Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information
for

Piperidine and piperazine analogs in action: zinc(II)-mediated formation of amidines

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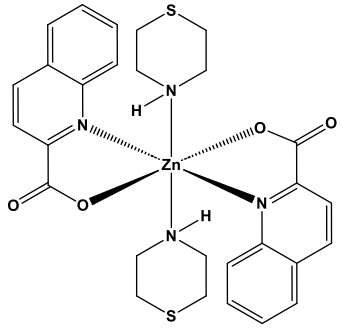
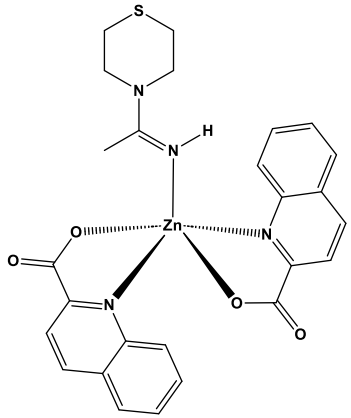
Contents

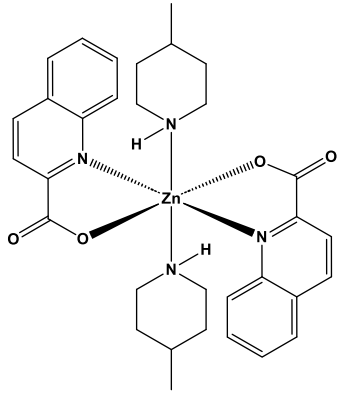
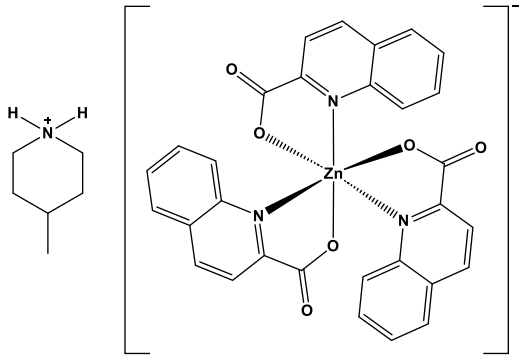
1. List of compounds with numbering scheme and chemical structures. Solvent molecules of crystallization were omitted for clarity.

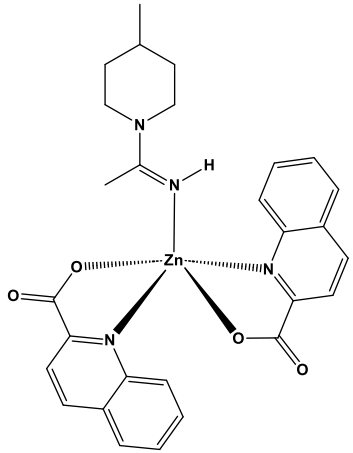
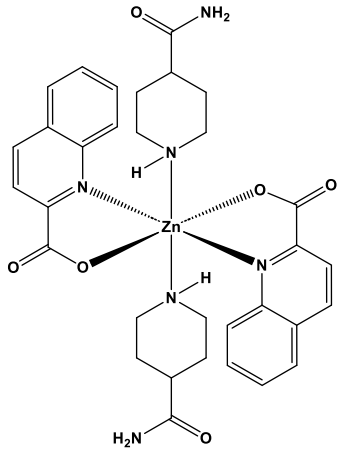
$[Zn(quin)_2(thiomorph)_2]$ **1**

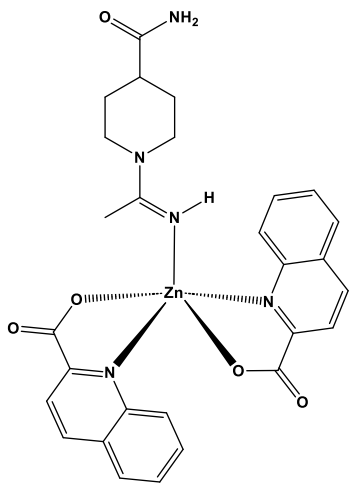
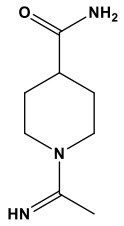


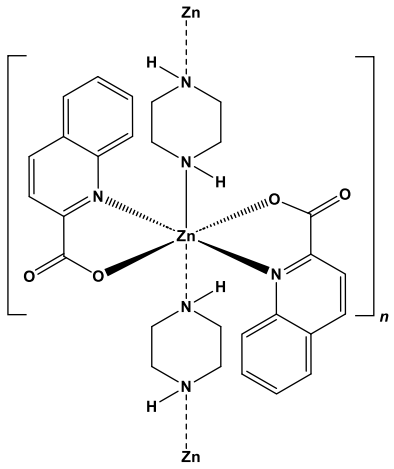
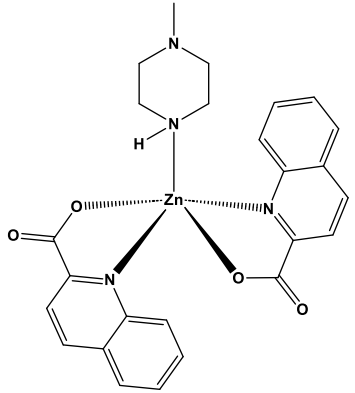
$[Zn(quin)_2(thiomorpham)]\cdot CH_3OH\cdot CH_3CN$ **2**

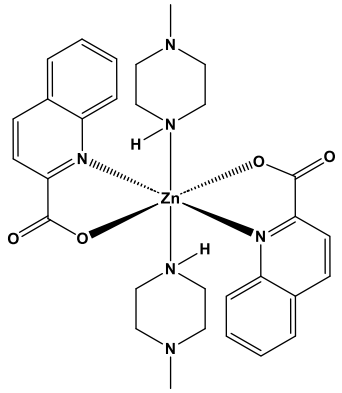
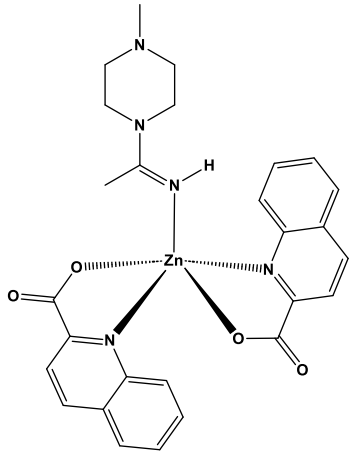


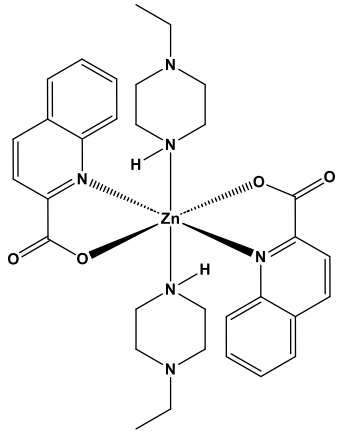
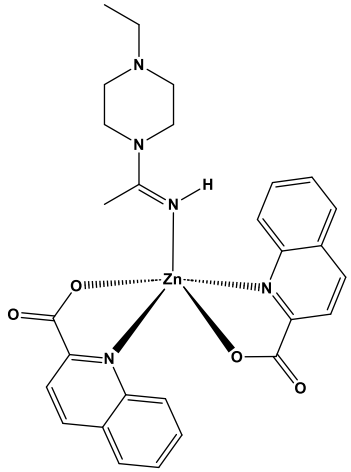
$[Zn(quin)_2(4\text{-}Mepipe)_2]$	**3**	
4-MepipeH$[Zn(quin)_3]$	**4**	

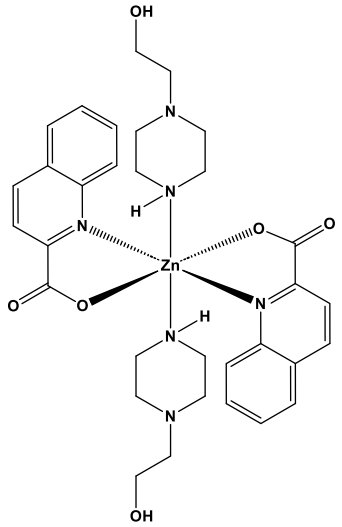
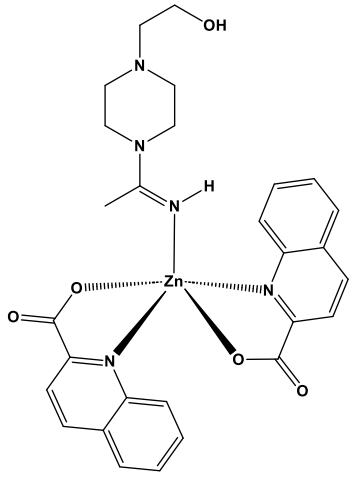
$[Zn(quin)_2(4\text{-Mepipeam})]\cdot CH_3CN$	**5**	
$[Zn(quin)_2(4\text{-amidepipe})_2]\cdot 2CH_3CN$	**6**	

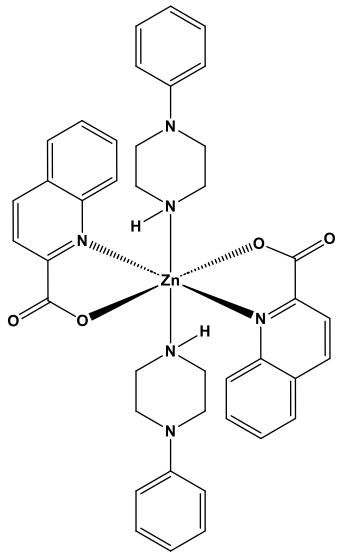
[Zn(quin)$_2$(4-amidepipeam)]	**7**	
4-amidepipeam	**8**	

$[Zn(quin)_2(pz)]_n$	**9**	
$[Zn(quin)_2(1\text{-}Mepz)]$	**10**	

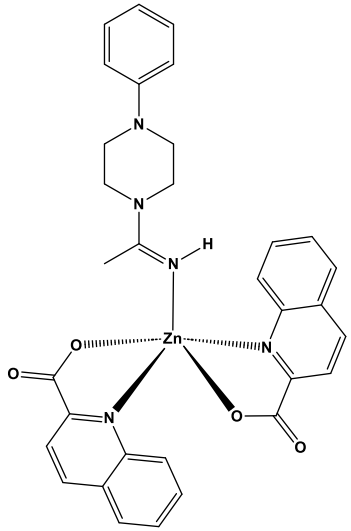
$[Zn(quin)_2(1\text{-}Mepz)_2]\cdot 0.5CH_3CN$	**11**	
$[Zn(quin)_2(1\text{-}Mepzam)]$	**12**	

$[Zn(quin)_2(1\text{-}Etpz)_2]\cdot 0.5CH_3CN$	**13**	
$[Zn(quin)_2(1\text{-}Etpzam)]\cdot H_2O$	**14**	

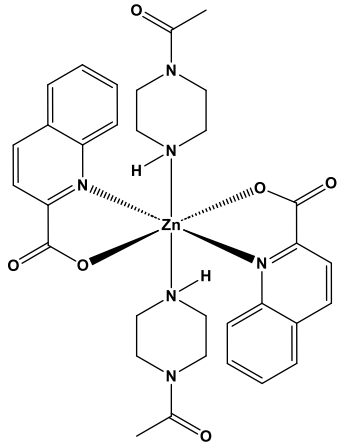
$[Zn(quin)_2(1\text{-}OHEtpz)_2]\cdot 2CH_3CN$	**15**	
$[Zn(quin)_2(1\text{-}OHEtpzam)]$	**16**	

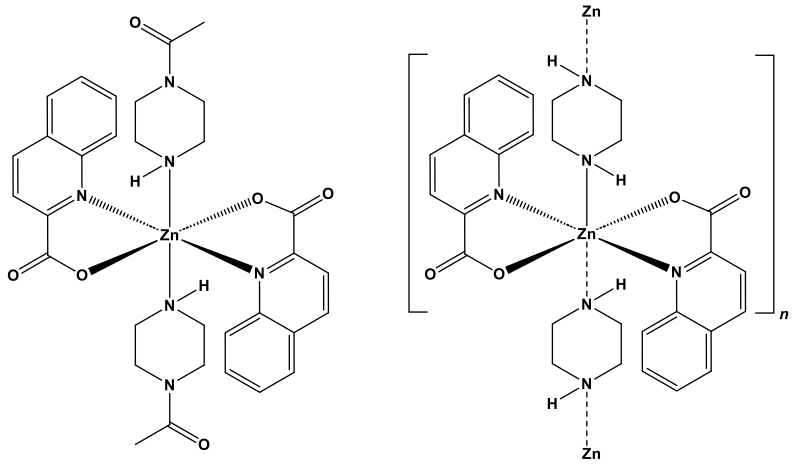
$[Zn(quin)_2(1\text{-}Phpz)_2]\cdot CH_3CN$	**17**	
$[Zn(quin)_2(1\text{-}Phpz)_2]\cdot 2$acetamide	**18** (polymorphs **18a** and **18b**)	see above

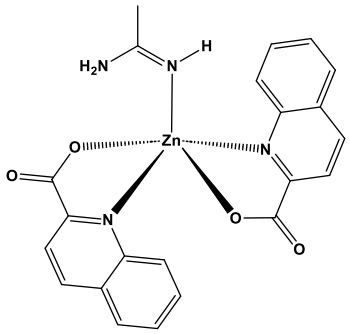
$[Zn(quin)_2(1\text{-}Phpzam)]\cdot 0.5(1\text{-}Phpz)\cdot CH_3CN$ **19**



$[Zn(quin)_2(1\text{-}Acpz)_2]$ **20**



$[Zn(quin)_2(1\text{-}Acpz)_2]\cdot 2CH_3CN$	**21** (polymorphs **21a** and **21b**)	see above
$[Zn(quin)_2(1\text{-}Acpz)_2]\cdot[Zn(quin)_2(pz)]_n\cdot 4CH_3CN$	**22**	

$[Zn(quin)_2(am)]\cdot 1.3CH_3CN\cdot 0.2H_2O$	**23**	

2. X-ray structure determinations

Table S1. Crystallographic data for **1**–**3**.

	[Zn(quin)$_2$(thiomorph)$_2$] (1)	**[Zn(quin)$_2$(thiomorpham)]·CH$_3$CN·CH$_3$OH[a] (2)**	**[Zn(quin)$_2$(4-Mepipe)$_2$] (3)**
Empirical formula	$C_{28}H_{30}N_4O_4S_2Zn$	$C_{29}H_{31}N_5O_5SZn$	$C_{32}H_{38}N_4O_4Zn$
Formula weight	616.05	627.02	608.03
Crystal system	monoclinic	triclinic	triclinic
Space group	$P\,2_1/c$	$P\,\bar{1}$	$P\,\bar{1}$
T **[K]**	150.00(10)	150.00(10)	150.00(10)
λ **[Å]**	0.71073	0.71073	0.71073
a **[Å]**	11.2469(3)	7.6502(2)	10.4859(3)
b **[Å]**	12.7175(3)	13.4372(4)	11.0143(4)
c **[Å]**	9.8919(3)	14.9144(4)	13.4761(3)
α **[°]**	90	82.689(2)	104.223(2)
β **[°]**	102.639(3)	80.642(2)	94.428(2)
γ **[°]**	90	76.138(2)	94.244(3)
V **[Å^3]**	1380.58(7)	1462.45(7)	1497.23(8)
Z	2	2	2
D_{calc} **[g/cm^3]**	1.482	1.424	1.349
μ **[mm^{-1}]**	1.083	0.958	0.863
Collected reflections	40131	28842	26192
Unique reflections	3988	7904	8186
Observed reflections	3484	6752	6638
R_{int}	0.0359	0.0361	0.0279
R_1 ($I > 2\sigma(I)$)	0.0280	0.0309	0.0333
wR_2 **(all data)**	0.0698	0.0761	0.0815

[a] The solvent mask function was applied.

Table S2. Crystallographic data for **5**–**10**.

	[Zn(quin)$_2$(4-Mepipeam)]·CH$_3$CN (5)	**[Zn(quin)$_2$(4-amidepipe)$_2$]·2CH$_3$CN (6)**	**4-amidepipeam (8)**	**[Zn(quin)$_2$(1-Mepz)] (10)**
Empirical formula	$C_{30}H_{31}N_5O_4Zn$	$C_{36}H_{42}N_8O_6Zn$	$C_8H_{15}N_3O$	$C_{25}H_{24}N_4O_4Zn$
Formula weight	590.97	748.14	169.23	509.85
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$	$P\,2_1$	$P\,2_1/n$
***T* [K]**	150.00(10)	150.00(10)	150.00(10)	150.00(10)
λ [Å]	0.71073	0.71073	1.54184	0.71073
***a* [Å]**	7.98150(10)	8.5710(5)	4.96280(10)	10.9883(4)
***b* [Å]**	12.0120(3)	10.9044(7)	12.41770(10)	12.0680(5)
***c* [Å]**	15.0991(3)	10.9382(6)	7.50220(10)	17.4386(6)
α [°]	81.099(2)	108.531(5)	90	90
β [°]	79.411(2)	108.117(5)	100.9800(10)	98.953(4)
γ [°]	85.675(2)	96.396(5)	90	90
***V* [Å^3]**	1404.17(5)	895.82(10)	453.871(12)	2284.30(15)
Z	2	1	2	4
D_{calc} [g/cm^3]	1.398	1.387	1.238	1.483
μ [mm^{-1}]	0.919	0.743	0.684	1.116
Collected reflections	41338	8006	12090	13353
Unique reflections	7828	4590	1759	6051
Observed reflections	6815	4099	1755	4260
R_{int}	0.0344	0.0383	0.0290	0.0351
R_1 ($I > 2\sigma(I)$)	0.0309	0.0397	0.0307	0.0358
wR_2 (all data)	0.0758	0.0849	0.0791	0.0828

Table S3. Crystallographic data for **11**–**13**.

	[Zn(quin)$_2$(1-Mepz)$_2$]·0.5CH$_3$CN (11)	**[Zn(quin)$_2$(1-Mepzam)][a] (12)**	**[Zn(quin)$_2$(1-Etpz)$_2$]·0.5CH$_3$CN (13)**
Empirical formula	$C_{31}H_{37.5}N_{6.5}O_4Zn$	$C_{27}H_{27}N_5O_4Zn$	$C_{33}H_{41.5}N_{6.5}O_4Zn$
Formula weight	630.54	550.90	658.59
Crystal system	triclinic	triclinic	triclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$	$P\,\bar{1}$
***T* [K]**	150.00(10)	150.00(10)	150.00(10)
λ [Å]	0.71073	0.71073	0.71073
***a* [Å]**	10.4192(2)	7.9372(2)	10.5552(4)
***b* [Å]**	14.5738(4)	11.9685(4)	12.0176(5)
***c* [Å]**	20.2693(5)	15.1081(4)	13.4817(6)
α [°]	78.682(2)	79.394(3)	72.156(4)
β [°]	87.613(2)	79.461(2)	86.674(3)
γ [°]	86.401(2)	82.938(2)	86.036(3)
***V* [Å^3]**	3010.68(13)	1380.97(7)	1622.75(12)
Z	4	2	2
D_{calc} [g/cm^3]	1.391	1.325	1.348
μ [mm^{-1}]	0.863	0.929	0.804
Collected reflections	59679	26942	14788
Unique reflections	16415	7547	8464
Observed reflections	12708	6261	6753
R_{int}	0.0294	0.0328	0.0231
R_1 ($I > 2\sigma(I)$)	0.0330	0.0376	0.0371
wR_2 (all data)	0.0899	0.1004	0.0948

[a] The solvent mask function was applied.

Table S4. Crystallographic data for **14**–**16**.

	$[Zn(quin)_2(1\text{-}Etpzam)]\cdot H_2O$ (14)	**$[Zn(quin)_2(1\text{-}OHEtpz)_2]\cdot 2CH_3CN$ (15)**	**$[Zn(quin)_2(1\text{-}OHEtpzam)]$[a] (16)**
Empirical formula	$C_{28}H_{31}N_5O_5Zn$	$C_{36}H_{46}N_8O_6Zn$	$C_{28}H_{29}N_5O_5Zn$
Formula weight	582.95	752.18	580.93
Crystal system	monoclinic	triclinic	triclinic
Space group	$P\,2_1/c$	$P\,\bar{1}$	$P\,\bar{1}$
***T* [K]**	150.00(10)	150.00(10)	150.00(10)
λ [Å]	0.71073	0.71073	0.71073
***a* [Å]**	7.9223(4)	7.8233(2)	7.6949(4)
***b* [Å]**	22.5925(13)	11.2495(2)	13.1323(7)
***c* [Å]**	15.2268(8)	20.2794(6)	15.2125(7)
α [°]	90	87.078(2)	77.884(4)
β [°]	102.820(5)	85.696(2)	78.618(4)
γ [°]	90	86.042(2)	77.812(5)
***V* [Å^3]**	2657.4(3)	1773.59(8)	1450.17(13)
Z	4	2	2
D_{calc} [g/cm^3]	1.457	1.408	1.330
μ [mm^{-1}]	0.973	0.750	0.891
Collected reflections	11925	34681	13965
Unique reflections	5208	9721	7470
Observed reflections	3444	8058	5499
R_{int}	0.0472	0.0368	0.0345
R_1 ($I > 2\sigma(I)$)	0.0464	0.0374	0.0473
wR_2 (all data)	0.0885	0.0899	0.1052

[a] The solvent mask function was applied.

Table S5. Crystallographic data for **17**–**18b**.

	[Zn(quin)$_2$(1-Phpz)$_2$]·CH$_3$CN (17)	**[Zn(quin)$_2$(1-Phpz)$_2$]·2acetamide (18a)**	**[Zn(quin)$_2$(1-Phpz)$_2$]·2acetamide (18b)**
Empirical formula	$C_{42}H_{43}N_7O_4Zn$	$C_{44}H_{50}N_8O_6Zn$	$C_{44}H_{50}N_8O_6Zn$
Formula weight	775.20	852.29	852.29
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P\,2_1/n$	$P\,\bar{1}$	$P\,2_1/c$
T **[K]**	150.00(10)	150.00(10)	150.00(10)
λ **[Å]**	1.54184	0.71073	0.71073
a **[Å]**	13.61490(10)	7.9641(2)	11.2690(2)
b **[Å]**	10.83280(10)	10.7052(4)	17.3987(3)
c **[Å]**	25.0497(3)	12.7812(5)	11.4134(2)
α **[°]**	90	101.629(4)	90
β **[°]**	93.3260(10)	101.475(3)	115.978(2)
γ **[°]**	90	101.582(3)	90
V **[Å^3]**	3688.29(6)	1012.52(6)	2011.68(7)
Z	4	1	2
D_{calc} **[g/cm^3]**	1.396	1.398	1.407
μ **[mm^{-1}]**	1.358	0.667	0.671
Collected reflections	17736	20001	78590
Unique reflections	7509	5524	5875
Observed reflections	6690	4918	5038
R_{int}	0.0237	0.0358	0.0348
R_1 ($I > 2\sigma(I)$)	0.0315	0.0335	0.0297
wR_2 **(all data)**	0.0870	0.0801	0.0791

Table S6. Crystallographic data for **19**–**21a**.

	[Zn(quin)$_2$(1-Phpzam)]·0.5(1-Phpz)·CH$_3$CN[a] (19)	**[Zn(quin)$_2$(1-Acpz)$_2$] (20)**	**[Zn(quin)$_2$(1-Acpz)$_2$]·2CH$_3$CN (21a)**
Empirical formula	$C_{39}H_{39}N_7O_4Zn$	$C_{32}H_{36}N_6O_6Zn$	$C_{36}H_{42}N_8O_6Zn$
Formula weight	735.14	666.04	748.14
Crystal system	triclinic	monoclinic	triclinic
Space group	*P* –1	*P* $2_1/n$	*P* –1
***T* [K]**	150.00(10)	150.00(10)	150.00(10)
λ [Å]	0.71073	0.71073	0.71073
***a* [Å]**	7.6458(2)	9.9752(3)	10.5815(4)
***b* [Å]**	15.0408(4)	11.1948(3)	12.3264(5)
***c* [Å]**	16.2179(4)	14.1436(4)	13.5644(6)
α [°]	72.152(2)	90	86.699(4)
β [°]	81.180(2)	105.524(3)	87.372(3)
γ [°]	80.559(2)	90	82.306(3)
***V* [Å^3]**	1740.66(8)	1521.80(8)	1749.09(12)
Z	2	2	2
D_{calc} [g/cm^3]	1.403	1.454	1.421
μ [mm^{-1}]	0.758	0.863	0.761
Collected reflections	34456	29908	17384
Unique reflections	9515	4320	9087
Observed reflections	8029	3716	6266
R_{int}	0.0354	0.0396	0.0331
R_1 ($I > 2\sigma(I)$)	0.0319	0.0297	0.0395
wR_2 (all data)	0.0830	0.0728	0.0820

[a] The solvent mask function was applied.

Table S7. Crystallographic data for **21b**–**23**.

