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Transition metal and radical free 1,2-dicarbofunctionalisation of 1,1-arylboryl alkenes through dual C(sp³)-C(sp³) bond formation

Sara González,[a] Oriol Salvado [a] and Elena Fernández*[a]

We reveal here the regioselective nucleophilic addition of C(sp³) to 1,1-arylboryl alkenes, followed by nucleophilic attack of the α-boryl carbanionic intermediates to C(sp³) electrophiles, at room temperature. We envisioned this goal through engaged C(sp³) chemical entities avoiding metal catalysts, additives, radical initiators or specific irradiation. This multicomponent reaction guarantees that the new tetrasubstituted carbon formed retains all the C atoms from the three starting materials involved in the assembly.

Introduction

Multicomponent reactions (MCRs), wherein three compounds intermolecularly combine in a sequential manner, are revealed as ideal strategies in diversity-oriented synthesis. 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 multicomponent reactions. This type of dicarbofunctionalisation sequence provides 1,2-substituted alkanes, principally with the aid of catalytic amounts of Pd, Cu or Ni complexes.[1] The intrinsic sequences along the catalytic cycles, with the mentioned transition metal complexes, involves the formation of undesired byproducts, due to the cross coupling between both reagents or Heck-type products formation, as a consequence of inherent β-H-elimination pathways. These drawbacks limit the application of this method to essentially C(sp²) or C(sp) hybridised reagents, R¹-X and R²-Y, (Scheme 1A). Current efforts are focused to permit the efficient metal catalysed assembly of the three components, alkene / R¹-X / R²-Y, with particular emphasis to the formation of two C(sp³)–C(sp³) 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.

Since the intermolecular addition of two different C(sp³) alkyl groups across an alkene remains one of the most challenging 1,2-dicarbofunctionalization reactions, the use of accessible alkenylboronic esters as substrates represents a synthetic opportunity. Four strategic platforms were launched to allow the formation of two C(sp³)–C(sp³) bonds on vinylboronic acid pinacol ester **1** (Scheme 1B-E).
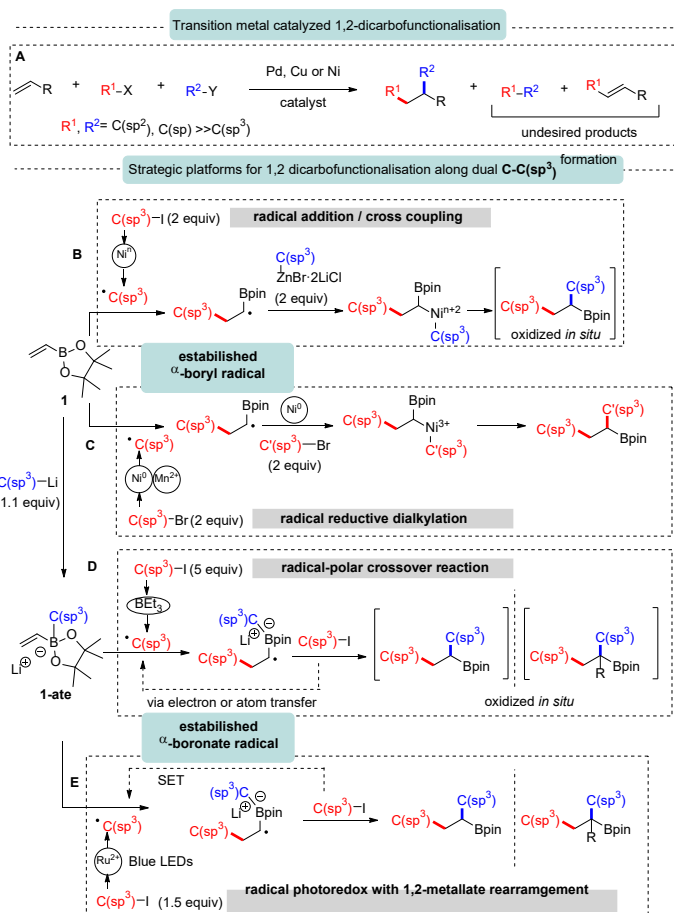
Scheme 1. Conceptual dicarbofunctionalisation of alkenes with formation of two C(sp³)–C(sp³) bonds: (A) Transition metal catalysed reactions, (B) Ni/radical catalytic process, (C) Ni/radical reductive dialkylation, (D) radical-polar crossover on boronate systems initiated by BEt₃, (E) radical photoredox with 1,2-metallate rearrangement.

