Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Inversion of selectivity in anion recognition with conformationally blocked calix[4]pyrroles

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Supplementary Information

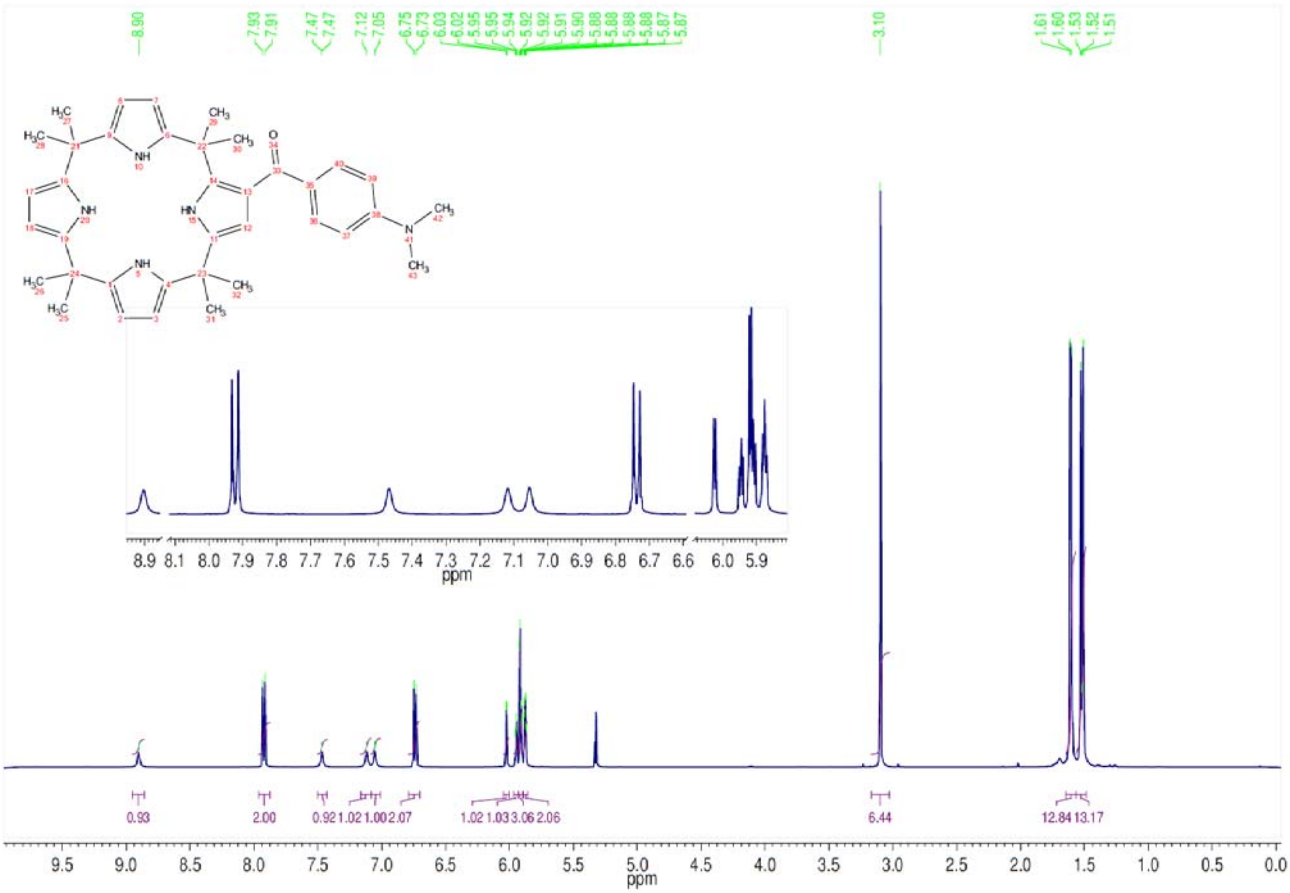


Figure S-1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

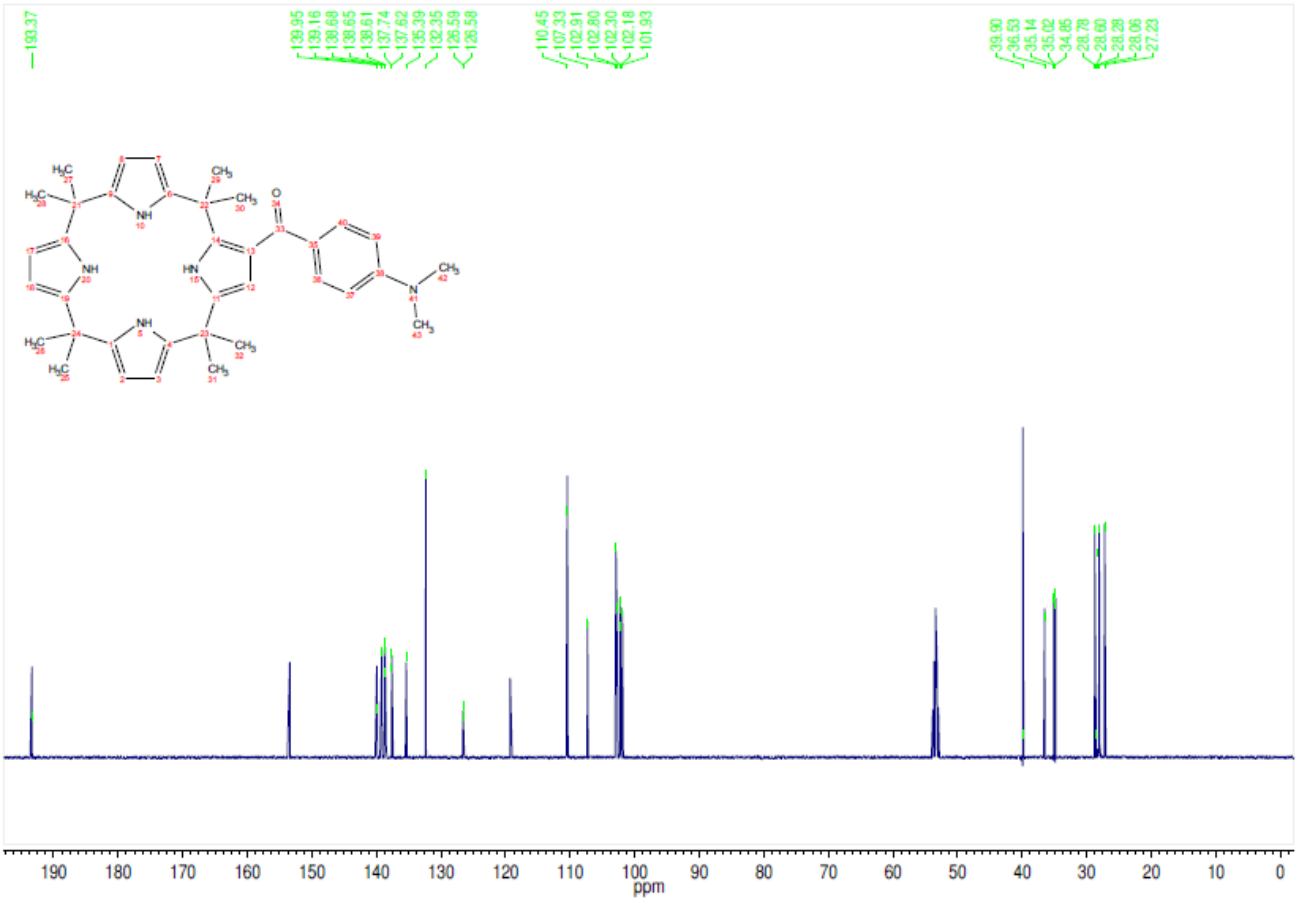


Figure S-2. ^{13} NMR spectrum of compound **1** in $CDCl_3$.

