Supporting Materials

Cationic dinitrosyl iron complexes with thiourea exhibit selective toxicity to brain tumor cells
in vitro

N.A. Sanina[a,b,c*], I.V. Sulimenkov[d], N.S. Emel'yanova[a], A.S. Konyukhova[c], T.S. Stupina[a], A.A. Balakina[a], A.A. Terent'ev[a,b,c] and S.M. Aldoshin[a]

[a]Institute of Problems of Chemical Physics, The Russian Academy of Sciences, 142432, Chernogolovka, Russia

[b]Scientific and Educational Center "Medical Chemistry" of Moscow State Regional University, 141014, Mytishchi, Russia

[c]Faculty of Fundamental Physicochemical Engineering, Moscow State University, 119991, Moscow, Russia

[d]Chernogolovka Branch of N.N. Semenov Federal Research Center of Chemical Physics, The Russian Academy of Sciences, 142432, Chernogolovka, Russia

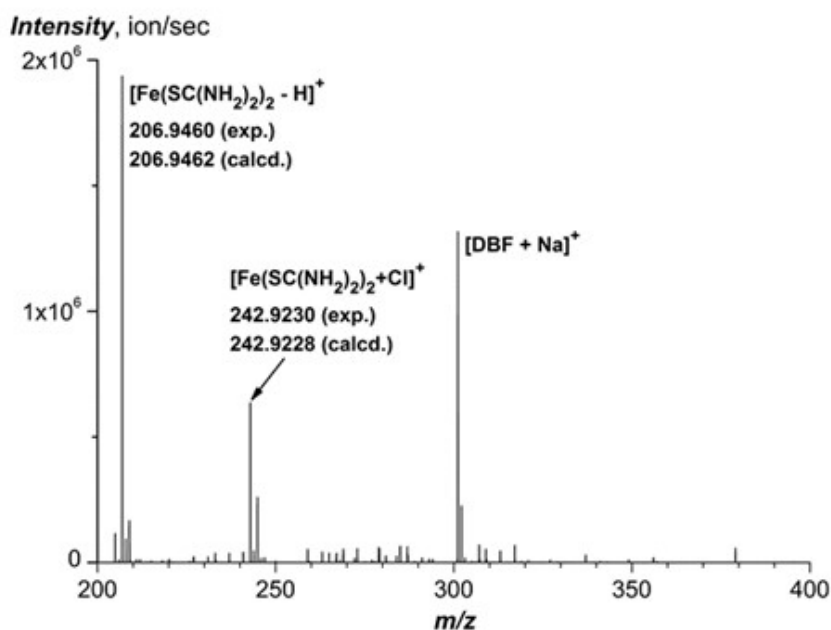**Corresponding author:** sanina@icp.ac.ru (Nataliya A. Sanina)

Figure S1. The ESI mass spectrum of MeOH solution of DNIC **I** (100μM). The $[DBF + Na]^+$ ion appearance in the mass spectrum is related to a design feature of our home-build electrospray ion source.
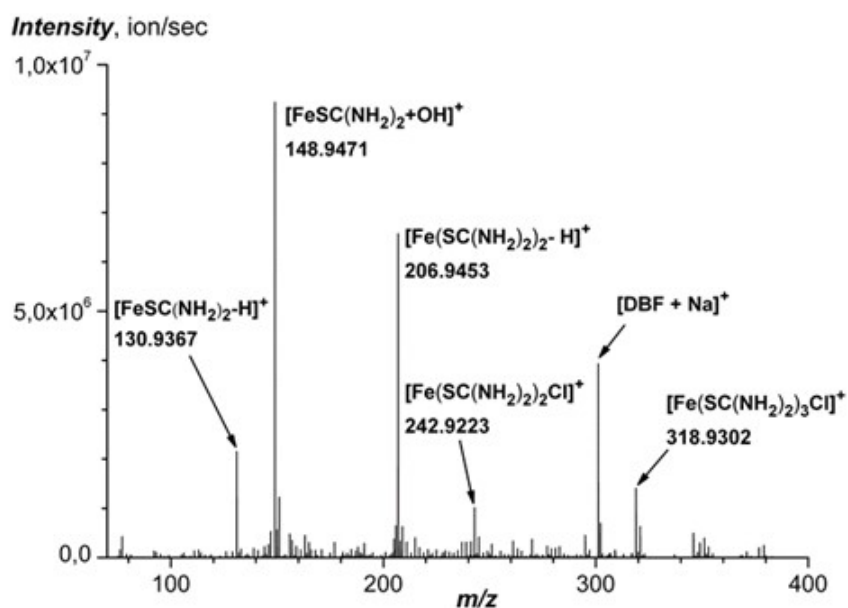
Figure S2 The ESI mass spectrum for MeOH solution (ca. 100 µM) of DNIC **II**. The [DBF + Na]+ ion appearance is a result of a design feature of our home-made electrospray ion source.

