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The seriatim Cu(I) activation of 1,1,1′,1′-tetrapinacolborylethane to prospective ring closing

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ABSTRACT

The synthesis and characterization of 1,1,1′1′-tetrapinacolborylethane is conducted to study the functionalization of that densely borylated small molecules through Cu-catalyzed coupling with allyl halides. A second Cu-catalyzed allylic alkylation of the homoallyl triboronate products gave access to mixed dihomoallyl diboronates. The intramolecular concatenated allylic alkylation version produced methylenecyclopentane-1,2-dipinacolboronic ester with 2:1 diastereoselection on the *trans*-diastereoisomer.

Tetraborylethane compounds are considered densely borylated small molecules with potential functionalization. Siebert, Gleiter and co-workers developed a detailed investigation into the Pt-catalyzed reactions of bis(catecholato)diboron (B_2cat_2) with diborylacetylenes to access air-stable tetraborylethenes **I**, that can be subsequently hydrogenated, with Pd catalysts, to afford tetracatecholborylethane compound **1** (Scheme 1a) [1]. Natural Bond Orbital (NBO) analyses revealed an intramolecular stabilization of the boron p_z orbital in **1**, through B–O, B–B, and agostic interactions, justifying the enhanced stability. More recently, Zhang et al., patented the synthesis of 1,1,1′1′-tetrapinacolborylethane (**2**) from dipinacolborylmethane via activation with lithium diisopropylamide (LDA) to generate dipinacolborylmethide lithium salt **II** that subsequently react with I_2 to form **2** in moderate yields (Scheme 1b, *methods A and C*) [2]. Complementary synthesis of the lithium salt **II** has been developed by Masarwa and co-workers [3], with $^{i}Pr_2NH$ and $^{n}BuLi$ (Scheme 1b, *method B*). Cho and co-workers established the use of NFSI for the halogenative step transforming **II** into the coupled product **2** (Scheme 1b, *method D*) [4]. Whereas the synthesis of the polyborated **2** compound has been well established, its structural characterization and reactivity received less attention, being only covered by stoichiometric activation modes with LDA, to promote the single deprotonation, followed by electrophilic trapping with RX (Scheme 2a) [2] or via nucleophilic mono trifluorination towards the desymmetrization of **2** (Scheme 2b) [3]. In our relentless pursuit of generating new knowledge towards organoboron activation modes and subsequent reactivity we became interested to launch a systematic study on the catalytic Cu(I) activation of 1,1,1′1′-tetrapinacolborylethane (**2**) to be subsequently trapped by a general scope of allyl halides (Scheme 2c).

We prepared compound **2** adapting the protocol from Zhang et al. [2], and we conducted its full characterization through X-Ray diffraction to establish the relative orientation of the "empty" boron p_z orbital and the plausible intramolecular electron-donor interactions. Unlike compound **1**, compound 1,1,1,1′-tetrapinacolborylethane (**2**) does not present intramolecular interactions (Scheme 3), in agreement with the lower Lewis acid properties of Bpin moiety compared with Bcat motif.

We were aware of the benefits of Cu (I) complexes in the activation of 1,1-diborylalkanes to deliver the corresponding α-borylalkyl copper species [5], as key intermediates in copper-catalyzed allylic alkylation reactions, forming linear or branched homoallyl boronates via S_N2 or S_N2'mechanisms [6–11]. Copper-deborylation of 1,1-diborylalkanes is essentially performed *in situ*, assisted by alkoxy bases (-OR') that favour the σ-bond metathesis pathway. But also the addition of stabilizing ligands, such as phosphines or N-heterocyclic carbenes, contribute to the steric and electronic tuning of the borylalkyl copper(I) catalytic system. From this background, we launched a preliminary study of the CuCl catalyzed allylic alkylation of 1,1,1′,1′-tetrapinacolborylethane (**2**) with allyl bromide in the presence of $LiO^{t}Bu$ as base, at 60 °C, in THF. The reaction outcome showed a high conversion of **2** into the major product **3** (67%), identified as the monoalkylated compound, together with 23% of dialkylated byproduct, as a result of the double allylic alkylation, within a mixture of 1:1 diastereoisomers **4**/**4'** (Table 1, entry 1). The

