Direct evidence of a mesogenic dendrimer with free void space by CF-VT-HP ^{129}Xe-NMR spectroscopy

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Supporting information

Experimental section

General: Reagents were used as received without further purification. Elemental analyses were performed using an Elementar Unicube analyzer (EA000600). The spectra of ^{1}H were recorded on a Bruker AMX-300 spectrometer. Thermogravimetric analyses were completed under N_2 with a Perkin-Elmer TGA-7 TG analyzer. The mass spectra were obtained from Microflex MALDI-TOF MS. All ^{129}Xe NMR spectra were obtained on a Bruker AMX300 spectrometer operating at 83.013 MHz (magnetic field 7.05 T) using a customized probe from Morris Instruments. The majority of the experiments were performed using a continuous flow of hyperpolarized Xe gas. The flow rate was monitored using a Fathom Technologies flow controller (model GR-116 3-A-PV). The gas flow was set to 0.3 L/h in order to achieve a good signal-to-noise ratio and kept constant for each experiment.

Preparation of dendrimers:

C_8G_3NH (9.18 g, 3 mmol) and 1,3,5-benzenetricarboxylic acid chloride (0.27 g, 1 mmol) was dissolved in dry THF (20 mL), and the resulting solution was stirred for 1 hour. The resulting solution was stirred for 30 min in an ice-bath. K_2CO_3 (0.5 g, 3.6 mmol) was added and the resulting mixture was heated in a sealed tube at 170 ^{o}C for 72 hours. Water (40 mL) was added to the mixture and the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The combined extracts were dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by chromatography (SiO_2: 2.1 cm × 15 cm; eluent: CH_2Cl_2) to give **$(G_3N)_3B$** in 35.2% yield (3.27 g).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.14 (s, Ar-H, 3H), 3.81+3.79 (2s, 84×CH_2, 168H), 3.46 (br s, 48×CH_2, 96H), 1.50-1.60 (m, 48×CH_2, 96H), 1.28 (br s, 240×CH_2, 480H), 0.89 (t, J = 6.9 Hz, 48×CH_3, 144H). MS m/z: M^+ calcd for $C_{540}H_{987}N_{129}O_3$, 9335.12; found, 9335.27. Anal. Cacld. for $C_{540}H_{987}N_{129}O_3$: C, 69.47; H, 10.66; N, 19.35. Found: C, 69.55; H, 10.82; N, 19.12.

In a similar manner, **$(G_2N)_3B$**, was obtained in a 40.6% yield (1.85 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ): δ 7.62 (s, 3×CH, 3H), 3.76-3.82 (m, 36×CH_2, 72H), 3.45 (br s, 24×CH_2, 48H), 1.57 (br s, 24×CH_2, 48H), 1.27 (br s, 120×CH_2, 240H), 0.88 (t, J = 6.9 Hz, 24×CH_3, 72H). MS m/z: M^+ calcd for $C_{254}H_{483}N_{57}O_3$ $(M)^+$, 4504.16; found, 4504.40 Anal. Cacld. for $C_{254}H_{483}N_{57}O_3$: C, 70.40; H, 10.81; N, 17.73. Found C, 70.15; H, 10.90; N, 17.65.