Figure S3. The ESI mass spectrum of a DNIC **III** solution in MeOH in the positive-ion mode (the concentration of complex **III** was 100 µM). The spectrum is averaged over the first minute of acquisition, i.e. at the third minute after preparation of the solution. The accuracy of determination of m/z values < 5 ppm. The inset shows the detailed experimental isotopic distribution of one of the ions and the calculated isotopic distribution for this ion (the numerical values).
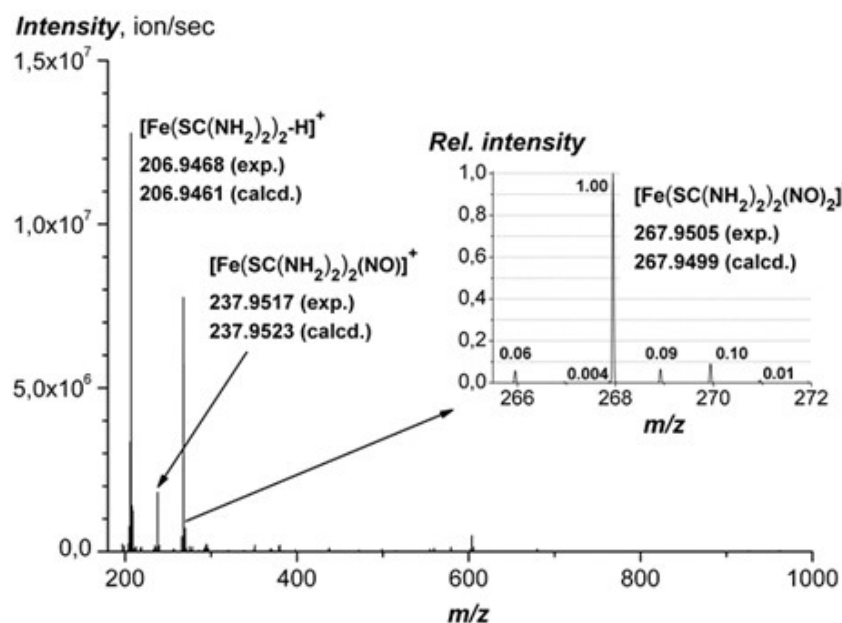
Figure S4. The ESI mass spectrum of a DNIC **III** in MeOH in the negative-ion mode (the concentration of complex **III** was 100 μM). The spectrum is averaged over the first minute of acquisition, i.e. at the third minute after preparation of the solution. The accuracy of determination of m/z values < 5 ppm. The inset shows the detailed experimental isotopic distribution of one of the ions and the calculated isotopic distribution for that ion (the numerical values).
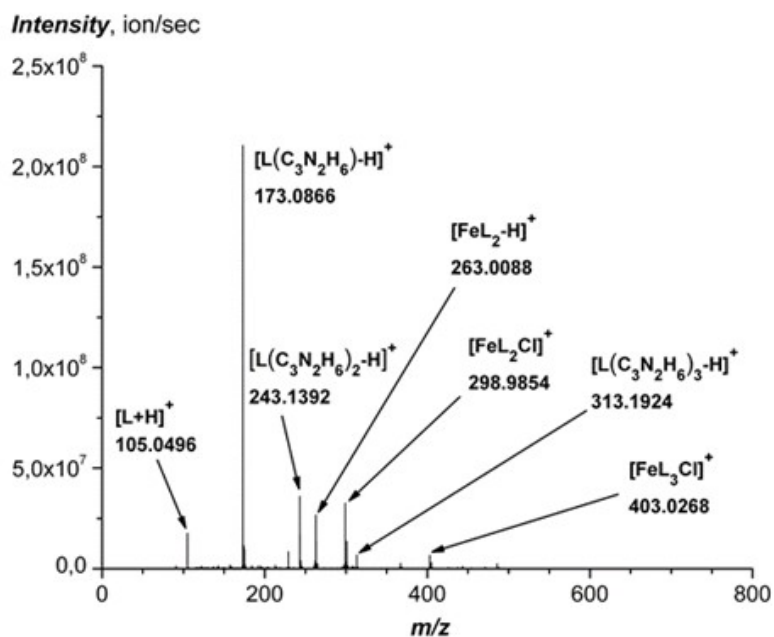
Figure S5. The ESI mass spectrum of MeOH of DNIC **IV** (L = SC3N2H8, N'-ethylthiourea) in the positive-ion mode (the concentration of complex **IV** was 100 μM). The spectrum is averaged over the first minute of registration, i.e. at the third minute after preparation of the solution (the determination accuracy of m/z values < 5 ppm).
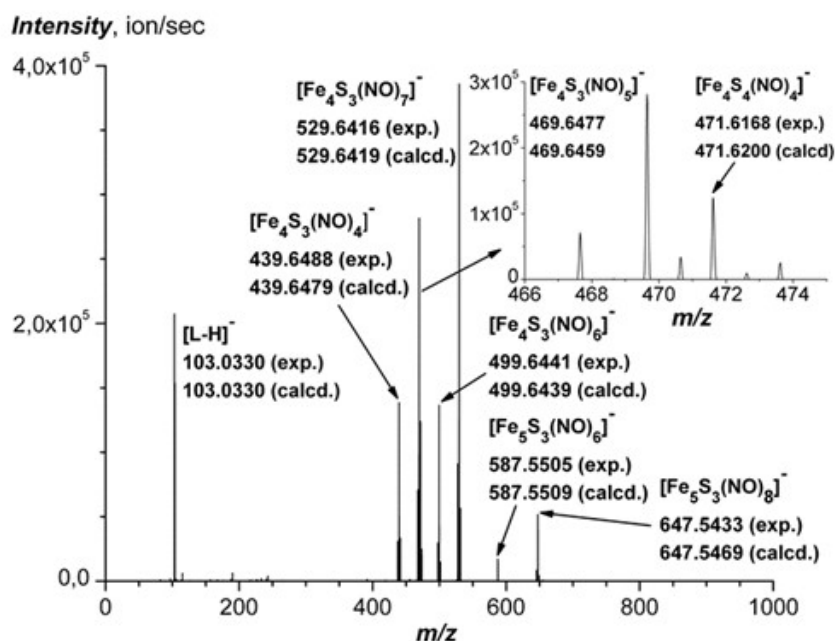
Figure S6. The ESI mass spectrum of MeOH of DNIC **IV** (L = SC3N2H8 is N'-ethylthiourea) in the negative-ion mode (the concentration of complex **IV** was 100 μM). The spectrum is averaged over the first minute of registration, i.e. at the third minute after preparation of the solution (the determination accuracy of m/z values < 5 ppm). The inset shows the detailed experimental isotopic distribution of one of the ions and the calculated isotopic distribution for that ion (the numerical values).
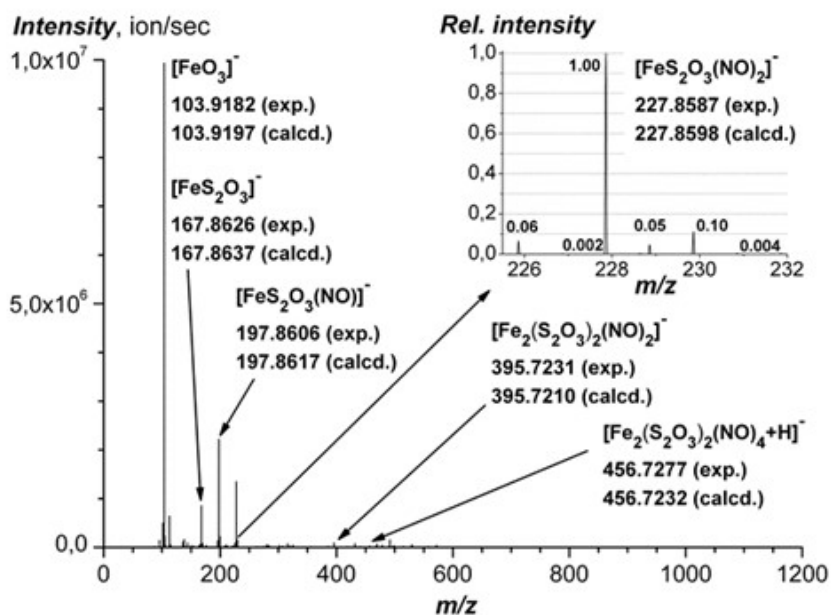

Figure S7. The ESI mass spectrum of MeOH of DNIC **V** (L = C3H8N2S is dimethylthiourea) in the positive-ion mode (the concentration of complex **V** was 100 μM). The spectrum is averaged over the first minute of registration, i.e. at the third minute after preparation of the solution (the determination accuracy of m/z values < 5 ppm). The inset shows the detailed experimental isotopic

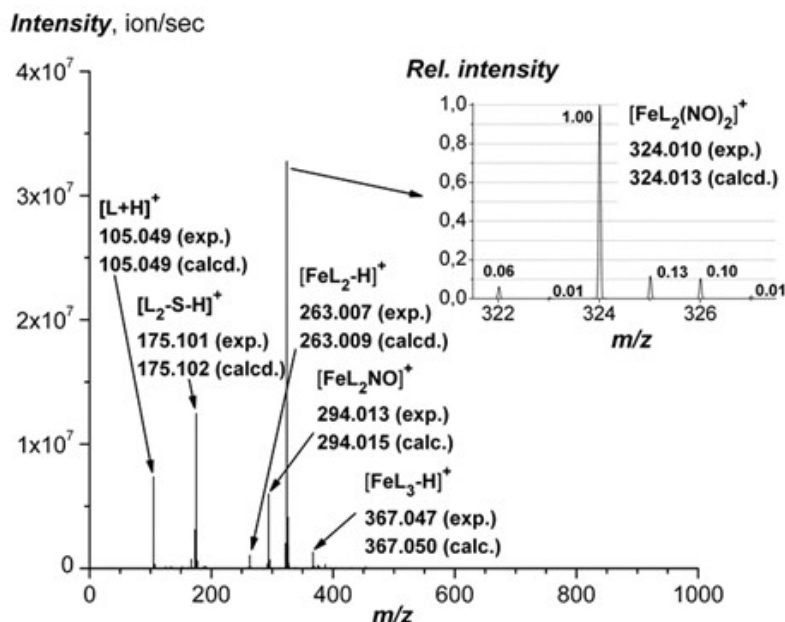distribution of one of the ions and the calculated isotopic distribution for this ion (the numerical values).

