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Surefire generation of stannylpotassium: highly reactive stannyl anions and applications†

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Organometallic reagents such as organolithium and Grignard reagents have long been esteemed in chemical synthesis for their exceptional reactivity. In contrast, the application of their sodium and potassium counterparts has been comparatively sluggish, notwithstanding their augmented reactivity stemming from their heightened ionic character. This inertia persists due to the constrained accessibility of these heavy alkali metal reagents. In this study, our focus was directed towards devising a convenient and pragmatic approach for fabricating heavy alkali metal-based reagents, particularly those grounded in potassium. Herein, we present a novel, direct method for generating stannylpotassium (Sn–K) reagents through the simple combination of readily available silylstannanes and *t*-BuOK. Subsequently, the generated Sn–K reagents were effectively harnessed for stannylative substitution of aryl halides, furnishing an array of arylstannanes straightforwardly under transition metal-free conditions. This application distinctly underscores the potential utility of highly reactive Sn–K species, hitherto sparingly tapped into within the realm of synthetic organic chemistry. Furthermore, our investigation confirms that Sn–K reagents manifest notably superior reactivity compared with their well-established stannyllithium (Sn–Li) counterparts. This heightened reactivity can be ascribed to the increasing ionic character of Sn–K, which was supported by computational experiments.

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Introduction

The indispensable role of organometallic reagents as nucleophilic species in chemical synthesis is firmly established. Among the plethora of metallic elements, highly electropositive alkali and alkaline earth metals, notably lithium^{1,2} and magnesium,³ have been extensively harnessed across various synthetic endeavors, yielding a rich spectrum of organic compounds. This preference is attributed to their widespread availability and myriad advantages, including exceptionally high reactivity and versatility in reaction modalities. In accordance with Fajans' rule,⁴ organometallic reagents featuring heavy alkali metals as counter-cations tend to have a greater ionic character, thus implying heightened nucleophilicity and promising synthetic potential. Despite these prospects, their utilization in chemical synthesis has not always been pervasive, likely constrained by limited accessibility to such organometallic reagents. Notably, the contrast in reactivity between lithium and potassium-based organometallic species is stark: while the most commonly employed organolithium, *n*-BuLi, exhibits a half-life of 24 hours at 0 °C in THF,⁵ the infrequently

utilized *n*-BuK swiftly undergoes reaction with THF, even at –30 °C (Fig. 1a).⁶

A parallel scenario emerges in stannyl anion chemistry, where the application of stannyl anion species featuring various counter-cations (Sn–M: M = Li, Na, MgX, ZnX, Cu, *etc.*)⁷ facilitates direct and efficient routes to a broad spectrum of organostannanes of high synthetic importance. Notably, stannyl lithiums^{8–10} and sodiums^{11–13} have emerged as the most prevalent stannyl nucleophiles (Fig. 1a and b), albeit traditional methods for their generation often entail labor-intensive processes lacking in practicality. For instance, the synthesis of R₃Sn–Na typically entails the direct reduction of R₃Sn–Cl with metallic sodium in liquid ammonia, a procedure fraught with operational challenges such as the handling of ammonia gas under cryogenic conditions and the use of highly reactive metallic sodium (Fig. 1b).^{14,15} Similarly, established protocols for R₃Sn–Li, involving either direct reduction of R₃Sn–Cl with metallic lithium or the reaction of R₃Sn–SnR₃ with organolithium reagents, are beset by inefficiencies in generation and prone to side reactions.^{16,17} In 2015, Uchiyama and Wang addressed these limitations by employing naphthalene as a catalyst in the preparation of R₃Sn–Li from metallic lithium and R₃Sn–Cl, leading to notable improvements in efficiency and stability (Fig. 1c).¹⁸ Furthermore, the synthetic utility of this methodology was underscored by its successful application in stannylative substitution reactions of aryl halides, illustrating

