Supplementary information for:

$FeC_4H_2^{2+}$ Encompassing Planar Tetracoordinate Iron: Structure and Bonding Patterns

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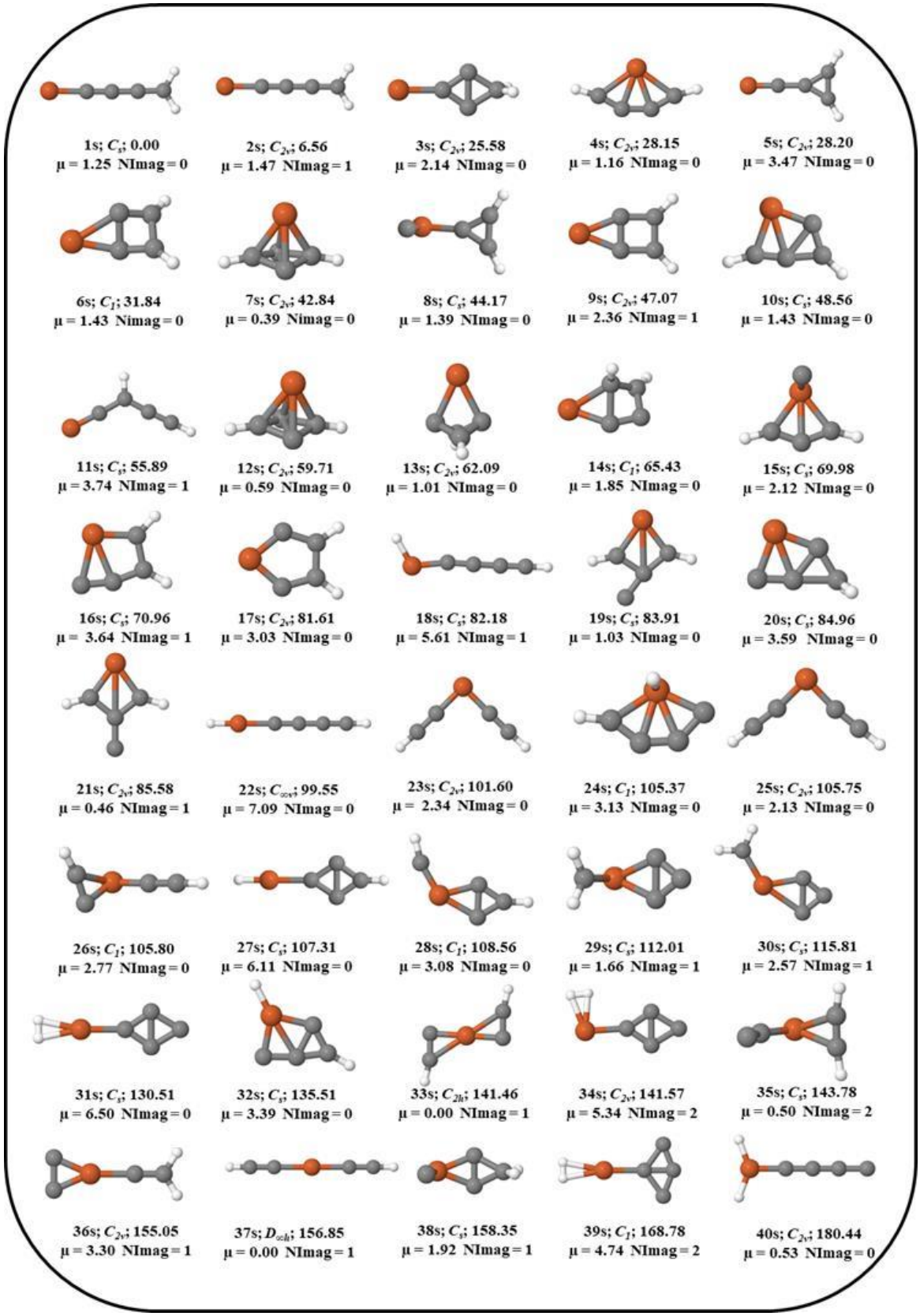


Figure S1. Isomers of $FeC_4H_2^{2+}$ in the singlet electronic state with ZPVE-corrected relative energies (in kcal mol^{-1}), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained using ωB97X-D functional with SDD and 6-311++G(2d,2p) basis sets.

