Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION

Chemical Control of Molecular Spin Switch in Presence of Gate

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Contents:

1. Computational Details:

The pure singlet (S=0) and high spin quintet state (S=2) geometry optimization of the Fe(II) complex of 2,5-di-(2-pyridyl)-1,3,4-thiazole are performed with B3LYP[1] functional at the density functional level of theory and the basis sets used are, 6-31G(d) for C, H, N and effective core potential corrected LANL2DZ[2] for Fe and S atom. After that, we have placed the acceptors (-NO_2 and -CN) and a donor (-OMe) in a suitable position of Fe(II) complex. Besides, we have also put same type of substituents (-NO_2, -CN and –OMe) separately in two suitable positions of Fe(II) complex and re-optimized these singly and doubly substituted derivatives using the same level of theory. On these optimized geometries, we have performed single point energy calculation to extract the dielectric properties, like dipole moment (p) and polarizability (α). To study the basis set effect, we have re-calculated p and α using cc-pVDZ basis for C, H, S, O and aug-cc-pVDZ for N and all electron Wachters + f basis for Fe and found that basis set has little impact on these parameters. All the geometry optimizations and single point calculations have been performed in Gaussian09 suite of programs.[3] The optimized coordinates of all the systems are supplied in the SI.

In the next step, we have carried out spin-polarized quantum transport calculation on the pure and -2NO_2 derivatives of Fe(II) complex of 2,5-di-(2-pyridyl)-1,3,4-thiazole by employing nonequilibrium Green's function technique within density functional theory and the relevant calculations are implemented in ATK 12.2.2.[4] The two-probe configuration with the sandwiched Fe^{II} complex in between two Au electrodes as presented in the Fig. 1clearly reveals that two (6 x 6) layers of Au atoms make a contact with the central complex through coordination with the S atom which eventually locates in the hollow site of the Au(111) surface. It is worth noting that, due to larger size of the -2NO_2 derivative, we have used (8 x 6) layer of Au electrodes. The transport calculations have been done with PBE[5,6] functional and double ζ + polarization basis functions for all elements except Au atoms. Considering the large number of Au atoms in the electrodes, we have chosen single ζ basis for Au and a cutoff energy of 150 Ry for the convergence of two-probe configuration. In the present investigation, the range of bias applied is 0-500mV. In this bias range, the transport calculations on the -2NO_2 derivatives have also been repeated by employing a critical gate voltage of ~1V.

References of Computational Section:

1 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372.

2 (a) M. Dupuis, J. Rys and H. F. King, *J. Chem. Phys.* 1976, **65**, 111. (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270. (c) W. R. Wadt and P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284. (d) P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299.

3 GAUSSIAN09, revision A.1, Gaussian, Inc., Wallingford, CT, 2009.

4 http://www.quantumwise.com.

5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

6 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

2. Geometrical representation of the Fe(II) complex and its double $-NO_2$ derivative involved in the present study. The green, pink, blue yellow and red colours denote the C, H, N, S and O atoms, respectively.

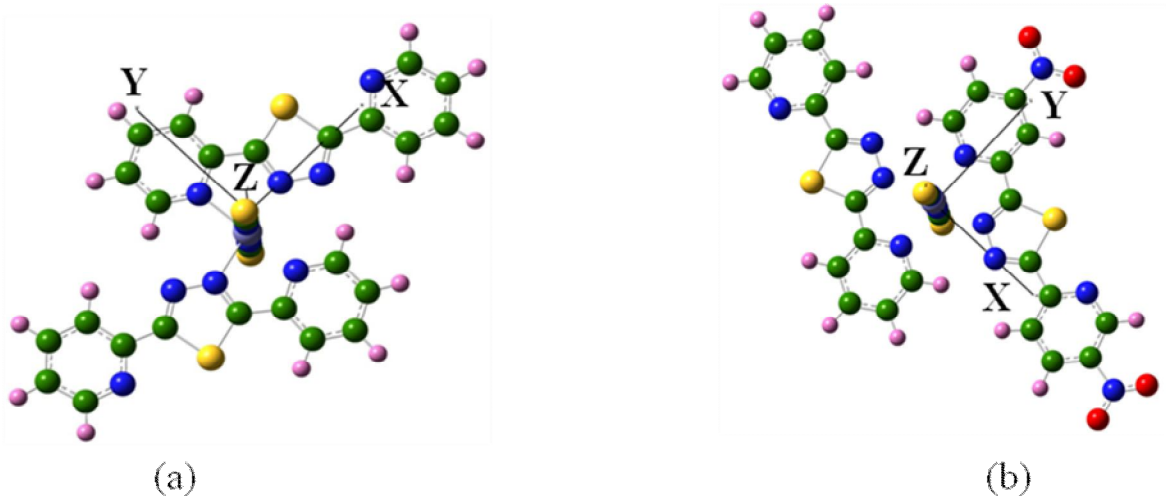

Fig. S1

3. I-V characteristics for the Fe^{II} complex in the high (black) and low-spin (red) states. The inset shows separate α (black) and β (red) spin channel contribution to the current in the high spin state.

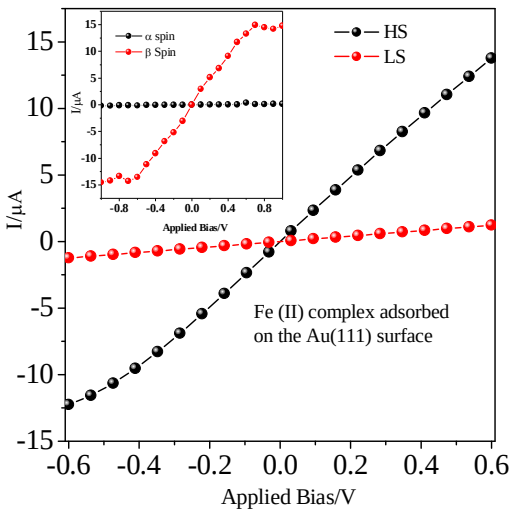

Fig. S2

Spin filter efficiency can be calculated by using the standard formula given by equation 1

$$SFE = \frac{T_{\uparrow}(E_F) - T_{\downarrow}(E_F)}{T_{\uparrow}(E_F) + T_{\downarrow}(E_F)} \times 100\% \qquad (1)$$

Where $T_{\uparrow}(E_F)$ and $T_{\downarrow}(E_F)$ are the transmission coefficients (T(E)) of the up and down spin channels, respectively.

4. *I-V* characteristics for the double –NO_2 derivative in the high-spin (blue) and low-spin (magenta) state. The α (violet) and β (green) contribution to the current in the spin polarized high-spin state is shown in the inset.

