Telescoped and tandem mechanochemical reactions: Ligand and complex synthesis in one pot with no or minimal added solvent

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Supplementary Information

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Ligand Analysis

2,2'-[1,2-ethanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol; (compound 1):

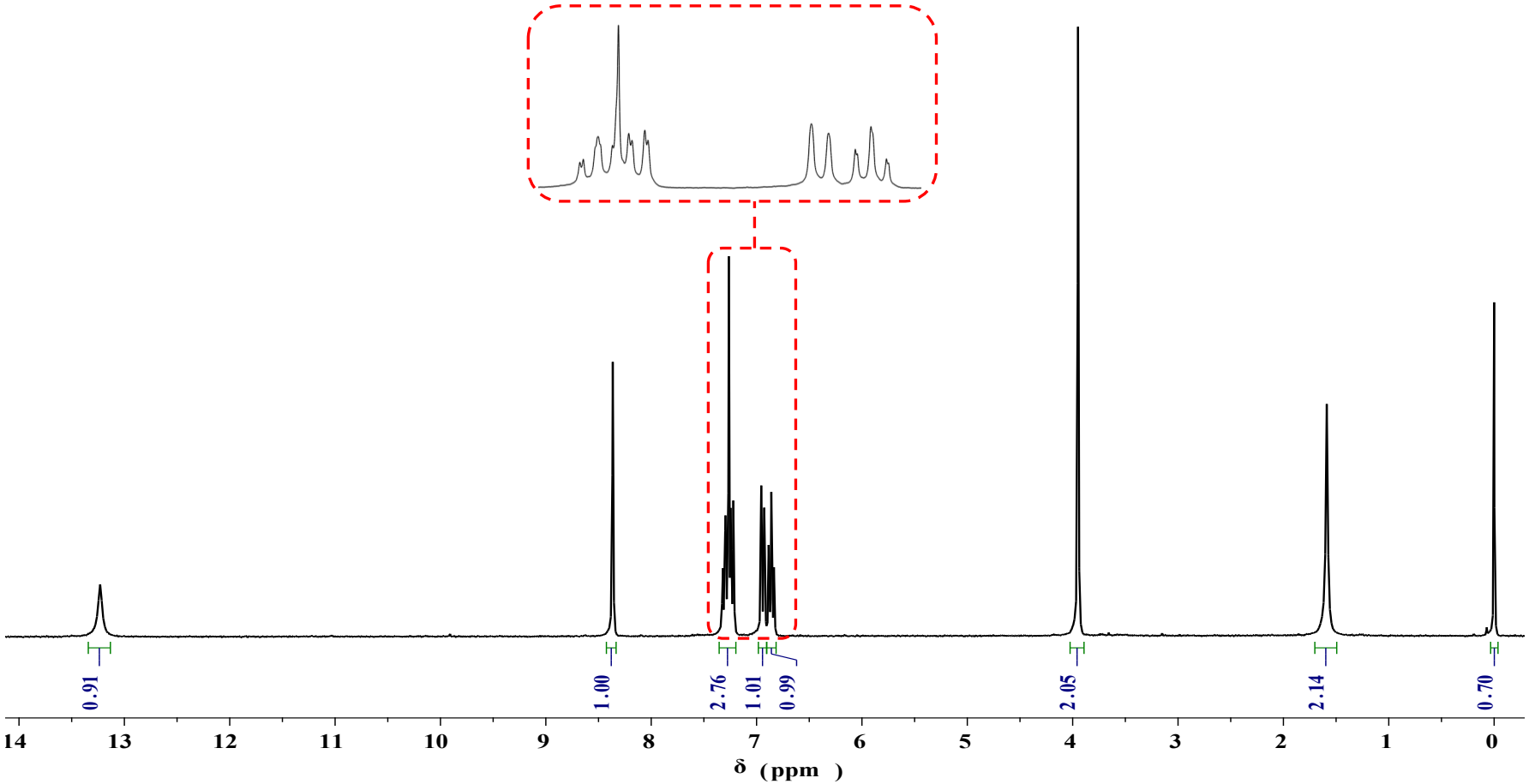

Figure S1: Solution state ($CDCl_3$) ^1H NMR spectrum of salenH_2, **1**, obtained mechanochemically.

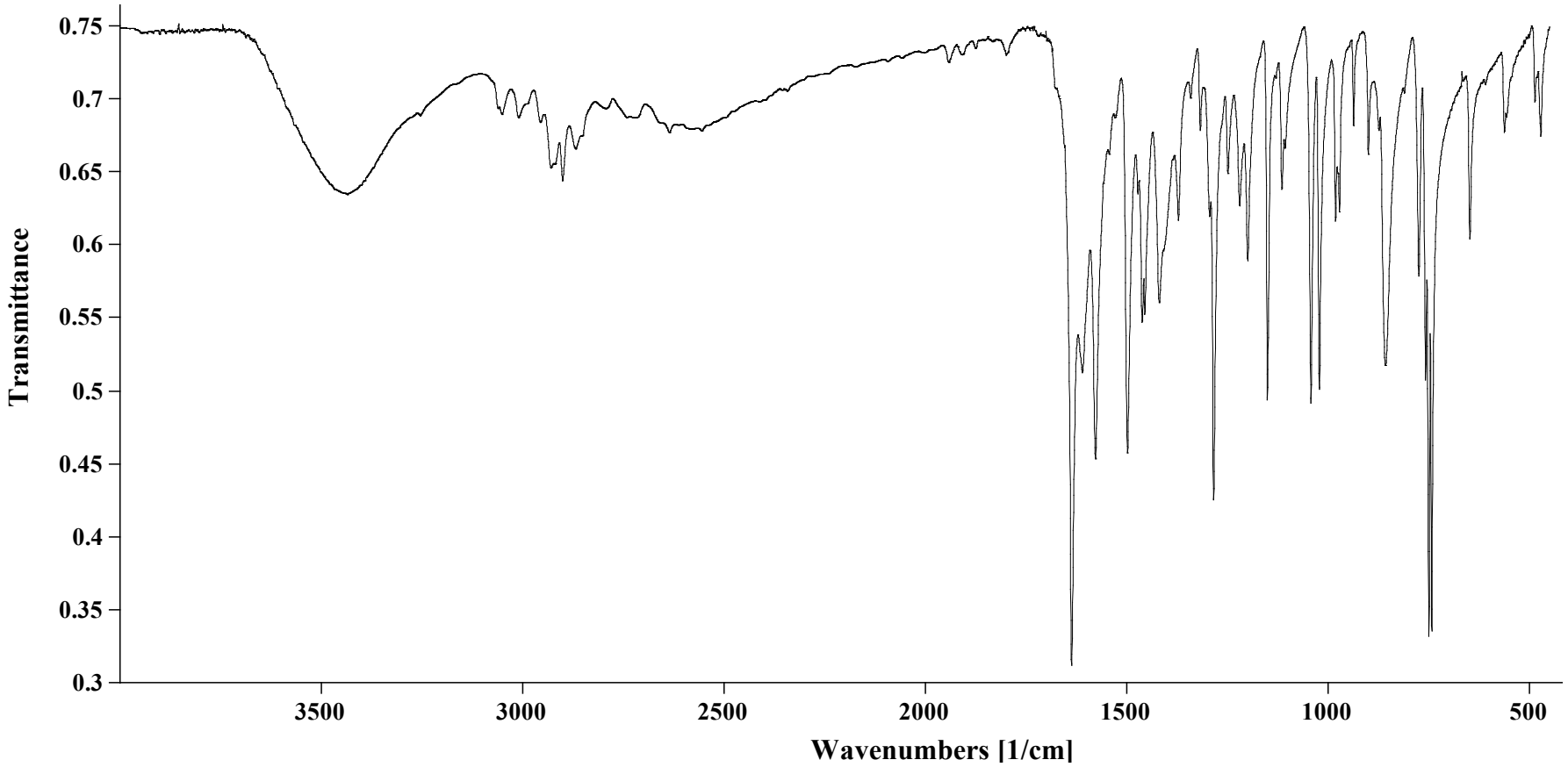

Figure S2: Solid state IR (KBr disc) spectrum of salenH_2, **1**, obtained mechanochemically.

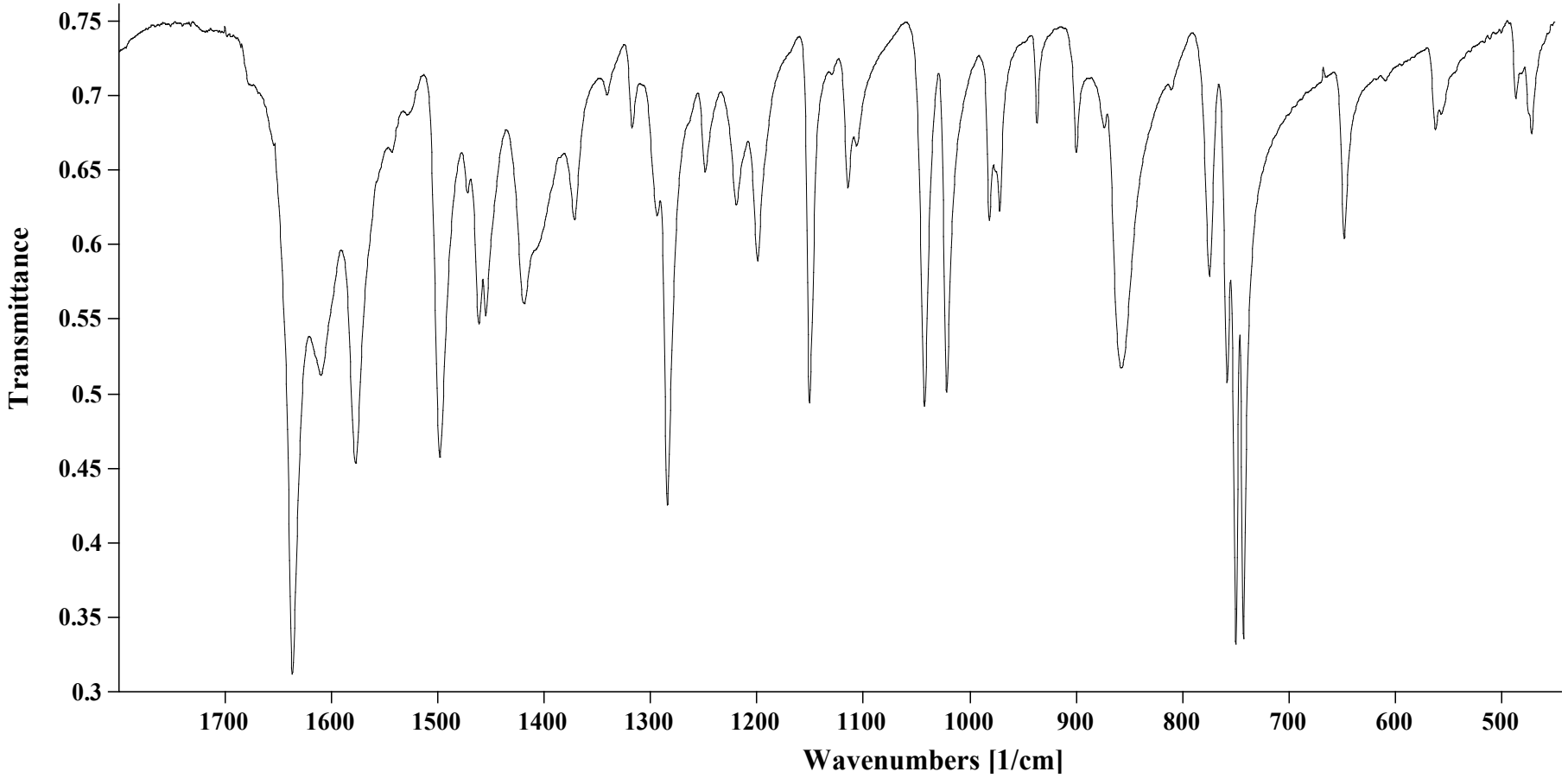

Figure S3: Expanded fingerprint region of the solid state IR spectrum of salenH_2, **1**, obtained mechanochemically.

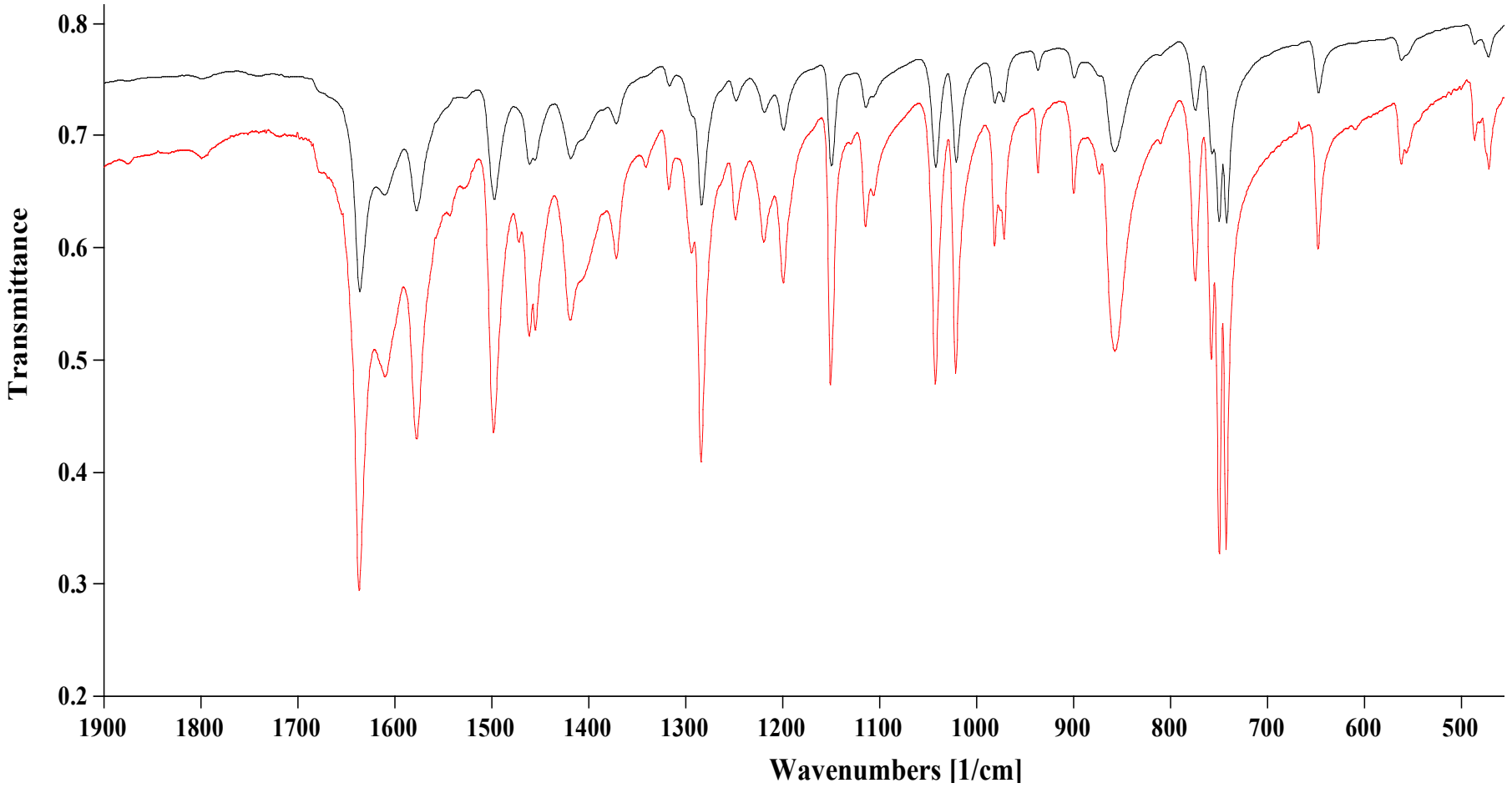

Figure S4: Comparison of the fingerprint regions of the solid state IR spectra of salenH_2 obtained through conventional solution based techniques (black) and mechanochemical synthesis, **1** (red).

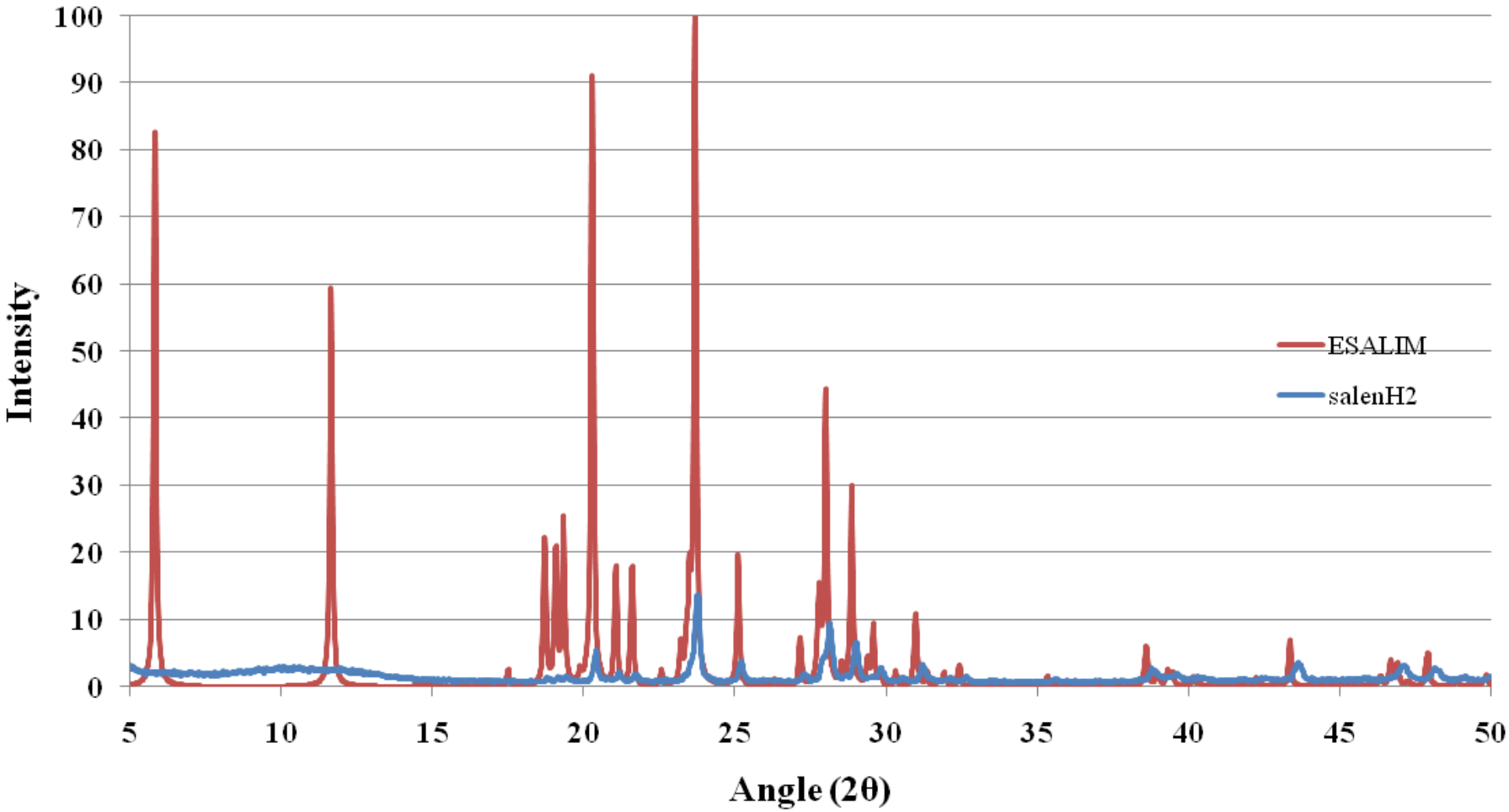

Figure S5: X-Ray powder diffraction spectra of salenH_2 obtained mechanochemically, **1**, and a simulated pattern from the Cambridge Structural Database (CCD code ESALIM).

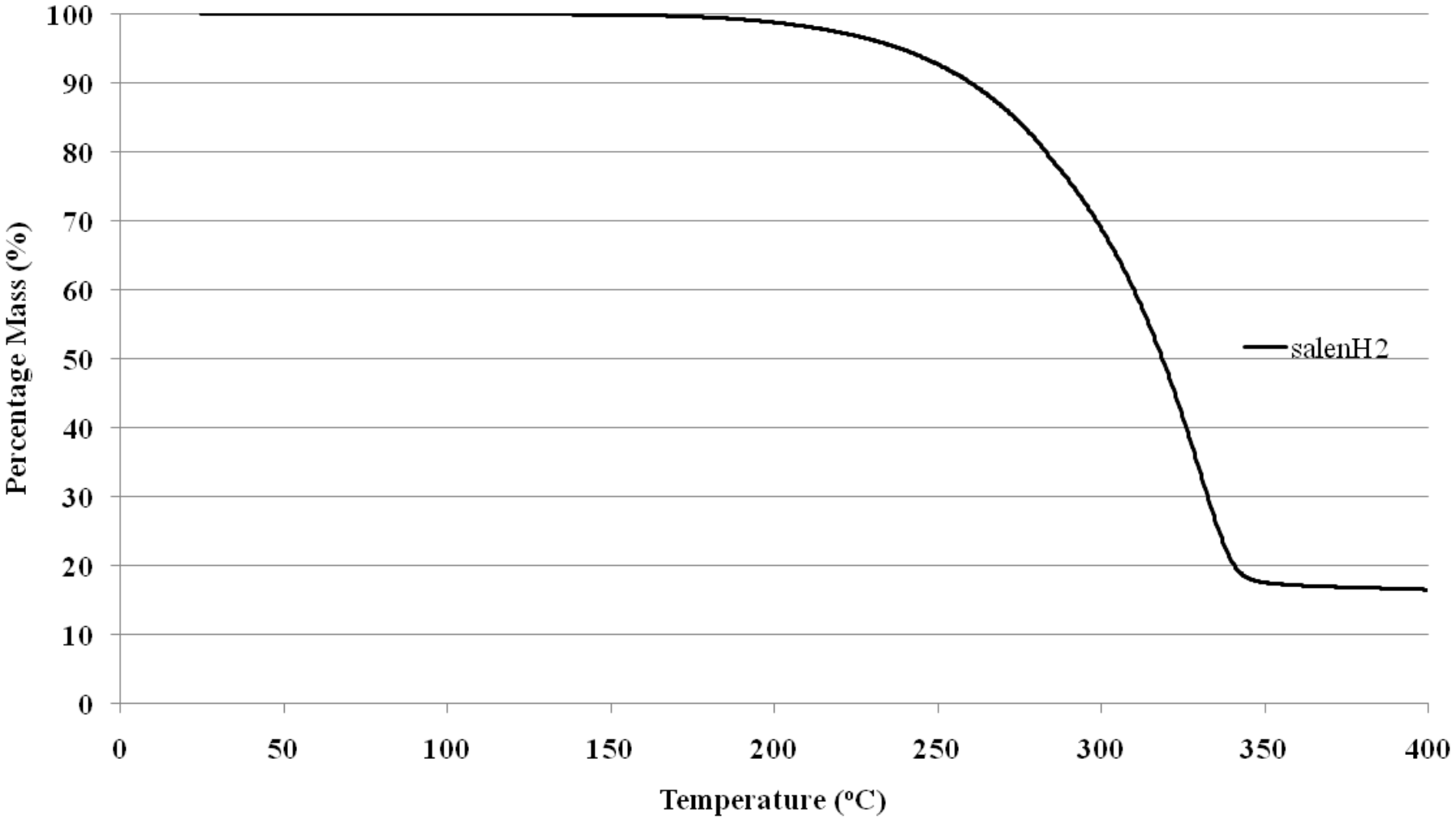

Figure S6: Thermogravimetric analysis of salenH_2 obtained mechanochemically, **1**, showing thermal decomposition onset at 160°C.

