Supporting Information

Materials

All chemicals were used as received. The perovskite solutions were prepared in a N_2-filled glove box from 1.2 M of SnI_2 (Tokyo Chemical Industry), and formamidinium iodide (FAI, Dyenamo), methylammonium iodide (MAI, Dyenamo) or CsI (abcr GmbH, 99.999%) in DMSO-d6 (Sigma) or DMF-d7 (Sigma). The different additives were dissolved from SnI_2 or $FASnI_3$ solutions: SnI_4 (Sigma), SnF_2 (Aldrich), I_2 (Sigma, beads) and dimethyl sulfide (Sigma).

Preparation of solutions

All solutions were prepared in N_2-filled glove box. Solutions suffered no air exposure during preparation or transport to characterization instruments.

SnI_2 solutions of different molarity (0.01-1.2 M) were prepared dissolving the powder in the corresponding volume of solvent (DMSO or DMF).

1 M $FASnI_3$, $MASnI_3$ and $CsSnI_3$ solutions in DMSO and DMF were prepared by preparing nominal 1.2 M stock solutions of SnI_2 in the corresponding solvent, and adding the corresponding volume to previously weighed FAI, MAI or CsI powder in 1:1 stoichiometry.

10% SnF_2-containing solutions were prepared by preparing a 0.4 M stock solution of SnF_2 in DMSO and adding the corresponding volume to the 1 M $FASnI_3$ solution in DMSO for a final 0.8 M solution with 10% of SnF_2.

DMS-containing solutions were prepared by adding 73 μL to 1 mL of 1 M $FASnI_3$ solution in DMSO.

1% SnI_4-containing solutions were prepared by dissolving 6.26 mg of SnI_4 in 1 mL of 1 M $FASnI_3$ solution in DMSO.

10% I_2-containing solutions were prepared by dissolving 25.4 mg of I_2 in 1 mL of 1 M $FASnI_3$ solution in DMSO.

Methods

Solid-state ^{119}Sn-NMR

The spectra were collected on a Bruker Avance II 400 spectrometer equipped with a 4 mm broadband Magic Angle Spinning (MAS) probe. Powder samples were packed in 4 mm zirconia rotors sealed with Vespel caps and spun at a rate of 12 or 13 kHz. A Direct Polarization (DP) scheme was applied, with a $\pi/2$ pulse width of 4 μs, a recycle delay of 40 s and averaging over 4096 scans.

Liquid-state ^{119}Sn-NMR

The spectra were all acquired on a Bruker AVII 400 MHz or Bruker AVIII 500 MHz equipped with room-temperature TBO or BBO-probe heads respectively. Typically, a sweep width of 504.3 ppm was used and 64k points were acquired, resulting in a total acquisition time of 435.81 ms. The centre frequency had to be adjusted from sample to sample in order to detect the desired signal, therefore, on new samples, a full scan of the possible shift range was acquired (1000 to -3000ppm). We used a 30° pulse in order to minimize the recycle delay down to 2s. The number of scans thus ranged from 128 for very concentrated samples to 16k scans for very dilute samples.

Liquid-state ^{1}H- and ^{13}C-NMR

All other spectra were measured with standardized parameter sets from Bruker Topspin version 2.1 (AV400) and 3.0 (AV500).

