Supplementary materials

Figure S1. Geometry of complexes **1, 2**.

Figure S2. IR spectrum of **1** in CH_2Cl_2 (ν(CO) region)

Figure S3. ^1H NMR spectrum of **1** in CD_2Cl_2

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2

Figure S5. (**a**) Cyclic voltammograms of **1** (1.9 mM) in CH_2Cl_2-$[Bu_4N][PF_6]$ (0.2 M) under Ar at 0.2 Vs^{-1}. (**b**) Variation of the current intensity (*I*p) as a function of the square root of the scan rate ($v^{1/2}$). (**c**) Scan rate dependence of the current for the reduction of **1** in CH_2Cl_2-$[Bu_4N][PF_6]$ (0.2M) (vitreous carbon electrode).

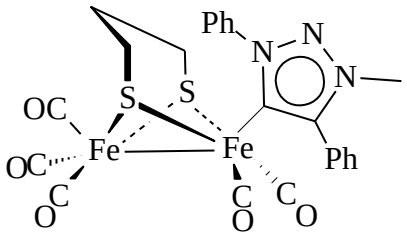
Figure S6. **A**) thermodynamic speciation of $\mathbf{2}^-$ and **B**) optimized structure of $\mathbf{2a}^-$ with relevant geometrical parameters (distances in Å) in comparison with the ones of its neutral counterpart **2**. Atom colouring: Fe = orange, S = yellow, C = grey, N = blue, O = red. H atoms are omitted for clarity. For simplification, net charges on structures are not reported.

Figure S7. A) thermodynamic speciation of $\mathbf{2}^{2-}$ and **B**) optimized structure of $\mathbf{2a}^{2-}$ with relevant geometrical parameters (distances in Å). Atoms colouring: Fe = orange, S = yellow, C = grey, N = blue, O = red. H atoms are omitted for clarity. For simplification, net charges on structures are not reported.

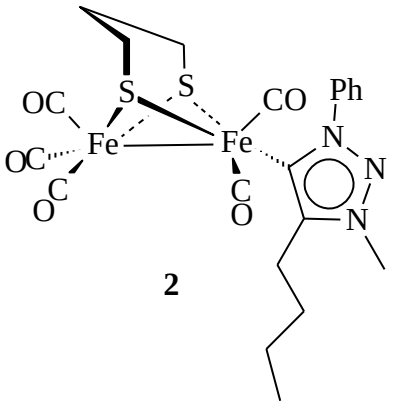
Table S1. Calculated ν(CO) (cm^{-1}) of complexes **1**, **2** and their most stable mono-anion and di-anion

Table S2. Crystallographic data and refinement parameters of **1.C_4H_8O.**

Table S3. XYZ Coordinates of selected optimized structures.



1



2

Figure S1. Geometry of complexes **1, 2**.

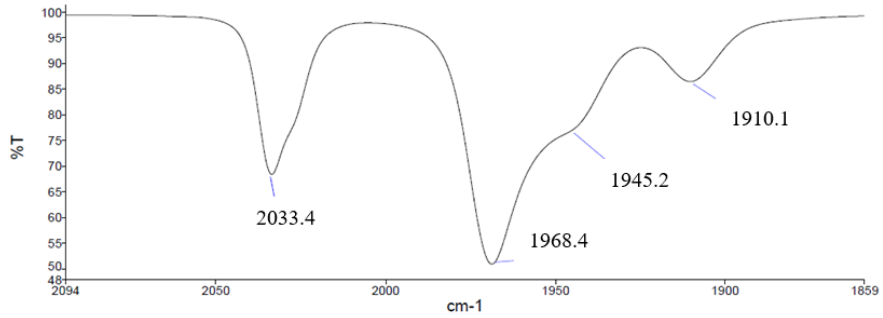


Figure S2. IR spectrum of **1** in CH_2Cl_2 (ν(CO) region)

