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Very Important Publication

1,2-Dialkylation of 1,1-Arylboryl Alkenes Via Borata-Alkene Intermediate

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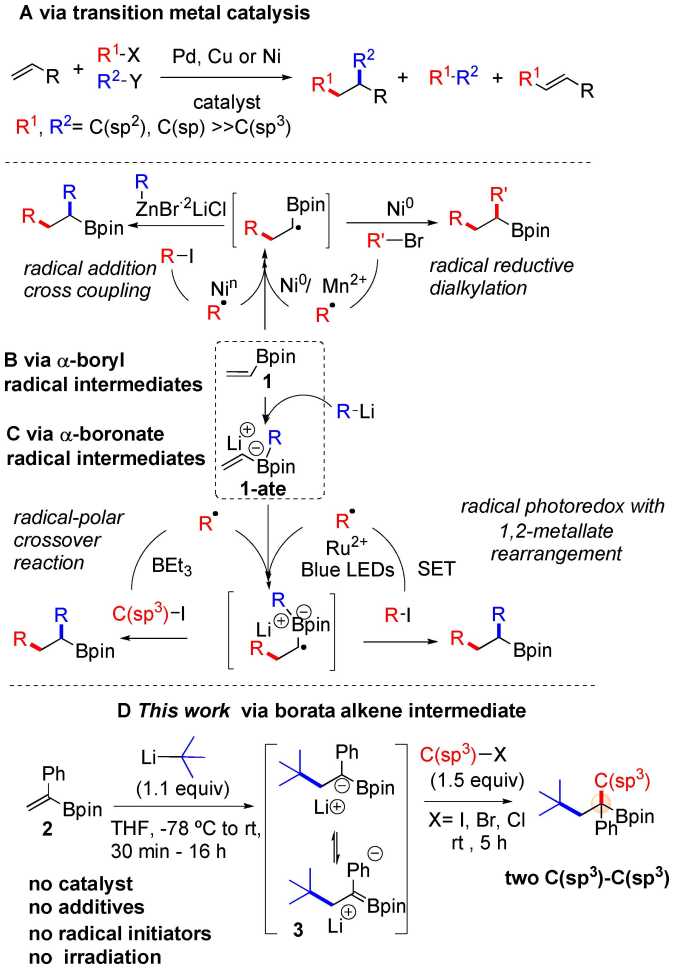
Abstract: We describe here the conjugate addition of tert-butyllithium to vinyl systems of boronic esters to generate a borata-alkene intermediate, followed by a sequential S_N2 reaction with alkyl halides, at room temperature. We envisioned this goal through engaged C(sp^3) chemical entities avoiding metal catalysts, additives, radical initiators or specific irradiation. This reaction guarantees that the new tetrasubstituted carbon formed retains all the C atoms from the three starting materials involved in the assembly.

Keywords: 1,2-dicarbofunctionalization; borata-alkene; tertiary boronic esters; tertiary alcohols; cyclopropanation

The formation of two new vicinal carbon-carbon bonds by addition of two different reagents across terminal and internal olefins is one of the most challenging intermolecular reactions. This type of dicarbofunctionalization sequence provides selective 1,2-substituted alkanes, principally with the aid of catalytic amounts of Pd, Cu or Ni complexes.[1] However, the catalytic cycles might generate undesired byproducts, due to the cross coupling between both reagents or Heck-type sequences through inherent β-H-elimination pathways. These drawbacks limit the application of this method to essentially C(sp^2) or C(sp) hybridized reagents (Scheme 1A). Current efforts are focused to permit the efficient metal catalyzed assembly of the three components, with particular emphasis to the formation of two C(sp^3)–C(sp^3) bonds across the alkene. However, this ambitious goal has scarcely succeed and the most remarkable examples are based on the use of Ni,[2–4] Ti,[5,6] Fe[7] or Co[8] catalysts.

