Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information to

Benchmarking magnetic and spectroscopic properties on highly stable 3d metal complexes with tunable bisheterocyclomethanide ligands

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S1 Crystallographic data

The diffraction data were collected using an Incoatec Mo Microsource[1] and a Bruker Apex II detector. The data were integrated with SAINT.[2] A multi-scan absorption correction was applied using SADABS[3], respectively. For structures **1b**, **2b**, **3b**, and **4b** a 3 λ correction was applied.[4] The structures were solved by SHELXT[5] and refined on F^2 using SHELXL[6] in the graphical user interface ShelXle.[7] An overview of the crystallographic data can be found in Table **S1a** and **S1b**, while individual bond lengths and angles are listed in Table **S2a – S5a** for **1a -4a** and **S2b – S5b** for **1b-4b** respectively.

Table S1a. Crystal data and structure refinement for compounds **1a – 4a** at 100(2) K.

Compound	**1a**	**2a**	**3a**	**4a**
CCDC	2095985	2095986	2095987	2095988
Empirical Formula	$C_{38}H_{34}MnN_4O_6$	$C_{38}H_{34}FeN_4O_6$	$C_{30}H_{18}CoN_4O_4$	$C_{30}H_{18}NiN_4O_4$
Formula weight	697.63	698.54	557.41	557.19
Temperature (K)	100(2) K	100(2) K	100(2) K	100(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c	$P2_1/n$	$P2_1/n$
a (Å)	36.870(4)	36.725(3)	20.023(3)	19.760(3)
b (Å)	8.799(2)	8.803(2	7.758(2)	7.758(2)
c (Å)	22.995(3)	23.004(2)	31.980(4)	32.276(3)
β (deg)	119.49(3)	119.97(2)	102.30(2)	102.250(2)
V (Å^3)	6494(2)	6443(2)	4853.7(16)	4835.2(16)
Z	8	8	8	8
μ (mm^{-1})	0.462	0.524	0.754	0.850
Crystal size(mm)	0.332 · 0.233 · 0.218	0.450 · 0.347 · 0.061	0.245 · 0.143 · 0.118	0.234 · 0.132 · 0.050
Θ max (deg)	26.497	26.043	27.526	25.349

Reflections collected	56345	88097	135554	71101
Independent reflections	6684	6361	11334	8859
R_{int}	0.0393	0.0610	0.0999	0.0726
Data/restraints/parameters	6684 / 146 / 487	6361 / 146 / 487	11334 / 0 / 704	8859 / 0 / 703
$R1^a$ ($I > 2\sigma(I)$)	0.0308	0.0311	0.0615	0.0988
$wR2^b$(all data)	0.0822	0.0703	0.1584	0.1998
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	0.301/-0.328	0.298/-0.347	1.218/-1.158	1.067/-1.446
Shape and color	light green blocks	yellow needles	red needles	dark green needles

$^a R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $^b wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma(F_0^2)^2]^{1/2}$

Table S1b. Crystal data and structure refinement for compounds **1b – 4b** at 100 (2) K.

Compound	**1b**	**2b**	**2b'**	**3b**	**4b**
CCDC	2095989	2095990	2095991	2095992	2095993
Empirical Formula	$C_{42}H_{42}MnN_4O_6$	$C_{42}H_{42}FeN_4O_6$	$C_{34}H_{26}FeN_4O_4$	$C_{34}H_{26}CoN_4O_4$	$C_{34}H_{26}NiN_4O_4$
Formula weight	753.73	754.64	610.44	613.52	613.30
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.886(2)	9.930(2)	11.299(2)	11.174(2)	11.207(2)
b (Å)	12.349(2)	12.250(2)	14.937(2)	14.946(2)	14.891(3)
c (Å)	14.910(3)	14.847(3)	16.803(3)	16.818(3)	16.859(3)
α (deg)	88.59(2)	88.59(2)	90	90	90
β (deg)	88.40(2)	89.09(2)	93.65(2)	93.62 (2)	93.74(3)
γ (deg)	87.210(2)	87.26(2)	90	90	90
V (Å^3)	1816.9(6)	1803.2(6)	2830.1(8)	2803.1(9)	2807.5(9)
Z	2	2	4	4	4
μ/mm^{-1}	0.419	0.474	0.580	0.660	0.739
Crystal size(mm)	0.278 x 0.237 x 0.103	0.442 x 0.268 x 0.196	0.408 x 0.323 x 0.262	0.183 x 0.160 x 0.108	0.350 x 0.247 x 0.198
Θ max (deg)	28.402	30.950	28.350	30.773	30.685
Reflections collected	89253	150733	54594	98624	85389
Independent reflections	9072	11339	7045	8715	8686
R_{int}	0.0678	0.0415	0.0272	0.0637	0.0425

Data/restraints/parameters	9072 / 0 / 482	11339 / 0 / 482	7045 / 0 / 392	8715 / 0 / 392	8686 / 0 / 392
$R1^a$ ($I > 2\sigma(I)$)	0.0341	0.0353	0.0271	0.0395	0.0394
$wR2^b$(all data)	0.0826	0.0929	0.0719	0.0943	0.0957
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	0.371 / -0.372	0.576 / -0.359	0.367 / -0.294	0.486 / -0.489	0.451 / -0.601
Shape and color	Yellow blocks	red-orange blocks	Red blocks	Orange-red blocks	Blue blocks

$^a R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $^b wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma(F_0^2)^2]^{1/2}$

General procedures for processing XRD data

Applied methods to determine twist angles : Twist Angles are the angles between the N(1)N(2)C(2) and N(3)N(4)C(5), and between the N(3)N(4)C(32) and N(6)N(5)C(35) moieties. To determine the twist angles of the ligands, two planes were constructed through both benzoxazole moiety. For the first ligand one plane was constructed through N1, C2, and N2, and a second plane through N3, C5, and N4. For **3a** and **4a** additional planes were constructed through N5 C32, and N6 and a second plane through N7, C35, and N8. SHELXL[6] was then used to calculate the angles between these two planes, or rather four planes for **3a** and **4a**.

Crystal structure **1a**

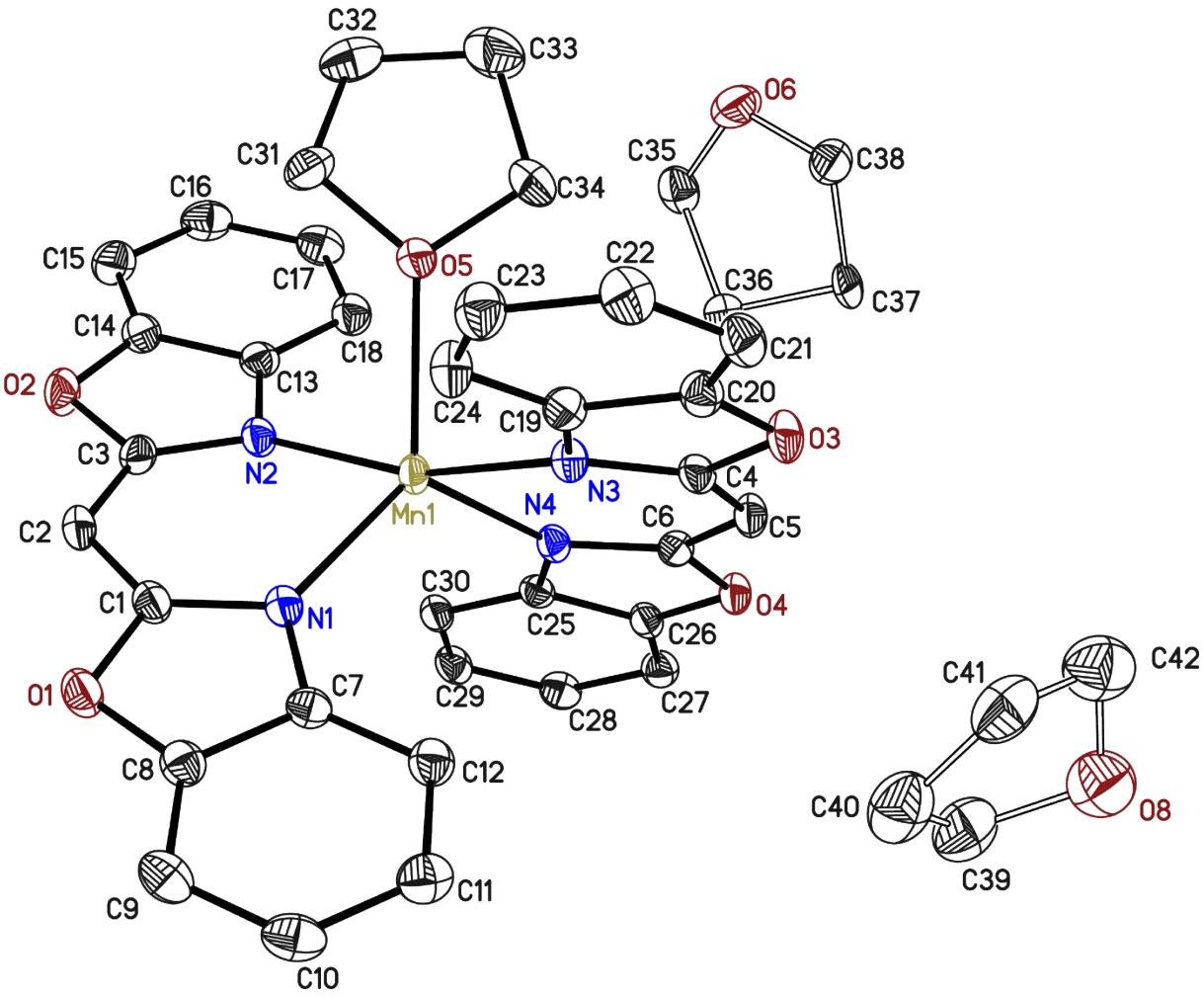

Figure S1: Molecular structure of **1a**. Hydrogen atoms are omitted for clarity and ADPs are depicted at 50% probability level.

The asymmetric unit contains one complex molecule with one thf molecules attached to the Mn(II) metal center. Additional, two thf molecules are found in the crystal lattice, disordered about symmetry elements.. They are refined with distance restraints and restraints for the anisotropic displacement parameters.

Table S2a: Bond lengths (Å) and angles (°) for **1a**.

Mn(1)-N(4)	2.1368(15)	C(20)-C(19)-N(3)	108.31(14)
Mn(1)-N(1)	2.1447(15)	C(24)-C(19)-N(3)	131.81(15)
Mn(1)-N(2)	2.1486(13)	C(1)-N(1)-C(7)	105.50(13)
Mn(1)-N(3)	2.1588(13)	C(1)-N(1)-Mn(1)	124.22(11)
Mn(1)-O(5)	2.2507(13)	C(7)-N(1)-Mn(1)	129.96(10)
O(1)-C(8)	1.385(2)	C(1)-C(2)-C(3)	121.73(15)
O(1)-C(1)	1.385(2)	C(34)-C(33)-C(32)	105.37(16)
C(1)-N(1)	1.343(2)	C(30)-C(29)-C(28)	121.93(15)
C(1)-C(2)	1.385(2)	C(29)-C(28)-C(27)	121.23(16)
C(34)-O(5)	1.439(2)	C(3)-N(2)-C(13)	105.82(13)
C(34)-C(33)	1.518(3)	C(3)-N(2)-Mn(1)	123.74(11)
C(19)-C(20)	1.389(2)	C(13)-N(2)-Mn(1)	127.38(10)
C(19)-C(24)	1.389(2)	C(3)-O(2)-C(14)	105.41(12)
C(19)-N(3)	1.398(2)	C(4)-N(3)-C(19)	105.81(13)
N(1)-C(7)	1.402(2)	C(4)-N(3)-Mn(1)	125.49(11)
C(2)-C(3)	1.388(2)	C(19)-N(3)-Mn(1)	127.72(11)
C(33)-C(32)	1.525(3)	C(4)-O(3)-C(20)	105.17(12)
C(29)-C(30)	1.392(2)	N(2)-C(3)-O(2)	112.42(14)
C(29)-C(28)	1.395(2)	N(2)-C(3)-C(2)	129.71(15)
C(28)-C(27)	1.401(2)	O(2)-C(3)-C(2)	117.87(14)
N(2)-C(3)	1.334(2)	C(31)-C(32)-C(33)	102.88(15)
N(2)-C(13)	1.401(2)	N(3)-C(4)-O(3)	112.68(14)
O(2)-C(3)	1.3838(19)	N(3)-C(4)-C(5)	129.54(14)
O(2)-C(14)	1.385(2)	O(3)-C(4)-C(5)	117.77(14)
N(3)-C(4)	1.331(2)	O(5)-C(31)-C(32)	104.69(15)
O(3)-C(4)	1.3805(19)	C(6)-N(4)-C(25)	105.17(13)
O(3)-C(20)	1.386(2)	C(6)-N(4)-Mn(1)	125.64(11)
C(32)-C(31)	1.511(3)	C(25)-N(4)-Mn(1)	129.18(10)
C(4)-C(5)	1.391(2)	C(6)-O(4)-C(26)	105.58(12)
C(31)-O(5)	1.446(2)	C(7)-C(12)-C(11)	117.31(16)
N(4)-C(6)	1.3380(19)	N(4)-C(6)-O(4)	112.80(13)
N(4)-C(25)	1.406(2)	N(4)-C(6)-C(5)	130.12(15)
O(4)-C(6)	1.3767(19)	O(4)-C(6)-C(5)	117.07(13)
O(4)-C(26)	1.3846(18)	C(6)-C(5)-C(4)	121.93(14)
C(12)-C(7)	1.388(2)	C(34)-O(5)-C(31)	107.07(14)
C(12)-C(11)	1.394(2)	C(34)-O(5)-Mn(1)	123.73(11)
C(6)-C(5)	1.391(2)	C(31)-O(5)-Mn(1)	129.19(10)

C(9)-C(8)	1.371(2)	C(8)-C(9)-C(10)	115.86(16)
C(9)-C(10)	1.397(3)	C(11)-C(10)-C(9)	121.26(16)
C(10)-C(11)	1.390(3)	C(9)-C(8)-O(1)	127.87(15)
C(8)-C(7)	1.391(2)	C(9)-C(8)-C(7)	124.12(16)
C(18)-C(13)	1.387(2)	O(1)-C(8)-C(7)	108.00(14)
C(18)-C(17)	1.393(2)	C(10)-C(11)-C(12)	121.75(17)
C(15)-C(14)	1.373(2)	C(12)-C(7)-C(8)	119.70(15)
C(15)-C(16)	1.391(3)	C(12)-C(7)-N(1)	131.66(15)
C(14)-C(13)	1.389(2)	C(8)-C(7)-N(1)	108.61(14)
C(17)-C(16)	1.391(3)	C(13)-C(18)-C(17)	117.23(16)
C(24)-C(23)	1.389(2)	C(14)-C(15)-C(16)	116.18(16)
C(21)-C(20)	1.372(2)	C(15)-C(14)-O(2)	128.47(15)
C(21)-C(22)	1.394(2)	C(15)-C(14)-C(13)	123.55(16)
C(23)-C(22)	1.395(2)	O(2)-C(14)-C(13)	107.99(14)
C(25)-C(26)	1.389(2)	C(16)-C(17)-C(18)	121.54(17)
C(25)-C(30)	1.390(2)	C(15)-C(16)-C(17)	121.40(17)
C(26)-C(27)	1.371(2)	C(18)-C(13)-C(14)	120.10(16)
O(8)-C(42)	1.420(6)	C(18)-C(13)-N(2)	131.54(15)
O(8)-C(39)	1.435(10)	C(14)-C(13)-N(2)	108.36(14)
C(39)-C(40)	1.531(8)	C(23)-C(24)-C(19)	117.18(15)
C(40)-C(41)	1.534(11)	C(20)-C(21)-C(22)	115.94(15)
C(41)-C(42)	1.525(9)	C(21)-C(20)-O(3)	127.95(15)
O(6)-C(35)	1.409(10)	C(21)-C(20)-C(19)	124.02(16)
O(6)-C(38)	1.420(10)	O(3)-C(20)-C(19)	108.03(14)
C(35)-C(36)	1.530(11)	C(24)-C(23)-C(22)	121.89(16)
C(36)-C(37)	1.523(5)	C(21)-C(22)-C(23)	121.09(16)
C(37)-C(38)	1.528(11)	C(26)-C(25)-C(30)	119.93(15)
		C(26)-C(25)-N(4)	108.60(13)
N(4)-Mn(1)-N(1)	120.90(6)	C(30)-C(25)-N(4)	131.42(15)
N(4)-Mn(1)-N(2)	104.74(5)	C(27)-C(26)-O(4)	127.73(14)
N(1)-Mn(1)-N(2)	85.82(5)	C(27)-C(26)-C(25)	124.38(15)
N(4)-Mn(1)-N(3)	86.20(5)	O(4)-C(26)-C(25)	107.83(13)
N(1)-Mn(1)-N(3)	98.52(5)	C(26)-C(27)-C(28)	115.50(15)
N(2)-Mn(1)-N(3)	164.14(5)	C(25)-C(30)-C(29)	116.99(15)
N(4)-Mn(1)-O(5)	113.73(5)	C(42)-O(8)-C(39)	105.0(5)
N(1)-Mn(1)-O(5)	125.30(5)	O(8)-C(39)-C(40)	106.5(7)
N(2)-Mn(1)-O(5)	83.19(5)	C(39)-C(40)-C(41)	103.7(6)
N(3)-Mn(1)-O(5)	81.87(5)	C(42)-C(41)-C(40)	103.3(6)

C(8)-O(1)-C(1)	105.49(12)	O(8)-C(42)-C(41)	104.6(5)
N(1)-C(1)-C(2)	129.89(15)	C(35)-O(6)-C(38)	110.7(3)
N(1)-C(1)-O(1)	112.36(14)	O(6)-C(35)-C(36)	106.5(8)
C(2)-C(1)-O(1)	117.75(14)	C(37)-C(36)-C(35)	102.7(10)
O(5)-C(34)-C(33)	106.89(16)	C(36)-C(37)-C(38)	101.5(10)
C(20)-C(19)-C(24)	119.87(15)	O(6)-C(38)-C(37)	106.9(8)

Crystal structure **2a**

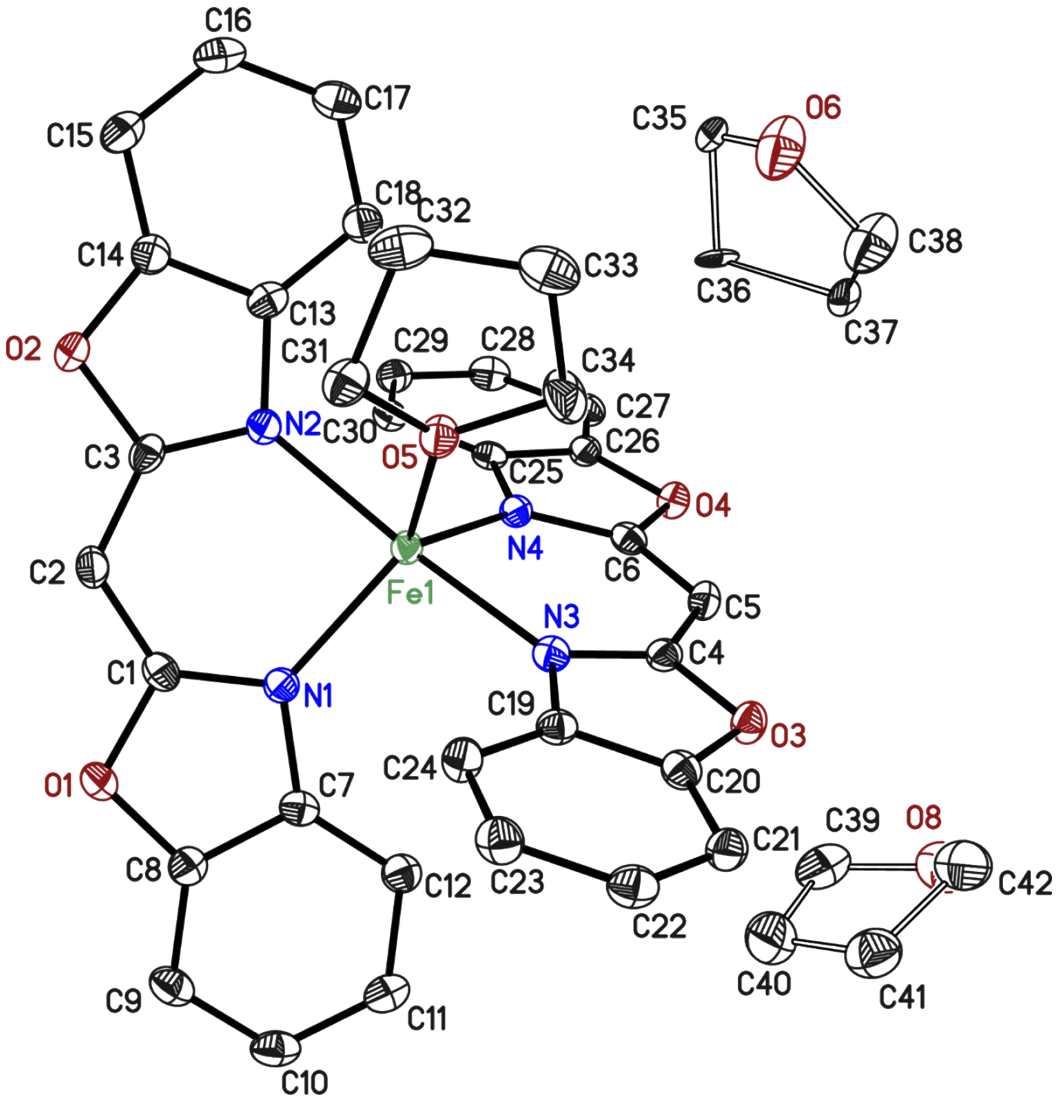

Figure S2: Molecular structure of **2a**. Hydrogen atoms are omitted for clarity and ADPs are depicted at 50% probability level.

The asymmetric unit contains one complex molecule with one thf molecules attached to the Fe(II) metal center. Additional, two thf molecules are found in the crystal lattice, disordered about symmetry elements, the C35-C38 unit about a 2-fold axes and the C39-C42 unit about an inversion center. They are refined with distance restraints and restraints for the anisotropic displacement parameters.

Table S3a: Bond lengths (Å) and angles (°) for **2a**

Fe(1)-N(4)	2.0837(15)	C(9)-C(8)	1.378(2)
Fe(1)-N(1)	2.0849(15)	C(9)-C(10)	1.396(3)
Fe(1)-N(2)	2.0959(14)	C(10)-C(11)	1.394(3)
Fe(1)-N(3)	2.1026(14)	C(8)-C(7)	1.392(2)
Fe(1)-O(5)	2.1778(13)	C(18)-C(13)	1.386(2)
O(1)-C(8)	1.384(2)	C(18)-C(17)	1.393(2)
O(1)-C(1)	1.390(2)	C(15)-C(14)	1.375(2)
C(1)-N(1)	1.343(2)	C(15)-C(16)	1.393(3)
C(1)-C(2)	1.385(2)	C(14)-C(13)	1.389(2)
C(34)-O(5)	1.442(2)	C(17)-C(16)	1.393(3)
C(34)-C(33)	1.523(3)	C(24)-C(23)	1.392(2)
C(19)-C(20)	1.384(2)	C(21)-C(20)	1.378(2)
C(19)-C(24)	1.390(2)	C(21)-C(22)	1.392(3)
C(19)-N(3)	1.405(2)	C(23)-C(22)	1.397(3)
N(1)-C(7)	1.407(2)	C(25)-C(26)	1.387(2)
C(2)-C(3)	1.389(2)	C(25)-C(30)	1.390(2)
C(33)-C(32)	1.529(3)	C(27)-C(26)	1.377(2)
C(29)-C(28)	1.394(3)	O(8)-C(42)	1.415(7)
C(29)-C(30)	1.397(2)	O(8)-C(39)	1.437(11)
C(28)-C(27)	1.395(3)	C(39)-C(40)	1.525(9)
N(2)-C(3)	1.333(2)	C(40)-C(41)	1.547(12)
N(2)-C(13)	1.408(2)	C(41)-C(42)	1.523(9)
O(2)-C(3)	1.385(2)	O(6)-C(38)	1.437(11)
O(2)-C(14)	1.390(2)	O(6)-C(35)	1.444(10)
N(3)-C(4)	1.331(2)	C(35)-C(36)	1.528(10)
O(3)-C(4)	1.382(2)	C(36)-C(37)	1.529(5)
O(3)-C(20)	1.388(2)	C(37)-C(38)	1.516(10)
C(32)-C(31)	1.516(3)		
C(4)-C(5)	1.392(2)	N(4)-Fe(1)-N(1)	117.18(6)
C(31)-O(5)	1.455(2)	N(4)-Fe(1)-N(2)	103.45(5)
N(4)-C(6)	1.343(2)	N(1)-Fe(1)-N(2)	87.14(6)
N(4)-C(25)	1.412(2)	N(4)-Fe(1)-N(3)	87.22(5)
O(4)-C(6)	1.377(2)	N(1)-Fe(1)-N(3)	98.07(5)
O(4)-C(26)	1.387(2)	N(2)-Fe(1)-N(3)	164.49(6)
C(12)-C(7)	1.393(2)	N(4)-Fe(1)-O(5)	115.86(5)
C(12)-C(11)	1.396(2)	N(1)-Fe(1)-O(5)	126.91(5)
C(6)-C(5)	1.390(2)	N(2)-Fe(1)-O(5)	82.96(5)

N(3)-Fe(1)-O(5)	82.25(5)	N(4)-C(6)-C(5)	130.05(15)
C(8)-O(1)-C(1)	105.39(13)	O(4)-C(6)-C(5)	116.95(15)
N(1)-C(1)-C(2)	129.86(16)	C(6)-C(5)-C(4)	121.14(16)
N(1)-C(1)-O(1)	112.33(14)	C(34)-O(5)-C(31)	107.19(13)
C(2)-C(1)-O(1)	117.81(15)	C(34)-O(5)-Fe(1)	123.50(11)
O(5)-C(34)-C(33)	106.73(16)	C(31)-O(5)-Fe(1)	129.30(10)
C(20)-C(19)-C(24)	119.91(16)	C(8)-C(9)-C(10)	115.87(17)
C(20)-C(19)-N(3)	108.52(15)	C(11)-C(10)-C(9)	121.34(17)
C(24)-C(19)-N(3)	131.56(16)	C(9)-C(8)-O(1)	127.59(16)
C(1)-N(1)-C(7)	105.57(14)	C(9)-C(8)-C(7)	124.11(17)
C(1)-N(1)-Fe(1)	123.66(11)	O(1)-C(8)-C(7)	108.29(14)
C(7)-N(1)-Fe(1)	130.18(11)	C(10)-C(11)-C(12)	121.73(17)
C(1)-C(2)-C(3)	120.93(16)	C(8)-C(7)-C(12)	119.55(16)
C(34)-C(33)-C(32)	105.26(16)	C(8)-C(7)-N(1)	108.38(15)
C(28)-C(29)-C(30)	122.00(16)	C(12)-C(7)-N(1)	132.05(16)
C(29)-C(28)-C(27)	121.21(16)	C(13)-C(18)-C(17)	117.32(17)
C(3)-N(2)-C(13)	105.33(14)	C(14)-C(15)-C(16)	116.04(17)
C(3)-N(2)-Fe(1)	123.67(11)	C(15)-C(14)-C(13)	123.68(17)
C(13)-N(2)-Fe(1)	128.31(11)	C(15)-C(14)-O(2)	128.31(16)
C(3)-O(2)-C(14)	105.07(13)	C(13)-C(14)-O(2)	108.01(15)
C(4)-N(3)-C(19)	105.22(14)	C(18)-C(17)-C(16)	121.58(17)
C(4)-N(3)-Fe(1)	126.25(11)	C(17)-C(16)-C(15)	121.30(17)
C(19)-N(3)-Fe(1)	127.84(11)	C(18)-C(13)-C(14)	120.07(16)
C(4)-O(3)-C(20)	104.77(13)	C(18)-C(13)-N(2)	131.36(16)
N(2)-C(3)-O(2)	113.02(15)	C(14)-C(13)-N(2)	108.57(15)
N(2)-C(3)-C(2)	129.14(16)	C(19)-C(24)-C(23)	117.18(17)
O(2)-C(3)-C(2)	117.84(15)	C(20)-C(21)-C(22)	115.81(16)
C(31)-C(32)-C(33)	103.26(15)	C(21)-C(20)-C(19)	124.14(16)
N(3)-C(4)-O(3)	113.24(14)	C(21)-C(20)-O(3)	127.61(16)
N(3)-C(4)-C(5)	128.75(16)	C(19)-C(20)-O(3)	108.25(14)
O(3)-C(4)-C(5)	118.01(15)	C(24)-C(23)-C(22)	121.75(17)
O(5)-C(31)-C(32)	104.06(14)	C(21)-C(22)-C(23)	121.21(17)
C(6)-N(4)-C(25)	104.84(13)	C(26)-C(25)-C(30)	119.89(15)
C(6)-N(4)-Fe(1)	125.46(11)	C(26)-C(25)-N(4)	108.62(14)
C(25)-N(4)-Fe(1)	129.69(11)	C(30)-C(25)-N(4)	131.44(15)
C(6)-O(4)-C(26)	105.44(13)	C(26)-C(27)-C(28)	115.67(16)
C(7)-C(12)-C(11)	117.39(16)	C(27)-C(26)-O(4)	127.57(15)
N(4)-C(6)-O(4)	112.99(14)	C(27)-C(26)-C(25)	124.30(16)

O(4)-C(26)-C(25)	108.07(14)	C(38)-O(6)-C(35)	109.2(5)
C(25)-C(30)-C(29)	116.91(16)	O(6)-C(35)-C(36)	103.4(8)
C(42)-O(8)-C(39)	104.8(5)	C(35)-C(36)-C(37)	101.9(9)
O(8)-C(39)-C(40)	106.6(7)	C(38)-C(37)-C(36)	102.9(10)
C(39)-C(40)-C(41)	103.9(6)	O(6)-C(38)-C(37)	107.4(8)
C(42)-C(41)-C(40)	102.4(7)		
O(8)-C(42)-C(41)	105.3(6)		

Crystal structure of **3a**

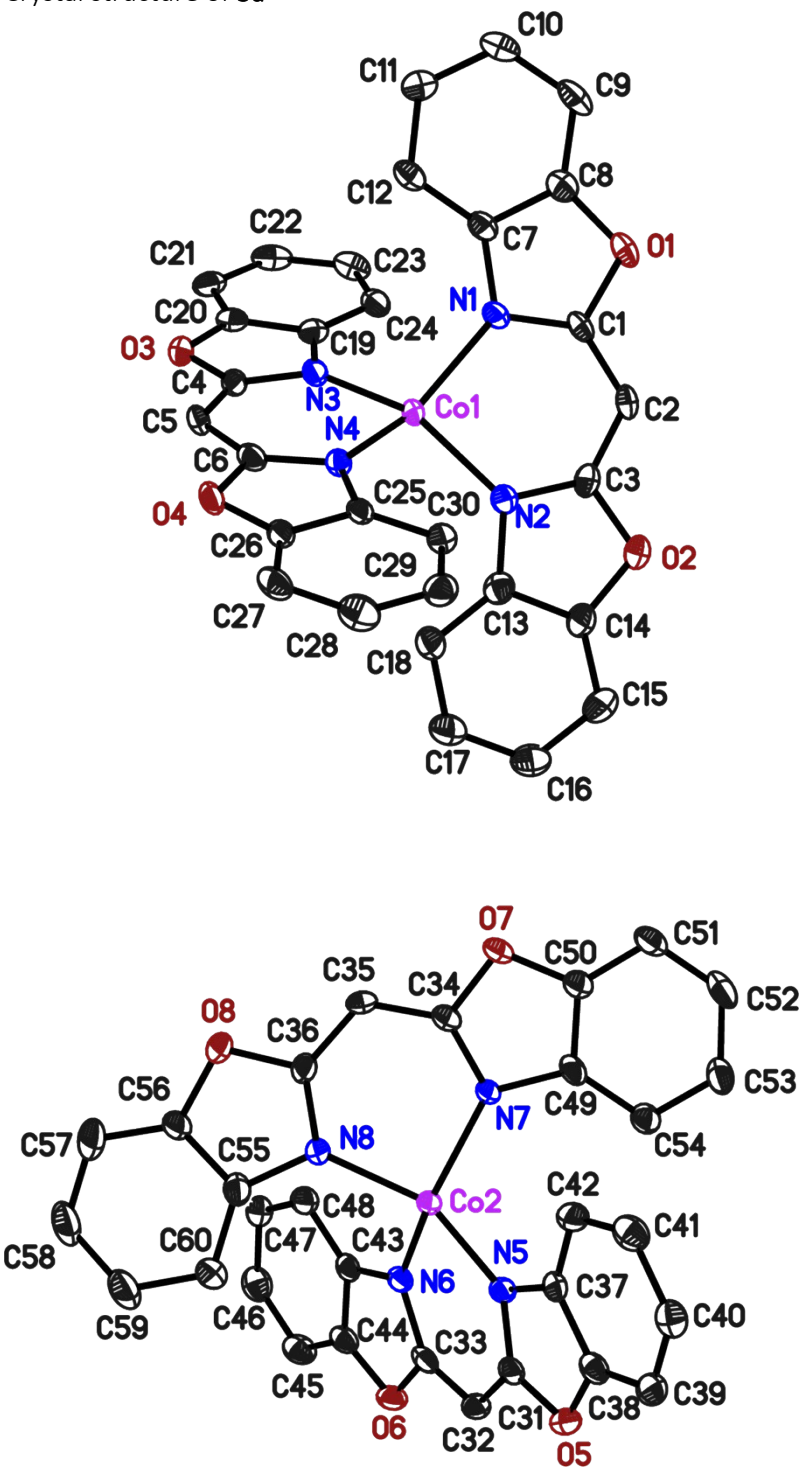

Figure S3: Molecular structure of **3a**. Hydrogen atoms are omitted for clarity and ADPs are depicted at 50% probability level.

The asymmetric unit contains two complex molecules and no solvent molecules. The measured crystal was non-merohedrally twinned with the twin law 1 0 0 0 -1 0 -0.68 0 -1. The fractional contribution refines to 0.0515(6).

