Synthesis, Structural Characterization, and Chemical Properties of Pentacoordinate Model Complexes for the Active Site of [Fe]-Hydrogenase

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Table S1 Crystallographic data for **2** and **3**

	2	**3**
Empirical formula	$C_{30}H_{36}FeI_2N_2O_3$	$C_{30}H_{38}FeI_2N_2O_3$
CCDC no.	1429929	1429930
Formula weight	782.26	784.27
Space group	Cc	P2(1)/n
T (K)	110(2)	113(2)
Wavelength (Å)	0.71073	0.71073
Crystal size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.18 × 0.12
Crystal system	Monoclinic	Orthorhombic
a (Å)	33.960(7)	18.490(4)
b (Å)	10.340(2)	10.356(2)
c (Å)	18.590(4)	33.072(7)
α (º)	90	90
β (º)	98.22(3)	90
γ (º)	90	90
V (Å^3)	6461(2)	6333(2)
Z	8	8
ρ (g/cm^3)	1.608	1.645
θ range (º)	1.21 -28.32	2.0607-27.8625
μ (mm^{-1})	2.409	2.458
F(000)	3088.0	3104.0
Tmin and Tmax	0.644,0.795	0.639 and 0.757
Data/restraints/parameters	14872 / 2 / 701	15063 /20/702
goodness-of-fit on F^2	1.052	1.092
R [I≥2σ]	0.0537 wR2 = 0.1014	0.0629 wR2 =0.1279
R (all data)	R1 = 0.0763 wR2 = 0.1091	0.0915 wR2 =0.1463

Table S2 Crystallographic data for **5-8**

	5	**6**	**7**	**8**
Empirical formula	$C_{29}H_{31}FeN_3O_2S$	$C_{35}H_{41}FeN_3O_2S$	$C_{35}H_{43}FeN_3O_2S$	$C_{13}H_{13}FeN_3O_2S$
CCDC no.	1429932	1429933	1429934	1429935
Formula weight	541.48	623.62	625.63	331.17
Space group	P2(1)/n	P-1	P-1	P-1
T (K)	113	113	113	113
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm)	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.10	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.10
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
a (Å)	10.308(2)	11.478(2)	11.416(2)	7.6045(15)
b (Å)	19.262(4)	14.306(3)	14.213(3)	8.7041(17)
c (Å)	13.340(3)	20.809(4)	20.749(4)	22.191(4)
α (º)	90	82.76(3)	82.99(3)	89.29(3)
β (º)	93.79(3)	80.15(3)	80.48(3)	87.47(3)
γ (º)	90	76.45(3)	76.34(3)	71.63(3)
V (Å^3)	2642.9(9)	3259.6(11)	3214.3(11)	1392.6(5)
Z	4	4	4	4
ρ (g/cm^3)	1.361	1.271	1.293	1.580
θ range (º)	1.5299-27.8824	1.7008-27.8267	1.4800-27.9745	1.8372-28.0107
μ (mm^{-1})	1.361	0.561	0.569	1.236
F(000)	1136.0	1320.0	1328.0	680.0
Tmin and Tmax	0.876 and 0.923	0.896 and 0.946	0.895 and 0.935	0.790 and 0.886
Data/restraints/parameters	6325/1/335	11358/2/780	15149/2/781	6479/2/373
goodness-of-fit on F^2	1.021	1.023	1.031	1.070
R [I≥2σ]	0.0462 wR2 = 0.0921	0.0935 wR2 = 0.2409	0.0509 wR2 = 0.0933	0.0572 wR2 =0.1550
R (all data)	0.0655 wR2 =0.1002	0.1225 wR2 =0.2569	0.0840 wR2 =0.1050	0.0783 wR2 =0.1596

Table S3 Selected bond lengths and bond angles of complex **5**

Bond length (Å)			
Fe(1)-C(1)	1.768(2)	Fe(1)-N(1)	1.8636(18)
Fe(1)-C(2)	1.777(2)	Fe(1)-C(20)	1.954(2)
Fe(1)-S(1)	2.2376(8)	C(20)-N(3)	1.341(3)
Bond angles (deg)			
S(1)-Fe(1)-C(2)	172.24(7)	S(1)-Fe(1)-N(1)	85.06(6)
N(1)-Fe(1)-C(1)	140.15(9)	N(3)-C(20)-N(2)	107.44(17)
C(1)-Fe(1)-C(20)	100.66(9)		

Table S4 Selected bond lengths and bond angles of complex **6**

Bond length (Å)			
Fe(1)-C(1)	1.737(7)	Fe(1)-N(1)	1.865(5)
Fe(1)-C(2)	1.774(7)	Fe(1)-C(23)	1.957(6)
Fe(1)-S(1)	2.2450(19)	C(23)-N(3)	1.379(7)
Bond angles (deg)			
S(1)-Fe(1)-C(2)	168.9(2)	S(1)-Fe(1)-N(1)	84.44(17)
N(1)-Fe(1)-C(1)	142.9(3)	N(3)-C(23)-N(2)	103.3(5)
C(1)-Fe(1)-C(23)	100.0(3)		

Table S5 Selected bond lengths and bond angles of complex **7**

Bond length (Å)			
Fe(1)-C(1)	1.763(2)	Fe(1)-N(1)	1.864(2)
Fe(1)-C(2)	1.766(3)	Fe(1)-C(23)	1.951(2)
Fe(1)-S(1)	2.2337(9)	C(23)-N(3)	1.356(3)
Bond angles (deg)			
S(1)-Fe(1)-C(1)	167.17(8)	S(1)-Fe(1)-N(1)	84.33(7)
N(1)-Fe(1)-C(2)	143.03(10)	N(3)-C(23)-N(2)	107.04(19)
C(2)-Fe(1)-C(23)	100.33(11)		

Table S6 Selected bond lengths and bond angles of complex **8**

Bond length (Å)			
Fe(1)-C(1)	1.783(5)	Fe(1)-N(1)	1.858(4)
Fe(1)-C(2)	1.730(5)	Fe(1)-C(12)	1.965(5)
Fe(1)-S(1)	2.2259(15)	C(12)-N(3)	1.353(6)
Bond angles (deg)			
S(1)-Fe(1)-C(2)	97.78(16)	S(1)-Fe(1)-C(12)	159.92(14)
N(1)-Fe(1)-C(1)	156.4(2)	N(3)-C(12)-N(2)	103.3(4)
C(1)-Fe(1)-C(12)	88.6(2)		

