Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Extremely large differences in DFT energies for nitrogenase models

Lili Cao and Ulf Ryde *

Department of Theoretical Chemistry, Lund University, Chemical Centre, P. O. Box 124,

SE-221 00 Lund, Sweden

Correspondence to Ulf Ryde, E-mail: Ulf.Ryde@teokem.lu.se,

Tel: +46 – 46 2224502, Fax: +46 – 46 2228648

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Figure S1. Energies for the **1**→**5**, **4**→**5**, **3**→**4**, **2**→**3** and **1**→**2** reactions, obtained with all the 13 DFT methods. The cyan line shows %HF for the methods (right axis). It the same as Figure 3, but also with the results of the BHLYP, M06-2X and M06-HF methods.

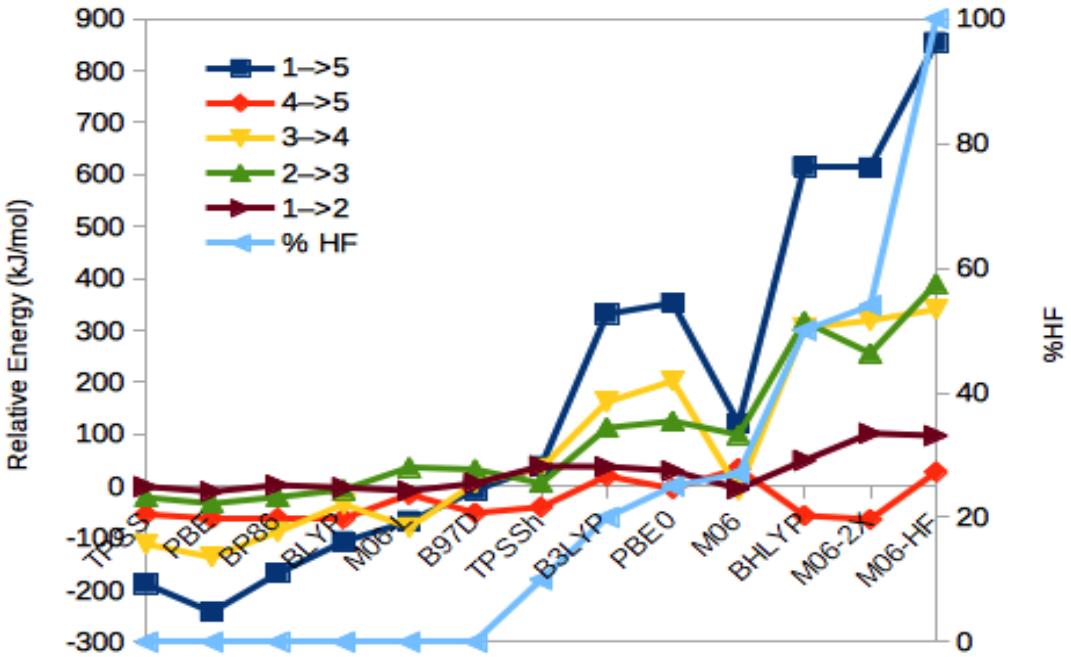

Figure S2. Energies for the **6**→**7**, **5**/**1**→**6**, **8**→**9**, **5**/**1**→**9**/**8** + H_2 and **9**/**8**→**0** + H_2 reactions obtained with all 13 different DFT methods (using the structure with the lowest energy for **5**/**1** and **9**/**8**). It is the same as Figure 5, but also with the results of the BHLYP, M06-2X and M06-HF methods.

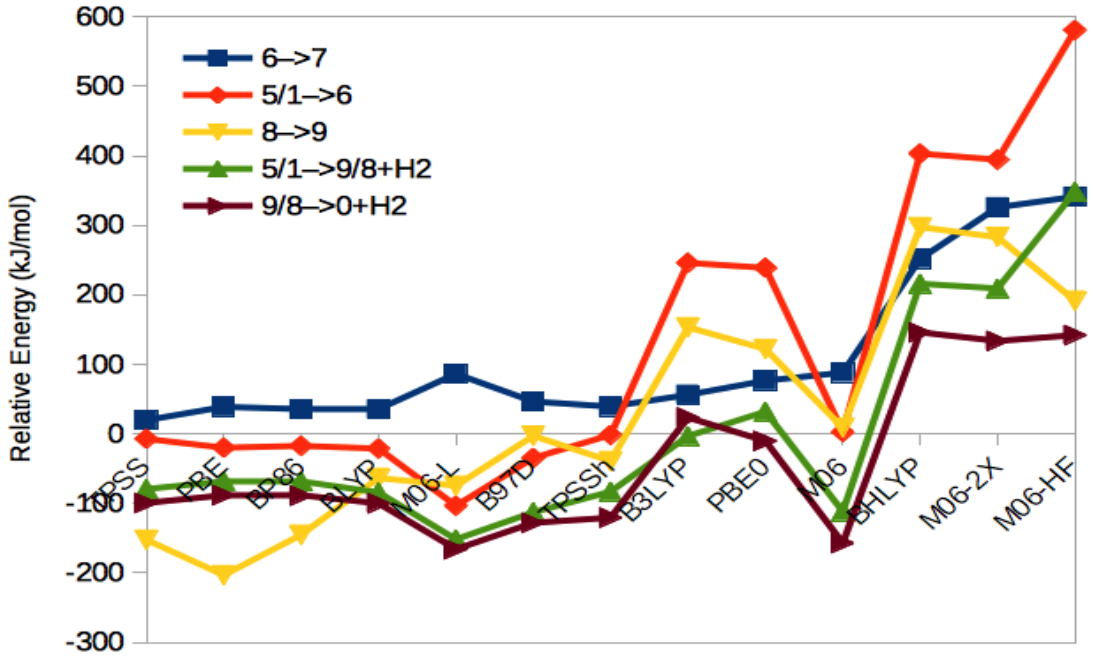

Figure S3. Performance of the various DFT methods for the structure of the resting E_0 state. For each method, the RMSD for the Mo, Fe, S and C atoms of the cluster, as well as the directly connected ligand S, O and N atoms are given, together with the MAD and maximum deviation for the 34 metal–ligand distances and the 15 short (< 3 Å) metal–metal distances. Same as Figure 6, but also with BHLYP, M06-2X and M06-HF. The maximum deviations of M06-HF are truncated (1.78 and 1.86 Å). It is the same as Figure 6, but also with the results of the BHLYP, M06-2X and M06-HF methods.

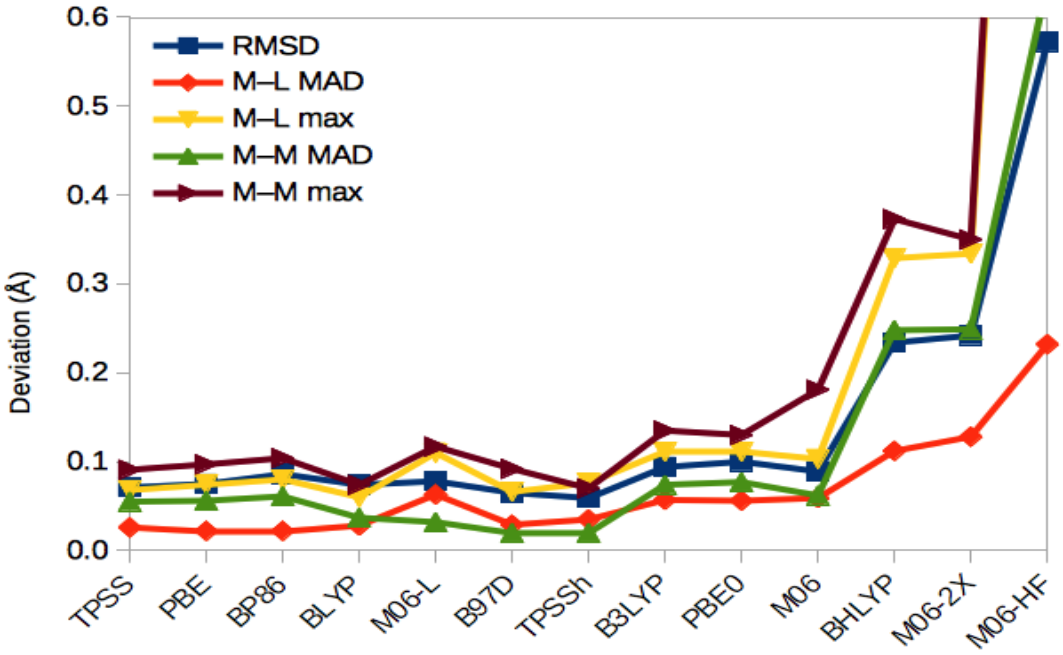

Table S1. H–X distances (Å) in the various models, optimised with the various DFT methods. Entries marked in magenta have changed qualitatively, compared to the other structures.

1	S2B	C	C	C		
TPSS	1.37	1.12	1.16	1.11		
PBE	1.38	1.14	1.18	1.12		
BP86	1.38	1.13	1.17	1.12		
B-LYP	1.38	1.12	1.15	1.11		
M06-L	1.36	1.11	1.11	1.11		
B97D	1.37	1.11	1.12	1.11		
TPSSh	1.36	1.11	1.12	1.11		
B3LYP	1.36	1.10	1.10	1.10		
PBE0	1.36	1.10	1.11	1.11		
M06	1.36	1.10	1.11	1.11		
BHLYP	1.35	1.08	1.10	1.09		
M06-2X	1.36	1.09	1.10	1.11		
M06-HF	1.35	1.09	1.10	1.09		
2	S2B	C	C	S2A		
TPSS	1.37	1.15	1.15	1.37		
PBE	1.38	1.17	1.16	1.38		
BP86	1.38	1.17	1.16	1.38		
B-LYP	1.38	1.15	1.15	1.38		
M06-L	1.36	1.13	1.13	1.37		
B97D	1.37	1.13	1.13	1.37		
TPSSh	1.36	1.13	1.13	1.37		
B3LYP	1.36	1.11	1.11	1.36		
PBE0	1.36	1.12	1.12	1.36		
M06	1.36	1.12	1.12	1.37		
BHLYP	1.35	1.10	1.09	1.35		
M06-2X	1.36	1.11	1.10	1.36		
M06-HF	1.35	1.11	1.10	1.36		
3	C	S2B	S2A	Fe2	Fe6	Fe7
TPSS	1.18	1.37	1.38	2.13	1.54	
PBE	1.19	1.38	1.39	2.15	1.53	
BP86	1.18	1.38	1.39	2.14	1.53	
B-LYP	1.17	1.38	1.38	2.09	1.54	
M06-L	1.15	1.36	1.37	2.38	1.57	2.28
B97D	1.16	1.37	1.37	2.15	1.51	
TPSSh	1.14	1.36	1.37	2.38	1.55	2.15
B3LYP	1.12	1.36	1.36		1.55	2.04
PBE0	1.13	1.36	1.36		1.57	1.97
M06	1.12	1.36	1.37		1.58	2.05
BHLYP	1.10	1.35	1.35		1.66	1.92
M06-2X	1.11	1.36	1.36		1.71	1.98
M06-HF	1.11	1.35	1.35		1.76	2.04

4	S2B	Fe2	Fe6	Fe3	Fe7	S5A
TPSS	1.36	1.60	1.69	1.92	1.53	1.37
PBE	1.37	1.62	1.68	1.93	1.53	1.38
BP86	1.37	1.61	1.68	1.93	1.52	1.38
B-LYP	1.37	1.62	1.69	1.93	1.53	1.38
M06-L	1.35	1.64	1.88	1.95	1.64	1.36
B97D	1.36	1.62	1.68	1.94	1.52	1.37
TPSSh	1.36	1.62	1.69	1.92	1.54	1.36
B3LYP	1.36	1.66	1.69	1.93	1.52	1.36
PBE0	1.35	1.59	1.80	1.85	1.61	1.36
M06	1.35	1.67	1.83	1.87	1.69	1.36
BHLYP	1.34	1.77	1.74	1.80	1.76	1.35
M06-2X	1.35	1.77	1.79	1.82	1.82	1.36
M06-HF	1.35	1.82	2.01	1.79	1.87	1.35

5	S2B	Fe2	Fe6	Fe4	Fe5	S3A
TPSS	1.37	1.70	1.65	1.55	1.55	
PBE	1.38	1.74	1.63	1.55	1.55	
BP86	1.38	1.72	1.63	1.54	1.54	
B-LYP	1.38	1.73	1.63	1.55	1.55	
M06-L	1.36	1.68	1.74	1.56	1.60	
B97D	1.37	1.73	1.62	1.55	1.55	
TPSSh	1.36	1.83	1.57	1.56	1.55	
B3LYP	1.36	1.77	1.60	1.57	1.55	
PBE0	1.36	1.74	1.64	1.57	1.55	
M06	1.36	1.72	1.70	1.56	1.62	
BHLYP	1.35	1.58	2.68	1.71		1.34
M06-2X	1.35	1.83	1.96	1.76		1.35
M06-HF	1.35	1.80	1.86	1.75		1.35

6	S2B	Fe2	Fe6	Fe5	H	C	S1A	Fe5
TPSS	1.37	1.52	2.35	1.82	0.78			
PBE	1.38	1.77	1.60	1.77	0.81			
BP86	1.38	1.76	1.60	1.76	0.81			
B-LYP	1.38	1.80	1.59	1.76	0.80			
M06-L	1.36	1.56	2.41	1.82	0.78			
B97D	1.37	1.50	2.47	1.83	0.79			
TPSSh	1.36	1.52	2.37	1.82	0.78			
B3LYP	1.36	1.52	2.48	1.83	0.78			
PBE0	1.36	1.52	2.46	1.82	0.78			
M06	1.36	1.54	2.50	1.83	0.78			
BHLYP	1.35	2.24	2.08	2.21	0.76	1.12		
M06-2X	1.35	2.21	2.13	2.25	0.76	1.13		
M06-HF	1.35			1.88	0.76		1.35	2.20

7	S2B	Fe4	Fe2	Fe6	Fe2	H
TPSS	1.38	1.55	1.75	2.38	1.71	0.83
PBE	1.39	1.55	1.67	2.35	1.64	0.89
BP86	1.39	1.55	1.67		1.64	0.88
B-LYP	1.39	1.55	1.77	2.44	1.74	0.83
M06-L	1.36	1.58	1.77	2.43	1.72	0.84
B97D	1.37	1.56	1.68		1.66	0.85
TPSSh	1.37	1.55	1.70		1.67	0.84
B3LYP	1.37	1.56	1.71		1.69	0.82
PBE0	1.36	1.55	1.69	2.41	1.67	0.83
M06	1.37	1.58	1.69	2.50	1.67	0.85
BHLYP	1.35	1.65				0.75
M06-2X	1.36	1.68				0.76
M06-HF	1.35	1.78	2.15		2.18	0.77

8	C	C
TPSS	1.13	1.16
PBE	1.13	1.16
BP86	1.13	1.16
B-LYP	1.13	1.16
M06-L	1.13	1.16
B97D	2.35	1.16
TPSSh	1.13	1.16
B3LYP	1.13	1.15
PBE0	1.13	1.16
M06	1.13	1.16
BHLYP	1.13	1.15
M06-2X	1.13	1.15
M06-HF	1.13	1.15

9	S2B	Fe2	Fe6	C2
TPSS	1.37	1.53	2.30	
PBE	1.38	1.52	2.44	
BP86	1.38	1.51	2.48	
B-LYP	1.38	1.52	2.58	
M06-L	1.36	1.57	2.33	
B97D	1.37	1.51	2.58	
TPSSh	1.36	1.53	2.41	
B3LYP	1.36	1.53	2.54	
PBE0	1.36	1.53	2.51	
M06	1.36	1.56	2.71	
BHLYP	1.35	1.57	2.62	
M06-2X	1.35	1.61	2.67	
M06-HF	1.35			1.11

Table S2. Relative energies (kJ/mol) for the various reactions, obtained with the 13 DFT methods, using structures optimised for each functional. The five final entries in the table give the minimum, maximum (these values are shown in bold face in the table), average and range of the reaction energies, as well as the correlation between the reaction energies and %HF (given in the second column).