Alternatively, the use of accessible vinylboronic esters, as unsaturated substrates, for dual C–C(sp^3) formation, represents a synthetic opportunity due to the advantageous adjacent empty p orbital on boron atom. The formation of stable α-boryl radical intermediates on vinylboronic acid pincol ester (**1**) can be performed via Ni/radical catalytic process adding C(sp^3)I followed by cross coupling with C(sp^3)ZnBr·2LiCl (Scheme 1B).[9] Alternatively, the nickel-catalyzed reductive dialkylation of **1** with a variety of alkyl bromides, provides an interesting approach towards alkylboronates, being required up to 3 equiv. of Mn to complete the redox process (Scheme 1B).[10] Contemporary work on alkylarylation of vinyl boronates, through Ni photoredox dual catalysis or Ni-photoredox conjunctive cross-coupling has been reported,[11–14] however examples on formation of two C(sp^3)–C(sp^3) bonds across the alkenyl boronate are not described.

Alternatively, the vinylboronic ester "ate" complex **1-ate**, can react with electrophilic carbon radicals generating the corresponding radical anionic adducts. Subsequent 1,2-alkyl shift from boron to the α carbon, results in the formation of secondary or tertiary alkylboronic esters, (Scheme 1C).[15] This significant advance do not require transition metal catalyst but BEt_3 (5 mol%) is used as radical initiator.[15,16] Other approaches involving the palladium-induced metalate rearrangement enabled 1,2-difunctionalized products although examples on formation of two C(sp^3)–C(sp^3) bonds across the alkenyl boronates are not described.[17] Eventually, the radical addition of an electron-deficient alkyl radical to **1-ate**, in the presence



Scheme 1. Dicarbofunctionalization of alkenes with formation of two C(sp^3)–C(sp^3) bonds.

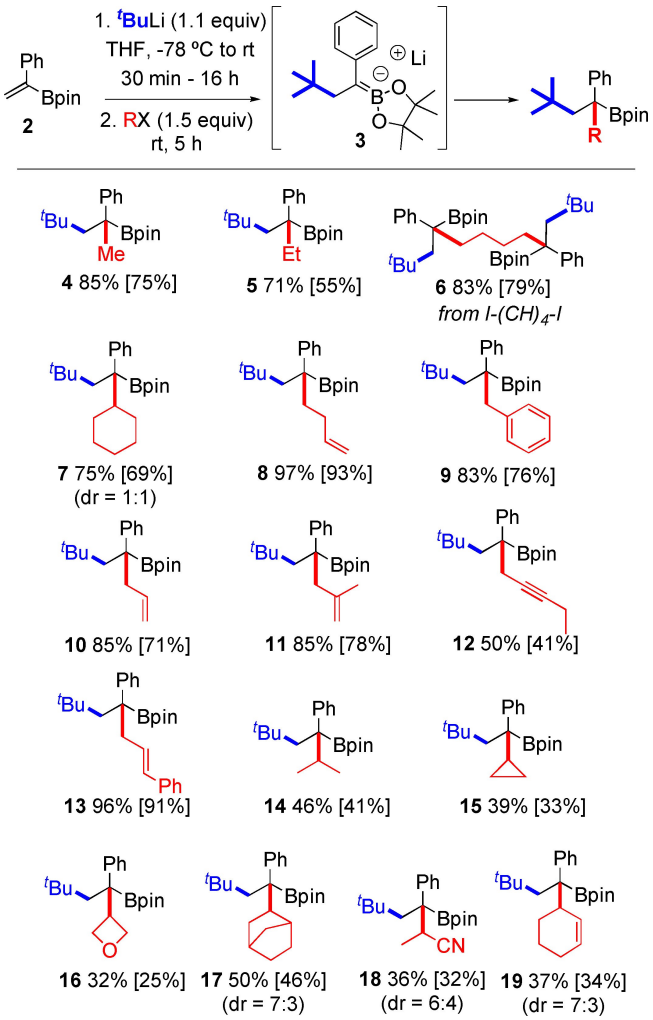
of visible light-irradiation, can be followed by electron transfer with another molecule of alkyl iodide, triggering a 1,2-metalate rearrangement (Scheme 1C).[18]

