Electronic Supplementary Information

Three routes to nickel(II) salicylaldehyde 4-phenyl and 4-methylthiosemicarbazonato complexes: mechanochemical, electrochemical and conventional approach

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Content:

Figure S1. ORTEP view of the asymmetric unit of **2** with atom-labelling scheme. The displacement ellipsoids are drawn at the 50 % probability level at 296(2) K. Intramolecular and one intermolecular hydrogen bond with CH_3OH solvent of crystallization are represented by dashed lines.

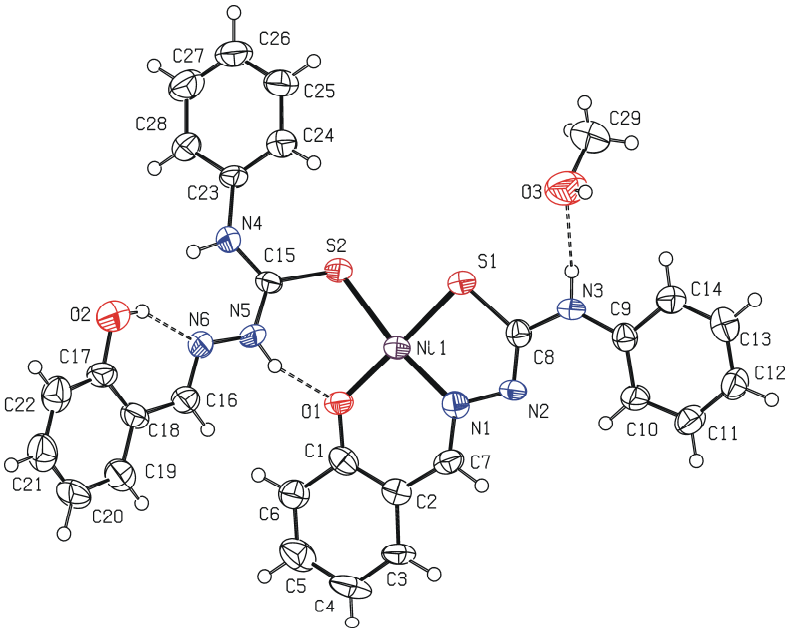
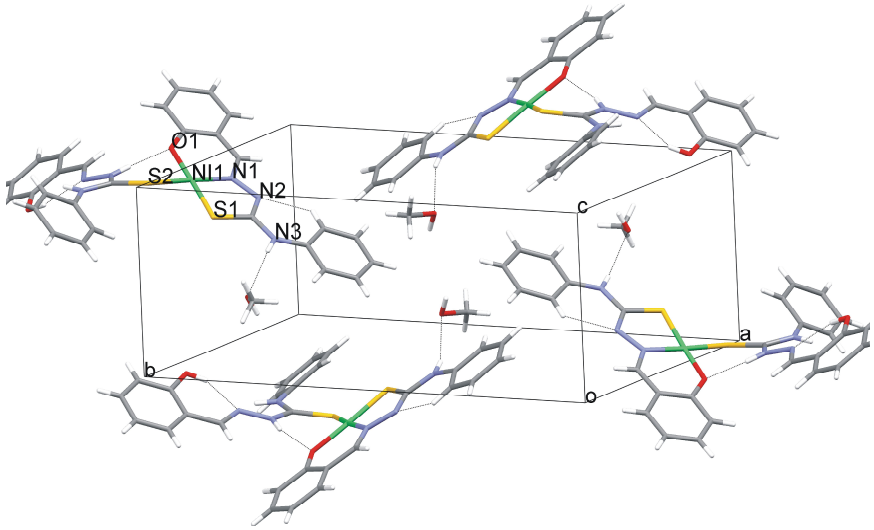
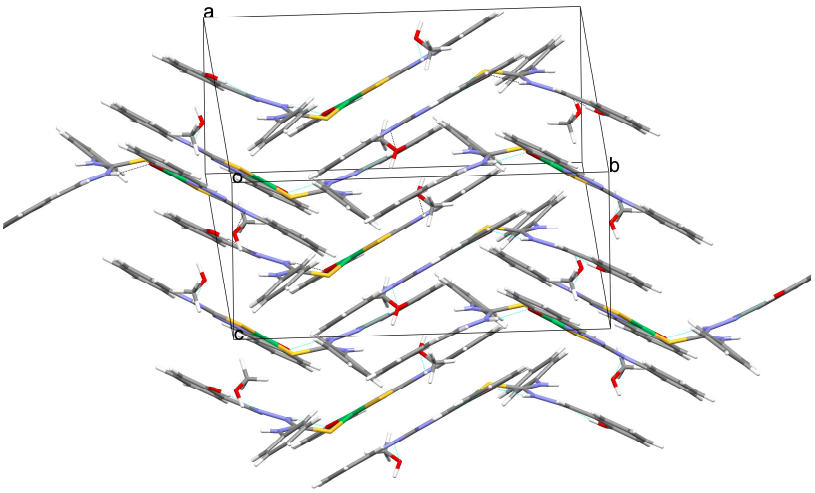


Figure S2. a) Packing arrangement of **2** b) Packing arrangement of **2** showing spreading molecules along *c* axis by N4-H4N···O3 intermolecular hydrogen bond with the methanol oxygen O3 atom.

