Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis and mutual transformations of nitronium tetrakis(nitrooxy)- and tetrakis(2,2,2-trifluoroacetoxy)borates

Victor P. Zelenov, Evgeny Yu. Gorshkov, Mikhail V. Zavaruev, Artem O. Dmitrienko, Ivan A. Troyan, Alla N. Pivkina, Dmitry V. Khakimov, and Alexander V. Pavlikov

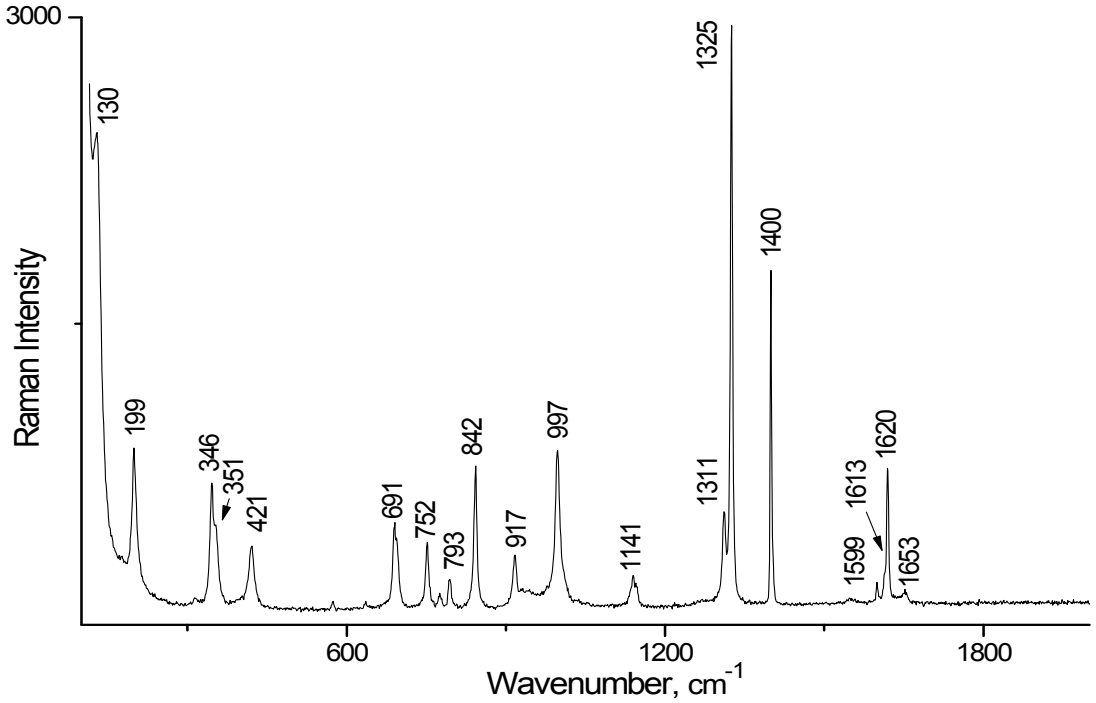

Figure S1. Raman spectrum of $NO_2[B(NO_3)_4]$ (**1**).

