Electronic Supplementary Material (ESI) for CrystEngComm

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TUNING OF COORDINATION GEOMETRY *VIA* COOPERATION OF INTER- AND INTRAMOLECULAR HYDROGEN BONDS IN BIS(BENZOYLACETONATO)MANGANESE(II) ADDUCTS WITH PYRIDINE DERIVATIVES

(SUPPORTING INFORMATION)

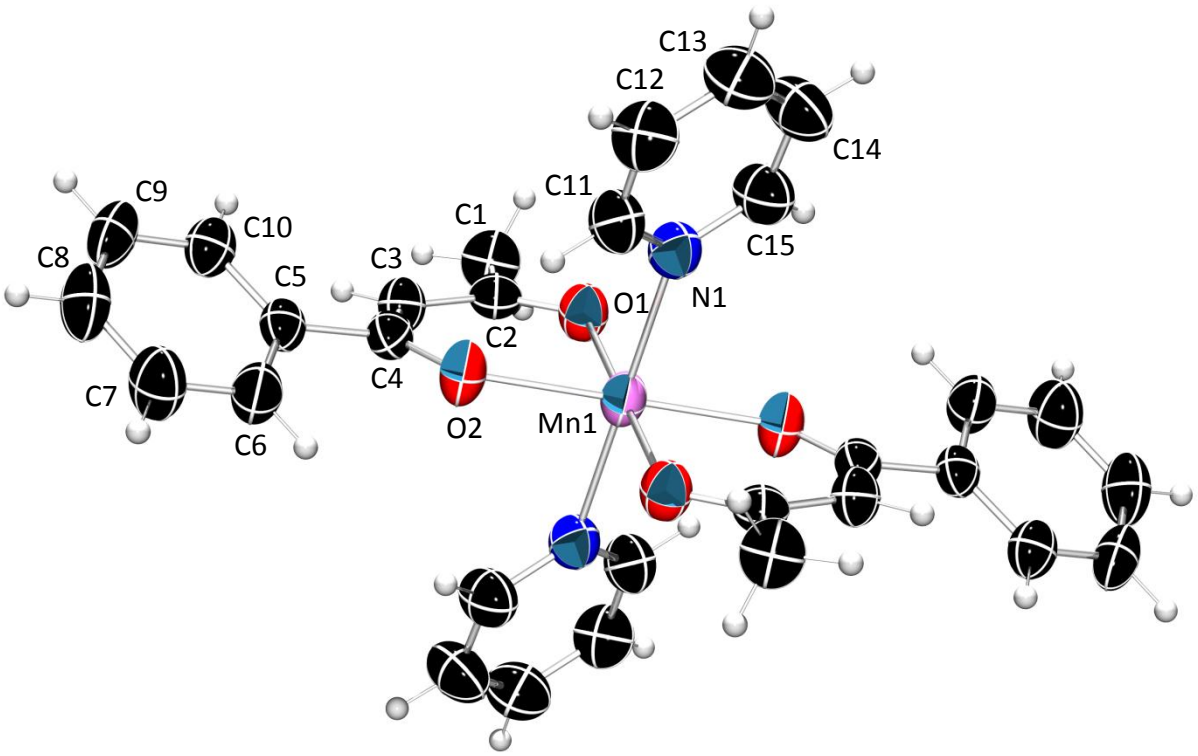

Figure S1. ORTEP plot of **I**. Thermal ellipsoids are drawn with 50% probability and hydrogen atoms are shown as spheres of arbitrary radius.

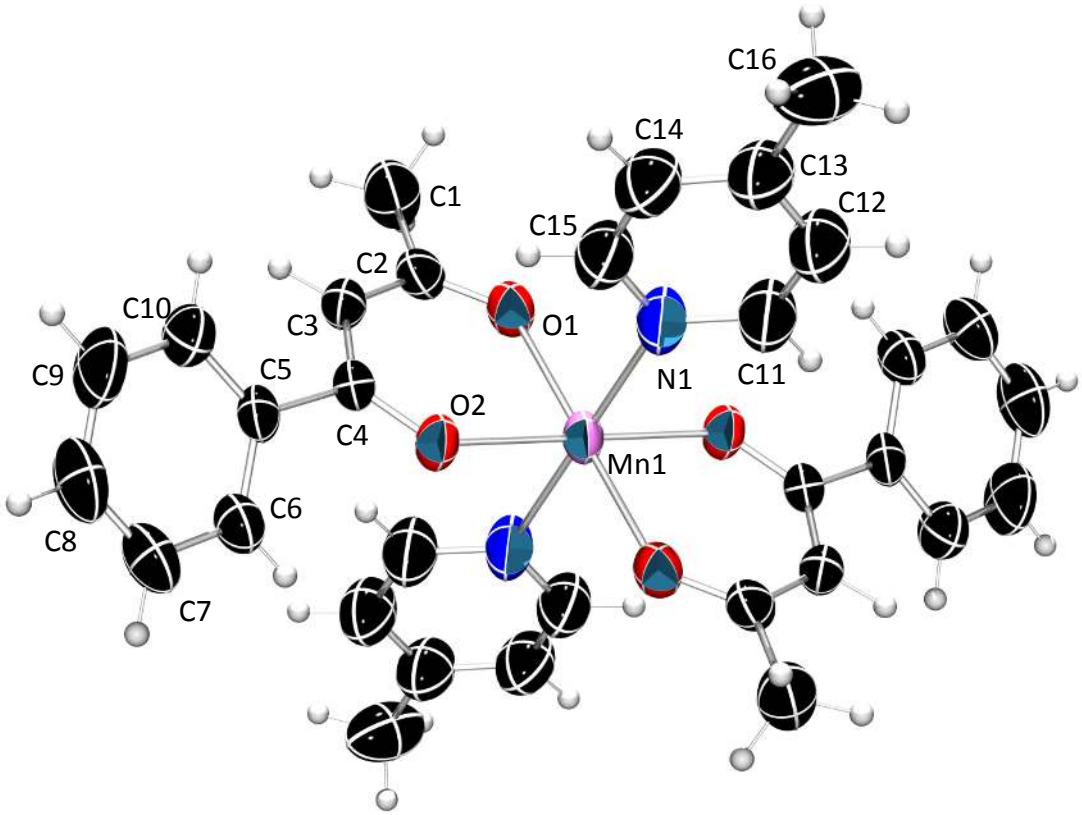

Figure S2. ORTEP plot of **II**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

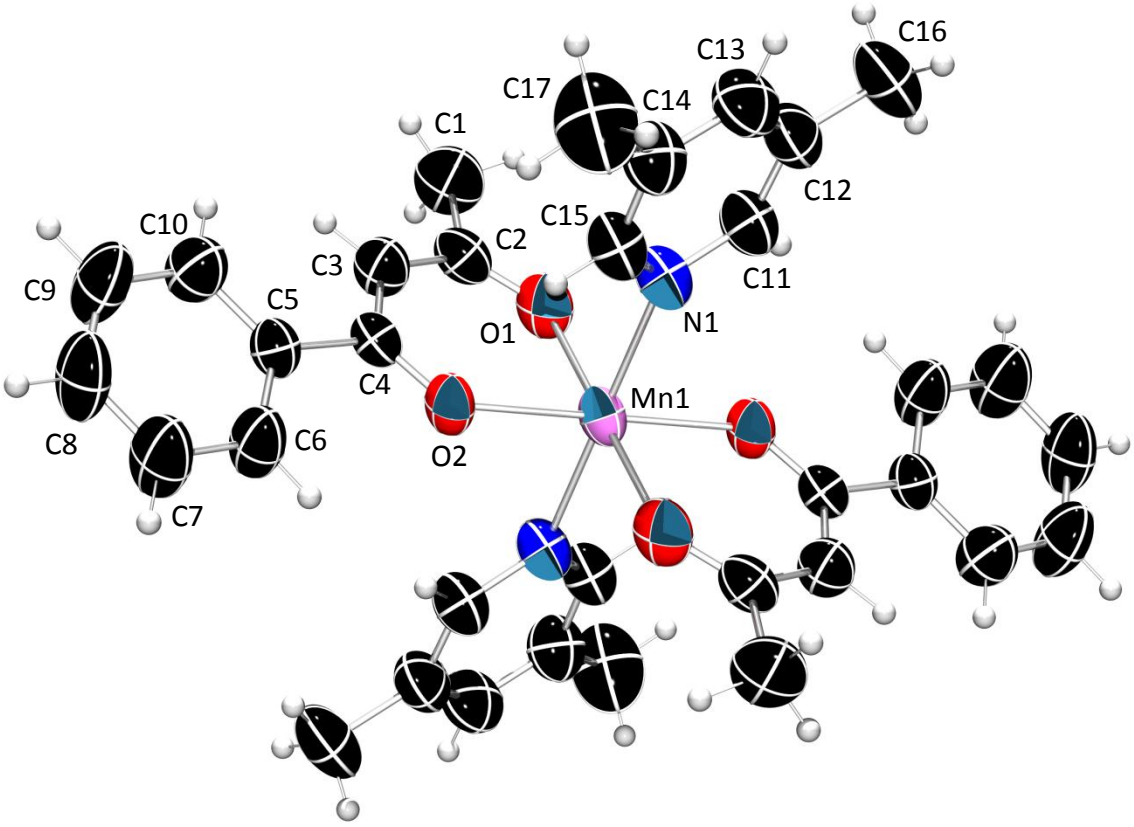

Figure S3. ORTEP plot of **III**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