DFT	%HF	ΔE_{15}	ΔE_{45}	ΔE_{34}	ΔE_{23}	ΔE_{12}	ΔE_{67}	ΔE_{56}	ΔE_{16}	ΔE_{89}	ΔE_{59}	ΔE_{18}	ΔE_{90}	ΔE_{81}
TPSS	0	-188	-54	-111	-22	-1	**20**	**-7**	-195	-153	79	115	100	252
PBE	0	**-242**	-62	**-137**	**-33**	**-10**	39	-20	**-262**	**-203**	**68**	107	88	**292**
BP86	0	-168	-62	-88	-21	2	35	-17	-185	-145	69	91	89	234
BLYP	0	-107	-62	-35	-7	-3	35	-21	-128	-64	84	128	100	164
M06-L	0	-67	-16	-79	36	-9	86	-104	-171	-75	152	**144**	**166**	241
B97D	0	-8	-51	6	32	5	46	-35	-43	-3	113	118	128	131
TPSSh	10	39	-64	58	5	39	39	-40	-2	-39	122	44	121	160
B3LYP	20	332	**-78**	259	112	38	56	-86	246	153	182	3	130	-23
PBE0	25	353	-5	203	125	29	76	-114	239	122	199	-32	132	10
M06	27	121	**34**	-8	99	-5	88	-118	2	9	224	112	**166**	157
BHLYP	50	615	-57	305	317	50	252	-212	403	**298**	101	-216	152	**-146**
M06-2X	54	613	-64	319	256	**102**	326	-219	395	283	121	-209	149	-134
M06-HF	100	**855**	27	**340**	**390**	97	**341**	**-274**	**581**	192	**315**	**-348**	**50**	-142
Min		-242	-78	-137	-33	-10	20	-274	-262	-203	68	-348	50	-146
Max		855	34	340	390	102	341	-7	581	298	315	144	166	292
Range		1097	112	477	423	112	322	266	844	501	246	493	78	438
R^2		0.88	0.22	0.70	0.92	0.75	0.85	0.88	0.84	0.61	0.51	0.90	0.04	0.73

Table S3. Relative energies (kJ/mol) for the various reactions, obtained with the 13 DFT methods, using the same structures optimised either by TPSS or B3LYP. The five final entries are the same as in Table S3. R^2 Opt is the correlation between the reaction energies in this table and those based on optimised structures in Table S3.

DFT	%HF	ΔE_{15}	ΔE_{45}	ΔE_{34}	ΔE_{23}	ΔE_{12}	ΔE_{67}	ΔE_{56}	ΔE_{16}	ΔE_{89}	ΔE_{59}	ΔE_{18}	ΔE_{90}	ΔE_{81}
TPSS	0	-289	-42	-158	-31	-58	21	-12	-301	-179	86	196	96	275
PBE	0	**-358**	-50	**-200**	**-37**	**-72**	20	-4	**-363**	**-236**	76	198	**85**	**321**
BP86	0	-294	-50	-159	-26	-60	**16**	**-2**	-296	-169	**75**	201	**85**	254
BLYP	0	-176	-49	-73	-10	-44	20	-11	-187	-83	93	186	98	181
M06-L	0	-114	-35	-38	23	-65	85	-82	-196	-59	160	**214**	161	220
B97D	0	-48	-40	-2	29	-35	56	-36	-83	1	120	168	125	124
TPSSh	10	80	-38	89	30	-1	52	-52	28	37	134	92	120	83
B3LYP	20	479	-46	380	108	38	76	-92	387	290	191	2	140	-150
PBE0	25	504	-53	404	122	31	95	-119	384	256	214	-34	138	-118
M06	27	253	**-54**	216	95	-5	125	-120	133	130	221	97	**182**	52
BHLYP	50	1298	0	900	307	91	136	-216	1082	732	331	-234	163	-570
M06-2X	54	1247	-3	870	304	75	180	-232	1015	672	347	-228	180	-492
M06-HF	100	**1915**	**79**	**1266**	**458**	**111**	**227**	**-274**	**1641**	**1089**	**357**	**-468**	122	**-968**
Min		-358	-54	-200	-37	-72	16	-274	-363	-236	75	-468	85	-968
Max		1915	79	1266	458	111	227	-2	1641	1089	357	214	182	321
Range		2273	132	1466	495	184	211	272	2003	1326	282	683	97	1289
R^2		0.94	0.81	0.93	0.96	0.83	0.88	0.89	0.94	0.94	0.84	0.96	0.17	0.95
R^2 Opt		0.98	0.13	0.87	0.98	0.81	0.85	0.99	0.95	0.81	0.38	0.98	0.64	0.29

Table S4. Reaction energies for the $N_2 + H_2 \rightarrow 2\ NH_3$, $N_2 + H_2 \rightarrow 2\ NH_3$ and $N_2 + H_2 \rightarrow 2\ NH_3$ reactions obtained with the 13 DFT methods. The five final entries are the same as in Table S3.

		ΔE (kJ/mol)		
	%HF	N_2H_2	N_2H_4	NH_3
TPSS	0	175	-84	**-138**
PBE	0	153	-103	-149
BP86	0	157	-98	-149
BLYP	0	173	-85	-146
M06-L	0	157	-103	**-172**
B97D	0	175	**-83**	-148
TPSSh	10	172	-93	-145
B3LYP	20	168	-102	-157
PBE0	25	**152**	**-121**	-161
M06	27	161	-106	-162
BHLYP	50	167	-120	-170
M06-2X	54	180	-110	-158
M06-HF	100	**188**	-113	-147
Min		152	-121	-172
Max		188	-83	-138
Av.		167	-102	-154
Range		37	38	35
R^2		0.29	0.42	0.03

Table S5. Performance of the various DFT methods for the structure of the resting E_0 state, compared to the crystal structure[1] (average over the two subunits). For each method, the RMSD, as well as the MAD and maximum deviation is given for the 34 metal–ligand distances and the 15 short (< 3 Å) metal–metal distances. The distance giving the maximum deviation is also indicated. The last column is the sum of the five entries for each method. The best result in each column is emphasized in bold face.

	RMSD	Metal–ligand			Metal–metal			Sum
		MAD	max	bond	MAD	max	bond	
TPSS	0.071	0.026	0.068	Fe2–C	0.055	0.091	Fe1–Fe2	0.311
PBE	0.075	**0.022**	0.074	Fe2–C	0.056	0.097	Fe1–Fe2	0.324
BP86	0.086	**0.022**	0.080	Fe2–C	0.061	0.104	Fe1–Fe2	0.353
BLYP	0.074	0.028	**0.060**	Fe4–S4A	0.037	**0.074**	Fe1–Fe2	0.273
M06-L	0.078	0.063	0.110	Fe3–S2A	0.032	0.117	Fe5–Mo	0.400
B97D	0.065	0.029	0.066	Fe4–S4A	**0.020**	0.092	Fe5–Mo	0.272
TPSSh	**0.059**	0.035	0.076	Mo–O1	**0.020**	0.070	Fe5–Mo	**0.260**
B3LYP	0.094	0.057	0.111	Fe3–S2A	0.074	0.135	Fe5–Mo	0.471
PBE0	0.100	0.056	0.111	Fe3–C	0.077	0.130	Fe1–Fe3	0.474
M06	0.089	0.059	0.103	Fe3–S2A	0.062	0.181	Fe5–Mo	0.494
BHLYP	0.234	0.112	0.329	Fe3–C	0.248	0.373	Fe7–Mo	1.296
M06-2X	0.242	0.128	0.334	Fe3–C	0.249	0.350	Fe5–Fe6	1.303
M06-HF	0.572	0.232	1.781	Fe6–C	0.639	1.857	Fe3–Fe4	5.081

Table S6. Mulliken spin populations of the metals in all the optimised structures.

DFT	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Mo
1								
TPSS	3.30	-3.31	-3.40	-3.41	3.08	2.77	3.14	-0.99
PBE	3.21	-3.24	-3.31	-3.32	3.01	2.64	3.05	-0.95
BP86	3.21	-3.23	-3.30	-3.31	3.00	2.65	3.04	-0.95
BLYP	3.14	-3.17	-3.24	-3.27	2.98	2.59	3.01	-0.93
M06-L	3.50	-3.52	-3.56	-3.54	3.43	3.27	3.41	-1.65
B97D	3.42	-3.38	-3.42	-3.41	3.23	3.01	3.23	-1.58
TPSSh	3.51	-3.58	-3.65	-3.57	3.45	3.40	3.48	-1.82
B3LYP	3.59	-3.66	-3.68	-3.63	3.59	3.56	3.62	-2.33
PBE0	3.71	-3.75	-3.77	-3.73	3.71	3.68	3.74	-2.54
M06	3.64	-3.69	-3.74	-3.66	3.61	3.59	3.69	-2.32
BHLYP	3.87	-3.86	-3.87	-3.85	3.85	3.87	3.86	-2.86
M06-2X	3.83	-3.85	-3.85	-3.83	3.82	3.84	3.85	-2.92
M06-HF	3.98	-3.98	-3.98	-3.96	3.95	3.96	3.97	-3.34
2								
TPSS	3.21	-3.30	-3.42	-3.26	3.12	2.63	3.01	-0.93
PBE	3.08	-3.15	-3.33	-3.15	3.11	2.30	2.96	-0.88
BP86	3.08	-3.12	-3.30	-3.13	3.09	2.25	2.95	-0.87
BLYP	3.03	-3.07	-3.29	-3.08	3.03	2.26	2.91	-0.84
M06-L	3.51	-3.50	-3.61	-3.47	3.34	3.19	3.37	-1.57
B97D	3.28	-3.34	-3.46	-3.31	3.21	2.92	3.17	-1.47
TPSSh	3.50	-3.49	-3.66	-3.58	3.34	3.25	3.42	-1.70
B3LYP	3.57	-3.55	-3.70	-3.63	3.47	3.45	3.60	-2.21
PBE0	3.68	-3.68	-3.79	-3.74	3.61	3.63	3.73	-2.48
M06	3.63	-3.59	-3.73	-3.70	3.50	3.56	3.66	-2.28
BHLYP	3.82	-3.84	-3.86	-3.85	3.83	3.82	3.86	-2.85
M06-2X	3.80	-3.82	-3.85	-3.82	3.80	3.79	3.85	-2.89
M06-HF	3.95	-3.96	-3.96	-3.97	3.97	3.94	3.95	-3.30
3								
TPSS	-3.21	-3.16	3.37	3.26	-2.99	0.92	2.90	-0.15
PBE	-3.04	-3.05	3.30	3.20	-2.82	0.43	2.83	-0.03
BP86	-3.06	-3.04	3.29	3.19	-2.77	0.44	2.80	-0.04
BLYP	-3.11	-3.00	3.23	2.98	-2.74	0.90	2.83	-0.16
M06-L	-3.52	-3.41	3.57	3.48	-3.58	2.33	3.38	-1.00
B97D	-3.34	-3.29	3.41	3.29	-3.11	1.37	3.09	-0.37
TPSSh	-3.55	-3.52	3.66	3.37	-3.39	2.42	3.35	-0.87
B3LYP	-3.60	-3.58	3.71	3.48	-3.56	2.78	3.46	-1.10
PBE0	-3.70	-3.71	3.81	3.64	-3.70	3.04	3.58	-1.25
M06	-3.65	-3.64	3.75	3.54	-3.68	2.97	3.49	-0.96
BHLYP	-3.82	-3.84	3.90	3.80	-3.81	3.60	3.79	-1.84
M06-2X	-3.81	-3.82	3.88	3.76	-3.81	3.59	3.76	-1.91
M06-HF	-3.95	-3.96	3.97	3.91	-3.97	3.80	3.92	-2.34
4								
TPSS	-3.33	2.11	-3.15	2.64	2.21	1.42	-0.12	-0.39
PBE	-3.19	2.03	-2.95	2.44	2.11	1.23	-0.07	-0.36
BP86	-3.18	2.02	-2.93	2.41	2.10	1.23	-0.06	-0.37
BLYP	-3.16	2.05	-2.97	2.43	2.12	1.27	-0.09	-0.38