Qantum chemical calculations

1.Coordinates of optimized geometries of complexes
 Complex IV

Figure 3

Complex 2

26	0.104400000	1.450834000	-0.002559000
16	1.347315000	0.036729000	-1.421919000
16	-1.339775000	0.019744000	1.218316000
6	-2.388338000	-0.802932000	0.079301000
7	-3.649274000	-1.019430000	0.441948000
1	-3.936077000	-0.620090000	1.329028000
6	-4.647697000	-1.765955000	-0.341491000
1	-4.238510000	-2.756715000	-0.569502000
1	-4.824571000	-1.237756000	-1.285905000
7	-1.938777000	-1.251406000	-1.091667000
1	-2.547236000	-1.695914000	-1.769676000
1	-0.968607000	-1.101637000	-1.358153000
6	2.272487000	-1.039005000	-0.393169000
7	-0.614928000	2.607382000	-1.004680000
8	-0.931664000	3.625738000	-1.507127000
7	3.435269000	-1.483991000	-0.863592000
1	3.744839000	-1.066346000	-1.734108000
7	1.812759000	-1.432697000	0.793945000
1	2.337237000	-2.049123000	1.403658000
1	0.869419000	-1.180722000	1.083764000
8	1.658367000	2.826310000	1.940633000
7	1.064607000	2.103122000	1.225716000
6	4.337959000	-2.447237000	-0.212203000
1	4.876550000	-2.948663000	-1.018718000
1	3.727662000	-3.208237000	0.283953000
6	-5.945363000	-1.893150000	0.449527000
1	-6.673974000	-2.451466000	-0.143843000
1	-6.368094000	-0.908194000	0.671866000
1	-5.780694000	-2.430872000	1.388415000
6	5.315649000	-1.781656000	0.760476000
1	5.965800000	-2.545622000	1.198052000
1	4.791047000	-1.269583000	1.573317000
1	5.940757000	-1.051957000	0.237636000

Complex 3

26	1.283862000	-0.187943000	-0.021338000
16	0.027270000	1.717881000	-0.630940000
17	0.440884000	-1.883362000	-1.351922000
6	-1.622889000	1.322654000	-0.227221000
7	-2.058283000	0.066091000	-0.178212000
1	-1.411701000	-0.656589000	-0.501038000

5

7	2.897335000	0.282534000	-0.287194000
7	-2.466322000	2.329849000	0.022260000
1	-3.466856000	2.193509000	0.101189000
1	-2.123379000	3.281027000	0.016124000
6	-3.424812000	-0.342448000	0.183224000
1	-4.116523000	-0.043715000	-0.614362000
1	-3.707966000	0.185458000	1.100684000
8	4.003761000	0.635229000	-0.066187000
7	0.945048000	-0.489797000	1.613330000
6	-3.478879000	-1.851477000	0.401080000
1	-4.498953000	-2.141498000	0.666819000
1	-2.809592000	-2.152619000	1.212792000
1	-3.196153000	-2.390091000	-0.509055000
8	0.990541000	-0.504107000	2.794380000

Complex 4

26	-1.419561000	-0.102660000	-0.138273000
16	0.584697000	-1.213911000	-0.597333000
8	-2.039986000	0.227914000	2.604370000
8	-3.352630000	-2.146821000	-0.526278000
7	-1.624116000	0.323031000	1.503722000
7	-2.561122000	-1.279046000	-0.589988000
7	1.780970000	0.547051000	1.082413000
1	0.856341000	0.790026000	1.411582000
7	3.155517000	-0.818726000	-0.184532000
6	1.936451000	-0.414469000	0.171172000
1	3.190538000	-1.511830000	-0.923676000
1	2.564212000	1.003804000	1.533827000
6	4.437953000	-0.281777000	0.298986000
1	4.347165000	-0.074377000	1.369827000
1	5.161849000	-1.092576000	0.196994000
6	4.892816000	0.954166000	-0.482227000
1	4.169393000	1.771201000	-0.398399000
1	5.021882000	0.712498000	-1.541348000
1	5.852035000	1.301673000	-0.085927000
6	-2.193367000	2.857124000	-0.732300000
1	-3.264272000	2.690798000	-0.864102000
1	-1.953821000	3.000978000	0.319388000
1	-1.857314000	3.713494000	-1.318090000
8	-1.446584000	1.681052000	-1.157772000
1	-1.522830000	1.592467000	-2.125293000

Complex 5

26	-0.140306000	0.042855000	-0.024025000
17	0.146592000	2.215613000	0.616409000
7	-1.428230000	-0.125259000	-1.138008000
8	-2.469833000	-0.445863000	-1.594560000
7	-0.323385000	-1.030122000	1.299347000
8	-0.841412000	-1.808683000	2.023221000
8	1.511409000	-0.574149000	-1.075854000
6	2.808621000	-0.853111000	-0.479187000
1	3.311087000	0.078342000	-0.210270000

1	2.606035000	-1.447027000	0.410337000
1	3.405969000	-1.427120000	-1.189024000
1	1.641082000	-0.147944000	-1.942048000

Complex 6

26	-0.015635000	0.121330000	-0.185395000
7	0.103793000	0.070988000	1.529080000
8	0.284795000	0.490752000	2.615188000
7	0.285321000	1.722967000	-0.719807000
8	0.544948000	2.869458000	-0.650198000
8	1.505819000	-1.020640000	-0.917439000
1	2.092763000	-0.611836000	-1.577976000
6	2.237446000	-2.035768000	-0.172915000
1	3.002462000	-1.563174000	0.445966000
1	1.502378000	-2.545139000	0.446331000
1	2.684145000	-2.735366000	-0.880333000
8	-1.990225000	-0.232427000	-0.599993000
1	-2.276713000	-0.032483000	-1.509389000
6	-2.773803000	-1.344629000	-0.080460000
1	-2.527111000	-2.262839000	-0.616857000
1	-2.507295000	-1.432361000	0.971180000
1	-3.832464000	-1.103828000	-0.183768000