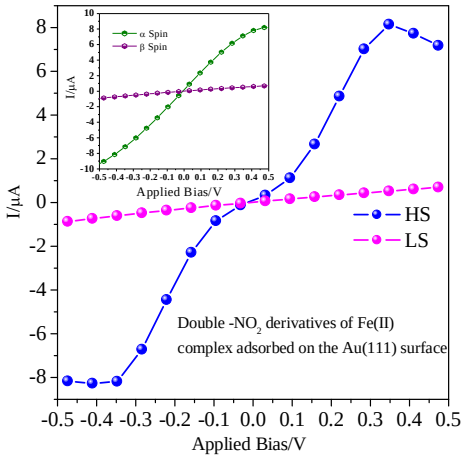

Fig. S3

5. Spin polarized transmission spectrum and projected device density of states (PDDOS) of the high-spin state of pristine Fe(II) complex adsorbed on the Au(111) surface at zero bias.

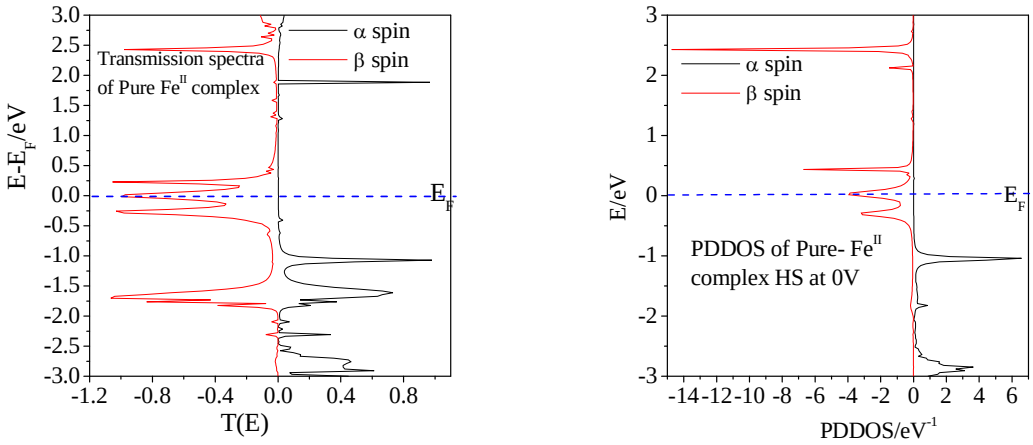

Fig. S4

The candidature of the Fe (II) complex material as a molecular spin filter is well in agreement with the spin polarized transmission spectra of the system. The spin polarized projected device density of states (PDDOS) (in Fig. S4) analyses clearly reveal that the transmission across the Fermi level of the β spin channel is strongly associated with the t_{2g} orbitals centred on the Fe^{II} ion of the complex. Earlier, Aravena et al.[1] performed the quantum transport calculation on the HS and LS states of trans-bis(3-(2-pyridyl)[1,2,3]triazolo[1,5-a]-pyridine)bis(isothiocyanato)iron(II) complex and found similar spin-polarized transport feature like us. In their study, Aravena et al.[1] got an energy difference of 0.54 eV with a very small polarizability difference of 14 a.u. between the HS and LS state which eventually prohibits electrostatic spin-crossover (ESC) at experimentally achievable electric field strength. In brief, although the system chosen in the present study and that of Aravena et al.[1] could have act as spin filtered molecular spin switch, the experimental verification of this particular spin-device action is rather unfeasible since

the energy difference of the two spin states is quite large and the chance of energy re-ordering of the HS and LS states through second order Stark energy gain is very remote due to small polarizability difference between the spin states.

Reference 1.
D. Aravena and E. Ruiz, *J. Am. Chem. Soc.* 2012, ***134*** , 777.

6. Spin polarized transmission spectrum of the high-spin state of double –NO_2 derivative in adsorbed on the Au(111) surface at zero bias.

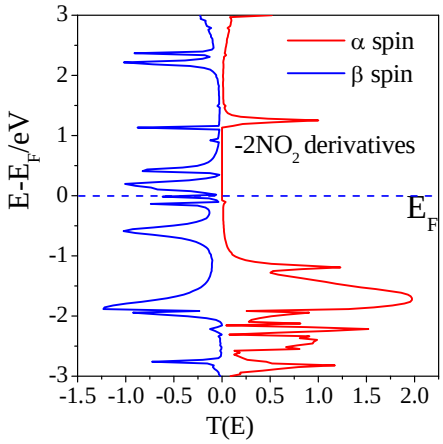

Fig. S5

The transmission spectra of the double –NO_2 derivative of Fe(II) complex, which points out that the major transmission across the Fermi level of this system also occurs through the β spin channel and the orbitals involved are again t_{2g} type. The consistency between the transmission spectra of the pristine and modified complex suggests that the substitution by two -NO_2 group hardly affects the spin polarized transport mechanism involved with the present study.

7. Energy, perpendicular component of the dipole moment and polarizability of the mono- and di-substituted Fe^{II} complex in the high spin and low spin states (where substitutents are -NO_2, -OMe, -CN).

X	LS			HS			E_{ESC}/a.u.	E_{ESC}/Vnm^{-1}
	ε/a.u.	$p_\perp$/a.u.	$\alpha_\perp$/a.u.	ε/a.u.	$p_\perp$/a.u.	$\alpha_\perp$/a.u.		
-NO_2	-4609.206	-0.009	726.568	-4609.172	1.721	1432.807	0.01	5.2
-OMe	-4519.214	-0.392	719.427	-4519.173	0.178	1700.338	0.0085	4.42
-CN	-4496.929	0.001	718.319	-4496.892	1.684	1526.831	0.01	5.2
-2NO_2	-4813.730	-2.431	882.583	-4813.703	6.606	1217.846	0.0028	1.45
-2OMe	-4633.743	-0.275	789.047	-4633.753	-0.284	742.059	-0.02	-10.4
-2CN	-4589.177	-2.320	838.792	-4589.188	-2.567	755.897	-0.0195	-10.14