M06-L	-3.69	2.87	-3.48	3.52	3.34	3.10	-3.22	-0.90
B97D	-3.43	2.41	-3.24	2.89	2.42	2.12	-1.15	-0.63
TPSSh	-3.67	2.67	-3.43	3.22	2.87	2.60	-1.94	-0.73
B3LYP	-3.71	3.42	-3.49	3.65	3.57	3.03	-2.97	-2.42
PBE0	-3.92	3.16	-3.65	3.65	3.63	3.47	-3.15	-1.30
M06	-3.82	3.44	-3.69	3.79	3.64	3.50	-3.65	-1.98
BHLYP	-4.18	3.76	-3.86	3.85	3.81	3.67	-3.80	0.98
M06-2X	-4.18	3.73	-3.86	3.81	3.78	3.65	-3.79	1.03
M06-HF	-3.99	3.85	-3.94	3.93	3.87	3.82	-3.94	1.05
5								
TPSS	-3.30	2.06	2.66	2.39	-1.64	1.69	-2.53	0.17
PBE	-3.09	1.97	2.56	2.27	-1.62	1.41	-2.36	0.24
BP86	-3.08	1.92	2.51	2.26	-1.58	1.44	-2.33	0.23
BLYP	-3.10	2.00	2.53	2.28	-1.64	1.49	-2.38	0.25
M06-L	-3.78	2.55	3.34	2.79	-2.96	2.86	-3.31	0.48
B97D	-3.45	2.32	2.94	2.51	-2.28	1.99	-2.81	0.44
TPSSh	-3.72	3.19	3.24	2.78	-2.57	1.63	-2.99	0.30
B3LYP	-3.85	3.18	3.43	2.96	-2.90	2.61	-3.40	0.42
PBE0	-3.99	3.35	3.59	3.13	-3.15	3.01	-3.63	0.51
M06	-3.93	3.08	3.52	2.77	-3.37	3.20	-3.59	0.67
BHLYP	-4.16	3.48	3.80	3.93	-3.83	3.75	-3.80	0.92
M06-2X	-4.16	3.71	3.77	3.89	-3.82	3.70	-3.87	1.00
M06-HF	-4.37	3.83	3.83	3.88	-3.97	3.93	-3.98	0.99
6								
TPSS	3.30	0.67	-2.86	-2.76	2.53	-2.39	2.55	-0.29
PBE	3.01	-1.46	-2.50	-2.46	2.54	-0.49	2.47	-0.50
BP86	3.00	-1.43	-2.48	-2.44	2.51	-0.51	2.45	-0.48
BLYP	3.01	-1.54	-2.49	-2.44	2.54	-0.45	2.48	-0.50
M06-L	3.68	2.73	-3.52	-3.48	3.34	-3.52	3.37	-1.42
B97D	3.40	1.21	-3.12	-3.09	2.82	-2.77	2.85	-0.48
TPSSh	3.63	1.97	-3.45	-3.44	3.14	-3.23	3.15	-0.60
B3LYP	3.63	2.66	-3.63	-3.62	3.39	-3.47	3.41	-0.91
PBE0	3.73	2.93	-3.76	-3.75	3.56	-3.64	3.58	-1.03
M06	3.74	2.62	-3.72	-3.71	3.46	-3.67	3.51	-0.83
BHLYP	3.84	3.85	-3.86	-4.17	3.81	-3.82	3.80	-1.86
M06-2X	3.82	3.82	-3.83	-4.17	3.77	-3.82	3.77	-1.89
M06-HF	3.94	3.86	-4.01	-3.95	3.78	-3.95	3.93	-1.06
7								
TPSS	3.33	-0.11	-2.95	-2.35	2.09	-1.42	2.32	-0.27
PBE	3.20	-0.16	-2.80	-2.23	1.92	-1.19	2.17	-0.27
BP86	3.19	-0.14	-2.78	-2.22	1.87	-1.18	2.14	-0.26
BLYP	3.16	-0.23	-2.79	-2.21	1.97	-1.20	2.19	-0.28
M06-L	3.75	1.39	-3.50	-3.05	3.38	-3.43	3.31	-1.26
B97D	3.46	0.12	-3.06	-2.70	2.73	-2.60	2.83	-0.42
TPSSh	3.72	0.38	-3.40	-2.86	2.97	-2.97	3.09	-0.41
B3LYP	3.83	0.19	-3.59	-2.99	3.41	-3.36	3.34	-0.61
PBE0	3.95	0.15	-3.75	-3.16	3.59	-3.52	3.52	-0.71
M06	3.88	0.94	-3.67	-3.17	3.69	-3.68	3.67	-1.62
BHLYP	4.17	-0.05	-3.87	-3.69	3.99	-3.77	3.79	-0.97
M06-2X	4.14	0.00	-4.08	-3.64	3.99	-3.74	3.77	-0.95

M06-HF	3.94	-0.11	-4.00	-3.86	3.95	-3.94	3.96	-1.04
8								
TPSS	3.41	3.40	-3.31	-3.39	-3.15	3.03	3.04	-0.37
PBE	3.18	3.27	-3.16	-3.24	-3.00	2.92	2.99	-0.34
BP86	3.20	3.01	-3.09	-3.19	-2.91	2.92	2.96	-0.34
BLYP	3.22	3.21	-3.15	-3.18	-2.94	2.87	2.93	-0.34
M06-L	3.64	3.56	-3.55	-3.64	-3.43	3.31	3.43	-0.66
B97D	3.45	3.38	-3.36	-3.41	-3.22	3.11	3.18	-0.61
TPSSh	3.63	3.56	-3.54	-3.61	-3.35	3.33	3.37	-0.73
B3LYP	3.68	3.73	-3.60	-3.68	-3.55	3.50	3.55	-0.96
PBE0	3.79	3.87	-3.71	-3.76	-3.70	3.63	3.67	-1.13
M06	3.76	3.71	-3.65	-3.77	-3.57	3.60	3.58	-0.90
BHLYP	3.86	4.13	-3.84	-3.87	-3.82	3.82	3.86	-1.91
M06-2X	3.83	4.12	-3.81	-3.84	-3.80	3.78	3.83	-1.90
M06-HF	3.98	3.92	-3.94	-3.91	-3.96	3.93	3.94	-2.28
9								
TPSS	3.31	1.90	-2.78	-2.85	2.69	-1.64	2.47	-0.38
PBE	3.17	1.76	-2.59	-2.65	2.49	-1.39	2.30	-0.35
BP86	3.17	1.75	-2.56	-2.62	2.46	-1.38	2.26	-0.35
BLYP	3.15	1.82	-2.62	-2.65	2.50	-1.41	2.29	-0.36
M06-L	3.68	2.79	-3.47	-3.47	3.36	-2.87	3.30	-0.54
B97D	3.41	2.26	-3.07	-3.10	2.96	-2.06	2.81	-0.56
TPSSh	3.67	2.63	-3.40	-3.40	3.27	-2.80	3.15	-0.51
B3LYP	3.79	2.89	-3.58	-3.58	3.48	-3.26	3.40	-0.60
PBE0	3.89	3.09	-3.72	-3.71	3.62	-3.47	3.57	-0.67
M06	3.82	3.13	-3.67	-3.68	3.56	-3.36	3.52	-0.62
BHLYP	4.14	3.50	-4.09	-3.86	4.08	-3.80	3.80	-0.96
M06-2X	4.14	3.53	-4.06	-3.82	4.03	-3.77	3.76	-0.98
M06-HF	4.35	3.95	-4.00	-3.99	3.91	-3.93	3.96	-1.08
0								
TPSS	3.29	-2.70	-2.82	3.09	-2.78	2.37	2.47	-0.20
PBE	3.15	-2.45	-2.60	2.94	-2.63	2.16	2.28	-0.16
BP86	3.14	-2.42	-2.57	2.92	-2.61	2.14	2.24	-0.16
BLYP	3.13	-2.47	-2.61	2.92	-2.64	2.19	2.30	-0.16
M06-L	3.67	-3.49	-3.50	3.56	-3.46	3.24	3.29	-0.54
B97D	3.41	-3.02	-3.09	3.23	-3.06	2.74	2.80	-0.38
TPSSh	3.65	-3.41	-3.43	3.52	-3.36	3.13	3.16	-0.57
B3LYP	3.72	-3.63	-3.57	3.67	-3.55	3.41	3.43	-0.90
PBE0	3.82	-3.80	-3.70	3.82	-3.70	3.59	3.61	-1.09
M06	3.79	-3.71	-3.68	3.74	-3.70	3.52	3.53	-0.79
BHLYP	3.86	-4.15	-3.85	4.15	-3.84	3.80	4.03	-1.87
M06-2X	3.83	-4.12	-3.83	4.15	-3.81	3.76	4.01	-1.89
M06-HF	3.97	-3.92	-3.97	4.00	-3.92	3.93	3.98	-2.38

Table S7. Coordinates (in PDB format) of the 10 structures studied in this paper. The structures were obtained with TPSS for models **0**, **4**–**7** and **9**, and by B3LYP for models **1**–**3** and **8**.

Structure **0** Resting state optimised with TPSS fucntional

```
REMARK Energies (QM/MM, QM+ptch) = -16163.019178 -15323.450724 H
REMARK /pfs/nobackup/home/l/lili/DFT/Def2-SVP/E0/Tpss
ATOM      1  H   ???     1       3.503   2.240 -29.686
ATOM      2  C   ???     1       3.916   2.092 -30.704
ATOM      3  H   ???     1       5.020   2.132 -30.633
ATOM      4  H   ???     1       3.623   1.099 -31.081
ATOM      5  N   ???     1       3.485   3.122 -31.637
ATOM      6  H   ???     1       4.007   4.012 -31.602
ATOM      7  C   ???     1       2.826   2.872 -32.782
ATOM      8  N   ???     1       1.959   1.827 -32.864
ATOM      9  H   ???     1       1.813   1.228 -32.049
ATOM     10  H   ???     1       1.754   1.419 -33.787
ATOM     11  N   ???     1       3.025   3.660 -33.838
ATOM     12  H   ???     1       3.573   4.545 -33.717
ATOM     13  H   ???     1       2.363   3.660 -34.619
ATOM     14  H   ???     1       7.271   1.572 -41.612
ATOM     15  C   ???     1       7.566   2.059 -40.675
ATOM     16  N   ???     1       8.383   3.175 -40.723
ATOM     17  C   ???     1       8.463   3.603 -39.467
ATOM     18  H   ???     1       9.004   4.477 -39.104
ATOM     19  N   ???     1       7.734   2.821 -38.627
ATOM     20  H   ???     1       7.634   3.011 -37.608
ATOM     21  C   ???     1       7.141   1.829 -39.377
ATOM     22  H   ???     1       6.492   1.076 -38.929
ATOM     23  H   ???     1       2.973   9.552 -40.109
ATOM     24  C   ???     1       3.081   8.696 -39.401
ATOM     25  H   ???     1       2.357   7.910 -39.680
ATOM     26  H   ???     1       2.852   9.065 -38.386
ATOM     27  S   ???     1       4.826   8.062 -39.472
ATOM     28  H   ???     1      13.631  11.344 -31.928
ATOM     29  C   ???     1      12.717  10.655 -31.974
ATOM     30  H   ???     1      12.873   9.949 -31.134
ATOM     31  H   ???     1      11.736  11.192 -31.789
ATOM     32  C   ???     1      12.890   9.819 -33.263
ATOM     33  O   ???     1      14.028   9.612 -33.687
ATOM     34  N   ???     1      11.791   9.235 -33.800
ATOM     35  H   ???     1      10.832   9.464 -33.496
ATOM     36  C   ???     1      11.928   8.138 -34.758
ATOM     37  H   ???     1      12.856   7.598 -34.521
ATOM     38  H   ???     1      11.062   7.475 -34.592
ATOM     39  C   ???     1      12.007   8.521 -36.253
ATOM     40  O   ???     1      13.056   8.366 -36.891
ATOM     41  N   ???     1      10.841   8.980 -36.776
ATOM     42  H   ???     1      10.005   8.919 -36.180
ATOM     43  C   ???     1      10.639   9.222 -38.212
ATOM     44  H   ???     1      11.639   9.370 -38.656
ATOM     45  H   ???     1      10.197   8.313 -38.665
ATOM     46  H   ???     1       9.970  10.066 -38.478
ATOM     47  H   ???     1       6.094  12.252 -32.940
ATOM     48  C   ???     1       5.946  11.599 -32.054
ATOM     49  H   ???     1       6.678  10.768 -32.122
ATOM     50  H   ???     1       6.136  12.196 -31.139
ATOM     51  N   ???     1       4.571  11.109 -32.064
ATOM     52  H   ???     1       3.975  11.247 -32.892
ATOM     53  C   ???     1       4.025  10.369 -31.084
ATOM     54  N   ???     1       4.710  10.131 -29.957
ATOM     55  H   ???     1       5.653  10.512 -29.833
ATOM     56  H   ???     1       4.398   9.437 -29.269
ATOM     57  N   ???     1       2.776   9.892 -31.253
ATOM     58  H   ???     1       2.284  10.154 -32.118
```

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ATOM     59  H   ???     1       2.188   9.704 -30.441
ATOM     60  H   ???     1       8.407   7.461 -28.183
ATOM     61  C   ???     1       9.355   7.502 -28.739
ATOM     62  N   ???     1       9.569   6.749 -29.884
ATOM     63  C   ???     1      10.870   6.851 -30.165
ATOM     64  H   ???     1      11.382   6.382 -31.008
ATOM     65  N   ???     1      11.493   7.644 -29.259
ATOM     66  H   ???     1      12.500   7.886 -29.277
ATOM     67  C   ???     1      10.553   8.063 -28.339
ATOM     68  H   ???     1      10.817   8.744 -27.530
ATOM     69  O   ???     1      10.674   5.261 -25.618
ATOM     70  C   ???     1      10.954   4.623 -26.695
ATOM     71  O   ???     1      12.099   4.355 -27.136
ATOM     72  C   ???     1       9.738   4.229 -27.556
ATOM     73  H   ???     1       8.848   4.129 -26.909
ATOM     74  H   ???     1       9.554   5.103 -28.206
ATOM     75  C   ???     1       9.866   3.023 -28.487
ATOM     76  H   ???     1      10.857   3.042 -28.971
ATOM     77  H   ???     1       9.804   2.070 -27.924
ATOM     78  C   ???     1       8.807   3.090 -29.626
ATOM     79  O   ???     1       9.298   3.982 -30.615
ATOM     80  H   ???     1      10.002   3.062 -31.400
ATOM     81  C   ???     1       7.483   3.613 -29.049
ATOM     82  O   ???     1       7.113   4.758 -29.494
ATOM     83  O   ???     1       6.844   2.957 -28.193
ATOM     84  C   ???     1       8.516   1.727 -30.309
ATOM     85  H   ???     1       8.141   0.979 -29.591
ATOM     86  H   ???     1       7.724   1.915 -31.066
ATOM     87  C   ???     1       9.727   1.173 -31.044
ATOM     88  O   ???     1      10.434   2.091 -31.696
ATOM     89  O   ???     1       9.998  -0.028 -31.045
ATOM     90 FE   ???     1       7.017   8.344 -35.388
ATOM     91 MO   ???     1       8.091   5.602 -31.267
ATOM     92 FE   ???     1       5.376   7.555 -37.297
ATOM     93 FE   ???     1       5.922   6.235 -32.603
ATOM     94 FE   ???     1       6.868   5.860 -36.054
ATOM     95 FE   ???     1       8.043   7.614 -33.134
ATOM     96 FE   ???     1       7.827   5.142 -33.816
ATOM     97 FE   ???     1       4.890   6.995 -34.816
ATOM     98  C   ???     1       6.758   6.712 -34.307
ATOM     99  S   ???     1       7.688   7.421 -37.401
ATOM    100  S   ???     1       9.689   6.038 -32.973
ATOM    101  S   ???     1       4.686   5.531 -36.570
ATOM    102  S   ???     1       8.033   4.031 -35.678
ATOM    103  S   ???     1       8.469   9.568 -34.158
ATOM    104  S   ???     1       6.564   4.071 -32.298
ATOM    105  S   ???     1       4.821   9.080 -35.628
ATOM    106  S   ???     1       6.873   7.660 -31.182
ATOM    107  S   ???     1       3.748   6.577 -32.921
ATOM    108  O   ???     1       4.511   5.539 -29.468
ATOM    109  H   ???     1       5.461   5.247 -29.519
ATOM    110  H   ???     1       4.394   6.128 -30.249
ATOM    111  O   ???     1       1.102   8.384 -34.233
ATOM    112  H   ???     1       1.955   8.023 -33.885
ATOM    113  H   ???     1       0.588   8.665 -33.420
END
```

Structure **1** Best E_4 structure optimised with B3LYP functional. One of the protons is on S2B atom, the other three are on centre carbide ion.