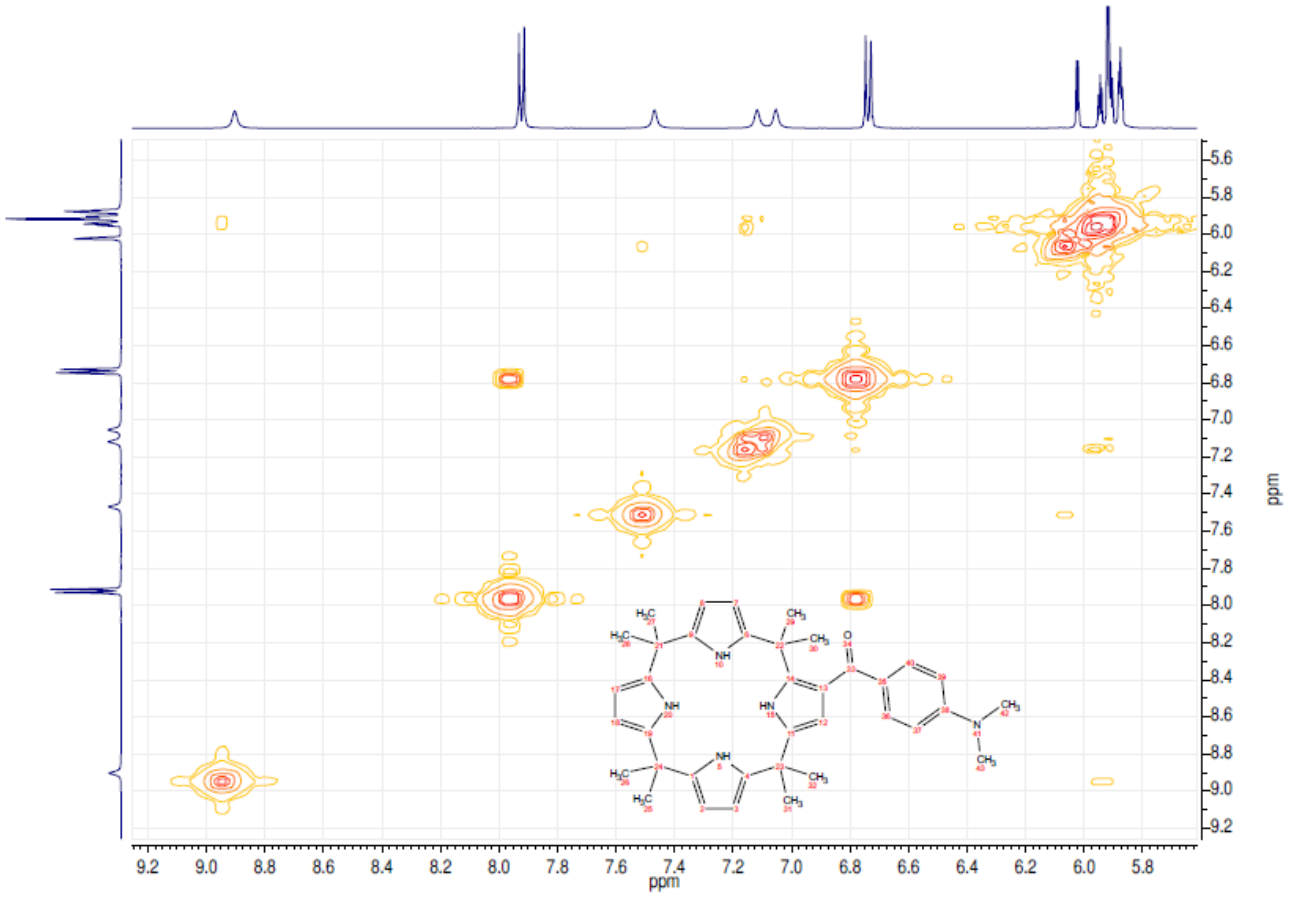


Figure S-3. COSY spectrum of compound **1** in $CDCl_3$

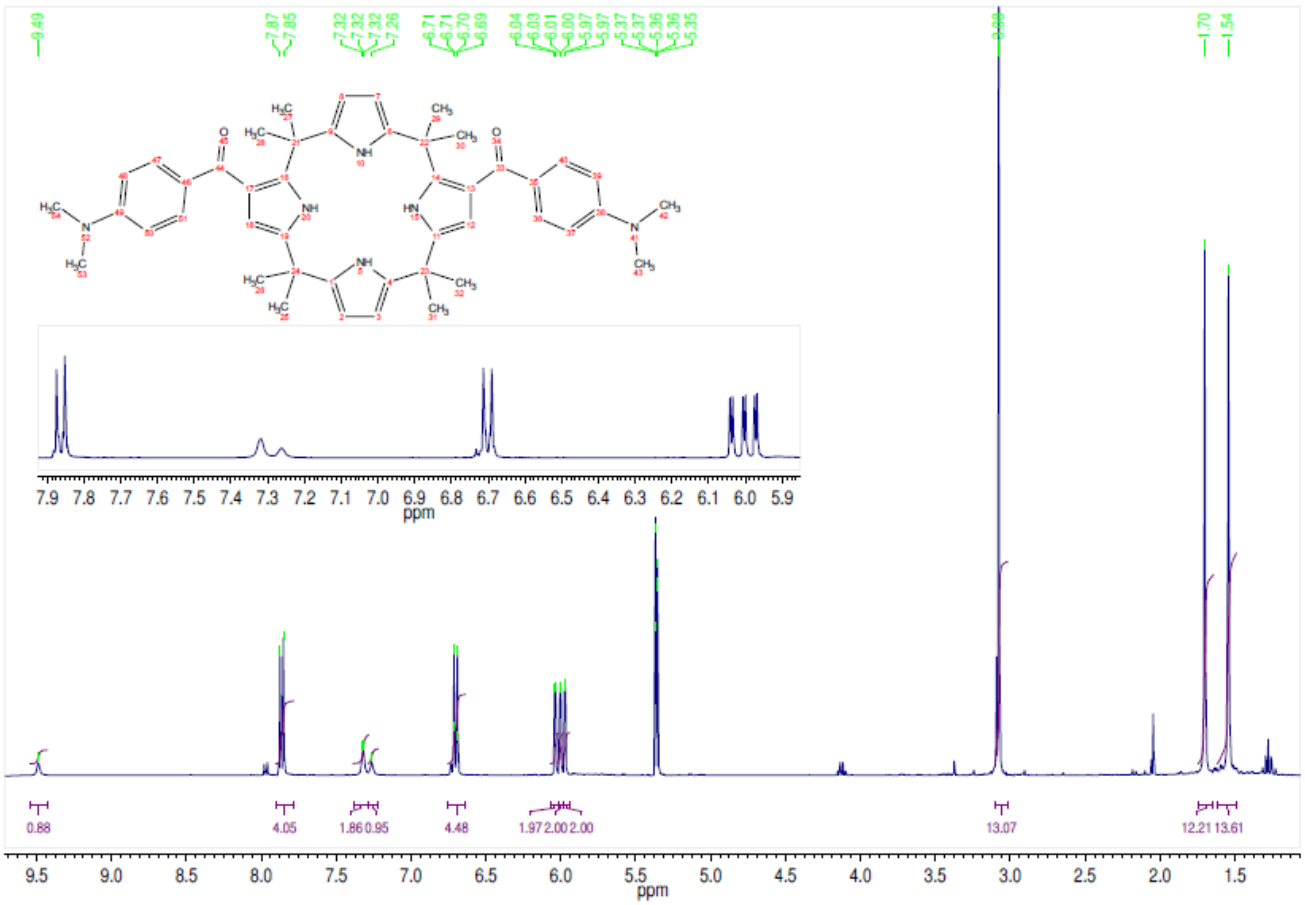


Figure S-4. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

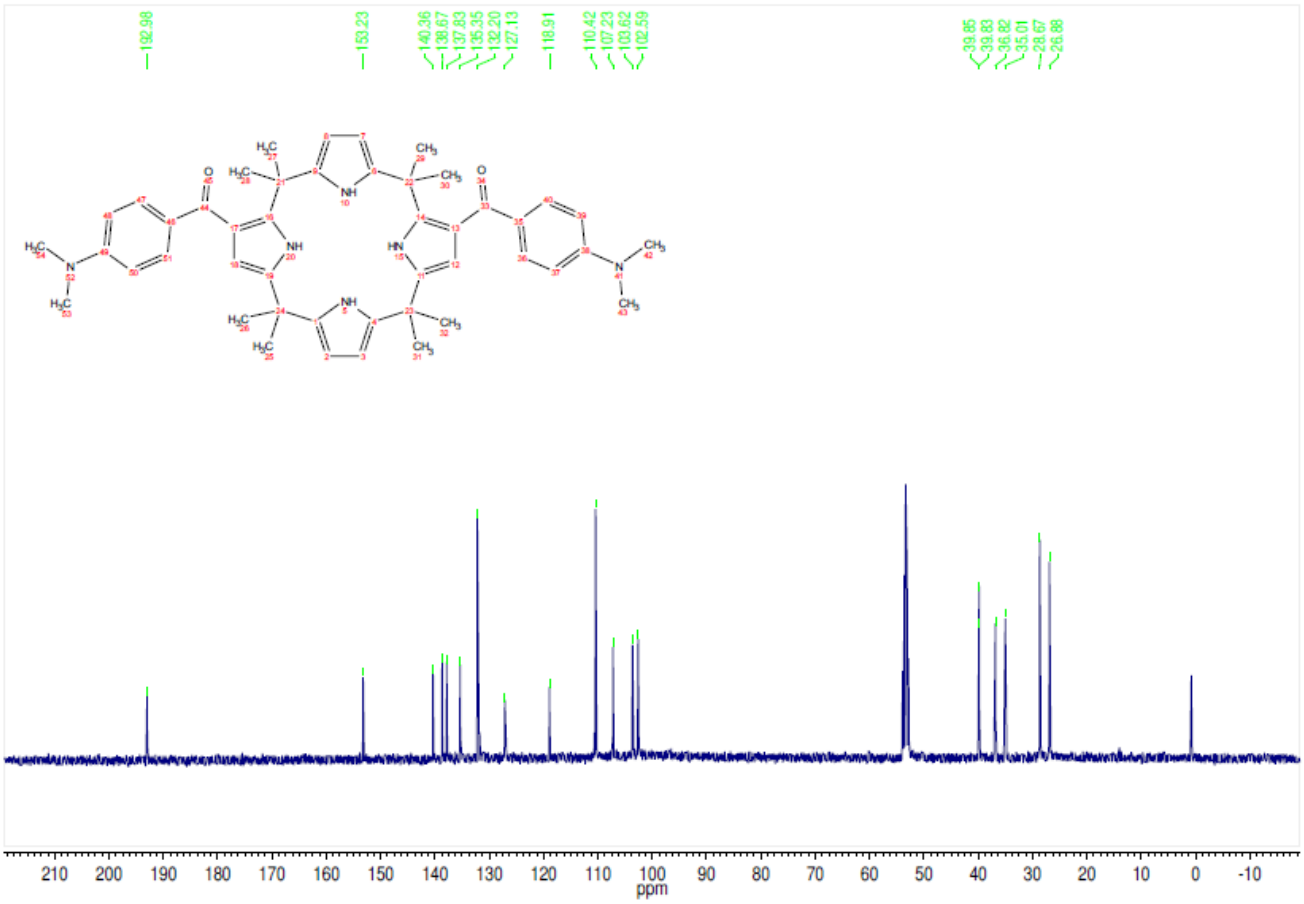


Figure S-5. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

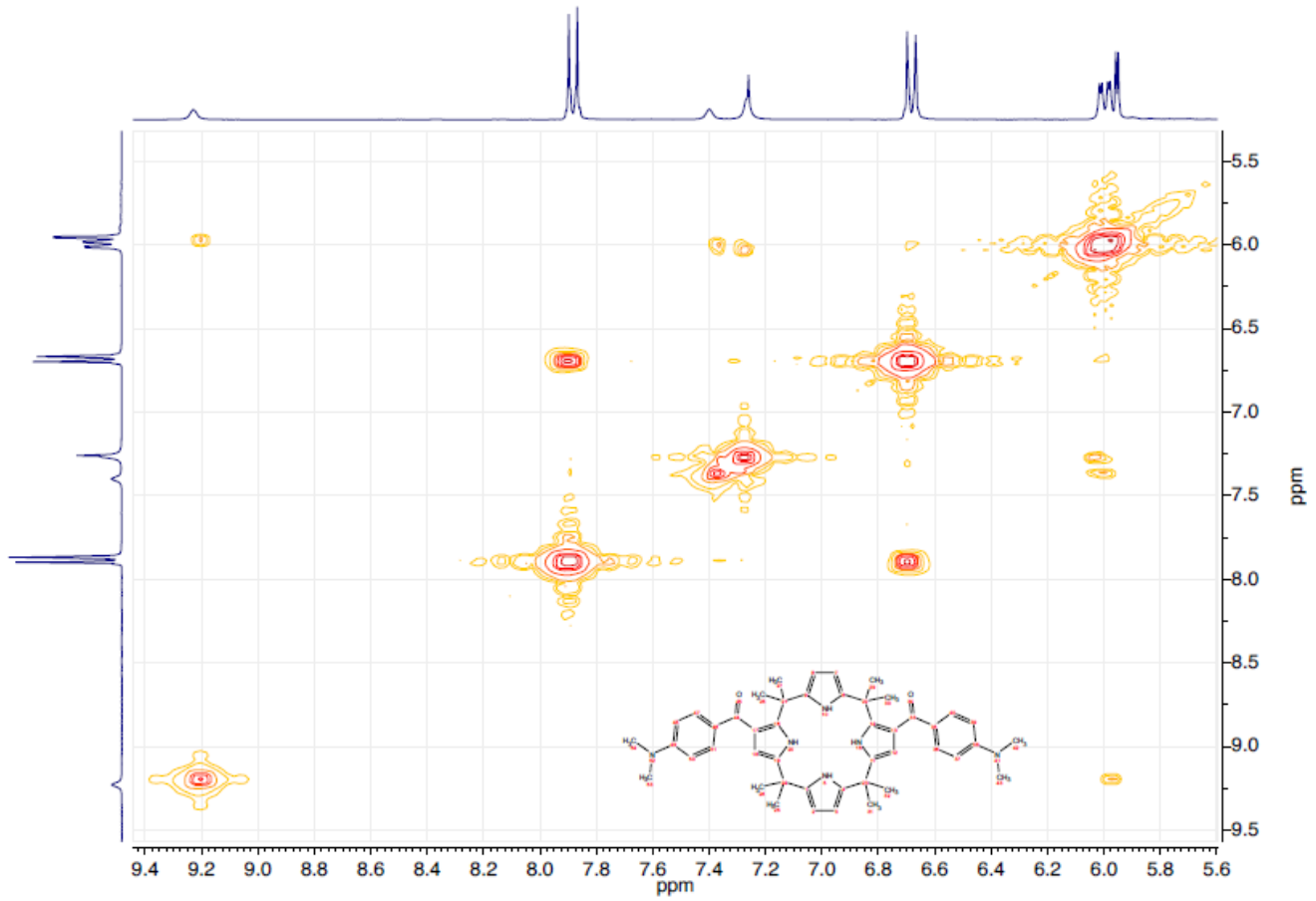


Figure S-6. COSY spectrum of compound **2** in $CDCl_3$

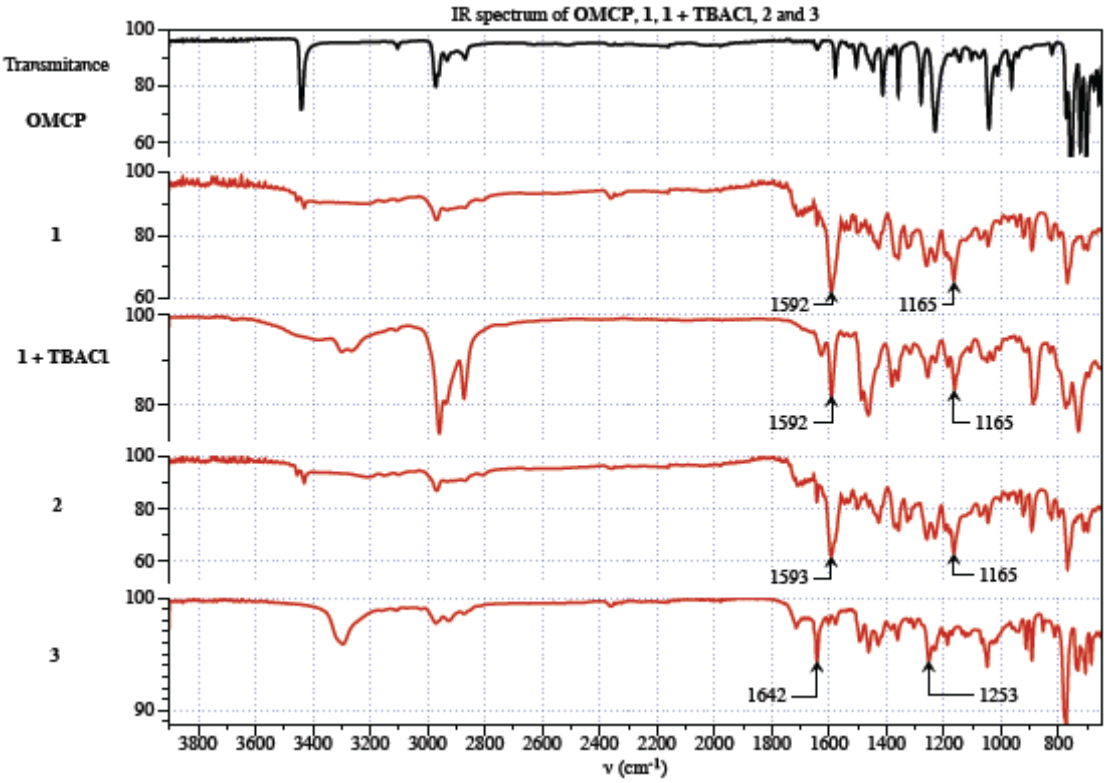


Figure S-7. IR spectra of **OMCP**, **1**, **2**, **3**, and **1+TBACl**

Table S.1. Comparison between Infrared N-H and C=O vibrations and the ^{1}H-NMR shift of the N-H$_a$ proton of the different calixpyrrole derivatives

