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1,2-Diborylsilanes: Catalytic Enantioselective Synthesis and Site-Selective Cross-coupling

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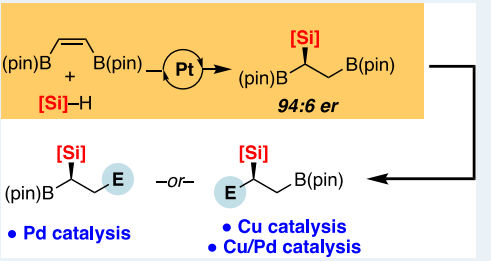
ABSTRACT: A Pt-catalyzed enantioselective hydrosilylation of (*Z*)-1,2-diborylethylene provides a 1,2-diboryl-1-silylalkane that can be used in catalytic cross-coupling reactions. Depending on the catalyst employed and the cross-coupling reaction conditions, the coupling can occur at either α or β relative to the silane center.



KEYWORDS: *organoboron compounds, catalysis, silanes, enantioselective catalysis, cross-coupling*

Due to their high reactivity and their ability to undergo stereospecific transformations, chiral organometallic compounds are valuable reagents in modern organic chemistry.[1] Among these species, structures bearing two or more organometallic groups can be employed to address complexity-generating synthesis *via* sequential chemoselective transformations.[2] As alternatives to reactive organometallic reagents such as organolithium compounds[3] or Grignard reagents, organoboron and organosilicon reagents have attracted attention in recent years due to their configurational stability, low toxicity, and versatility.[4] These compounds can undergo an array of C−C and C−heteroatom bond formation *via* transition metal-catalyzed cross-coupling reactions such as the Suzuki−Miyaura[5] and Hiyama−Denmark reactions.[6] While significant effort has been directed toward the preparation and utilization of motifs bearing multiple boronic esters such as diboryl[7] and triborylalkanes,[8] due to challenges in the stereoselective synthesis of requisite reagents, the utility of dimetallic reagents bearing silanes has been less explored. Considering the polyfunctionalization that might emanate from silylborylalkanes,[9] we initiated studies on a modular route to these materials along with a study of their transformations.

Often employed as carbanion precursors or masked alcohols, organosilanes possess unique electronic properties. Despite the large size of silanes, the elongated Si−C bond distance reduces steric hindrance[10] while still offering electronic modulation of reactivity due to the α[11] and β[12] silicon effect. These unique properties offer useful reactivity to silylboronate intermediates, especially *geminal* borylsilylalkanes.[13] It was hypothesized that a chiral trifunctional diborylsilylalkane might allow sequential functionalization, thereby affording useful routes to enantiomerically enriched building blocks. Pioneering investigations by Yun showed that these reagents could be prepared by enantioselective Cu-catalyzed double borylation of silylacetylenes (Figure 1a).[14] As an alternate route, the Chen group accessed α-silyl-β-boryl-allylboronates by diboration of allenylsilanes (Figure 1b).[15] Whereas these two studies examined oxidation and allylation of diborylsilylalkanes, studies in cross-coupling have not been undertaken. Addressing related compounds, regioselective coupling of enantiomerically enriched *vicinal* bis(boronates) with either palladium catalysts[16] or copper catalysts (Figure 1c)[17] have been described. These processes occur by transmetalation at the less hindered primary boronate, followed by coupling with the electrophile. In this connection, our interest in examining 1,2-diborylsilanes (**1**, Figure 1d) compounds that contain the structural features of both *vicinal* bis(boronates) and α-boryl silanes derives from fundamental questions about whether the boronate or the silyl group participates in transmetalation preferentially, whether the site selectivity of the coupling depends on the nature of the catalyst, and whether steric effects or electronic effects dictate regioselectivity of coupling.[11] In this report, we show that coupling of electrophiles can be controlled by the catalyst and offer a route for the rapid synthesis of diverse molecules based on the simple diborylsilane skeleton.

