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Accepted Version

Cafeo, G., Colquhoun, H. M., Cuzzola, A., Gattuso, M., Kohnke, F. H., Valenti, L. and White, A. J. P. (2010) Synthesis, x-ray structure and anion binding properties of a cryptand-like hybrid calixpyrrole. *Journal of Organic Chemistry*, 75 (18). pp. 6263-6266. ISSN 1520-6904 doi: 10.1021/jo1010262 Available at <https://centaur.reading.ac.uk/16568/>

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To link to this article DOI: <http://dx.doi.org/10.1021/jo1010262>

Publisher: American Chemical Society

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Synthesis, X-ray Structure and Anion Binding Properties of a Cryptand-Like Hybrid Calixpyrrole

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General experimental procedures

Ethanol was dried on molecular sieves (4 Å). Pyrrole was distilled before use. All other chemicals were standard reagent grade and were used without further purification. All air-sensitive and/or moisture-sensitive reactions were conducted under an inert atmosphere. Thin-layer chromatography was carried out by using Merck SiO₂ 60F254 plastic plates. Compounds were visualized with vanillin or by examination under UV light. Column chromatography was conducted by using silica gel (Aldrich, 230–400 mesh, 60 Å). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ or CD₂Cl₂ by using a Varian 500 spectrometer at 500 and 125 MHz, respectively. Melting points were determined by using a Kofler hot-stage apparatus, and are not corrected. The TBA salts were dried in a vacuum oven for at least 24 h. Solvents were used as supplied in sealed ampoules, and care was taken to minimize exposure to moisture. However, trace amounts of water could not be removed owing to the extremely hydrophilic nature of the salts. Because water has been demonstrated to lower the values of the observed binding constants, the data given should be considered to be the minimum observable value if operating under strictly anhydrous conditions.

Mass spectra were obtained from an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, Ont., Canada), equipped with a Turbo-V ionspray (TIS) source. The operative parameters used were as follows: ionspray voltage (IS), 5.5 kV; gas source 1 (GS1), 25; gas source 2 (GS2), 25; turbo temperature (TEM), 300 °C; entrance potential (EP), 10 V; declustering potential (DP), 20 V; scan range, m/z = 300–1500. Each sample for MS (ESI) was prepared by a 1:100 dilution of a dichloromethane solution (2 mg/mL) of the target compound with methanol, and it was infused by a syringe pump Harvard Mod. 22 (Harvard Apparatus, Holliston, MA, USA).

MS–MS product ions were produced by collisional induced dissociation (CID) of selected precursor ions in the LINAC collision cell (Q2) and mass-analyzed in the second mass filter (Q3). Additional experimental conditions for MS–MS product ions spectra included collision (CAD) gas, nitrogen; CAD gas pressure, 4 mPa; collision energy (CE), 30 eV, collision cell exit potential (CXP), 15V.

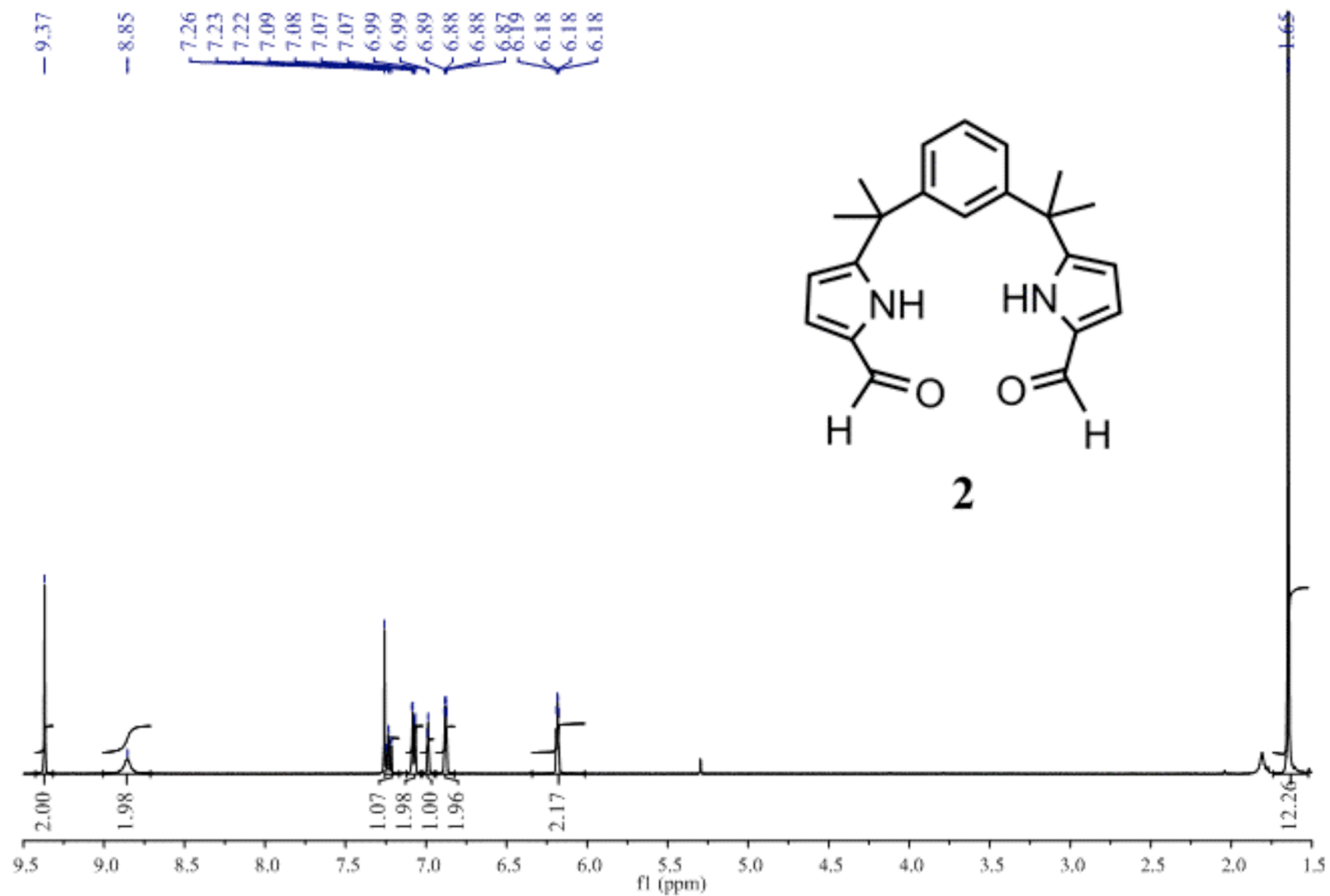


Figure S1. ^1H NMR (CDCl_3 , 125 MHz) of 1,3-Bis[1'-(pyrrol-2-carboxaldehyde-5-yl)-1',1'-(dimethyl)methyl]benzene **2**