Product	IR wave numbers (cm^{-1})			NMR shift (ppm)	
	N-H	C=O $_{maioritary}$ conformer	C=O minoritary conformer	^{1}H N-H$_a$	^{13}C C=O
OMCP	3441(s)	-	-	7.08	-
1	3500-3130 (b)	1590(s)	1730-1650(w)	8.90	193.25
2	3510-3100 (b)	1589(s)	1710-1650 (w)	9.26	192.99
3	3314(s), 3296(s)	1642(s)	1716(w)	8.29	
4$^{\dagger\dagger(x)}$	-	-	-	8.56	174.9***
4†††	3438(s), 3414(s), 3315(b)	1650(s)	1721(w)	7.35	

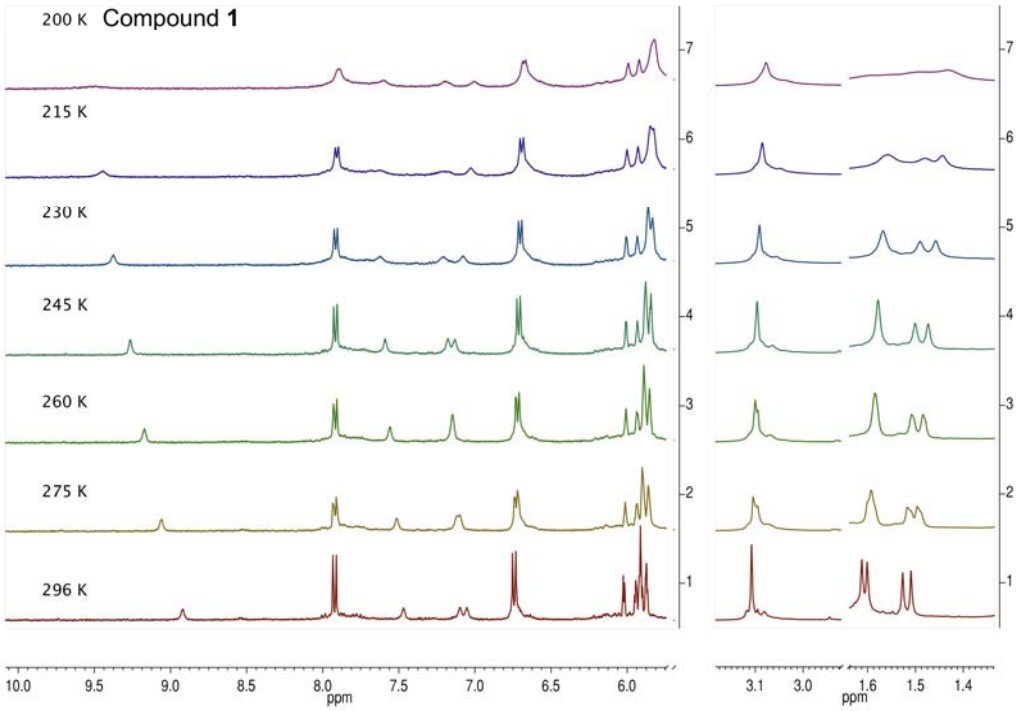


Figure S-8. Variable temperature NMR spectrum of compound **1** in CD_2Cl_2.

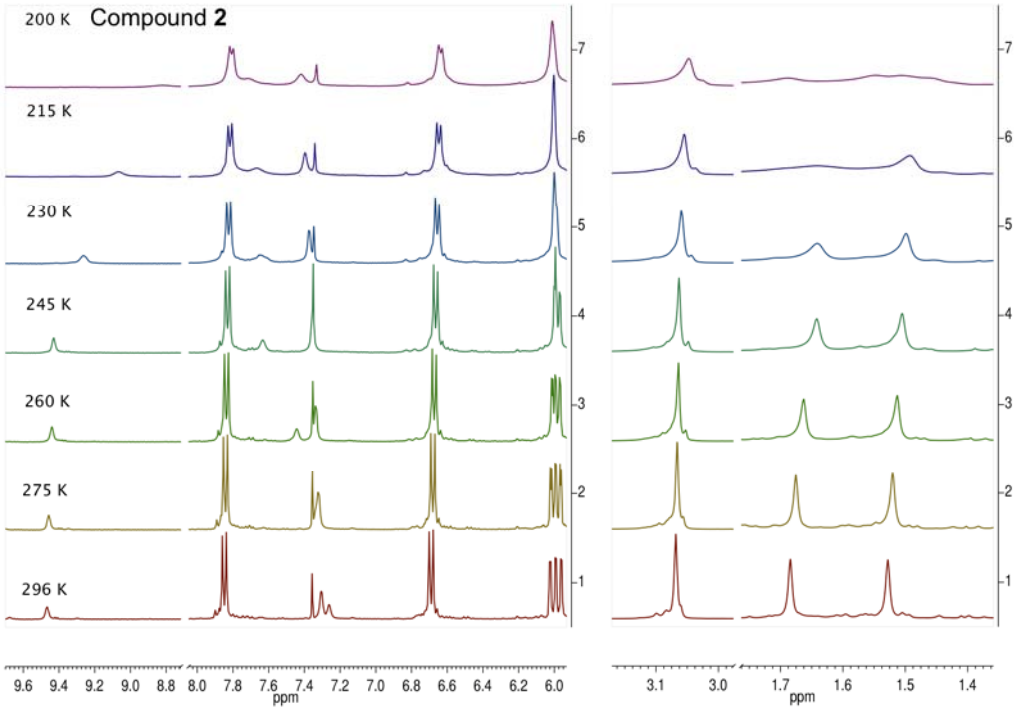


Figure S-9. Variable temperature NMR spectrum of compound **2** in $CDCl_3$.