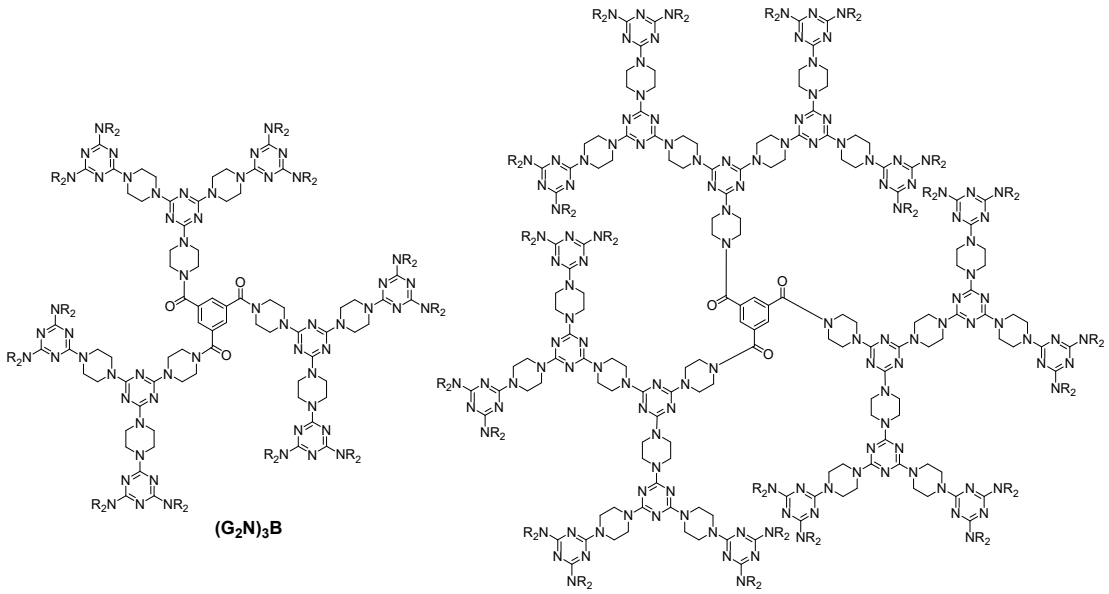


Figure S1. The mass spectrum of **$(G_3N)_3B$**, obtained by MALDI-TOF technique.

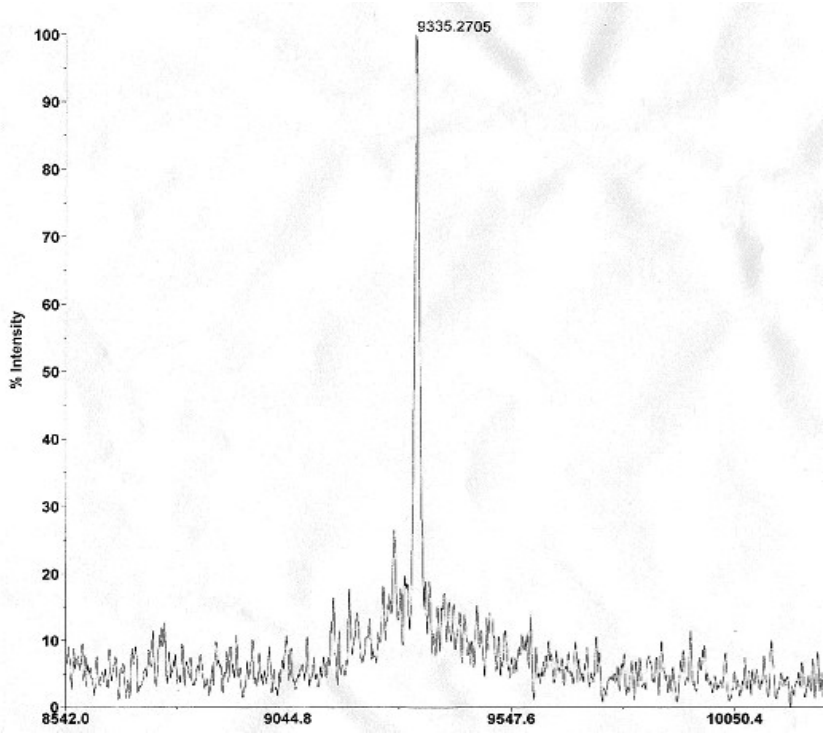


Figure S2. Thermogravimetric analysis of **$(G_3N)_3B$** (up panel) and **$(G_2N)_3B$** (down panel) at a heating rate of 10 °C min^{-1} under an N_2 atmosphere

