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Supporting Information

69451 Weinheim, Germany

Synthesis and Characterization of a Two-Coordinate Manganese Complex and its Reaction with Molecular Hydrogen at Room Temperature**

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Supporting Information

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S1. Magnetic Susceptibility Measurements

Temperature-dependent magnetic susceptibility measurements were carried out with a *Quantum-Design* MPMS-XL-5 SQUID magnetometer equipped with a 5 Tesla magnet in the range from 2 to 295 K at a magnetic field of 0.5 T. The powdered sample was contained in a teflon bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the sample holder and the teflon bucket. Molar susceptibility data were corrected for the diamagnetic contribution using Pascal's constants.[1] Temperature-independent paramagnetism (*TIP*) was included according to $\chi_{calc} = \chi + TIP$.[2] Before simulation, the experimental data were corrected for *TIP*.

Experimental data for **2** were modelled using a fitting procedure to the appropriate Heisenberg-Dirac-van Vleck spin Hamiltonian for one manganese S = 5/2 and two S = 1/2 radical centres with isotropic exchange coupling, Zeemann splitting and zero-field splitting.

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + g\mu_B\vec{B}\sum_{i=1}^{3}\vec{S} + D_2(\hat{S}_{z2}^2 - \frac{1}{3}S_2(S_2+1)) \quad \textbf{(eq. 1)}$$

The best fit gave values of g(radical) = 2.00 (fixed), g(Mn) = 2.10, J = –350 cm^{-1} (–504 K), $|D_{Mn}|$ = 1.4 cm^{-1} (2.0 K), and *TIP* = 86·10^{-6} cm^{3}mol^{-1} (subtracted). The J value represents a lower limit of the coupling strengths. To confirm this, simulations were performed with J fixed at different values in the range –200 cm^{-1} to –500 cm^{-1}. The quality of fit as a function of J is shown in the Figure S1. For J values beyond –350 cm^{-1} the quality of fit remains constant. Therefore, the lower limit of the coupling strength is ca. –350 cm^{-1} (–504K).

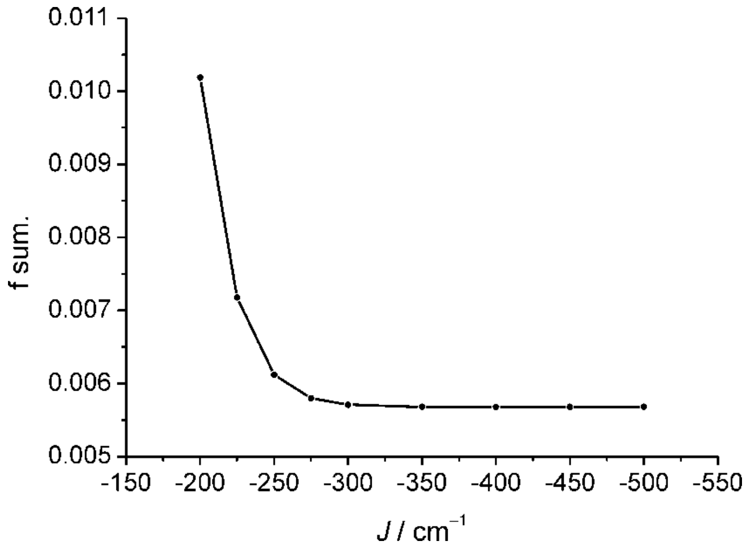


Figure S1. Total squared error of simulation as a function of exchange coupling parameter *J*.

Magnetization measurements at variable temperature and variable field (VTVH; see Figure 2 in the main text) were performed to provide further support for the magnitude of the *D* value, which cannot reliably be deduced from powder susceptibility measurements. To avoid any over-parameterization the *J* value and *TIP* were fixed to –350 cm^{-1} (–504 K) and $86 \cdot 10^{-6}$ cm^3mol^{-1}, respectively. Therefore, only *g* and *D* values of manganese ion were optimized. The obtained values *g* = 2.10 and *D* = +1.4 cm^{-1} (+2.0 K) are in excellent agreement with those derived from susceptibility data and evidence the positive sign of zero field splitting.

The magnetic properties of **3** were analyzed according to

$$\hat{H} = g\mu_B \vec{B}\vec{S} + D(\hat{S}_z^2 - \frac{1}{3}S(S+1)) \qquad \textbf{(eq. 2)}$$

The best fit values are *g* = 1.97, |*D*| = 0.6 cm^{-1} (0.86 K), and *TIP* = $340 \cdot 10^{-6}$ cm^3mol^{-1} (subtracted). Magnetization measurements at variable temperature and variable field (VTVH; Figure S2) gave *g* = 1.96 and *D* = +0.5 cm^{-1} (+0.72 K) in excellent agreement with the values derived from susceptibility data, thus evidencing a small, but non-negligible, zero-field splitting of positive sign.

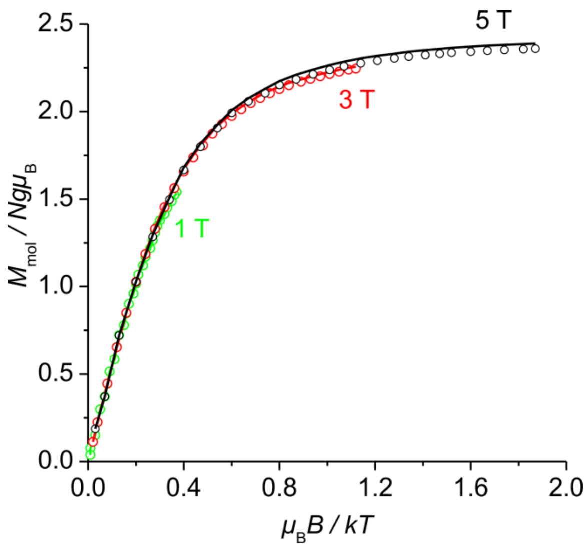


Figure S2. Variable temperature–variable field (VTVH) magnetization measurements as M_{mol} versus *B*/*T* for **3**. Solid lines represent the calculated curve fits (see text).

S2. EPR spectroscopy

Further elucidation of the magnetic structure of **2** and **3** was achieved using Electron Paramagnetic Resonance (EPR) on a Bruker X-band (9.45 GHz) EPR spectrometer. Powder samples of both **2** and **3** were measured at 290 and 140 K. We used a locally developed computer program to solve the spin Hamiltonian in Eq.3, by diagonalizing the Hamiltonian matrix, as detailed elsewhere.[3]

$$\hat{H} = g\mu_B \vec{B}\cdot\hat{S} + D(\hat{S}_z^2 - \hat{S}^2/3) + E(\hat{S}_x{}^2 - \hat{S}_y{}^2) + A\hat{I}\cdot\hat{S} \qquad \textbf{(eq. 3)}$$

In this Hamiltonian, g is the Landé factor, A is the hyperfine constant, and D and E are the axial and rhombic second order zero-field splitting parameters, and the other terms have their usual meaning.[4]

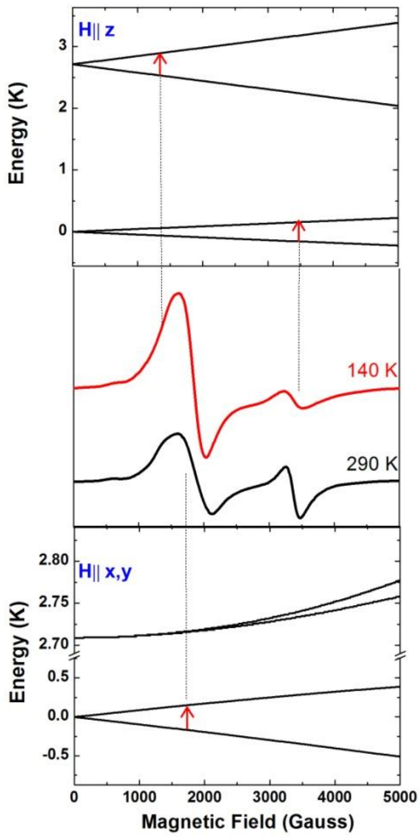


Figure S3. The experimental spectra of (**2**) are shown at 290 and 140K along with the energy level diagram for the H $_{\|}$ Z and H $_{\|}$ X,Y directions. The red arrows mark the EPR transition assignments. The sign of D was determined by comparison of the relative line intensities in the 290K and 140K spectra. The transitions in both spectra occur at 1730 and 3398 Gauss. At 290K the low field transition is less intense than the high field transition, while at 140K the opposite is true. As shown in the energy level diagram the low field line is a contributed both from a ground state and excited state transition, while the high field transition arises only from an excited state transition, thus it is expected that the low field transition will intensify upon cooling, while the high field line will intensify upon heating, as was observed.

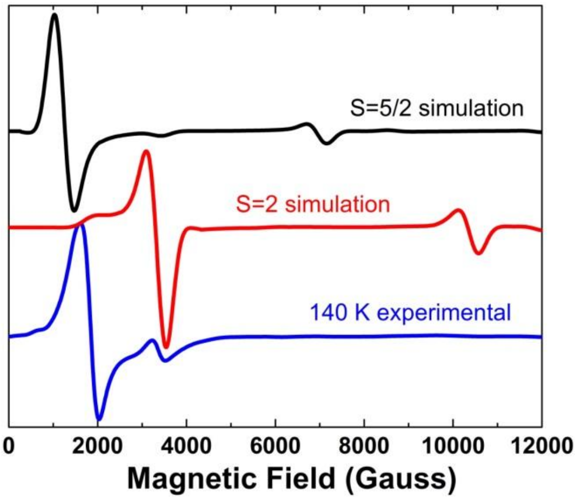


Figure S4. The experimental spectrum of **2** is shown with the best fit simulations using an S =2 and $^5/_2$. The unacceptable fits provide unambiguous evidence that **2** is not an S=2 or $^5/_2$ system.