Figure 4

TS1

26	-2.514881000	-0.006321000	0.251508000
16	-0.854452000	1.350677000	-0.480017000
7	-3.898955000	0.939423000	0.509131000
8	-4.748026000	1.556510000	1.035847000
7	-2.072902000	-0.994560000	1.548362000
8	-1.903304000	-1.403555000	2.642995000
6	2.371536000	-1.728376000	-0.428205000
16	0.833748000	-1.049813000	-0.938894000
6	0.795947000	0.695110000	0.028939000
7	2.473122000	-3.063592000	-0.364658000
1	3.361447000	-3.531826000	-0.233073000
1	1.657570000	-3.640077000	-0.524483000
7	3.387174000	-0.941560000	-0.122153000
6	4.672011000	-1.397348000	0.432623000
1	5.222627000	-1.944009000	-0.344065000
1	4.466714000	-2.087207000	1.260797000
6	5.491969000	-0.206554000	0.920790000
1	6.444549000	-0.560918000	1.322906000
1	4.966864000	0.332415000	1.715490000
1	5.708160000	0.486393000	0.101330000
7	1.010500000	0.480329000	1.399335000
1	1.686285000	1.106603000	1.822803000
7	1.908020000	1.438682000	-0.541385000
6	2.057930000	2.845690000	-0.062252000
1	1.083594000	3.348956000	-0.044156000
1	2.448584000	2.824222000	0.960798000

7

1	4.010468000	3.087323000	-0.996088000
6	3.036181000	3.586702000	-0.968821000
1	2.651115000	3.655314000	-1.992647000
1	3.183068000	4.605912000	-0.600474000
1	0.164508000	0.408009000	1.952096000
1	3.194033000	0.072697000	-0.245698000
1	1.764737000	1.463720000	-1.553458000
8	-2.835672000	-1.080863000	-1.513220000
6	-4.144886000	-1.515484000	-1.974446000
1	-4.579456000	-2.082564000	-1.152684000
1	-4.773664000	-0.653949000	-2.214329000
1	-4.020986000	-2.161845000	-2.845699000
1	-2.358868000	-0.644877000	-2.243169000

Complex 7

26	-2.608474000	0.102901000	0.031349000
16	-0.847529000	1.249611000	-0.838689000
7	-3.941068000	1.132379000	-0.165574000
8	-4.765898000	1.951844000	0.041525000
7	-2.387054000	-0.366841000	1.651801000
8	-2.479619000	-0.317616000	2.832039000
6	2.455666000	-1.710440000	-0.343526000
16	0.886687000	-1.099224000	-0.922335000
6	0.778682000	0.596796000	-0.128640000
7	2.574469000	-3.034467000	-0.243248000
1	3.471928000	-3.483352000	-0.100448000
1	1.774462000	-3.637509000	-0.387099000
7	3.439137000	-0.881789000	-0.068905000
6	4.735038000	-1.276654000	0.507630000
1	5.327393000	-1.784068000	-0.262909000
1	4.547496000	-1.986862000	1.321059000
6	5.472097000	-0.048109000	1.031178000
1	6.426925000	-0.359090000	1.463432000
1	4.887817000	0.455664000	1.807159000
1	5.677651000	0.661370000	0.223376000
7	0.871504000	0.440540000	1.294316000
1	0.684907000	1.335514000	1.751091000
7	1.898310000	1.395285000	-0.602993000
6	2.063328000	2.721309000	0.042990000
1	1.110190000	3.268502000	0.059739000
1	2.382922000	2.550781000	1.075122000
1	4.081796000	2.991685000	-0.716606000
6	3.125489000	3.524659000	-0.702358000
1	2.819924000	3.718699000	-1.736861000
1	3.273856000	4.489373000	-0.207816000
1	0.152496000	-0.205373000	1.617271000
1	3.207326000	0.120894000	-0.229719000
1	1.786176000	1.526886000	-1.610500000
8	-2.800036000	-1.628237000	-1.082415000
6	-3.283906000	-2.892562000	-0.551590000
1	-2.742429000	-3.053791000	0.378763000

```
1      -4.358631000     -2.839774000     -0.364059000
1      -3.053715000     -3.685532000     -1.264817000
1      -3.165731000     -1.499306000     -1.975933000


TS2
26     -2.886555000      0.090374000      0.012221000
16     -1.206296000      1.306256000     -0.921161000
7      -4.267189000      1.062333000     -0.141258000
8      -5.118087000      1.847378000      0.092054000
7      -2.589977000     -0.363061000      1.625288000
8      -2.643862000     -0.312935000      2.807886000
6       2.773316000     -1.698122000     -0.321501000
16      1.161068000     -1.155514000     -0.847365000
6       1.009314000      0.537724000     -0.054889000
7       2.950992000     -3.015592000     -0.221896000
1       3.870891000     -3.425915000     -0.109005000
1       2.172538000     -3.652189000     -0.336429000
7       3.729989000     -0.827900000     -0.083210000
6       5.060399000     -1.165794000      0.449247000
1       5.646673000     -1.651100000     -0.339957000
1       4.930945000     -1.879904000      1.270540000
6       5.762797000      0.094667000      0.943774000
1       6.744149000     -0.174290000      1.343599000
1       5.184925000      0.576696000      1.738148000
1       5.910460000      0.808826000      0.127484000
7       1.157524000      0.391305000      1.364418000
1       0.949338000      1.279538000      1.825005000
7       2.077439000      1.380453000     -0.569747000
6       2.208760000      2.714852000      0.066650000
1       1.234626000      3.221715000      0.114877000
1       2.570558000      2.562074000      1.087570000
1       4.186760000      3.066410000     -0.762942000
6       3.209974000      3.558925000     -0.717068000
1       2.861115000      3.735772000     -1.740904000
1       3.334629000      4.531017000     -0.230493000
1       0.477812000     -0.282826000      1.713724000
1       3.450883000      0.163531000     -0.238562000
1       1.925277000      1.503127000     -1.573121000
8      -3.043465000     -1.651801000     -1.089690000
6      -3.455265000     -2.933101000     -0.539131000
1      -2.875803000     -3.067713000      0.372380000
1      -4.524169000     -2.924599000     -0.314720000
1      -3.216657000     -3.718643000     -1.257792000
1      -3.444780000     -1.541948000     -1.970377000


Complex 8
26      0.158268000     -0.014907000     -0.036461000
16      0.320062000     -1.835401000     -1.200469000
7       1.469981000      0.175265000      1.036651000
8       2.565075000      0.010386000      1.495214000
7      -0.186388000      1.463280000     -0.934862000
```

8	0.243417000	2.569681000	-1.168579000
8	-1.550626000	-0.125347000	1.225900000
6	-2.870198000	-0.059413000	0.630851000
1	-2.886216000	0.858809000	0.045303000
1	-3.043403000	-0.921318000	-0.019165000
1	-3.623171000	-0.016249000	1.421108000
1	-1.510062000	-0.918357000	1.790335000

