Supplementary Information

for:

Long-range Supramolecular Synthon Polymophism. An Insight from the Case Study of Vinylic Tellurium Trihalides *Z*-Cl(Ph)C=C(Ph)TeX$_3$. (X = Cl, Br, I).

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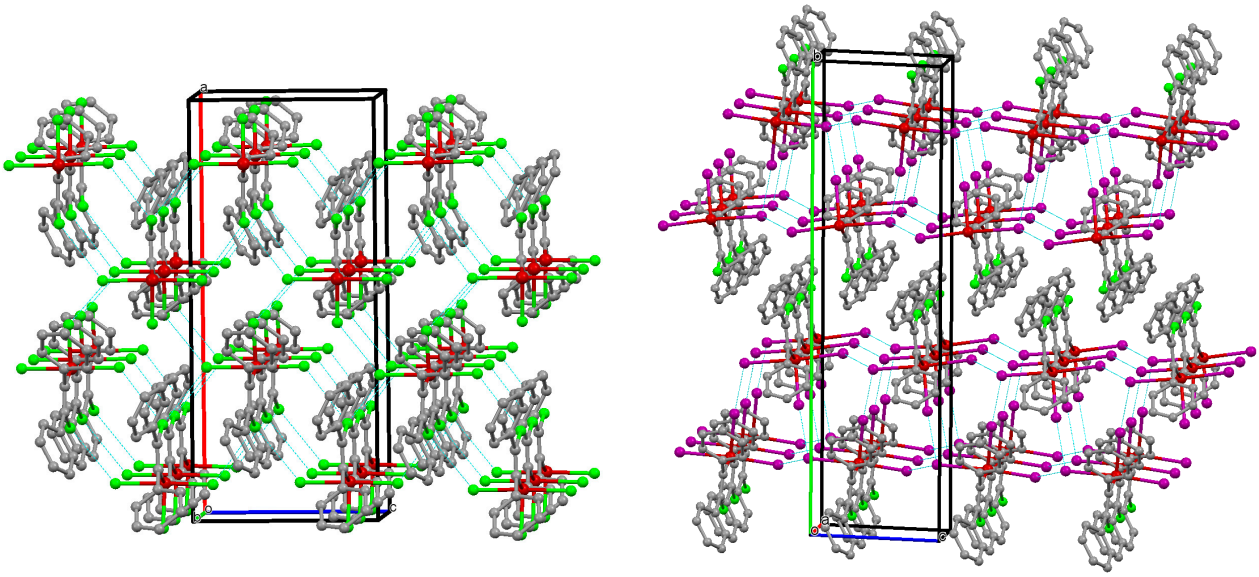

Figure S1
Fragments of the packing in (a) **1*α*** *Pca2*$_1$ **a** 21.031(3) **b 8.2010(8) c** 9.215(1) and (b) **2*α*** *P2*$_1$*/c* **a 8.2395(5) b** 27.9101(17) **c** 8.7289(5)

Table S1. Lattice energy
Calculated in Crystal Explorer 17.5 (CE-B3LYP-DGDZVP, 25 Å cluster)

1*α*	-247,6 kJ/mol
1β	-243,2 kJ/mol
	-4,4 kJ/mol

2*α*	-246,7 kJ/mol
2β	-242 kJ/mol
	-4.7 kJ/mol

Powder XRD

The compound was analyzed by powder X-Ray diffraction method to estimate the purity of the sample and check of possible presence of other crystal phases. The overlay of the experimental powder diffraction pattern with the theoretically calculated one shows good correlation of the crystal structures with the material. But in both cases we observe the presence of impurity components.

The PXRD analysis of **1β (***Cc***)** sample revealed the ~20% admixture of **1*α*** (*P*2_1/*c*) in addition to 80% of **1β** (see Fig. S2, S3). Further recrystallization of this **1β** sample afforded only **1*α*** as the main product (90%) (see Fig. S4, S5), contaminated with the unidentified admixtures, which possibly may be the products of hydrolysis of **1**. Hydrolytic cleavage of Te-Cl bonds in tellurium triclorides is well documented and earlier we have particularly demonstrated such a possibility for **1**, resulting in Cl(Ph)C=C(Ph)$TeCl_2$OH-DMSO solvate [1]. Although the detailed study of the decomposition byproducts is out of the focus of this work, we can note that much higher phase purity of **2β** and **2*α* -β** even after several recrystallizations is in good agreement with the increasing stability of tellurium trihallides towards the hydrolysis in a row $RTeI_3$>$RTeBr_3$>$RTeCl_3$.

