Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Syntheses, Emission Properties and Intramolecular Ligand Exchange of Zinc Complexes with Ligands Belonging to the Tmpa Family

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1. Crystallographic Data

The single crystal X-ray crystallography for **1c**, **3a**, **3c** and **3d** was carried out at 193(2) K and for **3d** at 203(2) K using a STOE IPDS diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K_α radiation (λ= 0.71073 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved by Direct Methods in SHELXS97, and refined by using full-matrix least squares in SHELXL97.[1]
The data for **1a** was collected on a Nonius MACH3 diffractometer at 173(2) K and for **1b**, **2** and **3b** on a Nonius KappaCCD respectively. Single crystals of **1b** and **3b** were measured at 100(2) K, whereas the crystals of **2** were measured at 173(2) K. The structures were solved using the SHELXTL 5.10 program based on the SHELX program packages.[2]
All non-hydrogen atoms were refined anisotropically. The single crystals were coated with protective Perfluorpolyether and mounted on a glass fiber.

1.1 Crystallographic Data for [**L2**$ZnCl_2$] (**1a**)

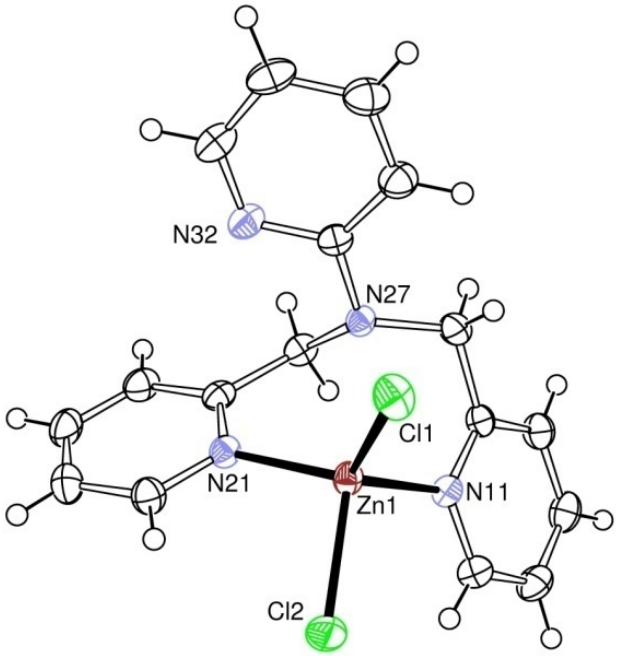


Fig. 1 SI Thermal ellipsoid representation (50% probability) of the molecular structure of [**L2**$ZnCl_2$] (**1a**).

Crystallographic data for **[L2ZnCl$_2$] (1a)**

Molecular formula	$C_{17}H_{16}Cl_2N_4Zn$	
CCDC no.	724313	
M_r	412.61	
Temperature [K]	173(2)	
Wavelength [Å]	0.71073	
Crystal description	colourless block	
Crystal size [mm]	0.30 × 0.30 × 0.30	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unitcell dimension	*a* [Å] = 9.2065(18)	α [°] = 90
	b [Å] = 11.230(2)	β [°] = 101.09(3)
	c [Å] = 17.138(3)	γ [°] = 90

[1] Sheldrick, G.M. (1997), SHELXS97 and SHELXL97. University of Göttingen, Germany
[2] SHELXTL 5.10 (Bruker AXS, 1998)

V [Å^3]	1738.7(6)
Z	4
F(000)	840
$\rho_{calc.}$ [g cm^{-3}]	1.576
μ [mm^{-1}]	1.725
Total reflections	7223
Unique reflections	3519
R(int)	0.0773
Scan range θ [°]	2.89 to 26.30
Completeness to $\theta_{max.}$ [%]	99.9
Index ranges	$-11 \le h \le 11$ $-7 \le k \le 13$ $-21 \le l \le 21$
Data / restraints / parameters	3519 / 0 / 273
Goodness-of-fit on F^2 [c]	0.873
$R1$,[a][b] $wR2$ [$I > 2\sigma(I)$][c]	0.0292, 0.0683
$R1$,[a][d] $wR2$ (all data)[c][d]	0.0459, 0.0789
Max./min. el. density [e.Å^{-3}]	+0.331, –0.458

Selected bond lengths [Å] and angles [°] for **[L2ZnCl$_2$] (1a)**

Zn(1)–N(11)	2.0819(18)	N(11)–Zn(1)–N(21)	110.59(8)
Zn(1)–Cl(2)	2.2941(8)	N(11)–Zn(1)–Cl(2)	101.07(6)
Zn(1)–N(21)	2.0513(19)	N(11)–Zn(1)–Cl(1)	114.39(6)
Zn(1)–Cl(1)	2.2143(7)	N(21)–Zn(1)–Cl(2)	100.00(6)
		N(21)–Zn(1)–Cl(1)	119.93(6)

1.2 Crystallographic Data for [**L2**Zn(OTf)(H$_2$O)]OTf (**1b**)

A sphere of data was collected with ω-scans (2.0° frame width; Irradiation times/frame: 20 s) and a semi empirical absorption correction from equivalent signals was applied (SORTAV) with T_{min} = 0.650 and T_{max} = 0.808. Hydrogen atoms were found and isotropically refined. The refinement showed an acetonitrile molecule in the independent unit.

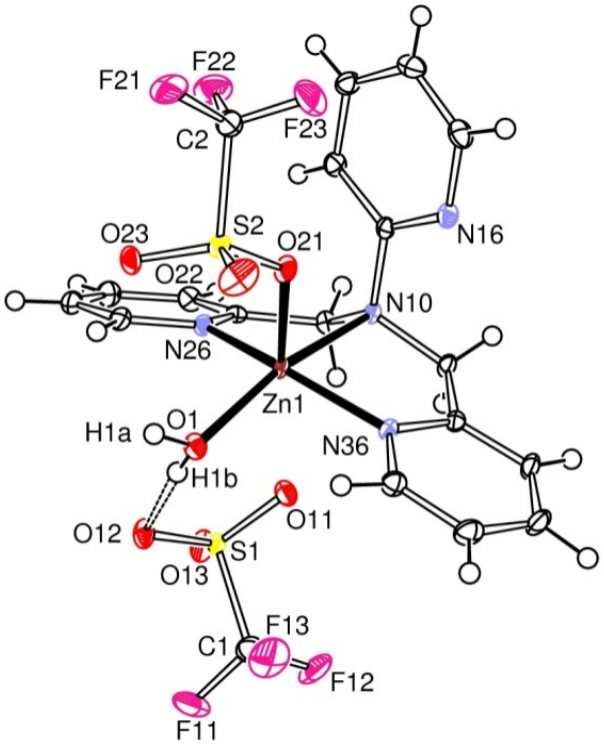


Fig. 2 SI Thermal ellipsoid representation (50% probability) of the molecular structure of [**L2**Zn(OTf)(H$_2$O)]OTf (**1b**).

Crystallographic data for [**L2**Zn(OTf)(H_2O)]OTf (**1b**)

Molecular formula	$C_{19}H_{18}F_6N_4O_7S_2Zn$	
M_r	657.86	
CCDC no.	796270	
Temperature [K]	100(2)	
Wavelength [Å]	0.71073	
Crystal description	colourless prism	
Crystal size [mm]	$0.28 \times 0.23 \times 0.17$	
Crystal system	triclinic	
Space group	*P*-1 (No. 2)	
Unitcell dimension	*a* [Å] = 9.4941(1)	α [°] = 100.878(1)
	b [Å] = 10.8919(2)	β [°] = 94.965(2)
	c [Å] = 12.8792(2)	γ [°] = 108.341(1)
V [Å^3]	1226.14(3)	
Z	2	
F(000)	664	
$\rho_{calc.}$ [g cm^{-3}]	1.782	
μ [mm^{-1}]	1.267	
Total reflections	33004	
Unique reflections	7118	
R(int)	0.0574	
Scan range θ [°]	3.42 to 30.00	
Completeness to $\theta_{max.}$ [%]	99.3	
Index ranges	$-13 \le h \le 13$	
	$-15 \le k \le 15$	
	$-18 \le l \le 18$	
Data / restraints / parameters	7118 / 0 / 406	
Goodness-of-fit on F^2 [c]	1.125	
R1,[a][b] *wR2* [$I > 2\sigma(I)$][c]	0.0323, 0.0856	
R1,[a][d] *wR2* (all data)[c][d]	0.0479, 0.0910	
Max./min. el. density [e.Å^{-3}]	+0.470, –0.558	

Selected bond lengths [Å] and angles [°] for [**L2**Zn(OTf)(H_2O)]OTf (**1b**)

Zn(1)–N(36)	2.023(2)	N(36)–Zn(1)–N(26)	150.73(6)
Zn(1)–O(21)	2.070(2)	N(36)–Zn(1)–O(21)	97.07(6)
O(1)...O(12)	2.703(2)	N(36)–Zn(1)–N(10)	79.80(6)
Zn(1)–N(26)	2.033(2)	O(21)–Zn(1)–N(10)	99.78(5)
Zn(1)–N(10)	2.319(2)	O(1)–Zn(1)–O(11)	81.93(5)
O(1)...O(23)*	2.755(2)	O(1)–H(1B)...O(12)	172(3)
Zn(1)–O(1)	2.058(2)	N(36)–Zn(1)–O(1)	97.23(6)
Zn(1)–O(11)	2.599(2)	N(26)–Zn(1)–O(21)	105.95(6)
		N(26)–Zn(1)–N(10)	78.71(6)
		N(36)–Zn(1)–O(11)	76.73(5)
		O(21)–Zn(1)–O(11)	173.26(5)
		O(1)–H(1A)...O(23)*	164(2)
		N(26)–Zn(1)–O(1)	97.88(6)
		O(1)–Zn(1)–O(21)	96.44(6)
		O(1)–Zn(1)–N(10)	163.79(6)
		N(26)–Zn(1)–O(11)	80.76(5)

1.3 Crystallographic Data for [(**L2**)$_3$Cu$_2$](BPh$_4$)$_2$ (**1c**)

Cell parameters were refined by using up to 5000 reflections. A sphere of data (310 frames) was collected with the φ-oscillation mode (0.6° frame width; Irradiation times/frame: 27.5 min). The refinement showed an acetone solvent molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically. The coordination geometry around the copper is best described as distorted tetragonal.

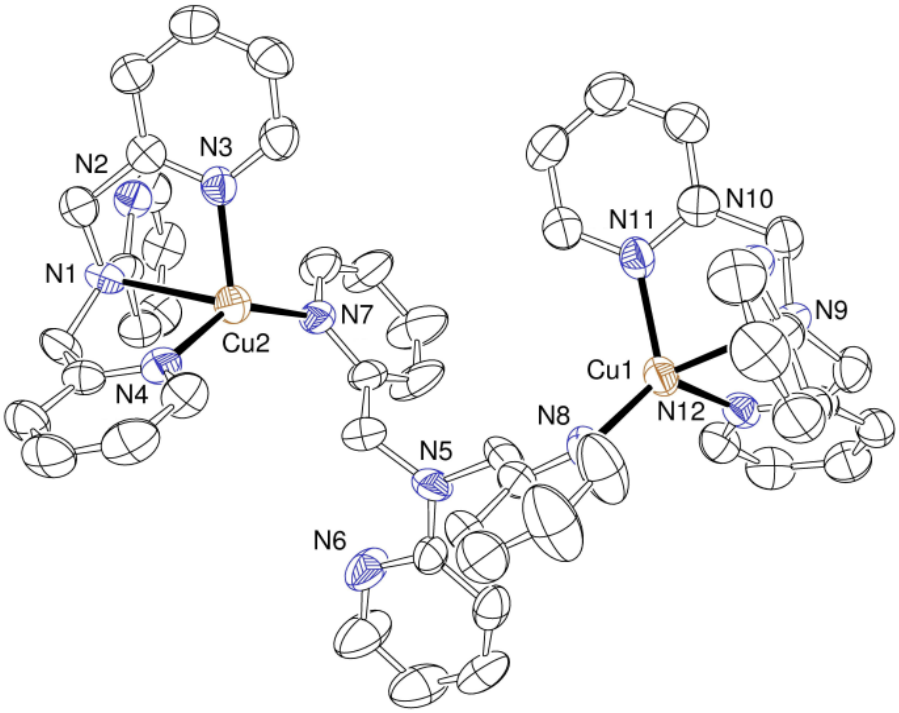


Fig. 3 SI Thermal ellipsoid representation (50% probability) of the molecular structure of $[(\mathbf{L2})_3Cu_2](BPh_4)_2$ (**1c**). Hydrogen atoms and anions are omitted for clarity.