	[Zn(quin)$_2$(1-Acpz)$_2$]·2CH$_3$CN (21b)	**[Zn(quin)$_2$(1-Acpz)$_2$]·[Zn(quin)$_2$(pz)]$_n$·4CH$_3$CN (22)**	**[Zn(quin)$_2$(am)]·1.3CH$_3$CN·0.2H$_2$O (23)**
Empirical formula	$C_{36}H_{42}N_8O_6Zn$	$C_{64}H_{70}N_{14}O_{10}Zn_2$	$C_{24.7}H_{22.4}N_{5.3}O_{4.2}Zn$
Formula weight	748.14	1326.08	526.12
Crystal system	monoclinic	triclinic	triclinic
Space group	$P\,2_1/n$	$P\,\bar{1}$	$P\,\bar{1}$
T **[K]**	150.00(10)	150.00(10)	150.00(10)
λ **[Å]**	1.54184	0.71073	0.71073
a **[Å]**	13.7663(4)	7.3460(2)	8.1567(3)
b **[Å]**	7.4819(2)	13.6349(3)	9.9520(4)
c **[Å]**	17.7683(5)	15.7320(4)	15.1357(6)
α **[°]**	90	90.652(2)	77.896(4)
β **[°]**	103.158(3)	96.810(2)	78.984(3)
γ **[°]**	90	96.254(2)	84.021(3)
V **[Å^3]**	1782.05(9)	1554.85(7)	1176.56(8)
Z	2	1	2
D_{calc} **[g/cm^3]**	1.394	1.416	1.485
μ **[mm^{-1}]**	1.432	0.842	1.088
Collected reflections	7240	45344	10357
Unique reflections	3602	8691	5608
Observed reflections	3134	6913	4591
R_{int}	0.0254	0.0397	0.0280
R_1 ($I > 2\sigma(I)$)	0.0496	0.0368	0.0388
wR_2 (all data)	0.1439	0.0969	0.0894

Crystal structures of zinc(II) complexes with amines

Figure S1. ORTEP diagram of $[Zn(quin)_2(thiomorph)_2]$ (**1**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

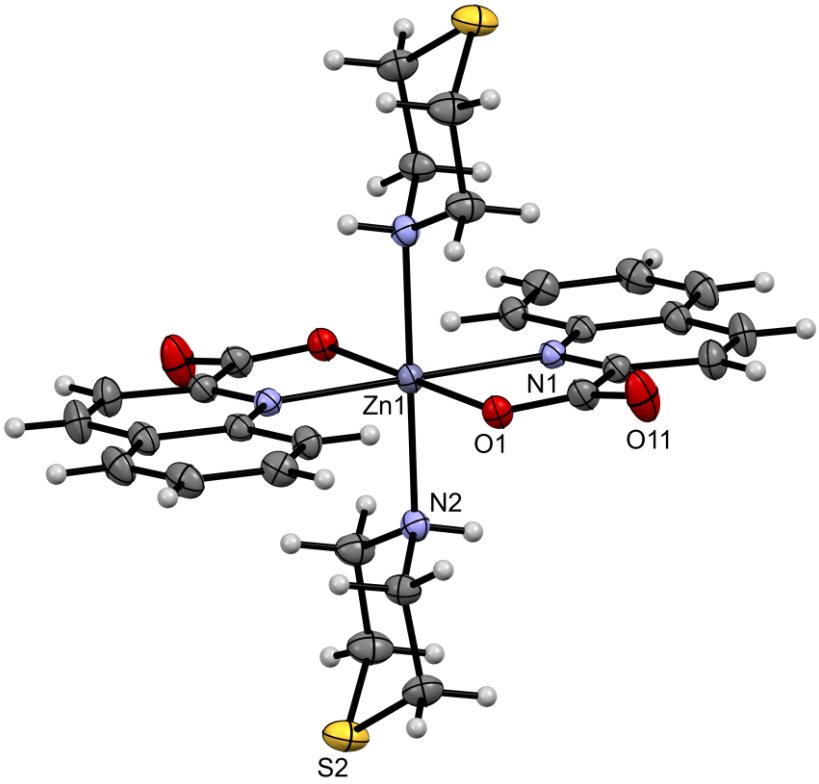


Figure S2. ORTEP diagram of [Zn(quin)$_2$(4-Mepipe)$_2$] (**3**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

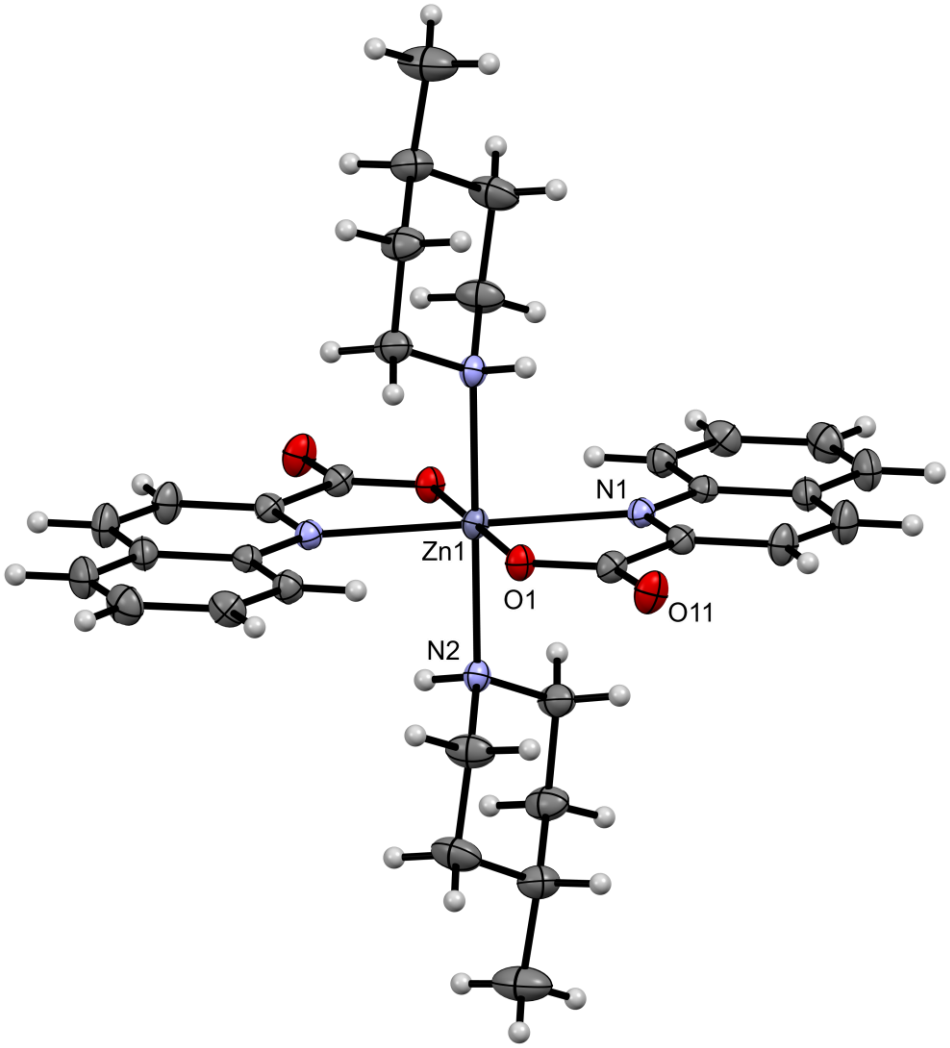


Figure S3. ORTEP diagram of $[Zn(quin)_2(4\text{-amidepipe})_2]$, found in **6**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

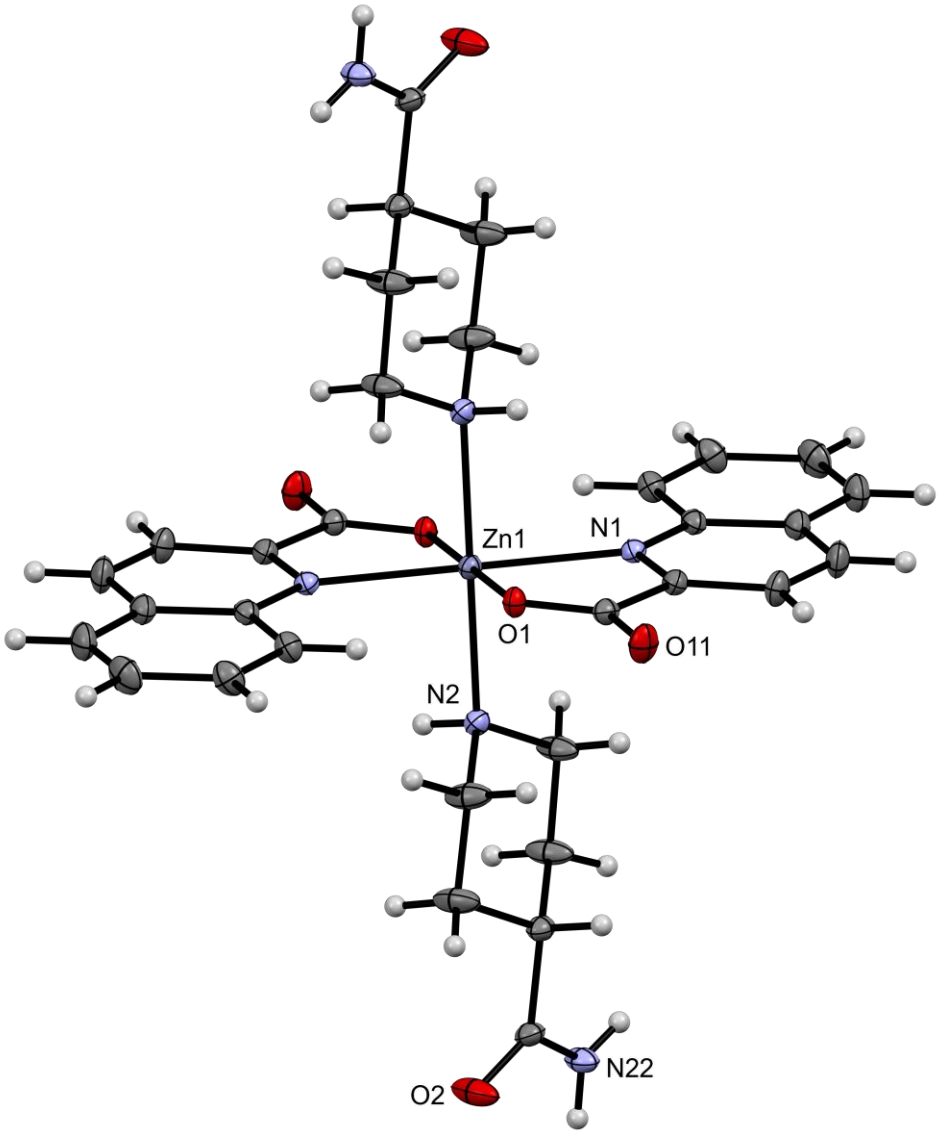


Figure S4. ORTEP diagram of $[Zn(quin)_2(1\text{-}Etpz)_2]$, found in **13**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

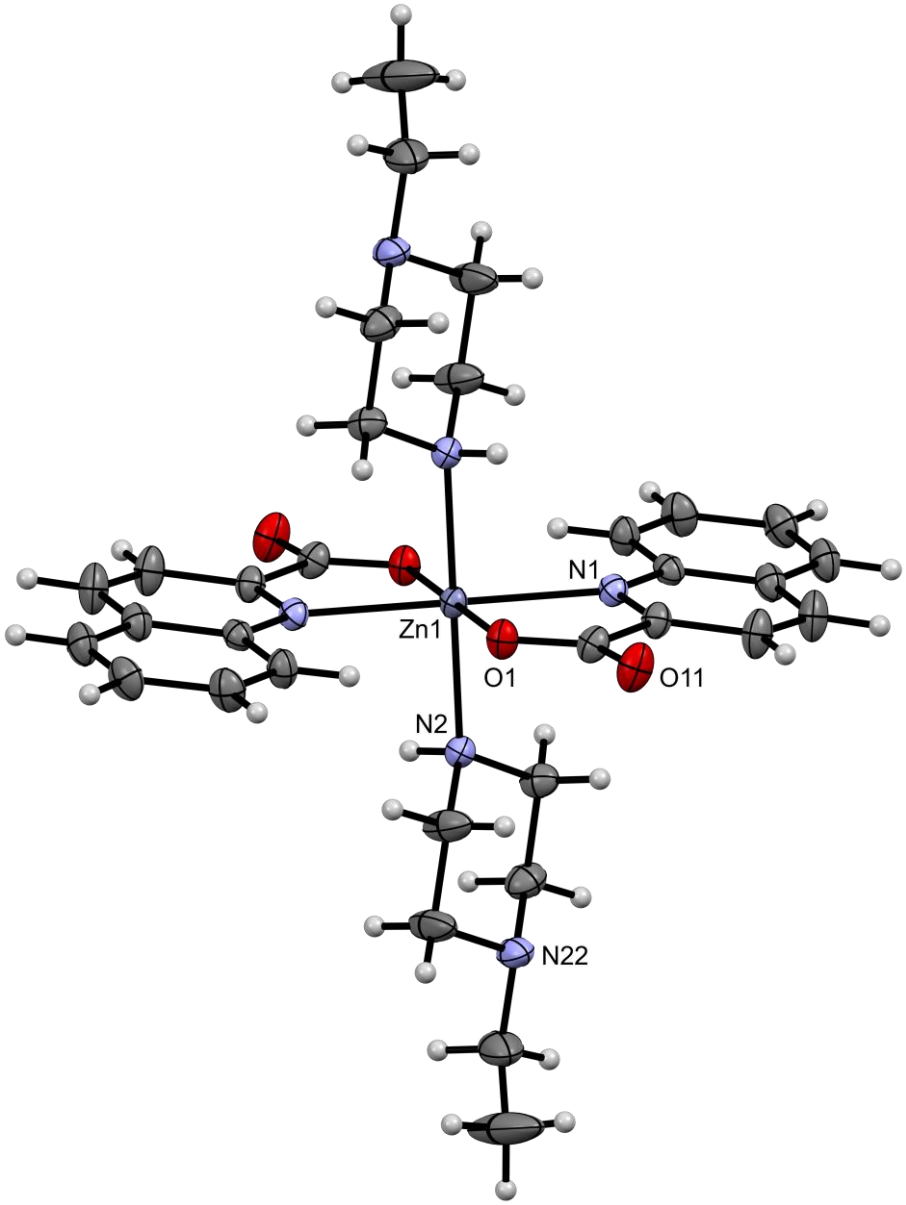


Figure S5. ORTEP diagram of $[Zn(quin)_2(1\text{-}OHEtpz)_2]$, found in **15**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

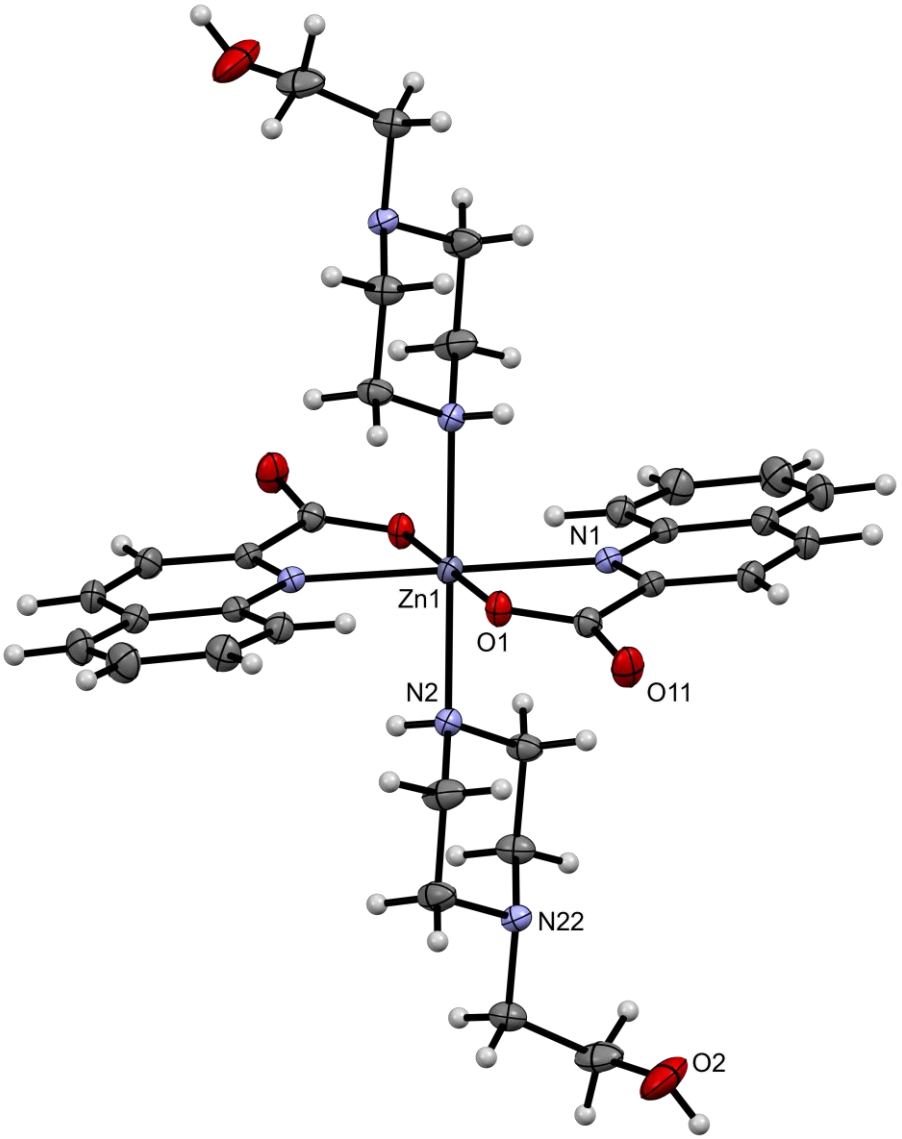


Figure S6. ORTEP diagram of [Zn(quin)$_2$(1-Phpz)$_2$], found in **17**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

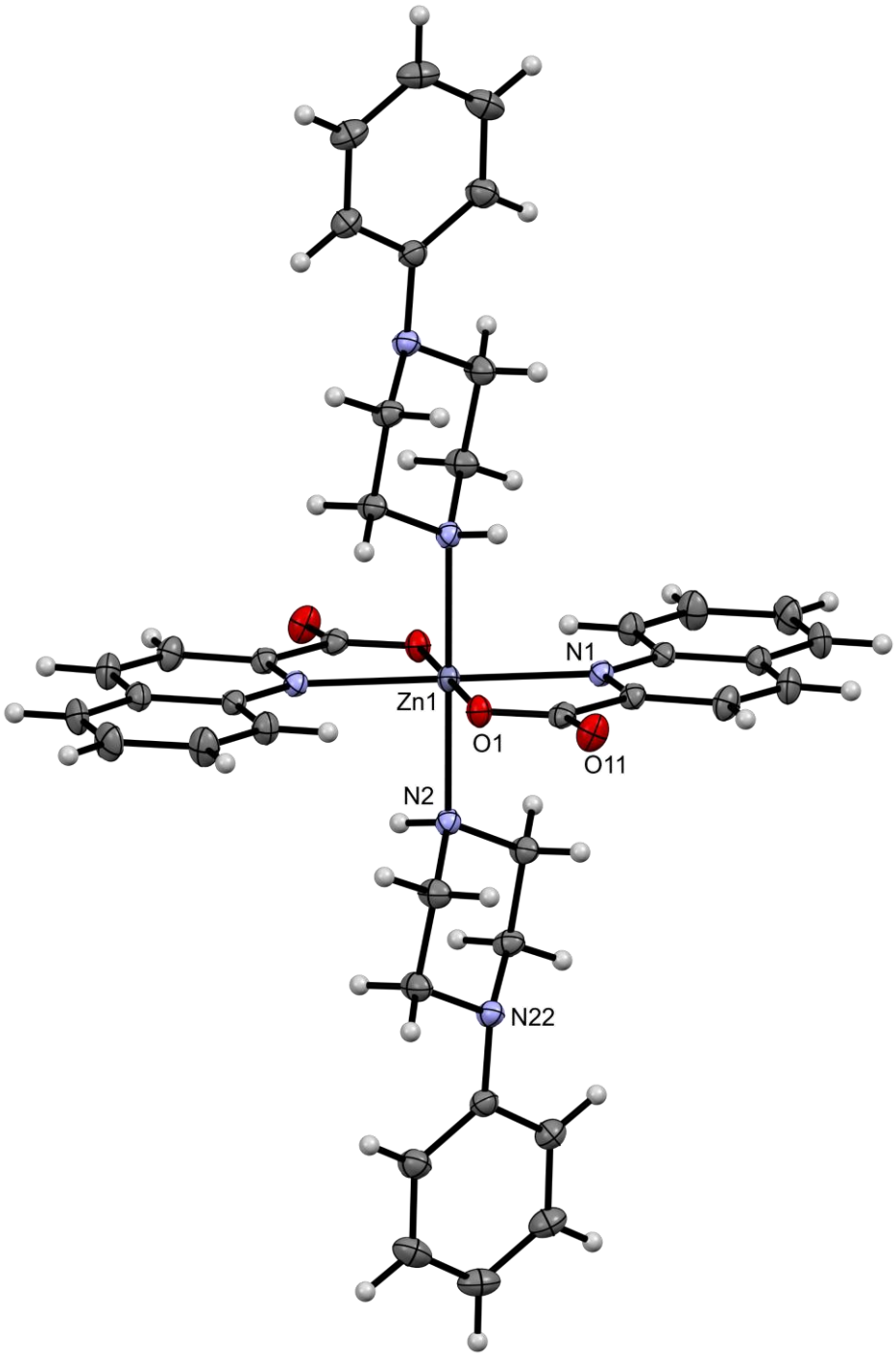
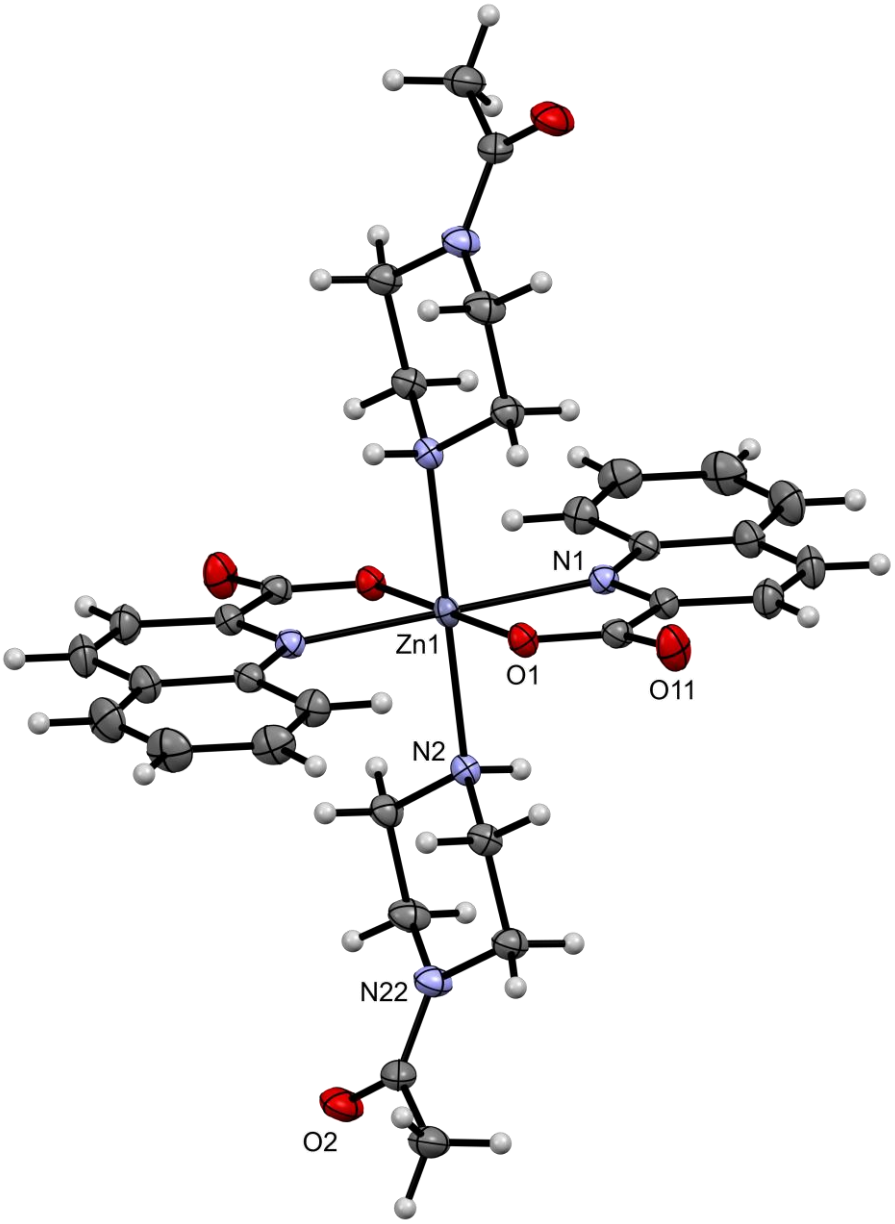


Figure S7. ORTEP diagram of $[Zn(quin)_2(1\text{-}Acpz)_2]$ (**20**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



Crystal structures of zinc(II) complexes with amidines

Figure S8. ORTEP diagram of [Zn(quin)$_2$(thiomorpham)], found in **2**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

