Supplementary Information

Dinuclear Spin Cross-Over Complexes Based on Tetradentate and Bridging Cyanocarbanion Ligands.

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Contents: Figures and Tables not shown in the main text

Figure S1: ^{1}H NMR ($CDCl_3$) of 1-bromomethyl-2-nitrobenzene at 25 °C (300 MHz)

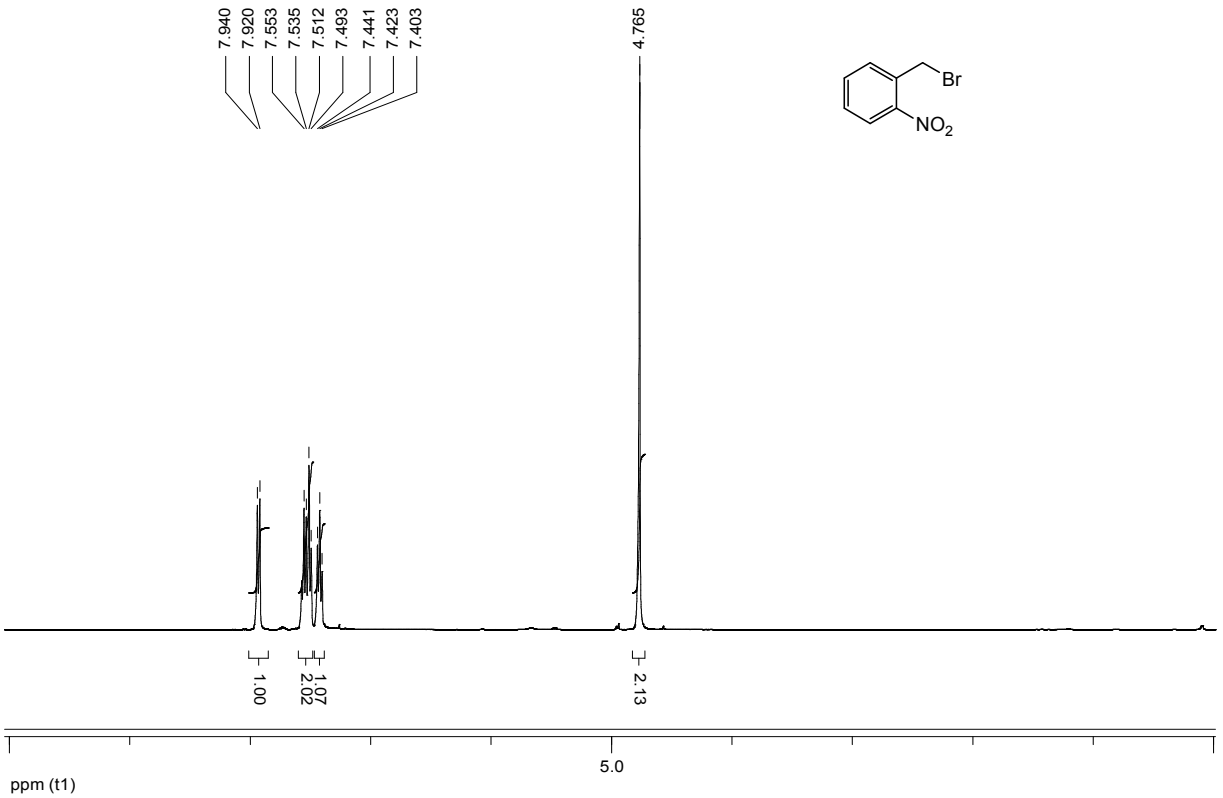


Figure S2: ^{1}H NMR ($CDCl_3$) of bis-(2-pyridylmethyl)aminomethyl)nitrobenzene at 25 °C (300 MHz)

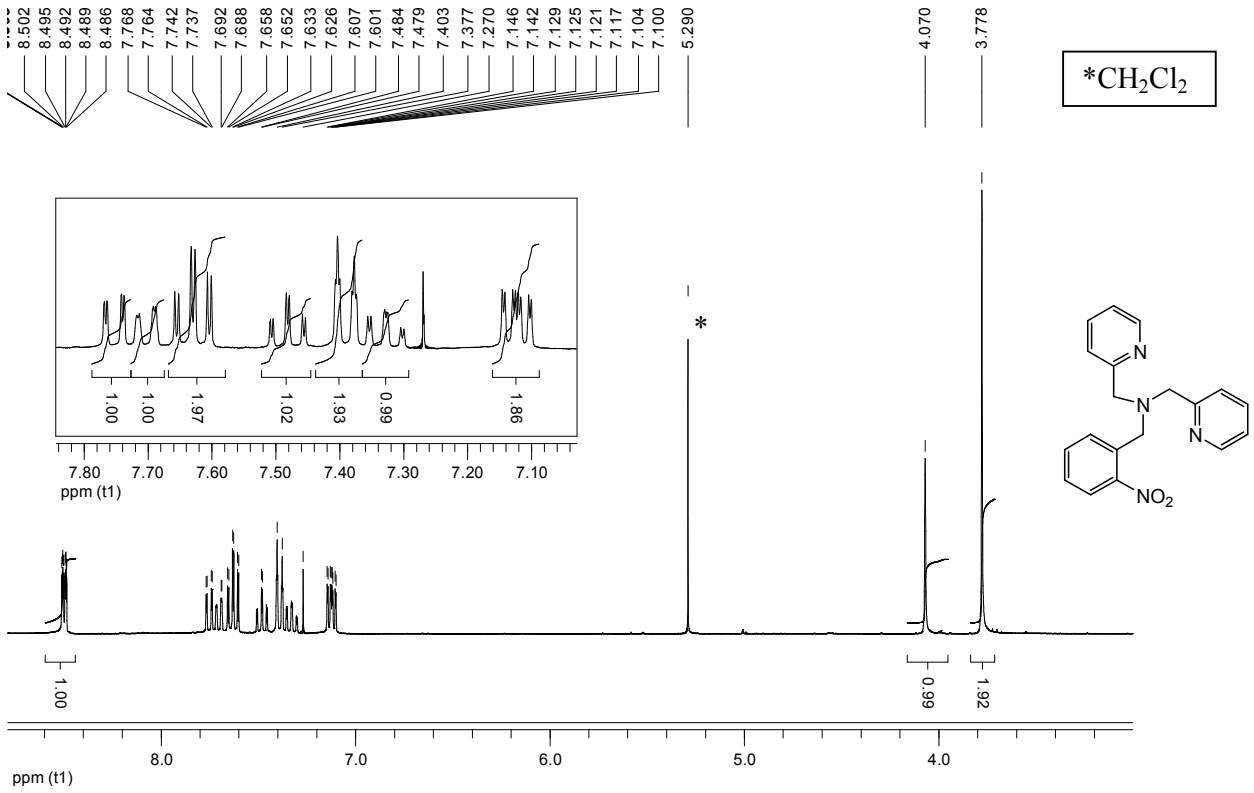


Figure S3: ^{13}C NMR ($CDCl_3$) of bis-(2-pyridylmethyl)aminomethyl)nitrobenzene at 25 °C (300 MHz)