Complex 9

16	-0.024367000	-1.624626000	-0.449329000
6	1.586793000	-0.884988000	-0.199897000
7	1.794452000	0.387748000	-0.467148000
1	1.070042000	0.892530000	-0.970559000
7	2.532015000	-1.712886000	0.211441000
1	3.517197000	-1.468173000	0.173059000
1	2.301238000	-2.639172000	0.553433000
6	3.050347000	1.122465000	-0.183492000
1	3.757219000	0.922569000	-0.995069000
1	3.457901000	0.721209000	0.748555000
6	2.762695000	2.613816000	-0.050710000
1	3.701602000	3.131728000	0.161240000
1	2.064993000	2.807510000	0.768649000
1	2.352031000	3.022714000	-0.979102000
6	-1.056933000	-0.426997000	0.387608000
7	-0.796033000	-0.079010000	1.636534000
1	-1.318742000	0.656325000	2.103626000
1	-0.110254000	-0.574723000	2.193988000
7	-2.107129000	0.002857000	-0.280448000
1	-2.146455000	-0.202903000	-1.275646000
6	-3.210074000	0.802066000	0.302282000
1	-2.848552000	1.824619000	0.450576000
1	-3.450174000	0.365339000	1.276815000
6	-4.421498000	0.775073000	-0.621841000
1	-5.218462000	1.369511000	-0.168267000
1	-4.184421000	1.211532000	-1.596878000
1	-4.786415000	-0.246175000	-0.761511000

Figure 5

TS3

26	-2.131595000	-0.103457000	-0.377912000
16	-0.351065000	0.591094000	-1.327005000
7	-3.605050000	-0.032926000	-1.166557000
8	-4.555680000	-0.037575000	-1.914767000
7	-1.979706000	-1.458835000	0.663934000
8	-2.461079000	-2.511154000	1.003543000
8	-1.978580000	1.221925000	1.438247000
6	-3.020807000	1.008844000	2.390866000
1	-3.955130000	1.232265000	1.872490000
1	-3.041791000	-0.031783000	2.733618000
1	-2.910220000	1.683623000	3.252269000
1	-1.153625000	0.813166000	1.767383000

6	0.784639000	3.173749000	0.327712000
1	0.207303000	2.934192000	1.232317000
1	1.063705000	4.243112000	0.350664000
1	0.156249000	2.955268000	-0.536818000
8	1.931206000	2.339860000	0.190193000
1	2.474976000	2.356029000	0.998680000
26	1.955423000	-0.168143000	-0.142297000
7	2.662674000	-0.504031000	-1.644945000
8	3.795670000	-0.633806000	-2.080761000
7	3.270736000	0.083961000	0.821311000
8	4.162001000	-0.402673000	1.485757000
16	1.324010000	-1.881696000	0.942596000

Complex 10

26	-1.763071000	-0.116742000	-0.248223000
16	0.007606000	-0.705685000	-1.463682000
7	-3.232818000	-0.205412000	-1.153141000
8	-4.299659000	-0.716067000	-1.358692000
7	-1.854161000	-1.049109000	1.169186000
8	-1.883914000	-1.986907000	1.906291000
8	-1.381907000	1.831236000	0.205692000
6	-2.024269000	2.465639000	1.325630000
1	-3.101487000	2.414401000	1.159188000
1	-1.771704000	1.959191000	2.263933000
1	-1.711908000	3.512905000	1.376626000
1	-0.346754000	1.954139000	0.309978000
26	1.787863000	-0.096494000	-0.063250000
7	1.825749000	-1.163049000	1.342769000
8	2.546416000	-1.979009000	1.881072000
7	3.205162000	-0.239276000	-0.983261000
8	4.160318000	0.051560000	-1.647628000
16	1.598352000	2.074503000	0.495685000

TS4

26	-1.151653000	0.164490000	0.376550000
16	0.475032000	0.514431000	1.797963000
7	-2.709620000	0.296106000	1.217826000
8	-3.705526000	0.995394000	1.288721000
7	-1.172712000	1.350850000	-0.846430000
8	-1.150532000	2.440690000	-1.341777000
8	-2.581919000	-1.783278000	-0.475728000
6	-3.713722000	-1.339409000	-1.200165000
1	-4.370158000	-0.857156000	-0.470950000
1	-3.448981000	-0.607528000	-1.977129000
1	-4.247096000	-2.183256000	-1.671432000
1	-1.913964000	-2.197666000	-1.081819000
26	1.726877000	-0.184703000	-0.033701000
7	1.865070000	1.177514000	-1.166554000
8	2.724197000	1.910097000	-1.622625000
7	3.283600000	-0.550246000	0.548058000
8	4.300245000	-1.084341000	0.914540000
16	0.509383000	-1.848211000	-0.853408000

Complex11

26	-1.397108000	0.044483000	-0.000028000
16	-0.000092000	-0.161164000	1.795555000
8	-3.302721000	2.114859000	-0.000636000
7	-2.219709000	1.577066000	-0.000579000
26	1.397087000	0.044491000	0.000076000
16	0.000065000	-0.162744000	-1.795331000
7	2.219701000	1.576957000	-0.000359000
8	3.302606000	2.114945000	-0.000372000
7	2.477981000	-1.236763000	0.000301000
8	3.137507000	-2.233176000	0.000153000
7	-2.478050000	-1.236759000	0.000335000
8	-3.137204000	-2.233416000	0.000516000

Figure 6

TS5

26	-1.866698000	-1.292148000	-0.302531000
8	-1.800947000	-3.513610000	1.308099000
7	-1.771793000	-2.358910000	0.943978000
26	-1.952750000	1.199951000	0.357846000
16	-3.714736000	-0.070995000	-0.107816000
7	-1.924482000	1.511411000	1.974086000
8	-2.057916000	2.340031000	2.848460000
7	-2.156414000	2.548152000	-0.486350000
8	-2.388292000	3.542451000	-1.126813000
7	-1.990965000	-2.070193000	-1.699607000
8	-2.130078000	-2.692618000	-2.721576000
26	2.827287000	-0.139602000	0.348291000
16	4.161230000	1.577430000	0.520940000
7	2.433011000	-0.943286000	1.860289000
8	2.728201000	-1.869741000	2.582513000
7	3.593832000	-1.299837000	-0.649286000
8	4.558626000	-1.898480000	-1.059332000
8	2.732382000	1.054797000	-2.204977000
1	3.462907000	1.214967000	-1.540734000
6	1.985211000	2.264021000	-2.234324000
1	0.916886000	2.018042000	-2.251530000
1	2.179390000	2.862197000	-1.334025000
1	2.239475000	2.874604000	-3.125885000
16	-0.154738000	0.122241000	-0.378647000

Complex 12

26	-1.376664000	-1.389804000	0.103439000
16	0.081308000	-0.057404000	-1.105562000
8	0.109075000	-3.398650000	1.496152000
7	-0.509515000	-2.562834000	0.916186000
26	-1.322166000	1.404629000	0.012662000

16	-2.283035000	0.078200000	1.598762000
7	-0.434956000	2.669378000	0.748422000
8	-0.172049000	3.821840000	0.953741000
7	-2.513722000	1.970414000	-1.029762000
8	-3.436238000	2.434724000	-1.628059000
7	-2.546200000	-2.055139000	-0.964188000
8	-3.078063000	-3.012005000	-1.461869000
8	2.333815000	0.615720000	2.556888000
7	2.116533000	-0.100188000	1.598766000
26	2.299731000	-0.084650000	-0.159765000
7	3.005689000	1.374071000	-0.690063000
8	3.765480000	2.079261000	-1.299569000
16	3.475202000	-1.744645000	-0.984359000