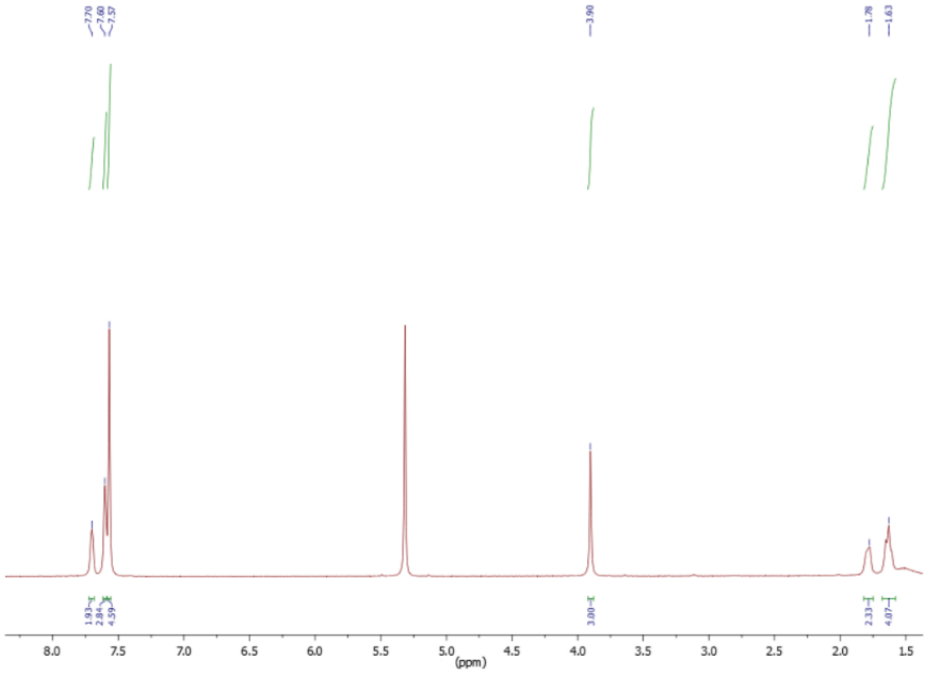


Figure S3. ^{1}H NMR spectrum of **1** in CD_2Cl_2