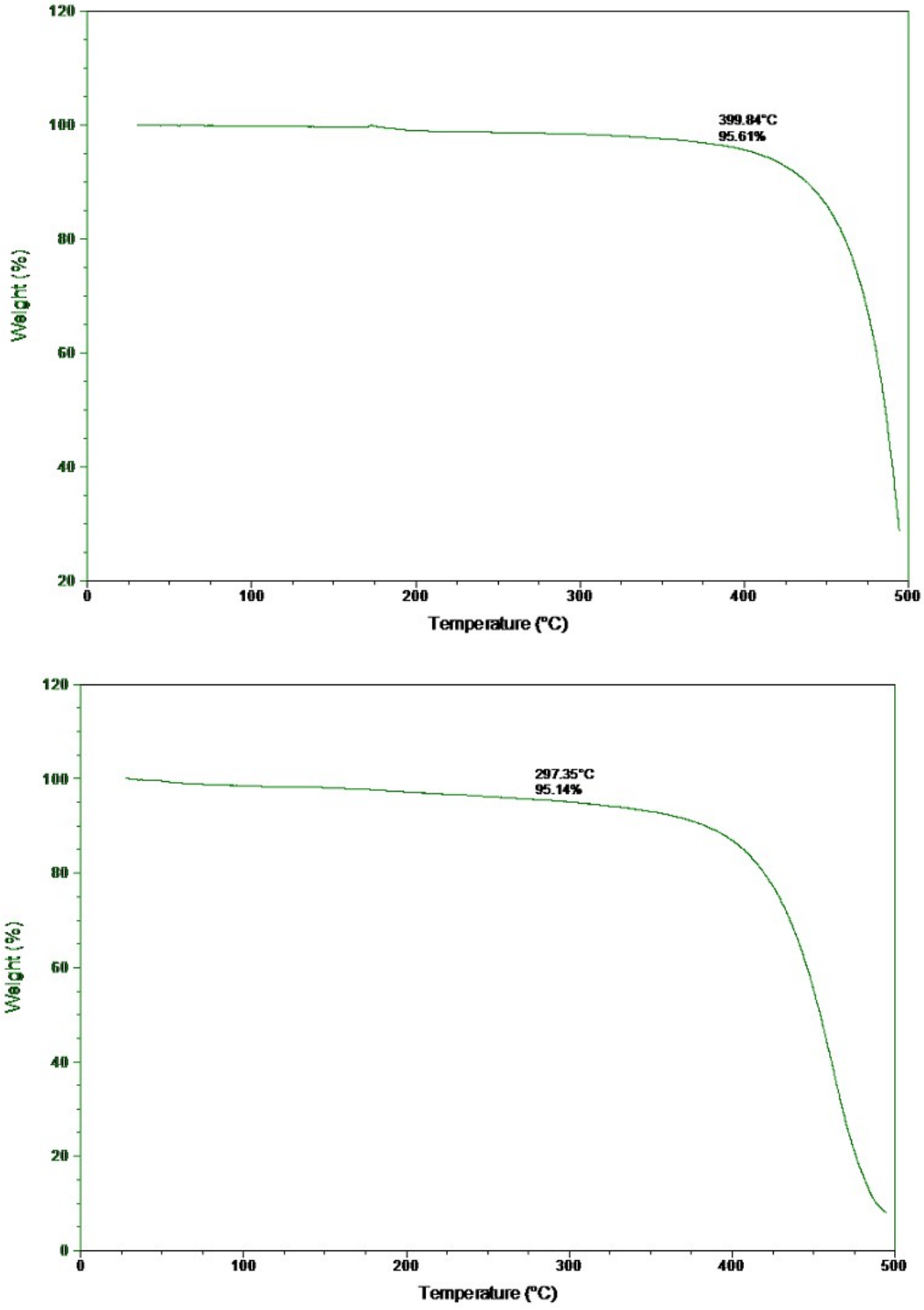


Figure S3. DSC of **$(G_3N)_3B$** in the second cycle at the heating and cooling rate of 5 °C/min.

