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Review

Palladium-Catalyzed Cross-Coupling Reactions of Borylated Alkenes for the Stereoselective Synthesis of Tetrasubstituted Double Bond

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Abstract: The stereoselective formation of tetrasubstituted alkenes remains one of the key goals of modern organic synthesis. In addition to other methods, the stereoselective synthesis of tetrasubstituted alkenes can be achieved by means of cross-coupling reactions of electrophilic and nucleophilic alkene templates. The use of electrophilic templates for the stereoselective synthesis of tetrasubstituted alkenes has previously been described. Therefore, the present review summarizes the procedures available for the stereoselective preparation of tetrasubstituted alkenes using stable and isolable nucleophilic templates.

Keywords: Suzuki reaction; stereoselective synthesis; borylation; transition-metal-catalyzed reactions; tetrasubstituted alkene

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1. Introduction

Alkenes are organic compounds with a double bond between two carbon atoms. Such compounds have undergone tumultuous development in terms of their preparation, reactivity, and applications in the fields of materials and medicinal chemistry. The applications of alkenes in organic synthesis include carbonyl olefin metathesis [1], alkene epoxidation [2], hydrogenation [3], and transition-metal-catalyzed functionalization [4,5]. Those alkenes with four different substituents represent a specific group of alkenes. They are usually referred to as tetrasubstituted alkenes, and they are considered attractive compounds due to their synthesis and application potential. An interesting feature of tetrasubstituted double bonds is the presence of four substituents, which allows for better modification of their properties via the introduction of different substituents. An example of a biologically relevant alkene is tamoxifen (**F1–1**). Variations of the substituents on the double bond can yield other biologically relevant derivatives of tamoxifen **F1–2** and GDC-0810 (**F1–3**), which have received considerable attention from synthetic [6] and biological [7–9] perspectives (Figure 1).

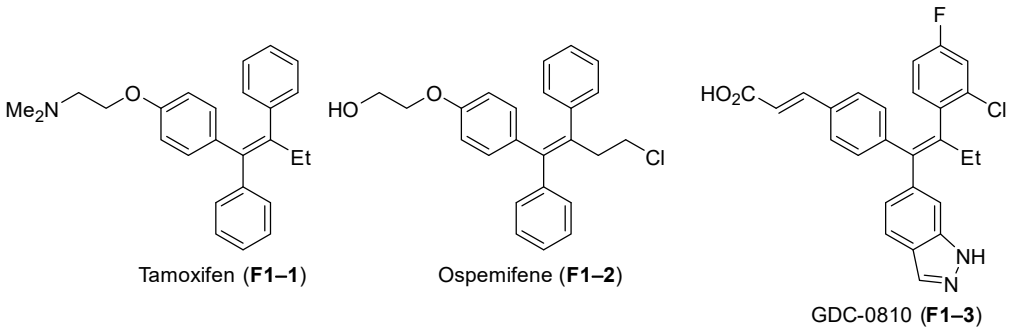
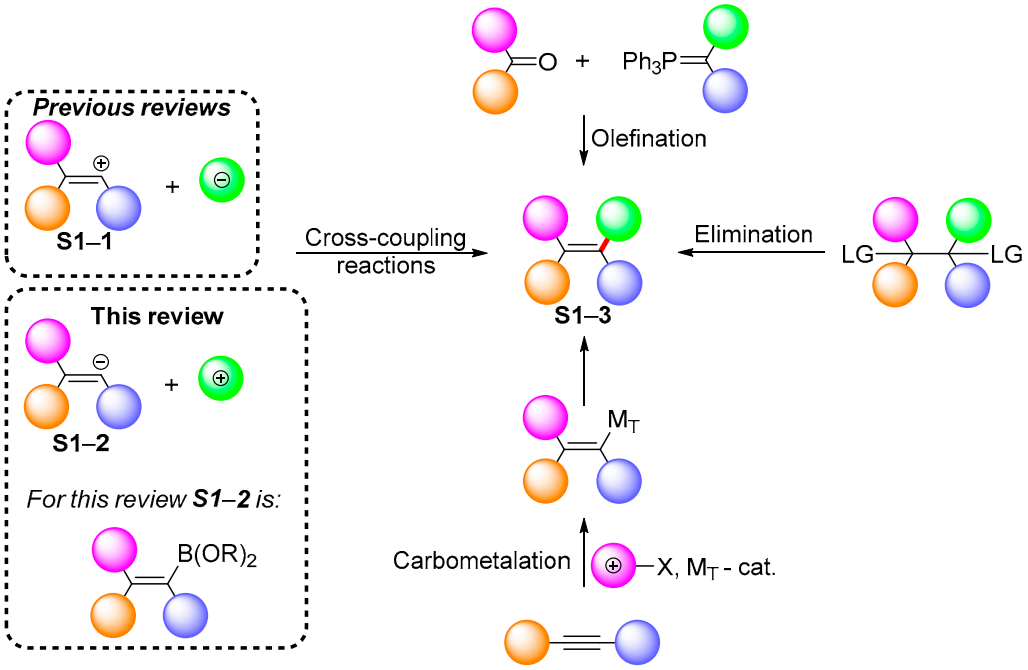


Figure 1. Structure of tamoxifen and related tetrasubstituted alkenes.

The general procedures available for the preparation of tetrasubstituted alkenes **S1–3** can be divided into several groups. The oldest procedures are arguably those involving elimination and olefination reactions, although it must be acknowledged that they are associated with a considerable disadvantage due to their low stereoselectivity in certain cases (Scheme 1) [10,11]. Carbometalation of alkynes [12–16] is a simple procedure for the preparation of tetrasubstituted alkenes. Yet, a typical drawback associated with the carbometallation of alkynes is the limited regioselectivity of the carbometallation step, especially for alkynes bearing substituents with similar electron and steric properties. The frequently used procedure for the stereoselective preparation of tetrasubstituted alkenes makes use of transition-metal-catalyzed cross-coupling reactions of electrophilic **S1–1** templates. The popularity of such procedures can be attributed to the availability of the electrophilic templates **S1–1** and organometallic compounds used for the cross-coupling reactions. This concept has been the subject of several reviews in previous years [17–21]. However, procedures that use nucleophilic alkene templates **S1–2** for the stereoselective synthesis of alkenes are also widely used, although this concept has not previously been the subject of a review article.



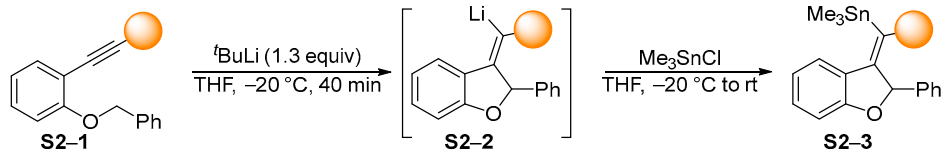
Scheme 1. General approaches to tetrasubstituted alkenes.

Nucleophilic alkene templates represented by a borylated double bond **S1–2** are an important alternative for the stereoselective preparation of tetrasubstituted alkenes for researchers involved in organic synthesis, materials, and medicinal chemistry. Therefore, the aim of this review is to summarize procedures developed for the stereoselective synthesis of tetrasubstituted alkenes based on the cross-coupling reactions of trisubstituted alkenylboronic acids and alkenylboronic acid esters over the last seven years. In addition, the procedures available for the preparation of alkenylboronic acids and alkenylboronates will also be briefly mentioned here, although it is not the aim of this review to provide a complete list of them, as prior work has already done so [21,22]. Although alkenylboronic acid derivatives have lower toxicity compared to alkenylstannanes, this review also briefly summarizes the most recent developments in the use of alkenylstannanes for the stereoselective preparation of tetrasubstituted alkenes.

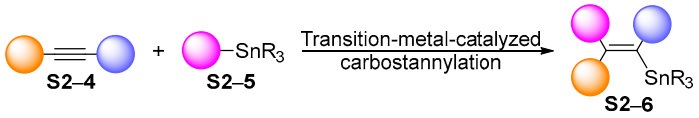
2. Recent Developments in Stereoselective Synthesis of Tetrasubstituted Alkenes by Palladium-Catalyzed Cross-Coupling Reactions of Trisubstituted Alkenylstannanes and Alkenylsilanes

Depending on the properties of the organometallic compounds, a variety of procedures can be used to prepare metalated tetrasubstituted alkenes. The use of Grignard and organozinc reagents is limited by their low stability in acidic conditions. Tetrasubstituted alkenyl stannanes exhibit substantially better stability when compared with Grignard and organozinc reagents. Recent approaches to stannylated double bonds include Li–Sn exchange reactions. In this case, the organolithium compounds generated in situ reacted with trialkyltin chlorides (Scheme 2a) [23]. A different procedure for the preparation of the stannylated tetrasubstituted double bond makes use of the transition-metal-catalyzed carbostannylation of internal alkynes (Scheme 2b) [24,25]. Finally, alkenyl stannanes can be prepared by means of cyclization procedures, including the cobalt-catalyzed Pauson–Khand reaction [26], radical cyclization [27], or [4 + 2] cycloaddition [28] (Scheme 2c).

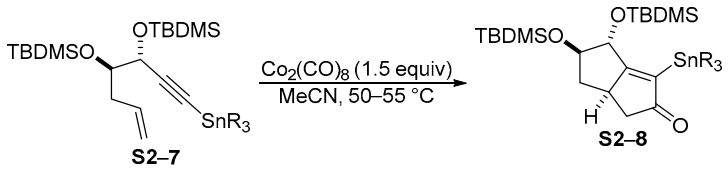
(a) *Synthesis of tetrasubstituted alkenyl stannanes by Li–Sn exchange reaction:*



(b) *Synthesis of tetrasubstituted alkenyl stannanes by transition-metal-catalyzed carbostannylation:*

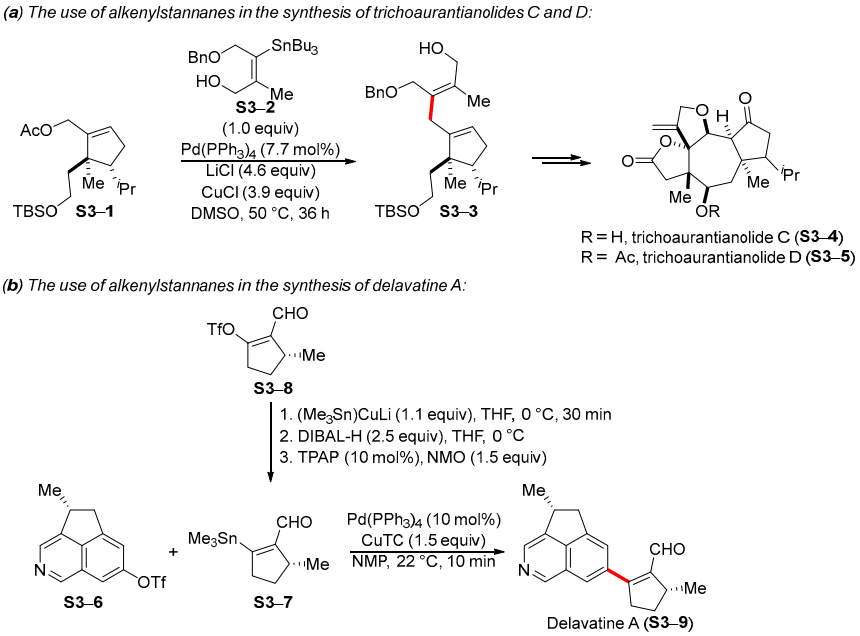


(c) *Synthesis of tetrasubstituted alkenyl stannanes by transition-metal-catalyzed carbocyclization:*



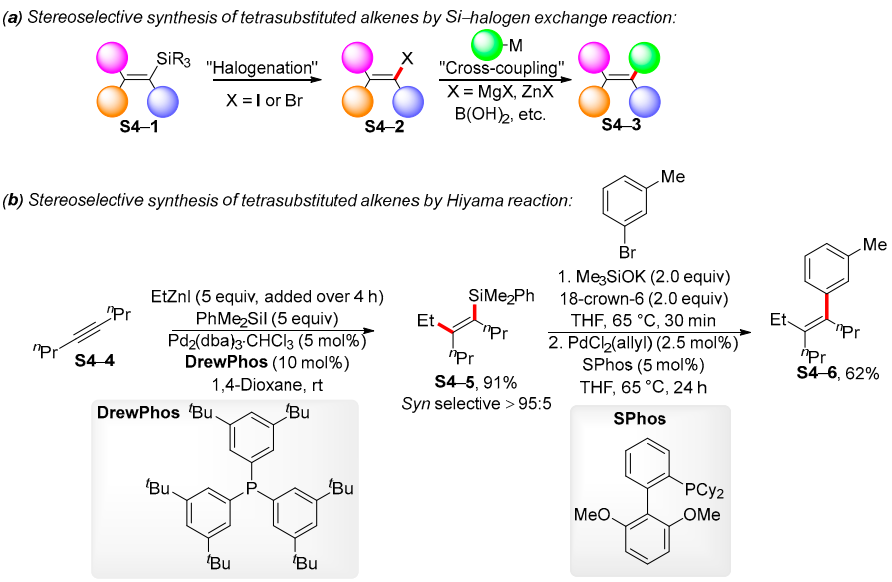
Scheme 2. Synthetic approaches to tetrasubstituted alkenyl stannanes (**a**–**c**).

