Half-sandwich manganese complexes $Cp(CO)_2Mn(NHC)$ as redox-active organometallic fragments

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Electronic Supplementary Information

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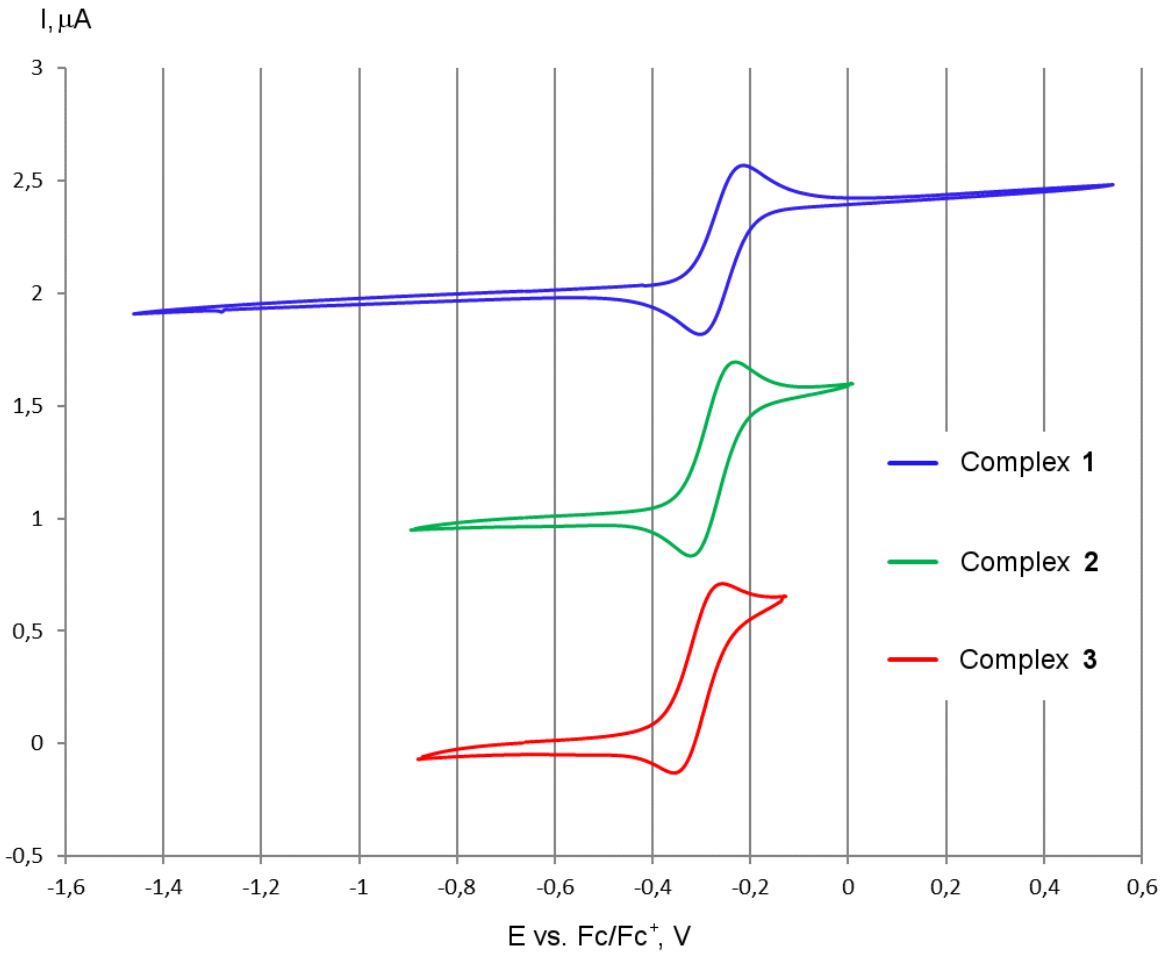

Figure S1. Superposition of cyclic voltammograms of Mn^{I} NHC complexes **1-3** (Pt electrode, CH_2Cl_2, 1 mM sample concentration, 0.1 M Bu_4NPF_6 as supporting electrolyte, 100 mV/s, potentials *vs.* Fc/Fc^+).

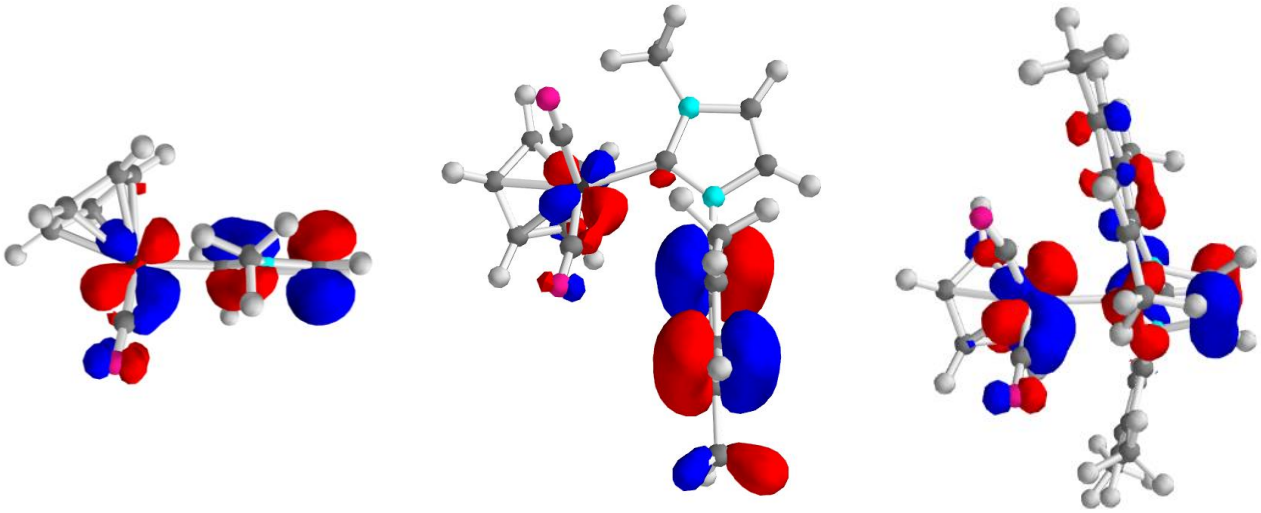

Figure S2. Plot of calculated SOMO orbitals for Mn^{II} complexes $[\mathbf{1}]^+$ (left), $[\mathbf{2}]^+$ (center) and $[\mathbf{3}]^+$ (right) on a 0.04 a.u. isodensity surface.

