Electronic Supplementary Material (ESI) for RSC Mechanochemistry.

SUPPORTING INFORMATION

FOR

Grinding and the anisotropic environment: Influences on the diastereoselective formation of Group 15 allyl complexes

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Abbreviations:

[A´] = $[1,3\text{-}(SiMe_3)_2C_3H_3]^-$
HMDSO = hexamethyldisiloxane
LAG = liquid assisted grinding
MM = mixer mill
PBM or PM = planetary ball mill
SS = stainless steel
THF = tetrahydrofuran
ZrO_2 = zirconia

General Considerations. All manipulations were performed with the rigorous exclusion of air and moisture using Schlenk and glovebox techniques under a nitrogen atmosphere. Unless otherwise indicated, the glovebox used was free of ethereal solvents; reactions involving THF or HMDSO were performed in another glovebox that stores ethereal solvents.

Proton (^1H) NMR spectra were obtained on an AV-400 spectrometer at 400 MHz or an AV-600 spectrometer at 600 MHz at room temperature and were referenced to the residual proton resonances of benzene-d_6 or toluene-d_8.

Materials. Anhydrous Group 15 halides ($AsCl_3$, AsI_3, $SbCl_3$, SbI_3) were purchased from Strem Chemicals and used as received. The potassium allyl K[A´] = $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ was synthesized by transmetallation of Li[A´][1] with potassium *tert*-butoxide in hexanes solution. Hexanes and THF were distilled under nitrogen over NaK/benzophenone radical,[2] then stored over 4 Å molecular sieves in a glovebox. Toluene was degassed with argon and dried over activated alumina using a solvent purification system, then stored over 4 Å molecular sieves in a glovebox. Benzene-d_6 and toluene-d_8 were obtained from Sigma Aldrich, degassed, and stored over 4 Å molecular sieves in a glovebox. HMDSO was used as received and stored over 4 Å molecular sieves in a glovebox.

Mechanochemical protocol. Planetary milling was performed in a Retsch PM100 or PM200 mill, with 50 mL stainless steel grinding jar type C, with a safety clamp for air-sensitive grinding, and 25 grams of “small” 4.8 mm stainless steel (440 grade) ball bearings (ca. 57 count, $^3/_{16}$ in, 0.44 g ball^{-1}). Select reactions used a 50 mL zirconia jar with 25 grams of 4 mm zirconia ball bearings (ca. 69 count, 0.36 g ball^{-1}).

Mixer milling was performed using a Retsch MM200 with a 15-mL stainless steel Formtech Smartsnap grinding jar and “large” 9.5 mm stainless steel (440 grade) ball bearings (2 count, 3.5 g ball^{-1}); select reactions used “small” stainless steel ball bearings (ca. 16 count, 7 g total). Select reactions used a 15-mL Teflon jar with 11 mm zirconia ball bearings (2 count, 2.9 g ball^{-1}).

In all cases, reagents were added to the jar in a nitrogen-filled glovebox, and after milling, reactions were worked up under nitrogen atmosphere. Ball bearings and jars were thoroughly cleaned with detergent and water, then washed with acetone, and dried prior to use. If needed, 10% aqueous hydrochloric acid was used to remove residual antimony metal before cleaning.

Table S1. Structural parameters for EX_3 (E = As, Sb; X = Cl, I)

EX_3	E-X length (Å)	X-E-X (deg)	Next closest E-X[b] [vdW radii][c] (Å)[4,5]	Coord. No.
$AsCl_3$ [3]	2.161(4)	98.4(5)	N/A [3.60]	3
AsI_3 [4,5]	2.56(7)	99.9(3)	3.55(9) [3.83]	3
$SbCl_3$ [6]	2.36[a]	94.1[a]	3.46–3.74 [3.81]	8 (3+2+3)
SbI_3 [4,5]	2.83(4)	95.2(2)	3.24(9) [4.04]	6 (**3**+3)

[a] averaged value
[b] length of E-X bond of next nearest neighbor.
[c] van der Waals radii, as specified in ref. 7 and 8, given in brackets

Each of the four group 15 halides used in this study ($AsCl_3$, AsI_3, $SbCl_3$, and SbI_3) possesses a unique structure. The bonding in each is best described as somewhere between ionic and covalent, with ionic character increasing from arsenic to antimony and from chloride to iodide.

Arsenic trichloride is a liquid at room temperature (mp = -16.2 °C). Its molecular structure is a regular trigonal pyramid.[3] There are no permanent intermolecular interactions in the liquid form.

Arsenic triiodide is a layered solid with identifiable AsI_3 units. The iodine anions are arranged in a hexagonal close packed lattice with arsenic cations filling two-thirds of the octahedral holes in every other layer.[4,5] The iodine layers are held together by van der Waals interactions. Each arsenic is covalently bonded to three iodine atoms, with another set of three iodine atoms further away but within the van der Waals radii.[4,5] Under high pressure (>1.7 GPa), the intermolecular separation of AsI_3 units decreases, new intermolecular bonds form, and the environment around arsenic becomes more symmetric.[9,10]

The structure of antimony chloride can be described as a zigzag layered structure. There are identifiable $SbCl_3$ units of pyramidal shape. The antimony atoms intermolecular bonds with five additional chlorides to give antimony a coordination number of eight and a bicapped trigonal prism geometry.[6,11] The chlorides pack in distorted hexagonal close packing.

Antimony iodide is isostructural with arsenic iodide, but its bonding can be described as more ionic in nature.[4,5] Discrete SbI_3 units are observed, with longer intermolecular bonds to three more iodide atoms within van der Waals radii. Under high pressure, the environment around antimony also becomes more symmetrical, shifting from three-coordinate to six-coordinate at pressures above 1.4 GPa.[12]

Experimental Details for the Preparation of [AsA´$_3$]

Synthetic procedures were based on the synthesis of [AsA´$_3$] as reported by Rightmire, et al.[13]

Sample mechanochemical synthesis of [AsA´$_3$] from AsI$_3$

Inside a glovebox, AsI$_3$ (red solid, 40 mg, 88 µmol) and K[A´] (tan solid, 63 mg, 280 µmol, 3.2 equiv.) were added to a grinding jar with ball bearings. The jar was sealed with a clamp and milled for the desired time. The jar was opened in the glovebox to reveal an orange solid. The product was extracted with minimal hexanes (< 30 mL) and filtered through a fine-porosity glass fritted funnel. The pale yellow filtrate was dried under vacuum to afford a pale yellow oil with small yellow crystals. The product mixture contained C$_1$ and C$_3$ isomers of [AsA´$_3$] and {A´}$_2$; the ratio of these products was determined by ^{1}H NMR in benzene-d$_6$ or toluene-d$_8$, using the resonances in the range of 1.9 to 2.6 ppm (Table S1).

Milling conditions (mill type, time, ball and jar material, ball size) were varied as shown in Table S2; C$_1$:C$_3$, yields of [AsA´$_3$], and the [AsA´$_3$]:{A´}$_2$ ratio are shown in Figures S1-S5.

Table S2. ^{1}H NMR shifts used to determine ratios of C$_1$ [AsA´$_3$], C$_3$ [AsA´$_3$], and {A´}$_2$

Product	Chemical shift in benzene-d$_6$ (ppm)	Chemical shift in toluene-d$_8$ (ppm)	Integration	Multiplicity
C$_3$ [AsA´$_3$]	2.55	2.50	3H	doublet
C$_1$ [AsA´$_3$]-a	2.48	2.44	1H	doublet
C$_1$ [AsA´$_3$]-b	2.27	2.23	1H	doublet
C$_1$ [AsA´$_3$]-c	2.61	2.57	1H	doublet
{A´}$_2$	2.02	1.99	2H	multiplet

Table S3. Milling conditions for the synthesis of [AsA´$_3$] without pre-grinding[a]

Mill type	Jar material	Ball size	Time (min)	Speed
PBM	SS	Small	5	600 rpm
PBM	SS	Small	10	600 rpm
PBM	SS	Small	60	600 rpm
PBM	ZrO_2	Small	10	600 rpm
PBM	ZrO_2	Small	30	600 rpm
PBM	ZrO_2	Small	60	600 rpm
MM	SS	Large	5	30 Hz
MM	SS	Large	10	30 Hz
MM	SS	Large	30	30 Hz
MM	SS	Large	60	30 Hz
MM	SS	Small	5	30 Hz
MM	SS	Small	10	30 Hz
MM	SS	Small	30	30 Hz
MM	SS	Small	60	30 Hz
MM	Teflon	Large	5	30 Hz
MM	Teflon	Large	10	30 Hz
MM	Teflon	Large	30	30 Hz
MM	Teflon	Large	60	30 Hz