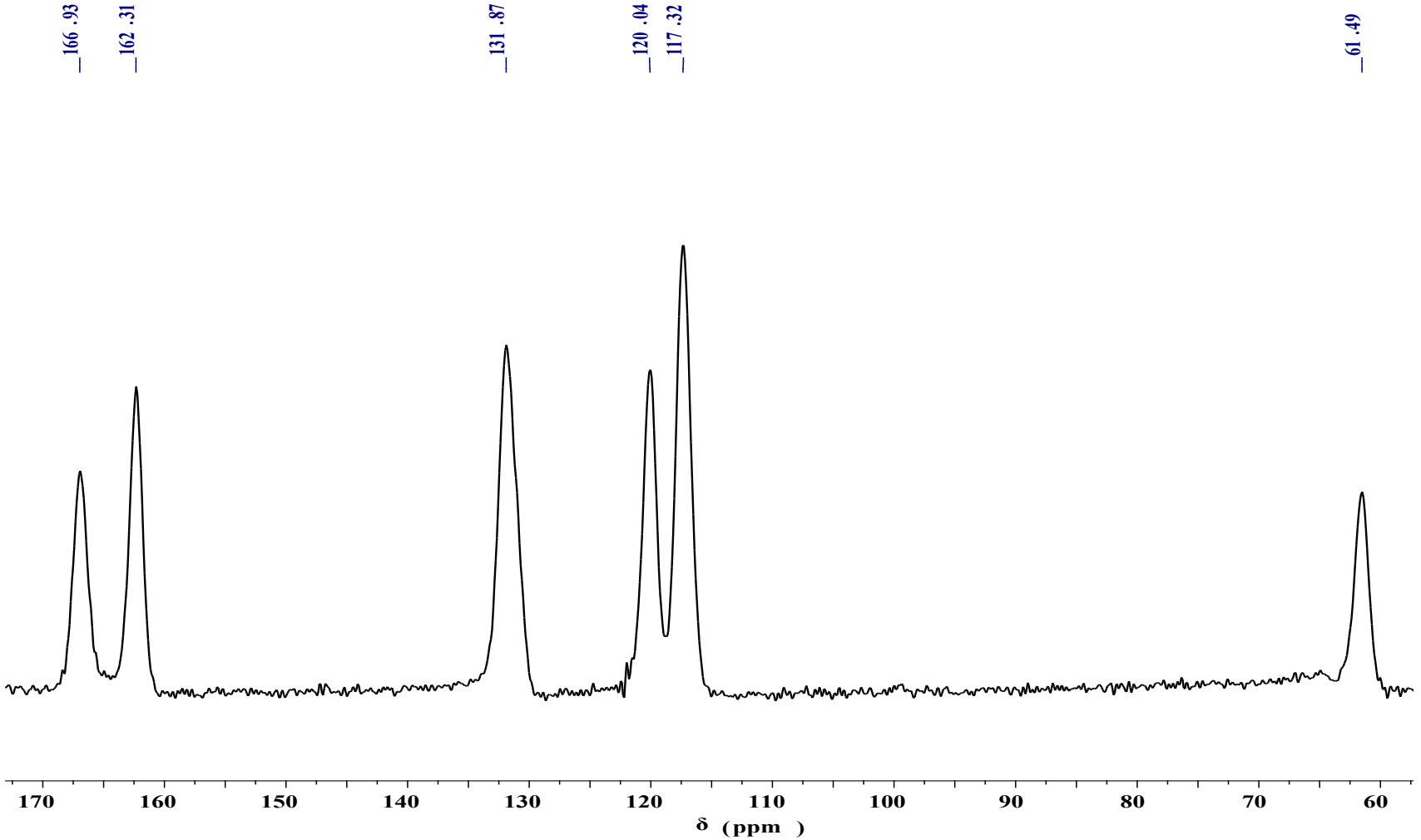

Figure S7: Solid state ^{13}C MAS NMR spectrum of salenH_2 formed mechanochemically, **1**.

Table ST1: Elemental analysis of salenH_2 from both conventional solution state synthesis and solventless mechanical (compound **1**) methods.

Element	**C**	**H**	**N**
Theoretical %	**71.62**	**6.01**	**10.44**
Solution %	**71.82**	**6.03**	**10.24**
Mechanochemical %	**71.63**	**6.03**	**10.57**

2,2'-[(±)-1,2-cyclohexanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol; (compound 2):

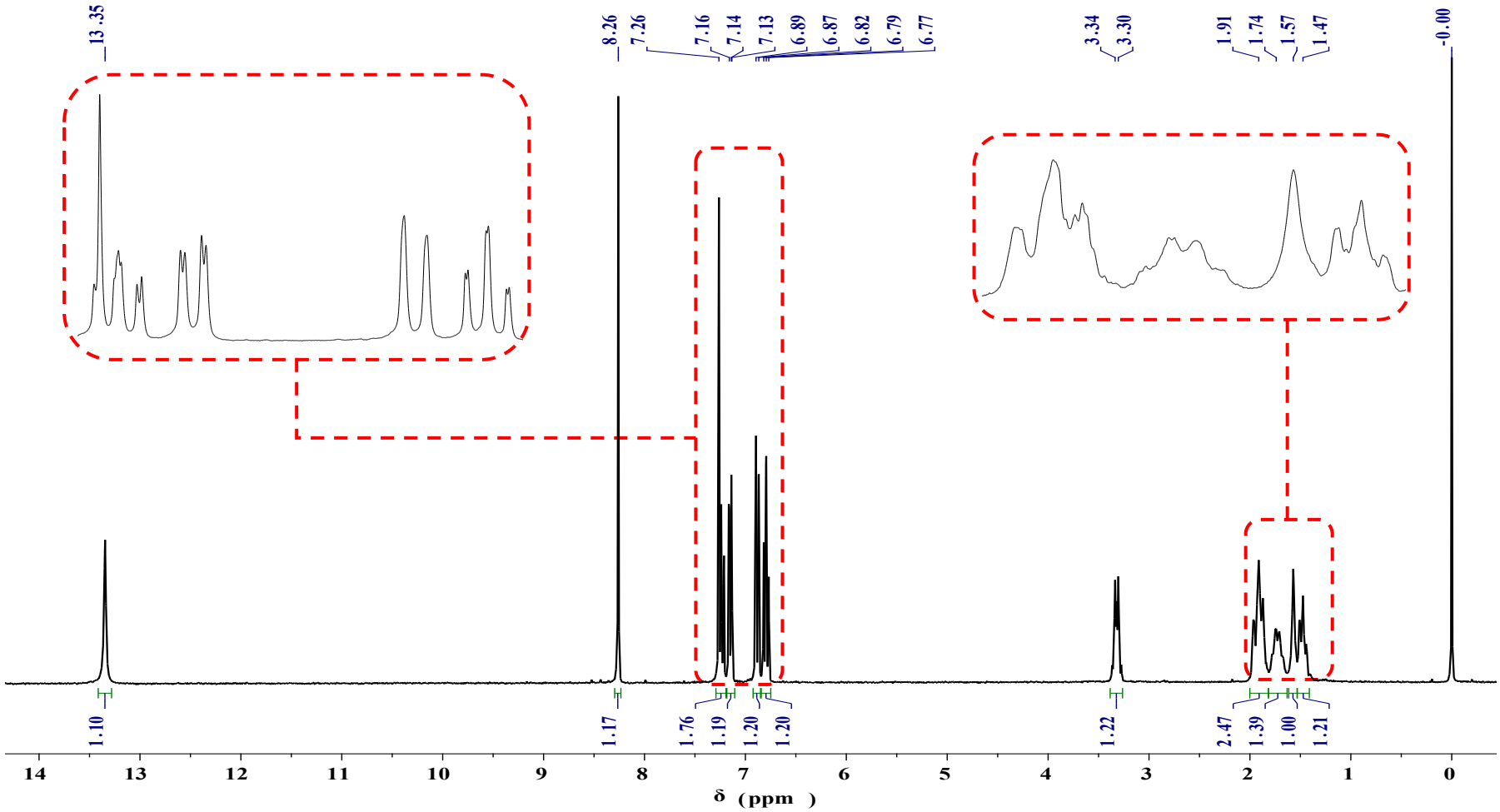

Figure S8: Solution state ($CDCl_3$) ^1H NMR spectrum of the cyclohexylsalen ligand, **2**, obtained mechanochemically.

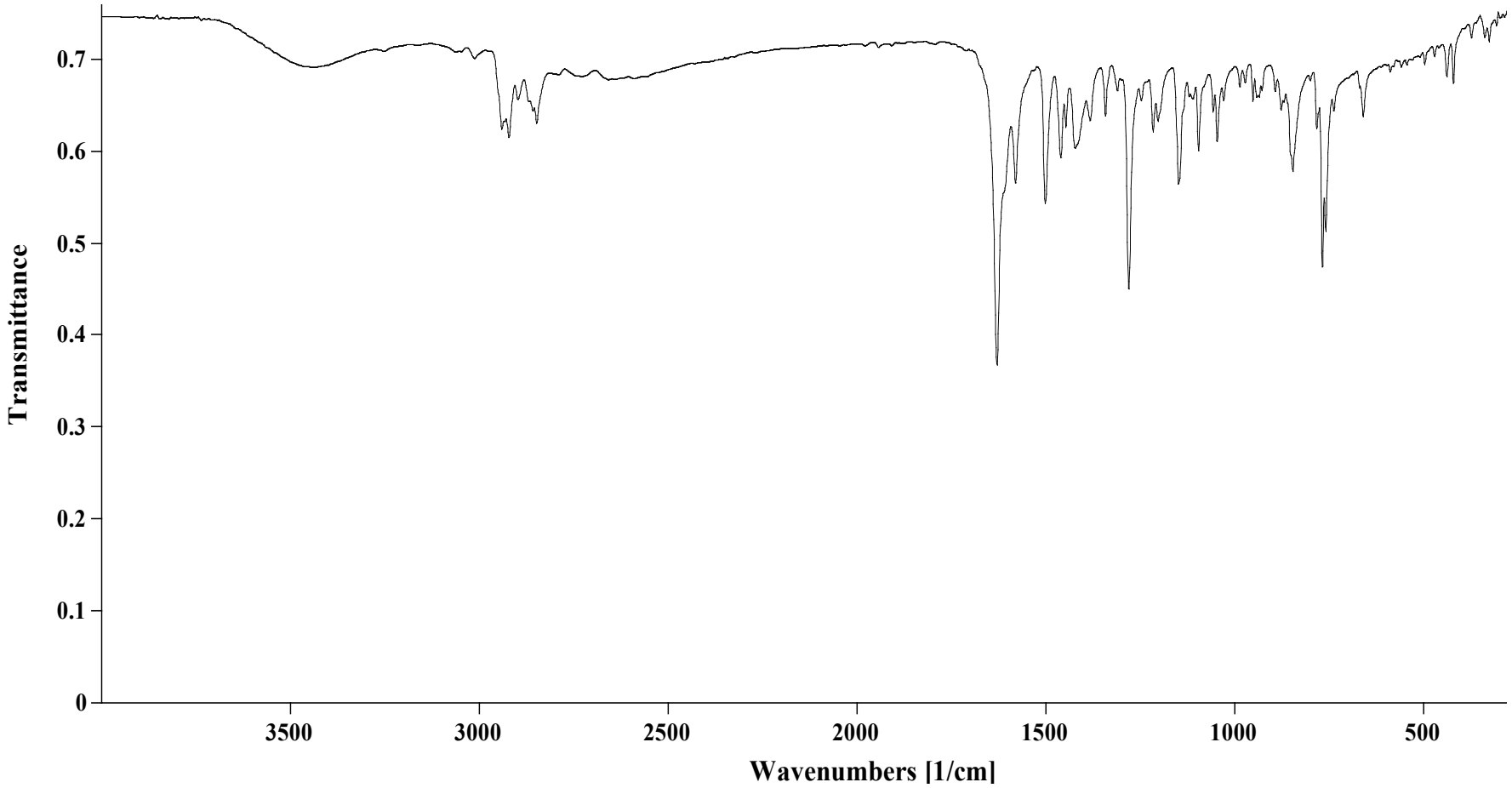

Figure S9: Solid state IR (KBr disc) spectrum of the cyclohexylsalen ligand, **2**, obtained mechanochemically.

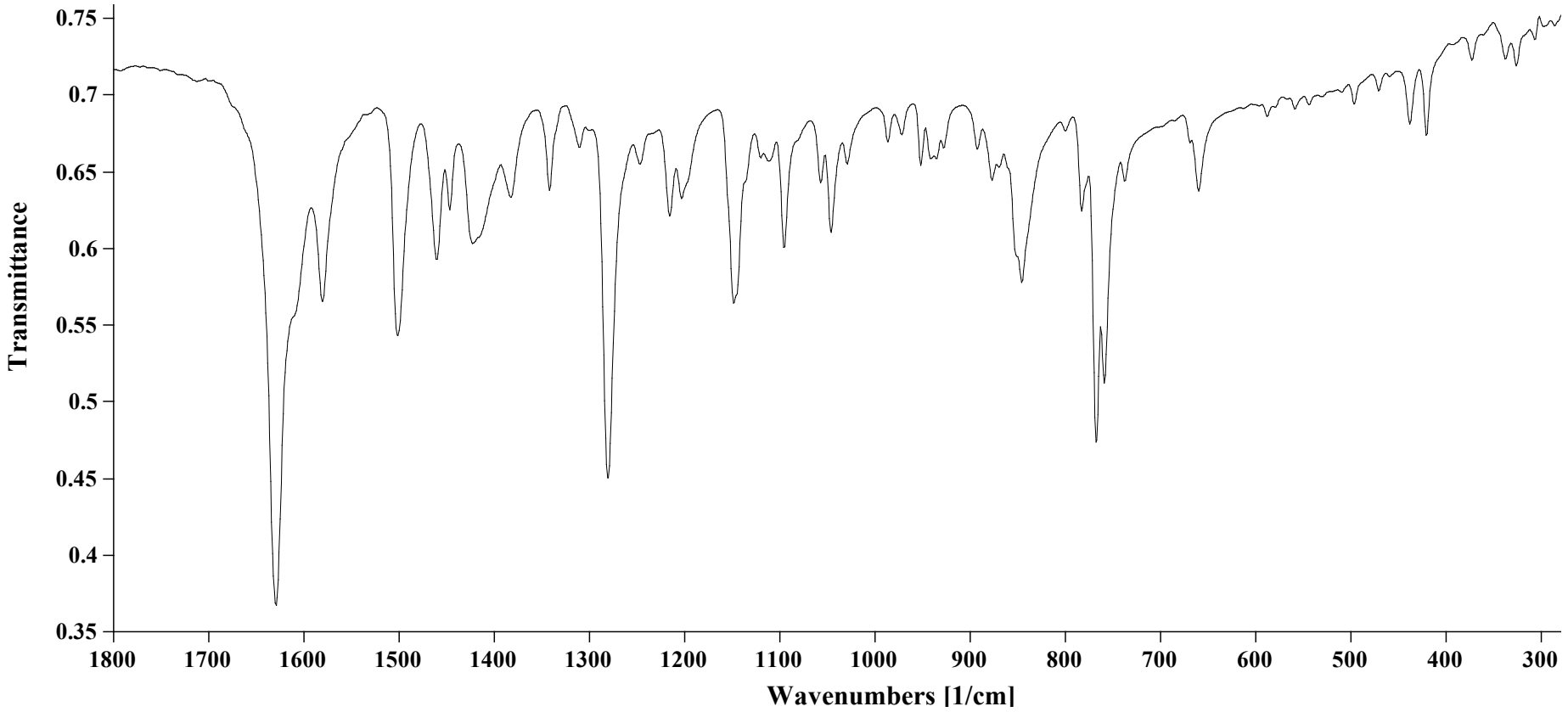

Figure S10: Expanded fingerprint region of the solid state IR spectrum of the cyclohexylsalen ligand, **2**, formed mechanochemically.

Table ST2: Elemental analysis of the cyclohexylsalen lignad, **2**, formed mechanochemically

Element	**C**	**H**	**N**
Theoretical %	**74.51**	**6.89**	**8.69**
Mechanochemical %	**74.58**	**6.91**	**8.92**

2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis-phenol; (compound 3):

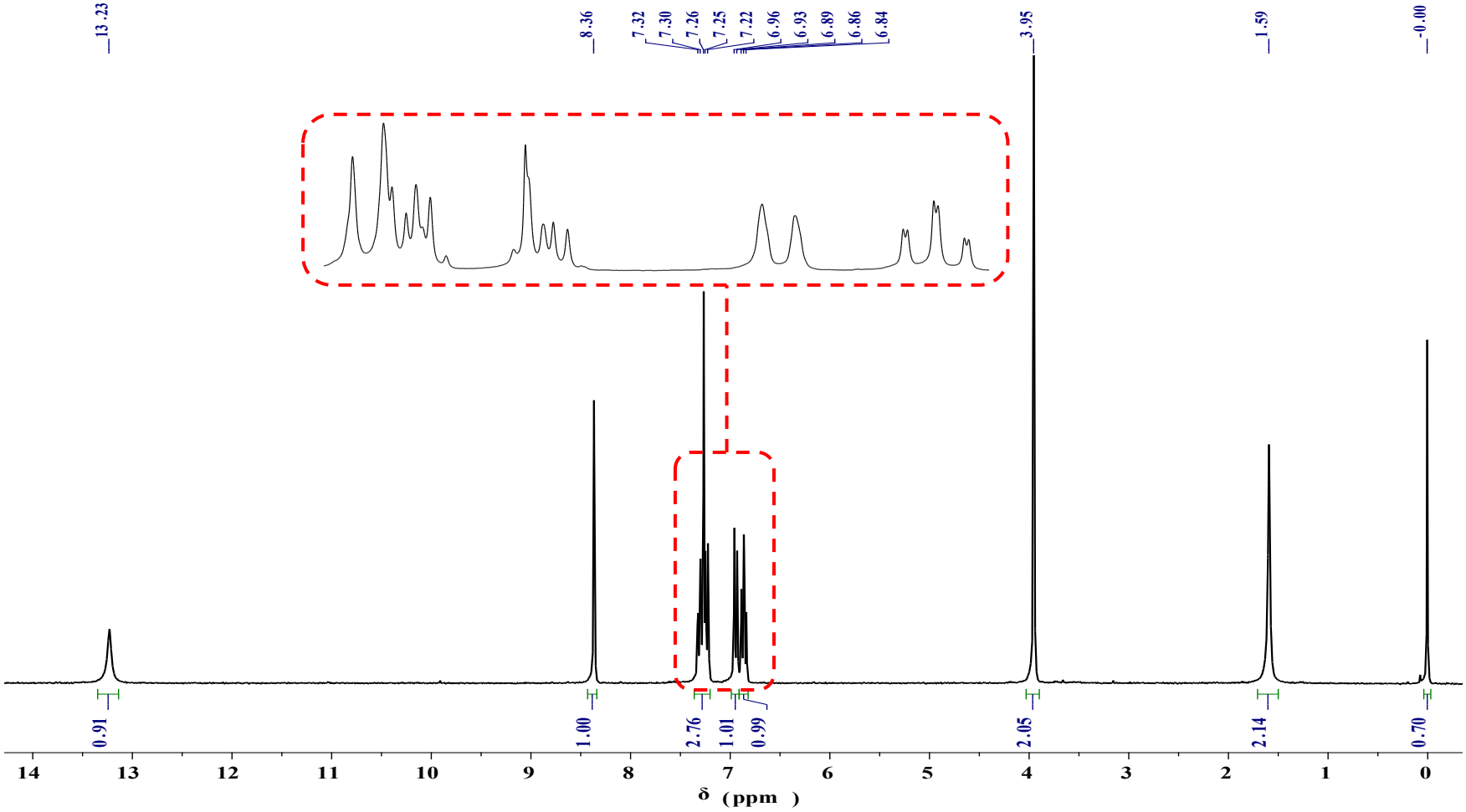

Figure S11: Solution state ($CDCl_3$) ^1H NMR spectrum of the salphen ligand, **3**, obtained mechanochemically.

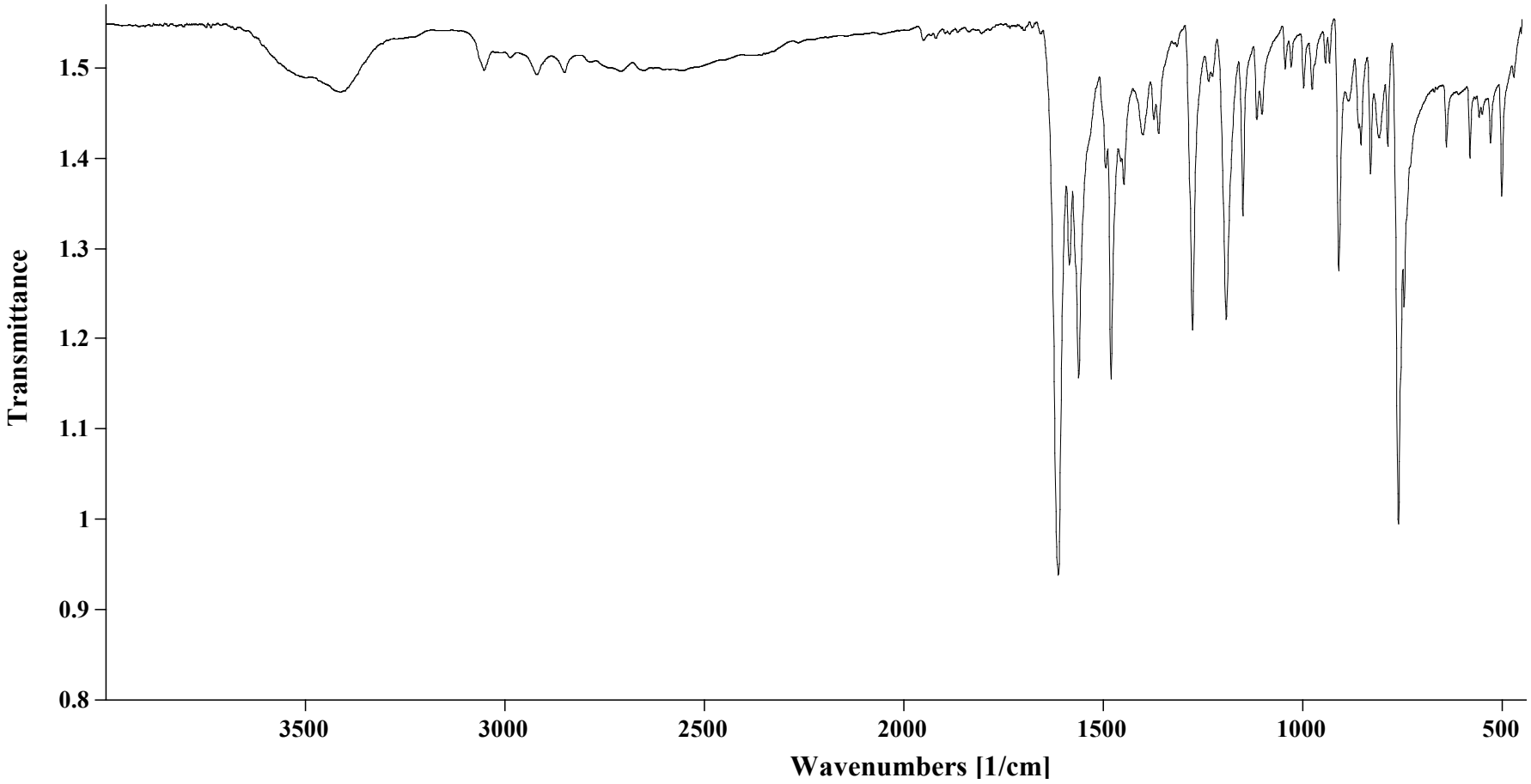

Figure S12: Solid state IR (KBr disc) spectrum of the salphen ligand, **3**, obtained mechanochemically.

