Supplementary Materials

How mechanochemistry affects the composition and properties of disordered fluorite $BaSnF_4$?

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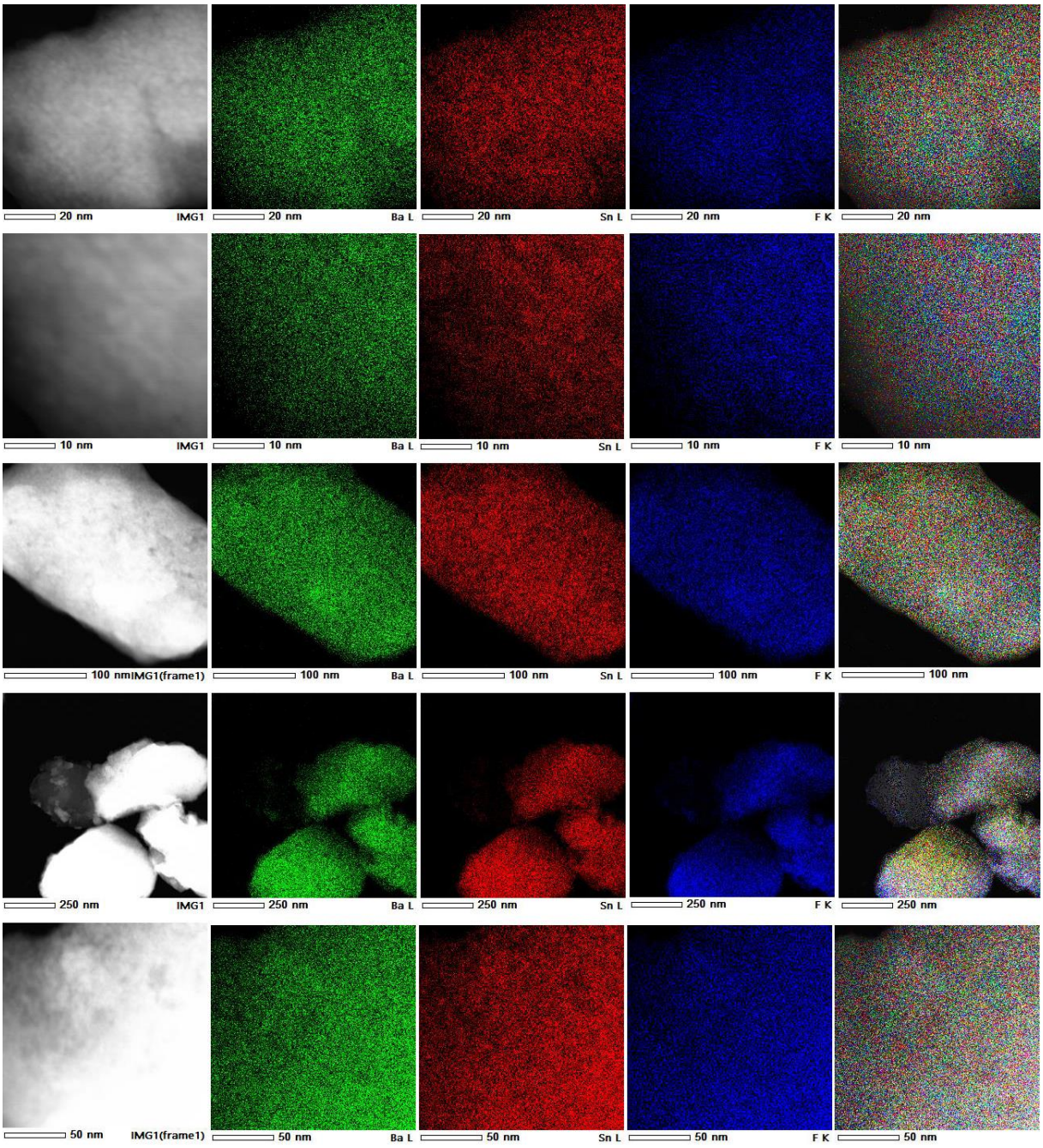

Figure S1. HAADF-STEM images and corresponding EDX elemental mapping for Ba L, Sn L and F K on c-$BaSnF_4$-99c.