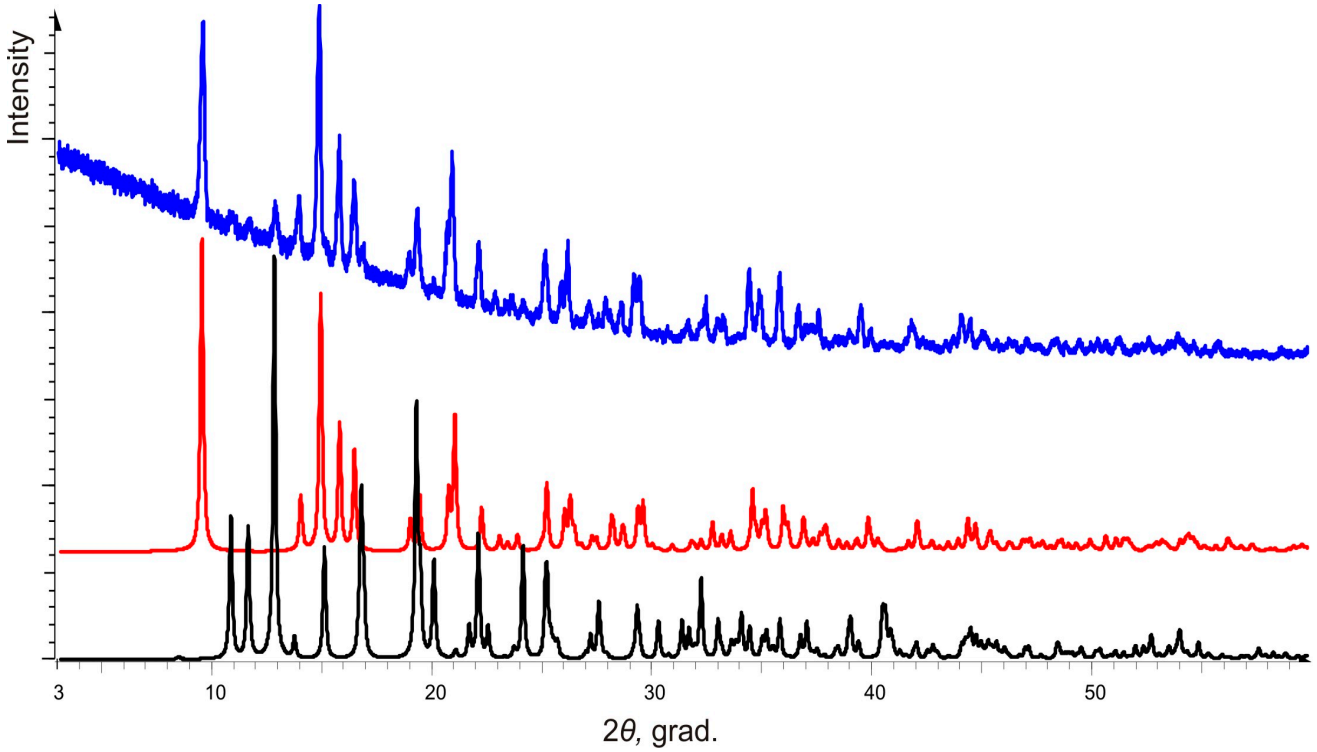

Figure S2

Theoretical powder diffraction patterns of **1α**-polymorph (black) and **1β**-polymorph (red) and experimental patterns of the crystalline sample **1β** (blue).

