

Supplementary material

for

**Beyond the simple copper(II) coordination chemistry with quinaldinate  
and secondary amines**

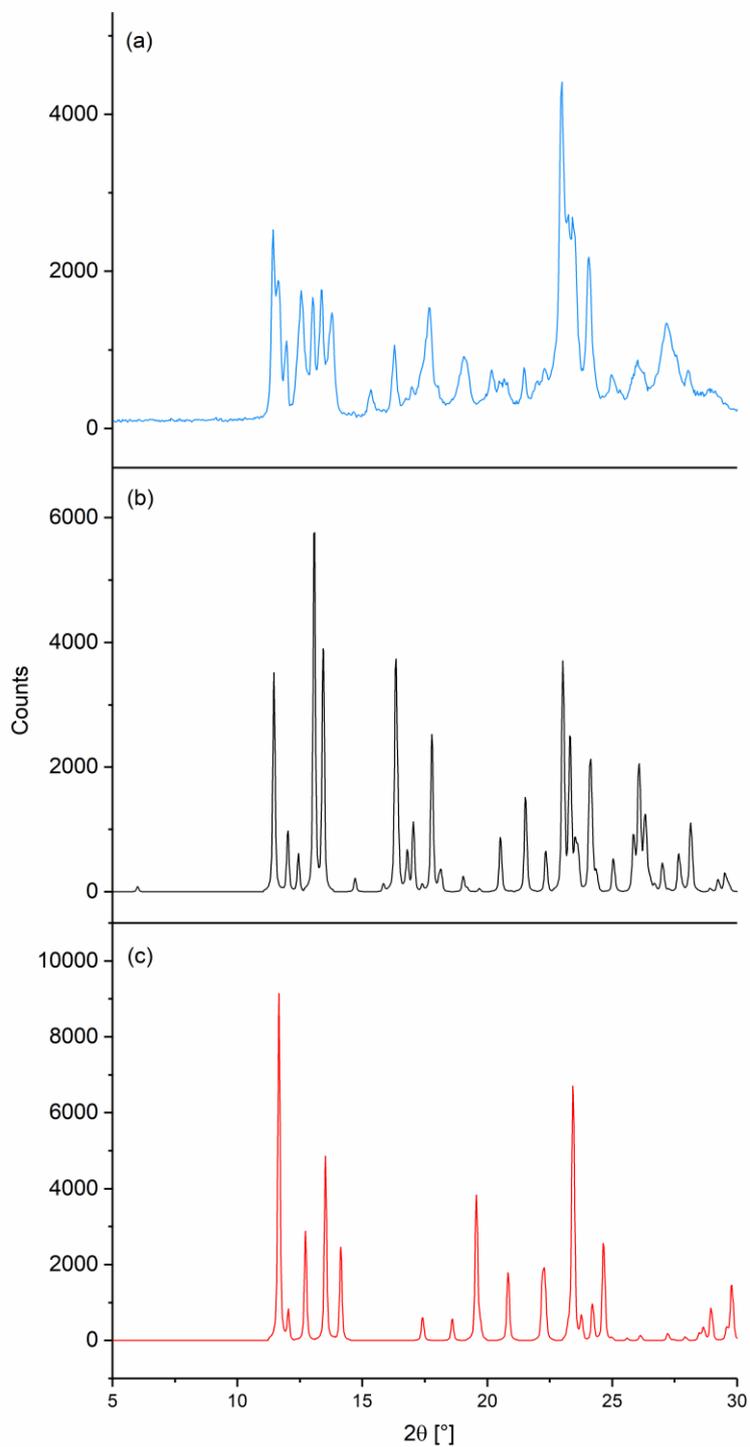
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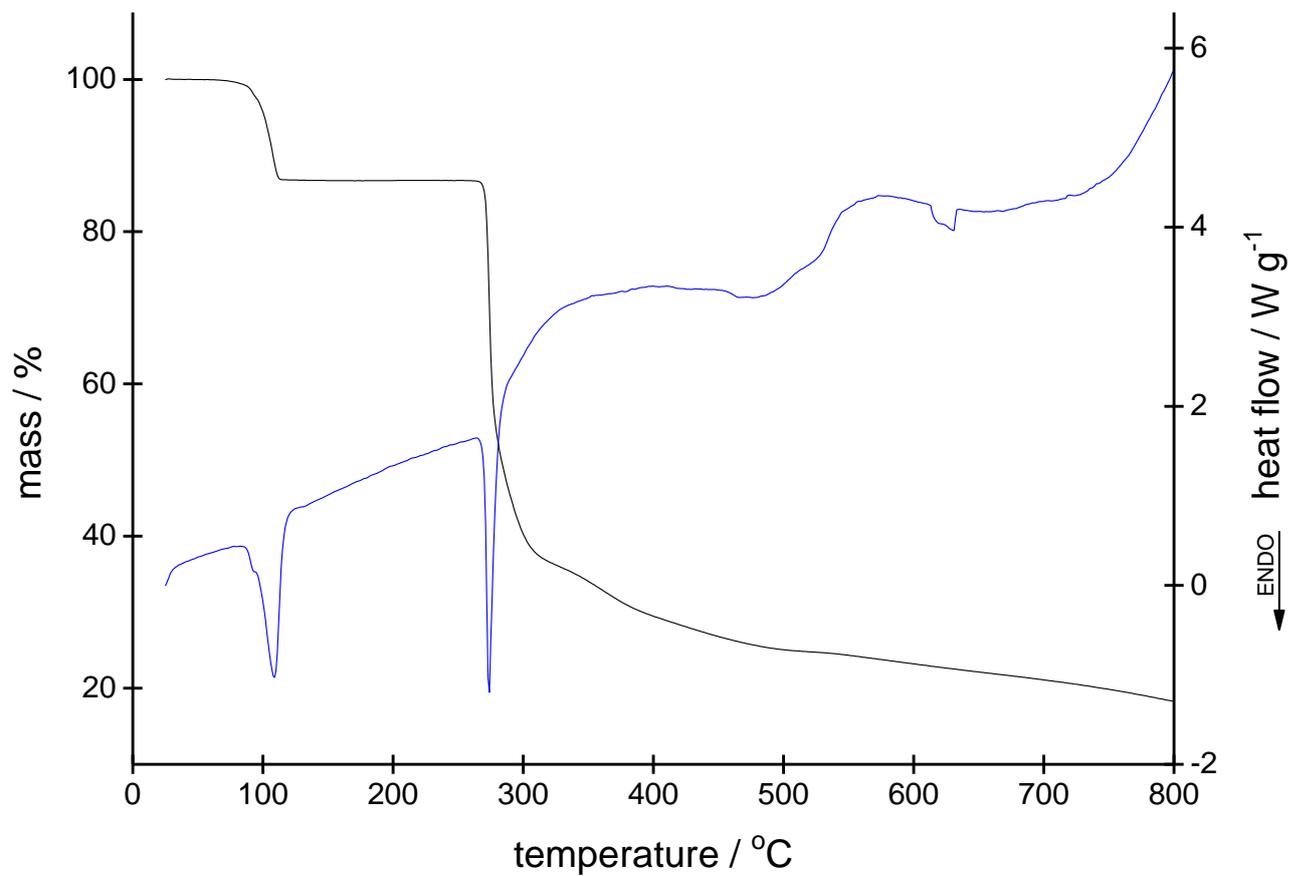
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**Figure S1.** Identification of the aged  $[\text{Cu}(\text{quin})_2(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$  (**1**): (a) measured PXRD, (b) calculated pattern for  $[\text{Cu}(\text{quin})_2(\text{H}_2\text{O})]$  [S1], and (c) calculated pattern for the new polymorph of  $[\text{Cu}(\text{quin})_2(\text{H}_2\text{O})]$ .



**Figure S2.** TG and DSC curves for  $[\text{Cu}(\text{quin})_2(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$  (**1**).



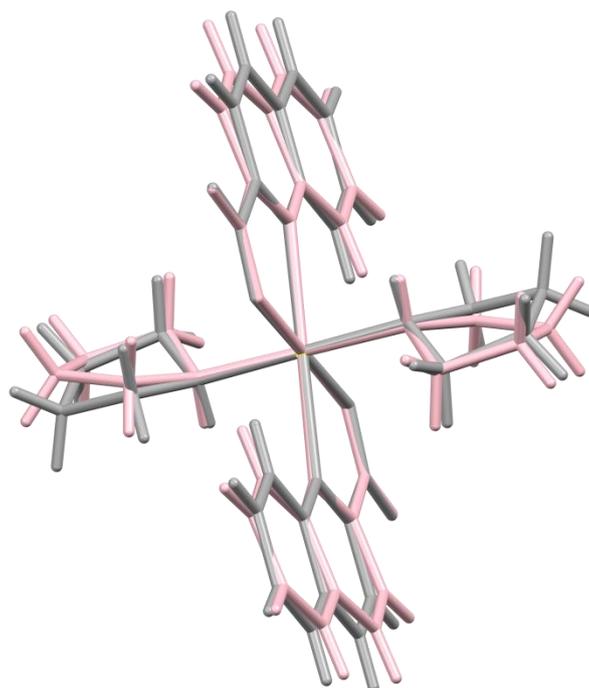
**A list of  $\pi\cdots\pi$  stacking interactions in [Cu(quin)<sub>2</sub>(CH<sub>3</sub>OH)]·CH<sub>3</sub>OH (1).**

The labels *Cg*(3) and *Cg*(4) pertain to the centroids of the pyridine parts of the quinaldinates, *i.e.*, N(1)-C(11)-C(12)-C(13)-C(14)-C(19) and N(2)-C(21)-C(22)-C(23)-C(24)-C(29), respectively, and the label *Cg*(6) to the arene part of one quinaldinate, *i.e.*, C(24)-C(25)-C(26)-C(27)-C(28)-C(29). Parameters *Cg*⋯*Cg*, interplanar distance, dihedral and offset angles are as defined in reference [S2].

**Table S1.**  $\pi\cdots\pi$  stacking interactions [Å, °] in [Cu(quin)<sub>2</sub>(CH<sub>3</sub>OH)]·CH<sub>3</sub>OH (1).

