Sulfur Difluoride and Sulfur Monofluoride as Ligands in Iron Carbonyl Chemistry

Xiaozhen Gao[a,b], Shida Gong[c], Nan Li,*[a,b] and R. Bruce King*[d]

[a]School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, China

[b]State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, PR China

[c]MOE Key Laboratory of Theoretical Environmental Chemistry, South China Normal University, Guangzhou 510631, P. R. China

[d]Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

Electronic Supplementary Information

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Table **S1 to S4** Coordinates of the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/ $Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

Tables **S5 to S8** Harmonic vibrational frequencies of the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

Table **S9 to S12** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/ $Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

Table **S13 to S16** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

Figures **S1 to S4** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/-$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

Table S1 Theoretical Cartesian coordinates (in Å) of the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, derivatives using the B3LYP* method (Note: The atomic number 6, 8, 9, 16 and 26 represent the C, O, F, S, Fe atoms, respectively. And the subsequent tables have the same arrangement)

Structures	Atom	X	Y	Z	Structures	Atom	X	Y	Z
4-1S (C_s)	6	-0.273514	-0.084057	1.844931	4-4S (C_s)	6	1.794334	0.904692	0.000000
	6	1.071300	1.344058	0.000000		6	-0.206022	1.330965	1.540707
	8	-0.273514	-0.308495	2.969848		6	-1.720906	-0.047808	0.000000
	8	1.965765	2.069002	0.000000		6	-0.206022	1.330965	-1.540707
	26	-0.322993	0.180840	0.000000		9	-0.206022	-2.435749	-1.182105
	16	0.989815	-1.738332	0.000000		9	-0.206022	-2.435749	1.182105
	9	2.575631	-1.207168	0.000000		16	0.623067	-1.628942	0.000000
	9	-1.636555	-1.193787	0.000000		8	-2.840816	-0.324361	0.000000
	6	-1.669297	1.436368	0.000000		8	-0.357183	1.908428	2.533673
	8	-2.546330	2.178766	0.000000		8	2.896867	1.252429	0.000000
	6	-0.273514	-0.084057	-1.844931		8	-0.357183	1.908428	-2.533673
	8	-0.273514	-0.308495	-2.969848		26	0.039905	0.416703	0.000000
4-2S (C_1)	6	-0.724240	1.740828	-0.345912	4-5S (C_1)	6	0.127125	1.663431	-0.647733
	6	-0.509281	0.025626	1.803339		6	0.841713	-1.523860	-0.944130
	8	-0.957956	2.823252	-0.645853		6	0.352297	-0.072908	1.795904
	8	-0.620906	0.059693	2.950541		6	2.186145	0.342018	0.017281
	26	-0.319745	-0.035460	0.000066		9	-2.448593	0.543680	-1.098117
	16	1.822680	0.858404	0.307861		9	-2.461203	-0.331610	1.111709
	9	2.735734	-0.097292	-0.692151		16	-1.629219	-0.615174	-0.274231
	9	-0.029675	-0.099766	-1.878294		8	0.338564	-0.110449	2.952916
	6	-2.004201	-0.673971	-0.398428		8	1.184571	-2.469037	-1.522987
	8	-3.036416	-1.066803	-0.713403		8	-0.026612	2.736810	-1.052854
	6	0.494696	-1.715772	-0.016704		8	3.319723	0.568923	0.032641
	8	1.022043	-2.728548	-0.097192		26	0.410847	-0.012612	-0.013088
4-3S (C_s)	6	0.381434	1.426772	1.323074					
	6	-0.909039	-0.841822	-1.317252					
	8	0.753815	2.132652	2.147049					
	8	-1.335987	-1.523362	-2.132504					
	26	-0.248925	0.296846	0.000000					
	16	1.779573	-0.852228	0.000000					
	9	1.210958	-2.437201	0.000000					
	9	-1.917083	1.231602	0.000000					
	6	0.381434	1.426772	-1.323074					
	8	0.753815	2.132652	-2.147049					
	6	-0.909039	-0.841822	1.317252					
	8	-1.335987	-1.523362	2.132504					

Table S2 Theoretical Cartesian coordinates (in Å) of the $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, derivatives using the B3LYP* method

Structures	Atom	X	Y	Z	Structures	Atom	X	Y	Z
3-1S (C_1)	6	-1.836615	0.240885	-0.951199	3-6T (C_1)	6	0.606976	1.799979	-0.594155
	6	0.333054	1.606343	-0.018058		6	1.795520	-1.129834	-0.183260
	8	-2.808389	0.392084	-1.547489		8	0.726926	2.873371	-0.984575
	8	0.721280	2.691137	0.018770		8	2.695670	-1.833857	-0.277198
	26	-0.241080	-0.103799	-0.100019		26	0.197580	-0.050662	-0.143950
	16	1.686525	-0.920695	-0.307333		16	-1.943368	0.090828	0.366457
	9	2.902777	0.185818	-0.096130		9	-2.580974	-1.248183	-0.350943
	9	-0.511346	-1.933763	-0.416379		9	-0.052576	-0.570752	-1.851452
	6	-0.956336	-0.137528	1.537785		6	0.456148	0.200564	1.671328
	8	-1.347869	-0.220322	2.618622		8	0.640767	0.336751	2.803956
3-2S (C_1)	6	-0.521313	-0.211212	1.596274	3-7T (C_1)	26	0.534151	0.025071	-0.313246
	6	-1.820684	-0.697382	-0.715604		6	0.588988	1.795075	-0.920860
	8	-0.667827	-0.344092	2.731977		6	0.781226	-1.736400	-0.893176
	8	-2.775103	-1.188432	-1.123849		6	1.611539	0.091807	1.180928
	26	-0.178749	-0.038034	-0.131742		8	0.625156	2.895443	-1.271824
	16	1.873854	0.569944	-0.271588		8	0.937000	-2.832400	-1.225109
	9	2.793900	-0.778862	-0.324609		8	2.302022	0.133764	2.111863
	9	0.326495	-1.795775	-0.369242		9	-2.353024	1.098585	0.210771
	6	-0.656061	1.709506	-0.240570		9	-2.250861	-1.303363	0.129232
	8	-0.985742	2.812030	-0.336284		16	-1.328556	-0.080386	0.747723
3-3T (C_1)	6	1.969416	0.567856	-0.396175	3-8S (C_s)	6	1.421349	1.776607	0.000000
	6	-1.386847	-1.055318	-0.607357		6	-0.561322	0.844280	1.530536
	8	3.031482	0.986660	-0.521401		6	-0.561322	0.844280	-1.530536
	8	-2.361909	-1.600016	-0.863177		8	2.251695	2.583604	0.000000
	26	0.279972	-0.228815	-0.268853		8	-1.189187	1.168595	2.449758
	16	-0.633835	1.735582	-0.051859		8	-1.189187	1.168595	-2.449758
	9	-2.262636	1.482795	0.210357		9	-0.561322	-2.493008	1.170604
	9	1.036545	-1.698497	-1.091423		9	-0.561322	-2.493008	-1.170604
	6	0.357019	-0.739991	1.702824		16	0.180862	-1.603690	0.000000
	8	0.362850	-0.950903	2.828800		26	0.247354	0.399070	0.000000
3-4S (C_1)	6	1.862231	0.756322	-0.291717	3-9T (C_1)	6	-2.097300	-0.970696	-0.484450
	6	-1.299607	-1.150962	-0.453136		6	-0.891688	1.608907	-0.416439
	8	2.913035	1.204853	-0.397029		6	-0.362780	-0.144876	1.681994
	8	-2.194565	-1.836369	-0.654783		8	-3.128818	-1.458566	-0.676298
	26	0.230793	-0.122889	-0.209093		8	-1.200814	2.719942	-0.538662
	16	-0.820789	1.687557	0.181198		8	-0.300008	-0.124601	2.837735
	9	-2.442524	1.347885	0.317799		9	2.481865	0.787016	0.297570
	9	0.989991	-1.248921	-1.506582		9	2.335982	-1.511802	-0.399239
	6	0.651924	-0.953089	1.284257		16	1.606126	-0.088729	-0.783686
	8	0.896218	-1.444746	2.301798		26	-0.458112	-0.158133	-0.162109
3-5T (C_1)	6	-2.176536	0.403262	-0.334328					
	6	0.033923	1.469570	0.676300					
	8	-3.267421	0.725235	-0.487267					
	8	0.264350	2.482031	1.179959					
	26	-0.341290	-0.122328	-0.168041					
	16	1.660799	-0.244477	-0.999905					
	9	2.714538	0.710173	-0.147752					
	9	-0.606269	-1.411859	-1.441727					
	6	-0.122781	-1.247742	1.458778					
	8	0.117910	-2.000165	2.290855					

