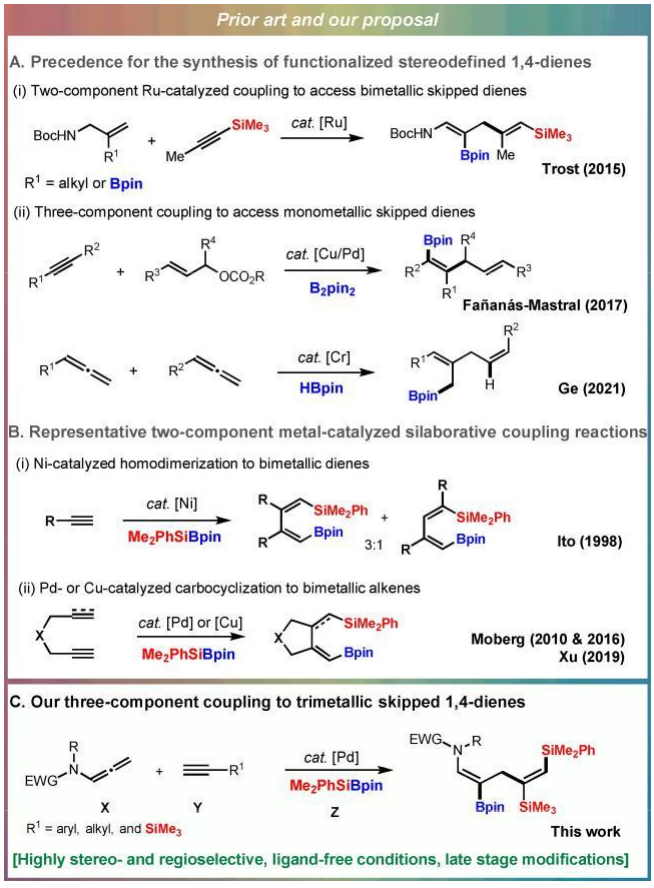
Silaborative Assembly of Allenamides and Alkynes: Highly Regio- and Stereocontrolled Access to Bi- or Trimetallic Skipped Dienes

Tapas R. Pradhan[+], Mukti Paudel[+], Taisiia Feoktistova, Paul Ha-Yeon Cheong, and Jin Kyoon Park**

Abstract: A highly stereo- and regiocontrolled multi-component approach to skipped 1,4-dienes decorated with one boryl and two silyl functionalities is described. This Pd-catalyzed atom-economical union of allena-mides, alkynes, and $Me_2PhSiBpin$ (or $Et_3SiBpin$) pro-ceeds without the use of phosphine ligands, instead relying on chelation through the internal amide group of the allenamide sulfonyl. A variety of alkynes, including those derived from complex bioactive molecules, can be efficiently coupled with allenamides and $Me_2PhSiBpin$ in good yields and with excellent selectivity. The synthetic potential was demonstrated through multiple valuable chemoselective transformations, establishing new disconnections for functionalized dienes. Density functional theory calculations revealed that the reaction first proceeded through borylation of the allenamide, followed by silylation of the alkyne and then reductive elimination, which convergently assemble the skipped 1,4-diene.

Introduction

The assembly of electronically distinct C C π-systems through catalytic functionalization is a widely deployed strategy for constructing valuable carbon synthons.[1] One of the hallmarks of organic synthesis is the development of facile and selective transformations that grant access to structural motifs that could have wide-ranging applications.[2] For instance, vinyl-boryl and -silyl structural units[3,4] are known to be excellent precursors for a wide variety of textbook reactions such as the Suzuki–Miyaura reaction,[5] Tamao–Fleming oxidation,[6] and Hiyama reaction.[7] As multi-substituted skipped 1,4-dienes are ubiquitous in natural products[8] and have high synthetic potential,[9] a modular atom- and step-economical synthetic approach to these compounds would have a significant impact. Numerous synthetic methods such as hydroallylation of alkynes,[10] hydroalkenylation of 1,3-dienes,[11] and cou-pling of vinyl metallic reagents with different allylic electrophiles[12] have reached impressive levels of sophisti-cation, and are powerful strategies for preparing skipped 1,4-dienes. However, the incorporation of metallic reagents in these processes to facilitate further functionalization is rare (Scheme 1A).[13] Trost et al. reported a pioneering work on Ru-catalyzed two-component alkene-alkyne coupling in 2015 (Scheme 1A(i)).[13c] They subsequently reported the successful installation of two metallic groups in 2020, integrating prefunctionalized π-systems.[13d] In terms of three-component coupling, Fañanás-Mastral et al. discov-



Scheme 1. Precedence and our approach to skipped dienes.