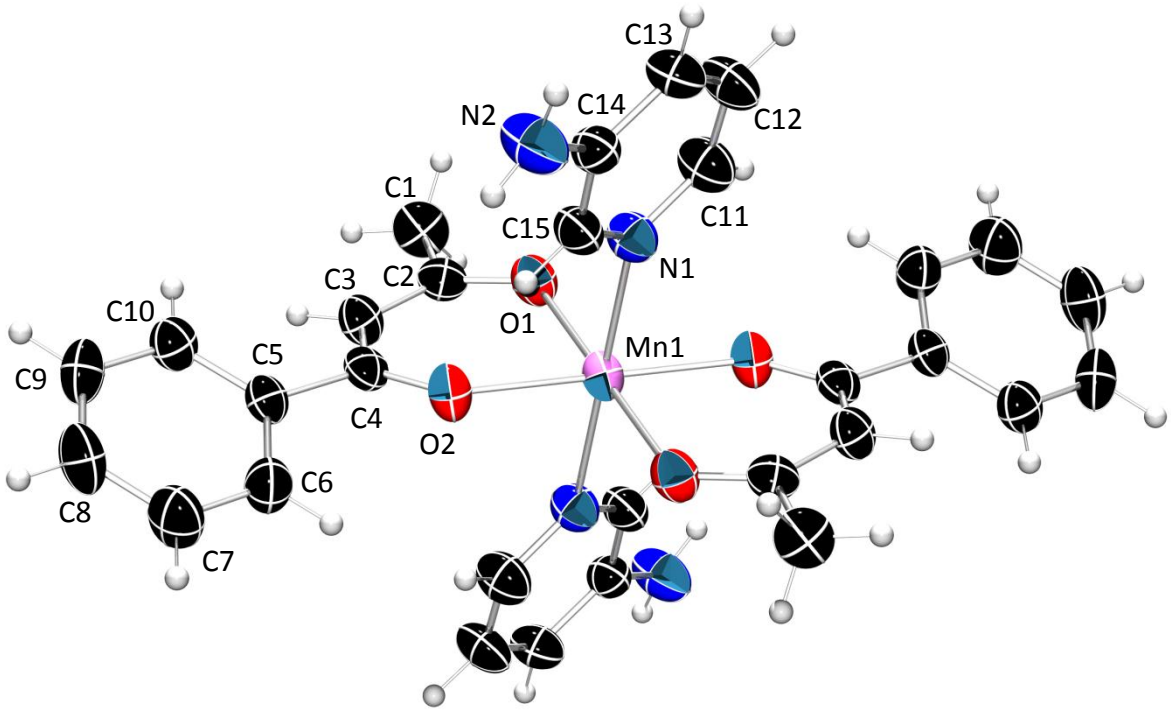

Figure S4. ORTEP plot of **IV**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

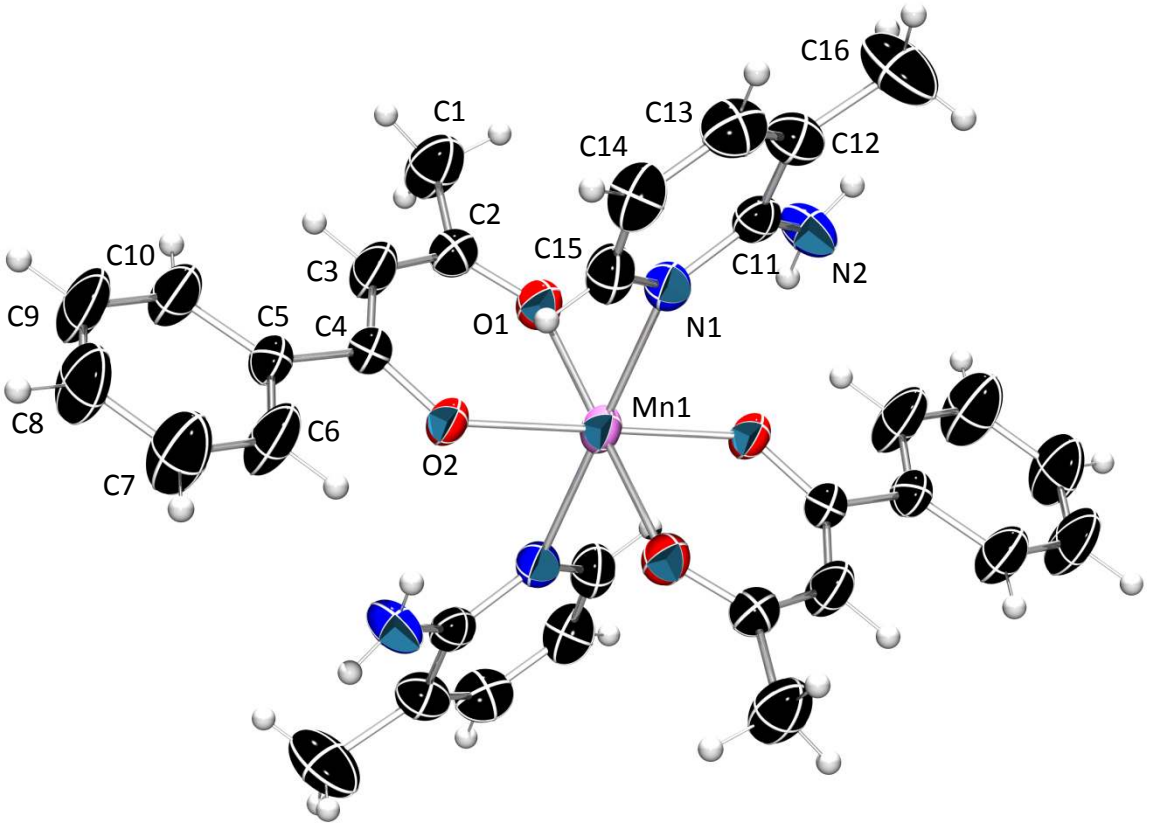

Figure S5. ORTEP plot of **V**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

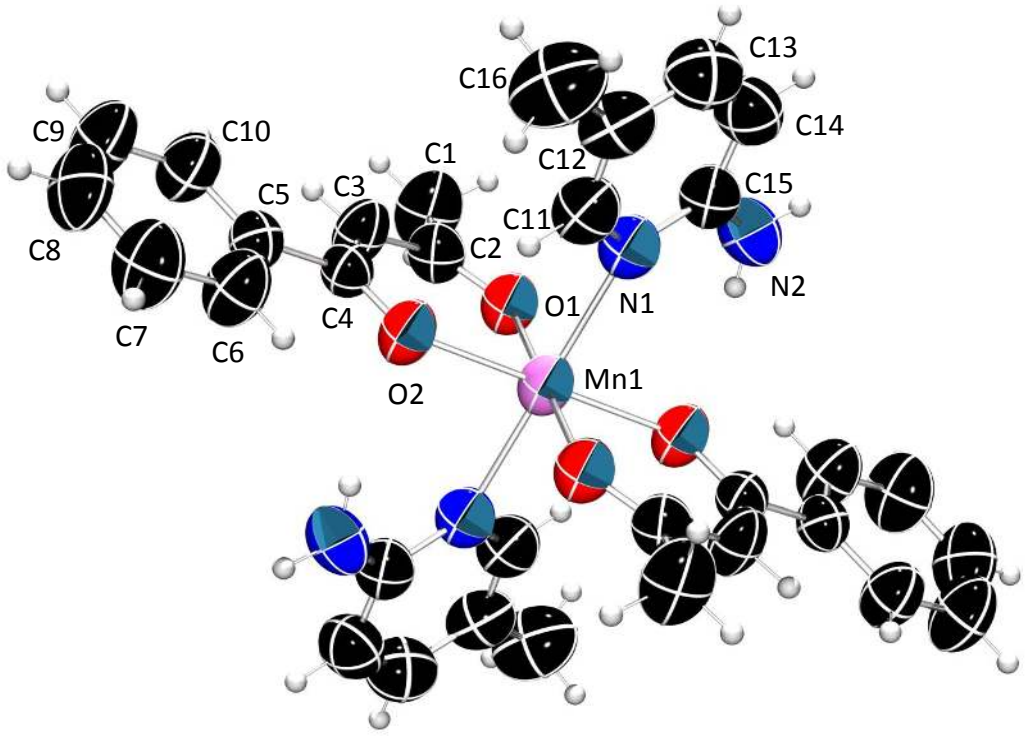

Figure S6. ORTEP plot of **VI**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

