

Supplementary Information

Anti-Le-Chatelier spin transition in a wine-rack supramolecular lattice with colossal anisotropic response

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Supplementary Table 1. Crystal data for 1·2MeOH.

<i>T</i> (K)	120
Empirical formula	C ₃₆ H ₂₈ N ₁₂ O ₂ F ₆ Fe
<i>Mr</i>	830.55
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> (Å)	12.7730(3)
<i>b</i> (Å)	9.9855(3)
<i>c</i> (Å)	28.7032(8)
<i>V</i> (Å ³)	3660.9(2)
<i>Z</i>	4
<i>D_c</i> (mg cm ⁻³)	1.507
<i>F</i> (000)	1696
μ (Mo-K α) (mm ⁻¹)	0.495
Crystal size (mm)	0.03 × 0.04 × 0.05
No. of total reflections	4002
No. of reflections [<i>I</i> > 2 σ (<i>I</i>)]	3227
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0436
<i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.1036
<i>S</i>	1.191

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

$$w = 1 / [\sigma^2(F_o^2) + (m P)^2 + n P] \text{ where } P = (F_o^2 + 2F_c^2) / 3; m = 0.0358; n = 4.3683$$

Supplementary Table 2. Crystal data for 1 in the LS and HS states.

<i>T</i> (K)	220 (LS)	317 (HS)
Empirical formula	C ₃₄ H ₂₀ N ₁₂ F ₆ Fe	
<i>Mr</i>	766.47	
Crystal system	orthorhombic	
Space group	<i>Pbcn</i>	
<i>a</i> (Å)	12.67660(10)	12.8539(2)
<i>b</i> (Å)	10.21388(13)	9.5164(2)
<i>c</i> (Å)	25.1175(3)	27.1630(5)
<i>V</i> (Å ³)	3252.15(6)	3322.65(11)
<i>Z</i>	4	
<i>D_c</i> (mg cm ⁻³)	1.56537	1.53215
Radiation Type	Synchrotron	
Wavelength (Å)	0.72979	
<i>R_p</i> (%)	2.02	1.82
<i>R_{wp}</i> (%)	2.26	2.22
<i>R_{exp}</i> (%)	0.68	0.68
GOF	3.31	3.26
<i>R_B</i> (%)	2.51	1.79

Supplementary Table 3. Key bond lengths, angles, and geometric details related to the FeN₆ coordination core.

Bond lengths (Å)	1·2MeOH (HS)	1 (HS)	1 (LS)
Fe1-N1	2.239(2)	2.273(8)	1.997(5)
Fe1-N2	2.139(2)	2.132(9)	1.898(6)
Fe1-N3	2.142(2)	2.014(12)	1.937(9)
Bond angles (°)			
N(1)-Fe-N(3)	72.18(7)	81.5(4)	78.2(4)
N(1)-Fe-N(3')	105.43(7)	92.3(4)	97.5(4)
N(1)-Fe-N(4)	91.32(7)	87.3(3)	82.8(4)
N(1)-Fe-N(4')	147.33(7)	161.3(5)	155.7(6)
N(3)-Fe-N(4)	75.17(7)	79.9(6)	77.6(7)
N(3)-Fe-N(4')	107.14(7)	106.4(6)	106.8(7)
N(3)-Fe-N(3')	176.57(7)	170.9(7)	173.2(6)
Geometrical parameters			
<Fe-N> ^{av} (Å)	2.173	2.140	1.944
V _{FeN₆} (Å ³)	12.6	12.2	9.4
Σ (°)	148.6	141.7	91.5
Θ (°)	487.3	348.0	267.0
α (°)	91.5	98.8	92.6

Supplementary Table 4. Intermolecular interactions for 1·2MeOH: close contacts smaller than the sum of the Van der Waals radii.

Interact.	Length/Å	Length-VdW/Å	Symm. op. 1	Symm. op. 2	Code Int.
H2...C13	2.736	-0.164	x,y,z	1-x,-1+y,1.5-z	(A)
H2...C12	2.837	-0.063	x,y,z	1-x,-1+y,1.5-z	(A)
F2...F2	2.933	-0.007	x,y,z	1-x,2-y,1-z	(B)
C1...N5	3.239	-0.011	x,y,z	-1/2+x,-1/2+y,1.5-z	(C)
C1...H7	2.725	-0.175	x,y,z	-1/2+x,-1/2+y,1.5-z	(D)
H1...N5	2.304	-0.446	x,y,z	-1/2+x,-1/2+y,1.5-z	(C)
C9...H16	2.878	-0.022	1-x,y,1.5-z	-1/2+x,-1/2+y,1.5-z	(E)
C3...C6	3.388	-0.012	1-x,y,1.5-z	-1/2+x,-1/2+y,1.5-z	(F)
N6...O1	2.785	-0.285	x,y,z	x,y,z	(G)
N6...H1A	1.946	-0.804	x,y,z	x,y,z	(G)
H5...O1	2.443	-0.277	x,y,z	1/2+x,-1/2+y,1.5-z	(H)
H5...H1A	2.254	-0.146	x,y,z	1/2+x,-1/2+y,1.5-z	(I)
H3...O1	2.339	-0.381	x,y,z	1/2+x,-1/2+y,1.5-z	(J)

(A): pyrazole...4CF₃Ph; **(B):** 4CF₃Ph...4CF₃Ph; **(C):** H-bonding pyrazole...triazole; **(D):** pyrazole...pyridine; **(E):** triazole...4CF₃Ph; **(F):** π-π stacking pyrazole...pyridine; **(G):** strong H-bonding triazole...CH₃OH; **(H):** weak H-bonding pyridine...CH₃OH; **(I):** pyridine...CH₃OH; **(J):** weak H-bonding pyrazole...CH₃OH.

Supplementary Table 5. Intermolecular interactions for **1** (HS): close contacts smaller than the sum of the Van der Waals radii.

Interaction	Length	Length-VdW	Symm. op. 1	Symm. op. 2	Code Int.
H6...H6	2.398	-0.002	x,y,z	-x,y,1.5-z	(A)
H2...C12	2.757	-0.143	x,y,z	1-x,-1+y,1.5-z	(B)
H2...C13	2.703	-0.197	x,y,z	1-x,-1+y,1.5-z	(B)
C1...N5	3.171	-0.079	1-x,y,1.5-z	1/2-x,-1/2+y,z	(C)
C1...H7	2.625	-0.275	1-x,y,1.5-z	1/2-x,-1/2+y,z	(D)
H1...N5	2.257	-0.493	1-x,y,1.5-z	1/2-x,-1/2+y,z	(C)
H1...H16	2.314	-0.086	1-x,y,1.5-z	1/2-x,-1/2+y,z	(B)

(A): pyridine...pyridine; (B): pyrazole...CF₃Ph; (C): pyrazole...triazole; (D): pyrazole...pyridine.

Supplementary Table 6. Intermolecular interactions for **1** (LS): close contacts smaller than the sum of the Van der Waals radii.

Interaction	Length	Length-VdW	Symm. op. 1	Symm. op. 2	Code Int.
H2...C13	2.740	-0.160	x,y,z	1-x,-1+y,1.5-z	(A)
H2...C14	2.746	-0.154	x,y,z	1-x,-1+y,1.5-z	(A)
C2...F3	3.133	-0.037	x,y,z	x,1-y,-1/2+z	(A)
N6...F2b	2.989	-0.031	1-x,y,1.5-z	x,1-y,-1/2+z	(B)
C12...C13	3.313	-0.087	1-x,y,1.5-z	x,1-y,-1/2+z	(C)
F3...F3b	2.871	-0.069	1-x,y,1.5-z	x,2-y,-1/2+z	(C)
F3b...F3b	2.788	-0.152	1-x,y,1.5-z	x,2-y,-1/2+z	(C)
C1...N5	3.141	-0.109	1-x,y,1.5-z	1/2-x,-1/2+y,z	(D)
C1...H7	2.660	-0.240	1-x,y,1.5-z	1/2-x,-1/2+y,z	(E)
H1...N5	2.241	-0.509	1-x,y,1.5-z	1/2-x,-1/2+y,z	(F)
H1...H16	2.396	-0.004	1-x,y,1.5-z	1/2-x,-1/2+y,z	(G)

(A): pyrazole...CF₃Ph, (B): triazole...CF₃Ph, (C): CF₃Ph...CF₃Ph, (E) pyrazole...pyridine, (F) pyrazole...triazole, (G) pyrazole...CF₃Ph

Supplementary Table 7. Evaluated thermodynamic parameters of the **1** under pressure.

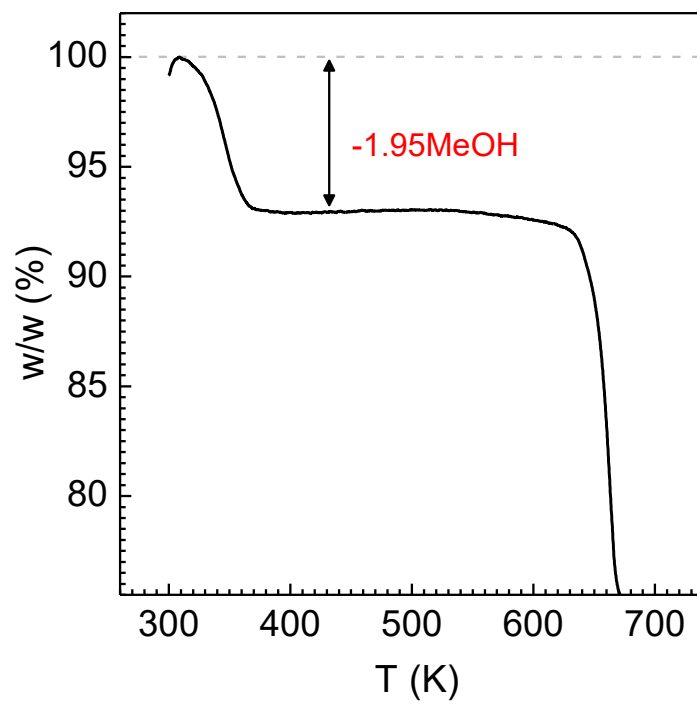
P (GPa)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔV (Å ³)	Δ _{elast} (J/mol)	Γ (J/mol)	Δ _{elast} -Γ+PΔV (J/mol)	γ _{HS}
0.0001	16.7	57.9	17.625	5280	5290	-10	1
0.05	16.7	57.9	17.625	4530	5520	-459	0
0.09	16.7	57.9	17.625	3910	5630	-764.2	0
0.28	16.7	57.9	17.625	3570	7400	-856.4	0.2
0.38	16.7	57.9	17.625	1160	7000	-1804.4	0.5
0.44	16.7	57.9	17.625	5380	9600	452.8	0.6
0.55	16.7	57.9	17.625	15333	17600	3574	0.8
0.64	16.7	57.9	17.625	13928	16500	4224.8	0.8

Supplementary Table 8. Cell parameters of 1 at varying temperature ($P = 0$ GPa) and pressure ($T = 298$ K).