Table S4a: Bond lengths (Å) and angles (°) for **3a.**

Co(1)-N(3)	1.977(3)	N(7)-C(49)	1.407(4)
Co(1)-N(2)	1.983(3)	O(7)-C(50)	1.384(4)
Co(1)-N(4)	1.987(3)	O(7)-C(34)	1.384(4)
Co(1)-N(1)	1.989(3)	C(7)-C(12)	1.378(5)
C(1)-N(1)	1.341(4)	C(7)-C(8)	1.393(5)
C(1)-O(1)	1.373(4)	N(8)-C(36)	1.336(5)
C(1)-C(2)	1.389(5)	N(8)-C(55)	1.403(4)
O(1)-C(8)	1.381(5)	O(8)-C(36)	1.379(4)
N(1)-C(7)	1.408(4)	O(8)-C(56)	1.393(5)
Co(02)-N(8)	1.981(3)	C(8)-C(9)	1.372(5)
Co(02)-N(5)	1.987(3)	C(10)-C(9)	1.392(6)
Co(02)-N(6)	1.987(3)	C(10)-C(11)	1.403(5)
Co(02)-N(7)	1.991(3)	C(11)-C(12)	1.399(5)
C(2)-C(3)	1.384(5)	C(13)-C(14)	1.381(5)
O(2)-C(3)	1.374(4)	C(13)-C(18)	1.386(5)
O(2)-C(14)	1.388(5)	C(14)-C(15)	1.380(6)
N(2)-C(3)	1.333(5)	C(15)-C(16)	1.389(6)
N(2)-C(13)	1.409(4)	C(16)-C(17)	1.392(6)
O(3)-C(4)	1.375(4)	C(18)-C(17)	1.394(5)
O(3)-C(20)	1.386(4)	C(19)-C(20)	1.390(5)
N(3)-C(4)	1.339(4)	C(19)-C(24)	1.391(5)
N(3)-C(19)	1.400(4)	C(21)-C(20)	1.363(5)
O(4)-C(6)	1.373(4)	C(21)-C(22)	1.394(5)
O(4)-C(26)	1.393(4)	C(23)-C(24)	1.390(5)
C(4)-C(5)	1.385(5)	C(23)-C(22)	1.397(6)
N(4)-C(6)	1.339(4)	C(25)-C(26)	1.380(5)
N(4)-C(25)	1.405(4)	C(25)-C(30)	1.392(5)
O(5)-C(31)	1.371(4)	C(26)-C(27)	1.363(5)
O(5)-C(38)	1.386(4)	C(27)-C(28)	1.395(5)
C(5)-C(6)	1.403(5)	C(28)-C(29)	1.387(5)
N(5)-C(31)	1.345(4)	C(29)-C(30)	1.391(5)
N(5)-C(37)	1.395(5)	C(31)-C(32)	1.391(5)
N(6)-C(33)	1.342(4)	C(32)-C(33)	1.381(5)
N(6)-C(43)	1.400(5)	C(34)-C(35)	1.381(5)
O(6)-C(33)	1.382(4)	C(35)-C(36)	1.387(5)
O(6)-C(44)	1.387(4)	C(37)-C(42)	1.387(5)
N(7)-C(34)	1.346(4)	C(37)-C(38)	1.388(5)

C(38)-C(39)	1.368(5)	N(8)-Co(02)-N(7)	92.86(12)
C(39)-C(40)	1.397(5)	N(5)-Co(02)-N(7)	107.36(12)
C(40)-C(41)	1.397(5)	N(6)-Co(02)-N(7)	134.99(12)
C(41)-C(42)	1.389(5)	C(3)-C(2)-C(1)	121.3(3)
C(43)-C(44)	1.386(5)	C(3)-O(2)-C(14)	105.3(3)
C(43)-C(48)	1.391(5)	C(3)-N(2)-C(13)	105.2(3)
C(44)-C(45)	1.370(5)	C(3)-N(2)-Co(1)	123.3(2)
C(45)-C(46)	1.384(6)	C(13)-N(2)-Co(1)	129.9(2)
C(46)-C(47)	1.402(5)	C(4)-O(3)-C(20)	105.4(3)
C(47)-C(48)	1.384(6)	N(2)-C(3)-O(2)	113.0(3)
C(49)-C(50)	1.381(5)	N(2)-C(3)-C(2)	129.3(3)
C(49)-C(54)	1.387(5)	O(2)-C(3)-C(2)	117.6(3)
C(50)-C(51)	1.384(5)	C(4)-N(3)-C(19)	105.6(3)
C(51)-C(52)	1.385(6)	C(4)-N(3)-Co(1)	124.3(2)
C(52)-C(53)	1.388(6)	C(19)-N(3)-Co(1)	130.1(2)
C(53)-C(54)	1.405(5)	C(6)-O(4)-C(26)	105.1(2)
C(55)-C(56)	1.385(5)	N(3)-C(4)-O(3)	112.7(3)
C(55)-C(60)	1.389(5)	N(3)-C(4)-C(5)	129.2(3)
C(56)-C(57)	1.373(5)	O(3)-C(4)-C(5)	118.1(3)
C(57)-C(58)	1.390(6)	C(6)-N(4)-C(25)	105.5(3)
C(58)-C(59)	1.389(7)	C(6)-N(4)-Co(1)	123.6(2)
C(59)-C(60)	1.393(5)	C(25)-N(4)-Co(1)	130.9(2)
N(3)-Co(1)-N(2)	137.33(12)	C(31)-O(5)-C(38)	105.4(3)
N(3)-Co(1)-N(4)	92.80(12)	C(4)-C(5)-C(6)	120.6(3)
N(2)-Co(1)-N(4)	102.90(12)	C(31)-N(5)-C(37)	105.5(3)
N(3)-Co(1)-N(1)	104.78(12)	C(31)-N(5)-Co(02)	123.8(2)
N(2)-Co(1)-N(1)	92.89(12)	C(37)-N(5)-Co(02)	130.7(2)
N(4)-Co(1)-N(1)	133.20(12)	C(33)-N(6)-C(43)	105.9(3)
N(1)-C(1)-O(1)	112.4(3)	C(33)-N(6)-Co(02)	123.2(2)
N(1)-C(1)-C(2)	129.1(3)	C(43)-N(6)-Co(02)	130.5(2)
O(1)-C(1)-C(2)	118.5(3)	C(33)-O(6)-C(44)	105.6(3)
C(1)-O(1)-C(8)	105.9(3)	N(4)-C(6)-O(4)	112.8(3)
C(1)-N(1)-C(7)	105.7(3)	N(4)-C(6)-C(5)	129.4(3)
C(1)-N(1)-Co(1)	122.6(2)	O(4)-C(6)-C(5)	117.9(3)
C(7)-N(1)-Co(1)	130.7(2)	C(34)-N(7)-C(49)	105.3(3)
N(8)-Co(02)-N(5)	133.98(13)	C(34)-N(7)-Co(02)	122.0(2)
N(8)-Co(02)-N(6)	101.43(12)	C(49)-N(7)-Co(02)	132.0(2)
N(5)-Co(02)-N(6)	92.78(12)	C(50)-O(7)-C(34)	105.6(3)

C(12)-C(7)-C(8)	119.7(3)	C(27)-C(26)-O(4)	126.9(3)
C(12)-C(7)-N(1)	132.4(3)	C(25)-C(26)-O(4)	108.4(3)
C(8)-C(7)-N(1)	107.9(3)	C(26)-C(27)-C(28)	115.2(3)
C(36)-N(8)-C(55)	105.6(3)	C(29)-C(28)-C(27)	121.5(4)
C(36)-N(8)-Co(02)	123.5(2)	C(28)-C(29)-C(30)	122.3(3)
C(55)-N(8)-Co(02)	129.6(2)	C(29)-C(30)-C(25)	116.2(3)
C(36)-O(8)-C(56)	104.8(3)	N(5)-C(31)-O(5)	112.5(3)
C(9)-C(8)-O(1)	127.5(3)	N(5)-C(31)-C(32)	129.2(3)
C(9)-C(8)-C(7)	124.4(4)	O(5)-C(31)-C(32)	118.3(3)
O(1)-C(8)-C(7)	108.1(3)	C(33)-C(32)-C(31)	120.6(3)
C(9)-C(10)-C(11)	121.6(4)	N(6)-C(33)-C(32)	130.3(3)
C(12)-C(11)-C(10)	121.0(4)	N(6)-C(33)-O(6)	112.0(3)
C(7)-C(12)-C(11)	117.7(3)	C(32)-C(33)-O(6)	117.7(3)
C(14)-C(13)-C(18)	119.9(3)	N(7)-C(34)-C(35)	130.2(3)
C(14)-C(13)-N(2)	108.5(3)	N(7)-C(34)-O(7)	112.1(3)
C(18)-C(13)-N(2)	131.5(3)	C(35)-C(34)-O(7)	117.6(3)
C(15)-C(14)-C(13)	124.4(4)	C(34)-C(35)-C(36)	120.7(3)
C(15)-C(14)-O(2)	127.4(4)	N(8)-C(36)-O(8)	112.9(3)
C(13)-C(14)-O(2)	108.0(3)	N(8)-C(36)-C(35)	129.3(3)
C(14)-C(15)-C(16)	115.3(4)	O(8)-C(36)-C(35)	117.7(3)
C(15)-C(16)-C(17)	121.6(4)	C(42)-C(37)-C(38)	120.6(3)
C(13)-C(18)-C(17)	117.0(4)	C(42)-C(37)-N(5)	131.0(3)
C(16)-C(17)-C(18)	121.8(4)	C(38)-C(37)-N(5)	108.4(3)
C(20)-C(19)-C(24)	120.2(3)	C(39)-C(38)-O(5)	128.2(3)
C(20)-C(19)-N(3)	108.3(3)	C(39)-C(38)-C(37)	123.7(3)
C(24)-C(19)-N(3)	131.4(3)	O(5)-C(38)-C(37)	108.1(3)
C(20)-C(21)-C(22)	116.3(3)	C(38)-C(39)-C(40)	115.7(3)
C(24)-C(23)-C(22)	121.8(4)	C(41)-C(40)-C(39)	121.6(4)
C(21)-C(22)-C(23)	121.1(4)	C(42)-C(41)-C(40)	121.4(4)
C(8)-C(9)-C(10)	115.6(4)	C(37)-C(42)-C(41)	116.9(3)
C(21)-C(20)-O(3)	128.2(3)	C(44)-C(43)-C(48)	119.7(3)
C(21)-C(20)-C(19)	123.8(3)	C(44)-C(43)-N(6)	108.4(3)
O(3)-C(20)-C(19)	108.0(3)	C(48)-C(43)-N(6)	132.0(3)
C(23)-C(24)-C(19)	116.8(3)	C(45)-C(44)-C(43)	124.5(3)
C(26)-C(25)-C(30)	120.1(3)	C(45)-C(44)-O(6)	127.3(3)
C(26)-C(25)-N(4)	108.3(3)	C(43)-C(44)-O(6)	108.1(3)
C(30)-C(25)-N(4)	131.6(3)	C(44)-C(45)-C(46)	115.5(3)
C(27)-C(26)-C(25)	124.8(3)	C(45)-C(46)-C(47)	121.5(4)

C(48)-C(47)-C(46)	121.7(4)	C(56)-C(55)-C(60)	119.8(3)
C(47)-C(48)-C(43)	117.1(3)	C(56)-C(55)-N(8)	108.3(3)
C(50)-C(49)-C(54)	119.8(3)	C(60)-C(55)-N(8)	131.8(3)
C(50)-C(49)-N(7)	108.6(3)	C(57)-C(56)-C(55)	124.4(4)
C(54)-C(49)-N(7)	131.6(3)	C(57)-C(56)-O(8)	127.2(4)
C(49)-C(50)-O(7)	108.3(3)	C(55)-C(56)-O(8)	108.4(3)
C(49)-C(50)-C(51)	124.3(4)	C(56)-C(57)-C(58)	115.2(4)
O(7)-C(50)-C(51)	127.4(3)	C(59)-C(58)-C(57)	122.1(4)
C(50)-C(51)-C(52)	115.5(4)	C(58)-C(59)-C(60)	121.3(4)
C(51)-C(52)-C(53)	121.8(3)	C(55)-C(60)-C(59)	117.1(4)
C(52)-C(53)-C(54)	121.5(4)		
C(49)-C(54)-C(53)	117.0(3)		

Crystal structure of **4a**

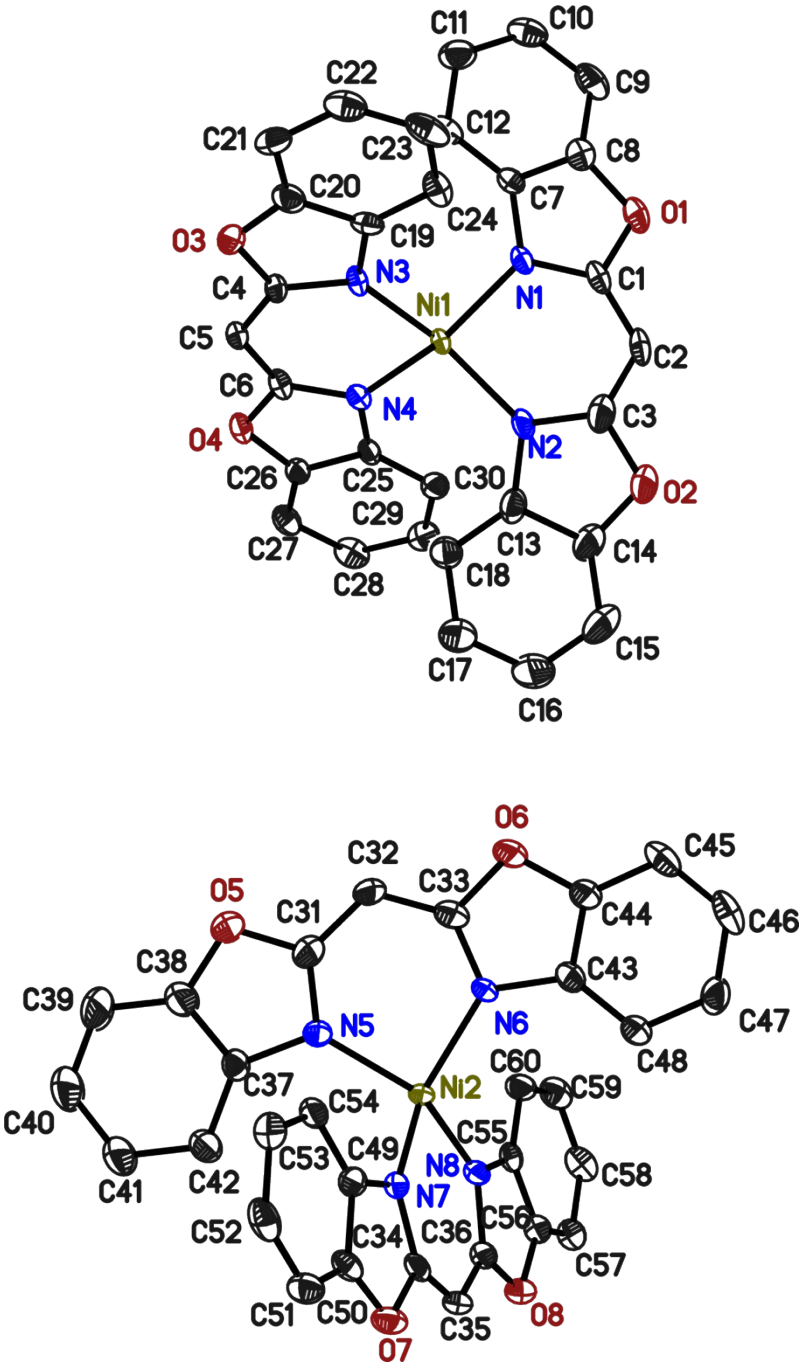

Figure S4: Molecular structure of **4a**. Hydrogen atoms are omitted for clarity and ADPs are depicted at 50% probability level.

The XRD data was in general relatively weak in comparison with the other complexes. The asymmetric unit contains two complex molecules and no solvent molecules. The measured crystal was non-merohedrally twinned with the twin law 1 0 0 0 -1 0 -0.68 0 -1. But an integration with two orientation matrices does not lead to an improvement of the data. Therefore, the integration was performed with a fixed integration box (x = y = z = 0.4).

Table S5a: Bond lengths (Å) and angles (°) for **4a.**

Ni(1)-N(2)	1.953(5)	N(7)-C(49)	1.409(9)
Ni(1)-N(3)	1.958(5)	O(7)-C(50)	1.374(8)
Ni(1)-N(4)	1.968(5)	O(7)-C(34)	1.391(7)
Ni(1)-N(1)	1.975(5)	C(7)-C(12)	1.375(9)
C(1)-N(1)	1.353(8)	C(7)-C(8)	1.382(9)
C(1)-C(2)	1.356(10)	N(8)-C(36)	1.352(8)
C(1)-O(1)	1.379(8)	N(8)-C(55)	1.401(8)
O(1)-C(8)	1.381(9)	O(8)-C(36)	1.366(8)
N(1)-C(7)	1.409(8)	O(8)-C(56)	1.391(8)
Ni(2)-N(5)	1.949(5)	C(8)-C(9)	1.375(10)
Ni(2)-N(7)	1.956(5)	C(9)-C(10)	1.374(11)
Ni(2)-N(8)	1.966(6)	C(21)-C(20)	1.361(10)
Ni(2)-N(6)	1.973(5)	C(21)-C(22)	1.402(9)
C(2)-C(3)	1.394(10)	C(10)-C(11)	1.385(10)
O(2)-C(3)	1.362(9)	C(11)-C(12)	1.404(9)
O(2)-C(14)	1.384(9)	C(13)-C(18)	1.377(9)
N(2)-C(3)	1.339(9)	C(13)-C(14)	1.388(10)
N(2)-C(13)	1.410(8)	C(14)-C(15)	1.368(12)
O(3)-C(20)	1.383(8)	C(15)-C(16)	1.402(12)
O(3)-C(4)	1.385(7)	C(16)-C(17)	1.366(12)
N(3)-C(4)	1.357(7)	C(17)-C(18)	1.391(10)
N(3)-C(19)	1.398(8)	C(19)-C(24)	1.387(9)
O(4)-C(6)	1.367(7)	C(19)-C(20)	1.392(9)
O(4)-C(26)	1.396(7)	C(24)-C(23)	1.370(10)
C(4)-C(5)	1.382(9)	C(23)-C(22)	1.406(10)
N(4)-C(6)	1.358(8)	C(25)-C(26)	1.388(8)
N(4)-C(25)	1.393(8)	C(25)-C(30)	1.399(9)
O(6)-C(44)	1.380(9)	C(26)-C(27)	1.351(9)
O(6)-C(33)	1.384(8)	C(27)-C(28)	1.398(9)
C(6)-C(5)	1.364(9)	C(28)-C(29)	1.398(9)
N(6)-C(33)	1.339(9)	C(29)-C(30)	1.362(9)
N(6)-C(43)	1.409(8)	C(31)-C(32)	1.404(10)
N(5)-C(31)	1.321(9)	C(32)-C(33)	1.381(10)
N(5)-C(37)	1.422(8)	C(34)-C(35)	1.367(9)
O(5)-C(31)	1.364(9)	C(35)-C(36)	1.393(9)
O(5)-C(38)	1.387(9)	C(37)-C(38)	1.361(10)
N(7)-C(34)	1.339(8)	C(37)-C(42)	1.387(9)

C(38)-C(39)	1.384(11)	N(5)-Ni(2)-N(6)	91.1(2)
C(39)-C(40)	1.390(12)	N(7)-Ni(2)-N(6)	138.2(2)
C(40)-C(41)	1.349(12)	N(8)-Ni(2)-N(6)	107.5(2)
C(41)-C(42)	1.399(10)	C(1)-C(2)-C(3)	120.4(6)
C(43)-C(44)	1.375(9)	C(3)-O(2)-C(14)	106.0(6)
C(43)-C(48)	1.380(10)	C(3)-N(2)-C(13)	105.0(6)
C(44)-C(45)	1.395(9)	C(3)-N(2)-Ni(1)	125.8(5)
C(45)-C(46)	1.367(11)	C(13)-N(2)-Ni(1)	128.9(4)
C(46)-C(47)	1.373(10)	C(20)-O(3)-C(4)	105.9(5)
C(47)-C(48)	1.420(9)	N(2)-C(3)-O(2)	113.0(6)
C(49)-C(50)	1.372(8)	N(2)-C(3)-C(2)	127.9(7)
C(49)-C(54)	1.402(9)	O(2)-C(3)-C(2)	118.9(6)
C(50)-C(51)	1.395(9)	C(4)-N(3)-C(19)	105.8(5)
C(51)-C(52)	1.360(10)	C(4)-N(3)-Ni(1)	125.7(4)
C(52)-C(53)	1.419(10)	C(19)-N(3)-Ni(1)	128.4(4)
C(53)-C(54)	1.369(10)	C(6)-O(4)-C(26)	106.2(4)
C(55)-C(60)	1.388(9)	N(3)-C(4)-C(5)	128.4(6)
C(55)-C(56)	1.395(9)	N(3)-C(4)-O(3)	111.5(5)
C(56)-C(57)	1.367(10)	C(5)-C(4)-O(3)	120.1(5)
C(57)-C(58)	1.403(9)	C(6)-N(4)-C(25)	105.9(5)
C(58)-C(59)	1.391(10)	C(6)-N(4)-Ni(1)	124.9(4)
C(59)-C(60)	1.377(10)	C(25)-N(4)-Ni(1)	129.0(4)
N(2)-Ni(1)-N(3)	140.4(2)	C(44)-O(6)-C(33)	105.1(5)
N(2)-Ni(1)-N(4)	103.2(2)	N(4)-C(6)-C(5)	129.2(6)
N(3)-Ni(1)-N(4)	91.3(2)	N(4)-C(6)-O(4)	111.6(6)
N(2)-Ni(1)-N(1)	91.7(2)	C(5)-C(6)-O(4)	119.1(5)
N(3)-Ni(1)-N(1)	104.4(2)	C(33)-N(6)-C(43)	105.4(5)
N(4)-Ni(1)-N(1)	134.2(2)	C(33)-N(6)-Ni(2)	123.9(4)
N(1)-C(1)-C(2)	129.8(6)	C(43)-N(6)-Ni(2)	130.1(4)
N(1)-C(1)-O(1)	110.4(6)	C(31)-N(5)-C(37)	104.2(5)
C(2)-C(1)-O(1)	119.8(6)	C(31)-N(5)-Ni(2)	127.1(5)
C(1)-O(1)-C(8)	107.2(5)	C(37)-N(5)-Ni(2)	128.5(4)
C(1)-N(1)-C(7)	106.5(5)	C(31)-O(5)-C(38)	104.8(6)
C(1)-N(1)-Ni(1)	123.2(4)	C(6)-C(5)-C(4)	120.3(6)
C(7)-N(1)-Ni(1)	129.1(4)	C(34)-N(7)-C(49)	105.2(5)
N(5)-Ni(2)-N(7)	101.7(2)	C(34)-N(7)-Ni(2)	126.1(5)
N(5)-Ni(2)-N(8)	135.9(2)	C(49)-N(7)-Ni(2)	128.7(4)
N(7)-Ni(2)-N(8)	90.6(2)	C(50)-O(7)-C(34)	105.0(5)

C(12)-C(7)-C(8)	119.6(6)	C(27)-C(26)-O(4)	127.4(6)
C(12)-C(7)-N(1)	132.3(5)	C(25)-C(26)-O(4)	107.5(5)
C(8)-C(7)-N(1)	108.0(6)	C(26)-C(27)-C(28)	115.7(6)
C(36)-N(8)-C(55)	104.6(5)	C(29)-C(28)-C(27)	120.5(6)
C(36)-N(8)-Ni(2)	126.5(5)	C(30)-C(29)-C(28)	122.5(6)
C(55)-N(8)-Ni(2)	128.8(4)	C(29)-C(30)-C(25)	117.5(6)
C(36)-O(8)-C(56)	105.8(5)	N(5)-C(31)-O(5)	114.0(6)
C(9)-C(8)-O(1)	128.0(6)	N(5)-C(31)-C(32)	127.9(6)
C(9)-C(8)-C(7)	124.1(7)	O(5)-C(31)-C(32)	118.0(6)
O(1)-C(8)-C(7)	107.9(6)	C(33)-C(32)-C(31)	119.1(7)
C(10)-C(9)-C(8)	116.4(6)	N(6)-C(33)-C(32)	130.2(6)
C(20)-C(21)-C(22)	116.5(6)	N(6)-C(33)-O(6)	112.3(6)
C(9)-C(10)-C(11)	120.9(7)	C(32)-C(33)-O(6)	117.4(6)
C(10)-C(11)-C(12)	122.0(7)	N(7)-C(34)-C(35)	128.9(6)
C(7)-C(12)-C(11)	117.0(6)	N(7)-C(34)-O(7)	112.3(6)
C(18)-C(13)-C(14)	119.7(7)	C(35)-C(34)-O(7)	118.7(5)
C(18)-C(13)-N(2)	131.9(6)	C(34)-C(35)-C(36)	120.7(6)
C(14)-C(13)-N(2)	108.3(6)	N(8)-C(36)-O(8)	113.2(6)
C(15)-C(14)-O(2)	128.0(8)	N(8)-C(36)-C(35)	127.0(6)
C(15)-C(14)-C(13)	124.2(8)	O(8)-C(36)-C(35)	119.8(5)
O(2)-C(14)-C(13)	107.7(6)	C(38)-C(37)-C(42)	120.2(6)
C(14)-C(15)-C(16)	115.0(8)	C(38)-C(37)-N(5)	108.6(6)
C(17)-C(16)-C(15)	121.9(8)	C(42)-C(37)-N(5)	131.2(6)
C(16)-C(17)-C(18)	121.8(7)	C(37)-C(38)-C(39)	124.1(7)
C(13)-C(18)-C(17)	117.3(7)	C(37)-C(38)-O(5)	108.4(6)
C(24)-C(19)-C(20)	119.2(6)	C(39)-C(38)-O(5)	127.5(8)
C(24)-C(19)-N(3)	132.3(6)	C(38)-C(39)-C(40)	114.7(8)
C(20)-C(19)-N(3)	108.5(5)	C(41)-C(40)-C(39)	122.7(8)
C(23)-C(24)-C(19)	118.4(6)	C(40)-C(41)-C(42)	121.7(7)
C(24)-C(23)-C(22)	121.6(6)	C(37)-C(42)-C(41)	116.6(7)
C(21)-C(22)-C(23)	120.3(6)	C(44)-C(43)-C(48)	120.3(6)
C(21)-C(20)-O(3)	127.8(6)	C(44)-C(43)-N(6)	108.2(6)
C(21)-C(20)-C(19)	124.0(6)	C(48)-C(43)-N(6)	131.6(6)
O(3)-C(20)-C(19)	108.2(6)	C(43)-C(44)-O(6)	108.9(6)
C(26)-C(25)-N(4)	108.7(5)	C(43)-C(44)-C(45)	124.0(7)
C(26)-C(25)-C(30)	118.7(6)	O(6)-C(44)-C(45)	127.1(7)
N(4)-C(25)-C(30)	132.6(5)	C(46)-C(45)-C(44)	115.6(7)
C(27)-C(26)-C(25)	125.1(6)	C(45)-C(46)-C(47)	122.0(6)

C(46)-C(47)-C(48)	121.9(7)	C(53)-C(54)-C(49)	118.0(6)
C(43)-C(48)-C(47)	116.1(6)	C(60)-C(55)-C(56)	119.4(6)
C(50)-C(49)-C(54)	119.3(6)	C(60)-C(55)-N(8)	131.5(6)
C(50)-C(49)-N(7)	108.4(6)	C(56)-C(55)-N(8)	109.1(5)
C(54)-C(49)-N(7)	132.3(6)	C(57)-C(56)-O(8)	128.3(6)
C(49)-C(50)-O(7)	109.1(5)	C(57)-C(56)-C(55)	124.3(6)
C(49)-C(50)-C(51)	123.9(6)	O(8)-C(56)-C(55)	107.4(6)
O(7)-C(50)-C(51)	127.0(6)	C(56)-C(57)-C(58)	115.3(6)
C(52)-C(51)-C(50)	116.3(6)	C(59)-C(58)-C(57)	121.4(7)
C(51)-C(52)-C(53)	121.2(7)	C(60)-C(59)-C(58)	121.8(7)
C(54)-C(53)-C(52)	121.3(7)	C(59)-C(60)-C(55)	117.7(6)

Crystal structure of **1b**

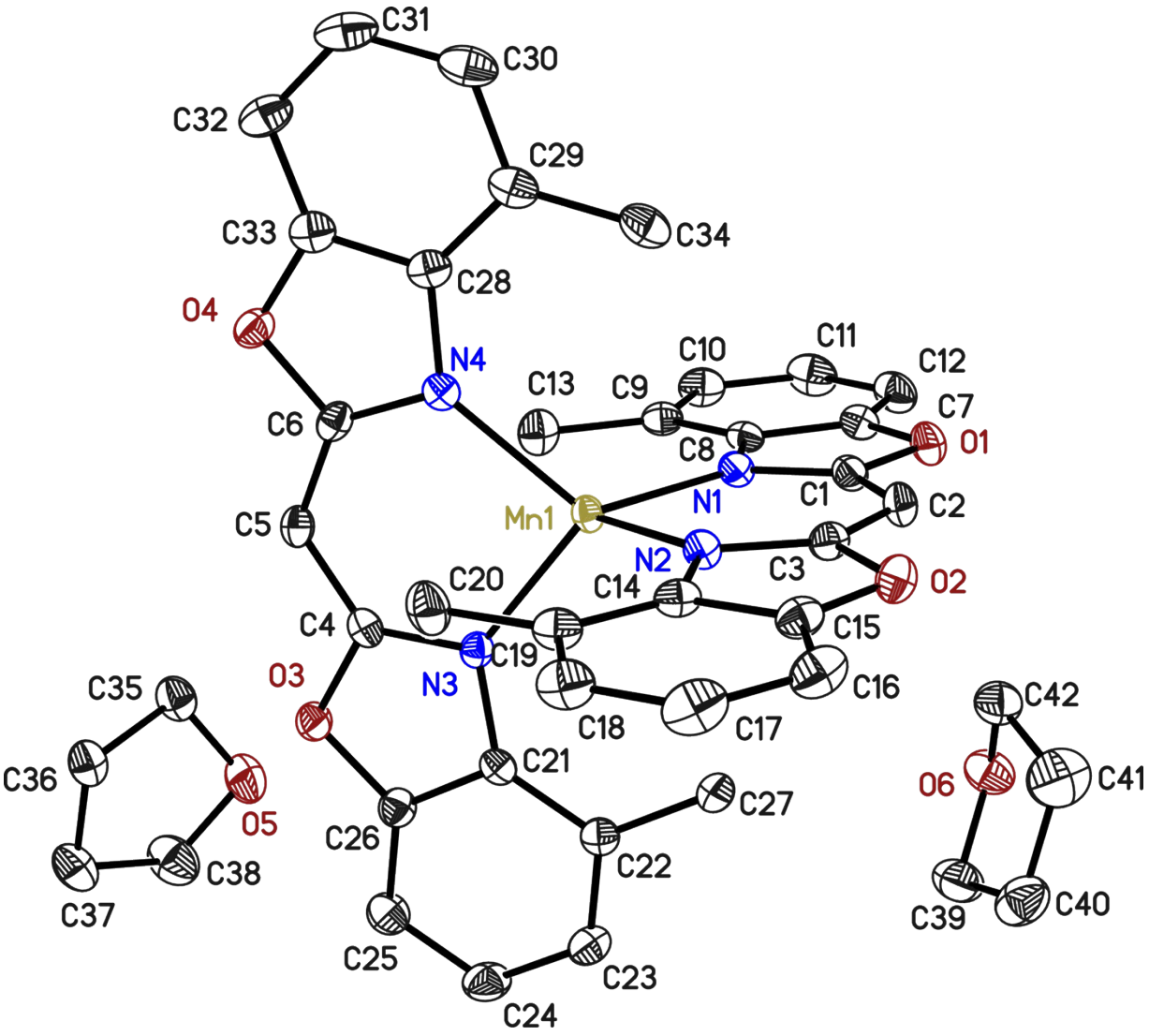

Figure S5: Molecular structure of **1b**.

The asymmetric unit contains one complex molecule and two thf molecules.

Table S2b: Bond lengths (Å) and angles (°) for **1b**.

Mn(1)-N(2)	2.1017(13)	C(15)-C(16)	1.374(2)
Mn(1)-N(4)	2.1043(13)	C(16)-C(17)	1.388(2)
Mn(1)-N(3)	2.1093(12)	C(17)-C(18)	1.397(2)
Mn(1)-N(1)	2.1098(13)	C(18)-C(19)	1.398(2)
O(1)-C(1)	1.3755(17)	C(19)-C(20)	1.505(2)
O(1)-C(7)	1.3847(18)	C(21)-C(26)	1.388(2)
O(2)-C(3)	1.3766(17)	C(21)-C(22)	1.395(2)
O(2)-C(15)	1.3842(19)	C(22)-C(23)	1.396(2)
O(3)-C(4)	1.3733(17)	C(22)-C(27)	1.501(2)
O(3)-C(26)	1.3823(18)	C(23)-C(24)	1.393(2)
O(4)-C(6)	1.3761(17)	C(24)-C(25)	1.388(2)
O(4)-C(33)	1.3822(18)	C(25)-C(26)	1.376(2)
O(5)-C(35)	1.423(2)	C(28)-C(33)	1.385(2)
O(5)-C(38)	1.428(2)	C(28)-C(29)	1.395(2)
O(6)-C(42)	1.423(2)	C(29)-C(30)	1.396(2)
O(6)-C(39)	1.430(2)	C(29)-C(34)	1.501(2)
N(1)-C(1)	1.3393(18)	C(30)-C(31)	1.394(3)
N(1)-C(8)	1.4071(18)	C(31)-C(32)	1.388(2)
N(2)-C(3)	1.3392(18)	C(32)-C(33)	1.379(2)
N(2)-C(14)	1.4067(18)	C(35)-C(36)	1.524(2)
N(3)-C(4)	1.3383(18)	C(36)-C(37)	1.537(2)
N(3)-C(21)	1.4084(18)	C(37)-C(38)	1.532(3)
N(4)-C(6)	1.3408(19)	C(39)-C(40)	1.528(3)
N(4)-C(28)	1.4066(18)	C(40)-C(41)	1.530(3)
C(1)-C(2)	1.390(2)	C(41)-C(42)	1.513(3)
C(2)-C(3)	1.387(2)	N(2)-Mn(1)-N(4)	122.00(5)
C(4)-C(5)	1.389(2)	N(2)-Mn(1)-N(3)	118.73(5)
C(5)-C(6)	1.387(2)	N(4)-Mn(1)-N(3)	91.98(5)
C(7)-C(12)	1.375(2)	N(2)-Mn(1)-N(1)	92.00(5)
C(7)-C(8)	1.387(2)	N(4)-Mn(1)-N(1)	117.76(5)
C(8)-C(9)	1.392(2)	N(3)-Mn(1)-N(1)	116.81(5)
C(9)-C(10)	1.394(2)	C(1)-O(1)-C(7)	105.61(11)
C(9)-C(13)	1.499(2)	C(3)-O(2)-C(15)	105.56(11)
C(10)-C(11)	1.393(2)	C(4)-O(3)-C(26)	105.64(11)
C(11)-C(12)	1.392(2)	C(6)-O(4)-C(33)	105.51(11)
C(14)-C(15)	1.386(2)	C(35)-O(5)-C(38)	105.11(13)
C(14)-C(19)	1.395(2)	C(42)-O(6)-C(39)	105.13(13)

C(1)-N(1)-C(8)	105.23(12)	C(15)-C(14)-C(19)	120.82(13)
C(1)-N(1)-Mn(1)	121.40(10)	C(15)-C(14)-N(2)	108.12(13)
C(8)-N(1)-Mn(1)	133.36(9)	C(19)-C(14)-N(2)	131.07(13)
C(3)-N(2)-C(14)	105.62(12)	C(16)-C(15)-O(2)	127.30(14)
C(3)-N(2)-Mn(1)	121.50(10)	C(16)-C(15)-C(14)	124.44(15)
C(14)-N(2)-Mn(1)	132.60(10)	O(2)-C(15)-C(14)	108.26(12)
C(4)-N(3)-C(21)	105.26(11)	C(15)-C(16)-C(17)	115.00(15)
C(4)-N(3)-Mn(1)	121.10(10)	C(16)-C(17)-C(18)	121.89(15)
C(21)-N(3)-Mn(1)	133.46(9)	C(17)-C(18)-C(19)	122.41(15)
C(6)-N(4)-C(28)	105.63(12)	C(14)-C(19)-C(18)	115.44(14)
C(6)-N(4)-Mn(1)	121.29(10)	C(14)-C(19)-C(20)	122.24(13)
C(28)-N(4)-Mn(1)	132.96(10)	C(18)-C(19)-C(20)	122.32(14)
N(1)-C(1)-O(1)	112.71(12)	C(26)-C(21)-C(22)	120.57(13)
N(1)-C(1)-C(2)	130.59(13)	C(26)-C(21)-N(3)	108.26(12)
O(1)-C(1)-C(2)	116.69(13)	C(22)-C(21)-N(3)	131.11(13)
C(3)-C(2)-C(1)	123.71(13)	C(21)-C(22)-C(23)	115.56(13)
N(2)-C(3)-O(2)	112.44(12)	C(21)-C(22)-C(27)	121.46(13)
N(2)-C(3)-C(2)	130.72(13)	C(23)-C(22)-C(27)	122.96(13)
O(2)-C(3)-C(2)	116.83(13)	C(24)-C(23)-C(22)	122.74(14)
N(3)-C(4)-O(3)	112.75(12)	C(25)-C(24)-C(23)	121.55(15)
N(3)-C(4)-C(5)	130.67(13)	C(26)-C(25)-C(24)	115.18(14)
O(3)-C(4)-C(5)	116.57(12)	C(25)-C(26)-O(3)	127.51(14)
C(6)-C(5)-C(4)	123.83(13)	C(25)-C(26)-C(21)	124.39(14)
N(4)-C(6)-O(4)	112.38(12)	O(3)-C(26)-C(21)	108.08(12)
N(4)-C(6)-C(5)	130.53(13)	C(33)-C(28)-C(29)	120.93(14)
O(4)-C(6)-C(5)	117.09(13)	C(33)-C(28)-N(4)	107.99(13)
C(12)-C(7)-O(1)	127.71(14)	C(29)-C(28)-N(4)	131.07(14)
C(12)-C(7)-C(8)	124.33(14)	C(28)-C(29)-C(30)	115.34(15)
O(1)-C(7)-C(8)	107.95(12)	C(28)-C(29)-C(34)	122.15(14)
C(7)-C(8)-C(9)	120.60(13)	C(30)-C(29)-C(34)	122.50(14)
C(7)-C(8)-N(1)	108.49(12)	C(31)-C(30)-C(29)	122.78(15)
C(9)-C(8)-N(1)	130.90(13)	C(32)-C(31)-C(30)	121.57(15)
C(8)-C(9)-C(10)	115.64(14)	C(33)-C(32)-C(31)	115.20(15)
C(8)-C(9)-C(13)	122.12(13)	C(32)-C(33)-O(4)	127.32(14)
C(10)-C(9)-C(13)	122.24(14)	C(32)-C(33)-C(28)	124.17(15)
C(11)-C(10)-C(9)	122.91(15)	O(4)-C(33)-C(28)	108.49(13)
C(12)-C(11)-C(10)	121.21(15)	O(5)-C(35)-C(36)	104.64(13)
C(7)-C(12)-C(11)	115.30(15)	C(35)-C(36)-C(37)	102.90(13)

C(38)-C(37)-C(36)	103.70(14)	C(39)-C(40)-C(41)	103.87(15)
O(5)-C(38)-C(37)	106.86(15)	C(42)-C(41)-C(40)	103.89(16)
O(6)-C(39)-C(40)	106.06(14)	O(6)-C(42)-C(41)	105.23(14)

Crystal structure **2b**

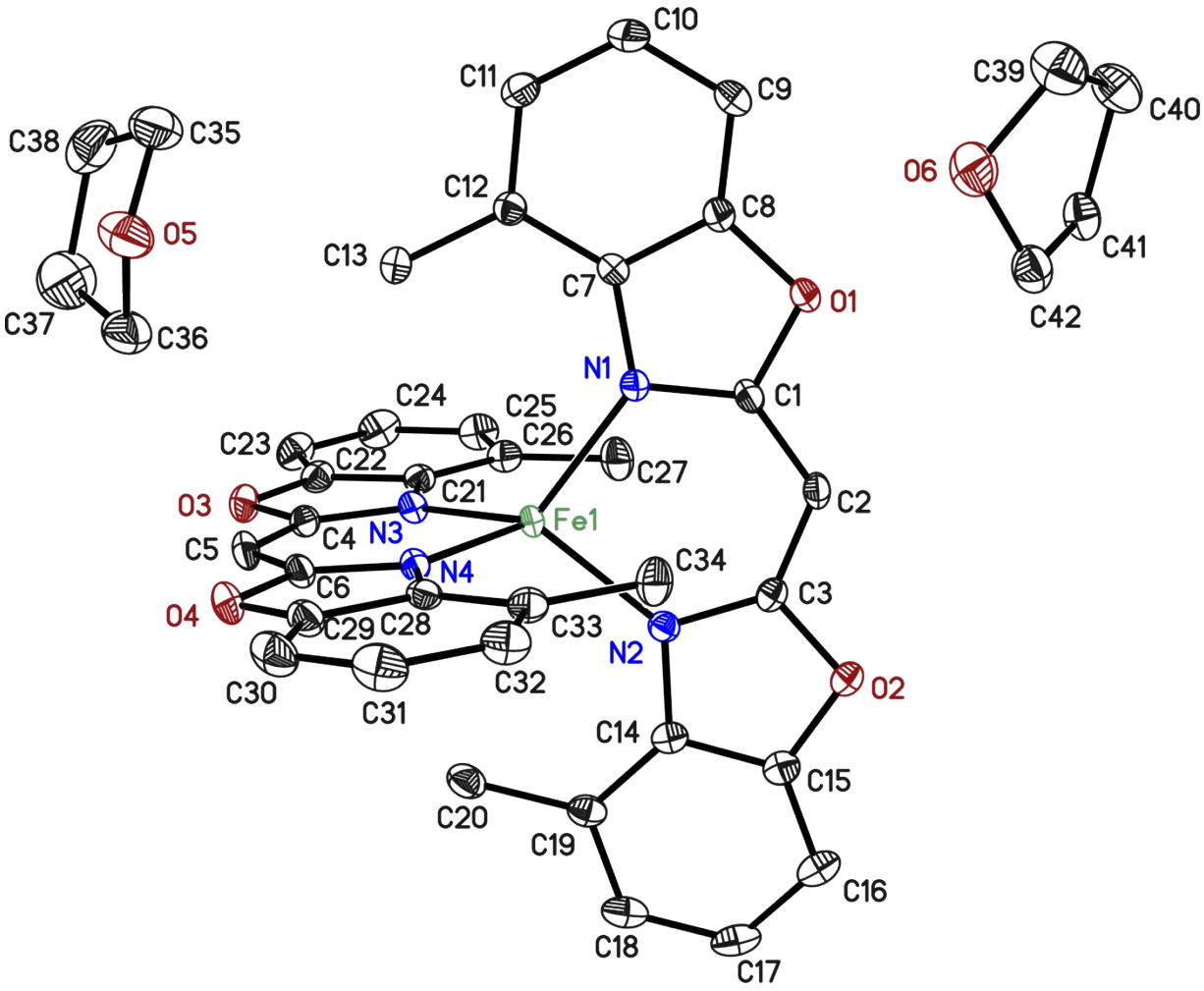

Figure S6: Molecular structure of **2b**.