Stannylated tetrasubstituted alkenes have a wide range of applications, including the synthesis of natural compounds. Aside from the other natural products that can be synthesized by means of the Stille reaction [29–33], the organostannanes attached to the acyclic **S3–2** and cyclic **S3–7** double bond have been used in the preparation of trichoaurantianolides C and D and delavatine A (Scheme 3). The preparation of intermediate **S3–3** during the synthesis of trichoaurantianolides C and D is accomplished via the cross-coupling reaction of allyl acetate with stannane **S3–2** [34]. Analogously, the formation of delavatine A (**S3–9**) is completed via the Stille reaction of aryl triflate **S3–6** with cyclic stannane **S3–7** [35]. It is worth noting that cyclic stannane **S3–7** is prepared from triflate **S3–8** by means of the reaction with the corresponding cuprate. In addition to the above-mentioned applications of organostannanes with a cyclic and acyclic tetrasubstituted double bond, the Stille reactions of similar stannylated tetrasubstituted alkenes have been used to synthesize substrates for the thermal ring expansion of boroles [36], palladium-catalyzed carbocyclization [37], the cascade reaction [38], and other reactions [39–43].



Scheme 3. The use of tetrasubstituted alkenylstannanes in the total synthesis (**a**,**b**).

An alternative method for the preparation of tetrasubstituted alkenes based on nucleophilic templates involves the use of a silylated double bond. This type of silane, as represented by the general structure **S4–1** (Scheme 4a), is not often used for the preparation of tetrasubstituted alkenes by means of their transition-metal-catalyzed reaction with electrophiles. The most common means of using alkenyl silane **S4–1** involves the substitution of the SiR_3 group for the halogen via halogenation [44,45]. Then, the obtained organohalide **S4–2** is subsequently used in cross-coupling reactions with organometallic reagents. In addition, the Hiyama reaction of silylated alkenes can be used for the preparation of tetrasubstituted alkenes. An example published in 2020 makes use of the *syn*-carbosilylation of oct-4-yne (**S4–4**), which is catalyzed by a palladium catalyst and a DrewPhos ligand to synthesize alkene **S4–5** (Scheme 4b) [46]. Interestingly, the use of a JessePhos ligand prefers *anti*-carbosilylation. Then, the stereoselective synthesis of the tetrasubstituted alkene **S4–6** is achieved via the Hiyama reaction under Denmark conditions [47].

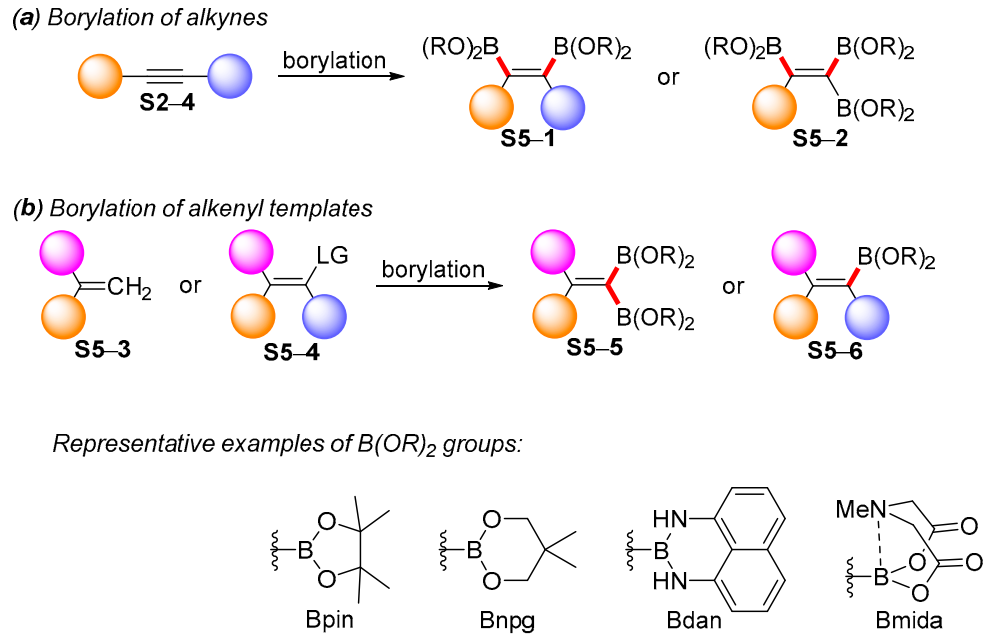


Scheme 4. An application of organosilanes for the stereoselective synthesis of tetrasubstituted alkenes (**a**,**b**).

3. Acyclic Boron-Based Tetrasubstituted Double Bond Templates

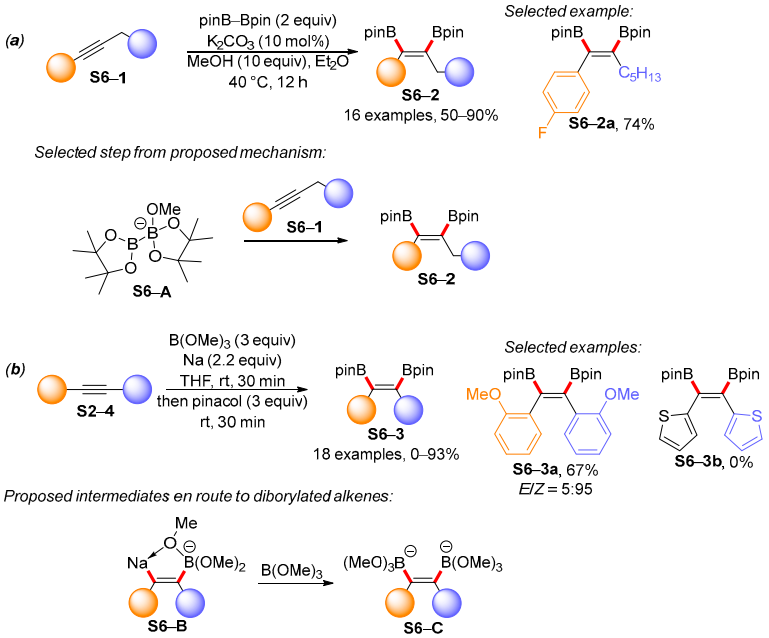
3.1. Synthetic Approaches to Acyclic Borylated Alkenes

Typically, the preparation of borylated tetrasubstituted alkenes begins with two readily available starting materials: alkyne **S2–4** and alkenes **S5–3** and **S5–4**. In this way, various types of borylated alkenes can be synthesized, including the mono-, di-, and triborylated templates **S5–1**, **S5–2**, **S5–5**, and **S5–6** (Scheme 5).



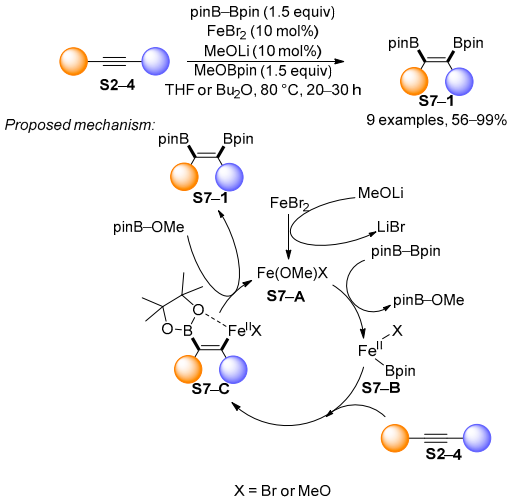
Scheme 5. Frequently synthesized borylated acyclic tetrasubstituted alkenes (**a**,**b**).

The preparation of diborylated alkenes is a widespread process that makes use of alkynes as the starting materials. The transition-metal-free borylation of alkyne **S6–1** can be performed in the presence of a catalytic amount of base, as described by Song (Scheme 6a) [48]. An optimization study determined that 10 mol% of potassium carbonate gave the best yields of borylated alkene **S6–2**. The reaction tolerates a minimal number of functional groups, and a reaction mechanism has been proposed based on experimental studies. This proposal involves the formation of an ate complex **S6–A** which reacts with the starting alkynes **S6–1** to give the borylated alkenes **S6–2**. An analogous procedure for the preparation of diborylated alkenes is shown in Scheme 6b [49]. The formation of the borylated product is achieved through the reduction of alkyne **S2–4** with sodium in the presence of trimethyl borate. The published reaction involves the preparation of 18 diborylated alkenes **S6–3**, while the proposed mechanism for the formation of the products **S6–3** considers the formation of the intermediate **S6–B** by means of the reduction of the triple bond via a SET (single electron transfer) mechanism, followed by transmetallation to give the ate complex **S6–A**, which reacts with pinacol to provide the major reaction products. It is important to note that internal alkynes with aryl and alkyl substituents require three equivalents of sodium dispersion.



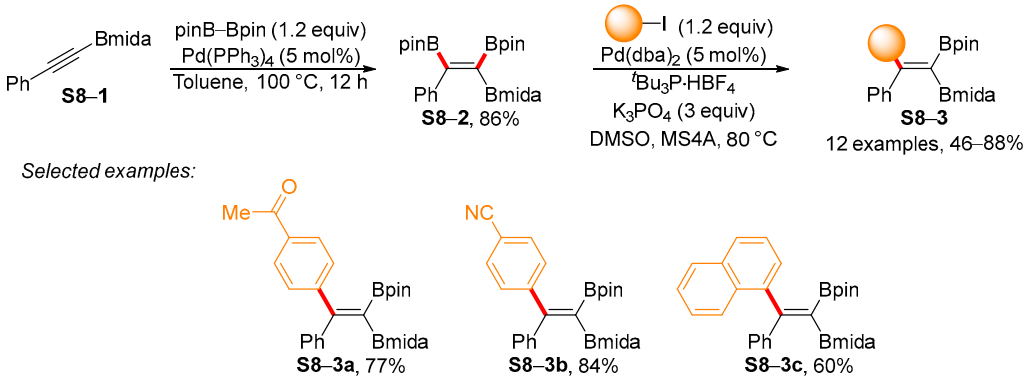
Scheme 6. Transition-metal-free route to diborylated alkenes by base-catalyzed borylation of internal alkynes (**a**) and sodium mediated borylation of internal alkynes (**b**).

The fact that borylmetallation remains a popular method for the preparation of diborylated tetrasubstituted alkenes was demonstrated by Nakamura (Scheme 7) [50]. Here, the starting internal alkyne **S2–4** is diborylated in the presence of a catalytic amount of iron (II) dichloride with limited scope and good functional group tolerance, which includes a substrate with a bromine atom or ester group. The authors also proposed and confirmed the mechanism behind the discovered reaction via quantum chemical calculations. The first step of the reaction involves transmetallation with lithium methoxide, and the resultant intermediate **S7–A** subsequently reacts with pinB–Bpin and then with alkynes **S2–4** to form the alkenyl complexes **S7–C**. Finally, the borylferration product **S7–C** reacts with MeOBpin to form the main reaction product **S7–1**. In addition to the above-mentioned examples of alkyne diborylation, examples of cobalt-catalyzed di- and monoborylation of internal alkynes have previously been published. This borylation has mostly been studied on pinacolborane affording a trisubstituted double bond with the Bpin moiety. However, for a limited number of internal alkynes, pinB–Bpin has been used to provide diborylation products with limited stereoselectivity [51].

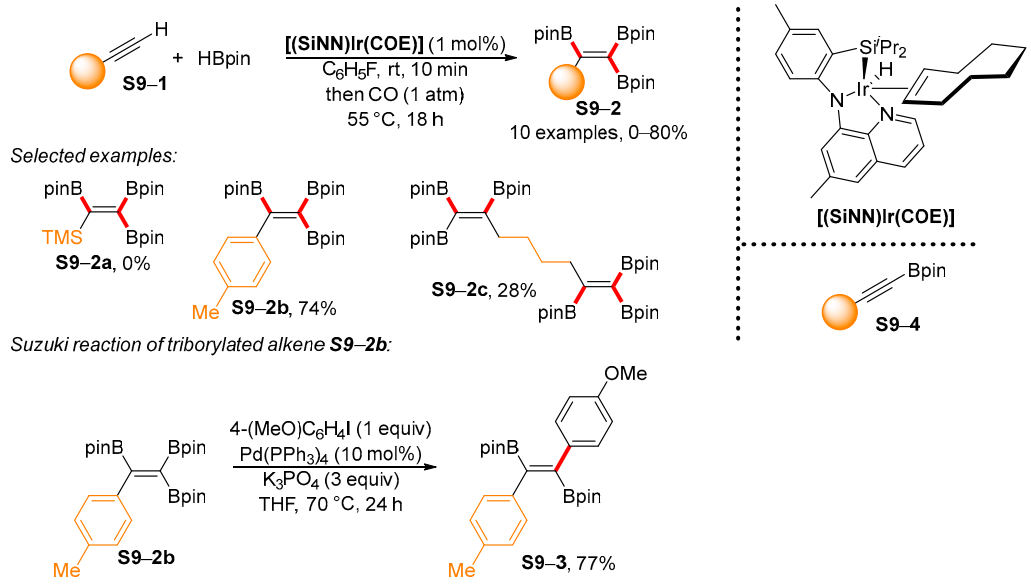


Scheme 7. Iron-catalyzed diborylation of internal alkynes.

