Supplementary Materials: Mono- and Hexanuclear Zinc Halide Complexes with Soft Thiopyridazine Based Scorpionate Ligands

Michael Tüchler, Melanie Ramböck, Simon Glanzer, Klaus Zangger, Ferdinand Belaj and Nadia C. Mösch-Zanetti

Table of contents

NMR Spectroscopy

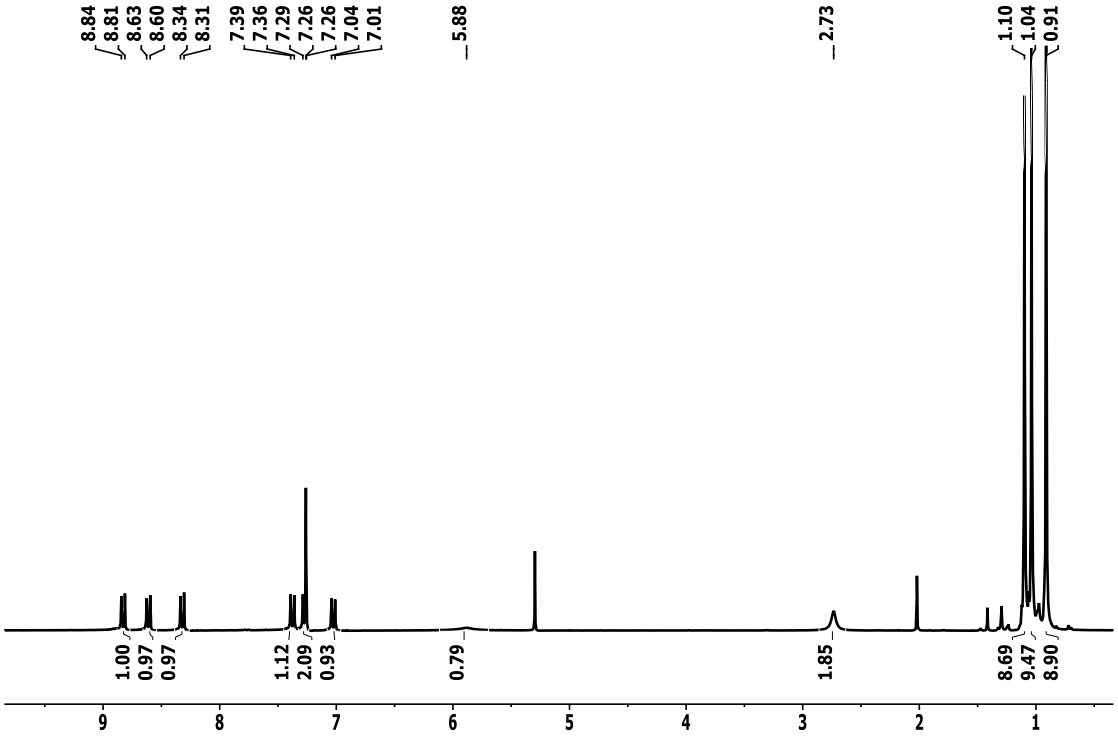

Figure S1. ^{1}H NMR spectrum of **1a**·H_2O in $CDCl_3$. Resonances at 5.30 and 2.17 ppm are residual CH_2Cl_2 and acetone.

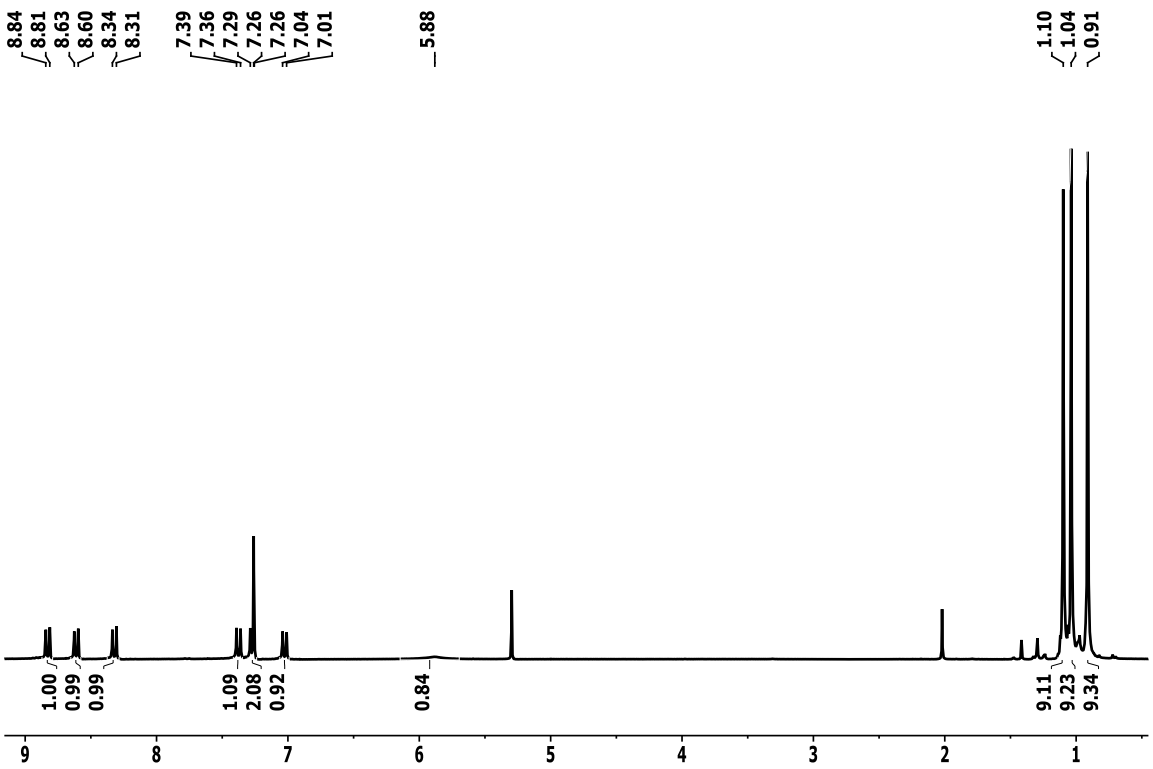

Figure S2. ^{1}H NMR spectrum of **1a**·H_2O in $CDCl_3$ after washing with D_2O. Resonances at 5.30 and 2.17 ppm are residual CH_2Cl_2 and acetone.

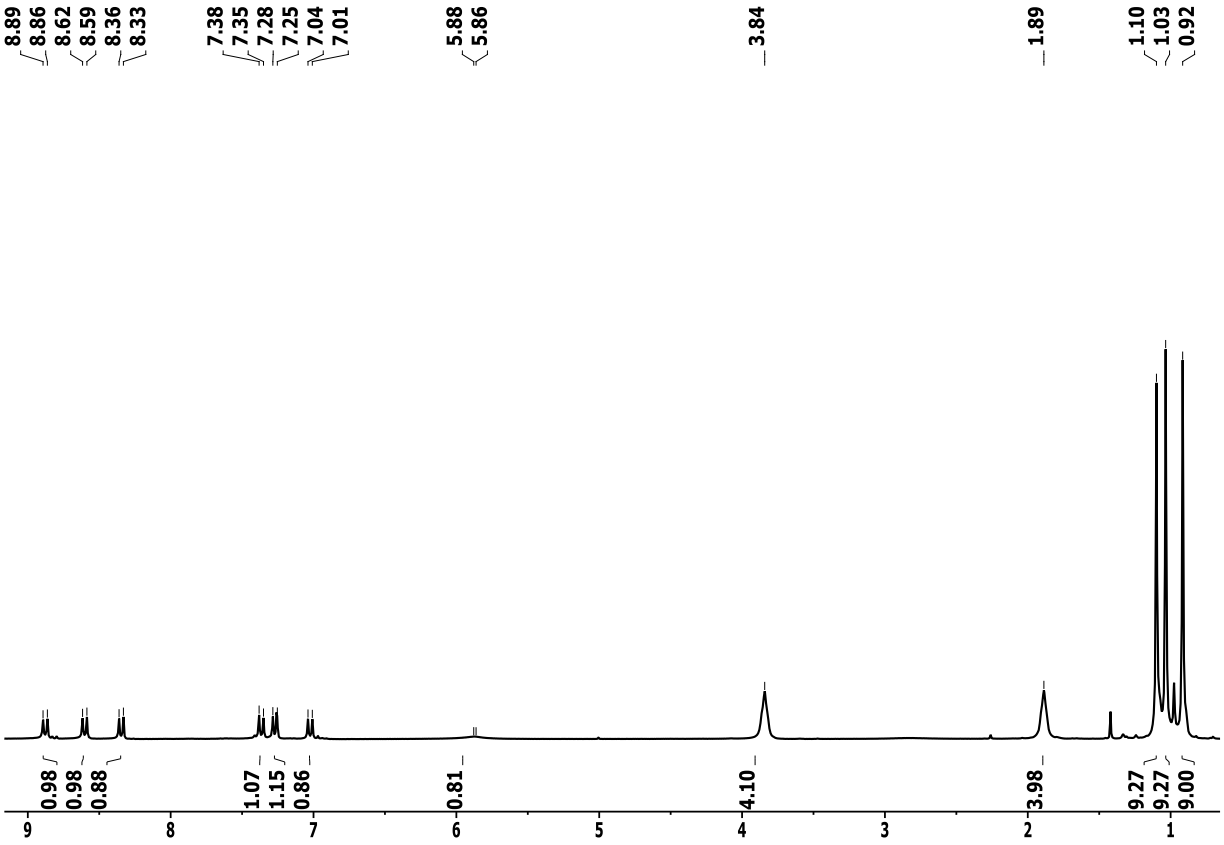

Figure S3. ^{1}H NMR spectrum of **1a**·THF in $CDCl_3$.