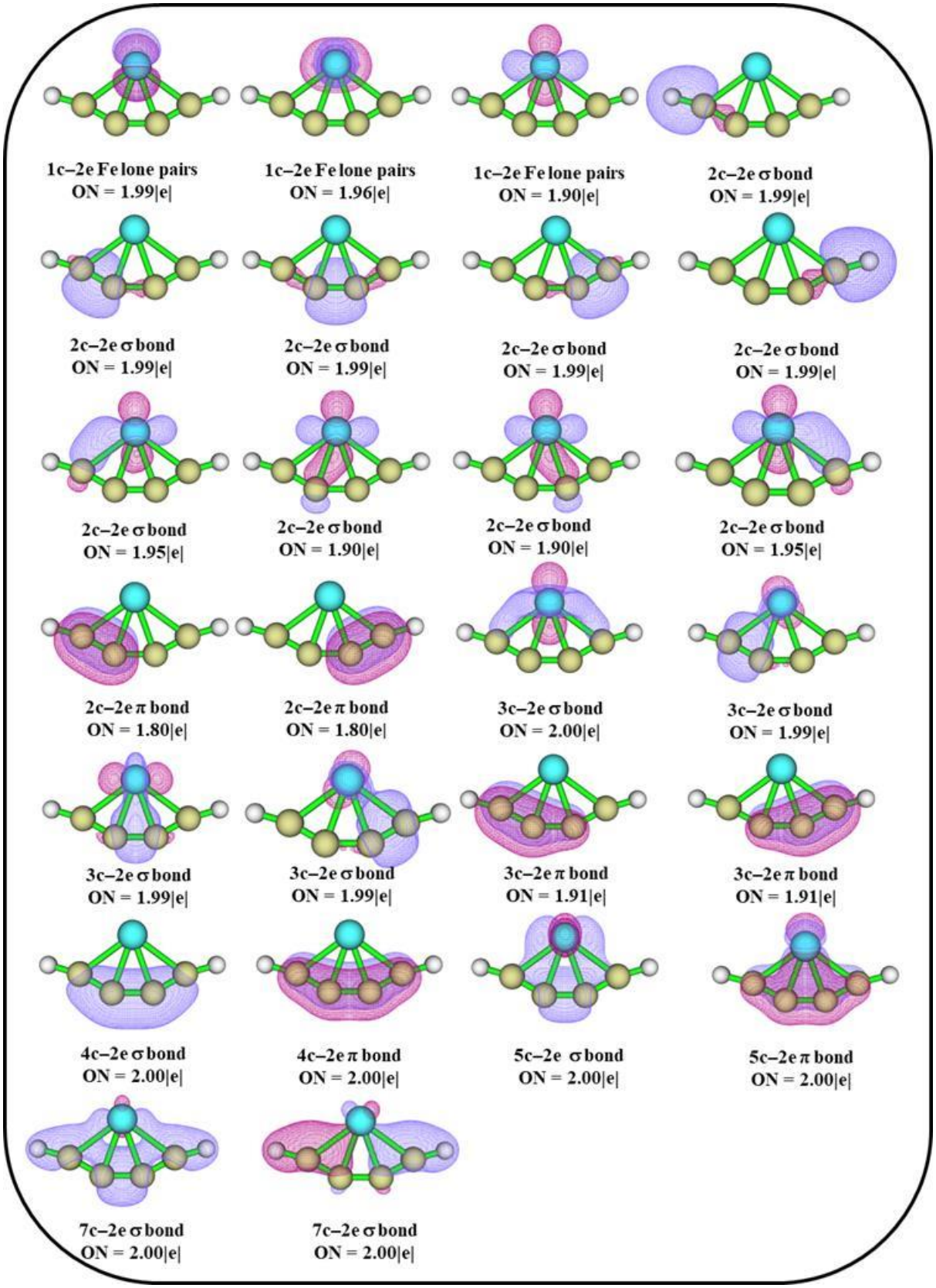


Figure S2. AdNDP bonding patterns of 4s with occupation numbers (ON).

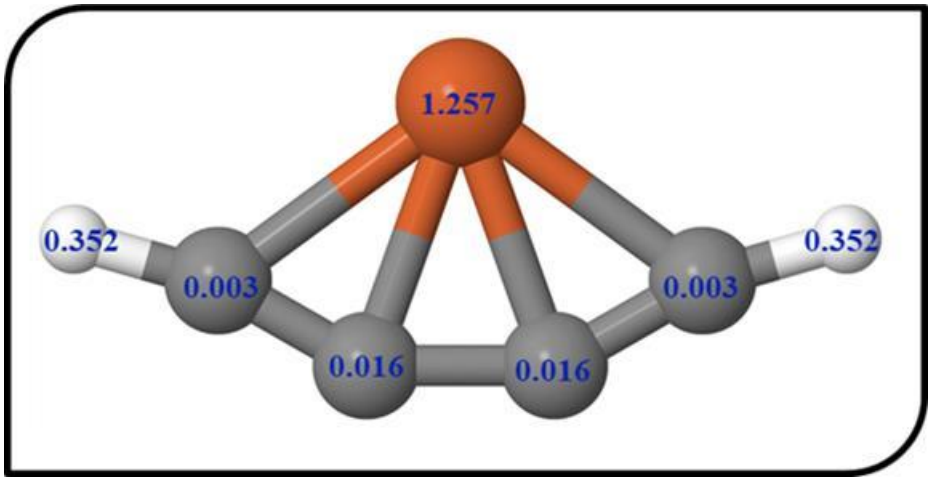
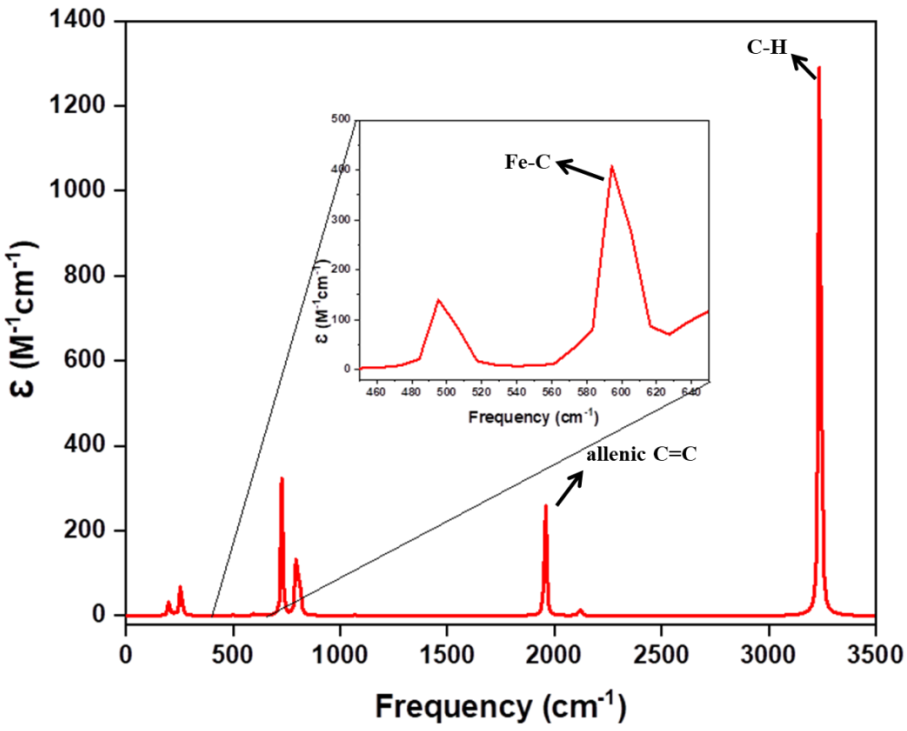
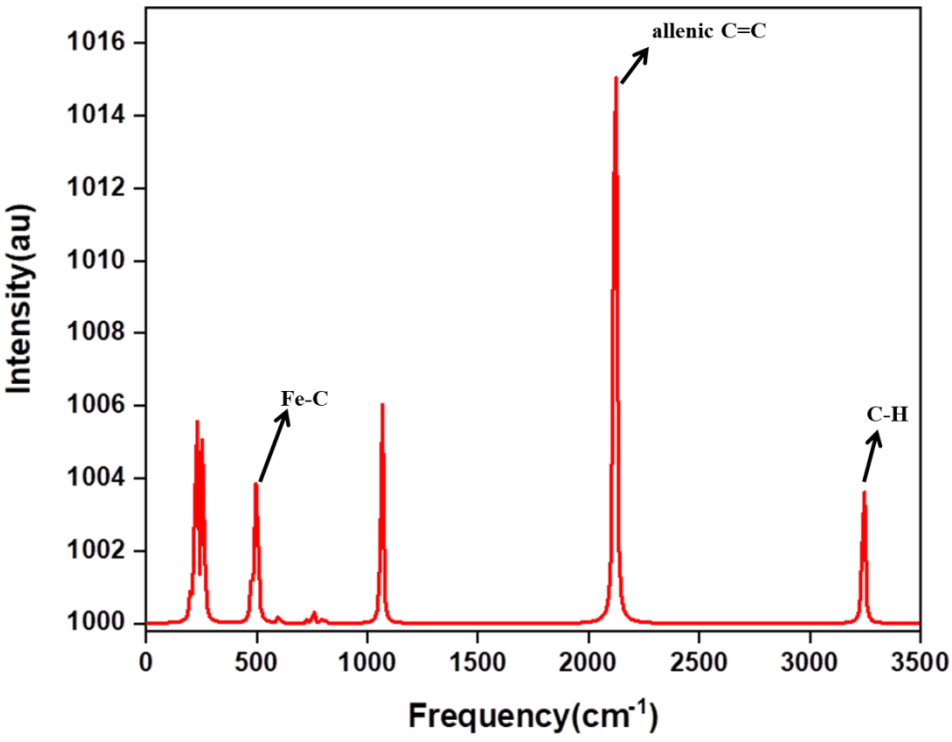


Figure S3. NBO charges (in |e|) on **4s** obtained using the ωB97X-D functional with SDD and 6-311++G (2d,2p) basis sets.



