Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

An ENDOR and DFT analysis of hindered methyl group rotations in frozen solutions of bis(acetylacetonato)-copper(II).

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Electronic Supplementary Information

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CW EPR spectra of "*wet*" and "*dry*" [Cu(acac)$_2$]

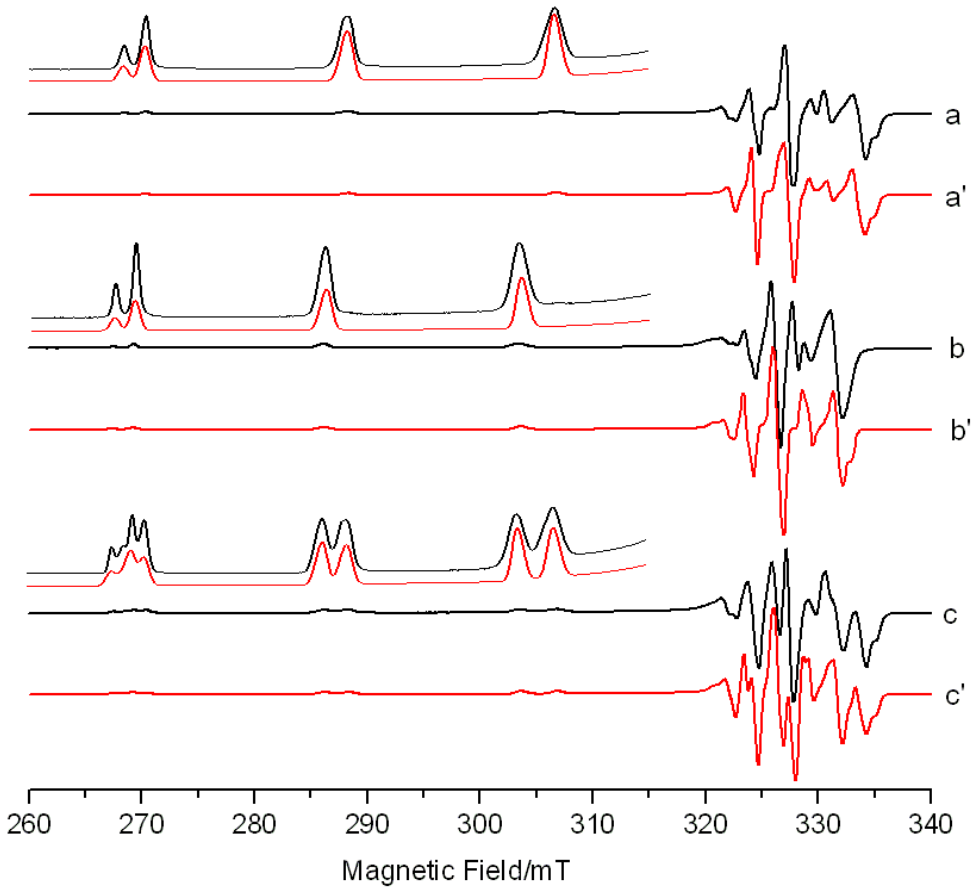

Figure S1: CW X-band EPR spectra of [Cu(acac)$_2$] dissolved in $CHCl_3$:$C_6H_5CH_3$ (2:3) under a) strict anhydrous conditions, b) under '*wet*' conditions, and c) '*mixed*' conditions (using '*bench-top*' solvents). All spectra were recorded at 140 K. Experimental spectra (a-c; black trace), simulated spectra (a′-c′; red trace). An expanded view of the low field parallel regions are also shown. Spin Hamiltonian parameters are given in Table 1 (main paper).

Q-band angular selective ^{1}H ENDOR (250 kHz RF modulation)