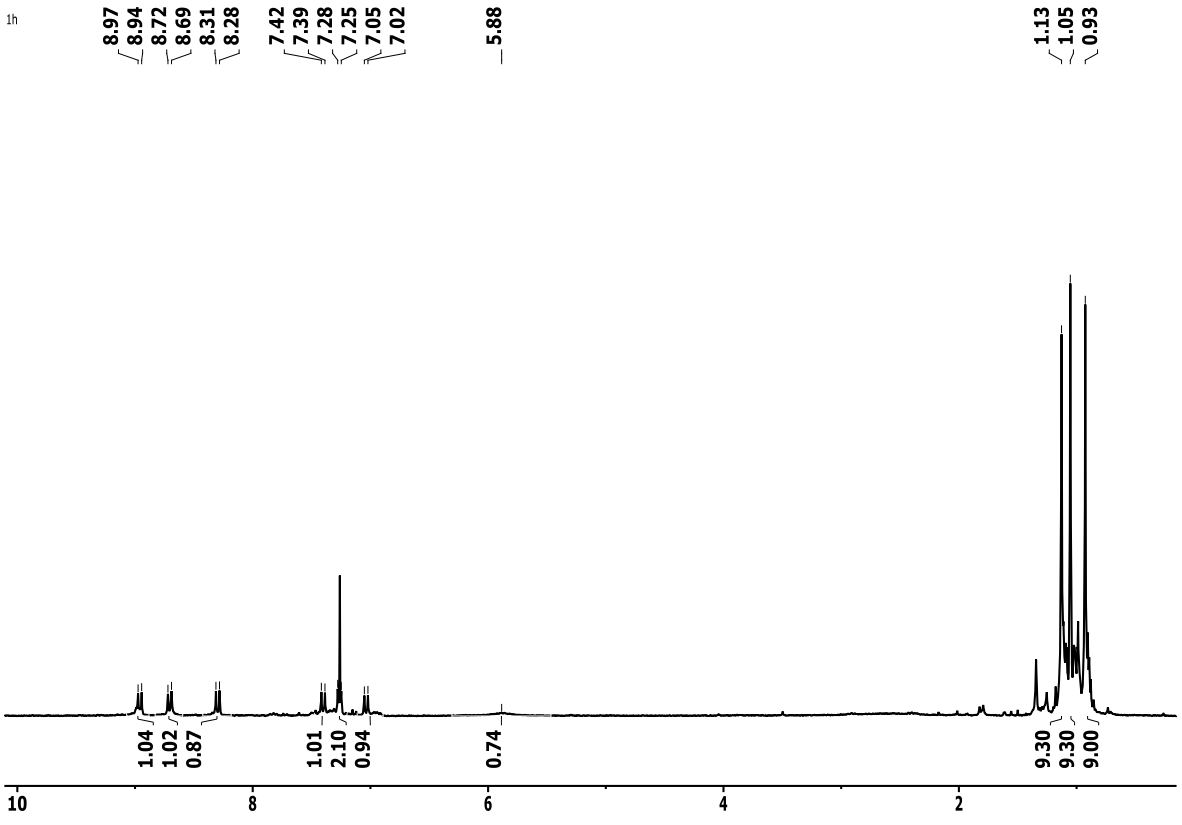

Figure S4. ^{1}H NMR spectrum of **1a** in $CDCl_3$ without donor molecules.

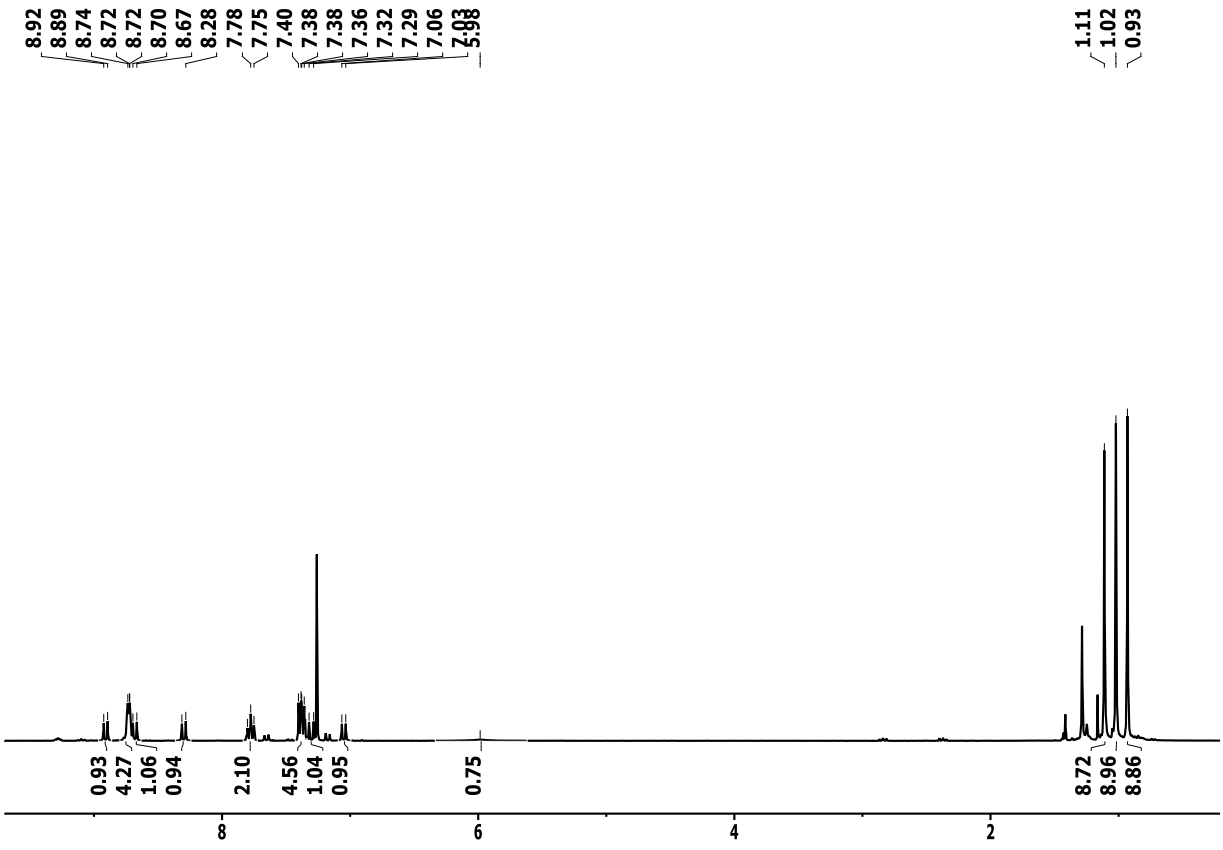

Figure S5. ^{1}H NMR spectrum of **1a**·**2Py** in $CDCl_3$.