Table S3 Theoretical Cartesian coordinates (in Å) of the $Fe_2(SF_2)_2(CO)_8$ derivatives using the B3LYP* method

Structures	Atom	X	Y	Z	Structures	Atom	X	Y	Z
8-1S(D_{2h})	6	-2.954973	0.000000	1.396285	8-3S(C_1)	6	1.833348	1.871135	-0.855994
	6	-1.803475	1.890301	0.000000		6	1.515860	-0.555214	-1.867831
	6	-1.803475	-1.890301	0.000000		6	3.421001	-0.180097	-0.122666
	8	-3.680920	0.000000	2.288318		8	2.002727	2.923329	-1.300696
	8	-2.061661	3.005319	0.000000		8	1.592549	-0.970879	-2.935910
	8	-2.061661	-3.005319	0.000000		8	4.546676	-0.417969	-0.087897
	9	0.000000	1.866992	-1.603611		9	-0.589162	-1.940822	-1.419711
	9	0.000000	-1.866992	-1.603611		9	2.371746	-2.036714	1.881289
	16	0.000000	0.000000	-1.584451		16	1.296083	-1.992404	0.588004
	26	-1.765426	0.000000	0.000000		26	1.652162	0.194224	-0.178362
	6	-2.954973	0.000000	-1.396285		6	1.626062	0.737176	1.571619
	8	-3.680920	0.000000	-2.288318		8	1.725780	1.069743	2.671068
	6	2.954973	0.000000	-1.396285		6	-0.821121	2.335674	0.421327
	6	1.803475	1.890301	0.000000		6	-3.060491	0.970933	0.135515
	6	1.803475	-1.890301	0.000000		6	-1.088745	0.758995	-1.690292
	8	3.680920	0.000000	-2.288318		8	-0.595005	3.449187	0.630190
	8	2.061661	3.005319	0.000000		8	-4.165542	1.286005	0.121786
	8	2.061661	-3.005319	0.000000		8	-1.075619	0.912670	-2.832735
	9	0.000000	1.866992	1.603611		9	-3.128847	-1.483240	1.041108
	9	0.000000	-1.866992	1.603611		9	-2.930166	-1.711922	-1.291507
	16	0.000000	0.000000	1.584451		16	-1.802548	-1.696025	-0.108406
	26	1.765426	0.000000	0.000000		26	-1.271080	0.603765	0.127786
	6	2.954973	0.000000	1.396285		6	-1.156684	0.205993	1.930796
	8	3.680920	0.000000	2.288318		8	-1.148096	-0.007852	3.059940
8-2S(C_1)	6	3.094843	-0.213335	1.482852					
	6	2.140300	1.675522	0.101538					
	6	1.751180	-1.980246	0.289089					
	8	3.782378	-0.241519	2.407560					
	8	2.345637	2.808637	0.146350					
	8	1.832546	-3.103894	0.521427					
	9	0.579205	1.500836	-2.226159					
	9	-0.447618	-2.180879	-0.716612					
	16	0.237147	-0.011523	-1.548832					
	26	1.982862	-0.152105	0.055058					
	6	-2.709113	0.824410	-1.134210					
	6	-0.890420	2.281392	0.115347					
	8	-3.525518	1.051199	-1.909626					
	8	-0.703947	3.419052	0.119483					
	9	-3.580109	-1.341527	0.792792					
	9	-2.722721	-2.011166	-1.267296					
	16	-2.010566	-1.730464	0.172019					
	26	-1.346127	0.521510	0.118920					
	6	3.256643	-0.368570	-1.293425					
	8	4.022134	-0.500566	-2.143238					
	6	-2.385498	0.823319	1.592306					
	8	-2.980226	1.079366	2.541744					
	6	0.228269	0.086149	1.313653					
	8	0.282440	-0.038523	2.498569					

Table S4 Theoretical Cartesian coordinates (in Å) of the $Fe_2(SF_2)_2(CO)_7$ derivatives using the B3LYP* method

Structures	Atom	X	Y	Z	Structures	Atom	X	Y	Z
7-1S (C_1)	6	-2.956938	-0.140238	1.646396	7-4S (C_1)	6	-0.016928	0.078017	-1.423284
	6	-3.186818	-1.162876	-0.687963		6	-0.909236	2.177619	0.110983
	6	-1.410398	1.689503	0.726491		6	-2.780810	0.904336	-1.082283
	8	-3.437849	-0.351334	2.669626		8	0.050965	-0.122050	-2.578132
	8	-3.814711	-2.009587	-1.132421		8	-0.715197	3.307324	0.207513
	8	-0.918490	2.634384	1.153256		8	-3.664186	1.233657	-1.736574
	9	-0.597374	-2.355027	-0.534209		9	-3.220053	-1.894819	-0.951537
	9	-0.243862	-0.703028	-2.163281		9	-2.248323	-2.315940	1.176421
	16	-0.344787	-0.701538	-0.497956		16	-1.751926	-1.690423	-0.251201
	26	-2.229619	0.222619	0.032122		26	-1.403080	0.436217	-0.033027
	6	2.432807	-0.778612	-1.357538		6	0.858311	-1.100250	1.154094
	6	2.466646	-1.841885	0.934536		6	1.847462	1.765432	-0.887567
	8	2.943470	-1.042031	-2.344833		6	1.743764	1.208114	1.605539
	8	3.003564	-2.759879	1.370625		8	0.704312	-1.960161	1.900735
	9	4.102129	1.423402	-0.330758		8	2.211196	2.683749	-1.470731
	9	2.104391	2.338187	-1.196123		8	2.054742	1.776299	2.554239
	16	2.540946	1.551961	0.199829		9	2.362934	-2.275559	-1.276533
	26	1.664827	-0.371928	0.257300		9	3.749729	-1.507726	0.489695
	6	-3.060831	1.323056	-1.141670		16	2.913126	-0.809749	-0.749118
	8	-3.606273	2.021893	-1.873522		26	1.330965	0.300380	0.077156
	6	1.071477	-0.002556	1.941853		6	-2.047235	0.490704	1.680993
	8	0.720643	0.184693	3.018741		8	-2.476179	0.537908	2.743512
7-2S (C_1)	6	-1.330598	1.437389	1.168890	7-5S (C_1)	6	-1.910420	2.110937	-0.043727
	6	-3.247967	-0.181545	1.430374		6	-0.652423	0.703116	1.789560
	6	-2.546580	1.590912	-1.070357		6	0.191750	1.896318	-1.597385
	8	-0.901099	2.215495	1.890412		8	-2.919468	2.644625	-0.110276
	8	-3.962196	-0.434147	2.293397		8	-0.861793	0.403137	2.869857
	8	-2.822519	2.456119	-1.773159		8	0.466693	2.273098	-2.639569
	9	-0.559015	-2.439780	0.365786		9	-3.388943	-1.058586	-1.354807
	9	-0.409164	-1.547074	-1.796893		9	-3.121740	-0.555911	0.871645
	16	-0.355634	-0.915517	-0.263360		16	-2.599425	-1.807685	-0.033741
	26	-2.137584	0.230542	0.056503		26	-0.276866	1.314173	0.084832
	6	1.501217	-0.661772	1.925890		6	2.753073	0.183168	-0.982793
	6	3.471681	0.058764	0.432479		6	2.294327	-2.335300	-0.452824
	6	2.329900	-1.924228	-0.666626		6	2.262871	-0.657947	1.708068
	8	1.378119	-0.806572	3.060753		8	3.502167	0.789509	-1.612486
	8	4.568114	0.337054	0.616506		8	2.716441	-3.357394	-0.762614
	8	2.732877	-2.866195	-1.184787		8	2.714298	-0.583413	2.761784
	9	1.999945	2.700855	0.190117		9	-0.739504	-0.913187	-2.283858
	9	2.611277	1.787896	-1.892271		9	-1.685688	-2.289631	1.367969
	16	1.426559	1.474972	-0.775308		16	-0.316614	-0.760548	-0.678355
	26	1.750400	-0.405100	0.152991		26	1.595853	-0.753709	0.007821
	6	-3.121796	-0.898438	-0.999041		6	0.882939	2.502314	0.813280
	8	-3.767116	-1.583797	-1.647927		8	1.613306	3.262920	1.264673
7-3S (C_1)	6	1.943709	1.769416	-0.218631					
	6	3.541954	0.132022	-1.245174					
	6	2.766225	0.439946	1.811056					
	8	1.740151	2.877015	-0.438761					
	8	4.323785	0.203539	-2.085474					
	8	3.063036	0.714527	2.888137					
	9	0.359279	-1.385421	-1.826108					
	9	0.160403	-2.161921	0.380809					
	16	0.323014	-0.656565	-0.319331					
	26	2.341208	0.024308	0.104858					