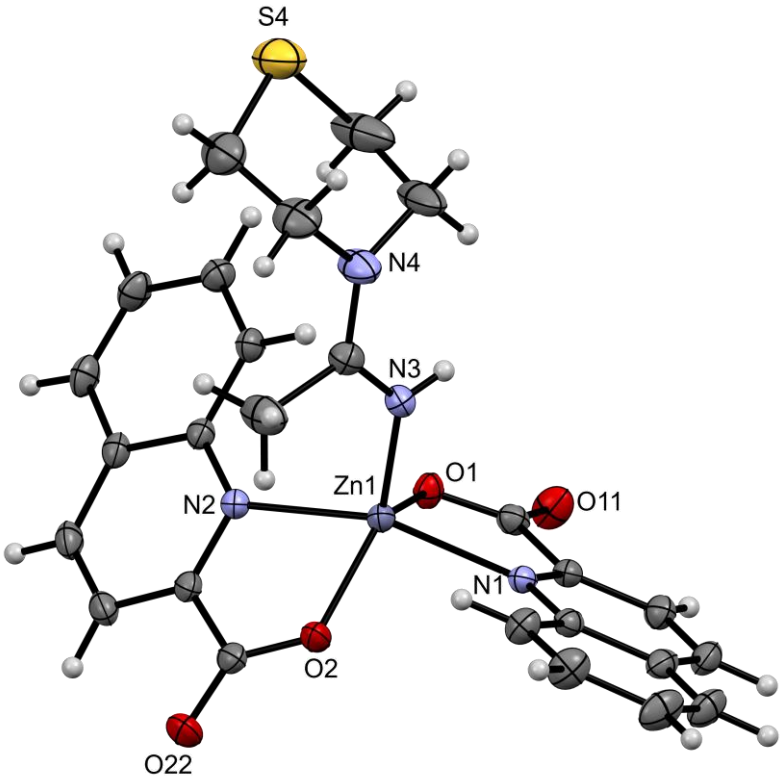


Figure S9. ORTEP diagram of [Zn(quin)$_2$(4-Mepipeam)], found in **5**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

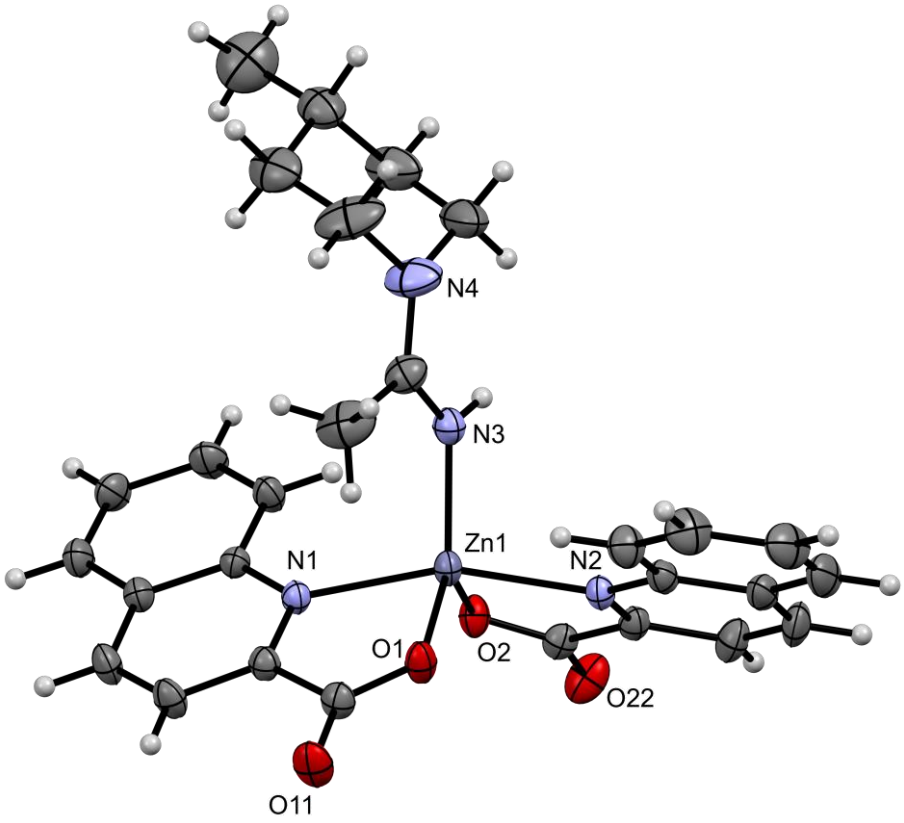


Figure S10. ORTEP diagram of [Zn(quin)$_2$(1-Mepzam)], found in **12**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

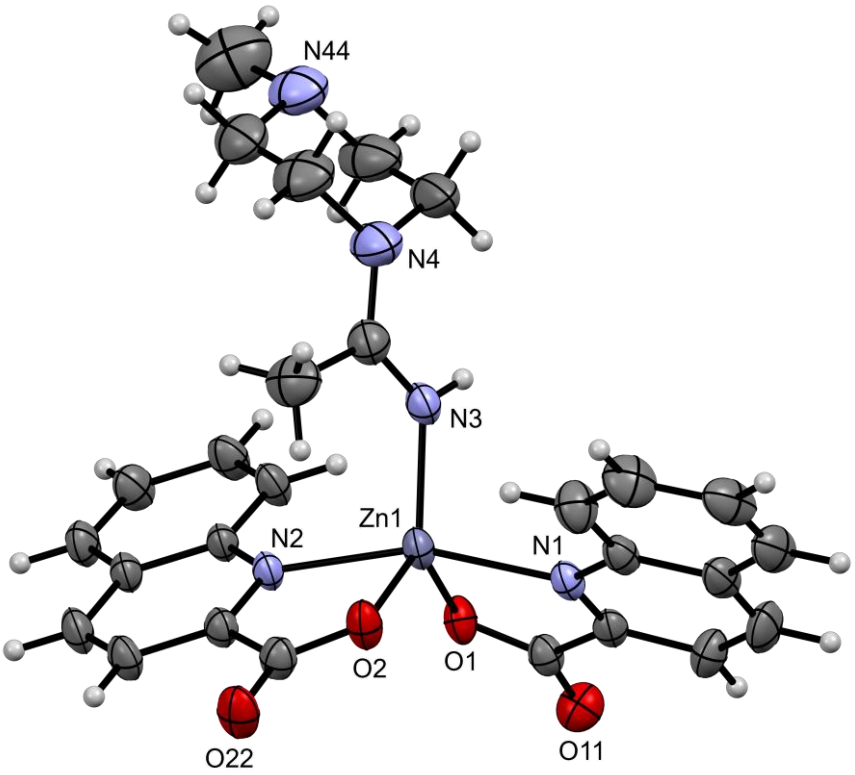


Figure S11. ORTEP diagram of [Zn(quin)$_2$(1-Etpzam)], found in **14**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

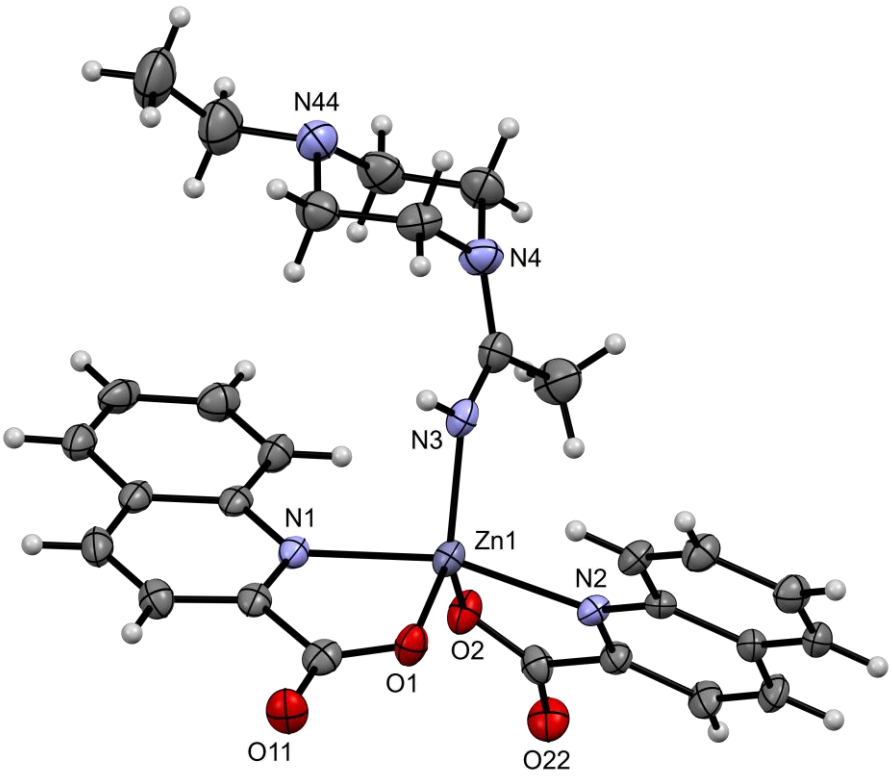
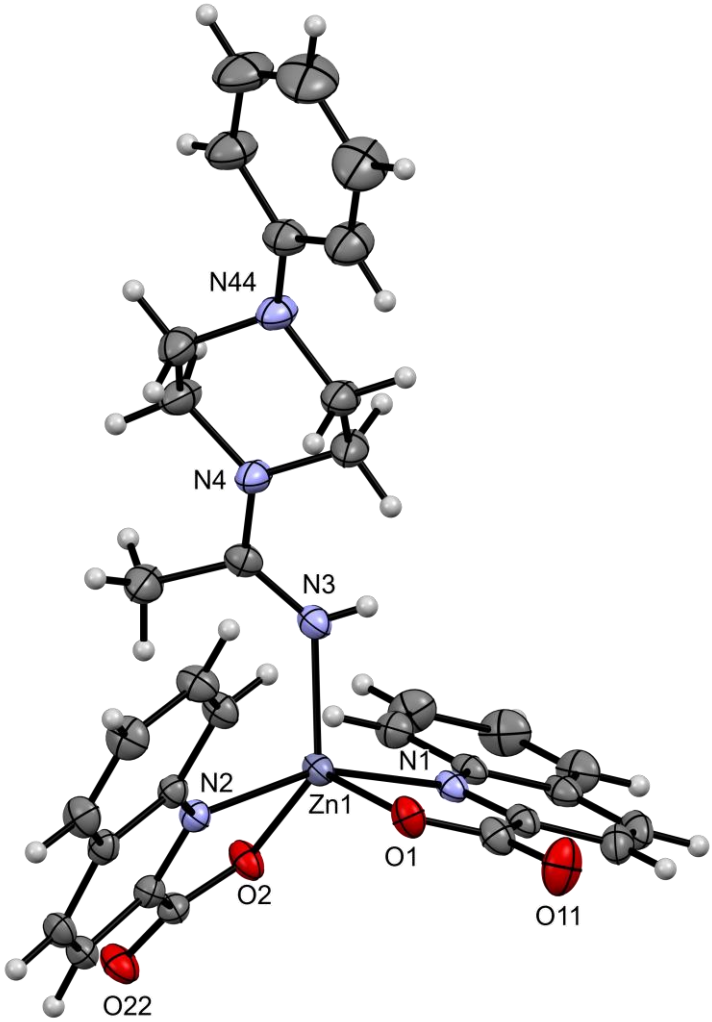
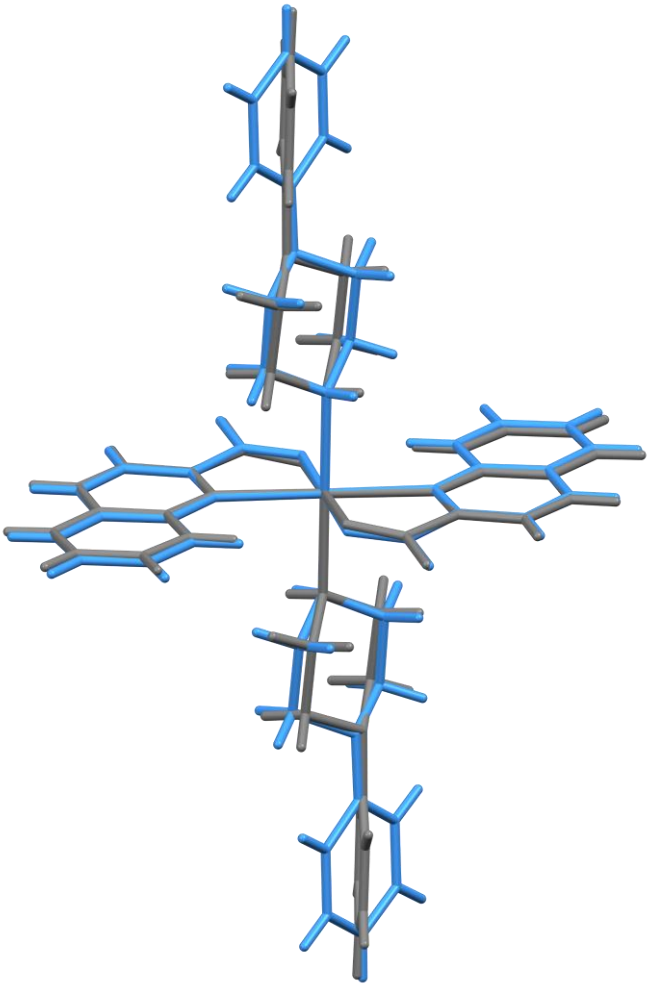


Figure S12. ORTEP diagram of [Zn(quin)$_2$(1-Phpzam)], found in **19**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



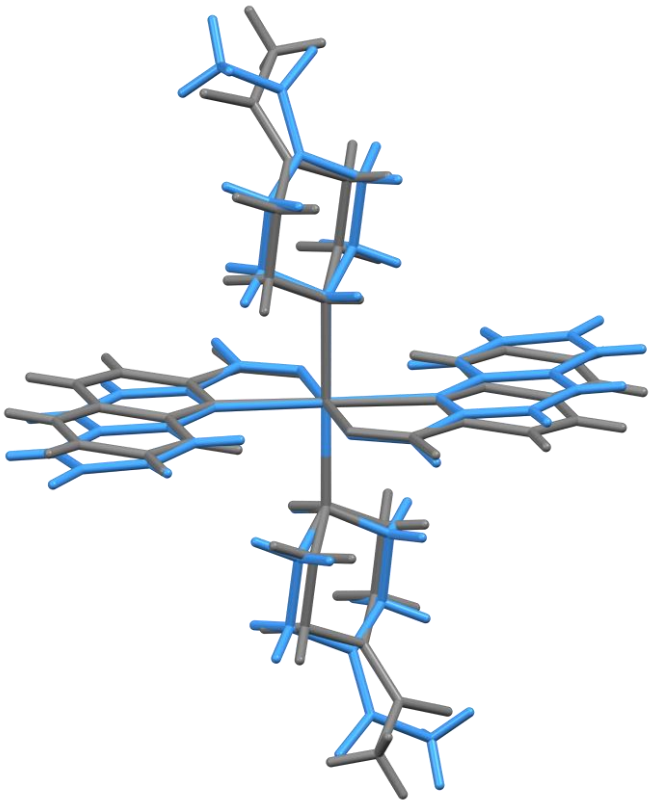
Polymorphism

Figure S13. Overlay of $[Zn(quin)_2(1\text{-}Phpz)_2]$ complex molecules, found in **18a** and **18b** polymorphs. The root mean square deviation value was 0.3471 and the maximum distance between equivalent atoms was 0.8221 Å. Color code: gray – **18a**, blue – **18b**. The overlay was done by Mercury.[S1]



[S1] Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; Wood, P.A. *J. Appl. Cryst.* **2020**, *53*, 226–235, doi:10.1107/S1600576719014092.

Figure S14. Overlay of $[Zn(quin)_2(1\text{-}Acpz)_2]$ complex molecules, found in **21a** and **21b** polymorphs. The RMSD values were 0.7989 and 0.8360 and the maximum distances were 2.8186 and 2.9406 Å. Two values are given because the asymmetric unit of **21a** contains two halves of complex molecules. Color code: gray – **21a**, blue – **21b**. The overlay was done by Mercury.[S1]



[S1] Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; Wood, P.A. *J. Appl. Cryst.* **2020**, *53*, 226–235, doi:10.1107/S1600576719014092.

Intermolecular interactions

Table S8. Hydrogen bond parameters for compounds with coordinated amines [Å].

Compound	Hydrogen bond	Donor···acceptor
$[Zn(quin)_2(thiomorph)_2]$ (**1**)	NH···COO^-	N···O [1–*x*, 0.5+*y*, 1.5–*z*] = 2.8782(15)
$[Zn(quin)_2(4\text{-Mepipe})_2]$ (**3**)	NH···COO^-	N···O = 2.9180(17)
	NH···COO^-	N···O [1–*x*, 1–*y*, 1–*z*] = 2.9756(18)
$[Zn(quin)_2(4\text{-amidepipe})_2]\cdot 2CH_3CN$ (**6**)	NH_2···COO^-	N···O [–1+*x*, *y*, *z*] = 2.912(2)
	NH_2···O(amide)	N···O [–*x*, –*y*, –*z*] = 2.916(2)
$[Zn(quin)_2(1\text{-Mepz})]$ (**10**)	NH···COO^-	N···O [0.5–*x*, –0.5+*y*, 1.5–*z*] = 2.905(2)
$[Zn(quin)_2(1\text{-Mepz})_2]\cdot 0.5CH_3CN$ (**11**)	NH···COO^-	N···O = 2.9983(16)
	NH···COO^-	N···O = 2.8685(16)
	NH···COO^-	N···O = 3.0076(16)
$[Zn(quin)_2(1\text{-Etpz})_2]\cdot 0.5CH_3CN$ (**13**)	NH···COO^-	N···O = 2.892(2)
	NH···COO^-	N···O [*x*, *y*, 1+*z*] = 3.007(2)
$[Zn(quin)_2(1\text{-OHEtpz})_2]\cdot 2CH_3CN$ (**15**)	OH···COO^-	O···O = 2.6823(18)
	NH···OH	N···O [1+*x*, *y*, *z*] = 3.057(2)
$[Zn(quin)_2(1\text{-Phpz})_2]\cdot CH_3CN$ (**17**)	NH···COO^-	N···O = 2.9177(15)
	NH···COO^-	N···O [1+*x*, *y*, *z*] = 3.0236(14)
$[Zn(quin)_2(1\text{-Phpz})_2]\cdot$2acetamide, triclinic (**18a**)	NH···O(acetamide)	N···O [–1+*x*, –1+*y*, *z*] = 2.9871(17)
	NH_2(acetamide)···O(acetamide)	N···O [2–*x*, 2–*y*, 1–*z*] = 2.8955(19)
	NH_2(acetamide)···COO^-	N···O = 2.8939(17)
$[Zn(quin)_2(1\text{-Phpz})_2]\cdot$2acetamide, monoclinic (**18b**)	NH···O(acetamide)[a]	N···O = 2.9821(15)
$[Zn(quin)_2(1\text{-Acpz})_2]$ (**20**)	NH···O(1-Acpz)	N···O [0.5–*x*, 0.5+*y*, 1.5–*z*] = 2.9130(14)
$[Zn(quin)_2(1\text{-Acpz})_2]\cdot 2CH_3CN$, triclinic (**21a**)	NH···COO^-	N···O = 2.903(2)
	NH···COO^-	N···O [*x*, *y*, 1+*z*] = 2.977(2)
$[Zn(quin)_2(1\text{-Acpz})_2]\cdot 2CH_3CN$, monoclinic (**21b**)	NH···COO^-	N···O [1–*x*, 2–*y*, 1–*z*] = 2.944(2)
$[Zn(quin)_2(1\text{-Acpz})_2]\cdot[Zn(quin)_2(pz)]_n\cdot 4CH_3CN$ (**22**)	NH···COO^-	N···O [–1+*x*, *y*, *z*] = 2.910(2)
	NH···O(1-Acpz)	N···O = 3.028(2)

[a] Contact NH_2(acetamide)···COO^- (3.0704(17) Å) is longer than the sum of van der Waals radii.[S2]

[S2] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451, doi:10.1021/j100785a001.

Table S9. Hydrogen bond parameters for compounds with coordinated amidines [Å].

Compound	Hydrogen bond	Donor···acceptor
$[Zn(quin)_2(thiomorpham)]\cdot CH_3CN\cdot CH_3OH$ (**2**)	$OH(CH_3OH)\cdots COO^-$	O···O [*x*, 1+*y*, *z*] = 2.690(2)
	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 2.9473(17)
$[Zn(quin)_2(4\text{-}Mepipeam)]\cdot CH_3CN$ (**5**)	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 3.0239(16)
$[Zn(quin)_2(1\text{-}Mepzam)]$ (**12**)	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 2.991(2)
$[Zn(quin)_2(1\text{-}Etpzam)]\cdot H_2O$ (**14**)	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 3.012(3)
	$OH(H_2O)\cdots COO^-$	O···O [1–*x*, –0.5+*y*, 1.5–*z*] = 2.783(4)
	$OH(H_2O)\cdots N(pz)$	O···N [1+*x*, *y*, *z*] = 2.970(4)
$[Zn(quin)_2(1\text{-}OHEtpzam)]$ (**16**)	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 2.974(3)
	$OH(pz)\cdots COO^-$	O···O [–1+*x*, 1+*y*, *z*] = 2.735(3)
$[Zn(quin)_2(1\text{-}Phpzam)]\cdot 0.5(1\text{-}Phpz)\cdot CH_3CN$ (**19**)	$NH\cdots COO^-$	N···O [1+*x*, *y*, *z*] = 3.0533(17)
$[Zn(quin)_2(am)]\cdot 1.3CH_3CN\cdot 0.2H_2O$ (**23**)	$NH\cdots COO^-$	N···O [–1+*x*, *y*, *z*] = 2.928(2)
	$NH_2\cdots COO^-$	N···O [*x*, 1+*y*, *z*] = 2.862(3)

Figure S15. Hydrogen bonding pattern in $[Zn(quin)_2(4\text{-Mepipe})_2]$ (**3**). The N–H···COO^- bonds link the complex molecules into supramolecular chains that run along the *c*-axis. A section of a chain is shown.

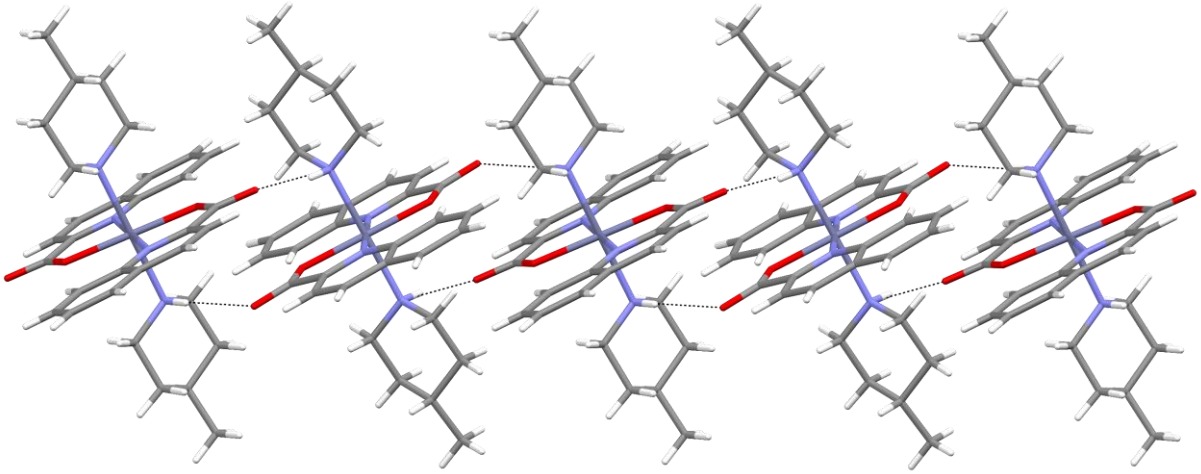


Figure S16. Hydrogen bonding pattern in $[Zn(quin)_2(1\text{-Mepz})]$ (**10**). The N–H···COO^- bonds link the complex molecules into supramolecular chains that run along the *b*-axis. A section of a chain is shown.

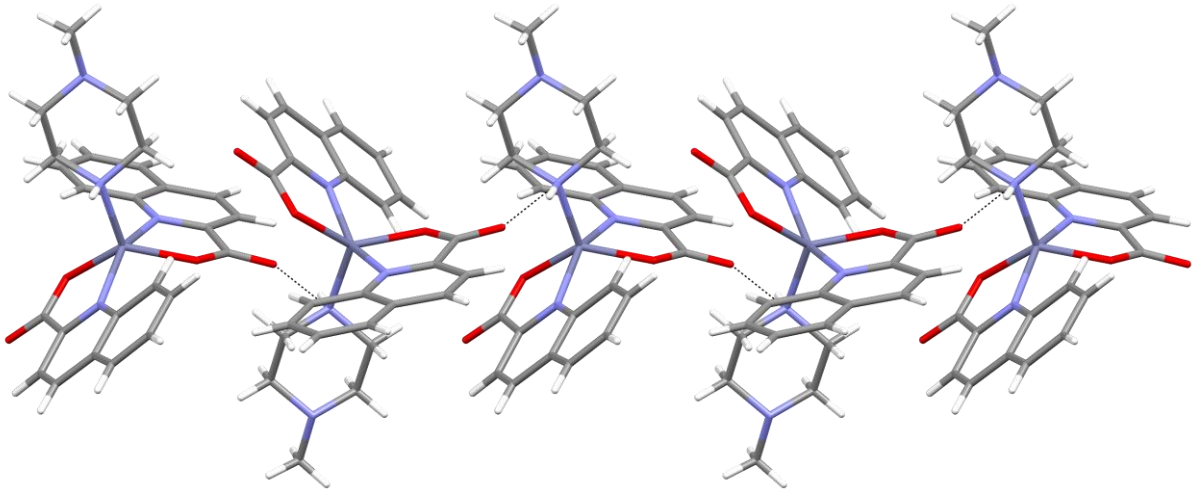


Figure S17. Hydrogen bonding pattern in 4-carboxamidopiperidinoacetamidine (**8**). The NH_2(amine)···NH(imine) (N···N = 2.961(2) Å) and NH_2(amine)···O(carbonyl) (N···O = 2.935(2) Å) bonds link the molecules into supramolecular layers (top). Stacking of such layers is shown in the bottom figure.