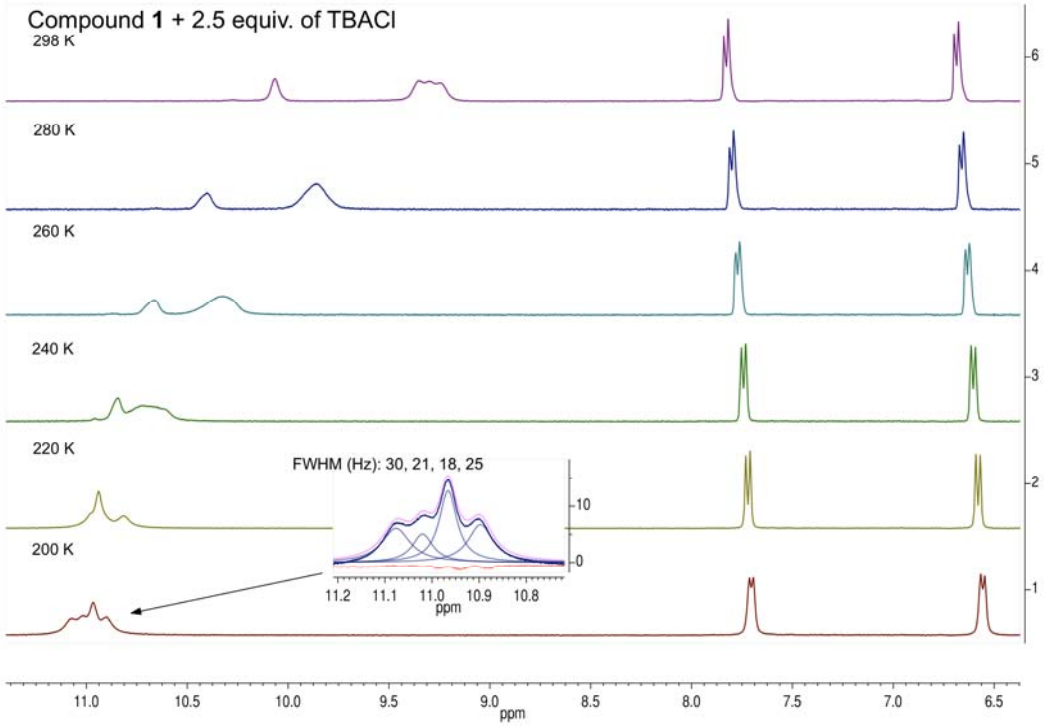


Figure S-10. Variable temperature NMR spectrum of compound **1** +TBACl in CD_2Cl_2.

Table S.2. Normalised association constants quotient $((K\text{-}K_{OMCP})/K_{OMCP}\cdot 100)$ of synthesised calixpyrrole derivatives 1 and 2 in relation to OMCP

Compound	Cl^-	AcO^-	$H_2PO_4^-$	HPO_4^{2-}	HSO_4^-	$pTsO^-$	MsO^-

Compound	Cl^-	AcO^-	$H_2PO_4^-$	HPO_4^{2-}	HSO_4^-	$pTsO^-$	MsO^-
1	-86	-47	-89	-77	394	143	596
2	-92	-55	-98	-92	490	899	263

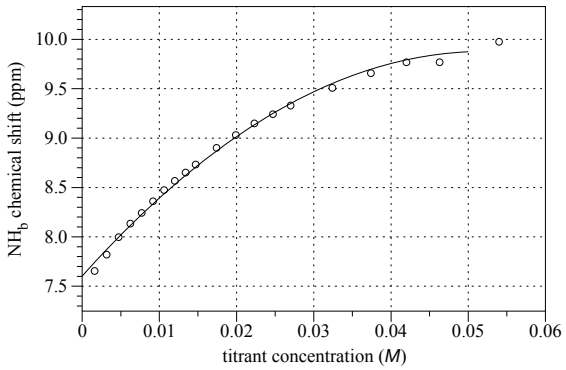


Figure S-11. NMR titration curve for compound **1** (0.01 M) and Cl^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S-3. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with Cl^- anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.655	7.662	0.00160	0.00990
7.820	7.828	0.00318	0.00980
7.997	7.979	0.00472	0.00971
8.134	8.118	0.00623	0.00962
8.242	8.245	0.00771	0.00952
8.360	8.364	0.00917	0.00943
8.474	8.472	0.01060	0.00935
8.566	8.571	0.01200	0.00926
8.651	8.664	0.01340	0.00917
8.732	8.746	0.01470	0.00909
8.901	8.901	0.01740	0.00893
9.031	9.029	0.01990	0.00877
9.148	9.140	0.02230	0.00862
9.242	9.240	0.02470	0.00847
9.329	9.327	0.02700	0.00833
9.508	9.504	0.03240	0.00800
9.657	9.639	0.03740	0.00769
9.767	9.744	0.04200	0.00741
9.768	9.829	0.04630	0.00714
9.975	9.956	0.05400	0.00667

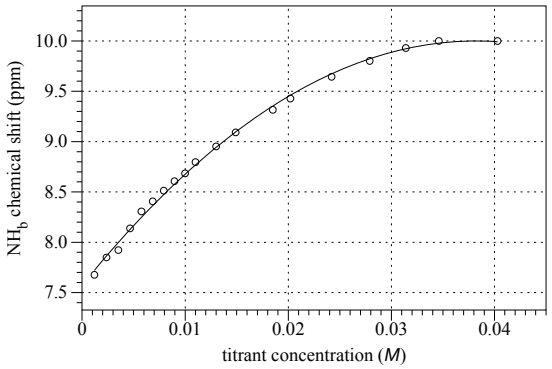


Figure S-12. NMR titration curve for compound **1** (0.01 M) and AcO^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S.4. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with AcO^- anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.676	7.679	0.00120	0.00990
7.849	7.839	0.00237	0.00980
7.922	7.989	0.00352	0.00971
8.138	8.128	0.00465	0.00962
8.306	8.258	0.00576	0.00952
8.406	8.378	0.00685	0.00943
8.512	8.490	0.00792	0.00935
8.606	8.593	0.00896	0.00926
8.684	8.690	0.00999	0.00917
8.796	8.780	0.01100	0.00909
8.952	8.943	0.01300	0.00893
9.091	9.084	0.01490	0.00877
9.000	9.204	0.01670	0.00862
9.316	9.313	0.01850	0.00847
9.428	9.408	0.02020	0.00833
9.644	9.600	0.02420	0.00800
9.802	9.747	0.02790	0.00769
9.930	9.865	0.03140	0.00741
10.000	9.958	0.03460	0.00714
10.000	10.097	0.04030	0.00667

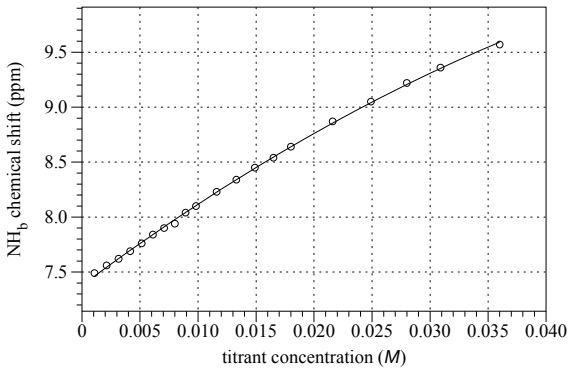


Figure S-13. NMR titration curve for compound **1** (0.01 M) and $H_2PO_4^-$ anion in CD_2Cl_2. Circles represent experimental data points.

TableS-5. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with $H_2PO_4^-$ anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.490	7.460	0.00107	0.00990
7.560	7.542	0.00212	0.00980
7.620	7.621	0.00315	0.00971
7.690	7.697	0.00415	0.00962
7.760	7.771	0.00514	0.00952
7.840	7.843	0.00611	0.00943
7.900	7.912	0.00707	0.00935
7.940	7.979	0.00800	0.00926
8.040	8.044	0.00892	0.00917
8.100	8.106	0.00982	0.00909
8.230	8.227	0.01160	0.00893
8.340	8.340	0.01330	0.00877
8.450	8.443	0.01490	0.00862
8.540	8.544	0.01650	0.00847
8.640	8.636	0.01800	0.00833
8.870	8.849	0.02160	0.00800
9.050	9.035	0.02490	0.00769
9.220	9.202	0.02800	0.00741
9.360	9.351	0.03090	0.00714
9.570	9.599	0.03600	0.00667

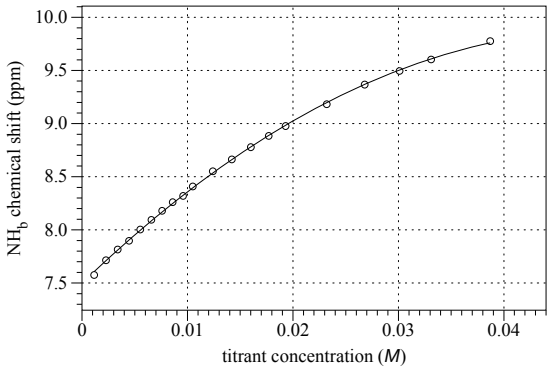


Figure S-14. NMR titration curve for compound **1** (0.01 M) and HPO_4^{2-} anion in CD_2Cl_2. Circles represent experimental data points.

Table S-6. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with HPO_4^{2-} anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.575	7.585	0.00115	0.00990
7.714	7.698	0.00227	0.00980
7.815	7.805	0.00338	0.00971
7.897	7.906	0.00446	0.00962
8.003	8.001	0.00552	0.00952

8.094	8.093	0.00657	0.00943
8.179	8.178	0.00759	0.00935
8.260	8.260	0.00859	0.00926
8.319	8.338	0.00958	0.00917
8.408	8.408	0.01050	0.00909
8.551	8.545	0.01240	0.00893
8.663	8.668	0.01420	0.00877
8.778	8.783	0.01600	0.00862
8.884	8.886	0.01770	0.00847
8.977	8.977	0.01930	0.00833
9.182	9.182	0.02320	0.00800
9.367	9.349	0.02680	0.00769
9.495	9.487	0.03010	0.00741
9.603	9.602	0.03310	0.00714
9.776	9.790	0.03870	0.00667

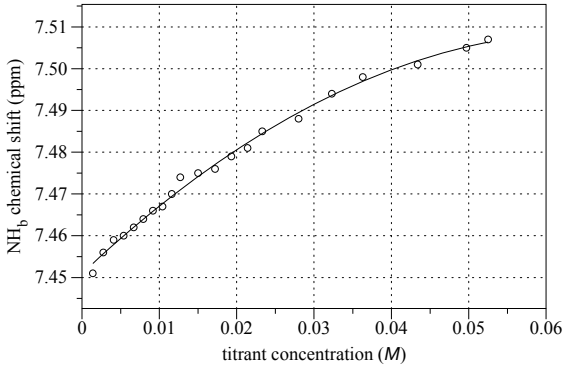


Figure S-15. NMR titration curve for compound **1** (0.01 M) and HSO_4^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S-7. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with HSO_4^- anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.451	7.453	0.00139	0.00990
7.456	7.455	0.00275	0.00980
7.459	7.457	0.00408	0.00971
7.460	7.460	0.00538	0.00962
7.462	7.462	0.00667	0.00952
7.464	7.464	0.00792	0.00943
7.466	7.466	0.00916	0.00935
7.467	7.468	0.01040	0.00926
7.470	7.470	0.01160	0.00917
7.474	7.472	0.01270	0.00909
7.475	7.475	0.01500	0.00893
7.476	7.478	0.01720	0.00877
7.479	7.480	0.01930	0.00862
7.481	7.482	0.02140	0.00847

7.485	7.485	0.02330	0.00833
7.488	7.489	0.02800	0.00800
7.494	7.493	0.03230	0.00769
7.498	7.496	0.03630	0.00741
7.501	7.501	0.04340	0.00690
7.505	7.505	0.04970	0.00645

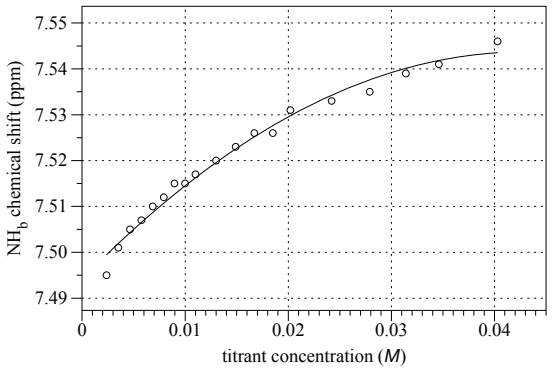


Figure S-16. NMR titration curve for compound **1** (0.01 M) and $MeSO_3^-$ anion in CD_2Cl_2. Circles represent experimental data points.