6	-2.359432	-0.887569	-1.320551
6	-1.846256	1.629730	-1.395354
8	-2.856565	-1.626438	-2.035625
8	-2.031203	2.468737	-2.159406
9	-4.589339	-0.061563	0.462108
9	-3.265832	-1.750242	1.441779
16	-3.129073	-0.116596	1.238874
26	-1.604091	0.328849	-0.172331
6	2.939270	-1.680753	0.399207
8	3.351403	-2.731724	0.585249
6	-0.985216	1.540196	1.041035
8	-0.621883	2.314707	1.806477

Table S5 Theoretical harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$ derivatives by the B3LYP* method

4-1S (C_s)	34.6 (a", 1.7) 59.0 (a', 0.3) 82.6 (a", 0.0) 82.7 (a', 0.3) 95.4 (a", 0.0) 98.3 (a', 3.0) 101.8 (a', 1.5) 129.4 (a", 1.9) 132.3 (a', 0.9) 145.2 (a", 3.8) 193.4 (a', 1.5) 336.3 (a', 0.2) 358.3 (a", 6.7) 377.5 (a', 2.4) 403.1 (a", 4.7) 429.0 (a", 1.6) 431.4 (a', 10.4) 435.4 (a', 7.2) 453.5 (a', 6.8) 514.9 (a', 24.0) 526.2 (a", 10.7) 542.9 (a', 46.0) 597.5 (a", 50.3) 599.0 (a', 91.4) 636.2 (a', 38.8) 724.5 (a', 111.4) 2107.6 (a', 658.7) 2131.4 (a', 421.2) 2132.2 (a", 968.0) 2177.2 (a', 134.6)
4-2S (C_1)	44.7 (a, 0.8) 66.5 (a, 0.1) 81.1 (a, 0.0) 90.7 (a, 0.3) 95.0 (a, 0.1) 103.1 (a, 0.3) 111.1 (a, 0.7) 116.9 (a, 0.7) 142.8 (a, 2.9) 157.0 (a, 2.8) 217.0 (a, 6.2) 306.1 (a, 0.2) 375.8 (a, 5.3) 377.8 (a, 4.4) 414.1 (a, 5.0) 420.8 (a, 1.9) 427.5 (a, 5.0) 429.8 (a, 14.4) 457.6 (a, 4.5) 513.8 (a, 8.2) 530.3 (a, 6.5) 550.6 (a, 50.8) 594.5 (a, 81.3) 609.8 (a, 62.0) 621.4 (a, 57.1) 752.0 (a, 90.0) 2098.9 (a, 665.3) 2132.2 (a, 508.3) 2140.4 (a, 879.9) 2184.3 (a, 116.3)
4-3S (C_s)	15.5 (a", 0.9) 62.6 (a", 0.8) 71.6 (a', 1.2) 89.9 (a", 0.0) 91.7 (a', 0.0) 96.3 (a', 0.2) 96.8 (a", 0.1) 100.3 (a', 1.7) 124.9 (a', 1.7) 146.3 (a", 1.7) 202.0 (a', 4.2) 320.7 (a', 2.1) 353.7 (a", 0.0) 379.3 (a', 5.5) 387.3 (a", 12.9) 399.1 (a", 20.7) 400.6 (a', 26.9) 454.7 (a", 0.5) 456.0 (a', 0.8) 499.4 (a", 0.0) 527.3 (a', 87.1) 548.6 (a', 0.7) 610.5 (a", 75.6) 611.7 (a', 67.3) 637.6 (a', 60.0) 712.5 (a', 80.7) 2130.6 (a", 969.2) 2132.3 (a', 1003.2) 2155.2 (a", 91.8) 2194.2 (a', 48.1)
4-4S (C_s)	36.4 (a", 0.0) 49.1 (a", 0.7) 57.2 (a', 0.2) 94.6 (a", 0.0) 95.7 (a', 0.1) 97.9 (a", 0.2) 99.8 (a', 0.1) 111.9 (a', 0.8) 215.4 (a", 0.4) 231.0 (a', 5.5) 358.0 (a', 22.5) 373.9 (a", 0.0) 388.0 (a', 41.4) 392.7 (a", 3.4) 427.9 (a', 5.8) 443.7 (a', 7.4) 446.5 (a', 2.1) 471.4 (a', 3.0) 472.8 (a", 7.5) 518.1 (a', 20.7) 562.9 (a", 0.0) 602.8 (a', 101.4) 633.3 (a", 18.0) 644.4 (a', 201.3) 674.8 (a", 184.0) 713.0 (a', 230.6) 2054.3 (a", 1174.8) 2068.4 (a', 681.9) 2080.5 (a', 950.7) 2136.8 (a', 206.7)
4-5S (C_1)	13.7 (a, 0.3) 51.1 (a, 0.5) 65.3 (a, 0.2) 96.6 (a, 0.1) 99.4 (a, 0.0) 106.3 (a, 0.1) 110.3 (a, 0.1) 112.3 (a, 0.6) 226.5 (a, 0.1) 237.7 (a, 2.3) 349.7 (a, 13.2) 365.5 (a, 0.5) 380.6 (a, 38.8) 392.1 (a, 2.1) 421.1 (a, 5.7) 424.1 (a, 1.5) 465.4 (a, 8.4) 466.0 (a, 1.4) 485.2 (a, 2.3) 504.9 (a, 10.5) 514.0 (a, 23.2) 599.8 (a, 131.8) 621.8 (a, 49.6) 624.3 (a, 89.3) 707.1 (a, 149.2) 725.1 (a, 267.6) 2043.3 (a, 1124.7) 2060.6 (a, 1041.8) 2071.4 (a, 497.8) 2126.2 (a, 346.3)

Table S6 Theoretical harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of $Fe(SF)(F)(CO)_3$/ $Fe(SF_2)(F)(CO)_3$ derivatives by the B3LYP* method

