Electronic Supplementary Material (ESI) for Dalton Transactions.

New modular manganese(I) tricarbonyl complexes as PhotoCORMs: *In vitro* detection of photoinduced carbon monoxide release using COP-1 as a fluorogenic switch-on probe

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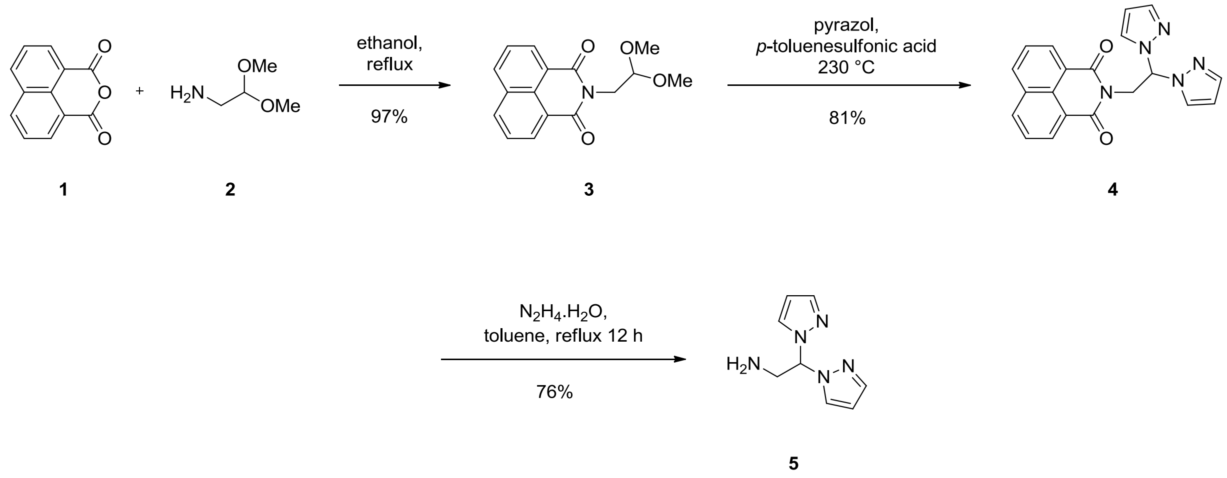
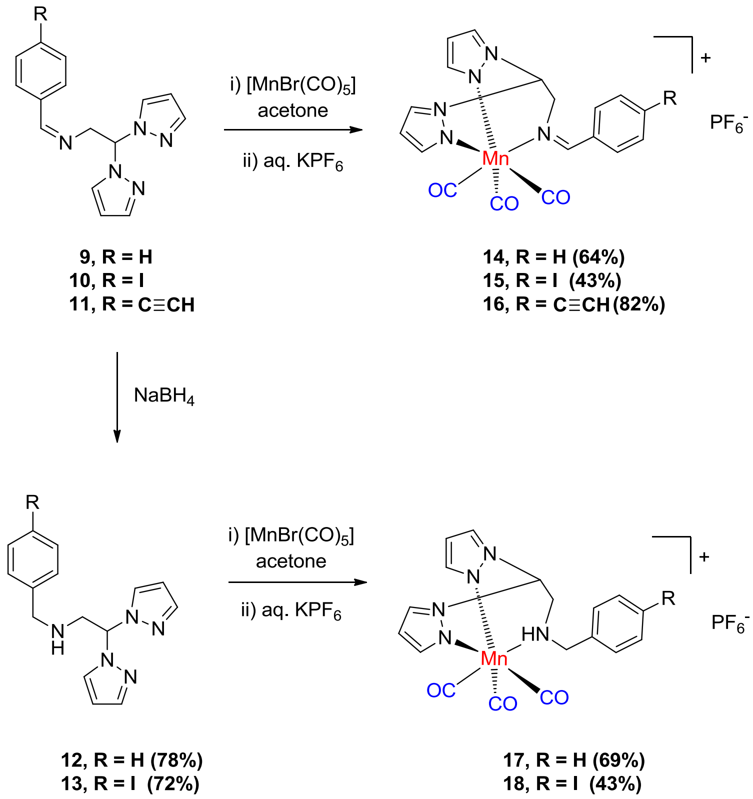
Supporting Information



Scheme S1 Synthesis of bis(2-pyrazolyl)ethylamine (bpea) ligand precursor **5**.



Scheme S2 Synthesis of manganese(I) tricarbonyl complexes **14–18**.