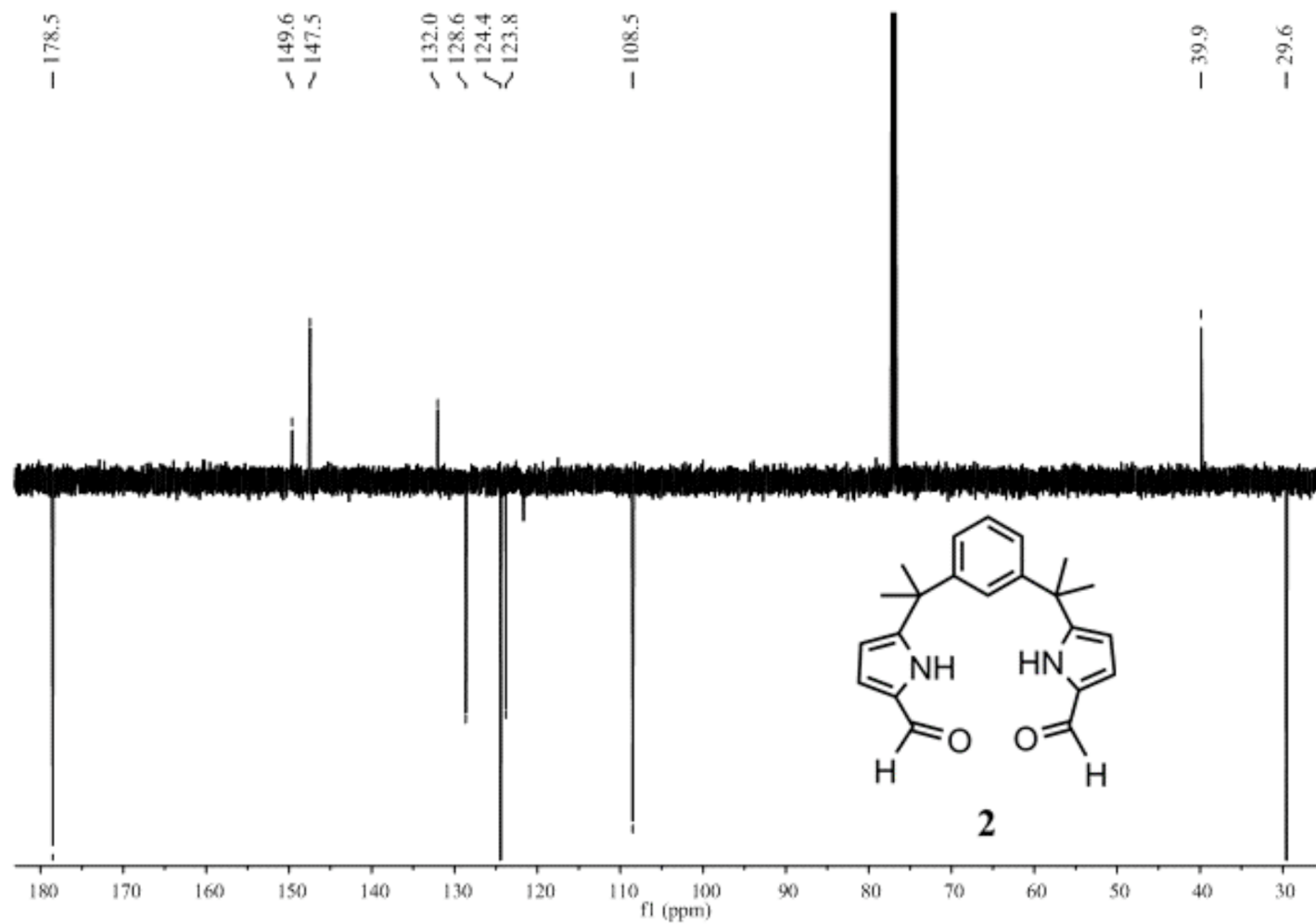


Figure S2. ¹³C NMR (CDCl₃, 125 MHz) of 1,3-Bis[1'-(pyrrol-2-carboxaldehyde-5-yl)-1'-(dimethyl)methyl]benzene **2**

