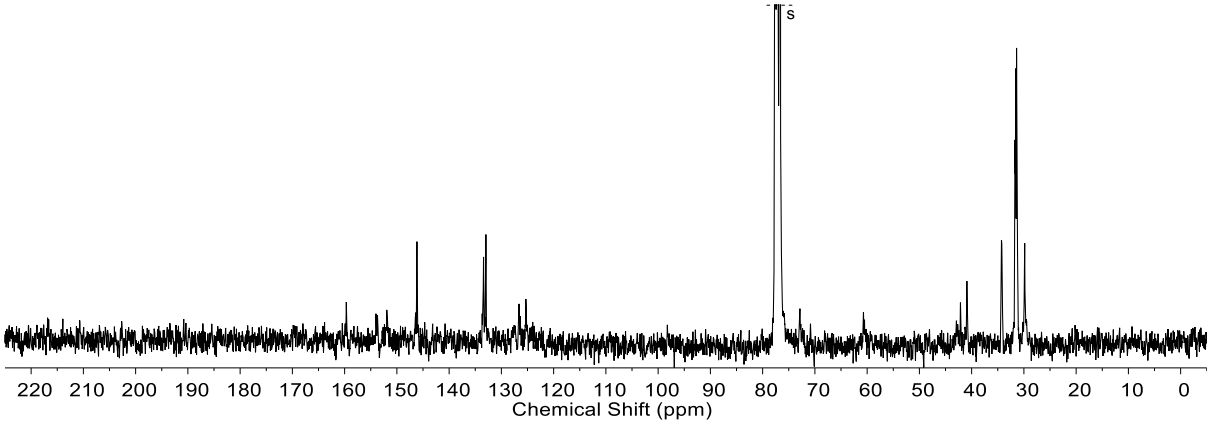

Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of calixarene **3**. s: solvent.

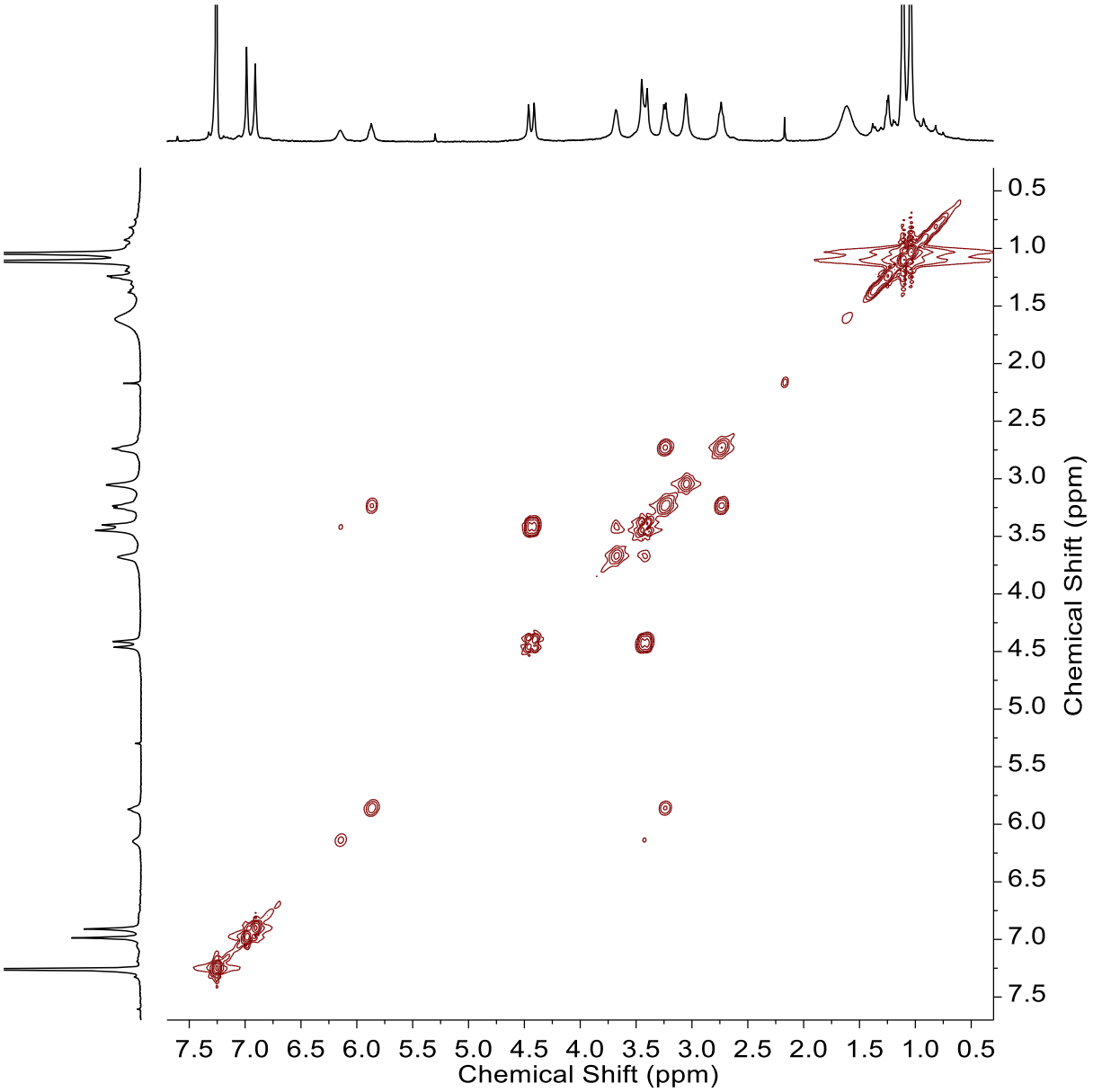

Figure S7. ^{1}H dqfCOSY NMR spectrum (300 MHz, $CDCl_3$, 298 K) of calixarene **3**.

