Supporting Information

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NMR SPECTRA OF COMPOUNDS:

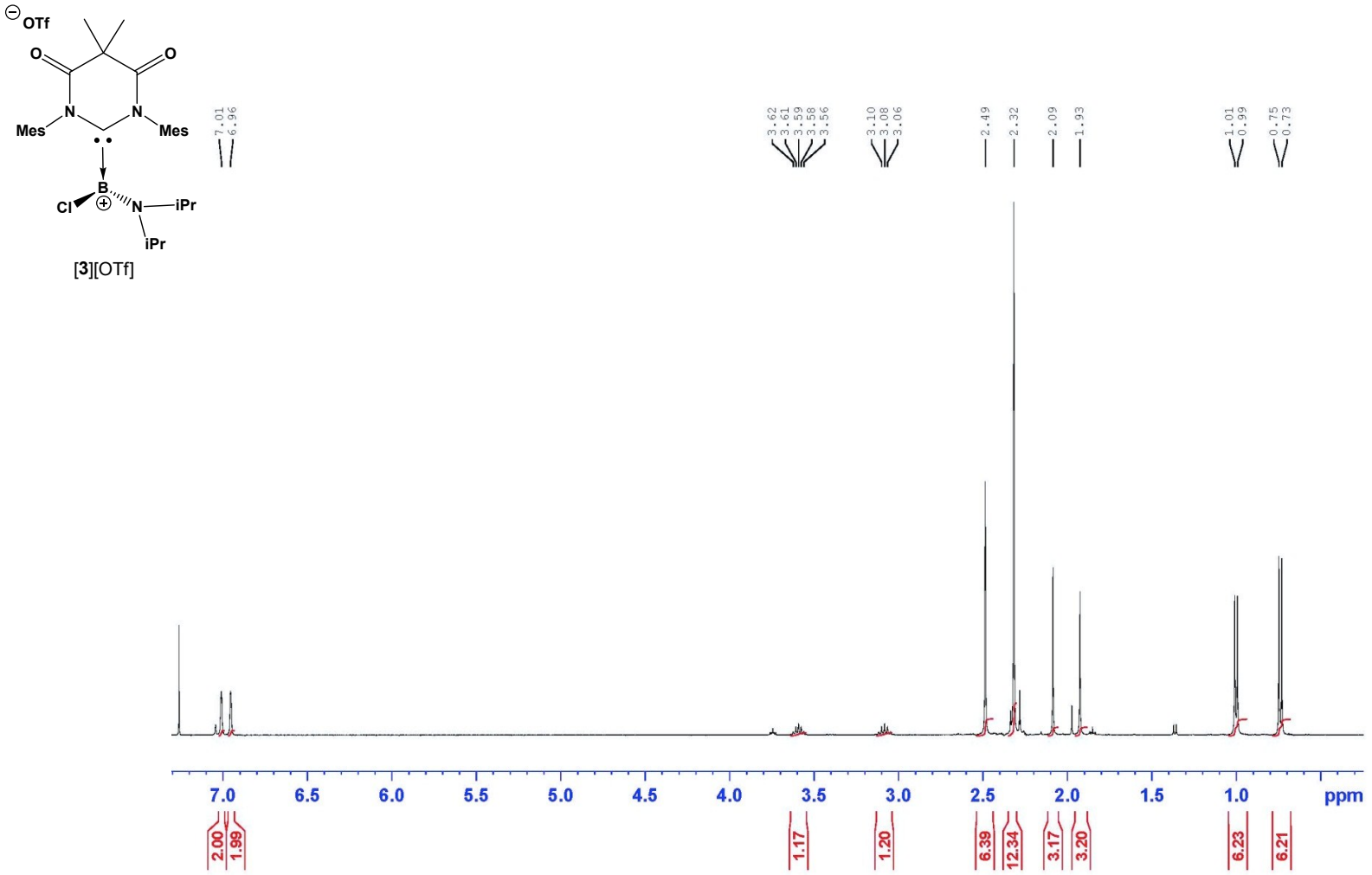


Figure S1: ^{1}H NMR of [**3**][OTf] ($CDCl_3$).