TS6
26	-2.459472000	-0.947496000	0.217074000
16	-0.592076000	-0.670546000	-1.126811000
8	-2.918511000	-3.115391000	1.957205000
7	-2.341256000	-2.135446000	1.514562000
26	-0.418169000	1.669316000	-0.044283000
16	-2.581033000	1.166391000	0.938259000
7	0.059090000	2.692285000	1.316490000
8	0.096753000	3.862526000	1.630348000
7	-0.799712000	2.760785000	-1.317445000
8	-1.322174000	3.663616000	-1.916751000
7	-3.832984000	-1.293785000	-0.729497000
8	-4.864110000	-1.171232000	-1.350236000
8	3.256588000	-2.877298000	-1.932742000
7	2.526506000	-1.904883000	-1.802656000
26	1.646961000	-1.015776000	-0.543838000
7	1.910580000	-1.784006000	0.946956000
8	2.194662000	-1.957613000	2.104587000
16	2.229314000	1.119669000	-0.394839000

Complex 13
26	2.014893000	-0.552168000	0.005937000
26	-0.296341000	1.738823000	-0.110329000
16	0.121110000	-0.354367000	1.322556000
16	1.805314000	1.327436000	-1.212309000
8	1.827347000	-2.610936000	-1.962869000
8	4.455832000	-1.164485000	1.252174000
8	1.058889000	2.634836000	2.232597000
7	3.439803000	-0.544622000	1.021339000
7	1.986164000	-1.891622000	-1.017289000
7	0.403734000	2.571095000	1.222213000
16	-1.544536000	0.289085000	-1.509680000
26	-1.766833000	-1.078078000	0.264919000
7	-1.716382000	-2.678291000	-0.243953000
8	-1.537271000	-3.734331000	-0.778880000
7	-3.141640000	-0.727033000	1.276683000
8	-4.127757000	-1.205372000	1.793475000
7	-1.321786000	3.015817000	-0.693794000

| 8 | -1.977561000 | 3.425928000 | -1.628891000 |

TS7

26	1.890984000	-1.207458000	0.055321000
16	-0.099946000	-0.755430000	1.208513000
8	2.295236000	-3.371561000	-1.695535000
7	1.791736000	-2.361919000	-1.233716000
26	0.183217000	1.394592000	0.020771000
16	2.302036000	0.873014000	-0.636475000
7	0.391726000	3.832801000	-1.568840000
8	0.459561000	4.962428000	-1.128427000
7	0.287798000	2.733324000	0.924223000
8	0.351505000	3.686377000	1.656827000
7	3.110693000	-1.679843000	1.119546000
8	4.140445000	-1.769182000	1.752531000
8	-3.258692000	-3.067811000	-1.259467000
7	-2.437097000	-2.206375000	-0.987760000
26	-2.122348000	-0.852500000	0.056204000
7	-3.404537000	-0.689313000	1.141597000
8	-4.380236000	-0.324158000	1.758081000
16	-1.814151000	1.068044000	-1.064358000

Complex 14

26	1.925731000	-0.550685000	0.106430000
26	-0.029668000	1.507804000	-0.154313000
16	0.014355000	-0.206404000	1.383172000
16	2.000506000	1.396074000	-1.080871000
8	1.993722000	-2.964136000	-1.394963000
8	4.229992000	-1.028747000	1.711373000
8	-0.243943000	4.285159000	0.236936000
7	3.239365000	-0.660254000	1.156603000
7	1.796939000	-1.905693000	-0.881951000
7	-0.185440000	3.092922000	0.264451000
16	-1.796988000	1.038064000	-1.437118000
26	-1.884250000	-0.628414000	0.112010000
7	-1.832318000	-2.125519000	-0.635525000
8	-2.017382000	-3.220083000	-1.066587000
7	-3.230751000	-0.473123000	1.128930000
8	-4.250850000	-0.783249000	1.671017000

Figure 7

TS8

26	2.702047000	-0.252299000	0.424701000
26	-1.141585000	-0.668330000	-1.065900000
16	0.696513000	0.437489000	-1.293825000
16	-0.920151000	-2.217506000	0.392090000
8	-1.713727000	-1.912567000	-3.503896000
7	-1.470174000	-1.368002000	-2.481583000
26	-2.515564000	-0.814847000	1.083042000
16	-2.771274000	0.651378000	-0.573656000

7	-3.895066000	-1.673230000	1.170781000
8	-4.903485000	-2.212626000	1.484445000
7	-2.109415000	-0.073761000	2.479600000
8	-2.103676000	0.316653000	3.598641000
26	-0.900814000	1.859064000	-0.661466000
7	-0.575840000	2.537532000	0.786709000
8	-0.360466000	3.317212000	1.653435000
7	-1.081578000	2.944659000	-1.860788000
8	-1.159411000	3.916023000	-2.536682000
8	3.473574000	-1.764453000	-1.464123000
1	4.392958000	-1.646274000	-1.757626000
6	3.031948000	-3.120416000	-1.735098000
1	3.564460000	-3.826289000	-1.092923000
1	3.202890000	-3.349583000	-2.788798000
1	1.965707000	-3.131397000	-1.515401000
8	3.618027000	1.657998000	0.585628000
1	4.044250000	1.970329000	-0.231906000
6	3.152802000	2.802127000	1.351465000
1	2.332860000	3.296016000	0.828654000
1	2.814608000	2.404306000	2.306490000
1	3.987826000	3.488556000	1.503501000
7	2.952759000	-0.714828000	2.034826000
8	3.543734000	-1.136943000	2.963865000
7	4.264865000	-0.552898000	-0.180087000
8	5.375367000	-0.949711000	-0.191303000

Complex 15

26	-2.457435000	-1.188486000	-0.147904000
26	0.950284000	-0.377829000	1.464597000
16	-1.326048000	0.163646000	1.348892000
16	1.547206000	-2.122859000	0.251173000
8	1.750813000	-1.179762000	4.103677000
7	1.374068000	-0.655608000	3.105785000
26	2.457802000	-0.347470000	-0.891156000
16	1.936721000	1.462889000	0.493123000
7	4.146841000	-0.451774000	-0.958383000
8	5.250892000	-0.456451000	-1.405620000
7	1.765807000	-0.110029000	-2.407867000
8	1.550688000	0.105921000	-3.556326000
26	-0.328556000	1.987488000	0.286626000
7	-0.843395000	2.091287000	-1.309907000
8	-1.327987000	2.374594000	-2.354242000
7	-0.636944000	3.384224000	1.192042000
8	-1.025932000	4.469756000	1.478445000
8	-4.340936000	-0.360991000	-0.298951000
1	-4.858219000	-0.374157000	0.526713000
6	-4.568585000	0.904023000	-0.980190000
1	-4.154775000	1.727704000	-0.394208000
1	-4.055239000	0.825372000	-1.936746000
1	-5.640887000	1.033980000	-1.133251000
7	-1.858104000	-1.221332000	-1.746842000

8	-1.335686000	-1.647000000	-2.720370000
7	-2.550706000	-2.746461000	0.534548000
8	-2.317216000	-3.886599000	0.746605000

