Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information to

"Sulfate templated assembly of neutral receptors in aqueous DMSO – orthogonal *versus* biplane structures"

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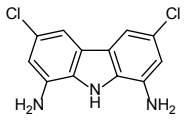
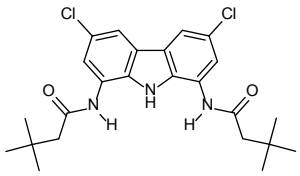
1. Synthesis and characterisation of model ligands.

1.1. Instruments and methods. The NMR spectra were measured on Varian UnityPlus 200 MHz or Varian INOVA 500 MHz spectrometers. The chemical shifts are given in ppm with the solvent signal being internal standard (DMSO-d_6 = 2.500 ppm); the coupling constants are in hertz. The ESI mass spectra were obtained using a Quattro (ESI TOF) mass spectrometer with methanol as a spray solvent. The melting points are uncorrected.

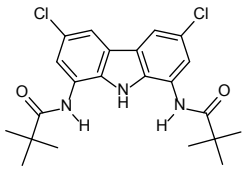
1.2. Synthesis. All precursors for the syntheses were obtained from Sigma-Aldrich or Alfa Aesar and were used as received. TLC was carried out on Merck silica gel 60 F_{254} plates; for column chromatography, Merck silica gel 60 (230 – 400 mesh) was used.



1,8-Diamino-3,6-dichlorocarbazole was synthesised as described previously[1] and purified by column chromatography: 1 g of crude 1,8-diamino-3,6-dichlorocarbazole was dissolved in THF (freshly distilled from potassium to exclude peroxides which cause oxidation of the amine) and the solution evaporated with ca. 4 g of silica gel. The preloaded mixture was put on top of a chromatographic column (100 g of silica suspended in 1% CH_3OH/CH_2Cl_2) and eluted with 500ml each: 1%, 1.2%, 1.4%, 1.6%, 1.8%, 2.0% CH_3OH in CH_2Cl_2. The progress of separation was followed by TLC using 10% CH_3OH as an eluent. Fractions containing pure product were combined and evaporated to yield ca. 0.9 g of the desired diamine.



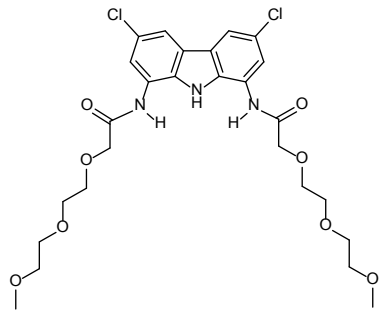
1,8-Bis(3,3-dimethylbutyrylamino)-3,6-dichlorocarbazole 1. As above, except that 3,3-dimethylbutyryl chloride (0.278 mL, 2.00 mmol) was used. Yield 0.293g (63.3%). Decomposes above 300°C.
^{1}H NMR (DMSO-d_6) δ_{DMSO}: 10.42 (s, 1H, carbazole NH), 10.11 (s, 2H, amide NH), 8.12 (d, *J* = 1.8 Hz, 2H, aromatic H-4 and H-5), 7.59 (d, *J* = 1.9 Hz, 2H, aromatic H-2 and H-7), 2.34 (s, 4H, CH_2), 1.09 (s, 18H, *t*-Bu);
^{13}C NMR (DMSO-d_6) δ_{DMSO}: 170.4, 131.1, 124.4, 124.2, 123.3, 119.1, 116.4, 49.0, 30.9, 29.6;
HR MS (ESI): m/z calcd. for $C_{24}H_{29}Cl_2N_3O_2Na$ $[M+Na]^+$: 484.1535, found: 484.1519;
Elemental Analysis calcd. for $C_{24}H_{29}Cl_2N_3O_2$: C, 62.34; H, 6.32; Cl, 15.33; N, 9.09; found: C, 60.18; H, 6.07; Cl, 15.36; N, 8.94.



1,8-Bis(trimethylacetylamino)-3,6-dichlorocarbazole 2. To a 50 mL round-bottomed flask equipped with a magnetic stirrer, 1,8-diamino-3,6-dichlorocarbazole (0.266g, 1.00 mmol) was added. The flask was closed with a septum and purged with argon. Afterwards, freshly dried CH_3CN (20 mL) and triethylamine (0.28 mL, 2.00 mmol) were added using syringes. After cooling the mixture to 0^0C, a solution of trimethylacetyl chloride (0.246 ml, 2.00 mmol) in freshly dried CH_3CN (5 ml) was slowly added dropwise via a syringe. White precipitate forms, typically within minutes. The reaction mixture was allowed to warm up to room temperature and left overnight. The next day the precipitate was filtered off, washed with 3 portions of CH_3CN (in total ca. 20 ml) and dried thoroughly to yield 0.322g (74.1%) of pure product as white powder. Decomposes above 335°C.
^{1}H NMR (DMSO-d_6) δ_{DMSO}: 9.73 (s, 2H, amide NH), 9.61 (s, 1H, carbazole NH), 8.16 (d, *J* = 1.9 Hz, 2H, aromatic H-4 and H-5), 7.41 (d, *J* = 1.9 Hz, 2H, aromatic H-2 and H-7), 1.31 (s, 18H, *t*-Bu);
^{13}C NMR (DMSO-d_6) δ_{DMSO}: 177.1, 132.4, 124.7, 124.4, 123.3, 121.0, 117.1, 39.0, 27.3;
HR MS (ESI): m/z calcd. for $C_{22}H_{25}Cl_2N_3O_2Na$ $[M+Na]^+$: 456.1222, found: 456.1219;
Elemental Analysis calcd. for $C_{22}H_{25}Cl_2N_3O_2$: C, 60.83; H, 5.80; Cl, 16.32; N, 9.67; found: C, 60.76; H, 5.62; Cl, 16.28; N, 9.81.

[1] M. J. Chmielewski, M. Charon, J. Jurczak, *Org. Lett.* **2004**, *6*, 3501-3504.

1,8-Bis(2-(2-(2-methoxyethoxy)ethoxy)acetylamino)-3,6-dichlorocarbazole 3.



Acid chloride was prepared according to Gong and coworkers.[2] 1,8-diamino-3,6-dichlorocarbazole was reacted with 20% molar excess of acid chloride according to the procedure described above, except for dry CH_2Cl_2 was used instead of CH_3CN. No precipitate was observed. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with 1M HCl (2x50 mL) and brine (2x50 ml). The organic layer was dried with $MgSO_4$ and evaporated to give crude product, which was further purified by column chromatography on 60 g of silica gel using gradient elution with CH_3OH/CH_2Cl_2 from 0.5 to 2%. The progress of chromatographic separation was monitored with TLC using 3% CH_3OH/CH_2Cl_2 as an eluent. Fractions containing pure product were combined and evaporated to yield 0.49 g (60%) of white solid.

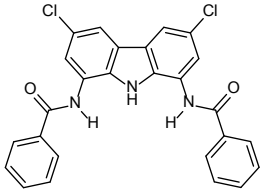
m.p. 81.7 – 83.5 ºC;

^{1}H NMR (DMSO-d_6) δ_{DMSO}: 10.79 (s, 1H), carbazole NH), 9.96 (s, 2H, NH), 8.16 (d, *J* = 1.9 Hz, 2H, aromatic H-4 and H-5), 7.74 (d, *J* = 1.8 Hz, 2H, aromatic H-2 and H-7), 4.25 (s, 4H, CH_2-C=O), 3.76 (dd, *J* = 5.8, 3.1 Hz, 4H), 3.65 (dd, *J* = 5.8, 3.0 Hz, 4H), 3.56 (dd, *J* = 5.9, 3.3 Hz, 4H), 3.41 (dd, *J* = 5.8, 3.3 Hz, 4H), 3.14 (s, 6H, OCH_3);

^{13}C NMR (DMSO-d_6) δ_{DMSO}: 169.03, 131.55, 124.14, 123.40, 123.24, 120.09, 116.95, 71.18, 70.45, 70.16, 69.65, 69.63, 57.96;

HR MS (ESI): m/z calcd. for $C_{26}H_{33}Cl_2N_3O_8Na$ $[M+Na]^+$: 608.1542, found: 608.1556;

Elemental Analysis calcd. for $C_{26}H_{33}Cl_2N_3O_8$: C, 53.25; H, 5.67; Cl, 12.09; N, 7.17; found: C,53.28; H, 5.58; Cl, 11.93; N, 7.11.



1,8-Di(benzoylamino)-3,6-dichlorocarbazole was obtained as described previously. Decomposes above 260°C.

2. Binding studies.

2.1. Materials:

Tetra(n-butyl)ammonium sulfate (TBA sulfate) was purchased from Alfa Aesar as a 50% aqueous solution. Before drying, the pH of this solution was checked and found to be neutral (pH=7.3 upon dilution to 1M concentration), confirming that the sample is essentially free from hydrogensulfate. Anhydrous salt was obtained in the following way: ca. 1g of the 50% solution was transferred to a 25 ml round bottom flask and most of the water was removed on rotary evaporator with gentle heating for a few hours. Viscous residue was then further dried under high vacuum over KOH to a constant mass (in total ca. 47% loss of weight was reached). The resulting white crystalline solid was stored in a vacuum desiccator over KOH and used both for crystallisations and titrations.

Tetrabutylammonium hydrogen sulfate and tetrabutylammonium chloride were obtained from Sigma-Aldrich and used as received.

DMSO-d_6 (99.8% isotopic purity, containing less than 0.02% water) was obtained from Eurisotop in septum-sealed vials and used as received.

2.2. ^{1}H NMR titration procedure.

DMSO-d_6/H_2O mixtures were obtained using distilled H_2O and their concentrations expressed as weight-weight percentage.

Typical ^{1}H NMR titration procedure. To a solution of host (600µl, typically 0.002M or 0.005M) in a septum-sealed screw-cap NMR tube appropriate aliquots of titrant (typically 15 times more concentrated than the host, dissolved in the solution of host to avoid dilution) were added with a 25 µl gas-tight microsyringe. NMR spectra were measured on Varian UnityPlus 200 MHz spectrometer. Association

[2] J. Zhang, X. Wu, K. Yamato, F. Liu, T. Su, C. Zheng, L. He, B. Gong, *Chem. Comm.* **2010**, *7*, 1062-1064.

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constants were calculated from changes in chemical shifts of most affected protons of the ligands, as indicated in each case below. Nonlinear curve fit was carried out using the WinEQNMR software (version 1.10).[3] Association constants $ß_{1:1}$ and $ß_{2:1}$ and chemical shifts of both 1:1 and 2:1 complexes were set as free parameters for fitting, whereas chemical shifts of free ligands were constrained to be equal to experimentally measured values. If titration curve was obtained for more than one proton in a single ligand, logarithms of association constants were averaged using arithmetic mean.

2.3. UV-Vis titration procedure.

To a solution of host (3 mL, 0.0001M) in a septum-sealed screw-cap precision cell made of Quartz SUPRASIL (light path: 10 mm) appropriate aliquots of titrant were added with a 25 µl gas-tight microsyringe. UV spectra were obtained on Thermo Spectronic UNICAM 540 UV-vis spectrometer. Association constants were calculated from absorbance changes for fixed wavelength. Nonlinear curve fit was carried out using the Hyperquad 2006 software. Association constants $ß_{1:1}$ and $ß_{2:1}$ and molar absorption coefficients of both 1:1 and 2:1 complexes were set as free parameters for fitting, whereas molar absorption coefficients of free ligand were constrained to be equal to experimentally measured values.

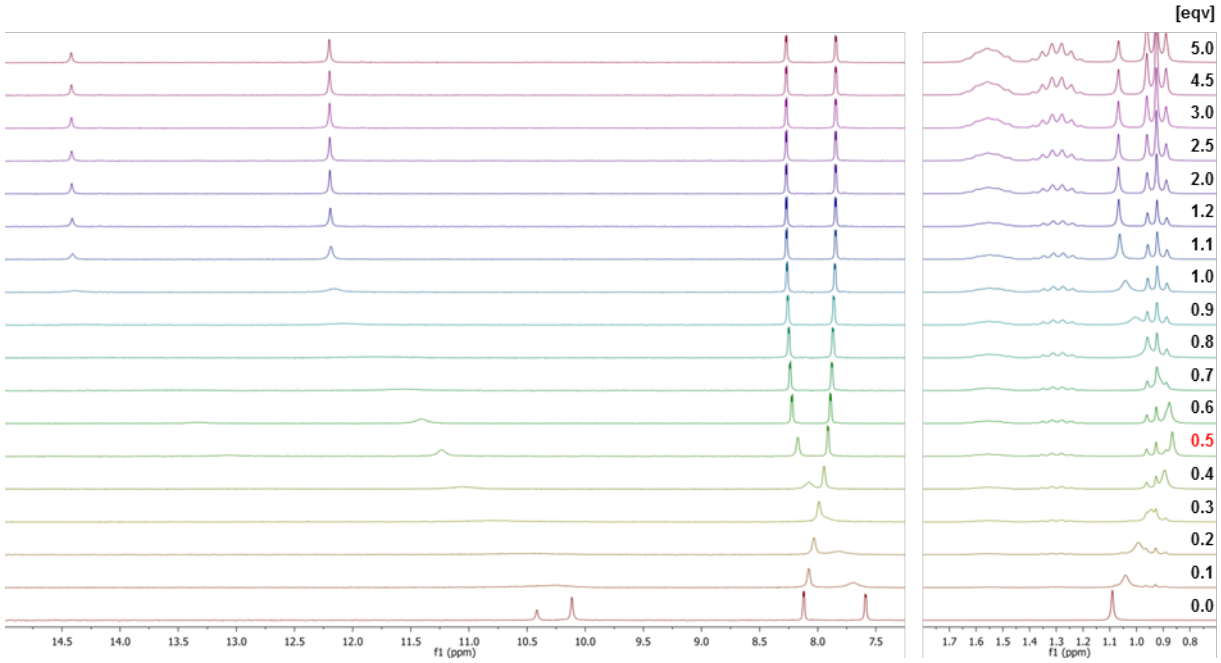
2.4. Self-association studies.

In order to check whether receptors **1 – 4** undergo self-association under conditions used for the anion binding studies, dilution experiments were carried out. Solutions of each receptor spanning concentration range 5 mM - 0.25 mM were prepared and their ^{1}H NMR spectra were recorded. No evidence of any self-association was found: dilution-induced chemical shift changes were small (< 0.016 ppm for all signals and all receptors) and random.

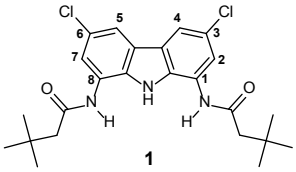
[3] M. J. Hynes, *J. Chem. Soc. Dalton. Trans.* **1993**, 311-312.

2.5. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **1** in DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

2.5a. ^{1}H NMR spectra.



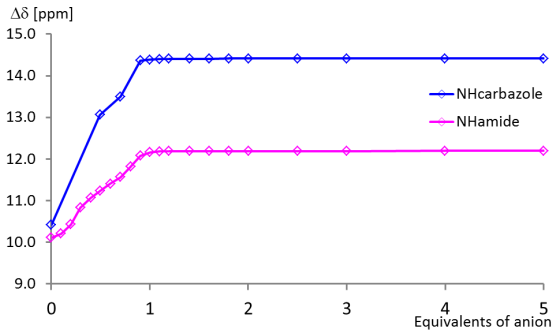
2.5b. Raw data:

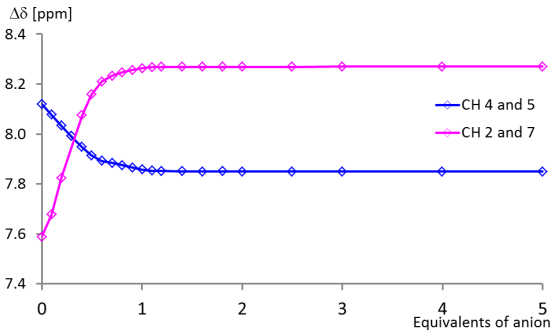


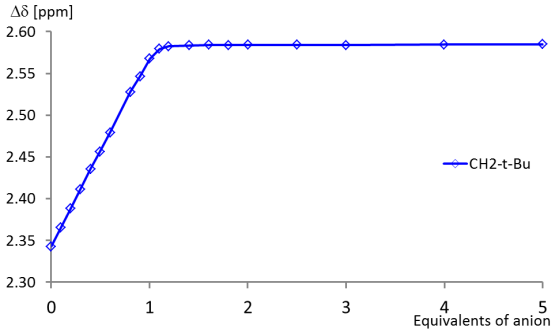
1

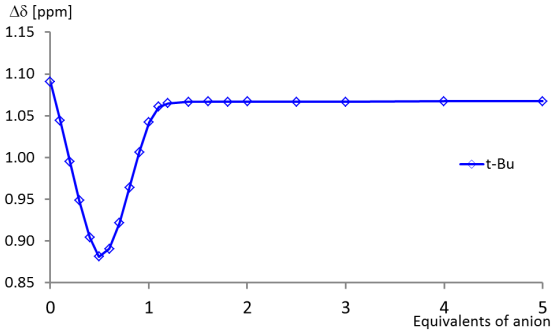
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH 4 and 5	CH 2 and 7	CH_2	*t*-Bu
0.0	0	10.4161	10.1110	8.1199	7.5883	2.3427	1.0910
4.0	0.10	broad	10.2094	8.0768	7.6773	2.3657	1.0443
8.0	0.20	broad	10.4279	8.0328	7.8245	2.3883	0.9949
12.0	0.29	broad	10.8337	7.9911	overlap	2.4108	0.9485
16.5	0.40	broad	11.0676	7.9474	8.0746	2.4356	0.9045
20.5	0.50	13.0643	11.2337	7.9148	8.1580	2.4560	0.8812
25.0	0.60	broad	11.4042	7.8928	8.2105	2.4791	0.8907
29.5	0.70	13.4990	11.5646	7.8847	8.2328	overlap	0.9217
34.0	0.80	broad	11.8147	7.8746	8.2464	2.5278	0.9642
38.5	0.90	14.3659	12.0778	7.8659	8.2564	2.5465	1.0063
43.0	1.00	14.3866	12.1629	7.8572	8.2633	2.5675	1.0422
47.5	1.10	14.4018	12.1823	7.8525	8.2672	2.5794	1.0608
52.0	1.20	14.4085	12.1882	7.8513	8.2684	2.5824	1.0650
62.0	1.40	14.4099	12.1892	7.8503	8.2688	2.5836	1.0665
72.0	1.61	14.4095	12.1897	7.8499	8.2687	2.5842	1.0670
82.0	1.80	14.4115	12.1907	7.8503	8.2689	2.5839	1.0667
92.5	2.00	14.4125	12.1918	7.8497	8.2691	2.5842	1.0670
120.0	2.50	14.4121	12.1911	7.8493	8.2693	2.5842	1.0665
150.0	3.00	14.4128	12.1921	7.8498	8.2695	2.5838	1.0668
218.0	4.00	14.4147	12.1942	7.8498	8.2699	2.5847	1.0672
300.0	5.00	14.4146	12.1941	7.8491	8.2702	2.5850	1.0674

2.5c. Titration curves.



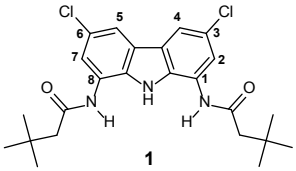






2.6. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **1** in DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

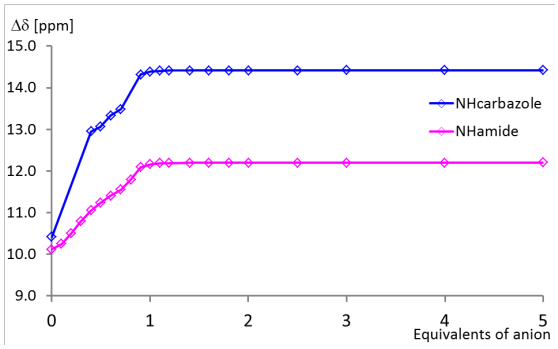
2.6a. Raw data:

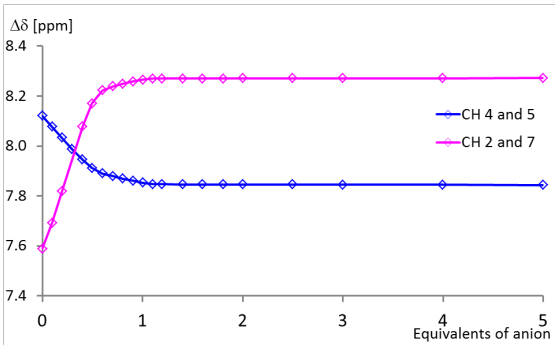


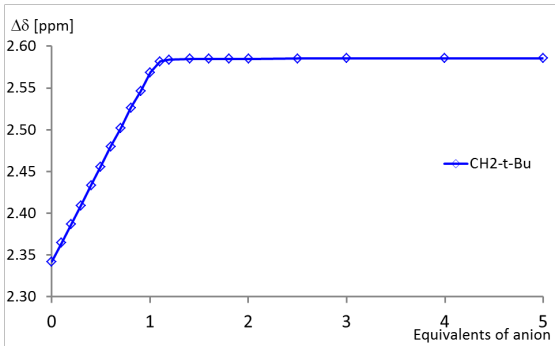
1

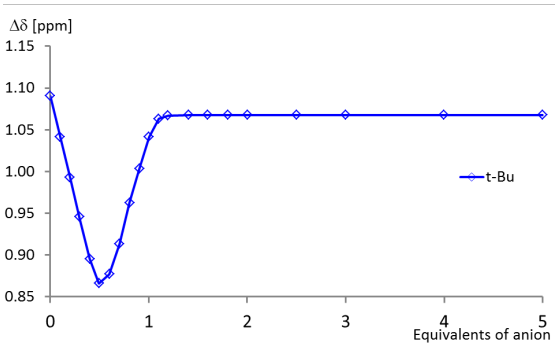
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH 4 and 5	CH 2 and 7	CH_2	*t*-Bu
0.0	0	10.4162	10.1149	8.1210	7.5889	2.3421	1.0906
4.0	0.10	broad	10.2449	8.0773	7.6927	2.3644	1.0416
8.0	0.20	broad	10.5053	8.0330	7.8178	2.3870	0.9930
12.0	0.29	broad	10.7874	7.9886	overlap	2.4088	0.9457
16.5	0.40	12.9531	11.0520	7.9454	8.0777	2.4335	0.8954
20.5	0.50	13.0595	11.2327	7.9115	8.1709	2.4554	0.8661
25.0	0.60	13.3308	11.4085	7.8904	8.2224	2.4798	0.8772
29.5	0.70	13.4828	11.5516	7.8791	8.2391	2.5021	0.9135
34.0	0.80	broad	11.7972	7.8697	8.2497	2.5265	0.9625
38.5	0.90	14.3204	12.0902	7.8613	8.2584	2.5461	1.0031
43.0	1.00	14.3855	12.1617	7.8530	8.2655	2.5685	1.0415
47.5	1.10	14.4097	12.1871	7.8473	8.2697	2.5817	1.0633
52.0	1.20	14.4130	12.1922	7.8467	8.2702	2.5840	1.0669
62.0	1.40	14.4138	12.1942	7.8466	8.2702	2.5848	1.0676
71.5	1.60	14.4148	12.1944	7.8457	8.2705	2.5849	1.0677
82.0	1.80	14.4142	12.1946	7.8464	8.2706	2.5848	1.0676
92.5	2.00	14.4155	12.1956	7.8459	8.2708	2.5850	1.0677
120.0	2.50	14.4172	12.1967	7.8456	8.2712	2.5853	1.0677
150.0	3.00	14.4189	12.1983	7.8454	8.2715	2.5857	1.0678
218.0	4.00	14.4190	12.1993	7.8450	8.2715	2.5855	1.0677
300.0	5.00	14.4213	12.2012	7.8442	8.2720	2.5855	1.0676

2.6b. Titration curves.