```
REMARK Energies (QM/MM, QM+ptch) = -16161.846309 -15322.290188 H
REMARK /pfs/nobackup/home/l/lili/DFT/B0-S2bC123/B3lyp
REMARK Fri Oct  5 14:42:48 CEST 2018
ATOM      1  H   ???     1       3.492   2.230 -29.683
ATOM      2  C   ???     1       3.887   2.063 -30.701
ATOM      3  H   ???     1       4.987   2.150 -30.656
ATOM      4  H   ???     1       3.633   1.043 -31.024
ATOM      5  N   ???     1       3.382   3.026 -31.658
ATOM      6  H   ???     1       3.870   3.925 -31.698
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ATOM      7  C   ???     1       2.715   2.702 -32.775
ATOM      8  N   ???     1       1.894   1.632 -32.796
ATOM      9  H   ???     1       1.741   1.082 -31.954
ATOM     10  H   ???     1       1.655   1.212 -33.700
ATOM     11  N   ???     1       2.881   3.440 -33.864
ATOM     12  H   ???     1       3.350   4.371 -33.768
ATOM     13  H   ???     1       2.227   3.363 -34.643
ATOM     14  H   ???     1       7.269   1.569 -41.622
ATOM     15  C   ???     1       7.560   2.054 -40.694
ATOM     16  N   ???     1       8.352   3.181 -40.728
ATOM     17  C   ???     1       8.408   3.610 -39.479
ATOM     18  H   ???     1       8.914   4.504 -39.118
ATOM     19  N   ???     1       7.686   2.809 -38.656
ATOM     20  H   ???     1       7.602   2.954 -37.643
ATOM     21  C   ???     1       7.128   1.810 -39.408
ATOM     22  H   ???     1       6.487   1.046 -38.975
ATOM     23  H   ???     1       2.970   9.556 -40.132
ATOM     24  C   ???     1       3.081   8.692 -39.460
ATOM     25  H   ???     1       2.330   7.930 -39.723
ATOM     26  H   ???     1       2.922   9.034 -38.425
ATOM     27  S   ???     1       4.811   8.073 -39.685
ATOM     28  H   ???     1      13.630  11.348 -31.930
ATOM     29  C   ???     1      12.721  10.661 -31.982
ATOM     30  H   ???     1      12.875   9.953 -31.147
ATOM     31  H   ???     1      11.738  11.193 -31.792
ATOM     32  C   ???     1      12.907   9.827 -33.267
ATOM     33  O   ???     1      14.044   9.615 -33.666
ATOM     34  N   ???     1      11.819   9.256 -33.820
ATOM     35  H   ???     1      10.864   9.540 -33.581
ATOM     36  C   ???     1      11.956   8.162 -34.771
ATOM     37  H   ???     1      12.866   7.604 -34.522
ATOM     38  H   ???     1      11.084   7.508 -34.620
ATOM     39  C   ???     1      12.058   8.531 -36.265
ATOM     40  O   ???     1      13.097   8.328 -36.889
ATOM     41  N   ???     1      10.921   9.028 -36.793
ATOM     42  H   ???     1      10.095   9.019 -36.194
ATOM     43  C   ???     1      10.711   9.271 -38.221
ATOM     44  H   ???     1      11.694   9.470 -38.677
ATOM     45  H   ???     1      10.308   8.357 -38.689
ATOM     46  H   ???     1      10.004  10.089 -38.480
ATOM     47  H   ???     1       6.092  12.251 -32.942
ATOM     48  C   ???     1       5.939  11.597 -32.061
ATOM     49  H   ???     1       6.704  10.799 -32.110
ATOM     50  H   ???     1       6.085  12.199 -31.145
ATOM     51  N   ???     1       4.592  11.055 -32.113
ATOM     52  H   ???     1       4.020  11.171 -32.955
ATOM     53  C   ???     1       4.028  10.343 -31.131
ATOM     54  N   ???     1       4.695  10.133 -29.990
ATOM     55  H   ???     1       5.646  10.478 -29.872
ATOM     56  H   ???     1       4.331   9.524 -29.259
ATOM     57  N   ???     1       2.790   9.865 -31.310
ATOM     58  H   ???     1       2.301  10.104 -32.179
ATOM     59  H   ???     1       2.219   9.581 -30.523
ATOM     60  H   ???     1       8.417   7.472 -28.156
ATOM     61  C   ???     1       9.386   7.533 -28.660
ATOM     62  N   ???     1       9.673   6.738 -29.747
ATOM     63  C   ???     1      10.973   6.877 -29.996
ATOM     64  H   ???     1      11.524   6.395 -30.804
ATOM     65  N   ???     1      11.526   7.737 -29.118
ATOM     66  H   ???     1      12.521   8.007 -29.128
ATOM     67  C   ???     1      10.542   8.161 -28.251
ATOM     68  H   ???     1      10.744   8.899 -27.478
ATOM     69  O   ???     1      10.695   5.270 -25.575
ATOM     70  C   ???     1      10.973   4.628 -26.636
ATOM     71  O   ???     1      12.105   4.389 -27.101
ATOM     72  C   ???     1       9.761   4.188 -27.461
ATOM     73  H   ???     1       8.873   4.126 -26.812
ATOM     74  H   ???     1       9.583   5.026 -28.149
```

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ATOM     75  C   ???     1       9.894   2.936 -28.313
ATOM     76  H   ???     1      10.878   2.931 -28.799
ATOM     77  H   ???     1       9.847   2.017 -27.702
ATOM     78  C   ???     1       8.855   2.951 -29.458
ATOM     79  O   ???     1       9.388   3.856 -30.428
ATOM     80  H   ???     1       9.940   3.198 -31.113
ATOM     81  C   ???     1       7.522   3.510 -28.931
ATOM     82  O   ???     1       7.237   4.703 -29.275
ATOM     83  O   ???     1       6.798   2.850 -28.171
ATOM     84  C   ???     1       8.619   1.595 -30.140
ATOM     85  H   ???     1       8.365   0.819 -29.404
ATOM     86  H   ???     1       7.754   1.709 -30.820
ATOM     87  C   ???     1       9.796   1.116 -31.003
ATOM     88  O   ???     1      10.422   2.041 -31.652
ATOM     89  O   ???     1      10.020  -0.095 -31.049
ATOM     90 FE   ???     1       7.185   8.902 -35.884
ATOM     91 MO   ???     1       8.214   5.558 -31.026
ATOM     92 FE   ???     1       4.733   6.801 -35.040
ATOM     93 FE   ???     1       5.400   5.974 -31.916
ATOM     94 FE   ???     1       8.333   4.411 -33.486
ATOM     95 FE   ???     1       8.349   7.866 -32.944
ATOM     96 FE   ???     1       6.983   5.734 -36.441
ATOM     97 FE   ???     1       5.387   7.549 -37.593
ATOM     98  C   ???     1       6.838   6.450 -34.382
ATOM     99  S   ???     1       7.848   7.522 -37.635
ATOM    100  S   ???     1       9.846   5.991 -32.799
ATOM    101  S   ???     1       4.774   5.333 -36.911
ATOM    102  S   ???     1       8.360   3.739 -35.737
ATOM    103  S   ???     1       8.558   9.757 -34.227
ATOM    104  S   ???     1       6.629   3.902 -32.024
ATOM    105  S   ???     1       4.862   9.065 -35.791
ATOM    106  S   ???     1       6.870   7.618 -31.104
ATOM    107  S   ???     1       3.517   6.404 -33.042
ATOM    108  H   ???     1       6.687   5.576 -33.740
ATOM    109  H   ???     1       9.640   3.977 -36.138
ATOM    110  H   ???     1       7.889   6.572 -34.693
ATOM    111  H   ???     1       6.514   7.357 -33.845
ATOM    112  O   ???     1       4.769   5.686 -29.425
ATOM    113  H   ???     1       5.658   5.257 -29.291
ATOM    114  H   ???     1       4.960   6.644 -29.457
ATOM    115  O   ???     1       1.083   8.389 -34.226
ATOM    116  H   ???     1       1.885   7.951 -33.866
ATOM    117  H   ???     1       0.558   8.670 -33.429
END
```

Structure **2** Second Best E_4 structure optimised with B3lyp functional. Two of the protons are on center carbide ion, the other two are on S2B and S2A atoms.

```
REMARK Energies (QM/MM, QM+ptch) = -16160.683272 -15321.126692 H
REMARK /pfs/nobackup/home/l/lili/DFT/BE2C12/B3svp
REMARK Fri Oct  5 14:47:31 CEST 2018
ATOM      1  H   ???     1       3.498   2.233 -29.683
ATOM      2  C   ???     1       3.902   2.071 -30.699
ATOM      3  H   ???     1       5.002   2.147 -30.640
ATOM      4  H   ???     1       3.644   1.057 -31.035
ATOM      5  N   ???     1       3.425   3.050 -31.655
ATOM      6  H   ???     1       3.948   3.930 -31.688
ATOM      7  C   ???     1       2.749   2.745 -32.769
ATOM      8  N   ???     1       1.917   1.683 -32.803
ATOM      9  H   ???     1       1.769   1.119 -31.969
ATOM     10  H   ???     1       1.676   1.272 -33.710
ATOM     11  N   ???     1       2.913   3.496 -33.853
ATOM     12  H   ???     1       3.392   4.411 -33.758
ATOM     13  H   ???     1       2.259   3.429 -34.632
ATOM     14  H   ???     1       7.270   1.566 -41.621
ATOM     15  C   ???     1       7.567   2.043 -40.691
ATOM     16  N   ???     1       8.400   3.139 -40.711
ATOM     17  C   ???     1       8.501   3.520 -39.447
ATOM     18  H   ???     1       9.069   4.362 -39.055
```

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ATOM     19  N   ???     1       7.767   2.725 -38.632
ATOM     20  H   ???     1       7.699   2.876 -37.609
ATOM     21  C   ???     1       7.152   1.777 -39.403
ATOM     22  H   ???     1       6.490   1.024 -38.981
ATOM     23  H   ???     1       2.975   9.554 -40.123
ATOM     24  C   ???     1       3.093   8.694 -39.438
ATOM     25  H   ???     1       2.346   7.927 -39.698
ATOM     26  H   ???     1       2.916   9.050 -38.411
ATOM     27  S   ???     1       4.822   8.053 -39.632
ATOM     28  H   ???     1      13.630  11.347 -31.930
ATOM     29  C   ???     1      12.720  10.660 -31.981
ATOM     30  H   ???     1      12.873   9.953 -31.144
ATOM     31  H   ???     1      11.738  11.193 -31.792
ATOM     32  C   ???     1      12.903   9.825 -33.266
ATOM     33  O   ???     1      14.038   9.619 -33.673
ATOM     34  N   ???     1      11.813   9.250 -33.811
ATOM     35  H   ???     1      10.858   9.515 -33.547
ATOM     36  C   ???     1      11.948   8.158 -34.766
ATOM     37  H   ???     1      12.861   7.602 -34.525
ATOM     38  H   ???     1      11.080   7.500 -34.615
ATOM     39  C   ???     1      12.041   8.533 -36.257
ATOM     40  O   ???     1      13.079   8.345 -36.887
ATOM     41  N   ???     1      10.896   9.021 -36.783
ATOM     42  H   ???     1      10.072   9.008 -36.182
ATOM     43  C   ???     1      10.687   9.256 -38.212
ATOM     44  H   ???     1      11.673   9.440 -38.669
ATOM     45  H   ???     1      10.276   8.341 -38.674
ATOM     46  H   ???     1       9.992  10.081 -38.477
ATOM     47  H   ???     1       6.091  12.251 -32.941
ATOM     48  C   ???     1       5.938  11.599 -32.059
ATOM     49  H   ???     1       6.701  10.799 -32.113
ATOM     50  H   ???     1       6.090  12.201 -31.143
ATOM     51  N   ???     1       4.587  11.062 -32.103
ATOM     52  H   ???     1       4.007  11.188 -32.938
ATOM     53  C   ???     1       4.026  10.355 -31.115
ATOM     54  N   ???     1       4.705  10.132 -29.984
ATOM     55  H   ???     1       5.657  10.475 -29.874
ATOM     56  H   ???     1       4.339   9.535 -29.244
ATOM     57  N   ???     1       2.779   9.896 -31.279
ATOM     58  H   ???     1       2.280  10.138 -32.140
ATOM     59  H   ???     1       2.222   9.587 -30.491
ATOM     60  H   ???     1       8.414   7.467 -28.165
ATOM     61  C   ???     1       9.377   7.520 -28.685
ATOM     62  N   ???     1       9.647   6.735 -29.786
ATOM     63  C   ???     1      10.946   6.864 -30.038
ATOM     64  H   ???     1      11.493   6.384 -30.849
ATOM     65  N   ???     1      11.516   7.707 -29.152
ATOM     66  H   ???     1      12.513   7.971 -29.165
ATOM     67  C   ???     1      10.542   8.131 -28.276
ATOM     68  H   ???     1      10.757   8.855 -27.493
ATOM     69  O   ???     1      10.683   5.262 -25.597
ATOM     70  C   ???     1      10.958   4.623 -26.662
ATOM     71  O   ???     1      12.091   4.373 -27.119
ATOM     72  C   ???     1       9.742   4.203 -27.497
ATOM     73  H   ???     1       8.860   4.117 -26.844
ATOM     74  H   ???     1       9.556   5.061 -28.158
ATOM     75  C   ???     1       9.870   2.980 -28.395
ATOM     76  H   ???     1      10.856   2.991 -28.880
ATOM     77  H   ???     1       9.819   2.043 -27.811
ATOM     78  C   ???     1       8.824   3.028 -29.539
ATOM     79  O   ???     1       9.323   3.911 -30.511
ATOM     80  H   ???     1      10.039   3.004 -31.318
ATOM     81  C   ???     1       7.492   3.555 -28.981
ATOM     82  O   ???     1       7.165   4.719 -29.380
ATOM     83  O   ???     1       6.811   2.896 -28.177
ATOM     84  C   ???     1       8.554   1.663 -30.210
ATOM     85  H   ???     1       8.225   0.902 -29.487
ATOM     86  H   ???     1       7.739   1.818 -30.942
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ATOM     87  C   ???     1       9.746   1.133 -30.987
ATOM     88  O   ???     1      10.438   2.054 -31.633
ATOM     89  O   ???     1      10.002  -0.060 -31.027
ATOM     90 FE   ???     1       7.132   8.512 -35.465
ATOM     91 MO   ???     1       8.182   5.567 -31.130
ATOM     92 FE   ???     1       5.383   7.677 -37.449
ATOM     93 FE   ???     1       5.453   6.078 -32.077
ATOM     94 FE   ???     1       6.984   5.793 -36.198
ATOM     95 FE   ???     1       8.040   4.870 -33.811
ATOM     96 FE   ???     1       8.243   7.711 -33.066
ATOM     97 FE   ???     1       4.136   7.034 -35.037
ATOM     98  C   ???     1       6.820   6.745 -34.280
ATOM     99  S   ???     1       7.781   7.562 -37.457
ATOM    100  S   ???     1       9.826   5.971 -32.840
ATOM    101  S   ???     1       4.697   5.501 -36.658
ATOM    102  S   ???     1       8.194   3.903 -35.834
ATOM    103  S   ???     1       8.554   9.752 -34.125
ATOM    104  S   ???     1       6.592   4.018 -32.191
ATOM    105  S   ???     1       4.804   9.165 -35.727
ATOM    106  S   ???     1       6.894   7.623 -31.094
ATOM    107  S   ???     1       3.393   6.504 -32.931
ATOM    108  H   ???     1       6.150   7.542 -33.845
ATOM    109  H   ???     1       6.123   5.830 -34.178
ATOM    110  O   ???     1       4.684   5.687 -29.348
ATOM    111  H   ???     1       5.589   5.277 -29.316
ATOM    112  H   ???     1       4.845   6.640 -29.470
ATOM    113  O   ???     1       1.019   8.396 -34.237
ATOM    114  H   ???     1       1.805   7.966 -33.838
ATOM    115  H   ???     1       0.484   8.700 -33.452
END
```

Structure **3** E_4 state with a hydride on the Fe6 ion. The other three protons are on the central carbide and on the S2B and S2A atoms. Structure is optimised with TPSS functional.