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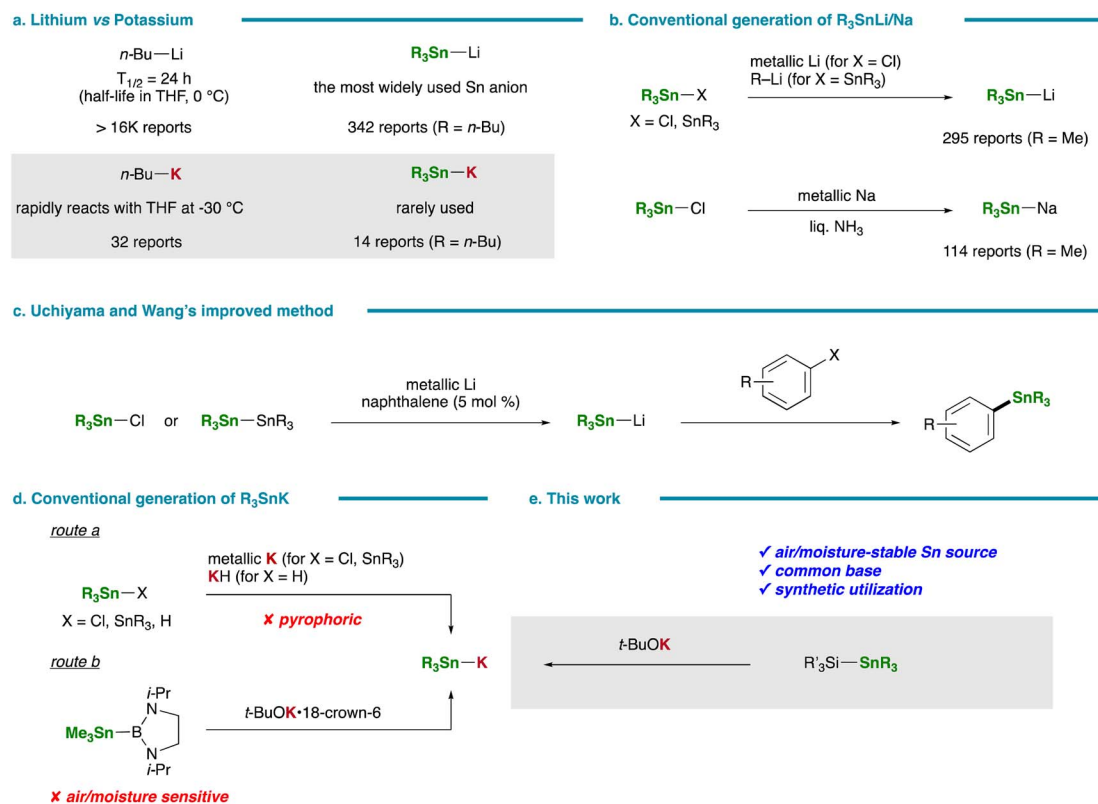


Fig. 1 Backgrounds and this work. (a) Lithium- and potassium-based nucleophilic species. (b) Conventional generation of $\text{R}_3\text{Sn-Li}$ and -Na reagents. (c) Uchiyama and Wang's improved method for generating $\text{R}_3\text{Sn-Li}$ reagents. (d) Conventional generation of $\text{R}_3\text{Sn-K}$ species. (e) This work: generation of $\text{R}_3\text{Sn-K}$ species from silylstannanes and *t*-BuOK.

the potential of developing practical and efficient synthesis approaches to stannyl anion species for fostering novel tin-based synthetic transformations.

In stark contrast to the well-established preparations and subsequent transformations of $\text{R}_3\text{Sn-Li/Na}$, the utilization of $\text{R}_3\text{Sn-K}$ in synthetic organic chemistry has been markedly scarce (Fig. 1a), despite its anticipated superior nucleophilicity arising from heightened ionicity. This disparity primarily stems from the lack of usability and practicality inherent in existing preparation methods: route a necessitates the use of hazardous, spontaneously combustible metallic potassium or potassium hydride as a potassium source,^{19–21} while route b requires stannylboranes, which are exceedingly sensitive to water and air,²² as a tin source (Fig. 1d). On the other hand, silicon- or aryl-stabilized stannyl potassiums $[(\text{R}_3\text{Si})_3\text{Sn-K or ArSnK}_3]$ have been reported to be readily generated *via* the reaction of $(\text{R}_3\text{Si})_4\text{Sn}$ or $\text{ArSn}(\text{SiHMe}_2)_3$ with a common base, *t*-BuOK.²³ These species have found utility in the synthesis of various compounds, including $(\text{R}_3\text{Si})_3\text{Sn}$ -substituted spirooligosilanes²⁴ and tetraacylstannanes.^{25,26} Given this context, our focus was directed towards harnessing (triorganosilyl)stannanes, characterized by their stable and facile handling properties, as a tin source for generating $\text{R}_3\text{Sn-K}$. While (triorganosilyl)stannanes have conventionally served as silylating/silylstannylating agents in transition metal-catalyzed reactions,^{27–32} we demonstrated for the first time their potential as a tin source for generating