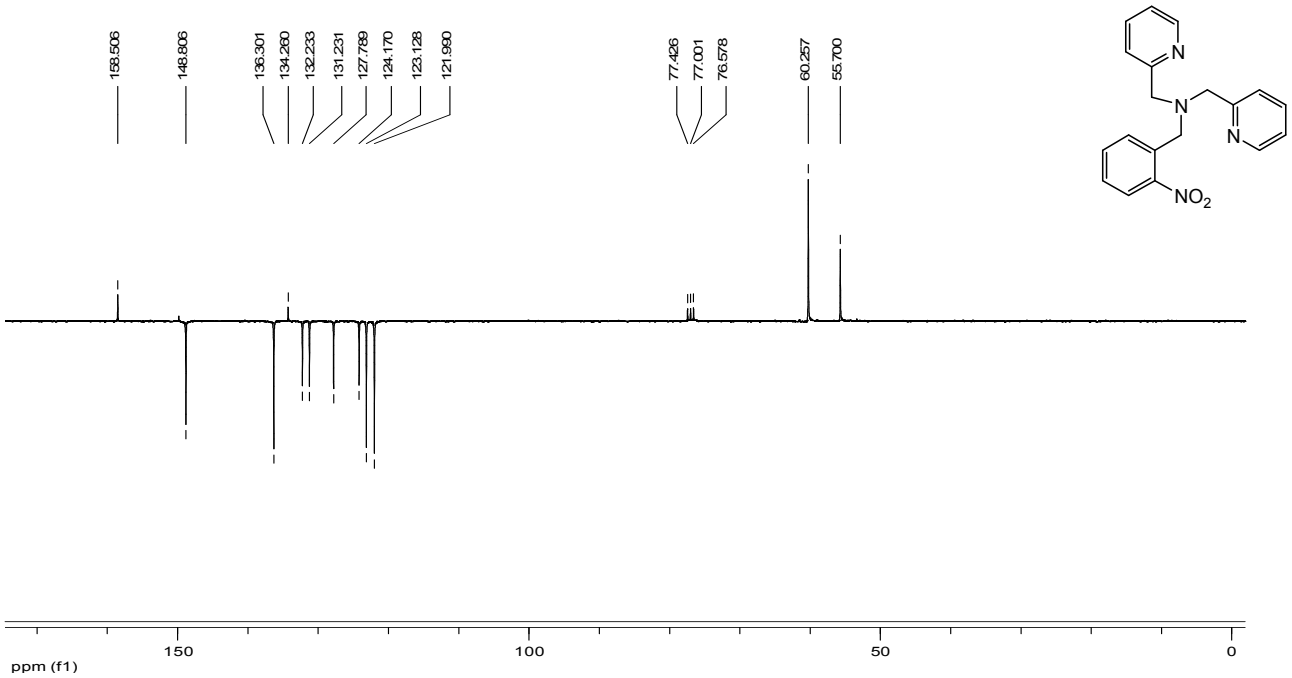


Figure S4: IR spectrum of bis-(2-pyridylmethyl)aminomethyl)nitrobenzene

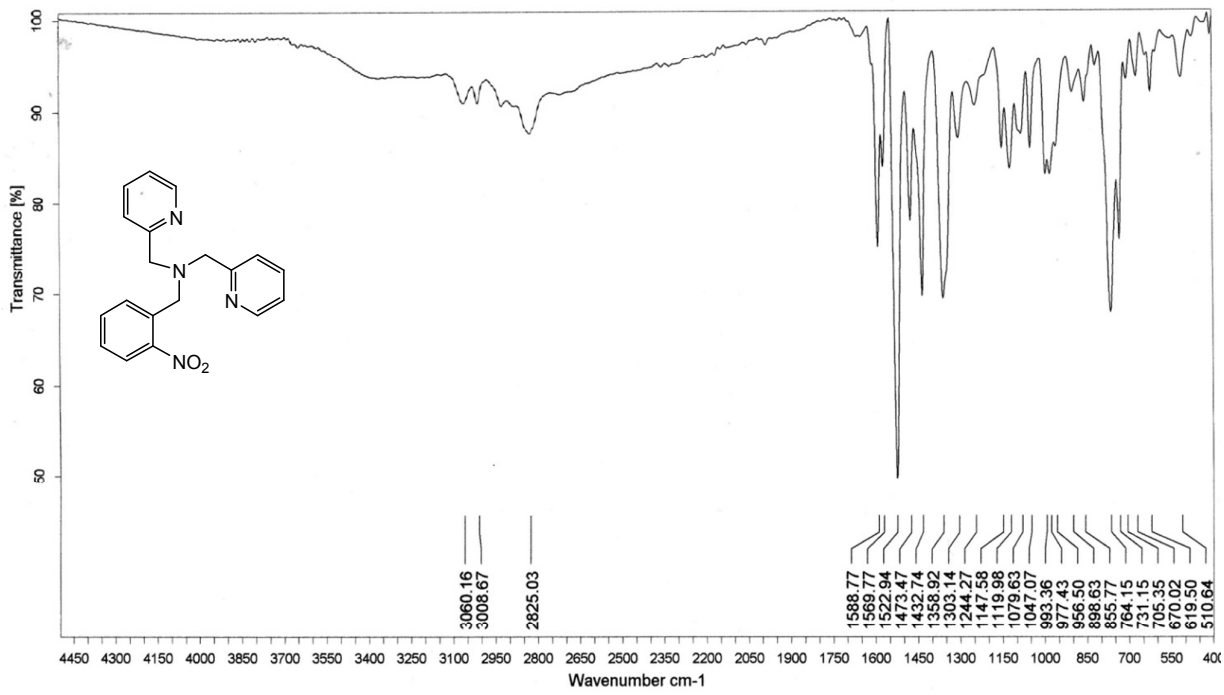


Figure S5: ^{1}H NMR ($CDCl_3$) of andmpa ligand at 25 °C (300 MHz)