```
REMARK Energies (QM/MM, QM+ptch) = -16161.789107 -15322.234618 H
REMARK /pfs/nobackup/home/l/lili/DFT/B1-S2bS2aC2F67/B3svp
REMARK Fri Oct  5 14:53:50 CEST 2018
ATOM      1  H   ???     1       3.498   2.228 -29.680
ATOM      2  C   ???     1       3.905   2.056 -30.690
ATOM      3  H   ???     1       5.004   2.140 -30.628
ATOM      4  H   ???     1       3.657   1.035 -31.017
ATOM      5  N   ???     1       3.430   3.019 -31.662
ATOM      6  H   ???     1       3.959   3.894 -31.709
ATOM      7  C   ???     1       2.735   2.702 -32.758
ATOM      8  N   ???     1       1.914   1.631 -32.773
ATOM      9  H   ???     1       1.790   1.062 -31.939
ATOM     10  H   ???     1       1.659   1.221 -33.676
ATOM     11  N   ???     1       2.869   3.449 -33.853
ATOM     12  H   ???     1       3.241   4.427 -33.733
ATOM     13  H   ???     1       2.167   3.364 -34.588
ATOM     14  H   ???     1       7.272   1.568 -41.620
ATOM     15  C   ???     1       7.571   2.050 -40.690
ATOM     16  N   ???     1       8.374   3.167 -40.730
ATOM     17  C   ???     1       8.468   3.576 -39.477
ATOM     18  H   ???     1       9.005   4.452 -39.115
ATOM     19  N   ???     1       7.763   2.775 -38.643
ATOM     20  H   ???     1       7.687   2.943 -37.627
ATOM     21  C   ???     1       7.171   1.794 -39.396
ATOM     22  H   ???     1       6.534   1.029 -38.957
ATOM     23  H   ???     1       2.964   9.556 -40.121
ATOM     24  C   ???     1       3.060   8.698 -39.435
ATOM     25  H   ???     1       2.318   7.933 -39.712
ATOM     26  H   ???     1       2.862   9.045 -38.409
ATOM     27  S   ???     1       4.768   8.015 -39.589
ATOM     28  H   ???     1      13.631  11.347 -31.929
ATOM     29  C   ???     1      12.724  10.659 -31.979
ATOM     30  H   ???     1      12.877   9.956 -31.140
ATOM     31  H   ???     1      11.740  11.192 -31.792
ATOM     32  C   ???     1      12.919   9.821 -33.260
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ATOM     33  O   ???     1      14.056   9.626 -33.670
ATOM     34  N   ???     1      11.834   9.234 -33.798
ATOM     35  H   ???     1      10.878   9.493 -33.525
ATOM     36  C   ???     1      11.963   8.149 -34.759
ATOM     37  H   ???     1      12.871   7.581 -34.521
ATOM     38  H   ???     1      11.086   7.500 -34.614
ATOM     39  C   ???     1      12.066   8.533 -36.249
ATOM     40  O   ???     1      13.099   8.323 -36.879
ATOM     41  N   ???     1      10.937   9.055 -36.779
ATOM     42  H   ???     1      10.103   9.034 -36.194
ATOM     43  C   ???     1      10.737   9.292 -38.211
ATOM     44  H   ???     1      11.720   9.502 -38.661
ATOM     45  H   ???     1      10.360   8.368 -38.685
ATOM     46  H   ???     1      10.017  10.099 -38.476
ATOM     47  H   ???     1       6.091  12.255 -32.940
ATOM     48  C   ???     1       5.937  11.609 -32.054
ATOM     49  H   ???     1       6.705  10.814 -32.096
ATOM     50  H   ???     1       6.081  12.220 -31.143
ATOM     51  N   ???     1       4.590  11.064 -32.104
ATOM     52  H   ???     1       4.019  11.178 -32.947
ATOM     53  C   ???     1       4.037  10.338 -31.127
ATOM     54  N   ???     1       4.704  10.128 -29.987
ATOM     55  H   ???     1       5.645  10.498 -29.862
ATOM     56  H   ???     1       4.361   9.490 -29.269
ATOM     57  N   ???     1       2.804   9.846 -31.310
ATOM     58  H   ???     1       2.312  10.085 -32.176
ATOM     59  H   ???     1       2.240   9.543 -30.525
ATOM     60  H   ???     1       8.411   7.464 -28.179
ATOM     61  C   ???     1       9.364   7.511 -28.726
ATOM     62  N   ???     1       9.582   6.770 -29.871
ATOM     63  C   ???     1      10.874   6.886 -30.163
ATOM     64  H   ???     1      11.380   6.428 -31.013
ATOM     65  N   ???     1      11.491   7.677 -29.260
ATOM     66  H   ???     1      12.494   7.917 -29.278
ATOM     67  C   ???     1      10.554   8.080 -28.334
ATOM     68  H   ???     1      10.814   8.758 -27.525
ATOM     69  O   ???     1      10.688   5.273 -25.592
ATOM     70  C   ???     1      10.968   4.646 -26.664
ATOM     71  O   ???     1      12.103   4.389 -27.110
ATOM     72  C   ???     1       9.761   4.246 -27.519
ATOM     73  H   ???     1       8.863   4.192 -26.883
ATOM     74  H   ???     1       9.606   5.094 -28.200
ATOM     75  C   ???     1       9.886   3.000 -28.385
ATOM     76  H   ???     1      10.871   2.991 -28.870
ATOM     77  H   ???     1       9.829   2.080 -27.778
ATOM     78  C   ???     1       8.839   3.006 -29.523
ATOM     79  O   ???     1       9.331   3.909 -30.518
ATOM     80  H   ???     1       9.907   3.252 -31.175
ATOM     81  C   ???     1       7.510   3.553 -28.984
ATOM     82  O   ???     1       7.183   4.714 -29.387
ATOM     83  O   ???     1       6.833   2.901 -28.172
ATOM     84  C   ???     1       8.612   1.638 -30.184
ATOM     85  H   ???     1       8.336   0.880 -29.437
ATOM     86  H   ???     1       7.768   1.740 -30.890
ATOM     87  C   ???     1       9.815   1.143 -31.005
ATOM     88  O   ???     1      10.472   2.060 -31.624
ATOM     89  O   ???     1      10.025  -0.074 -31.041
ATOM     90 FE   ???     1       6.979   6.095 -36.227
ATOM     91 MO   ???     1       8.099   5.586 -31.167
ATOM     92 FE   ???     1       5.725   8.501 -37.582
ATOM     93 FE   ???     1       5.522   5.947 -32.483
ATOM     94 FE   ???     1       7.363   8.702 -35.377
ATOM     95 FE   ???     1       7.508   5.190 -33.809
ATOM     96 FE   ???     1       8.134   7.720 -32.983
ATOM     97 FE   ???     1       4.378   7.143 -35.054
ATOM     98  C   ???     1       6.830   6.996 -34.346
ATOM     99  S   ???     1       7.913   7.813 -37.493
ATOM    100  S   ???     1       9.599   5.892 -32.989
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ATOM    101  S   ???     1       4.750   5.403 -36.775
ATOM    102  S   ???     1       8.059   3.951 -35.751
ATOM    103  S   ???     1       8.663   9.782 -33.865
ATOM    104  S   ???     1       6.616   3.895 -32.093
ATOM    105  S   ???     1       4.880   9.350 -35.637
ATOM    106  S   ???     1       6.704   7.525 -31.113
ATOM    107  S   ???     1       3.352   6.443 -33.085
ATOM    108  H   ???     1       6.030   5.004 -34.222
ATOM    109  H   ???     1       9.399   4.180 -35.834
ATOM    110  H   ???     1       4.585   4.344 -35.932
ATOM    111  H   ???     1       5.883   7.398 -33.895
ATOM    112  O   ???     1       4.598   5.579 -29.332
ATOM    113  H   ???     1       5.518   5.225 -29.372
ATOM    114  H   ???     1       4.654   6.458 -29.743
ATOM    115  O   ???     1       1.029   8.398 -34.253
ATOM    116  H   ???     1       1.821   7.953 -33.876
ATOM    117  H   ???     1       0.508   8.696 -33.458
END
```

Structure **4** Hoffman like structure optimised with TPSS functional. Two of the protons are on S2B and S3A atoms, the other two are bridging Fe2 and Fe6 ions, Fe3 and Fe7 ions.

```
REMARK Energies (QM/MM, QM+ptch) = -16165.277110 -15325.712269 H
REMARK /pfs/nobackup/home/l/lili/DFT/T2-hoff/Tpss
REMARK Fri Oct  5 14:14:45 CEST 2018
ATOM      1  H   ???     1       3.499   2.237 -29.684
ATOM      2  C   ???     1       3.905   2.086 -30.701
ATOM      3  H   ???     1       5.010   2.063 -30.635
ATOM      4  H   ???     1       3.552   1.125 -31.106
ATOM      5  N   ???     1       3.522   3.181 -31.580
ATOM      6  H   ???     1       4.026   4.068 -31.405
ATOM      7  C   ???     1       2.914   3.028 -32.767
ATOM      8  N   ???     1       2.040   2.006 -32.962
ATOM      9  H   ???     1       1.822   1.380 -32.185
ATOM     10  H   ???     1       1.851   1.651 -33.910
ATOM     11  N   ???     1       3.150   3.916 -33.735
ATOM     12  H   ???     1       3.965   4.571 -33.653
ATOM     13  H   ???     1       2.607   3.948 -34.602
ATOM     14  H   ???     1       7.269   1.577 -41.616
ATOM     15  C   ???     1       7.560   2.076 -40.687
ATOM     16  N   ???     1       8.380   3.185 -40.769
ATOM     17  C   ???     1       8.440   3.674 -39.537
ATOM     18  H   ???     1       8.982   4.560 -39.206
ATOM     19  N   ???     1       7.688   2.937 -38.680
ATOM     20  H   ???     1       7.611   3.174 -37.675
ATOM     21  C   ???     1       7.107   1.908 -39.389
ATOM     22  H   ???     1       6.451   1.175 -38.919
ATOM     23  H   ???     1       2.969   9.553 -40.106
ATOM     24  C   ???     1       3.069   8.698 -39.391
ATOM     25  H   ???     1       2.334   7.922 -39.669
ATOM     26  H   ???     1       2.840   9.076 -38.380
ATOM     27  S   ???     1       4.793   8.023 -39.435
ATOM     28  H   ???     1      13.631  11.344 -31.928
ATOM     29  C   ???     1      12.717  10.654 -31.975
ATOM     30  H   ???     1      12.873   9.949 -31.134
ATOM     31  H   ???     1      11.736  11.192 -31.789
ATOM     32  C   ???     1      12.888   9.818 -33.264
ATOM     33  O   ???     1      14.027   9.615 -33.691
ATOM     34  N   ???     1      11.790   9.230 -33.796
ATOM     35  H   ???     1      10.827   9.452 -33.495
ATOM     36  C   ???     1      11.926   8.135 -34.757
ATOM     37  H   ???     1      12.852   7.591 -34.522
ATOM     38  H   ???     1      11.056   7.477 -34.589
ATOM     39  C   ???     1      12.005   8.519 -36.251
ATOM     40  O   ???     1      13.054   8.361 -36.892
ATOM     41  N   ???     1      10.840   8.979 -36.775
ATOM     42  H   ???     1      10.005   8.934 -36.173
ATOM     43  C   ???     1      10.638   9.221 -38.211
ATOM     44  H   ???     1      11.637   9.368 -38.656
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ATOM     45  H   ???     1      10.193   8.312 -38.663
ATOM     46  H   ???     1       9.969  10.066 -38.477
ATOM     47  H   ???     1       6.094  12.246 -32.943
ATOM     48  C   ???     1       5.947  11.583 -32.063
ATOM     49  H   ???     1       6.660  10.737 -32.161
ATOM     50  H   ???     1       6.164  12.159 -31.141
ATOM     51  N   ???     1       4.558  11.129 -32.052
ATOM     52  H   ???     1       3.966  11.258 -32.884
ATOM     53  C   ???     1       3.991  10.446 -31.042
ATOM     54  N   ???     1       4.703  10.155 -29.944
ATOM     55  H   ???     1       5.690  10.419 -29.887
ATOM     56  H   ???     1       4.361   9.496 -29.237
ATOM     57  N   ???     1       2.696  10.088 -31.149
ATOM     58  H   ???     1       2.188  10.395 -31.988
ATOM     59  H   ???     1       2.133   9.916 -30.316
ATOM     60  H   ???     1       8.406   7.458 -28.190
ATOM     61  C   ???     1       9.349   7.492 -28.759
ATOM     62  N   ???     1       9.543   6.757 -29.921
ATOM     63  C   ???     1      10.840   6.858 -30.219
ATOM     64  H   ???     1      11.333   6.402 -31.080
ATOM     65  N   ???     1      11.481   7.632 -29.308
ATOM     66  H   ???     1      12.490   7.866 -29.330
ATOM     67  C   ???     1      10.556   8.040 -28.368
ATOM     68  H   ???     1      10.836   8.706 -27.552
ATOM     69  O   ???     1      10.669   5.261 -25.616
ATOM     70  C   ???     1      10.952   4.629 -26.696
ATOM     71  O   ???     1      12.098   4.358 -27.131
ATOM     72  C   ???     1       9.741   4.246 -27.569
ATOM     73  H   ???     1       8.842   4.164 -26.931
ATOM     74  H   ???     1       9.577   5.114 -28.231
ATOM     75  C   ???     1       9.867   3.026 -28.482
ATOM     76  H   ???     1      10.854   3.033 -28.973
ATOM     77  H   ???     1       9.808   2.081 -27.906
ATOM     78  C   ???     1       8.801   3.062 -29.613
ATOM     79  O   ???     1       9.292   3.964 -30.625
ATOM     80  H   ???     1       9.885   3.272 -31.271
ATOM     81  C   ???     1       7.483   3.609 -29.054
ATOM     82  O   ???     1       7.115   4.754 -29.500
ATOM     83  O   ???     1       6.842   2.959 -28.194
ATOM     84  C   ???     1       8.541   1.700 -30.291
ATOM     85  H   ???     1       8.197   0.954 -29.555
ATOM     86  H   ???     1       7.729   1.850 -31.033
ATOM     87  C   ???     1       9.772   1.167 -31.051
ATOM     88  O   ???     1      10.455   2.076 -31.677
ATOM     89  O   ???     1       9.996  -0.056 -31.037
ATOM     90 FE   ???     1       5.489   7.537 -37.296
ATOM     91 MO   ???     1       8.053   5.619 -31.306
ATOM     92 FE   ???     1       4.894   7.053 -34.795
ATOM     93 FE   ???     1       7.711   5.161 -33.844
ATOM     94 FE   ???     1       6.846   5.806 -35.965
ATOM     95 FE   ???     1       8.080   7.601 -33.115
ATOM     96 FE   ???     1       5.853   6.203 -32.644
ATOM     97 FE   ???     1       7.103   8.298 -35.390
ATOM     98  C   ???     1       6.804   6.777 -34.216
ATOM     99  S   ???     1       7.725   7.338 -37.404
ATOM    100  S   ???     1       9.648   5.975 -33.027
ATOM    101  S   ???     1       4.681   5.495 -36.489
ATOM    102  S   ???     1       8.377   3.882 -35.711
ATOM    103  S   ???     1       8.502   9.555 -34.158
ATOM    104  S   ???     1       6.523   4.102 -32.293
ATOM    105  S   ???     1       4.996   9.155 -35.675
ATOM    106  S   ???     1       6.835   7.664 -31.223
ATOM    107  S   ???     1       3.830   7.299 -32.577
ATOM    108  H   ???     1       6.438   4.715 -34.866
ATOM    109  H   ???     1       5.056   5.473 -33.724
ATOM    110  H   ???     1       7.412   2.942 -35.503
ATOM    111  H   ???     1       2.886   6.325 -32.789
ATOM    112  O   ???     1       4.508   5.485 -29.618
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ATOM    113  H   ???     1       5.464   5.200 -29.573
ATOM    114  H   ???     1       4.520   6.206 -30.294
ATOM    115  O   ???     1       1.145   8.418 -34.228
ATOM    116  H   ???     1       2.071   8.330 -33.893
ATOM    117  H   ???     1       0.615   8.701 -33.427
END
```

Structure **5** Best E_4 state optimised with TPSS functional. Three hydrides are on Fe4, Fe5 and bridging Fe2 and Fe6 ions. The fourth proton binds to the S2B atom.