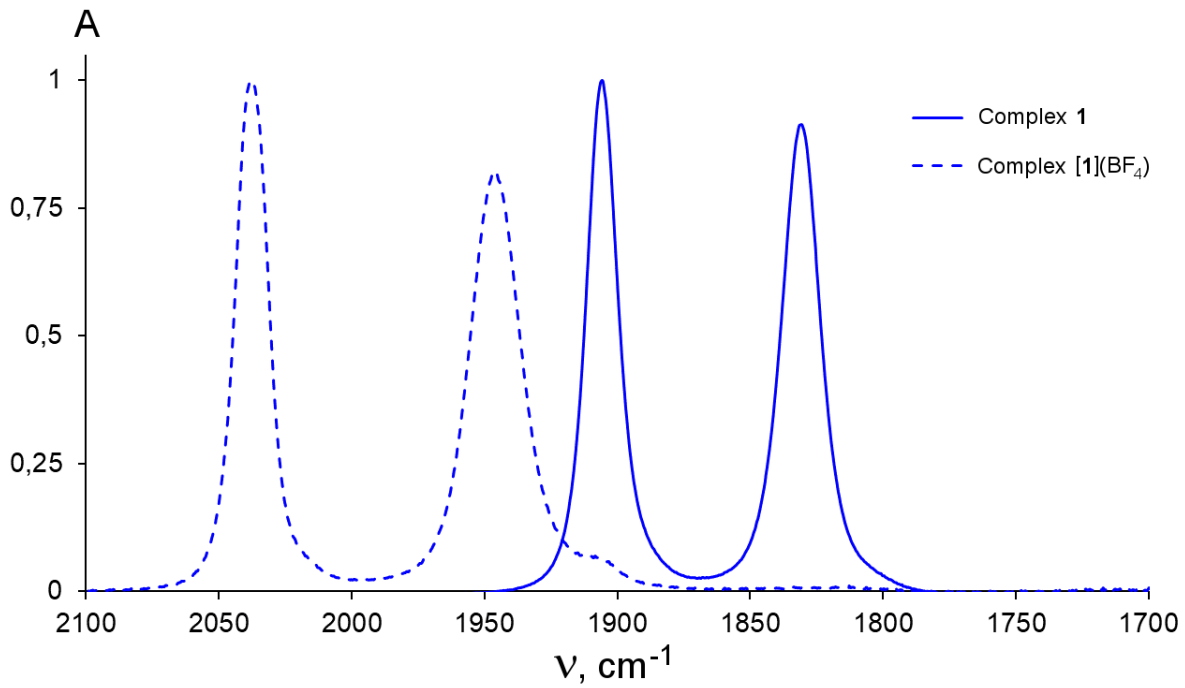

Figure S3. Superposition of normalized IR spectra of NHC complexes **1** and [**1**](BF_4) in 2100-1700 cm^{-1} range (CH_2Cl_2, 0.5 cm^{-1} resolution).

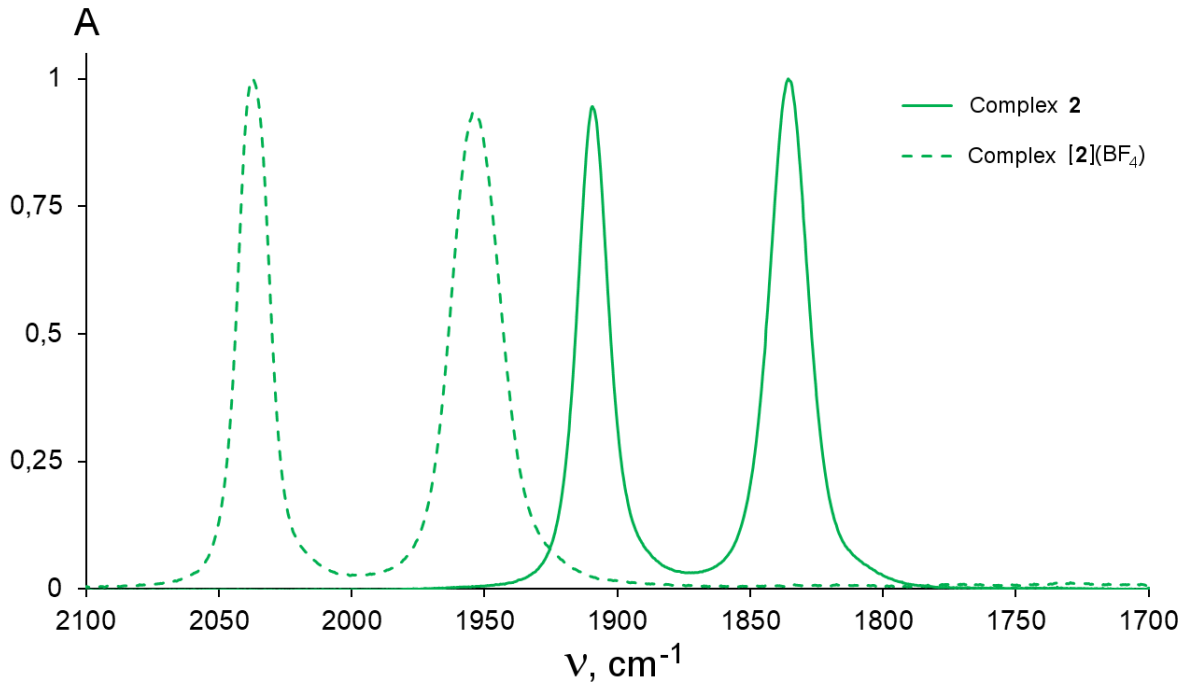

Figure S4. Superposition of normalized IR spectra of NHC complexes **2** and [**2**](BF_4) in 2100-1700 cm^{-1} range (CH_2Cl_2, 0.5 cm^{-1} resolution).

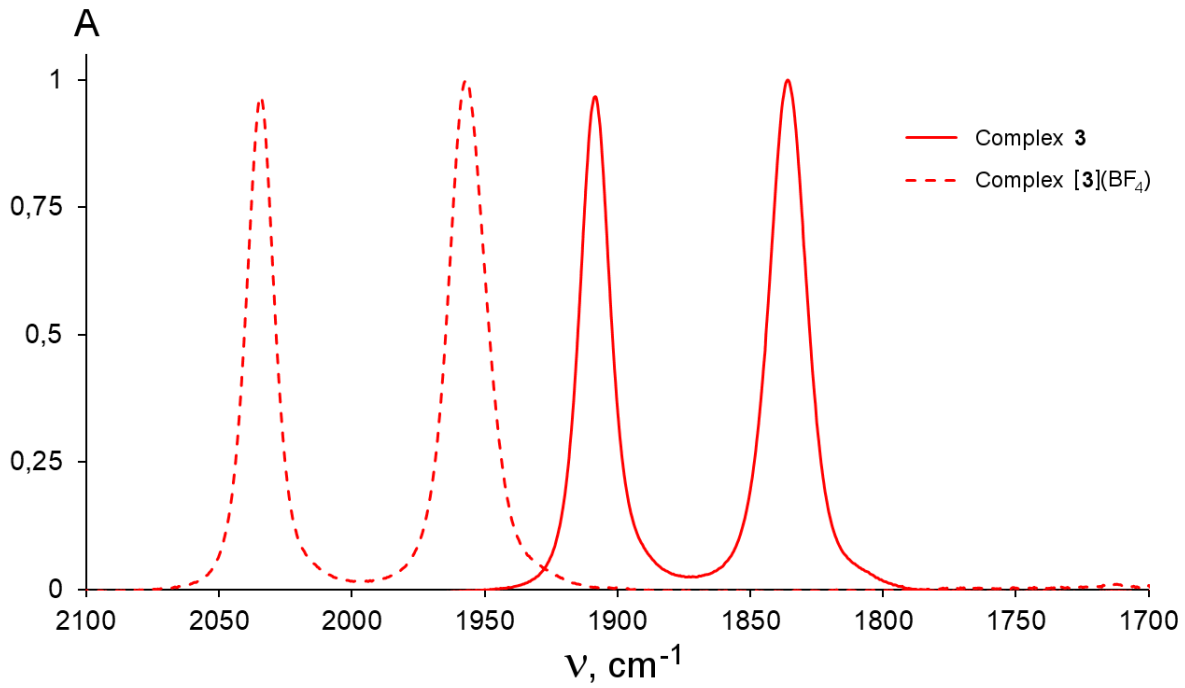

Figure S5. Superposition of normalized IR spectra of NHC complexes **3** and [**3**](BF_4) in 2100-1700 cm^{-1} range (CH_2Cl_2, 0.5 cm^{-1} resolution).

