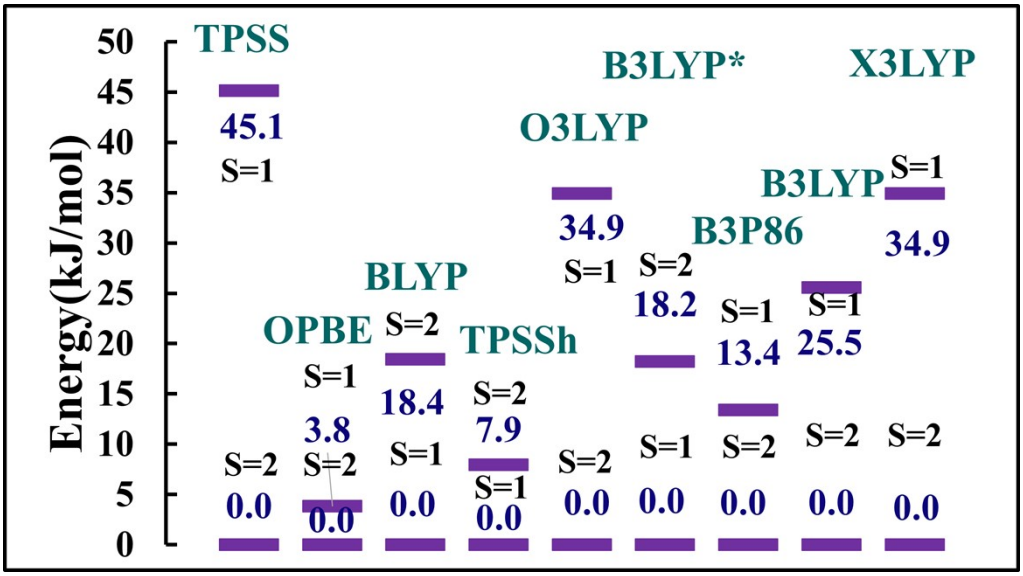
Electronic Supporting Information

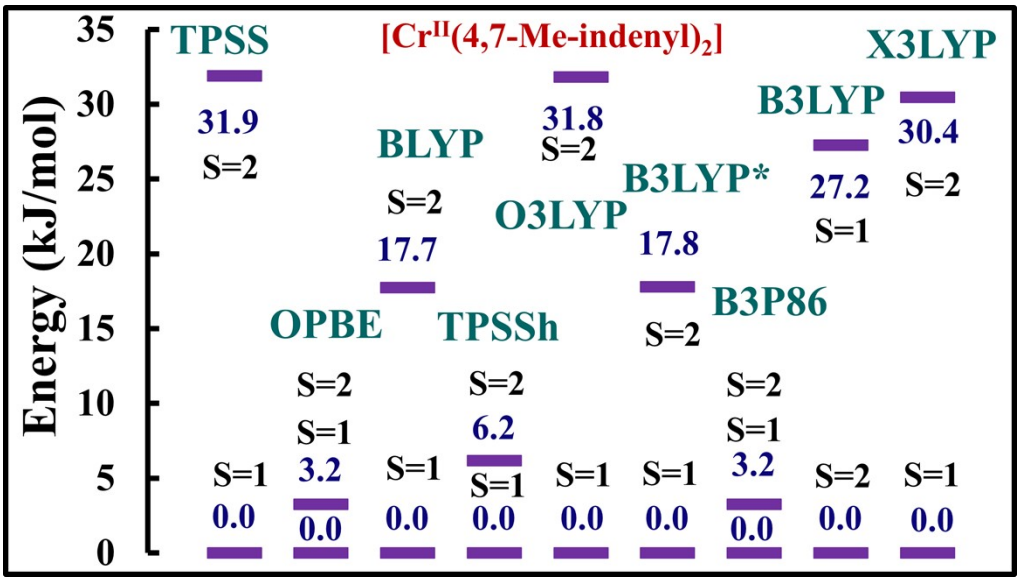
A Systematic Comparison of Density Functional Methods for Determining Spin-state Energy Gaps and Spin Transition Temperature of Spin Crossover Complexes

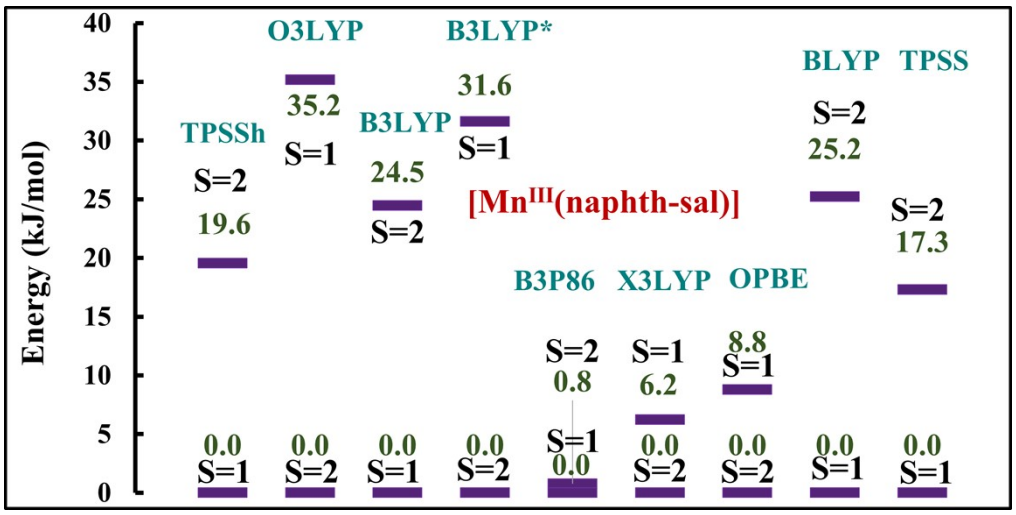
Esha Gera [a], Kuduva R. Vignesh [a, *]

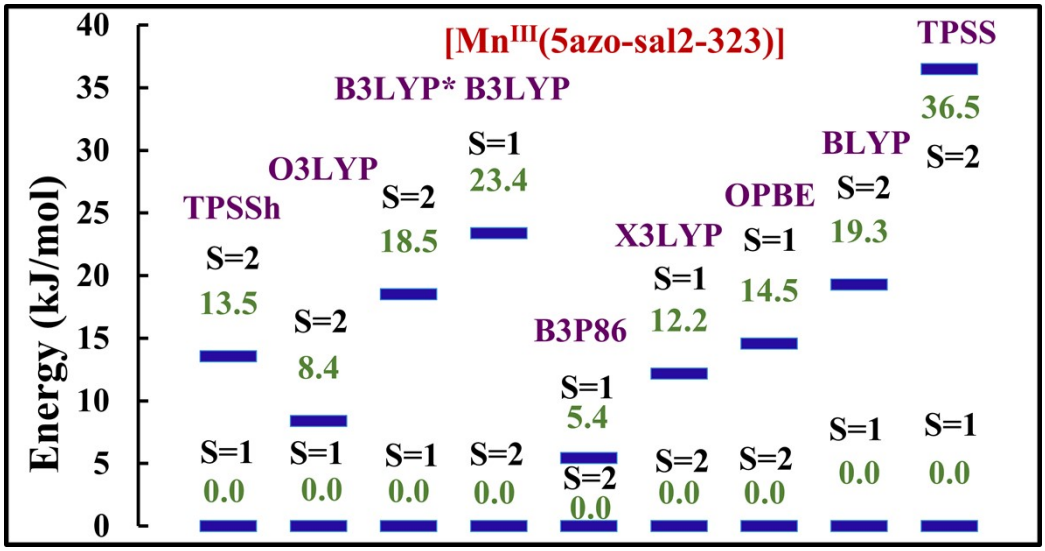
Table S1. Electronic Energy Differences (HS − LS) in kJ/mol for the 26 Systems Studied in this work. (The values in bold and with positive signs are the ones with the correct ground state.)

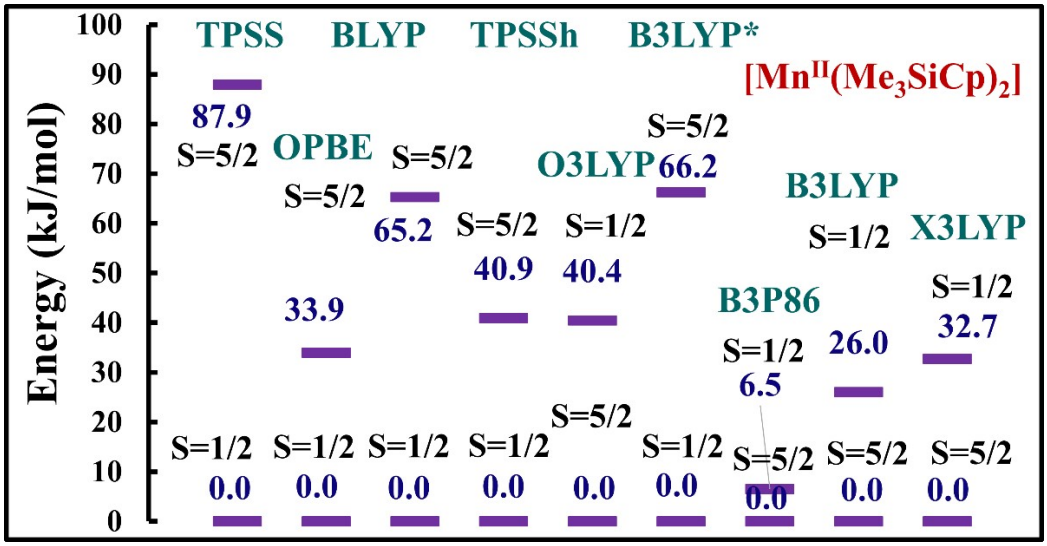
C. No	Molecular formula	OPBE	TPSS	TPSSh	BLYP	B3LYP*	B3LYP	B3P86	O3LYP	X3LYP
1	[Cr(1,3-Si-indenyl)$_2$]	−3.8	**45.2**	**7.9**	**18.4**	**18.2**	−25.5	−13.4	−3.8	−34.9
2	[Cr(4,7-Me-indenyl)$_2$]	**3.23**	**31.9**	**6.2**	**17.7**	**17.8**	−27.2	**3.2**	−31.8	−30.4
3	[Mn(naphth-sal-1,5,8,12)]	−8.8	**17.3**	**19.6**	**25.2**	**31.6**	−24.5	**0.8**	−35.2	−6.2
4	[Mn(5azo-sal2-323)](Cl)	−14.5	**36.5**	**13.5**	**19.3**	**18.5**	−23.4	−5.4	**8.4**	−12.2
5	[Mn(Me_3SiCp)$_2$]	**33.9**	**87.9**	**40.9**	**65.2**	**66.2**	−26	−6.5	−40.4	−32.6
6	[Mn(1,3-(tBu)$_2$Cp)$_2$]	**25.2**	**93.8**	**43.6**	**70.7**	**70.1**	−20.5	−1.6	−39.9	−27.3
7	[Fe(bztpen)(OEtg)](PF$_6$)$_2$	−18.6	**79.5**	**29.9**	**48.9**	**48.8**	−17.7	−1.4	−64.5	−26.2
8	[Fe(bztpen)(OButn)](PF$_6$)$_2$	−17.6	**78.2**	**0.5**	**49.5**	**49.5**	−17.5	**0.6**	−62.9	−26.2
9	[Fe(bztpen)(OProp)](PF$_6$)$_2$	−17.7	**83.9**	**32.4**	**50.1**	**50.1**	−12.6	**1.5**	−62.7	−23.4
10	[Fe(2amp)$_3$]Cl$_2$	**7.6**	**82.2**	**34.6**	**54.1**	**10.7**	−6.7	**1.9**	−62.6	**19.2**
11	[Fe(tacn)$_2$](OTf)$_2$	−10.3	**76.2**	**29.1**	**53.4**	**51.6**	−11.2	−1.1	−50.4	−17.9
12	[Fe($L^{OMe\text{-}Nap}$)$_2$(NCS)$_2$]	−19.5	**57.8**	**10.2**	**36.6**	**38.4**	−45.2	−22	−74.2	−45.2
13	[Fe (L^{npdtz})$_2$(NCS)$_2$]	−21.5	**54.7**	**9.3**	**35.4**	**38.1**	**38.1**	−22.9	−55.1	−46.2
14	[Fe (L^{npdtz})$_2$($NCSe$)$_2$]	−16.3	**58.5**	**15.7**	**43**	**44.2**	−46.0	**225.5**	**155.5**	−38.7
15	[Fe(bpte)(bim)]X$_2$	**16.3**	**82.1**	**19.3**	**56.1**	**54.6**	−25.5	−13.0	−55.3	−38.2
16	[Fe(H-ptp$^-$)$_2$]^0	**57.8**	**120.2**	**51.4**	**92.9**	**92**	−3.3	**12.2**	−22.6	−15.5
17	[Fe(CH_2OH-ptp$^-$)$_2$]^0	**55.7**	**109.2**	**49.6**	**91.2**	**89.8**	−5.7	**10.0**	−25.0	−17.2
18	[Fe($COOCH_3$-ptp$^-$)$_2$]^0	**55.7**	**125.2**	**49.6**	**97.7**	**89.8**	−5.7	**10.0**	−25.0	−17.2
19	[Fe($L^{OMe\text{-}Nap}$)$_2$($NCBH_3$)$_2$]	**11.9**	**84.9**	**34.6**	**68.7**	**69.1**	−23.4	**0.02**	−49.6	−24
20	[Fe(L^{Nap})$_2$($NCBH_3$)$_2$]	**11.0**	**83.1**	**34.3**	**68.1**	**78.4**	−26.9	−0.2	−49.9	−24.3
21	[Fe(bpte)($NCBH_3$)$_2$]	**19.5**	**71.6**	**17.2**	**42.3**	**41.3**	−35.8	−18.2	−57.5	−46.3
22	[Fe(H_2L^1)$_2$] (BF_4)$_2$·*x*(solv.)	**23.2**	**101.2**	**30.6**	**68.5**	**67.1**	−15.2	−6.3	−47.8	−31.6
23	[Co(L)$_2$] (ClO_4)$_2$	**31.3**	**54.4**	**15.9**	**43.9**	**43.5**	**7.2**	**6.7**	**15.9**	−8.9
24	[Co(L)($N(CN)_2$)$_2$]	−17.3	**30.1**	−0.8	**30.1**	**28.1**	−8.9	−4.7	−14.8	−17.9
25	[Co(Brphtpy)$_2$](OTf)$_2$·DMF·2H_2O	**36.6**	**57.4**	**12.0**	**49.9**	**49.3**	−1.5	**0.4**	−11.1	−16.1
26	[Co(tppz)$_2$](tcm)$_2$	**36.4**	**60.7**	**13.7**	**52.3**	**51.9**	−1.6	**12.8**	**4.7**	−0.9

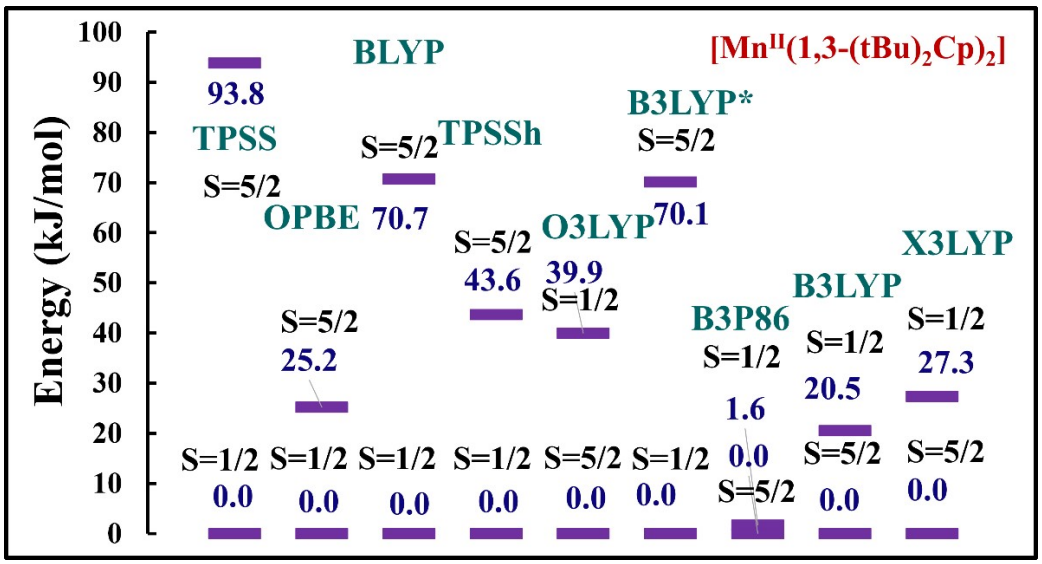

Energy(kJ/mol)
50
45
40
35
30
25
20
15
10
5
0
TPSS
45.1
S=1
B3LYP*
O3LYP
34.9
S=1
X3LYP
B3LYP
S=1
34.9
B3P86
S=2
18.2
S=1
13.4
S=1
25.5
S=2
S=2
BLYP
S=2
18.4
TPSSh
S=2
7.9
S=1
OPBE
S=1
3.8
S=2
S=2
0.0
0.0
S=1
0.0
S=2
0.0
S=1
0.0
S=2
0.0
S=2
0.0
0.0
0.0
0.0

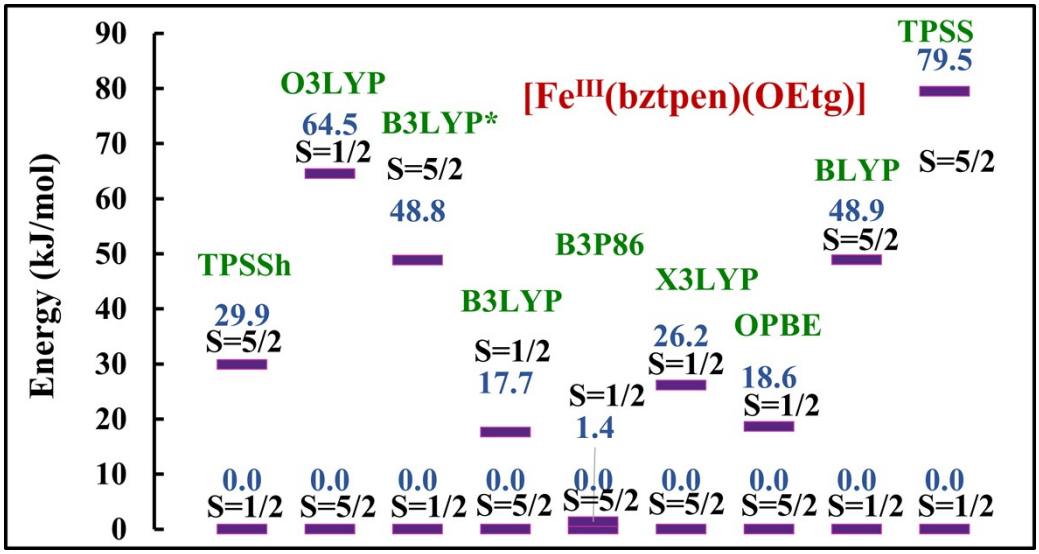

Energy (kJ/mol)
35
30
25
20
15
10
5
0
TPSS
31.9
S=2
[Cr^II(4,7-Me-indenyl)2]
31.8
S=2
X3LYP
B3LYP
30.4
S=2
27.2
S=1
BLYP
S=2
17.7
B3LYP*
O3LYP
17.8
S=2
B3P86
OPBE
TPSSh
S=2
S=1
3.2
S=2
S=2
6.2
S=1
S=2
S=1
3.2
S=1
S=1
S=1
S=1
S=2
S=1
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0

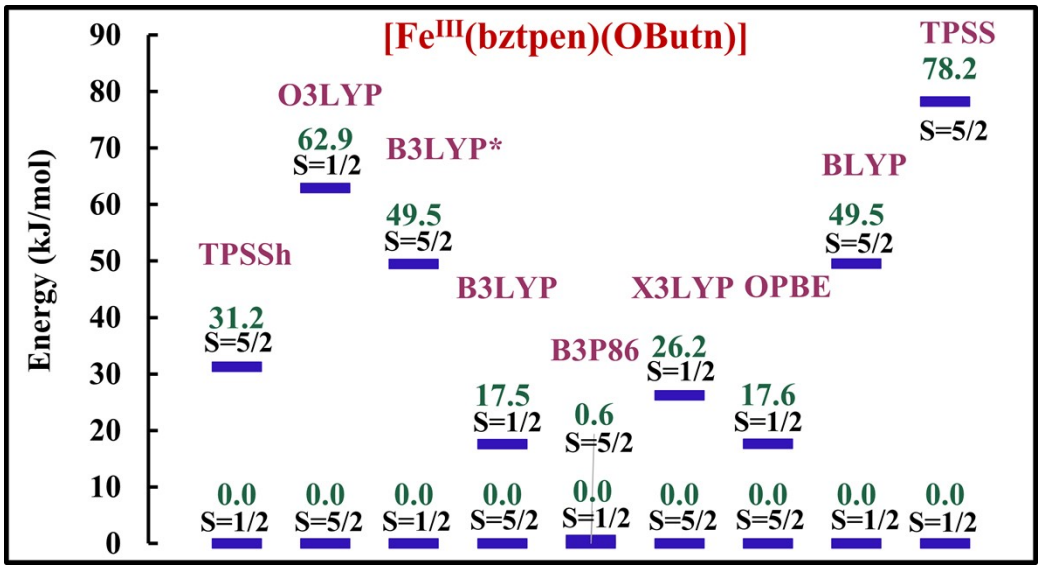

Energy (kJ/mol)
40
35
30
25
20
15
10
5
0
O3LYP
B3LYP*
BLYP
TPSS
TPSSh
35.2
S=1
31.6
S=1
B3LYP
S=2
24.5
S=2
S=2
25.2
S=2
17.3
19.6
S=2
[Mn^III(naphth-sal)]
B3P86
X3LYP
OPBE
S=2
0.8
S=1
6.2
8.8
S=1
0.0
S=1
0.0
S=2
0.0
S=2
0.0
S=1
0.0
S=2
0.0
S=1
0.0
S=1
0.0
S=2
0.0
S=1
0.0
S=2
0.0
S=2
0.0
S=1
0.0
S=1