Under this panoramic overview, we envisioned a polar addition of ^{t}BuLi reagent to the terminal carbon of 1-phenylvinylboronic acid pinacol ester **2**, promoted by the stability of the resulting α-boryl carbanion **3**, followed by electrophilic trapping with C(sp^3)X (X = I, Br and Cl), via substitution pathways (Scheme 1D). It has been demonstrated that α-boryl carbanions show a remarkable stability due to the valence deficiency of the adjacent three coordinate boron center, as illustrated in the borata-alkene resonance forms (Scheme 1D).[19,20]

This "all-alkyl" cross-coupling reaction inverts the trends of ^{t}BuLi addition to form alkenylboronates and is capable of generate two new C(sp^3)–C(sp^3) bonds across the alkene, delivering valuable tetrasubstituted carbon centers, in the absence of catalyst, additives or any type of radical initiators. To the best of our knowledge, the tert-butyl motif can form C–C(sp^3) bond at the terminal position of **1**, only as radical tert-butyl generated from ^{t}BuI and AIBN/Bu_3SnH,[21,22] or generated from visible light-activated Ir or Ru catalysts.[11,12]

As a proof of concept, we explored the addition of 1.1 equiv. of ^{t}BuLi to 1-phenylvinylboronic acid pinacol ester **2**, at −78 °C for 30 minutes, and 16 h at room temperature, in THF as solvent. Subsequently, 1.5 equiv. of MeI was added and the reaction mixture was stirred for 5 h. Substrate **2** was converted into product **4** in 85% by NMR (in comparison with internal standard naphthalene) and 75% isolated yield (Scheme 2). The formation of two new C(sp^3)–C(sp^3) bonds across the 1,1-arylboryl alkene was conducted regioselectively placing the ^{t}Bu group at the terminal position and the Me group at the internal position.

The simplicity of the three component assembly, where neither catalysts or radical precursors nor photo-

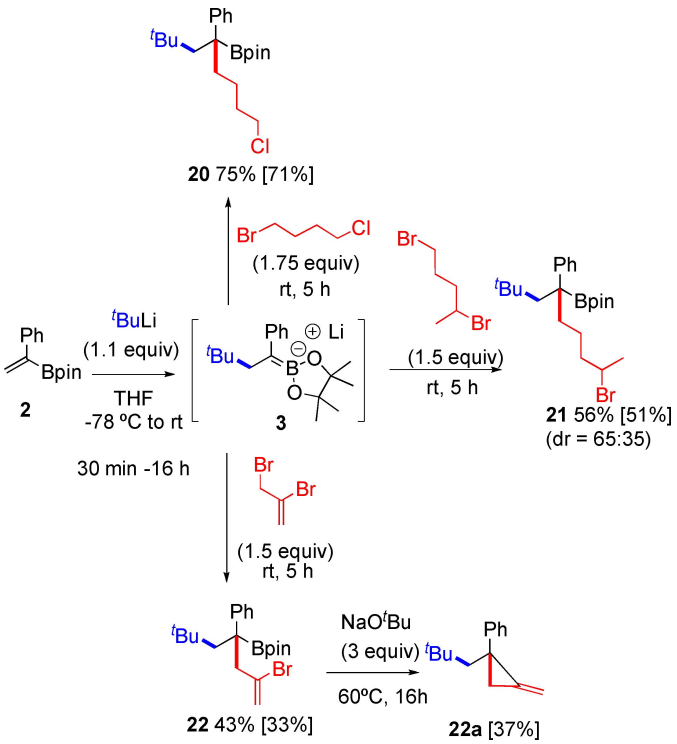


Scheme 2. Dicarbofunctionalization with ^{t}BuLi and primary/secondary C(sp^3)-X. Yields calculated by ^{1}H NMR with naphthalene as internal standard. Yields in brackets represent isolated yields after purification with silica gel chromatography.