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ered a copper/palladium catalytic system for combining allyl carbonates and alkynes with B_2Pin_2 to synthesize 1,4-dienes that feature a single boryl group (Scheme 1A(ii)).[13e] Last year, Ge and Zhao reported an elegant catalytic method to access borylated (*E*,*Z*)-1,4-dienes[13g] through a chromium(I) hydride intermediate.

Although selective three-component reactions are feasible for the synthesis of skipped dienes, they are restricted to the use of a single boryl group, leaving room to expand the boundaries for the synthesis of 1,4-dienes bearing multiple organometallic linkages. However, analogous coupling strategies for this that employ unsymmetrical metallic reagents (e.g., [Si] [B]) and two types of electronically different C C π-systems remain elusive.[14] Since Ito reported the Ni-catalyzed silaborative homodimerization of alkynes (albeit in poor regisoselectivity),[15] only intramolecular attempts employing tethered enyne substrates have been reported (Scheme 1B).[16] Thus, the development of *an intermolecular cross-coupling* to densely functionalized skipped dienes with multiple functionalizable metallic groups is highly desirable.

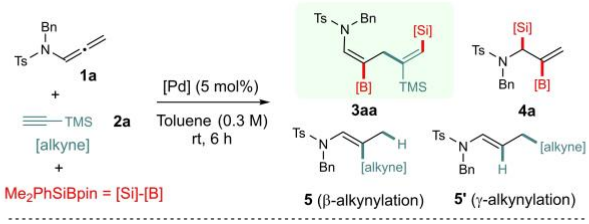
Realization of this process is a formidable challenge because of 1) chemoselectivity issues due to unselective interception of silylboranes by either an allene[17] or alkyne;[16a, 18] 2) the regioselectivity of the allene-alkyne coupling[19] (e.g., **5** or **5'**, Table 1) through hydroalkynylation;[19b] 3) the chemoselectivity of the allenamide, which can react through, for example, a hydroalkynylation/silaboration[20] or silaboration/alkyne coupling[16,17e] pathway (Scheme S1); and 4) regioselectivity issues due to ligands[18d] or additives.[17c]

During the past few years, our group has been engaged in stereo- and regioselective functionalization through selective interception of intermediates in allenamide chemistry.[19b,21] Herein, we report the discovery, scope, synthetic versatility, and computational mechanistic studies of a highly selective multicomponent reaction that grants access to 1,4-dienes bearing chemically distinct C [B] and C [Si] bonds (Scheme 1C).

Results and Discussion

In our continued efforts to extend the opportunities provided by sulfonyl-assisted allene functionalization to synthetically important unsaturated compounds, we exam-ined the feasibility of catalytic multicomponent reactions of an allenamide (**1 a**) and an alkyne (**2 a**) with dimethylphenylsilyl boronic acid pinacol ester ($Me_2PhSiBpin$) (Table 1). Preliminary investigations started with our previously reported regiodivergent alkynylation conditions[19b] featuring (*o*-OMePh)$_3$P, Brettphos, and Da-

Table 1: Representative reaction results from screening.[a,b]



Entry[a]	[Pd]/ligand[b]	Conv of **1a** [%][c]	Yield of **3aa**, **4a**, **5**, and **5'** **[%]**[c]
1	$Pd(OAc)_2$/(*o*-OMePh)$_3$P[d]	100	0:0:94:0
2	$Pd(OAc)_2$/Brettphos[d]	100	0:0:6:79
3	$Pd(OAc)_2$/Davephos	100	0:0:21:59
4	$Pd_2(dba)_3$/Davephos	44	0:10:0:0
5	$Pd_2(dba)_3$/(*p*-CF_3Ph)$_3$P	100	0:87:0:0
6	$Pd(OAc)_2$/–	100	67:10:0:0
7	$PdCl_2$/–	100	29:10:0:0
8	**$Pd_2(dba)_3$**/–	**100**	**78** : < **5** : **0** : **0 [71]**[e]
9	$Pd(dba)_2$/–	100	57:16:0:0
10	Cp(allyl)Pd/–	100	56:9:0:0
11	Cp(cinnamyl)Pd/–	100	38:11:0:0
12	(PivOH as acid additive)	100	37:14:0:0
13	(K_2CO_3 as base additive)	100	57[f] :10:0 :0
14	(other parameters)[g]	65	41[h] :12:0:0
15	[Si] [B] = Et_3SiBpin	100	75: 7:0:0 [70][e,i]