Expecting that 1,2-diboryl-1-silylalkanes might be a useful chiral building block, we initiated studies on the development of a method to prepare these compounds in a catalytic asymmetric fashion. Strategies involving enantioselective diboration[18] of vinylsilanes[19] were examined first, and as

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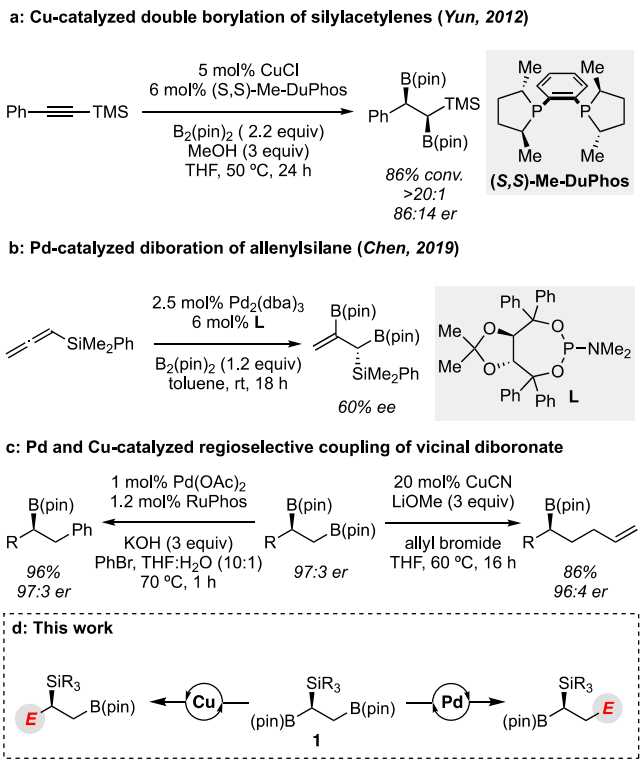
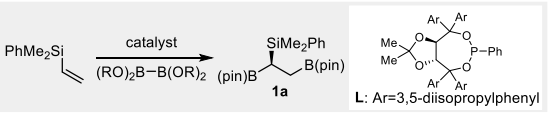


Figure 1. (a) Catalytic enantioselective preparation of 1,2-diborylsilanes from alkynes. (b) Enantioselective diboration of allenylsilanes. (c) Catalytic coupling reactions involving *vicinal* bis(boronates). (d) This work: complementary site-selective couplings of 1,2-diboryl-1-silylalkanes.

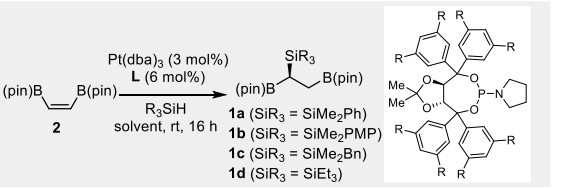
depicted in Figure 2A (entries 1−4, see the Supporting Information for additional data), either provided a modest yield or modest selectivity. We suspect that the diminished selectivity relative to that of reactions of 1-alkenes and styrenes[20] results from an elongated C−Si bond that results in lessened catalyst substrate interaction. As an alternative method, Pt-catalyzed hydrosilylation of diboryl ethylene was examined and was found to occur with good efficiency (entries 5−16).[21] The requisite (*Z*)-diborylethylene (**2**) could be accessed in quantitative yield from Zr-mediated reduction of diborylacetylene.[22] Examination of a collection of TADDOL-derived phosphoramidite ligands revealed **L6** (Figure 2B, entries 11 and 12) to be highly effective, providing quantitative yield and 94:6 er when the reaction was conducted in tetrahydrofuran solvent. Other TADDOL-derived ligands were also surveyed and gave moderate reactivity and enantioselectivity (Figure 2B, entries 5−10). Of note, because (*Z*)-**2** is symmetrically substituted, its reaction does not suffer from regiochemical concerns and, in a quadrant diagram analysis[23] (Figure 2C), the two prochiral faces of the alkene are well-distinguished. The use of (*Z*)-diborylethylene was crucial to obtain a high level of enantioselectivity as the analogous (*E*)-diborylalkene reacted with diminished selectivity despite furnishing the same enantiomer of the product (entry 13). Quadrant diagram analysis (Figure 2C) suggests that steric bulk from the catalyst ensemble may extend from quadrant *a* into quadrant *b*, thereby enhancing selectivity for the *cis* alkene but diminishing selectivity for the *trans* alkene. In addition to Me_2PhSiH, $Me_2PMPSiH$, Me_2BnSiH, and Et_3SiH also showed high reactivity and modest to good enantioselectivity (entries 14−16, Figure 2B).