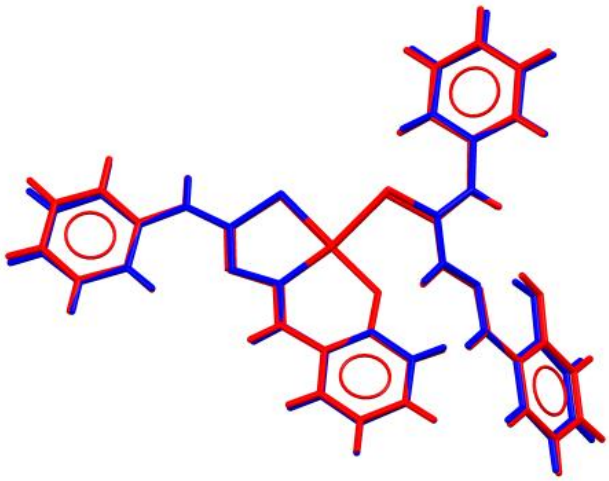


(a)



(b)

Figure S3. Overlaying* molecular structures of **2** (in blue) and [Ni(4-Phtsc-sal)(4-Phtsc-salH$_2$)]·H$_2$O[1] (in red)



*Isostructurality of two crystal structures can be established on the basis of several parameters: a) molecules should not differ substantially in their structure, *i.e.* they should be isometric (the inspected two structures differ in solvent molecules; H_2O *vs.* MeOH); b) similar crystal packing patterns should be approved by overlaying of molecular structures (Fig. S3) although there are differences in occurrence of weak hydrogen bonds; c) unit-cell similarity index should be close to zero; d) comparison of powder patterns should indicate unit-cell similarity.

The unit-cell similarity index Π calculated for structures **2** and [Ni(4-Phtsc-sal)(4-Phtsc-salH$_2$)]·H$_2$O[1] according to formula given in ref. 2 amounts 0.0151 (ideal value is zero).

[1] V. V. Bon, S. I. Orysyk, V. L. Pekhuyo and S. V. Volkov, J. Mol. Struct. 2010, **984**, 15.
[2] L. Fábián, A. Kálmán, Acta Crystallogr., Sect. B 1999, **55**, 1099.

Figure S4. a) Packing arrangement of **3** and b) Packing arrangement of **4**

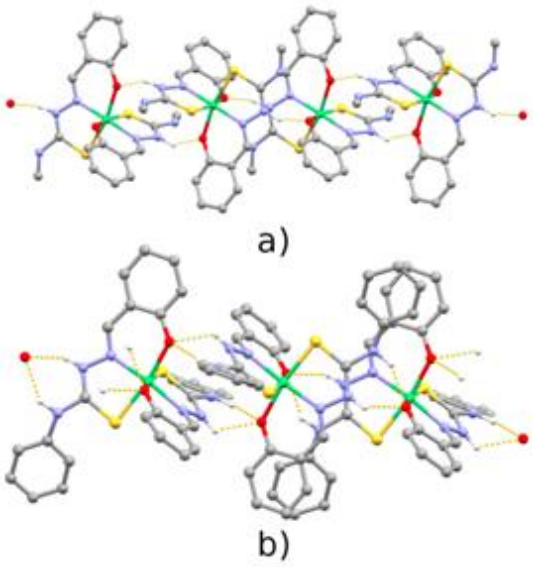


Table S5. General and Crystallographic data for compound **2**.

	2
Condensed formula	[Ni(4-Phtsc-sal)(4-Phtsc-salH$_2$)] × CH$_3$OH
Chemical formula	$C_{29}H_{28}N_6NiO_3S_2$
M_r	631.40
Crystal system, color and habit	monoclinic, red needle
Crystal dimensions (mm^3)	0.62 × 0.21 × 0.19
Space group	*P* 2$_1$/*c*
Z	4
Unit cell parameters:	
a (Å)	19.386(2)
b (Å)	18.7538(17)
c (Å)	7.9689(13)

β (°)	99.188(13)
V (Å^3)	2860.1(6)
T (K)	296(2)
Reflections collected, unique, R_{int}, observed [I Ó2σ(I)]	16245, 5004, (0.1451) , 2976
R_1[a] [I Ó2σ(I)]	0.0914
wR_2[b] (all data)	0.1926
Goodness of fit on F^2, S[c]	1.085
Max., min. electron density (e Å$^{ï 3}$)	0.597, –0.649

[a] $R = \Sigma||F_o|$ ï $|F_c||/\Sigma|F_o|$; [b] $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$; [c] $wR = \{\Sigma[w(F_o^2$ ï $F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S6. Selected bond distances and angles (Å,°) for **2**.

