Electronic Supplementary Information:

The two new derivatives of scandium borohydride, $MSc(BH_4)_4$, M = Rb, Cs, prepared via a one-pot solvent-mediated method

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Contents:

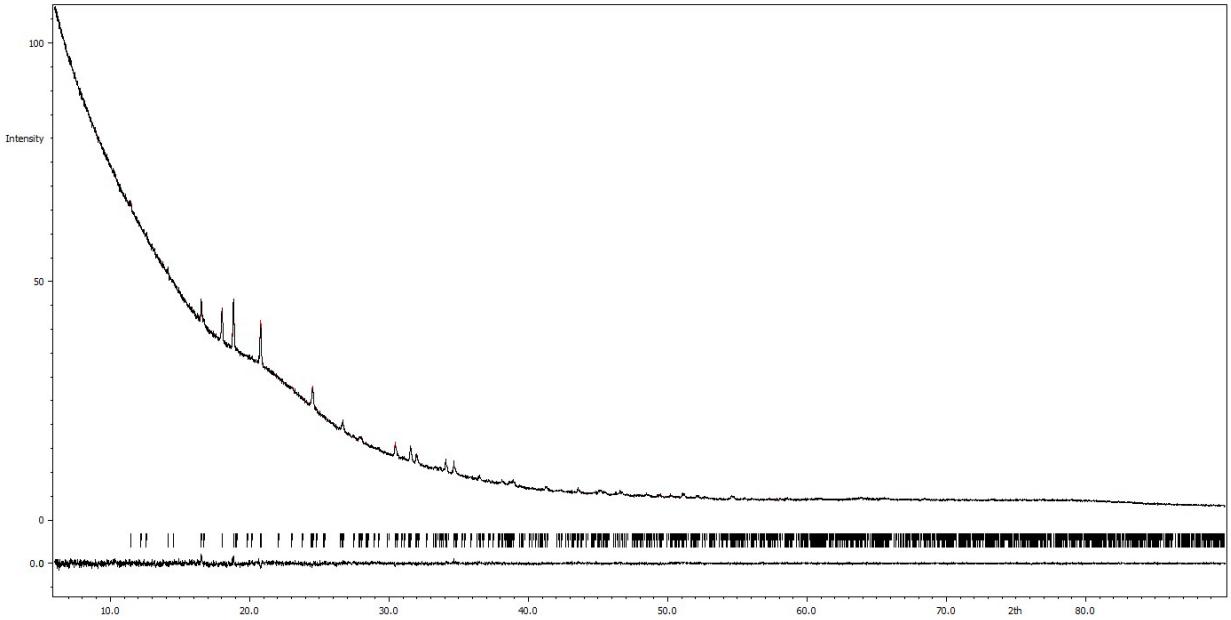

Figure S1. Rietveld refinement of PXRD (Cu K_α) data collected for $CsSc(BH_4)_4$ at room temperature, wRp = 1.17%, R(obs)= 4.72%.

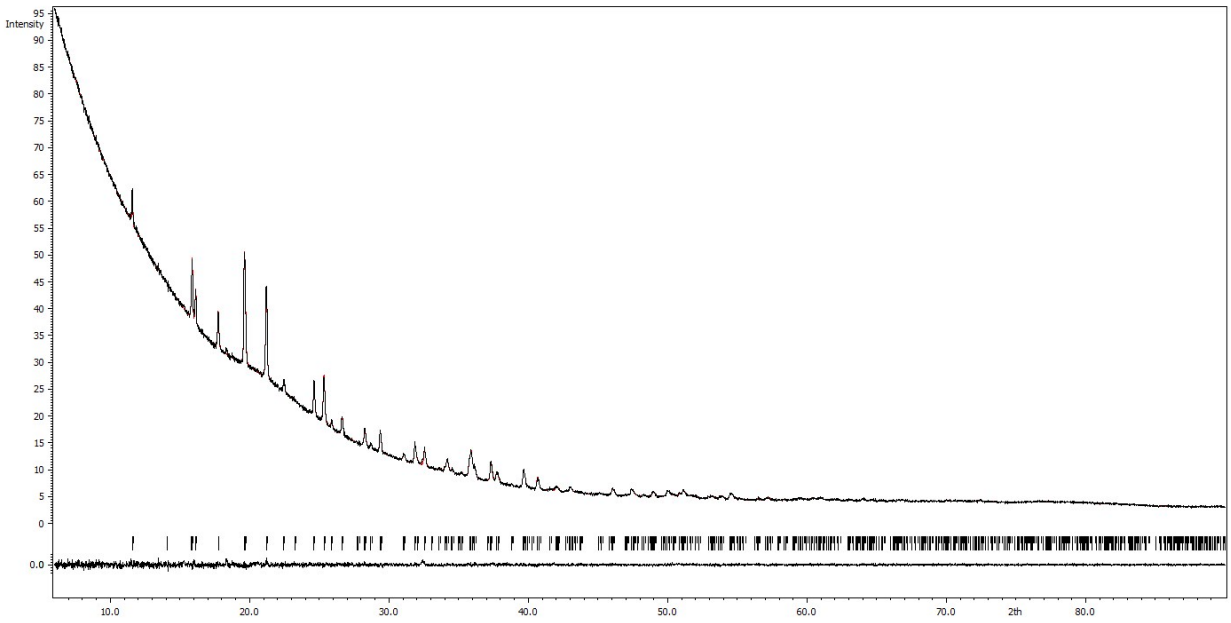

Figure S2. Rietveld refinement of PXRD (Cu K_α) data collected for $RbSc(BH_4)_4$ at room temperature, wRp = 1.23%, R(obs)= 2.29%.