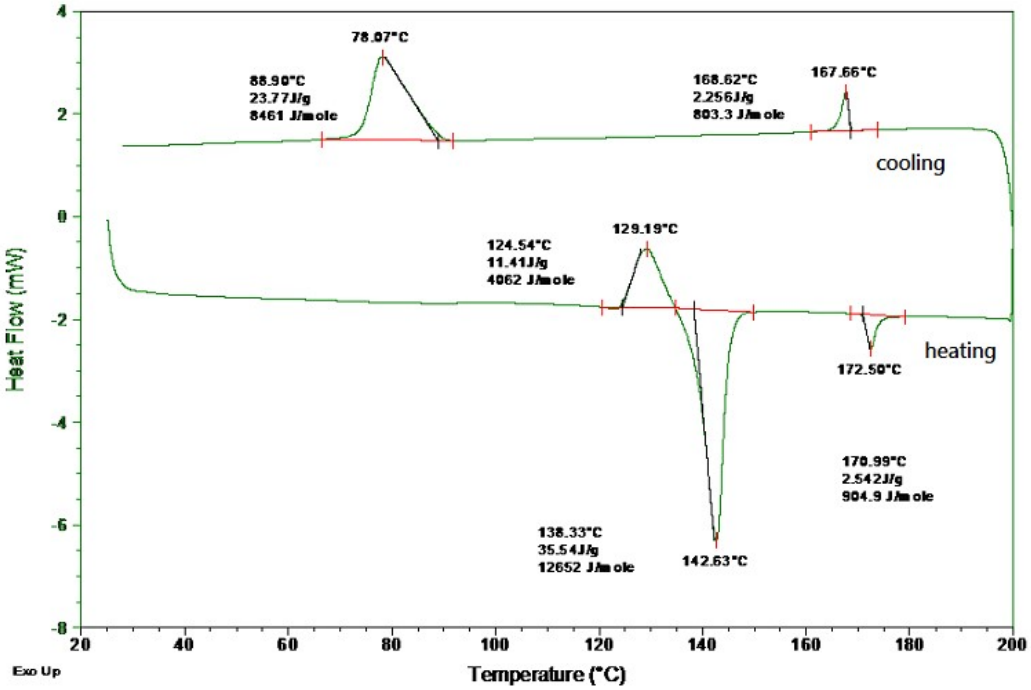
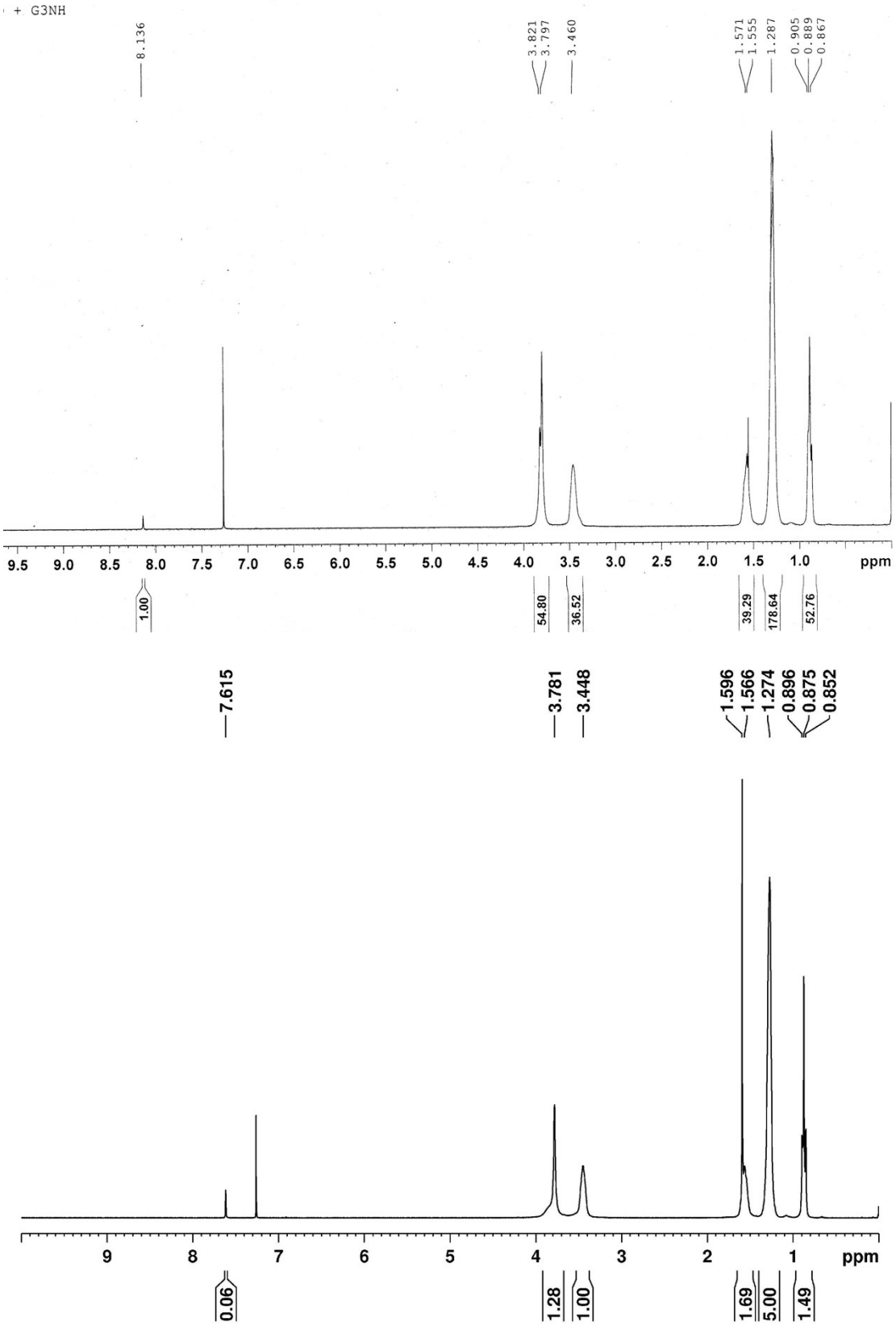
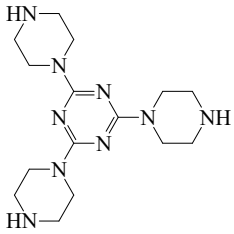