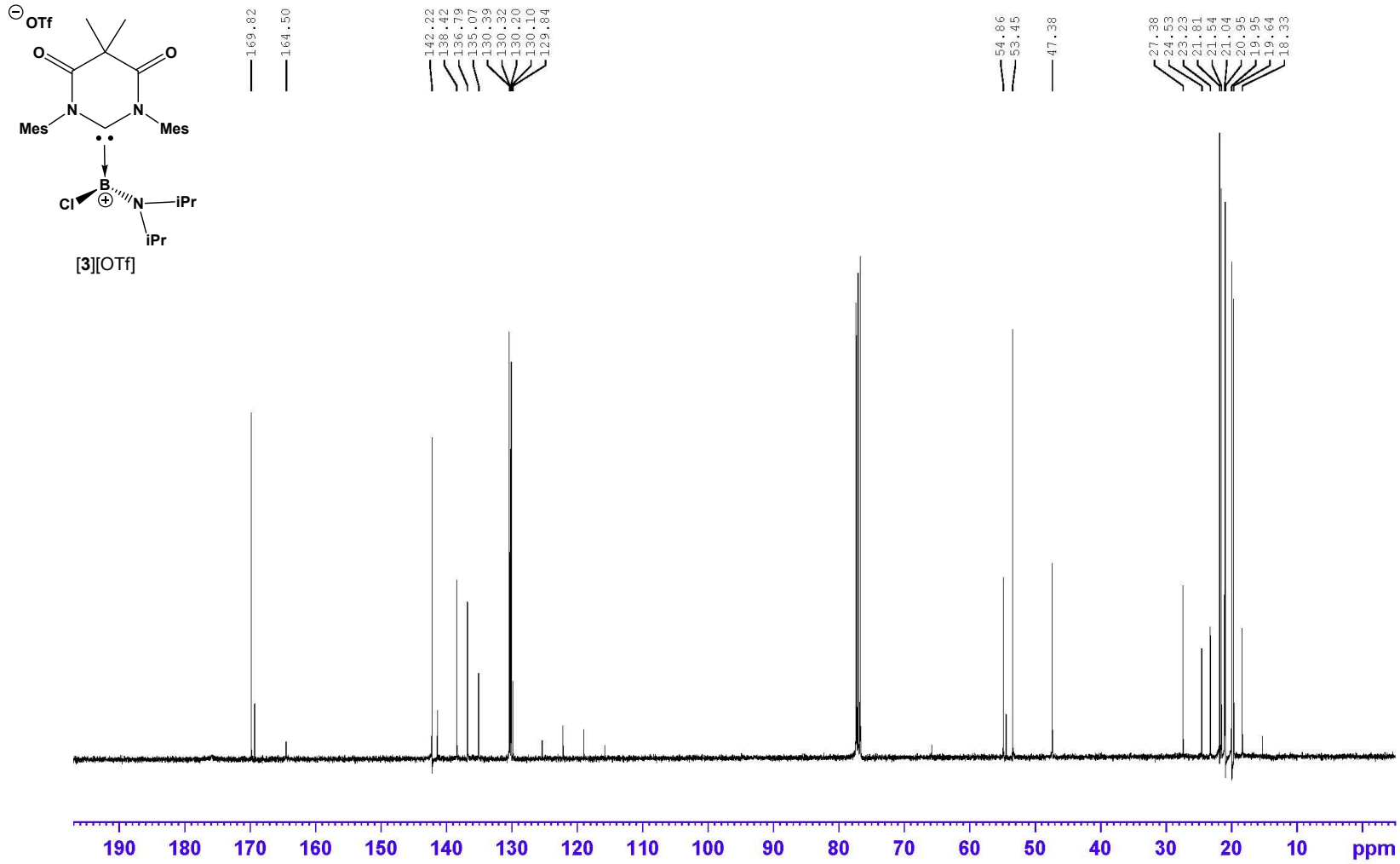
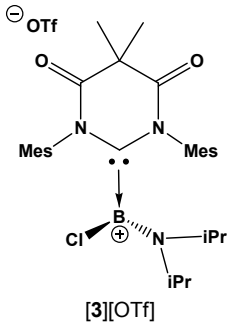


Figure S2: ^{13}C NMR of [**3**][OTf] ($CDCl_3$).



[**3**][OTf]

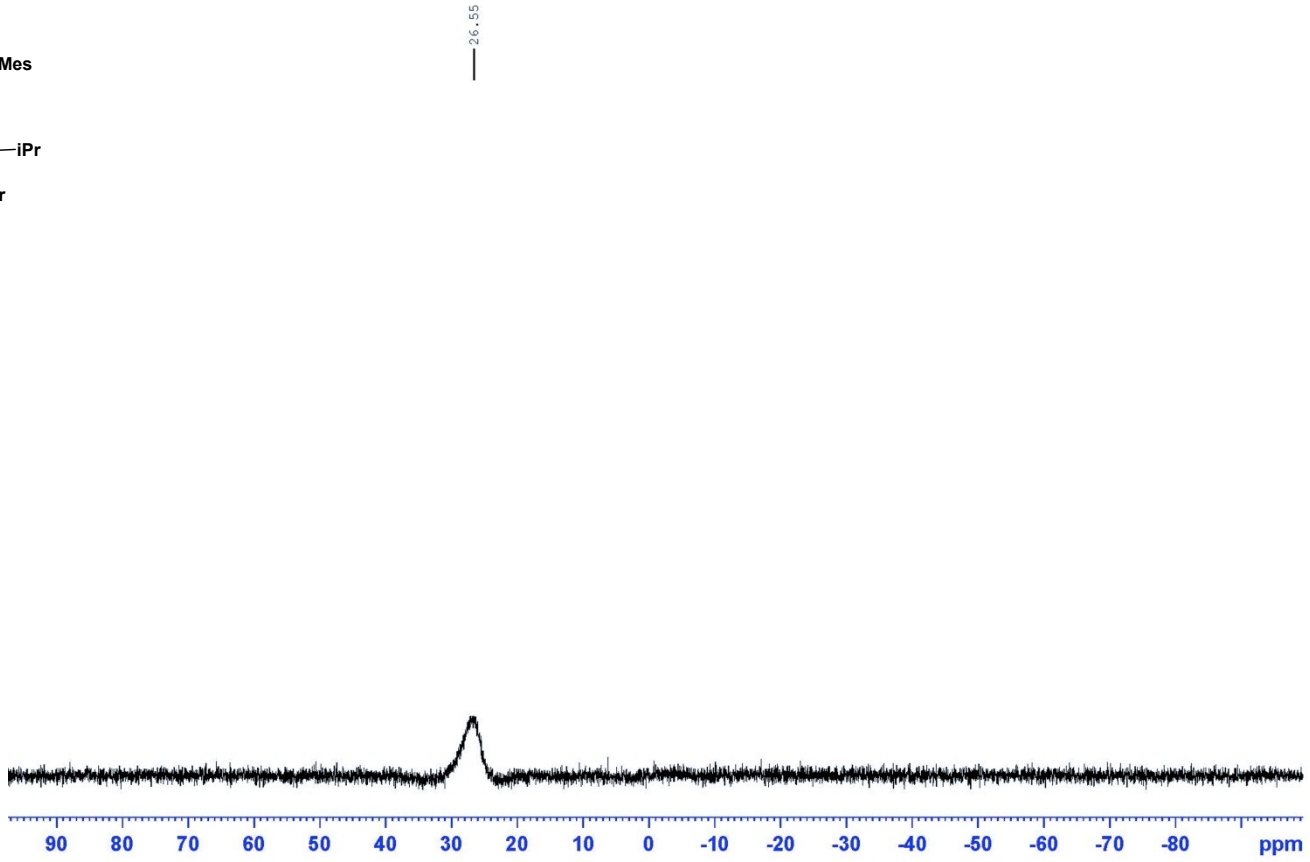
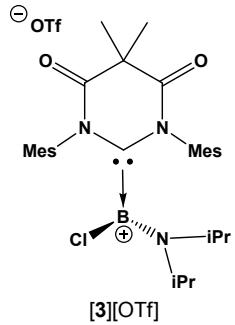