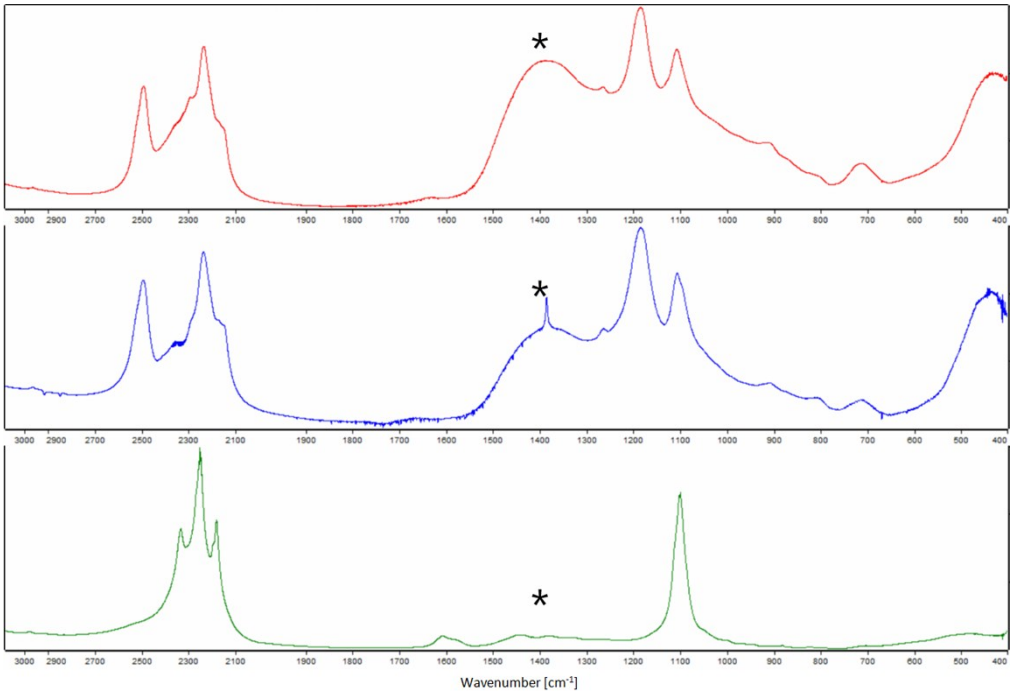

Figure S3. FTIR spectra of $CsSc(BH_4)_4$ obtained via mechanochemical (top) and solvent-mediated (middle) synthesis as well as of by-products of solvent-mediated synthesis (down, site **B**), * - background compensation error.

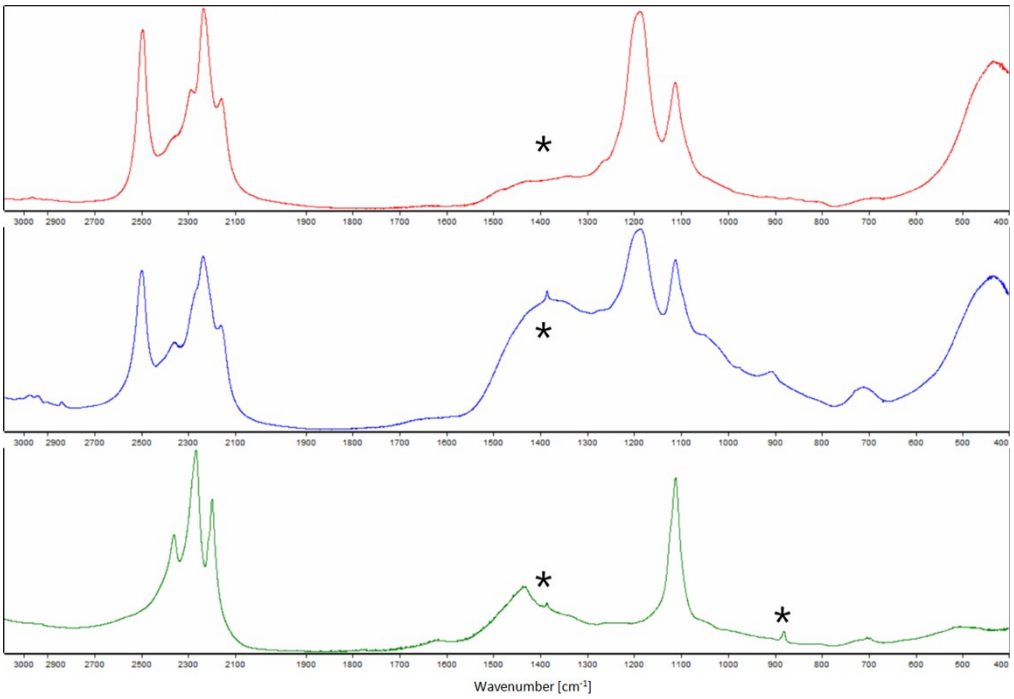

Figure S4. FTIR spectra of $RbSc(BH_4)_4$ obtained via mechanochemical (top) and solvent-mediated (middle) synthesis as well as of by-products of solvent-mediated synthesis (down, site **B**), * - background compensation errors.

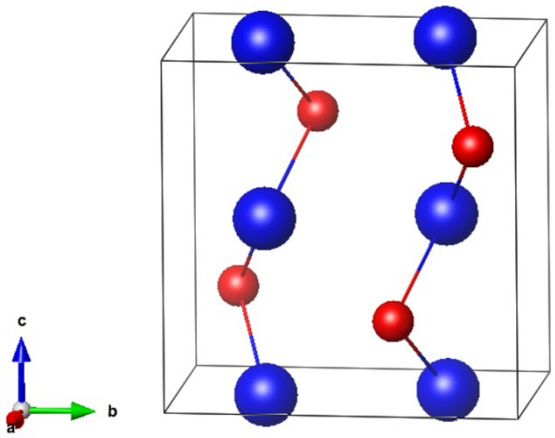

Figure S5. Sc-Rb zigzag lines along the *c*-axis in $RbSc(BH_4)_4$. Rb atoms in blue, Sc in red, Sc-Rb distance 4.487(5) Å.

