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Supporting information

for

Amidines from cyclic amines and nitriles in the presence of zinc(II): Other nitriles in place of acetonitrile

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Contents

List of compounds

$[Zn(quin)_2(pipe)]\cdot CH_3CH_2CN$	**1·CH_3CH_2CN**
$[Zn(quin)_2(pipe)_2]\cdot CH_3CH_2CN$	**2·CH_3CH_2CN**
$[Zn(quin)_2(pipe)_2]\cdot 2.5PhCN$	**2·2.5PhCN**
$[Zn(quin)_2(pyro)]$	**3**
$[Zn(quin)_2(pyro)_2]$	**4**
$[Zn(quin)_2(pipepropioam)]$	**5**
pipepropioamH$[Zn(quin)_3]$	**6**
pyropropioamH$[Zn(quin)_3]$	**7**
$[Zn(quin)_2(pipebenzoam)]$	**8a**, **8b**
$[Zn(quin)_2(pyrobenzoam)]$	**9a**, **9b**
pipebenzoamH$[Zn(quin)_3]$	**10**
pyrobenzoamH$[Zn(quin)_3]$	**11**
pyrobenzoamH$[Zn(quin)_3]\cdot[Zn(quin)_2(pyrobenzoam)]$	**12**

1. Crystal structures of zinc(II) complexes with intact amines

The zinc(II) complexes with amines, piperidine, pyrrolidine and morpholine, form part of our previous study.[S1] During current investigation, single-crystals of a few more complexes with piperidine or pyrrolidine were obtained. Of particular importance are the crystal structures of the pyrrolidine complexes which have not been determined before. A brief description of the structures of $[Zn(quin)_2(pyro)]$ (**3**) and $[Zn(quin)_2(pyro)_2]$ (**4**) is given below. The crystal data of the complexes with amines are given in Table S1.

Table S1. Crystallographic data for **1·CH_3CH_2CN**–**4**.

	1·CH_3CH_2CN	**2·CH_3CH_2CN**	**2·2.5PhCN**	**3**	**4**
Empirical formula	$C_{28}H_{28}N_4O_4Zn$	$C_{33}H_{39}N_5O_4Zn$	$C_{47.5}H_{46.5}N_{6.5}O_4Zn$	$C_{24}H_{21}N_3O_4Zn$	$C_{28}H_{30}N_4O_4Zn$
Formula weight	549.91	635.06	837.78	480.81	551.93
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	*Cc*	*P* $2_1/n$	*P* –1	*C* 2/*c*	*P* 2/*c*
***T* [K]**	150.00(10)	150.05(10)	150.00(10)	150.00(10)	150.00(10)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
***a* [Å]**	9.57440(10)	13.8766(5)	7.6600(2)	13.7196(4)	18.6335(9)
***b* [Å]**	24.2668(4)	7.5530(2)	14.7528(5)	8.0117(2)	13.7763(6)
***c* [Å]**	10.97570(10)	14.5911(5)	18.8900(6)	19.1729(5)	19.9630(13)
α [°]	90	90	91.319(3)	90	90
β [°]	96.5300(10)	91.303(3)	97.791(2)	105.783(3)	103.298(6)
γ [°]	90	90	97.798(2)	90	90
***V* [Å^3]**	2533.55(5)	1528.90(9)	2093.56(11)	2027.98(10)	4987.1(5)
Z	4	2	2	4	8
D_{calc} [g/cm^3]	1.442	1.379	1.329	1.575	1.470
μ [mm^{-1}]	1.012	0.849	0.639	1.250	1.028
Collected reflections	37001	13910	37788	29139	31372
Unique reflections	6999	4156	11268	2929	13077
Observed reflections	6796	3707	9346	2815	6040
R_{int}	0.0231	0.0228	0.0306	0.0338	0.0583
R_1 ($I > 2\sigma(I)$)	0.0233	0.0268	0.0331	0.0243	0.0581
wR_2 (all data)	0.0580	0.0687	0.0827	0.0663	0.1731

[S1] N. Podjed, B. Modec, M. M. Alcaide and J. López-Serrano, *RSC Adv.*, 2020, **10**, 18200–18221.

The [Zn(quin)$_2$(pyro)] complex molecules of **3** feature a metal ion in a five-coordinate environment which consists of two *N*,*O*-bidentate chelating quinaldinate ions and a monodentate pyrrolidine bound *via* amine nitrogen. As shown by the τ parameter of 0.04, the N_3O_2 donor set defines vertices of a slightly distorted square pyramid. The quinaldinate-to-zinc(II) and the amine-to-zinc(II) bonds are comparable to the ones observed for [Zn(quin)$_2$(pipe)], a monopiperidine complex which was found in [Zn(quin)$_2$(pipe)]·*cis*-[Zn(quin)$_2$(pipe)$_2$].[S1] The differences between the pair may be ascribed to crystallographic disorder of pyrrolidine ligand in **3**. Hydrogen bonds of the NH···COO$^-$ type with the length of 2.856(2) Å link the [Zn(quin)$_2$(pyro)] complex molecules into supramolecular layers. These layers stack along *c* axis.

Figure S1. ORTEP drawing of the [Zn(quin)$_2$(pyro)] complex molecule in **3**. The displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

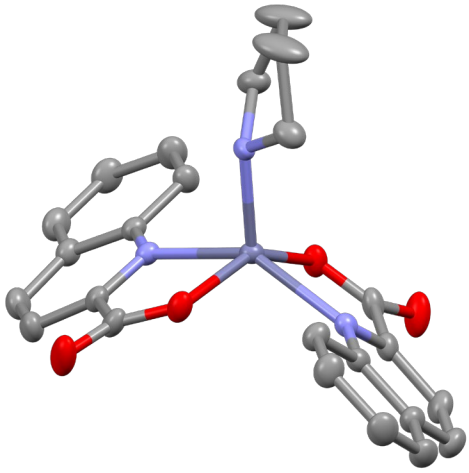


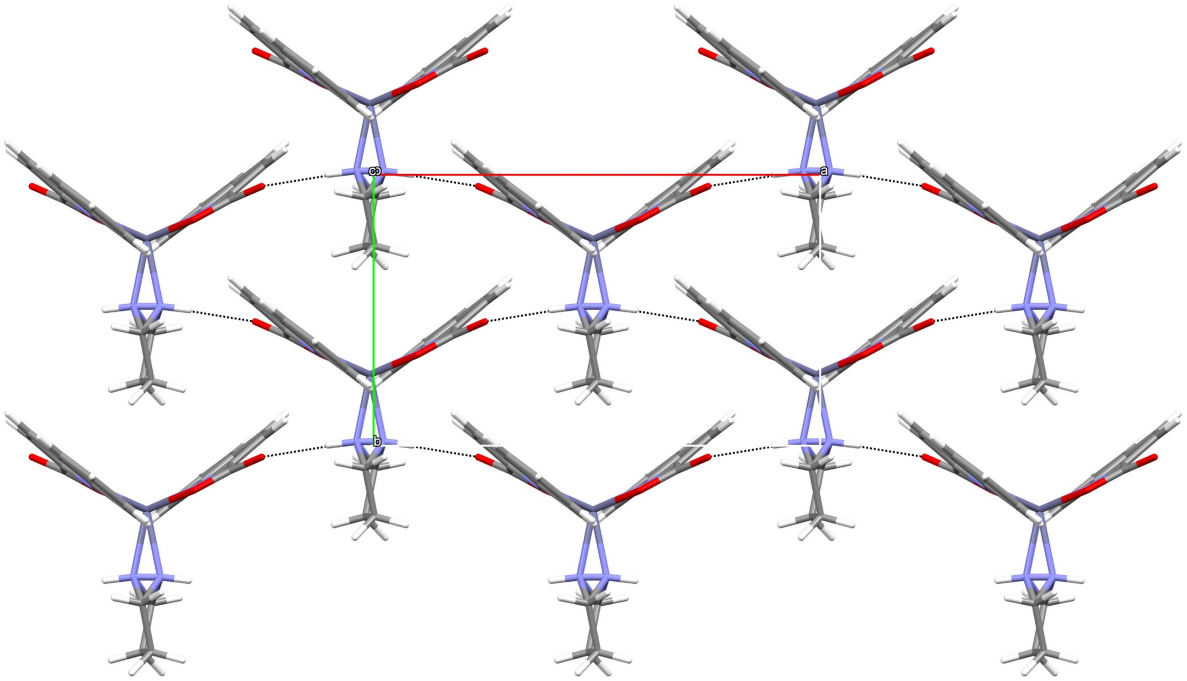
Table S2. Relevant geometric parameters [Å] of [Zn(quin)$_2$(pyro)] (**3**) as compared to a piperidine analogue.

Compound	Zn–N(amine)	Zn–N(quin$^-$)	Zn–O(quin$^-$)	τ
[Zn(quin)$_2$(pyro)] (**3**)	2.0291(19)	2.2093(10)	1.9921(9)	0.04
[Zn(quin)$_2$(pipe)]·*cis*-[Zn(quin)$_2$(pipe)$_2$][a]	2.0670(18)	2.1906(18), 2.1962(17)	1.9785(15), 1.9888(14)	0.35

[a] Previous work.[S1] The data pertain to the five-coordinate species.

[S1] N. Podjed, B. Modec, M. M. Alcaide and J. López-Serrano, *RSC Adv.*, 2020, **10**, 18200–18221.

Figure S2. Intermolecular interactions in [Zn(quin)$_2$(pyro)] (**3**). Section of a supramolecular layer, viewed along *c* axis.



The $[Zn(quin)_2(pyro)_2]$ complex molecules of **4** feature zinc(II) in a six-coordinate environment which consists of two *N*,*O*-bidentate chelating quinaldinate ions and two monodentate pyrrolidine ligands. The N_4O_2 donor set defines vertices significantly longer than the ones found in a monoamine complex $[Zn(quin)_2(pyro)]$ (**3**). As shown in Table S3, the coordination bonds in $[Zn(quin)_2(pyro)_2]$ are similar to the ones in the piperidine analogue, $[Zn(quin)_2(pipe)_2]$.[S1] In **4**, hydrogen bonds of the NH···COO^- type with the lengths of 2.921(4)–2.987(4) Å link complex molecules into supramolecular chains. The chains propagate along *b* axis.

Figure S3. ORTEP drawing of the $[Zn(quin)_2(pyro)_2]$ complex molecule in **4**. The displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

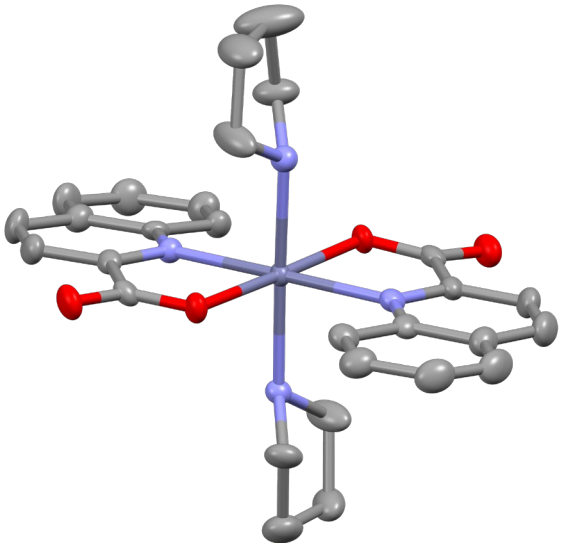


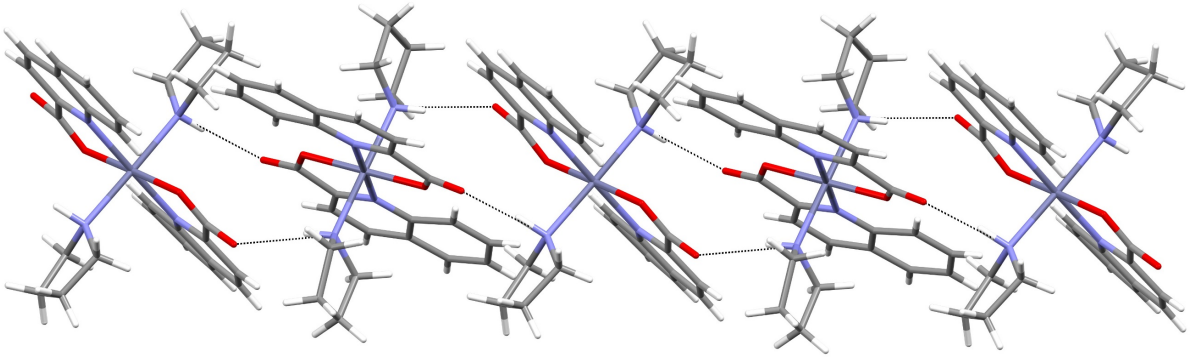
Table S3. Relevant geometric parameters [Å] of $[Zn(quin)_2(pyro)_2]$ (**4**) as compared to a piperidine analogue.

Compound	Zn–N(amine)	Zn–N($quin^-$)	Zn–O($quin^-$)
$[Zn(quin)_2(pyro)_2]$ (**4**)	2.166(3)–2.189(3)	2.240(3)–2.279(3)	2.060(2)–2.083(3)
$[Zn(quin)_2(pipe)_2]\cdot 2CH_3CN$[a]	2.2168(15)	2.2520(14)	2.0526(12)

[a] Previous work.[S1]

[S1] N. Podjed, B. Modec, M. M. Alcaide and J. López-Serrano, *RSC Adv.*, 2020, **10**, 18200–18221.

Figure S4. Intermolecular interactions in $[Zn(quin)_2(pyro)_2]$ (**4**). Section of a supramolecular chain.



2. Intermolecular interactions and connectivity patterns in the structures of amidine compounds

Table S4. Hydrogen bond parameters in the structures of 6–12.

Compound	Hydrogen bond	Donor···acceptor distance [Å]
pipepropioamH[Zn(quin)$_3$] (**6**)	$NH_2^+\cdots COO^-$	2.866(2)
	$NH_2^+\cdots N(quin^-)$	2.938(2)
pyropropioamH[Zn(quin)$_3$] (**7**)	$NH_2^+\cdots COO^-$	2.900(2)
	$NH_2^+\cdots N(quin^-)$	2.991(2)
[Zn(quin)$_2$(pipebenzoam)] (**8a**)	$NH\cdots COO^-$	2.898(2)
	$NH\cdots COO^-$	2.9114(18)
[Zn(quin)$_2$(pipebenzoam)] (**8b**)	$NH\cdots COO^-$	2.941(3)
[Zn(quin)$_2$(pyrobenzoam)] (**9a**)	$NH\cdots COO^-$	3.0016(19)
[Zn(quin)$_2$(pyrobenzoam)] (**9b**)	$NH\cdots COO^-$	2.915(2)
	$NH\cdots COO^-$	2.970(2)
pyrobenzoamH[Zn(quin)$_3$] (**11**)	$NH_2^+\cdots COO^-$	2.830(5)
pyrobenzoamH[Zn(quin)$_3$]·[Zn(quin)$_2$(pyrobenzoam)] (**12**)	$NH\cdots COO^-$	2.950(3)
	$NH_2^+\cdots COO^-$	2.831(4)
	$NH_2^+\cdots COO^-$	2.955(4)

Figure S5. Section of a supramolecular chain in pyrobenzoamH[Zn(quin)$_3$] (**11**): the $NH_2^+\cdots COO^-$ and the $NH_2^+\cdots N(quin^-)$ contacts are 2.830(5) and 3.141(5) Å, respectively.