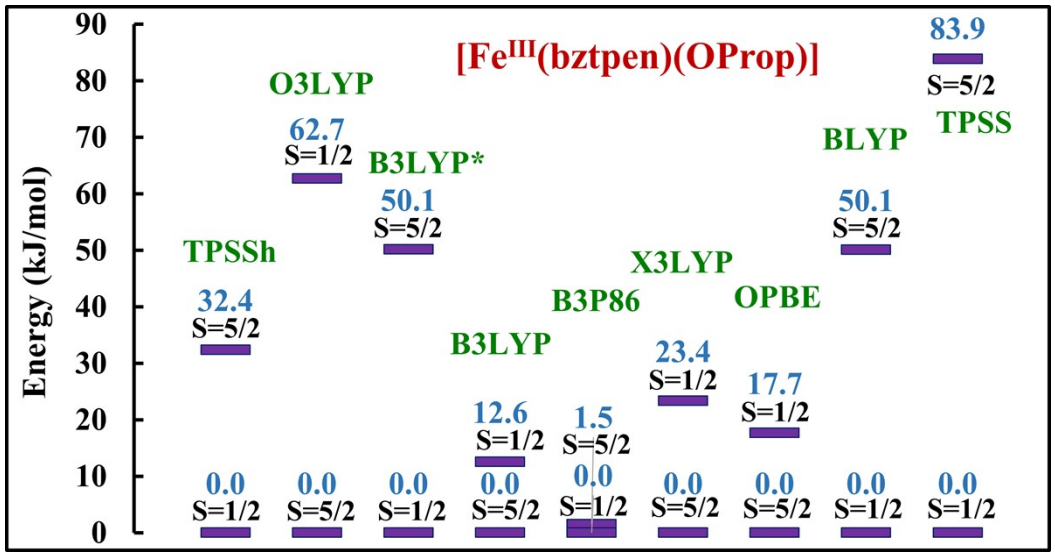

[Mn^III(5azo-sal2-323)]
Energy (kJ/mol)
TPSSh
S=2
13.5
S=1
0.0
O3LYP
S=2
8.4
S=1
0.0
B3LYP*
S=2
18.5
S=1
0.0
B3LYP
S=1
23.4
S=2
0.0
B3P86
S=1
5.4
S=2
0.0
X3LYP
S=1
12.2
S=2
0.0
OPBE
S=1
14.5
S=2
0.0
BLYP
S=2
19.3
S=1
0.0
TPSS
S=2
36.5
S=1
0.0

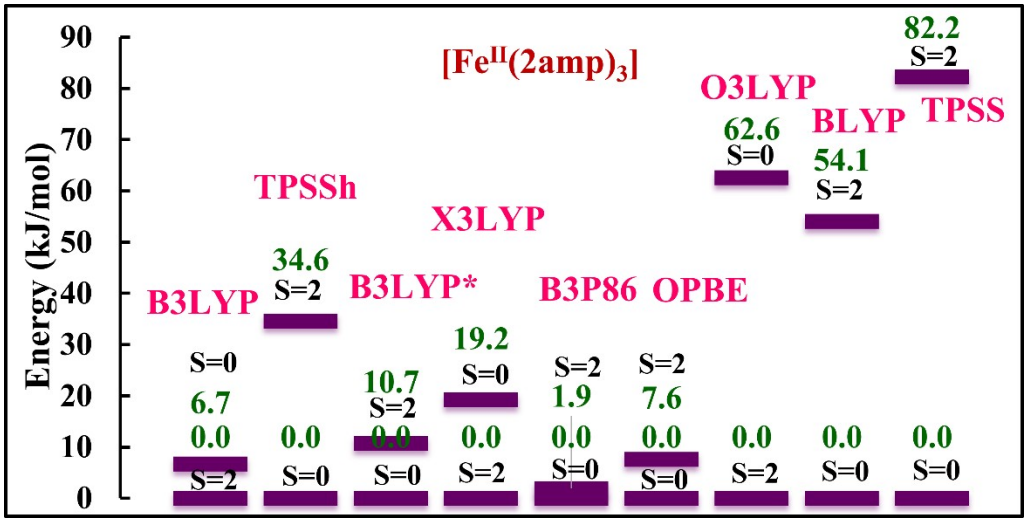

[Mn^II(Me3SiCp)2]
Energy (kJ/mol)
TPSS
S=5/2
87.9
S=1/2
0.0
BLYP
S=5/2
65.2
S=1/2
0.0
TPSSh
S=5/2
40.9
S=1/2
0.0
B3LYP*
S=5/2
66.2
S=1/2
0.0
OPBE
S=5/2
33.9
S=1/2
0.0
O3LYP
S=1/2
40.4
S=5/2
0.0
B3P86
S=1/2
6.5
S=5/2
0.0
B3LYP
S=1/2
26.0
S=5/2
0.0
X3LYP
S=1/2
32.7
S=5/2
0.0

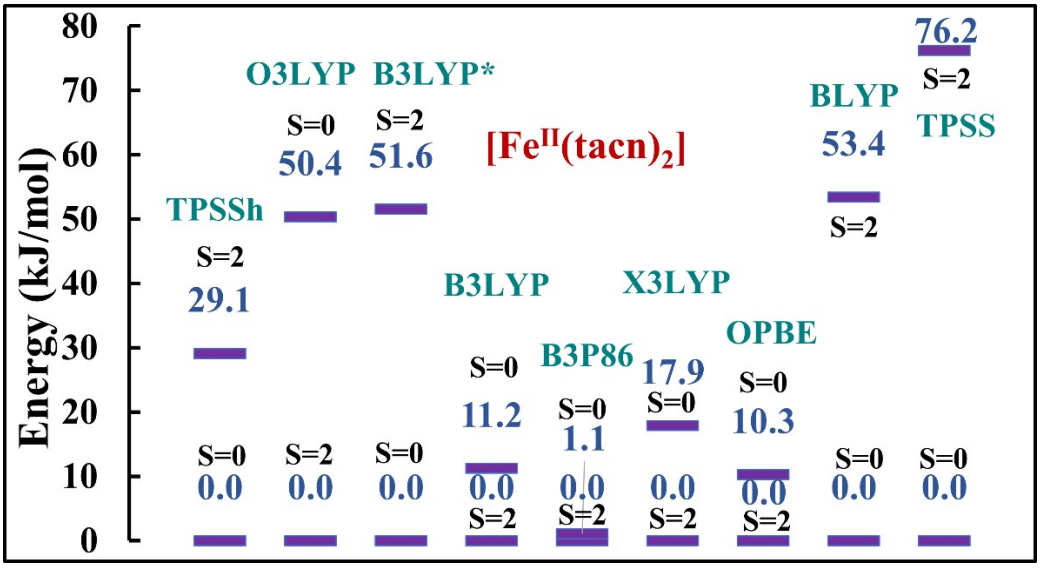

[Mn^II(1,3-(tBu)2Cp)2]
Energy (kJ/mol)
TPSS
S=5/2
93.8
S=1/2
0.0
BLYP
S=5/2
70.7
S=1/2
0.0
TPSSh
S=5/2
43.6
S=1/2
0.0
B3LYP*
S=5/2
70.1
S=1/2
0.0
OPBE
S=5/2
25.2
S=1/2
0.0
O3LYP
S=1/2
39.9
S=5/2
0.0
B3P86
S=1/2
1.6
S=5/2
0.0
B3LYP
S=1/2
20.5
S=5/2
0.0
X3LYP
S=1/2
27.3
S=5/2
0.0

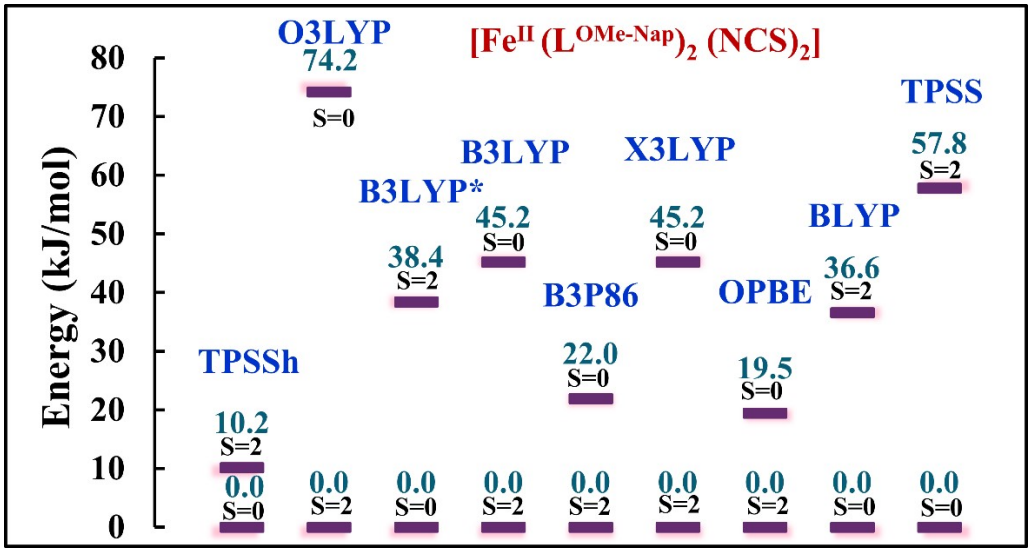

[Fe^III(bztpen)(OEtg)]
Energy (kJ/mol)
90
80
70
60
50
40
30
20
10
0
TPSS
79.5
S=5/2
O3LYP
64.5
S=1/2
B3LYP*
S=5/2
BLYP
48.8
48.9
S=5/2
B3P86
TPSSh
X3LYP
B3LYP
OPBE
29.9
S=5/2
26.2
S=1/2
S=1/2
17.7
18.6
S=1/2
S=1/2
1.4
0.0 S=1/2
0.0 S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=5/2
0.0 S=5/2
0.0 S=5/2
0.0 S=1/2
0.0 S=1/2

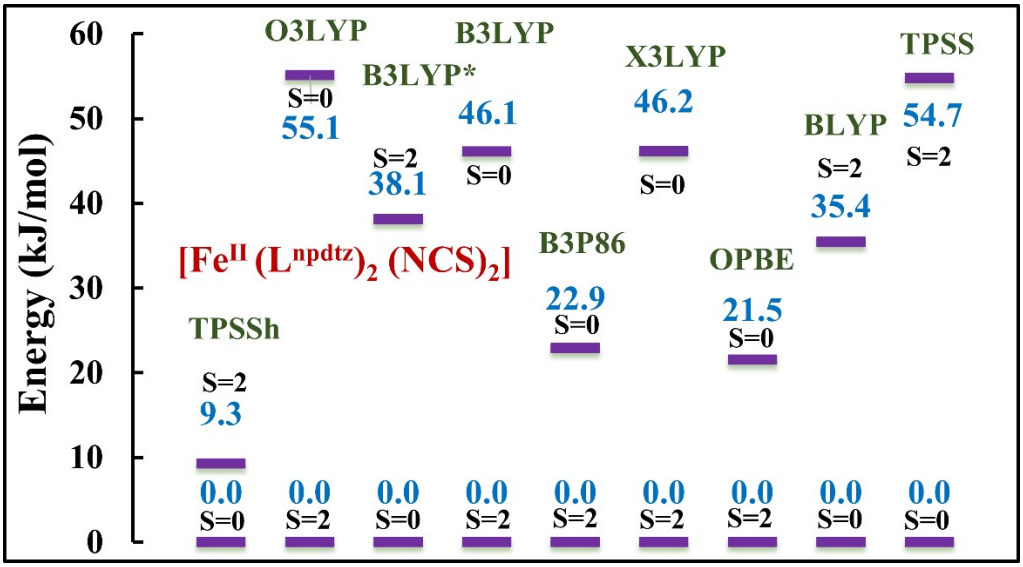

[Fe^III(bztpen)(OButn)]
Energy (kJ/mol)
90
80
70
60
50
40
30
20
10
0
TPSS
78.2
S=5/2
O3LYP
62.9
S=1/2
B3LYP*
BLYP
49.5
S=5/2
49.5
S=5/2
TPSSh
B3LYP
X3LYP
OPBE
31.2
S=5/2
B3P86
26.2
S=1/2
17.5
S=1/2
0.6
S=5/2
17.6
S=1/2
0.0 S=1/2
0.0 S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=5/2
0.0 S=1/2
0.0 S=1/2

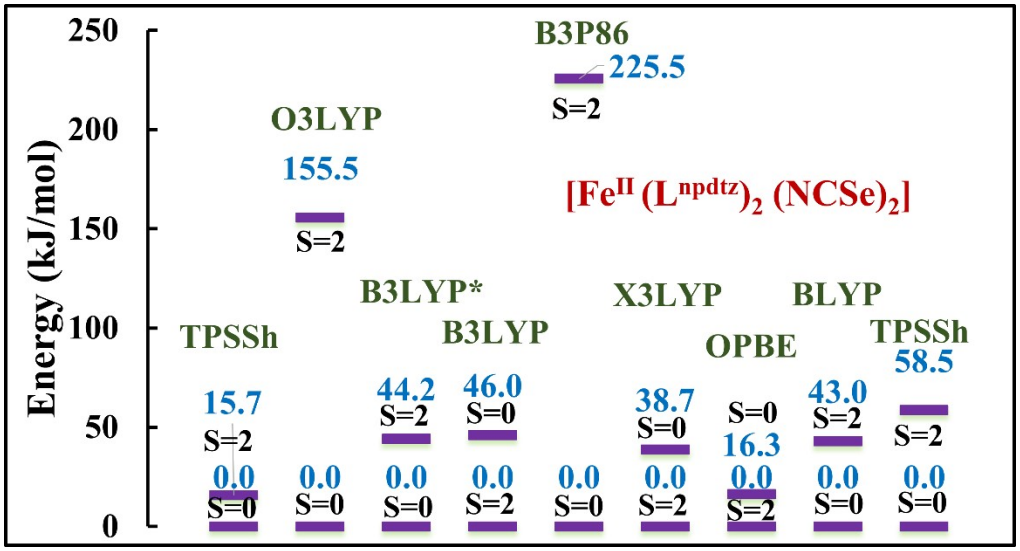

[Fe^III(bztpen)(OProp)]
Energy (kJ/mol)
90
80
70
60
50
40
30
20
10
0
83.9
S=5/2
TPSS
O3LYP
62.7
S=1/2
BLYP
B3LYP*
50.1
S=5/2
50.1
S=5/2
TPSSh
X3LYP
B3P86
OPBE
32.4
S=5/2
B3LYP
23.4
S=1/2
17.7
S=1/2
12.6
S=1/2
1.5
S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=1/2
0.0 S=5/2
0.0 S=5/2
0.0 S=1/2
0.0 S=1/2

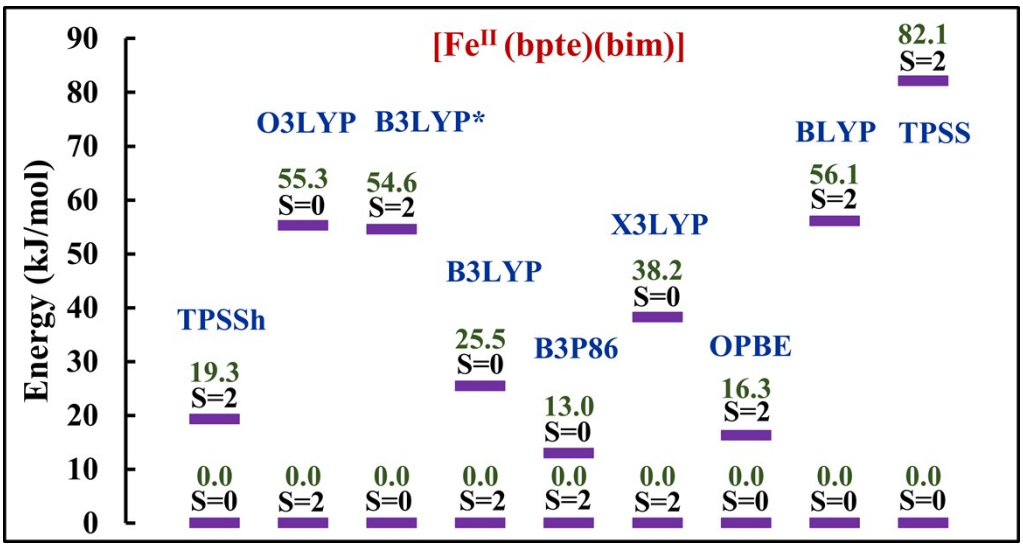

[Fe^II(2amp)3]
Energy (kJ/mol)
B3LYP
TPSSh
B3LYP*
X3LYP
B3P86
OPBE
O3LYP
BLYP
TPSS
S=0
S=2
6.7
0.0
34.6
10.7
19.2
1.9
7.6
62.6
54.1
82.2

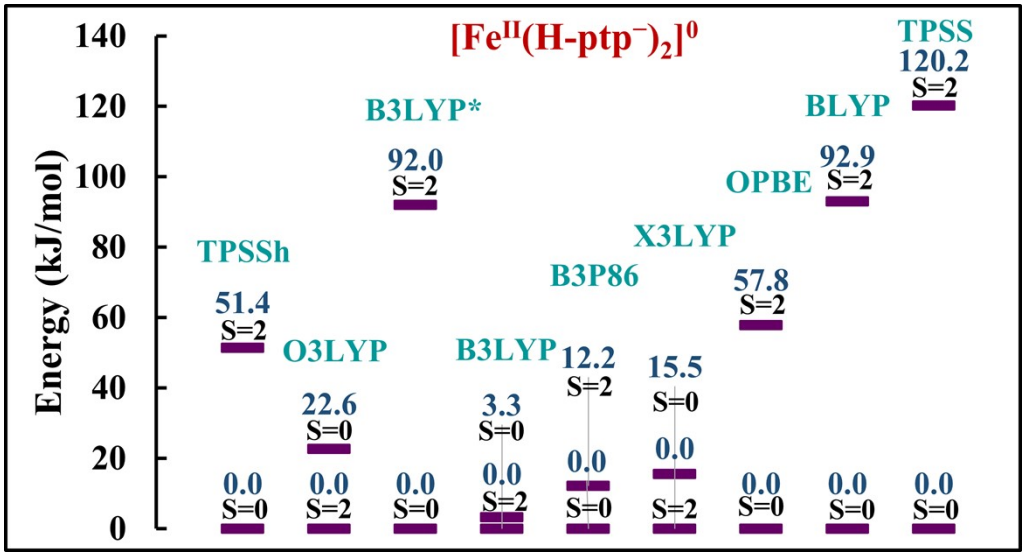

[Fe^II(tacn)2]
Energy (kJ/mol)
O3LYP
B3LYP*
TPSSh
B3LYP
X3LYP
B3P86
OPBE
BLYP
TPSS
S=0
S=2
50.4
51.6
29.1
11.2
1.1
17.9
10.3
53.4
76.2
0.0

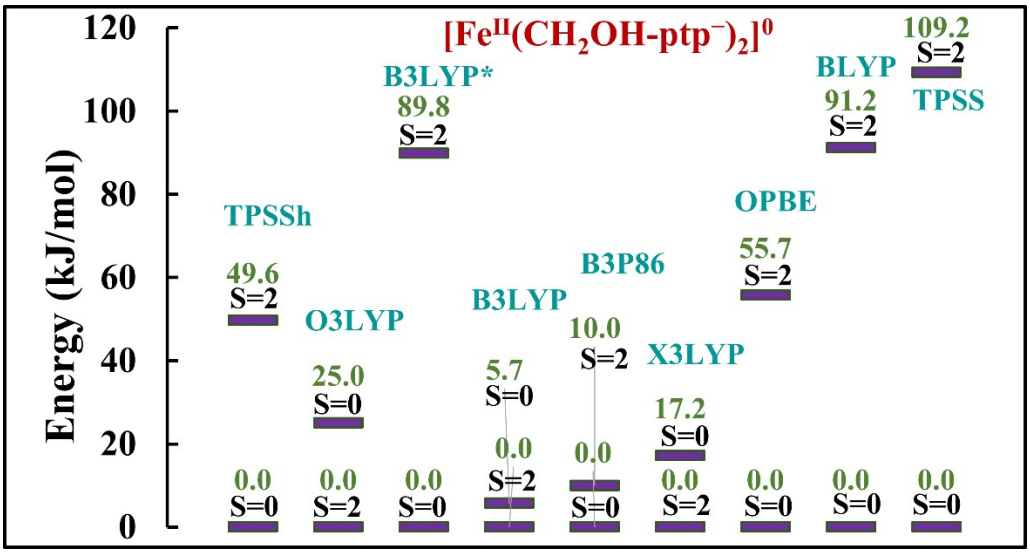

[Fe^II (L^OMe-Nap)2 (NCS)2]
Energy (kJ/mol)
O3LYP
TPSSh
B3LYP
B3LYP*
X3LYP
B3P86
OPBE
BLYP
TPSS
S=0
S=2
74.2
10.2
38.4
45.2
22.0
19.5
36.6
57.8
0.0

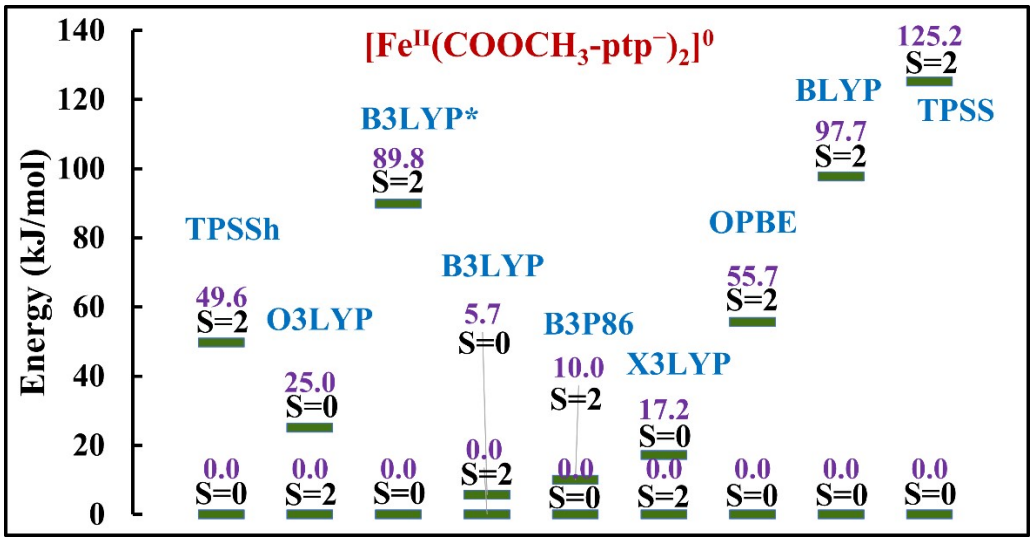

Energy (kJ/mol)
60
50
40
30
20
10
0
[Fe^II (L^npdtz)_2 (NCS)_2]
O3LYP
S=0
55.1
B3LYP*
S=2
38.1
B3LYP
46.1
S=0
B3P86
22.9
S=0
X3LYP
46.2
S=0
OPBE
21.5
S=0
BLYP
S=2
35.4
TPSS
54.7
S=2
TPSSh
S=2
9.3
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0