Mathematic relations of theoretical calculations

Free energy in gas phase= Electronic energy + Thermal correction to free

Free energy in solution phase= Free energy in gas phase + Solvation free energy

Variation of free energy in gas phase= Free energy in gas phase of **6-NH$^+$/6-SH$^+$/6-NH$^+$-SH$^+$/7-NH$^+$/7-SH$^+$/7-NH$^+$-SH$^+$** - Free energy in gas phase of **6**/**7**

Variation of free energy in solution phase = Free energy in solution phase of **6-NH$^+$/6-SH$^+$/6-NH$^+$-SH$^+$/7-NH$^+$/7-SH$^+$/7-NH$^+$-SH$^+$** - Free energy in solution phase of **6**/**7**

Table S7 Computed energy values of complex **6**

	Electronic energy (Hartree)	Thermal correction to free energy (Hartree)	Free energy in gas phase (Hartree)
6	-3336.026279	0.59356	-3335.432719
6-NH$^+$	-3336.414831	0.605493	-3335.809338
6-SH$^+$	-3336.396467	0.603051	-3335.793416
6-NH$^+$-SH$^+$	-3336.662189	0.615845	-3336.046344

Solvation free energy (Hartree)	Free energy in solution phase (Hartree)	Variation of free energy in gas phase (kJ/mol)	Variation of free energy in solution phase (kJ/mol)
-0.035780196	-3335.468499	0.00	0.00
-0.088451696	-3335.89779	-962.51	-40.30
-0.081103496	-3335.87452	-920.70	20.80

-0.229925396	-3336.27627	-1558.45	52.81

Table S8 Computed energy values of complex **7**

	Electronic energy (Hartree)	Thermal correction to free energy (Hartree)	Free energy in gas phase (Hartree)
7	-3337.222589	0.615906	-3336.606683
7-NH$^+$	-3337.611785	0.629035	-3336.98275
7-SH$^+$	-3337.593128	0.625094	-3336.968034
7-NH$^+$-SH$^+$	-3337.865006	0.638905	-3337.226101

Solvation free energy (Hartree)	Free energy in solution phase (Hartree)	Variation of free energy in gas phase (kJ/mol)	Variation of free energy in solution phase (kJ/mol)
-0.036698896	-3336.643381	0.00	0.00
-0.087929196	-3337.070679	-961.05	-35.06
-0.081943496	-3337.049978	-922.42	19.29
-0.229139296	-3337.455241	-1573.66	42.08

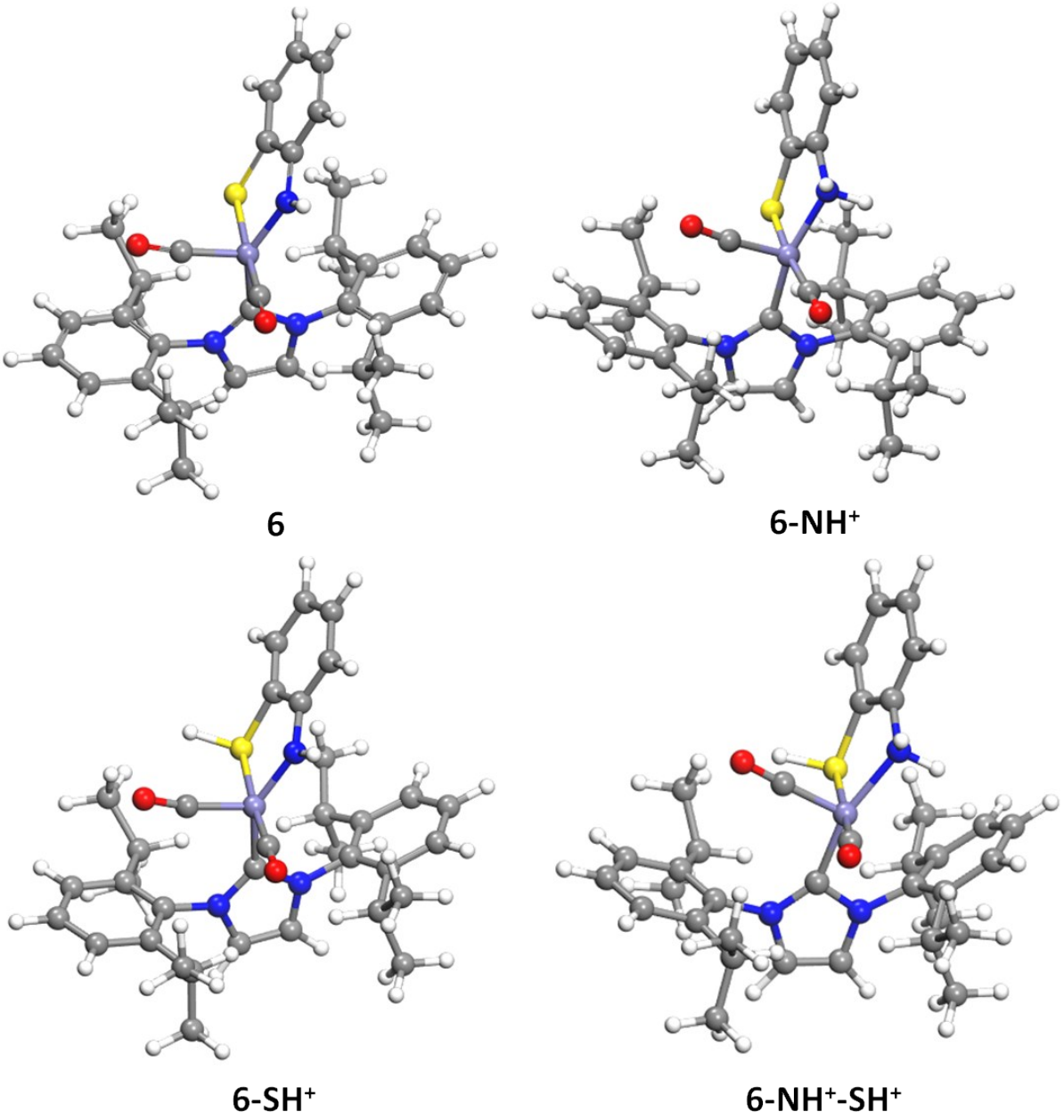

Fig. S1 The optimized structures of complex **6** and corresponding protonated species **6-NH$^+$**, **6-SH$^+$** and **6-NH$^+$-SH$^+$**.