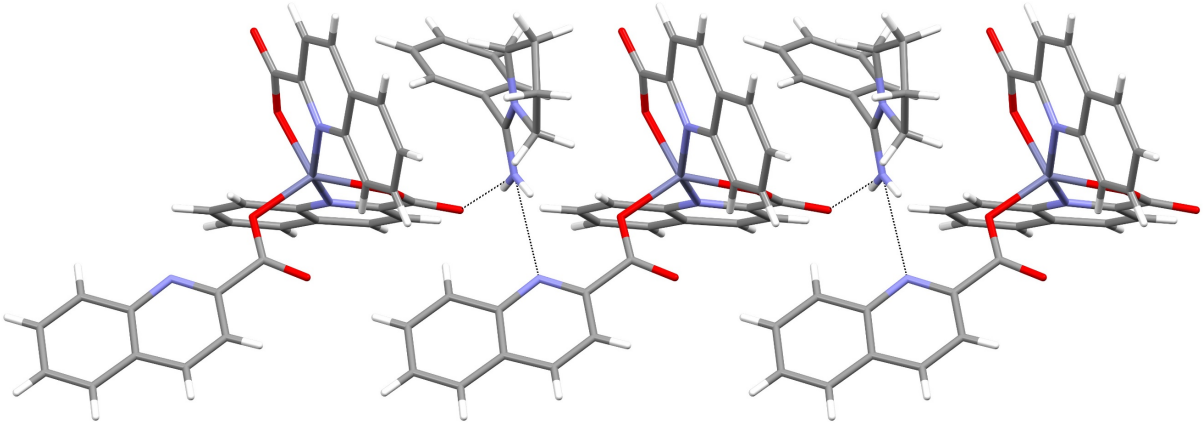


Figure S6. Supramolecular connectivity in pyrobenzoamH[Zn(quin)$_3$]·[Zn(quin)$_2$(pyrobenzoam)] (**12**): a short section of an infinite chain of ions (top) and a dimer of complex molecules (bottom).

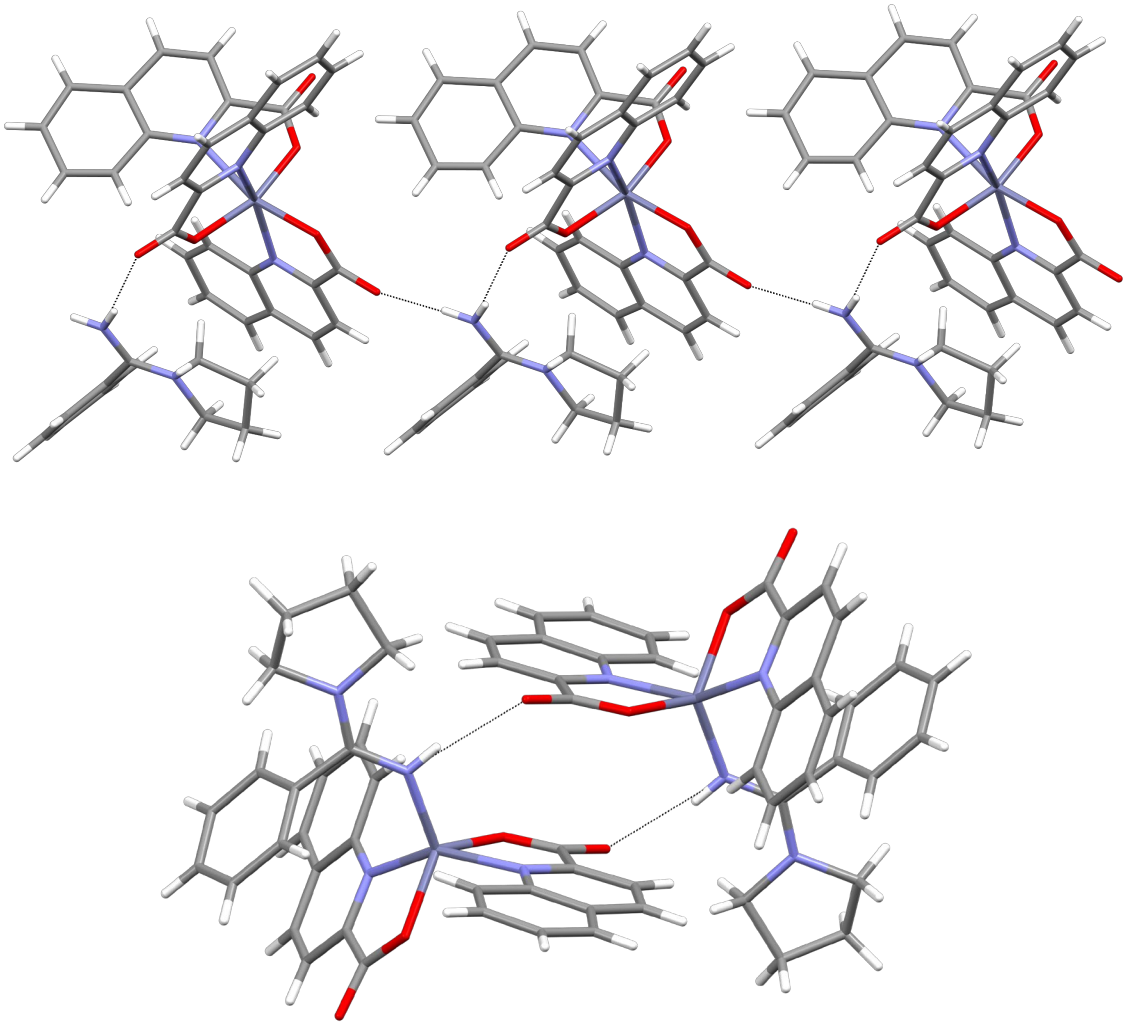
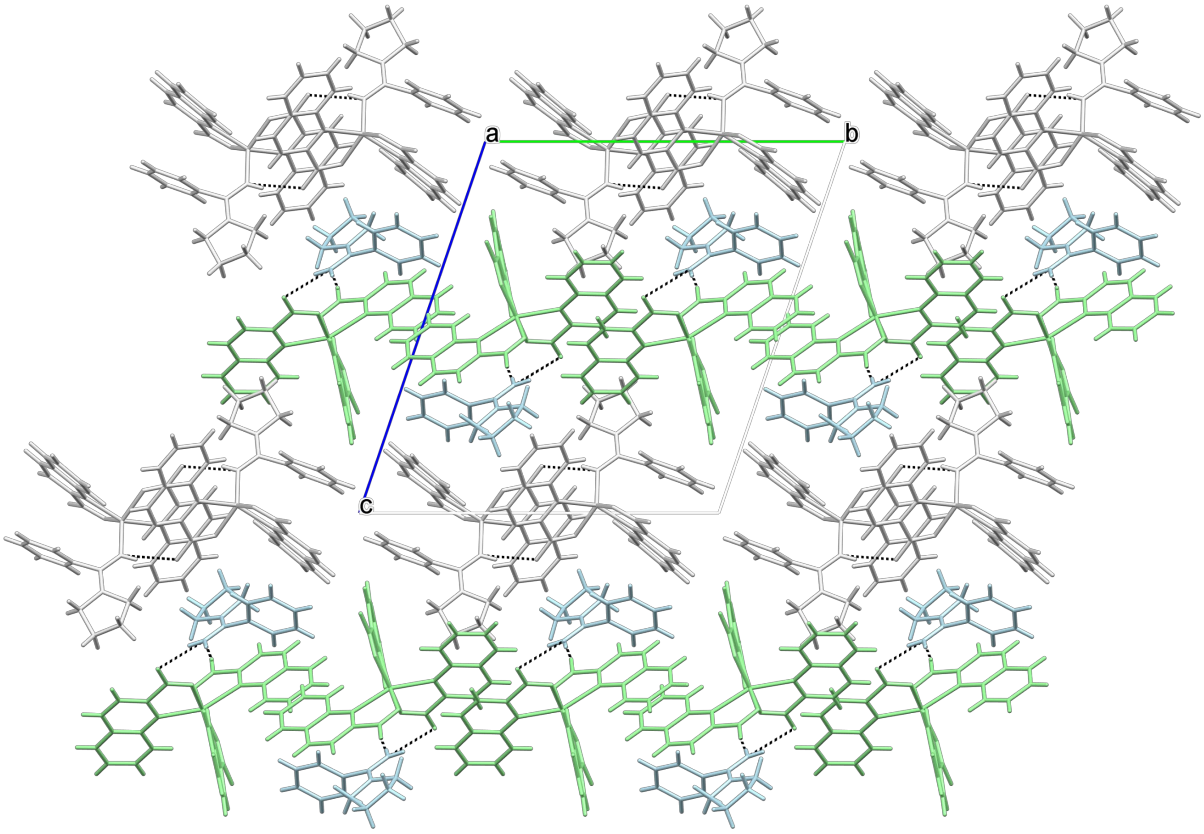


Figure S7. Packing in the structure of **12**. Layers of the [Zn(quin)$_2$(pyrobenzoam)] molecules, shown in grey colour, alternate with layers of the chains consisting of pyrobenzoamH$^+$ cations (coloured blue) and [Zn(quin)$_3$]$^-$ anions (coloured green). The supramolecular chains propagate along *a* axis. The view is along the chains.



3. Additional remarks on the infrared spectra

Presence of the coordinated amines, *i.e.*, piperidine and pyrrolidine, in compounds **1·CH_3CH_2CN–3** is corroborated by the stretching vibrations of the N–H and C–H bonds. The N–H stretching absorptions appear in the 3231–3126 cm^{-1} spectral region, whereas the C–H stretching bands occur in the 2960–2855 cm^{-1} region. With the amines being secondary amines, one ν(N–H) band is observed. The respective bands are of weak to medium intensity.

Table S5. Characteristic bands [cm^{-1}] in the spectra of Zn(II) complexes with amines.

Compound	ν(N–H)	ν(C–H)
$[Zn(quin)_2(pipe)]\cdot CH_3CH_2CN$ (**1·CH_3CH_2CN**)	3126	bands around 2937
$[Zn(quin)_2(pipe)_2]\cdot CH_3CH_2CN$ (**2·CH_3CH_2CN**)	3221	2931, 2854
$[Zn(quin)_2(pipe)_2]\cdot 2.5PhCN$ (**2·2.5PhCN**)	3231	2932, 2855
$[Zn(quin)_2(pyro)]$ (**3**)	3171	bands around 2956
$[Zn(quin)_2(pyro)_2]$ (**4**)[a]	3188	2953, 2873

[a] Previous work.[S1]

Nitrile solvent molecules are characterized by the C≡N stretching frequency which occurs according to the literature data for the aliphatic nitriles at 2260–2240 cm^{-1} and for benzonitriles at 2240–2220 cm^{-1}.[S2] Accordingly, $[Zn(quin)_2(pipe)]\cdot CH_3CH_2CN$ (**1·CH_3CH_2CN**) shows a band at 2244 cm^{-1}, whereas $[Zn(quin)_2(pipe)_2]\cdot 2.5PhCN$ (**2·2.5PhCN**) absorbs at 2226 cm^{-1}.

[S1] N. Podjed, B. Modec, M. M. Alcaide and J. López-Serrano, *RSC Adv.*, 2020, **10**, 18200–18221.

[S2] N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego, CA, 3rd. edn., 1990.

Figure S8. Infrared spectrum of [Zn(quin)$_2$(pipe)]·CH_3CH_2CN (**1·CH_3CH_2CN**).

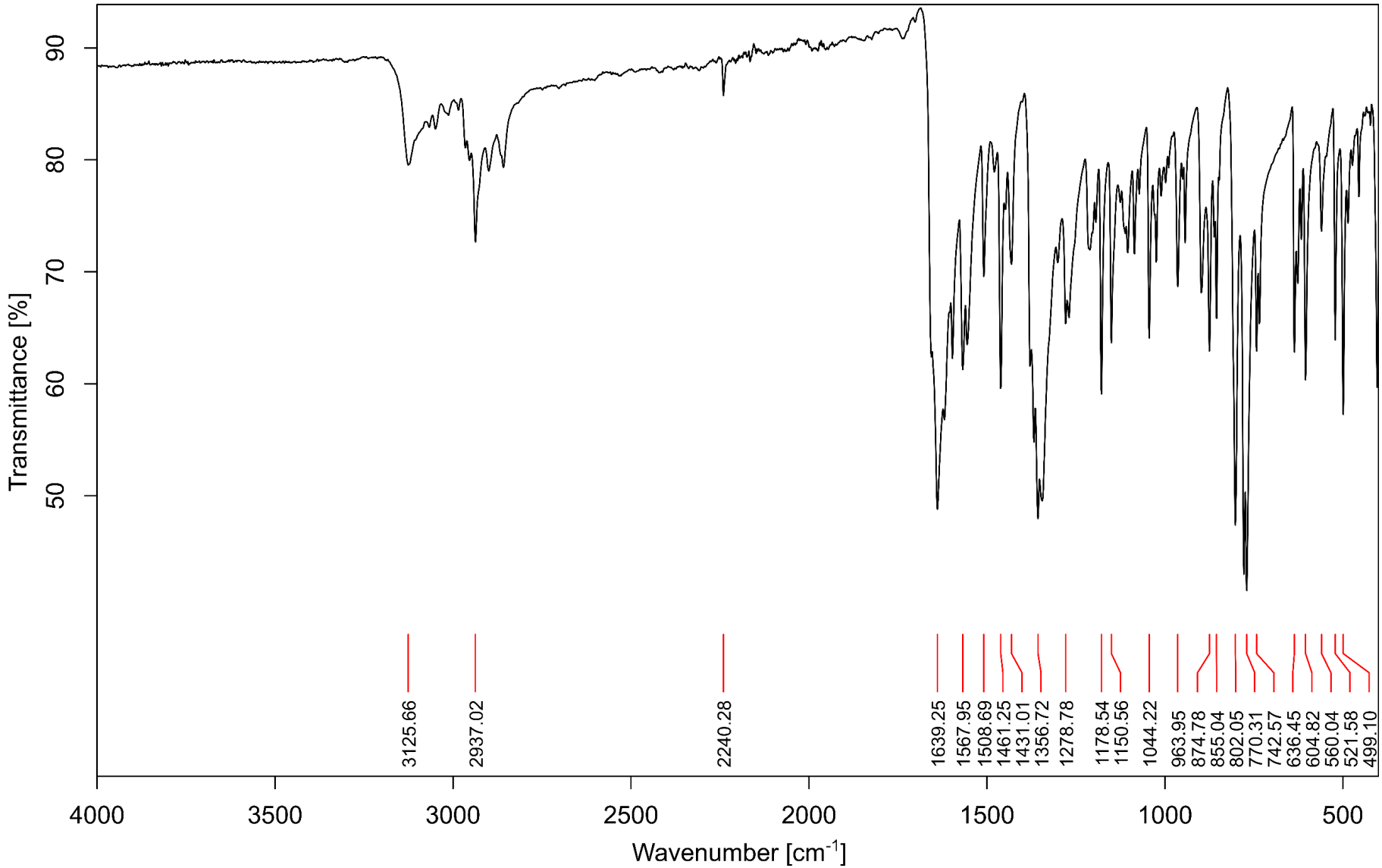


Figure S9. Infrared spectrum of $[Zn(quin)_2(pipe)_2]\cdot CH_3CH_2CN$ (**2·CH_3CH_2CN**).