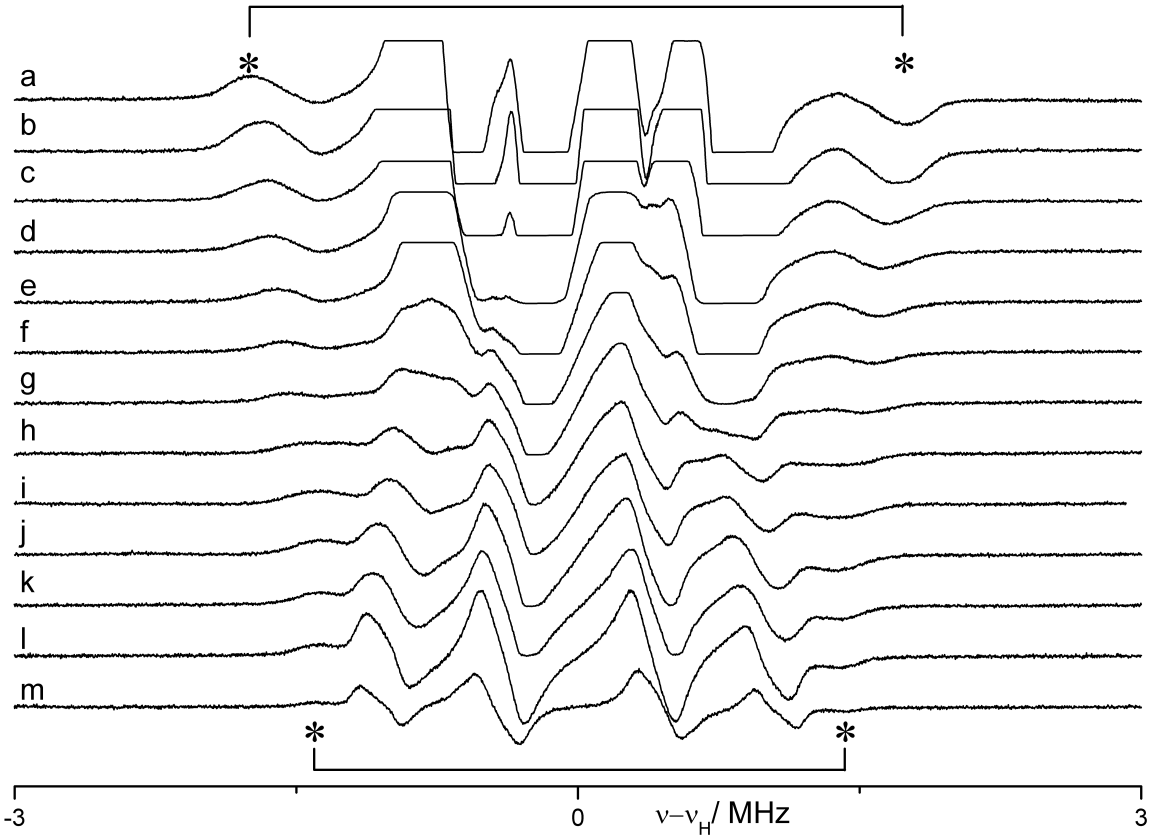

Figure S2: Angular selective ^{1}H ENDOR spectra, recorded at 10 K and Q-band frequency, of [Cu(acac)$_2$] recorded at 250 kHz RF modulation amplitude at different field positions (mT): (a) 1190.5 (b) 1186.2 (c) 1181.9 (d) 1176.6 (e) 1169.0 (f) 1160.6 (g) 1153.5 (h) 1139.4 (i) 1129.2 (j) 1113.7 (k) 1099.4 (l) 1072.4 and (m) 1046.8 mT. The peaks arising from the hindered rotational methyl groups (labelled *) are more clearly visible at this increased RF modulation.