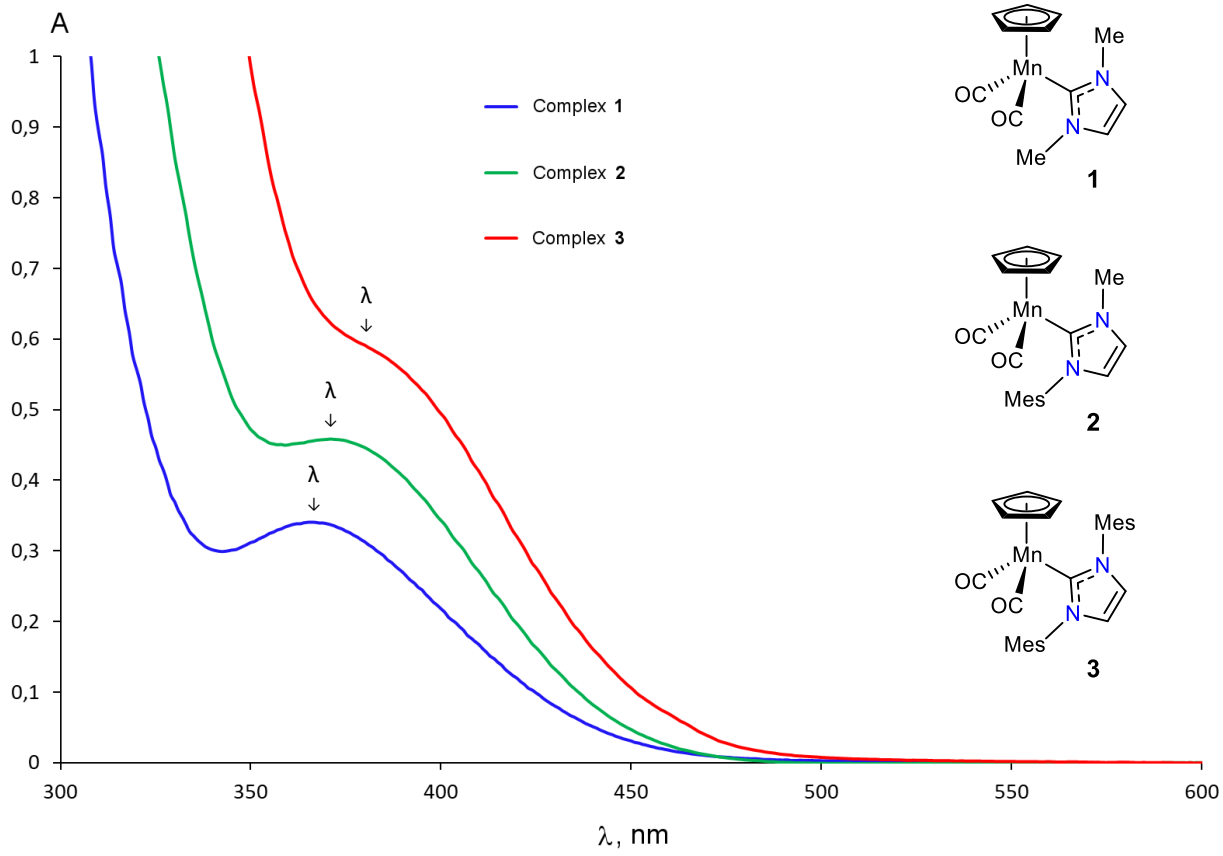

Figure S6. Superposition of normalized UV-Vis spectra of Mn^{I} NHC complexes **1-3** in CH_2Cl_2 solution.

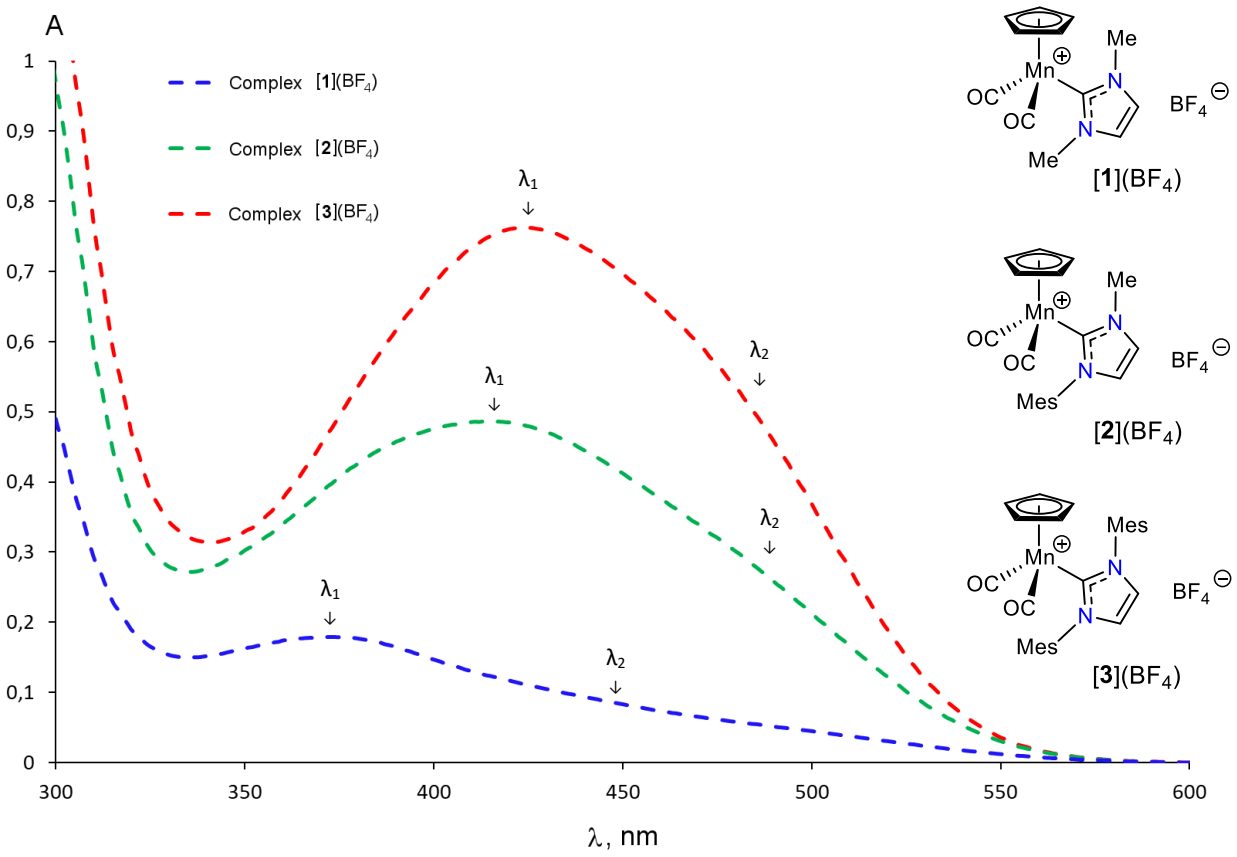

Figure S7. Superposition of normalized UV-Vis spectra of Mn^{II} NHC complexes [**1**-**3**](BF_4) in CH_2Cl_2 solution.