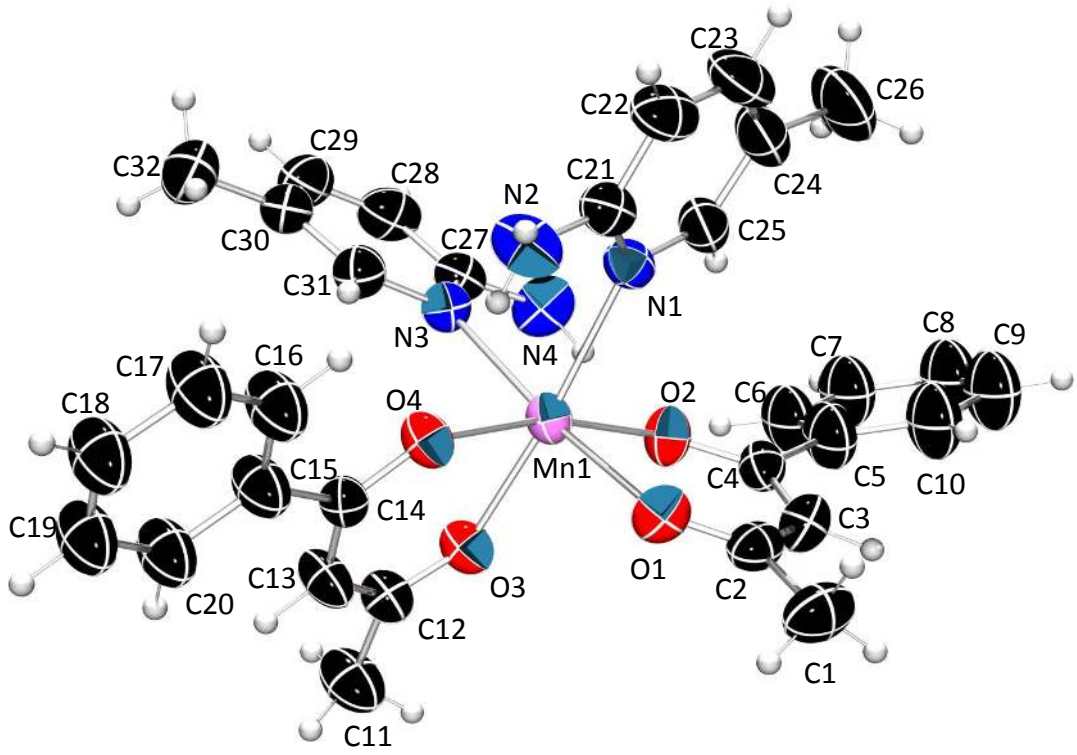

Figure S7. ORTEP plot of **VII**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

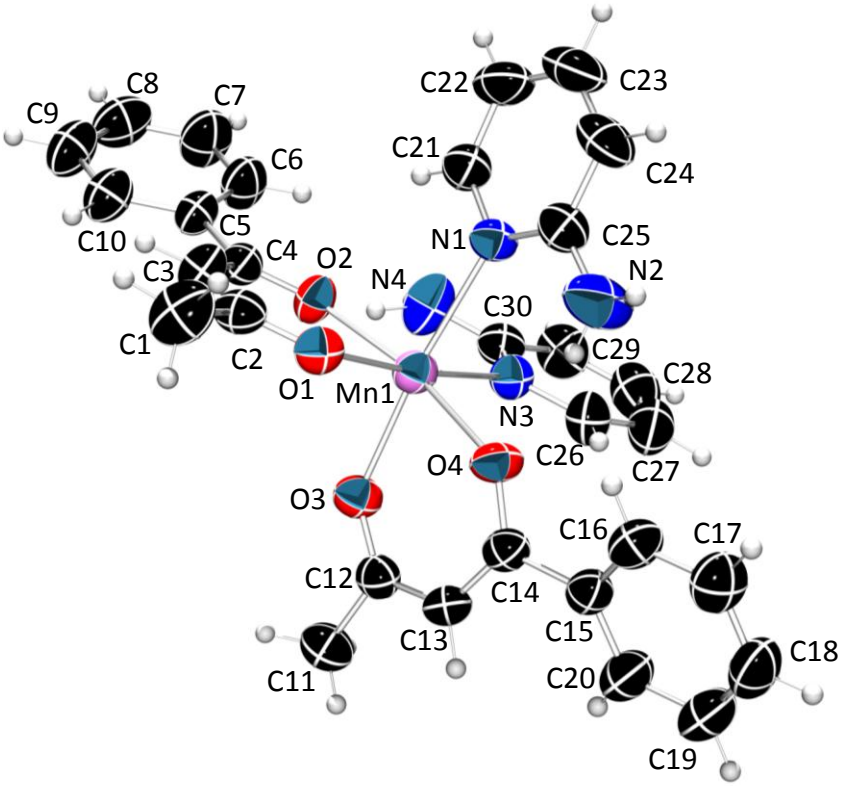

Figure S8. ORTEP plot of **VIII**. Thermal ellipsoids are shown with 50% probability and hydrogen atoms as spheres of arbitrary radius.

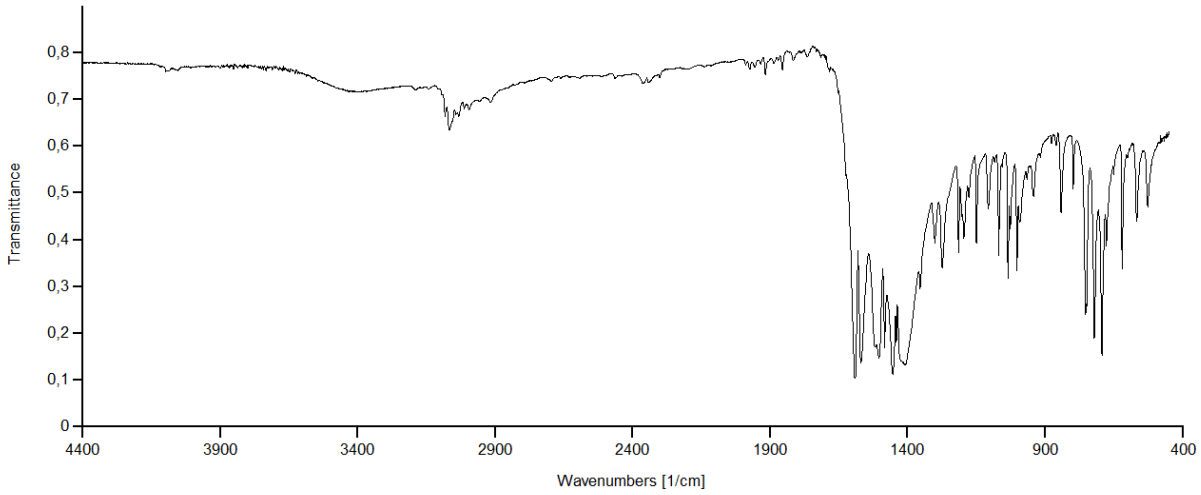

Figure S9. IR spectrum of **I**.