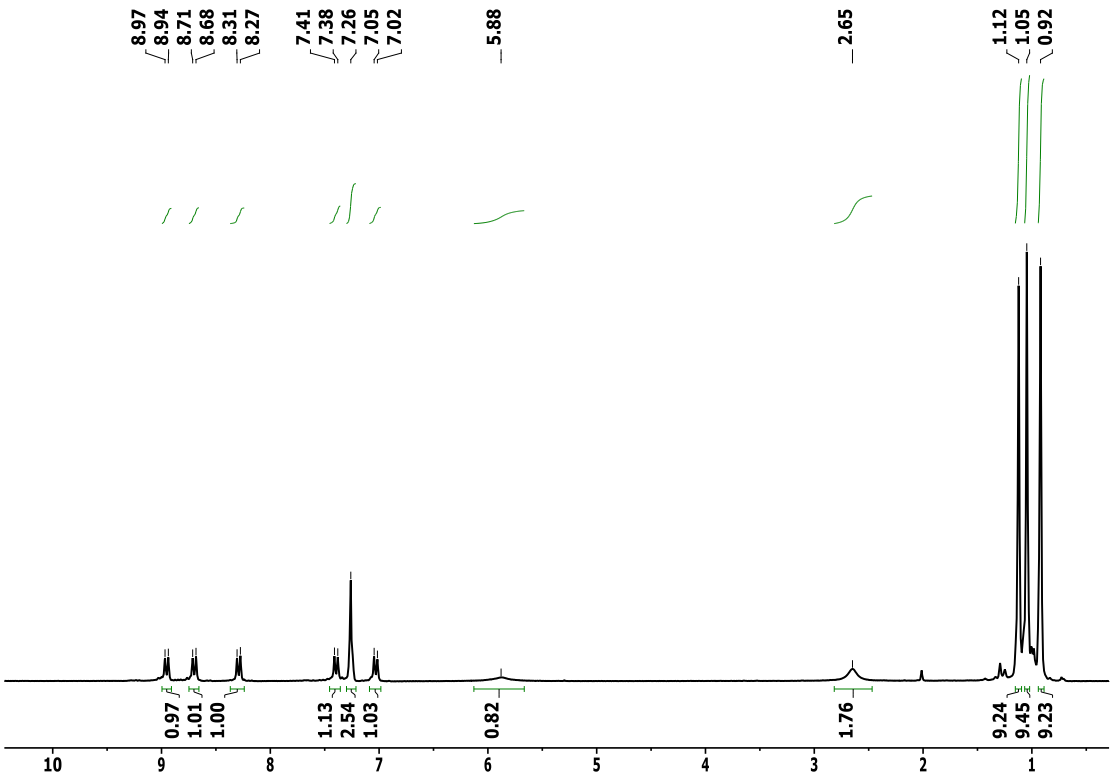

Figure S6. ^{1}H NMR spectrum of **1b**·H_2O in $CDCl_3$.

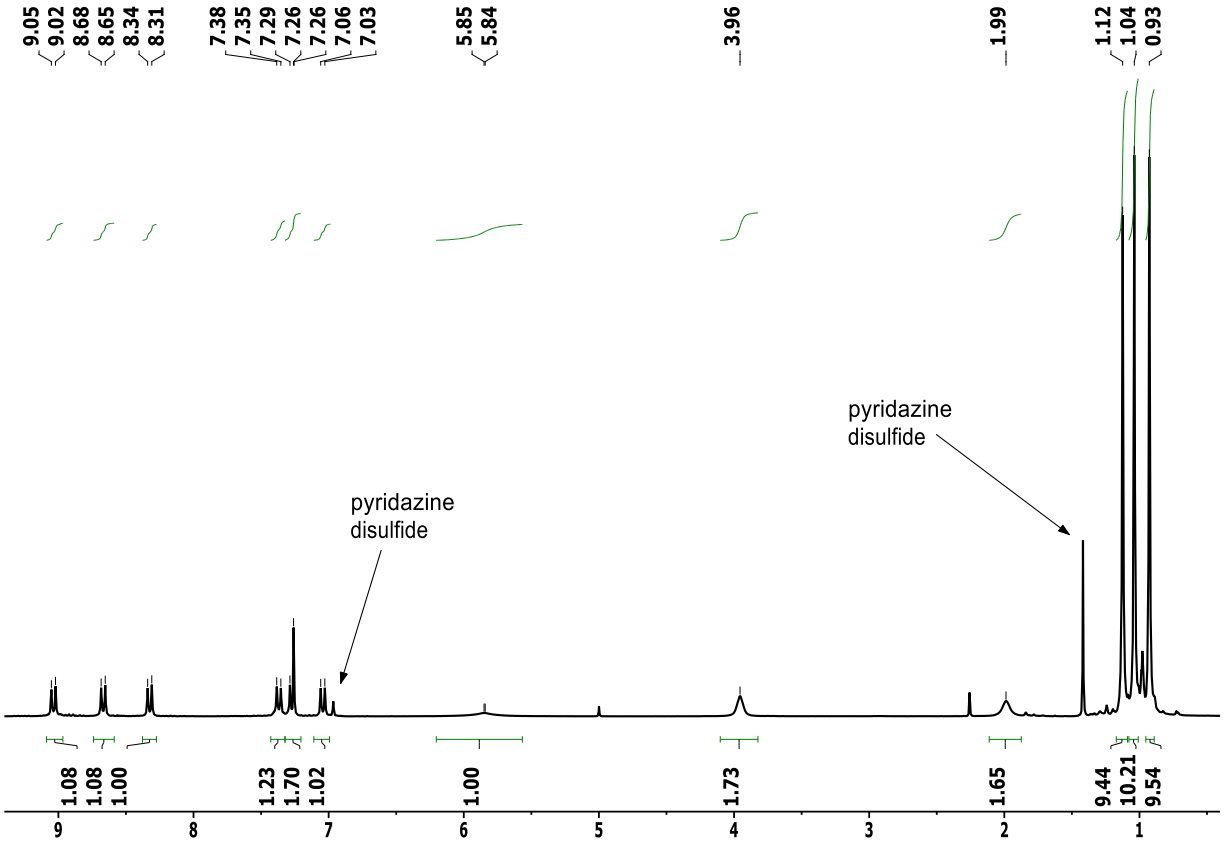

Figure S7. 1H NMR spectrum of **1b**·THF in $CDCl_3$.

