Supplementary Materials for

Crystal chemistry of zinc quinaldinate complexes with pyridine-based ligands

by

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Figure S1. The ORTEP drawing of [Zn(quin)$_2$(3,5-Lut)$_2$] (**2**). Atoms are represented by displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) = 2.2277(16), Zn(1)–O(1) = 2.0147(14), Zn(1)–N(2) = 2.2395(17), N(1)–Zn(1)–O(1) = 78.66(6), N(1)–Zn(1)–N(2) = 92.50(6), O(1)–Zn(1)–N(2) = 90.22(6).

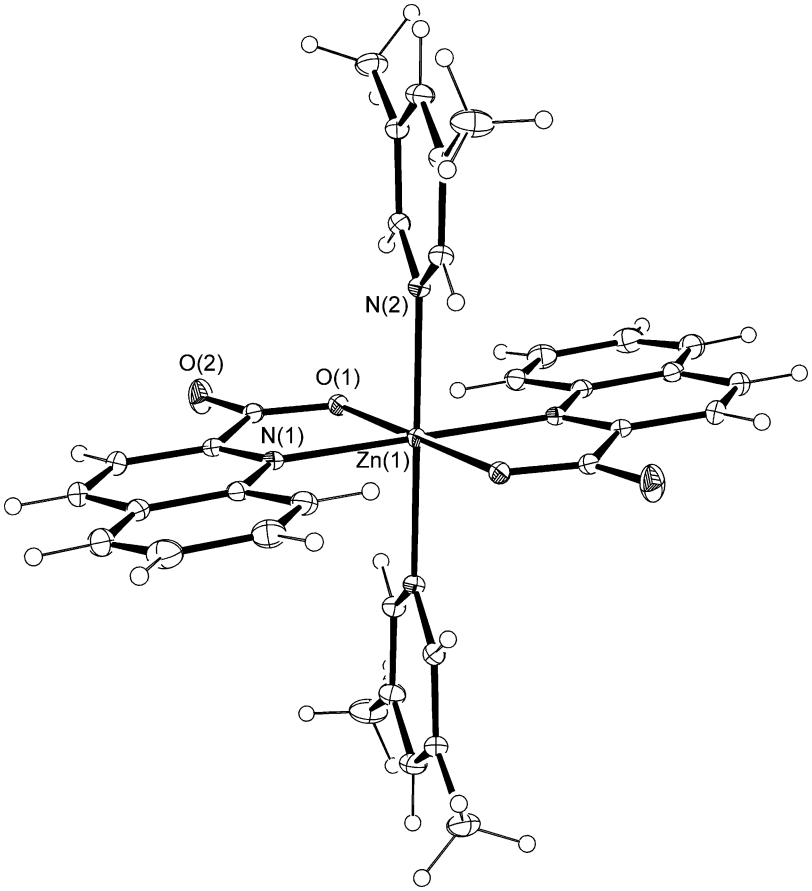


Figure S2. The ORTEP drawing of [Zn(quin)$_2$(3-Hmpy)$_2$] (**5**). Atoms are represented by displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) = 2.2462(17), Zn(1)–O(1) = 2.0500(13), Zn(1)–N(2) = 2.1868(16), O(1)–Zn(1)–N(1) = 77.94(6), O(1)–Zn(1)–N(2) = 90.49(6), N(1)–Zn(1)–N(2) = 91.55(6).

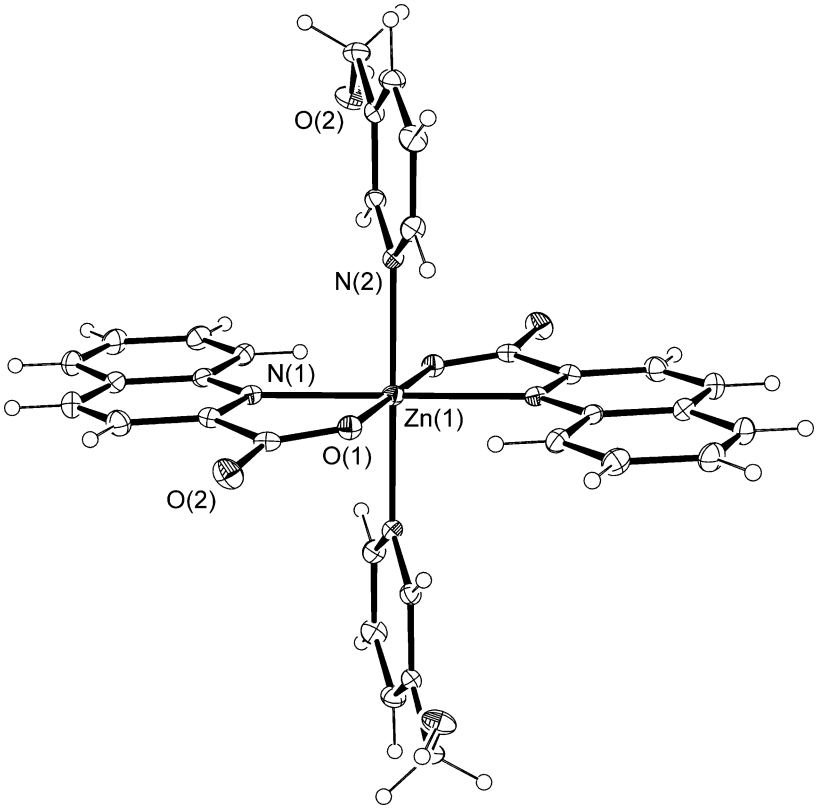


Figure S3. The ORTEP drawing of [Zn(quin)$_2$(4-Hmpy)$_2$] (**7**). Atoms are represented by displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) = 2.2214(14), Zn(1)–O(1) = 2.0208(11), Zn(1)–N(2) = 2.2420(14), O(1)–Zn(1)–N(1) = 78.06(5), O(1)–Zn(1)–N(2) = 90.11(5), N(1)–Zn(1)–N(2) = 90.25(5).

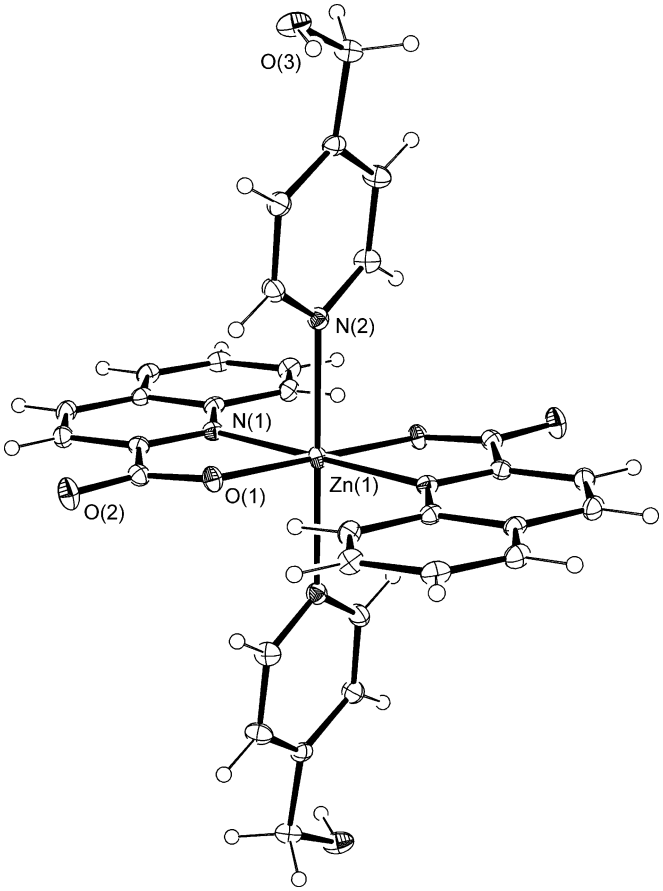


Figure S4. Packing of molecules in $[Zn(quin)_2(Py)_2]$ (**1**), a view along *a* axis.

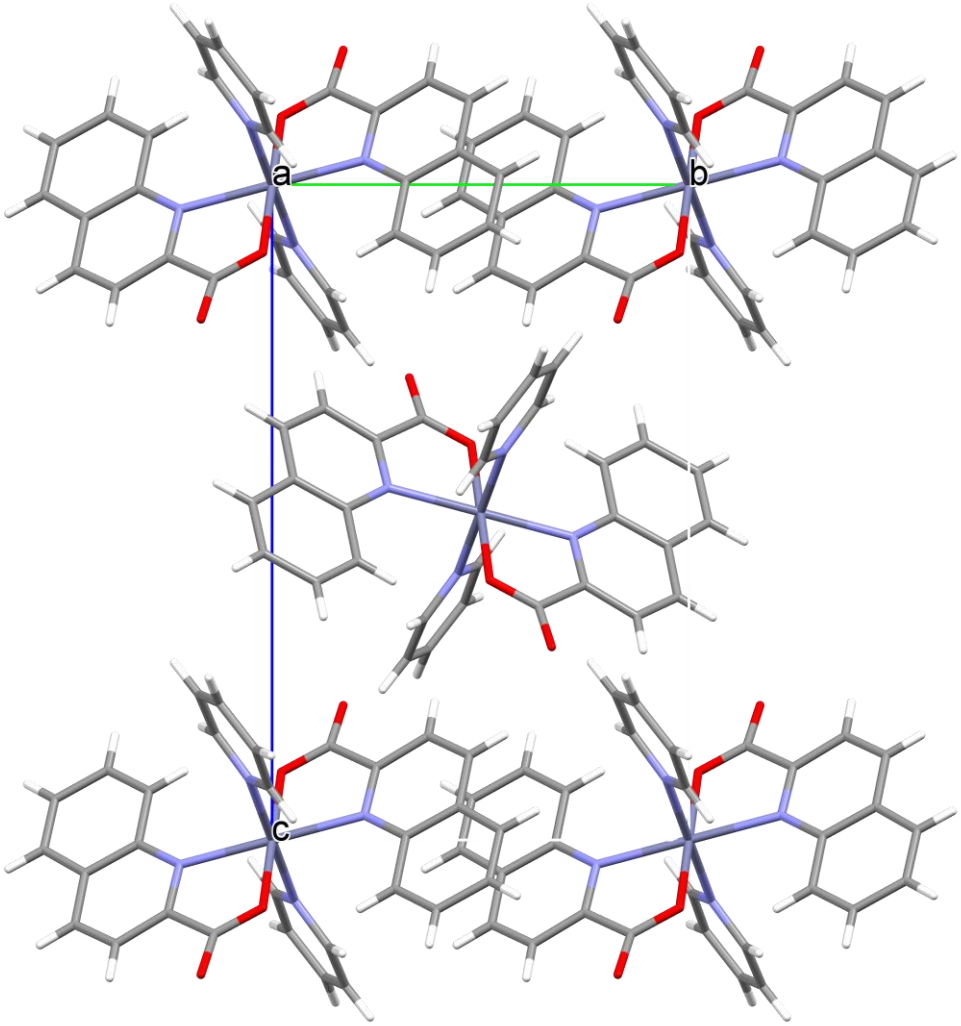


Figure S5. Packing of molecules in [Zn(quin)$_2$(3,5-Lut)$_2$] (**2**), a view along *a* axis.