(a)



(b)

Figure S4. (a)The IR vibrational spectrum and (b) Raman spectrum of **4s** obtained using the ωB97X–D functional with SDD and 6–311++G (2d,2p) basis sets.

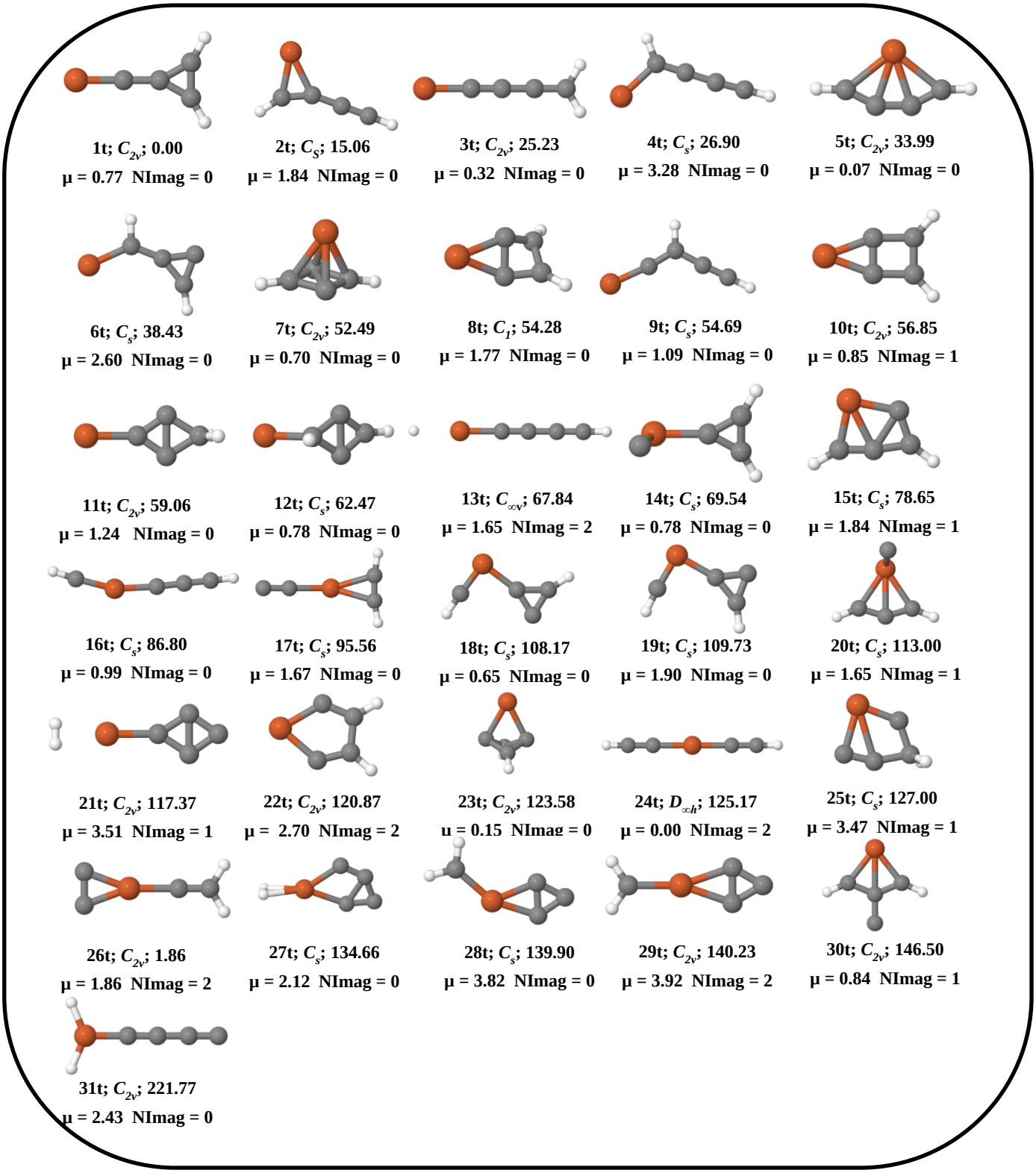


Figure S5. Isomers of $FeC_4H_2^{2+}$ in the triplet electronic state with ZPVE-corrected relative energies (in kcal mol^{-1}), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained using the (U)ωB97X–D functional with SDD and 6–311++G (2d,2p) basis sets.