$\pi\cdots\pi$ interactions	type	<i>Cg</i> ⋯ <i>Cg</i>	interplanar distance	dihedral angle	offset angle
<i>Cg</i> (4)⋯ <i>Cg</i> (4) [1- <i>x</i> , 1- <i>y</i> , 2- <i>z</i> ]	pyridine⋯pyridine	3.6148(11)	3.3167(8)	0.02(10)	23.4
<i>Cg</i> (3)⋯ <i>Cg</i> (6) [- <i>x</i> , - <i>y</i> , 2- <i>z</i> ]	pyridine⋯arene	4.0098(12)	2.9564(9)	20.83(10)	23.1

**Figure S3.** Overlay of the  $[\text{Cu}(\text{quin})_2(\text{pyro})_2]$  molecules in **2**, done by Mercury [S3].



**Table S2.** Overlay parameters for pairs of complex molecules in **2**, **4** and **7**.<sup>a</sup>

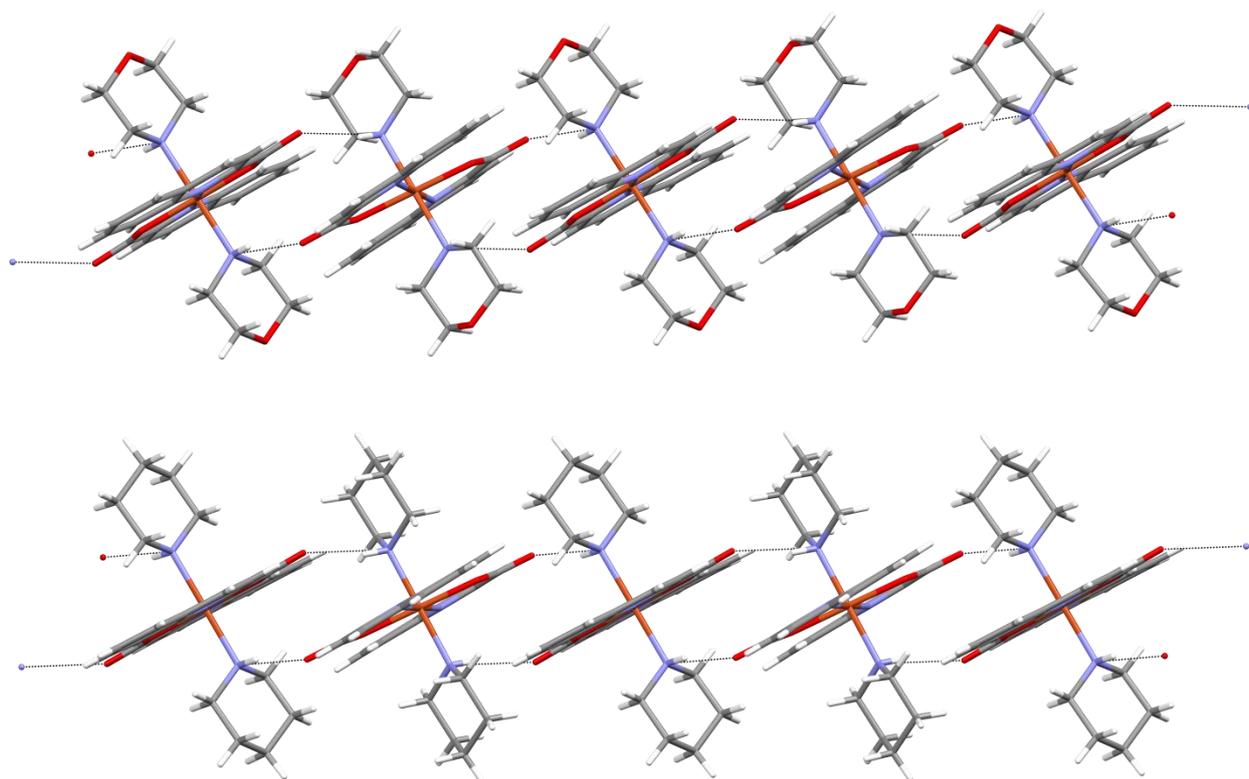
Compound	RMSD <sup>b</sup>	Max. distance <sup>c</sup>
<b>2</b>	0.2082	0.6469
<b>4</b>	0.2270	0.4844
<b>7</b>	0.1594	0.2959

<sup>a</sup> Overlay was done by Mercury [S3].

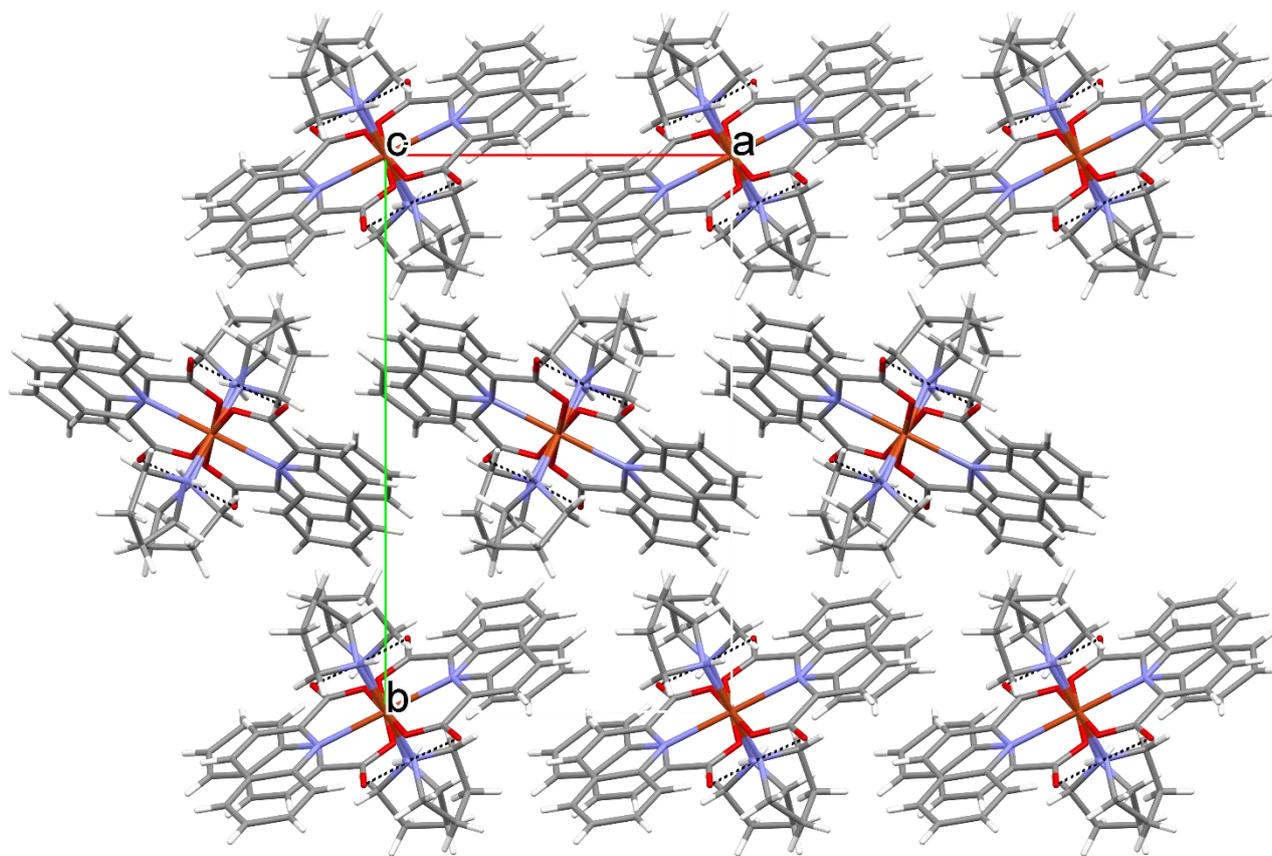
<sup>b</sup> Root-mean-square deviation.

<sup>c</sup> Maximum distance in Å between two equivalent atoms in the overlaid molecules.

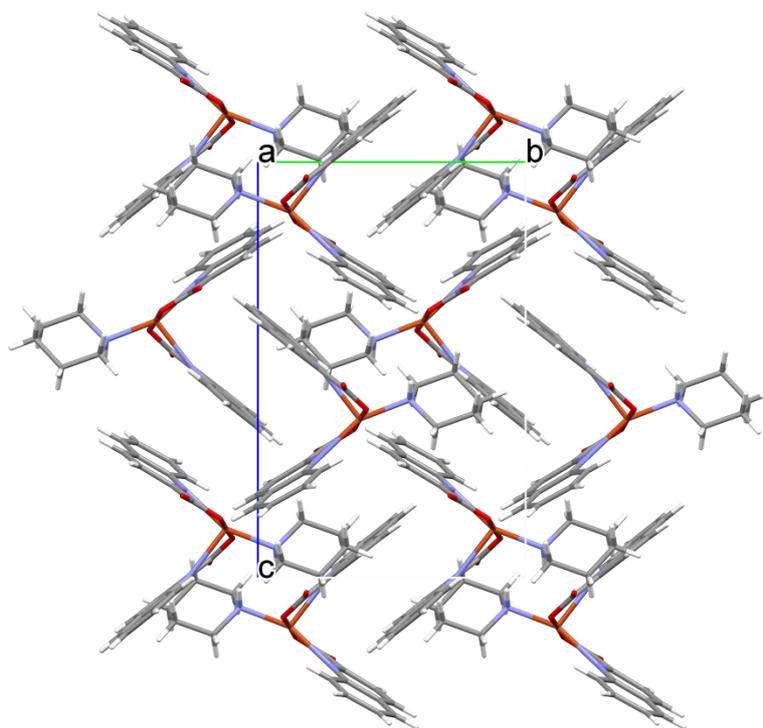
**Figure S4.** Chains in the structures of  $[\text{Cu}(\text{quin})_2(\text{morph})_2]$  (**4**) (top) and  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$  (**7**) (bottom).



**Figure S5.** A view along the chains in the structure of  $[\text{Cu}(\text{quin})_2(\text{pyro})_2]$  (**2**). The chains pack in a compact manner: each chain is surrounded by six adjacent ones.



**Figure S6.** Packing in the structure of [Cu(quin)<sub>2</sub>(pipe)] (**6**). Complex molecules are held together with the agency of  $\pi\cdots\pi$  stacking interactions between pairs of quinaldinate rings.