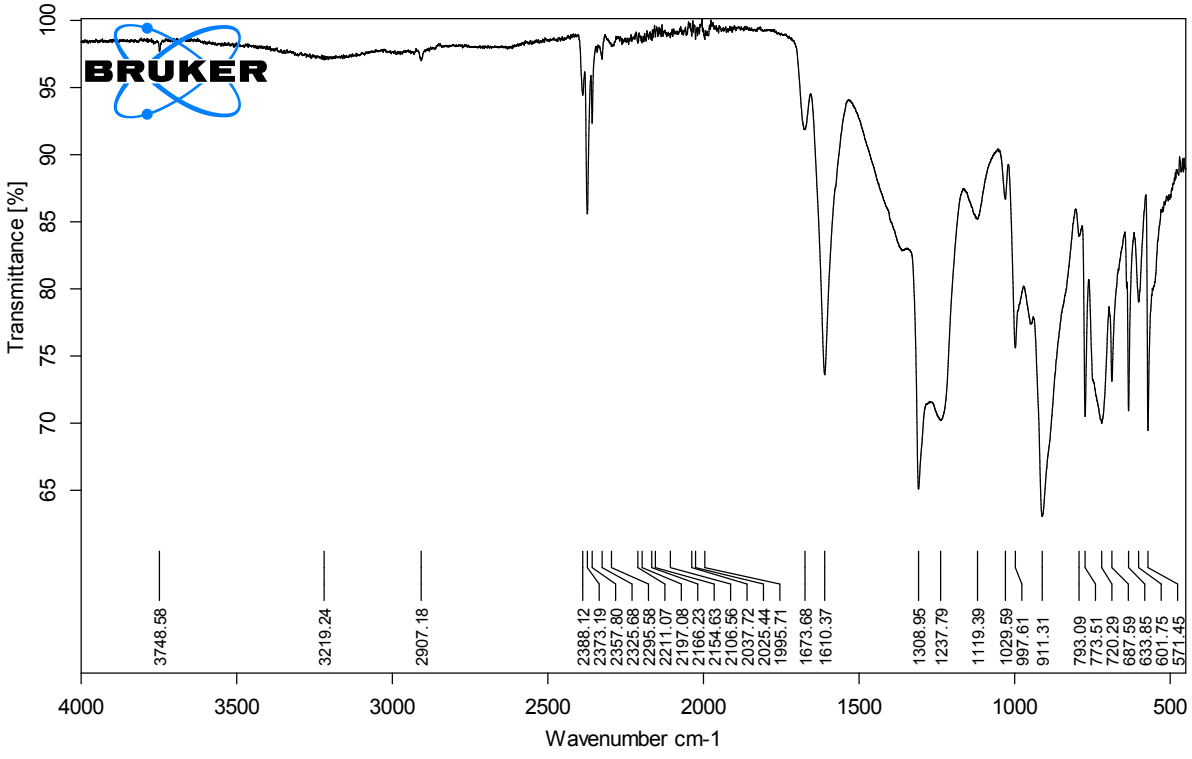

Figure S2. IR spectrum of $NO_2[B(NO_3)_4]$ (**1**).