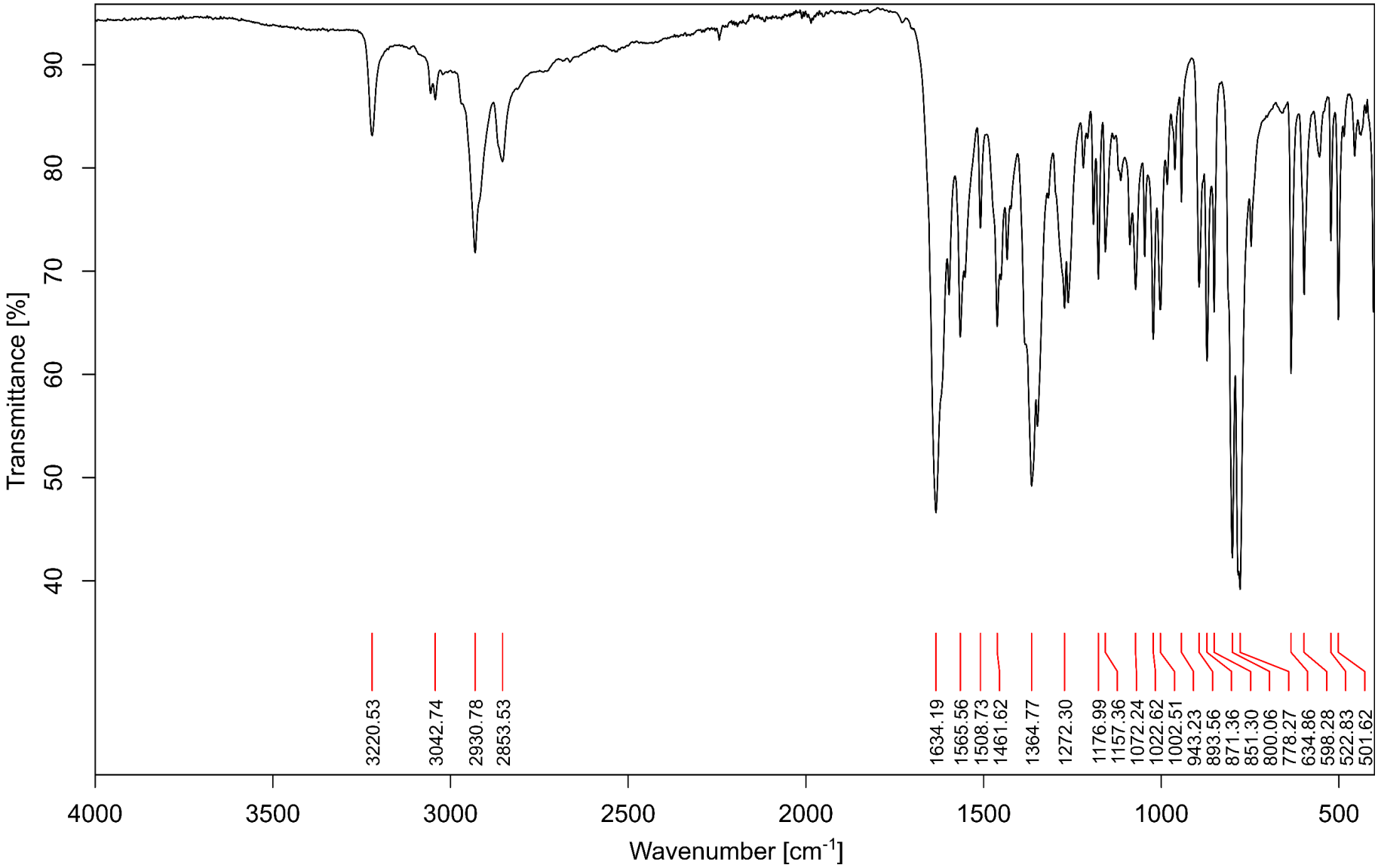


Figure S10. Infrared spectrum of $[Zn(quin)_2(pipe)_2]\cdot 2.5PhCN$ (**2·2.5PhCN**).

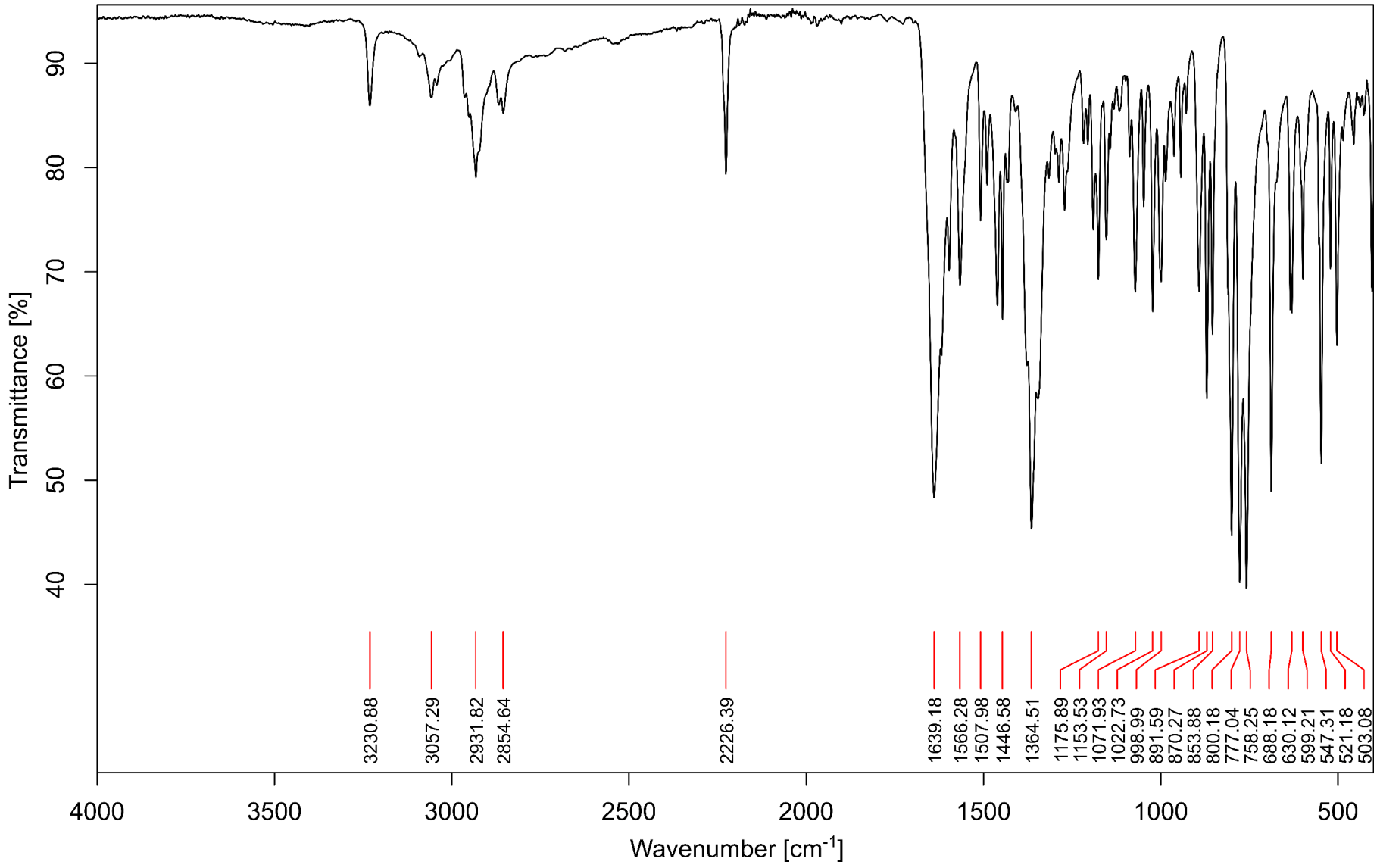


Figure S11. Infrared spectrum of [Zn(quin)$_2$(pyro)] (**3**).

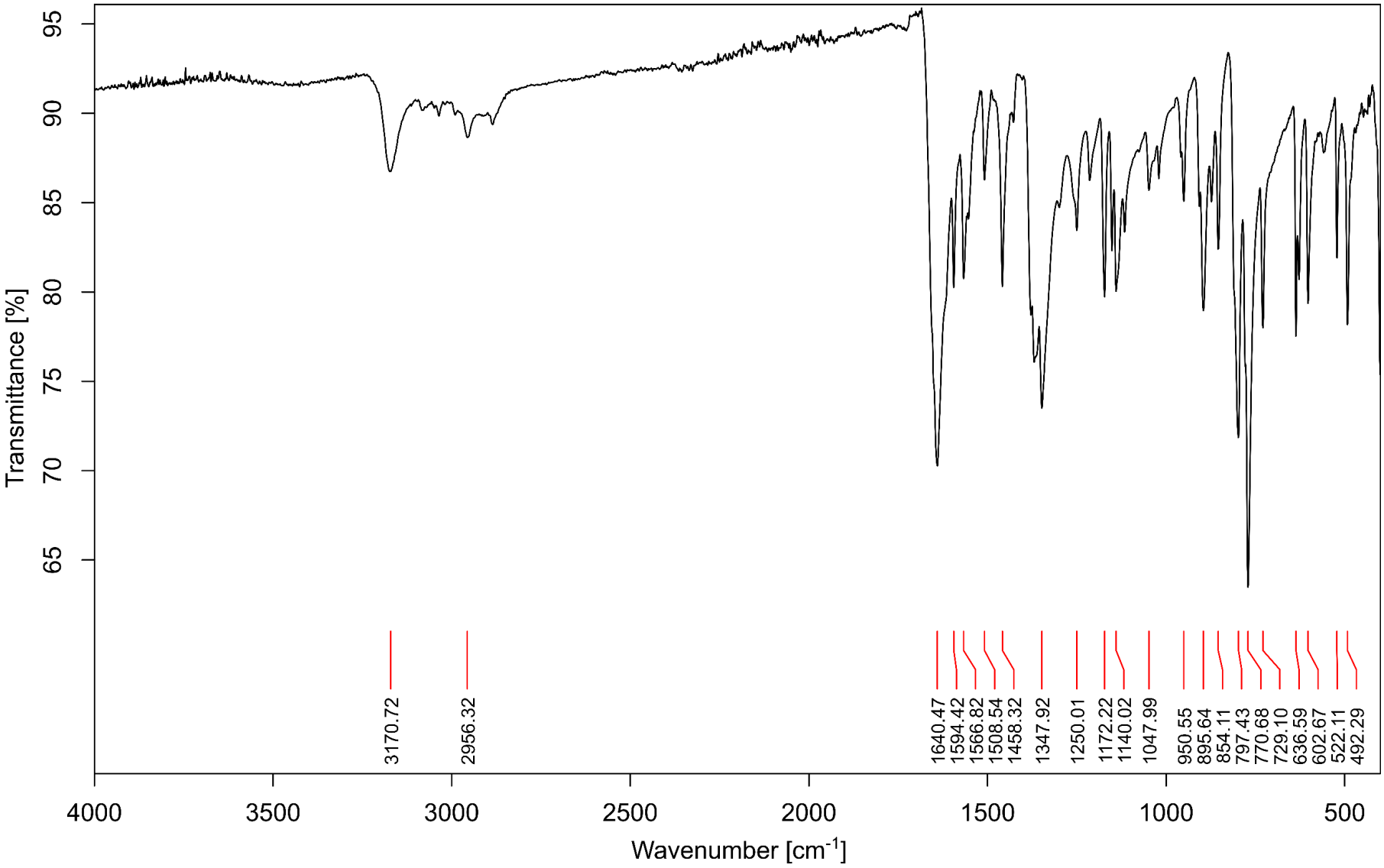


Figure S12. Infrared spectrum of [Zn(quin)$_2$(pipepropioam)] (**5**).

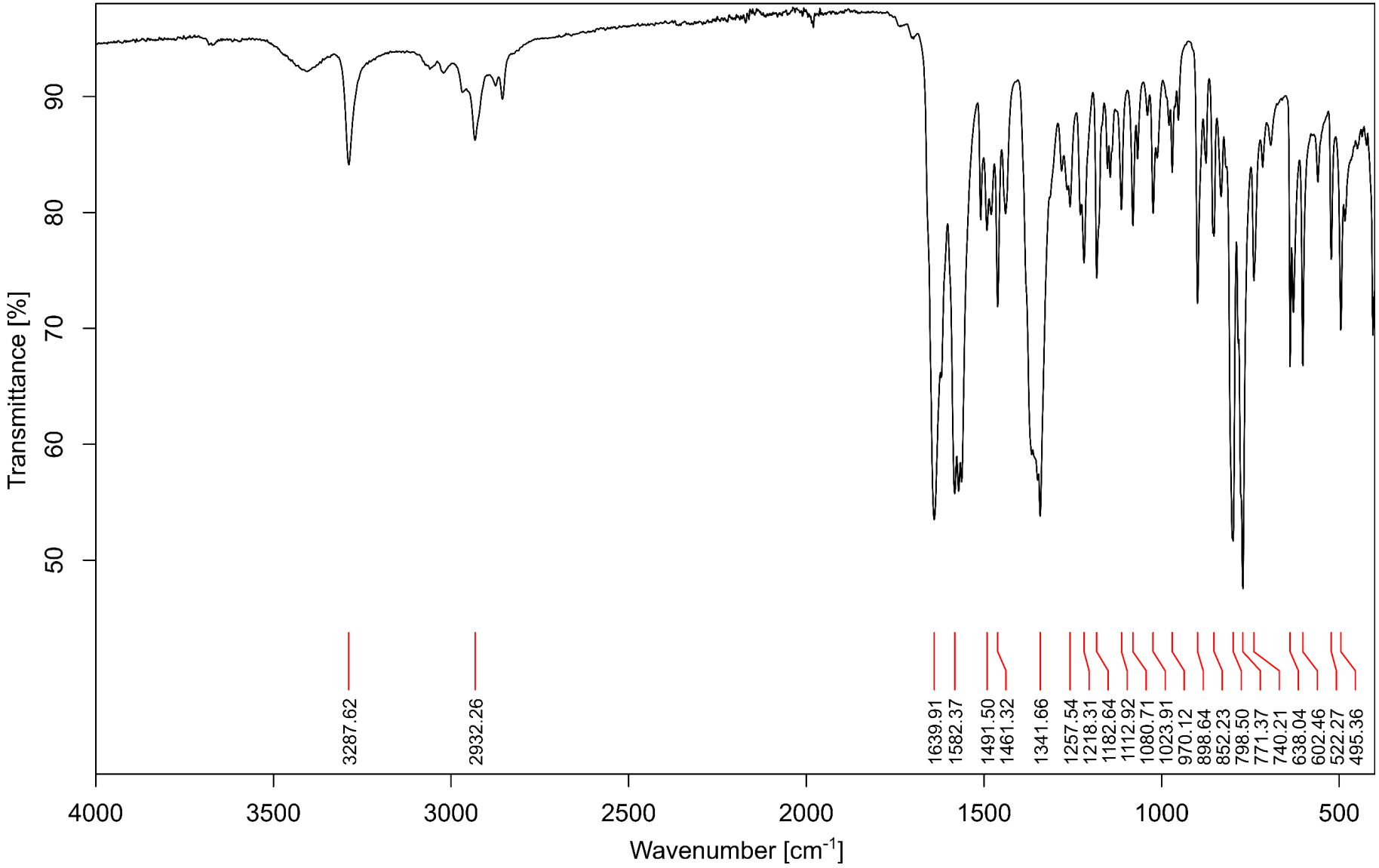


Figure S13. Infrared spectrum of pipepropioamH[Zn(quin)$_3$] (**6**).

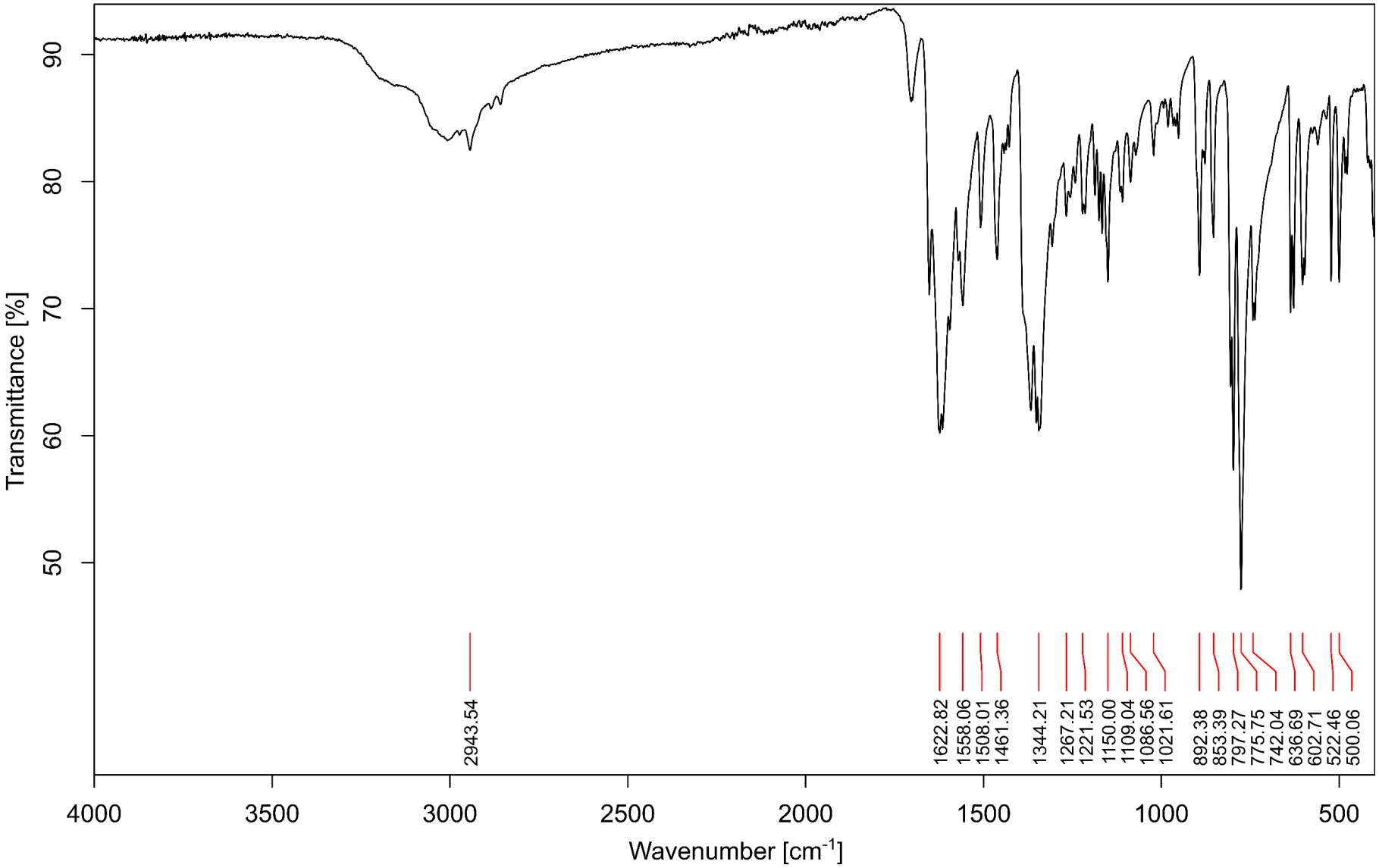


Figure S14. Infrared spectrum of pyropropioamH[Zn(quin)$_3$] (**7**).