a. Dept. Química Física i Inorgànica. University Rovira i Virgili, 43005, Tarragona, Spain. e-mail: mariaelena.fernandez@urv.cat
† Electronic Supplementary Information (ESI) available

In a first platform, a Ni/radical catalytic process adds C(sp³)I across **1**, followed by cross coupling with C(sp³)ZnBr·2LiCl (Scheme 1B).[9] The *in situ* oxidation of the C-B bond generates secondary alcohols in an enantioselective manner when chiral ligands modify the nickel complex. In a second platform, the nickel-catalysed 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 1C).[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(sp³)–C(sp³) bonds across the alkenyl boronate are not described. In a third platform, the *in situ* combination of vinylboronic esters and organolithium reagents (C(sp³)Li) forms the vinylboronic ester "ate" complex **1-ate**, that 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, converted *in situ* to secondary or tertiary alcohols by treatment with NaOH/H₂O₂ (Scheme 1D).[15] This significant advance do not require transition metal catalyst but BEt₃ (5 mol%) is used as radical initiator.[15,16] Interestingly, alkenylboronate complexes acted as good radical acceptors (proved only for perfluoroalkyl iodides, α-iodoesters and iodoacetonitrile) in the radical-polar crossover reaction. Other approaches explored that vinylboronic ester "ate" complexes participate in palladium-induced metalate rearrangement enabling 1,2-difunctionalized products although examples on formation of two C(sp³)–C(sp³) bonds across the alkenyl boronate are not described.[17] The fourth strategic platform is based on a radical addition of an electron-deficient alkyl radical to the vinylboronic ester "ate" complex **1-ate**, in the presence of visible light-irradiation, followed by electron transfer with another molecule of alkyl iodide, continuing the chain, and triggering a 1,2-metalate rearrangement (Scheme 1E).[18] With this methodology, two new C–C bonds can be created and the scope of the radical precursor includes α-iodo ketones, esters, nitriles, primary amides, α-fluorinated halo-acetates and perfluoroalkyl iodides.