Crystallographic data for $[(\mathbf{L2})_3Cu_2](BPh_4)_2$ (**1c**)

Molecular formula	$C_{102}H_{94}B_2Cu_2N_{12}O$	
M_r	1652.59	
CCDC no.	796271	
Temperature [K]	193(2)	
Wavelength [Å]	0.71073	
Crystal description	yellow block	
Crystal size [mm]	0.52 x 0.24 x 0.24	
Crystal system	monoclinic	
Space group	Cc	
Unitcell dimension	*a* [Å] = 17.762(4)	α [°] = 90
	b [Å] = 20.211(4)	β [°] = 100.35(3)
	c [Å] = 24.377(5)	γ [°] = 90
V [Å^3]	8609(3)	
Z	4	
F(000)	3464	
$\rho_{calc.}$ [g cm^{-3}]	1.275	
μ [mm^{-1}]	0.552	
Total reflections	27816	
Unique reflections	13806	
R(int)	0.0517	
Scan range θ [°]	2.02 to 25.02	
Completeness to $\theta_{max.}$ [%]	99.3	
Index ranges	$-21 \le h \le 21$	
	$-22 \le k \le 23$	
	$-28 \le l \le 28$	
Data / restraints / parameters	13806 / 2 / 1074	
Goodness-of-fit on F^2 [c]	0.924	
R1,[a][b] *wR2* [$I > 2\sigma(I)$][c]	0.0461, 0.0941	
R1,[a][d] *wR2* (all data)[c][d]	0.0795, 0.1057	
Max./min. el. density [e.Å^{-3}]	0.459 / -0.237	

Selected bond lengths [Å] and angles [°] for [(**L2**)$_3$Cu$_2$](BPh$_4$)$_2$ (**1c**)

Cu(1)-N(8)	1.979(4)	N(8)-Cu(1)-N(12)	126.25(16)
Cu(1)-N(12)	1.995(4)	N(8)-Cu(1)-N(11)	116.68(18)
Cu(1)-N(11)	2.007(4)	N(12)-Cu(1)-N(11)	115.88(16)
Cu(1)-N(9)	2.424(5)	N(8)-Cu(1)-N(9)	123.22(17)
Cu(2)-N(4)	1.952(4)	N(12)-Cu(1)-N(9)	77.74(15)
Cu(2)-N(7)	1.954(4)	N(11)-Cu(1)-N(9)	78.47(16)
Cu(2)-N(3)	2.051(4)	N(4)-Cu(2)-N(7)	141.53(17)
Cu(2)-N(1)	2.417(5)	N(4)-Cu(2)-N(3)	110.74(16)
Cu(1)-Cu(2)	7.364	N(7)-Cu(2)-N(3)	107.33(16)
		N(4)-Cu(2)-N(1)	78.06(16)
		N(7)-Cu(2)-N(1)	116.54(16)
		N(3)-Cu(2)-N(1)	76.81(15)

1.4 Crystallographic Data for [(**Me-bispic**)ZnCl$_2$] (**2**)

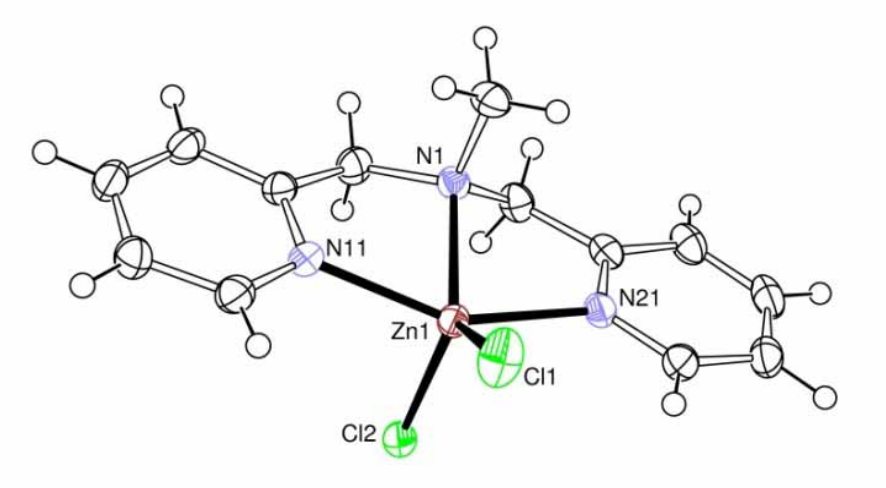


Fig. 4 SI Thermal ellipsoid representation (50% probability) of the molecular structure of [(**Me-bispic**)ZnCl$_2$] (**2**).

Crystallographic data for [(**Me-bispic**)ZnCl$_2$] (**2**)

Molecular formula	C_{13} H_{15} Cl_2 N_3 Zn	
M_r	349.55	
CCDC no.	724312	
Temperature [K]	173	
Wavelength [Å]	0.71073	
Crystal description	colourless block	
Crystal size [mm]	0.20 x 0.20 x 0.10	
Crystal system	monoclinic	
Space group	$P2_1/n$ (No. 14)	
Unitcell dimension	a [Å] = 8.5048(1)	α [°] = 90
	b [Å] = 13.0128(1)	β [°] = 95.250(1)
	c [Å] = 13.1424(1)	γ [°] =
V [Å3]	1448.38(4)	
Z	4	
F(000)	712	
ρcalc. [g cm–3]	1.603	
μ [mm–1]	2.053 mm^{-1}	
Total reflections	5650	
Unique reflections	3228	
R(int)	0.0179	
Scan range θ [°]	2.21 to 27.48	

Completeness to θmax. [%]	97.5 %
Index ranges	-9≤h≤10
	-16≤k≤15
	-17≤l≤17
Data / restraints / parameters	3228 / 0 / 232
Goodness-of-fit on F2 [c]	1.122
R1,[a][b] wR2 [I > 2σ(I)][c]	0.0262, 0.0754
R1,[a][d] wR2 (all data)[c][d]	0.0311, 0.0781
Max./min. el. density [e.Å–3]	+0.272, -0.536

Selected bond lengths [Å] and angles [°] for [(**Me-bispic**)$ZnCl_2$] (**2**)

Zn(1)–N(11)	2.1483(15)	N(11)–Zn(1)–N(21)	152.01(6)
Zn(1)–Cl(1)	2.2709(5)	N(11)–Zn(1)–Cl(1)	97.95(5)
Zn(1)–N(21)	2.1497(15)	N(11)–Zn(1)–Cl(2)	95.16(4)
Zn(1)–Cl(2)	2.2783(5)	Cl(1)–Zn(1)–Cl(2)	120.62(2)
Zn(1)–N(1)	2.2151(14)	N(11)–Zn(1)–N(1)	76.37(6)
		N(21)–Zn(1)–Cl(1)	96.44(4)
		N(21)–Zn(1)–Cl(2)	97.97(4)
		N(21)–Zn(1)–N(1)	76.04(6)
		N(1)–Zn(1)–Cl(1)	130.80(4)
		N(1)–Zn(1)–Cl(2)	108.58(4)

1.5 Crystallographic Data for **L1**H(OTf) (**3a**)

Cell parameters were refined by using up to 5000 reflections. A sphere of data (190 frames) was collected with the φ-oscillation mode (1.0° frame width; Irradiation times/frame: 8 min). The refinement showed a water molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically. The N-H and O-H hydrogen atoms were found and isotropically refined.

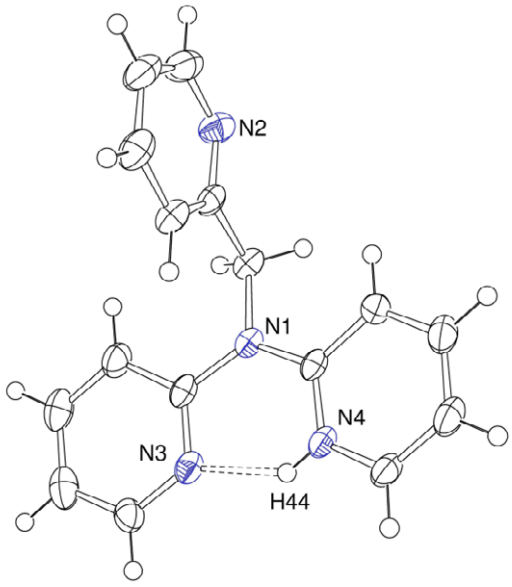


Fig. 5 SI Thermal ellipsoid representation (50% probability) of the molecular structure of **L1**H(OTf) (**3a**). Anion and solvent molecules are omitted for clarity.

Crystallographic data for **L1**H(OTf) (**3a**)

Molecular formula	$C_{17}H_{17}F_3N_4O_4S$
M_r	430.41
CCDC no.	796272
Temperature [K]	193(2)
Wavelength [Å]	0.71073

Crystal description	colourless block	
Crystal size [mm]	0.52 x 0.48 x 0.36	
Crystal system	triclinic	
Space group	P-1	
Unitcell dimension	a [Å] = 9.2409(18)	α [˚] = 75.35(3)
	b [Å] = 9.5985(19)	β [˚] = 83.59(3)
	c [Å] = 10.721(2)	γ [˚] = 88.29(3)
V [Å3]	914.2(3)	
Z	2	
F(000)	444	
ρcalc. [g cm–3]	1.564	
μ [mm–1]	0.241	
Total reflections	8133	
Unique reflections	3970	
R(int)	0.0715	
Scan range θ [˚]	3.12 to 28.06	
Completeness to θmax. [%]	89.3	
Index ranges	$-12 \le h \le 11$	
	$-12 \le k \le 12$	
	$-12 \le l \le 13$	
Data / restraints / parameters	3970 / 0 / 275	
Goodness-of-fit on F2 [c]	1.108	
R1,[a][b] wR2 [I > 2σ(I)][c]	0.0573, 0.1593	
R1,[a][d] wR2 (all data)[c][d]	0.0631, 0.1656	
Max./min. el. density [e.Å–3]	0.471 / -0.913	

Bond lengths [Å] and angles [°] for **L1**H(OTf) (**3a**)

C(1)-N(1)	1.459(3)	N(1)-C(1)-C(2)	114.22(15)
C(1)-C(2)	1.519(3)	N(2)-C(2)-C(3)	123.21(18)
C(2)-N(2)	1.327(3)	N(2)-C(2)-C(1)	114.20(17)
C(2)-C(3)	1.384(3)	C(3)-C(2)-C(1)	122.59(19)
C(3)-C(4)	1.392(3)	C(2)-C(3)-C(4)	117.8(2)
C(4)-C(5)	1.363(4)	C(5)-C(4)-C(3)	119.6(2)
C(5)-C(6)	1.376(4)	C(4)-C(5)-C(6)	118.5(2)
C(6)-N(2)	1.338(3)	N(2)-C(6)-C(5)	123.3(2)
C(7)-N(3)	1.328(3)	N(3)-C(7)-C(8)	121.2(2)
C(7)-C(8)	1.400(3)	N(3)-C(7)-N(1)	117.62(17)
C(7)-N(1)	1.408(3)	C(8)-C(7)-N(1)	121.2(2)
C(8)-C(9)	1.372(3)	C(9)-C(8)-C(7)	118.2(2)
C(9)-C(10)	1.374(4)	C(8)-C(9)-C(10)	120.6(2)
C(10)-C(11)	1.373(3)	C(11)-C(10)-C(9)	117.8(2)
C(11)-N(3)	1.343(3)	N(3)-C(11)-C(10)	122.5(2)
C(12)-N(4)	1.336(3)	N(4)-C(12)-N(1)	120.18(19)
C(12)-N(1)	1.377(2)	N(4)-C(12)-C(13)	117.81(17)
C(12)-C(13)	1.409(3)	N(1)-C(12)-C(13)	122.02(18)
C(13)-C(14)	1.371(3)	C(14)-C(13)-C(12)	119.3(2)
C(14)-C(15)	1.382(3)	C(13)-C(14)-C(15)	120.9(2)
C(15)-C(16)	1.362(3)	C(16)-C(15)-C(14)	118.41(19)
C(16)-N(4)	1.351(2)	N(4)-C(16)-C(15)	120.4(2)
N(3)-H(44)	1.827	C(14)-C(13)-C(12)	119.3(2)
		C(13)-C(14)-C(15)	120.9(2)
		C(16)-C(15)-C(14)	118.41(19)
		N(4)-C(16)-C(15)	120.4(2)
		C(12)-N(1)-C(7)	124.48(17)
		C(12)-N(1)-C(1)	117.54(17)
		C(7)-N(1)-C(1)	117.92(16)
		C(2)-N(2)-C(6)	117.6(2)
		C(7)-N(3)-C(11)	119.46(18)
		C(12)-N(4)-C(16)	123.17(19)

1.6 Crystallographic Data for [**L1**$ZnCl_2$] (**3b**)

A sphere of data was collected with ϕ– and ω-scans (0.8° frame width; Irradiation times/frame: 8 s). A numerical absorption correction was applied (Gauss-integration) with T_{min} = 0.608 and T_{max} = 0.726. An occupation disorder is observable where N16 and C12 swap their positions. The occupancies were refined and gave 67(2) % for the main and 33(2) % for the minor component. Hydrogen atoms were found and isotropically refined.

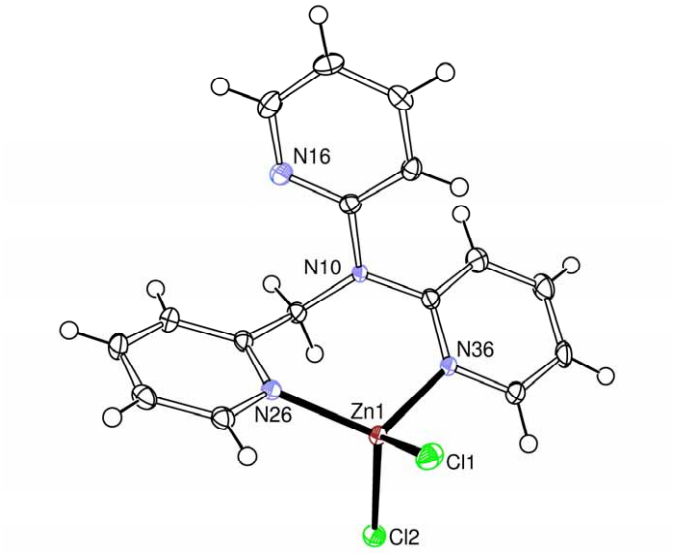


Fig. 6 SI Thermal ellipsoid representation (50% probability) of the molecular structure of [**L1**$ZnCl_2$] (**3b**).