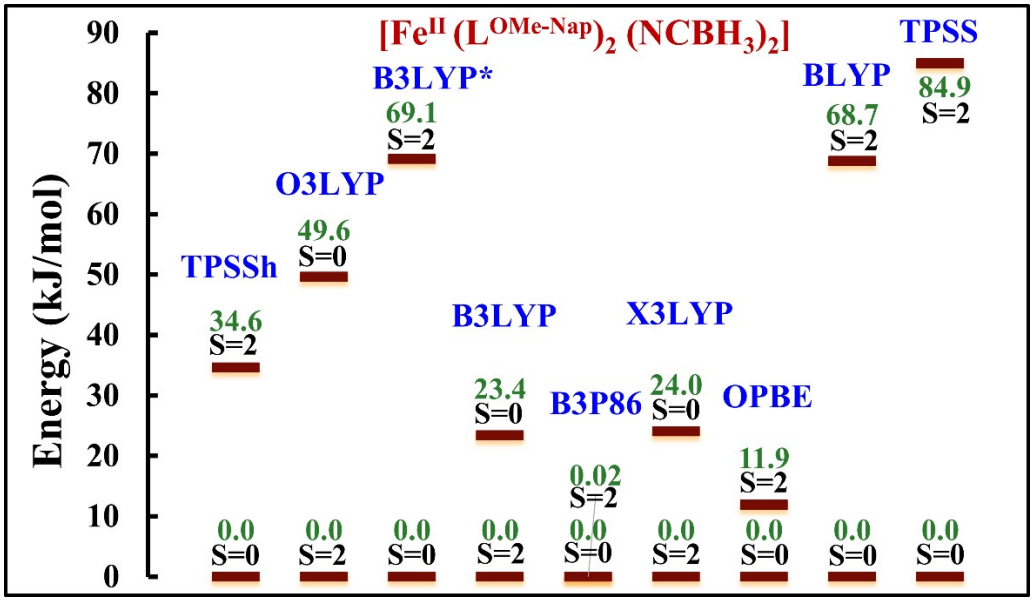

Energy (kJ/mol)
250
200
150
100
50
0
[Fe^II (L^npdtz)_2 (NCSe)_2]
B3P86
225.5
S=2
O3LYP
155.5
S=2
B3LYP*
44.2
S=2
B3LYP
46.0
S=0
X3LYP
38.7
S=0
OPBE
S=0
16.3
S=2
BLYP
43.0
S=2
TPSSh
58.5
S=2
TPSSh
15.7
S=2
0.0 S=0
0.0 S=0
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0

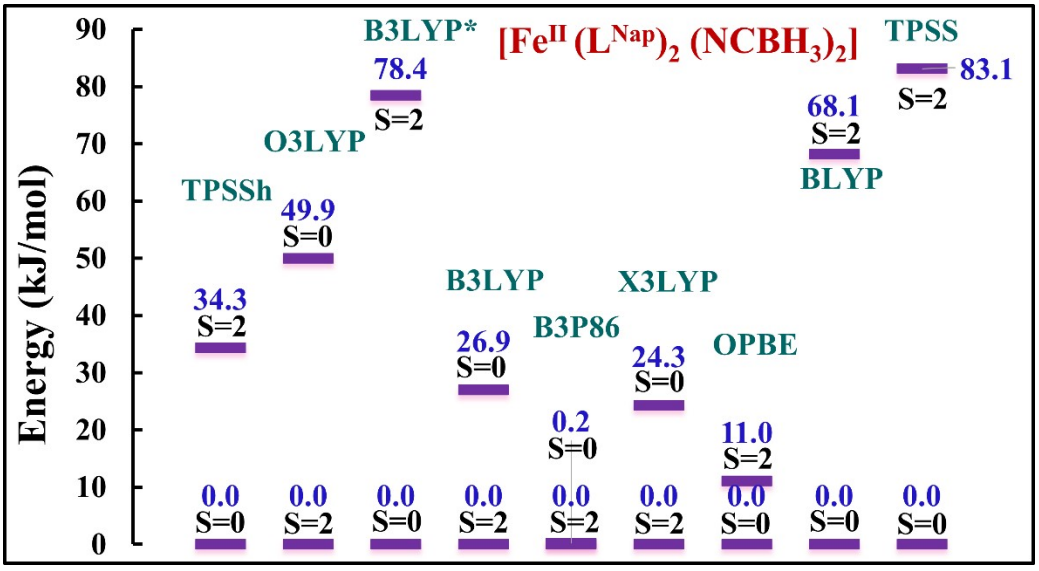

Energy (kJ/mol)
90
80
70
60
50
40
30
20
10
0
[Fe^II (bpte)(bim)]
O3LYP
55.3
S=0
B3LYP*
54.6
S=2
B3LYP
25.5
S=0
B3P86
13.0
S=0
X3LYP
38.2
S=0
OPBE
16.3
S=2
BLYP
56.1
S=2
TPSS
82.1
S=2
TPSSh
19.3
S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0

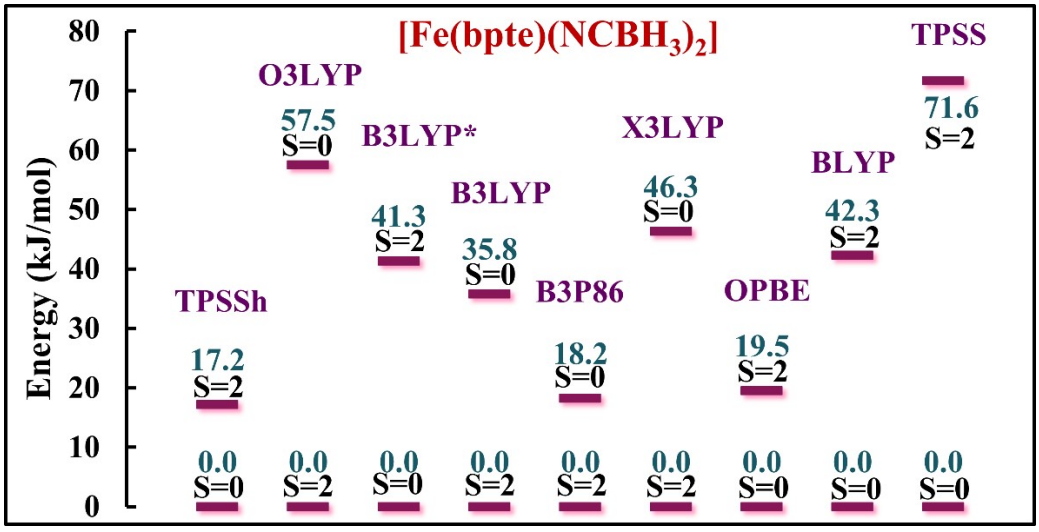

[Fe^II(H-ptp^-)2]^0
Energy (kJ/mol)
140
120
100
80
60
40
20
0
TPSSh
51.4
S=2
O3LYP
22.6
S=0
B3LYP*
92.0
S=2
B3LYP
3.3
S=0
0.0
S=2
B3P86
12.2
S=2
0.0
S=0
X3LYP
15.5
S=0
0.0
S=2
OPBE
57.8
S=2
BLYP
92.9
S=2
TPSS
120.2
S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0
0.0 S=0

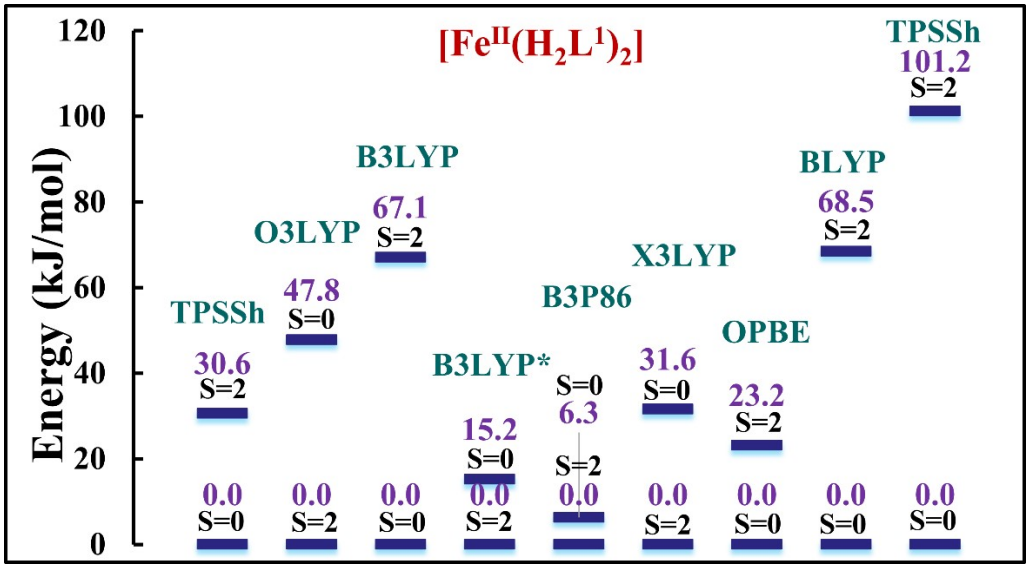

[Fe^II(CH2OH-ptp^-)2]^0
Energy (kJ/mol)
120
100
80
60
40
20
0
TPSSh
49.6
S=2
O3LYP
25.0
S=0
B3LYP*
89.8
S=2
B3LYP
5.7
S=0
0.0
S=2
B3P86
10.0
S=2
0.0
S=0
X3LYP
17.2
S=0
0.0
S=2
OPBE
55.7
S=2
BLYP
91.2
S=2
TPSS
109.2
S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0
0.0 S=0

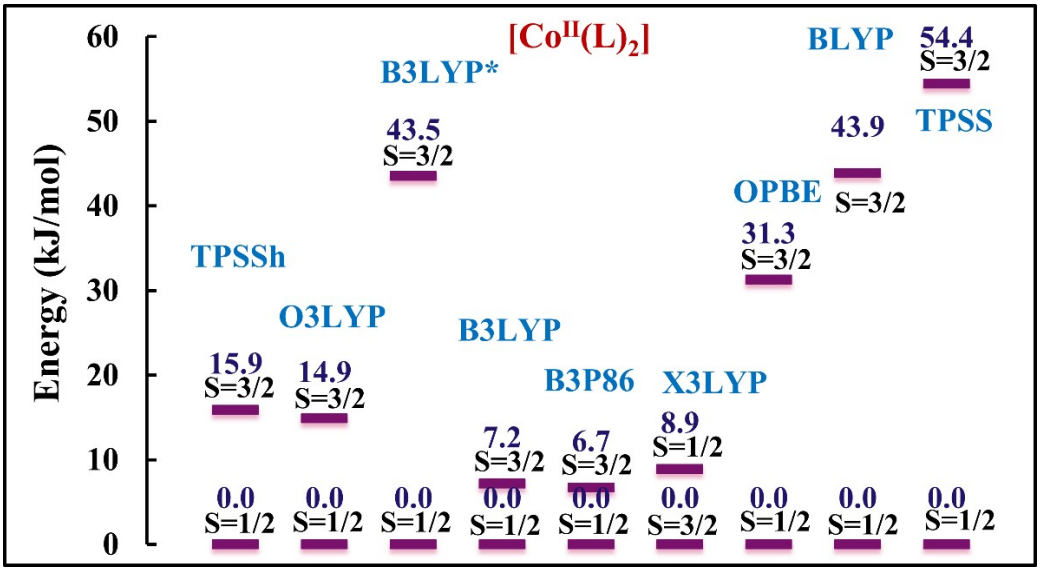

[Fe^II(COOCH3-ptp^-)2]^0
Energy (kJ/mol)
140
120
100
80
60
40
20
0
TPSSh
49.6
S=2
O3LYP
25.0
S=0
B3LYP*
89.8
S=2
B3LYP
5.7
S=0
0.0
S=2
B3P86
10.0
S=2
0.0
S=0
X3LYP
17.2
S=0
0.0
S=2
OPBE
55.7
S=2
BLYP
97.7
S=2
TPSS
125.2
S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0
0.0 S=0

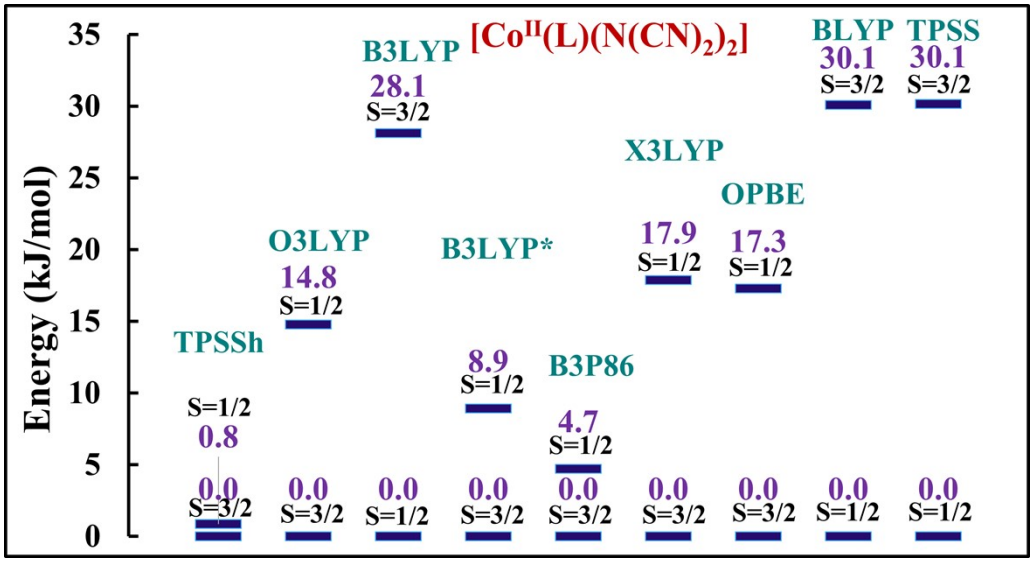

[Fe^II (L^OMe-Nap)2 (NCBH3)2]
Energy (kJ/mol)
TPSSh
34.6 S=2
O3LYP
49.6 S=0
B3LYP*
69.1 S=2
B3LYP
23.4 S=0
B3P86
0.02 S=2
X3LYP
24.0 S=0
OPBE
11.9 S=2
BLYP
68.7 S=2
TPSS
84.9 S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0


[Fe^II (L^Nap)2 (NCBH3)2]
Energy (kJ/mol)
TPSSh
34.3 S=2
O3LYP
49.9 S=0
B3LYP*
78.4 S=2
B3LYP
26.9 S=0
B3P86
0.2 S=0
X3LYP
24.3 S=0
OPBE
11.0 S=2
BLYP
68.1 S=2
TPSS
83.1 S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0


[Fe(bpte)(NCBH3)2]
Energy (kJ/mol)
TPSSh
17.2 S=2
O3LYP
57.5 S=0
B3LYP*
41.3 S=2
B3LYP
35.8 S=0
B3P86
18.2 S=0
X3LYP
46.3 S=0
OPBE
19.5 S=2
BLYP
42.3 S=2
TPSS
71.6 S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0


[Fe^II(H2L^1)2]
Energy (kJ/mol)
120
100
80
60
40
20
0
TPSSh
101.2
S=2
BLYP
68.5
S=2
B3LYP
67.1
S=2
O3LYP
47.8
S=0
X3LYP
B3P86
OPBE
TPSSh
30.6
S=2
B3LYP*
15.2
S=0
S=0
6.3
S=2
31.6
S=0
23.2
S=2
0.0 S=0
0.0 S=2
0.0 S=0
0.0 S=2
0.0 S=2
0.0 S=0
0.0 S=0
0.0 S=0


[Co^II(L)2]
Energy (kJ/mol)
60
50
40
30
20
10
0
BLYP
54.4
S=3/2
B3LYP*
43.5
S=3/2
TPSS
43.9
S=3/2
OPBE
31.3
S=3/2
TPSSh
O3LYP
B3LYP
15.9
S=3/2
14.9
S=3/2
B3P86
X3LYP
7.2
S=3/2
6.7
S=3/2
8.9
S=1/2
0.0 S=1/2
0.0 S=1/2
0.0 S=1/2
0.0 S=1/2
0.0 S=1/2
0.0 S=3/2
0.0 S=1/2
0.0 S=1/2
0.0 S=1/2


[Co^II(L)(N(CN)2)2]
Energy (kJ/mol)
35
30
25
20
15
10
5
0
B3LYP
28.1
S=3/2
BLYP
30.1
S=3/2
TPSS
30.1
S=3/2
X3LYP
OPBE
O3LYP
14.8
S=1/2
B3LYP*
17.9
S=1/2
17.3
S=1/2
TPSSh
S=1/2
0.8
8.9
S=1/2
B3P86
4.7
S=1/2
0.0 S=3/2
0.0 S=3/2
0.0 S=1/2
0.0 S=3/2
0.0 S=3/2
0.0 S=3/2
0.0 S=3/2
0.0 S=1/2
0.0 S=1/2

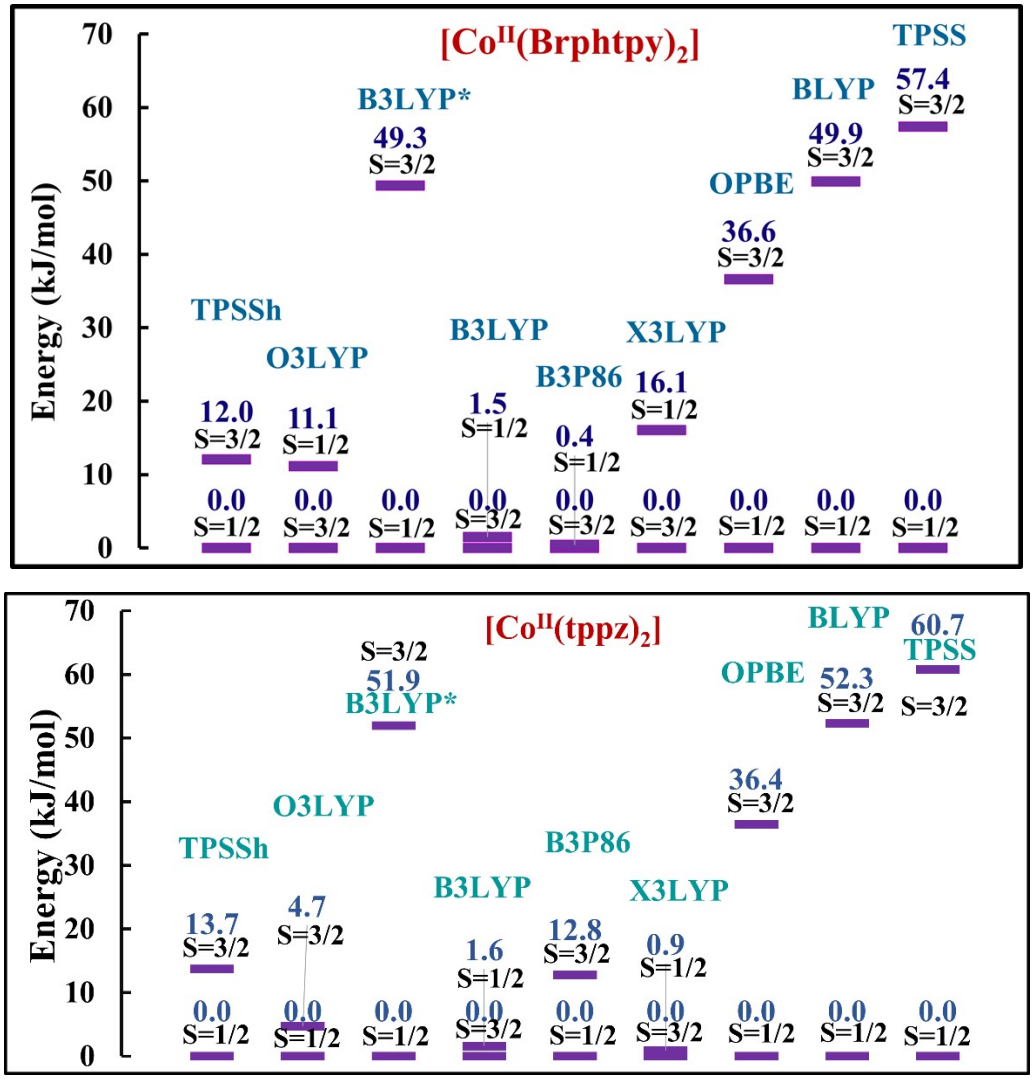


Figure S1: The energy difference between two spin states, expressed in kJ mol^{-1}, was calculated for each of the 26 complexes using OPBE, TPSS, TPSSh, O3LYP, B3LYP*, BLYP, B3LYP, B3P86, and X3LYP.

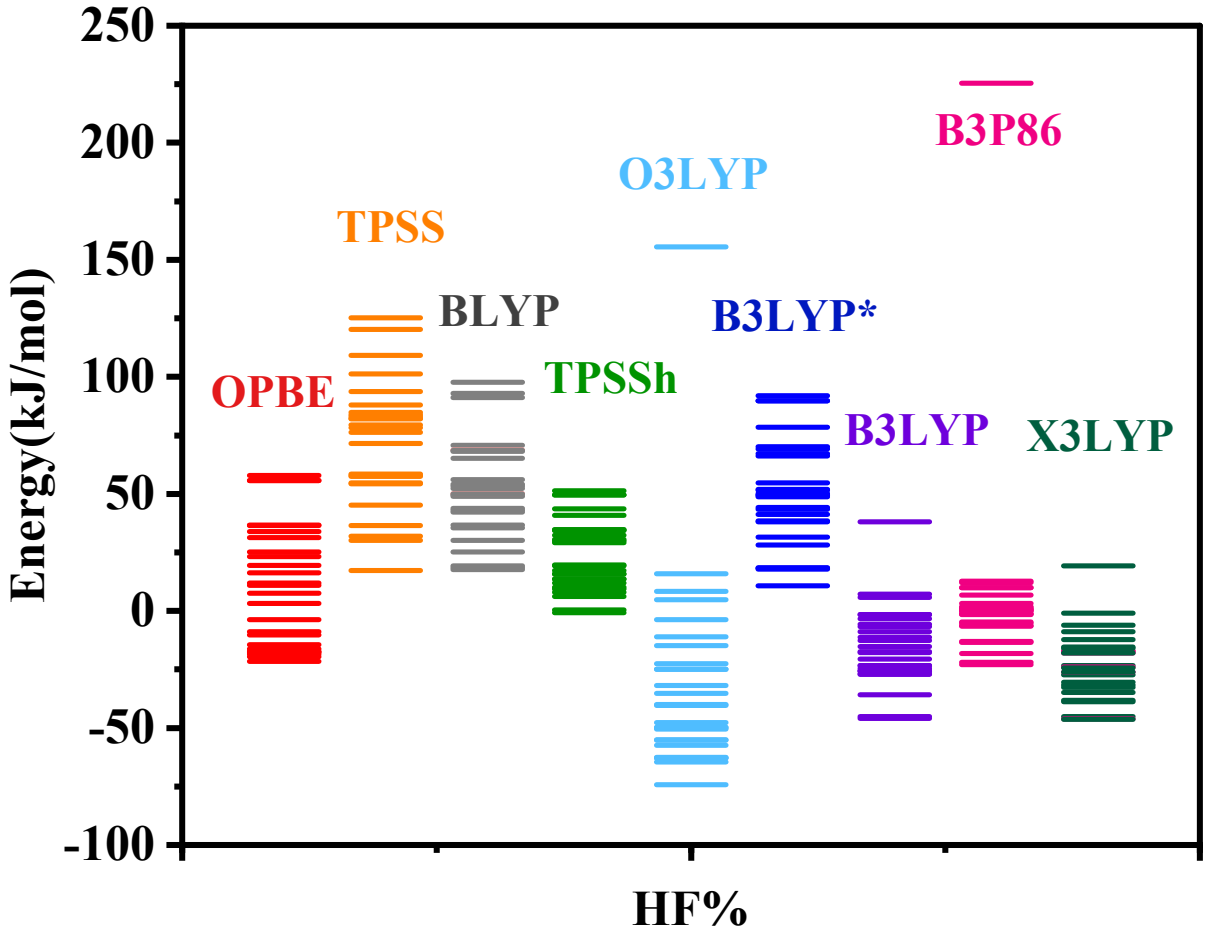


Figure S2. Energy difference (HS − LS) for the 26 studied systems plotted against the amount of exact Hartree−Fock mixed into the corresponding exchange-correlation functional.