The original procedure for the preparation of the triborylated alkene **S8–2** starts with alkyne **S8–1** substituted with the Bmida moiety (Scheme 8). The subsequent Suzuki reaction of boronate **S8–2** with aryliodides proceeds with different regioselectivity when compared with the Suzuki reaction given in Scheme 9. The reaction scope of the Suzuki reaction is limited to 12 examples, albeit with satisfactory functional group tolerance [52].



Scheme 8. Palladium-catalyzed diborylation of Bmida alkynes and subsequent Suzuki reaction.

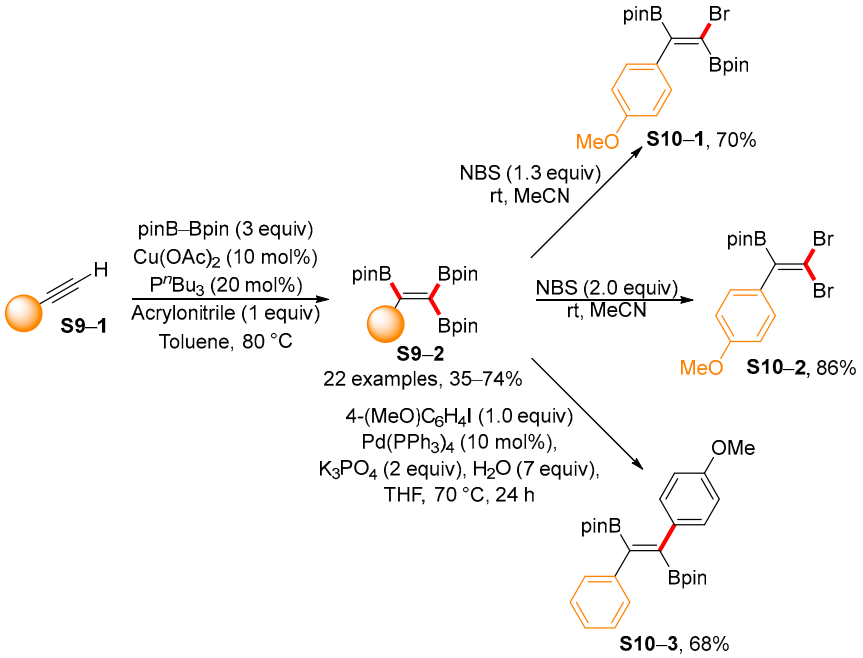


Scheme 9. Synthesis of triborylated alkenes via C–H borylation of terminal alkenes followed by diborylation.

A slightly different procedure for the preparation of triborylated alkenes relies on the iridium-catalyzed C–H borylation of terminal alkynes to form the borylated alkynes **S9–4**, which are then further borylated in the presence of carbon monoxide (Scheme 9) [53,54]. The reaction is limited in terms of its scope and functional group tolerance (see unreactive alkyne **S9–2a**), although the selected example **S9–2c** illustrates how diborylated dienes can also be prepared via this procedure. In addition, the authors showed that borylated alkene **S9–2b** reacts in the Suzuki reaction with trans selectivity, thereby affording the diborylated alkene **S9–3** in a 77% isolated yield.

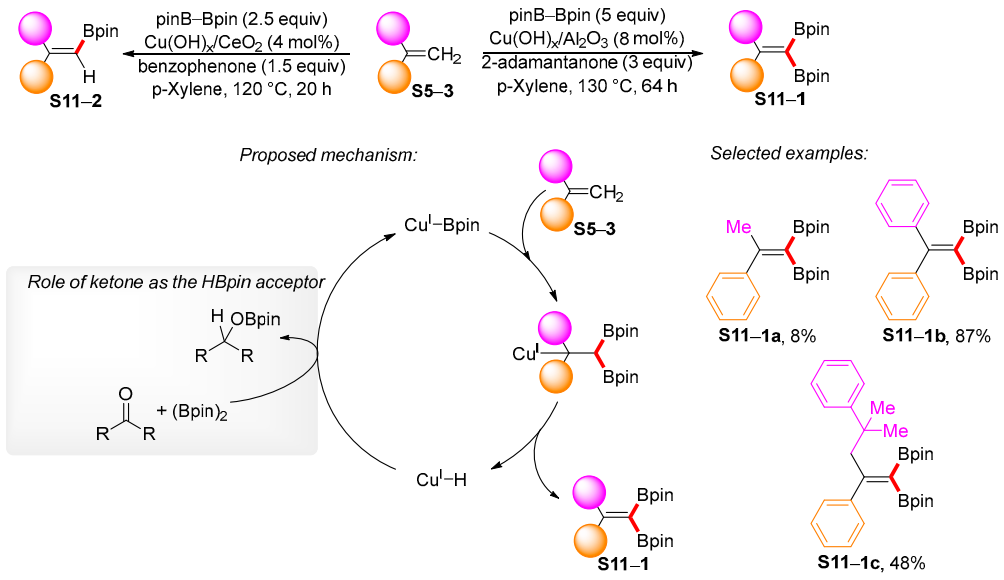
A similar approach for the preparation of mono- and diborylated alkenes was published in 2020 (Scheme 10) [55]. The starting terminal alkyne **S9–1** is triborylated in the presence of a catalytic amount of copper acetate and a tributylphosphine ligand. The developed borylation conditions tolerate a wide variety of functional groups, including –CN, –Cl, –F, or –CO_2Me groups. The proposed mechanism involves the borylation of

terminal alkyne followed by *syn*-cupraborylation. The triborylated alkene **S9–2** can be used in a Suzuki reaction with trans regioselectivity or in a Bpin–halogen exchange reaction.



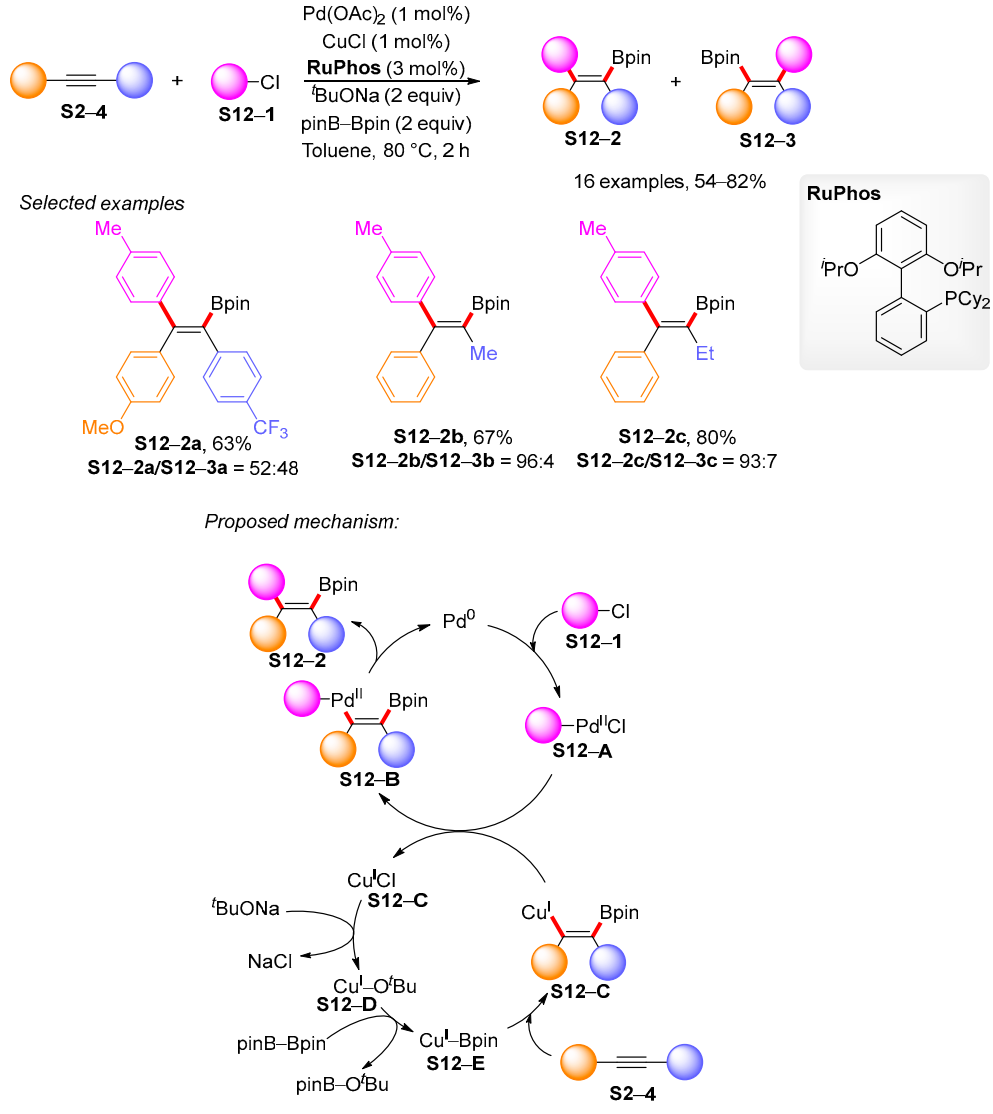
Scheme 10. Synthesis of 1,2-diborylated tetrasubstituted alkenes via the manipulation of triborylated alkenes.

A rapid approach to the preparation of 1,1-diborylated alkenes by means of the copper-catalyzed dehydrogenative borylation of the terminal alkene **S5–3** has been published by Yamaguchi (Scheme 11) [56]. Different reaction conditions allow for the formation of the mono- and diborylated products **S11–2** and **S11–1**. However, the borylation of disubstituted terminal alkenes to the borylated products **S11–1** is associated with a long reaction time and only moderate isolated yields of alkenes **S11–1a** and **S11–1c**. Other tetrasubstituted alkenes have not been synthesized. The authors proposed that 2-adamantanone and benzophenone are used as HBpin acceptors as can be seen from proposed mechanism for the formation of the alkenes **S11–1**.



Scheme 11. Alternative synthesis of 1,1-diborylated alkenes.

The monoborylated tetrasubstituted alkene **S12–2** can also be prepared via cooperative catalysis (Scheme 12) [57]. The starting materials are usually the symmetrical internal alkynes **S2–4**, which can be converted into monoborylated alkenes **S12–2** by means of the reaction with aryl chlorides. The reaction proceeds well for symmetric alkenes, although unsymmetric alkynes with similar substituents give a stereoselective mixture of the regioisomers **S12–2a** and **S12–3a**. High regioselectivity is achieved only for alkynes with the aromatic and aliphatic substituents **S12–2b** and **S12–2c**. The proposed mechanism assumes the oxidative addition of Pd^0 to the C–Cl bond, while the alkenylcopper reagent **S12–C** is used for the transmetallation step, which results in the formation of the borylcupration product **S12–B**. The final step is reductive elimination. A similar approach was published by Brown [58], although in that work the prepared monoborylated alkenes are oxidized to the corresponding ketones. In addition, Pd/Cu cooperative catalysis has been used to prepare symmetrical monoborylated tetrasubstituted alkenes from allenylic carbonates [59].