stannyl copper species ($\text{R}_3\text{Sn-Cu}$) upon treatment with a copper alkoxide ($\text{R}'\text{OCu}$), which served as a key intermediate in the copper-catalyzed hydrostannylation of terminal alkynes.³³ Herein, we unveil a straightforward and practical method for the preparation of $\text{R}_3\text{Sn-K}$, achievable without the need for specialized equipment or stringent handling precautions, simply by mixing readily available (triorganosilyl)silylstannanes and *t*-BuOK, focusing mainly on elucidating the synthetic potential of this facile method (Fig. 1e). The *in situ*-generated $\text{R}_3\text{Sn-K}$ was demonstrated to react smoothly with a diverse array of aryl halides to furnish arylstannanes. Furthermore, the heightened reactivity of $\text{R}_3\text{Sn-K}$, surpassing that of $\text{R}_3\text{Sn-Li}$, aligns with expectations, given its markedly ionic nature inherent in the Sn-K bond.

Results and discussion

Generation of stannyl potassiums from (triorganosilyl)stannanes

Our initial investigation focused on the synthesis of stannyl potassiums ($\text{R}_3\text{Sn-K}$) from (triorganosilyl)stannanes. Treatment of (dimethylphenylsilyl)trimethylstannane (**1a**) with *t*-BuOK in the presence of 18-crown-6 yielded $\text{Me}_3\text{Sn-K} \cdot 18\text{-crown-6}$ (**2a**) smoothly in 90% yield, as evidenced by NMR spectra (^1H , ^{13}C , ^{119}Sn) consistent with those reported by Kleeberg, Grunenberg, and Xie (Fig. 2a).²² The resulting **2a** exhibited sufficient