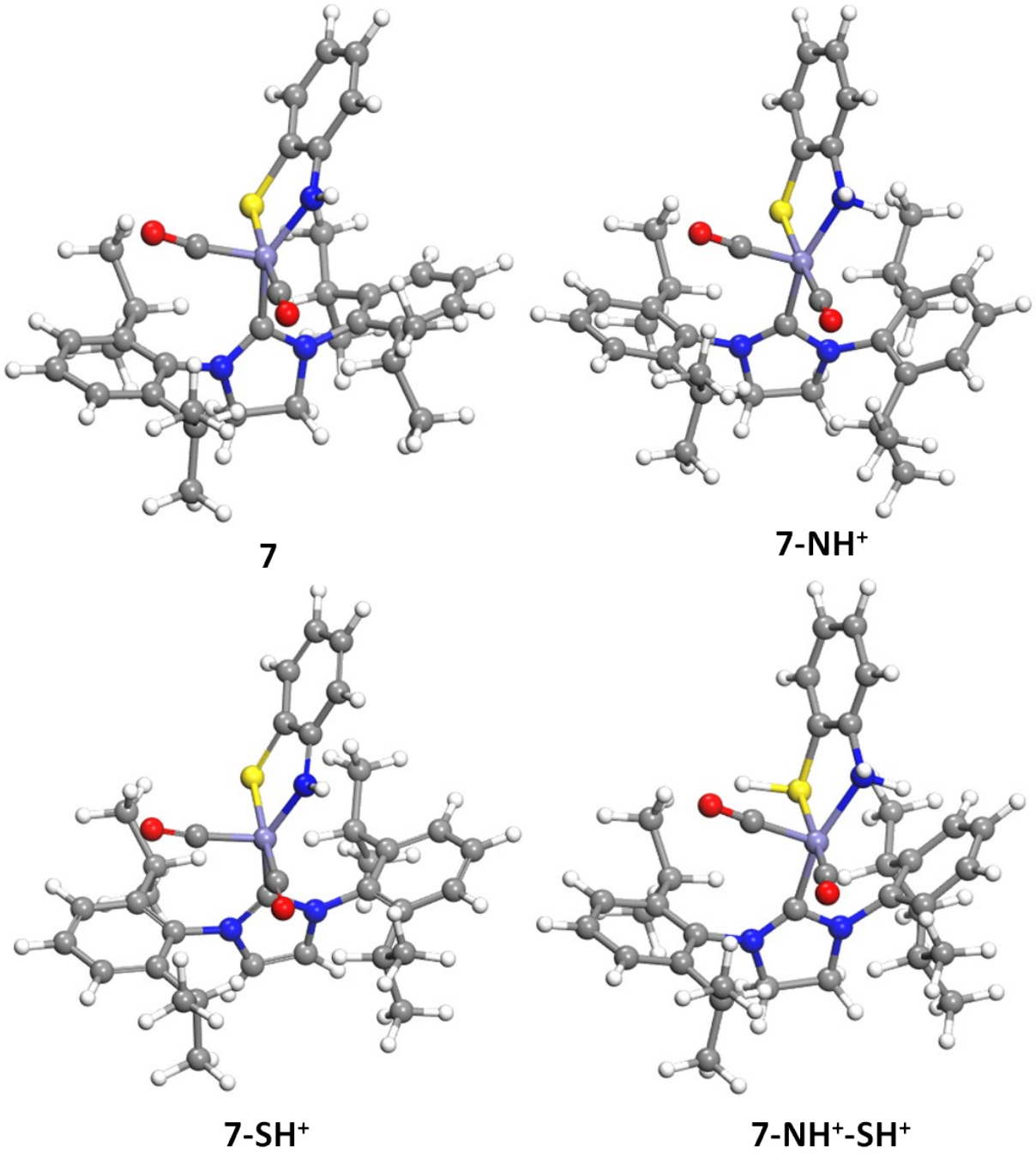

Fig. S2 The optimized structures of complex **7** and corresponding protonated species **7-NH$^+$**, **7-SH$^+$** and **7-NH$^+$-SH$^+$**.