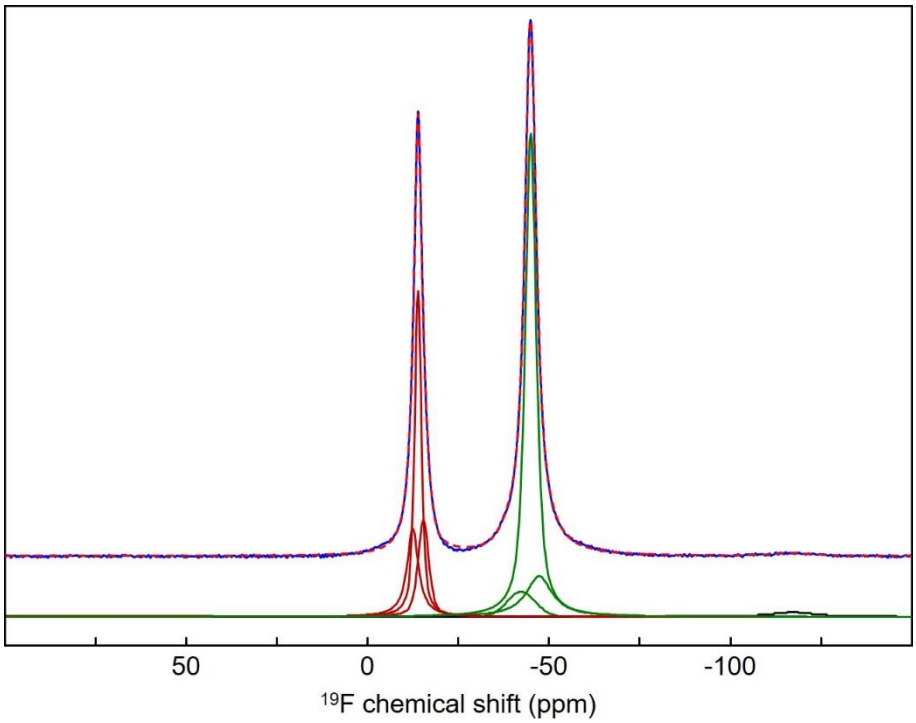

Figure S2. Experimental (blue) and fitted (dashed red line) ^{19}F MAS (64 kHz) NMR spectra of c-$BaSnF_4$-24c. The lower section of the figure shows the individual resonances (**Table S1**) used in the fit.

Table S1. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (64 kHz) NMR spectrum of c-$BaSnF_4$-24c (**Figure S2**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-117.3	13.8	1.2		1.2	-117.3
-47.4	8.7	10.2			
-45.0	3.6	46.2			
-42.4	9.1	5.2	Sn-rich	61.6	-45.2
-15.5	3.5	8.4			
-14.0	2.2	18.8			
-12.5	3.7	10.1	Ba-rich	37.3	-13.9

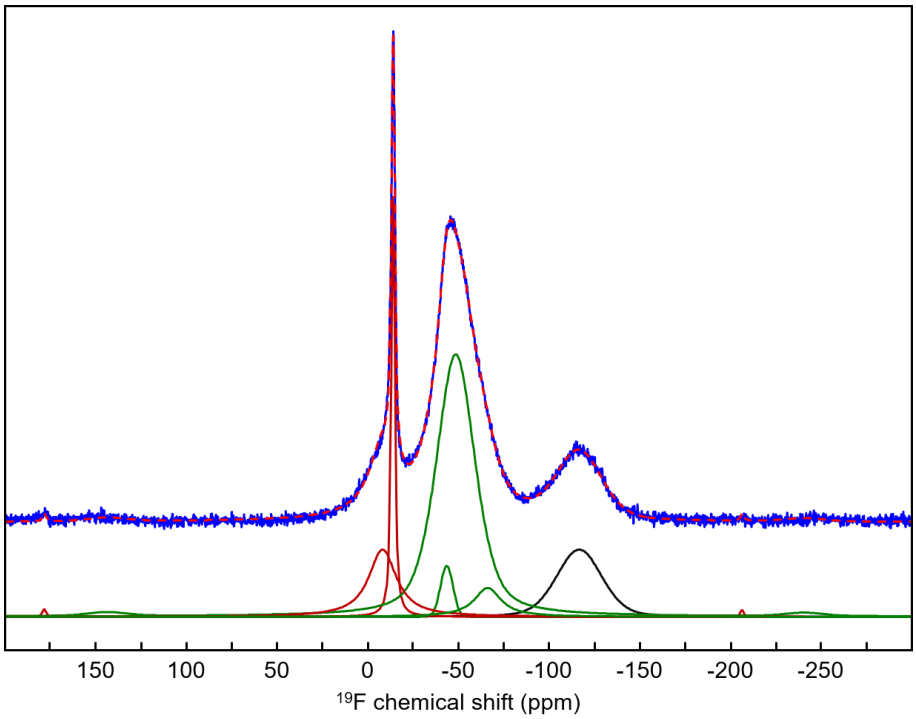

Figure S3. Experimental (blue) and fitted (dashed red line) ^{19}F MAS (54 kHz) NMR spectra of c-$BaSnF_4$-99c. The lower section of the figure shows the individual resonances (**Table S2**) used in the fit.