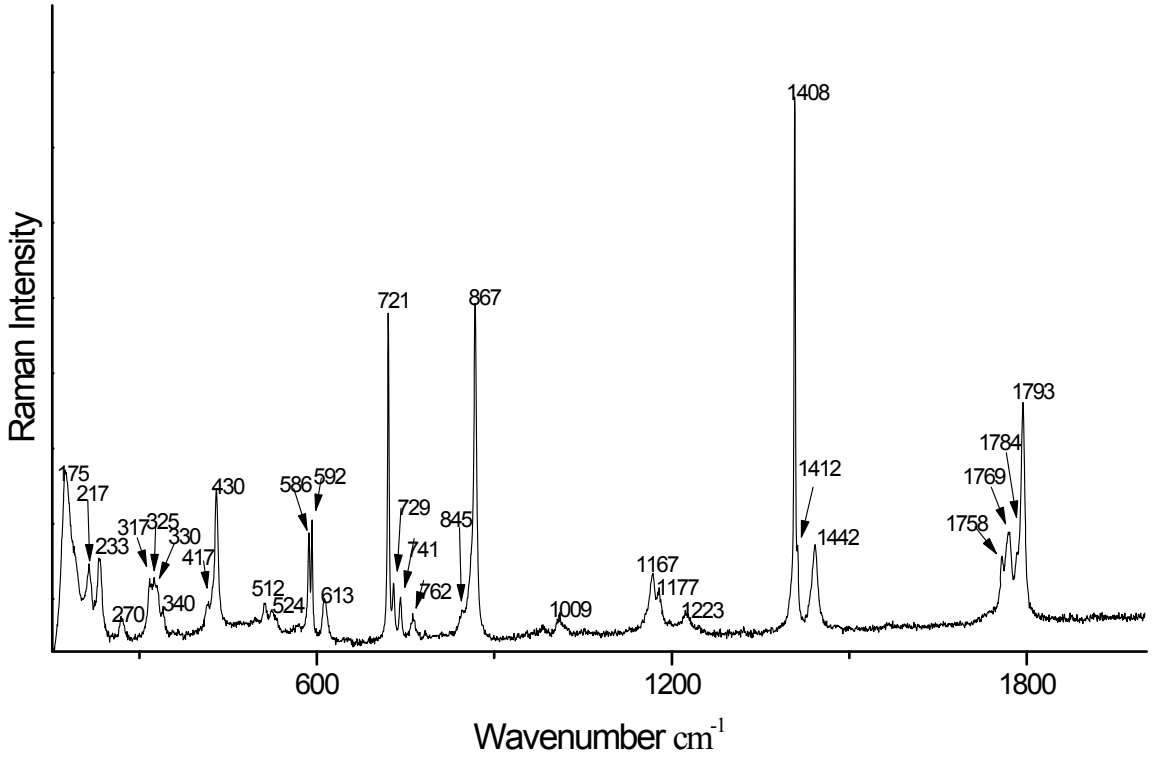

Figure S3. Raman spectrum of $NO_2[B(CF_3COO)_4]$ (**2**).

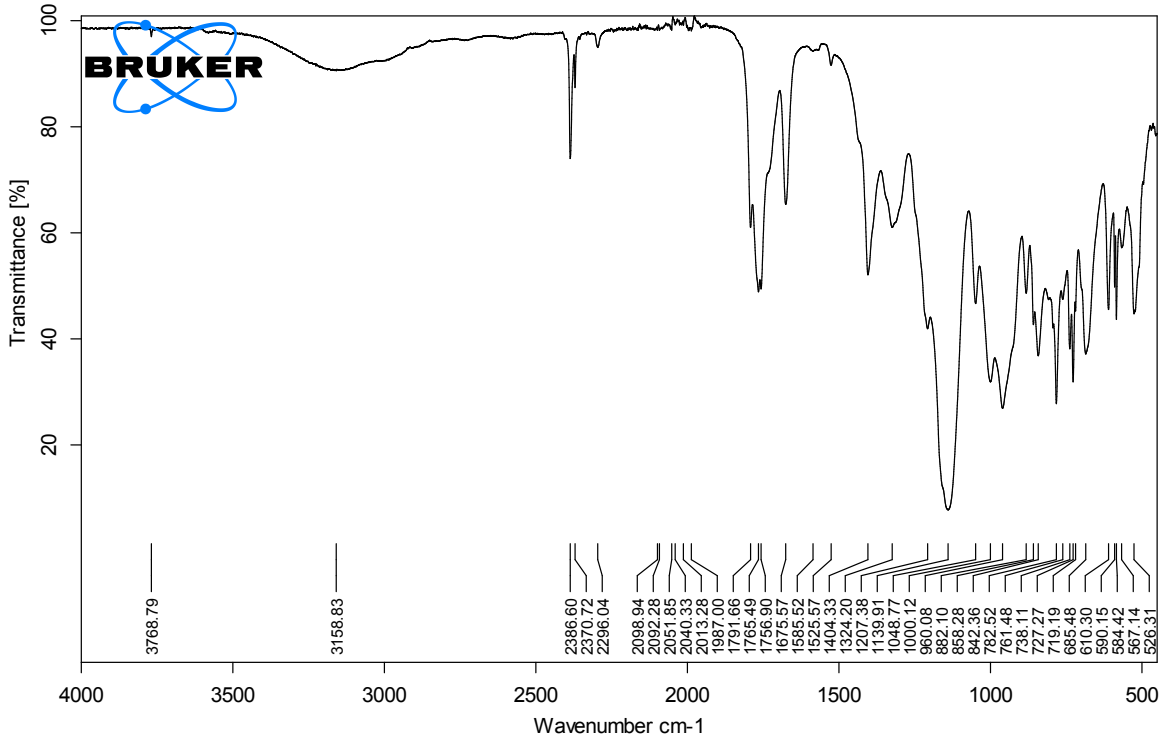

Figure S4. IR spectrum of $NO_2[B(CF_3COO)_4]$ (**2**).