**Table S3.** Overlay parameters for the [Cu(quin)<sub>2</sub>(pipe)<sub>2</sub>] complex molecules in **7**, **8** and **9**.<sup>a</sup>

<b>Pairs of compounds</b>	<b>RMSD<sup>b</sup></b>	<b>Max. distance<sup>c</sup></b>
<b>7 and 8<sup>d</sup></b>	0.1836	0.3717
	0.2458	0.4394
<b>7 and 9<sup>d</sup></b>	0.2452	0.4392
	0.2962	0.5059
<b>8 and 9</b>	0.0690	0.1281

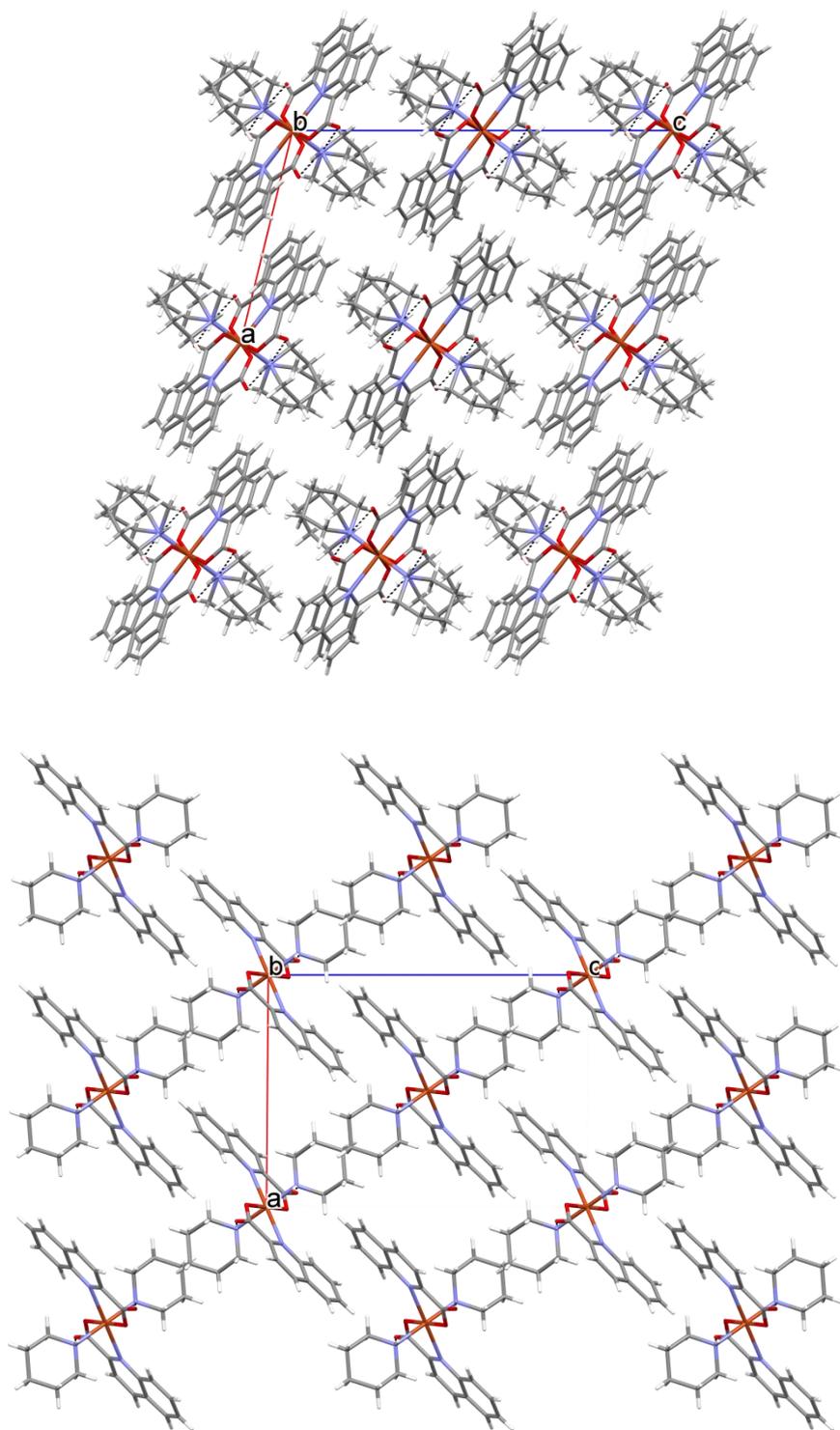
<sup>a</sup> Overlay was done by Mercury [S3].

<sup>b</sup> Root-mean-square deviation.

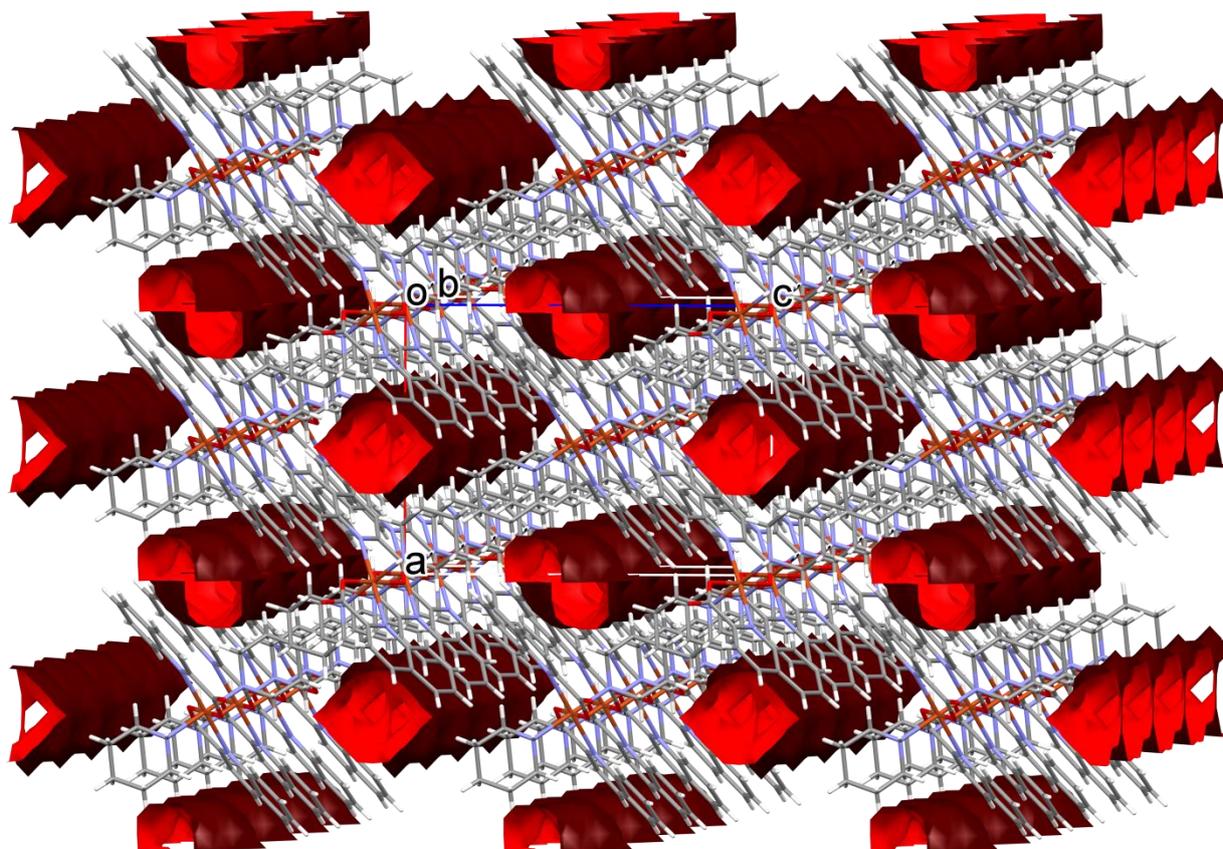
<sup>c</sup> Maximum distance in Å between two equivalent atoms in the overlaid molecules.

<sup>d</sup> As there are two complex molecules in the asymmetric unit of **7**, two sets of parameters are given.

**Figure S7.** Packing motifs in  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$  (**7**) (top) and  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]\cdot\text{CH}_3\text{CN}$  (**8**) (bottom). Both views are along the chains. Please note that  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]\cdot\text{CH}_3\text{CN}$  (**8**) and  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]\cdot\text{CH}_3\text{CH}_2\text{CN}$  (**9**) are isomorphous. The packing of chains in **8** and **9** creates hydrophobic channels.



**Figure S8.** A view along the channels, shown in red colour, in the structure of  $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$  (**8**). Solvent molecules of crystallization that are accommodated in the channels are not shown.



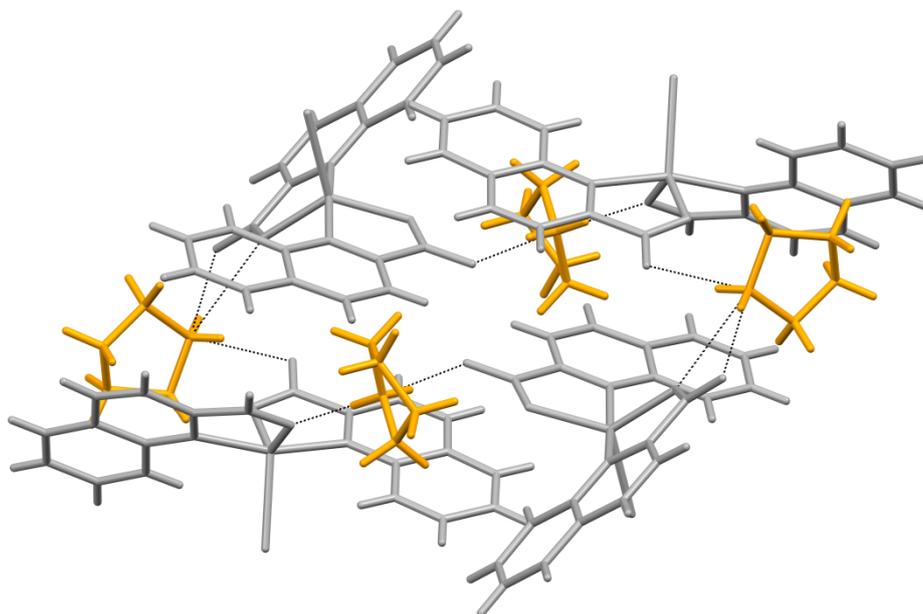
**A list of intermolecular interactions in [Cu(quin)<sub>2</sub>(pipe)] (6).**

The labels *Cg*(3) and *Cg*(4) pertain to the centroids of the pyridine parts of the quinaldinates, *i.e.*, N(1)-C(11)-C(12)-C(13)-C(14)-C(19) and N(2)-C(21)-C(22)-C(23)-C(24)-C(29), respectively, and the labels *Cg*(6) and *Cg*(7) to the corresponding arene parts, *i.e.*, C(14)-C(15)-C(16)-C(17)-C(18)-C(19) and C(24)-C(25)-C(26)-C(27)-C(28)-C(29), respectively. Parameters *Cg*...*Cg*, interplanar distance, dihedral and offset angles are as defined in reference [S2].