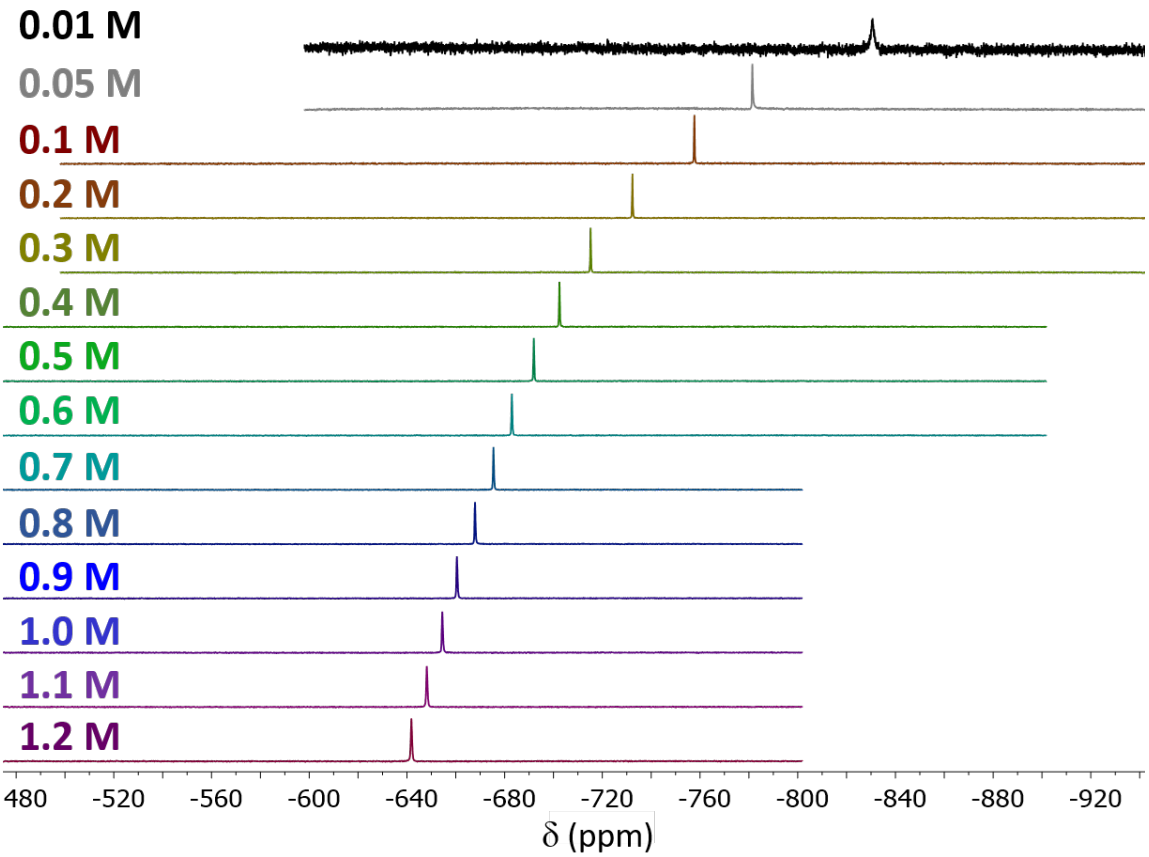

Figure S1. ^{119}Sn-NMR Sn(II) signal chemical shift for SnI_2 in DMSO at different solution concentrations.

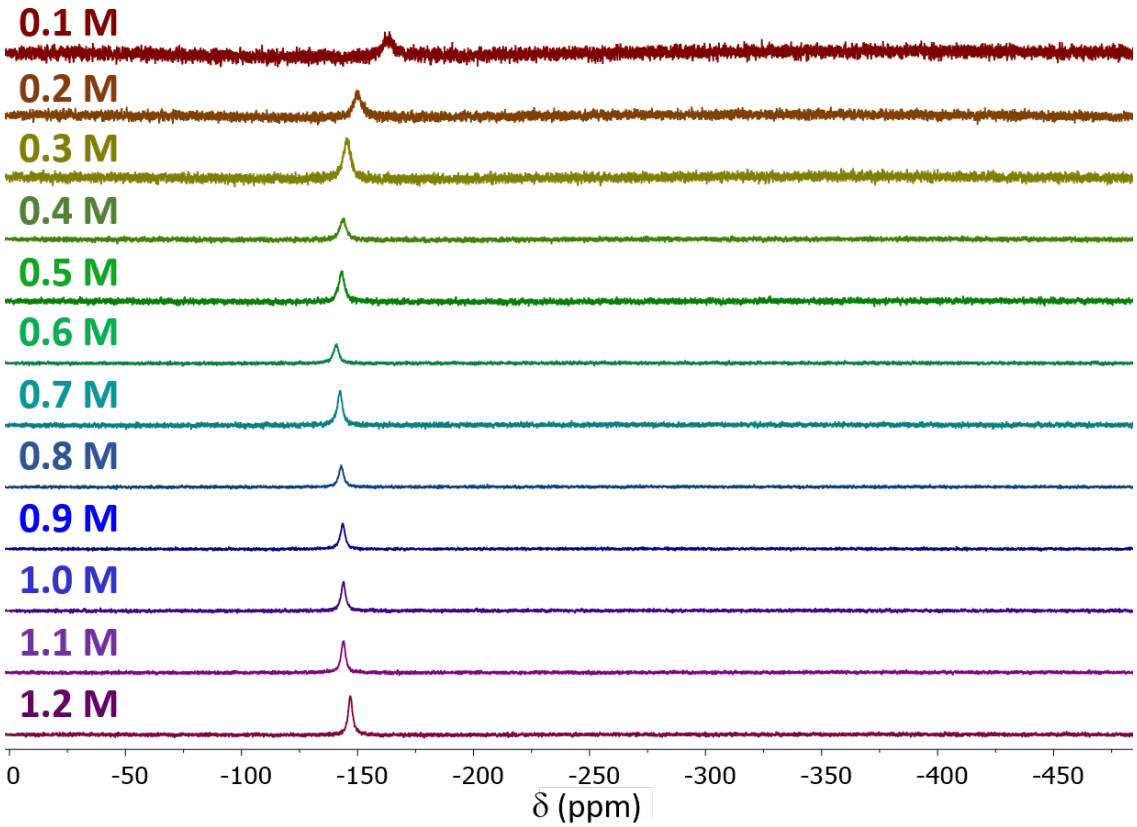

Figure S2. ^{119}Sn-NMR Sn(II) signal chemical shift for SnI_2 in DMF at different solution concentrations.