```
REMARK Energies (QM/MM, QM+ptch) = -16165.297723 -15325.728172 H
REMARK /pfs/nobackup/home/l/lili/DFT/Def2-SVP/E4/S2bF26F4F5
ATOM      1  H   ???     1       3.507   2.242 -29.687
ATOM      2  C   ???     1       3.928   2.098 -30.704
ATOM      3  H   ???     1       5.031   2.100 -30.616
ATOM      4  H   ???     1       3.613   1.119 -31.098
ATOM      5  N   ???     1       3.537   3.155 -31.626
ATOM      6  H   ???     1       4.038   4.052 -31.529
ATOM      7  C   ???     1       2.883   2.945 -32.782
ATOM      8  N   ???     1       2.012   1.906 -32.900
ATOM      9  H   ???     1       1.858   1.285 -32.104
ATOM     10  H   ???     1       1.804   1.522 -33.832
ATOM     11  N   ???     1       3.089   3.766 -33.813
ATOM     12  H   ???     1       3.634   4.650 -33.666
ATOM     13  H   ???     1       2.427   3.790 -34.594
ATOM     14  H   ???     1       7.267   1.574 -41.616
ATOM     15  C   ???     1       7.552   2.068 -40.682
ATOM     16  N   ???     1       8.358   3.190 -40.732
ATOM     17  C   ???     1       8.383   3.657 -39.489
ATOM     18  H   ???     1       8.899   4.551 -39.138
ATOM     19  N   ???     1       7.628   2.892 -38.655
ATOM     20  H   ???     1       7.485   3.102 -37.644
ATOM     21  C   ???     1       7.078   1.870 -39.396
ATOM     22  H   ???     1       6.424   1.121 -38.950
ATOM     23  H   ???     1       2.970   9.553 -40.109
ATOM     24  C   ???     1       3.073   8.697 -39.399
ATOM     25  H   ???     1       2.341   7.918 -39.675
ATOM     26  H   ???     1       2.855   9.067 -38.383
ATOM     27  S   ???     1       4.803   8.032 -39.473
ATOM     28  H   ???     1      13.631  11.341 -31.927
ATOM     29  C   ???     1      12.718  10.650 -31.970
ATOM     30  H   ???     1      12.872   9.948 -31.127
ATOM     31  H   ???     1      11.736  11.190 -31.788
ATOM     32  C   ???     1      12.888   9.815 -33.258
ATOM     33  O   ???     1      14.022   9.639 -33.710
ATOM     34  N   ???     1      11.796   9.209 -33.783
ATOM     35  H   ???     1      10.853   9.346 -33.394
ATOM     36  C   ???     1      11.950   8.132 -34.760
ATOM     37  H   ???     1      12.885   7.600 -34.536
ATOM     38  H   ???     1      11.095   7.453 -34.599
ATOM     39  C   ???     1      12.017   8.525 -36.252
ATOM     40  O   ???     1      13.058   8.354 -36.901
ATOM     41  N   ???     1      10.853   8.992 -36.774
ATOM     42  H   ???     1      10.017   8.953 -36.176
ATOM     43  C   ???     1      10.653   9.233 -38.210
ATOM     44  H   ???     1      11.652   9.390 -38.652
ATOM     45  H   ???     1      10.223   8.319 -38.668
ATOM     46  H   ???     1       9.976  10.072 -38.477
ATOM     47  H   ???     1       6.093  12.253 -32.939
ATOM     48  C   ???     1       5.943  11.604 -32.050
ATOM     49  H   ???     1       6.678  10.774 -32.107
ATOM     50  H   ???     1       6.127  12.205 -31.136
ATOM     51  N   ???     1       4.570  11.109 -32.065
ATOM     52  H   ???     1       3.971  11.260 -32.889
ATOM     53  C   ???     1       4.019  10.370 -31.087
ATOM     54  N   ???     1       4.705  10.125 -29.961
ATOM     55  H   ???     1       5.659  10.481 -29.849
ATOM     56  H   ???     1       4.392   9.428 -29.277
ATOM     57  N   ???     1       2.765   9.907 -31.254
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ATOM     58  H   ???     1       2.273  10.174 -32.118
ATOM     59  H   ???     1       2.179   9.707 -30.444
ATOM     60  H   ???     1       8.406   7.463 -28.177
ATOM     61  C   ???     1       9.356   7.509 -28.724
ATOM     62  N   ???     1       9.588   6.745 -29.856
ATOM     63  C   ???     1      10.892   6.859 -30.124
ATOM     64  H   ???     1      11.417   6.394 -30.960
ATOM     65  N   ???     1      11.497   7.668 -29.221
ATOM     66  H   ???     1      12.502   7.916 -29.236
ATOM     67  C   ???     1      10.542   8.087 -28.315
ATOM     68  H   ???     1      10.788   8.785 -27.515
ATOM     69  O   ???     1      10.670   5.258 -25.614
ATOM     70  C   ???     1      10.952   4.623 -26.692
ATOM     71  O   ???     1      12.098   4.364 -27.135
ATOM     72  C   ???     1       9.738   4.220 -27.553
ATOM     73  H   ???     1       8.851   4.105 -26.906
ATOM     74  H   ???     1       9.544   5.098 -28.195
ATOM     75  C   ???     1       9.881   3.020 -28.491
ATOM     76  H   ???     1      10.873   3.044 -28.971
ATOM     77  H   ???     1       9.822   2.063 -27.936
ATOM     78  C   ???     1       8.828   3.072 -29.633
ATOM     79  O   ???     1       9.338   3.976 -30.636
ATOM     80  H   ???     1       9.916   3.280 -31.286
ATOM     81  C   ???     1       7.506   3.621 -29.088
ATOM     82  O   ???     1       7.126   4.749 -29.570
ATOM     83  O   ???     1       6.870   2.984 -28.214
ATOM     84  C   ???     1       8.557   1.716 -30.320
ATOM     85  H   ???     1       8.195   0.974 -29.589
ATOM     86  H   ???     1       7.757   1.881 -31.072
ATOM     87  C   ???     1       9.788   1.172 -31.067
ATOM     88  O   ???     1      10.479   2.076 -31.692
ATOM     89  O   ???     1      10.009  -0.052 -31.044
ATOM     90 FE   ???     1       5.931   6.293 -32.618
ATOM     91 MO   ???     1       8.131   5.671 -31.295
ATOM     92 FE   ???     1       5.447   7.634 -37.320
ATOM     93 FE   ???     1       7.020   8.638 -35.354
ATOM     94 FE   ???     1       6.999   6.128 -35.901
ATOM     95 FE   ???     1       7.969   5.404 -33.893
ATOM     96 FE   ???     1       8.145   7.751 -33.010
ATOM     97 FE   ???     1       4.951   7.107 -34.825
ATOM     98  C   ???     1       6.746   6.923 -34.224
ATOM     99  S   ???     1       7.692   7.667 -37.350
ATOM    100  S   ???     1       9.789   6.169 -32.921
ATOM    101  S   ???     1       4.874   5.581 -36.521
ATOM    102  S   ???     1       8.011   3.913 -35.684
ATOM    103  S   ???     1       8.509   9.640 -34.111
ATOM    104  S   ???     1       6.695   4.175 -32.492
ATOM    105  S   ???     1       4.784   9.139 -35.733
ATOM    106  S   ???     1       6.853   7.657 -31.135
ATOM    107  S   ???     1       3.773   6.706 -32.931
ATOM    108  H   ???     1       9.024   8.541 -32.013
ATOM    109  H   ???     1       9.271   4.117 -36.176
ATOM    110  H   ???     1       8.563   6.161 -35.234
ATOM    111  H   ???     1       7.286   9.953 -36.124
ATOM    112  O   ???     1       4.526   5.520 -29.508
ATOM    113  H   ???     1       5.482   5.240 -29.542
ATOM    114  H   ???     1       4.444   6.160 -30.255
ATOM    115  O   ???     1       1.096   8.385 -34.238
ATOM    116  H   ???     1       1.951   8.029 -33.886
ATOM    117  H   ???     1       0.583   8.671 -33.426
END
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Stucture **6** H_2 bound end-on to Fe5 ion, optimised with TPSS functional. The other two protons are on S2B atom and bridging Fe2 and Fe6 ions respectly.

```
REMARK Energies (QM/MM, QM+ptch, MM3) =  -16165.300501 -15325.732779 H
REMARK /pfs/nobackup/home/l/lili/DFT/THendon-F5S2bF26/Tpss
REMARK Fri Oct  5 14:26:28 CEST 2018
ATOM      1  H   ???     1       3.499   2.239 -29.685
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ATOM      2  C   ???     1       3.907   2.091 -30.704
ATOM      3  H   ???     1       5.009   2.159 -30.644
ATOM      4  H   ???     1       3.635   1.086 -31.067
ATOM      5  N   ???     1       3.434   3.096 -31.645
ATOM      6  H   ???     1       3.938   3.997 -31.642
ATOM      7  C   ???     1       2.773   2.799 -32.777
ATOM      8  N   ???     1       1.919   1.743 -32.820
ATOM      9  H   ???     1       1.764   1.178 -31.983
ATOM     10  H   ???     1       1.713   1.309 -33.731
ATOM     11  N   ???     1       2.962   3.547 -33.862
ATOM     12  H   ???     1       3.494   4.448 -33.775
ATOM     13  H   ???     1       2.294   3.514 -34.638
ATOM     14  H   ???     1       7.268   1.569 -41.625
ATOM     15  C   ???     1       7.556   2.056 -40.698
ATOM     16  N   ???     1       8.361   3.179 -40.739
ATOM     17  C   ???     1       8.390   3.628 -39.489
ATOM     18  H   ???     1       8.903   4.520 -39.125
ATOM     19  N   ???     1       7.640   2.848 -38.668
ATOM     20  H   ???     1       7.507   3.036 -37.654
ATOM     21  C   ???     1       7.088   1.838 -39.416
ATOM     22  H   ???     1       6.431   1.086 -38.978
ATOM     23  H   ???     1       2.968   9.552 -40.117
ATOM     24  C   ???     1       3.069   8.689 -39.420
ATOM     25  H   ???     1       2.325   7.921 -39.694
ATOM     26  H   ???     1       2.879   9.047 -38.394
ATOM     27  S   ???     1       4.797   8.025 -39.543
ATOM     28  H   ???     1      13.631  11.341 -31.930
ATOM     29  C   ???     1      12.713  10.655 -31.976
ATOM     30  H   ???     1      12.870   9.947 -31.138
ATOM     31  H   ???     1      11.734  11.193 -31.789
ATOM     32  C   ???     1      12.859   9.819 -33.267
ATOM     33  O   ???     1      13.988   9.586 -33.701
ATOM     34  N   ???     1      11.742   9.256 -33.795
ATOM     35  H   ???     1      10.794   9.520 -33.496
ATOM     36  C   ???     1      11.848   8.143 -34.741
ATOM     37  H   ???     1      12.756   7.575 -34.491
ATOM     38  H   ???     1      10.957   7.513 -34.573
ATOM     39  C   ???     1      11.954   8.519 -36.234
ATOM     40  O   ???     1      13.024   8.391 -36.846
ATOM     41  N   ???     1      10.790   8.948 -36.783
ATOM     42  H   ???     1       9.937   8.883 -36.209
ATOM     43  C   ???     1      10.624   9.213 -38.217
ATOM     44  H   ???     1      11.635   9.365 -38.636
ATOM     45  H   ???     1      10.187   8.314 -38.695
ATOM     46  H   ???     1       9.963  10.063 -38.480
ATOM     47  H   ???     1       6.092  12.251 -32.939
ATOM     48  C   ???     1       5.941  11.599 -32.052
ATOM     49  H   ???     1       6.670  10.765 -32.124
ATOM     50  H   ???     1       6.128  12.195 -31.136
ATOM     51  N   ???     1       4.566  11.107 -32.068
ATOM     52  H   ???     1       3.969  11.255 -32.893
ATOM     53  C   ???     1       4.015  10.365 -31.092
ATOM     54  N   ???     1       4.688  10.140 -29.954
ATOM     55  H   ???     1       5.634  10.512 -29.831
ATOM     56  H   ???     1       4.384   9.430 -29.278
ATOM     57  N   ???     1       2.772   9.876 -31.274
ATOM     58  H   ???     1       2.289  10.129 -32.147
ATOM     59  H   ???     1       2.173   9.697 -30.468
ATOM     60  H   ???     1       8.398   7.455 -28.196
ATOM     61  C   ???     1       9.329   7.483 -28.778
ATOM     62  N   ???     1       9.481   6.751 -29.948
ATOM     63  C   ???     1      10.778   6.822 -30.264
ATOM     64  H   ???     1      11.246   6.362 -31.135
ATOM     65  N   ???     1      11.454   7.575 -29.360
ATOM     66  H   ???     1      12.466   7.792 -29.393
ATOM     67  C   ???     1      10.554   7.999 -28.403
ATOM     68  H   ???     1      10.864   8.646 -27.583
ATOM     69  O   ???     1      10.665   5.259 -25.633
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ATOM     70  C   ???     1      10.941   4.629 -26.716
ATOM     71  O   ???     1      12.085   4.354 -27.154
ATOM     72  C   ???     1       9.723   4.254 -27.587
ATOM     73  H   ???     1       8.831   4.156 -26.942
ATOM     74  H   ???     1       9.548   5.132 -28.232
ATOM     75  C   ???     1       9.843   3.053 -28.527
ATOM     76  H   ???     1      10.831   3.074 -29.019
ATOM     77  H   ???     1       9.788   2.098 -27.966
ATOM     78  C   ???     1       8.770   3.106 -29.656
ATOM     79  O   ???     1       9.231   3.996 -30.664
ATOM     80  H   ???     1       9.933   3.120 -31.412
ATOM     81  C   ???     1       7.446   3.614 -29.067
ATOM     82  O   ???     1       7.042   4.745 -29.521
ATOM     83  O   ???     1       6.835   2.956 -28.193
ATOM     84  C   ???     1       8.501   1.732 -30.324
ATOM     85  H   ???     1       8.154   0.981 -29.594
ATOM     86  H   ???     1       7.696   1.891 -31.072
ATOM     87  C   ???     1       9.719   1.201 -31.070
ATOM     88  O   ???     1      10.400   2.131 -31.724
ATOM     89  O   ???     1      10.007   0.002 -31.069
ATOM     90 FE   ???     1       6.809   8.322 -35.466
ATOM     91 MO   ???     1       7.957   5.602 -31.317
ATOM     92 FE   ???     1       4.795   6.784 -35.011
ATOM     93 FE   ???     1       5.741   6.130 -32.705
ATOM     94 FE   ???     1       7.093   5.956 -36.080
ATOM     95 FE   ???     1       7.786   7.555 -33.177
ATOM     96 FE   ???     1       7.720   5.110 -33.884
ATOM     97 FE   ???     1       5.332   7.435 -37.417
ATOM     98  C   ???     1       6.637   6.653 -34.407
ATOM     99  S   ???     1       7.583   7.629 -37.473
ATOM    100  S   ???     1       9.535   6.039 -33.036
ATOM    101  S   ???     1       4.898   5.308 -36.713
ATOM    102  S   ???     1       7.993   3.884 -35.791
ATOM    103  S   ???     1       8.209   9.572 -34.298
ATOM    104  S   ???     1       6.486   4.023 -32.369
ATOM    105  S   ???     1       4.590   8.890 -35.859
ATOM    106  S   ???     1       6.587   7.548 -31.178
ATOM    107  S   ???     1       3.604   6.516 -33.102
ATOM    108  H   ???     1       9.054   8.683 -31.462
ATOM    109  H   ???     1       9.342   4.026 -35.985
ATOM    110  H   ???     1       8.537   6.291 -35.745
ATOM    111  H   ???     1       8.970   8.563 -32.232
ATOM    112  O   ???     1       4.472   5.551 -29.420
ATOM    113  H   ???     1       5.417   5.245 -29.478
ATOM    114  H   ???     1       4.422   6.276 -30.081
ATOM    115  O   ???     1       1.069   8.389 -34.259
ATOM    116  H   ???     1       1.920   7.999 -33.935
ATOM    117  H   ???     1       0.574   8.663 -33.434
END
```