Crystallographic data for [**L1**$ZnCl_2$] (**3b**)

Molecular formula	$C_{16}H_{14}Cl_2N_4Zn$	
M_r	398.58	
CCDC no.	796273	
Temperature [K]	100(2)	
Wavelength [Å]	0.71073	
Crystal description	colourless prism	
Crystal size [mm]	0.29 × 0.19 × 0.19	
Crystal system	monoclinic	
Space group	*C*2/*c* (No. 15)	
Unitcell dimension	*a* [Å] = 15.2535(4)	α [°] = 90
	b [Å] = 7.4124(1)	β [°] = 92.344(2)
	c [Å] = 29.1536(6)	γ [°] = 90
V [Å^3]	3293.5(2)	
Z	8	
F(000)	1616	
$\rho_{calc.}$ [g cm^{-3}]	1.608	
μ [mm^{-1}]	1.819	
Total reflections	32273	
Unique reflections	5707	
R(int)	0.0699	
Scan range θ [°]	3.34 to 32.00	
Completeness to $\theta_{max.}$ [%]	99.8	
Index ranges	$-22 \le h \le 22$	
	$-11 \le k \le 11$	
	$-43 \le l \le 41$	
Data / restraints / parameters	5707 / 1 / 254	
Goodness-of-fit on F^2 [c]	1.015	
R1,[a][b] *wR2* [$I > 2\sigma(I)$][c]	0.0359, 0.0705	
R1,[a][d] *wR2* (all data)[c][d]	0.0714, 0.0762	
Max./min. el. density [e.Å^{-3}]	+0.488, –0.427	

Selected bond lengths [Å] and angles [°] for [**L1**$ZnCl_2$] (**3b**)

Zn(1)–N(36)	2.075(2)	N(36)–Zn(1)–N(26)	112.42(6)
Zn(1)–Cl(2)	2.2399(5)	N(36)–Zn(1)–Cl(2)	102.24(5)
Zn(1)–N(26)	2.039(2)	N(36)–Zn(1)–Cl(1)	108.70(4)
Zn(1)–Cl(1)	2.2413(5)	N(26)–Zn(1)–Cl(2)	110.37(4)
		N(26)–Zn(1)–Cl(1)	108.43(5)
		Cl(1)–Zn(1)–Cl(2)	114.65(2)

1.7 Crystallographic Data for [(**L1**)$_2$Zn(MeOH)$_2$](OTf)$_2$ (**3c**)

Cell parameters were refined by using up to 4992 reflections. A sphere of data (210 frames) was collected with the φ-oscillation mode (0.9° frame width; Irradiation times/frame: 30 min). The refinement showed only half of the molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically, the O-H hydrogen atom was found and isotropically refined. The coordination sphere of the metal centre is best described as an octahedron.

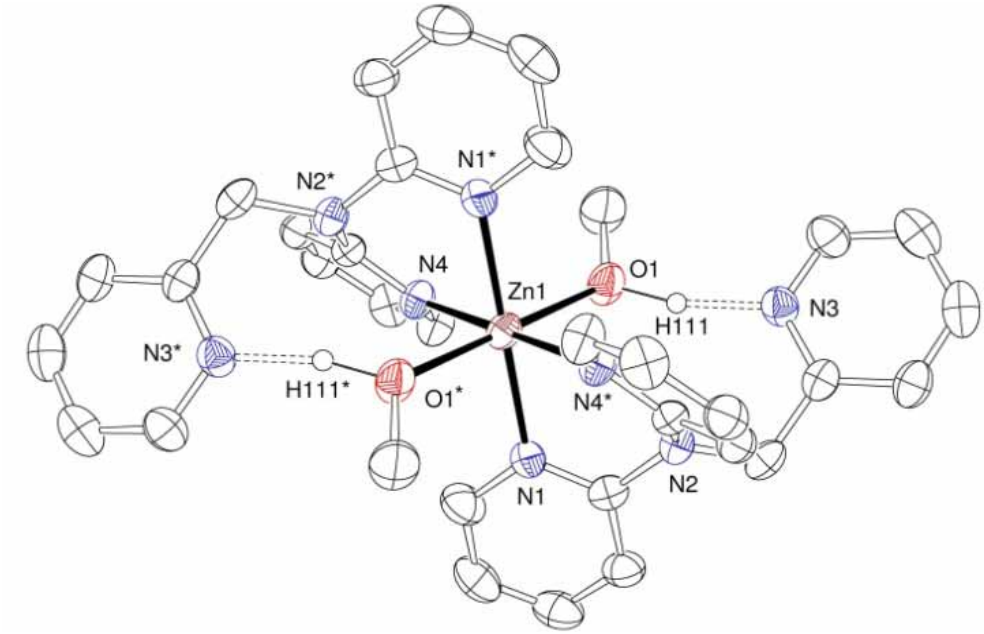


Fig. 7 SI Thermal ellipsoids representation (50% probability) of the molecular structure of [(**L1**)$_2$Zn(MeOH)$_2$](OTf)$_2$ (**3c**). Hydrogen atoms and anions are omitted for clarity.

Crystallographic data for [(**L1**)$_2$Zn(MeOH)$_2$](OTf)$_2$ (**3c**)

Molecular formula	$C_{36}H_{36}F_6N_8O_8S_2Zn$	
M_r	952.22	
CCDC no.	796274	
Temperature [K]	193(2)	
Wavelength [Å]	0.71073	
Crystal description	yellow block	
Crystal size [mm]	0.38 x 0.24 x 0.12	
Crystal system	monoclinic	
Space group	C2/c	
Unitcell dimension	*a* [Å] = 23.404(5)	α [°] = 90
	b [Å] = 12.220(2)	β [°] = 123.83(3)
	c [Å] = 17.155(3)	γ [°] = 90.0
V [Å^3]	4075.8(14)	
Z	4	
F(000)	1952	
$\rho_{calc.}$ [g cm^{-3}]	1.552	
μ [mm^{-1}]	0.794	
Total reflections	14581	
Unique reflections	4942	
R(int)	0.1493	

Scan range θ [°]	2.43 to 28.13
Completeness to $\theta_{max.}$ [%]	99.1
Index ranges	$-30 \le h \le 30$
	$-16 \le k \le 16$
	$-22 \le l \le 22$
Data / restraints / parameters	4942 / 0 / 326
Goodness-of-fit on F^2 [c]	0.860
$R1$,[a][b] $wR2$ $[I > 2\sigma(I)]$[c]	0.0588, 0.1183
$R1$,[a][d] $wR2$ (all data)[c][d]	0.1456, 0.1453
Max./min. el. Density [e.Å^{-3}]	0.566 / -0.592

Selected bond lengths [Å] and angles [°] for $[(\mathbf{L1})_2Zn(MeOH)_2](Otf)_2$ (**3c**)

N(1)-Zn(1)	2.130(4)	N(4)*-Zn(1)-N(4)	180.0(2)
N(4)-Zn(1)	2.108(3)	N(4)*-Zn(1)-N(1)	83.68(14)
O(1)-Zn(1)	2.158(3)	N(4)-Zn(1)-N(1)	96.32(14)
Zn(1)-N(4)*	2.108(3)	N(4)*-Zn(1)-N(1)*	96.32(14)
Zn(1)-N(1)*	2.130(4)	N(4)-Zn(1)-N(1)*	83.68(14)
Zn(1)-O(1)*	2.158(3)	N(1)-Zn(1)-N(1)*	180.0
N(3)-H(111)	1.59(7)	N(4)*-Zn(1)-O(1)*	88.31(13)
		N(4)-Zn(1)-O(1)*	91.69(12)
		N(1)-Zn(1)-O(1)*	89.11(13)
		N(1)*-Zn(1)-O(1)*	90.89(13)
		N(4)*-Zn(1)-O(1)	91.69(12)
		N(4)-Zn(1)-O(1)	88.31(12)
		N(1)-Zn(1)-O(1)	90.89(13)
		N(1)*-Zn(1)-O(1)	89.11(13)
		O(1)*-Zn(1)-O(1)	180.0

*Symmetry operation used to generate equivalent atoms: -x+1/2, -y+1/2, -z+1

1.8 Crystallographic Data for $[(\mathbf{L1})_2Cu_2](Otf)_2$ (**3d**)

Cell parameters were refined by using up to 5000 reflections. A sphere of data (235 frames) was collected with the φ-oscillation mode (0.8° frame width; Irradiation times/frame: 13 min). The refinement shows a half molecule of **3d** and a DMF molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically. The coordination geometry around the copper is best described as distorted trigonal planar.

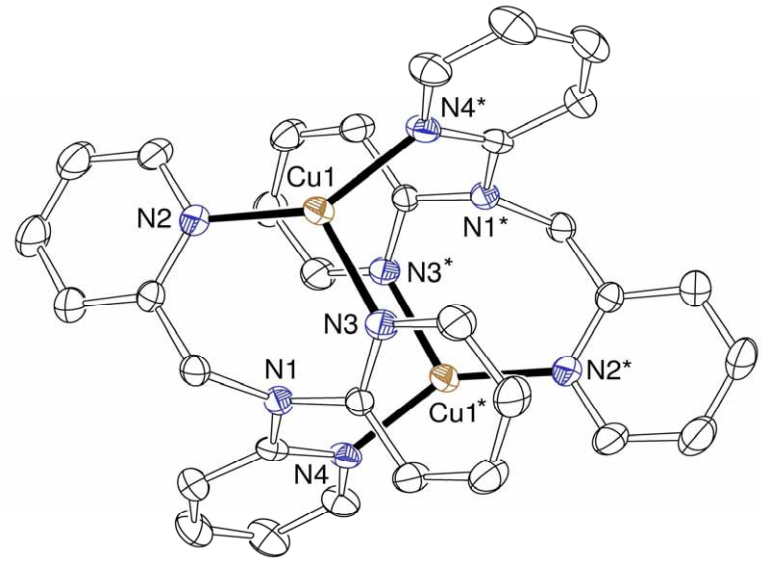


Fig. 8 SI Thermal ellipsoid representation (50% probability) of the molecular structure of $[(\mathbf{L1})_2Cu_2](Otf)_2$ * 2 DMF (**3d**). Hydrogen atoms and anions are omitted for clarity

Crystallographic data for $[(\mathbf{L1})_2Cu_2](Otf)_2$ (**3d**)

Molecular formula	$C_{40}H_{42}Cu_2F_6N_{10}O_8S_2$	
M_r	1096.04	
CCDC no.	796275	
Temperature [K]	203(2)	
Wavelength [Å]	0.71073	
Crystal description	yellow block	
Crystal size [mm]	0.80 x 0.32 x 0.24	
Crystal system	monoclinic	
Space group	P21/n	
Unitcell dimension	a [Å] = 13.411(3)	α [°] = 90
	b [Å] = 9.5300(19)	β [°] = 95.72(3)
	c [Å] = 17.636(4)	γ [°] = 90
V [Å^3]	2242.8(8)	
Z	2	
F(000)	1120	
$\rho_{calc.}$ [g cm^{-3}]	1.623	
μ [mm^{-1}]	1.130	
Total reflections	19621	
Unique reflections	5123	
R(int)	0.0624	
Scan range θ [°]	2.81 to 28.09	
Completeness to $\theta_{max.}$ [%]	93.6	
Index ranges	$-17 \le h \le 17$	
	$-11 \le k \le 11$	
	$-23 \le l \le 23$	
Data / restraints / parameters	5123 / 0 / 340	
Goodness-of-fit on F^2 [c]	1.070	
$R1$,[a][b] $wR2$ [$I > 2\sigma(I)$][c]	0.0410, 0.1126	
$R1$,[a][d] $wR2$ (all data)[c][d]	0.0502, 0.1182	
Max./min. el. density [e.Å^{-3}]	0.624 / -0.585	

Bond lengths [Å] and angles [°] for [(**L1**)$_2$Cu$_2$](OTf)$_2$ (**3d**)

Cu(1)-N(2)	1.956(2)	N(2)-Cu(1)-N(4)*	140.54(8)
Cu(1)-N(4)*	1.9834(17)	N(2)-Cu(1)-N(3)	117.56(7)
Cu(1)-N(3)	2.0725(19)	N(4)*-Cu(1)-N(3)	100.98(8)
Cu(1)-Cu(1)*	4.114		

*Symmetry operation used to generate equivalent atoms: -x+1, -y+2, -z

2. NMR Spectroscopy

2.1 ^{1}H NMR Spectra at Ambient Temperature

Chemical shifts and multiplicity of the ^{1}H NMR spectra for the compounds **1a**, **1b**, **2**, **3b**, **3c** and **3e** reported in the experimental section are taken from the spectra at ambient temperature depicted in the following Figures. Furthermore, the ^{1}H NMR spectrum of the compound [**tpa**$ZnCl_2$] at ambient temperature is shown in order to compare our data with data already published by Wang et al.[3]

[**L2**$ZnCl_2$] (**1a**)

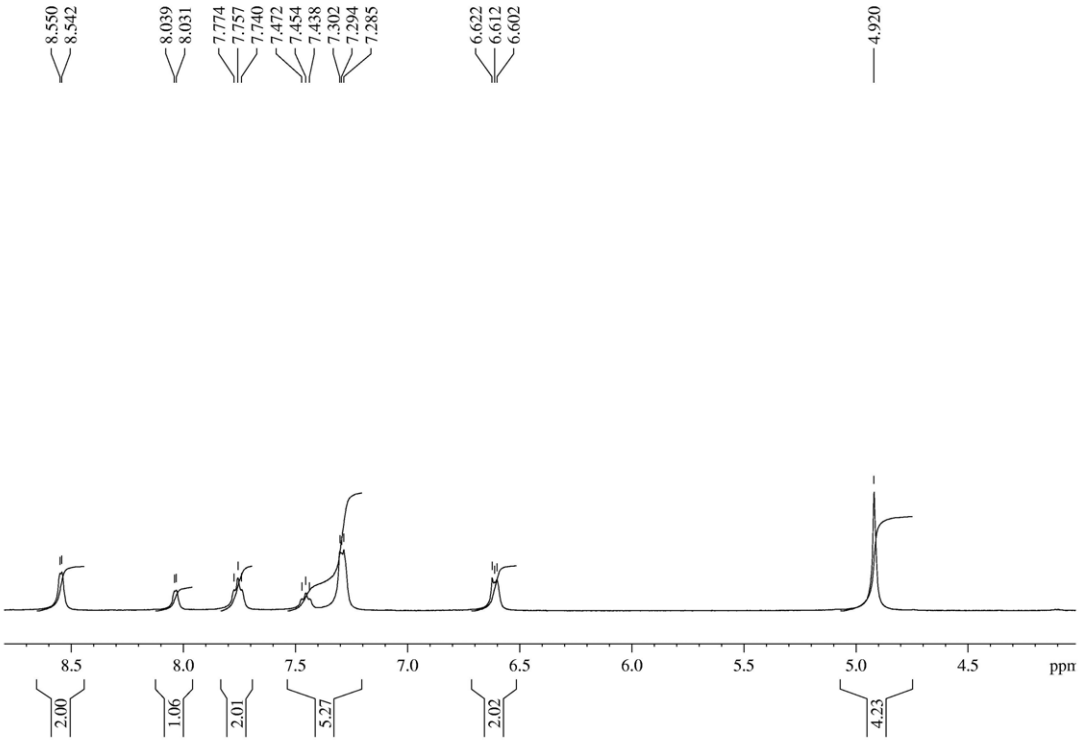


Fig. 9 SI Section of ^{1}H NMR spectrum of **1a** at 296 K in DMSO-D_6

[3] W. Y. Yang, H. Schmider, Q. G. Wu, Y. S. Zhang and S. N. Wang, *Inorg. Chem.*, 2000, **39**, 2397-2404.