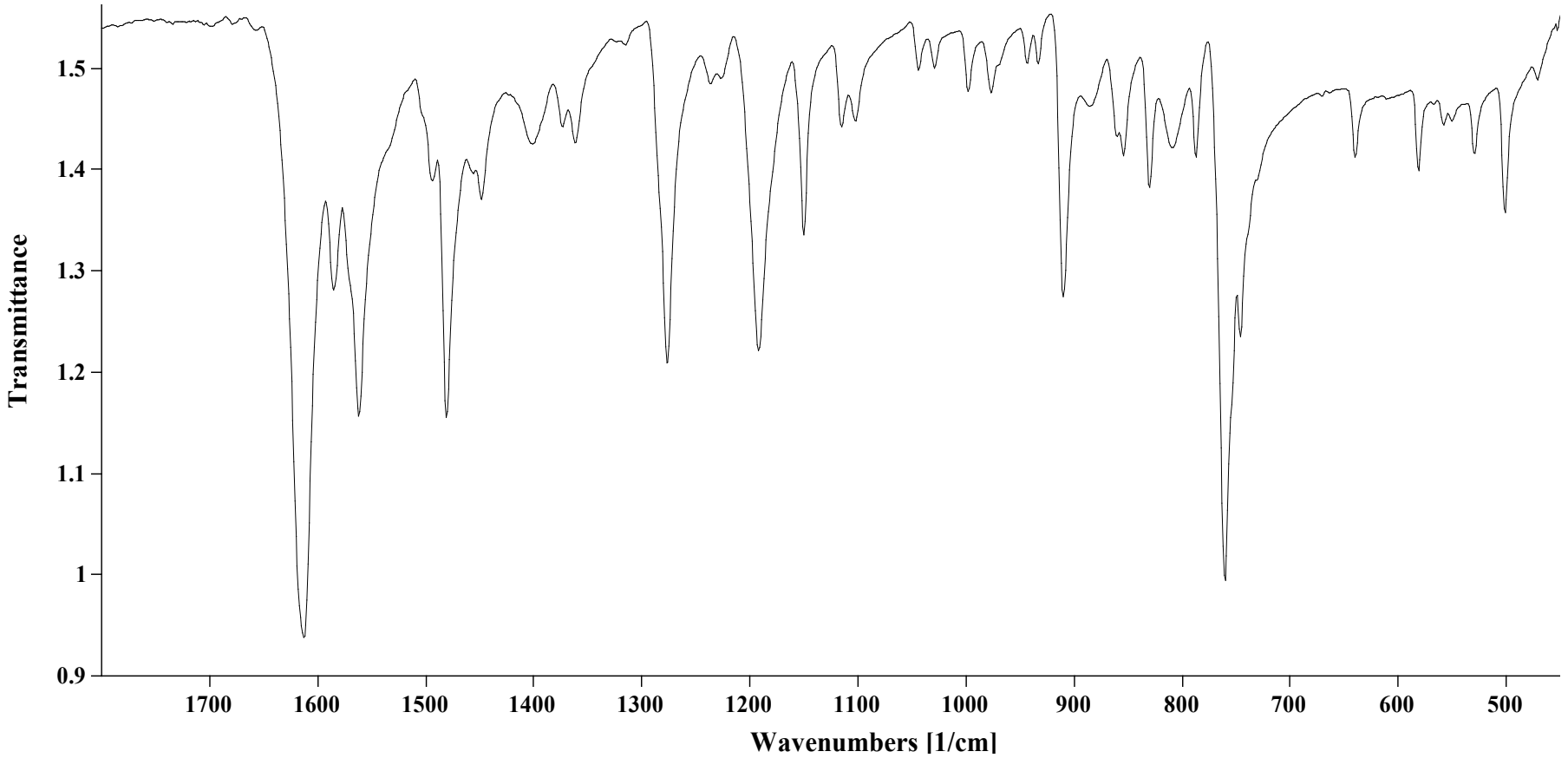

Figure S13: Expanded fingerprint region of the solid state IR spectrum of the salphen ligand, **3**, obtained mechanochemically.

Table ST3: Elemental analysis of the salphen ligand, **3**, formed mechanochemically.

Element	**C**	**H**	**N**
Theoretical %	**75.93**	**5.10**	**8.86**
Mechanochemical %	**75.92**	**4.97**	**8.68**

2-[[(2-aminophenyl)imino]methyl]-phenol; (compound 4):

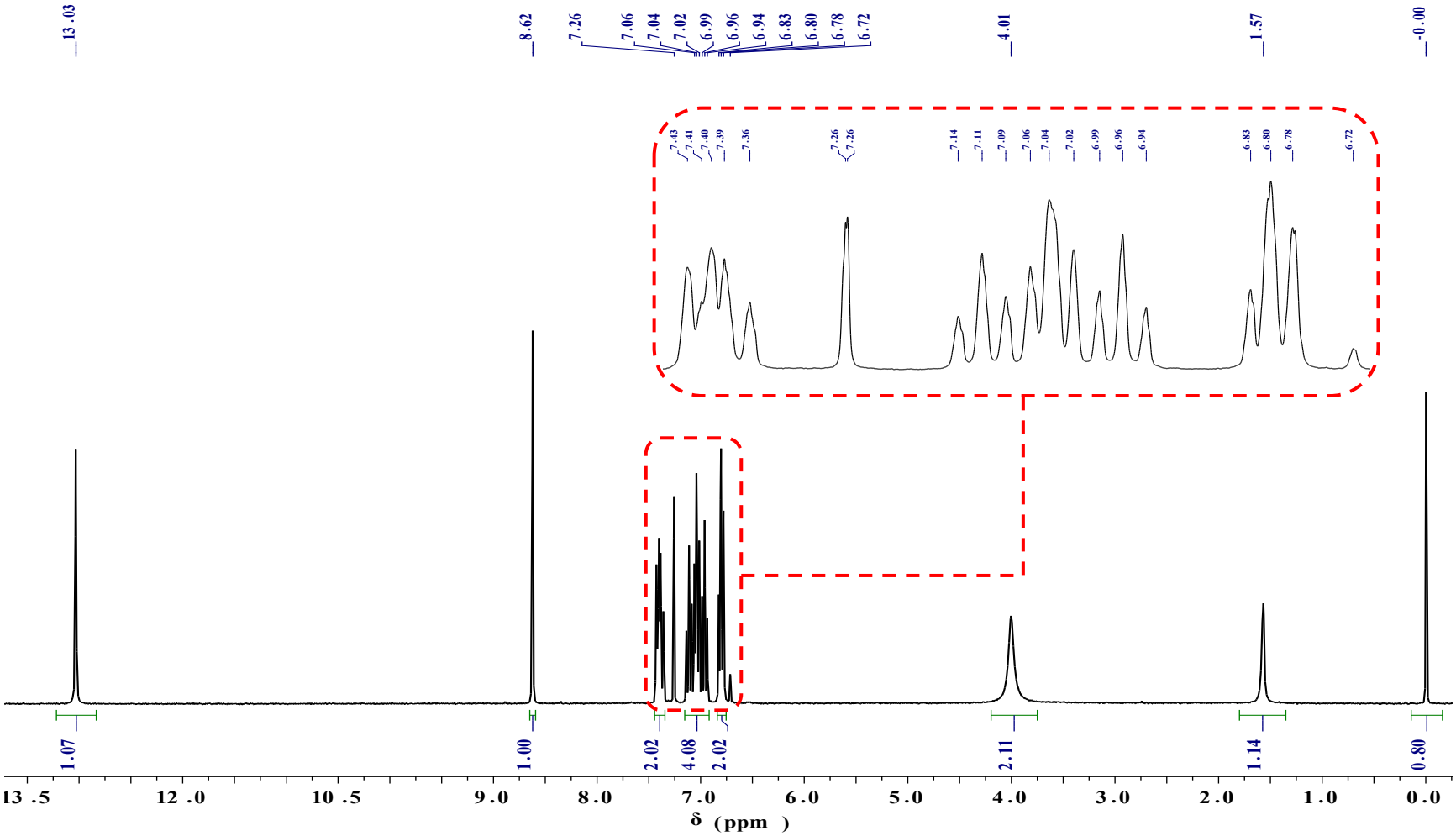

Figure S14: Solution state ($CDCl_3$) ^1H NMR spectrum of the unsymmetrical salphen ligand, **4**, obtained mechanochemically.

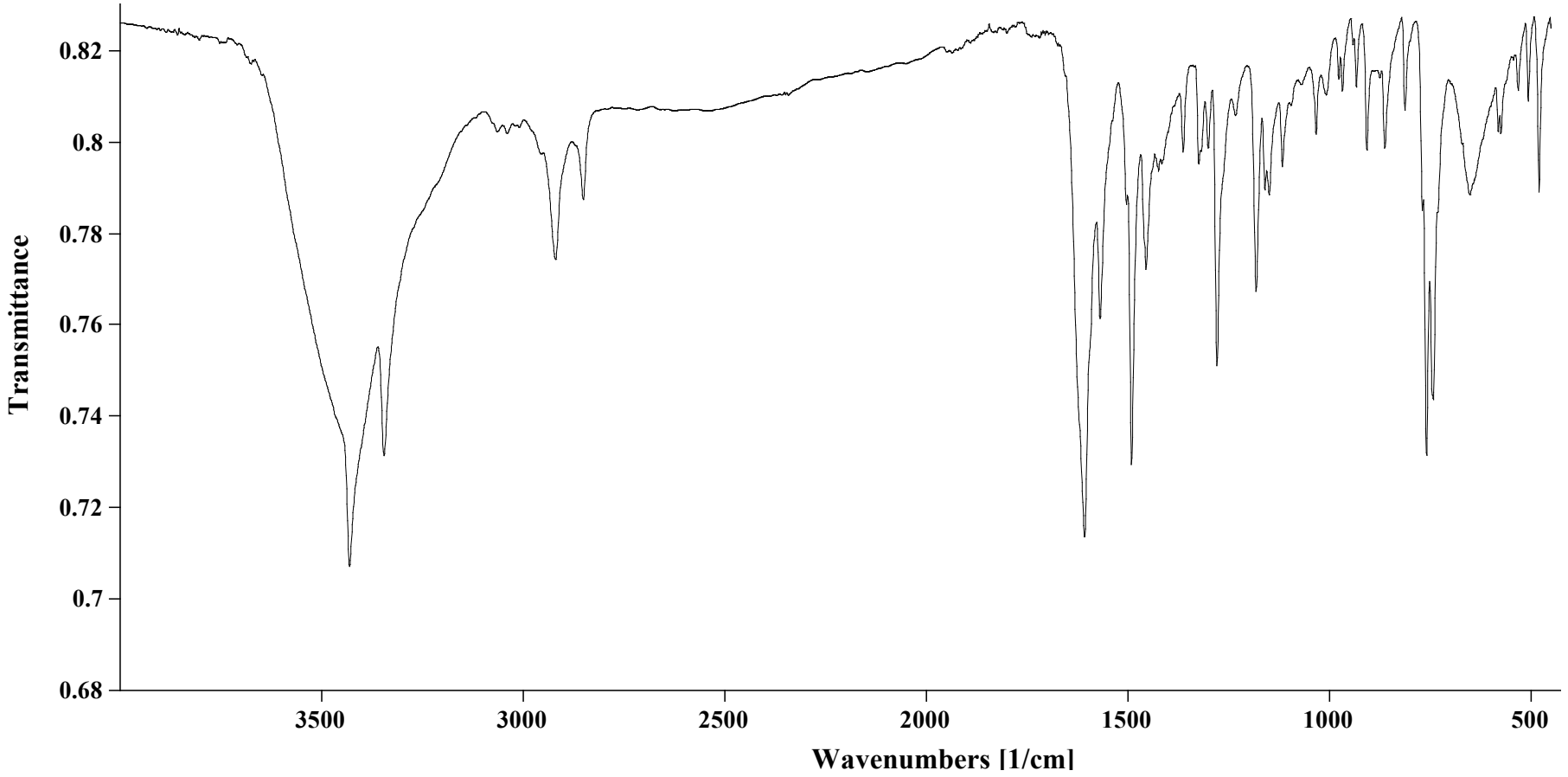

Figure S15: Solid state IR (KBr disc) spectrum of the asymmetrical salphen ligand, **4**, formed mechanochemically.

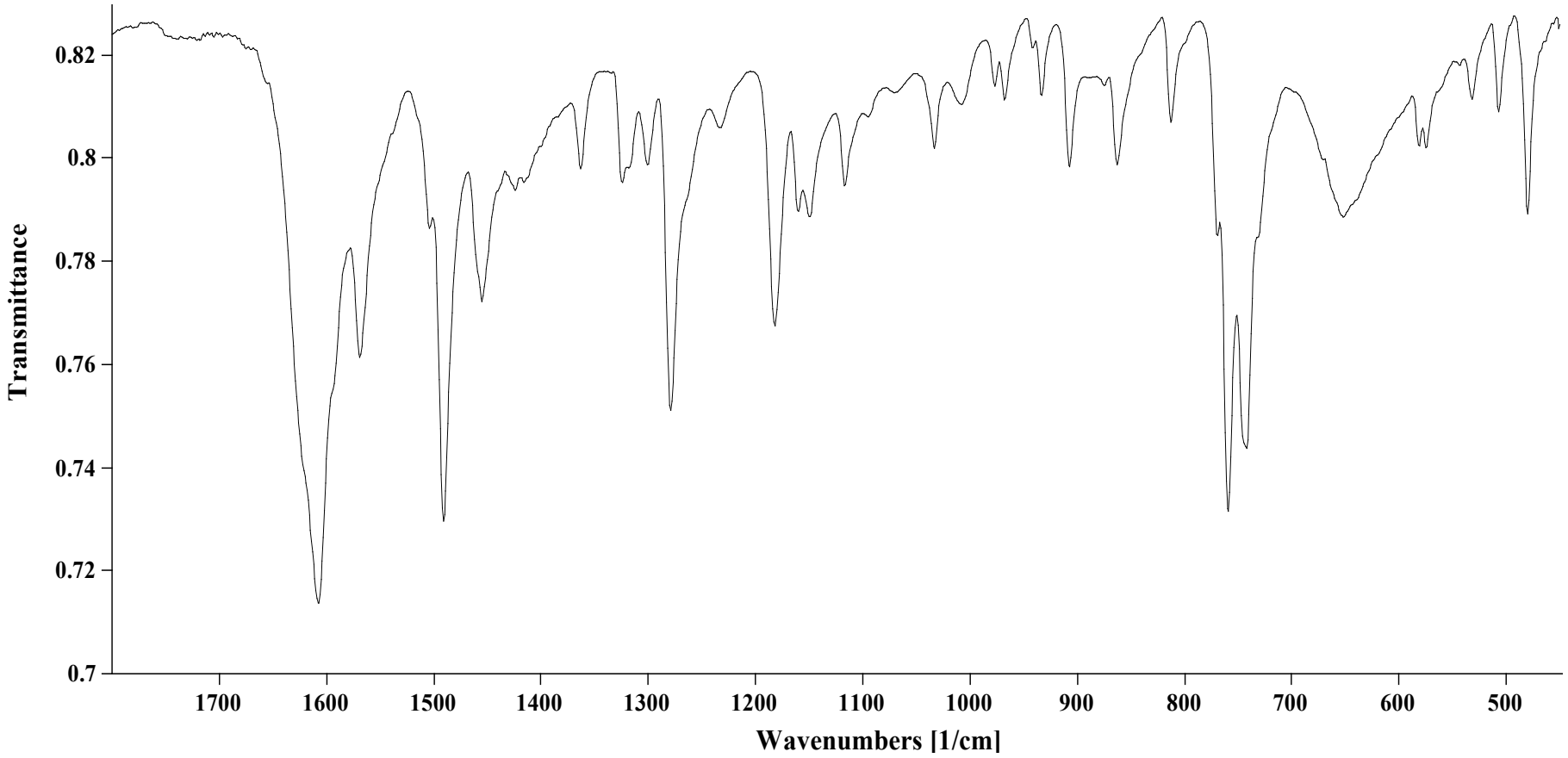

Figure S16: Expanded fingerprint region of the solid state IR spectrum of the asymmetric salphen ligand, **4**, obtained mechanochemically.

Table ST4: Elemental analysis of the asymmetrical salphen ligand, **4**, formed mechanochemically

Element	**C**	**H**	**N**
Theoretical %	**73.56**	**5.70**	**13.20**
Mechanochemical %	**73.49**	**5.69**	**13.09**

2,2'-[(±)-1,2-cyclohexanediylbis[(*E*)-nitrilomethylidyne]] bis[4,6-bis(1,1-dimethylethyl)]-phenol; (compound 5):

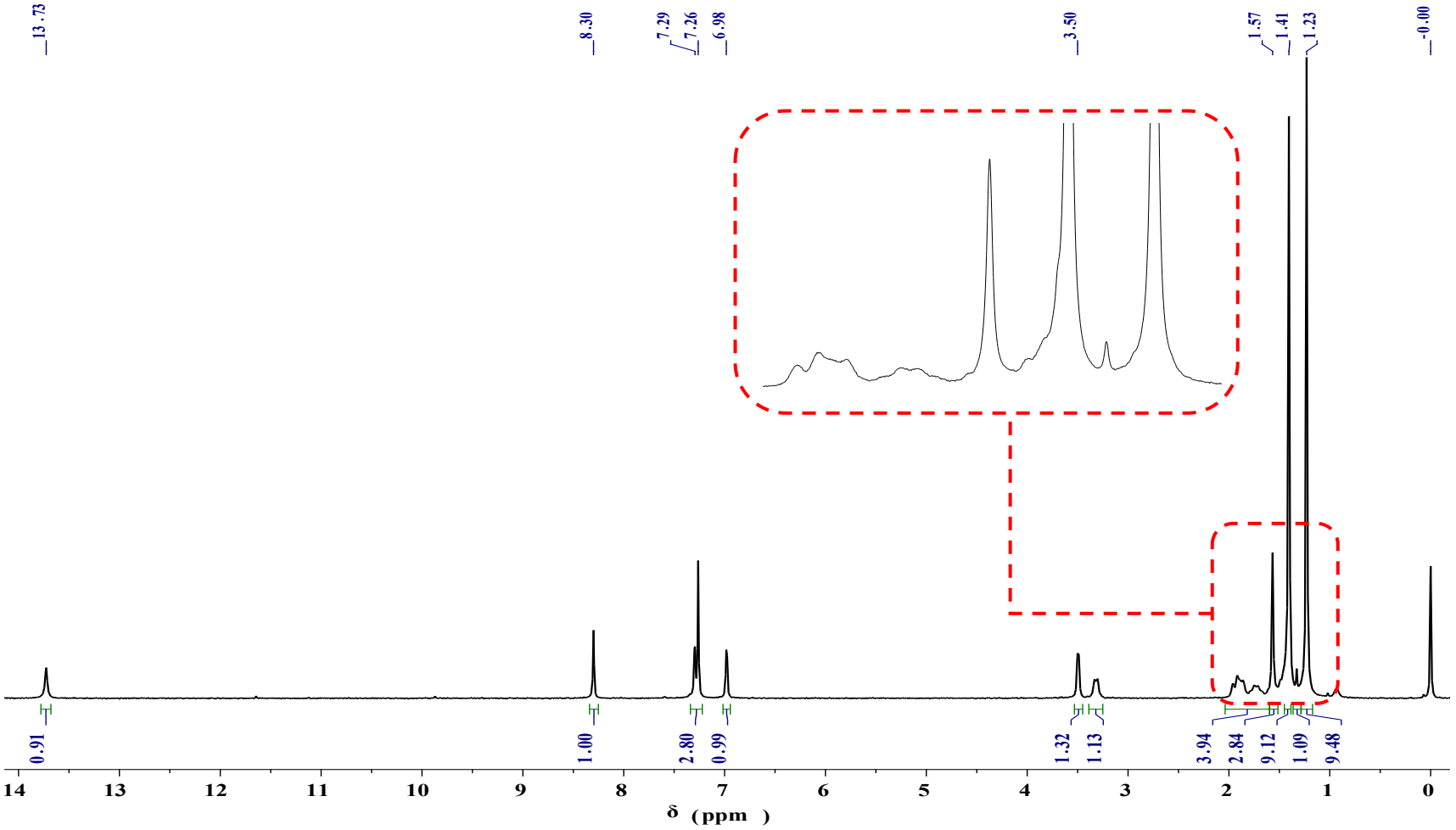

Figure S17: Solution state ($CDCl_3$) ^1H NMR spectrum of the 'Jacobsen' ligand, 5, obtained mechanochemically.

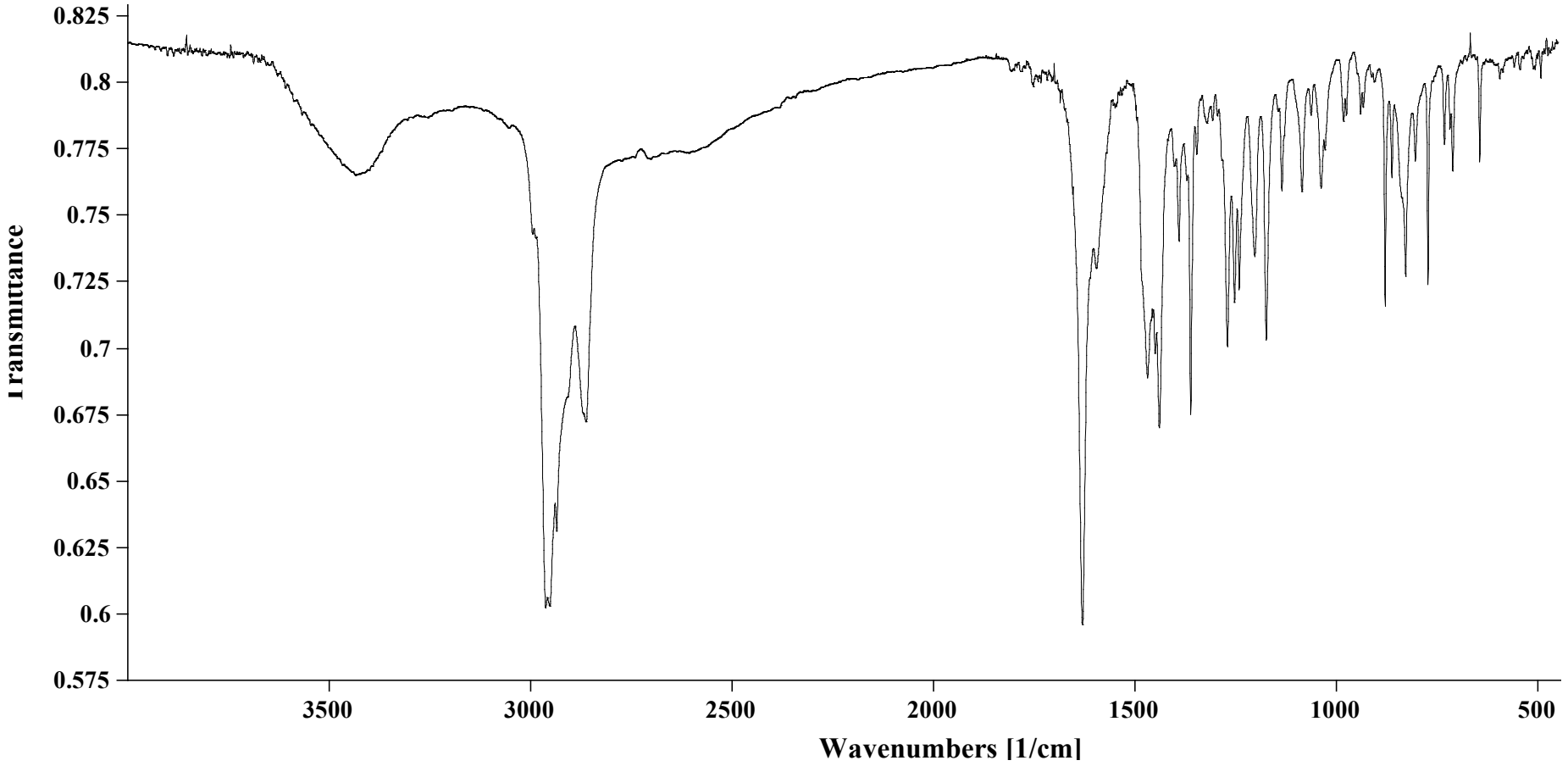

Figure S18: Solid state IR (KBr disc) spectrum of the 'Jacobsen' ligand, **5**, obtained mechanochemically.