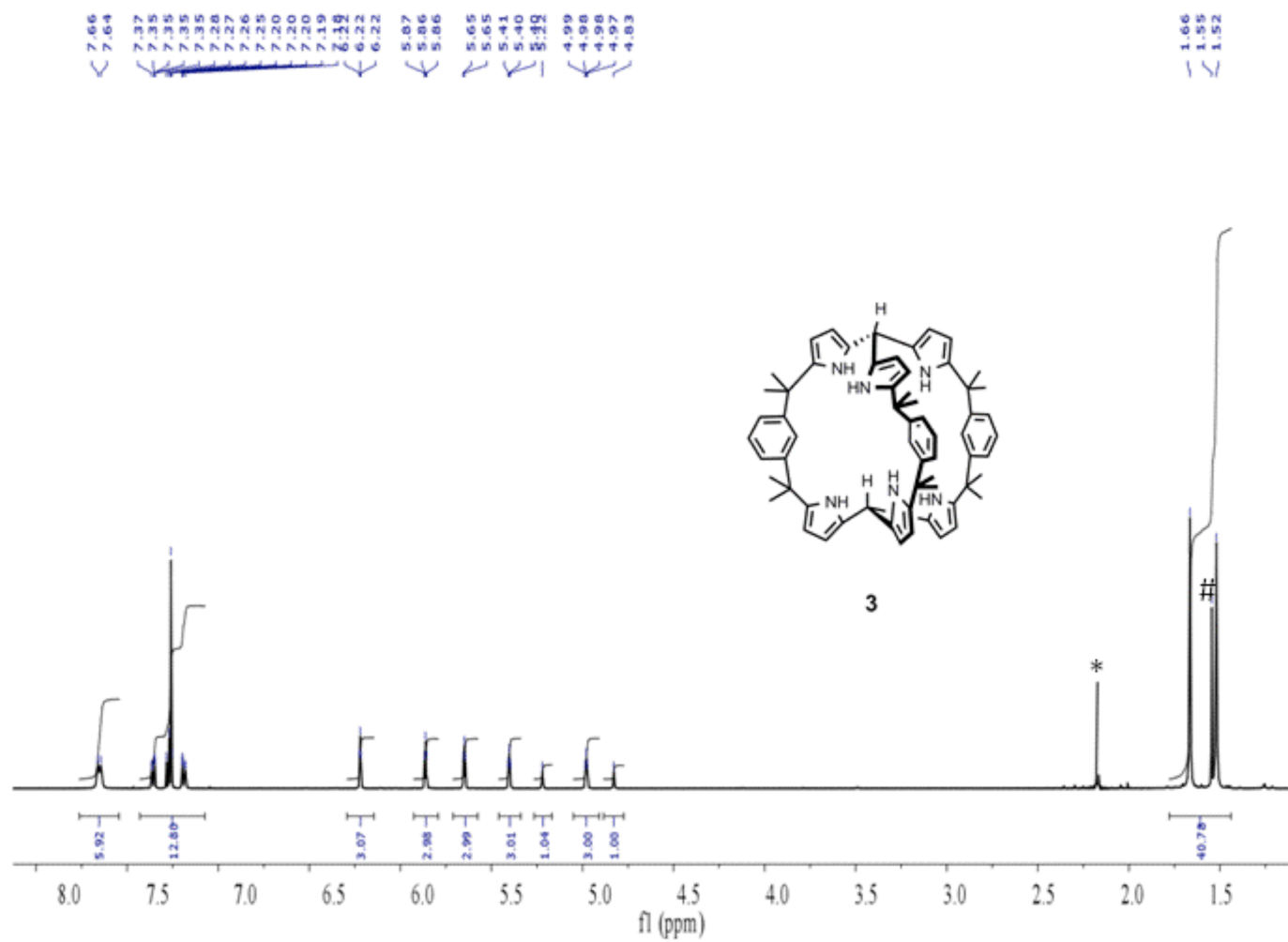


Figure S3. ¹H NMR (CDCl₃, 500 MHz) spectrum of cryptand *in/out*-**3**

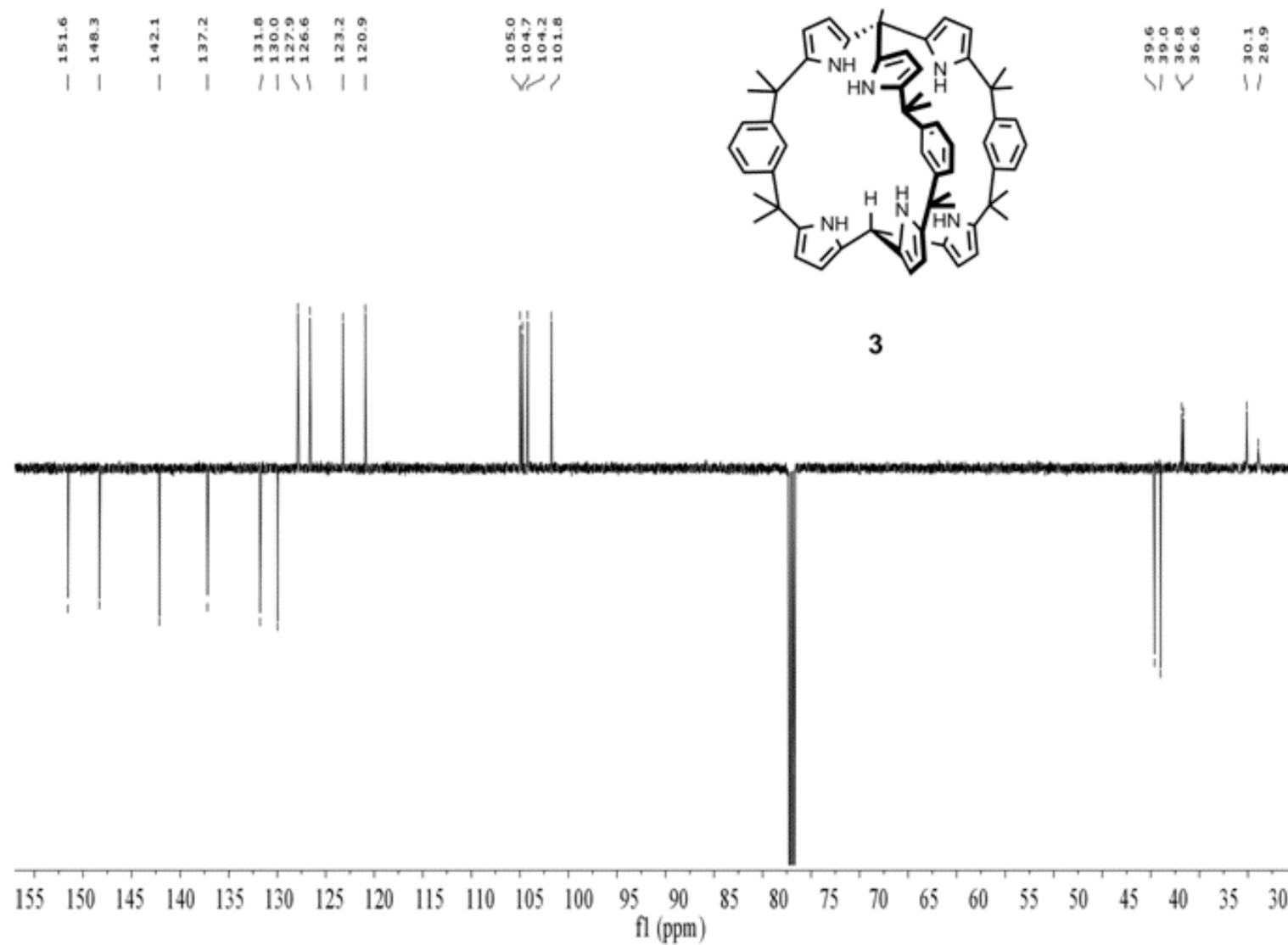


Figure S4. ^{13}C NMR (CDCl_3 , 125 MHz) spectrum of cryptand *in/out*-3

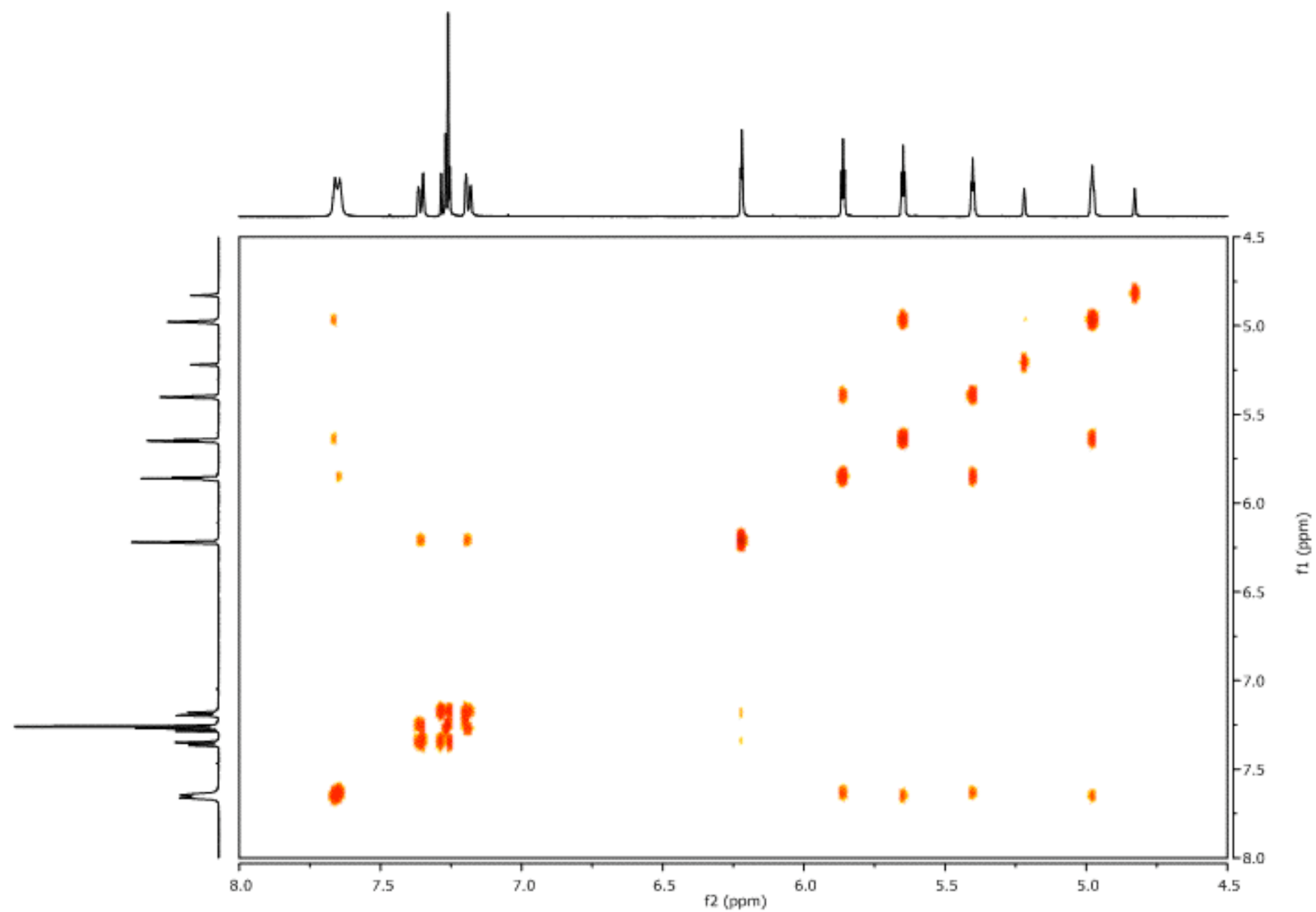


Figure S5. gCOSY (CDCl₃, 500 MHz) for cryptand *in/out*-3

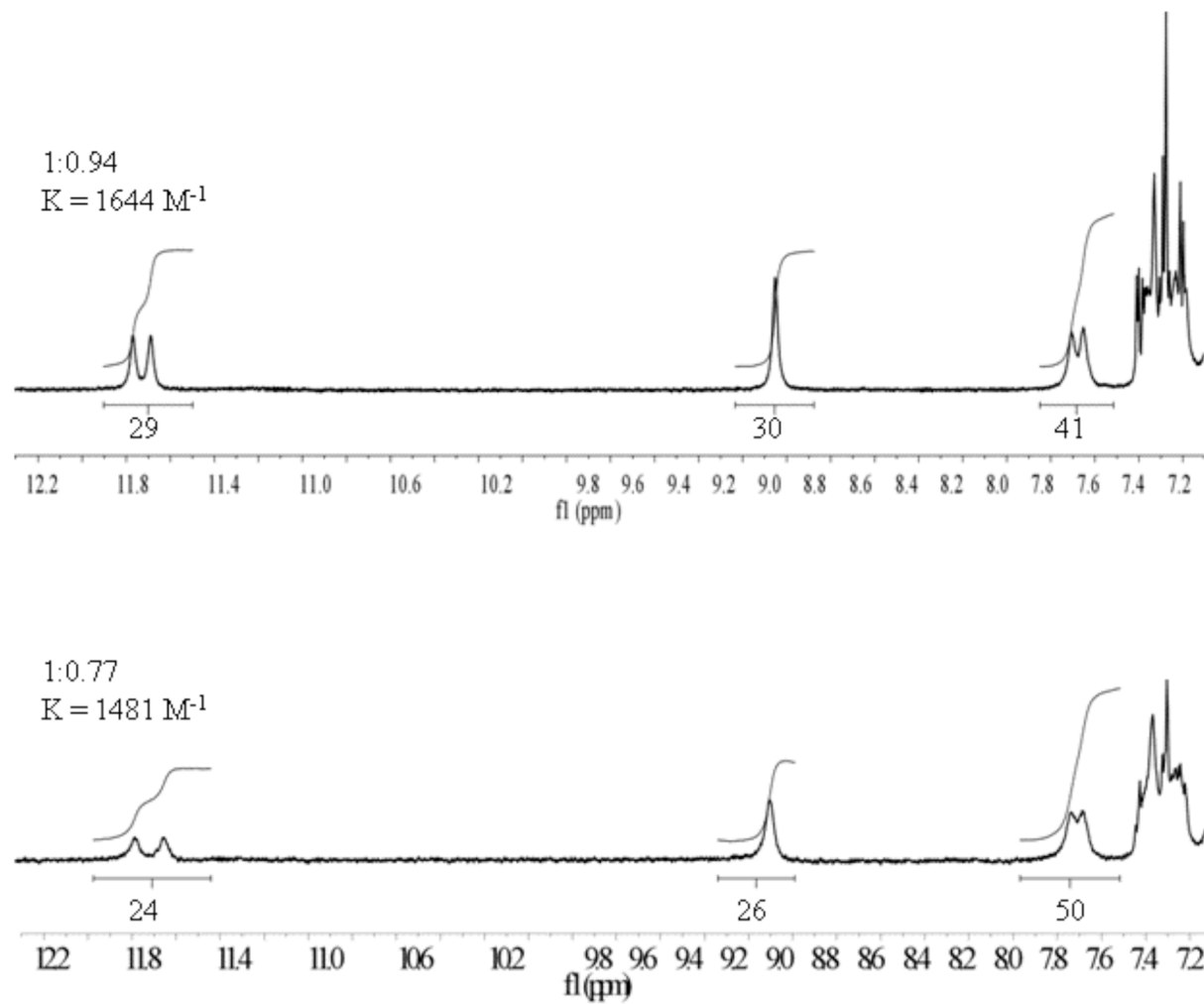


Figure S6. Partial ^1H NMR (CD_2Cl_2 , 500 MHz) spectra of two mixtures of free and complexed *in/out-3* and $\text{TBA}[\text{in/out-3}\cdot\text{F}^-]$ used for the determination of the 1:1 association constant

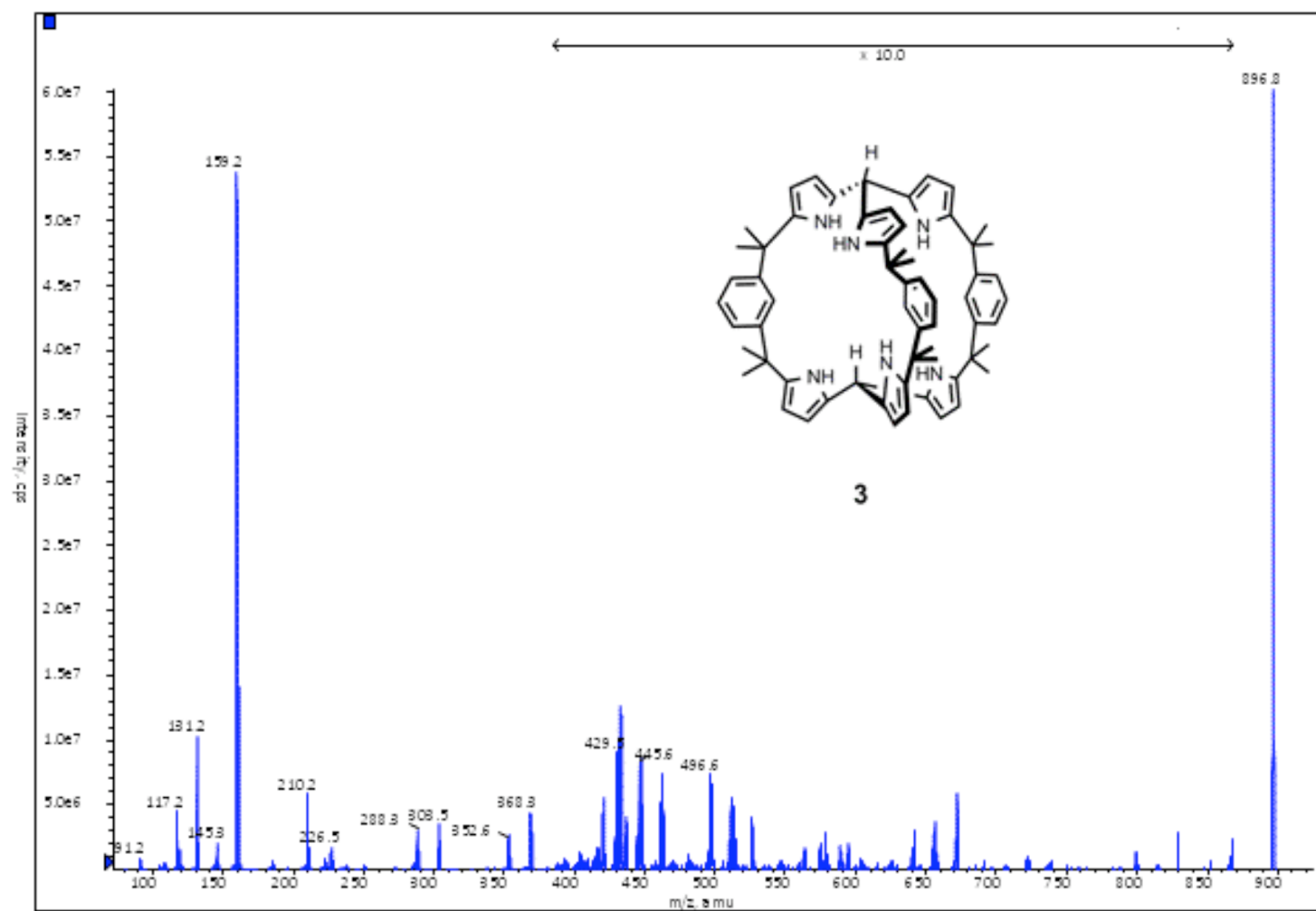


Figure S7. Positive ESI MS-MS of cryptand *in/out*-3.

X-Ray Crystallography

All six of the N–H hydrogen atoms in the structure of *in/out-3* were located from $_F$ maps and refined freely subject to an N–H distance constraint of 0.90 Å. Two of the three included acetone solvent molecules were found to be disordered. In each case two partial occupancy orientations were identified, of *ca.* 74 and 26% occupancy for the O(80)-based molecule, and *ca.* 77 and 23% occupancy for the O(90)-based molecule. Only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically. The methyl hydrogen atoms of the acetone molecules were added in idealised tetrahedral positions and, as they are each on an sp^3 centre bonded to an sp^2 centre, the groups were allowed to rotate about the C–C bond to find the best fit with the electron density map (the SHELXL HFIX/AFIX 137 command).