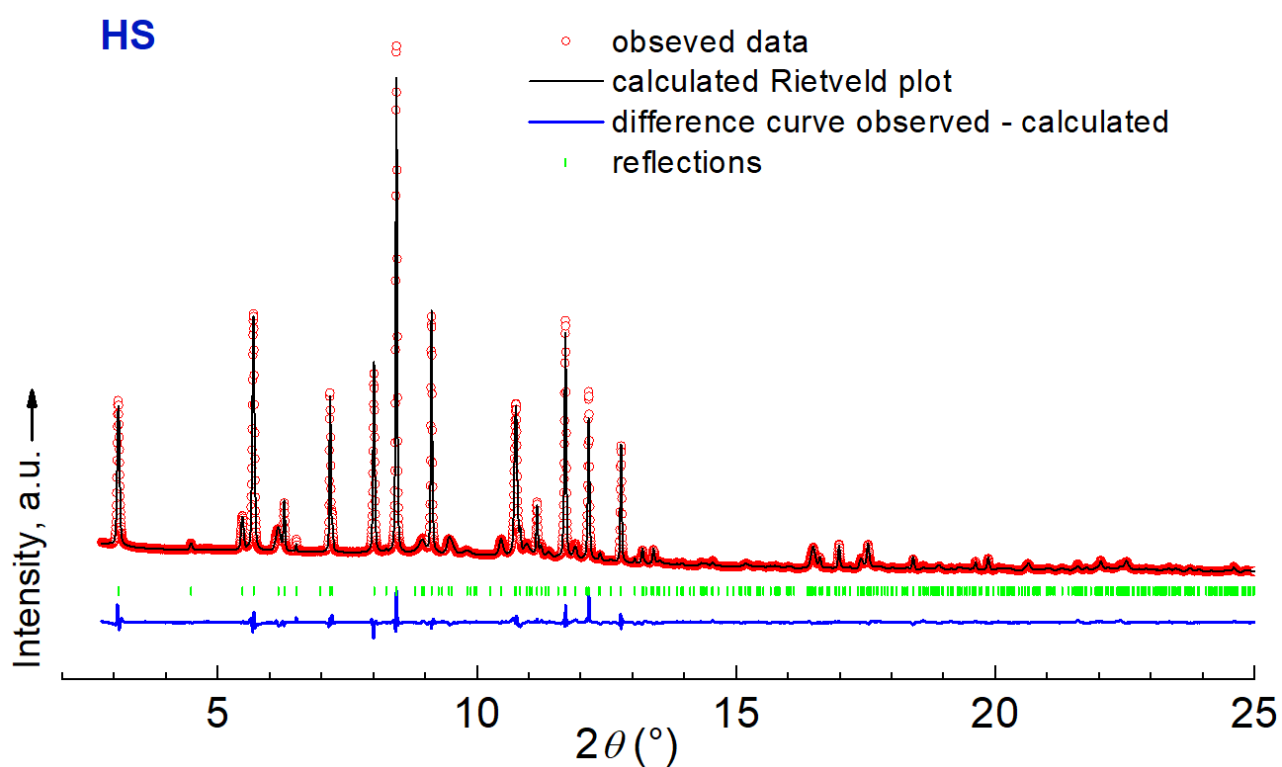
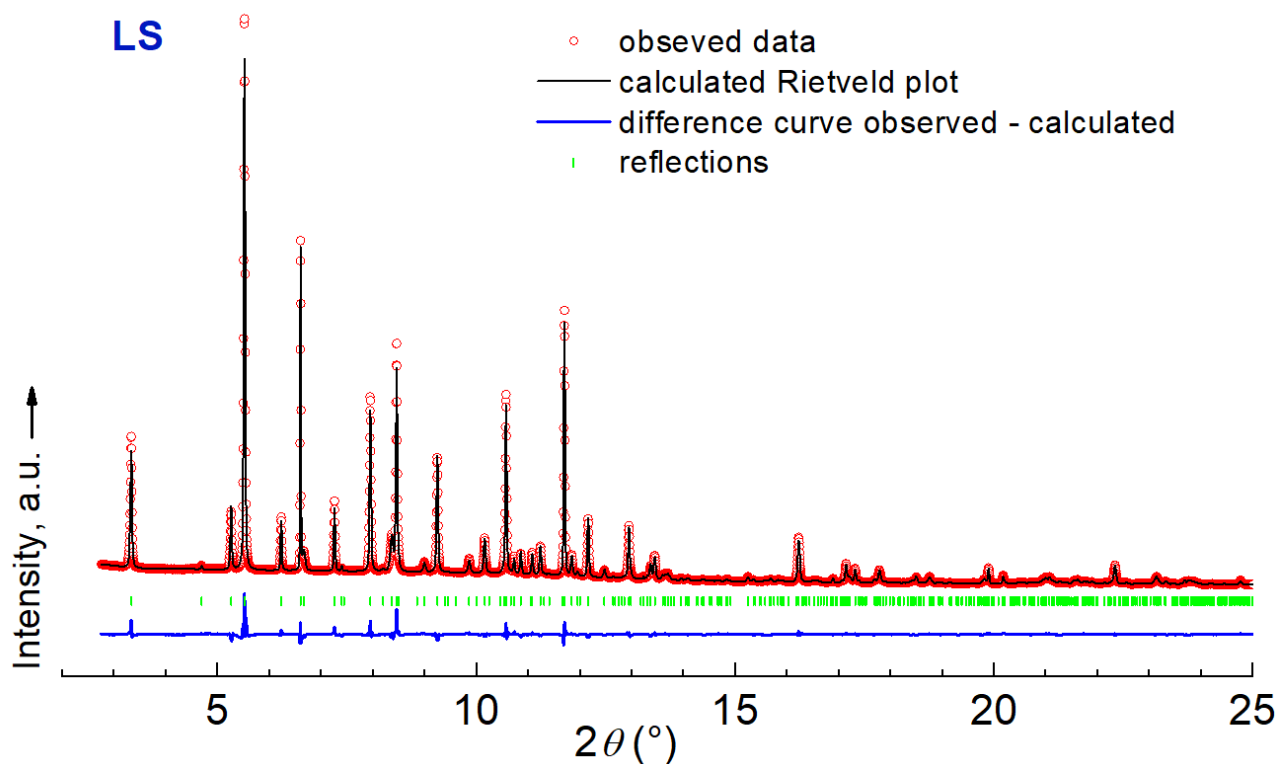
T, K	$a_{HS} (\text{\AA})$	$a_{LS} (\text{\AA})$	$b_{HS} (\text{\AA})$	$b_{LS} (\text{\AA})$	$c_{HS} (\text{\AA})$	$c_{LS} (\text{\AA})$	$V_{HS} (\text{\AA}^3)$	$V_{LS} (\text{\AA}^3)$
220		12.6767		10.21361		25.11747		3252.083
230		12.67949		10.21213		25.14927		3256.441
240		12.68223		10.21096		25.17966		3260.526
250		12.6856		10.21026		25.21016		3265.302
260		12.68842		10.20914		25.23892		3269.396
270		12.69266		10.20859		25.2664		3273.874
275		12.69482		10.20773		25.28155		3276.118
280		12.69732		10.20711		25.294		3278.178
285		12.69938		10.20666		25.30234		3279.643
290		12.70263		10.20574		25.31436		3281.748
293	12.81347	12.70554	9.52761	10.20451	27.10665	25.32306	3309.227	3283.233
296	12.82624		9.51568		27.13177		3311.444	
299	12.83162		9.49873		27.17735		3312.487	
302	12.83368		9.50352		27.16291		3312.929	
305	12.83949		9.51266		27.1381		3314.583	
308	12.84601		9.5067		27.16058		3316.935	
311	12.85224		9.51011		27.17182		3321.107	
314	12.85299		9.51373		27.1653		3321.77	
317	12.85346		9.5144		27.16631		3322.249	

P (GPa)	a (\text{\AA})	b (\text{\AA})	c (\text{\AA})	V (\text{\AA}^3)
0	12.83935	9.55434	27.03517	3316.445
0.05	12.79993	9.54024	26.9753	3294.071
0.08	12.84397	9.54072	26.97836	3305.947
0.14	12.74031	10.25628	24.89923	3253.538
0.2	12.71417	10.31368	24.80512	3252.695
0.25	12.72005	10.40793	24.66765	3265.735
0.3	12.71218	10.3853	24.45005	3227.890
0.35	12.66847	10.36904	24.51024	3219.660
0.41	12.64229	10.49613	24.57454	3233.589
0.47	12.63781	10.49949	24.5083	3252.020
0.52	12.66414	10.49825	24.47774	3254.346

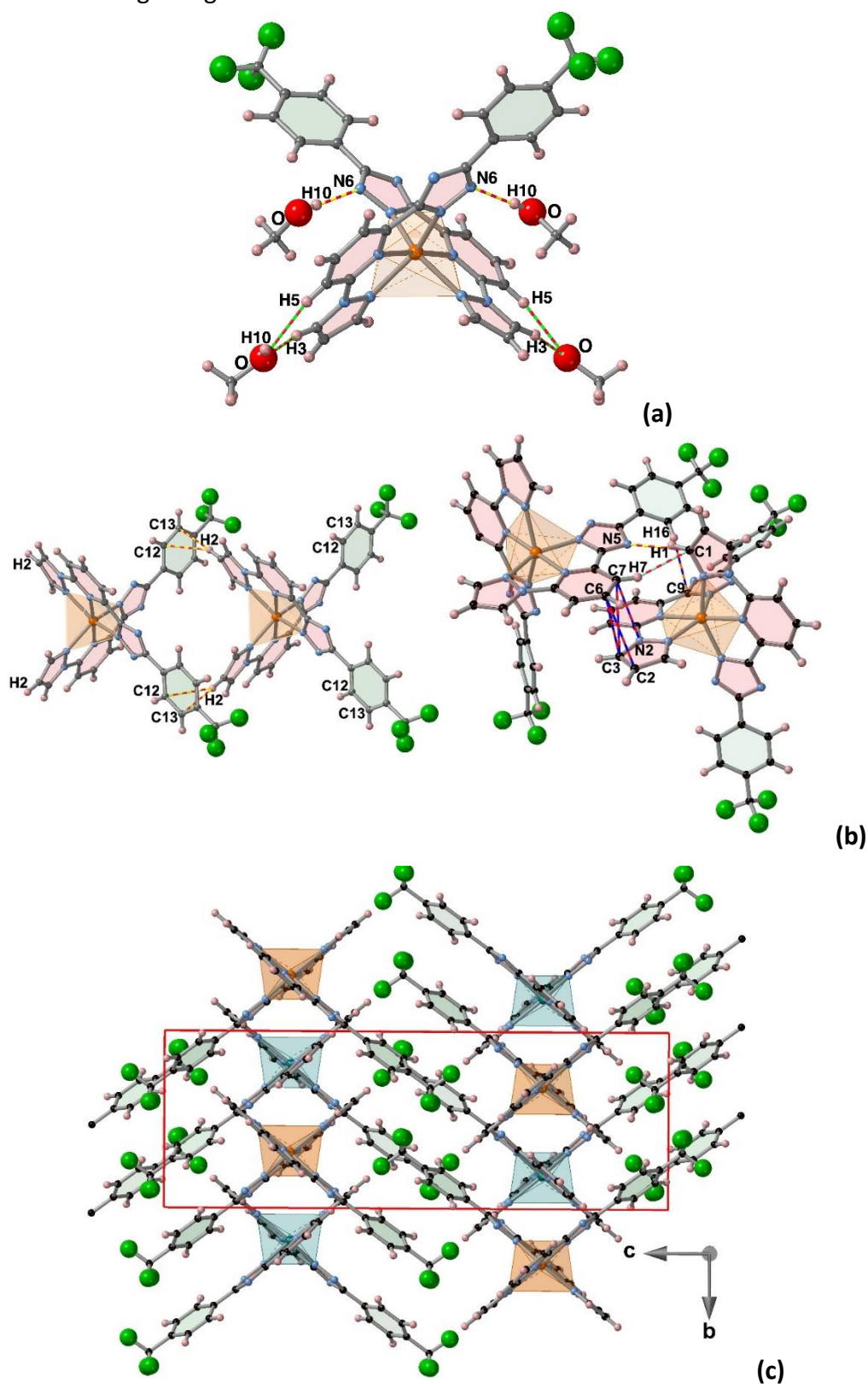
Supplementary Fig. 1. TGA data of the **1·2MeOH** and **1** (above 370 K).



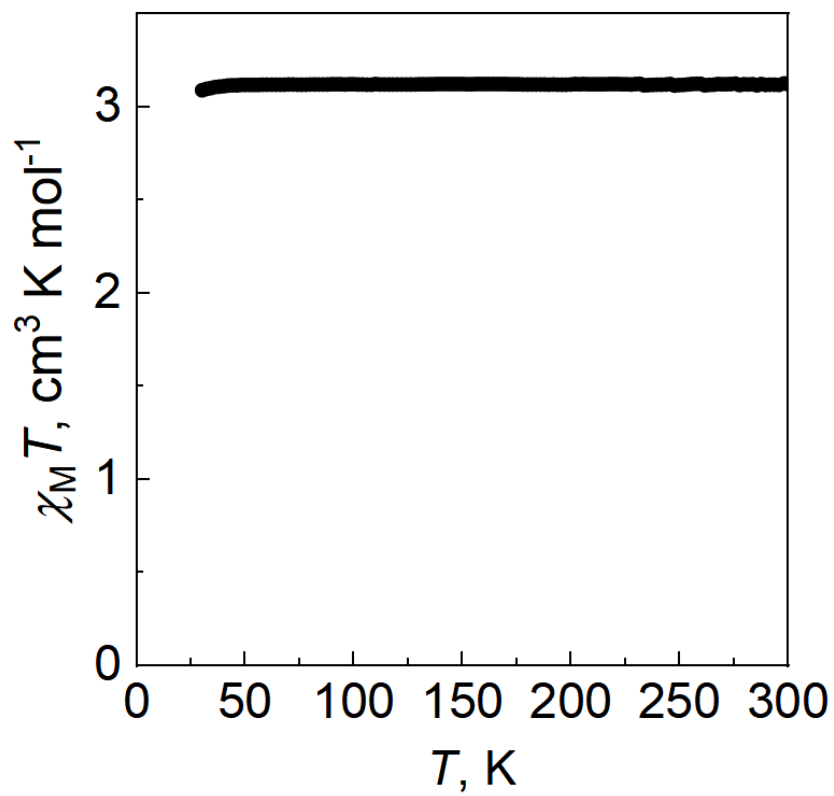
Supplementary Fig. 2. Final Rietveld refinement plots for **1** (LS) and (HS) phases, showing the experimental (red circles), calculated (black line) and difference (blue line) profiles; green marks indicate reflection positions.



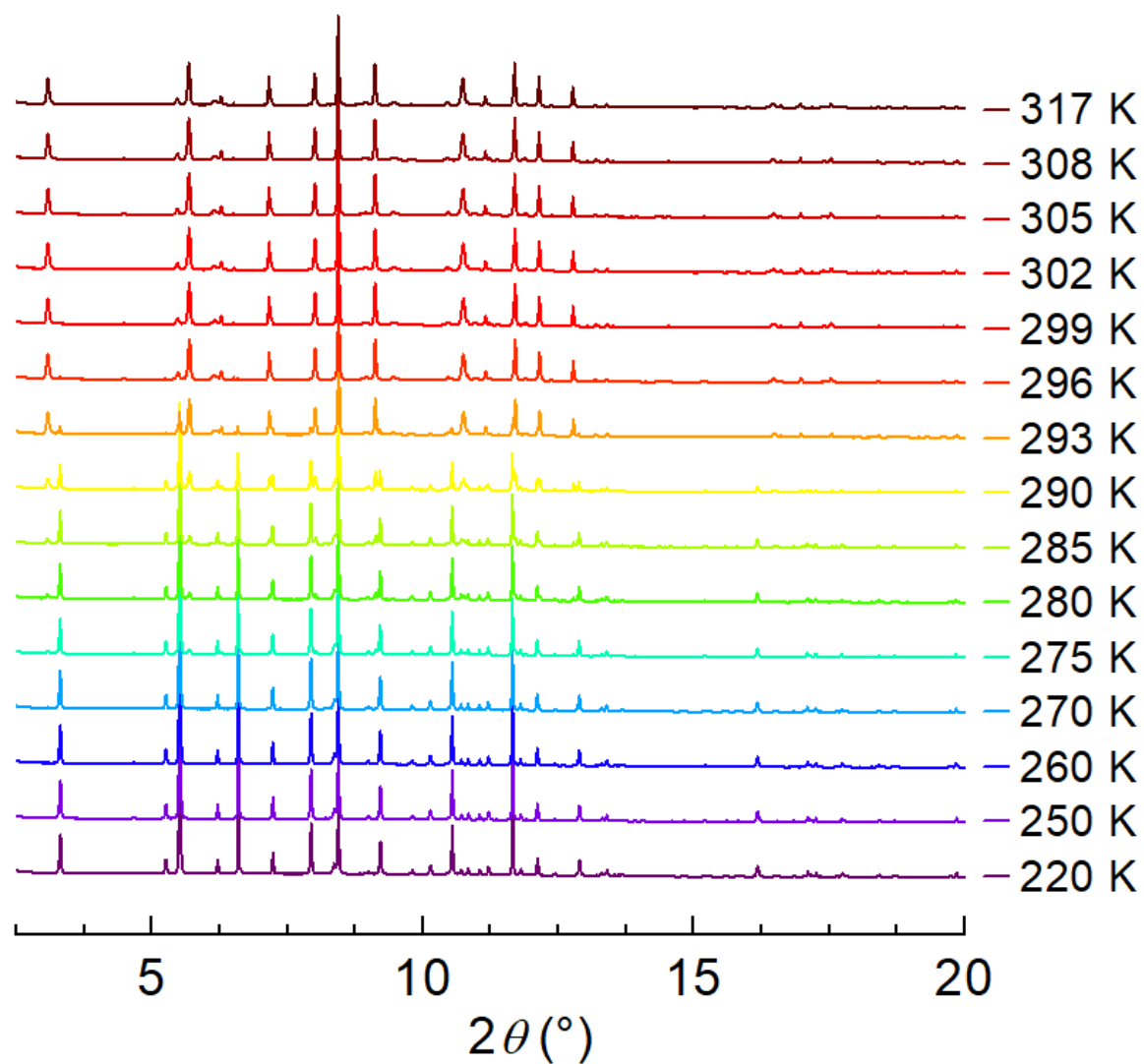
Supplementary Fig. 3. (a) Hydrogen bonding interactions between CH₃OH molecules and complex in 1·2MeOH; (b) Short contacts between the pyrazoles and CF₃ph rings of consecutive molecules of the same chain running along *b*; (c) Short contacts including π - π stacking (pyridine...pyrazole) and strong [N5...H1-C1 (triazole...pyrazole)] hydrogen bonding between molecules belonging to two adjacent chains running along *b*.