3-1S (C_1)	12.8 (a, 0.2) 80.6 (a, 0.0) 84.8 (a, 0.2) 98.4 (a, 0.1) 103.1 (a, 0.2) 122.7 (a, 1.8) 156.3 (a, 4.7) 189.9 (a, 4.1) 237.2 (a, 4.3) 362.4 (a, 6.4) 384.6 (a, 7.0) 429.2 (a, 5.9) 441.1 (a, 3.3) 447.5 (a, 7.0) 479.8 (a, 15.5) 491.0 (a, 34.8) 550.3 (a, 34.0) 584.5 (a, 22.2) 594.9 (a, 30.7) 648.4 (a, 19.5) 736.5 (a, 170.6) 2094.8 (a, 762.5) 2102.9 (a, 751.9) 2149.6 (a, 447.2)
3-2S (C_1)	38.2 (a, 0.7) 74.0 (a, 1.1) 81.4 (a, 0.4) 89.9 (a, 0.6) 100.5 (a, 0.5) 109.2 (a, 1.2) 155.0 (a, 1.7) 194.9 (a, 0.4) 264.1 (a, 8.9) 340.1 (a, 9.4) 380.8 (a, 2.1) 409.3 (a, 2.3) 427.9 (a, 7.4) 441.6 (a, 3.3) 487.6 (a, 10.1) 499.7 (a, 18.3) 551.0 (a, 47.6) 586.1 (a, 24.6) 600.6 (a, 35.3) 647.2 (a, 32.8) 778.8 (a, 143.9) 2083.7 (a, 773.7) 2107.7 (a, 705.9) 2151.3 (a, 491.3)
3-3T (C_1)	43.0 (a, 1.0) 55.6 (a, 1.4) 62.7 (a, 2.8) 73.4 (a, 0.1) 88.6 (a, 0.2) 99.3 (a, 0.4) 111.0 (a, 4.3) 139.1 (a, 1.4) 223.1 (a, 4.4) 258.5 (a, 9.0) 277.6 (a, 0.5) 306.2 (a, 1.4) 352.1 (a, 3.9) 358.8 (a, 10.1) 403.7 (a, 23.5) 419.3 (a, 22.1) 456.6 (a, 16.4) 511.6 (a, 15.5) 540.7 (a, 78.7) 591.6 (a, 27.3) 719.9 (a, 107.0) 2115.4 (a, 1107.4) 2135.1 (a, 526.5) 2168.2 (a, 94.6)
3-4S (C_1)	52.6 (a, 1.0) 81.0 (a, 0.3) 87.8 (a, 1.0) 92.1 (a, 0.0) 98.4 (a, 0.1) 110.7 (a, 1.4) 139.9 (a, 1.3) 147.8 (a, 1.6) 244.2 (a, 3.5) 351.4 (a, 12.6) 380.9 (a, 1.9) 391.0 (a, 3.3) 403.8 (a, 4.7) 417.4 (a, 18.6) 468.1 (a, 9.8) 479.8 (a, 12.7) 555.4 (a, 78.9) 573.9 (a, 10.7) 600.3 (a, 35.1) 609.4 (a, 60.8) 730.2 (a, 124.5) 2085.5 (a, 696.5) 2131.8 (a, 1005.2) 2177.0 (a, 111.7)
3-5T (C_1)	31.1 (a, 0.5) 52.8 (a, 0.4) 62.0 (a, 0.7) 78.6 (a, 0.3) 86.0 (a, 0.9) 107.0 (a, 2.9) 112.3 (a, 0.7) 168.9 (a, 2.6) 216.6 (a, 5.0) 280.9 (a, 17.4) 301.6 (a, 3.2) 325.1 (a, 8.1) 332.8 (a, 17.1) 360.2 (a, 1.2) 390.6 (a, 2.7) 418.2 (a, 7.5) 453.4 (a, 33.8) 498.6 (a, 17.6) 544.4 (a, 20.2) 608.2 (a, 12.3) 740.5 (a, 157.3) 2081.3 (a, 596.3) 2114.9 (a, 803.8) 2141.8 (a, 601.4)
3-6T (C_1)	48.6 (a, 0.0) 53.1 (a, 0.3) 74.2 (a, 0.1) 76.1 (a, 0.1) 82.7 (a, 0.4) 120.4 (a, 2.0) 129.0 (a, 3.1) 158.1 (a, 2.0) 223.4 (a, 6.2) 287.5 (a, 13.0) 315.7 (a, 8.6) 331.4 (a, 6.8) 350.2 (a, 1.4) 370.2 (a, 3.9) 385.8 (a, 1.0) 410.4 (a, 5.4) 448.2 (a, 27.1) 516.3 (a, 29.2) 539.4 (a, 13.8) 620.8 (a, 40.1) 759.9 (a, 142.4) 2075.9 (a, 625.1) 2113.3 (a, 760.5) 2145.1 (a, 569.6)
3-7T (C_1)	24.5 (a, 0.3) 51.4 (a, 0.3) 65.9 (a, 0.1) 75.1 (a, 0.1) 76.0 (a, 1.3) 89.7 (a, 1.1) 185.5 (a, 1.1) 203.7 (a, 7.1) 310.7 (a, 0.0) 317.8 (a, 0.4) 337.6 (a, 26.2) 345.0 (a, 4.8) 375.6 (a, 33.2) 407.8 (a, 9.6) 438.2 (a, 22.1) 454.7 (a, 1.5) 473.6 (a, 36.8) 495.8 (a, 27.7) 513.6 (a, 37.1) 683.6 (a, 82.6) 708.0 (a, 292.0) 2037.6 (a, 957.8) 2051.6 (a, 1620.7) 2102.9 (a, 278.5)
3-8S (C_s)	45.3 (a", 1.4) 48.6 (a', 1.5) 77.2 (a', 1.3) 78.4 (a", 0.1) 87.0 (a', 0.2) 91.3 (a", 0.0) 217.5 (a", 1.1) 218.0 (a', 5.1) 319.1 (a', 10.5) 369.1 (a", 0.0) 390.5 (a', 5.1) 402.0 (a", 0.1) 427.6 (a', 3.8) 450.7 (a', 1.5) 480.8 (a', 4.6) 516.7 (a", 6.6) 538.0 (a', 29.0) 603.2 (a', 16.9) 608.8 (a", 34.9) 664.3 (a", 110.6) 731.5 (a', 475.3) 2048.0 (a", 1136.4) 2051.7 (a', 873.1) 2107.1 (a', 477.2)
3-9T (C_1)	29.6 (a, 0.6) 50.4 (a, 0.1) 67.8 (a, 0.2) 74.7 (a, 0.2) 77.4 (a, 1.6) 83.2 (a, 1.5) 187.6 (a, 1.0) 206.6 (a, 5.0) 304.4 (a, 28.9) 312.6 (a, 1.6) 328.7 (a, 27.0) 382.4 (a, 27.7) 384.4 (a, 0.7) 398.1 (a, 0.9) 441.7 (a, 26.7) 455.0 (a, 13.9) 497.2 (a, 29.0) 510.6 (a, 45.5) 519.2 (a, 19.0) 694.2 (a, 112.7) 713.9 (a, 322.6) 2038.8 (a, 967.8) 2045.0 (a, 1107.8) 2096.2 (a, 527.9)

Table S7 Theoretical harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of $Fe_2(SF_2)_2(CO)_8$ derivatives by the B3LYP* method