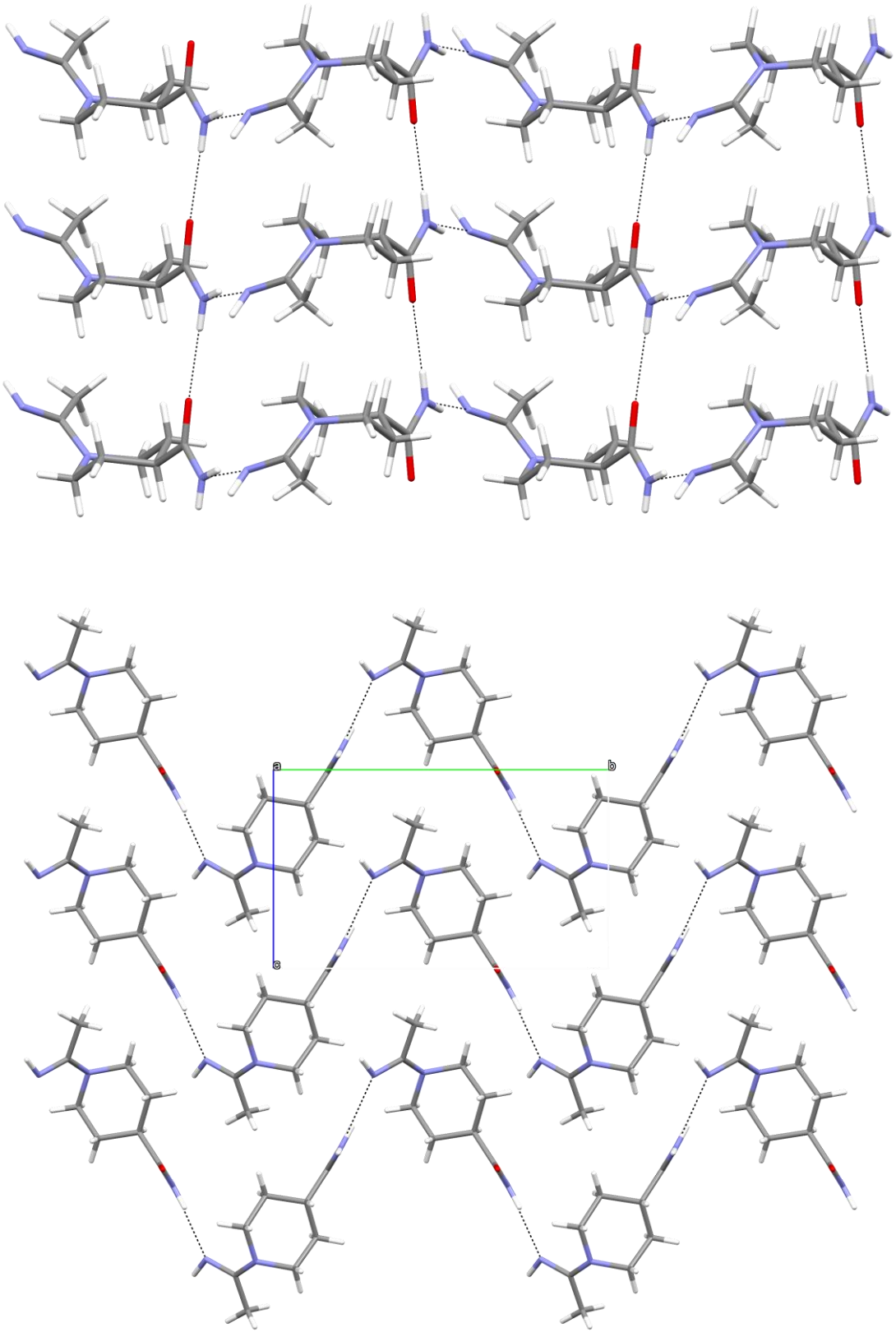


Figure S18. Hydrogen bonding pattern in $[Zn(quin)_2(1\text{-}Etpzam)]\cdot H_2O$ (**14**). A section of a layer of hydrogen bonded complex molecules and water is shown.

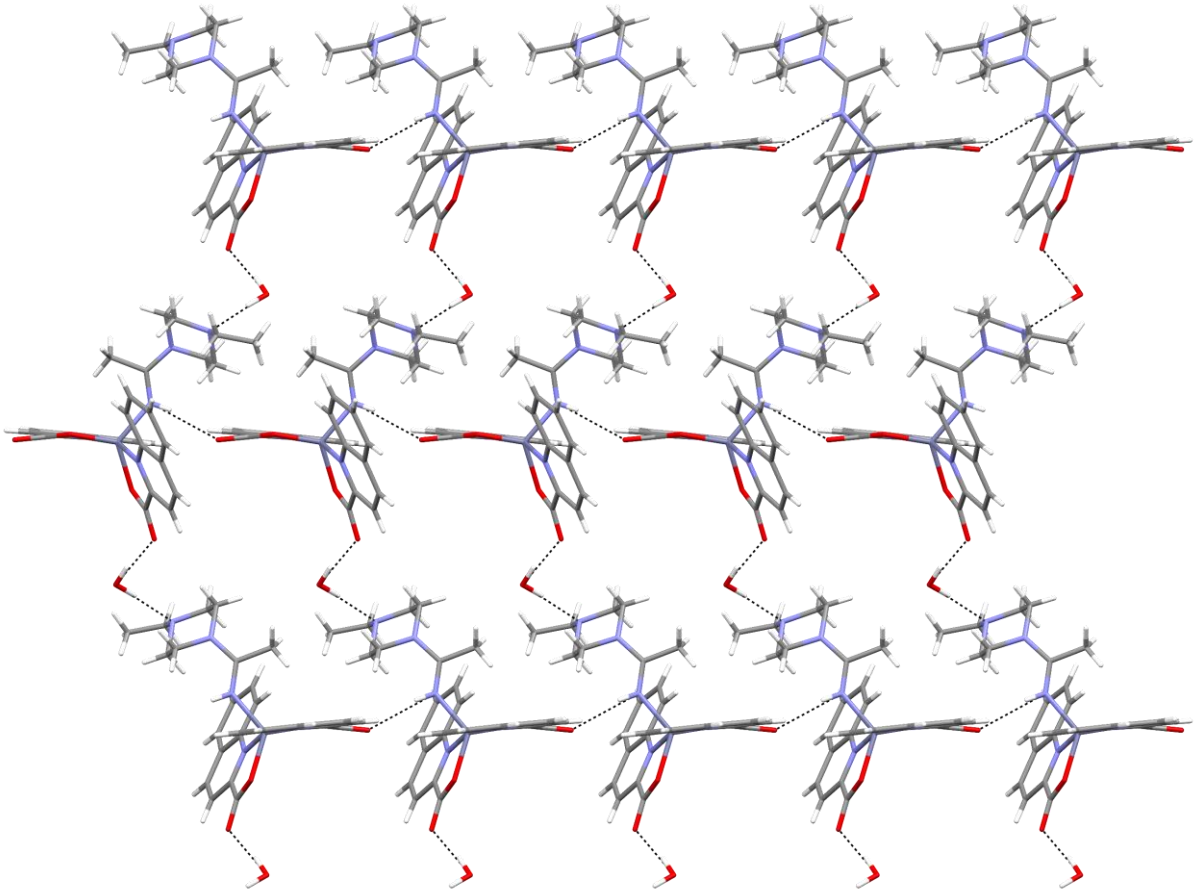


Figure S19. Differences in the crystal structures of the $[Zn(quin)_2(1\text{-}Phpz)_2]\cdot 2$acetamide polymorphs: packing in **18a** (top) and **18b** (bottom). The complex molecules are colored gray and acetamide is colored red.

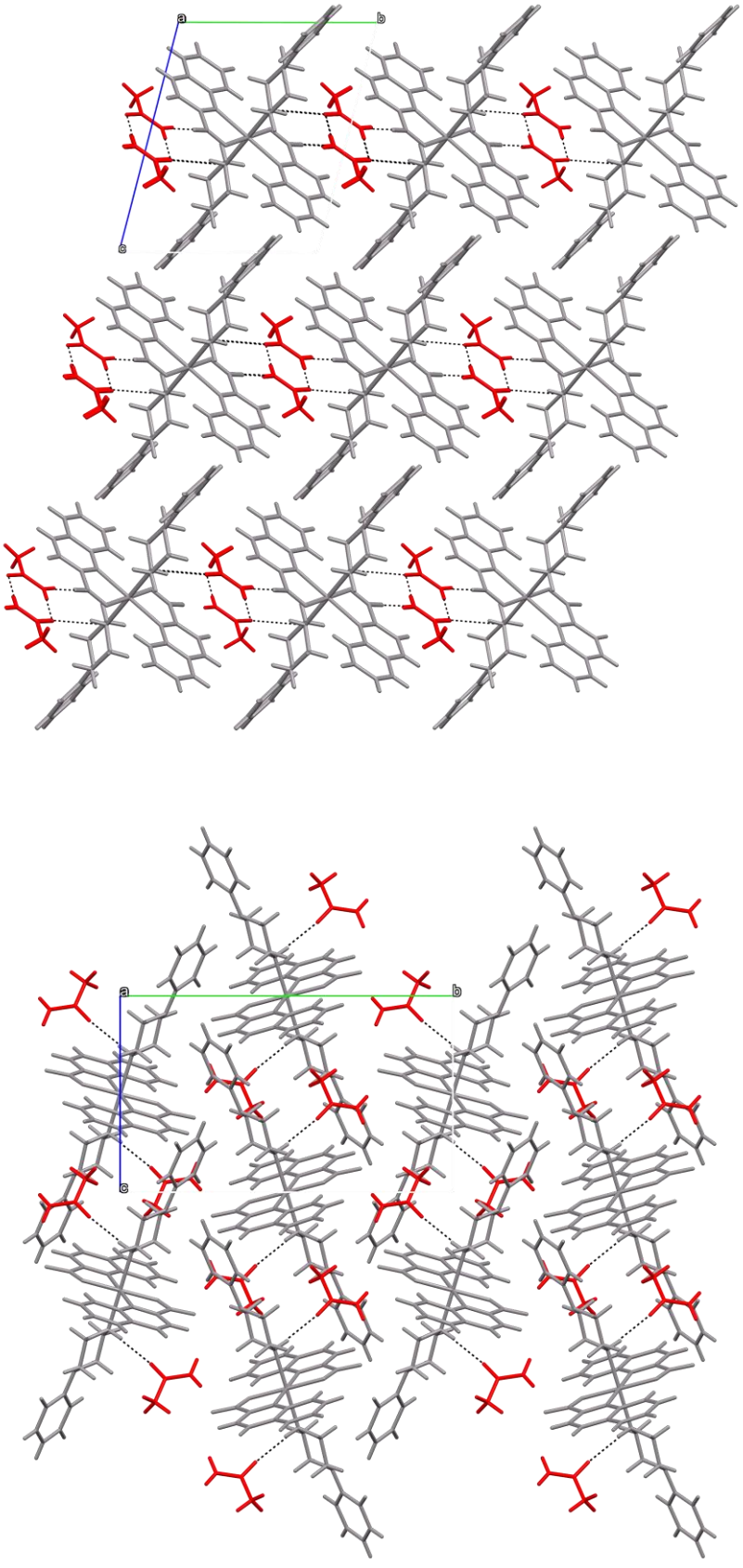
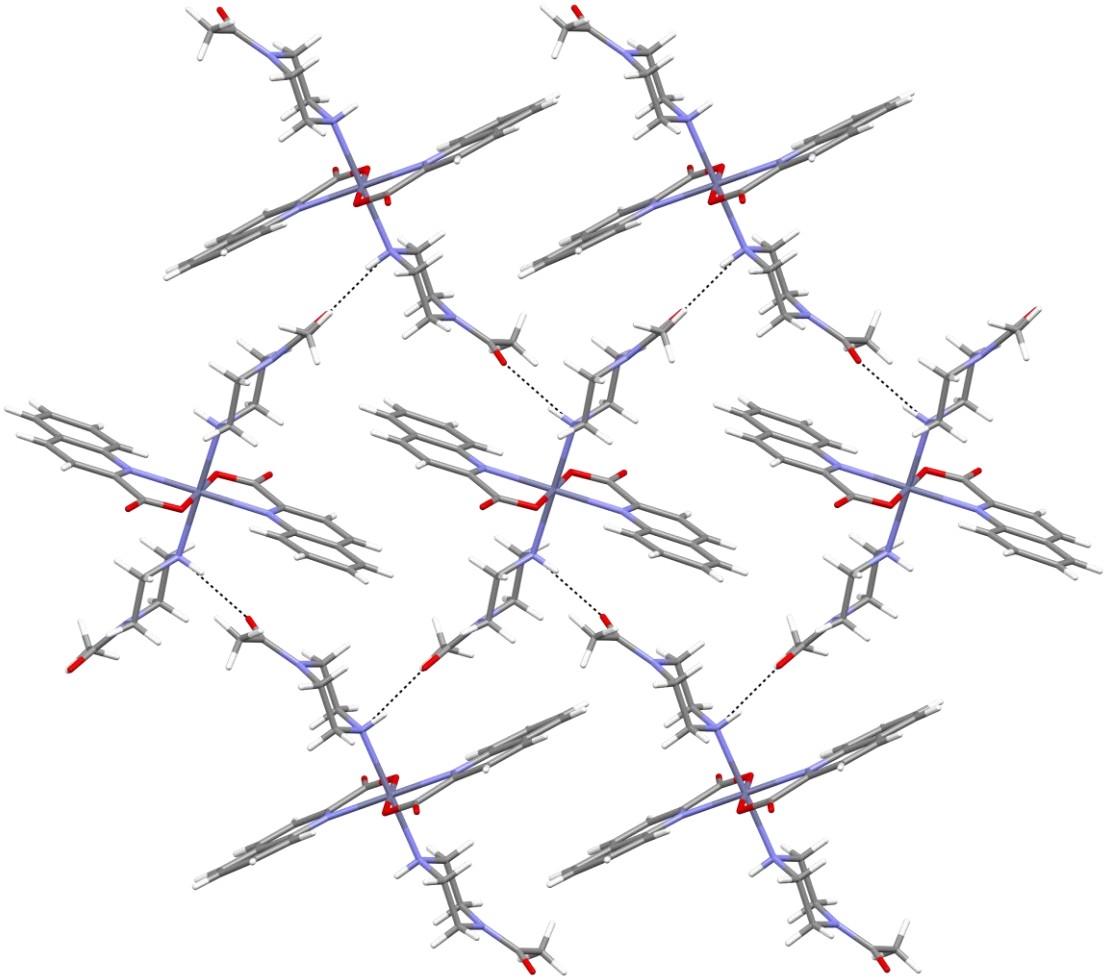


Figure S20. Hydrogen bonding in [Zn(quin)$_2$(1-Acpz)$_2$] (**20**). A section of a layer is shown. The resulting cyclic motif is denoted in graph set notation as $R_4^4(32)$.[S3]



[S3] Etter, M.C.; MacDonald, J.C.; Bernstein, J. *Acta Crystallogr., Sect. B* **1990**, *46*, 256–262, doi:10.1107/S0108768189012929.

Figure S21. Differences in the crystal structures of the $[Zn(quin)_2(1\text{-}Acpz)_2]\cdot 2CH_3CN$ polymorphs: a perpendicular view of the chains in **21a** (top) and **21b** (bottom). In **21a**, the molecules constituting the chains are arranged in two different directions. In contrast, in **21b**, the molecules are fully aligned. The complex molecules are colored gray and acetonitrile is colored red.

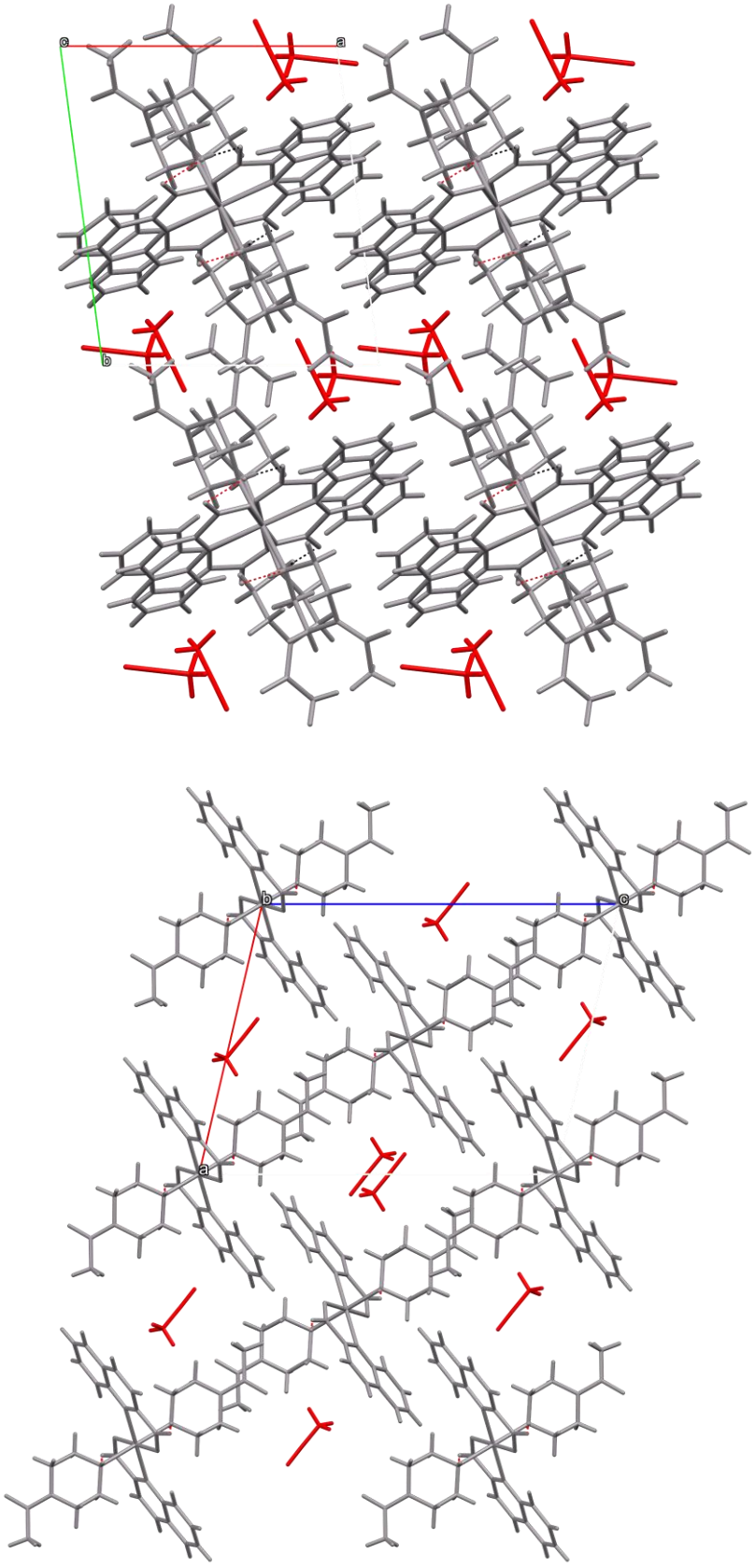


Figure S22. Hydrogen bonding pattern in $[Zn(quin)_2(1\text{-}Acpz)_2]\cdot[Zn(quin)_2(pz)]_n\cdot 4CH_3CN$ (**22**). A section of a layer is shown. The $[Zn(quin)_2(1\text{-}Acpz)_2]$ complex molecules are colored gray and the one-dimensional polymer $[Zn(quin)_2(pz)]_n$ is colored blue. Acetonitrile molecules are not drawn.

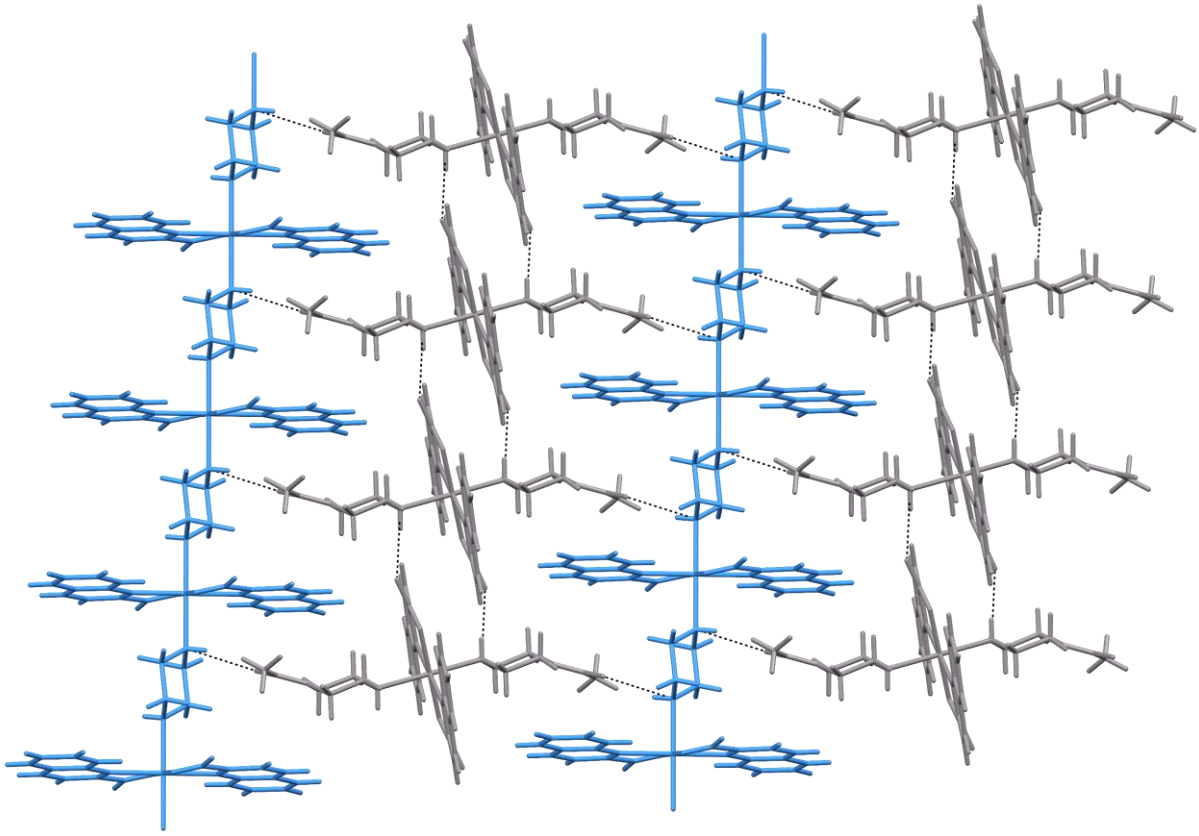
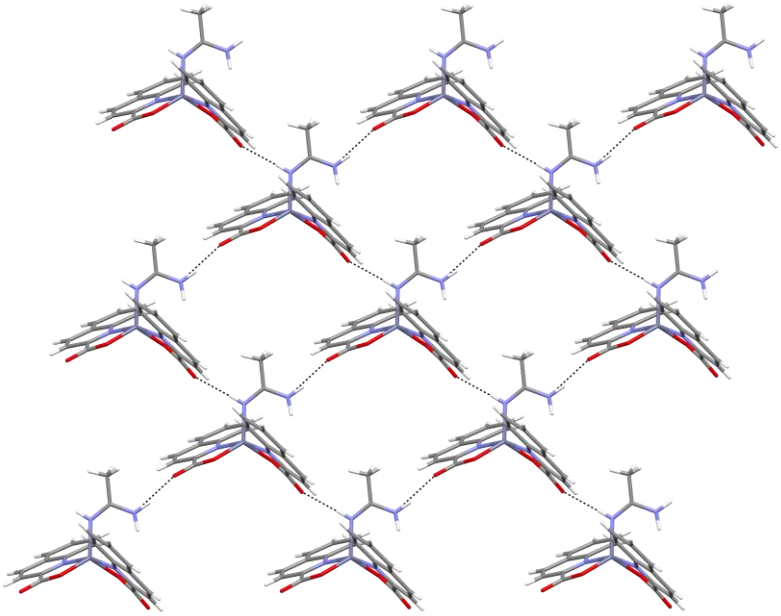
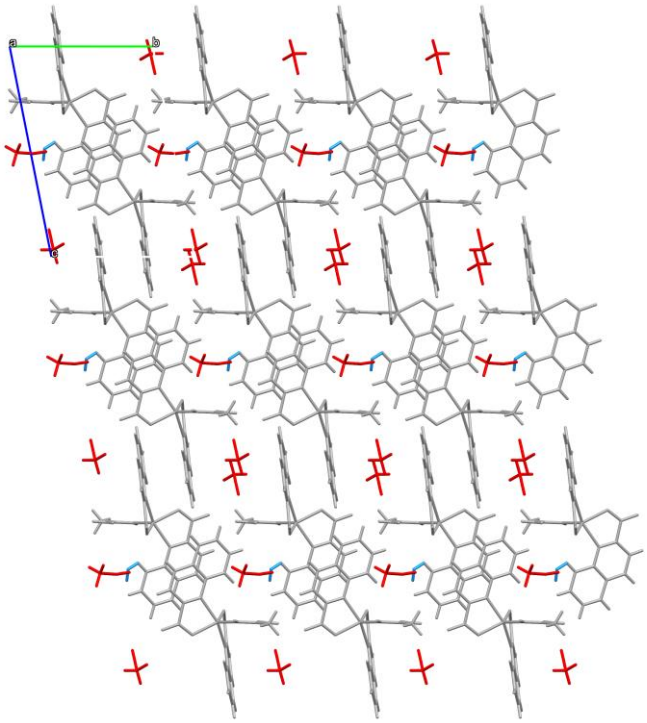


Figure S23. Hydrogen bonding pattern in $[Zn(quin)_2(am)]\cdot 1.3CH_3CN\cdot 0.2H_2O$ (**23**). Hydrogen bonds of two types ($NH\cdots COO^-$ and $NH_2\cdots COO^-$) link complex molecules into supramolecular layers. The resulting cyclic motif is denoted in graph set notation as $R_4^4(26)$.[S3] The layers stack along the *c*-axis. Solvent molecules are located in the channels that form.