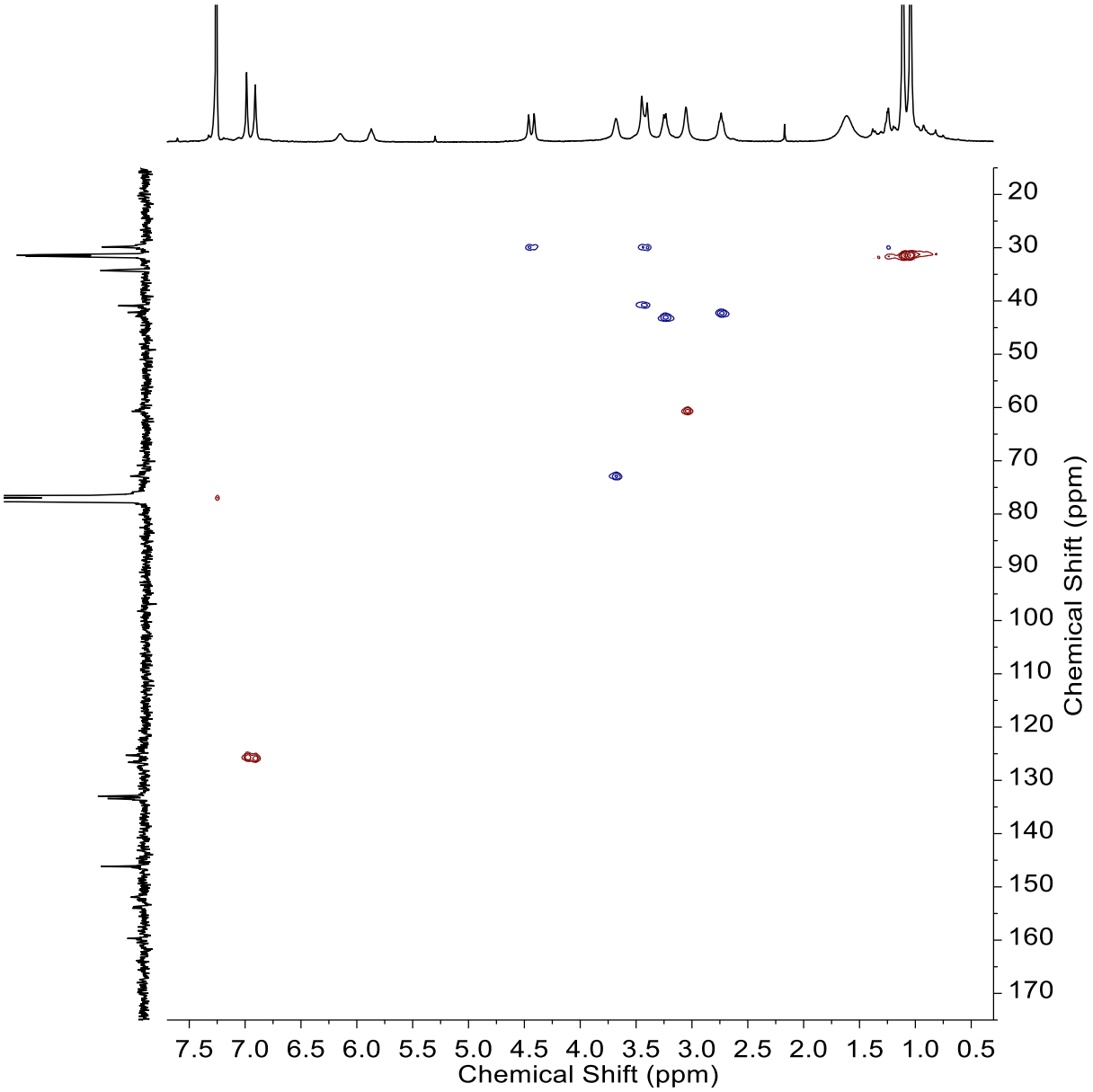

Figure S8. Edited ^{1}H-^{13}C HSQC NMR spectrum (7.0 Tesla, $CDCl_3$, 298 K) of calixarene **3**.

1.3. Calixarene C6U

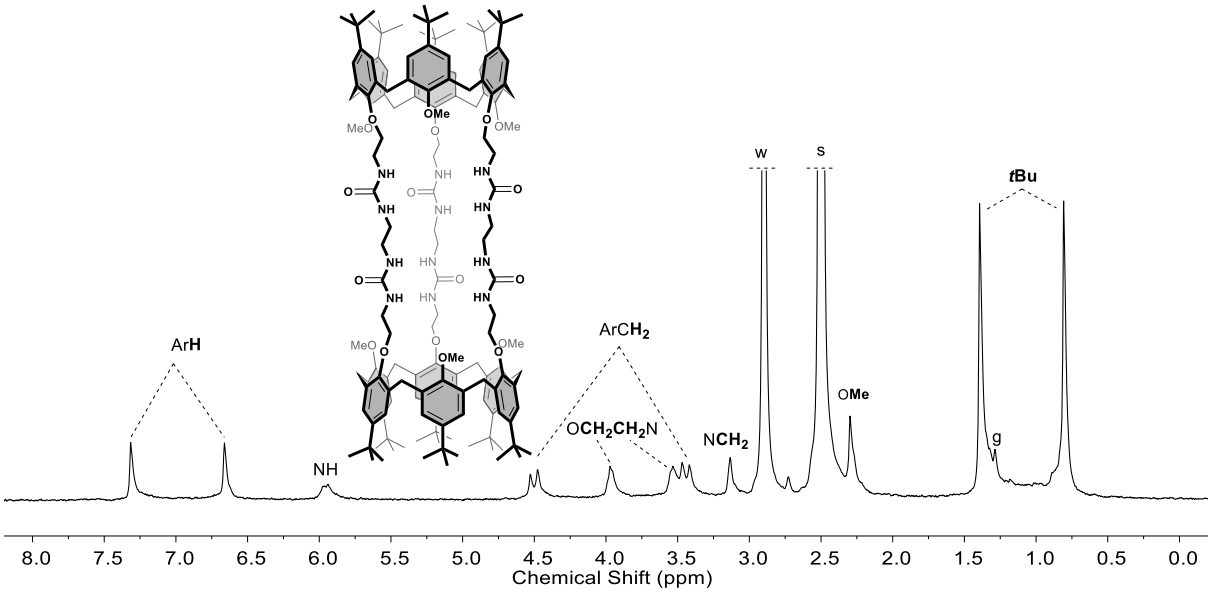

Figure S9. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 373 K) of calixarene **C6U**. s: solvent; w: water; g: grease.

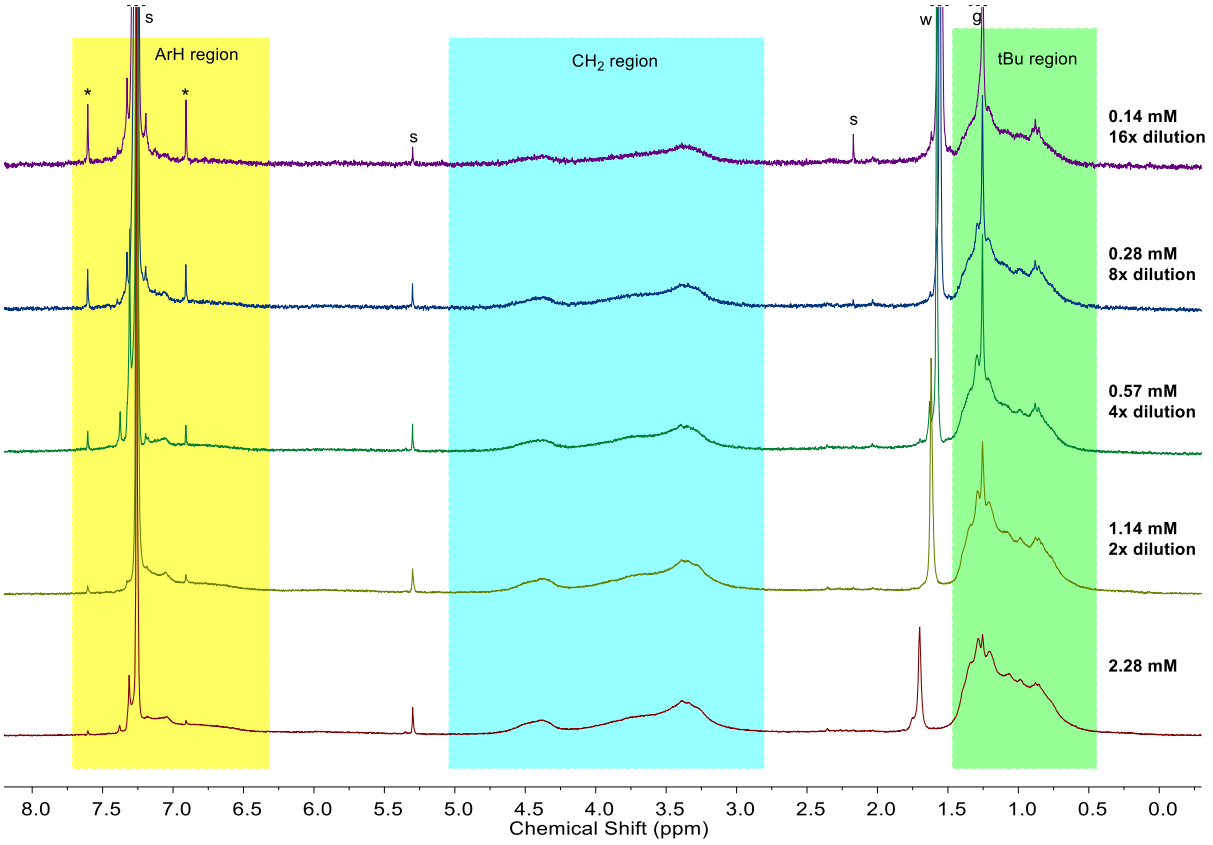

Figure S10. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of calixarene **C6U** at variable concentration. s: solvent; w: water; g: grease; *: ^{13}C satellite peaks.