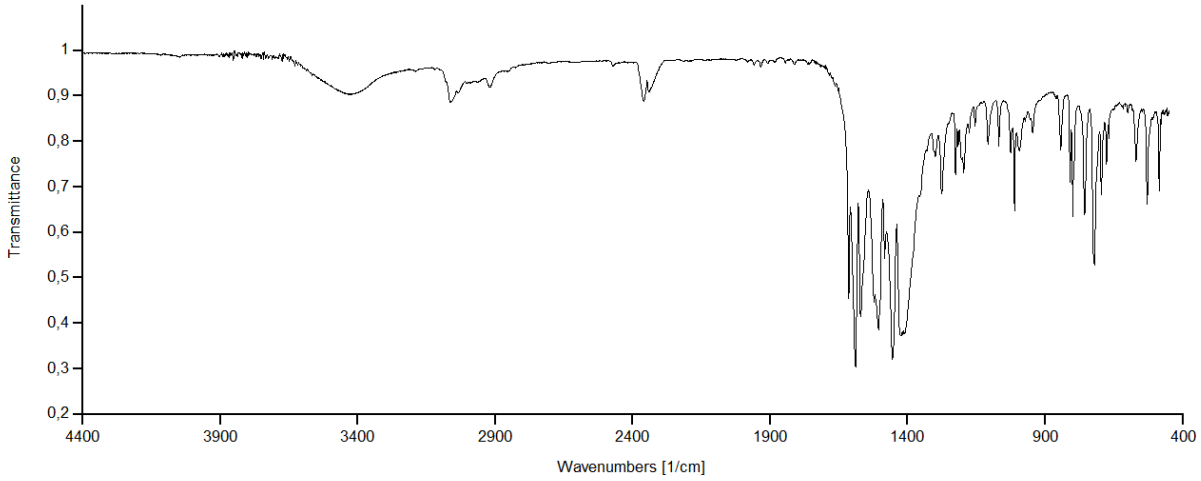

Figure S10. IR spectrum of **II**.

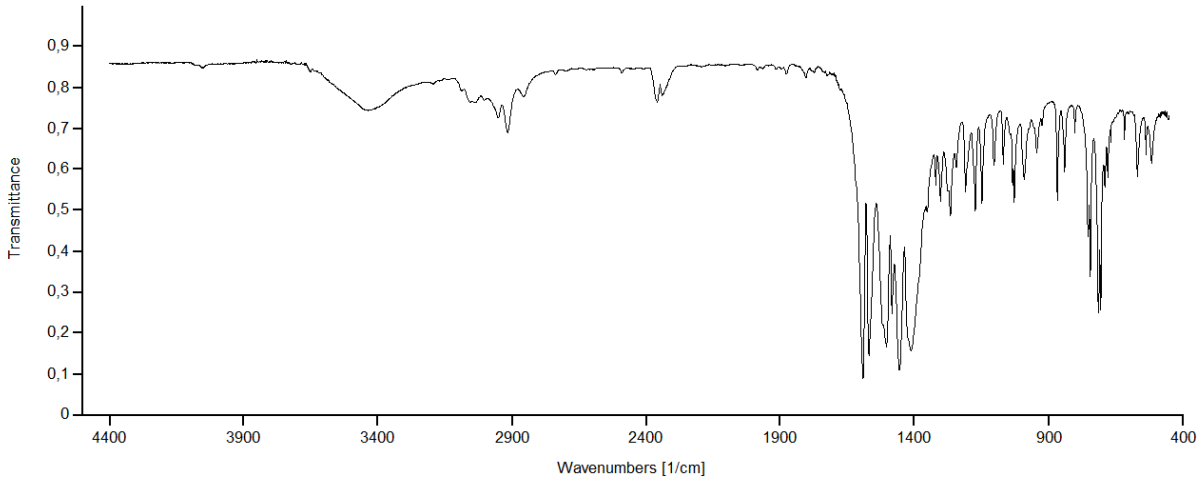

Figure S11. IR spectrum of **III**.

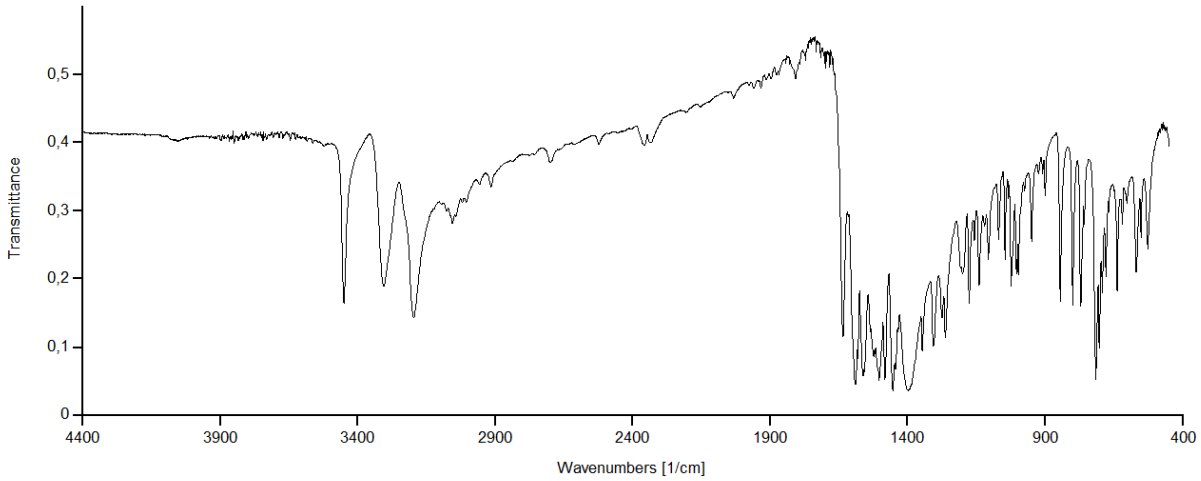

Figure S12. IR spectrum of **IV**.

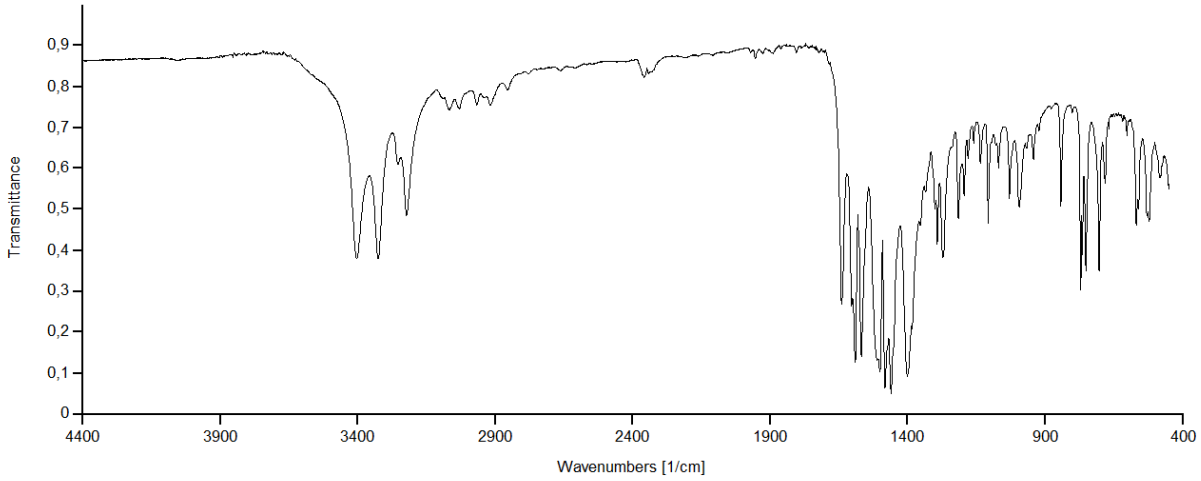

Figure S13. IR spectrum of **V**.

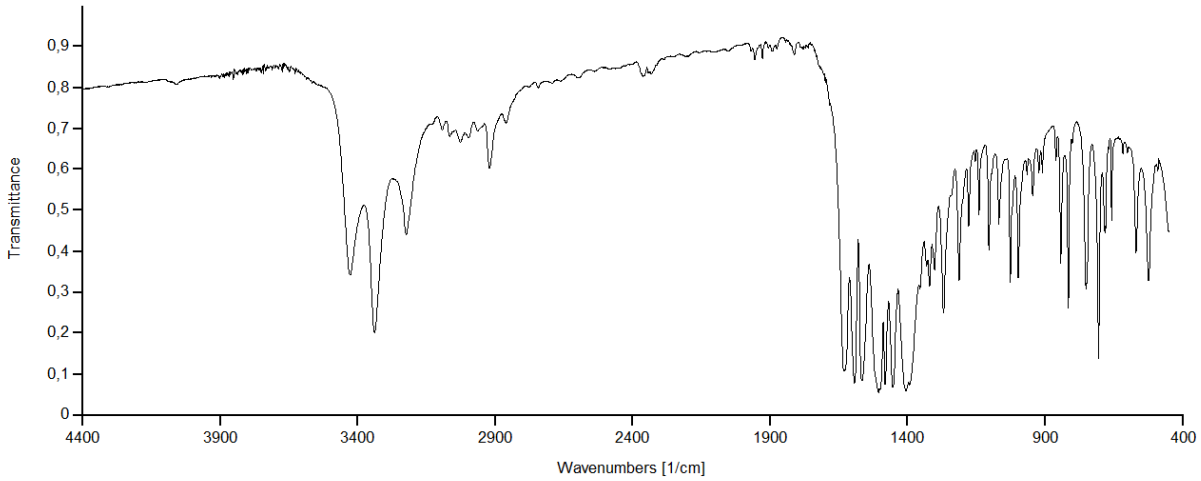

Figure S14. IR spectrum of **VI**.