DFT calculated relative energies as a function of dihedral angle

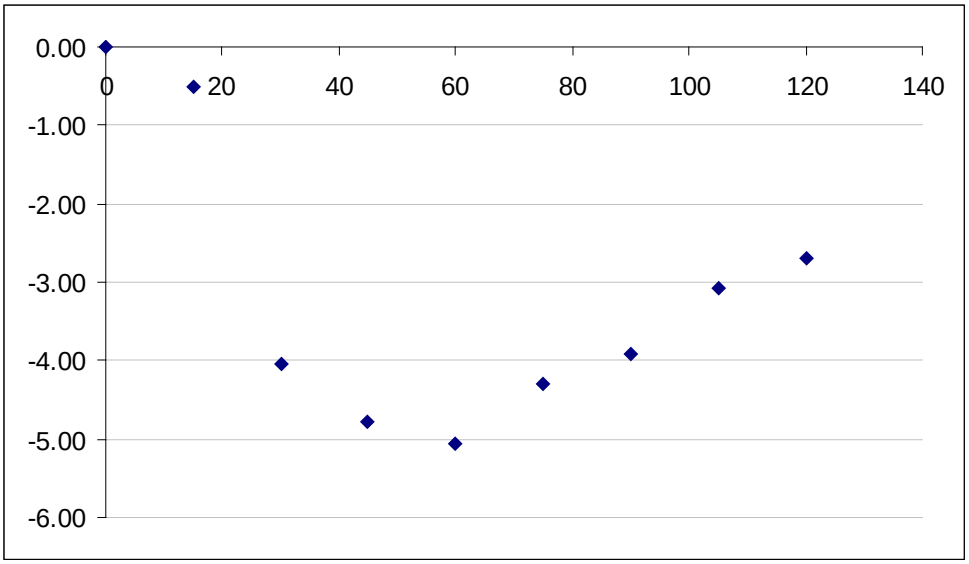

Figure S3: Relative DFT energies (Y-axis) as a function of dihedral angle (X-axis), defined as H-C-C-O, for the rotation of the methyl group.

DFT calculated hyperfine couplings as a function of rotation angle

Table S1: DFT calculated hyperfine couplings for the **methyl group protons** in [$Cu(acac)_2$], as a function of the rotation angle. See main text for a definition of the rotation angle θ.

Rotation Angle	Atom	α	β	γ	A_x	A_y	A_z	a_{iso}
0	8H	-17.7	69.8	-30.2	-1.02	-1.49	1.32	-0.40
0	9H	1.8	87.4	30.5	-2.11	1.89	-1.29	-0.50
0	10H	20.3	61.3	53	-0.38	1.88	-0.85	0.22
15	8H	12.9	22.3	-47.1	0.9	-1.99	-1.54	-0.88
15	9H	-35.2	9.1	66.5	-1.36	1.8	-2.16	-0.57
15	10H	-42	74.9	-23.6	0.26	-0.22	2.45	0.83
30	8H	-41.4	31.1	3	0.5	-2.61	-2.15	-1.42
30	9H	-30.5	24	61.3	-1.68	1.37	-2.37	-0.89
30	10H	24.1	82.6	-21.4	0.79	1.29	3.4	1.83
45	8H	36	39.2	13.5	-2.71	0.54	-2.21	-1.46
45	9H	-29.4	31.6	59.9	-1.88	1.12	-2.51	-1.09
45	10H	14.1	85.7	-21.2	1.13	1.64	3.73	2.17
60	8H	-28.7	37.9	60.2	-2	0.94	-2.59	-1.22
60	9H	29.5	45.1	19.4	-2.7	0.64	-2.19	-1.42
60	10H	7.1	87.7	-20.2	1.24	1.76	3.84	2.28
75	8H	-30.5	32.3	62.2	-1.85	1.14	-2.48	-1.06
75	9H	36.3	37.3	14.4	-2.7	0.5	-2.23	-1.48
75	10H	13.9	84.7	-19.8	1.1	1.61	3.7	2.14
90	8H	8.6	77	26.9	-2.23	1.63	-1.48	-0.69
90	9H	5.4	67.6	-40.1	-1.89	-2.33	0.63	-1.20
90	10H	19.4	39.1	49.3	0.7	2.86	0.22	1.26
105	8H	-34	9.1	60.3	-1.36	1.77	-2.16	-0.58
105	9H	15.6	22.5	-54.7	0.9	-1.97	-1.52	-0.86
105	10H	-22.1	43.8	77.6	-0.32	2.34	0.15	0.72
120	8H	-33.1	2.6	58.2	-1.3	1.85	-2.11	-0.52
120	9H	-29.3	72.1	-32.6	-0.48	-0.95	1.77	0.11
120	10H	21.1	72	48	-1	1.32	-1.45	-0.38

Table S2: DFT calculated hyperfine couplings for the **methine protons** in $Cu(acac)_2$, as a function of the rotation angle. See main text for a definition of the rotation angle θ.

Rotation Angle	Atom	α	β	γ	A_x	A_y	A_z	a_{iso}
0	16H	-4.7	0.1	4.7	1.06	-1.75	2.34	0.55
0	20H	0	89.9	0.1	-2.35	-1.75	1.06	-1.01
15	16H	0.2	89.5	0.7	-2.34	-1.75	1.05	-1.01
15	20H	31.3	0.2	-30.6	1.05	-1.75	-2.35	-1.02
30	16H	44.8	0.4	-45.6	1.05	-1.75	-2.35	-1.02
30	20H	0.2	90	-0.8	-2.36	-1.75	1.05	-1.02
45	16H	0.2	90	-1.5	-2.36	-1.75	1.05	-1.02