2. Binding studies

2.1. Binding studies with C3U

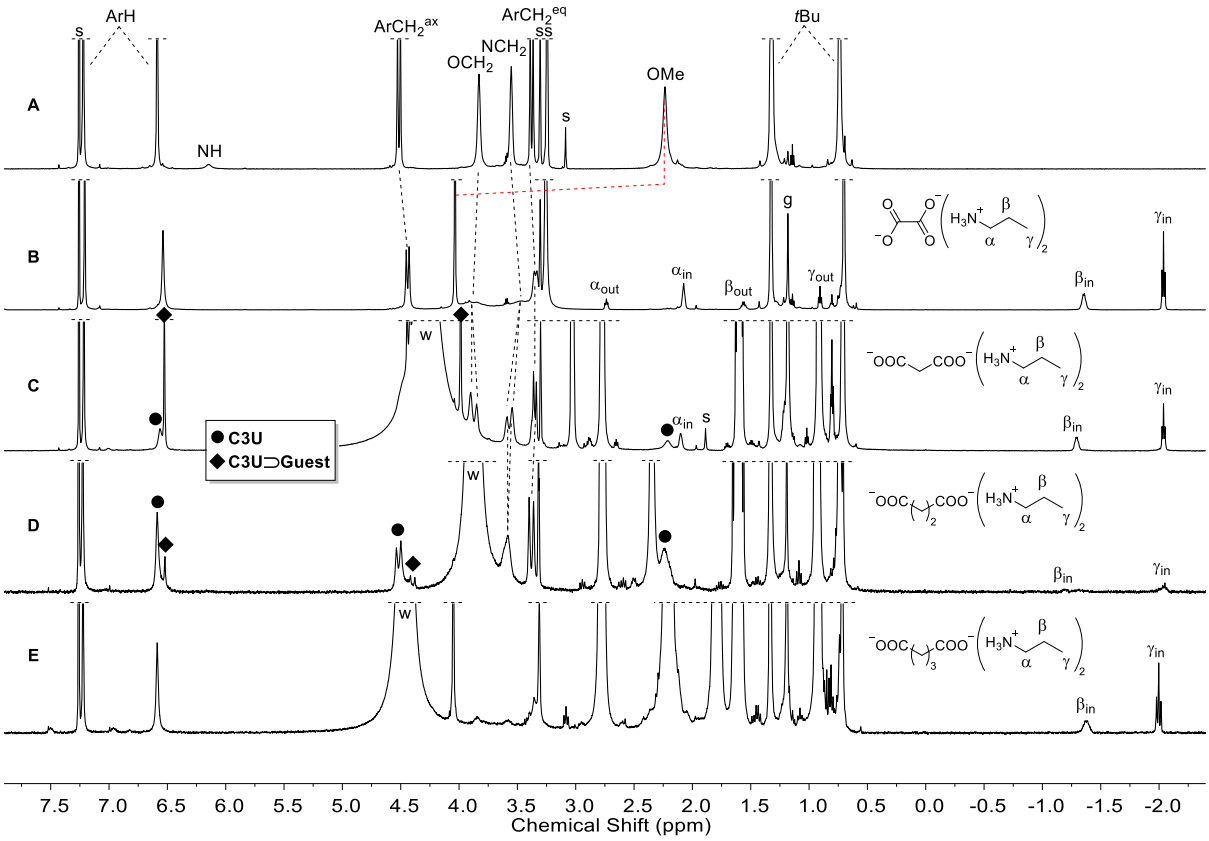

Figure S11. ^{1}H NMR spectra ($CDCl_3/CD_3OD$, 10:1, 298 K) of **C3U** and its inclusion complexes with dicarboxylate salts $(n\text{PrNH}_3^+)_2X^{2-}$. (A) **C3U** (600 MHz); (B) $(n\text{PrNH}_3^+)_2$-oxalate (600 MHz); (C) $(n\text{PrNH}_3^+)_2$-malonate (600 MHz); (D) $(n\text{PrNH}_3^+)_2$-succinate (400 MHz); (E) $(n\text{PrNH}_3^+)_2$-glutarate (400 MHz). s: solvents; w: water; g: grease.