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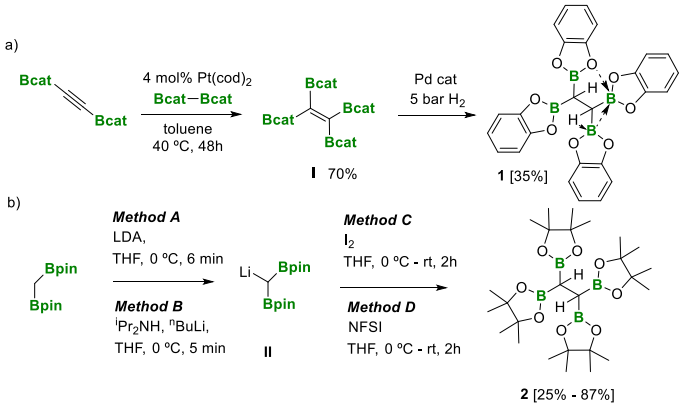
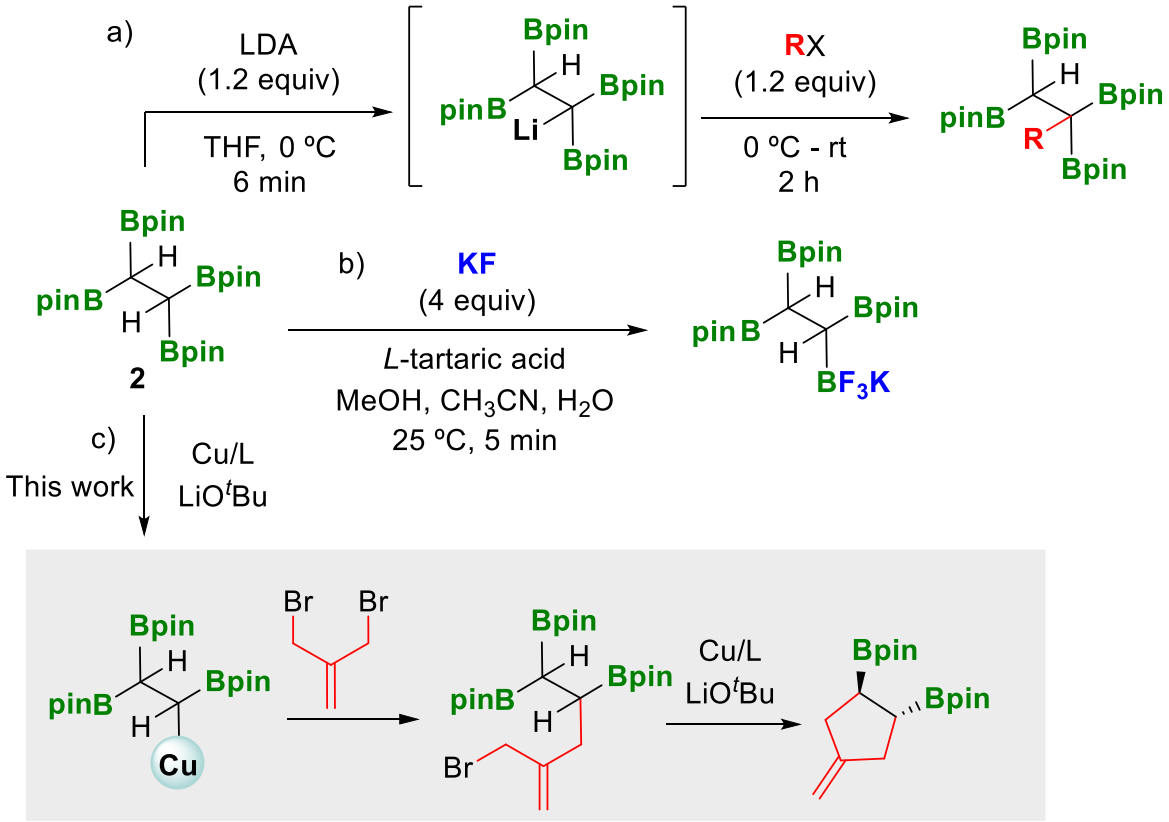