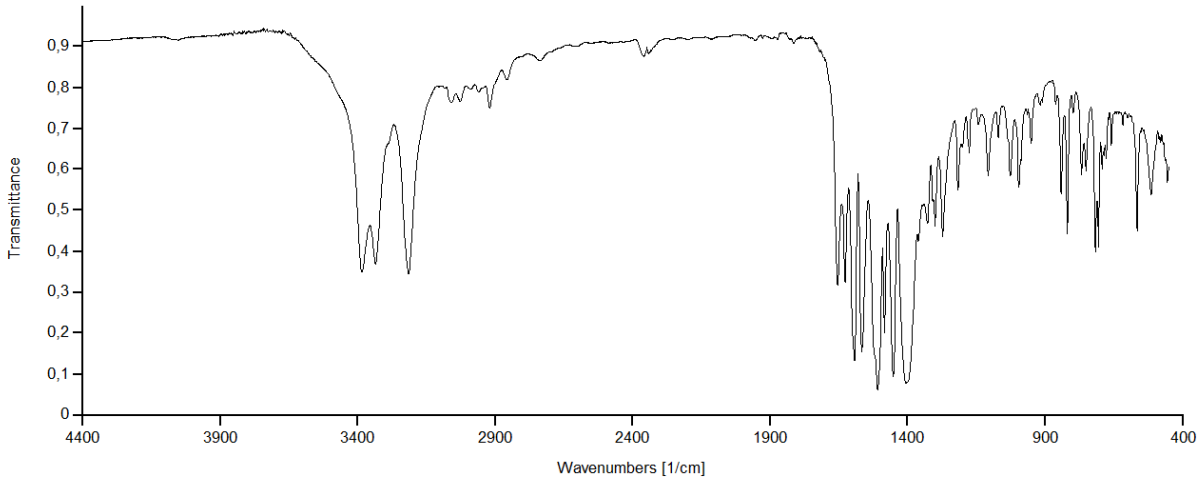

Figure S15. IR spectrum of **VII**.

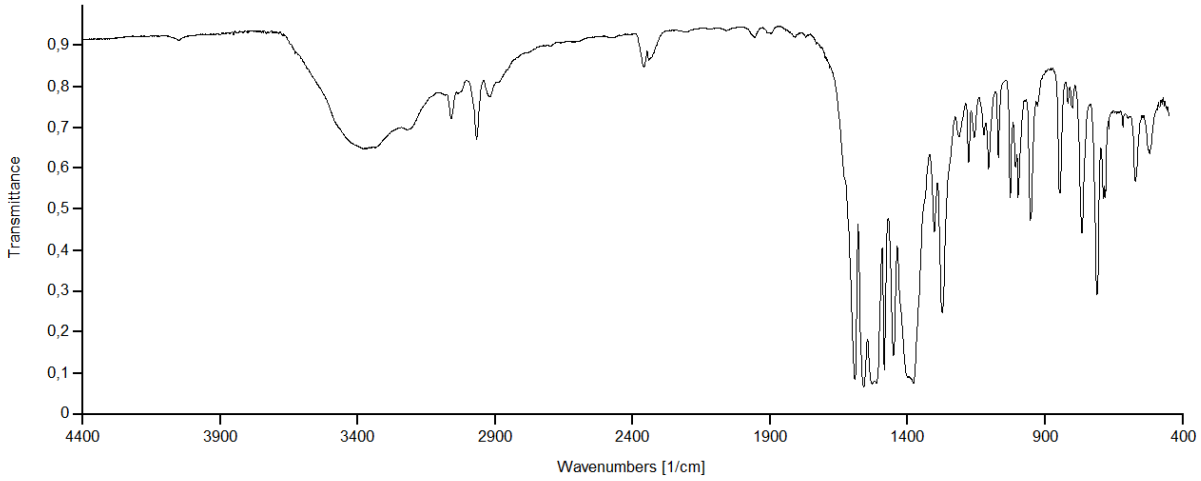

Figure S16. IR spectrum of **VIII**.

Table S1. Overview of the prepared compounds.

Compound	Formula	Mol. formula	Molar mass	C-H...O
I	trans-Mn(BzAc)$_2$(Py)$_2$	$C_{30}H_{28}N_2O_4Mn$	535.48	H3-Py
II	trans-Mn(BzAc)$_2$(4-MePy)$_2$	$C_{32}H_{32}N_2O_4Mn$	563.54	H3-Ph(BzAc)
III	trans-Mn(BzAc)$_2$(3,5-dMePy)$_2$	$C_{34}H_{36}N_2O_4Mn$	591.59	H3-Ph(BzAc)
IV	trans-Mn(BzAc)$_2$(3-AmPy)$_2$	$C_{30}H_{30}N_4O_4Mn$	565.52	N3-H...O (Py)
V	trans-Mn(BzAc)$_2$(2-Am-3MePy)$_2$	$C_{32}H_{34}N_4O_4Mn$	593.57	N2-H...O (Py)
VI	trans-Mn(BzAc)$_2$(2-Am-5MePy)$_2$	$C_{32}H_{34}N_4O_4Mn$	593.57	N2-H...O (Py)
VII	cis-Mn(BzAc)$_2$(2-Am-5MePy)$_2$	$C_{32}H_{34}N_4O_4Mn$	593.57	N2-H...O (Py)
VIII	cis-Mn(BzAc)$_2$(2-AmPy)$_2$	$C_{30}H_{30}N_4O_4Mn$	565.52	N2-H...O (Py)

Table S2. Crystallographic data for the prepared compounds

	I	**II**	**III**	**IV**
Chemical formula	$C_{30}H_{28}N_2O_4Mn$	$C_{32}H_{32}N_2O_4Mn$	$C_{34}H_{36}N_2O_4Mn$	$C_{30}H_{30}N_4O_4Mn$
M_r	535.48	563.54	591.59	565.52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/n$
a/Å	10.6425(7)	9.5507(19)	13.5786(8)	7.5573(3)
b/Å	17.5482(9)	17.045(3)	13.5686(12)	17.7535(7)
c/Å	11.5193(8)	9.6962(18)	18.240(2)	10.6145(4)
α/°	90	90	90	90
β/°	141.110(3)	110.425(18)	104.845(8)	101.146(3)
γ/°	90	90	90	90
V/Å^3	1350.65(17)	1479.2(5)	3248.3(5)	1397.27(9)
Z	2	2	4	2
Z'	1/2	1/2	1/2	1/2
ρ_{calc}/(g cm^{-3})	1.317	1.265	1.210	1.344
u/mm^{-1}	0.526	0.484	0.444	0.514
F[000]	558	590	1244	590
Crystal size/mm^3	0.4×0.2×0.1	0.3×0.1×0.1	0.5×0.1×0.1	0.58×0.15×0.15
Reflections collected	6161	6825	10147	13272
Unique reflections	2906	3176	3523	3025
Observed reflections	1857	2427	2133	2011
Parameters	170	180	190	185
R_1(obs)	0.0344	0.0734	0.0366	0.0315
wR_2(all)	0.0834	0.2106	0.0950	0.0712
S	0.844	1.145	0.874	0.907
Max./min $\Delta\rho$/(e/Å^3)	0.278/–0.206	0.776/–0.571	0.202/–0.156	0.209/–0.193

Table S2. (cont.)