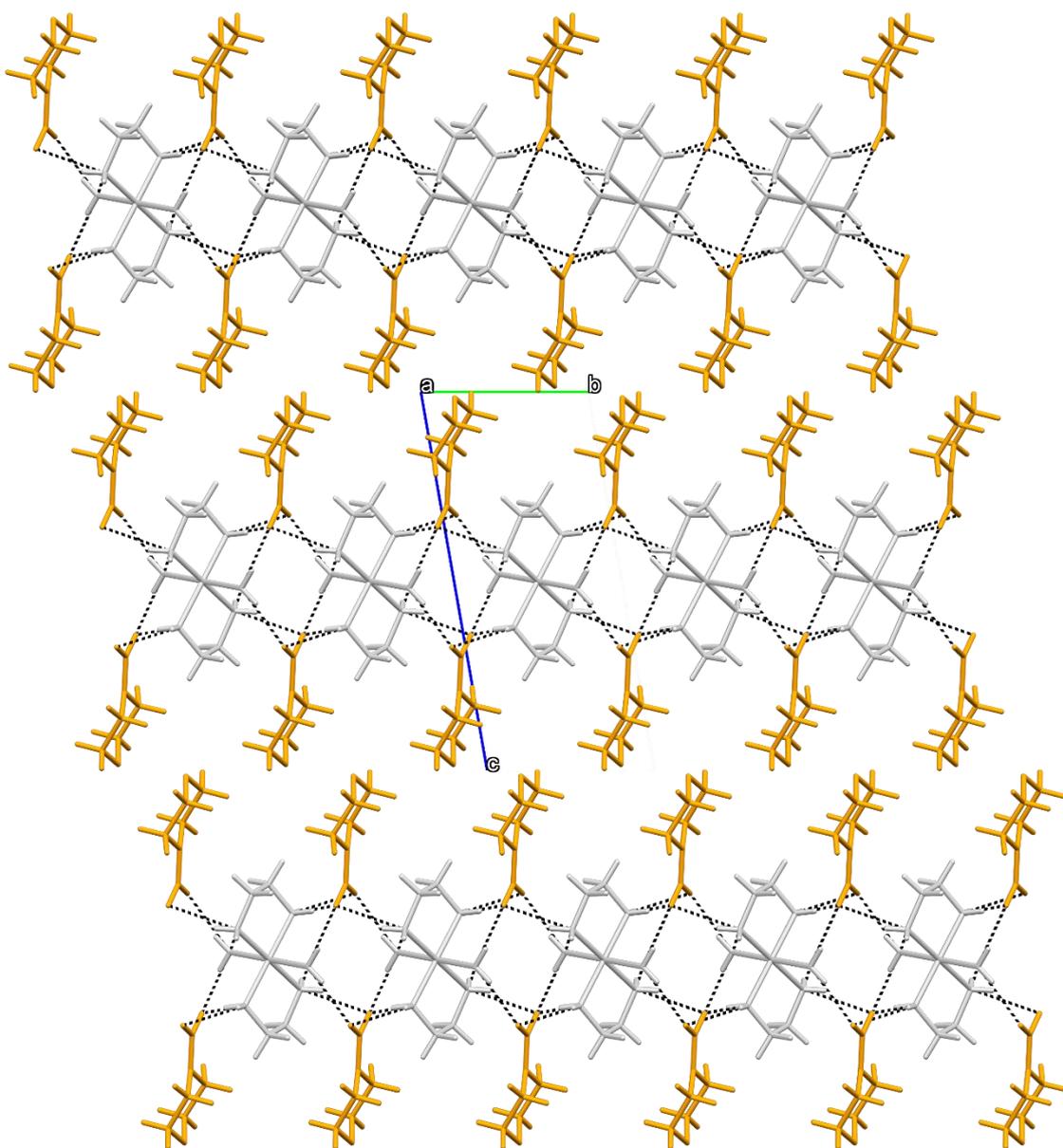
**Table S4.** Intermolecular interactions [Å, °] in [Cu(quin)<sub>2</sub>(pipe)] (6).

<b><math>\pi</math>...<math>\pi</math> interactions</b>	<b>type</b>	<b><i>Cg</i>...<i>Cg</i></b>	<b>interplanar distance</b>	<b>dihedral angle</b>	<b>offset angle</b>
<i>Cg</i> (4)... <i>Cg</i> (6) [ <i>x</i> , 1/2- <i>y</i> , -1/2+ <i>z</i> ]	pyridine...arene	3.7087(10)	3.5616(7)	11.77(8)	27.2
<i>Cg</i> (6)... <i>Cg</i> (7) [ <i>x</i> , 1/2- <i>y</i> , 1/2+ <i>z</i> ]	arene...arene	3.9004(10)	3.4550(7)	11.41(8)	23.9
<b>C-H...<math>\pi</math> interactions</b>	<b>H...<i>Cg</i></b>	<b>C-H...<i>Cg</i></b>	<b>C...<i>Cg</i></b>	<b>X-H, <math>\pi</math></b>	
C(32)-H... <i>Cg</i> (3) [ <i>x</i> , 1+ <i>y</i> , <i>z</i> ]	3.00	159	3.918(2)	67	
C(33)-H... <i>Cg</i> (7) [ <i>x</i> , 1+ <i>y</i> , <i>z</i> ]	2.78	146	3.630(2)	60	

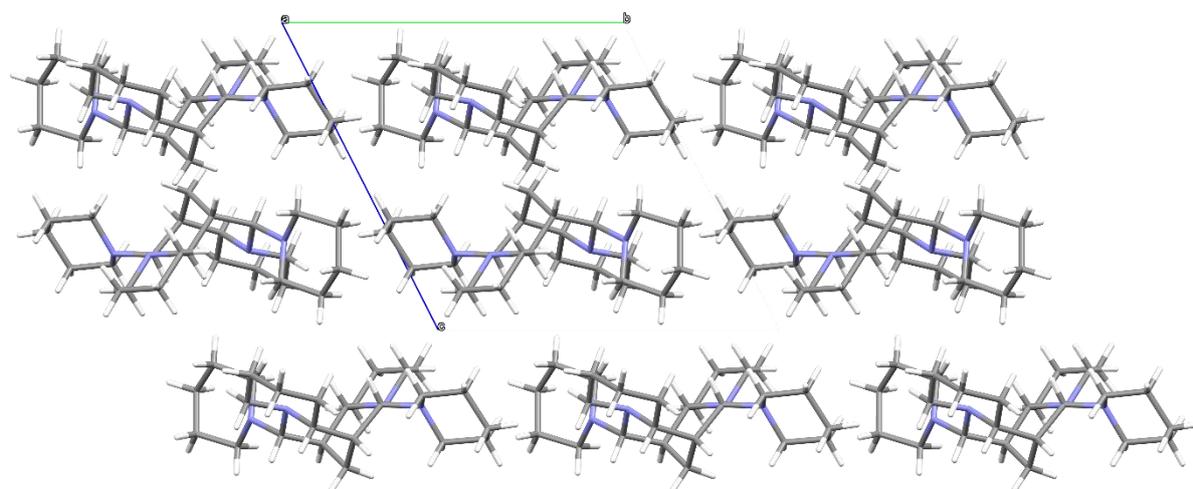
**Figure S9.** Hydrogen bonding pattern in (pyroH)[Cu(quin)<sub>2</sub>Cl] (**3**): NH<sub>2</sub><sup>+</sup>...COO<sup>-</sup> interactions link four pyrrolidinium cations with four complex anions into a cyclic supramolecular motif, described in graph set notation as  $R_8^8(36)$  [S4]. Colour code: complex anions - grey, pyrrolidinium cations - gold.



**Figure S10.** Hydrogen bonds in  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{morphCOO})_2$  (**5**): intricate pattern of H-bonds (dotted lines) links complex cations (light grey) and counteranions (gold) into infinite 2D array. The surface of the layers is covered with the hydrophobic part of the morphCOO<sup>-</sup> anions. The layers stack along *c*-axis.



**Figure S11.** Packing arrangement in the structure of **10**.



**Table S5.** Hydrogen bonds in compounds **1–11**.

Compound	Donor...acceptor	Description	Distance [Å]
[Cu(quin) <sub>2</sub> (CH <sub>3</sub> OH)]·CH <sub>3</sub> OH ( <b>1</b> )	O1M...O12[1-x, -y, 2-z]	CH <sub>3</sub> OH(ligand)...COO <sup>-</sup>	2.752(2)
	O2M...O22	CH <sub>3</sub> OH...COO <sup>-</sup>	2.743(2)
[Cu(quin) <sub>2</sub> (pyro) <sub>2</sub> ] ( <b>2</b> )	N3...O22	NH(pyro)...COO <sup>-</sup>	2.903(3)
	N4...O12[2-x, -y, 4-z]	NH(pyro)...COO <sup>-</sup>	2.916(2)
(pyroH)[Cu(quin) <sub>2</sub> Cl] ( <b>3</b> )	N5...O11	NH <sub>2</sub> <sup>+</sup> (pyroH <sup>+</sup> )...COO <sup>-</sup>	2.828(3)
	N5...O32	NH <sub>2</sub> <sup>+</sup> (pyroH <sup>+</sup> )...COO <sup>-</sup>	2.730(3)
	N6...O22	NH <sub>2</sub> <sup>+</sup> (pyroH <sup>+</sup> )...COO <sup>-</sup>	2.802(3)
	N6...O42[1-x, 1-y, 1-z]	NH <sub>2</sub> <sup>+</sup> (pyroH <sup>+</sup> )...COO <sup>-</sup>	2.879(3)
[Cu(quin) <sub>2</sub> (morph) <sub>2</sub> ] ( <b>4</b> )	N3...O22	NH(morph)...COO <sup>-</sup>	2.924(4)
	N4...O12	NH(morph)...COO <sup>-</sup>	2.952(4)
<i>trans</i> -[Cu(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](morphCOO) <sub>2</sub> ( <b>5</b> )	N1...O1[1+x, y, z]	NH <sub>2</sub> ...H <sub>2</sub> O	3.056(2)
	N1...O31	NH <sub>2</sub> ...COO <sup>-</sup>	3.001(2)
	N2...O31[x, -1+y, z]	NH <sub>2</sub> ...COO <sup>-</sup>	2.987(2)
	N2...O32[1+x, -1+y, z]	NH <sub>2</sub> ...COO <sup>-</sup>	2.907(2)
	O1...O31[-x, 2-y, 1-z]	H <sub>2</sub> O...COO <sup>-</sup>	2.7773(19)
	O1...O32	H <sub>2</sub> O...COO <sup>-</sup>	2.7447(18)
[Cu(quin) <sub>2</sub> (pipe) <sub>2</sub> ] ( <b>7</b> )	N3...O22[2-x, 1-y, 1-z]	NH(pipe)...COO <sup>-</sup>	2.924(2)
	N4...O12[2-x, -y, 1-z]	NH(pipe)...COO <sup>-</sup>	2.994(2)
[Cu(quin) <sub>2</sub> (pipe) <sub>2</sub> ]·CH <sub>3</sub> CN ( <b>8</b> )	N2...O12[x, -1+y, z]	NH(pipe)...COO <sup>-</sup>	3.0103(17)
[Cu(quin) <sub>2</sub> (pipe) <sub>2</sub> ]·CH <sub>3</sub> CH <sub>2</sub> CN ( <b>9</b> )	N2...O12[x, -1+y, z]	NH(pipe)...COO <sup>-</sup>	2.9973(17)
(pipeH)[Cu(quin) <sub>2</sub> Cl] ( <b>11</b> )	N5...O22[1-x, -y, 2-z]	NH <sub>2</sub> <sup>+</sup> (pipeH <sup>+</sup> )...COO <sup>-</sup>	2.8505(18)
	N5...O42[1-x, -y, 2-z]	NH <sub>2</sub> <sup>+</sup> (pipeH <sup>+</sup> )...COO <sup>-</sup>	2.8222(18)
	N6...O12	NH <sub>2</sub> <sup>+</sup> (pipeH <sup>+</sup> )...COO <sup>-</sup>	2.7886(18)
	N6...O32[-x, 1-y, 2-z]	NH <sub>2</sub> <sup>+</sup> (pipeH <sup>+</sup> )...COO <sup>-</sup>	2.8471(18)