redox reaction conditions were involved, could be extended to other primary and secondary alkyl iodides, achieving comparable 1,2-dicarbofunctionalization reaction outcomes (Scheme 2). In particular, the tertiary boronic esters **5**–**7** were isolated, by adding EtI, $I(CH_2)_4I$ and CyI respectively, highlighting the double dicarbofunctionalized product **6**, where two tetrasubstituted carbon atoms are simultaneously formed (Scheme 2). Remarkably, this significant increase of the molecular complexity involves five-components assembly in a simple operational step. However, ^{t}BuI, PhI and vinyl-I resulted not suitable alkylating agents. Next, we were committed to prove whether alternative functional groups were compatible with this 1,2-dicarbofunctionalization strategy and to our delight the primary alkyl bromide 4-bromobut-1-ene was efficiently trapped to generate product **8** in 93% isolated yield (Scheme 2). Benzyl bromide was next assembled to **2**, in the presence of ^{t}BuLi, and the new C–C bond was conveniently performed to generate product **9** in 76% isolated yield (Scheme 2). Allyl bromides were also explored and the tertiary homoallylic boronic esters **10** and **11** could be efficiently prepared (Scheme 2). The tolerance of alternative functional groups along the 1,2-dicarbofunctionalization process was studied with the introduction of the electrophile 1-bromopent-2-yne, preserving the triple bond intact since no allene group was detected at the isolated product **12** (Scheme 2).

In order to check whether an allylic rearrangement is operating though the C–C bond formation, we selected cinnamyl chloride to react with **2**, in the presence of ^{t}BuLi. However, to the light of the exclusive formation of product **13**, where no conjugative process was observed, we could confirm that the substitution of chloride took place preferentially (Scheme 2). The most challenging secondary alkyl bromide electrophiles, were also explored to be trapped with the borata-alkene intermediate **3**, and tertiary boronic esters **14**–**19** could be prepared in modest yields, introducing diverse sterically hindered cyclic systems, as well as compatible functional groups, such as cyanide in product **18** (Scheme 2).

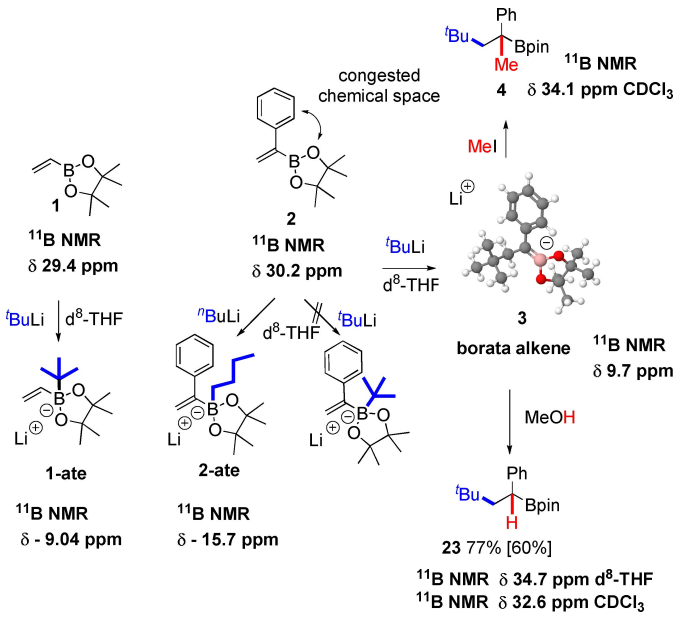
The preference in the coupling with alkyl bromides versus alkyl chlorides could be demonstrated when 1-bromo-4-chlorobutane reacted with **2** and ^{t}BuLi, generating only monoalkylated product **20**, preserving the C–Cl functionality throughout the three-component assembly (Scheme 3). Interestingly, selective alkyl trapping has also been observed when the borata-alkene intermediate **3** reacted with 1,4-dibromopentane or 2,3-dibromoprop-1-ene to form the tertiary boronic esters **21** and **22**, respectively (Scheme 3), demonstrating the preference for primary *versus* secondary alkyl bromides along the trapping sequence. An excess of NaO^{t}Bu base allowed the intramolecular deborylative cyclization towards **22a**. To the best of our knowledge,