(i) A perpendicular view of a section of a layer. Solvent molecules are not drawn.



(ii) A view along the layers. Complex molecules are colored gray, acetonitrile red and water is colored blue.



[S3] Etter, M.C.; MacDonald, J.C.; Bernstein, J. *Acta Crystallogr., Sect. B* **1990**, *46*, 256–262, doi:10.1107/S0108768189012929.

3. Infrared spectroscopy

Figure S24. Infrared spectrum of [Zn(quin)$_2$(thiomorph)$_2$] (**1**).

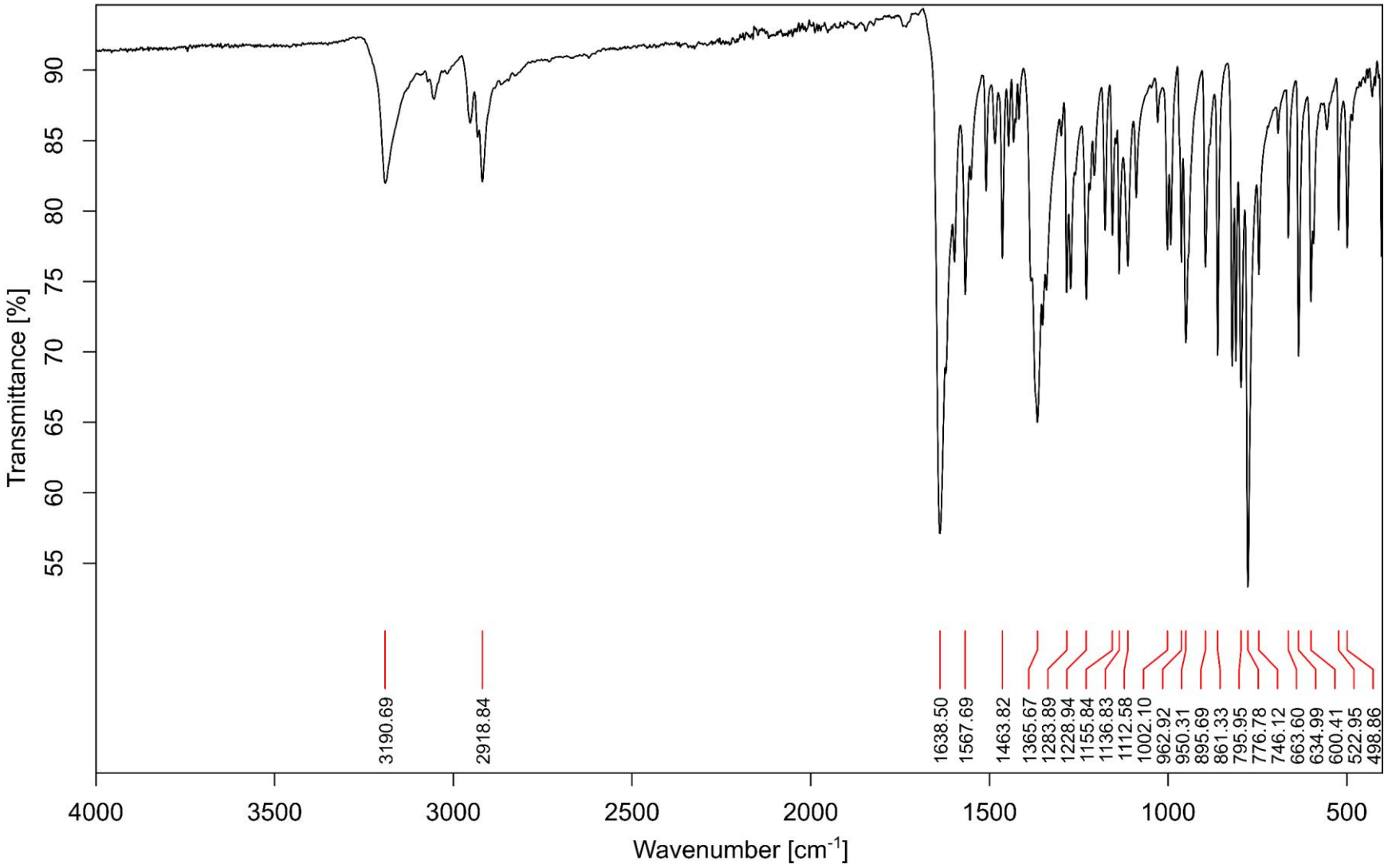


Figure S25. Infrared spectrum of [Zn(quin)$_2$(thiomorpham)]·CH_3OH·CH_3CN (**2**).

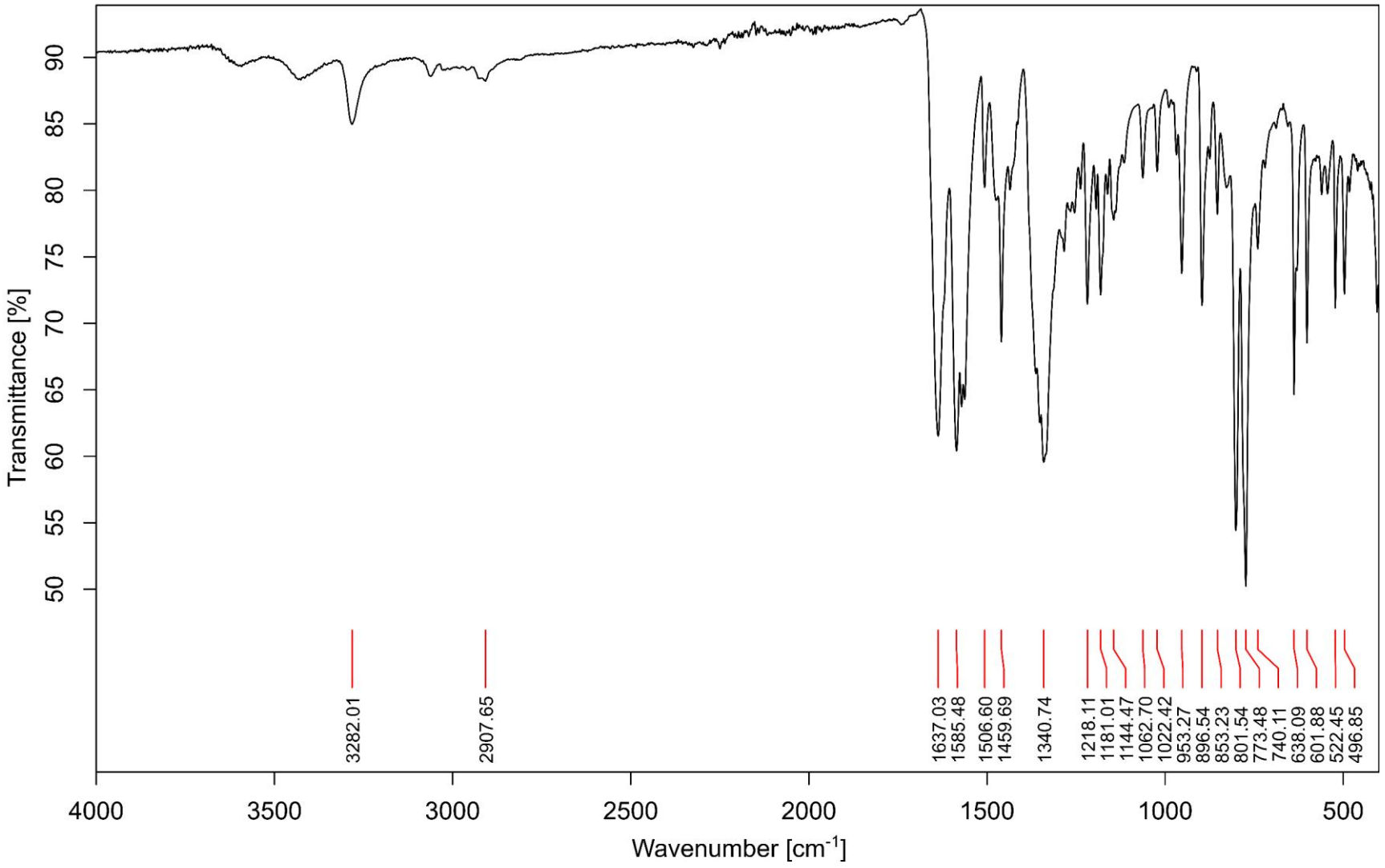


Figure S26. Infrared spectrum of [Zn(quin)$_2$(4-Mepipe)$_2$] (**3**).

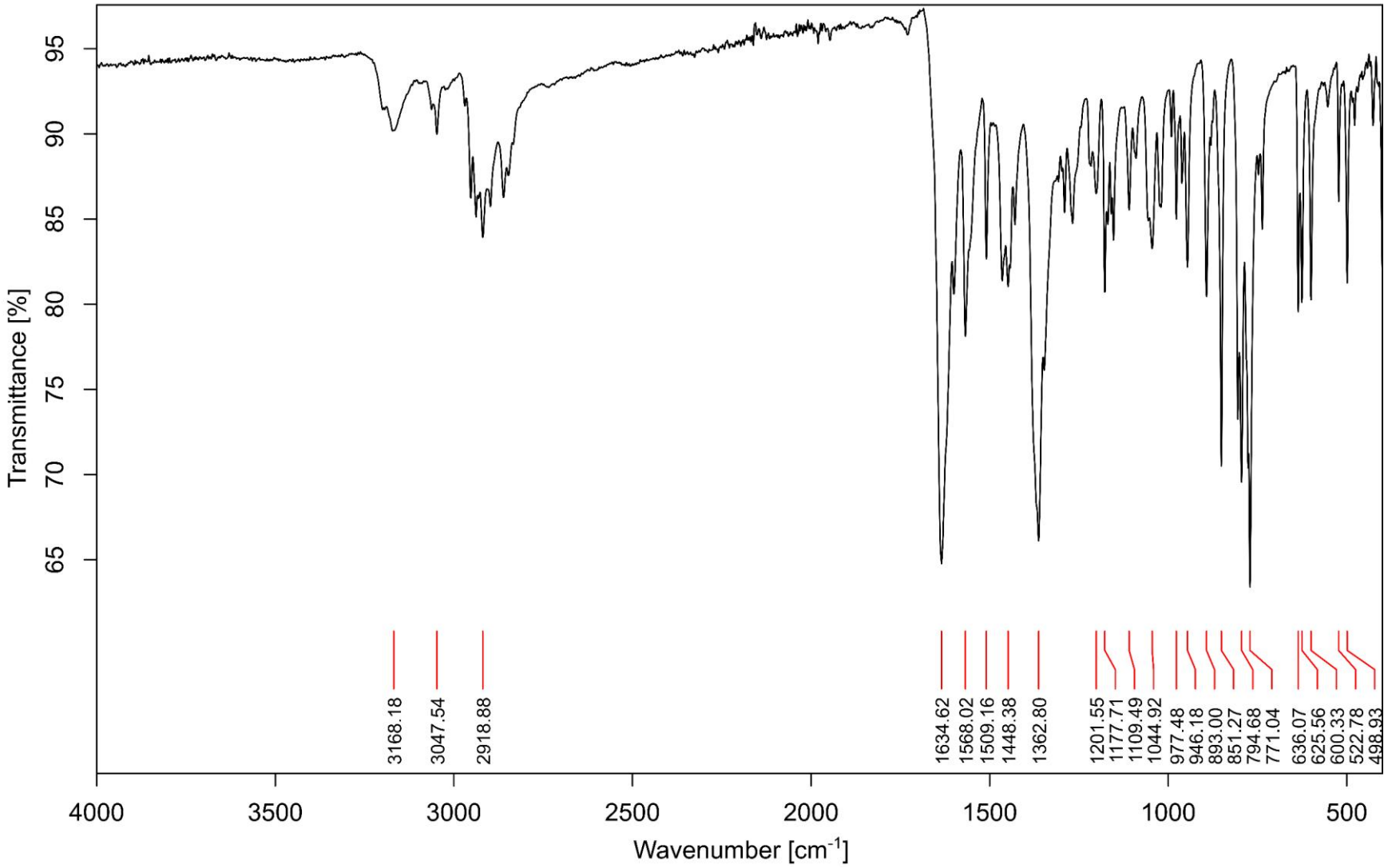


Figure S27. Infrared spectrum of 4-MepipeH[Zn(quin)$_3$] (**4**).

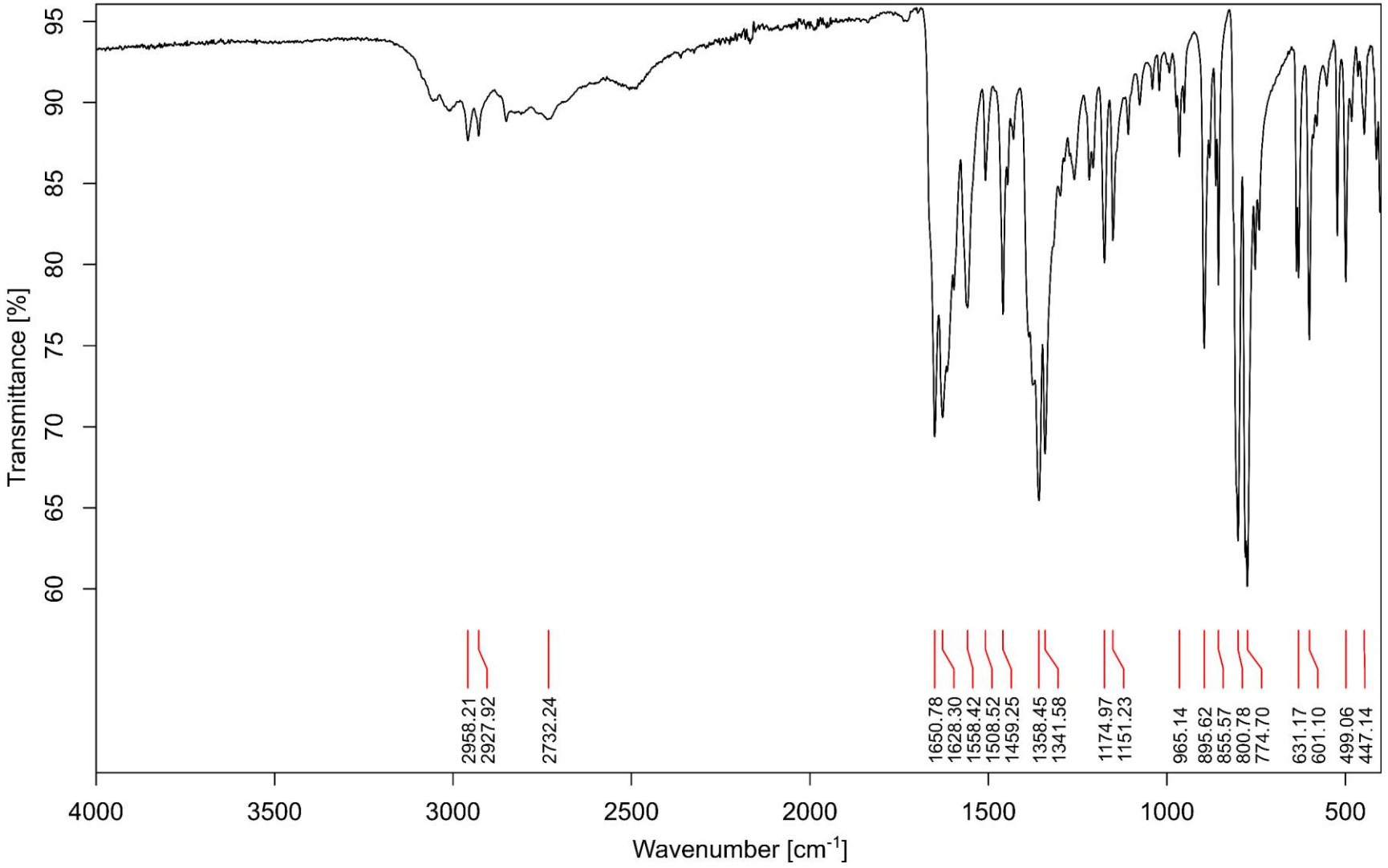


Figure S28. Infrared spectrum of [Zn(quin)$_2$(4-Mepipeam)]·CH_3CN (**5**).

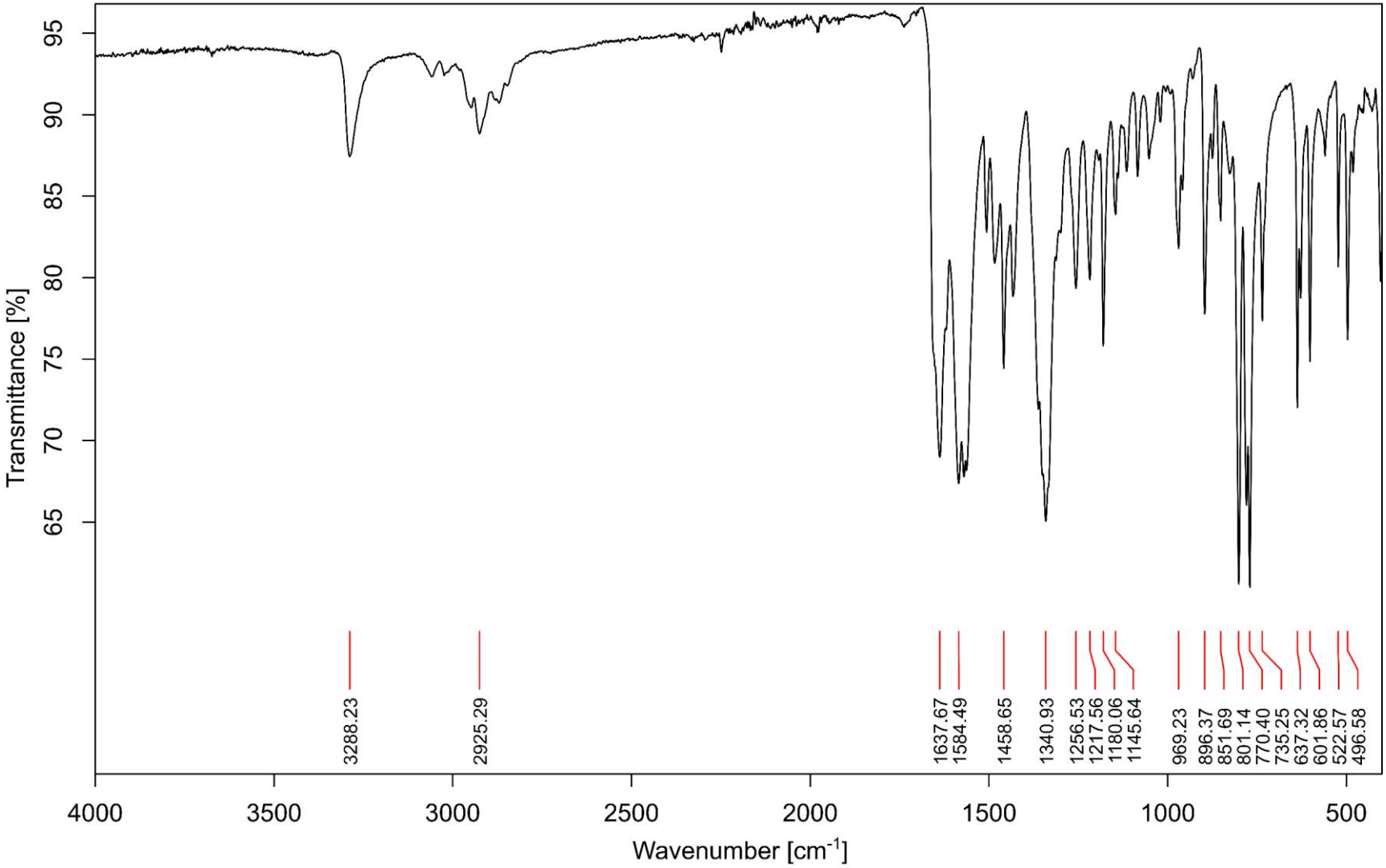


Figure S29. Infrared spectrum of $[Zn(quin)_2(4\text{-amidepipe})_2]\cdot 2CH_3CN$ (**6**).

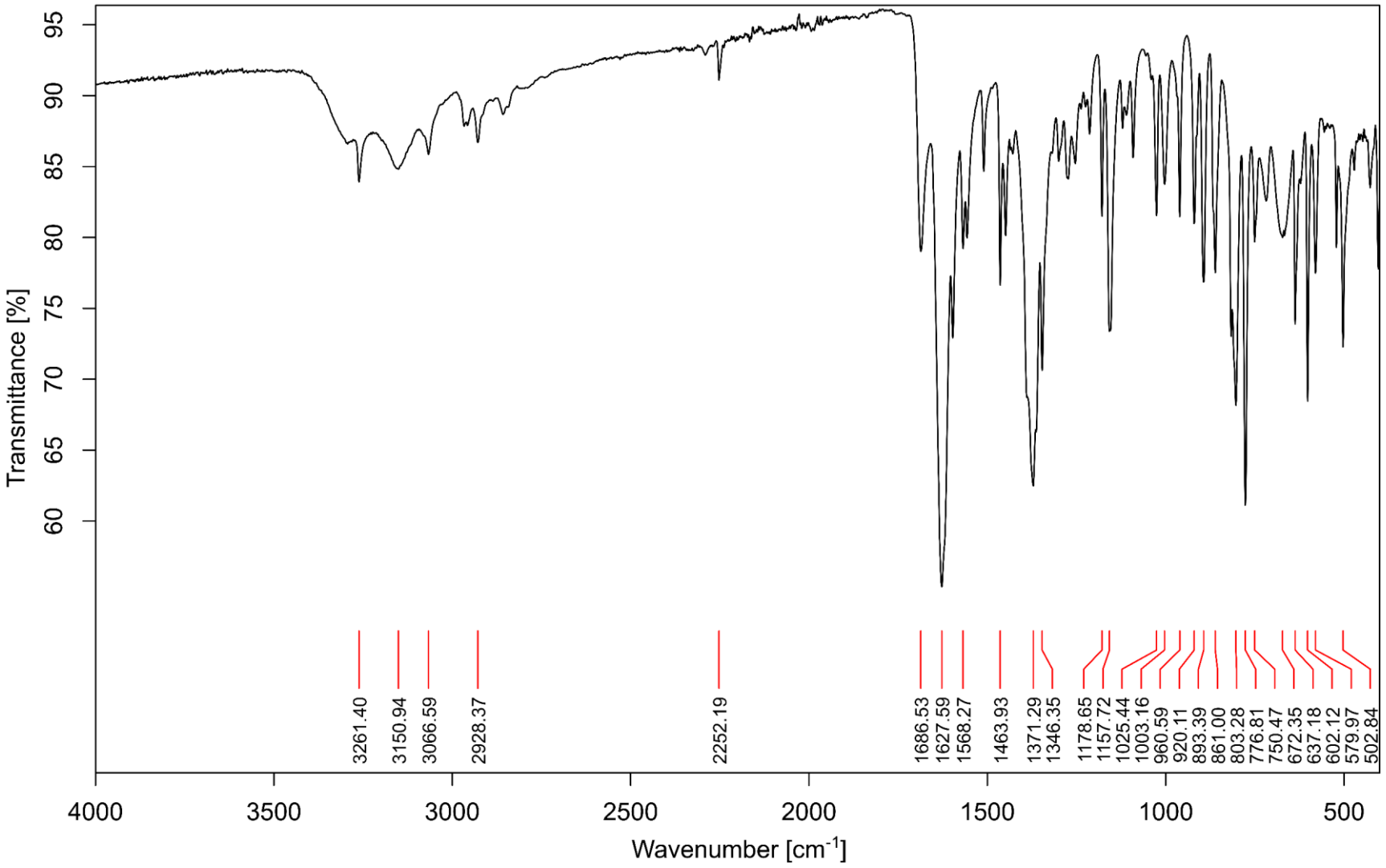


Figure S30. Infrared spectrum of [Zn(quin)$_2$(4-amidepipeam)] (**7**).