Table S2. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (54 kHz) NMR spectrum of c-$BaSnF_4$-99c (**Figure S3**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-116.7	29.4	14.7	Sn(IV)-bonded	14.7	-116.7
-66.2	17.8	5.0			
-48.6	25.3	55.9			
-43.7	8.1	2.8	Sn-rich	63.7	-49.8
-14.1	2.4	9.6			
-8.3	18.4	12.0	Ba-rich	21.6	-10.8

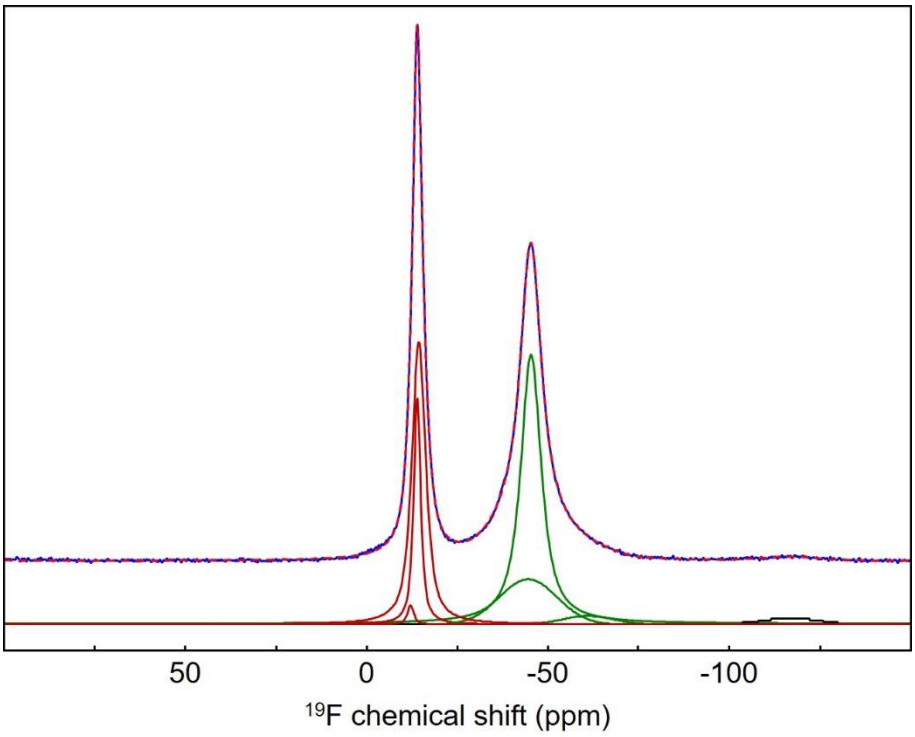

Figure S4. Experimental (blue) and fitted (dashed red line) ^{19}F MAS (44 kHz) NMR spectra of c-$BaSnF_4$-24c. The lower section of the figure shows the individual resonances (**Table S3**) used in the fit.

Table S3. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (44 kHz) NMR spectrum of c-$BaSnF_4$-24c (**Figure S4**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-116.8	18.4	1.1		1.1	-116.8
-61.0	16.5	2.3			
-45.3	6.7	40.8			
-44.5	18.7	13.9	Sn-rich	57.0	-45.8
-14.4	4.5	28.9			
-13.9	2.3	12.1			
-12.1	2.1	0.9	Ba-rich	41.9	-14.2