Table S1

8. Optimized Coordinates of low-spin and high-spin states of Fe^{II} complex of 2, 5-di-(2-pyridyl)-1,3,4-thiazole.

(a) Optimized coordinates of low-spin Fe^{II} complex

Fe	-0.00003	0.00005	-0.00002
N	0.13102	-2.04245	0.00254
N	-3.10302	0.27603	-0.00161
N	-6.53605	-0.82275	-0.00019
C	1.24145	-2.78755	0.00361
H	2.1735	-2.23688	0.00292
C	1.21106	-4.18374	0.00559
H	2.14367	-4.73797	0.00642
C	-0.01723	-4.83861	0.00649
H	-0.07376	-5.92267	0.00806
C	-1.17972	-4.07251	0.00532
H	-2.15913	-4.53935	0.00594
C	-1.06362	-2.68203	0.00333
C	-2.19568	-1.77361	0.00182
C	-4.19692	-0.42604	-0.00062
C	-5.56263	0.10278	-0.00151
C	-5.80949	1.48174	-0.00353
H	-4.98278	2.1824	-0.00454
C	-7.13468	1.9092	-0.00415
H	-7.36741	2.97001	-0.0057
C	-8.15319	0.95627	-0.00276
H	-9.19849	1.24843	-0.00316
C	-7.79964	-0.39642	-0.00081
H	-8.56451	-1.16996	0.0003
S	-3.91787	-2.2055	0.00232
N	-1.97655	-0.47909	-0.00022
N	-0.00126	0.00256	1.95601
C	-0.00316	0.00574	3.13602
S	-0.00588	0.01025	4.80621
N	-0.13106	2.04254	-0.0026
N	3.10297	-0.27595	0.00162
N	6.53602	0.8228	0.00026
C	-1.24148	2.78765	-0.0037
H	-2.17354	2.237	-0.003
C	-1.21108	4.18384	-0.00571
H	-2.14369	4.73808	-0.00656
C	0.01721	4.8387	-0.00661
H	0.07375	5.92276	-0.0082
C	1.1797	4.07259	-0.00541
H	2.15911	4.53942	-0.00602
C	1.06359	2.68212	-0.00338
C	2.19564	1.7737	-0.00184
C	4.19688	0.42612	0.00066
C	5.56259	-0.10272	0.00159
C	5.80942	-1.48169	0.00364
H	4.9827	-2.18233	0.00465
C	7.13461	-1.90917	0.0043
H	7.36732	-2.96999	0.00587
C	8.15313	-0.95625	0.00291
H	9.19842	-1.24843	0.00333
C	7.7996	0.39645	0.00092
H	8.56448	1.16997	-0.00019
S	3.91783	2.20557	-0.0023
N	1.9765	0.47918	0.0002
N	0.00122	-0.00249	-1.95605
C	0.00327	-0.00595	-3.13605
S	0.00621	-0.01083	-4.80625

(b) Optimized coordinates of high-spin Fe^{II} complex

Fe	0.	0.	0.
N	0.	0.	2.29208
N	2.19927	0.	0.66761
N	3.35431	-0.00056	-0.04487
N	6.7534	-0.00376	1.16557
S	4.07136	-0.00217	2.46763
C	-1.09431	0.0003	3.05504
H	-2.03985	0.00069	2.51972
C	-1.03903	0.00011	4.4511
H	-1.95536	0.00037	5.03204
C	0.20974	-0.00041	5.0683
H	0.29467	-0.00058	6.15077
C	1.35698	-0.00071	4.27676
H	2.34331	-0.00112	4.72919
C	1.2109	-0.00047	2.8864
C	2.35581	-0.00073	1.96706
C	4.42102	-0.00174	0.70054
C	5.8035	-0.00273	0.21593
C	6.08437	-0.00264	-1.15693
H	5.27207	-0.00177	-1.8744
C	7.41942	-0.00371	-1.55189
H	7.67819	-0.0037	-2.60673
C	8.4143	-0.00479	-0.5739
H	9.46665	-0.00567	-0.83982
C	8.02711	-0.00476	0.76935
H	8.77306	-0.00557	1.56134
N	0.00085	-2.02906	0.00006
C	0.00277	-3.21473	0.00039
S	0.00538	-4.87222	0.00081
N	-0.00001	-0.00003	-2.29207
N	-2.19927	-0.00001	-0.66759
N	-3.3543	0.00053	0.0449
N	-6.75341	0.00351	-1.1655
S	-4.07137	0.0021	-2.4676
C	1.09428	-0.00033	-3.05505
H	2.03984	-0.00068	-2.51974
C	1.03899	-0.00019	-4.45111
H	1.95532	-0.00044	-5.03206
C	-0.20978	0.0003	-5.06829
H	-0.29473	0.00044	-6.15077
C	-1.35701	0.0006	-4.27674
H	-2.34335	0.00098	-4.72917
C	-1.21092	0.0004	-2.88639
C	-2.35582	0.00066	-1.96705
C	-4.42102	0.00163	-0.70051
C	-5.80349	0.00255	-0.21588
C	-6.08435	0.00248	1.15698
H	-5.27204	0.00168	1.87445
C	-7.4194	0.00347	1.55196
H	-7.67815	0.00348	2.6068
C	-8.41428	0.00449	0.57398
H	-9.46663	0.0053	0.83992
C	-8.02711	0.00444	-0.76927
H	-8.77307	0.0052	-1.56126
N	-0.00099	2.02906	-0.00008
C	-0.00417	3.21472	-0.00074
S	-0.00853	4.87221	-0.00165

9. Optimized coordinates of low-spin and high-spin states of -NO_2 derivatives.

(a) Optimized coordinates of low-spin Fe^{II} complex

Fe	0.00684	0.00582	0.21088
N	0.12595	-2.03811	0.21101
N	-3.09631	0.29932	0.21071

N	-6.53285	-0.78805	0.2108
C	1.23196	-2.78929	0.21112
H	2.16743	-2.24472	0.21107
C	1.19327	-4.18536	0.21128
H	2.12253	-4.74506	0.21136
C	-0.03876	-4.83268	0.21134
H	-0.1018	-5.91633	0.21147
C	-1.19688	-4.05964	0.21123
H	-2.1789	-4.52085	0.21126
C	-1.07263	-2.67016	0.21106
C	-2.19992	-1.75543	0.21094
C	-4.19439	-0.39697	0.21075
C	-5.55831	0.13638	0.2107
C	-5.80308	1.51548	0.21058
H	-4.97639	2.21616	0.21051
C	-7.12786	1.94488	0.21056
H	-7.35903	3.00596	0.21046
C	-8.14729	0.99315	0.21066
H	-9.19215	1.28675	0.21065
C	-7.79581	-0.36031	0.21078
H	-8.56166	-1.13275	0.21086
S	-3.92402	-2.1773	0.21098
N	-1.97401	-0.4624	0.21081
N	0.00749	-0.00626	2.1641
C	0.00733	-0.07611	3.34263
S	0.00745	-0.1683	5.00806
N	-0.1167	2.03539	0.21073
N	3.10678	-0.28821	0.21108
N	6.54125	0.80489	0.21086
C	-1.23124	2.77671	0.21059
H	-2.16247	2.22443	0.21065
C	-1.21087	4.1718	0.21039
H	-2.12504	4.75092	0.21028
C	0.02643	4.79922	0.21034
C	1.2013	4.06205	0.21048
H	2.16257	4.56037	0.21045
C	1.08114	2.67282	0.21068
C	2.2128	1.76526	0.21083
C	4.2043	0.40989	0.21102
C	5.56862	-0.12146	0.21099
C	5.81477	-1.50018	0.21103
H	4.98853	-2.20143	0.21112
C	7.14052	-1.92697	0.21094
H	7.37388	-2.98757	0.21097
C	8.15824	-0.9735	0.21081
H	9.20359	-1.26532	0.21073
C	7.80489	0.3797	0.21078
H	8.56937	1.15343	0.21067
S	3.93481	2.19088	0.21083
N	1.98511	0.47214	0.21096
N	0.00778	-0.00641	-1.74233
C	0.00835	-0.07618	-2.92087
S	0.00944	-0.16827	-4.58631
N	0.10143	6.275	0.21015
O	1.22108	6.77852	0.21017
O	-0.96136	6.88855	0.21