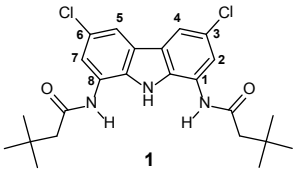






2.7. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **1** in 5% H_2O/DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

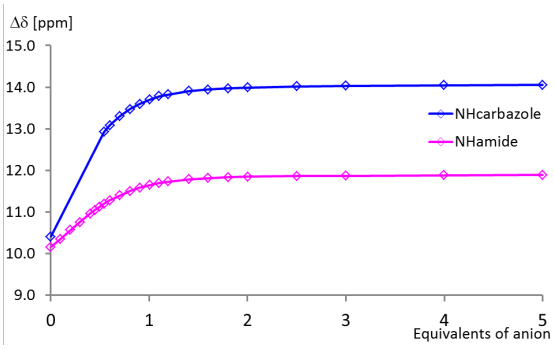
2.7a. Raw data:

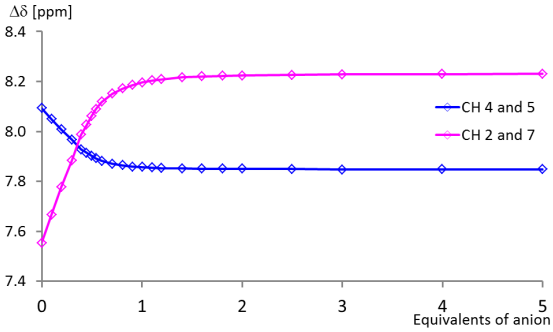


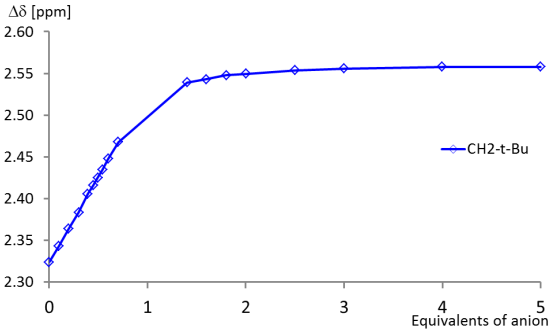
1

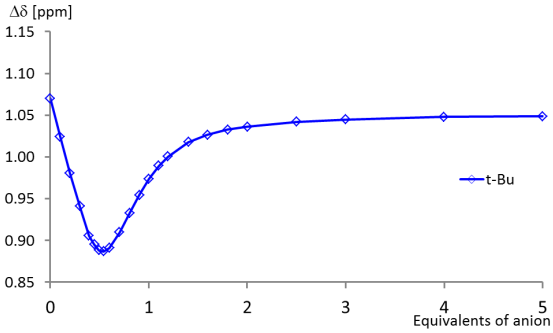
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH 4 and 5	CH 2 and 7	CH_2	*t*-Bu
0	0.00	10.4101	10.1578	8.0932	7.5543	2.3238	1.0702
4	0.10	broad	10.3535	8.0491	7.6664	2.3434	1.0244
8	0.20	broad	10.5657	8.0075	7.7774	2.364	0.9803
12	0.29	broad	10.7547	7.9678	7.8826	2.3837	0.9407
16.5	0.40	broad	10.9649	7.9285	7.9873	2.4058	0.9054
18.5	0.45	broad	11.0462	7.9142	8.0268	2.4158	0.895
20.5	0.50	broad	11.1247	7.9024	8.0609	2.425	0.8881
22.5	0.54	12.9251	11.1964	7.8924	8.0893	2.4346	0.8867
25	0.60	13.0848	11.2807	7.8817	8.1188	2.4477	0.891
29.5	0.70	13.3032	11.4019	7.8707	8.1512	2.4679	0.9098
34	0.80	13.4697	11.5023	7.8645	8.1719	overlap	0.9324
38.5	0.90	13.5977	11.5827	7.8592	8.1862	overlap	0.9544
43.1	1.01	13.6983	11.6516	7.8573	8.1964	overlap	0.9739
47.5	1.10	13.7826	11.6992	7.8553	8.2044	overlap	0.9892
52	1.20	13.8275	11.7338	7.8535	8.2089	overlap	1.0005
62	1.40	13.908	11.7893	7.8523	8.2166	2.539	1.0176
71.5	1.60	13.9431	11.815	7.8510	8.2200	2.543	1.0266
82	1.80	13.9706	11.8336	7.8502	8.2224	2.548	1.0327
92.5	2.00	13.9897	11.847	7.8508	8.2241	2.5494	1.036
120	2.50	14.0169	11.8634	7.8492	8.2266	2.5537	1.0419
150	3.00	14.0299	11.8719	7.8477	8.2279	2.5557	1.0448
218	4.00	14.0471	11.8855	7.8485	8.2296	2.5579	1.0478
300	5.00	14.0545	11.8902	7.8485	8.2302	2.5579	1.0486

2.7b. Titration curves.

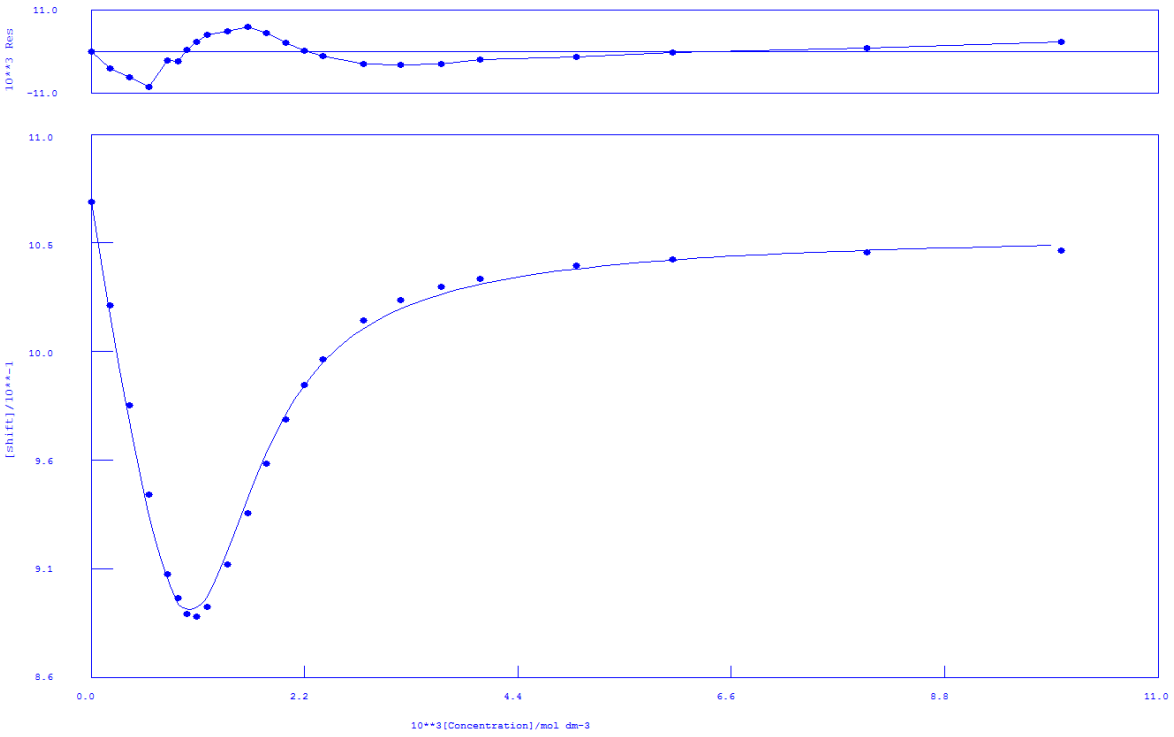




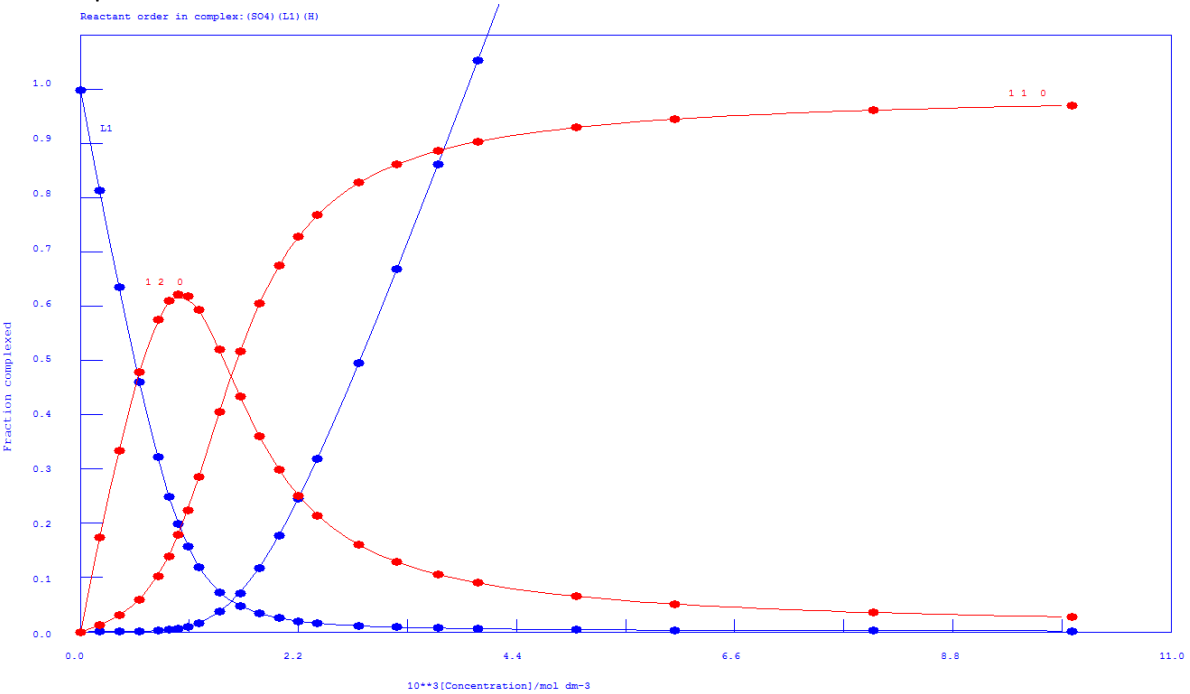




2.7c. Fitting of (2:1 & 1:1) model to the data for *t*-Bu protons using WinEQNMR.
$\log\beta_1$= 4.88±0.078; $\log\beta_2$= 8.52±0.15 $\delta_{max(2:1)}$= 0.782±0.012 ppm; $\delta_{max(1:1)}$= 1.058±0.0035 ppm.

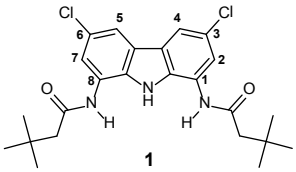


Simulated speciation:



2.8. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **1** in 10% H_2O/DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

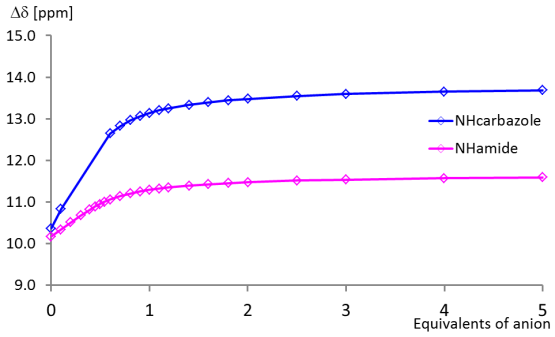
2.8a. Raw data:

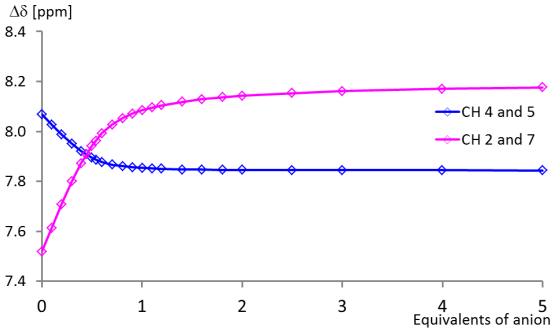


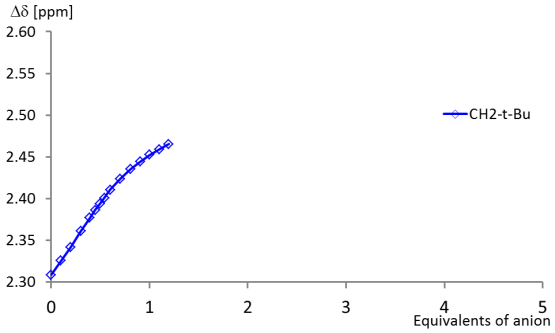
1

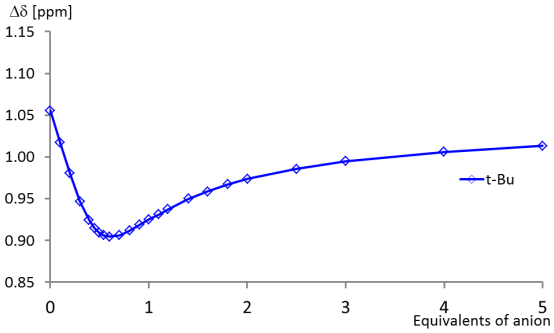
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	CH_2	*t*-Bu
0.0	0.00	10.3680	10.1732	8.0685	7.5184	2.3086	1.0556
4.0	0.10	10.8314	10.3411	8.0279	7.6127	2.3256	1.0171
8.0	0.20	broad	10.5092	7.9887	7.7071	2.3421	0.9803
12.3	0.30	broad	10.6803	7.9508	7.8003	2.3610	0.9468
16.1	0.39	broad	10.8134	7.9215	7.8727	2.3769	0.9246
18.5	0.45	broad	10.8946	7.9088	7.9088	2.3862	0.9150
20.5	0.50	broad	10.9516	7.8960	7.9403	2.3935	0.9092
22.5	0.54	broad	11.0006	7.8870	7.9632	2.4009	0.9062
25.0	0.60	12.6445	11.0608	7.8774	7.9923	2.4105	0.9044
29.5	0.70	12.8299	11.1445	7.8673	8.0275	2.4239	0.9060
34.1	0.81	12.9646	11.2057	7.8606	8.0528	2.4352	0.9117
38.5	0.90	13.0595	11.2518	7.8561	8.0708	2.4443	0.9185
43.0	1.00	13.1421	11.2945	7.8543	8.0849	2.4524	0.9251
47.5	1.10	13.2056	11.3252	7.8523	8.0960	2.4591	0.9310
52.0	1.20	13.2515	11.3509	7.8505	8.1047	2.4653	0.9374
62.0	1.40	13.3327	11.3938	7.8477	8.1188	overlap	0.9500
71.5	1.60	13.3959	11.4274	7.8476	8.1289	overlap	0.9586
82.0	1.80	13.4444	11.4532	7.8461	8.1368	overlap	0.9670
92.5	2.00	13.4818	11.4744	7.8458	8.1429	overlap	0.9736
120.0	2.50	13.55	11.5141	7.8454	8.1539	overlap	0.9857
150.0	3.00	13.5964	11.5399	7.8451	8.1612	overlap	0.9950
218.0	4.00	13.6537	11.5747	7.8447	8.1705	overlap	1.0060
300.0	5.00	13.6896	11.5957	7.8442	8.1765	overlap	1.0133

2.8b. Titration curves.

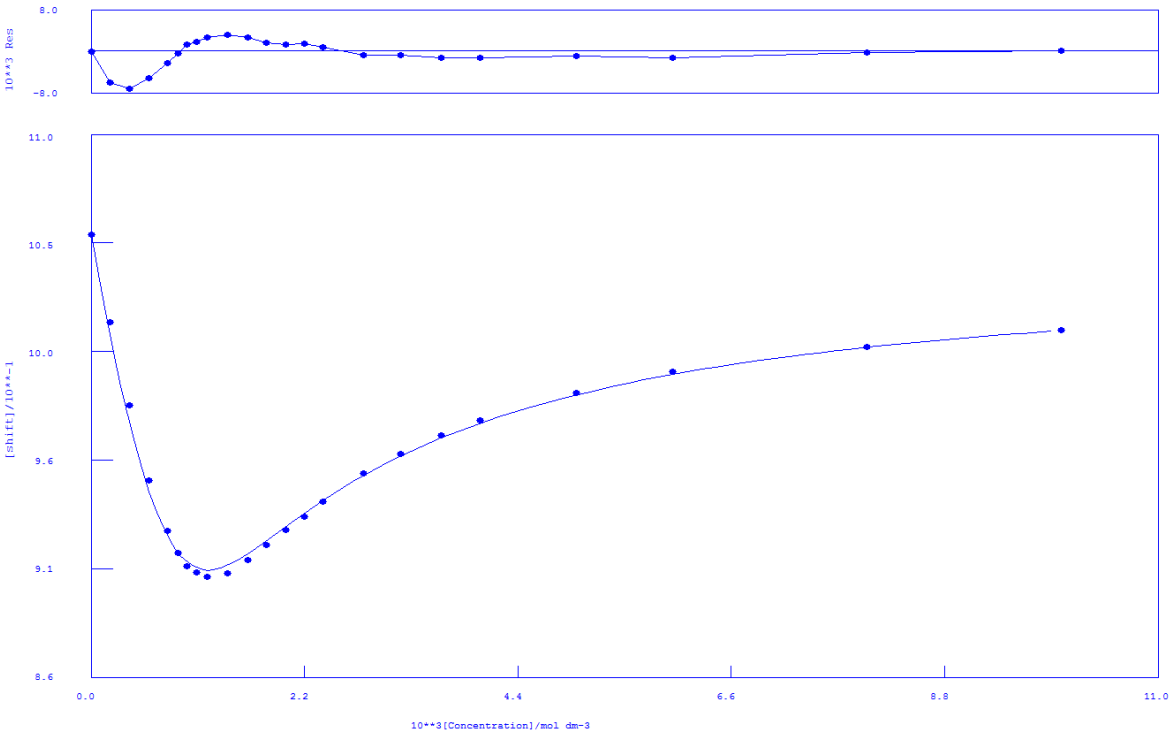




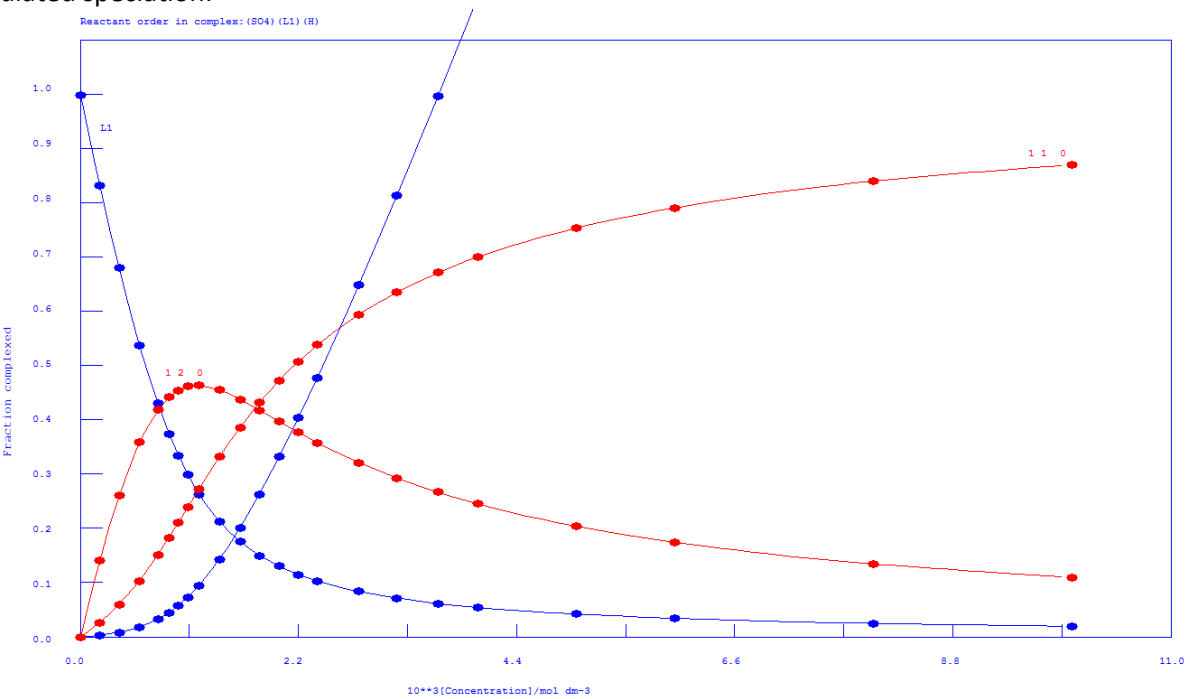




2.8c. Data fitting. Fitting of (2:1 & 1:1) model to the data for *t*-Bu protons using WinEQNMR. $\log\beta_1$= 3.74±0.045; $\log\beta_2$= 6.95±0.11 $\delta_{max(2:1)}$= 0.741±0.021 ppm; $\delta_{max(1:1)}$= 1.047±0.0066 ppm.

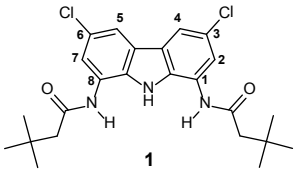


Simulated speciation:



2.9. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **1** in 10% H_2O/DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

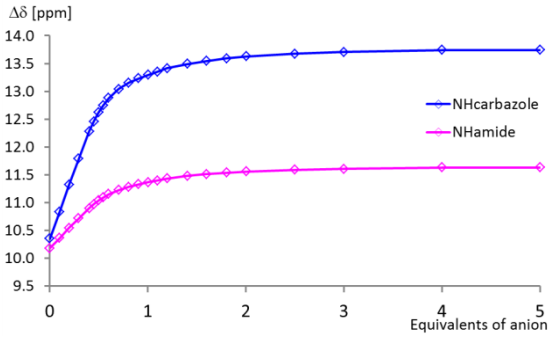
2.9a. Raw data:

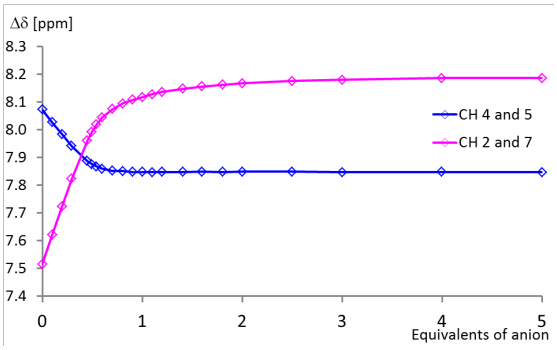


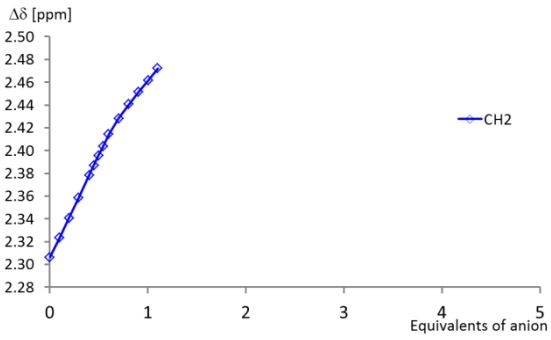
1

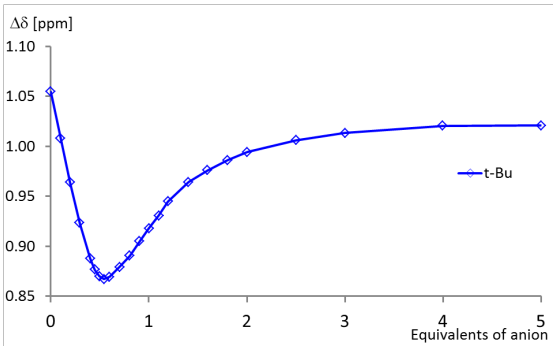
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	CH_2	*t*-Bu
0.0	0	10.3553	10.1815	8.0723	7.5154	2.3063	1.0546
4.0	0.10	10.8360	10.3609	8.0260	7.6205	2.3234	1.0081
8.0	0.20	11.3211	10.5435	7.9834	7.7226	2.3408	0.9641
12.0	0.29	11.7883	10.7192	7.9412	7.8225	2.3586	0.9233
16.5	0.40	12.2831	10.9009	overlap	overlap	2.3784	0.8880
18.5	0.45	12.4590	10.9737	7.8868	7.9596	2.3869	0.8766
20.5	0.50	12.6203	11.0388	7.8754	7.9922	2.3957	0.8699
22.5	0.54	12.7446	11.0922	7.8668	8.0177	2.4036	0.8672
25.0	0.60	12.8793	11.1516	7.8589	8.0436	2.4141	0.8693
29.5	0.70	13.0384	11.2274	7.8513	8.0738	2.4282	0.8793
34.0	0.80	13.1527	11.2860	7.8499	8.0934	2.4407	0.8904
38.5	0.90	13.2340	11.3298	7.8478	8.1070	2.4515	0.9049
43.0	1.00	13.2958	11.3656	7.8469	8.1170	2.4615	0.9178
47.5	1.10	13.3553	11.3993	7.8467	8.1265	2.4721	0.9307
52.0	1.20	13.4143	11.4341	7.8471	8.1350	overlap	0.9448
62.0	1.40	13.4951	11.4811	7.8475	8.1472	overlap	0.9642
71.5	1.60	13.5470	11.5126	7.8478	8.1549	overlap	0.9759
82.0	1.80	13.5908	11.5383	7.8473	8.1610	overlap	0.9861
92.5	2.00	13.6274	11.5599	7.8484	8.1667	overlap	0.9942
120.0	2.50	13.6764	11.5907	7.8478	8.1744	overlap	1.0061
150.0	3.00	13.7053	11.6066	7.8462	8.1786	overlap	1.0131
218.0	4.00	13.7443	11.6334	7.8468	8.1848	overlap	1.0204
300.0	5.00	13.7448	11.6331	7.8459	8.18485	overlap	1.0207

2.9b. Titration curves.

