Supporting information
for

3-amino-1-propanol and *N*-methylaminoethanol: coordination to zinc(II) *vs*. decomposition to ammonia?

Nina Podjed,[a,*] Petra Stare,[a] Romana Cerc Korošec,[a] María M. Alcaide,[b] Joaquín López-Serrano[b] and Barbara Modec[a,*]

[a] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113 1000 Ljubljana, Slovenia

[b] Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Avenida Américo Vespucio 49, 41092 Sevilla, Spain

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* Corresponding authors. E-mail: nina.podjed@fkkt.uni-lj.si; barbara.modec@fkkt.uni-lj.si

1. Crystal structures

Table S1. Bond lengths and angles in [Zn(quin)$_2$(NH$_3$)] (**1**).

Coordination bonds [Å]	
Zn1−O1	2.0039(13)
Zn1−O2	1.9949(13)
Zn1−N1	2.1593(15)
Zn1−N2	2.1599(16)
Zn1−N3	2.0281(19)
Angles [°]	
O1–Zn1–N1	79.44(6)
O1–Zn1–N2	91.82(6)
O1–Zn1–N3	118.50(7)
O2–Zn1–O1	125.45(6)
O2–Zn1–N1	94.15(6)
O2–Zn1–N2	79.49(6)
O2–Zn1–N3	115.99(7)
N1–Zn1–N2	163.54(6)
N3–Zn1–N1	94.53(7)
N3–Zn1–N2	101.91(7)
Carboxylate bonds [Å]	
C19−O1	1.275(2)
C19−O11	1.227(2)
C29−O2	1.273(2)
C29−O22	1.231(2)

Table S2. Bond lengths and angles in $[Zn(quin)_2(3\text{-apOH})]\cdot CH_3CN$ (**2a**), $[Zn(quin)_2(3\text{-apOH})]\cdot EtOH$ (**2b**), $[Zn(quin)_2(3\text{-apOH})]\cdot 2\text{-PrOH}$ (**2c**) and $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

	2a	**2b**	**2c**	**2d**
Coordination bonds [Å]				
Zn1−O1	1.9935(14)	2.0028(12)	1.9928(12)	1.984(3)
Zn1−O2	2.0149(13)	2.0150(12)	2.0137(12)	2.004(3)
Zn1−N1	2.1695(16)	2.1808(14)	2.1921(13)	2.150(3)
Zn1−N2	2.1785(15)	2.1834(14)	2.1882(13)	2.193(3)
Zn1−N3	2.0445(17)	2.0433(14)	2.0438(14)	2.028(4)
Angles [°]				
O1–Zn1–O2	128.35(6)	133.48(5)	131.42(5)	124.85(13)
O1–Zn1–N1	79.77(6)	79.52(5)	79.30(5)	79.84(12)
O1–Zn1–N2	89.64(6)	92.56(5)	92.32(5)	93.48(12)
O1–Zn1–N3	116.44(7)	110.67(6)	111.66(6)	121.36(15)
O2–Zn1–N1	95.24(6)	93.29(5)	93.60(5)	92.01(12)
O2–Zn1–N2	78.79(6)	78.68(5)	78.87(5)	78.68(12)
O2–Zn1–N3	115.16(7)	115.85(5)	116.91(5)	113.74(14)
N1–Zn1–N2	160.85(6)	159.87(5)	160.72(5)	162.73(14)
N3–Zn1–N1	98.19(6)	98.73(5)	97.40(5)	101.69(15)
N3–Zn1–N2	100.81(6)	101.39(5)	101.83(5)	95.39(15)
Carboxylate bonds [Å]				
C19−O1	1.278(2)	1.274(2)	1.274(2)	1.276(5)
C19−O11	1.225(3)	1.234(2)	1.234(2)	1.231(5)
C29−O2	1.267(2)	1.264(2)	1.266(2)	1.264(5)
C29−O22	1.236(2)	1.239(2)	1.244(2)	1.250(5)

Table S3. Parameters of the overlay procedure for pairs of [Zn(quin)$_2$(3-apOH)] compounds.[a]

Pair of compounds	RMSD[b]	Max. distance[c]
2a and **2b**	0.2156	0.5767
2a and **2c**	0.1682	0.4325
2a and **2d**	0.1757	0.4261
2b and **2c**	0.0821	0.1836
2b and **2d**	0.3059	0.7806
2c and **2d**	0.2348	0.6338

[a] Overlay was done by Mercury.[1]

[b] Root-mean-square deviation.

[c] Maximum distance between two equivalent atoms in the overlaid molecules.

[1] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.

Table S4. Bond lengths and angles in [Zn(quin)$_2$(*N*-maeOH)] (**3**).

Coordination bonds [Å]	
Zn1−O1	2.0269(16)
Zn1−O2	2.425(4)
Zn1−N1	2.234(2)
Zn1−N2	2.036(4)
Angles [°]	
N1[a]–Zn1–N1	106.17(11)
N1–Zn1–O2	74.44(10)
N1[a]–Zn1–O2	164.12(10)
O1–Zn1–N1	77.95(8)
O1–Zn1–N1[a]	99.37(8)
O1[a]–Zn1–N1	99.37(8)
O1[a]–Zn1–N1[a]	77.95(8)
O1[a]–Zn1–O1	175.62(11)
O1[a]–Zn1–N2	90.71(11)
O1–Zn1–N2	93.34(11)
O1[a]–Zn1–O2	86.26(11)
O1–Zn1–O2	96.28(11)
N2–Zn1–N1[a]	104.73(13)
N2–Zn1–N1	148.85(13)
N2–Zn1–O2	76.93(15)
Carboxylate bonds [Å]	
C19−O1	1.256(3)
C19−O11	1.237(3)

[a] Related through symmetry: 1–*x*, *y*, 1.5–*z*.

2. Intermolecular interactions

Figure S1. Hydrogen bonding pattern in $[Zn(quin)_2(NH_3)]$ (**1**): section of a layer, as viewed along *c*-axis.

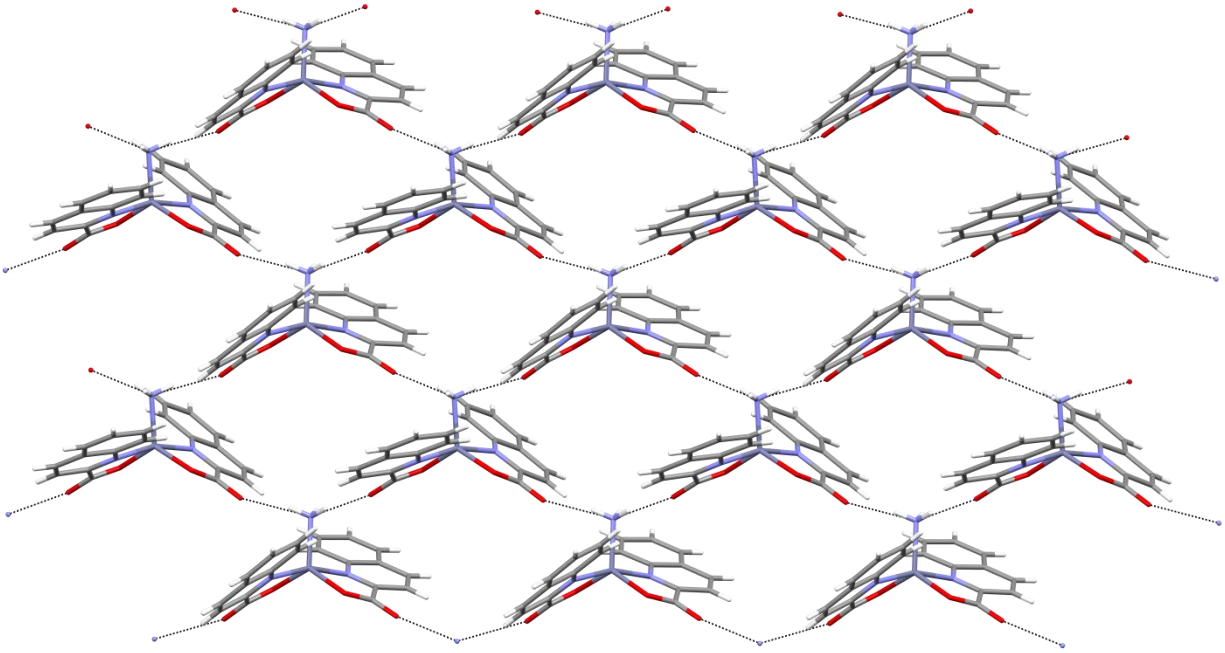


Figure S2. Depiction of channels that run along *a*-axis in $[Zn(quin)_2(3\text{-apOH})]\cdot CH_3CN$ (**2a**). Solvent molecules of acetonitrile, located in these channels, are not drawn.

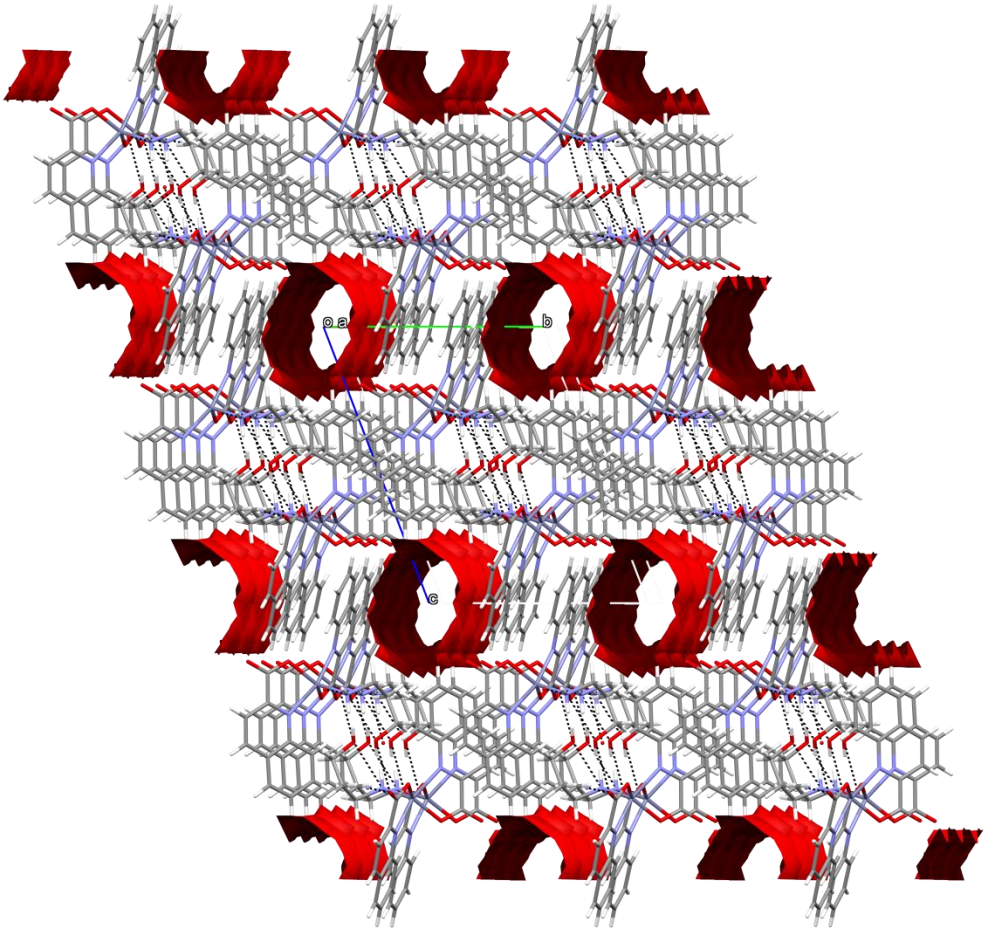
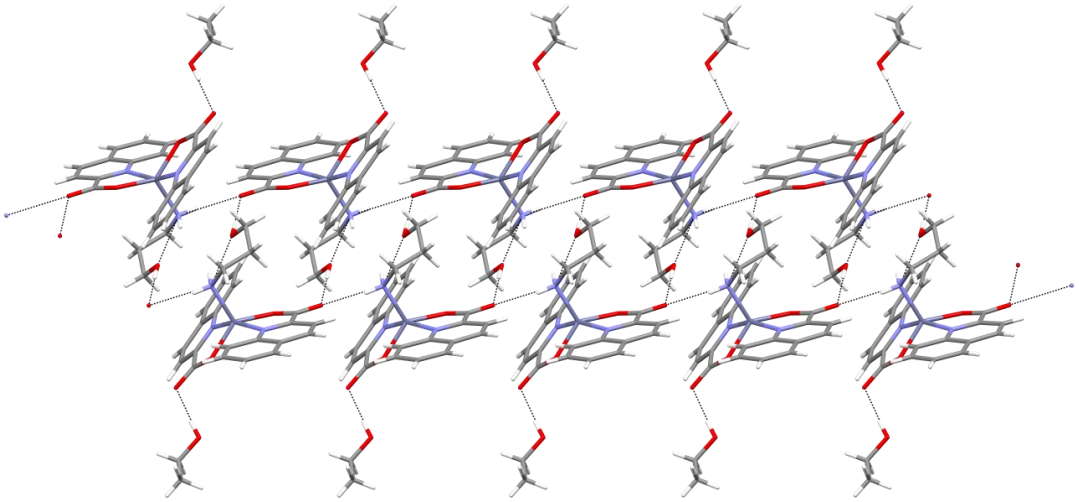


Figure S3. Hydrogen bonding pattern in [Zn(quin)$_2$(3-apOH)]·EtOH (**2b**): (i) a chain with appended ethanol molecules, (ii) a view along channels filled with ethanol solvent molecules. Colour code: complex molecules are light grey, ethanol molecules are coloured orange.

(i)



(ii)

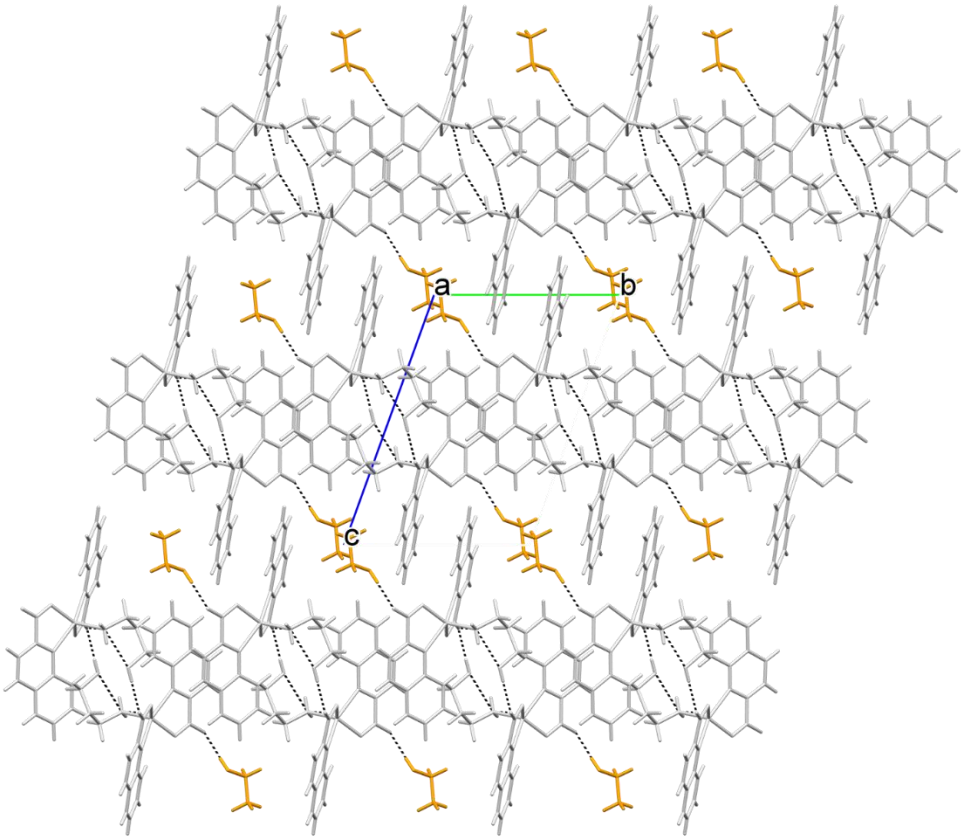
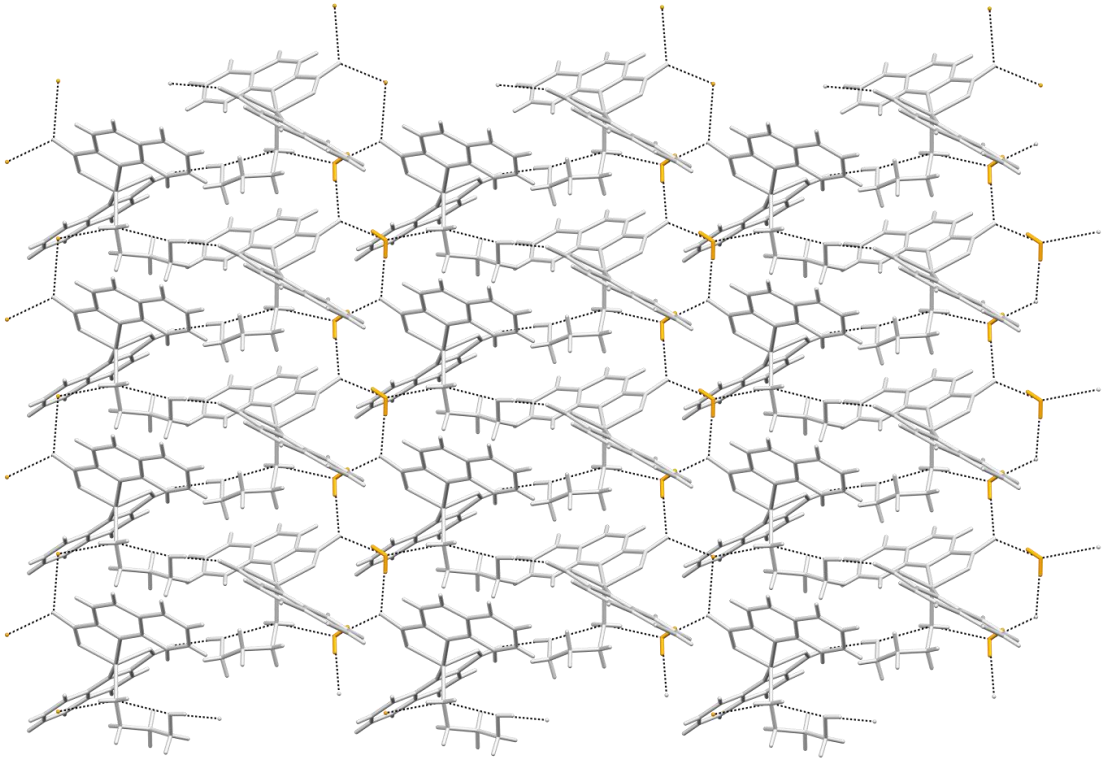


Figure S4. Hydrogen bonding pattern in $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**): (i) a layer of H-bonded water and complex molecules viewed along *c*-axis, (ii) a view along the layer. Colour code: complex molecules are light grey, water molecules are coloured orange.