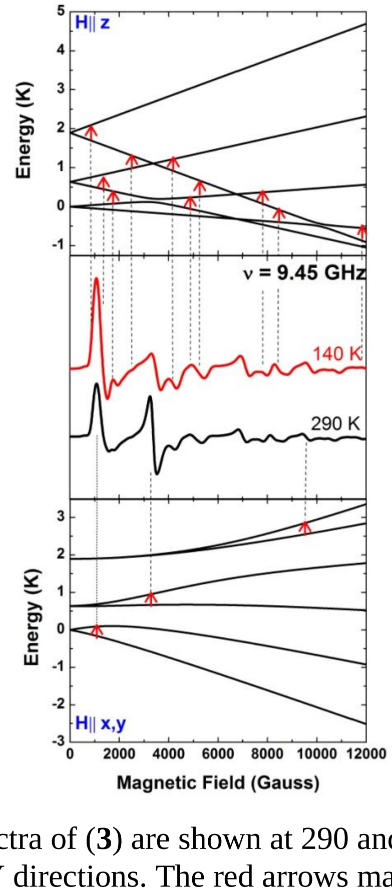


Figure S5. The experimental spectra of (**3**) are shown at 290 and 140K along with the energy level diagram for the H ∥ Z and H ∥ X,Y directions. The red arrows mark the EPR transition assignments. The sign of D was determined by comparison of the relative line intensities in the 290K and 140K spectra. The two sharpest transitions in both spectra occur at 1200 and 3360 Gauss. At 290K the low field transition is less intense than the high field transition, while at 140K the opposite is true. As shown in the energy level diagram the low field line is a mixture of several low lying $M_s \rightarrow M_s \pm 1$ transitions while the high field transition is due to the an excited state transition, thus it is expected that the low field transition will intensify upon cooling, while the high field line will intensify upon heating, as was observed.

S3. Crystallographic Information

Crystal structure determination: Molecular structures of compounds **2** and **3** were established by single-crystal X-ray crystallographic studies. X-ray intensity data sets for **2** were collected at beamline P11 at the new PETRA-III storage ring at DESY in Hamburg. The crystallography endstation at P11 is equipped with a high precision one-axis goniometer and Pilatus 6M single photon counting detector. The beam size was adjusted to 150 µm. Data were collected at a temperature of 100 K and an X-ray energy of 20 keV (λ = 0.6199 Å). In total 1800 frames were collected in rotation increments of 0.2 ° and an exposure time of 0.086 seconds per frame. Data were processed using the XDS program package.[5] Crystal of compound 3 was measured on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area detector and a CuKα rotating anode. Integrations were performed with SAINT.[6] Intensity data for both compounds were corrected for absorption and scaled with SADABS.[7] Structures were solved by direct methods and initially refined by full-matrix least-squares methods on F^2 with the program SHELXL-2013,[8] utilizing anisotropic displacement parameters for non-hydrogen atoms. Visualization and modeling was done using SHELXLE.[9]

Packing of molecules in the crystal: Both compounds **2** and **3** crystallize in space group *P*-1 with one half molecule and an additional solvent molecule (toluene) in the asymmetric unit. Inversion symmetry as part of the space group symmetry generates the other half of the main molecule and another solvent molecule, thereby filling the unit cell. In the deposited structure of **2** the manganese atom was chosen to lie at x=0.5 y=0.00 and z=0.0. To facilitate the generation of a packing diagram the origin of the Mn atom was shifted to lie in the center of the unit cell at x=0.5, y=0.5 and z=0.5, one of the eight inversion centers in space group *P*-1. The solvent was then translated back into the unit cell by shifting it 0, -1, -1. With that choice of origin, the complete main molecule is placed within the unit cell. Simple translation of the whole unit cell then generates the packing diagram shown in figure S6. The figure (left) shows a rendering of the packing in the bc-plane. The ARU codes are given in the figure in right side. A number of 1446.01 refers to a translation of the main molecule (residue 01) by symmetry operation 1 (x,y,z) by (-1, -1, +1)

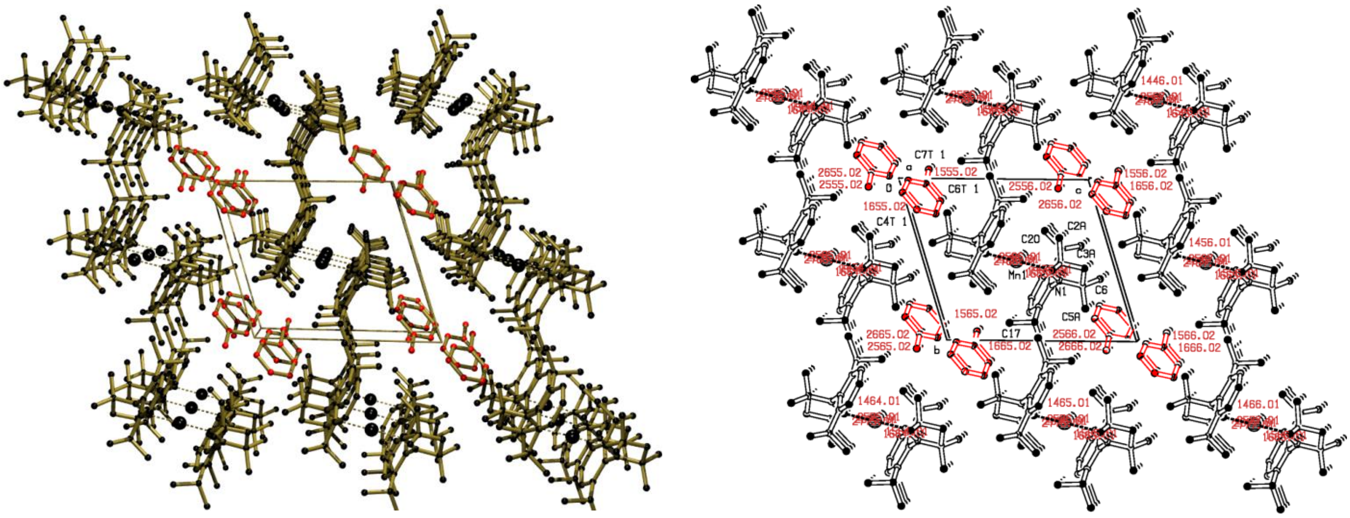


Figure S6. (left) Packing of molecules of **2** and toluene in the crystal. Hydrogen atoms were omitted for clarity. All non-solvent atoms are black; (right) ARU symmetry/translation codes.

Compound **3** (distinguishable from the pyramidal ‘carbene’ carbon atom in the ligand) had a Mn origin of x+0.5, y=0.0 and z=1.0. Shifting it to 0.5, 0.5, 0.5 again facilitated the generation of the packing diagram. Figure S7 shows the view of packing through the a-axis with most non-solvent atoms in grey color.

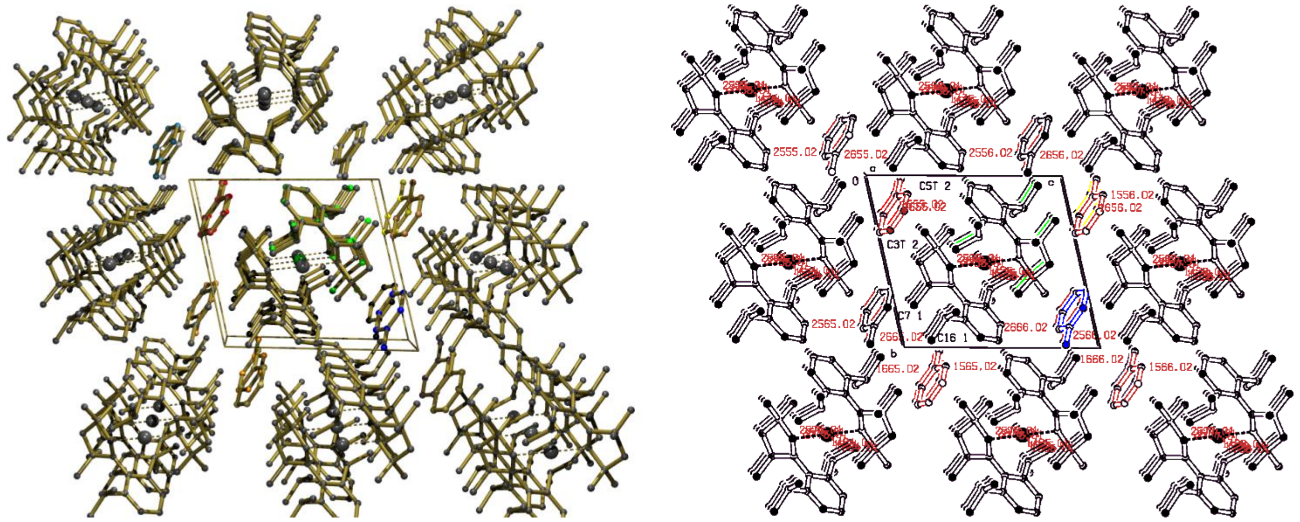


Figure S7. (left) Packing of molecules of **3** and toluene in the crystal. Hydrogen atoms were omitted for clarity; (right) ARU symmetry/translation codes.

Table S1. Crystal and Structure Refinement parameters for compounds **2**, and **3**.