TS9

26	-2.403955000	-0.184940000	0.539609000
26	1.154458000	0.108659000	1.222862000
16	-0.666680000	1.293090000	1.163582000
16	0.333609000	-1.763915000	1.370489000
8	2.436872000	0.831959000	3.584885000
7	1.876310000	0.661491000	2.558197000
26	1.381341000	-1.637768000	-0.562507000
16	2.351236000	0.355434000	-0.533238000
7	2.547977000	-2.756723000	-0.617702000
8	3.327680000	-3.626871000	-0.820396000
7	0.290057000	-1.720294000	-1.776828000
8	-0.236013000	-2.039911000	-2.787746000
26	0.670246000	1.837831000	-0.566099000
7	-0.009393000	1.710481000	-2.030892000
8	-0.315466000	1.780317000	-3.181919000
7	1.333653000	3.301736000	-0.299636000
8	1.712122000	4.408702000	-0.491293000
8	-2.842735000	1.253025000	-0.896986000
1	-2.003522000	1.749196000	-1.024686000
6	-3.306766000	0.789493000	-2.182908000
1	-2.568393000	0.131730000	-2.649069000
1	-4.226424000	0.238335000	-1.988105000
1	-3.512992000	1.649399000	-2.827526000
7	-2.340859000	-1.564592000	-0.317317000
8	-2.677225000	-2.638408000	-0.712048000
7	-3.437148000	-0.297368000	1.767991000
8	-4.257387000	-0.621413000	2.568796000

Complex 16

26	-0.219141000	2.035912000	0.259261000
26	-0.001003000	-0.001683000	-1.250782000
16	-1.869261000	0.827255000	-0.597418000
16	1.648519000	1.203020000	-0.595311000
8	-0.232081000	2.245076000	3.034757000
8	-0.492518000	4.701517000	-0.518020000
8	-0.001554000	-0.004843000	-4.043228000
7	-0.375827000	3.537124000	-0.333485000
7	-0.208397000	1.963178000	1.885319000
7	0.000029000	-0.004920000	-2.860487000
26	1.874461000	-0.829635000	0.260773000
16	0.216325000	-2.030959000	-0.587476000
7	3.251990000	-1.441263000	-0.337793000
8	4.320772000	-1.917413000	-0.523082000
7	1.816708000	-0.803243000	1.887329000

```
8      2.081563000    -0.922022000    3.034910000
26    -1.657664000    -1.205127000    0.261624000
7     -1.602719000    -1.155614000    1.887553000
8     -1.834886000    -1.316583000    3.037002000
7     -2.877583000    -2.095279000   -0.329829000
8     -3.825259000    -2.782615000   -0.511058000
```

2. Table S1 Charges and spin densities on the most relevant atoms

Complex	Atom	Charges on the most relevant atoms	Spin densities on the most relevant atoms
2	Fe	0.914	2.725
	N	0.007;0.002	-0.501;-0.506
	S	-0.336;-0.347	0.050;0.048
	O	-0.266;-0.269	-0.427;-0.429
3	Fe	0.913	2.863
	N	-0.015 ; -0.022	-0.551 ; -0.541
	S	-0.308	0.051
	O	-0.270 ; -0.277	-0.455 ; -0.452
	Cl	-0.600	0.070
4	Fe	1.034	2.876
	N	-0.055 ; -0.003	-0.533 ; -0.517
	S	-0.303	0.052
	O	-0.236 ; -0.250	-0.477 ; -0.451
	O(met)	-0.687	0.035
5	Fe	1.051	3.038
	N	-0.036 ; -0.045	-0.584 ; -0.587
	Cl	-0.614	0.074
	O	-0.263 ; -0.261	-0.489 ; -0.482
	O(met)	-0.692	0.031
6	Fe	1.101	2.967
	N	-0.056 ; -0.049	-0.510 ; -0.504
	O	-0.170 ; -0.174	-0.511 ; -0.510
	O(met)	-0.694	0.024
TS1	Fe	0.931	2.749
	N	-0.039 ; -0.017	-0.503 ; -0.476
	S	-0.335 ; 0.144	0.001 ; 0.072
	O	-0.250 ; -0.222	-0.451 ; -0.447
	O(met)	-0.678	0.024

7	Fe	0.915	2.770
	N	-0.019 ; -0.080	-0.474 ; -0.513
	S	0.226 ; -0.329	0.086 ; 0.003
	O	-0.224 ; -0.225	-0.472 ; -0.449
	O(met)	-0.676	0.029
TS2	Fe	0.894	2.749
	N	-0.019 ; -0.074	-0.514 ; -0.478
	S	0.248 ; -0.493	0.001 ; 0.124
	O	-0.231 ; -0.247	-0.443 ; -0.460
	O(met)	-0.674	0.028
8	Fe	0.825	2.979
	N	-0.163 ; -0.095	-0.714 ;
	S	-1.071	0.263
	O	-0.333 ; -0.307	-0.526 ; -0.454
	O(met)	-0.669	0.028
TS3	Fe	0.546 ; 0.607	
	N	-0.080 ; -0.090 ; -0.064 ; -0.087	
	S	-0.778 ; -0.617	
	O	-0.452 ; -0.358 ; -0.364 ; -0.362	
	O(met)	-0.602 ; -0.581	
10	Fe	0.772 ; 0.915	2.935 ; -2.916
	N	-0.154 ; -0.067 ; -0.068 ; -0.109	-0.731 ; -0.563 ; 0.572 ; 0.653
	S	-0.925 ; -1.085	0.157 ;
	O	-0.320 ; -0.301 ; -0.321 ; -0.348	-0.517 ; -0.412 ; 0.447 ; 0.498
	O(met)	-0.698	-0.041
TS4	Fe	0.477 ; 0.344	
	N	-0.172 ; -0.233 ; -0.122 ; -0.142	
	S	-1.067 ; -1.065	
	O	-0.009 ; -0.033 ; -0.028 ; -0.034	
	O(met)	-0.105	
11	Fe	0.694 ; 0.694	2.754 ; -2.754
	N	-0.026 ; -0.026 ; -0.117 ; -0.117	-0.668 ; -0.540 ; 0.668 ; 0.539