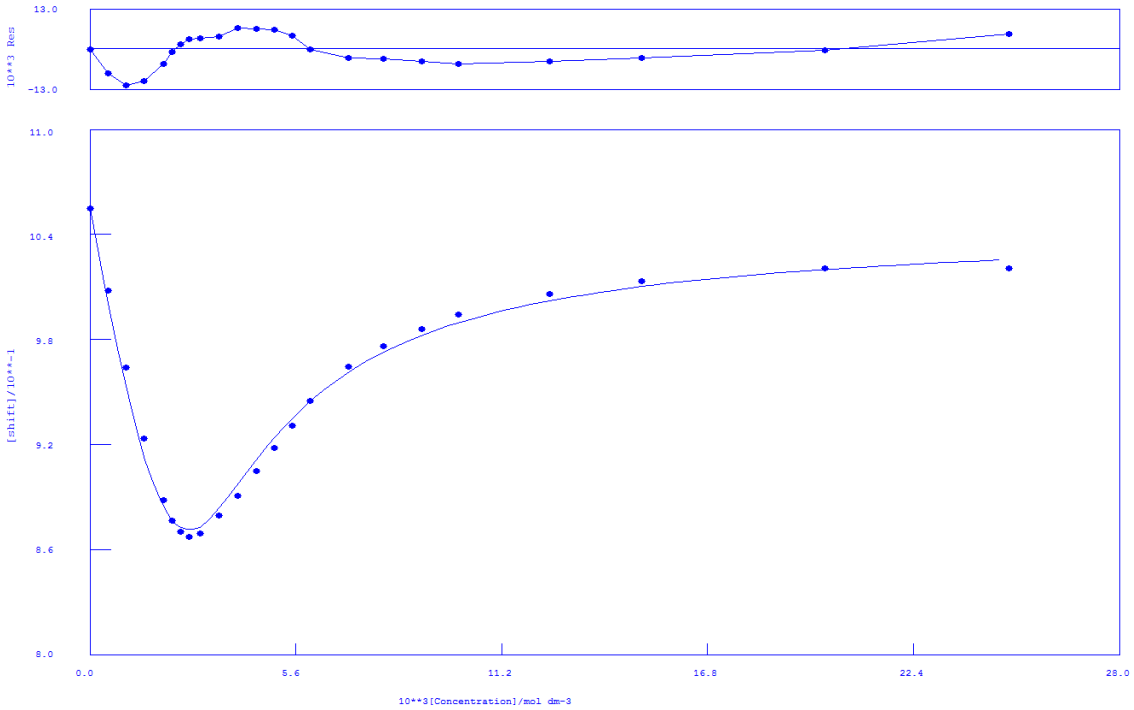




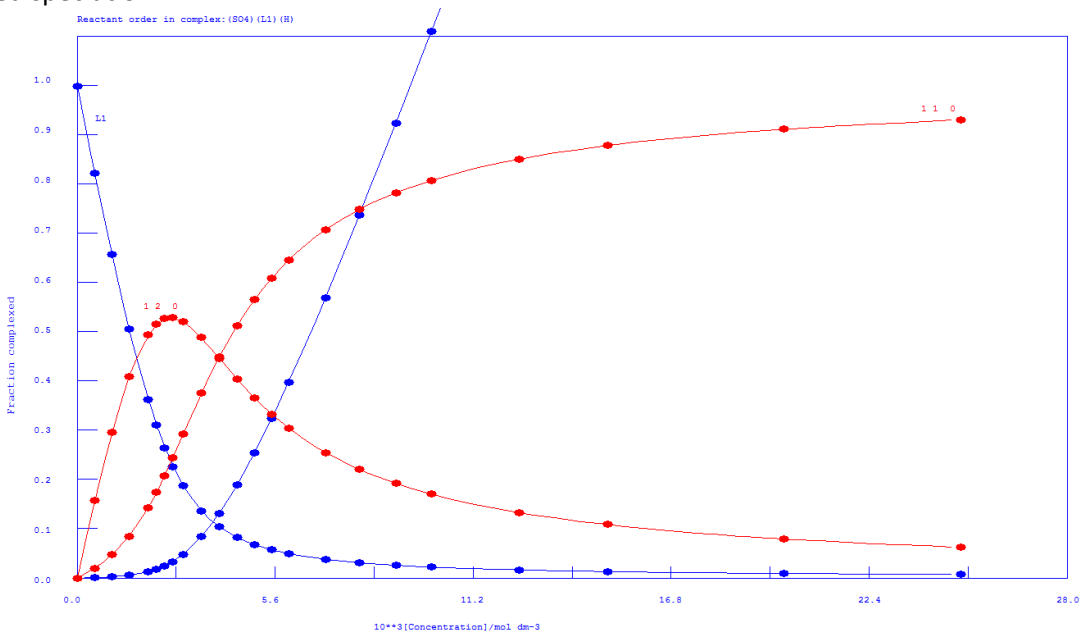




2.9c. Fitting of (2:1 & 1:1) model to the data for *t*-Bu protons using WinEQNMR.
$\log\beta_1$= 3.82±0.112; $\log\beta_2$= 6.80±0.238 $\delta_{max(2:1)}$= 0.710±0.032 ppm; $\delta_{max(1:1)}$= 1.046±0.007 ppm.

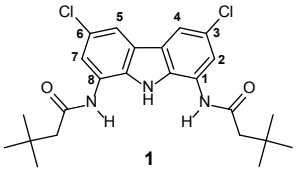


Simulated speciation:



2.10. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **1** in DMSO-d_6 with 0.075M TBACl.

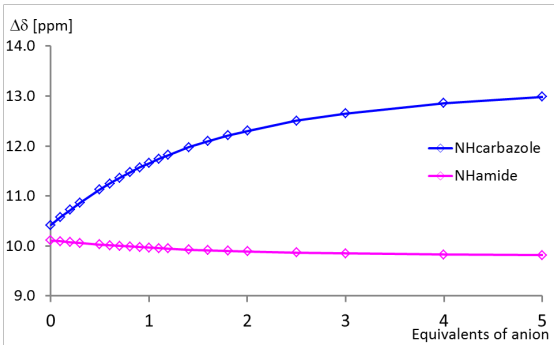
2.10a. Raw data:

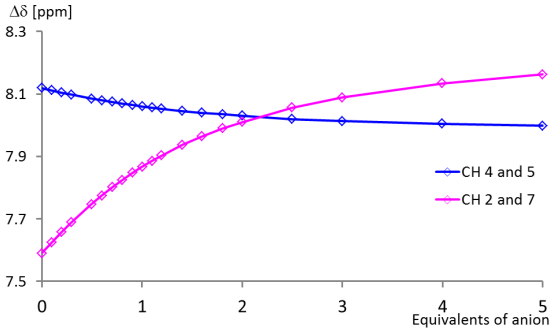


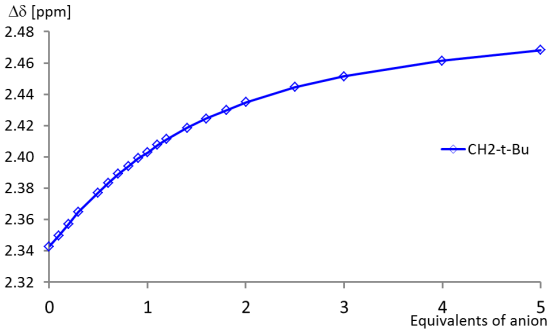
1

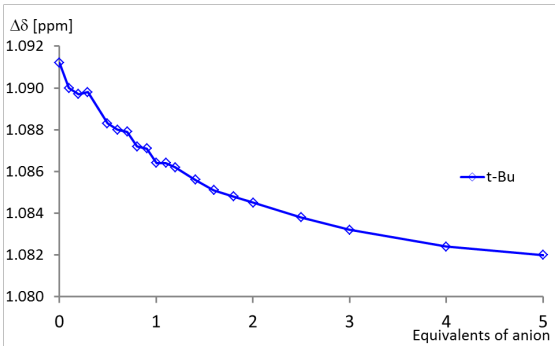
Added volume of titrant solution [µl]	Equivalents of TBACl	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	CH_2	*t*-Bu
0.0	0.00	10.4175	10.1115	8.1194	7.5895	2.3427	1.0912
4.0	0.10	10.5759	10.0921	8.1117	7.6238	2.3497	1.0900
8.0	0.20	10.7214	10.0738	8.1046	7.6568	2.3572	1.0897
12.0	0.29	10.8614	10.0595	8.0982	7.6887	2.3647	1.0898
20.5	0.50	11.1248	10.0259	8.0853	7.7468	2.3769	1.0883
25.0	0.60	11.2496	10.0115	8.0792	7.7750	2.3833	1.0880
29.5	0.70	11.3649	10.0001	8.0747	7.8012	2.3891	1.0879
34.0	0.80	11.4712	9.9878	8.0696	7.8249	2.3939	1.0872
38.5	0.90	11.5701	9.9751	8.0646	7.8472	2.3991	1.0871
43.0	1.00	11.6589	9.9639	8.0599	7.8668	2.4029	1.0864
47.5	1.10	11.7427	9.9550	8.0564	7.8855	2.4076	1.0864
52.0	1.20	11.8220	9.9467	8.0527	7.9030	2.4113	1.0862
62.0	1.40	11.9729	9.9272	8.0452	7.9370	2.4185	1.0856
71.5	1.60	12.0941	9.9144	8.0401	7.9638	2.4244	1.0851
82.0	1.80	12.2104	9.9013	8.0348	7.9898	2.4298	1.0848
92.5	2.00	12.3071	9.8898	8.0307	8.0106	2.4349	1.0845
120.0	2.50	12.5047	9.8666	8.0199	8.0561	2.4446	1.0838
150.0	3.00	12.6529	9.8504	8.0131	8.0890	2.4515	1.0832
218.0	4.00	12.8567	9.8288	8.0044	8.1338	2.4615	1.0824
300.0	5.00	12.9876	9.8137	7.9979	8.1628	2.4682	1.0820

2.10b. Titration curves.

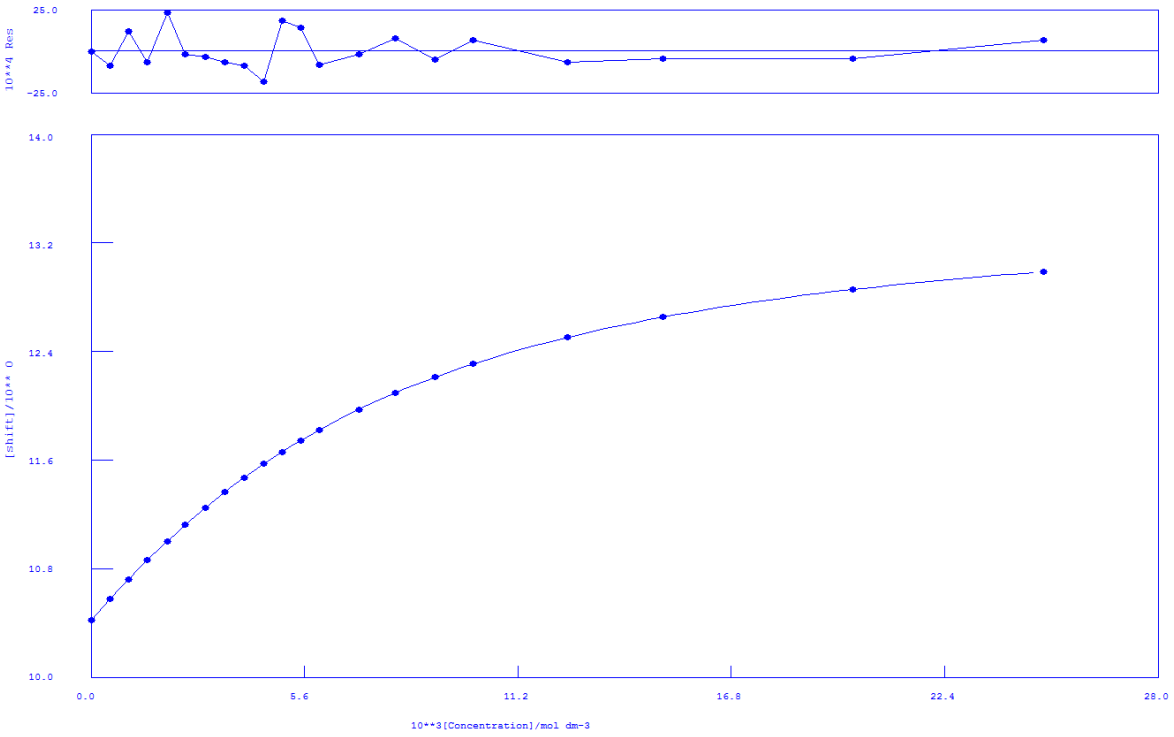




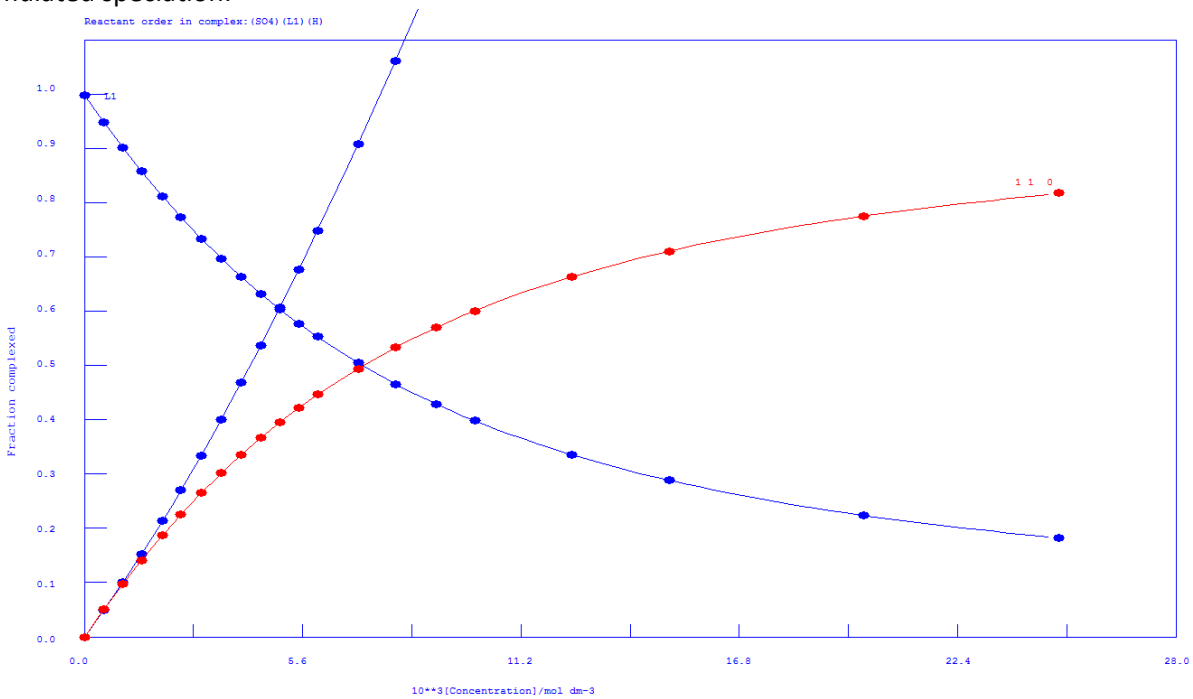




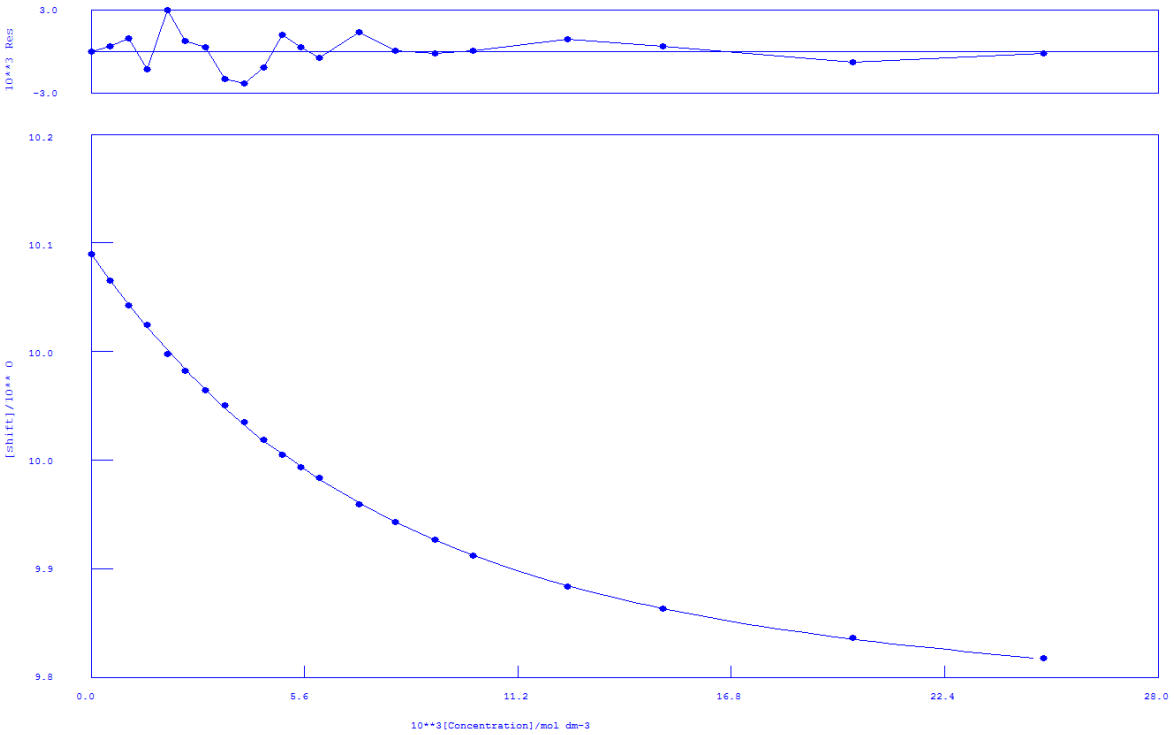
2.10c. Data fitting. Fitting of (1:1) model to the data for $NH_{carbazole}$ protons using WinEQNMR. $\log\beta_1$= 2.33±0.00094; $\delta_{max(1:1)}$= 13.558±0.0019 ppm.



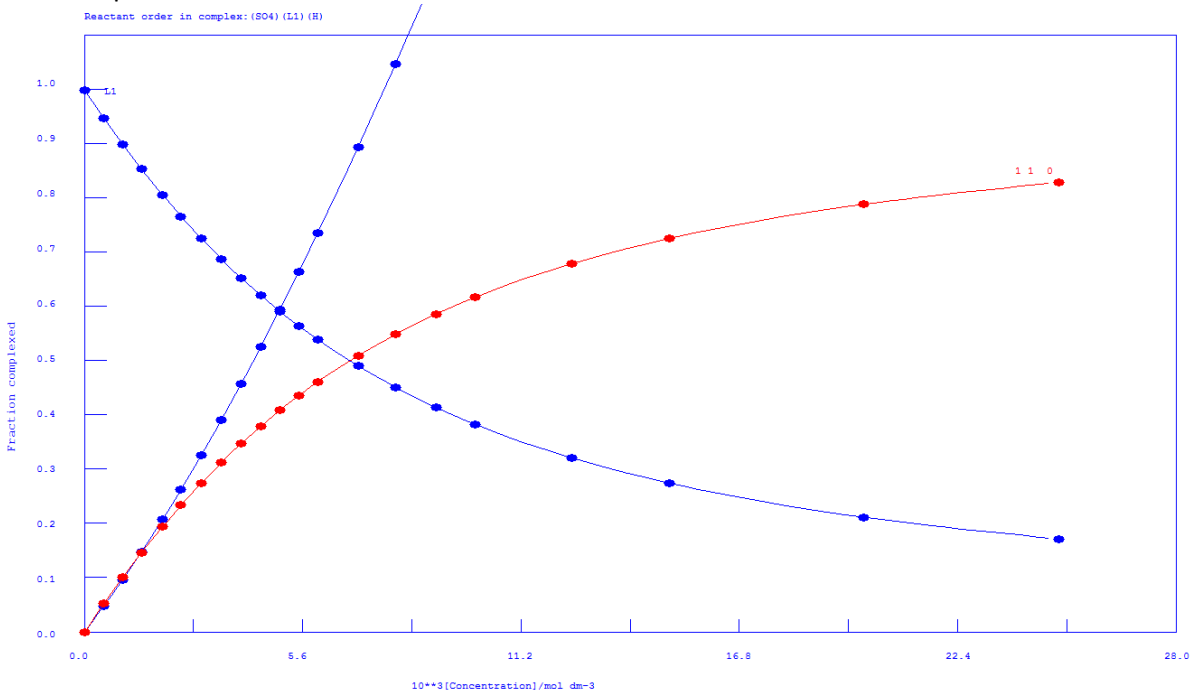
Simulated speciation:



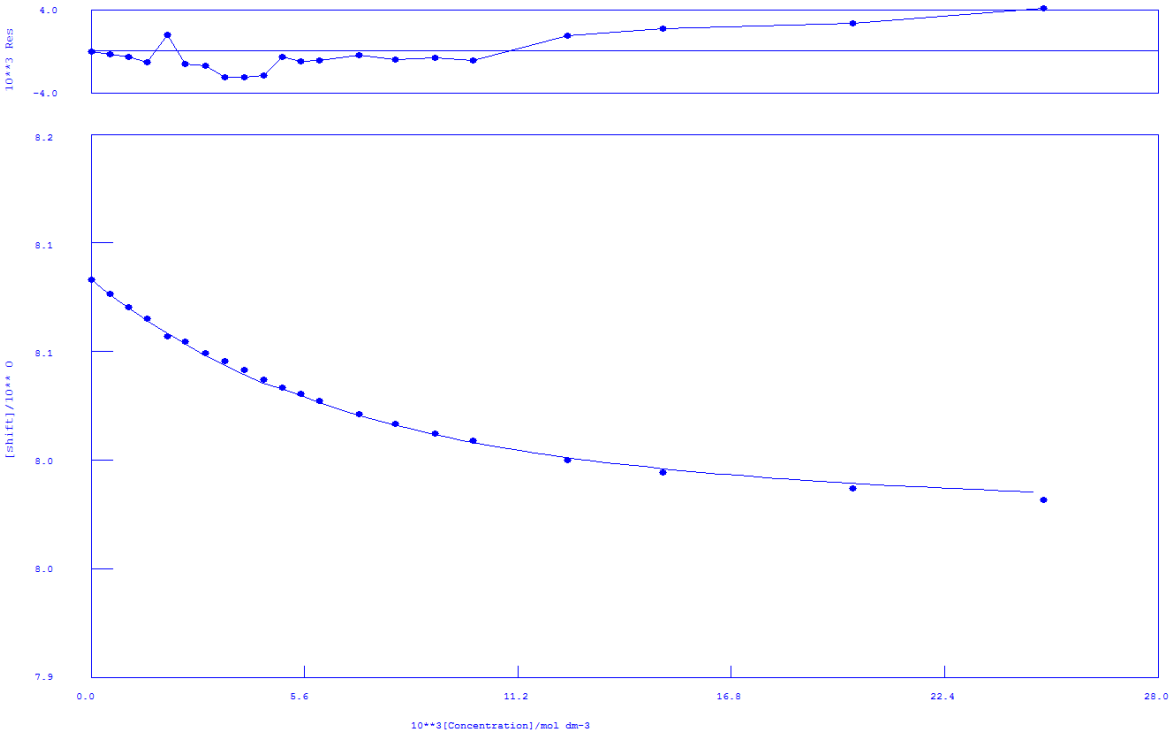
Fitting of (1:1) model to the data for NH_{amide} protons using WinEQNMR.
$\log\beta_1$= 2.37±0.0093; $\delta_{max(1:1)}$= 9.751±0.0021 ppm.