Alkyl radicals can be regioselectively added to the unhindered position of terminal alkenes under Giese type reaction conditions.[19] In that context, the radical tert-butyl can be viewed as surrogate of C(sp³)-hybridized nucleophile with the ability to form C-C(sp³) bond at the terminal position of vinylB(pin) **1**, when is generated from ʹBuI and AIBN/Bu₃SnH,[20] or generated from visible light-activated Ir or Ru catalysts, (Scheme 2A).[11,12] However the merger of Ni/photoredox dual catalyst has only provided regioselective alkylation / arylation in the dicarbofunctionalization of **1** (Scheme 2A).[11,12] Alternatively, the addition of ʹBuLi to **1**, through alkenylboronate complex formation, incorporates an electrophile by radical addition at the terminal position with concomitant [1,2]-metalate shift placing the ʹBu group regioselectively at the internal position (Scheme 2B).[16] Under this panoramic overview, we envisioned a polar addition of the nucleophilic ʹBuLi 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(sp³)X (X=I, Br and Cl), via substitution pathways (Scheme 2C). 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 borataalkene resonance forms (Scheme 2C).[21,22] This new three component "all-alkyl" cross-coupling reaction inverts the trends of ʹBuLi addition to alkenylboronates and is capable of generate two new C(sp³)–C(sp³) bonds across the alkene, delivering valuable tetrasubstituted carbon centers, in the absence of catalyst, additives or any type of radical initiators.[23]
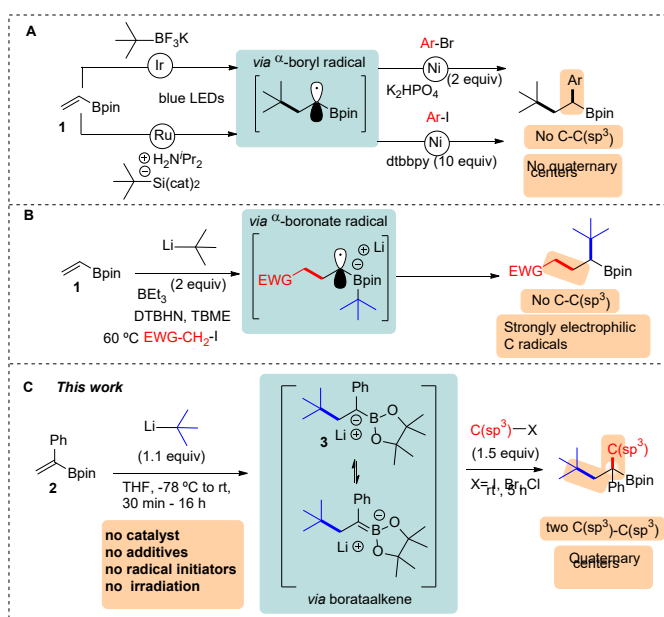
Scheme 2. Dicarbofunctionalisation with ʹBu moieties: (A) alkylarylation of vinyl boronates, via Ni photoredox dual catalysis, (B) alkenylboronate complex acting as good radical acceptor in the radical-polar crossover reaction. (C) This work: discovery of ʹBuLi and C(sp³)-X addition to **2**, generating two C(sp³)–C(sp³) bonds across the alkene, forming valuable tetrasubstituted carbon atoms, in the absence of catalyst, additives or radical initiators.

Results and Discussion

As a proof of concept, we explored the addition of 1.1 equiv of ʹBuLi to 1-phenylvinylboronic acid pinacol ester **2**, at -78 ºC 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 3). The formation of two new C(sp³)–C(sp³) bonds across the 1,1-arylboryl alkene was conducted regioselectively placing the ʹBu group at the terminal position and the Me group at the internal position, providing a valuable quaternary carbon atom.
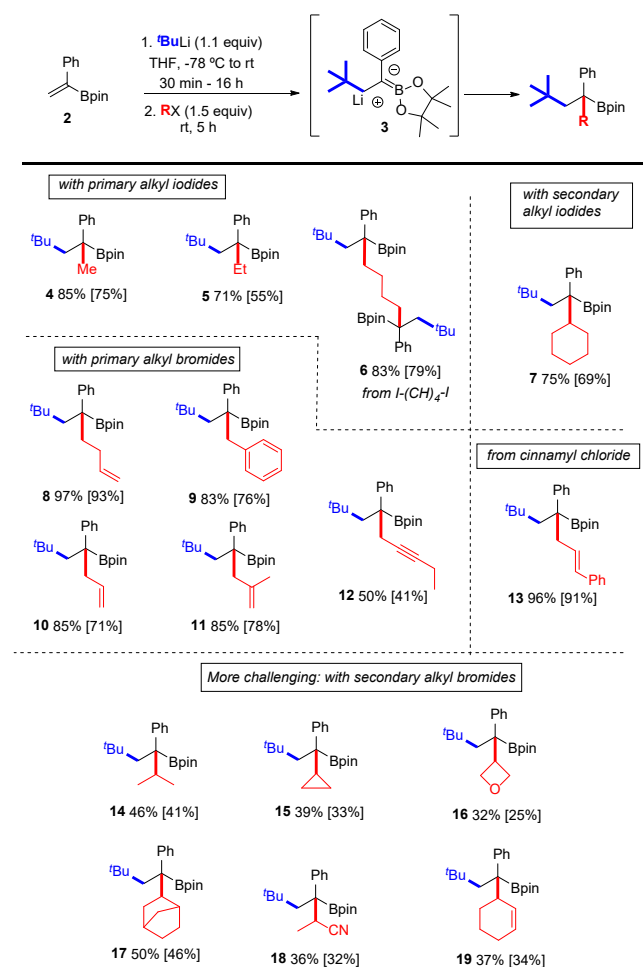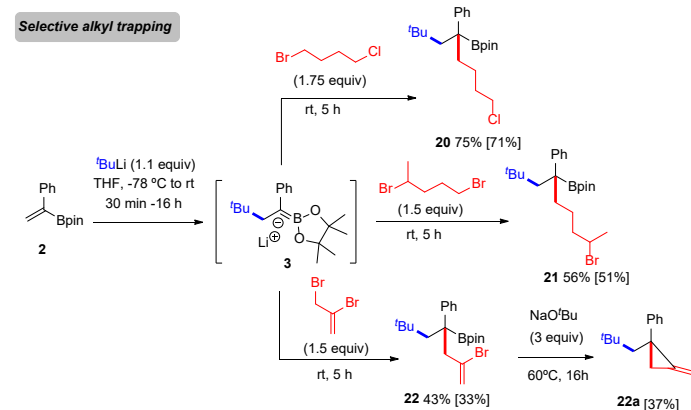
Scheme 3. Dicarbofunctionalisation with ^{t}BuLi and primary / secondary C(sp^3)-X. Reactions were run on a 0.3 mmol scale. Yields values reflect product quantification by ^{1}H NMR with naphthalene as internal standard. Yields in brackets represent isolated yields after purification with silica gel chromatography.

