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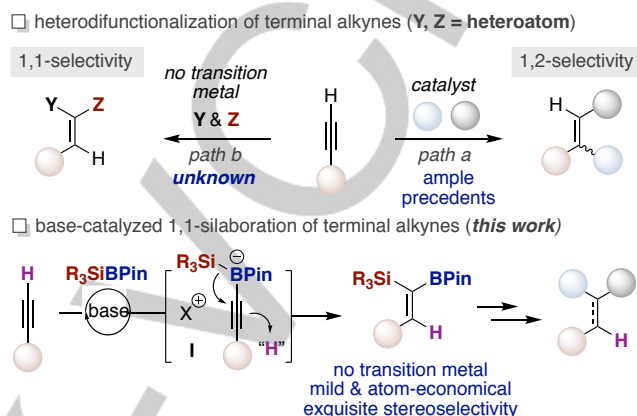
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Stereoselective Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

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Abstract: A base-catalyzed protocol that enables a stereoselective 1,1-silaboration of terminal alkynes is described. This method does not only offer a new strategy to functionalize simple and readily accessible alkynes beyond 1,2-difunctionalization events, but also provides an unconventional atom- and step-economical approach to rapidly and reliably access versatile geminal silylboranes in the absence of transition metals with an exquisite stereoselectivity pattern.

In recent years, the catalytic functionalization of π -systems has gained momentum as a powerful, yet practical, alternative to the use of organic (pseudo)halides for building up molecular complexity.^[1] Among these, particular attention has been devoted to designing *de novo* catalytic routes en route to densely functionalized alkenes via site-selective difunctionalization of alkyne congeners.^[2] Although 1,2-difunctionalizations of alkynes via one or two-electron manifolds have become routine (Scheme 1, *top right*),^[3-5] a related 1,1-difunctionalization event is not as commonly practiced as one might initially anticipate. At present, these techniques remain primarily confined to the use of transition metal catalysts – in most instances requiring sophisticated ligand sets –,^[6] or stoichiometric organometallic reagents.^[7] Despite the advances realized,^[8] a stereoselective catalytic 1,1-heterodifunctionalization blueprint that obviates the need for transition metals while forging two different C–heteroatom bonds still constitutes an elusive cartography in catalytic endeavors (Scheme 1, *top left*).

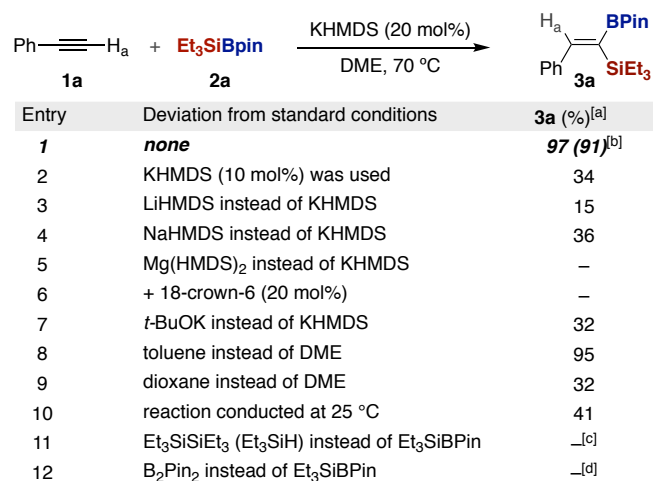


Scheme 1. Base-catalyzed heterodifunctionalization of terminal alkynes.