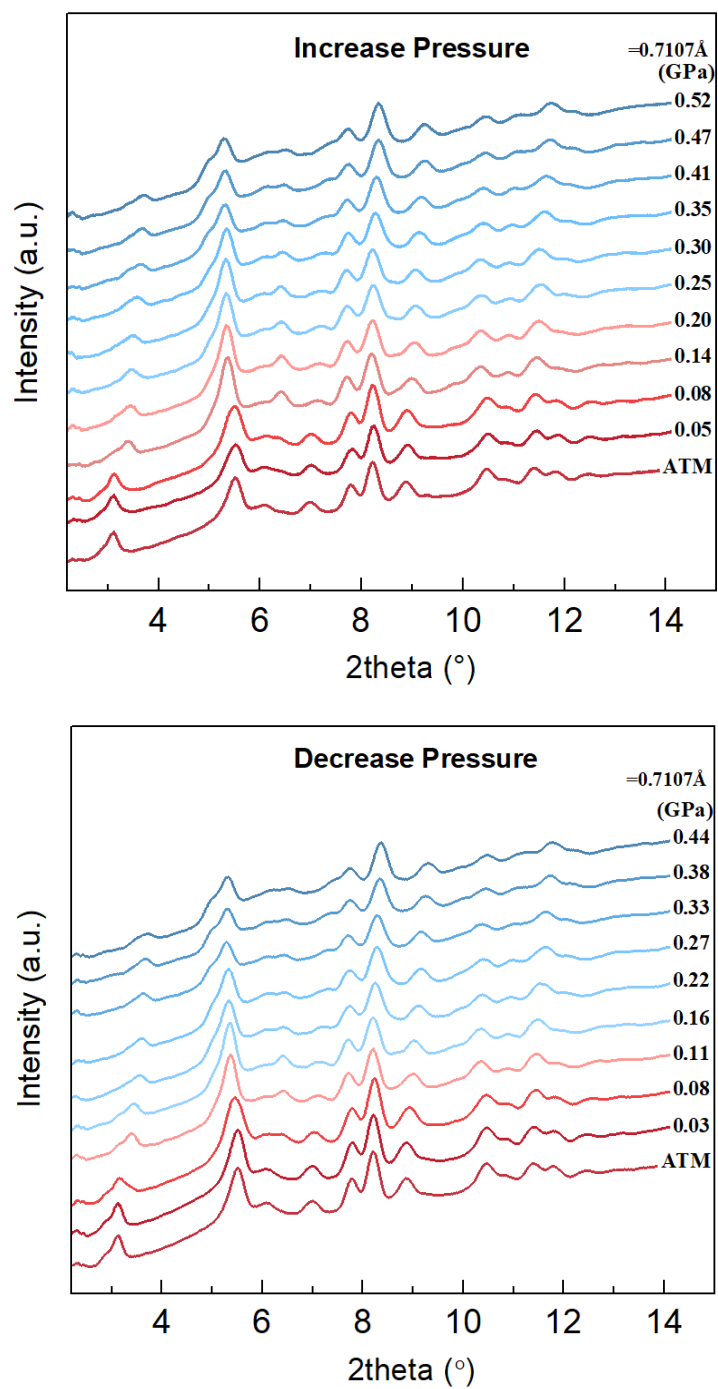
Supplementary Fig. 4. Magnetic properties of the **1·2MeOH**.



Supplementary Fig. 5. XRD of **1** at indicated temperature ($P = 0$ GPa).



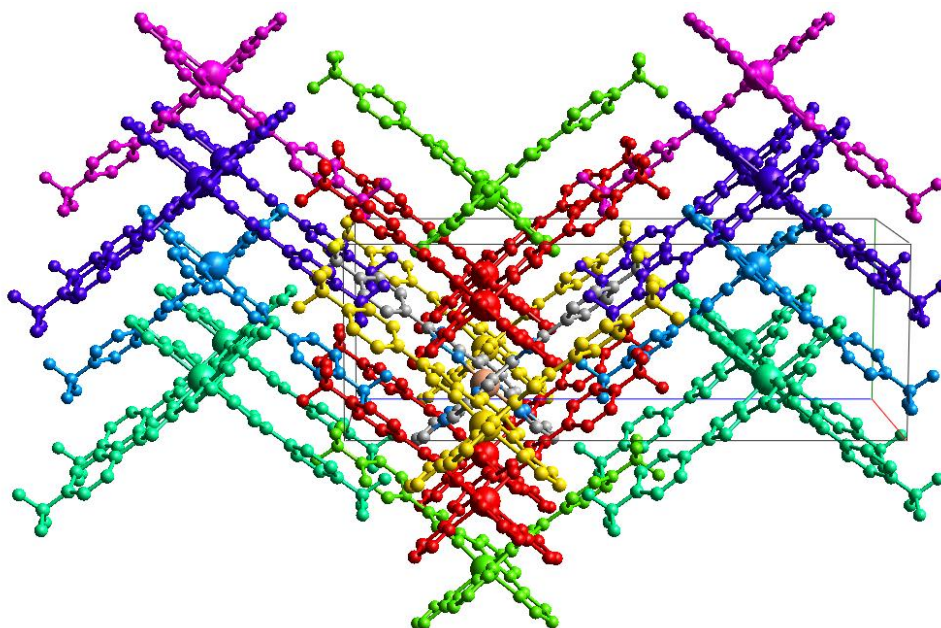
Supplementary Fig. 6. XRD of **1** at indicated pressure ($T = 298$ K).



Supplementary Note 1. Difference energy framework analysis

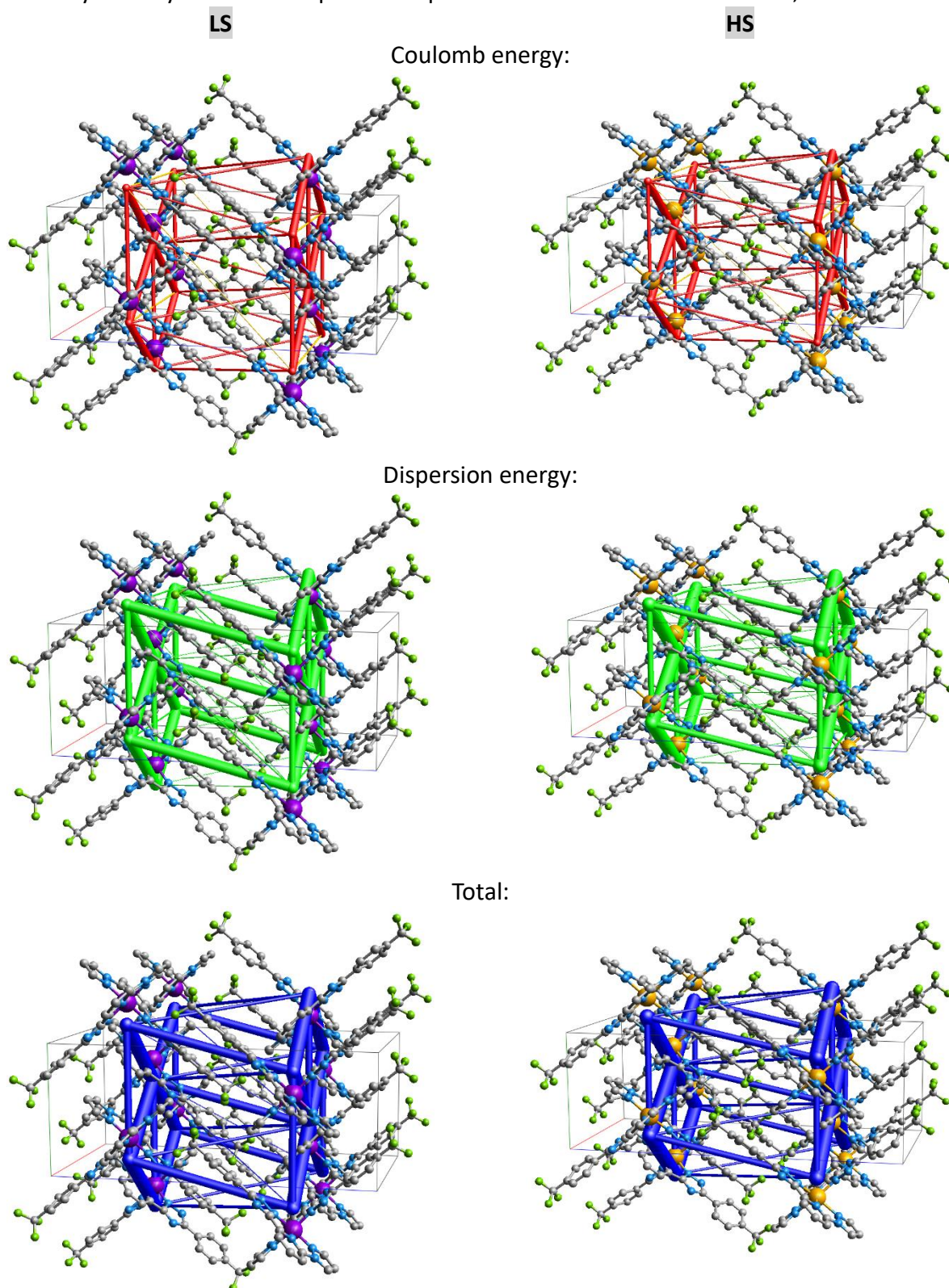
The method¹ visualizes the interaction energies between molecular pairs, independent of the type of the interactions, as cylinders connecting the centroids of molecules, with cylinder radius proportional to the magnitude of the interaction energy. The individual contributions (electrostatic, dispersion, polarization, and repulsive) to the total interaction energy for each spin state were calculated using the B3LYP6-31G(d,p) basis set and are presented in Supplementary Table 9. The resulting interaction topologies reveal strong cohesive forces, mostly within the layers in the *ab* planes, depicted by thicker tubes in the total energy framework diagrams (Supplementary Fig. 7). The difference energy framework² (Supplementary Fig. 8) highlights significant energetic changes of opposite sign during the LS→HS transition; however, these changes are not balanced, with destabilizing interactions reaching up to $\Delta E^{\text{HS-LS}} = +13.9 \text{ kJ mol}^{-1}$, surpassing the absolute value of stabilizing interactions (down to $\Delta E^{\text{HS-LS}} = -10.8 \text{ kJ mol}^{-1}$). This disparity is consistent with the abrupt but weakly hysteretic behavior of the compound.

Supplementary Table 9. The color-coded interaction mappings of a central reference molecule with the nearest neighbors of **1** and the contributions to the total energy in both spin states as calculated by B3LYP/6-31G(d,p) method.

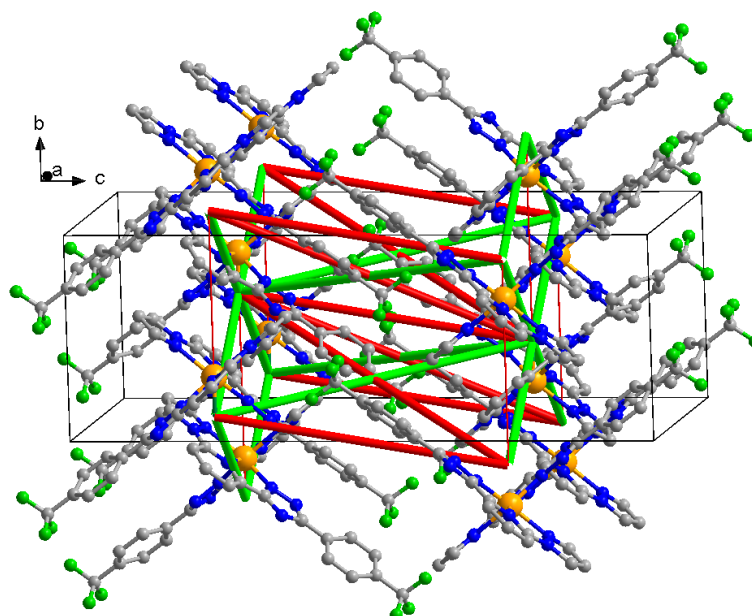


Color code	Symmetry operation	Spin state	$R, \text{\AA}$	$\Delta R^{\text{HS-LS}}, \text{\AA}$	$E, \text{kJ mol}^{-1}$					
					Electrostatic	Polarization	Dispersion	Exchange-repulsion	Total	$\Delta E^{\text{HS-LS}}$
Red	$x+1/2, y+1/2, -z+1/2$	$\text{HS}^{\uparrow}$	8.00	-0.14	-42.9	-19.5	-93.3	85.9	-87.9	-10.80
		LS	8.14		-40.5	-18.6	-76.9	75.1	-77.1	
Yellow	x, y, z	$\text{HS}^{\uparrow}$	12.85	0.17	7.5	-2.7	-13.1	10.2	0.8	-2.80
		LS	12.68		9.4	-2.1	-9.9	6.0	3.6	
Cyan	$-x+1/2, -y+1/2, z+1/2$	$\text{HS}^{\uparrow}$	15.25	-0.68	-10.7	-1.3	-5.5	1.2	-16.3	-10.50
		LS	15.93		0.3	-0.6	-8.2	2.3	-5.8	
Magenta	x, y, z	$\text{HS}^{\uparrow}$	9.52	-0.69	-19.0	-5.0	-38.4	34.0	-36.3	4.10
		LS	10.21		-21.6	-5.6	-39.9	34.6	-40.4	
Blue	$-x+1/2, -y+1/2, z+1/2$	$\text{HS}^{\uparrow}$	16.53	2.2	0.6	-0.5	-5.8	0.5	-4.5	13.90
		LS	14.33		-12.3	-1.4	-5.2	0.3	-18.4	
Orange	$-x, -y, -z$	$\text{HS}^{\uparrow}$	13.75	0.97	-11.5	-3.4	-42.6	23.0	-37.6	12.20
		LS	12.78		-10.1	-7.6	-67.8	41.3	-49.8	
Pink	$-x, -y, -z$	$\text{HS}^{\uparrow}$	17.90	0.13	3.6	-0.4	-4.3	0.3	-0.1	-1.20
		LS	17.77		5.6	-0.6	-5.1	0.1	1.1	

Supplementary Fig. 7. Energy components (above) of the total energy frameworks of **1** in both spin states. The yellow cylinders correspond to repulsive interactions. Tube size is 70, cut-off is zero.