A: *Diboration of Vinylsilane:*



entry	conditions	yield (%)[a]	er
1	3% $Pt(dba)_3$, 6% **L**, $B_2(pin)_2$ THF, 60 °C, 48 h	85	48:52
2	3% $Pt(nbd)_3$, 6% **L**, $B_2(cat)_2$ THF, 60 °C, 16 h, then pinacol	10	33:67
3	5% Rh(acac)(nbd), 5% R-Quinap, $B_2(cat)_2$ THF, 22 °C, 16 h, then pinacol	95	72:28
4	5% Rh(acac)(nbd), 5.5% R-Tol-binap $B_2(cat)_2$, THF, 22 °C, 16 h, then pinacol	19	7:93

B: *Hydrosilylation of Alkenyldiboronates:*



entry	L	SiR_3	R	solvent	yield (%)[a]	er
5	**L1**	$PhMe_2Si$	H	THF	40	50:50
6	**L2**	$PhMe_2Si$	Me	THF	95	87:13
7	**L3**	$PhMe_2Si$	F	MTBE	43	77:23
8	**L4**	$PhMe_2Si$	OMe	MTBE	52	95:5
9	**L4**	$PhMe_2Si$	OMe	THF	90	90:10
10	**L5**	$PhMe_2Si$	OEt	THF	91	92:8
11	**L6**	$PhMe_2Si$	O^{i}Pr	MTBE	91	93:7
12	**L6**	$PhMe_2Si$	O^{i}Pr	***THF***	***>98***	***94:6***
13	**L6**	$PhMe_2Si$	O^{i}Pr	THF	90	82:18
14	**L6**	Me_2PMPSi	O^{i}Pr	THF	98	94:6
15	**L6**	Me_2BnSi	O^{i}Pr	THF	96	90:10
16	**L6**	Et_3Si	O^{i}Pr	THF	92	79:21

C: *Quadrant Diagram Analysis for Reactions of Z–2 and E–2*

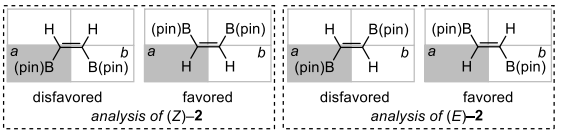


Figure 2. Development of a catalytic enantioselective synthesis of silyldiboronates. (A) Diboration of vinyl silanes. (B) Hydrosilation of 1,2-diborylethylene. (C) Analysis of selectivity with cis *versus* trans substrates. [a]Yields are of isolated material after purification by column chromatography. Reactions were carried out with a 0.20 mmol concentration of the substrate and 1 mL of solvent. [b]Reaction carried out using (*E*)-diborylalkene.

With a route to chiral enantiomerically enriched 1,2-diboryl organosilanes established, we initiated studies on the reactivity of these species. Initial studies focused on the copper-catalyzed reaction of *racemic* 1,2-diborylsilanes, which were readily prepared by diboration of commercially available dimethylphenylvinylsilane.[24,25] Similar to previous studies on copper-catalyzed coupling of *vicinal* diboronates,[17] CuCN was initially employed as a catalyst for coupling reactions with allyl bromide serving as the electrophile. In contrast to reactions with 1,2-diborylalkanes, when the 1,2-diborylsilane **1a** was used as the substrate, the reaction occurred at the more substituted carbon

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and produced allylation product **3a** as a single regioisomer (Figure 3). We considered that the reversal of regioselectivity