[**L2**Zn(OTf)(H_2O)]OTf (**1b**)

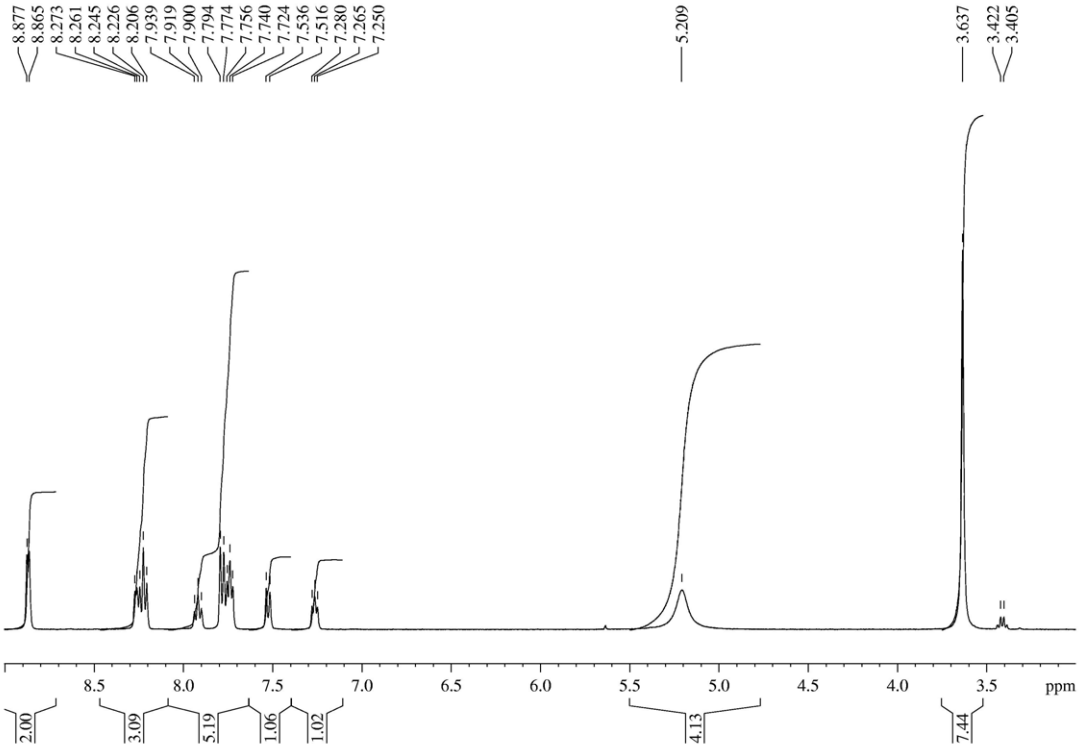


Fig. 10 SI Section of ^{1}H NMR spectrum of **1b** at 296 K in CD_6CO

[**Mebispic**$ZnCl_2$] (**2**)

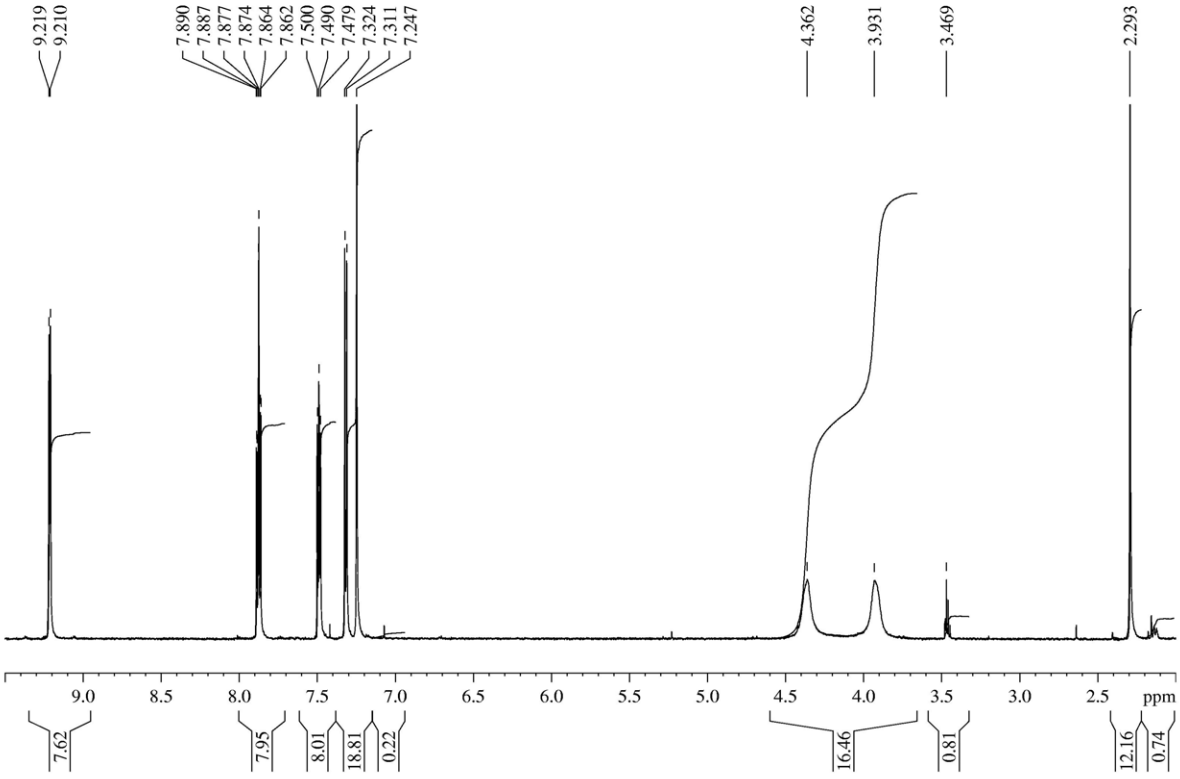


Fig. 11 SI Section of ^{1}H NMR spectrum of **2** at 295 K in $CDCl_3$

[**L1**$ZnCl_2$] (**3b**)

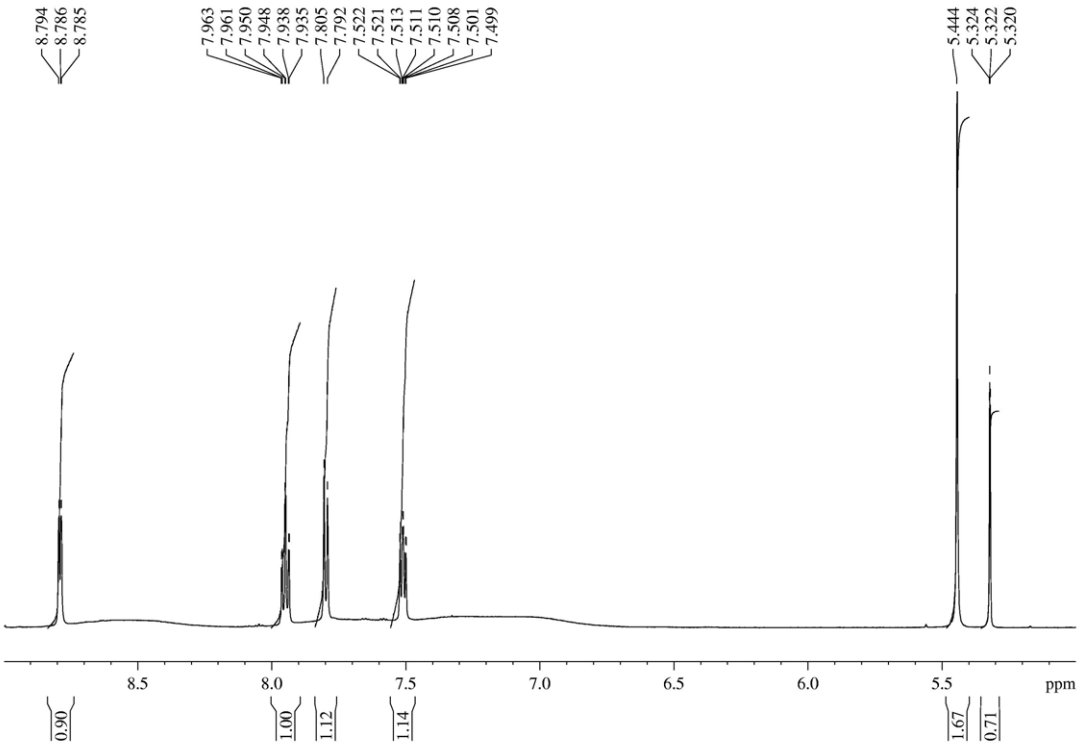


Fig. 12 SI Section of ^{1}H NMR spectrum of **3b** at 296 K in CD_2Cl_2

[(**L1**)$_2$Zn(MeOH)$_2$]OTf_2 (**3c**)

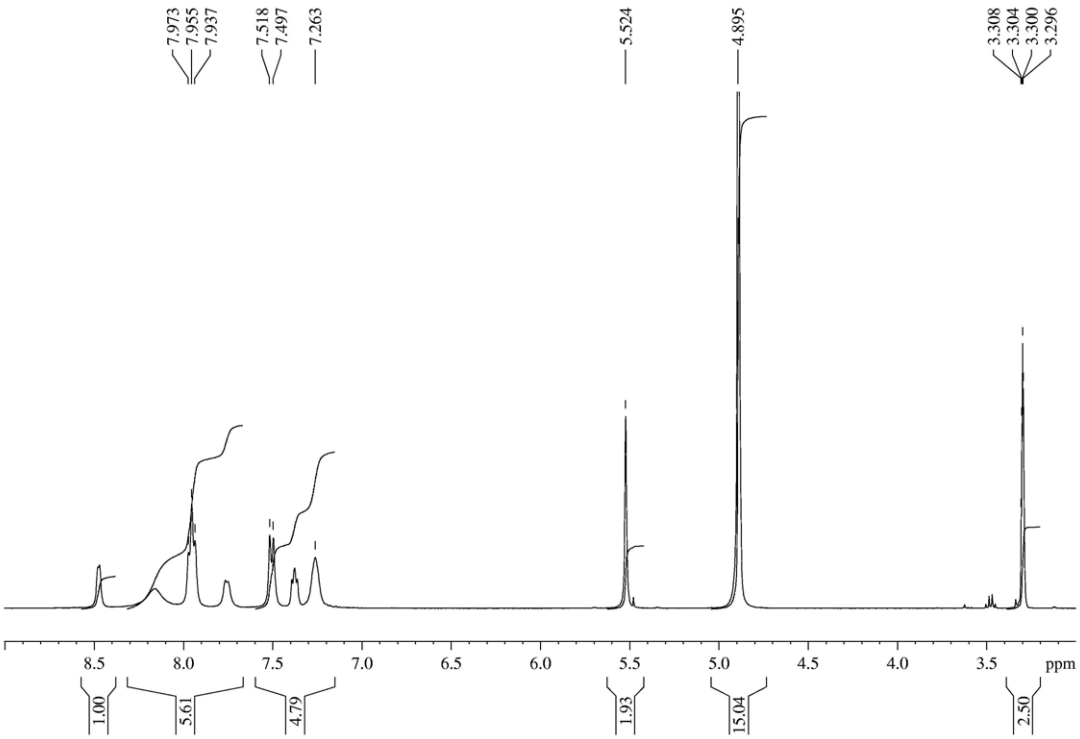


Fig. 13 SI Section of ^{1}H NMR spectrum of **3c** at 295 K in $CH_3OH + D_2O$

Mixture of **L1** and $Zn(OTf)_2$ (**3e**)

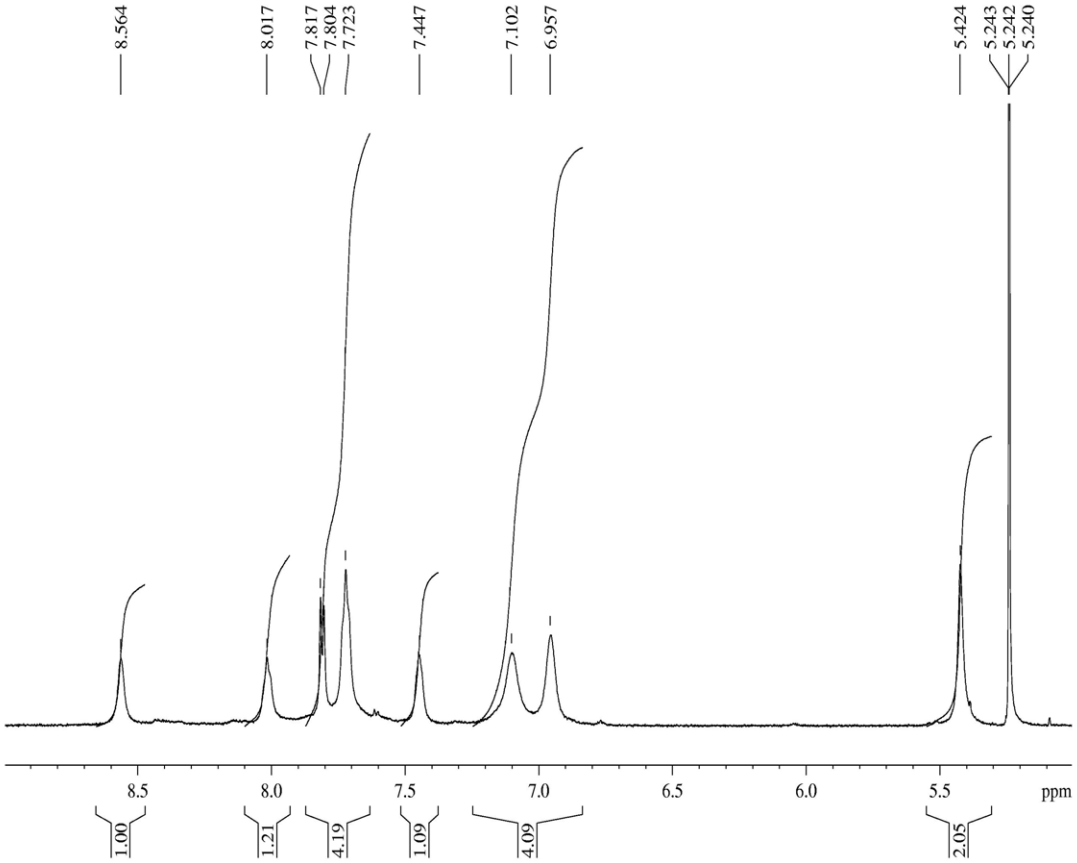


Fig. 14 SI Section of ^{1}H NMR spectrum of **3e** at 296 K in CD_2Cl_2

[**tpa**$ZnCl_2$]

