

## SUPPORTING INFORMATION

### Schiff base derived from 2-hydroxy-1-naphthaldehyde and liquid-assisted mechanochemical synthesis of its isostructural Cu(II) and Co(II) complexes

Dominik Cinčić\* and Branko Kaitner

*Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia,*

Email: dominik@chem.pmf.hr

Fax: +385 1 4606 341

Tel: +385 1 4606 362

#### Table of Contents

<b>Figure S1.</b>	IR spectrum for compound <b>1</b>	3
<b>Figure S2.</b>	IR spectrum for compound <b>2</b> synthesised by solution-based method	3
<b>Figure S3.</b>	IR spectrum for compound <b>2</b> synthesised via grinding	3
<b>Figure S4.</b>	IR spectrum for compound <b>3</b> synthesised by solution-based method	4
<b>Figure S5.</b>	IR spectrum for compound <b>3</b> synthesised via grinding	4
<b>Figure S6.</b>	IR spectrum for the product of grinding of Co(II) acetate and compound <b>1</b> , i.e. the acetic acid solvate of compound <b>3</b>	4
<b>Figure S7.</b>	IR spectra for compound <b>2</b> synthesised by solution-based method (black) and via grinding (red)	5
<b>Figure S8.</b>	IR spectra for compound <b>3</b> synthesised by solution-based method (black) and via grinding (red)	5
<b>Figure S9.</b>	IR spectra for the product of grinding of Co(II) acetate and compound <b>1</b> , i.e. the acetic acid solvate of compound <b>3</b> (red) and compound <b>3</b> after three days standing in acetic acid vapour (black)	5
<b>Figure S10.</b>	DSC curve for compound <b>1</b>	6
<b>Figure S11.</b>	TG curve for compound <b>1</b>	6
<b>Figure S12.</b>	DSC curve of nonisothermal crystallisation experiment for compound <b>1</b>	7
<b>Figure S13.</b>	PXRD patterns for compound <b>1</b> before (red) and after (black) experiment of nonisothermal crystallisation	7
<b>Figure S14.</b>	TG (black) and DTA (red) curves for compound <b>2</b> synthesised by solution-based method	8
<b>Figure S15.</b>	TG (black) and DTA (red) curves for compound <b>2</b> synthesised via grinding	8
<b>Figure S16.</b>	TG (black) and DTA (red) curves for compound <b>3</b> synthesised by solution-based method	9
<b>Figure S17.</b>	TG (black) and DTA (red) curves for compound <b>3</b> synthesised via grinding	9
<b>Figure S18.</b>	TG (black) and DTA (red) curves for the product of grinding of Co(II) acetate and compound <b>1</b> , i.e. the acetic acid solvate of compound <b>3</b>	10
<b>Figure S19.</b>	TG curve of isothermal experiment at 160 °C for the product of grinding of Co(II) acetate and compound <b>1</b> , i.e. the acetic acid solvate of compound <b>3</b> .	10
<b>Figure S20.</b>	PXRD patterns of: a) pure 2-hydroxy-1-naphthaldehyde, b) compound <b>1</b> and c) simulated pattern for compound <b>1</b>	11
<b>Figure S21.</b>	PXRD patterns for mechanochemical and solution-based experiments involving copper(II) acetate monohydrate and the compound <b>1</b> : a)	

compound **1**, b) copper acetate monohydrate, c) compound **2** obtained by grinding of Cu(II) acetate monohydrate and compound **1** in the presence of 30  $\mu\text{L}$  triethylamine, d) compound **2** obtained by solution-based method, e) compound **2** after three days standing in acetic acid vapour and f) simulated pattern for compound **2**

11

**Figure S22.** PXRD patterns for mechanochemical and solution-based experiments involving cobalt(II) acetate tetrahydrate and compound **1**: a) compound **1**, b) cobalt(II) acetate tetrahydrate, c) LAG product obtained by grinding of Co(II) acetate tetrahydrate and compound **1** in the presence of 40  $\mu\text{L}$  triethylamine (the acetic acid solvate of compound **3** is a major product and compound **3** is in traces), d) LAG product obtained by grinding of Co(II) acetate tetrahydrate and compound **1** in the presence of 50  $\mu\text{L}$  triethylamine (the acetic acid solvate of compound **3** is a major product and compound **3** is in traces), e) compound **3** obtained by annealing of LAG product, f) compound **3** obtained by solution-based method, g) simulated pattern for compound **3** and h) compound **3** after three days standing in acetic acid vapour

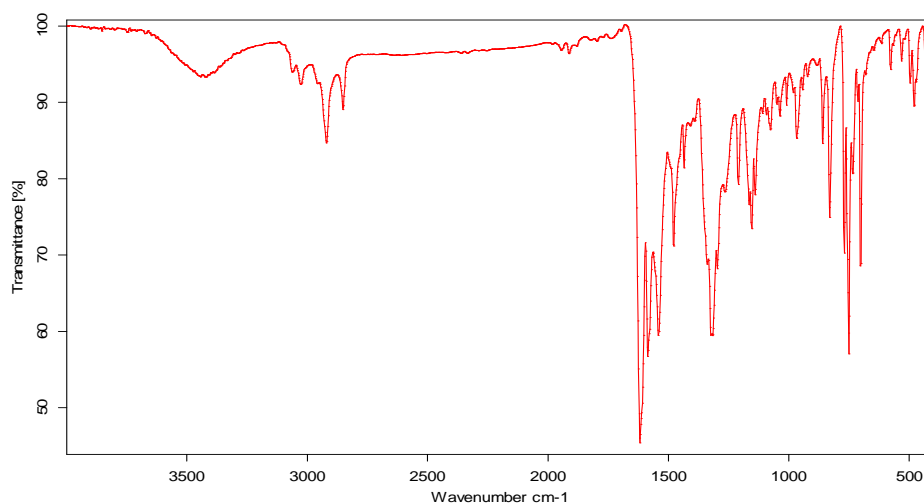
12

**Figure S23.** PXRD patterns for mechanochemical and solution-based experiments involving copper(II) acetate monohydrate and the compound **1**: a) compound **1**, b) copper acetate monohydrate, c) product obtained by neat grinding, d) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  acetonitrile (compound **2**), e) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  methanol (compound **2**), f) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  triethylamine (compound **2**) and g) compound **2** obtained by solution-based method.