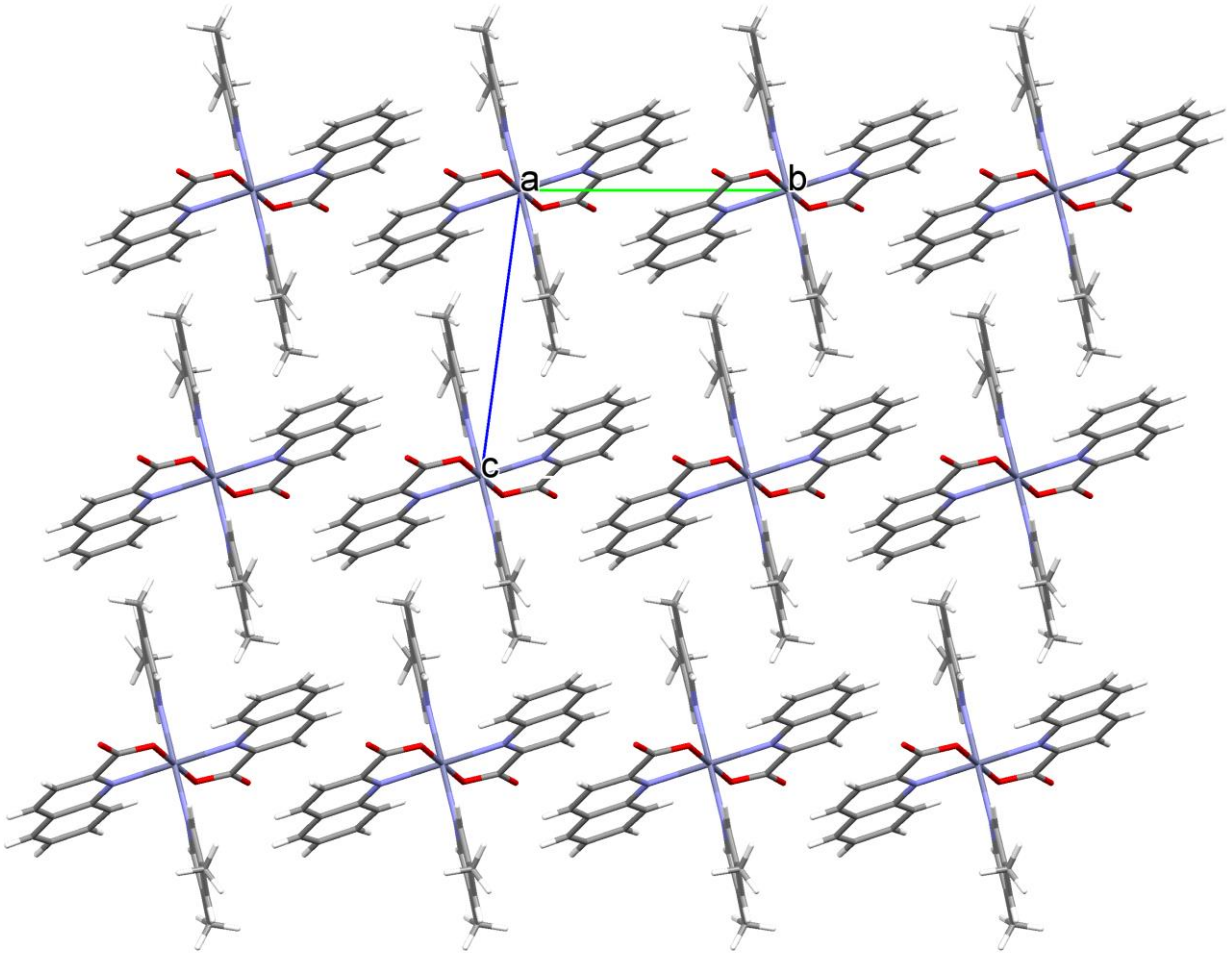
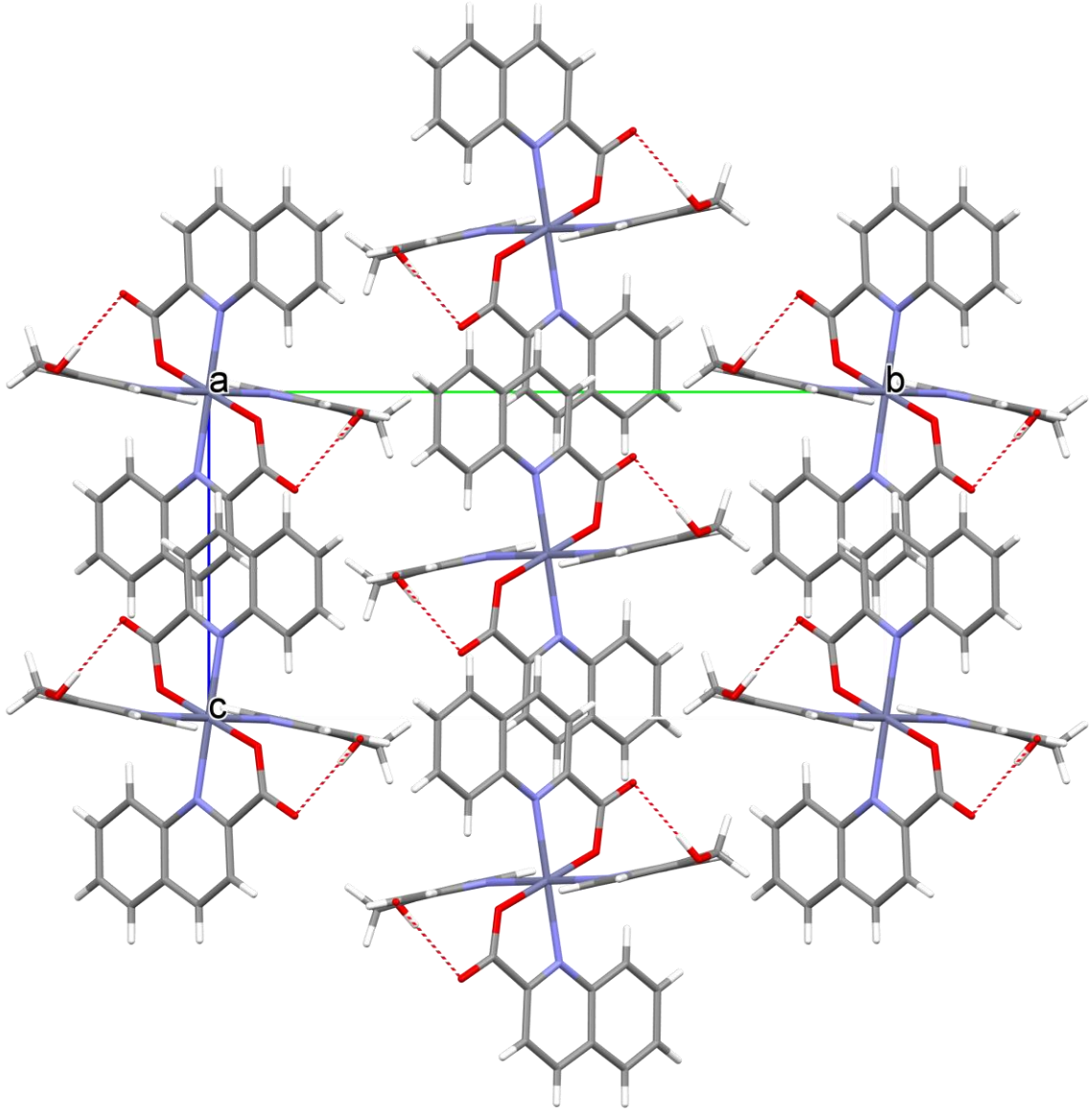


Figure S6. The chains in [Zn(quin)$_2$(4-Hmpy)$_2$] (**7**) propagate along *a* axis. Each chain is surrounded by six others.



Lists of intermolecular interactions.

Unless stated otherwise, the labels *Cg(3)* and *Cg(5)* pertain to the centroids of pyridine, *i.e.*, N(1)-C(1)-C(2)-C(3)-C(4)-C(9), and arene, *i.e.*, C(4)-C(5)-C(6)-C(7)-C(8)-C(9), parts of quinaldinate rings, respectively. Parameters *Cg*···*Cg*, interplanar distance, dihedral and offset angles are as defined in reference [63].

Table S1. Intermolecular interactions (Å, °) in $[Zn(quin)_2(Py)_2]$ (**1**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(3)* [–*x*, –*y*+1, –*z*]	pyridine···pyridine	3.967(2)	3.361(1)	0	32.1
Cg(3)···*Cg(5)* [–*x*, –*y*+1, –*z*]	pyridine···arene	3.593(2)	3.351(1)	1.5(1)	21.1
Cg(5)···*Cg(5)* [–*x*, –*y*+1, –*z*]	arene···arene	4.658(2)	3.381(1)	0	43.5
Cg(5)···*Cg(5)* [–*x*+1, –*y*+1, –*z*]	arene···arene	4.869(2)	3.225(1)	0	48.5

C–H···O contacts
C(21)[a]···O(2) [–*x*, *y*+0.5, –*z*+0.5] = 3.101(4)
C(22)[a]···O(2) [–*x*, *y*+0.5, –*z*+0.5] = 3.106(5)

[a] C(21) and C(22) are pyridine (Py) carbon atoms.

[63] Janiak, C. A critical account on π–π stacking in metal complexes with aromatic nitrogen-containing ligands. *J. Chem. Soc., Dalton Trans*. **2000**, 3885–3896, DOI 10.1039/b003010o.

Table S2. Intermolecular interactions (Å, °) in $[Zn(quin)_2(3,5\text{-}Lut)_2]$ (**2**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(3)* [–*x*+2, –*y*+1, –*z*]	pyridine···pyridine	3.718(1)	3.4032(8)	0	23.7
Cg(3)···*Cg(5)* [–*x*+2, –*y*+1, –*z*]	pyridine···arene	3.801(1)	3.4152(8)	2.1(1)	26.0
Cg(5)···*Cg(5)* [–*x*+2, –*y*+1, –*z*]	arene···arene	5.162(1)	3.4585(10)	0	47.9
Cg(4)···*Cg(4)* [–*x*+2, –*y*, –*z*+1]	3,5-Lut···3,5-Lut	4.712(1)	3.4402(9)	0	43.1

C–H···π interactions				
	H···*Cg*	**C–H···*Cg***	**C···*Cg***	**X–H, π**
C(23)–H(23)[a]···*Cg(5)* [*x*, *y*, *z*+1]	2.76	174	3.687(2)	82

C–H···O contacts
C(2)···O(2) [–*x*+3, –*y*+1, –*z*] = 3.191(3)

[a] C(23) is part of 3,5-lutidine.