The asymmetric unit consists of one complex molecule and two thf molecules.

Table S7: Bond lengths (Å) and angles (°)

Fe(1)-N(3)	2.0368(11)	C(15)-C(16)	1.3782(17)
Fe(1)-N(2)	2.0385(10)	C(16)-C(17)	1.390(2)
Fe(1)-N(1)	2.0415(10)	C(17)-C(18)	1.393(2)
Fe(1)-N(4)	2.0427(10)	C(18)-C(19)	1.3968(17)
O(1)-C(1)	1.3721(14)	C(19)-C(20)	1.4998(18)
O(1)-C(8)	1.3780(14)	C(21)-C(22)	1.3884(16)
O(2)-C(3)	1.3718(14)	C(21)-C(26)	1.3924(16)
O(2)-C(15)	1.3813(15)	C(22)-C(23)	1.3768(17)
O(3)-C(4)	1.3713(14)	C(23)-C(24)	1.388(2)
O(3)-C(22)	1.3798(15)	C(24)-C(25)	1.3976(19)
O(4)-C(6)	1.3740(14)	C(25)-C(26)	1.4000(17)
O(4)-C(29)	1.3823(15)	C(26)-C(27)	1.5019(18)
O(5)-C(36)	1.4213(17)	C(28)-C(29)	1.3879(16)
O(5)-C(35)	1.4296(18)	C(28)-C(33)	1.3908(16)
O(6)-C(42)	1.4214(18)	C(29)-C(30)	1.3786(17)
O(6)-C(39)	1.4283(19)	C(30)-C(31)	1.390(2)
N(1)-C(1)	1.3411(14)	C(31)-C(32)	1.3924(19)
N(1)-C(7)	1.4089(14)	C(32)-C(33)	1.3973(17)
N(2)-C(3)	1.3401(15)	C(33)-C(34)	1.4943(17)
N(2)-C(14)	1.4081(15)	C(35)-C(38)	1.533(3)
N(3)-C(4)	1.3402(15)	C(36)-C(37)	1.516(2)
N(3)-C(21)	1.4100(15)	C(37)-C(38)	1.529(3)
N(4)-C(6)	1.3415(14)	C(39)-C(40)	1.534(2)
N(4)-C(28)	1.4073(14)	C(40)-C(41)	1.536(2)
C(1)-C(2)	1.3857(16)	C(41)-C(42)	1.5221(18)
C(2)-C(3)	1.3890(16)	N(3)-Fe(1)-N(2)	119.87(4)
C(4)-C(5)	1.3884(17)	N(3)-Fe(1)-N(1)	118.05(4)
C(5)-C(6)	1.3883(17)	N(2)-Fe(1)-N(1)	93.73(4)
C(7)-C(8)	1.3873(16)	N(3)-Fe(1)-N(4)	93.71(4)
C(7)-C(12)	1.3923(15)	N(2)-Fe(1)-N(4)	116.70(4)
C(8)-C(9)	1.3759(17)	N(1)-Fe(1)-N(4)	116.83(4)
C(9)-C(10)	1.3923(19)	C(1)-O(1)-C(8)	105.57(9)
C(10)-C(11)	1.3934(18)	C(3)-O(2)-C(15)	105.28(9)
C(11)-C(12)	1.3990(16)	C(4)-O(3)-C(22)	105.52(9)
C(12)-C(13)	1.4959(17)	C(6)-O(4)-C(29)	105.56(9)
C(14)-C(15)	1.3852(17)	C(36)-O(5)-C(35)	104.98(12)
C(14)-C(19)	1.3946(17)	C(42)-O(6)-C(39)	104.87(11)

C(1)-N(1)-C(7)	105.20(9)	C(15)-C(14)-C(19)	120.81(11)
C(1)-N(1)-Fe(1)	121.15(8)	C(15)-C(14)-N(2)	107.82(10)
C(7)-N(1)-Fe(1)	133.49(7)	C(19)-C(14)-N(2)	131.36(11)
C(3)-N(2)-C(14)	105.41(9)	C(16)-C(15)-O(2)	126.90(12)
C(3)-N(2)-Fe(1)	121.40(8)	C(16)-C(15)-C(14)	124.39(12)
C(14)-N(2)-Fe(1)	133.07(8)	O(2)-C(15)-C(14)	108.68(10)
C(4)-N(3)-C(21)	105.38(9)	C(15)-C(16)-C(17)	115.08(12)
C(4)-N(3)-Fe(1)	121.66(8)	C(16)-C(17)-C(18)	121.44(12)
C(21)-N(3)-Fe(1)	132.85(8)	C(17)-C(18)-C(19)	122.98(12)
C(6)-N(4)-C(28)	105.30(9)	C(14)-C(19)-C(18)	115.29(12)
C(6)-N(4)-Fe(1)	121.48(8)	C(14)-C(19)-C(20)	122.39(11)
C(28)-N(4)-Fe(1)	133.21(8)	C(18)-C(19)-C(20)	122.31(11)
N(1)-C(1)-O(1)	112.76(10)	C(22)-C(21)-C(26)	120.88(11)
N(1)-C(1)-C(2)	130.33(10)	C(22)-C(21)-N(3)	107.80(10)
O(1)-C(1)-C(2)	116.90(10)	C(26)-C(21)-N(3)	131.31(11)
C(1)-C(2)-C(3)	122.86(10)	C(23)-C(22)-O(3)	126.96(11)
N(2)-C(3)-O(2)	112.80(10)	C(23)-C(22)-C(21)	124.50(12)
N(2)-C(3)-C(2)	130.03(10)	O(3)-C(22)-C(21)	108.52(10)
O(2)-C(3)-C(2)	117.18(10)	C(22)-C(23)-C(24)	114.86(12)
N(3)-C(4)-O(3)	112.76(10)	C(23)-C(24)-C(25)	121.83(12)
N(3)-C(4)-C(5)	130.09(11)	C(24)-C(25)-C(26)	122.59(12)
O(3)-C(4)-C(5)	117.14(10)	C(21)-C(26)-C(25)	115.31(11)
C(6)-C(5)-C(4)	122.91(10)	C(21)-C(26)-C(27)	122.60(11)
N(4)-C(6)-O(4)	112.69(10)	C(25)-C(26)-C(27)	122.09(11)
N(4)-C(6)-C(5)	130.10(10)	C(29)-C(28)-C(33)	120.48(11)
O(4)-C(6)-C(5)	117.21(10)	C(29)-C(28)-N(4)	108.20(10)
C(8)-C(7)-C(12)	120.65(10)	C(33)-C(28)-N(4)	131.31(10)
C(8)-C(7)-N(1)	108.02(10)	C(30)-C(29)-O(4)	127.44(11)
C(12)-C(7)-N(1)	131.27(10)	C(30)-C(29)-C(28)	124.31(12)
C(9)-C(8)-O(1)	127.05(11)	O(4)-C(29)-C(28)	108.25(10)
C(9)-C(8)-C(7)	124.48(11)	C(29)-C(30)-C(31)	115.33(12)
O(1)-C(8)-C(7)	108.44(10)	C(30)-C(31)-C(32)	121.29(12)
C(8)-C(9)-C(10)	115.09(12)	C(31)-C(32)-C(33)	122.80(12)
C(9)-C(10)-C(11)	121.48(12)	C(28)-C(33)-C(32)	115.79(11)
C(10)-C(11)-C(12)	122.73(11)	C(28)-C(33)-C(34)	122.22(10)
C(7)-C(12)-C(11)	115.56(11)	C(32)-C(33)-C(34)	121.99(11)
C(7)-C(12)-C(13)	121.91(10)	O(5)-C(35)-C(38)	105.80(13)
C(11)-C(12)-C(13)	122.50(11)	O(5)-C(36)-C(37)	105.70(13)

C(36)-C(37)-C(38)	103.69(14)	C(39)-C(40)-C(41)	103.78(11)
C(37)-C(38)-C(35)	103.97(13)	C(42)-C(41)-C(40)	102.86(11)
O(6)-C(39)-C(40)	106.47(12)	O(6)-C(42)-C(41)	104.83(11)

Crystal structure **2b'**

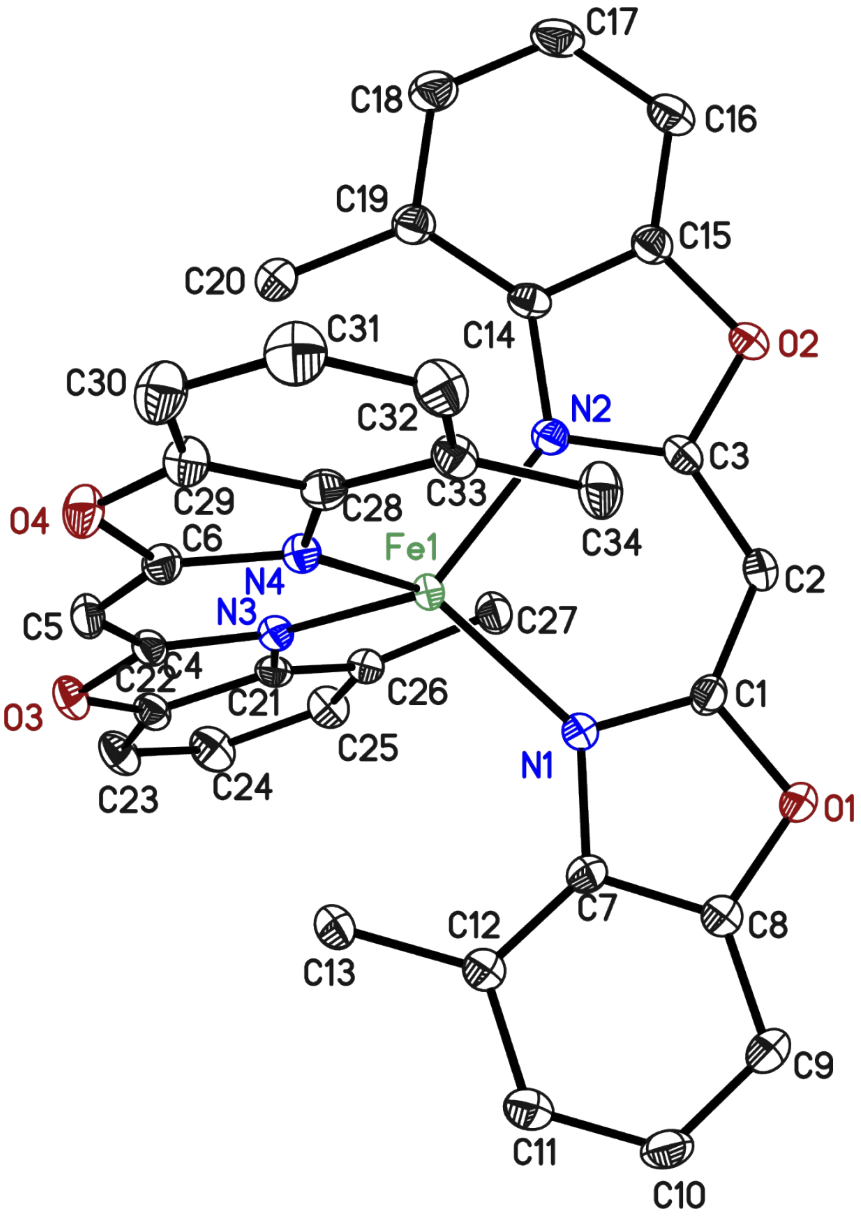

Figure S7: Molecular structure of **2b'**.

The asymmetric unit contains one complex molecule.

Table S8 : Bond lengths (Å) and angles (°) for **2b**

Fe(1)-N(1)	2.0339(11)	C(3)-N(2)-C(14)	105.33(10)
Fe(1)-N(4)	2.0345(11)	C(3)-N(2)-Fe(1)	120.16(8)
Fe(1)-N(2)	2.0358(10)	C(14)-N(2)-Fe(1)	134.36(8)
Fe(1)-N(3)	2.0363(10)	C(4)-N(3)-C(21)	105.43(9)
O(1)-C(1)	1.3755(14)	C(4)-N(3)-Fe(1)	120.56(8)
O(1)-C(8)	1.3835(15)	C(21)-N(3)-Fe(1)	133.15(8)
O(2)-C(3)	1.3718(14)	C(6)-N(4)-C(28)	105.32(10)
O(2)-C(15)	1.3847(15)	C(6)-N(4)-Fe(1)	121.32(8)
O(3)-C(4)	1.3795(14)	C(28)-N(4)-Fe(1)	132.62(8)
O(3)-C(22)	1.3867(14)	N(1)-C(1)-O(1)	112.75(10)
O(4)-C(6)	1.3709(14)	N(1)-C(1)-C(2)	130.22(11)
O(4)-C(29)	1.3835(15)	O(1)-C(1)-C(2)	117.02(10)
C(4)-N(3)	1.3443(15)	C(1)-C(2)-C(3)	123.82(11)
C(4)-C(5)	1.3855(17)	N(2)-C(3)-O(2)	112.94(10)
N(1)-C(1)	1.3437(15)	N(2)-C(3)-C(2)	130.07(11)
N(1)-C(7)	1.4110(15)	O(2)-C(3)-C(2)	116.98(10)
N(2)-C(3)	1.3406(15)	C(4)-C(5)-C(6)	122.60(11)
N(2)-C(14)	1.4117(15)	N(4)-C(6)-O(4)	112.97(10)
N(3)-C(21)	1.4076(14)	N(4)-C(6)-C(5)	129.81(11)
N(4)-C(6)	1.3352(15)	O(4)-C(6)-C(5)	117.22(10)
N(4)-C(28)	1.4087(15)	C(8)-C(7)-C(12)	120.69(11)
C(1)-C(2)	1.3869(16)	C(8)-C(7)-N(1)	108.12(10)
C(2)-C(3)	1.3926(17)	C(12)-C(7)-N(1)	131.18(11)
C(5)-C(6)	1.3944(17)	C(9)-C(8)-O(1)	127.02(11)
C(7)-C(8)	1.3872(16)	C(9)-C(8)-C(7)	124.53(12)
C(7)-C(12)	1.3968(16)	O(1)-C(8)-C(7)	108.45(10)
C(8)-C(9)	1.3783(17)	C(9)-C(10)-C(11)	121.51(12)
C(10)-C(9)	1.3953(19)	C(8)-C(9)-C(10)	115.03(12)
C(10)-C(11)	1.3957(19)	C(10)-C(11)-C(12)	122.73(12)
C(11)-C(12)	1.4005(17)	C(7)-C(12)-C(11)	115.49(11)
C(12)-C(13)	1.5007(17)	C(7)-C(12)-C(13)	122.09(11)
C(14)-C(15)	1.3903(16)	C(11)-C(12)-C(13)	122.42(11)
C(14)-C(19)	1.3981(17)	C(15)-C(14)-C(19)	120.50(11)
C(18)-C(17)	1.3972(19)	C(15)-C(14)-N(2)	107.88(10)
C(18)-C(19)	1.3980(17)	C(19)-C(14)-N(2)	131.61(11)
C(15)-C(16)	1.3773(17)	C(17)-C(18)-C(19)	123.09(12)
C(19)-C(20)	1.5044(17)	C(16)-C(15)-O(2)	126.85(11)

C(16)-C(17)	1.392(2)	C(16)-C(15)-C(14)	124.73(12)
C(21)-C(22)	1.3903(16)	O(2)-C(15)-C(14)	108.41(10)
C(21)-C(26)	1.3946(16)	C(18)-C(19)-C(14)	115.29(11)
C(22)-C(23)	1.3754(17)	C(18)-C(19)-C(20)	121.69(11)
C(23)-C(24)	1.3950(18)	C(14)-C(19)-C(20)	123.00(11)
C(24)-C(25)	1.3951(18)	C(15)-C(16)-C(17)	114.98(12)
C(25)-C(26)	1.4009(17)	C(16)-C(17)-C(18)	121.39(12)
C(26)-C(27)	1.5023(16)	C(22)-C(21)-C(26)	120.48(11)
C(28)-C(29)	1.3868(17)	C(22)-C(21)-N(3)	108.23(10)
C(28)-C(33)	1.3917(17)	C(26)-C(21)-N(3)	131.18(11)
C(29)-C(30)	1.3803(17)	C(23)-C(22)-O(3)	127.20(11)
C(30)-C(31)	1.392(2)	C(23)-C(22)-C(21)	124.53(11)
C(31)-C(32)	1.3968(19)	O(3)-C(22)-C(21)	108.26(10)
C(32)-C(33)	1.3996(17)	C(22)-C(23)-C(24)	115.14(11)
C(33)-C(34)	1.5007(17)	C(23)-C(24)-C(25)	121.43(11)
N(1)-Fe(1)-N(4)	118.59(4)	C(24)-C(25)-C(26)	122.68(11)
N(1)-Fe(1)-N(2)	95.57(4)	C(21)-C(26)-C(25)	115.64(11)
N(4)-Fe(1)-N(2)	114.43(4)	C(21)-C(26)-C(27)	122.06(11)
N(1)-Fe(1)-N(3)	118.52(4)	C(25)-C(26)-C(27)	122.23(11)
N(4)-Fe(1)-N(3)	94.04(4)	C(29)-C(28)-C(33)	120.99(11)
N(2)-Fe(1)-N(3)	117.43(4)	C(29)-C(28)-N(4)	108.05(10)
C(1)-O(1)-C(8)	105.44(9)	C(33)-C(28)-N(4)	130.92(11)
C(3)-O(2)-C(15)	105.43(9)	C(30)-C(29)-O(4)	127.61(12)
C(4)-O(3)-C(22)	105.45(9)	C(30)-C(29)-C(28)	124.16(12)
C(6)-O(4)-C(29)	105.43(9)	O(4)-C(29)-C(28)	108.22(10)
N(3)-C(4)-O(3)	112.57(10)	C(29)-C(30)-C(31)	115.16(12)
N(3)-C(4)-C(5)	130.10(11)	C(30)-C(31)-C(32)	121.52(12)
O(3)-C(4)-C(5)	117.31(10)	C(31)-C(32)-C(33)	122.61(12)
C(1)-N(1)-C(7)	105.21(10)	C(28)-C(33)-C(32)	115.53(11)
C(1)-N(1)-Fe(1)	120.05(8)	C(28)-C(33)-C(34)	121.96(11)
C(7)-N(1)-Fe(1)	134.72(8)	C(32)-C(33)-C(34)	122.51(11)

Crystal structure **3b**

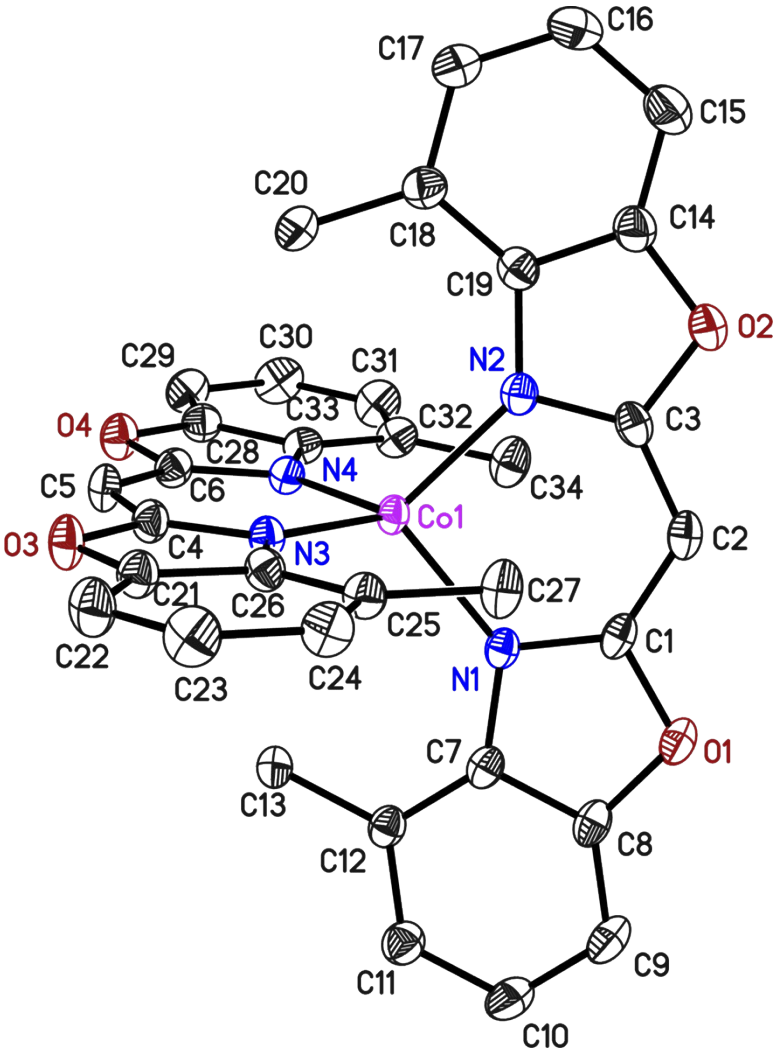

Figure S8 : Molecular structure of **3b**.

The asymmetric unit contains one complex molecule.

Table S9 : Bond lengths (Å) and angles (°) for **3b**

Co(1)-N(2)	1.9852(14)	C(18)-C(19)	1.388(2)
Co(1)-N(4)	1.9867(14)	C(18)-C(20)	1.500(2)
Co(1)-N(3)	1.9878(14)	C(21)-C(22)	1.375(2)
Co(1)-N(1)	1.9896(14)	C(21)-C(26)	1.388(2)
O(1)-C(1)	1.377(2)	C(22)-C(23)	1.390(3)
O(1)-C(8)	1.382(2)	C(23)-C(24)	1.392(3)
O(2)-C(3)	1.368(2)	C(24)-C(25)	1.397(2)
O(2)-C(14)	1.380(2)	C(25)-C(26)	1.393(2)
O(3)-C(4)	1.3760(19)	C(25)-C(27)	1.497(2)
O(3)-C(21)	1.381(2)	C(28)-C(29)	1.373(2)
O(4)-C(6)	1.371(2)	C(28)-C(33)	1.386(2)
O(4)-C(28)	1.380(2)	C(29)-C(30)	1.385(3)
N(1)-C(1)	1.342(2)	C(30)-C(31)	1.395(3)
N(1)-C(7)	1.407(2)	C(31)-C(32)	1.394(2)
N(2)-C(3)	1.339(2)	C(32)-C(33)	1.397(2)
N(2)-C(19)	1.404(2)	C(32)-C(34)	1.498(3)
N(3)-C(4)	1.341(2)	N(2)-Co(1)-N(4)	113.56(6)
N(3)-C(26)	1.414(2)	N(2)-Co(1)-N(3)	118.50(6)
N(4)-C(6)	1.339(2)	N(4)-Co(1)-N(3)	96.72(6)
N(4)-C(33)	1.411(2)	N(2)-Co(1)-N(1)	95.50(6)
C(1)-C(2)	1.378(2)	N(4)-Co(1)-N(1)	117.56(6)
C(2)-C(3)	1.382(2)	N(3)-Co(1)-N(1)	116.51(6)
C(4)-C(5)	1.381(2)	C(1)-O(1)-C(8)	105.49(13)
C(5)-C(6)	1.385(2)	C(3)-O(2)-C(14)	105.64(13)
C(7)-C(8)	1.385(2)	C(4)-O(3)-C(21)	105.47(12)
C(7)-C(12)	1.392(2)	C(6)-O(4)-C(28)	105.48(13)
C(8)-C(9)	1.375(2)	C(1)-N(1)-C(7)	105.34(13)
C(9)-C(10)	1.385(3)	C(1)-N(1)-Co(1)	120.61(11)
C(10)-C(11)	1.393(3)	C(7)-N(1)-Co(1)	133.58(11)
C(11)-C(12)	1.397(2)	C(3)-N(2)-C(19)	105.45(14)
C(12)-C(13)	1.500(2)	C(3)-N(2)-Co(1)	120.88(11)
C(14)-C(15)	1.377(3)	C(19)-N(2)-Co(1)	133.12(11)
C(14)-C(19)	1.385(2)	C(4)-N(3)-C(26)	105.21(13)
C(15)-C(16)	1.381(3)	C(4)-N(3)-Co(1)	120.06(11)
C(16)-C(17)	1.393(3)	C(26)-N(3)-Co(1)	134.73(11)
C(17)-C(18)	1.393(3)	C(6)-N(4)-C(33)	105.14(13)

C(6)-N(4)-Co(1)	120.10(11)	C(15)-C(16)-C(17)	121.55(18)
C(33)-N(4)-Co(1)	134.65(11)	C(18)-C(17)-C(16)	122.61(18)
N(1)-C(1)-O(1)	112.51(15)	C(19)-C(18)-C(17)	115.65(17)
N(1)-C(1)-C(2)	129.67(15)	C(19)-C(18)-C(20)	121.88(16)
O(1)-C(1)-C(2)	117.79(14)	C(17)-C(18)-C(20)	122.47(16)
C(1)-C(2)-C(3)	122.49(15)	C(14)-C(19)-C(18)	120.75(16)
N(2)-C(3)-O(2)	112.61(15)	C(14)-C(19)-N(2)	108.02(15)
N(2)-C(3)-C(2)	129.79(16)	C(18)-C(19)-N(2)	131.20(16)
O(2)-C(3)-C(2)	117.60(15)	C(22)-C(21)-O(3)	126.93(16)
N(3)-C(4)-O(3)	112.83(14)	C(22)-C(21)-C(26)	124.54(17)
N(3)-C(4)-C(5)	129.95(15)	O(3)-C(21)-C(26)	108.53(14)
O(3)-C(4)-C(5)	117.22(14)	C(21)-C(22)-C(23)	115.04(16)
C(4)-C(5)-C(6)	123.22(15)	C(22)-C(23)-C(24)	121.58(16)
N(4)-C(6)-O(4)	112.93(14)	C(23)-C(24)-C(25)	122.77(17)
N(4)-C(6)-C(5)	129.89(15)	C(26)-C(25)-C(24)	115.55(15)
O(4)-C(6)-C(5)	117.18(15)	C(26)-C(25)-C(27)	122.23(15)
C(8)-C(7)-C(12)	120.46(16)	C(24)-C(25)-C(27)	122.21(16)
C(8)-C(7)-N(1)	108.24(14)	C(21)-C(26)-C(25)	120.50(15)
C(12)-C(7)-N(1)	131.20(15)	C(21)-C(26)-N(3)	107.95(14)
C(9)-C(8)-O(1)	127.22(15)	C(25)-C(26)-N(3)	131.55(14)
C(9)-C(8)-C(7)	124.39(17)	C(29)-C(28)-O(4)	126.65(16)
O(1)-C(8)-C(7)	108.37(15)	C(29)-C(28)-C(33)	124.92(16)
C(8)-C(9)-C(10)	115.38(16)	O(4)-C(28)-C(33)	108.41(14)
C(9)-C(10)-C(11)	121.34(17)	C(28)-C(29)-C(30)	114.94(17)
C(10)-C(11)-C(12)	122.73(17)	C(29)-C(30)-C(31)	121.25(17)
C(7)-C(12)-C(11)	115.60(15)	C(32)-C(31)-C(30)	123.48(17)
C(7)-C(12)-C(13)	122.22(15)	C(31)-C(32)-C(33)	114.85(16)
C(11)-C(12)-C(13)	122.08(16)	C(31)-C(32)-C(34)	121.73(16)
C(15)-C(14)-O(2)	127.69(17)	C(33)-C(32)-C(34)	123.41(15)
C(15)-C(14)-C(19)	124.05(18)	C(28)-C(33)-C(32)	120.52(16)
O(2)-C(14)-C(19)	108.26(15)	C(28)-C(33)-N(4)	108.04(14)
C(14)-C(15)-C(16)	115.35(18)	C(32)-C(33)-N(4)	131.43(16)

Crystal structure **4b**

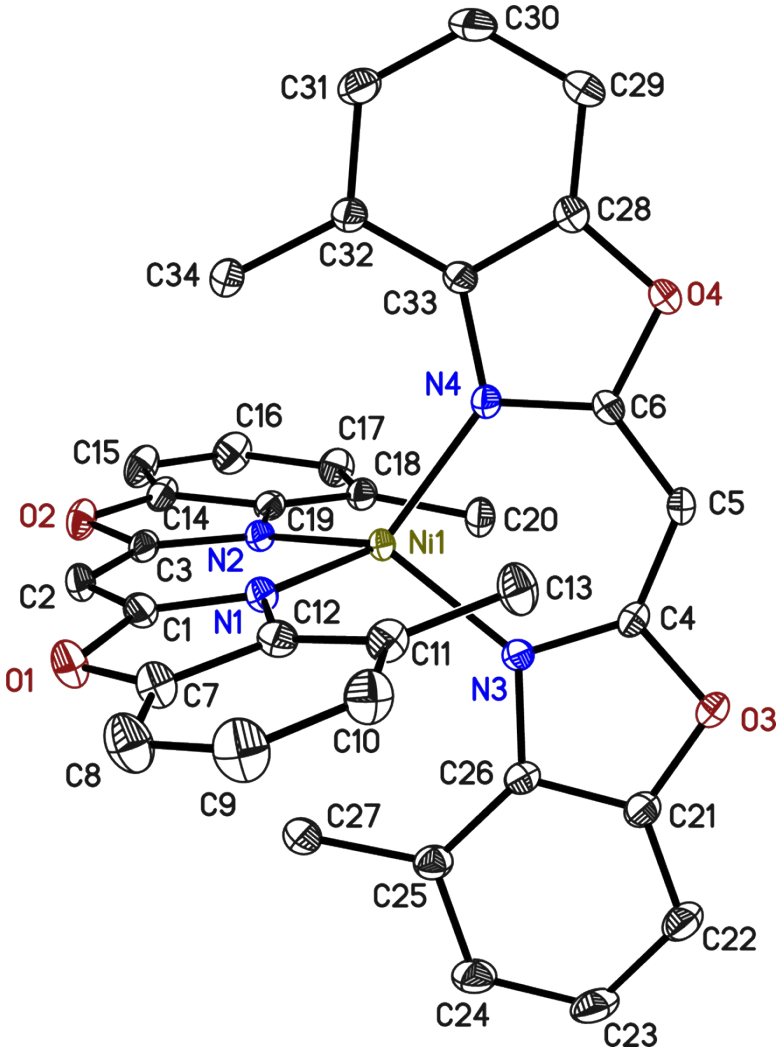

Figure S9: Molecular structure of **4b**.

The asymmetric unit contains one complex molecule.

Table S10: Bond lengths (Å) and angles (°) for **4b**.