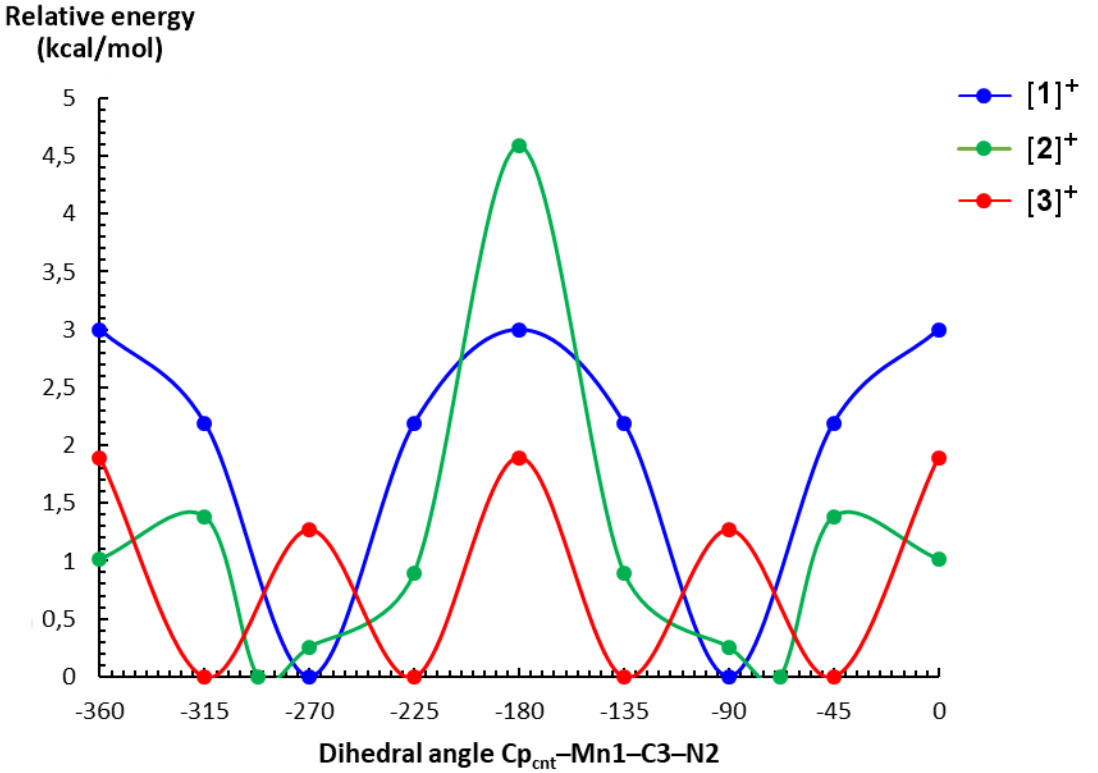

Figure S8. Energy profile (kcal/mol) of the DFT geometry-optimized cations [**1**]$^+$ (blue), [**2**]$^+$ (green) and [**3**]$^+$ (red) in a gas phase with a constrained Cp_{cnt}–Mn1–C3–N2 dihedral angle. The values of Cp_{cnt}–Mn1–C3–N2 −45° (−135°), −90° (−270°) and −180° correspond to eclipsed, horizontal and vertical NHC ligand orientations, respectively.

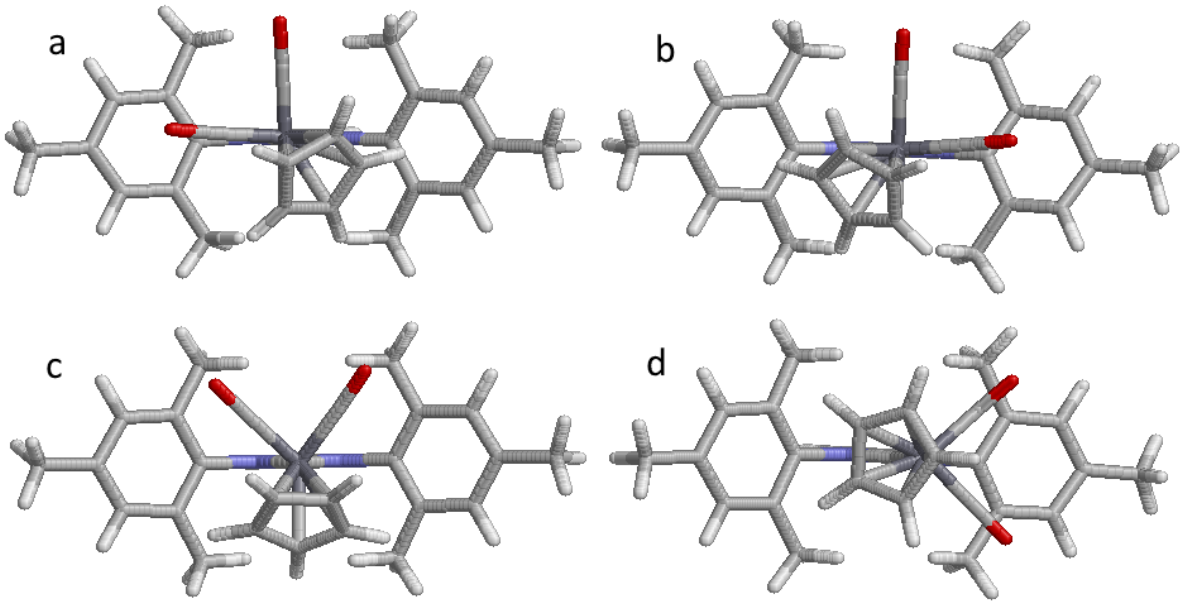

Figure S9. Molecular geometries of the conformations corresponding to four extrema points on the energy profile of [**3**]$^+$ with eclipsed (−45°, (**a**); −135° (**b**)), horizontal (−90°C, (**c**)) and vertical (−180° (**d**)) IMes ligand orientation.

Table S1. Calculated values of g_3 component for cations [**1-3**]$^+$ in a gas phase with a variation of Cp_{cnt}−Mn1−C3−N2 dihedral angle (45° step).