Figure S4. ^{1}H NMR of **$(G_3N)_3B$** and **$(G_2N)_3B$**:



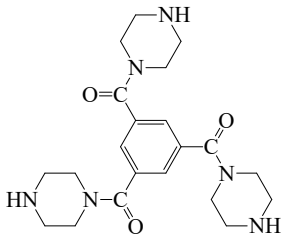
Scheme S1. The calculation details of compounds **1** and **2**.



1:

Cartesian Coordinates (Å)				Cartesian Coordinates (Å)			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.30944	-0.00436	0.09062	H	5.32185	2.061121	-0.10375
N	0.694259	-1.19745	0.000589	H	4.438693	1.23976	-1.41317
C	-0.63351	-1.12775	-0.20394	H	6.350263	-0.03269	-0.52713
N	-1.34625	0.007059	-0.3219	H	5.30041	-2.11243	-0.08652
C	-0.62316	1.135725	-0.20818	H	4.425698	-1.2929	-1.40274
N	0.70544	1.193938	-0.00425	H	3.683821	-1.32744	1.563738
N	2.665342	-0.01043	0.280686	H	2.783422	-2.08491	0.229186
C	3.429991	1.216034	0.489135	H	-2.86519	-2.68419	-1.66165
C	4.713395	1.18194	-0.34304	H	-3.15928	-1.36888	-0.5015
N	5.472399	-0.02614	-0.01511	H	-4.49185	-3.4737	-0.02248
C	4.701	-1.22905	-0.3331	H	-3.44579	-2.97078	1.327525
C	3.417462	-1.24283	0.499293	H	-3.28095	-5.3587	0.754015
N	-1.3185	-2.31049	-0.28753	H	-0.92998	-5.57692	0.53293
C	-2.74024	-2.3666	-0.61531	H	-1.28166	-4.24923	1.665293
C	-3.44855	-3.37089	0.295926	H	-0.61946	-4.00873	-1.31051
N	-2.78778	-4.67281	0.189093	H	0.380345	-3.45827	0.054067
C	-1.39041	-4.58628	0.61714	H	-0.59046	4.022686	-1.3137
C	-0.64252	-3.60467	-0.28707	H	0.412149	3.456981	0.042664
N	-1.29703	2.324245	-0.29702	H	-0.88021	5.582839	0.540598
C	-0.61125	3.613176	-0.29243	H	-1.23683	4.25098	1.666585
C	-1.34762	4.595158	0.620969	H	-3.2317	5.381038	0.770476
N	-2.74615	4.694688	0.199532	H	-4.46035	3.510231	-0.01229
C	-3.41663	3.397286	0.301328	H	-3.41297	2.991003	1.330493
C	-2.71949	2.393016	-0.61863	H	-2.84573	2.718209	-1.66243
H	3.697108	1.307089	1.552867	H	-3.14561	1.397806	-0.50931
H	2.804641	2.06228	0.211851				