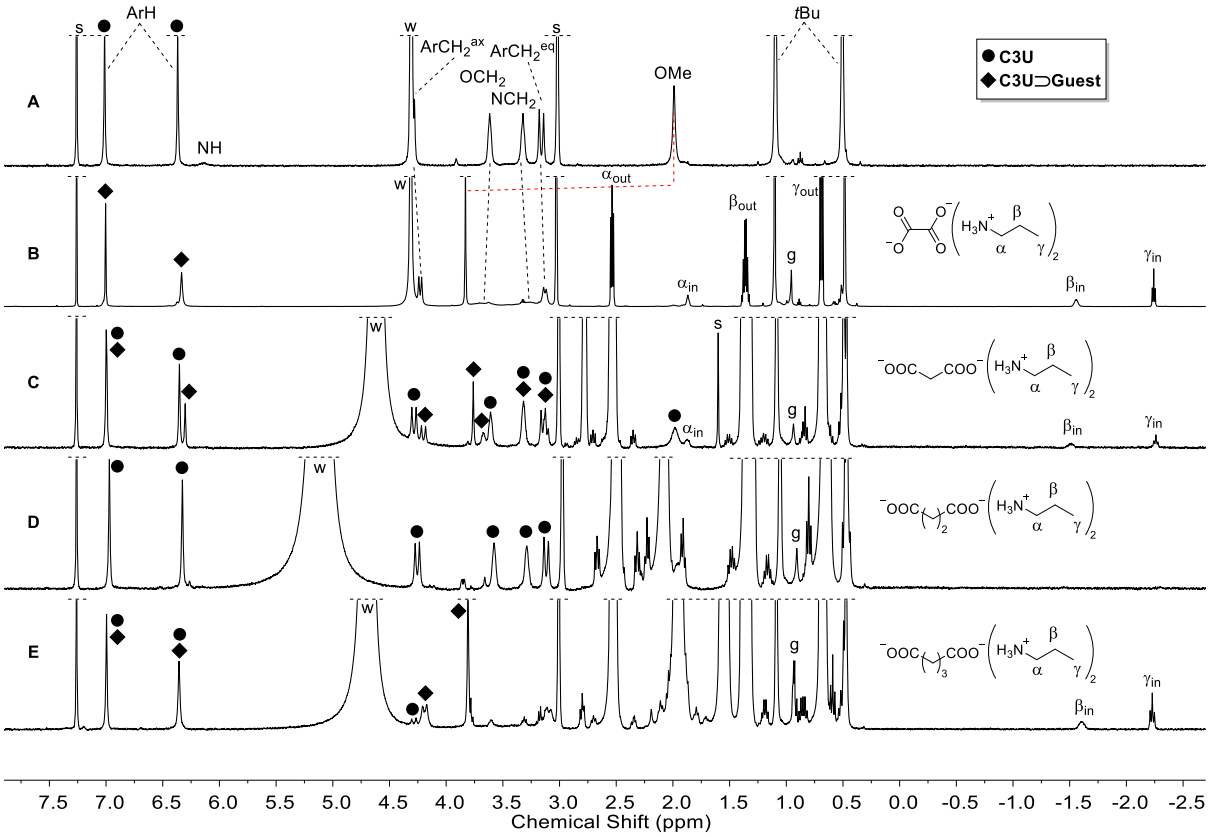

Figure S12. ^{1}H NMR spectra ($CDCl_3/CD_3OD$, 1:1, 298 K) of **C3U** and its inclusion complexes with dicarboxylate salts (n-$PrNH_3^+)_2X^{2-}$. (A) **C3U** (400 MHz); (B) (n-$PrNH_3^+)_2$-oxalate (600 MHz); (C) (n-$PrNH_3^+)_2$-malonate (400 MHz); (D) (n-$PrNH_3^+)_2$-succinate (400 MHz); (E) (n-$PrNH_3^+)_2$-glutarate (400 MHz). s: solvents; w: water; g: grease.

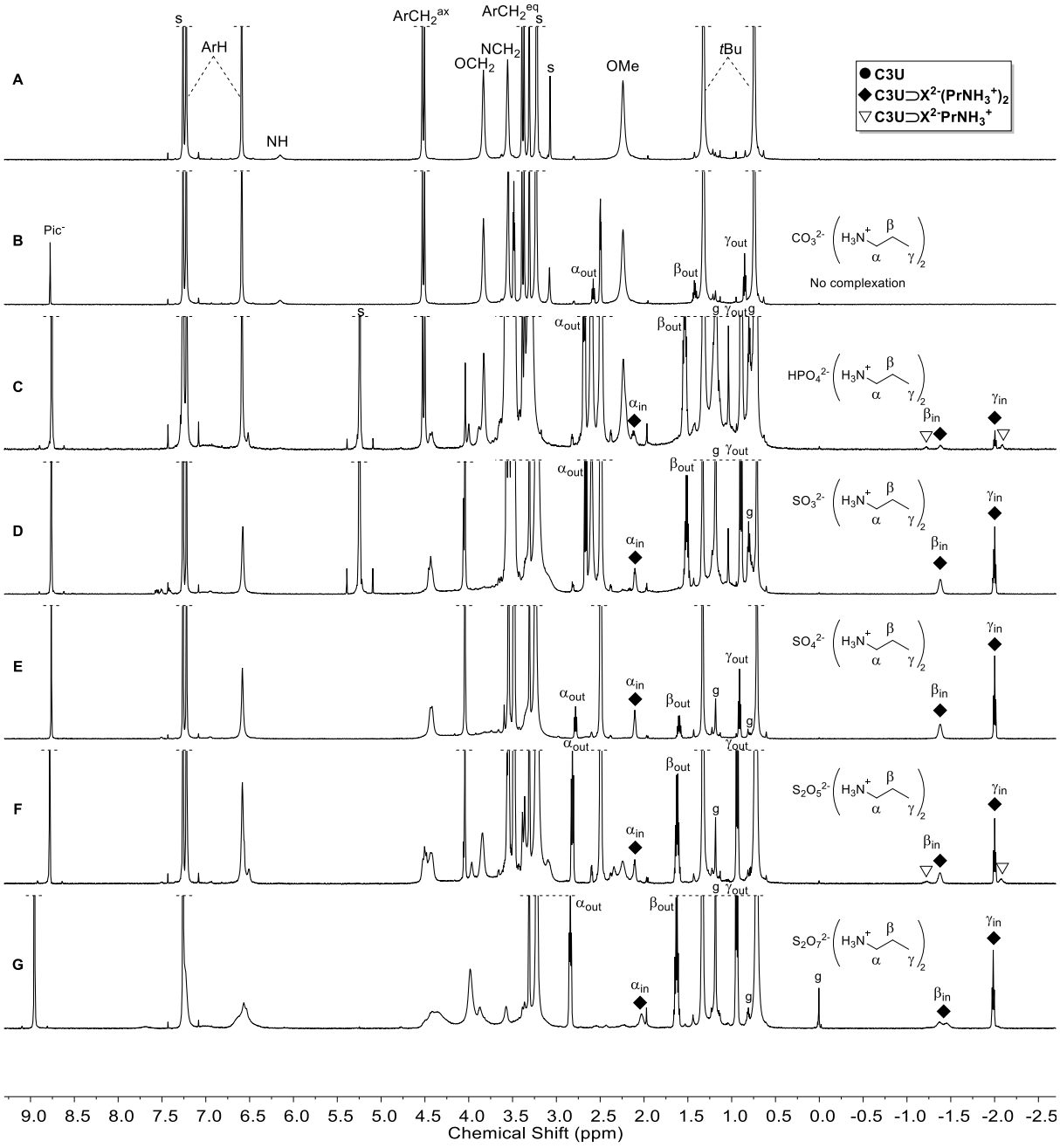

Figure S13. ^{1}H NMR spectra (600MHz, $CDCl_3/CD_3OD$, 10:1, 298 K) of **C3U** and its inclusion complexes with salts (nPrNH$_3^+$)$_2$X^{2-} added as a mixture of nPrNH$_3^+$Pic$^-$ and K_2X in the presence of Kryptofix® 222. (A) **C3U**; (B) (nPrNH$_3^+$)$_2$CO$_3^{2-}$ (no inclusion); (C) (nPrNH$_3^+$)$_2$HPO$_4^{2-}$; (D) (nPrNH$_3^+$)$_2$SO$_3^{2-}$; (E) (nPrNH$_3^+$)$_2$SO$_4^{2-}$; (F) (nPrNH$_3^+$)$_2$S$_2$O$_5^{2-}$; (G) (nPrNH$_3^+$)$_2$S$_2$O$_7^{2-}$. s: solvents; g: grease.