	V	**VI**	**VII**	**VIII**
Chemical formula	$C_{32}H_{34}N_4O_4Mn$	$C_{32}H_{34}N_4O_4Mn$	$C_{32}H_{34}N_4O_4Mn$	$C_{30}H_{30}N_4O_4Mn$
M_r	593.57	593.57	593.57	565.52
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	P-1
a/Å	7.3008(6)	7.3129(16)	10.1610(4)	9.0001(7)
b/Å	17.1487(10)	8.752(2)	12.6475(5)	12.7277(10)
c/Å	13.0737(13)	24.543(7)	12.9842(6)	14.1367(14)
α/°	90	90	85.849(4)	66.042(9)
β/°	113.591(7)	90.83(2)	73.618(4)	76.101(7)
γ/°	90	90	74.865(4)	73.393(7)
V/Å^3	1500.0(2)	1570.6(7)	1545.34(11)	1403.8(2)
Z	2	2	2	2
Z'	1/2	1/2	1	1
ρ_{calc}/(g cm^{-3})	1.314	1.255	1.276	1.338
u/mm^{-1}	0.482	0.461	0.468	0.512
F[000]	622	622	622	590
Crystal size/mm^3	0.57×0.10×0.10	0.50×0.21×0.11	0.8×0.3×0.3	0.5×0.1×0.1
Reflections collected	7284	12765	11979	7777
Unique reflections	2577	3437	5965	4790
Observed reflections	1525	1791	4081	2409
Parameters	197	197	388	370
R_1(obs)	0.0345	0.0379	0.0545	0.0364
wR_2(all)	0.0838	0.0945	0.1567	0.0677
S	0.881	0.832	1.024	0.731
Max./min $\Delta\rho$/(e/Å^3)	0.208/–0.195	0.215/–0.140	1.096/–0.793	0.219/–0.226

Table S3a. Bond lengths and angles in the first coordination sphere of manganese atoms.

Compound	d(Mn–O_{Ac}) (Å)	d(Mn–O_{Bz}) (Å)	d(Mn–N) (Å)	φ(O_{Ac}–Mn–O_{Bz}) (°)	φ(O_{Ac}–Mn–N) (°)	φ(O_{Bz}–Mn–N) (°)
I	2.1413(12)	2.1150(11)	2.3262(16)	84.69(4)	84.76(5)	90.59(5)
II	2.130(3)	2.121(2)	2.342(4)	83.66(10)	89.49(13)	88.95(12)
III	2.1398(14)	2.1232(11)	2.3026(17)	84.63(5)	88.50(6)	90.22(5)
IV	2.1414(11)	2.1044(10)	2.3361(14)	85.02(4)	86.22(5)	90.43(5)
V	2.1608(17)	2.0909(16)	2.419(2)	85.68(6)	88.72(7)	88.31(6)
VI	2.1420(14)	2.1037(14)	2.3727(19)	85.95(5)	87.72(6)	91.49(6)
VII	2.174(2) 2.170(2)	2.145(2) 2.168(2)	2.356(3) 2.315(3)	82.29(9) 82.20(8)	90.79(9) 90.77(9)	92.10(9) 93.82(9)
VIII	2.184(2) 2.1792(17)	2.1616(17) 2.1476(16)	2.335(2) 2.355(2)	81.59(7) 82.19(6)	90.09(7) 88.96(7)	92.76(7) 93.91(8)

Table S3b. Angles in coordination octahedra of Mn atoms in **VII** and **VIII**.

Bond angle	**VII**	**VIII**
φ($O1_{Ac}$–Mn–$O2_{Bz}$) (°)	82.29(9)	81.59(7)
φ($O3_{Ac}$–Mn–$O4_{Bz}$) (°)	82.20(8)	82.19(6)
φ($O1_{Ac}$–Mn–N1) (°)	90.79(9)	90.09(7)
φ($O3_{Ac}$–Mn–N3) (°)	90.77(9)	88.96(7)
φ($O2_{Bz}$–Mn–N1) (°)	92.10(9)	92.76(7)
φ($O4_{Bz}$–Mn–N3) (°)	93.82(9)	93.91(8)
φ($O1_{Ac}$–Mn–$O3_{Ac}$) (°)	94.92(9)	96.17(7)
φ($O1_{Ac}$–Mn–$O4_{Bz}$) (°)	88.46(8)	90.32(7)
φ($O2_{Bz}$–Mn–N3) (°)	96.35(9)	94.83(8)
φ($O2_{Bz}$–Mn–$O3_{Ac}$) (°)	88.75(8)	90.71(6)
φ($O4_{Bz}$–Mn–N1) (°)	97.90(8)	95.24(7)
φ(N1–Mn–N3) (°)	83.52(9)	84.96(7)

Table S3. Bond lengths and angles in the first coordination sphere of manganese atoms for compounds **I**–**VI**.

Cmpd.	d(Mn–O_{Ac}) (Å)	d(Mn–O_{Bz}) (Å)	d(Mn–N) (Å)	φ(O_{Ac}–Mn–O_{Bz}) (°)	φ(O_{Ac}–Mn–N) (°)	φ(O_{Bz}–Mn–N) (°)	φ(O2-Mn-N1-C11)/°
I	2.1413(12)	2.1150(11)	2.3262(16)	84.69(4)	95.24(5)	89.41(5)	29.66
II	2.130(3)	2.121(2)	2.342(4)	83.66(10)	89.49(13)	88.95(12)	−26.41
III	2.1398(14)	2.1232(11)	2.3026(17)	84.63(5)	91.50(6)	89.78(5)	21.61
IV	2.1414(11)	2.1044(10)	2.3361(14)	85.02(4)	93.78(5)	89.57(5)	27.04
V	2.1608(17)	2.0909(16)	2.419(2)	85.68(6)	91.28(7)	91.69(6)	19.07
VI	2.1420(14)	2.1037(14)	2.3727(19)	85.95(5)	92.18(6)	88.51(6)	29.99
VII	2.174(2) 2.170(2)	2.145(2) 2.168(2)	2.356(3) 2.315(3)	82.29(9) 82.20(8)	90.79(9) 90.77(9)	92.10(9) 93.82(9)	13.23 12.34
VIII	2.184(2) 2.1792(17)	2.1616(17) 2.1476(16)	2.335(2) 2.355(2)	81.59(7) 82.19(6)	90.09(7) 88.96(7)	92.76(7) 93.91(8)	13.19 8.70

Table S4. Significant hydrogen bonds and C—H···O contacts

Contact	*d*(D,H)/Å	*d*(D,A)/Å	*d*(A,H)/Å	ϕ(D,H,A)/ °
I				
C11—H11···O2	0.930(4)	3.199(4)	2.633(2)	119.8(2)
C15—H15···O2[a]	0.930(2)	3.326(3)	2.839(2)	113.9(1)
C12—H12···O1[b]	0.930(2)	3.414(4)	2.622(2)	143.4(1)
II				
C15—H15···O2	0.930(7)	3.318(7)	2.790(3)	117.0(3)
C11—H11···O2[c]	0.930(6)	3.242(6)	2.703(3)	117.7(3)
C7—H7···O1[d]	0.930(4)	3.351(6)	2.654(3)	132.3(3)
III				
C15—H15···O2	0.930(2)	3.249(3)	2.699(1)	118.7(1)
C11—H11···O2[e]	0.930(2)	3.166(3)	2.584(1)	121.1(1)
C7—H7···O1[f]	0.930(2)	3.490(2)	2.748(1)	137.5(1)
IV				
C11—H11···O2	0.930(2)	3.220(2)	2.657(1)	119.6(1)
C15—H15···O2[g]	0.930(2)	3.270(2)	2.753(1)	116.1(1)
N2—H17···O1[h]	0.82(2)	2.962(2)	2.15(2)	168(2)
V				
C15—H15···O2	0.930(3)	3.122(3)	2.491(1)	125.3(2)
N2—H1···O1[i]	0.79(3)	3.084(4)	2.35(3)	154(3)
N2—H1···O2[a]	0.84(2)	2.867(3)	2.10(2)	151(3)
VI				
C11—H11···O2[j]	0.930(2)	3.131(3)	2.567(2)	119.5(2)
N2—H18···O2	0.85(2)	2.971(3)	2.20(2)	152(2)
N2—H17···O1[h]	0.82(2)	3.101(3)	2.36(2)	150(2)
VII				
C25—H25···O2	0.930(4)	3.162(5)	2.484(3)	129.9(2)
C31—H31···O4	0.930(3)	3.154(5)	2.458(2)	131.7(2)
N2—H34···O4	0.78(5)	2.935(5)	2.19(4)	159(4)
N4—H35···O2	0.86(6)	2.900(4)	2.08(5)	158(5)
N2—H33···O1[k]	0.79(4)	2.966(4)	2.18(4)	172(4)
N4—H36···O3[l]	0.78(5)	2.994(3)	2.22(4)	169(5)
VIII				
C21—H21···O2	0.930(4)	3.164(4)	2.486(2)	129.9(2)
C26—H26···O4	0.930(3)	3.202(3)	2.507(2)	131.8(2)
N2—H1···O4	0.82(3)	2.864(4)	2.07(3)	164(3)
N4—H4···O2	0.97(4)	2.873(3)	2.01(3)	146(3)
N2—H2···O1[j]	0.89(4)	3.050(5)	2.16(4)	174(3)
N4—H3···O3[h]	0.89(3)	3.010(4)	2.12(3)	176(2)

a) $-x, -y, -z$; b) $x+1, y, z+1$; c) $-x, -y+1, -z+1$; d) $x, y, z+1$; e) $-x+3/2, -y+1/2, -z+1$; f) $x+1/2, -y+1/2, z+1/2$; g) $-x+1, -y, -z+1$; h) $x-1, y, z$; i) $-x+1, -y, -z$; j) $-x+1, -y+1, -z+1$; k) $-x+1, -y+2, z+1$; l) $-x+2, -y+1, z+1$