8-1S(D_{2h})	24.4 ($b3_g$, 0.0) 41.8 ($b2_u$, 0.0) 54.3 (a_u, 0.0) 57.9 ($b1_u$, 0.2) 69.2 ($b2_g$, 0.0) 79.4 (a_g, 0.0) 81.7 ($b3_u$, 0.5) 90.0 ($b2_u$, 8.1) 92.6 ($b1_g$, 0.0) 96.6 ($b3_g$, 0.0) 97.9 (a_u, 0.0) 108.7 (a_g, 0.0) 137.2 ($b2_u$, 8.0) 138.1 ($b1_u$, 0.0) 146.9 ($b2_g$, 0.0) 148.1 ($b3_u$, 0.4) 153.3 (a_u, 0.0) 154.5 ($b1_g$, 0.0) 166.2 ($b1_g$, 0.0) 170.1 ($b3_g$, 0.0) 176.6 (a_g, 0.0) 181.3 ($b2_g$, 0.0)189.5 ($b1_u$, 25.6) 211.7 ($b3_u$, 48.8) 212.0 ($b2_u$, 1.9) 213.1 (a_g, 0.0) 320.5 ($b3_g$, 0.0) 328.3 ($b2_u$, 104.0) 330.0 ($b1_u$, 10.6) 348.1 ($b2_g$, 0.0) 356.4 (a_g, 0.0) 357.6 ($b3_u$, 3.1) 358.9 ($b1_g$, 0.0) 369.1 (a_g, 0.0) 373.2 (a_u, 0.0) 381.3 ($b3_u$, 10.1) 405.3 ($b1_u$, 4.8) 410.0 ($b2_u$, 17.7) 411.7 (a_g, 0.0) 426.7 ($b2_g$, 0.0) 426.7 ($b1_u$, 3.5) 428.9 ($b3_u$, 1.8) 437.7 ($b1_g$, 0.0) 442.1 (a_g, 0.0) 447.9 ($b2_g$, 0.0) 466.2 ($b1_u$, 0.6) 474.1 ($b3_g$, 0.0) 494.6 ($b3_u$, 10.0) 512.9 (a_g, 0.0) 532.0 (a_u, 0.0) 555.9 ($b2_u$, 300.3) 557.1 ($b3_g$, 0.0) 572.0 ($b2_g$, 0.0) 590.8 ($b1_u$, 165.1)596.1 ($b3_u$, 262.0) 597.3 ($b1_g$, 0.0) 600.3 ($b2_u$, 120.8) 611.7 (a_g, 0.0) 2106.5 ($b2_g$, 0.0) 2106.7 ($b1_u$, 1143.4) 2127.1 ($b3_u$, 1018.2) 2132.5 (a_g, 0.0) 2151.0 ($b1_g$, 0.0) 2157.2 ($b2_u$, 1222.3) 2177.5 ($b3_u$, 696.8) 2193.5 (a_g, 0.0)
8-2S(C_1)	28.5 (a, 0.2) 32.3 (a, 0.3) 49.7 (a, 0.2) 57.6 (a, 0.1) 69.1 (a, 0.0) 71.2 (a, 0.3) 76.6 (a, 0.1) 78.2 (a, 0.2) 88.1 (a, 0.2) 93.0 (a, 0.1) 97.5 (a, 0.5) 101.0 (a, 0.4) 110.5 (a, 1.6) 116.1 (a, 2.0) 121.1 (a, 0.7) 125.9 (a, 0.9) 139.1 (a, 0.3) 149.3 (a, 0.7) 155.7 (a, 3.7) 169.4 (a, 1.7) 183.4 (a, 2.9) 198.0 (a, 5.7) 207.3 (a, 8.2) 213.2 (a, 2.2) 238.5 (a, 12.1) 288.1 (a, 4.6) 313.4 (a, 3.8) 322.1 (a, 11.4) 324.3 (a, 2.9) 355.3 (a, 14.0) 373.4 (a, 7.7) 378.4 (a, 8.7) 382.1 (a, 26.6) 390.0 (a, 5.3) 398.3 (a, 16.0) 411.7 (a, 0.7) 420.9 (a, 21.8) 424.3 (a, 0.1) 427.3 (a, 2.3) 435.3 (a, 6.1) 445.0 (a, 11.3) 458.0 (a, 24.0) 460.9 (a, 12.1) 480.8 (a, 33.3) 488.5 (a, 15.9) 501.9 (a, 14.7) 514.4 (a, 4.0) 528.0 (a, 0.2) 531.4 (a, 163.7) 564.8 (a, 17.2) 593.2 (a, 53.0) 598.6 (a, 340.5) 605.2 (a, 103.0) 620.4 (a, 126.8) 626.5 (a, 95.8) 647.9 (a, 140.4) 678.9 (a, 102.6) 764.3 (a, 105.9) 1812.9 (a, 336.0) 2076.9 (a, 37.7) 2090.9 (a, 579.5) 2100.3 (a, 1091.5) 2104.3 (a, 395.4) 2113.6 (a, 596.4) 2133.5 (a, 1655.9) 2159.2 (a, 154.5)
8-3S(C_1)	29.6 (a, 0.3) 37.8 (a, 0.1) 45.4 (a, 0.6) 59.5 (a, 0.3) 63.0 (a, 0.1) 70.9 (a, 0.8) 78.8 (a, 0.1) 82.1 (a, 0.1) 86.8 (a, 0.3) 94.6 (a, 0.2) 97.5 (a, 0.2) 100.3 (a, 1.1) 106.3 (a, 0.4) 107.5 (a, 0.4) 110.4 (a, 0.6) 112.9 (a, 0.3) 116.2 (a, 0.8) 124.9 (a, 0.5) 128.3 (a, 0.5) 136.6 (a, 0.0) 148.6 (a, 0.1) 155.3 (a, 1.7) 167.5 (a, 1.2) 189.6 (a, 0.7) 193.5 (a, 1.0) 203.5 (a, 5.0) 307.6 (a, 7.9) 321.2 (a, 2.1) 374.5 (a, 11.4) 378.5 (a, 4.2) 392.0 (a, 4.3) 392.2 (a, 6.6) 397.4 (a, 15.1) 403.8 (a, 5.1) 406.5 (a, 4.2) 412.5 (a, 1.6) 417.7 (a, 3.8) 425.1 (a, 0.7) 442.9 (a, 2.9) 454.7 (a, 1.2) 460.7 (a, 0.6) 463.0 (a, 7.5) 464.0 (a, 4.9) 484.7 (a, 4.6) 487.4 (a, 9.8) 494.2 (a, 12.6) 508.1 (a, 6.3) 527.4 (a, 11.4) 544.1 (a, 1.8) 572.9 (a, 75.0) 595.2 (a, 76.4) 600.8 (a, 117.2) 605.7 (a, 50.5) 610.4 (a, 91.5) 615.4 (a, 355.4) 627.8 (a, 92.7) 704.3 (a, 134.5) 748.4 (a, 163.2) 2063.2 (a, 52.4) 2078.0 (a, 63.8) 2090.6 (a, 554.3) 2095.5 (a, 812.3) 2114.9 (a, 716.0) 2118.7 (a, 648.3) 2130.4 (a, 1661.0) 2168.4 (a, 181.8)

Table S8 Theoretical harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of $Fe_2(SF_2)_2(CO)_7$ derivatives by the B3LYP* method