Figure S12. Infrared spectrum of [Cu(quin)<sub>2</sub>(H<sub>2</sub>O)].

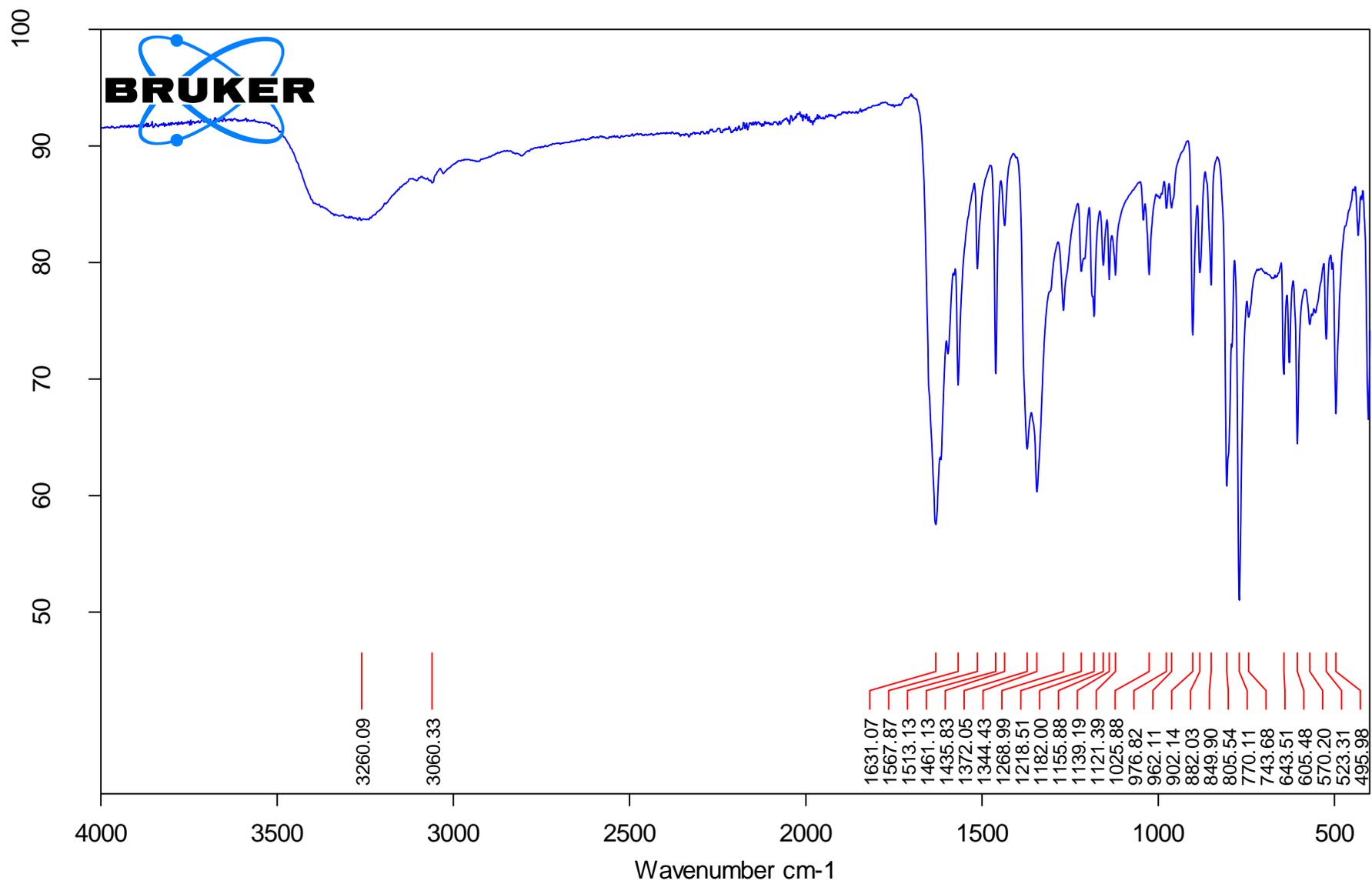


Figure S13. Infrared spectrum of [Cu(quin)<sub>2</sub>(CH<sub>3</sub>OH)]·CH<sub>3</sub>OH (1).

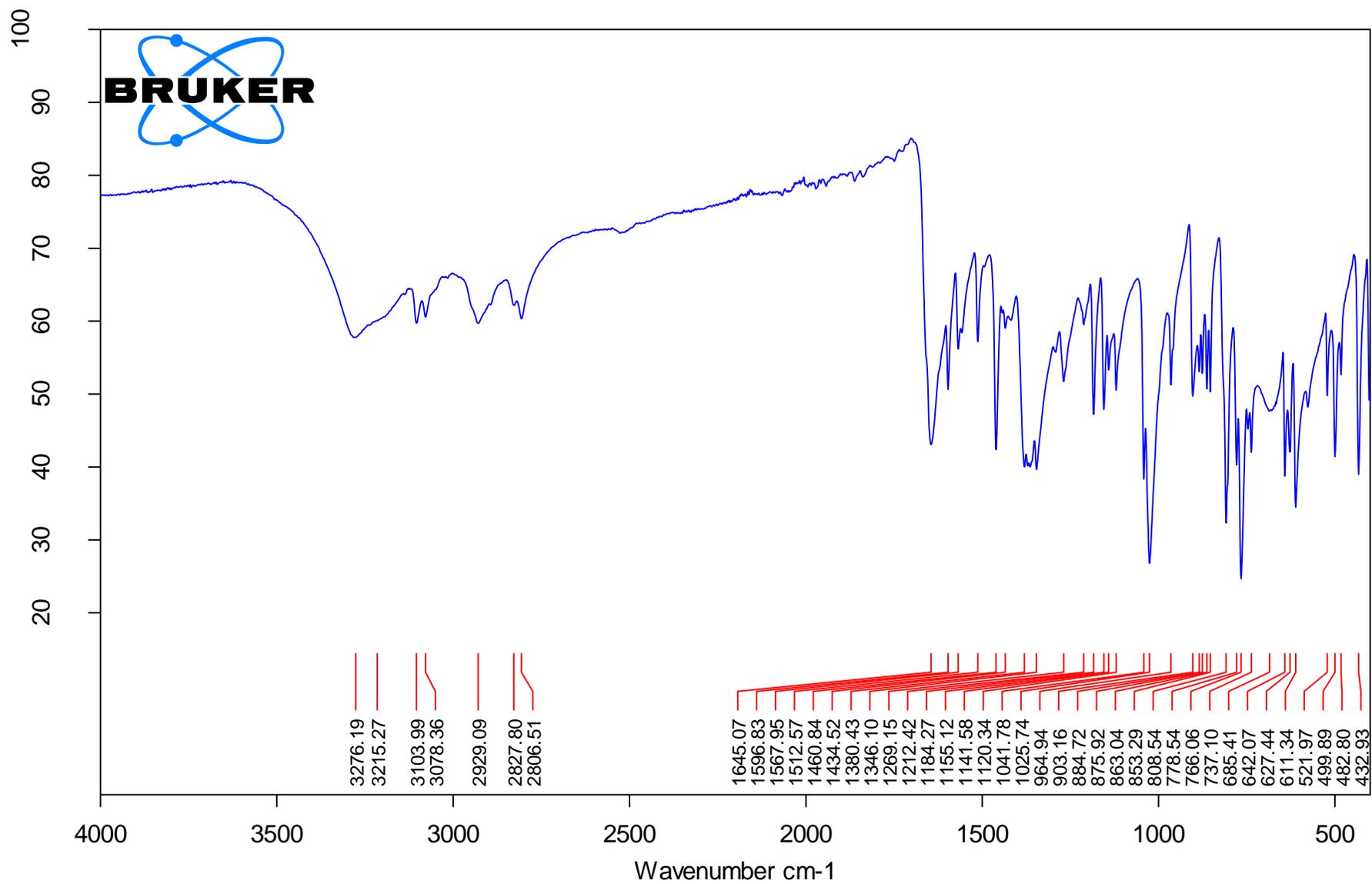


Figure S14. Infrared spectrum of [Cu(quin)<sub>2</sub>(pyro)<sub>2</sub>] (2).