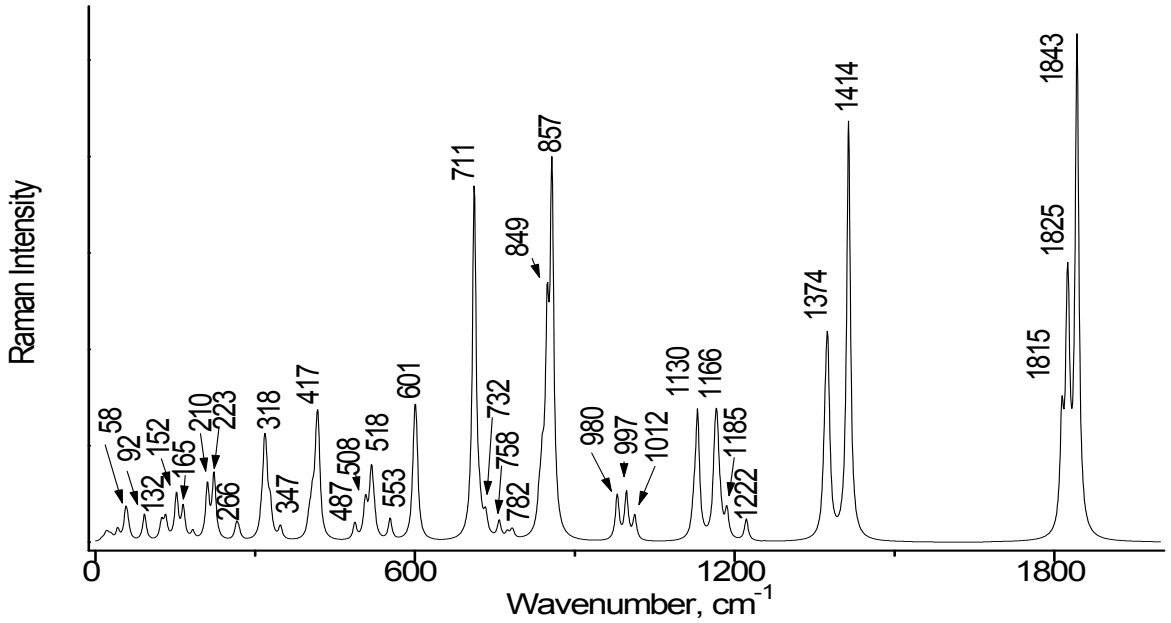

Figure S5. Calculated Raman spectrum of $B(CF_3COO)_4]^-$ ion.

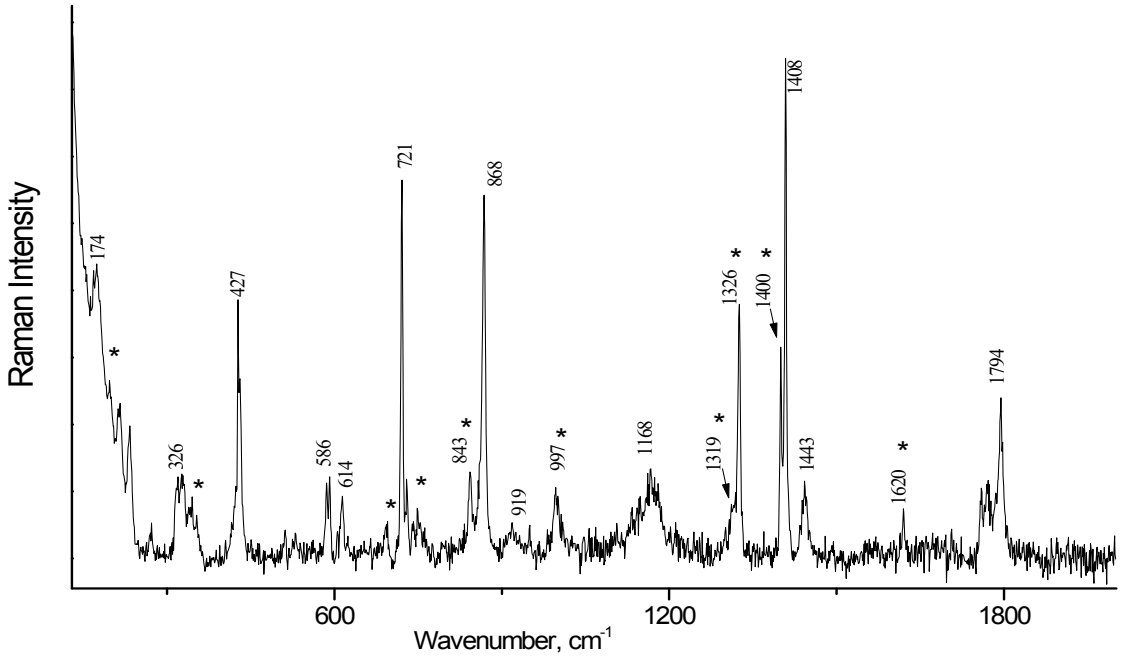

Figure S6. Raman spectrum of mixture of $NO_2[B(CF_3COO)_4]$ (**2**) with $NO_2[B(NO_3)_4]$ (**1**), which was obtained from $B(CF_3COO)_3$ and N_2O_5. The bands corresponding to the spectrum of compound **1** are marked with asterisks.

