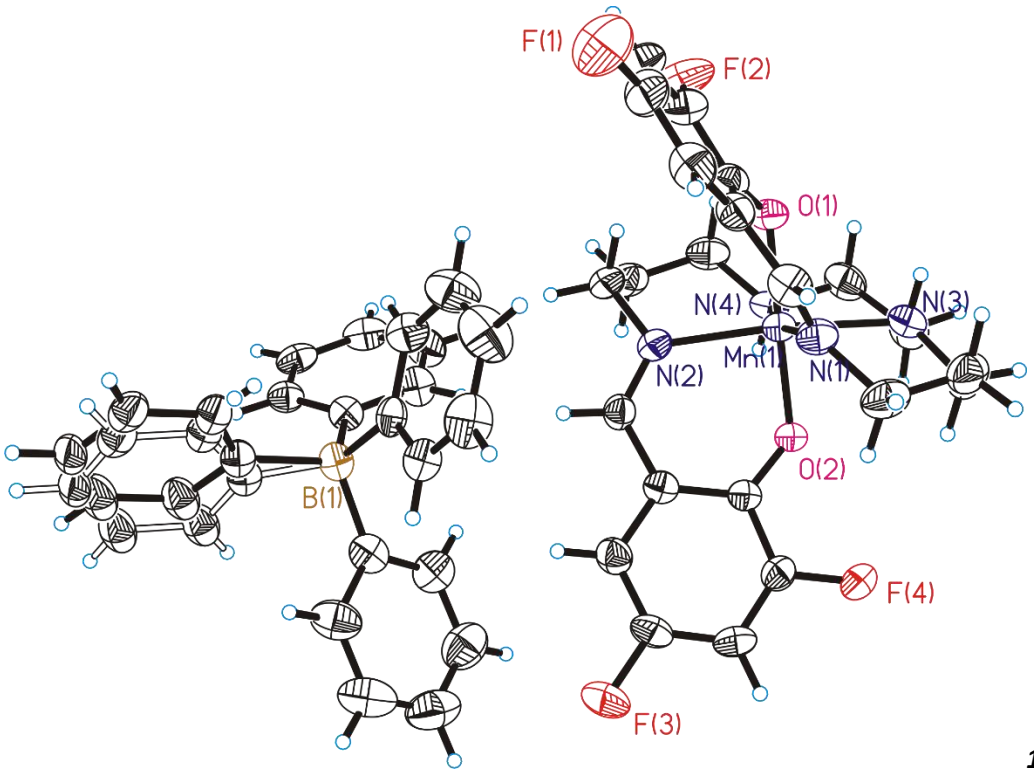
ELECTRONIC SUPPORTING INFORMATION (ESI) for New Journal Chemistry