2.2. Binding studies with C3TU

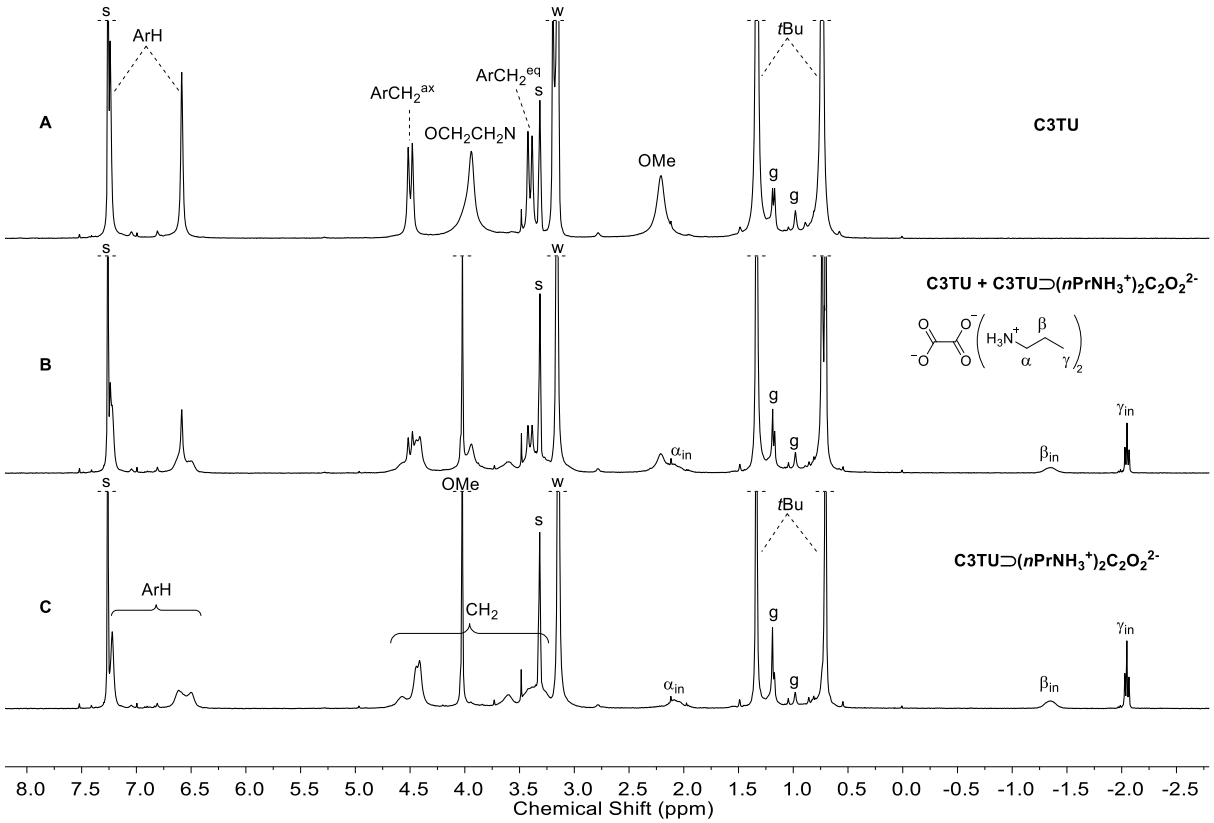

Figure S14. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3OD$, 10:1, 298 K) of **C3TU** and its inclusion complex with bis-propylammonium oxalate **C3TU**⊃$(n\text{PrNH}_3^+)_2C_2O_2^{2-}$. (A) **C3TU** ($1.7 \times 10^{-3}$ M); (B) **C3TU** + 0.6 equiv. $(n\text{PrNH}_3^+)_2C_2O_2^{2-}$; (C) **C3TU** + 1.0 equiv. $(n\text{PrNH}_3^+)_2C_2O_2^{2-}$. s: solvents; w: water; g: grease.

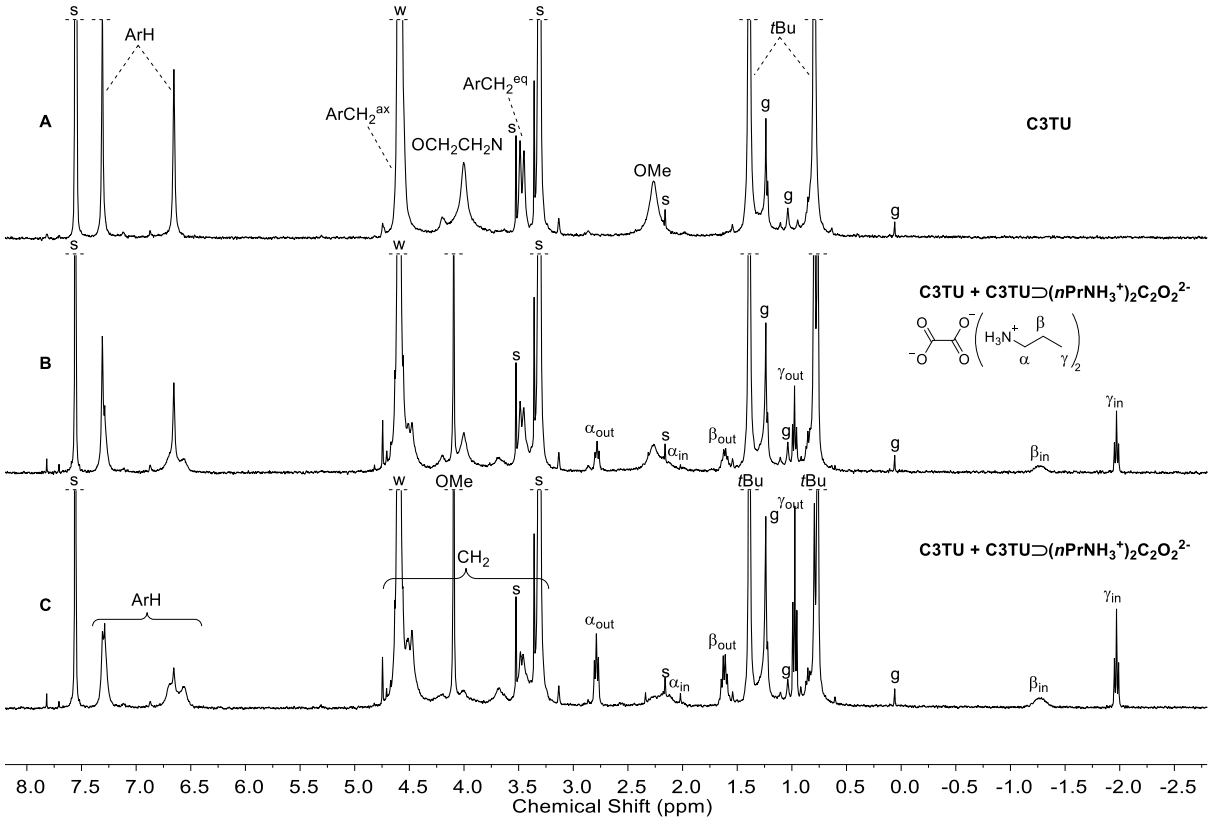

Figure S15. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3OD$, 1:1, 298 K) of **C3TU** and its inclusion complex with bis-propylammonium oxalate **C3TU⊃**(nPrNH$_3^+$)$_2$C$_2$O$_2^{2-}$. (A) **C3TU** (2.7×10^{-4} M); (B) **C3TU** + 1.1 equiv. (nPrNH$_3^+$)$_2$C$_2$O$_2^{2-}$; (C) **C3TU** + 2.5 equiv. (nPrNH$_3^+$)$_2$C$_2$O$_2^{2-}$. s: solvents; w: water; g: grease.