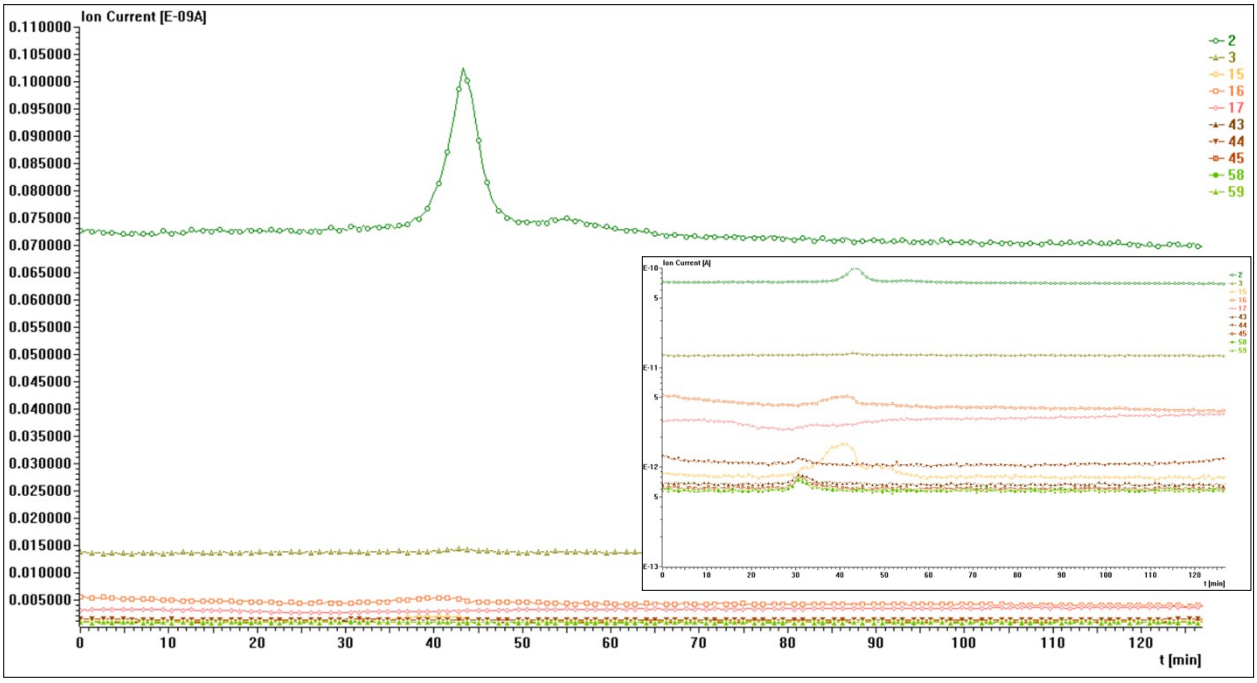

Figure S6. Mass spectrum of gaseous decomposition products of $RbSc(BH_4)_4$ obtained mechanochemically (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 15 °C.

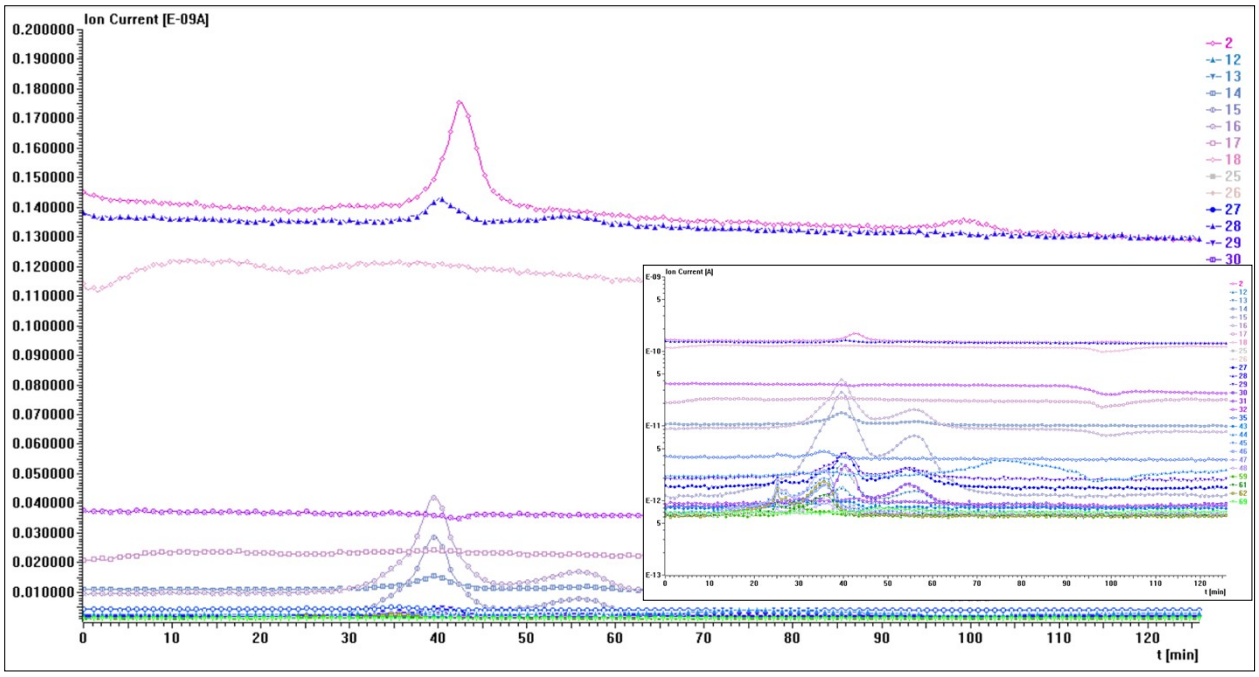

Figure S7. Mass spectrum of gaseous decomposition products of $RbSc(BH_4)_4$ obtained via DMS-mediated synthesis (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 20 °C.