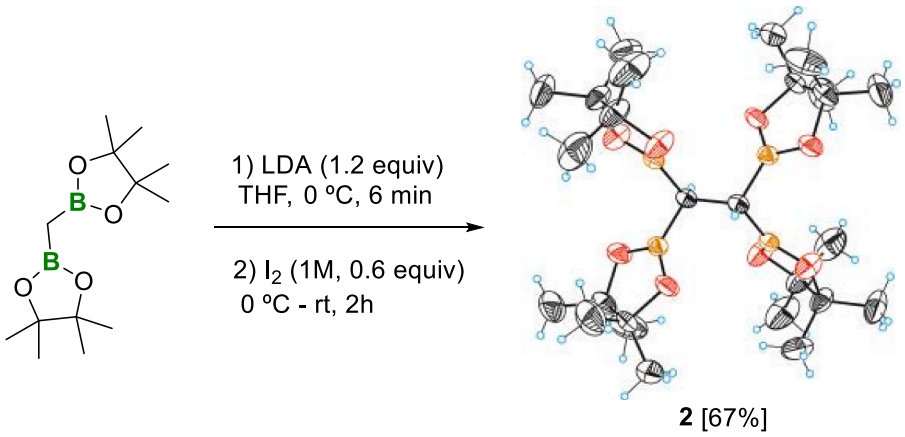
Scheme 1. Synthetic approaches towards 1,1,1′,1′-tetraborylethane.



Scheme 2. Activation of 1,1,1′,1′-tetraborylethane and subsequent reactivity.

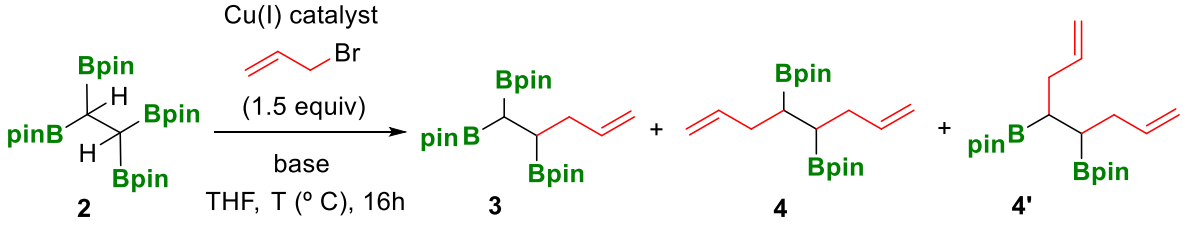
addition of ligand PPh_3 to the Cu(I) catalytic system, favoured the formation of homoallyl triboronate product **3** versus the dialkylated byproduct **4** (Table 1, entry 2), suggesting that the sterically hindered catalytic system Cu-PPh_3 diminished the double allylic alkylation. Replacement of LiO^tBu by NaO^tBu decreased the percentage formation on the desired monoalkylated product **3**, since protodeborylated byproducts (pdb) were formed together with byproducts **4**/**4'** (Table 1, entry 3). The pronounced influence of the base in the reaction coupling is in agreement with Cho and co-workers observations about the benefits of LiO^tBu in CuCl catalyzed allylic alkylation of 1,1-diborylalkanes [7]. When $[Cu(MeCN)_4]PF_6$ was used as Cu(I) source, product **3** could be isolated in 54% working conducting the reaction at 60 °C, noting that higher reaction temperatures (90 °C) did not favour the formation of **3**, since protodeborylated byproducts (pdb) were also observed (Table 1, entries 4, 5). Reduction of LiO^tBu loading resulted in a suppression of the byproducts (Table 1, entry 6), conditioning the use of 1.5 equiv of base in the optimized reaction conditions within the catalytic system $[Cu(MeCN)_4]PF_6/PPh_3$ to synthesize product **3** in 65% isolated yield, minimising the formation of double alkylation byproducts (Table 1, entry 7).

For comparison, we have also explored the reactivity of **2** with 3-bromo-3,3-difluoroprop-1-ene, to give the corresponding 3-substituted 1,1-difluoroalkene (Table 2, entries 1, 2). To our delight, the nucleophilic attack took place regioselectively on the γ position, facilitating the synthesis of the polyborylated 1,1-difluoroalkene **5**, in 68% isolated yield. The access to *gem*-difluoroalkene compounds is of fundamental interest since C═CF_2 motifs are considered critical for certain mechanism-based enzyme inhibitors, and they can also function as bioisosteres for aldehydes and ketones [12,13]. The influence of alkyl substituents on the allyl moiety was next studied. As a general trend, allyl bromides containing the functional groups R^2 = methyl,



Scheme 3. Synthesis of 1,1,1′,1′-tetrapinacolborylethane (**2**). CCDC number 2284601.