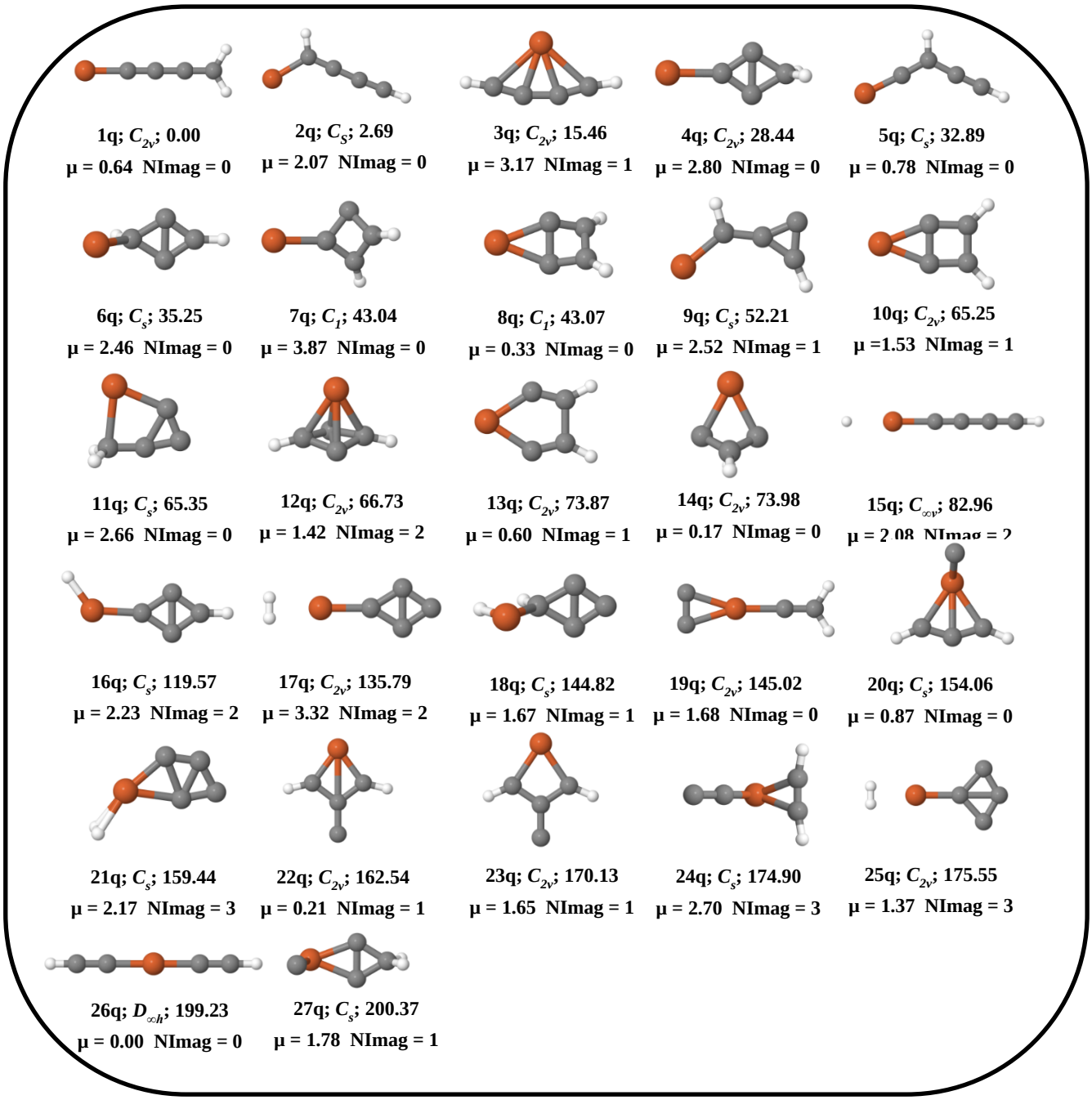


Figure S6. Isomers of $FeC_4H_2^{2+}$ in the quintet electronic state with ZPVE-corrected relative energies (in kcal mol^{-1}), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained using the (U)ωB97X–D functional with SDD and 6–311++G (2d,2p) basis sets.

Table S1. Total energy (in a.u)**,** point group**,** zero-point correction (in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye), and the number of imaginary frequencies (NImag) of $FeC_4H_2^{2+}$ in their corresponding singlet electronic state calculated using ωB97X-D functional with SDD and 6-311++G(2d,2p) basis sets.

Isomer	Energy(a.u)	Poin Group	Zero correction (a.u)	E+ZPVE (a.u)	ΔE+ZPVE (a.u)	ΔE+ZPVE (kcal/mol)	|μ| Debye	Nimag
1s	-276.5081389	Cs	0.037799	-276.470339	0	0	1.2507	0
2s	-276.49663	C2v	0.036733	-276.45989	0.010449	6.556846442	1.4746	1
3s	-276.4701718	C2v	0.0406	-276.429572	0.040767	25.58167852	2.1359	0
4s	-276.4641642	C2v	0.03868	-276.425484	0.044855	28.14693723	1.1615	0
5s	-276.4650087	C2v	0.039613	-276.425396	0.044943	28.20215807	3.4711	0
6s	-276.4586515	C1	0.039059	-276.419592	0.050747	31.84422302	1.4264	0
7s	-276.4396313	C2v	0.037565	-276.402067	0.068272	42.84132647	0.3921	0
8s	-276.4388896	Cs	0.038943	-276.399946	0.070393	44.17227405	1.3917	0
9s	-276.4350436	C2v	0.039717	-276.395327	0.075012	47.07074029	2.356	1
10s	-276.4311395	Cs	0.038187	-276.392952	0.077387	48.56107528	1.4325	0
11s	-276.417843	Cs	0.036571	-276.381272	0.089067	55.89038588	3.7408	1
12s	-276.4143135	C2v	0.039124	-276.37519	0.095149	59.70689847	0.5863	0
13s	-276.4093772	C2v	0.037981	-276.371396	0.098943	62.08766939	1.0148	0
14s	-276.4048176	C1	0.038744	-276.366074	0.104265	65.42727479	1.8522	0
15s	-276.3956551	Cs	0.03683	-276.358826	0.111513	69.97546342	2.1238	0
16s	-276.3943499	Cs	0.037093	-276.357257	0.113082	70.96002577	3.6407	1
17s	-276.3789125	C2v	0.038623	-276.340289	0.13005	81.60760644	3.0324	0
18s	-276.3729568	Cs	0.033573	-276.339384	0.130955	82.17550251	5.608	1
19s	-276.3728461	Cs	0.036234	-276.336612	0.133727	83.91495876	1.0319	0
20s	-276.3718337	Cs	0.036893	-276.334941	0.135398	84.96352708	3.5905	0
21s	-276.3703426	C2v	0.03639	-276.333953	0.136386	85.58350644	0.4851	1
22s	-276.3467418	C∞v	0.03505	-276.311692	0.158647	99.55249473	7.0915	0
23s	-276.3443286	C2v	0.035893	-276.308436	0.161903	101.5956656	2.3403	0
24s	-276.3374112	C1	0.034991	-276.302421	0.167918	105.370135	3.1321	0
25s	-276.3482493	C2v	0.036284	-276.301818	0.168521	105.7485232	2.1256	0
26s	-276.3378629	C1	0.036123	-276.30174	0.168599	105.797469	2.7657	0
27s	-276.3345036	Cs	0.035167	-276.299337	0.171002	107.3053742	6.1113	0
28s	-276.3330531	Cs	0.035719	-276.297334	0.173005	108.5622757	3.0815	0
29s	-276.3267376	Cs	0.034893	-276.291845	0.178494	112.0066752	1.656	1
30s	-276.3204053	Cs	0.034621	-276.285784	0.184555	115.8100101	2.5687	1
31s	-276.2917441	C2v	0.029389	-276.262355	0.207984	130.5119294	6.5043	0
32s	-276.2884172	Cs	0.034028	-276.25439	0.215949	135.5100423	3.3857	0

33s	**-276.2799614**	**C2h**	**0.035053**	**-276.244909**	**0.22543**	**141.4594596**	**0**	**1**
34s	**-276.2746893**	**Cs**	**0.029951**	**-276.244739**	**0.2256**	**141.5661362**	**5.3431**	**2**
35s	**-276.2721261**	**Cs**	**0.030915**	**-276.241211**	**0.229128**	**143.7799896**	**0.4958**	**2**
36s	**-276.2552366**	**C2v**	**0.031991**	**-276.223246**	**0.247093**	**155.0531972**	**3.3015**	**1**
37s	**-276.2547452**	**D∞h**	**0.034358**	**-276.220387**	**0.249952**	**156.8472468**	**0**	**1**
38s	**-276.2525505**	**Cs**	**0.034557**	**-276.217994**	**0.252345**	**158.348877**	**1.9223**	**1**
39s	**-276.2293873**	**C2v**	**0.028009**	**-276.201378**	**0.268961**	**168.7755743**	**4.7392**	**2**
40s	**-276.2099469**	**C2v**	**0.027158**	**-276.182789**	**0.28755**	**180.4403478**	**0.528**	**0**

Table S2. Total energy (in a.u)**,** point group**,** zero-point correction (in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye), and the number of imaginary frequencies (NImag) of $FeC_4H_2^{2+}$ in their corresponding triplet electronic state calculated using ROHF with SDD and 6-311++G(2d,2p) basis sets.