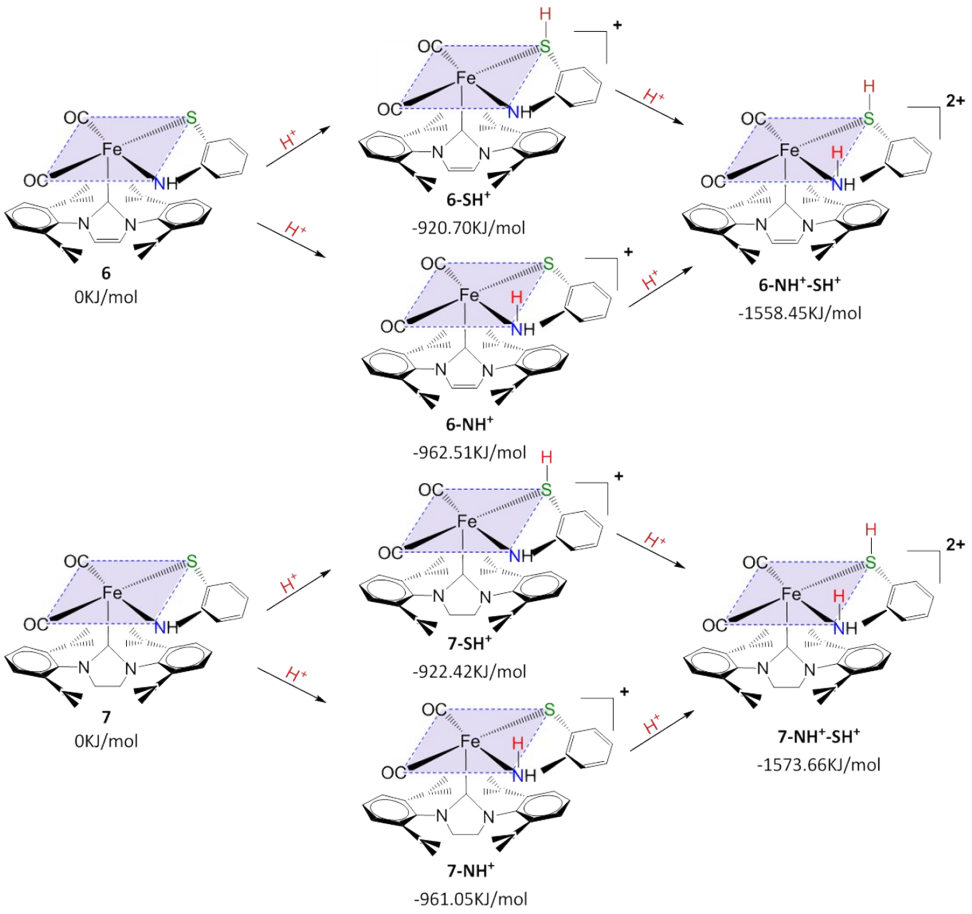

Fig. S3 The free energy comparison between the possible protonated products in gas phase.

Table S9 The atomic coordinate of optimized species of complex **6**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.251	-0.392	-1.253
2	S	1.073	-2.082	0.041
3	O	-1.769	-2.235	-2.214
4	O	-0.630	1.690	-3.103
5	N	1.857	-0.551	-2.172
6	H	2.066	-0.008	-3.018
7	N	-1.800	0.321	0.902
8	N	0.116	1.312	1.174
9	C	-1.015	-1.471	-1.737
10	C	-0.275	0.887	-2.319
11	C	2.550	-2.395	-0.838
12	C	3.466	-3.426	-0.531

13	H	3.256	-4.100	0.307
14	C	4.627	-3.577	-1.295
15	H	5.339	-4.374	-1.052
16	C	4.885	-2.711	-2.385
17	H	5.795	-2.841	-2.981
18	C	3.985	-1.698	-2.711
19	H	4.178	-1.028	-3.559
20	C	2.804	-1.520	-1.939
21	C	-2.696	-2.300	3.404
22	H	-2.877	-1.251	3.702
23	H	-1.982	-2.740	4.124
24	H	-3.652	-2.846	3.496
25	C	-2.140	-2.401	1.963
26	H	-1.194	-1.831	1.924
27	C	-1.802	-3.866	1.613
28	H	-2.676	-4.532	1.738
29	H	-1.008	-4.236	2.285
30	H	-1.438	-3.957	0.576
31	C	-3.113	-1.769	0.967
32	C	-4.268	-2.471	0.571
33	H	-4.439	-3.481	0.958
34	C	-5.197	-1.904	-0.308
35	H	-6.087	-2.471	-0.605
36	C	-4.991	-0.614	-0.811
37	H	-5.726	-0.178	-1.497
38	C	-3.857	0.138	-0.450
39	C	-2.929	-0.466	0.437
40	C	-3.688	1.566	-0.971
41	H	-2.634	1.860	-0.821
42	C	-3.991	1.690	-2.480
43	H	-3.405	0.968	-3.073
44	H	-3.735	2.705	-2.831
45	H	-5.061	1.526	-2.699
46	C	-4.570	2.548	-0.161
47	H	-5.639	2.286	-0.258
48	H	-4.437	3.581	-0.531
49	H	-4.315	2.534	0.913
50	C	-1.915	1.119	2.044
51	H	-2.836	1.160	2.619
52	C	-0.714	1.741	2.213
53	H	-0.366	2.442	2.967

54	C	-0.541	0.419	0.336
55	C	1.480	1.801	1.045
56	C	2.507	1.179	1.804
57	C	3.808	1.707	1.688
58	H	4.623	1.243	2.251
59	C	4.076	2.812	0.873
60	H	5.098	3.201	0.796
61	C	3.037	3.432	0.170
62	H	3.252	4.312	-0.445
63	C	1.715	2.951	0.245
64	C	0.585	3.717	-0.445
65	H	-0.254	3.017	-0.604
66	C	0.982	4.283	-1.824
67	H	1.709	5.110	-1.736
68	H	0.089	4.686	-2.334
69	H	1.420	3.506	-2.473
70	C	0.076	4.858	0.471
71	H	-0.296	4.473	1.436
72	H	-0.751	5.406	-0.018
73	H	0.885	5.580	0.683
74	C	2.239	0.034	2.782
75	H	1.291	-0.448	2.487
76	C	3.330	-1.057	2.752
77	H	3.506	-1.424	1.728
78	H	3.013	-1.914	3.373
79	H	4.289	-0.695	3.165
80	C	2.080	0.581	4.222
81	H	3.006	1.084	4.556
82	H	1.870	-0.246	4.925
83	H	1.255	1.311	4.302

Table S10 The atomic coordinate of optimized species of complex **6-NH$^+$**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.419	-0.409	-1.079
2	S	1.339	-1.652	0.481
3	O	-1.453	-2.468	-1.845
4	O	-0.563	1.356	-3.218
5	N	1.913	-1.088	-2.289
6	H	1.646	-1.183	-3.280
7	N	-1.772	0.436	0.884

8	N	0.031	1.657	0.979
9	C	-0.753	-1.603	-1.496
10	C	-0.162	0.712	-2.331
11	C	2.475	-2.615	-0.484
12	C	3.185	-3.715	0.043
13	H	3.062	-3.987	1.096
14	C	4.018	-4.464	-0.799
15	H	4.559	-5.325	-0.394
16	C	4.150	-4.132	-2.161
17	H	4.791	-4.732	-2.814
18	C	3.460	-3.029	-2.689
19	H	3.568	-2.758	-3.746
20	C	2.640	-2.276	-1.840
21	C	-2.575	-1.790	3.809
22	H	-2.925	-0.746	3.896
23	H	-1.878	-1.987	4.642
24	H	-3.453	-2.449	3.937
25	C	-1.881	-2.058	2.450
26	H	-1.018	-1.372	2.372
27	C	-1.327	-3.499	2.404
28	H	-2.116	-4.249	2.592
29	H	-0.561	-3.630	3.188
30	H	-0.863	-3.725	1.430
31	C	-2.837	-1.756	1.296
32	C	-3.863	-2.666	0.976
33	H	-3.933	-3.607	1.531
34	C	-4.796	-2.388	-0.030
35	H	-5.585	-3.113	-0.259
36	C	-4.735	-1.179	-0.733
37	H	-5.482	-0.965	-1.504
38	C	-3.735	-0.225	-0.461
39	C	-2.787	-0.552	0.544
40	C	-3.742	1.119	-1.191
41	H	-2.753	1.592	-1.051
42	C	-3.978	0.975	-2.711
43	H	-3.275	0.260	-3.171
44	H	-3.848	1.953	-3.207
45	H	-5.003	0.631	-2.936
46	C	-4.800	2.063	-0.568
47	H	-5.814	1.636	-0.669
48	H	-4.791	3.043	-1.078