Table 1
Optimization of the reaction conditions for Cu catalyzed coupling of 1,1,1′,1′-tetrapinacolborylethane with allyl bromide.[a].

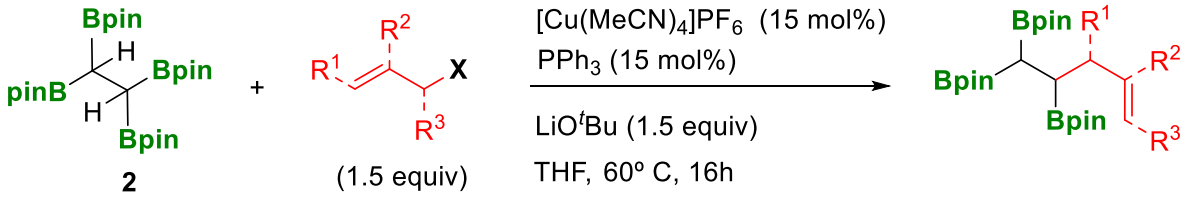


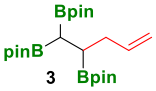
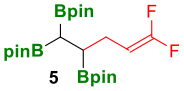
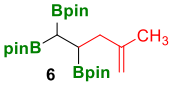
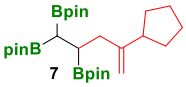
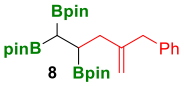
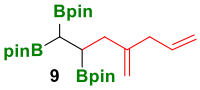
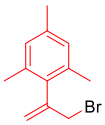
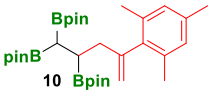
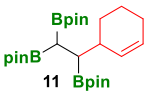
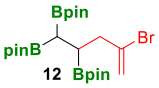
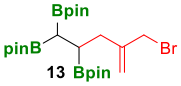
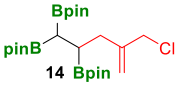
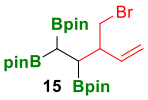
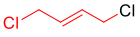
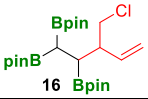
Entry	Cu(I) (mol%)	Base (equiv)	T (°C)	Conversion (%)[b]	3 (%)[b][%][c]	4/4′ (%)[b]
1	CuCl (10)	LiO^{t}Bu (2)	60	90	67 [31]	23
2	CuCl/PPh_3 (10/10)	LiO^{t}Bu (2)	60	88	78 [51]	10
3	CuCl/PPh_3 (10/10)	NaO^{t}Bu (2)	60	85	45	11 (and 29% **pdb**)[d]
4	$[Cu(MeCN)_4]PF_6$(10)	LiO^{t}Bu (2)	60	70	58 [54]	12
5	$[Cu(MeCN)_4]PF_6$(10)	LiO^{t}Bu (2)	90	95	54	31 (and 10% **pdb**)[d]
6	$[Cu(MeCN)_4]PF_6$(10)	LiO^{t}Bu (1.5)	90	62	60	–
7	$[Cu(MeCN)_4]PF_6/PPh_3$ (15/15)	LiO^{t}Bu (1.5)	60	72	70 [65]	2

[a] Reactions performed at 0.15 mmol scale of **2**, allyl bromide (1.5 equiv), CuCl or $[Cu(MeCN)_4]PF_6$ (10–15 mol%), PPh_3 (10–15 mol%), LiO^{t}Bu (1.5–2 equiv), THF (2 mL), 16 h.
[b] Conversion and yields determined by NMR with naphthalene as internal standard.
[c] Isolated yield.
[d] Protodeborylated byproducts (**pdb**).