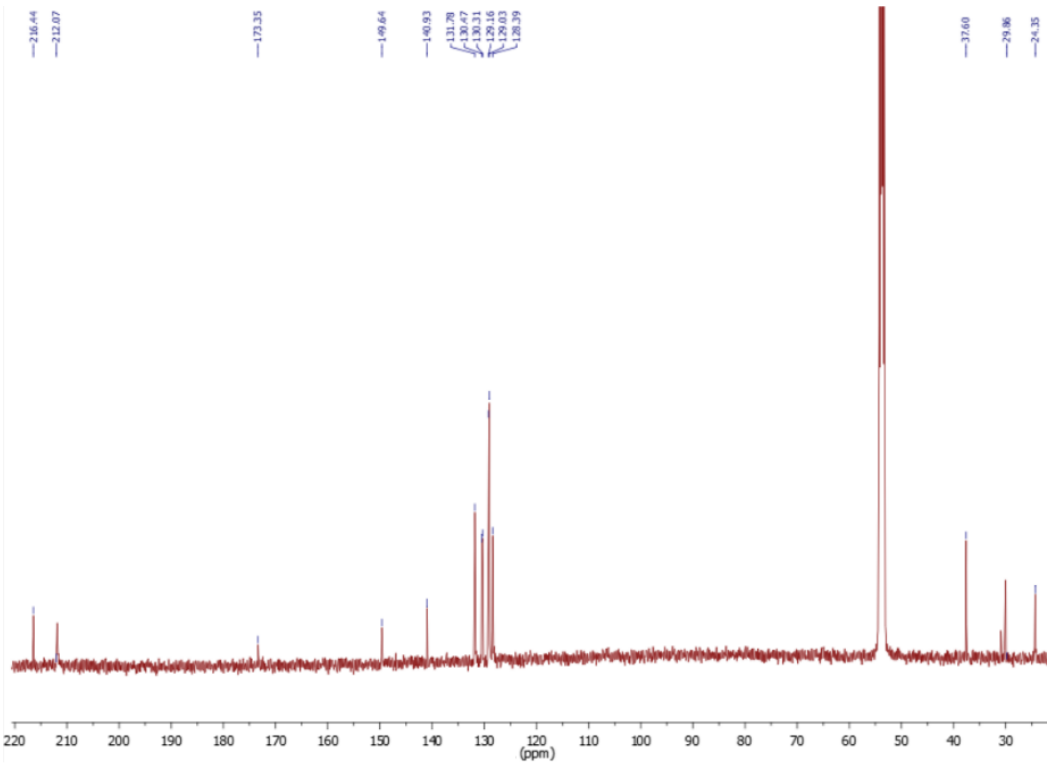


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2