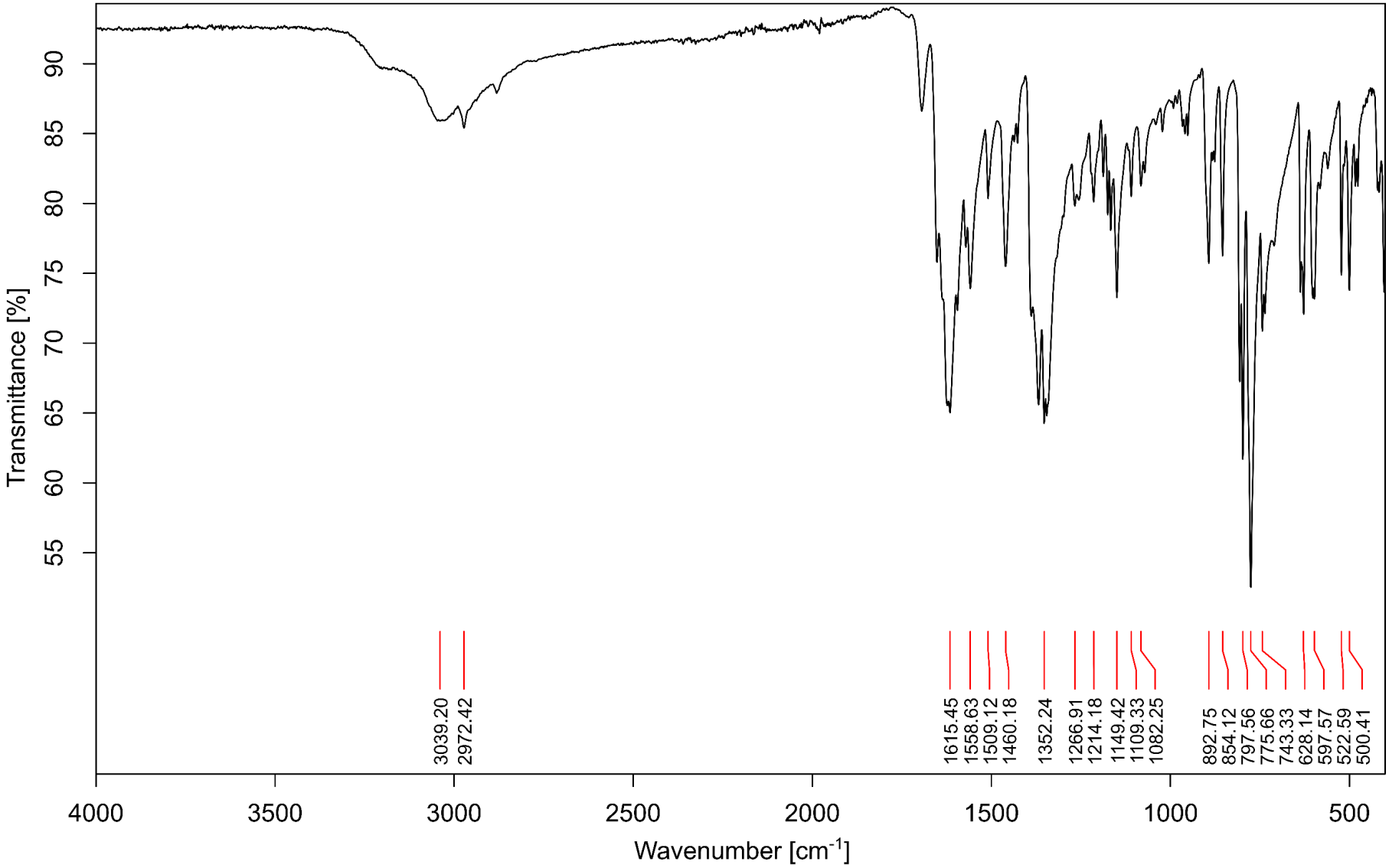


Figure S15. Infrared spectrum of [Zn(quin)$_2$(pipebenzoam)] (**8**).

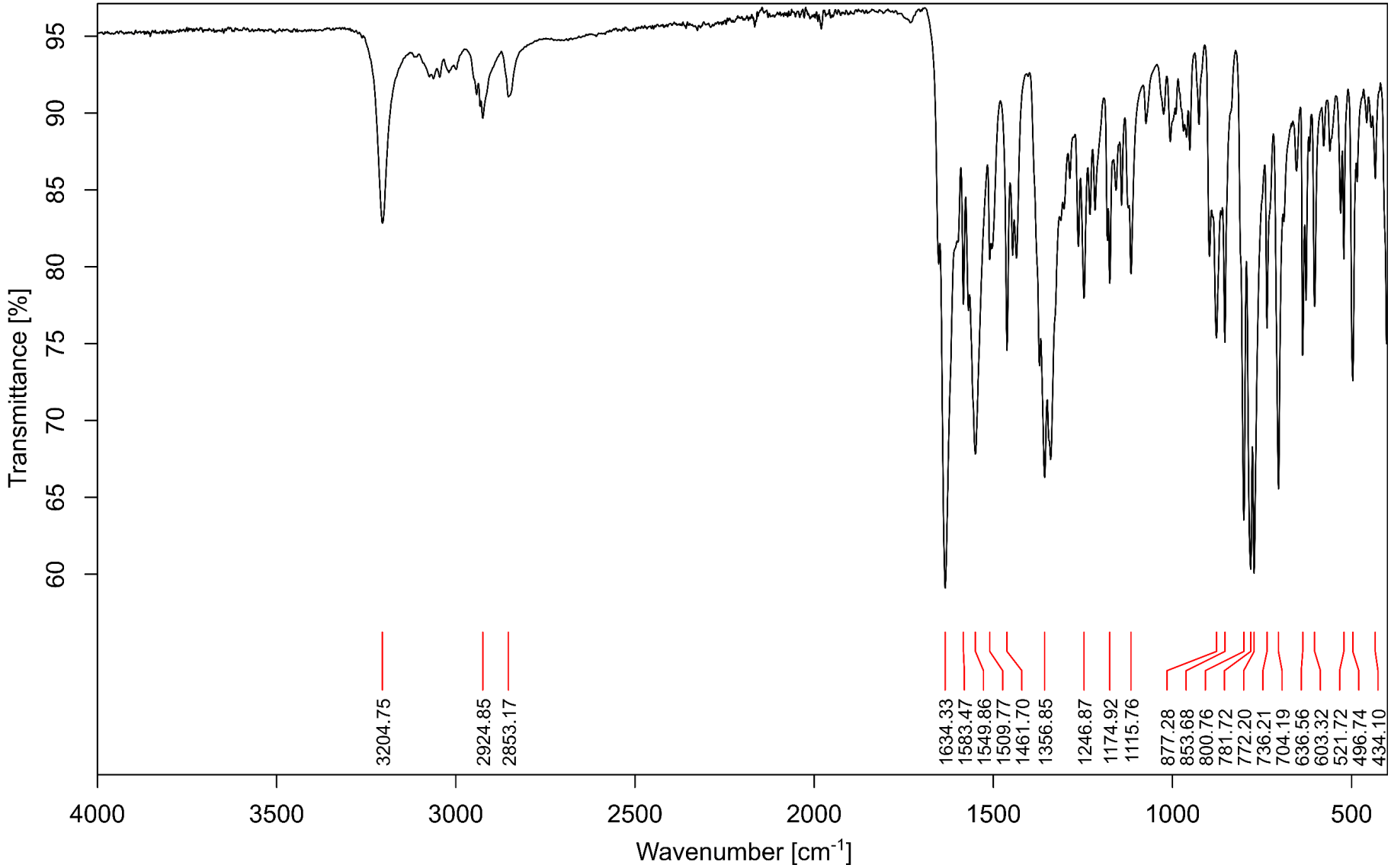


Figure S16. Infrared spectrum of [Zn(quin)$_2$(pyrobenzoam)] (**9**).

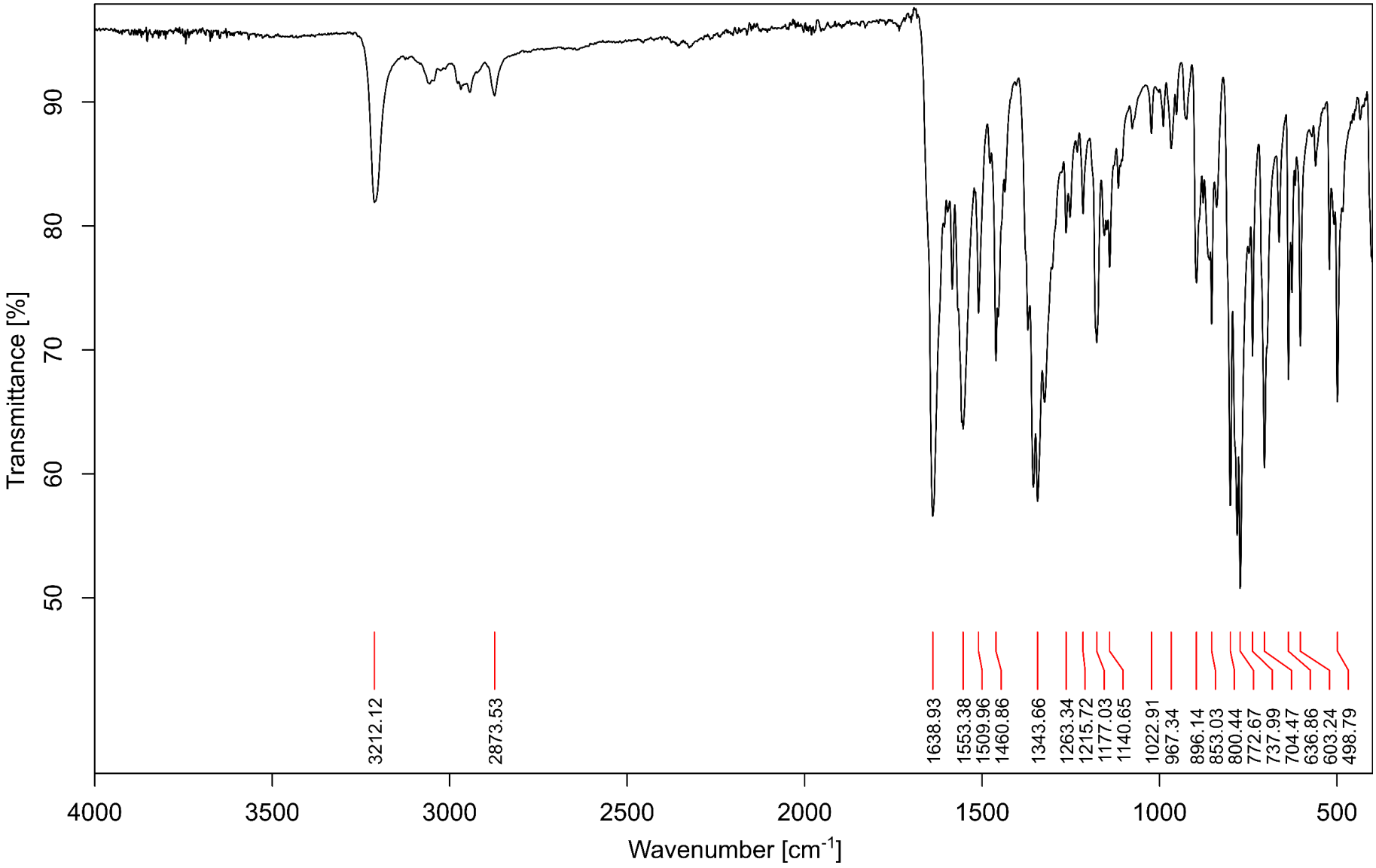


Figure S17. Infrared spectrum of pipebenzoamH[Zn(quin)$_3$] (**10**).

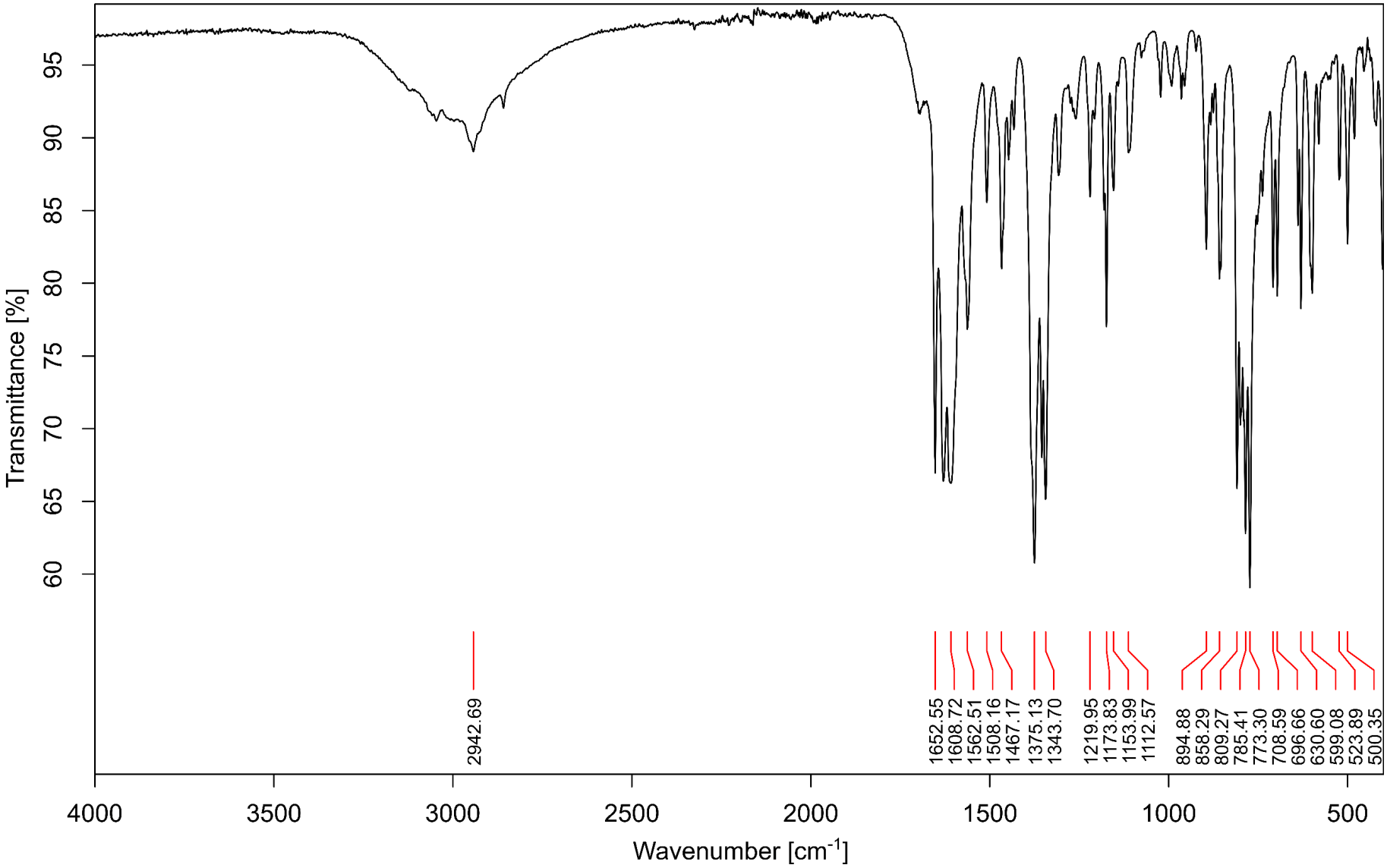


Figure S18. Infrared spectrum of pyrobenzoamH[Zn(quin)$_3$] (**11**).

