Supporting Information

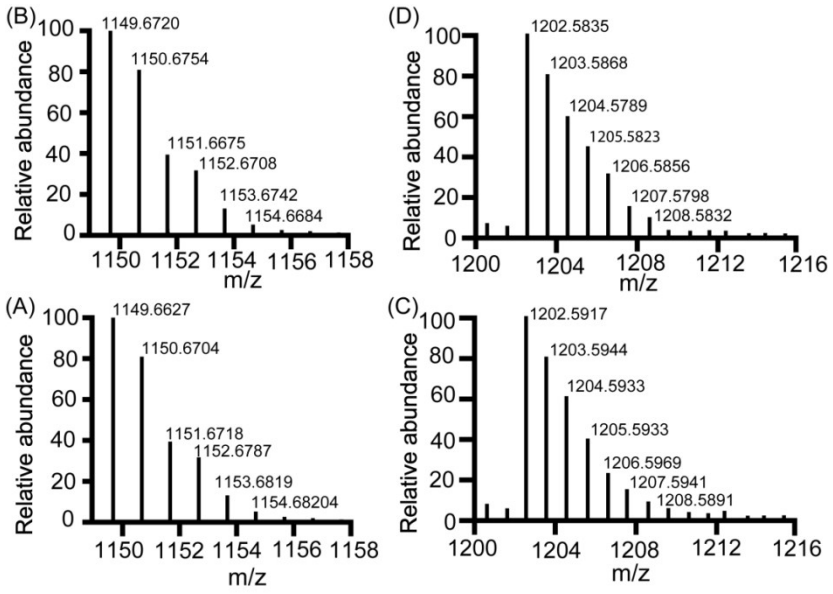

Figure S1. Isotopic distribution pattern of the (A) experimental and (B) simulated ESI-MS spectrum (positive ion mode) of Ni-PD, and (C) experimental and (D) simulated ESI-MS spectrum (positive ion mode) of FeNi-PD.

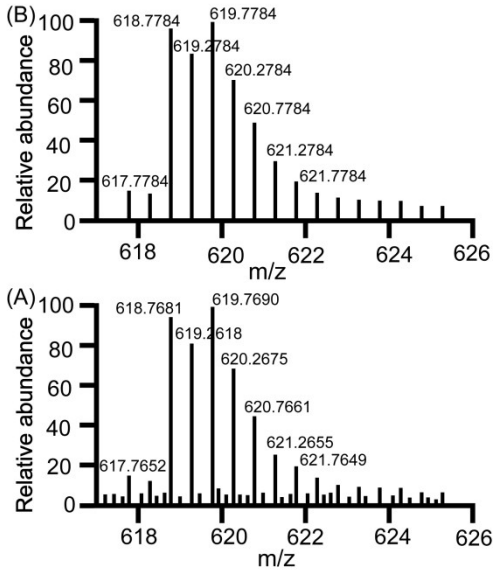

Figure S2. Isotopic distribution pattern of the (A) experimental and (B) simulated ESI-MS spectrum (positive ion mode) of FeNi-PD•2$FeCl_4$.