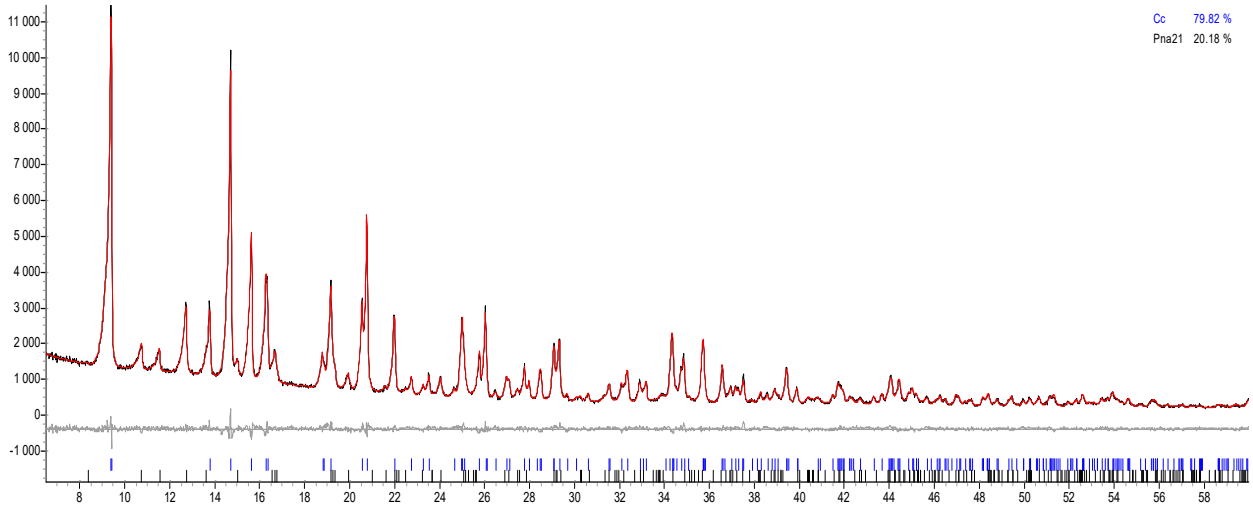

Figure S3

Final fit of the Rietveld refinement of the structure 1**β** (R_{wp} = 0.031)**:** experimental X-ray diffraction pattern (black), Pawley fit (red) and difference profile (gray). .