Table S2. Computed transition temperatures ($T_{1/2}$) in K, enthalpy and entropy differences ($\Delta H = H_{HS}-H_{LS}$) in kcal/mol and ($\Delta S = S_{HS}-S_{HS}$) in cal/K.mol for the 26 studied systems, using the TPSSh functional and 12 systems for which the B3P86 functional predicted correct GS, together with the experimental transition temperatures and computed transition temperatures.

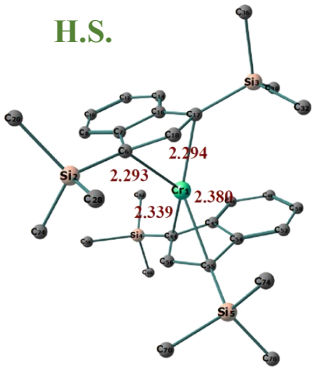
Complex No.	Molecular formula	$T_{1/2\ Exp}$	TPSSh			B3P86		
			ΔH	ΔS	$T_{1/2}$	ΔH	ΔS	$T_{1/2}$
1	$[Cr(1,3\text{-Si-indenyl})_2]$	350	2.47	10.37	239	---	---	---
2	$[Cr(4,7\text{-Me-indenyl})_2]$	250	2.02	6.61	266	3.24	6.45	503
3	[Mn(naphth-sal-1,5,8,12)]	164	5.61	10.7	521	1.03	10.1	103
4	[Mn(5azo-sal2-323)]	560	4.12	10.2	406	---	---	---
5	$[Mn(Me_3SiCp)_2]$	125	10.83	14.9	724	---	---	---
6	$[Mn(1,3\text{-}(tBu)_2Cp)_2]$	314, 327	11.7	20.4	574	---	---	---
7	$[Fe(bztpen)(OEtg)](PF_6)_2$	284	8.32	14.3	580	---	---	---
8	$[Fe(bztpen)(OButn)](PF_6)_2$	282	8.69	17.4	497	1.25	17.5	73
9	$[Fe(bztpen)(OProp)](PF_6)_2$	255	8.94	15.6	570	1.42	14.6	97
10	$[Fe(2amp)_3]Cl_2$	196	6.83	20	341	0.98	18.5	53
11	$[Fe(tacn)_2](OTf)_2$	330	8.22	14.7	558	---	---	---
12	$[Fe(L^{OMe\text{-}Nap})_2(NCS)_2]$	100	3.70	22.5	164	---	---	---
13	$[Fe\ (L^{npdtz})_2(NCS)_2]$	110	3.48	22.8	153	---	---	---
14	$[Fe\ (L^{npdtz})_2(NCSe)_2]$	154	5.0	22.0	229	55.8	17.2	324
15	$[Fe(bpte)(bim)]X_2$	330	5.8	15.4	375	---	---	---
16	$[Fe(H\text{-}ptp^-)_2]^0$	296	13.8	20.4	675	19.5	22	887
17	$[Fe(CH_2OH\text{-}ptp^-)_2]^0$	302	13.3	20.1	664	-16.4	19.85	829
18	$[Fe(COOCH_3\text{-}ptp^-)_2]^0$	347	14.8	20.5	722	5.23	20.2	259
19	$[Fe(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$	290	9.85	24.6	399	1.42	23.8	60
20	$[Fe(L^{Nap})_2(NCBH_3)_2]$	160, 300	9.77	24.6	396	---	---	---
21	$[Fe(bpte)(NCBH_3)_2]$	243	5.07	13.5	373	---	---	---
22	$[Fe(H_2L^1)_2]\ (BF_4)_2{\cdot}x(solv.)$	200	9.15	25.3	361	---	---	---
23	$[Co(L)_2]\ (ClO_4)_2$	175	4.45	9.3	480	2.19	8.17	268
24	$[Co(L)(N(CN)_2)_2]$	238	---	---	---	---	---	---
25	$[Co(Brphtpy)_2](OTf)_2{\cdot}DMF{\cdot}2H_2O$	360	3.48	12.04	289	0.43	9.25	47
26	$[Co(tppz)_2](tcm)_2$	200	3.82	8.12	471	3.44	4.74	725

Table S3: Computed transition temperatures ($T_{1/2}$) in K, enthalpy and entropy differences ($\Delta H = H_{HS} - H_{LS}$) in kcal/mol and ($\Delta S = S_{HS} - S_{HS}$) in cal/K.mol for the 26 studied systems using the B3LYP* functional, together with the experimental transition temperatures and computed transition temperatures.

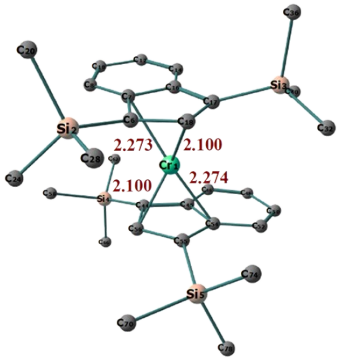
B3LYP*					
Complex No.	Molecular formula	ΔH	ΔS	$T_{I/2}$	$T_{I/2\ Exp}$
1	$[Cr(1,3\text{-Si-indenyl})_2]$	3.27	12.55	260	350
2	$[Cr(4,7\text{-Me-indenyl})_2]$	4.82	8.15	591	250
3	[Mn(naphth-sal-1,5,8,12)]	6.24	4.36	1429	164
4	[Mn(5azo-sal2-323)]	5.37	12.54	429	560
5	$[Mn(Me_3SiCp)_2]$	16.59	12.9	1284	125
6	$[Mn(1,3\text{-}(tBu)_2Cp)_2]$	17.0	9.2	1836	314, 327
7	$[Fe(bztpen)(OEtg)](PF_6)_2$	12.4	10.6	1168	284
8	$[Fe(bztpen)(OButn)](PF_6)_2$	11.8	-0.65	18042	282
9	$[Fe(bztpen)(OProp)](PF_6)_2$	12.05	1.52	7896	255
10	$[Fe(2amp)_3]Cl_2$	13.71	14.3	955	91
11	$[Fe(tacn)_2](OTf)_2$	11.97	-1.60	7446	330
12	$[Fe(L^{OMe\text{-}Nap})_2(NCS)_2]$	9.79	13.604	720	100
13	$[Fe\ (L^{npdtz})_2(NCS)_2]$	10.15	16.6	613	110
14	$[Fe\ (L^{npdtz})_2(NCSe)_2]$	11.13	11.96	930	150
15	$[Fe(bpte)(bim)]X_2$	13.7	9.2	1496	330
16	$[Fe(H\text{-}ptp^-)_2]^0$	23.2	17.04	1361	296
17	$[Fe(CH_2OH\text{-}ptp^-)_2]^0$	22.47	10.87	2066	302
18	$[Fe(COOCH_3\text{-}ptp^-)_2]^0$	24.2	10.67	2269	347
19	$[Fe(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$	17.05	8.75	1948	290
20	$[Fe(L^{Nap})_2(NCBH_3)_2]$	19.75	13.4	1477	160, 300
21	$[Fe(bpte)(NCBH_3)_2]$	10.75	11.4	941	243
22	$[Fe(H_2L^1)_2]\ (BF_4)_2{\cdot}x$(solv.)	16.78	11.16	1504	200
23	$[Co(L)_2]\ (ClO_4)_2$	10.6	4.13	2570	175
24	$[Co(L)(N(CN)_2)_2]$	6.75	0.21	32656	238
25	$[Co(Brphtpy)_2](OTf)_2{\cdot}DMF{\cdot}2H_2O$	12.44	7.27	1711	360
26	$[Co(tppz)_2](tcm)_2$	13.06	6.19	2108	200

$[Cr^{II}(1,3\text{-Si-indenyl})_2]$

H.S.

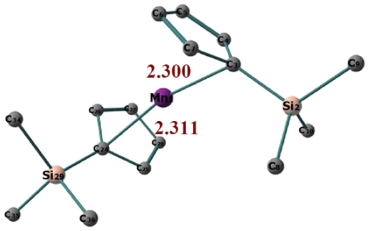


L.S.

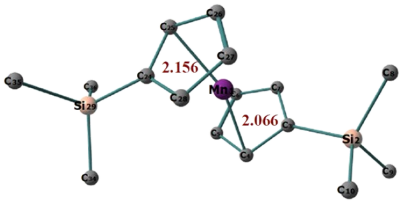


$[Mn^{II}(Me_3SiCp)_2]$

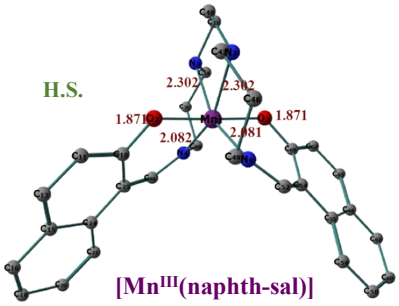
H.S.



L.S.

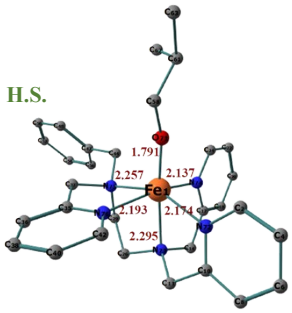


H.S.



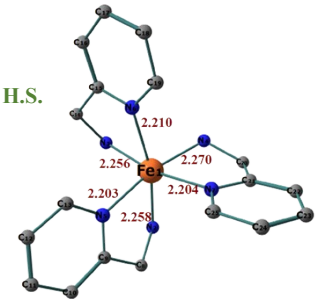
$[Mn^{III}(naphth\text{-}sal)]$

H.S.



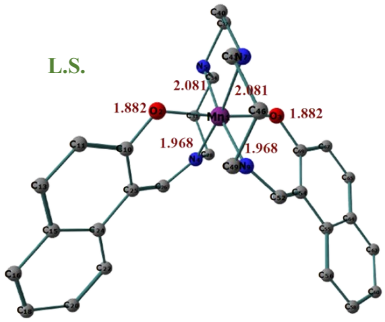
$[Fe^{III}(bztpen)(OEtg)]$

H.S.

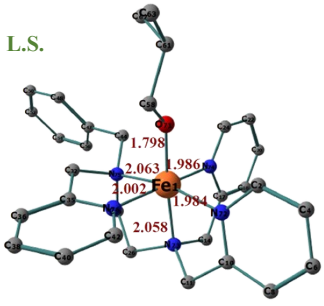


$[Fe^{II}(2amp)_3]$

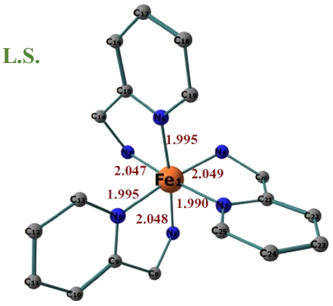
L.S.



L.S.

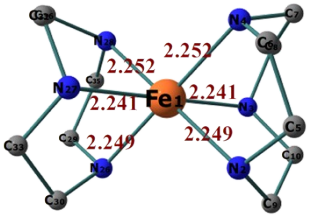


L.S.

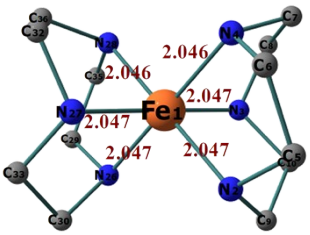


$[Fe^{II}(tacn)_2]$

H.S.

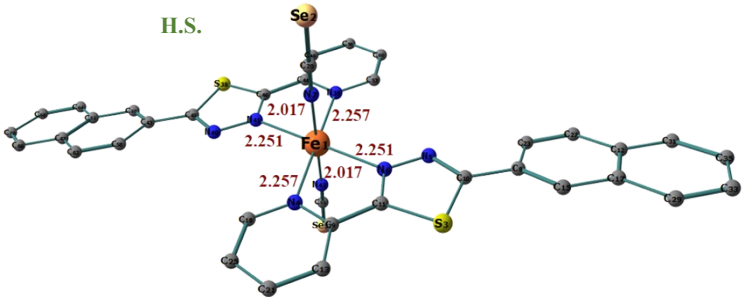


L.S.

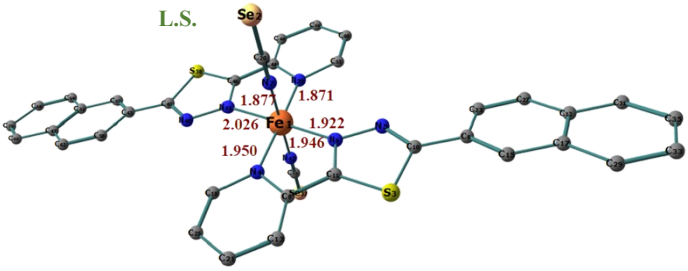


$[Fe^{II}(L^{npdtz})_2(NCSe)_2]$

H.S.

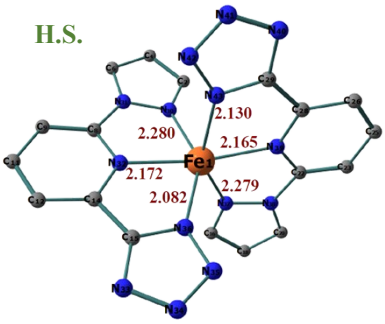


L.S.

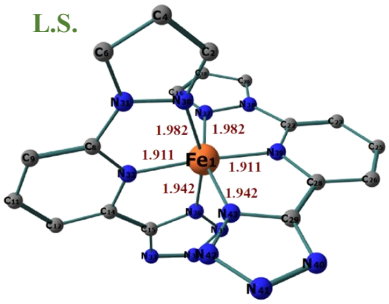


$[Fe^{II}(H\text{-}ptp^{-})_2]^0$

H.S.

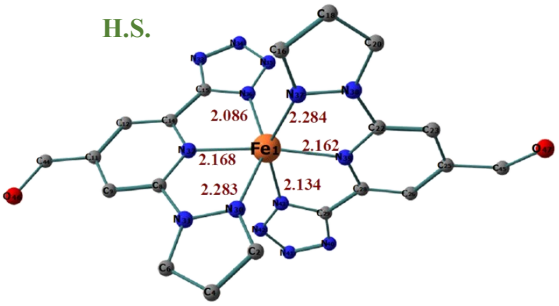


L.S.

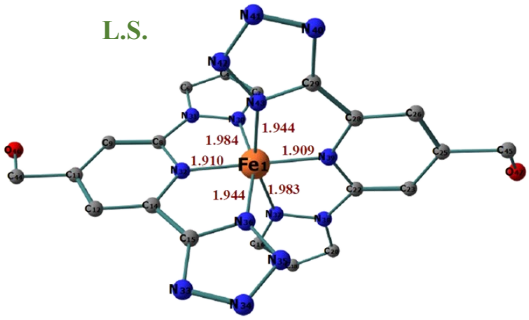


$[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$

H.S.

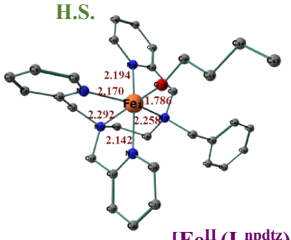


L.S.

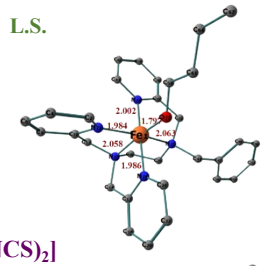


$[Fe^{III}(bztpen)(OButn)]$

H.S.

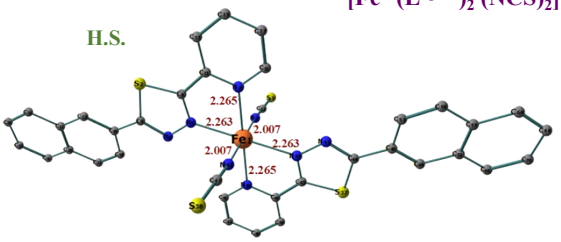


L.S.

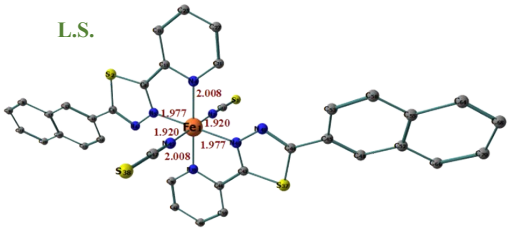


$[Fe^{II}(L^{npdtz})_2(NCS)_2]$

H.S.

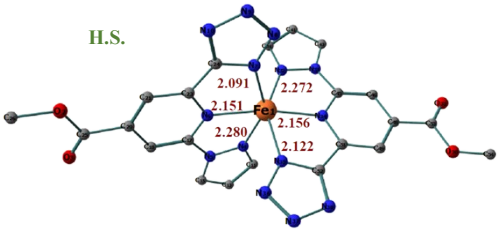


L.S.

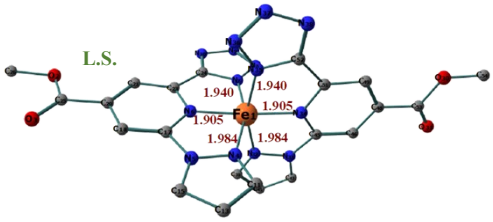


$[Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$

H.S.

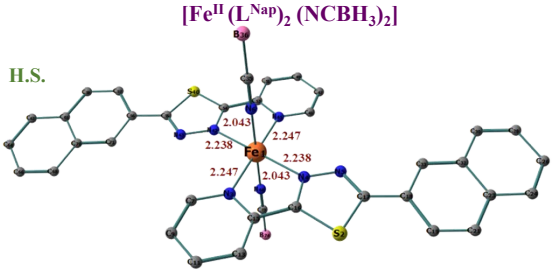


L.S.

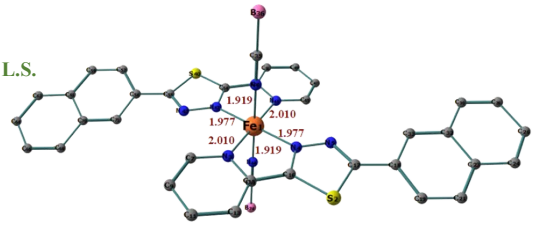


$[Fe^{II}(L^{Nap})_2(NCBH_3)_2]$

H.S.

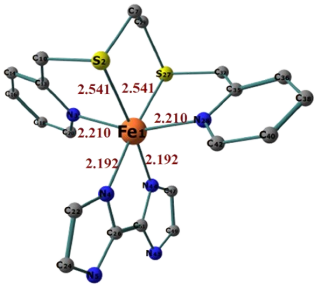


L.S.

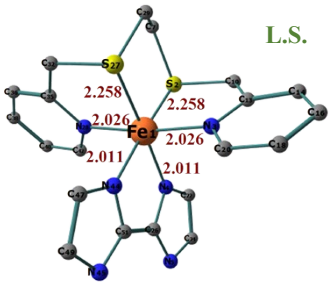


$[Fe^{II}(bpte)(bim)]$

H.S.

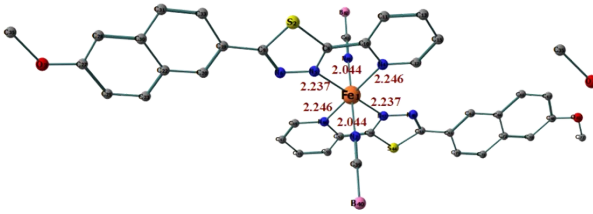


L.S.

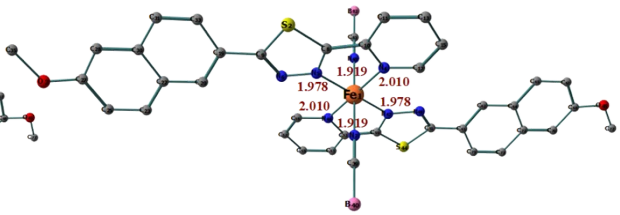


$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$

H.S.



L.S.