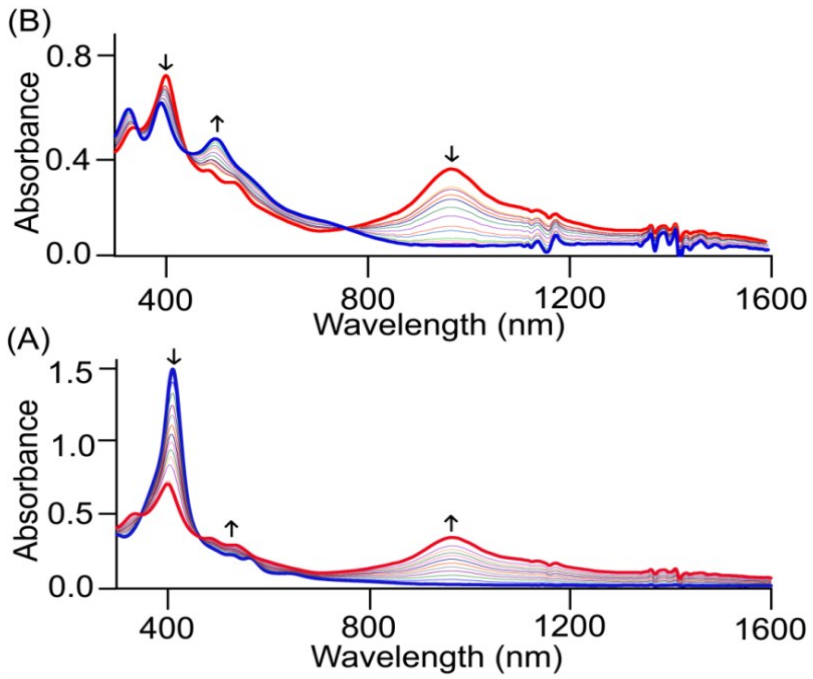

Figure S3. UV-vis-NIR (in $CHCl_3$ at 295 K) spectral changes of 1 x 10^{-5} (M) solution of FeNi-PD upon gradual addition of (A) 0 to 1.0 eq. and (B) 1.0 to 2.0 eq. of $Fe(ClO_4)_3$.

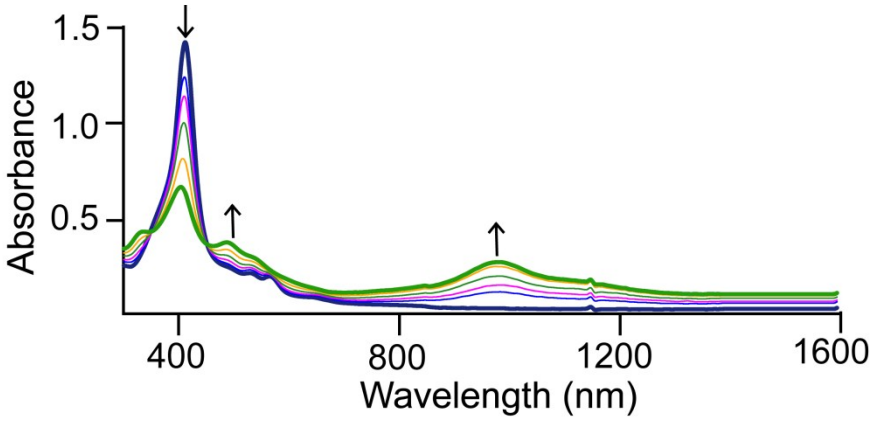

Figure S4. UV-vis-NIR (in $CHCl_3$ at 295 K) spectral changes of 1 x 10^{-5} (M) solution of FeNi-PD upon gradual addition of 0 to 8.0 eq. of $AgClO_4$. Similar spectral changes are also obtained upon additions of $AgSbF_6$ and $AgBF_4$.

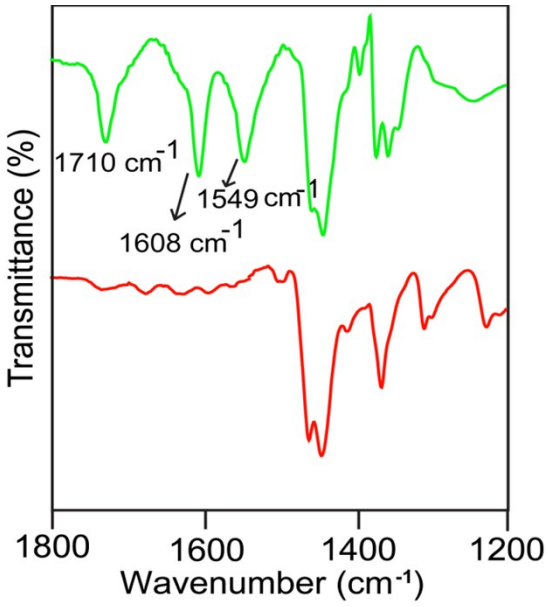

Figure S5. IR spectra (selected portion only) of solid polycrystalline samples of FeNi-PD (red-line) and FeNi-PD•2$FeCl_4$ (green-line). The π-cation radical marker bands in FeNi-PD•2$FeCl_4$ have been labeled.