[a] Unless otherwise noted, all reactions were performed using **1 a** (0.1 mmol), **2a** (0.3 mmol), and $Me_2PhSiBpin$ (0.12 mmol) at rt. [b] For details of employed conditions, see Supporting Information. [c] % conversion of **1a** and % yield of the formed compounds were determined from the crude ^{1}H NMR results using CH_2Br_2 as an internal standard. [d] Our previous regioselective alkynylation conditions for allenamides. [e] Isolated yield. [f] Highest % yield under the conditions is given; for details, refer to the Supporting Information. [g] Effects of solvent and temperature were studied. [h] Toluene at 0 °C. [i] Yield of **3aa**' under the condition of entry 8 (an analogue of **3aa** with [Si] = Et_3Si). Ts = 4-toluenesulfonyl. Bn = benzyl. TMS = trimethylsilyl. Davephos = 2-dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl. TDMPP = tris(2,6-dimethoxyphenyl)phosphine. Cp = cyclopentadienyl.

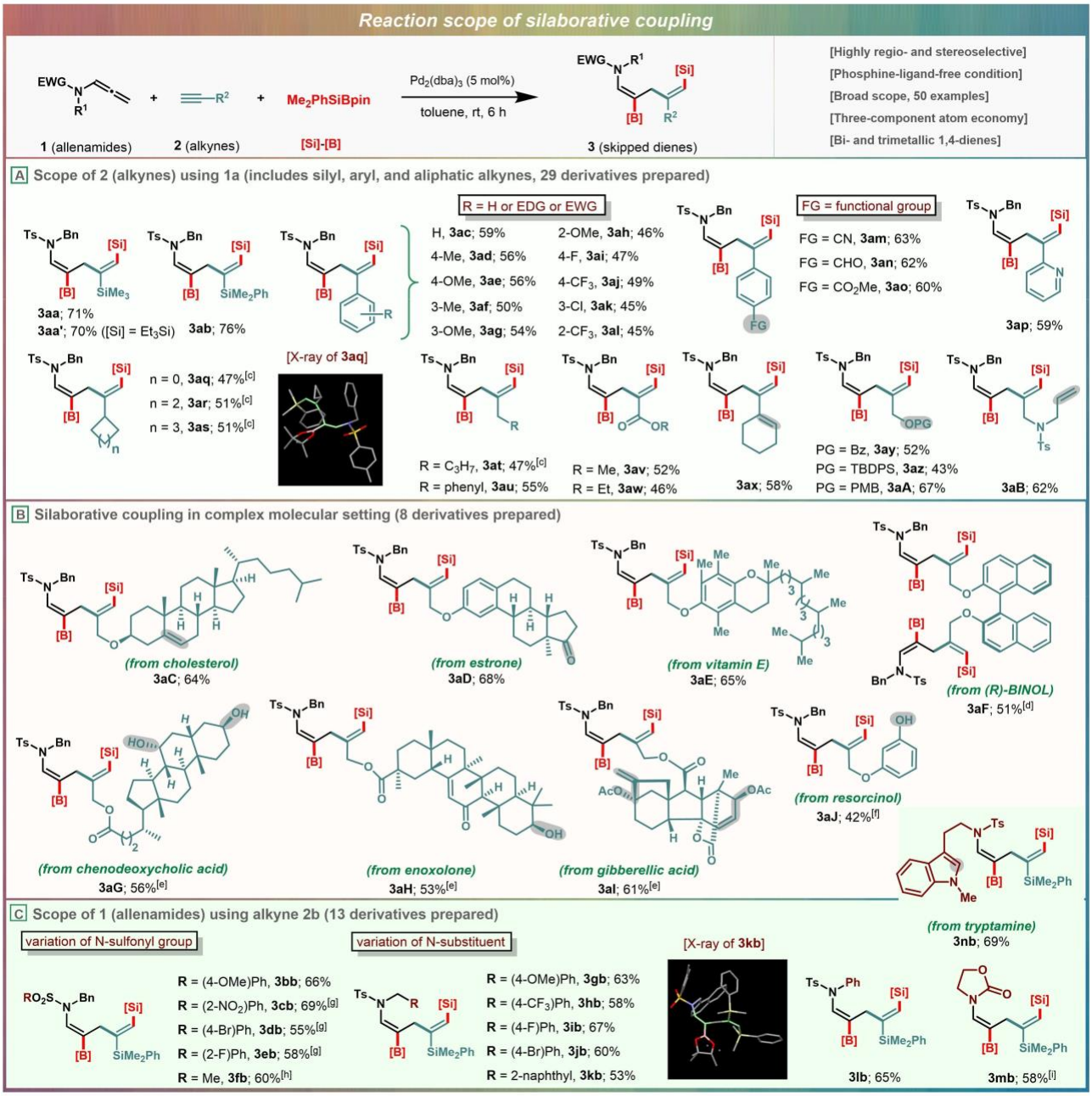
vephos in the presence of $Pd(OAc)_2$; unfortunately, desired product **3 aa** was not detected. Instead, alkynylation products identical to those in the previous study were obtained (entries 1–3). When $Pd(OAc)_2$ was replaced with tris-(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), two-component silaboration product **4 a** was formed exclusively. Electron-deficient ligand (p-$CF_3Ph)_3P$ led to a better yield (87 %) of **4 a** than did electron-rich Davephos (entry 4 versus 5). Surmising that phosphines are responsible for the fast reductive elimination of the Si Pd B intermediate, we omitted the phosphine ligand. To our excitement, we were able to find suitable optimum conditions by carefully screening various palladium catalysts without phosphine ligands (entries 6–9 show representative cases, see Support-ing Information for more details). Notably, Pd^0 precursors such as Cp(allyl)Pd or Cp(cinnamyl)Pd both led to the full conversion of **1 a**, albeit in lower yields compared with ligand dba (entries 10 and 11), indicating Pd^0 is the active catalyst. It is worth noting that the goal for the proposed transformation was an efficient catalytic system that does not require any precious phosphine ligands at room temperature. Target **3 aa** was furnished in the highest yield under standard conditions comprising 5 mol% of $Pd_2(dba)_3$ with a 1 : 3: 1.2 mixture of **1 a**, **2 a**, and $Me_2PhSiBpin$ in toluene (0.3 M) (entry 8). Product **3 aa** was isolated in a synthetically acceptable yield (71 %); the stereo- and regiochemistry were unambiguously confirmed to be *Z*,*E* and 1-silyl-4-boryl, respectively, based on the spectral data of similar compounds **3 aq** and **3 kb**, for which X-ray crystal structures were obtained (see Supporting Information). Another noteworthy advantage is that the present challeng-ing three-component silaborative coupling proceeds in the absence of any additives, either acidic or basic (entries 12 and 13). We also screened other parameters; however, all attempts to reduce the yield of allenamide silaboration product **4 a** below 5 % were futile (entry 14). As antici-pated, this silaborative coupling employing other silyl variant (Et_3Si instead of Me_2PhSi) was equally efficient to provide **3 aa**' under the identical condition as entry 8 (entry 15).