Figure S3: ^{11}B NMR of [**3**][OTf] ($CDCl_3$).



[**3**][OTf]

Figure S4: ^{19}F NMR of [**3**][OTf] ($CDCl_3$).

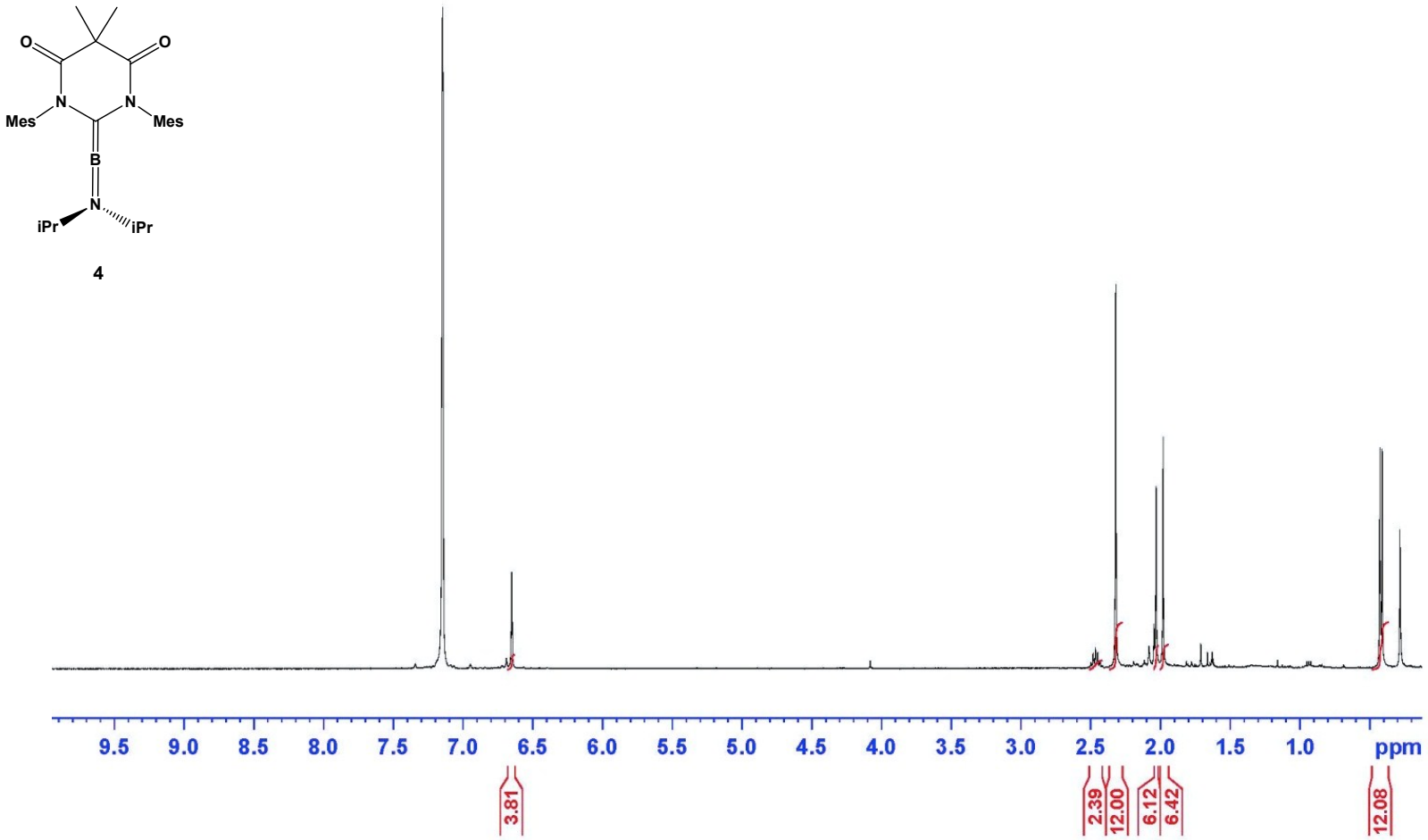


Figure S5: ^{1}H NMR of **4** (C_6D_6).