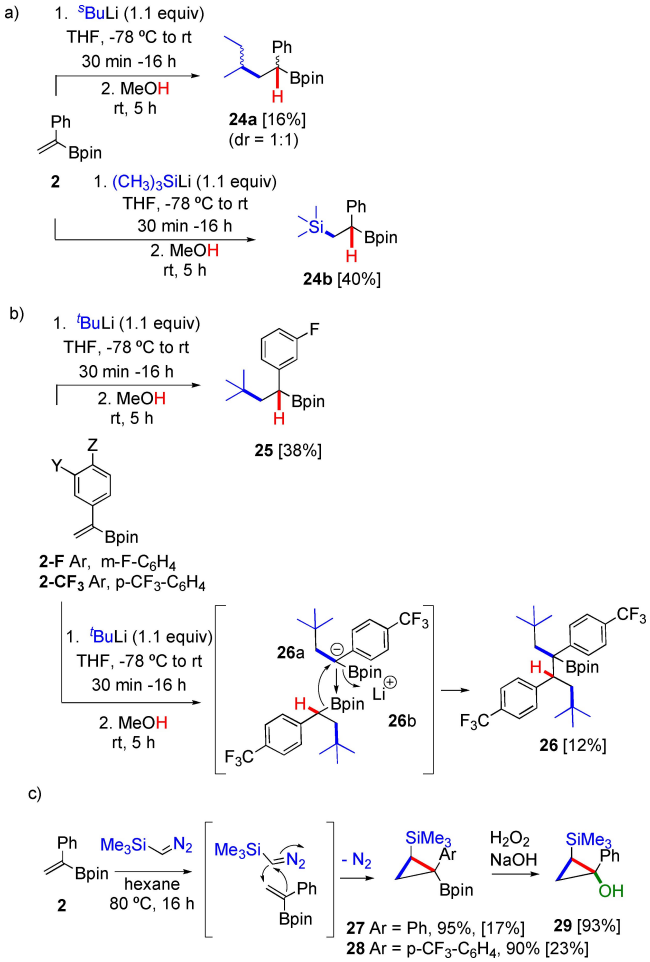
Scheme 3. Selective alkyl trapping with alkyldihalides. Yields calculated by ^{1}H NMR with naphthalene as internal standard. Yields in brackets represent isolated yields after purification with silica gel chromatography.

compounds **4**–**22** are prepared for the first time in this work.

Our work hypothesis, to justify the unexpected reactivity observed between alkenyl boronic ester **2** and ^{t}BuLi, is based on the olefin activation to nucleophilic addition of ^{t}Bu by virtue of the presence of the polarizing pinacolboryl substituent. In addition, the presence of the Ph group, in geminal position to the Bpin group, is of fundamental importance, because the Ph group in alpha position suppressed the formation of the boron "ate" complex, which led to the borata alkene as the favoured intermediate. The expected direct interaction of the ^{t}Bu group with the empty p orbital of boron seems to be precluded in this case due to the congested chemical space in the 1,1-disubstituted alkene **2** (Scheme 4). Whereas vinylboronic ester "ate" complex formation between unhindered vinylborane **1** and ^{t}BuLi (**1-ate**), or between ^{n}BuLi and **2** (**2-ate**) is favoured, to the best of our knowledge the vinylboronic ester "ate" complex formed between **2** and ^{t}BuLi, is unknown. This suppression of boron "ate" complex formation was unambiguously confirmed by ^{11}B nuclear magnetic resonance spectroscopy (in deuterated tetrahydrofuran solvent) by mixing **2** and ^{t}BuLi (1:1), since only one characteristic borata-alkene signal at $\delta = 9.7$ ppm was observed,[19] in contrast to the signals observed about



Scheme 4. ^{11}B NMR spectroscopic studies about ^{t}BuLi addition to alkenylboronates, followed by alkylation with MeI or protonated with MeOH.