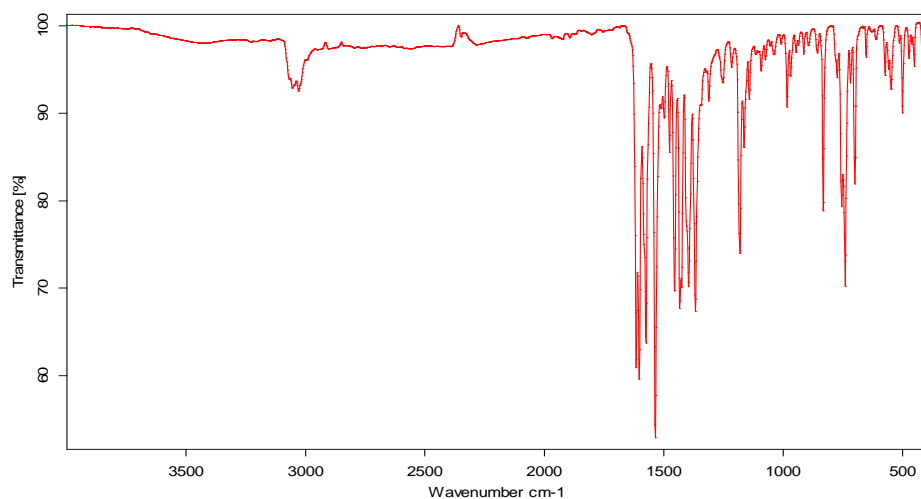
13

**Figure S24.** PXRD patterns for mechanochemical experiments involving cobalt(II) acetate tetrahydrate and **1**: a) compound **1**, b) cobalt(II) acetate tetrahydrate, c) product obtained by neat grinding, d) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  acetonitrile (acetic acid solvate of compound **3** is a major product and cobalt(II) acetate tetrahydrate is in traces), e) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  methanol (acetic acid solvate of compound **3**), f) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  triethylamine (acetic acid solvate of compound **3** is a major product and compound **3** is in traces), g) compound **3** obtained by solution-based method and h) compound **3** after three days standing in acetic acid vapour.

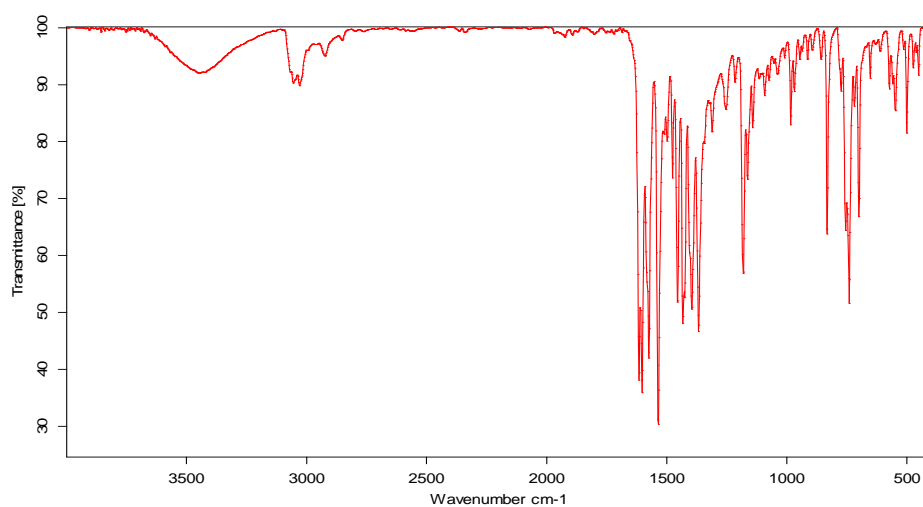
14



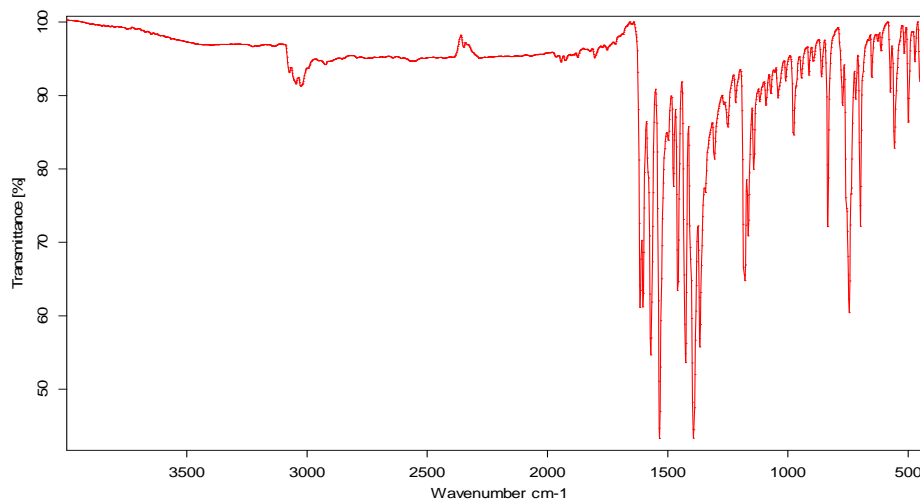
**Figure S1.** IR spectrum for compound **1**.



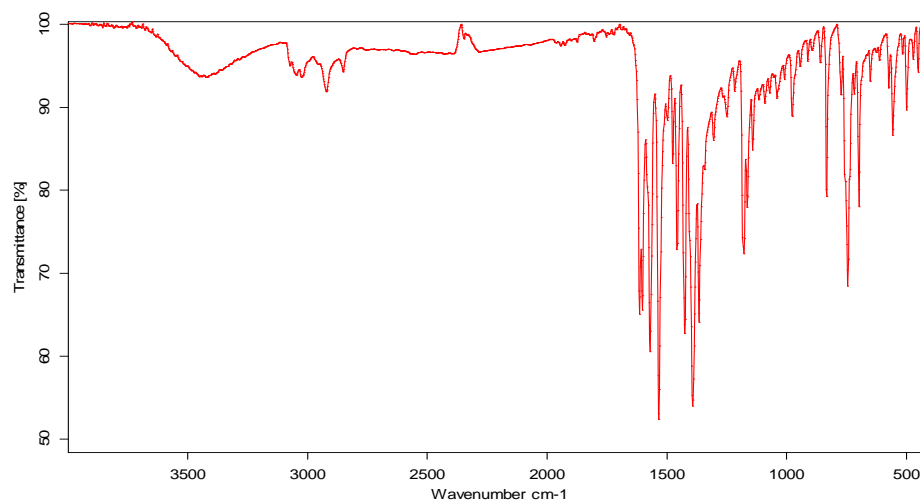
**Figure S2.** IR spectrum for compound **2** synthesised by solution-based method.



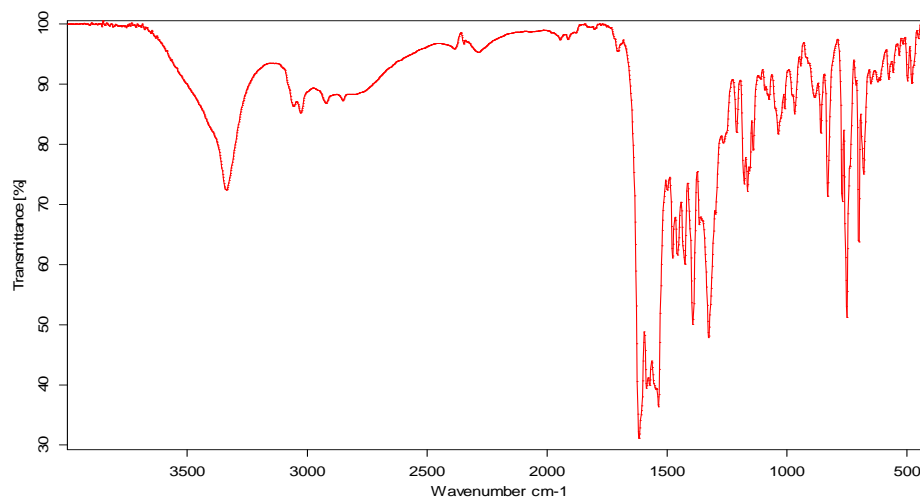
**Figure S3.** IR spectrum for compound **2** synthesised via grinding.