Isomer	Energy (a.u)	Point Group	Zero correction(a.u)	E+ZPVE (a.u)	ΔE+ZPVE (a.u)	ΔE+ZPVE (kcal/mol)	|μ| Debye	Nimag
1t	-274.8298502	C2v	0.041499	-274.788351	0	0	4.6044	0
2t	-274.8256918	C2v	0.042439	-274.783253	0.005098	3.199043273	4.0318	0
3t	-274.7419577	C2v	0.038729	-274.703228	0.085123	53.41548853	0.4864	1
4t	-274.5868034	Cs	0.030855	-274.555949	0.232402	145.8344556	2.6412	1

Table S3. Total energy (in a.u)**,** point group, zero-point correction (in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye),and the number of imaginary frequencies (NImag) of $FeC_4H_2^{2+}$ in their corresponding quintet electronic state calculated using ROHF with SDD and 6-311++G(2d,2p) basis sets.

Isomer	Energy (a.u)	Point Group	Zero correction (a.u)	E+ZPVE (a.u)	ΔE+ZPVE (a.u)	ΔE+ZPVE (kcal/mol)	Dipole moment (Debye)	NImag
1q	**-274.9305578**	**C_{2v}**	**0.042217**	**-274.888341**	**0**	**0**	**4.4949**	**0**
2q	**-274.8551817**	**C_{2v}**	**0.039958**	**-274.815223**	**0.073118**	**45.88223735**	**2.0085**	**1**
3q	**-274.8389778**	**C_{2v}**	**0.037276**	**-274.801702**	**0.086639**	**54.36679288**	**3.341**	**2**
4q	**-274.6103434**	**C_{2v}**	**0.038443**	**-274.5719**	**0.316441**	**198.5697239**	**2.8418**	**2**

Table S4. Cartesian coordinates of optimized geometries of $FeC_4H_2^{2+}$ in the singlet electronic state (in Angström units) obtained using ωB97X-D functional with SDD and 6-311++G(2d,2p) basis sets.

1s				2s			
C	0.000000	0.000000	0.103840	C	0.000000	0.000000	-2.695925
C	0.000000	0.000000	-1.116934	C	0.000000	0.769099	-1.428945
C	0.000000	0.000000	-2.447412	C	0.000000	-0.769099	-1.428945
C	0.000000	0.000000	-3.719511	C	0.000000	0.000000	-0.313882
Fe	0.000000	0.000000	1.986466	Fe	0.000000	0.000000	1.605833
H	0.000000	0.938049	-4.284009	H	0.923129	0.000000	-3.272742
H	0.000000	-0.938049	-4.284009	H	-0.923129	0.000000	-3.272742
3s				4s			
C	0.000000	1.748412	-0.513345	Fe	0.000000	0.000000	1.651523
C	0.000000	0.677309	-1.126090	C	0.000000	0.682065	-2.546768
C	0.000000	-0.677309	-1.126090	C	0.000000	-0.682065	-2.546768
C	0.000000	-1.748412	-0.513345	C	0.000000	0.000000	-1.364237
H	0.000000	2.791092	-0.212855	C	0.000000	0.000000	0.069870
H	0.000000	-2.791092	-0.212855	H	0.000000	1.624126	-3.085073
Fe	0.000000	0.000000	0.773036	H	0.000000	-1.624126	-3.085073
5s				6s			
C	-0.477895	-0.563707	0.250297	C	0.000000	1.142732	-0.814358
C	-1.912969	0.649325	0.164077	C	0.811343	0.000000	-1.008920
C	-1.794237	-0.776891	-0.075053	C	-0.811343	0.000000	-1.008920
C	-0.677450	0.729305	-0.449283	C	0.000000	-1.142732	-0.814358
Fe	1.312637	0.001098	0.017337	Fe	0.000000	0.000000	0.920300
H	-2.393904	-1.554556	-0.544010	H	0.000000	2.207151	-1.024234
H	-2.559361	1.297827	0.753014	H	0.000000	-2.207151	-1.024234
7s				8s			
C	-0.113306	2.049251	0.678644	C	0.000000	0.708276	-1.911323
C	1.292191	-1.237962	0.000000	C	0.000000	-0.708276	-1.911323
C	-0.113306	2.049251	-0.678644	C	0.000000	0.714875	-0.460385
C	-0.113306	0.862046	0.000000	C	0.000000	-0.714875	-0.460385
Fe	-0.211363	-1.059729	0.000000	Fe	0.000000	0.000000	1.300319
H	-0.109106	2.608716	1.606317	H	0.000000	1.486677	-2.673904
H	-0.109106	2.608716	-1.606317	H	0.000000	-1.486677	-2.673904
9s				10s			
C	-0.910388	-1.682103	0.000000	H	1.270773	1.958017	0.000003
C	-1.158983	-0.397993	0.000000	H	4.147374	-1.214669	0.000000
C	0.408776	-1.091873	0.000000	C	-0.196920	0.347653	0.000000
C	1.452225	-0.382779	0.000000	C	1.147771	0.869130	0.000003
Fe	0.000000	0.929949	0.000000	C	2.224787	0.068015	0.000002
H	-1.262109	-2.713620	0.000000	C	3.247804	-0.615004	0.000001
H	2.512333	-0.136563	0.000000	Fe	-1.690723	-0.183158	-0.000002
11s				12s			