[a] Each set of conditions was run a minimum of two times

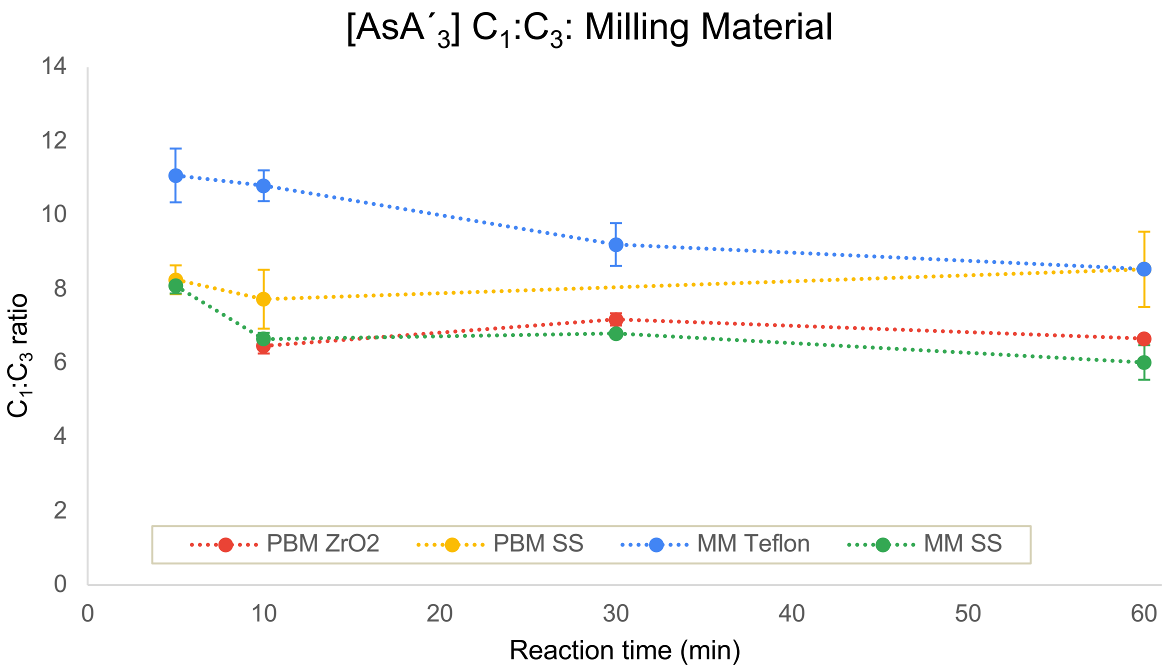

Figure S1. [AsA´$_3$] C$_1$:C$_3$: Milling Material

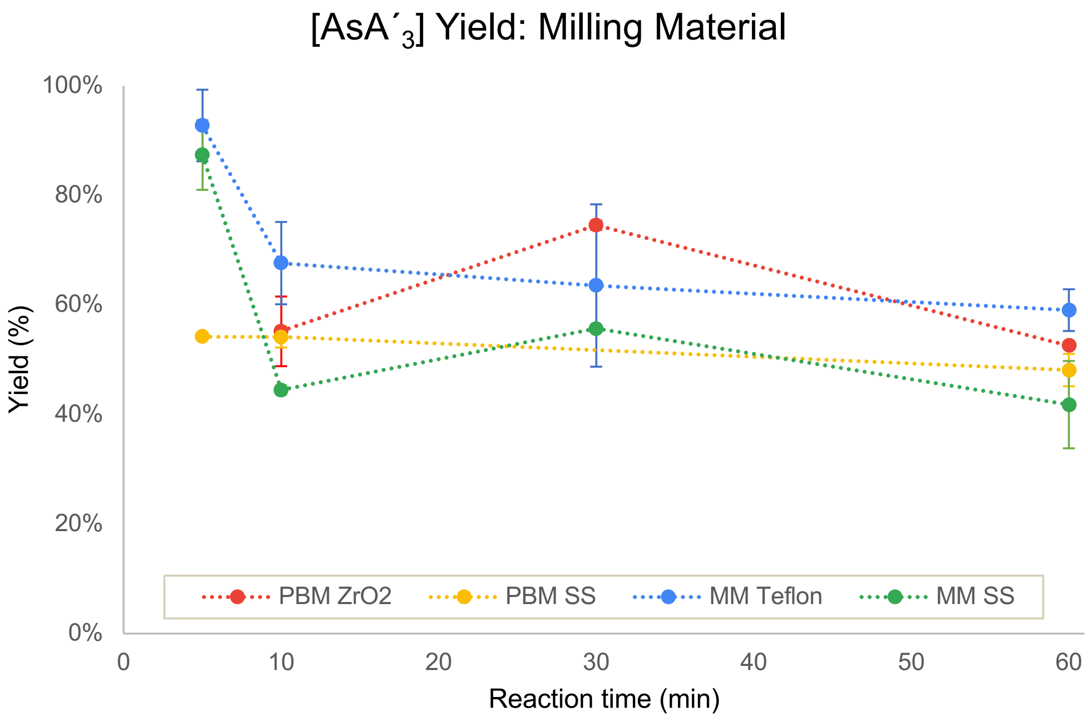

Figure S2. [AsA´$_3$] Yield: Milling Material

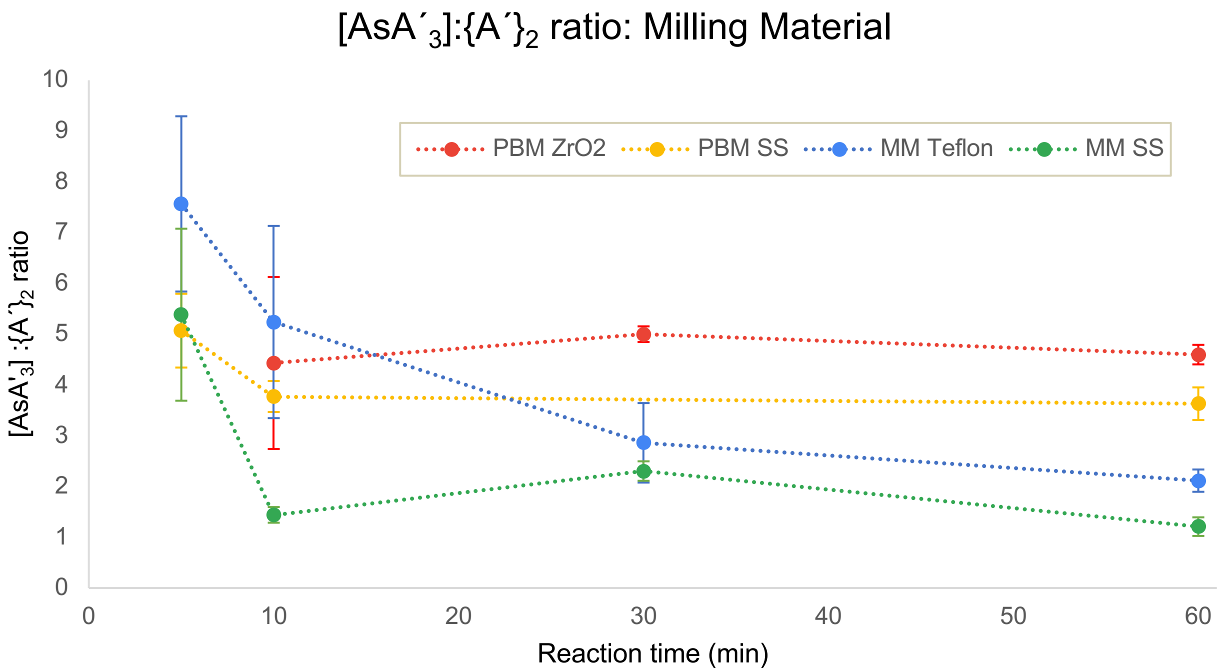

Figure S3. [AsA´$_3$]:{A´}$_2$ ratio: Milling Material

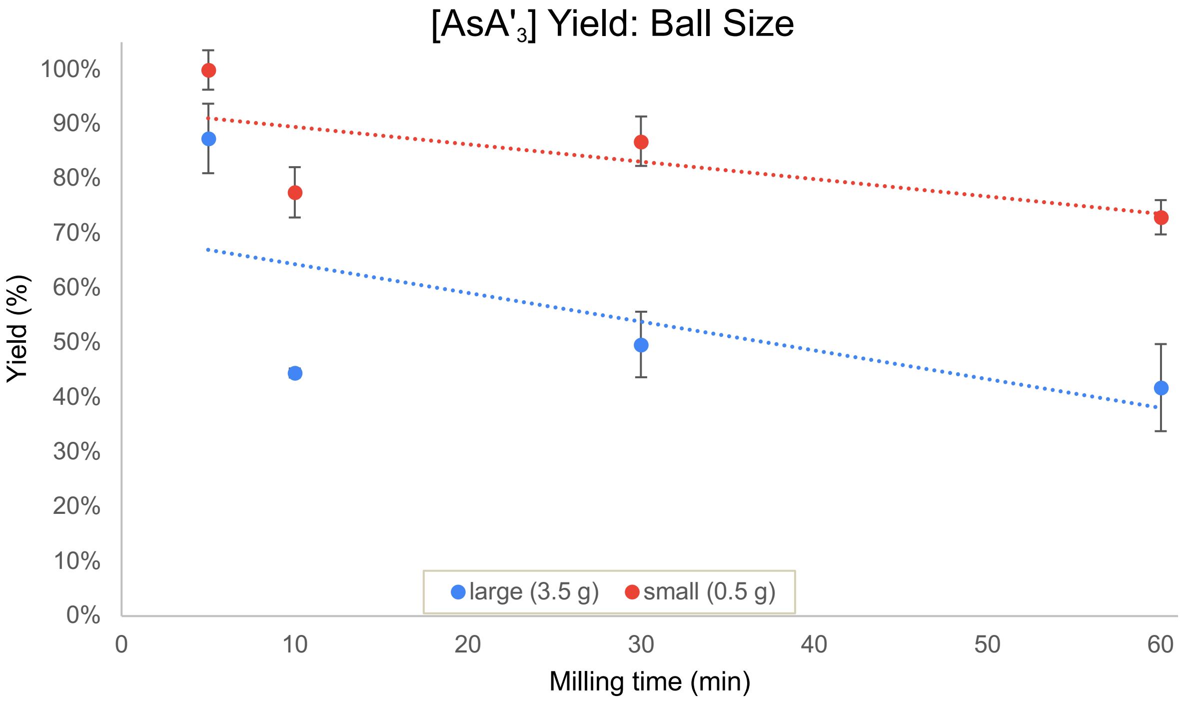

Figure S4. [AsA´$_3$] Yield: Ball Size

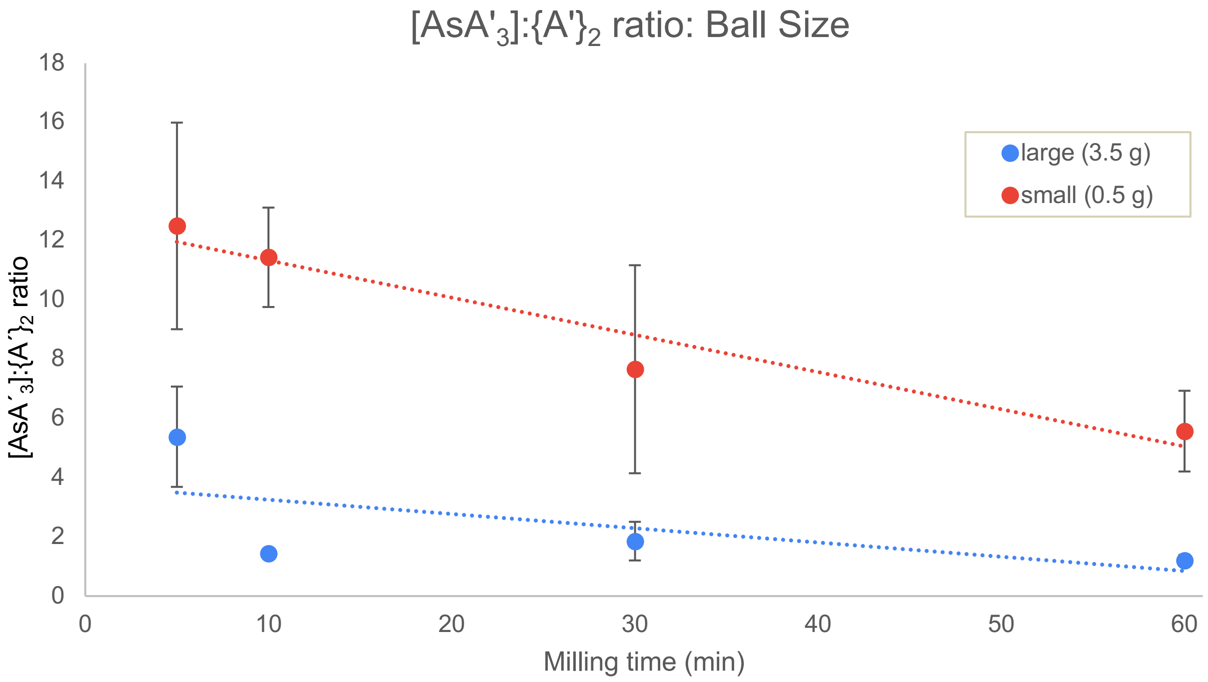

Figure S5. $[AsA'_3]:\{A'\}_2$ ratio: Ball Size

Mechanochemical synthesis of [AsA'_3] from $AsCl_3$

SAFETY NOTE: This reaction is highly exothermic and should not be performed on a larger scale!