The simplicity of the three component assembly, where neither catalysts or radical precursors nor photoredox reaction conditions were involved, could be extended to other primary and secondary alkyl iodides, achieving comparable 1,2-dicarbofunctionalisation reaction outcomes (Scheme 3). In particular, the tertiary boronic esters **5**-**7** were isolated, by adding EtI, I(CH$_2$)$_4$I and CyI respectively, highlighting the double dicarbofunctionalised product **6**, where two tetrasubstituted carbon atoms are simultaneously formed (Scheme 3). Remarkably, this significant increase of the molecular complexity involves five-components assembly in a simple operational step. However, the addition of the tertiary alkyl iodide ^{t}BuI, PhI and vinyl-I resulted inefficient through the electrophilic trapping with the borataalkene intermediate **3**. 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 3). Benzyl bromide was the next challenging reagent to be 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 3). Allyl bromides were explored next and the tertiary homoallylic boronic esters **10** and **11** could be efficiently prepared (Scheme 3). The tolerance of alternative functional groups along the 1,2-dicarbofunctionalisation process was studied with the introduction of the electrophile 1-bromopent-2-yne, preserving the triple bond intact since no allene group was detected in the isolated product **12** (Scheme 3).

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 product **13** formed, where no conjugative process was observed, we could confirm that the substitution of chloride took place preferentially (Scheme 3). The most challenging secondary alkyl bromide electrophiles, were also explored to be trapped with the borataalkene intermediate **3**, and tertiary boronic esters **14**-**19** could be easily prepared in modest yields, introducing diverse sterically hindered cyclic systems, as well as compatible functional groups, such as cyanide in product **18** (Scheme 3).

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 4). Interestingly, selective alkyl trapping has also been observed when the borataalkene intermediate **3** reacted with 1,4-dibromopentane or 2,3-dibromoprop-1-ene to form the tertiary boronic esters **21** and **22**, respectively (Scheme 4), demonstrating the preference for primary versus secondary alkyl bromides along the trapping sequence. An excess of NaO^{t}Bu base allowed the deborylative cyclization towards **22a**. To the best of our knowledge, all the tertiary boronic esters **4**-**22**, synthesised through the polar nucleophilic tactics, are new.


Scheme 4. Selective alkyl trapping with alkyldihalides. Reactions were run on a 0.3 mmol scale. Yields values reflect product quantification by ^{1}H NMR with naphthalene as internal standard. Yields in brackets represent isolated yields after purification with silica gel chromatography.