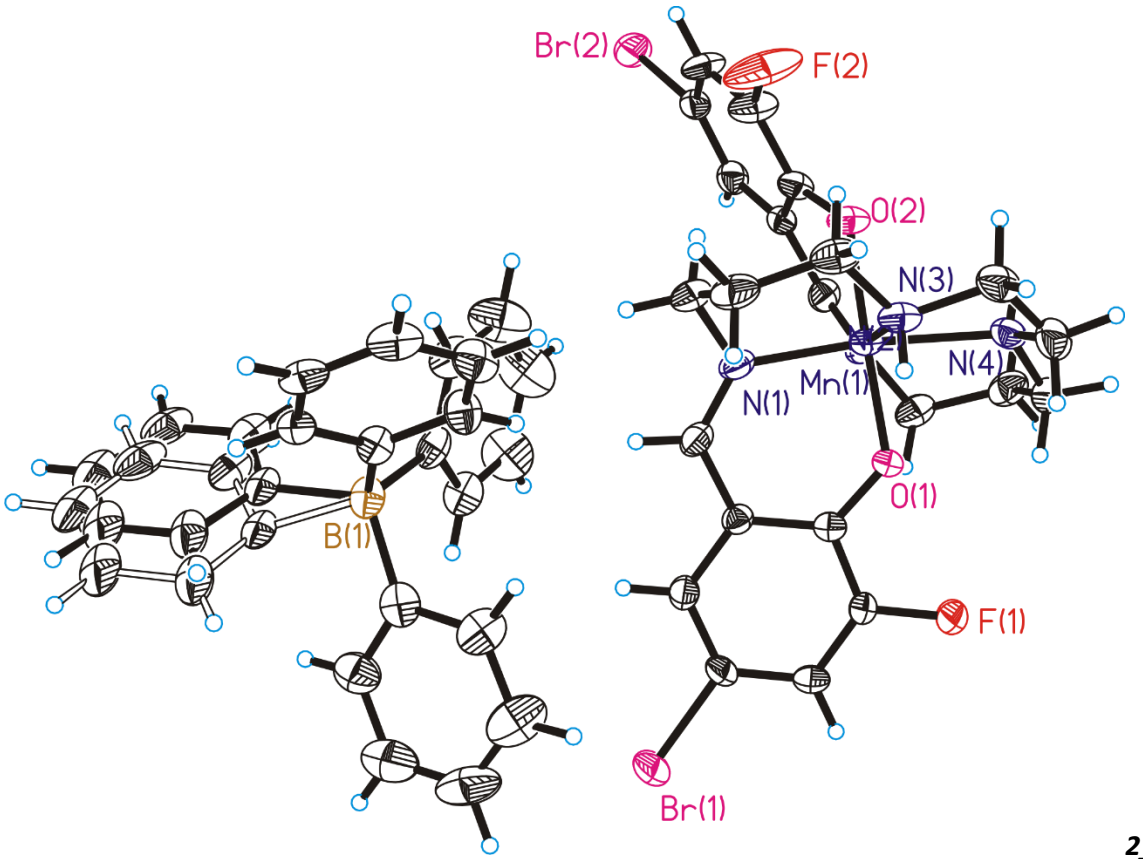
Effect of fluorine substituents on crystal structure and spin crossover behavior of cation $[Mn^{III}(3,5\text{-diHal-sal}_2323)]^+$ complexes family with BPh_4 anion

A.V. Tiunova,[a,b] A.V. Kazakova,[b*] D.V. Korchagin,[b*] G.V. Shilov,[b] K.V. Zakharov,[a] A.N. Vasiliev,[a,c] and E.B. Yagubskii[b*]

[a]*Lomonosov Moscow State University,119991 Moscow, Russia*
[b]*Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, MD, Russia, E-mail: kazakova@icp.ac.ru, korden@icp.ac.ru, yagubski@gmail.com*
[c]*National University of Science and Technology "MISiS",119049 Moscow, Russia*


F(1)
F(2)
O(1)
N(4)
N(3)
N(2)
Mn(1)
N(1)
O(2)
B(1)
F(4)
F(3)

1_240K


Br(2)
F(2)
O(2)
N(3)
N(4)
N(1)
Mn(1)
O(1)
B(1)
F(1)
Br(1)