(i)



(ii)

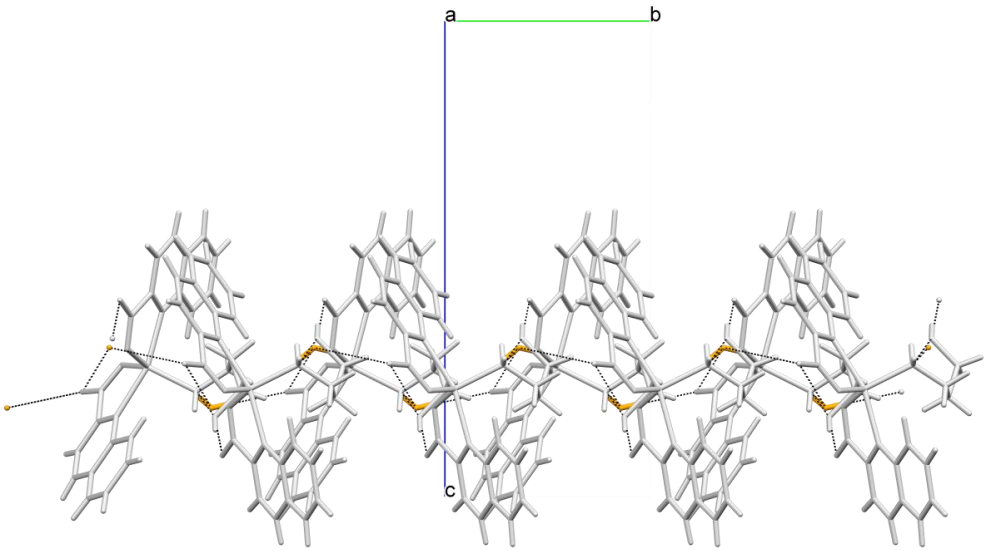
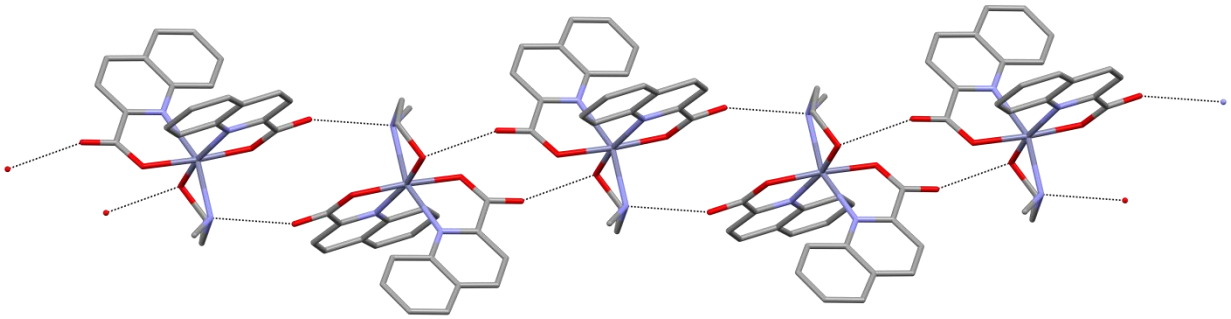


Figure S5. Hydrogen bonding pattern in *cis*-[Zn(quin)$_2$(*N*-maeOH)] (**3**). Hydrogen atoms are omitted for clarity.



3. Lists of $\pi\cdots\pi$ interactions

For compounds **1**–**2d**, *Cg*(3) is defined as a centroid of a pyridine part of one quinaldinate [N1, C10, C15, C16, C17 and C18], and *Cg(*4) as a centroid of a pyridine part of another quinaldinate [N2, C20, C25, C26, C27 and C28]. *Cg*(5) and *Cg*(6) pertain to centroids of the corresponding arene parts of quinaldinates, *i.e.*, C10, C11, C12, C13, C14 and C15, and C20, C21, C22, C23, C24 and C25, respectively. For compound **3**, *Cg*(2) is a centroid of an arene part of quinaldinate. *Cg*···*Cg* is a distance between ring centroids, dihedral angle is an angle between planes of two rings and slippage is a distance between centroid of one ring and perpendicular projection of centroid of the second ring to the first one.[2] Only interactions that have *Cg*···*Cg* distances shorter than 4 Å are given.

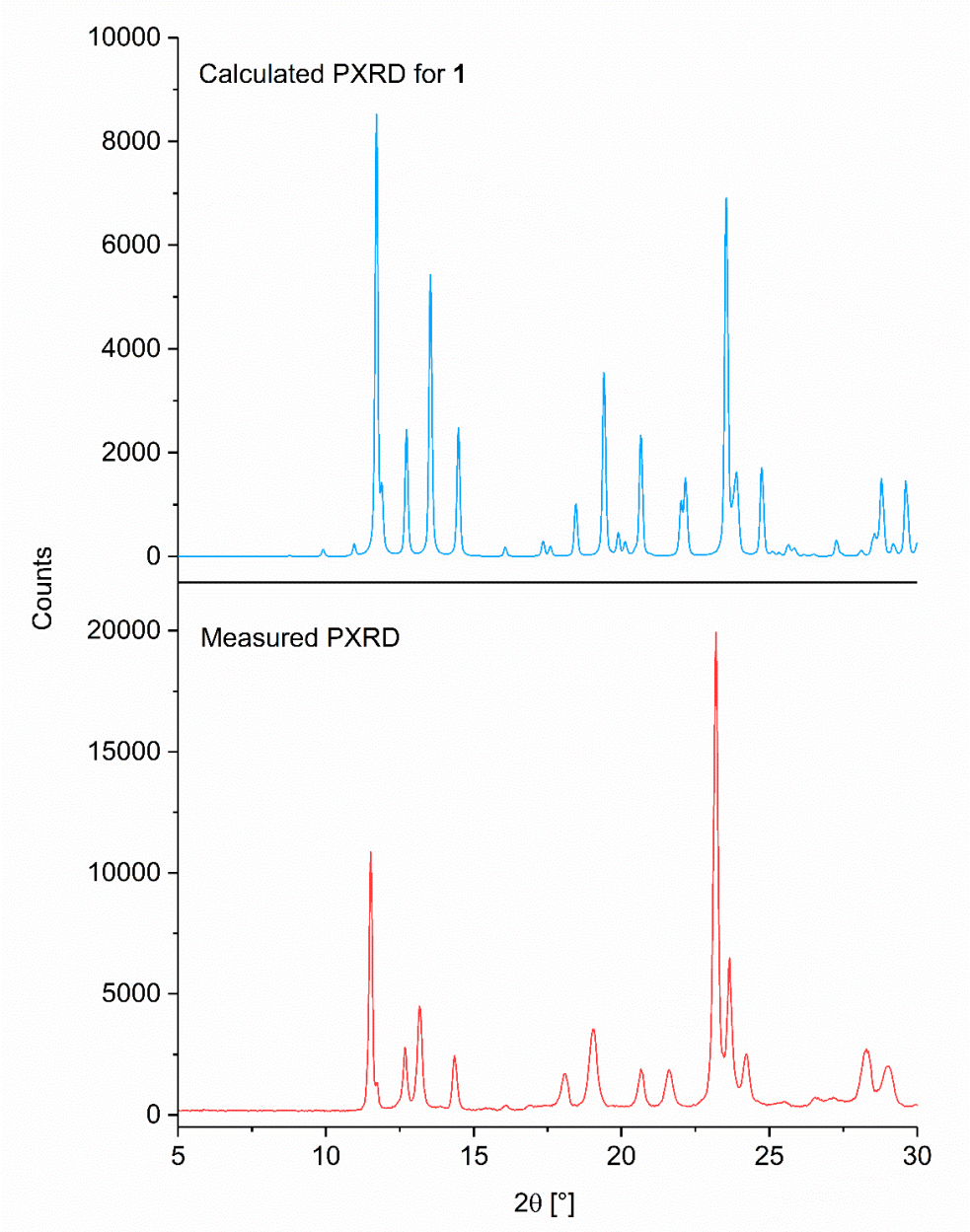
Table S5. $\pi\cdots\pi$ interactions in **1**–**3**.

$\pi\cdots\pi$ interactions	type	*Cg*···*Cg* [Å]	Dihedral angle [°]	Slippage [Å]
1				
Cg(3)···*Cg*(5) [1–*x*, 1–*y*, 1–*z*]	pyridine···arene	3.7657(11)	0.41(9)	1.172
Cg(4)···*Cg*(4) [1–*x*, 1–*y*, –*z*]	pyridine···pyridine	3.9904(11)	0.02(9)	2.055
Cg(4)···*Cg*(6) [1–*x*, 1–*y*, –*z*]	pyridine···arene	3.6020(11)	1.31(9)	1.042
2a				
Cg(3)···*Cg*(3) [1–*x*, –*y*, 1–*z*]	pyridine···pyridine	3.6781(12)	0.00(10)	1.426
Cg(3)···*Cg*(5) [1–*x*, –*y*, 1–*z*]	pyridine···arene	3.6181(13)	1.13(10)	1.236
Cg(4)···*Cg*(6) [1–*x*, 1–*y*, –*z*]	pyridine···arene	3.6099(13)	1.06(11)	0.230
2b				
Cg(3)···*Cg*(3) [1–*x*, 1–*y*, 1–*z*]	pyridine···pyridine	3.5880(11)	0.00(9)	1.145
Cg(3)···*Cg*(5) [1–*x*, 1–*y*, 1–*z*]	pyridine···arene	3.7120(12)	2.25(9)	1.425
Cg(4)···*Cg*(6) [1–*x*, 1–*y*, –*z*]	pyridine···arene	3.5863(11)	1.12(9)	0.926
Cg(6)···*Cg*(6) [1–*x*, 1–*y*, –*z*]	arene···arene	3.8764(12)	0.00(10)	1.768
2c				
Cg(3)···*Cg*(3) [1–*x*, 2–*y*, 1–*z*]	pyridine···pyridine	3.6562(10)	0.02(8)	1.296
Cg(3)···*Cg*(5) [1–*x*, 2–*y*, 1–*z*]	pyridine···arene	3.6810(11)	1.78(9)	1.323
Cg(4)···*Cg*(6) [1–*x*, 1–*y*, 2–*z*]	pyridine···arene	3.5409(10)	0.83(8)	1.083
Cg(6)···*Cg*(6) [1–*x*, 1–*y*, 2–*z*]	arene···arene	3.9271(11)	0.00(9)	2.048
2d				
Cg(3)···*Cg*(3) [1–*x*, 1–*y*, 1–*z*]	pyridine···pyridine	3.573(3)	0.0(2)	1.347
Cg(3)···*Cg*(5) [1–*x*, 1–*y*, 1–*z*]	pyridine···arene	3.568(3)	1.6(2)	1.271
Cg(4)···*Cg*(6) [1–*x*, 1–*y*, 2–*z*]	pyridine···arene	3.931(3)	1.4(2)	1.936
Cg(5)···*Cg*(5) [1–*x*, 2–*y*, 1–*z*]	arene···arene	3.786(3)	0.0(2)	1.701
Cg(6)···*Cg*(6) [1–*x*, 1–*y*, 2–*z*]	arene···arene	3.617(3)	0.0(2)	1.091
3				
Cg(2)···*Cg*(2) [0.5–*x*, 1.5–*y*, 1–*z*]	arene···arene	3.9056(18)	0.02(16)	1.697

[2] C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885-3896.

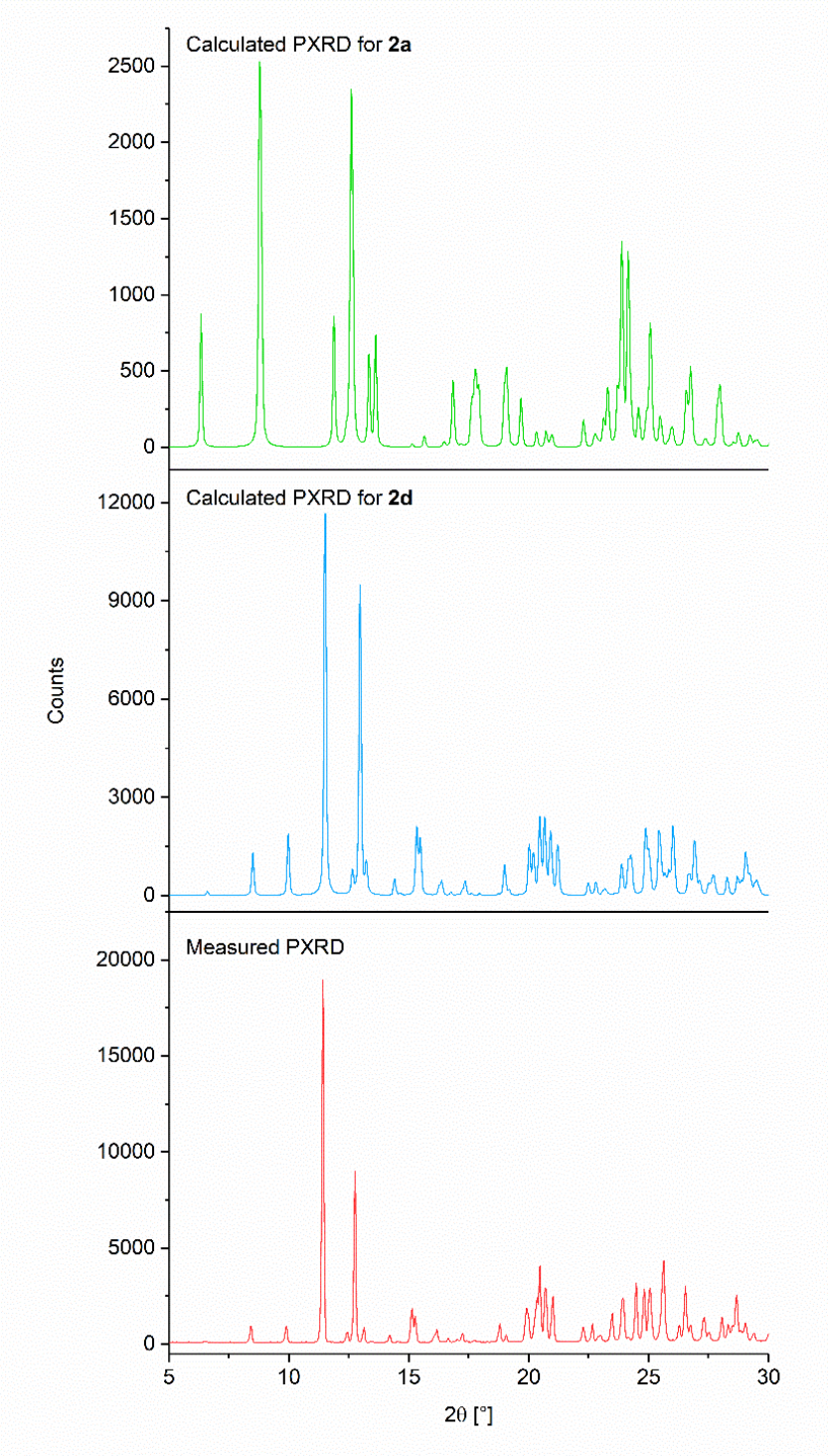
4. Conversion of $[Zn(quin)_2(H_2O)]$ into $[Zn(quin)_2(NH_3)]$ (1)

Figure S6. Comparison of the PXRD of the solid product, obtained by bubbling ammonia gas through the acetonitrile suspension of $[Zn(quin)_2(H_2O)]$ (red line), and the calculated powder diffractogram of $[Zn(quin)_2(NH_3)]$ (**1**) (blue line).



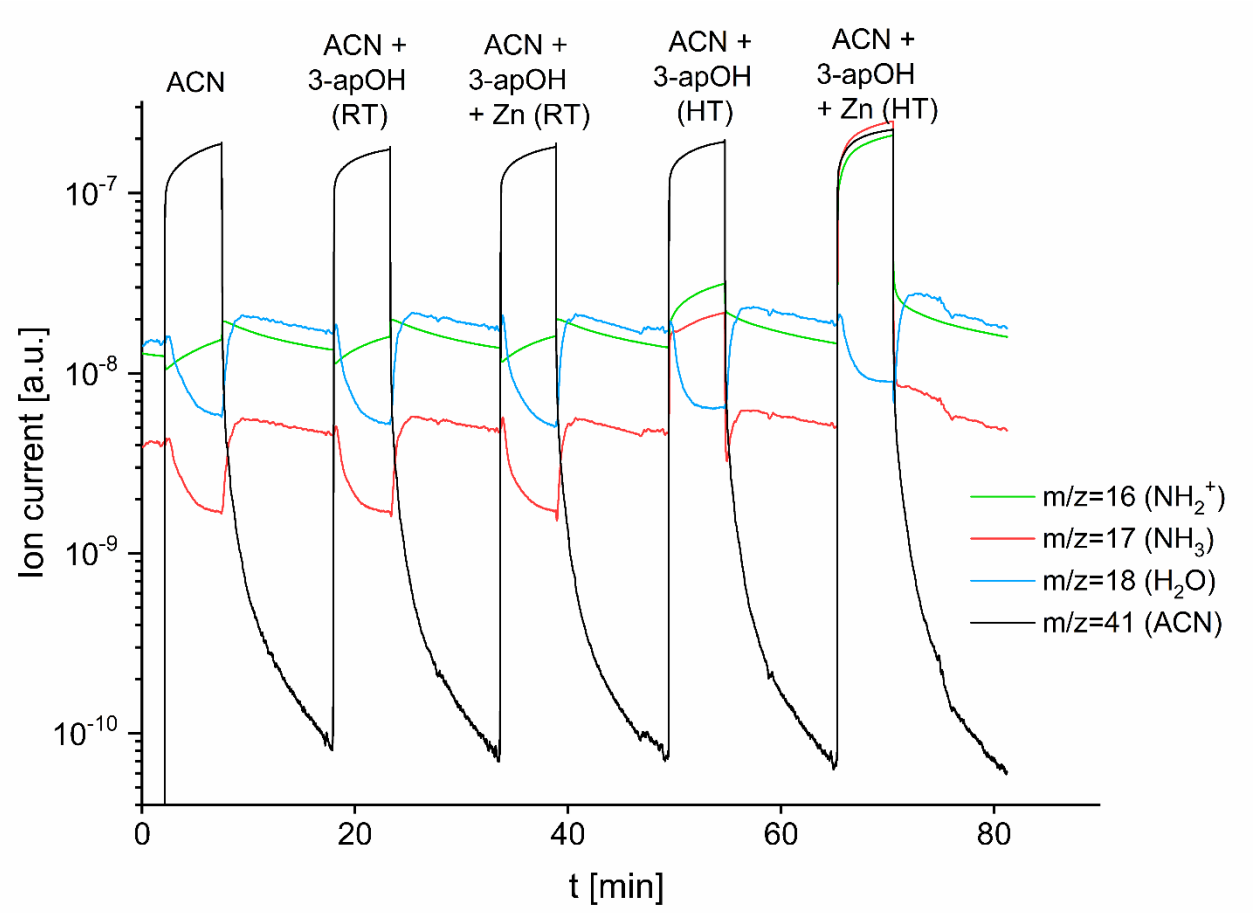
5. Conversion of [Zn(quin)$_2$(3-apOH)]·CH$_3$CN (2a) into [Zn(quin)$_2$(3-apOH)]·H$_2$O (2d)

Figure S7. Comparison of the calculated powder patterns for [Zn(quin)$_2$(3-apOH)]·CH$_3$CN (**2a**) (green line) and [Zn(quin)$_2$(3-apOH)]·H$_2$O (**2d**) (blue line) with the measured one for the aged acetonitrile solvate (red line).