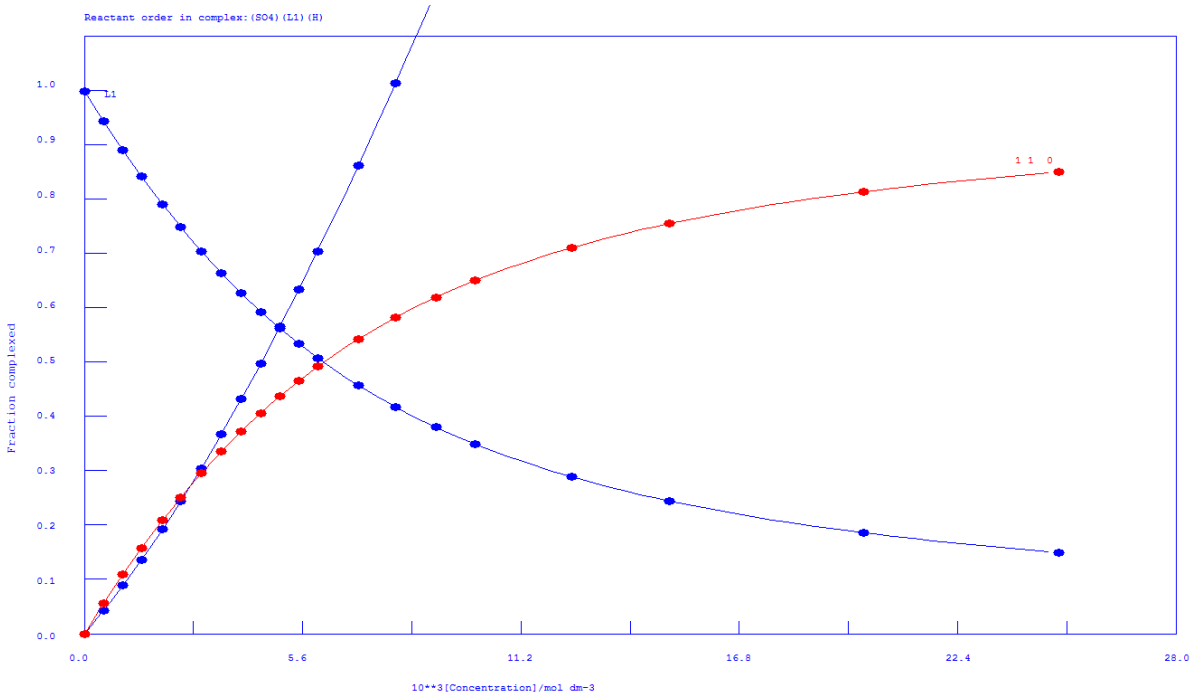


Simulated speciation:



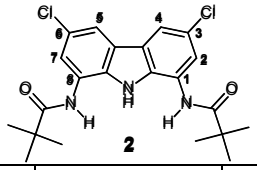
Fitting of (1:1) model to the data for CH 2 protons using WinEQNMR.
$\log\beta_1$= 2.44±0.0035, $\delta_{max(1:1)}$= 8.119±0.0008ppm





2.11. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **2** in DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

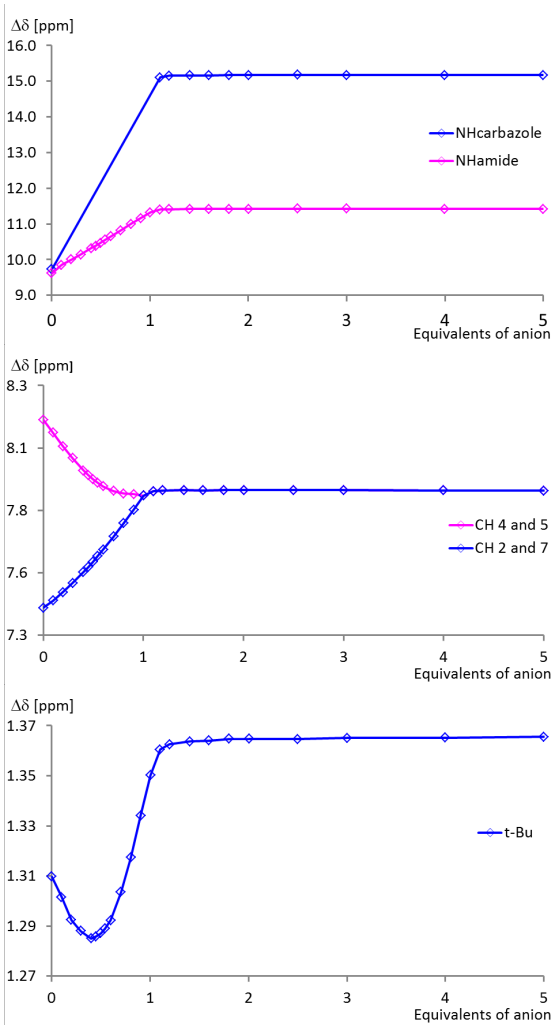
2.11a. Raw data:



2

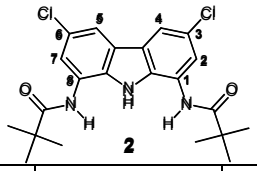
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*t*-Bu
0	0	9.7324	9.6126	8.1627	7.4094	1.3097
4	0.10	broad	9.8532	8.1112	7.4388	1.3015
8	0.20	broad	10.0001	8.0573	7.47225	1.2924
12	0.29	broad	10.1438	8.0094	7.5095	1.2880
16.5	0.40	broad	10.3213	7.9596	7.5535	1.2850
18.5	0.45	broad	10.3846	7.9410	7.5726	1.2858
20.5	0.50	broad	10.4653	7.9249	7.5934	1.2871
22.5	0.54	broad	10.5508	7.9109	7.6165	1.2889
25	0.6	broad	10.6471	7.8961	7.6434	1.2923
29.5	0.70	broad	10.8233	7.8772	7.6952	1.3035
34	0.80	broad	10.9952	7.8678	7.7490	1.3174
38.5	0.90	broad	11.1628	7.8651	7.8024	1.3341
43	1.00	broad	11.3188	7.8594	7.8594	1.3502
47.5	1.10	15.1082	11.3989	7.8768	7.8768	1.3605
52	1.20	15.1508	11.4134	7.8799	7.8799	1.3626
62	1.40	15.1634	11.4186	7.881	7.8810	1.3637
71.5	1.60	15.165	11.4215	7.8805	7.8805	1.3640
82	1.80	15.1699	11.4215	7.8813	7.8813	1.3648
92.5	2.00	15.1697	11.4215	7.8809	7.8809	1.3648
120	2.50	15.1758	11.4234	7.8815	7.8815	1.3646
150	3.00	15.172	11.4227	7.8807	7.8807	1.3651
218	4.00	15.1705	11.4207	7.8795	7.8795	1.3652
300	5.00	15.1714	11.4198	7.8792	7.8792	1.3655

2.11b. Titration curves.



2.12. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **2** in 10% H_2O/DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

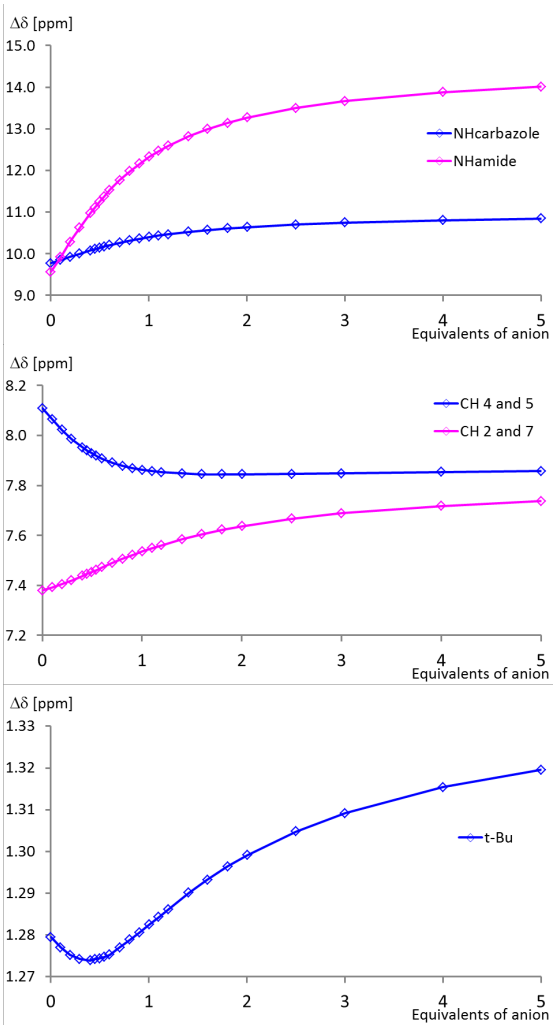
2.12a. Raw data:



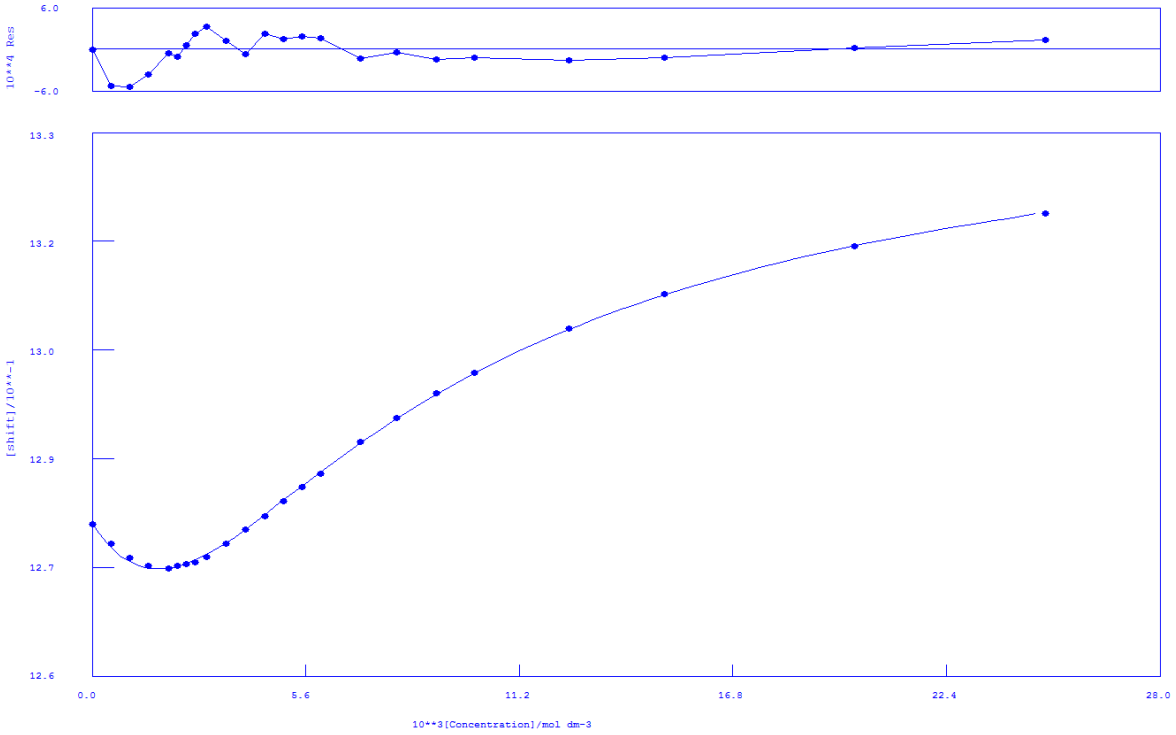
2

Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*t*-Bu
0	0	9.7698	9.5619	8.1096	7.3796	1.2795
4	0.10	9.8466	9.9172	8.0652	7.3914	1.2770
8	0.20	9.9245	10.2807	8.0225	7.4049	1.2752
12	0.29	10.0009	10.6233	7.9856	7.4198	1.2742
16.5	0.40	10.0780	10.9672	7.9525	7.4375	1.2739
18.5	0.45	10.1090	11.1094	7.9400	7.4458	1.2742
20.5	0.50	10.1397	11.2432	7.9288	7.4536	1.2744
22.5	0.54	10.1706	11.3721	7.9187	7.4611	1.2747
25	0.60	10.2068	11.5289	7.9068	7.4724	1.2753
29.5	0.70	10.2652	11.7690	7.8907	7.4895	1.2770
34	0.80	10.3144	11.9795	7.8785	7.5059	1.2789
38.5	0.90	10.3579	12.1647	7.8692	7.5209	1.2806
43	1.00	10.3981	12.3256	7.8624	7.5359	1.2825
47.5	1.10	10.4335	12.4655	7.8571	7.5496	1.2843
52	1.20	10.4638	12.5912	7.8532	7.5611	1.2861
62	1.40	10.5220	12.8201	7.8480	7.5853	1.2901
71.5	1.60	10.5658	12.9910	7.8453	7.6045	1.2932
82	1.80	10.6059	13.1403	7.8442	7.6225	1.2964
92.5	2.00	10.6389	13.2675	7.8442	7.6370	1.2991
120	2.50	10.7021	13.5007	7.8459	7.6668	1.3048
150	3.00	10.7458	13.6672	7.8486	7.6887	1.3092
218	4.00	10.8054	13.8816	7.8536	7.7180	1.3154
300	5.00	10.8440	14.0140	7.8573	7.7371	1.3196

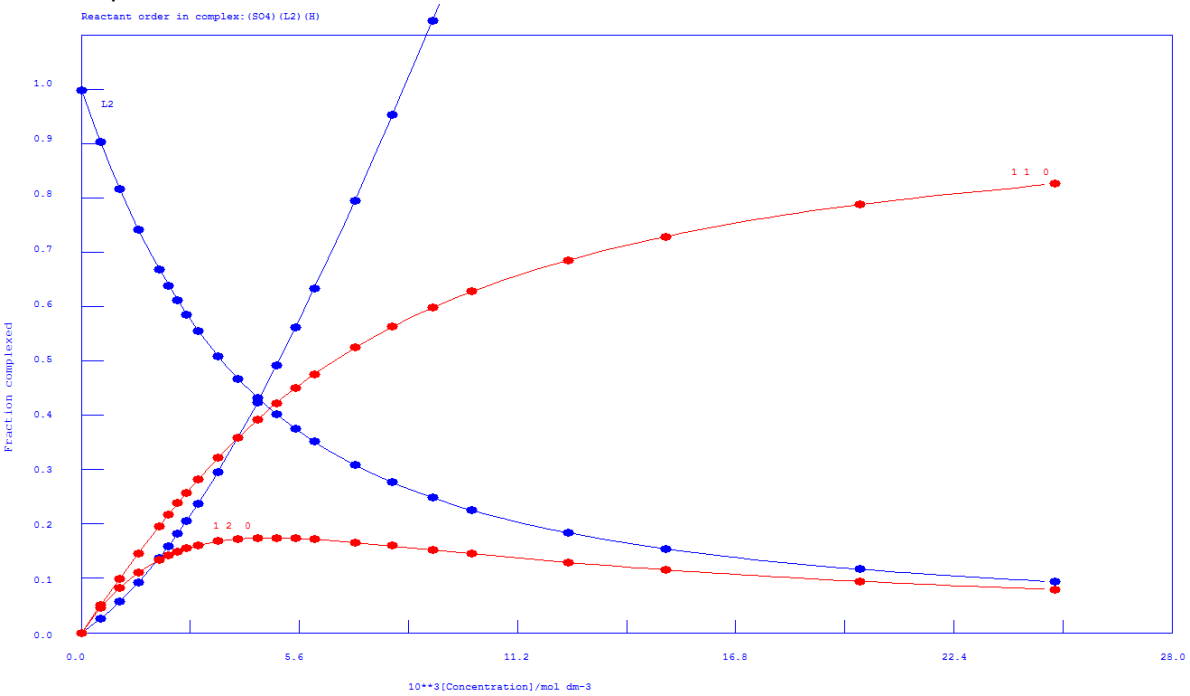
2.12b. Titration curves.



2.12c. Fitting of (2:1 & 1:1) model to the data for *t*-Bu protons using WinEQNMR.
$\log\beta_1$= 2.63±0.01; $\log\beta_2$= 4.64±0.01; $\delta_{max(2:1)}$= 1.149± 0.0011 ppm; $\delta_{max(1:1)}$= 1.341± 0.00060 ppm.

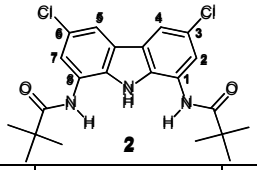


Simulated speciation:



2.13. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **2** in DMSO-d_6 with 0.075M TBACl.

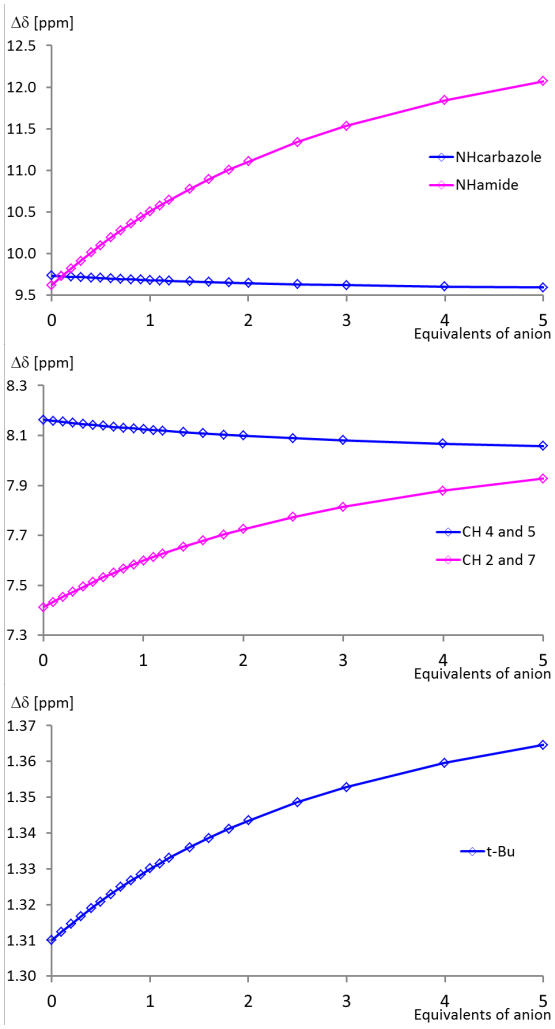
2.13a. Raw data:



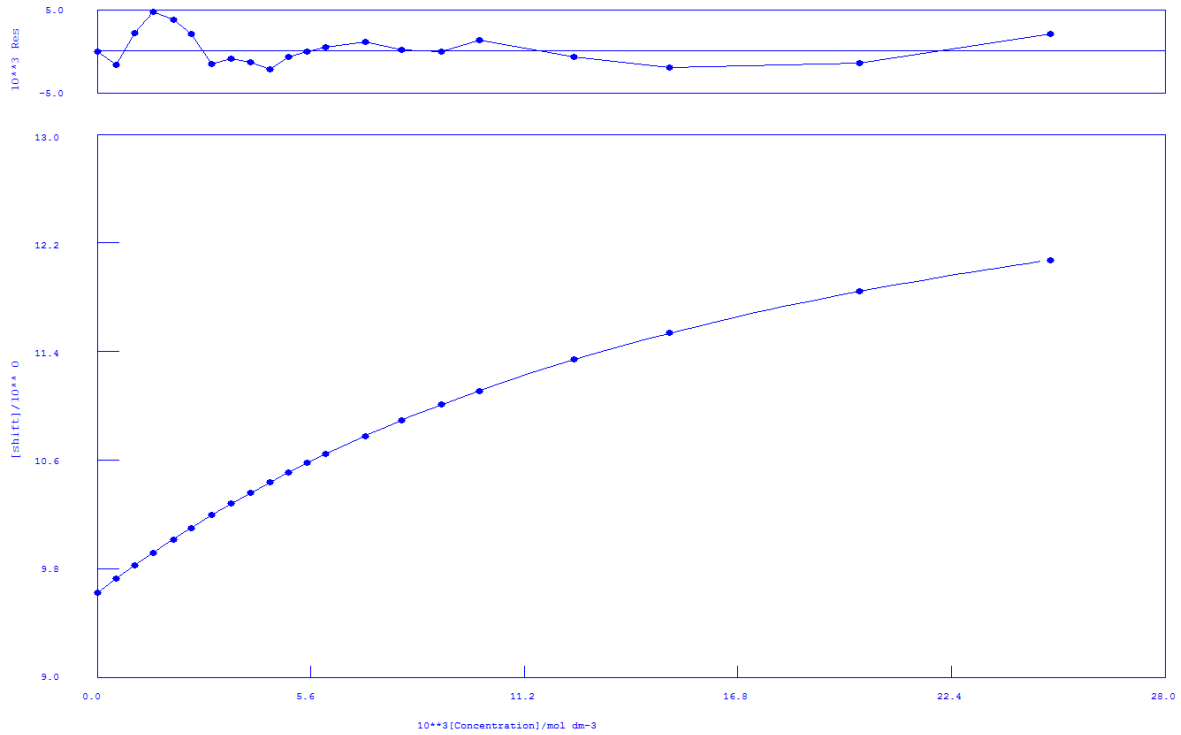
2

Added volume of titrant solution [µl]	Equivalents of TBACl	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*t*-Bu
0	0	9.7348	9.6223	8.1636	7.4118	1.3100
4	0.10	9.7278	9.7278	8.1589	7.4332	1.3124
8	0.20	9.7234	9.8226	8.1547	7.4542	1.3146
12	0.29	9.7176	9.9137	8.1507	7.4733	1.3167
16.5	0.40	9.7114	10.0146	8.1461	7.4947	1.3189
20.5	0.50	9.7067	10.1005	8.1426	7.5126	1.3208
25	0.60	9.7005	10.1940	8.1388	7.5322	1.3229
29.5	0.70	9.6958	10.2785	8.1347	7.5501	1.3249
34	0.80	9.6907	10.3597	8.1312	7.5674	1.3267
38.5	0.90	9.6869	10.4373	8.1280	7.5833	1.3283
43	1.00	9.6821	10.5089	8.1247	7.5988	1.3301
47.5	1.10	9.6785	10.5773	8.1220	7.6129	1.3315
52	1.20	9.6739	10.6424	8.1188	7.6268	1.3331
62	1.40	9.6667	10.7761	8.1133	7.6551	1.3360
71.5	1.60	9.6598	10.8922	8.1085	7.6792	1.3386
82	1.80	9.6531	11.0073	8.1035	7.7036	1.3412
92.5	2.00	9.6475	11.1096	8.0991	7.7253	1.3435
120	2.50	9.6335	11.3396	8.0887	7.7733	1.3486
150	3.00	9.6231	11.5353	8.0812	7.8146	1.3528
218	4.00	9.6054	11.8431	8.0676	7.8792	1.3596
300	5.00	9.5925	12.0730	8.0575	7.9275	1.3646

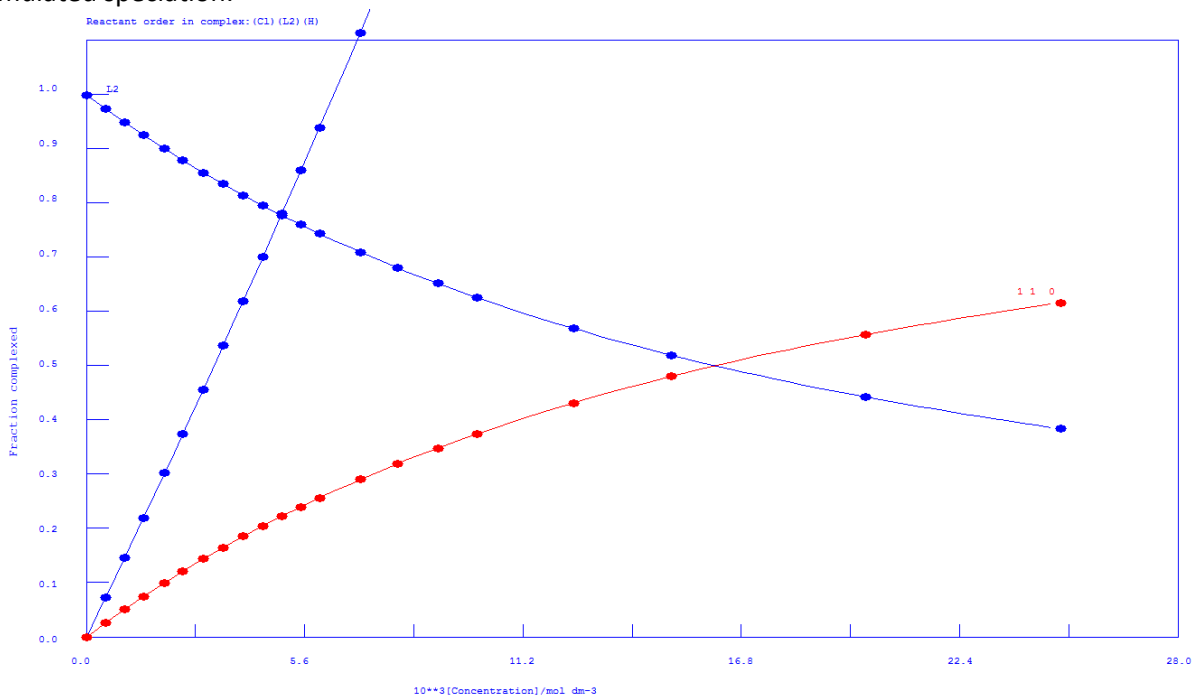
2.13b. Titration curves.