Driven by the versatility and inherent modularity of organosilicon and organoboron reagents as synthons in organic synthesis,^[9] we recently wondered whether it would be possible to design an atom-economical stereoselective 1,1-silaboration of alkynes in the absence of transition metals or organometallic species. To this end, we hypothesized that a base-catalyzed protocol in the presence of readily available silylborane might be suited for our purposes (Scheme 1, *bottom*). Specifically, we anticipated that in situ generated ate-complexes of type I might enable a stereoselective [1,2]-silyl shift^[10] with concomitant deprotonation of the acetylenic *sp* C–H bond, thus setting the basis for the base catalyst turnover. If successful, such a route would represent, conceptually and practicality aside, a new platform for preparing geminal organometallic linkages bearing two chemically distinct, yet modular, C–B and C–Si bonds. In our continuing interest in silylation and borylation reactions,^[11] we report herein the successful realization of this goal. The salient features of our 1,1-silaboration reaction are the mild conditions, atom-economy and ease of execution, thus representing a bonus from a simplicity and practical standpoint. In addition, we have found an intriguing dichotomy exerted by the solvent on diastereoselectivity, suggesting the intermediacy of both contacted or separated ion pairs. Unlike related 1,1-diborations that typically require either transition metal catalysts or organometallic reagents,^[12] our catalytic 1,1-silaboration event offers a strategic gateway to rapidly and reliably access densely functionalized alkenes in a highly stereocontrolled manner via orthogonal C–Si and C–B cleavage, thus leading to new knowledge in retrosynthetic design.

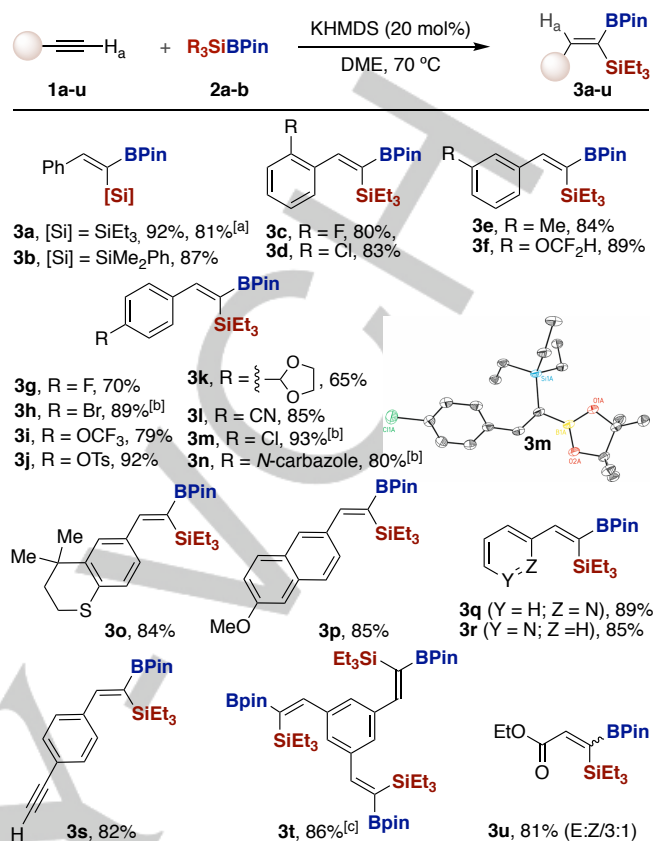
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Scheme 2. Optimization of the reaction conditions. **1a** (0.40 mmol), **2a** (0.4 mmol), KHMDS (0.08 mmol, 20 mol%) in DME (2 mL) at 70 °C for 12 h. ^[a] Yields determined by GC using decane as internal standard. ^[b] Isolated yield, average of two independent runs. ^[c] no traces of hydro(di)silylation were found. ^[d] no traces of hydro(di)boration were found. DME = 1,2-dimethoxyethane; BPin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl. HMDS = hexamethyldisilazide.