7-1S (C_1)	9.1 (a, 0.1) 18.6 (a, 0.0) 32.6 (a, 0.1) 39.5 (a, 0.6) 44.8 (a, 0.2) 51.8 (a, 0.1) 56.3 (a, 0.4) 71.1 (a, 0.1) 82.0 (a, 0.2) 85.7 (a, 0.1) 96.5 (a, 0.6) 99.5 (a, 0.4) 100.8 (a, 0.2) 103.2 (a, 0.3) 107.3 (a, 0.4) 109.3 (a, 0.0) 116.9 (a, 1.2) 150.5 (a, 0.6) 187.8 (a, 0.7) 210.0 (a, 0.9) 213.5 (a, 2.0) 230.5 (a, 1.0) 246.6 (a, 3.8) 260.1 (a, 8.4) 357.0 (a, 37.4) 367.6 (a, 20.9) 376.5 (a, 3.9) 388.7 (a, 154.7) 394.6 (a, 23.3) 401.3 (a, 28.2) 420.4 (a, 14.1) 421.3 (a, 2.2) 423.4 (a, 3.6) 428.3 (a, 9.3) 431.3 (a, 2.1) 450.9 (a, 47.7) 462.1 (a, 17.4) 464.2 (a, 8.5) 471.4 (a, 7.0) 481.3 (a, 28.5) 501.8 (a, 57.3) 525.7 (a, 35.1) 564.5 (a, 0.4) 587.5 (a, 40.8) 599.6 (a, 29.6) 604.6 (a, 197.0) 611.3 (a, 14.5) 626.8 (a, 43.9) 640.2 (a, 194.1) 646.5 (a, 179.6) 661.8 (a, 155.5) 663.9 (a, 229.5) 705.9 (a, 273.6) 2056.6 (a, 655.4) 2063.7 (a, 712.1) 2073.2 (a, 424.4) 2079.9 (a, 1264.9) 2089.8 (a, 1259.8) 2128.6 (a, 856.3) 2147.8 (a, 138.0)
7-2S (C_1)	10.6 (a, 0.3) 21.3 (a, 0.1) 27.4 (a, 0.1) 40.8 (a, 0.0) 47.6 (a, 0.5) 54.2 (a, 0.1) 59.8 (a, 0.5) 67.9 (a, 0.1) 81.5 (a, 0.3) 86.1 (a, 0.1) 94.1 (a, 0.1) 98.7 (a, 0.1) 101.1 (a, 0.1) 102.0 (a, 0.1) 104.1 (a, 0.5) 109.4 (a, 0.9) 112.6 (a, 0.2) 154.9 (a, 1.8) 191.1 (a, 0.3) 200.5 (a, 1.0) 215.2 (a, 2.4) 236.2 (a, 3.0) 245.1 (a, 0.8) 246.3 (a, 3.5) 364.7 (a, 70.1) 365.8 (a, 32.3) 369.1 (a, 3.8) 376.4 (a, 8.2) 384.8 (a, 4.6) 398.9 (a, 7.8) 405.3 (a, 39.3) 421.0 (a, 7.1) 425.5 (a, 4.8) 435.0 (a, 2.2) 445.5 (a, 20.3) 450.5 (a, 8.6) 460.3 (a, 12.7) 466.1 (a, 6.9) 473.4 (a, 7.2) 481.8 (a, 56.2) 500.6 (a, 9.2) 504.9 (a, 129.8) 562.7 (a, 0.6) 567.2 (a, 40.5) 598.9 (a, 66.2) 600.7 (a, 47.2) 602.5 (a, 91.5) 620.6 (a, 71.9) 634.3 (a, 130.6) 646.1 (a, 55.5) 655.6 (a, 254.4) 674.0 (a, 358.7) 699.2 (a, 188.7) 2055.5 (a, 536.4) 2068.8 (a, 1193.7) 2079.6 (a, 547.5) 2086.6 (a, 586.0) 2095.7 (a, 1076.0) 2116.2 (a, 1241.1) 2150.5 (a, 221.5)
7-3S (C_1)	12.0 (a, 0.2) 19.2 (a, 0.1) 22.1 (a, 0.0) 35.7 (a, 0.2) 46.7 (a, 0.0) 52.3 (a, 0.1) 59.4 (a, 0.4) 74.8 (a, 0.1) 82.2 (a, 0.4) 85.5 (a, 0.1) 95.7 (a, 0.9) 98.6 (a, 0.3) 100.1 (a, 0.3) 104.9 (a, 0.2) 109.9 (a, 0.3) 113.1 (a, 0.6) 116.7 (a, 0.5) 147.5 (a, 0.9) 184.4 (a, 3.2) 203.0 (a, 2.6) 220.2 (a, 5.0) 231.3 (a, 2.5) 247.3 (a, 0.1) 258.7 (a, 15.3) 359.7 (a, 54.9) 363.8 (a, 26.9) 373.2 (a, 10.8) 389.5 (a, 177.5) 391.8 (a, 38.2) 400.7 (a, 29.7) 416.6 (a, 3.5) 420.4 (a, 4.3) 425.4 (a, 1.0) 427.6 (a, 3.3) 431.3 (a, 4.7) 450.1 (a, 48.3) 462.5 (a, 13.5) 468.1 (a, 5.7) 472.6 (a, 8.3) 487.2 (a, 33.0) 501.4 (a, 47.8) 520.9 (a, 33.8) 564.6 (a, 0.5) 586.8 (a, 27.6) 600.5 (a, 108.8) 604.5 (a, 111.6) 611.9 (a, 49.9) 625.8 (a, 52.4) 641.8 (a, 149.9) 648.8 (a, 201.7) 659.7 (a, 126.0) 669.9 (a, 195.8) 712.1 (a, 350.0) 2053.6 (a, 517.8) 2066.7 (a, 1209.1) 2068.6 (a, 367.7) 2076.4 (a, 306.9) 2092.0 (a, 1823.3) 2128.1 (a, 791.8) 2148.4 (a, 154.8)
7-4S (C_1)	13.9 (a, 0.1) 27.9 (a, 0.2) 36.8 (a, 0.0) 43.7 (a, 0.7) 50.2 (a, 0.2) 55.7 (a, 0.3) 66.4 (a, 0.2) 79.2 (a, 0.1) 86.1 (a, 0.1) 92.2 (a, 0.4) 98.0 (a, 0.3) 102.3 (a, 0.1) 103.9 (a, 0.8) 106.6 (a, 0.3) 109.9 (a, 0.2) 115.6 (a, 1.6) 121.4 (a, 0.6) 129.3 (a, 0.5) 167.1 (a, 0.9) 217.2 (a, 1.1) 227.1 (a, 15.8) 232.5 (a, 17.4) 241.8 (a, 1.2) 257.4 (a, 4.3) 341.4 (a, 76.8) 351.4 (a, 37.5) 356.6 (a, 11.0) 367.9 (a, 26.6) 378.1 (a, 4.0) 394.7 (a, 25.5) 403.2 (a, 0.6) 416.1 (a, 50.1) 417.1 (a, 22.6) 424.5 (a, 2.2) 433.0 (a, 9.8) 446.2 (a, 14.8) 463.7 (a, 47.9) 467.6 (a, 12.6) 478.7 (a, 27.0) 484.5 (a, 3.4) 513.6 (a, 2.3) 520.0 (a, 23.3) 545.0 (a, 0.5) 569.5 (a, 11.2) 593.9 (a, 261.8) 595.9 (a, 347.9) 611.5 (a, 57.8) 614.1 (a, 43.9) 623.1 (a, 130.8) 680.1 (a, 120.0) 706.7 (a, 208.6) 716.9 (a, 149.9) 731.2 (a, 222.0) 1882.0 (a, 527.3) 2048.4 (a, 34.8) 2059.1 (a, 540.4) 2067.2 (a, 394.4) 2078.0 (a, 1496.1) 2092.9 (a, 1074.7) 2132.6 (a, 611.9)
7-5S (C_1)	19.3 (a, 0.0) 21.4 (a, 0.3) 33.4 (a, 0.3) 42.0 (a, 0.1) 50.6 (a, 0.2) 58.6 (a, 0.3) 68.2 (a, 0.7) 74.2 (a, 0.3) 80.1 (a, 0.6) 82.4 (a, 0.3) 88.7 (a, 0.1) 96.2 (a, 1.3) 99.9 (a, 0.3) 102.6 (a, 0.0) 109.8 (a, 1.0) 111.8 (a, 2.4) 115.0 (a, 2.6) 129.6 (a, 4.2) 138.6 (a, 2.1)155.9 (a, 0.9) 172.3 (a, 5.2) 200.6 (a, 2.4) 252.2 (a, 24.3) 309.5 (a, 7.8) 340.3 (a, 20.0) 371.0 (a, 0.5) 381.2 (a, 0.4) 385.0 (a, 0.4) 388.5 (a, 0.8) 402.5 (a, 7.6) 411.1 (a, 5.8) 417.3 (a, 3.3) 433.4 (a, 27.9) 435.4 (a, 6.7) 447.4 (a, 21.2) 449.9 (a, 14.5) 460.3 (a, 6.0) 472.7 (a, 2.8) 474.0 (a, 13.5) 479.2 (a, 6.5) 485.5 (a, 15.0) 498.8 (a, 23.1) 509.3 (a, 32.0) 548.9 (a, 57.1) 556.3 (a, 8.4) 580.5 (a, 44.4) 591.1 (a, 72.0) 611.4 (a, 178.1) 617.1 (a, 54.4) 627.9 (a, 118.8) 649.8 (a, 56.6) 684.7 (a, 391.0) 749.2 (a, 137.1) 2049.1 (a, 408.1) 2060.2 (a, 279.5) 2083.2 (a, 861.6) 2101.4 (a, 1742.4) 2111.8 (a, 701.0) 2118.2 (a, 842.2) 2162.6 (a, 344.5)