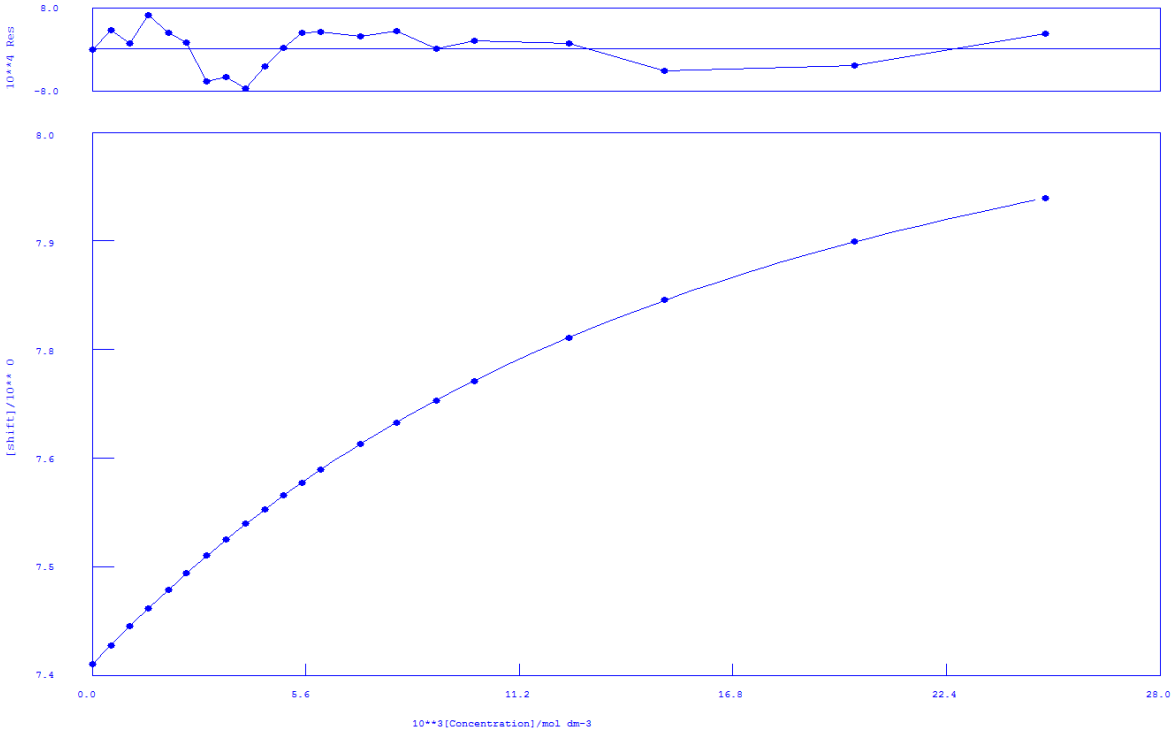
2.13c. Data fitting. Fitting of (1:1) model to the data for NH_{amide} protons using WinEQNMR. $\log\beta_1 = 1.87 \pm 0.0022$; $\delta_{max(1:1)} = 13.599 \pm 0.0089$ ppm.



Simulated speciation:

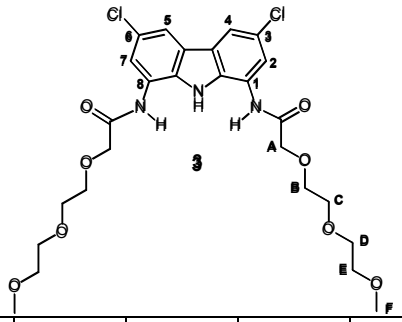


Fitting of (1:1) model to the data for CH 2 and 7 protons using WinEQNMR.
$\log\beta_1$= 1.87±0.0020; $\delta_{max(1:1)}$= 8.246±0.0018 ppm.



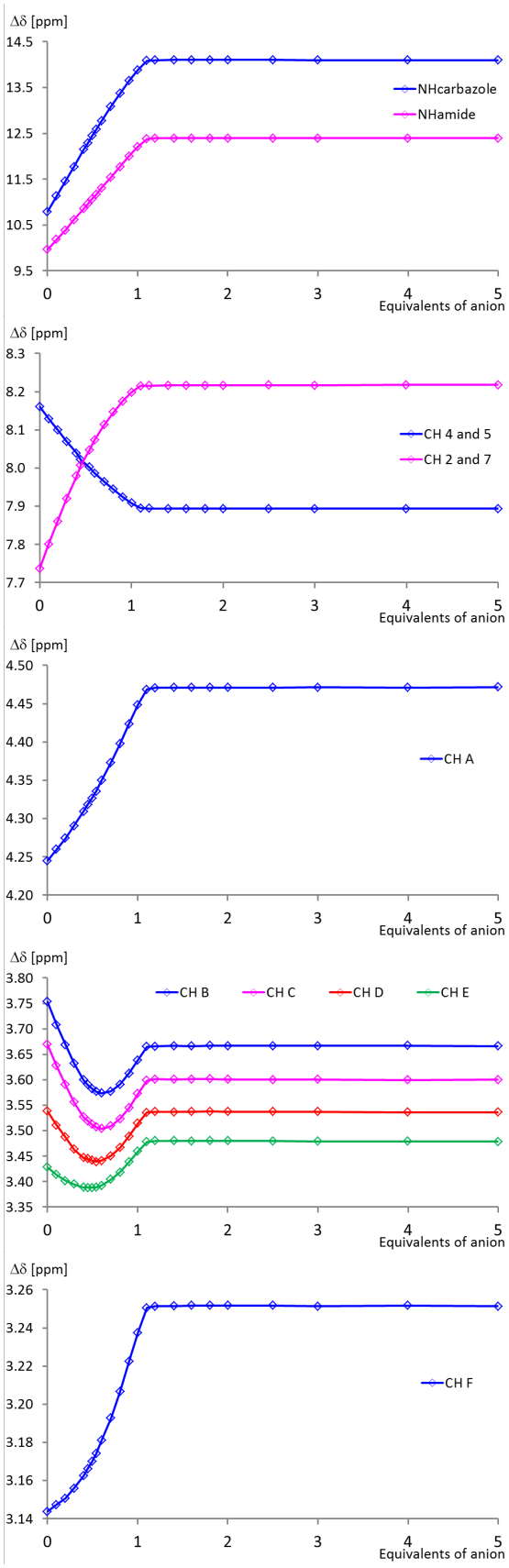
2.14. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **3** in DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

2.14a. Raw data:



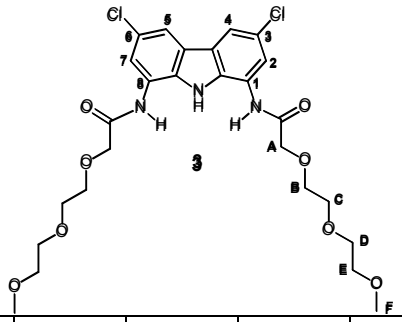
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	CH A	CH B	CH C	CH D	CH E	CH F
0	0	10.7865	9.9608	8.1610	7.7360	4.2447	3.7537	3.6693	3.5384	3.4282	3.1438
4	0.10	11.1294	10.1793	8.1294	7.8008	4.2598	3.7084	3.6276	3.5106	3.4133	3.1473
8	0.20	11.4596	10.3844	8.1002	7.8599	4.2741	3.6685	3.5901	3.4872	3.4014	3.1507
12	0.29	11.7712	10.6154	8.0696	7.9201	4.2904	3.6323	3.5557	3.4636	3.3945	3.1559
16.5	0.40	12.1474	10.8530	8.0388	7.9790	4.3092	3.5998	3.5269	3.4466	3.3884	3.1624
18.5	0.45	12.2864	10.9577	8.0220	8.0072	4.3181	3.5904	3.5190	3.4446	3.3880	3.1662
20.5	0.50	12.4453	11.0635	overlap	overlap	4.3267	3.5825	3.5120	3.4413	3.3880	3.1700
22.5	0.54	12.5874	11.1645	8.0024	8.0465	4.3355	3.5768	3.5070	3.4389	3.3885	3.1741
25	0.60	12.7675	11.3075	7.9865	8.0735	4.3497	3.5734	3.5040	3.4412	3.3923	3.1811
29.5	0.70	13.0867	11.5407	7.9644	8.1135	4.3729	3.5774	3.5091	3.4502	3.4041	3.1927
34	0.80	13.3729	11.7718	7.9437	8.1463	4.3975	3.5908	3.5229	3.4664	3.4183	3.2066
38.5	0.90	13.6490	11.9999	7.9241	8.1752	4.4235	3.6127	3.5446	3.4886	3.4383	3.2223
43	1.00	13.8868	12.2080	7.9080	8.1986	4.4486	3.6386	3.5723	3.5142	3.4592	3.2375
47.5	1.10	14.0842	12.3789	7.8950	8.2150	4.4688	3.6649	3.5987	3.5355	3.4781	3.2505
52	1.20	14.0996	12.3933	7.8943	8.2160	4.4707	3.6658	3.6009	3.5371	3.4798	3.2514
62	1.40	14.1046	12.3956	7.8937	8.2162	4.4709	3.6668	3.6005	3.5367	3.4798	3.2515
71.5	1.60	14.1029	12.3967	7.8936	8.2162	4.4711	3.6663	3.6010	3.5371	3.4797	3.2517
82	1.80	14.1023	12.3965	7.8934	8.2164	4.4712	3.6672	3.6014	3.5377	3.4800	3.2517
92.5	2.00	14.1017	12.3953	7.8934	8.2164	4.4709	3.6666	3.6008	3.5370	3.4801	3.2517
120	2.50	14.1023	12.3967	7.8933	8.2169	4.4711	3.6666	3.6003	3.5370	3.4794	3.2517
150	3.00	14.0999	12.3961	7.8934	8.2167	4.4713	3.6666	3.6007	3.5370	3.4792	3.2514
218	4.00	14.1003	12.3953	7.8931	8.2176	4.4711	3.6674	3.5998	3.5363	3.4792	3.2517
300	5.00	14.0977	12.3935	7.8935	8.2178	4.4717	3.6662	3.5999	3.5361	3.4785	3.2513

2.14b. Titration curves.



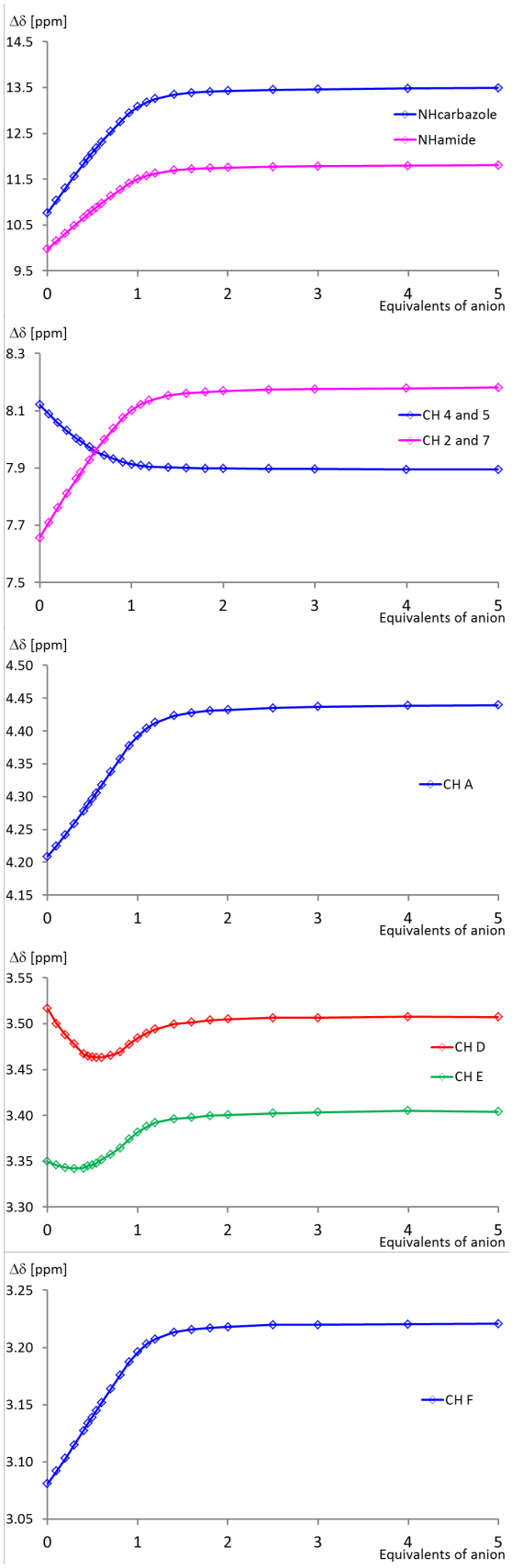
2.15. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **3** in 10% H_2O/DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

2.15a. Raw data:

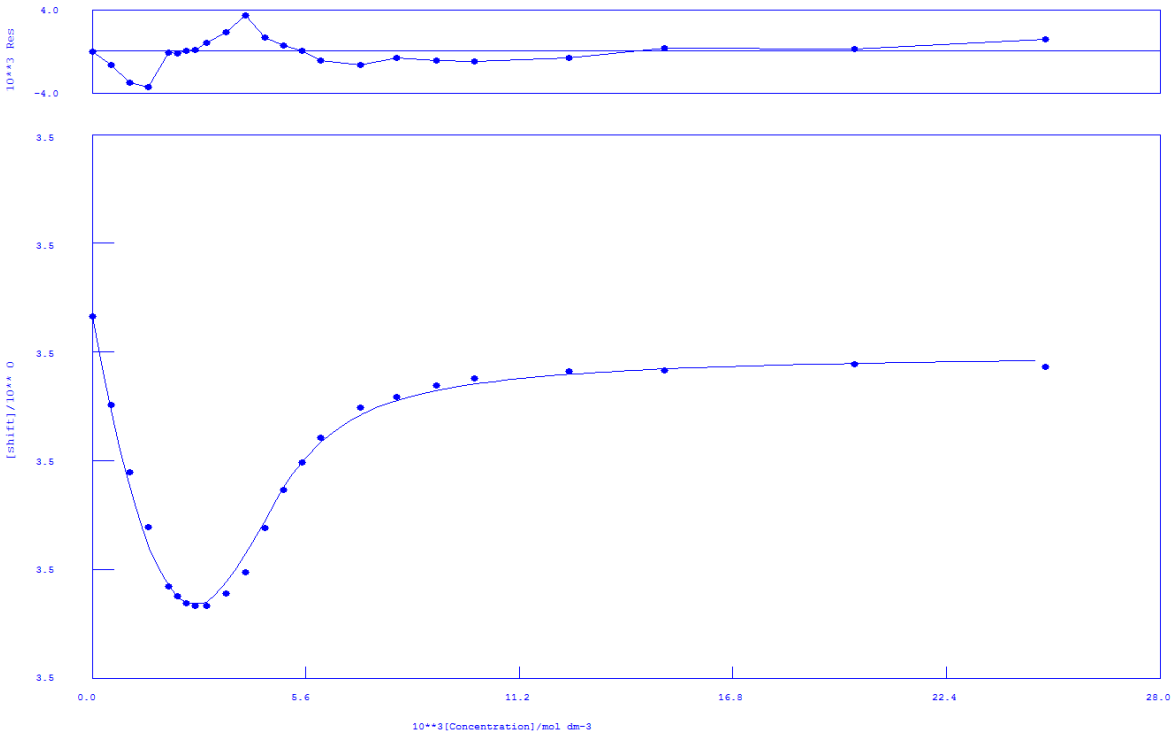


Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	CH A	CH B	CH C	CH D	CH E	CH F
0	0	10.7672	9.9762	8.1207	7.6564	4.2088	overlap	overlap	3.5166	3.3497	3.0810
4	0.10	11.0375	10.1450	8.0884	7.7088	4.2248	overlap	overlap	3.5003	3.3457	3.0920
8	0.20	11.3051	10.3151	8.0582	7.7603	4.2417	overlap	overlap	3.4879	3.3430	3.1031
12	0.29	11.5654	10.4830	8.0302	7.8104	4.2590	overlap	overlap	3.4778	3.3420	3.1147
16.5	0.40	11.8359	10.6566	8.0032	7.8622	4.2782	overlap	overlap	3.4669	3.3426	3.1274
18.5	0.45	11.9540	10.7344	7.9926	7.8849	4.2881	overlap	overlap	3.4650	3.3448	3.1336
20.5	0.50	12.0715	10.8120	7.9824	7.9073	4.2966	overlap	overlap	3.4637	3.3457	3.1389
22.5	0.54	12.1779	10.8830	7.9730	7.9281	4.3059	overlap	overlap	3.4633	3.3476	3.1447
25	0.60	12.3162	10.9754	7.9587	7.9587	4.3176	overlap	overlap	3.4632	3.3518	3.1516
29.5	0.70	12.5409	11.1292	7.9446	7.9988	4.3380	overlap	overlap	3.4656	3.3575	3.1639
34	0.80	12.7460	11.2684	7.9314	8.0378	4.3576	overlap	overlap	3.4694	3.3645	3.1758
38.5	0.90	12.9418	11.4048	7.9203	8.0752	4.3775	overlap	overlap	3.4776	3.3741	3.1873
43	1.00	13.0791	11.5022	7.9131	8.1017	4.3926	overlap	overlap	3.4846	3.3819	3.1961
47.5	1.10	13.1825	11.5756	7.9089	8.1221	4.4042	overlap	overlap	3.4897	3.3877	3.2032
52	1.20	13.2571	11.6290	7.9050	8.1359	4.4130	overlap	overlap	3.4942	3.3921	3.2073
62	1.40	13.3468	11.6933	7.9017	8.1532	4.4232	overlap	overlap	3.4997	3.3963	3.2133
71.5	1.60	13.3878	11.7238	7.9002	8.1611	4.4280	overlap	overlap	3.5017	3.3976	3.2158
82	1.80	13.4121	11.7419	7.8987	8.1657	4.4310	overlap	overlap	3.5038	3.3998	3.2171
92.5	2.00	13.4287	11.7543	7.8987	8.1689	4.4324	overlap	overlap	3.5051	3.4005	3.2181
120	2.50	13.4504	11.7707	7.8975	8.1736	4.4350	overlap	overlap	3.5065	3.4022	3.2198
150	3.00	13.4642	11.7826	7.8966	8.1757	4.4371	overlap	overlap	3.5066	3.4035	3.2199
218	4.00	13.4802	11.7947	7.8951	8.1789	4.4386	overlap	overlap	3.5077	3.4051	3.2202
300	5.00	13.4895	11.8039	7.8948	8.1809	4.4395	overlap	overlap	3.5073	3.4040	3.2207

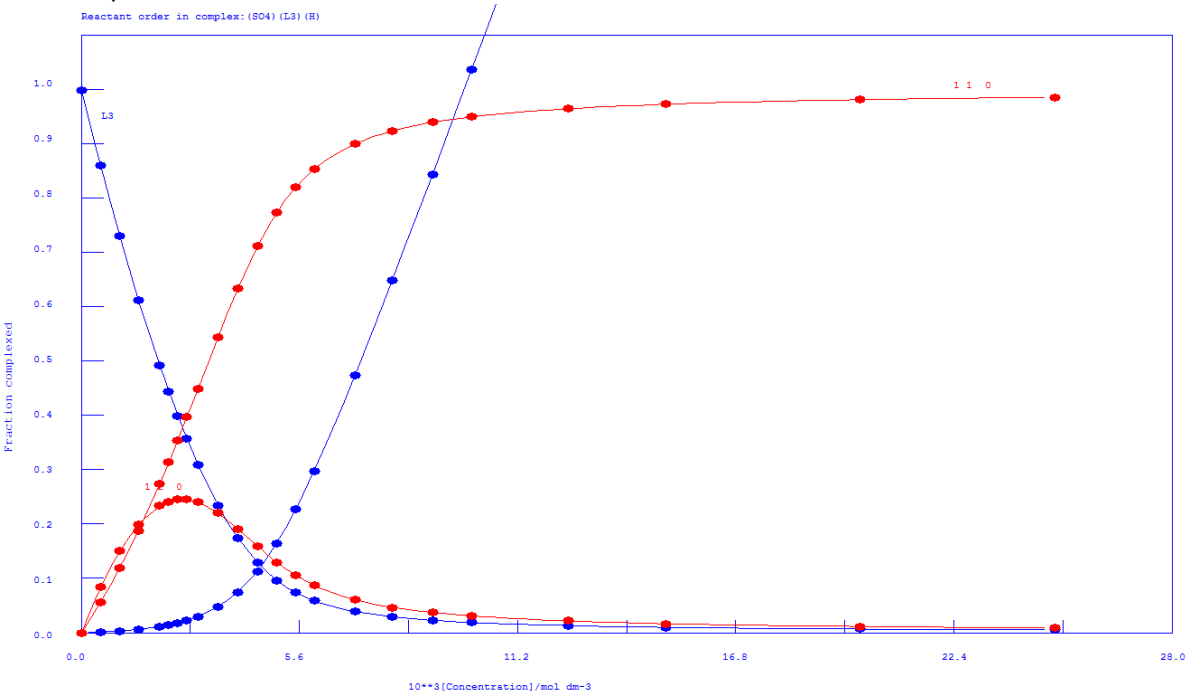
2.15b. Titration curves.