(b) Optimized coordinates of high-spin Fe^{II} complex

Fe	0.08521	0.0748	0.14384
N	-0.04123	-2.28102	0.14372
N	2.00852	-0.53139	0.14375
N	3.08498	0.28379	0.14375
N	6.56079	-0.66874	0.14362

S	4.01571	-2.16428	0.14359
C	-1.09353	-3.09837	0.14375
H	-2.06059	-2.60504	0.1438
C	-0.96322	-4.4905	0.14372
H	-1.84754	-5.11894	0.14375
C	0.31721	-5.04359	0.14366
H	0.45636	-6.12035	0.14363
C	1.42258	-4.19621	0.14363
H	2.43181	-4.59527	0.14359
C	1.20026	-2.81413	0.14367
C	2.26957	-1.82656	0.14367
C	4.21243	-0.36537	0.14368
C	5.55158	0.21932	0.14368
C	5.74357	1.60766	0.14375
H	4.89091	2.27675	0.14379
C	7.05108	2.08606	0.14376
H	7.24171	3.15513	0.14381
C	8.10626	1.17309	0.1437
H	9.13926	1.50593	0.14371
C	7.80637	-0.19279	0.14363
H	8.60129	-0.93539	0.14358
N	0.09425	0.00064	-1.74052
C	0.06551	-0.20996	-2.9099
S	0.03965	-0.49351	-4.52426
N	0.26885	2.33468	0.144
N	-1.78218	0.61289	0.14386
N	-2.83552	-0.21192	0.14375
N	-6.32962	0.6814	0.14352
S	-3.81787	2.23464	0.14381
C	1.32221	3.16036	0.14411
H	2.29013	2.66967	0.14412
C	1.22028	4.54497	0.14419
H	2.08855	5.18864	0.14427
C	-0.08123	5.09084	0.14416
C	-1.195	4.27616	0.14406
H	-2.18629	4.71322	0.14404
C	-0.99485	2.88388	0.14399
C	-2.05143	1.9343	0.1439
C	-3.9783	0.41543	0.14369
C	-5.30212	-0.18868	0.14355
C	-5.48288	-1.58216	0.14347
H	-4.62212	-2.24099	0.14351
C	-6.7812	-2.07827	0.14333
H	-6.95686	-3.1504	0.14327
C	-7.85255	-1.18133	0.14329
H	-8.88076	-1.52875	0.14319
C	-7.56826	0.18625	0.14339
H	-8.37286	0.91904	0.14336
N	0.09431	0.0004	2.02817
C	0.06542	-0.21034	3.19753
S	0.03935	-0.49408	4.81185
N	-0.26098	6.53775	0.14423
O	-1.41446	6.98072	0.14422
O	0.76113	7.23179	0.14431

10. Optimized coordinates of low-spin and high-spin states of -OMe derivatives.

(a) Optimized coordinates of low-spin –OMe derivatives Fe^{II} complex

Fe	0.03507	-0.31628	0.00009
N	0.20426	-2.3547	0.0004
N	-3.06899	-0.09398	-0.00025
N	-6.4829	-1.25181	-0.00025
C	1.32807	-3.07975	0.00063
H	2.25009	-2.51232	0.00065

C	1.32294	-4.47622	0.00082
H	2.26546	-5.01348	0.00101
C	0.1067	-5.1534	0.00077
H	0.06995	-6.23832	0.00091
C	-1.06944	-4.40856	0.00054
H	-2.0402	-4.89316	0.00049
C	-0.97858	-3.01612	0.00036
C	-2.12659	-2.12812	0.00012
C	-4.15045	-0.81518	-0.00023
C	-5.52517	-0.31009	-0.00035
C	-5.7957	1.06449	-0.00052
H	-4.98061	1.77863	-0.00059
C	-7.12791	1.46926	-0.00059
H	-7.37891	2.52594	-0.00072
C	-8.13024	0.49927	-0.00048
H	-9.18036	0.7736	-0.00053
C	-7.75361	-0.84707	-0.00032
H	-8.50513	-1.6336	-0.00024
S	-3.84112	-2.58966	0.00003
N	-1.92983	-0.82984	-0.00005
N	0.0313	-0.31316	1.95728
C	0.00142	-0.2966	3.13664
S	-0.03966	-0.27421	4.80696
N	-0.13499	1.72583	-0.00014
N	3.14265	-0.5306	0.00017
N	6.55583	0.62867	-0.00015
C	-1.2485	2.46222	-0.00022
H	-2.17722	1.90541	-0.00029
C	-1.25128	3.85735	-0.00021
H	-2.19857	4.38155	-0.00028
C	-0.02828	4.5363	-0.00011
C	1.14921	3.77416	-0.00003
H	2.10969	4.27699	0.00005
C	1.04869	2.39094	-0.00005
C	2.19798	1.50216	0.00004
C	4.22332	0.19178	0.00004
C	5.59822	-0.31317	-0.00006
C	5.86876	-1.68775	-0.00009
H	5.05403	-2.4023	-0.00004
C	7.20099	-2.09255	-0.00021
H	7.45179	-3.14926	-0.00024
C	8.2032	-1.12244	-0.00029
H	9.25334	-1.39674	-0.00039
C	7.82654	0.2239	-0.00026
H	8.57805	1.01045	-0.00032
S	3.91173	1.96524	-0.00002
N	2.00222	0.20405	0.00016
N	0.03175	-0.31373	-1.9571
C	0.0021	-0.29751	-3.13647
S	-0.0387	-0.27562	-4.80681
O	0.12736	5.87392	-0.00008
C	-1.03837	6.69649	-0.00013
H	-0.67286	7.72369	-0.00006
H	-1.64413	6.52256	-0.89729
H	-1.64425	6.52248	0.89695