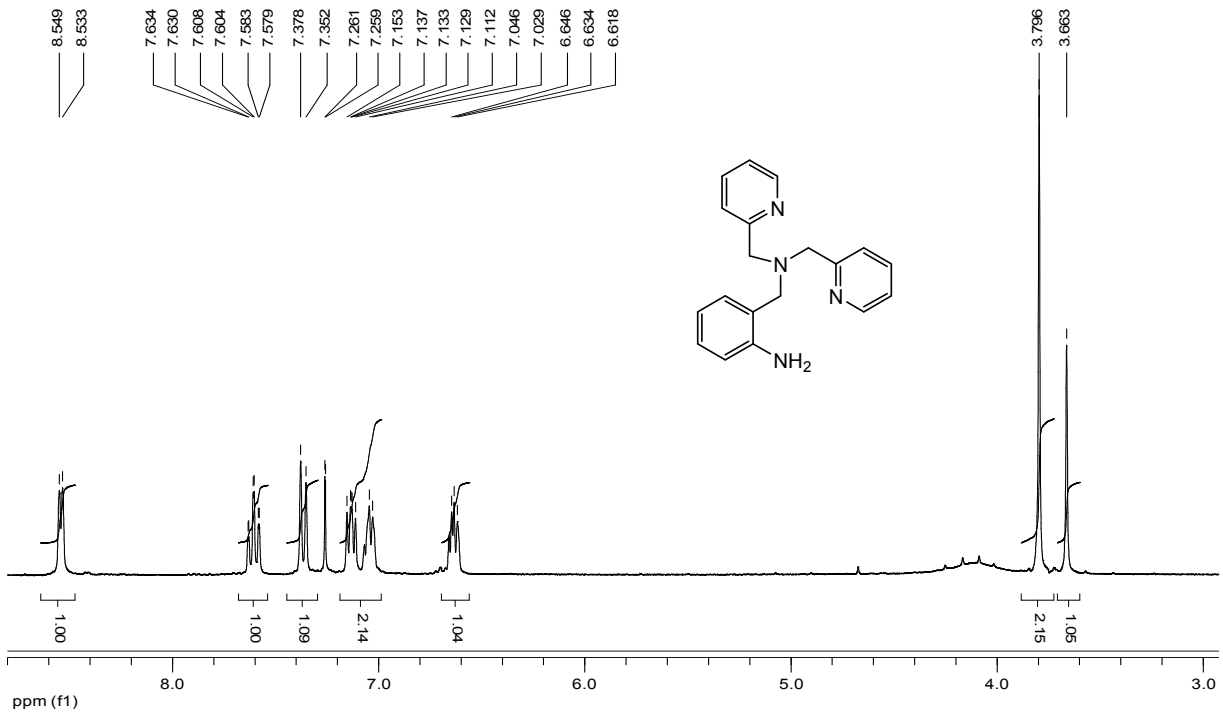


Figure S6: ^{13}C NMR ($CDCl_3$) of andmpa ligand at 25 °C (300 MHz)

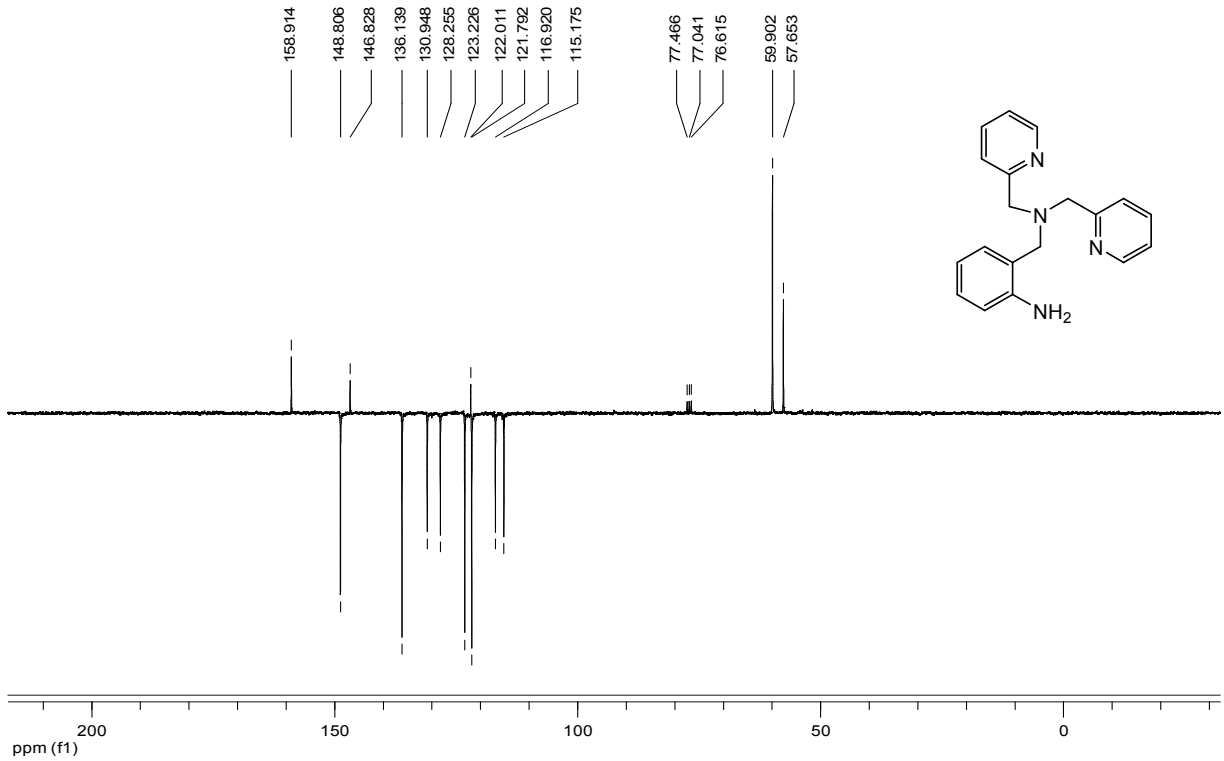


Figure S7: IR spectrum of andmpa ligand

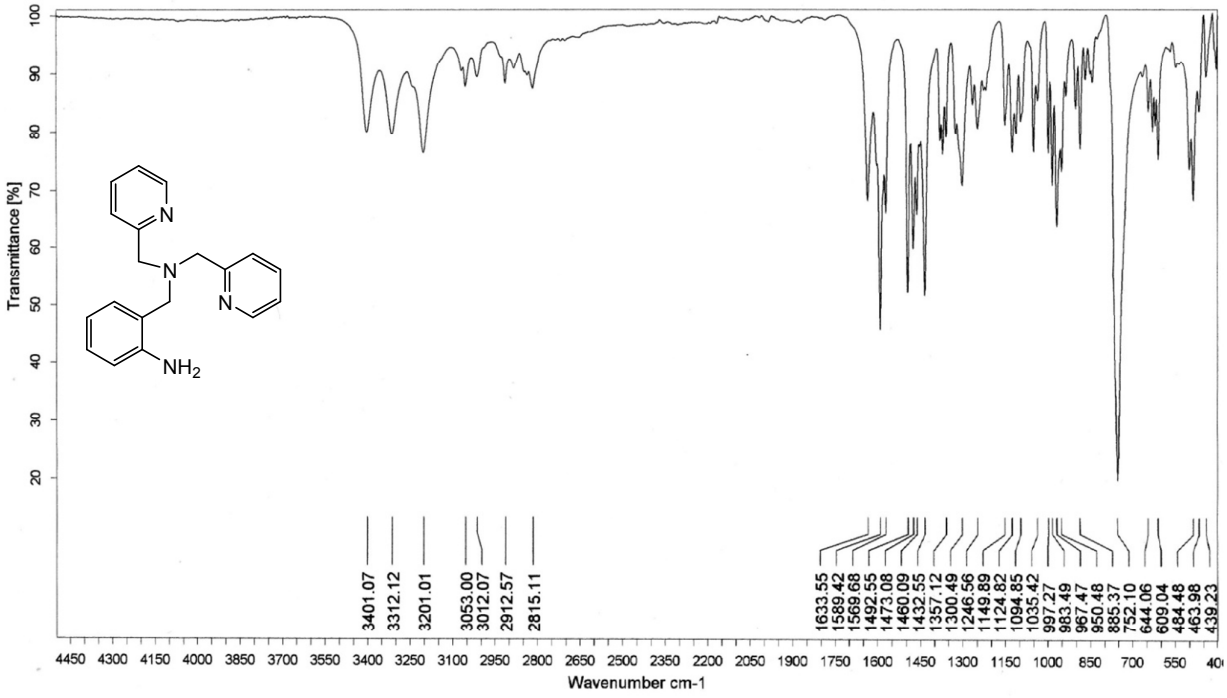


Figure S8 : TGA analysis of compound **2.MeOH.** The sample starts to lose weight from ca. 65°C and loses 2,7 % of its mass when heated up to 135 °C.