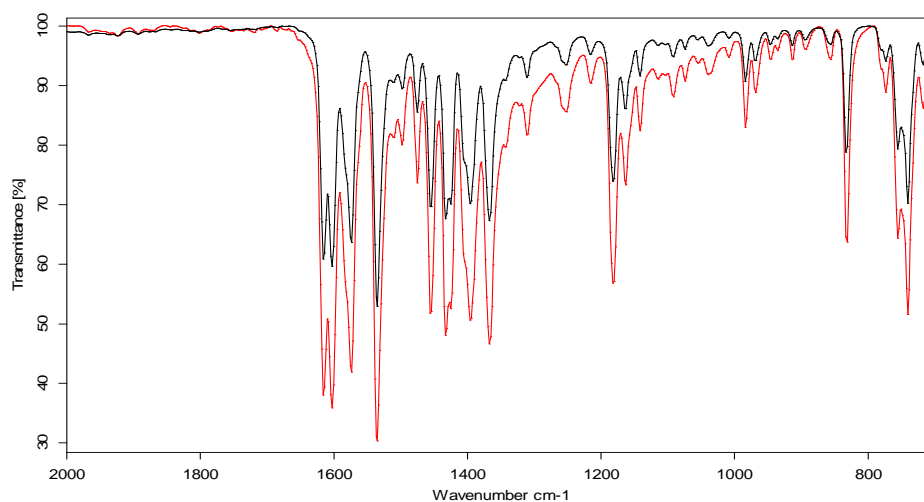
**Figure S4.** IR spectrum for compound **3** synthesised by solution-based method.



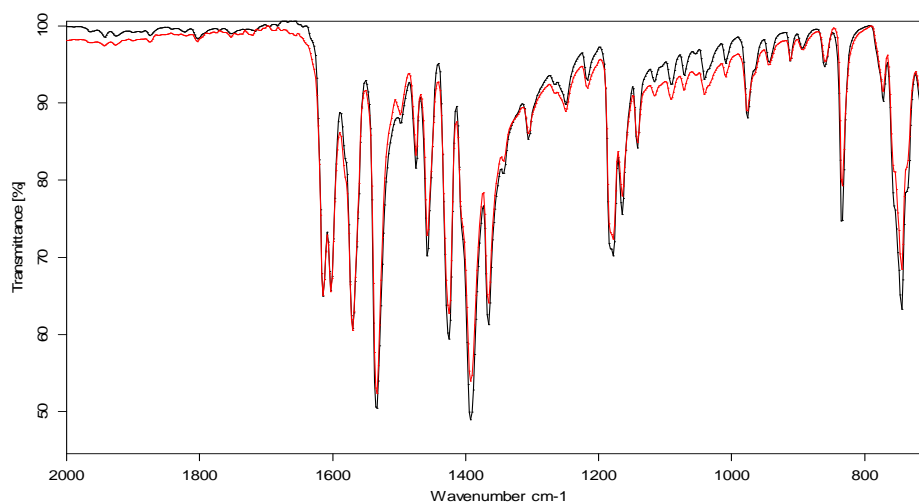
**Figure S5.** IR spectrum for compound **3** synthesised via grinding.



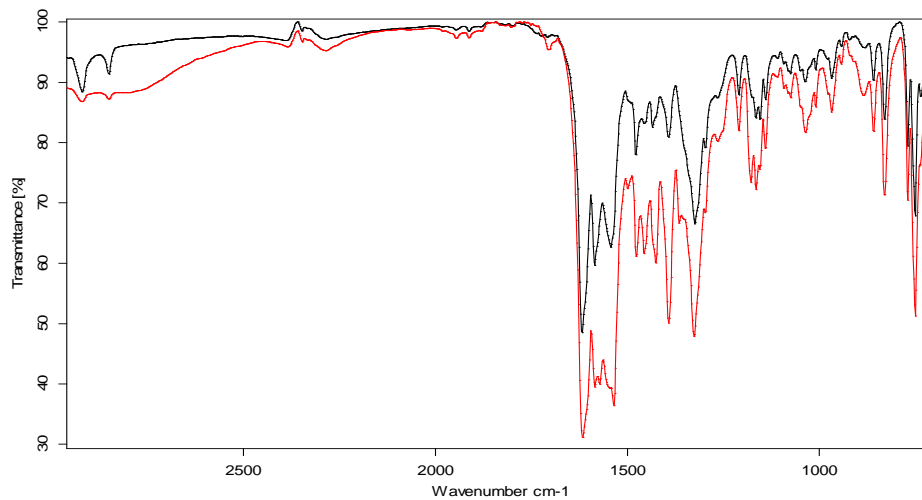
**Figure S6.** IR spectrum for the product of grinding of Co(II) acetate and compound **1**, i.e. the acetic acid solvate of compound **3**.



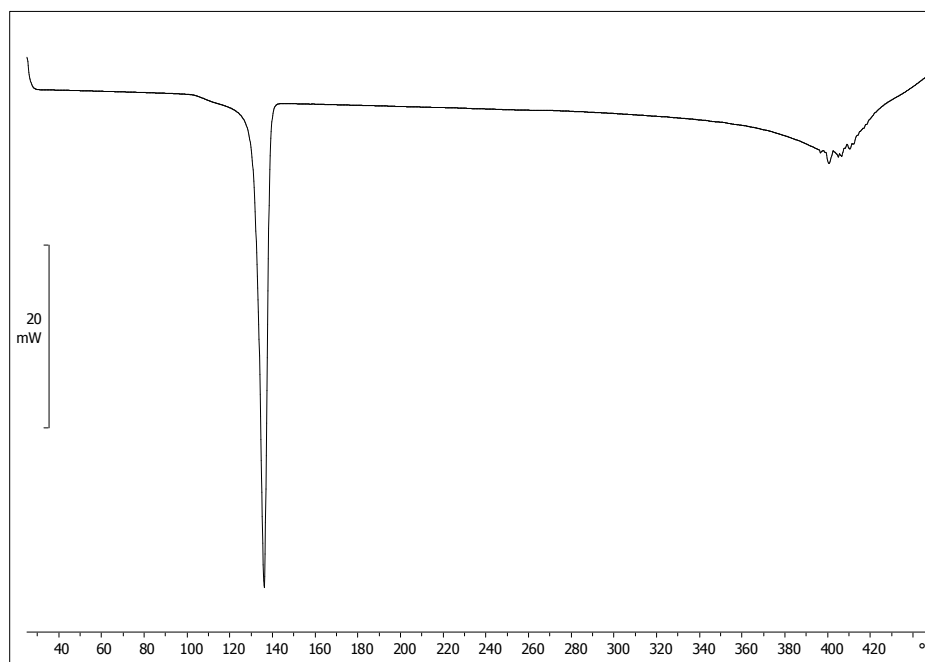
**Figure S7.** IR spectra for compound **2** synthesised by solution-based method (black) and via grinding (red).