(b) Optimized coordinates of high-spin –OMe derivatives Fe^{II} complex

Fe	0.01707	-0.34674	-0.00012
N	0.26824	-2.63474	0.
N	-1.84199	-0.96881	-0.00017
N	-2.92652	-0.19015	-0.00011
N	-6.38669	-1.22307	0.00032
S	-3.80687	-2.67523	0.00012

C	1.35052	-3.41309	0.00005
H	2.2984	-2.88367	0.00004
C	1.28435	-4.80744	0.00011
H	2.19477	-5.39706	0.00016
C	0.02108	-5.41415	0.00009
H	-0.07148	-6.49642	0.00012
C	-1.11565	-4.6207	0.00004
H	-2.10716	-5.06205	0.00001
C	-0.9645	-3.21898	0.
C	-2.05642	-2.29474	-0.00004
C	-4.04669	-0.86483	0.00004
C	-5.39004	-0.31502	0.00012
C	-5.62329	1.07227	0.00002
H	-4.78686	1.76171	-0.00015
C	-6.93825	1.51983	0.00012
H	-7.15309	2.5849	0.00004
C	-7.97691	0.58403	0.00033
H	-9.01721	0.89344	0.00041
C	-7.64186	-0.77203	0.00043
H	-8.41988	-1.53331	0.00057
N	0.02266	-0.33538	1.8902
C	0.00301	-0.28031	3.07624
S	-0.01866	-0.20687	4.71595
N	-0.21899	1.95043	-0.00024
N	1.89648	0.29695	-0.00011
N	2.99052	-0.47841	0.00008
N	6.44125	0.57927	0.0005
S	3.84898	2.00691	0.00012
C	-1.29453	2.73359	-0.00032
H	-2.24606	2.2106	-0.00032
C	-1.23761	4.12874	-0.0004
H	-2.15624	4.70135	-0.00046
C	0.02553	4.74107	-0.00041
C	1.16726	3.93065	-0.00033
H	2.14781	4.39342	-0.00035
C	1.00594	2.54368	-0.00023
C	2.10828	1.61237	-0.00012
C	4.10288	0.20581	0.00019
C	5.45296	-0.33601	0.00035
C	5.69112	-1.72069	0.00034
H	4.85838	-2.41448	0.0002
C	7.00981	-2.16046	0.00049
H	7.23116	-3.22397	0.00048
C	8.04118	-1.21795	0.00065
H	9.08335	-1.52095	0.00077
C	7.69935	0.13701	0.00065
H	8.47274	0.90268	0.00075
N	0.02277	-0.33555	-1.89048
C	0.00317	-0.28063	-3.07652
S	-0.01838	-0.20727	-4.71625
O	0.24278	6.07295	-0.0005
C	-0.88194	6.94855	-0.00059
H	-1.49685	6.8048	0.89592
H	-0.4689	7.95783	-0.00066
H	-1.49681	6.80467	-0.89711

11. Optimized coordinates of low-spin and high-spin states of -CN derivatives.

(a) Optimized coordinates of low-spin –CN derivatives Fe^{II} complex

Fe	-0.00286	-0.23256	0.00004
N	0.11987	-2.27556	0.00025
N	-3.10506	0.05724	-0.00016
N	-6.5404	-1.03431	-0.00011
C	1.22702	-3.0252	0.00039

H	2.16162	-2.47911	0.00038
C	1.19054	-4.42131	0.00054
H	2.12068	-4.97957	0.00065
C	-0.04051	-5.07061	0.00055
H	-0.10183	-6.15436	0.00066
C	-1.1998	-4.29938	0.0004
H	-2.18111	-4.76209	0.0004
C	-1.07771	-2.90965	0.00026
C	-2.20626	-1.99655	0.0001
C	-4.2022	-0.64048	-0.00012
C	-5.56682	-0.10888	-0.00019
C	-5.81326	1.26993	-0.0003
H	-4.98713	1.97125	-0.00036
C	-7.13849	1.69784	-0.00034
H	-7.37099	2.75864	-0.00042
C	-8.15693	0.74502	-0.00026
H	-9.20211	1.03745	-0.00028
C	-7.80385	-0.60799	-0.00014
H	-8.56883	-1.38132	-0.00008
S	-3.92987	-2.42061	0.00002
N	-1.98185	-0.7032	-0.00002
N	-0.00254	-0.23845	1.95397
C	-0.001	-0.27669	3.13384
S	0.00138	-0.32699	4.80146
N	-0.12887	1.8008	-0.00014
N	3.09709	-0.51949	0.00018
N	6.53067	0.57662	0.00003
C	-1.24145	2.54446	-0.00024
H	-2.1736	1.9934	-0.00024
C	-1.21873	3.93765	-0.00035
H	-2.14633	4.49807	-0.00043
C	0.01629	4.5972	-0.00035
C	1.18568	3.82827	-0.00024
H	2.15969	4.30399	-0.00024
C	1.06679	2.4401	-0.00014
C	2.19984	1.5329	-0.00002
C	4.1938	0.17936	0.00011
C	5.55876	-0.35049	0.00011
C	5.8061	-1.72902	0.00017
H	4.98038	-2.43088	0.00022
C	7.13215	-2.15478	0.00014
H	7.36634	-3.2152	0.00018
C	8.14915	-1.2005	0.00006
H	9.19473	-1.49148	0.00004
C	7.79466	0.15235	0.00001
H	8.55856	0.92666	-0.00005
S	3.92194	1.96002	0.00001
N	1.97417	0.2395	0.00009
N	-0.00234	-0.2388	-1.95388
C	-0.00071	-0.27732	-3.13375
S	0.00186	-0.32797	-4.80136
C	0.08636	6.0296	-0.00047
N	0.13969	7.19067	-0.00056

(b) Optimized coordinates of high-spin –CN derivatives Fe^{II} complex

Fe	-0.00777	-0.16814	0.00036
N	-0.15908	-2.50892	0.00026
N	1.90735	-0.78174	0.00013
N	2.98912	0.02312	0.00002
N	6.45804	-0.95905	-0.00066
S	3.90089	-2.4346	-0.00039
C	-1.22003	-3.31518	0.0004
H	-2.18157	-2.8112	0.00054
C	-1.10564	-4.70844	0.00036