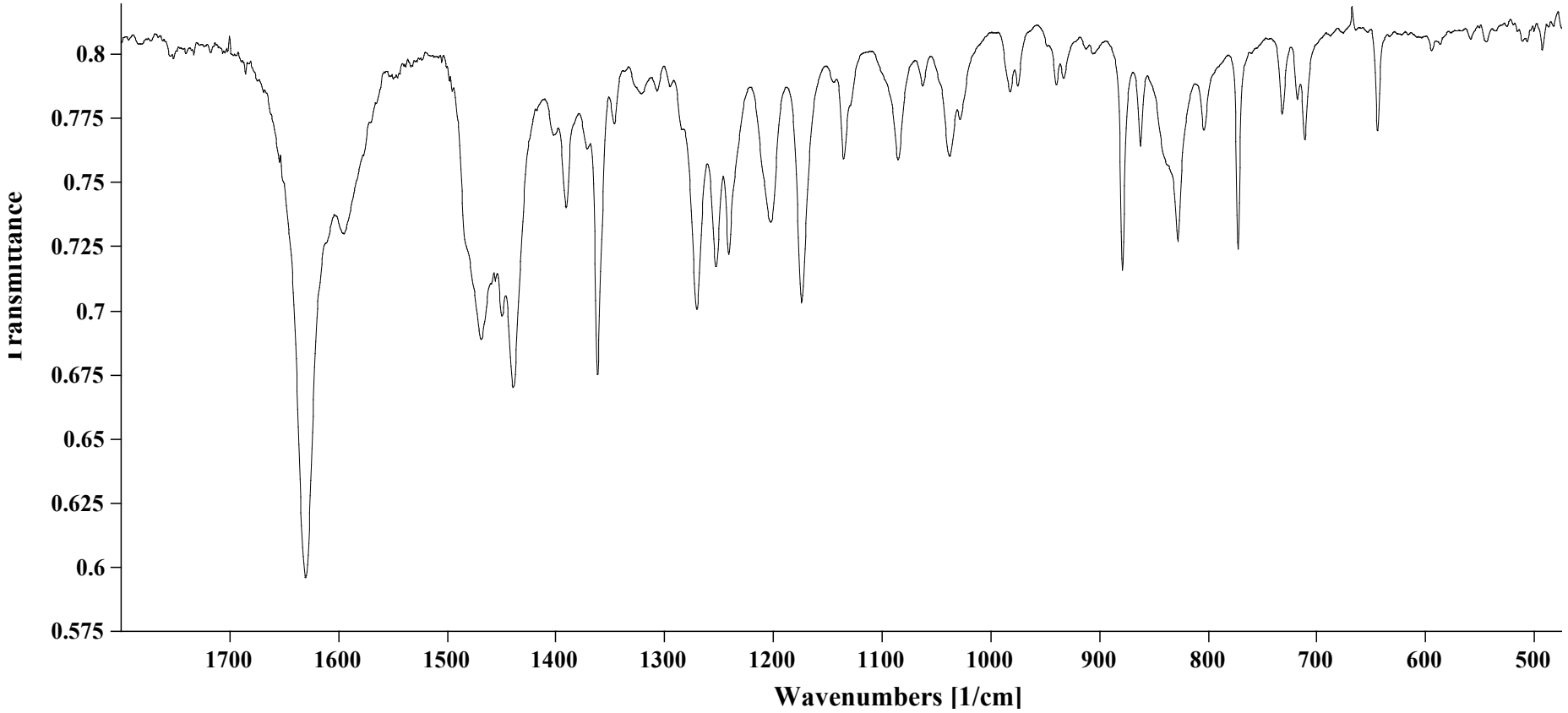

Figure S19: Expanded fingerprint region of the solid state IR spectrum of the 'Jacobsen' ligand, **5**, obtained mechanochemically.

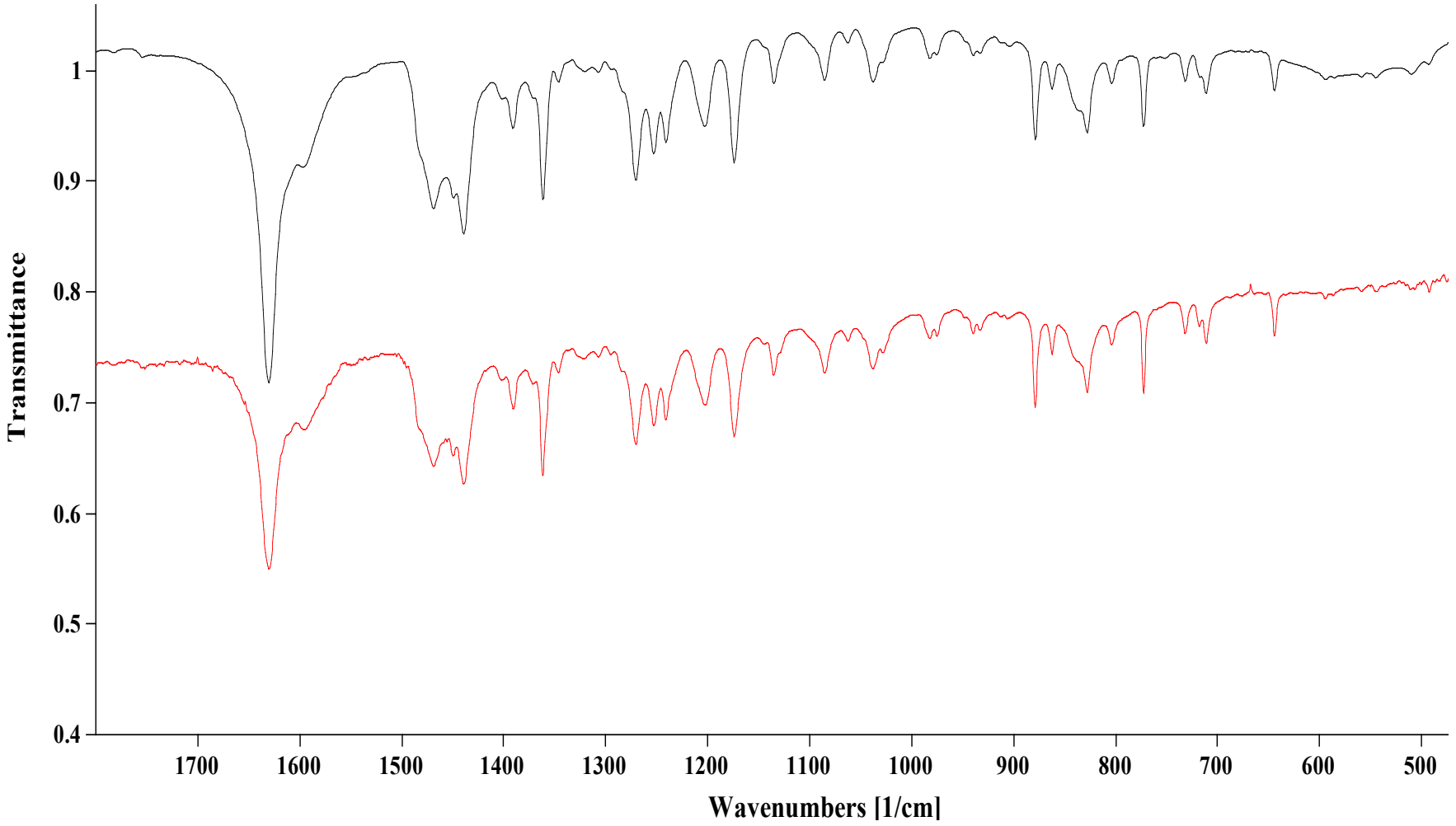

Figure S20: Comparison of the expanded fingerprint regions of the solid state IR spectra of the 'Jacobsen' ligand obtained through conventional solution based techniques (black) and mechanochemical synthesis, **5**, (red).

Element	**C**	**H**	**N**
Theoretical %	**79.07**	**9.95**	**5.12**
Mechanochemical %	**79.16**	**10.17**	**5.13**

Table ST5: Elemental analysis of the 'Jacobsen' ligand, **5**, obtained mechanochemically.

Complex Analysis

2,2'-[1,2-ethanediylbis[(*E*)-nitrilomethylidyne]]bis[phenolato]-κN,N',O,O'-zinc(II); (compound 6):

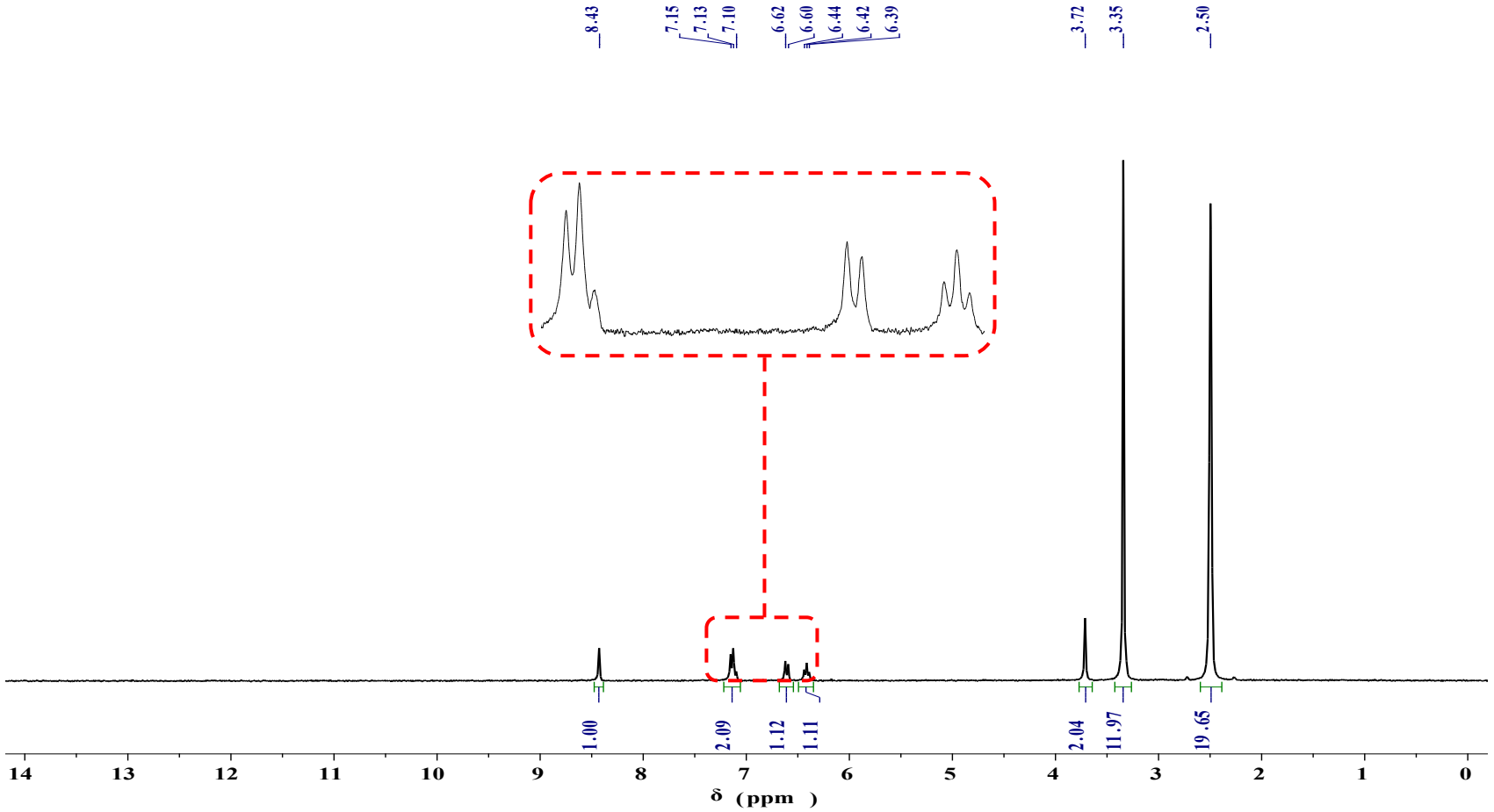

Figure S21: Solution state (d^6-DMSO) ^{1}H NMR spectrum of Zn(salen), **6**, obtained by a 2-step mechanochemical process.

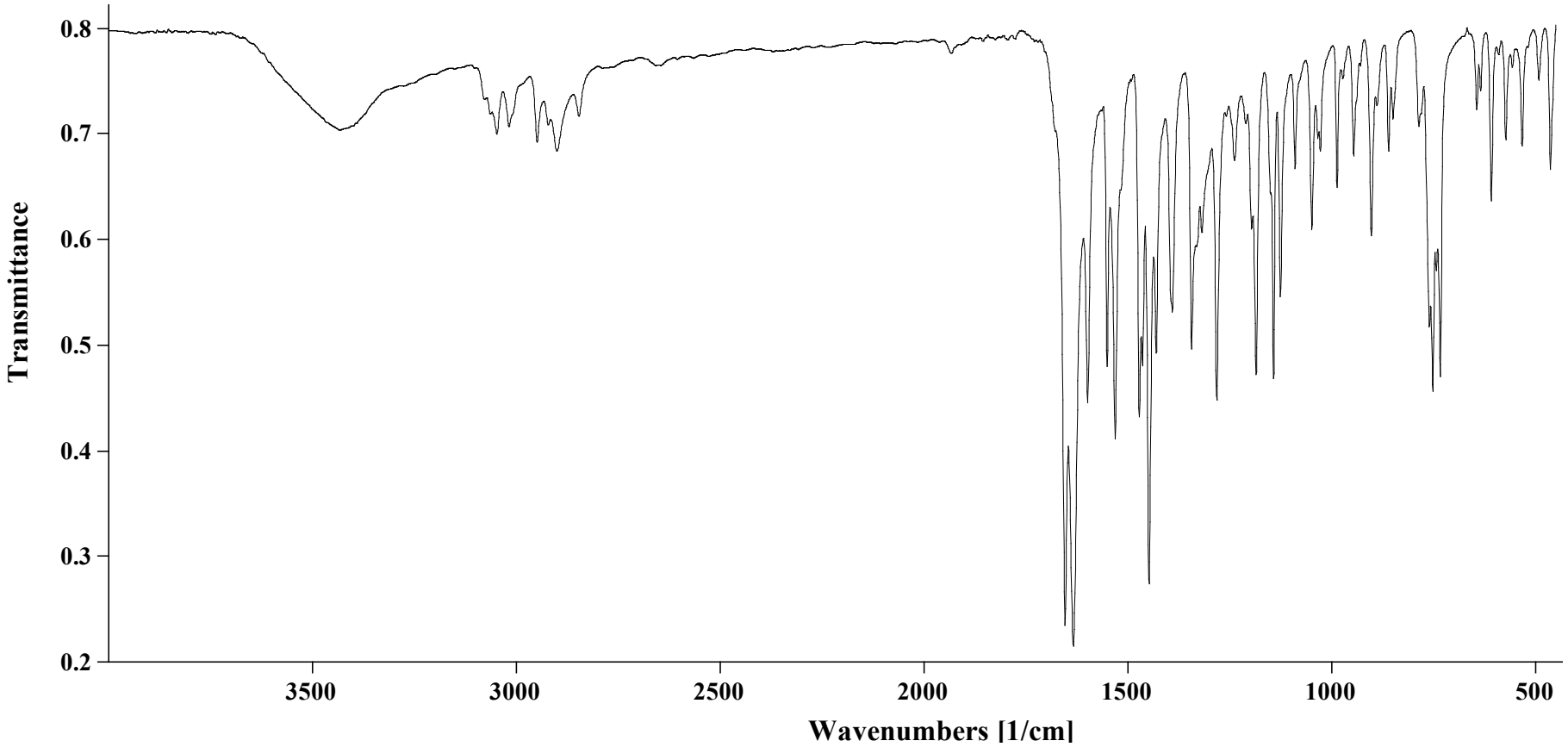

Figure S22: Solid state IR (KBr disc) spectrum of Zn(salen), **6**, obtained mechanochemically.

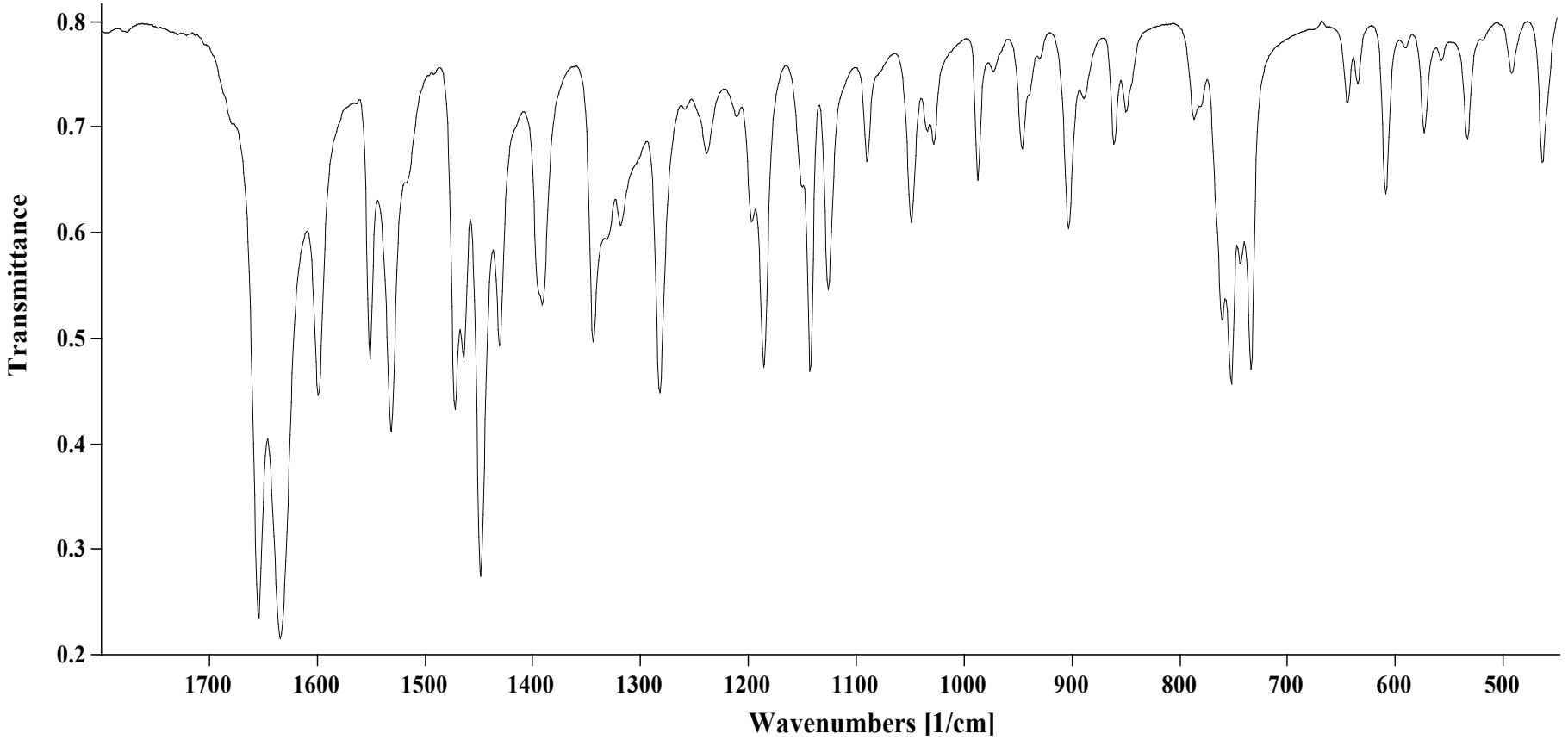

Figure S23: Expanded fingerprint region of the solid state spectrum of Zn(salen), **6**, obtained mechanochemically.

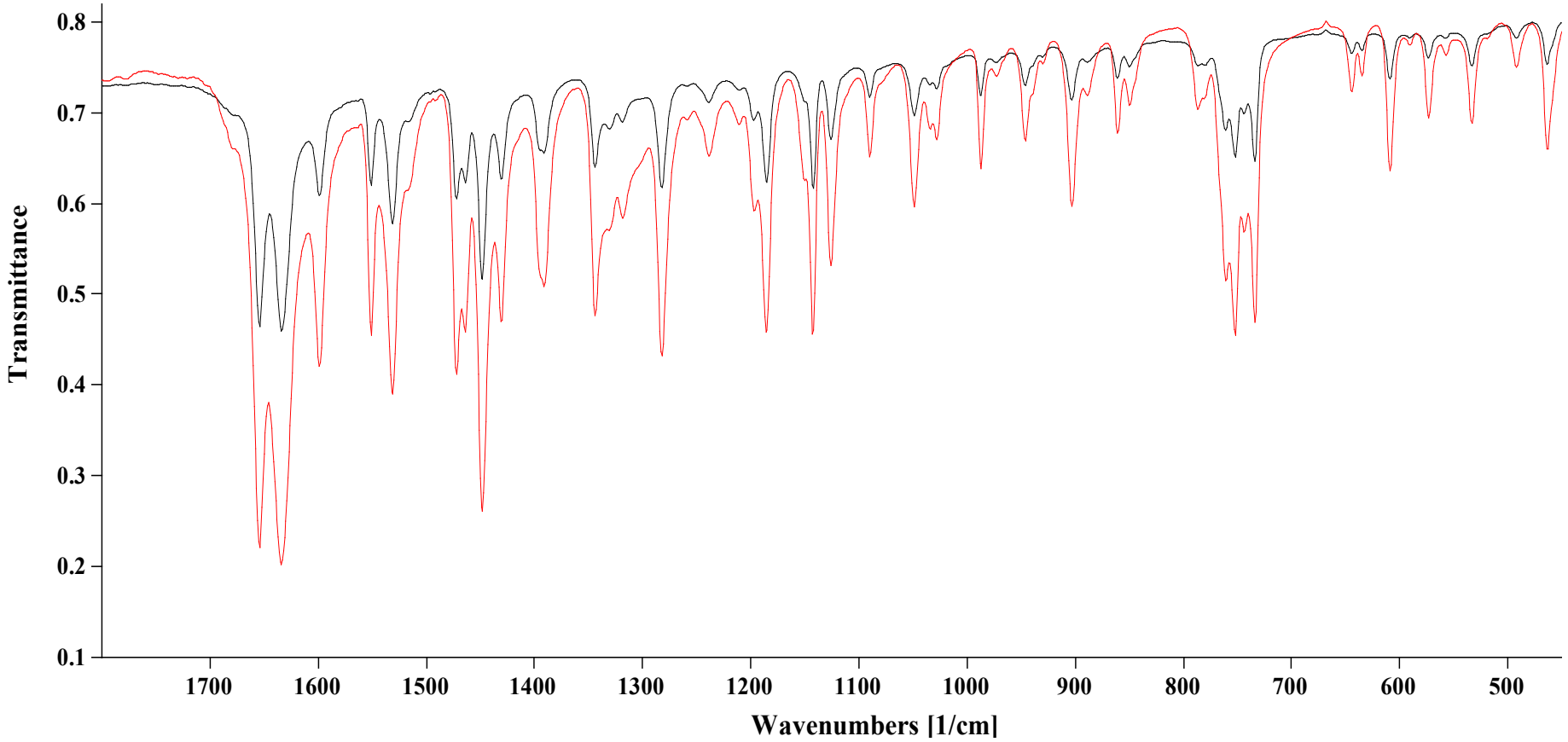

Figure S24: Comparison of the expanded fingerprint regions of the solid state IR spectra of Zn(salen) obtained through conventional solution based techniques (black) and mechanochemical synthesis, **6**, (red).