C	0.000000	1.128150	-0.822134	C	0.000000	0.941538	-1.305390
C	0.841633	0.000000	-0.979080	C	-0.928827	0.000000	-0.773077
C	-0.841633	0.000000	-0.979080	C	0.000000	-0.941538	-1.305390
C	0.000000	-1.128150	-0.822134	C	0.928827	0.000000	-0.773077
Fe	0.000000	0.000000	0.905745	Fe	0.000000	0.000000	1.100466
H	0.000000	2.204588	-0.967405	H	0.000000	1.895059	-1.835256
H	0.000000	-2.204588	-0.967405	H	0.000000	-1.895059	-1.835256
		13s				14s	
C	-1.783429	0.480513	0.423095	C	0.453407	-0.885266	1.213576
C	-1.707394	-0.816620	-0.082470	C	0.453407	1.593437	0.000000
C	-0.400162	-0.879081	-0.188170	C	0.676433	-1.278023	0.000000
Fe	1.183827	0.031926	0.089128	C	0.453407	-0.885266	-1.213576
H	-2.346403	0.970173	1.217144	Fe	-0.516602	0.420839	0.000000
H	-0.838406	1.171771	-1.479165	H	0.605860	-1.105553	2.270271
C	-0.708129	0.719850	-0.495006	H	0.605860	-1.105553	-2.270271
		15s				16s	
C	-0.697427	-1.116647	0.000000	C	0.000000	0.701611	-1.622319
C	0.580050	-1.591118	0.000000	C	0.000000	-0.701611	-1.622319
C	-1.760934	-0.337194	0.000000	C	0.000000	1.109062	-0.252284
C	1.321102	-0.340443	0.000000	C	0.000000	-1.109062	-0.252284
Fe	0.000000	0.891767	0.000000	Fe	0.000000	0.000000	1.058340
H	0.928832	-2.626177	0.000000	H	0.000000	1.337285	-2.510808
H	2.414422	-0.247354	0.000000	H	0.000000	-1.337285	-2.510808
		17s				18s	
C	3.376479	-1.620108	0.000000	C	-1.026358	-0.581161	0.000000
C	2.278868	-1.073548	0.000000	C	-0.501259	-2.413016	0.000000
C	1.110049	-0.476841	0.000000	C	0.233212	-1.276586	0.000000
C	0.000000	0.131458	0.000000	C	1.252937	-0.291034	0.000000
H	4.343306	-2.103180	0.000000	H	-2.079383	-0.882325	0.000000
Fe	-1.660284	0.697085	0.000000	H	2.328189	-0.489700	0.000000
H	-1.768300	2.213205	0.000000	Fe	0.000000	1.105493	0.000000
		19s				20s	
C	0.817812	-1.887580	0.000000	C	0.000000	1.115491	-0.391301
C	0.949511	-0.498235	0.000000	C	0.000000	0.000000	-2.664934
C	-1.563625	-0.055859	0.000000	C	0.000000	0.000000	-1.284770
C	-0.512732	-0.888431	0.000000	C	0.000000	-1.115491	-0.391301
Fe	0.000000	0.956659	0.000000	Fe	0.000000	0.000000	1.144685
H	0.927101	-2.446244	0.941113	H	0.000000	2.168060	-0.683983
H	0.927101	-2.446244	-0.941113	H	0.000000	-2.168060	-0.683983
		21s				22s	
C	0.000000	0.000000	-3.893290	C	0.000000	2.168121	-1.232321
C	0.000000	0.000000	-2.649729	C	0.000000	1.269845	-0.366819
C	0.000000	0.000000	-1.350823	C	0.000000	-1.269845	-0.366819
C	0.000000	0.000000	-0.058165	C	0.000000	-2.168121	-1.232321
H	0.000000	0.000000	-4.977033	Fe	0.000000	0.000000	0.888206
Fe	0.000000	0.000000	1.896762	H	0.000000	-2.975648	-1.951840
H	0.000000	0.000000	3.373275	H	0.000000	2.975648	-1.951840

23s				24s			
Fe	-0.125029	-0.638179	-0.068936	Fe	0.000000	0.000000	0.851992
C	-1.640910	0.399314	0.050234	C	0.000000	2.179000	-1.161395
C	-0.590942	1.238198	0.011786	C	0.000000	1.203460	-0.381544
C	0.716402	1.105001	-0.036800	C	0.000000	-1.203460	-0.381544
H	-0.060947	-0.819970	1.371504	C	0.000000	-2.179000	-1.161395
H	2.675432	-0.099884	0.111050	H	0.000000	3.040088	-1.818266
C	1.621496	0.176236	0.026409	H	0.000000	-3.040088	-1.818266
25s				26s			
C	-1.566899	0.927677	-0.339558	C	0.000000	0.461766	0.000000
C	1.320531	0.084480	-0.003545	C	-0.798027	1.673685	0.000000
C	-1.259559	0.513144	0.831033	C	-0.001659	2.797486	0.000000
C	2.487690	0.519334	0.013274	C	0.796742	1.674752	0.000000
H	-1.940477	1.518305	-1.172987	Fe	0.000727	-1.557938	0.000000
H	3.526610	0.828565	0.029999	H	0.001243	-3.027570	0.000000
Fe	-0.287566	-0.562103	-0.071701	H	-0.002483	3.887822	0.000000
27s				28s			
C	-0.770415	-2.093417	0.000000	C	-0.493191	1.765453	0.000000
C	-1.246231	-0.814065	0.000000	C	-0.493191	-1.050189	0.790579
C	0.158925	-1.114050	0.000000	C	-0.493191	-1.050189	-0.790579
C	1.574208	1.273503	0.000000	C	-1.100710	-1.872568	0.000000
Fe	0.000000	0.704296	0.000000	Fe	0.661194	0.337784	0.000000
H	-0.978794	-3.162371	0.000000	H	-0.854668	2.231292	0.925300
H	2.679873	1.338849	0.000000	H	-0.854668	2.231292	-0.925300
29s				30s			
C	1.784604	1.271103	0.000000	C	0.000000	0.000000	-0.586218
C	0.000081	-1.300537	0.000000	C	0.000000	0.772603	-1.727024
C	-1.593434	-0.990856	0.000000	C	0.000000	-0.772603	-1.727024
C	-0.972584	-2.131339	0.000000	C	0.000000	0.000000	-3.013246
Fe	0.000000	0.611657	0.000000	Fe	0.000000	0.000000	1.378952
H	1.997941	2.349831	0.000000	H	0.000000	0.390554	3.234159
H	2.690053	0.656860	0.000000	H	0.000000	-0.390554	3.234159
31s				32s			
C	-1.020311	-0.627698	0.000000	Fe	0.000000	0.000000	0.000000
C	0.439230	-1.137731	0.000000	C	1.275488	-1.696415	0.000000
C	1.463884	-0.133846	0.000000	C	0.000000	1.770386	0.000000
C	-0.652110	-1.950331	0.000000	C	0.000000	-1.770386	0.000000
Fe	0.000000	0.913750	0.000000	C	-1.275488	1.696415	0.000000
H	-0.409366	2.333901	0.000000	H	2.349640	-1.874741	0.000000
H	-0.974785	-2.993751	0.000000	H	-2.349640	1.874741	0.000000
33s				34s			
C	0.000000	0.510187	0.000000	C	1.748720	-1.809444	0.000000
C	-0.779946	1.647805	0.000000	C	0.463720	-1.406768	0.000000
C	-0.011001	2.937294	0.000000	C	0.463720	1.555413	0.610937
C	0.766369	1.651649	0.000000	C	0.463720	1.555413	-0.610937
Fe	-0.115945	-1.426598	0.000000	Fe	-0.768520	-0.106206	0.000000
H	1.532939	-2.088247	0.000000	H	0.571121	1.696836	1.679516