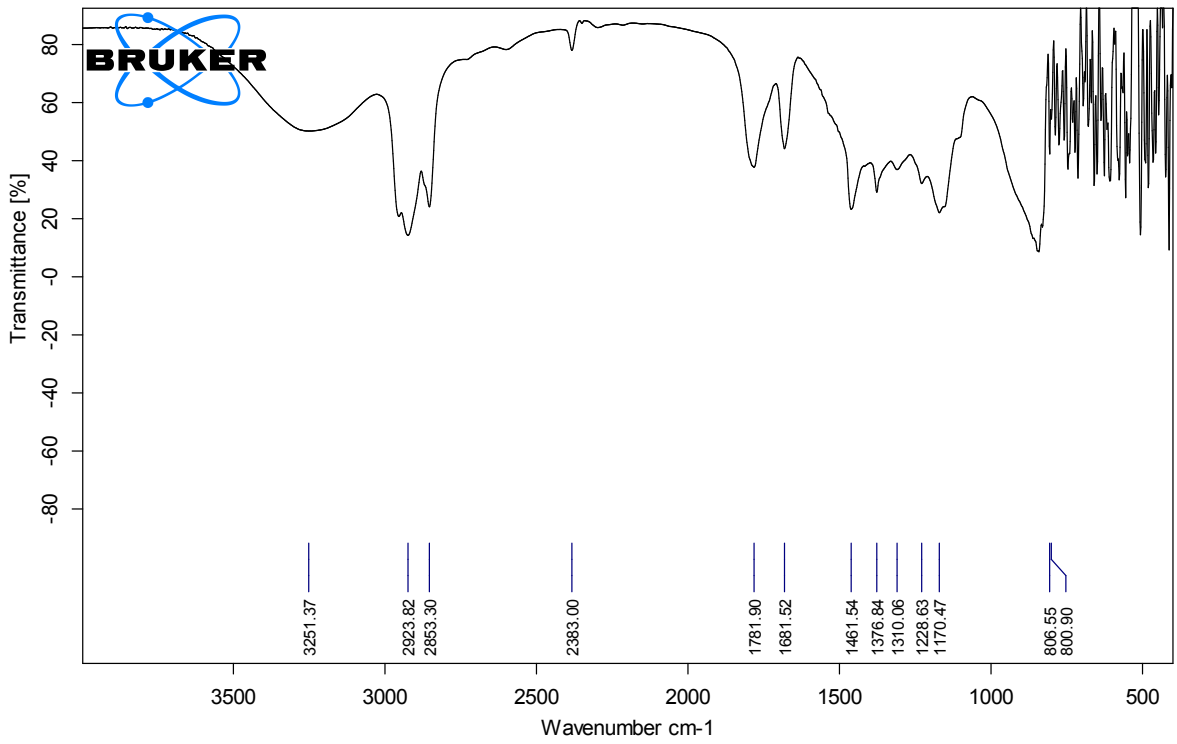

Figure S7. IR spectrum (Nujol mull) of mixture of $NO_2[B(CF_3COO)_4]$ (**2**) with $NO_2[B(NO_3)_4]$ (**1**), which was obtained from $B(CF_3COO)_3$ and N_2O_5.

Figure S8. Filtration of N_2O_5 under an argon stream.

The X-ray powder diffraction (details)

The X-ray powder diffraction pattern was measured using Cu $K_{\alpha 1}$ radiation in transmission mode on a Bruker D8 Advance diffractometer equipped with LynxEye 1D detector and Ge^{111} monochromator. The pattern of compound **1** was indexed using SVD-Index algorithm in tetragonal syngony; systematic absences agreed with space

groups $I\bar{4}$ and $I4$. Cell volume and the symmetry of the $B(NO_3)_4^-$ anion was consistent with $I\bar{4}$ space group and the independent part of the cell containing a single NO_3 group.