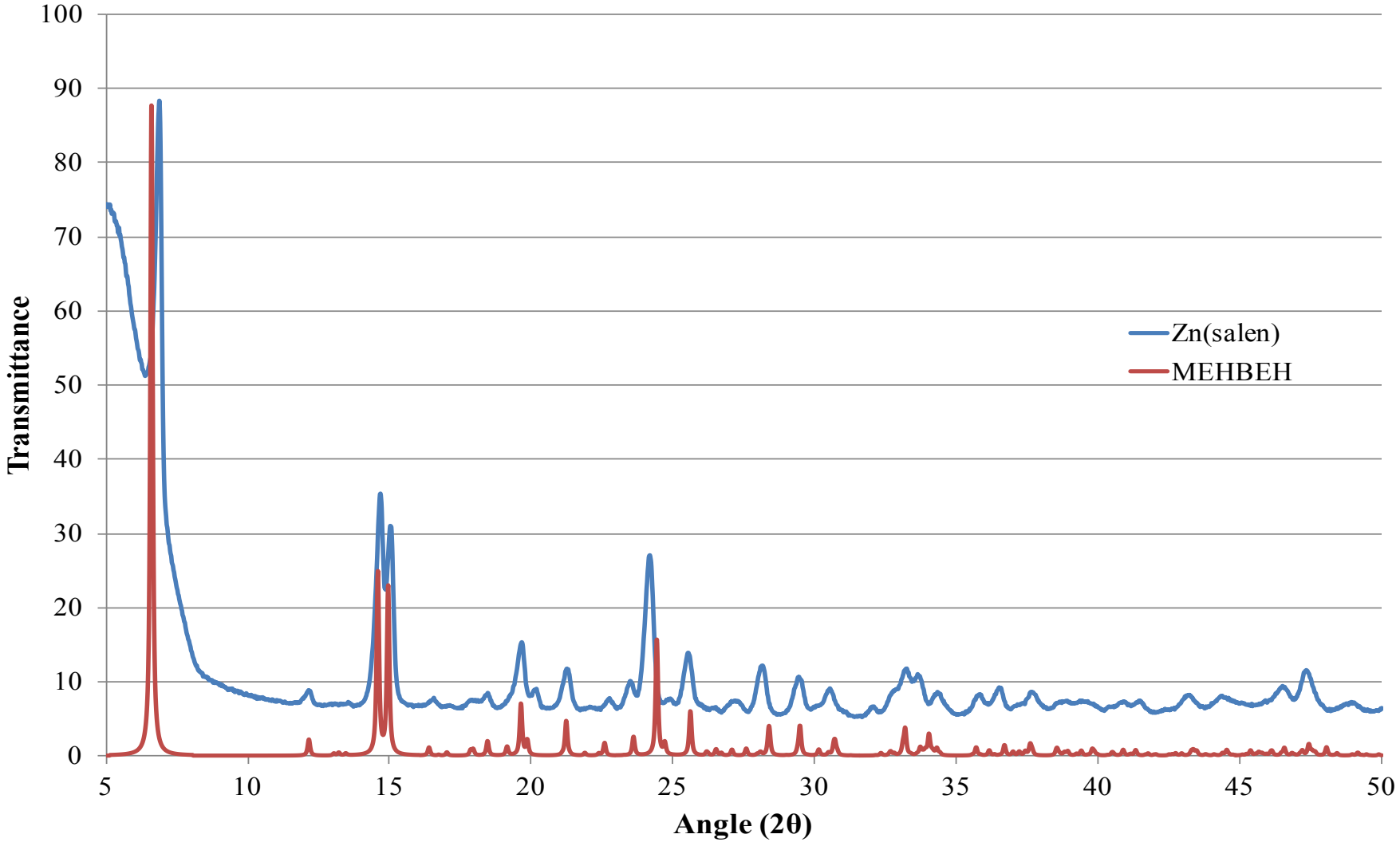

Figure S25: X-Ray powder diffraction spectra of Zn(salen), **6**, obtained mechanochemically and a simulated pattern from the Cambridge Structural Database (CCD code MEHBEH).

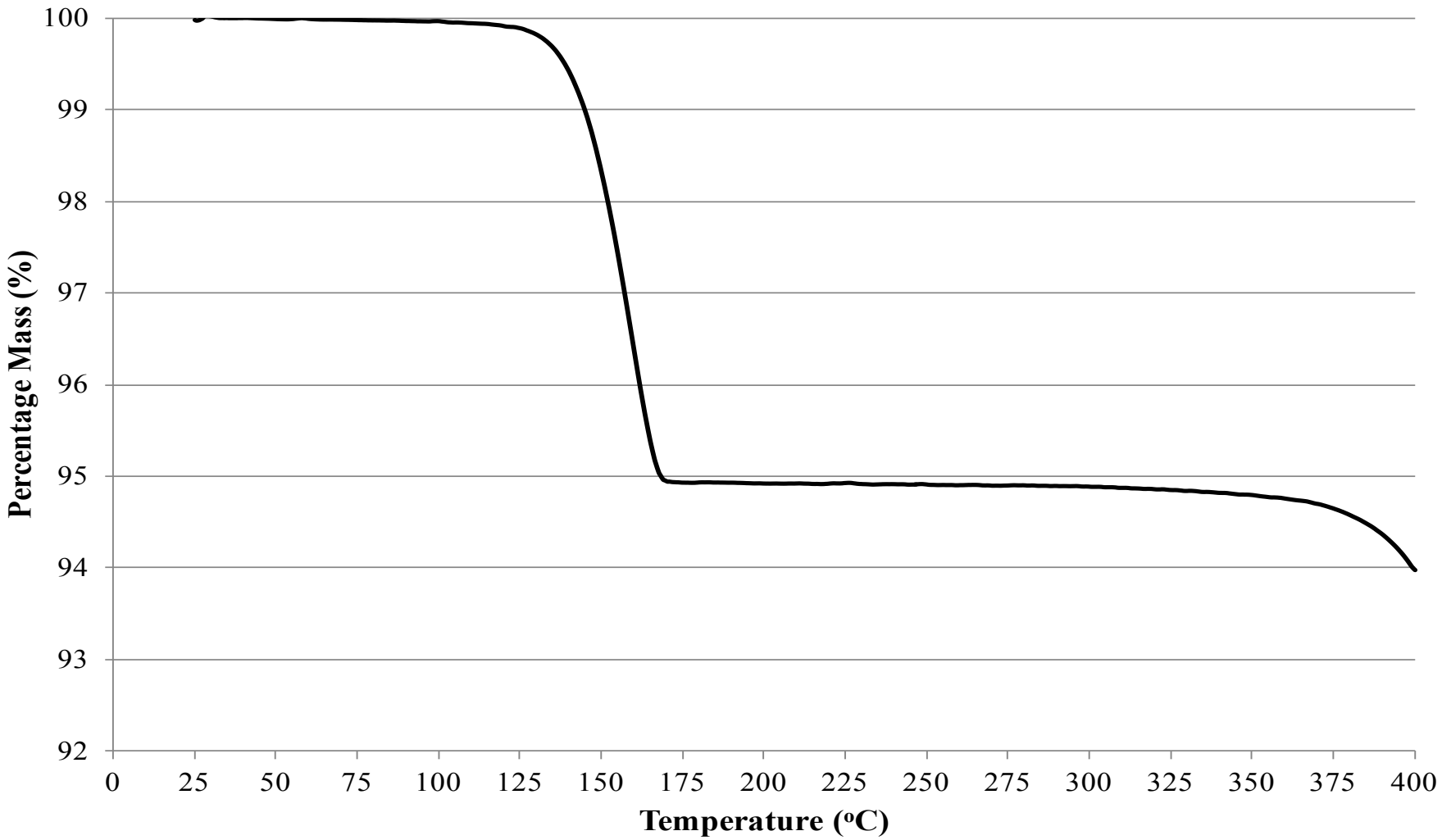

Figure S26: Thermal gravimetric analysis of Zn(salen), **6**, formed mechanochemically showing ≈5% mass loss at 150°C which is equivalent to one molecule of H_2O per molecule of complex.

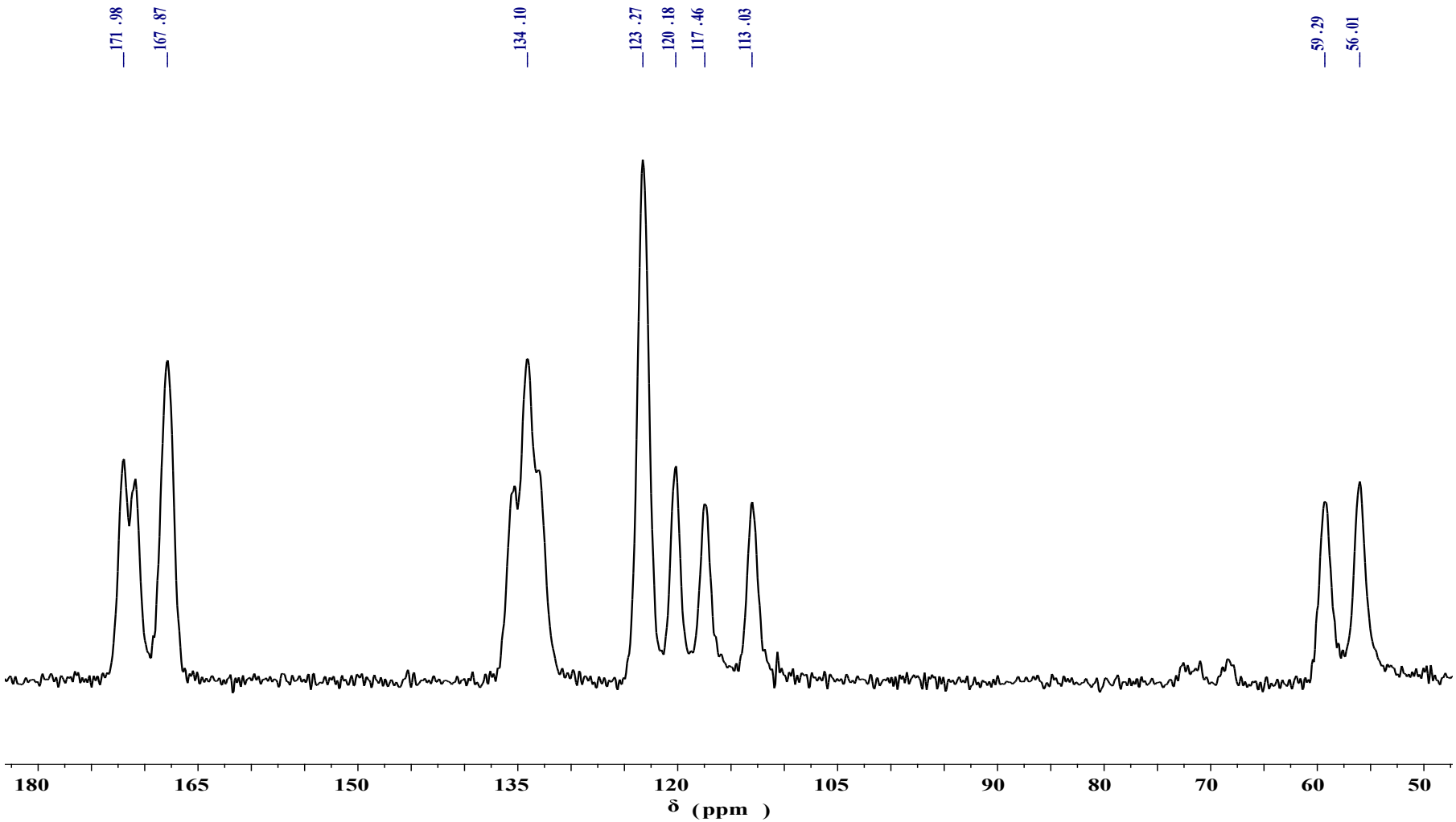

Figure S27: Solid state ^{13}C MAS NMR spectrum of Zn(salen), **6**, obtained by a two-step telescoped mechanochemical reaction.

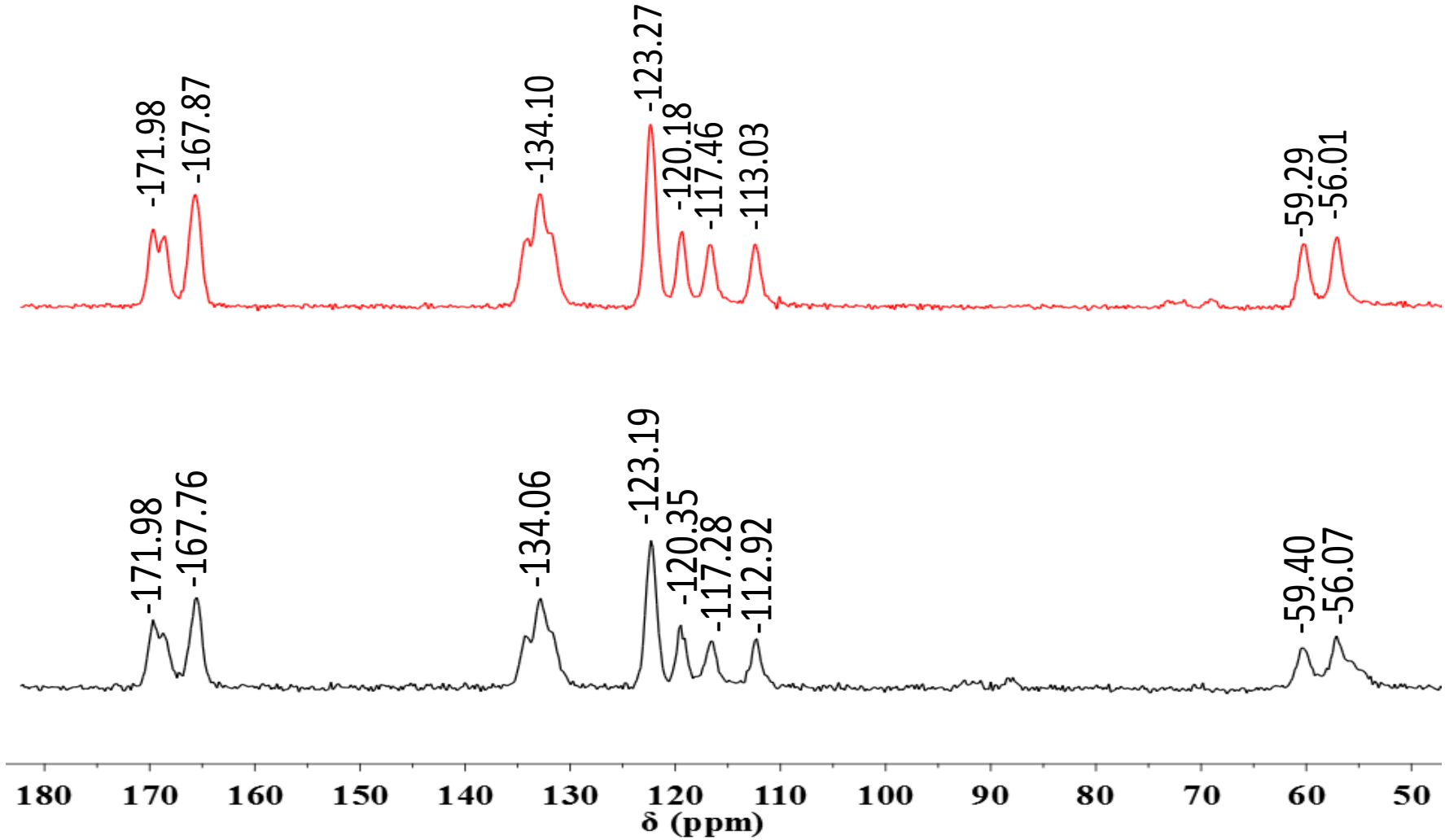

Figure S28: Comparison between the solid state ^{13}C MAS NMR spectra for Zn(salen) obtained from conventional solution state synthesis (black) and the two-step telescoped mechanical method (red, compound **6**).

Table ST6: Elemental analysis of Zn(salen) from both conventional solution state synthesis and mechanical methods (compound **6**).

Element	**C**	**H**	**N**
Theoretical %	**57.94**	**4.25**	**8.45**
Solution %	**58.67**	**4.46**	**8.57**
Mechanochemical %	**57.64**	**4.01**	**8.51**

2,2'-[1,2-ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κN,N',O,O'-nickel(II); (compound 7):

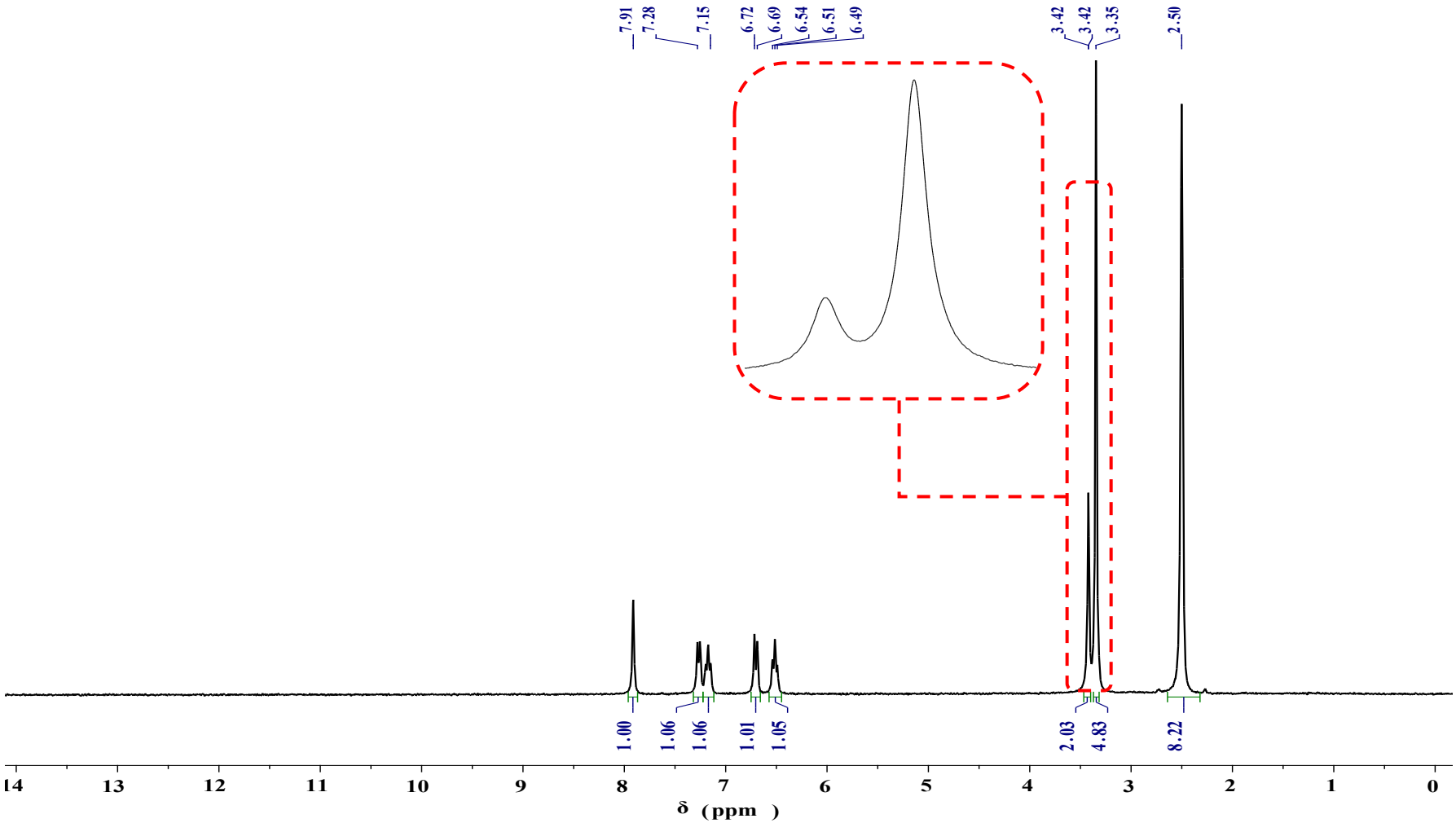

Figure S29: Solution state (d^6-DMSO) ^{1}H NMR spectrum of Ni(salen), **7**, obtained mechanochemically.