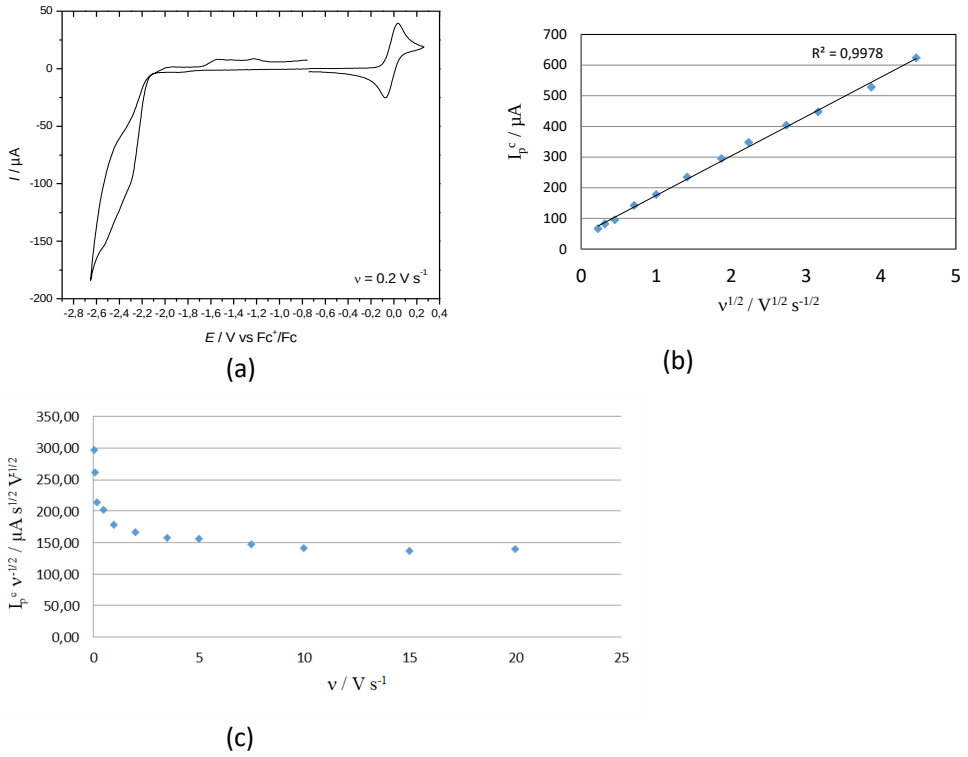
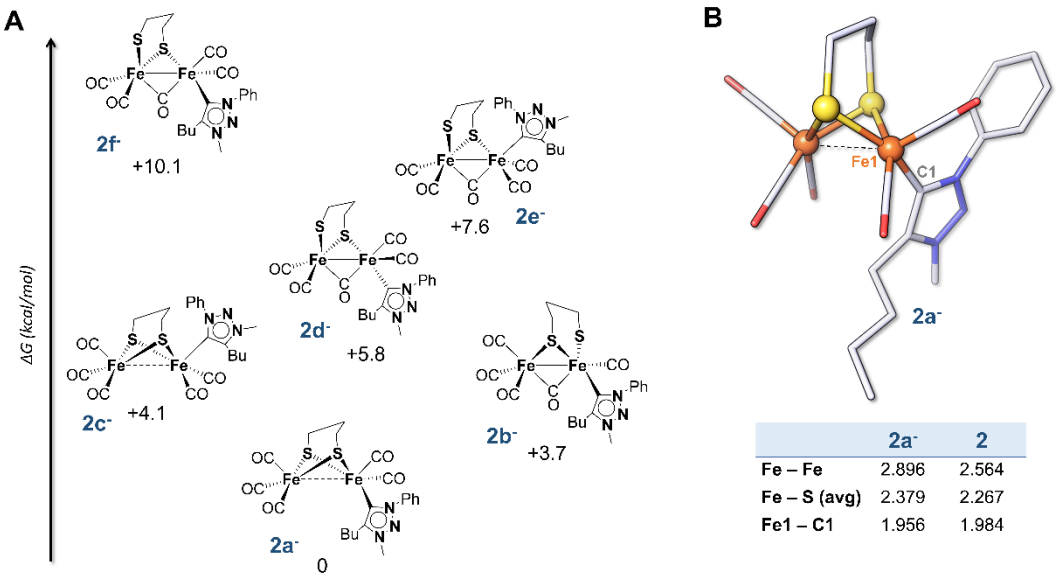
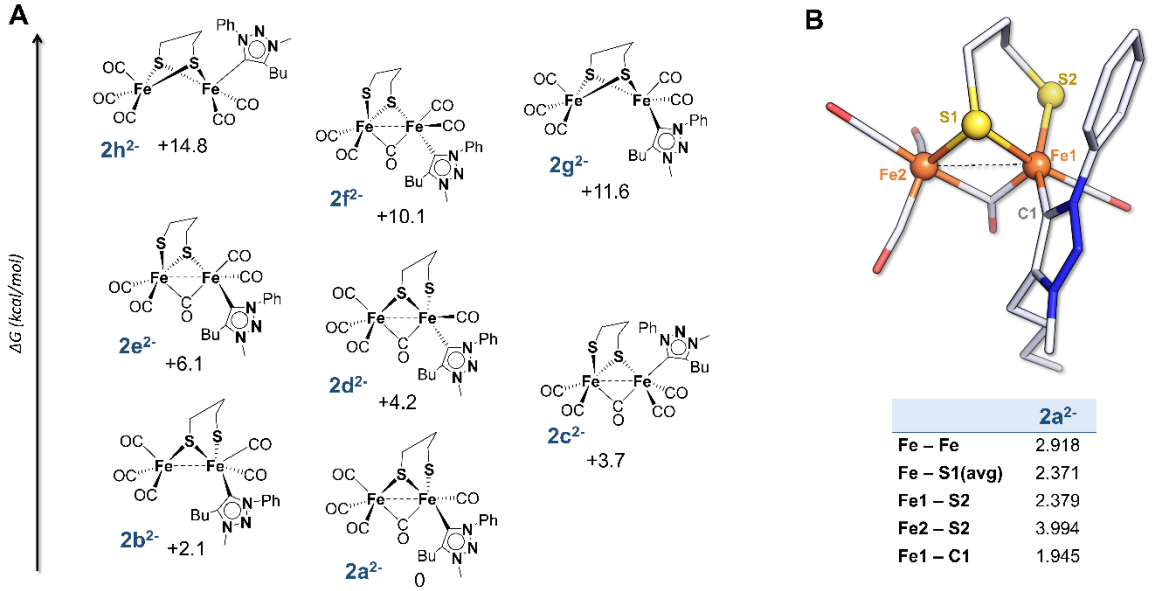