Table S3. Intermolecular interactions (Å, °) in $[Zn(quin)_2(Nia)_2]\cdot 2CH_3CN$ (**3**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(3)* [–*x*+1, –*y*, –*z*]	pyridine···pyridine	3.888(1)	3.4455(9)	0	27.6
Cg(3)···*Cg(5)* [–*x*+1, –*y*, –*z*]	pyridine···arene	5.358(2)	3.4164(9)	0.7(1)	50.4

Table S4. Intermolecular interactions (Å, °) in $[Zn(quin)_2(3\text{-Py-OH})_2]$ (**4**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(3)* [–*x*+1, –*y*+1, –*z*+1]	pyridine···pyridine	3.899(1)	3.3639(8)	0	30.4
Cg(3)···*Cg(5)* [–*x*+1, –*y*+1, –*z*+1]	pyridine···arene	3.777(1)	3.3811(8)	1.2(1)	26.5
Cg(5)···*Cg(5)* [–*x*+1, –*y*+1, –*z*+1]	arene···arene	4.989(1)	3.3953(8)	0	47.1
Cg(5)···*Cg(5)* [–*x*, –*y*+1, –*z*+1]	arene···arene	5.439(1)	2.9435(8)	0	57.2

C–H···π interactions				
	H···*Cg*	**C–H···*Cg***	**C···*Cg***	**X–H, π**
C(5)–H(5) ···*Cg(4)* [*x*, *y*+1, *z*][a]	2.78	170	3.703(2)	81

C–H···O contacts
C(21)[b]···O(2) [–*x*+1.5, *y*–0.5, –*z*+1.5] = 3.089(2)

[a] The label *Cg(4)* pertains to the centroid of 3-hydroxypyridine, N(2)-C(21)-C(22)-C(23)-C(24)-C(25).
[b] C(21) is a 3-hydroxypyridine atom.

Table S5. Intermolecular interactions (Å, °) in $[Zn(quin)_2(3\text{-}Hmpy)_2]$ (**5**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(5)* [–*x*+2, –*y*+1, –*z*]	pyridine···arene	4.367(1)	3.3808(8)	0.9(1)	39.3
Cg(3)···*Cg(5)* [*x*–1, *y*, *z*]	pyridine···arene	5.082(1)	3.2624(8)	0.9(1)	50.1
Cg(5)···*Cg(5)* [–*x*+2, –*y*+1, –*z*]	arene···arene	3.614(1)	3.4007(9)	0	19.8
Cg(4)···*Cg(4)* [–*x*+2, –*y*+2, –*z*+1]	3-Hmpy···3-Hmpy	4.297(1)	3.6011(8)	0	33.1

Table S6. Intermolecular interactions (Å, °) in $[Zn(quin)_2(4\text{-}Hmpy)_2]$ (**7**).

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(3)···*Cg(3)* [–*x*–1, –*y*, –*z*+1]	pyridine···pyridine	4.409(1)	3.4168(7)	0	39.2
Cg(3)···*Cg(3)* [–*x*, –*y*, –*z*+1]	pyridine···pyridine	5.038(1)	3.0811(7)	0	52.3
Cg(3)···*Cg(5)* [–*x*–1, –*y*, –*z*+1]	pyridine···arene	3.713(1)	3.3740(7)	1.4(1)	24.7
Cg(5)···*Cg(5)* [–*x*–1, –*y*, –*z*+1]	arene···arene	4.438(1)	3.3983(8)	0	40.0

C–H···π interactions				
	H···*Cg*	**C–H···*Cg***	**C···*Cg***	**X–H, π**
C(5)–H(5) ···*Cg(4)* [*x*–1, *y*, *z*–1][a]	2.56	169	3.479(2)	78

[a] The label *Cg(4)* pertains to the centroid of 4-hydroxymethylpyridine ring.

Table S7. Intermolecular interactions (Å, °) in [Zn(quin)$_2$(4-Pyridone)] (**6**).[a]

π···π interactions					
	type	***Cg*···*Cg***	**interplanar distance**	**dihedral angle**	**offset angle**
Cg(4)···*Cg(4)* [–*x*+1, –*y*+1, –*z*+1]	pyridine···pyridine	4.743(1)	3.4941(8)	0	42.6
Cg(4)···*Cg(7)* [–*x*+1, –*y*+1, –*z*+1]	pyridine···arene	3.741(1)	3.4657(8)	1.6(1)	22.1
Cg(6)···*Cg(6)* [–*x*, –*y*, –*z*+1]	arene···arene	5.525(1)	3.3092(9)	0	53.2
Cg(7)···*Cg(7)* [–*x*+1, –*y*+1, –*z*+1]	arene···arene	4.130(1)	3.4631(8)	0	33.0
Cg(5)···*Cg(7)* [–*x*+0.5, *y*–0.5, –*z*+0.5]	4-pyridone···arene	3.819(1)	3.5201(8)	16.6(1)	22.8
Cg(5)···*Cg(4)* [–*x*+0.5, *y*–0.5, –*z*+0.5]	4-pyridone···pyridine	4.55781	3.5661(8)	16.0(1)	38.5

C–H···π interactions				
	H···*Cg*	**C–H···*Cg***	**C···*Cg***	**X–H, π**
C(26)–H(26) ···*Cg(3)* [–*x*+0.5, *y*+0.5, –*z*+0.5]	2.53	151	3.369(2)	68

C–H···O contacts

C(31)[b]···O(11) [–*x*+0.5, *y*–0.5, –*z*+0.5] = 3.125(2)

C(32)[b]···O(12) [*x*+0.5, –*y*+0.5, *z*+0.5] = 3.153(2)

[a] The asymmetric unit contains two quinaldinato ligands. The labels *Cg(3)* and *Cg(4)* pertain to the centroids of their pyridine parts, whereas the labels *Cg(6)* and *Cg(7)* pertain to their arene parts. The label *Cg(5)* pertains to the centroid of 4-pyridone ring.

[b] C(31) and C(32) are 4-pyridone atoms.

Figure S7. TG and DSC curves for $[Zn(quin)_2(3,5\text{-}Lut)_2]$ (**2**).

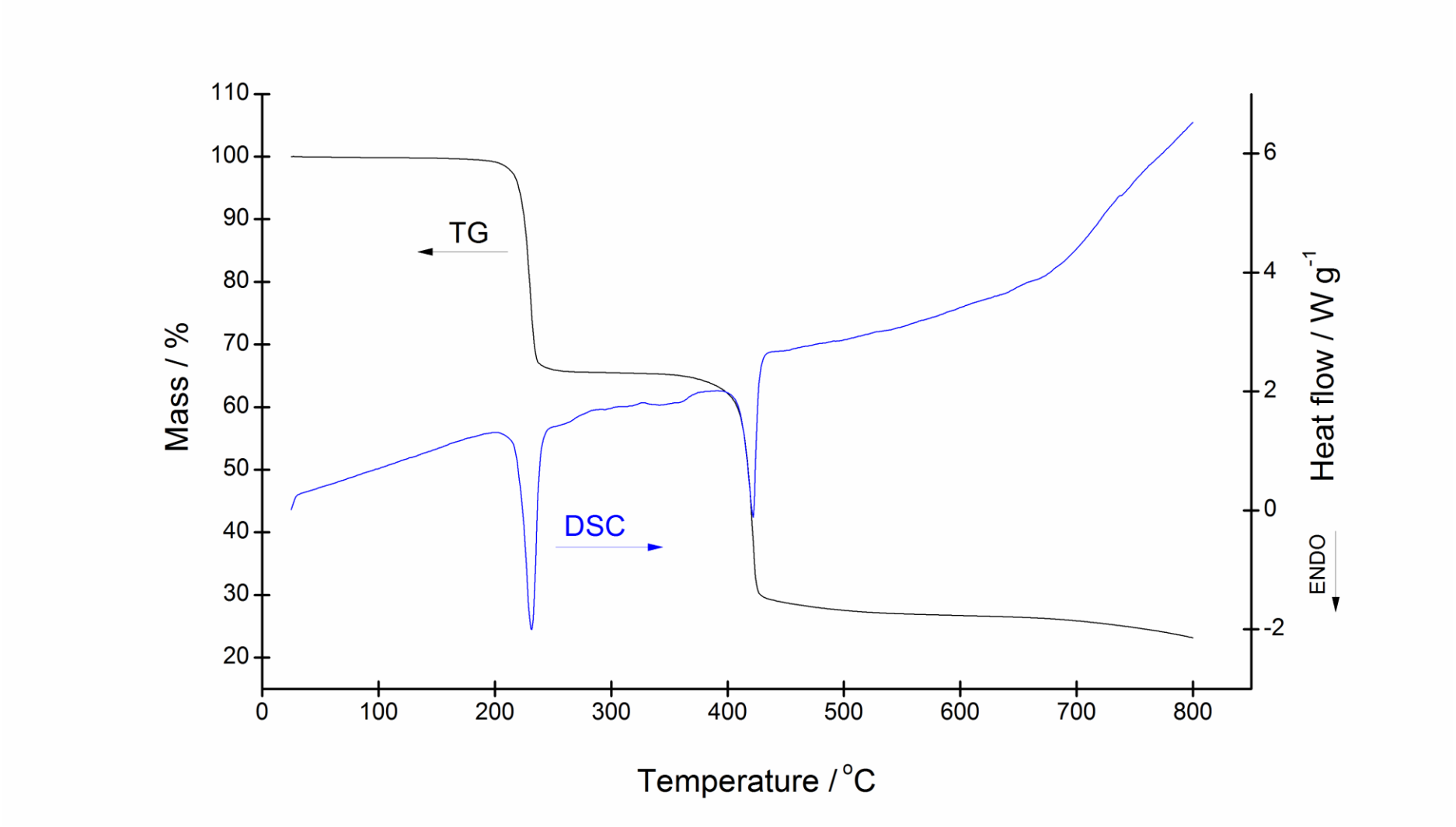


Figure S8. TG and DSC curves for $[Zn(quin)_2(4\text{-}Hmpy)_2]$ (**7**).