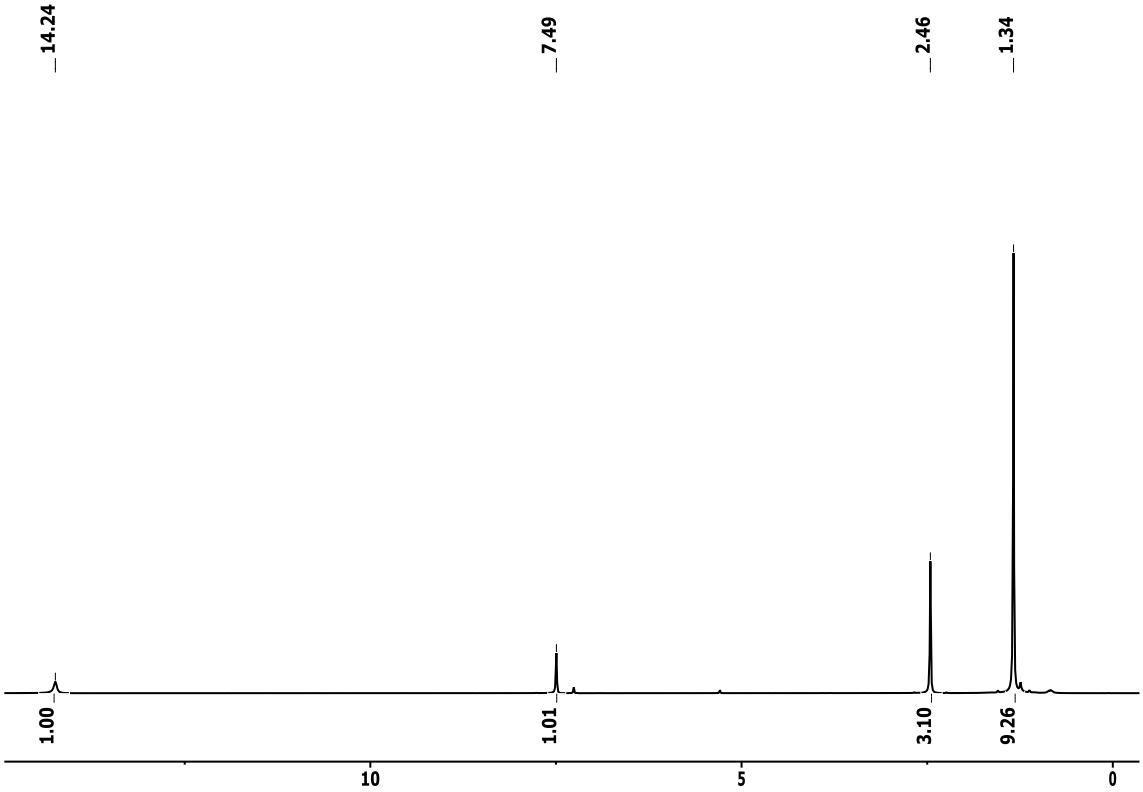

Figure S8. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

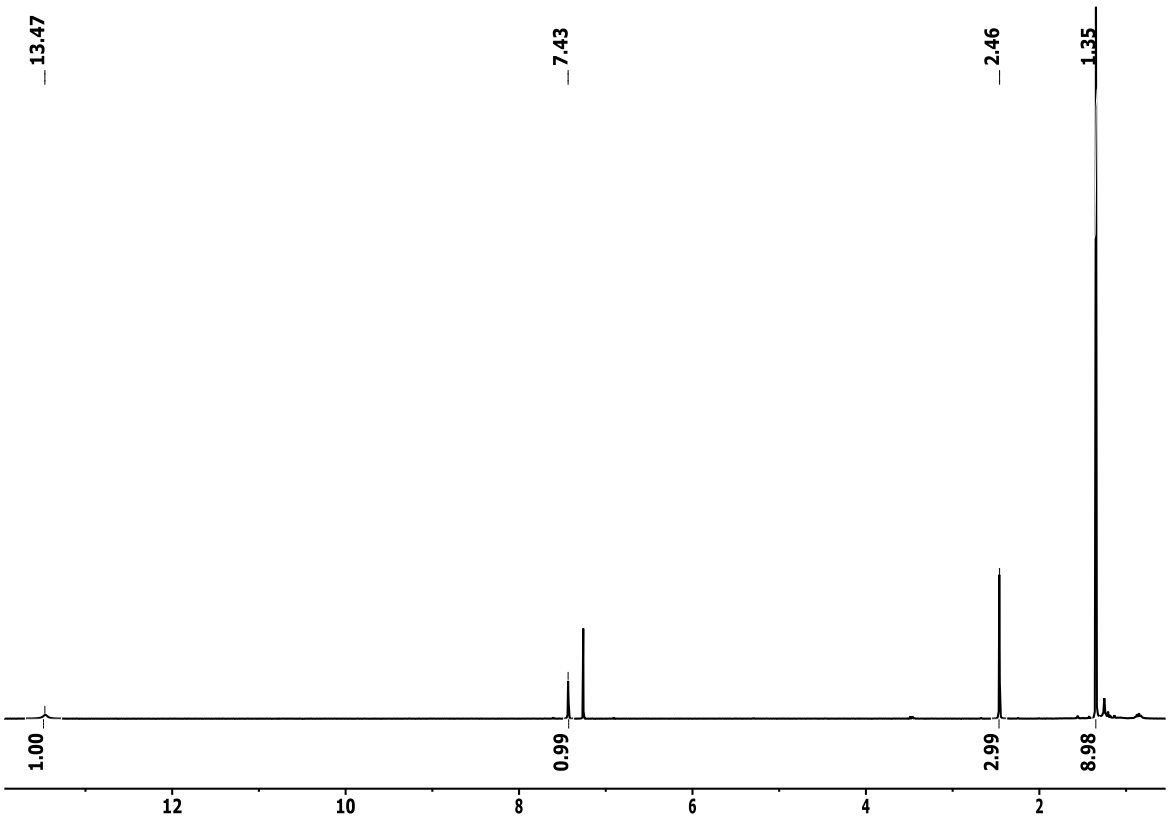

Figure S9. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

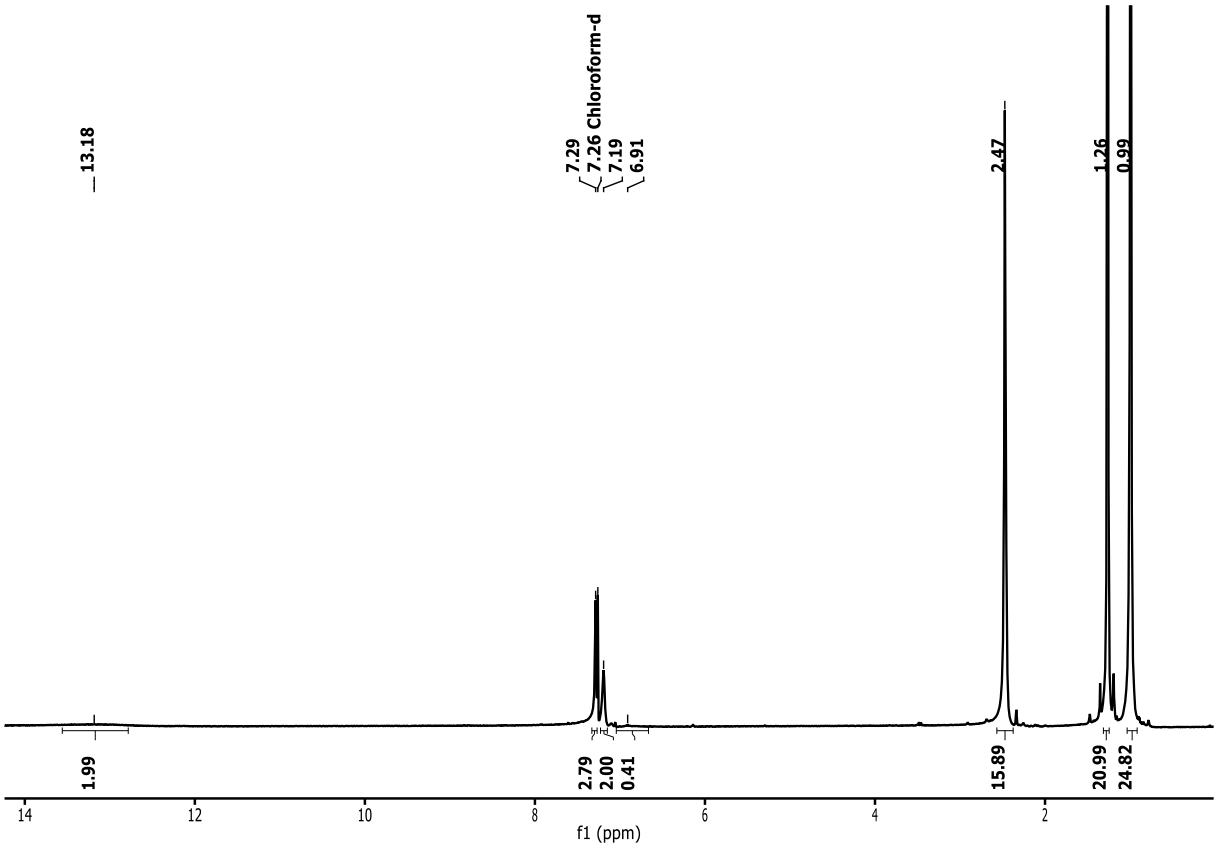

Figure S10. ^{1}H NMR spectrum of **3·HPn^{Me,tBu}** in $CDCl_3$.

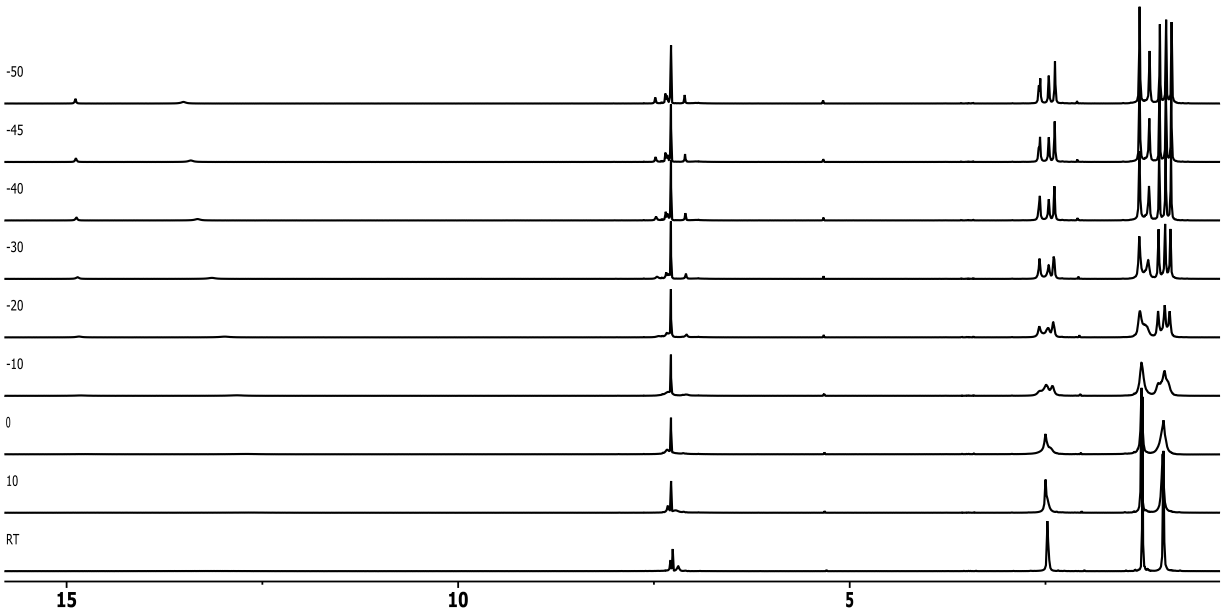

Figure S11. Variable temperature ^{1}H NMR spectra of **3·HPn^{Me,tBu}** in $CDCl_3$