After optimizing the conditions (entry 8, Table 1), we inspected the generality of the present silaborative coupling with a variety of alkynes **2** and allenamides **1** with $Me_2PhSiBpin$ (Table 2). Twenty-nine examples of skipped dienes **3** were synthesized from alkynes **2**, which included silylated, aryl, and aliphatic alkynes, with identical regio-and stereoselectivities (Table 2A). Notably, bulkier silylated alkyne **2b** furnished corresponding coupling product **3ab** in a slightly higher yield (5% higher). No significant yield differences were observed for most of the aryl alkynes, irrespective of the electronic nature (electron-rich or electron-poor) and position of the substituents on the aryl rings; the corresponding products (**3ac**–**l**) were isolated in yields of up to 59%. Pleasingly, the reaction conditions are compat-ible with modifiable functionalities such as nitriles, alde-hydes, and esters, further increasing the diversity of the coupling products (**3am**–**ao**). To our delight, heteroaryl alkynes were also compatible, as **3ap** was obtained in 59% yield. Likewise, various aliphatic alkynes, from cyclic alkynes of various ring sizes (n = 3, 5, and 6) to acyclic alkynes, were competent partners, smoothly affording the desired products (**3aq**–**au**). A crystal of product **3aq** was suitable for X-ray analysis,[22] which unambiguously confirmed the stereo- and regiochemistry, and the structures of the other products were determined based on analogy to product **3aq**. Most significantly, the site selectivity was not altered even for electron-deficient alkynes; both methyl and ethyl alkynoates were suitable candidates for the present transformation, allowing the synthesis of highly modifiable carbon skeletons (**3av** and **3aw**). A 1,3-enyne was also found to be a competent substrate, affording a valuable extended olefinic system, triene **3ax**, in 58% yield. The compatibility of labile O-COR (Bz), O-silyl (TBDPS), and O-*p*-methoxybenzyl (PMB) protecting groups will add further value to the present developed method, as **3ay**, **3az**, and **3aA** were synthesized as the sole products. 1,6-Enyne **2B** undergoes our intermolecular silaborative assembly over a more favorable silaborative carbocyclization process,[16a,b,18] affording **3aB** and leaving the terminal olefin intact, illustrating the orthogonality of this ligand-free protocol. Note that the direct use of propargyl amine is ineffective for the present silaborative coupling, presumably due to catalyst inactivation by labile nitrogen-lone pair (see details in Supporting Information, Table S2).