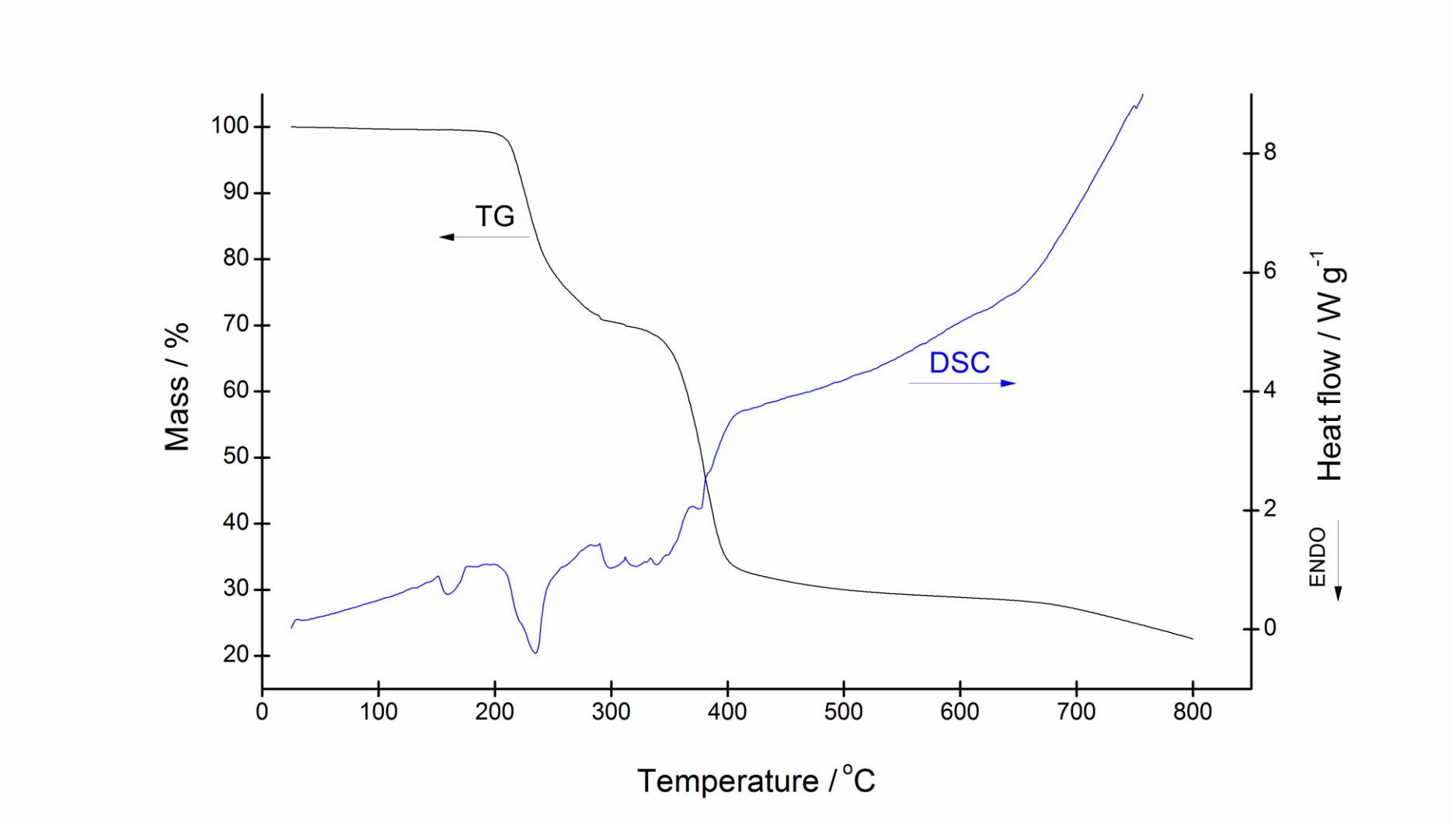


Figure S9. TG and DSC curves for $[Zn(quin)_2(3\text{-}Hmpy)_2]$ (**5**).

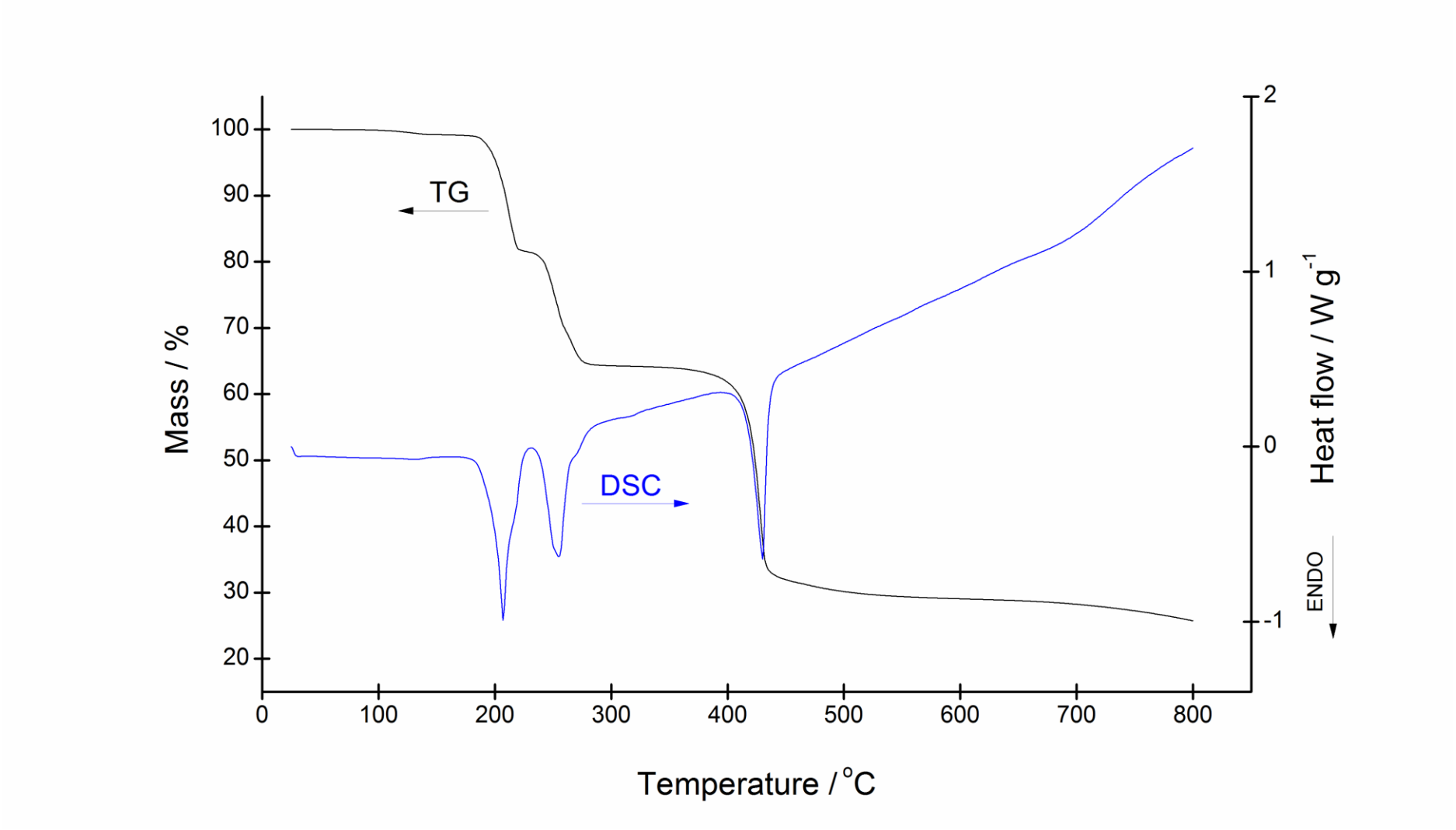


Figure S10. TG and DSC curves for [Zn(quin)$_2$(3-Hmpy)$_2$] (**5**). The sample was heated in the air.

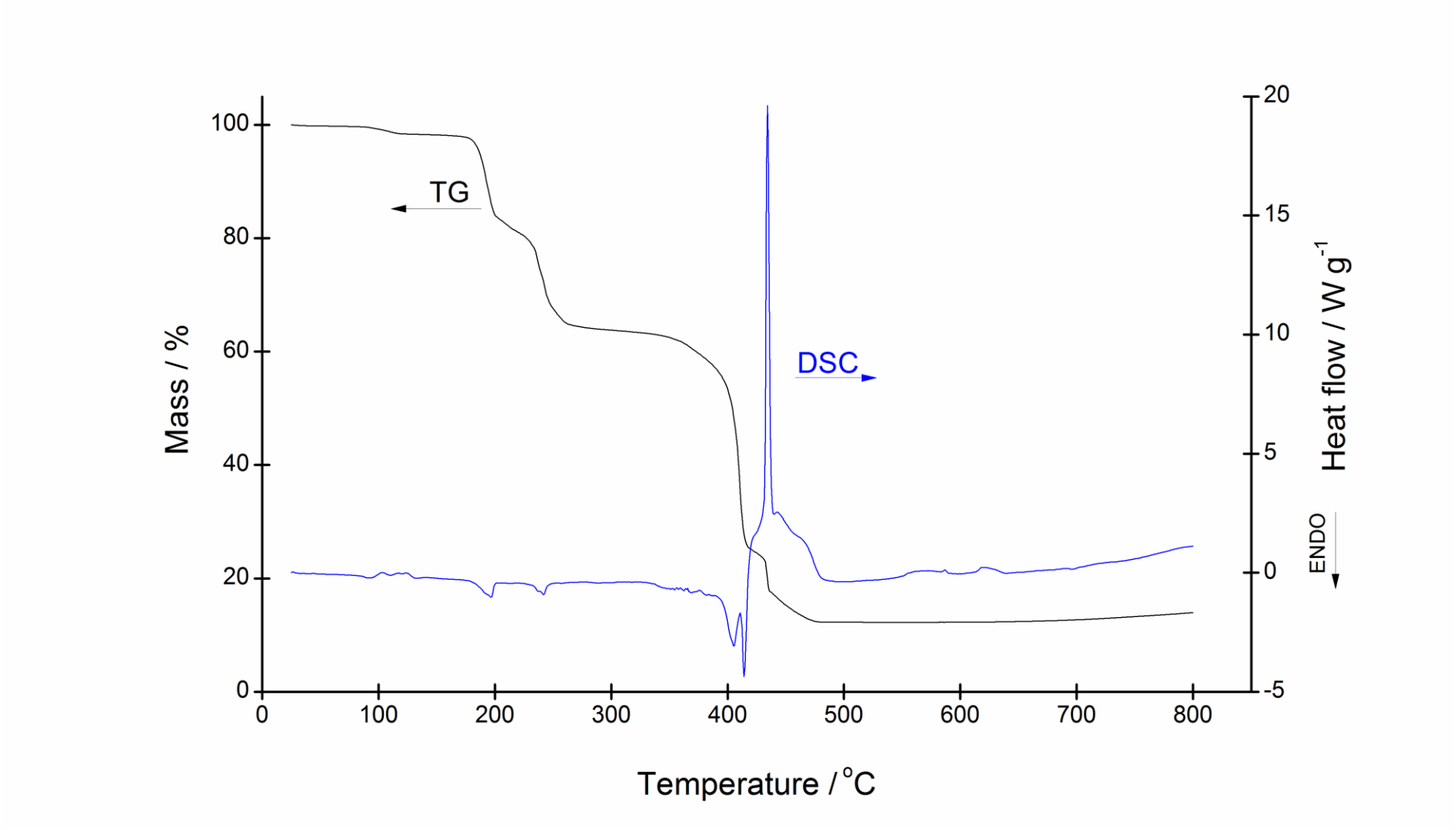


Figure S11. TG and DSC curves for [Zn(quin)$_2$(4-Pyridone)] (**6**).