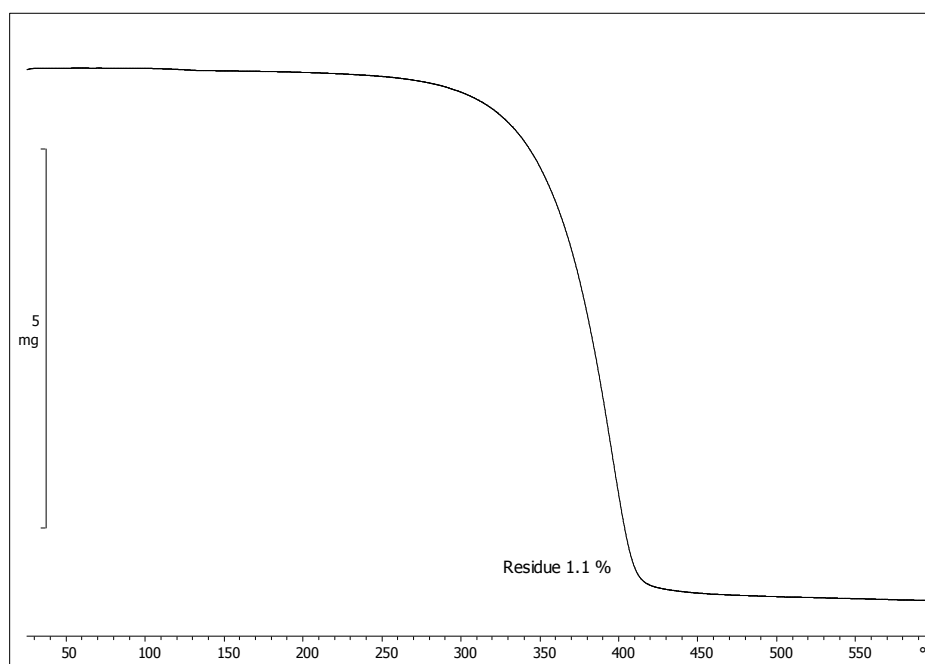
**Figure S8.** IR spectra for compound **3** synthesised by solution-based method (black) and via grinding (red).



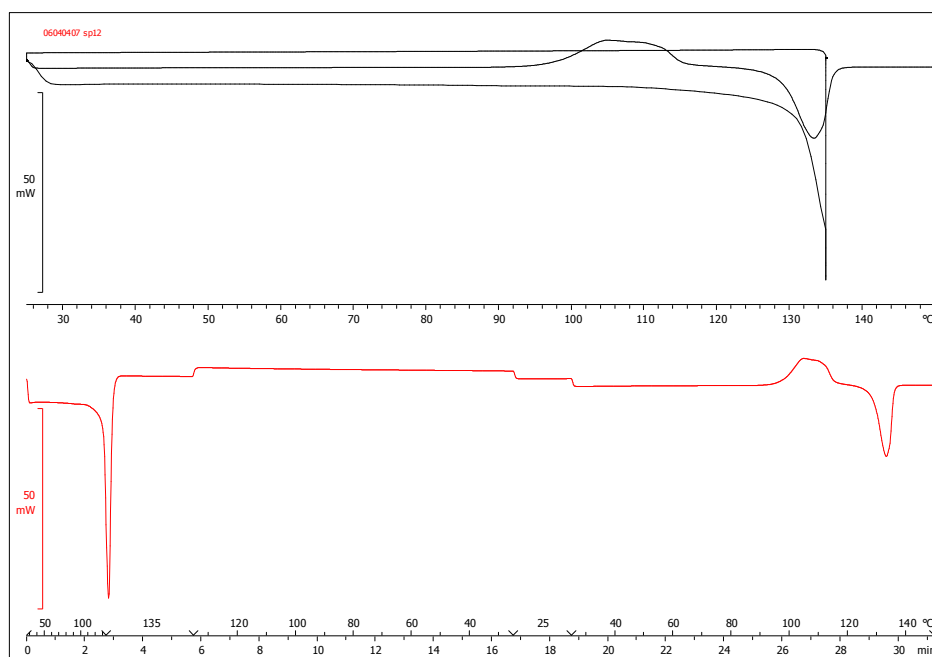
**Figure S9.** IR spectra for the product of grinding of Co(II) acetate and compound **1**, i.e. the acetic acid solvate of compound **3** (red) and compound **3** after three days standing in acetic acid vapour (black).



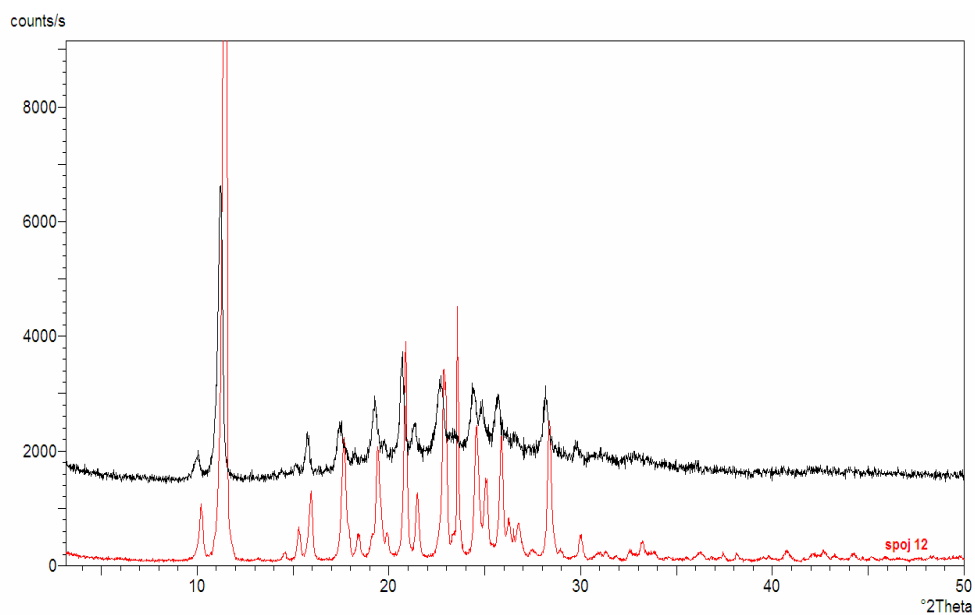
**Figure S10.** DSC curve for compound **1**.