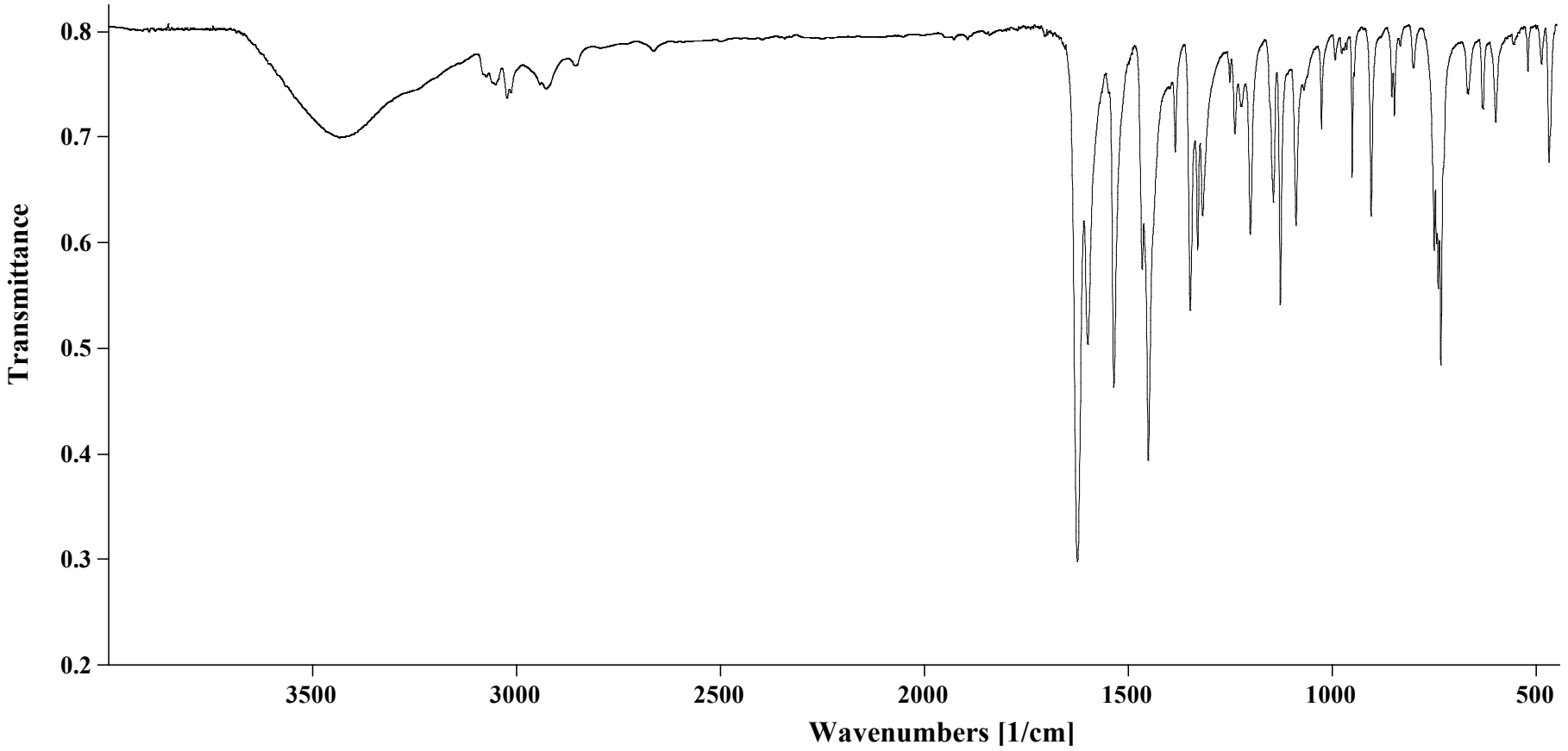

Figure S30: Solid state IR (KBr disc) spectrum of Ni(salen), **7**, obtained mechanochemically.

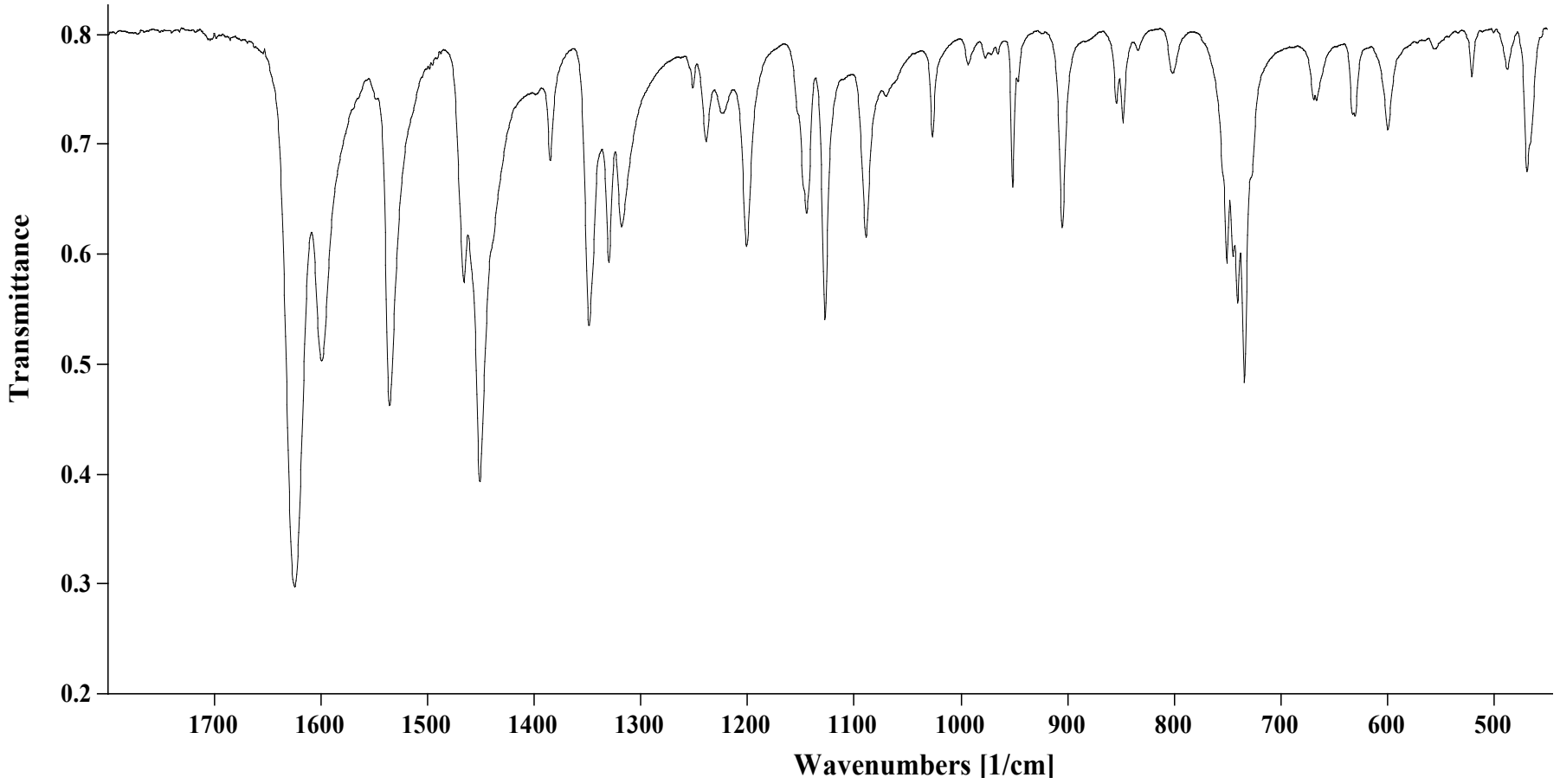

Figure S31: Expanded fingerprint region of the solid state IR spectrum of Ni(salen), **7**, obtained mechanochemically.

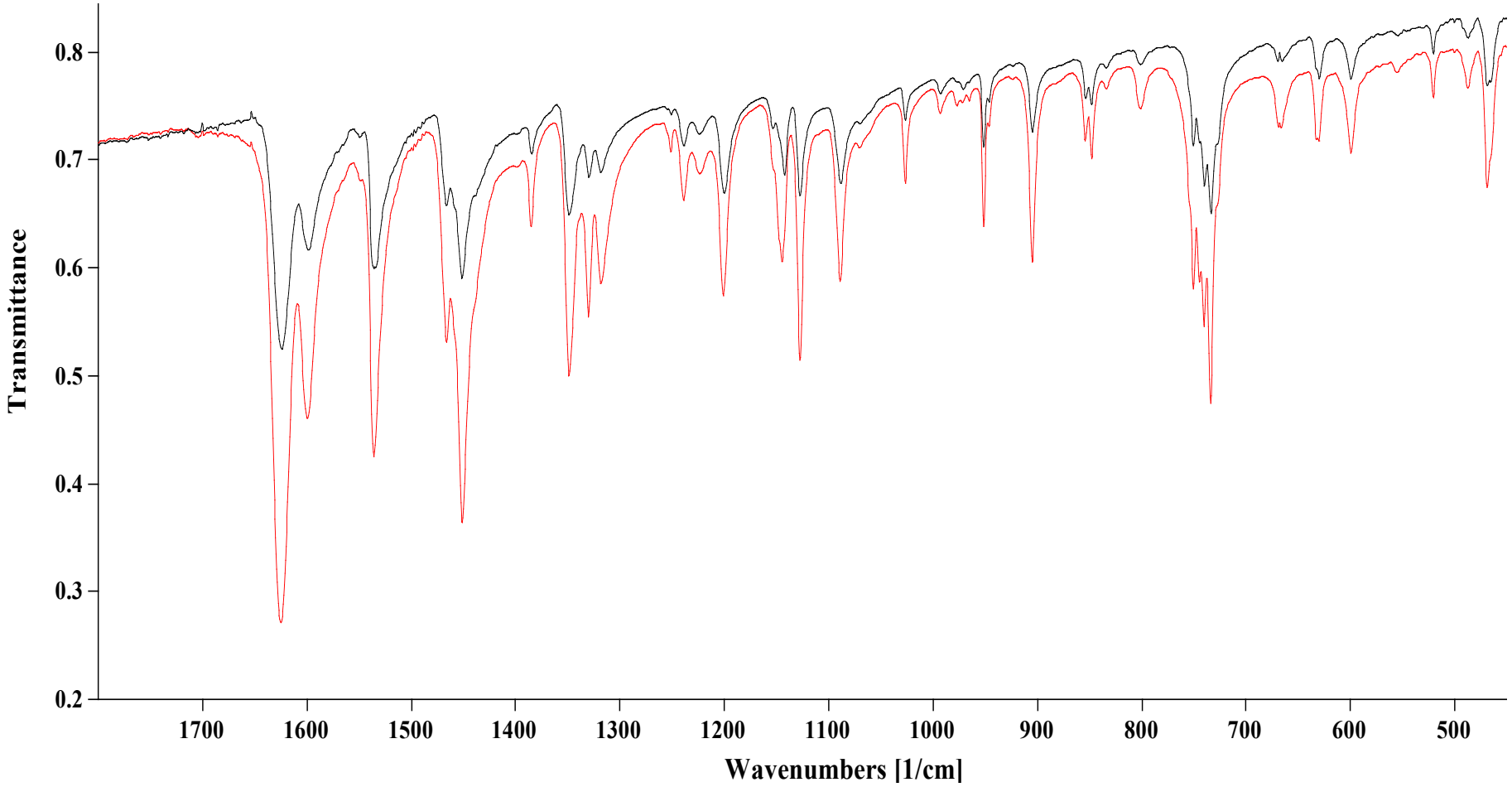

Figure S32: Comparison of the expanded fingerprint regions of the solid state IR spectra of Ni(salen) obtained through conventional solution based techniques (black) and mechanochemical synthesis, **7**, (red).

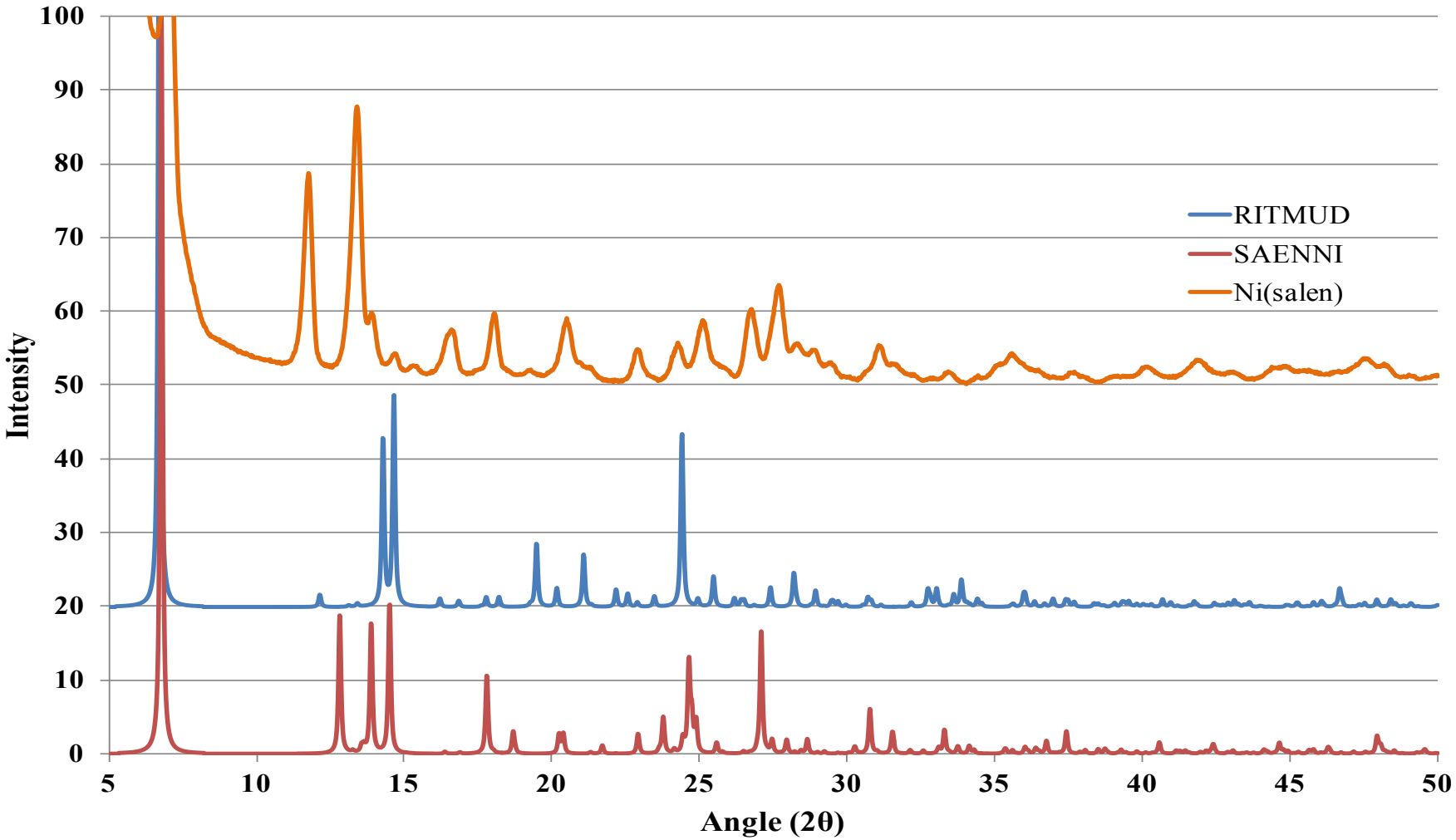

Figure S33: X-Ray powder diffraction spectra of Ni(salen) obtained mechanochemically, **7**, and the simulated patterns for a Ni(salen) monomer (CSD code SAENNI) and dimer (CSD code RITMUD) from the Cambridge Structural Database.

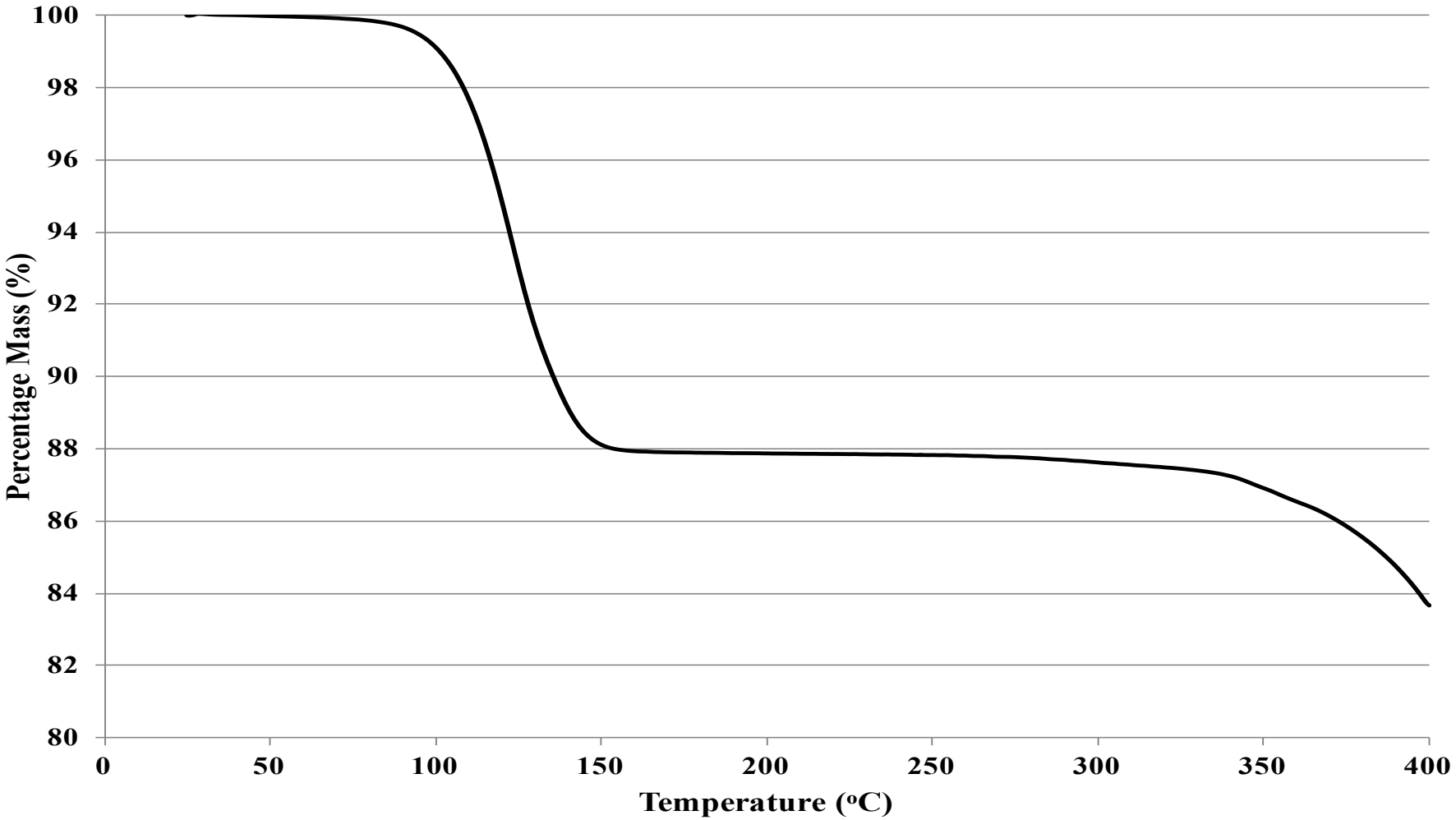

Figure S34: Therm0gravimetric analysis of Ni(salen) obtained mechanochemically, **7**, showing ≈12.25% mass loss at 115°C which is equivalent to one molecule of H_2O and molecule of MeOH per molecule of complex.

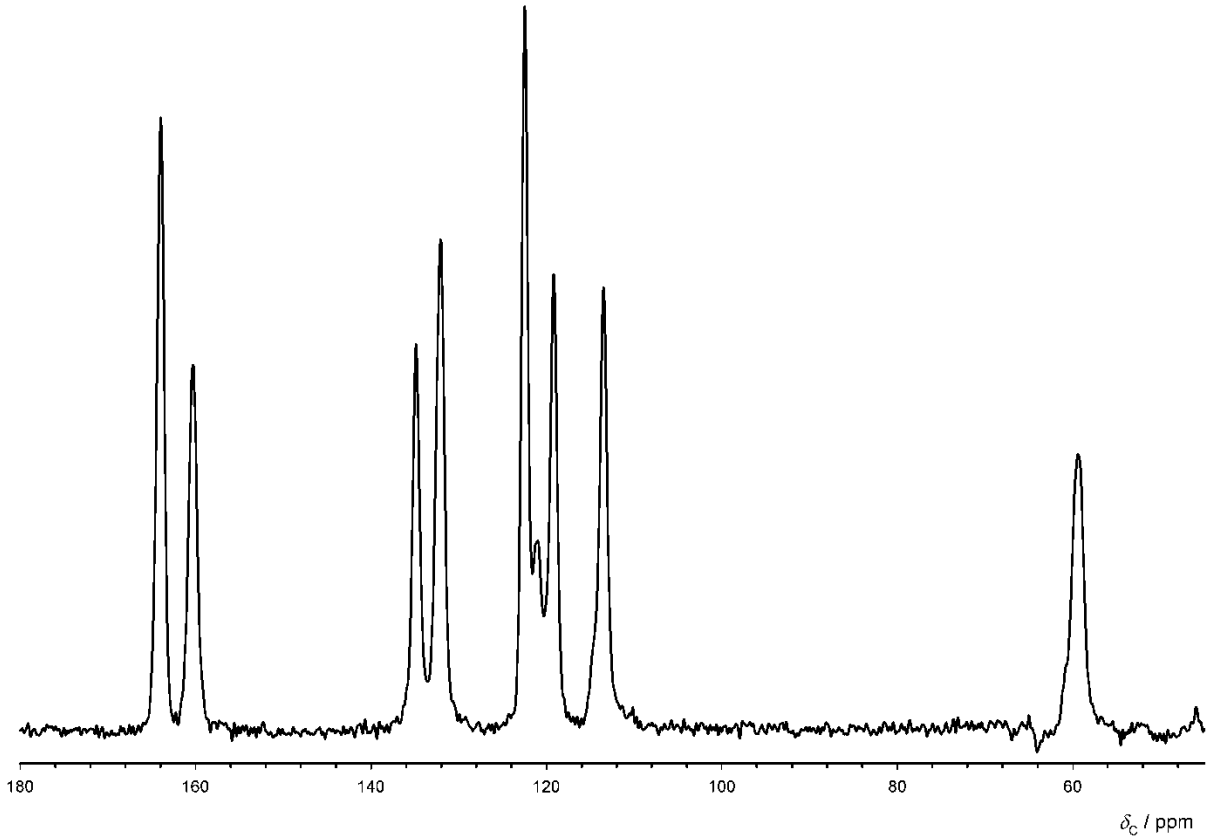

Figure S35: Solid state ^{13}C MAS NMR spectrum of Ni(salen), **7**, obtained mechanochemically.

Table ST7: Elemental analysis of Ni(salen) from both conventional solution state synthesis and mechanical methods (compound **7**).