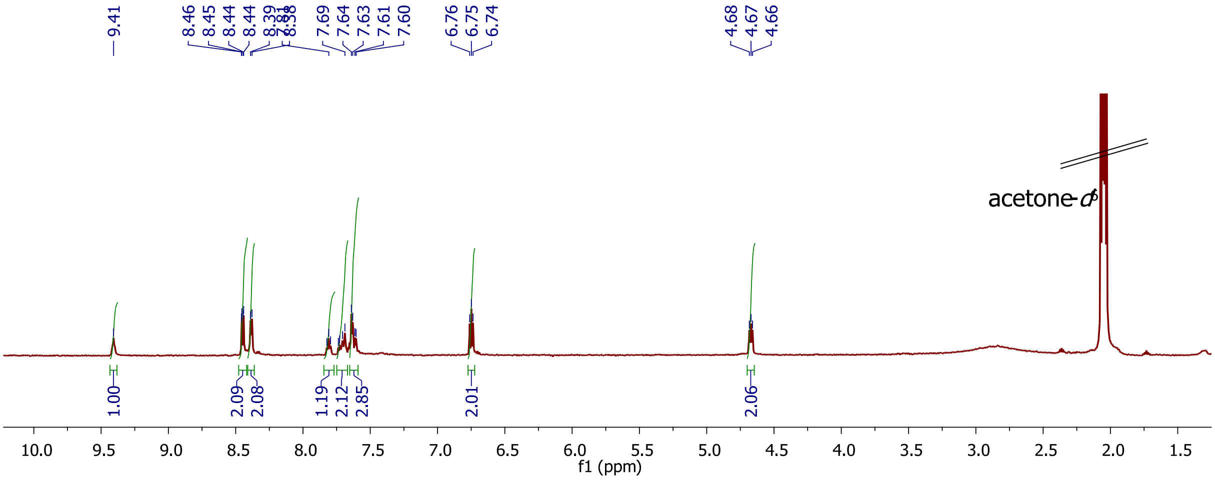


Fig. S1 400 MHz ^{1}H NMR spectrum of [Mn(CO)$_3$(bpea$^{\mathrm{N=CHC6H5}}$)]PF$_6$ **14** in acetone-*d*$_6$.

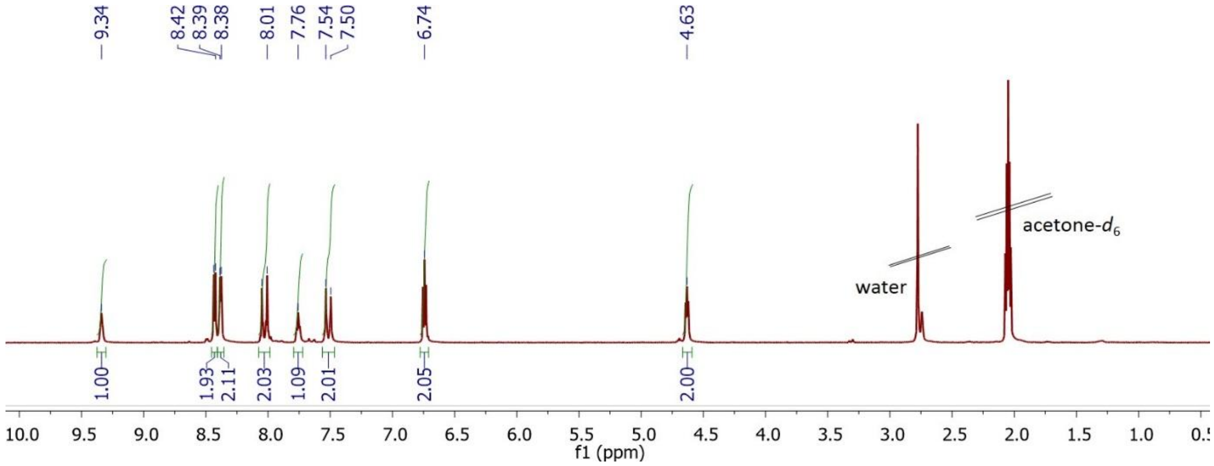


Fig. S2 400 MHz ^{1}H NMR spectrum of [Mn(CO)$_3$(bpea$^{\mathrm{N=CHC6H4I}}$)]PF$_6$ **15** in acetone-*d*$_6$.