In a glovebox, $AsCl_3$ (colorless liquid, 30 mg, 0.17 mmol) was added to a mixer mill jar with two large stainless steel ball bearings. K[A′] (112 mg, 0.50 mmol) was added, generating a small amount of white smoke from the exothermic reaction. The jar was sealed and milled for 10 min at 30 Hz. After milling, the jar was returned to the glovebox. The jar was opened to reveal a viscous orange substance. The product was extracted with minimal hexanes (< 30 mL) and filtered through a fine-porosity glass fritted funnel. The pale-yellow filtrate was dried under vacuum to afford small yellow crystals. The product mixture contained C_1 and C_3 isomers of [AsA'_3] and $\{A'\}_2$; the ratio of these was determined with ^1H NMR in benzene-d_6 or toluene-d_8, using the resonances in the range of 1.9 to 2.6 ppm (Table S1).

Solution synthesis of [AsA'_3] from AsI_3

Similar to the procedure in hexanes solution reported by Rightmire et al.,[13] [AsA'_3] can be prepared in toluene solution, however, the reaction does not proceed as cleanly. In a glovebox, AsI_3 (50 mg, 0.11 mmol) was dissolved in toluene (6 mL) in a vial to give a deep yellow solution. In a round bottom flask, K[A′] (80 mg, 0.36 mmol) was suspended in toluene (20 mL) to afford an orange suspension. The AsI_3 solution was slowly added to the K[A′] at room temperature and allowed to stir for 3 h. The turbid orange solution was filtered through a fine-porosity glass fritted funnel to provide a yellow filtrate. Toluene was removed by vacuum, affording a mixture of [AsA'_3] and $\{A'\}_2$ as a thin yellow oil and round colorless crystals.

Solution synthesis of [AsA'_3] from $AsCl_3$

In a glovebox, $AsCl_3$ (85 mg, 0.47 mmol) was dissolved in toluene (5 mL) in a vial to give a colorless solution. In a round bottom flask, K[A′] (320 mg, 1.43 mmol) was suspended in toluene (20 mL) to afford an orange suspension. The $AsCl_3$ solution was slowly added to the K[A′] at room temperature and allowed to stir overnight. The hazy yellow solution was filtered through a fine-porosity glass fritted funnel to give a yellow filtrate. Toluene was removed by vacuum, affording a mixture of [AsA'_3] and $\{A'\}_2$ as a yellow oil and yellow crystals.

LAG reactions with AsI_3

For selected mechanochemical reactions, a small amount of solvent was added to the dry AsI_3 and K[A´] before grinding. The solvent (hexanes, HMDSO, or THF) was measured with a 1-mL plastic pipette and added directly to the grinding jar. Immediately after the addition of solvent, the grinding jar was sealed and clamped to minimize evaporation. The reaction was milled in the planetary mill for 10 min at 600 rpm, using a 50 mL stainless steel jar and small ball bearings, and worked up as described above. The various LAG conditions are described in Tables S3 and S4; yields of [AsA´$_3$] and the ratio of [AsA´$_3$]:{A´}$_2$ are shown in Figures S6 and S7.

Table S4. Milling conditions for the synthesis of [AsA´$_3$] under LAG conditions

LAG solvent	Equiv. [a]	η (µL/mg)[b]
hexanes	1	0.12
hexanes	2	0.23
hexanes	3	0.35
hexanes	6	0.69
hexanes	14	1.6
hexanes	30	3.3
hexanes	60	6.9
HMDSO	3	0.56
HMDSO	5	0.97

Each set of conditions was run a minimum of two times. [a] Equiv. of LAG solvent relative to AsI_3. [b] µL of solvent divided by mg of total reagents

Table S5. Milling conditions for the synthesis of [AsA´$_3$] under LAG conditions and results

LAG solvent	Equiv. [a]	η (µL/mg)[b]	C_1:C_3	[AsA´$_3$]:{A´}$_2$
THF	4.5	0.33	N/A	N/A, K[A´] recovered
THF	11	0.81	3.5	0.42
THF	13	0.95	3.3	0.36

[a] Equiv. of LAG solvent relative to AsI_3. [b] µL of solvent divided by mg of total reagents

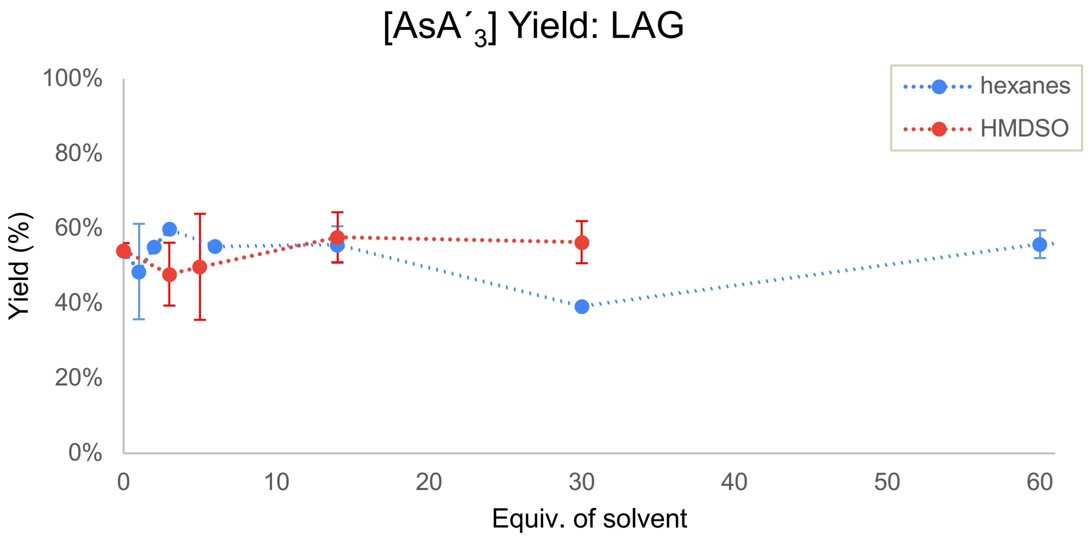

Figure S6. [AsA´$_3$] Yield: LAG

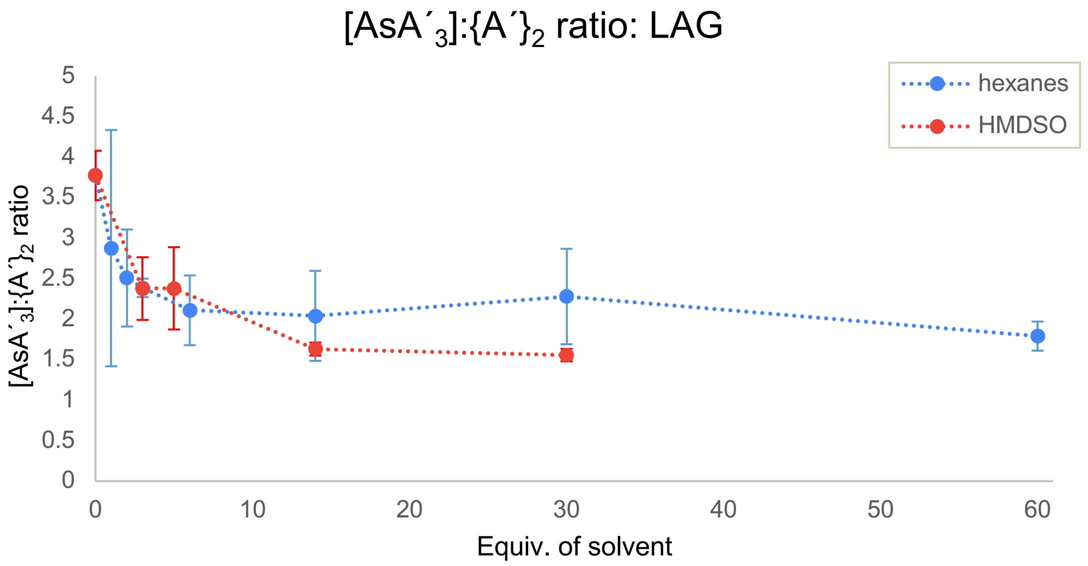

Figure S7. [AsA´$_3$]:{A´}$_2$ ratio: LAG

Pre-grinding of AsI_3

Select mechanochemical reactions, the metal halide precursor underwent “pre-grinding.” Specifically, the metal halide was added to the grinding jar with ball bearings in the glovebox, sealed in a clamp and milled for a specified time (pre-grind time). The jar was returned to the glovebox, then opened and 3 equiv. of K[A´] added. The jar was re-sealed and milled for the reaction time. The reaction was worked up as described above. The various milling conditions used are described in Table S6; yields of [AsA´$_3$] and the [AsA´$_3$]:{A´}$_2$ ratio are provided in Figures S8 and S9.

Table S6. Milling conditions for the synthesis of [AsA´$_3$] with pre-grinding[a]

Pre-grind time (min)	Pre-grind frequency	Reaction time (min)	Reaction frequency	Mill type
0	N/A	10	600 rpm	PBM
1	600 rpm	10	600 rpm	PBM
5	600 rpm	10	600 rpm	PBM
10	600 rpm	10	600 rpm	PBM
15	600 rpm	10	600 rpm	PBM
20	600 rpm	10	600 rpm	PBM
25	600 rpm	10	600 rpm	PBM
30	600 rpm	10	600 rpm	PBM
45	600 rpm	10	600 rpm	PBM
0	N/A	10	30 Hz	MM
0.5	30 Hz	10	30 Hz	MM
1	30 Hz	10	30 Hz	MM
2	30 Hz	10	30 Hz	MM
5	30 Hz	10	30 Hz	MM
10	30 Hz	10	30 Hz	MM
15	30 Hz	10	30 Hz	MM
30	30 Hz	10	30 Hz	MM
0	NA	5	30 Hz	MM

Table S6 (cont.)