We began our investigations by studying the 1,1-silaboration of phenylacetylene (**1a**) with Et₃SiBPin (**2a**) en route to **3a** (Scheme 2). The choice of **2a** instead of commonly employed PhMe₂SiBPin (**2b**) was not arbitrary.^[13] From a synthetic standpoint, the use of **2a** offers the advantage of selectively functionalizing the vinyl–Si bond in **3a** at later stages, thus avoiding unnecessary site-selectivity issues arising from the presence of multiple *sp*² C–Si bonds in **3b**.^[14] After systematic evaluation of all reaction parameters,^[15] we found that a protocol based on KHMDS (20 mol%) in DME at 70 °C provided the best results, affording **3a** in 91% isolated yield as a single diastereoisomer (entry 1).^[16] This transformation merits some further discussion: 1) no transition metal complex is required; 2) the reaction is conducted with a **1a**:**2a** ratio of 1:1 and catalytic amounts of KHMDS, thus offering a unique atom- and step-economical route to **3a**; 3) two different, yet chemically distinguishable, organometallic bonds can be forged from available alkynes with exquisite control of the stereoselectivity. Intriguingly, the escorting cation exerted a profound influence on the reaction outcome, as the corresponding Li, Na or Mg analogues provided lower yields of **3a**, if any (entries 2–5). The key role of potassium counterions was further corroborated by observing no conversion of **1a** to **3a** in the presence of 18-crown-6 (entry 6) whereas lower yields were found when KO^{*t*}Bu was used (entry 7). Likewise, the nature of the counteranion and the solvent employed was equally important (entry 8 and 9). The importance of boron–interelement reagents was illustrated by the lack of reactivity found when employing either Et₃SiH,^[17] (Et₃Si)₂ or B₂Pin₂, respectively (entry 11 and 12).

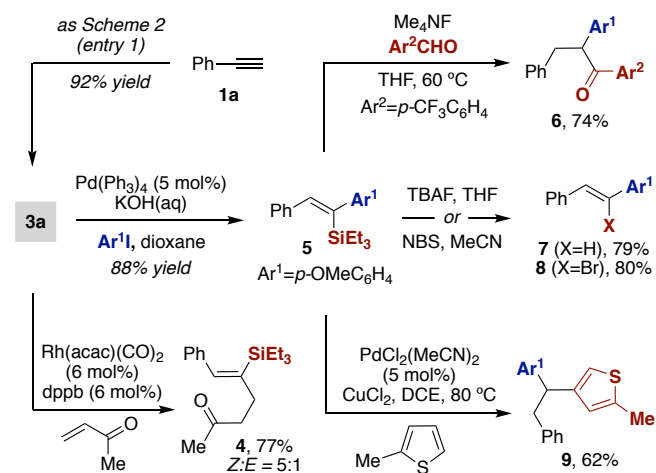


Scheme 3. Scope of terminal alkyne. Reaction conditions: As scheme 2, entry 1; Yield of Isolated product, average of at least two independent runs. ^[a] 10 mmol scale. ^[b] T = rt. ^[c] **2a** (3.5 equiv).

With a reliable set of conditions in hand, we focused our attention on studying the generality of our diastereoselective 1,1-silaboration of terminal alkynes catalyzed by KHMDS (Scheme 3). As evident from the results compiled in Scheme 3, the 1,1-silaboration turned out to be widely applicable for a wide range of arene substituents at the alkyne terminus. Moreover, **3b** was within reach in an otherwise identical yield to that shown for **3a**. Notably, the presence of nitriles (**3l**), carbazoles (**3n**) or esters (**3u**) could all be well-accommodated. Interestingly, aryl halides (**3c**, **3d**, **3g**, **3h** and **3m**),^[18] sulfonates (**3j**), ethers (**3f**, **3i**, **3k** and **3p**) or sulfides (**3o**) – all common counterparts in the cross-coupling arena –^[19] did not interfere with our targeted 1,1-silaboration, hence opening up an orthogonal gateway for further derivatization via conventional transition metal-catalyzed reactions. Particularly noteworthy was the observation that the 1,1-silaboration of **1a** could be executed on a gram scale, delivering **3a** in 81% yield without noticeable erosion in yield or diastereoselectivity. Equally relevant was the observation that the reaction could also be executed with nitrogen-containing heterocycles (**3q**, **3r**). The ability to obtain **3q** and **3r** as single products is particularly noteworthy if one takes into consideration the known proclivity of silylboranes to enable C2- or C4-silylation of electron-poor azines under basic conditions via nucleophilic aromatic substitution (S_NAr) pathways.^[11a] The successful preparation of **3s** and **3t** highlights another favorable feature of