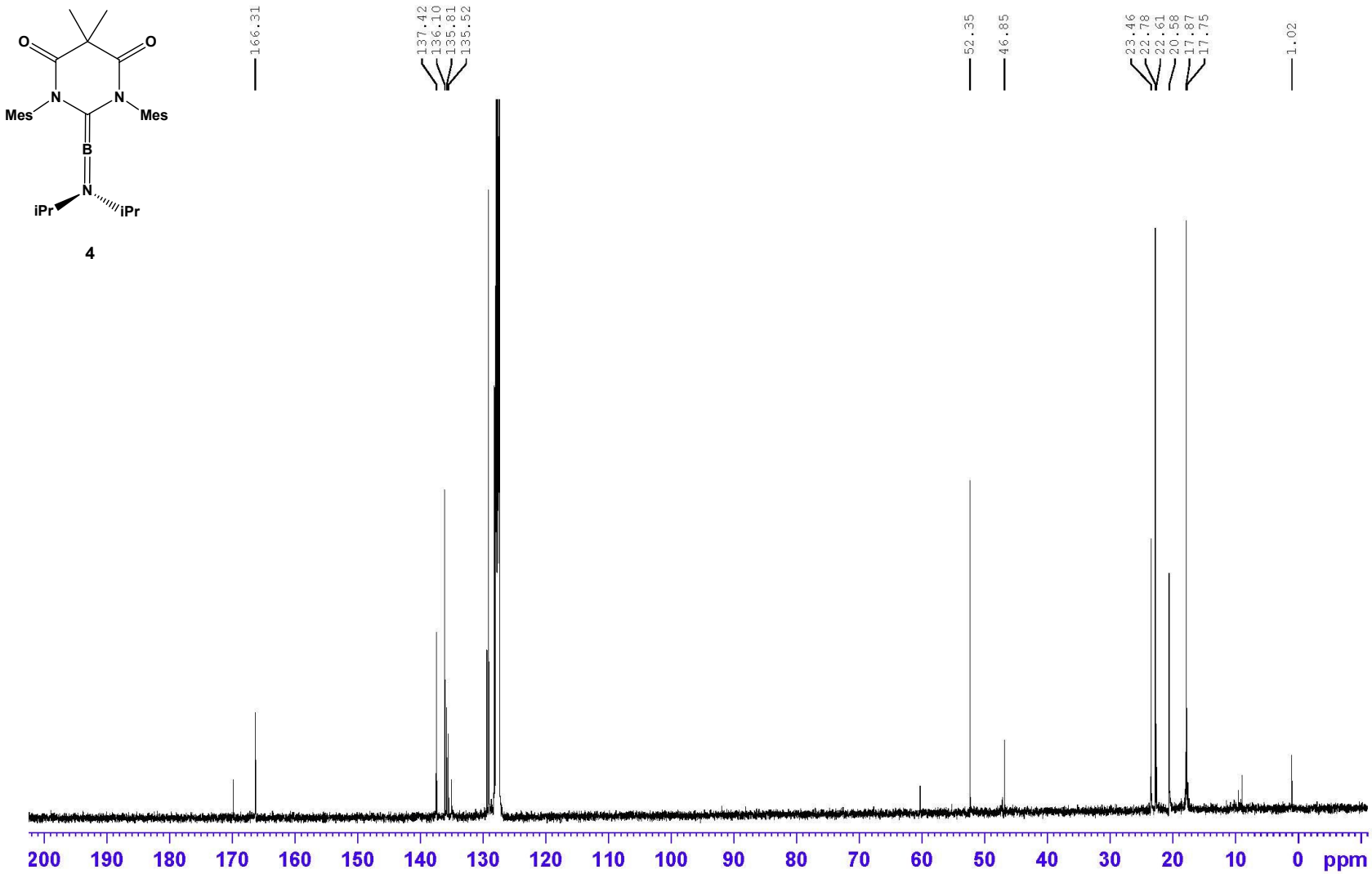
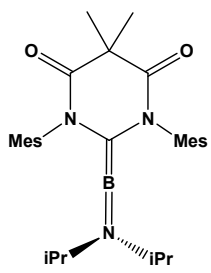


Figure S6: ^{13}C NMR of **4** (C_6D_6).