Ni(1)-N(1)	1.9751(14)	C(18)-C(20)	1.499(2)
Ni(1)-N(2)	1.9754(13)	C(21)-C(22)	1.376(2)
Ni(1)-N(3)	1.9755(13)	C(21)-C(26)	1.393(2)
Ni(1)-N(4)	1.9770(13)	C(22)-C(23)	1.385(3)
O(1)-C(1)	1.3678(19)	C(23)-C(24)	1.399(3)
O(1)-C(7)	1.386(2)	C(24)-C(25)	1.397(2)
O(2)-C(3)	1.3761(18)	C(25)-C(26)	1.399(2)
O(2)-C(14)	1.384(2)	C(25)-C(27)	1.500(2)
O(3)-C(4)	1.3692(18)	C(28)-C(29)	1.377(2)
O(3)-C(21)	1.383(2)	C(28)-C(33)	1.392(2)
O(4)-C(6)	1.3736(19)	C(29)-C(30)	1.393(3)
O(4)-C(28)	1.380(2)	C(30)-C(31)	1.389(3)
N(1)-C(1)	1.336(2)	C(31)-C(32)	1.404(2)
N(1)-C(12)	1.410(2)	C(32)-C(33)	1.395(2)
N(2)-C(3)	1.3414(19)	C(32)-C(34)	1.496(2)
N(2)-C(19)	1.409(2)	N(1)-Ni(1)-N(2)	93.43(6)
N(3)-C(4)	1.340(2)	N(1)-Ni(1)-N(3)	114.76(6)
N(3)-C(26)	1.416(2)	N(2)-Ni(1)-N(3)	118.93(5)
N(4)-C(6)	1.3438(19)	N(1)-Ni(1)-N(4)	119.37(6)
N(4)-C(33)	1.4171(19)	N(2)-Ni(1)-N(4)	117.83(5)
C(1)-C(2)	1.386(2)	N(3)-Ni(1)-N(4)	94.53(5)
C(2)-C(3)	1.383(2)	C(1)-O(1)-C(7)	105.36(13)
C(4)-C(5)	1.386(2)	C(3)-O(2)-C(14)	105.30(12)
C(5)-C(6)	1.383(2)	C(4)-O(3)-C(21)	105.42(12)
C(7)-C(8)	1.373(2)	C(6)-O(4)-C(28)	105.31(12)
C(7)-C(12)	1.389(2)	C(1)-N(1)-C(12)	105.32(13)
C(8)-C(9)	1.389(3)	C(1)-N(1)-Ni(1)	123.07(11)
C(9)-C(10)	1.393(3)	C(12)-N(1)-Ni(1)	131.11(11)
C(10)-C(11)	1.400(2)	C(3)-N(2)-C(19)	105.31(12)
C(11)-C(12)	1.395(2)	C(3)-N(2)-Ni(1)	122.92(11)
C(11)-C(13)	1.501(2)	C(19)-N(2)-Ni(1)	131.27(10)
C(14)-C(15)	1.376(2)	C(4)-N(3)-C(26)	105.42(13)
C(14)-C(19)	1.390(2)	C(4)-N(3)-Ni(1)	122.34(10)
C(15)-C(16)	1.390(3)	C(26)-N(3)-Ni(1)	132.18(10)
C(16)-C(17)	1.396(2)	C(6)-N(4)-C(33)	104.84(12)
C(17)-C(18)	1.398(2)	C(6)-N(4)-Ni(1)	122.43(11)
C(18)-C(19)	1.397(2)	C(33)-N(4)-Ni(1)	132.72(10)

N(1)-C(1)-O(1)	113.15(14)	C(16)-C(17)-C(18)	122.85(16)
N(1)-C(1)-C(2)	129.34(15)	C(19)-C(18)-C(17)	115.81(14)
O(1)-C(1)-C(2)	117.50(14)	C(19)-C(18)-C(20)	122.47(14)
C(3)-C(2)-C(1)	121.01(14)	C(17)-C(18)-C(20)	121.62(15)
N(2)-C(3)-O(2)	112.86(14)	C(14)-C(19)-C(18)	119.92(14)
N(2)-C(3)-C(2)	129.15(14)	C(14)-C(19)-N(2)	107.99(13)
O(2)-C(3)-C(2)	117.98(13)	C(18)-C(19)-N(2)	131.98(14)
N(3)-C(4)-O(3)	113.05(13)	C(22)-C(21)-O(3)	126.47(15)
N(3)-C(4)-C(5)	129.46(14)	C(22)-C(21)-C(26)	124.85(16)
O(3)-C(4)-C(5)	117.49(14)	O(3)-C(21)-C(26)	108.67(13)
C(6)-C(5)-C(4)	121.99(14)	C(21)-C(22)-C(23)	115.24(16)
N(4)-C(6)-O(4)	113.26(13)	C(22)-C(23)-C(24)	121.07(16)
N(4)-C(6)-C(5)	129.22(14)	C(25)-C(24)-C(23)	123.42(16)
O(4)-C(6)-C(5)	117.51(14)	C(24)-C(25)-C(26)	115.21(15)
C(8)-C(7)-O(1)	126.95(16)	C(24)-C(25)-C(27)	120.99(15)
C(8)-C(7)-C(12)	124.81(17)	C(26)-C(25)-C(27)	123.78(15)
O(1)-C(7)-C(12)	108.23(14)	C(21)-C(26)-C(25)	120.17(15)
C(7)-C(8)-C(9)	115.21(17)	C(21)-C(26)-N(3)	107.44(14)
C(8)-C(9)-C(10)	121.25(17)	C(25)-C(26)-N(3)	132.39(14)
C(9)-C(10)-C(11)	122.95(17)	C(29)-C(28)-O(4)	126.44(15)
C(12)-C(11)-C(10)	115.55(16)	C(29)-C(28)-C(33)	124.90(16)
C(12)-C(11)-C(13)	122.37(15)	O(4)-C(28)-C(33)	108.66(14)
C(10)-C(11)-C(13)	122.08(15)	C(28)-C(29)-C(30)	114.91(16)
C(7)-C(12)-C(11)	120.16(15)	C(31)-C(30)-C(29)	121.56(16)
C(7)-C(12)-N(1)	107.90(14)	C(30)-C(31)-C(32)	122.91(16)
C(11)-C(12)-N(1)	131.91(15)	C(33)-C(32)-C(31)	115.57(15)
C(15)-C(14)-O(2)	126.66(14)	C(33)-C(32)-C(34)	122.81(14)
C(15)-C(14)-C(19)	124.86(15)	C(31)-C(32)-C(34)	121.61(15)
O(2)-C(14)-C(19)	108.46(13)	C(28)-C(33)-C(32)	120.14(14)
C(14)-C(15)-C(16)	115.18(15)	C(28)-C(33)-N(4)	107.90(13)
C(15)-C(16)-C(17)	121.28(16)	C(32)-C(33)-N(4)	131.95(14)

Structural variation from distorted tetrahedron (τ4 and τ4')

The following equations were used to determine τ4 and τ4', according to the references cited in the main manuscript:

$$\tau_4 = \frac{360 - (\alpha + \beta)}{360 - 2 * 109{,}5}$$

and

$$\tau_{4'} = \frac{\beta - \alpha}{360 - 109{,}5} + \frac{180 - \beta}{180 - 109{,}5}$$

where α and β are the largest valence angles of the coordination center, with β >α.

The following results were obtained:

Table S11: Structural τ4 and τ4' parameters for **1-4a, b**

#	α angle (°)	β angle (°)	τ_4	τ_4'	REMARKS
1a	120,9	164,14	0,531631	0,397579	Without taking the coordinated THF into account
2a	117,18	164,49	0,555532	0,408862	Without taking the coordinated THF into account
3a	133,2	137,33	0,634539	0,621735	
4a	134,2	140,4	0,605674	0,586453	
1b	118,73	122	0,845887	0,835749	
2b	118,05	119,87	0,865816	0,860173	
2b no solv	118,52	118,59	0,87156	0,871343	
3b	117,56	118,5	0,879007	0,876093	
4b	118,93	119,37	0,863121	0,861756	

S2 Analytical details

NMR-spectroscopy data

The ^{1}H and ^{13}C NMR spectroscopic data were recorded at our Central Analytics Department, , located at the organic chemistry institute at University of Göttingen. All measurements were performed on a Bruker Avance 500 MHz, a Bruker Avance 400 MHz and a Bruker Avance 300 MHz spectrometer and referenced to a deuterated solvent signal (thf-d_8).

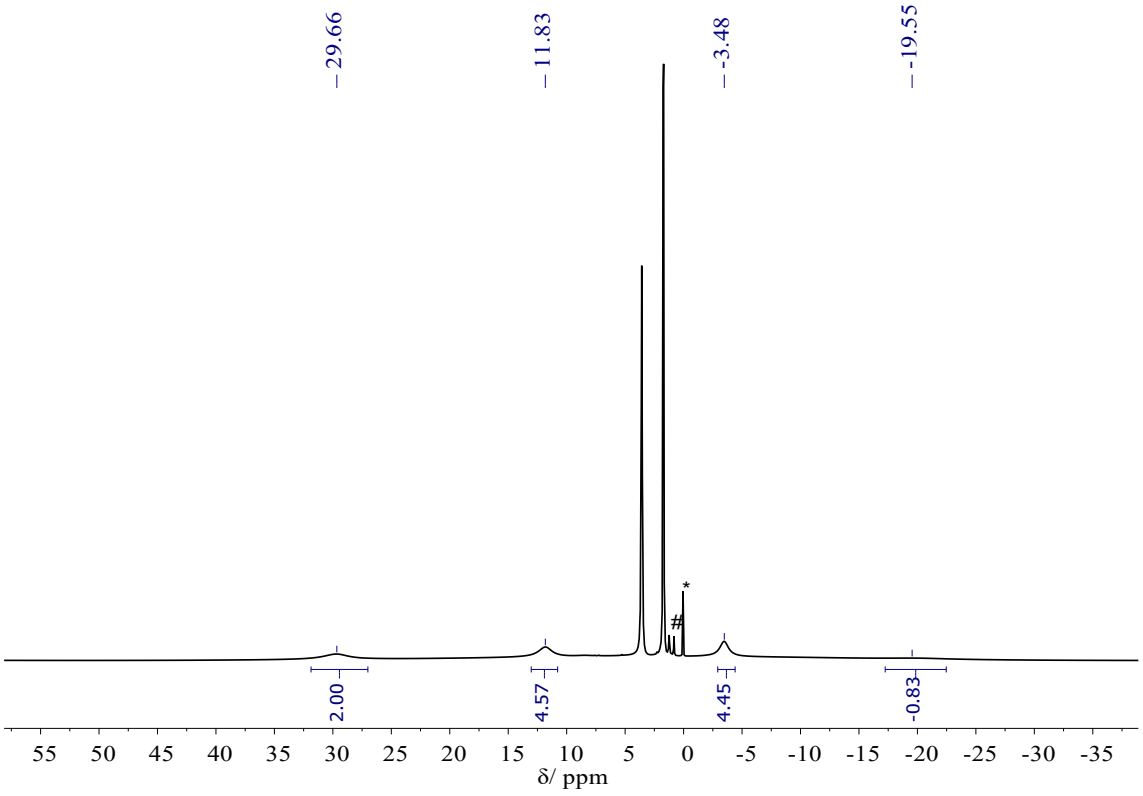

Figure S10: ^{1}H-NMR data for **1a** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

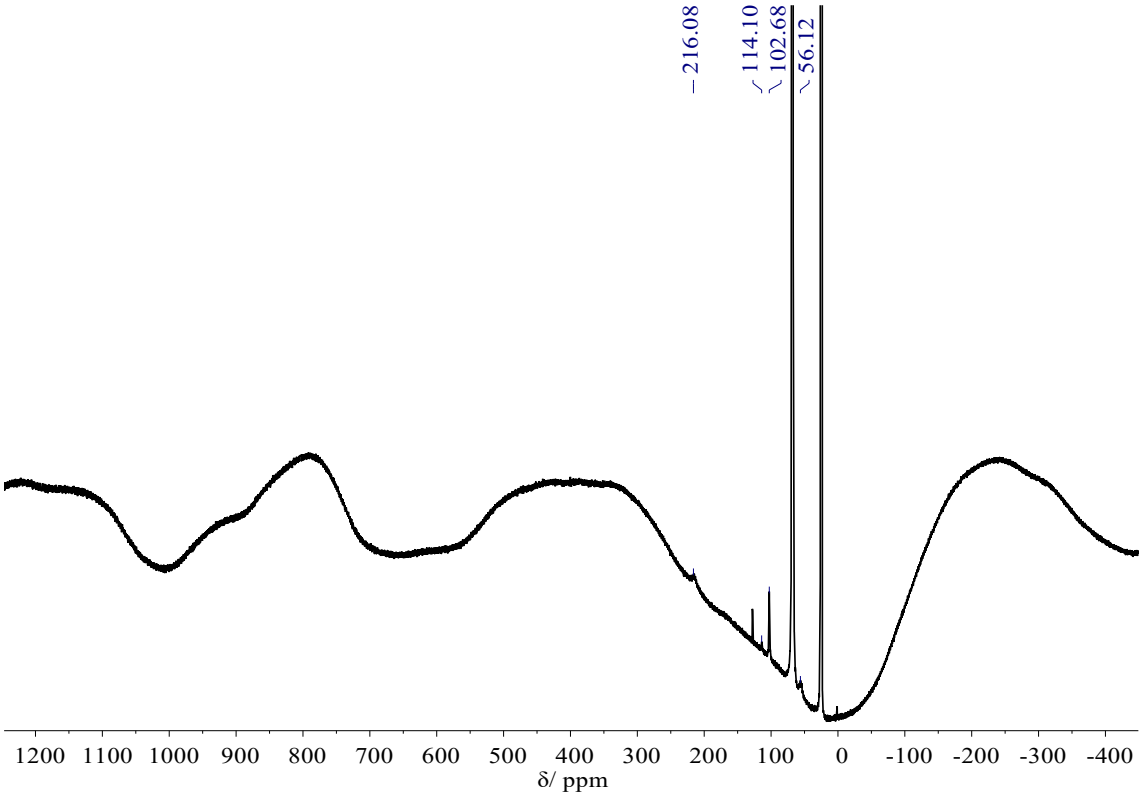

Figure S11: ^{13}C-NMR data for **1a** in thf-d_8 at 298 K. Attempts to record ^{13}C-NMR data for **1a** in thf-d_8 at any temperature failed due to strong signal broadening.

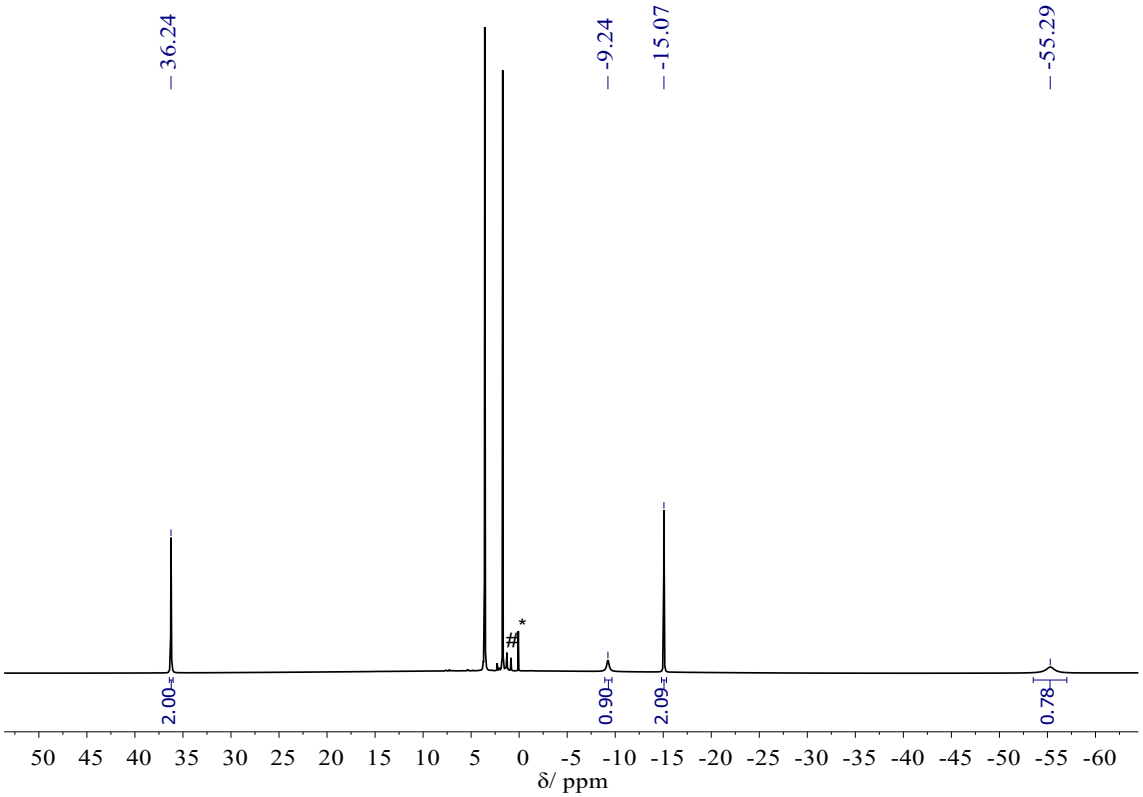

Figure S12: ^{1}H-NMR data for **2a** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

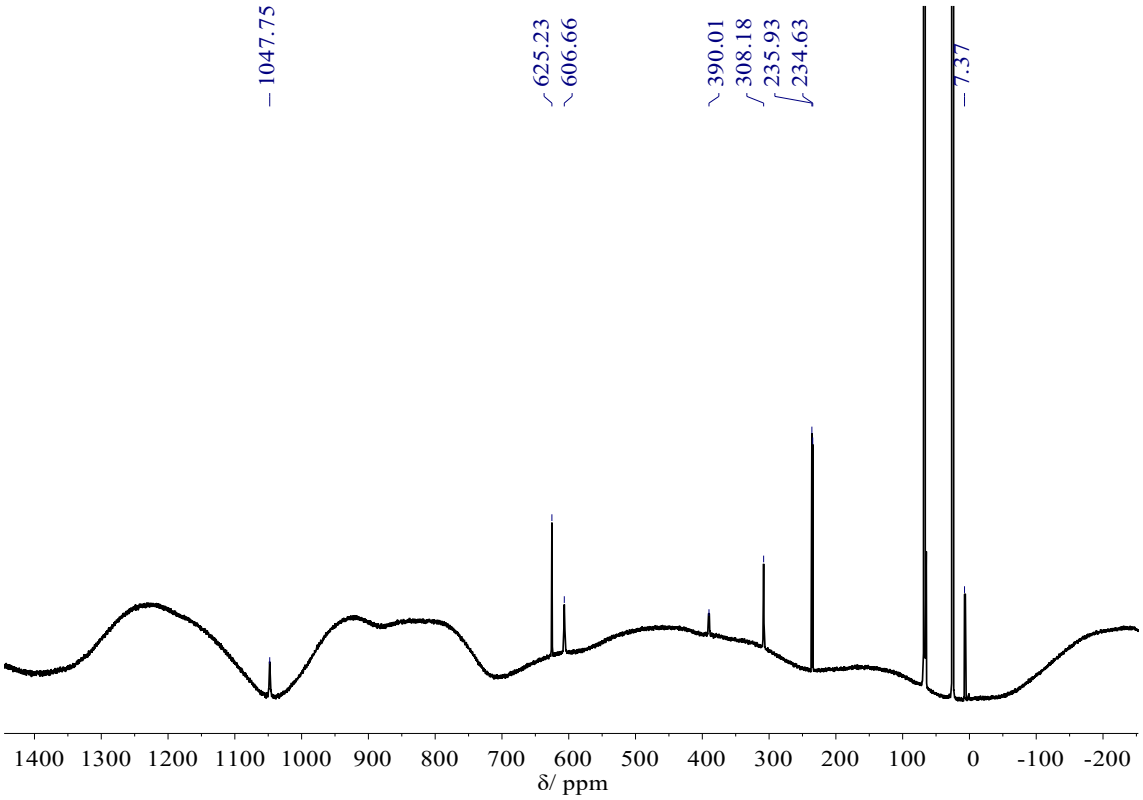

Figure S13: ^{13}C-NMR data for **2a** in thf-d_8 at 298 K.

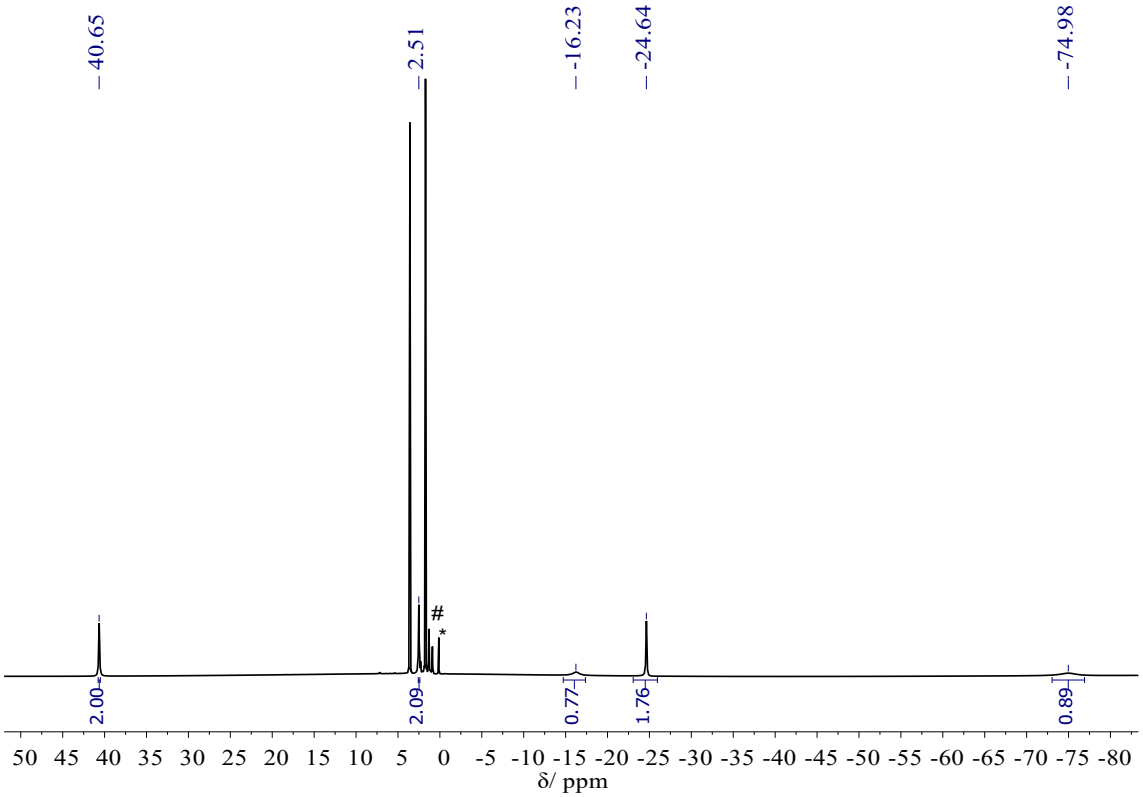

Figure S14: ^{1}H-NMR data for **3a** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

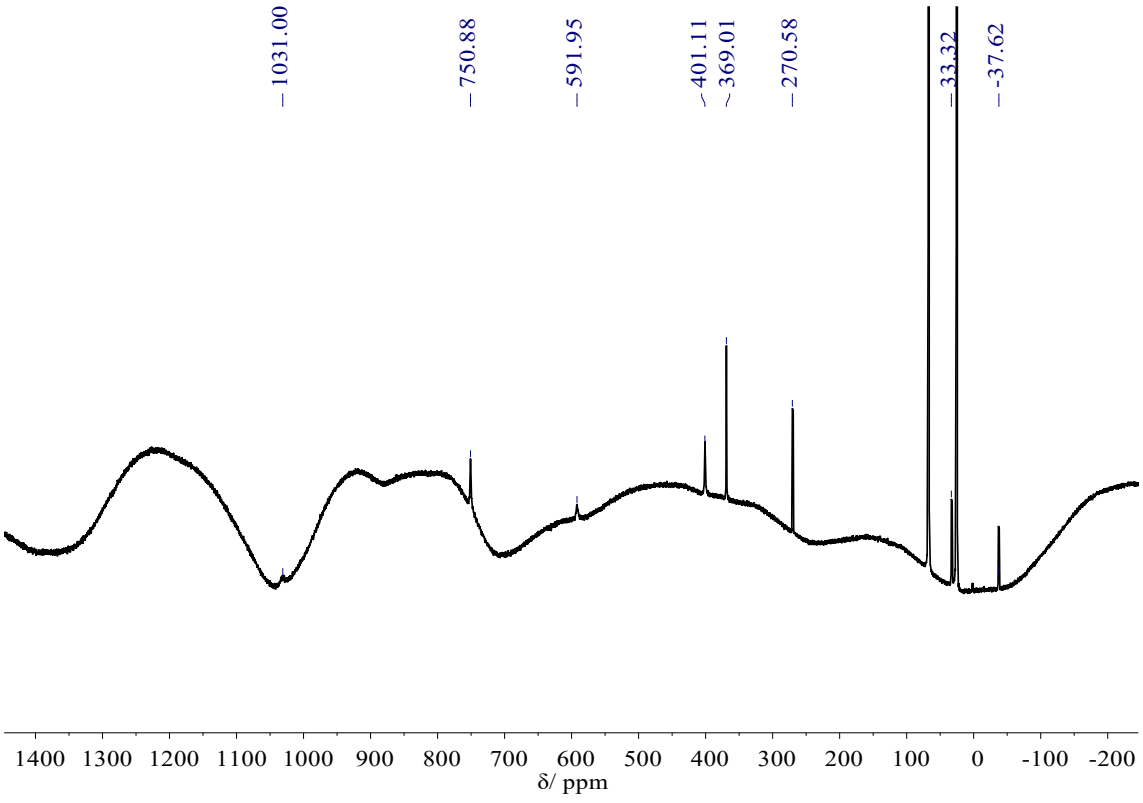

Figure S15: ^{13}C-NMR data for **3a** in thf-d_8 at 298 K.

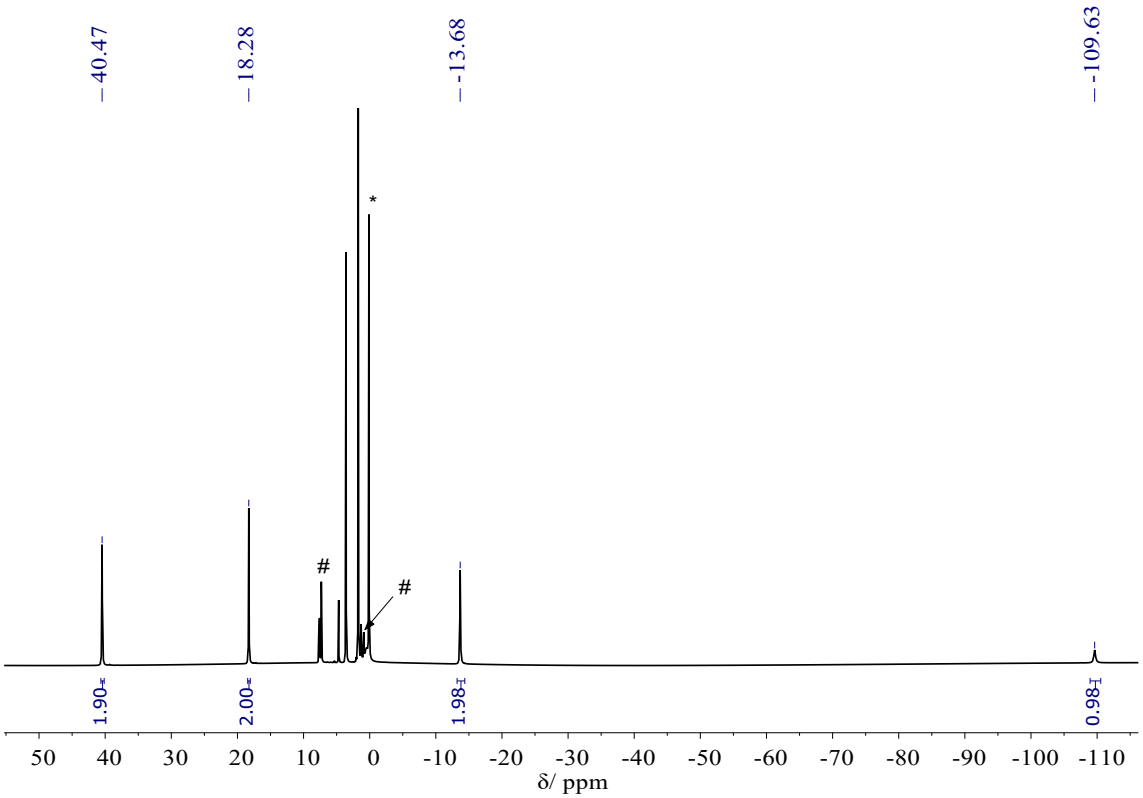

Figure S16: ^{1}H-NMR data for **4a** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

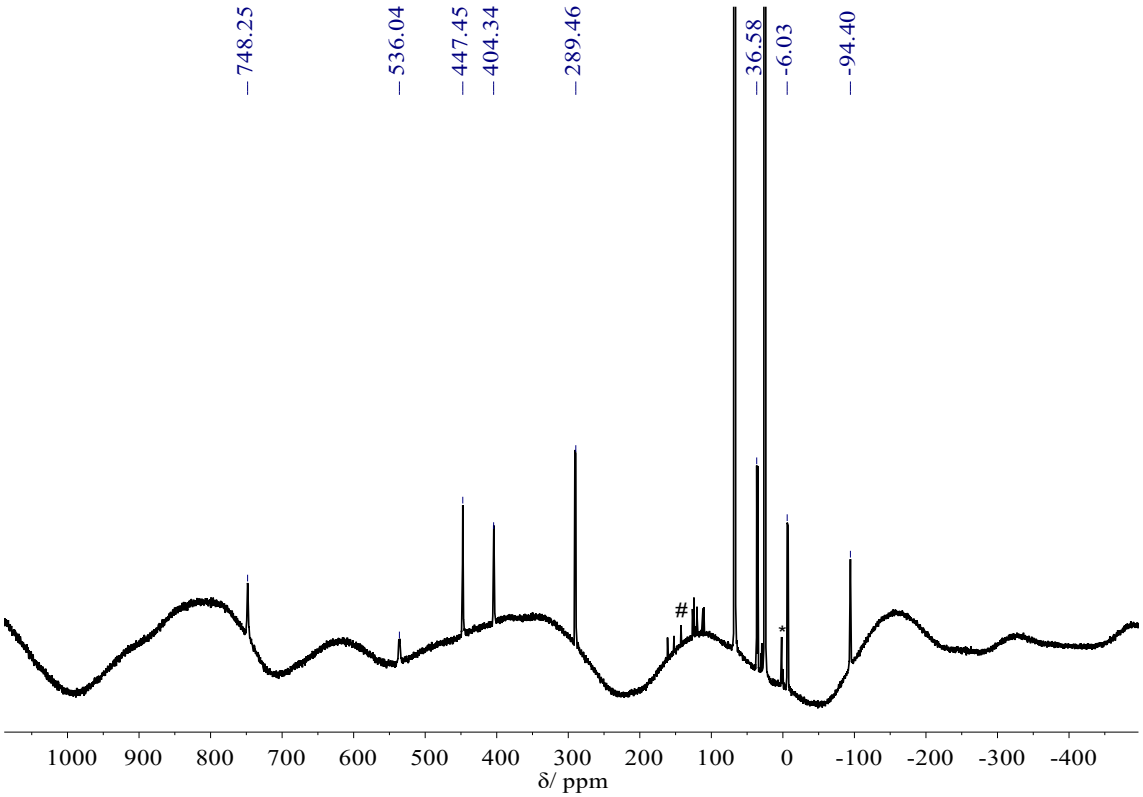

Figure S17: ^{13}C-NMR data for **4a** in thf-d_8 at 298 K. The Residual solvent signals are labeled with **#**.

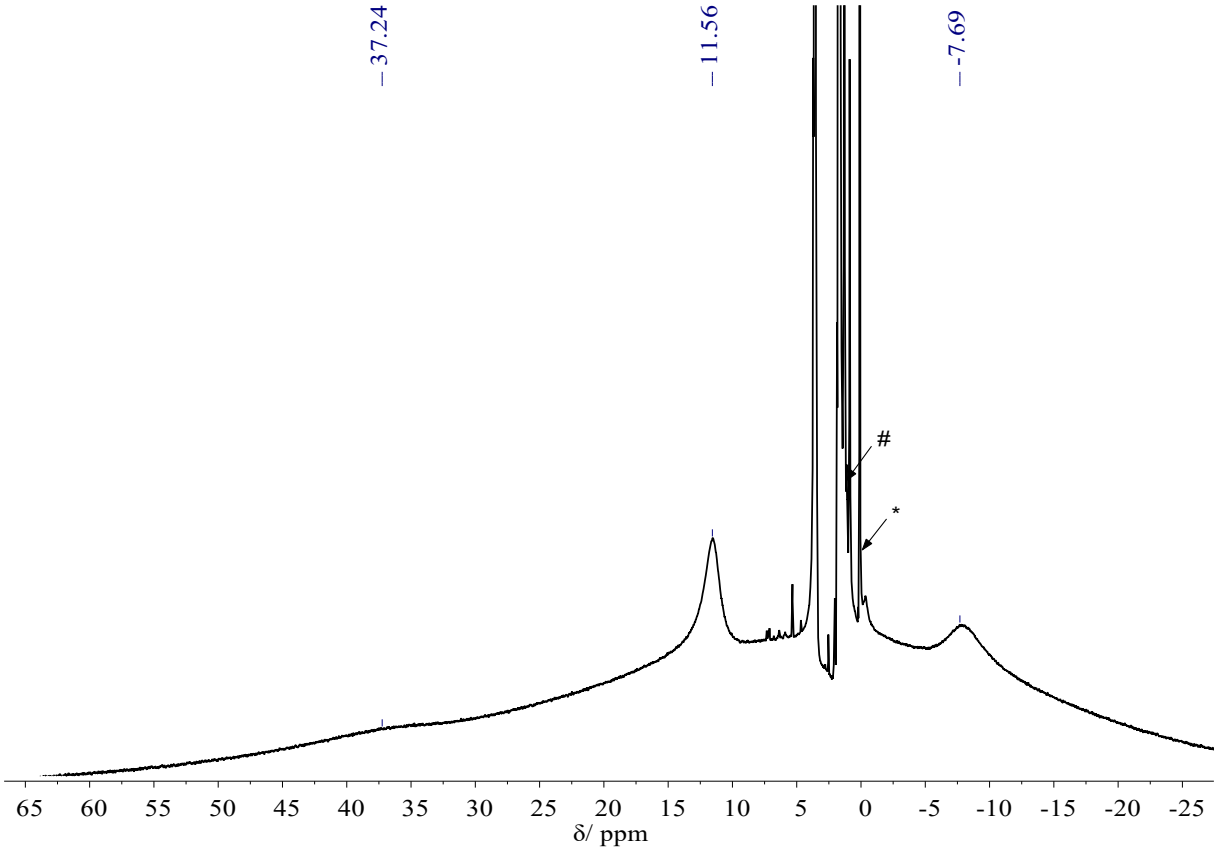

Figure S18: ^{1}H-NMR data for **1b** in thf-d_8 at 298 K. The strong paramagnetic metal center (Mn^{2+}) causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****. Attempts to record ^{13}C-NMR data for **1b** in thf-d_8 at any temperature failed due to strong signal broadening.

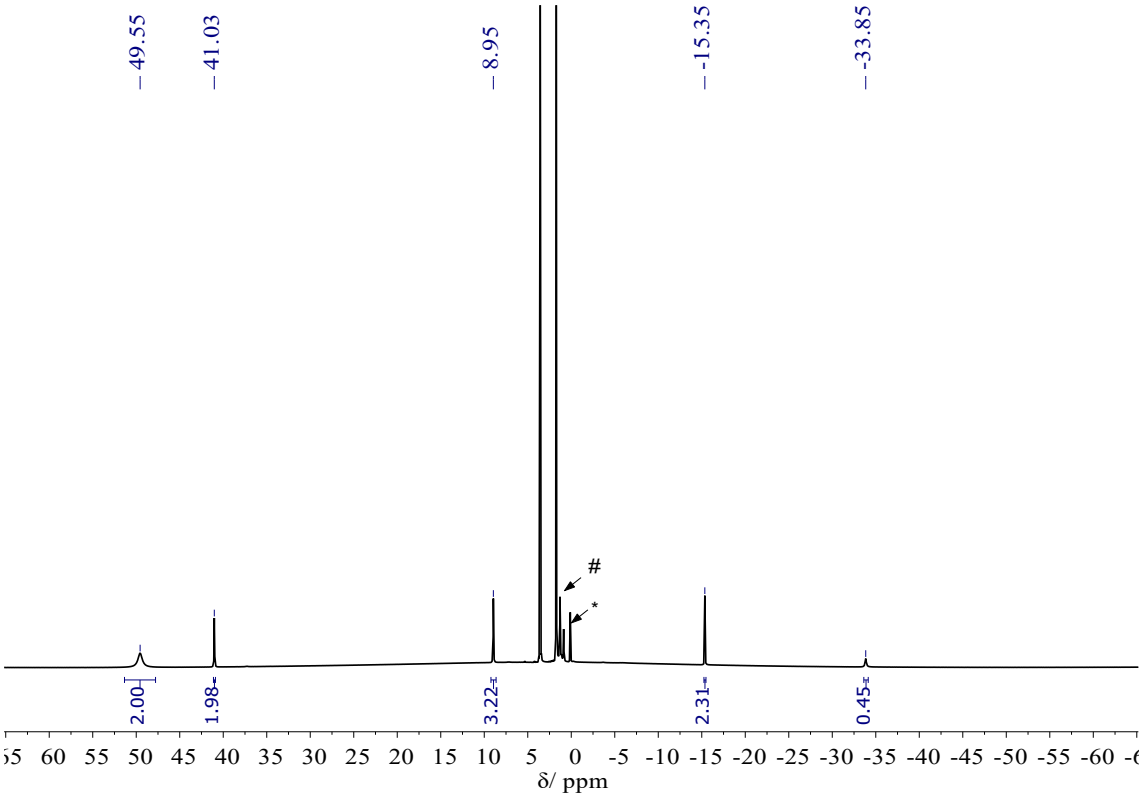

Figure S19: ^{1}H-NMR data for **2b** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

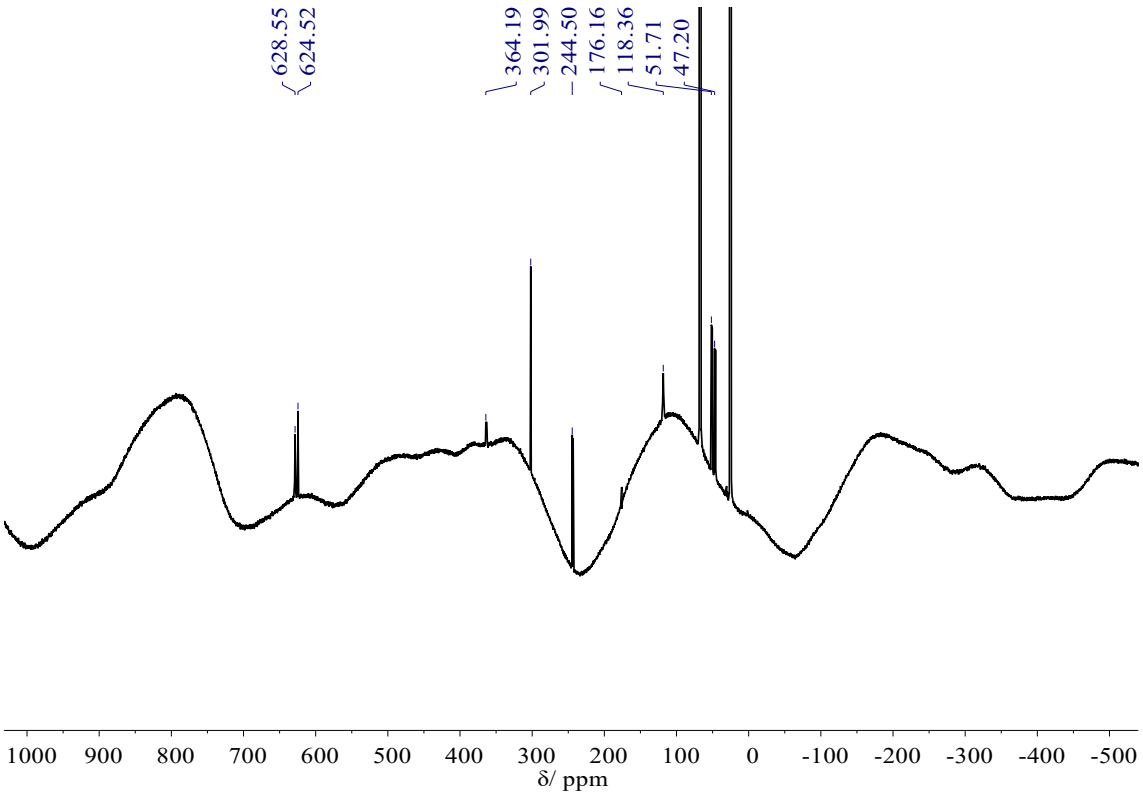

Figure S20: ^{13}C-NMR data for **2b** in thf-d_8 at 298 K.