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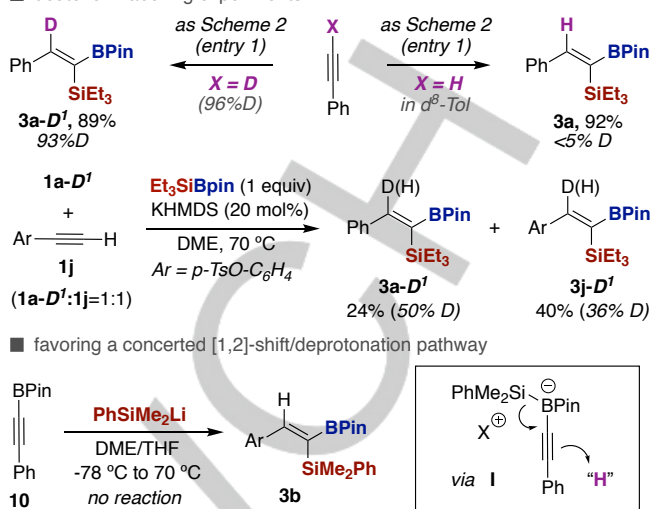
our 1,1-silaboration technique. In particular, substrates bearing more than one terminal alkyne can either be selectively (**3s**) or exhaustively coupled with silylborane (**3t**) by carefully adjusting the stoichiometry of the reaction. As shown for **3u**, the reaction can be applied to non-aromatic acetylenes. Note, however, that **3u** was obtained as *E/Z* mixtures, suggesting that allene-type intermediates might come into play in certain cases (see below).



Scheme 4. Synthetic Applicability.

The stereoselective synthesis of densely functionalized olefins – fundamental motifs in pharmaceuticals, material sciences and liquid crystals –,^[20] continues to pose a challenge in preparative organic chemistry.^[21] Driven by this observation, we wondered whether our 1,1-silaboration platform could be used for such purpose by selectively functionalizing two distinguishable organometallic C–Si and C–B bonds at later stages.^[22] As shown in Scheme 4, this was indeed the case. Specifically, **4** and **5** could easily be obtained from **3a** by selective C(*sp*²)–C(*sp*²) or C(*sp*²)–C(*sp*³) bond-forming reactions via either Pd-catalyzed Suzuki–Miyaura coupling with an aryl iodide^[23] or Rh-catalyzed 1,4-addition with α,β -unsaturated ketones.^[24] The versatility of the triethylsilyl group as a masked nucleophile is evident by the results compiled in Scheme 4 (*right pathways*). Indeed, proto- or bromodesilylation could easily be accomplished from **5** with TBAF (**7**) or NBS (**8**) whereas *sp*³–*sp*³ bonds can easily be forged in the presence of Me₄NF and an appropriate aldehyde counterpart (**6**).^[7a] The formal conversion of phenyl acetylene (**1a**) into **9** via the intermediacy of **5** is particularly noteworthy, allowing to incorporate three different aryl groups via β -selective C–H functionalization with Pd catalysts and Cu(II) as oxidant.^[25] Taken together, the results shown in Scheme 4 stand as a testament to the prospective impact of our base-catalyzed 1,1-silaboration of terminal alkynes.

■ deuterium labelling experiments



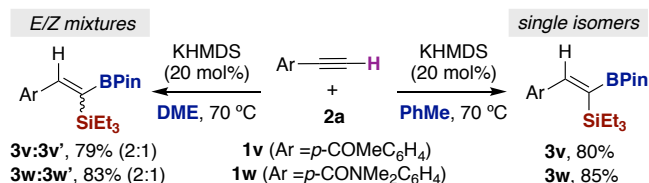
Scheme 5. Deuterium labelling experiments.