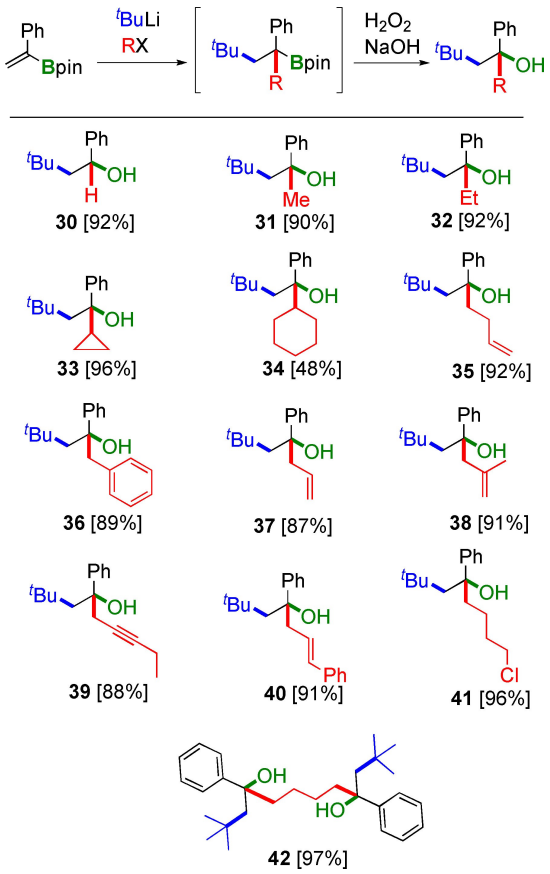


Scheme 5. Reactivity with a) alternative lithium bases, b) alternative 1,1-arylboryl alkenes and c) (trimethylsilyl)diazomethane (TMSDM).

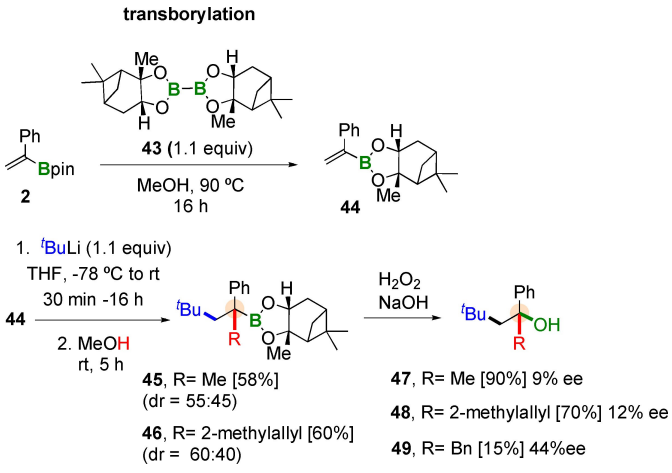
$\delta = -9.0$ and -15.7 ppm associated to boron "ate" species **1-ate** and **2-ate** (Scheme 4). A precedent on boron-activated nucleophilic addition to olefins by steric suppression of boron "ate" complex was reported for α-trimetylsilyl substituted vinyldimesitylboranes, although attempts to alkylate the borata-alkene intermediate were only successful with MeI.[23] The trapping of the α-boryl carbanion **3** with MeOH resulted in the formation of the secondary boronic ester **23** (Scheme 4), with a comparable yield to that obtained via iridium photoredox/nickel catalysis alkylation/arylation of **2**.[11]

When the alternative lithiated base sec-butyllithium (^{s}BuLi) was added to **2**, we were able to isolate the secondary boronic ester **24 a** (Scheme 5a), as a (1:1) mixture of the two diastereoisomers, by trapping of the borata-alkene intermediate with MeOH. The low conversion was due to an isolation issue. For comparison, the use of $(CH_3)_3SiLi$ to activate substrate **2**, followed by protonation with MeOH, allowed the isolation of the silylborylated specie **24 b** (Scheme 5a). The use of the alternative organometallic regent t-butyl-magnesium bromide was inefficient for the activation of **2**, and unreacted substrate was observed instead. The introduction of electron withdrawing substituents on the aryl group in **2-F, 2-CF$_3$**, was postulated to generate an extra stabilization of the carbanion lone pair on the α-boryl carbanion. When the ^{t}BuLi was added to the vinylboronic ester **2-F**, followed by MeOH, the corresponding secondary boronic ester **25** (Ar = m-F-C$_6$H$_4$) was isolated in 38% (Scheme 5b). However, when Ar = p-CF$_3$-C$_6$H$_4$, the reaction produced the tertiary boronic ester as a dimer **26** (Scheme 5b) suggesting a deborylative cross coupling pathway. We postulated a plausible interaction between the α-borylcarbanion **26 a** with the B of the secondary boronic ester **26 b**, via boron "ate" formation and 1,2-shift rearrangement (Scheme 5b).