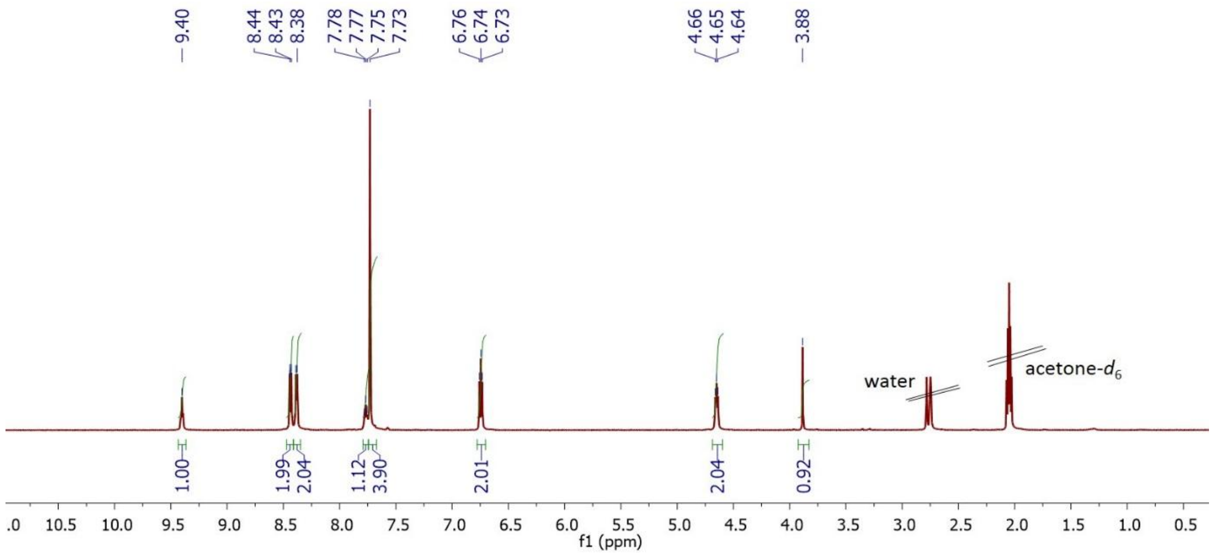


Fig. S3 400 MHz ^{1}HNMR spectrum of [Mn(CO)$_3$(bpea$^{\mathrm{N=CHC6H4C{\equiv}CH}}$)]PF$_6$ **16** in acetone-d_6.

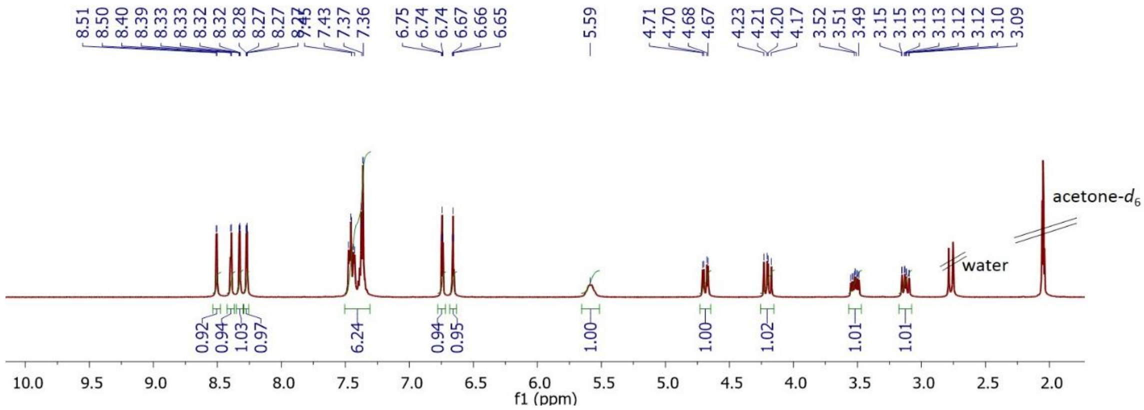


Fig. S4 400 MHz ^{1}H NMR spectrum of [Mn(CO)$_3$(bpea$^{\mathrm{NHCH2C6H5}}$)]PF$_6$ **17** in acetone-d_6.

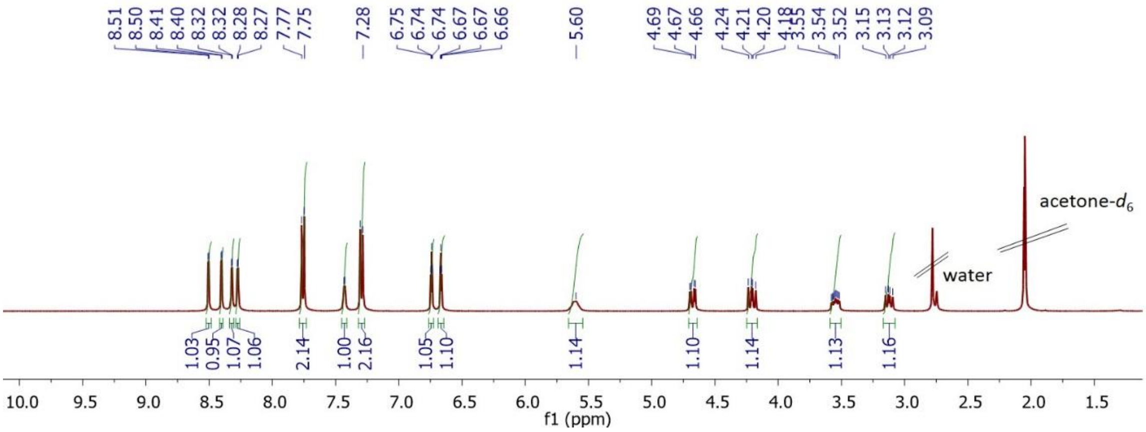


Fig. S5 400 MHz ^{1}H NMR spectrum of [Mn(CO)$_3$(bpea$^{\mathrm{NHCH2C6H4I}}$)]PF$_6$ **18** in acetone-*d*$_6$.