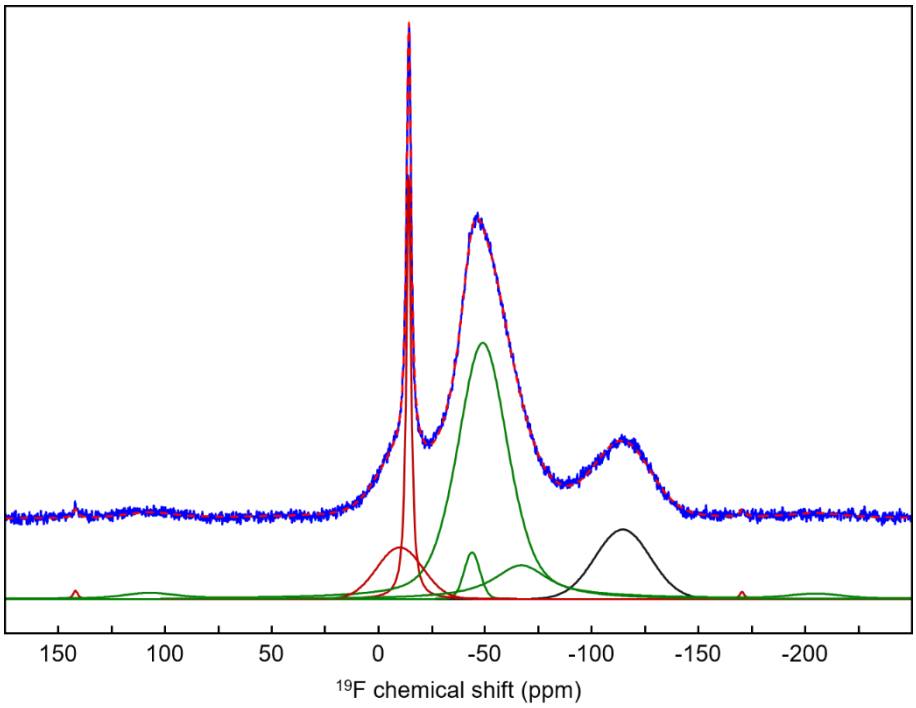

Figure S5. Experimental (blue) and fitted (dashed red line) ^{19}F MAS (44 kHz) NMR spectra of c-$BaSnF_4$-99c. The lower section of the figure shows the individual resonances (**Table S4**) used in the fit.

Table S4. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (44 kHz) NMR spectrum of c-$BaSnF_4$-99c (**Figure S5**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-114.5	30.3	13.5	Sn(IV)-bonded	13.5	-114.5
-67.0	31.8	9.8			
-49.0	27.7	55.1			
-43.9	8.7	2.7	Sn-rich	67.5	-51.4
-14.3	2.6	10.7			
-10.1	25.2	8.3	Ba-rich	19.0	-12.4

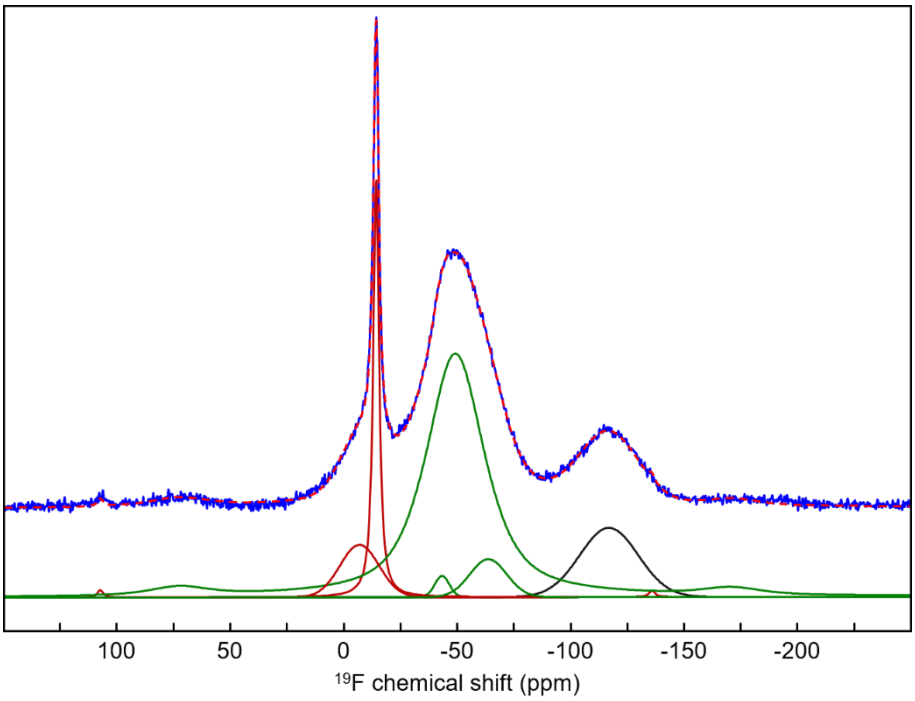

Figure S6. Experimental (blue) and fitted (dashed red line) ^{19}F MAS (34 kHz) NMR spectra of c-$BaSnF_4$-99c. The lower section of the figure shows the individual resonances (**Table S5**) used in the fit.