Supplementary Fig. 8. A fragment of the crystal packing of **1** in the HS state superimposed on the differential energy framework, constructed using the values from the Supplementary Table 9, column " $\Delta E_{\text{total}}^{\text{HS-LS}}$ ", showing destabilizing (red cylinders) and stabilizing (green cylinders) interactions due to the lattice changes during the ST event. Cylinder thickness is proportional to the absolute value of the interaction energy.

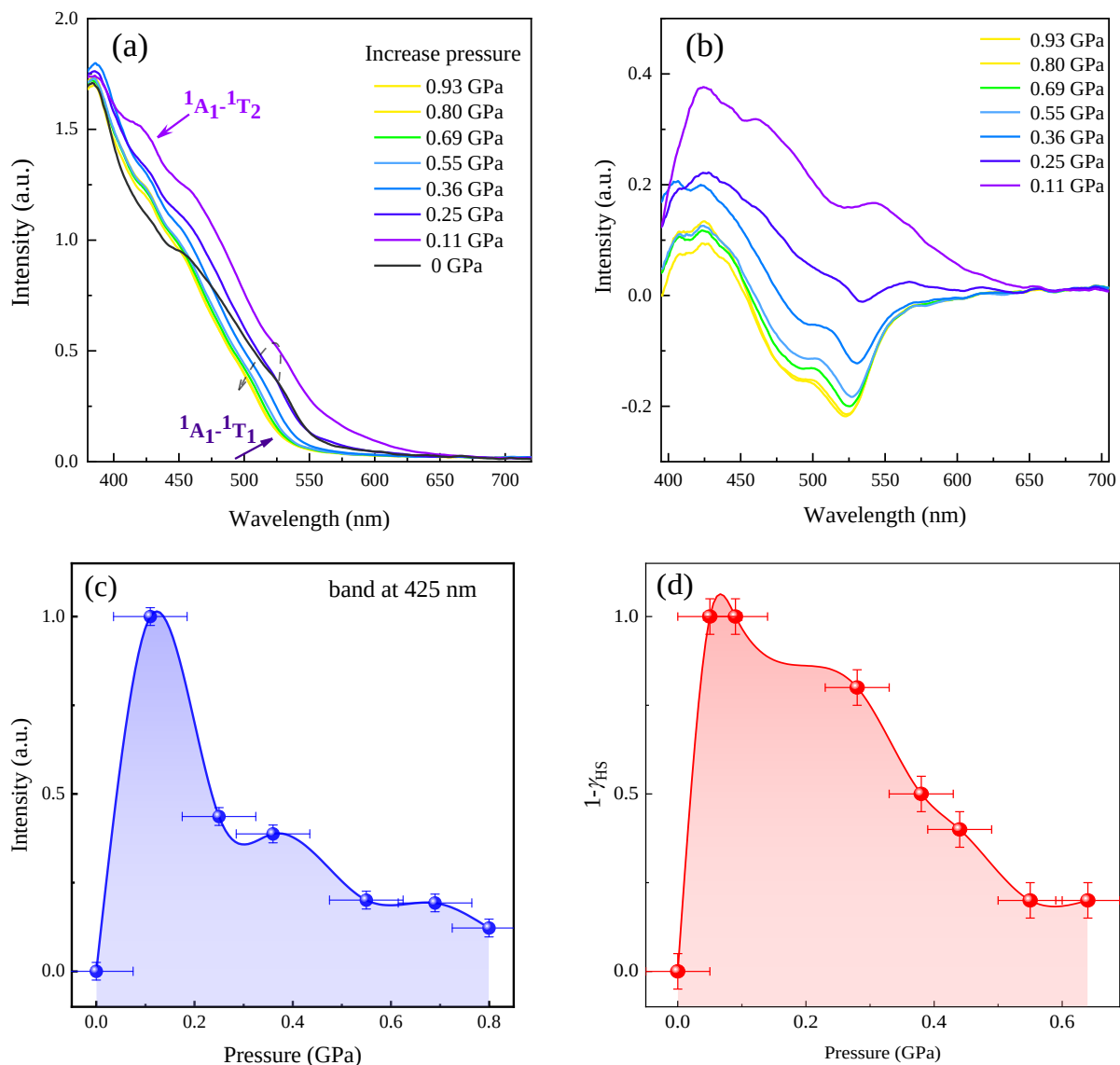


Supplementary Note 2. Optical and Raman properties under pressure at RT

The optical spectrum of **1** at ambient pressure is demonstrated by metal-to-ligand charge-transfer (MLCT) in the 400–600 nm region, which are typical for bis-azolyipyridine FeII complexes (Supplementary Fig. 9a)³, and LS absorption bands characterized by very strong absorption associated with bands $^1A_1-^1T_1$ and $^1A_1-^1T_2$ approximately at 425nm and 560nm, respectively^{4,5}.

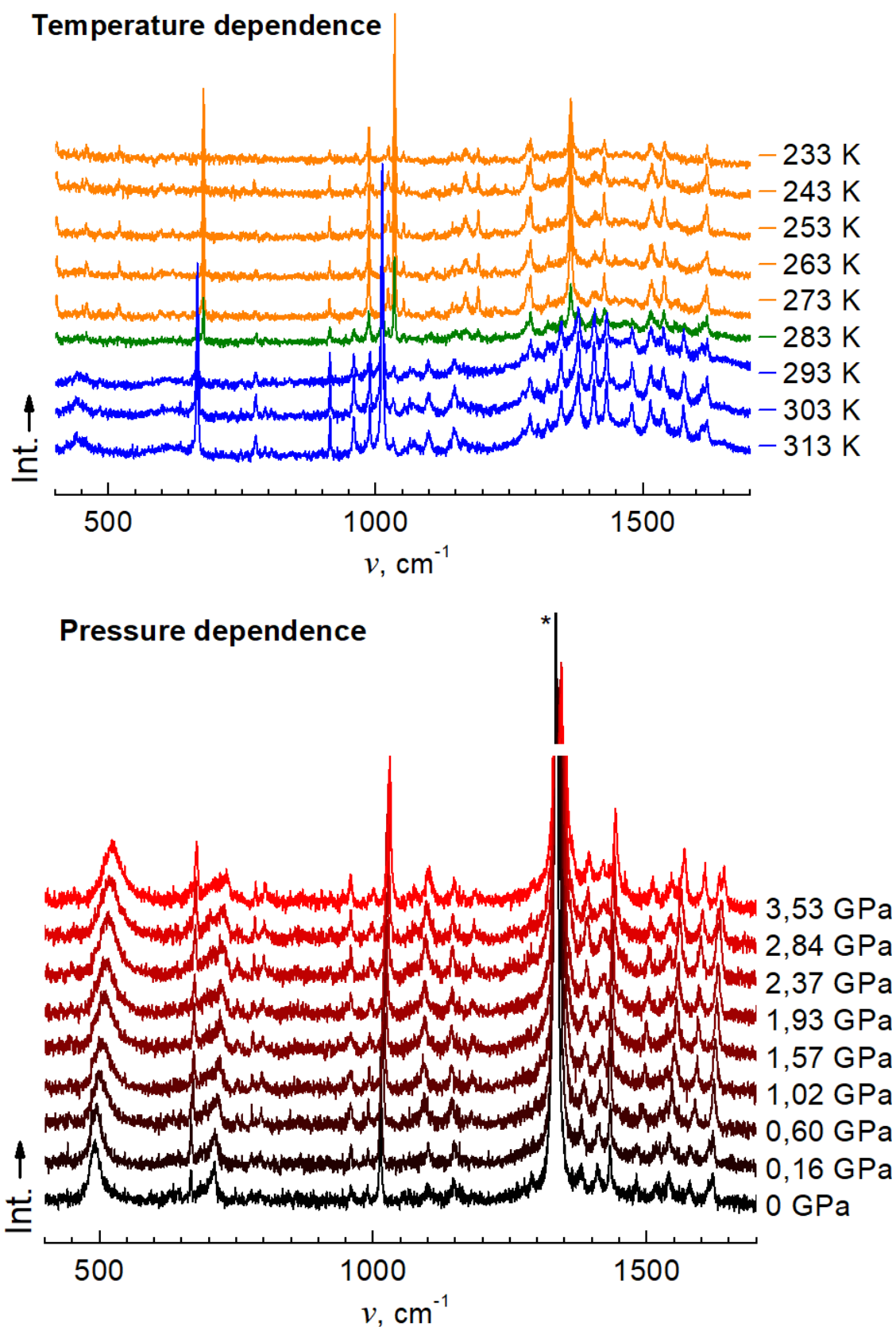
After subtracting the absorption intensity at ambient pressure from the intensity at high pressures (Supplementary Fig. 9b), the intensity of the received signal is proportional to the intensity of $^1A_1-^1T_1$ and $^1A_1-^1T_2$ bands more pronounced despite of large width of them. As follows from magnetic measurements, **1** is in HS state at ambient pressure and transforms to LS state at small pressure (around 0.05 GPa) (Fig. 5b). Upon pressurization to 0.11 GPa, the absorption bands at 425 nm and 560 nm abruptly increase in intensity indicating a complete conversion of the compound to the LS state supporting by this the magnetic measurements. On further pressurization to 0.25 GPa and higher, the bands intensity slowly decreases demonstrating the increase of the HS state (Supplementary Fig. 9c). The Supplementary Fig. 9d demonstrates the appearance of the HS state in the region of the LS state with an increase in pressure obtained from magnetic measurements. The behavior of this fraction is confirmed qualitatively by the change of the optical intensity of the absorption band at 425 nm^{12,15}. To get quantity agreement it is not possible because the experimental bands are very wide. But even at quality agreement it is seen that optical data reflect the magnetic behavior of ST. Therefore, observed behavior (increase and then decrease with pressure of these bands intensity) is caused with abrupt decrease of the HS fraction and then slowly increase it with pressure. This behavior completely supports the observed behavior of the ST with pressure in Fig. 5b, when the HS state fraction decreases under pressure to zero and then appears with increase the pressure in the range of LS state. At the same time the transition temperature decreases under pressure. The increase of the HS state under pressure is shown also in Supplementary Table 7 as increase of γ_{HS} with pressure increase.

Supplementary Fig. 9. (a) Pressure-dependent absorption spectra of **1** in the 400–700 nm range; (b) Dependence of the absorption intensity of **1** after subtracting curve at $P = 0$ GPa; (c) The change of the band optical intensity at 425 nm with pressure; (d) The appearance and behavior of the HS state fraction with pressure increase.

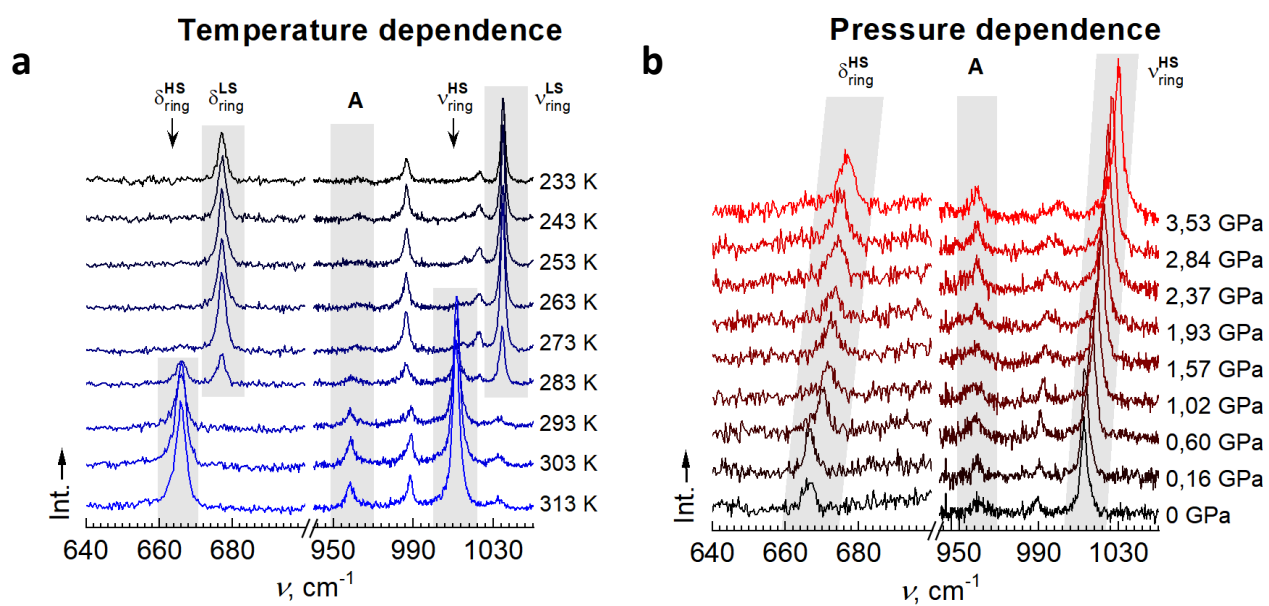


The ST process is typically accompanied by significant changes in atomic vibrational modes, making Raman spectroscopy a reliable tool for tracking the ST process. The compound exhibits intense characteristic peaks at 666 and 1011 cm^{-1} at RT, corresponding to the pyridine ring vibrations δ_{ring} and ν_{ring} ^{6,7}, respectively. Upon cooling these peaks are substituted by new bands at 677 and 1035 cm^{-1} , respectively, in the temperature interval 283–293 K (Supplementary Figs. 10 and 11a). Additionally, an unassigned peak A at 958 cm^{-1} almost disappears on transition to the LS state. This information on the ST effect was used to interpret the spectra under progressively increasing pressure up to 3.53 GPa (Supplementary Figs. 10 and 11b). Interestingly, in contrast to the temperature, the effect of pressure on the HS peaks does not involve a gradual reduction of their intensity in favor of two new LS peaks growing with pressure, but instead a progressive shift to the final location (678 cm^{-1} for δ_{ring} and 1036 cm^{-1} for ν_{ring}) of the HS ones is observed. Additionally, peak 6A does not change its position and intensity, remaining at about 958 cm^{-1} at all pressure values. Comparing this behavior with the magnetic and optical data at RT we conclude that as the lattice stiffens this induces gradual changes in the local environment of the pyridine ring directly coordinated to the Fe^{II} ion which, however, remains HS up to the highest pressure reached. Notably, a similar gradual shift of characteristic bands under pressure was reported for a related Fe^{II} bispyrazolpyridine complex in both spin states⁸. Also, complementary to the Raman studies, the infrared absorption spectroscopic measurements show no signs of the ST at up to 2.12 GPa (refer to the Supplementary Note 3).