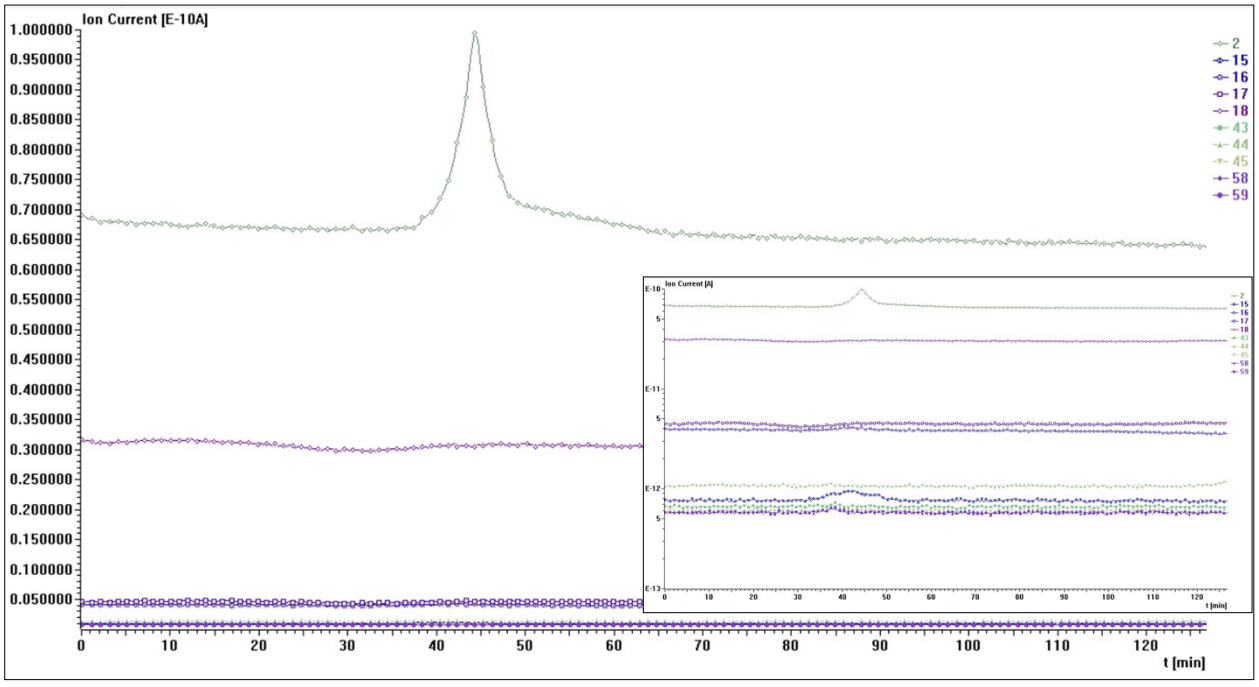

Figure S8. Mass spectrum of gaseous decomposition products of $CsSc(BH_4)_4$ obtained mechanochemically (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 15 °C.

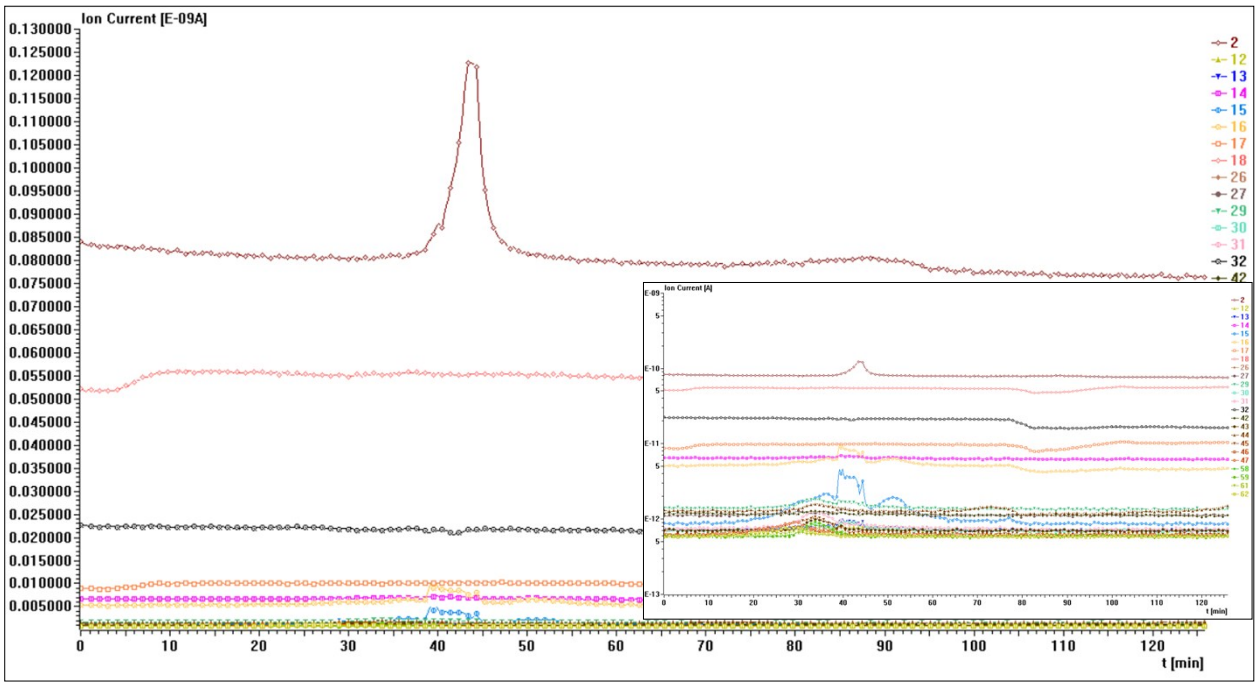

Figure S9. Mass spectrum of gaseous decomposition products of $CsSc(BH_4)_4$ obtained via DMS-mediated synthesis (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 20 °C.

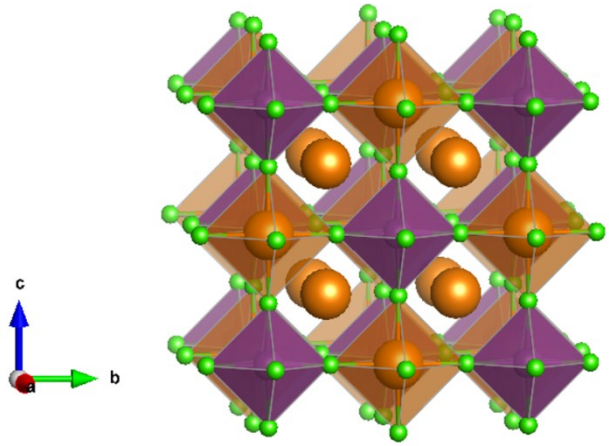

Figure S10. Crystal structure of M_3ScCl_6, M=Rb, Cs - the elpasolite-type structure. M atoms in orange, Sc - purple, Cl - green.