H	1.629089	-1.301807	0.000000	H	0.571121	1.696836	-1.679516
35s				36s			
C	0.000000	0.700964	1.986460	H	0.000000	0.000000	4.349293
C	0.000000	-0.700964	1.986460	C	0.000000	0.000000	3.265411
C	0.000000	0.000000	-1.593518	C	0.000000	0.000000	1.995264
C	0.000000	0.000000	-2.872714	Fe	0.000000	0.000000	0.000000
Fe	0.000000	0.000000	0.379451	C	0.000000	0.000000	-1.995264
H	0.000000	0.938416	-3.452930	C	0.000000	0.000000	-3.265411
H	0.000000	-0.938416	-3.452930	H	0.000000	0.000000	-4.349293
37s				38s			
C	-0.285915	1.731363	0.000000	C	0.000000	0.000000	-2.207208
C	-0.285915	-0.852251	0.679564	C	0.000000	1.292922	-1.710216
C	-0.285915	-0.852251	-0.679564	C	0.000000	0.000000	-0.773476
C	-1.414338	-1.604388	0.000000	C	0.000000	-1.292922	-1.710216
Fe	0.666290	0.516666	0.000000	Fe	0.000000	0.000000	1.228374
H	-2.453712	-1.271030	0.000000	H	0.000000	0.388393	3.234491
H	-1.237325	-2.697139	0.000000	H	0.000000	-0.388393	3.234491
39s							
C	0.000000	0.000000	-3.982106				
C	0.000000	0.000000	-2.614241				
C	0.000000	0.000000	-1.352902				
C	0.000000	0.000000	-0.055241				
Fe	0.000000	0.000000	1.678179				
H	0.000000	1.402314	2.197141				
H	0.000000	-1.402314	2.197141				

Table S5. Cartesian coordinates of optimized geometries of $FeC_4H_2^{2+}$ in the triplet electronic state (in Angström units) obtained using ROHF with SDD and 6-311++G(2d,2p) basis sets.

1t				2t			
C	0.000000	1.865449	-0.880508	C	0.000000	0.000000	-2.745979
C	0.000000	0.695563	-1.123010	C	0.000000	0.756046	-1.476615
C	0.000000	-0.695563	-1.123010	C	0.000000	-0.756046	-1.476615
C	0.000000	-1.865449	-0.880508	C	0.000000	0.000000	-0.360518
H	0.000000	2.925148	-0.746599	Fe	0.000000	0.000000	1.653100
H	0.000000	-2.925148	-0.746599	H	0.916034	0.000000	-3.311117
Fe	0.000000	0.000000	0.982131	H	-0.916034	0.000000	-3.311117
3t				4t			
C	0.000000	0.802015	-1.755424	C	-2.331797	-0.569765	0.000001
C	0.000000	-0.802015	-1.755424	C	-1.013041	-0.699463	0.000000
C	0.000000	1.113560	-0.524034	C	-1.771279	0.660222	0.000000
C	0.000000	-1.113560	-0.524034	C	-0.562966	1.153240	0.000000
Fe	0.000000	0.000000	1.259621	Fe	1.092920	-0.175606	0.000000
H	0.000000	1.324343	-2.698324	H	2.829283	0.650179	-0.380592
H	0.000000	-1.324343	-2.698324	H	2.829283	0.650178	0.380593

Table S6. Cartesian coordinates of optimized geometries of $FeC_4H_2^{2+}$ in the quintet electronic state (in Angström units) obtained using ROHF with SDD and 6-311++G(2d,2p) basis sets.

1q				2q			
C	0.000000	0.000000	-2.790069	C	0.000000	0.892823	-1.399766
C	0.000000	0.754352	-1.519461	C	-0.969850	0.000000	-0.862076
C	0.000000	-0.754352	-1.519461	C	0.000000	-0.892823	-1.399766
C	0.000000	0.000000	-0.401658	C	0.969850	0.000000	-0.862076
Fe	0.000000	0.000000	1.695903	Fe	0.000000	0.000000	1.194849
H	0.916035	0.000000	-3.354794	H	0.000000	1.811352	-1.961984
H	-0.916035	0.000000	-3.354794	H	0.000000	-1.811352	-1.961984
3q				4q			
C	0.000000	1.158305	-0.992589	C	0.000000	0.706185	-2.042402
C	0.769830	0.000000	-1.198734	C	0.000000	-0.706185	-2.042402
C	-0.769830	0.000000	-1.198734	C	0.000000	0.743314	-0.610582
C	0.000000	-1.158305	-0.992589	C	0.000000	-0.743314	-0.610582
Fe	0.000000	0.000000	1.117467	Fe	0.000000	0.000000	1.440995
H	0.000000	2.157146	-1.379131	H	0.000000	1.457727	-2.815034
H	0.000000	-2.157146	-1.379131	H	0.000000	-1.457727	-2.815034

Table S7. Total energy (in a.u)**,** point group, zero-point correction (in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye), the number of imaginary frequencies (NImag), the expectation value of the total spin, $<S^2>$ and calculated %error for spin contamination of $FeC_4H_2^{2+}$ in their corresponding triplet electronic state calculated using (U)ωB97X–D functional with SDD and 6-311++G(2d,2p) basis sets.