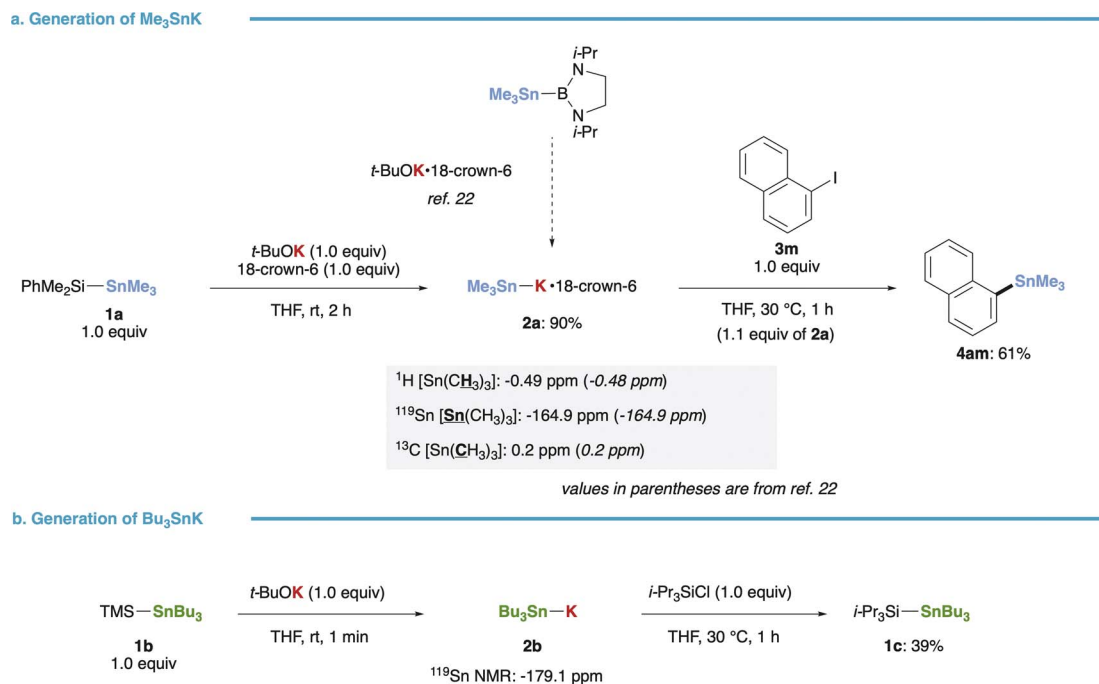


Fig. 2 Generation of R₃Sn–K species from silylstannanes. (a) Generation, NMR analysis and reaction of Me₃Sn–K. (b) Generation and reaction of Bu₃Sn–K.

nucleophilicity, as demonstrated by its reaction with 1-iodonaphthalene (**3m**) completing within 1 hour at 30 °C, affording the stannylated product (**4am**) in 61% yield. Furthermore, our method for preparing R₃Sn–K was successfully extended to (trimethylsilyl)tributylstannane (**1b**), yielding Bu₃Sn–K (**2b**) even

in the absence of 18-crown-6. This was confirmed by the upfield-shifted signal (–179.1 ppm) observed in the ¹¹⁹Sn NMR spectrum.³⁴ Subsequent addition of *i*-Pr₃SiCl resulted in the formation of the trapped product (**1c**) in 39% yield (Fig. 2b).

Table 1 Optimization of reaction conditions^a

Entry	Deviation from standard conditions	Yield ^b (%)	
		4ba	5
1	None	54	0
2	Toluene instead of THF	16	19
3	DMF instead of THF	0	0
4	CH ₃ CN instead of THF	0	18
5	1,4-Dioxane instead of THF	28	12
6	DME instead of THF	5	26
7	<i>t</i> -BuOLi instead of <i>t</i> -BuOK	0	0
8	<i>t</i> -BuONa instead of <i>t</i> -BuOK	0	30
9	MeOK instead of <i>t</i> -BuOK	10	18
10	EtOK instead of <i>t</i> -BuOK	7	28
11	KF/18-crown-6 instead of <i>t</i> -BuOK	0	32
12	<i>p</i> -iodotoluene (3b) instead of 3a	71	0
13	3b instead of 3a , 1.1 equiv. of 1b /1.1 equiv. of <i>t</i> -BuOK	78	0

^a Reaction conditions: **1b** (0.2 mmol), **3a** (0.2 mmol), *t*-BuOK (0.24 mmol, 1.2 equiv.), THF (0.67 mL), 30 °C, 1 h. ^b ¹¹⁹Sn NMR yield determined by using tributyl(vinyl)stannane as an internal standard.



Optimization of reaction conditions for stannylation of aryl halides with R_3Sn-K

Equipped with our straightforward and practical method for generating R_3Sn-K , we proceeded to investigate the reaction of $TMS-SnBu_3$ (**1b**) with *p*-bromotoluene (**3a**) in THF using *t*-BuOK as an additive, with a focus on the synthetic utility of the *in situ*-generated R_3Sn-K . Notably, the stannylation reaction proceeded smoothly at 30 °C within 1 hour, affording tributyl(*p*-tolyl)stannane (**4ba**) in 54% yield (Table 1, entry 1). However, the reaction encountered sluggishness when conducted in other solvents such as toluene, DMF, acetonitrile, 1,4-dioxane, and DME, resulting in the formation of $Bu_3SnSnBu_3$ (**5**) as a major side-product (entries 2–6). A counter-cation of bases significantly influenced the reaction outcome: no **4ba** was observed when employing *t*-BuOLi or *t*-BuONa as additives (entries 7 and 8). Moreover, less basic potassium alkoxides (MeOK and EtOK) and

fluoride ion (KF/18-crown-6), previously reported for generating stannyl anion species upon treatment with **1b**,³⁵ proved ineffective as additives (entries 9–11). Remarkably, the yield was substantially improved when *p*-iodotoluene (**3b**) was used instead of **3a**, resulting in a 78% yield of **4ba** while suppressing side-product formation (entries 12 and 13).