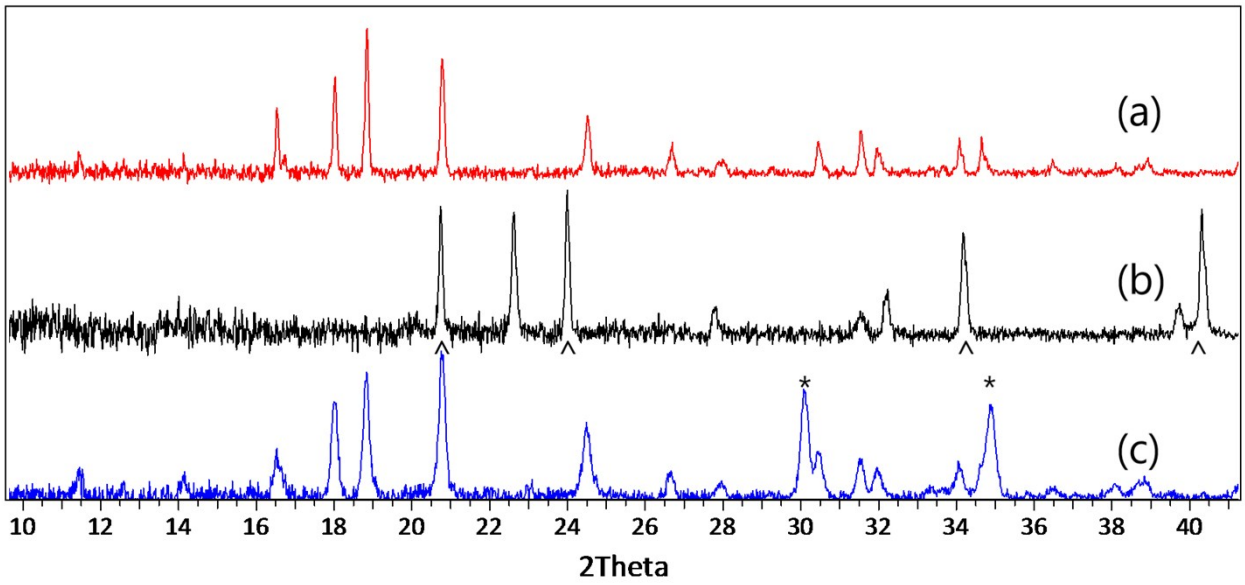

Figure S11. PXRD patterns of $CsSc(BH_4)_4$ samples obtained via the solvent-mediated (a) and the mechanochemical (c) synthesis and by-products of solvent-mediated synthesis (b), * - LiCl , ^ - $CsBH_4$, unmarked - $CsSc(BH_4)_4$ or Cs_3ScCl_6, respectively.

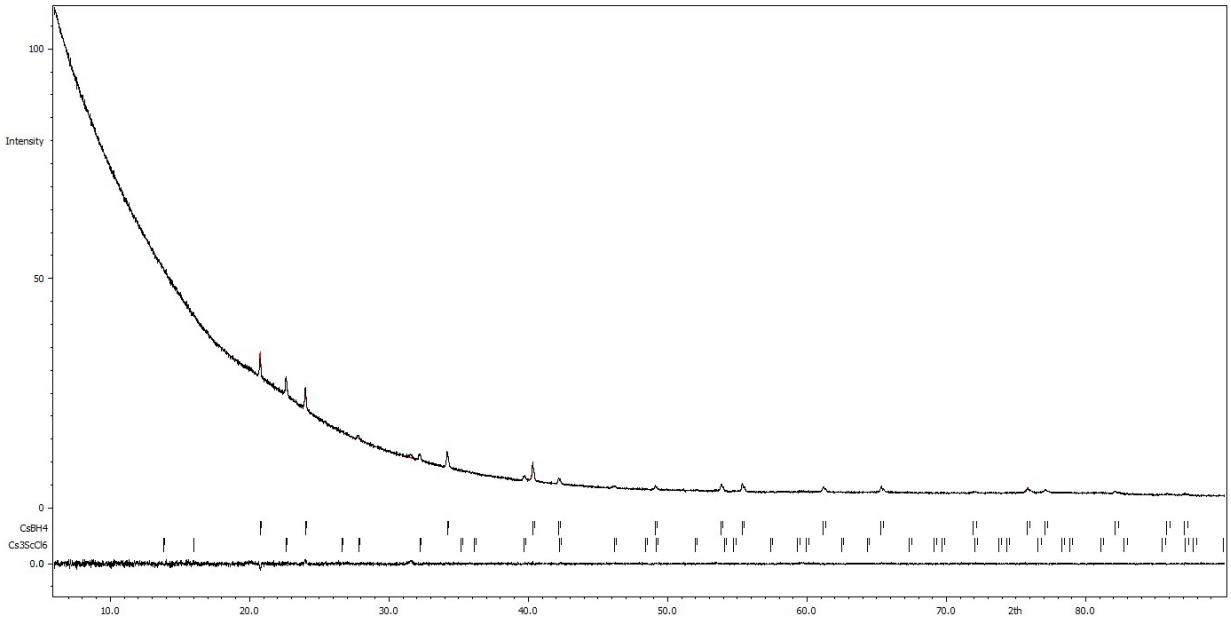

Figure S12. Rietveld refinement of PXRD (Cu K_α) data collected for Cs_3ScCl_6 sample at room temperature, wRp = 1.20%, $R(obs)_{CsBH4}$ = 3.66%, $R(obs)_{Cs3ScCl6}$ = 3.20%.