The three acetone molecules are hydrogen bonded to the N–H atoms of the pyrrole units linked to C(1). Hence, the O(70) acetone molecule is linked to the N(3)–H moiety, the O(80) acetone to N(43)–H, and the O(90) acetone to N(48)–H. The N $\cdots$ O, H $\cdots$ O distances (Å) and N–H $\cdots$ O angles (°) for the full or major occupancy orientations of the acetone molecules are 2.9303(16), 2.13 and 148 for the N(3)–H $\cdots$ O(70) interaction, 2.894(5), 2.08 and 151 for the N(43)–H $\cdots$ O(80) interaction, and 2.967(2), 2.18 and 146 for the N(48)–H $\cdots$ O(90) interaction respectively; the corresponding geometries for the minor occupancy acetone molecules are 2.872(13), 2.06 and 149 for the N(43)–H $\cdots$ O(80') interaction, and 2.998(9), 2.13 and 163 for the N(48)–H $\cdots$ O(90') interaction respectively.

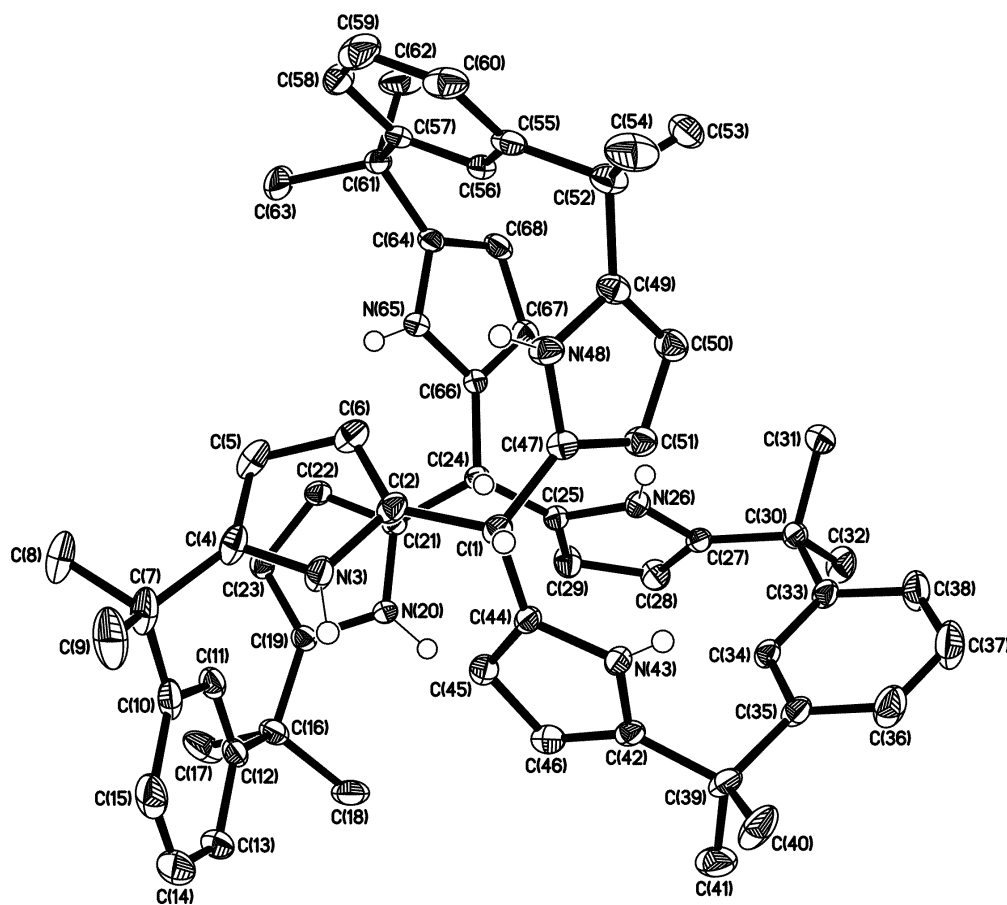
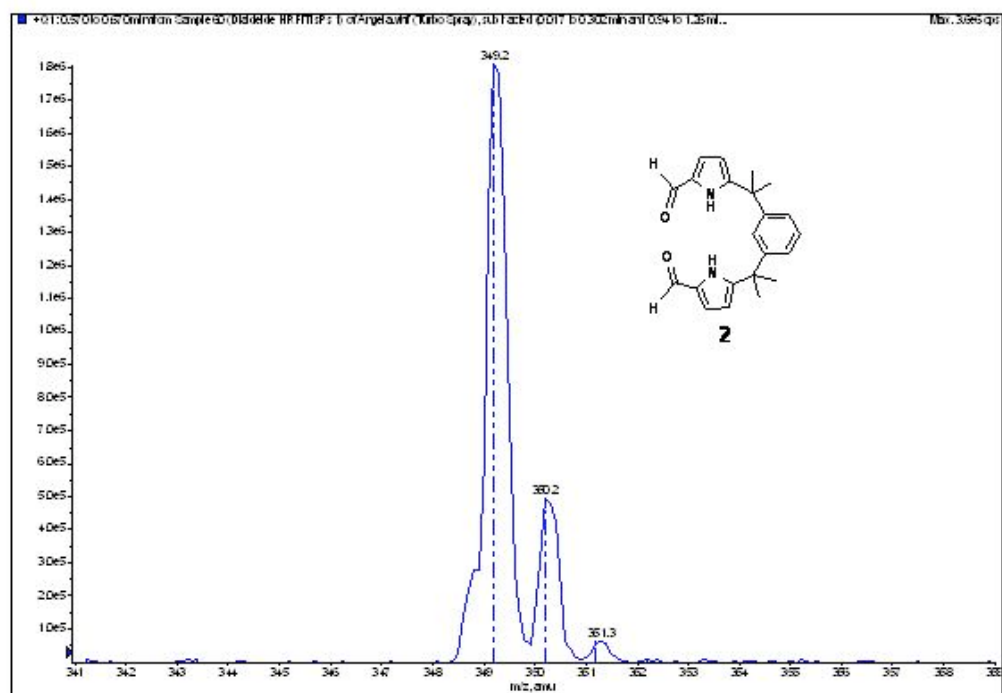


Figure S8. The X-Ray crystal structure of cryptand *in/out-3* showing the numbering of the atoms.

Match between measured (accurate MS-ESI) and calculated isotopic pattern for compound **2** (C₂₂H₂₄N₂O₂).