Element	**C**	**H**	**N**
Theoretical %	**59.13**	**4.34**	**8.62**
Solution %	**59.14**	**4.13**	**8.79**
Mechanochemical %	**58.73**	**4.20**	**8.69**

2,2'-[1,2-ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κN,N',O,O'-copper(II); (compound 8):

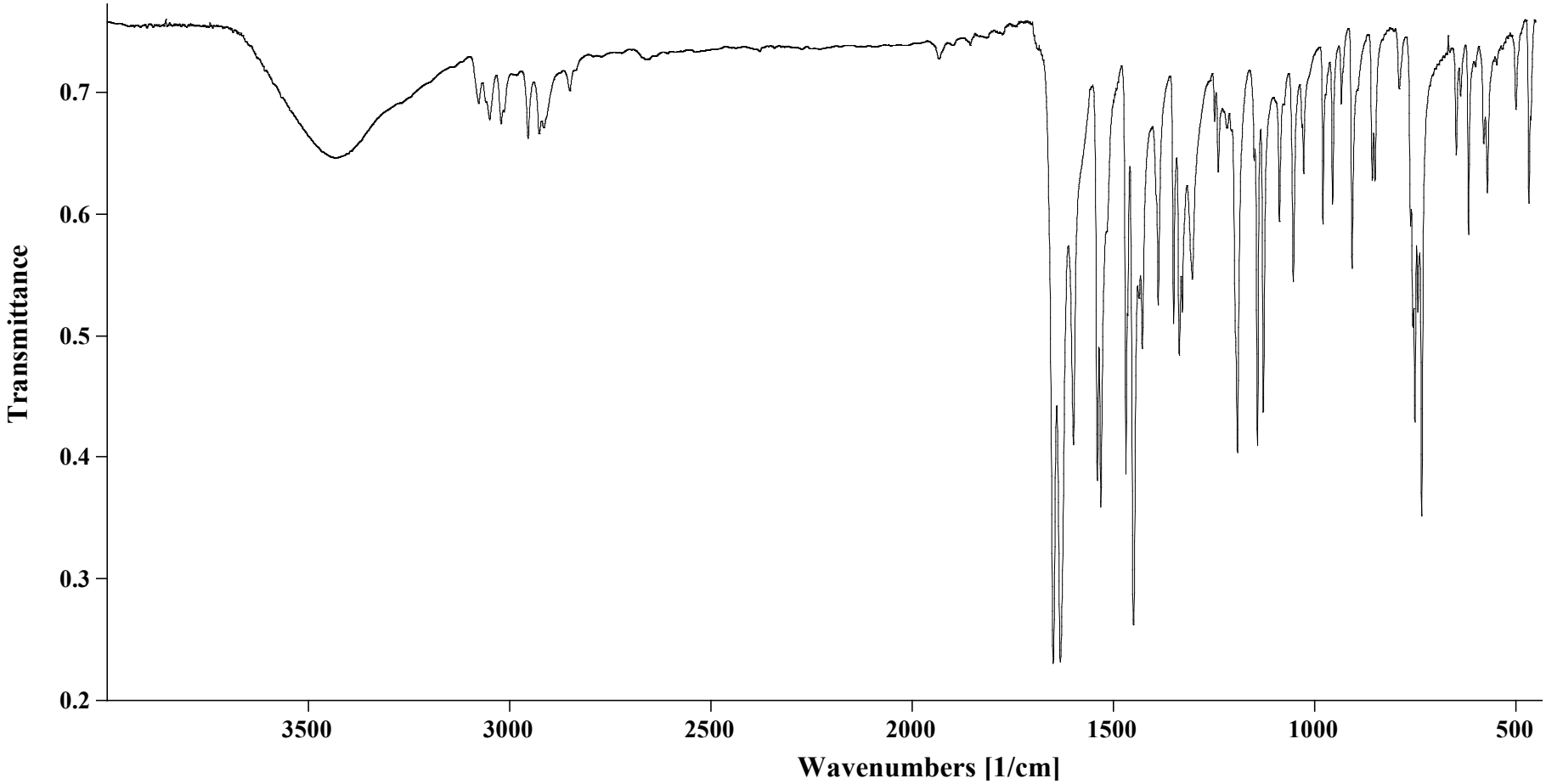

Figure S36: Solid state IR (KBr disc) spectrum of Cu(salen), **8**, obtained by a two-step telescoped mechanochemical reaction.

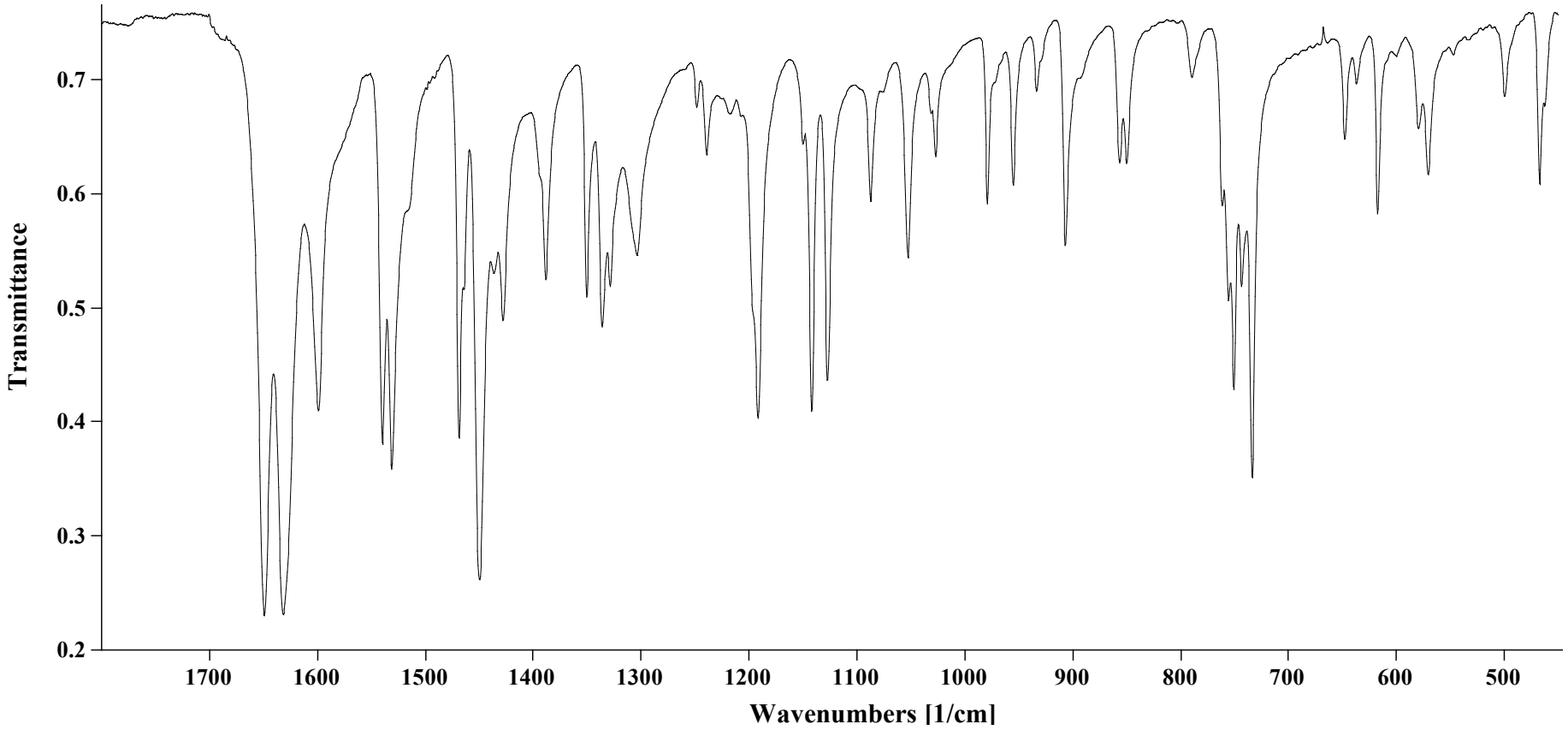

Figure S37: Expanded fingerprint region of the solid state IR spectrum of Cu(salen), **8**, obtained by a two-step telescoped mechanochemical reaction.

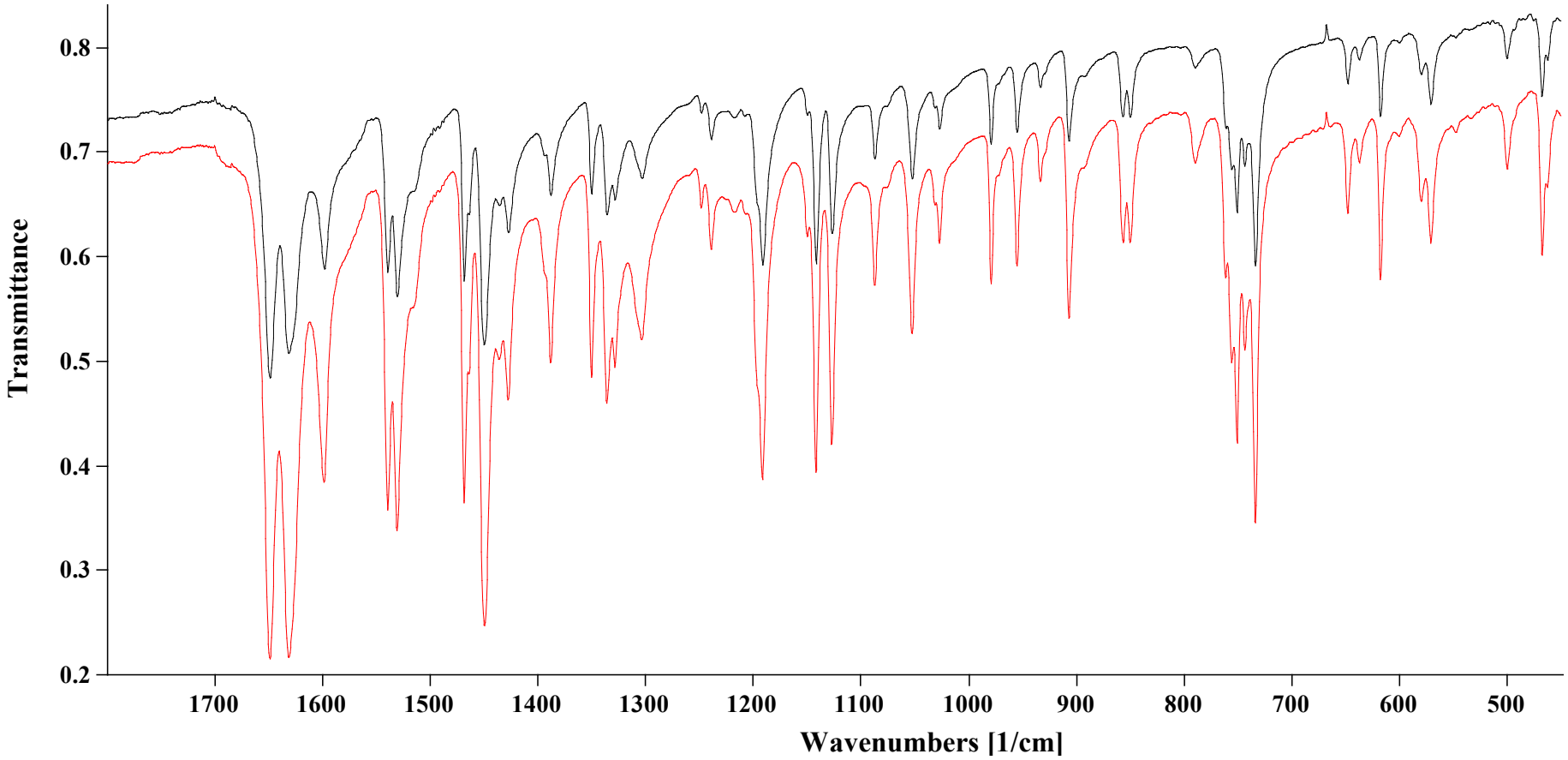

Figure S38: Comparison of the expanded fingerprint regions of the solid state IR spectra of Cu(salen) obtained through conventional solution based method (black) and mechanochemical method, **8**, (red).

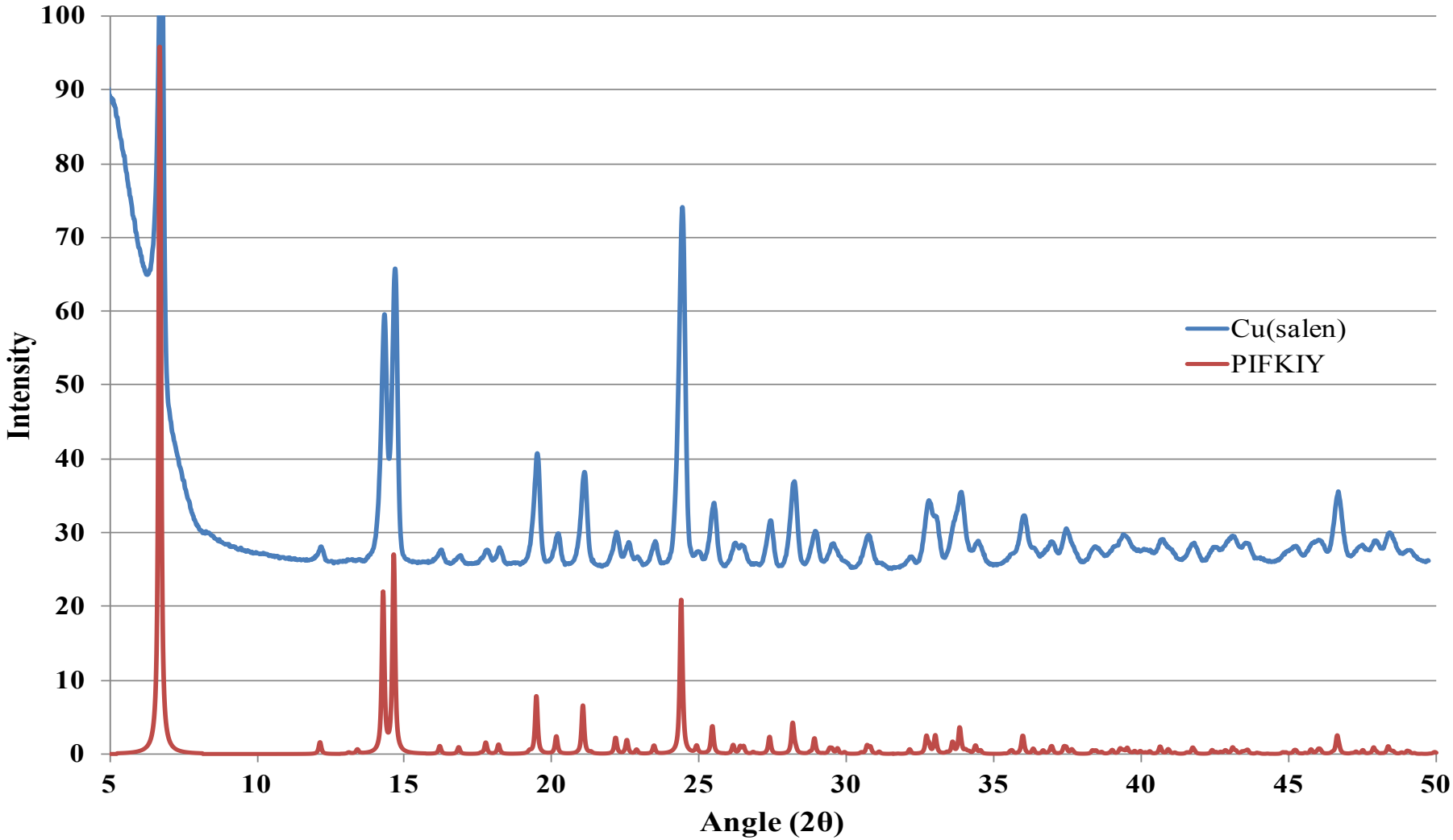

Figure S39: X-Ray powder diffraction spectra of Cu(salen), **8**, obtained mechanochemically and the simulated pattern from the Cambridge Structural Database (CSD code PIFKIY).

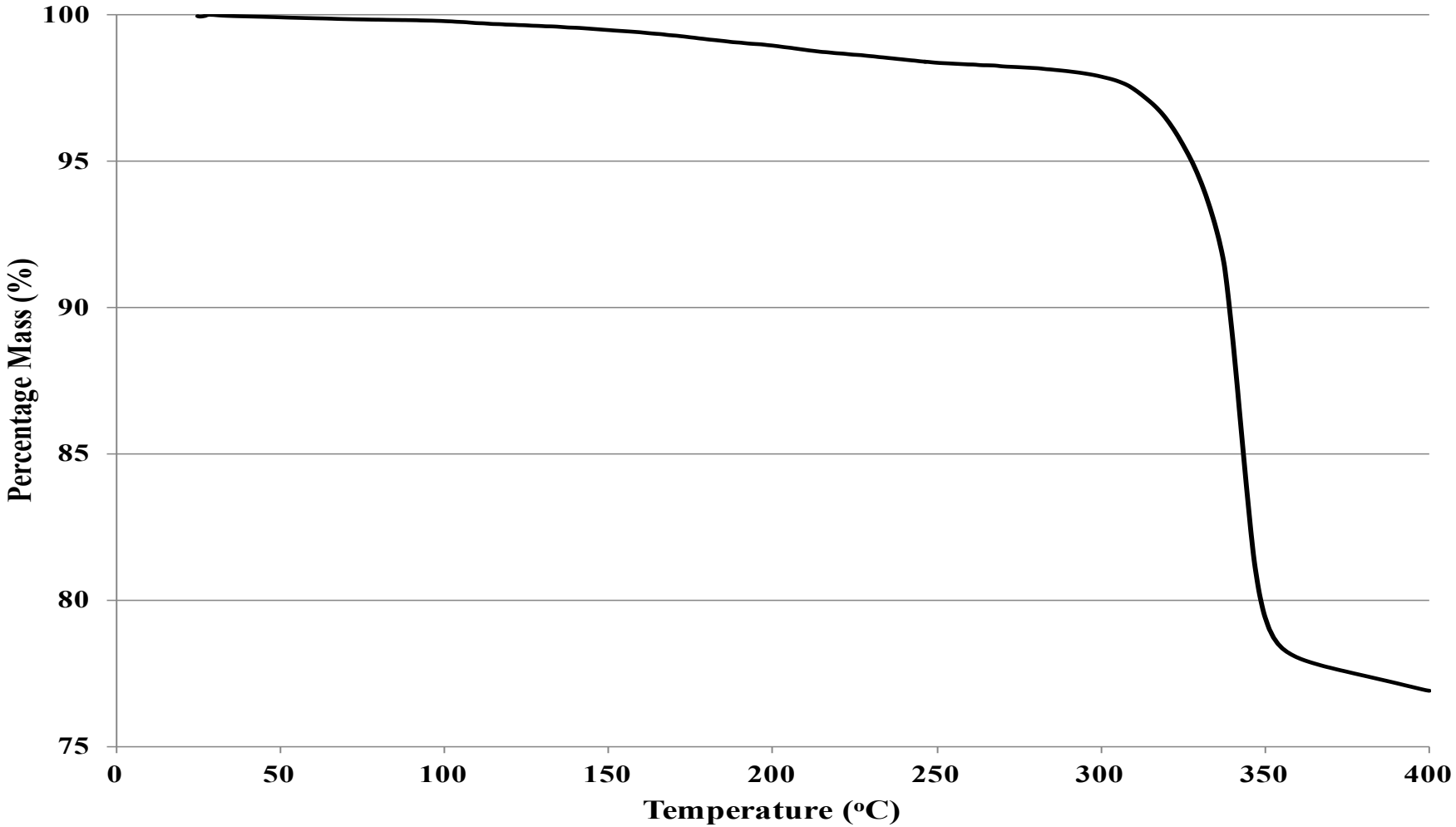

Figure S40: Thermogravimetric analysis of Cu(salen), **8**, obtained from a two-step telescoped mechanochemical reaction showing ≈1.3% mass loss at 175°C which is equivalent to 1/3 molecule of H_2O per molecule of complex.

Table ST8: Elemental analysis of Cu(salen) from both conventional solution state synthesis and mechanical methods (compound **8**).

Element	**C**	**H**	**N**
Theoretical %	**58.26**	**4.28**	**8.49**
Solution %	**58.77**	**4.06**	**8.73**
Mechanochemical %	**57.30**	**4.14**	**8.63**

'All in one' 2,2'-[1,2-ethanediylbis[(*E*)nitrilomethylidyne]]-bis[phenolato]-κN,N',O,O'-zinc(II); (compound 9):

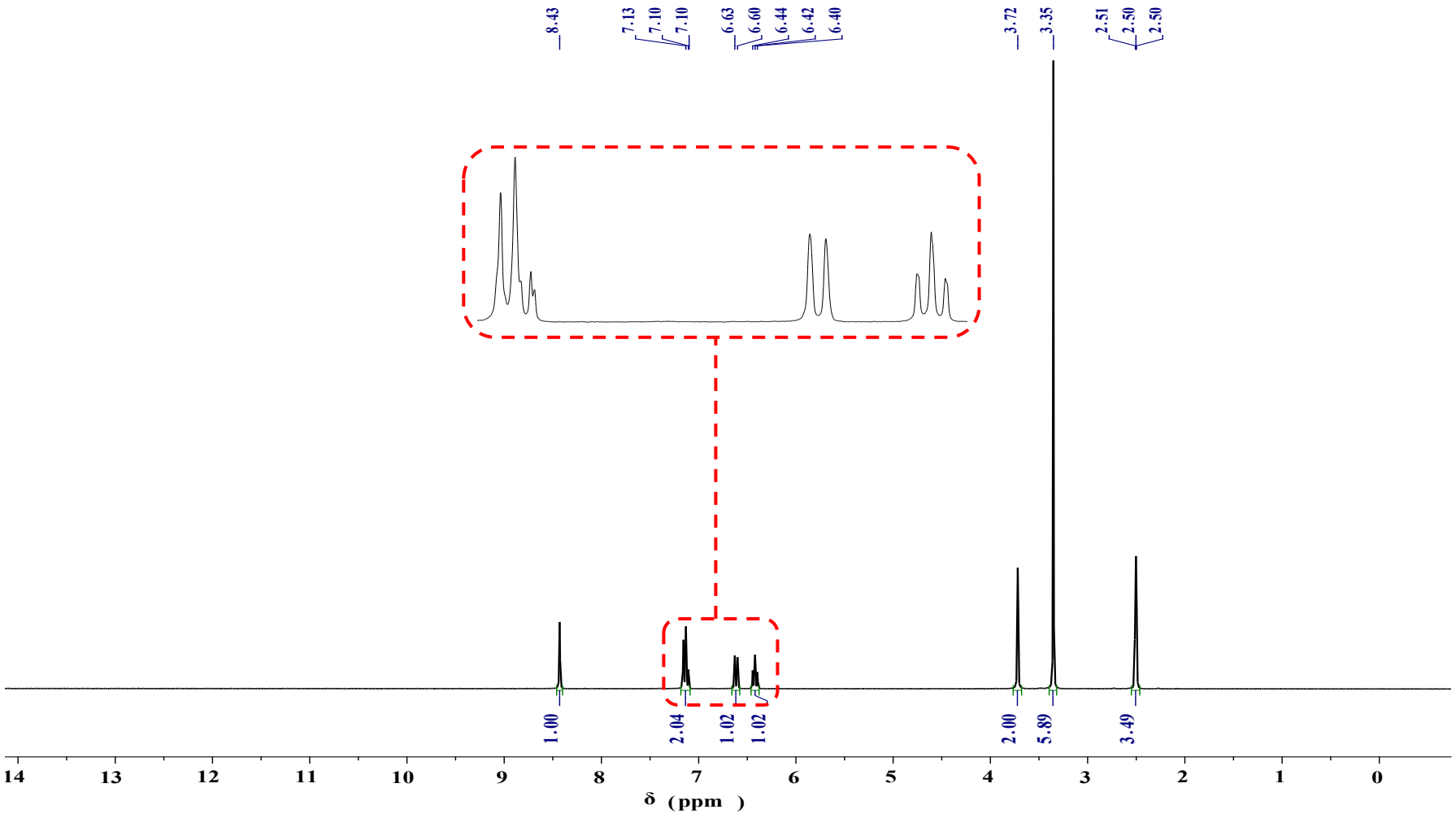

Figure S41: Solution state (d^6-DMSO) ^{1}H NMR spectrum of Zn(salen), **6'**, from tandem mechanochemical synthesis.