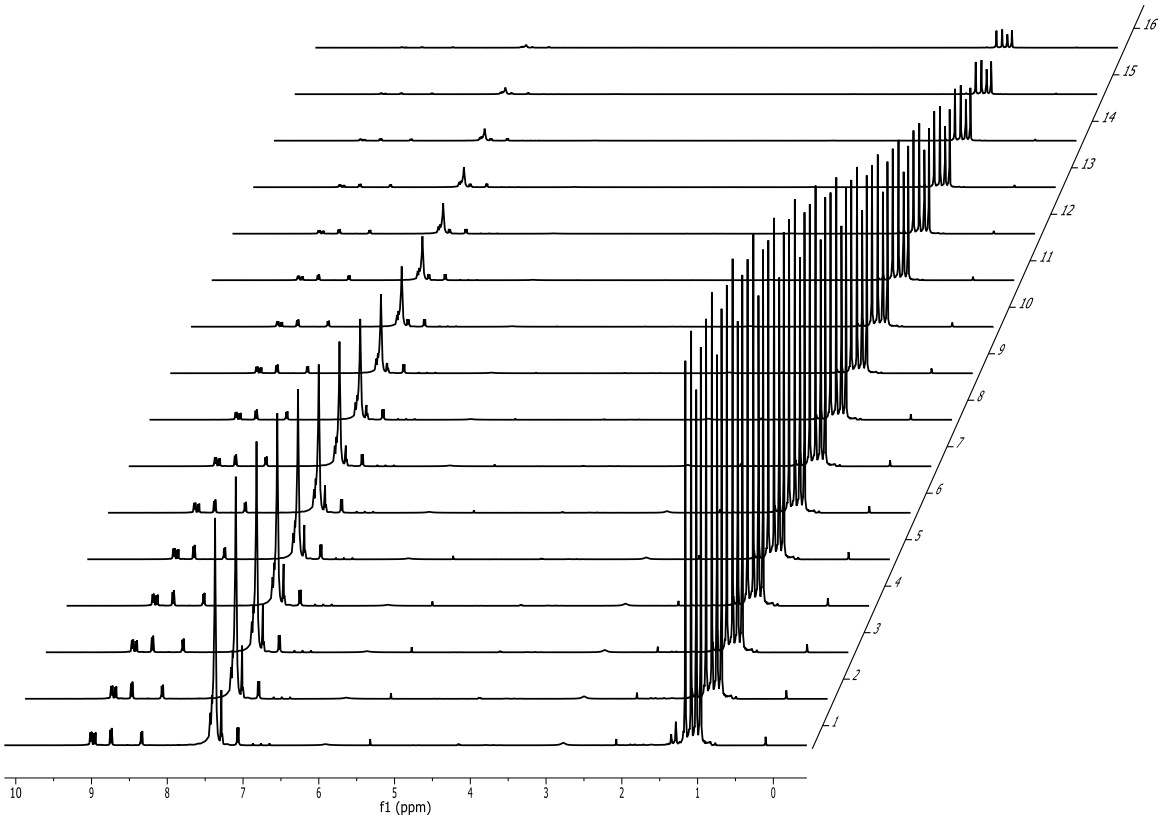

Figure S22. Diffusion weighted ^{1}H NMR spectra of **1a** and PPh_3 in $CDCl_3$.

For the determination of the hydrodynamic radius a 0.5 mM solution of **1a** in $CDCl_3$ was prepared and spiked with 3 mg of PPh_3 as internal standard. The hydrodynamic radius was calculated according to the Stokes – Einstein equation, where k_B is the Boltzmann constant, T the absolute temperature, η the dynamic viscosity of pure chloroform (due to the low concentration) and D the diffusion coefficient.

$$R_H = \frac{k_B T}{6\pi\eta D} \quad \text{(Eq. 1)}$$

In a similar experiment, to a solution of **1a**, two equiv of pyridine were added together with 0.5 µL of cyclooctene as an internal standard.[1] After calibration, the hydrodynamic radius and the partition coefficient were calculated according to equations 1 and 2.

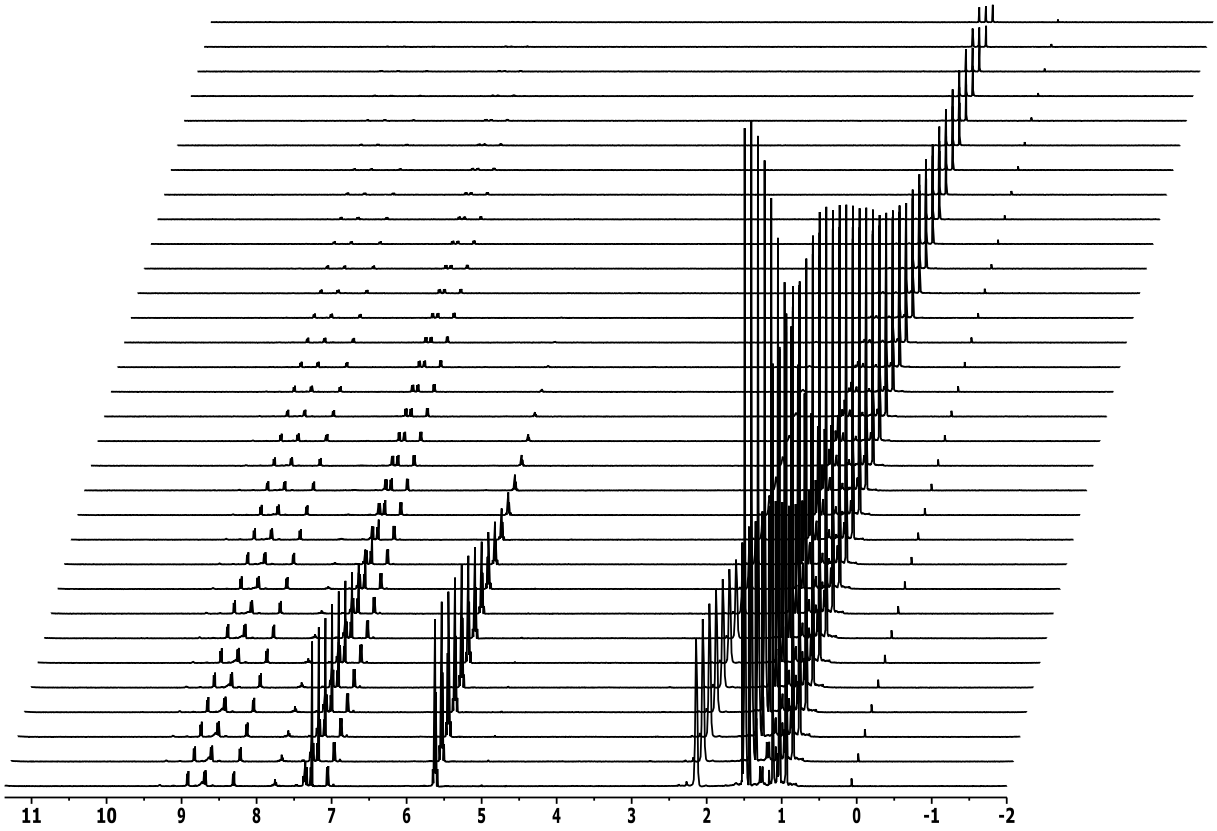

Figure S33. Diffusion weighted ^{1}H NMR spectra of **1a·2Py** and cyclooctene in $CDCl_3$.

Table S1. Diffusion coefficients of **1a**, cyclooctene (COE), pyridine in **1a·2Py** ($Py_{(1a)}$) and of free pyridine (Py)

	D [10^{-10} m^2/s]
1a	5.37
COE	20.3
$Py_{(1a)}$	19.1
Py	24.5

$$K = \frac{D_{Py(\mathbf{1a})} - D_{Py}}{D_{\mathbf{1a}} - D_{Py(\mathbf{1a})}} \quad \text{(Eq. 2)}$$

UV-Vis spectroscopy

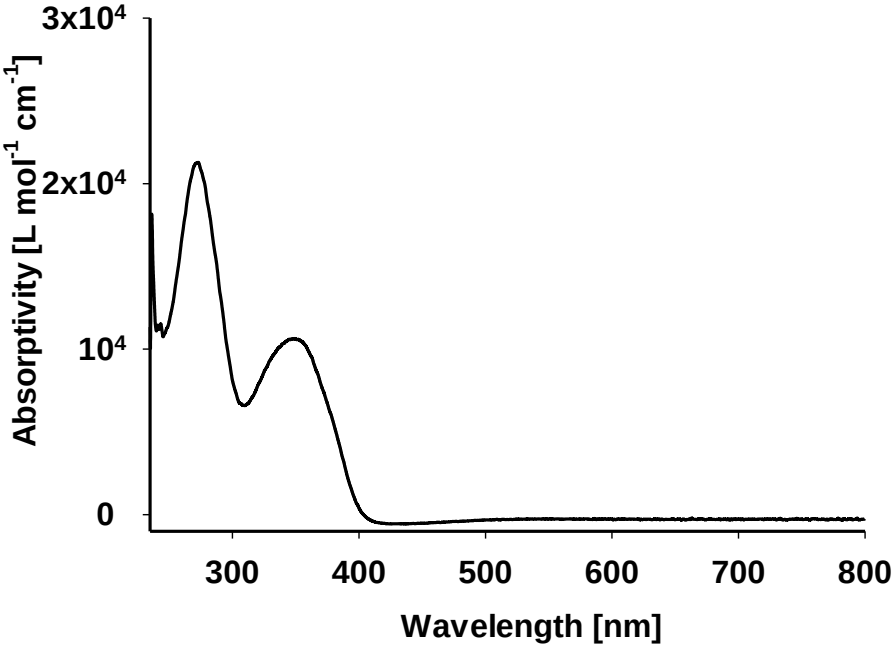

Figure S44. UV-Vis Spectrum of a 0.027 mM solution of **1a**·H_2O in dichloromethane.