Parameters	**2**·2tol	**3**·2tol
CCDC No.	925860	926052
Empirical formula	$C_{54}H_{78}MnN_2$	$C_{54}H_{80}MnN_2$
Formula Weight	810.12	812.14
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 10.484(3) Å b = 10.503(6) Å c = 11.954(3) Å α = 69.74(3) ° β= 73.71(4) ° γ = 75.03(2) °	a = 10.5432(3) Å b = 10.5666(3) Å c = 12.0659(4) Å α = 73.5122(14) ° β= 69.6414(14) ° γ = 74.8798(13) °
Volume, Z	1166.0(9) $Å^3$, 1	1188.61(6) $Å^3$, 1
Density (calcd)	1.154 Mg/m^3	1.135 Mg/m^3
Absorption coefficient	0.223 mm^{-1}	2.512 mm^{-1}
F (000)	441	443
Crystal size/mm	0.041 x 0.032 x 0.030	0.13 x 0.09 x 0.08
θ range for data collection	1.620 to 26.277 °	4.000 to 72.124 °
Limiting indices	$-14 \le h \le 14, -14 \le k \le 14, -17 \le l \le 17$	$-13 \le h \le 13, -13 \le k \le 12, -14 \le l \le 13$
Reflections collected	22225	28620
Independent reflections	6505 (R_{int} = 0.0908)	4557 (R_{int} = 0.0292)
Completeness to θ	94.1 %(θ = 21.835 °)	98.3 %(θ = 67.679 °)
Refinement method	Full-matrix least-squares on F^2	Full - matrix least - squares on F^2
Data/restraints/ parameters	6505 / 15 / 362	4557 / 126 / 373
Goodness - of - fit on F^2	1.043	1.156
Final R indices [I>2σ(I)]	$R1$ = 0.0590, $wR2$ = 0.1562	$R1$ = 0.0348, $wR2$ = 0.1006
R indices (all data)	$R1$ = 0.0592, $wR2$ = 0.1564	$R1$ = 0.0348, $wR2$ = 0.1006
Largest diff. peak and hole	0.470 and -0.454 e.$Å^{-3}$	0.653 and -0.455 e.$Å^{-3}$

S4. UV-Vis Spectra

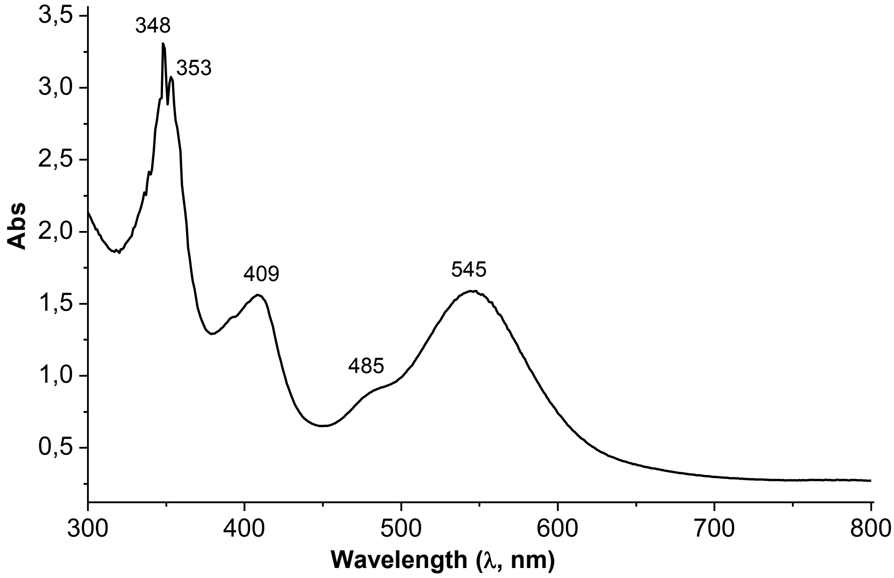


Figure S8. UV-Vis spectrum of compound **2** in *n*-hexane solution

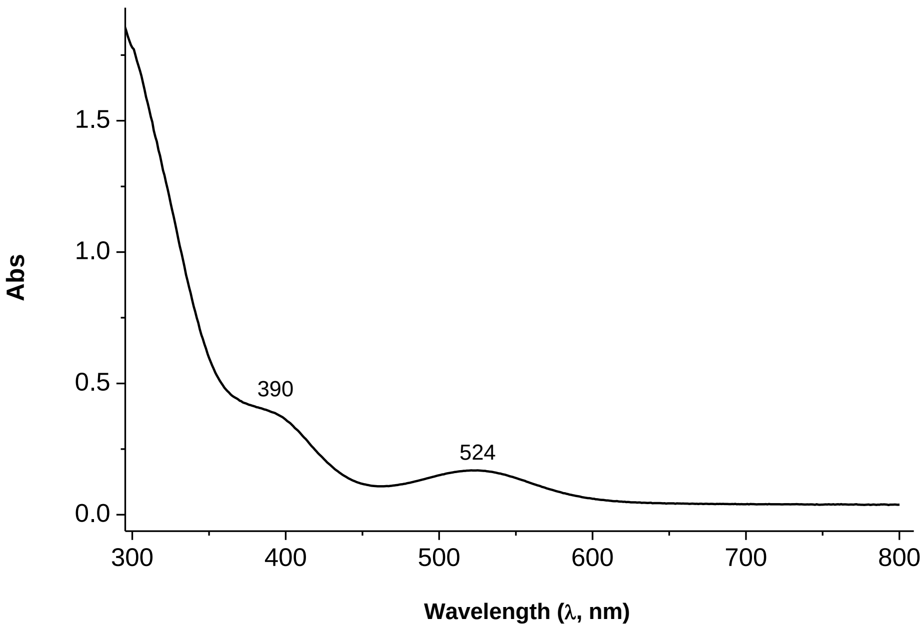
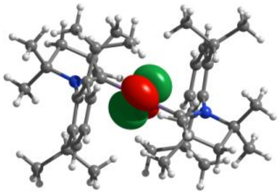
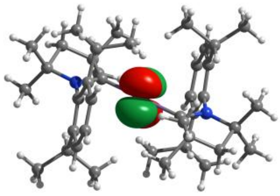
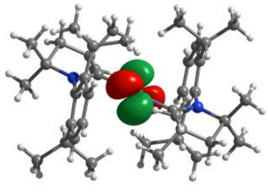
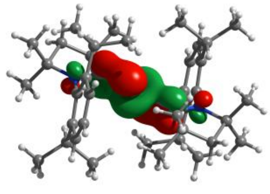
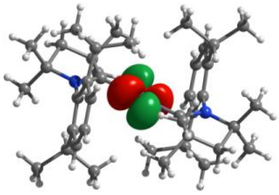
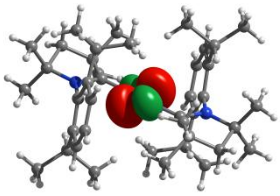
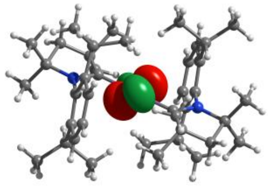
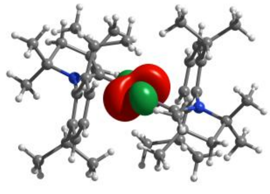
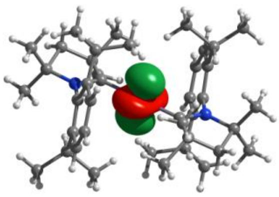
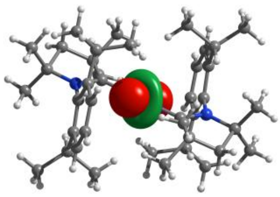
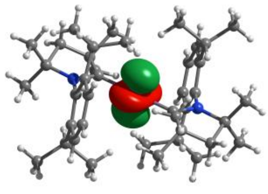
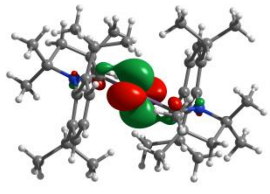
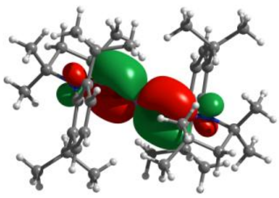
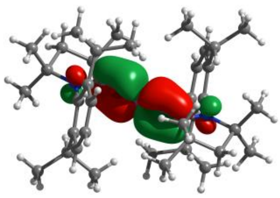
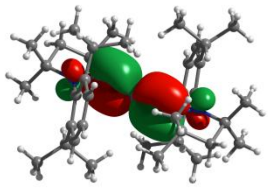
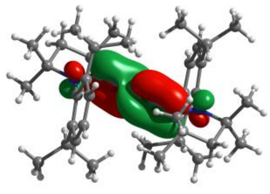
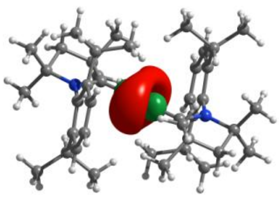
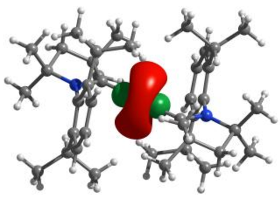
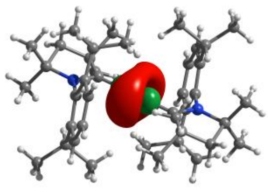
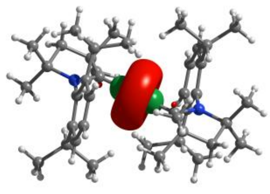


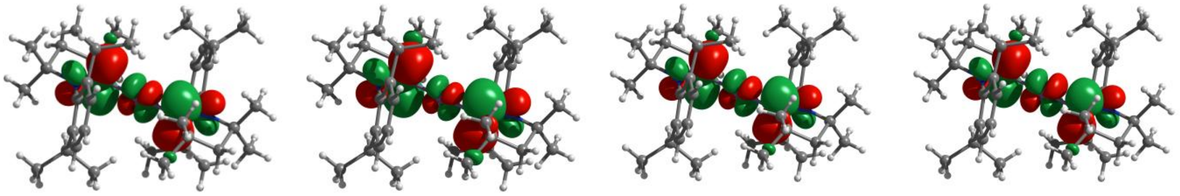
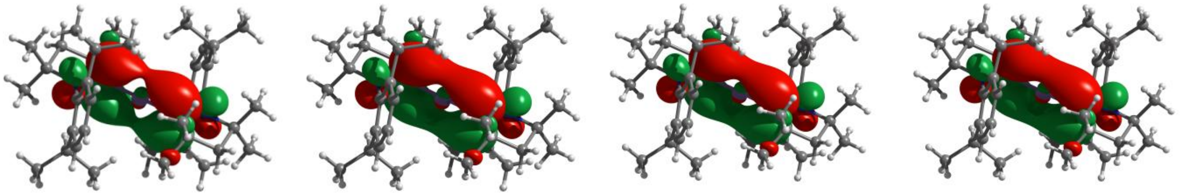
Figure S9. UV-Vis spectrum of compound **3** in *n*-hexane solution

S5. Ab initio calculations of 2 and 3

All *ab inito* calculations were done with MOLCAS 7.8 patch 82 program package. All basis sets were of relativistic ANO-RCC type. Complete Active Space Self Consistent Field (CASSCF) calculations combined with multiconfigurational second-order perturbation theory (CASPT2) were employed in order to estimate the ground spin quartet (gerade), two spin quintets (gerade and ungerade) and the spin octet (gerade). The active space of the CASSCF method consisted of five 3*d* orbitals of the Mn^{II} center, and two 2*p* orbitals of the carbon atoms (radicals). The inversion symmetry was employed in the calculation. Table S2 shows the active orbitals for the optimized states.