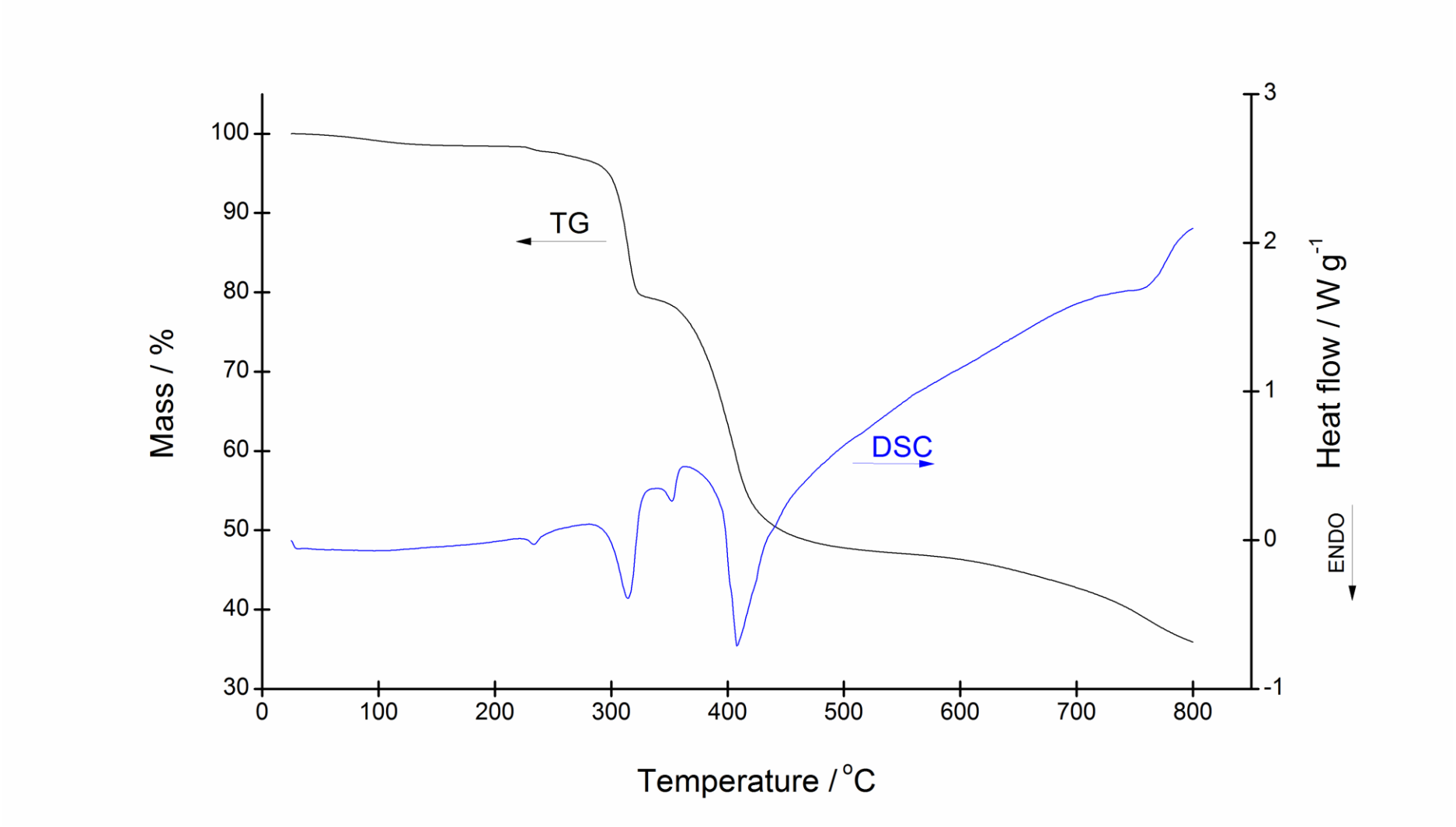


Figure S12. Infrared spectrum of $[Zn(quin)_2(Py)_2]$ (**1**).

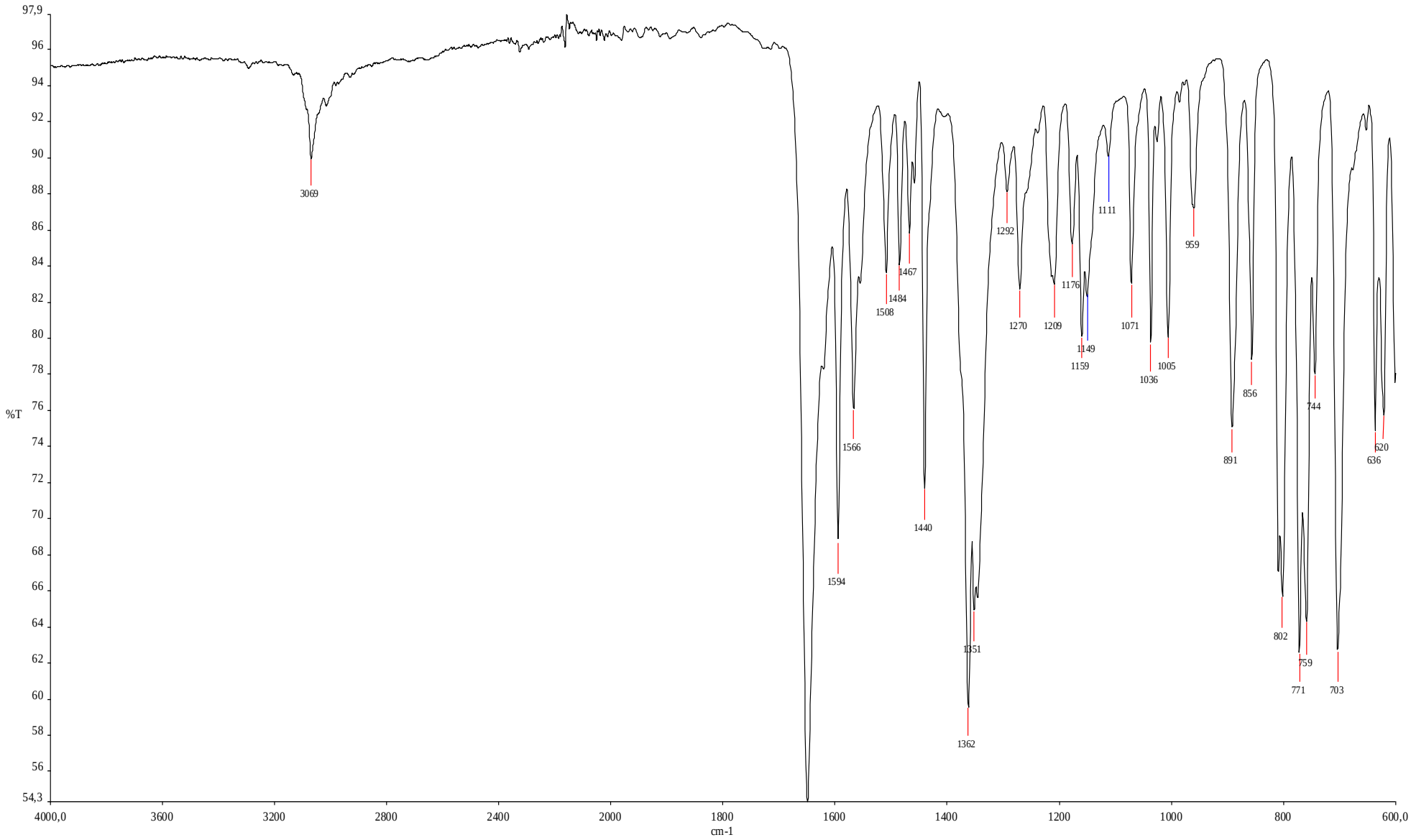


Figure S13. Infrared spectrum of [Zn(quin)$_2$(3,5-Lut)$_2$] (**2**).

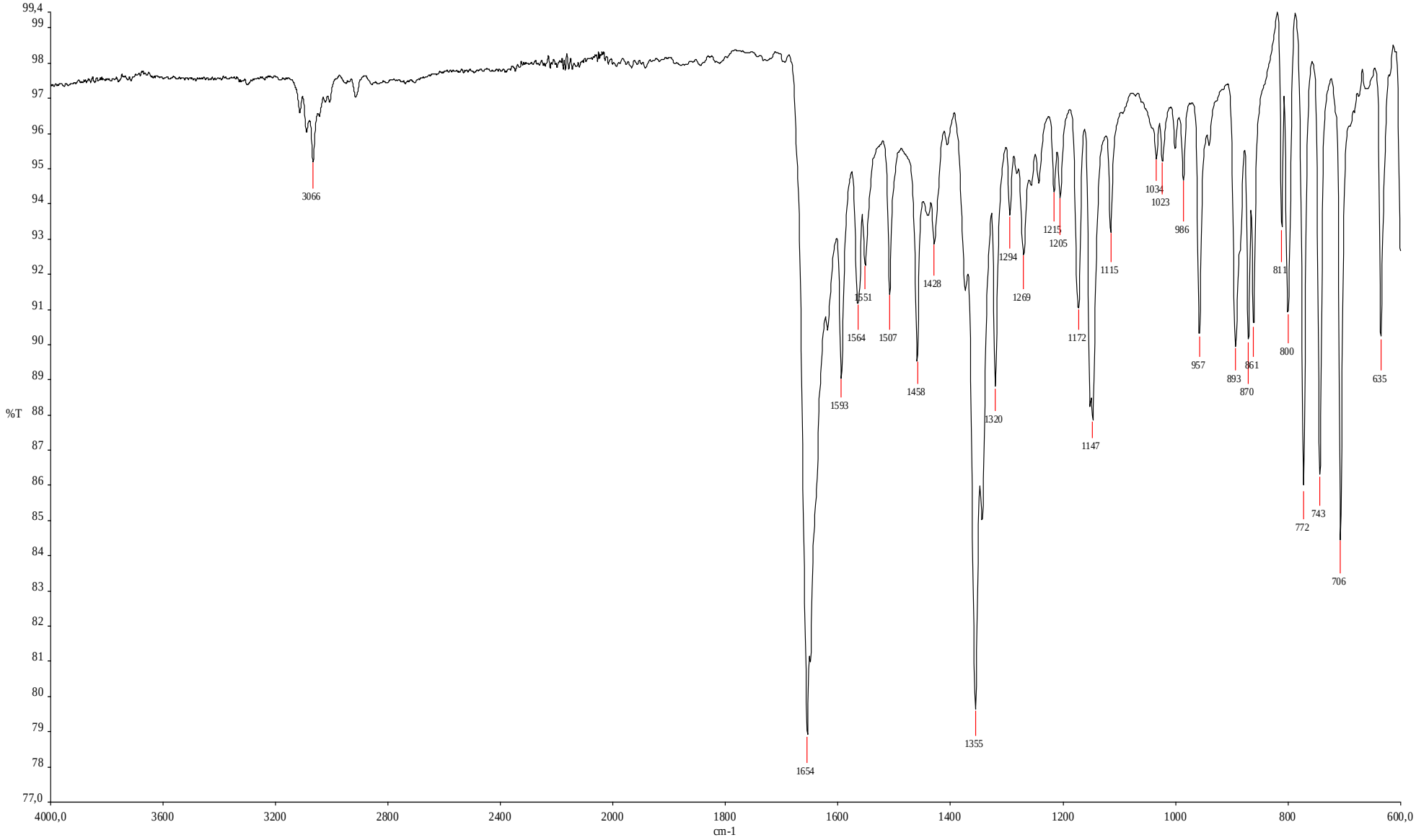


Figure S14. Infrared spectrum of $[Zn(quin)_2(Nia)_2]\cdot 2CH_3CN$ (**3**).