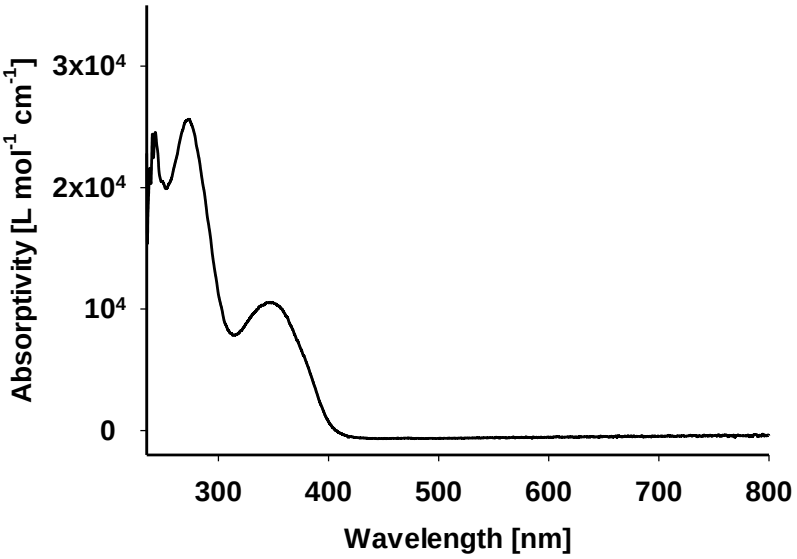

Figure S55. UV-Vis spectrum of a 0.018 mM solution of **1b**·H_2O in dichloromethane.

Thermogravimetric Analysis of 1a

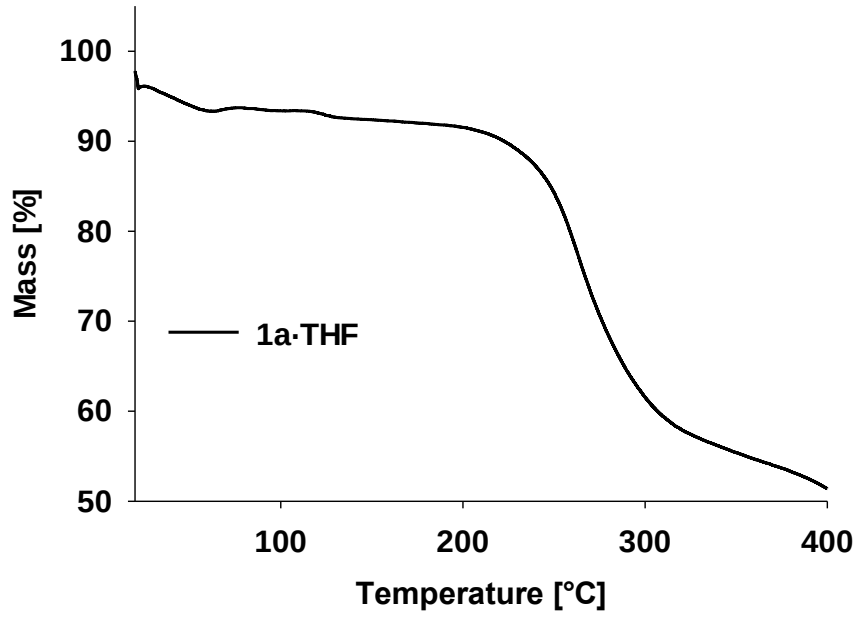

Figure S66. Thermogravimetric analysis of **1a**·THF

Molecular Structures

The molecular structures of complexes **1a**, **1b**, **2a** and **3** were determined, using single crystal X-ray diffraction analysis. Suitable crystals could be obtained by slow diffusion of pentane (**1a** and **1b**) into a chloroform solution and by slow evaporation of a chloroform solution (**2a** and **3**).

[Tn^{tBu}ZnBr]$_6$ (**1a**)

Due to the low quality of the X-ray data, no discussion of the bond lengths and angles is possible. However, the connectivity can be determined, showing the isotype structure to **1b** [*comp.* **1a**: a = 29.0374(15) Å, b = 29.8896(14) Å, c = 30.7411(16) Å, β = 102.387(2)°, C 2/c *vs.* **1b**: a = 29.161(3) Å, b = 30.102(3) Å, c = 31.045(3) Å, β = 102.323(2)°, C 2/c].

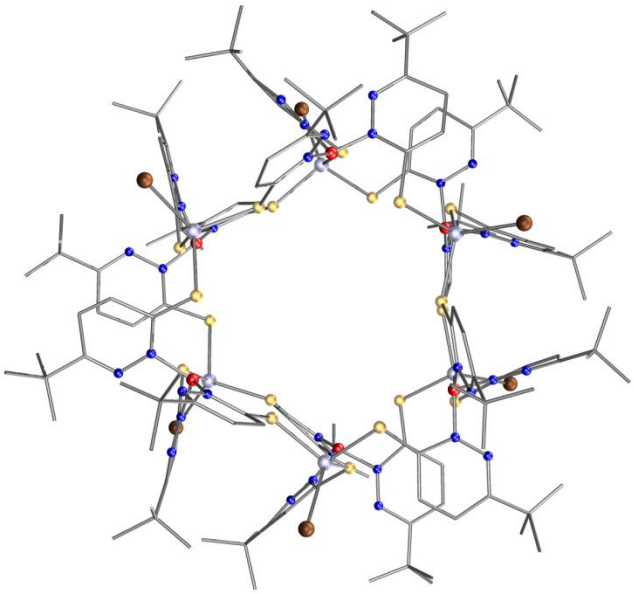

Figure S77. ORTEP/POV-Ray plot of **1a**. Hydrogen atoms and solvent molecules are omitted for clarity. Atom code: Zn gray, B red, Br brown, N blue, S yellow.

[Tn^{tBu}ZnI]$_6$ (1b)

Besides the described hexameric complex there are large regions containing disordered n-hexane molecules, both within as well as outside the hexameric molecules. Since it was not possible to describe the refined peaks of residual electron density as partially occupied individual solvent molecules, the diffuse electron density in these regions was removed by the SQUEEZE routine of the PLATON program.[3] The SQUEEZE routine computed a very large void volume of 10143 Å^3 (38.1% of the unit cell) with an electron count of approx. 3177 per unit cell (consistent with 64 n-hexane molecules with 50 electrons each). Two *tert*-butyl groups (bonded to C16, C36) were disordered over two orientations and refined with site occupation factors of 0.843(7) and 0.838(7), respectively, for the more prominent occupied orientations. The same anisotropic displacement parameters were used for equivalent C atoms of these disordered *tert*-butyl groups and the C–C distances were restrained to 1.53 Å. The largest peaks in a final difference Fourier map (1.12 - 1.14 eÅ^{-3}) were in the vicinity (0.32 - 0.84 Å) of the I atoms. For 1010 parameters final *R* indices of R1 = 0.0524 and wR^2 = 0.1624 (GOF = 1.079) were obtained.

Table S2. Selected bond lengths and angles for **1b**

Bond lengths	[Å]	Bond angles	[°]
I1 – Zn1	2.6158(4)	S4 – Zn1 – S2	101.14(3)
I2 – Zn2	2.6014(5)	S4 – Zn1 – S1'	109.03(3)
I3 – Zn3	2.5916(5)	S2 – Zn1 – S1'	98.87(3)
Zn1 – S1'	2.3506(8)	S4 – Zn1 – I1	114.68(2)
Zn1 – S2	2.3460(8)	S2 – Zn1 – I1	118.16(2)
Zn1 – S4	2.3316(9)	S1' – Zn1 – I1	113.23(2)
Zn2 – S3	2.3346(9)	S3 – Zn2 – S5	102.04(3)
Zn2 – S5	2.3466(9)	S3 – Zn2 – S7	108.48(4)
Zn2 – S7	2.3511(10)	S5 – Zn2 – S7	99.98(3)
Zn3 – S6	2.3435(9)	S3 – Zn2 – I2	112.53(3)
Zn3 – S8	2.3547(9)	S5 – Zn2 – I2	118.64(3)
Zn3 – S9'	2.3262(12)	S7 – Zn2 – I2	113.78(3)
B1 – N12	1.547(4)	S9' – Zn3 – S6	108.45(4)
B1 – N22	1.566(4)	S9' – Zn3 – S8	100.17(4)
B1 – N32	1.575(4)	S6 – Zn3 – S8	100.23(3)
B2 – N42	1.574(4)	S9' – Zn3 – I3	113.33(3)
B2 – N52	1.560(4)	S6 – Zn3 – I3	114.63(3)
B2 – N62	1.568(4)	S8 – Zn3 – I3	118.31(3)
B3 – N72	1.552(5)	C13 – S1 – Zn1'	102.45(10)
B3 – N82	1.564(5)	C23 – S2 – Zn1	107.97(10)
B3 – N92	1.564(5)	C33 – S3 – Zn2	107.42(11)
		C43 – S4 – Zn1	108.27(11)
		C53 – S5 – Zn2	107.58(12)
		C63 – S6 – Zn3	101.55(11)
		C73 – S7 – Zn2	101.14(12)
		C83 – S8 – Zn3	107.56(12)
		C93 – S9 – Zn3'	109.02(15)