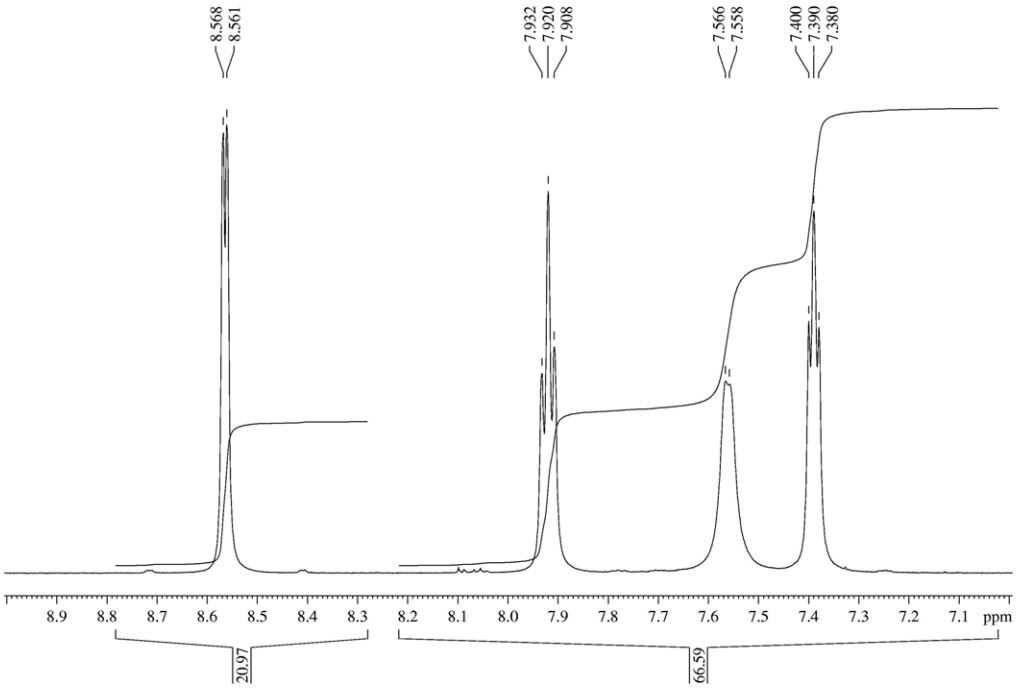


Fig. 15 SI Section of ^{1}H NMR spectrum of [**tpa**$ZnCl_2$] at 296 K in CD_2Cl_2

2.2 Variable Temperature ^{1}H NMR and 2D spectra

All spectra depicted in the following were measured in CD_2Cl_2 at 600 MHz using Brukers Avance III spectrometer if not mentioned otherwise.

[Mebispic$ZnCl_2$] (2)

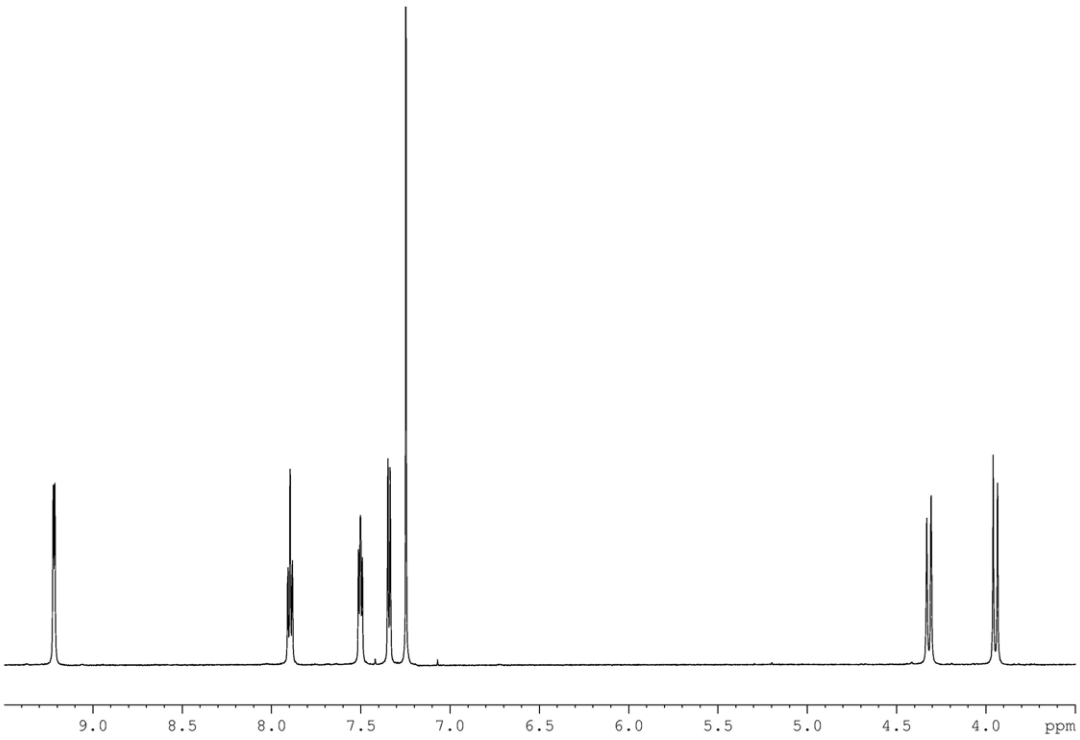
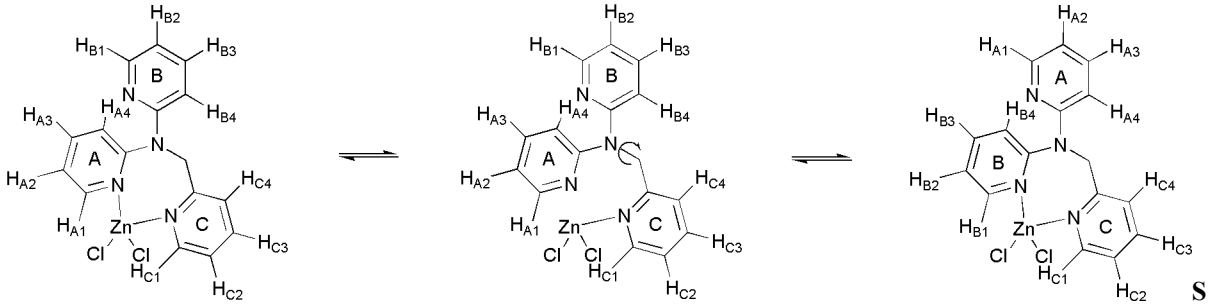


Fig. 16 SI Section of ^{1}H NMR spectrum of **2** at 260 K in $CDCl_3$

Unlike the ^{1}H NMR spectrum of **2** at ambient temperature in Figure 11, the spectrum at 260 K shows the resolved AB pattern of the diastereotope methylene protons (d, 4.32; d, 3.95).

[L1$ZnCl_2$] (3b)

Due to the unusual fluxional behaviour of 3b in solution that leads to the proposed rotation mechanism (Scheme 1), the assignment of protons in the NMR spectroscopy becomes difficult. With low temperature NMR measurements and 2D NMR spectroscopy, we are now able not only to clearly assign all protons to the according resonances but also prove the rotation mechanism by the exchange signals in the 2D-EXSY spectrum at 219 K.

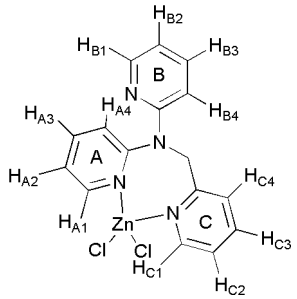


cheme 1 SI Proposed rotation mechanism of **3b** in solution

At this temperature the exchange of protons due to the rotation of the pyridyl rings labelled A and B is slow enough to follow by NMR spectroscopy. All expected exchange signals are visible in the depicted 2D-EXSY spectrum (Figure 20 SI), assignable and labelled with the number of the according proton in Scheme 1 SI.

Starting point of the assignment is the COSY signal of H_{C4} at δ = 7.84 ppm that shows 4J coupling to the methylene protons. Combining of COSY and 2D-EXSY signals finally leads to the assignment of ^{1}H NMR resonances to the full set of protons presented in the following

Table. Due to an overlap of the signals of H_{A3} and H_{C3} at δ = 7.95, 11 of the 12 expected resonances can be observed at 180 K.
In the ^{1}H NMR spectra at variable temperatures depicted in Figures 17 and 18, another interesting phenomenon can be detected. At 253 K, the signal for the methylene protons at a chemical shift of 5.36 starts to broaden and finally splits at 180 K. Two doublets indicate an AB system. Due to the lowered temperature, the two methylene protons become diastereotopic.



Scheme 2 SI ChemDraw representation of **3b** with H labelled A1 to C4

Proton assignment to ^{1}H signals of **3b** at 180 K

Proton No.	multiplicity	δ / ppm
H_{A1}	d	8.63
H_{A2}	t	7.41
H_{A3}	t	7.95
H_{A4}	d	7.52
H_{B1}	d	8.24
H_{B2}	t	6.84
H_{B3}	t	7.45
H_{B4}	d	6.88
H_{C1}	d	8.66
H_{C2}	t	7.50
H_{C3}	t	7.95
H_{C4}	d	7.86
methylene H	s	5.90; 4.74

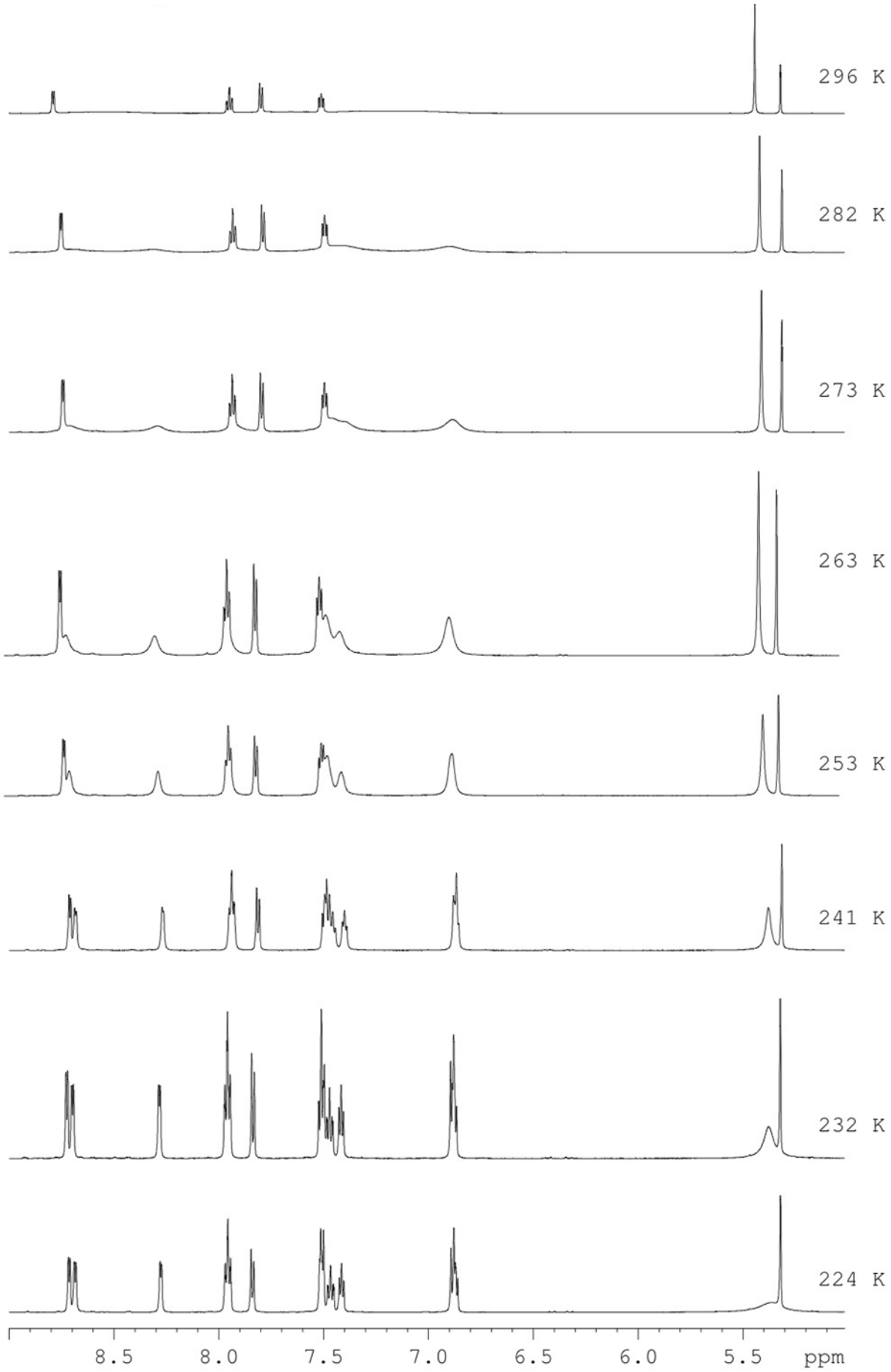


Fig. 17 SI Sections of ^{1}H NMR spectra of **3b** from 296 K to 224 K in CD_2Cl_2