Stucture **7** H_2 bound side-on to Fe2 ion, optimised at TPSS level. The other two protons are on S2B atom and Fe4 ion respectly.

```
REMARK Energies (QM/MM, QM+ptch, MM3) =  -16165.293001 -15325.724871H
REMARK /pfs/nobackup/home/l/lili/DFT/THsideon-F2S2bF4/Tpss
REMARK Fri Oct  5 14:29:27 CEST 2018
ATOM      1  H   ???     1       3.502   2.240 -29.685
ATOM      2  C   ???     1       3.913   2.093 -30.702
ATOM      3  H   ???     1       5.017   2.119 -30.635
ATOM      4  H   ???     1       3.607   1.106 -31.086
ATOM      5  N   ???     1       3.487   3.138 -31.622
ATOM      6  H   ???     1       4.006   4.027 -31.559
ATOM      7  C   ???     1       2.842   2.906 -32.777
ATOM      8  N   ???     1       1.975   1.863 -32.884
ATOM      9  H   ???     1       1.821   1.254 -32.079
ATOM     10  H   ???     1       1.776   1.465 -33.813
ATOM     11  N   ???     1       3.054   3.712 -33.820
ATOM     12  H   ???     1       3.594   4.599 -33.676
ATOM     13  H   ???     1       2.387   3.731 -34.597
```

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ATOM     14  H   ???     1       7.269   1.571 -41.616
ATOM     15  C   ???     1       7.558   2.057 -40.683
ATOM     16  N   ???     1       8.369   3.176 -40.725
ATOM     17  C   ???     1       8.421   3.614 -39.472
ATOM     18  H   ???     1       8.949   4.498 -39.111
ATOM     19  N   ???     1       7.681   2.833 -38.641
ATOM     20  H   ???     1       7.553   3.029 -37.626
ATOM     21  C   ???     1       7.110   1.832 -39.393
ATOM     22  H   ???     1       6.457   1.079 -38.952
ATOM     23  H   ???     1       2.956   9.554 -40.113
ATOM     24  C   ???     1       3.033   8.696 -39.411
ATOM     25  H   ???     1       2.299   7.927 -39.708
ATOM     26  H   ???     1       2.796   9.062 -38.398
ATOM     27  S   ???     1       4.753   8.024 -39.450
ATOM     28  H   ???     1      13.632  11.343 -31.928
ATOM     29  C   ???     1      12.718  10.654 -31.972
ATOM     30  H   ???     1      12.873   9.950 -31.131
ATOM     31  H   ???     1      11.736  11.192 -31.788
ATOM     32  C   ???     1      12.884   9.818 -33.259
ATOM     33  O   ???     1      14.017   9.615 -33.699
ATOM     34  N   ???     1      11.780   9.233 -33.784
ATOM     35  H   ???     1      10.827   9.442 -33.452
ATOM     36  C   ???     1      11.906   8.134 -34.740
ATOM     37  H   ???     1      12.831   7.585 -34.509
ATOM     38  H   ???     1      11.036   7.479 -34.561
ATOM     39  C   ???     1      11.984   8.515 -36.235
ATOM     40  O   ???     1      13.033   8.359 -36.874
ATOM     41  N   ???     1      10.818   8.967 -36.769
ATOM     42  H   ???     1       9.982   8.956 -36.170
ATOM     43  C   ???     1      10.636   9.223 -38.207
ATOM     44  H   ???     1      11.643   9.373 -38.634
ATOM     45  H   ???     1      10.203   8.317 -38.677
ATOM     46  H   ???     1       9.970  10.068 -38.476
ATOM     47  H   ???     1       6.093  12.253 -32.939
ATOM     48  C   ???     1       5.943  11.603 -32.050
ATOM     49  H   ???     1       6.678  10.774 -32.111
ATOM     50  H   ???     1       6.125  12.204 -31.136
ATOM     51  N   ???     1       4.570  11.107 -32.068
ATOM     52  H   ???     1       3.974  11.252 -32.895
ATOM     53  C   ???     1       4.019  10.366 -31.091
ATOM     54  N   ???     1       4.702  10.125 -29.962
ATOM     55  H   ???     1       5.659  10.473 -29.855
ATOM     56  H   ???     1       4.392   9.422 -29.282
ATOM     57  N   ???     1       2.768   9.898 -31.262
ATOM     58  H   ???     1       2.276  10.166 -32.125
ATOM     59  H   ???     1       2.183   9.686 -30.455
ATOM     60  H   ???     1       8.406   7.458 -28.186
ATOM     61  C   ???     1       9.351   7.493 -28.750
ATOM     62  N   ???     1       9.543   6.750 -29.905
ATOM     63  C   ???     1      10.841   6.848 -30.205
ATOM     64  H   ???     1      11.332   6.386 -31.063
ATOM     65  N   ???     1      11.482   7.629 -29.300
ATOM     66  H   ???     1      12.490   7.862 -29.322
ATOM     67  C   ???     1      10.556   8.043 -28.362
ATOM     68  H   ???     1      10.837   8.714 -27.550
ATOM     69  O   ???     1      10.668   5.259 -25.621
ATOM     70  C   ???     1      10.947   4.626 -26.701
ATOM     71  O   ???     1      12.092   4.361 -27.143
ATOM     72  C   ???     1       9.732   4.234 -27.565
ATOM     73  H   ???     1       8.839   4.140 -26.920
ATOM     74  H   ???     1       9.553   5.104 -28.220
ATOM     75  C   ???     1       9.860   3.019 -28.486
ATOM     76  H   ???     1      10.844   3.034 -28.982
ATOM     77  H   ???     1       9.809   2.071 -27.915
ATOM     78  C   ???     1       8.789   3.052 -29.613
ATOM     79  O   ???     1       9.270   3.963 -30.623
ATOM     80  H   ???     1       9.857   3.290 -31.273
ATOM     81  C   ???     1       7.469   3.596 -29.052
```

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ATOM     82  O   ???     1       7.098   4.740 -29.497
ATOM     83  O   ???     1       6.833   2.946 -28.190
ATOM     84  C   ???     1       8.537   1.694 -30.300
ATOM     85  H   ???     1       8.193   0.943 -29.568
ATOM     86  H   ???     1       7.727   1.848 -31.043
ATOM     87  C   ???     1       9.771   1.169 -31.059
ATOM     88  O   ???     1      10.449   2.079 -31.687
ATOM     89  O   ???     1      10.003  -0.054 -31.042
ATOM     90 FE   ???     1       6.911   8.660 -35.317
ATOM     91 MO   ???     1       8.027   5.636 -31.269
ATOM     92 FE   ???     1       4.910   7.030 -34.832
ATOM     93 FE   ???     1       5.849   6.287 -32.583
ATOM     94 FE   ???     1       7.271   6.270 -35.993
ATOM     95 FE   ???     1       7.973   7.559 -33.075
ATOM     96 FE   ???     1       7.701   5.201 -33.818
ATOM     97 FE   ???     1       5.331   7.702 -37.269
ATOM     98  C   ???     1       6.734   6.799 -34.251
ATOM     99  S   ???     1       7.525   8.000 -37.419
ATOM    100  S   ???     1       9.633   5.966 -32.991
ATOM    101  S   ???     1       5.125   5.554 -36.524
ATOM    102  S   ???     1       7.971   4.085 -35.761
ATOM    103  S   ???     1       8.483   9.518 -33.951
ATOM    104  S   ???     1       6.499   4.112 -32.323
ATOM    105  S   ???     1       4.649   9.105 -35.634
ATOM    106  S   ???     1       6.826   7.673 -31.118
ATOM    107  S   ???     1       3.703   6.671 -32.942
ATOM    108  H   ???     1       8.854   6.628 -35.336
ATOM    109  H   ???     1       9.336   4.085 -35.940
ATOM    110  H   ???     1       8.920   6.709 -36.162
ATOM    111  H   ???     1       7.025  10.108 -35.850
ATOM    112  O   ???     1       4.507   5.539 -29.466
ATOM    113  H   ???     1       5.456   5.244 -29.507
ATOM    114  H   ???     1       4.419   6.164 -30.222
ATOM    115  O   ???     1       1.092   8.388 -34.245
ATOM    116  H   ???     1       1.953   8.040 -33.897
ATOM    117  H   ???     1       0.582   8.670 -33.430
END
```

Structure **8** Best E_2 state optimised with B3LYP functional, with two protons on central carbide ion.

```
REMARK Energies (QM/MM, QM+ptch) = -16160.683272 -15321.126692 H
REMARK /pfs/nobackup/home/l/lili/DFT/BE2C12/B3svp
REMARK Fri Oct  5 15:10:08 CEST 2018
ATOM      1  H   ???     1       3.498   2.233 -29.683
ATOM      2  C   ???     1       3.902   2.071 -30.699
ATOM      3  H   ???     1       5.002   2.147 -30.640
ATOM      4  H   ???     1       3.644   1.057 -31.035
ATOM      5  N   ???     1       3.425   3.050 -31.655
ATOM      6  H   ???     1       3.948   3.930 -31.688
ATOM      7  C   ???     1       2.749   2.745 -32.769
ATOM      8  N   ???     1       1.917   1.683 -32.803
ATOM      9  H   ???     1       1.769   1.119 -31.969
ATOM     10  H   ???     1       1.676   1.272 -33.710
ATOM     11  N   ???     1       2.913   3.496 -33.853
ATOM     12  H   ???     1       3.392   4.411 -33.758
ATOM     13  H   ???     1       2.259   3.429 -34.632
ATOM     14  H   ???     1       7.270   1.566 -41.621
ATOM     15  C   ???     1       7.567   2.043 -40.691
ATOM     16  N   ???     1       8.400   3.139 -40.711
ATOM     17  C   ???     1       8.501   3.520 -39.447
ATOM     18  H   ???     1       9.069   4.362 -39.055
ATOM     19  N   ???     1       7.767   2.725 -38.632
ATOM     20  H   ???     1       7.699   2.876 -37.609
ATOM     21  C   ???     1       7.152   1.777 -39.403
ATOM     22  H   ???     1       6.490   1.024 -38.981
ATOM     23  H   ???     1       2.975   9.554 -40.123
ATOM     24  C   ???     1       3.093   8.694 -39.438
ATOM     25  H   ???     1       2.346   7.927 -39.698
ATOM     26  H   ???     1       2.916   9.050 -38.411
```