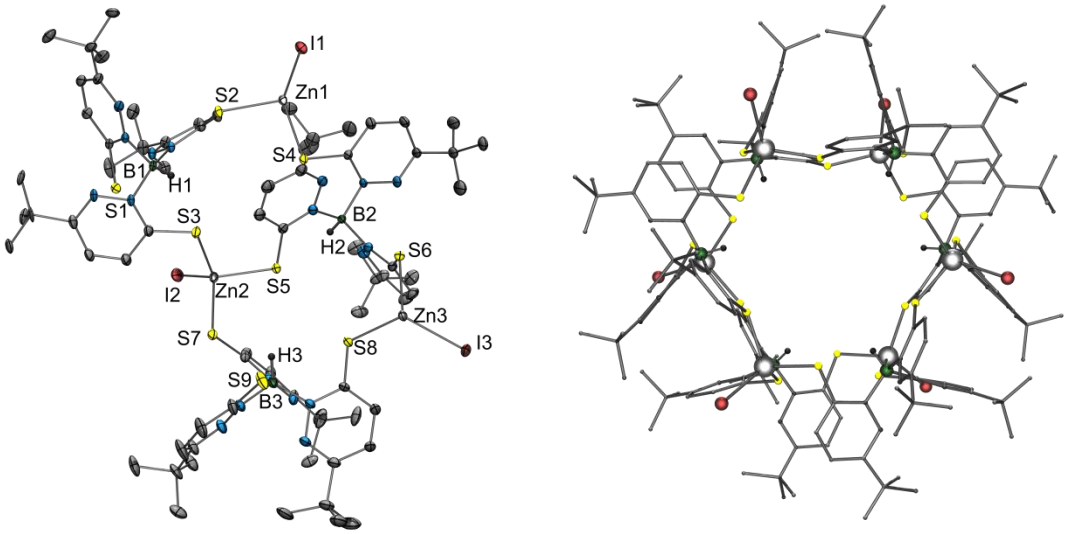

Figure S88. Left: ORTEP/POV-Ray plot of the asymmetric unit of **1b**. Hydrogen atoms, except for the B-H, solvent molecules and symmetric 2nd half of the hexamer are omitted for clarity, right: ORTEP/POV-Ray plot of **1b**, top view. Color Code: Zn gray, I brown, B green, S yellow, B-H black.

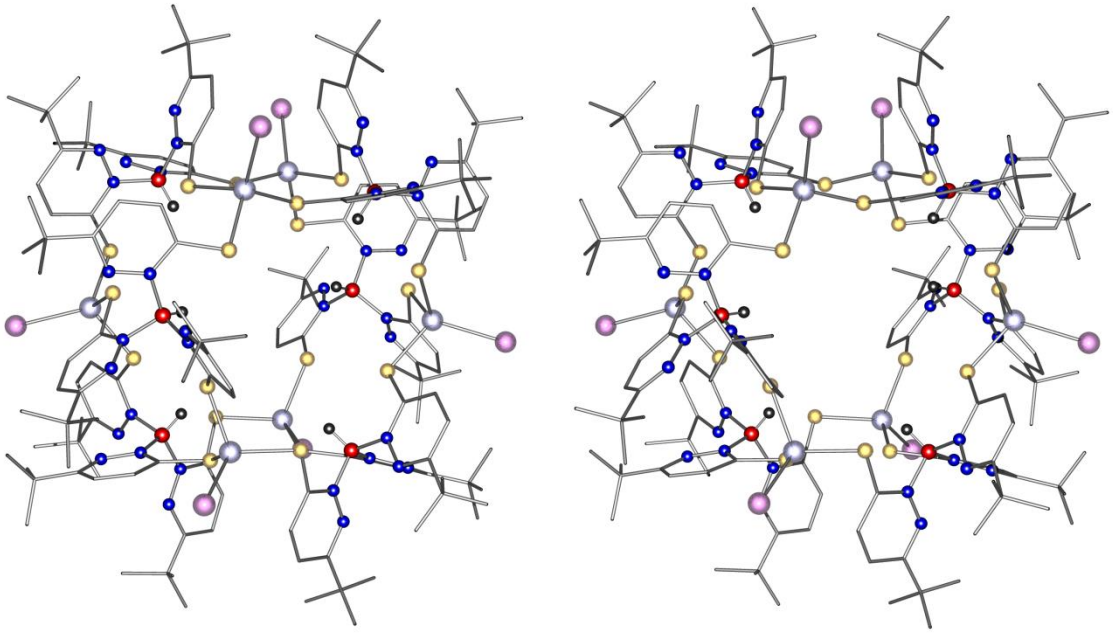

Figure S99. Stereoscopic ORTEP/PovRay plot of **1b**. The atoms are drawn with arbitrary radii. The H atoms except those bonded to boron were omitted for clarity reasons.

Table S3. Crystal data, data collection and refinement for $[Tn^{tBu}ZnI]_6$ (**1b**)

Crystal data	**1b**
Empirical formula	$C_{144}H_{20}O_4B_6I_6N_{36}S_{18}Zn_6 \cdot 16C_6H_{14}$
Formula weight	5613.72
Crystal description	Block, colourless
Crystal size	0.33 x 0.30 x 0.24mm
Crystal system, space group	monoclinic, C 2/c
Unit cell dimension	
a	29.161(3) Å
b	30.102(3) Å
c	31.045(3) Å
β	102.323(2)°
Volume	26624(5) $Å^3$
Z	4
Calculated density	1.401 mg/m^3
F(000)	12144
Linear absorption coefficient μ	1.428 mm^{-1}
Max. and min. transmission	1.0 and 0.735
Unit cell determination	2.45° < θ < 26.95°
	9343 reflections used at 100K
Data collection	
Temperature	100 K
Diffractometer	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube
Radiation and wavelength	MoKα, 0.71073Å
Monochromator	graphite
Scan type	ϕ and ω scans
θ range for data collection	1.97 to 26.00°
Reflections collected / unique	181208 / 26154
Significant unique reflections	19711 with I > 2σ(I)
R(int), R(sigma)	0.0405, 0.0389
Completeness (θ)	99.9% (26.0°)
Refinement	
Refinement method	Full-matrix least-squares on F2
Data / parameters / restraints	26154 / 1018 / 15
Goodness-of-fit on F2	1.134
Final R indices [I > 2σ(I)]	R1 = 0.0399, wR2 = 0.1100
R indices (all data)	R1 = 0.0537, wR2 = 0.1151
Extinction expression	none
Largest Δ/ σ in last cycle	0.003
Largest difference peak and hole	1.120 and -1.416 e/$Å^3$
Structure Solution Program	SHELXS-97[2]
Structure Refinement Program	SHELXL-2014/6[3]
CCDC number	1510468

[Zn(HPn^{Me,tBu})$_2$Br$_2$] (2a)

The positions of the H atoms H12 and H22 were taken from a difference Fourier map, the N–H distances were fixed to 0.88 Å, and these H atoms were refined without any constraints to the bond angles. For 268 parameters final *R* indices of R1 = 0.0224 and wR^2 = 0.0500 (GOF = 1.046) were obtained. The largest peak in a difference Fourier map was 0.656 eÅ^{-3}.