49	H	-4.614	2.236	0.506
50	C	-1.987	1.407	1.865
51	H	-2.920	1.454	2.420
52	C	-0.857	2.172	1.925
53	H	-0.599	3.025	2.546
54	C	-0.525	0.576	0.328
55	C	1.357	2.210	0.728
56	C	2.440	1.789	1.549
57	C	3.710	2.326	1.261
58	H	4.569	2.021	1.868
59	C	3.894	3.252	0.228
60	H	4.893	3.652	0.023
61	C	2.797	3.699	-0.519
62	H	2.946	4.461	-1.290
63	C	1.498	3.210	-0.276
64	C	0.299	3.848	-0.982
65	H	-0.523	3.109	-1.012
66	C	0.593	4.290	-2.432
67	H	1.264	5.167	-2.461
68	H	-0.346	4.588	-2.929
69	H	1.055	3.488	-3.032
70	C	-0.203	5.066	-0.163
71	H	-0.505	4.783	0.860
72	H	-1.076	5.527	-0.659
73	H	0.588	5.832	-0.082
74	C	2.258	0.881	2.767
75	H	1.328	0.299	2.629
76	C	3.411	-0.127	2.964
77	H	3.606	-0.712	2.049
78	H	3.152	-0.831	3.774
79	H	4.350	0.373	3.260
80	C	2.093	1.742	4.047
81	H	2.998	2.347	4.230
82	H	1.933	1.092	4.926
83	H	1.236	2.435	3.977
84	H	2.546	-0.266	-2.247

Table S11 The atomic coordinate of optimized species of complex **6-SH$^+$**

Tag	Atomic symbol	X	Y	Z

1	Fe	0.264	-0.390	-1.229
2	S	1.284	-2.031	0.092
3	O	-1.736	-2.267	-2.174
4	O	-0.798	1.661	-3.005
5	N	1.842	-0.457	-2.164
6	H	2.009	0.117	-2.999
7	N	-1.879	0.366	0.842
8	N	0.053	1.314	1.180
9	C	-1.021	-1.480	-1.690
10	C	-0.367	0.871	-2.265
11	C	2.757	-2.290	-0.905
12	C	3.734	-3.256	-0.638
13	H	3.617	-3.954	0.197
14	C	4.869	-3.311	-1.466
15	H	5.640	-4.064	-1.277
16	C	5.016	-2.396	-2.526
17	H	5.906	-2.441	-3.162
18	C	4.039	-1.427	-2.782
19	H	4.159	-0.720	-3.610
20	C	2.880	-1.364	-1.970
21	C	-2.695	-2.257	3.334
22	H	-2.890	-1.208	3.618
23	H	-1.976	-2.679	4.059
24	H	-3.644	-2.814	3.431
25	C	-2.142	-2.366	1.892
26	H	-1.207	-1.774	1.852
27	C	-1.782	-3.833	1.568
28	H	-2.632	-4.514	1.750
29	H	-0.954	-4.174	2.215
30	H	-1.485	-3.963	0.511
31	C	-3.126	-1.764	0.888
32	C	-4.251	-2.504	0.477
33	H	-4.393	-3.522	0.855
34	C	-5.196	-1.960	-0.401
35	H	-6.064	-2.554	-0.706
36	C	-5.039	-0.656	-0.884
37	H	-5.791	-0.240	-1.562
38	C	-3.936	0.137	-0.510
39	C	-2.988	-0.450	0.368
40	C	-3.833	1.580	-1.005
41	H	-2.794	1.925	-0.844

42	C	-4.142	1.718	-2.512
43	H	-3.539	1.026	-3.124
44	H	-3.926	2.748	-2.847
45	H	-5.207	1.523	-2.731
46	C	-4.765	2.505	-0.183
47	H	-5.819	2.193	-0.291
48	H	-4.681	3.548	-0.536
49	H	-4.519	2.489	0.894
50	C	-2.021	1.194	1.958
51	H	-2.964	1.272	2.491
52	C	-0.812	1.793	2.166
53	H	-0.483	2.510	2.913
54	C	-0.596	0.427	0.344
55	C	1.449	1.726	1.099
56	C	2.402	1.071	1.928
57	C	3.740	1.504	1.834
58	H	4.503	1.019	2.451
59	C	4.109	2.552	0.983
60	H	5.155	2.871	0.931
61	C	3.138	3.216	0.224
62	H	3.432	4.060	-0.407
63	C	1.784	2.830	0.270
64	C	0.732	3.657	-0.471
65	H	-0.172	3.034	-0.597
66	C	1.188	4.113	-1.873
67	H	1.979	4.882	-1.816
68	H	0.340	4.561	-2.418
69	H	1.577	3.274	-2.475
70	C	0.327	4.887	0.382
71	H	-0.078	4.590	1.366
72	H	-0.446	5.479	-0.139
73	H	1.198	5.543	0.560
74	C	2.020	0.013	2.968
75	H	1.061	-0.445	2.658
76	C	3.061	-1.119	3.104
77	H	3.338	-1.552	2.128
78	H	2.655	-1.926	3.738
79	H	3.988	-0.765	3.590
80	C	1.802	0.676	4.352
81	H	2.731	1.161	4.701
82	H	1.512	-0.083	5.101