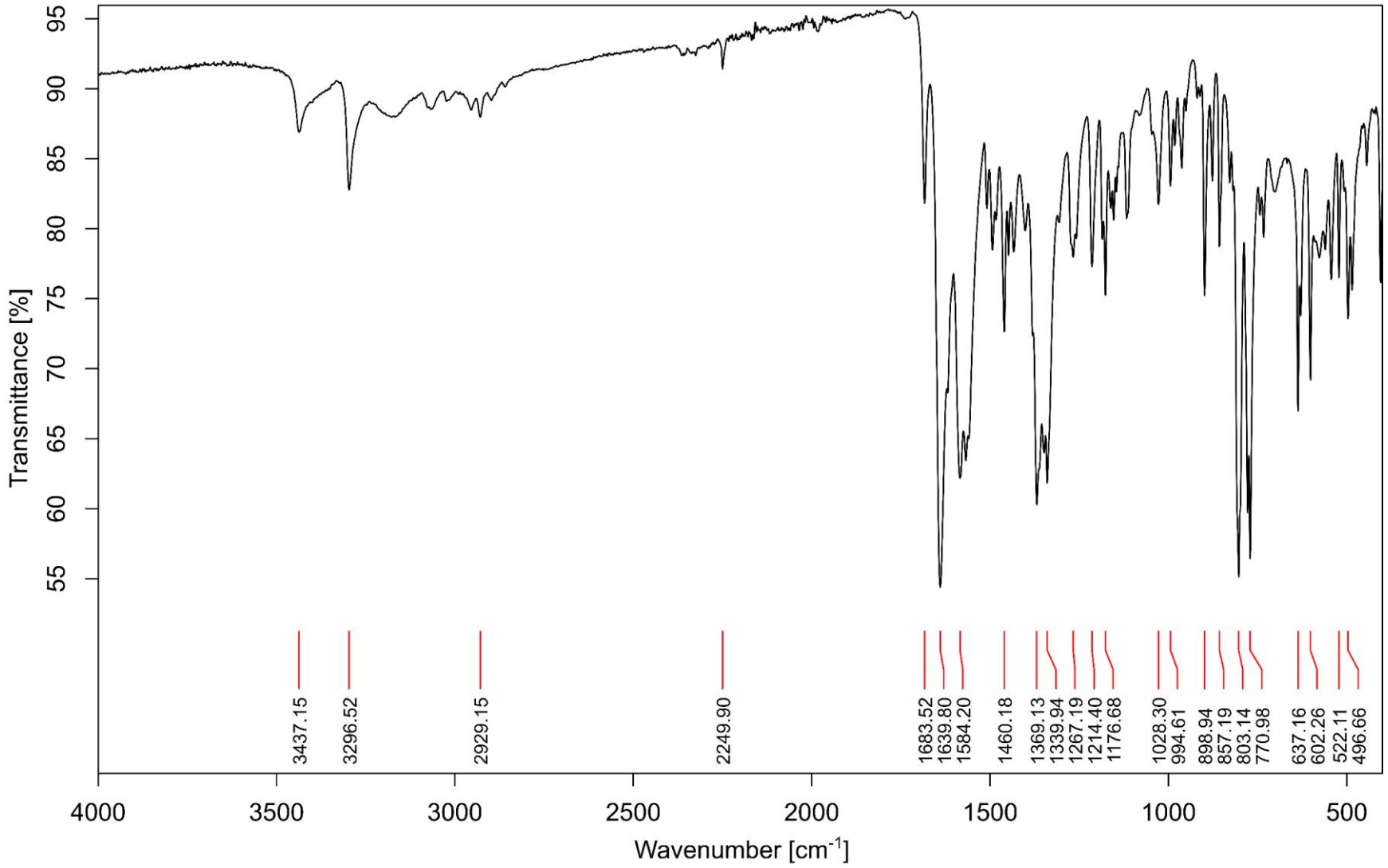


Figure S31. Infrared spectrum of 4-amidepipeam (**8**).

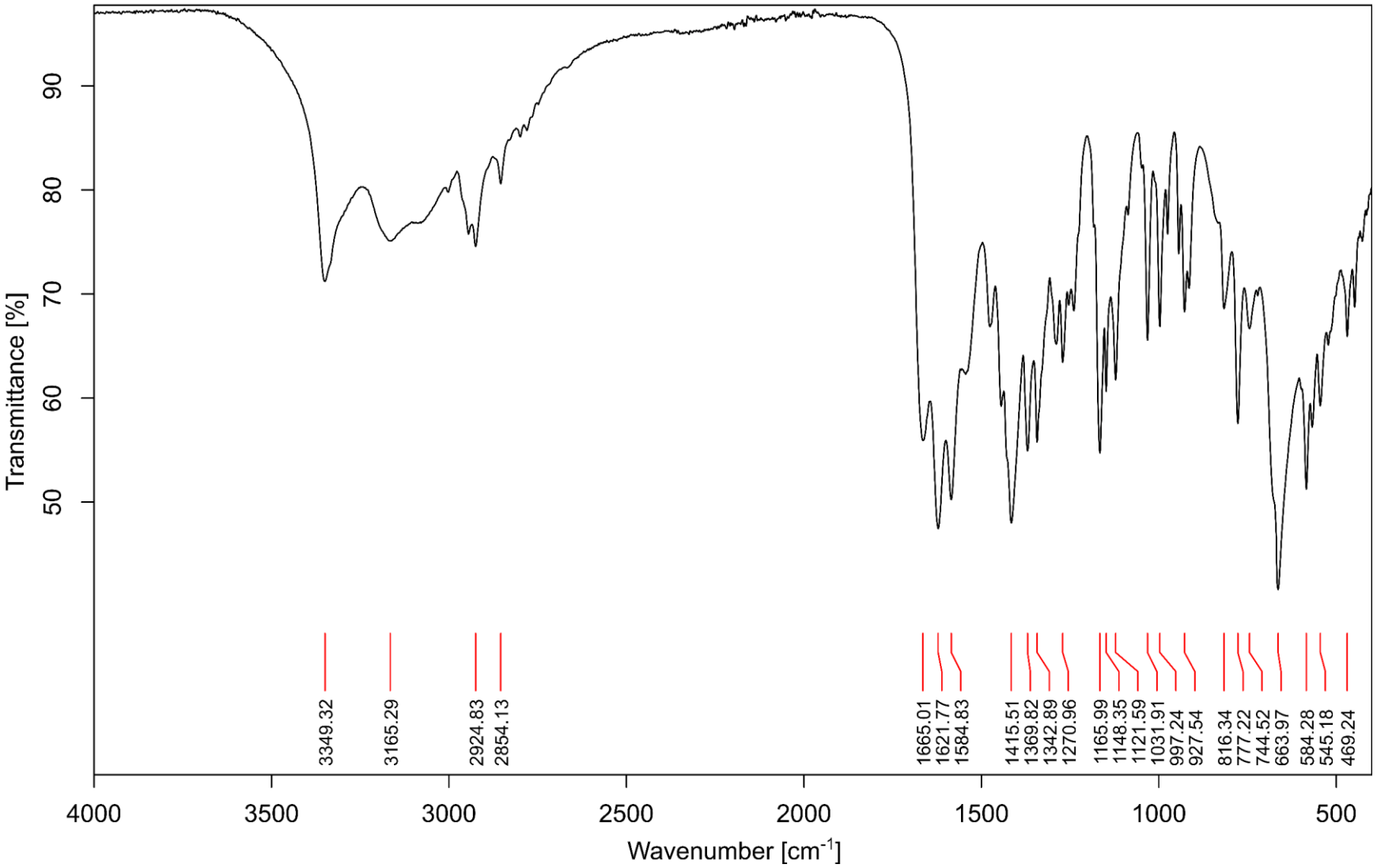


Figure S32. Infrared spectrum of $[Zn(quin)_2(pz)]_n$ (**9**).

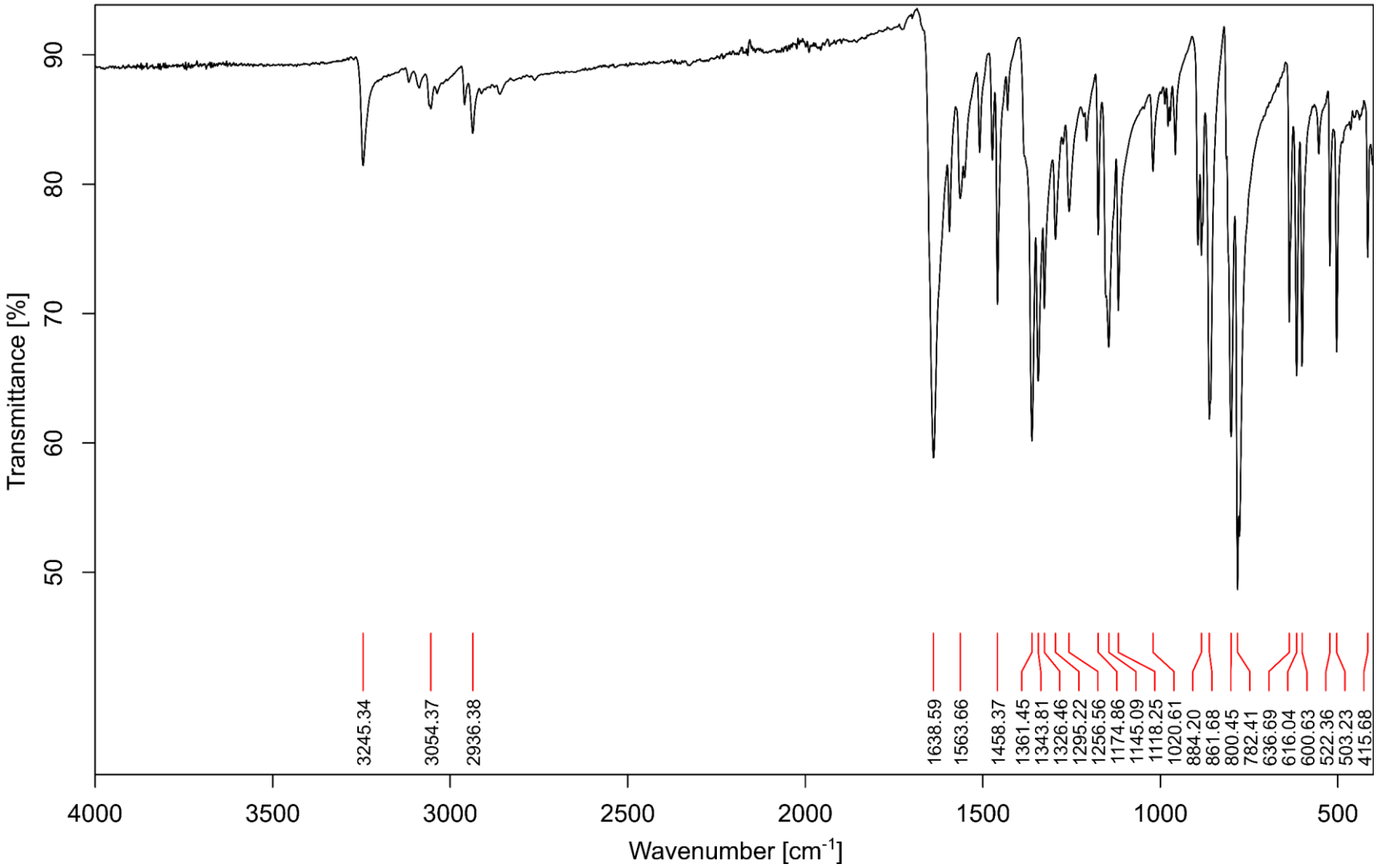


Figure S33. Infrared spectrum of [Zn(quin)$_2$(1-Mepz)] (**10**).

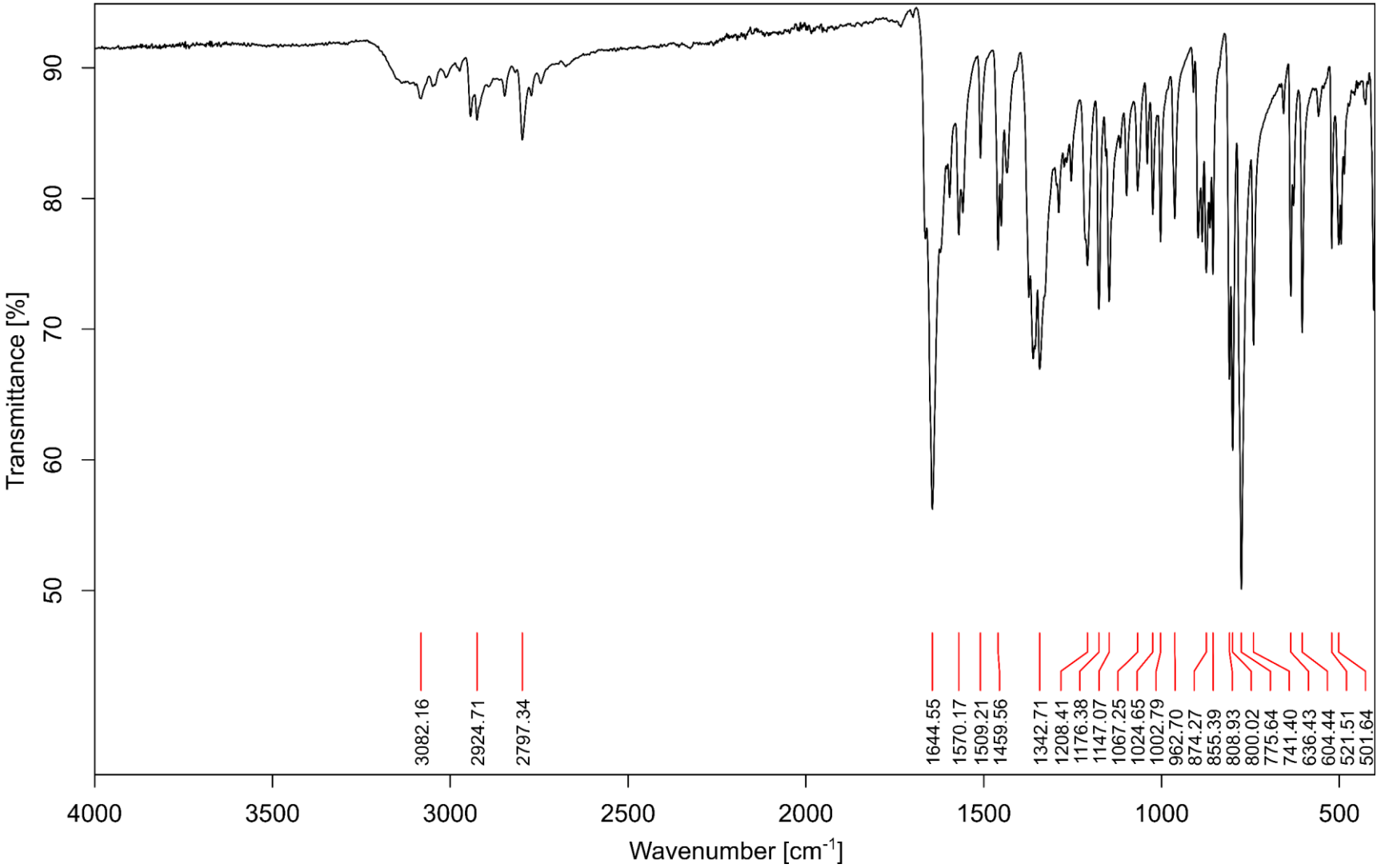


Figure S34. Infrared spectrum of $[Zn(quin)_2(1\text{-}Mepz)_2]\cdot 0.5CH_3CN$ (**11**).

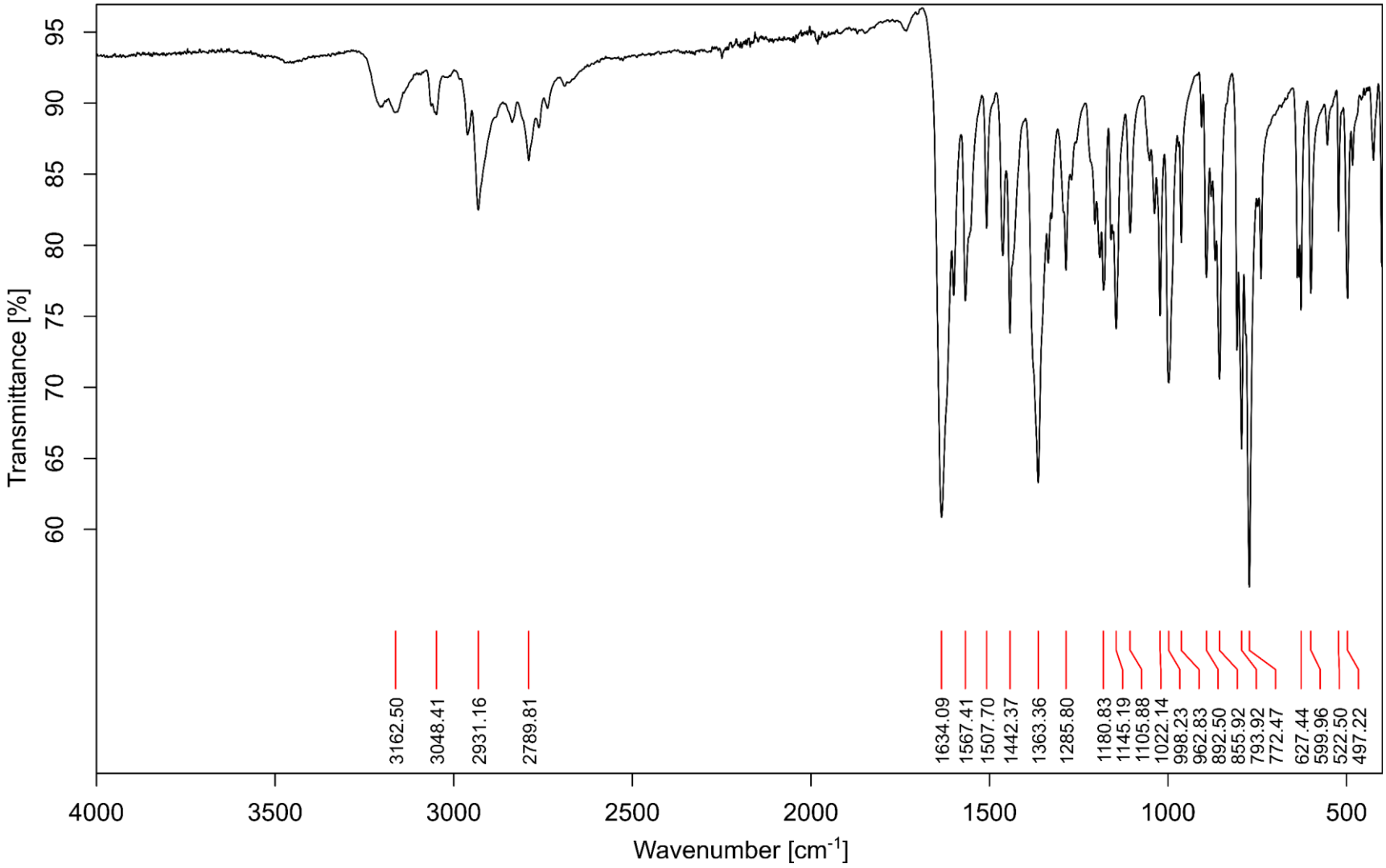


Figure S35. Infrared spectrum of [Zn(quin)$_2$(1-Mepzam)] (**12**).

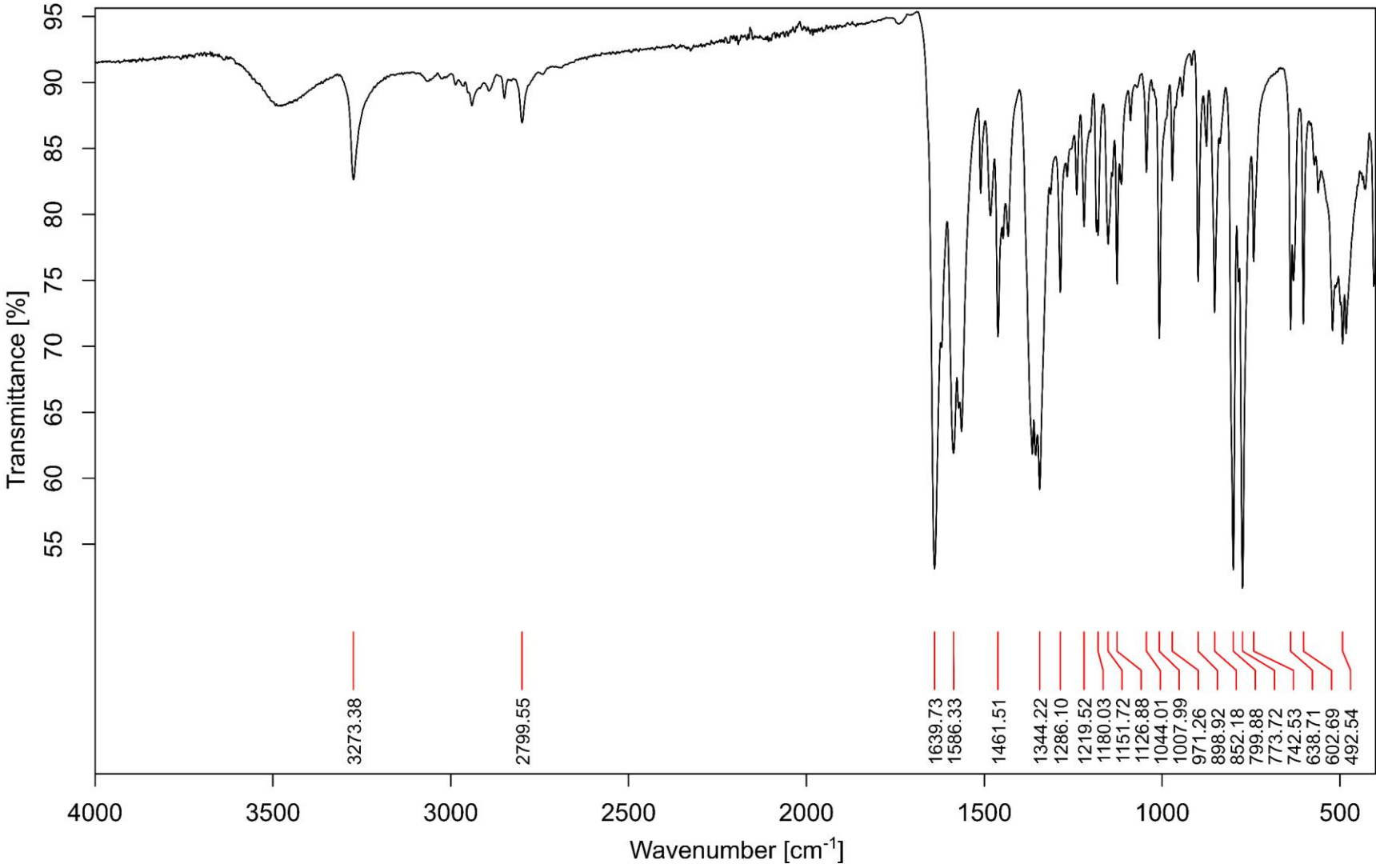


Figure S36. Infrared spectrum of $[Zn(quin)_2(1\text{-}Etpz)_2]\cdot 0.5CH_3CN$ (**13**).

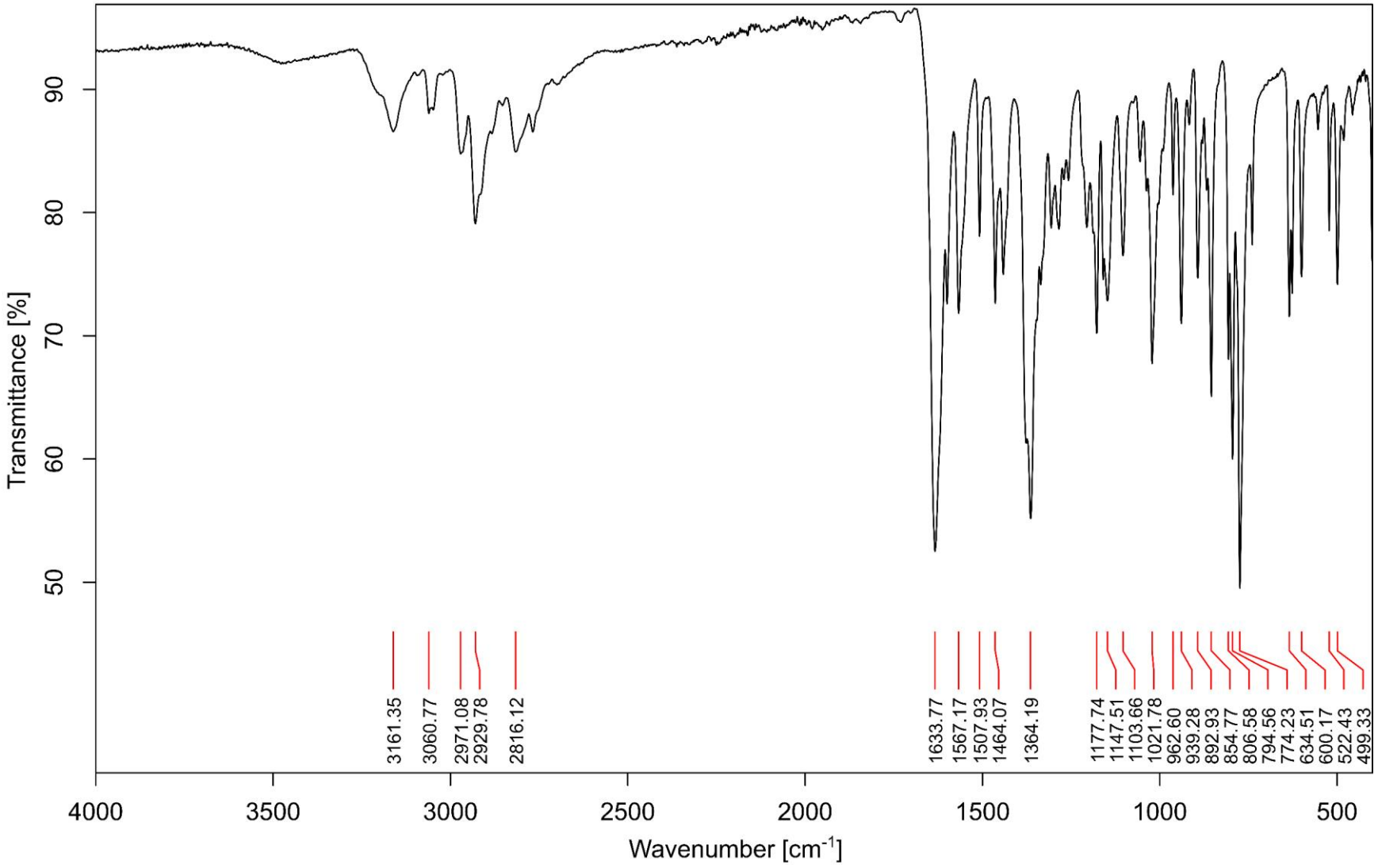


Figure S37. Infrared spectrum of [Zn(quin)$_2$(1-Etpzam)]·H_2O (**14**).