Table **S9** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$ derivatives

Structures		E	ΔE	Nimag	‹S^2›
$Fe(SF)(F)(CO)_4$	4-1S (C_s)	-2314.508961	0.0	0	0.00
$Fe(SF)(F)(CO)_4$	4-2S (C_1)	-2314.502285	4.2	0	0.00
$Fe(SF)(F)(CO)_4$	4-3S (C_s)	-2314.499223	6.1	0	0.00
$Fe(SF_2)(CO)_4$	4-4S (C_s)	-2314.493363	9.8	0	0.00
$Fe(SF_2)(CO)_4$	4-5S (C_1)	-2314.490738	11.4	0	0.00

Table **S10** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$ derivatives

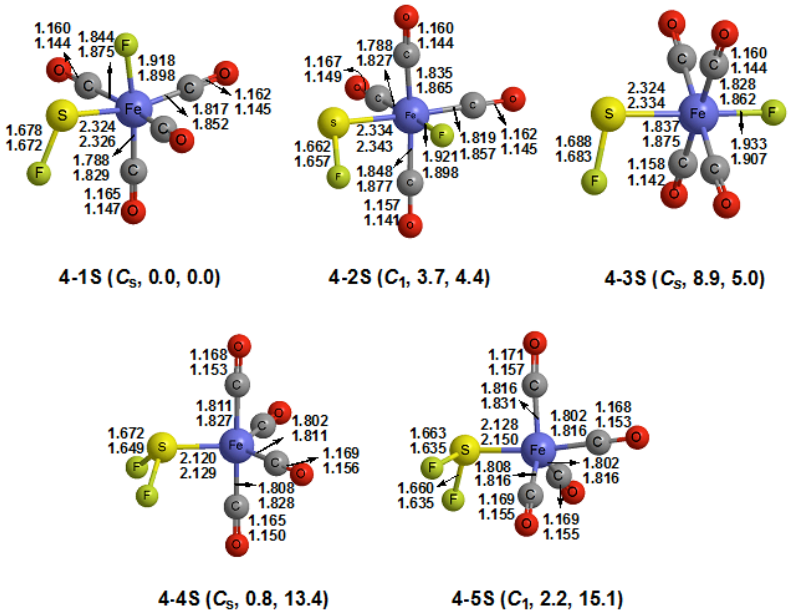
Structures		E	ΔE	Nimag	‹S^2›
$Fe(SF)(F)(CO)_3$	3-1S (C_1)	-2201.225127	0.0	0	0.00
$Fe(SF)(F)(CO)_3$	3-2S (C_1)	-2201.214985	6.4	0	0.00
$Fe(SF)(F)(CO)_3$	3-3T (C_1)	-2201.213957	7.0	0	2.05
$Fe(SF)(F)(CO)_3$	3-4S (C_1)	-2201.212318	8.0	0	0.00
$Fe(SF)(F)(CO)_3$	3-5T (C_1)	-2201.208765	10.3	0	2.05
$Fe(SF)(F)(CO)_3$	3-6T (C_1)	-2201.203555	13.5	0	2.05
$Fe(SF_2)(CO)_3$	3-7T (C_1)	-2201.176788	30.3	0	2.05
$Fe(SF_2)(CO)_3$	3-8S (C_s)	-2201.175860	30.9	0	0.00
$Fe(SF_2)(CO)_3$	3-9T (C_1)	-2201.174472	31.8	0	2.04

Table **S11** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe_2(SF_2)_2(CO)_8$ derivatives

Structures	E	ΔE	Nimag	Fe-Fe
8-1S(D_{2h})	-4629.022550	0.0	0	3.531
8-2S(C_1)	-4628.996242	16.5	0	3.397
8-3S(C_1)	-4628.989864	20.5	0	2.968

Table **S12** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe_2(SF_2)_2(CO)_7$ derivatives

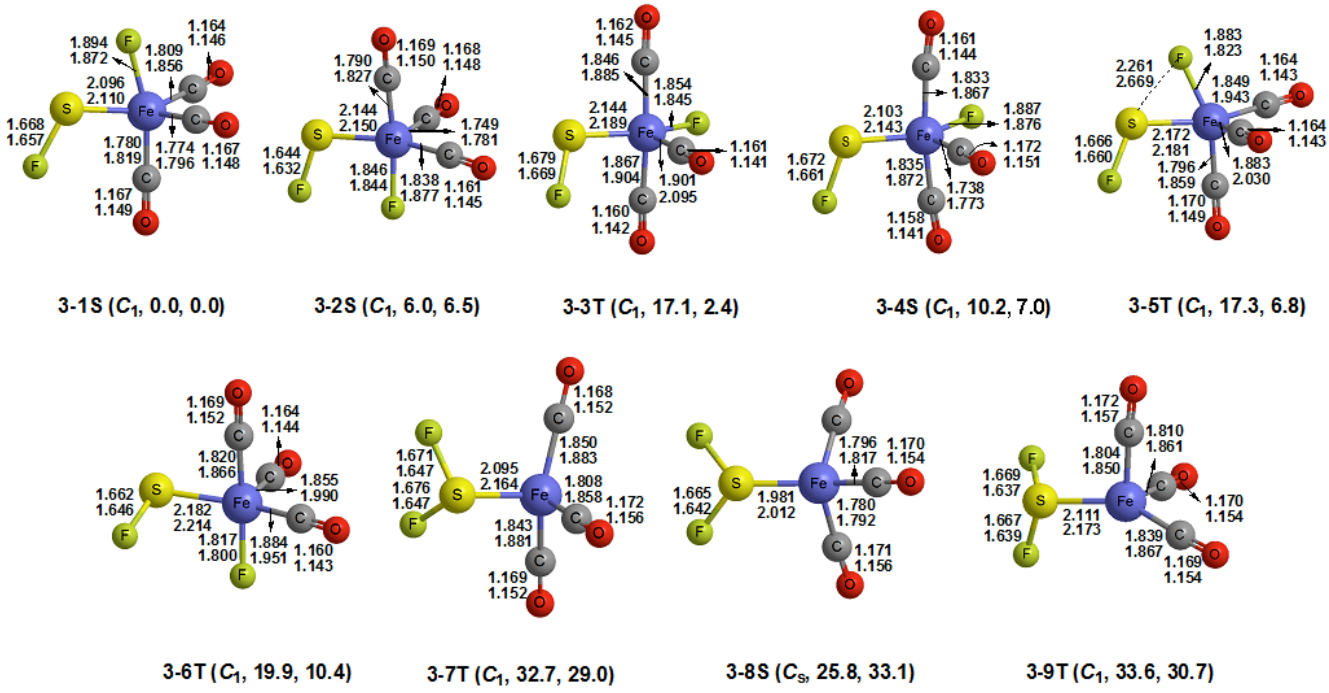
Structures	E	ΔE	Nimag	Fe-Fe
7-1S (C_1)	-4515.765651	0.0	0	3.946
7-2S (C_1)	-4515.764897	0.5	0	3.941
7-3S (C_1)	-4515.764587	0.7	0	3.967
7-4S (C_1)	-4515.750809	9.3	0	2.740
7-5S (C_1)	-4515.749553	10.1	0	2.791



Figures **S1** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$ derivatives

Table **S13** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) level of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$ derivatives

structures		BP86				B3LYP			
		E	ΔE	Nimag	Fe-S	E	ΔE	Nimag	Fe-S
$Fe(SF)(F)(CO)_4$	4-1S (C_s)	-2315.355811	0.0	0	2.324	-2315.087450	0.0	0	2.326
$Fe(SF)(F)(CO)_4$	4-2S (C_1)	-2315.349835	3.7	0	2.334	-2315.080469	4.4	0	2.343
$Fe(SF)(F)(CO)_4$	4-3S (C_s)	-2315.341615	8.9	1(16i)	2.324	-2315.079444	5.0	0	2.334
$Fe(SF_2)(CO)_4$	4-4S (C_s)	-2315.354480	0.8	0	2.120	-2315.066114	13.4	0	2.129
$Fe(SF_2)(CO)_4$	4-5S (C_1)	-2315.352332	2.2	0	2.128	-2315.063311	15.1	0	2.150