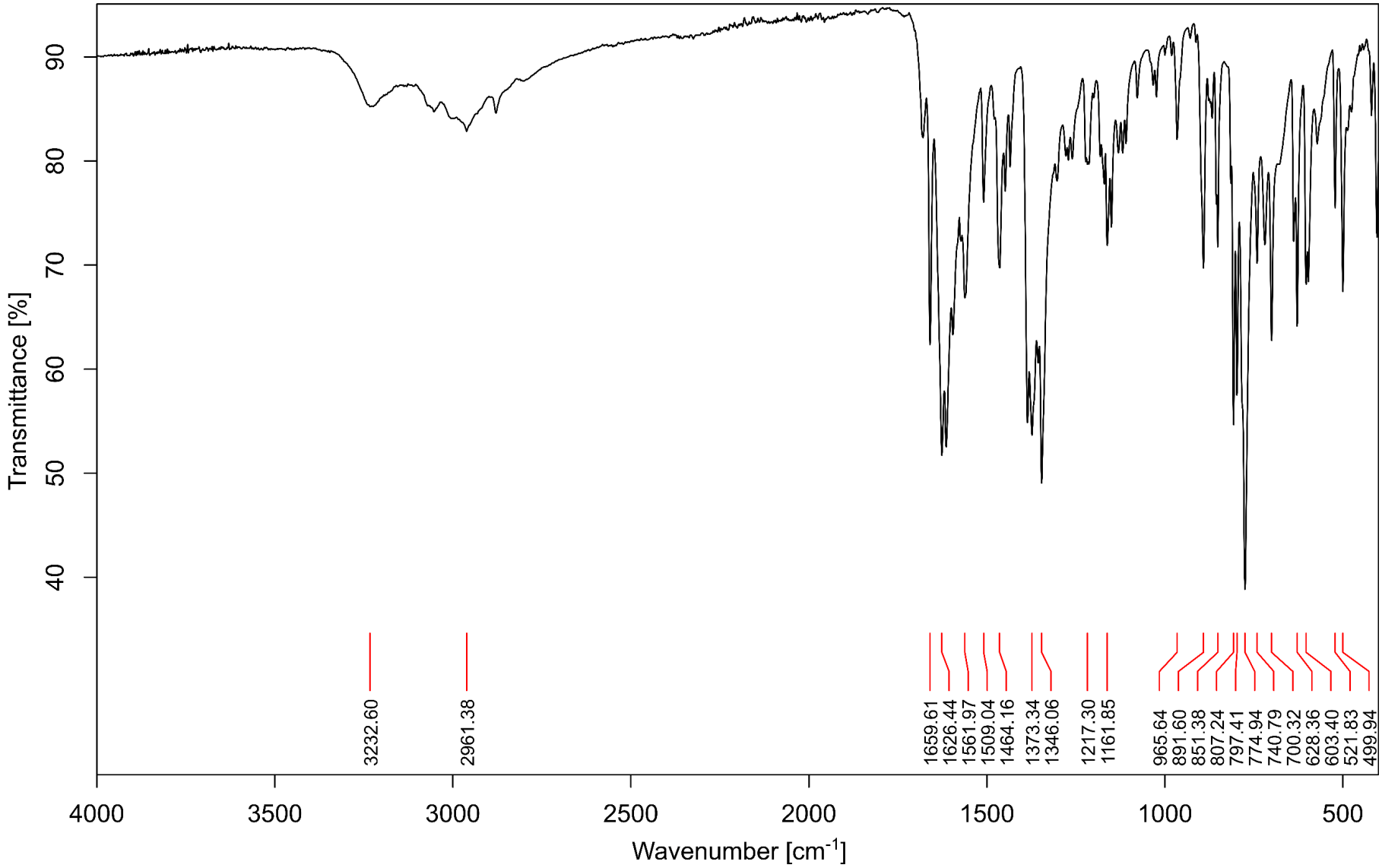
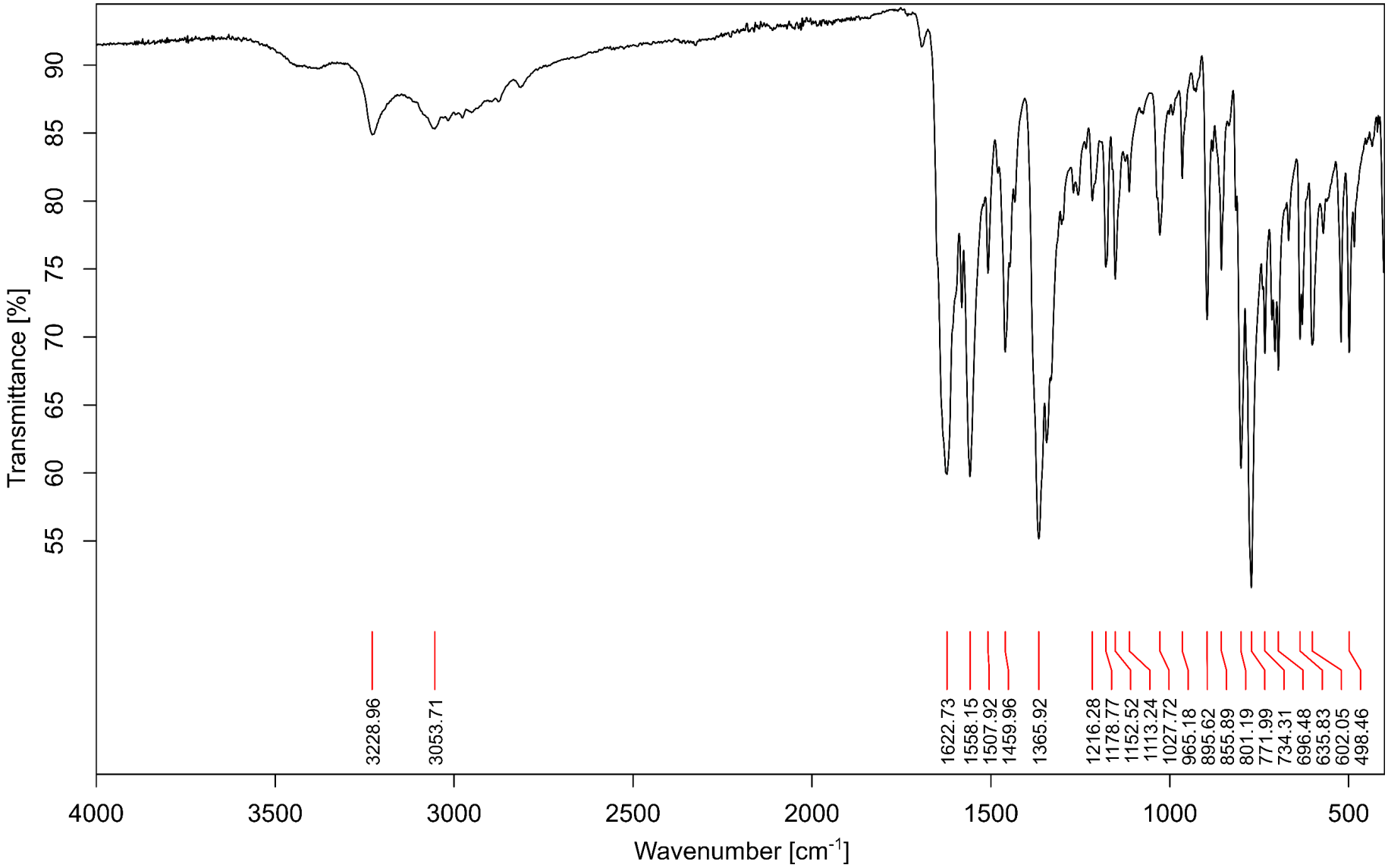


Figure S19. Infrared spectrum of pyrobenzoamH[Zn(quin)$_3$]·[Zn(quin)$_2$(pyrobenzoam)] (**12**).



5. ^{1}H and ^{13}C NMR spectroscopy

Figure S20. ^{1}H NMR spectrum of [Zn(quin)$_2$(pipe)]·CH_3CH_2CN (**1·CH_3CH_2CN**) in DMSO-d_6.

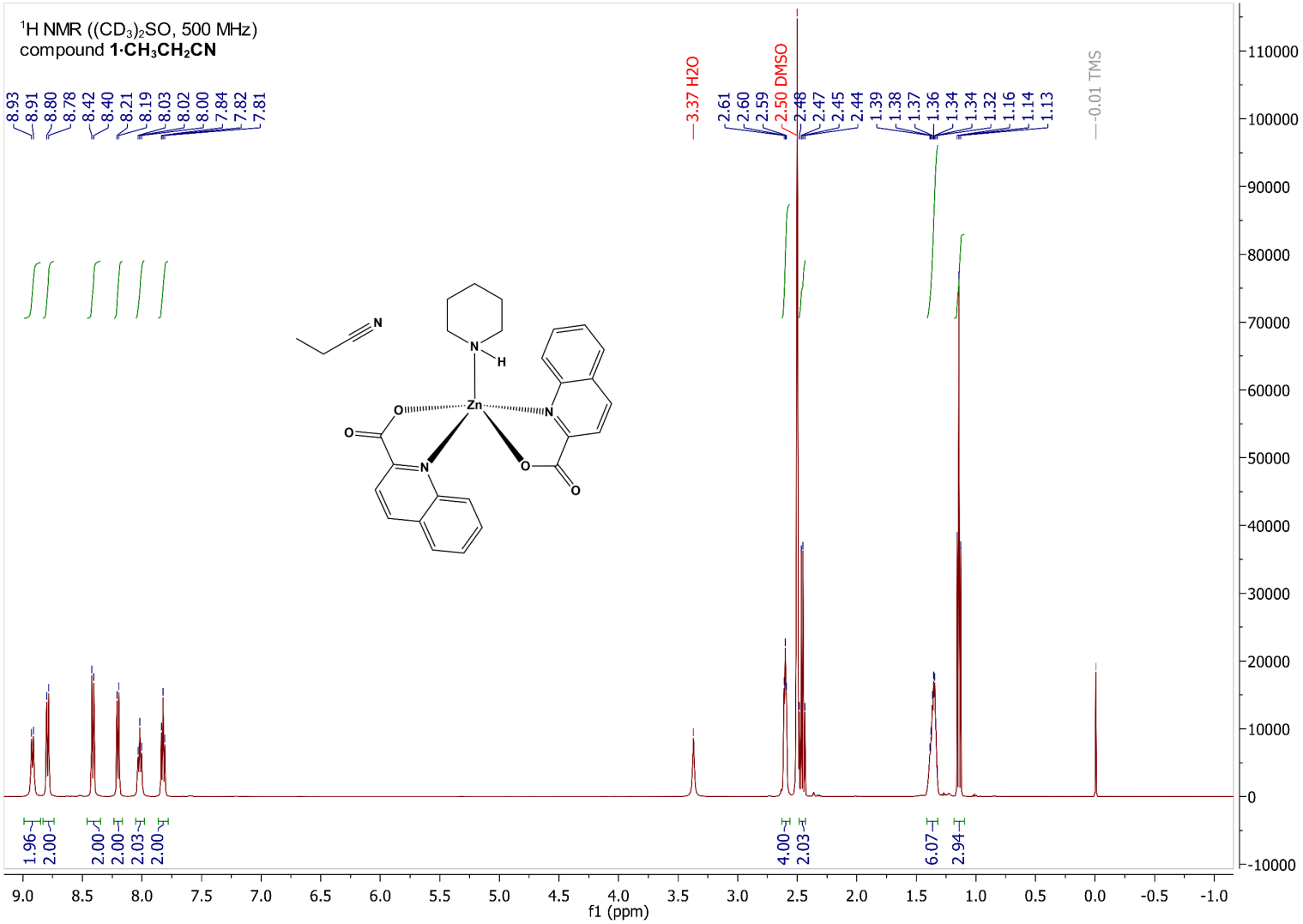


Figure S21. ^{1}H NMR spectrum of [Zn(quin)$_2$(pyro)] (**3**) in DMSO-d_6.

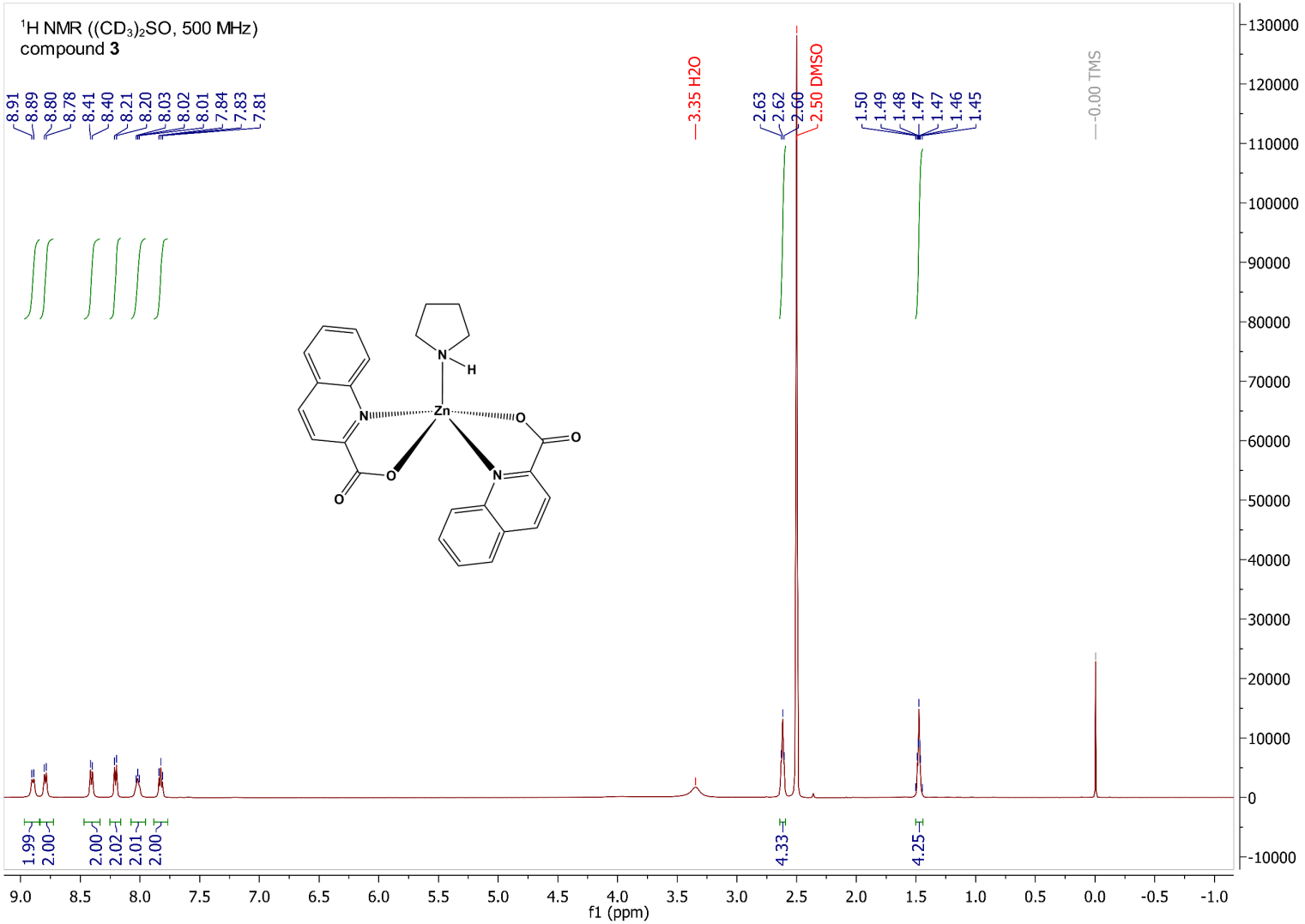


Figure S22. ^{1}H NMR spectrum of [Zn(quin)$_2$(pipepropioam)] (**5**) in DMSO-d_6 with the addition of trifluoroacetic acid.