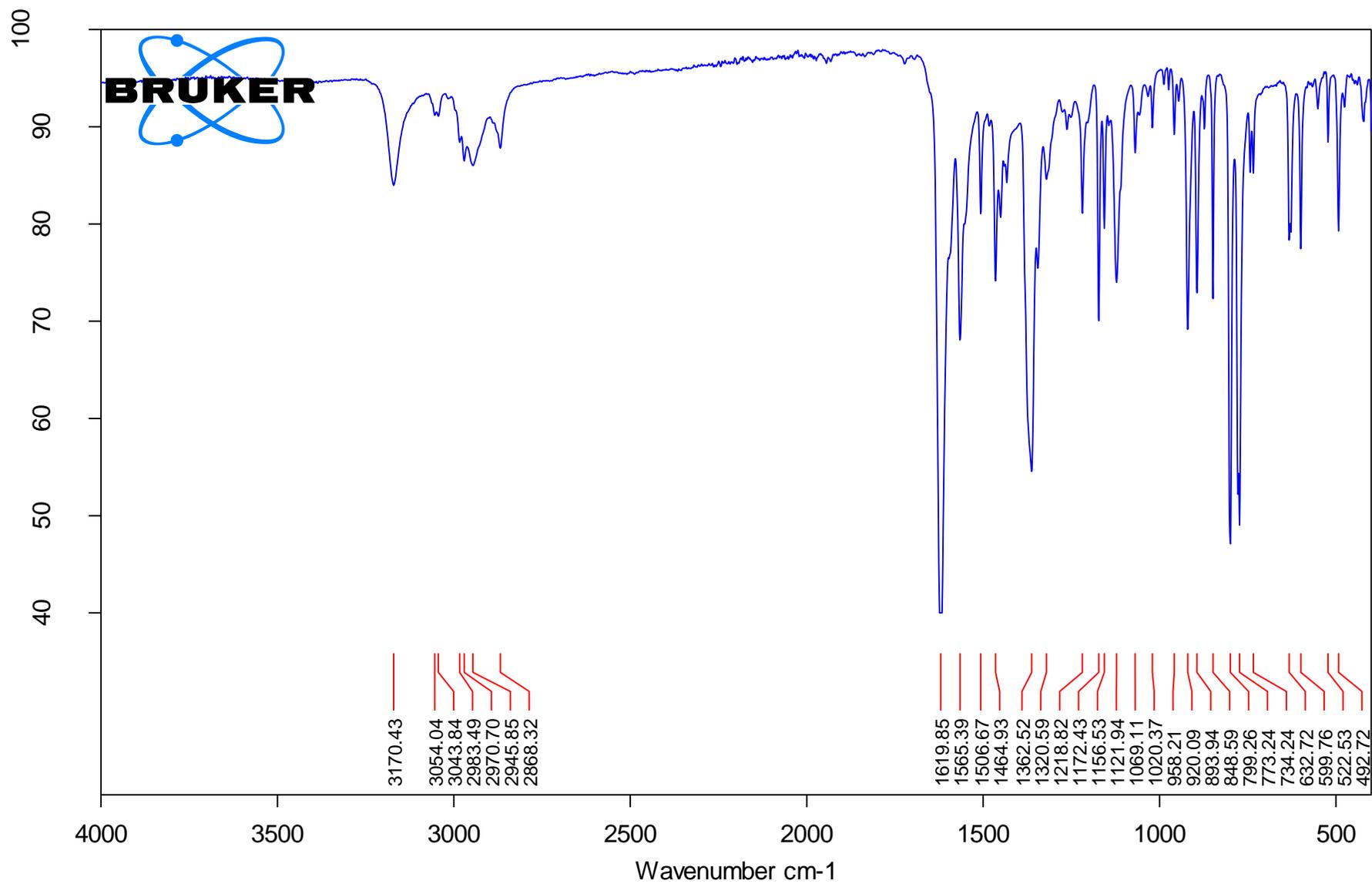


Figure S15. Infrared spectrum of (pyroH)[Cu(quin)<sub>2</sub>Cl] (3).

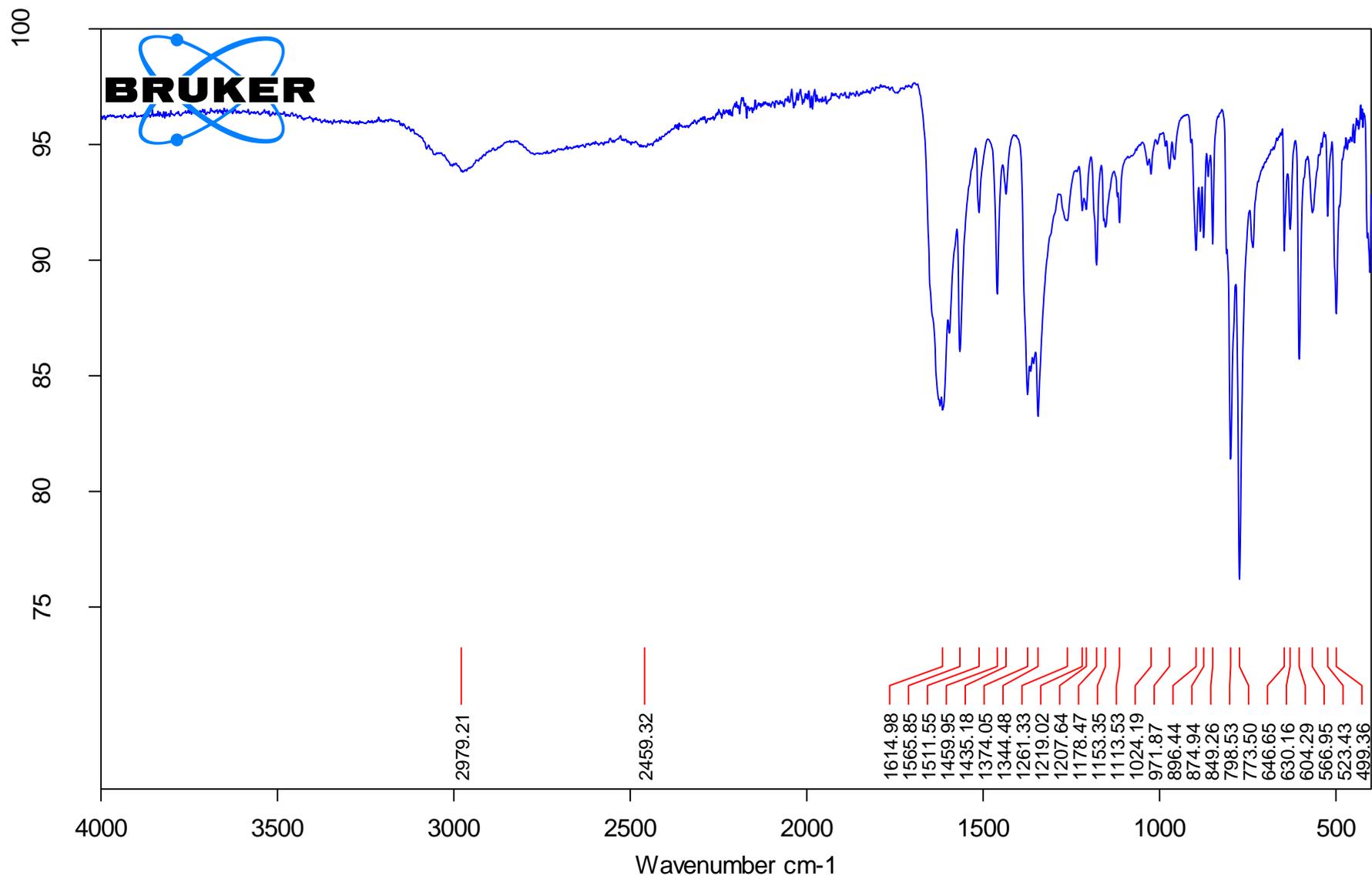


Figure S16. Infrared spectrum of [Cu(quin)<sub>2</sub>(morph)<sub>2</sub>] (4).

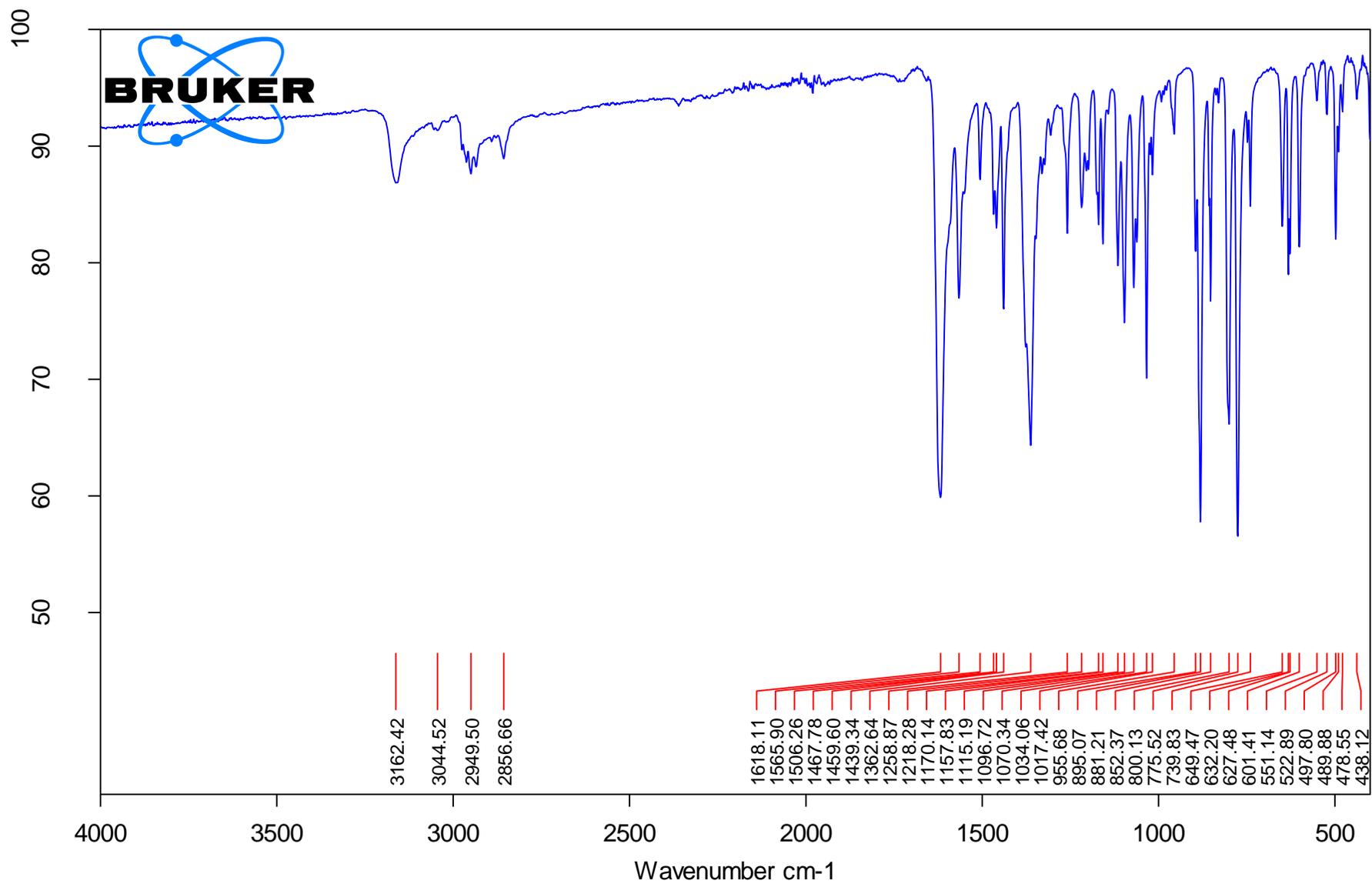


Figure S17. Infrared spectrum of [Cu(quin)<sub>2</sub>(pipe)] (6).