Bond distances			
Ni1- O1	1.858(5)	N1-N2	1.393(8)
Ni1- N1	1.871(6)	N2-C8	1.295(9)
Ni1- S1	2.139(2)	N3-C8	1.368(9)
Ni1- S2	2.234(2)	N3-C9	1.402(9)
S1-C8	1.744(7)	N4-C15	1.333(9)
S2-C15	1.712(7)	N4-C23	1.414(9)
O1-C1	1.308(9)	N5-C15	1.323(9)
O2-C17	1.348(10)	N5-N6	1.369(8)
N1-C7	1.308(10)	N6-C16	1.302(10)
Bond angles			
O1-Ni1-N1	94.5(2)	O1-Ni1-S2	93.26(16)

O1-Ni1-S1	178.08(18)	N1-Ni1-S2	170.89(19)
N1-Ni1-S1	86.8(2)	S1-Ni1-S2	85.59(8)

Table S7. Hydrogen bonding and interaction geometry (Å,º) for compound **2**.

Dï H···A	Dï H	H···A	D···A	∠Dï H···A	Symmetry code
O2-H1O2···N6	0.83(2)	1.92(8)	2.664(8)	149(6)	-
N3-H3N···O3	0.86	2.22	3.004(9)	151	-
N5-H5N···O1	0.86	1.87	2.664(7)	154	-
N4-H4N···O3	0.86	2.91	3.66(1)	147	x,–y+3/2,+z–1/2
O3-H1O3···O2	0.82(2)	2.64(1)	3.11(1)	118(8)	x, –y+3/2,+z+1/2
C10-H10···N2	0.93	2.28	2.88(1)	122	-
C14-H14···O3	0.93	2.82	3.51(1)	132	-
C6-H6···O1	0.93	2.98	3.57(1)	123	x,–y+3/2,+z–1/2
C28-H28···O3	0.93	2.80	3.39(1)	122	x,–y+3/2,+z–1/2

Table S8. Geometrical parameters of π···π interactions[a] (Å, °) for compound **2**.

Interaction[b]	C_g-C_g distance	C_g···P1[b]	C_g···P2[d]	α[e]	β[f]	Slippage
Cg4···Cg5[i]	3.652(5)	3.324	3.371	2.18	22.64	1.406
Cg5···Cg4[ii]	3.653(5)	3.371	3.324	2.18	24.49	1.514

[a]Those possible interactions for which perpendicular distance between two planes is longer than 3.8 Å (3.3 - 3.8 Å) (C_g···P1 and C_g···P2; the perpendicular distance of corresponding centroid to a plane) and dihedral angles (between P1 and P2) larger than 20° are not taken into account. The calculated slippage on the basis of Cg...Cg distances as well as the value of the angle between Cg...Cg vector and vertical line on corresponding plane has been taken into account as one of the geometrical criteria, too (approx. 1.5 Å for π···π stacking interactions).
[b]Rings Cg4 and Cg5 are defined by the atoms C9, C10, C11, C12, C13 and C14; C17, C18, C19, C20, C21, C22 in **1**, respectively.
[c,d]C_g···P1 (or P2) is the perpendicular distance of corresponding centroid to a plane. Planes P1 or P2 are defined by the atoms, which define the corresponding centroids; [e]dihedral angles between P1 and P2; [f]β is the angle between Cg···Cg vector and vertical line on corresponding plane. Symmetry codes: i = x,3/2-y,1/2+z, ii = x,3/2-y,1/2+z.

Table S9. General and Crystallographic data for compounds (**3**) and (**4**)

Compound	**3**	**4**
Molecular formula	$C_{18}H_{20}N_6NiO_2S_2$	$C_{28}H_{24}N_6NiO_2S_2$
Formula weight (g mol^{-1})	475.23	599.36
Space group	*Pbcn*	*C*2/*c*
a / Å	19.790(1)	11.8765(5)
b / Å	8.3659(3)	22.538(1)
c / Å	11.7972(4)	10.7802(5)
α / °		
β / °		116.174(3)
γ / °		
V / Å^3	1953.1(1)	2589.6(2)
Z	4	4
Calc. density (g cm^{-3})	1.616	1.537
Temperature (K)	293	293
Wavelength (Å)	1.5406	1.5406
R_{exp} (%)*	2.21	2.747
R_p (%)*	0.0318	0.0349
R_{wp} (%)*	0.0411	0.0448
*Gof**	1.86	1.63
$R(F^2)$ (%)*	0.0186	0.0162
Starting angle (° 2θ)	5	5
Final angle (° 2θ)	68	65
Step width (° 2θ)	0.0853	0.00853
Scan time (h)	~12	~12
No. of variables	100	96

Figure S10. Final Rietveld plot for compound **3** prepared by liquid-assisted grinding.