Cp_{cnt}−Mn1−C3−N2	0° (−360°)	−45° (−315°)	−90° (−270°)	−135° (−225°)	−180°
g_3 for [**1**]$^+$	2.073	2.084	2.100	2.084	2.073
g_3 for [**2**]$^+$	2.072	2.087	2.083	2.083	2.070
g_3 for [**3**]$^+$	2.069	2.078	2.087	2.078	2.069
Δg_3 [**1**]$^+$ *vs.* [**2**]$^+$	0.001	−0.003	**0.017**	0.001	0.003
Δg_3 [**1**]$^+$ *vs.* [**3**]$^+$	0.004	0.006	**0.013**	0.006	0.004
Δg_3 [**2**]$^+$ *vs.* [**3**]$^+$	0.003	0.007	−0.004	0.005	0.001

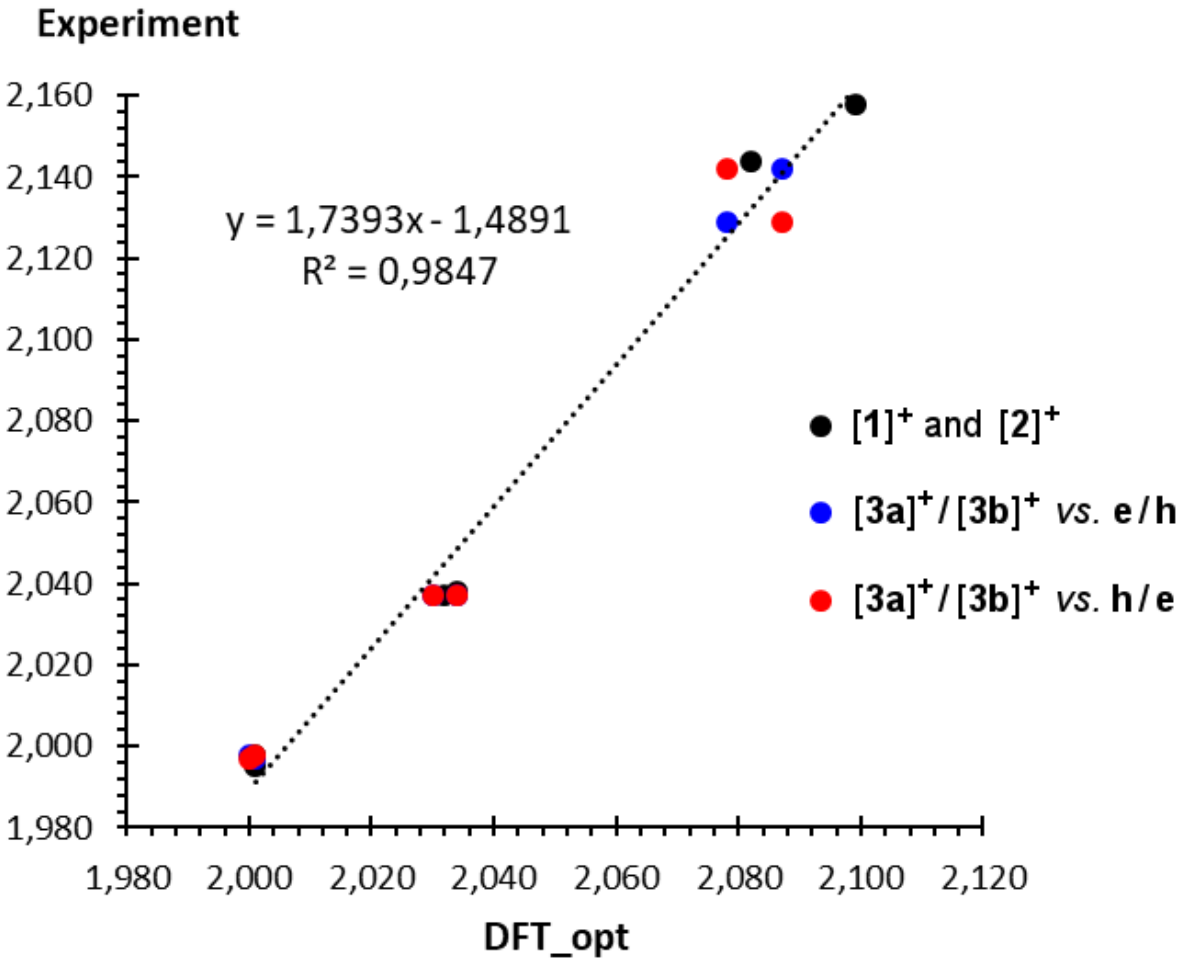

Figure S10. Plot of experimental *vs.* calculated g-tensor values for [**1**]$^+$, [**2**]$^+$ and both components [**3a**]$^+$ and [**3b**]$^+$. For calculated cation [**3**]$^+$ both geometry-optimized conformers with Cp_{cnt}–Mn1–C3–N2 dihedral angle values of −45° (e = eclipsed) and −90° (h = horizontal) were considered. In view of the good agreement between experimental (crystal) and *in vacuo* DFT geometry-optimized dihedral angles for [**1**]$^+$ and [**2**]$^+$, these data were used as a reference (black points and dotted correlation line).