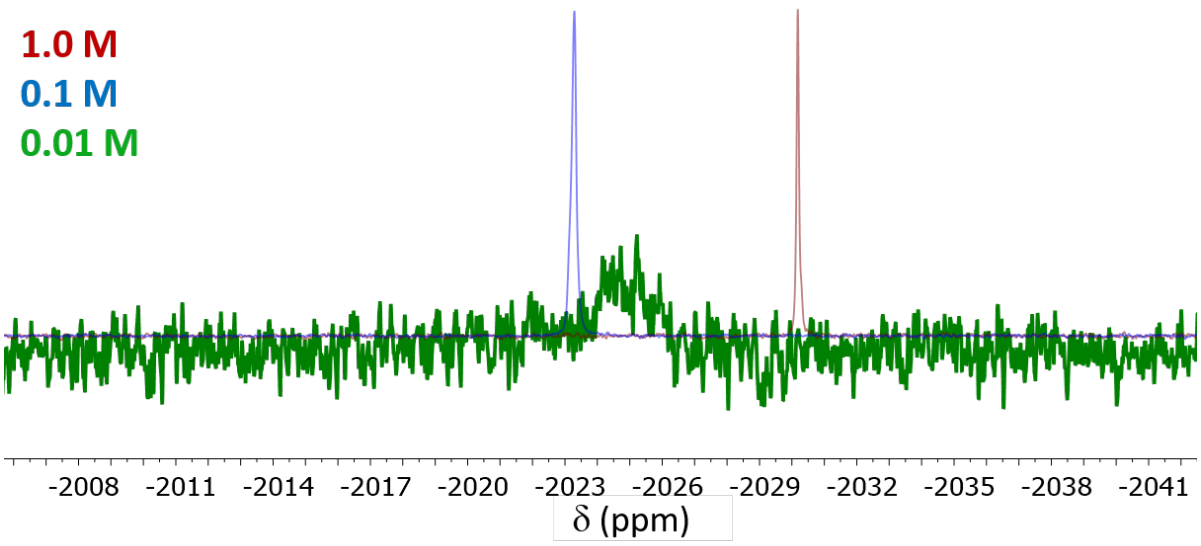

Figure S3. ^{119}Sn-NMR Sn(IV) signal for SnI_4 in DMSO at different solution concentrations.

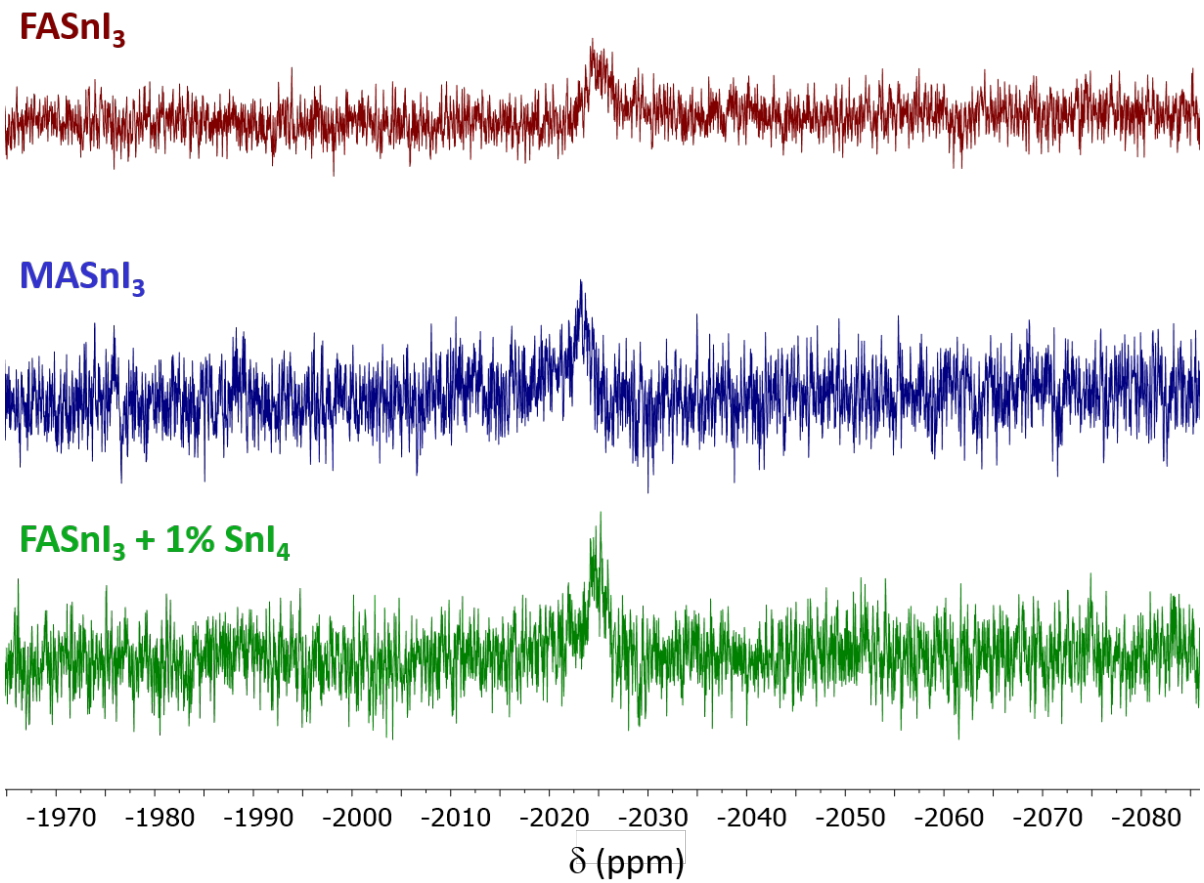

Figure S4. ^{119}Sn-NMR Sn(IV) signal for $FASnI_3$ and $MASnI_3$ after 30 min at 100°C and $FASnI_3$ with 1%mol of SnI_4 in DMSO at 1M. All measurements were carried out with the same sensitivity.