Stannylation of various aryl halides

The substrate scope of the stannylation reaction with the *in situ*-generated Bu_3Sn-K proved to be sufficiently broad (Fig. 3): a diverse array of aryl iodides bearing either electron-donating (**3b**, **3c**, **3i**) or -withdrawing groups (**3d–3f**, **3h**) underwent efficient conversion to the respective arylstannanes upon mixing with **1b** and *t*-BuOK, regardless of the electronic nature of the aryl rings (Fig. 3a). Chemoselective substitution occurred at the iodine site of 4-bromoiodobenzene, yielding 4-bromophenylstannane (**4bj**),

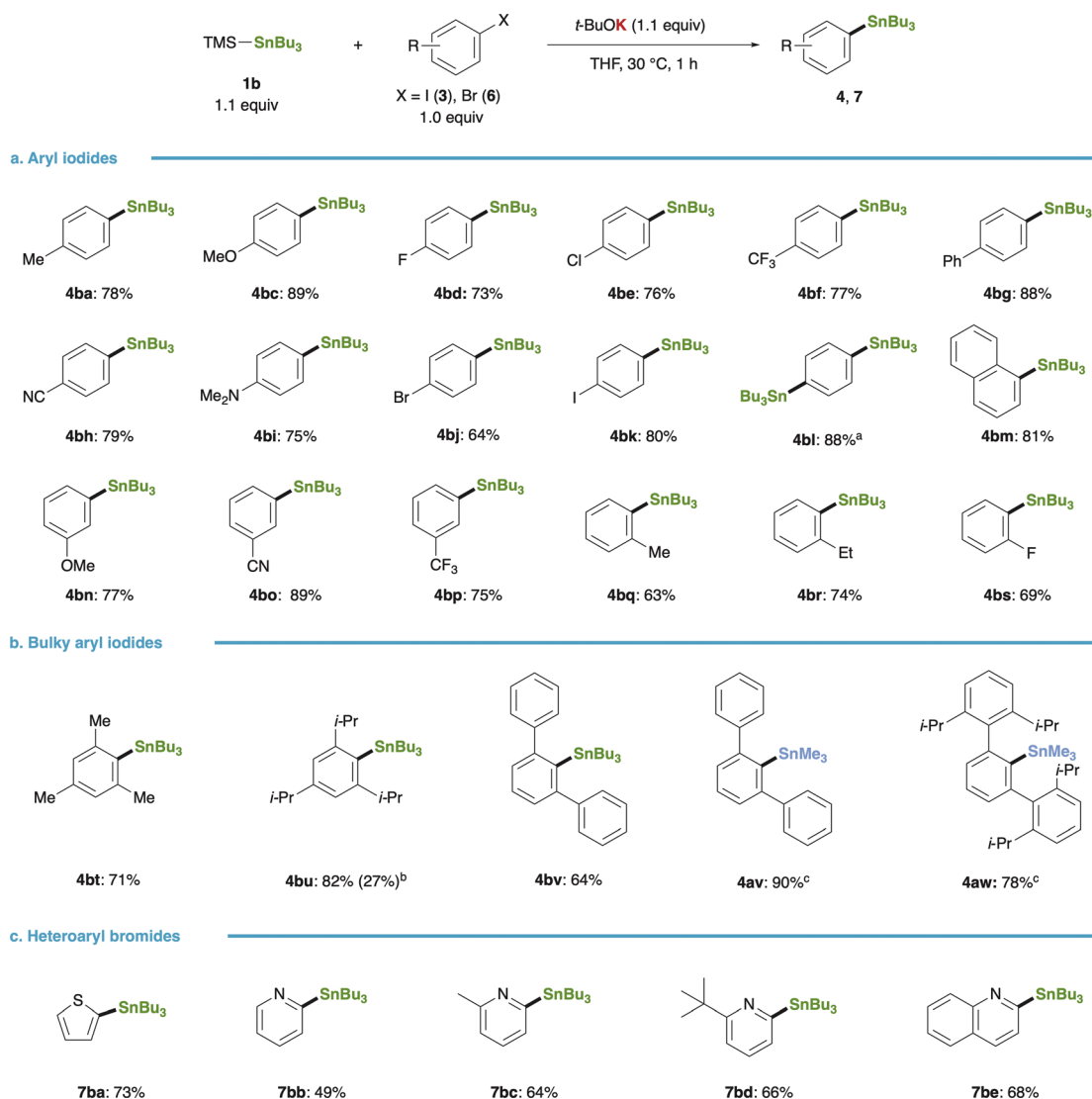


Fig. 3 Substrate scope of stannylation of aryl halides. (a) Stannylation of aryl iodides. (b) Stannylation of bulky aryl iodides. (c) Stannylation of heteroaryl bromides. Reaction conditions: **1b** (0.22 mmol), **3** or **6** (0.20 mmol), *t*-BuOK (0.22 mmol), THF (0.67 mL), 30 °C, 1 h. Isolated yields were given. ^aThe reaction was carried out with 1,4-diiodobenzene (**3k**, 0.20 mmol) using **1b** (0.44 mmol) and *t*-BuOK (0.44 mmol). ^bIsolated yield with Bu_3SnLi under Uchiyama and Wang's conditions was given in parentheses. ^c $PhMe_2Si-SnMe_3$ (**1a**) was used instead of **1b**.



while 4-iodophenylstannane (**4bk**) could be synthesized from 1,4-diiodobenzene; employing a twofold amount of **1b** and *t*-BuOK led to the formation of a distannylated product (**4bl**). The superior reactivity of Sn–K over Sn–Li was evident in reactions involving bulky substrates such as mesityl (**3t**), 2,4,6-triisopropylphenyl (**3u**), and *m*-terphenyl (**3v**) iodides, providing good yields of arylstannanes (**4bt–4bv**, Fig. 3b), whereas the yield of the target product (**4bu**) dropped to 27% with its lithium counterpart. Additionally, the present method facilitated Me₃Sn-installation using PhMe₂Si–SnMe₃ (**1a**), with the yield of **4av** reaching 90%, and even extremely bulky aryl iodide (**3w**) was amenable to transformation into **4aw** (78% yield), highlighting the exceptional nucleophilicity of Sn–K.

Heteroaryl bromides (**6a–6e**) also engaged in the reaction efficiently, affording 2-thienyl- (**7ba**), 2-pyridyl- (**7bb–7bd**), and 2-quinolyl-stannane (**7be**) in yields ranging from 49% to 73% (Fig. 3c).