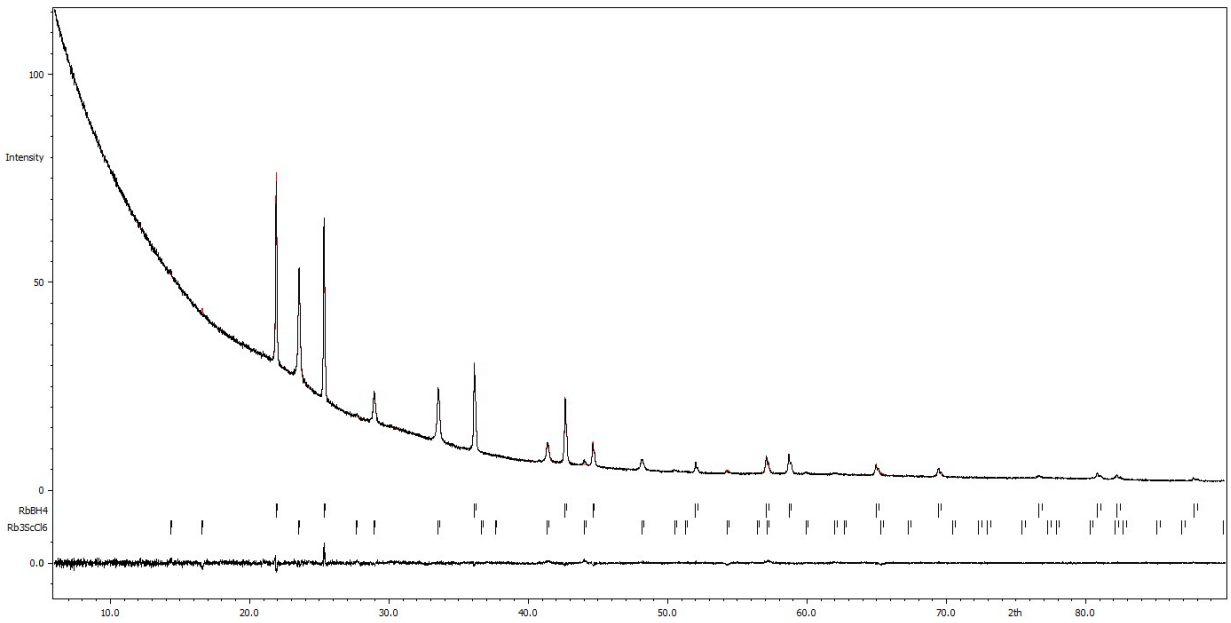

Figure S13. Rietveld refinement of PXRD (Cu K_α) data collected for Rb_3ScCl_6 sample at room temperature, wRp = 1.48%, $R(obs)_{RbBH4}$ = 2.57%, $R(obs)_{Rb3ScCl6}$ = 5.24%.

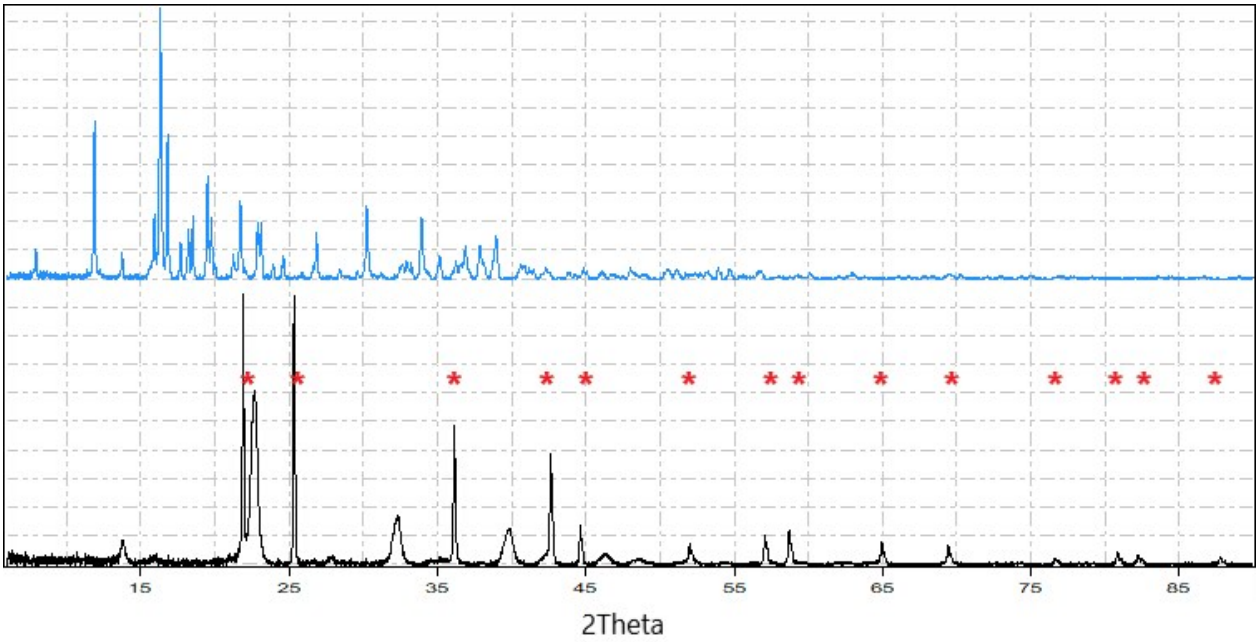

Figure S14. PXRD patterns of Rb-Y samples prepared via solvent-mediated method, site **A** - $Y(BH_4)_3$·DMS (top), and site **B** - $RbBH_4$ (marked with *) and ht-Rb_3YCl_6 (bottom).