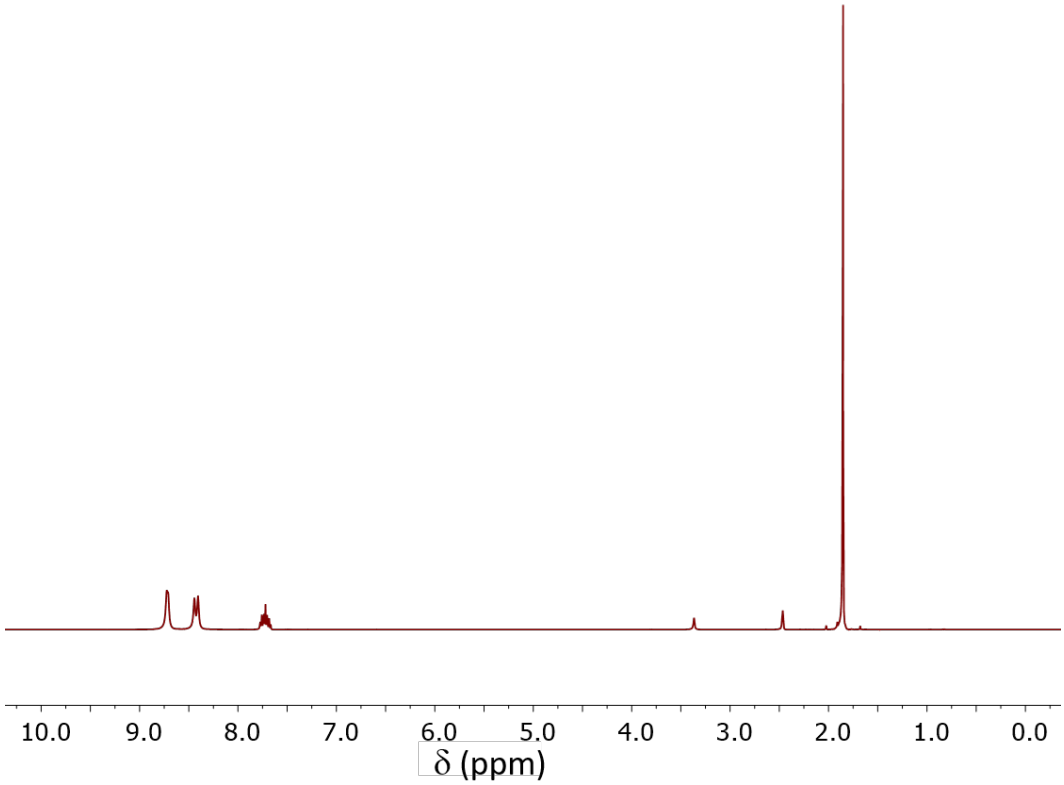

Figure S5. ^{1}H-NMR spectrum of $FASnI_3$ with 1 equivalent of DMS.

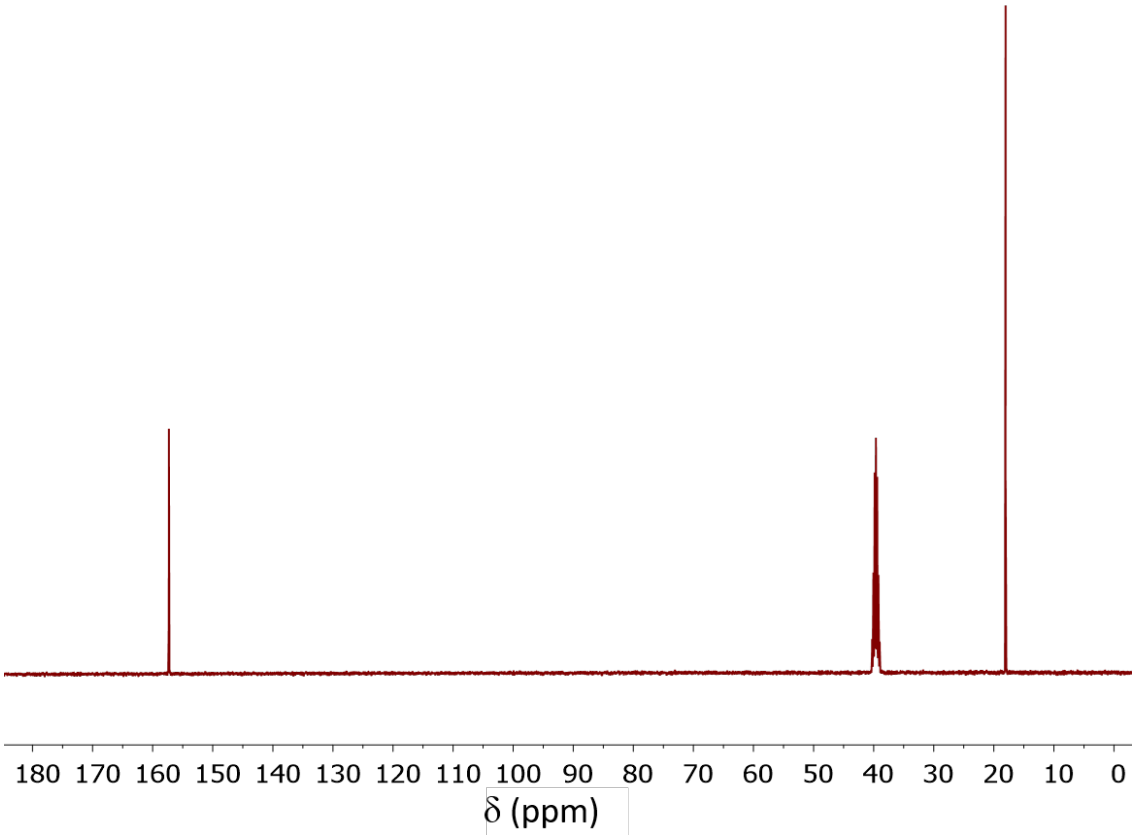

Figure S6. ^{13}C-NMR spectrum of $FASnI_3$ with 1 equivalent of DMS.