Table S2. CASSCF molecular orbitals of the ground S=3/2 and excited spin states for compound **2**.

Nr	$S_{ungerade}$=3/2	S_{gerade}=5/2	$S_{ungerade}$=5/2	$S_{ungerade}$=7/2
		gerade orbitals		
1				
2				
3				
4				
5				

6	
ungerade orbitals	
7	

Contractions of the employed basis sets for atoms:

Basis set 1:

Mn.ANO-RCC...5s4p2d.
N.ANO-RCC...3s2p.
C.ANO-RCC...3s2p.
H.ANO-RCC...1s.

Basis set 2:

Mn.ANO-RCC...6s5p3d2f1g.
N.ANO-RCC...4s3p2d1f. (close)
C.ANO-RCC...4s3p2d1f. (close)
N.ANO-RCC...3s2p. (distant)
C.ANO-RCC...3s2p. (distant)
H.ANO-RCC...2s.

Table S3. Main configurations of optimized wave functions of the excited spin states, and their calculated energies (cm^{-1}.)

	Active orbitals		Coeff.	Basis set 1		Basis set 2	
	gerade	ungerade		CASSCF	CASPT2	CASSCF	CASPT2
S=5/2, gerade	↑↑↑ 2 ↑↑	0	-0.41773	3211	4372	3417	4754
	↑↑↑↑↑ 2	0	0.46712				
	↑↑↑↑↑ 0	2	-0.73233				
	↑↑↑ 0 ↑↑	2	0.26645				
S=5/2, ungerade	↑↑↑ 2 ↑ 0	↑	-0.70078	1547	1632	1592	3080
	↑↑↑↓↑↑	↑	0.27079				
	↑↑↑↑↓↑	↑	0.06157				
	↑↑↑↑↑↓	↑	0.22665				
	↑↑↑↑↑↑	↓	-0.53270				
	↑↑↑ 0 ↑ 2	↑	-0.30925				
S=7/2, ungerade	↑↑↑↑↑↑	↑	1.00000	5566	8721	5922	9496

Table S4. Ab intio calculated spin-orbit countribution to the ZFS paramerers of the ground state spin *S* = 5/2 for compound **3**, in K. Active space of the CASSCF included five 3*d* orbitals. All spin quartet and spin doublet states were mixed by the spin-orbit coupling in RASSI.

	Basis set 1		Basis set 2
	CASSCF	CASPT2	CASSCF
	0.000	0.000	0.000
	0.000	0.000	0.000
	0.183	0.167	0.168
	0.183	0.167	0.168
	0.491	0.445	0.432
	0.491	0.445	0.432
Anisotropy parameters (K)			
D*	0.079	0.072	0.069
E*	-0.010	-0.009	-0.011

* *D*, and *E* parameters are for the spin *S* = 5/2.

g factor the ground state spin was obtained 2.0021.

S6. DFT Calculations for the geometry optimization.

Geometry optimizations of **2** and **3** have been carried out using the DFT functionals BP86[10] and TPSS[11] with def2-TZVPP basis sets.[12] The RI-Approximation was applied throughout.[13] The optimized geometry was verified as a minimum on the potential energy surface by calculation of the vibrational frequencies analytically. Calculations were carried out with the program packages Gaussian09[14] and TurboMole 6.3.[15]

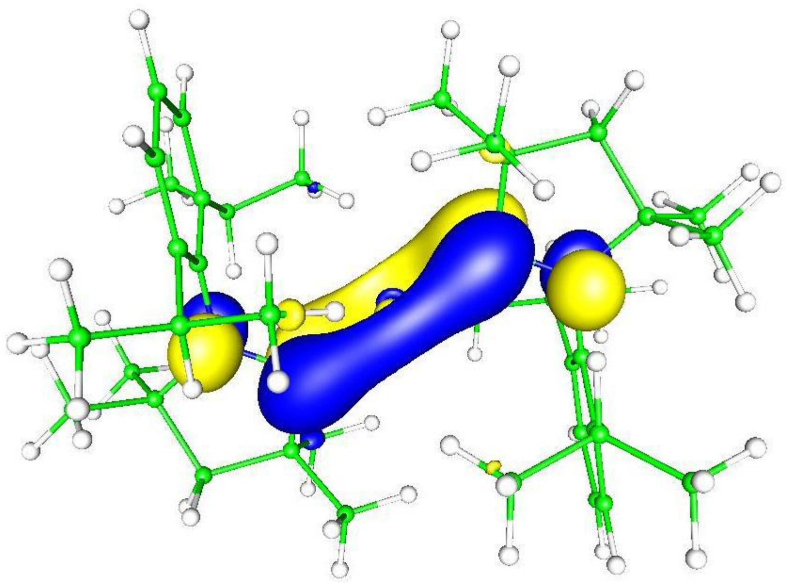


Figure S10. Highest lying singly occupied orbital of **2** in sextet state.

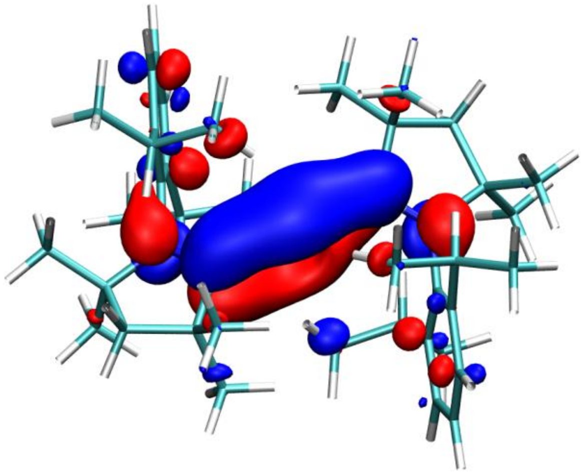
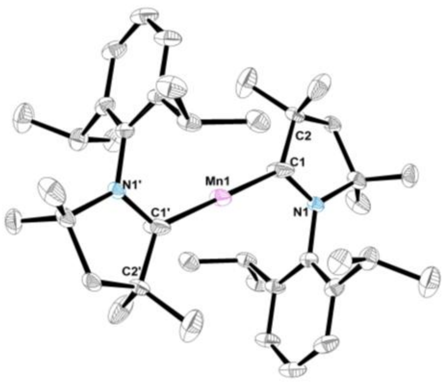
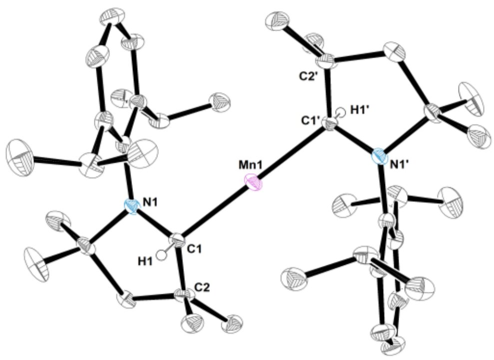


Figure S11. Lowest unoccupied molecular orbital of **2** in the quartet state.

Table S5: Comparison of bond lengths [Å] and bond angles [°] in **2** and **3**

	 **2**		 **3**	
	Experimental	Theoretical[a,c]	Experimental	Theoretical[b,c]
Mn1–C1	1.9655(14)	1.975;1.978/1.984	2.106(2)	2.102; 2.104
C1–C2	1.5075(17)	1.540;1.543/1.540	1.534(2)	1.548; 1.550
C1–N1	1.3589(16)	1.381;1.383/1.377	1.478(2)	1.466; 1.478
C1–Mn1–C1’	180	171.6/180.0	180	163.2
C2–C1–N1	107.82(10)	106.4;106.9/106.6	99.43(14)	102.6; 102.9
C2–C1–Mn1	132.43(10)	124.5;126.3/126.0	121.48(14)	118.0; 121.2
N1–C1–Mn1	119.75(10)	126.8;128.9/127.4	104.66(12)	106.5; 119.9
N1–C1–C1’-N1’	180.0	127.8/180.0	180.0	179.4

[a] calculated at BP86/def2-TZVPP for quartet/sextet state

[b] calculated at BP86/def2-TZVPP

[c] optimized structures of **2** (quartet state) and **3** do not posses C*i* symmetry where bond lengths and bond angles of the two ligands are slightly different from each other.

Full reference 19: Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Table S6. Coordinates and energies of the calculated molecules at BP86/TZVPP and TPSS/TZVPP.