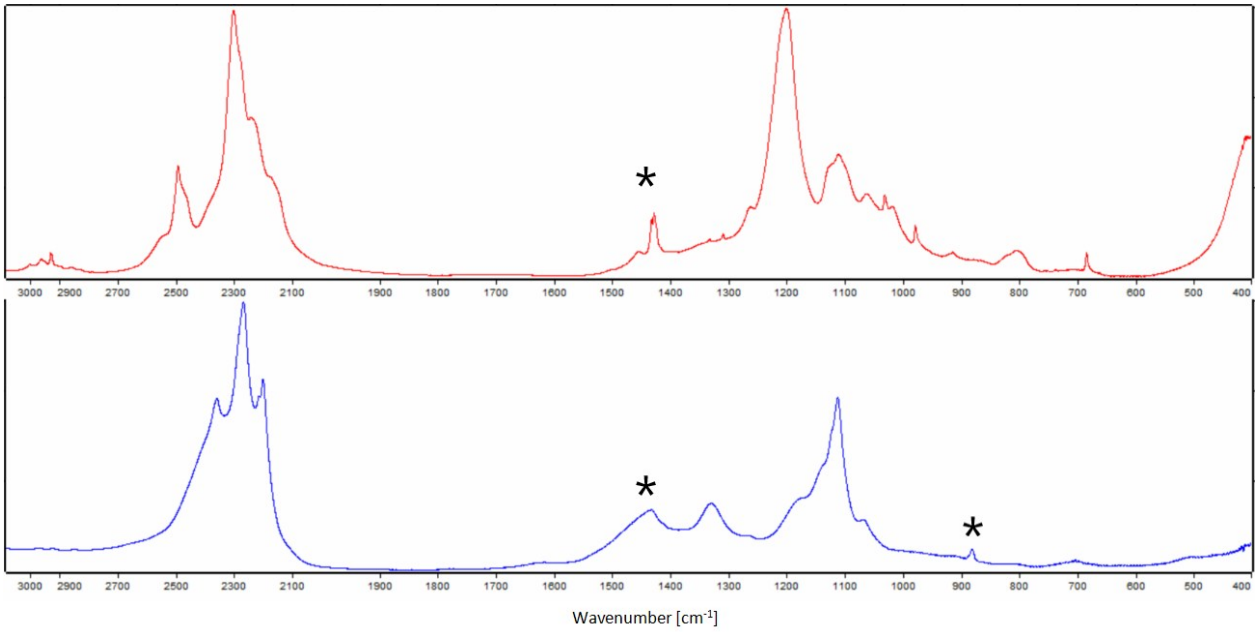

Figure S15. FTIR spectra of Rb-Y samples prepared via solvent-mediated method, site **A** - $Y(BH_4)_3 \cdot DMS$ (top), and site **B** - $RbBH_4$ and ht-Rb_3YCl_6 (bottom), * - background compensation errors.

The structures of $MSc(BH_4)_4$ optimized computationally

$RbSc(BH_4)_4$

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$CsSc(BH_4)_4$

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H19    H     0.42198   0.02115   0.14752   0.04200  Uiso   1.00
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Sc21   Sc    0.32111   0.16280   0.20685   0.04500  Uiso   1.00
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Table S1. Comparison of the selected parameters for the experimental and computed structures.

$MSc(BH_4)_4$	**Rb**		**Cs**	
Data	experimental	DFT	experimental	DFT
Space group	*P*bcm		$P2_1/c$	
Z	4		4	
a [Å]	7.6514(10)	7.6514	9.587(2)	9.5870
b [Å]	11.1821(14)	11.1821	10.727(3)	10.7270
c [Å]	11.2443(14)	11.2443	12.228(3)	12.2280
β [°]	90	90	126.351(3)	126.3510
V [$Å^3$]	962.1(2)	962.1	1012.8(5)	1012.8
Sc–H [Å]	2.255(8)	2.129–2.177	2.202(7)	2.143–2.184
M–Sc [Å]	4.487(4); 5.374–5.512(4)	4.334; 5.556– 5.57462	4.788(11)–4.993(7); 5.685–5.787(8)	4.553– 5.095; 5.594–5.974
Sc–B [Å]	2.360(8)	2.289–2.314	2.300(3)	2.289–2.303
M–B [Å]	3.494(7)– 3.806(6)	3.377–3.784	3.630(8)–4.165(11)	3.541–3.909