We also postulated that a carbene addition on the terminal position of the alkene might be followed by an intramolecular C–C bond formation through the borata-alkene, with the concomitant N_2 release. When **2** reacted with (trimethylsilyl)diazomethane (TMSDM), the polysubstituted cyclopropanes **27** and **28** were essentially formed although isolated in low yield (Scheme 5c), becoming the first transition metal free catalysed cyclopropanation of alkenylboranes with TMSDM.[24,25] The relative stereoselectivity shows an exclusive *trans* configuration of the SiMe$_3$ and Bpin vicinal substituents, as well as in the oxidized silylcyclopropanol **29** (Scheme 5c).



Scheme 6. Application of dicarbofunctionalization of 1,1-arylboryl alkenes towards the synthesis of tertiary alcohols.



Scheme 7. Transborylation of **2** with B_2pai_2 (**43**) to isolate the corresponding chiral substrate 1,1-disubstituted alkenyl (+)-pinanediolboronic esters **44**, and subsequent dicarbofunctionalization with ^{t}BuLi and C(sp^3)-X/oxidation. Yields in brackets represent isolated yields after purification and ee calculated by HPLC.

The oxidation of the tertiary boronic esters prepared in this work has been conducted with H_2O_2/NaOH and the resulting tertiary alcohols were isolated in quantitative yields (Scheme 6). It is worth mentioning that tertiary alcohols **32**–**42** have been synthetized for the first time in this work and only 4,4-dimethyl-2-phenylpentan-2-ol (**31**) was earlier prepared via air-assisted addition of Grignard reagents to olefins[26] or via multicomponent oxyalkylation of styrenes enabled by hydrogen-bond-assisted photoinduced electron transfer.[27] With the aim to induce asymmetry in the new tertiary boronic esters, and the corresponding tertiary alcohols, we postulated a transborylation of 1-phenylvinylboronic acid pinacol ester **2** with bis-(+)-pinanediolato diboron (B_2pai_2) (**43**) to isolate the corresponding chiral substrate 1,1-disubstituted alkenyl (+)-pinanediolboronic ester **44** (Scheme 7).[28] The addition of ^{t}BuLi to **44** and the subsequent trapping with methyliodide or 2-methylallylbromide, resulted in the formation of the diastereoisomeric mixture of tertiary boronic esters **45** and **46**. The modest diastereomieric ratio was confirmed when oxidation of **45** and **46** generated the tertiary alcohols **47** and **48**, in 9% and 12% enantiomeric excess, respectively (Scheme 7). However, when the electrophilic trapping of the chiral alkene borata **44** was performed with benzylbromide, the tertiary alcohol **49** was isolated in 44% enantiomeric excess (Scheme 7). Similar e.e. values were obtained in the enantioselective version of the radical-polar crossover reaction with commercially available chiral (+)-vinylboronic acid pinanediol ester.[15] The increased enantioselectivity for product **49** over **47** and **48** might be due to the increased sterically hindrance provided by the chiral boryl moiety on the trapping reagent.