Isomer	Energy(a.u)	Point Group	Zero correction(a.u)	E+ZPVE (a.u)	ΔE+ZPVE (a.u)	ΔE+ZPVE(kcal/mol)	|μ| Debye	Nimag	$<S^2>$	%error(Δ)
1t	-276.5994616	C_{2v}	0.039074	-276.560388	0	0	0.7687	0	3.484484	74.224
2t	-276.5730412	C_s	0.037363	-276.535678	0.02471	15.50575898	1.835	0	3.102027	55.101
3t	-276.5571365	C_{2v}	0.036949	-276.520188	0.0402	25.22588065	0.324	0	3.036149	51.807
4t	-276.5545701	C_s	0.037046	-276.517524	0.042864	26.89756588	3.2764	0	3.028073	51.404
5t	-276.542751	C_{2v}	0.036522	-276.506229	0.054159	33.98528533	0.0667	0	3.047113	52.356
6t	-276.5372374	C_s	0.038093	-276.499145	0.061243	38.43056241	2.6017	0	3.857944	92.897
7t	-276.5138829	C_{2v}	0.037147	-276.476736	0.083652	52.4924221	0.7009	0	2.85293	42.647
8t	-276.5139298	C_1	0.040042	-276.473888	0.0865	54.27956907	1.7737	0	2.472009	23.600
9t	-276.5107029	C_s	0.037468	-276.473235	0.087153	54.68933275	1.0944	0	3.087718	54.386
10t	-276.507312	C_{2v}	0.03752	-276.469792	0.090596	56.84984785	0.8467	1	3.108095	55.405
11t	-276.5065662	C_{2v}	0.040291	-276.466275	0.094113	59.05679866	1.2364	0	2.123818	6.191
12t	-276.5002374	C_s	0.039397	-276.46084	0.099548	62.46731262	0.785	0	2.21914	10.957
13t	-276.4816416	$C_{\infty v}$	0.029367	-276.452275	0.108113	67.84193122	1.6534	2	3.97294	98.647
14t	-276.4869775	C_s	0.037409	-276.449569	0.110819	69.53997185	0.7839	0	3.036699	51.835
15t	-276.4709338	C_s	0.035886	-276.435048	0.12534	78.65203684	1.8423	1	2.188823	9.441
16t	-276.4556008	C_s	0.033543	-276.422058	0.13833	86.80338485	0.9934	0	3.649029	82.451
17t	-276.4425235	C_s	0.034412	-276.408111	0.152277	95.55525941	1.6689	0	4.013586	100.679
18t	-276.4237408	C_s	0.035727	-276.388014	0.172374	108.1663172	0.6518	0	2.876221	43.811
19t	-276.4212597	C_s	0.03574	-276.38552	0.174868	109.7313258	1.8957	0	2.868263	43.413
20t	-276.414054	C_s	0.033738	-276.380316	0.180072	112.9968851	1.6528	1	3.13925	56.962
21t	-276.4016117	C_{2v}	0.028268	-276.373343	0.187045	117.3725086	3.5121	1	3.882687	94.134
22t	-276.4040746	C_{2v}	0.0363	-276.367774	0.192614	120.8671089	2.7037	2	3.78448	89.224
23t	-276.400137	C_{2v}	0.036683	-276.363454	0.196934	123.5779498	0.1534	0	2.027017	1.351
24t	-276.3949545	$D_{\infty h}$	0.034043	-276.360911	0.199477	125.1737063	0	2	3.829017	91.451
25t	-276.393331	C_s	0.035332	-276.357999	0.202389	127.0010139	3.472	1	3.192583	59.629
26t	-276.3780194	C_{2v}	0.032126	-276.345893	0.214495	134.5976436	1.8584	2	3.707389	85.369
27t	-276.3744789	C_s	0.028688	-276.345791	0.214597	134.6616495	2.1175	0	3.967814	98.391
28t	-276.3711398	C_s	0.033692	-276.337448	0.22294	139.896961	3.82	0	3.411628	70.581
29t	-276.3697092	C_{2v}	0.032789	-276.33692	0.223468	140.228286	3.9182	2	3.640274	82.014
30t	-276.3603695	C_{2v}	0.033446	-276.326924	0.233464	146.5008707	0.8358	1	2.661644	33.082
31t	-276.2341859	C_{2v}	0.027217	-276.206969	0.353419	221.773769	2.4268	1	2.288686	14.434

Table S8. Total energy (in a.u)**,** point group, zero-point correction (in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye), the number of imaginary frequencies (NImag), the expectation value of the total spin, $<S^2>$ and calculated %error for spin contamination of $FeC_4H_2^{2+}$ in their corresponding quintet electronic state calculated using (U)ωB97X–D functional with SDD and 6-311++G(2d,2p) basis sets.

Isomer	Energy(a.u)	Point Group	Zero correction(a.u)	E+ZPVE(a.u)	ΔE+ZPVE(a.u)	ΔE+ZPVE(kcal/mol)	|μ| Debye	Nimag	$<S^2>$	%error(Δ)
1q	-276.6166351	C_{2v}	0.037086	-276.579549	0	0	0.6393	0	6.033383	0.556
2q	-276.6135374	C_S	0.038268	-276.575269	0.00428	2.685740527	2.0744	0	6.020776	0.346
3q	-276.5930383	C_{2v}	0.038127	-276.554912	0.024637	15.45995079	3.1707	1	6.011035	0.184
4q	-276.5741543	C_{2v}	0.03993	-276.534225	0.045324	28.44123917	2.7959	0	6.007305	0.122
5q	-276.5649685	C_s	0.037827	-276.527142	0.052407	32.88588874	0.7852	0	6.255859	4.264
6q	-276.5625568	C_s	0.039181	-276.523376	0.056173	35.2490894	2.4625	0	6.009071	0.151
7q	-276.5499091	C_1	0.038945	-276.510964	0.068585	43.03773693	3.8661	0	6.00806	0.134
8q	-276.5500295	C_1	0.039121	-276.510909	0.06864	43.07224995	0.3283	0	6.010209	0.170
9q	-276.5341532	C_s	0.037813	-276.49634	0.083209	52.21443541	2.5186	1	6.851908	14.198
10q	-276.5149133	C_{2v}	0.03934	-276.475574	0.103975	65.24529704	1.5343	1	6.025566	0.426
11q	-276.5134145	C_s	0.038014	-276.4754	0.104149	65.35448369	2.6555	0	6.039035	0.651
12q	-276.5080959	C_{2v}	0.034882	-276.473214	0.106335	66.72621939	1.4181	2	6.02375	0.396
13q	-276.4972468	C_{2v}	0.035421	-276.461826	0.117723	73.87229722	0.5967	1	6.02958	0.493
14q	-276.4992438	C_{2v}	0.037591	-276.461653	0.117896	73.98085636	0.1703	0	6.025435	0.424
15q	-276.4766828	$C_{\infty v}$	0.029344	-276.447339	0.13221	82.9630269	2.0761	2	7.009057	16.818
16q	-276.4188288	C_s	0.029829	-276.389	0.190549	119.5713018	2.2322	2	6.590486	9.841
17q	-276.3912874	C_{2v}	0.028127	-276.363161	0.216388	135.785519	3.3188	2	6.805229	13.420
18q	-276.3814498	C_s	0.03269	-276.34876	0.230789	144.8222828	1.6729	1	6.212063	3.534
19q	-276.3798743	C_{2v}	0.031434	-276.348441	0.231108	145.0224584	1.6836	0	6.778556	12.976
20q	-276.3668015	C_s	0.032759	-276.334042	0.245507	154.0579672	0.8663	0	6.694701	11.578
21q	-276.3541483	C_s	0.028685	-276.325463	0.254086	159.4413709	2.1693	3	6.932344	15.539
22q	-276.3555894	C_{2v}	0.035064	-276.320525	0.259024	162.5400127	0.211	1	6.281732	4.696
23q	-276.3411154	C_{2v}	0.032692	-276.308423	0.271126	170.1341323	1.6494	1	6.440915	7.349
24q	-276.3335756	C_s	0.032745	-276.300831	0.278718	174.8981842	2.7004	3	6.190754	3.179
25q	-276.3243873	C_{2v}	0.024602	-276.299785	0.279764	175.5545591	1.3749	3	6.666643	11.111
26q	-276.2971748	$D_{\infty h}$	0.035115	-276.26206	0.317489	199.2273538	0	0	6.05478	0.913
27q	-276.2917557	C_s	0.031509	-276.260247	0.319302	200.3650285	1.7671	1	7.128387	18.806