Table S-8. Experimental and calculated shifts (ppm) of the NH_b proton of compound **1** during NMR titration with $MeSO_3^-$ anion.

Exp. δ	Calc. δ	[A-] (M)	[**1**]
7.472	7.488	0.00120	0.00990
7.495	7.493	0.00237	0.00980
7.501	7.496	0.00352	0.00971
7.505	7.500	0.00465	0.00962
7.507	7.503	0.00576	0.00952
7.510	7.506	0.00685	0.00943
7.512	7.509	0.00792	0.00935
7.515	7.512	0.00896	0.00926
7.515	7.515	0.00999	0.00917
7.517	7.517	0.01100	0.00909
7.520	7.521	0.01300	0.00893
7.523	7.524	0.01490	0.00877
7.526	7.527	0.01670	0.00862
7.526	7.529	0.01850	0.00847
7.531	7.531	0.02020	0.00833
7.533	7.535	0.02420	0.00800
7.535	7.538	0.02790	0.00769
7.539	7.540	0.03140	0.00741
7.541	7.541	0.03460	0.00714
7.546	7.544	0.04030	0.00667

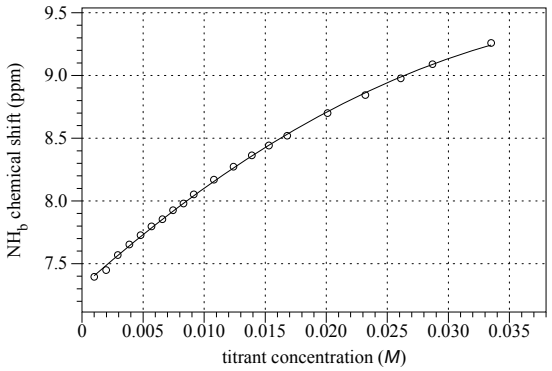


Figure S-17. NMR titration curve for compound **2** (0.01 M) and Cl^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S-9. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with Cl^- anion.

Exp. δ	Calc. δ	[A-] (M)	[**2**]
7.395	7.390	0.00100	0.00990
7.449	7.478	0.00197	0.00980
7.569	7.562	0.00293	0.00971
7.653	7.642	0.00387	0.00962
7.727	7.718	0.00479	0.00952
7.797	7.790	0.00569	0.00943
7.854	7.859	0.00658	0.00935
7.926	7.925	0.00745	0.00926
7.980	7.989	0.00831	0.00917
8.052	8.049	0.00915	0.00909
8.169	8.163	0.01080	0.00893
8.273	8.268	0.01240	0.00877
8.363	8.361	0.01390	0.00862
8.442	8.444	0.01530	0.00847
8.520	8.530	0.01680	0.00833
8.700	8.703	0.02010	0.00800
8.844	8.852	0.02320	0.00769
8.977	8.978	0.02610	0.00741
9.090	9.083	0.02870	0.00714
9.259	9.257	0.03350	0.00667

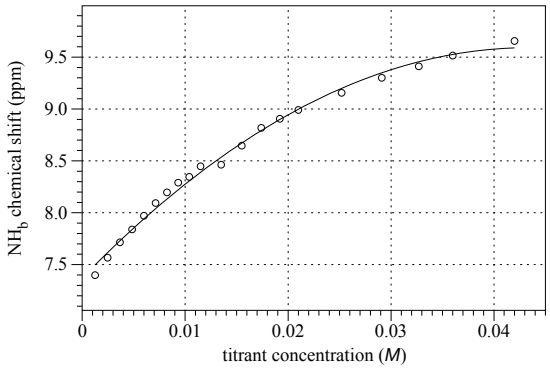


Figure S-18. NMR titration curve for compound **2** (0.01 M) and AcO^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S-10. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with AcO^- anion.

Exp. δ	Calc. δ	[A-] (M)	[**2**]
7.398	7.437	0.00125	0.00990
7.567	7.580	0.00247	0.00980
7.715	7.713	0.00367	0.00971
7.839	7.837	0.00485	0.00962
7.971	7.952	0.00600	0.00952
8.094	8.058	0.00713	0.00943
8.196	8.158	0.00824	0.00935
8.290	8.251	0.00933	0.00926
8.346	8.338	0.01040	0.00917
8.448	8.421	0.01150	0.00909
8.463	8.563	0.01350	0.00893
8.646	8.692	0.01550	0.00877
8.818	8.803	0.01740	0.00862
8.906	8.899	0.01920	0.00847
8.991	8.987	0.02100	0.00833
9.156	9.168	0.02520	0.00800
9.301	9.307	0.02910	0.00769
9.411	9.418	0.03270	0.00741
9.515	9.506	0.03600	0.00714
9.656	9.640	0.04200	0.00667

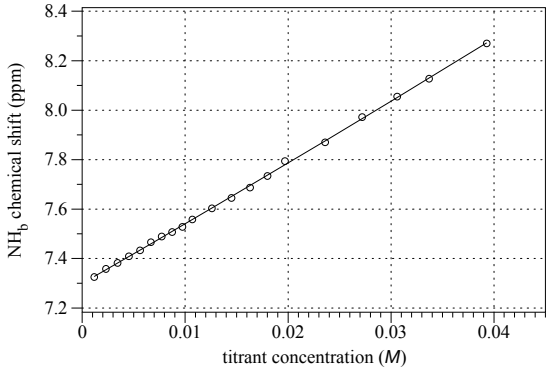


Figure S-19. NMR titration curve for compound **2** (0.01 M) and $H_2PO_4^-$ anion in CD_2Cl_2. Circles represent experimental data points.

Table S-11. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with $H_2PO_4^-$ anion.

Exp. δ	Calc. δ	[A-] (M)	[**2**]
7.325	7.315	0.00117	0.00990
7.358	7.345	0.00231	0.00980
7.382	7.375	0.00344	0.00971
7.409	7.403	0.00454	0.00962
7.433	7.432	0.00562	0.00952
7.466	7.459	0.00668	0.00943
7.489	7.486	0.00772	0.00935
7.507	7.512	0.00874	0.00926
7.528	7.538	0.00974	0.00917
7.558	7.563	0.01070	0.00909
7.603	7.611	0.01260	0.00893
7.645	7.659	0.01450	0.00877
7.687	7.703	0.01630	0.00862
7.734	7.746	0.01800	0.00847
7.794	7.788	0.01970	0.00833
7.870	7.883	0.02360	0.00800
7.972	7.970	0.02720	0.00769
8.055	8.050	0.03060	0.00741
8.127	8.123	0.03370	0.00714
8.270	8.252	0.03930	0.00667

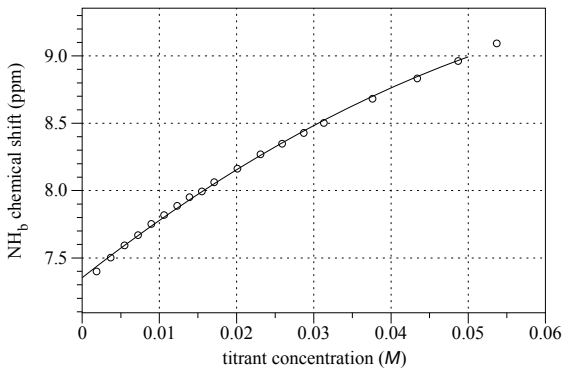


Figure S-20. NMR titration curve for compound **2** (0.01 M) and HPO_4^{2-} anion in CD_2Cl_2. Circles represent experimental data points.

Table S-12. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with HPO_4^{2-} anion.

Exp. δ	Calc. δ	[A-] (M)	[**2**]
7.399	7.424	0.00186	0.00990
7.502	7.509	0.00369	0.00980

7.593	7.589	0.00548	0.00971
7.669	7.666	0.00723	0.00962
7.752	7.739	0.00895	0.00952
7.818	7.807	0.01060	0.00943
7.887	7.875	0.01230	0.00935
7.951	7.937	0.01390	0.00926
7.994	7.997	0.01550	0.00917
8.062	8.057	0.01710	0.00909
8.163	8.163	0.02010	0.00893
8.269	8.264	0.02310	0.00877
8.348	8.355	0.02590	0.00862
8.428	8.441	0.02870	0.00847
8.502	8.518	0.03130	0.00833
8.682	8.693	0.03760	0.00800
8.833	8.839	0.04340	0.00769
8.962	8.963	0.04870	0.00741
9.093	9.072	0.05370	0.00714

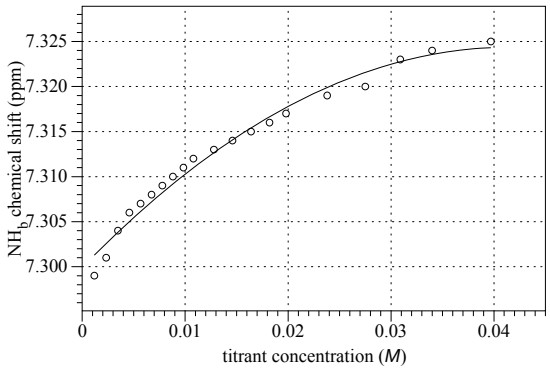


Figure S-21. NMR titration curve for compound **2** (0.01 M) and HSO_4^- anion in CD_2Cl_2. Circles represent experimental data points.

Table S-13. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with HSO_4^- anion.