2:



Cartesian Coordinates (Å)				Cartesian Coordinates (Å)			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.31988	-0.57502	-0.71011	H	-1.56517	1.471226	-1.29763
C	-0.88301	0.748276	-0.86346	H	2.317662	0.427007	0.204225
C	0.414765	1.116075	-0.50132	H	-0.73796	-2.56972	-0.10784
C	1.303654	0.133752	-0.04437	H	-4.74235	-3.35769	-1.10894
C	0.892776	-1.19386	0.084474	H	-4.77649	-1.88715	-2.12505
C	-0.42923	-1.53722	-0.22853	H	-6.84649	-2.17897	-0.68016
C	-2.69993	-0.91145	-1.21957	H	-5.97598	-0.65681	-0.37885
O	-3.08474	-0.40087	-2.27146	H	-6.56012	-1.92282	1.662048
N	-3.46219	-1.8162	-0.51879	H	-4.44726	-1.98784	2.730804
C	-4.73316	-2.2603	-1.10269	H	-4.51423	-0.54188	1.694533
C	-5.91909	-1.75664	-0.27858	H	-3.24152	-3.23841	1.011018
N	-5.75436	-2.19818	1.107844	H	-2.40856	-1.69996	1.299961
C	-4.5331	-1.64907	1.692637	H	3.969104	-4.25942	0.296831
C	-3.31705	-2.14889	0.902207	H	3.525891	-3.57464	1.866132
C	1.773782	-2.27069	0.664295	H	6.044719	-3.53084	1.421933
O	1.31404	-3.02048	1.524855	H	5.364184	-1.9299	1.727095
N	3.082652	-2.34552	0.246819	H	6.10193	-3.06073	-0.86878
C	3.954381	-3.33236	0.893115	H	5.412272	-1.07512	-1.88776
C	5.375895	-2.76492	1.014957	H	4.984216	-0.4148	-0.30742
N	5.932623	-2.27086	-0.24749	H	3.595143	-2.73357	-1.75366
C	5.013686	-1.33678	-0.9021	H	2.920293	-1.12491	-1.46676
C	3.585303	-1.88192	-1.05276	H	-0.11563	5.442737	-1.34011
C	0.974731	2.496442	-0.73522	H	1.537042	4.787957	-1.4693
O	2.094403	2.606333	-1.23509	H	1.355152	6.744877	0.16991
N	0.194717	3.588365	-0.43206	H	1.954059	5.258328	0.913693
C	0.687529	4.920746	-0.79924	H	-0.75521	6.355346	1.104055
C	1.074756	5.724128	0.451285	H	-1.34887	4.540548	2.45498
N	0.010577	5.784142	1.458877	H	0.297502	3.911568	2.320374
C	-0.49209	4.448412	1.778109	H	-1.78781	4.052391	0.075666
C	-0.89596	3.612273	0.546505	H	-1.14572	2.595267	0.84829