Calculated for C ₂₂ H ₂₄ N ₂ O ₂				Measured			
MZ	Relative_Abundance			MZ	Relative_Abundance		
349,1916	100			349,2	1,81E+06		
350,1948	25,54213			350,2	4,95E+05	27,29581	
351,1978	3,525478			351,3	6,13E+04	3,380795	
352,2006	0,345877						
353,2033	0,026483						
354,206	0,00165						
355,2087	0,000084						
356,2112	0,000003						

Atomic coordinates (.xyz) for the Dreiding II force field minimized molecular model of the complex [in/out-3F]:
Generated by CrystalMaker 8.0.3, (c) 1994-2008 CrystalMaker Software Limited.

		Fractional Coordinates			Orthogonal Coordinates [Å]		
Elmt	Label	x	y	z	xor	yor	zor
C	C1	1.381336	0.764498	0.836431	3.23219	21.59203	18.61986
C	C3	1.397575	0.765425	0.771154	1.93598	20.89407	18.76582
C	C6	1.370539	0.754562	0.666842	0.35141	19.33542	18.61902
C	C7	1.464300	0.783531	0.686949	-0.13778	20.36675	19.42222
C	C9	1.480889	0.790464	0.751802	0.85009	21.33359	19.51707
C	C11	1.314841	0.740342	0.600337	-0.30048	18.01723	18.28689
C	C12	1.302746	0.671364	0.597505	-0.43826	17.98550	16.72317
C	C16	1.377166	0.757388	0.549644	-1.74948	17.88357	18.86299
C	C20	1.214407	0.774831	0.584666	0.52344	16.88304	18.88481
C	C21	1.123548	0.751515	0.545868	0.67501	15.62796	18.24057
C	C23	1.027903	0.781941	0.531661	1.46483	14.56092	18.75484
C	C24	1.026651	0.839437	0.557338	2.09839	14.78777	20.00271
C	C26	1.115666	0.865271	0.593682	1.92983	15.99119	20.70320
C	C28	1.208153	0.833564	0.606378	1.14104	17.01328	20.15626
C	C30	0.934027	0.752531	0.490266	1.58259	13.25587	17.97199
C	C31	0.955117	0.745244	0.422393	0.16836	12.58011	17.94729
C	C35	0.832143	0.789095	0.482148	2.55880	12.20269	18.60273
C	C39	0.914471	0.693268	0.517170	2.06648	13.52532	16.56859
C	C42	0.928578	0.616518	0.582637	2.83724	14.61223	14.78442
C	C43	0.854142	0.602077	0.529254	2.59883	13.29915	14.39189
C	C45	0.845359	0.649903	0.488567	2.12034	12.62332	15.50352
C	C47	0.968917	0.580925	0.639418	3.32126	15.75100	13.98534
C	C49	0.892780	0.571386	0.678406	4.72535	15.60159	13.56701
C	C52	0.821957	0.578673	0.762044	6.90632	16.04519	13.47182
C	C53	0.754539	0.547098	0.715363	6.66371	14.90695	12.69988
C	C55	0.798450	0.542550	0.663254	5.30700	14.62872	12.75857
C	C57	0.806225	0.595895	0.826425	8.23660	16.70703	13.73442
C	C58	0.800847	0.537162	0.863949	8.76709	17.23594	12.35543
C	C62	0.699640	0.627028	0.820902	9.28821	15.65479	14.23065
C	C66	0.889664	0.638863	0.858238	8.09583	17.77611	14.81403
C	C67	0.906334	0.692076	0.826991	7.54652	17.43534	16.08257
C	C69	0.983078	0.734160	0.852385	7.35734	18.36488	17.13849
C	C70	1.040678	0.722723	0.914311	7.83322	19.68193	16.90656
C	C72	1.027100	0.670923	0.946879	8.37927	20.06443	15.67382
C	C74	0.953317	0.629368	0.918842	8.49466	19.12598	14.63933
C	C76	1.000584	0.789978	0.816938	6.73435	17.97330	18.47300
C	C77	0.933786	0.839835	0.837847	7.90992	17.57831	19.42841
C	C81	0.966655	0.785827	0.743117	5.76996	16.73528	18.41933
C	C85	1.113709	0.804242	0.831192	5.90726	19.12222	18.99329
C	C88	1.281873	0.791568	0.840018	4.35997	20.72554	19.02605
C	C89	1.268500	0.844604	0.869566	5.16745	20.90331	20.14482
C	C91	1.163946	0.852730	0.863854	6.12629	19.90320	20.13028
C	C93	1.390943	0.704043	0.862722	3.41338	22.11038	17.24772
C	C96	1.369694	0.607156	0.872350	3.49929	22.20334	15.02350
C	C97	1.444537	0.625836	0.924129	3.71848	23.49257	15.51402
C	C99	1.458012	0.686026	0.917946	3.65889	23.43464	16.89662
C	C101	1.332781	0.545111	0.854886	3.37266	21.75570	13.58735
C	C102	1.214132	0.545597	0.851913	4.49560	20.67979	13.37028
C	C106	1.380392	0.498301	0.905957	3.65133	22.90261	12.55959
C	C110	1.363082	0.527182	0.793762	1.95297	21.26414	13.33279
C	C111	1.301055	0.489734	0.748545	1.66486	20.20120	12.43783
C	C113	1.325429	0.473439	0.690158	0.35645	19.69040	12.20432
C	C114	1.419470	0.495210	0.678878	-0.70462	20.33256	12.89186