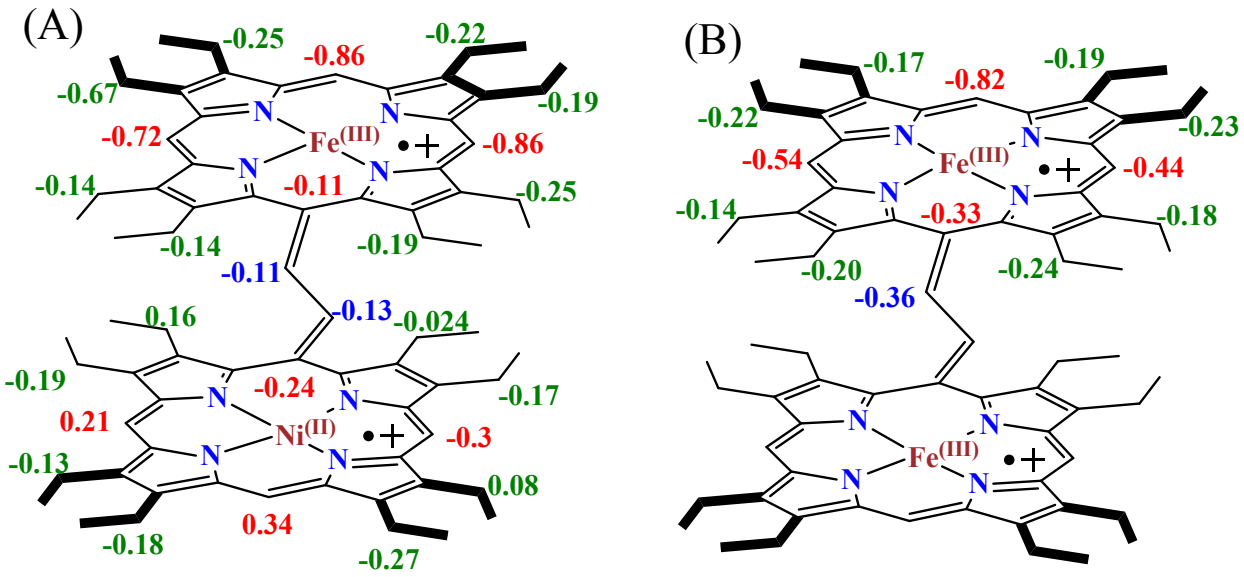

Figure S6. Calculated Mulliken spin densities ($\times 10^{-2}$) for (A) FeNi-PD•2$FeCl_4$ and (B) Fe_2-PD•2$FeCl_4$ at the UB97D/6-31G**/LANL2DZ level.

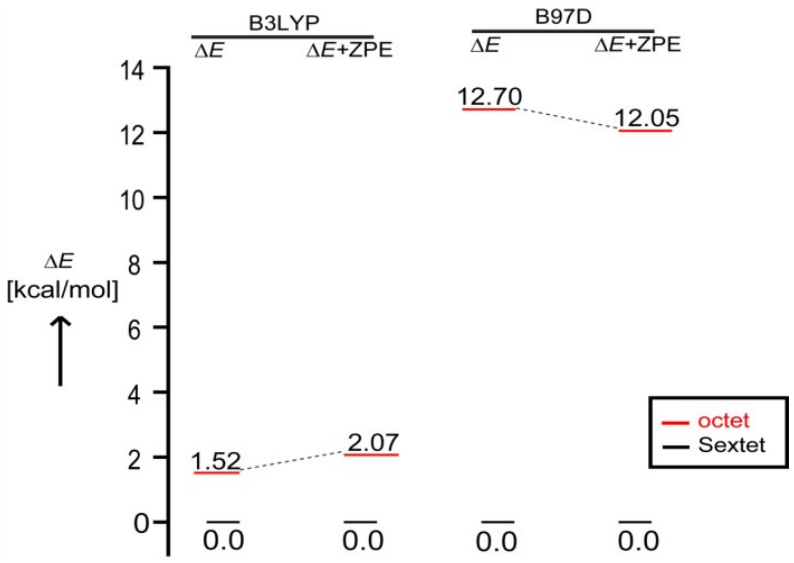

Figure S7. Relative spin-state energies of sextet (6), and octet (8) states of FeNi-PD•2$FeCl_4$ as calculated using B3LYP/BS1 and B97D/BS1 level of theory. All the ΔE and ΔE+ZPE value are relative to sextet (6) state.

Table S1. Selected Bond Distances (Å) and Angles (º).