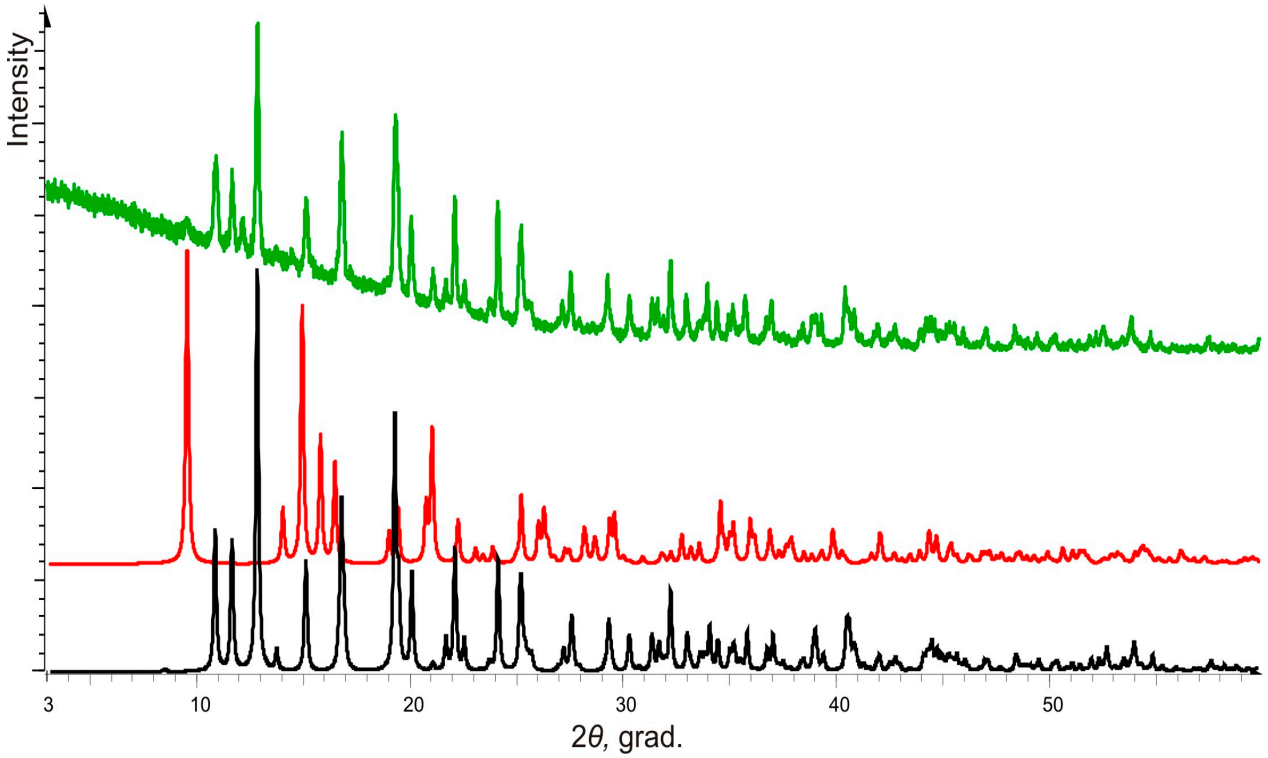

Figure S4
Theoretical powder diffraction patterns of **1*α***-polymorph (black) and **1β-**polymorph (red) and experimental patterns of the crystalline sample **1*α*** (green).

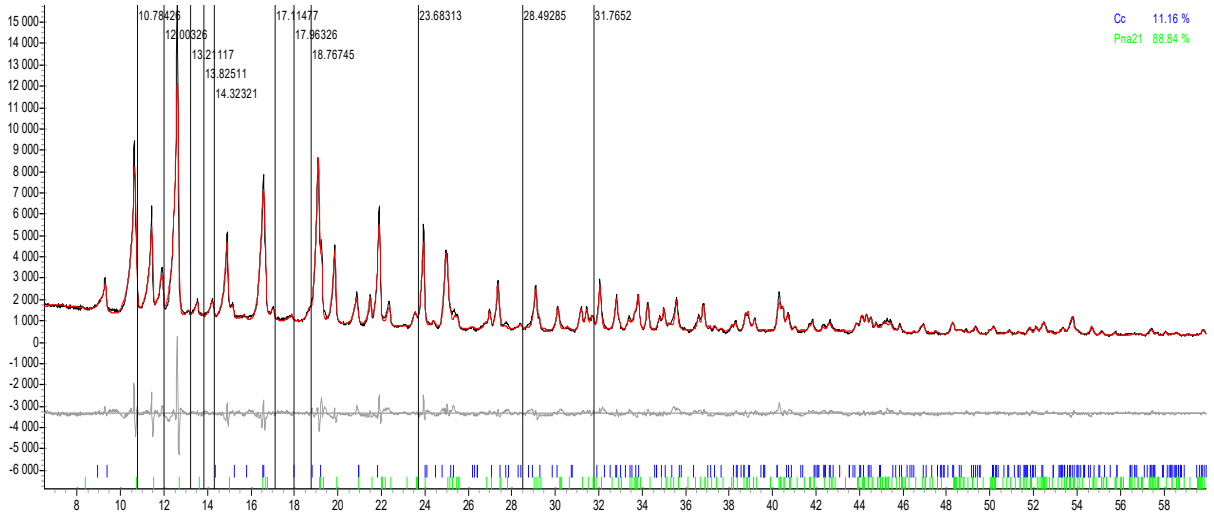

Figure S5

Final fit of the Rietveld refinement of the structure 1***α*** (R_{wp} = 0.067): experimental X-ray diffraction pattern (black), Pawley fit (red) and difference profile (gray).