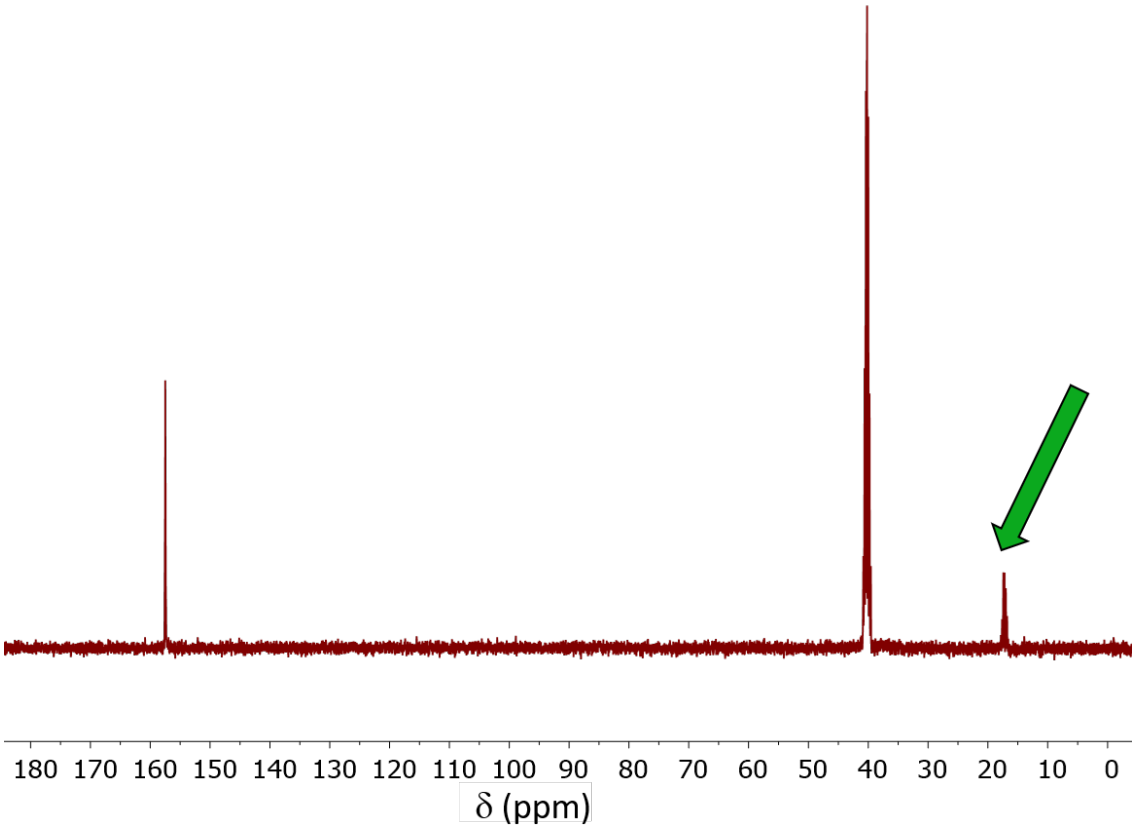

Figure S7. ^{13}C-NMR spectrum of $FASnI_3$ heated at 100°C for 30 min in DMSO at 1M. The green arrow highlights the peak of DMS originating from heating the solution.

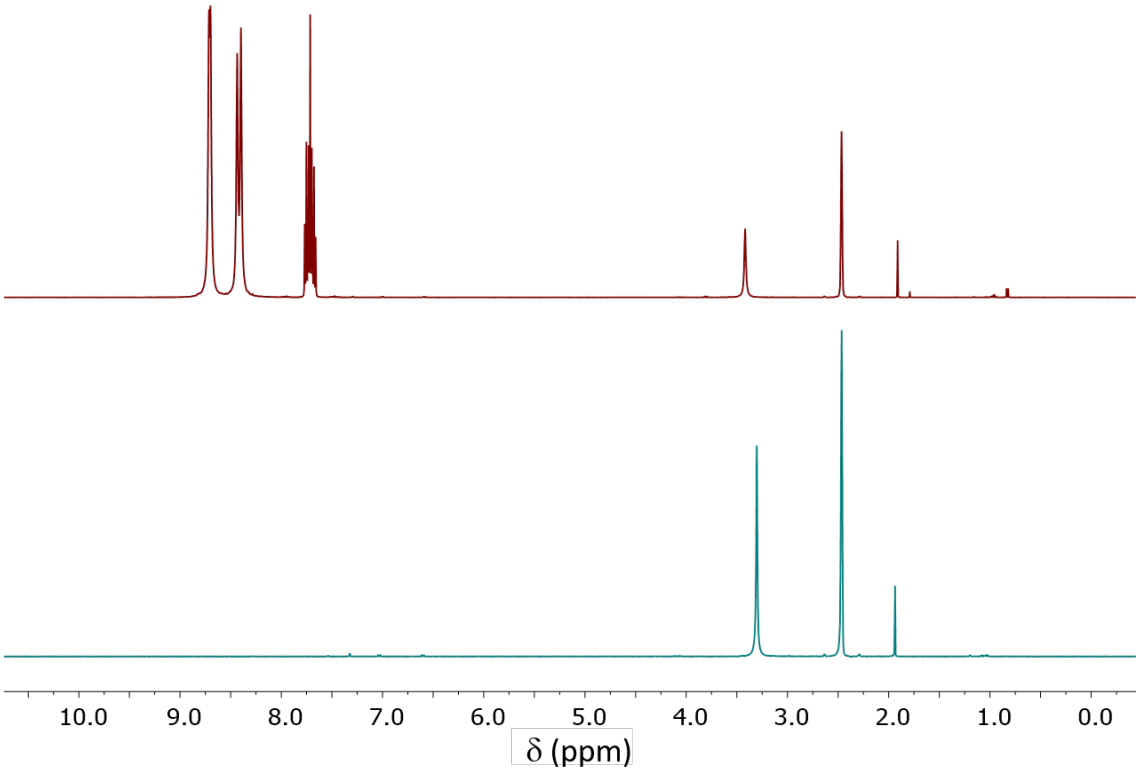

Figure S8. ^{1}H-NMR spectrum of $FASnI_3$ (red) and SnI_2 (turquoise), with the DMS peak at 1.90 ppm.