Compound **2**:

BP86/def2-TZVPP, quartet

-2822.902982624

Mn	-0.0088945	-0.3572041	0.4304301
N	2.9051909	0.4887676	0.2840261
C	1.6661627	0.5842147	0.8860615
C	1.7872481	1.6800931	1.9613111
C	0.5589487	2.6033084	1.9855519
C	3.0612458	2.4634811	1.5513414
C	3.9372280	1.5093249	0.7120733
C	5.0782660	0.8776246	1.5313732
C	4.5731065	2.2362242	-0.4806705
C	1.9360261	1.0389660	3.3606484
C	3.2311208	-0.6078276	-0.5934777
C	3.1235342	-0.4561592	-2.0016857
C	3.5313166	-1.5148966	-2.8273564
C	3.9996605	-2.7118603	-2.2973636
C	4.0299017	-2.8805021	-0.9157957
C	3.6447039	-1.8534183	-0.0434765
C	3.6246472	-2.1506796	1.4517890
C	4.9568270	-2.7153810	1.9748815
C	2.4686606	-3.1083344	1.7957618

C	2.4900186	0.7626579	-2.6630751
C	3.3917376	1.4122638	-3.7275522
C	1.1343318	0.3769329	-3.2865662
H	1.0410332	0.4535853	3.6128225
H	2.0630339	1.8169555	4.1305247
H	-0.3573462	2.0442606	2.2275280
H	0.4066982	3.0862073	1.0112642
H	0.6752101	3.3913964	2.7461891
H	2.7990831	0.3634056	3.4189161
H	3.6117890	2.8590839	2.4165548
H	2.7690852	3.3230076	0.9299543
H	4.7219919	0.4163143	2.4589698
H	5.8080468	1.6539145	1.8012948
H	5.6066661	0.1154943	0.9430540
H	5.1332569	1.5412705	-1.1211303
H	5.2811093	2.9919062	-0.1118369
H	3.8200779	2.7500639	-1.0895620
H	3.4623620	-1.4005961	-3.9100470
H	4.3172059	-3.5197846	-2.9576195
H	4.3573779	-3.8347849	-0.5011716
H	3.4214220	-1.2089371	1.9734240
H	4.9153125	-2.8343381	3.0670722
H	5.8023337	-2.0571033	1.7368026
H	5.1740777	-3.7047942	1.5479896
H	2.5823295	-4.0748273	1.2837594
H	1.5030576	-2.6746090	1.4970234
H	2.4326390	-3.2984890	2.8782001
H	2.2880373	1.5011625	-1.8761936
H	4.3729534	1.6903906	-3.3228493
H	2.9171202	2.3208414	-4.1249115
H	3.5611234	0.7350066	-4.5767720
H	1.2594106	-0.3922731	-4.0624777
H	0.6627197	1.2535576	-3.7524654
H	0.4439760	-0.0193327	-2.5262226
N	-2.9078125	-0.3946724	-0.4035535

C	-1.7259968	-1.0897681	-0.2233766
C	-1.9816537	-2.5372035	-0.6924356
C	-1.5624027	-3.5461911	0.3935630
C	-3.5146844	-2.5980606	-0.9298034
C	-3.9954867	-1.1454938	-1.1352998
C	-4.0428177	-0.7803143	-2.6327515
C	-5.3830881	-0.8995713	-0.5346558
C	-1.1787268	-2.8557897	-1.9723556
C	-3.1326433	0.8515520	0.2836844
C	-3.4576163	0.8216119	1.6702811
C	-3.7047941	2.0321690	2.3300338
C	-3.6407268	3.2526069	1.6612027
C	-3.2955620	3.2746636	0.3153772
C	-3.0222823	2.0933511	-0.3921926
C	-2.5636409	2.2148327	-1.8391622
C	-3.6154817	2.9020971	-2.7289486
C	-1.2219815	2.9663007	-1.9268456
C	-3.5326232	-0.4687772	2.4803357
C	-4.8511819	-0.6040618	3.2641380
C	-2.3332995	-0.5900438	3.4382295
H	-0.1000999	-2.7604180	-1.7835254
H	-1.3753185	-3.8867811	-2.3071575
H	-0.4816916	-3.4881388	0.5873712
H	-2.0854430	-3.3546802	1.3403844
H	-1.7892545	-4.5770299	0.0779533
H	-1.4279485	-2.1765026	-2.7972162
H	-3.7852839	-3.2401806	-1.7795808
H	-4.0071080	-3.0136803	-0.0374818
H	-3.0565775	-0.8677010	-3.1040453
H	-4.7306682	-1.4604045	-3.1558668
H	-4.4096696	0.2418431	-2.7852412
H	-5.6703018	0.1585268	-0.6034421
H	-6.1295702	-1.4856546	-1.0886249
H	-5.4299181	-1.2034075	0.5175668
H	-3.9601477	2.0178483	3.3904555

H	-3.8488713	4.1822755	2.1920533
H	-3.2206327	4.2325293	-0.2015852
H	-2.3953840	1.1995066	-2.2188122
H	-3.2931262	2.8991696	-3.7800508
H	-4.5924815	2.4036019	-2.6703895
H	-3.7645310	3.9502143	-2.4317388
H	-1.3129354	3.9936370	-1.5453790
H	-0.4441923	2.4545537	-1.3427309
H	-0.8836771	3.0268602	-2.9711864
H	-3.4684763	-1.3069199	1.7747220
H	-5.7285032	-0.4924443	2.6130757
H	-4.9059569	-1.5907745	3.7458419
H	-4.9312314	0.1512872	4.0586216
H	-2.3179726	0.2363537	4.1634599
H	-2.3779710	-1.5342257	4.0003140
H	-1.3847360	-0.5740524	2.8794564

BP86/def2-TZVPP, sextet

-2822.899090605

Mn	-0.0000458	-0.0000319	0.0000405
N	2.9714717	0.4657300	0.3275808
C	1.6824992	0.8789512	0.5781144
C	1.7891940	2.1730268	1.4056214
C	0.8228260	3.2577594	0.9029340
C	3.2641590	2.6142796	1.2122043
C	4.0742091	1.3476186	0.8683382
C	4.7602213	0.7420960	2.1083391
C	5.1675186	1.6282906	-0.1702182
C	1.4637079	1.8938176	2.8913847
C	3.2038332	-0.7314401	-0.4402977
C	3.2767267	-0.6494810	-1.8584062
C	3.5179467	-1.8243755	-2.5858179
C	3.6644049	-3.0548371	-1.9526888
C	3.5442637	-3.1317050	-0.5687345
C	3.3026083	-1.9902970	0.2107991

C	3.1155004	-2.1715765	1.7130284
C	4.3243947	-2.8566652	2.3765706
C	1.8288970	-2.9587985	2.0248717
C	3.0707536	0.6474907	-2.6354283
C	4.2587453	0.9727600	-3.5604566
C	1.7671407	0.6074488	-3.4541902
H	0.4124380	1.5982675	3.0033002
H	1.6308229	2.7980819	3.4985754
H	-0.2237045	2.9329886	1.0018297
H	1.0057771	3.4918524	-0.1542704
H	0.9375058	4.1842621	1.4876204
H	2.0775362	1.0850755	3.3071518
H	3.6699991	3.1297454	2.0939280
H	3.3214518	3.3155814	0.3662688
H	4.0526980	0.5342110	2.9186231
H	5.5102052	1.4493678	2.4904032
H	5.2829501	-0.1886946	1.8545302
H	5.6497091	0.6996531	-0.5056218
H	5.9438684	2.2614584	0.2815571
H	4.7729944	2.1555267	-1.0454757
H	3.5864164	-1.7713142	-3.6732888
H	3.8576960	-3.9544396	-2.5383450
H	3.6316444	-4.1016582	-0.0772447
H	2.9956284	-1.1752530	2.1534193
H	4.1961550	-2.8840308	3.4680748
H	5.2659742	-2.3361224	2.1576294
H	4.4341740	-3.8952757	2.0330214
H	1.8639443	-3.9712011	1.5969798
H	0.9449073	-2.4461350	1.6196979
H	1.6961958	-3.0564643	3.1121701
H	2.9629160	1.4586214	-1.9039920
H	5.2124734	0.9878168	-3.0178961
H	4.1162779	1.9560931	-4.0312050
H	4.3489808	0.2339668	-4.3695526
H	1.7871280	-0.2008943	-4.1997990

H	1.6233264	1.5566375	-3.9907149
H	0.8955996	0.4528571	-2.8010643
N	-2.9715568	-0.4657175	-0.3276411
C	-1.6825843	-0.8789693	-0.5781255
C	-1.7892732	-2.1731219	-1.4055101
C	-0.8229267	-3.2578143	-0.9026926
C	-3.2642464	-2.6143446	-1.2120848
C	-4.0742955	-1.3476553	-0.8683197
C	-4.7603355	-0.7422514	-2.1083634
C	-5.1675846	-1.6282478	0.1702769
C	-1.4637460	-1.8940595	-2.8912909
C	-3.2039036	0.7314828	0.4401965
C	-3.2767903	0.6495615	1.8583075
C	-3.5179095	1.8244890	2.5856986
C	-3.6642871	3.0549474	1.9525460
C	-3.5441496	3.1317780	0.5685894
C	-3.3025827	1.9903374	-0.2109246
C	-3.1154229	2.1715916	-1.7131511
C	-4.3242249	2.8568165	-2.3767217
C	-1.8287269	2.9586717	-2.0249689
C	-3.0709075	-0.6474073	2.6353564
C	-4.2587515	-0.9723669	3.5606845
C	-1.7670983	-0.6075852	3.4538162
H	-0.4124694	-1.5985344	-3.0032090
H	-1.6308591	-2.7983803	-3.4983979
H	0.2236087	-2.9330584	-1.0015883
H	-1.0059105	-3.4918062	0.1545285
H	-0.9375944	-4.1843712	-1.4872950
H	-2.0775517	-1.0853491	-3.3071531
H	-3.6700783	-3.1298737	-2.0937753
H	-3.3215555	-3.3155834	-0.3660982
H	-4.0528309	-0.5344333	-2.9186801
H	-5.5103190	-1.4495664	-2.4903485
H	-5.2830704	0.1885554	-1.8546287
H	-5.6497883	-0.6995869	0.5055967