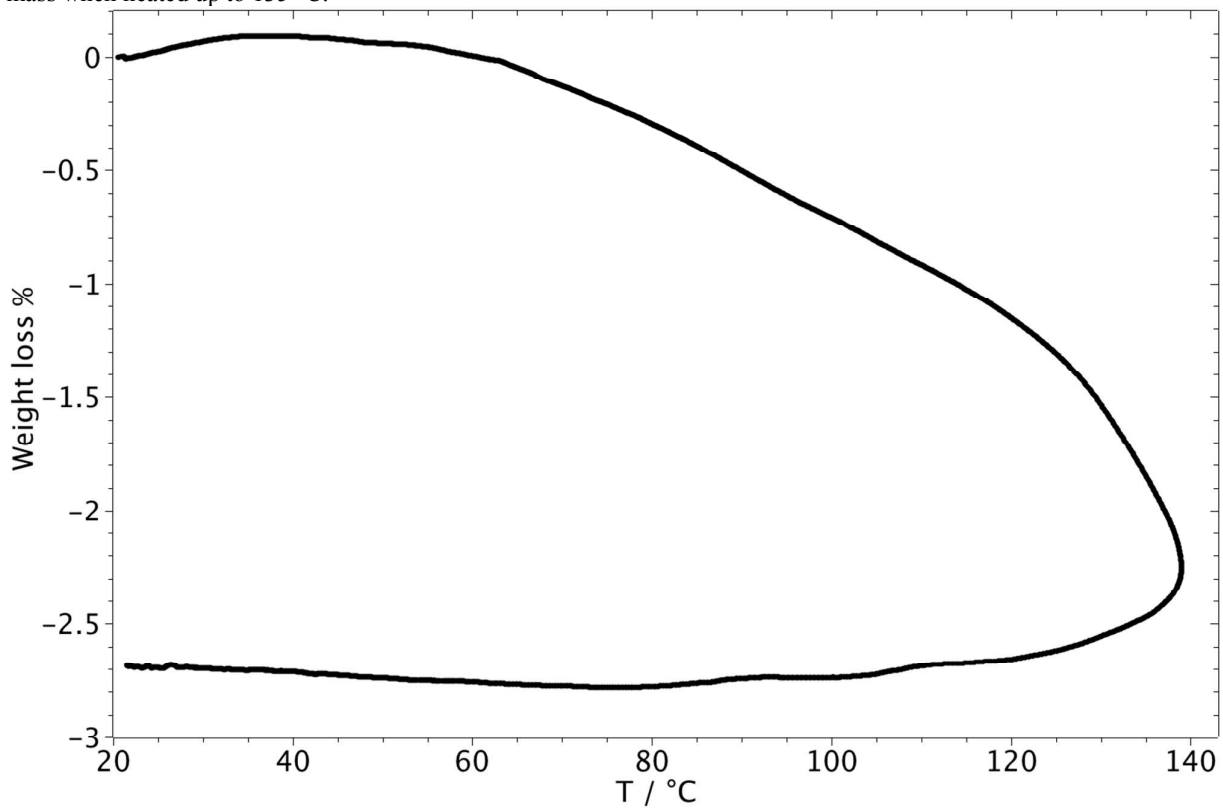
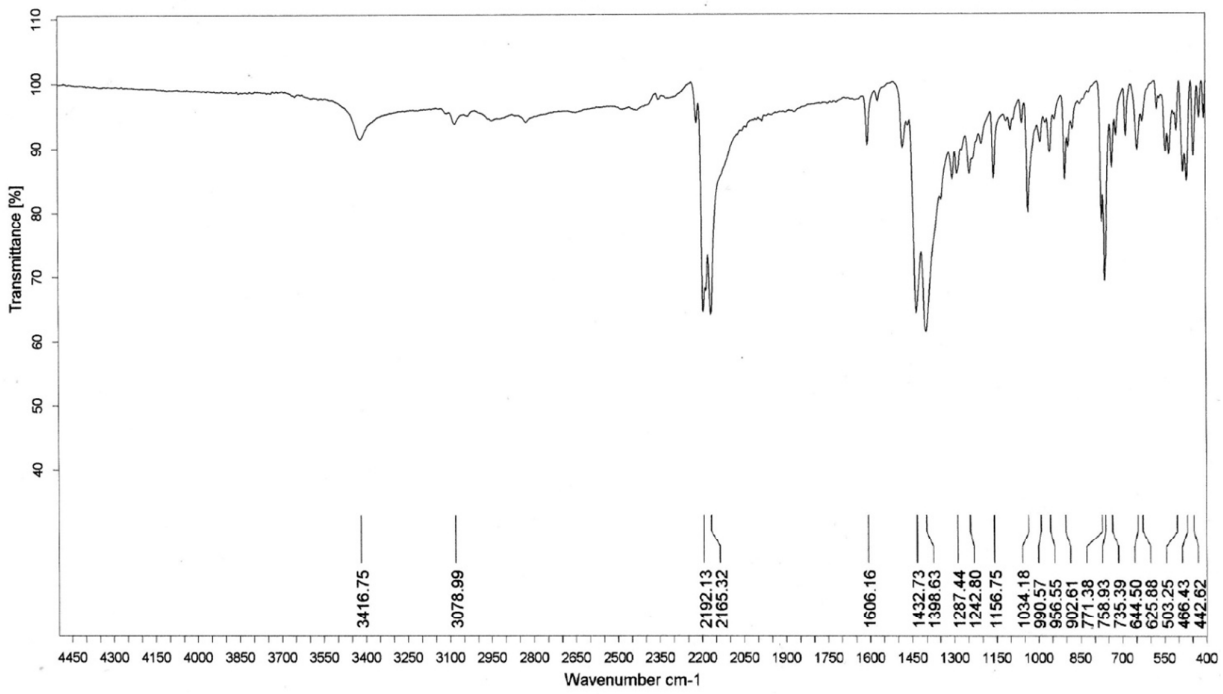
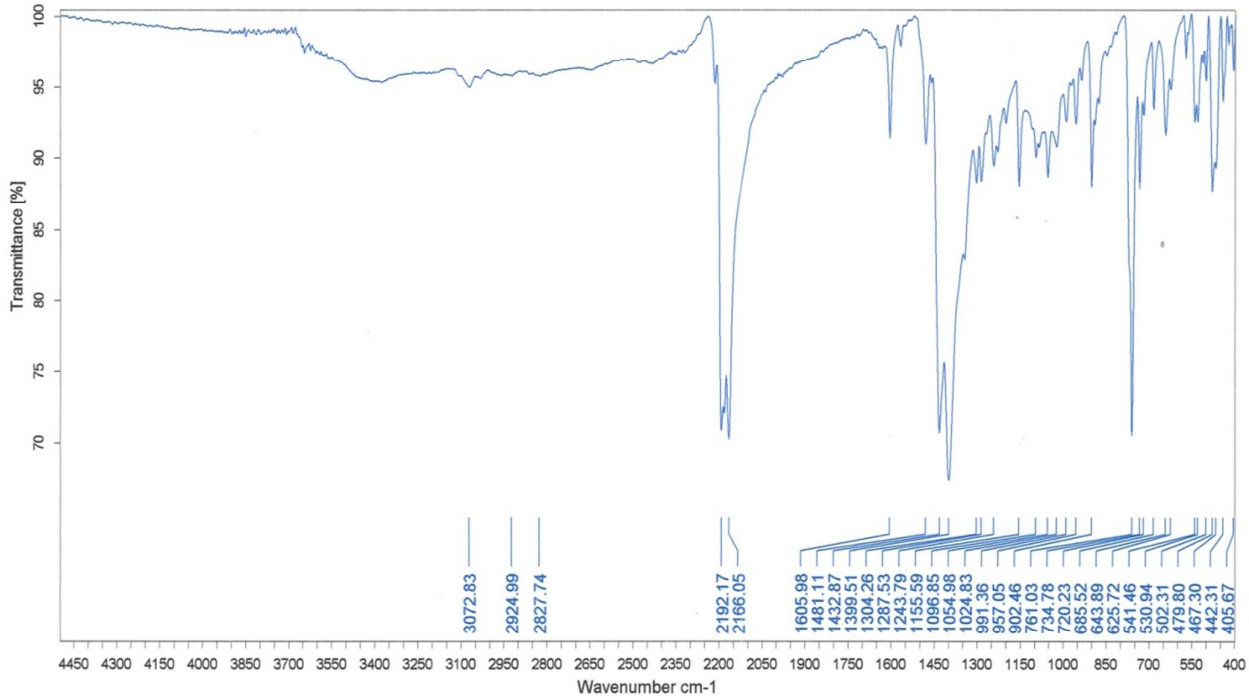