2_160K

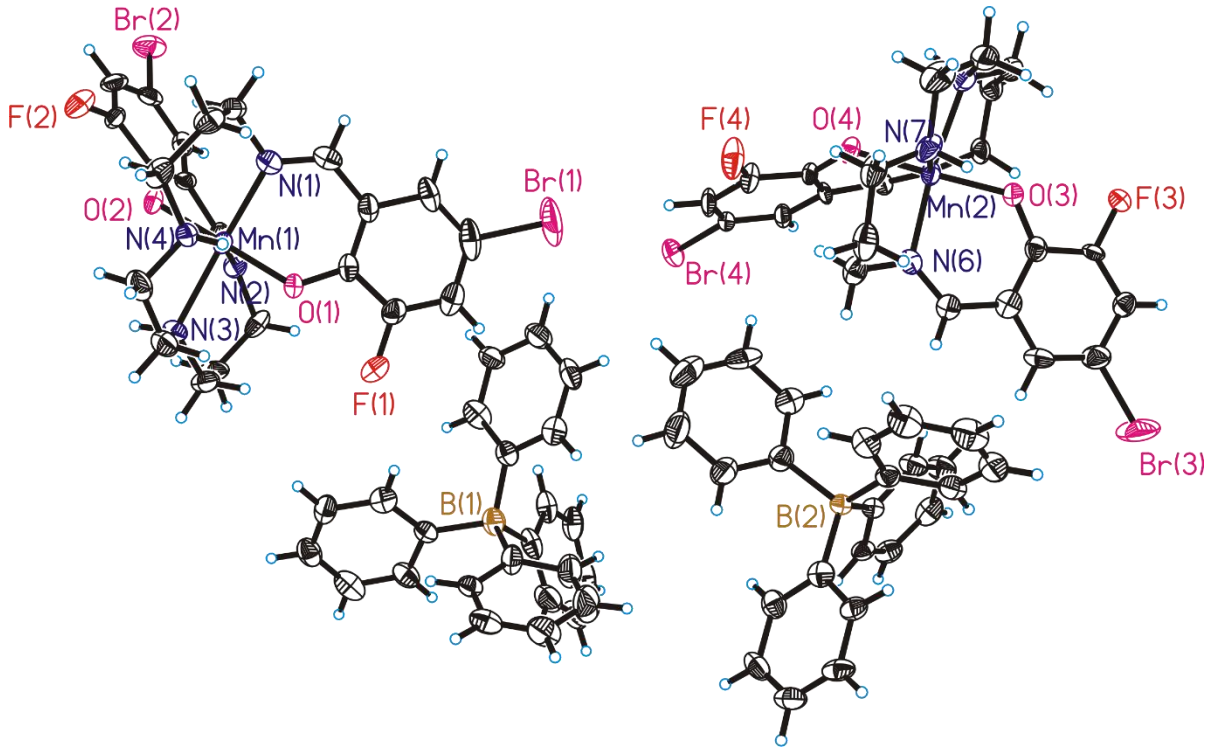


Figure S1. Asymmetric units of complexes **1-3** (50% ellipsoid probability). Minor positions of the disordered phenyl groups of the BPh_4 anions in **1** and **2** are shown by empty bonds.

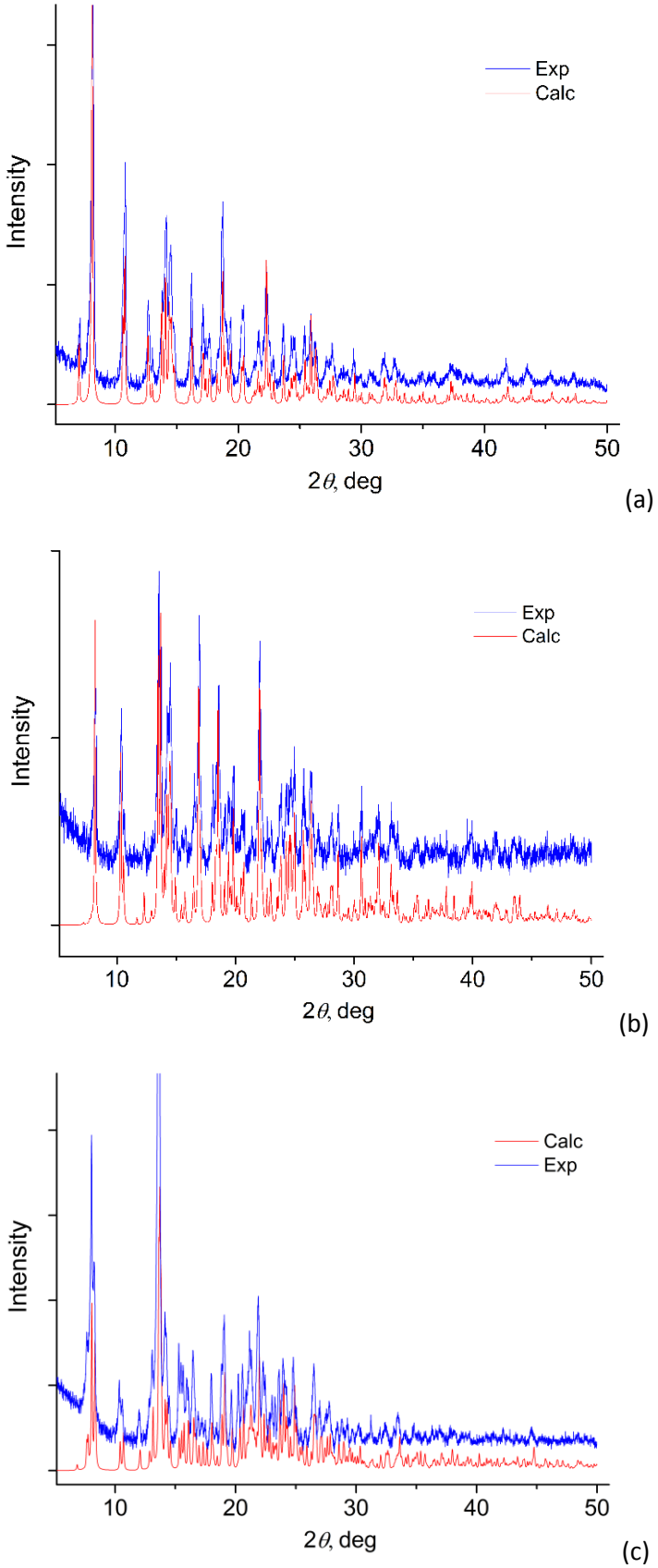


Figure S2. Powder X-ray diffraction pattern of polycrystalline samples of **1** (a), **2** (b) and **3** (c): experimental (blue), and calculated from single crystal data (red).