We have described here one operational simple unconventional intermolecular assembly across alkenylboranes. This methodology forms two C(sp^3)–C(sp^3) bonds through regioselective 1,2-dicarbofunctionalization of 1,1-arylboryl alkenes, generating tertiary boronic esters which are highly valuable compounds for diverse follow-up chemistry, such as oxidation towards tertiary alcohols. This methodology facilitates a rapid influx of molecular complexity inverting the trends of ^{t}BuLi, ^{s}BuLi, Me_3SiLi or Me_3SiCHN_2 addition to alkenylboronates allowing the generation of two new C(sp^3)–C(sp^3) bonds across the alkene, via borata-alkene intermediates, in the absence of catalyst, additives or any type of radical initiators.[29]

Experimental Section

Representative Procedure for 1,2-dialkylation. A flame dried 100 mL round-bottom flask equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane(**2**) (69.5 mg, 0.3 mmol, 1.0 equiv.) in dried THF (2 mL), then sealed with a rubber septum and put under a

nitrogen atmosphere at −78 °C. A solution of tert-butyllithium reagent (0.19 mL, 0.33 mmol, 1.1 equiv.) in hexane (1.7 M) was added dropwise and the reaction mixture was stirred for 30 minutes at −78 °C and then stirred at room temperature for 16 h. The reagent RX (0.45 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred for 5 h at room temperature. Finally, the reaction was quenched by addition of MeOH (5 mL) and extracted with Et_2O three times. The combined organic layers were dried by addition of $MgSO_4$ filtered through Celite and concentrated under reduced pressure. The NMR yield was calculated by comparison to an internal standard (naphthalene). The crude product was purified by flash column chromatography.

Representative Procedure for alkylation / protonation. A flame dried 100 mL round-bottom flask equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**2**) (69.5 mg, 0.3 mmol, 1.0 equiv.) in dried THF (2 mL), then sealed with a rubber septum and put under a nitrogen atmosphere at −78 °C. A solution of tert-butyllithium reagent (0.19 mL, 0.33 mmol, 1.1 equiv.) in hexane (1.7 M) was added dropwise and the reaction mixture was stirred for 30 minutes at −78 °C and then stirred at room temperature for 16 h. The reaction mixture was quenched by addition of MeOH (5 mL) and extracted with Et_2O three times. The combined organic layers were dried by addition of $MgSO_4$ filtered through Celite and concentrated under reduced pressure. The NMR yield was calculated by comparison to an internal standard (naphthalene). The crude product was purified by flash column chromatography.

Representative Procedure for cyclopropanation. A flame dried Schlenk tube equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**2**) (69.5 mg, 0.3 mmol, 1.0 equiv.) in dried hexane (0.5 mL), then sealed with a rubber septum and put under a nitrogen atmosphere. A solution of (trimethylsilyl)diazomethane (1.05 mL, 2.1 mmol, 7 equiv.) in hexane (2 M) was added dropwise and the reaction mixture was stirred for 16 h at 80 °C. After the reaction time, the solvent was evaporated in a rotatory evaporator and the NMR yield was calculated by comparison to an internal standard (naphthalene). The crude mixture was purified by silica gel chromatography.

Representative Procedure for oxidation of boronic esters. A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with the boronic ester (0.2 mmol) in THF (2 mL). A solution of NaOH (1.00 mL, 3 M) was added and the reaction mixture was stirred for 5 min. A solution of H_2O_2 (2.00 mL, 33%v/v) was added dropwise and the reaction mixture was stirred for 12 h. The crude was quenched with 2 mL of a saturated solution of $Na_2S_2O_3$ and extracted with diethyl ether. The organic phases were dried over $MgSO_4$ and concentrated in a rotatory evaporator. The oxidized product was purified by by silica gel chromatography.

Representative Procedure for transborylation of alkenylboranes. A flame dried Schlenk tube equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**2**) (69.5 mg, 0.3 mmol, 1.0 equiv.) and bis-(+)-pinanediolato diboron (0.6 mmol, 2 equiv.) in dried MeOH (2 mL), then sealed with a rubber septum and put under a nitrogen atmosphere. The reaction mixture was stirred for 16 h at 90 °C. After the reaction time, the solvent was evaporated in a rotatory evaporator and the NMR yield was calculated by comparison to an internal standard (naphthalene). The crude mixture was purified by silica gel chromatography.

Acknowledgements

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