The initial solutions for the structure were obtained by search in the direct space using Parallel Tempering as implemented in FOX. The resulting structure was used as a starting geometry for the Rietveld refinement as well as the DFT calculations in crystal with fixed and optimized unit-cell.

With only 13 atomic coordinates and 2 (one for the cation and one for the anion) isotropic thermal displacement parameters Rietveld refinement was performed without any restraints or constraints.

$R_{wp}/R_{wp}'/R_p/R_p'/R_{Bragg}$ =6.66/11.28/4.77/19.91/1.58 % and the difference curve was featureless.

The RMSD of the atomic positions in the Rietveld refined structure from ones obtained by a calculation with optimized unit cell was 0.044 Å — within the limits proposed by J. van de Streek and M. Neumann for correct powder structures.[1]

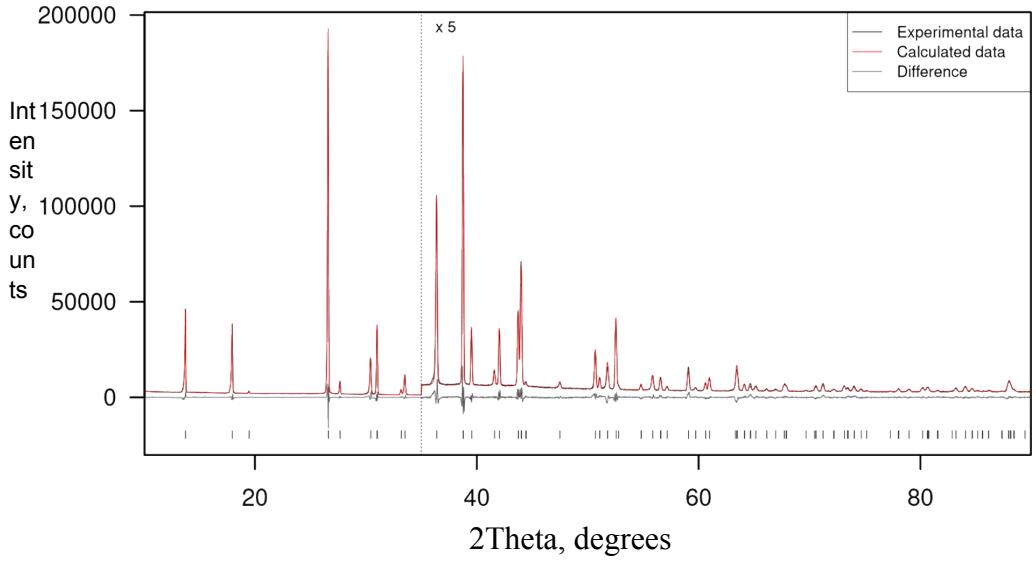

Figure S9. Final observed (black), calculated (red) and difference profiles for the Rietveld refinement of compound **1**.