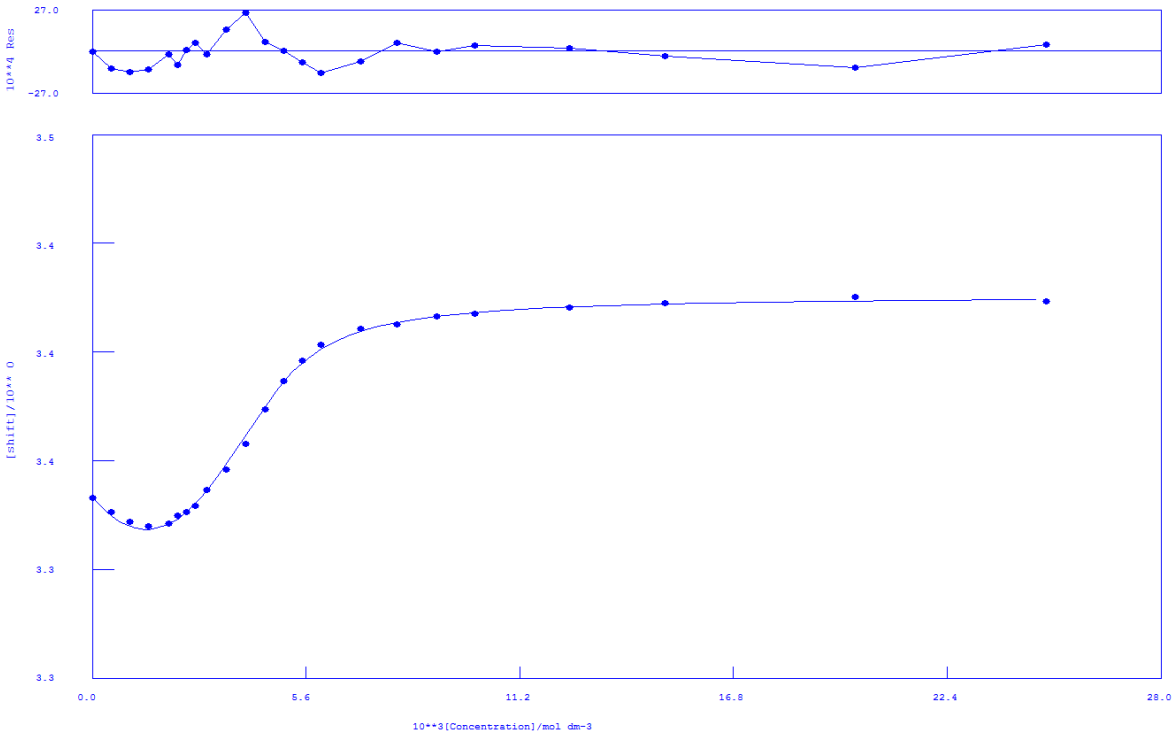
2.15c. Data fitting. Fitting of (2:1 & 1:1) model to the data for CH D protons using WinEQNMR. $\log\beta_1$= 3.99±0.05; $\log\beta_2$= 6.23±0.05 $\delta_{max(2:1)}$= 3.312±0.0037 ppm; $\delta_{max(1:1)}$= 3.510±0.00095 ppm.



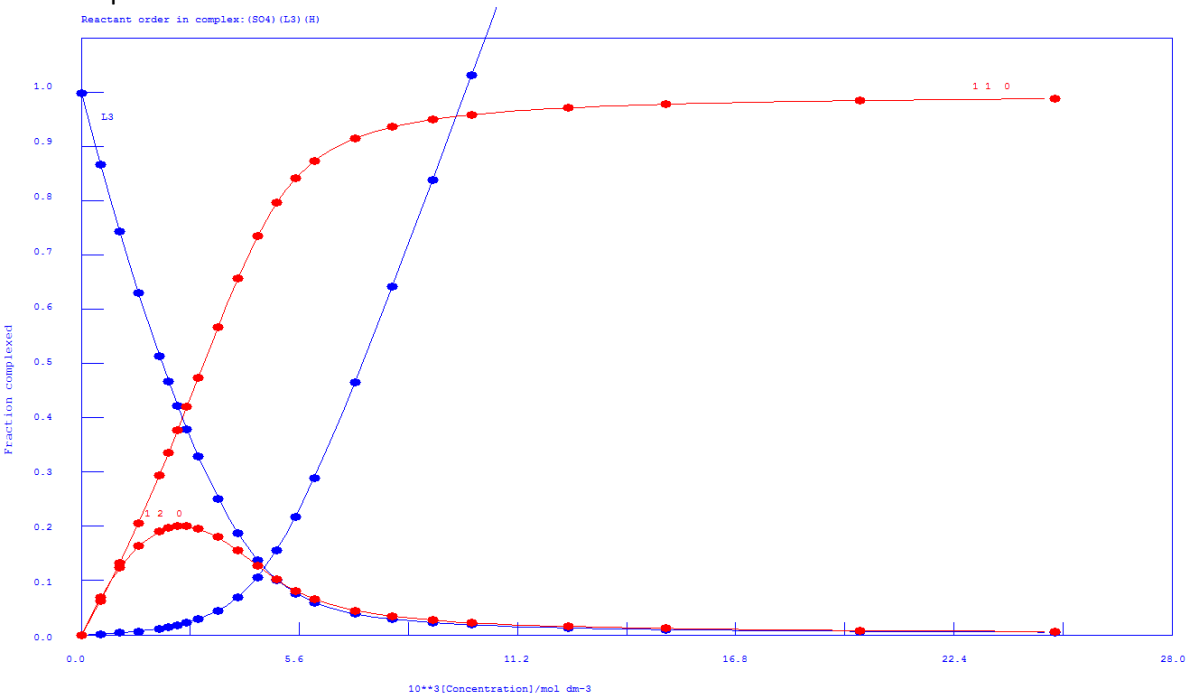
Simulated speciation:



Fitting of (2:1 & 1:1) model to the data for CH E protons using WinEQNMR.
$\log\beta_1$= 4.00±0.04; $\log\beta_2$= 6.10±0.04 $\delta_{max(2:1)}$= 3.226±0.0019 ppm; $\delta_{max(1:1)}$= 3.406±0.00071 ppm.

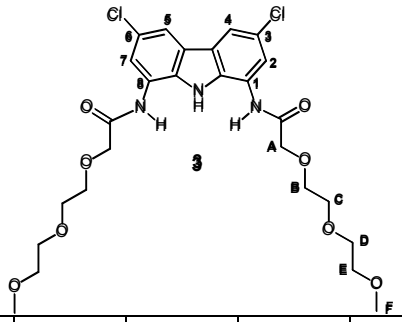


Simulated speciation:



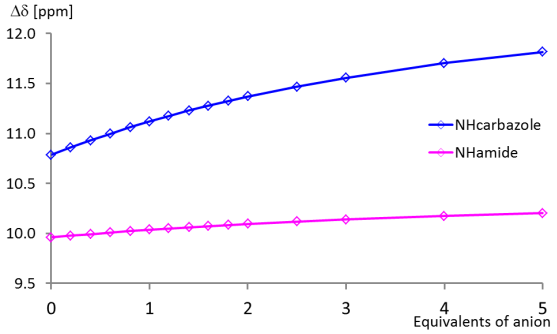
2.16. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **3** in DMSO-d_6 with 0.075M TBACl.

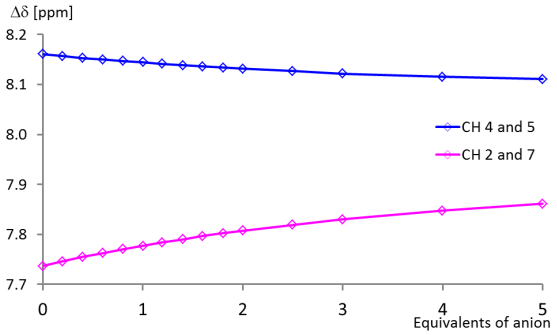
2.16a. Raw data:

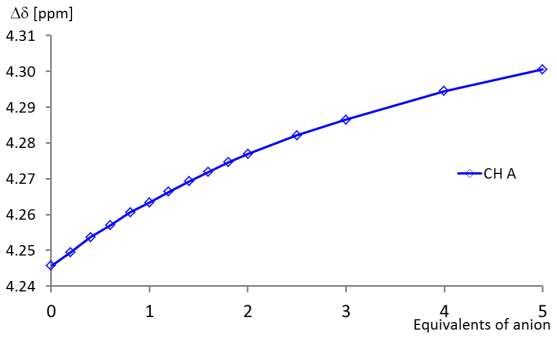


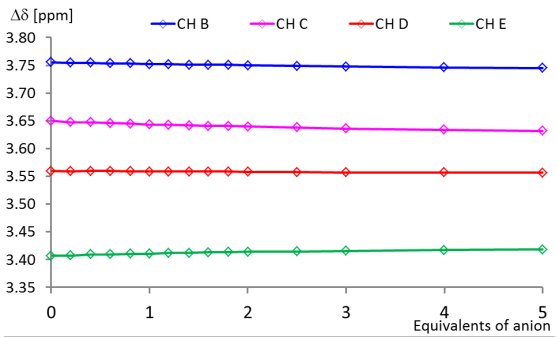
Added volume of titrant solution [µl]	Equivalents of TBACl	NH (carbazole)	NH (amide)	CH-4 and 5	CH-2 and 7	CH A	CH B	CH C	CH D	CH E	CH F
0	0	10.7850	9.9590	8.1608	7.7366	4.2457	3.7556	3.6498	3.5597	3.4068	3.1446
8	0.20	10.8594	9.9768	8.1570	7.7455	4.2495	3.7545	3.6475	3.5592	3.4073	3.1470
16.5	0.40	10.9309	9.9918	8.1531	7.7547	4.2537	3.7547	3.6472	3.5597	3.4091	3.1494
25	0.60	10.9968	10.0074	8.1499	7.7624	4.2570	3.7537	3.6458	3.5593	3.4095	3.1516
34	0.80	11.0623	10.0232	8.1470	7.7704	4.2606	3.7533	3.6448	3.5591	3.4102	3.1533
43	1.00	11.1206	10.0383	8.1448	7.7772	4.2634	3.7521	3.6434	3.5586	3.4104	3.1545
52	1.20	11.1746	10.0486	8.1412	7.7838	4.2664	3.7519	3.6428	3.5585	3.4117	3.1569
62	1.40	11.2290	10.0618	8.1388	7.7904	4.2693	3.7510	3.6420	3.5583	3.4121	3.1586
71.5	1.60	11.2768	10.0720	8.1361	7.7963	4.2719	3.7508	3.6408	3.5583	3.4127	3.1602
82	1.80	11.3266	10.0845	8.1340	7.8025	4.2746	3.7507	3.6407	3.5586	3.4136	3.1617
92.5	2.00	11.3709	10.0938	8.1314	7.8078	4.2770	3.7500	3.6397	3.5582	3.4141	3.1631
120	2.50	11.4685	10.1184	8.1269	7.8191	4.2821	3.7489	3.6380	3.5577	3.4147	3.1657
150	3.00	11.5576	10.1376	8.1216	7.8301	4.2865	3.7477	3.6362	3.5572	3.4156	3.1691
218	4.00	11.7026	10.1744	8.1156	7.8476	4.2945	3.7464	3.6341	3.5570	3.4173	3.1728
300	5.00	11.8160	10.2029	8.1105	7.8610	4.3006	3.7454	3.6317	3.5562	3.4184	3.1760

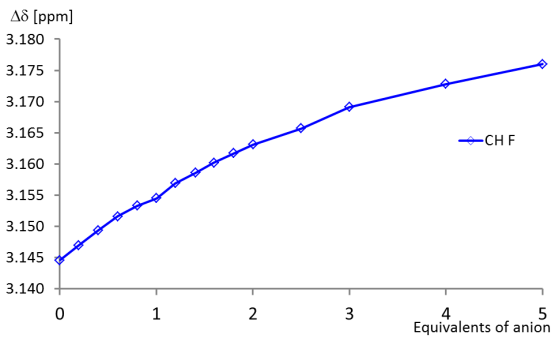
2.16b. Titration curves.



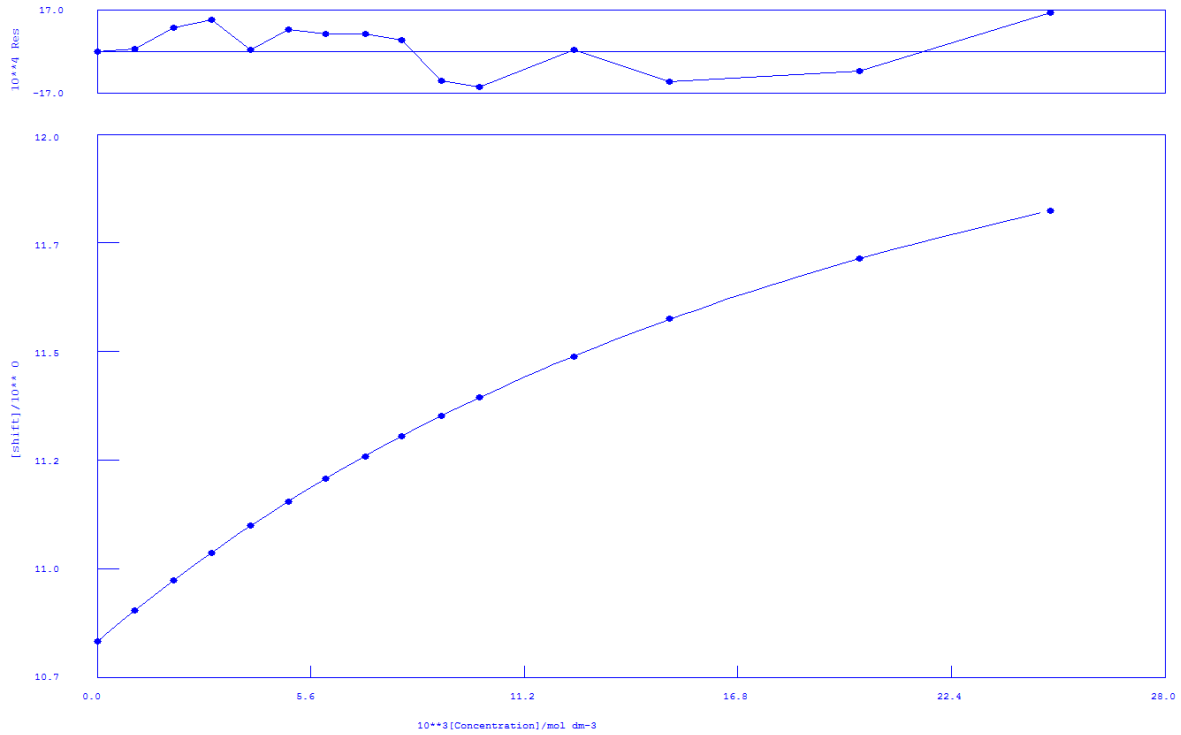




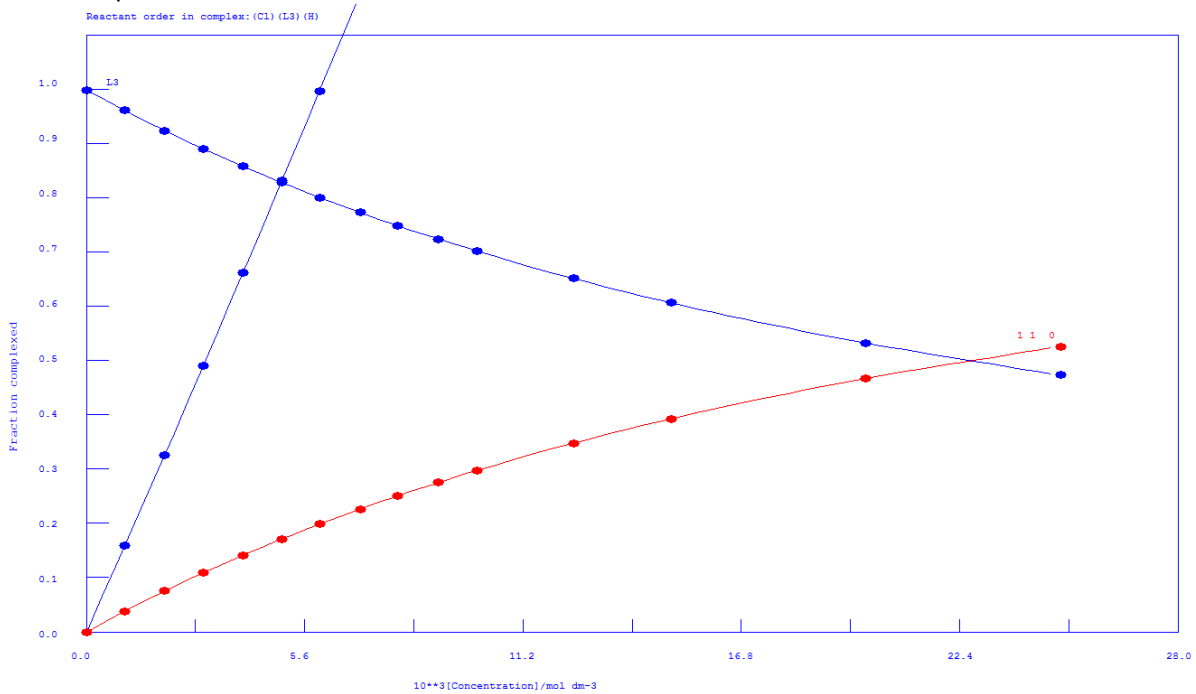




2.16c. Data fitting. Fitting of (1:1) model to the data for $NH_{carbazole}$ protons using WinEQNMR. $\log\beta_1$=1.70±0.0022; $\delta_{max(1:1)}$=12.745 ±0.0055 ppm

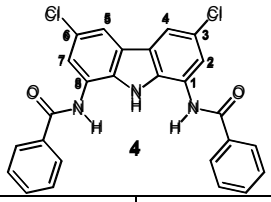


Simulated speciation:



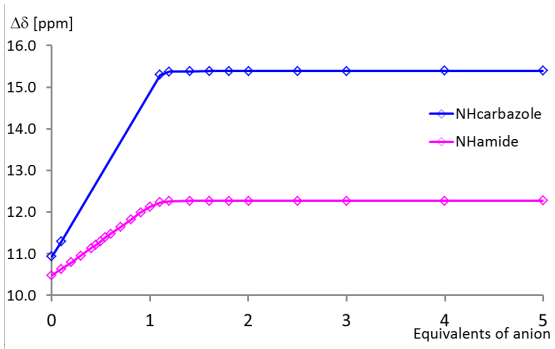
2.17. ^{1}H NMR titration of 0.002M solution of diamidocarbazole **4** in DMSO-d_6 with 0.03M $(TBA)_2SO_4$.

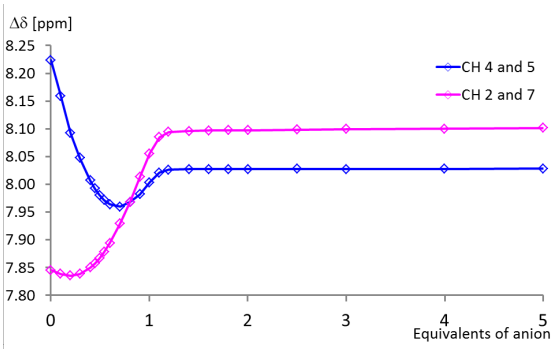
2.17a. Raw data:

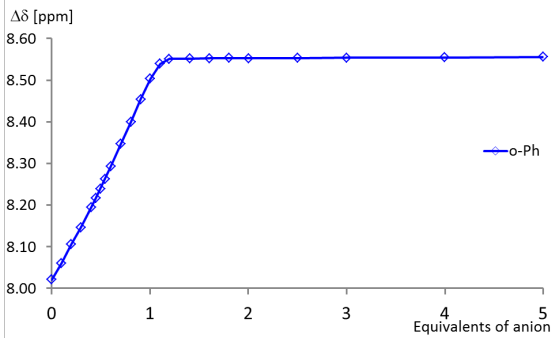


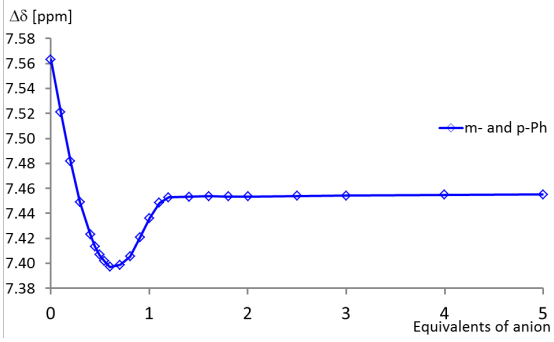
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*orto*-Ph	*Meta*- and *para*-Ph
0	0.00	10.9264	10.4760	8.2236	7.8455	8.0210	7.5632
4	0.10	11.2943	10.6314	8.1591	7.8385	8.0607	7.5213
8	0.20	broad	10.7936	8.0922	7.8355	8.1059	7.4817
12	0.29	broad	10.9525	8.0476	7.8385	8.1456	7.4492
16.5	0.40	broad	11.1324	8.0068	7.8498	8.1942	7.4232
18.5	0.45	broad	11.2086	7.9922	7.8573	8.2167	7.4135
20.5	0.50	broad	11.2884	7.9803	7.8666	8.2392	7.4069
22.5	0.54	broad	11.3862	7.9717	7.8779	8.2629	7.4020
25	0.60	broad	11.4755	7.9637	7.8944	8.2928	7.3972
29.5	0.70	broad	11.6452	7.9598	7.9296	8.3474	7.3988
34	0.80	broad	11.8180	7.9679	7.9679	8.3995	7.4054
38.5	0.90	broad	11.9903	7.9823	8.0134	8.4539	7.4206
43	1.00	broad	12.1299	8.0032	8.0551	8.5036	7.4361
47.5	1.10	15.2940	12.2312	8.0210	8.0852	8.5392	7.4483
52	1.20	15.3702	12.2618	8.0262	8.0945	8.5508	7.4528
62	1.40	15.3817	12.2656	8.0272	8.0960	8.5516	7.4533
72	1.61	15.3843	12.2685	8.0271	8.0967	8.5529	7.4538
82	1.80	15.3862	12.2692	8.0272	8.0973	8.5532	7.4535
92.5	2.00	15.3860	12.2685	8.0270	8.0977	8.5526	7.4534
120	2.50	15.3880	12.2686	8.0276	8.0985	8.5535	7.4539
150	3.00	15.3891	12.2694	8.0273	8.0994	8.5540	7.4541
218	4.00	15.3904	12.2702	8.0276	8.1002	8.5544	7.4549
300	5.00	15.3929	12.2709	8.0282	8.1018	8.5560	7.4552

2.17b. Titration curves.