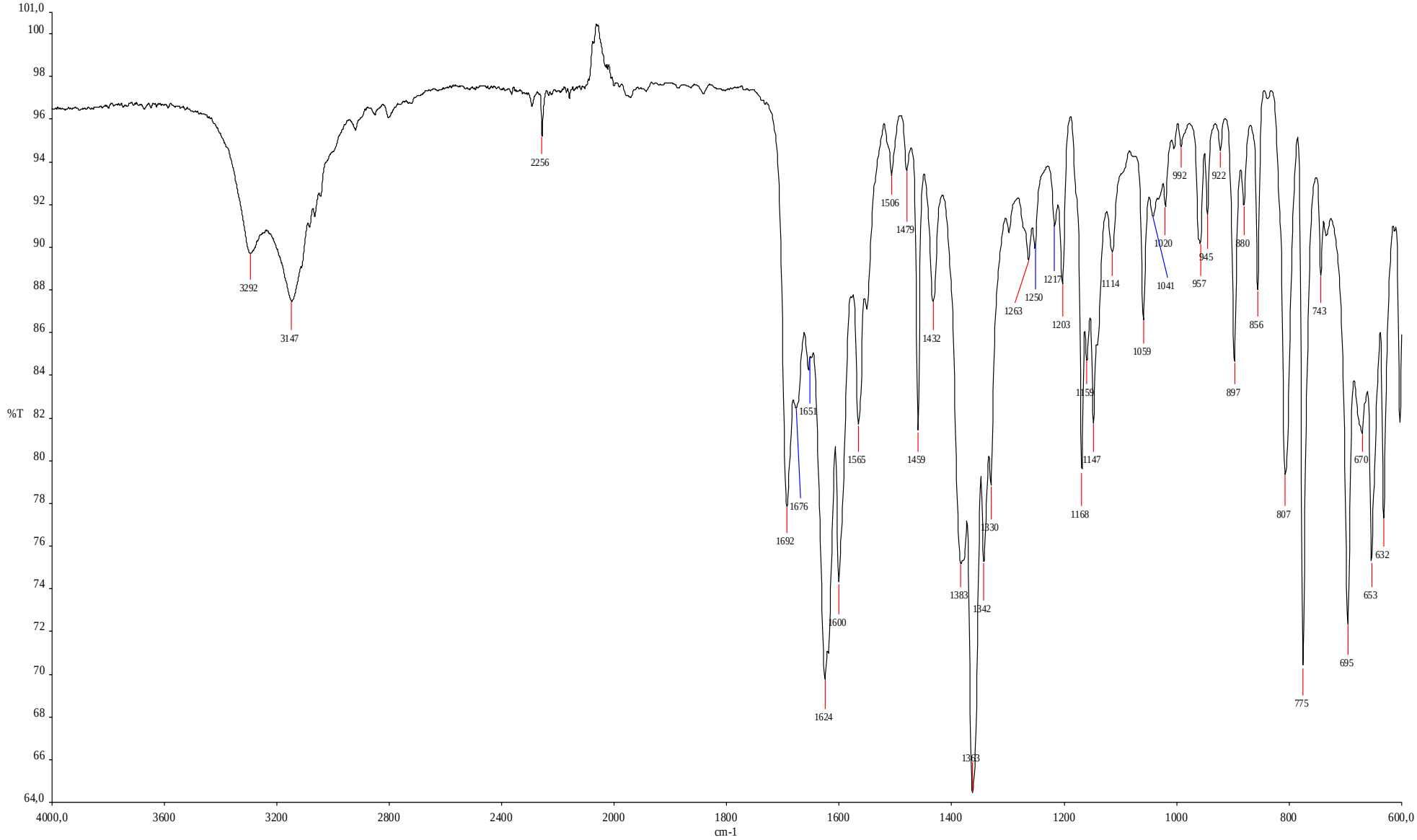


Figure S15. Infrared spectrum of [Zn(quin)$_2$(3-Hmpy)$_2$] (**5**).

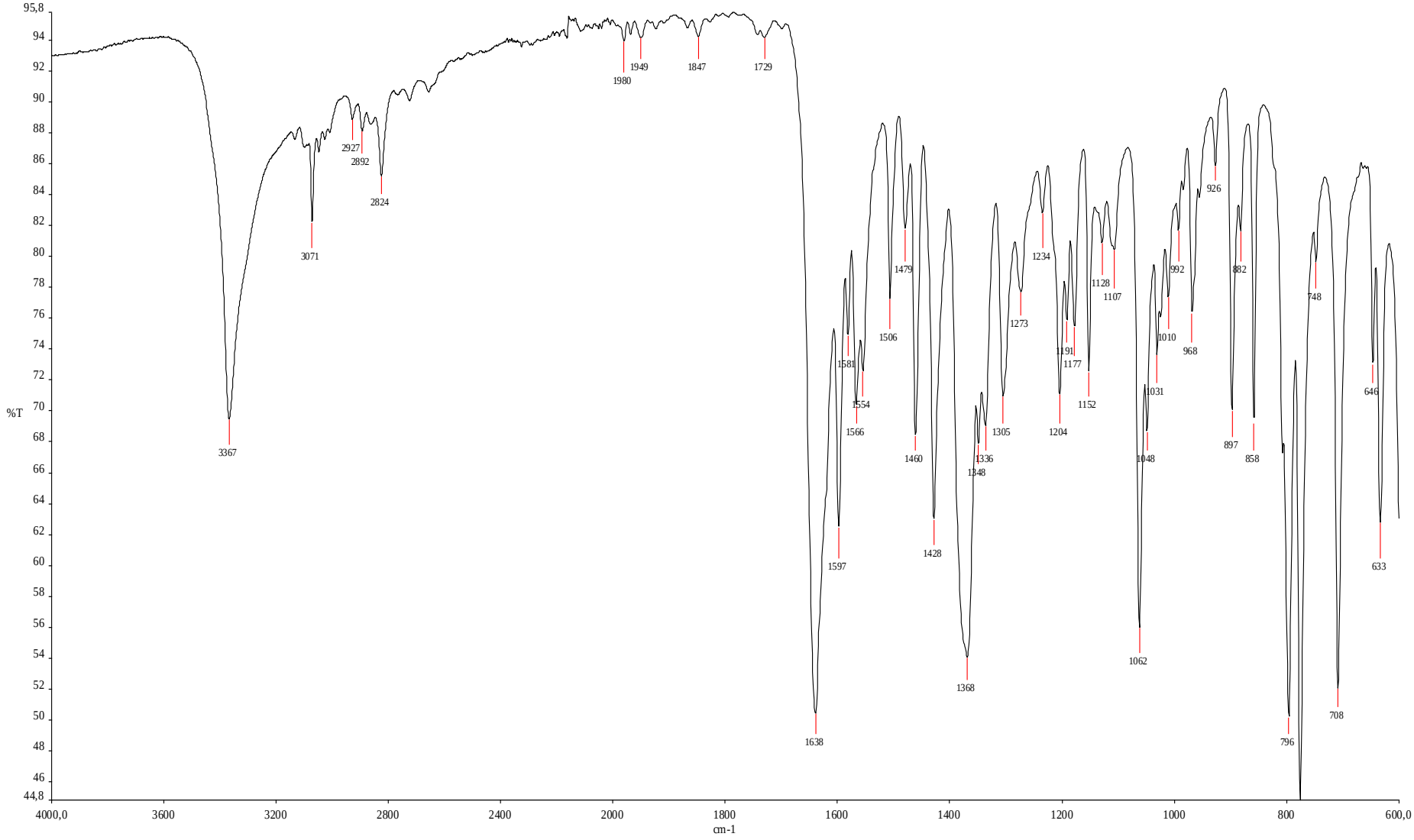


Figure S16. Infrared spectrum of [Zn(quin)$_2$(4-Pyridone)] (**6**).

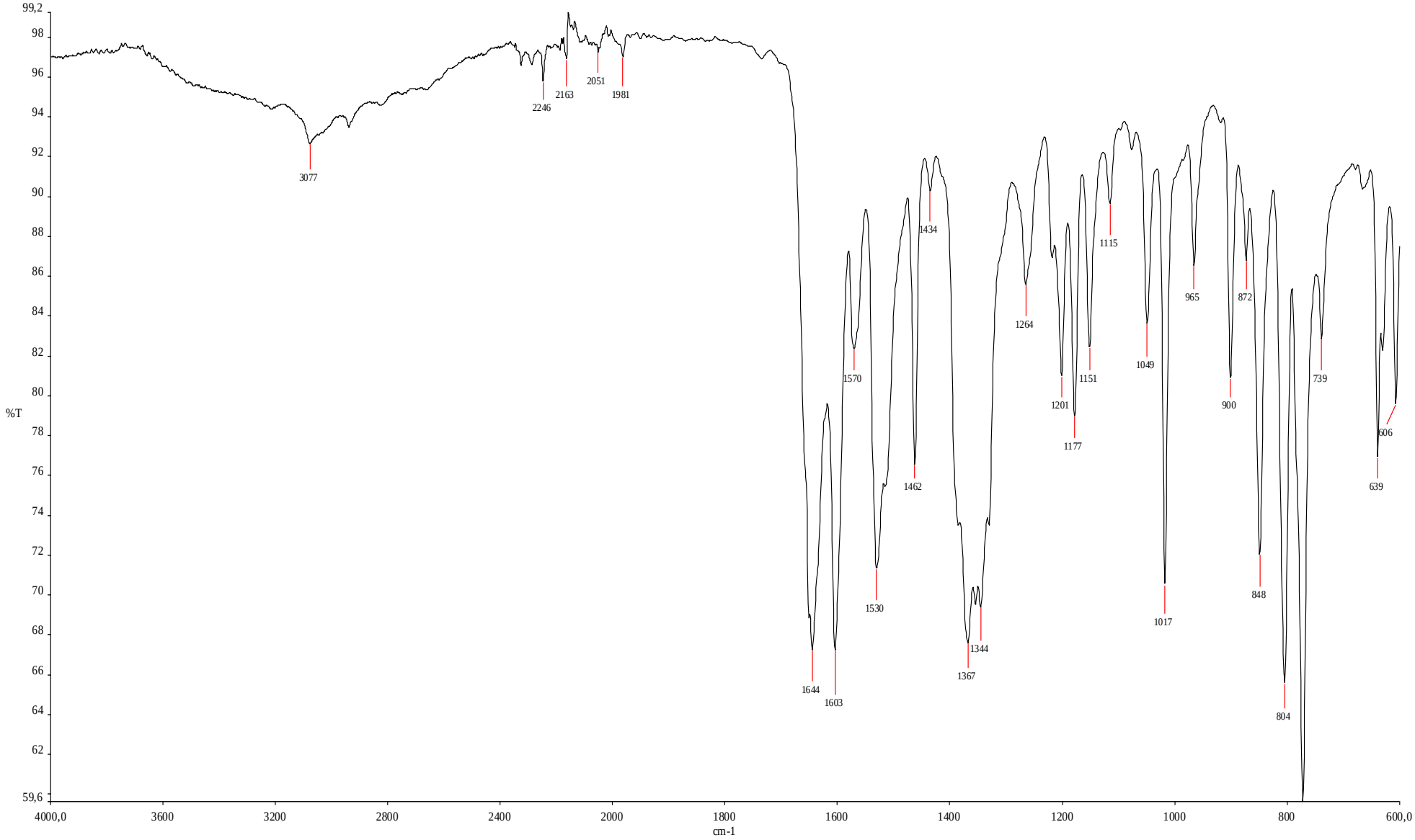


Figure S17. Infrared spectrum of [Zn(quin)$_2$(4-Hmpy)$_2$] (**7**).