Pre-grind time (min)	Pre-grind frequency	Reaction time (min)	Reaction frequency	Mill type
0.5	10 Hz	5	30 Hz	MM
1	10 Hz	5	30 Hz	MM
2	10 Hz	5	30 Hz	MM
5	10 Hz	5	30 Hz	MM
10	10 Hz	5	30 Hz	MM
15	10 Hz	5	30 Hz	MM

[a] Each set of conditions was used a minimum of two times

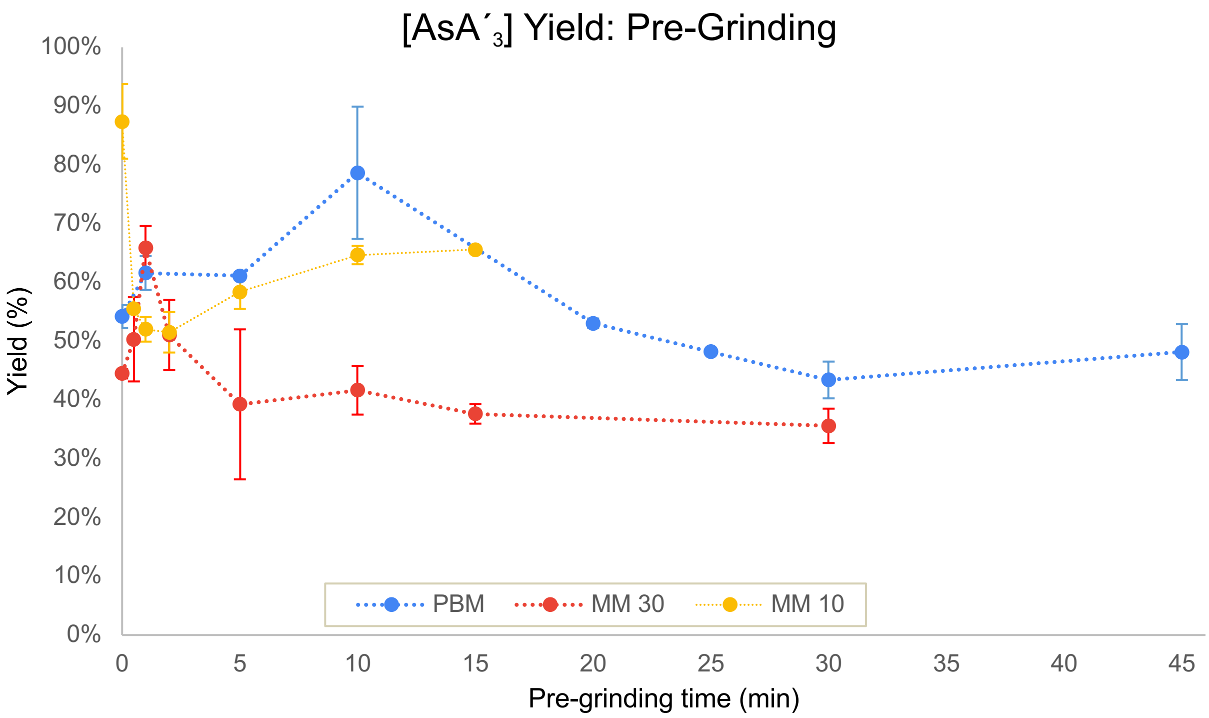

Figure S8. [AsA´$_3$] Yield: Pre-Grinding

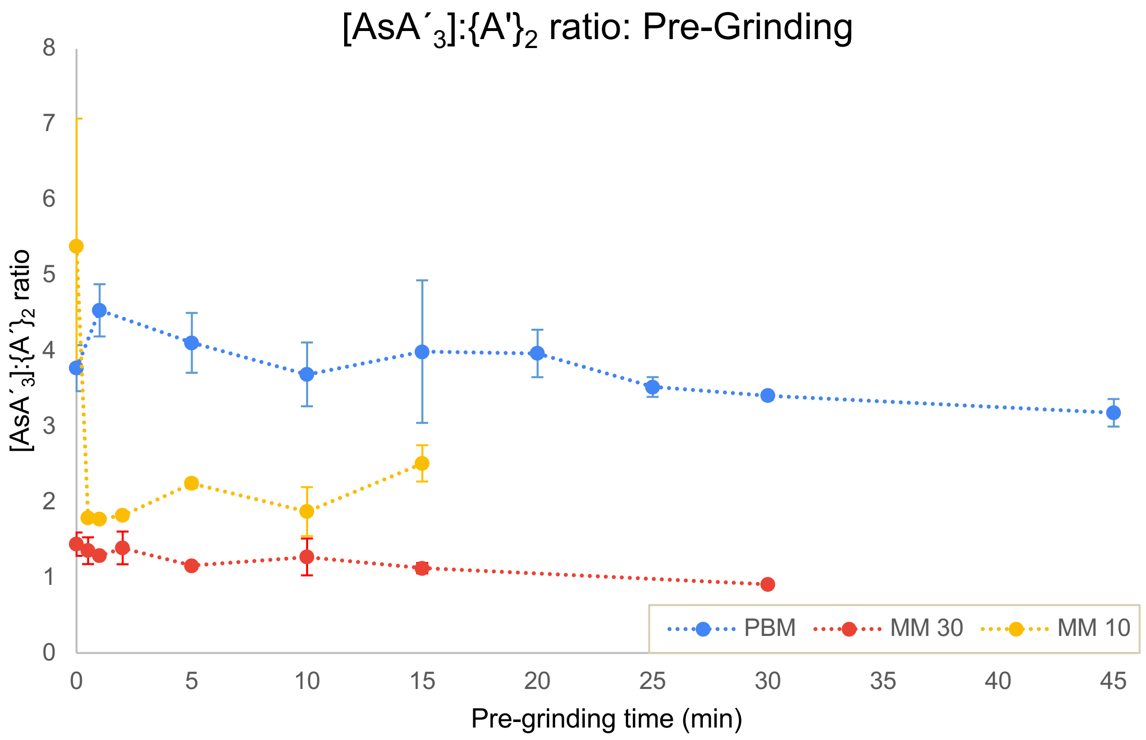

Figure S9. [AsA´$_3$] to {A´}$_2$ ratio: Pre-Grinding

Decomposition study: Milling [AsA´$_3$] alone or with KI

Prepared [AsA´$_3$] with {A´}$_2$ (30 mg) was loaded into a mixer mill stainless jar with either 2 large ball bearings or 16 small ball bearings (total mass of 7 g) and milled at 30 Hz for either 30 or 60 min. ^{1}H NMR (in C_6D_6) was taken after milling; the ratio of C_1:C_3 and [AsA´$_3$]:{A´}$_2$ were compared before and after milling, as shown in Figures S10 and S11 (green arrows).

Prepared [AsA´$_3$] containing {A´}$_2$ (30 mg) and potassium iodide (3 equiv.) were loaded into a mixer mill stainless steel jar with either 2 large ball bearings or 16 small ball bearings (total mass of 7 grams) and milled at 30 Hz for either 30 or 60 min. The product was extracted with benzene-d$_6$, filtered over Celite and glass wool, and ^{1}H NMR was obtained. The ratio of C_1:C_3 and [AsA´$_3$]:{A´}$_2$ were compared before and after milling, as shown in Figures S10 and S11 (blue arrows).

Table S7. Conditions for milling decomposition studies.

[AsA´$_3$] source	Alone or with 3 KI	Ball size	Mill time (min)
Sample A	Alone	Large	30
Sample A	With KI	Large	30
Sample B	Alone	Large	60
Sample B	With KI	Large	60
Sample B	Alone	Small	60
Sample B	With KI	Small	60

Decomposition study: Heating [AsA´$_3$] in toluene-d$_8$

A solution of [AsA´$_3$] in toluene-d$_8$ (pale yellow) was prepared in an NMR tube fitted with a septum NMR cap. The cap was wrapped with Parafilm, after which an initial ^{1}H NMR spectrum was obtained. The tube was connected to the Schlenk line under nitrogen and heated in a 90 °C oil bath for 7.5 h. After heating the solution was a very pale yellow and some brown precipitate formed. A subsequent ^{1}H NMR spectrum was obtained. This process was repeated once with a different [AsA´$_3$] sample. The ratios of C_1:C_3 and [AsA´$_3$]:{A´}$_2$ were compared before and after heating, as shown in Figures S10 and S11.

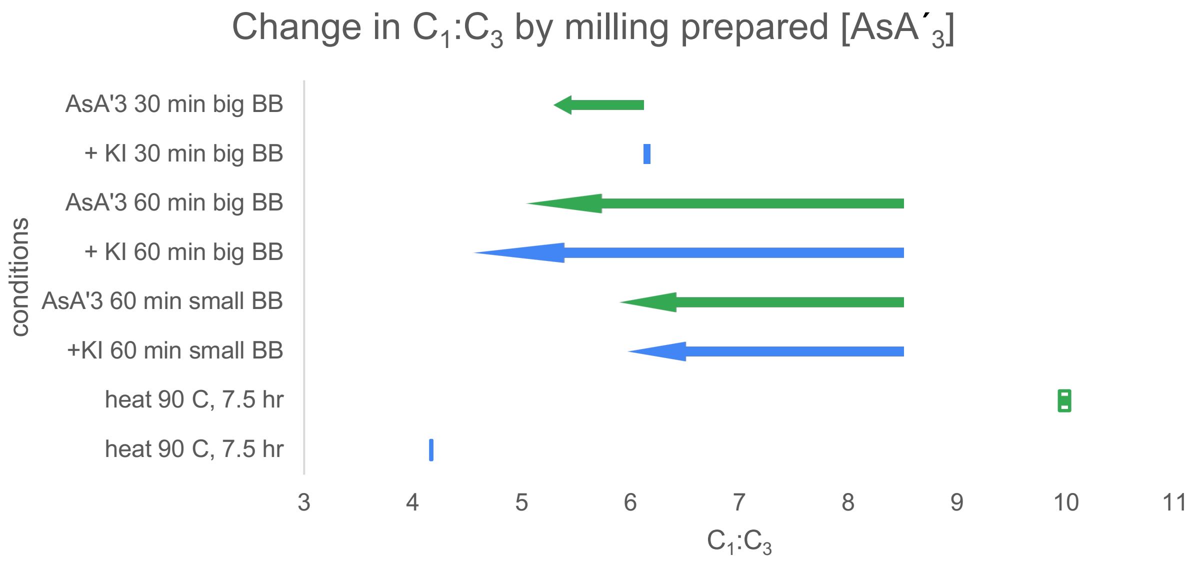

Figure S10. Change in C_1:C_3 by milling prepared [AsA'$_3$]

Green arrows show [AsA´$_3$] milled alone; blue arrows show [AsA´$_3$] milled with KI. Arrows point from starting value to value after milling or heating.