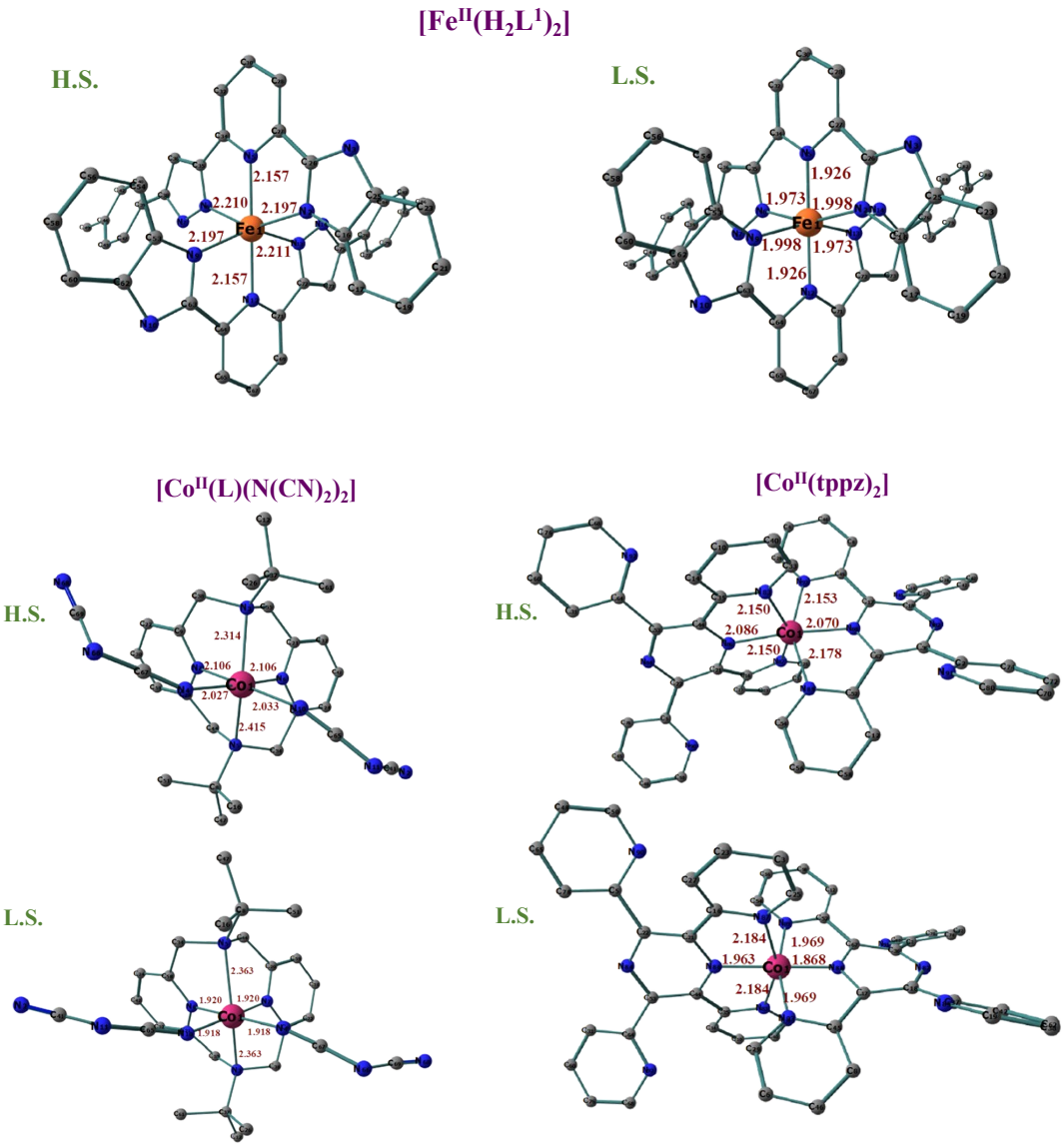


Figure S3: Structure optimization for complexes ([Cr(1,3-Si-indenyl)$_2$](**1**), [Mn(naphth-sal-1,5,8,12)](**3**), [Mn(Me$_3$SiCp)$_2$](5), [Fe(bztpen)(OEtg)] (PF$_6$)$_2$(**7**), [Fe(bztpen)(OButn) (**8**), ([Fe(bztpen)(OProp)] (PF$_6$)$_2$(**9**), [Fe(2amp)$_3$](**10**), [Fe(tacn) $_2$](**11**), [Fe (L^{npdtz})$_2$(NCS)$_2$] (**13**), [Fe (L^{npdtz})$_2$(NCSe)$_2$](**14**) , [Fe(H-ptp$^-$)$_2$](**16**), [Fe(bpte)(bim)](**15**), [Fe(CH$_2$OH-ptp$^-$)$_2$]^0 (**17**),[Fe(COOCH$_3$-ptp$^-$)$_2$](**18**), [Fe(L$^{OMe-Nap}$)$_2$(NCBH$_3$)$_2$] (**19**), [Fe(L^{Nap})$_2$(NCBH$_3$)$_2$](**21**), [Fe(H$_2$L^1)$_2$] (BF$_4$)$_2$(**22**), [Co(L)$_2$] (ClO$_4$)$_2$(**23**), [Co(L)(N(CN)$_2$)$_2$](**24**), and [Co(tppz)$_2$] (tcm)$_2$ (**26**)using the TPSSh functional and a few chosen bond values in the first coordination environment. The color code is as follows: Orange stands for iron, blue for nitrogen, red for oxygen, grey for carbon, pink for boron, yellow for sulfur, green for bromine and hydrogen atoms are left out for clarity.

Table S4: The TPSSh calculated parameters for complexes compared with X-ray structural parameters for some of the selected complexes [Cr^{II}(1,3-Si-indenyl)$_2$](**1**), [Cr^{II}(4,7-Me-indenyl)$_2$](**2**), [Mn^{III}(naphth-sal-N-1,5,8,12)](**3**), [Mn^{II}(Me_3SiCp)$_2$](**5**), [Mn^{II}(1,3-(tBu)$_2$Cp)$_2$](**6**), [Fe^{III}(bztpen)(OProp)](**9**, [Fe(2amp)$_2$]$^{2+}$(**10**), [Fe(tacn)$_2$]$^{2+}$(**11**), [Fe^{II}($L^{OMe\text{-}Nap}$)$_2$ (NCS)$_2$](**12**), [Co(L)(N(CN)$_2$)$_2$](**24**), [Fe^{II} (L^{npdtz})$_2$(NCSe)$_2$](**14**), [Fe^{II}H-ptp$^-$)$_2$]^0(**16**), ((**4**)[Mn^{III}(5azo-sal2-323)], (**7**)[Fe^{III}(bztpen)(OEtg)], (**8**)[Fe^{III}(bztpen)(OButn)], (**13**)[Fe^{II} (L^{npdtz})$_2$ (NCS)$_2$], (**15**)[Fe^{II}(bpte)(bim)], (**19**)[Fe^{II}($L^{OMe\text{-}Nap}$)$_2$($NCBH_3$)$_2$], (**22**)[Fe^{II}(H_2L^1)$_2$](BF_4)$_2$·*x*(solv.), (**21**)[Fe^{II}(bpte)($NCBH_3$)$_2$] and (**25**)[Co^{II} (Brphtpy)$_2$]).

[Mn^{III}(naphth-sal-N-1,5,8,12)]				**[Fe^{III}(bztpen)(OProp)]**				**[Fe(2amp)$_2$]$^{2+}$**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Mn-O2	1.865	1.871	1.882	**Fe-O71**	1.804	1.791	1.798	**Fe-N2**	2.017	2.258	2.048
Mn-O3	1.861	1.871	1.882	**Fe-N72**	1.963	2.174	1.984	**Fe-N3**	2.021	2.256	2.047
Mn-N4	2.093	2.082	1.968	**Fe-N73**	2.036	2.295	2.058	**Fe-N4**	2.024	2.270	2.049
Mn-N5	2.231	2.302	2.081	**Fe-N74**	1.977	2.137	1.986	**Fe-N5**	1.977	2.203	1.995
Mn-N7	2.252	2.302	2.081	**Fe-N75**	2.045	2.257	2.063	**Fe-N6**	1.970	2.210	1.995
Mn-N9	2.096	2.081	1.968	**Fe-N76**	1.985	2.193	2.002	**Fe-N7**	1.973	2.204	1.990
[Fe(tacn) $_2$]$^{2+}$				**[Fe^{II}($L^{OMe\text{-}Nap}$)$_2$ (NCS)$_2$]**				**[Co(L)(N(CN)$_2$)$_2$]**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N2	2.043	2.249	2.047	**Fe-N5**	2.187	2.262	1.978	**Co-N3**	2.340	2.314	2.363
Fe-N3	2.035	2.241	2.047	**Fe-N7**	2.204	2.263	2.008	**Co-N4**	1.927	2.027	1.918
Fe-N4	2.023	2.252	2.046	**Fe-N8**	2.101	2.009	1.921	**Co-N5**	2.315	2.415	2.363
Fe-N26	2.043	2.249	2.047	**Fe-N44**	2.187	2.262	1.978	**Co-N6**	1.909	2.106	1.920
Fe-N27	2.035	2.241	2.047	**Fe-N46**	2.204	2.263	2.008	**Co-N7**	1.920	2.106	1.920
Fe-N28	2.023	2.252	2.046	**Fe-N47**	2.101	2.009	1.921	**Co-N10**	1.942	2.033	1.918
[Fe^{II} (L^{npdtz})$_2$(NCSe)$_2$]				**[Fe^{II}H-ptp$^-$)$_2$]^0**				**[Cr^{II}(4,7-Me-indenyl)$_2$]**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N4	2.203	2.257	1.977	**Fe-N30**	1.969	2.280	1.982	**Cr-C2**	2.218	2.275	2.257
Fe-N6	2.161	2.251	1.922	**Fe-N32**	1.898	2.171	1.911	**Cr-C5**	2.127	2.263	2.094
Fe-N7	2.137	2.017	1.877	**Fe-N36**	1.957	2.082	1.941	**Cr-C27**	2.122	2.275	2.257
Fe-N39	2.203	2.257	1.887	**Fe-N37**	1.951	2.279	1.982	**Cr-C31**	2.235	2.266	2.094
Fe-N41	2.161	2.251	2.026	**Fe-N39**	1.906	2.165	1.911				
Fe-N42	2.137	2.017	1.946	**Fe-N43**	1.958	2.130	1.942				

[Cr^{II}(1,3-Si-indenyl)$_2$]				**[Mn^{II}(1,3-(tBu)$_2$Cp)$_2$**				**[Mn^{II}(Me_3SiCp)$_2$]**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Cr-C7	2.268	2.293	2.273	**Mn-C5**	2.071	2.370	2.068	**Mn-C3**	2.331	2.300	2.066
Cr-C18	2.113	2.294	2.100	**Mn-C8**	2.164	2.421	2.186	**Mn-C24**	2.331	2.311	2.156
Cr-C54	2.265	2.339	2.273	**Mn-C39**	2.071	2.359	2.068				
Cr-C56	2.102	2.380	2.100	**Mn-C42**	2.164	2.430	2.186				

(2)[Mn^{III}(5azo-sal2-323)]				**(4)[[[Fe^{III}(bztpen)(OButn)]**				**(8)[[Fe^{II}(L^{npdtz})$_2$(NCS)$_2$]**			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Mn-O2	1.886	1.870	1.880	**Fe-O71**	1.800	1.786	1.797	**Fe-N4**	2.200	2.265	2.008
Mn-N3	1.985	2.100	1.982	**Fe-N72**	1.962	2.170	1.984	**Fe-N5**	2.200	2.263	1.977
Mn-N4	2.033	2.300	2.077	**Fe-N73**	2.037	2.292	2.058	**Fe-N7**	2.091	2.007	1.920
Mn-O42	1.886	1.870	1.880	**Fe-N74**	1.981	2.142	1.986	**Fe-N39**	2.200	2.265	2.008
Mn-N43	1.985	2.100	1.982	**Fe-N75**	2.044	2.258	2.063	**Fe-N40**	2.200	2.263	1.977
Mn-N44	2.033	2.300	2.077	**Fe-N76**	1.981	2.194	2.002	**Fe-N42**	2.091	2.007	1.920
(18)[Fe^{II} (H_2L^1)$_2$]				**(13)[Fe^{II}(bpte)(bim)]**				**(17)[Fe^{II}($L^{OMe\text{-}Nap}$)$_2$($NCBH_3$)$_2$]**			

Bond parameters	X-ray	HS	LS	Bond parameters	X-ray	HS	LS	Bond parameters	X-ray	HS	LS
Fe-N2	2.137	2.197	1.998	**Fe-S2**	2.236	2.541	2.258	**Fe-N4**	2.034	2.246	2.010
Fe-N5	2.088	2.157	1.926	**Fe-N3**	2.003	2.210	2.026	**Fe-N5**	1.996	2.237	1.978
Fe-N6	2.168	2.210	1.973	**Fe-N4**	2.004	2.192	2.011	**Fe-N7**	1.947	2.044	1.919
Fe-N9	2.140	2.197	1.998	**Fe-S27**	2.236	2.541	2.258	**Fe-N46**	2.034	2.246	2.010
Fe-N12	2.081	2.157	1.926	**Fe-N28**	2.003	2.210	2.026	**Fe-N47**	1.996	2.237	1.978
Fe-N13	2.162	2.213	1.973	**Fe-N44**	2.004	2.192	2.011	**Fe-N49**	1.947	2.044	1.919
(19)[Fe^{II}(bpte)($NCBH_3$)$_2$]				**(21)[Co^{II}(Brphtpy)$_2$]**				**(3)[Fe^{III}(bztpen)(OEtg)]**			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Fe-S2	2.250	2.677	2.269	**Co-N2**	1.891	2.077	1.937	**Fe-O64**	1.810	1.799	1.801
Fe-N3	1.960	2.030	1.925	**Co-N3**	1.879	2.056	1.868	**Fe-N66**	1.973	2.172	1.990
Fe-N4	2.008	2.209	1.999	**Co-N4**	2.093	2.200	2.003	**Fe-N67**	2.029	2.294	2.057
Fe-S25	2.250	2.677	2.269	**Co-N5**	2.050	2.169	2.003	**Fe-N68**	1.980	2.133	1.991
Fe-N26	1.960	2.026	1.925	**Co-N6**	2.082	2.170	2.189	**Fe-N69**	2.050	2.244	2.057
Fe-N42	2.008	2.209	1.999	**Co-N7**	2.050	2.180	2.189	**Fe-N70**	1.995	2.186	2.002

Table S5: The TPSSh calculated parameters for complexes compared with X-ray structural parameters for some of the selected complexes $[Fe^{II}(CH_2OH\text{-}ppt^{-})_2]^0$(**13**), $[Fe^{II}(COOCH_3\text{-}ppt^{-})_2]^0$(**14**), $[Fe^{II}\ (L^{Nap})_2\ (NCBH_3)_2]$(**16**), $[Fe^{II}(H_2L^1)_2]\ (BF_4)_2{\cdot}x$(solv.)(**18**), $[Co^{II}(L)_2]\ (ClO_4)_2$(**21**), $[Co^{II}(tppz)_2]\ (tcm)_2$(**22**).

$[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$				**$[Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$**				**$[Fe^{II}\ (L^{Nap})_2\ (NCBH_3)_2]$**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N30	1.969	2.283	1.984	**Fe-N4**	1.955	2.280	1.984	**Fe-N3**	2.115	2.247	2.010
Fe-N32	1.898	2.168	1.910	**Fe-N6**	1.902	2.151	1.905	**Fe-N4**	2.096	2.238	1.977
Fe-N36	1.957	2.086	1.944	**Fe-N7**	1.942	2.091	1.940	**Fe-N6**	2.045	2.043	1.919
Fe-N37	1.958	2.284	1.983	**Fe-N32**	1.955	2.272	1.940	**Fe-N41**	2.115	2.247	2.010
Fe-N39	1.906	2.162	1.909	**Fe-N34**	1.902	2.156	1.905	**Fe-N42**	2.096	2.238	1.977
Fe-N43	1.951	2.134	1.944	**Fe-N35**	1.942	2.122	1.984	**Fe-N44**	2.045	2.043	1.919
$[Fe^{II}(H_2L^1)_2]\ (BF_4)_2{\cdot}x$(solv.)				**$[Co^{II}(L)_2]\ (ClO_4)_2$**				**$[Co^{II}(tppz)_2]\ (tcm)_2$**			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N2	2.133	2.197	1.998	**Co-S2**	2.470	2.484	2.514	**Co-N83**	2.158	2.150	2.184
Fe-N5	2.089	2.157	1.926	**Co-S3**	2.472	2.484	2.514	**Co-N86**	1.936	2.086	1.963
Fe-N6	2.168	2.210	1.973	**Co-N8**	2.027	2.177	2.020	**Co-N87**	2.160	2.150	2.184
Fe-N9	2.140	2.197	1.998	**Co-N9**	2.019	2.177	2.020	**Co-N88**	1.864	2.070	1.868
Fe-N12	2.082	2.157	1.926	**Co-N11**	1.981	2.097	1.942	**Co-N89**	1.978	2.178	1.969
Fe-N13	2.161	2.211	1.973	**Co-N12**	1.980	2.097	1.942	**Co-N93**	1.977	2.153	1.969

Table S6: The comparison of optimized and X-ray bond parameters for all 26 complexes using the B3LYP* functional.

$[Mn^{III}(5azo\text{-}sal2\text{-}323)]$				$[Fe^{III}(bztpen)(OButn)]$				$[Fe^{II}(L^{npdtz})_2(NCS)_2]$			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Mn-O2	1.886	1.873	1.889	**Fe-O71**	1.800	1.785	1.795	**Fe-N4**	2.200	2.291	2.032
Mn-N3	1.985	2.116	2.002	**Fe-N72**	1.962	2.186	2.009	**Fe-N5**	2.200	2.290	2.001
Mn-N4	2.033	2.326	2.096	**Fe-N73**	2.037	2.319	2.090	**Fe-N7**	2.091	2.014	1.936
Mn-O42	1.886	1.873	1.889	**Fe-N74**	1.981	2.158	2.012	**Fe-N39**	2.200	2.291	2.032
Mn-N43	1.985	2.116	2.002	**Fe-N75**	2.044	2.288	2.096	**Fe-N40**	2.200	2.290	2.001
Mn-N44	2.033	2.326	2.096	**Fe-N76**	1.981	2.211	2.034	**Fe-N42**	2.091	2.014	1.936
$[Fe^{II}(H_2L^1)_2]$				$[Fe^{II}(bpte)(bim)]$				$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Fe-N2	2.137	2.217	2.024	**Fe-S2**	2.236	2.573	2.289	**Fe-N4**	2.034	2.269	2.033
Fe-N5	2.088	2.173	1.944	**Fe-N3**	2.003	2.229	2.055	**Fe-N5**	1.996	2.261	2.001
Fe-N6	2.168	2.237	2.002	**Fe-N4**	2.004	2.210	2.035	**Fe-N7**	1.947	2.051	1.935
Fe-N9	2.140	2.217	2.024	**Fe-S27**	2.236	2.573	2.289	**Fe-N46**	2.034	2.268	2.033
Fe-N12	2.081	2.173	1.944	**Fe-N28**	2.003	2.229	2.055	**Fe-N47**	1.996	2.261	2.002
Fe-N13	2.162	2.237	2.002	**Fe-N44**	2.004	2.210	2.035	**Fe-N49**	1.947	2.051	1.935
$[Fe^{II}(bpte)(NCBH_3)_2]$				$[Co^{II}(Brphtpy)_2]$				$[Fe^{III}(bztpen)(OEtg)]$			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Fe-S2	2.250	2.698	2.307	**Co-N2**	1.891	2.078	1.951	**Fe-O64**	1.810	1.801	1.804
Fe-N3	1.960	2.041	1.941	**Co-N3**	1.879	2.078	1.883	**Fe-N66**	1.973	2.184	2.007
Fe-N4	2.008	2.246	2.028	**Co-N4**	2.093	2.215	2.033	**Fe-N67**	2.029	2.322	2.084
Fe-S25	2.250	2.699	2.307	**Co-N5**	2.050	2.187	2.033	**Fe-N68**	1.980	2.145	2.010
Fe-N26	1.960	2.246	2.028	**Co-N6**	2.082	2.215	2.218	**Fe-N69**	2.050	2.279	2.087
Fe-N42	2.008	2.041	1.941	**Co-N7**	2.050	2.187	2.218	**Fe-N70**	1.995	2.201	2.024

$[Mn^{III}(naphth\text{-}sal\text{-}N\text{-}1,5,8,12)]$				$[Fe^{III}(bztpen)(OProp)]$				$[Fe(2amp)_2]^{2+}$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Mn-O2	1.865	1.874	1.890	**Fe-O71**	1.804	1.790	1.796	**Fe-N2**	2.017	2.275	2.068
Mn-O3	1.861	1.874	1.890	**Fe-N72**	1.963	2.188	2.010	**Fe-N3**	2.021	2.274	2.068
Mn-N4	2.093	2.096	1.986	**Fe-N73**	2.036	2.322	2.090	**Fe-N4**	2.024	2.287	2.071
Mn-N5	2.231	2.330	2.101	**Fe-N74**	1.977	2.154	2.012	**Fe-N5**	1.977	2.221	2.023
Mn-N7	2.252	2.330	2.101	**Fe-N75**	2.045	2.290	2.096	**Fe-N6**	1.970	2.233	2.025
Mn-N9	2.096	2.096	1.986	**Fe-N76**	1.985	2.210	2.034	**Fe-N7**	1.973	2.221	2.018
$[Fe(tacn)_2]^{2+}$				$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCS)_2]$				$[Co(L)(N(CN)_2)_2]$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N2	2.043	2.272	2.081	**Fe-N5**	2.187	2.289	2.001	**Co-N3**	2.340	2.348	2.425
Fe-N3	2.035	2.262	2.081	**Fe-N7**	2.204	2.289	2.032	**Co-N4**	1.927	2.026	1.927
Fe-N4	2.023	2.275	2.080	**Fe-N8**	2.101	2.016	1.937	**Co-N5**	2.315	2.541	2.425
Fe-N26	2.043	2.272	2.081	**Fe-N44**	2.187	2.289	2.001	**Co-N6**	1.909	2.123	1.939
Fe-N27	2.035	2.262	2.081	**Fe-N46**	2.204	2.289	2.032	**Co-N7**	1.920	2.120	1.939
Fe-N28	2.023	2.275	2.080	**Fe-N47**	2.101	2.016	1.937	**Co-N10**	1.942	2.030	1.927
$[Fe^{II}(L^{npdtz})_2(NCSe)_2]$				$[Fe^{II}H\text{-}ptp^{-})_2]^0$				$[Cr^{II}(4,7\text{-}Me\text{-}indenyl)_2]$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N4	2.203	2.282	2.033	**Fe-N30**	1.969	2.313	2.012	**Cr-C2**	2.218	2.288	2.116
Fe-N6	2.161	2.278	2.002	**Fe-N32**	1.898	2.181	1.928	**Cr-C5**	2.127	2.297	2.286
Fe-N7	2.137	2.024	1.933	**Fe-N36**	1.957	2.138	1.960	**Cr-C27**	2.122	2.298	2.115
Fe-N39	2.203	2.282	2.033	**Fe-N37**	1.951	2.308	2.012	**Cr-C31**	2.235	2.288	2.286
Fe-N41	2.161	2.278	2.002	**Fe-N39**	1.906	2.197	1.928				
Fe-N42	2.137	2.025	1.933	**Fe-N43**	1.958	2.096	1.960				

$[Cr^{II}(1,3\text{-Si-indenyl})_2]$				$[Mn^{II}(1,3\text{-}(tBu)_2Cp)_2$				$[Mn^{II}(Me_3SiCp)_2]$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Cr-C7	2.268	2.319	2.309	**Mn-C5**	2.071	2.386	2.092	**Mn-C3**	2.331	2.353	2.093
Cr-C18	2.113	2.320	2.121	**Mn-C8**	2.164	2.446	2.215	**Mn-C24**	2.331	2.383	2.093
Cr-C54	2.265	2.359	2.309	**Mn-C39**	2.071	2.386	2.092				
Cr-C56	2.102	2.409	2.121	**Mn-C42**	2.164	2.446	2.215				

$[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$				$[Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$				$[Fe^{II}\ (L^{Nap})_2\ (NCBH_3)_2]$			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Fe-N30	1.969	2.318	2.015	**Fe-N4**	1.955	2.299	2.014	**Fe-N3**	2.115	2.226	2.033
Fe-N32	1.898	2.169	1.928	**Fe-N6**	1.902	2.181	1.923	**Fe-N4**	2.096	2.218	2.000
Fe-N36	1.957	2.130	1.963	**Fe-N7**	1.942	2.115	1.958	**Fe-N6**	2.045	2.068	1.934
Fe-N37	1.958	2.321	2.013	**Fe-N32**	1.955	2.299	2.014	**Fe-N41**	2.115	2.226	2.033
Fe-N39	1.906	2.174	1.927	**Fe-N34**	1.902	2.181	1.923	**Fe-N42**	2.096	2.218	2.000
Fe-N43	1.951	2.115	1.963	**Fe-N35**	1.942	2.115	1.958	**Fe-N44**	2.045	2.068	1.934
$[Fe^{II}(H_2L^1)_2]\ (BF_4)_2{\cdot}x$(solv.)				$[Co^{II}(L)_2]\ (ClO_4)_2$				$[Co^{II}(tppz)_2]\ (tcm)_2$			
Bond parameters	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**	**Bond parameters**	**X-ray**	**HS**	**LS**
Fe-N2	2.133	2.217	2.024	**Co-S2**	2.470	2.518	2.573	**Co-N83**	2.158	2.166	2.217
Fe-N5	2.089	2.173	1.944	**Co-S3**	2.472	2.518	2.573	**Co-N86**	1.936	2.098	1.979
Fe-N6	2.168	2.237	2.002	**Co-N8**	2.027	2.189	2.035	**Co-N87**	2.160	2.181	2.217
Fe-N9	2.140	2.217	2.024	**Co-N9**	2.019	2.188	2.035	**Co-N88**	1.864	2.088	1.882
Fe-N12	2.082	2.173	1.944	**Co-N11**	1.981	2.113	1.962	**Co-N89**	1.978	2.195	1.991
Fe-N13	2.161	2.237	2.002	**Co-N12**	1.980	2.113	1.962	**Co-N93**	1.977	2.088	1.991

Table S7: The comparison of optimized and X-ray bond parameters for the 13 complexes, which shows the correct ground state using the B3P86 functional.