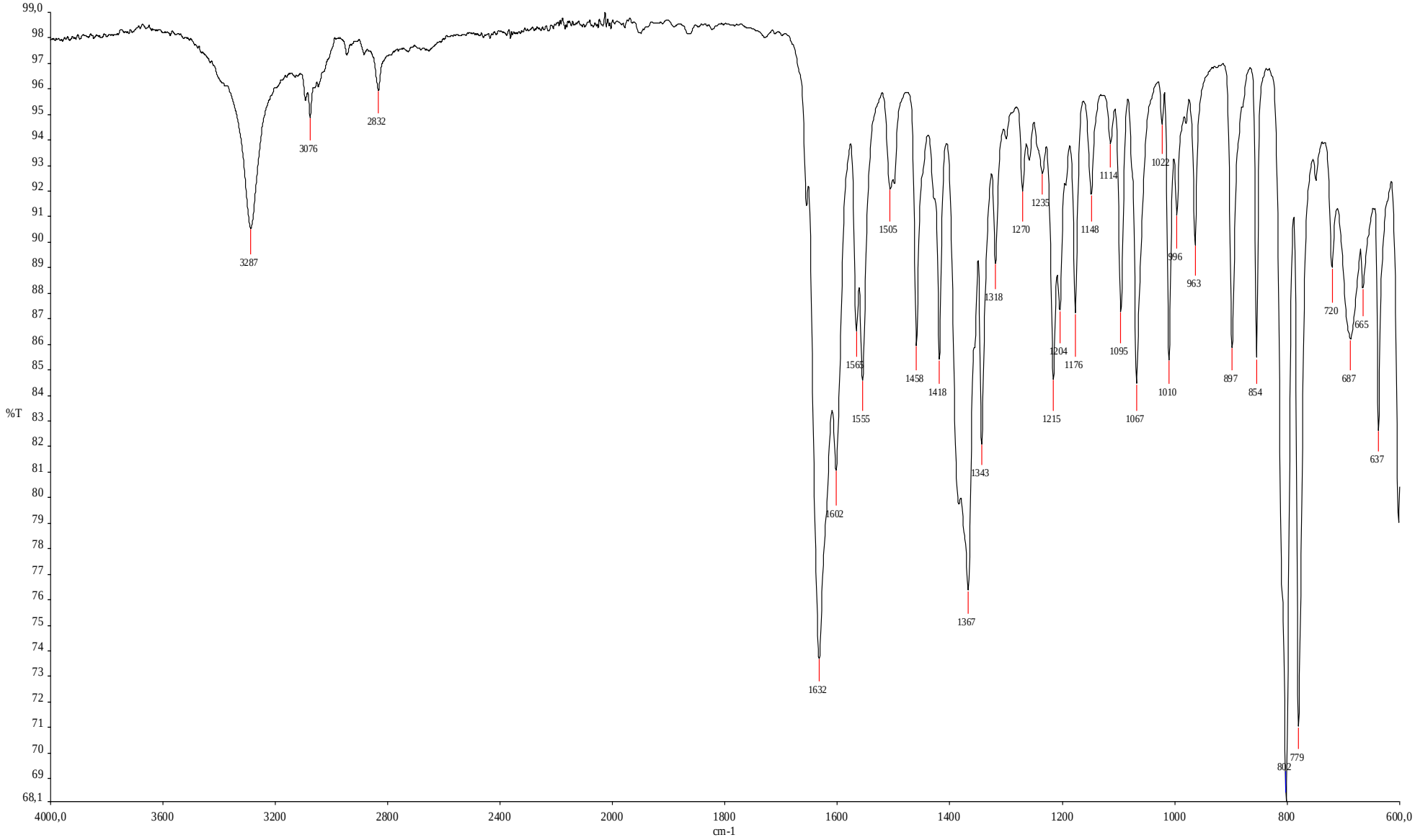
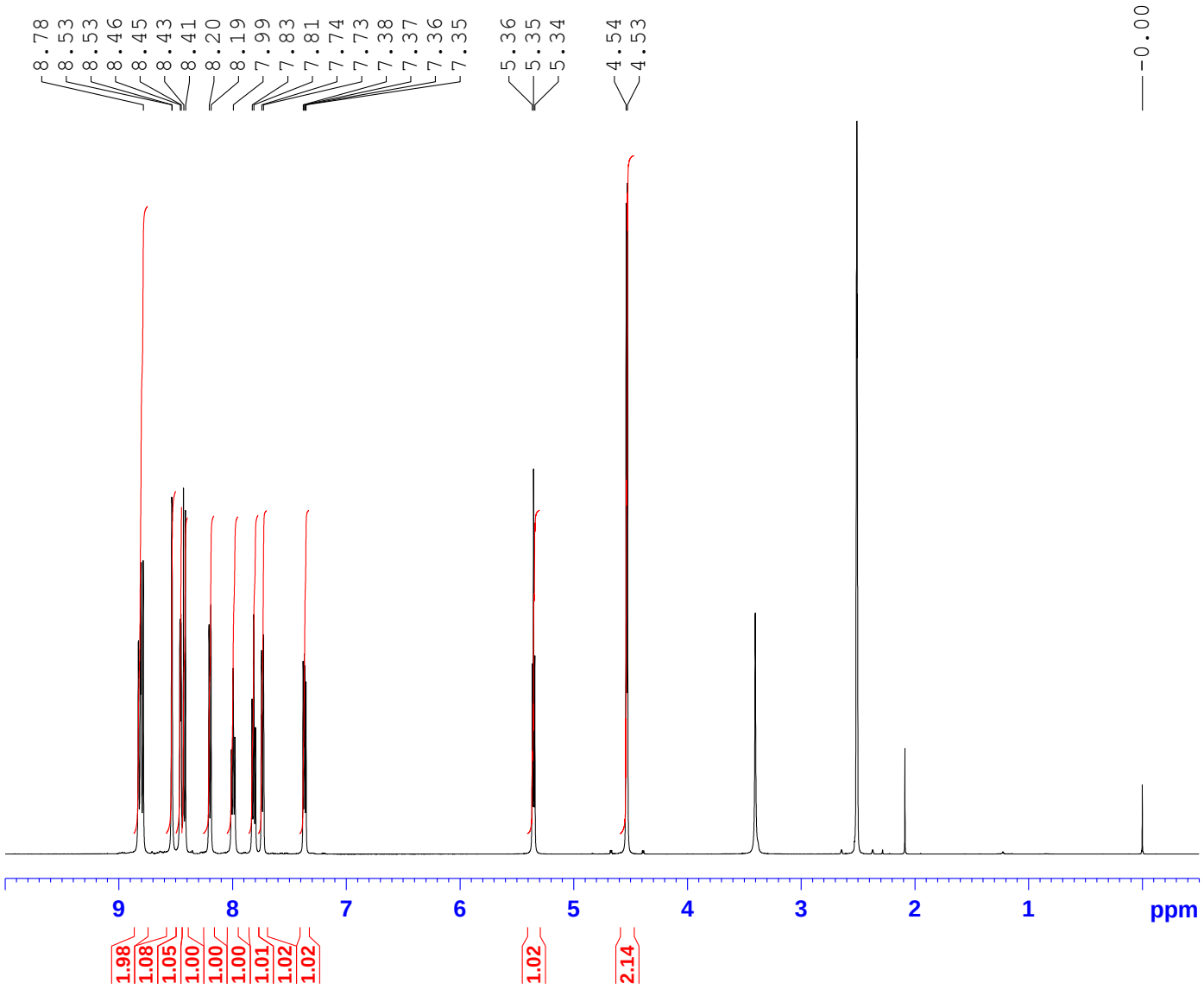


Figure S18. ^{1}H NMR spectrum of a DMSO-d_6 solution of [Zn(quin)$_2$(3-Hmpy)$_2$] (**5**).

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DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                    1

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P1                 8.70 usec
PLW1        26.00000000 W