Exp. δ	Calc. δ	[A^-] (M)	[**2**]
7.299	7.302	0.00118	0.00990
7.301	7.303	0.00233	0.00980
7.304	7.304	0.00347	0.00971
7.306	7.305	0.00458	0.00962
7.307	7.306	0.00567	0.00952
7.308	7.307	0.00674	0.00943
7.309	7.308	0.00779	0.00935
7.310	7.309	0.00881	0.00926
7.311	7.310	0.00983	0.00917

7.312	7.311	0.01080	0.00909
7.313	7.313	0.01280	0.00893
7.314	7.314	0.01460	0.00877
7.315	7.315	0.01640	0.00862
7.316	7.316	0.01820	0.00847
7.317	7.317	0.01980	0.00833
7.319	7.319	0.02380	0.00800
7.320	7.321	0.02750	0.00769
7.323	7.323	0.03090	0.00741
7.324	7.324	0.03400	0.00714
7.325	7.326	0.03970	0.00667

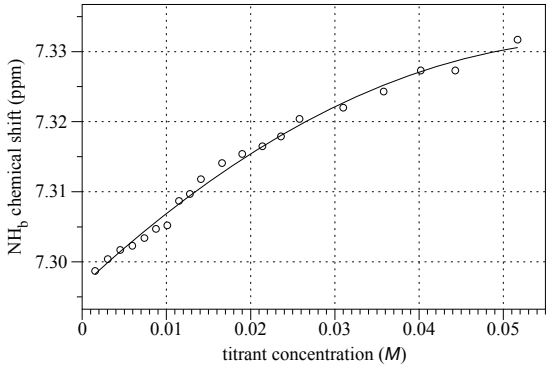


Figure S-22. NMR titration curve for compound **2** (0.01 M) and $MeSO_3^-$ anion in CD_2Cl_2. Circles represent experimental data points.

Table S-14. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with $MeSO_3^-$ anion.

Exp. δ	Calc. δ	[A-] (M)	[**2**]
7.299	7.298	0.00153	0.00990
7.300	7.299	0.00304	0.00980
7.302	7.301	0.00451	0.00971
7.302	7.303	0.00596	0.00962
7.303	7.304	0.00738	0.00952
7.305	7.306	0.00877	0.00943
7.305	7.308	0.01010	0.00935
7.309	7.309	0.01150	0.00926
7.310	7.310	0.01280	0.00917
7.312	7.311	0.01410	0.00909
7.314	7.313	0.01660	0.00893
7.315	7.315	0.01900	0.00877
7.317	7.317	0.02140	0.00862
7.318	7.318	0.02360	0.00847
7.320	7.319	0.02580	0.00833
7.322	7.322	0.03100	0.00800
7.324	7.325	0.03580	0.00769
7.327	7.327	0.04020	0.00741

7.327	7.328	0.04430	0.00714
7.332	7.331	0.05170	0.00667

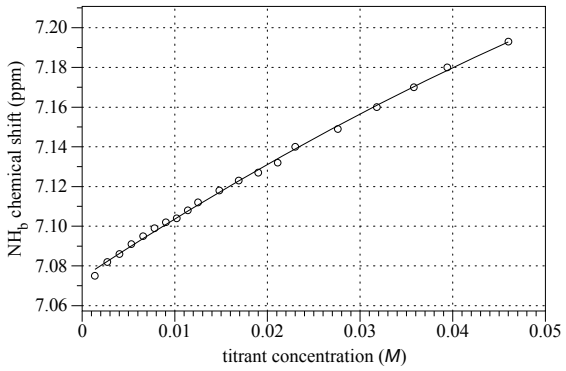


Figure S-23 NMR titration curve for **OMCP** (0.01 M) and $MeSO_3^-$ anion in CD_2Cl_2. Circles represent experimental data points.

Exp. δ	Calc. δ	[A-] (M)	[**OMCP**]
7.075	7.077	0.00137	0.00990
7.082	7.082	0.00271	0.00980
7.086	7.086	0.00402	0.00971
7.091	7.090	0.00531	0.00962
7.095	7.094	0.00657	0.00952
7.099	7.097	0.00781	0.00943
7.102	7.101	0.00903	0.00935
7.104	7.105	0.01020	0.00926
7.108	7.108	0.01140	0.00917
7.112	7.111	0.01250	0.00909
7.118	7.118	0.01480	0.00893
7.123	7.123	0.01690	0.00877
7.127	7.129	0.01900	0.00862
7.132	7.135	0.02110	0.00847
7.140	7.139	0.02300	0.00833
7.149	7.151	0.02760	0.00800
7.160	7.161	0.03180	0.00769
7.170	7.170	0.03580	0.00741
7.180	7.178	0.03940	0.00714
7.193	7.192	0.04600	0.00667

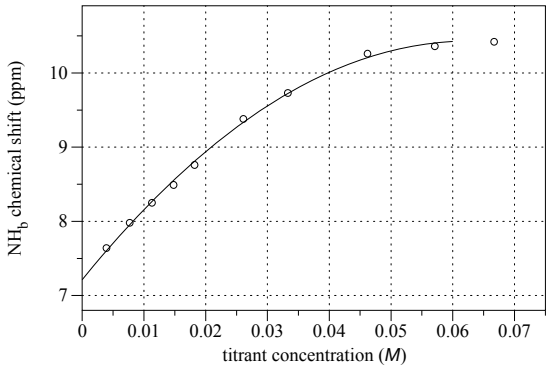


Figure S-24. NMR titration curve for compound **1** (0.01 M) and *p*-nitrophenolate$^-$ anion in CD_2Cl_2. Circles represent experimental data points.

Table S-16. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with *p*-nitrophenolate$^-$ anion.

Exp. ∂	Calc. ∂	[A-] (M)	[**1**]
7.640	7.558	0.00392	0.00980
7.980	7.967	0.00769	0.00962
8.250	8.309	0.01130	0.00943
8.490	8.599	0.01480	0.00926
8.760	8.846	0.01820	0.00909
9.380	9.319	0.02610	0.00870
9.730	9.653	0.03330	0.00833
10.260	10.096	0.04620	0.00769
10.360	10.366	0.05710	0.00714
10.420	10.552	0.06670	0.00667

Table S-21. Experimental and calculated shifts (ppm) of the NH_b proton of compound **2** during NMR titration with *p*-nitrophenolate$^-$ anion.

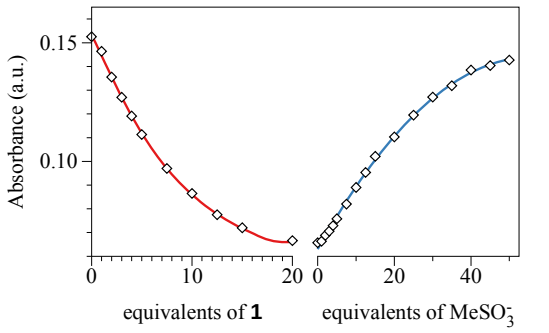
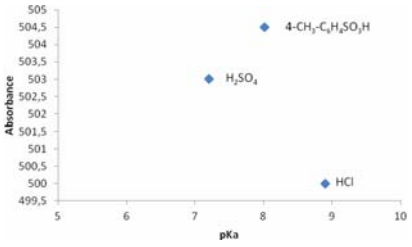
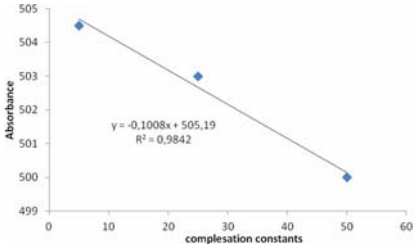


Figure S-25. Titration curve profiles for 10^{-5}M CH_2Cl_2 solutions of *p*-nitrophenolate (as TBA salt) *a)* after the addition of 0 to 20 equivalents of compound **1** (as 10^{-3} M CH_2Cl_2 solution) followed by *b)* addition of 0 to 50 equivalents of tetrabutylammonium mesylate (as 10^{-2} M CH_2Cl_2 solution).

(a)



(b)



(1) Eckert et al. *J. Comp. Chem*. **2009**, *30*, 799-810.

Figure S-26. Representation of the wavelength of compound 1 in the presence of acids (a) in the presence of *p*Ka acids in acetonitrile[1] and (b) in the presence of the calculated complexation constants.

Crystallographic Data

Compound 1:

Table S-24. Crystal structure data and details of structure refinement for compound **1**.

Empirical formula	C_{37} H_{45} N_5 O
Formula weight	575.78
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 13.1700(7) Å alpha = 90º.
	b = 12.2955(5) Å beta = 103.669(5)º.
	c = 20.5036(9) Å gamma = 90º.
Volume	3226.1(3) Å ^{3}
Z, Calculated density	4, 1.185 mg/m^3
Absorption coefficient	0.072 mm^{-1}
F(000)	1240
Crystal size	0.13 x 0.08 x 0.04 mm
Theta range for data collection	3.18 to 25.00º.
Limiting indices	-15<=h<=10, -14<=k<=14, -21<=l<=24
Reflections collected / unique	15338 / 5686 [R(int) = 0.0584]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9971 and 0.9906
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5686 / 0 / 404
Goodness-of-fit on F^2	1035
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1196
R indices (all data)	R1 = 0.1243, wR2 = 0.1513
Largest diff. peak and hole	0.201 and -0.236 e. Å $^{-3}$

Table S-25. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for compound **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1C)	4494(3)	1149(2)	2655(2)	52(1)
C(2C)	3491(2)	2177(2)	1685(1)	45(1)
N(3C)	4040(2)	2165(2)	2393(1)	39(1)
C(4C)	3826(2)	2969(2)	2805(1)	31(1)
C(5C)	3277(2)	3899(2)	2542(2)	39(1)
C(6C)	3072(2)	4710(2)	2955(1)	40(1)
C(7C)	3400(2)	4637(2)	3649(1)	33(1)
C(8C)	3957(2)	3707(2)	3911(1)	36(1)
C(9C)	4161(2)	2894(2)	3508(1)	35(1)
C(10C)	3194(2)	5498(2)	4098(2)	38(1)
O	3550(2)	5443(2)	4714(1)	49(1)
N(1)	1752(2)	8021(2)	3632(1)	28(1)
C(11)	2497(2)	6419(2)	3809(1)	32(1)
C(12)	1447(2)	6291(2)	3427(1)	33(1)
C(13)	996(2)	7292(2)	3329(1)	28(1)
C(14)	2669(2)	7517(2)	3930(1)	30(1)
C(1)	-99(2)	7660(2)	3020(1)	29(1)
C(1A)	-771(2)	6695(2)	2702(1)	38(1)
C(1B)	-108(2)	8516(2)	2470(1)	38(1)
N(2)	-571(2)	7552(2)	4136(1)	31(1)
C(21)	-527(2)	8155(2)	3577(1)	29(1)
C(22)	-886(2)	9164(2)	3675(1)	38(1)
C(23)	-1148(2)	9174(2)	4309(1)	44(1)
C(24)	-941(2)	8168(2)	4586(1)	34(1)
C(2)	-1125(2)	7674(3)	5223(1)	40(1)
C(2A)	-2103(3)	6950(3)	5050(2)	59(1)
C(2B)	-1304(3)	8586(3)	5694(2)	63(1)
N(3)	765(2)	7439(2)	5815(1)	32(1)
C(31)	-201(2)	6986(2)	5555(1)	34(1)
C(32)	-87(2)	5897(2)	5655(1)	40(1)
C(33)	970(2)	5685(2)	5975(1)	37(1)
C(34)	1488(2)	6652(2)	6069(1)	30(1)
C(3)	2603(2)	6939(2)	6404(1)	33(1)
C(3A)	3269(2)	5904(2)	6501(2)	51(1)
C(3B)	2638(3)	7447(3)	7094(1)	54(1)
N(4)	3180(2)	7430(2)	5363(1)	31(1)
C(41)	3004(2)	7744(2)	5970(1)	31(1)
C(42)	3147(2)	8842(2)	6017(1)	37(1)

C(43)	3421(2)	9204(2)	5426(1)	38(1)
C(44)	3434(2)	8322(2)	5028(1)	32(1)
C(4)	3585(2)	8181(2)	4323(1)	35(1)
C(4A)	4624(2)	7611(3)	4329(2)	49(1)
C(4B)	3617(2)	9303(2)	3999(2)	48(1)

Figure S-27. Unit cell of compound **1**.