6. Detection of ammonia by mass spectrometry

Figure S8. Mass spectrometry of gaseous phases in the 3-apOH system.



7. TG analysis

Figure S9. TG-DSC diagram for $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

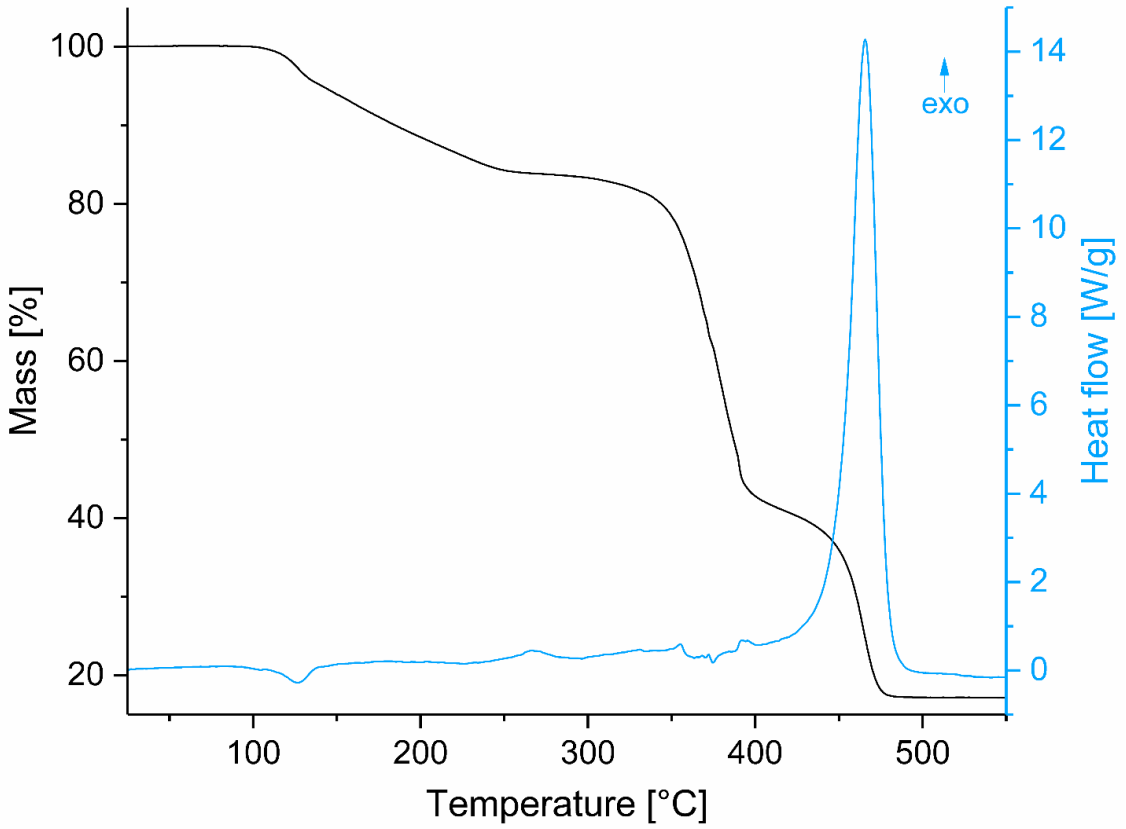
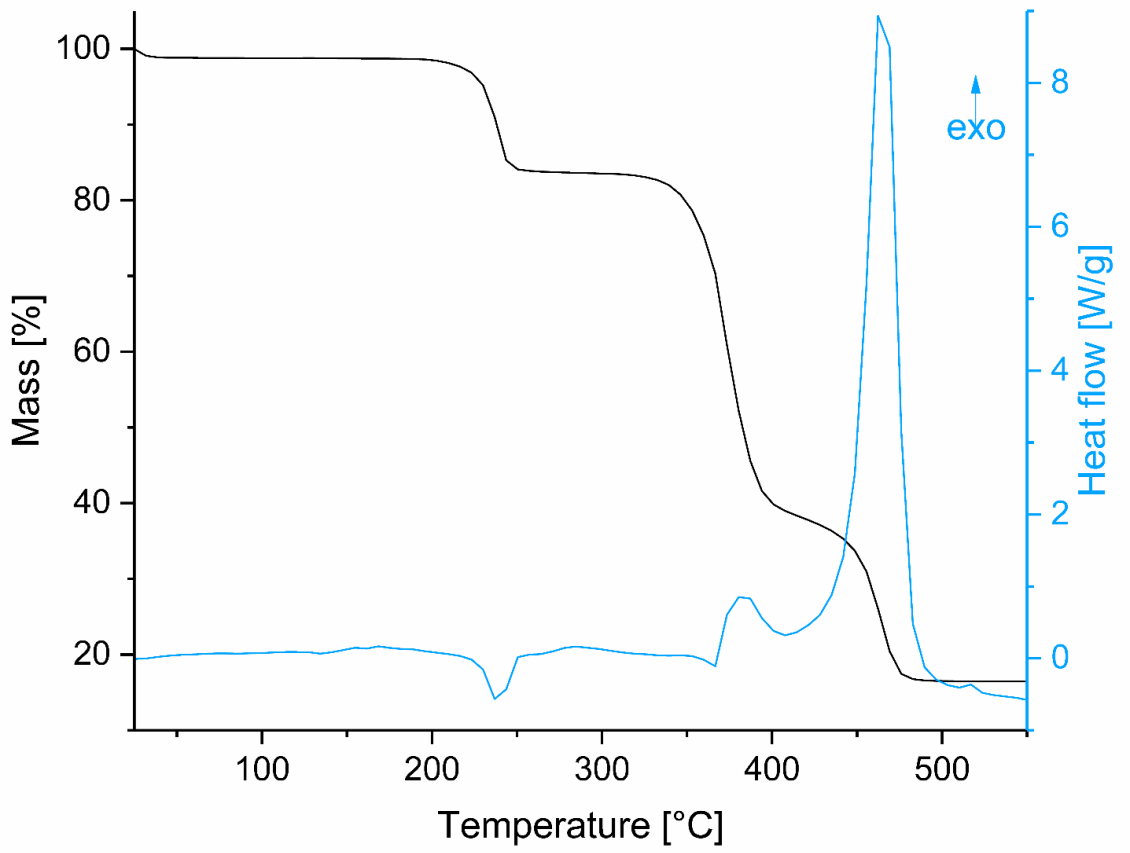


Figure S10. TG-DSC diagram for [Zn(quin)$_2$(*N*-maeOH)] (**3**).



8. Infrared spectroscopy

Figure S11. Infrared spectrum of starting material, $[Zn(quin)_2(H_2O)]$.

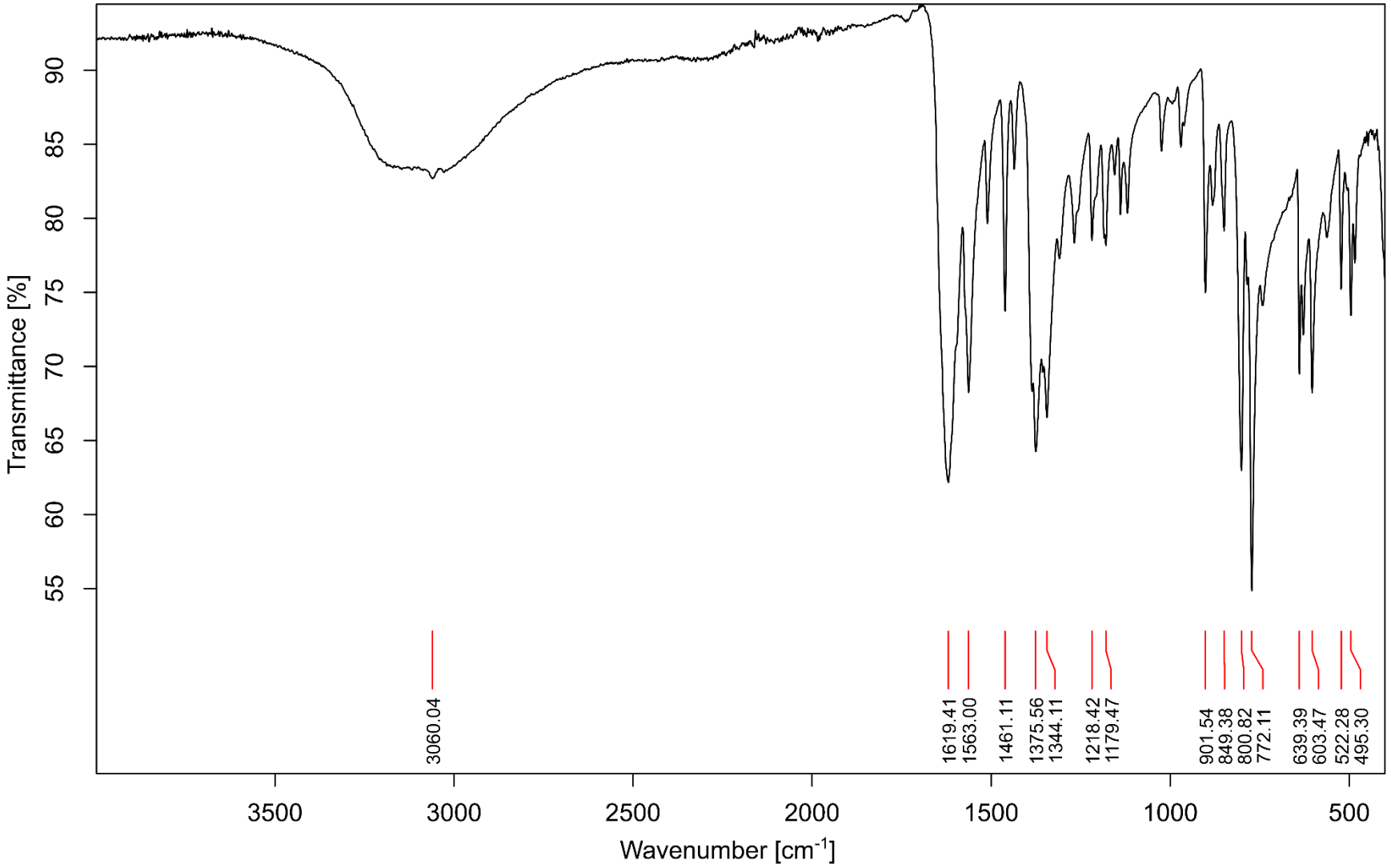


Figure S12. Infrared spectrum of $[Zn(quin)_2(NH_3)]$ (**1**).

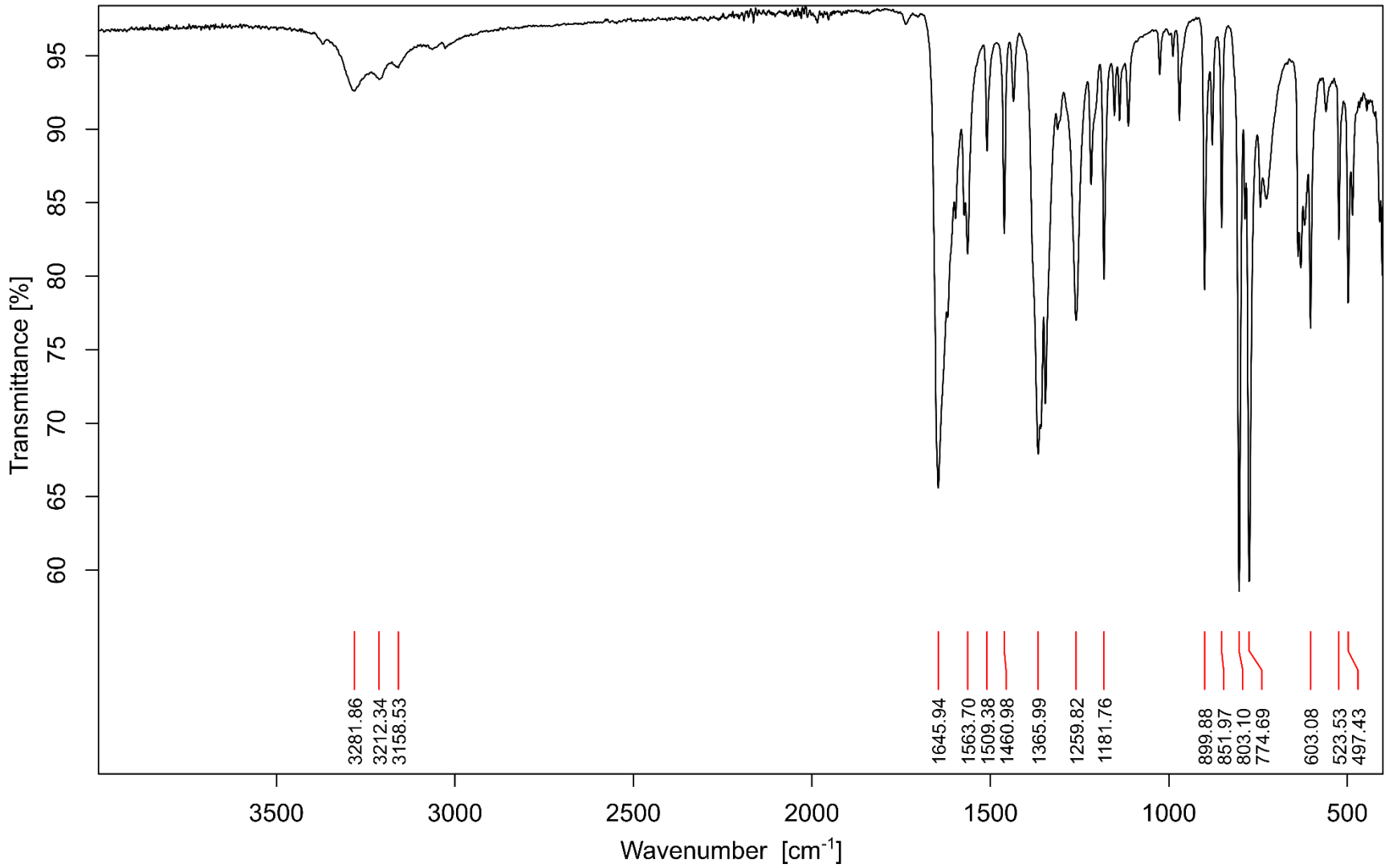


Figure S13. Infrared spectrum of $[Zn(quin)_2(3\text{-apOH})]\cdot CH_3CN$ (**2a**).

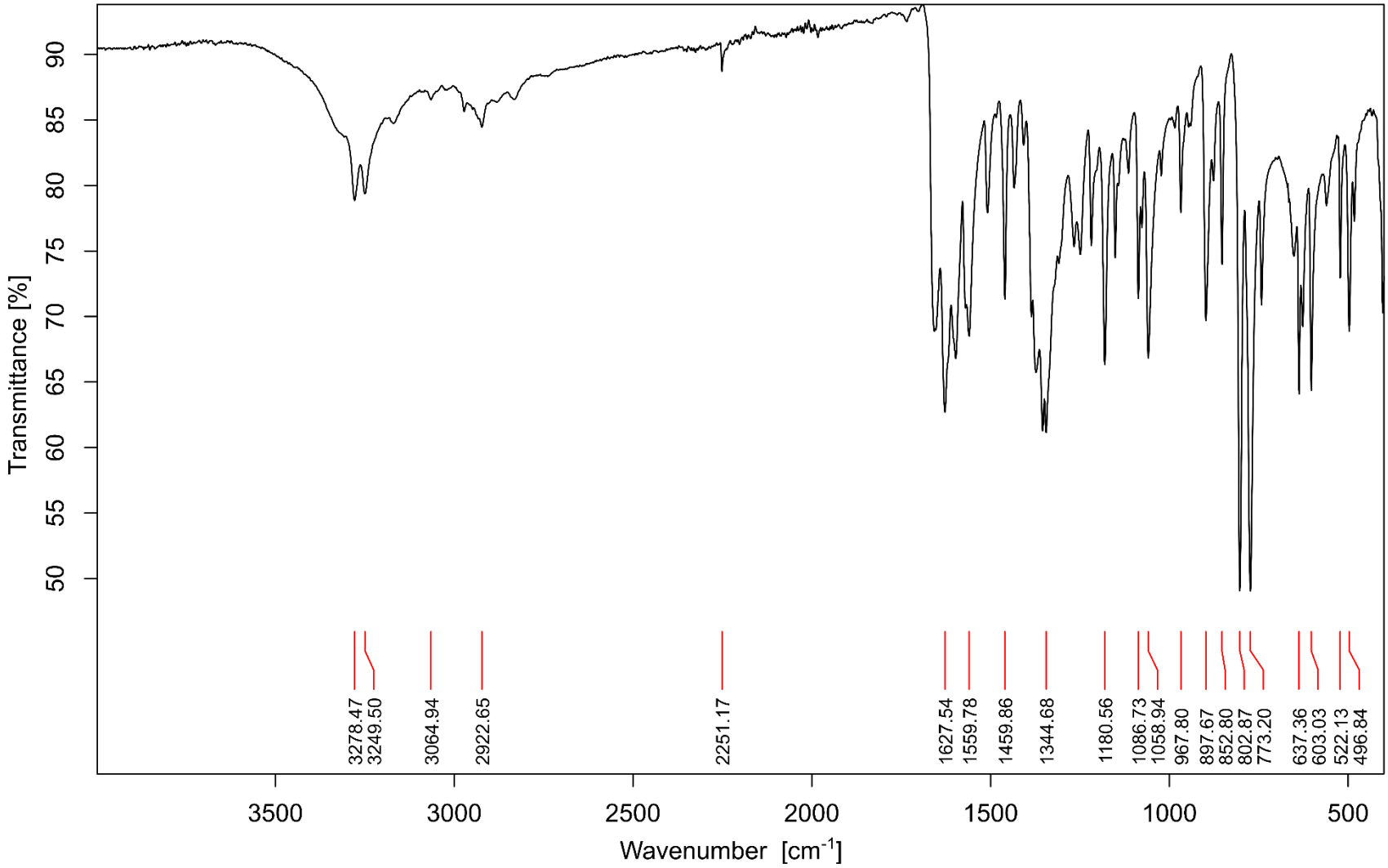


Figure S14. Infrared spectrum of [Zn(quin)$_2$(3-apOH)]·EtOH (**2b**).