Table S1. Crystal data and structure refinement parameters for compounds **1-3**.

Temperature, K	100	160	240	100	160	240	100	160	240
Empirical formula	$[C_{22}H_{24}F_4N_4O_2Mn]^+[(C_6H_5)_4B]^-$			$[C_{22}H_{24}F_2Br_2N_4O_2Mn]^+[(C_6H_5)_4B]^-$			$2[C_{22}H_{24}Br_2Cl_2N_4O_2Mn]^+2[(C_6H_5)_4B]$		
Molecular weight	826.60			948.42			1896.84		
Crystal system, space group	monoclinic, $P2_1/c$			monoclinic, $P2_1/n$			triclinic, $P1$		
a, Å	14.2148(6)	14.2739(7)	14.3158(5)	14.2242(5)	14.2815(6)	14.3588(9)	13.0486(7)	13.0849(7)	13.1318(9)
b, Å	21.5308(6)	21.7237(6)	21.8648(6)	22.6477(7)	22.824(1)	22.9189(12)	13.4558(9)	13.4898(9)	13.500(1)
c, Å	14.5452(6)	14.5807(6)	14.6437(6)	14.5139(6)	14.4290(8)	14.4698(9)	14.2222(9)	14.2694(6)	14.320(1)
α, °	90	90	90	90	90	90	105.615(6)	105.671(5)	105.613(7)
β, °	118.483(6)	118.570(6)	118.711(5)	117.877(5)	117.062(6)	116.719(7)	102.221(5)	102.257(4)	102.473(6)
γ, °	90	90	90	90	90	90	111.652(6)	111.727(6)	111.889(8)
Volume, $Å^3$	3912.8(3)	3970.7(3)	4020.1(3)	4133.0(3)	4188.4(4)	4253.4(5)	2096.0(2)	2111.0(2)	2121.7(3)
Z, ρ_3 (calc.), g/cm	4, 1.403	4, 1.383	4, 1.366	4, 1.524	4, 1.504	4, 1.481	1, 1.503	1, 1.492	1, 1.485
μ, mm^{-1}	0.398	0.396	0.391	2.306	2.276	2.241	2.274	2.258	2.246
F(000)	1720			1928			964		
Crystal size, mm^3	0.45 x 0.2 x 0.15			0.35 x 0.2 x 0.15			0.45 x 0.2 x 0.2		
θ range, °	2.93 – 29.07	2.92 – 29.07	2.78–26.32	2.89–26.32	2.86–26.32	2.84–26.32	2.98–29.07	2.97–29.07	2.96–29.05
Reflections collected	35119	34504	29041	18730	18484	17664	18399	21030	17180
Reflections unique [R_{int}]	10460 [0.0432]	10602 [0.0441]	8169 [0.0322]	8409 [0.0296]	8504 [0.0292]	8628 [0.0296]	14200 [0.0358]	14503 [0.0341]	13019 [0.0338]
Completeness to θ	0.999	0.999	0.999	0.999	0.998	0.998	0.999	0.999	0.999
Number of parameters	531	531	526	531	520	531	1045		
Goodness-of-fit on F^2	1.002	0.994	1.020	1.015	1.016	0.928	1.049	1.041	1.038
Final R_1, wR_2 [$I>2\sigma(I)$]	0.0395, 0.0808	0.0486, 0.0929	0.0427, 0.0870	0.0322, 0.0661	0.0399, 0.0733	0.0479, 0.0623	0.0760, 0.1975	0.0789, 0.2163	0.0797, 0.2103
R_1, wR_2 (all data)	0.0645, 0.0872	0.0818, 0.1063	0.0640, 0.0955	0.0463, 0.0716	0.0660, 0.0816	0.1006, 0.0799	0.0916, 0.2100	0.0988, 0.2329	0.1117, 0.2410
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, $e \cdot Å^{-3}$	0.412 / -0.687	0.539 / -0.516	0.472 / -0.447	0.429 / -0.391	0.591 / -0.549	0.598 / -0.538	2.678 / -2.319	1.881 / -1.932	1.041 / -1.130
CCDC code	2162851	2162852	2162853	2162854	2162855	2162856	2162857	2162858	2162859