cyclopentyl and benzyl, reacted with **2** allowing the isolation of homoallyl triboronate products **6** to **8**, in moderate yields (Table 2, entries 3–5). Interestingly, the Cu-catalyzed coupling between **2** and 2-(bromomethyl)penta-1,4-diene enabled the formation of the polyborylated product **9**, (Table 2, entry 6). When R^2 = mesityl group, the reaction resulted efficient towards the allylic alkylation in spite of the steric hindrance associated to the aryl group, isolating compound **10** in 73% (Table 2, entry 7). Notably, the cyclic 3-bromocyclohex-1-ene was a suitable electrophile along the Cu(I) catalyzed allylic alkylation of **2**, since product **11** was efficiently synthesized and isolated in 67% yield, within 1:1 dr (Table 2, entry 8). To broaden the scope of our methodology we explored next the reactivity of **2** with 2,3-dibromoprop-1-ene that would offer a high synthetic versatility to the products. By increasing temperature up to 90 °C, product **12** was exclusively formed as a result of a chemoselective C–Br coupling (Table 2, entry 9) retaining the C (sp^2)-Br bond for downstream transformations [14,15]. By extension, the reaction of **2** with 3-bromo-2-(bromomethyl)prop-1-ene and 3-chloro-2-(chloromethyl)prop-1-ene allowed the isolation of compounds **13** and **14**, in similar moderate yields, despite the differences on the leaving group (Table 2, entries 10 and 11). Internal allyl halides were next studied when we conducted the copper catalyzed allylic alkylation between **2** and (*E*)-1,4-dibromo-2-butene or (*E*)-1,4-dichloro-2-butene. The coupling was exclusively achieved at the γ position of the allyl halides, generating products **15** and **16** in 53% and 86% isolated yield, respectively, within 1:1 dr (Table 2, entries 12 and 13). According to the overall reactivity found, we suggest that the Cu catalyzed allylic alkylation between 1,1,1′,1′-tetrapinacolborylethane and the allyl halides depicted in Table 2 might undergo a S_N2' mechanism. This is in agreement with the reported copper-catalyzed S_N2'-selective allylic alkylation reactions involving diborylmethane [6–10], *gem*-diborylalkanes [11] as well as *gem*-diborylalkenes [15]. However, when we performed the Cu-catalyzed coupling between **2** and (*E*)-1-bromobut-2-ene, the reaction evolved to the formation of products **17** and **18,** in about 2:1 ratio respectively, with a favoured α-selectvity versus γ-selectvity (Scheme 4). In this case, the S_N2 mechanism seems to be favoured as previously pointed by Liu and Fu [10]. The formation of **17** via base assisted deborylation, followed by nucleophilic addition to the α-position of the allyl halide [16] has been discarded due to the lack

Table 2
Scope of Cu catalyzed coupling between 1,1,1′,1′-tetrapinacolborylethane and allyl halides.[a].

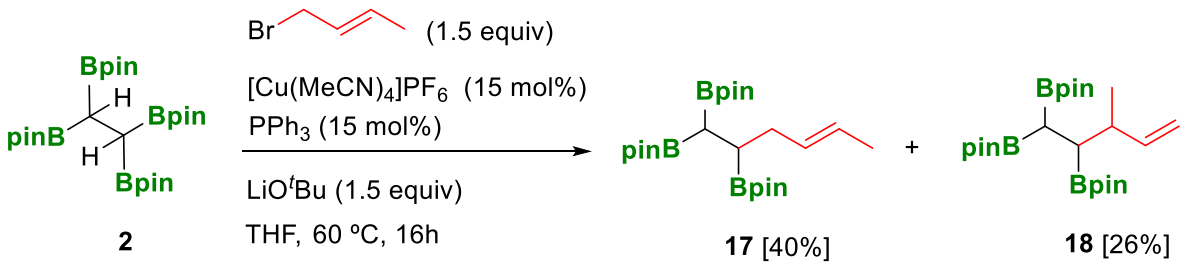


Entry	Allyl halide	Product	Isolated Yield [%][b]
1		 **3**	[65%]
2		 **5**	[74%]
3		 **6**	[58%]
4		 **7**	[51%]
5		 **8**	[68%]
6		 **9**	[31%]
7		 **10**	[73%]
8		 **11**	[67%] (dr = 1/1)
9[c]		 **12**	[55%]
10		 **13**	[41%]
11		 **14**	[43%]
12[c]		 **15**	[53%] (dr = 1/1)
13[c]		 **16**	[86%] (dr = 1/1)

[a] Reactions performed at 0.15 mmol scale of **2**, allyl bromide (1.5 equiv), $[Cu(MeCN)_4]PF_6$ (15 mol%), PPh_3 (15 mol%), LiO^tBu (1.5 equiv), THF (2 mL), 60 °C, 16 h.
[b] Isolated yield after flash column chromatography purification.
[c] 90 °C, base (1.75 equiv).