83	H	1.012	1.446	4.328
84	H	0.607	-3.174	-0.231

Table S12 The atomic coordinate of optimized species of complex **6-NH$^+$-SH$^+$**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.545	-0.031	-0.907
2	S	1.523	-1.642	0.504
3	O	-0.835	-2.206	-2.238
4	O	-0.671	1.661	-2.958
5	N	2.344	-0.133	-1.869
6	H	2.268	0.077	-2.875
7	N	-2.028	0.178	0.878
8	N	-0.250	1.388	1.253
9	C	-0.302	-1.336	-1.686
10	C	-0.174	1.061	-2.098
11	C	2.852	-2.184	-0.596
12	C	3.606	-3.342	-0.344
13	H	3.388	-3.976	0.522
14	C	4.633	-3.686	-1.237
15	H	5.213	-4.598	-1.064
16	C	4.912	-2.872	-2.348
17	H	5.711	-3.147	-3.043
18	C	4.173	-1.700	-2.577
19	H	4.399	-1.062	-3.439
20	C	3.140	-1.356	-1.692
21	C	-2.749	-2.746	3.215
22	H	-3.197	-1.791	3.538
23	H	-2.050	-3.081	4.001
24	H	-3.563	-3.489	3.146
25	C	-2.019	-2.604	1.857
26	H	-1.221	-1.846	1.995
27	C	-1.340	-3.939	1.475
28	H	-2.059	-4.777	1.456
29	H	-0.562	-4.204	2.213
30	H	-0.886	-3.907	0.462
31	C	-2.977	-2.103	0.775
32	C	-3.943	-2.974	0.236
33	H	-3.975	-4.016	0.570
34	C	-4.876	-2.528	-0.709
35	H	-5.621	-3.223	-1.109
36	C	-4.870	-1.193	-1.132

37	H	-5.616	-0.858	-1.859
38	C	-3.931	-0.269	-0.633
39	C	-2.990	-0.762	0.309
40	C	-4.003	1.199	-1.059
41	H	-3.053	1.691	-0.769
42	C	-4.168	1.371	-2.586
43	H	-3.399	0.818	-3.153
44	H	-4.095	2.439	-2.855
45	H	-5.155	1.020	-2.932
46	C	-5.149	1.923	-0.309
47	H	-6.126	1.474	-0.560
48	H	-5.183	2.989	-0.597
49	H	-5.029	1.868	0.787
50	C	-2.283	0.972	2.005
51	H	-3.235	0.917	2.528
52	C	-1.171	1.736	2.245
53	H	-0.967	2.474	3.017
54	C	-0.773	0.435	0.425
55	C	1.105	1.823	0.922
56	C	2.218	1.309	1.675
57	C	3.502	1.623	1.194
58	H	4.379	1.231	1.717
59	C	3.685	2.470	0.084
60	H	4.700	2.706	-0.255
61	C	2.586	3.094	-0.527
62	H	2.754	3.842	-1.307
63	C	1.266	2.836	-0.092
64	C	0.117	3.765	-0.498
65	H	-0.817	3.177	-0.564
66	C	0.334	4.511	-1.831
67	H	1.126	5.275	-1.743
68	H	-0.592	5.044	-2.105
69	H	0.592	3.843	-2.670
70	C	-0.074	4.810	0.640
71	H	-0.307	4.342	1.611
72	H	-0.907	5.485	0.381
73	H	0.836	5.422	0.765
74	C	2.033	0.593	3.012
75	H	1.080	0.030	2.976
76	C	3.168	-0.382	3.386
77	H	3.370	-1.129	2.600

78	H	2.892	-0.927	4.305
79	H	4.110	0.150	3.605
80	C	1.905	1.670	4.128
81	H	2.847	2.237	4.229
82	H	1.696	1.181	5.095
83	H	1.100	2.398	3.931
84	H	2.847	0.682	-1.453
85	H	0.684	-2.720	0.383

Table S13 The atomic coordinate of optimized species of complex **7**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.181	-0.362	-1.255
2	S	1.165	-1.985	-0.006
3	O	-1.783	-2.297	-2.143
4	O	-0.895	1.680	-3.047
5	N	1.731	-0.452	-2.281
6	H	1.852	0.076	-3.153
7	N	-1.845	0.436	0.832
8	N	0.179	1.226	1.205
9	C	-1.052	-1.498	-1.688
10	C	-0.465	0.891	-2.288
11	C	2.599	-2.239	-0.973
12	C	3.581	-3.222	-0.715
13	H	3.458	-3.895	0.142
14	C	4.695	-3.330	-1.552
15	H	5.458	-4.089	-1.347
16	C	4.840	-2.469	-2.667
17	H	5.714	-2.566	-3.320
18	C	3.872	-1.505	-2.946
19	H	3.977	-0.840	-3.813
20	C	2.738	-1.371	-2.098
21	C	-2.781	-2.443	3.249
22	H	-3.065	-1.455	3.653
23	H	-2.047	-2.899	3.939
24	H	-3.689	-3.074	3.259
25	C	-2.193	-2.347	1.820
26	H	-1.272	-1.739	1.864
27	C	-1.786	-3.752	1.321
28	H	-2.643	-4.451	1.328
29	H	-1.007	-4.173	1.981

30	H	-1.378	-3.713	0.299
31	C	-3.177	-1.654	0.875
32	C	-4.351	-2.334	0.498
33	H	-4.516	-3.354	0.861
34	C	-5.307	-1.735	-0.329
35	H	-6.211	-2.285	-0.612
36	C	-5.107	-0.430	-0.791
37	H	-5.864	0.038	-1.430
38	C	-3.953	0.301	-0.445
39	C	-2.982	-0.335	0.379
40	C	-3.817	1.748	-0.921
41	H	-2.774	2.064	-0.745
42	C	-4.107	1.910	-2.430
43	H	-3.489	1.231	-3.038
44	H	-3.888	2.945	-2.747
45	H	-5.169	1.712	-2.664
46	C	-4.745	2.683	-0.105
47	H	-5.806	2.417	-0.265
48	H	-4.608	3.734	-0.418
49	H	-4.550	2.621	0.980
50	C	-1.971	1.136	2.136
51	H	-2.048	0.392	2.952
52	C	-0.669	1.937	2.196
53	H	-0.197	1.928	3.191
54	C	-0.559	0.436	0.359
55	C	1.583	1.577	1.144
56	C	2.483	0.941	2.047
57	C	3.829	1.352	2.040
58	H	4.538	0.865	2.719
59	C	4.278	2.369	1.191
60	H	5.332	2.670	1.202
61	C	3.372	3.011	0.341
62	H	3.722	3.824	-0.304
63	C	2.013	2.642	0.305
64	C	1.060	3.445	-0.581
65	H	0.100	2.901	-0.630
66	C	1.583	3.592	-2.026
67	H	2.480	4.237	-2.070
68	H	0.811	4.051	-2.668
69	H	1.849	2.610	-2.452
70	C	0.787	4.841	0.031