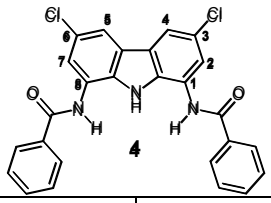






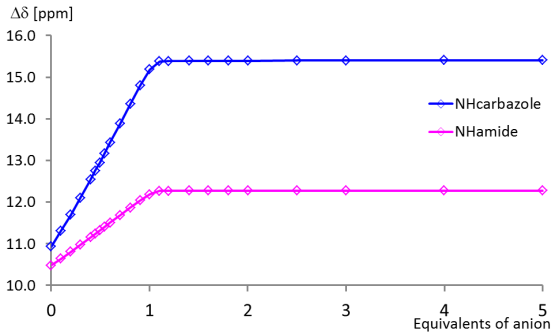
2.18. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **4** in DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

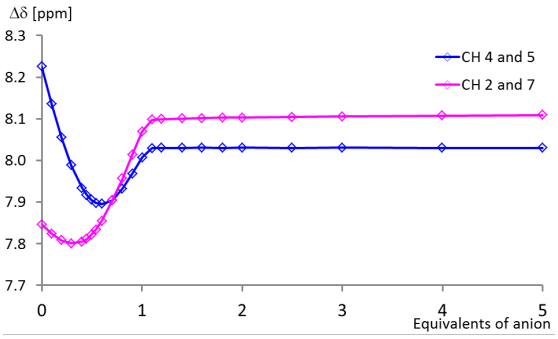
2.18a. Raw data:

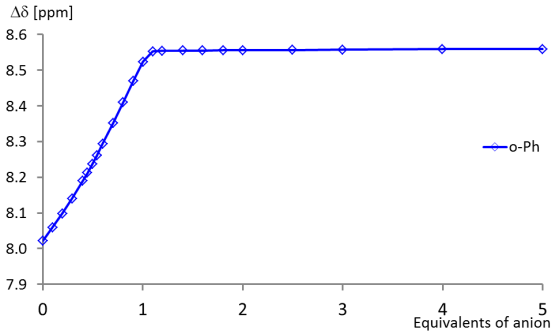


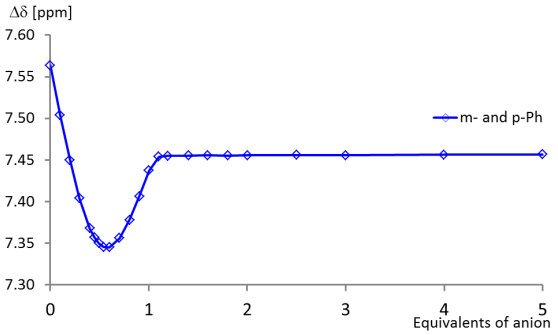
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*orto*-Ph	*Meta*- and *para*-Ph
0	0.00	10.9318	10.4803	8.2254	7.8464	8.0216	7.5637
4	0.10	11.3091	10.6414	8.1361	7.8245	8.0595	7.5038
8	0.20	11.6938	10.8049	8.0557	7.8085	8.0985	7.4500
12	0.29	12.0930	10.9690	7.9884	7.8007	8.1404	7.4043
16.5	0.40	12.5387	11.1532	7.9339	7.8051	8.1901	7.3681
18.5	0.45	12.7548	11.2341	7.9169	7.8112	8.2126	7.3572
20.5	0.50	12.9380	11.3175	7.9053	7.8211	8.2361	7.3499
22.5	0.54	13.1599	11.4010	7.8978	7.8341	8.2611	7.3455
25	0.60	13.4330	11.5060	7.8957	7.8549	8.2938	7.3452
29.5	0.70	13.8911	11.6883	7.9038	7.9038	8.3510	7.3562
34	0.80	14.3514	11.8670	7.9325	7.9566	8.4106	7.3781
38.5	0.90	14.7943	12.0367	7.9684	8.0142	8.4693	7.4064
43	1.00	15.1854	12.1864	8.0071	8.0693	8.5233	7.4372
47.5	1.10	15.3768	12.2646	8.0292	8.0977	8.5525	7.4539
52	1.20	15.3886	12.2696	8.0303	8.0997	8.5543	7.4549
62	1.40	15.3935	12.2717	8.0302	8.1009	8.5550	7.4552
71.5	1.60	15.3948	12.2727	8.0305	8.1013	8.5553	7.4555
82	1.80	15.3966	12.2731	8.0298	8.1025	8.5563	7.4553
92.5	2.00	15.3966	12.2727	8.0308	8.1026	8.5557	7.4555
120	2.50	15.3995	12.2748	8.0303	8.1043	8.5571	7.4559
150	3.00	15.4007	12.2746	8.0305	8.1054	8.5573	7.4558
218	4.00	15.4045	12.2761	8.0302	8.1073	8.5590	7.4562
300	5.00	15.4080	12.2772	8.0300	8.1091	8.5595	7.4568

2.18b. Titration curves.



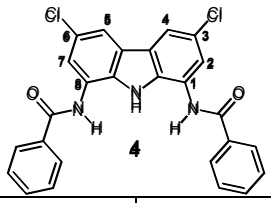






2.19. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **4** in 10% H_2O/DMSO-d_6 with 0.075M $(TBA)_2SO_4$.

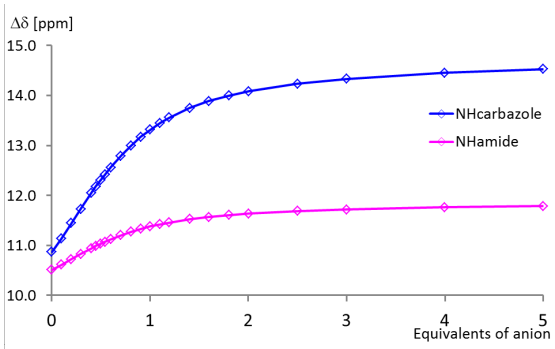
2.19a. Raw data:

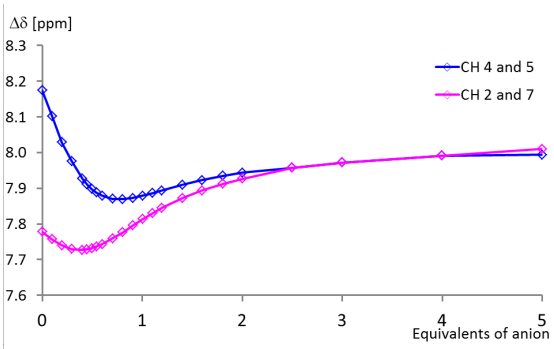


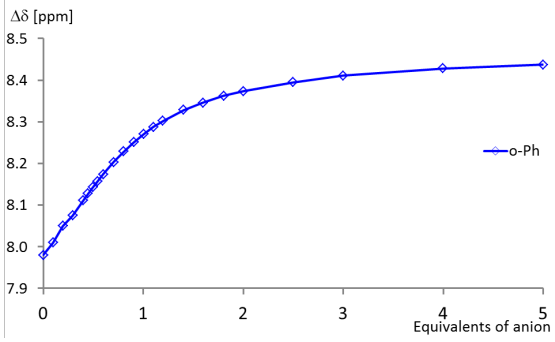
4

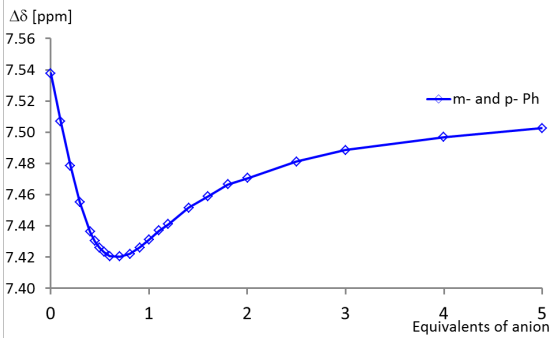
Added volume of titrant solution [µl]	Equivalents of $(TBA)_2SO_4$	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*orto*-Ph	*meta*- and *para*-Ph
0	0	10.8687	10.5110	8.1745	7.9796	7.7779	7.5377
4	0.10	11.1409	10.6124	8.1026	8.0094	7.7571	7.5070
8	0.20	11.4421	10.7206	8.0283	8.0497	7.7402	7.4786
12	0.29	11.7296	10.8261	7.9763	8.0746	7.7293	7.4552
16.5	0.40	12.0442	10.9381	7.9272	8.1112	7.7273	7.4363
18.5	0.45	12.1786	10.9861	7.9105	8.1274	7.7286	7.4304
20.5	0.50	12.3003	11.0300	7.8979	8.1426	7.7319	7.4260
22.5	0.54	12.4168	11.0713	7.8879	8.1567	7.7365	7.4233
25	0.60	12.5596	11.1206	7.8788	8.1737	7.7431	7.4206
29.5	0.70	12.7882	11.1995	7.8705	8.2028	7.7593	7.4203
34	0.80	12.9949	11.2695	7.8694	8.2283	7.7766	7.4221
38.5	0.90	13.1701	11.3294	7.8729	8.2510	7.7956	7.4260
43	1.00	13.3181	11.3784	7.8791	8.2705	7.8134	7.4312
47.5	1.10	13.4488	11.4234	7.8862	8.2878	7.8301	7.4369
52	1.20	13.5559	11.4585	7.8935	8.3019	7.8448	7.4410
62	1.40	13.7484	11.5235	7.9098	8.3285	7.8730	7.4515
72	1.61	13.8854	11.5681	7.9225	8.3459	7.8939	7.4588
82	1.80	13.9995	11.6059	7.9347	8.3622	7.9124	7.4665
92.5	2.00	14.0826	11.6340	7.9442	8.3737	7.9270	7.4707
120	2.50	14.2367	11.6852	7.9576	8.3953	7.9576	7.4812
150	3.00	14.3343	11.7189	7.9723	8.4108	7.9723	7.4885
218	4.00	14.4564	11.7607	7.9911	8.4284	7.9911	7.4968
300	5.00	14.5269	11.7862	7.9943	8.4375	8.0102	7.5026

2.19b. Titration curves.

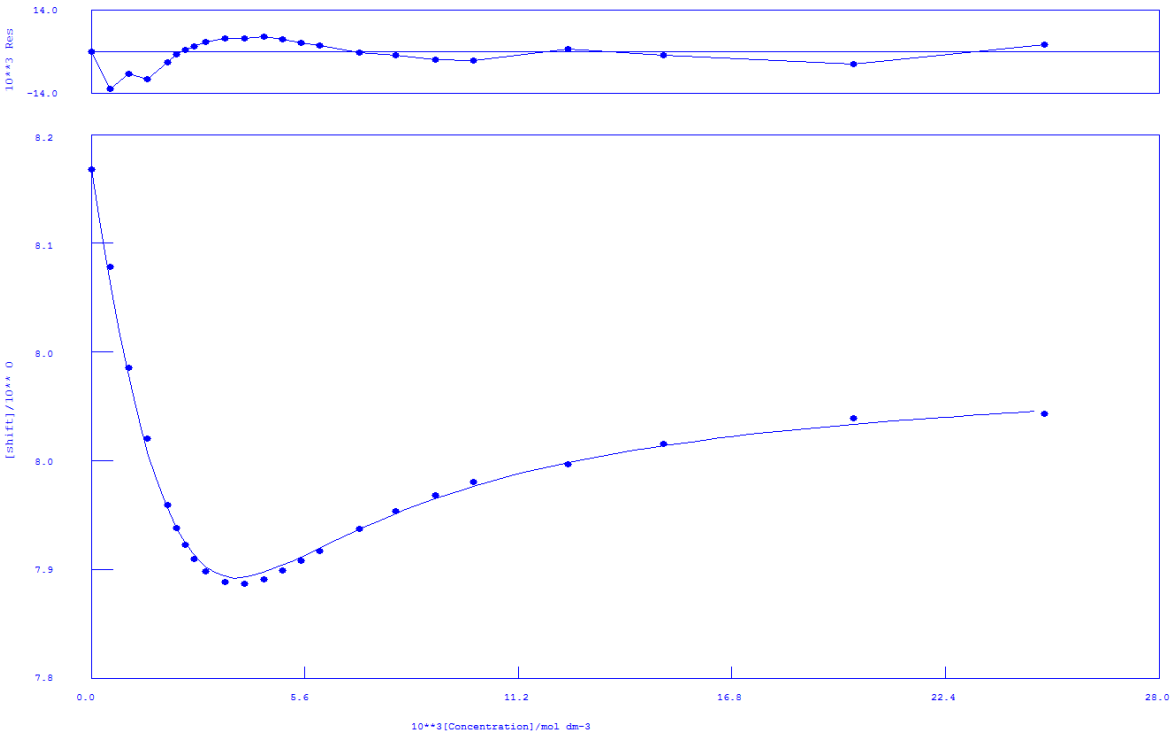




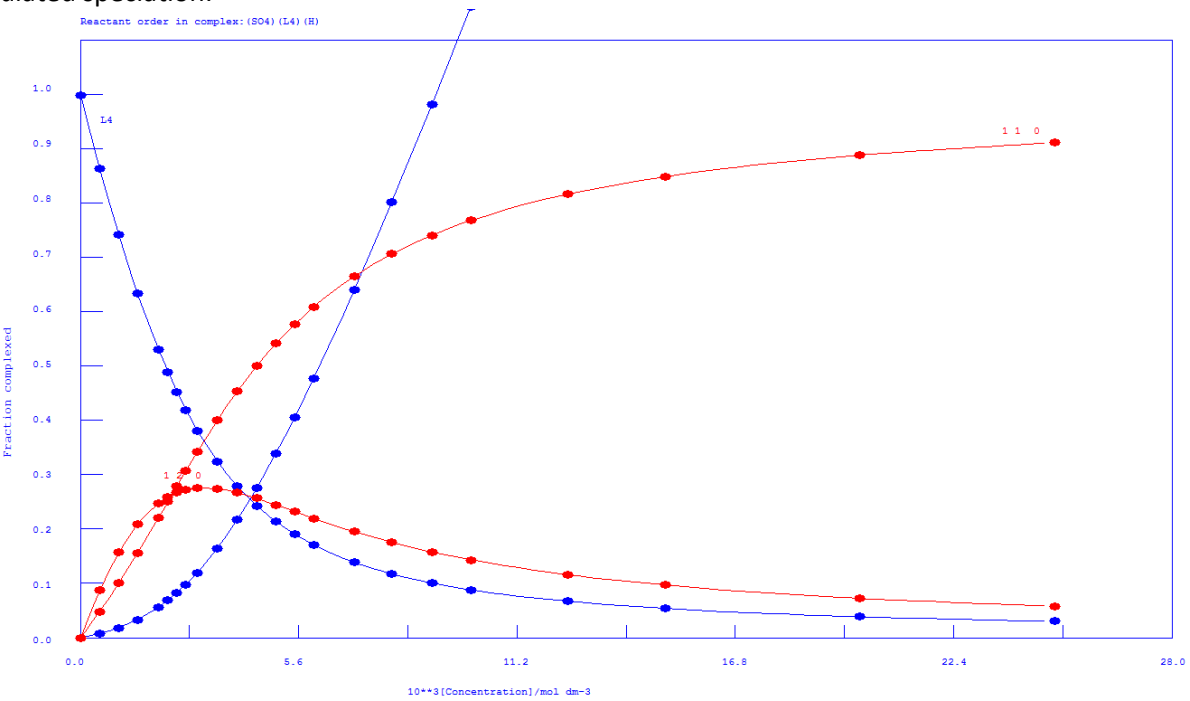




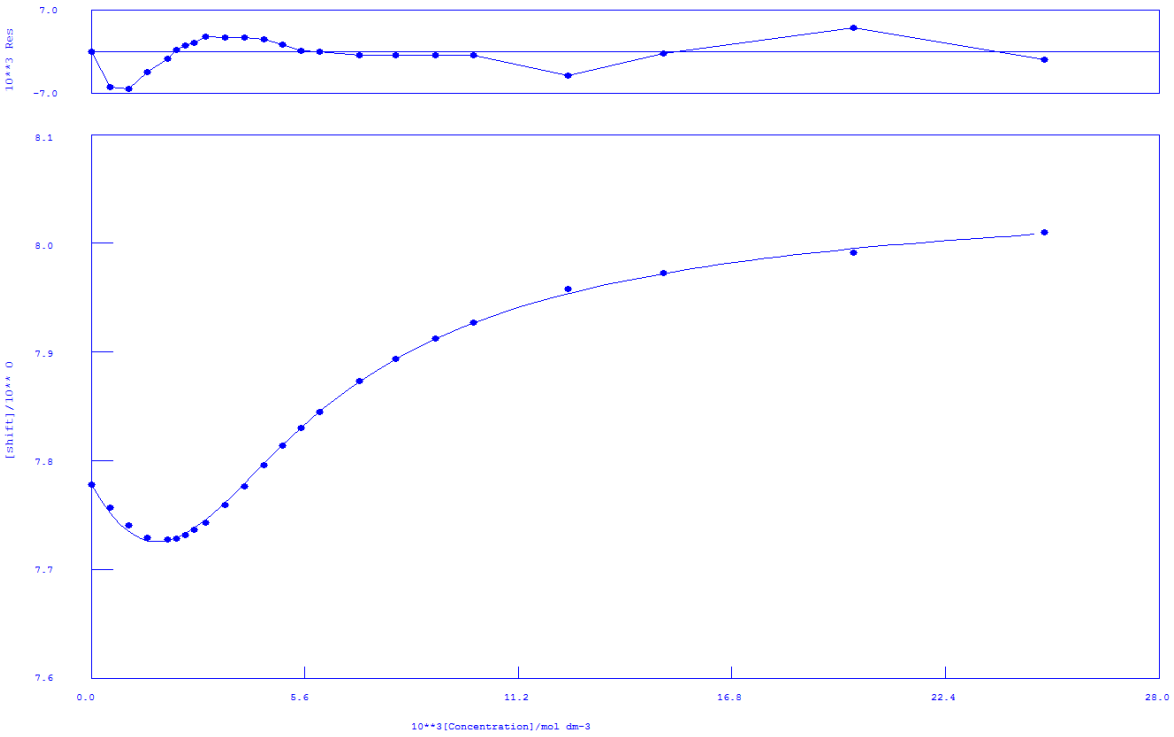
2.19c. Data fitting. Fitting of (2:1 & 1:1) model to the data for CH 4 and 5 protons using WinEQNMR. $\log\beta_1$= 3.18±0.02; $\log\beta_2$= 5.50±0.02 $\delta_{max(2:1)}$= 7.289±0.0061 ppm; $\delta_{max(1:1)}$= 8.035±0.00049 ppm.



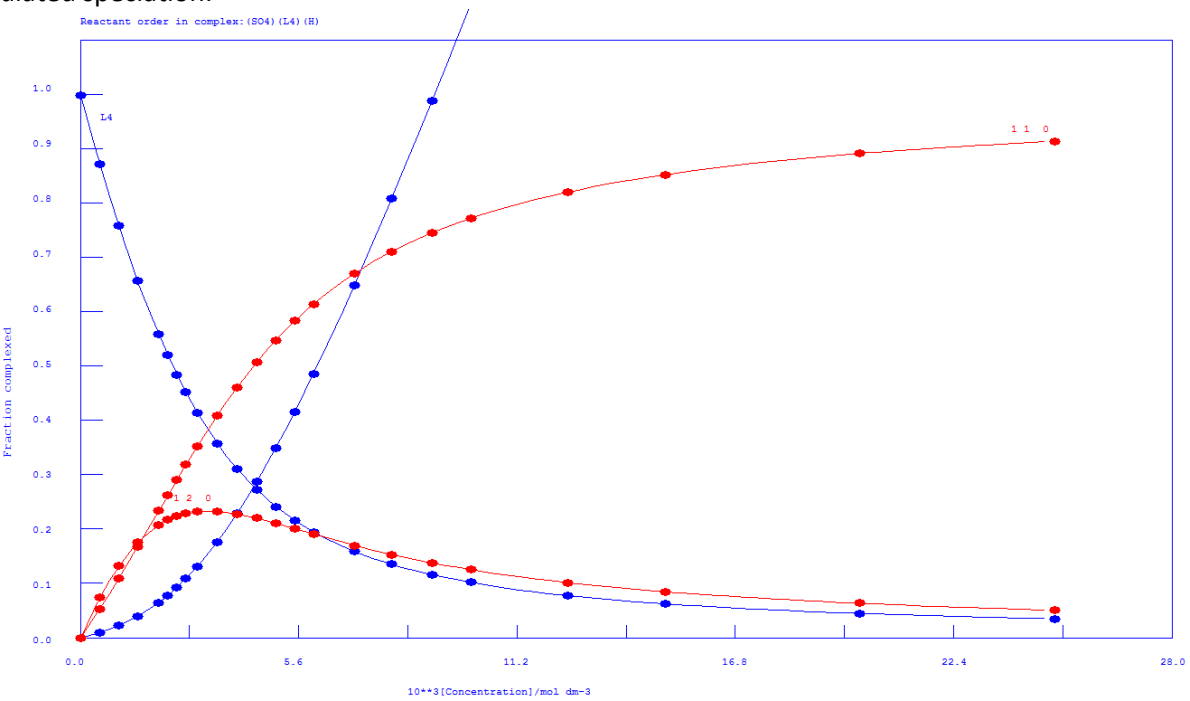
Simulated speciation:



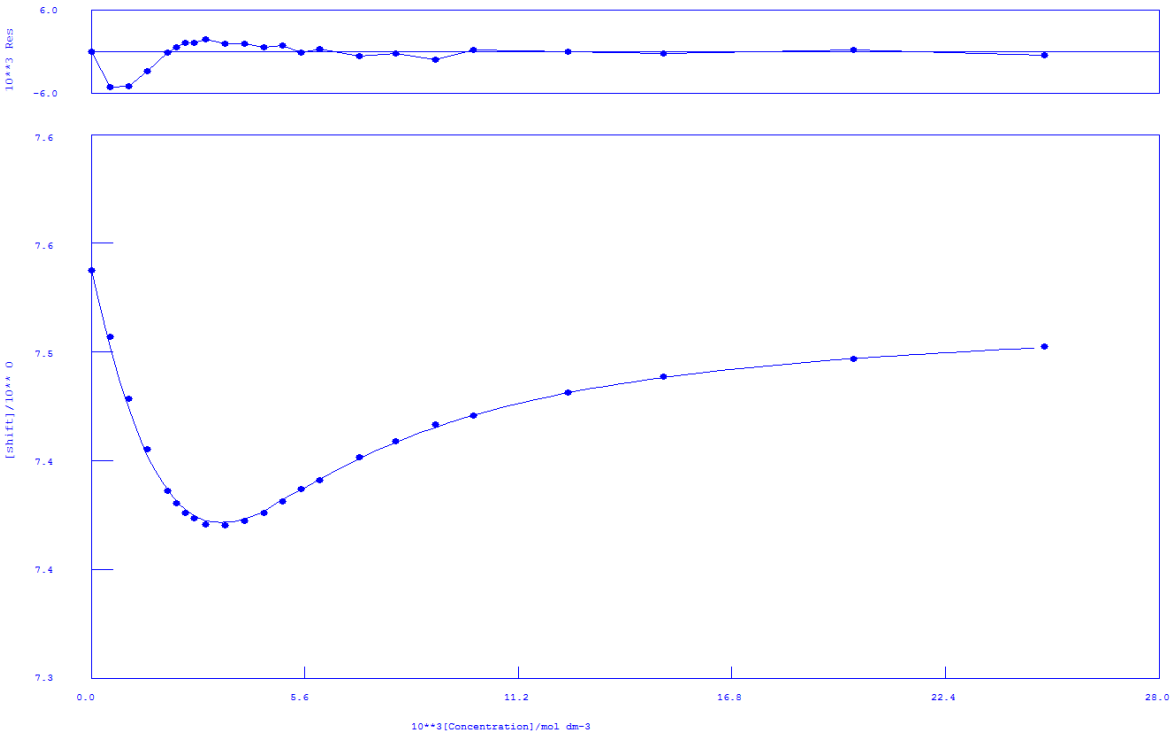
Fitting of (2:1 & 1:1) model to the data for CH 2 and 7 protons using WinEQNMR.
$\log\beta_1$= 3.11±0.01 $\log\beta_2$= 5.32±0.02 $\delta_{max(2:1)}$= 7.212±0.0031 ppm; $\delta_{max(1:1)}$= 8.061±0.0025 ppm.



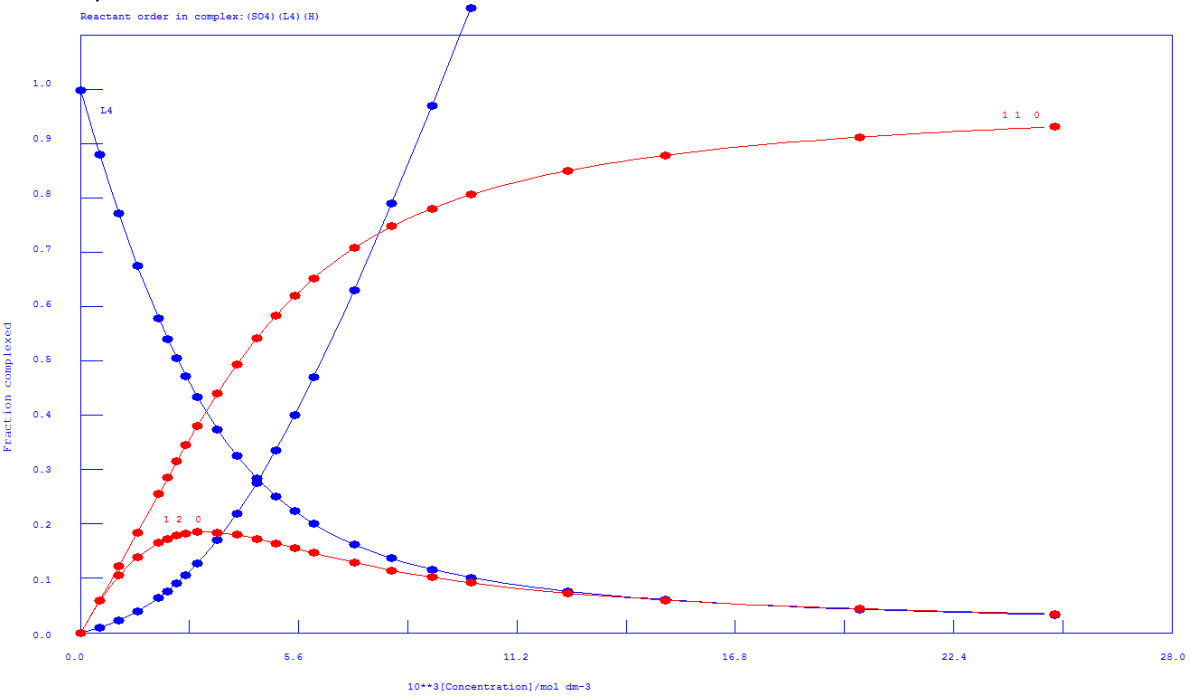
Simulated speciation:



Fitting of (2:1 & 1:1) model to the data for *m*- and *p*-Ph protons using WinEQNMR.
$\log\beta_1$= 3.14±0.02 $\log\beta_2$= 5.19±0.02 $\delta_{max(2:1)}$= 6.953±0.0023 ppm; $\delta_{max(1:1)}$= 7.520±0.0018 ppm.