Supplementary Fig. 10. Normalized Raman spectra of **1** at varying temperature and pressure (* – peak of diamond anvil).



Supplementary Fig. 11. Raman spectra of **1** in regions with characteristic peaks at varying temperature (a) and pressure (b).



Supplementary Note 3. Infrared spectroscopic data and evaluation

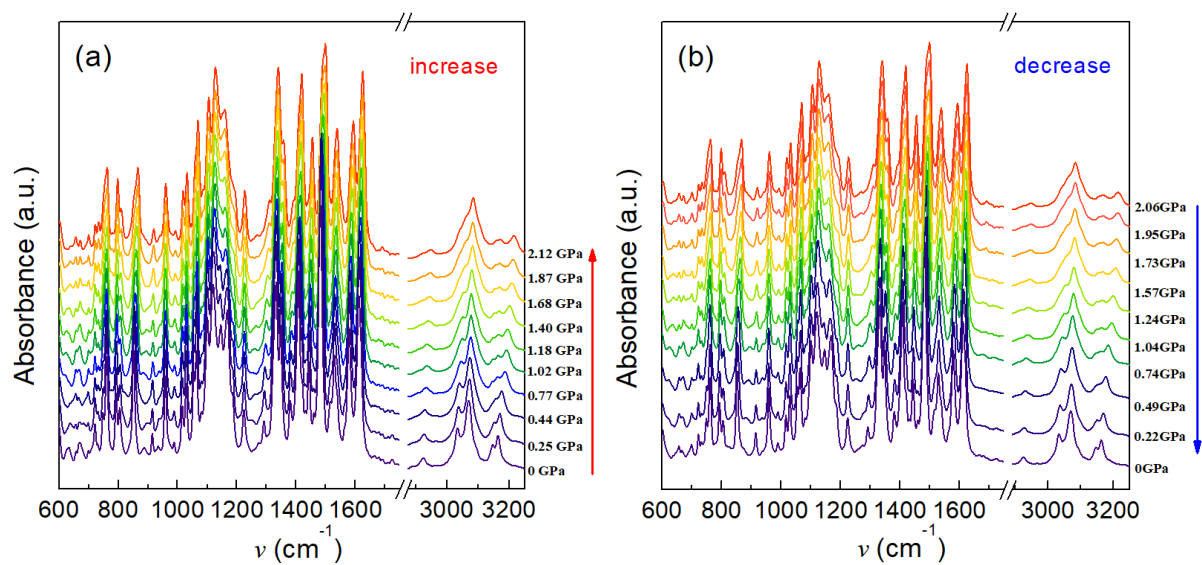
A powerful tool for indirectly confirming the appearance of the ST under pressure is the infrared (IR) spectroscopy. Typically, for ST compounds, both the IR vibrational modes associated with changing spin state from HS to LS state and the movement of $T_{1/2}$ towards higher temperatures occur upon increasing external pressure⁹. However, in this study, we observe another remarkable behavior. We recorded the IR spectra under different pressures ranging from ambient conditions up to 2.12 GPa at 299 K over a wide frequency range of 600–5000 cm^{-1} , using KBr solids as a pressure transfer medium (see Supplementary Fig. 12).

While the intensity and shape of most peaks do not undergo noticeable changes, we noted a blue shift due to the changing distances between different vibrational bonds showing in Supplementary Fig. 13. Also, two bands at 1459 and 1515 cm^{-1} vanish at 0.22 GPa.

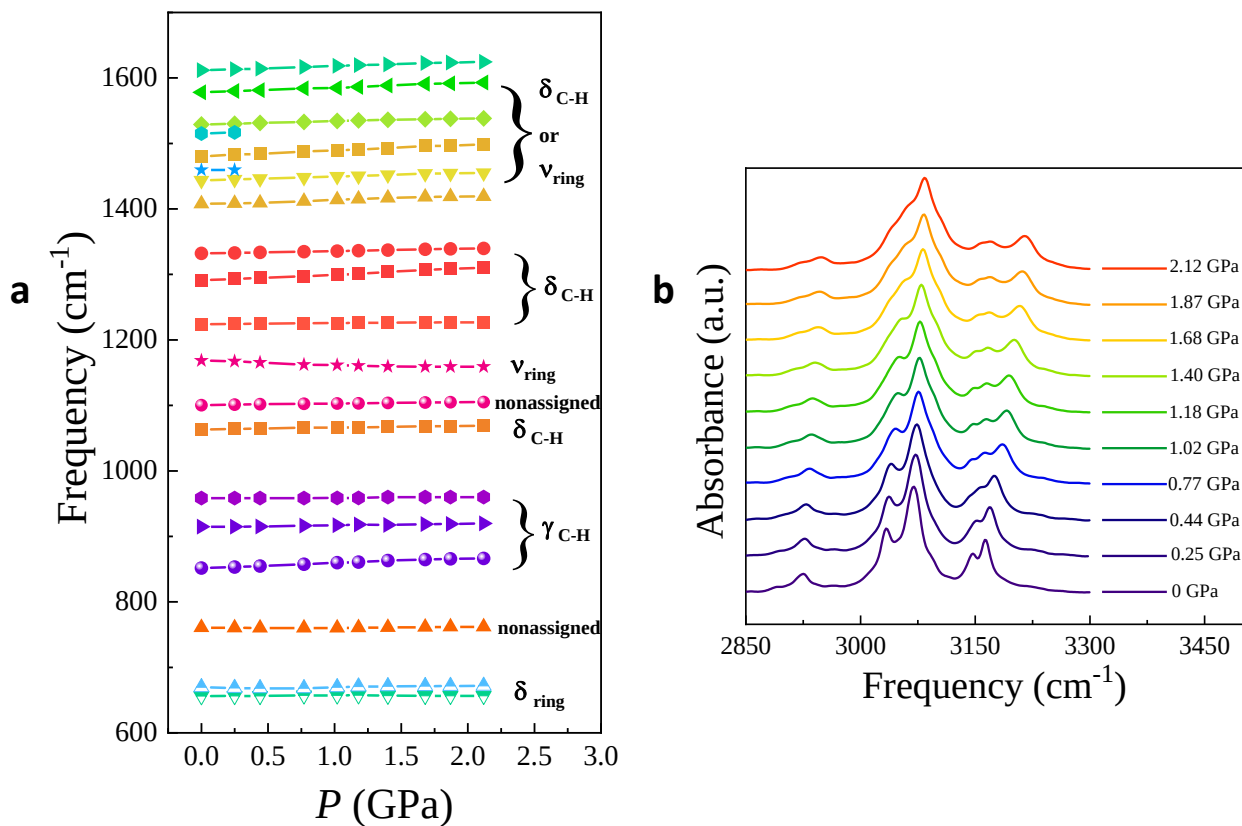
Except those changes there no evidence of ST of Fe^{II} , indicating that the HS state persists at RT under pressure up to 2.12 GPa, which may be caused by a shift of $T_{1/2}$ towards low temperatures under pressure.

One of the most commonly used vibration modes for monitoring the ST is associated with the C–H stretching at around 3100 cm^{-1} ⁹, but it does not exhibit transition, only some broadening is observed (Supplementary Fig. 13). All these observations are consistent and corroborate the magnetic data at RT.

Supplementary Fig. 12. IR spectra of the **1** upon increasing (a) and decreasing (b) pressure at RT.



Supplementary Fig. 13. (a) Pressure dependence of the peak positions for the most pronounced IR modes of **1** at RT (ν is stretching, δ is in-plane bending, and γ is out of-plane bending); (b) IR spectra of the **1** under different pressures at room temperature for the selected frequency range.



Supplementary Note 4. Thermodynamic analysis

For theoretical description of the ST behavior, a variety of models, including thermodynamic^{10,11}, microscopic Ising-like¹² and Landau-type¹³ were proposed. Within these models the main features of the ST behavior, *i.e.* the characteristics of the thermal ST (gradual and abrupt, with and without hysteresis), the two-step nature of the ST phenomenon in mononuclear compounds, and the occurrence of irreversible or incomplete transitions have been successfully explained¹⁴. In addition, other aspects concerning the analysis of: i) the interaction parameters in terms of the elasticity theory¹⁵; ii) the relationship between thermodynamic and microscopic parameters¹⁶; and the different behavior of ST depending on the internal and external perturbations¹⁷ have been achieved.

In particular, to analyze the behavior of the ST under pressure, it is possible to consider two approaches: i) based on the Ising model, in which the order parameter of the phase transition is a pseudospin whose value is -1 for LS and +1 for HS¹⁸; ii) based on the model of elastic interactions, whose order parameter is the square of the spin¹⁹. Both approaches give the same result, but the second one has a real physical meaning in contrast to the pseudospin used in the Ising model. Therefore, here we use the second approach. For every spin state the Gibbs free energy can be written as $G_n = H_n - T \cdot S_n + P \cdot V_n$ ($n = \text{HS or LS}$), where P , V_n , H_n , and S_n are, respectively, pressure, volume, enthalpy, and entropy associated with the HS and LS states¹⁹. For a compound with mean-field interaction Γ between HS and LS molecules, the equation of state is obtained from the equilibrium condition $dG/d\gamma_{\text{HS}} = 0$ and takes the form⁸:

$$\Delta H_{\text{HL}} - T \cdot \Delta S_{\text{HL}} + P \cdot \Delta V_{\text{HL}} + \Delta_{\text{elastic}} - \Gamma + \Gamma(1 - 2\gamma_{\text{HS}}) - N_A k_B T \cdot \ln\left(\frac{1 - \gamma_{\text{HS}}}{\gamma_{\text{HS}}}\right) = 0 \quad (\text{S1})$$

In this equation ΔH_{HL} , ΔS_{HL} , ΔV_{HL} , and Δ_{elastic} correspond to the enthalpy, entropy, molecular volume, and elastic energy changes at ST. Γ is an interaction energy and γ_{HS} is the reduced molar fraction of HS molecules. Using equation (S1) it is easy to obtain the relationship between the temperature and HS molar fraction:

$$T(\gamma_{\text{HS}}) = \frac{\Delta H_{\text{HL}} + (\Delta_{\text{elastic}} - \Gamma) + P \cdot \Delta V_{\text{HL}} + \Gamma(1 - 2\gamma_{\text{HS}})}{\Delta S_{\text{HL}} + N_A k_B \cdot \ln\left(\frac{1 - \gamma_{\text{HS}}}{\gamma_{\text{HS}}}\right)} \quad (\text{S2})$$

At $\gamma_{\text{HS}} = 1/2$, it is easy to get the ST temperature under pressure:

$$T_{1/2} = \frac{\Delta H_{\text{HL}} + (\Delta_{\text{elastic}} - \Gamma) + P \cdot \Delta V_{\text{HL}}}{\Delta S_{\text{HL}}} \quad (\text{S3})$$

Equation S3 shows that the transition temperature is governed by pressure and by difference $(\Delta_{\text{elastic}} - \Gamma)$. The results of many experimental^{20,21} and theoretical^{10,15,19,22} studies demonstrate that the ST temperature increases invariably with pressure. As far as we know, there is only one exception in which the average temperature $T_{1/2}$ decreased under pressure due to a huge down-shift of the low-temperature branch of the hysteresis which is not compensated by the up-shift of the high-temperature branch²⁰, *i.e.* the decrease in $T_{1/2}$ occurs due to an increase in the interaction energy Γ and an asymmetric increase of hysteresis width.

Exceptionally different behavior is observed for **1**. As seen in Fig. 5b under applying pressure the narrow hysteresis loop linearly shifts to the lower temperature. At low pressure the ST hysteresis loop has a rectangular shape and becomes inclined and incomplete with the pressure increase, thereby increasing significantly the HS fraction in the region of the LS state.

A related pressure-induced HS molar fraction in the low-temperature region was previously reported²¹, but as expected the ST temperature increased with pressure increase. Based on the results indicated in refs. ^{17,22-26} it can be assumed that the increase in the transition temperature with an increase in pressure is an established phenomenon, but for **1** a decrease of $T_{1/2}$, $T_{1/2}^{\downarrow}$ and $T_{1/2}^{\uparrow}$ with pressure contradicts this expectation.

As follows from ref. ²², for decreasing the transition temperature due to the pressure, the term $((\Delta_{\text{elast}} - \Gamma) + P\Delta V)$ must decrease with increasing pressure or be negative and increase. But, as known from the literature, the change of the splitting energy of the iron 3d-levels in the octahedral environment always increases as pressure increases^{19,22}. The $P\Delta V$ term also increases, and Γ can increase or decrease depending on the structure behavior under pressure^{10,19,27}. Therefore, for the reduction of the transition temperature under pressure the negative or decreasing term $((\Delta_{\text{elast}} - \Gamma) + P\Delta V)$ under pressure with small Δ_{elast} and large Γ should be observed. It is known that with a trigonal distortion of the Fe^{II} ligand environment, the splitting of the $e_g - t_{2g}$ levels decreases with a pressure increase²⁸. This behavior might be a plausible mechanism for decreasing term $((\Delta_{\text{elast}} - \Gamma) + P\Delta V)$ and even for its sign change. In our opinion, this is observed for **1**.

Computation

As shown in Fig. 5b, at ambient pressure and at 0.05 and 0.09 GPa, the ST is complete and the $T_{1/2}$ decreases. Therefore, we can use the equation (S2) for simulating the ST curve. At pressure of 0.44 GPa and higher the ST becomes incomplete and, consequently, for such transitions²⁹ equation (S2) should be modified.