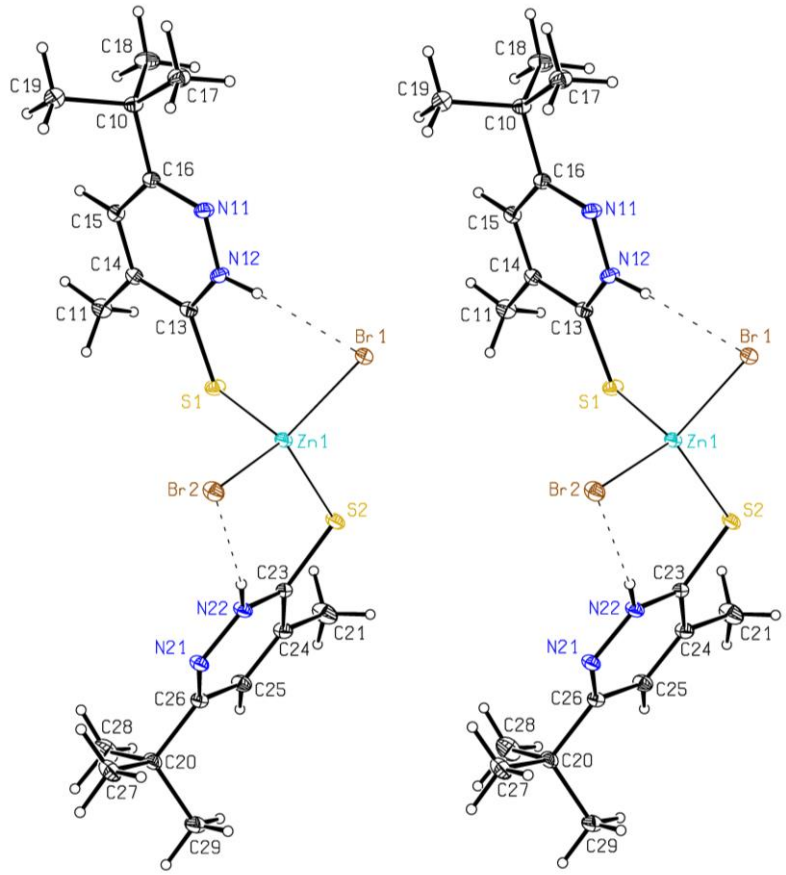

Figure S20. Stereoscopic ORTEP1 plot of **2a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii. The hydrogen bonds are indicated by dashed lines

[(Tn^{Me,tBu})Zn(HPn^{Me,tBu})Br] (**3**)

The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. Since racemic twinning was detected a twin matrix (-1 0 0 / 0 -1 0 / 0 0 -1) was applied and a scale factor was refined [0.078(11)] between the two unequal components. The non-hydrogen atoms of both complexes of the asymmetric unit were refined with anisotropic displacement parameters without any constraints. The H atoms bonded to B and co-ordinated to Zn were clearly identified in a difference Fourier map and were refined without any positional constraints with individual isotropic displacement parameters. The positions of the H atoms of the NH groups were taken from a difference Fourier map, the N–H distances were fixed to 0.88Å, and these H atoms were refined with a common isotropic displacement parameter without any constraints to the bond angles. Besides the described molecules there are four large regions containing disordered solvent molecules. Since it was not possible to describe the refined peaks of residual electron density as partially occupied individual solvent molecules, the diffuse electron density in these regions was removed by the SQUEEZE routine of the PLATON program[4]. The solvent contribution to the calculated structure factors for each reflection hkl is included in the FAB file. The SQUEEZE routine resulted in a void volume of 1469 Å^{-3} (15.1% of the unit cell) with an electron count of 358 per unit cell. Since the atoms of the unknown solvent molecules are not included in the UNIT instruction, the values of the reported chemical formula, molecular weight, density, F000, and of the absorption coefficient are too low. For 961 parameters final *R* indices of R1 = 0.0526 and wR^2 = 0.1315 (GOF = 1.014) were obtained. The largest peak in a difference Fourier map was 0.662 eÅ^{-3}.

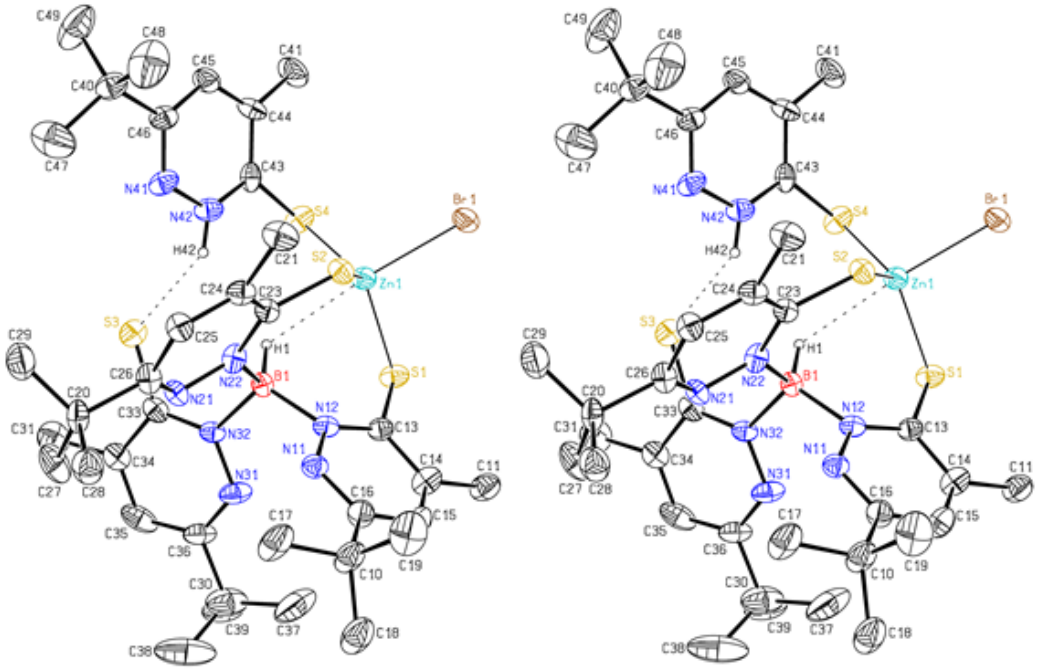

Figure S21. Stereoscopic ORTEP[1] plot of complex **3** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 30% probability level. The H atoms bonded to B or N are drawn with arbitrary radii, the others were omitted for clarity. The hydrogen bond and the contact Zn1···H1 [2.45(5) Å] is indicated by a dotted line.

Table S4. Crystal data, data collection and refinement for [Zn(HPn^{Me,tBu})$_2$Br$_2$] (**2a**) and [(Tn^{Me,tBu})Zn(HPn^{Me,tBu})Br] (**3**)

Crystal data	**2a**	**3**
Empirical formula	$C_{18}H_{28}Br_2N_4S_2Zn$	$C_{36}H_{54}BBrN_8S_4Zn$
Formula weight	589.75	883.20
Crystal description	block, colourless	needle, yellow
Crystal size	0.30 x 0.28 x 0.15mm	0.19 x 0.17 x 0.14mm
Crystal system, space group	monoclinic, P 21/c	orthorhombic, P 21 21 21
Unit cell dimensions:		
a	10.2147(3) Å	16.6456(19) Å
b	8.6489(2) Å	16.9851(19) Å
c	27.2498(8) Å	34.357(4) Å
β	96.6196(13)°	
Volume	2391.36(11) Å^3	9713.6(19) Å^3
Z	4	8
Calculated density	1.638 mg/m^3	1.208 mg/m^3
F(000)	1184	3680
Linear absorption coefficient μ	4.554 mm^{-1}	1.532 mm^{-1}
Max. and min. transmission	1.000 and 0.736	1.000 and 0.790
Unit cell determination	2.47° < θ < 35.70°	2.40° < θ < 21.32°
	9905 reflections used at 100K	9890 reflections used at 100K
Data collection		
Temperature	100K	
Diffractometer	Bruker APEX-II CCD	
Radiation source	Incoatec microfocus sealed tube	
Radiation and wavelength	MoKα, 0.71073Å	
Monochromator	multilayer monochromator	
Scan type	ϕ and ω scans	
θ range for data collection	2.01 to 35.00°	2.08 to 25.00°
Reflections collected / unique	38304 / 10517	65878 / 16976
Significant unique reflections	9146 with I > 2σ(I)	11043 with I > 2σ(I)
R(int), R(sigma)	0.0236, 0.0233	0.0711, 0.0946
Completeness (θ)	100.0 % (35.0°)	99.9% (25.0°)
Refinement		
Refinement method	Full-matrix least-squares on F2	
Data / parameters / restraints	10517 / 268 / 2	16976 / 961 / 2
Goodness-of-fit on F2	1.046	1.014
Final R indices [I > 2σ(I)]	R1 = 0.0224, wR2 = 0.0481	R1 = 0.0526, wR2 = 0.1160
R indices (all data)	R1 = 0.0299, wR2 = 0.0500	R1 = 0.0975, wR2 = 0.1315
Extinction expression	none	none
Largest Δ/ σ in last cycle	0.005	0.001
Largest difference peak and hole	0.656 and -0.359e/Å3	0.662 and -0.577e/Å3
Structure Solution Program	SHELXS-97[2]	
Structure Refinement Program	SHELXL-2014/6[3]	
CCDC number	1850650	1850651

References

1. Li, D.; Kagan, G.; Hopson, R.; Williard,P. G. *J. Am. Chem. Soc.* **2009**, *131*, 5627.
2. Sheldrick, G. M. *Acta Crystallogr., A* **2008**, *64*, 112.
3. Sheldrick, G. M. *Acta Crystallogr., C Struct. Chem*. **2015**, *71*, 3.