Mechanistic studies

A plausible pathway for the stannylation, initiated by the generation of R₃Sn–K *via* nucleophilic attack of *t*-BuOK on a silicon center of a silyl stannane, is delineated in Fig. 4a. The co-production of a *tert*-butyl silyl ether (**8**) was confirmed in the stannylation of **3w** (Fig. 4b). Subsequent halogen–metal exchange between the resulting R₃Sn–K and an aryl halide, leading to the formation of an aryl anion, followed by its nucleophilic coupling with R₃Sn–X, yields an

arylstannane.^{13,36,37} The intermediary formation of an aryl anion is supported by treating **6f** with isolated Me₃Sn–K (**2a'**):³⁸ an aryl anion intermediate (**6f'**) undergoes intramolecular cyclization at an ester carbonyl moiety prior to stannylation, resulting in the formation of **9** (Fig. 4c). Although the reaction of 2,4,6-tri-*tert*-butylphenyl bromide (**6g**) fails to yield the corresponding arylstannane, likely due to excessive steric hindrance, the preferential formation of a reduced product, 1,3,5-tri-*tert*-butylbenzene, also strongly implies the generation of an aryl anion intermediate (**10'**) that abstracts a C2 proton of THF.⁶ Notably, conducting the same reaction in THF-*d*₈ indeed results in the formation of deuterated tri-*tert*-butylbenzene (**10**) with a deuterium incorporation ratio of 52% (Fig. 4c), providing further support for the proposed ionic pathway. While an initially formed tin-based by-product would be Bu₃SnBr in the reaction of **6g**, it was rapidly converted into Bu₃SnOt-Bu and Bu₃SnSnBu₃ by reacting with remaining *t*-BuOK or Bu₃Sn–K.³⁹

Fig. 5a presents an alternative pathway for the stannylation involving the formation of an aryl radical intermediate through single-electron transfer, a mechanism reported to be operative in certain stannylation reactions of aryl halides with Sn–Li/Na.^{36,37,40,41} Despite the propensity of the respective aryl radical to undergo rapid cyclization, as evidenced by a high rate constant for ring closure ($k = 7.9 \times 10^9 \text{ s}^{-1}$ at 323 K),⁴² a radical