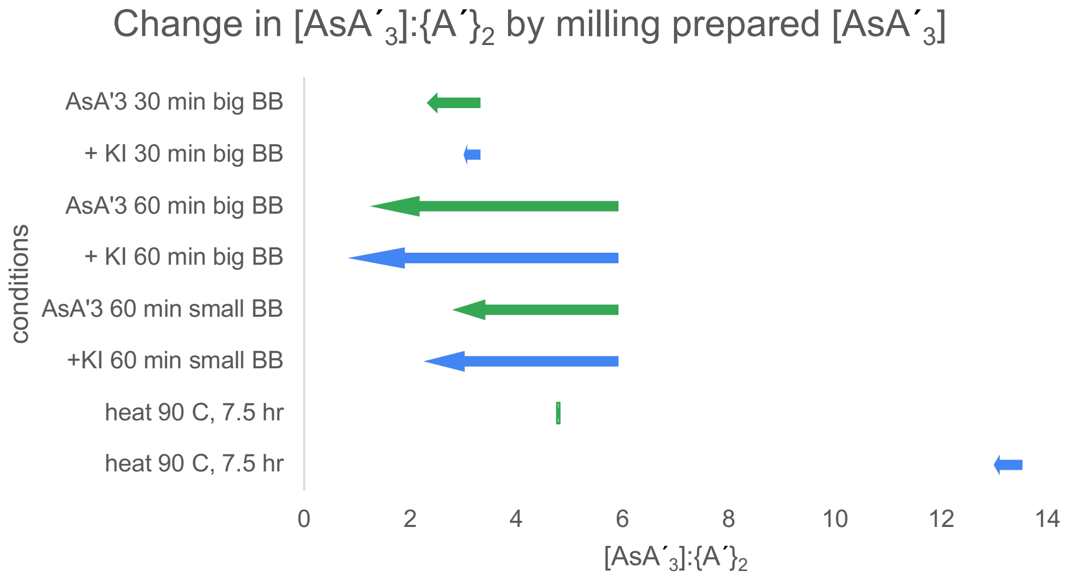

Figure S11. Change in [AsA´$_3$] to {A´}$_2$ by milling prepared [AsA´$_3$]

Green arrows show [AsA´$_3$] milled alone; blue arrows show [AsA´$_3$] milled with KI. Arrows point from starting value to value after milling or heating.

Experimental Details for the Preparation of [SbA´$_3$]

Synthetic procedures were based on the synthesis of [SbA´$_3$] as reported by Rightmire et al.[13]

Sample mechanochemical synthesis of [SbA´$_3$] from $SbCl_3$

Inside a glovebox, $SbCl_3$ (solid, 50 mg, 221 µmol) and K[A´] (solid, 155 mg, 690 µmol, 3.1 equiv.) were added to a grinding jar with ball bearings. The jar was sealed with a clamp and milled for the desired time. The jar was opened in the glovebox to reveal a black solid. The product was extracted with minimal hexanes (< 30 mL) and filtered through a fine-porosity glass fritted funnel. The pale-yellow filtrate was dried under vacuum to afford a pale yellow oil with small yellow crystals. The product mixture contained C_1 and C_3 isomers of [SbA´$_3$] along with {A´}$_2$; the ratio of these products was determined with ^{1}H NMR spectra in benzene-d$_6$ or toluene-d$_8$, using the resonances in the range of 1.9 to 2.6 ppm (Table S8). The various milling conditions are described in Table S9; the C_1:C_3 ratio, yields of [SbA´$_3$] and the [SbA´$_3$]:{A´}$_2$ ratio are provided in Figures S12–S14.

Table S8. ^{1}**H NMR shifts used to determine ratios of** C_1 **[SbA´$_3$],** C_3 **[SbA´$_3$], and {A´}$_2$**

Product	Chemical shift in C_6D_6 (ppm)	Chemical shift in $CH_3C_6H_5$ (ppm)	Integration	Multiplicity
C_3	2.59	2.54	3H	d
C_1-a	2.21	2.17	1H	d
C_1-b	2.55	2.50	1H	d
C_1-c	2.36	2.31	1H	d
A´$_2$	2.02	1.99	2H	m

Sample mechanochemical synthesis of [SbA´$_3$] from SbI_3

Inside a glovebox, SbI_3 (pink solid, 31 mg, 61 µmol) and K[A´] (tan solid, 47 mg, 210 µmol, 3.4 equiv.) were added to a grinding jar with ball bearings. The jar was sealed with a clamp and milled for the desired time. The jar was opened in the glovebox to reveal a black solid. The product was extracted with minimal hexanes (< 30 mL) and filtered through a fine-porosity glass fritted funnel.

The pale yellow filtrate was dried under vacuum to afford a brown-yellow oil with small crystals. The product mixture contained the C_1 and C_3 isomers of [SbA´$_3$] along with {A´}$_2$. The various milling conditions are described in Table S9; the C_1:C_3 ratio, yields of [SbA´$_3$] and the [SbA´$_3$]:{A´}$_2$ ratio are provided in Figures S12–S14.

Table S9. Milling conditions for the synthesis of [SbA´$_3$] without pre-grinding[a]

Sb precursor	Mill type	Jar material	Ball size	Time (min)	Speed
SbI_3	PBM	SS	Small	5	300 rpm
SbI_3	PBM	SS	Small	10	300 rpm
SbI_3	PBM	SS	Small	60	300 rpm
SbI_3	PBM	ZrO_2	Small	10	300 rpm
SbI_3	PBM	ZrO_2	Small	60	300 rpm
SbI_3	MM	SS	Large	10	20 Hz
SbI_3	MM	SS	Large	15	20 Hz
SbI_3	MM	SS	Large	60	20 Hz
$SbCl_3$	PBM	SS	Small	5	300 rpm
$SbCl_3$	PBM	SS	Small	10	300 rpm
$SbCl_3$	PBM	SS	Small	60	300 rpm
$SbCl_3$	PBM	ZrO_2	Small	5	300 rpm
$SbCl_3$	PBM	ZrO_2	Small	10	300 rpm
$SbCl_3$	PBM	ZrO_2	Small	60	300 rpm
$SbCl_3$	MM	SS	Large	10	30 Hz
$SbCl_3$	MM	SS	Large	10	20 Hz
$SbCl_3$	MM	SS	Large	15	20 Hz
$SbCl_3$	MM	SS	Large	60	20 Hz

[a]Each set of conditions was used a minimum of two times.