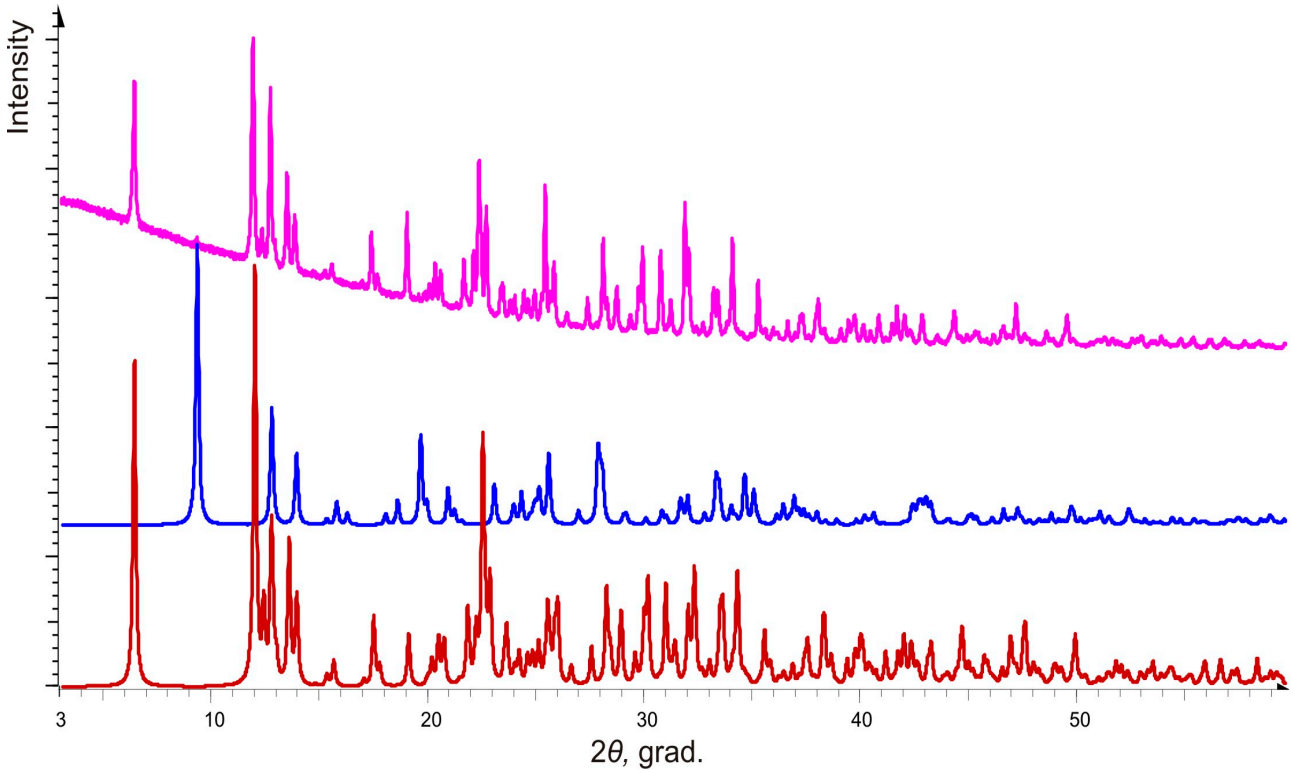

Figure S6
Figure 5. Theoretical powder diffraction patterns of 2α-polymorph (brown) and 2β-polymorph (blue) and experimental patterns of the crystalline sample 2β (magenta).

Table S2. Interaction Energies (kJ/mol) in **1α**

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	x+1/2, -y, z	11.14	B3LYP/DGDZVP	-3.1	-0.5	-10.6	4.7	-10.0
	1	-x+1/2, y, z+1/2	6.49	B3LYP/DGDZVP	-15.1	-3.0	-48.8	43.8	-33.6
	0	-x, -y, z+1/2	8.78	B3LYP/DGDZVP	0.8	-0.9	-8.5	7.5	-2.6
	1	-x+1/2, y, z+1/2	10.46	B3LYP/DGDZVP	-2.6	-0.6	-5.2	2.6	-6.2
	0	x, y, z	8.20	B3LYP/DGDZVP	-19.6	-1.7	-32.4	38.3	-26.5
	1	-x+1/2, y, z+1/2	10.46	B3LYP/DGDZVP	-7.2	-1.2	-8.5	9.5	-10.0
	0	-x, -y, z+1/2	8.37	B3LYP/DGDZVP	-19.3	-3.0	-27.8	28.1	-29.4

R is the distance between molecular centroids (mean atomic position) in Å.
Total energies are the sum of the four energy components, scaled appropriately [2]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