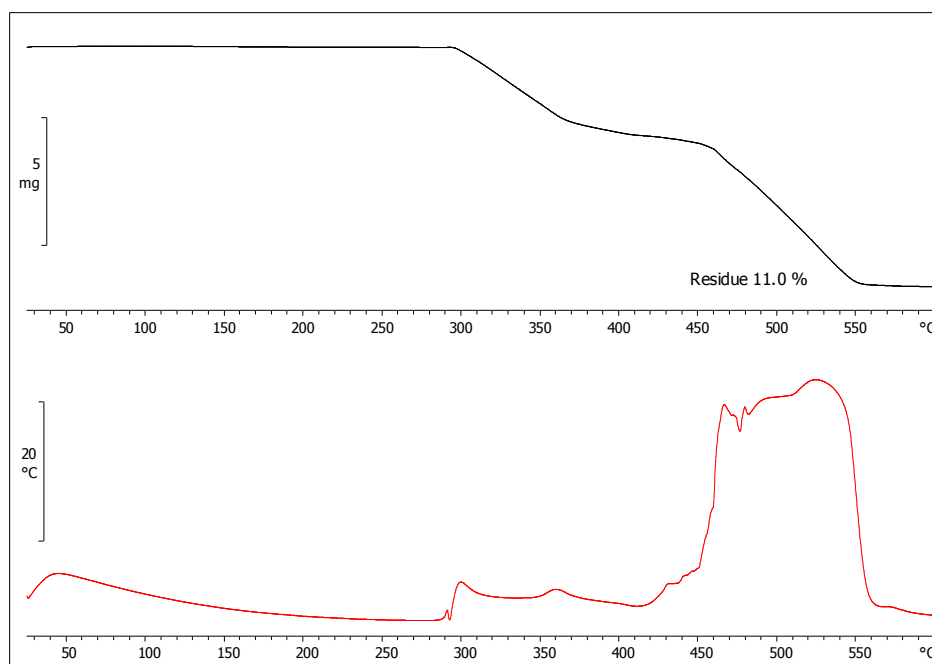
**Figure S11.** TG curve for compound **1**.



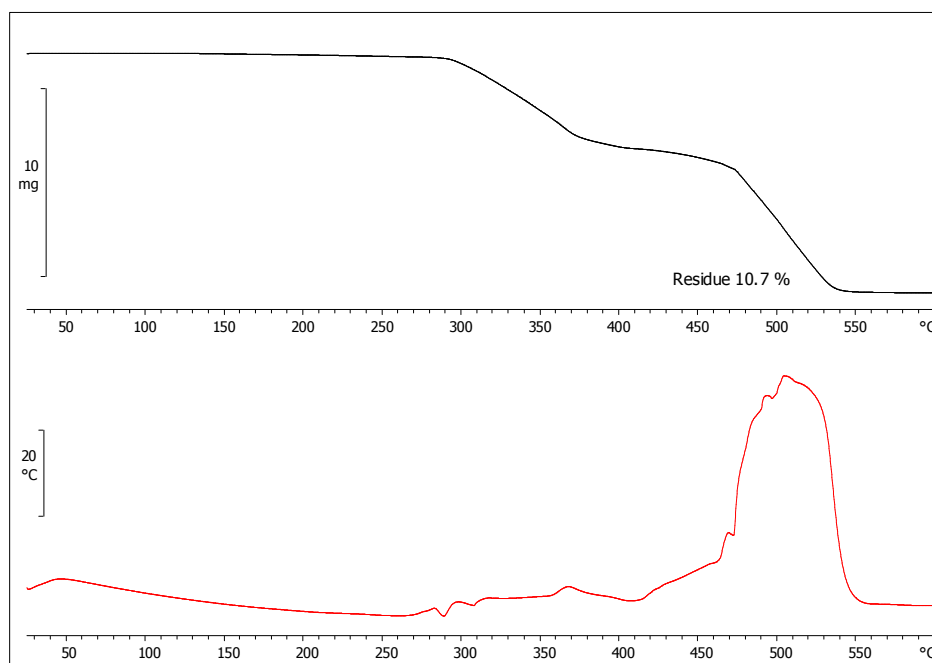
**Figure S12.** DSC curve of nonisothermal crystallisation experiment for compound **1**.



**Figure S13.** PXRD patterns for compound **1** before (red) and after (black) experiment of nonisothermal crystallisation.