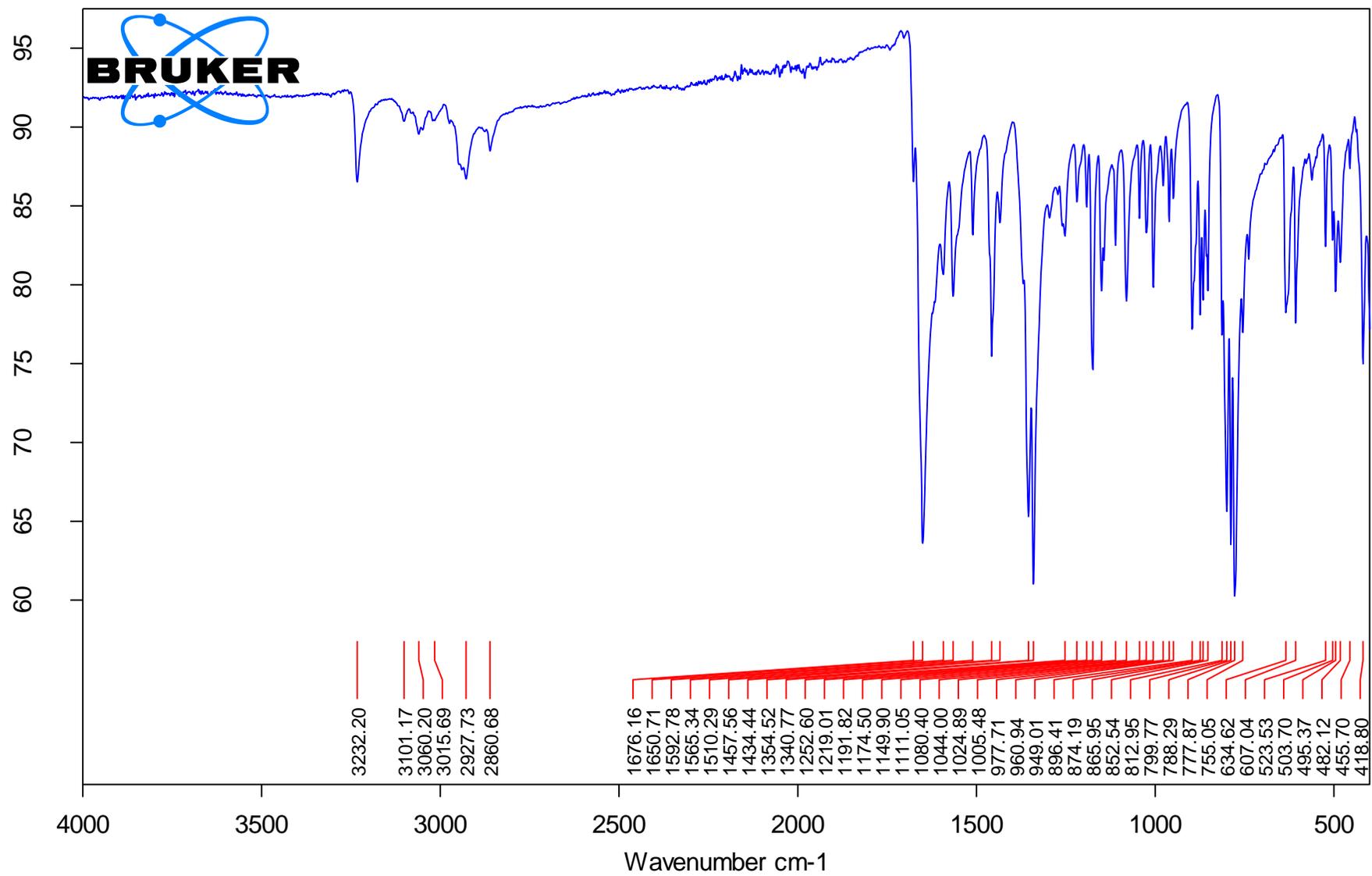


Figure S18. Infrared spectrum of  $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$  (7).

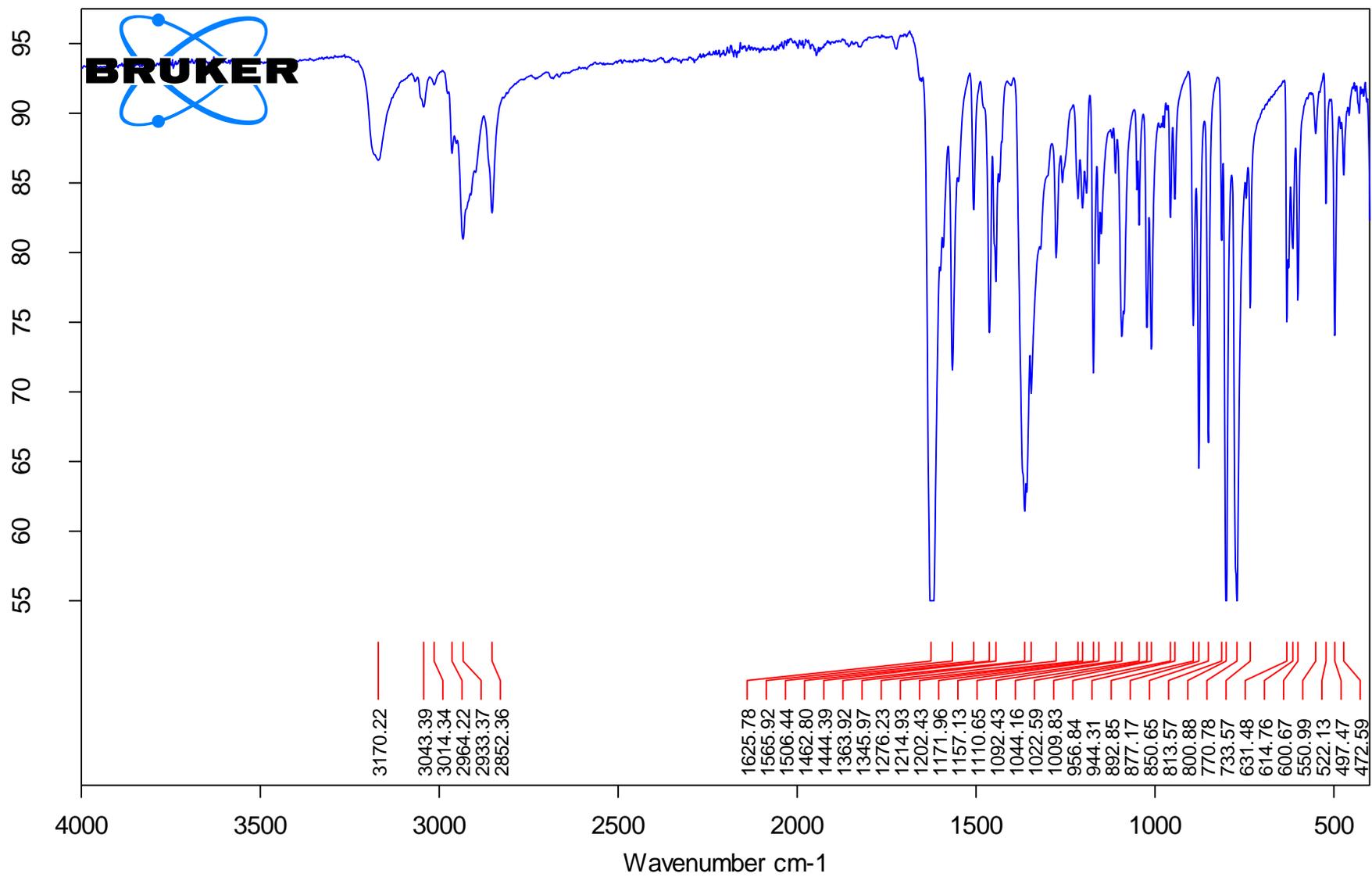


Figure S19. Infrared spectrum of  $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$  (**8**).