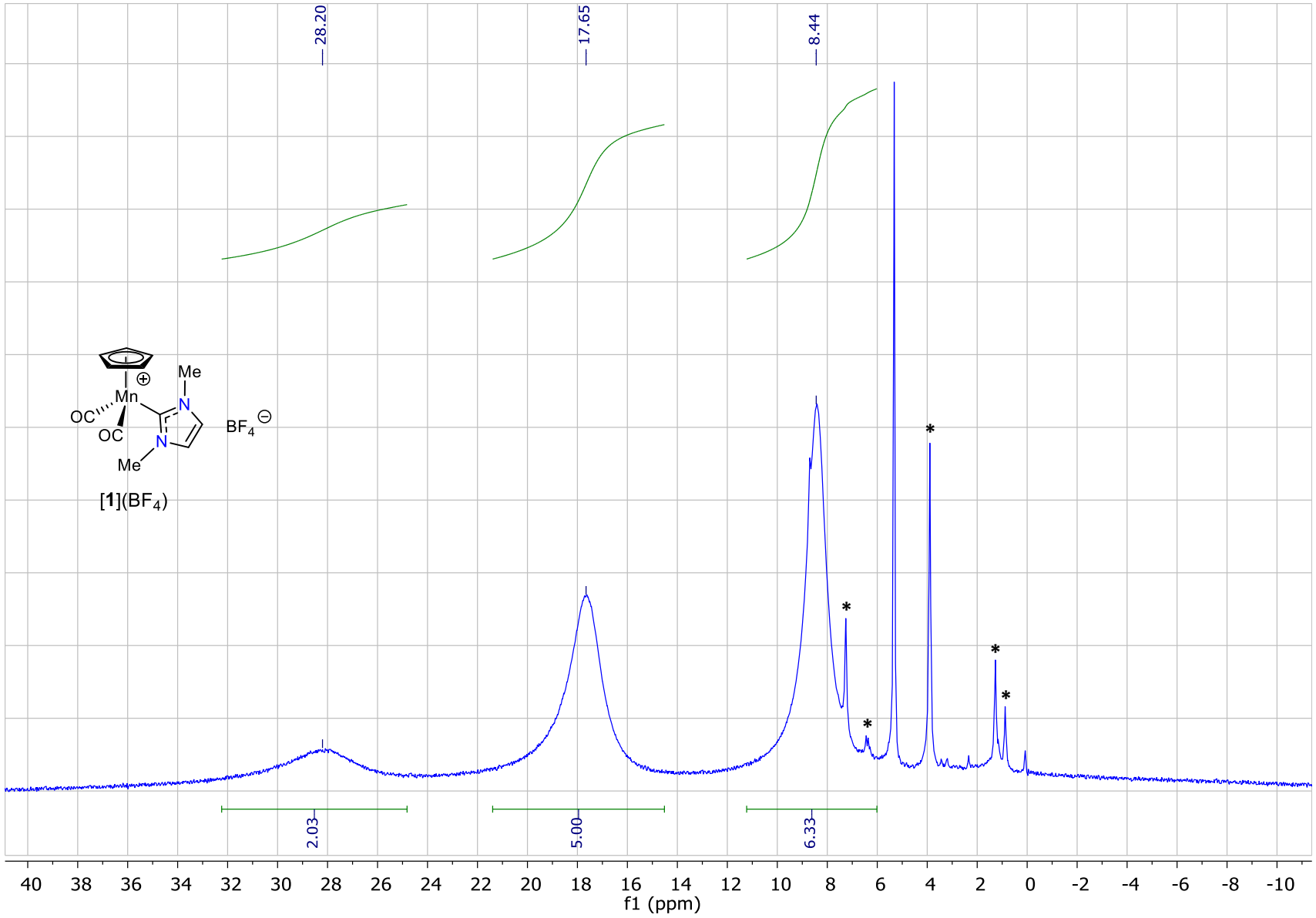

Figure S11. ^{1}H NMR spectrum of complex [**1**]BF_4 (400.1 MHz, CD_2Cl_2, 25°C), the signals of unidentified diamagnetic impurities are marked with asterisk

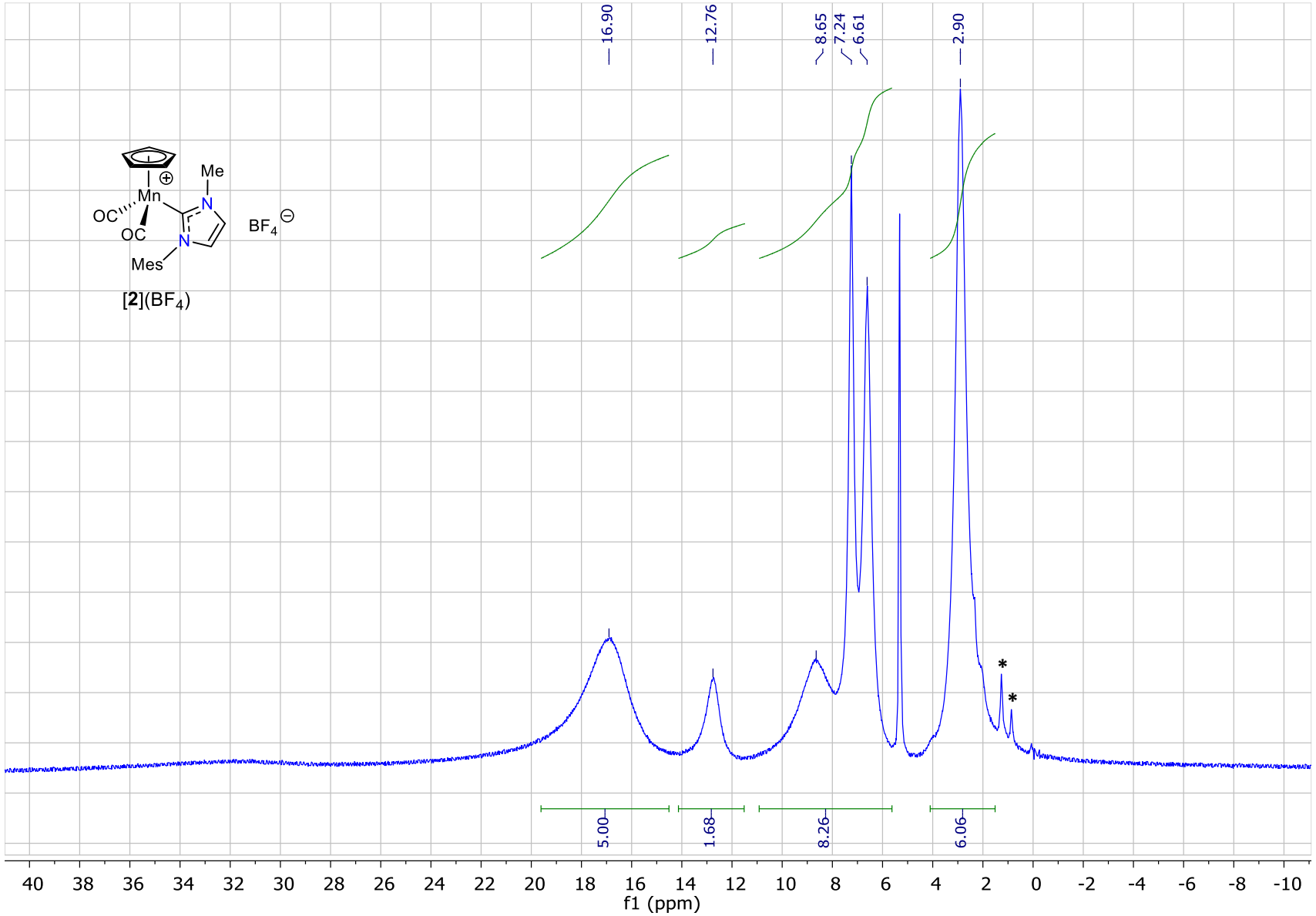

Figure S12. ^{1}H NMR spectrum of complex [**2**]BF_4 (400.1 MHz, CD_2Cl_2, 25°C), the signals of unidentified diamagnetic impurities are marked with asterisk