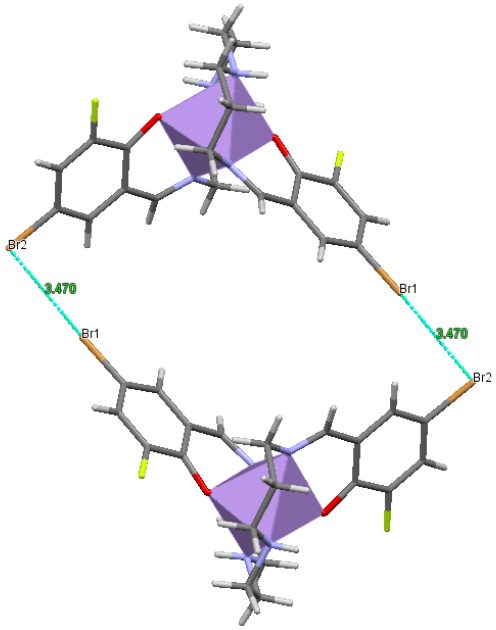


Figure S3. Br…Br contacts in dimers of cationic complexes in crystal structure of **2**.

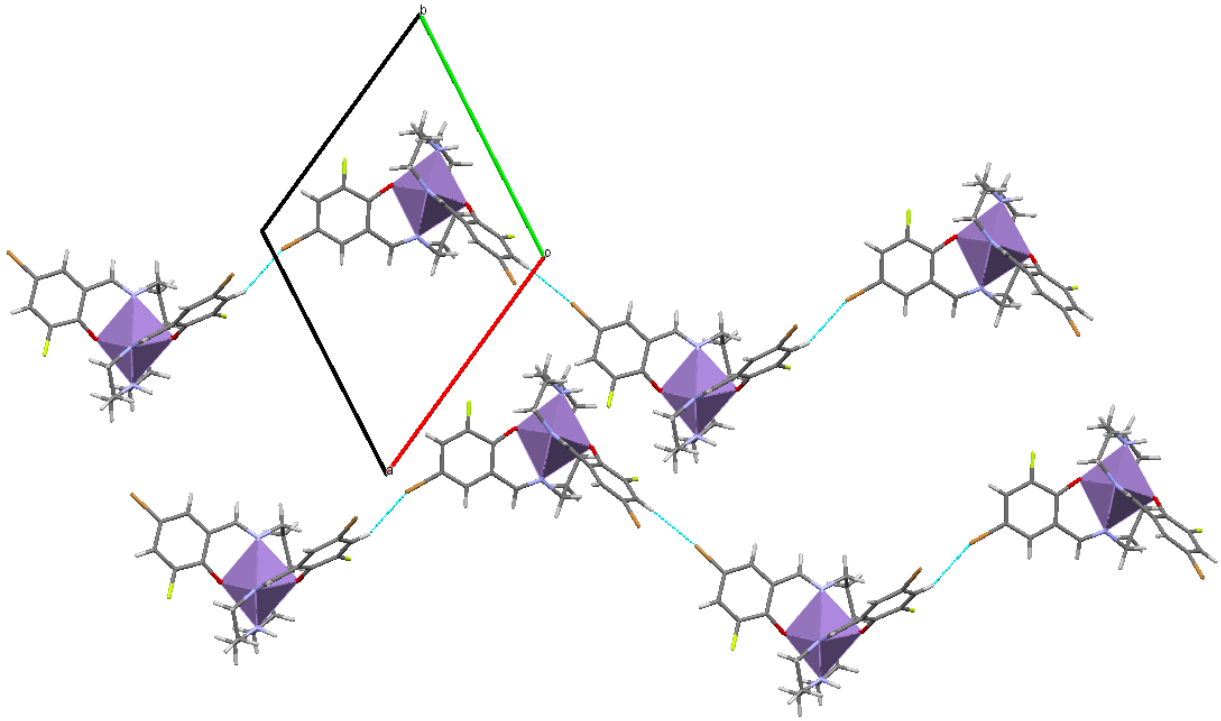


Figure S4. View of C–H···Br interactions (cyan lines) forming a 1D chains in **3**.