Next, we turned our attention to unravelling the mechanistic intricacies of our 1,1-silaboration event via deuterium-labelling experiments (Scheme 5, *top*). As shown, reliable deuterium transfer en route to **3a-D**¹ was only observed if **1a-D**¹ was used as substrate (*top left*), arguing against radical-type scenarios via hydrogen atom transfer (HAT) with solvents possessing weak C–H bonds such as toluene (*top right*).^[26] Notably, a deuterium-labelling crossover experiment with **1a-D**¹ and **1j** revealed a non-negligible H/D scrambling in the 1,1-silaboration products **3a** and **3j**. These experiments suggested that our 1,1-difunctionalization might operate via initial deprotonation of the acetylenic *sp* C–H bond (pK_a (PhC≡C–H) = 23) by KHMDS (pK_a = 27) followed by addition to Et₃SiBPin. The resulting silylboronate species (**1**, Scheme 1) might evolve via a concerted pathway consisting of a [1,2]-shift^[27] followed by a downhill protonolysis of an in situ generated vinyl organometallic reagent ($pK_a \approx 40$ –45) with the acetylenic *sp* C–H bond, thus turning over the key potassium acetylide species.^[28,30] This notion could be corroborated by the lack of reactivity found when exposing **10** to PhSiMe₂Li (*bottom*). While our available data suggested a stereoselective [1,2]-shift of in situ generated **I** en route to *Z*-configured 1,1-silylborated alkenes (**3a–3u**, Scheme 3), care should be taken when generalizing this. Indeed, we found an intriguing dichotomy exerted by both the substituents on the arene and the solvent utilized (Scheme 6). Specifically, a significant erosion in stereoselectivity was found upon exposing **1v** or **1w** to **2a** in DME (*top left*), whereas *Z*-configured **3v** and **3w** were exclusively obtained under a toluene regime (*top right*). The former result can tentatively be interpreted on the basis of the strong coordination of DME to the escorting potassium counterion,^[31] thus generating a separated silylboronated ion pair that precedes the formation of allene-type intermediates via [1,2]-shift from **I**.^{[8], [32]} This notion was corroborated by the formal defluorosilylation of **1x** observed under our optimized reaction conditions (Scheme 6, *bottom*) as well as by the *E/Z* mixtures obtained for **3u** (Scheme 3). In toluene as solvent, however, a contacted ion pair is more likely, thus

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attenuating the reactivity of **1** while forming the targeted **3v-3w** in a highly stereoselective fashion.

■ solvent-dependent stereoselectivity pattern



■ involvement of allene-type intermediates



Scheme 6. Solvent-dependent selectivity and intermediacy of allene species.

In summary, we have documented an unconventional atom-economical 1,1-silaboration of terminal alkynes enabled by catalytic amounts of KHMDS. This protocol is characterized by its excellent stereoselectivity pattern, constituting a complementary approach to existing methods en route to geminal organometallic reagents that typically require transition metal complexes and a new gateway to rapidly and reliably convert simple alkynes into stereodefined trisubstituted alkenes via orthogonal C–Si and C–B bond-cleavage. Further extensions to other related processes are currently underway in our laboratories.

Acknowledgements

We thank ICIQ and FEDER/MICIU – AEI/PGC2018-096839-B-100 for financial support. Y. G. and Y. S. thank Severo and China Scholarship Council (CSC) for predoctoral fellowships.

Keywords: alkyne • 1,1-difunctionalization • silaboration • atom-economy

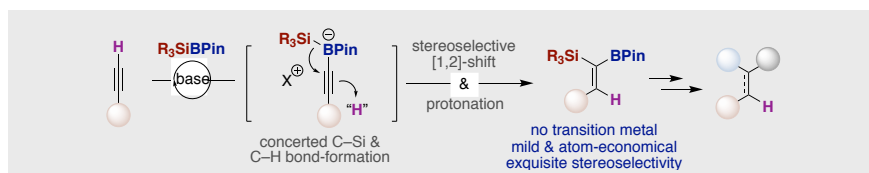
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Layout 1:

COMMUNICATION



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Ruben Martin*

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**Stereoselective Base-Catalyzed 1,1-
Silaboration of Terminal Alkynes**

A base-catalyzed protocol that enables an atom-economical 1,1-silaboration of terminal alkyne is described. This protocol is distinguished by its mild conditions and exquisite stereoselectivity pattern, offering a complementary approach to conventional 1,2- or 1,1-difunctionalization techniques that typically require transition metal complexes or stoichiometric organometallics, and an opportunity to build up molecular complexity by subsequent orthogonal C-Si and C-B cleavage.