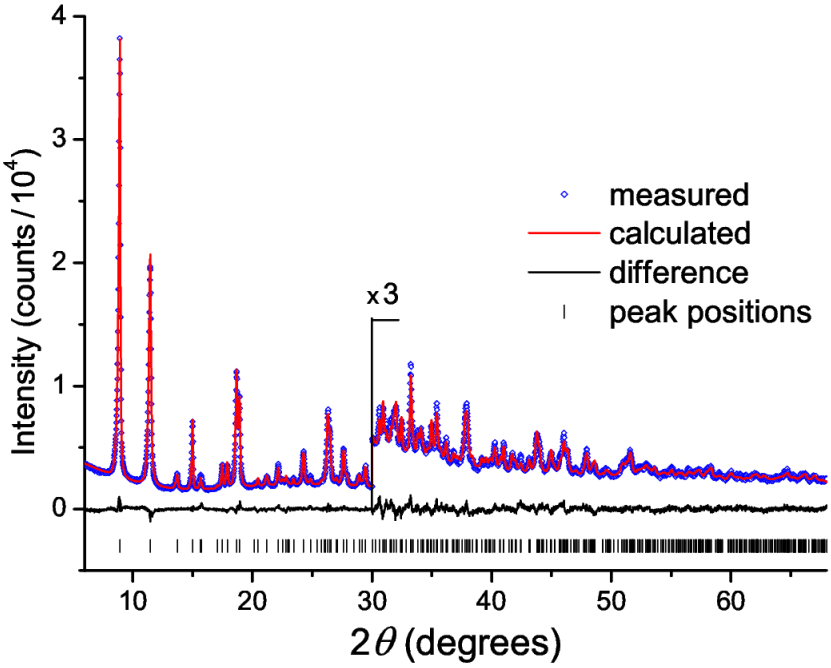
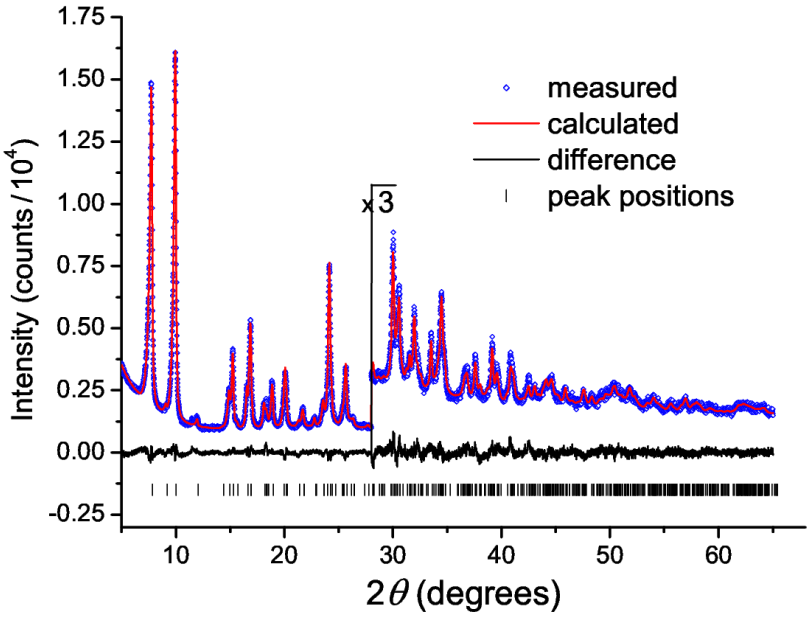


Figure S11. Final Rietveld plot for compound (**4**) prepared by liquid-assisted grinding.