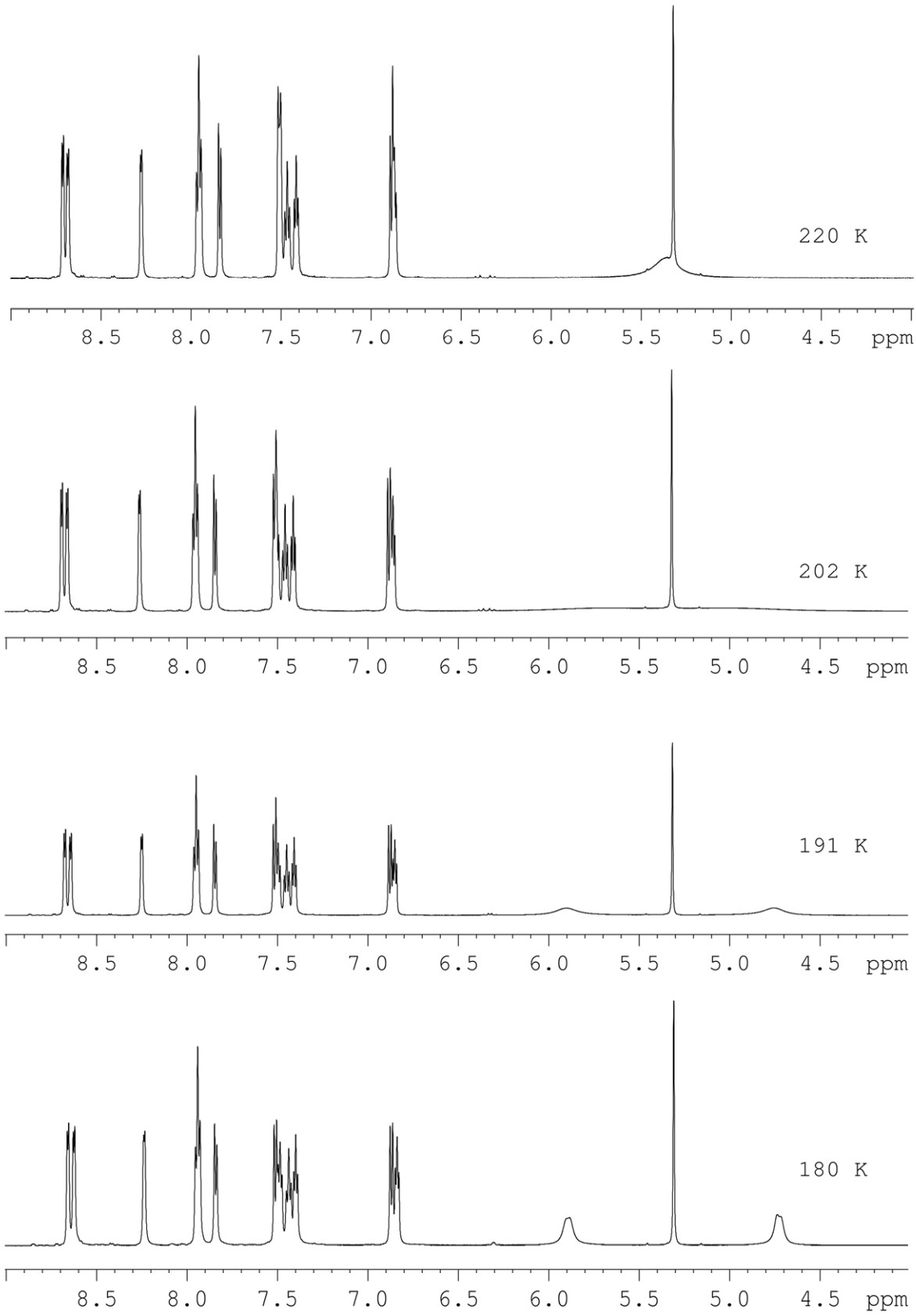


Fig. 18 SI Sections of ^{1}H NMR spectra of **3b** from 220K to 180 K in CD_2Cl_2

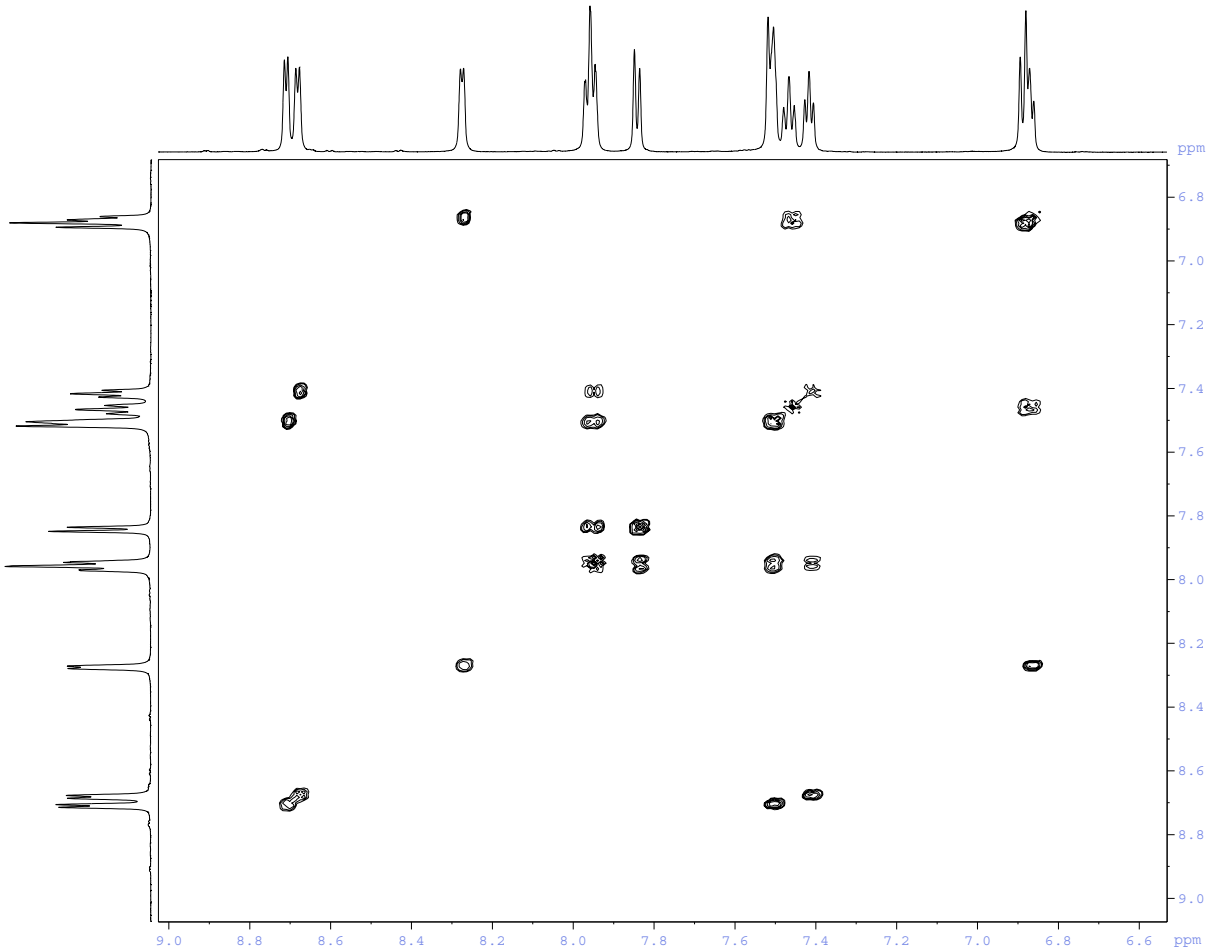


Fig. 19 SI Section of COSY spectrum of **3b** at 219 K in CD_2Cl_2

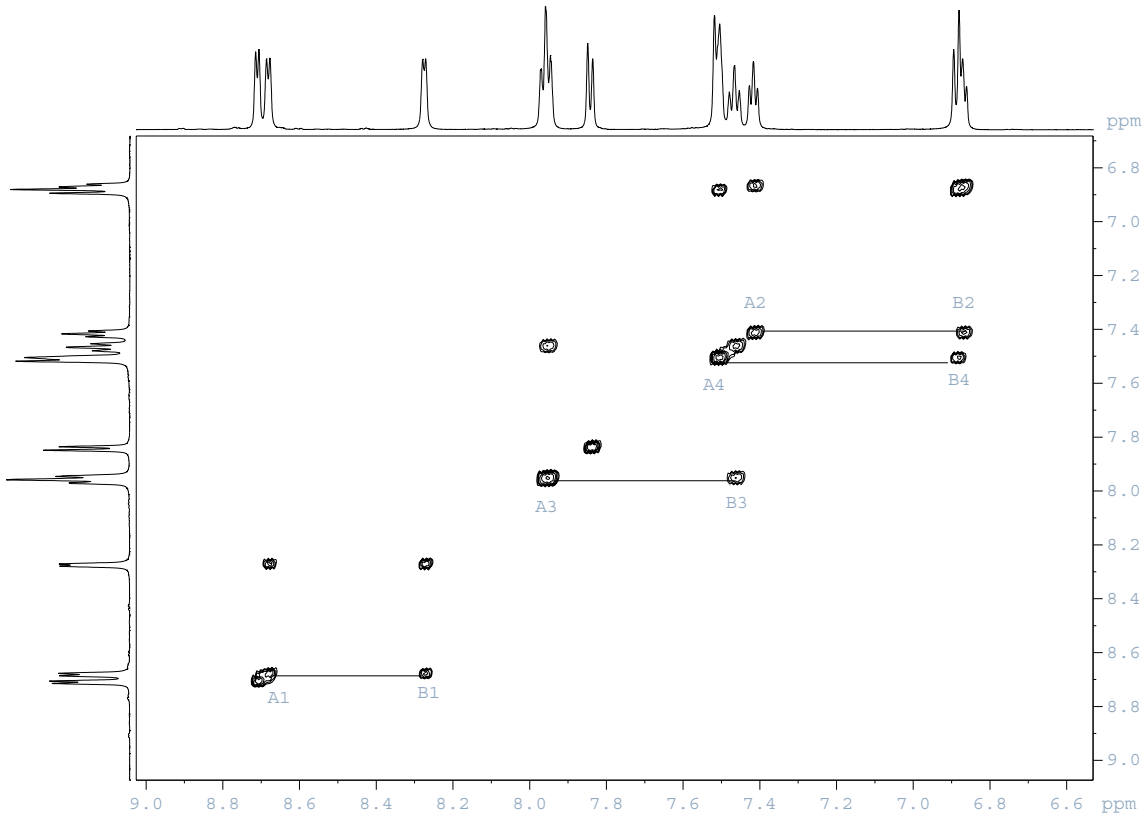
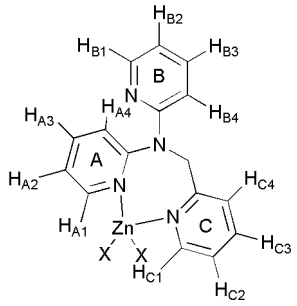


Fig. 20 SI Section of 2D-EXSY spectrum of **3b** at 219 K in CD_2Cl_2

Mixture of **L1** and $Zn(OTf)_2$ (**3e**)

Unlike the spectra of **3b,** the ^1H NMR spectra of **3e** in CD_2Cl_2 show no sign of diastereotopic protons at low temperatures. The proton resonances in the room temperature spectrum are broad and not clearly assignable. Lowering of the temperature leads to a shift of signals and additional signals sharpen. At 230 K, COSY (Figure 22) and 2D-EXSY (Figure 23 SI) spectra of **3e** point to an exchange mechanism as is shown for **3b** in Figures 19 and 20 . The exchange signals, that prove the proposed mechanism are labelled with the number of the according proton in Scheme 3. Again, all exchange signals are visible and an assignment of the full set of protons at 230 K is possible. Starting point of the assignment the proton C4, close to the methylene protons. The chemical shifts and multiplicity of the signals are reported in the following Table.
Further decrease of temperature to 213 K clearly shows a broad underlying signal at 7.66 (most likely assignable as coordinated water) that disappears again at 186 K. The 2D-EXSY spectrum (Figure 25 SI) at 213 K shows additional exchange signals indicating of a second dynamic process. Therefore, we unfortunately have not been able to clearly state the coordination mode so far. Additional experiments to prove the coordination mode of the complex **3e** are in progress.



Scheme 3 SI ChemDraw representation of **3e** with H-atoms labelled A1 to C4

Proton assignment to ^1H signals of **3e** at 213 K

Proton No.	multiplicity	δ / ppm
H_{A1}	d	8.04
H_{A2}	t	7.12
H_{A3}	t	7.85
H_{A4}	d	7.31
H_{B1}	d	7.31
H_{B2}	t	6.85
H_{B3}	t	7.79
H_{B4}	d	7.37
H_{C1}	d	8.35
H_{C2}	t	7.22
H_{C3}	t	7.79
H_{C4}	d	7.59
methylene H	s	4.49