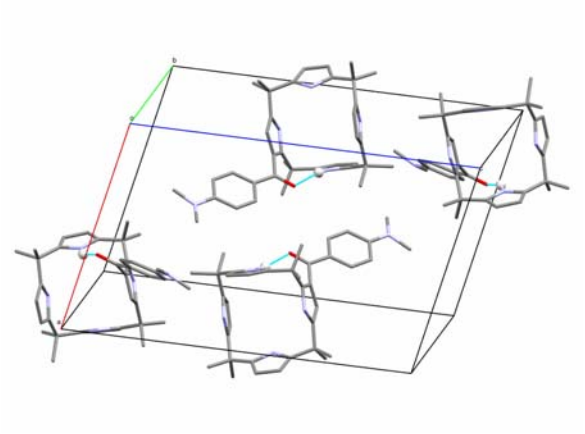
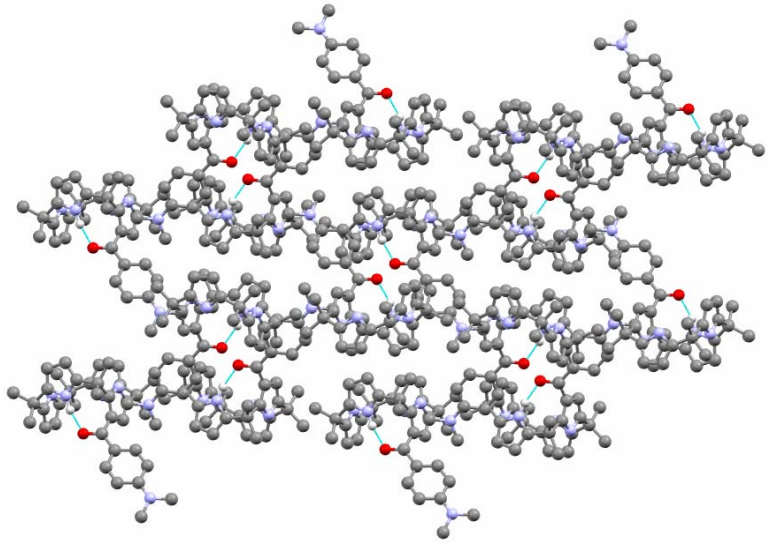


Figure S-28. Packing diagram along c axes.



Planes defined by dimethylamino and pyrrole rings (pN1, pN3, pN2, pN4,) and each intersection angle:

Least-squares planes (x,y,z in the crystal coordinates) and deviations from them (* indicates the atom used to define the plane).

11.7529 (0.0073) x + 5.5307 (0.0132) y - 5.0395 (0.0240) z = 4.7254 (0.0086)

* -0.0010 (0.0020) C4C
* 0.0016 (0.0021) C5C
* 0.0011 (0.0022) C6C
* -0.0043 (0.0021) C7C
* 0.0051 (0.0020) C8C
* -0.0024 (0.0020) C9C

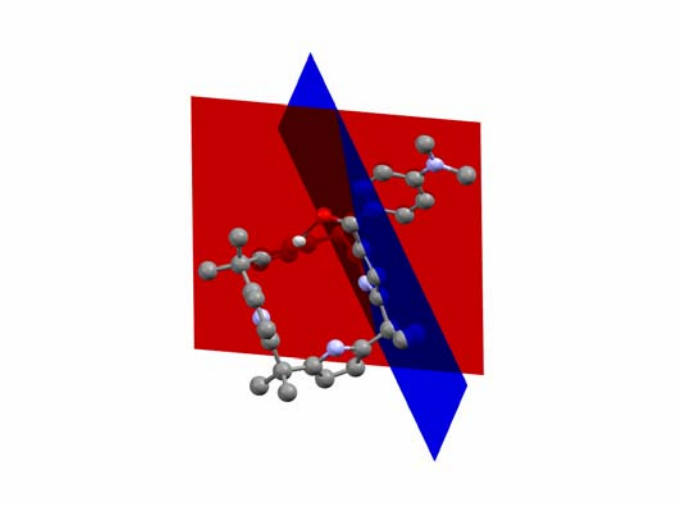
Rms deviation of fitted atoms = 0.0030

- 6.8637 (0.0157) x - 1.0915 (0.0163) y + 19.4363 (0.0093) z = 4.9856 (0.0139)

Angle to previous plane (with approximate esd) = 57.62 (0.11)

* -0.0035 (0.0015) N1

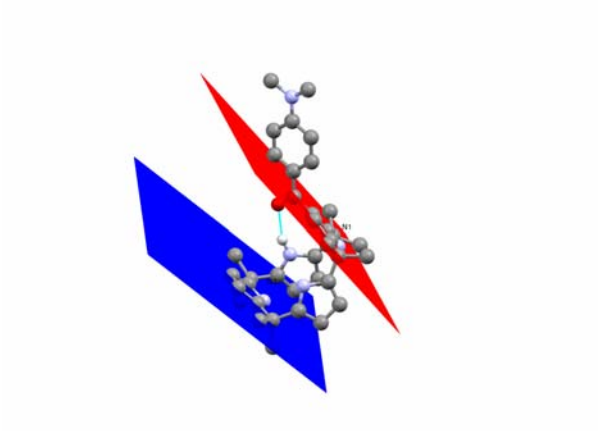
* 0.0022 (0.0016) C11
* -0.0043 (0.0017) C12
* 0.0049 (0.0016) C13
* 0.0007 (0.0016) C14
Rms deviation of fitted atoms = 0.0035



- 5.8215 (0.0163) x + 1.1635 (0.0166) y + 19.9129 (0.0069) z = 11.9952 (0.0107)

Angle to previous plane (with approximate esd) = 11.73 (0.13)

* 0.0039 (0.0015) N3
* -0.0039 (0.0016) C31
* 0.0024 (0.0017) C32
* -0.0001 (0.0017) C33
* -0.0023 (0.0016) C34
Rms deviation of fitted atoms = 0.0029



11.2321 (0.0102) x + 3.5179 (0.0177) y + 4.5695 (0.0295) z = 3.9086 (0.0191)

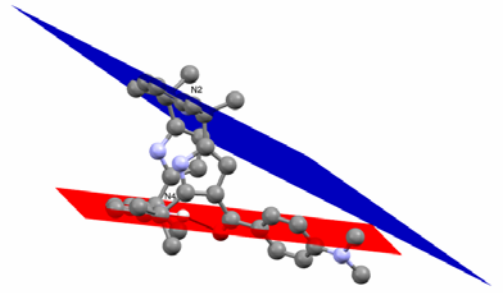
* -0.0039 (0.0017) N2
* 0.0027 (0.0017) C21
* -0.0005 (0.0019) C22
* -0.0018 (0.0019) C23
* 0.0035 (0.0018) C24
Rms deviation of fitted atoms = 0.0028

11.7240 (0.0087) x - 1.7383 (0.0169) y + 4.3145 (0.0291) z = 4.7503 (0.0204)

Angle to previous plane (with approximate esd) = 24.78 (0.14)

* 0.0001 (0.0016) N4
* 0.0011 (0.0017) C41
* -0.0019 (0.0018) C42
* 0.0019 (0.0018) C43
* -0.0013 (0.0017) C44

Rms deviation of fitted atoms = 0.0014



Hydrogen bonds with H..A < r(A) + 2,000 Angstroms and <DHA > 110º:

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N3-H3	0.878				
N1-H1	0.872				
N2-H2	0.858				
N4-H	0.996	1.944	155.40	2.879	O

Compound 2:

Table S-27. Crystal structure data and details of structure refinement for compound **2**.

Empirical formula	$C_{46}\,H_{54}\,N_6\,O_2$
Formula weight	722.95
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.051(3) Å alpha = 76.98(4)º.
	b = 10.220(5) Å beta = 76.86(3)º.
	c = 20.088(7) Å gamma = 86.88(3)º.
Volume	1957.7(13) $Å^3$
Z, Calculated density	2, 1.226 mg/m^3
Absorption coefficient	0.076 mm^{-1}
F(000)	776
Crystal size	0.06 x 0.03 x 0.02 mm
Theta range for data collection	2.92 to 25.00º.
Limiting indices	-11<=h<=9, -11<=k<=12, -23<=l<=23
Reflections collected / unique	8850 / 5810 [R(int) = 0.0957]
Completeness to theta = 25.00	84.2 %
Max. and min. transmission	0.9985 and 0.9954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5810 / 84 / 508
Goodness-of-fit on F^2	0.972
Final R indices [I>2sigma(I)]	R1 = 0.1000, wR2 = 0.1336

R indices (all data)	R1 = 0.2362, wR2 = 0.1997
Extinction coefficient	0.0026(3)
Largest diff. peak and hole	0.271 and -0.292 e. $Å^{-3}$