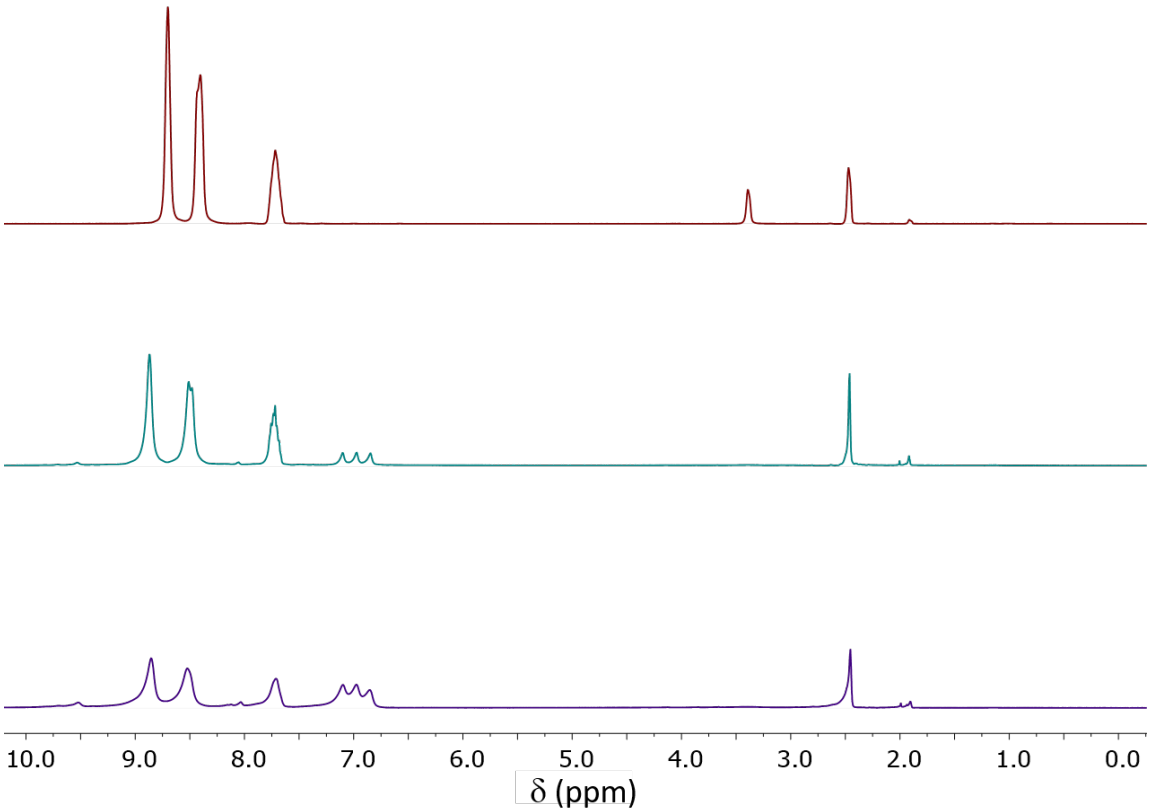

Figure S9. ^{1}H-NMR spectra of $FASnI_3$ solution in DMSO without heating (red) and heated at 100°C for 2 (turquoise) and 4 days (purple).