For 0.44 GPa the equation becomes:

$$T(\gamma_{\text{HS}}) = \frac{0.4\Delta H_{\text{HL}} + (\Delta_{\text{elastic}} - \Gamma) + 0.4P \cdot \Delta V_{\text{HL}} + \Gamma(1.34 - 2\gamma_{\text{HS}})}{0.4\Delta S_{\text{HL}} + N_A k_B \cdot \ln\left(\frac{0.87 - \gamma_{\text{HS}}}{\gamma_{\text{HS}} - 0.47}\right)} \quad (\text{S4})$$

Here the coefficient 0.4 comes from the part of the molecules transformed into the LS state. In the numerator, the term $(1 - 2\gamma_{\text{HS}})$ is replaced by $(1.34 - 2\gamma_{\text{HS}})$, since 1.34 equals to the $2\gamma_{\text{HS}}$ at transition temperature $T_{1/2} = 179$ K at 0.44 GPa. In the denominator, the value 0.47 equals molar HS fraction γ_{HS} at finishing temperature of the transition under pressure of 0.44 GPa and 1 is the value of γ_{HS} at room temperature. Similarly, the formula for the incomplete ST at 0.55 GPa should be rewritten as:

$$T(\gamma_{\text{HS}}) = \frac{0.15\Delta H_{\text{HL}} + (\Delta_{\text{elastic}} - \Gamma) + 0.15P \cdot \Delta V_{\text{HL}} + \Gamma(1.56 - 2\gamma_{\text{HS}})}{0.15\Delta S_{\text{HL}} + N_A k_B \cdot \ln\left(\frac{0.87 - \gamma_{\text{HS}}}{\gamma_{\text{HS}} - 0.72}\right)} \quad (\text{S5})$$

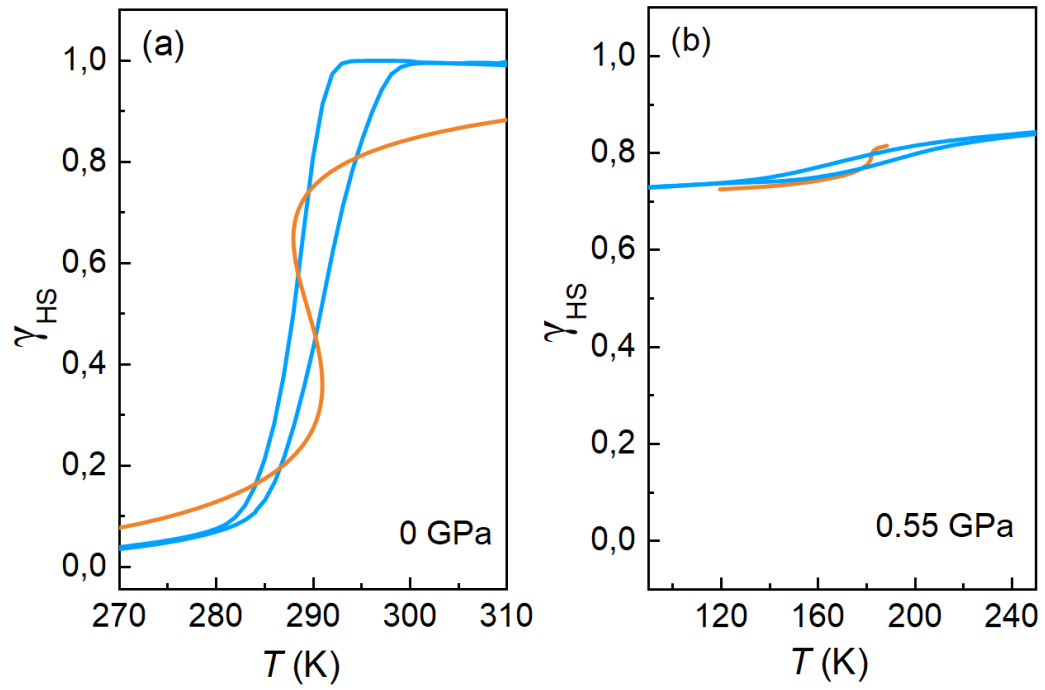
Here coefficient 0.15 equals the part of the transformed molecules to the LS state under pressure 0.55 GPa, value 1.56 equals to $2\gamma_{\text{HS}}$ at $T_{1/2} = 172$ K at 0.55 GPa, while the value 0.72 equals γ_{HS} at the end of the transition at 0.55 GPa, being 1 the value of γ_{HS} at room temperature and ambient

pressure.

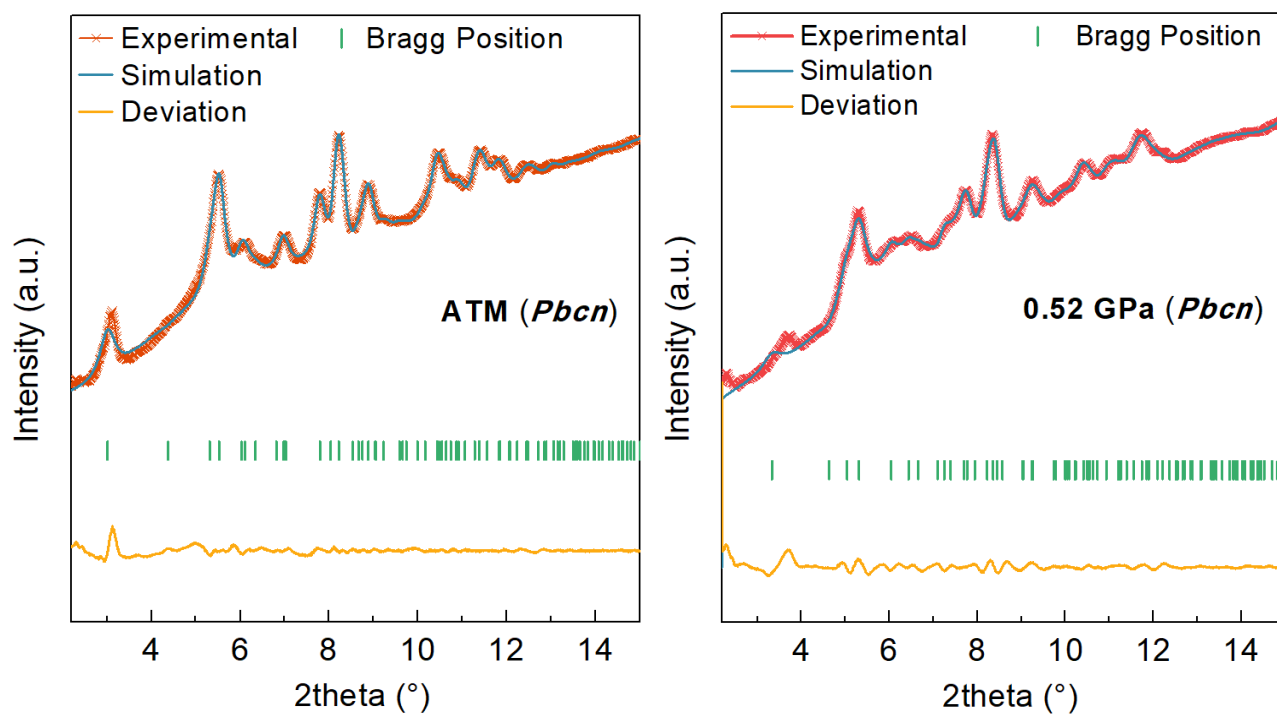
The behavior of the parameters Δ_{elast} , Γ and $((\Delta_{\text{elast}} - \Gamma) + P\Delta V)$ with increasing pressure was obtained by fitting the experimental ST curves ($\gamma_{\text{HS}}(T)$) at different pressures using a modified equation (S2) as described above. For this, the changes in enthalpy and entropy ($\Delta H = 16.7 \text{ kJ mol}^{-1}$, $\Delta S = 57.9 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively) were obtained from differential DSC measurements. The change of volume at ST was obtained from XRD measurements at room temperature and equals $\Delta V = 17.625 \text{ \AA}^3 \text{ mol}^{-1}$. Representative fits at ambient pressure and at 0.55 GPa are shown in Supplementary Fig. 14. The results of calculations are presented in Supplementary Table 7 together with the amount of HS fraction appearing in the region of LS state.

Overall, the analysis shows that the ST response under pressure is governed by changes in the elastic and interaction energies, together with the combines term $((\Delta_{\text{elast}} - \Gamma) + P\Delta V)$.

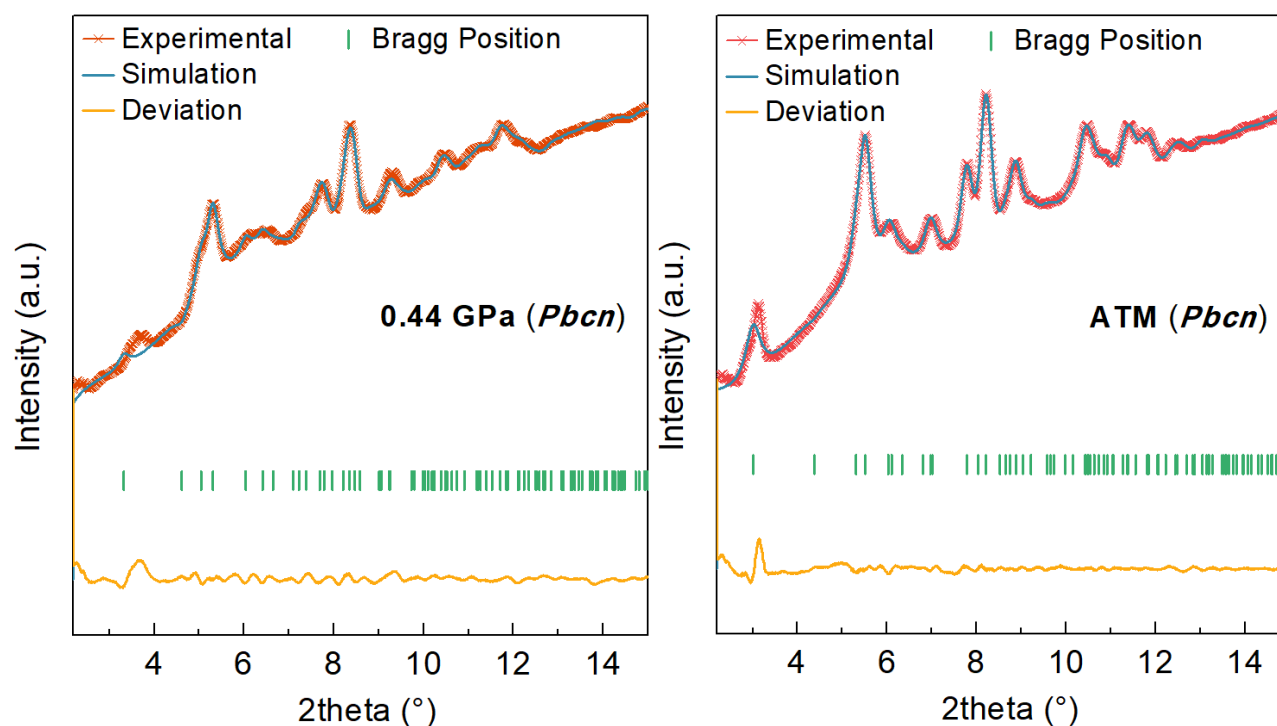
Supplementary Fig. 14. Fitting of ST curves ($\gamma_{\text{HS}}(T)$) at ambient (a) and 0.55 GPa (b) pressures, where the blue curve is experimental, and orange is the fitting curve.



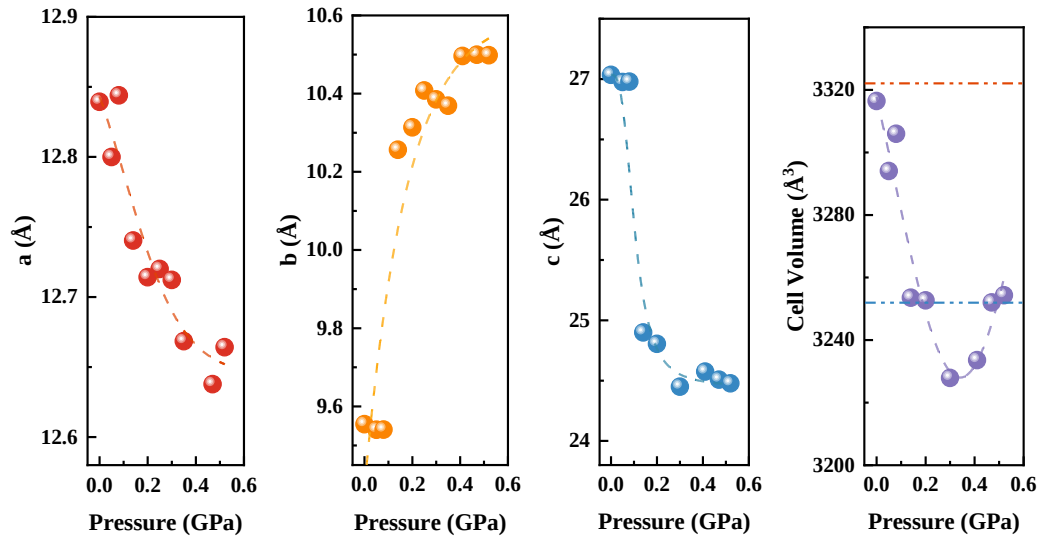
Supplementary Fig. 15. Fitting results obtained using Rietveld (increasing pressure).



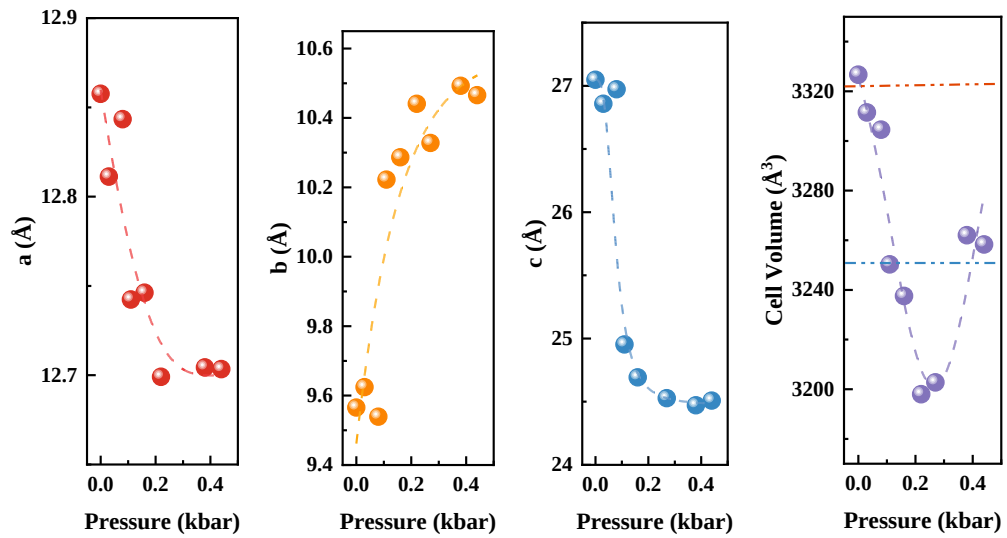
Supplementary Fig. 16. Fitting results obtained using Rietveld (decreasing pressure).