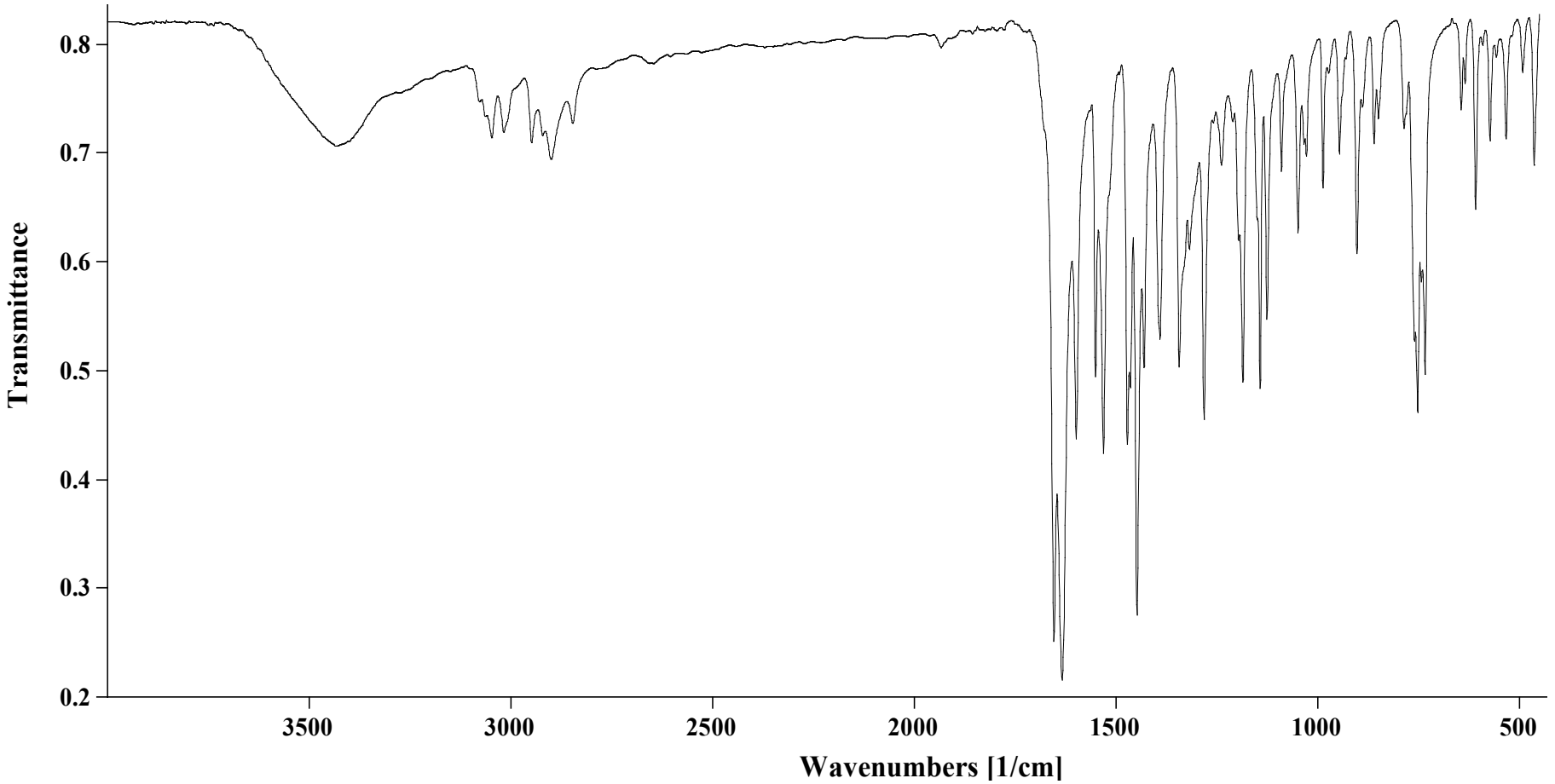

Figure S42: Solid state IR (KBr disc) spectrum of Zn(salen), **6'**, obtained from tandem mechanochemical synthesis.

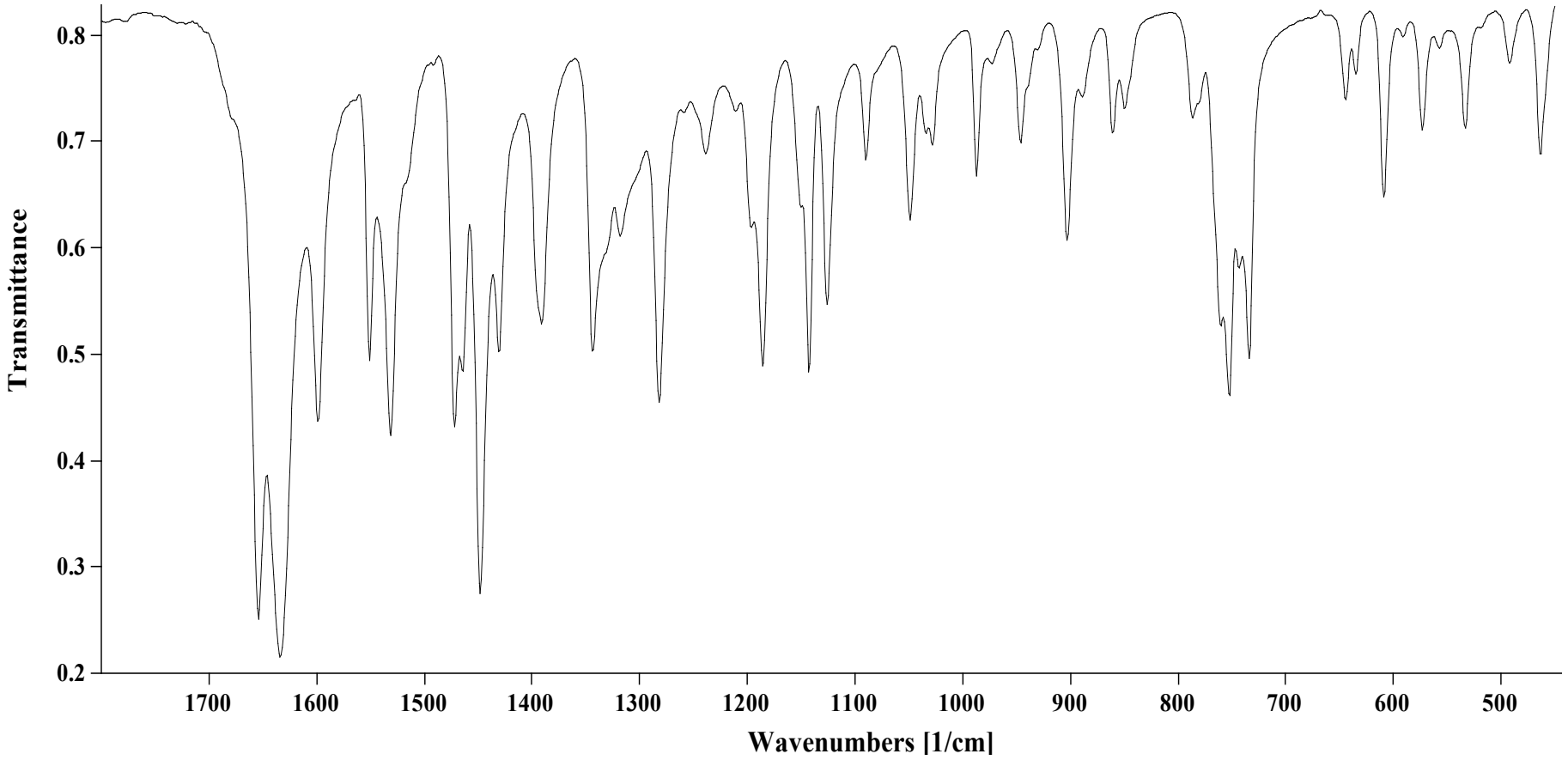

Figure S43: Expanded fingerprint region of the solid state IR spectrum of Zn(salen), **6'**, obtained from tandem mechanochemical synthesis.

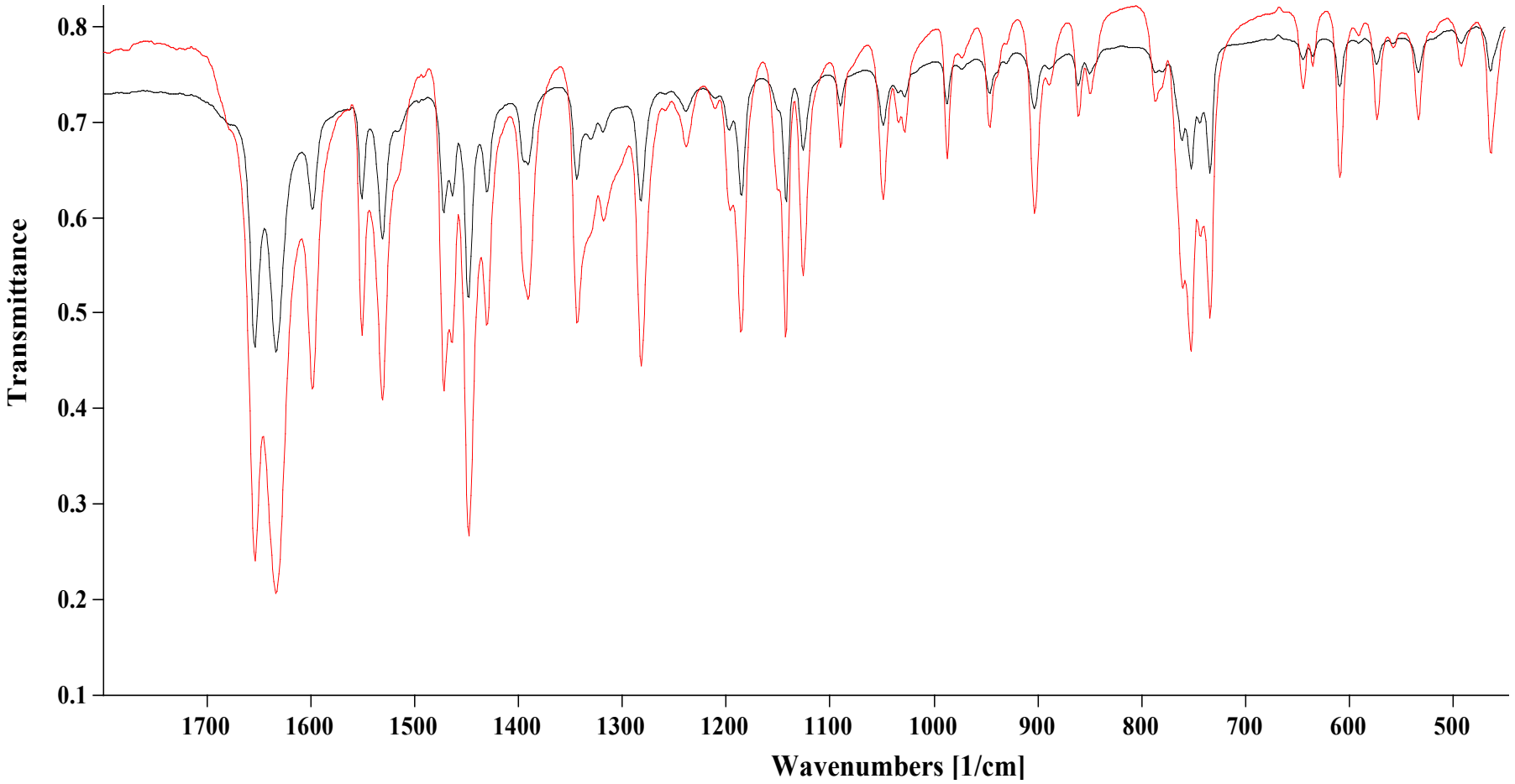

Figure S44: Comparison of the expanded fingerprint regions of the solid state IR spectra of Zn(salen) obtained through conventional solution based techniques (black) and tandem mechanochemical synthesis, **6'**, (red).

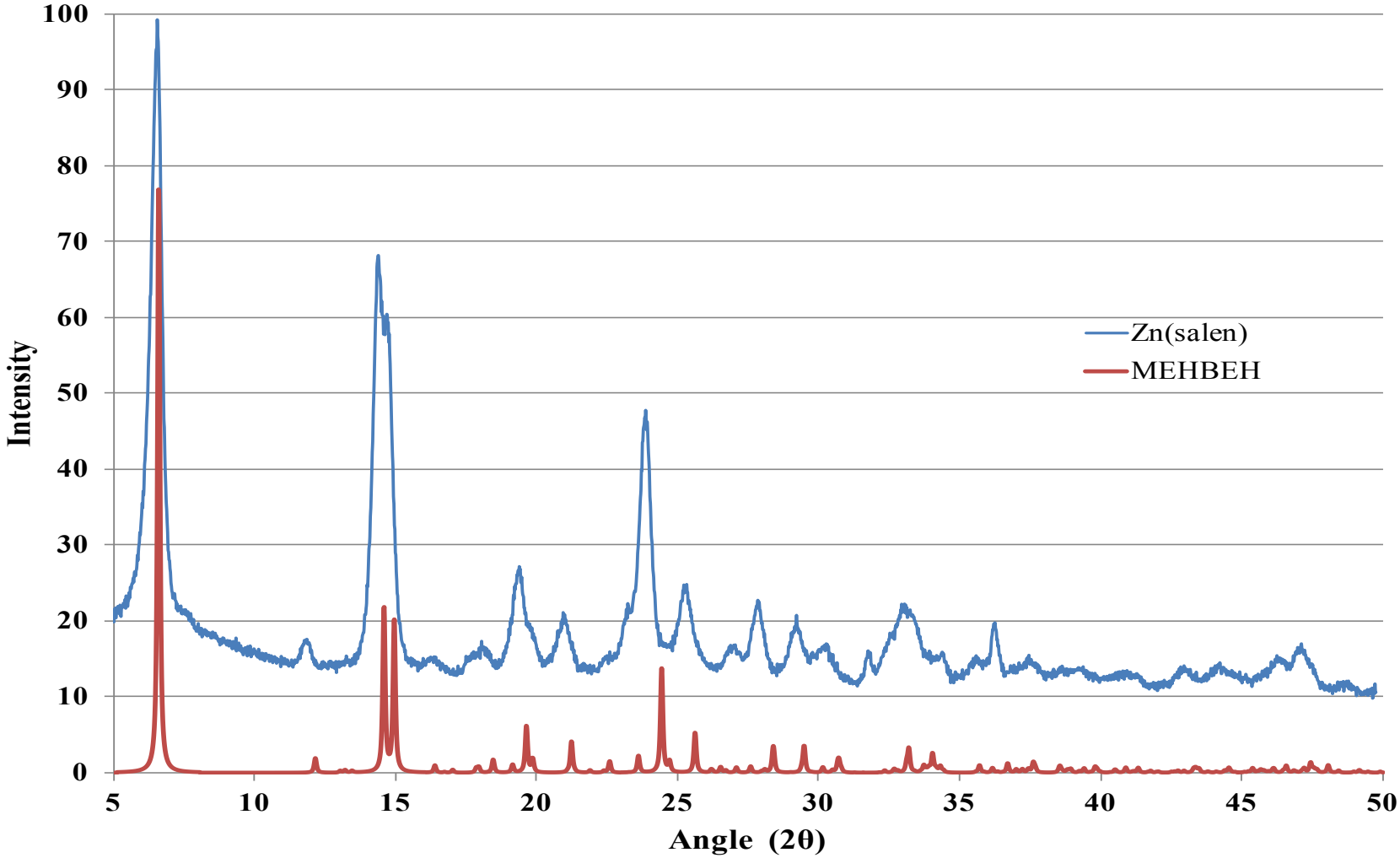

Figure S45: X-Ray powder diffraction spectra of Zn(salen) obtained by tandem mechanochemical reaction, **6'**, and the simulated pattern from the Cambridge Structural Database (CSD code MEHBEH).

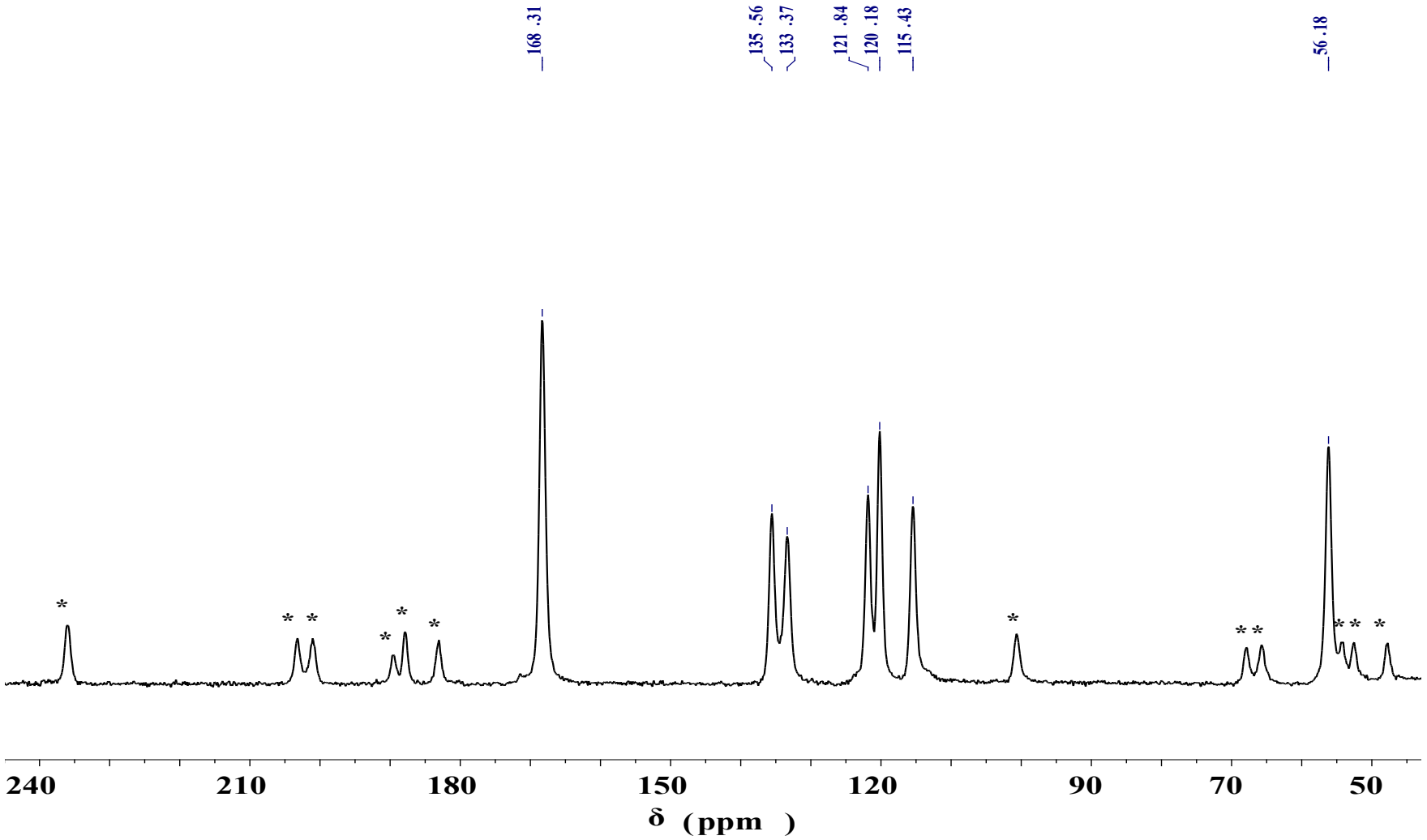

Figure S46: Solid state ^{13}C MAS NMR spectrum of Zn(salen), **6'**, obtained by tandem mechanochemical reaction. * represents a spinning side

band.

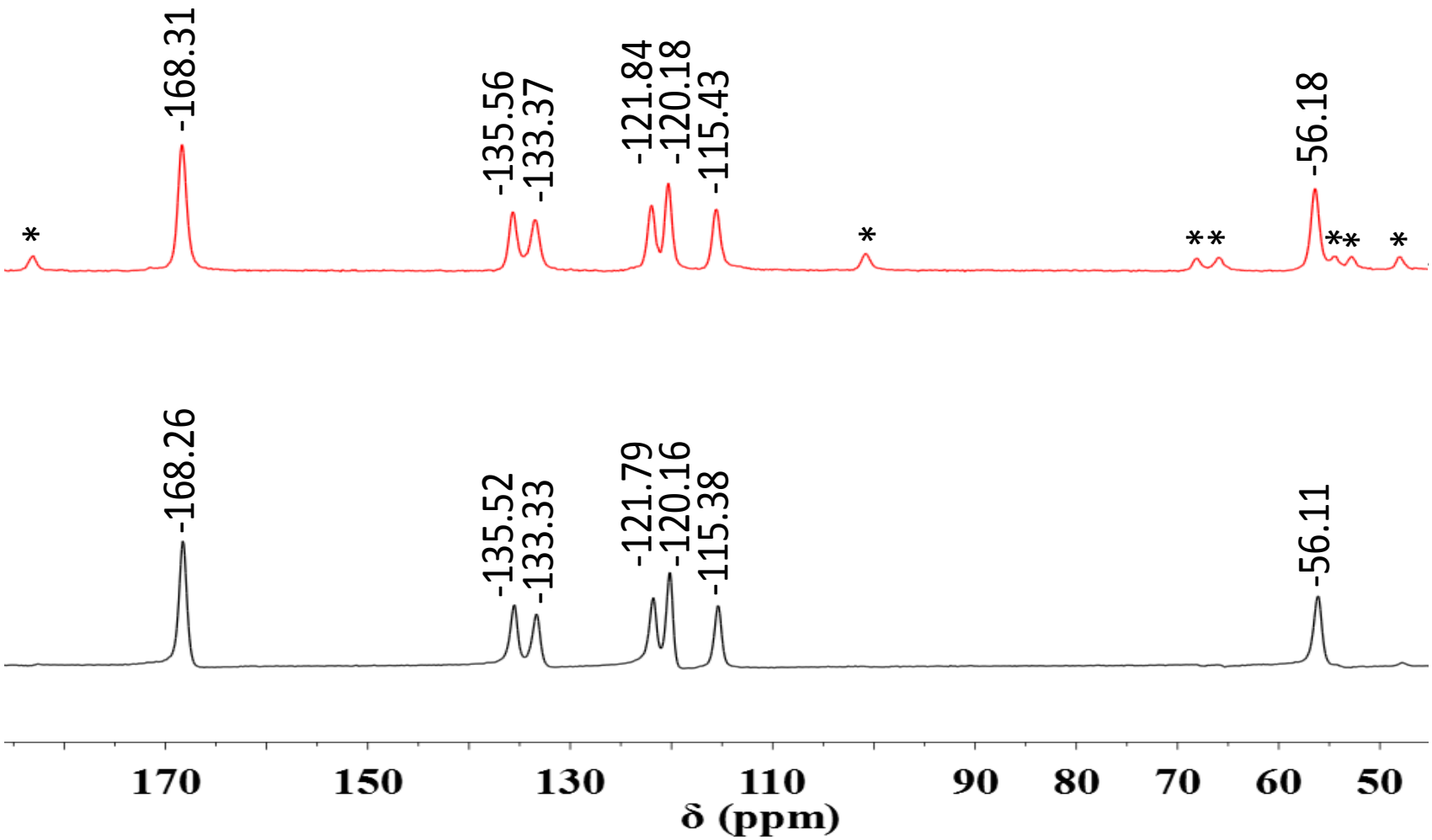

Figure S47: Comparison of ^{13}C SSNMR of Zn(salen) obtained from the tandem mechanochemical reaction, **6'**, (red) and the hydrated product from the two step mechanochemical reaction, **6**. * represents a spinning side band.

Table ST9: Elemental analysis of Zn(salen) from the tandem mechanical method (compound **6'**).

Element	**C**	**H**	**N**
Theoretical %	**57.94**	**4.25**	**8.45**
Mechanochemical %	**57.58**	**4.26**	**8.50**