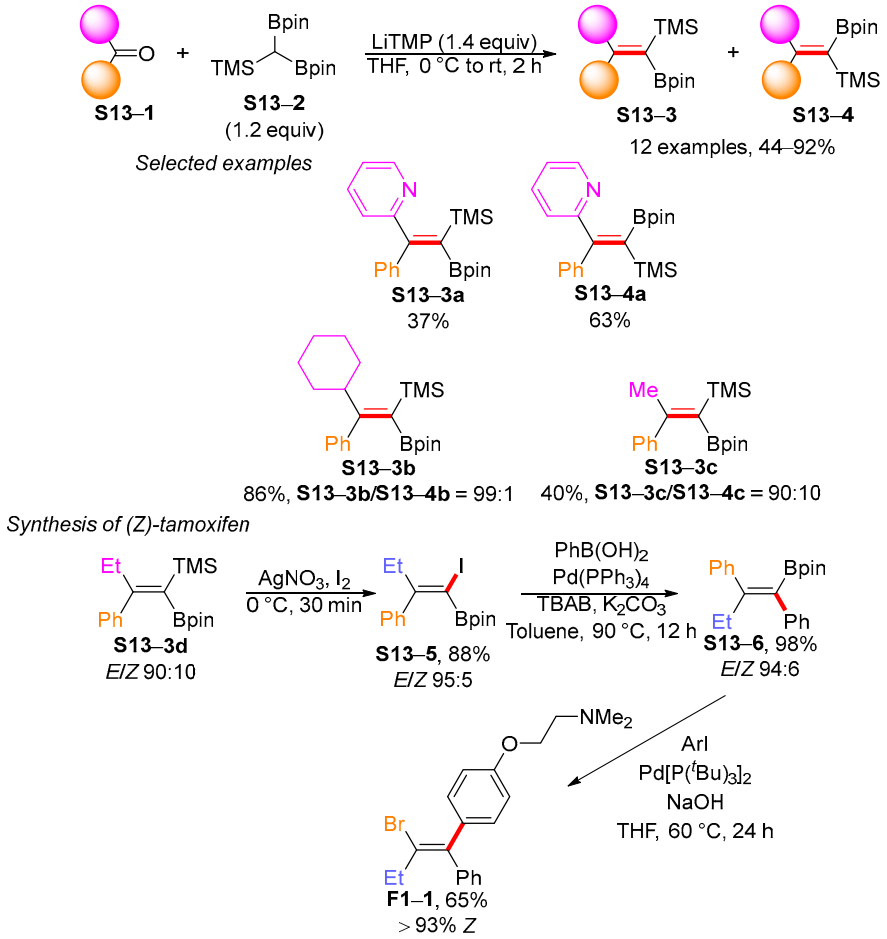
Scheme 12. Pd/Cu cooperative catalysis for the carboborylation of alkynes.

3.2. Applications of the Borylated Acyclic Double Bond for Stereoselective Synthesis of Tetrasubstituted Alkenes

In the previous section, various procedures for the synthesis of the borylated tetrasubstituted double bond were briefly introduced. This type of organometallic reagent can be used for the nonstereoselective preparation of tetrasubstituted fluoroalkenes [60] or corrphycene derivatives [61]. However, this review focuses on their conversion into

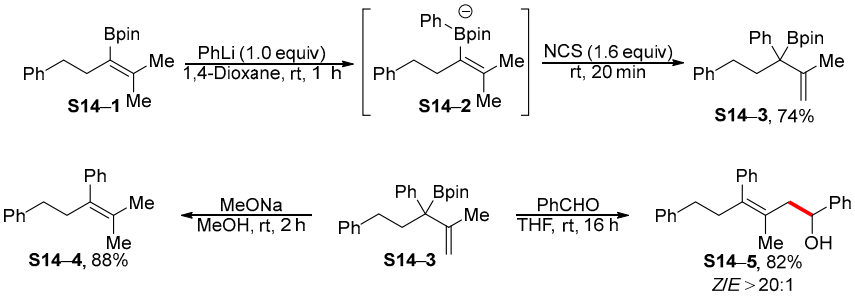
tetrasubstituted alkenes. Therefore, in this section, the use of the borylated tetrasubstituted double bond for the stereoselective synthesis of tetrasubstituted alkenes is discussed. These applications go hand in hand with the preparation of the borylated double bond, which led to the inclusion of the synthesis of borylated alkenes in this paper.

The reaction of carbonyl compounds **S13–1** with the C1 synthon **S13–2** can directly afford the silylborylation products **S13–3** and **S13–4** (Scheme 13) [62]. The selected examples show that the reaction is sensitive to the structures of the starting ketones. Ketones with aliphatic and aromatic substituents undergo silylborylation with high regioselectivity. In contrast, ketones with two similar substituents give a mixture of both regioisomers. The preparation of (*Z*)-tamoxifen (**F1–1**) can be performed starting with the alkene **S13–3d**, which is iodinated before a double Suzuki reaction gives (*Z*)-tamoxifen as >93% *Z*. Thus, the above-mentioned examples of the stereoselective synthesis of (*Z*)-tamoxifen complement previous preparations of (*Z*)-tamoxifen via the cross-coupling reactions of borylated alkenes [63,64].



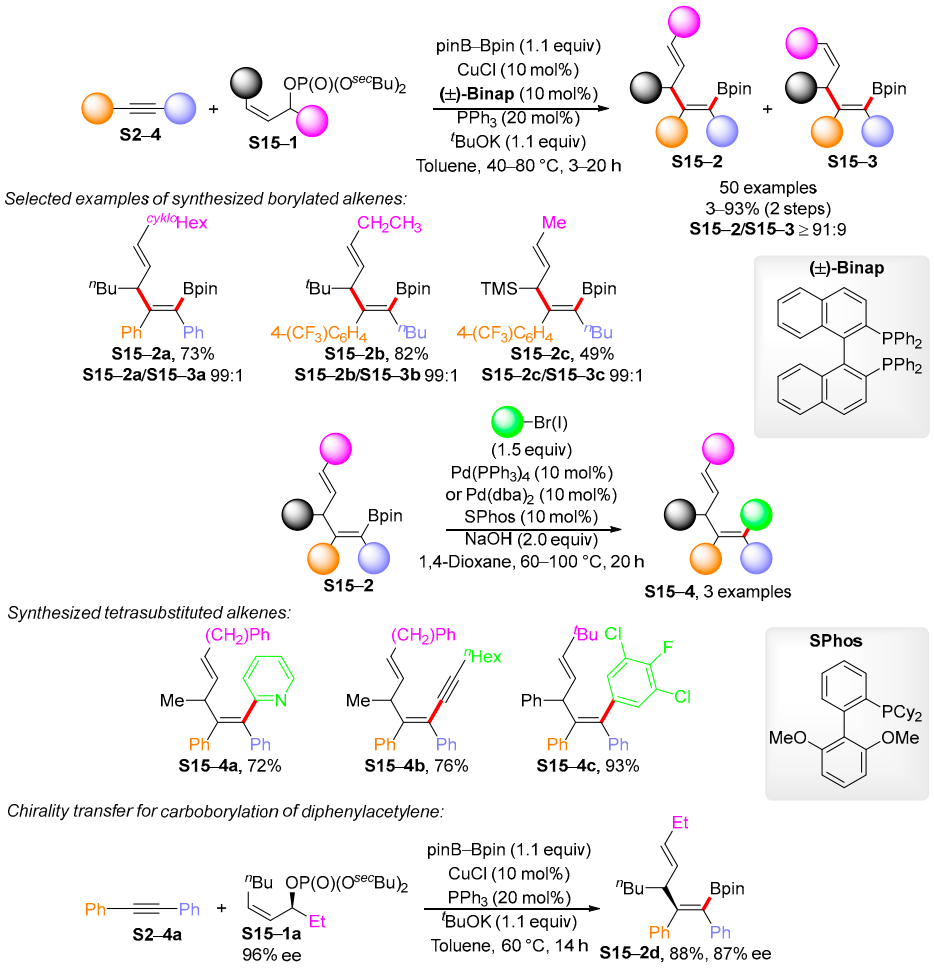
Scheme 13. Synthesis of (*Z*)-tamoxifen by means of the Suzuki reaction of borylated alkenes.

The synthesis of tetrasubstituted alkenes without the use of transition metal catalysis was published by Liu in 2021 (Scheme 14) [65]. The reaction starts with the isomerization of boronate **S14–1** into **S14–3** by means of Zweifel-type deprotonative olefination. Subsequently, the reaction of the allylboronate **S14–3** with benzaldehyde resulted in the tetrasubstituted alkene **S14–5** in a high yield and with high stereoselectivity. Alternatively, protodeborylation into the symmetrical alkene **S14–4** can also be performed. The use of highly reactive organolithium reagents and resulting low functional group tolerance, as well as the limited scope of synthesized tetrasubstituted alkenes is a major drawback of this protocol.



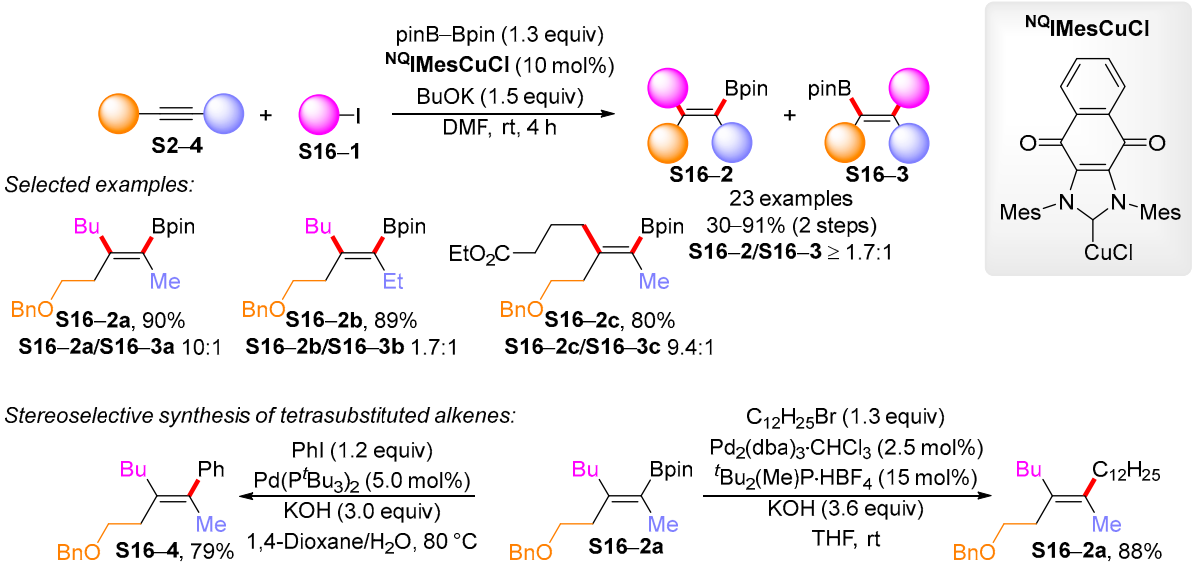
Scheme 14. Transition-metal-free synthesis of tetrasubstituted alkenes from allylboronates.

A comprehensive solution for the preparation of the tetrasubstituted skipped diene **S15–2** was published by Zhong (Scheme 15) [66]. The developed procedure makes use of copper-catalyzed borylation of internal and terminal alkynes. Terminal alkynes are suitable for the preparation of trisubstituted alkenes. In contrast, a tetrasubstituted double bond with a Bpin group is formed from the internal alkynes as the major stereo- and regioisomer **S15–2**. The published reaction was optimized to determine the influence of the structures of allyl phosphate **S15–1** and alkyne **S2–4** on the regio- and stereoselectivity of the carboboration reaction. The findings were then used for the regio- and stereoselective preparation of a wide variety of skipped dienes containing both trisubstituted and tetrasubstituted double bonds. Unfortunately, the scope of the reaction includes only simple functional groups (MeO, F, Cl, CF_3, and TMS). In addition, chirality retention can be observed in relation to the borylation of the diphenylacetylene **S2–4a** with the chiral allyl phosphate **S15–1a**.



Scheme 15. Stereoselective synthesis of skipped dienes by means of the substrate-controlled carboborylation of internal alkynes.