4

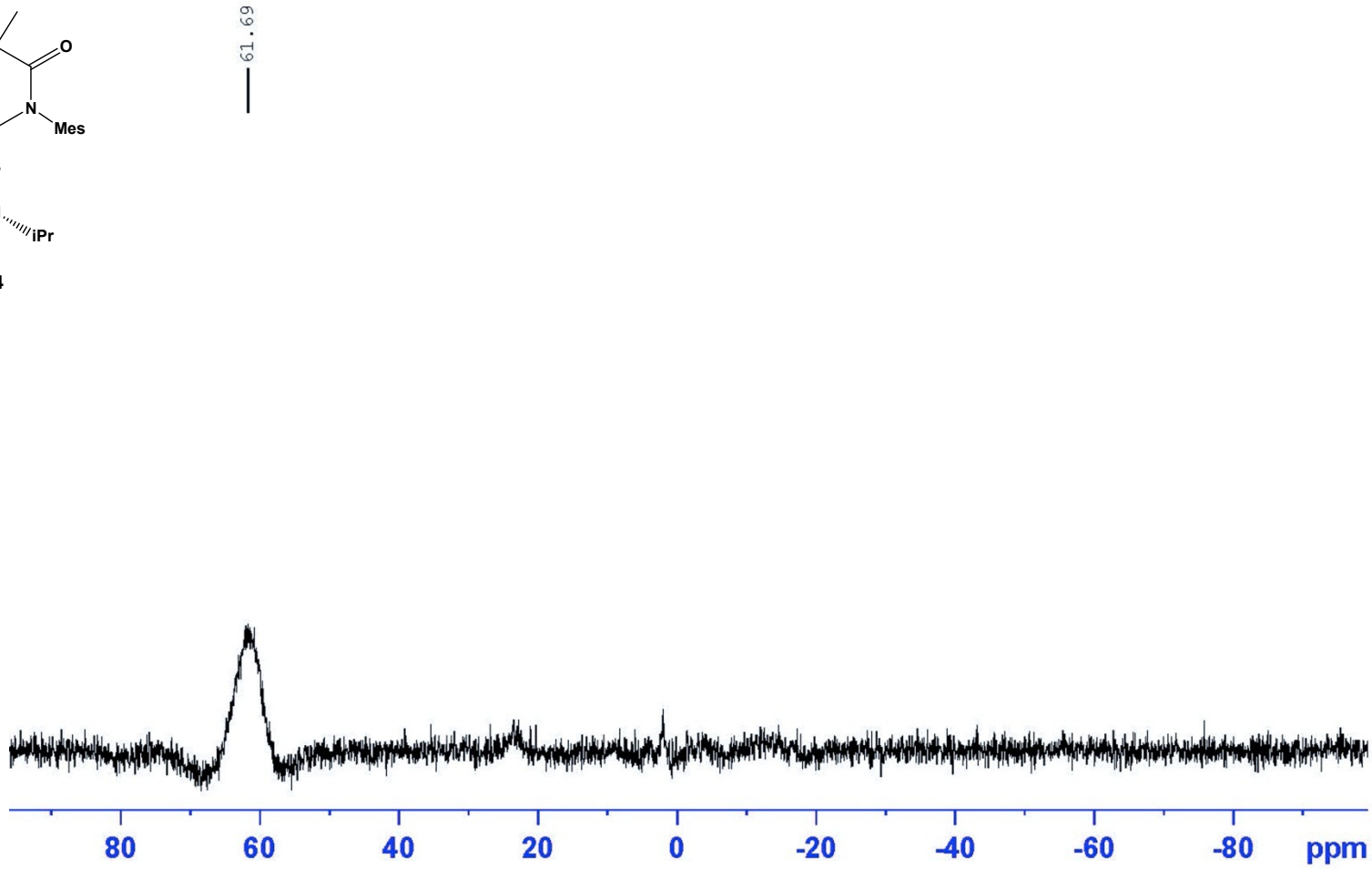


Figure S7: ^{1}H coupled ^{11}B NMR of **4** (C_6D_6).

CRYSTALLOGRAPHY

General Considerations: All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 223 K using an Oxford Cryostream low-temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using Crystal Clear Expert 2.0. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen. Colourless, single crystals of [**3**][OTf] – CH_2Cl_2 were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution saturated with [**3**][OTf]. This compound crystallized in the monoclinic space group $P2_{1/n}$ with one interstitial molecule of dichloromethane in the unit cell. Orange, single crystals of $\mathbf{3}^{\cdot}$ – C_6H_6 were grown by slow evaporation of benzene solution saturated with the radical. This compound crystallized in the triclinic space group *P*–1. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for [**3**][OTf] – CH_2Cl_2 and $\mathbf{3}^{\cdot}$ – C_6H_6 were assigned as 1448866 and 1448867, respectively.