45	20H	-7.6	0.4	6.1	1.05	-1.75	-2.36	-1.02
60	16H	0.1	90	-0.8	-2.36	-1.75	1.05	-1.02
60	20H	0.4	90	-0.8	-2.36	-1.75	1.05	-1.02
75	16H	0	89.5	-0.2	-2.36	-1.75	1.05	-1.02
75	20H	0	89.8	-0.2	-2.36	-1.75	1.05	-1.02
90	16H	-43.8	0.3	40.8	1.05	-1.75	-2.35	-1.02
90	20H	0.1	89.9	-2.9	-2.35	-1.75	1.05	-1.02
105	16H	0.1	89.8	-4.3	-2.35	-1.75	1.05	-1.02
105	20H	0.2	90	-4.2	-2.36	-1.75	1.05	-1.02
120	16H	0.1	90	-5.4	-2.35	-1.75	1.05	-1.02
120	20H	0	90	-5.2	-2.35	-1.75	1.05	-1.02

Table S3; Atomic coordinates for [Cu(acac)$_2$] as a function of the methyl group rotation.

Dihedral Angle = 0				Dihedral = 15			
Cu	-0.002923	0.000075	-0.002826	Cu	-0.001929	0.000430	0.006133
O	1.336337	-1.416569	-0.002412	O	1.337444	-1.415357	-0.005246
O	1.336443	1.416668	0.003209	O	1.336914	1.418011	0.005621
O	-1.344168	1.414147	-0.001109	O	-1.343348	1.413931	0.006176
O	-1.344256	-1.413923	-0.003172	O	-1.342655	-1.413969	0.006470
C	2.605140	-1.243354	0.001048	C	2.606272	-1.241795	-0.013267
C	2.605213	1.243314	0.004046	C	2.605444	1.245005	-0.009014
C	3.437986	-2.511993	0.003202	C	3.437284	-2.510873	0.001831
H	4.087166	-2.544299	0.891579	H	3.849556	-2.670141	1.010897
H	2.780525	-3.388980	0.001340	H	2.805010	-3.370397	-0.249925
H	4.090909	-2.544457	-0.882117	H	4.281138	-2.445029	-0.698447
C	3.438240	2.511804	0.005860	C	3.438474	2.513305	-0.011627
H	2.781093	3.388947	0.018022	H	2.781601	3.390713	-0.012930
H	4.098094	2.537780	0.886345	H	4.089189	2.547023	0.875455
H	4.080549	2.550462	-0.887166	H	4.090081	2.543796	-0.898028
C	3.261872	-0.000046	0.003591	C	3.262437	0.001501	-0.022463
H	4.352818	-0.000080	0.006208	H	4.352953	0.002325	-0.035889
C	-2.613301	-1.243073	-0.004030	C	-2.611753	-1.243594	0.005448
C	-2.613223	1.243375	-0.002464	C	-2.612380	1.242904	0.004369
C	-3.272566	0.000172	-0.003742	C	-3.271340	-0.000503	0.005074
H	-4.361777	0.000207	-0.004285	H	-4.360727	-0.000774	0.004516
C	-3.426669	-2.520260	-0.005532	C	-3.424652	-2.521069	0.005027
H	-3.167239	-3.115730	-0.893831	H	-3.170162	-3.113634	-0.886712
H	-3.159610	-3.122944	0.875512	H	-3.152114	-3.126461	0.882475
H	-4.506369	-2.326219	-0.000445	H	-4.504379	-2.327574	0.016740
C	-3.426517	2.520613	-0.002476	C	-3.425975	2.519929	0.001802
H	-3.160012	3.121902	0.879696	H	-3.155702	3.125723	0.879685
H	-3.166441	3.117464	-0.889658	H	-3.169978	3.112394	-0.889564
H	-4.506228	2.326625	0.001603	H	-4.505615	2.325806	0.011387
Dihedral = 30				Dihedral = 45			
Cu	0.005168	0.000410	-0.001610	Cu	0.006843	0.000462	0.000306
O	1.344180	-1.416833	-0.040895	O	1.347157	-1.415193	-0.036009
O	1.347101	1.411871	-0.005798	O	1.347875	1.413015	-0.019500
O	-1.335033	1.414952	0.035211	O	-1.333737	1.415278	0.038355
O	-1.336085	-1.412711	0.002822	O	-1.333739	-1.413271	0.011121
C	2.612559	-1.247224	-0.058943	C	2.615898	-1.244151	-0.054558
C	2.616234	1.238994	-0.034173	C	2.616611	1.241997	-0.044667
C	3.433283	-2.520956	-0.052694	C	3.431325	-2.520211	-0.051215
H	3.604073	-2.834118	0.990338	H	3.362920	-2.986933	0.944582
H	2.876727	-3.324460	-0.551655	H	3.003169	-3.232778	-0.770008
H	4.411891	-2.381053	-0.530203	H	4.488293	-2.339198	-0.285292
C	3.430855	2.515477	-0.035479	C	3.431175	2.518829	-0.052902
H	3.152593	3.124220	-0.908838	H	3.154524	3.120400	-0.931696
H	3.184828	3.105422	0.860142	H	3.183943	3.114469	0.838248
H	4.510124	2.320050	-0.057341	H	4.510845	2.323740	-0.071761
C	3.272966	-0.003937	-0.064155	C	3.275268	-0.001060	-0.064625
H	4.362243	-0.006237	-0.088895	H	4.364144	-0.001172	-0.091587
C	-2.605027	-1.241771	0.019528	C	-2.602593	-1.242414	0.030879
C	-2.603998	1.244464	0.049076	C	-2.602517	1.244031	0.054410
C	-3.263758	0.001463	0.042102	C	-3.261776	0.000672	0.050516
H	-4.352949	0.001716	0.055072	H	-4.350910	0.000380	0.063782
C	-3.418517	-2.518846	0.014175	C	-3.415909	-2.519697	0.029227
H	-3.161426	-3.110479	-0.877230	H	-3.157340	-3.115382	-0.858936
H	-3.149213	-3.125351	0.891952	H	-3.147826	-3.122001	0.910368
H	-4.498135	-2.324784	0.023579	H	-4.495573	-2.325817	0.036638
C	-3.416761	2.521778	0.075220	C	-3.415984	2.520956	0.076572
H	-3.140131	3.111025	0.962387	H	-3.132698	3.118608	0.955933
H	-3.166303	3.130493	-0.806579	H	-3.172946	3.121370	-0.812901
H	-4.496401	2.328054	0.088881	H	-4.495355	2.326696	0.100714