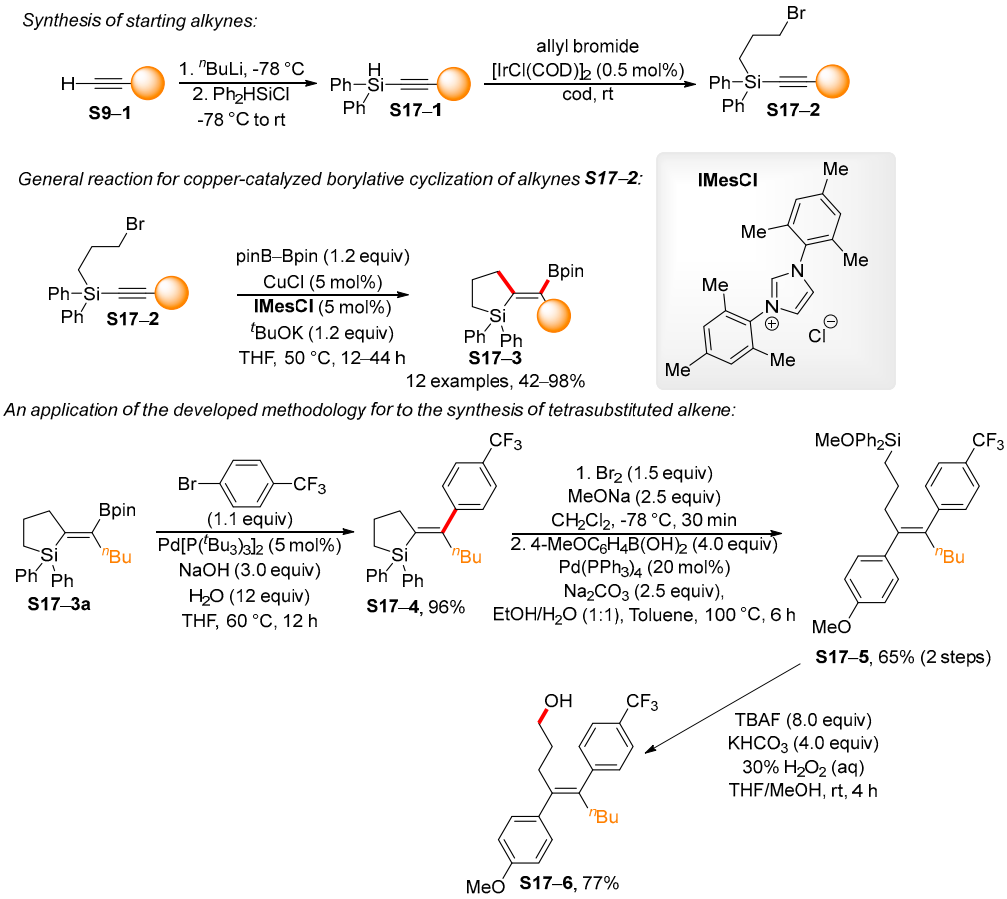
In 2016, Kanai et al. published a procedure for the preparation of compounds with tetraalkylated and monoarylated double bonds (Scheme 16) [67]. Borylated trialkylethylenes were prepared via the ^{NQ}IMesCuCl-catalyzed [68] reaction of the internal alkynes **S2–4** with the alkyl iodide **S16–1** in the presence of pinB–Bpin with satisfactory regioselectivity. This method tolerates a variety of functional groups, including the ether (BnO, TBSO), ester (CO_2Me, PivO), dialkyamino (Bn_2N), and amide (NH_2(O)C) groups. The priming of tetralkyl olefins is completed via the reaction of the borylated alkene **S16–2a** with dodecyl bromide or iodobenzene in the presence of a catalytic amount of a palladium complex and potassium hydroxide as a base.



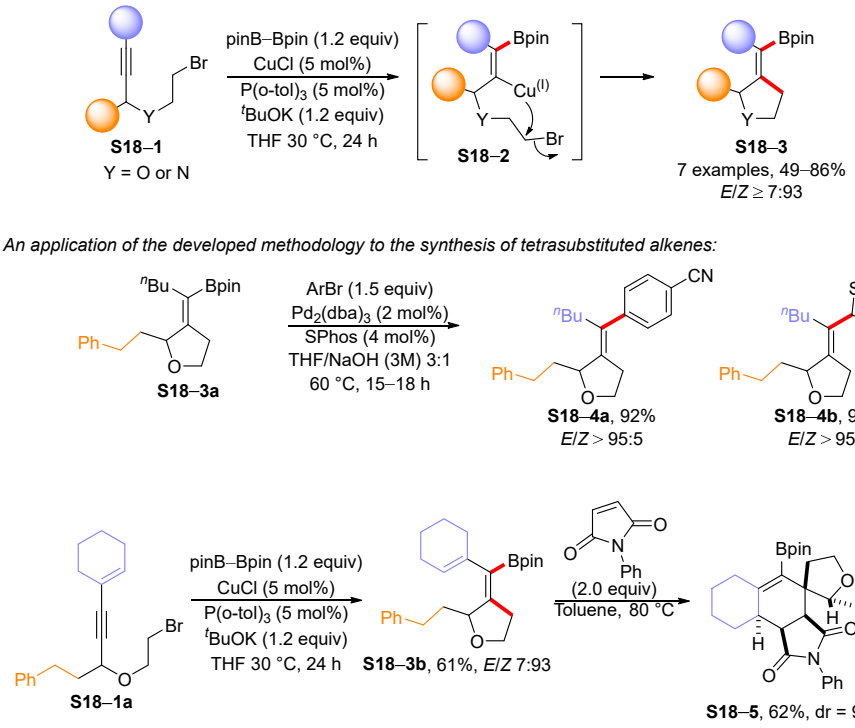
Scheme 16. Alkyne carboboration for the stereoselective synthesis of tetraalkylated alkenes.

Two reports describing the borylative cyclization of alkynyl bromides were published by Ito's research group. In the first report, the copper-catalyzed silicon-tethered cyclization of the silylated alkyne **S17–2** was shown to result in products with the borylated tetrasubstituted double bond **S17–3** (Scheme 17) [69]. Starting alkynes **S17–1** are readily available by means of the iridium-catalyzed hydrosilylation of alkynes, as reported by Rahaim's group [70]. However, the method suffers from low functional group tolerance, where only alkynes with Cl, OTBS, OTHP, and OMe groups are used. The products of the carboborylation reaction can be used to prepare tetrasubstituted acyclic alkenes. This has been demonstrated through the preparation by means of stereoselective synthesis of the alkene **S17–6** via the Suzuki reaction of borylated alkene **S17–3a**. Then, the opening of the silacyclopentane ring via the reaction of alkene **S17–4** with bromine followed by the Suzuki reaction with 4-methoxyphenylboronic acid resulting in the alkene **S17–5**. The preparation of the tetrasubstituted alkene was completed by Tamao oxidation [71].

Subsequently, Ito et al. used copper-catalyzed borylation of the internal alkyne **S18–1** to prepare tetrasubstituted alkenes (Scheme 18). [72] Similar to their previous work [69], the authors proposed that the cupraborylation of the triple bond forms the cuprate **S18–2**, which completes the stereoselective synthesis of the borylated alkene **S18–3** by means of intramolecular alkylation. The reaction is also suitable for the preparation of trisubstituted double bonds. The obtained borylated alkene **S18–3**, in conjunction with the Suzuki reaction or the Diels–Alder reaction, allows for the preparation of the tetrasubstituted alkenes **S18–4a** and **S18–4b** or the cyclic boronate **S18–5**.

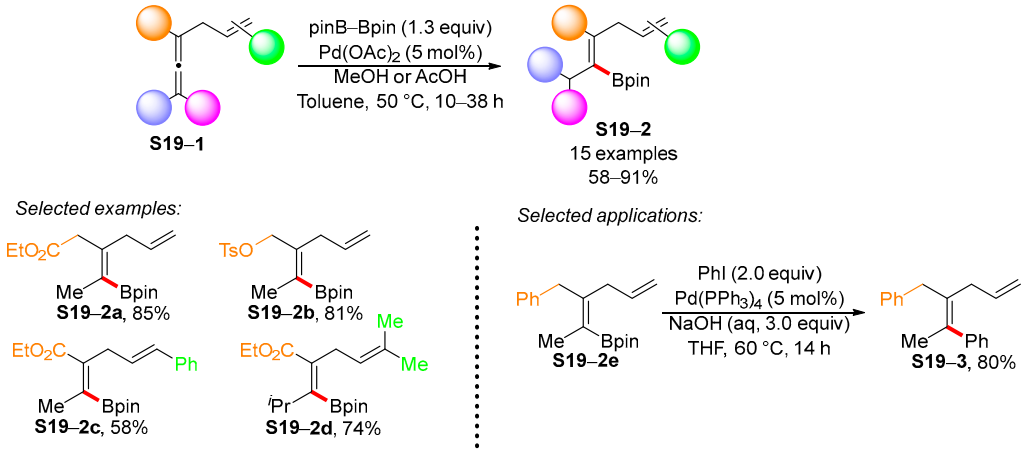


Scheme 17. Silicon-tethered borylative cyclization of alkynyl bromides for the synthesis of tetrasubstituted alkenes.

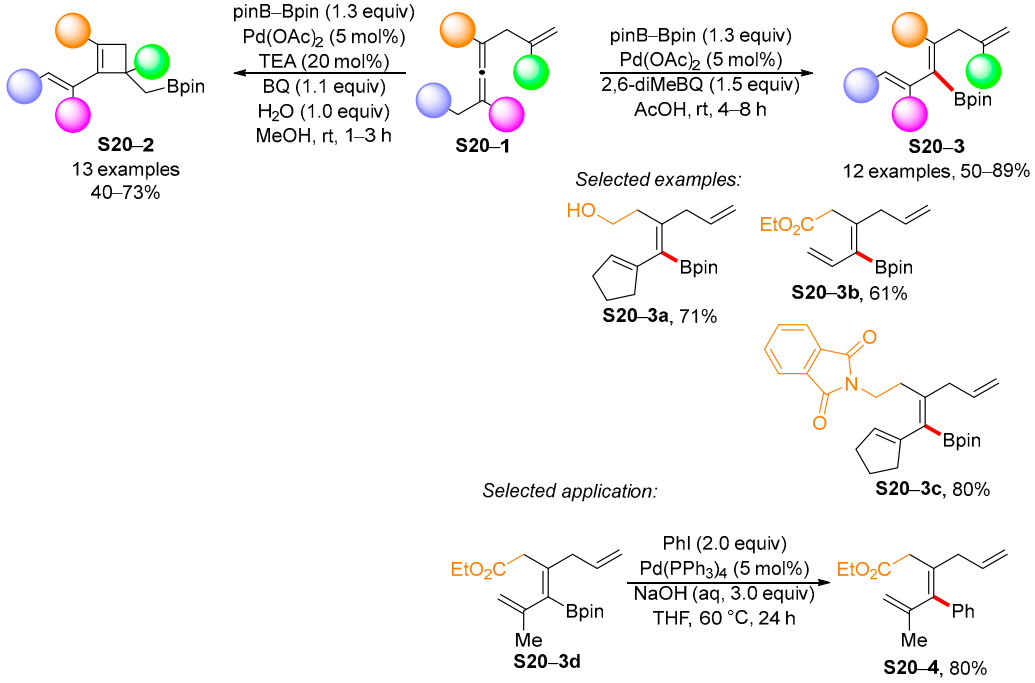


Scheme 18. Preparation of tetrasubstituted exocyclic double bond by means of the copper-catalyzed alkylative borylation of internal alkynes.

In addition, allenes can also be used for the stereoselective formation of tetrasubstituted alkenes via borylated intermediates (Scheme 19 [73] and Scheme 20 [74]). The borylated alkenes **S19–2** and **S20–3** are prepared via palladium-catalyzed hydroboration or oxidative borylation of allenes. These reactions are characterized by good functional group tolerance and a good reaction scope. Moreover, the oxidative borylation of allenes is sensitive to additives and the utilized oxidant. Benzoquinone (BQ) prefers the carbocyclization of the starting allenes into cyclobutene **S20–2**, while the formation of borylated tetrasubstituted alkenes was accomplished by means of 2,6-dimethylbenzoquinone (2,2-diMeBQ) (Scheme 20). The prepared borylated alkenes were used for the stereoselective formation of tetrasubstituted alkenes by means of the Suzuki reaction catalyzed by tetrakis(triphenylphosphine)palladium.

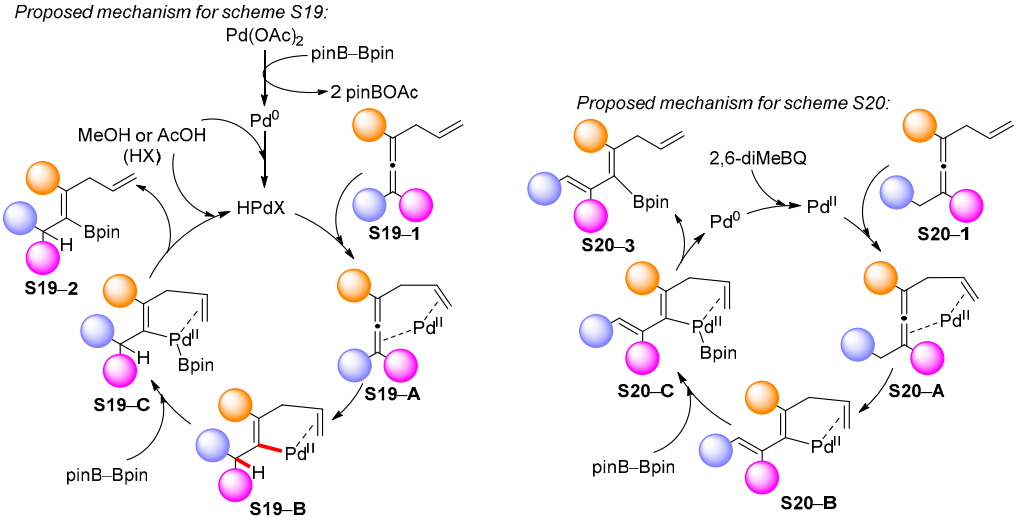


Scheme 19. Palladium-catalyzed hydroboration of allenes en route to boralyted alkenes as well as stereoselective synthesis of tetrasubstituted alkenes.