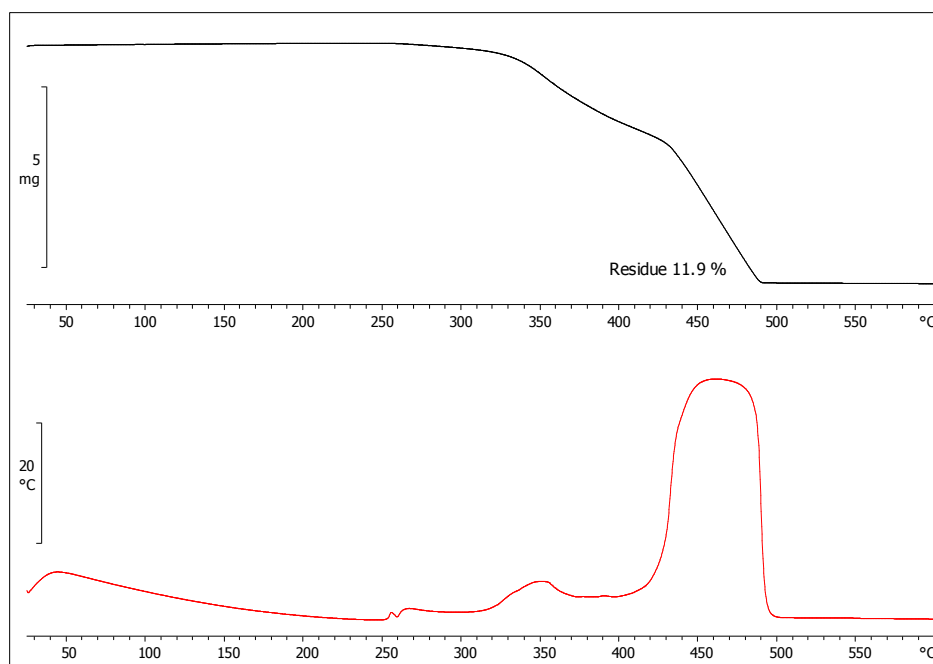


**Figure S14.** TG (black) and DTA (red) curves for compound **2** synthesised by solution-based method.

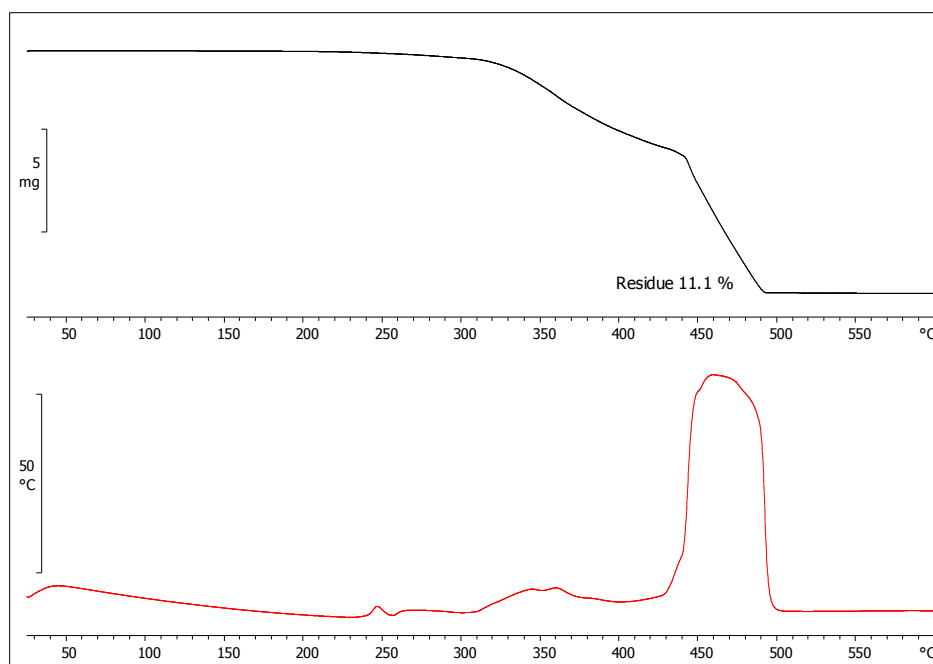


**Figure S15.** TG (black) and DTA (red) curves for compound **2** synthesised via grinding.

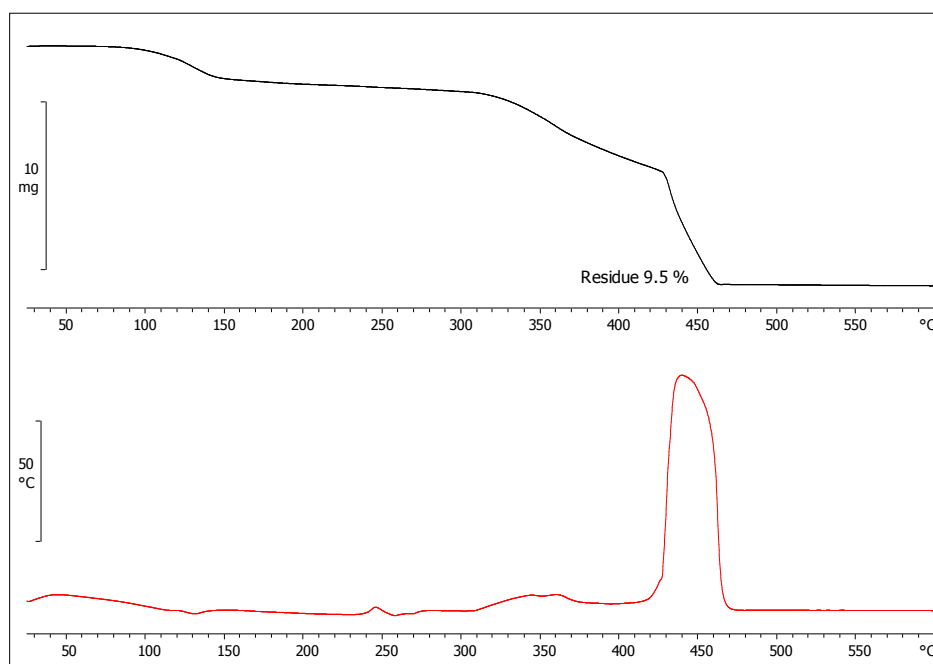




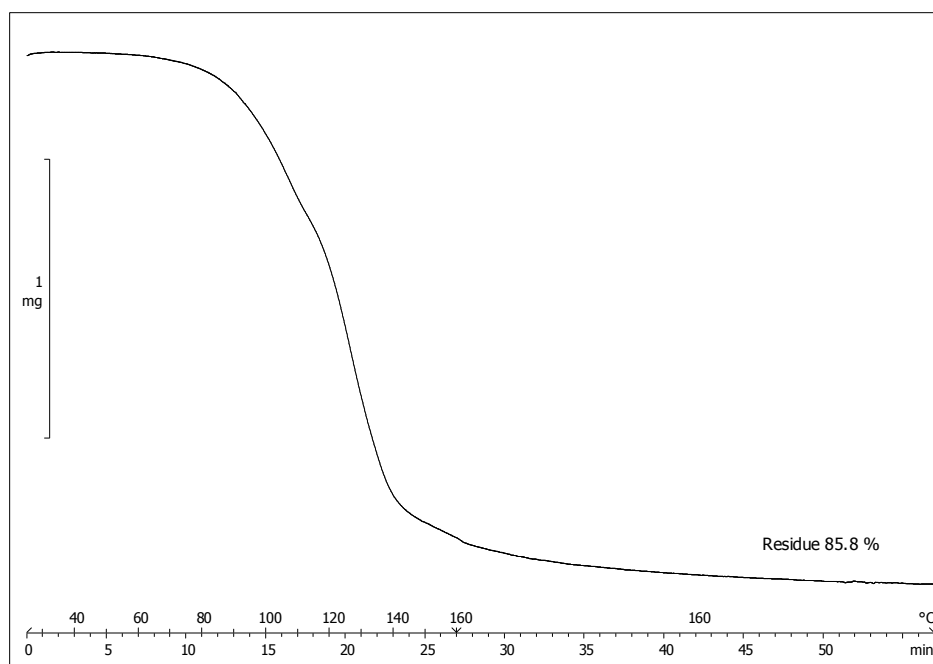
**Figure S16.** TG (black) and DTA (red) curves for compound **3** synthesised by solution-based method.



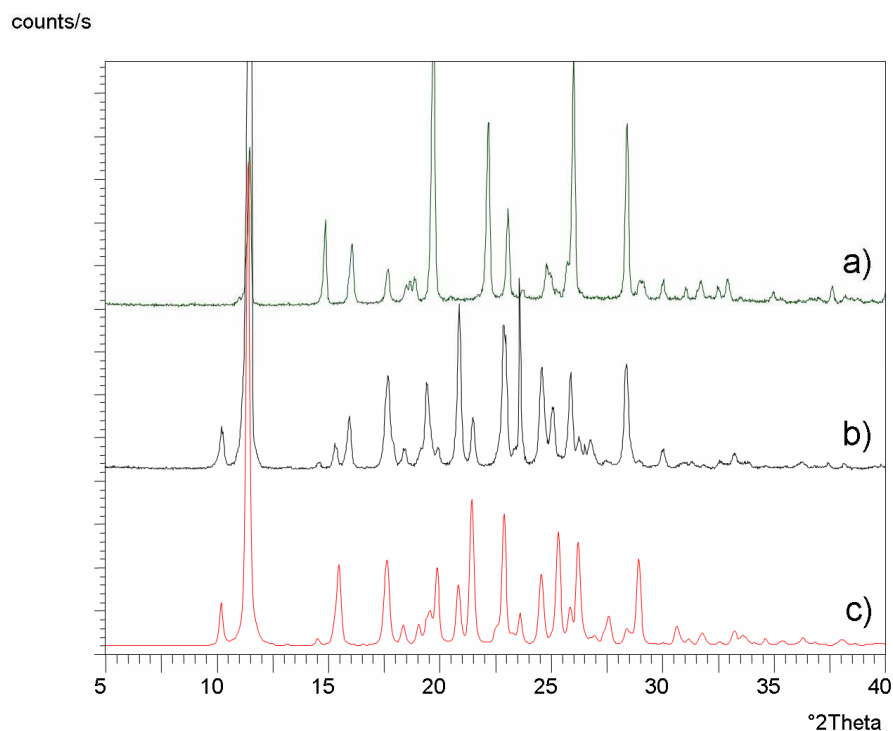
**Figure S17.** TG (black) and DTA (red) curves for compound **3** synthesised via grinding.