H	-5.9439285	-2.2614753	-0.2814248
H	-4.7730346	-2.1553903	1.0455797
H	-3.5863735	1.7714540	3.6731714
H	-3.8575056	3.9545760	2.5381863
H	-3.6314523	4.1017292	0.0770820
H	-2.9956490	1.1752551	-2.1535376
H	-4.1959631	2.8841563	-3.4682240
H	-5.2658702	2.3363889	-2.1577920
H	-4.4338869	3.8954437	-2.0331853
H	-1.8636691	3.9710773	-1.5970755
H	-0.9448018	2.4459086	-1.6197808
H	-1.6959949	3.0563250	-3.1122647
H	-2.9634033	-1.4586028	1.9039411
H	-5.2126115	-0.9872519	3.0183531
H	-4.1163833	-1.9557013	4.0314604
H	-4.3486359	-0.2335028	4.3697556
H	-1.7867462	0.2008033	4.1993847
H	-1.6233564	-1.5567731	3.9903611
H	-0.8956768	-0.4532096	2.8004811

TPSS/def2-TZVPP, sextet

-2822.994935266

Mn	0.0000372	-0.0001035	-0.0000524
N	2.9437564	0.4969903	0.3345712
C	1.6503854	0.9143794	0.5970237
C	1.7674985	2.2058608	1.4336654
C	0.7948061	3.2970664	0.9450185
C	3.2467871	2.6436574	1.2245555
C	4.0535403	1.3702748	0.8713756
C	4.7442709	0.7524533	2.1083185
C	5.1449838	1.6495313	-0.1767018
C	1.4576259	1.9150307	2.9242189
C	3.1608258	-0.7035449	-0.4309956
C	3.2311044	-0.6256195	-1.8578220
C	3.4652396	-1.8102564	-2.5871323
C	3.6040107	-3.0469533	-1.9464113

C	3.4793367	-3.1214371	-0.5543318
C	3.2450338	-1.9697336	0.2264606
C	3.0321963	-2.1388866	1.7313898
C	4.2037795	-2.8656801	2.4212820
C	1.6987152	-2.8573824	2.0249216
C	3.0113118	0.6763917	-2.6311118
C	4.1650296	0.9955292	-3.6033827
C	1.6639271	0.6537295	-3.3820029
H	0.4012975	1.6042656	3.0467638
H	1.6220661	2.8228162	3.5453064
H	-0.2609060	2.9693419	1.0505500
H	0.9680096	3.5404843	-0.1225745
H	0.9132576	4.2305123	1.5370458
H	2.0880818	1.1016894	3.3339027
H	3.6688234	3.1708296	2.1047038
H	3.2969458	3.3479770	0.3678439
H	4.0334598	0.5492405	2.9308239
H	5.5140682	1.4521156	2.4939555
H	5.2569544	-0.1942307	1.8474963
H	5.6265819	0.7115540	-0.5204550
H	5.9349770	2.2863635	0.2709033
H	4.7454392	2.1827564	-1.0590414
H	3.5345191	-1.7606679	-3.6850328
H	3.7940610	-3.9577847	-2.5353622
H	3.5585030	-4.1006149	-0.0567834
H	2.9483527	-1.1256822	2.1657506
H	4.0560900	-2.8854656	3.5210422
H	5.1766072	-2.3743530	2.2176778
H	4.2887575	-3.9199775	2.0844976
H	1.6874252	-3.8877374	1.6115839
H	0.8456700	-2.3005605	1.5827814
H	1.5268114	-2.9290393	3.1193071
H	2.9448329	1.4930720	-1.8859866
H	5.1491357	1.0026722	-3.0942180
H	4.0141190	1.9906153	-4.0710499

H	4.2230228	0.2548712	-4.4281205
H	1.6365466	-0.1481223	-4.1497268
H	1.4861705	1.6209233	-3.8970559
H	0.8219056	0.4854230	-2.6767788
N	-2.9436671	-0.4969844	-0.3345775
C	-1.6503567	-0.9145650	-0.5970585
C	-1.7676773	-2.2061173	-1.4335548
C	-0.7951669	-3.2974218	-0.9447633
C	-3.2470407	-2.6436524	-1.2244107
C	-4.0535842	-1.3700997	-0.8713536
C	-4.7441348	-0.7522326	-2.1083769
C	-5.1451259	-1.6490571	0.1767044
C	-1.4577373	-1.9155178	-2.9241380
C	-3.1605493	0.7036028	0.4309530
C	-3.2308460	0.6257282	1.8577833
C	-3.4649438	1.8103994	2.5870512
C	-3.6036590	3.0470784	1.9462819
C	-3.4789996	3.1215016	0.5541969
C	-3.2447402	1.9697606	-0.2265541
C	-3.0320344	2.1388131	-1.7315139
C	-4.2037929	2.8653364	-2.4213907
C	-1.6986923	2.8575007	-2.0252158
C	-3.0111893	-0.6762820	2.6311128
C	-4.1650744	-0.9954121	3.6031884
C	-1.6639273	-0.6536308	3.3822225
H	-0.4013680	-1.6048988	-3.0467013
H	-1.6222748	-2.8233621	-3.5451139
H	0.2605973	-2.9698953	-1.0503722
H	-0.9683890	-3.5406474	0.1228706
H	-0.9137987	-4.2309345	-1.5366488
H	-2.0880851	-1.1021531	-3.3339429
H	-3.6691558	-3.1708391	-2.1045121
H	-3.2973236	-3.3478809	-0.3676315
H	-4.0332144	-0.5490795	-2.9308025
H	-5.5139411	-1.4518406	-2.4940928

H	-5.2567720	0.1944964	-1.8476217
H	-5.6264994	-0.7109489	0.5204152
H	-5.9352676	-2.2857049	-0.2709011
H	-4.7457435	-2.1823529	1.0590766
H	-3.5342516	1.7608500	3.6849514
H	-3.7936895	3.9579383	2.5351952
H	-3.5581628	4.1006598	0.0566095
H	-2.9480639	1.1255782	-2.1657832
H	-4.0561830	2.8850482	-3.5211631
H	-5.1765168	2.3738517	-2.2176728
H	-4.2889341	3.9196483	-2.0846940
H	-1.6875633	3.8879122	-1.6120154
H	-0.8455165	2.3008932	-1.5830551
H	-1.5268670	2.9290472	-3.1196206
H	-2.9446041	-1.4929682	1.8860058
H	-5.1490887	-1.0025767	3.0938452
H	-4.0142366	-1.9904889	4.0708987
H	-4.2232241	-0.2547417	4.4279036
H	-1.6366470	0.1482378	4.1499345
H	-1.4862717	-1.6208192	3.8973205
H	-0.8217929	-0.4853617	2.6771242

TPSS/def2-TZVPP, quartet

-2822.998675439

Mn	-0.0113732	-0.1152254	0.0591963
N	2.8372826	0.5718272	-0.6792435
C	1.9613156	-0.2943646	-0.0425886
C	2.8081970	-1.4625851	0.4999932
C	2.5012673	-2.7739712	-0.2580331
C	2.5134050	-1.7034575	1.9941991
C	4.2754924	-0.9967477	0.3049627
C	4.2599688	0.0798178	-0.8003404
C	4.5442599	-0.5372047	-2.1851807
C	5.2815966	1.1934254	-0.5452618
C	2.4449050	1.9358080	-0.9342747
C	2.0937900	2.3665592	-2.2358316

C	1.7537943	3.7123515	-2.4332499
C	1.7293363	4.6165967	-1.3802672
C	2.0374020	4.1768653	-0.0962636
C	2.3980768	2.8486506	0.1544472
C	2.7097715	2.4454888	1.5919229
C	1.4269562	2.4161740	2.4459738
C	3.7555165	3.3668399	2.2511301
C	2.0149689	1.4247652	-3.4297287
C	2.9720152	1.8453238	-4.5627078
C	0.5720716	1.3420694	-3.9679788
H	1.4484977	-3.0483173	-0.1301626
H	2.6901879	-2.6820391	-1.3307900
H	3.1175010	-3.5953582	0.1302387
H	2.6959566	-0.7992218	2.5837088
H	1.4689037	-1.9992075	2.1409798
H	3.1477892	-2.5072453	2.3902191
H	4.6381309	-0.5431680	1.2353585
H	4.5721327	0.2284887	-2.9639861
H	5.5223982	-1.0314348	-2.1687211
H	3.7911171	-1.2808210	-2.4564751
H	5.1858325	1.9984041	-1.2808412
H	5.1672570	1.6198038	0.4538467
H	6.2934225	0.7819246	-0.6258099
H	1.4901423	4.0489526	-3.4325831
H	1.4622097	5.6552410	-1.5544001
H	2.0039880	4.8813505	0.7305190
H	3.1120084	1.4293374	1.5729982
H	4.9504683	-1.8227050	0.0569659
H	0.9585391	3.4059590	2.4864601
H	0.7007400	1.7082723	2.0279822
H	1.6540165	2.1035727	3.4715325
H	3.3696399	4.3836706	2.3797080
H	4.0162919	2.9859680	3.2448085
H	4.6720517	3.4320816	1.6569856
H	2.2964200	0.4273107	-3.0848078