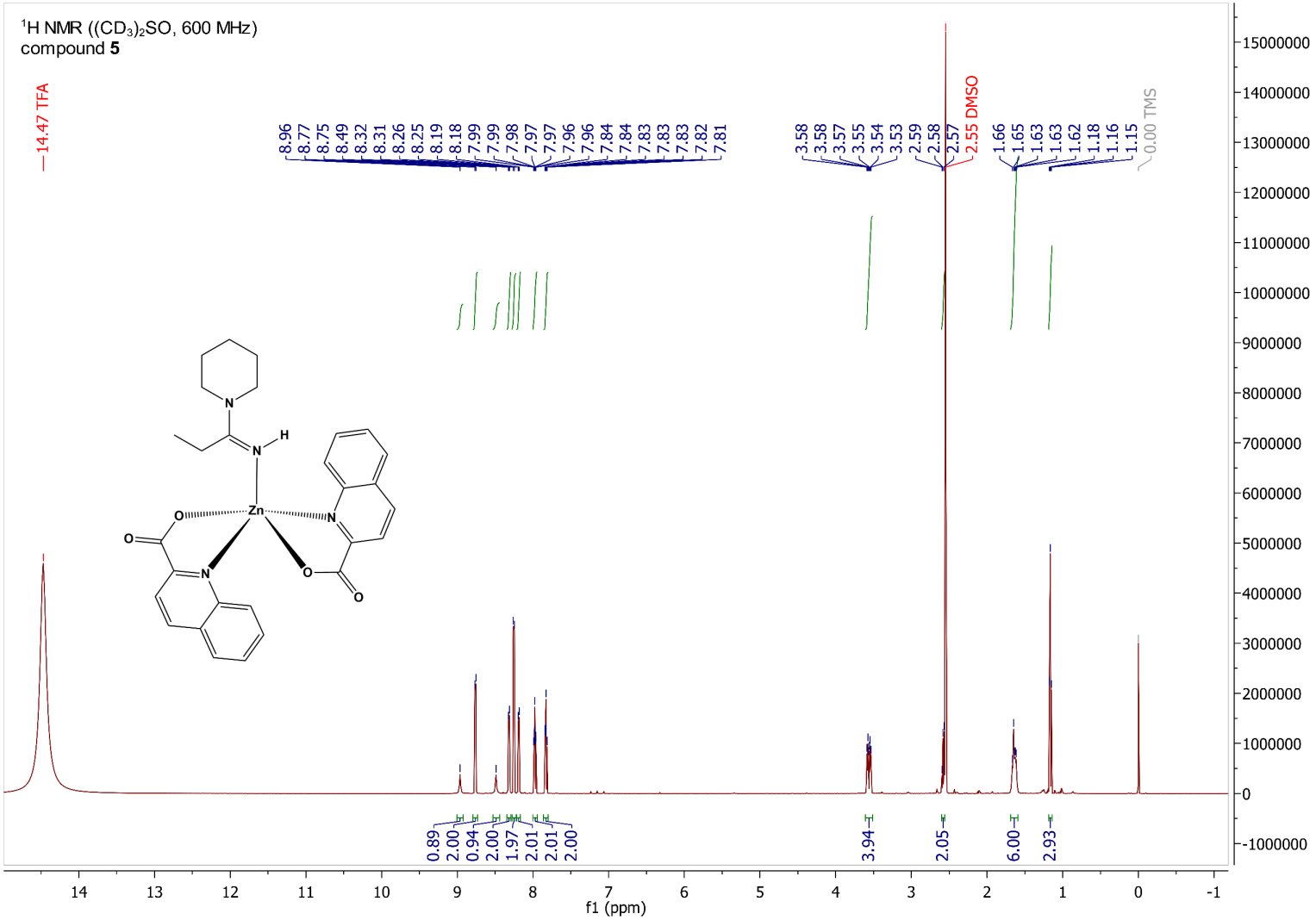


Figure S23. ^{1}H NMR spectrum of pipepropioamH[Zn(quin)$_3$] (**6**) in DMSO-d_6.

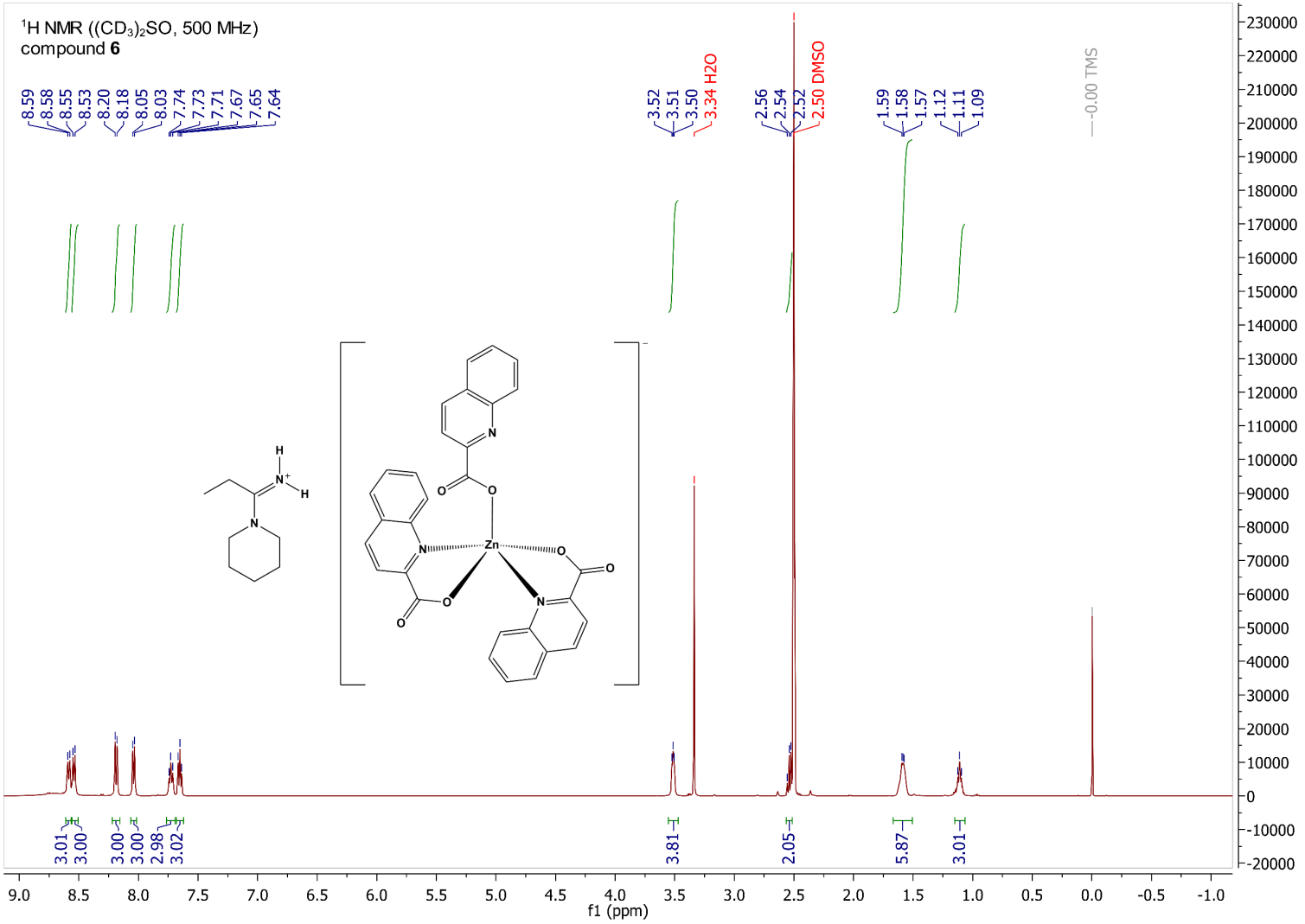


Figure S24. ^{13}C NMR spectrum of pipepropioamH[Zn(quin)$_3$] (**6**) in DMSO-d_6.

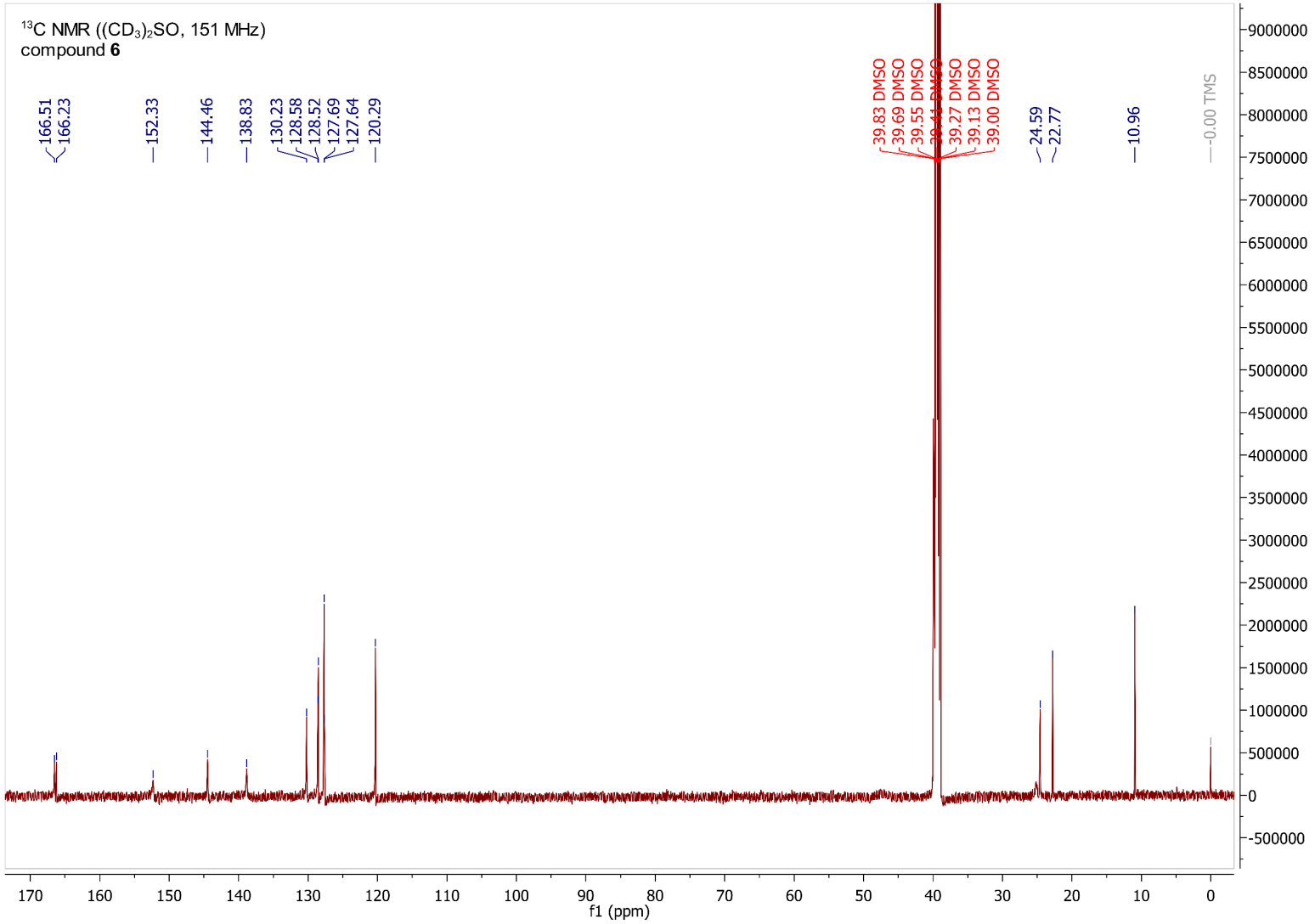


Figure S25. ^{1}H NMR spectrum of pyropropioamH[Zn(quin)$_3$] (**7**) in DMSO-d_6.

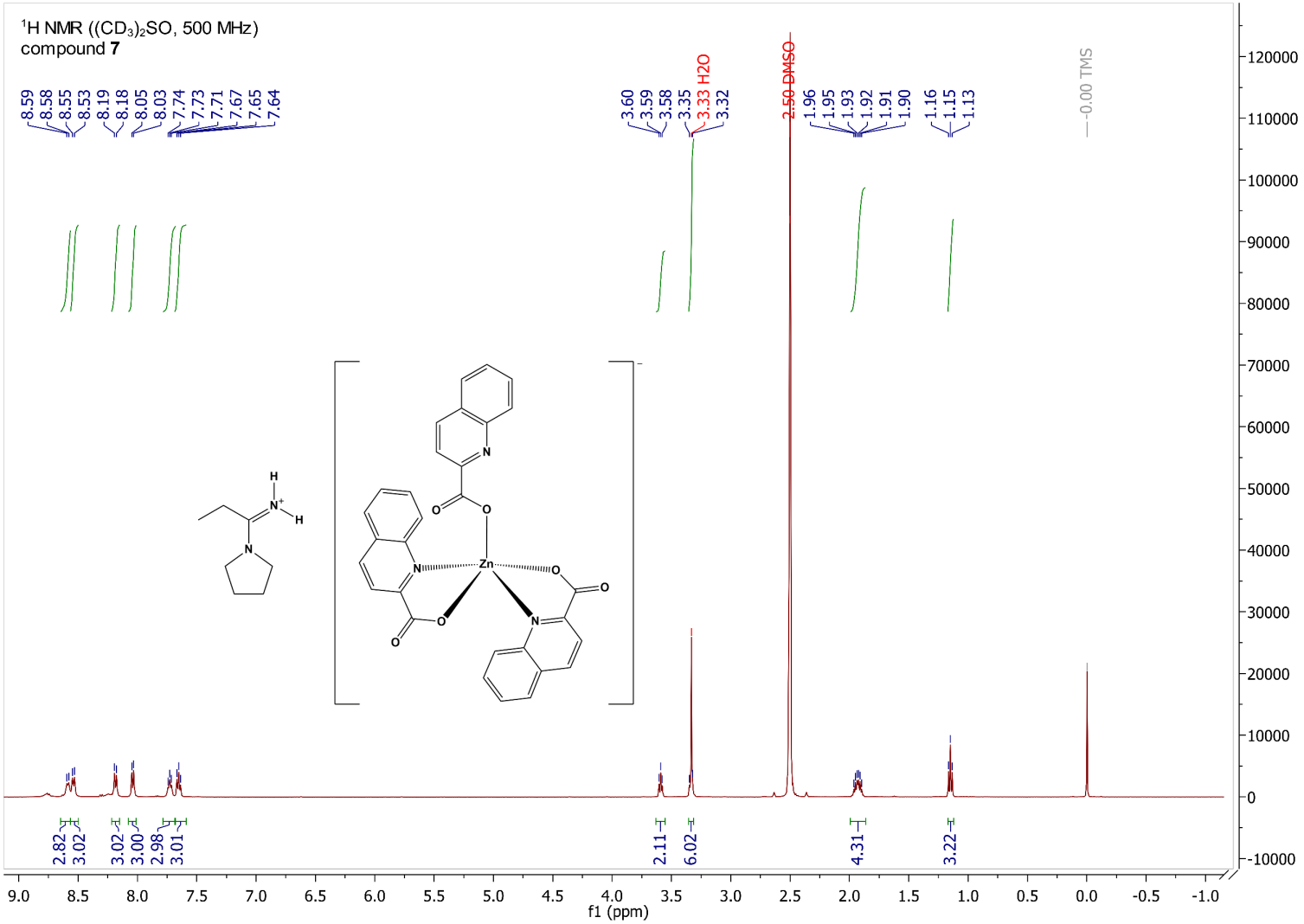


Figure S26. ^{13}C NMR spectrum of pyropropioamH[Zn(quin)$_3$] (**7**) in DMSO-d_6.