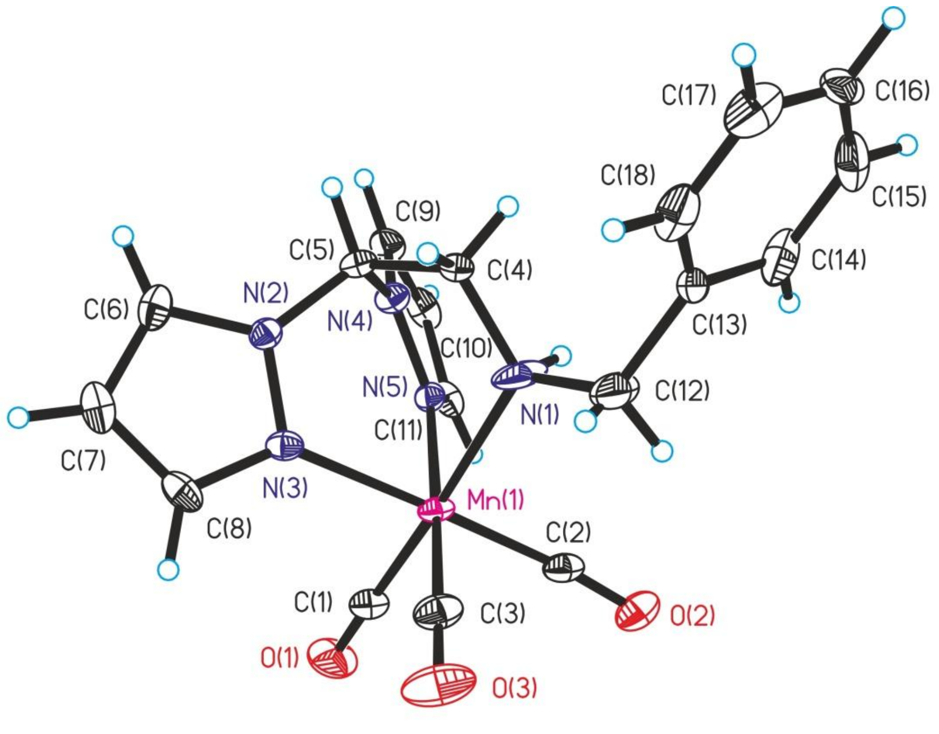


Fig. S6 Molecular structure of the cationic unit of **17** drawn at the 50% probability level. Only one of the two nearly identical molecules in the unit cell is shown and the hexafluorophosphate counterions are removed for clarity.

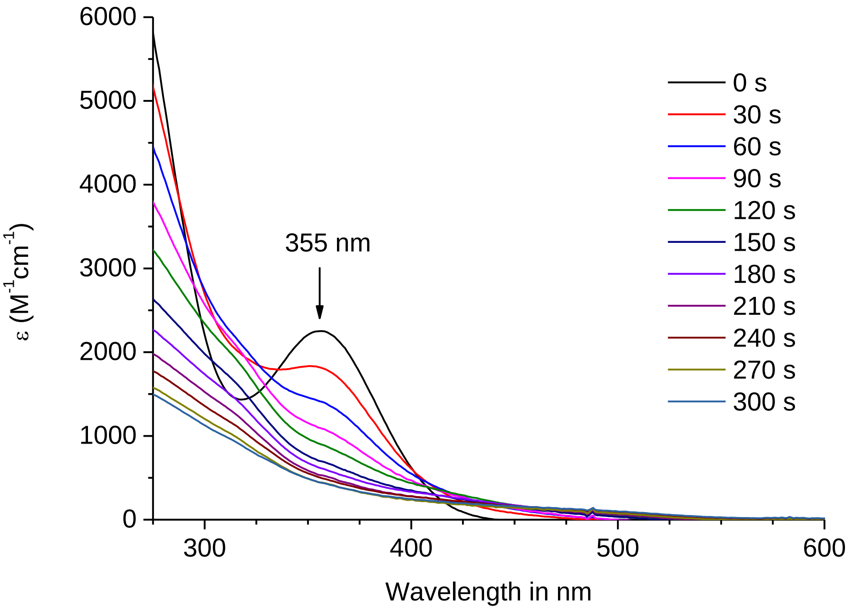


Fig. S7 UV/Vis spectral changes of **17** (0.2 mM solution in DMSO) with increasing illumination time (0–300 s) at 365 nm.