71	H	0.375	4.770	1.054
72	H	0.067	5.403	-0.591
73	H	1.718	5.434	0.092
74	C	2.041	-0.113	3.065
75	H	1.028	-0.450	2.781
76	C	2.957	-1.356	3.077
77	H	3.057	-1.785	2.068
78	H	2.532	-2.130	3.743
79	H	3.967	-1.115	3.457
80	C	1.976	0.496	4.489
81	H	2.981	0.813	4.824
82	H	1.599	-0.251	5.212
83	H	1.321	1.384	4.543
84	H	-0.804	2.990	1.883
85	H	-2.874	1.767	2.153

Table S14 The atomic coordinate of optimized species of complex **7-NH$^+$**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.598	-0.265	-0.926
2	S	1.043	-1.932	0.485
3	O	-1.108	-2.091	-2.368
4	O	0.175	1.822	-2.944
5	N	2.353	-0.769	-1.830
6	H	2.378	-0.604	-2.847
7	N	-1.786	0.167	0.913
8	N	-0.068	1.546	1.133
9	C	-0.466	-1.339	-1.749
10	C	0.335	1.056	-2.079
11	C	2.382	-2.719	-0.373
12	C	2.909	-3.967	0.024
13	H	2.504	-4.470	0.907
14	C	3.928	-4.559	-0.733
15	H	4.326	-5.534	-0.431
16	C	4.429	-3.926	-1.886
17	H	5.214	-4.404	-2.480
18	C	3.922	-2.678	-2.280
19	H	4.315	-2.173	-3.171
20	C	2.913	-2.083	-1.512
21	C	-3.180	-2.289	3.526
22	H	-3.611	-1.277	3.637

23	H	-2.630	-2.531	4.453
24	H	-4.025	-2.994	3.441
25	C	-2.245	-2.401	2.296
26	H	-1.399	-1.703	2.442
27	C	-1.659	-3.828	2.209
28	H	-2.455	-4.591	2.150
29	H	-1.064	-4.046	3.113
30	H	-1.006	-3.943	1.328
31	C	-2.984	-1.989	1.021
32	C	-3.980	-2.838	0.500
33	H	-4.171	-3.800	0.988
34	C	-4.735	-2.474	-0.620
35	H	-5.504	-3.151	-1.007
36	C	-4.519	-1.236	-1.235
37	H	-5.132	-0.950	-2.097
38	C	-3.540	-0.341	-0.762
39	C	-2.759	-0.752	0.356
40	C	-3.409	1.033	-1.423
41	H	-2.488	1.516	-1.045
42	C	-3.287	0.945	-2.961
43	H	-2.478	0.263	-3.273
44	H	-3.082	1.944	-3.385
45	H	-4.223	0.582	-3.421
46	C	-4.607	1.937	-1.038
47	H	-5.555	1.513	-1.416
48	H	-4.489	2.944	-1.478
49	H	-4.711	2.049	0.056
50	C	-2.218	1.124	1.974
51	H	-2.642	0.577	2.829
52	C	-0.913	1.865	2.314
53	H	-0.435	1.474	3.230
54	C	-0.573	0.501	0.418
55	C	1.167	2.222	0.787
56	C	2.418	1.696	1.237
57	C	3.594	2.295	0.735
58	H	4.568	1.905	1.047
59	C	3.539	3.414	-0.105
60	H	4.466	3.866	-0.476
61	C	2.304	3.996	-0.418
62	H	2.277	4.911	-1.019
63	C	1.094	3.430	0.026

64	C	-0.224	4.173	-0.212
65	H	-1.051	3.445	-0.101
66	C	-0.354	4.822	-1.607
67	H	0.363	5.651	-1.740
68	H	-1.364	5.254	-1.719
69	H	-0.199	4.098	-2.422
70	C	-0.393	5.270	0.874
71	H	-0.311	4.871	1.900
72	H	-1.376	5.764	0.772
73	H	0.388	6.043	0.763
74	C	2.511	0.663	2.361
75	H	1.601	0.037	2.331
76	C	3.727	-0.278	2.259
77	H	3.785	-0.782	1.279
78	H	3.656	-1.061	3.034
79	H	4.679	0.257	2.429
80	C	2.545	1.404	3.725
81	H	3.458	2.021	3.812
82	H	2.548	0.674	4.555
83	H	1.680	2.076	3.860
84	H	-1.047	2.952	2.420
85	H	-2.997	1.792	1.561
86	H	2.945	-0.027	-1.407

Table S15 The atomic coordinate of optimized species of complex **7-SH**$^{+}$

Tag	Atomic symbol	X	Y	Z
1	Fe	0.214	-0.315	-1.233
2	S	1.315	-1.943	0.012
3	O	-1.747	-2.205	-2.227
4	O	-0.966	1.755	-2.913
5	N	1.759	-0.320	-2.229
6	H	1.877	0.267	-3.064
7	N	-1.909	0.428	0.801
8	N	0.113	1.211	1.241
9	C	-1.049	-1.422	-1.713
10	C	-0.488	0.958	-2.210
11	C	2.762	-2.148	-1.035
12	C	3.768	-3.094	-0.815