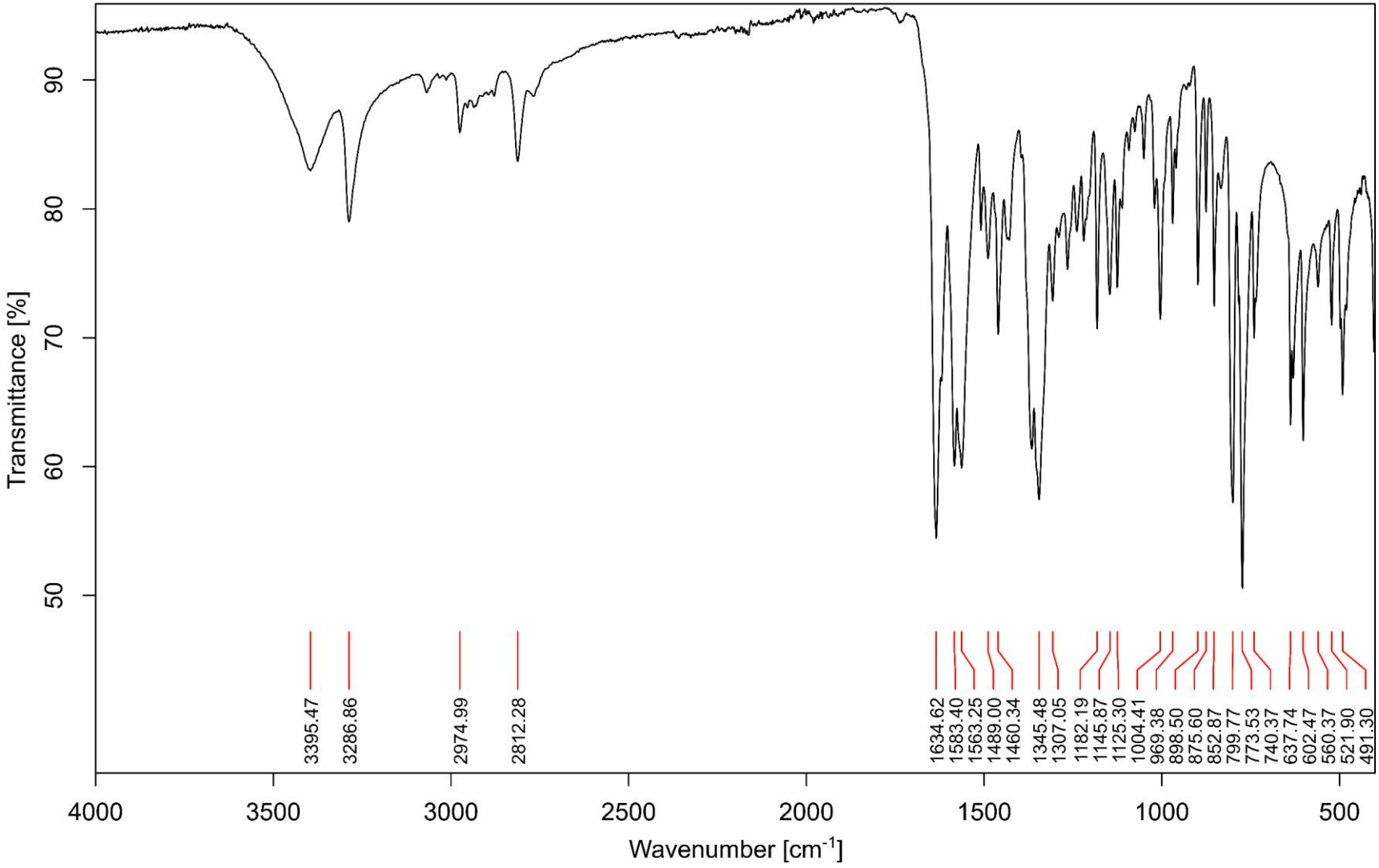


Figure S38. Infrared spectrum of $[Zn(quin)_2(1\text{-}OHEtpz)_2]\cdot 2CH_3CN$ (**15**).

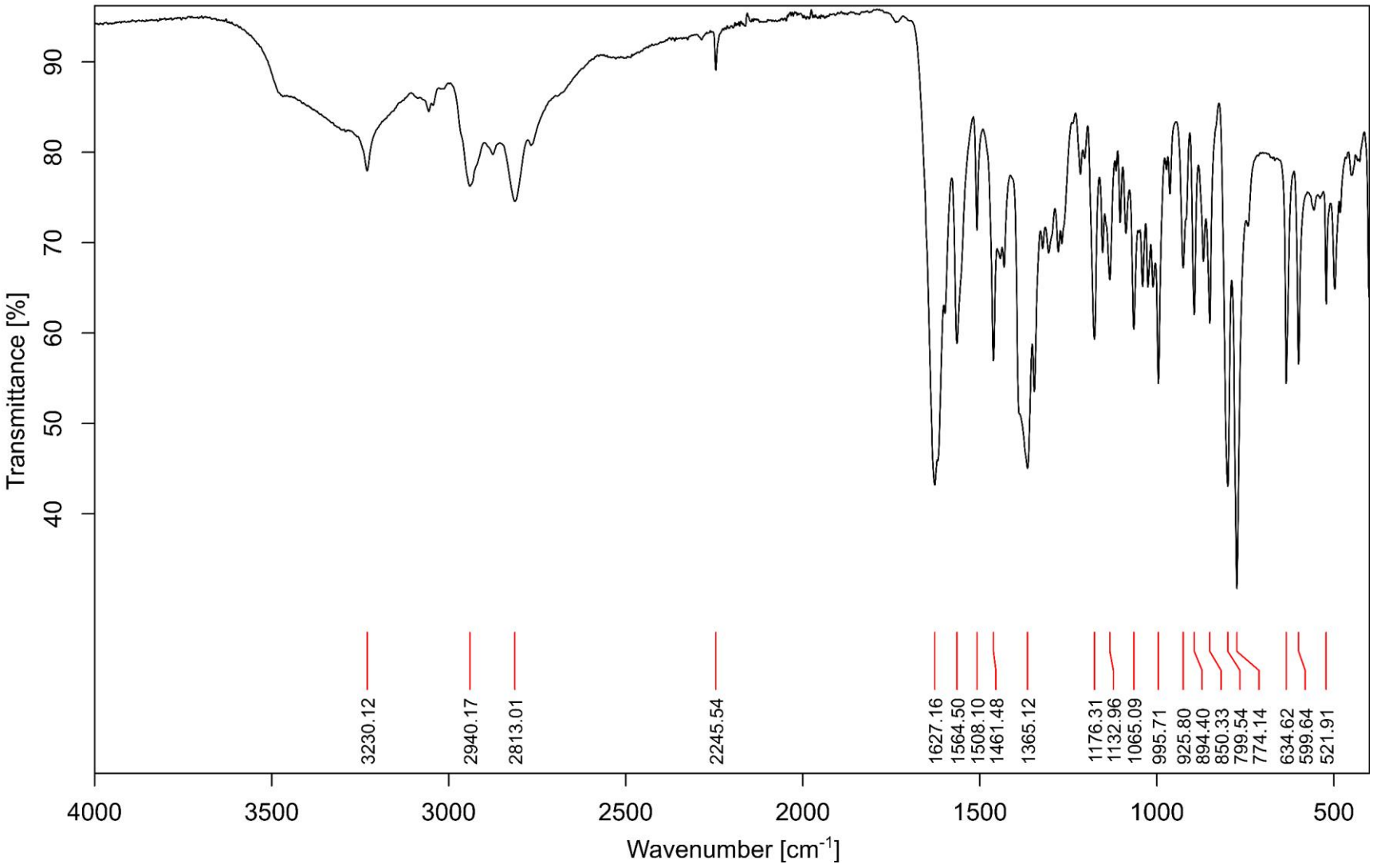


Figure S39. Infrared spectrum of [Zn(quin)$_2$(1-OHEtpzam)] (**16**).

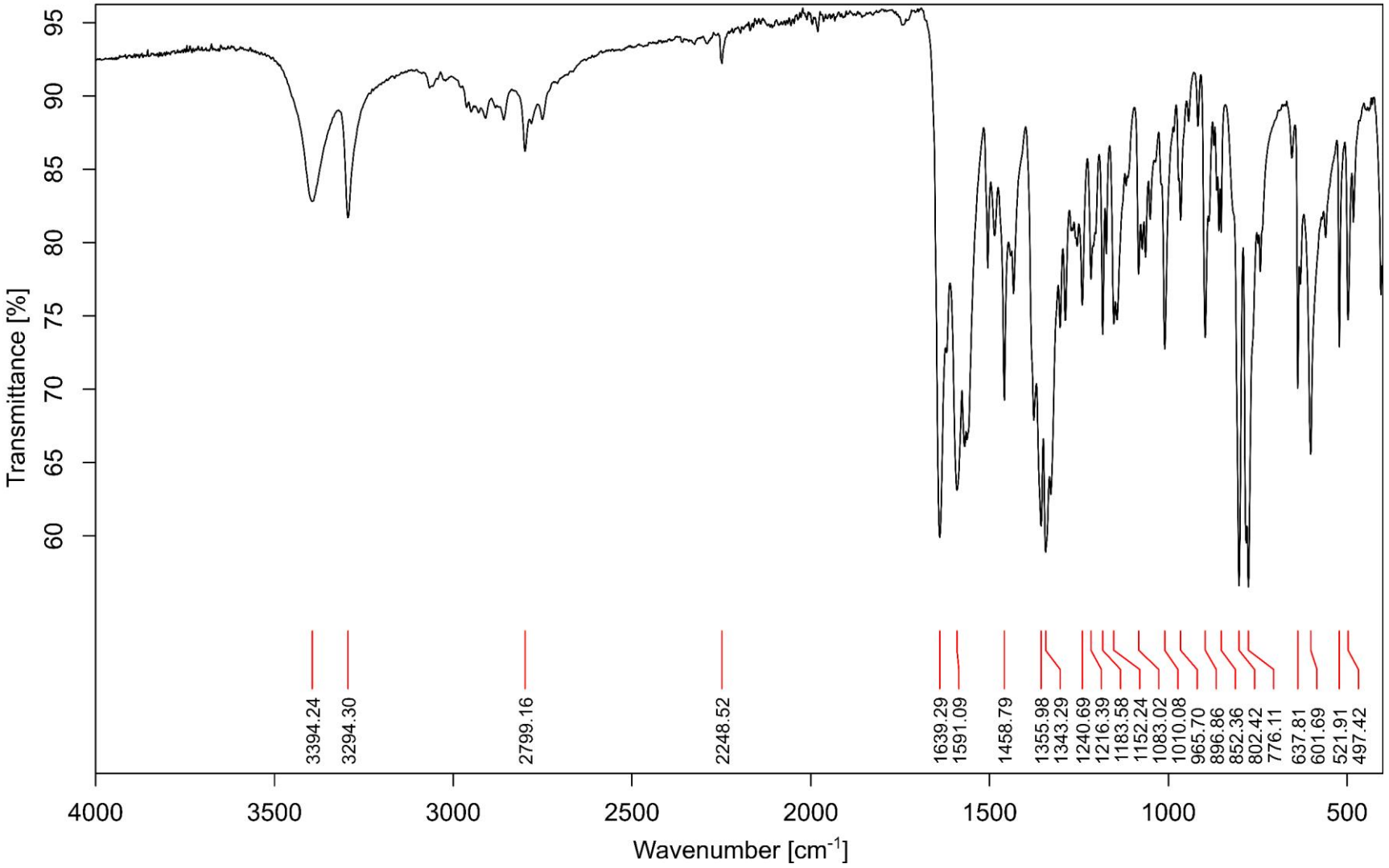


Figure S40. Infrared spectrum of $[Zn(quin)_2(1\text{-}Phpz)_2]\cdot CH_3CN$ (**17**).

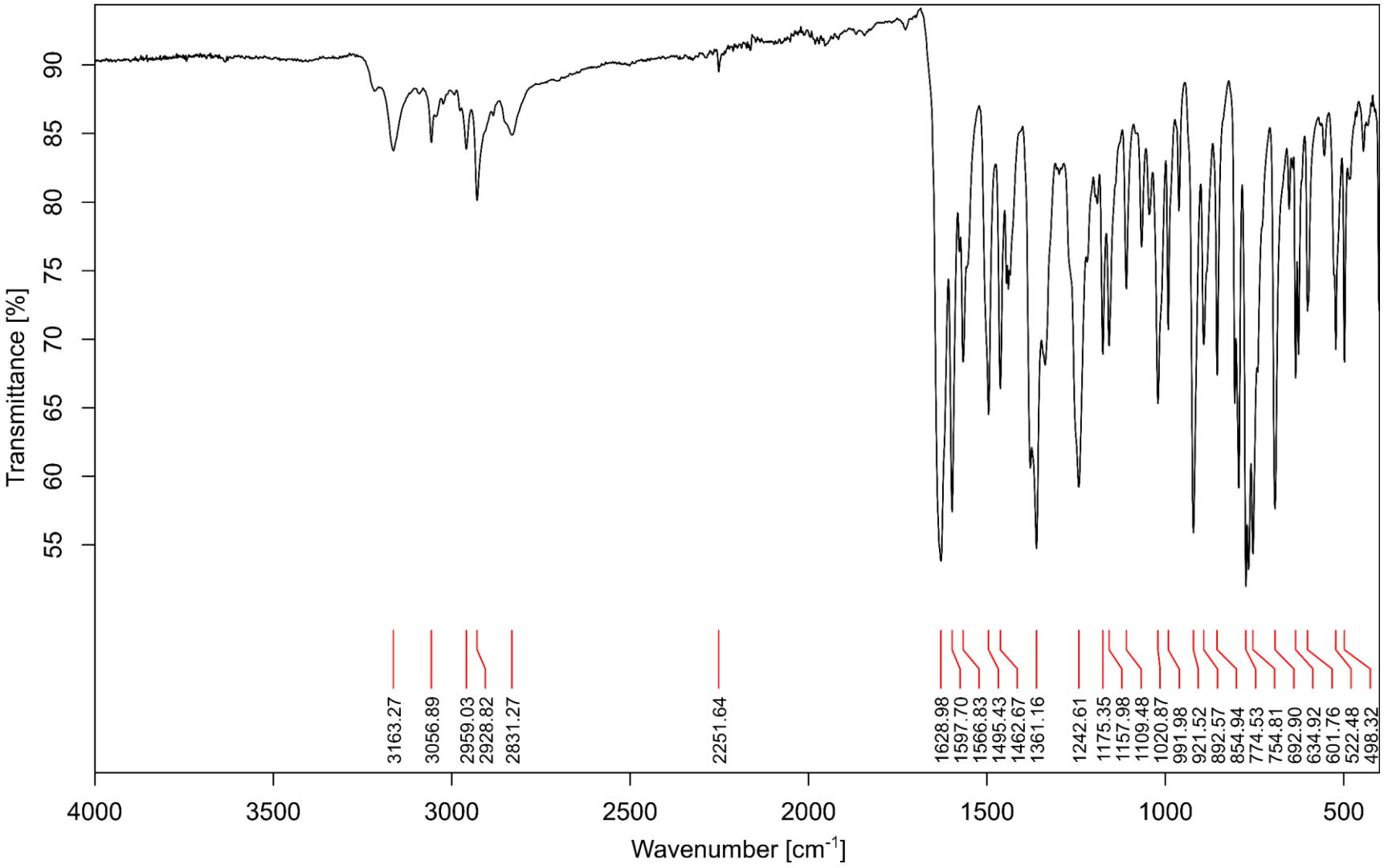


Figure S41. Infrared spectrum of the first polymorph of $[Zn(quin)_2(1\text{-}Phpz)_2]\cdot 2$acetamide.

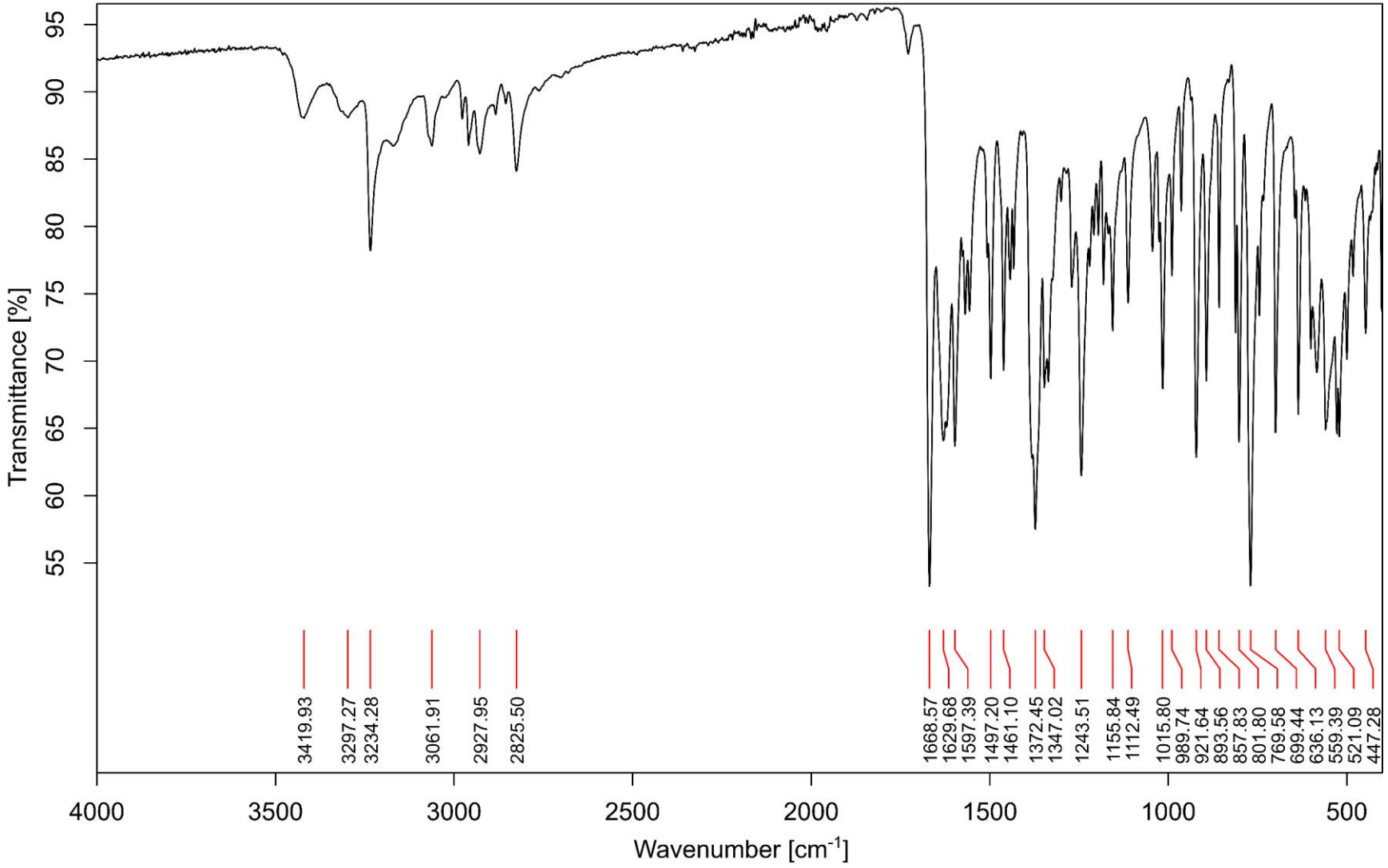


Figure S42. Infrared spectrum of the second polymorph of $[Zn(quin)_2(1\text{-}Phpz)_2]\cdot 2acetamide$.

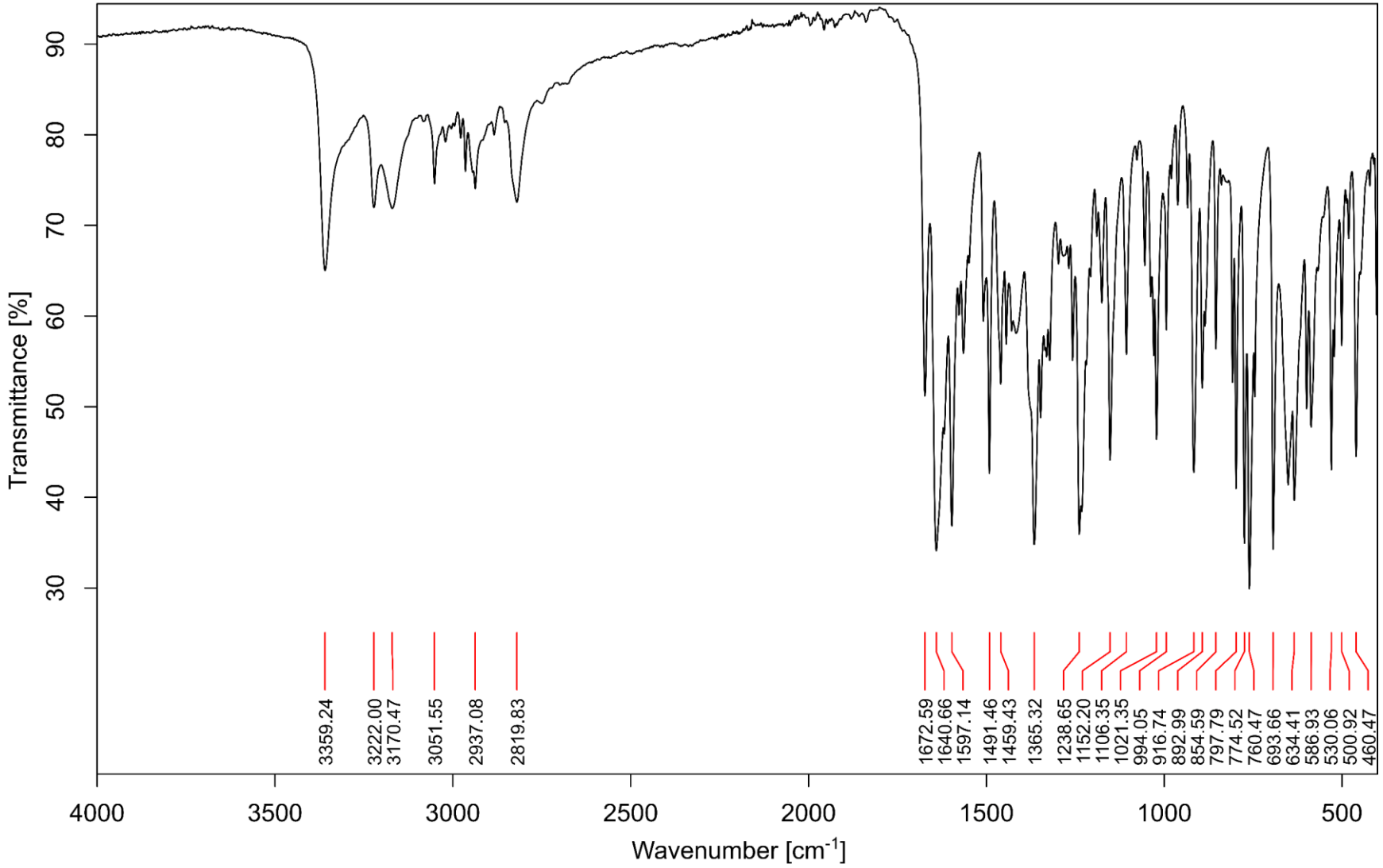


Figure S43. Infrared spectrum of [Zn(quin)$_2$(1-Phpzam)]·0.5(1-Phpz)·CH_3CN (**19**).