Figure S9: IR spectra of (**a**) $[Fe_2(tmpa)_2(\mu_2\text{-tcpd})_2]\bullet xCH_3OH$ (**1.MeOH**) and (**b**) $[Fe_2(tmpa)_2(\mu_2\text{-tcpd})_2]$ (**1**).

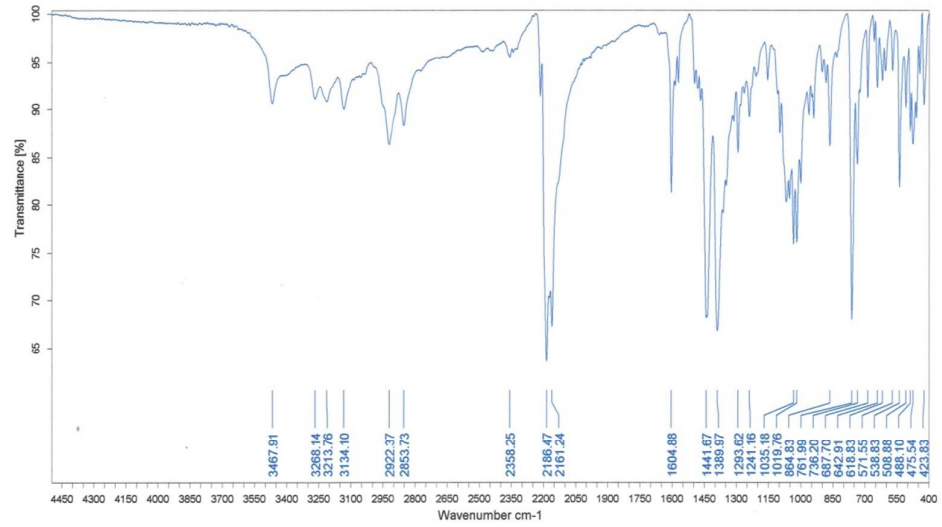


(**a**)

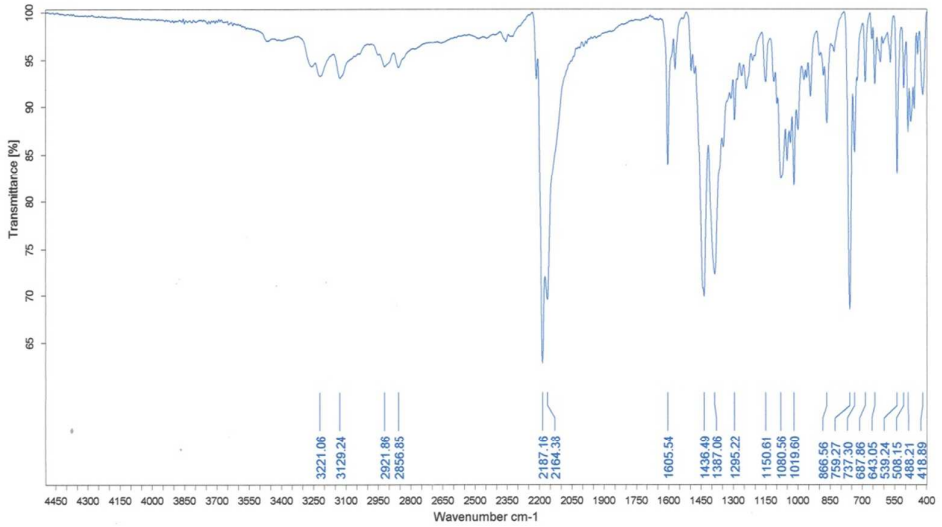


(**b**)

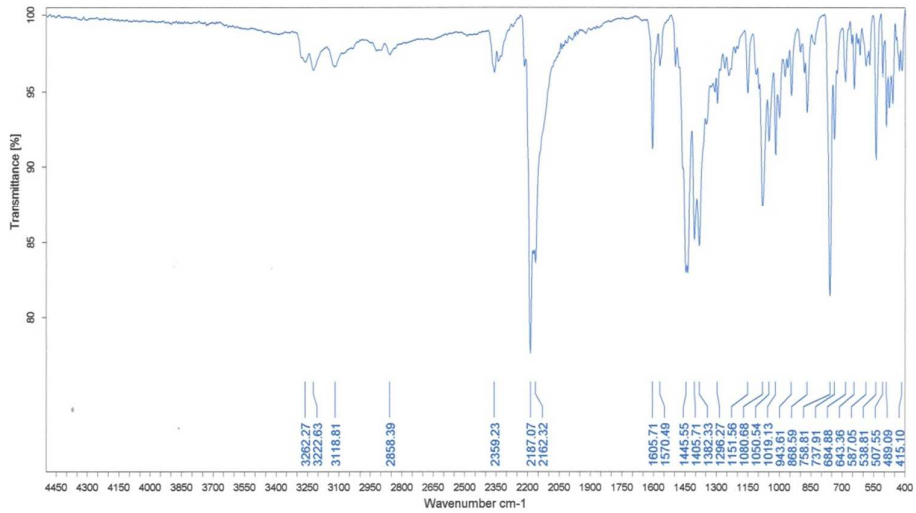
Figure S10: IR spectra of $[Fe_2(andmpa)_2(\mu_2\text{-}tcpd)_2]\bullet 2CH_3OH$ (**2.MeOH**) (**a**); $[Fe_2(andmpa)_2(\mu_2\text{-}tcpd)_2]$ (**2**) prepared at 100 °C (**b**) and at 150 °C (**c**).