Scheme 20. Oxidative borylation of allenes for the synthesis of trienes containing a tetrasubstituted double bond.

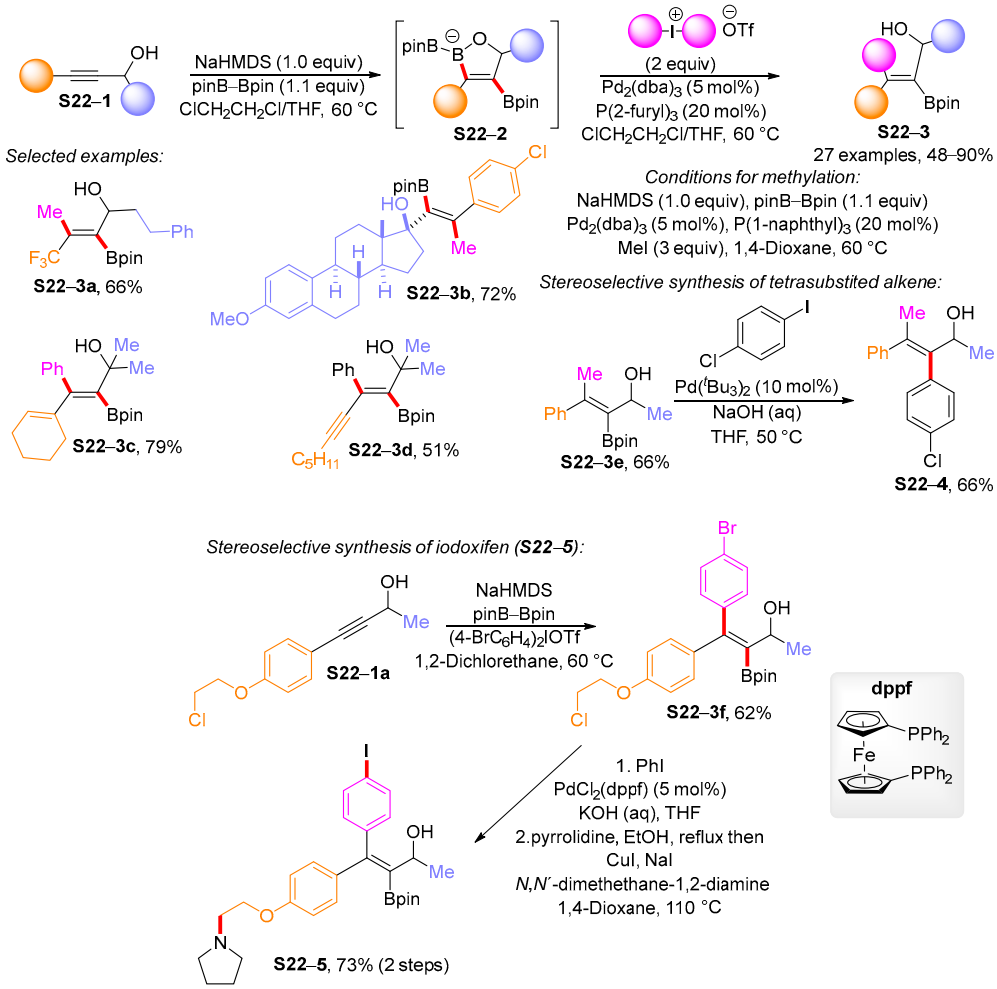
The above-mentioned reactions differ significantly in terms of the mechanism behind the formation of borylated alkenes (Scheme 21). Thus, the palladium-catalyzed hydroboration of allenes begins with the reduction of palladium acetate by pinB–Bpin, which is followed by the oxidative addition of palladium to the H–O bond of methanol or acetic acid to obtain the catalytic species HPdX [73]. The next step involves the coordination of the allene, followed by the hydropalladation of the allenic double bond to **S19–B**. The reaction product **S19–2** is obtained via transmetallation and reductive elimination. In contrast, the oxidative borylation of allenes can be explained by the coordination of palladium acetate to the starting material and the subsequent isomerization to the vinyl intermediate **S20–B**. Next, transmetallation and reductive elimination complete the synthesis of the borylated alkene **S20–3**. The oxidation of Pd^0 into Pd^{II} is achieved using 2,6-dimethylbenzoquinone [74].



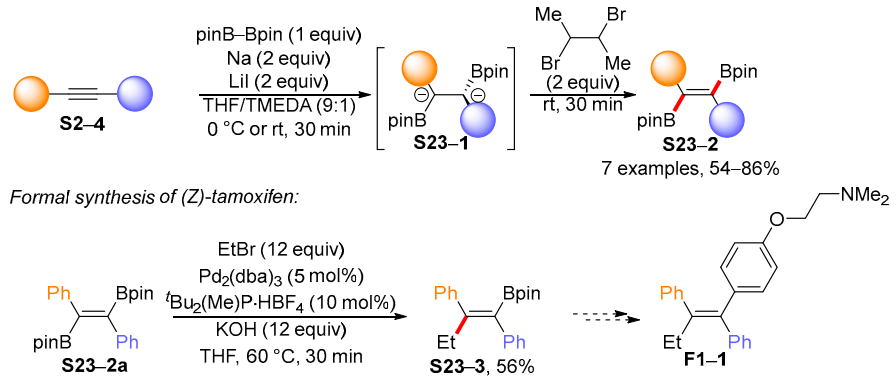
Scheme 21. Proposed mechanisms for the synthesis of borylated alkenes.

An unusual trans borylation of propargyl alcohol **S22–1** was reported by Fürstner in 2019 (Scheme 22) [75]. The starting material is converted into the ate complex **S22–2** via the reaction with NaHMDS and pinB–Bpin. Subsequently, the borylated alkene **S22–3** is formed in excellent isolated yields and with excellent reaction scopes via the palladium-catalyzed reaction with methyliodide or diaryliodonium triflate under different conditions. The selected examples illustrate how the methodology is suitable for the preparation of the conjugated diene **S22–3c**, the enyne **S22–3d**, and the tetrasubstituted double bond with a steroid skeleton **S22–3b**. In addition, the methodology can be used for the preparation of tetrasubstituted alkene **S22–4** and the nonsteroidal estrogen receptor modulator iodoxifen (**S22–5**).

The diborylated tetrasubstituted double bond has also been used for the synthesis of (*Z*)-tamoxifen (Scheme 23). Nogi et al. extended the sodium-mediated preparation of cis diborylated alkenes [49] to the preparation of trans diborylated alkene **S23–2** [76]. The authors experimentally verified that the dianion **S23–1** acts as an intermediate in the formation of the alkene **S23–2**, which is formed by means of the oxidation of **S23–1** with 2,3-dibromobutane. The formal synthesis of (*Z*)-tamoxifen was performed via the palladium-catalyzed ethylation of alkene **S23–2a** in a 56% isolated yield.



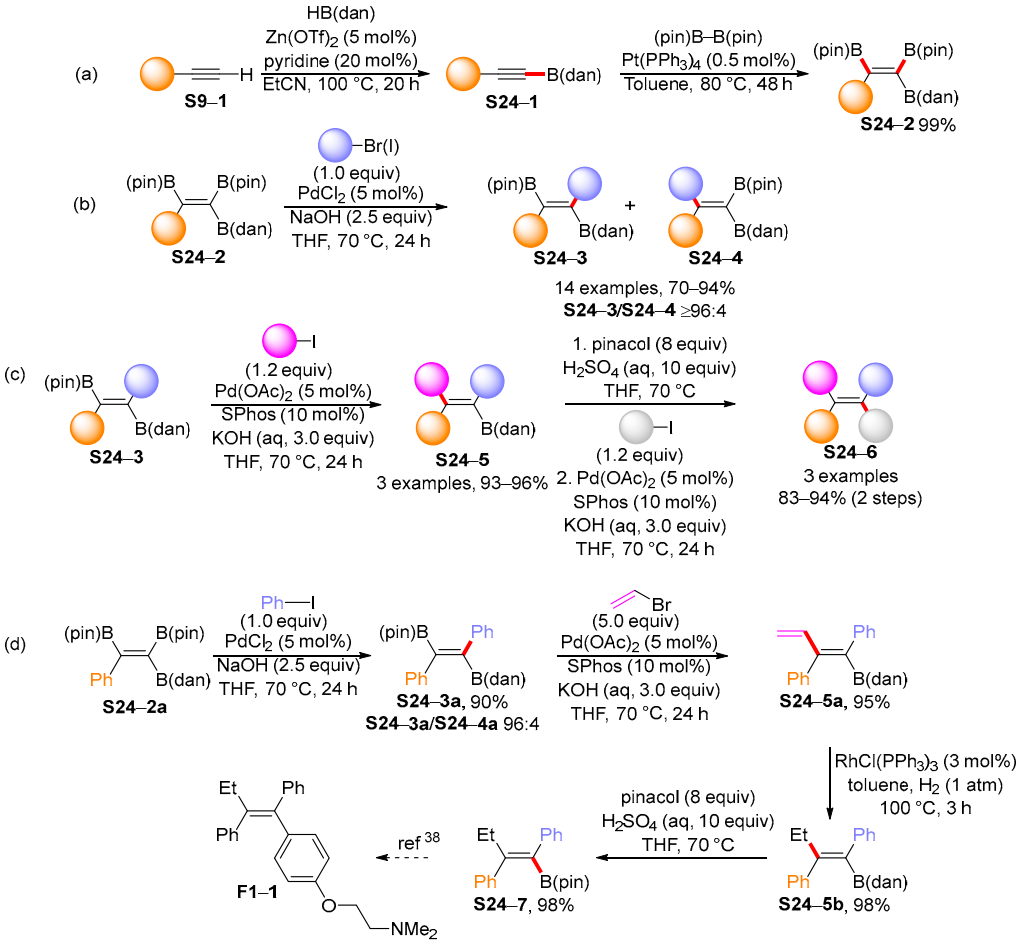
Scheme 22. Stereoselective trans diborylation of internal alkynes for the synthesis of allylic alcohols with tetrasubstituted double bonds.



Scheme 23. Borylation of internal alkynes en route to (Z)-tamoxifen.

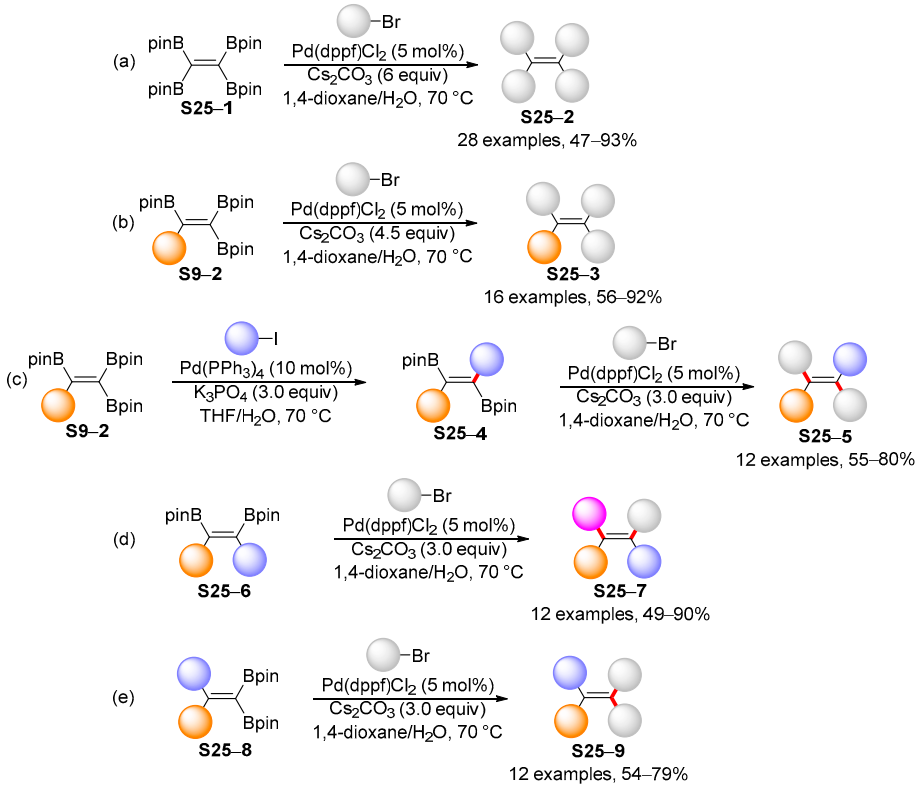
A similar iterative approach for the stereoselective preparation of tetrasubstituted alkenes was reported by Tsuchimoto (Scheme 24) [77]. This work builds on previous results concerning the preparation of borylated compounds reported by Tsuchimoto's research group [78,79]. Thus, the starting triborylated alkene **S24–2** is synthesized by means of the dehydrogenative coupling of the terminal alkyne **S9–1** with 1,8-naphthalenediamineborane (HB(dan)) followed by the diborylation of the internal alkyne **S24–1** (Scheme 24a). In a further step, the triborylated alkene is trans arylated with high regioselectivity to form the diborylated alkene **S24–3** as the major product (Scheme 24b). The second introduction of

aryl substituents was performed with only a limited amount of aryl iodides, as illustrated in Scheme 24c. Subsequently, the B(dan) group was esterified via the reaction with pinacol under acidic conditions, and the stereoselective synthesis of tetrasubstituted alkenes was completed by the Suzuki reaction with aryl iodides. In addition, a complementary series of (*E*)- and (*Z*)-tetraarylethylenes can be prepared using this procedure. The developed procedure can also be used for the formal synthesis of (*Z*)-tamoxifen from the triborylated alkene **S24–2a**. The starting compound was initially used in the Suzuki reaction with iodobenzene and vinyl bromide under optimized reaction conditions. The reduction of the vinyl group with hydrogen gives the B(dan) derivative **S24–5b** in a high yield (86% in three steps). The substitution of the dan group for pinacol provides the intermediate needed for the preparation of (*Z*)-tamoxifen in a 98% yield [63].