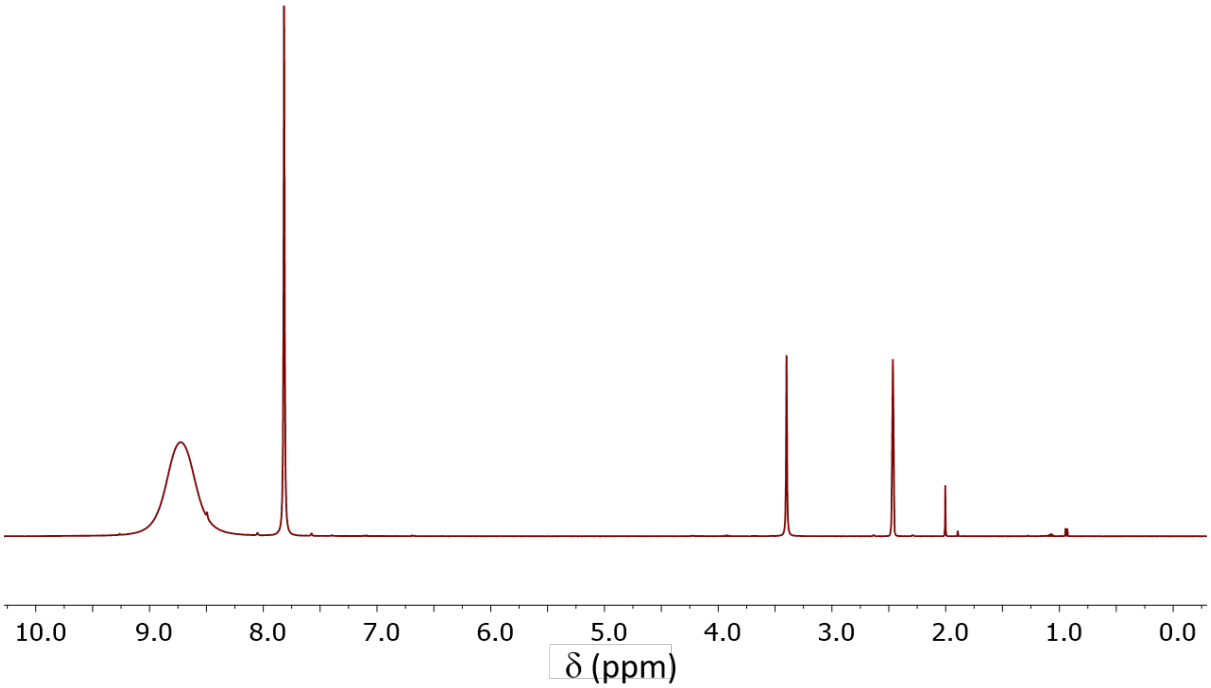

Figure S10. ^{1}H-NMR spectra of FAI solution in DMSO at 1 M after heating the solution at 100°C for 30 min.

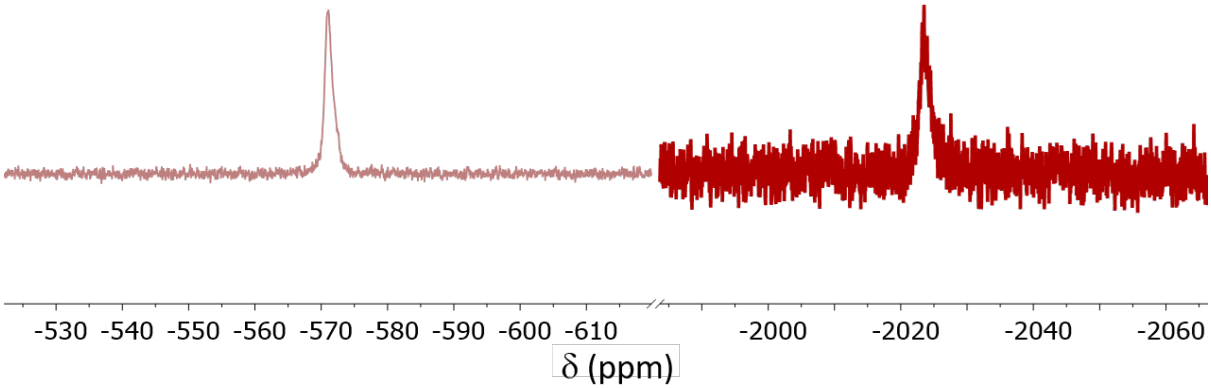

Figure S11. ^{119}Sn-NMR spectra of $FASnI_3$ in DMSO after adding 10% mol of I_2 beads.

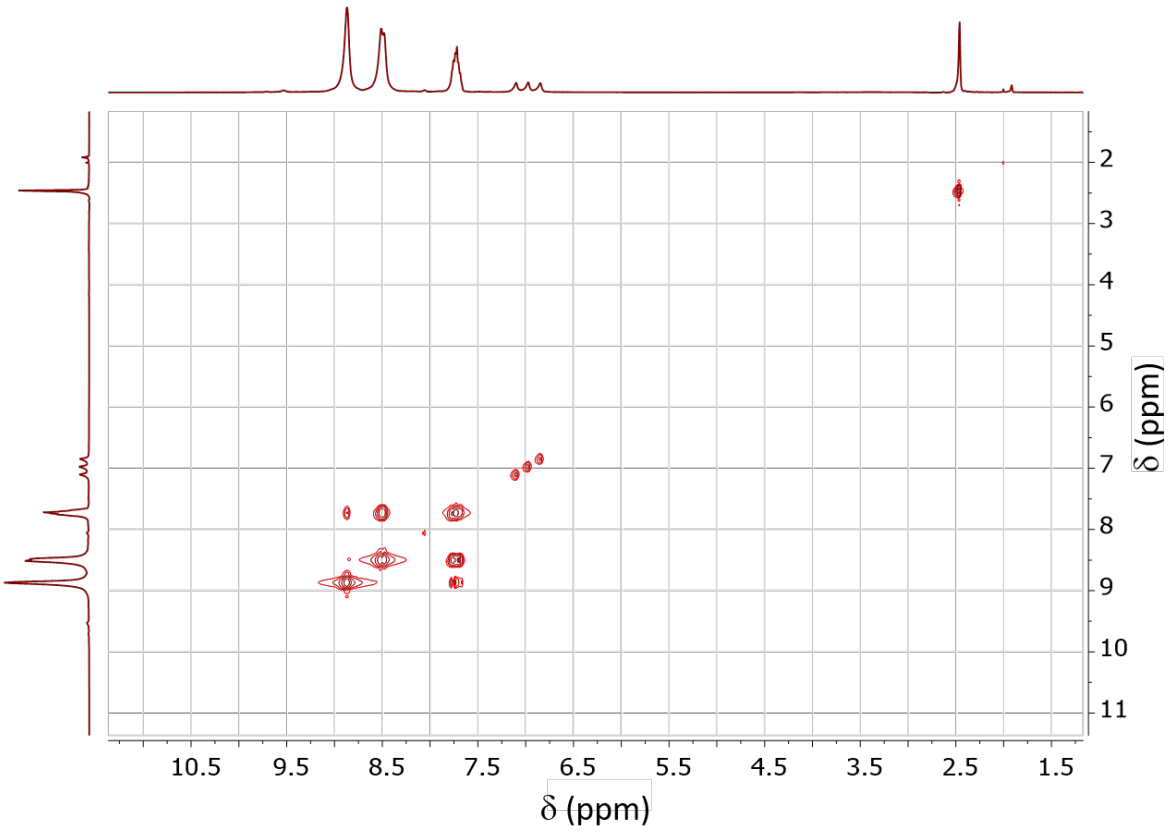

Figure S12. ^{1}H-^{1}H COSY spectrum of $FASnI_3$ solution in DMSO heated at 100°C for 2 days.