Supplementary Fig. 17. Variation of the unit cell parameters under pressure (increasing pressure).



Supplementary Fig. 18. Variation of the unit cell parameters under pressure (decreasing pressure).



Supplementary Note 6. Evaluation of the cell parameters at varying temperature and pressure

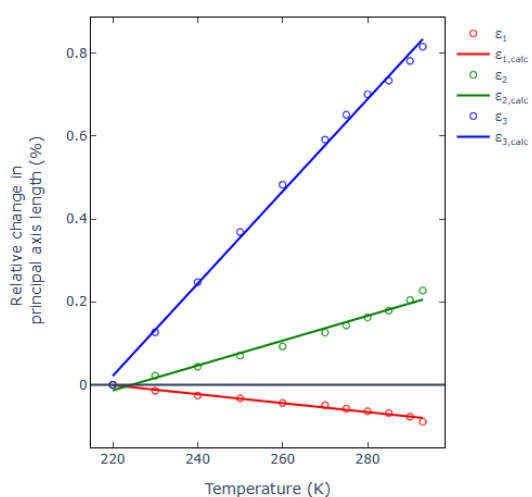
At low T before ST

Supplementary Table 10. The fitting results for **1** from *PASCal* in the range of 220–293 K (before ST).

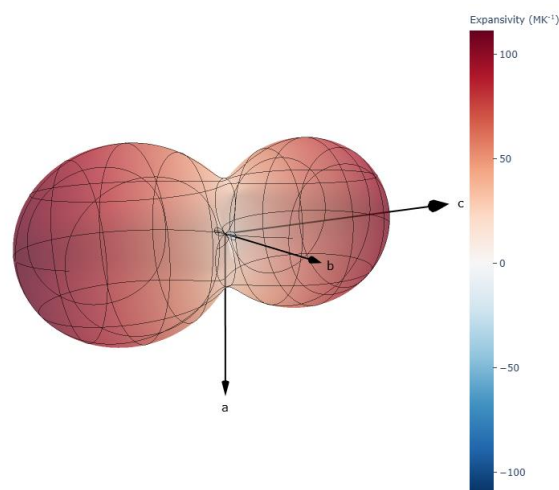
Axes	α (MK ⁻¹)	σ_α (MK ⁻¹)	Direction		
			a	b	c
X ₁	-10.7972	0.5139	0.0	1.0	0.0
X ₂	29.9774	1.5053	1.0	0.0	0.0
X ₃	111.2637	2.0514	0.0	0.0	1.0
V	131.0933	0.9062			

Supplementary Fig. 19. (a) Plot of the pressure-dependent changes in the principal tensor lengths for **1** in the range of 220–293 K with solid lines representing the best-fitting results (before ST) and (b) the corresponding expansivity tensor plots for **1** evaluated by *PASCal*.

a



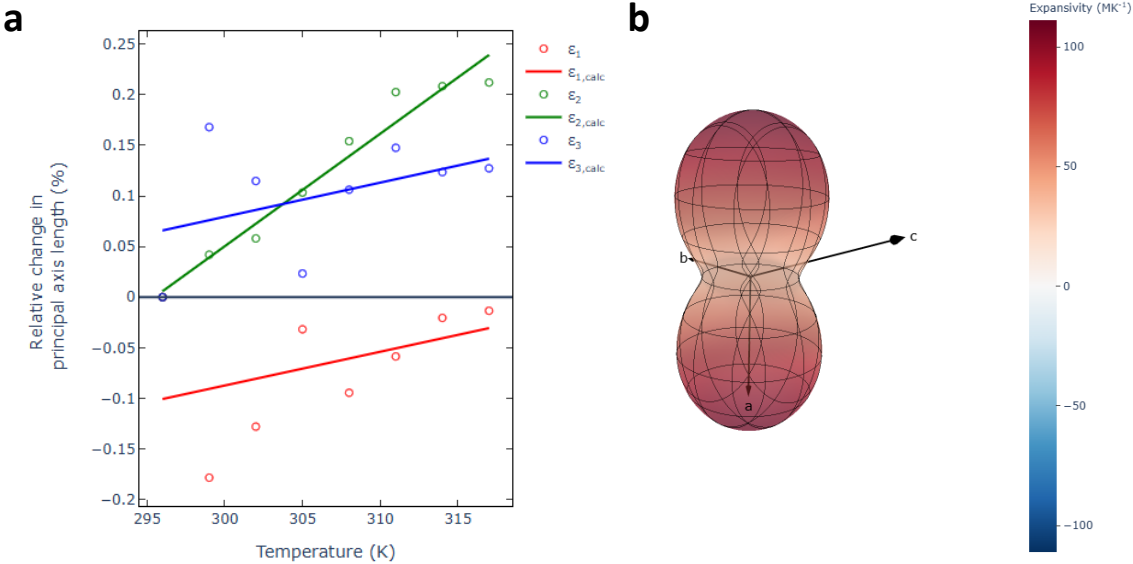
b



Supplementary Table 11. The fitting results for **1** (295–317 K) from *PASCaI* in the range of 295–317 K (after ST).

Axes	α (MK ⁻¹)	σ_α (MK ⁻¹)	Direction		
			a	b	c
X ₁	33.3362	34.0435	0.0	1.0	0.0
X ₂	111.123	8.7345	1.0	0.0	0.0
X ₃	33.7308	26.6068	0.0	0.0	1.0
V	178.4861	13.0301			

Supplementary Fig. 20. (a) Plot of the pressure-dependent changes in the principal tensor lengths for **1** in the range of 295–317 K with solid lines representing the best-fitting results (after ST) and (b) the corresponding expansivity tensor plots for **1** evaluated by *PASCaI*.



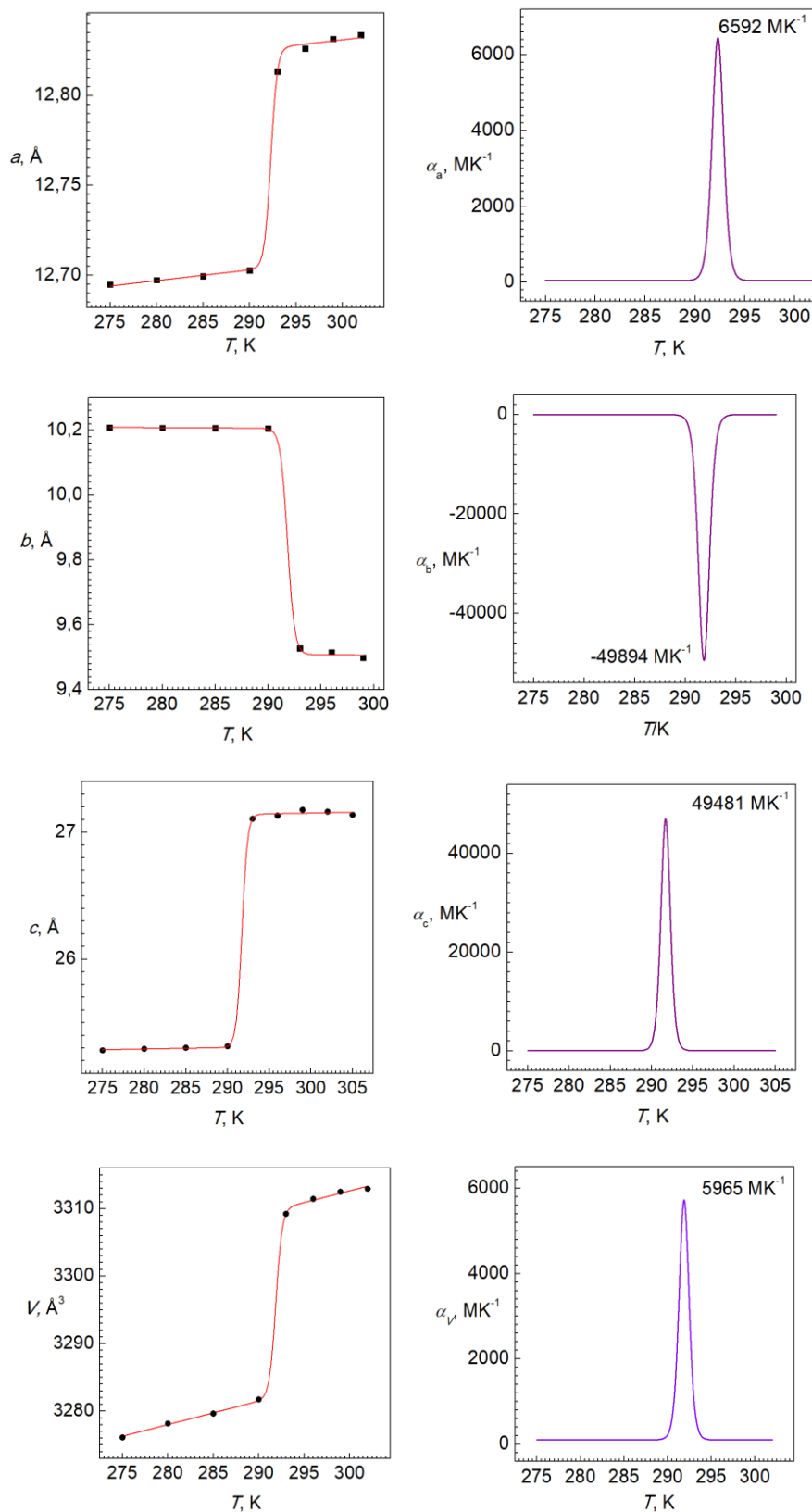
Across the ST region

Supplementary Table 12. Best fitting results of the principal axes parameters and unit cell volume over the temperature range 275-302 K by equation (2) for **1**.

	a	b	c	V
A	0.12221	-0.6978	1.83602	27.68001
B	292.2903	291.8355	291.71796	291.87683
C	0.33*	0.33*	0.33*	0.33*
D	12.5307	10.25468	24.9663	3181.08718
E	5.93984E-4	-1.67144E-4	0.00117	0.34622
R ²	0.99944	0.99966	0.99962	0.99974

* fixed value

Supplementary Fig. 21. Left: Plot of the temperature-dependent changes in the axes for **1** in the range 275–305 K across the ST. The red lines represent the nonlinear fitting using the sigmoidal function (1). Right: the corresponding thermal expansion coefficients α calculated by equation (2).



At low *P* before transition

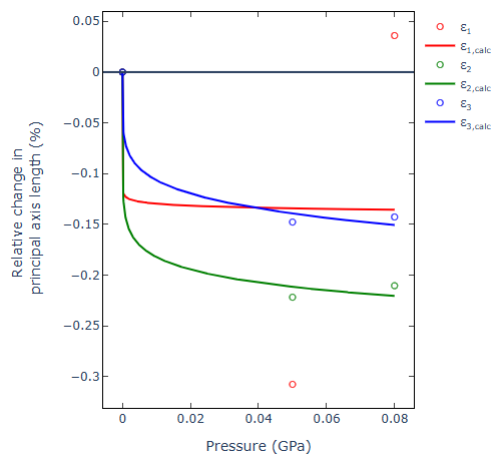
Supplementary Table 13. The fitting results for **1** from online program *PASCal* in the range of 0–0.09 GPa (before transition).

Axes	K (TPa ⁻¹)	σK (TPa ⁻¹)	Direction		
			a	b	c
X ₁	0.5786	—*	1.0	0.0	0.0
X ₂	3.801	—*	0.0	0.0	1.0
X ₃	4.5969	—*	0.0	1.0	0.0
V	49.2962	27.5202			

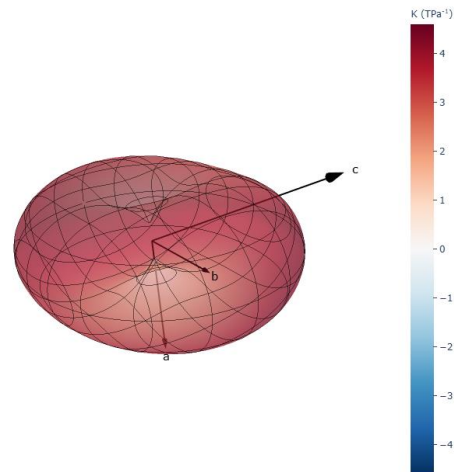
* Not enough data points for error estimation.

Supplementary Fig. 22. (a) Plot of the pressure-dependent changes in the principal tensor lengths for **1** with solid lines representing the best-fitting results and (b) expansivity tensor plots for **1** in the range of 0–0.09 GPa (before transition) evaluated by *PASCal*.

a



b

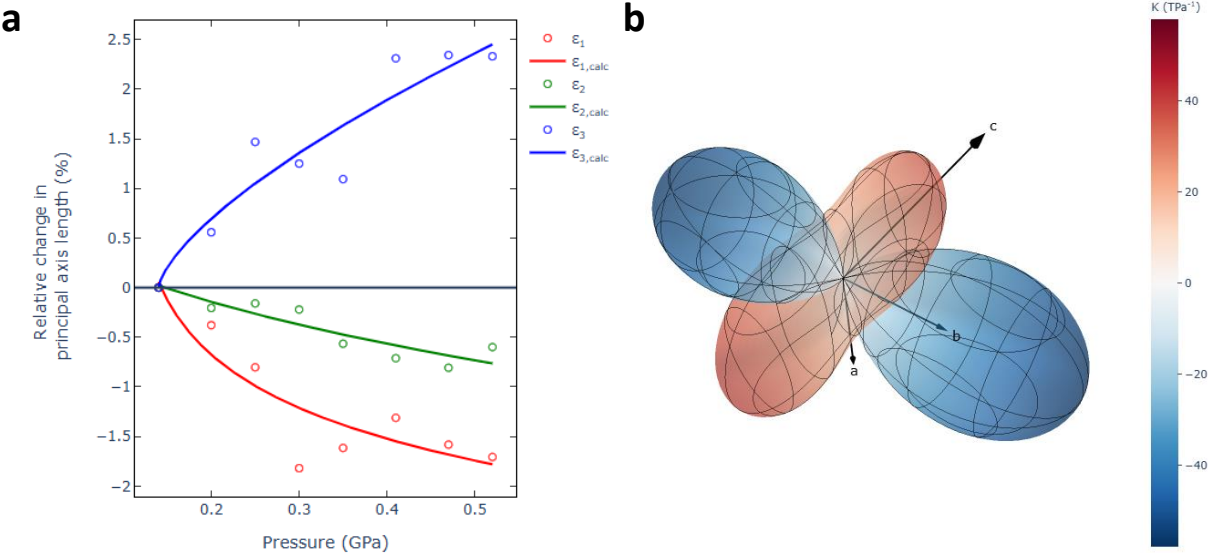


At high *P* after transition

Supplementary Table 14. The fitting results for **1** from web tool PASCAL in the range of 0.14–0.52 GPa (after transition).