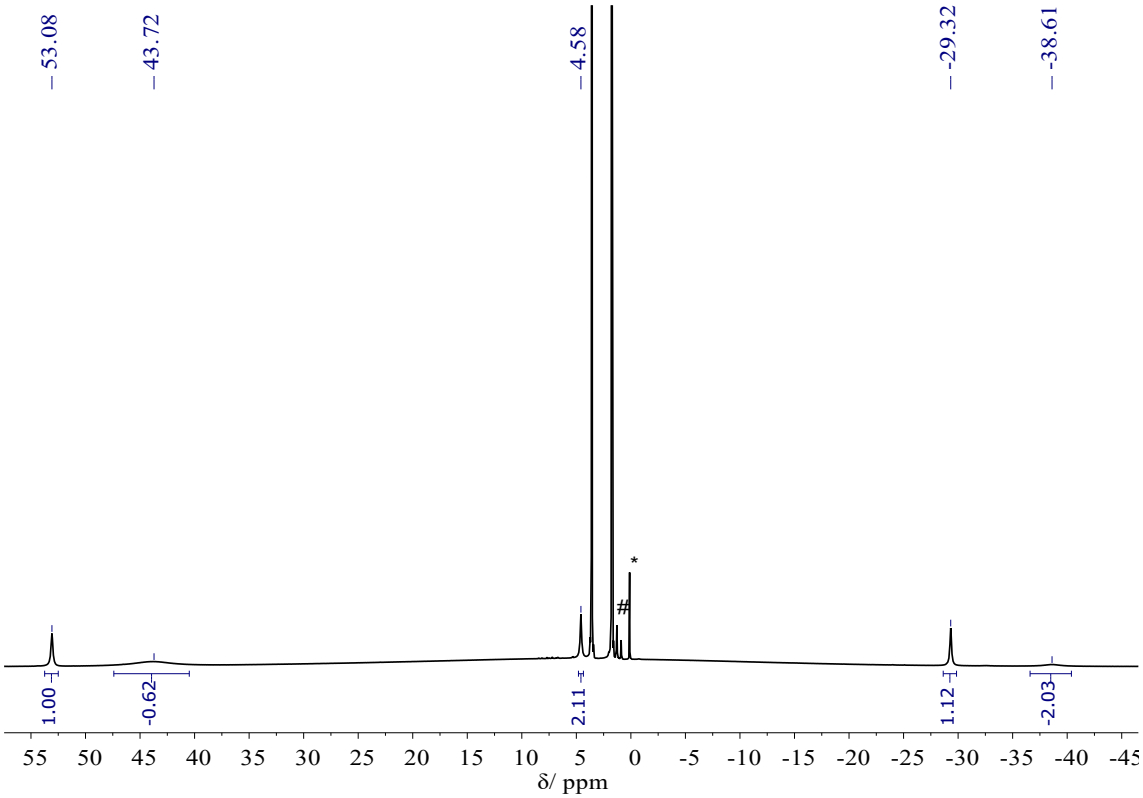

Figure S21: ^{1}H-NMR data for **3b** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

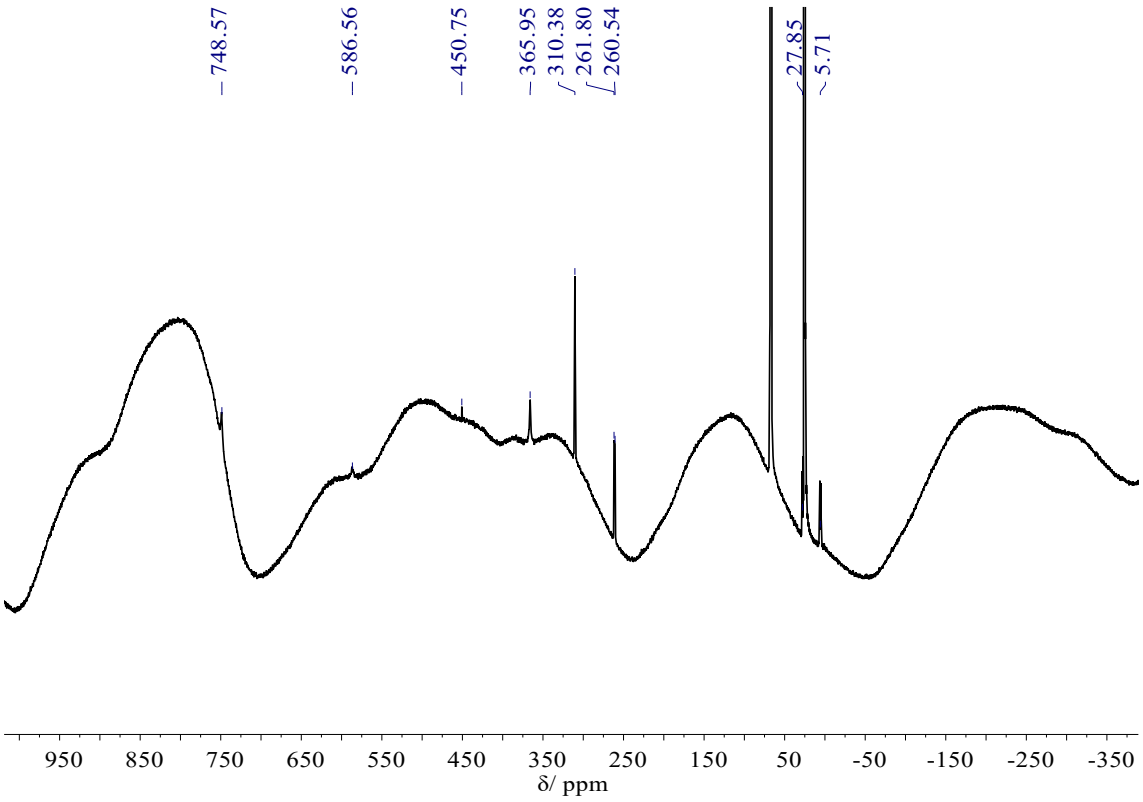

Figure S22: ^{13}C-NMR data for **3b** in thf-d_8 at 298 K.

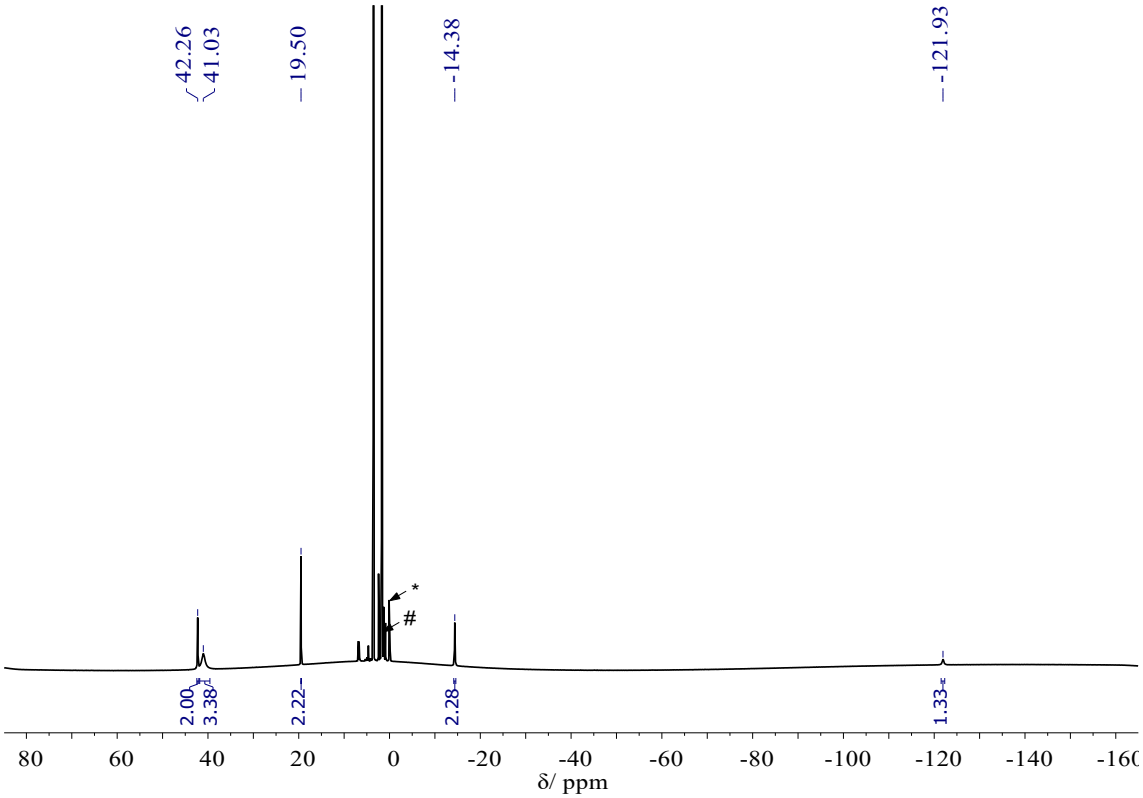

Figure S23: ^{1}H-NMR data for **4b** in thf-d_8 at 298 K. The strong paramagnetic metal center causes strong signal broadening since integral values do not align with expected hydrogen stoichiometry. The Residual solvent signals are labeled with **#** and grease is labeled with *****.

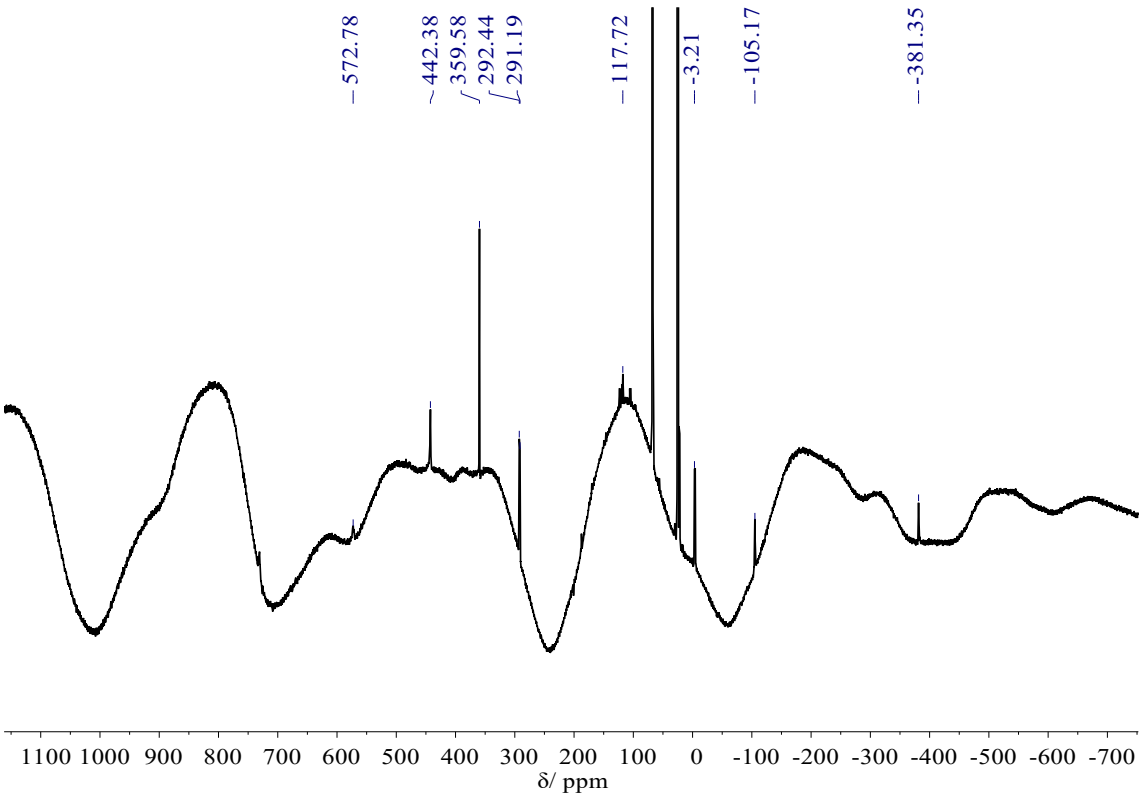

Figure S24: ^{13}C-NMR data for **4b** in thf-d_8 at 298 K.

Mass spectrometry data

The mass spectrometry data was recorded at our Central Analytics Department, located at the organic chemistry institute at University of Göttingen. All experiments were performed applying the LIFDI-MS method and spectra were conducted with a *Jeol* AccuTOF spectrometer.

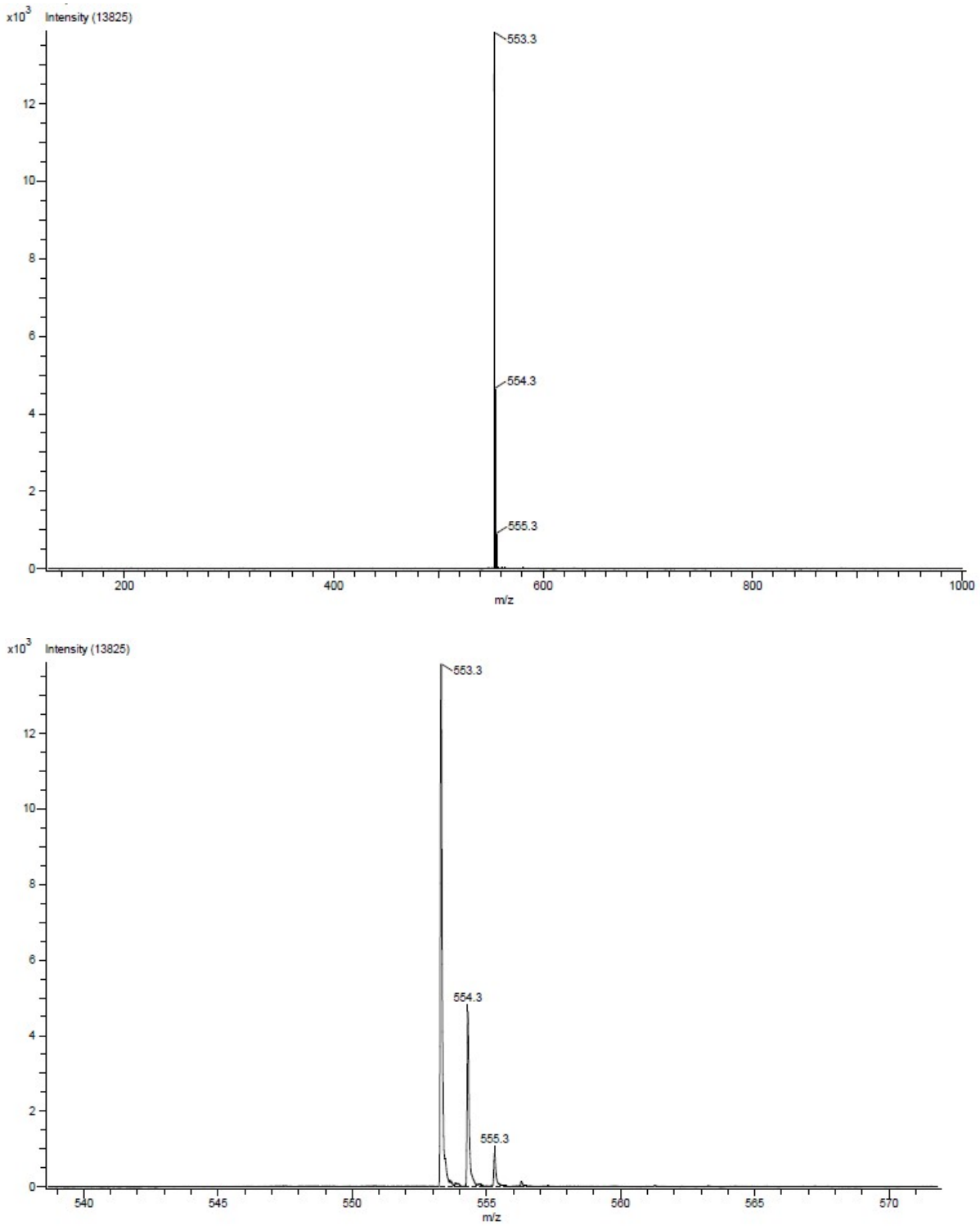

Figure S25: Mass spectrum for 1a, detected fragment refers to $[Mn(Box)_2]$, solvent coordination is not provided by this method.

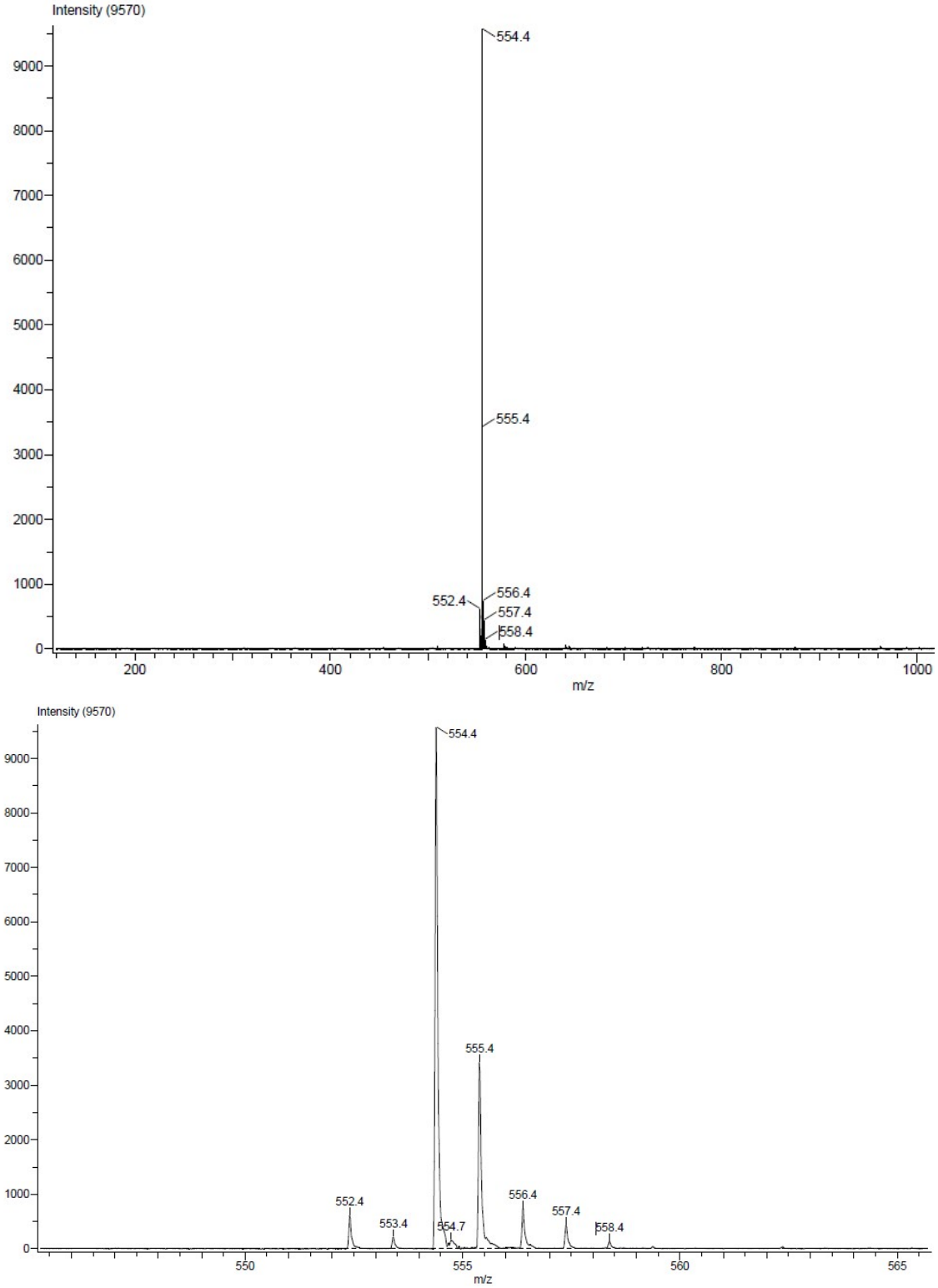

Figure S26: Mass spectrum for 2a, detected fragment refers to $[Fe(Box)_2]$.

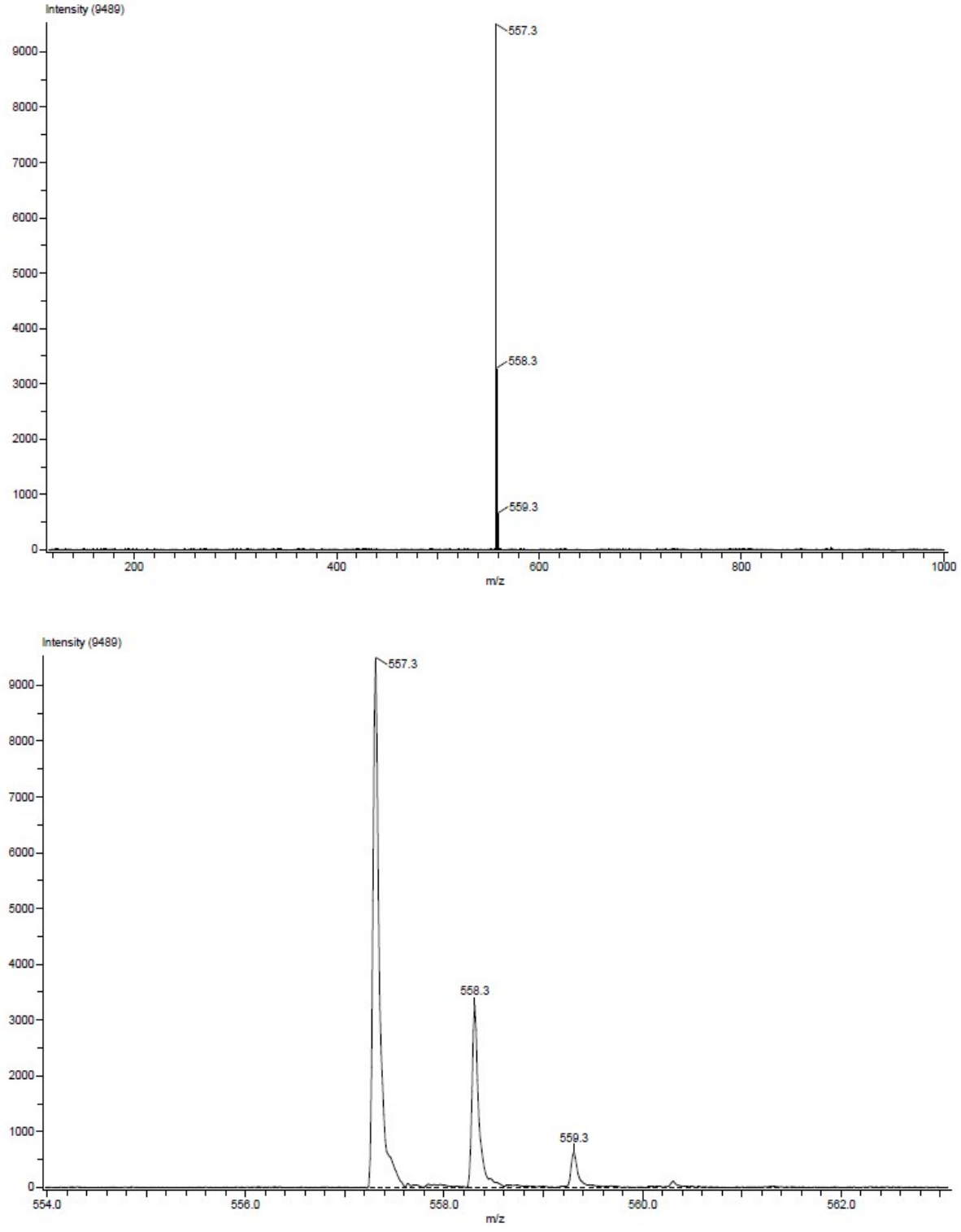

Figure S27: Mass spectrum for 3a, detected fragment refers to $[Co(Box)_2]$,

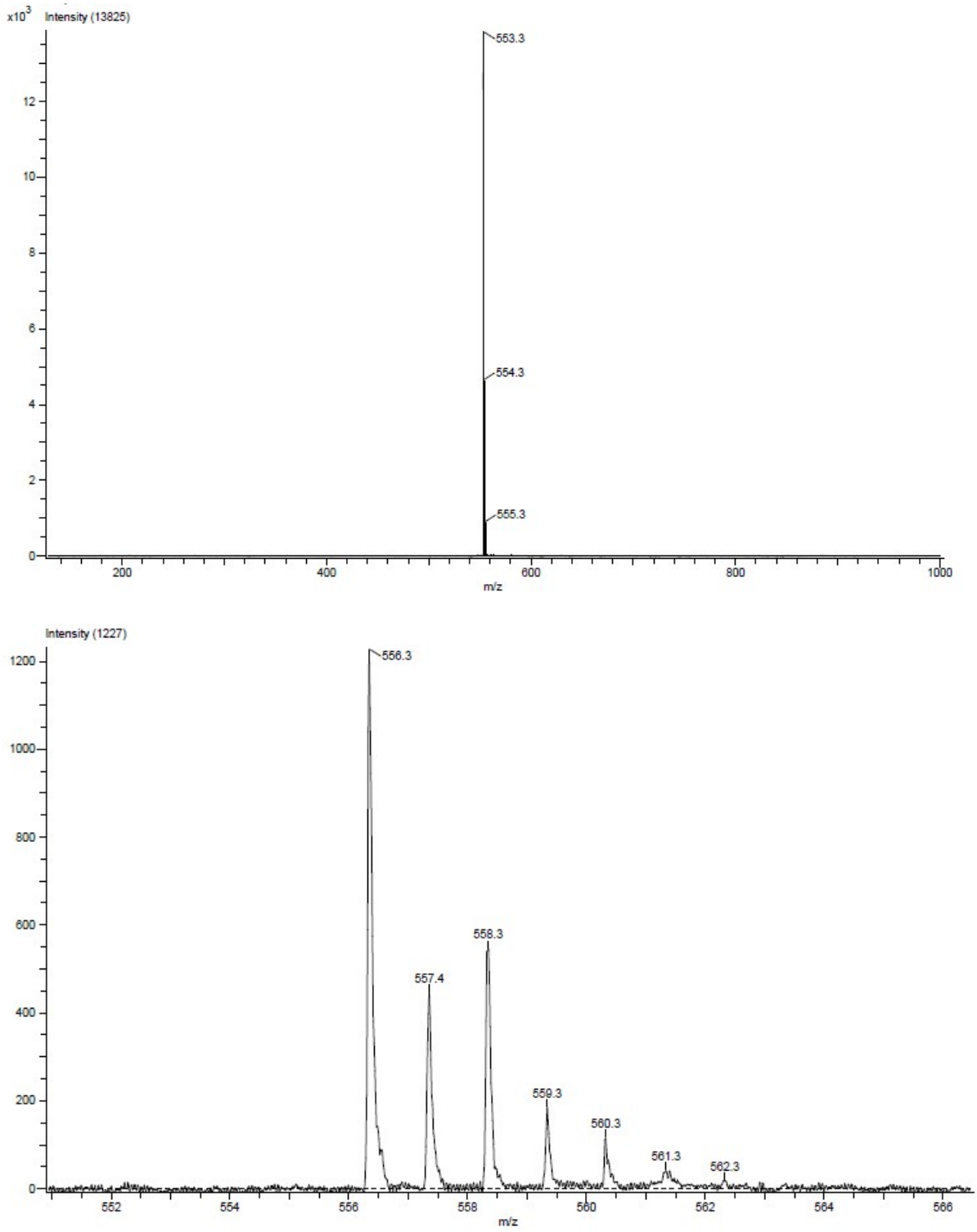

Figure S28: Mass spectrum for 4a, detected fragment refers to $[Ni(Box)_2]$,

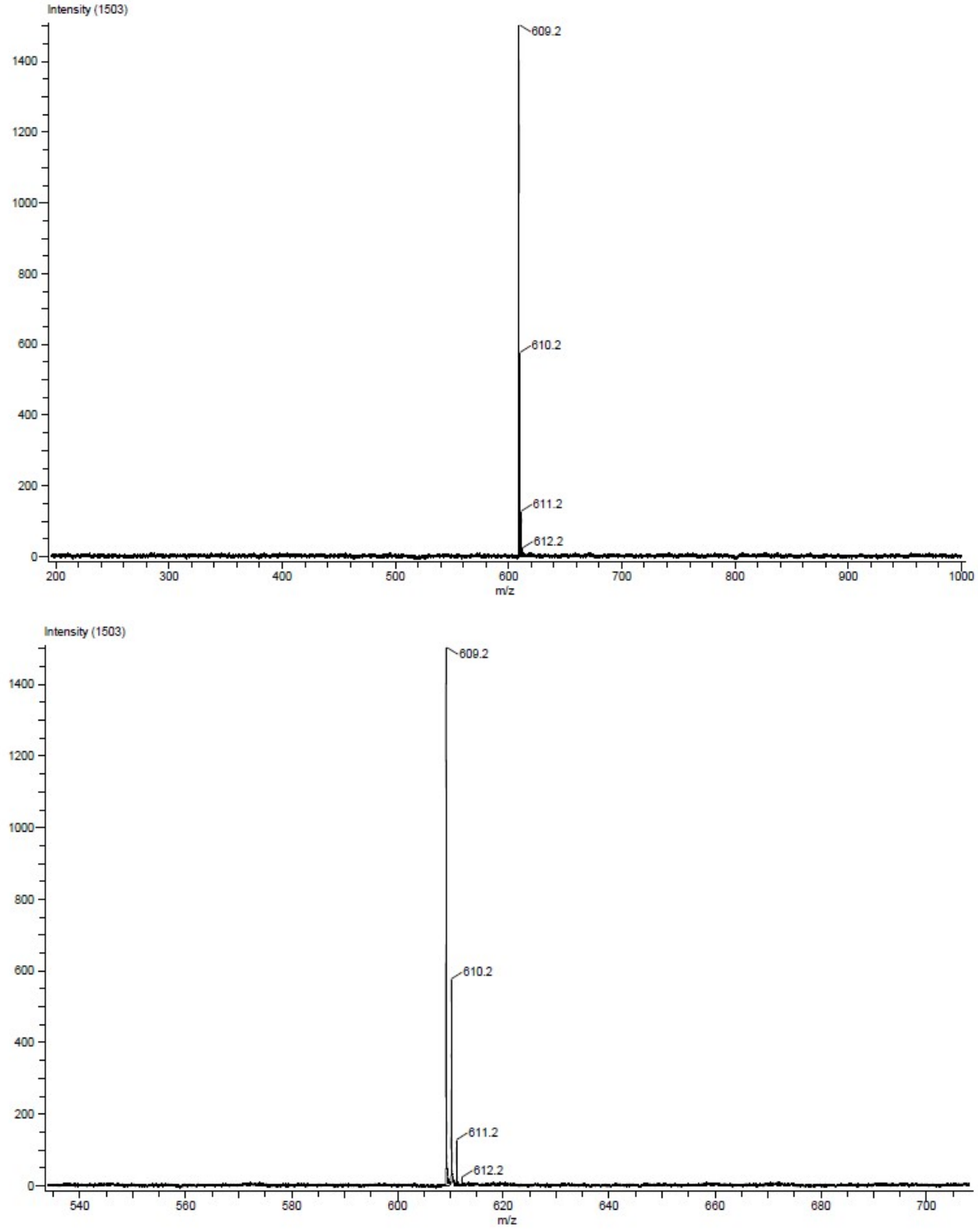

Figure S29: Mass spectrum for 1b, detected fragment refers to $[Mn(MeBox)_2]$.

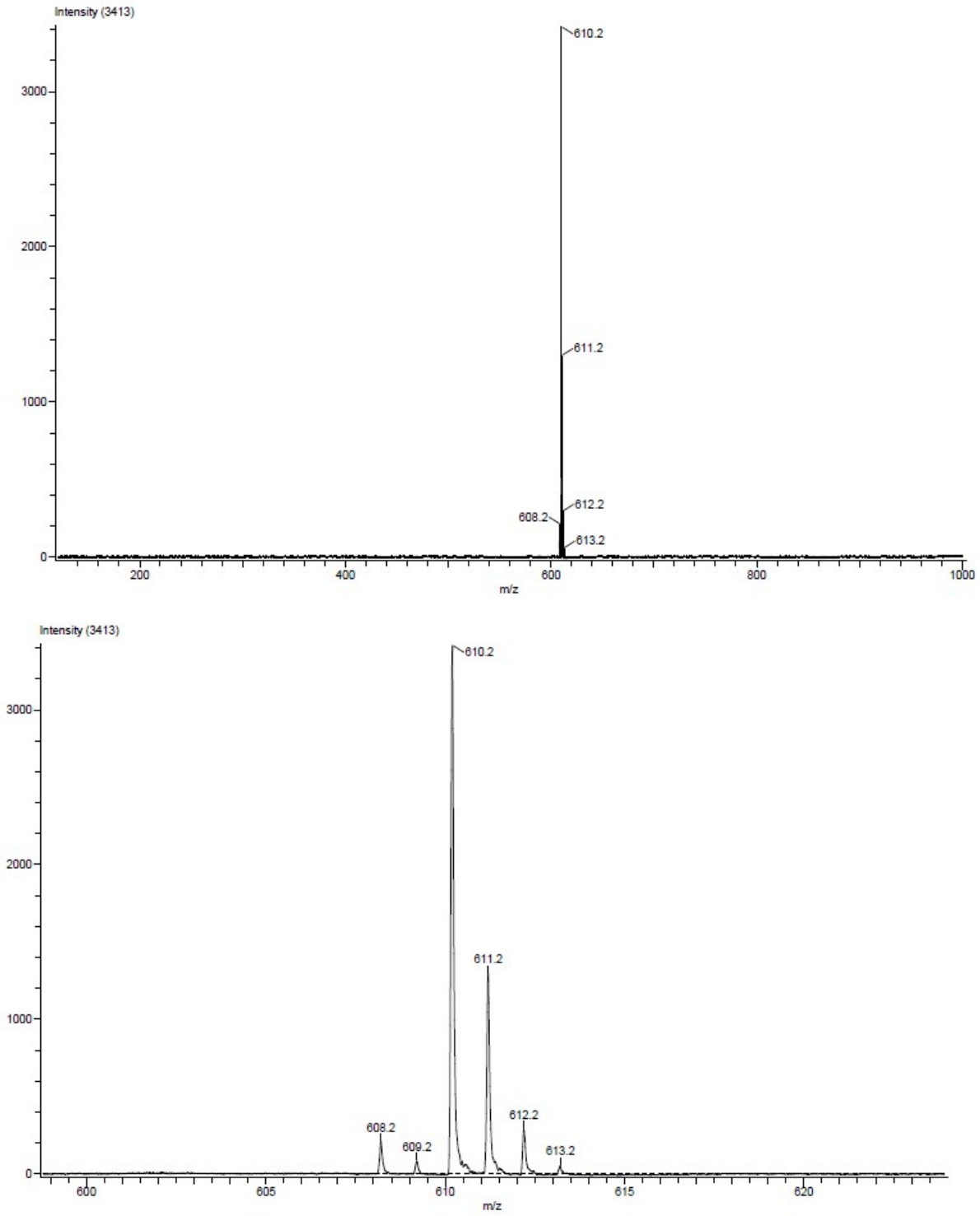

Figure S30: Mass spectrum for 2b, detected fragment refers to [Fe(MeBox)$_2$].