To further demonstrate the functional group compatibility of this coupling, we explored several additional examples in complex molecular settings (Table 2B). *O*-Propargyl derivatives of chiral complex bioactive molecules such as cholesterol, estrone, and vitamin E were successfully coupled under these mild conditions in good yields and with excellent selectivity (**3aC**–**aE**). Double silaborative couplings are also feasible, as two dienamide arms were installed on the chiral (*R*)-BINOL ligand (**3aF**). In addition to *O*-propargyl ethers, propiolates derived from chenodeoxy-cholic acid, enoxolone, and gibberellic acid, possessing both competing and modifiable functional group footprints, provided their corresponding skipped dienes (**3aG**–**aI**) in acceptable yields. Internal and terminal olefins, hydroxyl groups, ketones, esters, and lactones in these complex molecules were also tolerated. Notably, allyl acetates, well known to be easily reactive in palladium chemistry, are also tolerated under the reaction conditions (**3aI**), illustrating the selectivity of the Pd^0 catalyst toward allenamides and $Me_2PhSiBpin$ in the presence of an alkyne. Additional challenging substrate includes alkyne derived from resorci-nol (mainly used in the treatment of acne vulgaris as a peeling agent)[23] with a nucleophilic phenolic OH group that furnished the desired product **3aJ**, albeit in longer reaction time (24 h).

Finally, the applicability of this three-component protocol was examined for allenamides bearing different chelating groups on the N atom using **2b** as the alkyne coupling partner (Table 2C). Substrates with several different sulfonyl-based directing groups, including aryl and alkyl sulfonamides, participated in this reaction with slight variations in the standard conditions (**3bb**–**fb**). While the same conditions are applicable to substrates with electron-donating substituents (OMe), those with electron-with-

Table 2: Substrate scope with respect to alkynes (**2**) and allenamides (**1**).[a,b]



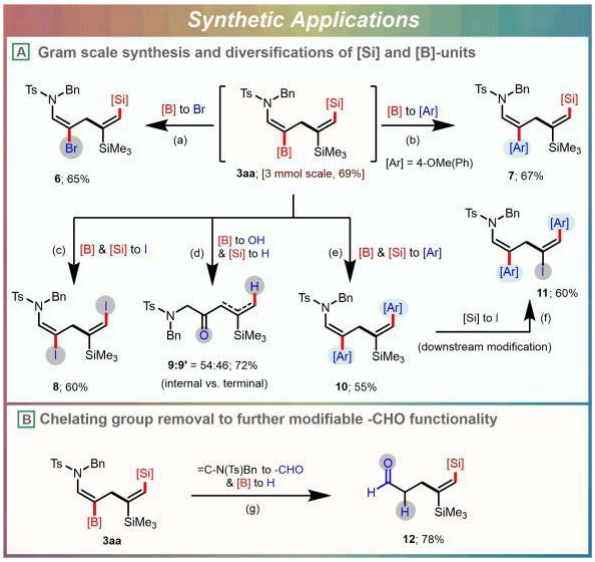
[a] Unless otherwise noted, all reactions were carried out using 0.2 mmol of **1**, 0.6 mmol of **2**, and 0.24 mmol of $Me_2PhSiBpin$ under the standard conditions. [b] Isolated yield of **3**. [c] The desired coupling product and **4 a** were obtained as a 6 :1 mixture (see Supporting Information). [d] 0.1 mmol of bis-alkyne **2F** was used for smooth purification. [e] 0.2 mmol of alkyne was used for smooth purification. [f] Based on 34% recovery of **1a** after 24 h. [g] The reaction was carried out at 40 °C for 8 h. [h] Full conversion after 3 h. [i] 27% of **4 m** was formed.

drawing substituents (2-NO_2, 4-Br, and 2-F) required a temperature of 40 °C for full conversion after 8 h. The electronic nature of the benzyl group could also be varied; products **3gb–jb** were formed under identical conditions without reduced selectivity. Allenamides with polyaryl substituents and aryl rings directly attached to the N atom were also suitable coupling partners (**3kb** and **3 lb**). The stereochemical configurations of the products obtained from the allenamide scope study were found to be the same based on the X-ray crystal structure of **3kb**.[22] In addition, an oxazolidinone ring was amenable to this protocol, acting as a chelating group to provide analogous silaborated 1,4-diene **3mb** (58% yield), albeit with 27% yield of the two-component silaboration adduct. An indolamine metabolite, tryptamine, was also incorporated into an allenamide partner without obstructing this mild silaborative coupling.