$[Mn^{III}$(naphth-sal-N-1,5,8,12)]				$[Fe^{III}$(bztpen)(OProp)]				$[Fe^{III}$(bztpen)(OButn)]			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Mn-O2	1.865	1.862	1.878	**Fe-O71**	1.804	1.781	1.785	**Fe-O71**	1.800	1.775	1.784
Mn-O3	1.861	1.862	1.878	**Fe-N72**	1.963	2.162	1.978	**Fe-N72**	1.962	2.158	1.978
Mn-N4	2.093	2.079	1.967	**Fe-N73**	2.036	2.296	2.059	**Fe-N73**	2.037	2.295	2.059
Mn-N5	2.231	2.290	2.074	**Fe-N74**	1.977	2.128	1.981	**Fe-N74**	1.981	2.133	1.981
Mn-N7	2.252	2.290	2.074	**Fe-N75**	2.045	2.255	2.061	**Fe-N75**	2.044	2.256	2.061
Mn-N9	2.096	2.078	1.967	**Fe-N76**	1.985	2.181	2.000	**Fe-N76**	1.981	2.183	2.000
$[Fe(2amp)_2]^{2+}$				$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$				$[Fe^{II}\ (L^{npdtz})_2(NCSe)_2]$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N2	2.017	2.253	2.046	**Fe-N4**	2.034	2.239	2.012	**Fe-N4**	2.203	2.497	2.013
Fe-N3	2.021	2.253	2.046	**Fe-N5**	1.996	2.236	1.984	**Fe-N6**	2.161	2.783	1.984
Fe-N4	2.024	2.265	2.048	**Fe-N7**	1.947	2.045	1.918	**Fe-N7**	2.137	1.952	1.917
Fe-N5	1.977	2.198	2.000	**Fe-N46**	2.034	2.239	2.012	**Fe-N39**	2.203	2.119	2.013
Fe-N6	1.970	2.209	2.002	**Fe-N47**	1.996	2.236	1.984	**Fe-N41**	2.161	2.386	1.984
Fe-N7	1.973	2.200	1.995	**Fe-N49**	1.947	2.045	1.918	**Fe-N42**	2.137	1.965	1.917
$[Fe^{II}H\text{-}ptp^{-})_2]^0$				$[Co^{II}\ (Brphtpy)_2]$				$[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N30	1.969	2.290	1.990	**Co-N2**	1.891	2.063	1.934	**Fe-N30**	1.969	2.292	1.993
Fe-N32	1.898	2.159	1.911	**Co-N3**	1.879	2.063	1.869	**Fe-N32**	1.898	2.175	1.911
Fe-N36	1.957	2.111	1.943	**Co-N4**	2.093	2.192	2.010	**Fe-N36**	1.957	2.093	1.945
Fe-N37	1.951	2.292	1.990	**Co-N5**	2.050	2.165	2.010	**Fe-N37**	1.958	2.294	1.991
Fe-N39	1.906	2.159	1.911	**Co-N6**	2.082	2.192	2.194	**Fe-N39**	1.906	2.158	1.910
Fe-N43	1.958	2.106	1.943	**Co-N7**	2.050	2.165	2.194	**Fe-N43**	1.951	2.129	1.945
Fe-N30	1.969	2.290	1.990	**Bond parameters**	**Exp**	**HS**	**LS**	**Fe-N30**	1.969	2.292	1.993
$[Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$				$[Co^{II}(L)_2]\ (ClO_4)_2$				$[Co^{II}(tppz)_2]\ (tcm)_2$			
Bond parameters	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**	**Bond parameters**	**Exp**	**HS**	**LS**
Fe-N4	1.955	2.283	1.991	**Co-S2**	2.470	2.483	2.527	**Co-N83**	2.158	2.144	2.191
Fe-N6	1.902	2.173	1.906	**Co-S3**	2.472	2.483	2.527	**Co-N86**	1.936	2.055	1.961
Fe-N7	1.942	2.087	1.940	**Co-N8**	2.027	2.163	2.013	**Co-N87**	2.160	2.144	2.191
Fe-N32	1.955	2.289	1.991	**Co-N9**	2.019	2.163	2.013	**Co-N88**	1.864	2.055	1.870
Fe-N34	1.902	2.160	1.906	**Co-N11**	1.981	2.094	1.943	**Co-N89**	1.978	2.144	1.971
Fe-N35	1.942	2.124	1.940	**Co-N12**	1.980	2.094	1.942	**Co-N93**	1.977	2.144	1.971

$[Cr^{II}(4,7\text{-Me-indenyl})_2]$			
Bond parameters	**Exp**	**HS**	**LS**
Cr-C2	2.218	2.263	2.256
Cr-C5	2.127	2.277	2.095
Cr-C27	2.122	2.277	2.256
Cr-C31	2.235	2.263	2.095

Table S8: Comparison of bond parameters using TPSSh, B3LYP*, and B3P86 functionals. Here, a negative value shows the expansion of the low-spin state bond length compared to the X-ray bond parameters.

For the comparison of bond parameters, here we have chosen the 13 complexes that predict the correct ground state with TPSSh, B3LYP*, and B3P86 functionals. This represents an average of the difference between the X-ray bond parameters and the low-spin state bond parameters. As it is clear from Table S8 that 9 complexes show the average bond length expansion, whereas the other 3 complexes show the compression in their average bond parameters. As it is observed that the percentage change is less for TPSSh, followed by B3P86 and B3LYP*. So, we can conclude that TPSSh and B3P86 are considerably functional for SCO calculations.

C.No.	Molecular formula	TPSSh	B3LYP*	B3P86
2	$[Cr^{II}(4,7\text{-Me-indenyl})_2]$	0	-0.0252	0
3	$[Mn^{III}(\text{naphth-sal-1,5,8,12})]$	0.089	0.074	0.094
8	$[Fe^{III}(\text{bztpen})(\text{OButn})]\ (PF_6)_2$	-0.014	-0.0385	-0.0097
9	$[Fe^{III}(\text{bztpen})(\text{OProp})]\ (PF_6)_2$	-0.0135	-0.038	-0.009
10	$[Fe^{II}(2amp)_3]^{2+}$	-0.02367	-0.0485	-0.0258
14	$[Fe^{II}\ (L^{npdtz})_2(NCSe)_2]$	0.228	0.177	0.195
16	$[Fe^{II}(H\text{-}ptp^{-})_2]^0$	-0.005	-0.0268	-0.0081
17	$[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$	-0.006	-0.028	-0.009
18	$[Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$	-0.01	-0.032	-0.0126
15	$[Fe^{II}(L^{OMeNap})_2(NCBH_3)_2]$	0.023	0.0033	0.021
23	$[Co^{II}(L)_2]\ (ClO_4)_2$	-0.0005	-0.0318	-0.0027
25	$[Co^{II}\ (Brphtpy)_2]$	-0.024	-0.0485	-0.027
26	$[Co^{II}(tppz)_2]\ (tcm)_2$	-0.0106	-0.034	-0.0137

Table S9: Spin density values for some of the selected first coordination environment atoms coordinated to the metal center for (**4**)[Mn^{III}(5azo-sal2-323)], (**8**)[Fe^{III}(bztpen)(OButn)], (**12**)[Fe^{II} $(L^{npdtz})_2$ $(NCS)_2$], (**15**)[Fe^{II}(bpte)(bim)], (**19**)[Fe^{II} $(L^{OMe\text{-}Nap})_2$ $(NCBH_3)_2$], (**21**)[Fe^{II}(bpte)$(NCBH_3)_2$], and (**25**)[Co^{II} $(Brphtpy)_2$]).

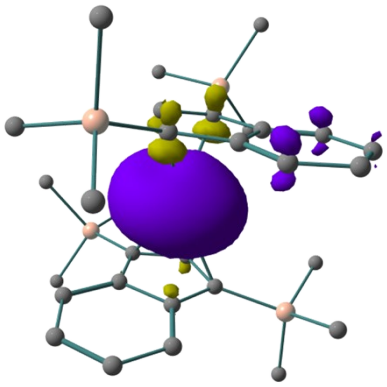
(4)[Mn^{III}(5azo-sal2-323)]			**(8)[Fe^{III}(bztpen)(OButn)]**		
	HS	**LS**		**HS**	**LS**
Mn1	3.8263	1.999652	Fe1	4.043024	0.846988
O2	0.0044	0.043443	O71	0.457898	0.20382
N3	-0.0080	-0.025432	N72	0.070175	-0.005155
N4	0.0364	-0.028004	N73	0.061692	-0.015037
O42	0.004475	0.043443	N74	0.065859	-0.014858
N43	-0.008087	-0.025432	N75	0.096825	-0.011235
N44	0.036432	-0.028004	N76	0.072056	-0.015113

(12)[Fe^{II} $(L^{npdtz})_2$ $(NCS)_2$]		**(15)[Fe^{II}(bpte)(bim)]**		**(19)[Fe^{II} $(L^{OMe\text{-}Nap})_2$ $(NCBH_3)_2$]**	
HS		**HS**		**HS**	
Fe1	3.678413	Fe1	3.716876	Fe1	3.734222
N4	0.02644	S2	0.053373	N4	0.027668
N5	0.019727	N3	0.03525	N5	0.020453
N6	-0.00038	N4	0.02269	N7	0.005334
N7	0.011672	S27	0.053373	N46	0.027663
N39	0.026441	N28	0.03525	N47	0.020456
N40	0.019726	N44	0.02269	N49	0.00532
N42	0.0117	N45	0.003693		

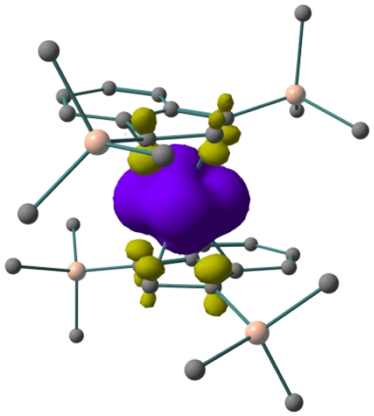
(21)[Fe^{II}(bpte)$(NCBH_3)_2$]		**(25)[Co^{II} $(Brphtpy)_2$]**			**(24)[Co^{II}(L)$(N(CN)_2)_2$]**		
HS			**HS**	**LS**		**HS**	**LS**
Fe1	3.717526	Co1	2.68572	0.927329	Co1	2.666807	0.96
S2	0.047889	N2	0.058211	0.000342	N3	0.055652	0.047093
N3	0.013317	N3	0.040996	-0.014282	N4	0.027091	-0.00386
N4	0.028249	N4	0.0328	0.007907	N5	0.043343	0.047098
S25	0.046608	N5	0.060252	0.007927	N6	0.047645	-0.003171
N26	0.026991	N6	0.053638	0.061055	N7	0.050544	-0.003169
N42	0.00993	N7	0.047527	0.061042	N10	0.025459	-0.00386

$[Cr^{II}(1,3\text{-Si-indenyl})_2]$

H.S.

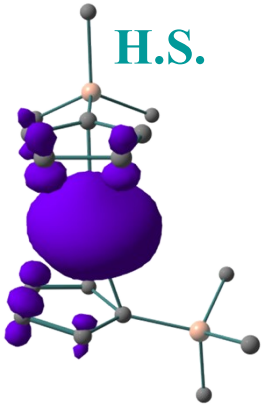


L.S.

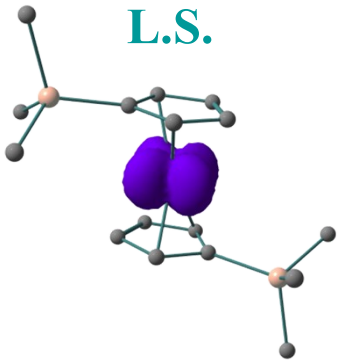


$[Mn^{II}(Me_3SiCp)_2]$

H.S.

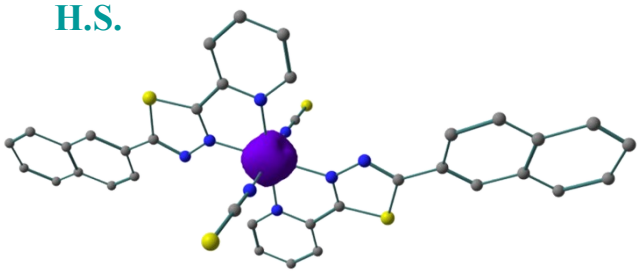


L.S.



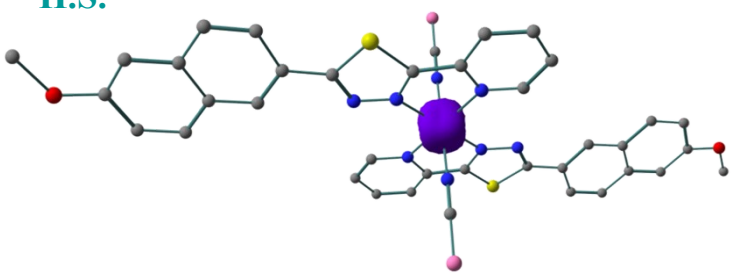
$[Fe^{II}(L^{npdtz})_2(NCS)_2]$

H.S.



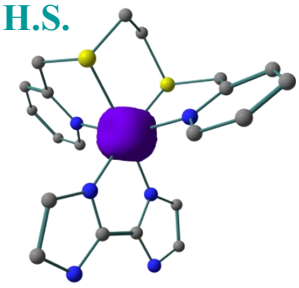
$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$

H.S.



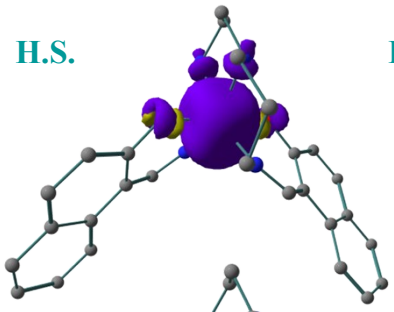
[Fe(bpte)(bim)]

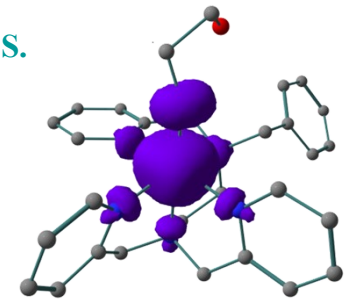
H.S.

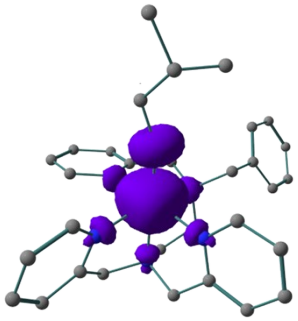


$[Mn^{III}(naphth\text{-}sal)]$ $[Fe^{III}(bztpen)(OEtg)]$ $[Fe^{III}(bztpen)(OProp)]$

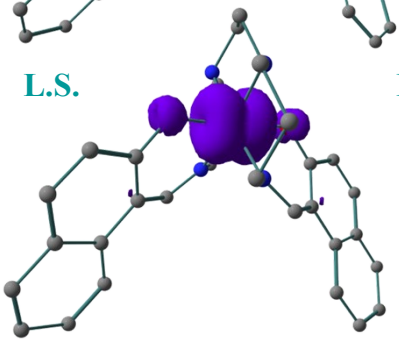
H.S.

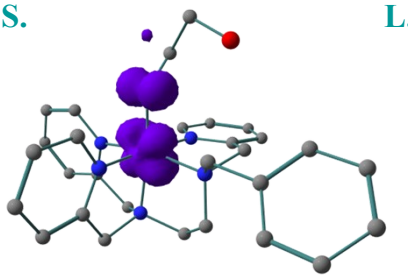


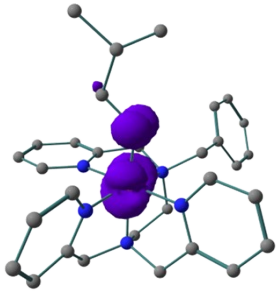




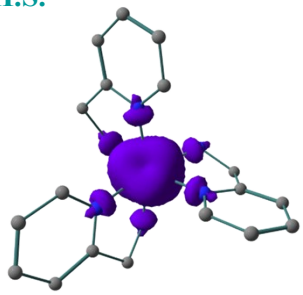
L.S.



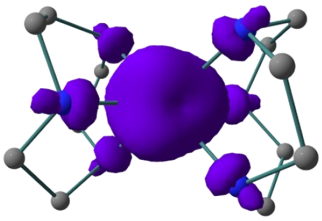




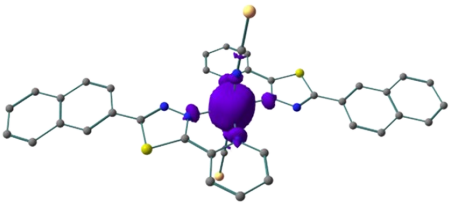
H.S. $[Fe^{II}(2amp)_3]$



H.S. $[Fe^{II}(tacn)_2]$

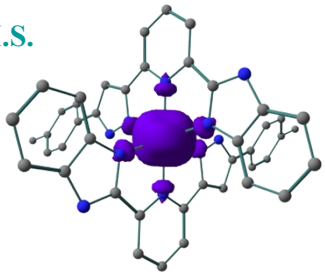


H.S. $[Fe^{II}(L^{npdtz})_2(NCSe)_2]$

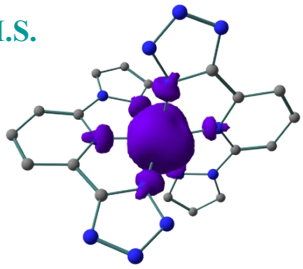


$[Fe^{II}(H_2L^1)_2]$ $[Fe^{II}(H\text{-}ptp^{-})_2]^0$ $[Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$

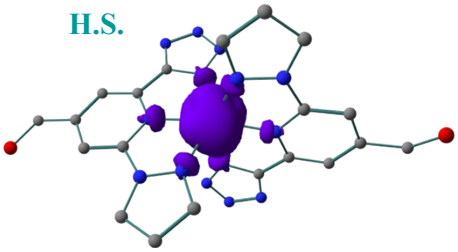
H.S.



H.S.



H.S.