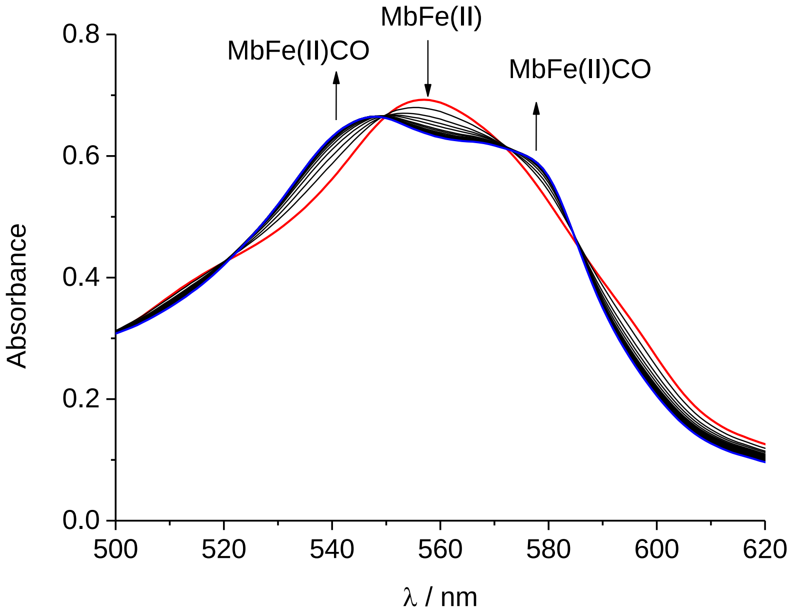


Fig. S8 UV/Vis spectral changes in the Q-band region of myoglobin (60 *μ*M) upon incubation with complex **17** (10 *μ*M solution in 0.1 M PBS pH 7.4) with increasing illumination time at 365 nm.

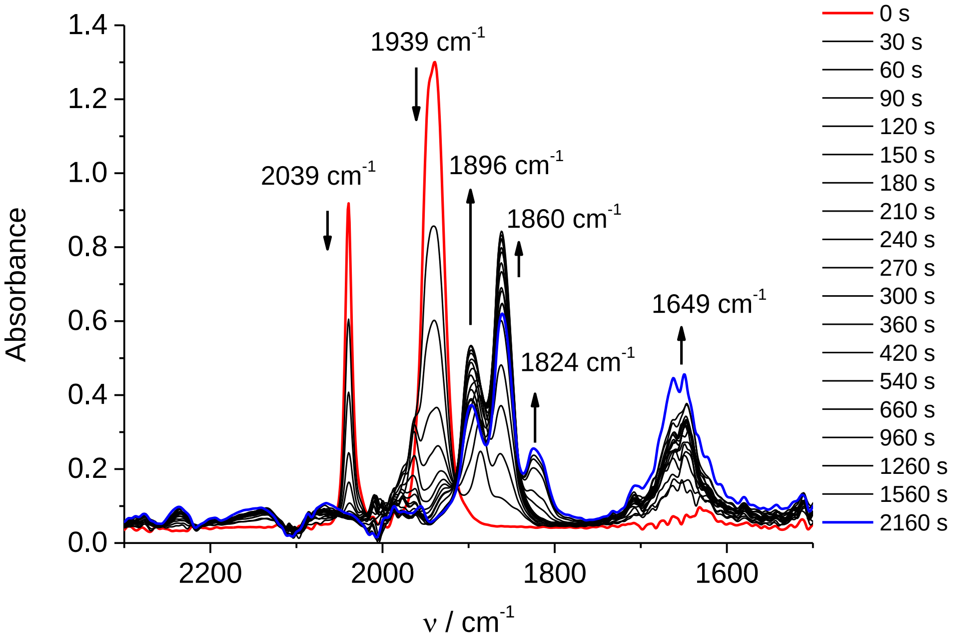


Fig. S9 Spectral changes in the solution IR of **14** (9 mM solution in DMSO) upon illumination (0–2160 s) at 365 nm. The red trace was recorded on a freshly prepared solution before start of the illumination whereas the blue trace shows the final spectrum recorded after about 20 min of illumination.

Table S1 Comparison of ^{1}H NMR chemical shifts of (a) imine ligands **9–11** and corresponding manganese complexes **14–16** and (b) amine ligands **12–13** and corresponding manganese complexes **17–18**. The chemical shifts δ are reported in ppm.

(a)

compound	C*H*	C*H*$_2$	N=C*H*	*H*$_{3,3'}$-pz	*H*$_{4,4'}$-pz	*H*$_{5,5'}$-pz
9	6.80	4.66	8.20	7.67	6.25	7.56
10	6.77	4.64	8.11	7.65	6.25	7.55
11	6.78	4.67	8.17	7.66	6.25	7.55
14	7.81	4.67	9.41	8.38	6.75	8.45
15	7.76	4.63	9.34	8.38	6.75	8.43
16	7.73	4.63	9.39	8.37	6.74	8.43

(b)

compound	C*H*	C*H*$_2$	N*H*	C*H*$_2$-Ph	*H*$_{3,3'}$-pz	*H*$_{4,4'}$-pz	*H*$_{5,5'}$-pz
12	6.54	3.70	[a]	3.83	7.58	6.27	7.50
13	6.52	3.66	[a]	3.76	7.57	6.27	7.55
17[b]	7.41	3.52, 3.12	5.59, br	4.69, 4.20	8.51, 8.39	6.74, 6.66	8.33, 8.27
18[b]	7.43	3.55, 3.12	5.60, br	4.68, 4.21	8.51, 8.40	6.74, 6.67	8.32, 8.27

[a] not detected.