H	4.0048996	1.9340462	-4.2120360
H	2.9471444	1.1111114	-5.3756148
H	2.6813856	2.8154788	-4.9808564
H	0.2246941	2.3208658	-4.3168496
H	0.5222070	0.6475143	-4.8139167
H	-0.1167962	0.9926414	-3.1926681
N	-2.9026015	-0.8721290	-0.5037007
C	-1.9723857	0.0844585	-0.1365104
C	-2.7442870	1.4090405	-0.0087265
C	-3.0124724	1.7276518	1.4816175
C	-1.9652063	2.5873398	-0.6166553
C	-4.0616646	1.1528224	-0.7852163
C	-4.3006285	-0.3713649	-0.7876756
C	-5.3101097	-0.8179562	0.2869447
C	-4.8283158	-0.8565651	-2.1451314
C	-2.5781702	-2.2778227	-0.4629877
C	-2.6365483	-2.9765881	0.7719256
C	-2.3751003	-4.3516767	0.7808106
C	-2.0491293	-5.0365141	-0.3849524
C	-1.9354241	-4.3339813	-1.5776231
C	-2.1758089	-2.9547158	-1.6417005
C	-1.8919776	-2.2410883	-2.9587701
C	-0.3800547	-2.2863038	-3.2647725
C	-2.6770055	-2.8315656	-4.1458965
C	-2.9097677	-2.2871642	2.1037168
C	-4.0366692	-2.9609647	2.9093376
C	-1.6236374	-2.2208749	2.9510882
H	-2.0676436	1.8688326	2.0164975
H	-3.5594462	0.9230435	1.9809478
H	-3.6014676	2.6494253	1.5762786
H	-1.7626596	2.4179565	-1.6783672
H	-1.0032629	2.7266894	-0.1089392
H	-2.5308530	3.5227897	-0.5174907
H	-3.9405345	1.4973582	-1.8186585
H	-5.3558968	-1.9098793	0.3432541

H	-6.3081303	-0.4545707	0.0185088
H	-5.0643350	-0.4266242	1.2760144
H	-4.9089732	-1.9479131	-2.1704103
H	-4.1859568	-0.5285451	-2.9653445
H	-5.8294356	-0.4437372	-2.3119653
H	-2.4256252	-4.8933946	1.7215708
H	-1.8624470	-6.1065617	-0.3584498
H	-1.6358977	-4.8600326	-2.4803057
H	-2.1714566	-1.1915247	-2.8376710
H	-4.9144850	1.6906207	-0.3573035
H	-0.0319864	-3.3208087	-3.3615375
H	0.1993083	-1.8066848	-2.4677087
H	-0.1677343	-1.7674180	-4.2056188
H	-2.3752631	-3.8660806	-4.3426430
H	-2.4766595	-2.2521959	-5.0541032
H	-3.7554889	-2.8255638	-3.9676911
H	-3.2035461	-1.2585556	1.8901498
H	-4.9636871	-3.0288712	2.3329986
H	-4.2412511	-2.3865194	3.8197398
H	-3.7578427	-3.9745888	3.2165440
H	-1.2445937	-3.2239482	3.1763875
H	-1.8166971	-1.7069354	3.8995277
H	-0.8411540	-1.6688024	2.4191028

Compound **3**

BP86/def2-TZVPP

-2824.100813024

Mn	-0.0283588	0.2711469	0.1614916
N	2.4007019	0.1432528	-1.7686840
C	1.8796768	0.7826432	-0.5562295
C	3.0756062	0.6884656	0.4256903
C	4.2716580	0.9242652	-0.5335584
C	3.8837876	0.3575379	-1.9271829
C	3.1618008	-0.6949874	1.0946999
C	3.0201130	1.7653014	1.5153392

C	4.2640622	1.3551219	-3.0397032
C	4.6302587	-0.9556245	-2.2292835
C	1.5283052	-0.1537716	-2.8670205
C	0.8938363	0.8714350	-3.6331792
C	0.0262136	0.5155485	-4.6762661
C	-0.2253715	-0.8143833	-4.9960306
C	0.3780931	-1.8167534	-4.2439845
C	1.2380530	-1.5172893	-3.1781058
C	1.0887004	2.3626567	-3.3660925
C	1.5713000	3.1253197	-4.6137926
C	-0.1957289	3.0120852	-2.8193942
C	1.7742265	-2.6798178	-2.3509020
C	2.5175725	-3.7257697	-3.1994080
C	0.6474589	-3.3577533	-1.5506518
H	1.7157832	1.8859156	-0.7175519
H	4.4450094	2.0079279	-0.6172906
H	5.2045954	0.4748380	-0.1620223
H	4.1070872	-0.8128246	1.6467521
H	3.0968198	-1.5040480	0.3560475
H	2.3419958	-0.8298955	1.8173111
H	3.9221657	1.7358550	2.1446199
H	2.1557104	1.6187683	2.1816538
H	2.9461225	2.7713702	1.0771134
H	5.3580657	1.4572412	-3.0919045
H	3.8497095	2.3533021	-2.8548129
H	3.9161369	1.0054291	-4.0219789
H	4.4991425	-1.6969310	-1.4319335
H	5.7068868	-0.7569625	-2.3302258
H	4.2873767	-1.3956323	-3.1752143
H	-0.4585083	1.3029583	-5.2560056
H	-0.8954486	-1.0674697	-5.8185346
H	0.1637877	-2.8611232	-4.4770262
H	1.8592929	2.4651501	-2.5942936
H	1.7832896	4.1744032	-4.3610914
H	0.8099640	3.1264105	-5.4064347

H	2.4854678	2.6835137	-5.0296406
H	-0.0307108	4.0778946	-2.6050013
H	-0.5270607	2.5298121	-1.8885006
H	-1.0208729	2.9371251	-3.5421623
H	2.4778511	-2.2514758	-1.6282323
H	3.3240126	-3.2750465	-3.7922646
H	1.8382058	-4.2359259	-3.8978357
H	2.9614908	-4.4967887	-2.5531915
H	1.0525844	-4.1624127	-0.9199836
H	-0.1080133	-3.7993760	-2.2167265
H	0.1295145	-2.6422355	-0.8962397
N	-2.4009348	-0.1413584	1.7681534
C	-1.8331076	-0.7420372	0.5424184
C	-3.0187158	-0.6674044	-0.4507186
C	-4.2204352	-0.9556801	0.4886003
C	-3.8841204	-0.3781329	1.8901670
C	-3.1403719	0.7223603	-1.1019837
C	-2.9193259	-1.7235878	-1.5567428
C	-4.2712370	-1.3773661	2.9981446
C	-4.6638147	0.9218409	2.1671611
C	-1.5379250	0.1449643	2.8766928
C	-0.8909285	-0.8889517	3.6235509
C	-0.0180323	-0.5428660	4.6650691
C	0.2296658	0.7834240	5.0033467
C	-0.3875087	1.7946862	4.2750750
C	-1.2570721	1.5071698	3.2133461
C	-1.0809944	-2.3761483	3.3360077
C	-1.5746448	-3.1502504	4.5723911
C	0.2099039	-3.0168257	2.7936728
C	-1.8265284	2.6819800	2.4256579
C	-2.5865360	3.6810606	3.3153200
C	-0.7264118	3.4167864	1.6393015
H	-1.6085031	-1.8282052	0.6815843
H	-4.3468670	-2.0462163	0.5670440
H	-5.1656286	-0.5471149	0.1011020

H	-4.0843138	0.8225302	-1.6600288
H	-3.1063881	1.5256103	-0.3537256
H	-2.3199238	0.8862489	-1.8174596
H	-3.8138874	-1.7059650	-2.1973563
H	-2.0482649	-1.5440159	-2.2036862
H	-2.8264000	-2.7341410	-1.1332187
H	-5.3642423	-1.4971978	3.0277237
H	-3.8362544	-2.3687758	2.8263751
H	-3.9505442	-1.0185907	3.9865923
H	-4.5239310	1.6643655	1.3723426
H	-5.7390844	0.7031003	2.2354513
H	-4.3596395	1.3700888	3.1225353
H	0.4760498	-1.3363439	5.2281843
H	0.9060749	1.0269039	5.8234328
H	-0.1807581	2.8362457	4.5267083
H	-1.8440669	-2.4690012	2.5555454
H	-1.7813310	-4.1972927	4.3077739
H	-0.8205603	-3.1568687	5.3720021
H	-2.4939479	-2.7147193	4.9837024
H	0.0453910	-4.0795403	2.5649460
H	0.5495635	-2.5238055	1.8728238
H	1.0261901	-2.9538399	3.5276474
H	-2.5285528	2.2612151	1.6968698
H	-3.3728440	3.1877638	3.9009115
H	-1.9128928	4.1854089	4.0232608
H	-3.0592606	4.4597926	2.6998396
H	-1.1534646	4.2334235	1.0400254
H	0.0343666	3.8443444	2.3078450
H	-0.1964276	2.7425326	0.9434244

TPSS/def2-TZVPP

-2824.197289086

Mn	-0.2179100	-0.4312600	-0.2655441
N	2.2899307	0.0767657	-1.6928371
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C	2.6376715	0.4836520	0.5692663

C	3.9030698	0.7892172	-0.2024383
C	3.7483473	0.2977985	-1.6299142
C	2.6583426	-0.9064411	1.1579430
C	2.4475107	1.4883138	1.6755174
C	4.2661208	1.3331699	-2.6282491
C	4.5609432	-0.9847009	-1.8724138
C	1.6064630	-0.1010192	-2.9143618
C	1.1041830	1.0478528	-3.5944542
C	0.3813153	0.8842531	-4.7632579
C	0.1578204	-0.3743353	-5.3057794
C	0.6411015	-1.5008199	-4.6493908
C	1.3576561	-1.3935112	-3.4510335
C	1.3367804	2.4464980	-3.0470231
C	1.8701456	3.4044833	-4.1234701
C	0.0628724	3.0313318	-2.4287460
C	1.8025574	-2.6693955	-2.7454901
C	2.6940112	-3.5557020	-3.6426147
C	0.5934709	-3.4889807	-2.2540261
H	1.3994262	1.6868425	-0.6344416
H	4.0257314	1.8619182	-0.2177158
H	4.7885513	0.3664973	0.2533433
H	3.5408903	-1.0678579	1.7732856
H	2.6535353	-1.6716027	0.3796022
H	1.7823891	-1.0469185	1.7908987
H	3.2444000	1.4163393	2.3993040
H	1.5158003	1.3365033	2.2066715
H	2.4462421	2.4913547	1.2788411
H	5.3516089	1.4145566	-2.5423409
H	3.8512244	2.3239961	-2.4463169
H	4.0346671	1.0411827	-3.6602572
H	4.2980707	-1.7669203	-1.1604427
H	5.6255313	-0.7727322	-1.7561694
H	4.3966222	-1.3629906	-2.8863501
H	-0.0057177	1.7569334	-5.2710189
H	-0.3999949	-0.4798298	-6.2299250