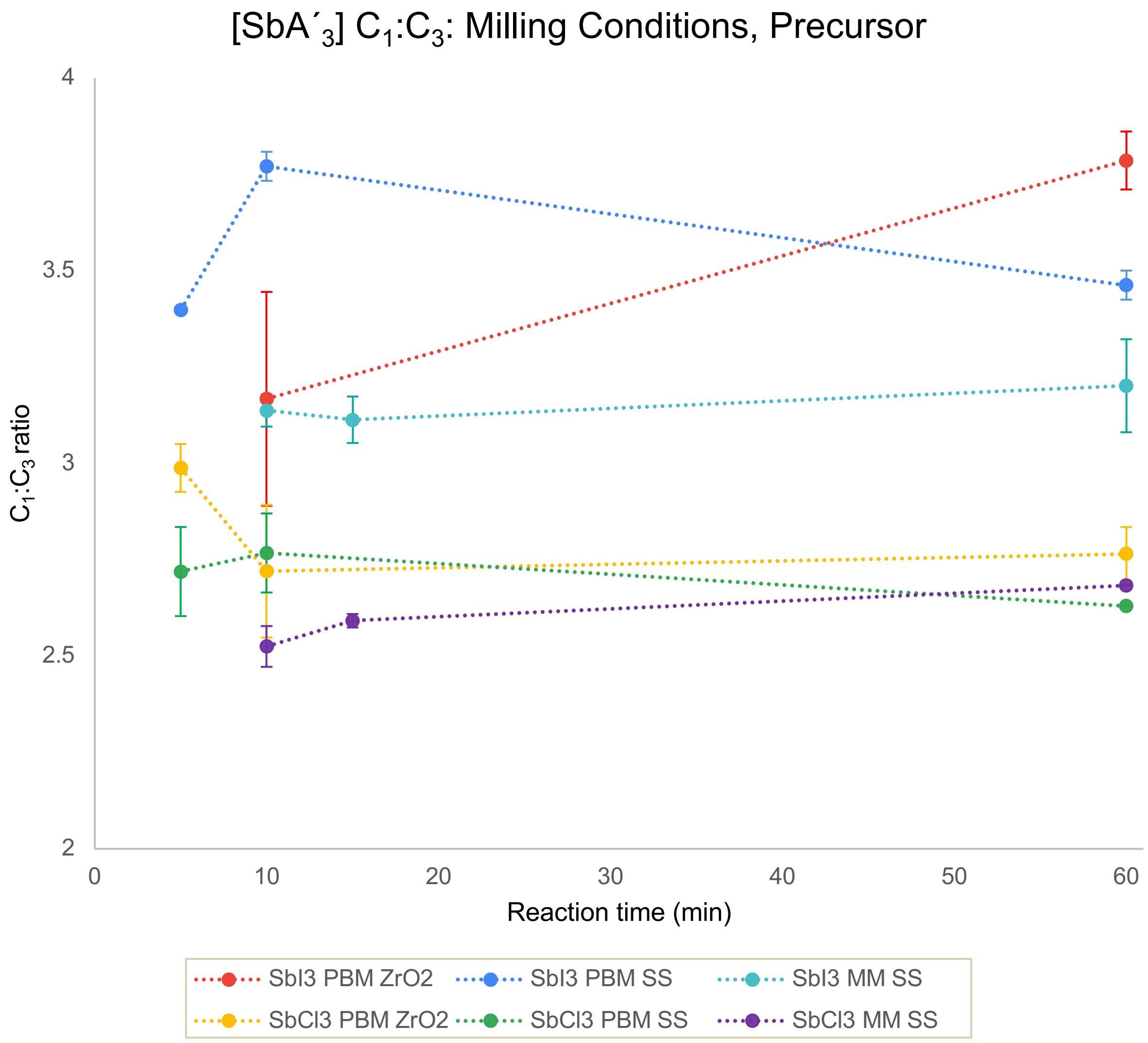

Figure S12. [SbA´$_3$] C$_1$:C$_3$: Mill, Material, Sb source

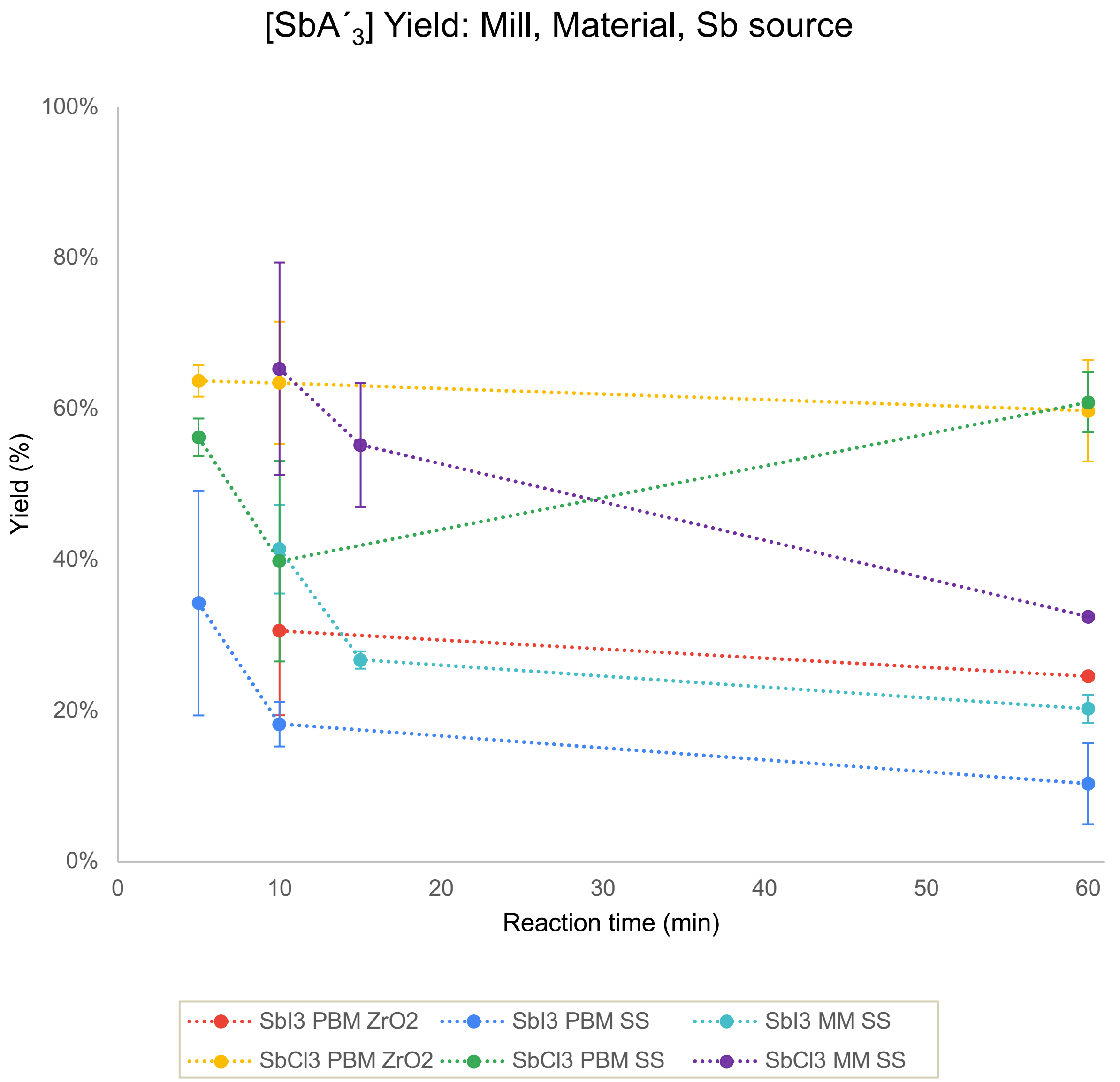

Figure S13. [SbA´$_3$] Yield: Mill, Material, Sb source

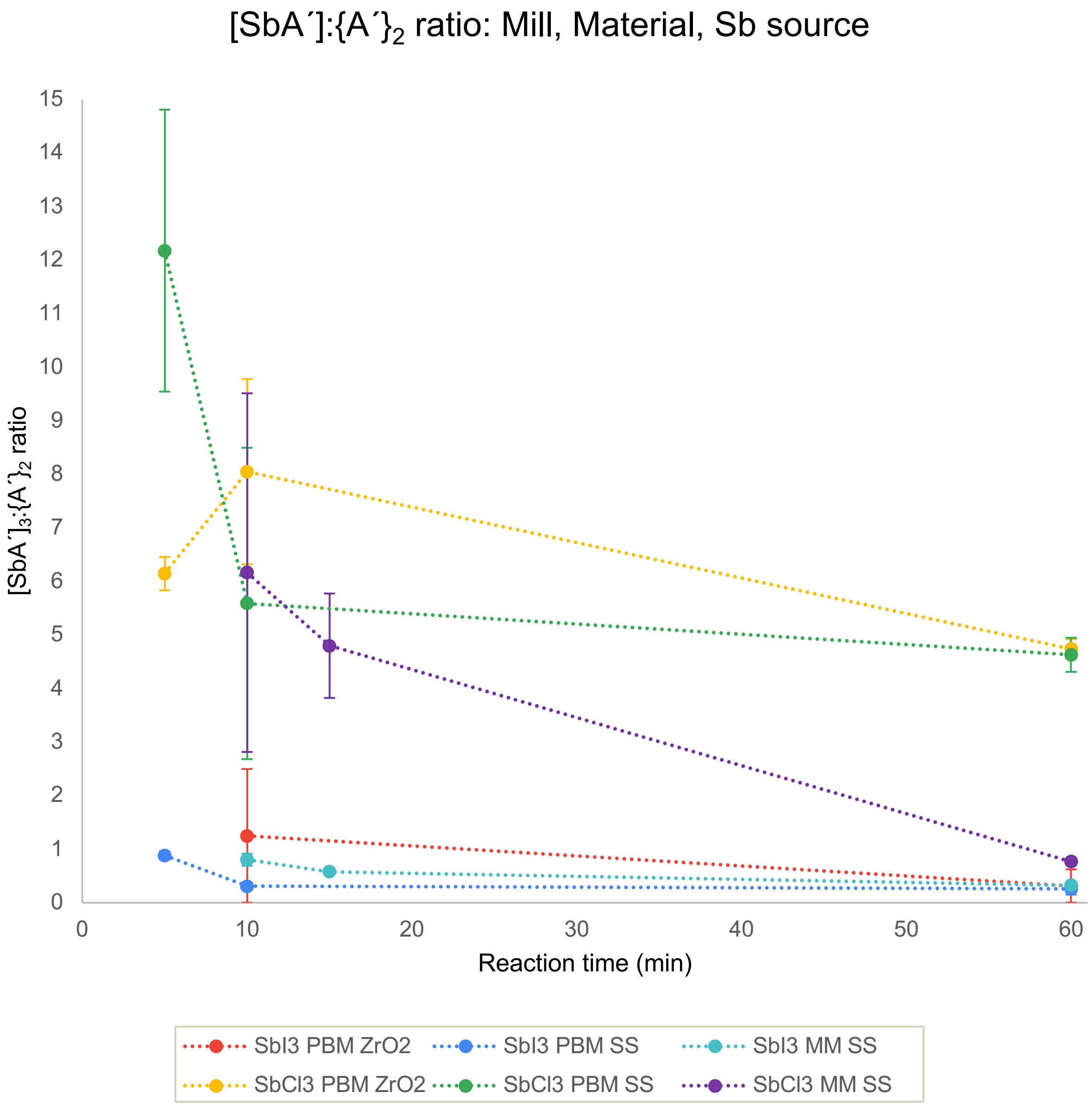

Figure S14. [SbA´$_3$] to {A´}$_2$ ratio: Mill, Material, Sb source

LAG reactions with $SbCl_3$

For select mechanochemical reactions, a small quantity of hexanes was added to the dry $SbCl_3$ and K[A´] before grinding. Hexanes was measuring with a 1-mL plastic pipette and added directly to the grinding jar. Immediately after the addition of solvent, the grinding jar was sealed and clamped to minimize evaporation. The reaction was milled in the planetary mill for 10 minutes at 600 rpm, using a 50 mL stainless steel jar and small ball bearings, and worked up as described above. The various LAG conditions are described in Table S10; yields of [SbA´$_3$] and the [SbA´$_3$]:{A´}$_2$ ratio are shown in Figures S15 and S16.

Solution synthesis of [SbA´$_3$] from $SbCl_3$

In a glovebox, $SbCl_3$ (51 mg, 0.22 mmol) was suspended in hexanes (3.49 mL, 120 equiv.) in a vial to give a colorless solution. K[A´] (tan solid, 155 mg, 0.68 mmol) was added slowly while stirring at room temperature and allowed to stir for 2 h. The hazy dark solution was filtered through a fine-porosity glass fritted funnel to give a colorless filtrate and black solid. Hexanes was removed from the filtrate by vacuum, affording a mixture of [SbA´$_3$] and {A´}$_2$ as a pale-yellow oil and colorless crystals.

Table S10. Conditions for the synthesis of [SbA´$_3$] from $SbCl_3$ under LAG or solution conditions

Equiv.	η (µL/mg)
0 [a]	0
1 [a]	0.16
2 [a]	0.27
3 [a]	0.40
6 [a]	0.87
14 [a]	2.0
30 [a]	4.2
60 [a]	8.5
93 [b]	13.6
120 [b]	17.0

[a] Each set of LAG conditions was used a minimum of two times. [b] Reactions conducted once in hexanes solution with stirring.