H	-1.99692	-5.3269	0.00048
C	0.16951	-5.27564	0.00017
H	0.29661	-6.35395	0.00014
C	1.28382	-4.44145	0.00002
H	2.28857	-4.85165	-0.00012
C	1.07848	-3.05551	0.00007
C	2.15595	-2.08206	-0.00004
C	4.11245	-0.6354	-0.00023
C	5.45534	-0.0628	-0.00039
C	5.66099	1.32431	-0.00028
H	4.81417	2.00077	-0.00006
C	6.97212	1.79119	-0.00047
H	7.17221	2.85862	-0.0004
C	8.02002	0.86929	-0.00076
H	9.05585	1.19318	-0.00091
C	7.70759	-0.49351	-0.00084
H	8.496	-1.24316	-0.00106
N	0.00462	-0.22305	-1.88514
C	-0.00756	-0.38932	-3.06168
S	-0.0128	-0.61247	-4.68608
N	0.19074	2.10443	0.00053
N	-1.87054	0.38757	0.00052
N	-2.92882	-0.42547	0.00021
N	-6.4182	0.49347	-0.00103
S	-3.89441	2.03027	-0.00016
C	1.2494	2.91721	0.0007
H	2.21338	2.41801	0.00081
C	1.15592	4.30428	0.00073
H	2.04297	4.92575	0.00087
C	-0.13897	4.88257	0.00056
C	-1.25517	4.05529	0.0004
H	-2.25415	4.47751	0.00031
C	-1.06767	2.65711	0.00039
C	-2.1285	1.7139	0.0003
C	-4.06924	0.20962	-0.00021
C	-5.39566	-0.38374	-0.00061
C	-5.58717	-1.77668	-0.00056
H	-4.73117	-2.4417	-0.00021
C	-6.8885	-2.26354	-0.00094
H	-7.07142	-3.3345	-0.00091
C	-7.95417	-1.35923	-0.00137
H	-8.98477	-1.69954	-0.00167
C	-7.65994	0.00611	-0.00139
H	-8.45974	0.74431	-0.00171
N	0.00503	-0.22332	1.88586
C	-0.00691	-0.38969	3.06237
S	-0.01198	-0.6131	4.68675
C	-0.29697	6.30691	0.00058
N	-0.41282	7.46453	0.00059

12. Optimized coordinates of low-spin and high-spin states of double -NO_2 derivatives.

(a) Optimized coordinates of low-spin double -NO_2 derivatives Fe^{II} complex

Fe	-0.08535	0.0574	-0.13036
N	0.20199	-1.97114	-0.1302
N	-3.20146	0.09533	-0.13039
N	-6.53418	-1.2773	-0.13042
C	1.36476	-2.63131	-0.13017
H	2.25428	-2.01507	-0.1302
C	1.43953	-4.02575	-0.13011
H	2.41092	-4.50861	-0.13009
C	0.264	-4.77063	-0.13008

H	0.28901	-5.85576	-0.13003
C	-0.95261	-4.09355	-0.13011
H	-1.89389	-4.63303	-0.13009
C	-0.94121	-2.69848	-0.13018
C	-2.13915	-1.87888	-0.13024
C	-4.2384	-0.68934	-0.13037
C	-5.64233	-0.27287	-0.13045
C	-6.00389	1.08011	-0.13055
H	-5.2405	1.8493	-0.13056
C	-7.36073	1.3946	-0.13062
H	-7.68196	2.43195	-0.1307
C	-8.29499	0.35918	-0.13059
H	-9.36112	0.56219	-0.13064
C	-7.82909	-0.95941	-0.13049
H	-8.52597	-1.79457	-0.13046
S	-3.82227	-2.44115	-0.13022
N	-2.02007	-0.57149	-0.13032
N	-0.06969	0.04243	1.82106
C	0.00782	-0.03775	2.99671
S	0.11356	-0.14192	4.65693
N	-0.37714	2.06716	-0.13053
N	3.03222	0.02855	-0.1303
N	6.36496	1.39802	-0.13037
C	-1.55003	2.71285	-0.13056
H	-2.43265	2.08563	-0.13051
C	-1.64633	4.10495	-0.13065
H	-2.60607	4.60511	-0.13067
C	-0.46687	4.83507	-0.13071
C	0.76564	4.1992	-0.13067
H	1.68108	4.77765	-0.13072
C	0.76198	2.80486	-0.13058
C	1.96606	1.99682	-0.13051
C	4.06446	0.82047	-0.13036
C	5.46592	0.39842	-0.1303
C	5.81663	-0.95975	-0.13018
H	5.04783	-1.72279	-0.13012
C	7.16623	-1.28963	-0.13013
H	7.51125	-2.31665	-0.13003
C	8.0879	-0.24654	-0.1302
C	7.65761	1.08245	-0.13032
H	8.3776	1.89387	-0.13038
S	3.64409	2.56915	-0.13046
N	1.85052	0.68693	-0.1304
N	-0.06967	0.04205	-2.08178
C	0.00794	-0.03871	-3.25738
S	0.11386	-0.1437	-4.91754
N	-0.51628	6.31205	-0.13081
O	0.55739	6.90704	-0.13087
O	-1.62707	6.83312	-0.13083
N	9.52735	-0.54413	-0.13016
O	10.29887	0.41193	-0.13024
O	9.85604	-1.7282	-0.13005

(b) Optimized coordinates of high-spin double -NO_2 derivatives Fe^{II} complex

Fe	0.15771	0.08609	-0.09732
N	0.43007	-2.26004	0.03616
N	2.16306	-0.19804	-0.02185
N	3.09359	0.78574	-0.04642
N	6.67434	0.41476	0.08077
S	4.40741	-1.47014	0.1136

C	-0.47389	-3.23886	0.06122
H	-1.50851	-2.91399	0.01279
C	-0.11472	-4.58836	0.14403
H	-0.88314	-5.35404	0.16179
C	1.23686	-4.92073	0.20239
H	1.55148	-5.95768	0.26718
C	2.18773	-3.90095	0.17655
H	3.24832	-4.12694	0.22049
C	1.73888	-2.5804	0.09259
C	2.63359	-1.42486	0.0578
C	4.3092	0.3304	0.01439
C	5.5374	1.12643	0.00868
C	5.50084	2.52413	-0.0671
H	4.55179	3.04451	-0.12334
C	6.71429	3.20844	-0.06732
H	6.73051	4.29264	-0.12477
C	7.90133	2.48024	0.00716
H	8.86664	2.97617	0.00957
C	7.8269	1.08521	0.07947
H	8.7306	0.48298	0.13872
N	0.24371	-0.07532	-1.96718
C	0.32973	-0.31624	-3.12849
S	0.45955	-0.6414	-4.728
N	-0.04052	2.35136	-0.22436
N	-1.77113	0.30072	-0.16673
N	-2.65532	-0.68707	-0.14038
N	-6.25628	-0.4258	-0.26219
S	-4.05256	1.55252	-0.30175
C	0.85928	3.33922	-0.25022
H	1.89598	3.02144	-0.20218
C	0.52541	4.68642	-0.33222
H	1.27176	5.46801	-0.35165
C	-0.84546	4.99628	-0.38982
C	-1.80837	4.01	-0.36595
H	-2.8583	4.27259	-0.41142
C	-1.37635	2.67074	-0.28145
C	-2.25841	1.55857	-0.24846
C	-3.89988	-0.26959	-0.19989
C	-5.08035	-1.09426	-0.19123
C	-5.00994	-2.50323	-0.11385
H	-4.04612	-2.99513	-0.05867
C	-6.18564	-3.22914	-0.11036
H	-6.19874	-4.31082	-0.05299
C	-7.39356	-2.5253	-0.18421
C	-7.38286	-1.12771	-0.25851
H	-8.31809	-0.58006	-0.31585
N	0.13105	0.12503	1.78091
C	0.1468	0.0096	2.96434
S	0.18012	-0.14269	4.59427
N	-1.26694	6.39879	-0.47739
O	-2.47493	6.63582	-0.52624
O	-0.37668	7.25077	-0.49623
N	-8.6561	-3.24402	-0.1838
O	-9.69442	-2.58056	-0.25057
O	-8.61076	-4.47636	-0.1166