13	H	3.697	-3.806	0.013
14	C	4.874	-3.112	-1.683
15	H	5.668	-3.849	-1.531
16	C	4.962	-2.179	-2.735
17	H	5.829	-2.196	-3.402
18	C	3.955	-1.231	-2.942
19	H	4.029	-0.510	-3.765
20	C	2.824	-1.205	-2.089
21	C	-2.740	-2.509	3.156
22	H	-3.037	-1.529	3.569
23	H	-2.002	-2.961	3.842
24	H	-3.640	-3.150	3.157
25	C	-2.157	-2.388	1.726
26	H	-1.251	-1.753	1.784
27	C	-1.720	-3.786	1.227
28	H	-2.543	-4.519	1.300
29	H	-0.890	-4.172	1.845
30	H	-1.404	-3.768	0.168
31	C	-3.154	-1.716	0.780
32	C	-4.290	-2.437	0.366
33	H	-4.418	-3.472	0.701
34	C	-5.261	-1.857	-0.457
35	H	-6.136	-2.438	-0.765
36	C	-5.120	-0.529	-0.873
37	H	-5.894	-0.078	-1.502
38	C	-4.008	0.246	-0.490
39	C	-3.015	-0.374	0.320
40	C	-3.946	1.716	-0.908
41	H	-2.927	2.089	-0.694
42	C	-4.216	1.919	-2.417
43	H	-3.563	1.289	-3.042
44	H	-4.041	2.974	-2.693
45	H	-5.263	1.684	-2.677
46	C	-4.947	2.562	-0.080
47	H	-5.986	2.248	-0.285
48	H	-4.859	3.631	-0.342
49	H	-4.784	2.461	1.008
50	C	-2.079	1.147	2.096
51	H	-2.233	0.409	2.905
52	C	-0.755	1.908	2.231
53	H	-0.318	1.847	3.238

54	C	-0.616	0.443	0.382
55	C	1.530	1.520	1.178
56	C	2.415	0.838	2.068
57	C	3.784	1.165	2.008
58	H	4.485	0.651	2.674
59	C	4.262	2.147	1.135
60	H	5.331	2.385	1.109
61	C	3.368	2.851	0.321
62	H	3.745	3.651	-0.324
63	C	1.988	2.570	0.332
64	C	1.047	3.467	-0.473
65	H	0.056	2.978	-0.520
66	C	1.529	3.699	-1.923
67	H	2.440	4.321	-1.954
68	H	0.753	4.226	-2.504
69	H	1.757	2.747	-2.433
70	C	0.863	4.830	0.242
71	H	0.488	4.711	1.274
72	H	0.148	5.464	-0.313
73	H	1.823	5.374	0.301
74	C	1.933	-0.138	3.145
75	H	0.908	-0.461	2.882
76	C	2.810	-1.405	3.273
77	H	2.946	-1.914	2.305
78	H	2.342	-2.117	3.975
79	H	3.811	-1.167	3.674
80	C	1.881	0.570	4.525
81	H	2.897	0.861	4.846
82	H	1.464	-0.108	5.292
83	H	1.271	1.490	4.511
84	H	-0.844	2.974	1.950
85	H	-2.959	1.807	2.054
86	H	0.656	-3.096	-0.311

Table S16 The atomic coordinate of optimized species of complex **7-NH$^+$-SH$^+$**

Tag	Atomic symbol	X	Y	Z
1	Fe	0.515	-0.039	-0.877
2	S	1.489	-1.650	0.528
3	O	-0.894	-2.210	-2.190
4	O	-0.711	1.629	-2.940

5	N	2.290	-0.189	-1.888
6	H	2.186	-0.006	-2.898
7	N	-2.011	0.192	0.881
8	N	-0.176	1.384	1.262
9	C	-0.357	-1.341	-1.638
10	C	-0.210	1.044	-2.072
11	C	2.800	-2.217	-0.581
12	C	3.548	-3.376	-0.317
13	H	3.339	-3.989	0.566
14	C	4.557	-3.749	-1.219
15	H	5.132	-4.662	-1.036
16	C	4.823	-2.962	-2.353
17	H	5.608	-3.260	-3.055
18	C	4.090	-1.789	-2.595
19	H	4.307	-1.173	-3.475
20	C	3.076	-1.416	-1.700
21	C	-2.755	-2.810	3.179
22	H	-3.234	-1.878	3.527
23	H	-2.052	-3.149	3.960
24	H	-3.550	-3.570	3.085
25	C	-2.021	-2.614	1.828
26	H	-1.228	-1.856	1.990
27	C	-1.337	-3.936	1.409
28	H	-2.055	-4.774	1.370
29	H	-0.556	-4.220	2.137
30	H	-0.890	-3.878	0.394
31	C	-2.977	-2.084	0.758
32	C	-3.952	-2.944	0.218
33	H	-3.988	-3.989	0.542
34	C	-4.892	-2.484	-0.713
35	H	-5.644	-3.170	-1.114
36	C	-4.882	-1.144	-1.117
37	H	-5.636	-0.794	-1.829
38	C	-3.934	-0.232	-0.615
39	C	-2.971	-0.734	0.306
40	C	-4.020	1.240	-1.024
41	H	-3.091	1.746	-0.691
42	C	-4.131	1.430	-2.554
43	H	-3.327	0.907	-3.099
44	H	-4.079	2.503	-2.807
45	H	-5.094	1.055	-2.941

46	C	-5.215	1.931	-0.318
47	H	-6.171	1.486	-0.646
48	H	-5.242	3.006	-0.567
49	H	-5.172	1.831	0.781
50	C	-2.348	0.996	2.102
51	H	-2.577	0.309	2.934
52	C	-1.075	1.850	2.359
53	H	-0.625	1.651	3.344
54	C	-0.771	0.461	0.471
55	C	1.165	1.782	0.861
56	C	2.309	1.277	1.584
57	C	3.581	1.557	1.055
58	H	4.469	1.165	1.559
59	C	3.740	2.375	-0.081
60	H	4.746	2.585	-0.460
61	C	2.631	3.007	-0.662
62	H	2.784	3.739	-1.460
63	C	1.323	2.785	-0.171
64	C	0.199	3.760	-0.533
65	H	-0.767	3.222	-0.508
66	C	0.352	4.457	-1.902
67	H	1.181	5.186	-1.892
68	H	-0.566	5.026	-2.124
69	H	0.519	3.758	-2.737
70	C	0.159	4.857	0.574
71	H	0.044	4.442	1.589
72	H	-0.684	5.542	0.383
73	H	1.089	5.452	0.562
74	C	2.165	0.610	2.950
75	H	1.193	0.081	2.975
76	C	3.278	-0.397	3.308
77	H	3.413	-1.180	2.543
78	H	3.027	-0.896	4.260
79	H	4.250	0.105	3.461
80	C	2.135	1.730	4.032
81	H	3.111	2.242	4.083
82	H	1.933	1.287	5.022
83	H	1.370	2.501	3.834
84	H	-1.267	2.931	2.268
85	H	-3.240	1.608	1.898
86	H	2.816	0.630	-1.510

87	H	0.640	-2.722	0.418