Table S-28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for compound **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(4)	-455(6)	12052(7)	3632(3)	22(2)
C(4A)	-1350(6)	12971(6)	3179(3)	26(2)
C(4B)	-458(6)	12657(7)	4263(3)	34(2)
C(41)	-1486(6)	8556(7)	3734(3)	26(2)
C(42)	-1903(6)	8588(6)	4436(3)	26(2)
C(43)	-1627(6)	9866(7)	4525(3)	30(2)
C(44)	-1044(6)	10656(7)	3867(3)	22(2)
N(4)	-970(5)	9823(6)	3404(3)	28(2)
C(1)	4531(6)	10922(7)	3330(3)	23(2)
C(1A)	5760(6)	11088(7)	2703(3)	30(2)
C(1B)	4829(6)	11698(7)	3849(3)	28(2)
C(10C)	821(7)	12128(7)	1910(3)	29(2)
C(2)	3298(6)	6101(7)	3526(3)	28(2)
C(2A)	4553(6)	5643(7)	3022(3)	34(2)
C(2B)	2835(6)	4906(6)	4162(3)	35(2)
C(3)	-1495(6)	7487(6)	3338(3)	23(2)
C(3A)	-2283(6)	7957(7)	2754(3)	30(2)
C(3B)	-2203(6)	6212(6)	3831(3)	38(2)
C(9C)	1301(6)	13080(6)	1245(3)	21(2)
C(8C)	2143(6)	14162(7)	1182(3)	34(2)
C(7C)	868(6)	12919(7)	653(3)	29(2)
C(6C)	2574(6)	15034(7)	538(3)	30(2)
C(5C)	1280(6)	13768(7)	23(3)	29(2)
C(4C)	2148(7)	14869(7)	-57(3)	33(2)
C(1C)	2198(7)	15500(8)	-1325(3)	50(2)
C(11)	986(6)	11934(6)	3195(3)	22(2)
C(2C)	3680(7)	16657(8)	-803(4)	66(3)
C(12)	1534(6)	12050(7)	2502(3)	26(2)
C(21C)	456(7)	7449(7)	1669(4)	30(2)
C(13)	2985(6)	11750(6)	2419(3)	25(2)
C(14)	3270(6)	11460(6)	3079(3)	23(2)

C(20C)	1315(7)	8480(7)	1106(4)	36(2)
C(18C)	1200(7)	8642(8)	423(4)	43(2)
C(19C)	2224(6)	9314(7)	1253(4)	38(2)
C(16C)	1947(7)	9575(7)	-106(4)	41(2)
C(17C)	3005(7)	10254(7)	724(3)	33(2)
C(15C)	2884(7)	10405(8)	25(4)	38(2)
C(21)	4290(6)	9454(7)	3687(3)	20(2)
C(13C)	4554(6)	12270(7)	-367(3)	40(2)
C(22)	4485(6)	8709(7)	4308(3)	30(2)
C(12C)	3538(7)	11451(8)	-1226(3)	55(3)
C(23)	4114(6)	7348(7)	4376(3)	32(2)
C(24)	3708(6)	7259(7)	3798(3)	26(2)
C(31)	2179(7)	6501(6)	3151(3)	25(2)
C(32)	2140(7)	6718(7)	2454(4)	35(2)
C(33)	787(6)	7123(7)	2372(3)	28(2)
C(34)	-14(6)	7127(6)	3028(3)	20(2)
N(1)	2040(5)	11596(5)	3538(3)	23(1)
N(2)	3823(5)	8557(5)	3365(2)	25(1)
N(3)	858(5)	6766(5)	3501(3)	24(1)
N(3C)	2599(6)	15710(6)	-699(3)	39(2)
N(14C)	3668(6)	11322(6)	-508(3)	41(2)
O(11C)	-162(4)	11362(5)	2001(2)	38(1)
O(22C)	-504(4)	6887(5)	1554(2)	47(2)

Figure S-29. Unit cell of compound **2**

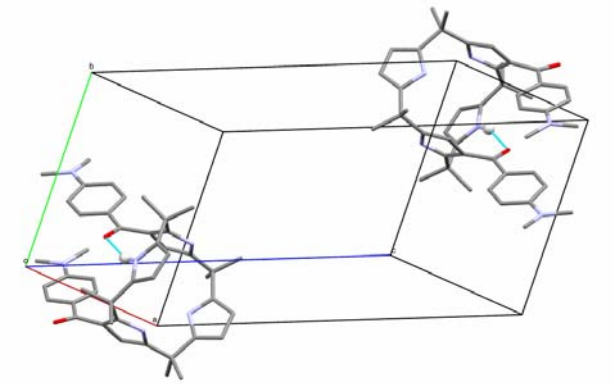
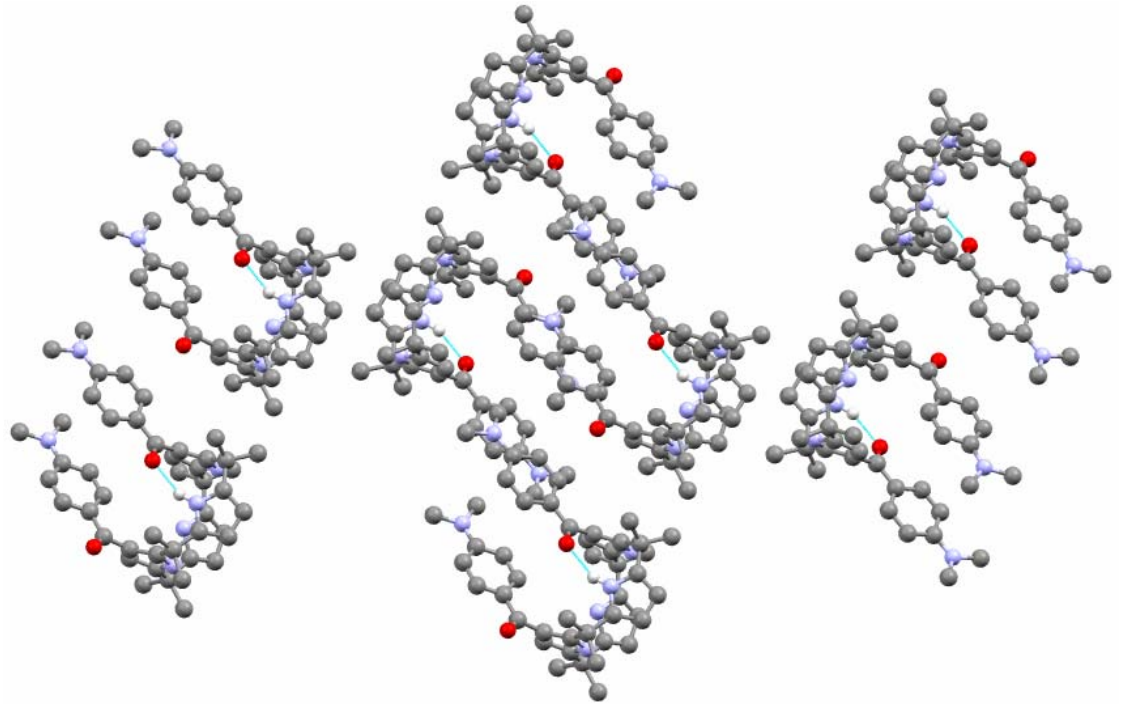


Figure S-30. Packing diagram along a axe.



Planes defined by dimethylamino and pyrrole rings (pN1, pN3, pN2, pN4,) and each intersection angle:

Least-squares planes (x,y,z in the crystal coordinates) and deviations from them (* indicates the atom used to define the plane).

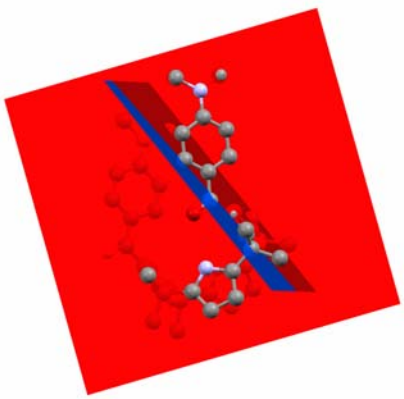
- 7.3955 (0.0256) x + 6.1217 (0.0293) y + 3.6097 (0.0712) z = 7.4933 (0.0462)
* -0.0036 (0.0073) C4C
* 0.0020 (0.0067) C5C
* -0.0003 (0.0074) C6C
* 0.0035 (0.0067) C7C
* 0.0059 (0.0069) C8C
* -0.0075 (0.0069) C9C

Rms deviation of fitted atoms = 0.0045

2.2360 (0.0415) x + 10.0169 (0.0104) y + 3.1968 (0.0834) z = 13.1966 (0.0316)

Angle to previous plane (with approximate esd) = 64.29 (0.27)

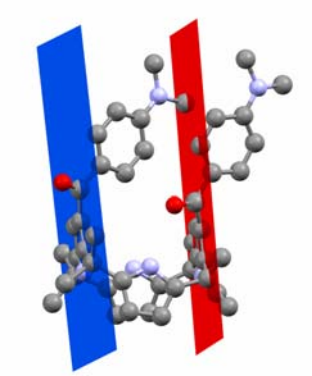
* 0.0060 (0.0049) N1
* -0.0093 (0.0049) C11
* 0.0089 (0.0053) C12
* -0.0054 (0.0054) C13
* -0.0003 (0.0051) C14
Rms deviation of fitted atoms = 0.0068



2.6788 (0.0422) x + 9.9070 (0.0128) y + 3.0170 (0.0923) z = 7.9855 (0.0319)

Angle to previous plane (with approximate esd) = 2.81 (0.30)

* 0.0147 (0.0055) N3
* -0.0059 (0.0057) C31
* -0.0051 (0.0054) C32
* 0.0143 (0.0052) C33
* -0.0179 (0.0053) C34
Rms deviation of fitted atoms = 0.0127



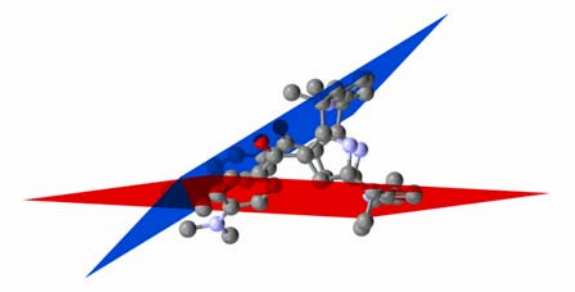
- 8.5587 (0.0227) x + 2.5600 (0.0375) y + 5.6301 (0.0819) z = 0.8224 (0.0570)

* -0.0001 (0.0053) N2
* 0.0055 (0.0052) C21
* -0.0089 (0.0054) C22
* 0.0089 (0.0056) C23
* -0.0054 (0.0055) C24
Rms deviation of fitted atoms = 0.0066

- 9.5414 (0.0139) x + 2.3603 (0.0398) y - 5.7320 (0.0750) z = 1.2979 (0.0540)

Angle to previous plane (with approximate esd) = 33.55 (0.30)

* -0.0003 (0.0050) N4
* -0.0012 (0.0050) C41
* 0.0022 (0.0050) C42
* -0.0024 (0.0050) C43
* 0.0016 (0.0050) C44
Rms deviation of fitted atoms = 0.0017



Hydrogen bonds with H..A < r(A) + 2,000 Angstroms and <DHA > 110°:

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1	0.880				
N2-H2	0.880				
N4-H4	0.887	2.052	151.33	2.862	O11C
N3-H3	0.873				