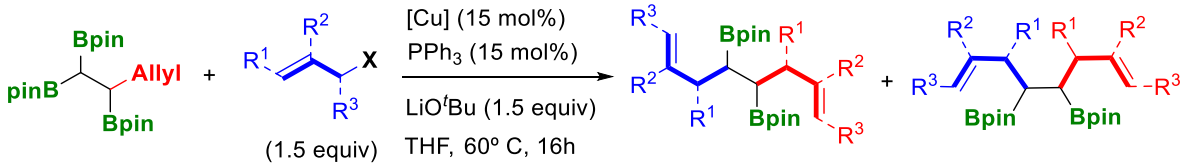
of reactivity when Cu(I) is removed.

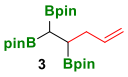
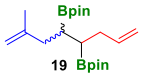
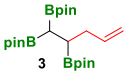
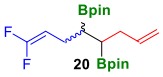
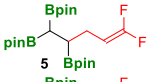
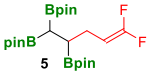
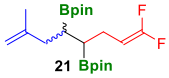
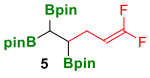
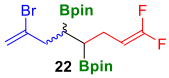
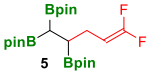
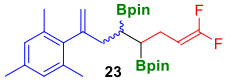
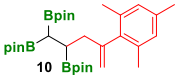
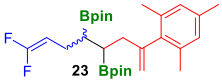
To the best of our knowledge, this is the first attempt to activate 1,1,1′,1′-tetraborylated ethane with Cu catalyst for carbon coupling since previous attempts to synthesize substituted tri or tetraborylated ethanes required multiple borylation of double or triple bonds [16–19], followed by alkylation with an excess of NaO^tBu. Under the optimized reaction conditions for our Cu-catalyzed first allylic alkylation of **2**, we aimed to perform a second allylic alkylation of the homoallyl triboronate systems, to generate mixed dihomoallyl diboronates (Table 3). We studied the coupling between compound **3** and 3-bromo-2-methylprop-1-ene, catalyzed by $[Cu(MeCN)_4]PF_6/PPh_3$, and to our delight the corresponding mixed dihomoallyl diboronate **19** could be isolated as



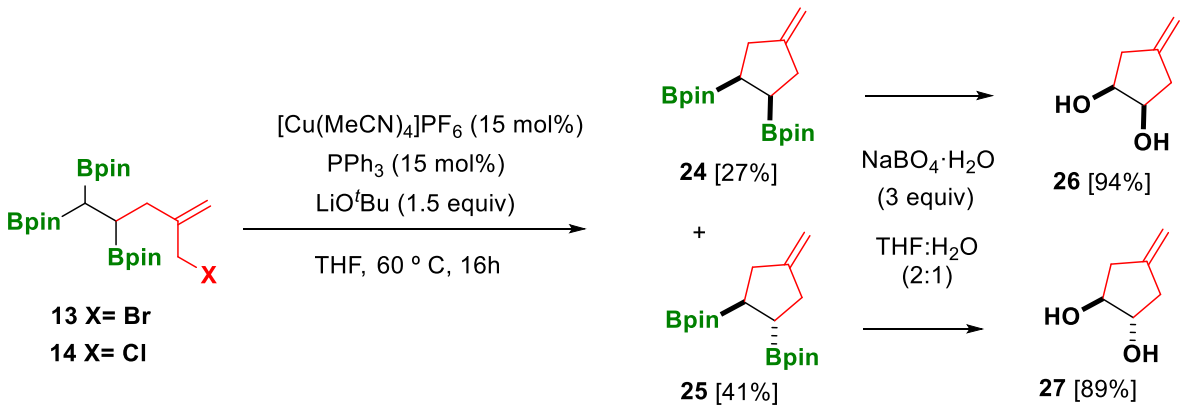
Scheme 4. Solvent-controlled regioselective allylic alkylation between **2** and (*E*)-1-bromobut-2-ene.