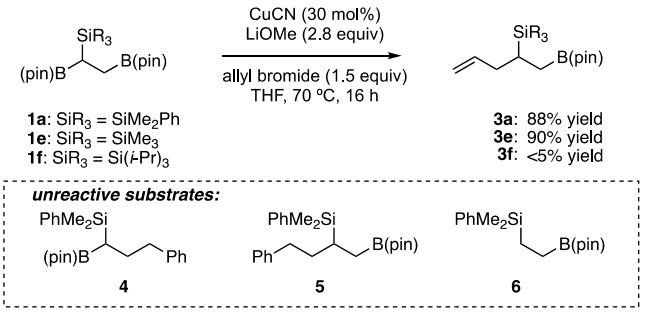

Figure 3. Copper-catalyzed coupling of allyl bromide with diborylsilanes (**1**). Reaction of other borylsilanes (**4**–**6**) do not provide the product.

might arise as a result of the α silicon effect: during transmetalation, the incipient σ_{C-Cu} may be stabilized by donation into the adjacent σ^{*}_{C-Si}.[26] To probe the role of the *vicinal* diboronate motif, experiments with α-boryl silane **4** and β-boryl silanes **5** and **6** were also conducted. These reactions did not provide any product and returned the substrate unchanged, thereby indicating the activating effect of the 1,2-diboryl motif in facilitating the reaction of substrates **1a** and **1e**.

With coupling conditions identified, we briefly examined the impact of reaction conditions and found that CuCN·2LiCl consistently provided the highest yields. The scope of the coupling was then examined with different classes of electrophiles (Figure 4). As noted in previous studies,[17] Cu complexes are known to engage a broad array of electrophiles. In addition to allyl bromide, electrophiles bearing other leaving groups such as allyl chloride, allyl iodide, and allyl phosphate reacted with a similar level of efficiency (**7**). Functionalized allyl electrophiles were also found to be effective coupling partners. Aromatic, aliphatic, and halogenated substituents were well-tolerated, and their presence did not alter the course of the reaction (products **8**–**12**). Of note, the 2-silyl-4-alkenol products of this reaction sequence have been employed by others in stereoselective electrophile-induced cyclization.[27,28] Coupling reactions with trichloropropene gave dichloroalkene **12** as the product, which could be transformed into an ester functional group in one step.[29] In addition, S_N2' coupling to substituted primary propargylic bromides afforded substituted terminal allenes (**13**–**18**) bearing different functional groups. These homoallenylsilanes are valuable synthetic intermediates and can undergo further chemoselective transformation.[30−32] Base-sensitive functional groups such as an alkyl bromide and an alkenyl silane survived the reaction intact. While most propargylic bromides gave rise to the S_N2' product, triisopropylsilyl-protected propargyl bromide gave the S_N2 product (**19**) only, presumably due to increased steric demand. Copper-catalyzed coupling with functionalized alkynyl bromides provided access to propargylic silanes **20**–**26**, which were previously prepared *via* the Cu-catalyzed 1,4-conjugate addition of silicon nucleophiles to alkyne-containing enones[33] or alkynyl carbene insertion into Si−H bonds.[34] Apart from aryl- and alkyl-substituted alkynes, alkenyl substituents were also incorporated in the product. Lastly, with access to enantiomerically enriched substrate **1** from enantioselective hydrosilylation, we examined the stereospecificity of coupling