[b] two sets of signals due to stereogenic center at the coordinated amine group.

Table S2 Crystallographic parameters for complex **17**.

Compound	**17**
Empirical formula	$C_{18}H_{17}F_6MnN_5O_3P$
Formula weight	551.28
Crystal system	Triclinic
Space group	P-1
a (Å)	11.225(2)
b (Å)	14.377(3)
c (Å)	14.529(3)
α (°)	79.31(3)
β (°)	75.74(3)
γ (°)	70.34(3)
V (Å^3)	2126.4(9)
Z	4
ρ_{calc} (g cm^{-3})	1.722
T (K)	110(2)
μ (mm^{-1})	0.781
λ (Å) (Mo K$_\alpha$)	0.71073
2Θ_{max} (°)	26.00
Reflections measured	28040
Unique refl. / [$I > 2\sigma(I)$]	8350 / 7763
Data completeness	0.998
Variables	612
R ($I \geq 2\sigma(I)$)	0.0545
wR ($I \geq 2\sigma(I)$)	0.1365
Largest difference map peak/hole in e Å^{-3}	-1.3282 / -1.0553
Goodness of fit (GOF)	1.0220

Table S3 Selected bond lengths (Å) and angles (°) for complex **17**.

	17[a]
Mn1-C1	1.804(4) / 1.804(4)
Mn1-C2	1.815(4) / 1.813(4)
Mn1-C3	1.811(4) / 1.826(4)
Mn1-N1	2.130(3) / 2.137(3)
Mn1-N3	2.052(3) / 2.055(3)
Mn1-N5	2.047(3) / 2.047(3)
C1-O1	1.139(5) / 1.146(5)
C2-O2	1.149(5) / 1.140(5)
C3-O3	1.139(5) / 1.132(5)
C5-N2	1.449(5) / 1.443(5)
C5-N4	1.454(4) / 1.452(4)
C4-C5	1.528(5) / 1.526(5)
C4-N1	1.462(5) / 1.468(4)
N1-C12	1.403(6) / 1.472(5)
C1-Mn1-N1	172.05(16) / 173.63 (15)
C2-Mn1-N3	178.32(14) / 178.37(15)
C3-Mn1-N5	176.12(15) / 175.38(14)
C1-Mn1-C3	92.00(17) / 89.76 (17)
C3-Mn1-N1	95.95(17) / 96.58(16)
N1-Mn1-N5	81.62(14) / 79.51(13)
N5-Mn1-C1	90.44(14) / 94.12(14)
C1-Mn1-C2	87.50(17) / 88.61(16)
C2-Mn1-N1	92.78(16) / 92.05(15)
N1-Mn1-N3	88.89(14) / 89.23(12)
N3-Mn1-C1	90.89(15) / 90.01(14)
C2-Mn1-N5	94.83(14) / 93.27(14)
N5-Mn1-N3	85.67(11) / 85.97(11)
N3-Mn1-C3	91.28(15) / 91.55(15)
C3-Mn1-C2	88.29(17) / 89.31(17)
(Mn1-N1-C4-C5)-(N1-C12-C13)	26.4° / 36°
(N1-C12-C13)-(C13-C14-C15-C16-C17-C18)	85.2° / 77.9°

[a] Parameters are listed for the two independent molecules in the unit cell but atomic labels in the left column only refer to one of them.

Table S4 Selected calculated bond lengths (Å) and angles (°) for structures **A** (imine) and **B** (amine).

	A (imine)	**B (amine)**
Mn-C1	1.708	1.703
Mn-C2	1.707	1.708
Mn-C3	1.708	1.707
Mn-N1	1.961	2.027
Mn-N3	1.920	1.917
Mn-N5	1.921	1.918
C1-O1	1.179	1.179
C2-O2	1.180	1.181
C3-O3	1.180	1.182
C5-N2	1.447	1.450
C5-N4	1.447	1.447
C4-C5	1.523	1.527
C4-N1	1.478	1.507
N1-C12	1.313	1.525
C1-Mn1-N1	176.30	174.16
C2-Mn1-N3	177.30	175.83
C3-Mn1-N5	177.30	178.45
C1-Mn1-C3	90.25	89.65
C3-Mn1-N1	92.34	90.24
N1-Mn1-N5	85.73	88.33
N5-Mn1-C1	91.59	91.71
C1-Mn1-C2	90.24	90.10
C2-Mn1-N1	92.38	95.74
N1-Mn1-N3	85.69	81.31
N3-Mn1-C1	91.60	92.86
C2-Mn1-N5	91.37	90.42
N5-Mn1-N3	86.61	86.56
N3-Mn1-C3	91.41	92.64
C3-Mn1-C2	90.55	90.31
(Mn1-N1-C4-C5)-(N1-C12-C13)	0.3°	42.7°
(N1-C12-C13)-(C13-C14-C15-C16-C17-C18)	0.8°	72.8°