(**a**)



(**b**)



(**c**)

Figure S11: Magnetic properties of compound **1** comparing the sweep and settle mode at a 1K/m, the temperature scan rate (top) and two temperature cycles (bottom).

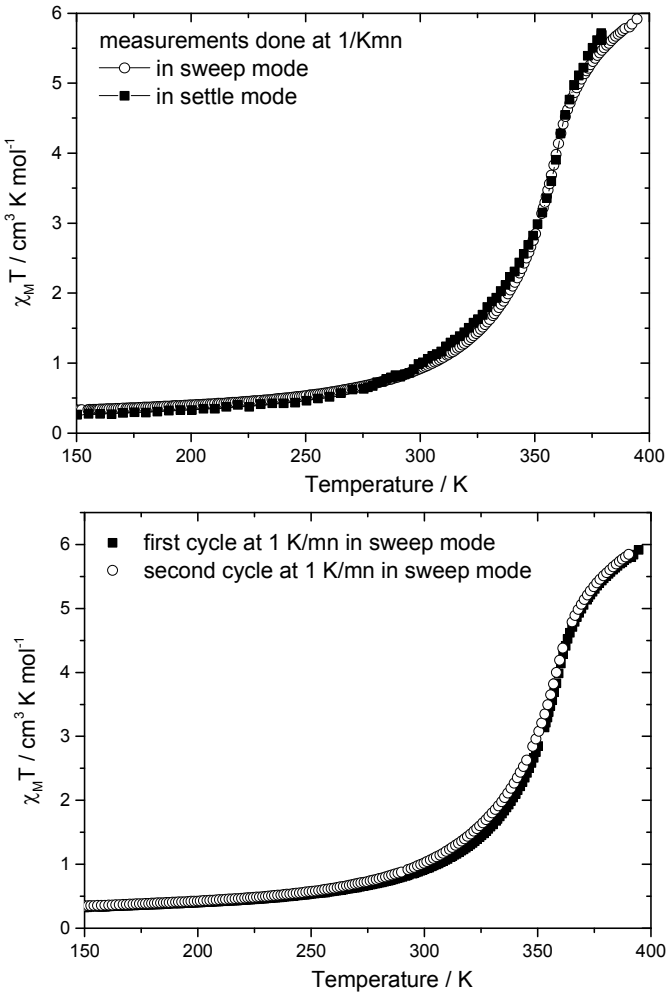


Figure S12: Magnetic properties of compound **2.MeOH** upon warming and cooling at 1 K/mn in settle mode.

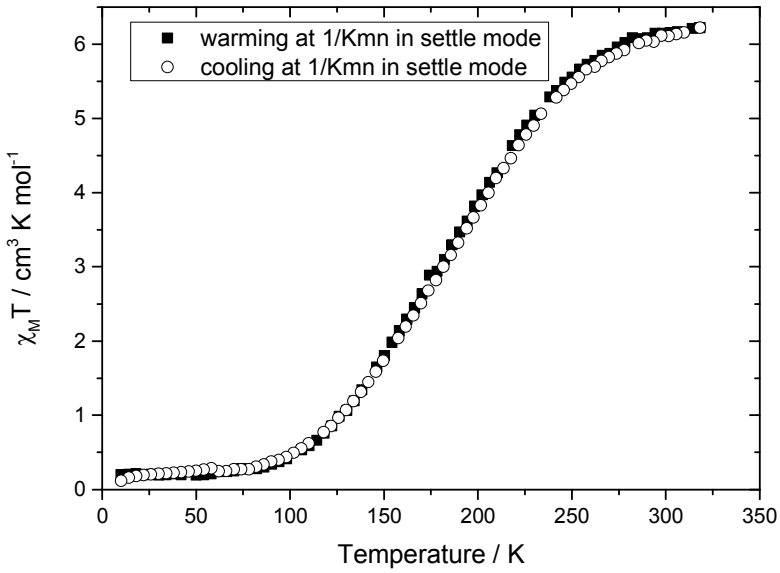


Figure S13: Magnetic properties of compound **2** upon warming and cooling at 1 K/mn in settle mode.