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. But also the presence of the Ph group, in geminal position to the Bpin group, is of fundamental importance. 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 5*)*. Whereas vinylborane 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 alkeneborata signal at δ = 9.7 ppm was observed, in contrast to the signals observed about δ = -9.0 and -15.7 ppm associated to boron "ate" species **1-ate** and **2-ate** (Scheme 5). A particular 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 alkeneborata intermediate were only successful with MeI.[24] Our hypothesis for the alkylation of alkeneborata intermediate **3**, via S_N2 nucleophilic substitution, gains strength since it occurs with aliphatic $C(sp^3)$ halides (including allyl halides) but it does not react with aryl or vinyl halides, or tertiary alkyl iodides. The quantification of the nucleophilic character of α-boryl carbanions towards organic electrophiles, was previously predicted through theoretical calculations for the S_N2 nucleophilic substitution reaction between bromoethane and alkeneborata carbanions, containing mesitylboranes or piancolboranes, demonstrating that the free-energy barriers ($\Delta G^{\ddagger}_{SN2}$) are significantly lower when pinacolboryl motifs are involved.[22] In addition, despite the fact that the Ph substituent on α-boryl carbanion **3** provides an extra stabilization of the carbanion lone pair,[22] the straightforward reactivity with aliphatic $C(sp^3)$ halides is predominant. Interestingly, the trapping of the α-boryl carbanion **3** with MeOH resulted in the formation of the secondary boronic ester **23** (Scheme 5), with a comparable yield to that obtained via iridium photoredox/nickel catalysis alkylation / arylation of **2**.[11]

To showcase the potential of this unpredicted 1,2-dicarbofunctionalization of alkenylborane, we launched a systematic study modifying the nucleophilic lithiated base, as well as the aryl moieties in the substrate. When sec-butyllithium (*s*BuLi) was added to **2**, instead of *t*BuLi, followed by MeOH trapping of the borataalkene intermediate, we were able to isolate the secondary boronic ester **24a** (Scheme 6), as a (1:1) mixture of the two diastereoisomers. For comparison, the use of $(CH_3)_3SiLi$ for the nucleophilic attack to **2**, followed by protonation with MeOH, allowed the isolation of the silylborylated specie **24b** (Scheme 6). Other organometallic reagents such as alkyl-magnesium, -copper or -zinc species were inefficient for the activation of **2**.
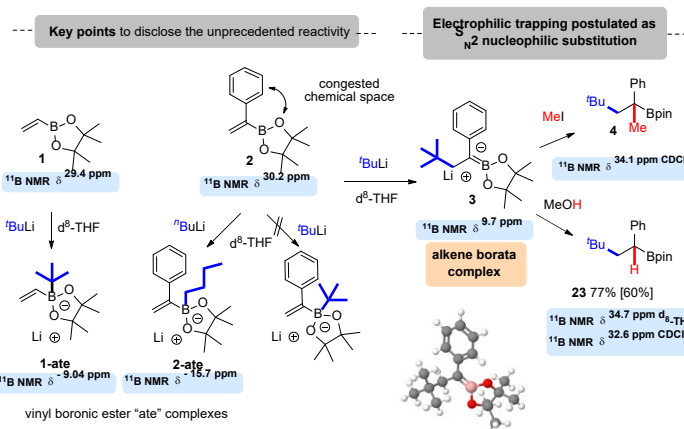

Scheme 5. ^{11}B NMR spectroscopic studies are consistent with the formation of intermediate borataalkene **3**, inverting the boron "ate" trends in *t*BuLi addition to alkenylboronates, followed by alkylation with MeI or protonated with MeOH
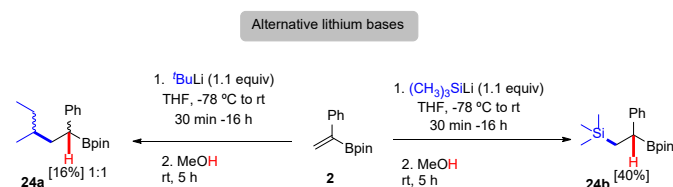

Scheme 6. Dicarbofunctionalisation of alkenylborane **2** with *s*BuLi and $(CH_3)_3SiLi$, as alternative lithium bases.