	FeNi-PD•2$FeCl_4$
Fe(1)-N(6)	2.010(4)
Fe(1)-N(7)	2.022(4)
Fe(1)-N(5)	2.047(4)
Fe(1)-N(8)	2.056(4)
Fe(1)-Cl(1)	2.2383(15)
Ni(1)-N(2)	1.903(4)
Ni(1)-N(3)	1.907(4)
Ni(1)-N(4)	1.917(4)
Ni(1)-N(1)	1.920(4)
C(20)-C(38)	1.353(7)
C(37)-C(60)	1.346(7)
C(37)-C(38)	1.427(6)
N(6)-Fe(1)-N(7)	88.39(15)
N(6)-Fe(1)-N(5)	87.62(15)

N(7)-Fe(1)-N(5)	156.58(16)
N(6)-Fe(1)-N(8)	157.21(16)
N(7)-Fe(1)-N(8)	88.47(15)
N(5)-Fe(1)-N(8)	86.34(15)
N(6)-Fe(1)-Cl(1)	104.61(12)
N(7)-Fe(1)-Cl(1)	105.42(12)
N(5)-Fe(1)-Cl(1)	97.92(12)
N(8)-Fe(1)-Cl(1)	97.99(12)
N(2)-Ni(1)-N(3)	90.78(16)
N(2)-Ni(1)-N(4)	177.79(16)
N(3)-Ni(1)-N(4)	90.12(16)
N(2)-Ni(1)-N(1)	90.29(16)
N(3)-Ni(1)-N(1)	177.33(17)
N(4)-Ni(1)-N(1)	88.73(16)

Cartesian coordinates of the optimized geometries:

FeNi-PD

Fe	4.885100	-0.028300	0.032500
N	3.524000	-1.359000	1.015300
N	6.421600	-1.452100	0.489400
N	6.451400	1.421100	0.251400
N	3.541700	1.493000	0.710400
C	2.160000	-1.151200	1.156100
C	1.512200	-2.424000	1.546500
C	2.512000	-3.355800	1.612600
C	3.747000	-2.670900	1.238400
C	4.999600	-3.331700	1.115900
H	4.990100	-4.395200	1.325700
C	6.218700	-2.786200	0.769900
C	7.489900	-3.518800	0.686200
C	8.443800	-2.591600	0.365500
C	7.743700	-1.304400	0.264000
C	8.382400	-0.062400	0.016600
H	9.453000	-0.099100	-0.151100
C	7.794900	1.188400	0.034000
C	8.509000	2.465400	-0.099800
C	7.572800	3.447800	0.071100
C	6.295500	2.759100	0.291500
C	5.063000	3.416500	0.544600
H	5.107300	4.498800	0.588500
C	3.825500	2.846000	0.769200
C	2.616700	3.592400	1.116800
C	1.611600	2.672600	1.247000
C	2.224700	1.353800	0.965100
C	1.532900	0.084000	0.973900
C	0.091900	-2.652700	1.991400
H	-0.118100	-3.726200	1.946500
H	-0.615500	-2.180900	1.308200
C	-0.172300	-2.157100	3.427000
H	-1.211100	-2.348000	3.714100
H	0.012900	-1.082500	3.521000
H	0.479700	-2.666900	4.143100
C	2.405300	-4.807800	1.991800
H	1.556300	-4.947900	2.668400
H	3.291400	-5.104700	2.565000
C	2.243500	-5.746000	0.779700
H	2.185400	-6.790000	1.104000
H	3.085100	-5.651300	0.086400
H	1.330800	-5.510000	0.223600
C	7.654900	-4.996600	0.893800
H	8.692200	-5.208700	1.176100
H	7.038300	-5.320700	1.741400
C	7.289400	-5.834000	-0.349100
H	7.414300	-6.901700	-0.142500
H	7.929900	-5.573300	-1.197600
H	6.251400	-5.663700	-0.651700
C	9.913600	-2.800900	0.132700
H	10.227700	-3.732700	0.615300
H	10.483000	-2.001800	0.624200
C	10.297900	-2.852400	-1.359900
H	11.378000	-2.988800	-1.475900
H	10.014100	-1.930400	-1.876600
H	9.792200	-3.681400	-1.865000
C	9.974900	2.616100	-0.390700
H	10.314600	3.597800	-0.044200
H	10.544800	1.878200	0.186600
C	10.313400	2.462200	-1.887200
H	11.390100	2.570900	-2.051900
H	9.797800	3.221800	-2.482300
H	10.007700	1.481200	-2.263900
C	7.774000	4.937600	0.079300
H	6.945800	5.425300	-0.449600
H	8.676400	5.182500	-0.490600
C	7.894500	5.531500	1.497300
H	8.029300	6.616700	1.450700
H	8.750500	5.103100	2.028400
H	6.999500	5.327000	2.093900
C	2.542500	5.084500	1.286600
H	3.464300	5.448300	1.755100
H	1.736300	5.334300	1.983600
C	2.315000	5.837300	-0.040100
H	2.286800	6.918300	0.130300
H	1.367600	5.538800	-0.499800
H	3.112600	5.625500	-0.759000
C	0.217800	2.967900	1.736500
H	-0.531100	2.475800	1.111800
H	0.031500	4.041200	1.629200
C	0.001800	2.574500	3.211000
H	-1.023300	2.797600	3.524200
H	0.686800	3.123000	3.865300
H	0.179600	1.506600	3.373400
C	0.064100	0.099700	0.671700
H	-0.654700	0.208400	1.481700
N	-3.886800	1.342900	-0.974300
N	-6.567800	1.375000	-0.185800
N	-6.574400	-1.385000	-0.145300
N	-3.887100	-1.389700	-0.928800
C	-2.518400	1.196200	-1.078600
C	-1.909200	2.454500	-1.502300
C	-2.938000	3.349600	-1.650600
C	-4.147000	2.661800	-1.266800
C	-5.366800	3.296200	-1.089200
H	-5.422600	4.350200	-1.331100
C	-6.477000	2.707800	-0.509100
C	-7.670600	3.425100	-0.102000
C	-8.484400	2.504200	0.507000
C	-7.797000	1.229600	0.414800
C	-8.362200	0.013500	0.763500
H	-9.347500	0.023500	1.213800
C	-7.807500	-1.214200	0.441300
C	-8.506700	-2.480900	0.556000
C	-7.693700	-3.424300	-0.017200
C	-6.489800	-2.727400	-0.429900
C	-5.371100	-3.344400	-0.961800
H	-5.424700	-4.409400	-1.151600
C	-4.146100	-2.722500	-1.148500
C	-2.932500	-3.435900	-1.465300
C	-1.902700	-2.537200	-1.349300
C	-2.515400	-1.251700	-1.020100
C	-1.842000	-0.023700	-0.912000
C	-0.484800	2.716200	-1.920300
H	-0.299400	3.794200	-1.862600
H	0.225400	2.256600	-1.232200
C	-0.183600	2.241100	-3.355000
H	0.855900	2.454300	-3.623100
H	-0.344800	1.163900	-3.460700
H	-0.835100	2.742500	-4.078000
C	-2.858300	4.786300	-2.092600
H	-2.035800	4.900500	-2.806800
H	-3.766700	5.054400	-2.643700
C	-2.655700	5.780000	-0.932200
H	-2.605300	6.808100	-1.305600
H	-3.477400	5.720000	-0.211400
H	-1.727000	5.568800	-0.392600
C	-7.901400	4.899100	-0.285500
H	-8.979300	5.089600	-0.344000
H	-7.488200	5.221400	-1.249100
C	-7.298700	5.764400	0.839300
H	-7.484600	6.827300	0.653300
H	-7.737000	5.507300	1.809300
H	-6.216400	5.616600	0.915200
C	-9.829800	2.721200	1.142900
H	-10.253500	3.661500	0.773500
H	-10.524000	1.933700	0.822300
C	-9.789400	2.759600	2.683700
H	-10.791900	2.922000	3.094100
H	-9.402600	1.821800	3.094900
H	-9.141000	3.567700	3.037900
C	-9.857100	-2.675600	1.190200
H	-10.297900	-3.605600	0.816300
H	-10.537000	-1.875000	0.872400
C	-9.811600	-2.721800	2.730700
H	-10.815300	-2.865000	3.145100
H	-9.178400	-3.545200	3.077000
H	-9.403800	-1.794000	3.144400
C	-7.959800	-4.891400	-0.215300
H	-7.064400	-5.469500	0.044400
H	-8.736100	-5.214600	0.486000
C	-8.397000	-5.249200	-1.649600
H	-8.572600	-6.325900	-1.744900
H	-9.321300	-4.727700	-1.917300
H	-7.633500	-4.964100	-2.379900
C	-2.850600	-4.900100	-1.806500
H	-3.748000	-5.202800	-2.358300
H	-2.013200	-5.067700	-2.492300
C	-2.680400	-5.809700	-0.573700
H	-2.633700	-6.862800	-0.870300
H	-1.759600	-5.567600	-0.032900
H	-3.514600	-5.688800	0.124800
C	-0.466700	-2.840700	-1.694400
H	0.222700	-2.365300	-0.995000
H	-0.306200	-3.918200	-1.579200
C	-0.092200	-2.441700	-3.135500
H	0.957900	-2.672700	-3.340400
H	-0.711700	-2.977300	-3.862400
H	-0.240200	-1.370900	-3.306400
C	-0.379600	-0.015800	-0.590100
H	0.347600	-0.119300	-1.393300
Ni	-5.226000	-0.014200	-0.541500
Cl	4.484600	-0.243900	-2.309800