Table S5. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (34 kHz) NMR spectrum of c-$BaSnF_4$-99c (**Figure S6**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-116.9	30.3	12.8	Sn(IV)-bonded	12.8	-116.9
-63.7	19.1	4.4			
-49.1	30.6	63.8			
-43.3	7.5	1.0	Sn-rich	69.2	-50.0
-14.2	3.0	11.6			
-6.9	20.2	6.5	Ba-rich	18.1	-11.6

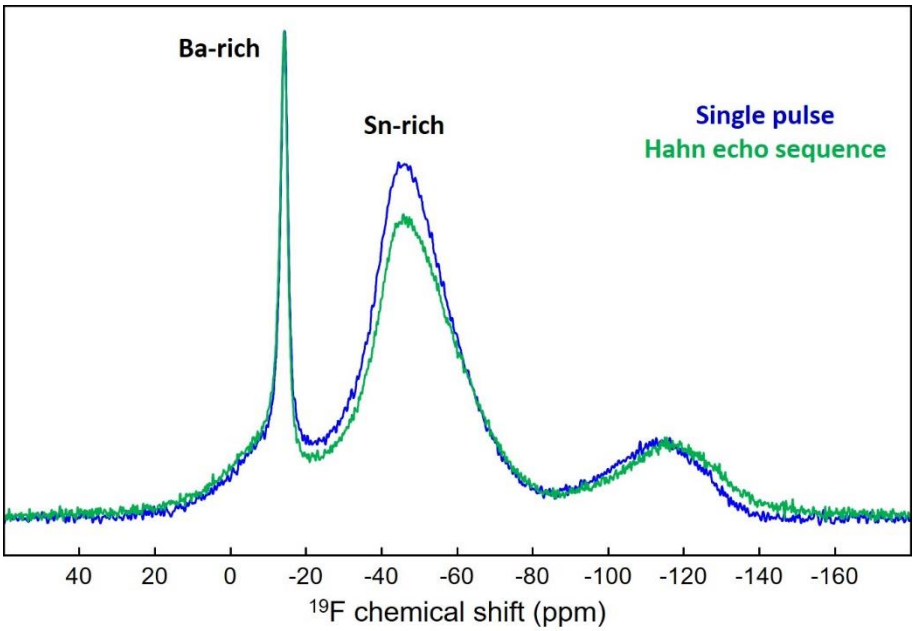

Figure S7. ^{19}F MAS (54 kHz) NMR spectra of c-$BaSnF_4$-99c recorded using a single pulse (blue) and using a rotor-synchronized Hahn echo sequence with an interpulse delay equal to one rotor period (green).