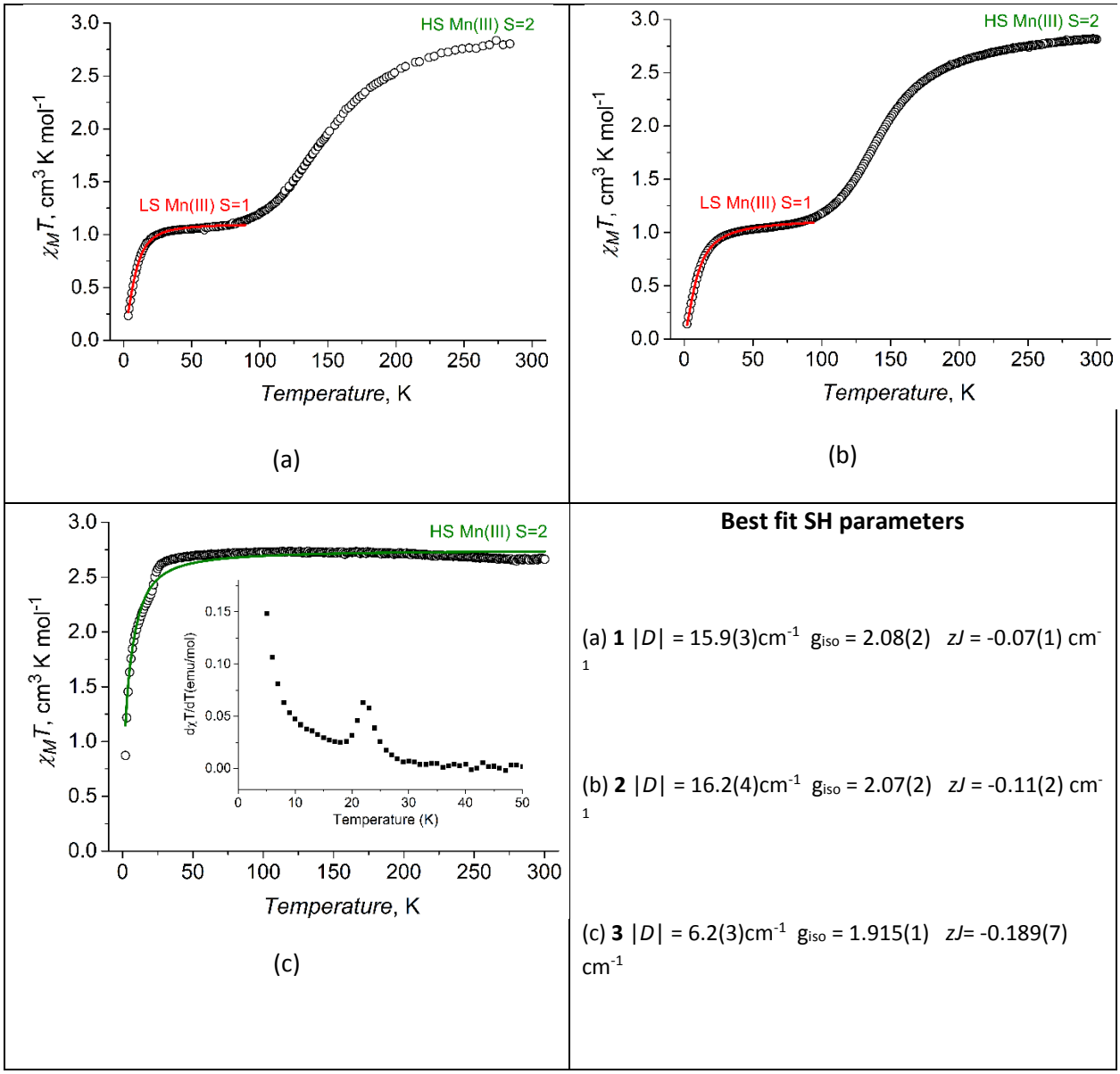


Figure S5. Temperature dependence of $\chi_M T$ product for **1-3**. The empty circles – experimental data, solid lines – best fit data with corresponding parameters. Inset (c): d($\chi_m T$)/dT *vs.* T for **3**. The magnetic data were fitted by the spin-Hamiltonian with corresponding parameters using *PHI* program [1].

References

1. N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, J. Comput. Chem. 2013, 34, 1164−1175.