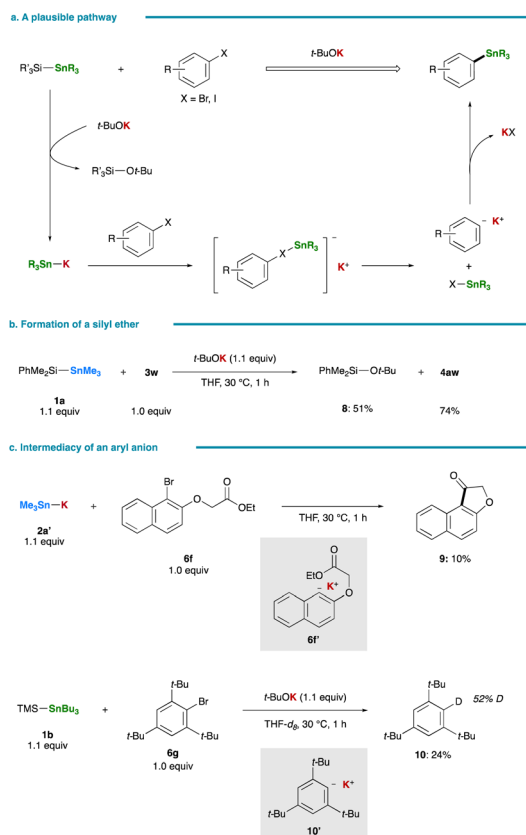


Fig. 4 Mechanistic studies. (a) A plausible pathway. (b) Formation of a silyl ether by-product. (c) Intermediacy of an aryl anion.

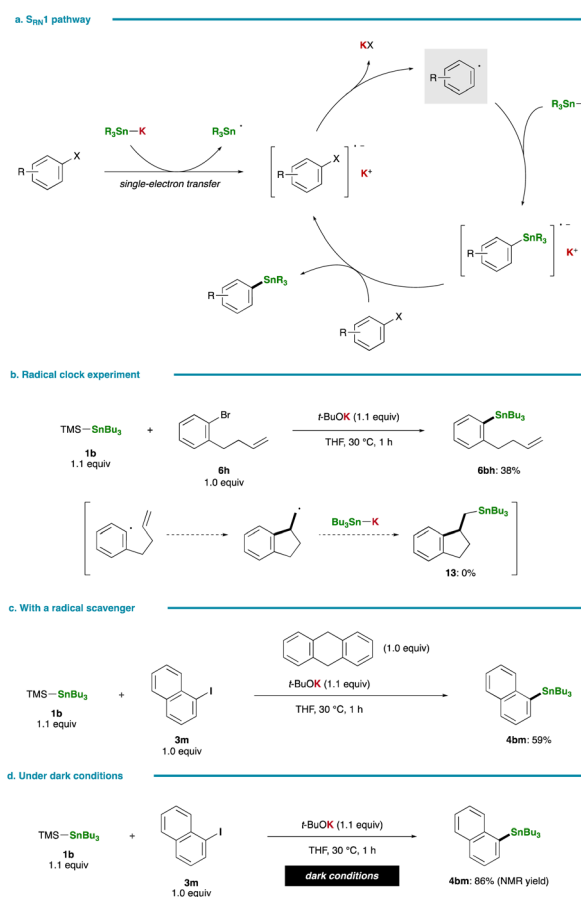


Fig. 5 Control experiments. (a) Stannylation via the SRN1 pathway. (b) Radical clock experiment. (c) Stannylation with a radical scavenger. (d) Stannylation under dark conditions.