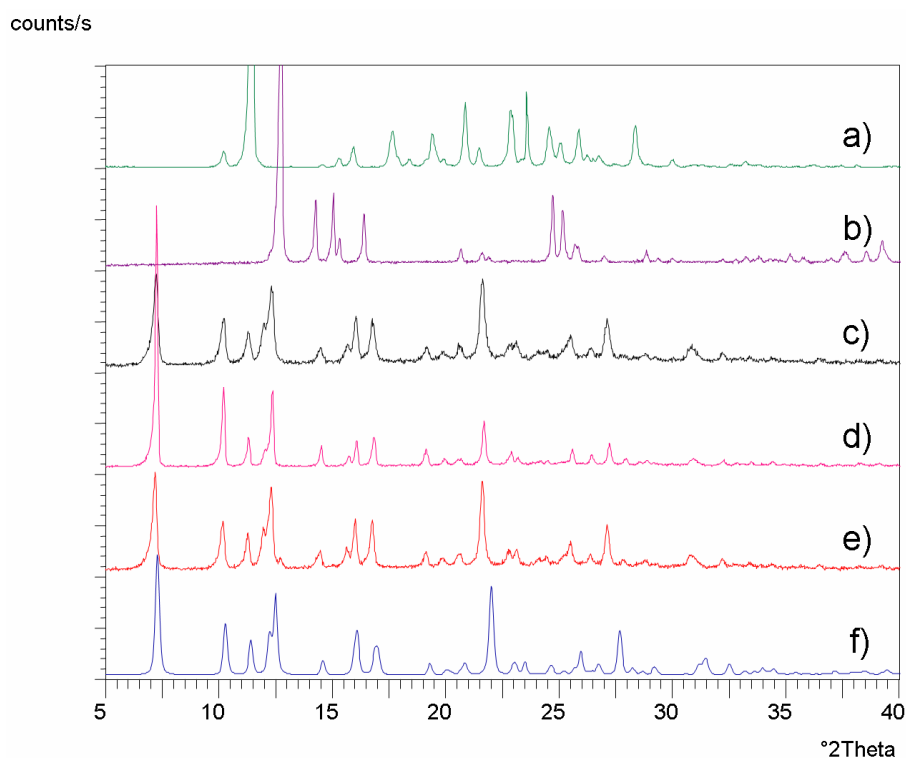
**Figure S18.** TG (black) and DTA (red) curves for the product of grinding of Co(II) acetate and compound **1**, i.e. the acetic acid solvate of compound **3**.



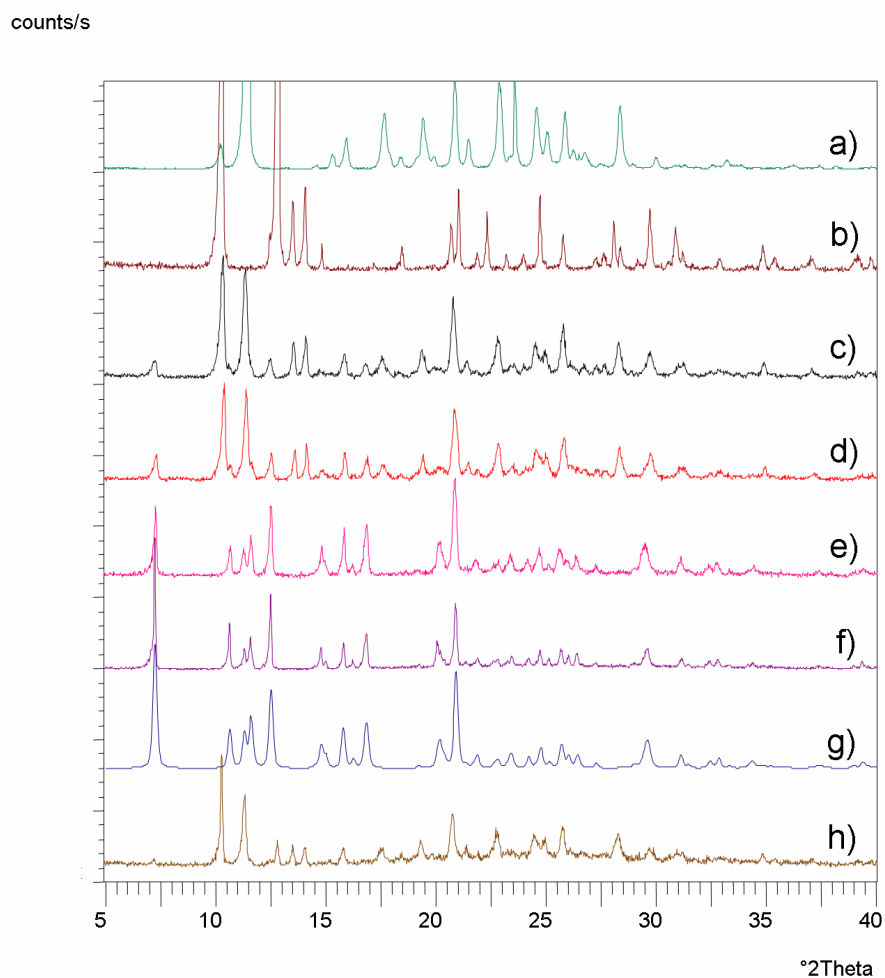
**Figure S19.** TG curve of isothermal experiment at 160 °C for the product of grinding of Co(II) acetate and compound **1**, i.e. the acetic acid solvate of compound **3**.