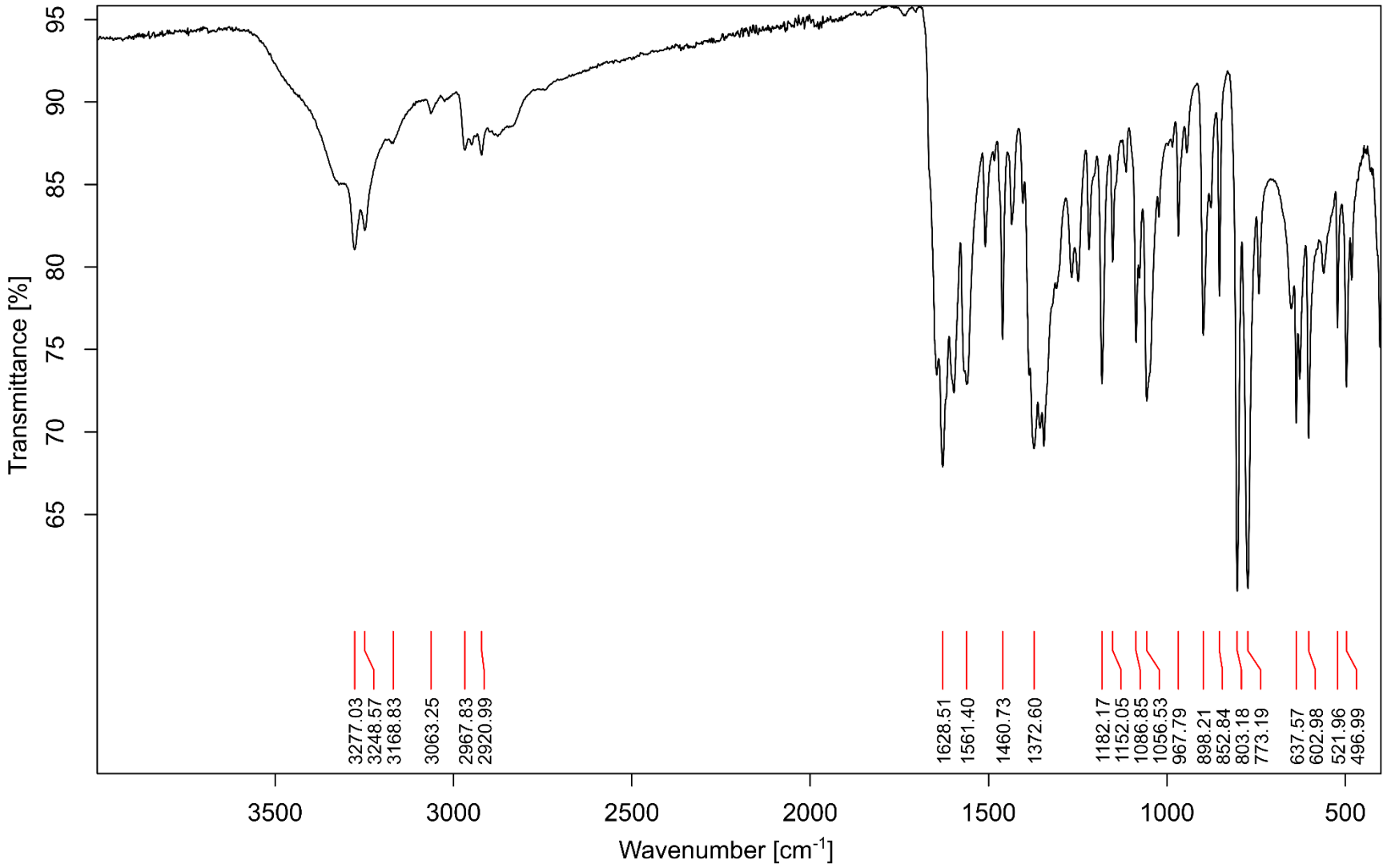


Figure S15. Infrared spectrum of [Zn(quin)$_2$(3-apOH)]·2-PrOH (**2c**).

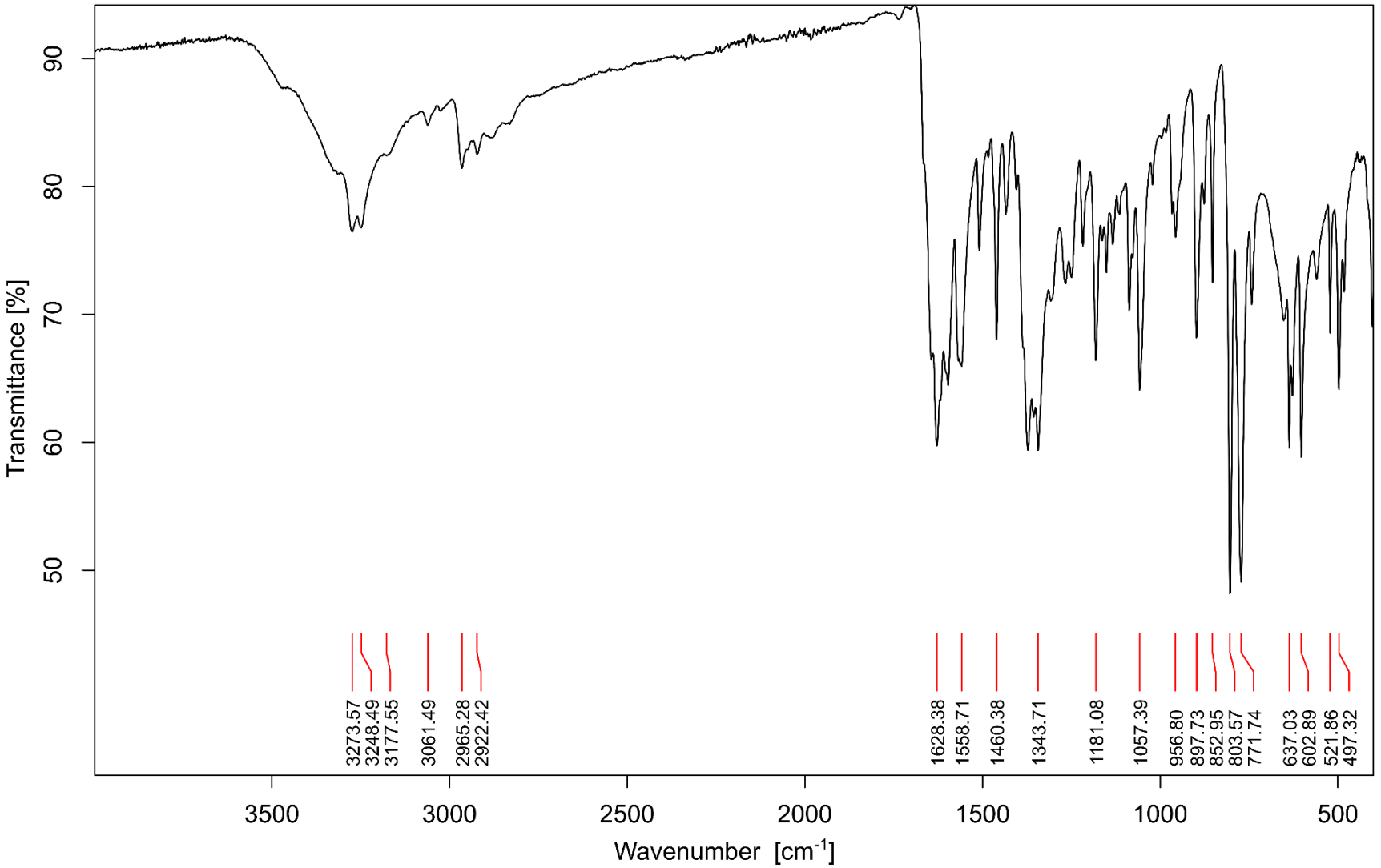


Figure S16. Infrared spectrum of $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

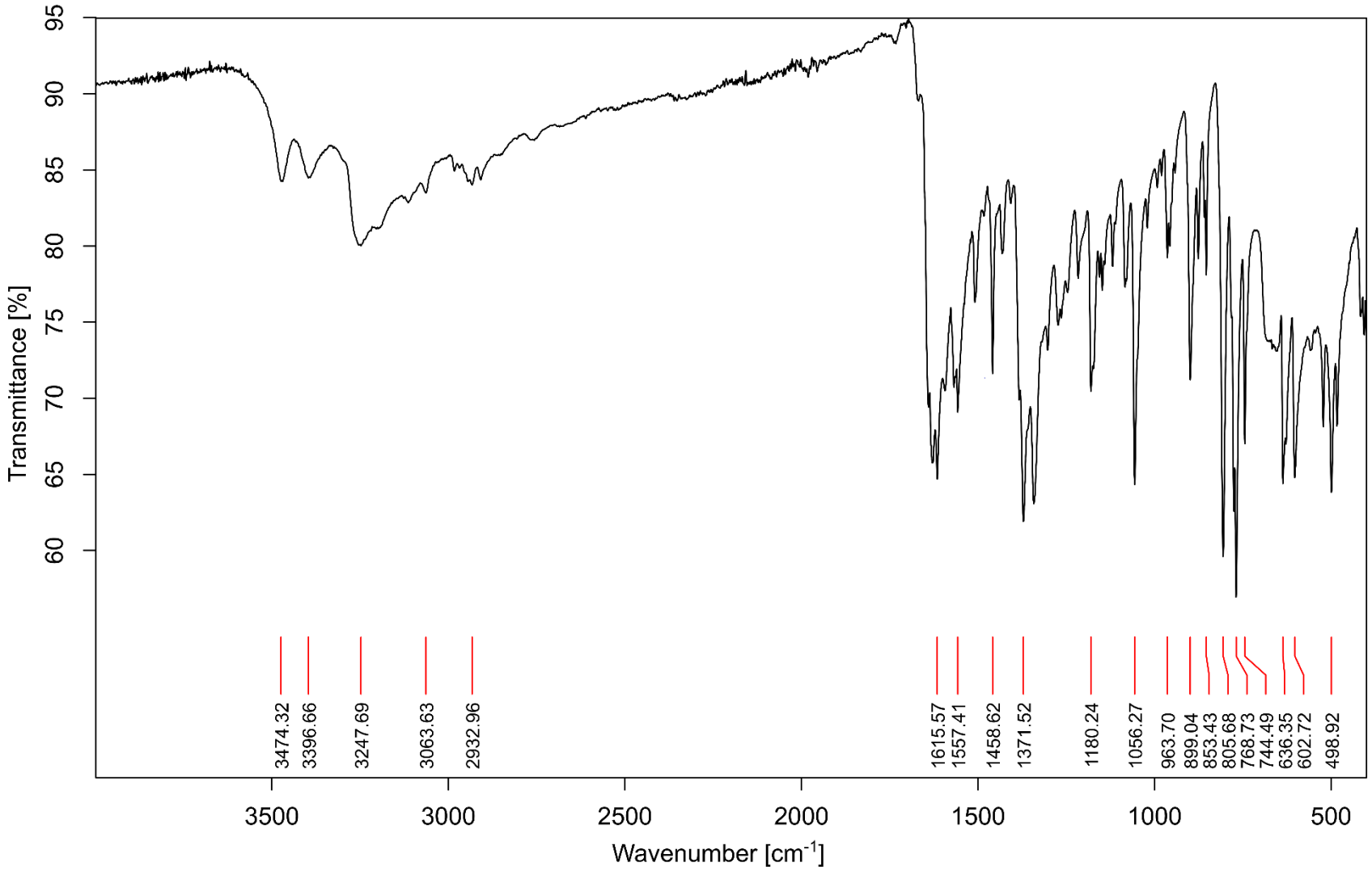
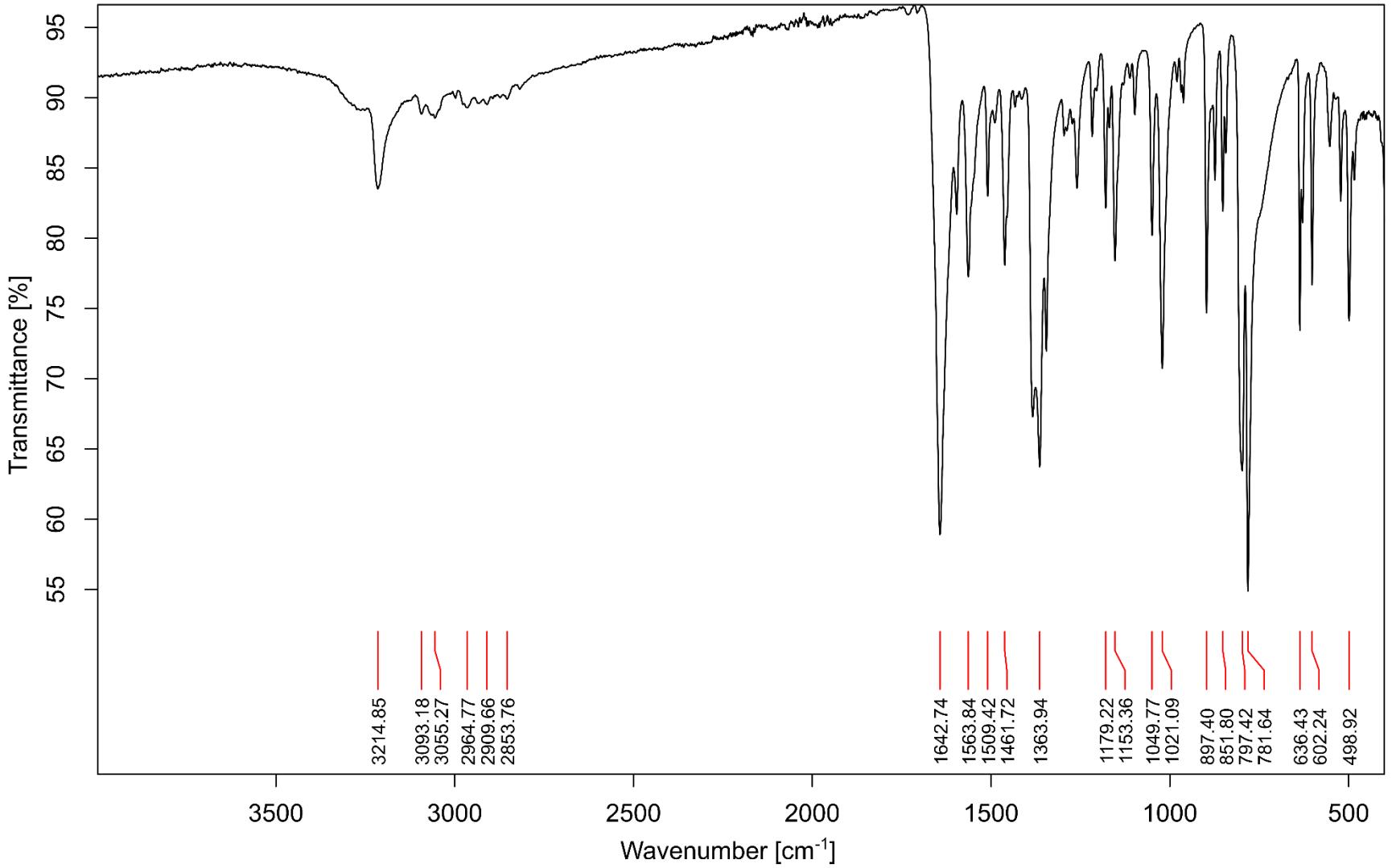


Figure S17. Infrared spectrum of [Zn(quin)$_2$(*N*-maeOH)] (**3**).



9. NMR spectroscopy

The ^{1}H, ^{13}C, $^{1}H–^{1}H$ COSY and $^{1}H–^{13}C$ HSQC NMR spectra were recorded for all stable compounds, [Zn(quin)$_2$(NH$_3$)] (**1**), [Zn(quin)$_2$(3-apOH)]·H$_2$O (**2d**) and [Zn(quin)$_2$(*N*-maeOH)] (**3**). All protons can be unambiguously determined using 2D NMR techniques. In ^{13}C NMR spectra, the peak for carboxylate carbon atom is located around 166 ppm. Quaternary carbons can be distinguished from other carbons, but they were assigned with the help of the literature data.[3] Assignments are presented as chemical shifts in ppm (red colour stands for proton shifts and blue for carbon chemical shifts). For all unstable compounds, [Zn(quin)$_2$(3-apOH)]·CH$_3$CN (**2a**), [Zn(quin)$_2$(3-apOH)]·EtOH (**2b**) and [Zn(quin)$_2$(3-apOH)]·2-PrOH (**2c**), only ^{1}H NMR spectra were recorded.

[3] SDBSWeb (National Institute of Advanced Industrial Science and Technology). https://sdbs.db.aist.go.jp (accessed 5. 11. 2019).

Figure S18. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(NH$_3$)] (**1**).

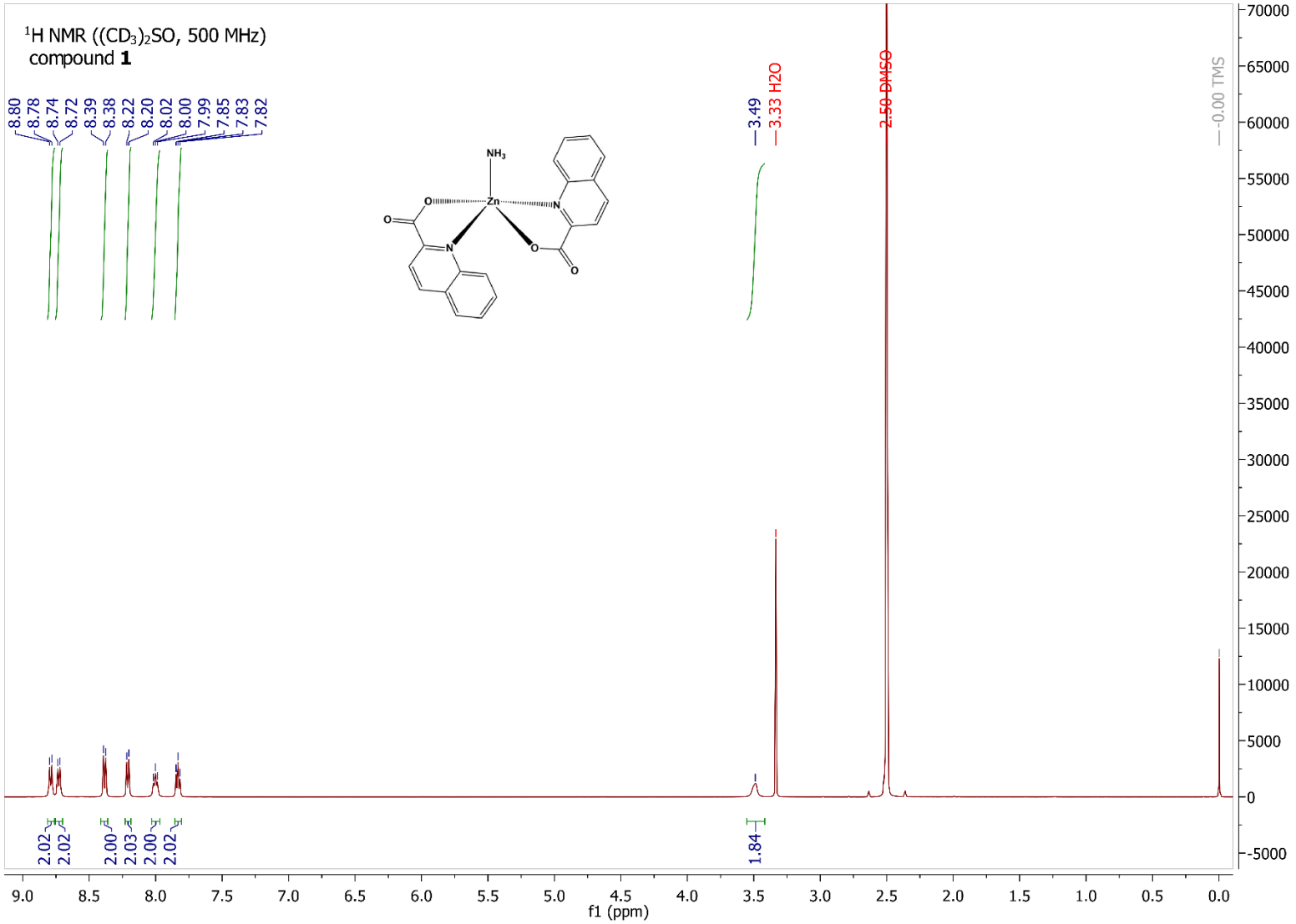


Figure S19. ^{13}C NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(NH$_3$)] (**1**).