Axes	K (TPa ⁻¹)	σ_K (TPa ⁻¹)	Direction		
			a	b	c
X ₁	38.4414	17.4464	0.0	0.0	1.0
X ₂	20.9367	20.747	1.0	0.0	0.0
X ₃	-57.9589	18.0049	0.0	1.0	0.0
V	1.132	6.6862			

Supplementary Fig. 23. (a) Plot of the pressure-dependent changes in the principal tensor lengths for **1** in the range of 0.14–0.52 GPa with solid lines representing the best-fitting results (after ST) and (b) expansivity tensor plots for **1** in the range of 295–317 K (after ST) evaluated by *PASCAL*.



Supplementary Note 7. Evaluation of the α in the HS^P phase

The molecule of **1** has a scissors shape with two long rigid ligand crossing at the Fe atom, which acts as the hinge (Supplementary Fig. 24). Crystal symmetry keeps the scissors in the same position with the line bisecting the molecule along the crystallographic b axis. Consequently, the lengths of the unit cell along b and c are set, almost entirely, by how far the scissors are open. Measuring the cell therefore allows calculating the opening angle α . The structures **1**(LS) and **1**(HS) in which the angle is independently known are used to calibrate it.

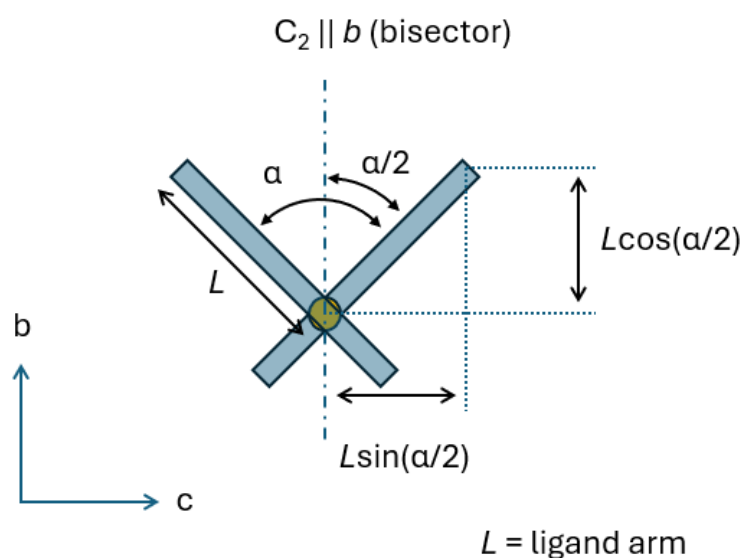
α is the angle between the planes of the two ligands. L is the arm length defined as the distance Fe...C17, which variability can be neglected [for **1**·MeOH and **1**(LS/HS) the $L = 9.79 \pm 0.06$ Å]. Because the crystallographic two-fold axis through Fe runs along b , the two ligands always locate symmetrically about b and each makes the angle $\alpha/2$ with it. The following equations connect the geometry of the molecule to the cell parameters b and c (Supplementary Fig. 24):

$$b = n_b L \cos(\alpha/2) + \delta_b \quad (S6)$$

$$c = n_c L \sin(\alpha/2) + \delta_c \quad (S7)$$

The four numbers n_b , δ_b , n_c , δ_c are packing constants, which compensate for the interlocking of the molecules and a slight tilt of the scissors plane from the bc plane.

Supplementary Fig. 24. Definition of the scissor model. The rigid ligand cross at Fe; the crystallographic two-fold axis along b bisects the opening angle α ; an arm of length L casts a projection $L\cos(\alpha/2)$ on b and $L\sin(\alpha/2)$ on c , and these projections multiplied by the packing constants build the cell edges (Equations S6–S7).



For the **1**(LS) and **1**(HS) both sides of Equations (S6)–(S7) are known, which can be used to calculate the constants. For the b axis:

$$n_b = (b_{HS} - b_{LS}) / L[\cos(\alpha_{HS}/2) - \cos(\alpha_{LS}/2)],$$

$$\delta_b = [b_{HS} \cos(\alpha_{HS}/2) - b_{LS} \cos(\alpha_{LS}/2)] / [\cos(\alpha_{HS}/2) - \cos(\alpha_{LS}/2)] \quad (S8)$$

For the c axis:

$$n_c = (c_{HS} - c_{LS}) / [L_{HS}\sin(\alpha_{HS}/2) - L_{LS}\sin(\alpha_{LS}/2)],$$

$$\delta_c = c_{HS} - n_c L_{LS}\sin(\alpha_{HS}/2)$$

The derived constants are:

$$n_b = 1.76; \delta_b = 1.70$$

$$n_c = 5.77; \delta_c = 15.73$$

To perform the back calculations for each measured pair (b , c) at as function of T and P , the two projections were calculated using equations:

$$X = (b - \delta_b) / n_b \quad Y = (c - \delta_c) / n_c \quad (S9)$$

$$\alpha = 2\arctan(Y/X) \quad (S10)$$

The derived values are collected in Supplementary Table 15.

Supplementary Table 15. Calculated α value of **1** at varying temperature ($P = 0$ GPa) and pressure ($T = 298$ K).

P (GPa)	α (°)	Phase	T (K)	α (°)	Phase
0.00	98.43	HS	220	92.57	LS
0.05	98.42		230	92.62	
0.08	98.42		240	92.67	
0.14	92.05	HS ^P	250	92.71	
0.20	91.65		260	92.76	
0.25	91.27		270	92.80	
0.30	91.03		275	92.82	
0.35	90.81		280	92.84	
0.41	90.45		285	92.86	
0.47	90.35		290	92.88	
0.52	90.31		293	98.66	HS
			297	98.75	
			299	98.90	
			302	98.85	
			305	98.77	
			308	98.83	
			311	98.83	
			314	98.80	
			317	98.80	

CheckCIF Explanation of A and B level alerts for 1 (LS) and 1 (HS)

1 (LS) CCDC 2468400

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds 0.07 Ang.

Author Response: *The structure was solved and refined from powder X-ray diffraction data by the Rietveld method. The lower precision of bond lengths is typical for powder data and is considered acceptable for the present discussion.*

1 (HS) CCDC 2468401

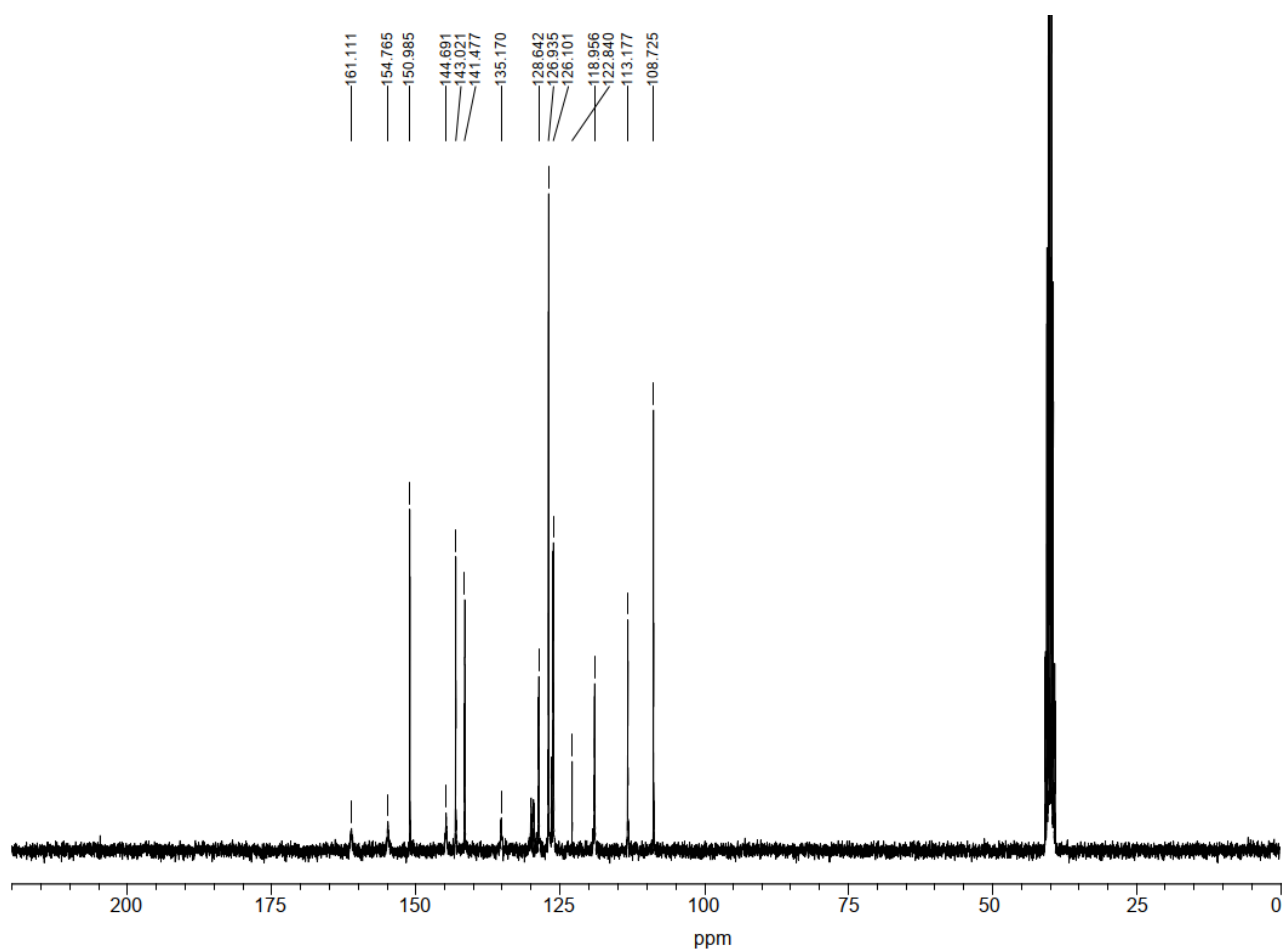
Alert level A

PLAT341_ALERT_3_A Low Bond Precision on C-C Bonds 0.09533 Ang.

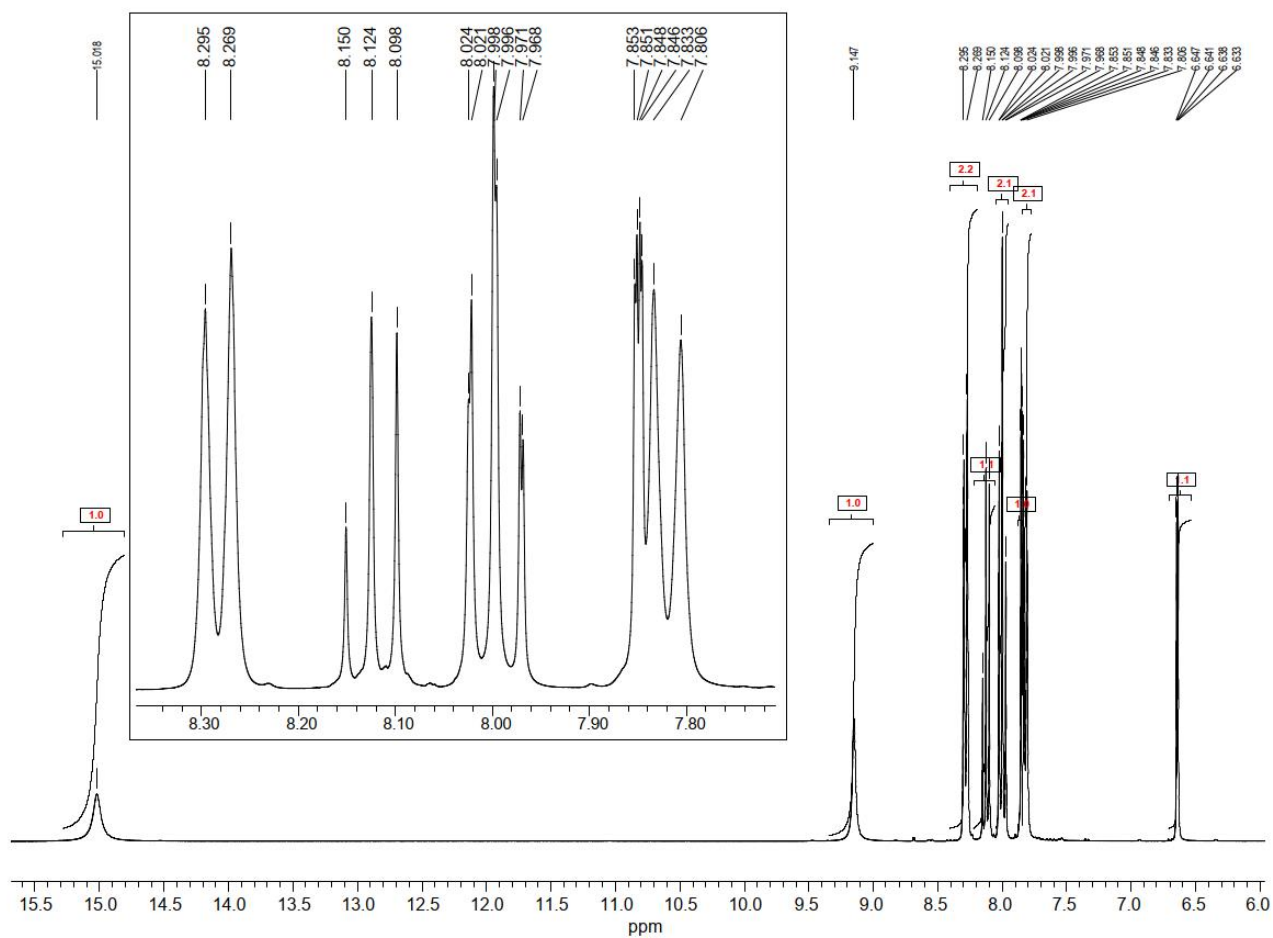
Author Response: *The structure was solved and refined from powder X-ray diffraction data by the Rietveld method. The lower precision of bond lengths is typical for powder data and is considered acceptable for the present discussion.*

NMR spectra of the ligand L in DMSO-d⁶

¹³C:



^1H :



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