2.3. Binding studies with C6U

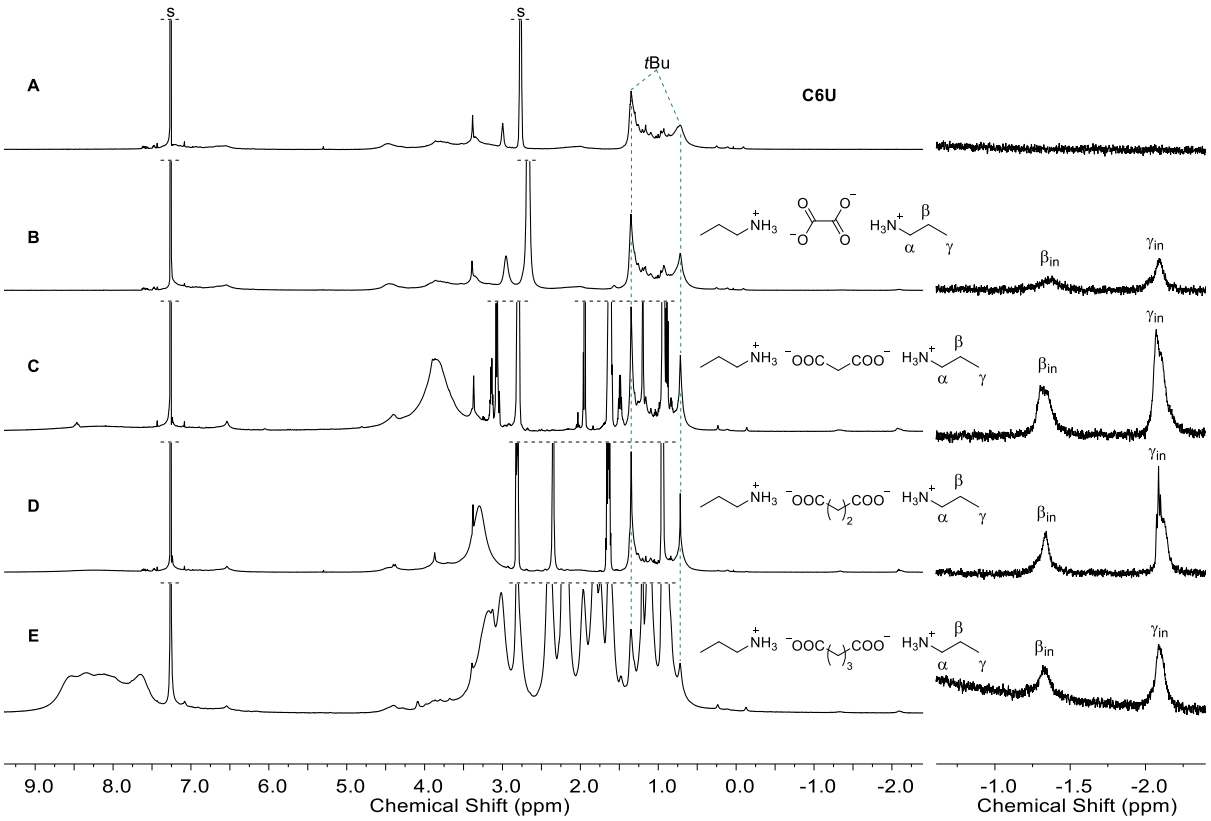

Figure S16. ^{1}H NMR spectra (600MHz, $CDCl_3/CD_3OD$, 50:1, 253 K) of **C6U** and its inclusion complexes with dicarboxylate salts (nPrNH$_3^+$)$_2$X$^-$. The spectra did not further evolve after 48 h at 65 °C. (A) **C6U**; (B) (nPrNH$_3^+$)$_2$-oxalate (excess solid, insoluble); (C) (nPrNH$_3^+$)$_2$-malonate; (D) (nPrNH$_3^+$)$_2$-succinate; (E) (nPrNH$_3^+$)$_2$-glutarate. s: solvents.

3. Molecular modeling

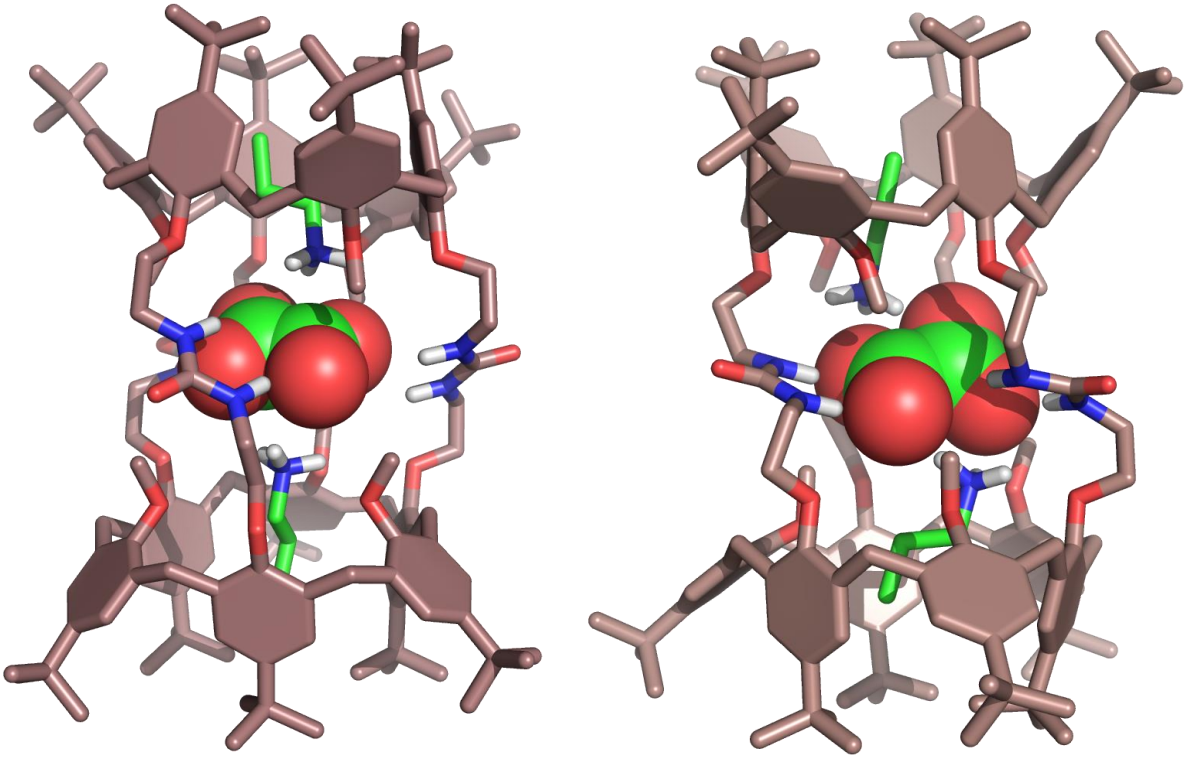

Figure S17. UFF (left) and PM6 (right) geometry optimized structure of **C3U⊃**(*n*PrNH$_3^+$)$_2$C$_2$O$_2^{2-}$. Non-polar hydrogen atoms are omitted for clarity.

Table S1. Cartesian coordinates (in Å) for the PM6 model of **C3U**⊃$(PrNH_3^+)_2C_2O_4^{2-}$.