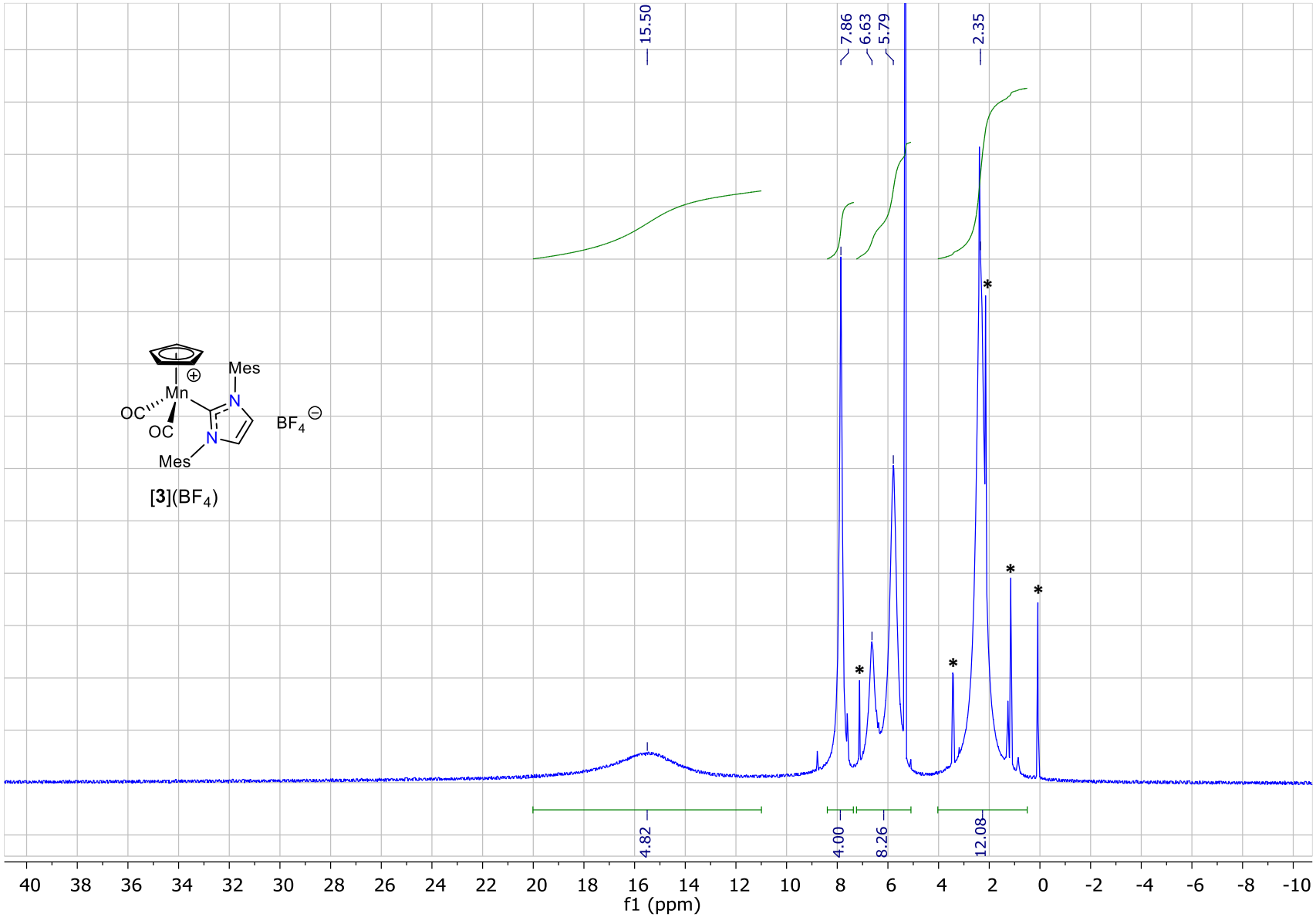

Figure S13. ^{1}H NMR spectrum of complex [**3**]BF_4 (400.1 MHz, CD_2Cl_2, 25°C), the signals of traces of ether, silicon grease and unidentified diamagnetic impurities are marked with asterisk

Table S2. Crystal data and structure refinement for manganese NHC complexes **1**, **2**, and [**1-3**](BF_4)

Complex	**1**	[**1**](BF_4)	**2**	[**2**](BF_4)	[**3**](BF_4)
Empirical formula	$C_{12}H_{13}MnN_2O_2$	$C_{12}H_{13}BF_4MnN_2O_2$	$C_{20}H_{21}MnN_2O_2$	$C_{20}H_{21}BF_4MnN_2O_2$	$C_{28}H_{29}BF_4MnN_2O_2$
M_r	272.18	358.99	376.33	463.14	567.28
T/K	173	100	173	173	173
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group (no.)	$P2_1/c$ (#14)	$P2_1$ (#4)	$P2_1/n$ (#14)	P1 bar (#2)	C2/c (#15)
a/Å	13.3975(8)	6.506(5)	11.5587(5)	8.160(5)	23.385(5)
b/Å	20.5591(13)	15.326(5)	10.2736(4)	11.501(5)	22.343(5)
c/Å	8.7407(5)	14.777(5)	15.0530(6)	11.720(5)	13.538(5)
α/°	90	90	90	88.848(5)	90
β/°	90.615(3)	90.876(5)	98.434(2)	76.657(5)	119.785(5)
γ/°	90	90	90	74.499(5)	90
V/Å^3	2407.4(3)	1473.3(13)	1768.20(13)	1030.3(9)	6139(3)
Z	4	2	4	2	8
D_c/g.cm^{-3}	1.502	1.619	1.414	1.493	1.228
μ/mm^{-1}	1.087	0.946	0.762	0.695	0.479
F(000)	1120	724	784	474	2344
θ_{max}/°	26.4	26.4	26.4	26.4	26.4
Completeness to θ_{max} (%)	0.998	0.999	0.998	0.998	0.998
Index range, *hkl*	-16<h<16 -25<k<25 -10<l<10	-8<h<8 -19<k<19 -18<l<18	-14<h<14 -12<k<12 -18<l<18	-10<h<10 -14<k<14 -14<l<14	-29<h<29 -27<k<27 -16<l<16
Reflections collected	80410	77300	87471	77840	81174
Independent reflections	4916	5238	3341	4214	6282
Parameters	311	402	230	275	349
GOF	1.13	1.04	0.98	1.024	1.036
R (all data)	0.0439	0.0552	0.0263	0.0237	0.076
R [I>2σ(I)]	0.0406	0.0473	0.0231	0.0229	0.0639
Rw (all data)	0.1054	0.1342	0.0773	0.0593	0.1792
R_w [I>2σ(I)]	0.1036	0.1255	0.072	0.0582	0.1712
$\Delta\rho_{max/min}$/e.Å^{-3}	−1.04/0.82	−0.74/1.06	−0.23/0.33	−0.26/0.32	−0.53/1.56

Cartesian coordinates for DFT optimized structures of Mn(II) NHC complexes

Complex $[1]^+$

Mn	0.0069	-0.0147	0.0037
C	1.0507	1.1978	0.8596
C	2.2080	-0.6807	-3.5708
H	2.6336	-1.3891	-4.2691
C	1.0584	-1.2020	0.8830
N	1.4953	1.0761	-2.4469
O	1.7087	1.9548	1.4314
N	1.5139	-1.0827	-2.4378
O	1.7196	-1.9437	1.4711
C	1.3401	-2.4880	-2.0745
H	2.1921	-2.8439	-1.4833
H	1.2609	-3.0848	-2.9884
H	0.4213	-2.6063	-1.4946
C	1.2993	2.4823	-2.0983
H	2.1625	2.8675	-1.5426
H	0.3994	2.5865	-1.4873
H	1.1730	3.0635	-3.0171
C	1.0725	-0.0040	-1.7271
C	2.1962	0.6763	-3.5766
H	2.6095	1.3860	-4.2810
C	-1.8915	-0.6763	-0.9024
H	-1.9710	-1.2600	-1.8135
C	-1.9018	0.7450	-0.8229
H	-1.9884	1.4265	-1.6628
C	-1.7831	1.1114	0.5486
H	-1.7749	2.1239	0.9392
C	-1.7032	-0.0841	1.3253
H	-1.6334	-0.1415	2.4058
C	-1.7676	-1.1911	0.4212
H	-1.7552	-2.2396	0.7005