Dihedral = 60

Cu	0.007740	0.000710	-0.002008
O	1.347782	-1.413432	-0.031293
O	1.348695	1.414407	-0.024366
O	-1.333216	1.414191	0.021759
O	-1.333060	-1.413255	0.026607
C	2.616774	-1.243256	-0.048654
C	2.617487	1.243097	-0.042193
C	3.429141	-2.520864	-0.069069
H	3.157899	-3.138602	0.800017
H	3.172780	-3.100188	-0.968934
H	4.508618	-2.327309	-0.058482
C	3.431236	2.519993	-0.053014
H	3.157976	3.117408	-0.935825
H	3.179057	3.120507	0.833679
H	4.510985	2.325784	-0.066196
C	3.276384	-0.000310	-0.053298
H	4.365478	0.000126	-0.068803
C	-2.601922	-1.242866	0.048567
C	-2.602123	1.243443	0.043853
C	-3.261292	0.000240	0.057748
H	-4.350348	0.000157	0.077716
C	-3.414642	-2.520300	0.066089
H	-3.158788	-3.126478	-0.815763
H	-3.143384	-3.112053	0.953401
H	-4.494352	-2.326710	0.074595
C	-3.415204	2.520759	0.056078
H	-3.128405	3.127187	0.928207
H	-3.175694	3.112282	-0.840399
H	-4.494515	2.326960	0.085975

Dihedral = 75

Cu	0.005373	-0.001608	-0.003644
O	1.345481	-1.415953	-0.025501
O	1.346545	1.411259	-0.037264
O	-1.333567	1.413626	0.019399
O	-1.336008	-1.414052	0.032374
C	2.614822	-1.246912	-0.058941
C	2.615251	1.239790	-0.056720
C	3.428154	-2.523425	-0.060098
H	3.028409	-3.231487	0.678176
H	3.373433	-2.991265	-1.056666
H	4.488080	-2.327033	0.150099
C	3.428870	2.516815	-0.063997
H	3.152709	3.121352	-0.940703
H	3.178156	3.112651	0.827128
H	4.507638	2.321679	-0.077520
C	3.273882	-0.003546	-0.066750
H	4.363199	-0.004987	-0.079622
C	-2.604528	-1.242073	0.057324
C	-2.602670	1.244448	0.048593
C	-3.262573	0.002008	0.067469
H	-4.351603	0.003601	0.087343
C	-3.418855	-2.518473	0.080543
H	-3.169495	-3.125914	-0.802465
H	-3.142589	-3.109597	0.966356
H	-4.498249	-2.323568	0.095463
C	-3.414214	2.522413	0.053268
H	-3.126572	3.131203	0.923516
H	-3.174537	3.111436	-0.844932
H	-4.493454	2.329237	0.083770