FeNi-PD•2FeCl$_4$

Fe	4.685400	-0.014300	0.588000
Ni	-4.943200	0.022300	-0.725200
N	-3.460500	1.196500	-1.122400
N	-6.078000	1.552800	-0.406200
N	-6.429800	-1.163700	-0.391100
N	-3.799300	-1.490500	-1.130100
N	3.362600	-1.268700	1.381600
N	5.961100	-1.517200	0.403500
N	6.178200	1.249600	0.293000
N	3.583300	1.481600	1.327000
C	-2.146300	0.883800	-1.185500
C	-1.377000	1.947400	-1.837500
C	-2.278700	2.946100	-2.107800
C	-3.565900	2.491200	-1.601400
C	-4.698600	3.271100	-1.462500
H	-4.657400	4.297800	-1.804000
C	-5.847100	2.846200	-0.793700
C	-6.944600	3.722300	-0.380100
C	-7.832300	2.930700	0.290500
C	-7.296500	1.566100	0.220800
C	-7.995800	0.427400	0.597700
H	-8.957100	0.554800	1.077700
C	-7.612700	-0.856400	0.227500
C	-8.481200	-2.036200	0.309700
C	-7.823000	-3.039200	-0.341100
C	-6.534000	-2.480400	-0.756300
C	-5.522200	-3.204600	-1.381200
H	-5.736700	-4.222300	-1.680600
C	-4.221600	-2.747600	-1.511700
C	-3.081100	-3.569200	-1.902500
C	-1.958800	-2.824300	-1.649600
C	-2.442000	-1.535800	-1.148500
C	-1.641300	-0.403500	-0.766600
C	0.040400	1.869100	-2.344600
H	0.674900	1.275500	-1.685300
H	0.470900	2.875500	-2.354300
C	0.112500	1.268600	-3.763900
H	1.151800	1.230900	-4.102200
H	-0.461700	1.865400	-4.479200
H	-0.285600	0.249200	-3.779500
C	-2.043100	4.260600	-2.796300
H	-2.921200	4.516600	-3.399700
H	-1.214600	4.148600	-3.502100
C	-1.728500	5.422800	-1.832000
H	-1.594300	6.351000	-2.395000
H	-0.810100	5.230400	-1.270400
H	-2.536300	5.578300	-1.110100
C	-7.006700	5.200700	-0.633300
H	-8.054600	5.516300	-0.633500
H	-6.626900	5.417500	-1.638500
C	-6.227700	6.037000	0.402200
H	-6.304400	7.101500	0.162700
H	-5.166600	5.768700	0.419000
H	-6.628200	5.884300	1.408700
C	-9.114400	3.314400	0.968000
H	-9.901000	2.597500	0.703200
H	-9.445300	4.282800	0.580900
C	-8.994200	3.396600	2.503800
H	-9.954900	3.681200	2.942200
H	-8.250400	4.142700	2.799000
H	-8.696000	2.436600	2.936700
C	-9.820100	-2.067500	0.985300
H	-10.384400	-2.929900	0.618500
H	-10.398700	-1.181400	0.697600
C	-9.725500	-2.139400	2.523200
H	-10.726800	-2.151900	2.962900
H	-9.186300	-1.280000	2.934100
H	-9.202100	-3.046000	2.840700
C	-8.255100	-4.459200	-0.564800
H	-7.932700	-4.790700	-1.558600
H	-9.348700	-4.500100	-0.574800
C	-7.723000	-5.438100	0.501900
H	-8.060600	-6.455200	0.283500
H	-8.083700	-5.165400	1.497900
H	-6.628900	-5.442700	0.532500
C	-3.175300	-4.957000	-2.466900
H	-2.273000	-5.160900	-3.052300
H	-4.013600	-5.007800	-3.171200
C	-3.340500	-6.060500	-1.399800
H	-3.389600	-7.041100	-1.881300
H	-4.255500	-5.925600	-0.815500
H	-2.498800	-6.065100	-0.701800
C	-0.537700	-3.191900	-1.990900
H	0.066800	-2.285800	-2.088600
H	-0.542400	-3.653400	-2.985300