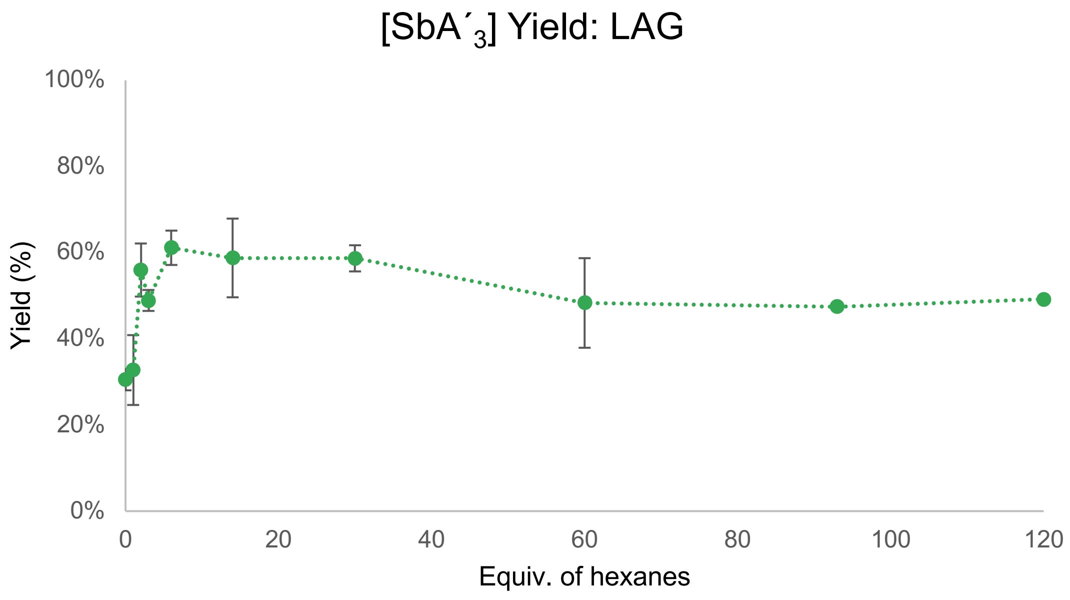

Figure S15. [SbA´₃] Yield: LAG

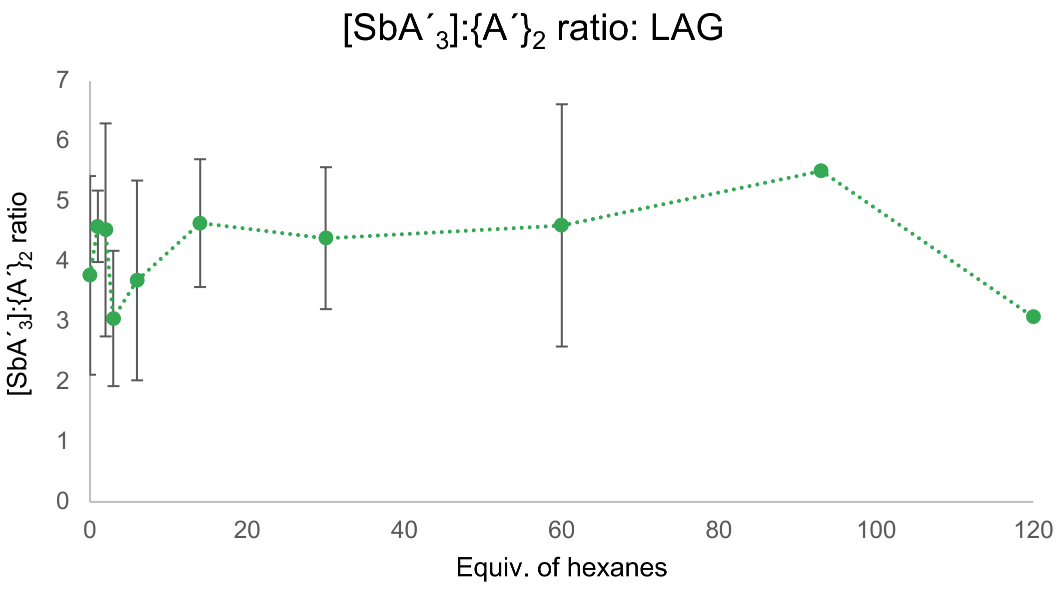

Figure S16. [SbA´₃] to {A´}₂ ratio: LAG

Pre-Grinding of $SbCl_3$ and SbI_3

For selected mechanochemical reactions, the metal halide precursor underwent pre-grinding, in which the metal halide was added to the grinding jar with ball bearings in the glovebox, sealed in a clamp and milled for a specified time (pre-grind time). The jar was returned to the glovebox, the jar was opened and 3 equiv. of K[A′] was added. The jar was re-sealed and milled for a specified time (reaction time). The reaction was worked up as described above. The various milling conditions used are described in Table S11; yields of [SbA'_3] and the [SbA'_3]:$\{A'\}_2$ ratio are provided in Figures S17–S18.

Table S11. Milling conditions for the synthesis of [SbA'_3] with pre-grinding

SbX_3 precursor	Pre-grind time (min)	Pre-grind Frequency	Reaction time (min)	Reaction frequency	Mill type
SbI_3	0	NA	10	300 rpm	PBM
SbI_3	1	300 rpm	10	300 rpm	PBM
SbI_3	5	300 rpm	10	300 rpm	PBM
SbI_3	10	300 rpm	10	300 rpm	PBM
SbI_3	15	300 rpm	10	300 rpm	PBM
SbI_3	30	300 rpm	10	300 rpm	PBM
SbI_3	45	300 rpm	10	300 rpm	PBM
$SbCl_3$	0	NA	10	300 rpm	PBM
$SbCl_3$	5	300 rpm	10	300 rpm	PBM
$SbCl_3$	10	300 rpm	10	300 rpm	PBM
$SbCl_3$	15	300 rpm	10	300 rpm	PBM
$SbCl_3$	30	300 rpm	10	300 rpm	PBM
$SbCl_3$	45	300 rpm	10	300 rpm	PBM
$SbCl_3$	60	300 rpm	10	300 rpm	PBM
$SbCl_3$	0	NA	10	20 Hz	MM
$SbCl_3$	1	20 Hz	10	20 Hz	MM
$SbCl_3$	5	20 Hz	10	20 Hz	MM
$SbCl_3$	10	20 Hz	10	20 Hz	MM
$SbCl_3$	15	20 Hz	10	20 Hz	MM
$SbCl_3$	30	20 Hz	10	20 Hz	MM
$SbCl_3$	45	20 Hz	10	20 Hz	MM