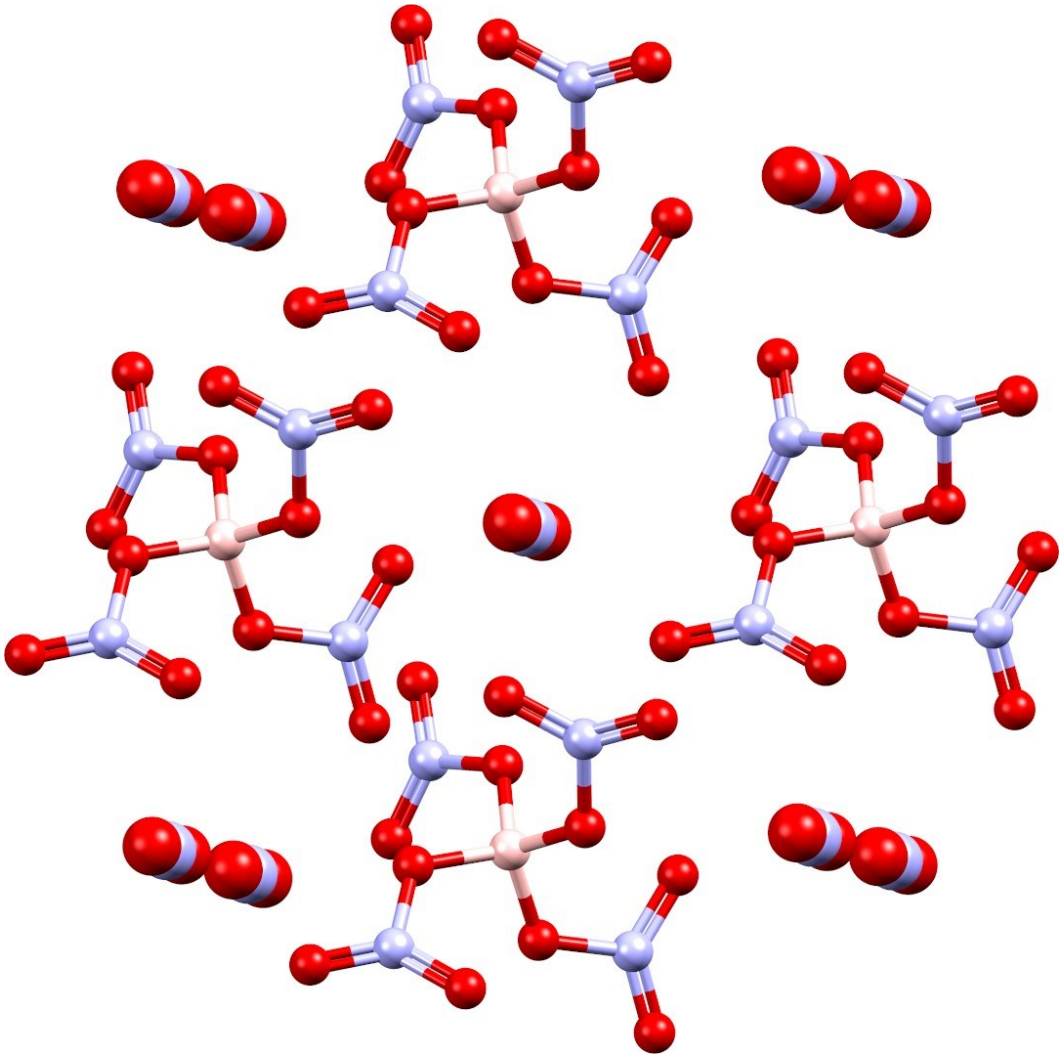

Figure S10. Fragment of the crystal packing of the compound **1**. Isotropic displacement parameters for atoms are drawn at 50 % probability.

The pattern of the compound **2** was indexed using SVD-Index algorithm in orthorhombic syngony; cell volume and systematic absences agreed with space group *Pbca* and Z = 8.

The initial solutions for the structure were obtained by search in the direct space using Parallel Tempering as implemented in FOX. The resulting structure was used as a starting geometry for the DFT calculations in crystal with fixed and optimized unit-cell.

Optimization results with fixed unit cell were used as the starting geometries and the sources of bond and angle restrains in the Rietveld refinements. The fit for resulting model was unsatisfactory. Since trifluoromethyl groups often show positional disorder, we considered it in the model. The new components were placed to the geometrically calculated (by rotating CF_3 groups about corresponding C-C bonds by 180°) positions and were subject to the same set of soft bond and angle restraints as the original CF_3 groups. Considering disorder lead to a 1.5% drop in R_{wp}, and the refined occupancies of

minor components were 0.149(10) for (F1, F2, F3) group, 0.160(11) for (F4, F5, F6) group, 0.132(9) for (F7, F8, F9) group, and 0.099(9) for (F10, F11, F12) group.

$R_{wp}/R_{wp}'/R_p/R_p'/R_{Bragg}$ = 3.62/7.92/2.66/7.96/1.57 %, the difference curve was featureless and the molecular geometry preserved well after the unrestrained refinement.

The RMSD of the atomic positions in the Rietveld refined structure from ones obtained by a calculation with optimized unit cell was 0.052 Å — within the limits proposed by J. van de Streek and M. Neumann for correct powder structures.