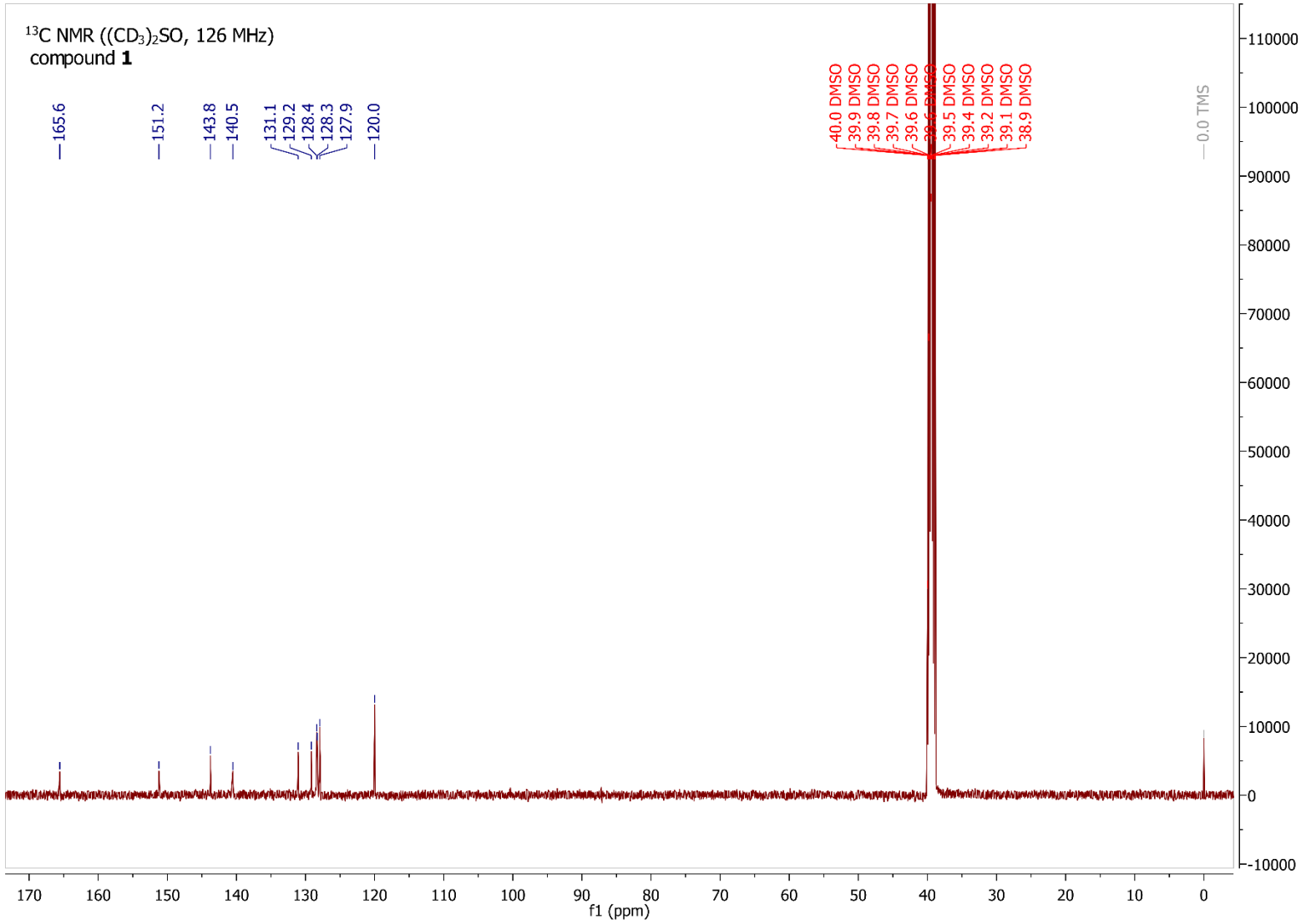


Figure S20. $^{1}H–^{1}H$ COSY NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(NH$_3$)] (**1**).

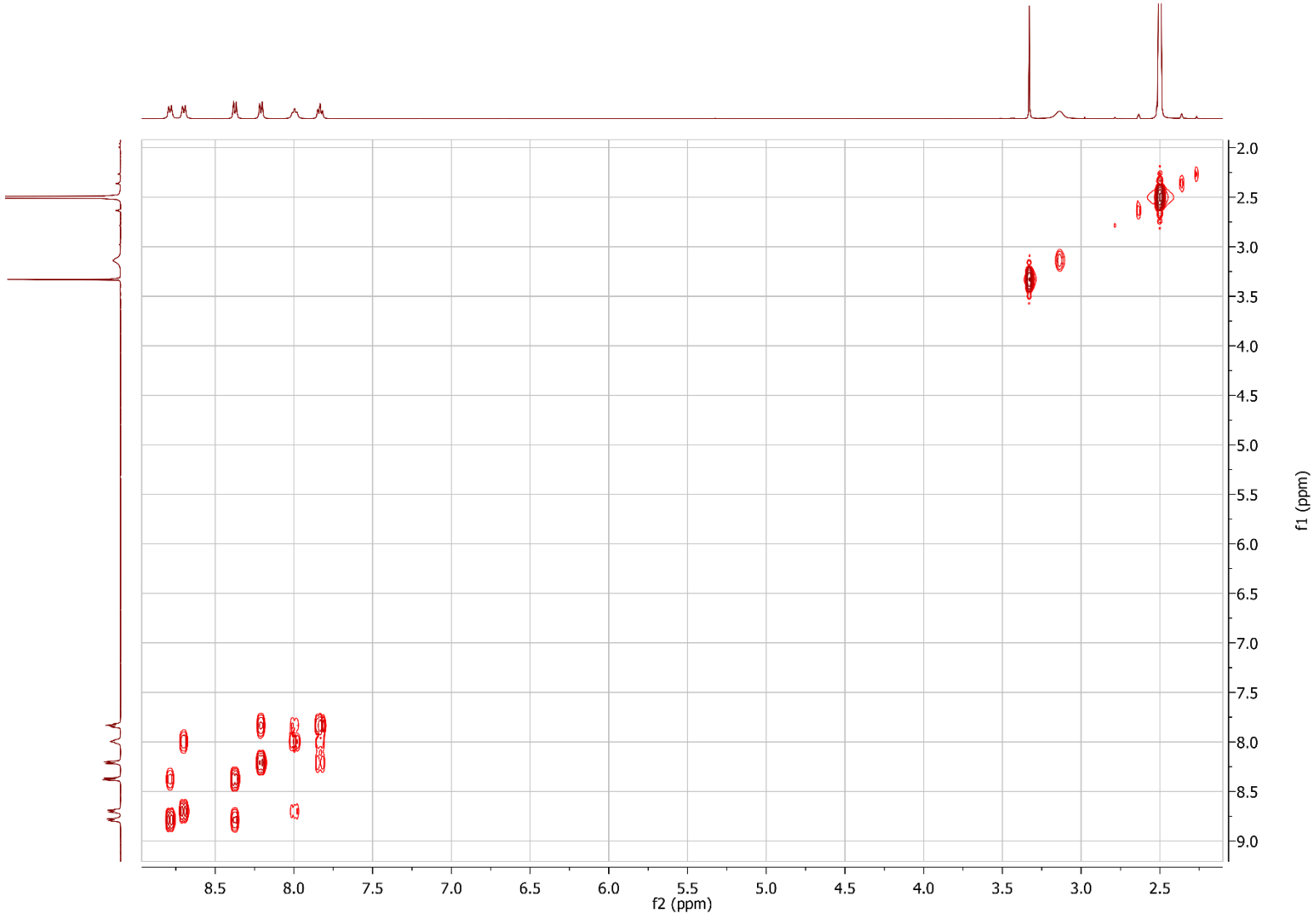


Figure S21. $^{1}H–^{13}C$ HSQC NMR spectrum of DMSO-d_6 solution of $[Zn(quin)_2(NH_3)]$ (**1**).

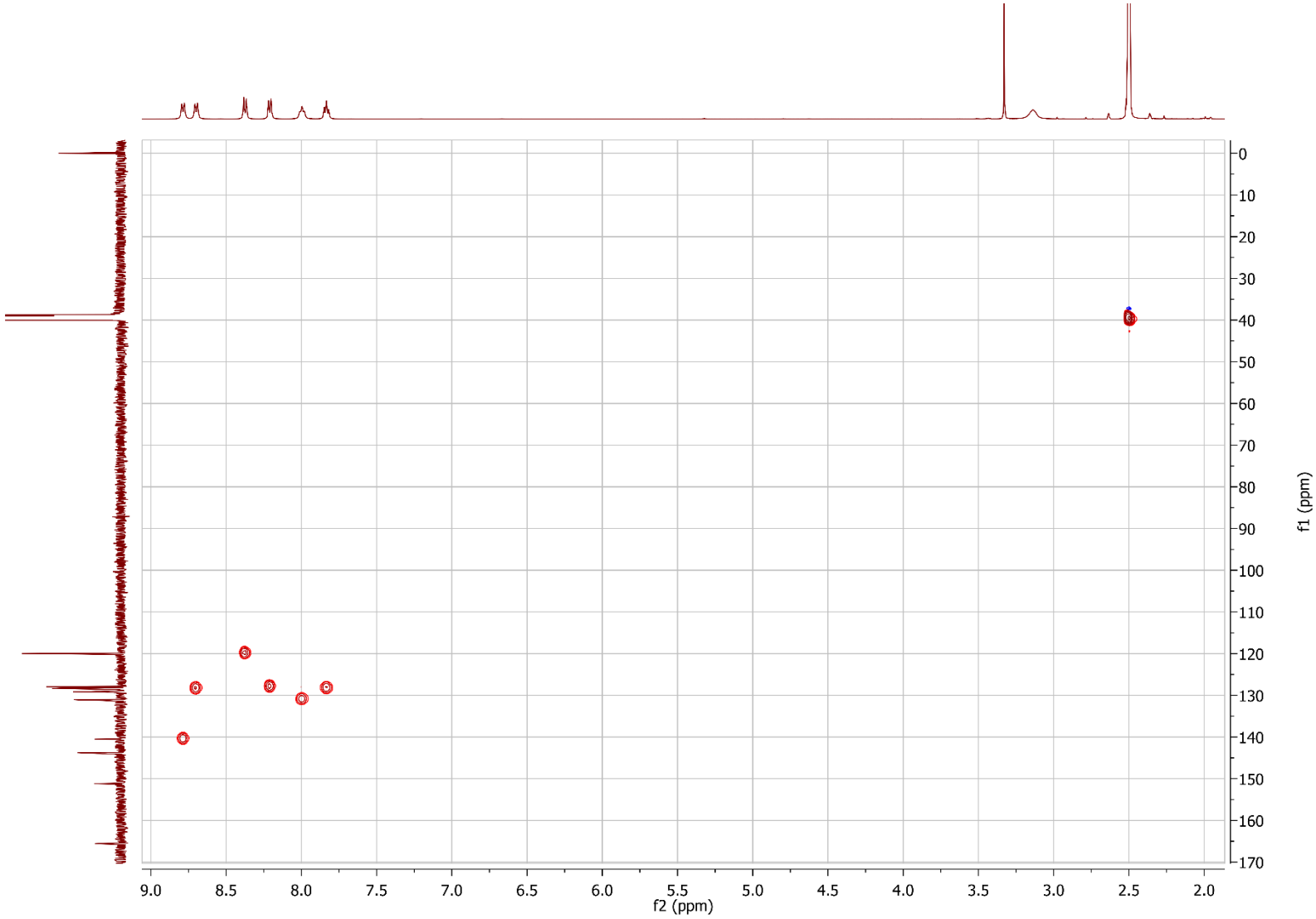


Figure S22. Assignment of NMR signals for $[Zn(quin)_2(NH_3)]$ (**1**) (ligands: quinaldinate and ammonia).

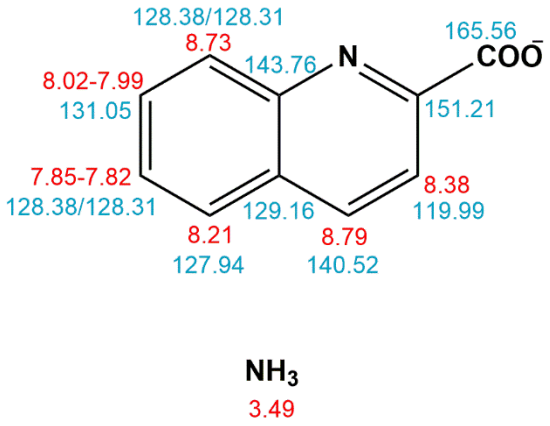


Figure S23. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(3-apOH)]·CH$_3$CN (**2a**).

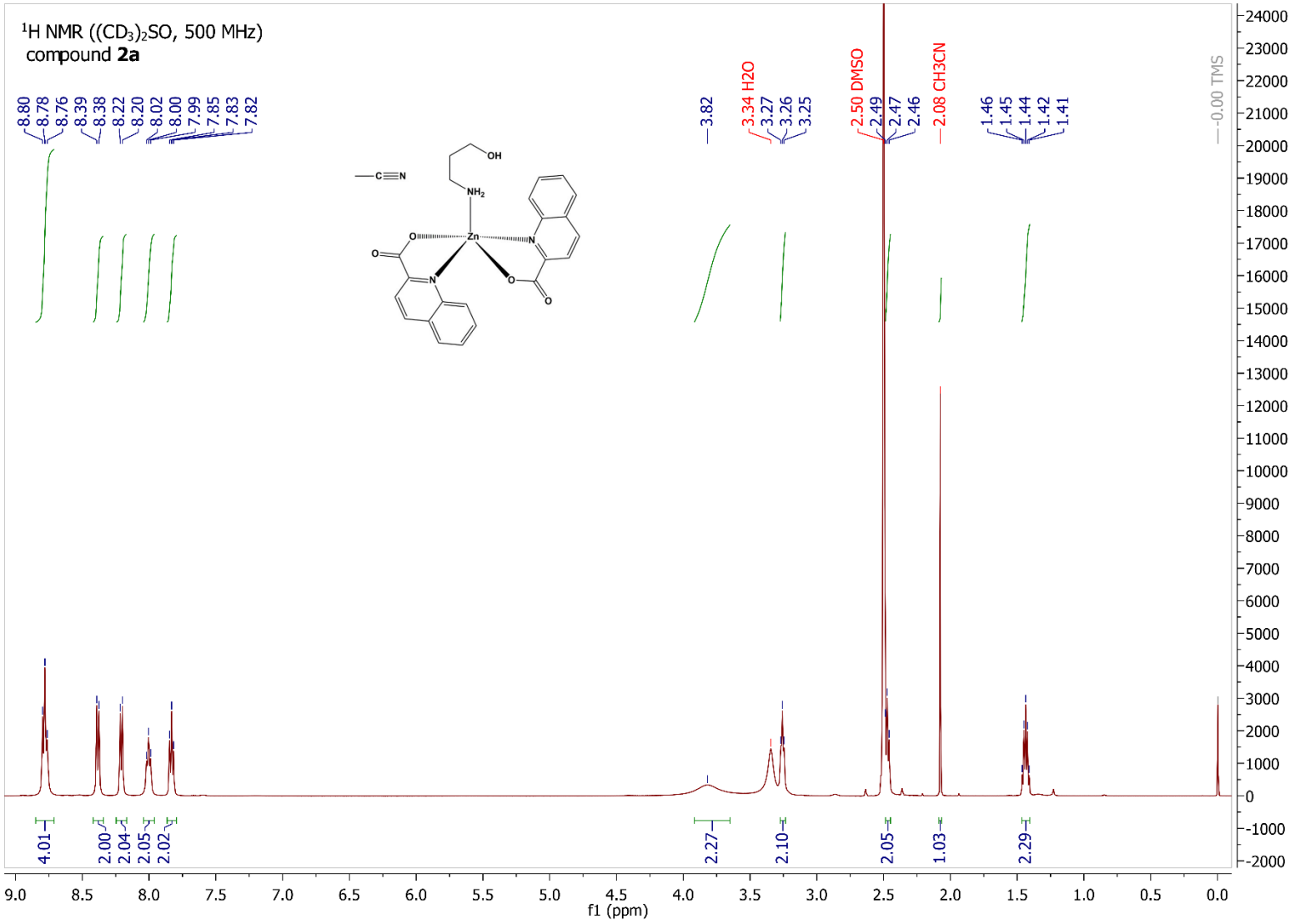


Figure S24. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(3-apOH)]·EtOH (**2b**).