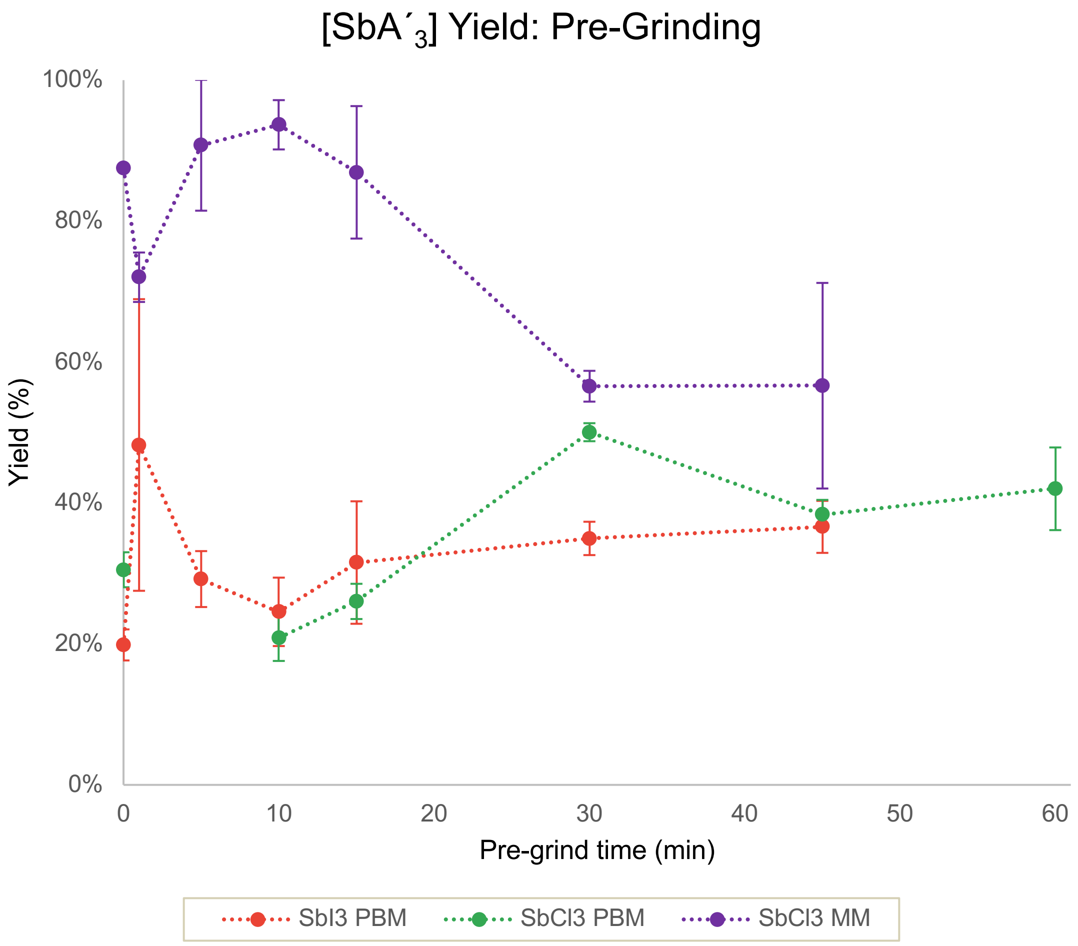

Figure S17. [SbA´$_3$] Yield: Pre-Grinding

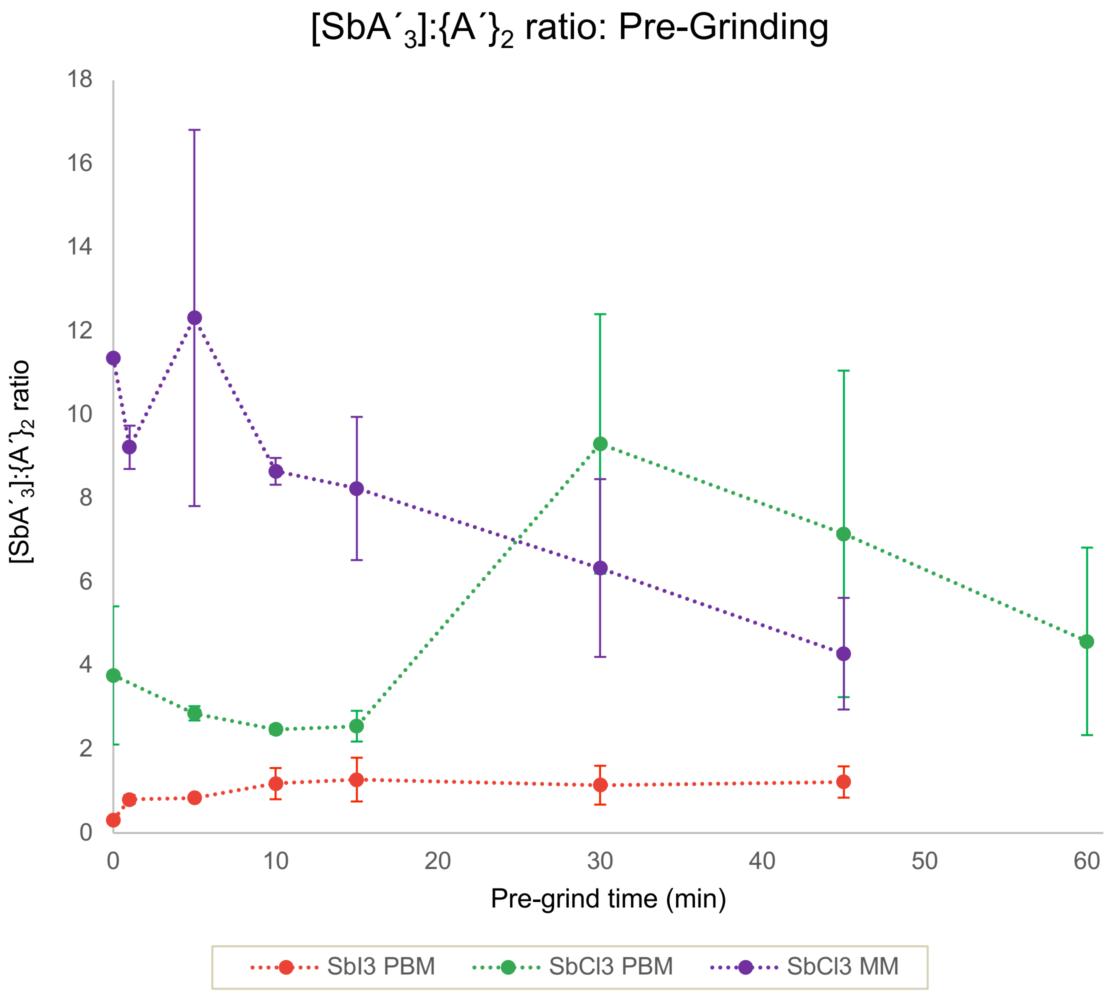

Figure S18. [SbA´$_3$] to {A´}$_2$ ratio: Pre-Grinding

Photographs of Pre-Ground Samples

The photographs below are of AsI_3 in the mixer mill grinding jar after pre-grinding, but before addition of K[A´]. Note that the color lightens from red-orange (Figure S19) to yellow (Figure S22) as pre-grinding time or frequency increases and the particle size decreases.

Figure S19. AsI_3 ground in the mixer mill at 10 Hz for 30 s.

Figure S20. AsI_3 ground in the mixer mill at 10 Hz for 1 min (left) or 2 min (right).

Figure S21. AsI_3 ground in the mixer mill at 10 Hz for 5 min. (left) or 10 min. (right).

Figure S22. AsI_3 ground in the mixer mill at 30 Hz for 2 min.
All pre-grind samples at 30 Hz (30 sec. to 30 min.) appear visually the same.

Scanning Electron Microscopy

Procedure for SEM

Two samples were prepared for analysis by scanning electron microscopy (SEM). The unground sample was obtained from commercially available AsI_3, as received. The ground sample was prepared by milling AsI_3 from the same source in the planetary mill for 45 min at 600 rpm using a 50 mL stainless steel jar and 25 g of small ball bearings. Bromopentafluorobenzene was used to transfer particles to a glass slide without dissolving them. The sample was sputter coated with gold for 20 sec. in an argon environment using a Cressington 108 Sputter Coater. Images were taken with a Zeiss Merlin Scanning Electron Microscope equipped with a GEMINI II column, using an accelerating voltage of 2.00 kV, a working distance of 9 mm, and the InLens secondary electron detector.

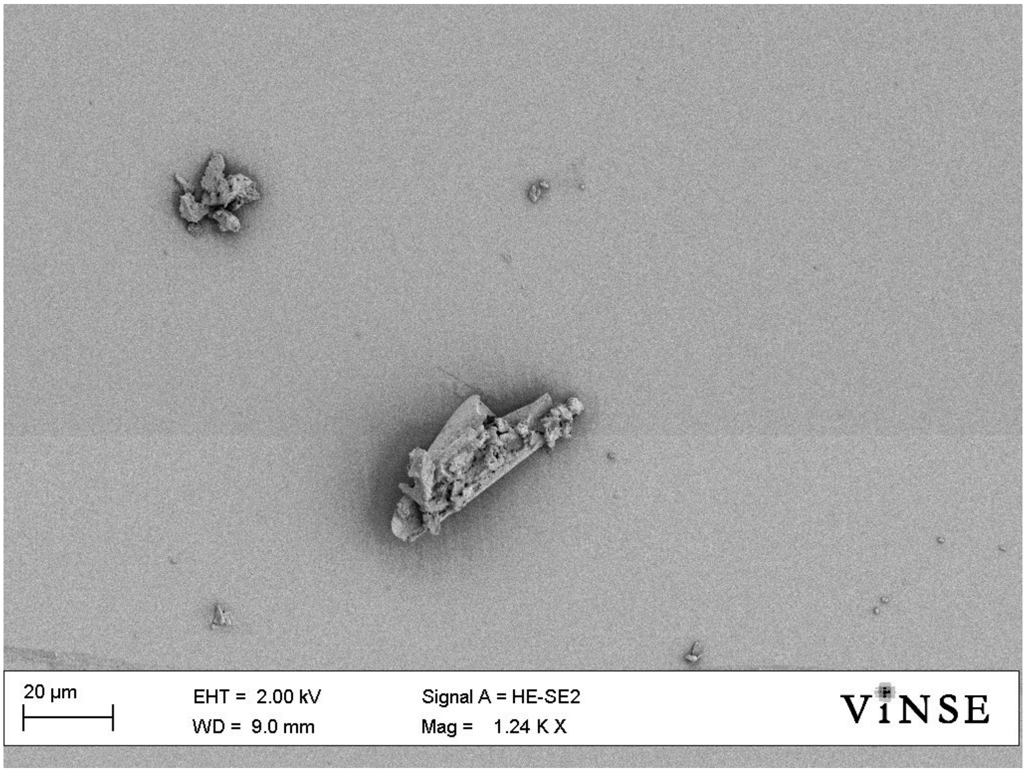

Figure S23. SEM image of unground AsI_3

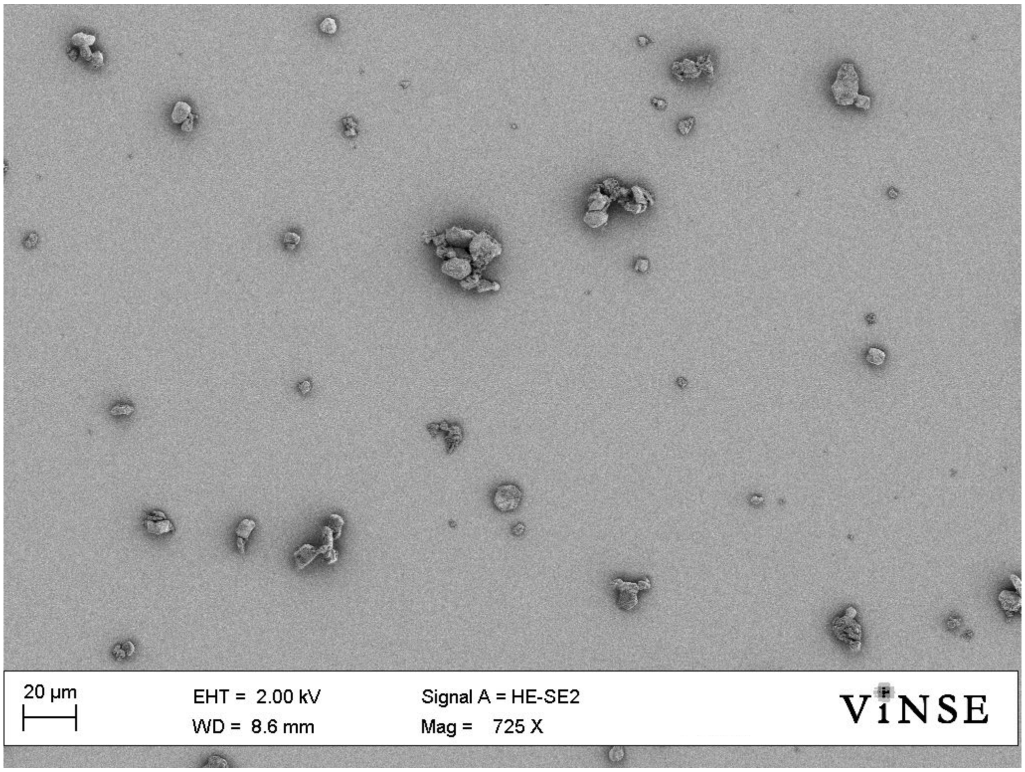

Figure S24. SEM Image of ground AsI_3

Powder X-Ray Diffraction

Procedure for PXRD

A sample of AsI_3 was ground in the planetary mill for 45 min at 600 rpm using a 50 mL stainless steel jar and 25 g of small ball bearings. A suspension of the powder in hexanes was drop-cast onto a low-background silicon XRD wafer in ambient conditions. Powder X-ray diffraction (XRD) spectra were obtained using a Rigaku SmartLab® X-ray Diffractometer with a CuKα source and a D/TeX Ultra 250 detector. The operating voltage and current were 40 kV and 44 mA, respectively. The step size was 0.1 degree at a rate of 10 degrees per minute. The data was used to confirm the sample contained only AsI_3 and no redox products.

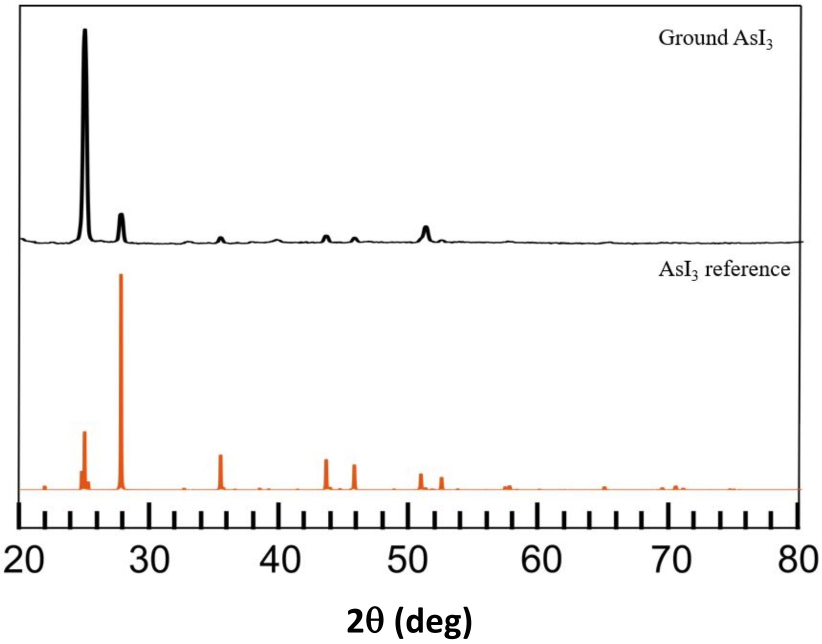

Figure S25. PXRD of AsI_3 after grinding

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