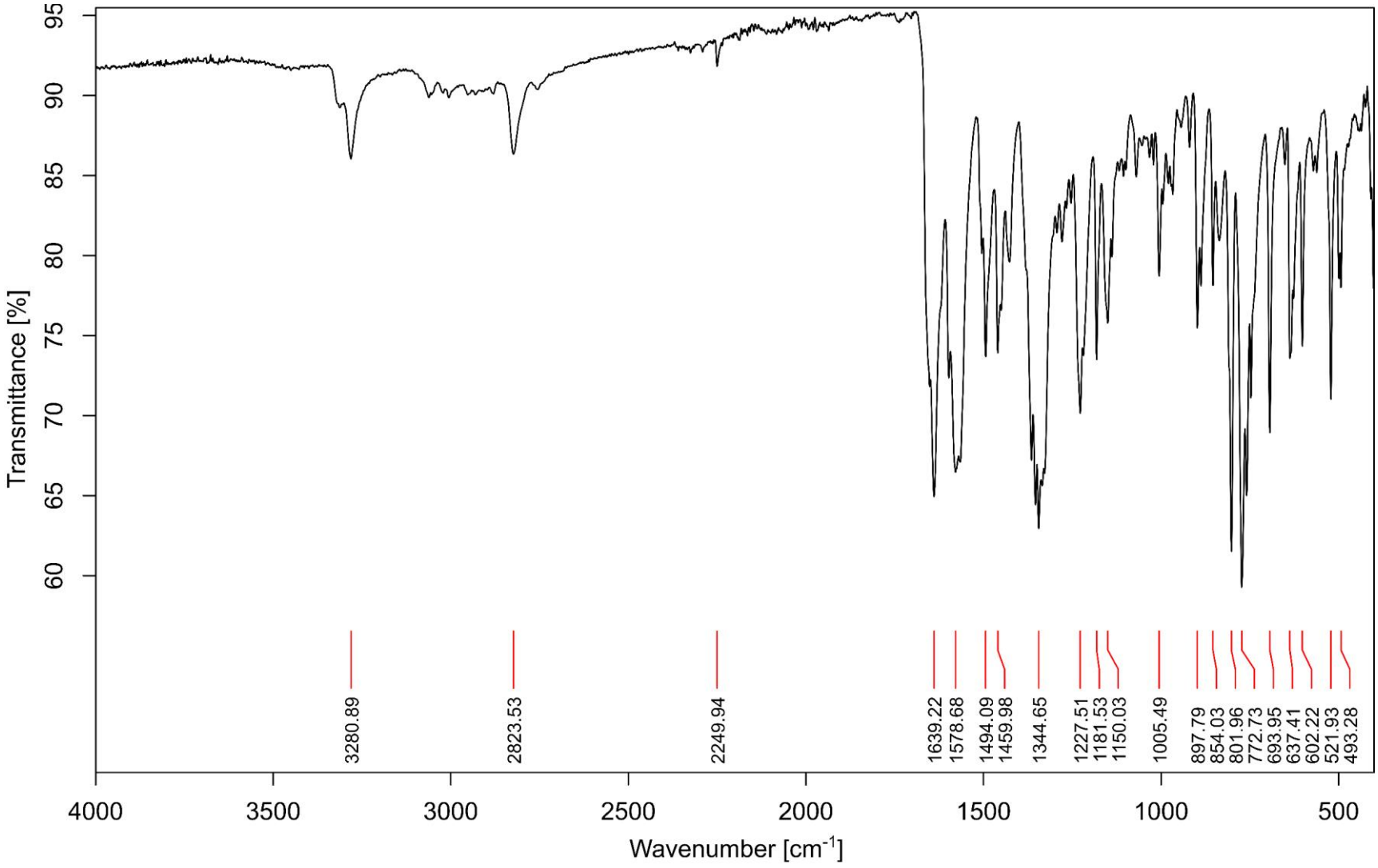


Figure S44. Infrared spectrum of $[Zn(quin)_2(1\text{-}Acpz)_2]\cdot 2CH_3CN$ (**21**).

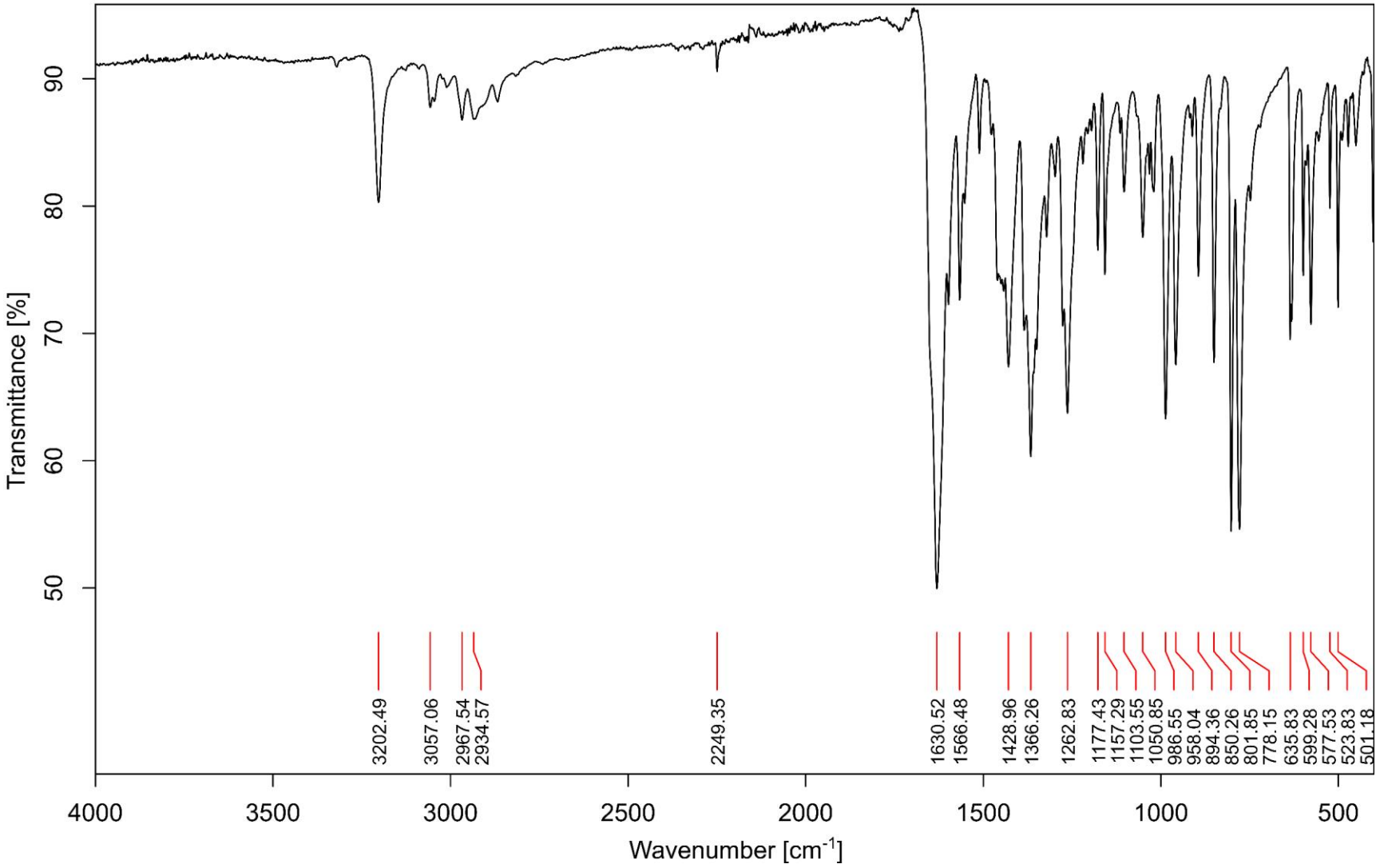


Figure S45. Infrared spectrum of $[Zn(quin)_2(1\text{-}Acpz)_2]\cdot[Zn(quin)_2(pz)]_n\cdot 4CH_3CN$ (**22**).

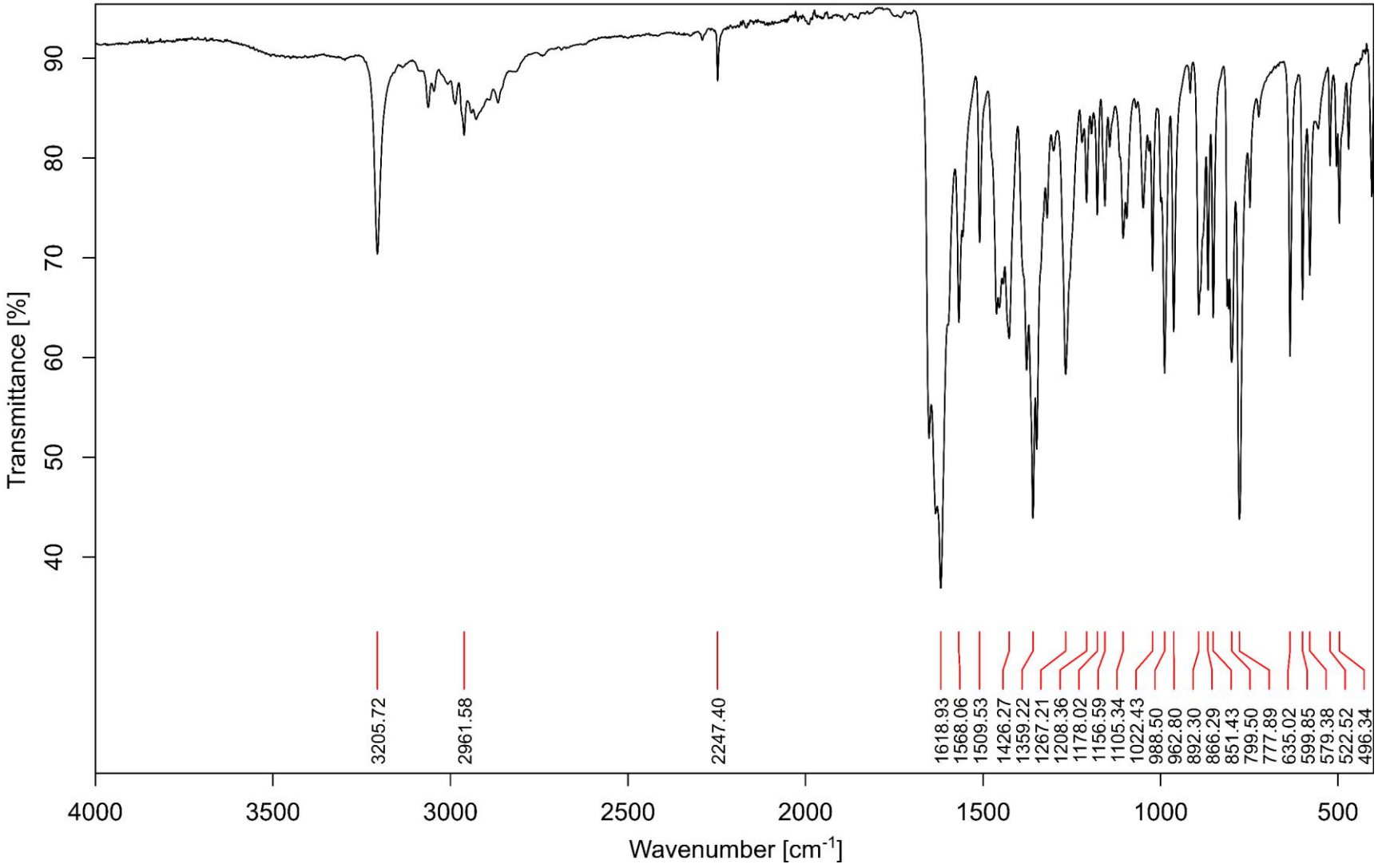
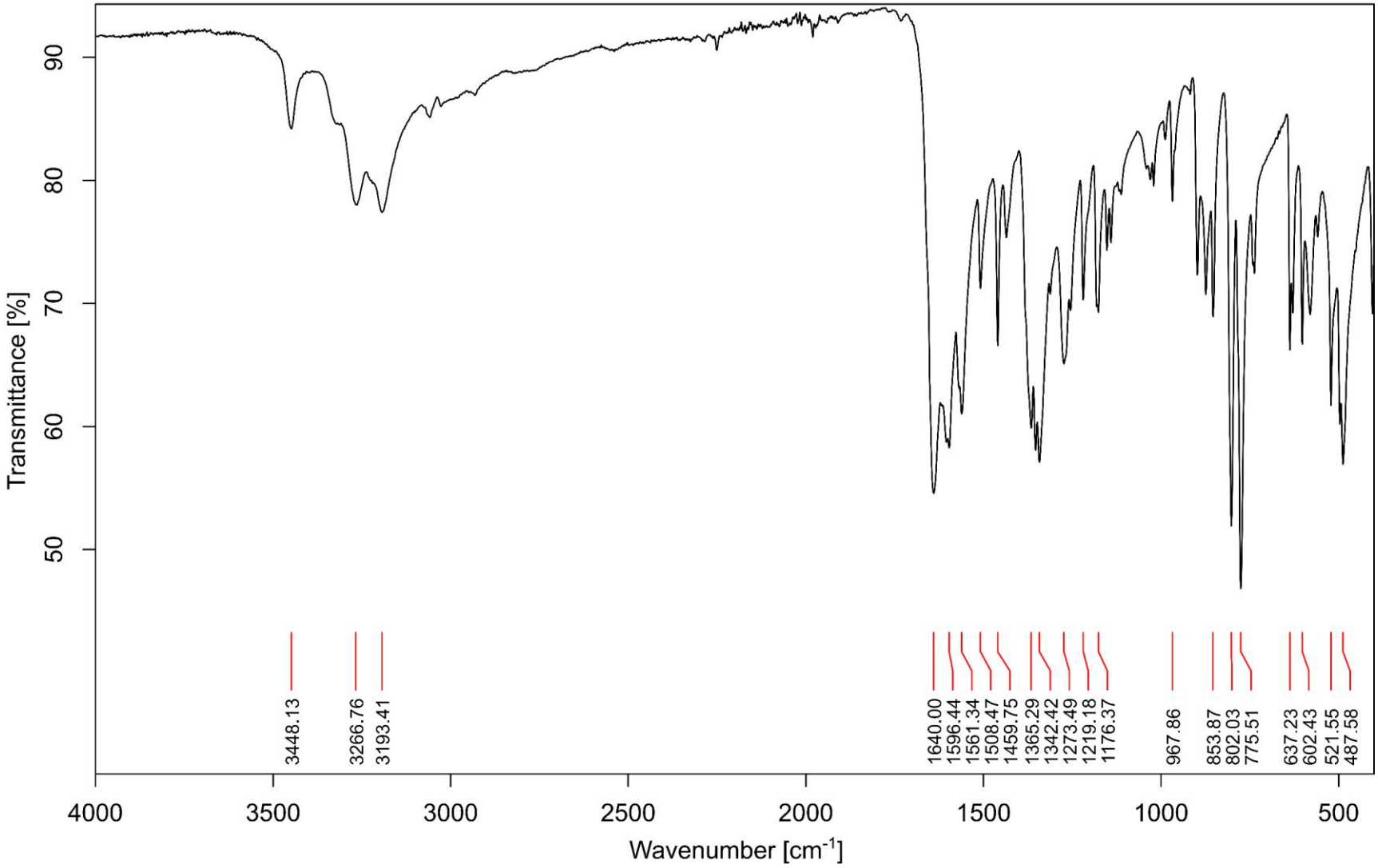


Figure S46. Infrared spectrum of $[Zn(quin)_2(am)]\cdot 1.3CH_3CN\cdot 0.2H_2O$ (**23**).



4. ^{1}H NMR spectroscopy

Figure S47. ^{1}H NMR spectrum of 4-MepipeH[Zn(quin)$_3$] (**4**) in DMSO-d_6.

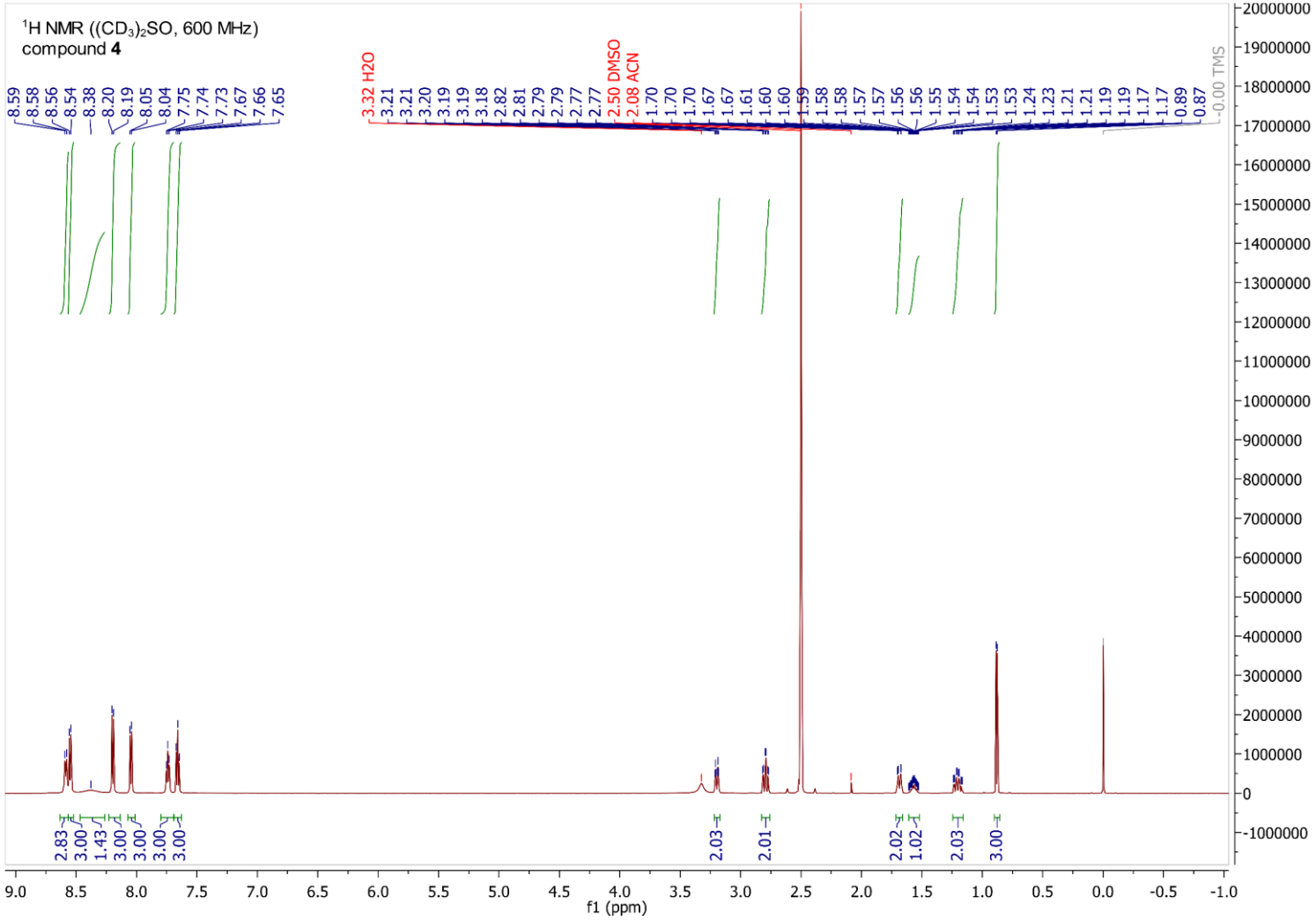


Figure S48. ^{1}H NMR spectrum of [Zn(quin)$_2$(4-amidepipeam)] (**7**) in DMSO-d_6.

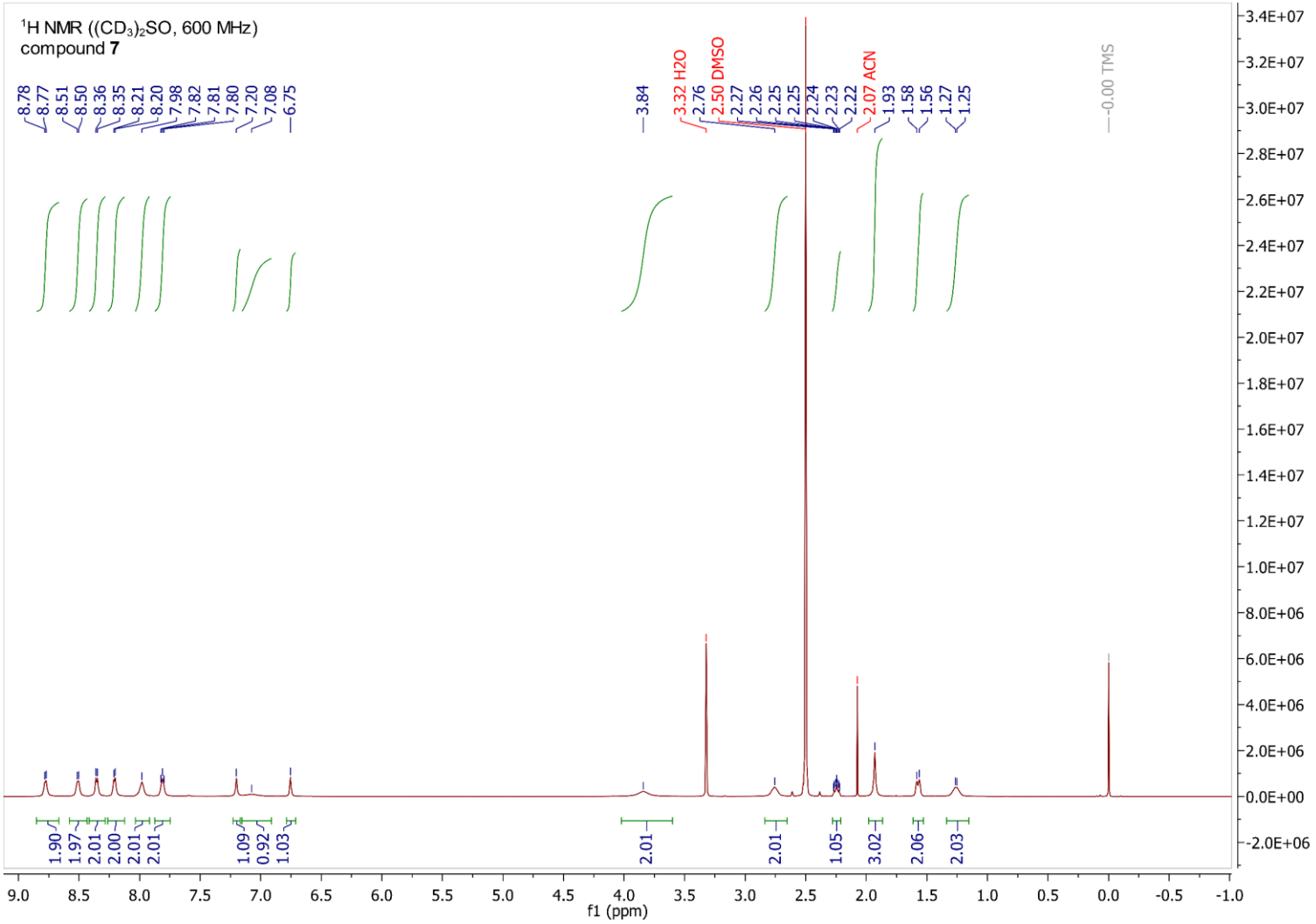


Figure S49. ^{1}H NMR spectrum of 4-amidepipeam (**8**) in DMSO-d_6.

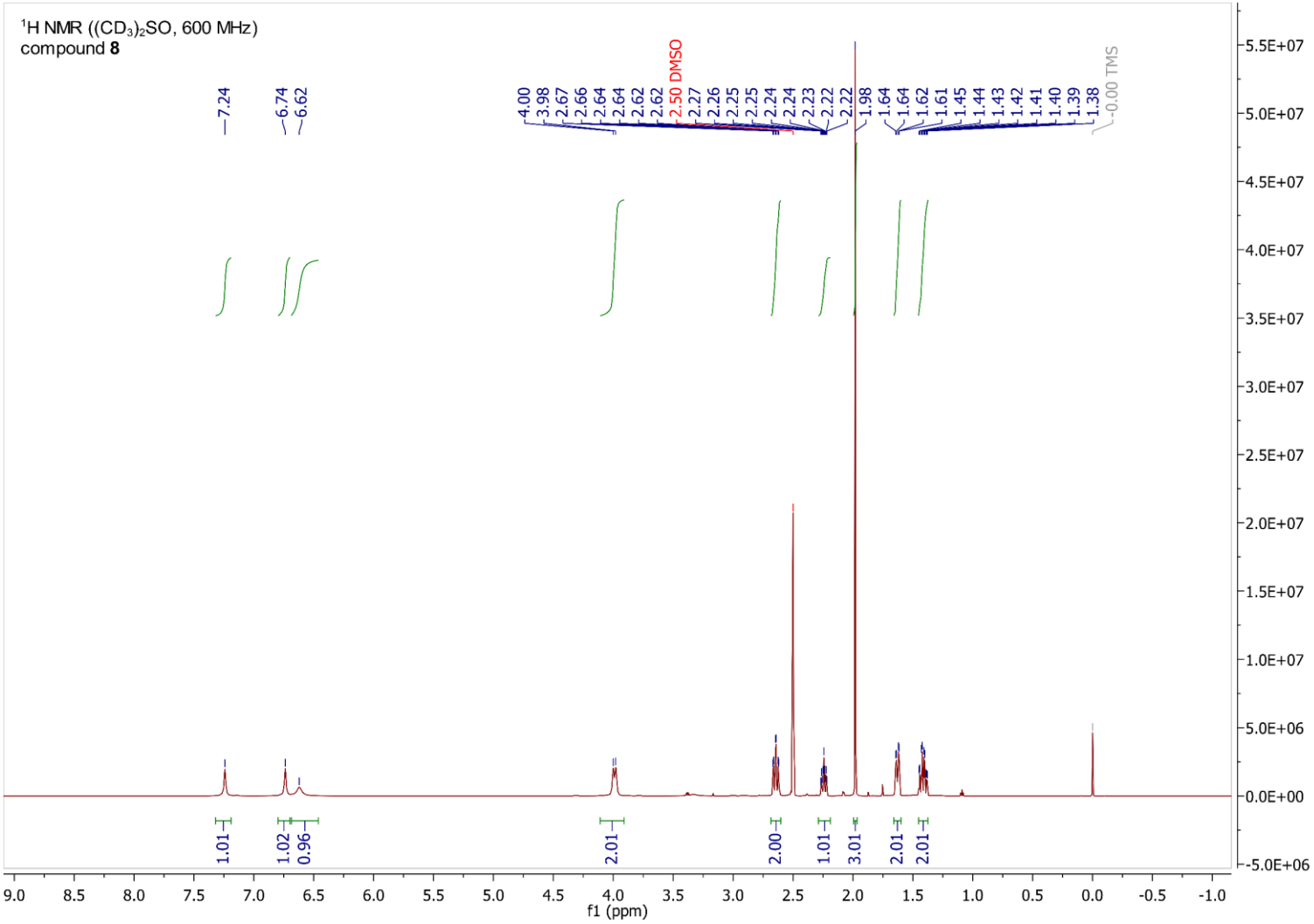


Figure S50. ^{1}H NMR spectrum of [Zn(quin)$_2$(pz)]$_n$ (**9**) in DMSO-d_6 with the addition of trifluoroacetic acid (TFA).