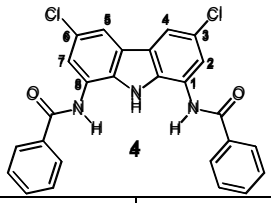


Simulated speciation:



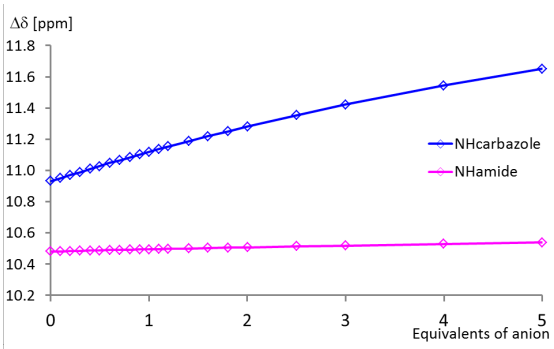
2.20. ^{1}H NMR titration of 0.005M solution of diamidocarbazole **4** in DMSO-d_6 with 0.075M TBACl.

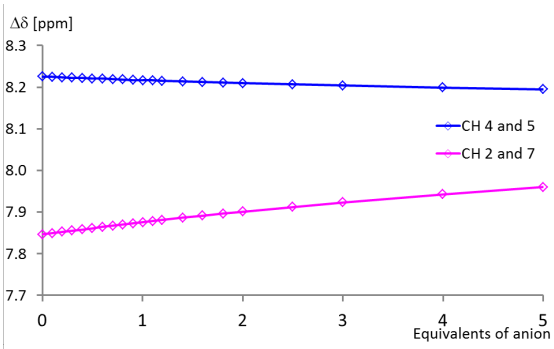
2.20a. Raw data:

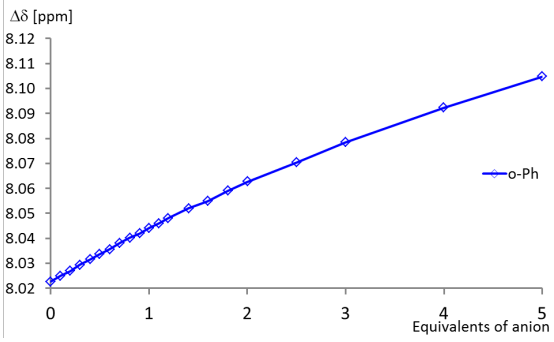


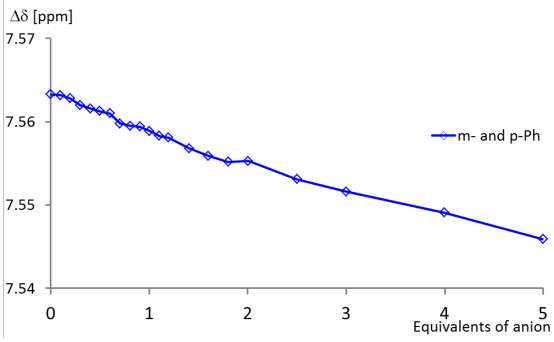
Added volume of titrant solution [µl]	Equivalents of TBACl	$NH_{(carbazole)}$	$NH_{(amide)}$	CH-4 and 5	CH-2 and 7	*orto*-Ph	*Meta*- and *para*-Ph
0	0.00	10.9320	10.4804	8.2254	7.8462	8.0227	7.5633
4	0.10	10.9510	10.4815	8.2247	7.8494	8.0249	7.5632
8	0.20	10.9703	10.4827	8.2234	7.8524	8.0270	7.5628
12	0.29	10.9883	10.4845	8.2227	7.8551	8.0294	7.5620
16.5	0.40	11.0097	10.4863	8.2219	7.8584	8.0316	7.5616
20.5	0.50	11.0271	10.4869	8.2206	7.8612	8.0337	7.5613
25	0.60	11.0484	10.4902	8.2205	7.8646	8.0356	7.5610
29.5	0.70	11.0660	10.4905	8.2193	7.8674	8.0381	7.5598
34	0.80	11.0843	10.4920	8.2184	7.8702	8.0402	7.5595
38.5	0.90	11.1023	10.4939	8.2175	7.8730	8.0420	7.5594
43	1.00	11.1196	10.4947	8.2165	7.8756	8.0441	7.5589
47.5	1.10	11.1365	10.4957	8.2162	7.8784	8.0460	7.5583
52	1.20	11.1532	10.4972	8.2154	7.8810	8.0481	7.5581
62	1.40	11.1879	10.4992	8.2135	7.8864	8.0520	7.5568
71.5	1.60	11.2185	10.5027	8.2125	7.8911	8.0549	7.5559
82	1.80	11.2503	10.5051	8.2110	7.8963	8.0590	7.5552
92.5	2.00	11.2818	10.5076	8.2098	7.9013	8.0627	7.5553
120	2.50	11.3537	10.5137	8.2071	7.9125	8.0704	7.5531
150	3.00	11.4219	10.5186	8.2040	7.9235	8.0784	7.5516
218	4.00	11.5441	10.5295	8.1993	7.9426	8.0923	7.5491
300	5.00	11.6520	10.5376	8.1948	7.9603	8.1048	7.5459

2.20b. Titration curves.

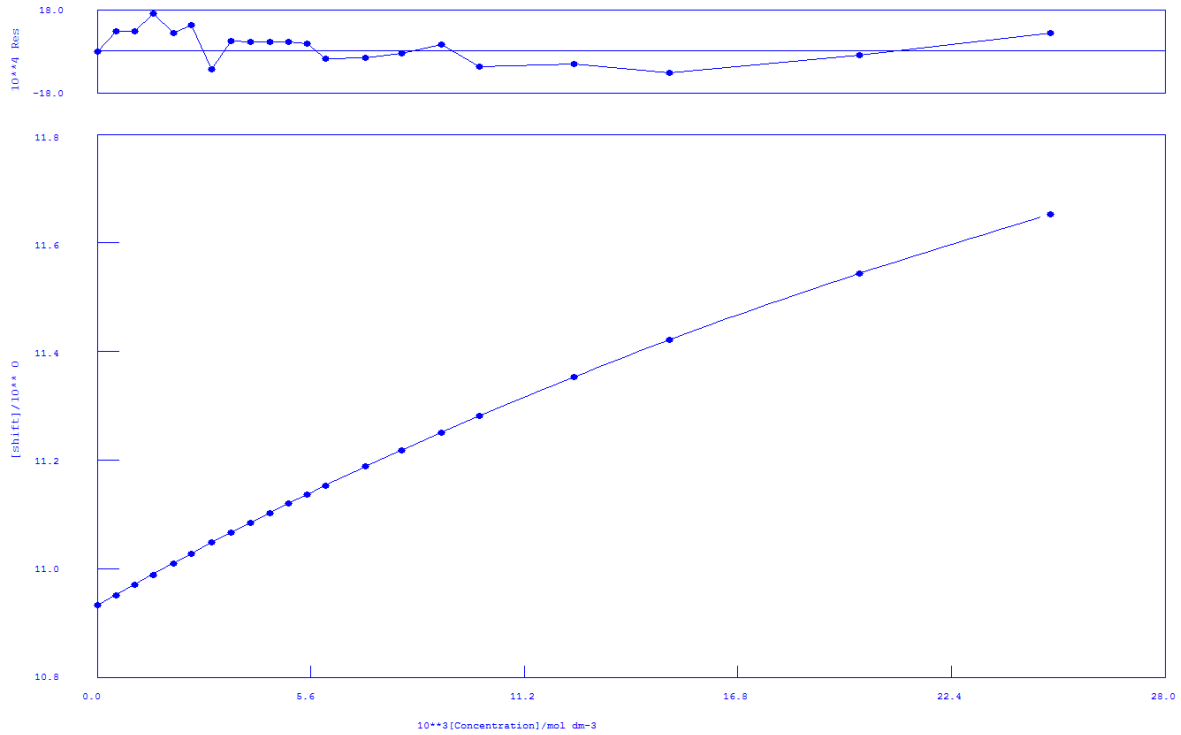




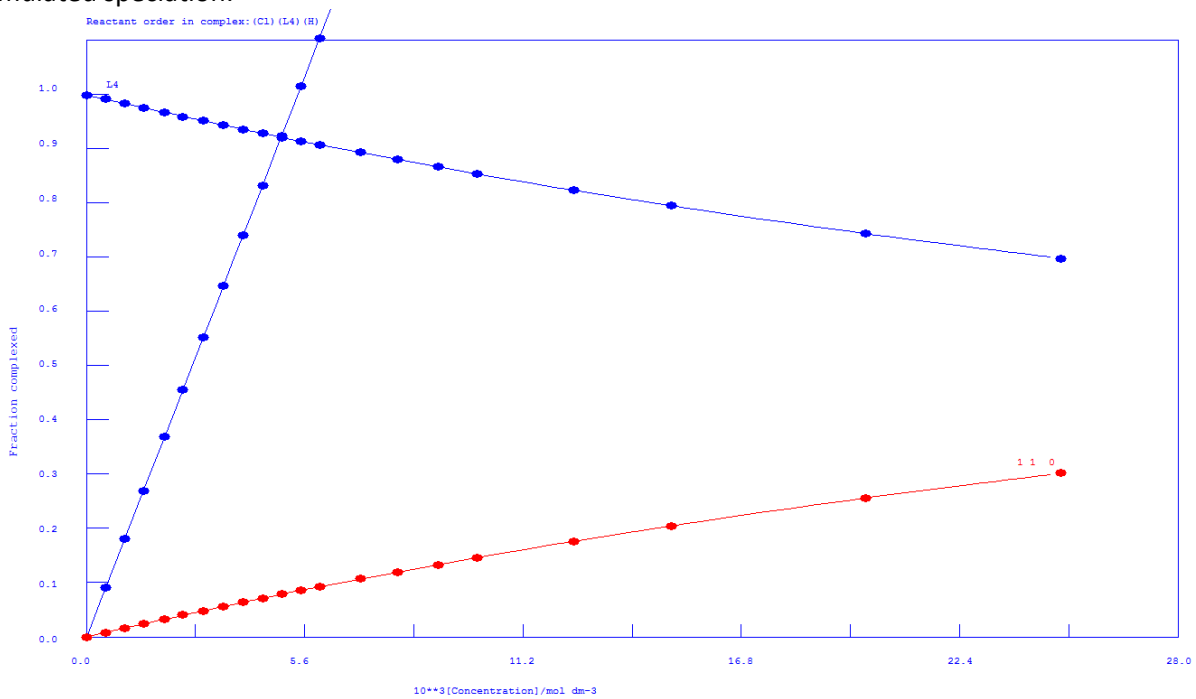




2.20c. Data fitting. Fitting of (1:1) model to the data for $NH_{carbazole}$ protons using WinEQNMR. $\log\beta_1 = 1.26 \pm 0.00049$; $\delta_{max(1:1)} = 13.317 \pm 0.019$ ppm

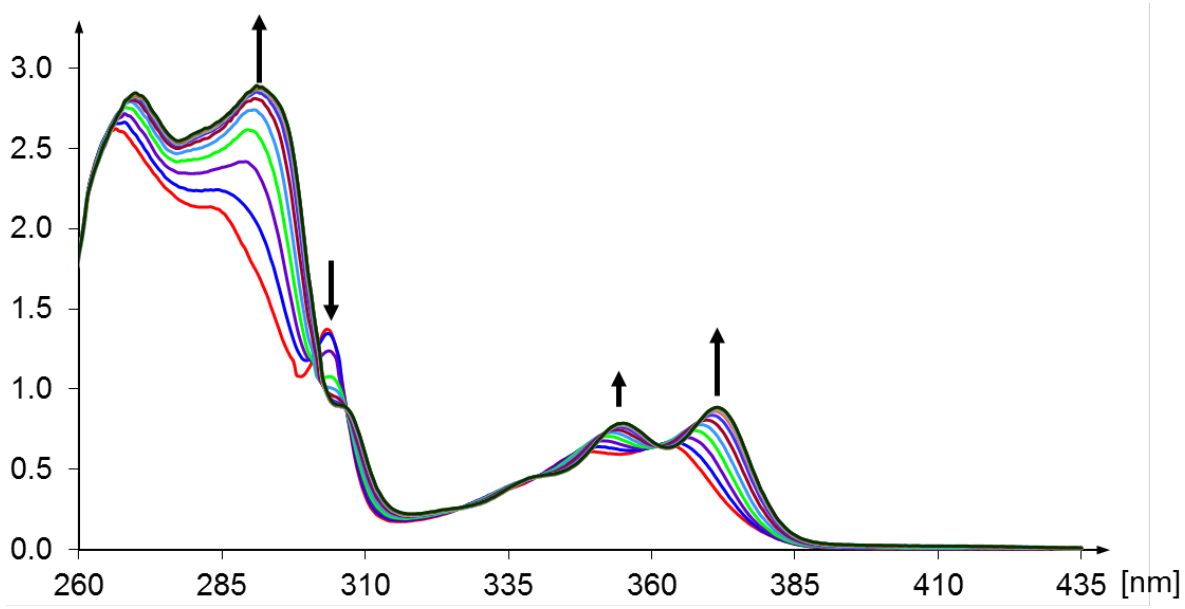


Simulated speciation:

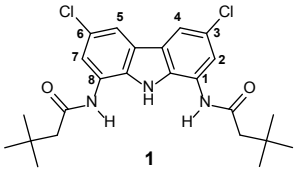


2.21. UV-Vis titration of 0.0001M solution of diamidocarbazole **1** in DMSO-d_6 with 0.0075M $(TBA)_2SO_4$

2.21a. UV-Vis spectra.

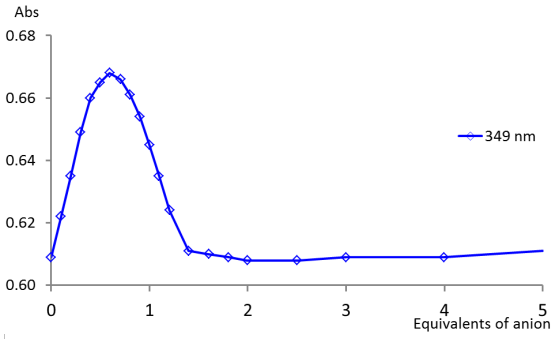


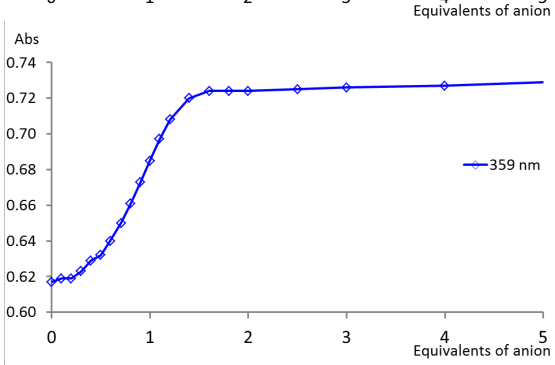
2.21b. Raw data: KB86

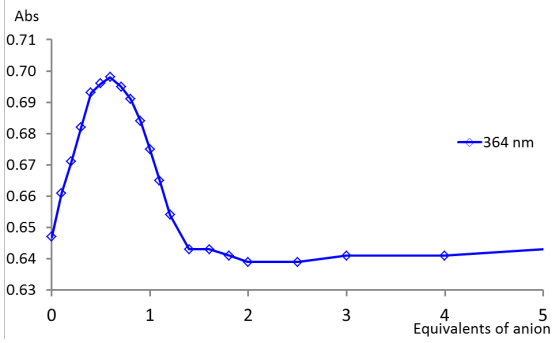


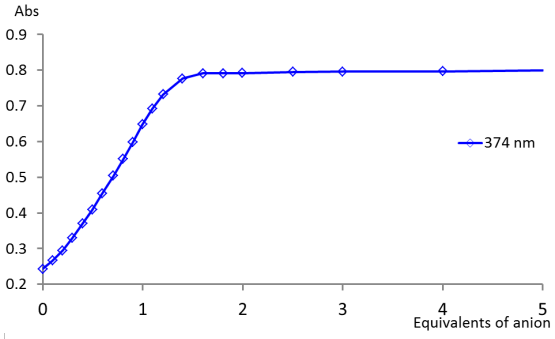
Added volume of titrant solution [µl]	Equivalents of $TBAHSO_4$	349 nm	358 nm	364 nm	374 nm	380 nm
0	0.00	0.609	0.617	0.647	0.243	0.090
4	0.10	0.622	0.619	0.661	0.266	0.092
8	0.20	0.635	0.619	0.671	0.295	0.093
12	0.30	0.649	0.623	0.682	0.330	0.098
16	0.40	0.660	0.629	0.693	0.370	0.106
20	0.50	0.665	0.632	0.696	0.409	0.114
24	0.60	0.668	0.640	0.698	0.454	0.128
28.5	0.71	0.666	0.650	0.695	0.504	0.147
32.5	0.80	0.661	0.661	0.691	0.551	0.166
36.5	0.90	0.654	0.673	0.684	0.599	0.188
40.5	1.00	0.645	0.685	0.675	0.648	0.212
44.5	1.10	0.635	0.697	0.665	0.692	0.234
49	1.21	0.624	0.708	0.654	0.732	0.253
57	1.40	0.611	0.720	0.643	0.777	0.278
65.5	1.60	0.610	0.724	0.643	0.791	0.286
74	1.81	0.609	0.724	0.641	0.791	0.287
82	2.00	0.608	0.724	0.639	0.792	0.287
103.6	2.50	0.608	0.725	0.639	0.795	0.289
125	3.00	0.609	0.726	0.641	0.796	0.291
169	4.00	0.609	0.727	0.641	0.797	0.291
214.5	5.00	0.611	0.729	0.643	0.799	0.294

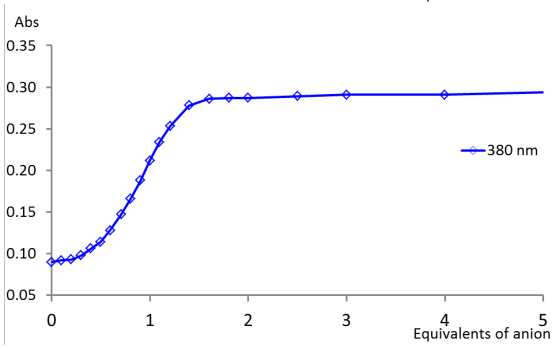
2.21c. Titration curves.











3. X-ray analysis:

Crystals of TBA_2[**1**×SO_4×**1**] and TBA_2[**4**×SO_4×**4**] (TBA = tetra(n-butyl)ammonium) were both grown by slow diffusion of diethyl ether into a solution of respective ligand and dry $(TBA)_2SO_4$ in dichloroethane $C_2H_4Cl_2$ (at 2:1 ratio).

Single crystal X-ray diffraction data were collected on a KM4CCD κ-axis diffractometer with graphite-monochromated MoK_α radiation. The crystals were positioned 50 mm from the CCD camera. 642 frames (TBA_2[**1**×SO_4×**1**]) or 694 frames (TBA_2[**4**×SO_4×**4**]) were measured at 1° intervals with a counting time of 60 sec (TBA_2[**1**×SO_4×**1**]) or 50 sec (TBA_2[**4**×SO_4×**4**]). The data were corrected for Lorentz and polarization effects. Multi-scan absorption correction have been applied. Data reduction and analysis were carried out with the Agilent programs.[4]

The structures were solved by direct methods and refined using SHELXL[5], Olex2[6] and WinGX Program System.[7] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Most of hydrogen atoms were located geometrically and their positions – except those engaged in hydrogen bonds - and temperature factors were not refined. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C.[8]

For disordered atoms from the main residues the ratios of occupancies were refined first for atoms with isotropic thermal motion parameters. After this procedure the anisotropic displacement parameters were refined together with the occupancies.

In the case of TBA_2[**1**×SO_4×**1**] structure, additional EADP constraint was used for equal anisotropic displacement parameters on the C34 and C33 carbon atoms. The sulphate ion SO_4^{2-} is situated almost exactly on the two fold axis. Consequently, all of the atoms from this sulphate ion are disordered and have occupancy equal to 0.5. The structure was solved in the centrosymmetric C2/c space group with Z = 4. Alternative solution in Cc space group is disfavoured by reflections statistics and does not solve the problem with disorder neither in the main residue nor in the sulphate anion.

For TBA_2[**4**×SO_4×**4**] structure the ISOR restraint was used on C62A C62 C63 C63A C64A C1G carbon atoms.

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under the deposition numbers: [**1**×SO_4×**1**]$^{2-}$ CCDC 968838, [**4**×SO_4×**4**]$^{2-}$ CCDC 968837. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223)336-033; E-mail:deposit@ccdc.cam.ac.uk).

Acknowledgements

The X-ray measurements were undertaken in the Structural Research Laboratory at the Chemistry Department of the University of Warsaw.

[4] CrysAlisPro, Agilent Technologies, Version 1.171.35.15 (release 03-08-2011 CrysAlis171.NET)
[5] G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122.
[6] *J. Appl. Cryst.*, **2009**, *42*, 339–341.
[7] L. J. Farrugia, *J. Appl. Cryst.*, **1999** ,*32*, 837-838.
[8] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.

	TBA_2[**1**×SO_4×**1**]	TBA_2[**4**×SO_4×**4**]
Identification code	kb71_xp	kb13_xp
Empirical formula	C80 H130 Cl4 N8 O8 S	C86 H110 Cl6 N8 O8 S
Formula weight	1505.78	1628.58
Temperature	100.15	100.00(10) K
Wavelength	0.71073	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Unit cell dimensions	a = 26.289(2)	a = 50.5530(9) Å
	b = 14.5923(6)	b = 12.8629(2) Å
	c = 24.1216(13)	c = 28.1196(4) Å
	α = 90.00°	α = 90.00°
	β = 114.437(7)°	β = 112.216(2)°
	γ = 90.00°	γ = 90.00°
Volume	8424.6(9) $Å^3$	16927.6(5) $Å^3$
Z	4	8
Density (calculated)	1.187	1.278
Absorption coefficient	0.221	0.287
F(000)	3256.0	6912.0
2Θ range for data collection	3.86 to 57.64	3.28 to 57.62^O
Index ranges	-35<=h<=32, -19<=k<=18, -31<=l<=32	-66<=h<=68, -16<=k<=16, -37<=l<=37
Reflections collected	42958	77045
Independent reflections	9955	20013
Completeness to theta = ??.??^{0}	0.903 to theta 28.820	0.904 to theta 28.810
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.9167 0.9633	0.9158 0.9609
Refinement method	Full matrix least squares method	Full matrix least squares method
Data/restraints/parameters	9955/0/633	20013/36/1046
Goodness-of-fit on F^2	1.024	1.036
Final R indices [I>2sigma(I)]	R_1 = 0.0485, wR_2 = 0.1072	R_1 = 0.0505, wR_2 = 0.1201
R indices (all data)	R_1 = 0.0914, wR_2 = 0.1287	R_1 = 0.0713, wR2 = 0.1320
Largest diff. peak and hole	0.27/-031 e $Å^{-3}$	0.65/-058 e $Å^{-3}$