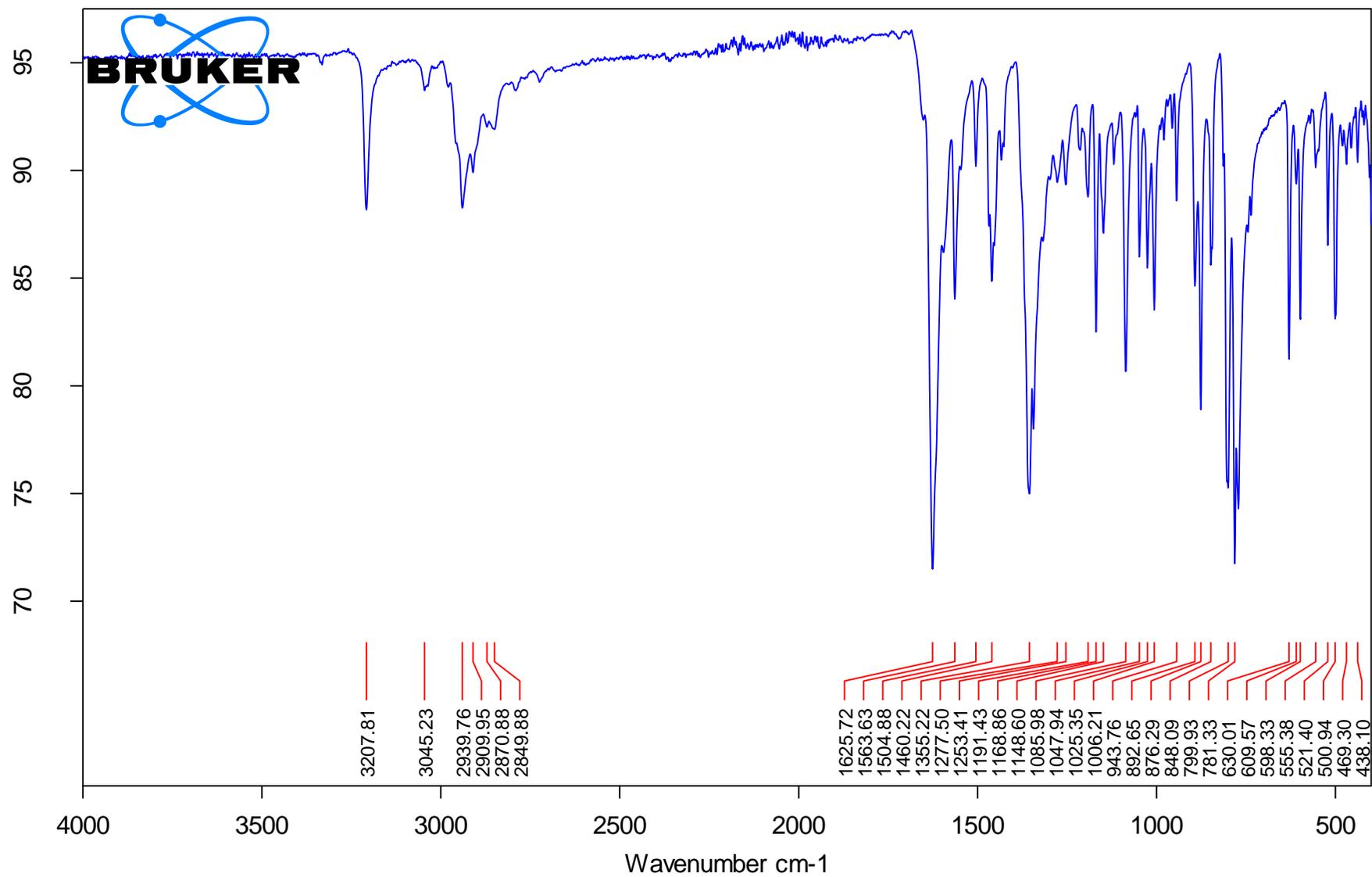


Figure S20. Infrared spectrum of [Cu(quin)<sub>2</sub>(pipe)<sub>2</sub>] $\cdot$ CH<sub>3</sub>CH<sub>2</sub>CN (9).

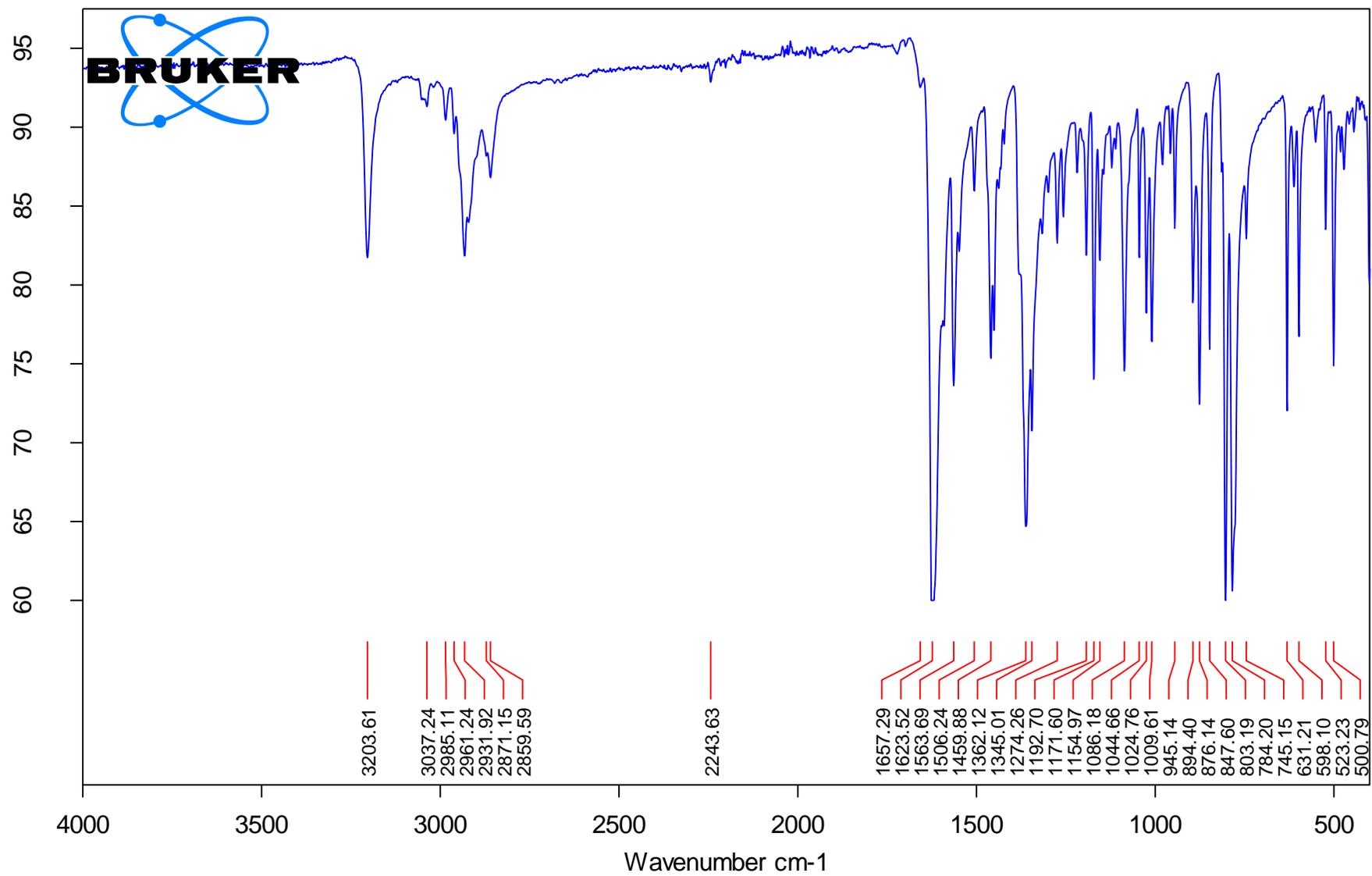
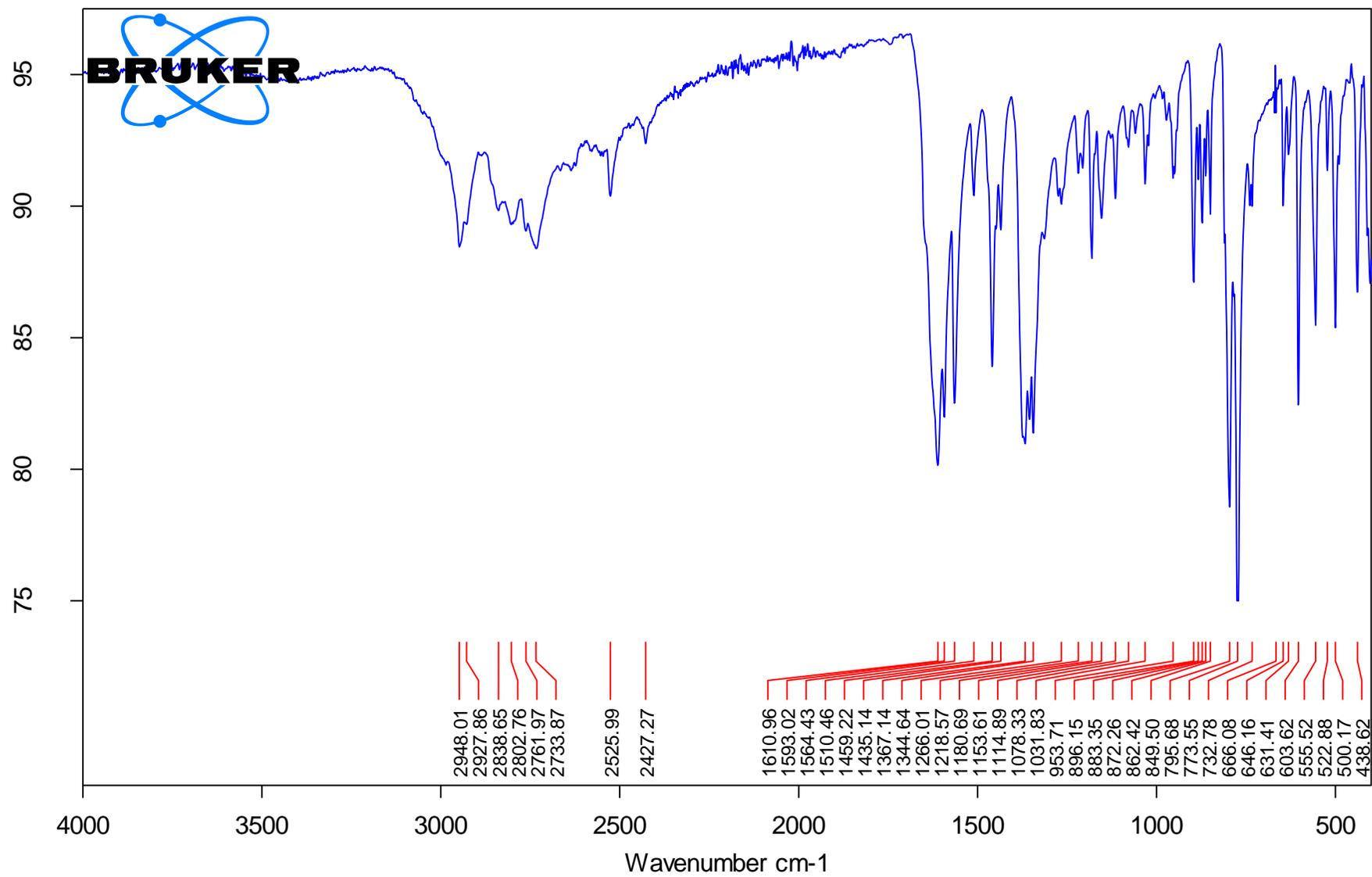


Figure S21. Infrared spectrum of (pipeH)[Cu(quin)<sub>2</sub>Cl] (**11**).



## References

- S1. Haendler, H.M. Copper quinaldinate monohydrate [aquabis(2-quinolinecarboxylato)copper(II)]; pentacoordinate copper. *Acta Crystallogr., Sect. C* **1986**, *42*, 147-149, doi:10.1107/S0108270186096981.
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