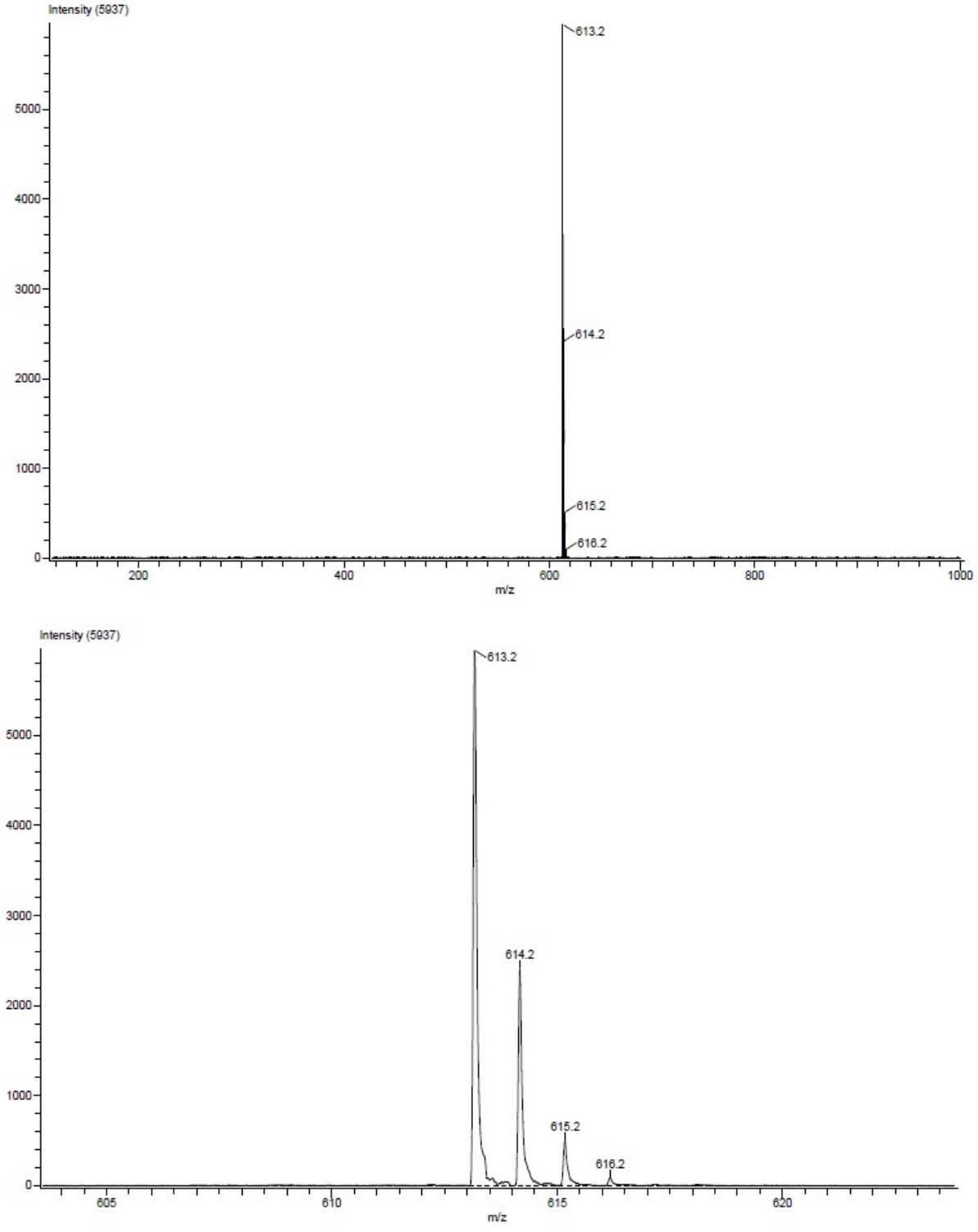

Figure S31: Mass spectrum for 3b, detected fragment refers to $[Co(MeBox)_2]$.

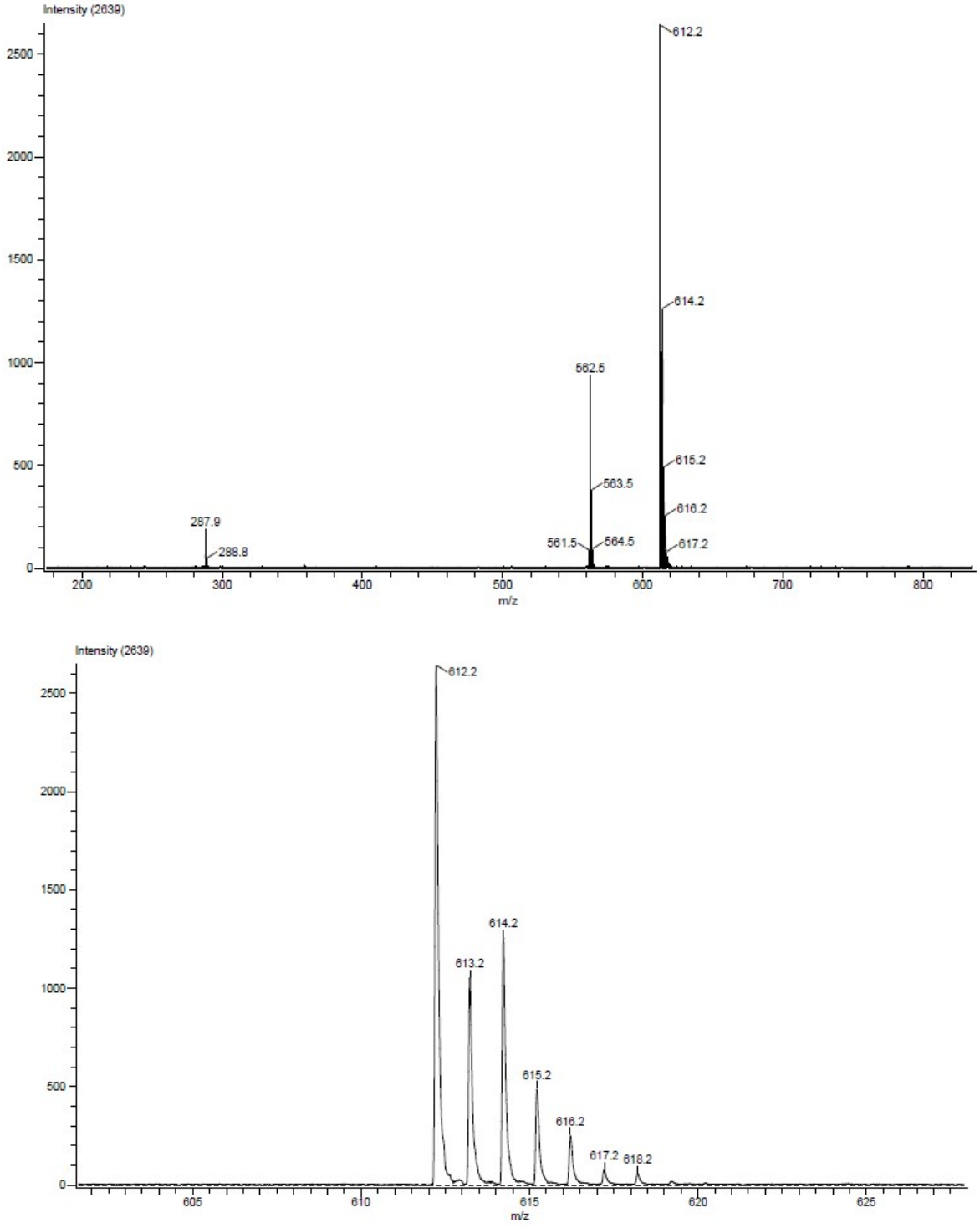

Figure S32: Mass spectrum for 4b, detected fragment refers to [Ni(MeBox)$_2$]. The peak at 287.9 corresponds to the bare ligand.

UV-vis data in solution

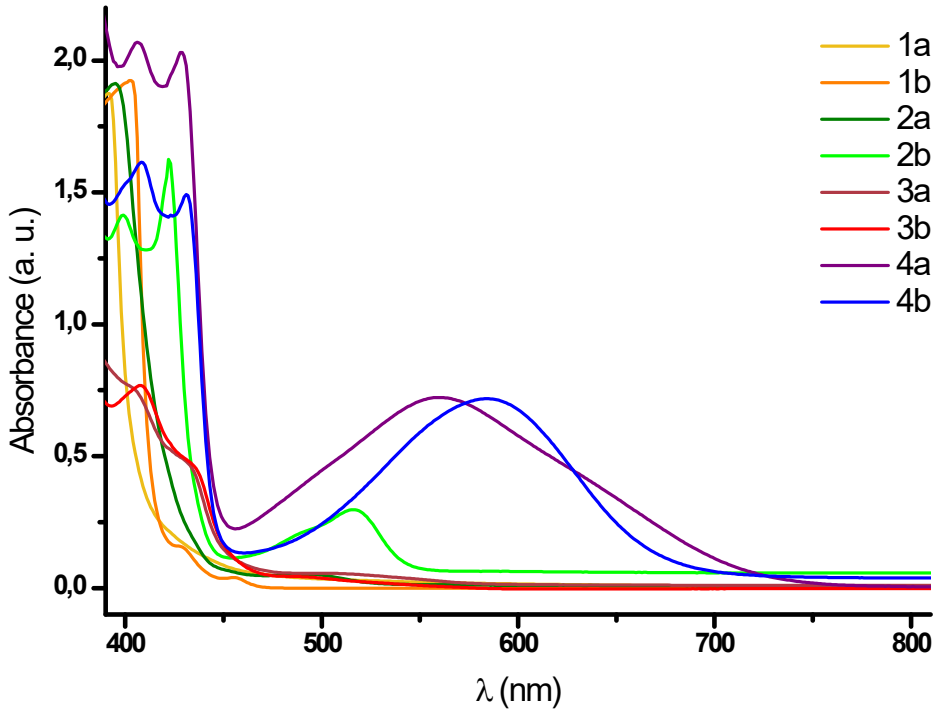

Figure S33: UV-vis/NIR (THF, 0.1 mM, 25 °C, ε is given in L · mol^{-1} · cm^{-1}) 1a: 391 (ε =18762) ; 1b: 402 (ε =19241) 2a: 395 (ε =19136); 2b: 399 (ε =14136), 422 (ε =16251); 3a 404 (ε =7579); 3b: 408 (ε =7680); 4a: 429 (ε =); 4b: 408 (ε =1615), 431 (ε =1492)

UV-vis data in the solid-state

All data was recorded on a HORIBA FLUOROLOG FL 322 spectrometer with a 450 W Xeon-lamp at room temperatures. Equipped with a double monochromator in the excitation compartment (1200l/mm, 300 nm blazed grating) and in the emission compartment (1200 l/mm, 500 nm blaze grating). Detection of emitted light was facilitated by a HAMAMATSU-928P photomultiplier tube. Samples were transferred under inert condition into quartz glass ampoules and sealed via a MIG-O-MAT Lötstar 301.

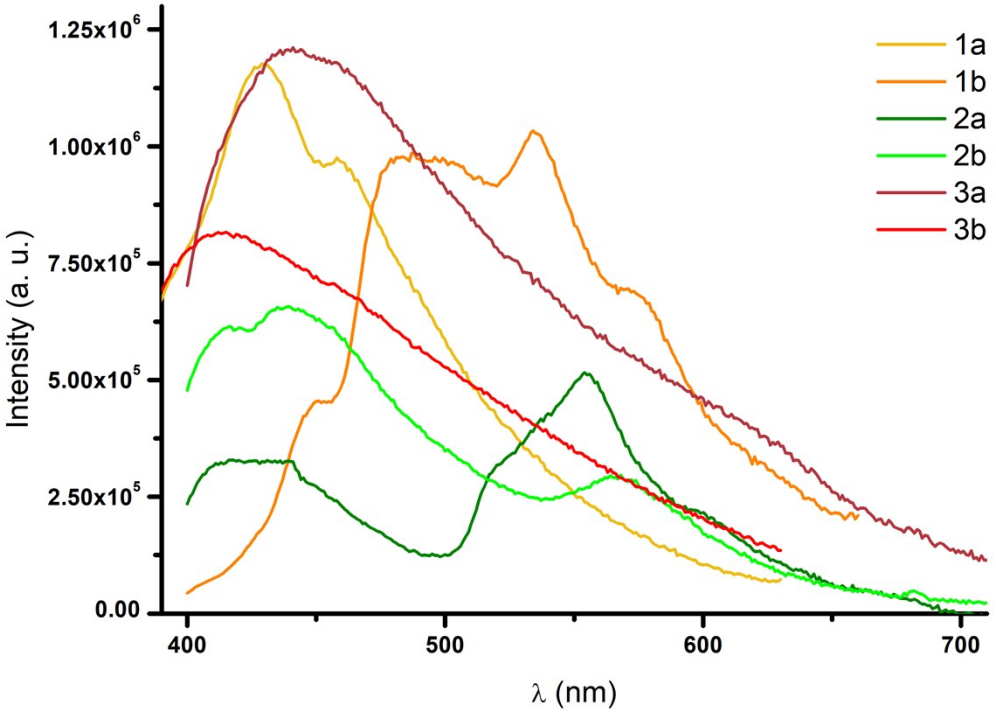

Figure S34: UV-vis (solid-state, 25 °C), 1a: 431; 1b: 534; 2a: 556; 2b: 439; 3a: 441; 3b: 415.

S3 Magnetic data

General procedures and data work-up:

Dc data:

The following spin Hamiltonian with Zeeman splitting, and zero-field splitting is used to fit the dc magnetic susceptibility data and VTVH data using the *JulX-Jul2s* program developed by E. Bill[38]:

$$\hat{H} = \mu_B(S_x g_x B_x + S_y g_y B_y + S_z g_z B_z) + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1) + E/D(\hat{S}_x^2 - \hat{S}_y^2)\right] \quad \textbf{(eq S1)}$$

Weighing issues for **1a** and **1b**, as well as **2a** and **2b**, might occur since there are several solvent molecules present in the structures. In each case, we reported the fitted dc data with the molecular mass verified by elemental analysis (which might be different than the value reported from mass spectrometry). However, considering the unexpected difference observed between the high temperature value of $\chi_M T$ for **1a** and **1b** (Figure 3 in the main manuscript), we additionally report here the $\chi_M T$ values for the different molar masses for **1a** and **1b** while taking more or less solvent molecules into account:

Table S12: Dependence of the number of THFs for the $\chi_M T$ values for **1a** and **1b**.

#	Without THF	With 1 THF	With 2 THFs
$\chi_M T$ for **1a** ($cm^3mol^{-1}K$)	4.10	4.60	5.16
$\chi_M T$ for **1b** ($cm^3mol^{-1}K$)	4.19	4.59	5.19

While taking into account 2 THF molecules is excluded (values much higher than the expected 4.38 $cm^3mol^{-1}K$), the $\chi_M T$ values for no THF and for 1 THF molecule are in good agreement for both complexes. Thus, we suggest than the observed differences between **1a** and **1b** are due to partial variable solvent loss prior to the magnetic measurement.

Ac data:

The presence of slow magnetic relaxation is first probed under 0 Oe and 1000 Oe from 2K to 10K or 20K for each complex at maximal frequency (1488Hz). In case of the observation of a maxima in the out-of-phase signal at a temperature *T*, the optimal field is probed at *T* by screening the applied dc field. Since no optimal field was reached for **1b** and **3a**, as it is a relaxation through phonon bottleneck process, in order to better compare the present complexes, we further chose to present the data at 1000 Oe as a compromise for the relevant complexes (maximum reached at 400 Oe and stable at 1000 Oe for **3b**). Additionally, while looking for SMM behavior, the smallest possible applied magnetic fields are desirable. Subsequently, ac data was recorded from 2K to *T* at H_{dc} = 1000 Oe.

Additional measurements of the out-of-phase susceptibility (χ_M'') at 2 K under a broader range of dc fields ranging from 0 Oe to 7 kOe were performed for **1b** (**figure S53**) and **3a** (**figure S46**)**.** Since **3b** (**figure S63**) exhibits no maximum of χ_M'' at 2K we conducted the analog experiment at 3K. For these measurements the reactions were reproduced, and fresh sample material was used, which further confirms the good reliability of the recorded data. In the light of these findings, the chosen field of 1000 Oe is the most appropriate one to compare **1b**, **3a**, and **3b**.

The Cole-Cole diagrams were analyzed with the CC-Fit program by N. F. Chilton.[39] Temperature dependence of the obtained relaxation times for the main process (Orbach process) were analyzed according to the Arrhenius law using:

$$\tau = \tau_0 \cdot \exp\left(U_{eff} \Big/ k_B T\right) \quad \textbf{(eq. S2)}$$

The full fits were performed according to the following equation:

$$\tau^{-1} = \tau_0{}^{-1} e^{-U_{eff}/k_B T} + CT^n + \tau_{QTM}^{-1} \textbf{ (eq S3)}$$

taking Orbach, Raman processes and, if necessary (for **1b**), QTM into account.

S3.1 Magnetic data for **1a**

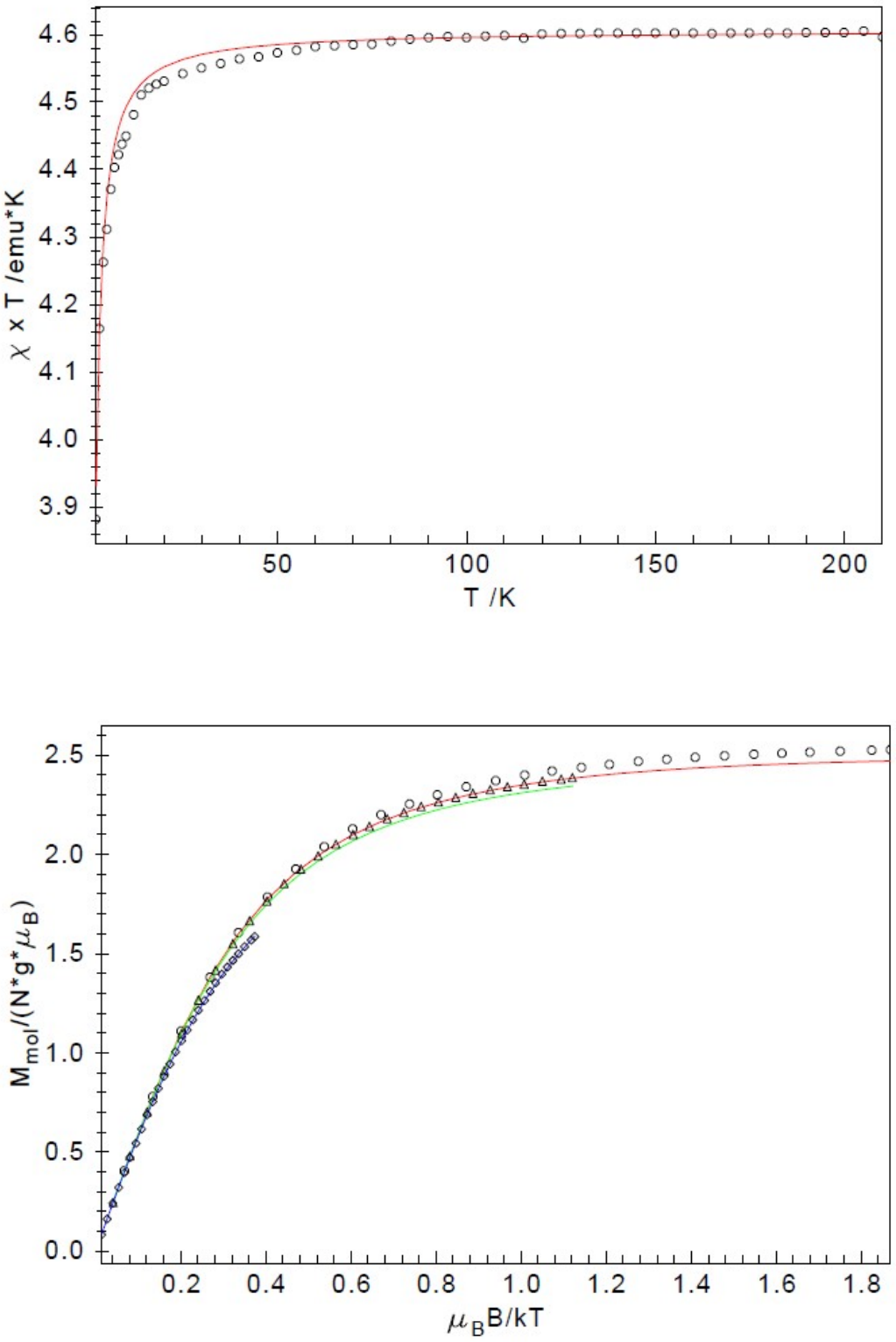

Figure S35: $\chi_M T$ vs T and VTVH data for **3a**. The following best fitting parameters were found: D = -0.03 cm^{-1}, E/D = 0, $g_{x1=y1=z1}$ = 2.052, TIP = 8.9 x 10^{-6} emu.

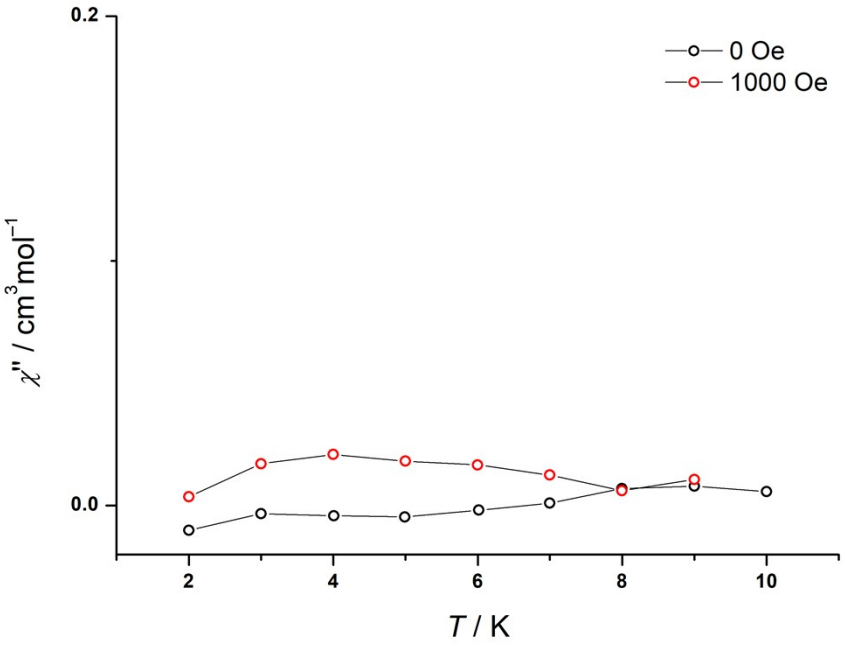

Figure S36: Temperature dependency of the imaginary part of the dynamic magnetic moment for **1a** with a small ac field of 3Oe at maximal frequency of 1488 Hz. No maxima are detected, even under applied dc field.

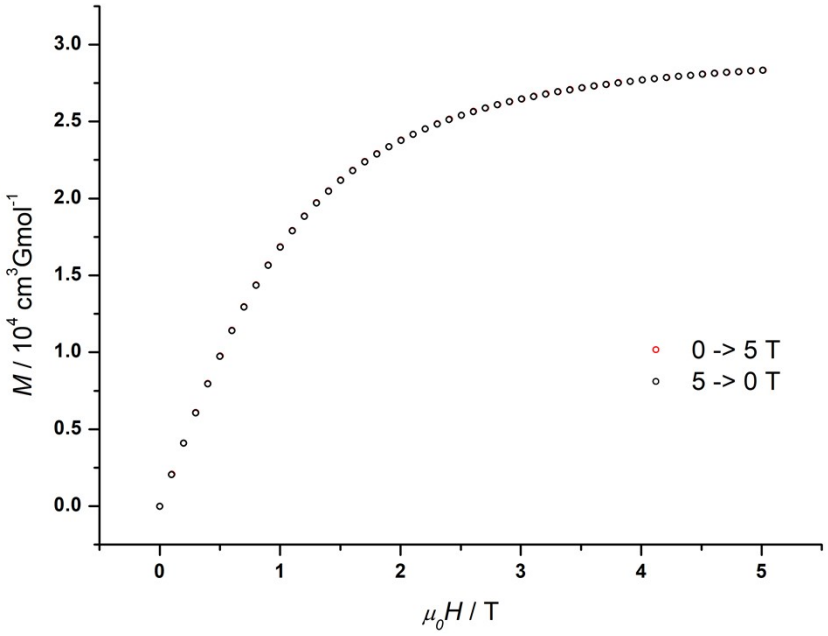

Figure S37: Field dependency of the magnetic moment of **1a** at 2K (field varied from 0 T to 5T and back).

S3.2 Magnetic data for **2a**

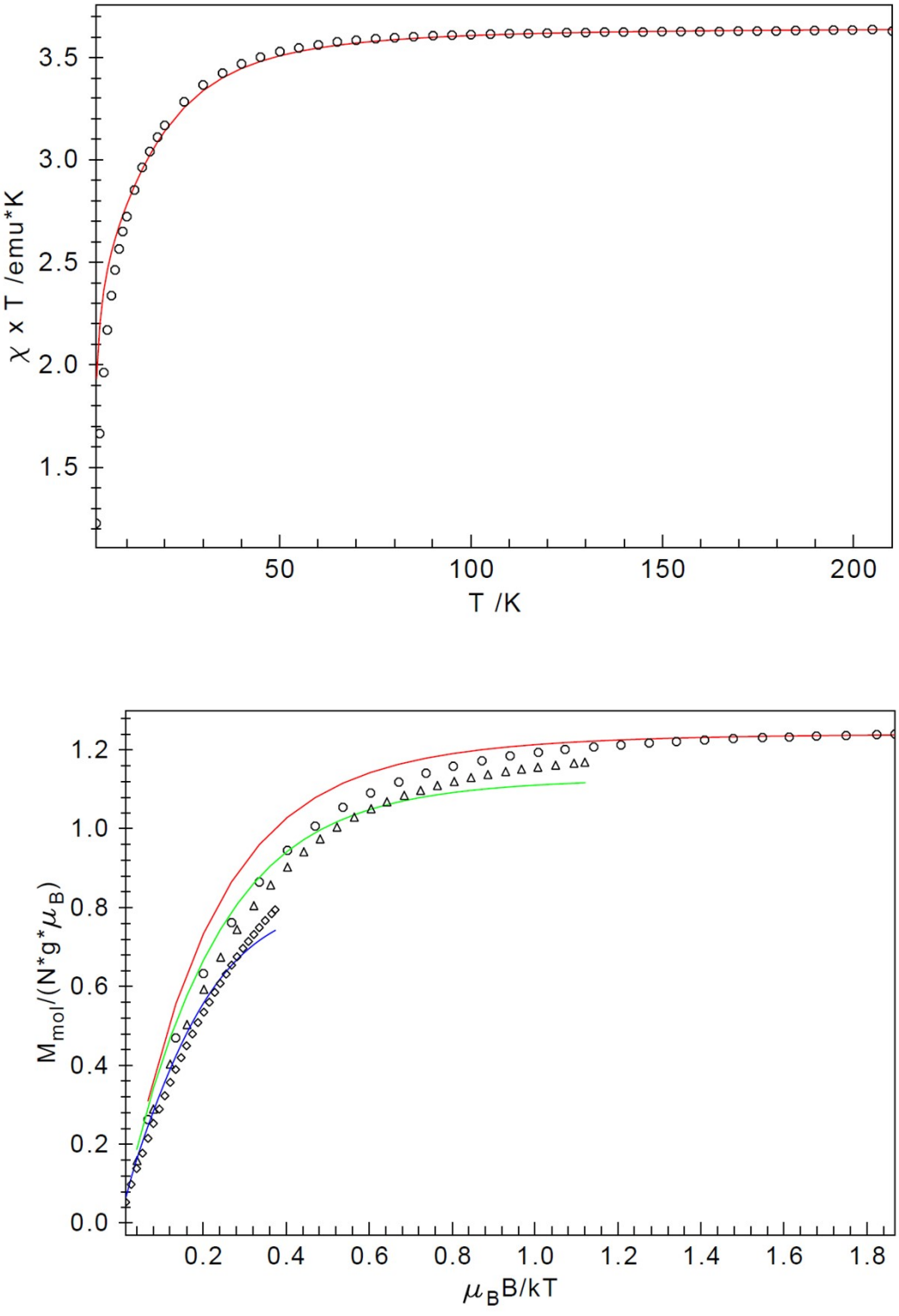

Figure S38: $\chi_M T$ vs T and VTVH data for **2a**. The following best fitting parameters were found: D = 11.74 cm^{-1}, E/D = 0.3 $g_{x1=y1=z1}$ = 2.21, TIP = 171.2 x 10^{-6} emu

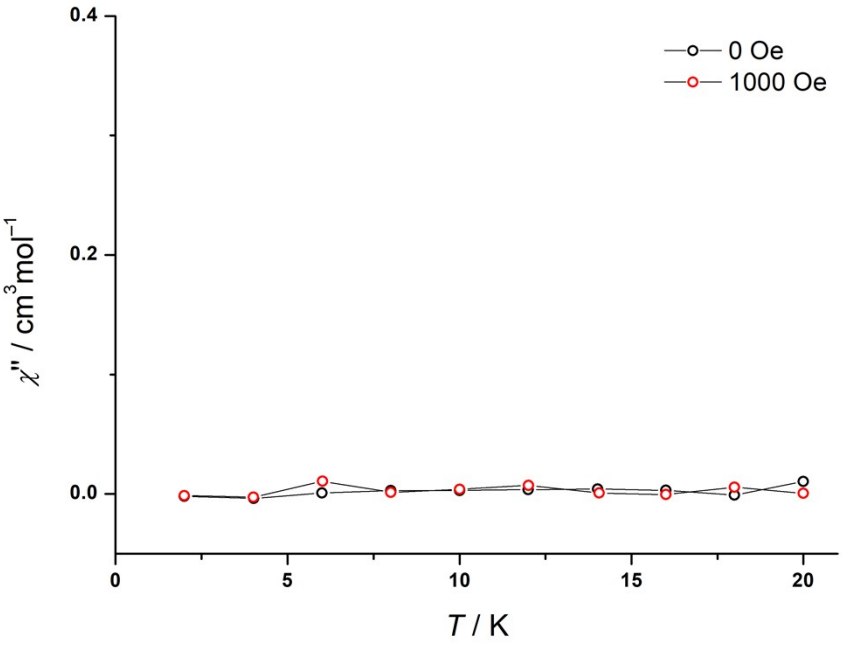

Figure S39: Temperature dependency of the imaginary part of the dynamic magnetic moment for **2a** with a small ac field of 3Oe at maximal frequency of 1488 Hz. No maxima are detected, even under applied dc field.

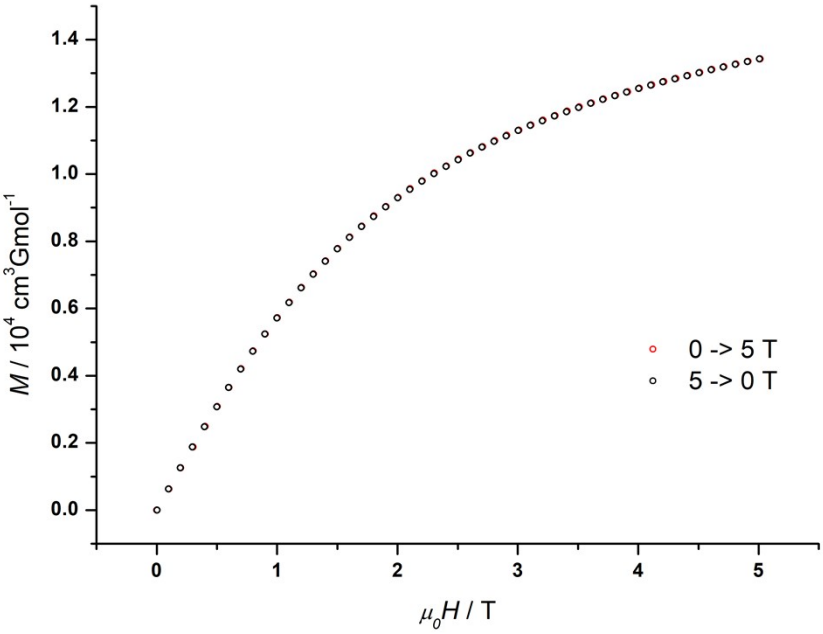

Figure S40: Field dependency of the magnetic moment of **2a** at 2K (field varied from 0 T to 5T and back).

S3.3 Magnetic data for **3a**

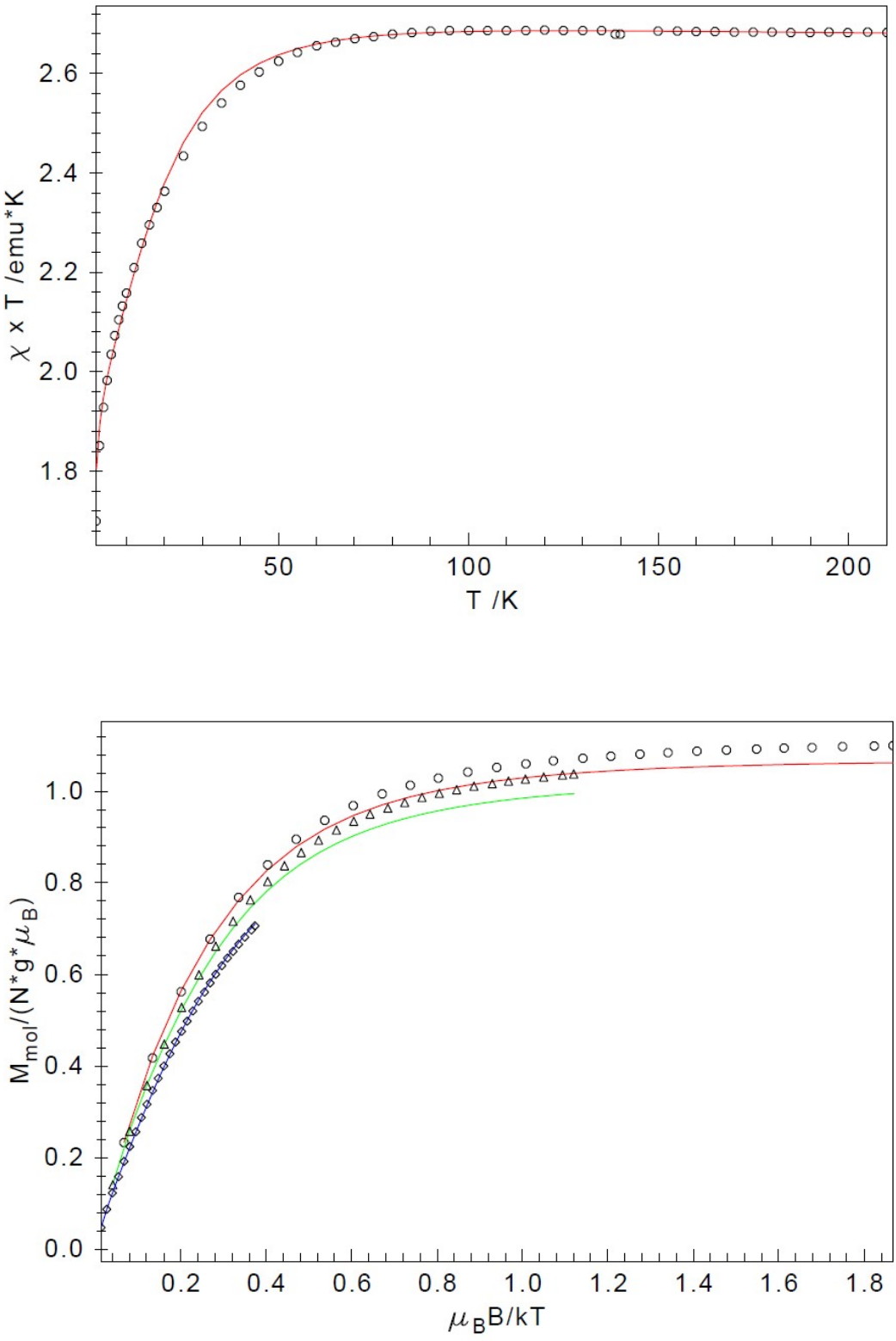

Figure S41: $\chi_M T$ vs T and VTVH data for **3a**. The following best fitting parameters were found: D = -24.95 cm^{-1}, E/D = 0, $g_{x1=y2}$ = 2.272, , g_{z1} = 2.58, TIP = 2.42 x 10^{-4} emu.