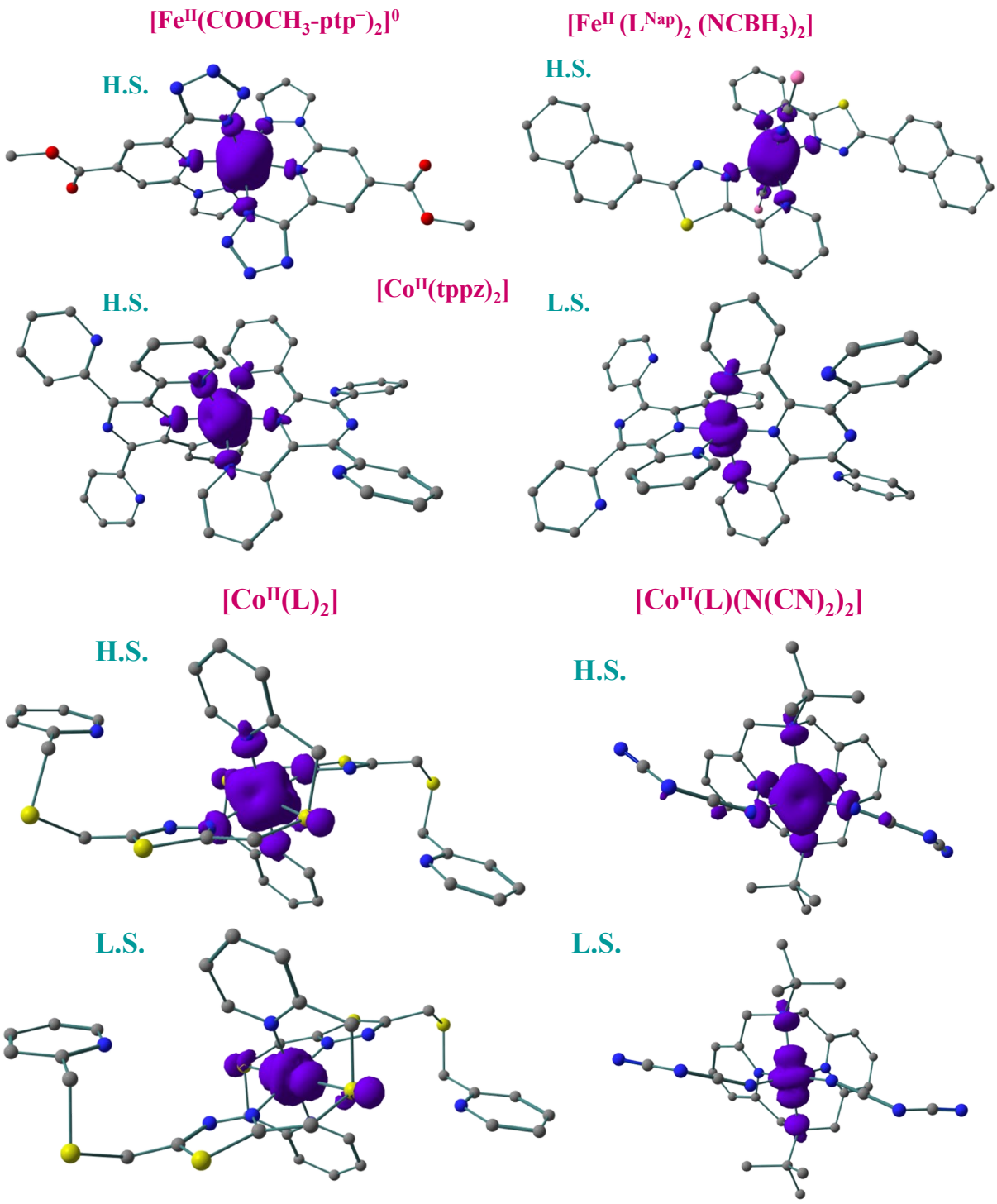
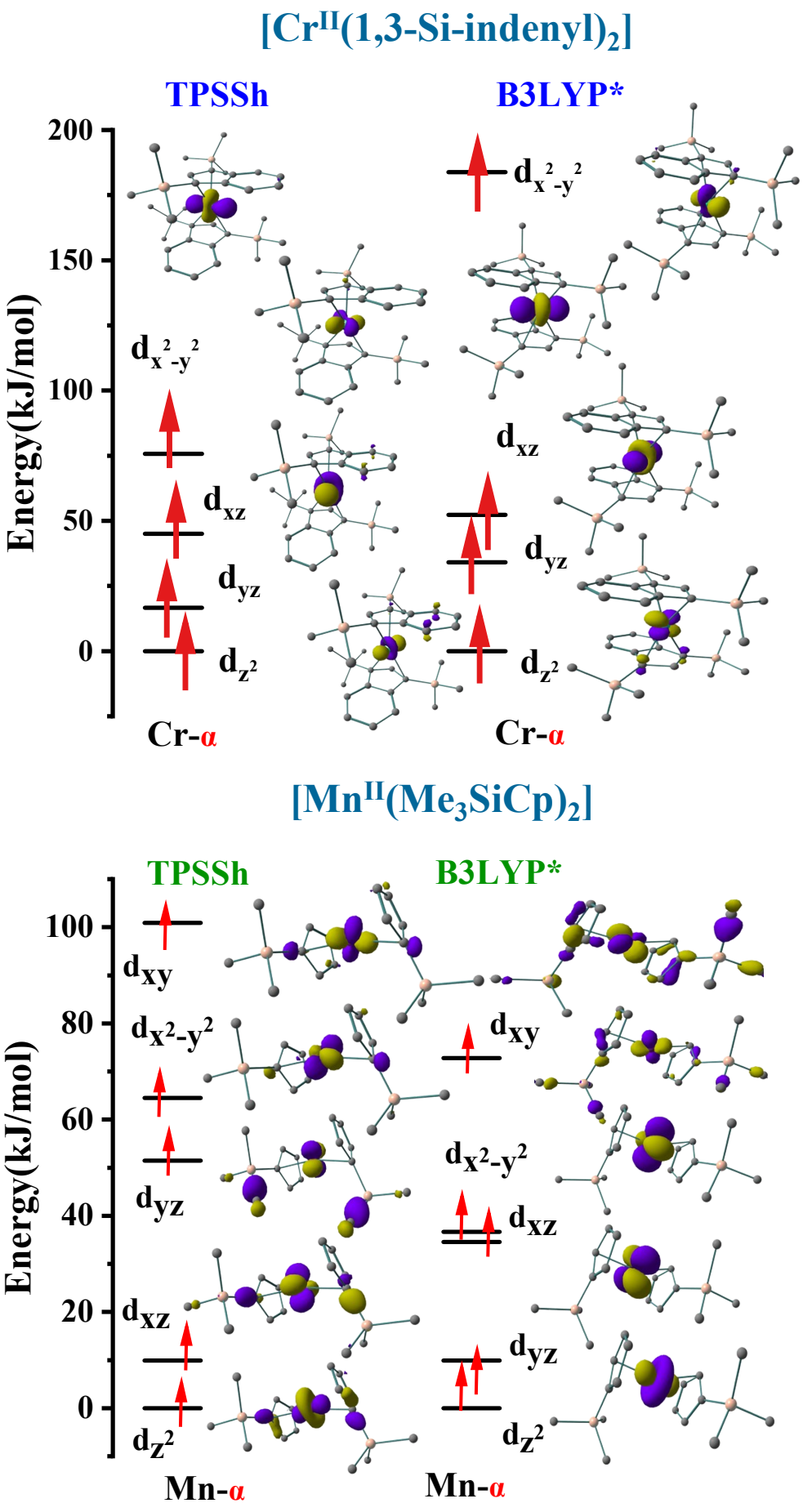
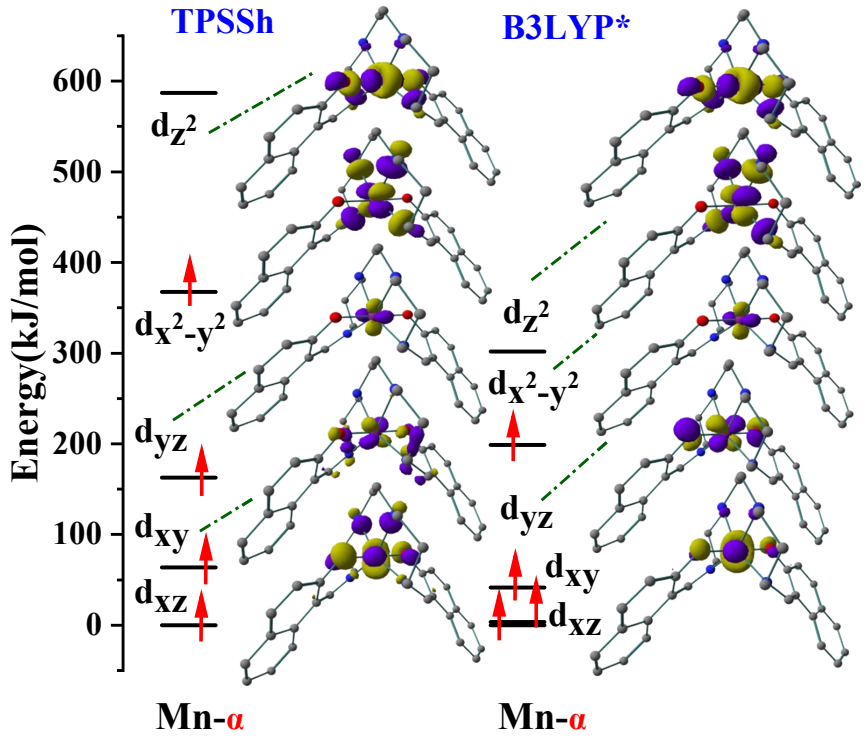


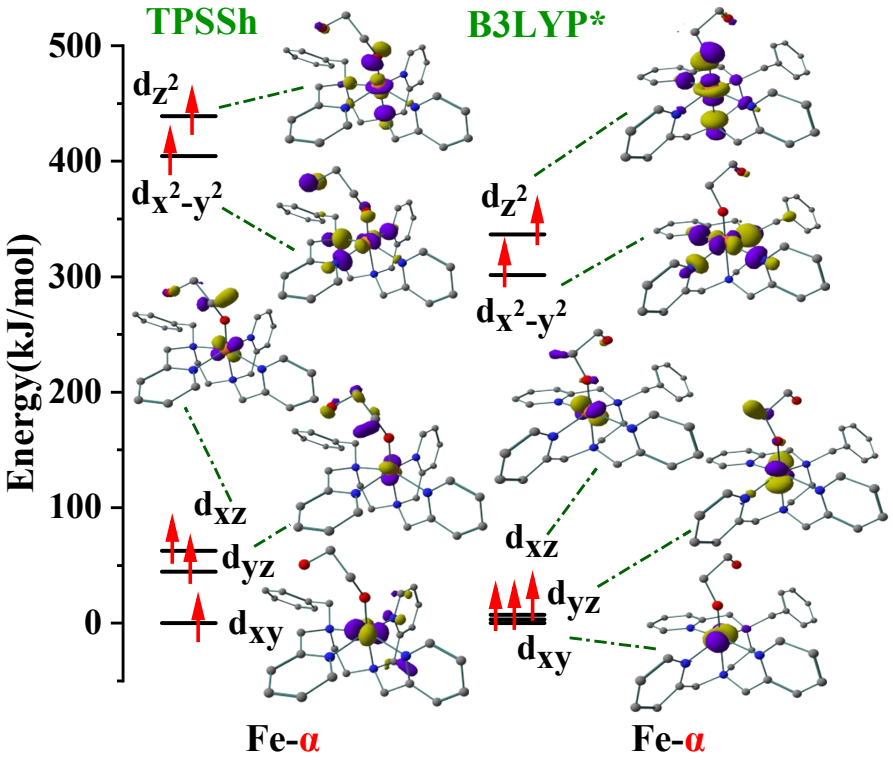
Figure S4: Spin density diagram with TPSSh optimized geometry for ([Cr^{II}(1,3-Si-indenyl)$_2$](**1**), [Mn^{II}(Me$_3$SiCp)$_2$](5), [Mn^{III}(naphth-sal)] (**3**), [Fe^{III}(bztpen)(OEtg)](**7**), [Fe^{III}(bztpen)(OProp)](**9**), [Fe^{II}(2amp)$_3$](**10**), [Fe^{II}(tacn)$_2$](**11**), [Fe^{II}(L$^{OMe-Nap}$)$_2$(NCS)$_2$](**12**), [Fe^{II} (L^{npdtz})$_2$(NCS)$_2$] (**13**), [Fe^{II}(bpte)(bim)](**15**), [Fe^{II}(L$^{OMe-Nap}$)$_2$(NCBH$_3$)$_2$] (**19**), [Fe^{II}(L^{npdtz})$_2$(NCSe)$_2$](**14**), [Fe^{II}(H-ptp$^-$)$_2$]^0(**16**), [Fe^{II}(CH$_2$OH)ptp$^-$)$_2$]^0(**17**), [Fe^{II}(COOCH$_3$-ptp$^-$)$_2$]^0 (**18**), [Fe^{II}(L^{Nap})$_2$(NCBH$_3$)$_2$](**20**), [Fe^{II}(H$_2$L^1)$_2$](**22**), [Co^{II}(L)$_2$](**23**), [Co^{II}(L)(N(CN)$_2$)$_2$](**24**) and [Co^{II}(tppz)$_2$](**26**).

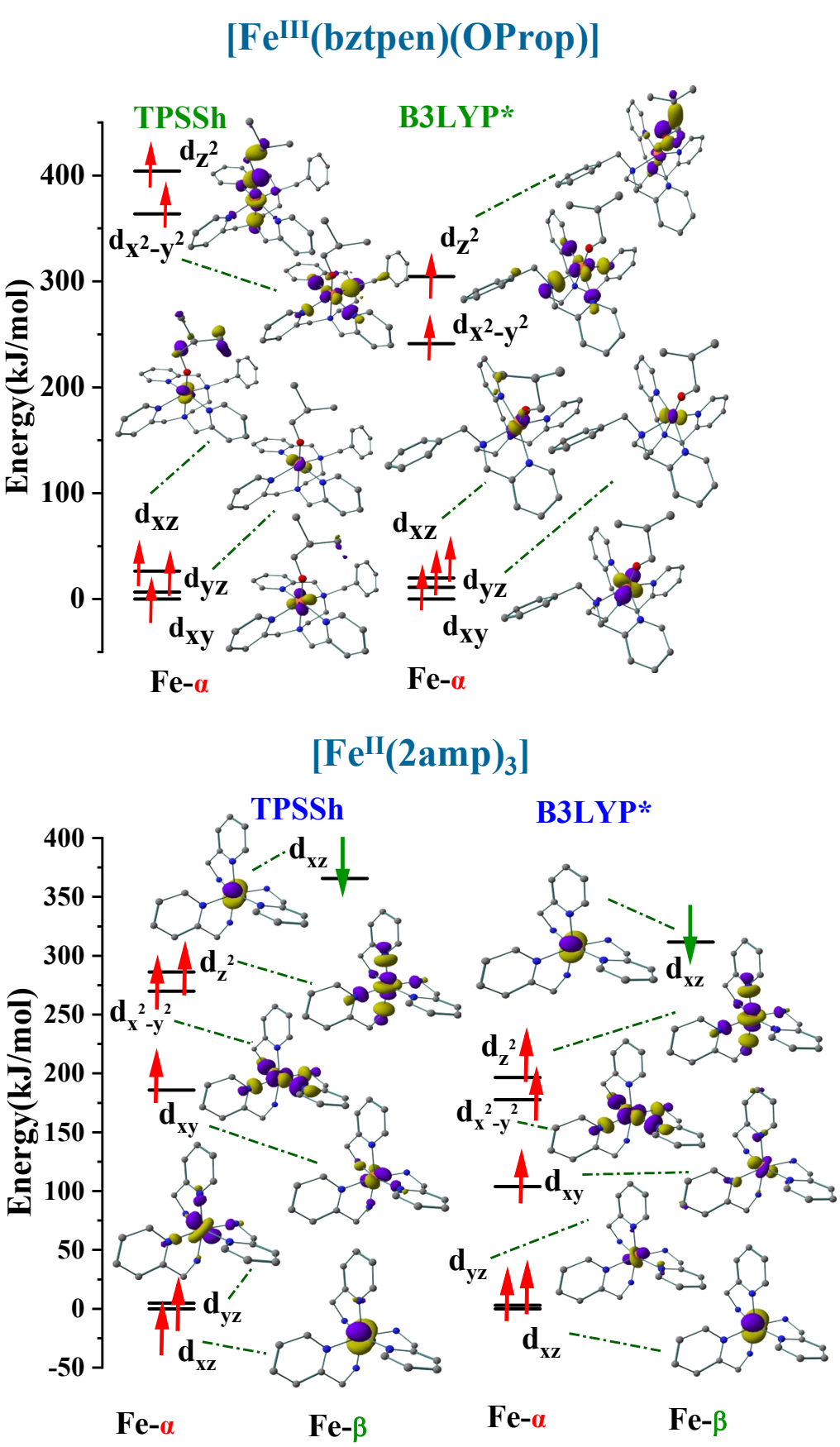

[Cr^II(1,3-Si-indenyl)2]
TPSSh
B3LYP*
Energy(kJ/mol)
200
150
100
50
0
d x2 -y2
dxz
dyz
dz2
Cr-α
[Mn^II(Me3SiCp)2]
TPSSh
B3LYP*
Energy(kJ/mol)
100
80
60
40
20
0
dxy
dx2-y2
dyz
dxz
dz2
Mn-α

[Mn^{III}(naphth-sal)]

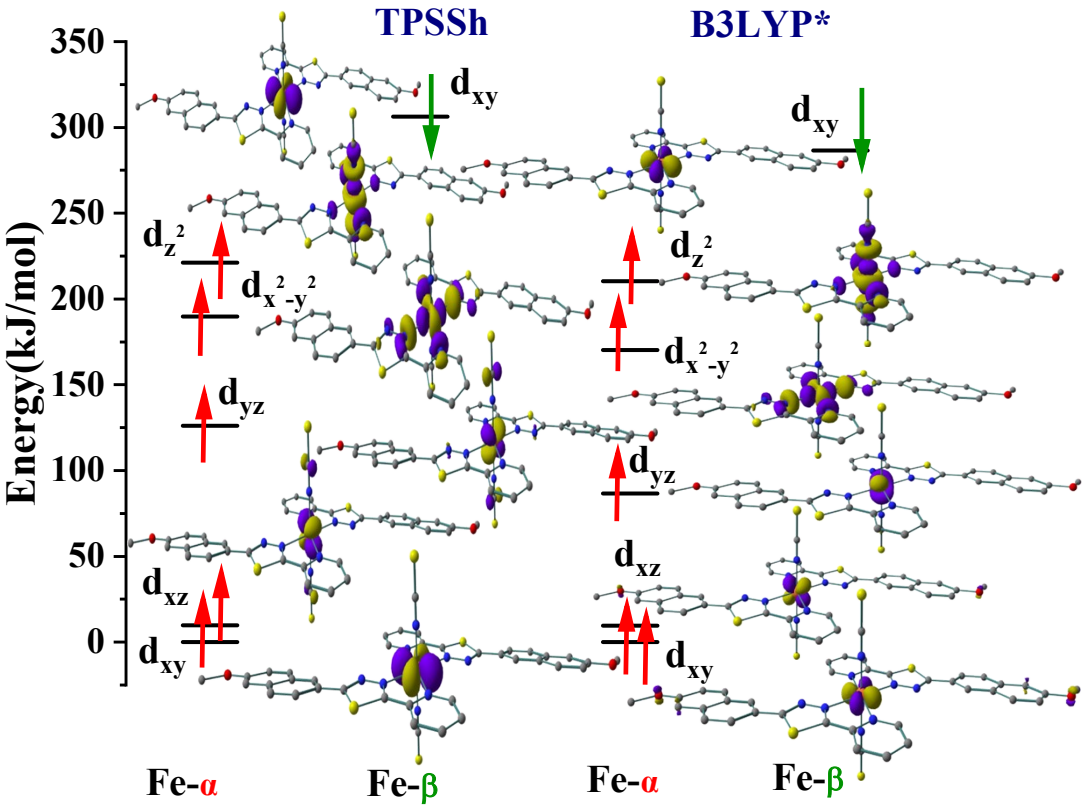


[Fe^{III}(bztpen)(OEtg)]

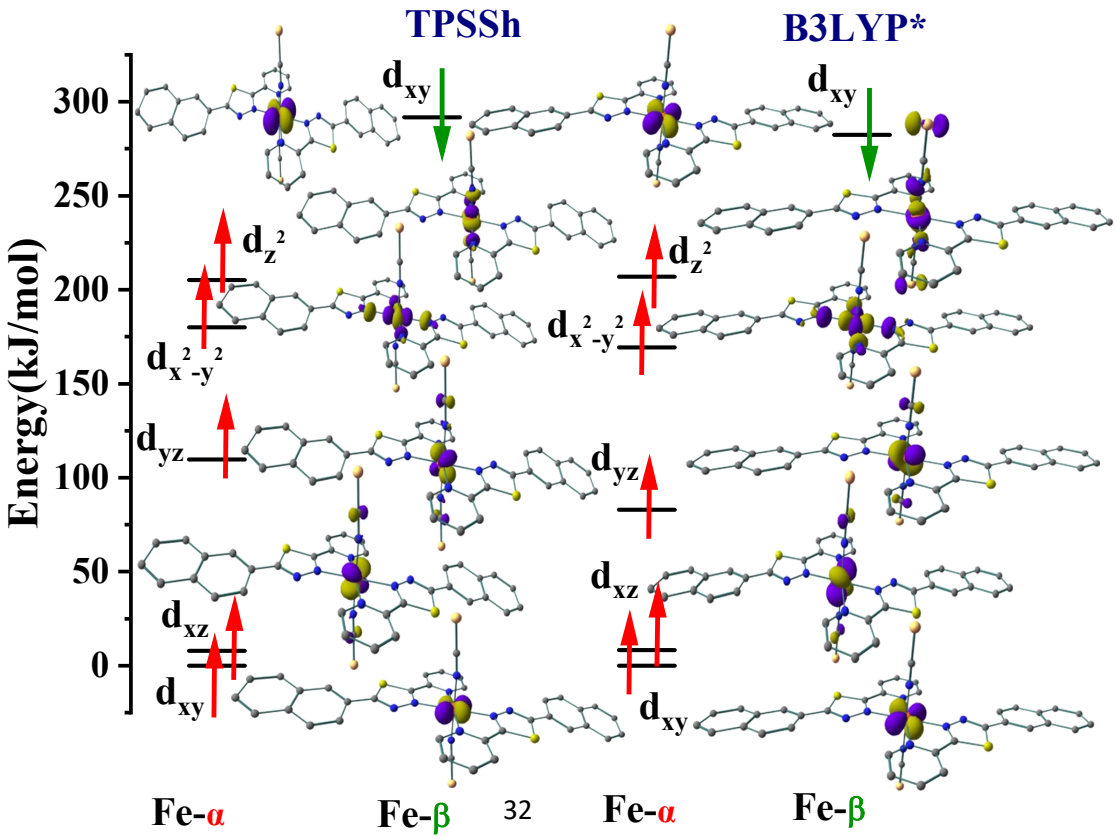



[Fe^III(bztpen)(OProp)]
TPSSh
B3LYP*
Energy(kJ/mol)
400
300
200
100
0
d_z^2
d_x^2-y^2
d_xz
d_yz
d_xy
Fe-α
[Fe^II(2amp)_3]
TPSSh
B3LYP*
Energy(kJ/mol)
400
350
300
250
200
150
100
50
0
-50
d_xz
d_z^2
d_x^2-y^2
d_xy
d_yz
Fe-α
Fe-β