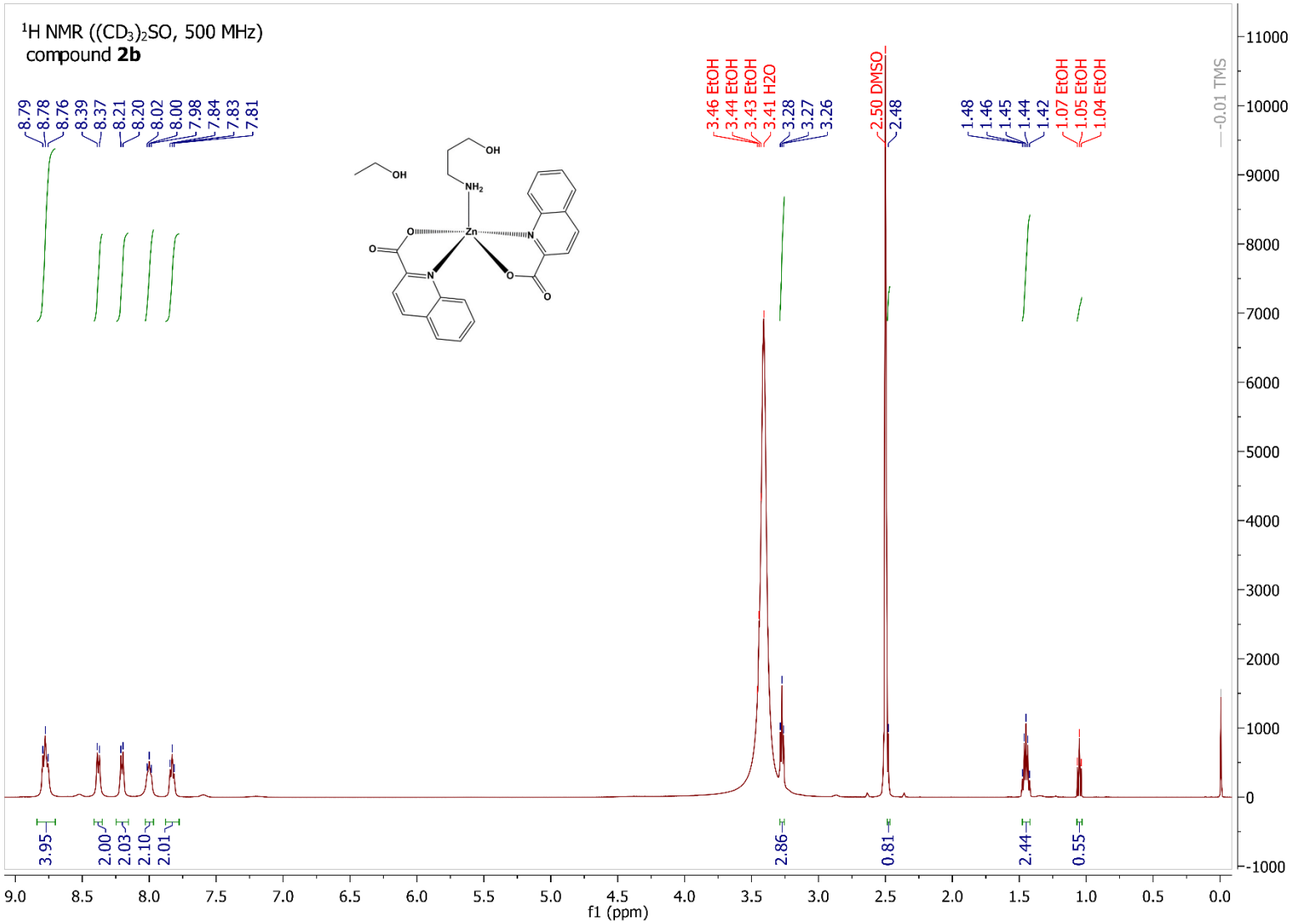


Figure S25. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(3-apOH)]·2-PrOH (**2c**).

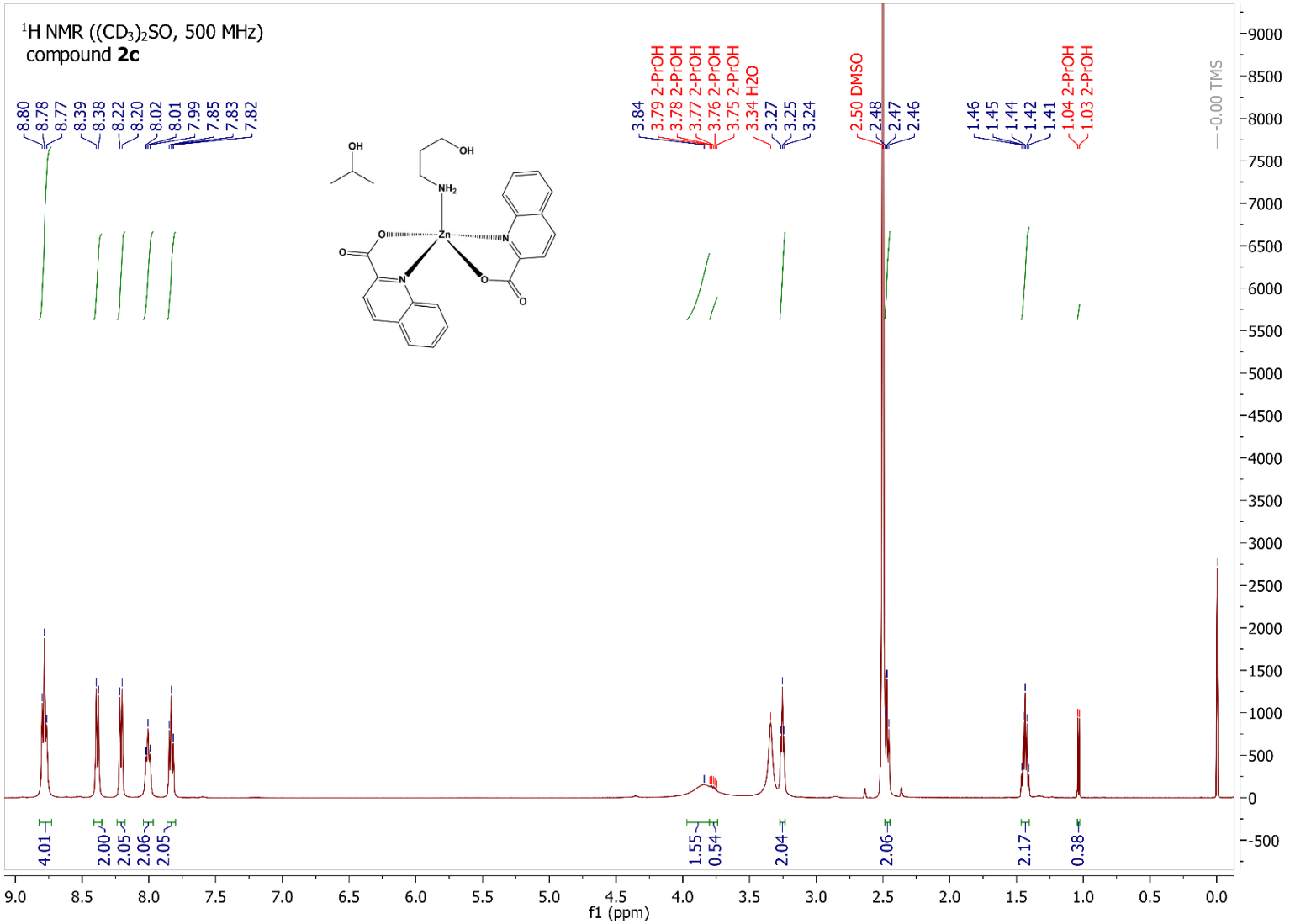


Figure S26. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(3-apOH)]·H$_2$O (**2d**).

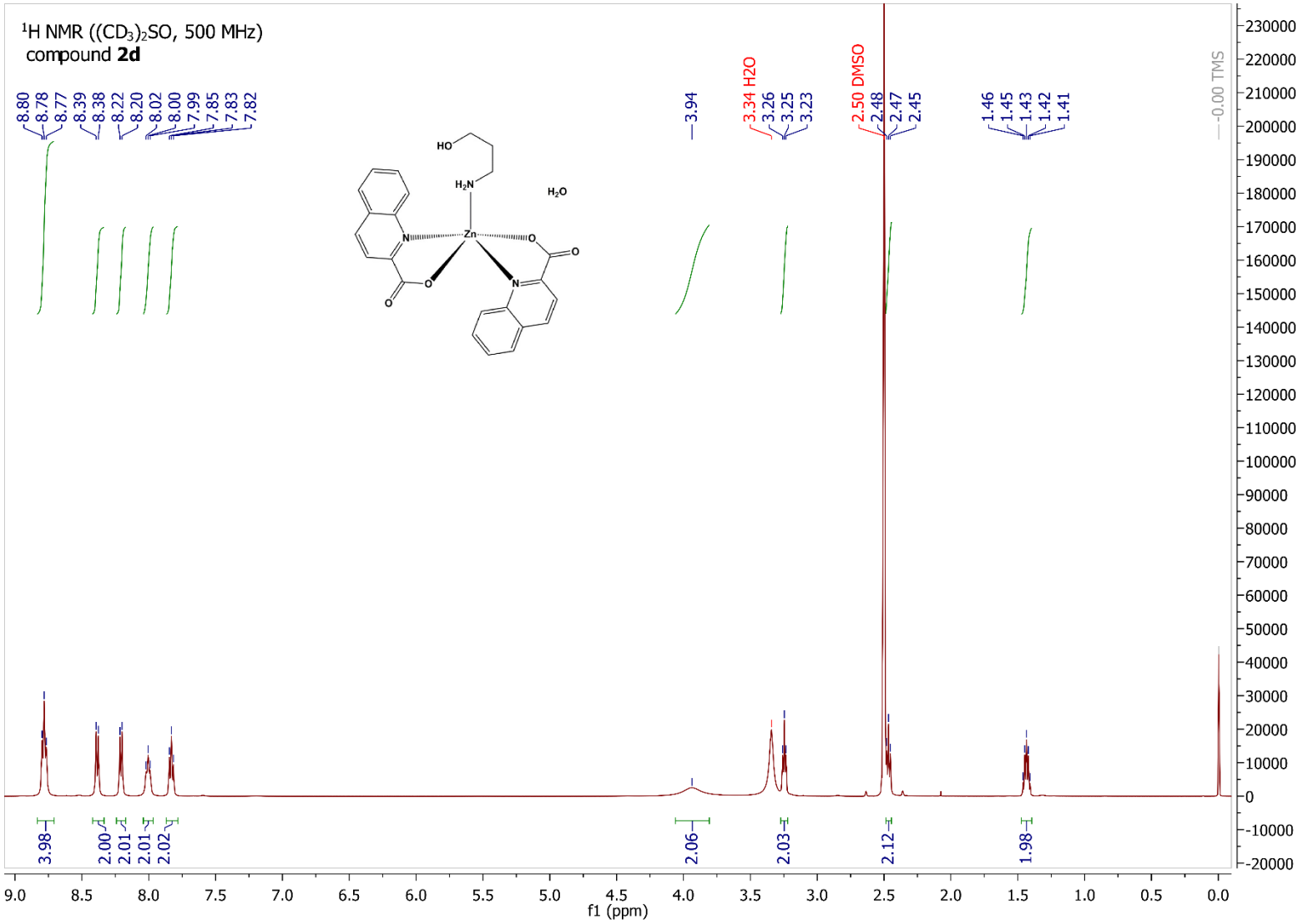


Figure S27. ^{13}C NMR spectrum of DMSO-d_6 solution of $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

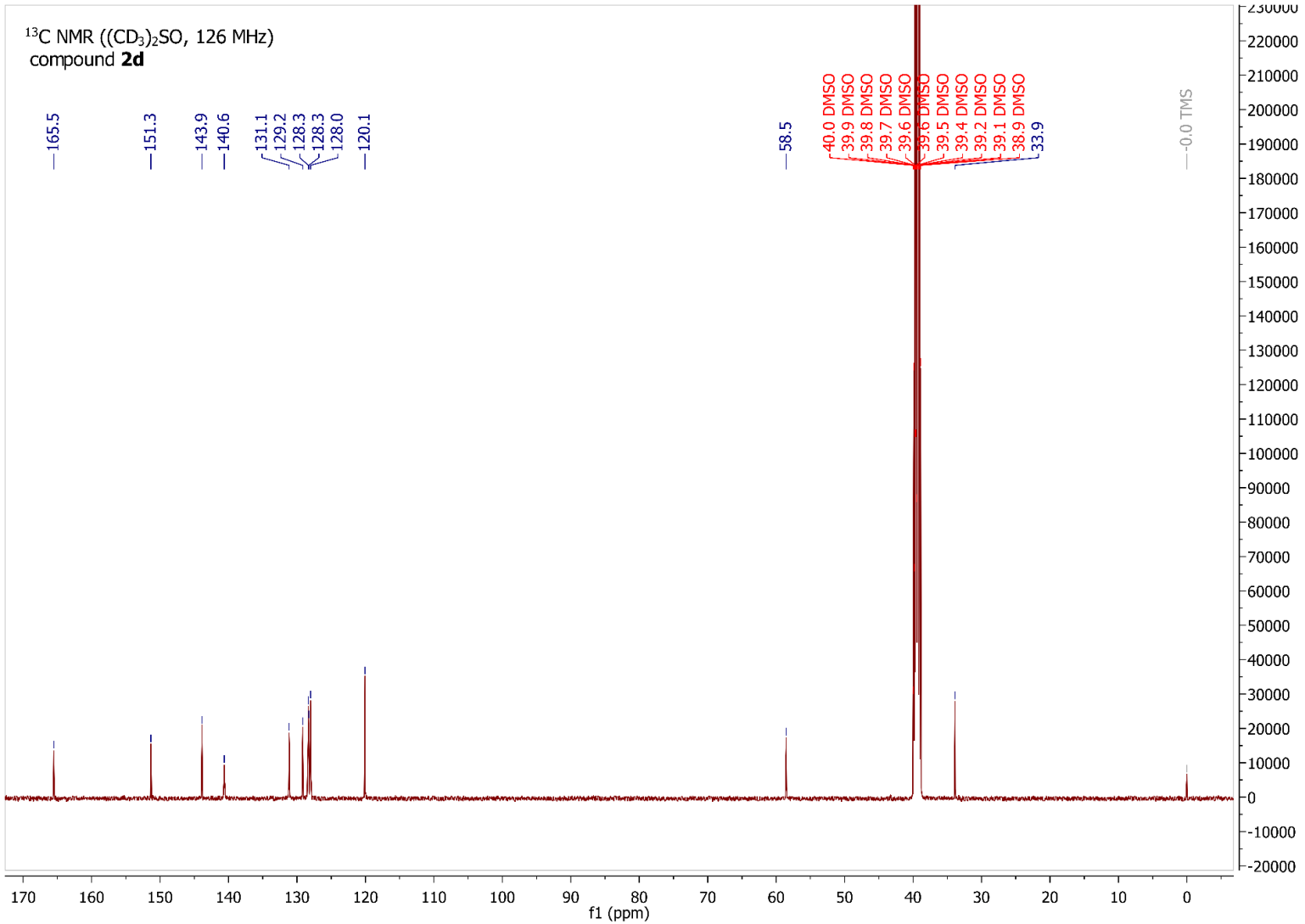


Figure S28. $^{1}H–^{1}H$ COSY NMR spectrum of DMSO-d_6 solution of $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

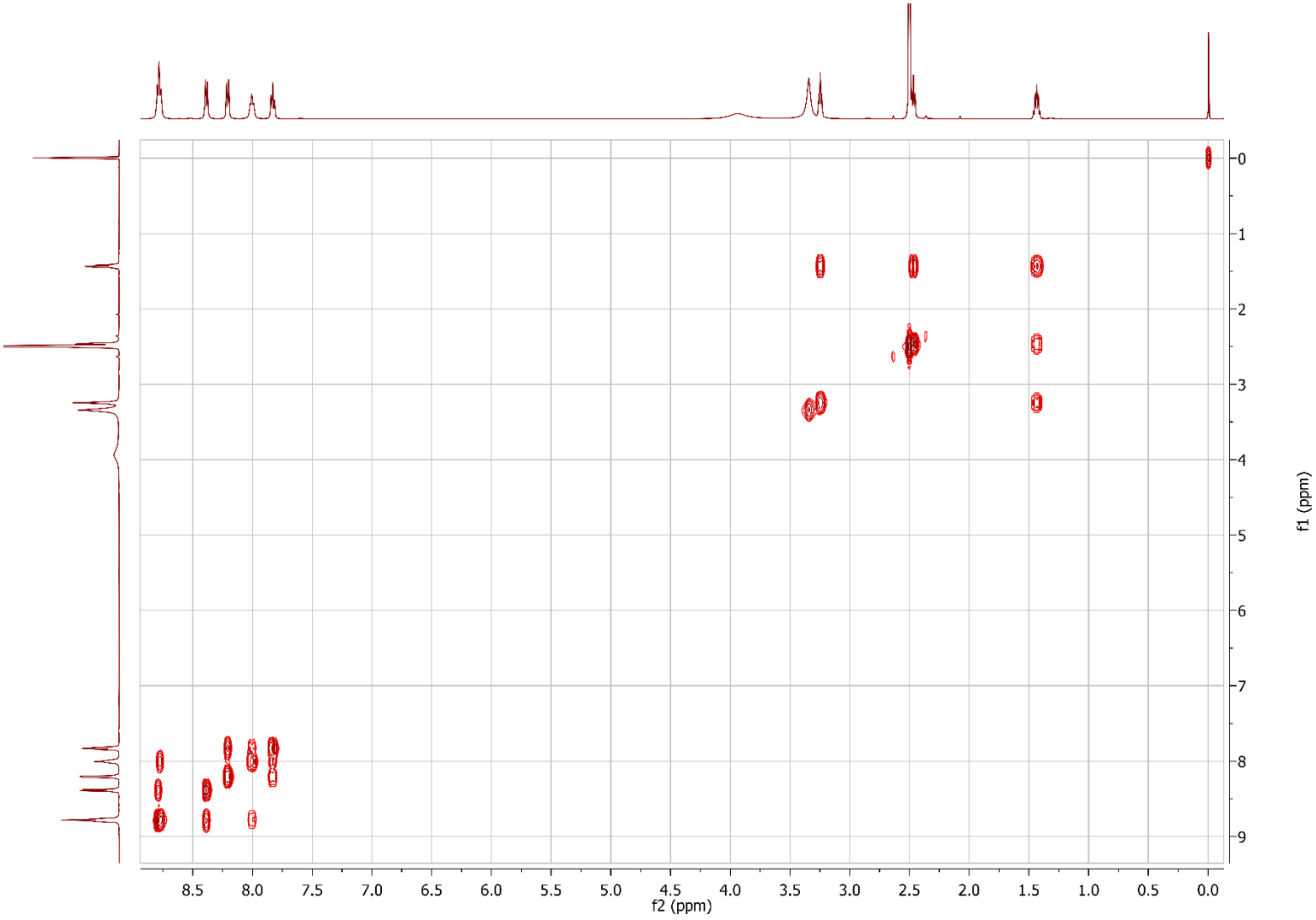


Figure S29. $^{1}H–^{13}C$ HSQC NMR spectrum of DMSO-d_6 solution of $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**).