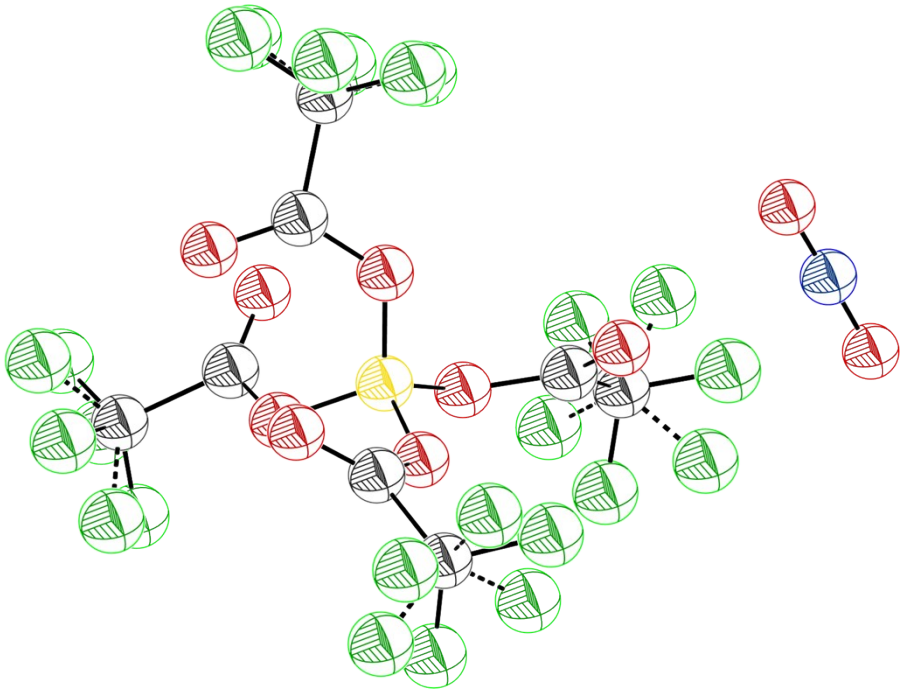

Figure S11. General view of the compound **2** in a crystal including disordered fluorine atoms. Isotropic displacement parameters for atoms are drawn at 50 % probability.

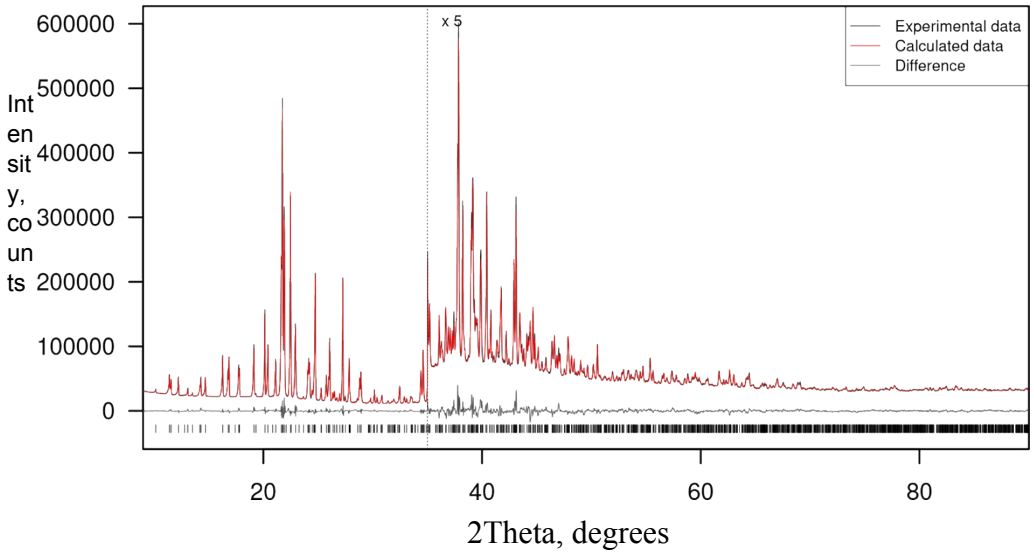

Figure S12. Final observed (black), calculated (red) and difference profiles for the Rietveld refinement of the compound **2**.

[1] J. van de Streek and M. A. Neumann, *Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials,* **2014**, *70*, 1020–1032. DOI:10.1107/s2052520614022902