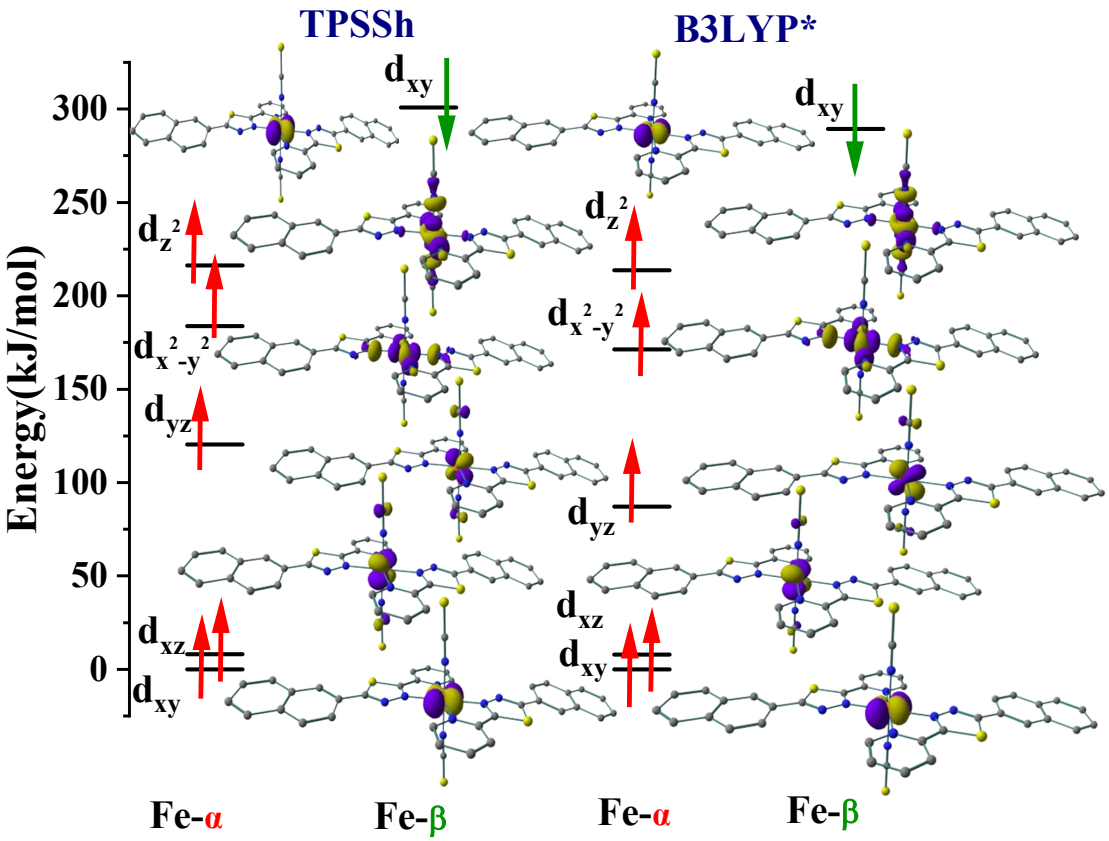
$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCS)_2]$



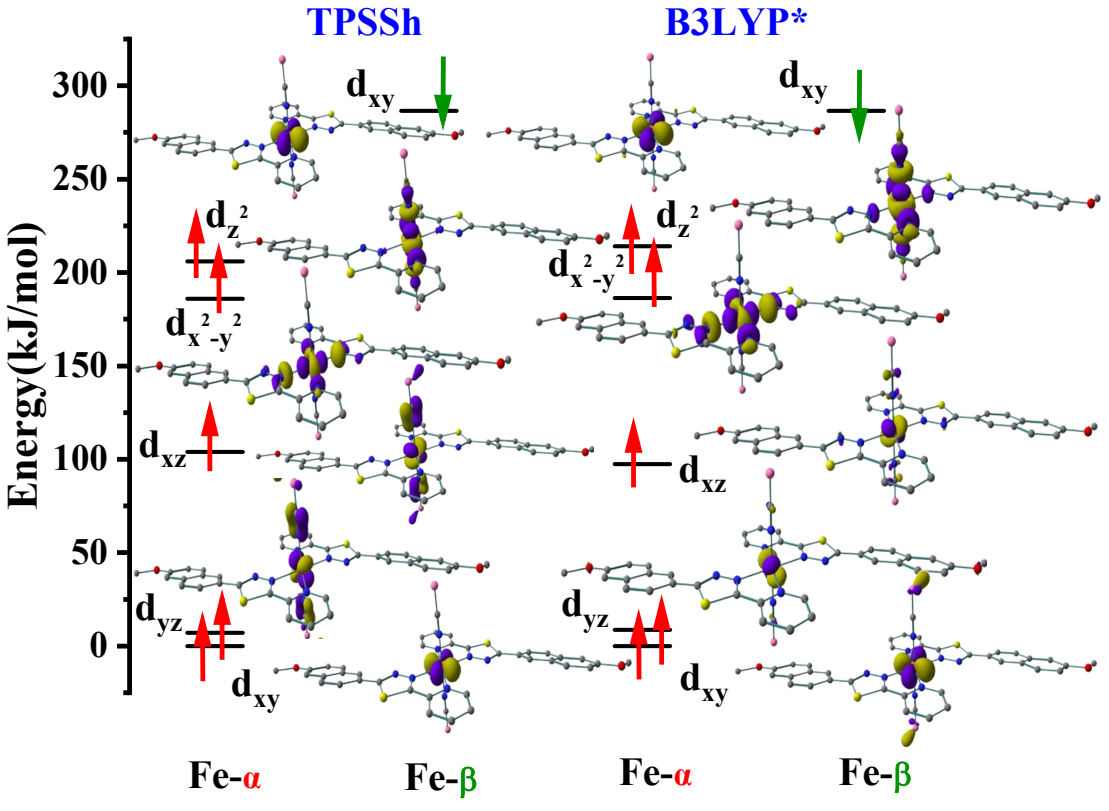
$[Fe^{II}(L^{npdtz})_2(NCSe)_2]$

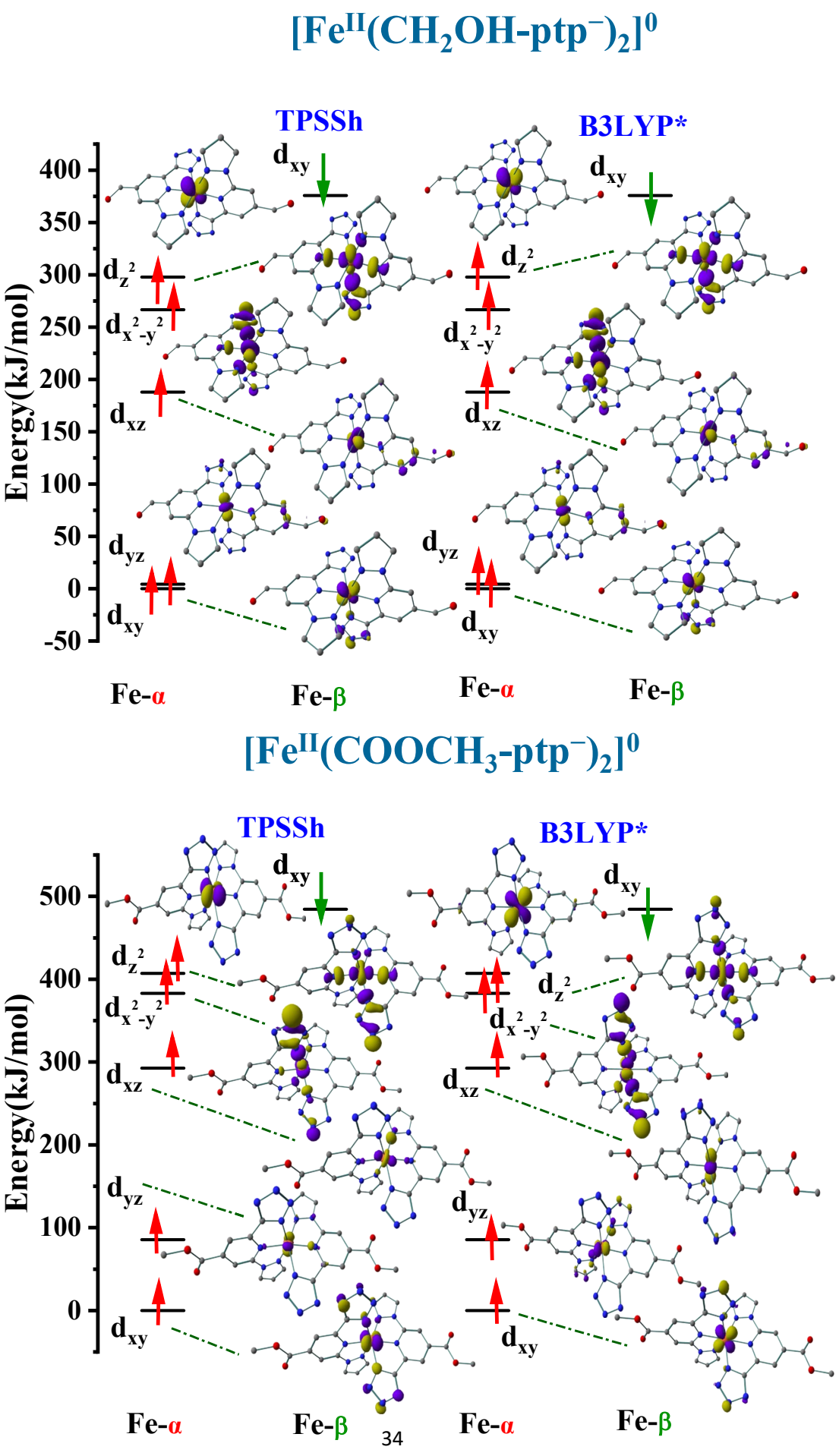


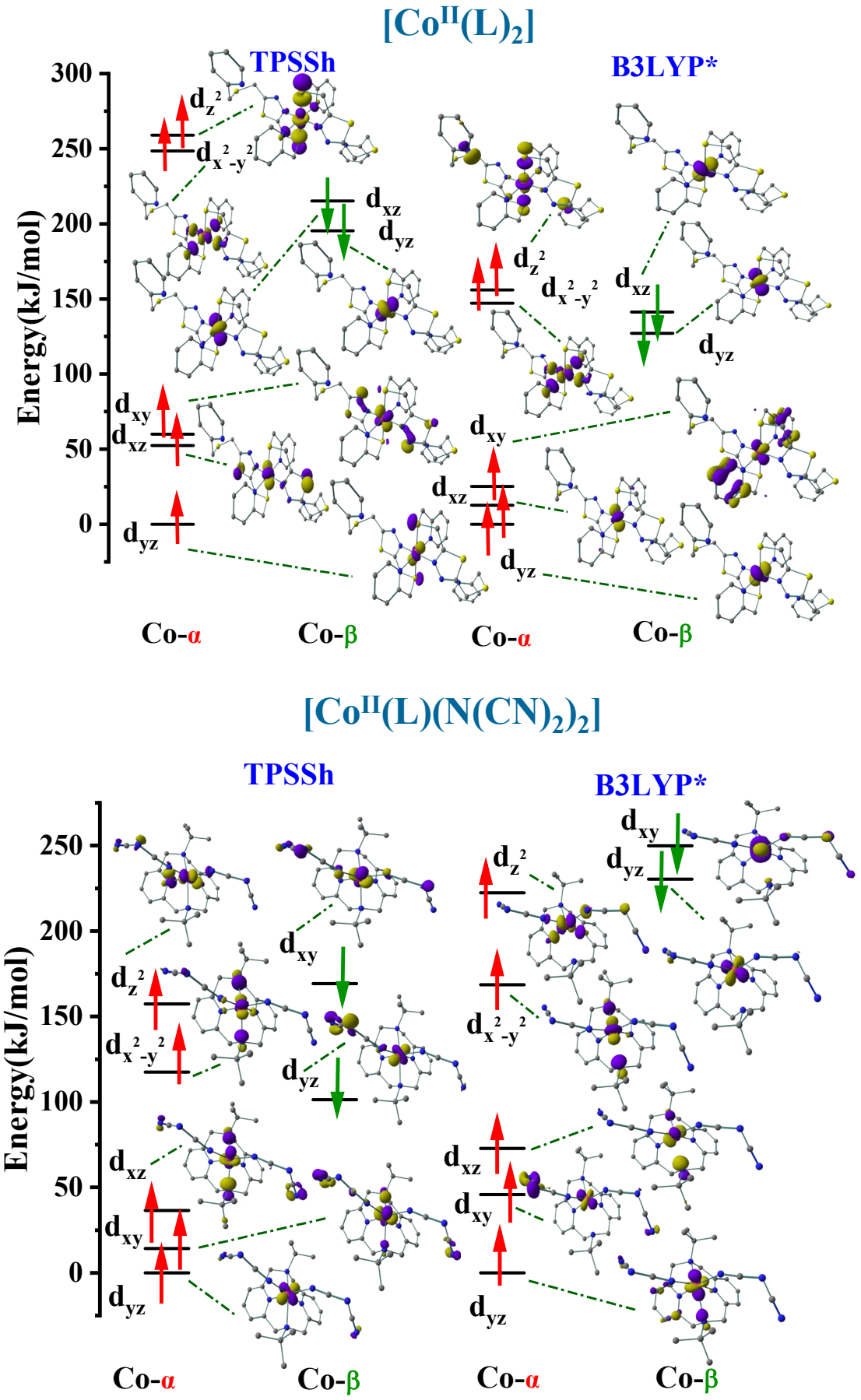
$[Fe^{II}(L^{npdtz})_2(NCS)_2]$



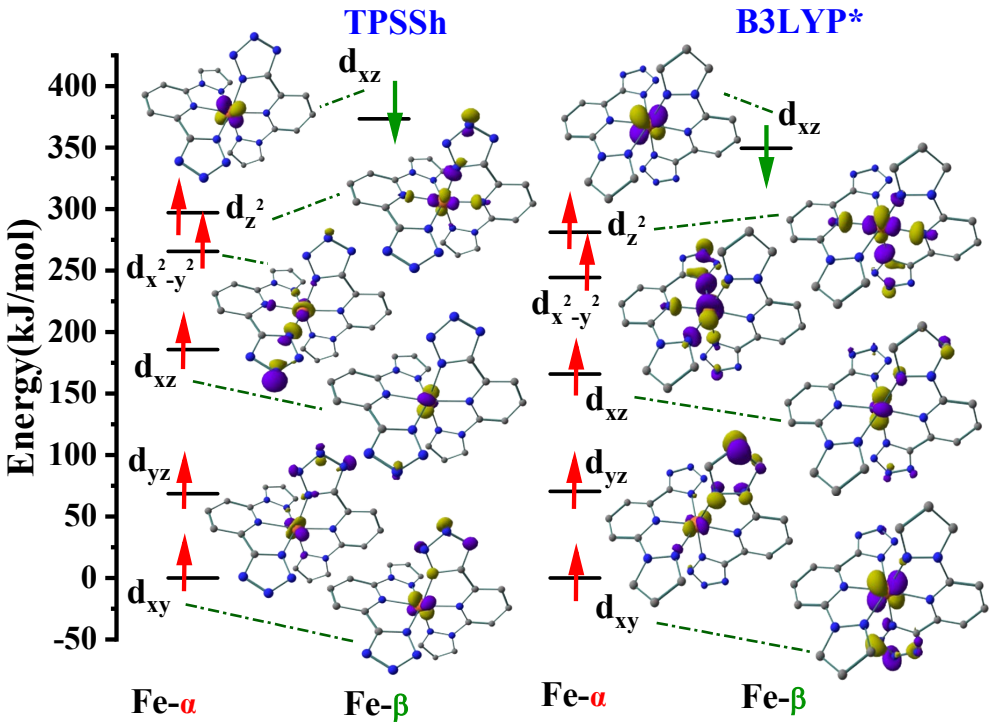
$[Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2]$



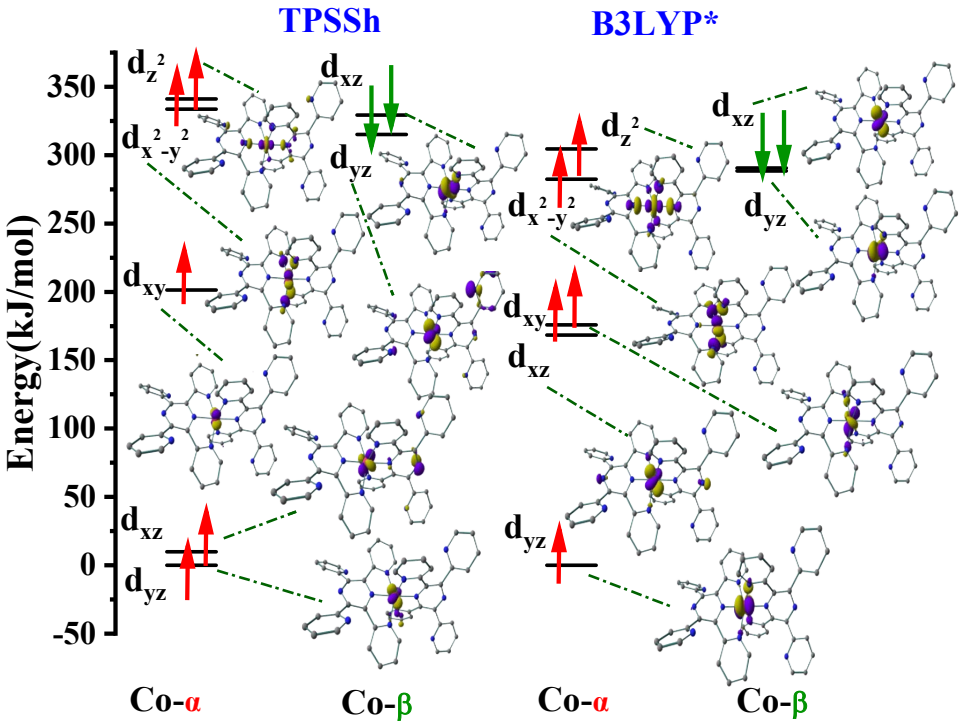

[Fe^II(CH2OH-ptp−)2]0
TPSSh
B3LYP*
Energy(kJ/mol)
400
350
300
250
200
150
100
50
0
-50
dxy
dz2
dx2-y2
dxz
dyz
dxy
Fe-α
Fe-β
Fe-α
Fe-β
[Fe^II(COOCH3-ptp−)2]0
TPSSh
B3LYP*
Energy(kJ/mol)
500
400
300
200
100
0
dxy
dz2
dx2-y2
dxz
dyz
dxy
Fe-α
Fe-β
Fe-α
Fe-β


[Co^II(L)2]
TPSSh
B3LYP*
Energy(kJ/mol)
300
250
200
150
100
50
0
dz2
dx2-y2
dxz
dyz
dxy
Co-α
Co-β
[Co^II(L)(N(CN)2)2]

$[Fe^{II}(H\text{-}ptp^{-})_2]^0$



$[Co^{II}(tppz)_2]$



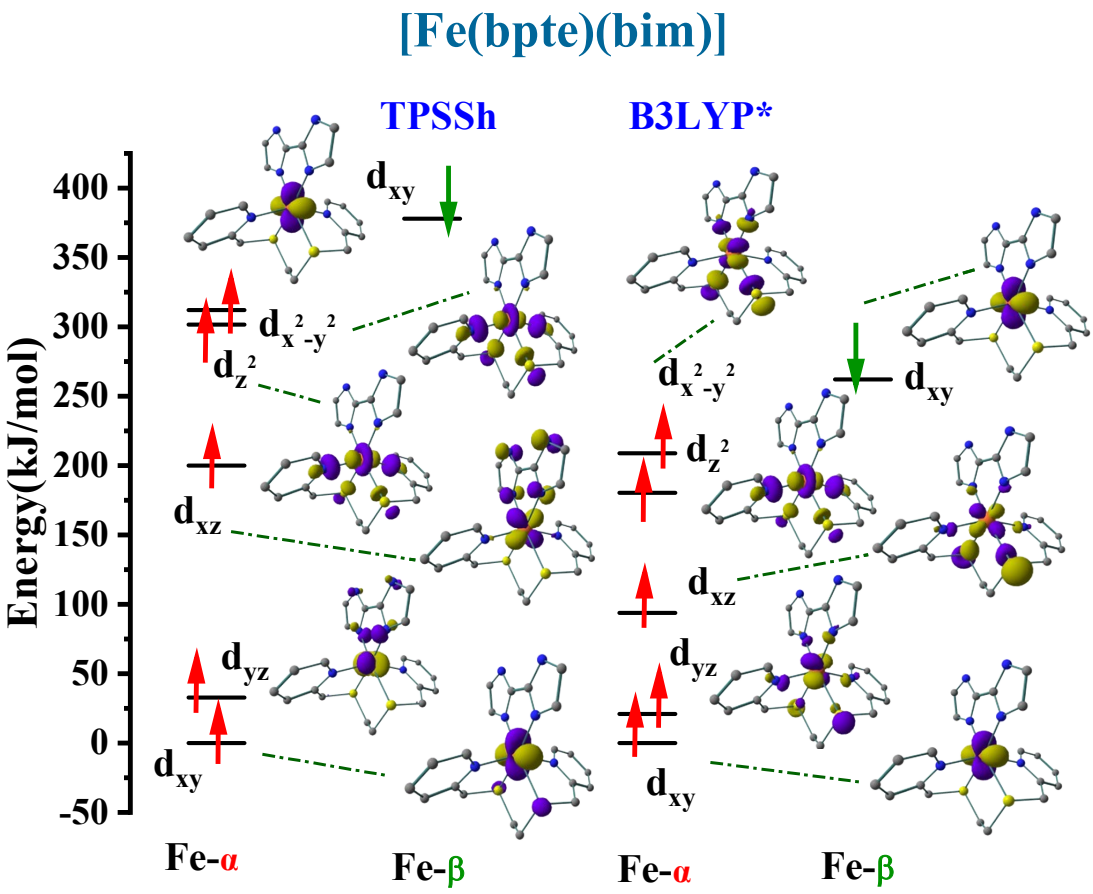


Figure S5: d-based eigenvalue plots for High-spin state computed with TPSSh and B3LYP* hybrid functionals for complexes **[**Mn^{III}(naphth-sal)] (**3**), [Fe^{III}(bztpen)(OEtg)](**7**), [Fe^{III}(bztpen)(OProp)](**9**), [$Fe^{II}(2amp)_3$](**10**),[$Fe^{II}(tacn)_2$](**11**), [$Fe^{II}(L^{OMe\text{-}Nap})_2(NCS)_2$](**12**), [$Fe^{II}(L^{npdtz})_2(NCSe)_2$](**14**), [$Fe^{II}$(bpte)(bim)](**15**), [$Fe^{II}(L^{npdtz})_2(NCS)_2$](**9**), [$Fe^{II}(L^{OMe\text{-}Nap})_2(NCBH_3)_2$](**15**), [$Fe^{II}(H\text{-}ptp^{-})_2]^0$(**12**), [$Fe^{II}(CH_2OH\text{-}ptp^{-})_2]^0$(**13**), [$Fe^{II}(COOCH_3\text{-}ptp^{-})_2]^0$ (**18**),[$Fe^{II}(L^{Nap})_2(NCBH_3)_2$](**20**), [$Fe^{II}(H_2L^1)_2$](**22**), [$Co^{II}(L)_2$](**23**), [$Co^{II}(L)(N(CN)_2)_2$](**24**) and [$Co^{II}(tppz)_2$](**26**). Spin-up electrons (α) are represented by the red arrow, while those that are spin-down (β) are represented by the green arrow. The energy has been scaled to the lowest spin-up orbitals for each scenario.