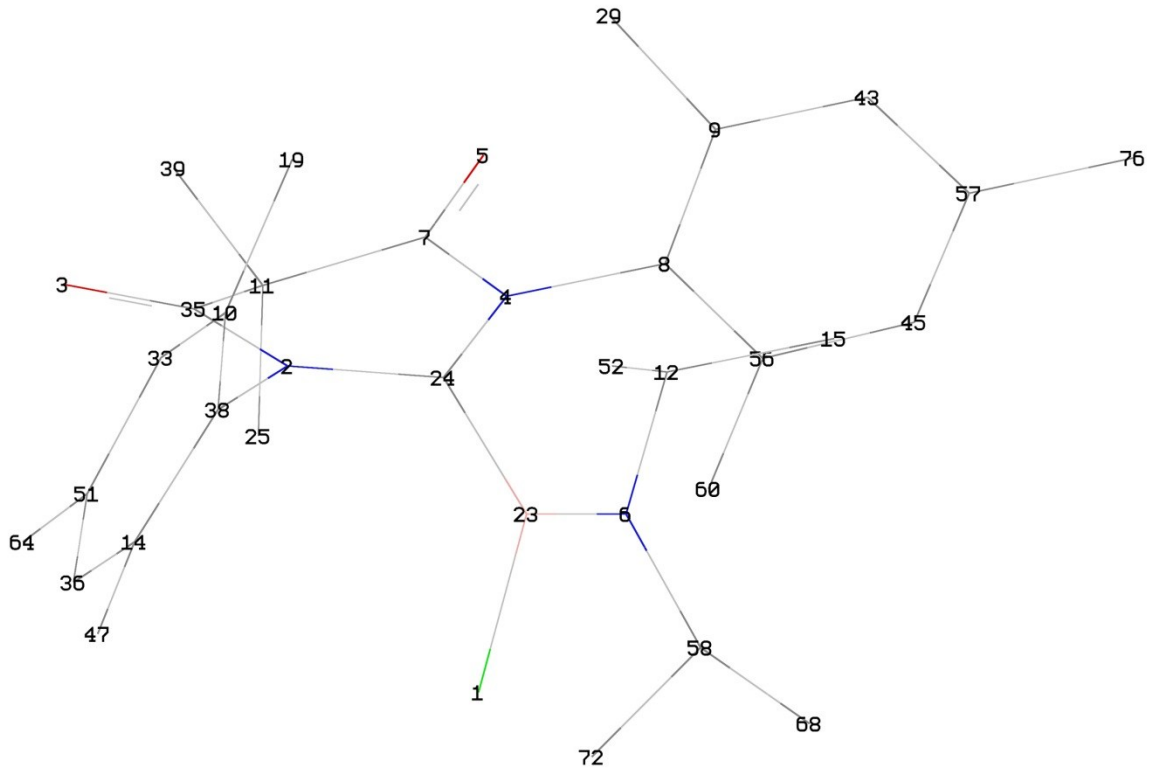
Table S1. Crystal Data, Data Collection and Structure Refinement for [**3**][OTf] – CH_2Cl_2, and $\mathbf{3}^{\cdot}$ – C_6H_6

	[**3**][OTf] – CH_2Cl_2		$\mathbf{3}^{\cdot}$ – C_6H_6	
Empirical Formula	$C_{32}H_{44}N_3O_5B_1Cl_3F_3S_1$		$C_{33}H_{45}N_3O_2B_1Cl_1$	
Formula Weight	756.92		561.98	
Temperature	100(2) K		100(2) K	
Wavelength	0.71075 Å		0.71073 Å	
Crystal System	Monoclinic		Triclinic	
Space Group	*P*21/n		*P*–1	
Unit Cell Dimensions	a = 13.8269(7) Å	α= 90.0°	a = 8.2331(18) Å	α= 75.271(5)°
	b = 17.9052(9) Å	β=107.190(8)°	b = 11.975(3)Å	β= 87.907(5)°
	c = 15.9013(11) Å	γ = 90.0°	c = 16.754(4) Å	γ = 84.925(4)°
Volume	3760.9(4) $Å^3$		1573.9(6) $Å^3$	
Z	4		2	
Density (calculated)	1.337 Mg/m3		1.186 Mg/m3	
Absorption coefficient	0.356 mm^{-1}		0.155 mm^{-1}	
F(000)	1584		604	
Crystal size	0.385 x 0.181 x 0.086 mm^3		0.32 x 0.20 x 0.12 mm^3	
Theta range for data collections	3.084 to 24.999°		2.99 3to 24.999°	
Index ranges	-16<=h<=16, -21<=k<=21, -18<=l<=18		-9<=h<=9, -14<=k<=14, -19<=l<=19	
Reflections collected	31927		21212	
Independent reflections	6614 [R(int) = 0.0443]		5540 [R(int) = 0.0632]	
Completeness to theta = 26.00°	99.8 %		99.8 %	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data/restraints/parameters	6614 / 0 / 433		540 / 0 / 361	
GooF on F^2	1.137		0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1320		R1 = 0.0592, wR2 = 0.1511	
R indices (all data)	R1 = 0.0719, wR2 = 0.1430		R1 = 0.0726, wR2 = 0.1619	
Largest diff. peak and hole	0.485 and -0.391 e.$Å^{-3}$		0.426 and -0.504 e.$Å^{-3}$	

COMPUTATIONAL DETAILS

General Considerations: Density functional theory (DFT) calculations (full geometry optimizations) were carried out on compounds **3•** and **4** using the Gaussian09[1] program (B3LYP/UB3LYP functional, with the 6-311++G(d',p') and 6-31+G basis sets for all atoms (compounds **3•** and **4**).[2] Frequency calculations performed on the DFT-optimized structures found no remaining imaginary frequencies. A Natural Bonding Order (NBO) analysis was performed on the optimized geometry of **3•** using the NBO Version 3.1 Software suite.[3]