Complex $[2]^+$

Mn	-0.0297	-0.0109	0.0517
C	-0.1317	0.3573	-1.7369
C	0.7386	1.6147	0.1410
C	1.8048	-0.8448	0.2686
C	3.6718	-2.0741	-0.1382
H	4.3217	-2.7260	-0.7070
C	3.8141	-1.5148	1.0898
H	4.6202	-1.5764	1.8088
C	2.4558	-0.0332	2.5717
C	-2.1917	-0.4068	0.0008
H	-2.7978	-0.3636	-0.8983
C	-1.9147	0.6823	0.8730
H	-2.2852	1.6957	0.7648
C	-1.0764	0.1947	1.9272
H	-0.7226	0.7735	2.7733
C	-0.8453	-1.1955	1.6961
H	-0.2669	-1.8628	2.3259
C	-1.5391	-1.5662	0.5094
H	-1.5564	-2.5518	0.0573
C	1.9618	-2.0387	-1.9427
C	2.3897	-1.2950	-3.0602
C	1.9744	-1.7276	-4.3210
C	1.1765	-2.8676	-4.4950
C	0.7931	-3.5853	-3.3585
C	1.1861	-3.2042	-2.0691
C	3.2822	-0.0871	-2.9227
C	0.7661	-3.3108	-5.8756
C	0.8491	-4.0860	-0.8918
N	2.4435	-1.6518	-0.6325
N	2.6688	-0.7646	1.3250
O	-0.2922	0.6761	-2.8336
O	1.2272	2.6625	0.1922
H	3.4241	0.3030	2.9551
H	1.8300	0.8419	2.3860
H	1.9787	-0.6744	3.3233
H	2.2907	-1.1582	-5.1965
H	0.1888	-4.4864	-3.4754
H	2.9056	0.6261	-2.1773
H	4.2966	-0.3725	-2.6073
H	3.3692	0.4376	-3.8799
H	0.2101	-2.5176	-6.3943
H	1.6484	-3.5389	-6.4896
H	0.1356	-4.2064	-5.8433
H	0.7214	-3.5214	0.0385
H	-0.0656	-4.6590	-1.0841
H	1.6529	-4.8169	-0.7152

Complex [3]$^+$ (dihedral angle Cp_{cnt}–Mn1–C3–N2 –45°)

N	0.0177	0.0199	-0.0963
C	1.3903	0.0229	-0.0207
Mn	2.6290	1.6603	-0.0099
C	1.4167	3.0395	-0.1250
O	0.8211	4.0255	-0.2014
C	2.6407	1.7597	-1.8288
O	2.6622	1.8590	-2.9811
C	-0.4790	-1.2713	-0.1799
C	0.5913	-2.1072	-0.1774
N	1.7230	-1.3122	-0.0748
C	3.7639	1.1521	1.8191
C	3.4381	2.5406	1.8203
C	4.0876	3.1463	0.6955
C	4.8046	2.1285	0.0096
C	4.6149	0.8997	0.7030
C	3.0485	-1.8934	-0.0114
C	3.5063	-2.3690	1.2333
C	4.7831	-2.9330	1.2860
C	5.5896	-3.0603	0.1467
C	5.0775	-2.6112	-1.0728
C	3.8035	-2.0368	-1.1864
C	3.2945	-1.6467	-2.5523
C	6.9475	-3.7101	0.2305
C	2.6531	-2.3253	2.4782
C	-0.8648	1.1657	-0.0122
C	-1.1998	1.6655	1.2588
C	-2.0982	2.7354	1.3184
C	-2.6662	3.2937	0.1690
C	-2.3249	2.7425	-1.0729
C	-1.4380	1.6704	-1.1940
C	-1.1344	1.0827	-2.5498
C	-3.6330	4.4466	0.2573
C	-0.6457	1.0635	2.5261
H	-1.5417	-1.4721	-0.2222
H	0.6559	-3.1855	-0.2426
H	5.6795	-2.7220	-1.9771
H	5.1554	-3.2931	2.2469
H	-2.7655	3.1584	-1.9811
H	-2.3659	3.1388	2.2964
H	3.4462	0.4228	2.5560
H	5.0461	-0.0583	0.4286
H	5.4024	2.2667	-0.8858
H	4.0493	4.1960	0.4233
H	2.8272	3.0578	2.5534
H	1.9793	-3.1943	2.5200
H	2.0194	-1.4314	2.5256
H	3.2780	-2.3603	3.3779
H	7.5988	-3.3931	-0.5921
H	6.8525	-4.8047	0.1716
H	7.4474	-3.4797	1.1793
H	2.3091	-1.1728	-2.5208
H	3.2162	-2.5377	-3.1913
H	3.9889	-0.9582	-3.0512
H	-0.9531	0.0135	2.6396
H	-1.0082	1.6117	3.4024
H	0.4526	1.0825	2.5415
H	-3.2915	5.2949	-0.3513
H	-3.7535	4.7935	1.2896
H	-4.6235	4.1571	-0.1209
H	-0.0632	0.8925	-2.6907
H	-1.4668	1.7591	-3.3448
H	-1.6545	0.1240	-2.6955

Complex [3]$^+$ (dihedral angle Cp_{cnt}–Mn1–C3–N2 –90°)

N	0.0000	0.0000	0.0000
C	1.3696	0.0000	0.0000
Mn	2.6688	1.5987	0.0000
C	1.7959	2.5636	-1.2860
O	1.3347	3.2250	-2.1124
C	3.7584	1.1466	-1.4091
O	4.4722	0.9763	-2.2999
C	-0.4961	-1.3002	0.0351
C	0.5749	-2.1310	0.0597
N	1.7096	-1.3258	0.0382
C	2.6849	1.7380	2.1916
C	2.2868	2.9952	1.6432
C	3.3837	3.5022	0.8769
C	4.4433	2.5605	0.9487
C	4.0172	1.4682	1.7606
C	3.0534	-1.8688	0.0553
C	3.6672	-2.1284	1.2951
C	4.9568	-2.6684	1.2827
C	5.6231	-2.9767	0.0902
C	4.9572	-2.7407	-1.1171
C	3.6667	-2.2025	-1.1653
C	2.9635	-2.0414	-2.4902
C	7.0003	-3.5901	0.1093
C	2.9545	-1.9094	2.6071

C	-0.8723	1.1577	-0.0413
C	-1.3196	1.7255	1.1627
C	-2.1748	2.8331	1.0834
C	-2.6072	3.3538	-0.1383
C	-2.1757	2.7233	-1.3131
C	-1.3220	1.6183	-1.2950
C	-0.9583	0.9276	-2.5863
C	-3.5330	4.5425	-0.1995
C	-0.9814	1.1551	2.5195
H	-1.5592	-1.5018	0.0388
H	0.6428	-3.2106	0.0894
H	5.4531	-2.9879	-2.0574
H	5.4494	-2.8672	2.2367
H	-2.5201	3.0987	-2.2786
H	-2.5268	3.2881	2.0116
H	2.0865	1.1153	2.8467
H	4.6065	0.5875	1.9955
H	5.4108	2.6537	0.4652
H	3.4047	4.4430	0.3362
H	1.3307	3.4880	1.7885
H	2.2807	-2.7511	2.8281
H	2.3390	-1.0028	2.6040
H	3.6701	-1.8436	3.4346
H	7.5575	-3.3569	-0.8057
H	6.9324	-4.6860	0.1817
H	7.5843	-3.2432	0.9703
H	2.3635	-1.1249	-2.5401
H	2.2800	-2.8847	-2.6717
H	3.6872	-2.0225	-3.3121
H	-1.8631	0.6599	2.9517
H	-0.6906	1.9475	3.2211
H	-0.1799	0.4110	2.4791
H	-3.0856	5.3629	-0.7776
H	-3.7711	4.9205	0.8010
H	-4.4772	4.2783	-0.6958
H	0.0584	0.5184	-2.5763
H	-1.0403	1.6203	-3.4310
H	-1.6432	0.0884	-2.7812