Figure S5. (**a**) Cyclic voltammograms of **1** (1.9 mM) in CH_2Cl_2-[Bu_4N][PF_6] (0.2 M) under Ar at 0.2 Vs^{-1}. (**b**) Variation of the current intensity (*I*p) as a function of the square root of the scan rate ($\nu^{1/2}$). (**c**) Scan rate dependence of the current for the reduction of **1** in CH_2Cl_2-[Bu_4N][PF_6] (0.2M) (vitreous carbon electrode).



	2a⁻	2
Fe – Fe	2.896	2.564
Fe – S (avg)	2.379	2.267
Fe1 – C1	1.956	1.984

Figure S6. **A**) thermodynamic speciation of **2**$^{-}$ and **B**) optimized structure of **2a**$^{-}$ with relevant geometrical parameters (distances in Å) in comparison with the ones of its neutral counterpart **2**. Atom colouring: Fe = orange, S = yellow, C = grey, N = blue, O = red. H atoms are omitted for clarity. For simplification, net charges on structures are not reported.



	$2a^{2-}$
Fe – Fe	2.918
Fe – S1(avg)	2.371
Fe1 – S2	2.379
Fe2 – S2	3.994
Fe1 – C1	1.945

Figure S7. **A**) thermodynamic speciation of $\mathbf{2}^{2-}$ and **B**) optimized structure of $\mathbf{2a}^{2-}$ with relevant geometrical parameters (distances in Å). Atoms colouring: Fe = orange, S = yellow, C = grey, N = blue, O = red. H atoms are omitted for clarity. For simplification, net charges on structures are not reported.

Table S1. Calculated ν(CO) (cm^{-1}) of complexes **1**, **2** and their most stable mono-anion and di-anion.

species	ν(CO) / cm^{-1}
1	1920, 1944, 1958, 1963, 2016
1^{-}	1852, 1854, 1884, 1894, 1933
1^{2-}	1657, 1791, 1825, 1844, 1886
2	1914, 1944, 1947, 1962, 2010
2^{-}	1818, 1857, 1860, 1877, 1927
2^{2-}	1646, 1783, 1811, 1821, 1869

Table S2. Crystallographic data and refinement parameters of **1.C_4H_8O**

		1.C_4H_8O
Empirical formula		$C_{27}H_{27}Fe_2N_3O_6S_2$
Formula weight		665.34
Temperature (°K)		170(2)
Wavelength (Å)		0.71073
Crystal system, space group		Triclinic, P-1
Unit cell dimensions	a (Å)	9.1679(8)
	b (Å)	9.7446(9)
	c (Å)	16.3731(14)
	α (°)	99.169(7)
	β (°)	97.263(2)
	γ(°)	94.410(7)
Volume ($Å^3$)		1424.9(2) $Å^3$
Z		2
Calculated density (Mg/m^3)		1.551
Absorption coefficient (mm^{-1})		1.211
F(000)		684
Crystal colour		Red
Crystal size (mm)		0.18 x 0.08 x 0.01
Theta range for data collection (°)		3.25 to 26.37
Limiting indices		$-9 \le h \le 11$, $-12 \le k \le 10$, $-17 \le l \le 20$
Reflections collected / unique		9784 / 5817 [R(int) = 0.0847]
Completeness to theta = 26.37 (%)		99.7
Absorption correction		Analytical
Max. and min. transmission		0.9880 and 0.8115
Refinement method		Full-matrix least-squares on F^2
Data / restraints / parameters		5817 / 0 / 362
Goodness-of-fit on F^2		0.938
Final R indices [I>2σ(I)]		$R_1 = 0.0636$, $wR_2 = 0.0956$
R indices (all data)		$R_1 = 0.1275$, $wR_2 = 0.1242$
Largest diff. peak and hole ($e.Å^{-3}$)		0.679 and -0.587

Table S3. XYZ Coordinates of selected optimized structures.

2

C	4.938346	5.239871	4.259887
C	3.207701	4.094470	2.723169
C	1.370404	6.066821	0.929079
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C	1.899799	8.770558	1.282333
C	5.268087	7.984426	1.810301
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C	5.512219	8.421556	3.243295
H	5.933221	7.586760	3.820819
H	6.278547	9.215876	3.232648
C	4.280600	8.959592	3.947580
H	3.863470	9.830993	3.424407
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C	0.131653	3.943896	3.683223
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C	0.153678	2.405981	3.616509
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C	3.176603	7.363717	7.384434
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C	4.239280	7.968506	8.059028
H	4.166778	9.016946	8.350173
C	5.392211	7.232311	8.356597
H	6.222937	7.709754	8.877964
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S	4.086010	6.570372	1.578766
S	2.885095	7.758006	4.159062
Fe	3.398318	5.636499	3.535756
Fe	1.960573	7.218012	2.140070

2a$^-$

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H	4.770508	8.733592	1.208114
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H	4.171086	8.960002	8.441759
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H	6.471869	5.315748	8.160744
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H	4.566251	4.215178	6.971747
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S	2.778274	7.673160	4.184025
Fe	3.513577	5.484401	3.612213
Fe	1.856140	7.289338	2.068453

2a^{2-}

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S	4.367555	5.977152	2.700021
S	1.854204	7.930461	4.231384
Fe	2.286472	5.676717	3.734524
Fe	0.749440	7.573310	2.136631