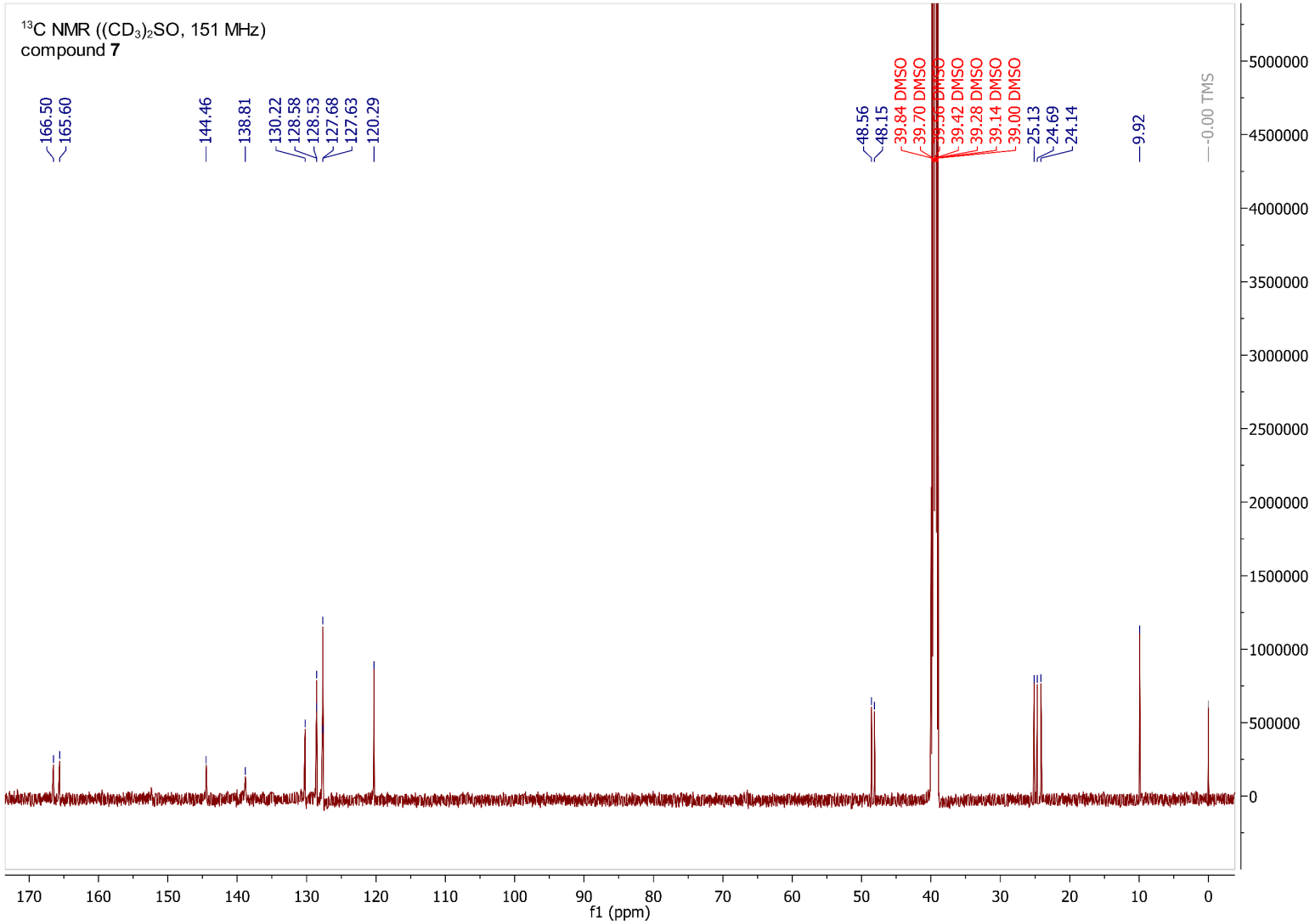


Figure S27. ^{1}H NMR spectrum of [Zn(quin)$_2$(pipebenzoam)] (**8**) in DMSO-d_6.

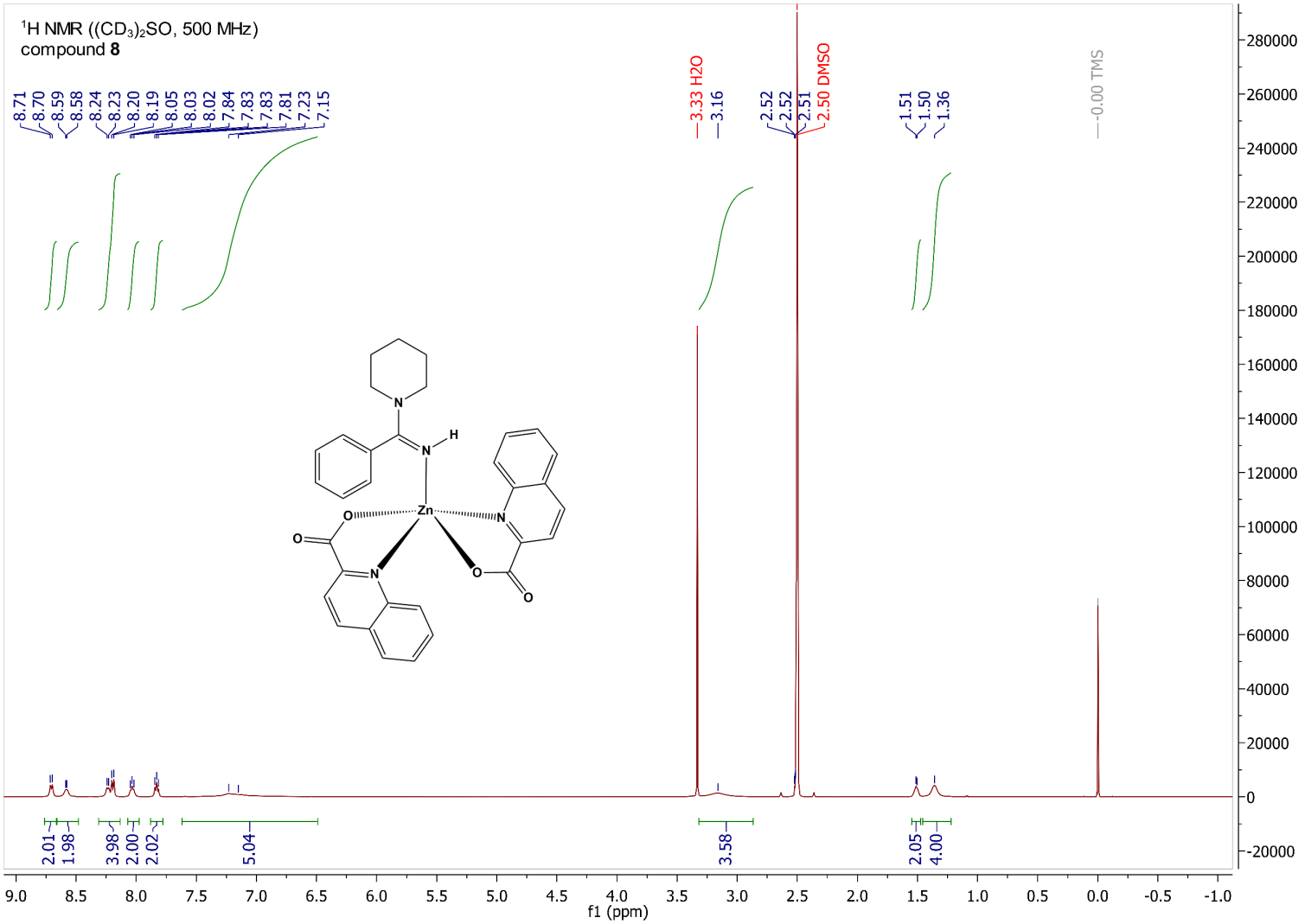


Figure S28. ^{13}C NMR spectrum of [Zn(quin)$_2$(pipebenzoam)] (**8**) in DMSO-d_6.

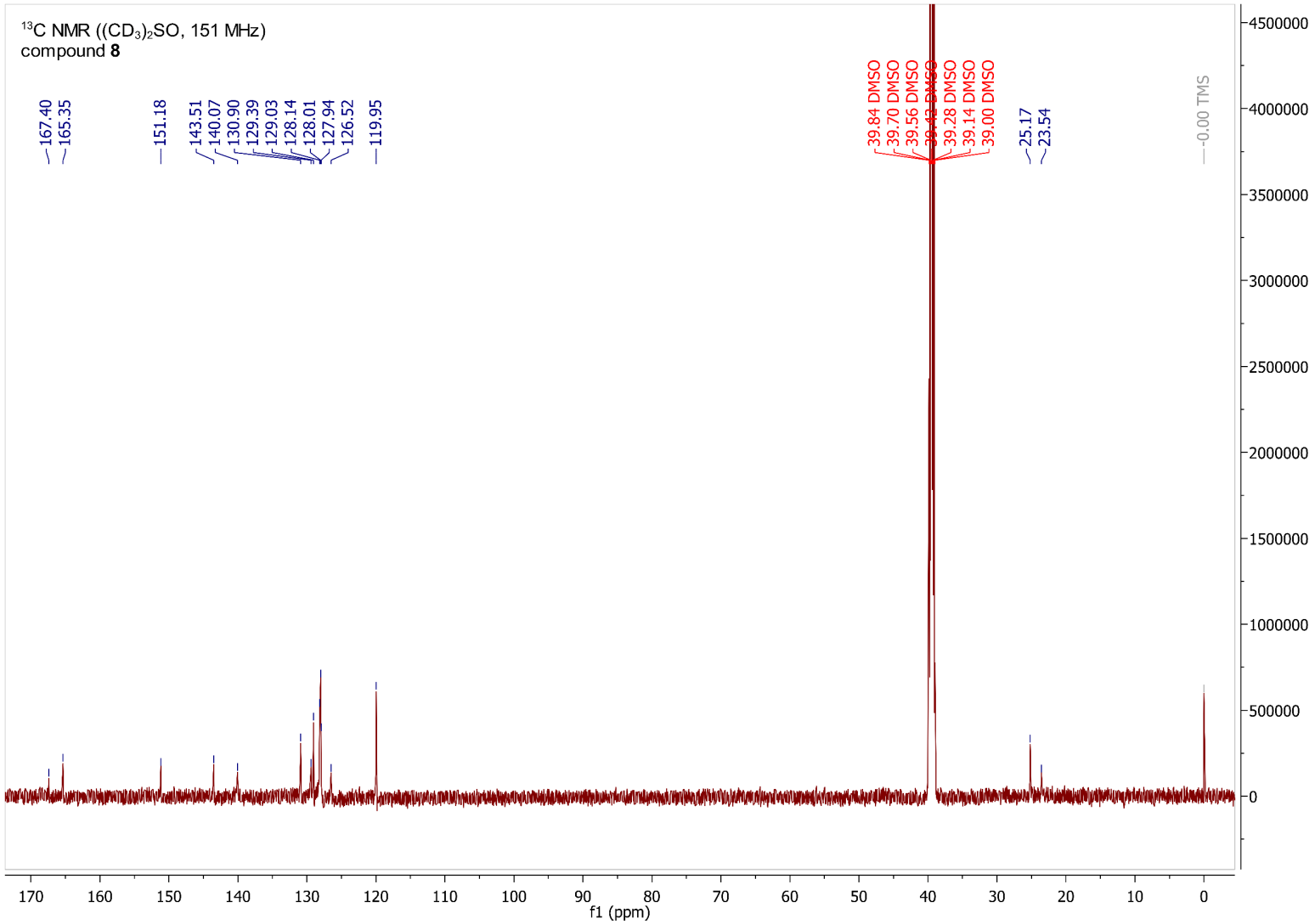


Figure S29. ^{1}H NMR spectrum of [Zn(qin)$_2$(pyrobenzoam)] (**9**) in DMSO-d_6.

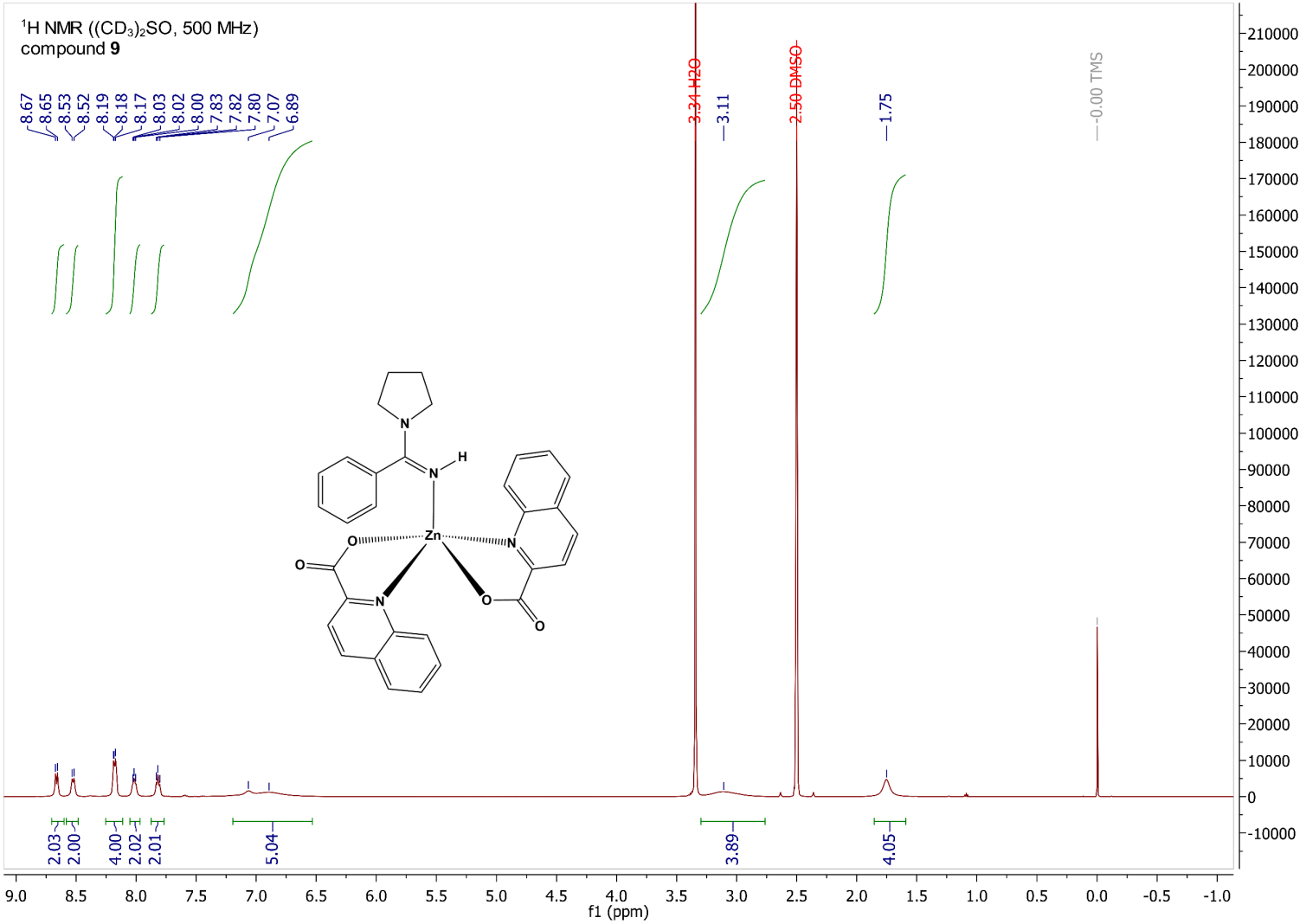


Figure S30. ^{13}C NMR spectrum of [Zn(qin)$_2$(pyrobenzoam)] (**9**) in DMSO-d_6.