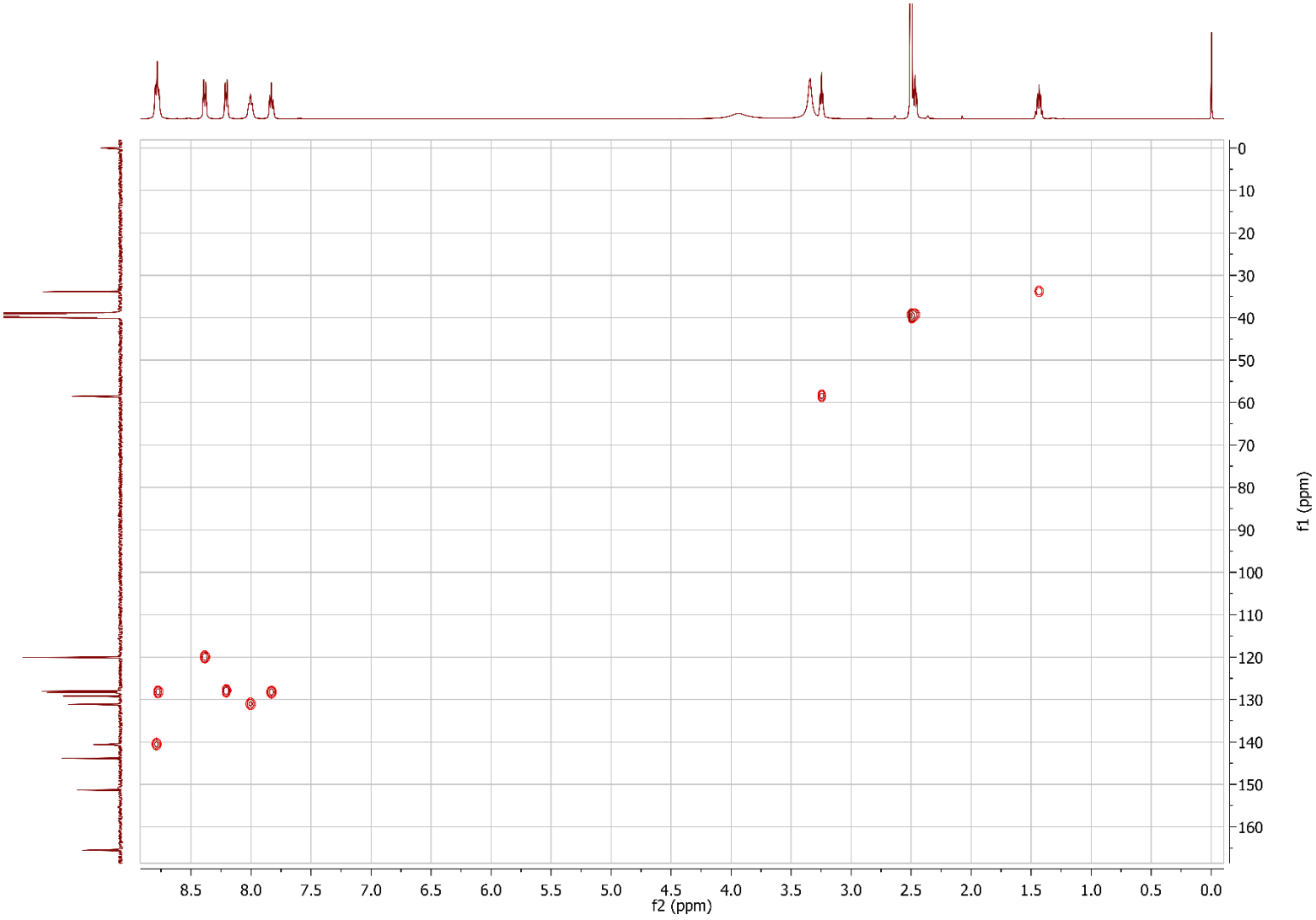


Figure S30. Assignment of NMR signals for $[Zn(quin)_2(3\text{-apOH})]\cdot H_2O$ (**2d**) (ligands: quinaldinate and 3-amino-1-propanol).

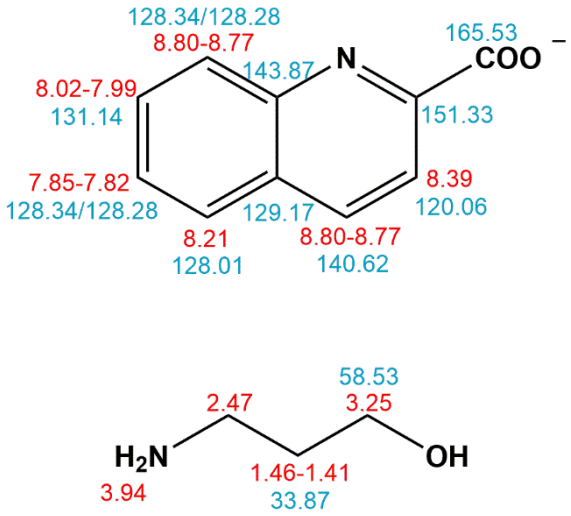


Figure S31. ^{1}H NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(*N*-maeOH)] (**3**).

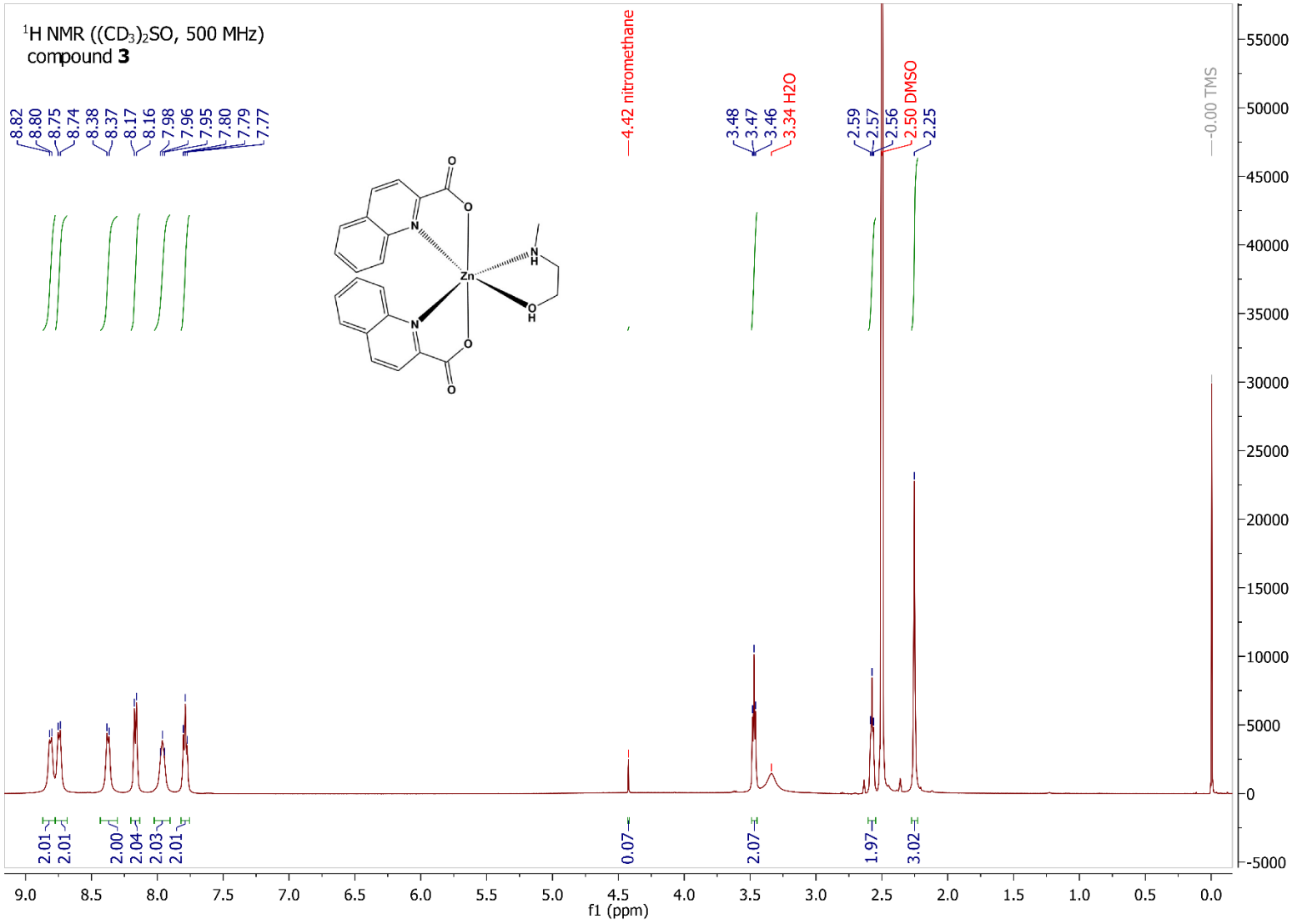


Figure S32. ^{13}C NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(*N*-maeOH)] (**3**).

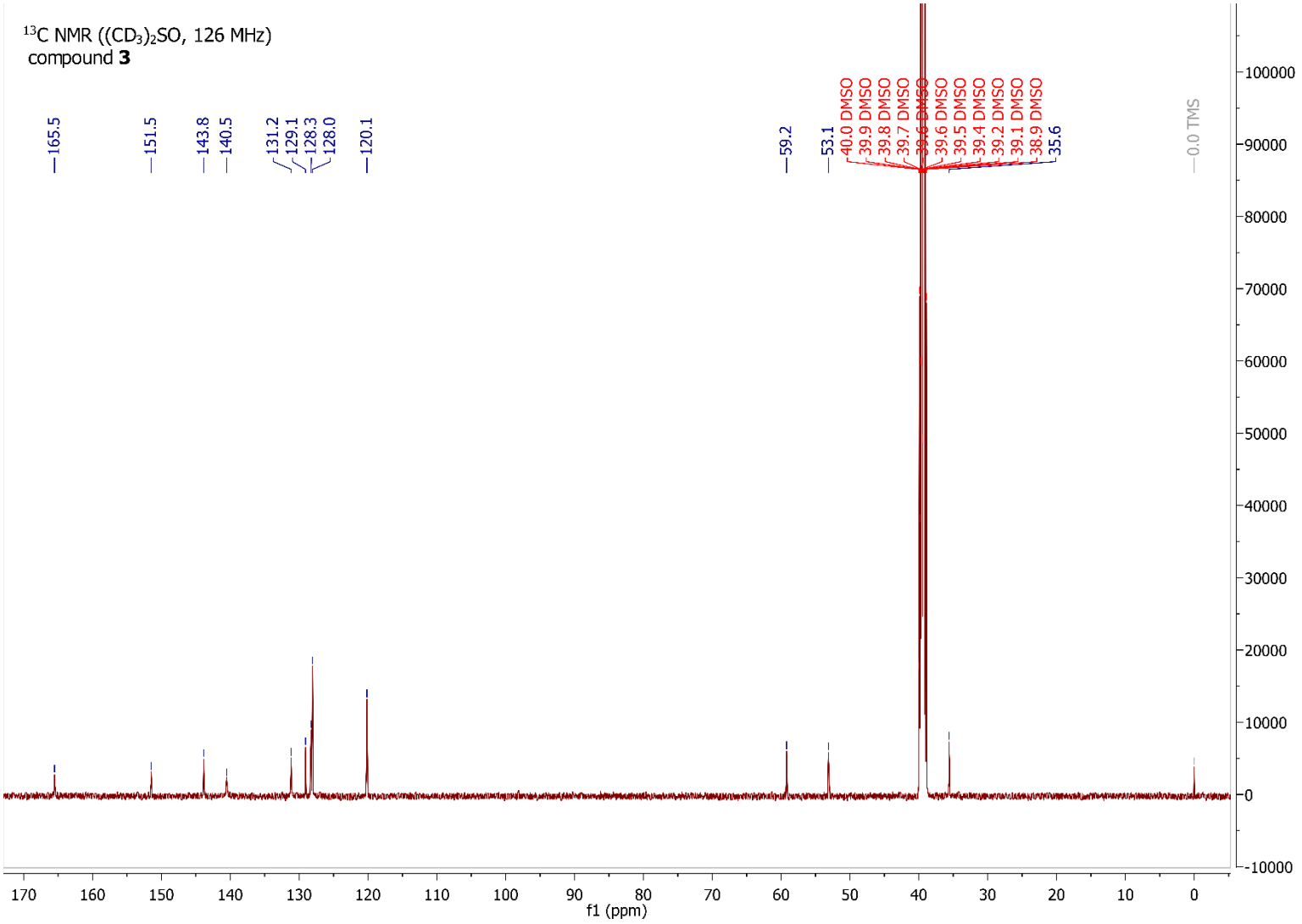


Figure S33. ^{1}H–^{1}H COSY NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(*N*-maeOH)] (**3**).

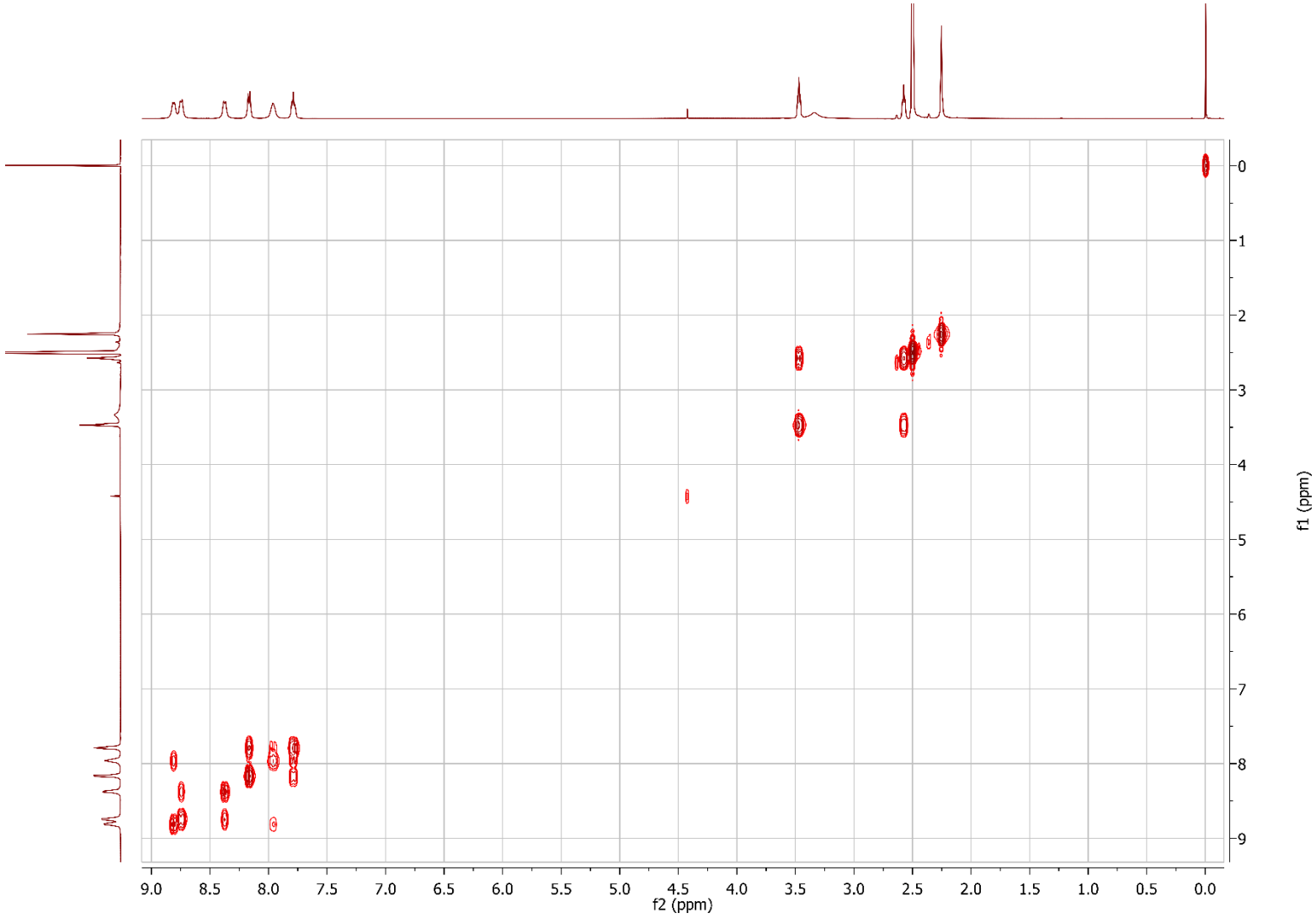


Figure S34. ^{1}H–^{13}C HSQC NMR spectrum of DMSO-d_6 solution of [Zn(quin)$_2$(*N*-maeOH)] (**3**).

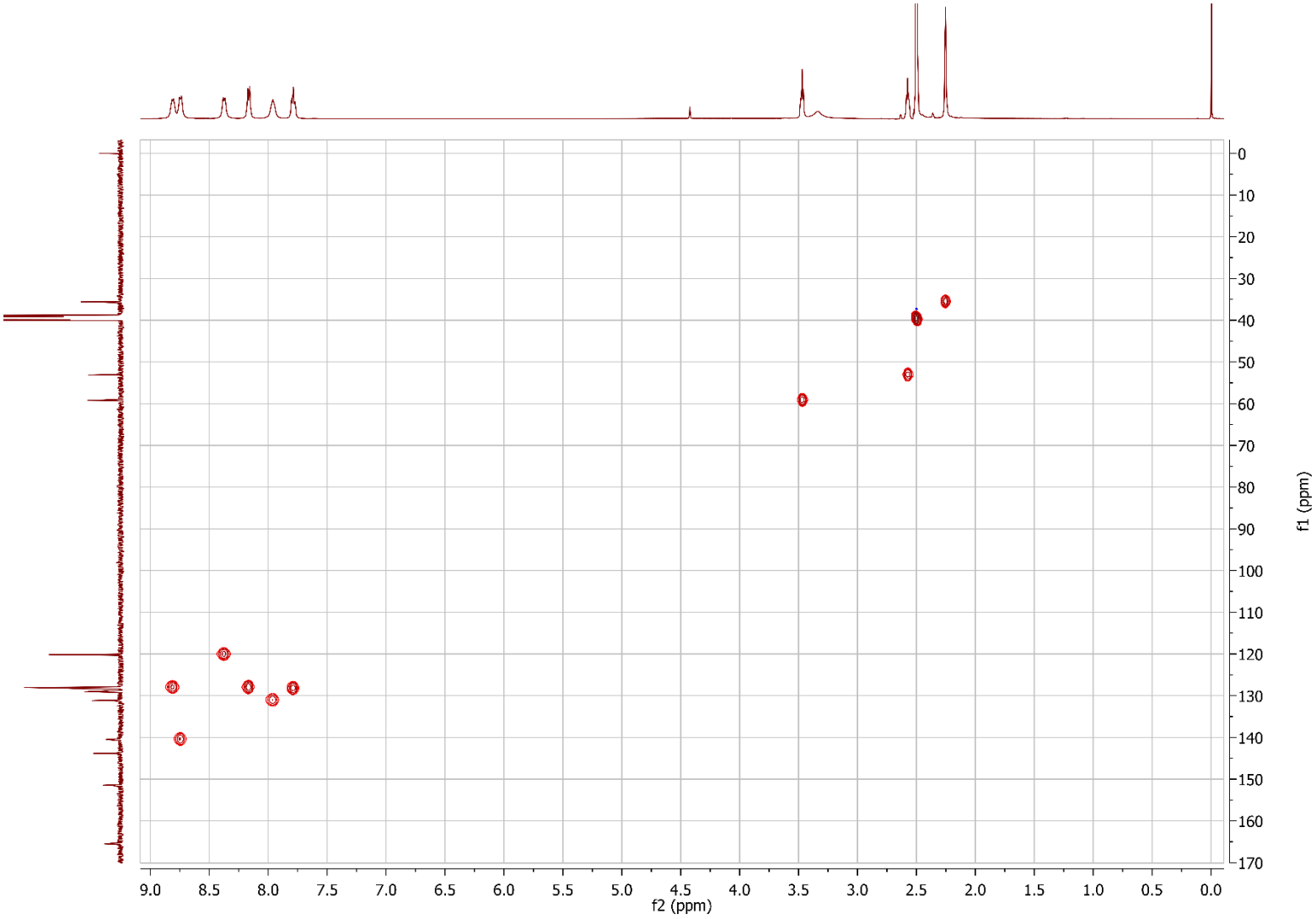
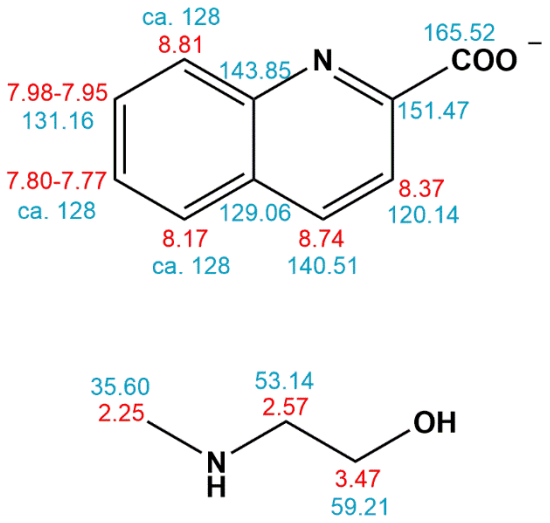


Figure S35. Assignment of NMR signals for [Zn(quin)$_2$(*N*-maeOH)] (**3**) (ligands: quinaldinate and *N*-methylaminoethanol).