13. Optimized coordinates of low-spin and high-spin states of double -OMe derivatives.

(a) Optimized coordinates of low-spin double -OMe derivatives Fe^{II} complex

Fe	0.38076	-0.24326	0.00268
N	0.06111	-2.26247	0.01034
N	3.49482	-0.25326	-0.0048

N	6.81204	-1.66457	-0.00717
C	-1.11399	-2.9014	0.01543
H	-1.99112	-2.26627	0.01476
C	-1.21261	-4.29436	0.02103
H	-2.19258	-4.75986	0.02505
C	-0.0504	-5.0606	0.02134
H	-0.09483	-6.14524	0.0256
C	1.17805	-4.40575	0.01607
H	2.10985	-4.9616	0.01612
C	1.19113	-3.01031	0.01071
C	2.40218	-2.21064	0.005
C	4.51891	-1.05379	-0.00431
C	5.92771	-0.65365	-0.00913
C	6.30074	0.69668	-0.0153
H	5.54166	1.4701	-0.0167
C	7.65961	1.00032	-0.01953
H	7.98915	2.03519	-0.02435
C	8.58637	-0.04217	-0.01752
H	9.65415	0.15233	-0.02068
C	8.10953	-1.35633	-0.01131
H	8.79983	-2.19714	-0.00959
S	4.07717	-2.79991	0.0031
N	2.3034	-0.90113	0.0005
N	0.38074	-0.25081	-1.95485
C	0.40746	-0.26626	-3.13419
S	0.44458	-0.28837	-4.80504
N	0.7022	1.77959	-0.00258
N	-2.73547	-0.22865	0.00358
N	-6.05767	1.18603	-0.00141
C	1.86701	2.43212	-0.00405
H	2.7527	1.80911	-0.00482
C	1.97294	3.8231	-0.00451
H	2.95667	4.27519	-0.00558
C	0.80312	4.59012	-0.00335
C	-0.42717	3.91694	-0.00199
H	-1.34796	4.48918	-0.00095
C	-0.42947	2.5298	-0.00155
C	-1.64107	1.72871	0.0003
C	-3.7612	0.57228	0.00098
C	-5.16548	0.17588	-0.0002
C	-5.552	-1.16773	-0.00069
H	-4.8006	-1.94904	-0.00006
C	-6.90899	-1.48151	-0.00242
H	-7.22521	-2.51818	-0.00298
C	-7.83662	-0.43381	-0.00362
C	-7.34695	0.8901	-0.003
H	-8.05702	1.71395	-0.00401
S	-3.3163	2.31933	-0.0021
N	-1.5436	0.42049	0.00317
N	0.38959	-0.23799	1.96024
C	0.4254	-0.24287	3.13943
S	0.47522	-0.25005	4.81008
O	0.74642	5.93596	-0.00335
C	1.96928	6.6701	-0.00367
H	1.68066	7.72155	-0.00313
H	2.56144	6.45201	0.89302
H	2.56059	6.45272	-0.90109
O	-9.18095	-0.56612	-0.00543
C	-9.7353	-1.87834	-0.00712
H	-9.43842	-2.43641	0.88955
H	-10.81728	-1.74255	-0.00898
H	-9.43525	-2.43543	-0.90334

(b) Optimized coordinates of high-spin double -OMe derivatives Fe^{II} complex

Fe	0.41971	-0.2027	0.00006
N	0.41044	-2.49983	0.00339
N	2.61983	-0.88654	-0.00134
N	3.77964	-0.18213	-0.00312
N	7.17229	-1.41082	-0.00168
S	4.48053	-2.69895	0.00166
C	-0.68774	-3.25726	0.00525
H	-1.63095	-2.71768	0.00496
C	-0.6394	-4.65362	0.00742
H	-1.55869	-5.22994	0.00889
C	0.60614	-5.27723	0.00762
H	0.68579	-6.36014	0.00928
C	1.75723	-4.49148	0.00563
H	2.7412	-4.94903	0.00569
C	1.61809	-3.10033	0.00352
C	2.7678	-2.18703	0.00125
C	4.84141	-0.93454	-0.00194
C	6.22644	-0.4572	-0.00322
C	6.51351	0.91453	-0.00582
H	5.70391	1.63502	-0.00696
C	7.85015	1.30345	-0.00682
H	8.11384	2.35712	-0.00881
C	8.84092	0.32122	-0.00522
H	9.89441	0.58269	-0.00591
C	8.44786	-1.02014	-0.00267
H	9.1903	-1.81545	-0.00137
N	0.43015	-0.23352	-2.03313
C	0.46589	-0.28265	-3.21687
S	0.51608	-0.35116	-4.87343
N	0.42425	2.07393	-0.00229
N	-1.77458	0.45591	0.00148
N	-2.9269	-0.26189	0.00233
N	-6.3375	0.93446	0.0005
S	-3.65143	2.25016	-0.00098
C	1.50679	2.85053	-0.00333
H	2.45998	2.32865	-0.00383
C	1.45936	4.24533	-0.00374
H	2.38194	4.812	-0.00456
C	0.20382	4.86429	-0.00301
C	-0.94323	4.0544	-0.0019
H	-1.92024	4.52465	-0.00123
C	-0.78879	2.67377	-0.00155
C	-1.9338	1.75402	-0.00025
C	-3.99759	0.48037	0.00126
C	-5.37354	-0.00723	0.00153
C	-5.65919	-1.37623	0.00266
H	-4.84863	-2.09604	0.00339
C	-6.98888	-1.79001	0.00274
H	-7.22676	-2.84753	0.00356
C	-7.99151	-0.81377	0.00168
C	-7.60158	0.54236	0.00058
H	-8.37123	1.31097	-0.00029
N	0.43659	-0.22742	2.03337
C	0.47953	-0.26954	3.21713
S	0.53982	-0.32835	4.87374
O	-0.01123	6.19472	-0.00324
C	1.11614	7.06833	-0.00417
H	1.72924	6.92188	-0.90134
H	0.70517	8.0783	-0.00413
H	1.7304	6.92227	0.89228
O	-9.32328	-1.0463	0.00158
C	-9.77572	-2.39651	0.00247