Scheme 24. Iterative synthesis of tetrasubstituted alkenes, including the formal stereoselective synthesis of (*Z*)-tamoxifen (**a**–**d**).

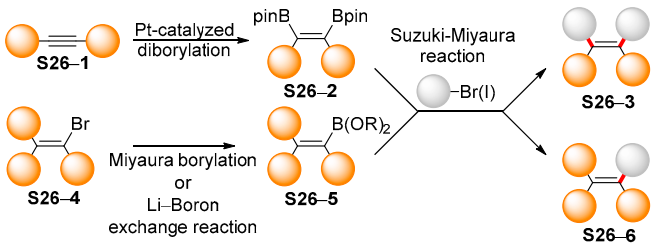
An exhaustive approach for the preparation of tetraarylated ethylenes was reported in 2020 (Scheme 25) [80]. In this work, various mono-, di-, tri-, and tetraborylated ethylenes were used in palladium-catalyzed Suzuki reactions to produce symmetrically and unsymmetrically substituted tetraarylethylenes. It is worth noting here that the triborylated alkene **S9–2** coupled with aryl iodide to give trans diarylated alkene **S25–4** (Scheme 25c). A wide reaction scope is typical for all starting alkenylboronic acid esters. In conclusion, the developed methodology enabled a Lego-based approach to the preparation of the tetraarylated alkenes **S25–2**, **S25–3**, **S25–5**, **S25–7**, and **S25–9** from the easily available borylated double bond.



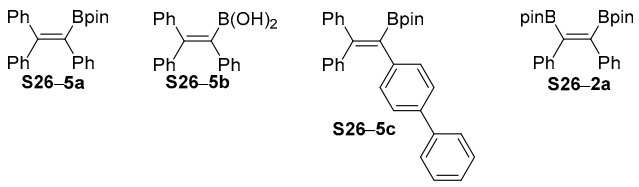
Scheme 25. Lego-based approach to tetraarylated ethylenes (**a**–**e**).

As mentioned in the introductory section, tetrasubstituted alkenes have a wide range of applications, including the field of materials chemistry. A detailed survey of the available literature has revealed that the symmetrical tetrasubstituted double bond is most commonly used for materials chemistry purposes. Examples of these borylated alkenes are given in Scheme 26. Miyaura borylation, [81–83], the Li–B exchange reaction [84], and platinum-catalyzed diborylation of internal alkynes [85–88] are commonly used for the synthesis of the borylated alkenes **S26–2** and **S26–5**. The applications of borylated alkenes **S26–2** and **S26–5** include the Suzuki–Miyaura reaction, which is commonly catalyzed by the tetrakis(triphenylphosphine)palladium complex along with inorganic bases (Na_2CO_3 [89], K_2CO_3 [82,90–92]), organic solvents (THF, toluene, MeOH, 1,4-dioxane), and water.

Frequently used approaches to tetrasubstituted alkenes synthesized for materials chemistry purposes:



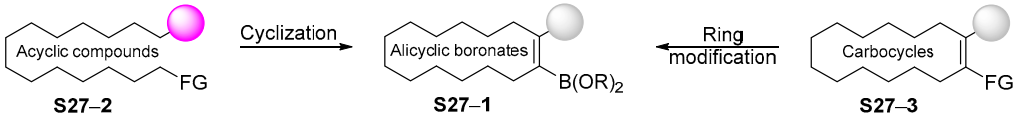
Examples of borylated alkenes synthesized for material chemistry purposes:



Scheme 26. Approaches to tetrasubstituted alkenes and examples of borylated alkenes used in materials chemistry.

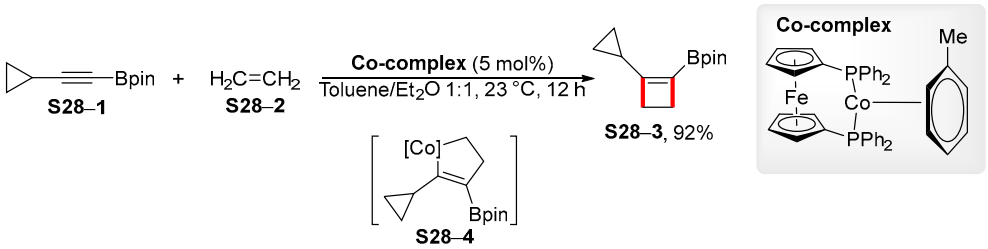
4. Synthetic Approaches to and Applications of Cycloalkenylboronates

In the previous section, we showed that the acyclic tetrasubstituted double bond with a boryl group is frequently synthesized from alkynes by means of triple bond borylation. The situation is different with regard to tetrasubstituted alicyclic alkenylboronic acids and alkenylboronic acid esters. Cyclooctyne is an isolable compound [93], although four-, five-, six-, and seven-membered cycloalkynes are unstable compounds under normal conditions that can be stabilized via, for example, the formation of cobalt complexes [94]. Therefore, cycloalkynes are considered unsuitable substrates for use in the preparation of cycloalkenyl boronic acids and their esters. In principle, the modification of the tetrasubstituted cycloalkene **S27–3** with a suitable functional group or the cyclization of the acyclic precursor **S27–2** can be used for the synthesis of cyclic boronic acid esters (Scheme 27).



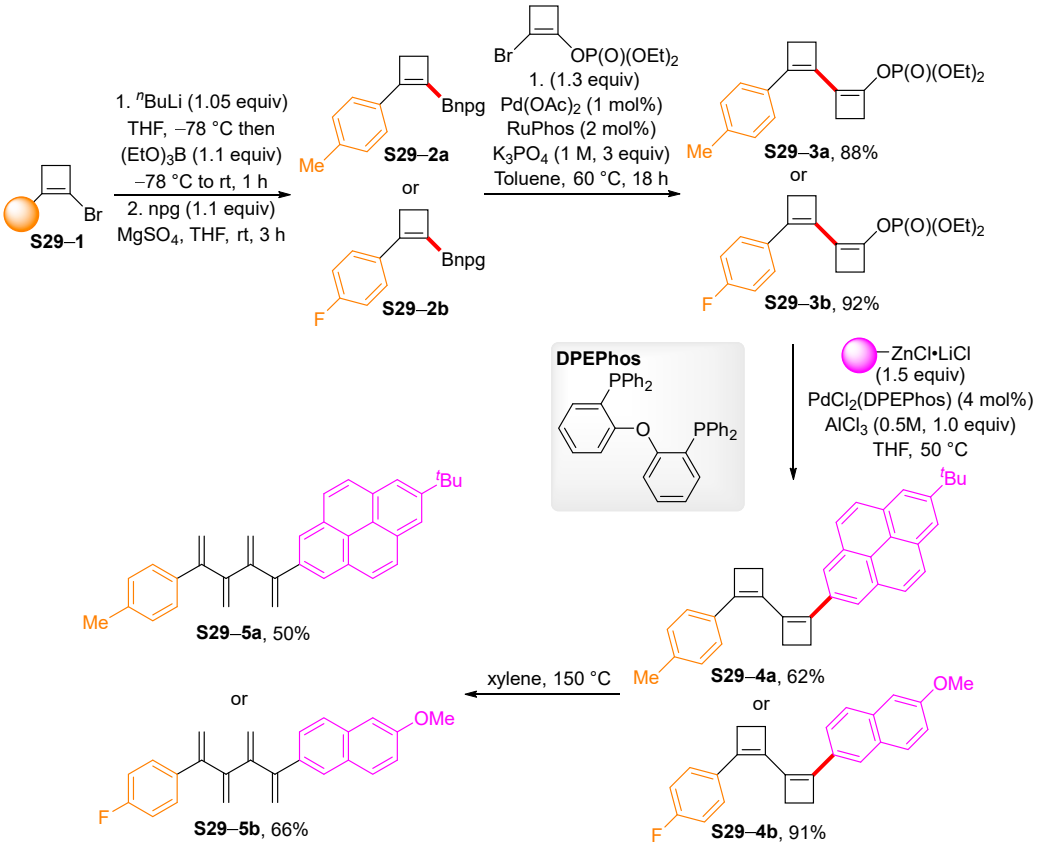
Scheme 27. Synthetic approaches toward alicyclic boronic acid esters.

The [2 + 2]-cycloaddition of borylated acetylene can be used to prepare the cyclobutenylboronate **S28–3** in a high yield (Scheme 28) [95]. The reaction is catalyzed by a cobalt complex and proceeds at room temperature. Unfortunately, the scope of the reaction is limited to the preparation of only the single cyclobutenylboronate **S28–3**. Based on mechanistic studies, it has been suggested that the reaction involves the formation of cobalt(III) metallacycle **S28–4**.



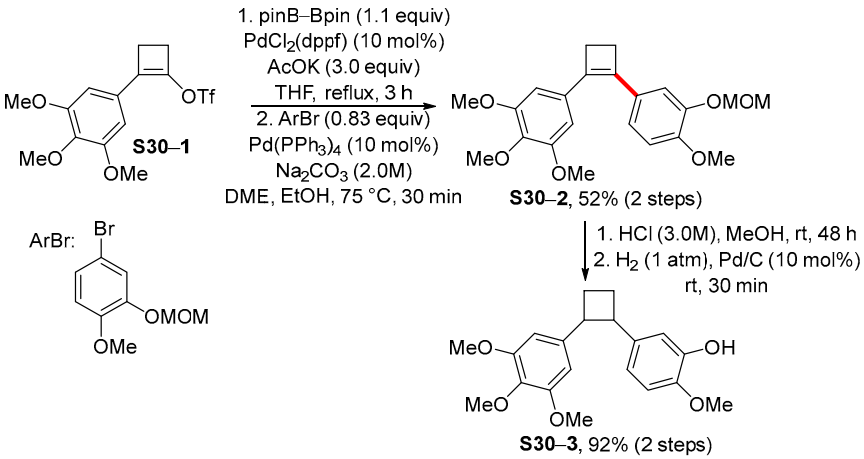
Scheme 28. [2 + 2]-Cycloaddition for the synthesis of borylated cyclobutene.

Cyclic boronates derived from cyclobutene can be used for the preparation of [4]dendralenes (Scheme 29) [96]. Starting neopentylglycol (npg) boronates are prepared via the reaction of cyclobutenyl lithium with triethylborate, which is followed by esterification with neopentylglycol. The Suzuki reaction of boronates **S29–2a** and **S29–2b** with diethyl 2-bromocyclobutenyl phosphate results in phosphates **S29–3a** and **S29–3b**. Subsequently, the phosphate group is replaced by means of the Negishi reaction with arylzinc chlorides in the presence of aluminum chloride, and [4]dendralenes are obtained via the thermal opening of cyclobutenes **S29–4a** and **S29–4b** in xylene at 150 °C.