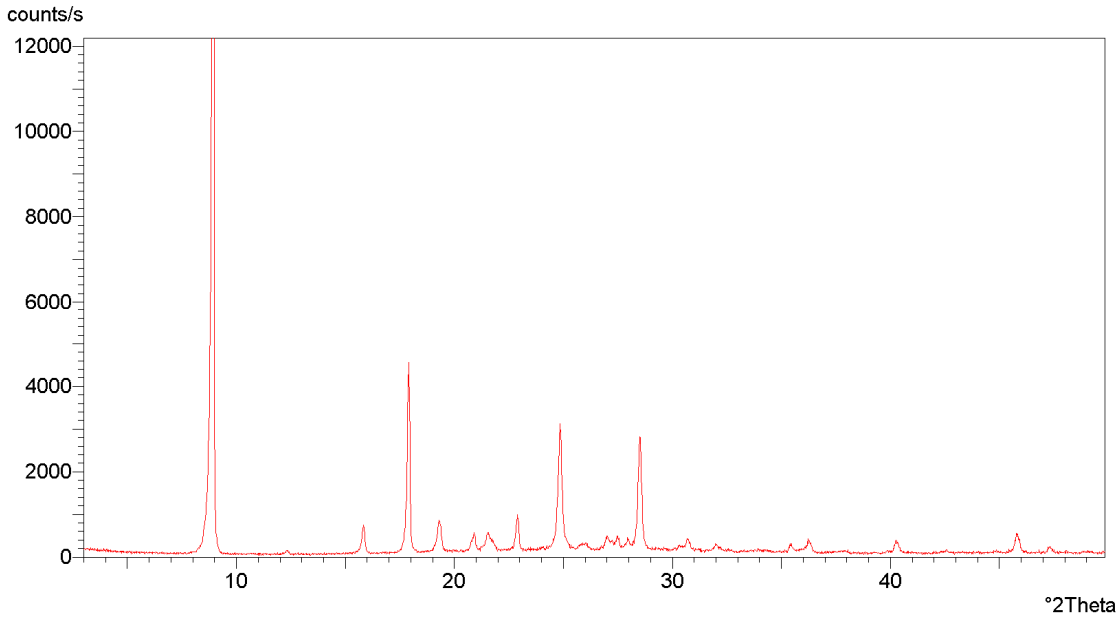


Figure S12. X-ray powder diffraction pattern of salicylaldehyde 4-methylthiosemicarbazone.

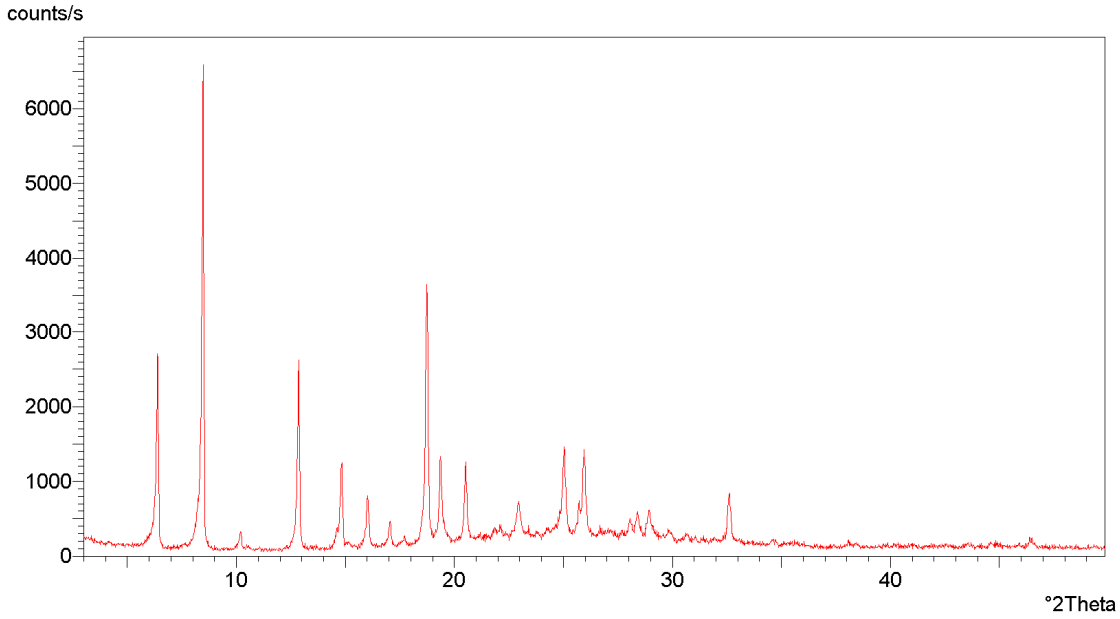


Figure S13. X-ray powder diffraction pattern of compound salicylaldehyde 4-phenylthiosemicarbazone.