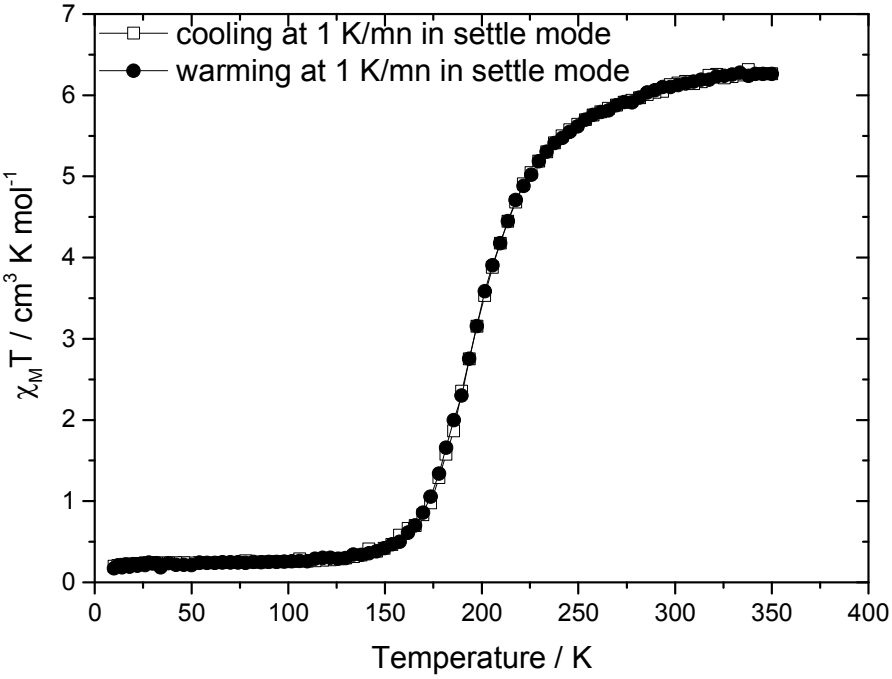


Figure S14: ^{1}H NMR ($CDCl_3$) of tmpa ligand

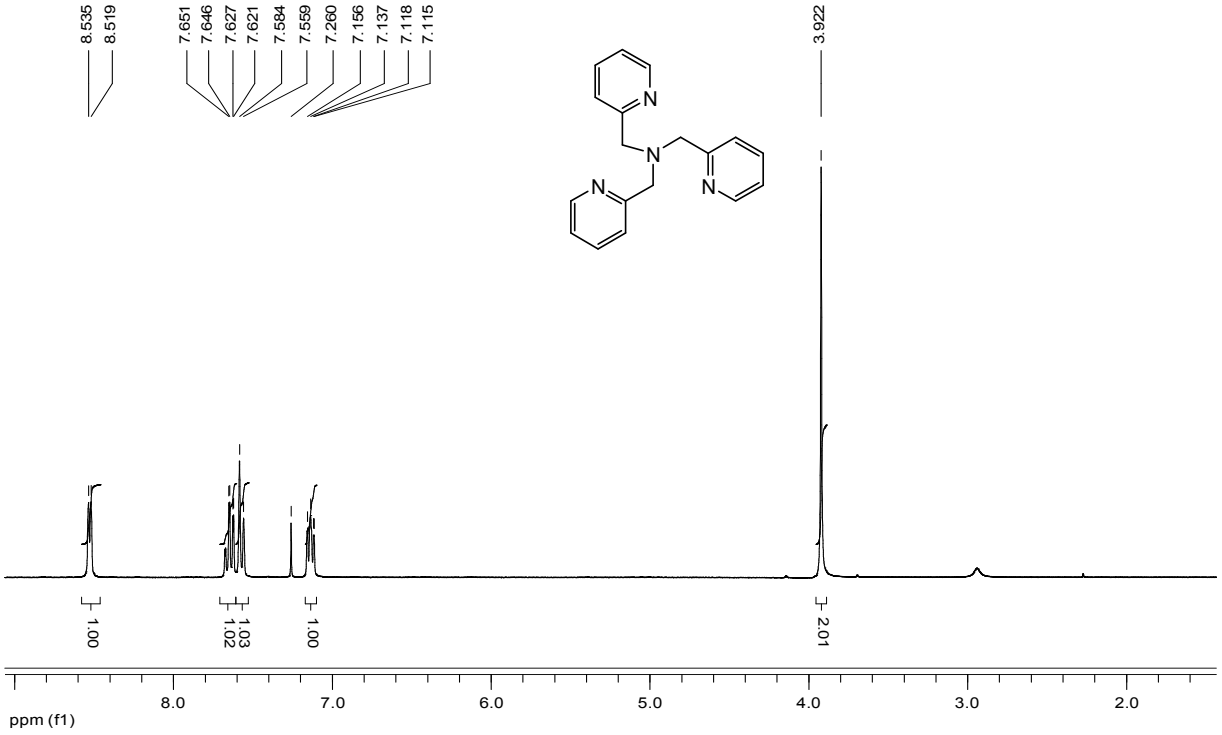


Figure S15: ^{13}C NMR ($CDCl_3$) of tmpa ligand

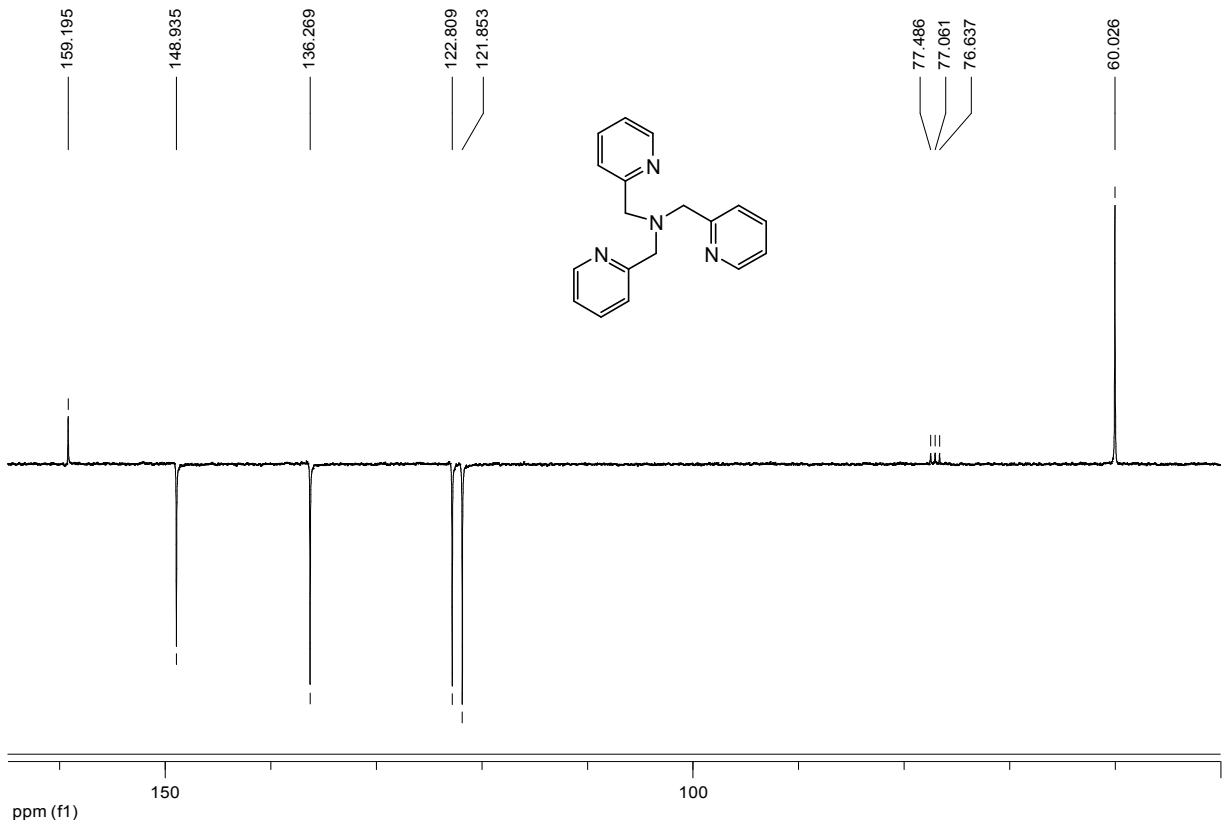


Figure S16: IR spectrum of tmpa ligand

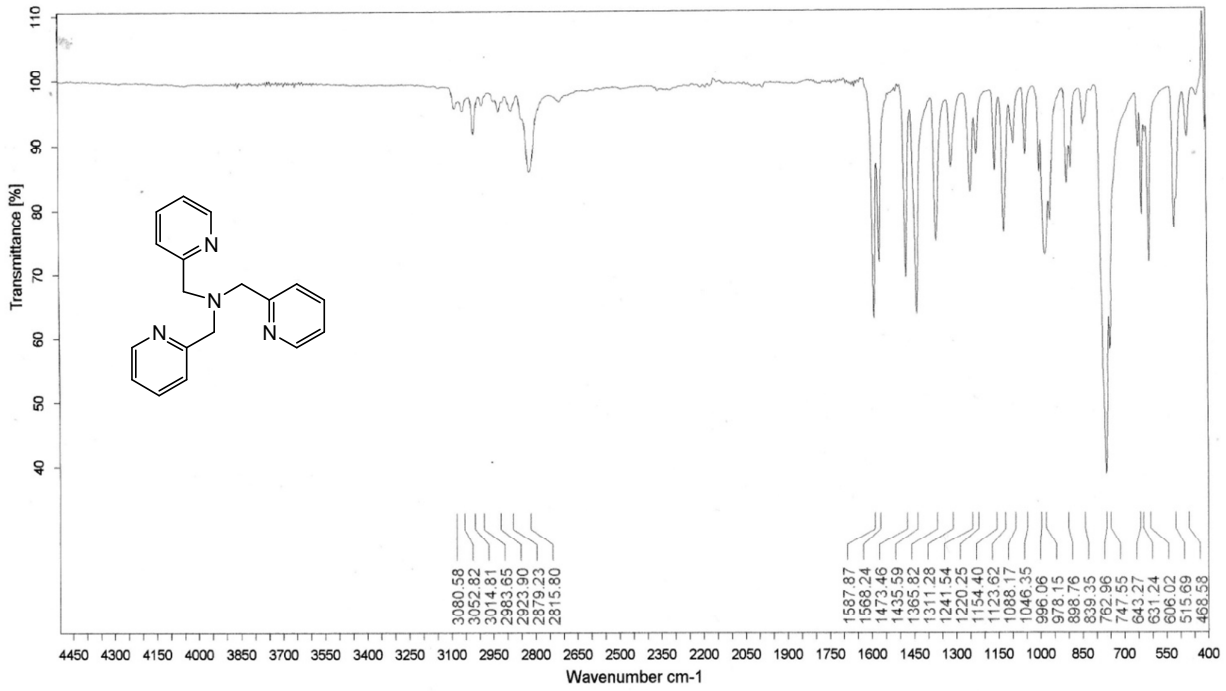


Table S1. Crystal data and structural refinement parameters for compounds **1.MeOH**, **1** and **2.MeOH**.