10. Tables of optimized geometries (Cartesian coordinates)

Table S6. 2_monodentate

E(wb97xd) = -3208.48841692 a.u.

C	3.40265	2.95210	0.03515
C	4.57379	2.24507	0.11959
C	0.84873	2.98267	-0.09842
C	2.18258	2.24291	-0.00827
C	4.53707	0.82876	0.15908
C	5.70799	0.02978	0.24192
C	3.26678	0.19352	0.11015
C	5.60987	-1.33945	0.27197
C	-4.21212	1.68740	-1.87435
C	-3.08486	1.20765	-1.25468
C	3.18877	-1.22134	0.14511
C	4.33965	-1.96676	0.22102
C	-5.49678	1.46797	-1.31548
C	-3.20090	0.47841	-0.04357
C	-5.63190	0.76843	-0.14227
C	-1.01911	-1.64387	-2.20908
C	-4.48552	0.25502	0.52054
C	-2.17621	-0.67996	1.68861
C	-0.86500	-1.17085	2.30341
C	-4.56104	-0.47856	1.73061
C	-1.04781	-2.88359	-1.32034
C	-3.41271	-0.94705	2.31434
C	0.01373	-3.91497	-1.65864
H	3.38457	4.03458	0.00161
H	5.53277	2.75414	0.15733
H	6.67555	0.52200	0.28079
H	-4.12164	2.24355	-2.80236
H	6.50642	-1.94850	0.33379
H	-2.09721	1.38293	-1.66858
H	0.14143	0.01667	-2.55052
H	-6.37408	1.86034	-1.82019
H	0.96408	-1.23486	-1.90853
H	2.21677	-1.70119	0.10275
H	4.27711	-3.05061	0.24567
H	-0.91887	-1.94367	-3.25934
H	-1.95710	-1.09461	-2.10966
H	-6.61039	0.59693	0.29740
H	1.97903	-3.95588	-1.74373
H	-0.95359	-2.59272	-0.26742
H	-0.11249	-4.25508	-2.69561
H	-5.53187	-0.66000	2.18333
H	-2.02513	-3.36525	-1.43298
H	-3.42520	-1.50974	3.23967
H	-0.08674	-4.78406	-0.99655
N	2.11643	0.92615	0.02829
N	0.08407	-0.71967	-1.84792
N	-2.07518	-0.00390	0.56035
O	0.86629	4.21636	-0.15991
O	-0.19337	2.24386	-0.10097
O	0.20253	-0.81217	1.69766
O	1.30167	-3.31806	-1.49473
O	-0.92179	-1.86079	3.32586
Zn	0.02503	0.23179	-0.01779

Table S7. 2_chelate

E(wb97xd) = -3208.48741959 a.u.

C	-4.08115	-3.14807	-0.53354
C	-3.57421	-2.17897	-1.43410
C	-3.70922	-3.12083	0.78764
C	-2.69613	-1.21160	-1.00965
C	1.85245	-2.23457	-2.30624
C	0.09174	-0.45744	-2.78853
C	2.84084	-2.74151	-1.50545
C	-2.80928	-2.12918	1.25907
C	1.18663	-1.05534	-1.90473
C	-2.28234	-1.17307	0.34706
C	-2.42417	-2.03735	2.61873
C	3.19433	-2.05882	-0.31578
C	4.23121	-2.50847	0.54390
C	2.48394	-0.87138	0.01023
C	-1.58099	-1.03354	3.01300
C	-1.08794	-0.13474	2.04075
C	4.55505	-1.79456	1.67051
C	2.84678	-0.14303	1.17206
C	-0.15027	0.99498	2.46414
C	3.86039	-0.59917	1.98002
H	-4.77173	-3.90533	-0.89140
H	-3.88686	-2.20124	-2.47376
H	1.56050	-2.71082	-3.23428
H	-4.09876	-3.84879	1.49415
H	-2.30930	-0.46455	-1.69406
H	3.36656	-3.65401	-1.77353
H	-2.81186	-2.75776	3.33402
H	4.76182	-3.42157	0.28818
H	0.97868	2.95096	-2.08279
H	-2.53246	2.14926	-0.06221
H	-1.27424	-0.90825	4.04376
H	5.34889	-2.13901	2.32669
H	2.31290	0.77240	1.40261
H	4.13429	-0.03665	2.86740
N	1.47090	-0.41077	-0.78708
N	-1.40213	-0.20726	0.75961
N	1.11804	2.84551	-1.07874
O	-0.14152	-1.00406	-3.87323
O	-0.49552	0.57635	-2.32679
O	-1.79505	2.59623	-0.49641
O	0.32867	1.70359	1.51917
O	0.07385	1.14368	3.67086
Zn	-0.04152	1.20145	-0.43324
H	2.09489	2.57957	-0.96371
C	0.88974	4.14529	-0.41272
H	1.08128	4.00341	0.65424
H	1.59793	4.89175	-0.79074
C	-0.53248	4.65767	-0.62113
H	-0.57072	5.68929	-0.25337
H	-0.76522	4.69499	-1.69344
C	-1.62271	3.89195	0.10717
H	-1.36565	3.76795	1.16566
H	-2.56973	4.43695	0.03375

Table S8. 3_chelate

E(wb97xd) = -3208.47806194 a.u.

C	4.70176	-1.85406	1.24543
C	3.83597	-0.98655	1.95625
C	4.53078	-2.04314	-0.10315
C	2.80839	-0.33531	1.31790
C	-1.58685	-2.05543	2.60275
C	-0.30939	0.13857	2.80353
C	-2.29587	-2.95460	1.85122
C	3.48307	-1.37846	-0.79320
C	-1.10002	-0.88350	1.98451
C	2.60078	-0.52717	-0.07202
C	3.28739	-1.51685	-2.18865
C	-2.54577	-2.68037	0.48459
C	-3.29567	-3.55466	-0.34552
C	0.11831	4.19857	0.54437
C	-2.03275	-1.47170	-0.05977
C	2.27844	-0.82153	-2.79951
C	1.43776	-0.00731	-2.00998
C	-1.28801	3.97190	0.01761
C	-3.53164	-3.23122	-1.65841
C	-2.30229	-1.15217	-1.41483
C	0.31411	0.78621	-2.67383
C	-3.03349	-2.01673	-2.19224
C	-3.05814	2.29706	-0.17494
H	5.50623	-2.35971	1.77049
H	3.99131	-0.83052	3.01952
H	-1.38393	-2.21604	3.65424
H	5.19372	-2.69410	-0.66614
H	2.15111	0.33912	1.85475
H	-2.67903	-3.87182	2.28961
H	0.13605	4.14760	1.63628
H	3.94731	-2.16424	-2.75936
H	-3.68119	-4.47612	0.08163
H	0.48790	5.18054	0.23383
H	-1.90864	2.68009	1.45663
H	1.17525	3.29622	-0.84715
H	-1.94708	4.77860	0.36562
H	2.09975	-0.88039	-3.86594
H	-4.10796	-3.89900	-2.29106
H	-1.93269	-0.21468	-1.81515
H	-1.28119	3.98591	-1.07752
H	-3.41534	1.35628	0.25053
H	-3.81883	3.07173	-0.01317
H	-3.23605	-1.76658	-3.22920
H	-2.90832	2.16273	-1.24881
N	-1.30004	-0.60653	0.70778
N	1.57195	0.12306	-0.70185
N	-1.77695	2.65346	0.44648
O	-0.17611	-0.06924	4.01484
O	0.15449	1.13508	2.15618
O	1.00979	3.16875	0.09645
O	-0.44042	1.44453	-1.88264
O	0.21641	0.74250	-3.90497
Zn	-0.20225	1.20941	0.14207

Table S9. 3_monodentate

E(wb97xd) = -3208.47233371 a.u.

C	-3.94789	-3.64596	-0.43487
C	-2.84724	-3.22918	-1.22298
C	-4.28543	-2.94844	0.69748
C	-2.10013	-2.13153	-0.87124
C	3.41276	-1.65326	-1.77502
C	1.13360	-0.87142	-2.59200
C	4.35713	-1.74220	-0.78687
C	-3.53241	-1.81074	1.08931
C	2.21336	-0.95948	-1.51315
C	-2.42479	-1.39929	0.29791
C	-3.84109	-1.06484	2.25141
C	4.11500	-1.13264	0.46732
C	5.04671	-1.19492	1.53657
C	-2.12974	2.53279	-1.81560
C	2.88693	-0.43995	0.65147
C	-3.06669	0.01395	2.58560
C	-1.97640	0.35310	1.75826
C	-0.89562	3.28095	-1.32220
C	4.76616	-0.58892	2.73541
C	2.62283	0.18520	1.89585
C	-1.08035	1.53151	2.13534
C	3.54422	0.10563	2.91121
C	1.51760	3.12160	-0.98874
H	-4.52231	-4.51771	-0.73177
H	-2.59197	-3.78527	-2.11993
H	3.55334	-2.10471	-2.74891
H	-5.12789	-3.25314	1.31180
H	-1.26798	-1.79939	-1.48177
H	5.29017	-2.27386	-0.95018
H	-2.28616	1.63383	-1.21006
H	-4.68612	-1.35942	2.86722
H	5.98075	-1.72795	1.38436
H	-1.98793	2.21451	-2.85795
H	0.41036	2.14227	-2.38369
H	-3.23923	4.06723	-2.28124
H	-0.75279	4.19882	-1.91172
H	-3.25922	0.61144	3.46771
H	5.47942	-0.63759	3.55206
H	1.69056	0.72495	2.02506
H	-1.03128	3.56329	-0.27387
H	2.37824	2.46634	-1.14348
H	1.66767	4.04898	-1.55544
H	3.33558	0.58469	3.86291
H	1.44136	3.35860	0.07466
N	1.95859	-0.37136	-0.35562
N	-1.66830	-0.31202	0.65610
N	0.29490	2.42170	-1.41019
O	1.38647	-1.34499	-3.70500
O	0.04313	-0.31558	-2.23522
O	-3.30656	3.31358	-1.68376
O	-0.07558	1.72064	1.37414
O	-1.37471	2.19175	3.13687
Zn	0.03720	0.57603	-0.34555

Table S10. 3_monodentate_2

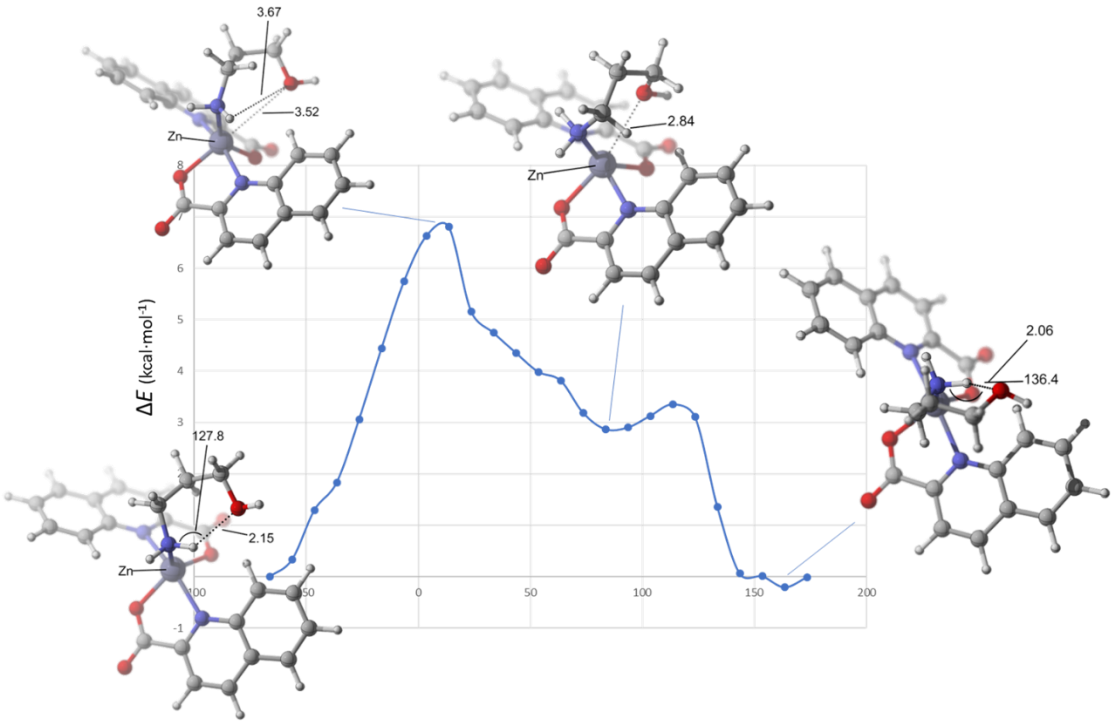
E(wb97xd) = -3208.47417732 a.u.

C	-4.40461	1.84132	-2.59579
C	-3.41556	2.42286	-1.76525
C	-4.47607	0.47706	-2.72664
C	-2.51352	1.64238	-1.08370
C	3.25123	2.49786	-0.81896
C	0.95856	2.72333	0.25093
C	4.27107	1.71916	-1.29656
C	-3.56105	-0.35834	-2.03321
C	2.10733	1.87034	-0.28255
C	-2.56435	0.23068	-1.20646
C	-3.60359	-1.76971	-2.12997
C	4.15755	0.30914	-1.23752
C	5.17420	-0.55620	-1.72043
C	-2.34897	-0.44198	3.06107
C	2.97661	-0.24780	-0.67309
C	-2.70218	-2.52151	-1.42474
C	-1.74238	-1.86490	-0.62750
C	-0.93737	-0.65547	3.56131
C	5.02001	-1.91758	-1.64376
C	2.84599	-1.65731	-0.59385
C	-0.74603	-2.68862	0.18656
C	3.84592	-2.46767	-1.07312
C	1.38720	0.04591	3.35767
H	-5.10470	2.47924	-3.12611
H	-3.37010	3.50317	-1.66448
H	3.29197	3.57994	-0.84000
H	-5.22979	0.01334	-3.35663
H	-1.75477	2.08439	-0.44665
H	5.16592	2.16592	-1.72057
H	-2.41789	-0.69653	1.99705
H	-4.35473	-2.23999	-2.75832
H	6.06979	-0.11763	-2.15133
H	-3.02643	-1.10285	3.61660
H	-0.27032	1.16761	2.97723
H	-0.88864	-0.44625	4.63941
H	-2.70024	-3.60378	-1.45938
H	5.79568	-2.57845	-2.01737
H	1.95128	-2.07519	-0.14551
H	-0.65583	-1.70007	3.40140
H	2.04590	0.76439	2.86374
H	1.43170	0.20972	4.44186
H	3.73487	-3.54587	-1.01188
H	1.74380	-0.96424	3.13881
N	1.96896	0.55695	-0.20806
N	-1.66505	-0.54771	-0.52229
N	0.01892	0.19968	2.84100
O	1.07988	3.95262	0.22031
O	-0.04861	2.07729	0.69046
O	0.11044	-2.01704	0.85236
O	-0.83530	-3.91979	0.14816
Zn	0.03215	0.01868	0.72675
O	-2.69463	0.92498	3.26640
H	-3.45597	1.13813	2.71690

11. Relaxed Potential Energy (PES) scan.

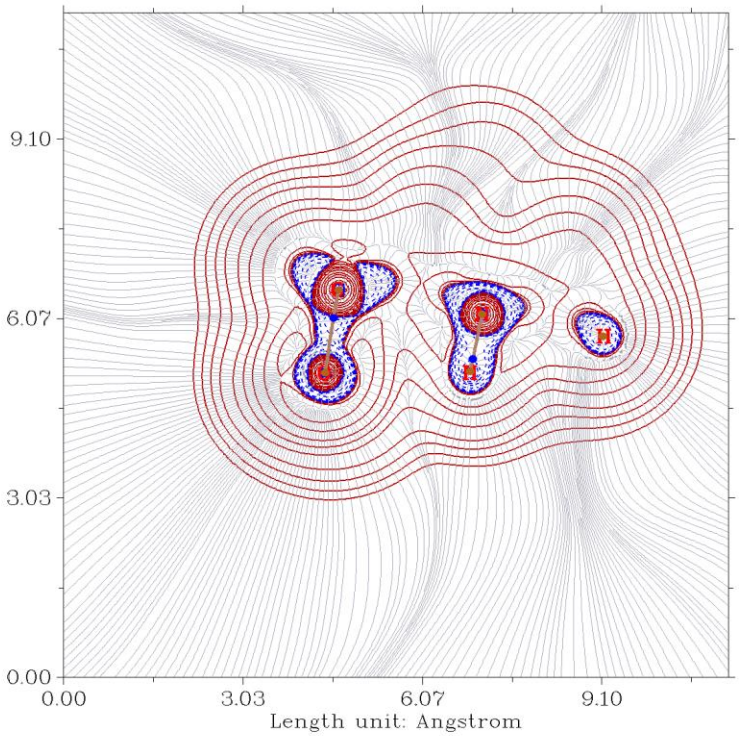
The stabilization induced by the hydrogen bond in **2_monodentate** was further investigated by a Relaxed Potential Energy scan of one of the H–N–C–C dihedral angles of the 3-amino-1-propanol ligand. Starting from the optimized geometry of **2_monodentate**, the energy reaches a relative maximum of *ca*. 7 kcal·mol^{-1} when the dihedral angle amounts to 13.6° and the H···O distance in N–H···O is 3.67 Å. Then, a local minimum (2.9 kcal·mol^{-1}) is located when the dihedral angle is 83.6°, which features a short Zn···OH contact of 2.84 Å. The energy values return to zero at higher values of the angle (*ca*. 160°) when another N–H···O hydrogen bond is installed in the amino alcohol ligand. By this scan, we were able to estimate that due to the N–H···O hydrogen bond in **2_monodentate** the energy lowers by *ca.* 3 kcal·mol^{-1}.

Figure S36. Relaxed Potential Energy scan of one of the H–N–C–C dihedral angles of the 3-amino-1-propanol ligand.



12. AIM analysis of the electron density.

Figure S37. Bond critical points (bcps, blue dots) and bond paths connecting the N–H and O–H atoms of the *N*-methylaminoethanol ligand of **3_monodentate**. No bcp connects the NH and O atoms. The bcps and paths are superimposed on the Laplacian of the electron density ($\nabla^2\rho$, solid red trace and dashed blue trace for positive and negative values, respectively).



The Pointcaré-Hopf relationship was satisfied in the topological analysis.