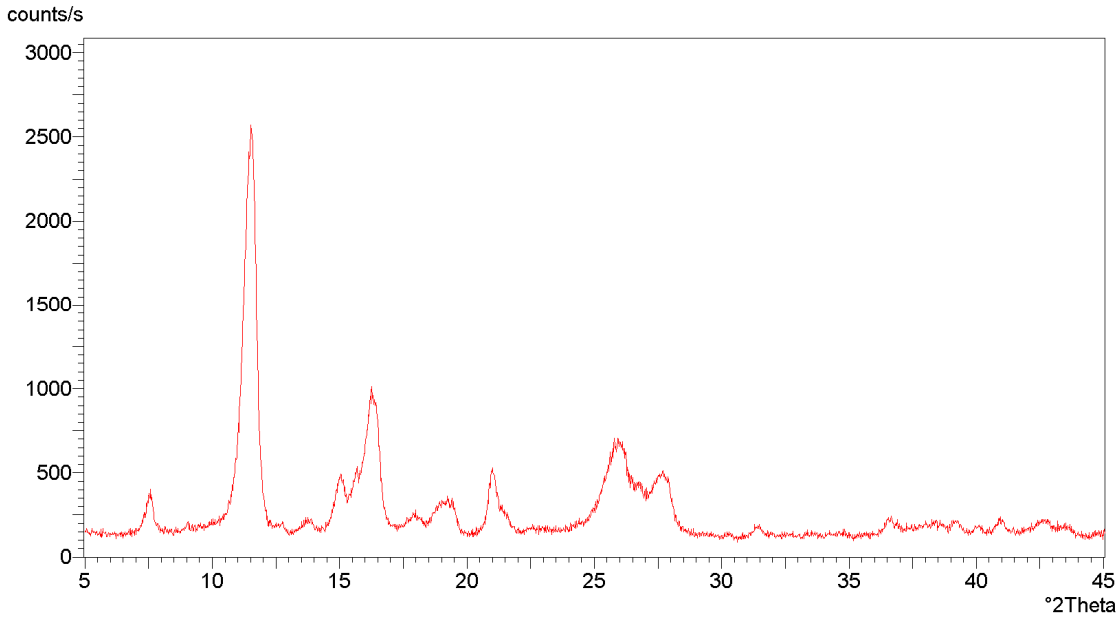


Figure S14. X-ray powder diffraction pattern of compound **1** prepared by solution-based method.

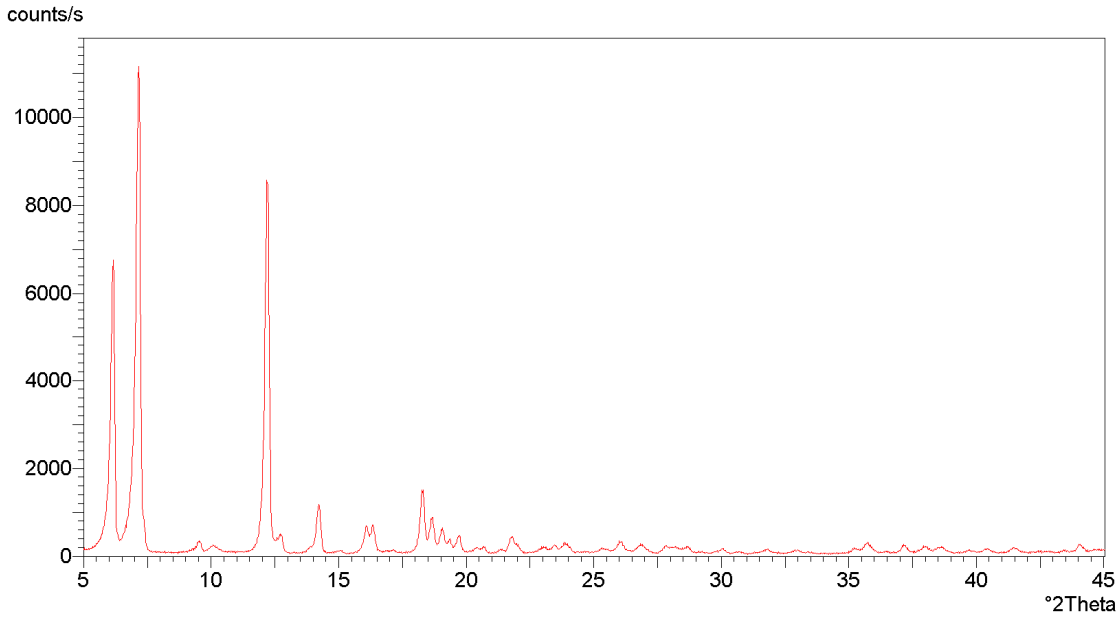


Figure S15. X-ray powder diffraction pattern of compound **2** prepared by solution-based method.