Table 3
Cu catalyzed second allylic alkyation of homoallyl triboronate systems.[a].



Entry	Substrate	Product	NMR Yield[b] (dr)[b] [%][c]
1	 3	 19	67% (dr = 1/1) [25%][29%]
2	 3	 20	99% (dr = 1/1.2) [34%][43%]
3	 5	 20	89% (dr = 1/1.5) [33%][50%]
4	 5	 21	64% (dr = 1/1.2) [23%][29%]
5	 5	 22	53% (dr = 1/1.4) [19%][25%]
6	 5	 23	43% (dr = 1/2) [11%][20%]
7	 10	 23	72% (dr = 2/1) [44%][21%]

[a] Reactions performed at 0.2 mmol scale of homoallyl triboronate, allyl bromide (1.5 equiv), $[Cu(MeCN)_4]PF_6$ (15 mol%), PPh_3 (15 mol%), LiO^tBu (1.5 equiv), THF (2 mL), 60 °C, 16 h.
[b] NMR yield and diastereo ratio calcultaed with naphthalene as internal standard.
[c] Isolated yield for each diastereoisomer.



Scheme 5. Intramolecular Cu catalyzed coupling of homoallyl triboronate systems **13** and **14**.

both diastereoisomers within 1:1 dr (Table 3, entry 1). Similar trend was observed when the allylic compound **3** reacted with 3-bromo-3, 3-difluoroprop-1-ene, to generate product **20** (Table 3, entry 2). However, when the same compound **20** was synthesized from the homoallyl triboronate system **5** by Cu-catalyzed coupling with the 3-bromoprop-1-ene, the dr slightly increased up 1:1.5 dr (Table 3, entry 3). To test whether the 1,1-difluoroalkenyl polyborated compound **5** could influence on the diasteroselection of the second Cu-catalyzed allylic alkylation, we coupled **5** with several allyl bromides noting an incipient diastereoselection, particularly on the formation of product **23** (Table 3, entries 4–6). Interestingly, the preparation of **23** from the homoallyl triboronate system **10**, gave also the same diastereoselection but with opposite preference on the major diasteroisomer, as a consequence of the steric hindrance of the mesityl group (Table 3, entry 7).

We complemented this study exploring the intramolecular Cu-catalyzed allylic alkylation of the homoallyl triboronate systems **13** and **14** with the aim to promote the synthesis of methylenecyclopentane-1,2-dipinacolboronic esters. Under the optimized reaction conditions, conversion into the desired product was similar independently of the leaving group in the substrate, with a diastereomeric ratio 2/1 in favour of the *trans* diastereoisomer **25** (Scheme 5). Interestingly, the oxidation gave access to *trans*-methylenecyclopentane-1,2-diol **27** in 89% isolated yield, becoming an alternative straightforward synthesis of this strategically key intermediate for the construction of cephalotaxine derivatives with antileukemic activity [20].

In summary, we have synthesized 1,1,1′1′-tetrapinacolborylethane (**2**) from dipinacolborylmethane and we conducted its full characterization through X-Ray diffraction to establish the relative orientation of the "empty" boron p_z orbital within the four Bpin moieties. We launched an unexplored Cu catalyzed coupling of 1,1,1′,1′-tetrapinacolborylethane with allyl bromide identifying the optimized reaction conditions with the catalytic system $[Cu(MeCN)_4]PF_6/PPh_3$ and LiO^tBu (1.5 equiv) minimising the formation of double alkylation byproducts. The substrate scope covered a representative examples of sterically hindered allyl halides that suggest a S_N2' mechanism for the Cu catalyzed allylic alkylation. A subsequent second allylic alkylation of the homoallyl triboronate systems, allowed the synthesis of mixed dihomoallyl diboronates. An intriguing intramolecular Cu-catalyzed allylic alkylation of the homoallyl triboronate systems **13** and **14** facilitated the synthesis of methylenecyclopentane-1,2-dipinacolboronic ester with 2:1 diastereoselection on the *trans*-diastereoisomer.

Contributions

Each author declares substantial contributions through the following:

(1) The conception and design of the study, or acquisition of data, or analysis and interpretation of data, (2) drafting the article or revising it critically for important intellectual content, Please indicate for each author the author contributions in the text field below. Signatures are not required.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tchem.2023.100045.

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