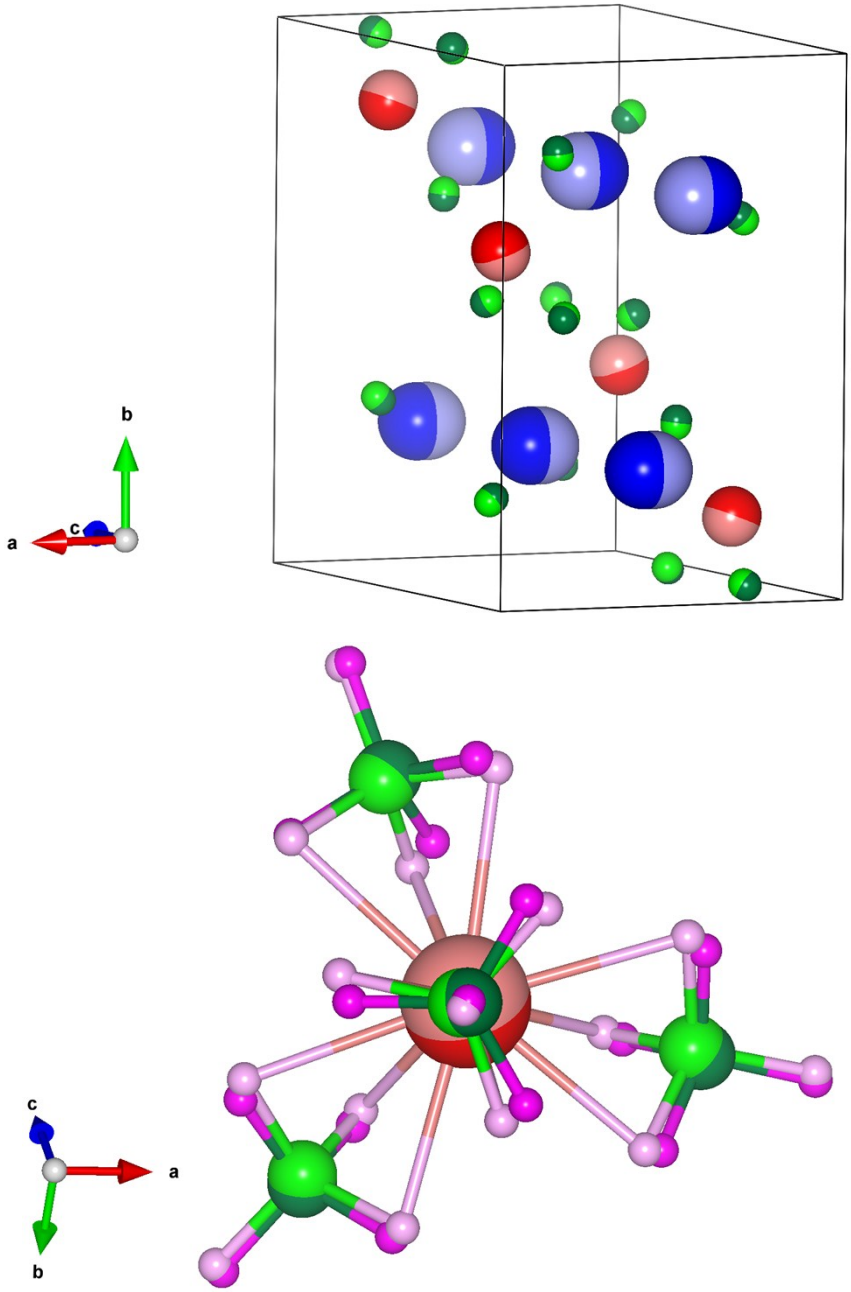

Figure S16. An overlay of the experimental (darker colors) and computationally optimized (brighter colors) structures of $RbSc(BH_4)_4$. Top – the sublattice of heavy atoms; bottom – the geometry of the $[Sc(BH_4)_4]^-$ complex anion.

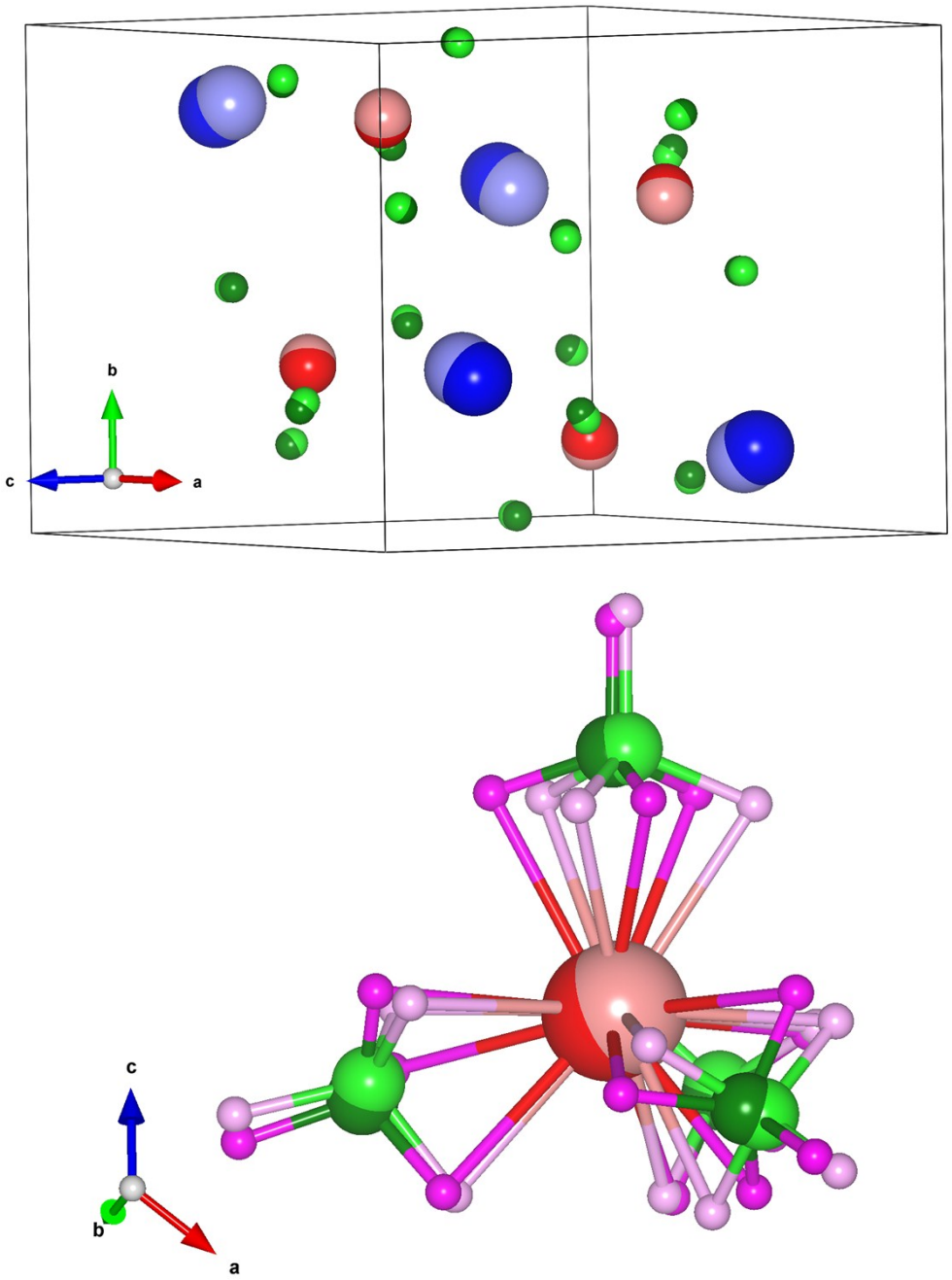

Figure S17. An overlay of the experimental (darker colors) and computationally optimized (brighter colors) structures of $CsSc(BH_4)_4$. Top – the sublattice of heavy atoms; bottom – the geometry of the $[Sc(BH_4)_4]^-$ complex anion.