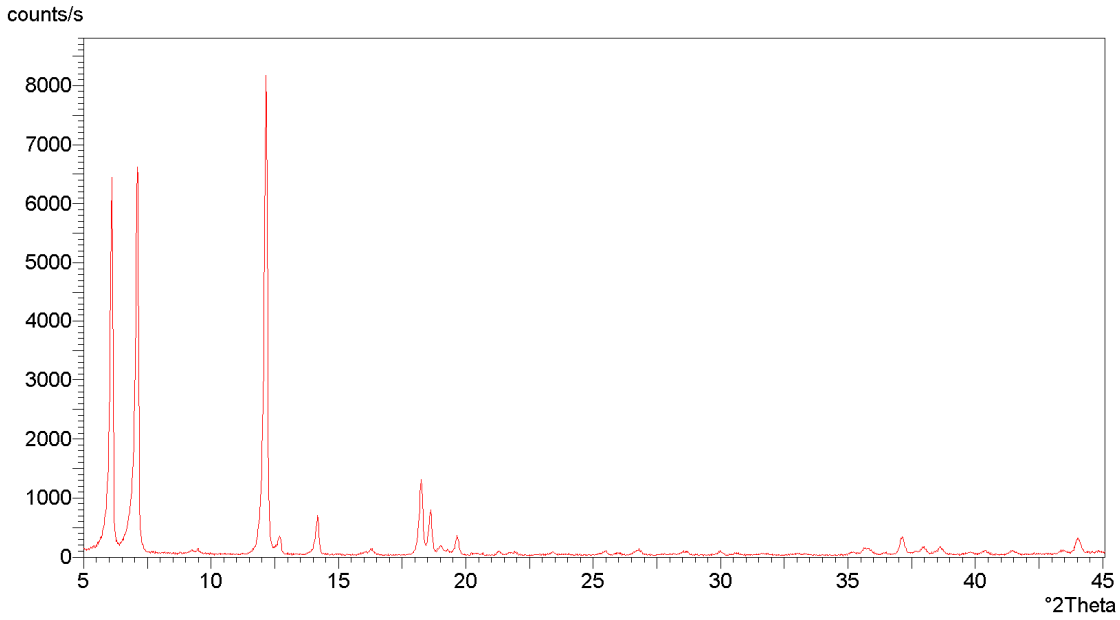


Figure S16. X-ray powder diffraction pattern of compound **2** prepared by electrochemical method.

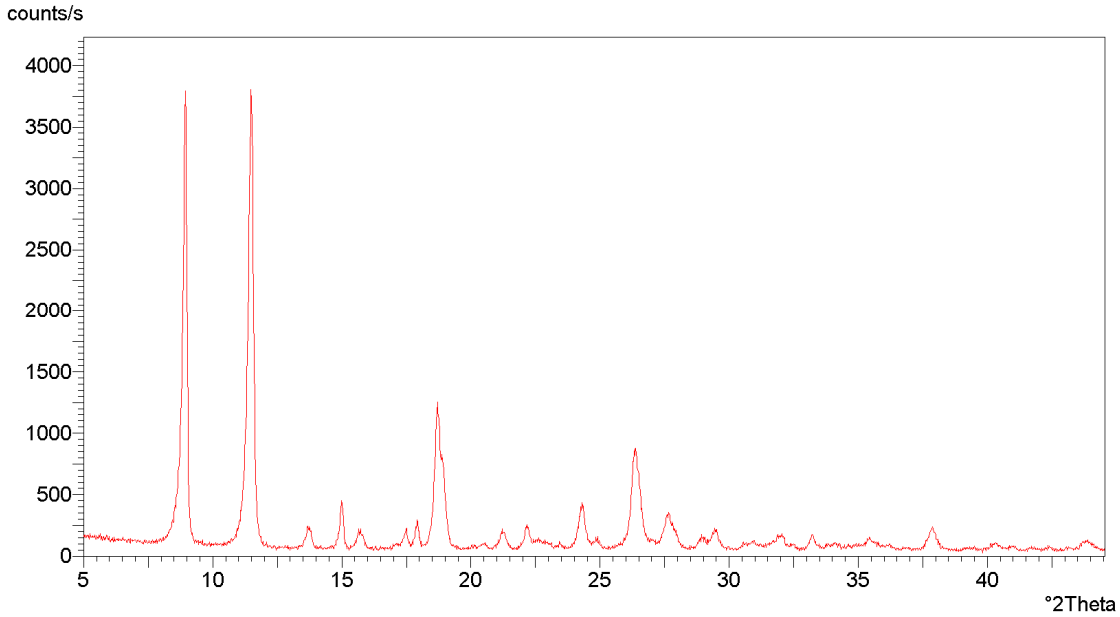


Figure S17. X-ray powder diffraction pattern of compound **3** prepared by electrochemical method.