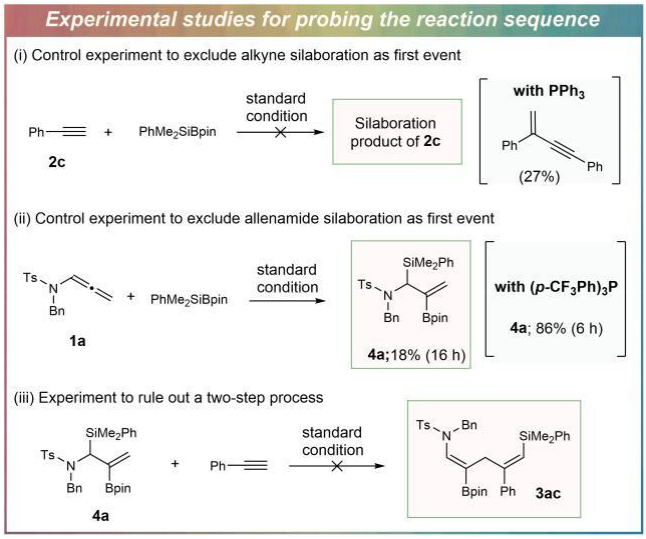
Attempts to further expand the scope toward other allene derivatives without N-sulfonyl or oxazolidinone groups, and internal allenamides were futile, suggesting that suitable chelation and steric factor around allene skeleton are key (details can be found in the Supporting Information, Table S1). Another limitation is that internal alkynes, including electronically tuned alkynes, were ineffective substrates, probably owing to steric congestion (see Ta-ble S2).

The versatility of this silaborative assembly also makes it a gateway to a wide variety of synthetic building blocks (Scheme 2). Because of the difference in reactivity of C [B] and C [Si] bonds, we decided to explore the synthetic applicability through the selective functionalization of trimetallic diene **3aa** (Scheme 2A). Employing the optimal conditions, even using 2.0 equiv of **2a**, 1.364 g of **3aa** was synthesized with identical selectivity, but in a slightly lower yield (69%). First, selective monofunctionalizations of the C [B] bond enabled controlled transformations to C Br (**6**) and C [Ar] (**7**) bonds, allowing further modification of the remaining C heteroatom bonds. Because of the diversity of vinyl iodides in cross-coupling reactions, we sought to modify both the C [B] and C [Si] bonds; the use of a simple electrophilic reagent (*N*-iodosuccinimide, NIS) rapidly led to monosilylated diiodo compound **8**. The conventional boryl oxidation method enabled simultaneous C O bond incorporation and protodesilylation to produce a mixture of inseparable skipped and conjugated β-silylenone **9** and **9**' in 72% yield. Note that the internal C [Si] bonds in all of these transformations remained intact, demonstrating the streamlining ability of **3aa**. Following double arylation of the boryl and terminal silyl units, the internal C [Si] bond of **10** was primed for use in downstream functionalization for installation of a C I bond, setting the stage for further modifications through **11**. Furthermore, chelating group removal could be achieved with the aid of single electron transfer reductant (Mg/MeOH) that resulted in the formation of aldehyde, especially a powerful intermediate for structural elaboration, via protodeboronation/enamine hydrolysis (Scheme 2B).

Our mechanistic hypotheses for this reaction are supported by control experiments, by-product isolation and re-subjection, and density functional theory (DFT) analysis. To probe the reaction sequence for the present phosphine-ligand-free three-component coupling, we first performed control experiments without the allenamide (**1a**) or alkyne (**2c**). At the outset, we considered three potential compet-itive mechanisms (Scheme 3): i) Pd-catalyzed alkyne silabo-ration followed by allenamide coordination, ii) allenamide silaboration followed by alkyne coordination, and iii) a two-step process. Under the standard reaction conditions, alkyne silaboration was not observed. However, with a phosphine ligand, the alkyne dimerization product was formed in 27% yield, ruling out alkyne silaboration as the first step. Allenamide silaboration proceeded, albeit sluggishly (18%). Surprisingly, the product formed significantly faster with the phosphine ligand (86% versus 18%). This suggests that the ligand disfavors tandem reaction with the alkyne; the presence of the phosphine ligand accelerates the reductive elimination process to give undesired silaborated allenamide **4a**. This is one of the reasons bismetallative intermolecular multicomponent processes have not yet been found. Anoth-