	1.MeOH	**1**		**2.MeOH**	
Temperature / K	296(2)	296(2)	380(2)	100(2)	296(2)
Empirical formula	$(C_{56}H_{36}Fe_2N_{20})$, $0.83(CH_3OH)$	$C_{56}H_{36}Fe_2N_{20}$		$(C_{58}H_{40}Fe_2N_{20})$, $2(CH_3OH)$	
Formula weight /g.mol^{-1}	1127.49	1100.75		1192.88	
Wavelength / Å	0.71073 Å	0.71073 Å		0.71073 Å	
Crystal system	Monoclinic	Monoclinic		Monoclinic	
Space group	$P2_1/n$	$P2_1/n$		$P2_1/n$	
a / Å	11.7269(5)	11.468(4)	10.894(4)	9.6690(10)	9.6831(12)
b / Å	16.6966(6)	17.0057(9)	18.7523(9)	24.658(2)	25.065(3)
c / Å	13.9317(6)	13.7743(6)	13.7750(6)	11.5670(10)	12.0485(16)
β /°	104.672(4)	105.098(9)	106.492(9)	102.631(6)	103.711(14)
Volume / Å^3	2638.87(19)	2593.6(10)	2698.3(11)	2691.0(4)	2840.9(7)
Z	2	2	2	2	2
D_{calc} / g.cm^{-3}	1.419	1.409	1.355	1.472	1.395
Abs. coef. / cm^{-1}	6.12	6.20	5.96	6.06	5.74
F(000)	1158	1128.0	1128.0	1232	1232
Crystal size / mm^3	0.22 x 0.15 x 0.11	0.2 × 0.15 × 0.1		0.28 x 0.07 x 0.06	
2θ range / °	6.664 - 50.496	7.196 - 50.504	7.104 - 50.502	7.03 - 50.504	6.894 - 50.502
Refl. collected	22679	17601	17702	18396	18091
Unique refl. / Rint	4765 / 0.0705	4688 / 0.0698	4844 / 0.1462	4864 / 0.1069	5120 / 0.1581
Data / restr. / N_v	4765/1/373	4688/0/352	4844/0/352	4864/0/389	5120/0/381
[b]R1/[c] wR2	0.0506 / 0.1366	0.0498 / 0.0798	0.0768 / 0.1485	0.0582 / 0.1400	0.0710/ 0.1270
[d]GooF	1.047	1.021	0.998	1.027	0.959
$\Delta\rho_{max/\,min}$ / eÅ^{-3}	+0.40 / -0.33	0.29/-0.25	0.28/-0.19	+1.00 / -0.63	+0.34 / -0.29
CCDC No.	1413422	1435809	1435810	1413424	1413423

[a]The asymmetric unit contains 0.5 of the chemical formula. [b]$R1 = \sum|F_o-F_c|/F_o$.
[c]$wR2= \{\Sigma[w(F_o^2-F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{1/2}$. [d]$GooF= \{\Sigma[w(F_o^2-F_c^2)^2]/ (N_{obs}-N_{var})\}^{1/2}$

Table S2. Selected bond lengths (Å), bond angles (°) and distortion parameters of the coordination sphere for **1.MeOH**, **1** and **2.MeOH**.

	1.MeOH	**1**		**2.MeOH**	
***T* / K**	**296**	**296**	**380**	**100**	**296**
Fe1-N1	1.985(2)	1.991(2)	2.191(4)	2.025(3)	2.232(4)
Fe1-N2	1.973(2)	1.973(2)	2.131(6)	1.973(3)	2.145(4)
Fe1-N3	1.966(2)	1.971(2)	2.149(5)	1.972(3)	2.136(4)
Fe1-N4	1.975(2)	1.973(2)	2.121(5)	2.068(3)	2.200(4)
Fe1-N5	1.949(3)	1.951(3)	2.118(6)	1.956(3)	2.149(4)
Fe1-N6[(a)]	1.939(3)	1.939(2)	2.055(5)	1.955(3)	2.100(4)
<Fe-N>	**1.965(3)**	**1.966(3)**	**2.128(5)**	**1.992(3)**	**2.160(4)**
N1-Fe1-N2	82.21(10)	82.16(10)	77.0(2)	81.30(12)	76.14(16)
N1-Fe1-N3	85.22(11)	85.13(10)	80.1(2)	84.68(13)	79.57(16)
N1-Fe1-N4	84.36(10)	83.85(10)	78.3(2)	90.95(13)	86.53(15)
N1-Fe1-N5	92.88(10)	93.58(10)	96.0(2)	95.87(12)	97.94(16)
N1-Fe1-N6[(a)]	177.91(10)	178.42(10)	175.8(2)	177.66(13)	173.21(17)
N2-Fe1-N3	93.11(10)	94.22(10)	97.31(18)	95.67(12)	95.62(15)
N2-Fe1-N4	166.42(11)	165.84(11)	155.0(2)	171.69(14)	161.50(15)
N2-Fe1-N5	89.14(10)	88.53(10)	87.4(2)	88.07(12)	86.95(16)
N2-Fe1-N6[(a)]	95.94(10)	96.44(10)	100.6(2)	97.07(12)	99.45(17)
N3-Fe1-N4	87.78(10)	86.76(10)	82.16(17)	86.56(13)	87.41(15)
N3-Fe1-N5	176.82(10)	176.77(10)	172.99(19)	176.26(12)	175.85(16)
N3-Fe1-N6[(a)]	95.87(10)	95.73(10)	97.0(2)	93.83(12)	95.89(16)
N4-Fe1-N5	89.50(10)	90.16(10)	91.37(19)	89.73(13)	89.13(15)
N4-Fe1-N6[(a)]	97.45(10)	97.52(10)	104.3(2)	90.76(13)	98.37(15)
N5-Fe1-N6[(a)]	86.12(9)	85.63(10)	87.24(19)	85.74(12)	86.88(15)
Distorsion					
[b]Σ(Fe1) (°)	51(2)	56(2)	94(3)	48(2)	75(2)
[c]Θ(Fe1) (°)	133(3)	143(3)	248(5)	141(4)	214(4)

(a) = 1-x,-y,-z+2 (**1**) or -x,-y+1,-z+1 (**2**)