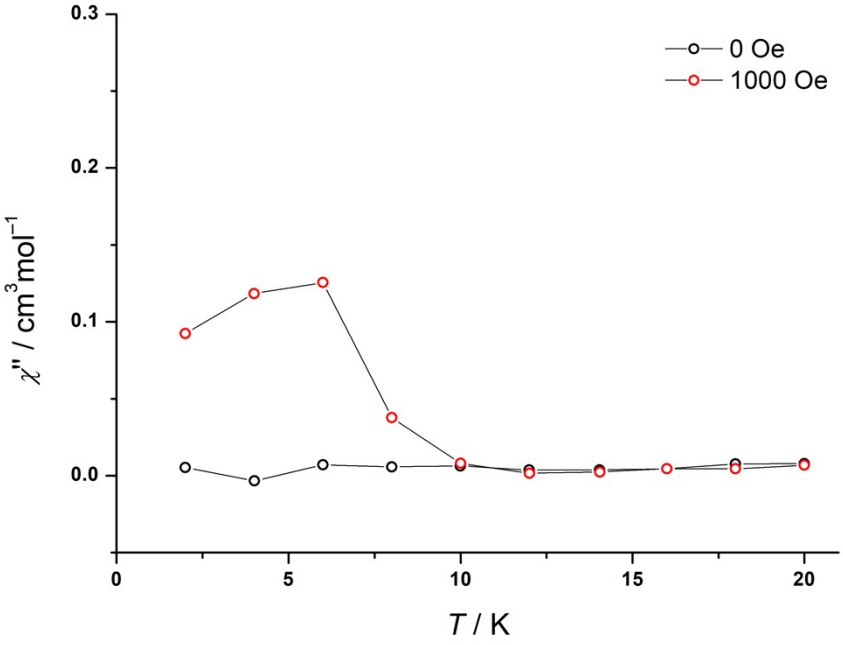

Figure S42: Temperature dependency of the imaginary part of the dynamic magnetic moment for 3a with a small ac field of 3Oe at maximal frequency of 1488 Hz. A small maximum is detected at 5 K under an applied dc field of 1000 Oe.

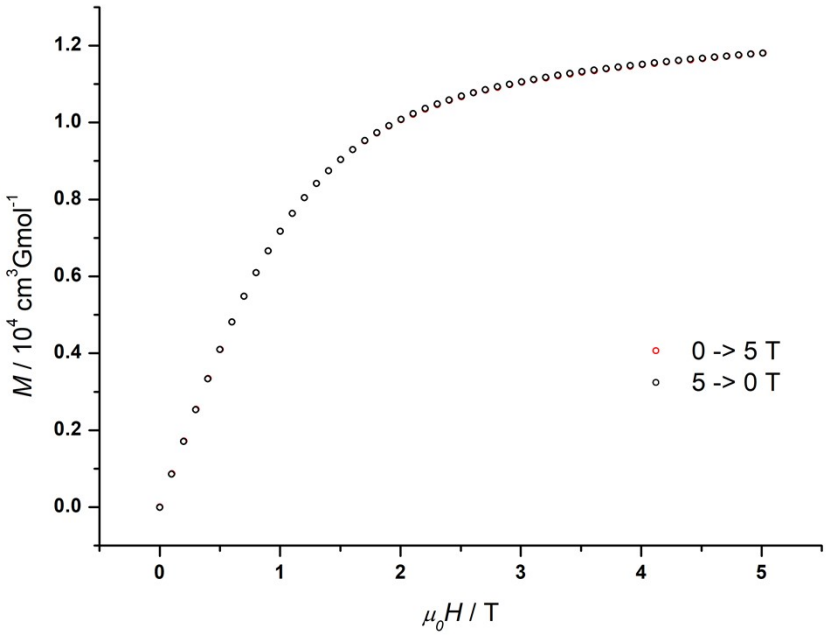

Figure S43: Field dependency of the magnetic moment of **3a** at 2K (field varied from 0 T to 5T and back).

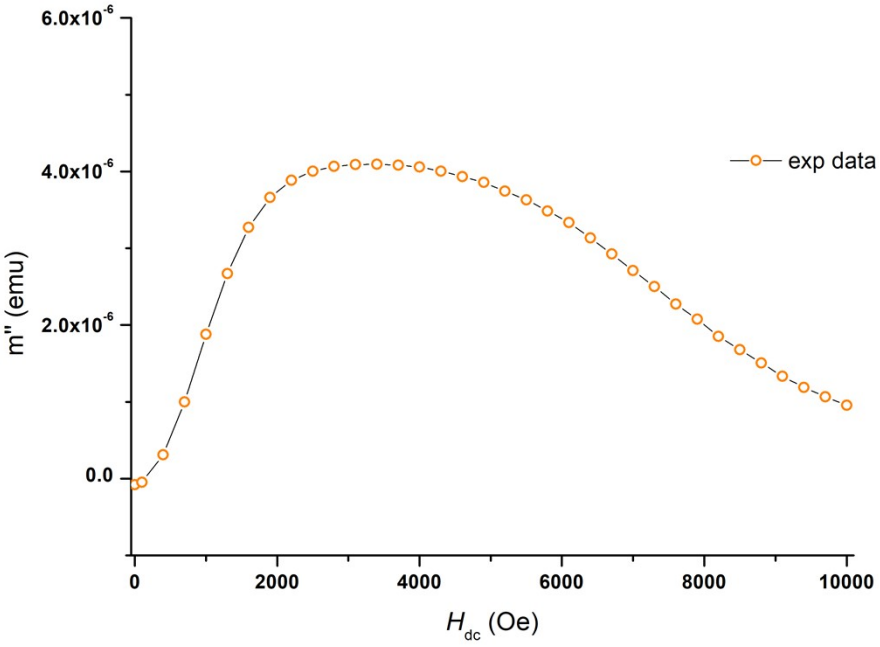

Figure S44: Field dependency of m" for **3a**. The value of m" constantly increases while increasing the external magnetic dc field.

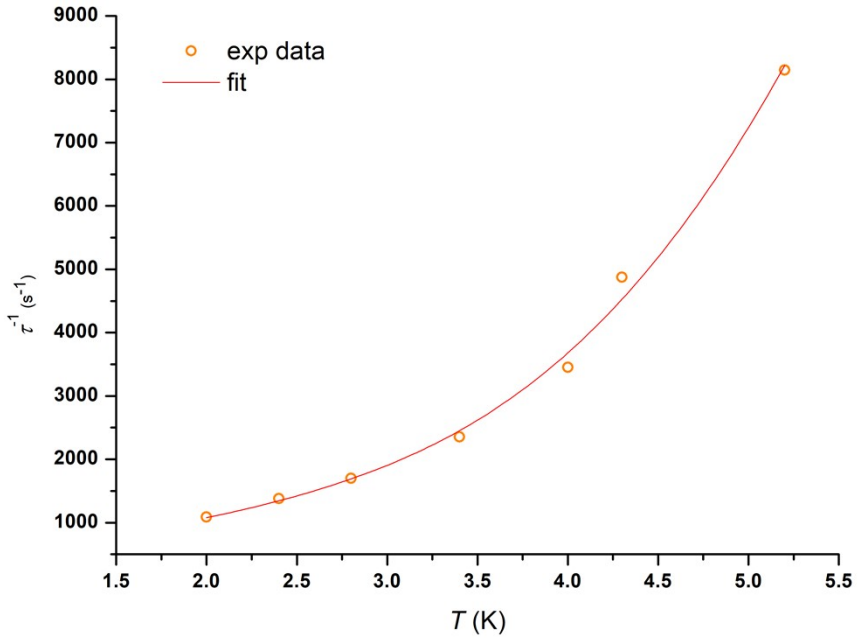

Figure S45: Relaxation curve for **3a**. The red line represents the relaxation fit according to **Eq S3**.

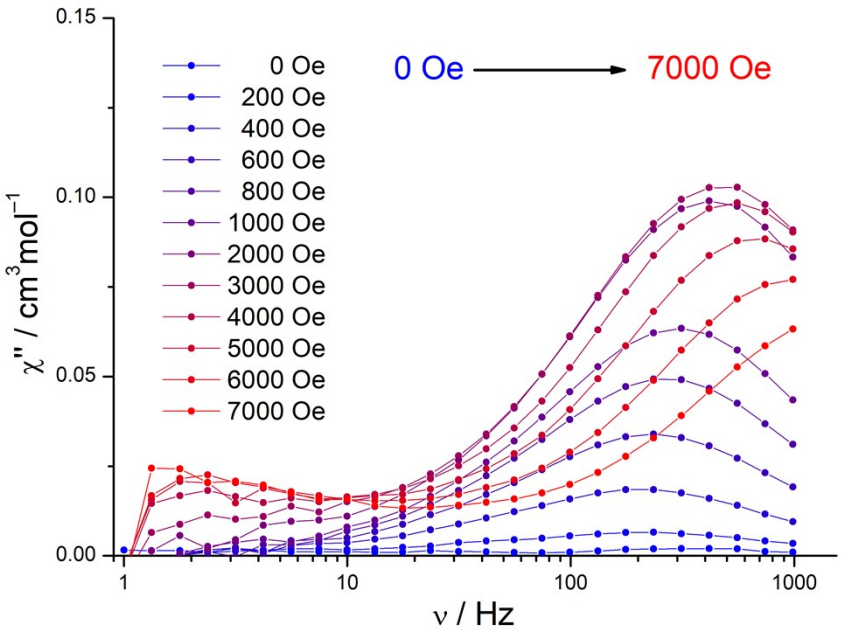

Figure S46: Out-of-phase susceptibility (χ_M'') conducted for **3a** at 2 K under dc fields ranging from 0 Oe to 7000 Oe.

S3.4 Magnetic data for **4a**

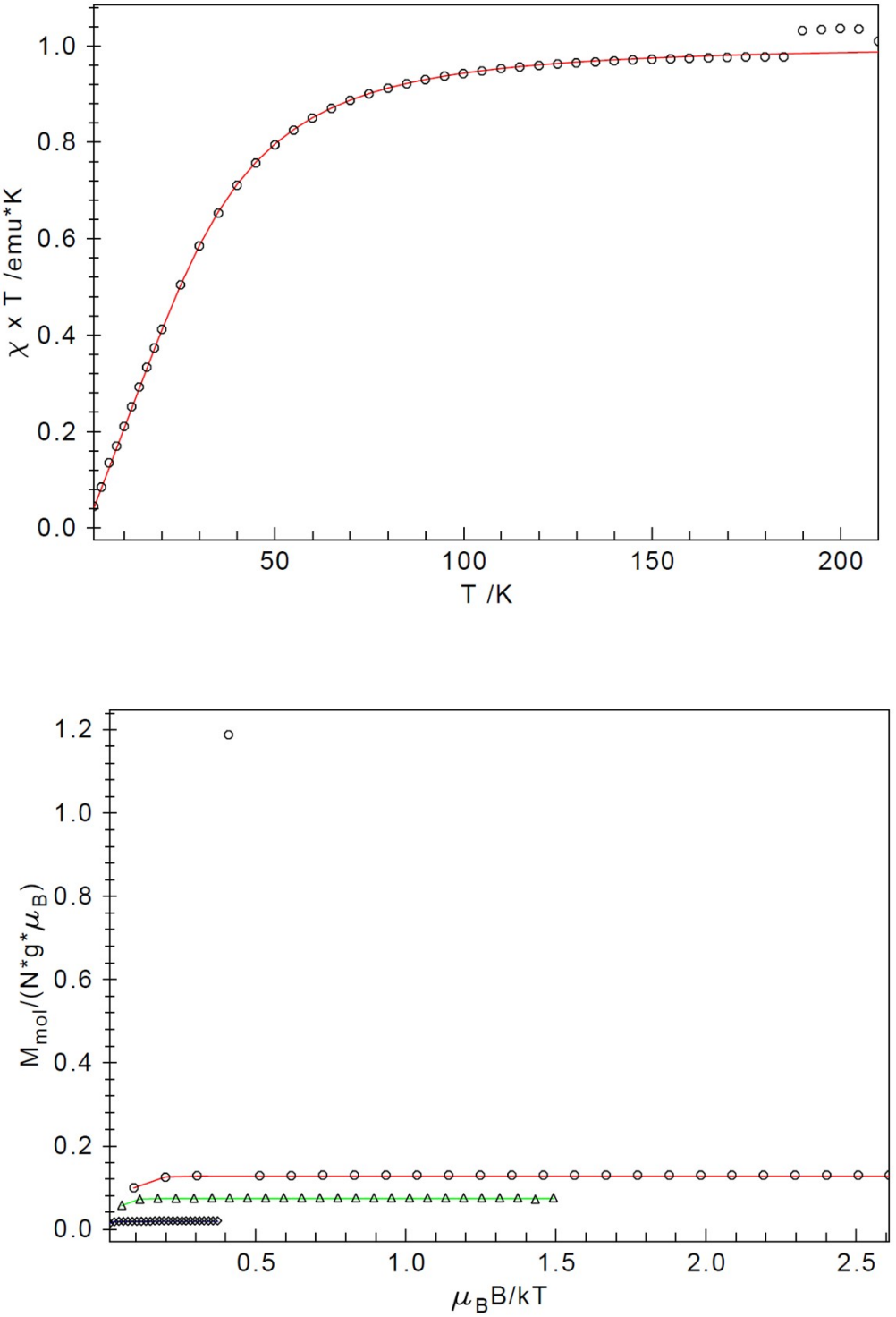

Figure S47: $\chi_M T$ vs T and VTVH data for **4a**. The following best fitting parameters were found: D = 67.54 cm^{-1}, E/D = 0, $g_{x1=y1=z1}$ = 2.00, TIP = 0.

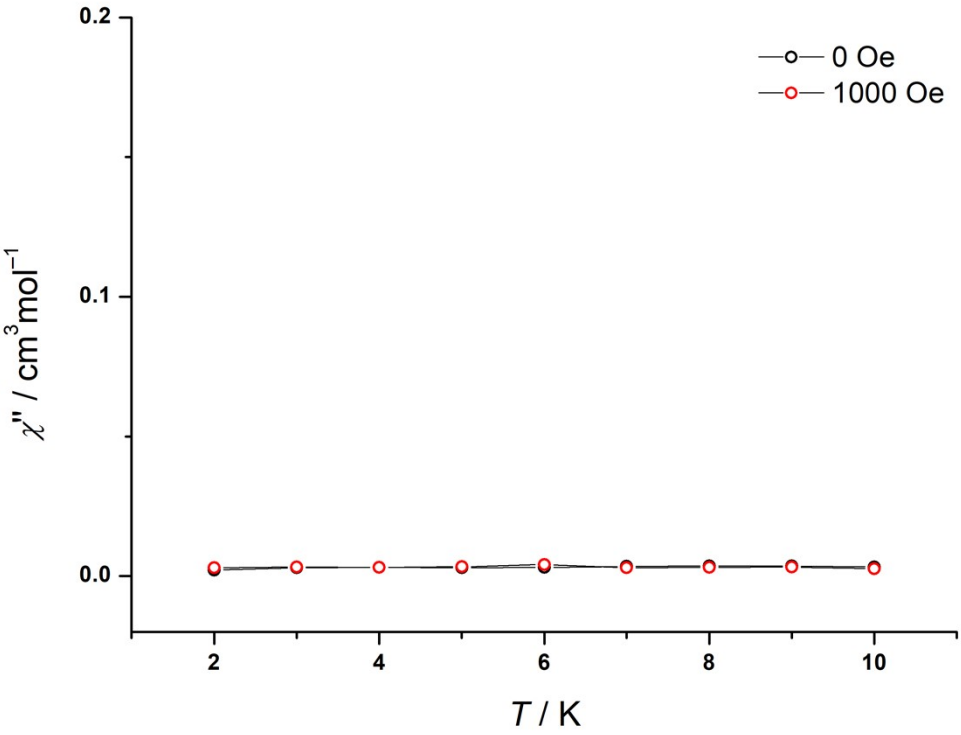

Figure S48: Temperature dependency of the imaginary part of the dynamic magnetic moment for **4a** with a small ac field of 3Oe at maximal frequency of 1488 Hz. No maxima are detected, even under applied dc field.

S3.5 Magnetic data for **1b**

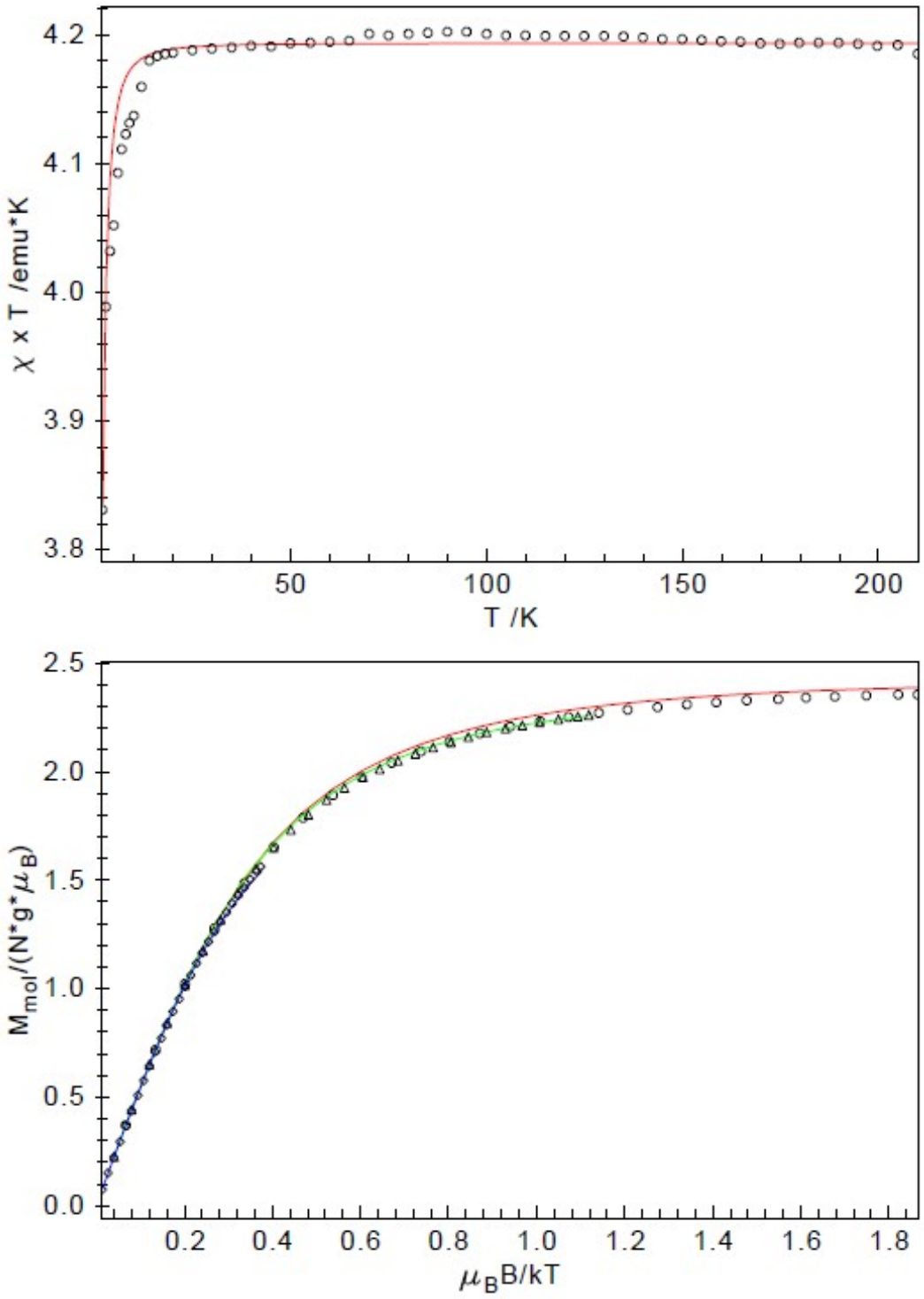

Figure S49: $\chi_M T$ vs T and VTVH data for **1b**. The following best fitting parameters were found: D = 0.45 cm^{-1}, E/D = 0, g_{iso} = 1.96, TIP = 4.9 x 10^{-6} emu.

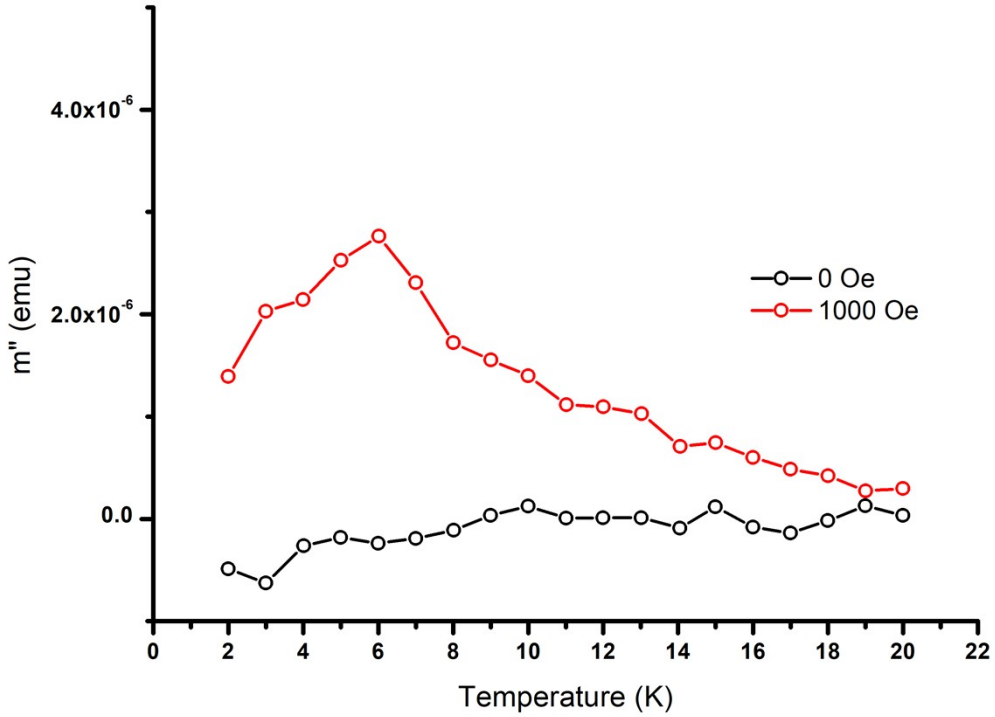

Figure S50: Temperature dependency of the imaginary part of the dynamic magnetic moment for **1b** with a small ac field of 3Oe at maximal frequency of 1488 Hz. A small maximum is detected at 6 K under an applied dc field of 1000 Oe.

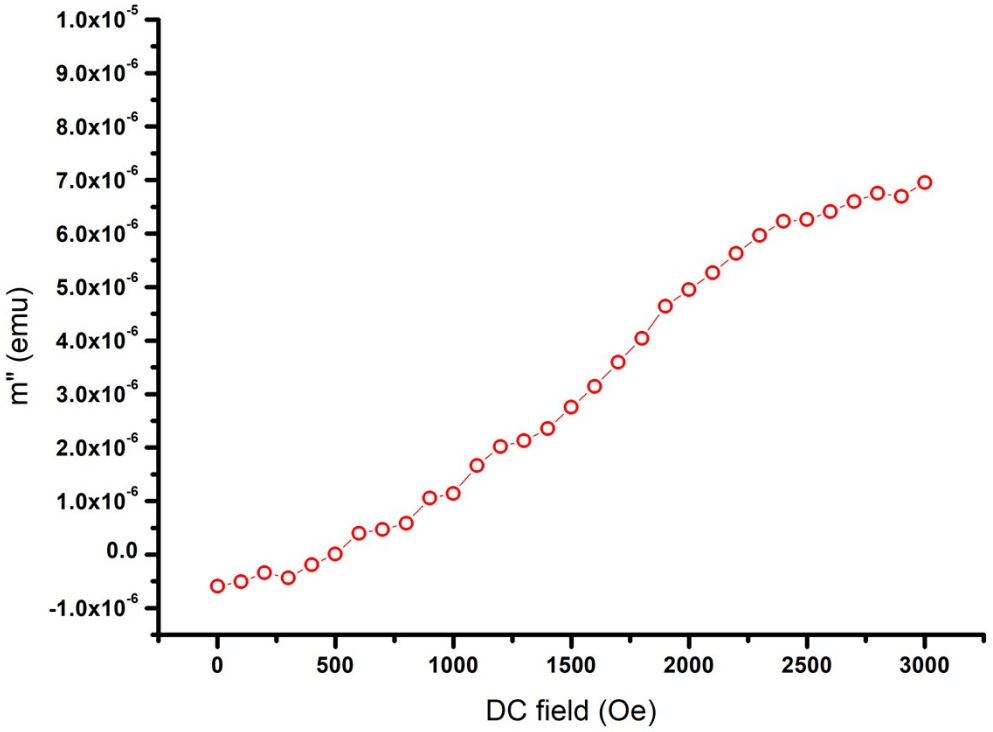

Figure S51: Field dependency of m" for **1b**. The value of m" constantly increases while increasing the external magnetic dc field.

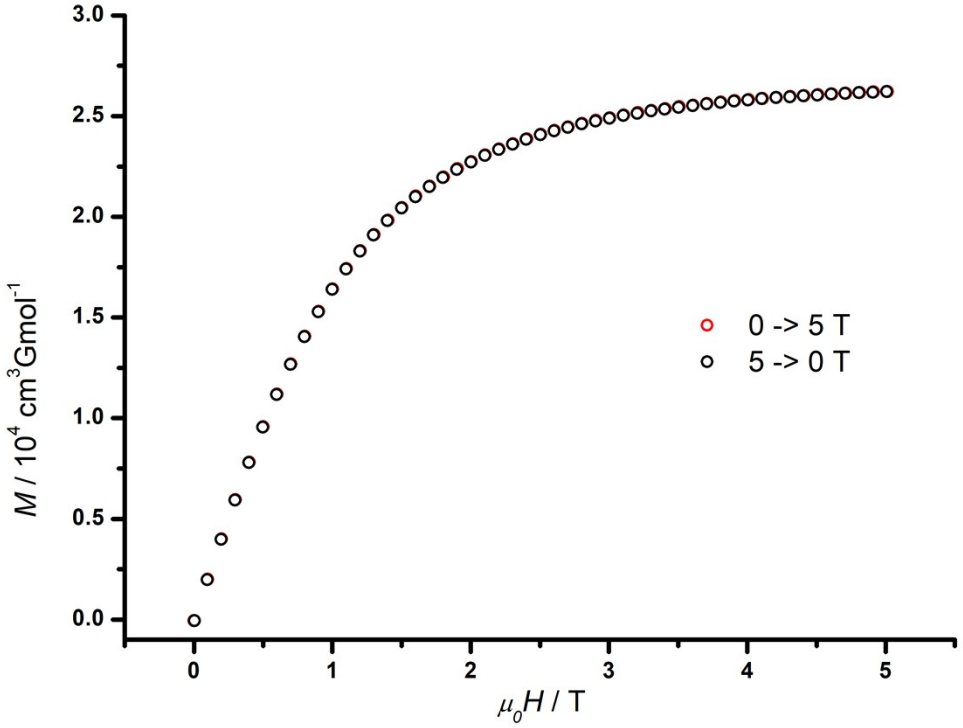

Figure S52: Field dependency of the magnetic moment of **1b** at 2K (field varied from 0 T to 5T and back).

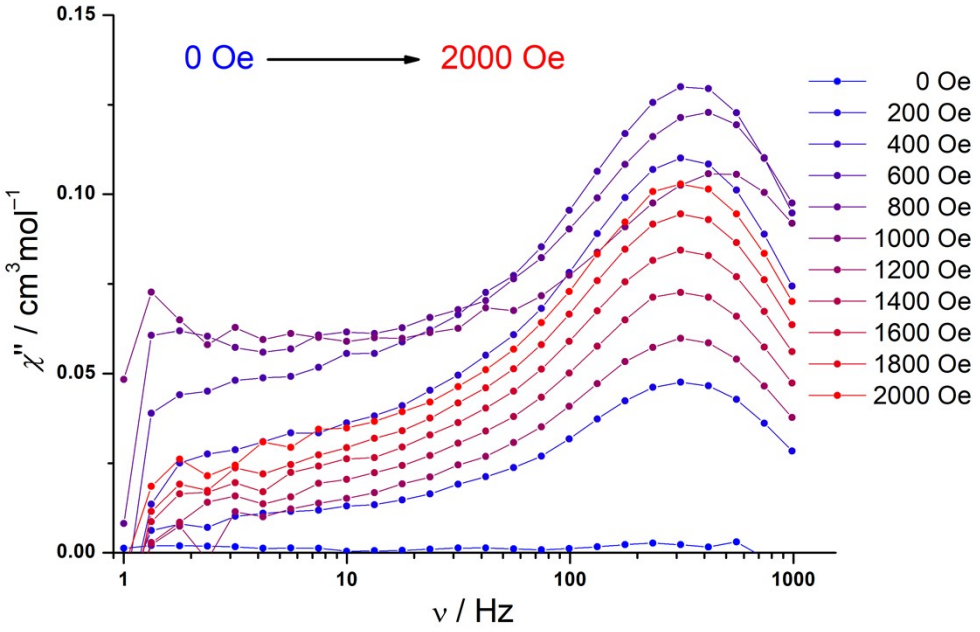

Figure S53: Out-of-phase susceptibility (χ_M'') conducted for **1b** at 2 K under dc fields ranging from 0 Oe to 2000 Oe.

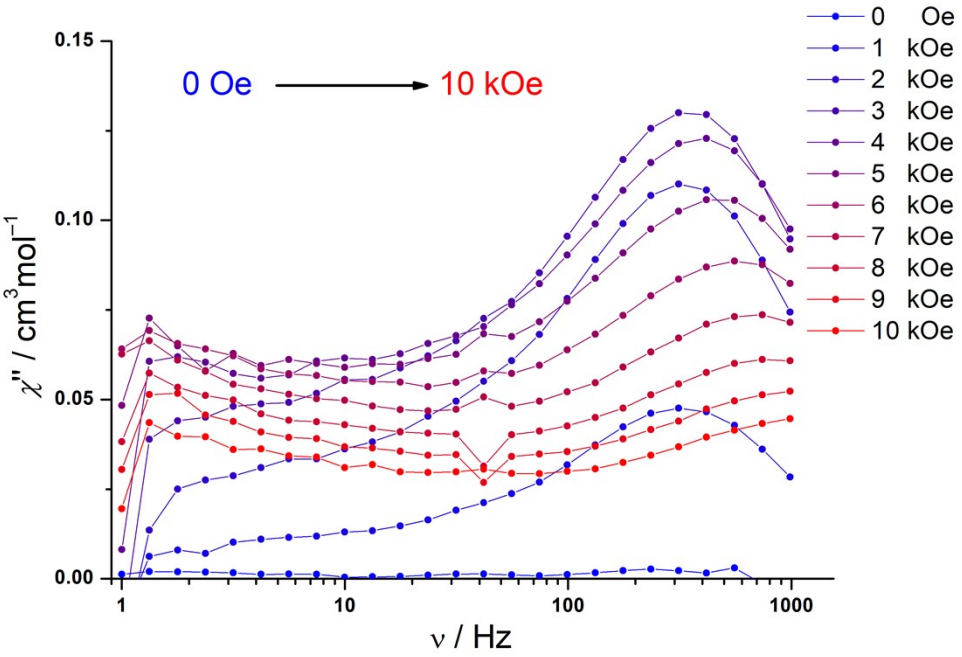

Figure S54: Out-of-phase susceptibility (χ_M'') conducted for **1b** at 2 K under dc fields ranging from 0 Oe to 10 kOe.

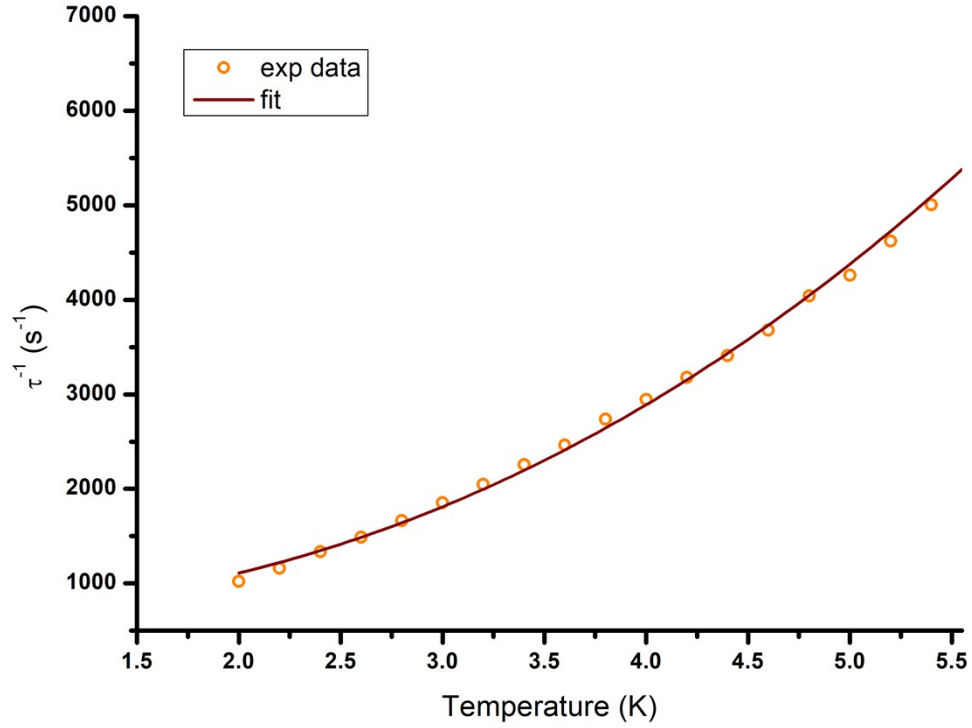

Figure S55: Relaxation curve for **1b**. The brown line represents the relaxation fit according to **Eq S3**.

S3.6 Magnetic data for **2b**

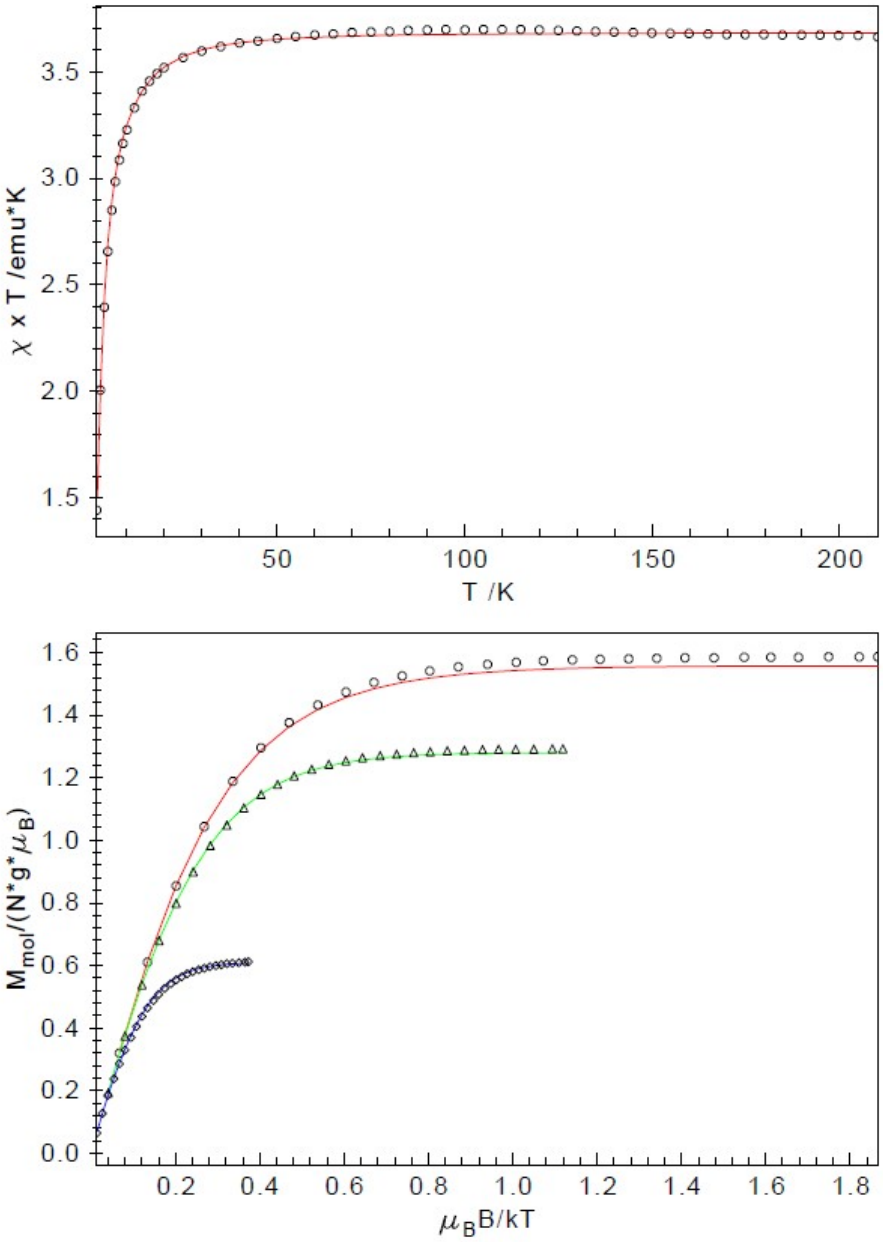

Figure S56: $\chi_M T$ vs T and VTVH data for **2b**. The following best fitting parameters were found: D = 6.93 cm^{-1}, E/D = 0, g_{iso} = 2.22, TIP = 578.4 x 10^{-6} emu.