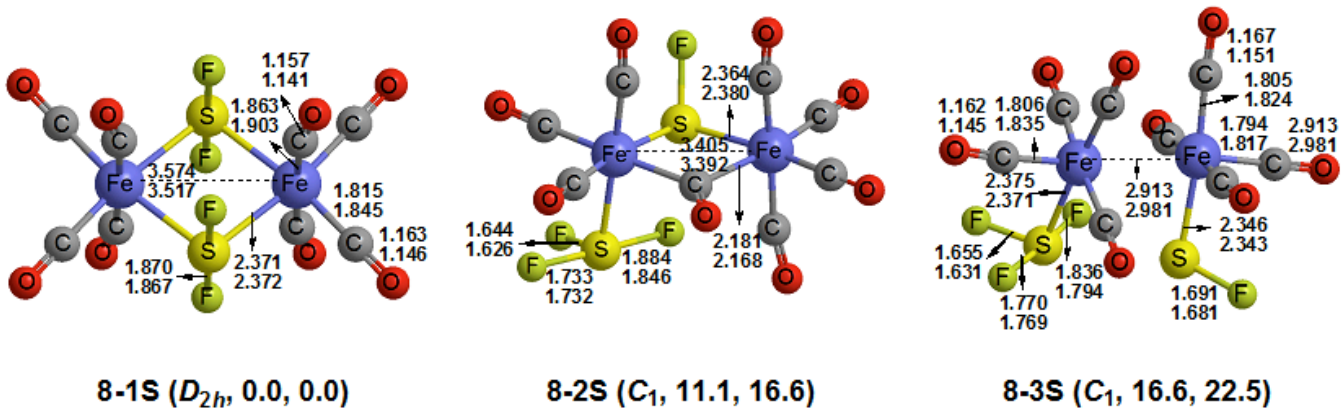


Figures **S2** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$ derivatives

Table **S14** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) level of theory for the $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$ derivatives

Structures		BP86					B3LYP				
		E	ΔE	Fe-S	Nimag	‹S^2›	E	ΔE	Fe-S	Nimag	‹S^2›
$Fe(SF)(F)(CO)_3$	3-1S (C_1)	-2202.010457	0.0	2.096	0	0.00	-2201.740901	0.0	2.110	0	0.00
$Fe(SF)(F)(CO)_3$	3-2S (C_1)	-2202.000885	6.0	2.144	0	0.00	-2201.730615	6.5	2.150	0	0.00
$Fe(SF)(F)(CO)_3$	3-3T (C_1)	-2201.983163	17.1	2.144	0	2.02	-2201.737038	2.4	2.189	0	2.05
$Fe(SF)(F)(CO)_3$	3-4S (C_1)	-2201.994189	10.2	2.103	0	0.00	-2201.729751	7.0	2.143	0	0.00
$Fe(SF)(F)(CO)_3$	3-5T (C_1)	-2201.982939	17.3	2.172	0	2.02	-2201.730044	6.8	2.181	0	2.06
$Fe(SF)(F)(CO)_3$	3-6T (C_1)	-2201.978773	19.9	2.182	0	2.02	-2201.724352	10.4	2.214	0	2.06
$Fe(SF_2)(CO)_3$	3-7T (C_1)	-2201.958401	32.7	2.095	1(10i)*	2.02	-2201.694720	29.0	2.164	0	2.07
$Fe(SF_2)(CO)_3$	3-8S (C_s)	-2201.969284	25.8	1.981	0	0.00	-2201.688120	33.1	2.012	0	0.00
$Fe(SF_2)(CO)_3$	3-9T (C_1)	-2201.956969	33.6	2.111	0	2.02	-2201.691954	30.7	2.173	0	2.05

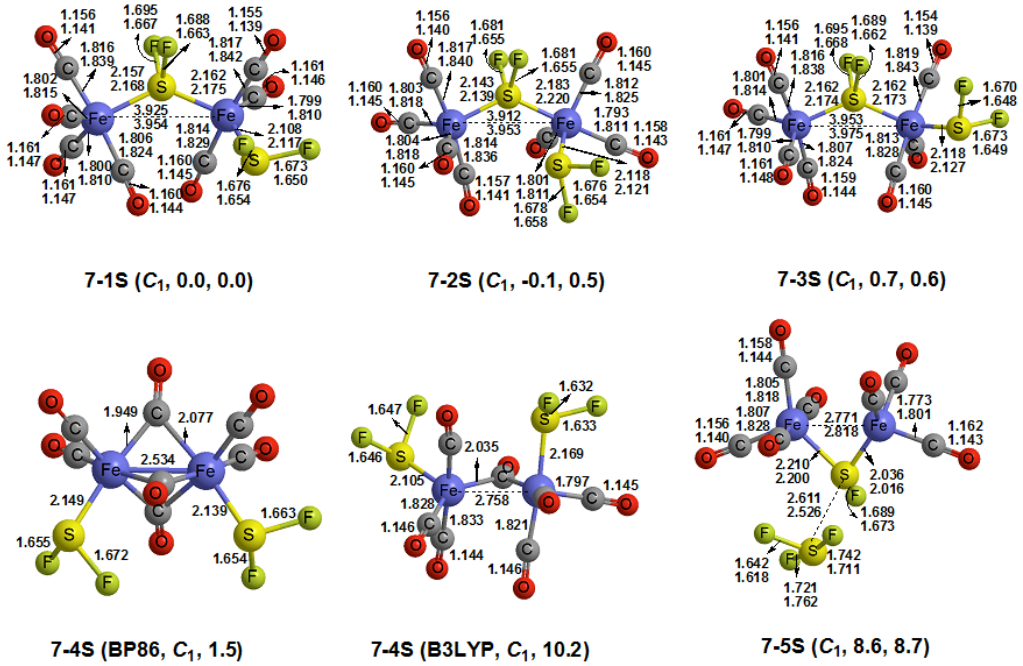
* denotes an imaginary vibrational frequency eliminated after using the finer (120, 974) grid.



Figures **S3** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe_2(SF_2)_2(CO)_8$ derivatives

Table **S15** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) level of theory for the $Fe_2(SF_2)_2(CO)_8$ derivatives

structures		BP86				B3LYP			
		E	ΔE	Nimag	Fe-S	E	ΔE	Nimag	Fe-S
$Fe_2(CO)_8(SF_2)_2$	8-1S (D_{2h})	-4630.731156	0.0	1(25i)	3.574	-4630.173133	0.0	0	3.517
$Fe_2(CO)_8(SF)(SF_3)$	8-2S (C_1)	-4630.713392	11.1	0	3.405	-4630.143130	18.8	0	3.392
$Fe_2(CO)_8(SF)(SF_3)$	8-3S (C_1)	-4630.704762	16.6	0	2.913	-4630.137285	22.5	0	2.981



Figures **S4** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe_2(SF_2)_2(CO)_7$ derivatives

Table **S16** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) level of theory for the $Fe_2(SF_2)_2(CO)_7$ derivatives

structures		BP86			B3LYP		
		E	ΔE	Fe-S	E	ΔE	Fe-S
$Fe_2(CO)_7(SF_2)_2$	7-1S (C_1)	-4517.418252	0.0	3.925	-4516.845280	0.0	3.954
$Fe_2(CO)_7(SF_2)_2$	7-2S (C_1)	-4517.418347	-0.1	3.912	-4516.844545	0.5	3.953
$Fe_2(CO)_7(SF_2)_2$	7-3S (C_1)	-4517.417151	0.7	3.953	-4516.844247	0.6	3.975
$Fe_2(CO)_7(SF_2)_2$	7-4S (C_1)	-4517.415862	1.5	2.534	-4516.828947	10.2	2.758
$Fe_2(CO)_7(SF)(SF_3)$	7-5S (C_1)	-4517.404516	8.6	2.771	-4516.831416	8.7	2.818