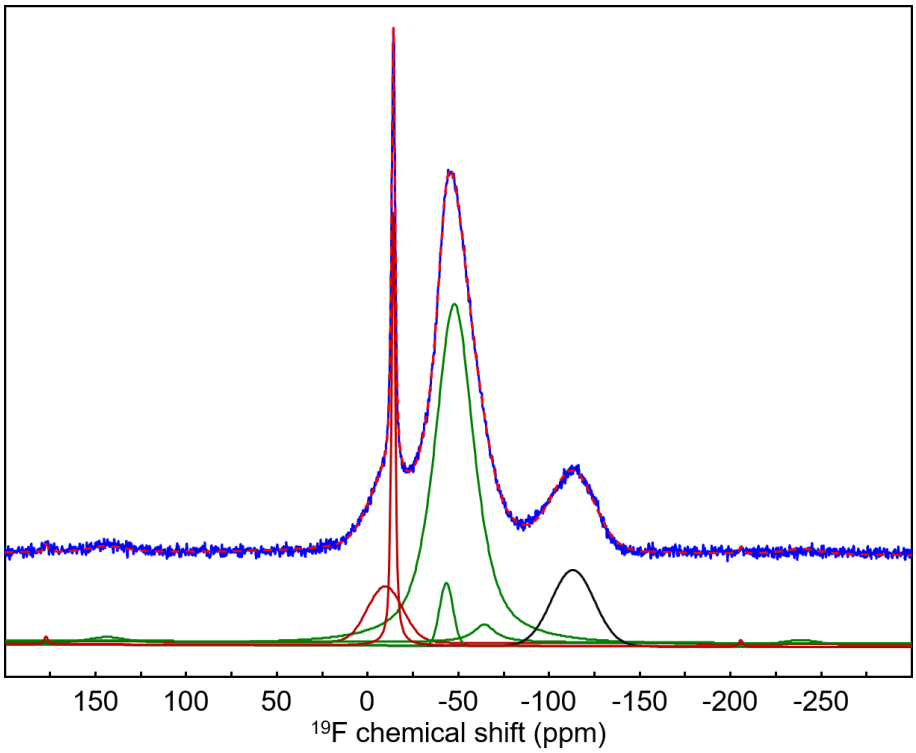

Figure S8. Experimental, recorded using a single pulse (blue), and fitted (dashed red line) ^{19}F MAS (54 kHz) NMR spectra of c-$BaSnF_4$-99c. The lower section of the figure shows the individual resonances (**Table S6**) used in the fit.

Table S6. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (54 kHz) NMR spectrum of c-$BaSnF_4$-99c, recorded using a single pulse (**Figure S8**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-113.2	27.7	12.2		12.2	-113.2
-43.4	8.6	3.1			
-48.0	25.5	66.7			
-64.5	14.5	2.1	Sn-rich	71.9	-48.3
-14.2	2.3	8.5			
-9.8	22.7	7.4	Ba-rich	15.9	-12.2

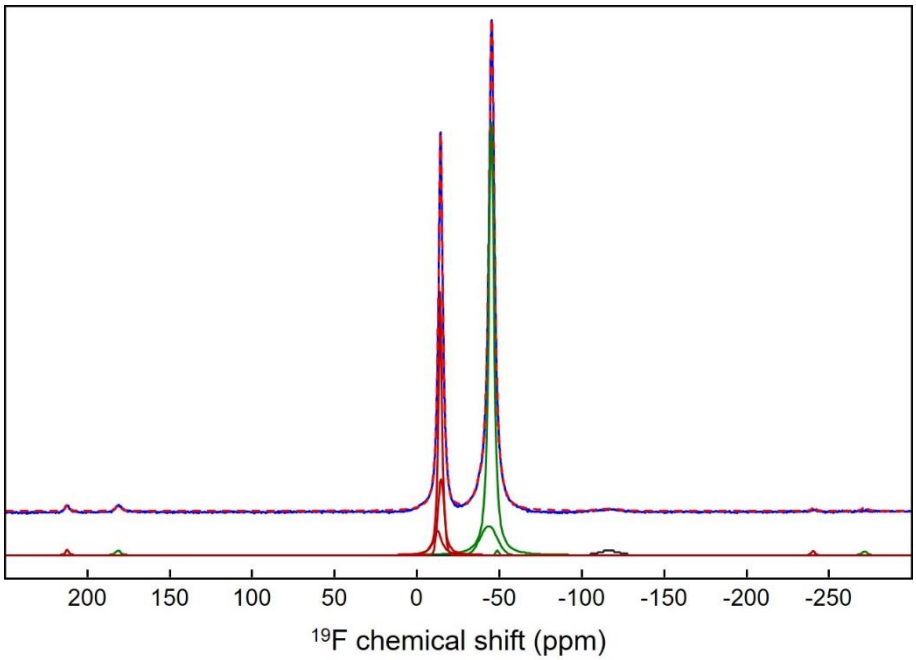

Figure S9. Experimental, recorded using a single pulse (blue), and fitted (dashed red line) ^{19}F MAS (64 kHz) NMR spectra of c-$BaSnF_4$-24c. The lower section of the figure shows the individual resonances (**Table S7**) used in the fit.

Table S7. Isotropic chemical shift (δ_{iso}, ppm), full width at half maximum (FWHM, ppm) and relative intensity (I, %) of the ^{19}F NMR lines used in the fit of the ^{19}F MAS (64 kHz) NMR spectrum of c-$BaSnF_4$-24c, recorded using a single pulse (**Figure S9**), and assignment of these lines to the types of fluorine atoms and the corresponding relative intensities (Σ I, %) and weighted average δ_{iso} values (<δ_{iso}>, ppm).

δ_{iso}	FWHM	I	Assignment	Σ I	<δ_{iso}>
-116.3	16.0	0.9		0.9	-116.3
-48.6	2.3	0.2			
-45.0	3.7	54.1			
-43.4	12.0	8.5	Sn-rich	62.8	-44.8
-14.6	4.6	8.3			
-14.0	2.5	22.6			
-12.4	6.1	5.4	Ba-rich	36.3	-13.9