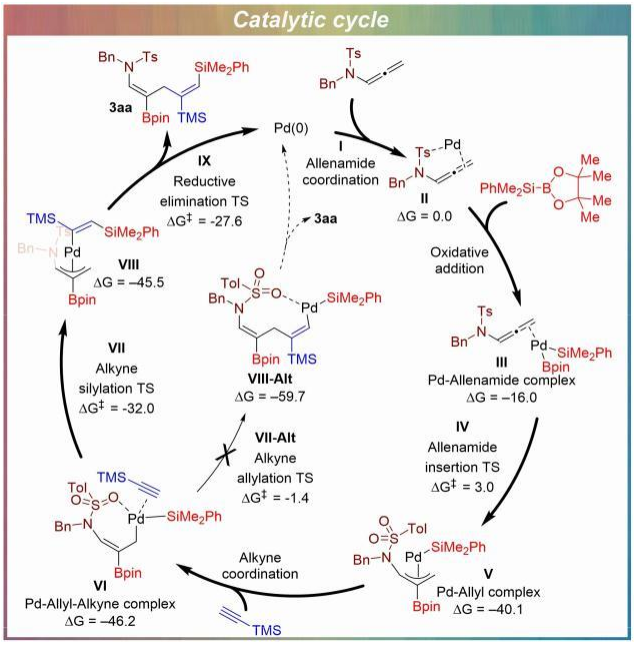


Scheme 2. Further transformations of **3aa**.[a,b] [a] Gram-scale synthesis of **3aa** was performed under the optimized conditions using 3 mmol of **1a**, 3.6 mmol of $Me_2PhSiBpin$, and 6 mmol of **2a**. [b] All trans-formations were carried out using 0.1 mmol of **3aa** under the described conditions. Reagents and conditions: a) *N*-bromosuccinimide (1.2 equiv), MeCN (0.3 M), 60 °C, 6 h, 65%; b) $Pd(PPh_3)_4$ (10 mol%), 4-iodoanisole (1.2 equiv), NaOH (3 equiv, 2 M aq. solution), 1,4-dioxane (0.3 M), 80 °C, 3 h, 67%; c) NIS (2.0 equiv), dichlorome-thane:1,1,1,3,3,3-hexafluoroisopropanol (4:1, 0.3 M), 60 °C, 6 h, 60%; d) 2 M NaOH:H_2O_2 (40% in H_2O) (2:1, 1.2 mL), Et_2O (0.1 M), 0 °C to rt, 4 h, 72%; e) $Pd(PPh_3)_4$ (10 mol%), 4-iodoanisole (2.5 equiv), NaOH (3 equiv, 2 M), 1,4-dioxane (0.3 M), 100 °C, 6 h, 55%; f) NIS (1.2 equiv), MeCN (0.3 M), 0 °C, 1 h, 71%; g) Mg (50 equiv), MeOH (0.04 M), sonication rt to 45 °C, 45 min, 78%.



Scheme 3. Probing the reaction sequence.

er conceivable pathway that was considered was a two-step process involving **4a**. To test whether this is operative, independently synthesized **4a** was treated with alkyne **2 c** under our standard conditions. The desired product was not formed (93% of **4a** was recovered), ruling out **4a** as an intermediate (Scheme 3, iii).



Scheme 4. Proposed catalytic cycle.

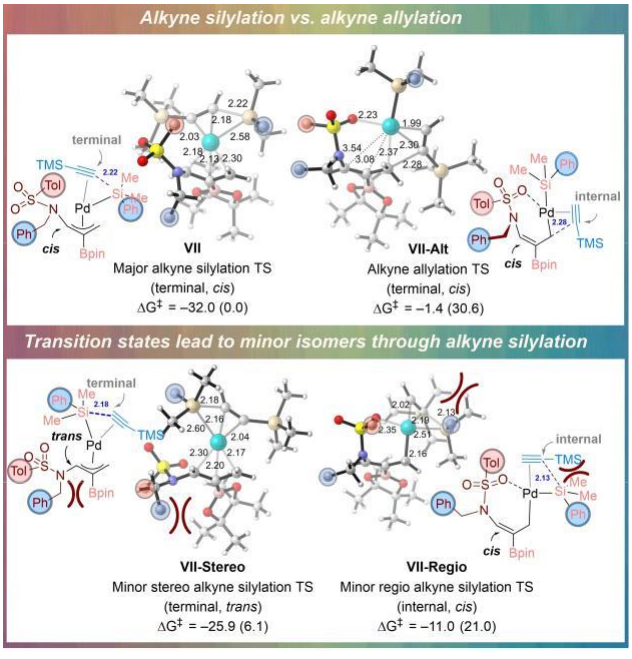


Figure 1. Computed transition state structures of the alkyne silylation and allylation processes. Arenes were condensed for clarity; highlighted red spheres represent tolyl groups and blue spheres represent phenyl groups. Relative energies are shown in parentheses. Distances in Å and energies in kcal mol ^{1}.