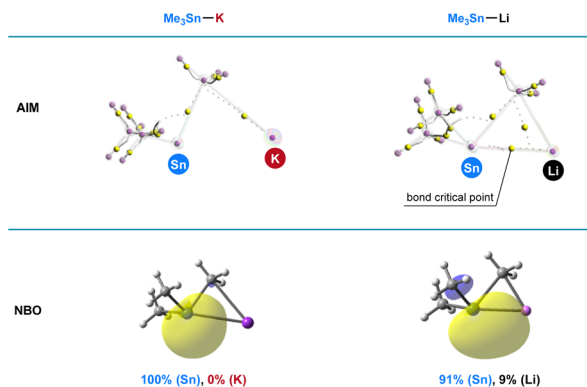


Fig. 6 Computational studies. Population analysis of $\text{Me}_3\text{Sn-K}$ and $\text{Me}_3\text{Sn-Li}$.

clock experiment with 1-bromo-2-(but-3-en-1-yl)benzene (**6h**) yielded the simple substitution product (**6bh**, 38%; **11**, 0%). This observation essentially rules out the possibility of the radical nucleophilic aromatic substitution pathway ($\text{S}_{\text{RN}}1$) in the present stannylation (Fig. 5b). Moreover, this conclusion is reinforced by the smooth stannylation reaction conducted in the presence of a radical scavenger, 9,10-dihydroanthracene (Fig. 5c). In 2021, Nagashima and Uchiyama reported on the generation of a photoexcited triplet stannyl diradical that could serve as a key species in photoinduced stannylation of aryl halides.⁴³ However, our reaction proceeded efficiently even under dark conditions, thereby excluding the involvement of a stannyl diradical species in the present case (Fig. 5d).

Computational studies

To illustrate the superior reactivity of $\text{R}_3\text{Sn-K}$ as stannyl nucleophiles compared with $\text{R}_3\text{Sn-Li}$, population analysis employing the Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) methods was conducted. Optimized structures of $\text{Me}_3\text{Sn-K}$ and $\text{Me}_3\text{Sn-Li}$ were obtained at the $\omega\text{b97xd/6-31+G(d)}/\text{LANL2DZ}$ level, and the bonding interactions between tin and alkali metal were thoroughly evaluated. As depicted in Fig. 6, AIM calculations revealed the absence of a bond critical point between tin and potassium in $\text{Me}_3\text{Sn-K}$, while a bond critical point was observed in the tin-lithium bond, indicating a significantly greater ionic character in the tin-potassium bonding compared with the tin-lithium bonding. NBO analysis further corroborated these findings; the electron distribution between tin and lithium was approximately 91% (Sn) and 9% (Li), indicative of its partially covalent character in the tin-lithium bonding. In contrast, the electron density was fully polarized towards the Sn atom in $\text{Me}_3\text{Sn-K}$. These results unequivocally demonstrate that the heightened reactivity of $\text{R}_3\text{Sn-K}$ observed in the stannylation of aryl halides can be attributed to the increased nucleophilicity arising from the pronounced ionic character in the tin-potassium bonding.

Conclusion

We have developed a straightforward and practical method for preparing $\text{R}_3\text{Sn-K}$ from readily available silylstannanes and *t*-

BuOK, presenting a promising avenue for its extensive utilization in tin-based synthetic transformations. Our methodology facilitated the facile transformation of diverse aryl halides into arylstannanes under mild conditions within 1 hour, simply by combining silylstannanes and *t*-BuOK. Moreover, $\text{R}_3\text{Sn-K}$ exhibited superior reactivity over commonly used $\text{R}_3\text{Sn-Li}$, enabling the smooth stannylation of extremely bulky aryl halides. Detailed mechanistic studies unveiled an ionic pathway underlying the stannylation process, wherein an aryl anion intermediate is generated *via* halogen-metal exchange. Furthermore, the exceptional nucleophilicity of $\text{R}_3\text{Sn-K}$ can be ascribed to the highly ionic character induced by the potassium cation, which was substantiated by population analysis (NBO and AIM) of the Sn-K bond. This study unequivocally underscores the synthetic significance of highly nucleophilic $\text{R}_3\text{Sn-K}$ reagents, which have hitherto been underutilized in synthetic organic chemistry. It presents promising avenues for addressing challenging stannylation reactions that are otherwise difficult to achieve with conventional stannyl anions featuring a light alkali metal cation.

Data availability

The data that support the findings of this study are available in the ESI† of this article.

Author contributions

Y. H.: conceptualization, investigation, writing – original draft, review & editing. T. I.: investigation. K. N.: investigation. H. K.: investigation. M. N.: validation. T. T.: validation. H. Y.: conceptualization, funding acquisition, supervision, writing – original draft, review & editing.

Conflicts of interest

The authors declare no conflict of interest.

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