H	-9.43575	-2.92935	0.89925
H	-10.86503	-2.3442	0.00207
H	-9.43521	-2.93072	-0.89329

14. Optimized coordinates of low-spin and high-spin states of double -CN derivatives.

(a) Optimized coordinates of low-spin double -CN derivatives Fe^{II} complex

Fe	-0.35373	-0.19123	0.00002
N	-0.12822	-2.2265	0.00014
N	-3.46535	-0.05647	-0.00012
N	-6.84013	-1.32264	-0.0001
C	1.01397	-2.92168	0.00022
H	1.92148	-2.33217	0.0002
C	1.04641	-4.31776	0.00032
H	2.00268	-4.82995	0.00038
C	-0.15124	-5.0267	0.00034
H	-0.15922	-6.1121	0.00042
C	-1.34671	-4.31305	0.00026
H	-2.30401	-4.82361	0.00028
C	-1.29304	-2.91892	0.00016
C	-2.46531	-2.06299	0.00007
C	-4.52626	-0.80835	-0.0001
C	-5.91632	-0.34753	-0.00015
C	-6.23426	1.01644	-0.00024
H	-5.44612	1.76022	-0.00028
C	-7.58018	1.37441	-0.00027
H	-7.86802	2.42154	-0.00034
C	-8.54737	0.36966	-0.00021
H	-9.60638	0.60701	-0.00024
C	-8.12418	-0.96317	-0.00013
H	-8.8476	-1.77546	-0.00009
S	-4.16531	-2.57253	0.00002
N	-2.30549	-0.75998	-0.00002
N	-0.34169	-0.1978	1.95266
C	-0.27519	-0.23135	3.13108
S	-0.18388	-0.27403	4.79551
N	-0.58336	1.83216	-0.00008
N	2.76015	-0.31377	0.00009
N	6.13615	0.94775	0.00005
C	-1.73278	2.51783	-0.00012
H	-2.63605	1.92056	-0.00011
C	-1.78162	3.91054	-0.00018
H	-2.73716	4.4219	-0.00021
C	-0.58304	4.63392	-0.0002
C	0.62444	3.92627	-0.00016
H	1.5722	4.45248	-0.00017
C	0.57685	2.53391	-0.00009
C	1.75537	1.68714	-0.00003
C	3.81716	0.4444	0.00006
C	5.20435	-0.02089	0.00008
C	5.51526	-1.38781	0.00012
H	4.72368	-2.12731	0.00015
C	6.85326	-1.75801	0.00013
H	7.1431	-2.8035	0.00016
C	7.83419	-0.75379	0.0001
C	7.415	0.59093	0.00006
H	8.14891	1.39262	0.00003
S	3.45152	2.20587	-0.00004
N	1.59923	0.38209	0.00004
N	-0.34154	-0.19809	-1.95263
C	-0.27501	-0.23284	-3.13101
S	-0.18366	-0.27724	-4.79539
C	-0.58748	6.06789	-0.00029
N	-0.59464	7.23011	-0.00037

C	9.22832	-1.07558	0.0001
N	10.36247	-1.33271	0.00011

(b) Optimized coordinates of high-spin double -CN derivatives Fe^{II} complex

Fe	-0.3938	-0.25958	0.00037
N	-0.51693	-2.54732	0.00191
N	-2.6139	-0.79535	0.00033
N	-3.72312	-0.01246	-0.0003
N	-7.18632	-1.0246	-0.00011
S	-4.59169	-2.47694	0.00116
C	0.52903	-3.37536	0.00262
H	1.50557	-2.89933	0.00254
C	0.39085	-4.76552	0.00338
H	1.27076	-5.40019	0.00394
C	-0.89263	-5.30686	0.00339
H	-1.04217	-6.38223	0.00396
C	-1.99033	-4.4478	0.00265
H	-3.00195	-4.84037	0.00263
C	-1.76152	-3.06879	0.00193
C	-2.84973	-2.08291	0.00113
C	-4.83354	-0.69159	-0.00002
C	-6.18583	-0.12832	-0.00055
C	-6.39082	1.25761	-0.00145
H	-5.54134	1.93059	-0.00176
C	-7.70243	1.72522	-0.0019
H	-7.90316	2.79256	-0.0026
C	-8.74908	0.80315	-0.00145
H	-9.78517	1.1265	-0.00178
C	-8.43643	-0.55964	-0.00057
H	-9.22458	-1.30948	-0.00019
N	-0.35429	-0.22522	2.02032
C	-0.26988	-0.15508	3.20179
S	-0.15185	-0.05683	4.84945
N	-0.30845	2.04833	-0.00106
N	1.84248	0.35976	0.00012
N	2.97487	-0.38298	0.00042
N	6.41151	0.71341	-0.00064
S	3.76623	2.10723	-0.0012
C	-1.38212	2.84012	-0.00141
H	-2.34276	2.33261	-0.00129
C	-1.294	4.23222	-0.00188
H	-2.18759	4.84562	-0.00215
C	-0.02113	4.81685	-0.002
C	1.1096	3.98909	-0.00163
H	2.10334	4.42261	-0.00168
C	0.9193	2.60594	-0.00116
C	2.03838	1.65469	-0.0007
C	4.06253	0.33339	-0.00015
C	5.42552	-0.19988	-0.00005
C	5.65639	-1.58315	0.00063
H	4.81961	-2.27134	0.00107
C	6.97008	-2.03088	0.00069
H	7.19869	-3.09149	0.0012
C	8.00787	-1.08504	0.00008
C	7.66743	0.28151	-0.00058
H	8.4472	1.03879	-0.00106
N	-0.35363	-0.22836	-2.01962
C	-0.26906	-0.16201	-3.20129
S	-0.1508	-0.06901	-4.84925
C	0.12858	6.24401	-0.0025
N	0.24738	7.40009	-0.00292
C	9.38096	-1.48746	0.00012
N	10.49812	-1.81075	0.00016

Electronic Supplementary Material (ESI) for RSC Advances