C	0.143400	-4.164300	-1.010500
H	1.161000	-4.381900	-1.347200
H	-0.401400	-5.110100	-0.947500
H	0.208100	-3.751600	0.000400
C	0.243200	0.426700	0.635400
H	-0.125000	1.439600	0.524500
C	-0.466000	-0.591800	-0.029000
H	-0.121100	-1.610400	0.100100
C	2.058200	-1.008100	1.619400
C	1.421500	-2.100400	2.319100
C	2.397200	-3.069500	2.477500
C	3.586700	-2.565500	1.837700
C	4.727400	-3.284700	1.568700
H	4.768100	-4.310700	1.915000
C	5.810900	-2.817800	0.808700
C	6.897900	-3.634600	0.337800
C	7.721900	-2.798100	-0.395800
C	7.140500	-1.482000	-0.308600
C	7.750500	-0.309900	-0.743900
H	8.681900	-0.406100	-1.288700
C	7.332800	0.971400	-0.410800
C	8.108300	2.171800	-0.606200
C	7.430800	3.182600	0.051600
C	6.233600	2.585200	0.585300
C	5.234200	3.283600	1.284100
H	5.428100	4.323600	1.516700
C	3.997800	2.779600	1.609900
C	2.889300	3.544300	2.135800
C	1.777700	2.727200	2.069600
C	2.249500	1.459000	1.555400
C	1.463200	0.273000	1.297500
C	0.058000	-2.103100	2.963100
H	-0.308400	-3.133700	3.016200
H	-0.665300	-1.555700	2.355000
C	0.077100	-1.494100	4.379300
H	-0.923500	-1.522500	4.821600
H	0.407800	-0.451000	4.352700
H	0.756100	-2.043200	5.038500
C	2.278400	-4.398000	3.170100
H	1.553200	-4.311200	3.985500
H	3.234100	-4.649200	3.642900
C	1.852500	-5.550400	2.237100
H	1.807000	-6.489800	2.795800
H	2.560200	-5.678500	1.412300
H	0.865400	-5.363900	1.804400
C	7.050800	-5.109500	0.582300
H	6.749000	-5.348000	1.608800
H	8.110900	-5.374400	0.514600
C	6.248500	-5.984200	-0.401700
H	6.404000	-7.044600	-0.181700
H	6.560000	-5.801400	-1.434300
H	5.175700	-5.776300	-0.335000
C	8.978700	-3.148800	-1.139100
H	9.390800	-4.076000	-0.728500
H	9.739500	-2.378900	-0.965300
C	8.764800	-3.318500	-2.657100
H	9.708400	-3.578600	-3.145700
H	8.387900	-2.397400	-3.112300
H	8.042700	-4.113300	-2.865700
C	9.395200	2.263000	-1.374400
H	10.039000	1.412100	-1.122800
H	9.940100	3.156800	-1.055200
C	9.191000	2.312300	-2.902500
H	10.157100	2.377800	-3.411600
H	8.593700	3.182000	-3.191300
H	8.674400	1.418200	-3.264500
C	7.817500	4.629700	0.174200
H	8.908900	4.710100	0.141200
H	7.520900	5.009900	1.158300
C	7.212700	5.526600	-0.924500
H	7.524200	6.565600	-0.781300
H	6.118800	5.493300	-0.908600
H	7.540900	5.207100	-1.917900
C	2.973500	4.953800	2.647400
H	3.904900	5.083700	3.210400
H	2.160500	5.118100	3.362600
C	2.896700	6.030000	1.543400
H	2.950600	7.027800	1.988200
H	1.961600	5.957200	0.981500
H	3.719200	5.932700	0.829000
C	0.399400	3.036300	2.598600
H	0.512300	3.506500	3.582900
H	-0.140700	2.102100	2.779300
C	-0.455800	3.963700	1.715700
H	-1.434100	4.125700	2.178500
H	-0.621000	3.545900	0.717800
H	0.019000	4.939900	1.587900
Cl	3.801600	-0.004600	-1.611600