F2 - Processing parameters
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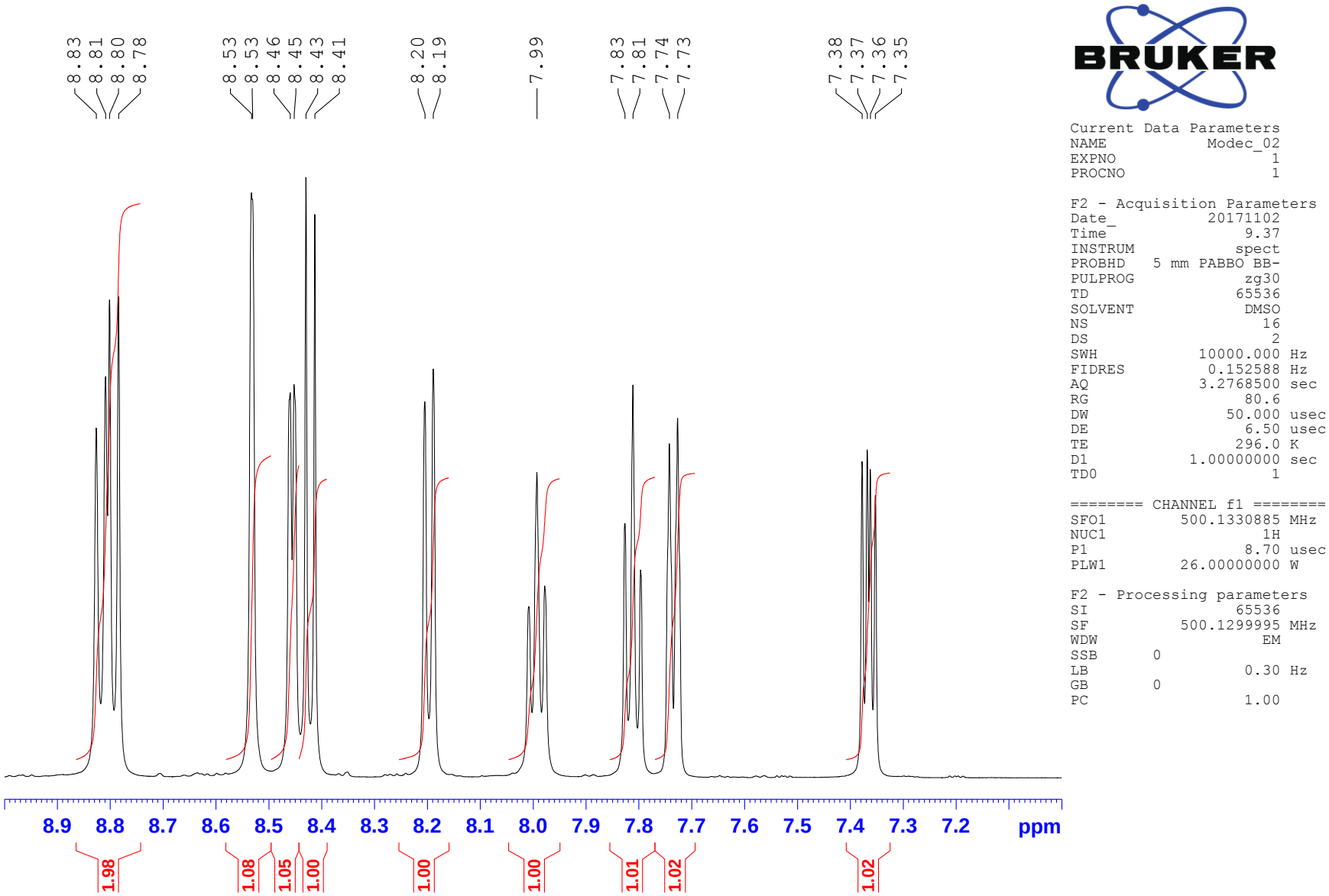
Figure S19. ^{1}H NMR spectrum of a DMSO-d_6 solution of [Zn(quin)$_2$(3-Hmpy)$_2$] (**5**).

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PROCNO                 1

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NS                     16
DS                      2
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DE                 6.50 usec
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D1            1.00000000 sec
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NUC1                1H
P1                 8.70 usec
PLW1        26.00000000 W

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WDW                  EM
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LB                 0.30 Hz
GB        0
PC                 1.00
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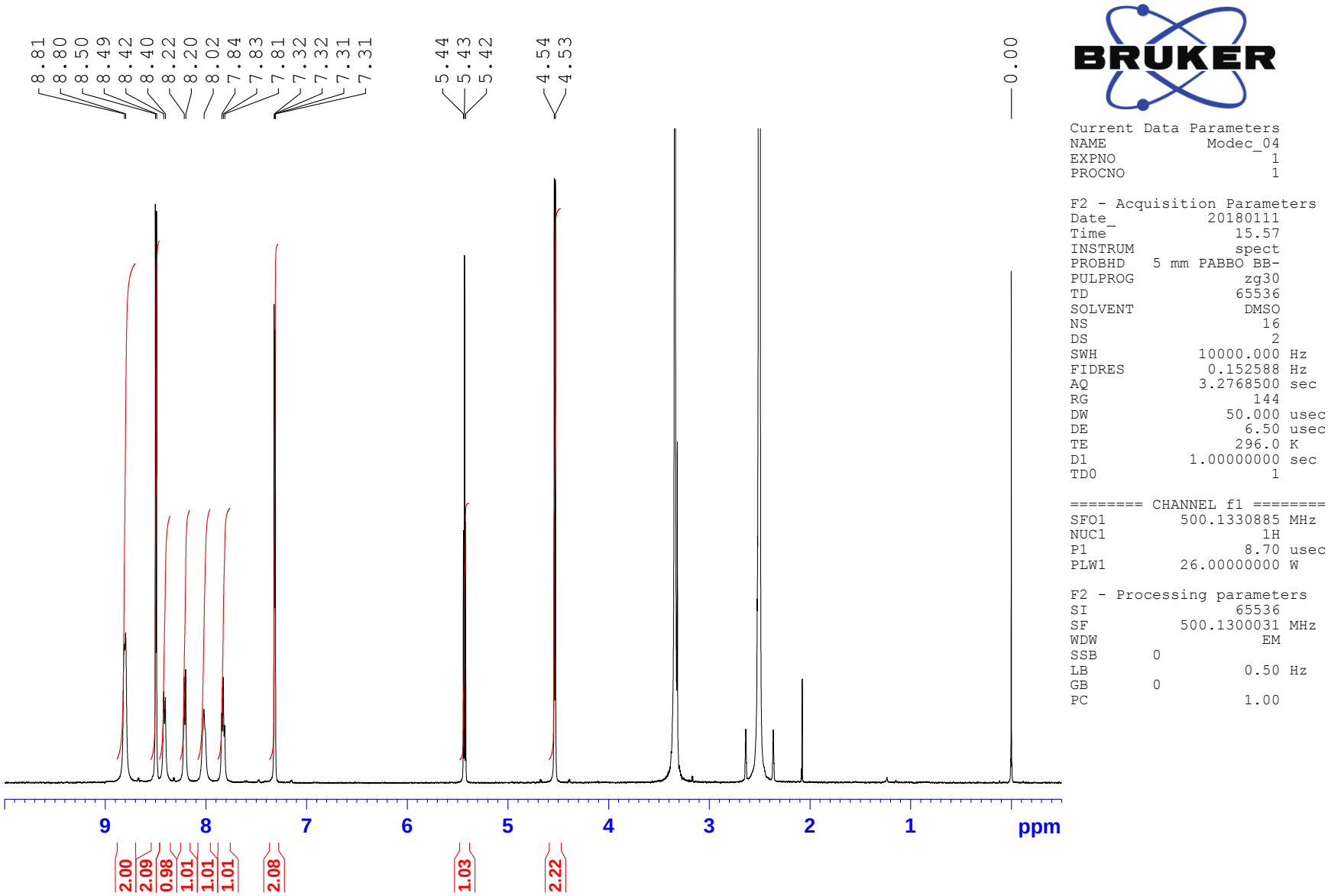
Figure S20. ^{1}H NMR spectrum of a DMSO-d_6 solution of [Zn(quin)$_2$(4-Hmpy)$_2$] (**7**).

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AQ             3.2768500 sec
RG                   144
DW                50.000 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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NUC1                   1H
P1                  8.70 usec
PLW1        26.00000000 W

F2 - Processing parameters
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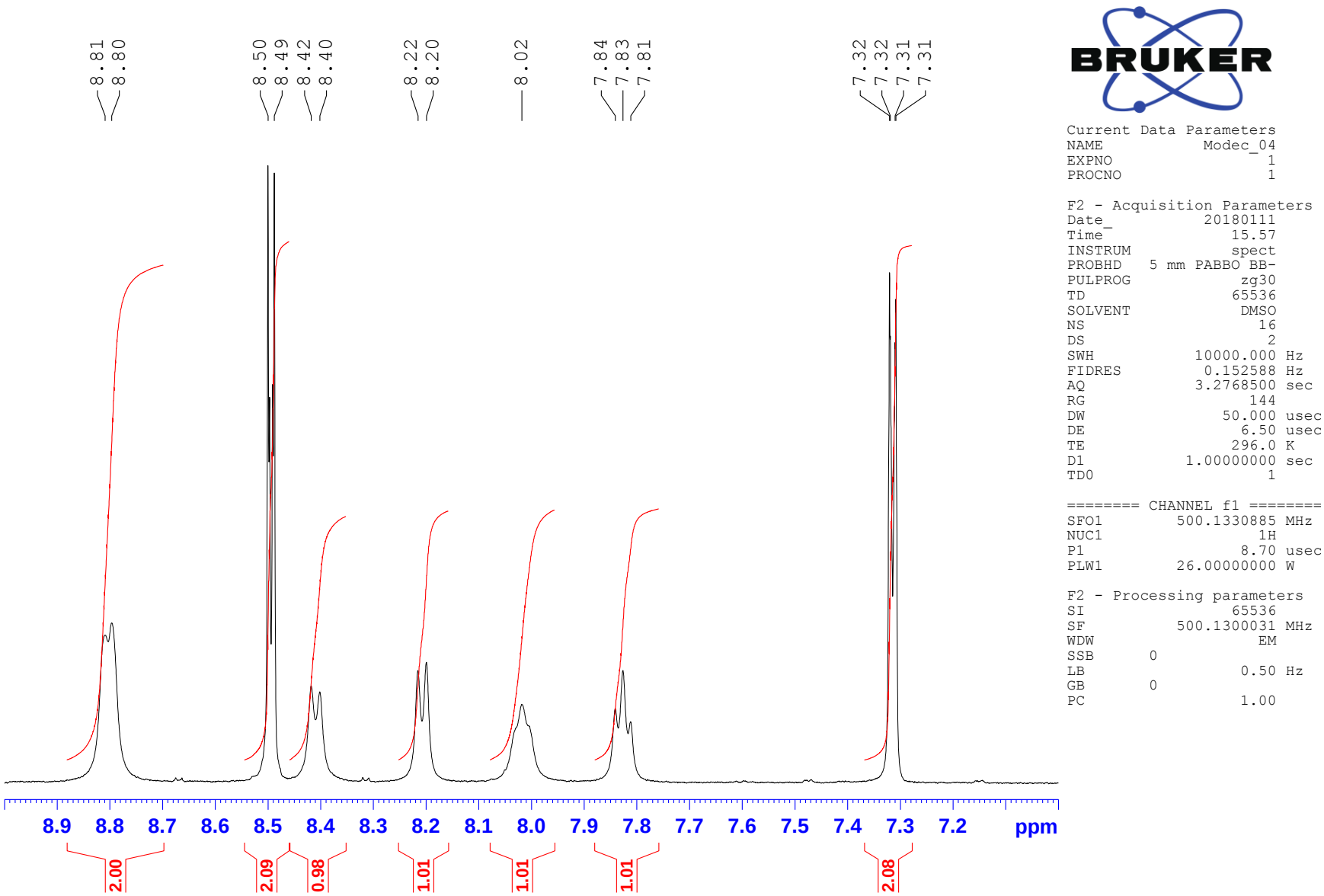
WDW                    EM
SSB      0
LB                  0.50 Hz
GB       0
PC                  1.00
```

Figure S21. ^{1}H NMR spectrum of a DMSO-d_6 solution of [Zn(quin)$_2$(4-Hmpy)$_2$] (**7**).




```
Current Data Parameters
NAME            Modec_04
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180111
Time                15.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ             3.2768500 sec
RG                    144
DW               50.000 usec
DE                6.50 usec
TE                296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                 8.70 usec
PLW1        26.00000000 W

F2 - Processing parameters
SI                  65536
SF           500.1300031 MHz
WDW                    EM
SSB      0
LB                 0.50 Hz
GB       0
PC                 1.00
```