Table S5 HOMO-5 to LUMO+5 of **A** calculated with B3LYP/TZVP. Isosurface values are plotted at ±0.05, with positive values shown in red and negative ones in blue.

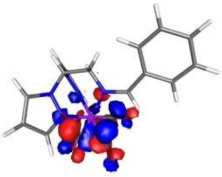
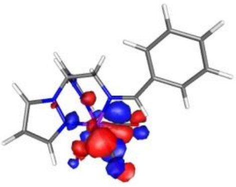
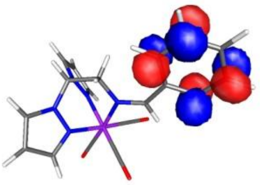
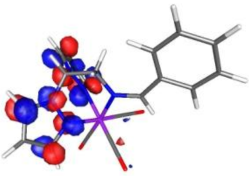
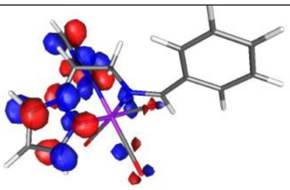
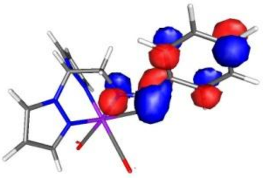
Orbital	Energy in eV (occupation)	Character	molecular orbital plot
108	-0.3684 (0)	π^*(CO)	
107	-0.4158 (0)	π^*(CO)	
106	-0.9185 (0)	π^*(phenyl)	
105	-1.2684 (0)	π^*(pyrazole)	
104	-1.6918 (0)	π^*(pyrazole)	
103 (LUMO)	-2.7947 (0)	π^*(phenyl+imine)	

Table S5 continued

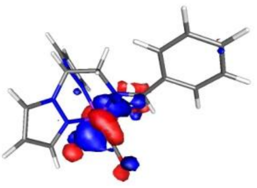
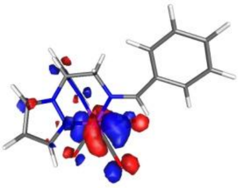
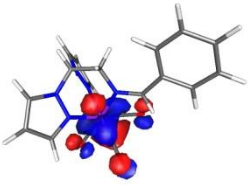
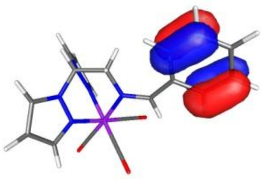
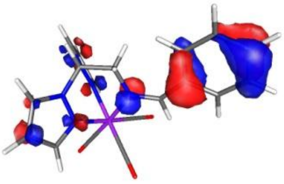
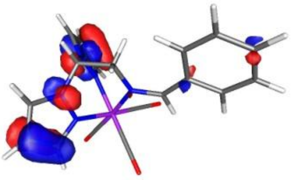
102 (HOMO)	-6.1884 (2)	d(Mn)	
101	-6.2108 (2)	d(Mn)	
100	-6.8045 (2)	d(Mn)	
99	-7.5917 (2)	π(phenyl)	
98	-7.7030 (2)	π(phenyl+imine)	
97	-8.0171 (2)	π(pyrazole)	

Table S6 TDDFT difference densities for the most important singlet excitations for **A** in the 250 to 600 nm range, calculated with B3LYP/TZVP. Isosurface values are plotted at ±0.002, with positive values shown in green and negative ones in red.

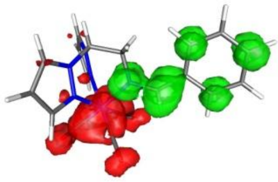
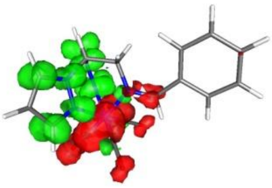
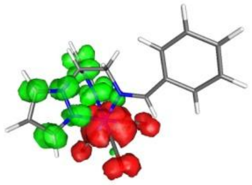
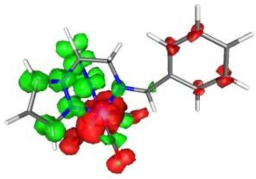
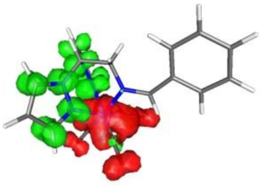
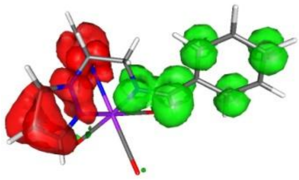
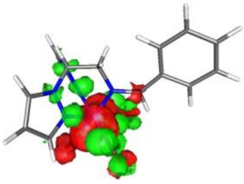
state	**λ nm**	**f_{osc}**	**difference density plot**
2	469.3	0.2602	
4	350.0	0.0168	
5	329.2	0.0528	
8	296.7	0.1258	
9	299.4	0.0941	
11	304.4	0.1377	
13	264.7	0.0850	