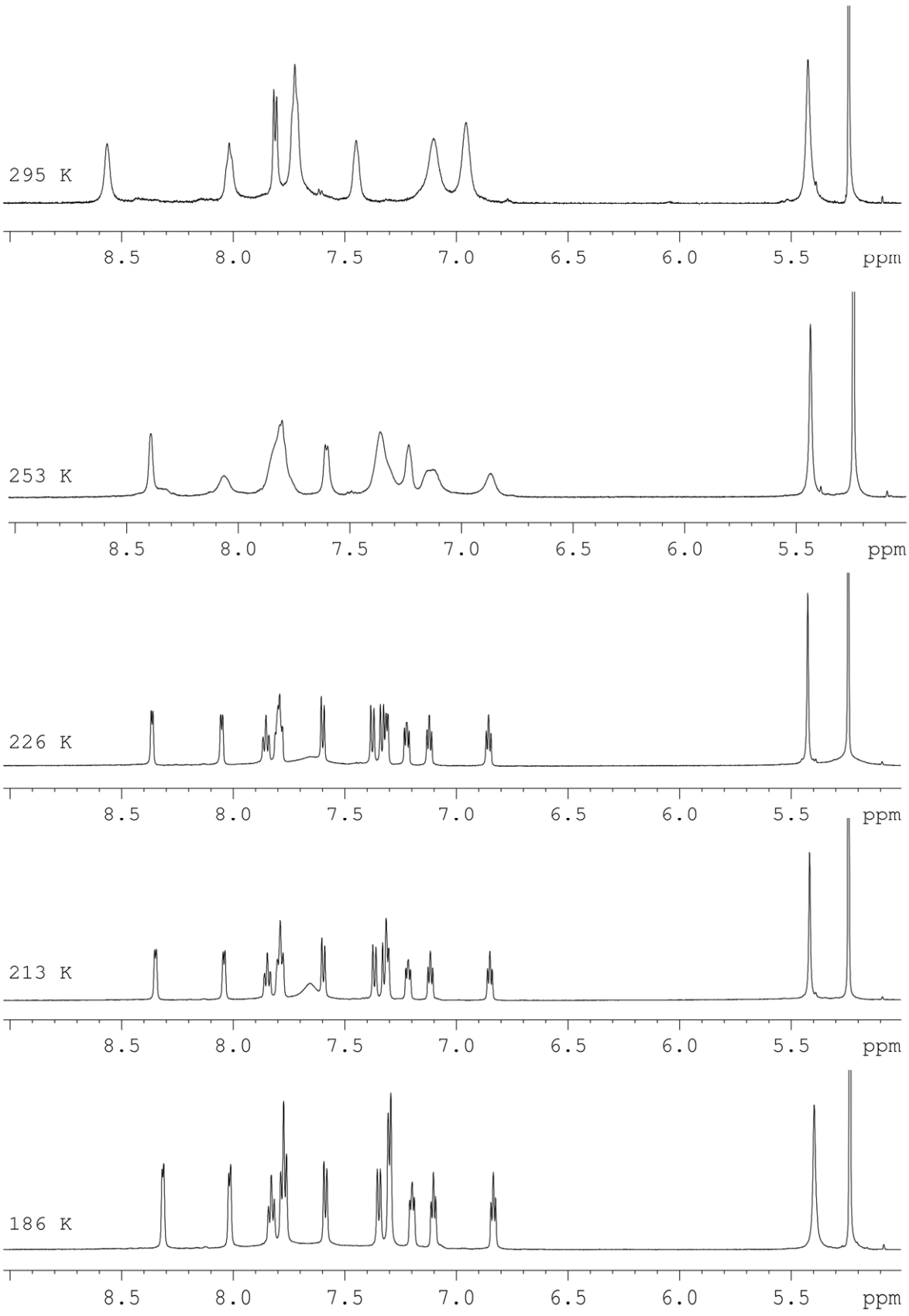


Fig. 21 SI Sections of ^{1}H NMR spectra of **3e** in CD_2Cl_2 at variable temperature