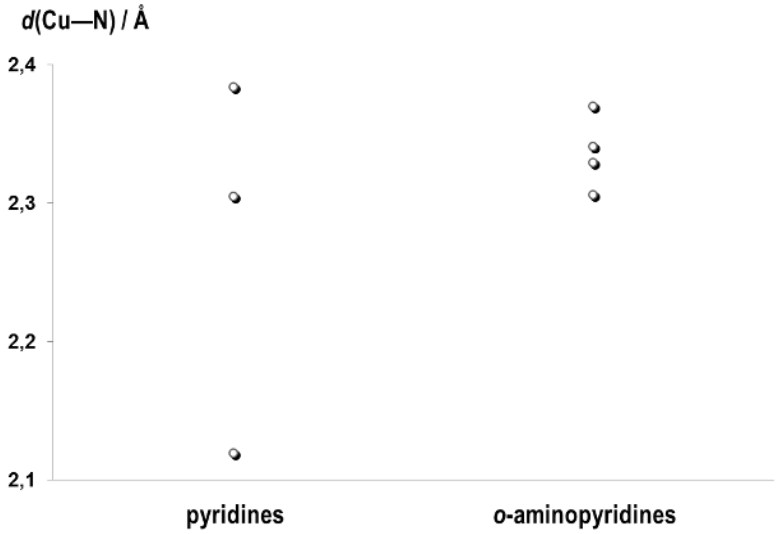

Figure S17. The comparison of Cu—N distances between adducts of $Cu(acac)_2$ with pyridines and *o*-aminopyridines (pyridines: ADAHIX, NULFUW, RAGQUN, HEGPEQ, *o*-aminopyridines: DAYQIF, DAYQOL, DAYQUR, WAWRUJ).

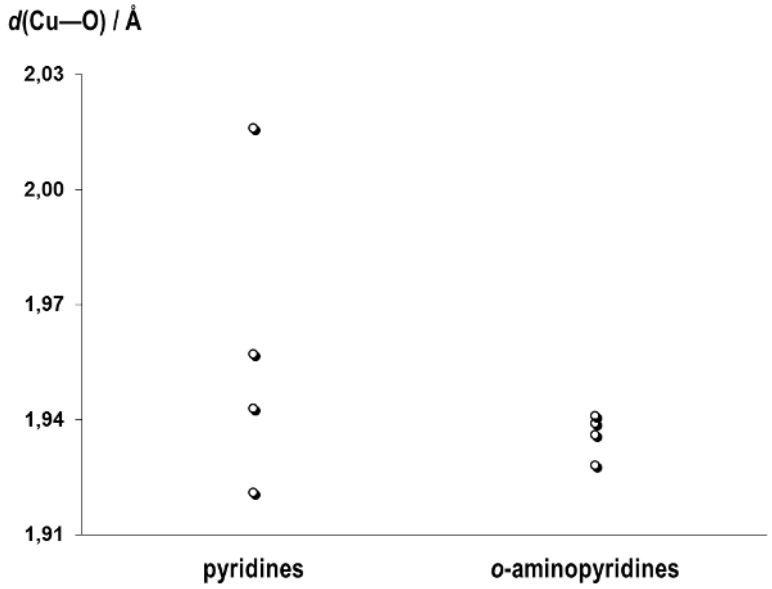

Figure S18. The comparison of Cu—O (oxygen atom hydrogen bonded to pyridine amino groups) distances between adducts of $Cu(acac)_2$ with pyridines and *o*-aminopyridines (pyridines: ADAHIX, NULFUW, RAGQUN, HEGPEQ, *o*-aminopyridines: DAYQIF, DAYQOL, DAYQUR, WAWRUJ).

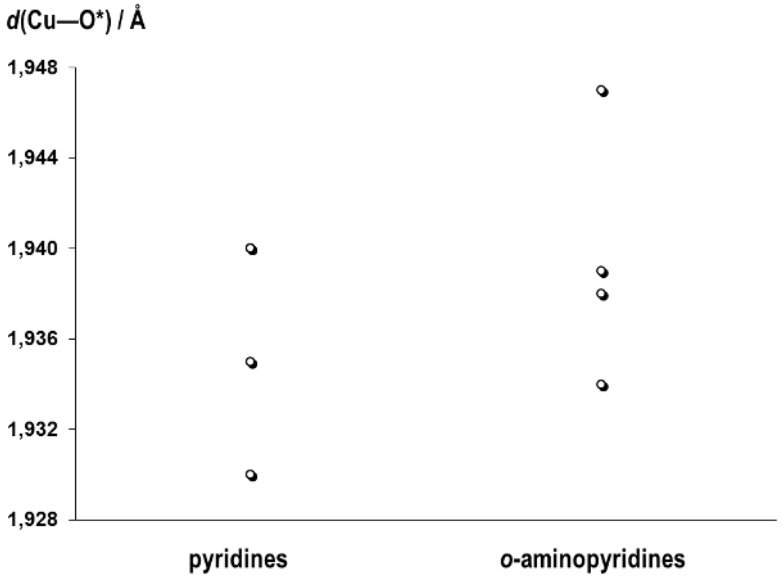

Figure S19. The comparison of Cu—O distances between adducts of $Cu(acac)_2$ with pyridines and *o*-aminopyridines (pyridines: ADAHIX, NULFUW, RAGQUN, HEGPEQ, *o*-aminopyridines: DAYQIF, DAYQOL, DAYQUR, WAWRUJ).

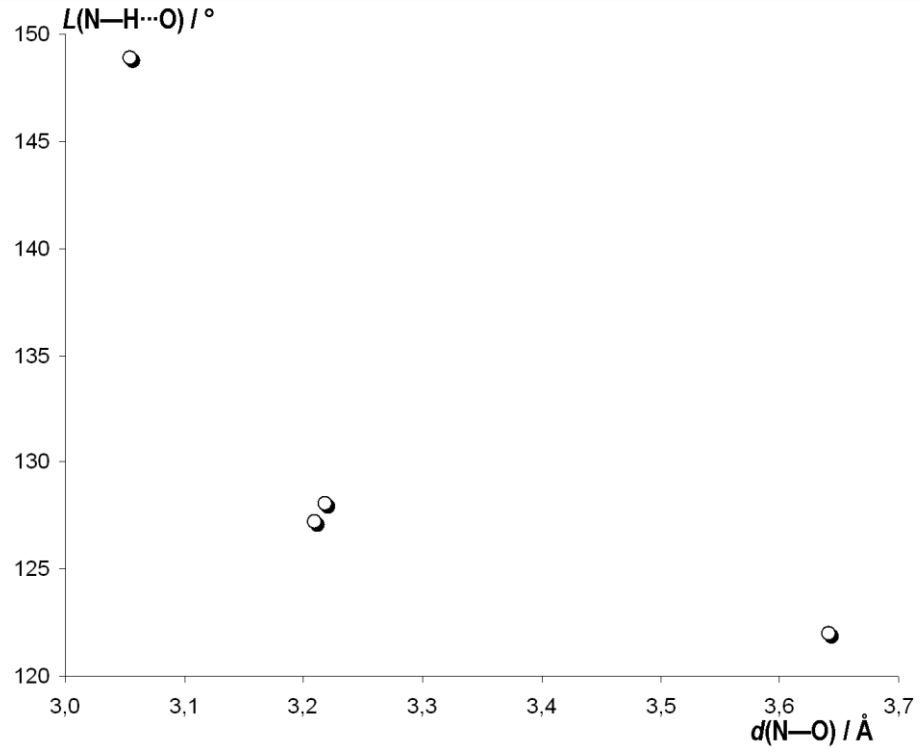

Figure S20. Hydrogen bond geometries in structures of adducts of $Cu(acac)_2$ with pyridines and *o*-aminopyridines (DAYQIF, DAYQOL, DAYQUR, WAWRUJ).

Table S5. Refcodes corresponding to structures of octahedrally coordinated metal(II) bis(diketonates), in which the metal is hexacoordinated, the diketone asymmetric with one aliphatic and one aromatic substituent, and the remaining two ligands monodentate neutral molecules.