The introduction of electron withdrawing substituents on the aryl group in **2-F, 2-CF₃,** 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_6H_4) was isolated in 38% (Scheme 7). However, when Ar = p-CF_3-C_6H_4, the reaction produced the tertiary boronic ester as a dimer **26** suggesting a deborylative cross coupling pathway (Scheme 7).
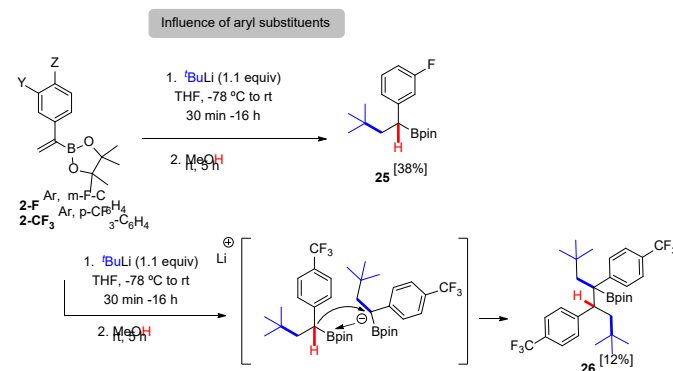
Scheme 7. Dicarbofunctionalisation of arylborylakenes **2-F** and **2-CF₃** with *t*BuLi / MeOH.

With the aim to complement the dicarbofunctionalisation of 1-phenylvinylboronic acid pinacol ester **2**, we explored a direct cyclopropanation process through the addition of (trimethylsilyl)diazomethane (TMSDM) to **2**. We postulated that the carbene addition on the terminal position of the alkene, might be followed by the intramolecular C-C bond formation through the α-boryl carbanion **3**, with the concomitant N_2 release. Polysubstituted cyclopropanes **27** and **28** were essentially formed although isolated in low yield (Scheme 8), becoming the first transition metal free catalysed cyclopropanation of alkenylboranes with TMSDM.[25-27] The relative stereoselectivity shows an exclusive *trans* conformation of the $SiMe_3$ and Bpin vicinal substituents on the new cyclopropanes which are prepared for the first time in this work (Scheme 8). Subsequent oxidation of **27**, with H_2O_2/NaOH, generated the corresponding silylcyclopropanol **29** retaining the *trans* conformation between $SiMe_3$ and OH (Scheme 8). This straightforward access to stereoselective polyfunctional cyclopropanes improves previous attempts involving titanium(II)-mediated coupling of vinylsilanes and esters to get enriched mixtures of stereoisomers.[28,29]
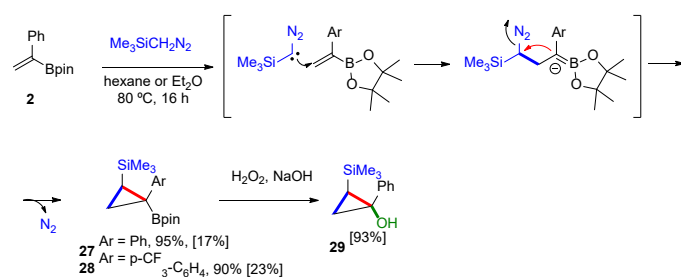
Scheme 8. Use of diazo compounds to perform a straightforward cyclopropanation followed by oxidation pathway. Yields values reflect product quantification by ^{1}H NMR with naphthalene as internal standard. Yields in brackets represent isolated yields after purification.