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ATOM     27  S   ???     1       4.822   8.053 -39.632
ATOM     28  H   ???     1      13.630  11.347 -31.930
ATOM     29  C   ???     1      12.720  10.660 -31.981
ATOM     30  H   ???     1      12.873   9.953 -31.144
ATOM     31  H   ???     1      11.738  11.193 -31.792
ATOM     32  C   ???     1      12.903   9.825 -33.266
ATOM     33  O   ???     1      14.038   9.619 -33.673
ATOM     34  N   ???     1      11.813   9.250 -33.811
ATOM     35  H   ???     1      10.858   9.515 -33.547
ATOM     36  C   ???     1      11.948   8.158 -34.766
ATOM     37  H   ???     1      12.861   7.602 -34.525
ATOM     38  H   ???     1      11.080   7.500 -34.615
ATOM     39  C   ???     1      12.041   8.533 -36.257
ATOM     40  O   ???     1      13.079   8.345 -36.887
ATOM     41  N   ???     1      10.896   9.021 -36.783
ATOM     42  H   ???     1      10.072   9.008 -36.182
ATOM     43  C   ???     1      10.687   9.256 -38.212
ATOM     44  H   ???     1      11.673   9.440 -38.669
ATOM     45  H   ???     1      10.276   8.341 -38.674
ATOM     46  H   ???     1       9.992  10.081 -38.477
ATOM     47  H   ???     1       6.091  12.251 -32.941
ATOM     48  C   ???     1       5.938  11.599 -32.059
ATOM     49  H   ???     1       6.701  10.799 -32.113
ATOM     50  H   ???     1       6.090  12.201 -31.143
ATOM     51  N   ???     1       4.587  11.062 -32.103
ATOM     52  H   ???     1       4.007  11.188 -32.938
ATOM     53  C   ???     1       4.026  10.355 -31.115
ATOM     54  N   ???     1       4.705  10.132 -29.984
ATOM     55  H   ???     1       5.657  10.475 -29.874
ATOM     56  H   ???     1       4.339   9.535 -29.244
ATOM     57  N   ???     1       2.779   9.896 -31.279
ATOM     58  H   ???     1       2.280  10.138 -32.140
ATOM     59  H   ???     1       2.222   9.587 -30.491
ATOM     60  H   ???     1       8.414   7.467 -28.165
ATOM     61  C   ???     1       9.377   7.520 -28.685
ATOM     62  N   ???     1       9.647   6.735 -29.786
ATOM     63  C   ???     1      10.946   6.864 -30.038
ATOM     64  H   ???     1      11.493   6.384 -30.849
ATOM     65  N   ???     1      11.516   7.707 -29.152
ATOM     66  H   ???     1      12.513   7.971 -29.165
ATOM     67  C   ???     1      10.542   8.131 -28.276
ATOM     68  H   ???     1      10.757   8.855 -27.493
ATOM     69  O   ???     1      10.683   5.262 -25.597
ATOM     70  C   ???     1      10.958   4.623 -26.662
ATOM     71  O   ???     1      12.091   4.373 -27.119
ATOM     72  C   ???     1       9.742   4.203 -27.497
ATOM     73  H   ???     1       8.860   4.117 -26.844
ATOM     74  H   ???     1       9.556   5.061 -28.158
ATOM     75  C   ???     1       9.870   2.980 -28.395
ATOM     76  H   ???     1      10.856   2.991 -28.880
ATOM     77  H   ???     1       9.819   2.043 -27.811
ATOM     78  C   ???     1       8.824   3.028 -29.539
ATOM     79  O   ???     1       9.323   3.911 -30.511
ATOM     80  H   ???     1      10.039   3.004 -31.318
ATOM     81  C   ???     1       7.492   3.555 -28.981
ATOM     82  O   ???     1       7.165   4.719 -29.380
ATOM     83  O   ???     1       6.811   2.896 -28.177
ATOM     84  C   ???     1       8.554   1.663 -30.210
ATOM     85  H   ???     1       8.225   0.902 -29.487
ATOM     86  H   ???     1       7.739   1.818 -30.942
ATOM     87  C   ???     1       9.746   1.133 -30.987
ATOM     88  O   ???     1      10.438   2.054 -31.633
ATOM     89  O   ???     1      10.002  -0.060 -31.027
ATOM     90 FE   ???     1       7.132   8.512 -35.465
ATOM     91 MO   ???     1       8.182   5.567 -31.130
ATOM     92 FE   ???     1       5.383   7.677 -37.449
ATOM     93 FE   ???     1       5.453   6.078 -32.077
ATOM     94 FE   ???     1       6.984   5.793 -36.198
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ATOM     95 FE   ???     1       8.040   4.870 -33.811
ATOM     96 FE   ???     1       8.243   7.711 -33.066
ATOM     97 FE   ???     1       4.136   7.034 -35.037
ATOM     98  C   ???     1       6.820   6.745 -34.280
ATOM     99  S   ???     1       7.781   7.562 -37.457
ATOM    100  S   ???     1       9.826   5.971 -32.840
ATOM    101  S   ???     1       4.697   5.501 -36.658
ATOM    102  S   ???     1       8.194   3.903 -35.834
ATOM    103  S   ???     1       8.554   9.752 -34.125
ATOM    104  S   ???     1       6.592   4.018 -32.191
ATOM    105  S   ???     1       4.804   9.165 -35.727
ATOM    106  S   ???     1       6.894   7.623 -31.094
ATOM    107  S   ???     1       3.393   6.504 -32.931
ATOM    108  H   ???     1       6.150   7.542 -33.845
ATOM    109  H   ???     1       6.123   5.830 -34.178
ATOM    110  O   ???     1       4.684   5.687 -29.348
ATOM    111  H   ???     1       5.589   5.277 -29.316
ATOM    112  H   ???     1       4.845   6.640 -29.470
ATOM    113  O   ???     1       1.019   8.396 -34.237
ATOM    114  H   ???     1       1.805   7.966 -33.838
ATOM    115  H   ???     1       0.484   8.700 -33.452
END
```

Structure **9** Best E_2 state optimised with TPSS functional. One proton is on S2B atom, the other one bridging the Fe2 and Fe6 ions.

```
REMARK Energies (QM/MM, QM+ptch) = -16164.154629 -15324.587561 H
REMARK /pfs/nobackup/home/l/lili/DFT/TE2S2bFe2/Opt/Tpss
REMARK Fri Oct  5 14:37:01 CEST 2018
ATOM      1  H   ???     1       3.506   2.241 -29.685
ATOM      2  C   ???     1       3.926   2.098 -30.701
ATOM      3  H   ???     1       5.029   2.124 -30.620
ATOM      4  H   ???     1       3.627   1.110 -31.089
ATOM      5  N   ???     1       3.509   3.141 -31.626
ATOM      6  H   ???     1       4.017   4.037 -31.557
ATOM      7  C   ???     1       2.854   2.909 -32.777
ATOM      8  N   ???     1       1.987   1.865 -32.874
ATOM      9  H   ???     1       1.833   1.260 -32.066
ATOM     10  H   ???     1       1.781   1.466 -33.801
ATOM     11  N   ???     1       3.055   3.712 -33.822
ATOM     12  H   ???     1       3.603   4.598 -33.691
ATOM     13  H   ???     1       2.389   3.725 -34.599
ATOM     14  H   ???     1       7.269   1.571 -41.617
ATOM     15  C   ???     1       7.558   2.058 -40.683
ATOM     16  N   ???     1       8.354   3.188 -40.725
ATOM     17  C   ???     1       8.400   3.626 -39.472
ATOM     18  H   ???     1       8.914   4.518 -39.110
ATOM     19  N   ???     1       7.670   2.833 -38.641
ATOM     20  H   ???     1       7.534   3.019 -37.627
ATOM     21  C   ???     1       7.114   1.825 -39.394
ATOM     22  H   ???     1       6.473   1.062 -38.953
ATOM     23  H   ???     1       2.968   9.554 -40.111
ATOM     24  C   ???     1       3.067   8.697 -39.406
ATOM     25  H   ???     1       2.335   7.920 -39.685
ATOM     26  H   ???     1       2.849   9.064 -38.389
ATOM     27  S   ???     1       4.799   8.036 -39.481
ATOM     28  H   ???     1      13.631  11.344 -31.929
ATOM     29  C   ???     1      12.717  10.655 -31.975
ATOM     30  H   ???     1      12.873   9.948 -31.136
ATOM     31  H   ???     1      11.735  11.192 -31.790
ATOM     32  C   ???     1      12.886   9.823 -33.265
ATOM     33  O   ???     1      14.024   9.616 -33.692
ATOM     34  N   ???     1      11.787   9.240 -33.805
ATOM     35  H   ???     1      10.827   9.460 -33.498
ATOM     36  C   ???     1      11.936   8.143 -34.761
ATOM     37  H   ???     1      12.867   7.610 -34.522
ATOM     38  H   ???     1      11.074   7.473 -34.595
ATOM     39  C   ???     1      12.014   8.521 -36.256
ATOM     40  O   ???     1      13.057   8.349 -36.901
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ATOM     41  N   ???     1      10.851   8.988 -36.779
ATOM     42  H   ???     1      10.015   8.955 -36.180
ATOM     43  C   ???     1      10.655   9.234 -38.214
ATOM     44  H   ???     1      11.655   9.396 -38.654
ATOM     45  H   ???     1      10.229   8.321 -38.678
ATOM     46  H   ???     1       9.978  10.072 -38.479
ATOM     47  H   ???     1       6.093  12.253 -32.939
ATOM     48  C   ???     1       5.944  11.602 -32.051
ATOM     49  H   ???     1       6.681  10.775 -32.115
ATOM     50  H   ???     1       6.125  12.202 -31.136
ATOM     51  N   ???     1       4.571  11.105 -32.067
ATOM     52  H   ???     1       3.975  11.248 -32.895
ATOM     53  C   ???     1       4.018  10.371 -31.087
ATOM     54  N   ???     1       4.700  10.134 -29.956
ATOM     55  H   ???     1       5.658  10.480 -29.850
ATOM     56  H   ???     1       4.388   9.435 -29.273
ATOM     57  N   ???     1       2.766   9.902 -31.256
ATOM     58  H   ???     1       2.277  10.170 -32.121
ATOM     59  H   ???     1       2.174   9.723 -30.444
ATOM     60  H   ???     1       8.407   7.461 -28.184
ATOM     61  C   ???     1       9.354   7.503 -28.742
ATOM     62  N   ???     1       9.560   6.769 -29.900
ATOM     63  C   ???     1      10.862   6.868 -30.183
ATOM     64  H   ???     1      11.367   6.412 -31.036
ATOM     65  N   ???     1      11.491   7.643 -29.265
ATOM     66  H   ???     1      12.500   7.879 -29.281
ATOM     67  C   ???     1      10.555   8.051 -28.336
ATOM     68  H   ???     1      10.824   8.722 -27.521
ATOM     69  O   ???     1      10.668   5.259 -25.624
ATOM     70  C   ???     1      10.953   4.626 -26.703
ATOM     71  O   ???     1      12.100   4.359 -27.138
ATOM     72  C   ???     1       9.742   4.239 -27.576
ATOM     73  H   ???     1       8.847   4.139 -26.936
ATOM     74  H   ???     1       9.564   5.116 -28.223
ATOM     75  C   ???     1       9.874   3.034 -28.509
ATOM     76  H   ???     1      10.861   3.050 -28.999
ATOM     77  H   ???     1       9.814   2.080 -27.949
ATOM     78  C   ???     1       8.809   3.080 -29.642
ATOM     79  O   ???     1       9.299   3.991 -30.650
ATOM     80  H   ???     1       9.879   3.312 -31.297
ATOM     81  C   ???     1       7.491   3.625 -29.082
ATOM     82  O   ???     1       7.112   4.761 -29.546
ATOM     83  O   ???     1       6.863   2.981 -28.209
ATOM     84  C   ???     1       8.544   1.723 -30.329
ATOM     85  H   ???     1       8.185   0.979 -29.597
ATOM     86  H   ???     1       7.741   1.887 -31.079
ATOM     87  C   ???     1       9.778   1.184 -31.078
ATOM     88  O   ???     1      10.462   2.089 -31.707
ATOM     89  O   ???     1      10.005  -0.040 -31.050
ATOM     90 FE   ???     1       6.970   8.501 -35.350
ATOM     91 MO   ???     1       8.072   5.682 -31.302
ATOM     92 FE   ???     1       5.380   7.660 -37.303
ATOM     93 FE   ???     1       5.904   6.322 -32.631
ATOM     94 FE   ???     1       7.121   6.110 -36.059
ATOM     95 FE   ???     1       8.046   7.685 -33.088
ATOM     96 FE   ???     1       7.817   5.295 -33.875
ATOM     97 FE   ???     1       4.926   6.957 -34.881
ATOM     98  C   ???     1       6.773   6.849 -34.312
ATOM     99  S   ???     1       7.645   7.834 -37.395
ATOM    100  S   ???     1       9.697   6.096 -32.988
ATOM    101  S   ???     1       4.929   5.516 -36.610
ATOM    102  S   ???     1       7.966   3.965 -35.707
ATOM    103  S   ???     1       8.441   9.669 -34.123
ATOM    104  S   ???     1       6.571   4.168 -32.413
ATOM    105  S   ???     1       4.736   9.086 -35.678
ATOM    106  S   ???     1       6.843   7.713 -31.146
ATOM    107  S   ???     1       3.745   6.663 -32.983
ATOM    108  H   ???     1       8.612   6.306 -35.785
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ATOM    109  H   ???     1       9.282   4.088 -36.070
ATOM    110  O   ???     1       4.512   5.529 -29.486
ATOM    111  H   ???     1       5.468   5.250 -29.530
ATOM    112  H   ???     1       4.419   6.179 -30.219
ATOM    113  O   ???     1       1.094   8.388 -34.243
ATOM    114  H   ???     1       1.956   8.040 -33.899
ATOM    115  H   ???     1       0.585   8.670 -33.428
END
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