Table S3. Interaction Energies (kJ/mol) in **1β**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x+1/2, -y+1/2, z+1/2	7.60	B3LYP/DGDZVP	-13.9	-2.9	-36.8	36.5	-26.5
2	x, -y, z+1/2	6.34	B3LYP/DGDZVP	-30.4	-3.4	-41.4	68.8	-28.2
2	x+1/2, -y+1/2, z+1/2	8.34	B3LYP/DGDZVP	-12.6	-2.3	-38.0	38.0	-24.6
2	x+1/2, y+1/2, z	10.82	B3LYP/DGDZVP	0.4	-0.5	-6.6	3.1	-3.8
2	x, y, z	7.79	B3LYP/DGDZVP	-5.3	-1.3	-12.7	10.2	-11.3
2	x, y, z	10.89	B3LYP/DGDZVP	-10.6	-1.6	-11.8	17.1	-12.1

R is the distance between molecular centroids (mean atomic position) in Å.
Total energies are the sum of the four energy components, scaled appropriately [2]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

Table S4. Interaction Energies (kJ/mol) in **3α**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-x, -y, -z	8.45	B3LYP/DGDZVP	-13.0	-2.1	-34.2	37.4	-22.0
0	x, y, z	8.73	B3LYP/DGDZVP	-9.5	-1.5	-19.6	31.9	-8.5
1	x, y, z	9.02	B3LYP/DGDZVP	-3.7	-0.8	-17.1	12.4	-11.8
1	-x, -y, -z	11.06	B3LYP/DGDZVP	-8.3	-1.3	-33.7	23.0	-24.8
1	x, y, z	8.24	B3LYP/DGDZVP	-21.3	-2.0	-39.3	42.3	-32.0
0	x, -y+1/2, z+1/2	9.61	B3LYP/DGDZVP	-7.1	-0.6	-13.2	18.2	-8.2
0	x, -y+1/2, z+1/2	7.48	B3LYP/DGDZVP	-71.2	-4.3	-31.9	156.2	-9.7
1	-x, -y, -z	9.93	B3LYP/DGDZVP	-18.8	-2.2	-38.2	40.8	-29.6
0	-x, -y, -z	14.92	B3LYP/DGDZVP	2.7	-0.7	-8.0	0.0	-4.7

R is the distance between molecular centroids (mean atomic position) in Å.
Total energies are the sum of the four energy components, scaled appropriately[2]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

Table S5. Interaction Energies (kJ/mol) in **3β**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x, -y, z+1/2	6.85	B3LYP/DGDZVP	-43.4	-3.0	-42.6	97.9	-24.7

	2	x, -y, z+1/2	12.32	B3LYP/DGDZVP	-3.7	-0.4	-4.0	0.0	-7.7
	2	x+1/2, -y+1/2, z+1/2	8.94	B3LYP/DGDZVP	-11.2	-1.6	-35.1	33.8	-22.7
	2	x, y, z	8.57	B3LYP/DGDZVP	-8.7	-1.1	-21.3	23.1	-14.2
	2	x+1/2, -y+1/2, z+1/2	7.74	B3LYP/DGDZVP	-49.4	-3.7	-41.4	111.5	-22.0
	2	x, y, z	11.17	B3LYP/DGDZVP	-12.2	-1.3	-17.1	25.8	-12.8
	2	x+1/2, y+1/2, z	11.33	B3LYP/DGDZVP	0.8	-0.3	-4.6	0.5	-3.1

R is the distance between molecular centroids (mean atomic position) in Å.
Total energies are the sum of the four energy components, scaled appropriately [2]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

1. Torubaev, Y.V.; Lyssenko, K.A.; Popova, A.E. Halogen and Hydrogen Bonds in Co-crystalline Ferrocenium Organotellurium Halide Salts. *Russian Journal of Coordination Chemistry* **2019**, *45*, 788-794, doi:10.1134/s1070328419110095.
2. Mackenzie, C.F.; Spackman, P.R.; Jayatilaka, D.; Spackman, M.A. CrystalExplorer model energies and energy frameworks: extension to metal coordination compounds, organic salts, solvates and open-shell systems. *IUCrJ* **2017**, *4*, 575-587, doi:10.1107/S205225251700848X.