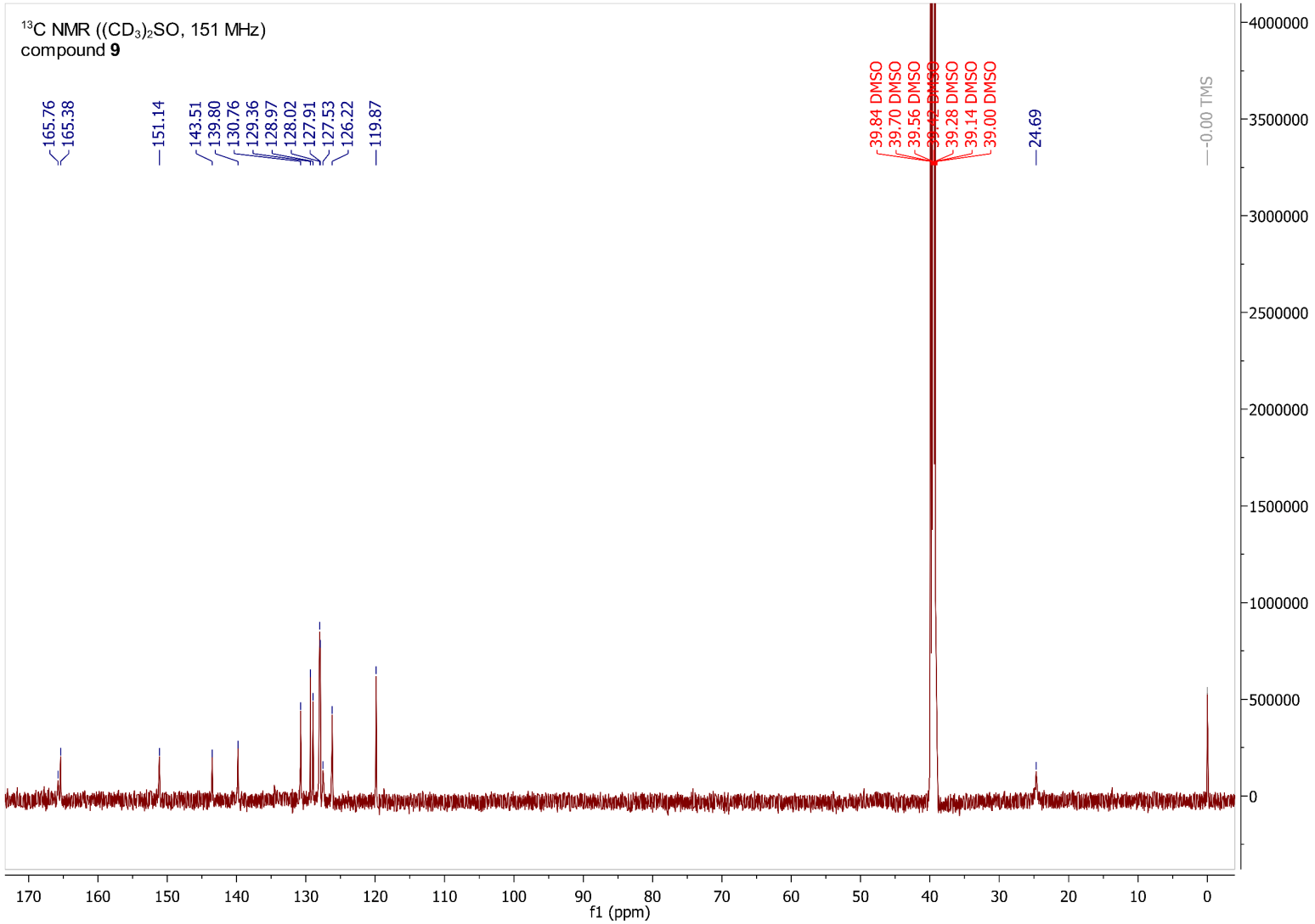


Figure S31. ^{1}H NMR spectrum of pipebenzoamH[Zn(quin)$_3$] (**10**) in DMSO-d_6.

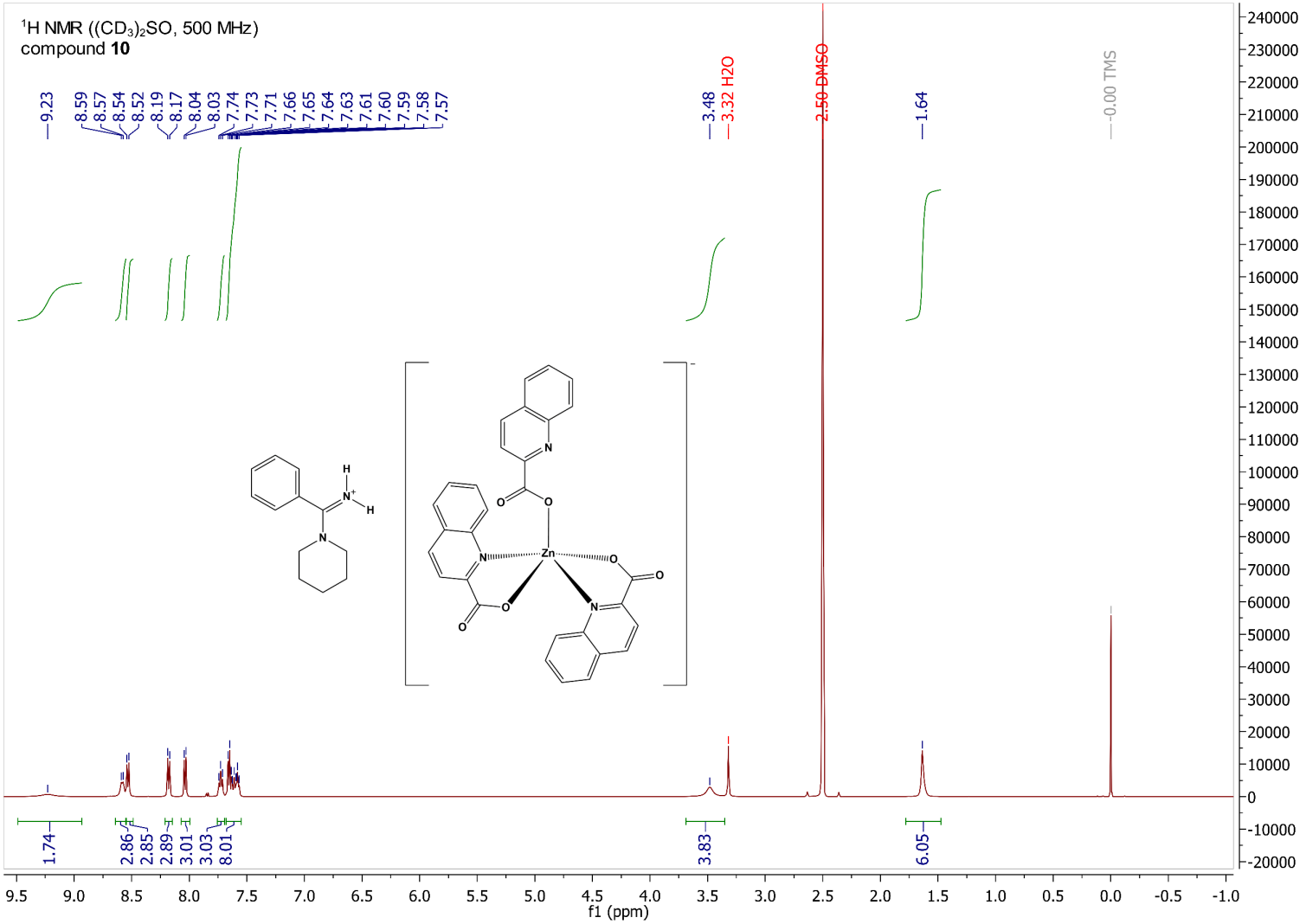


Figure S32. ^{13}C NMR spectrum of pipebenzoamH[Zn(quin)$_3$] (**10**) in DMSO-d_6.

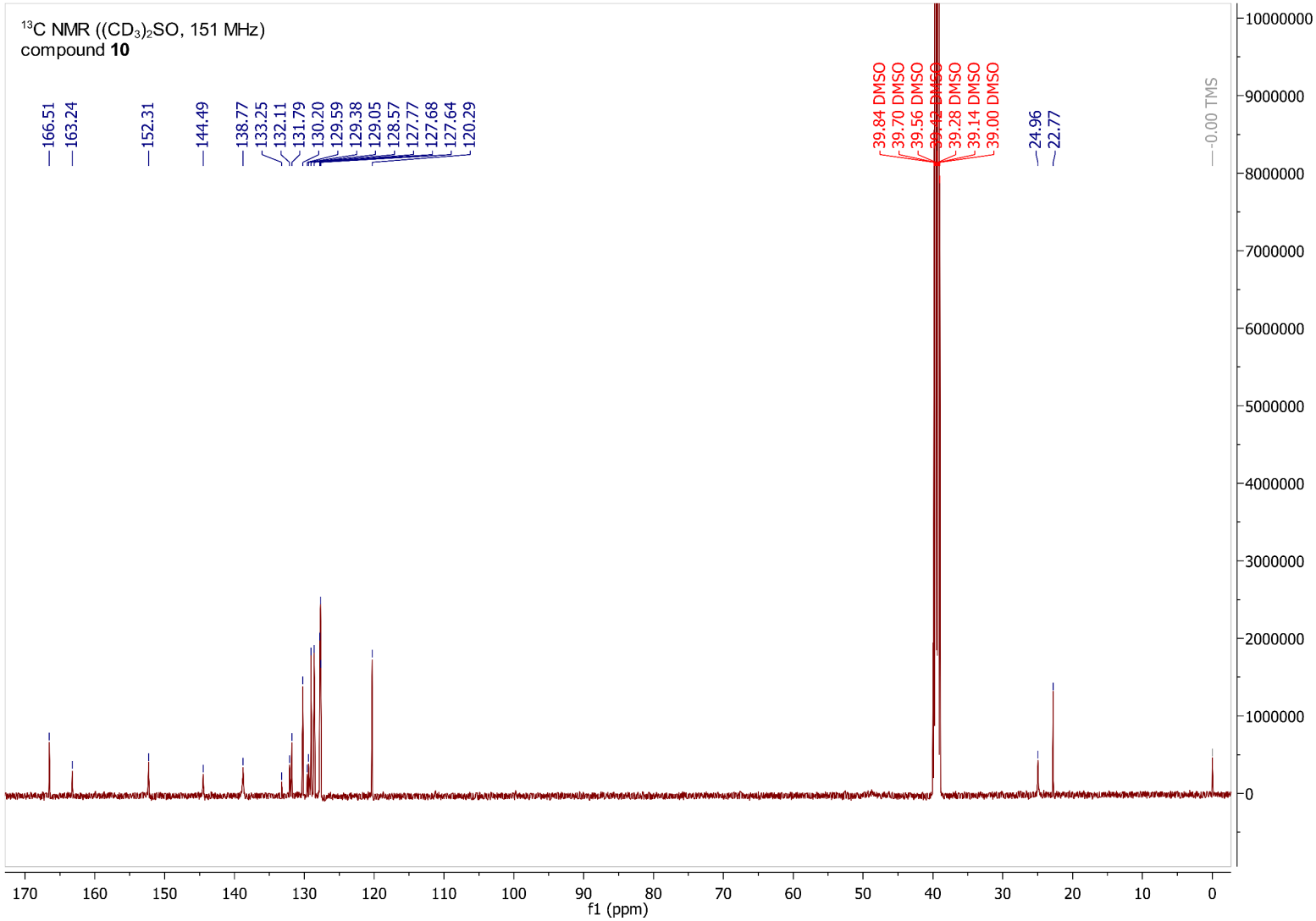


Figure S33. ^{1}H NMR spectrum of pyrobenzoamH[Zn(quin)$_3$] (**11**) in DMSO-d_6.

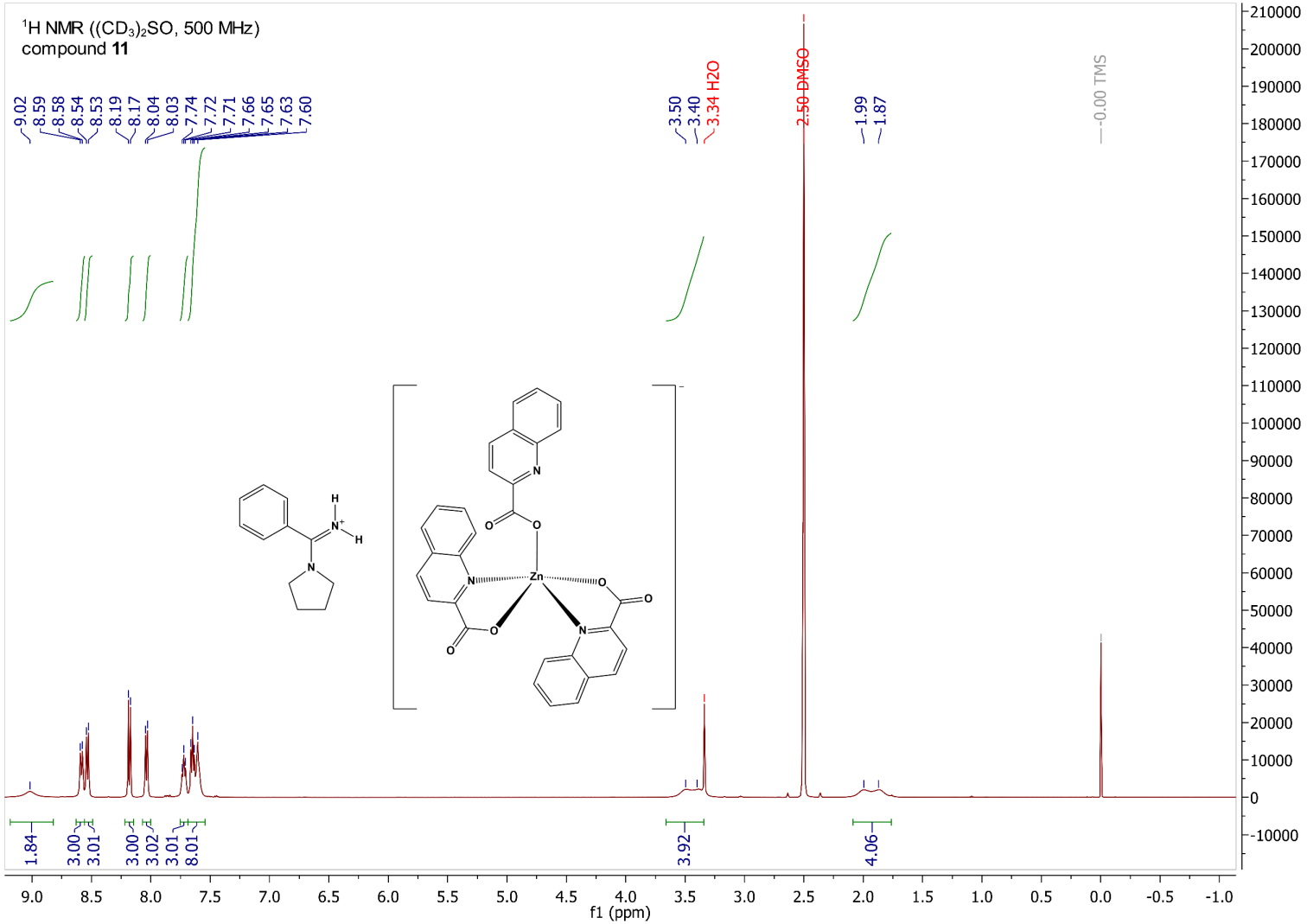


Figure S34. ^{13}C NMR spectrum of pyrobenzoamH[Zn(quin)$_3$] (**11**) in DMSO-d_6.