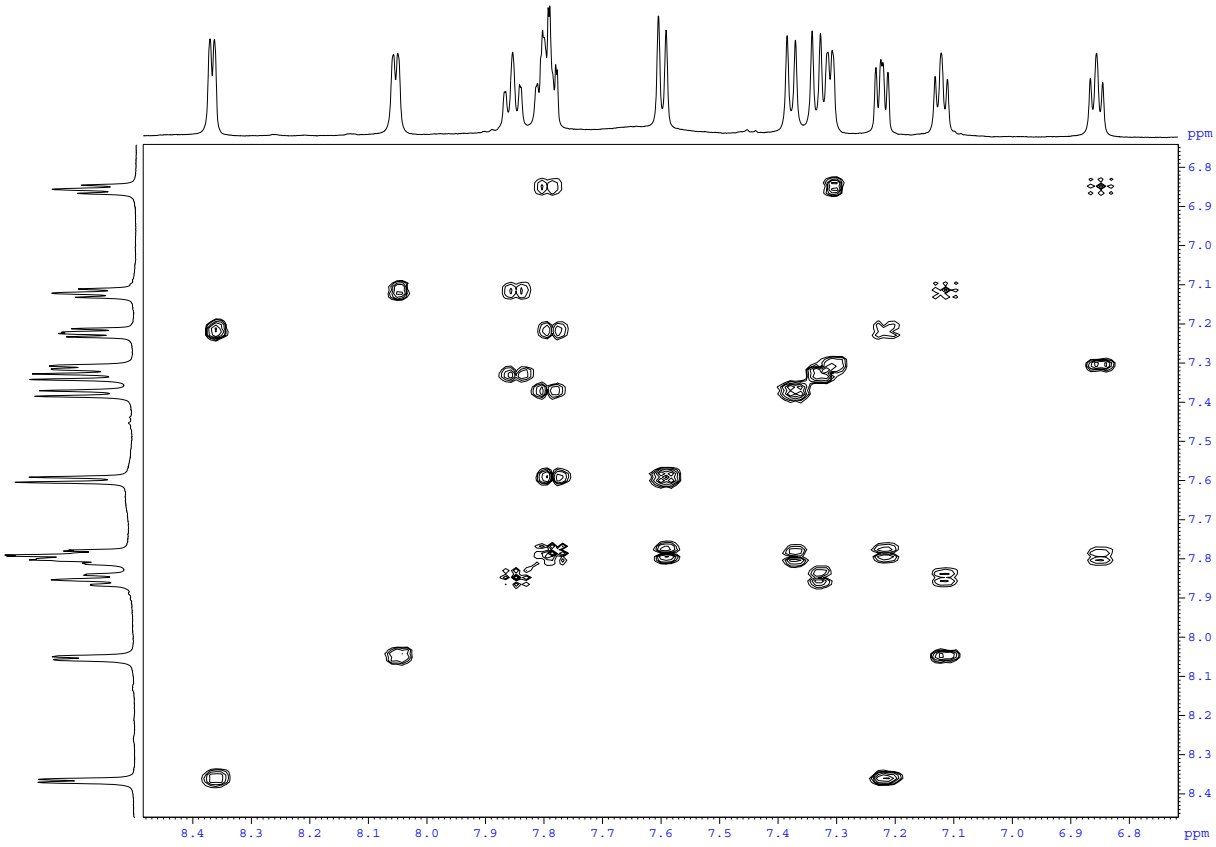


Fig. 22 SI Section of COSY spectrum of **3e** at 230 K in CD_2Cl_2

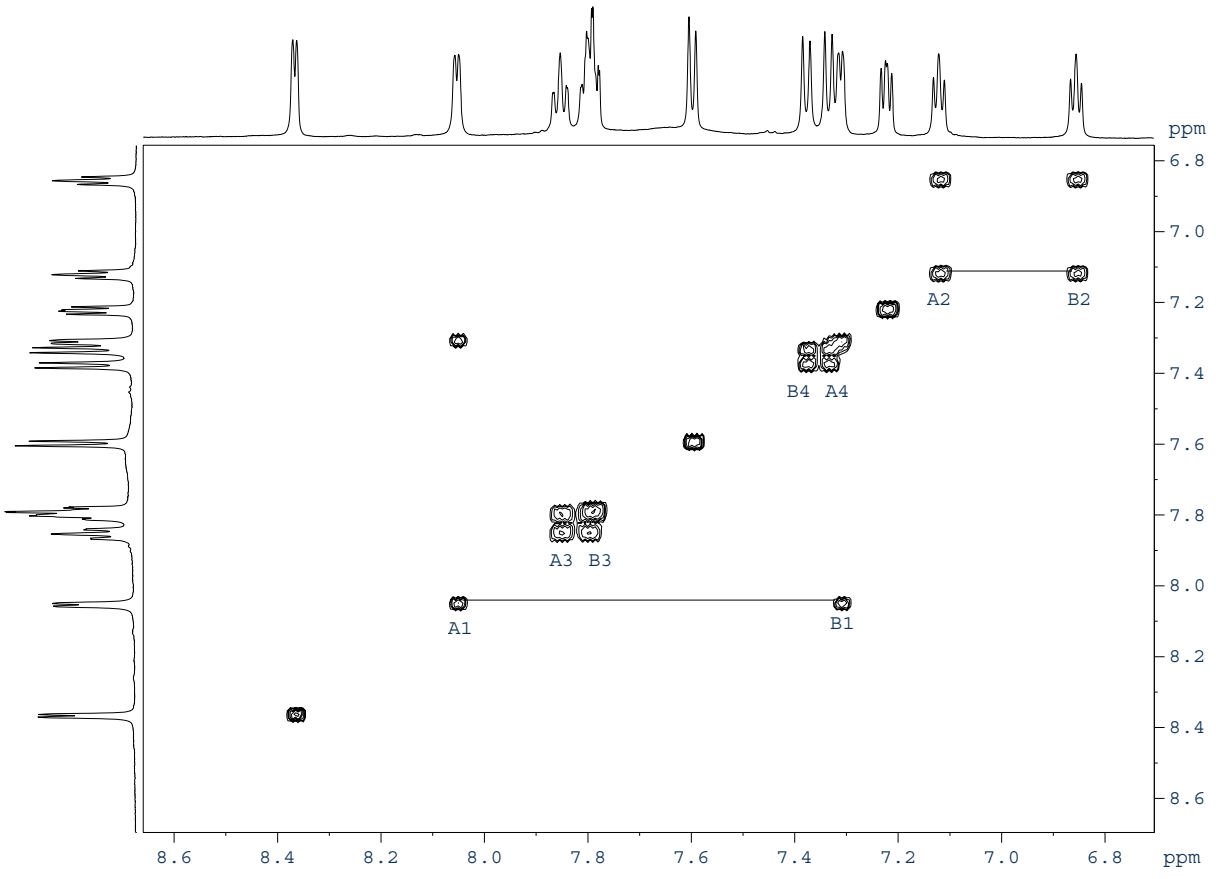


Fig. 23 SI Section of 2D-EXSY spectrum of **3e** at 230 K in CD_2Cl_2

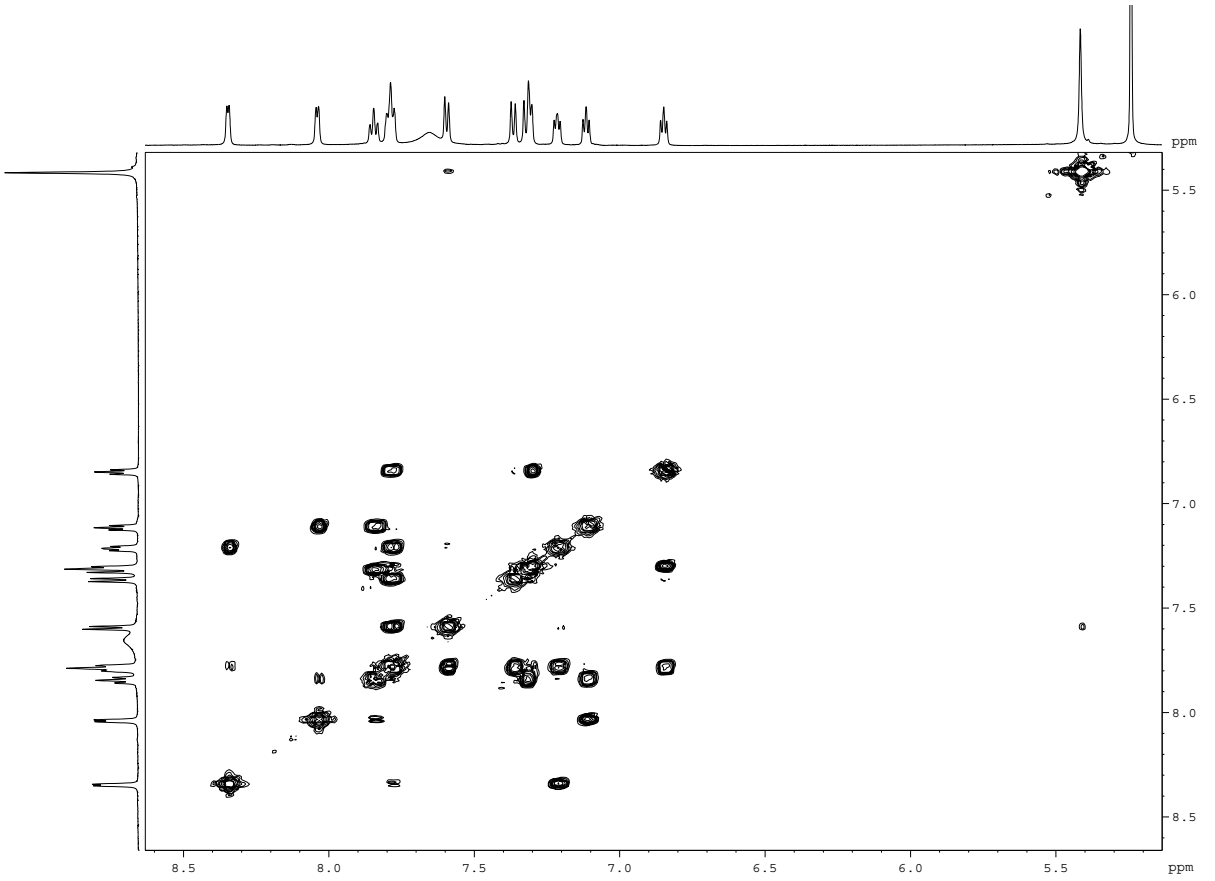


Fig. 24 SI Section of COSY spectrum of **3e** at 213 K in CD_2Cl_2

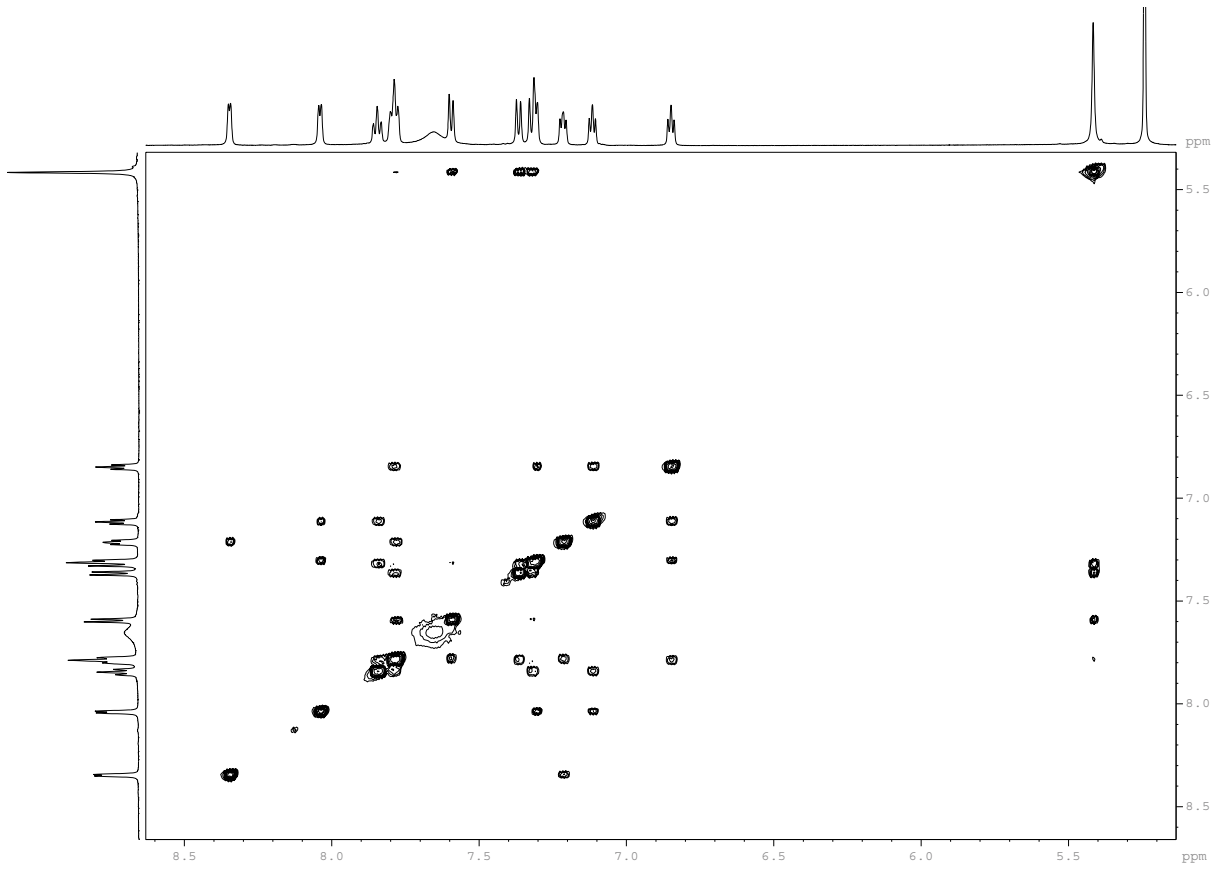
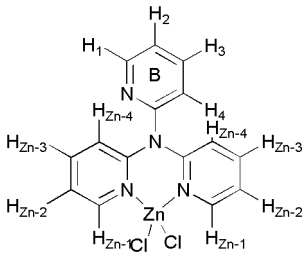


Fig. 25 SI Section of 2D-EXSY spectrum of **3e** at 213 K in CD_2Cl_2

[**tpa**$ZnCl_2$]

This complex has already been reported by Wang and coworkers.[3] A complete interpretation of the NMR data has not been possible so far. However, we are now able to clearly assign the full set of protons and prove the proposed exchange mechanism by the exchange signals occurring in the depicted 2D-EXSY spectrum at 186 K (Figure 28). Again, all expected resonances are detectable and assignable. They are labelled with the number of the according proton in Scheme 4. Like **3b** the ^{1}H NMR spectrum at ambient temperature of [**tpa**$ZnCl_2$] only shows the signals of the uncoordinated pyridyl residue indicating the rotation mechanism already published.[3] The COSY spectrum depicted in Figure 27 SI proves the expected 3 ABCD spin systems of the different pyridyl rings.



Scheme 4 SI Representation of [**tpa**$ZnCl_2$]

Proton assignment to ^{1}H signals of [**tpa**$ZnCl_2$] at 186 K

Proton No.	multiplicity	δ / ppm
H_{A1}	d	8.60
H_{A2}	t	7.57
H_{A3}	t	8.11
H_{A4}	d	7.85
H_{B1}	d	8.18
H_{B2}	t	7.02
H_{B3}	t	7.65
H_{B4}	d	6.83

[3] W. Y. Yang, H. Schmider, Q. G. Wu, Y. S. Zhang and S. N. Wang, *Inorg. Chem.*, 2000, **39**, 2397-2404.

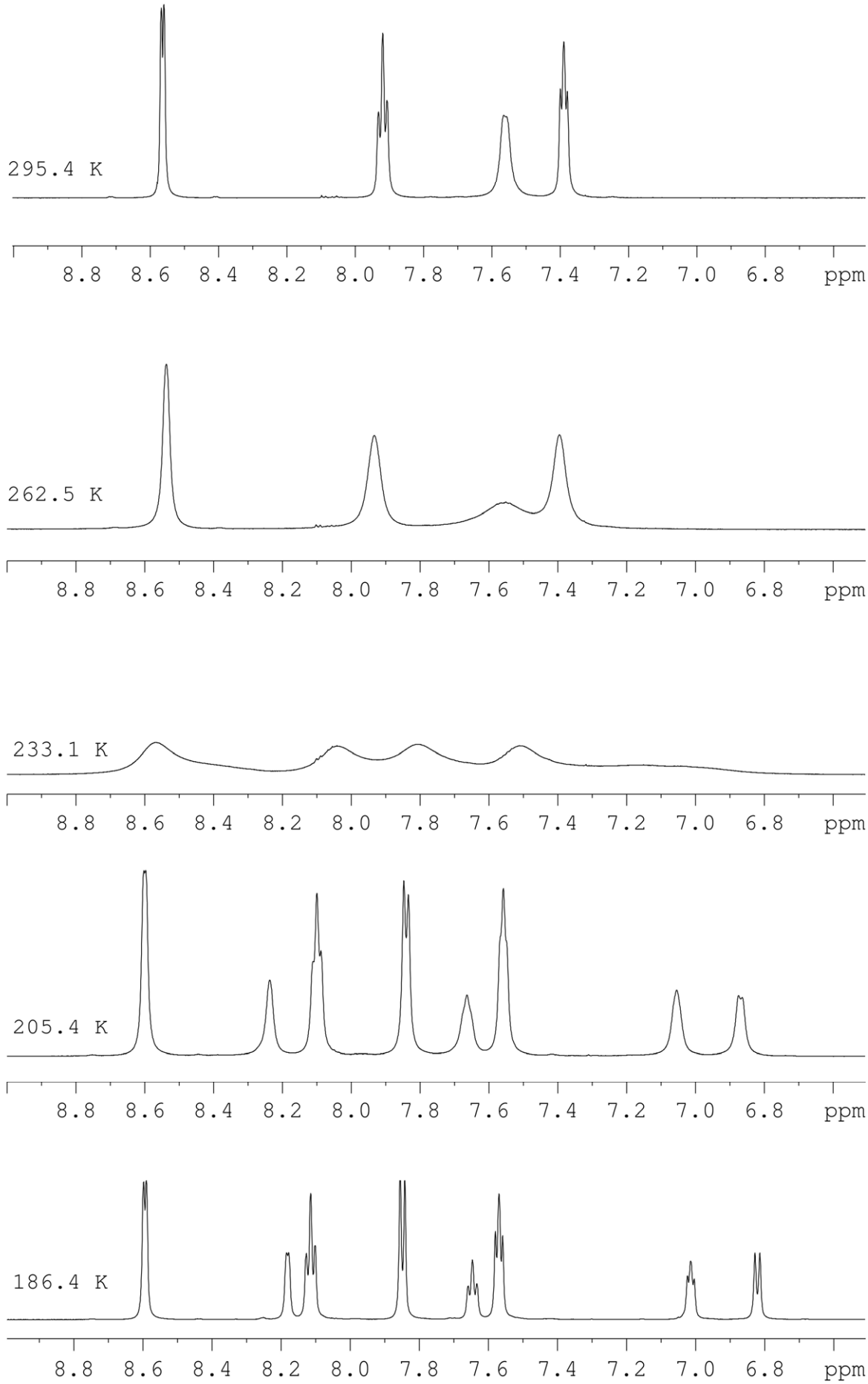


Fig. 26 SI Sections of ^{1}H NMR spectra of [**tpa**$ZnCl_2$] in CD_2Cl_2 at variable temperature

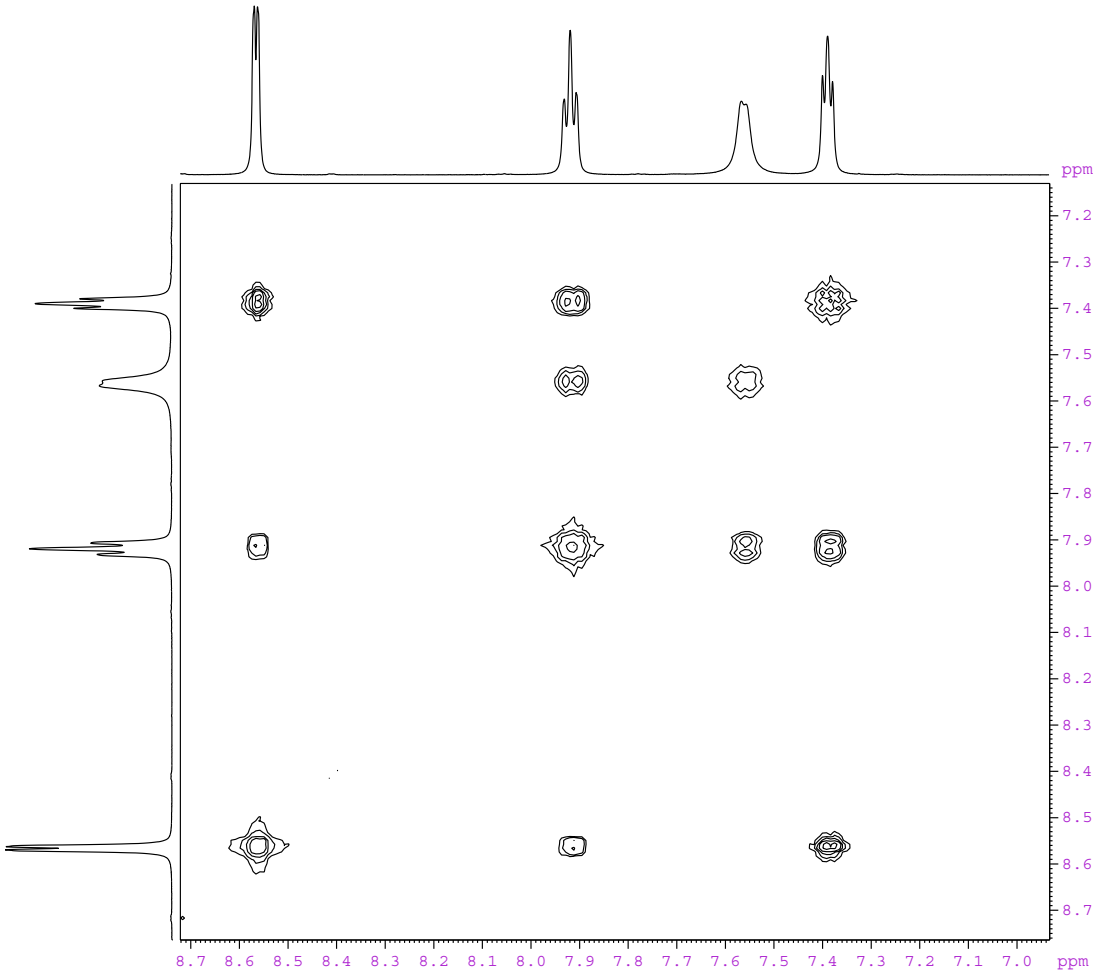


Fig. 27 SI Section of the COSY spectrum of [**tpa**$ZnCl_2$] at 296 K in CD_2Cl_2

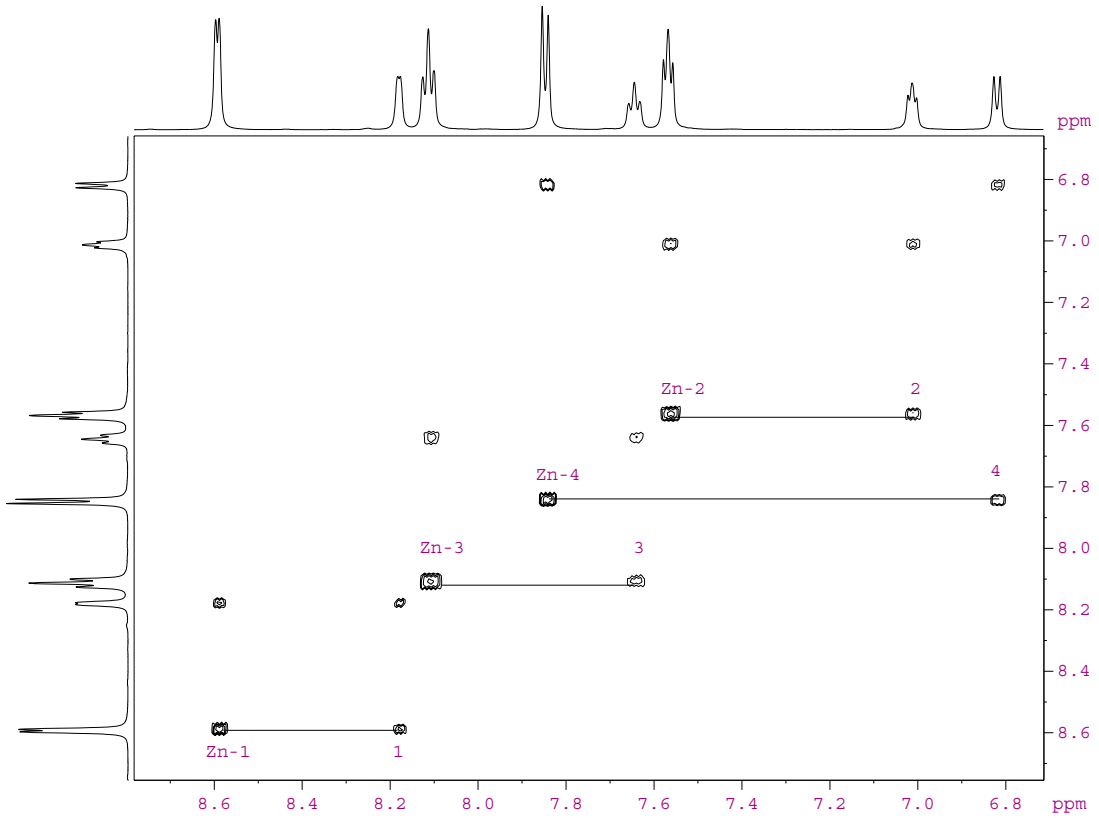


Fig. 28 SI Section of the 2D-EXSY spectrum of [**tpa**$ZnCl_2$] at 186 K in CD_2Cl_2