Table S6 continued

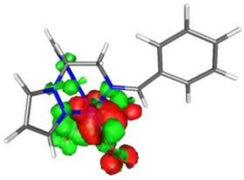
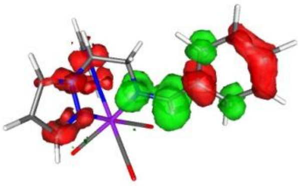
15	260.6	0.0362	
18	258.5	0.4138	

Table S7 HOMO-3 to LUMO+4 of **B** calculated with B3LYP/TZVP. Isosurface values are plotted at ±0.05, with positive values shown in red and negative ones in blue.

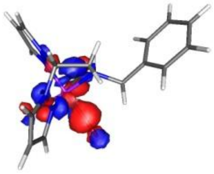
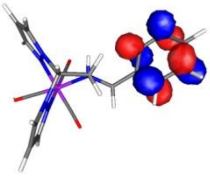
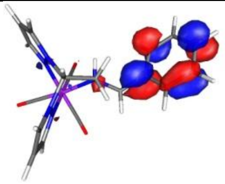
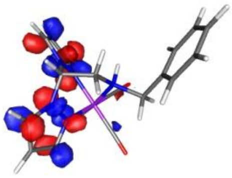
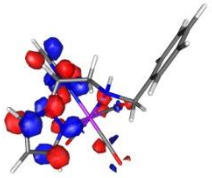
Orbital	**Energy in eV (occupation)**	**Character**	**molecular orbital plot**
108	-0.5461 (0)	π^*(CO)	
107	-0.7724 (0)	π^*(phenyl)	
106	-1.0045 (0)	π^*(phenyl)	
105	-1.3835 (0)	π^*(pyrazole)	
104 (LUMO)	-1.8241 (0)	π^*(pyrazole)	

Table S7 continued

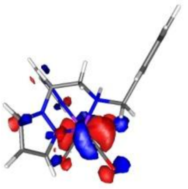
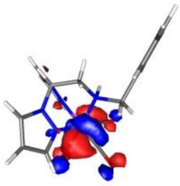
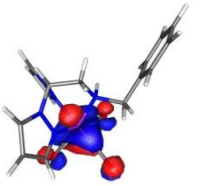
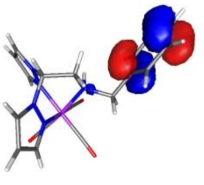
103 (HOMO)	-6.2363 (2)	Mn(d)	
102	-6.4139 (2)	d(Mn)	
101	-6.8481 (2)	d(Mn)	
100	-7.2998 (2)	π(phenyl)	

Table S8 TDDFT difference densities for the most important singlet excitations for **B** in the 250 to 600 nm range, calculated with B3LYP/TZVP. Isosurface values are plotted at ±0.002, with positive values shown in green and negative ones in red.

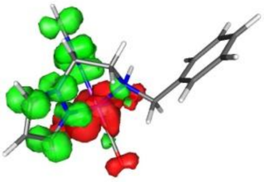
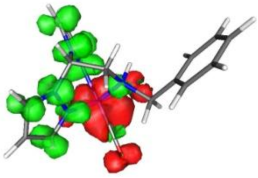
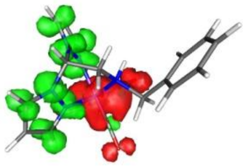
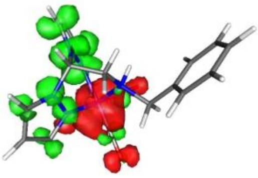
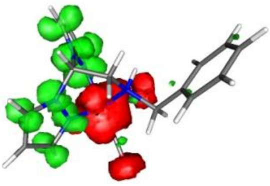
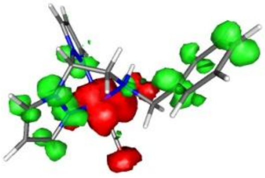
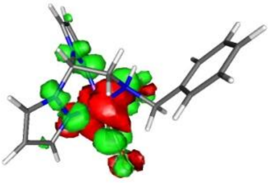
state	λ nm	f_{osc}	difference density plot
1	343.0	0.0110	
2	337.2	0.0781	
4	304.8	0.1017	
5	295.4	0.0660	
7	280.6	0.0127	
8	276.2	0.0446	

Table S8 continued

10	261.0	0.0545	
13	253.5	0.0190