	S	-0.870 ; -0.870	0 ; 0
	O	-0.321 ; -0.321 ; -0.359 ; -0.359	-0.403 ; -0.483 ; 0.483 ; 0.402
TS5	Fe	0.544 ; 0.552 ; 0.724	-0.079 ; -0.093 ; -0.045
	N	0.015 ; -0.032 ; 0.018 ; -0.029 ; -0.051 ; -0.069	0.047 ; 0.046 ; 0.014 ; 0.019 ; 0.227 ; 0.320
	S	-0.665 ; -0.619 ; -0.907	0.021 ; -0.002 ; 0.095
	O	-0.396 ; -0.448 ; -0.397 ; -0.449 ; -0.347 ; -0.373	0.025; 0.010; 0.150; 0.206; 0.033; 0.130
	O(met)	-0.625	0.002
12	Fe	0.664 ; 0.598 ; 0.560	-0.376 ; -0.033 ; 0.160
	N	-0.060 ; -0.103 ; -0.028 ; 0.007 ; 0.029 ; -0.056	-0.041 ; 0.050 ; -0.065 ; -0.037 ; 0.336 ; 0.384
	S	-0.640 ; -0.698 ; -0.810	0.182 ; 0.045 ; 0.001
	O	-0.407 ; -0.355 ; -0.384 ; -0.397 ; -0.383 ; -0.433	-0.029 ; -0.025 ; 0.029 ; -0.039 ; 0.209 ; 0.250
TS6	Fe	0.779 ; 0.771 ; 0.811	2.936 ; -0.831; 0.755
	N	-0.142 ; -0.066; -0.057 ; -0.029 ; -0.059 ; -0.117	-0.505 ; -0.508 ; 0.429 ; 0.611 ; -0.672 ; -0.586
	S	-0.912 ; -0.739 ; -0.883	0.259 ; 0.071 ; 0.041
	O	-0.362 ; -0.372 ; -0.378 ; -0.413 ; -0.349 ; -0.391	-0.253; -0.366; -0.409; -0.419; -0.429; -0.611
13	Fe	0.727 ; 0.747 ; 0.581	2.747 ; -1.247 ; -2.648
	S	-0.783 ; -0.784 ; -0.732	0.142 ; -0.120 ; -0.017
	N	-0.126 ; -0.053 ; -0.052 ; -0.054 ; -0.030 ; -0.071	0.726 ; 0.653 ; 0.717 ; 0.483 ; -0.520 ; -0.736
	O	-0.382 ; -0.389 ; -0.416 ; -0.397 ; -0.357 ; -0.360	0.442 ; 0.335 ; -0.456 ; -0.369 ;0.446 ; 0.423
TS7	Fe	0.756 ; 0.762 ; 0.604	2.693; 2.752; 1.076
	S	-0.737 ; -0.859 ; -0.769	0.137 ; 0.186 ; 0.108
	N	-0.065 ; -0.106 ; -0.116 ; -0.062 ; 0.031 ; -0.062	-0.563 ; -0.677 ; -0.659 ; -0.693 ; -0.242 ; -0.987
	O	-0.424, -0.381 ; -0.384 ; -0.419 ; -0.431 ; -0.341	-0.376 ; -0.440 ; -0.446 ; -0.380 ; -0.157 ; -0.419
14	Fe	0.772 ; 0.776 ; 0.515	2.597 ; 2.601 ; -1.508
	S	-0.763 ; -0.769 ; -0.752	0.165 ; 0.078 ; 0.178
	N	0.008 ; -0.049 ; -0.017 ; -0.029 ; -0.033	0.374 ; -0.561 ; -0.503 ; -0.522 ; -0.544
	O	-0.348 ; -0.322 ; -0.327 ; -0.330 ; -0.348	0.277 ; 0.427 ; 0.388 ; 0.402 ; 0.416
TS8	Fe	*-0.079 ; 0.495 ; 0.184*	

		;0.363 ;	
	S	*0.051 ; -0.517 ; 0.000 ;*	
	N	*-0.625 ;-0.509 ;-0.203 ; -0.175 ;-0.645 ; -0.314 ; -0.137*	
	O	*0.130 ; 0.073 ; 0.023 ;0.072 ; 0.147 ; 0.101 ; 0.060 ;*	
	O(met)	-0.163; -0.204	
15	Fe	1.002 ; 0.664 ; 0.661 ; 0.527	0.413 ; 0.586 ; -0.103 ; 0.250
	N	-0.060 ; -0.038 ; 0.005 ; 0.003 ; ; 0.019 ; 0.007 ; 0.028	*0.106 ; -0.118 ; -0.088 ; 0.043 ; -0.058 ; -0.244 ; -0.205*
	S	-0.539 ; -0.531 ; -0.725	*0.007 ; 0.103 ; -0.033*
	O	-0.282 ; -0.280 ; -0.300 ; -0.325 ; -0.335 ; -0.316 ; -0.324	*0.068 ; -0.090 ; -0.069 ; -0.034 ; -0.044 ; -0.211 ; -0.175*
	O(met)	-0.663	-0.002
TS9	Fe	*0.943 ; 0.489 ; 0.631 ; 0.555*	*2.233 ; -2.063 ; 1.577 ; -0.598*
	N	*0.057 ; 0.033 ; 0.011 ; -0.042 ; 0.027 ; -0.007 ; 0.006*	*0.282 ;-0.272 ; -0.295 ; 0.221 ; 0.185 ; -0.398 0.237*
	S	*-0.624 ; -0.493 ; -0.427*	*0.042 ; -0.006 ; 0.019 ;*
	O	*-0.322 ; -0.346 ; -0.321 ; -0.351 ; -0.325 ; -0.281 ; -0.318*	*-0.220 ; -0.233 ;0.180 ;0.153 ; ; -0.384 ; -0.339 ;-0.348*
	O(met)	-0.672	*0.023*
16	Fe	0.629 ; 0.329 ; 0.632 ; 0.599	-1.348 ; -0.265 ; 1.366 ; 0.328
	N	0.028 ; 0.033 ; 0.086 ; 0.028 ; 0.033 ; 0.039 ; 0.035	-0.037 ; -0.040 ; -0.250 ; -0.238 ; 0.018 ; 0.243 ; 0.258
	O	-0.310 ; -0.336 ; -0.327 ; -0.335 ; -0.310 ; -0.315 ; -0.338	0.211 ; 0.200 ; -0.033 ; -0.030 ; -0.205 ; -0.197 ; 0.017
	S	-0.392 ; -0.411 ; -0.398	-0.006 ; 0.003 ; 0.004

3. Input files for these calculations (the same for all stable structures)
%NPROC=12
%Mem=5000MB
%chk=etmks

utpssh/6-31G* iop(5/13=1) scf=qc   guess=mix freq
  test vshift=300
--Link1--
%NPROC=12
%Mem=5000MB
%chk=etmks
# utpssh/6-31G* iop(5/13=1) scf=(conver=5,maxcycle=1500) opt=(gdiis,readfc) scf=qc freq
guess=(read,mix) geom=check scrf=(pcm,solvent=methanol) test vshift=300
--Link1--
%NPROC=12
%Mem=5000MB
%chk=etmks
# utpssh/6-311++G** iop(5/13=1) scf=(conver=6,maxcycle=150) guess=(read,mix) geom=check
scrf=(pcm,solvent=methanol) test vshift=300

TS: (the same for all TS)
%NPROC=12
%Mem=5000MB
%chk=etmks
utpssh/6-31G* iop(5/13=1) Opt(TS,CalcFC,NoEigenTest) scf=qc guess=(r
 ead,mix) scrf=(pcm,solvent=methanol) geom=check Freq Test
--Link1--
%NPROC=12
%Mem=5000MB
%chk=etmks
utpssh/6-311++G** iop(5/13=1) scf=(conver=6,maxcycle=150) guess=(rea
 d,mix) geom=check scrf=(pcm,solvent=methanol) test vshift=300

%Nproc=8
%Mem=7000MB
# utpssh/6-31G* IRC(CalcFC,MaxPoints=500,Recorrect=Never) FREQ
scf=(VSHIFT=300,NoIncFock,MAXCYC=200,Tight,NoVarAcc) NOSYMM
IOP(5/13=1,5/36=1,8/11=1)