Dihedral = 90

Cu	0.004789	-0.000165	0.006261
O	0.343999	-1.418078	0.000324
O	1.346157	1.410933	-0.037376
O	1.335337	1.415017	0.018517
O	1.336516	-1.412532	0.045971
C	2.612086	-1.248819	-0.030509
C	2.615478	1.237362	-0.057876
C	3.432850	-2.522110	-0.066957
H	2.885024	-3.334238	0.426999
H	3.602256	-2.814303	-1.116193
H	4.414945	-2.385585	0.405111
C	3.429886	2.513615	-0.088275
H	3.150682	3.102333	-0.974980
H	3.184258	3.123657	0.793930
H	4.509189	2.318146	-0.106391
C	3.272440	-0.005588	-0.051737
H	4.361921	-0.008287	-0.068877
C	-2.605401	-1.241062	0.069059
C	-2.604130	1.245246	0.046126
C	-3.263914	0.002416	0.070572
H	-4.352978	0.003050	0.092374
C	-3.418661	-2.517911	0.097870
H	-3.166858	-3.129664	-0.781367
H	-3.143975	-3.104324	0.987583
H	-4.498263	-2.323797	0.109560
C	-3.416621	2.522985	0.051089
H	-3.133717	3.130555	0.923793
H	-3.172376	3.113070	-0.845012
H	-4.496129	2.329704	0.076409

Dihedral = 105

Cu	0.002676	-0.000199	0.001963
O	1.340930	-1.420256	-0.004768
O	1.344659	1.409313	-0.051601
O	-1.336614	1.415786	0.019984
O	-1.338755	-1.412142	0.047925
C	2.608577	-1.251928	-0.036409
C	2.614216	1.234259	-0.074612
C	3.436152	-2.522812	-0.056648
H	2.811118	-3.380584	0.218030
H	3.838851	-2.688026	-1.068768
H	4.292150	-2.448193	0.629229
C	3.429242	2.509947	-0.111564
H	3.146039	3.097513	-0.997750
H	3.188431	3.121705	0.770821
H	4.508323	2.313695	-0.134770
C	3.269622	-0.008636	-0.065601
H	4.359303	-0.013425	-0.085692
C	-2.607466	-1.240203	0.073938
C	-2.605360	1.246180	0.052081
C	-3.265468	0.003594	0.077810
H	-4.354446	0.004703	0.102839
C	-3.421443	-2.516628	0.103538
H	-3.174775	-3.126154	-0.778720
H	-3.142439	-3.105592	0.990191
H	-4.500817	-2.321719	0.121229
C	-3.417419	2.524174	0.061797
H	-3.134330	3.128357	0.936844
H	-3.172839	3.117588	-0.831976
H	-4.497030	2.331312	0.086657

Dihedral = 120

Cu	0.002452	0.000279	-0.003081
O	1.338964	-1.423039	-0.021040
O	1.344014	1.408321	-0.053564
O	-1.338060	1.416179	0.014780
O	-1.339987	-1.410473	0.047384
C	2.606122	-1.254650	-0.054964
C	2.613711	1.231631	-0.082470
C	3.437635	-2.522509	-0.061756
H	2.783143	-3.400441	-0.024482
H	4.055955	-2.568813	-0.971331
H	4.123362	-2.535932	0.798784
C	3.429267	2.506977	-0.116549
H	3.145189	3.097237	-1.000669
H	3.189835	3.116039	0.768100
H	4.508351	2.310450	-0.141077
C	3.267583	-0.011184	-0.084886
H	4.357347	-0.017172	-0.112019
C	-2.608423	-1.238768	0.084231
C	-2.606567	1.247210	0.051804
C	-3.266848	0.004731	0.087371
H	-4.355593	0.005754	0.118709
C	-3.421567	-2.515448	0.124987
H	-3.189041	-3.123469	-0.762186
H	-3.128264	-3.105852	1.006004
H	-4.500585	-2.320905	0.159804
C	-3.418697	2.525214	0.055794
H	-3.131336	3.136246	0.924702
H	-3.178761	3.111702	-0.843791
H	-4.498114	2.332312	0.087406