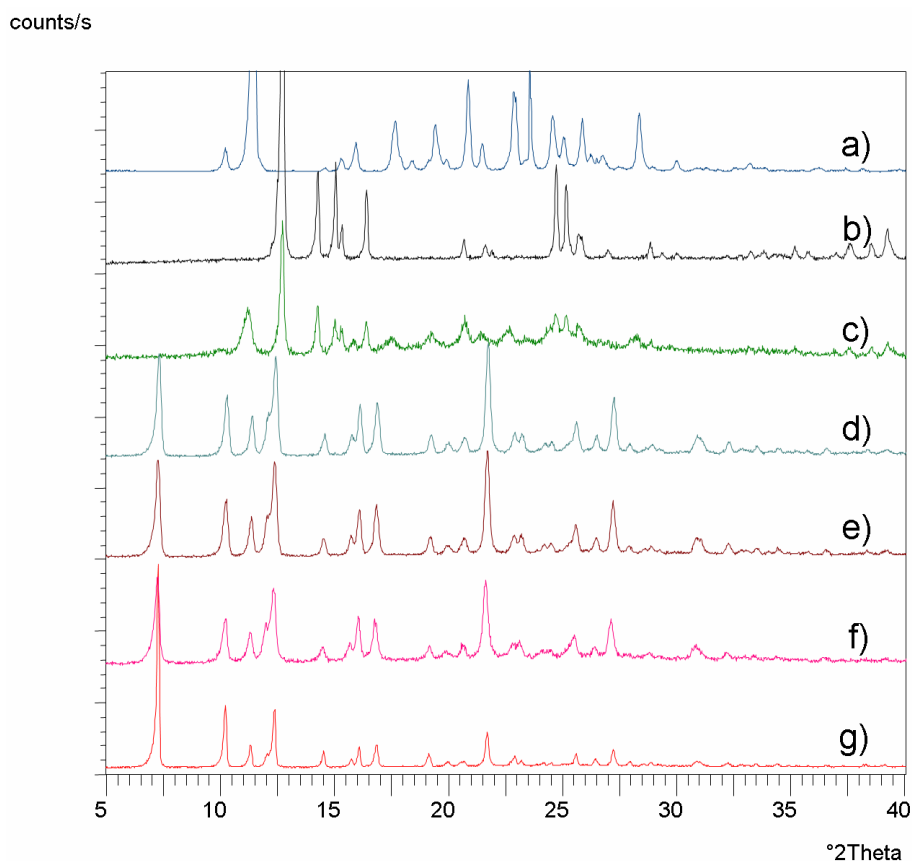
**Figure S20.** PXRD patterns of: a) pure 2-hydroxy-1-naphthaldehyde, b) compound **1** and c) simulated pattern for compound **1**.



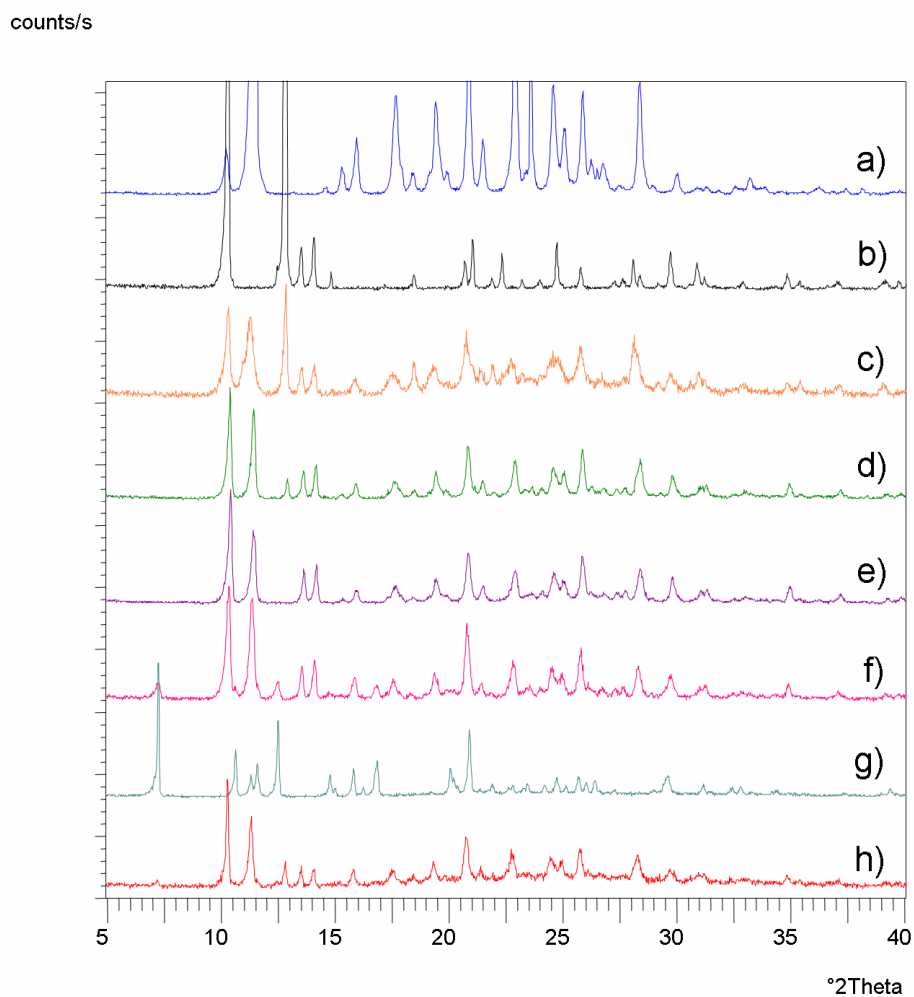
**Figure S21.** PXRD patterns for mechanochemical and solution-based experiments involving copper(II) acetate monohydrate and the compound **1**: a) compound **1**, b) copper(II) acetate monohydrate, c) compound **2** obtained by grinding of Cu(II) acetate monohydrate and compound **1** in the presence of 30  $\mu\text{L}$  triethylamine, d) compound **2** obtained by solution-based method, e) compound **2** after three days standing in acetic acid vapour and f) simulated pattern for compound **2**.



**Figure S22.** PXRD patterns for mechanochemical and solution-based experiments involving cobalt(II) acetate tetrahydrate and compound **1**: a) compound **1**, b) cobalt(II) acetate tetrahydrate, c) LAG product obtained by grinding of Co(II) acetate tetrahydrate and compound **1** in the presence of 40  $\mu\text{L}$  triethylamine (the acetic acid solvate of compound **3** is a major product and compound **3** is in traces), d) LAG product obtained by grinding of Co(II) acetate tetrahydrate and compound **1** in the presence of 50  $\mu\text{L}$  triethylamine (the acetic acid solvate of compound **3** is a major product and compound **3** is in traces), e) compound **3** obtained by annealing of LAG product, f) compound **3** obtained by solution-based method, g) simulated pattern for compound **3** and h) compound **3** after three days standing in acetic acid vapour.



**Figure S23.** PXRD patterns for mechanochemical and solution-based experiments involving copper(II) acetate monohydrate and the compound **1**: a) compound **1**, b) copper acetate monohydrate, c) product obtained by neat grinding, d) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  acetonitrile (compound **2**), e) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  methanol (compound **2**), f) LAG product obtained by grinding in the presence of 30  $\mu\text{L}$  triethylamine (compound **2**) and g) compound **2** obtained by solution-based method.



**Figure S24.** PXRD patterns for mechanochemical experiments involving cobalt(II) acetate tetrahydrate and **1**: a) compound **1**, b) cobalt(II) acetate tetrahydrate, c) product obtained by neat grinding, d) LAG product obtained by grinding in the presence of 30  $\mu$ L acetonitrile (acetic acid solvate of compound **3** is a major product and cobalt(II) acetate tetrahydrate is in traces), e) LAG product obtained by grinding in the presence of 30  $\mu$ L methanol (acetic acid solvate of compound **3**), f) LAG product obtained by grinding in the presence of 30  $\mu$ L triethylamine (acetic acid solvate of compound **3** is a major product and compound **3** is in traces), g) compound **3** obtained by solution-based method and h) compound **3** after three days standing in acetic acid vapour.