1

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H	3.679314	8.204797	-1.252757
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H	7.336508	7.325822	2.018407
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C	3.511468	1.406294	6.596894
H	3.111347	0.751440	7.372215
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O	4.774460	7.128688	6.297807
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S	1.624458	6.495864	2.269808
S	1.845517	5.247879	5.102062
Fe	3.275765	6.535699	3.867759
Fe	0.877019	7.177289	4.327069

1a^{-}

Fe	3.582549	6.914352	4.316609
Fe	0.824167	7.177838	3.393161
S	1.735353	5.713954	4.955596
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C	2.722531	3.869303	2.983554
C	2.464965	4.775461	1.790704
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C	4.779146	8.173178	3.453613
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C	3.500529	10.367229	3.609952
C	2.583057	10.701056	2.614042
C	1.514026	11.542212	2.930982
C	1.374855	12.038782	4.230472
C	2.305470	11.697017	5.217538
C	3.380167	10.859988	4.909186
C	7.672606	9.416538	1.558588
C	4.793849	5.708696	4.750748
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O	0.137278	8.969725	1.192095
C	0.581579	8.343383	4.694711
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H	1.438204	4.660246	1.414524
H	3.161827	4.519982	0.978581
H	7.860781	8.569397	0.890749
H	8.521106	9.542091	2.241567
H	7.516582	10.332844	0.981801
H	2.701524	10.291522	1.611123
H	0.783070	11.799606	2.163966
H	0.533117	12.687898	4.476469
H	2.188742	12.073952	6.234647
H	4.112019	10.588560	5.667598
H	8.525126	7.324409	3.691680
H	6.343690	3.610731	1.198862
H	5.141210	5.776253	1.533769
H	9.724662	5.181052	3.372631
H	8.634369	3.306389	2.138384

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N	5.777761	3.535560	2.588987
C	5.006487	3.966504	3.644626
C	4.647625	5.322058	3.400718

N	5.245214	5.512595	2.151306
N	5.942955	4.461934	1.656017
Fe	3.769325	6.746265	4.541326
Fe	1.146517	7.478401	3.735652
S	1.726362	5.576739	4.929933
C	1.474537	3.965724	4.053732
C	1.630360	3.937015	2.541040
C	0.474557	4.599101	1.789770
S	0.596273	6.435568	1.631155
C	4.640248	3.054237	4.731455
C	4.684804	3.479826	6.069529
C	4.277079	2.628834	7.097665
C	3.827443	1.334764	6.810460
C	3.787452	0.896759	5.482032
C	4.183525	1.750409	4.450922
C	5.205435	6.683390	1.326360
C	3.970656	7.276828	1.059435
C	3.941022	8.419263	0.256792
C	5.124097	8.956353	-0.264486
C	6.351885	8.341466	0.006821
C	6.397154	7.198592	0.812801
C	6.472896	2.262318	2.401635
C	4.664101	8.086652	3.892055
O	5.284613	9.051519	3.593143
C	4.483494	6.719318	6.118030
O	4.991275	6.877353	7.187072
C	1.320949	8.956073	2.835867
O	1.414316	9.983935	2.259457
C	-0.338276	7.845327	4.531629
O	-1.325508	8.183480	5.101573
C	2.407726	8.187674	5.011184
O	2.445438	9.153925	5.744886
H	2.183036	3.277553	4.528795
H	0.459293	3.638542	4.329952
H	2.579044	4.414944	2.256826
H	1.695770	2.874965	2.236226
H	-0.475884	4.328964	2.280733
H	0.432149	4.211569	0.760001
H	5.842408	1.558402	1.845223
H	6.713988	1.845233	3.383917
H	7.390442	2.461240	1.839166
H	3.042523	6.861245	1.464395
H	2.979881	8.892047	0.050819
H	5.090399	9.855013	-0.883630
H	7.277361	8.756439	-0.395860
H	7.345037	6.717115	1.054210
H	5.019840	4.490832	6.284742
H	4.311131	2.979690	8.130537
H	3.503650	0.673388	7.615950
H	3.423584	-0.104275	5.244121
H	4.090701	1.417898	3.416777