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. It is worth mentioning that tertiary alcohols **32–42** have been synthetized for the first time in this work (Scheme 9), and only 4,4-dimethyl-2-phenylpentan-2-ol (**31**) was earlier prepared via air-assisted addition of Grignard reagents to olefins[30] or via multicomponent oxyalkylation of styrenes enabled by hydrogen-bond-assisted photoinduced electron transfer.[31]

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 (B₂pai₂) (**43**) to isolate the corresponding chiral substrate 1,1-disubstituted alkenyl (+)-pinanediolboronic ester **44** (Scheme 10).[32] 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**.
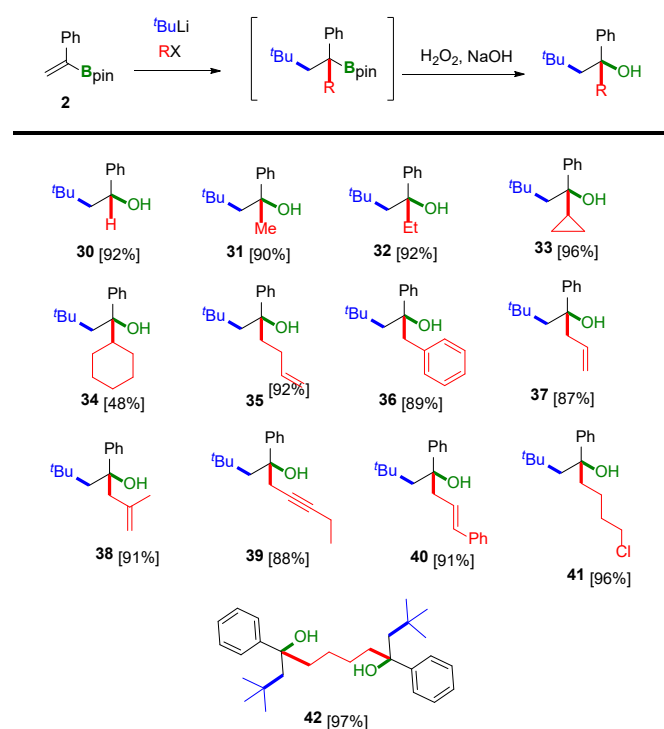
Scheme 9. Transfomation of tertiary boronic esters into tertiary alcohols by oxidation with H_2O_2/NaOH.

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 10). 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 10). 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]
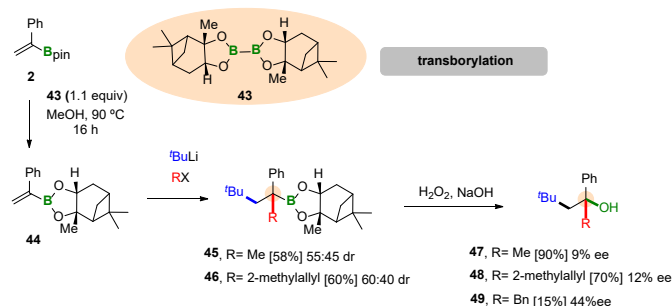
Scheme 10. Transborylation of **2** with B₂pai₂ (**43**) to isolate the corresponding chiral substrate 1,1-disubstituted alkenyl (+)-pinanediolboronic esters **44**, and subsequent dicarbofunctionalisation with *t*BuLi and C(sp³)-X / oxidation. Yields in brackets represent isolated yields after purification and ee calculated by HPLC.

Conclusions

We described here one operational simple multicomponent reaction for an unconventional intermolecular assembly of alkenylborane / R^1-X / R^2-Y forming two $C(sp^3)$–$C(sp^3)$ bonds through regioselective 1,2-dicarbofunctionalisation, generating tertiary boronic esters which are highly valuable compounds for diverse follow-up chemistry. Access to tertiary boronic esters, bearing tetrasubstituted carbon centers, contributes to enhance the molecular complexity field. This new three component "all-alkyl" cross-coupling reaction facilitates this rapid influx inverting the trends of ^{t}BuLi addition to alkenylboronates allowing the generation of two new $C(sp^3)$–$C(sp^3)$ bonds across the alkene, via borataalkene intermediates, in the absence of catalyst, additives or any type of radical initiators.

Author Contributions

S. G and O. S. performed the synthetic experiments and analysed the data. E. F. directed the project and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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