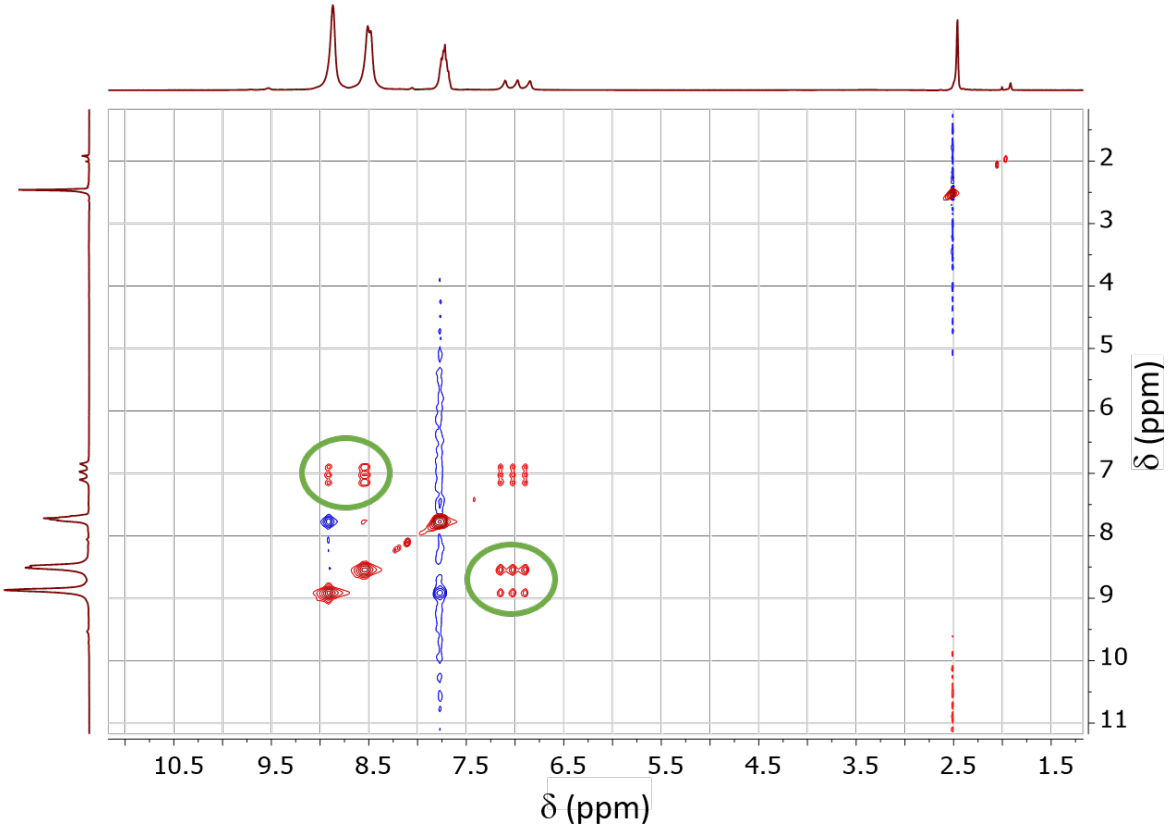

Figure S13. ^{1}H-^{1}H ROESY spectrum of $FASnI_3$ solution in DMSO heated at 100°C for 2 days. Green circles point to the chemical exchange between NH_4^+ and FA protons.

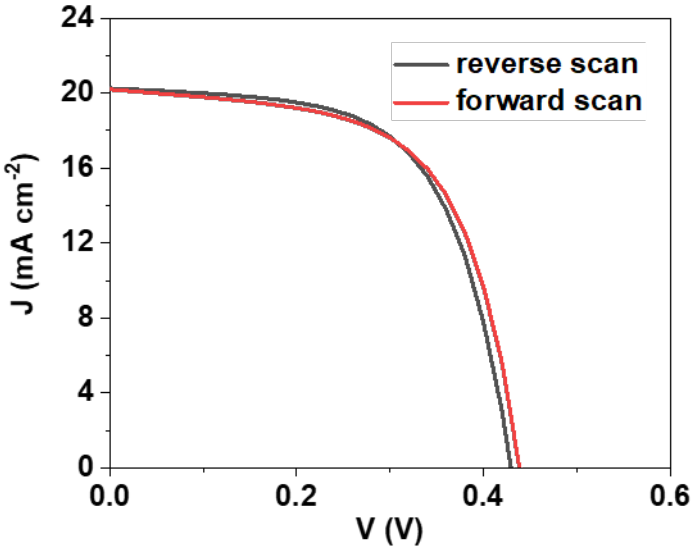

Figure S14. *J-V* curve (reverse and forward scans) of a standard $FASnI_3$ (10% SnF_2)-based perovskite solar cell processed with DMSO.