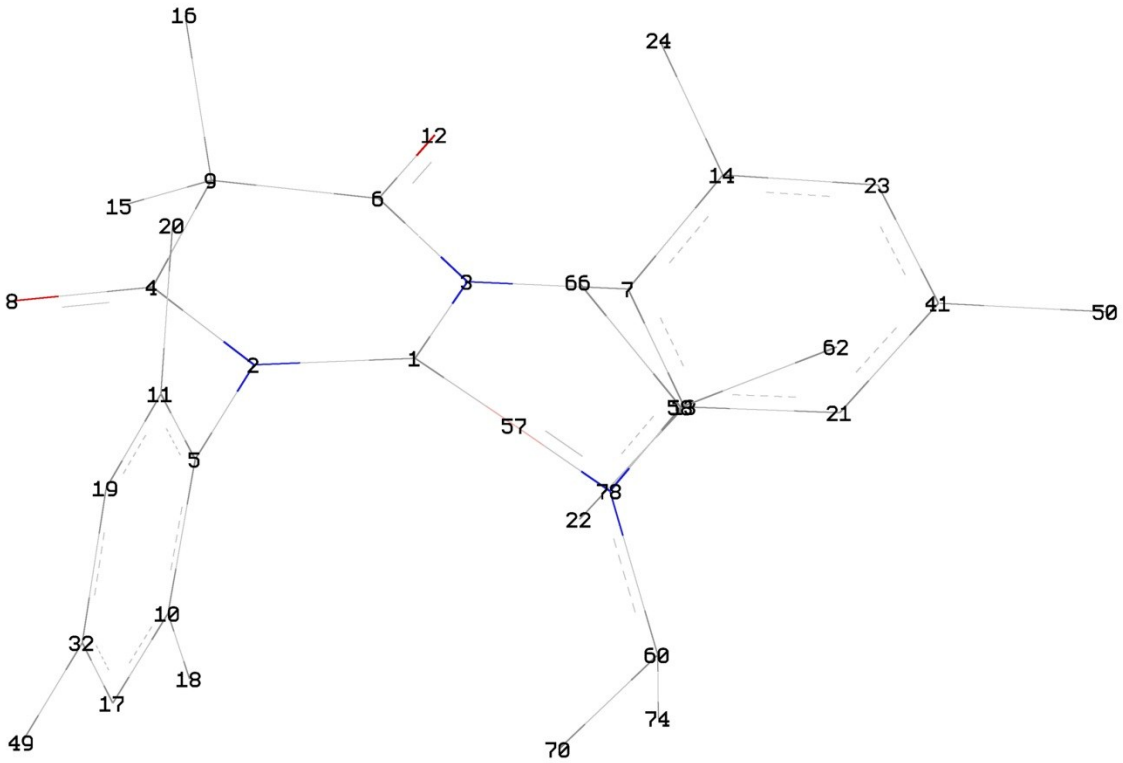
Figure S8: Wireframe rendering and Cartesian coordinates for **3•**



Center Number	Atom Symbol	Coordinates X	Y	Z	Center Number	Atom Symbol	Coordinates X	Y	Z
1	Cl	-0.51909	3.053447	0.817916	41	H	-3.24962	6.543149	5.611655
2	N	-1.2078	3.291628	4.152308	42	H	-1.87162	7.664878	5.400408
3	O	-3.01205	3.9782	5.368038	43	C	4.304909	5.048213	4.550863
4	N	0.633261	4.795363	3.873516	44	H	4.991402	4.871087	5.3777
5	O	0.503909	6.881339	4.788025	45	C	3.886825	5.821133	2.320049
6	N	1.524104	1.736651	2.198203	46	H	4.243361	6.254881	1.386911
7	C	-0.07236	5.865237	4.42195	47	C	-3.52193	2.482493	2.496833
8	C	2.058452	5.021954	3.67222	48	H	-4.01404	1.953291	1.674316
9	C	2.942589	4.790335	4.74307	49	H	-2.88911	3.260879	2.069212
10	C	-1.19342	1.050991	5.196592	50	H	-4.29784	2.974766	3.098213

11	C	-1.59395	5.723812	4.481309	51	C	-2.62919	-0.73393	4.331511
12	C	2.368467	1.401863	3.381361	52	C	2.163578	-0.04788	3.851027
13	H	2.018235	2.063679	4.177021	53	H	1.10671	-0.26197	4.036507
14	C	-2.75659	1.519132	3.370078	54	H	2.716859	-0.21059	4.78413
15	C	3.856173	1.709675	3.149497	55	H	2.540248	-0.77552	3.122054
16	H	4.000423	2.735186	2.799848	56	C	2.510824	5.595533	2.470055
17	H	4.316007	1.024025	2.427886	57	C	4.802227	5.545281	3.340664
18	H	4.3997	1.596062	4.094858	58	C	1.891354	0.963952	0.96693
19	C	-0.23086	1.520495	6.260129	59	H	2.721373	0.324232	1.278139
20	H	0.785752	1.648721	5.874187	60	C	1.562803	6.07808	1.398071
21	H	-0.18256	0.792684	7.076294	61	H	0.761502	5.369631	1.180678
22	H	-0.54723	2.480777	6.681769	62	H	2.103059	6.276156	0.46675
23	B	0.503759	2.684197	2.304633	63	H	1.093406	7.018512	1.717163
24	C	0.057068	3.539269	3.57027	64	C	-3.08156	-2.17541	4.353402
25	C	-2.16894	6.162692	3.102147	65	H	-3.04086	-2.59229	5.366229
26	H	-1.78521	5.550683	2.279615	66	H	-2.43861	-2.79956	3.717184
27	H	-1.9007	7.207979	2.913292	67	H	-4.10735	-2.27914	3.982987
28	H	-3.26116	6.080287	3.118433	68	C	2.444979	1.848902	-0.16141
29	C	2.448593	4.374325	6.107007	69	H	3.246057	2.497346	0.210084
30	H	1.705331	3.574699	6.060425	70	H	1.672856	2.47776	-0.6109
31	H	1.973197	5.228352	6.606964	71	H	2.862941	1.20951	-0.94916
32	H	3.278756	4.036005	6.735411	72	C	0.785115	0.007734	0.492875
33	C	-1.65749	-0.26924	5.225656	73	H	0.437023	-0.62407	1.317176
34	H	-1.26625	-0.94337	5.986447	74	H	1.188601	-0.64706	-0.28983
35	C	-2.0087	4.273034	4.733103	75	H	-0.07543	0.538565	0.080111
36	C	-3.17719	0.183009	3.430455	76	C	6.282332	5.780547	3.146021
37	H	-3.979	-0.13679	2.766487	77	H	6.765454	6.08161	4.082493
38	C	-1.70398	1.923958	4.21487	78	H	6.468574	6.561053	2.400116
39	C	-2.16027	6.627696	5.587849	79	H	6.785137	4.867386	2.798043
40	H	-1.77585	6.339297	6.571691					