C	0.000	0.000	0.000
C	10.481	0.000	0.000
C	2.345	2.336	0.000
C	4.027	-2.834	8.136
C	3.646	-7.420	0.565
C	0.618	0.894	0.897
C	9.754	-1.050	-0.603
C	3.719	2.719	0.581
C	5.362	-3.498	7.749
C	5.030	-6.755	0.430
O	1.982	1.136	0.749
O	8.364	-1.090	-0.447
C	-0.046	1.402	2.026
C	10.398	-2.111	-1.256
N	4.607	1.543	0.668
N	6.176	-2.677	6.825
N	5.460	-6.107	1.682
C	-1.355	0.964	2.275
C	11.802	-2.115	-1.312
C	4.932	0.872	-0.521
C	6.788	-1.528	7.372
C	6.216	-6.808	2.629
C	-1.987	0.046	1.429
C	12.552	-1.089	-0.732
O	4.823	1.397	-1.627
O	7.034	-1.452	8.575
O	6.583	-7.971	2.459
C	-1.302	-0.413	0.290
C	11.874	-0.053	-0.062
N	5.345	-0.473	-0.373
N	7.170	-0.529	6.472
N	6.603	-6.047	3.749
C	-3.388	-0.514	1.710
C	14.081	-1.017	-0.839
C	6.212	-1.034	-1.433
C	8.141	0.496	6.924
C	7.103	-6.720	4.963
C	-4.297	-0.228	0.493
C	14.427	0.220	-1.702
C	7.612	-0.402	-1.491
C	9.531	0.154	6.376
C	8.564	-7.162	4.792
C	-3.249	-2.037	1.938
C	14.703	-0.877	0.568
C	-4.039	0.118	2.960
C	14.688	-2.272	-1.505
C	0.663	2.376	2.932
C	9.606	-3.222	-1.893
C	0.473	2.050	4.385
C	10.014	-4.573	-1.373
C	1.351	1.162	5.027
C	9.721	-4.977	-0.060
C	3.693	1.460	4.683
C	7.738	-3.856	0.755
O	2.486	0.716	4.341
O	9.164	-4.114	0.874
C	1.084	0.670	6.317
C	10.106	-6.246	0.418
C	0.031	1.250	7.035
C	10.791	-7.108	-0.442
C	-0.806	2.222	6.459
C	11.123	-6.722	-1.752
C	-0.597	2.577	5.120
C	10.722	-5.459	-2.201
C	-1.947	2.815	7.294
C	11.932	-7.691	-2.623
C	-1.389	3.297	8.653
C	11.133	-9.004	-2.780
C	-2.622	4.020	6.602
C	12.221	-7.129	-4.033
C	-3.004	1.707	7.503
C	13.285	-7.954	-1.920
C	1.873	-0.482	6.865
C	9.798	-6.641	1.835
C	1.103	-1.776	6.945
C	10.898	-6.302	2.804
C	1.817	-2.977	7.139
C	10.604	-6.036	4.155
O	3.200	-2.966	6.944
O	9.284	-5.906	4.595
C	1.154	-4.193	7.365
C	11.610	-5.749	5.097
C	-0.246	-4.215	7.304
C	12.932	-5.662	4.646
C	-0.979	-3.063	6.998
C	13.264	-5.911	3.309
C	-0.290	-1.850	6.847
C	12.238	-6.233	2.406
C	-2.508	-3.129	6.877
C	14.709	-5.823	2.796
C	-3.090	-2.945	8.296
C	15.033	-7.088	1.966
C	-3.048	-2.021	5.945
C	14.825	-4.558	1.918
C	-2.942	-4.492	6.291
C	15.740	-5.728	3.945
C	1.906	-5.461	7.665
C	11.222	-5.582	6.545
C	1.435	-6.607	6.812
C	12.094	-4.629	7.311
C	1.698	-6.631	5.433
C	11.668	-3.318	7.584
C	3.587	-5.256	4.791
C	9.373	-3.240	8.211
O	2.155	-5.511	4.760
O	10.380	-2.926	7.199
C	1.374	-7.760	4.652
C	12.521	-2.386	8.206
C	0.661	-8.804	5.245
C	13.782	-2.823	8.628
C	0.294	-8.760	6.602
C	14.227	-4.135	8.396
C	0.721	-7.675	7.377
C	13.364	-5.029	7.752
C	-0.567	-9.895	7.169
C	15.646	-4.525	8.827
C	0.203	-11.226	7.022
C	15.733	-4.437	10.366
C	-0.910	-9.695	8.662
C	16.026	-5.958	8.392
C	-1.892	-9.937	6.371
C	16.644	-3.545	8.164
C	1.839	-7.830	3.227
C	12.134	-0.941	8.355
C	0.900	-7.219	2.225
C	12.590	-0.117	7.177
C	1.417	-6.595	1.072
C	11.752	0.875	6.630
O	2.777	-6.314	0.948
O	10.449	1.019	7.125
C	0.565	-6.092	0.072
C	12.201	1.738	5.616
C	-0.819	-6.145	0.278
C	13.482	1.532	5.084
C	-1.361	-6.713	1.436
C	14.302	0.495	5.538
C	-0.487	-7.265	2.390
C	13.856	-0.293	6.612
C	-2.871	-6.755	1.699
C	15.643	0.152	4.878
C	-3.307	-8.234	1.822
C	16.759	0.154	5.947
C	-3.162	-5.995	3.013
C	15.496	-1.251	4.242
C	-3.693	-6.096	0.569
C	16.034	1.155	3.770
C	1.163	-5.543	-1.197
C	11.326	2.863	5.122