H	0.4527951	-2.4866248	-5.0663213
H	2.0806161	2.3735418	-2.2581005
H	2.0977270	4.3803712	-3.6821271
H	1.1288642	3.5664283	-4.9083212
H	2.7798735	3.0185902	-4.5924400
H	0.2514591	4.0283552	-2.0241075
H	-0.3097472	2.4064409	-1.6163060
H	-0.7244362	3.1169511	-3.1717177
H	2.3814955	-2.3626703	-1.8686339
H	3.5417820	-2.9978480	-4.0508761
H	2.1218027	-3.9629143	-4.4831368
H	3.0921040	-4.4001880	-3.0681594
H	0.9274144	-4.3900045	-1.7276625
H	-0.0491996	-3.7963657	-3.0877459
H	-0.0404230	-2.9136683	-1.5643023
N	-2.4316925	-0.1420944	1.7556476
C	-2.0956202	-0.9407567	0.5539471
C	-3.4197390	-0.9281641	-0.2268232
C	-4.4546211	-1.0398902	0.9215228
C	-3.8634658	-0.3260978	2.1688863
C	-3.5977909	0.3675561	-1.0112410
C	-3.5344375	-2.1242007	-1.1826314
C	-4.0561222	-1.1869751	3.4294213
C	-4.5700623	1.0230344	2.4429938
C	-1.3859172	0.1875222	2.6627363
C	-0.6180172	-0.7748642	3.3883840
C	0.4150359	-0.3272644	4.2068520
C	0.7008713	1.0150376	4.3482290
C	-0.0353571	1.9399365	3.6506428
C	-1.0641076	1.5679038	2.8085192
C	-0.8410209	-2.2864041	3.3186313
C	-1.1592999	-2.8867272	4.7045399
C	0.3677706	-3.0165422	2.7023590
C	-1.7978972	2.6485714	2.0313565
C	-2.3612026	3.7445621	2.9525306

C	-0.9021997	3.2990147	0.9700169
H	-1.9481112	-2.0325201	0.7927839
H	-4.5925466	-2.1023758	1.1545261
H	-5.4374188	-0.6352659	0.6547060
H	-4.6197255	0.4710879	-1.3918988
H	-3.3806437	1.2431764	-0.3938882
H	-2.9282512	0.3839280	-1.8636614
H	-4.5091608	-2.1322686	-1.6801455
H	-2.7722847	-2.0936951	-1.9638548
H	-3.4253375	-3.0685027	-0.6384857
H	-5.1217829	-1.2449359	3.6825761
H	-3.7012591	-2.2111554	3.2877793
H	-3.5336171	-0.7525164	4.2894165
H	-4.5347326	1.6821249	1.5712122
H	-5.6246808	0.8446963	2.6862735
H	-4.1077386	1.5422072	3.2880955
H	1.0067282	-1.0553373	4.7531700
H	1.5042915	1.3360481	4.9993184
H	0.1972936	2.9898175	3.7564104
H	-1.6988893	-2.4698265	2.6697487
H	-1.3911464	-3.9543149	4.6104704
H	-0.3031295	-2.7939907	5.3809213
H	-2.0136096	-2.3904084	5.1714835
H	0.1726546	-4.0929974	2.6349679
H	0.5822349	-2.6515274	1.6923774
H	1.2684430	-2.8716167	3.3059685
H	-2.6207866	2.1569370	1.5125754
H	-2.9719345	3.3281429	3.7571892
H	-1.5535482	4.3244640	3.4091742
H	-2.9863829	4.4377641	2.3789353
H	-1.4632046	4.0589954	0.4166337
H	-0.0386053	3.7820705	1.4245944
H	-0.5220676	2.5655519	0.2558536

S7. DFT calculations for the determination of individual contributions to the ZFS parameters on Mn center

The following DFT calculations have been performed with ORCA 2.9.0 program package. The SVP basis set was used for all atoms. Experimental geometries were employed. Scalar relativistic effects were taken into account within second-order DKH Hamiltonian. TightSCF/Grid5 was used for these calculations. Calculations with BP86 functional were done with RI approximation. The calculation with B3LYP functional employed RIJCOSX approximation. Both approximations (RI and RIJCOSX) make use the auxiliary basis sets SV/J. The spin-orbit coupling was calculated using Couple-Perturbed equations. Spin-spin contribution was calculated using the spin-density from Unrestricted Natural Orbitals (UNO). The center of electric charge was chosen the origin of the molecule.

Table S7. The calculated Zero-Field Splitting parameters (K).

Complex	**Functional**	spin-spin contribution		spin-orbit coupling contribution		**Total**		**EPR**	
		D	E	D	E	D	E	D	E
2, S=3/2	BP86	1.029	-0.185	0.281	0.250	1.310	0.065	1.937	0.01
	B3LYP	1.165	0.348	0.842	-0.046	2.008	0.302		
3, S=5/2	BP86	0.314	0.007	0.311	0.040	0.626	0.047	0.45	0.015
	B3LYP	0.252	0.002	0.032	0.013	0.284	0.015		

For compound **2** a better agreement with experiment is obtained for the B3LYP functional.
For compound **3**, CASSCF/CASPT2/RASSI/SINGLE_ANISO calculations give for the spin-orbital contribution to D a value of 0.069 cm^{-1} (Table S3), which is close to the result obtained with B3LYP functional. We may conclude that for the calculations of ZFS parameters in the present compounds, the hybrid B3LYP functional performs much better than the pure BP86 functional.

S8. Synthetic methods

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. The cyclic alkyl(amino) carbene (cAAC:) was synthesized following a reported procedure.[16] Solvents were purified with the M-Braun solvent drying system. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. The powdered crystalline samples were subjected to evacuation for 5 h before magnetic measurement, elemental analysis and melting point determination.

Synthesis of **1**: To a mixture of $MnCl_2$ (0.629 g, 5 mmol) and cAAC: (1.43 g, 5 mmol) THF (15 mL) was added and stirred over night at room temperature. The precipitated product was separated by filtration and dried under vacuum to obtain **1** as a white powder. (Yield: 1.75 g, 85 %). Melting point: 278-280 °C; Decomposition temperature: 285-286 °C; Elemental analysis found (calcd.) [%] for $C_{20}H_{31}Cl_2MnN$: C 58.10 (58.40), H 7.61 (7.60), N 3.26 (3.41).

Synthesis of **2**: THF (50 mL) was added to a 1:1:2.1 mixture of **1** (0.82 g, 2 mmol), cAAC: (0.57 g, 2 mmol) and KC_8 (0.57 g, 4.2 mmol) at –78 ^{o}C while stirring. The reaction mixture was warmed to room temperature and the stirring was continued for 2 h. The resultant purple colored solution was then filtered and the filtrate was concentrated to dryness. The solid residue obtained was then extracted with toluene (100 mL). Storing a concentrated toluene solution at –4 ^{o}C afforded dark purple crystals of **2** suitable for X-ray diffraction. (Yield: 1.01 g, 81 %). Melting point: 136-138 °C; Decomposition temperature: 150 °C; Elemental analysis found (calcd.) [%] for $C_{40}H_{62}MnN_2$: C 76.42 (76.76), H 9.80 (9.98), N 4.49 (4.48). UV/Vis λ_{ab} = 545, 485 (sh), 409 (sh), 348 nm.

Synthesis of **3**: H_2 gas was bubbled through a solution of **2** (0.31 g, 0.5 mmol) in toluene (30 mL) at 25 ^{o}C under vigorous stirring for 2 minutes. Compound **3** precipitates as an alizarin crimson colored product which was then separated by filtration. Storing a saturated solution of **3** in toluene at –4 ^{o}C affords crystals suitable for X-ray diffraction. (Yield: 0.28 g, 91 %). Decomposition temperature: 182-183 °C; Elemental analysis found (calcd.) [%] for $C_{40}H_{64}MnN_2$: C 76.01 (76.51), H 9.98 (10.27), N 4.30 (4.46). UV/Vis λ_{ab} = 524, 398 nm.

Hydrogen splitting: The reaction of molecular hydrogen with compound **2** in toluene at room temperature is visible in the change of color. **2** shows a deep purple color in toluene solution. When hydrogen gas is passed for a few seconds, the deep purple color disappears and **3** precipitates as an alizarin crimson colored compound. The solubility of **3** is much less in toluene but enough to produce single crystals for X-ray diffraction. Figure S13 shows observed color change in the conversion of **2** to **3** in toluene on passing hydrogen gas.

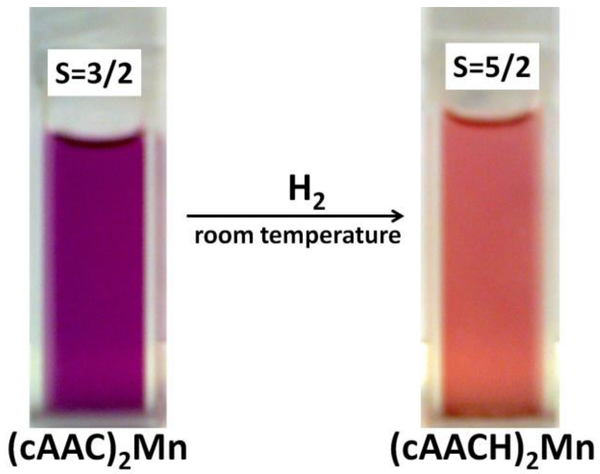

Figure S12. Room temperature activation of molecular hydrogen by compound 2 (purple) to form **3** (alizarin crimson)

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