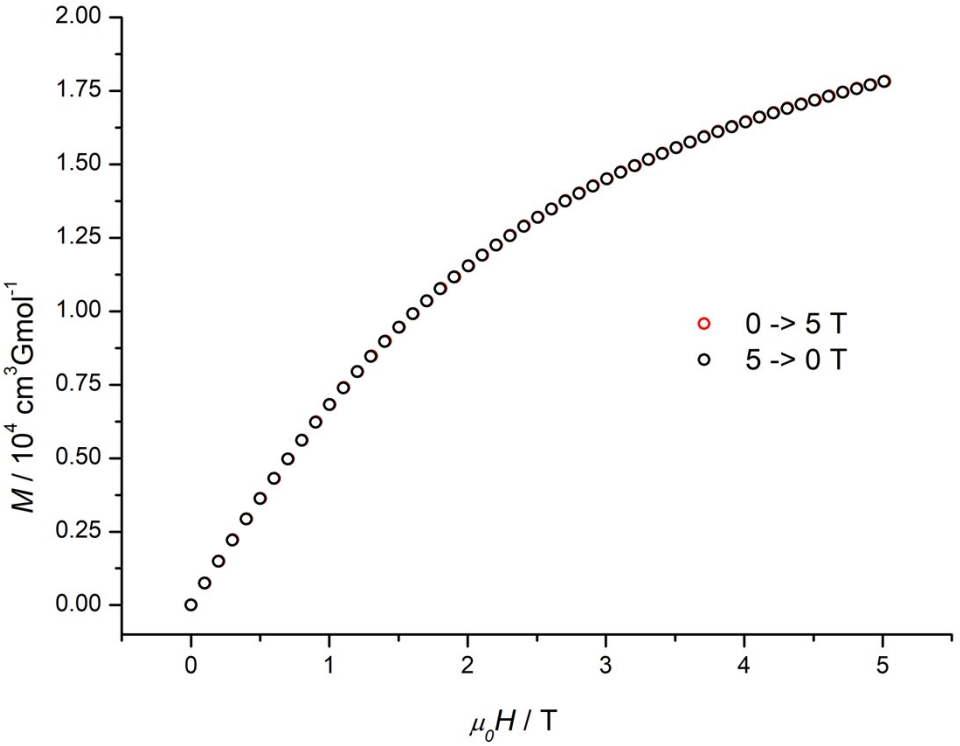

Figure S57: Field dependency of the magnetic moment of **2b** at 2K (field varied from 0 T to 5T and back).

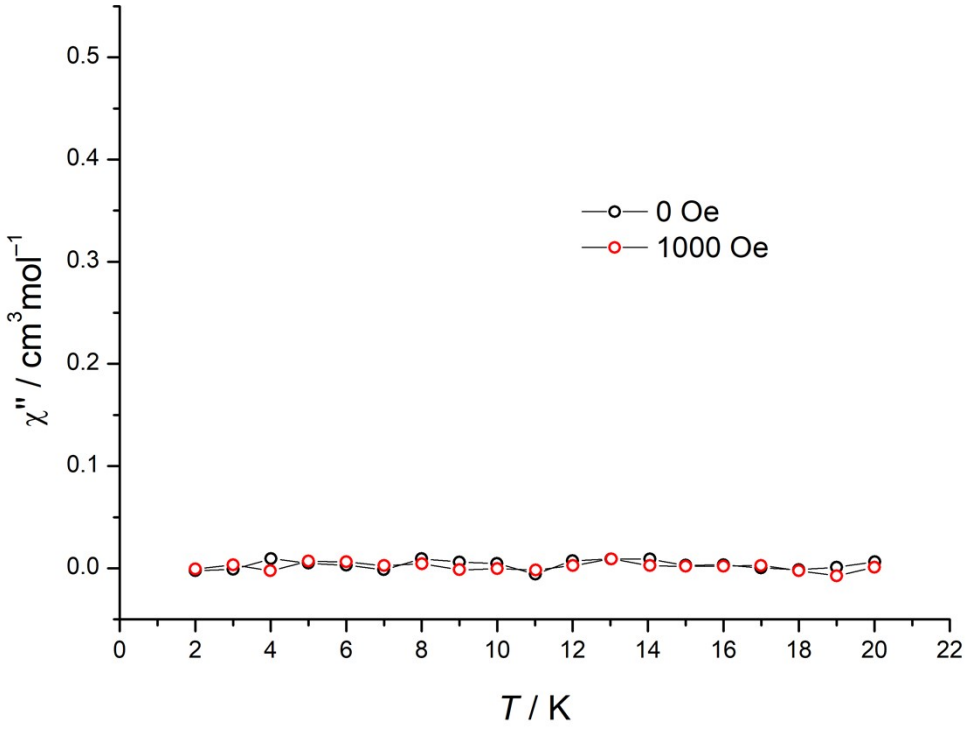

Figure S58: Figure SXX: Temperature dependency of the imaginary part of the dynamic magnetic moment for **2b** with a small ac field of 3Oe at maximal frequency of 1488 Hz. No maxima are detected, even under applied dc field.

S3.7 Magnetic data for **3b**

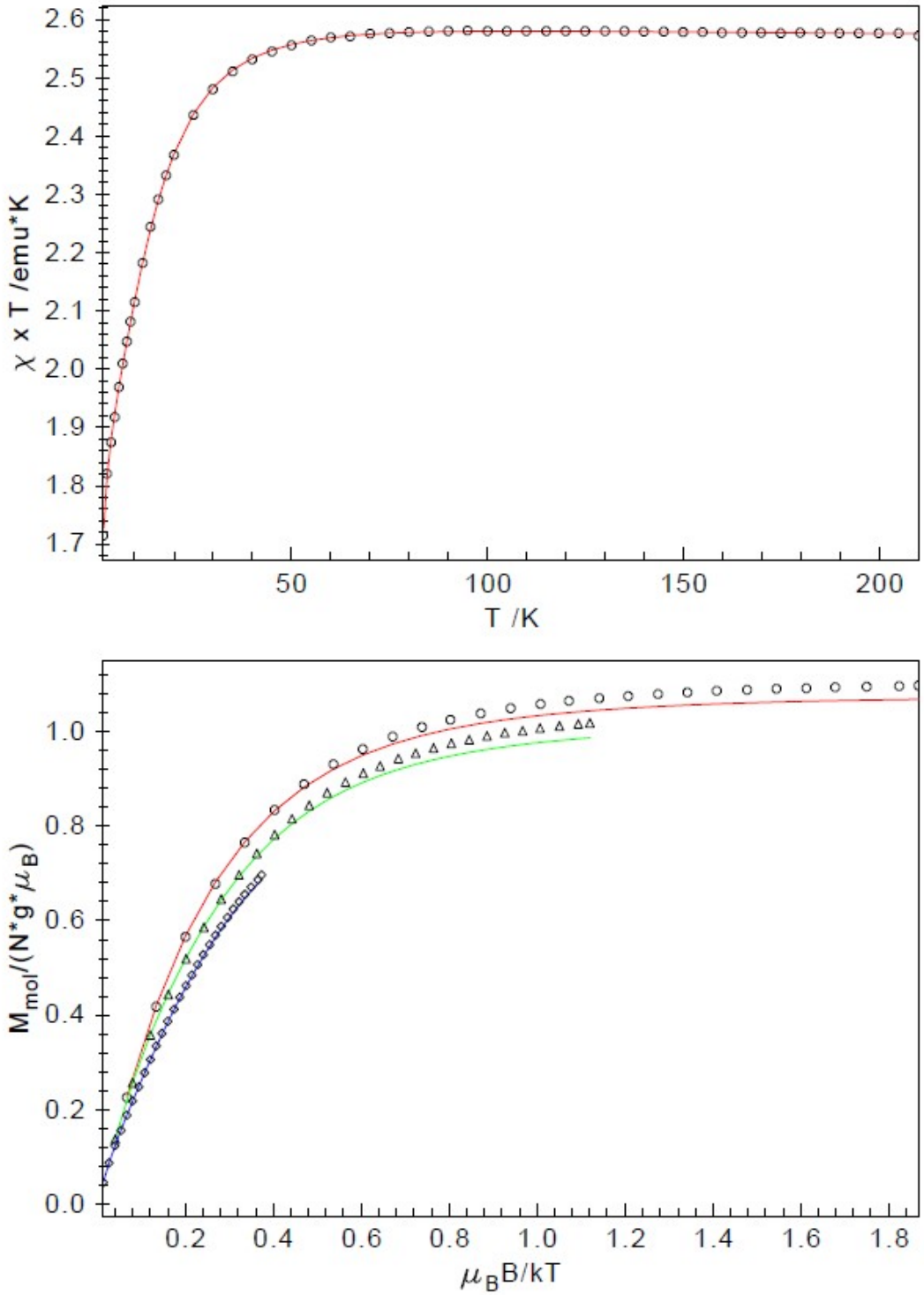

Figure S59: $\chi_M T$ vs T and VTVH data for **3b**. The following best fitting parameters were found: D = -18.4 cm^{-1}, E/D = 0.02, g_x = 2.28, g_y = 2.21, g_z = 2.51, TIP = 443.4 x 10^{-6} emu.

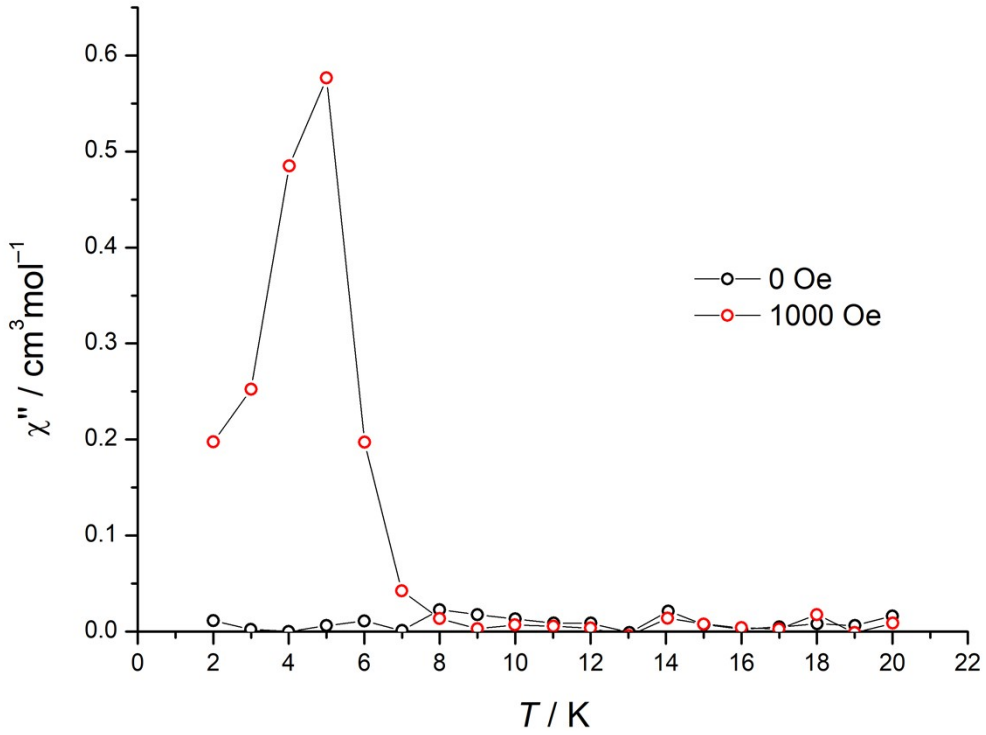

Figure S60: Temperature dependency of the imaginary part of the dynamic magnetic moment for **3b** with a small ac field of 3Oe at maximal frequency of 1488 Hz. A small maximum is detected at 6 K under an applied dc field of 1000 Oe.

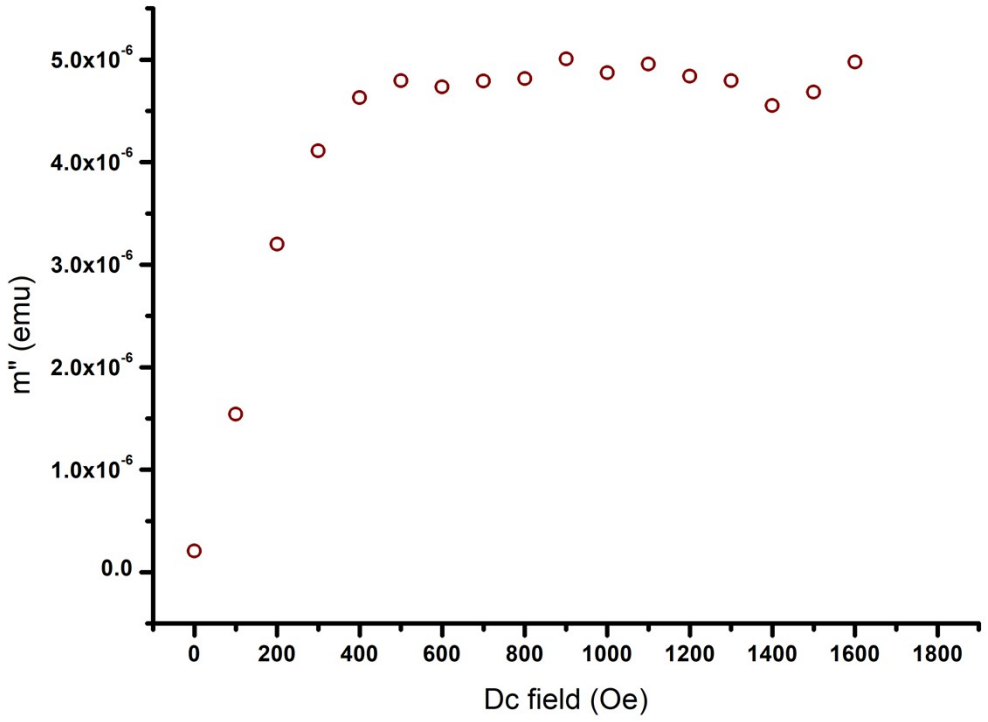

Figure S61 : Field dependency of m" for **3b**. The maximal value for m" is reached at 400 Oe and stays constant while increasing the external magnetic dc field.

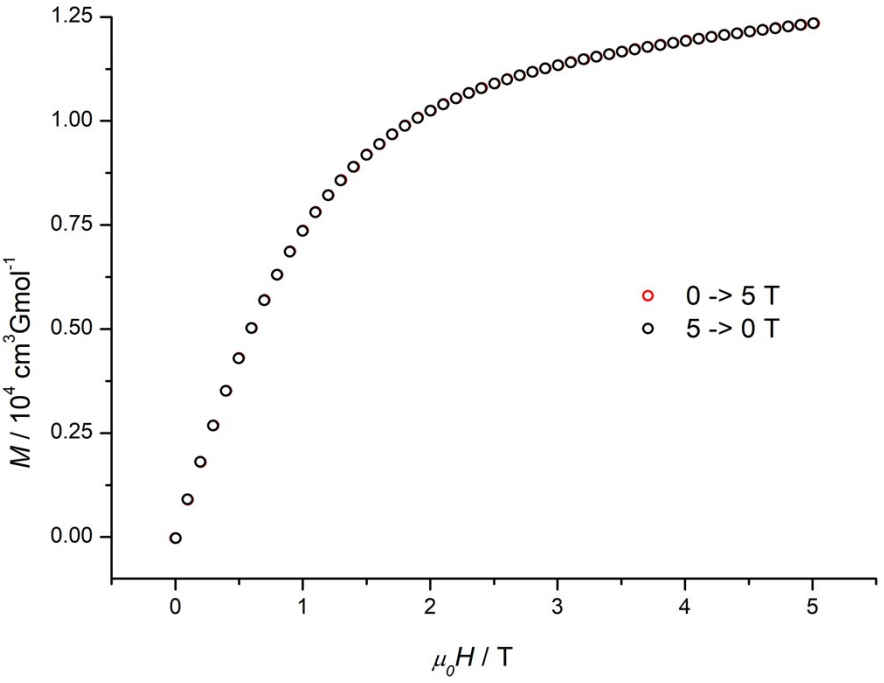

Figure S62: Field dependency of the magnetic moment of **3b** at 2K (field varied from 0 T to 5T and back).

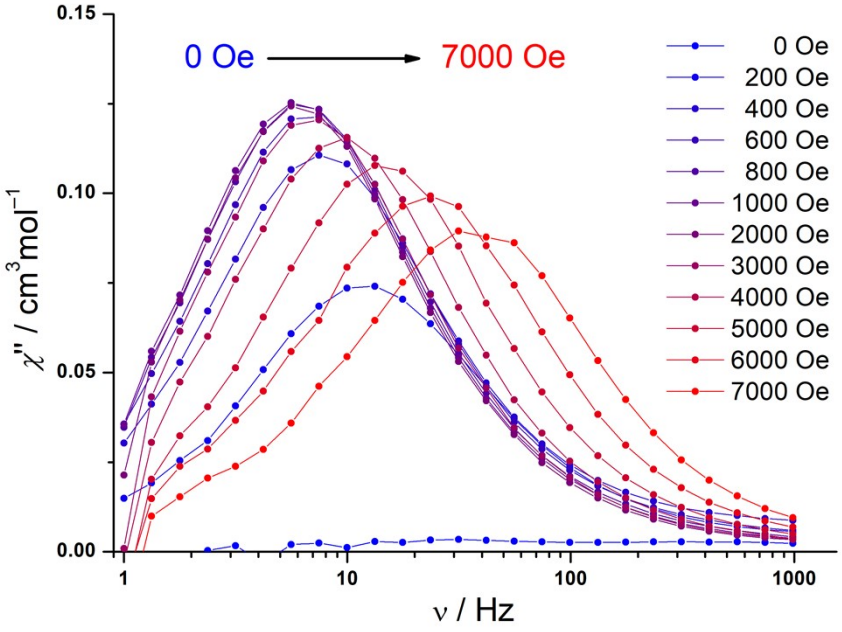

Figure S63: Out-of-phase susceptibility (χ_M'') conducted for **3b** at 3 K under dc fields ranging from 0 Oe to 7000 Oe.

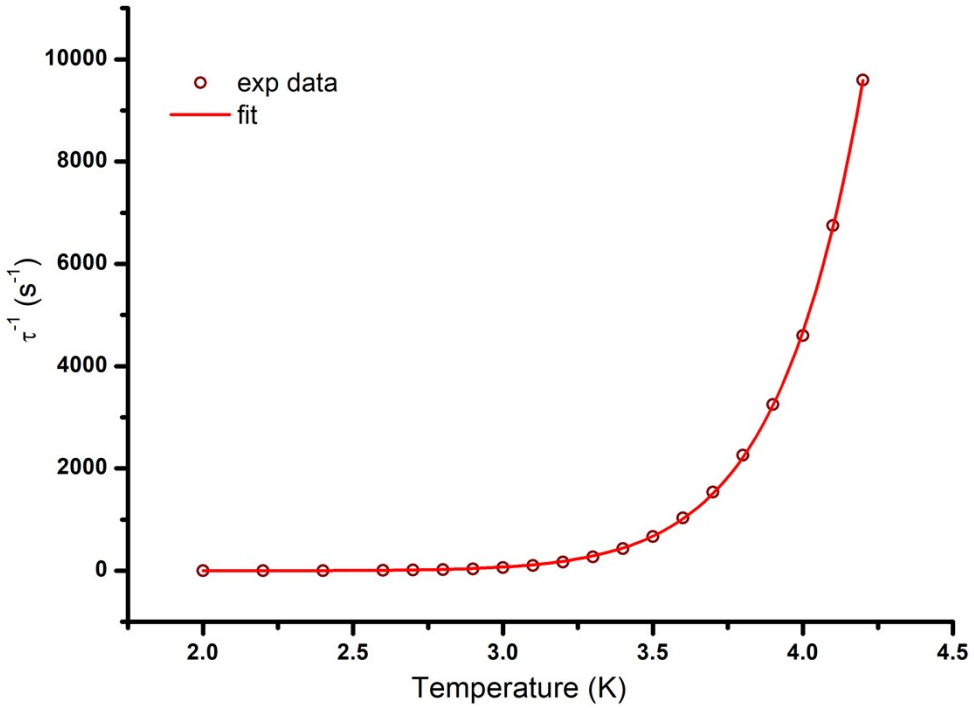

Figure S64: Relaxation curve for **3b**. The red line represents the relaxation fit according to **Eq S3**.

S3.8 Magnetic data for **4b**

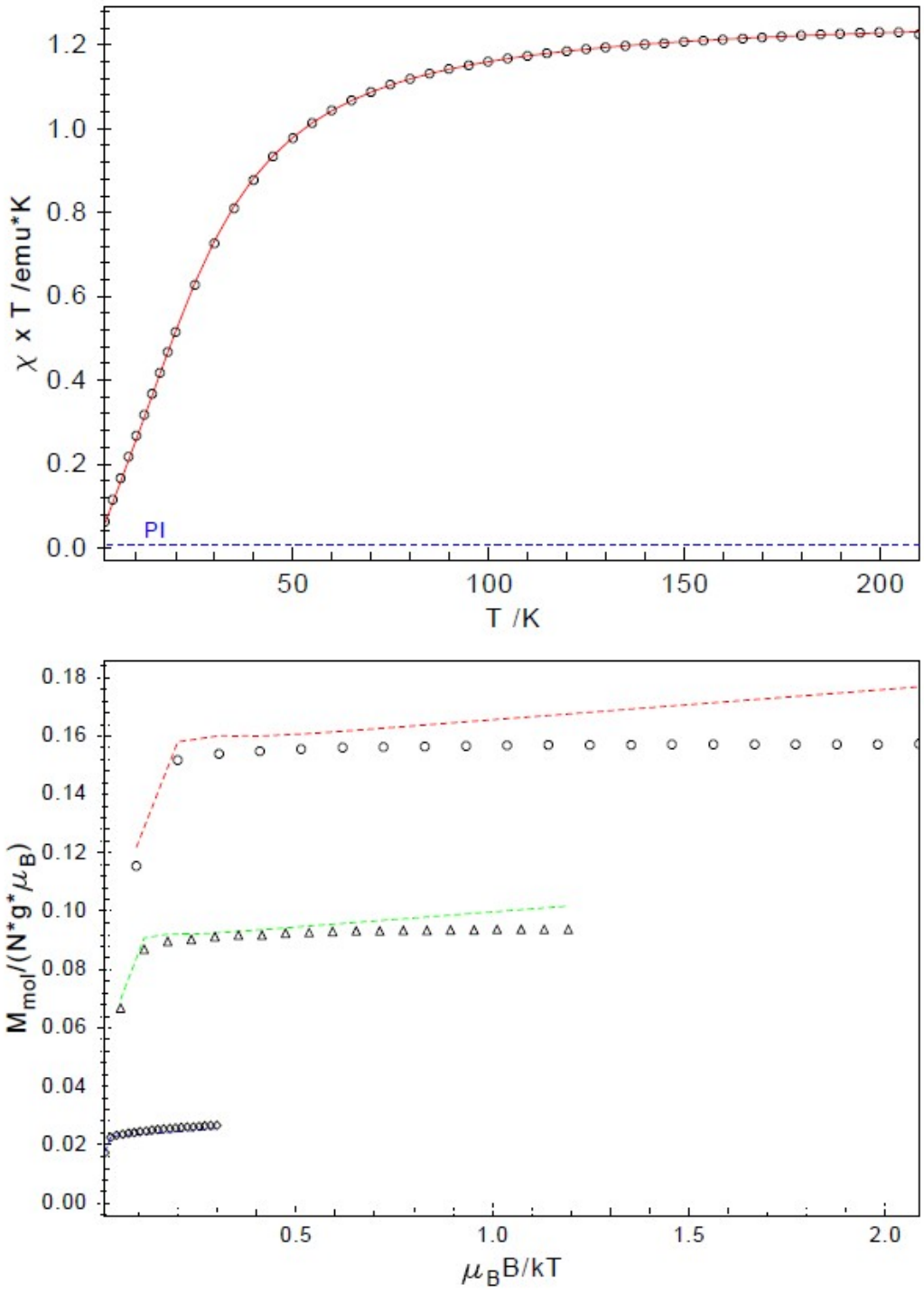

Figure S65: $\chi_M T$ vs T and VTVH data for **4b**. The following best fitting parameters were found: D = 55.0 cm^{-1}, E/D = 0, g_x = 2.00, g_y = 2.00, g_z = 2.71, TIP = 881.9 x 10^{-6} emu, diamagnetic impurities (S = 0): 0.8%.

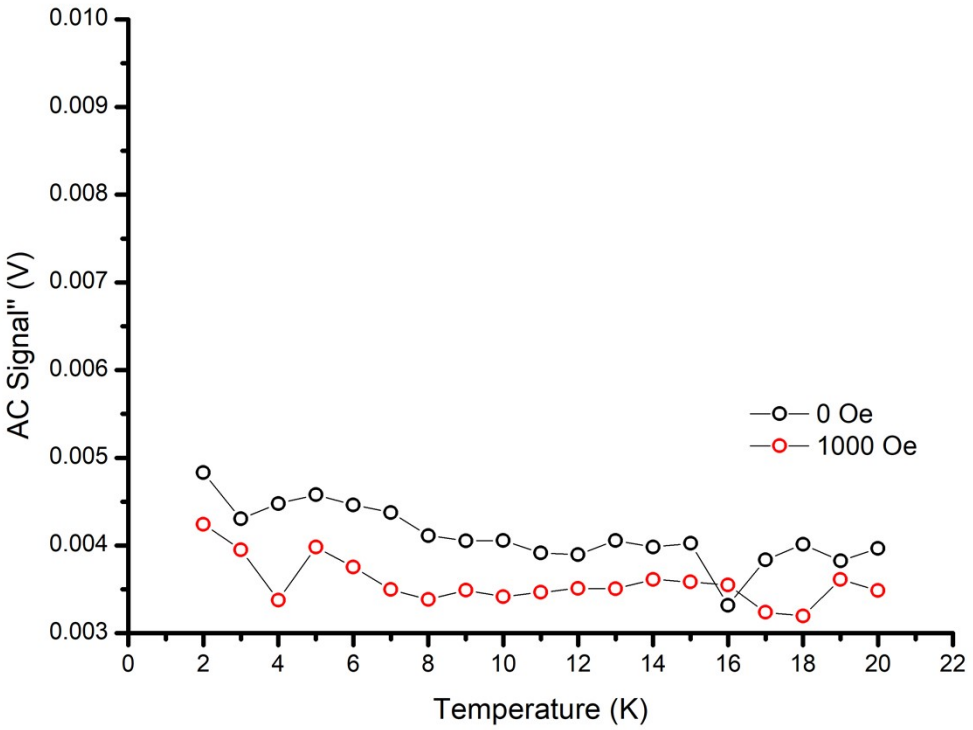

Figure S66: Temperature dependency of the imaginary part of the dynamic magnetic moment for **4b** with a small ac field of 3Oe at maximal frequency of 1488 Hz. No maxima are detected even with applied dc field.

S3.9 Magnetic details for Arrhenius plots analyses of complexes 1b and 3a-3b.

The full fits of the relaxation time according to **Eq S3** give the following best fitting parameters:

Table S13: Best fitting parameters for **1b**, **3a** and **3b**.

#	**1b**	**3a**	**3b**
τ_0 (s^{-1})	4.14 10^{-5} (±3.10 10^{-6})	1.84 10^{-6} (±2.30 10^{-7})	2.47 x 10^{-11} (±8.12 x 10^{-12})
U_{eff} (cm^{-1})	6.0 (±0.23)	17.93 (±1.22)	45.0 (±3.08)
n	2.28 (±0.17)	1.98 (±0.51)	9.02 (±3.41)
C ($s^{-1}K^{-n}$)	95.0 (±30.2)	150 (±40.65)	3.64 x 10^{-3} (±1.41 x 10^{-2})
τ_{QTM}^{-1} (s^{-1})	648.2 (±159.0)	484.7 (±304.8)	0

S4 Computational details

S4.1 UV-vis computation

Input file:

```
!  CAM-B3LYP RIJCOSX def2/J def2-SVP Grid6 Finalgrid7 Noautostart Normalprint
%scf
convergence VeryTight
end
%maxcore 1000
%tddft
maxdim 5
nroots 10
end
```

S4.2 CASSCF-NEVPT2 calculations

Input file:

```
! DKH DKH-DEF2-TZVP AUTOAUX NoFrozencore PAL8 tightscf
%rel
picturechange 2
end
%casscf nel 7
norb 5 #7 electrons in 5 d orbitals
nroots 10
mult 4 # 10 quartet states
actorbs dorbs
printwf true
trafostep rimo
nevpt2 SC
rel
nroots 10
printlevel 3      #Control the amount of printing
dosoc true        #Do the SOC calculation
gtensor true      # Request the G-tensor Calculation
dtensor true      # Request the ZFS-tensor Calculation
end
!Printbasis PrintMos
```

```
%scf print[p_mos] 1
maxcore 30000
end
```

S4.3 Coordinate file for **3a**

Co	0.00000	0.00000	0.00000
N	-1.44312	-0.10419	1.36370
N	1.43274	-0.14413	1.35710
O	2.37892	0.05268	3.40762
N	-0.55637	-1.12188	-1.54308
O	-0.77044	-1.76501	-3.70081
N	0.71131	1.43069	-1.17764
O	1.40576	2.40178	-3.09538
O	-2.35097	0.14532	3.41817
C	1.66306	3.23538	0.35601
H	1.37419	2.85981	1.17945
C	2.37639	4.42179	0.31438
H	2.58760	4.86543	1.12747
C	2.79476	4.98400	-0.90092
H	3.29968	5.78875	-0.88785
C	2.49609	4.40825	-2.09970
H	2.75242	4.80040	-2.92636
C	1.79276	3.20969	-2.03690
C	1.38679	2.61508	-0.86289
C	0.77003	1.33523	-2.51363
C	0.30751	0.30988	-3.34596
H	0.41756	0.38678	-4.28592
C	-0.30295	-0.80194	-2.82942
C	-1.34200	-2.75482	-2.89596
C	-1.93302	-3.91085	-3.29961
H	-2.00183	-4.15219	-4.21598
C	-2.43041	-4.71646	-2.27962
H	-2.84315	-5.54476	-2.49630
C	-2.33307	-4.32401	-0.92953
H	-2.69641	-4.88656	-0.25626
C	-1.72501	-3.14684	-0.56209
H	-1.65490	-2.88688	0.34910
C	-1.21535	-2.35089	-1.58997
C	2.82700	-0.06325	1.20839
C	3.62435	0.00019	0.06799
H	3.25437	-0.03745	-0.80608
C	5.00503	0.12344	0.28206
H	5.59279	0.11713	-0.46333
C	5.52669	0.25165	1.54479
H	6.46331	0.37368	1.64161
C	4.73726	0.21096	2.67767
H	5.09890	0.28972	3.55256
C	3.39201	0.04736	2.44963
C	1.21056	-0.06787	2.67059
C	-0.00000	0.00000	3.35558
H	0.00048	0.04356	4.30417
C	-1.18747	0.00545	2.67911
C	-3.38175	0.08051	2.50589
C	-4.73420	0.17238	2.77624
H	-5.07006	0.30355	3.65541
C	-5.56871	0.05991	1.66829
H	-6.50882	0.13199	1.78312
C	-5.05005	-0.15757	0.39364
H	-5.65014	-0.26650	-0.33460
C	-3.68171	-0.21948	0.15535
H	-3.33446	-0.33954	-0.72147
C	-2.84990	-0.09857	1.24854

S4.4 Coordinate file for **3b**

Co	0.00000	0.00000	0.00000
O	-0.10125	-2.31070	-3.42386
O	-0.07839	2.38482	-3.37489
O	-2.30904	-0.46333	3.38750
O	2.33478	0.33054	3.39738
N	0.00396	-1.47383	-1.33666
N	-0.04854	1.50475	-1.30180
N	-1.46748	-0.14006	1.33128
N	1.47678	0.02729	1.33548
C	-0.05573	-1.19311	-2.64241
C	-0.01218	-2.87438	-1.25435
C	0.01135	-3.74415	-0.16259
C	-0.08595	-5.10280	-0.47764
C	-0.17809	-5.57716	-1.78632
C	-0.15897	-4.70932	-2.87574
C	-0.08513	-3.37088	-2.55159
C	0.10622	-3.27588	1.25706
C	-0.08194	0.03693	-3.28730
C	-0.06092	1.25037	-2.61587
C	-0.08989	2.90249	-1.19396
C	-0.13487	3.74789	-0.08617
C	-0.16535	5.11775	-0.36719
C	-0.14802	5.62039	-1.66793
C	-0.11500	4.77168	-2.77442
C	-0.09295	3.42673	-2.48044
C	-0.16189	3.22672	1.31275
C	-1.20646	-0.18633	2.63799
C	-2.84306	-0.38438	1.21799
C	-3.68644	-0.39360	0.10961
C	-5.03234	-0.66147	0.37747

C	-5.51205	-0.91302	1.66341
C	-4.66597	-0.88273	2.77103
C	-3.34451	-0.59979	2.49406
C	-3.17840	-0.14060	-1.27205
C	0.00000	0.00000	3.31006
C	1.21003	0.11867	2.64341
C	2.86884	0.13922	1.22832
C	3.72696	-0.00082	0.13976
C	5.09072	0.15328	0.41556
C	5.57731	0.42481	1.69569
C	4.71650	0.52202	2.78993
C	3.38096	0.35251	2.50312
C	3.23035	-0.36845	-1.22427
H	-0.12850	-5.71098	0.21086
H	-0.27058	-6.53653	-1.92128
H	-0.18125	-5.00109	-3.78668
H	-0.67819	-2.78134	1.52959
H	0.20313	-3.99097	1.87002
H	0.88364	-2.67333	1.37748
H	-0.08019	0.06078	-4.25220
H	-0.13058	5.75656	0.34036
H	-0.23674	6.56988	-1.78739
H	-0.10672	5.10434	-3.64263
H	-0.20494	3.92567	1.94108
H	0.59029	2.69814	1.50157
H	-0.95458	2.67024	1.46367
H	-5.65377	-0.67674	-0.33561
H	-6.45101	-1.12569	1.79089
H	-4.99682	-1.05818	3.64430
H	-3.91398	-0.15833	-1.90251
H	-2.70093	0.69652	-1.32477
H	-2.54189	-0.76694	-1.53368
H	-0.06827	0.03839	4.23905
H	5.65335	0.03807	-0.32907
H	6.50660	0.48788	1.81722
H	5.03057	0.67190	3.62375
H	2.65804	-1.18412	-1.17937
H	2.71747	0.29988	-1.57914
H	3.99267	-0.55100	-1.81365

References

[1] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885-891.
[2] Bruker AXS Inc., in *Bruker Apex CCD, SAINT v8.30C* (Ed.: Bruker AXS Inst. Inc.), WI, USA, Madison, 2013.
[3] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr*. **2015**, *48*, 3-10.
[4] L. Krause, R. Herbst-Irmer, D. Stalke, *J. Appl. Crystallogr*. **2015**, *48*, 1907-1913.
[5] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.
[6] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.
[7] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.