C	0.498	-4.285	-1.675
C	11.328	2.938	3.621
C	0.952	-3.016	-1.261
C	10.445	2.150	2.860
C	3.323	-2.952	-0.829
C	8.151	1.933	3.478
O	1.966	-2.928	-0.310
O	9.495	1.368	3.518
C	0.314	-1.839	-1.685
C	10.553	2.074	1.461
C	-0.795	-1.945	-2.540
C	11.477	2.908	0.815
C	-1.287	-3.190	-2.945
C	12.340	3.739	1.539
C	-0.612	-4.349	-2.523
C	12.259	3.733	2.942
C	-2.565	-3.337	-3.779
C	13.419	4.586	0.855
C	-2.256	-4.168	-5.044
C	13.389	6.026	1.419
C	-3.617	-4.051	-2.897
C	14.782	3.915	1.149
C	-3.146	-1.977	-4.226
C	13.225	4.671	-0.675
C	0.763	-0.488	-1.203
C	9.716	1.098	0.686
H	1.586	3.127	0.148
H	2.432	2.014	-1.064
H	3.546	-3.351	8.990
H	4.149	-1.745	8.321
H	3.291	-7.824	-0.406
H	3.644	-8.187	1.365
H	4.191	3.476	-0.106
H	3.611	3.146	1.609
H	5.959	-3.654	8.692
H	5.169	-4.477	7.241
H	5.777	-7.550	0.149
H	4.979	-5.962	-0.360
H	4.709	1.078	1.584
H	5.965	-2.750	5.813
H	5.155	-5.126	1.835
H	-1.858	1.346	3.162
H	12.282	-2.954	-1.812
H	-1.783	-1.129	-0.377
H	12.451	0.726	0.437
H	5.423	-0.872	0.568
H	6.969	-0.582	5.463
H	6.275	-5.063	3.865
H	5.704	-0.842	-2.421
H	6.303	-2.136	-1.249
H	8.178	0.514	8.051
H	7.803	1.494	6.548
H	6.490	-7.637	5.185
H	7.033	-5.987	5.810
H	-3.966	-0.806	-0.396
H	-4.263	0.856	0.250
H	-5.344	-0.517	0.726
H	15.521	0.267	-1.880
H	14.107	1.152	-1.189
H	13.899	0.152	-2.678
H	8.098	-0.576	-2.473
H	7.586	0.676	-1.224
H	9.813	-0.902	6.601
H	9.625	0.411	5.293
H	8.968	-7.626	5.715
H	8.686	-7.813	3.899
H	-2.909	-2.548	1.011
H	-4.222	-2.471	2.248
H	-2.494	-2.224	2.733
H	15.806	-0.779	0.490
H	14.460	-1.779	1.170
H	14.307	0.017	1.095
H	-4.171	1.211	2.814
H	-3.412	-0.066	3.860
H	-5.037	-0.339	3.133
H	15.797	-2.192	-1.512
H	14.337	-2.363	-2.555
H	14.405	-3.183	-0.935
H	1.766	2.318	2.706
H	0.298	3.407	2.707
H	8.517	-3.071	-1.676
H	9.752	-3.166	-3.001
H	4.452	0.940	4.042
H	3.906	1.341	5.763
H	3.553	2.519	4.397
H	7.343	-4.159	1.747
H	7.278	-4.440	-0.060
H	7.674	-2.753	0.598
H	-0.138	0.919	8.059
H	11.072	-8.094	-0.074
H	-1.262	3.280	4.621
H	10.960	-5.131	-3.210
H	-2.163	3.878	9.200
H	-0.503	3.947	8.481
H	-1.089	2.439	9.290
H	11.651	-9.685	-3.488
H	10.117	-8.775	-3.170
H	11.029	-9.525	-1.805
H	-3.134	3.703	5.669
H	-1.865	4.801	6.371
H	-3.387	4.461	7.279
H	12.807	-7.872	-4.618
H	12.815	-6.193	-3.963
H	11.270	-6.933	-4.573
H	-3.377	1.358	6.516
H	-3.857	2.104	8.094
H	-2.564	0.846	8.050
H	13.934	-8.581	-2.568
H	13.133	-8.483	-0.956
H	13.793	-6.985	-1.721
H	2.767	-0.675	6.203
H	2.240	-0.227	7.892
H	8.860	-6.101	2.158
H	9.595	-7.742	1.879
H	-0.748	-5.167	7.476
H	13.704	-5.382	5.359
H	-0.850	-0.941	6.633
H	12.476	-6.413	1.357
H	-2.778	-1.962	8.708
H	-2.714	-3.747	8.968
H	-4.199	-2.992	8.259
H	16.125	-7.148	1.770
H	14.507	-7.065	0.989
H	14.716	-7.994	2.528
H	-2.964	-1.025	6.426
H	-4.119	-2.203	5.714
H	-2.471	-2.023	4.995
H	15.809	-4.533	1.407
H	14.724	-3.655	2.559
H	14.017	-4.543	1.153
H	-2.856	-5.300	7.048
H	-2.294	-4.737	5.419
H	-3.999	-4.451	5.952
H	16.768	-5.704	3.521
H	15.648	-6.612	4.611
H	15.590	-4.796	4.532
H	1.777	-5.697	8.751
H	2.997	-5.307	7.464
H	10.157	-5.216	6.575
H	11.257	-6.593	7.026
H	3.813	-5.059	3.717
H	4.145	-6.117	5.191
H	3.702	-4.330	5.403
H	8.549	-3.693	7.621
H	9.076	-2.260	8.656
H	9.768	-3.934	8.975
H	0.391	-9.662	4.632
H	14.428	-2.115	9.147
H	0.498	-7.633	8.440
H	13.661	-6.062	7.579
H	1.204	-11.130	7.496
H	0.341	-11.489	5.952

H	-0.358	-12.048	7.516
H	16.737	-4.765	10.710
H	14.959	-5.095	10.820
H	15.561	-3.397	10.714
H	0.017	-9.688	9.275
H	-1.553	-10.533	9.013
H	-1.467	-8.744	8.807
H	17.071	-6.179	8.703
H	15.961	-6.055	7.287
H	15.357	-6.702	8.877
H	-1.706	-10.204	5.309
H	-2.377	-8.937	6.406
H	-2.576	-10.692	6.810
H	17.686	-3.891	8.332
H	16.543	-2.526	8.592
H	16.448	-3.499	7.070
H	2.011	-8.899	2.942
H	2.818	-7.270	3.165
H	12.595	-0.505	9.278
H	11.019	-0.852	8.463
H	-1.463	-5.717	-0.487
H	13.812	2.191	4.282
H	-0.883	-7.725	3.294
H	14.500	-1.079	7.003
H	-4.412	-8.300	1.909
H	-2.853	-8.705	2.720
H	-2.976	-8.794	0.920
H	16.725	1.110	6.514
H	17.753	0.053	5.461
H	16.630	-0.689	6.657
H	-4.254	-5.965	3.206
H	-2.776	-4.954	2.930
H	-2.662	-6.493	3.871
H	14.631	-1.240	3.543
H	15.307	-2.020	5.020
H	16.417	-1.519	3.685
H	-4.774	-6.125	0.827
H	-3.546	-6.645	-0.386
H	-3.392	-5.034	0.443
H	16.148	2.174	4.197
H	15.262	1.168	2.970
H	17.001	0.852	3.313
H	2.250	-5.335	-0.991
H	1.097	-6.335	-1.984
H	11.698	3.819	5.568
H	10.276	2.697	5.489
H	3.899	-3.213	0.094
H	3.550	-1.934	-1.208
H	3.436	-3.716	-1.619
H	7.527	1.007	3.607
H	7.952	2.420	2.505
H	8.068	2.640	4.323
H	-1.269	-1.023	-2.871
H	11.511	2.877	-0.273
H	-0.961	-5.328	-2.849
H	12.932	4.356	3.528
H	-3.133	-4.169	-5.725
H	-2.017	-5.221	-4.783
H	-1.384	-3.724	-5.574
H	13.754	6.054	2.467
H	12.346	6.412	1.389
H	14.039	6.689	0.809
H	-4.584	-4.120	-3.440
H	-3.765	-3.477	-1.956
H	-3.283	-5.078	-2.637
H	14.768	2.865	0.782
H	14.985	3.906	2.241
H	15.596	4.470	0.637
H	-4.060	-2.143	-4.838
H	-2.405	-1.428	-4.845
H	-3.428	-1.364	-3.343
H	13.344	3.670	-1.143
H	13.989	5.349	-1.114
H	12.216	5.076	-0.908
H	0.647	0.265	-2.024
H	1.855	-0.536	-0.932
H	8.991	0.583	1.388
H	9.127	1.665	-0.078
N	2.733	-1.313	2.307
C	1.338	-1.914	2.354
C	1.368	-3.222	3.156
C	-0.037	-3.788	3.351
H	2.918	-0.792	3.219
H	2.864	-0.622	1.525
H	3.465	-2.091	2.192
H	0.999	-2.132	1.300
H	0.642	-1.173	2.827
H	1.981	-3.985	2.603
H	1.825	-3.054	4.165
H	-0.526	-3.959	2.367
H	-0.648	-3.109	3.980
H	0.061	-4.773	3.877
N	8.587	-2.985	4.380
C	10.037	-2.555	4.220
C	10.514	-2.764	2.782
C	11.959	-2.295	2.629
H	8.244	-2.726	5.331
H	8.475	-4.026	4.214
H	7.967	-2.417	3.694
H	10.669	-3.144	4.944
H	10.115	-1.462	4.461
H	9.866	-2.192	2.067
H	10.448	-3.850	2.507
H	12.035	-1.199	2.816
H	12.284	-2.502	1.582
H	12.618	-2.842	3.338
C	5.881	-1.203	3.082
C	5.585	-2.737	3.070
O	7.001	-0.878	3.523
O	4.979	-0.441	2.674
O	6.078	-3.367	4.042
O	4.945	-3.230	2.123