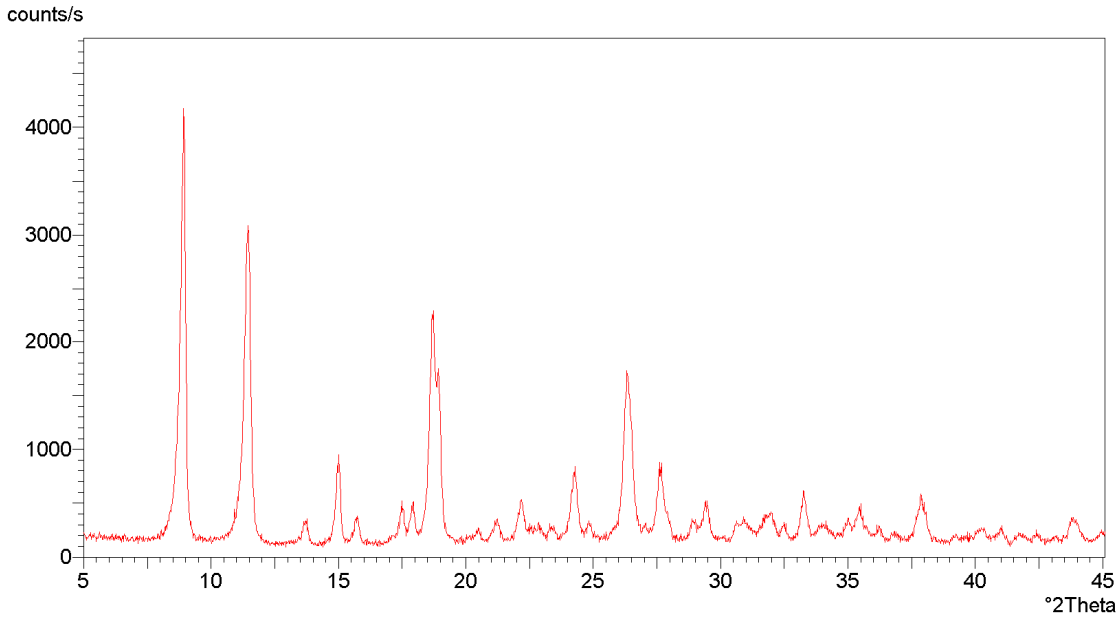


Figure S18. X-ray powder diffraction pattern of compound **3** prepared by liquid-assisted grinding.

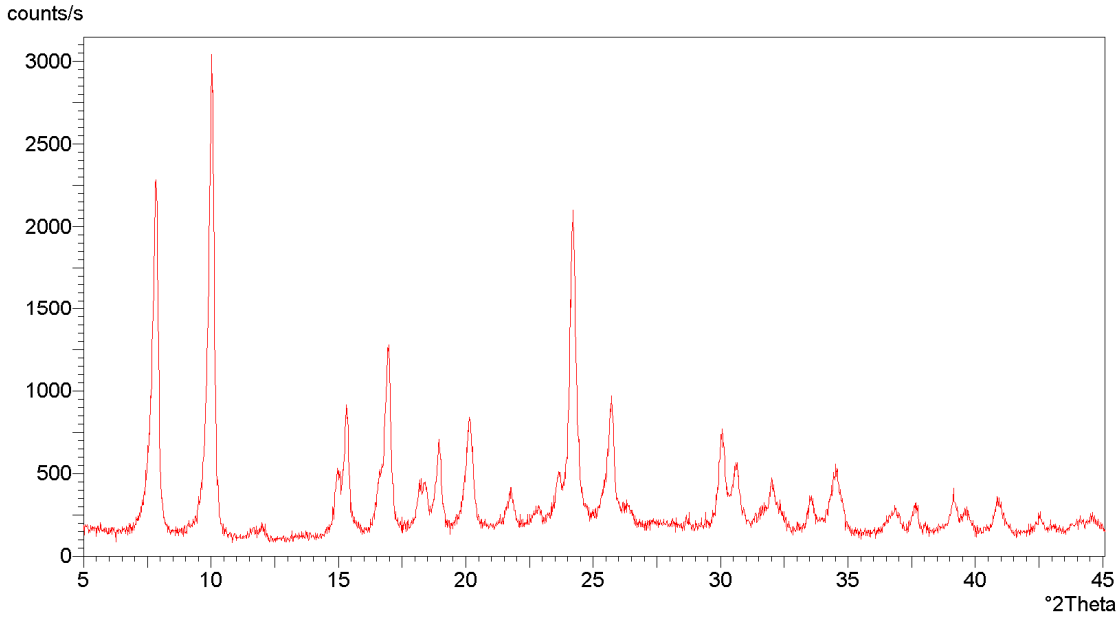


Figure S19. X-ray powder diffraction pattern of compound **4** prepared by liquid-assisted grinding.

Figure S20. The atom numbering of 4-phenylthiosemicarbazone used in the assignment of NMR resonances

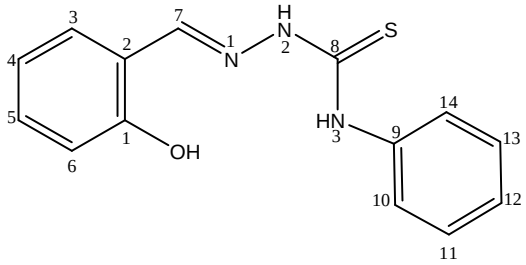


Table S21. Calculated Gibbs energies of conformers at the B3LYP/6-311++g (d, p) level (relative to the CS conformer)

Charge -2	$\frac{\Delta_r G}{\text{kcal mol}^{-1}}$	in CH_3OH	$\frac{\Delta_r G}{\text{kcal mol}^{-1}}$
Methyl TS	27.76	Methyl TS	22.32
Methyl SC	10.55	Methyl SC	3.71
Phenyl TS	30.64	Phenyl TS	25.34
Phenyl SC	11.17	Phenyl SC	3.24