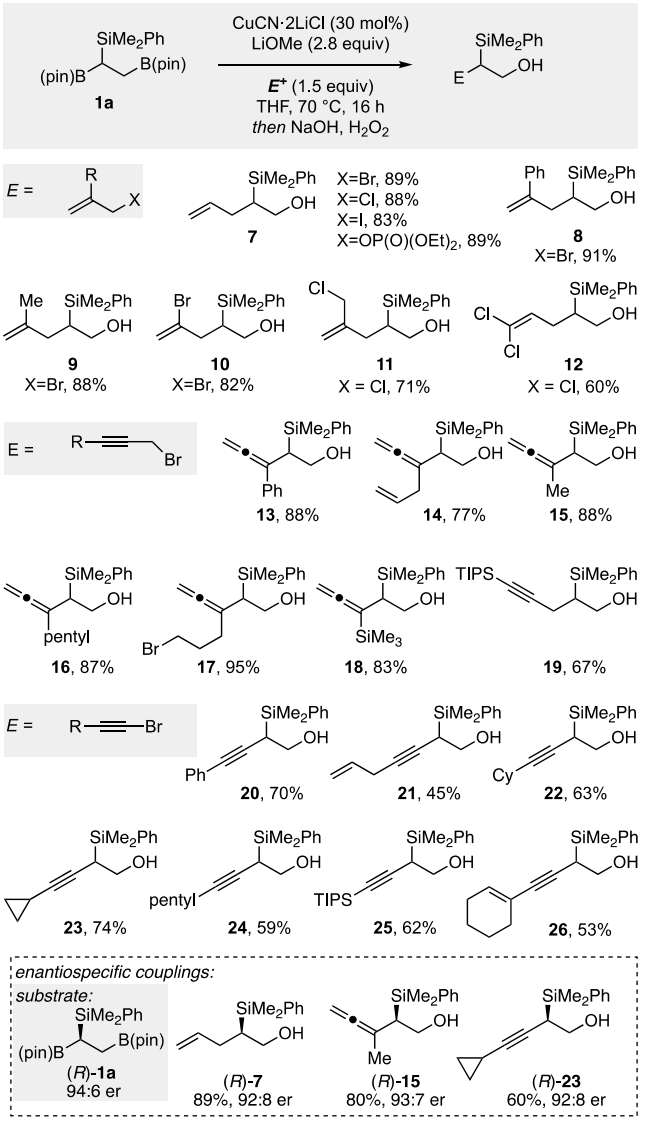

Figure 4. Scope of the Cu-catalyzed cross-coupling of α-boryl silylboronates and organic electrophiles. Yields are of isolated material after purification by column chromatography.

reactions. The products of coupling to allyl (*R*-**7**, Figure 4), propargyl (*R*-**15**), and alkynyl (*R*-**23**) electrophiles occurred with near-perfect stereospecificity, delivering chiral silane products. For compounds **20** and **7**, the overall process was determined to occur with retention of configuration at carbon by correlation of both the starting material and the product with compounds of known configuration.

With the knowledge that cooperative Pd/Cu co-catalysis might allow coupling of aromatic electrophiles,[35,36] we envisioned that the alkyl−Cu intermediate derived from diborylsilanes **1** might undergo Pd-catalyzed cross-coupling. Probing this strategy, 5 mol % of $Pd(OAc)_2$/RuPhos and an aryl bromide were introduced into the copper-catalyzed coupling reactions (Figure 5). After purification of the reaction mixture, the corresponding coupling products were obtained in synthetically useful yield for several substrates. In general, electron-rich aromatic electrophiles were effective coupling partners regardless of their steric encumbrance. When alkenyl electrophiles were engaged in the reaction, the process delivered allylsilanes (**33** and **34**), which are versatile reagents

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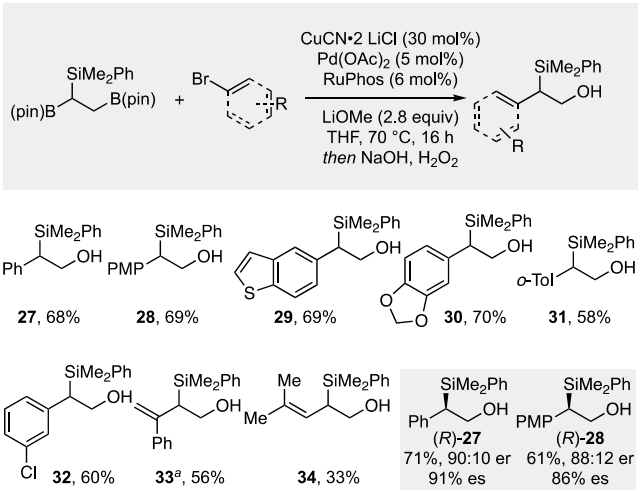

Figure 5. Scope of the Cu/Pd synergistic catalyzed cross-coupling of α-boryl silylboronates and organic electrophiles. Yields are of isolated material after purification by column chromatography. [a]$P(i\text{-}Pr)_3$ (6 mol %) was used instead of RuPhos.

in organic synthesis.[37,38] Lastly, similar to the examples in Figure 3, when an enantiomerically enriched substrate was employed in the reaction, this co-catalyzed coupling occurred with useful levels of enantiospecificity (91% es for **27** and 86% es for **28**), and comparison of the product configuration to the substrate configuration showed that the reaction occurred with net retention of configuration at carbon.