Figure S9: Wireframe rendering and Cartesian coordinates for **4**



Center Number	Atom Symbol	Coordinates X	Y	Z	Center Number	Atom Symbol	Coordinates X	Y	Z
1	C	0.006528	0.464619	0.058968	40	H	4.523118	-0.86917	-2.49775
2	N	-1.20112	1.241269	-0.01183	41	C	4.853199	-0.97835	-0.36781
3	N	1.219416	1.228364	-0.04996	42	H	2.384757	1.695976	-2.80945
4	C	-1.26586	2.615244	0.021466	43	H	1.174615	0.419283	-2.65766
5	C	-2.44987	0.502108	-0.10192	44	H	2.663867	0.121811	-3.57581
6	C	1.299949	2.601424	-0.0124	45	H	4.91734	-0.84019	1.781427
7	C	2.459466	0.476967	-0.15841	46	H	3.254915	0.13214	3.169362
8	O	-2.37293	3.208968	-0.05617	47	H	1.642003	0.491802	2.518221
9	C	0.023771	3.41473	0.191941	48	H	2.910459	1.720898	2.464169
10	C	-2.93673	0.129153	-1.37155	49	C	-6.1544	-1.70965	-0.38246
11	C	-3.17127	0.224221	1.073082	50	C	6.14141	-1.76504	-0.48804
12	O	2.411462	3.183378	-0.11252	51	H	-6.60036	-1.87201	0.604134
13	C	2.94711	0.135662	-1.43602	52	H	-5.99642	-2.69255	-0.84495
14	C	3.170462	0.15324	1.01115	53	H	-6.88975	-1.17627	-0.99835
15	C	0.016859	4.594935	-0.81498	54	H	6.572385	-1.97575	0.496089
16	C	0.046245	3.987964	1.644552	55	H	6.890677	-1.21285	-1.06974
17	C	-4.13524	-0.59532	-1.43632	56	H	5.97967	-2.72453	-0.99602
18	C	-2.22965	0.560754	-2.63539	57	B	-0.00142	-0.95577	0.196872
19	C	-4.366	-0.50775	0.961853	58	C	0.092694	-3.04087	1.642987
20	C	-2.7303	0.76989	2.411702	59	H	-0.47055	-3.97406	1.512068
21	C	4.136397	-0.60241	-1.51665	60	C	-0.12405	-3.27467	-0.84639

22	C	2.25108	0.613221	-2.68907	61	H	0.476235	-4.15013	-0.56336
23	C	4.359447	-0.58485	0.883741	62	C	1.561305	-3.3902	1.939319
24	C	2.715487	0.644941	2.366501	63	H	1.630861	-3.99693	2.850392
25	H	0.001336	4.230962	-1.84862	64	H	2.013329	-3.95811	1.118674
26	H	0.918556	5.194781	-0.67388	65	H	2.149379	-2.47781	2.080471
27	H	-0.8744	5.204302	-0.65045	66	C	-0.55477	-2.25955	2.788985
28	H	0.050723	3.18805	2.394074	67	H	-0.02563	-1.32001	2.979306
29	H	-0.84149	4.60804	1.799375	68	H	-1.59953	-2.0257	2.563769
30	H	0.945636	4.596467	1.776155	69	H	-0.52167	-2.85911	3.706189
31	H	-4.52241	-0.88383	-2.4111	70	C	-1.58716	-3.71513	-1.03325
32	C	-4.85927	-0.932	-0.27967	71	H	-1.6556	-4.47421	-1.82211
33	H	-2.64867	0.052323	-3.50956	72	H	-2.00156	-4.14576	-0.1149
34	H	-1.15581	0.351754	-2.59538	73	H	-2.20882	-2.85927	-1.31577
35	H	-2.34442	1.641887	-2.78681	74	C	0.465128	-2.69467	-2.13422
36	H	-4.93111	-0.72947	1.863965	75	H	-0.11066	-1.82938	-2.47739
37	H	-3.23962	0.254529	3.232347	76	H	1.503189	-2.382	-1.98774
38	H	-2.97555	1.837915	2.479272	77	H	0.437243	-3.45472	-2.92373
39	C	-1.99081	1.409105	0.056795	78	N	-0.01376	-2.31572	0.318451

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