DFT[24] was used to elucidate the mechanism and origin of the selectivity (Scheme 4 and Figure 1). All structures were computed using ωB97XD[25] with 6-31G(d),[26] LANL2DZ,[27] and SMD (toluene)[28] at room temperature.[29]

The coordination of allenamide to Pd **I** followed by its oxidative addition into the B Si bond of $PhMe_2SiBpin$ leads to Pd-allenamide complex **III** (see Figure S1 for Pd-coordination sequence). Facile insertion (**IV**) of the Bpin into the allenamide to generate the B C bond leads to Pd-allyl complex **V**. Bpin insertion occurs *anti* to the sulfonamide, presumably owing to the steric encumbrance experienced in the *syn* process. Alkyne coordination to Pd-allyl complex **V** leads to Pd-allyl-alkyne complex **VI**. Notably, substrate chelation with Pd ($SO_2\cdots Pd$) is observed in η^1 coordination mode. Insertion of the dimethylphenyl silyl group into the alkyne (**VII**) leads to the penultimate complex, **VIII**. The final reductive elimination (**IX**) of the nascent disilyl alkene with the allyl leads to the formation of product **3aa** and regeneration of the Pd catalyst (see Figure S3 for reaction coordinate diagram and computed geometries in Supporting Information).

Pd-allyl-alkyne-silyl complex **VI** can lead to the product in two ways (Figure 1, top). The first, as we have proposed, involves the alkyne silylation taking place first, which produces a C Si bond (**VII**). The second involves alkyne allylation occurring first, which produces a C C bond instead (**VII-Alt**). In this contra-chemoselective process, the formation of the weaker C Si bond in the favored alkyne silylation (**VII**) is surprisingly favored over the formation of the stronger C C bond by 30.6 kcal mol ^{1}. This surprising reversal in preference is attributed to the difficulty of forming a bond at the more sterically hindered internal position of the alkyne for C C bond formation versus the ostensibly more accessible terminal position for C Si bond formation. This is supported by the large distortion present in the Pd-allyl species in the C C bond process versus the C Si bond process (17.5 kcalmol ^{1} in **VII-Alt** versus 3.5 kcalmol ^{1} in **VII**, see Figure S5).

The alkyne silylation step **VII** also determines the *E*/*Z* product selectivity (Figure 1, bottom left). The *E* and *Z* selectivity come from the *cis* and *trans* configurations of the allenamide allyl, respectively. The *cis* transition state is favored over the *trans* one by 6.1 kcalmol ^{1} (**VII** versus **VII-Stereo**), presumably owing to the steric repulsion between the Bpin and N-substituents in the *trans* configuration (see Figure S4 for details). However, the distortion interaction analysis reveals that the *trans* is less distorted than the *cis* (1.3 versus 3.5 kcalmol ^{1}, see Figure S5). In fact, what determines the selectivity here is a favorable interaction energy in **VII** that is absent in **VII-Stereo** (87.2 versus

75.3 kcalmol ^{1}, see Figure S5). The regiocontrol of the alkyne silylation can be also rationalized based on the position of the alkyne at which C Si bond formation occurs (Figure 1, bottom right). Bond formation at the sterically accessible terminal alkyne position is favored over that at the congested internal position by 21.0 kcalmol ^{1} (**VII** versus **VII-Regio**).

Conclusion

In conclusion, we have discovered a novel atom- and step-economical multicomponent reaction that involves the highly selective union of allenamides, alkynes, and bimetallic reagents to afford silaborate-functionalized skipped 1,4-dienes. This phosphine-ligand-free and additive-free Pd-catalyzed reaction is compatible with a wide variety of functionalities, resulting in a broad substrate scope (50 ex-amples). The synthetic potential was showcased through late-stage modification of biologically active molecules and selective functionalization of [Si] and [B] units to provide value-added carbon skeletons. DFT computations revealed the reaction sequence and helped to pinpoint the important substrate chelation and steric interactions responsible for the observed regio- and stereoselectivity.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Allenamides · Multicomponent Reactions · Silaboration · Skipped Dienes · Stereocontrol

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