While the Cu-catalyzed cross-coupling reaction with LiOMe as the activator resulted in regioselective coupling α to the silyl group, coupling at the site β to the silicon group could be affected with alternate activation conditions. As depicted in Figure 6, when diborylsilane **1** was subjected to the Pd-

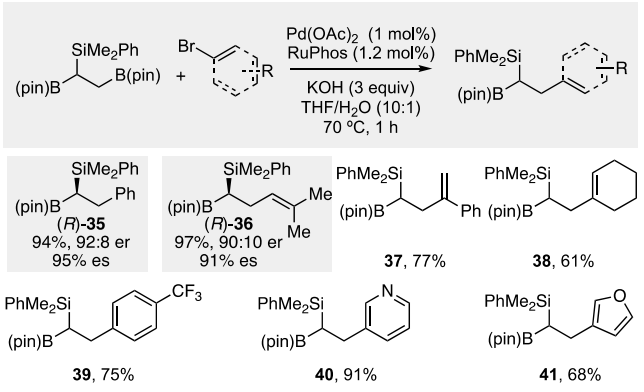

Figure 6. Direct Pd-catalyzed cross-coupling of a β-silyl boronate with C(sp^2) bromide electrophiles. Yields are of isolated material after purification by column chromatography.

catalyzed cross-coupling reaction in the absence of copper cyanide, efficient cross-coupling with the primary boronic ester was observed.[16] We suspect that the small size and linear nature of CuCN allow it to transmetalate at the more hindered secondary boronate and benefit from the α-silicon effect, whereas the dramatically increased steric demand of a four-coordinate ligand-bearing palladium center prohibits transmetalation at the more encumbered site, thereby resulting in the observed product. As expected, the configuration at the pre-existing stereocenter is essentially unperturbed during the coupling, and it is notable that this cross-coupling could be extended to a series of other electrophilic substrates to furnish **36**–**41**. The *geminal* silylboronates that arise from this reaction are known to be useful building blocks in the construction of allylsilanes, aminosilanes, and amino alcohol derivatives.[21,39]

The last feature that was probed with respect to synthesis utility was the possibility of conducting single flask hydrosilation/coupling sequences in such a way that the intermediate diborylsilane need not be isolated (Figure 7).

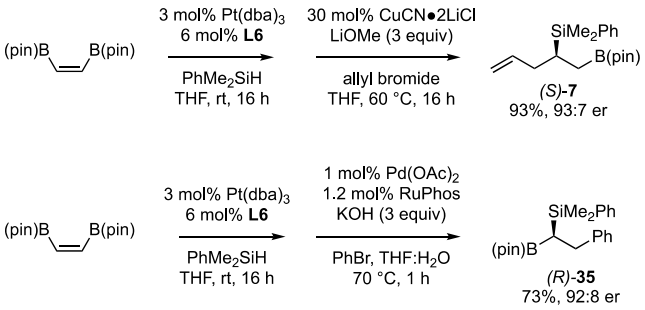

Figure 7. Single-flask sequential catalytic hydrosilylation/Cu-catalyzed allylation of 1,2-bis(boryl)ethylene and single-flask sequential catalytic hydrosilylation/Pd-catalyzed cross-coupling.

Thus, starting from (*Z*)-diborylethylene, Pt-catalyzed hydrosilylation and *in situ* Cu-catalyzed cross-coupling with allyl bromide furnished *vicinal* silylboronate (*S*)-**7** in good yield and enantioselectivity. Similarly, Pt-catalyzed hydrosilylation followed by *in situ* Pd-catalyzed cross-coupling with bromobenzene afforded *geminal* silylboronate (*R*)-**35** in good yield and enantioselectivity.

In summary, we have demonstrated the regiodivergent transformation of 1,2-diborylsilanes by transition-metal-catalyzed stereospecific reactions to afford functionalized organosilane products. The requisite reagents could be prepared with a high level of enantiomeric purity by Pt-catalyzed enantioselective hydrosilylation. This method offers a synthetic route to useful silicon-containing building blocks in an efficient fashion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c01789.

Procedures, characterization, and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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