Refcode	Central ion	Donor atom (L)	Configuration	Contacts with diketonate oxygen atoms
AMIQIW	Ni	N	*trans*	N—H···O
ASOWUA	Ni	O	*trans*	C—H···O*
CIGYOG	Cu	O	*trans*	C—H···O*
FAHHOL	Cu	N	*trans*	-
FIWJOL	Ni	N	*trans*	-
GISMIF	Co	N	*trans*	-
HIQWEK	Co	N	*trans*	-
ICACIY	Ni	P	*trans*	-
JIRCES	Cu	O	*trans*	-
KOWFIL	Cu	N	*trans*	-
LEKXEE	Fe	N	*trans*	-
LIMNAX	Zn	O	*trans*	C—H···O*
LUPJUB	Cu	N	*trans*	-
LUOKAI	Cu	N	*trans*	-
MIGGIT	Cu	N	*trans*	-
NAKFOW	Co	N	*trans*	-
NENMIE	Ni	N	*trans*	-
NENMOK	Co	N	*trans*	-
NENMUQ	Mn	N	*trans*	-
NENNAX	Mn	N	*trans*	N—H···O**
POJROW	Co	N	*trans*	-
REGLEV	Ca	O	*trans*	O—H···O
TAFACU	Cu	N	*trans*	-
TFBCOP	Co	N	*cis*	C—H···O
TFBCUP	Cu	N	*cis*	C—H···O
TFBONI01	Ni	N	*cis*	C—H···O
TFBZNP	Zn	N	*cis*	C—H···O
THFACO	Co	O	*cis*	O—H···O
THFAZN	Zn	O	*cis*	O—H···O
TTACOP	Co	N	*trans*	-
TTANIP	Ni	N	*trans*	-
TTAZNP	Zn	N	*cis*	-
WUXZOE	Co	N	*trans*	C—H···O***
YADKUJ	Co	N	*trans*	O—H···O**
YAFRII	Co	N	*cis*	-

* long contacts involving methyl groups
** contacts with (small) solvent molecules
*** long contact (3.455 Å) with a pyridine ring

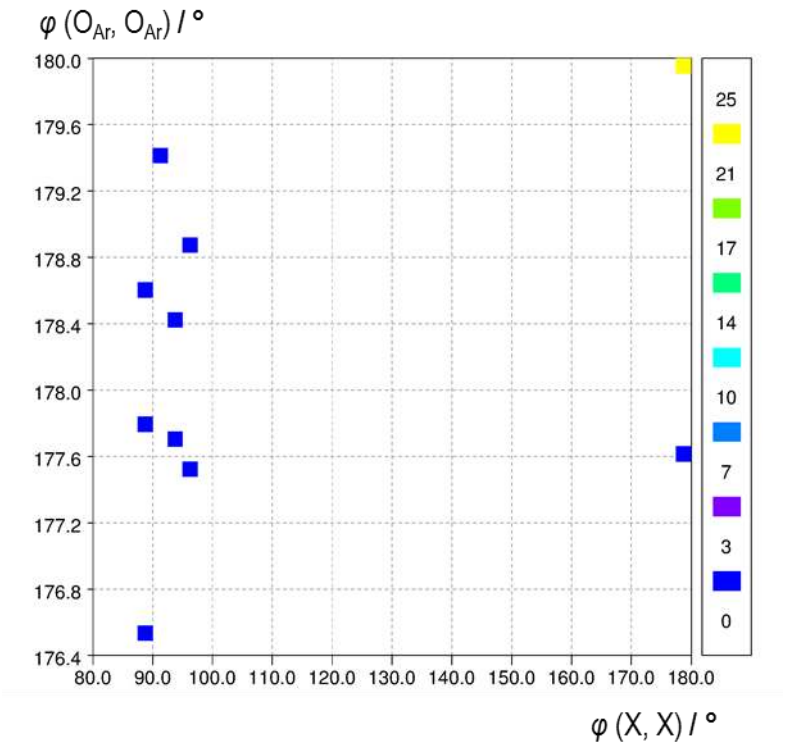

Figure S21. A plot of angles X—M—X *vs.* O_{Ar}—M—O_{Ar} in compounds M(diketonate)$_2$(L)$_2$, where X is the donor atom of ligand L. The colour of squares corresponds to number of compounds, as shown on the legend on the right side of the plot.

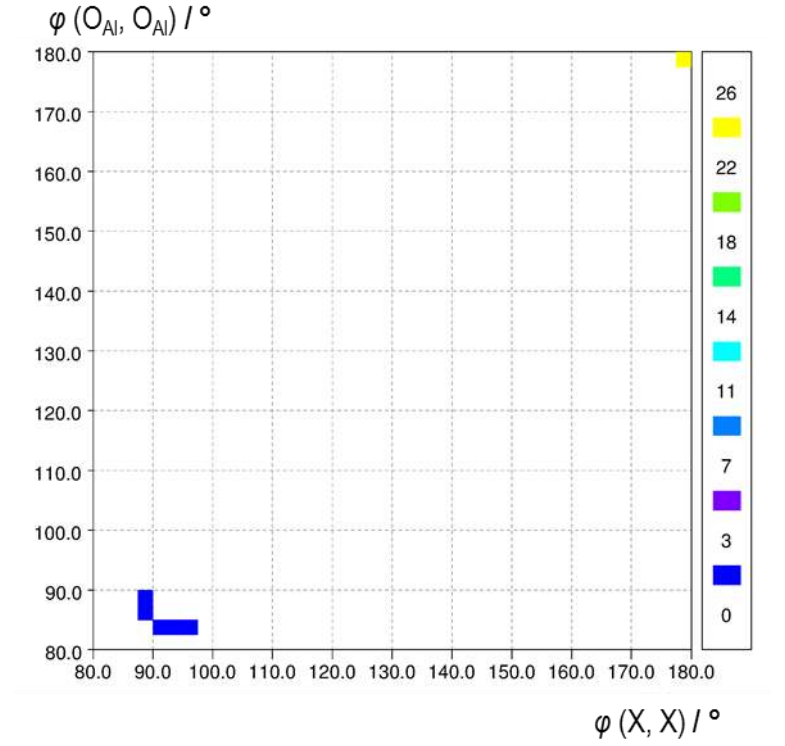

Figure S22. A plot of angles X—M—X *vs.* O_{Al}—M—O_{Al} in compounds M(diketonate)$_2$(L)$_2$, where X is the donor atom of ligand L. The colour of squares corresponds to number of compounds, as shown on the legend on the right side of the plot.

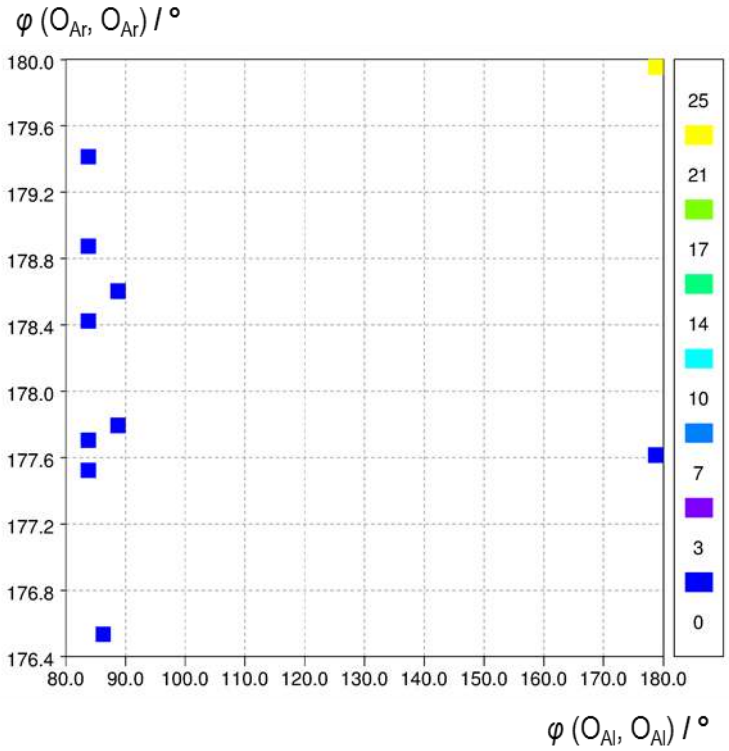

Figure S23. A plot of angles O_{Al}—M—O_{Al} *vs.* O_{Ar}—M—O_{Ar} in compounds M(diketonate)$_2$(L)$_2$, where X is the donor atom of ligand L. The colour of squares corresponds to number of compounds, as shown on the legend on the right side of the plot.