C	C116	1.485478	0.530141	0.723482	-0.47416	21.42643	13.73913
C	C118	1.457970	0.545244	0.780216	0.83283	21.89054	13.94218
C	C120	1.251908	0.434358	0.643808	0.15732	18.51508	11.25191
C	C121	1.248996	0.372136	0.674960	0.54177	18.98927	9.80877
C	C125	1.284388	0.423318	0.579522	-1.31829	17.99092	11.16035
C	C129	1.146086	0.461516	0.628374	1.01653	17.34855	11.67486
C	C132	1.019010	0.525946	0.625730	2.42139	16.10093	12.87223
C	C133	0.976084	0.475780	0.593398	2.13075	15.39078	11.71151
C	C135	1.055292	0.435727	0.595050	1.25549	16.16832	10.96755
F	F138	1.158295	0.666904	0.729759	3.28326	18.42883	16.15135
H	H2	1.442054	0.791259	0.865459	3.21868	22.45270	19.29620
H	H5	1.271583	0.722060	0.719706	2.15393	19.20155	17.62214
H	H8	1.512144	0.797971	0.659290	-1.04974	20.40655	19.87869
H	H10	1.542696	0.810601	0.779886	0.78937	22.20225	20.04861
H	H13	1.249548	0.656924	0.626344	0.54722	17.91408	16.25453
H	H14	1.376393	0.649549	0.615630	-0.91625	18.89683	16.35302
H	H15	1.274268	0.655379	0.549455	-1.04281	17.14506	16.37835
H	H17	1.450735	0.734248	0.558234	-2.39698	18.67389	18.47667
H	H18	1.392115	0.804816	0.550163	-1.74525	17.94501	19.95319
H	H19	1.334623	0.745642	0.502302	-2.18981	16.92252	18.58453
H	H22	1.126241	0.710446	0.527224	0.19939	15.47774	17.35319
H	H25	0.961111	0.863990	0.549833	2.68967	14.07931	20.43482
H	H27	1.113146	0.907179	0.610910	2.38157	16.12339	21.61174
H	H29	1.271590	0.854187	0.632291	1.02779	17.86752	20.70497
H	H32	0.974634	0.787770	0.404268	-0.21249	12.44985	18.96339
H	H33	0.887924	0.727978	0.389258	0.20292	11.59493	17.47669
H	H34	1.018475	0.714818	0.422251	-0.55241	13.18069	17.39038
H	H36	0.839313	0.831754	0.460058	2.23130	11.91340	19.60330
H	H37	0.812809	0.796691	0.527885	3.57054	12.60900	18.66946
H	H38	0.767452	0.766044	0.452270	2.60798	11.29046	18.00287
H	H41	1.012723	0.692296	0.604585	2.61640	15.50827	16.61402
H	H44	0.813726	0.563570	0.520946	2.73751	12.90084	13.46268
H	H46	0.797008	0.652508	0.445143	1.84905	11.63886	15.52937
H	H48	1.029568	0.607421	0.668258	3.30431	16.60907	14.65588
H	H51	0.964310	0.612720	0.760203	5.56914	17.21118	14.51521
H	H54	0.684756	0.530450	0.718526	7.35875	14.36433	12.18611
H	H56	0.766715	0.522192	0.621671	4.83424	13.84986	12.30026
H	H59	0.784878	0.546215	0.910299	9.76064	17.67720	12.46049
H	H60	0.873347	0.513051	0.870368	8.08937	17.99058	11.94839
H	H61	0.740059	0.508017	0.839169	8.84819	16.43304	11.61950
H	H63	0.691733	0.665182	0.789467	8.93322	15.12091	15.11427
H	H64	0.690699	0.642219	0.867206	10.22994	16.14705	14.48695
H	H65	0.636077	0.597132	0.802258	9.50149	14.90765	13.46370
H	H68	0.860539	0.700024	0.783803	7.27017	16.46771	16.23269
H	H71	1.094335	0.752266	0.936731	7.78269	20.39156	17.64082
H	H73	1.071072	0.663460	0.991058	8.69240	21.02808	15.52958
H	H75	0.946817	0.592186	0.944094	8.88721	19.45299	13.75812
H	H78	0.943228	0.881522	0.814342	7.53233	17.29223	20.41371
H	H79	0.955189	0.846945	0.888776	8.60788	18.40810	19.55657
H	H80	0.852402	0.828133	0.825811	8.46955	16.73118	19.02440
H	H82	0.883442	0.782604	0.726974	6.30162	15.80587	18.20742
H	H83	1.001387	0.747187	0.725842	5.00870	16.87877	17.64705
H	H84	0.991229	0.824865	0.720650	5.25283	16.59904	19.37345
H	H87	1.174598	0.733321	0.792110	4.40969	19.26587	17.58079
H	H90	1.325088	0.872425	0.891797	5.07944	21.63888	20.84653
H	H92	1.130755	0.887616	0.881460	6.86675	19.78344	20.82107
H	H95	1.284100	0.656394	0.799521	3.22408	20.44112	16.06244
H	H98	1.483885	0.600090	0.959906	3.87568	24.33716	14.96350
H	H100	1.508464	0.712036	0.948248	3.76686	24.22314	17.53424

H	H103	1.181224	0.501304	0.847240	4.60598	20.40303	12.32106
H	H104	1.174312	0.572049	0.811840	4.27029	19.77478	13.94184
H	H105	1.197359	0.564895	0.894723	5.46626	21.05217	13.70818
H	H107	1.350338	0.454230	0.891986	3.57200	22.53102	11.53420
H	H108	1.362082	0.508723	0.951410	4.65653	23.30970	12.69200
H	H109	1.463835	0.496579	0.912376	2.93291	23.71707	12.67515
H	H112	1.234677	0.473793	0.757938	2.43702	19.76723	11.93762
H	H115	1.442375	0.485848	0.638144	-1.66973	20.02455	12.78541
H	H117	1.553614	0.544625	0.714608	-1.25905	21.88477	14.20942
H	H119	1.508631	0.570150	0.811746	0.95681	22.69841	14.55374
H	H122	1.216375	0.374521	0.716826	1.60170	19.23808	9.73840
H	H123	1.326469	0.353898	0.689073	-0.03324	19.87679	9.53193
H	H124	1.202648	0.340871	0.642486	0.33951	18.21715	9.06466
H	H126	1.289056	0.465049	0.555025	-1.66584	17.65033	12.13871
H	H127	1.229205	0.395188	0.548134	-1.40481	17.15051	10.46757
H	H128	1.358905	0.401326	0.586979	-1.99146	18.77313	10.80321
H	H131	1.168650	0.544316	0.667974	1.73369	17.92191	13.51585
H	H134	0.900694	0.469112	0.572678	2.49482	14.47644	11.44436
H	H136	1.047791	0.394481	0.575557	0.86534	15.91838	10.05747
N	N4	1.334932	0.743434	0.719328	1.58533	19.71615	18.22511
N	N40	0.961088	0.671232	0.573905	2.52845	14.69667	16.08534
N	N50	0.904249	0.591258	0.737689	5.70573	16.43144	13.94946
N	N86	1.187692	0.769709	0.816607	4.81714	19.63673	18.38591
N	N94	1.338291	0.655953	0.837847	3.35525	21.40768	16.10376
N	N130	1.120072	0.515965	0.644658	1.72196	17.24324	12.81951