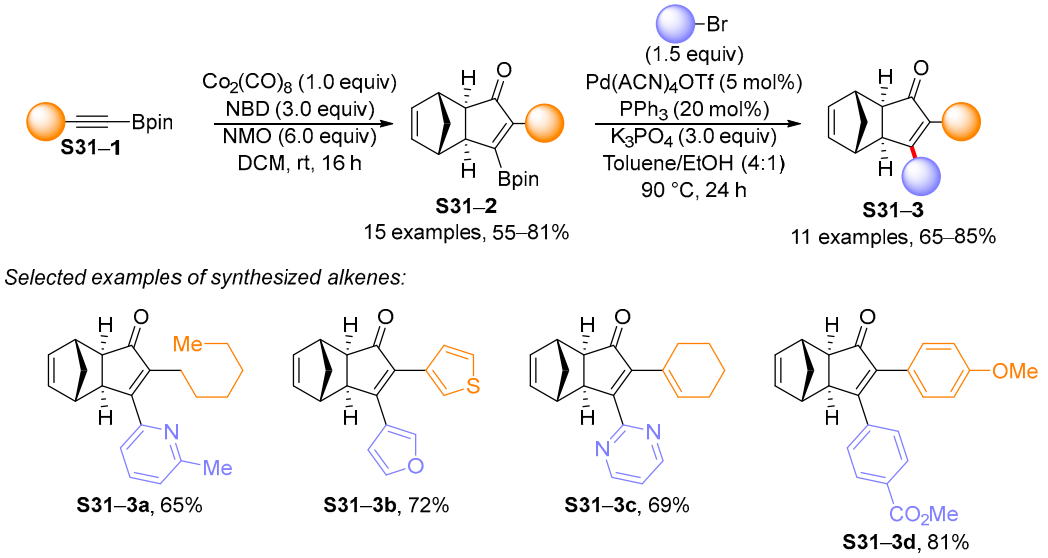
Scheme 29. Synthesis of [4]dendralenes by means of the ring-opening reaction of biscyclobutenes.

Pinacol cyclobutenylboronic acid ester can be prepared via the Miyaura borylation of triflate **S30–1** (Scheme 30) [97]. The subsequent Suzuki reaction of the borylated cyclobutene with aryl bromide (ArBr) gives 1,2-disubstituted cyclobutene **S30–2** in a 52% isolated yield. Removal of the MOM-protecting group and hydrogenation of the cyclobutene double bond result in combretastatin analogue A-4 **S30–3**.



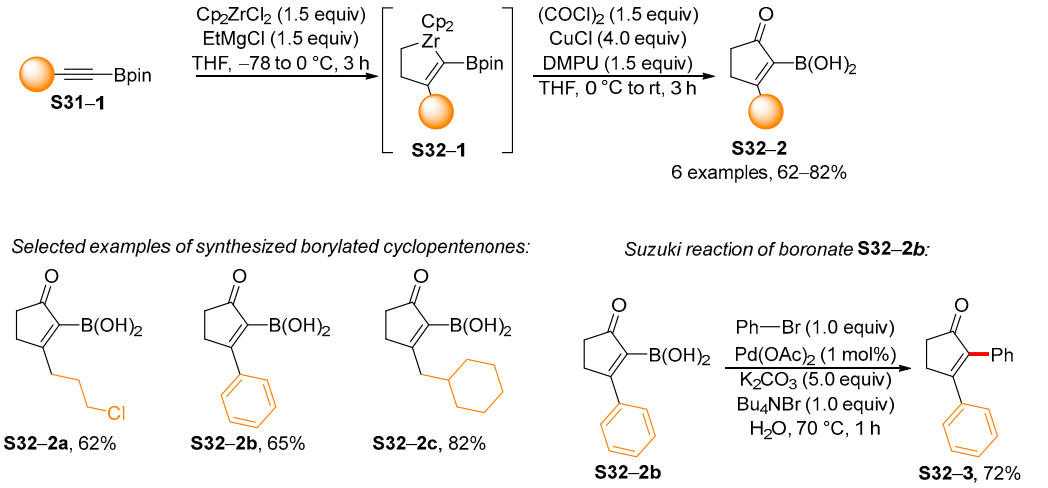
Scheme 30. Cyclobutenylboronic acid ester for the synthesis of the combretastatin A-4 analogue.

The cyclization procedure for the preparation of cyclopentenylboronic acid esters is shown in Scheme 31 [98]. The cobalt-mediated Pauson–Khand reaction is used to prepare the alicyclic boronate **S31–2**, which is subsequently used in a palladium-catalyzed Suzuki reaction. As the selected examples show, this procedure is useful for the preparation of tetrasubstituted cycloalkenes with a wide range of functional groups.



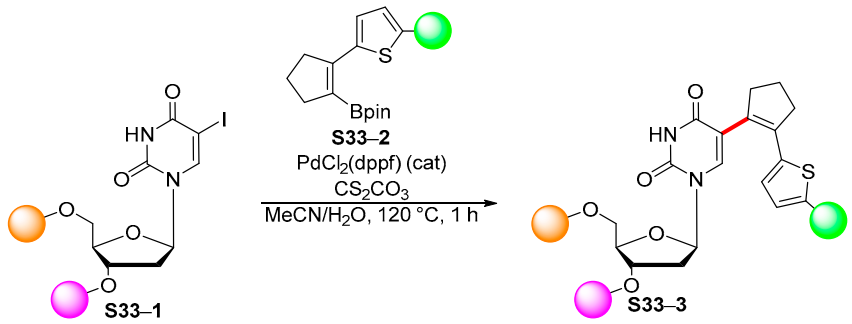
Scheme 31. The Pauson–Khand reaction for the synthesis of borylated tetrasubstituted cycloalkenes.

The further cyclization of alkynylboronic acid esters makes use of zirconium-mediated cyclization (Scheme 32) [99]. The zirconacyclopentene **S32–1** is proposed as an intermediate for the preparation of cyclopentenylboronate **S32–2**. Although the reaction is limited in terms of its scope, the prepared pinacol boronic acid ester **S32–2b** can be used for the preparation of the 2,3-disubstituted cyclopentenone **S32–3**.



Scheme 32. Zirconium-mediated cyclization of borylated alkynes en route to disubstituted cyclopentenone.

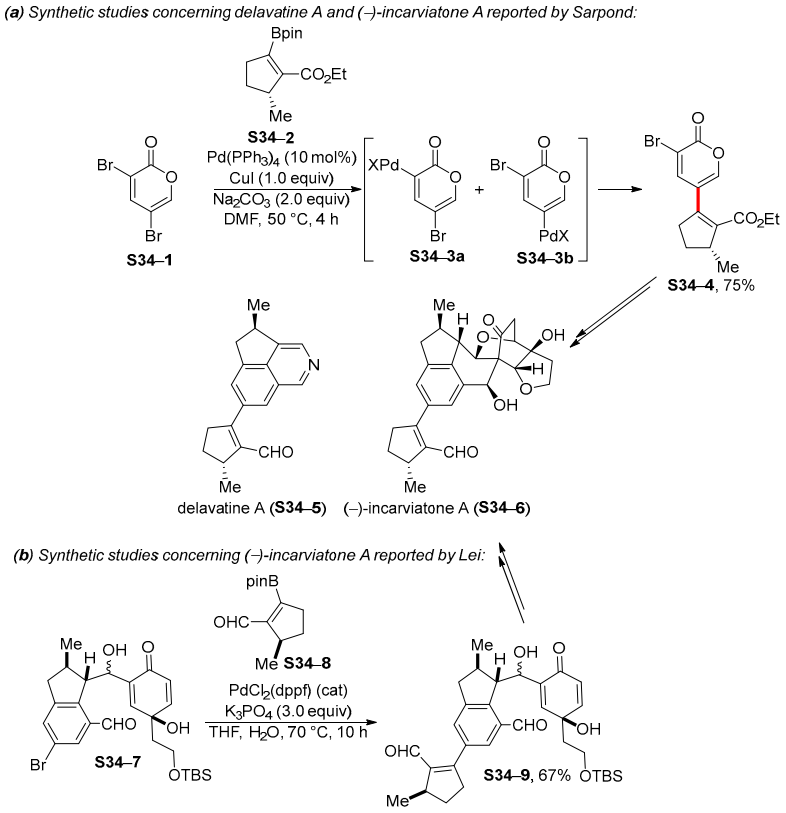
An application of the Suzuki reaction of cyclopentylboronate also involves the preparation of photoswitchable deoxyuridine nucleosides **S33–3** under standard reaction conditions (Scheme 33) [100–102]. In addition, a catalytic system based on $Pd_2(dba)_3$, along with an $AsPh_3$ ligand and silver oxide as a base, can be used for intramolecular Suzuki coupling in order to afford the tetrasubstituted double bond as a part of a tricyclic molecule [103,104].



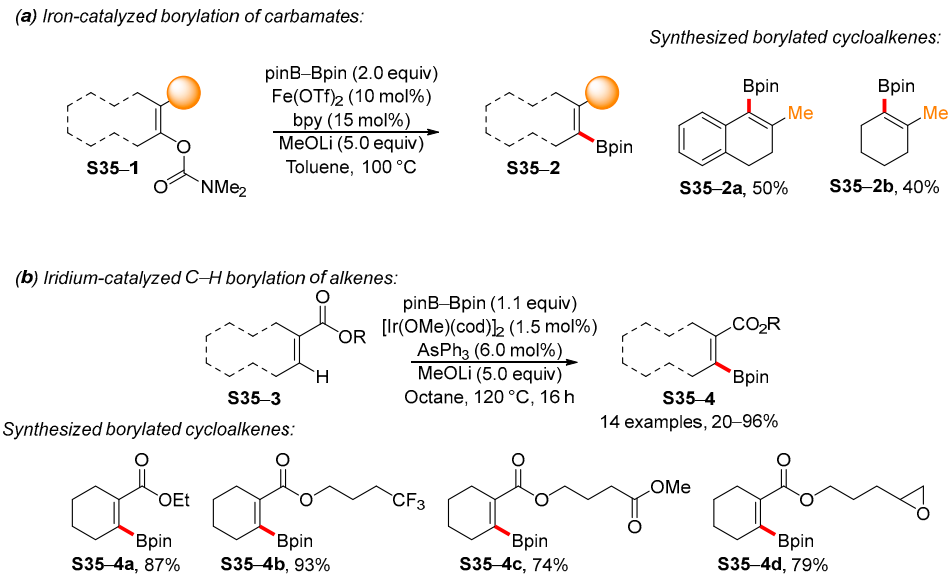
Scheme 33. Suzuki reaction of cyclopentenylboronic acid esters for the preparation of photoswitchable deoxyuridine nucleosides.

The Suzuki reactions of cyclic borylated alkenes have been used to synthesize the natural compounds delavatine A (**S34–5**) and (−)-incarviatone A (**S34–6**) (Scheme 34) [105,106]. The key step in the synthesis of the natural compounds **S34–5** and **S34–6** is the site-selective oxidative addition of a palladium catalyst at 3,5-dibromo-2-pyrone (**S34–1**). Moreover, it has been experimentally verified that the formation of oxidative addition products depends on the reaction conditions [105]. In *N*,*N*-dimethylformamide (DMF) and in the presence of CuI, the oxidative addition product **S34–3b** is preferentially formed. In addition, it has been shown that **S34–3a** undergoes conversion into the oxidative addition product **S34–3b** during the subsequent transmetallation and reductive elimination step. Thus, the complex **S34–3a** is a kinetic oxidative addition adduct, while complex **S34–3b** is a thermodynamic oxidative addition adduct. A detailed mechanism has been proposed based on quantum chemical calculations. The observed reactivity was used for the preparation of the natural compounds delavatine A (**S34–5**) and (−)-incarviatone A (**S34–6**). The similar borylated alkene **S34–8** can be used in the alternative total synthesis of (−)-incarviatone A (**S34–6**), although in this case the Suzuki reaction is performed under standard conditions [107]. The borylated alkenes **S34–2** and **S34–8** are prepared from the corresponding bromocyclopentenes by means of Miyaura borylation in the presence of a catalytic amount of Pd(dppf)Cl_2 and pinB–Bpin, and AcOK as a base in 1,4-dioxane at 80 °C.

Typical examples of the preparation of alicyclic alkenylboronates are shown in Scheme 35a,b. The first example illustrates the iron-catalyzed borolysis of carbamate **S35–1** in the presence of a bpy ligand and lithium methoxide as a base. The reaction leads to the preparation of different alkenyl and arylboronic acid esters as well as only two borylated tetrasubstituted alkenes **S35–2a** and **S35–2b** [108]. The second process relies on the iridium-catalyzed C–H borylation of the cyclohexenyl carboxylate **S35–3** [109]. The reaction tolerates a variety of functional groups, as illustrated by selected examples **S35–4a**, **S35–4b**, **S35–4c**, and **S35–4d**, and the overall isolated yields of the boronates are high. The C–H borylation process can also be used to prepare acyclic tetrasubstituted vinylboronic acid esters, although the cyclopentenyl-, cycloheptenyl-, and cyclooctenylboronic acid esters are only obtained in moderate isolated yields.

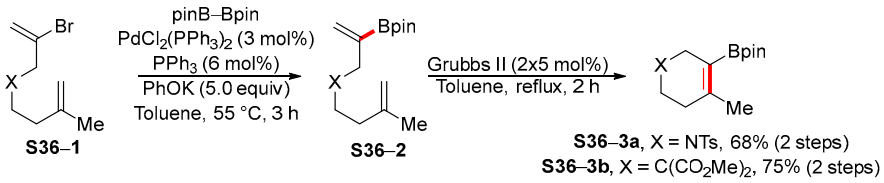


Scheme 34. Suzuki reaction of borylated tetrasubstituted alkenes en route to (−)-incarviatone A and delavatine A.



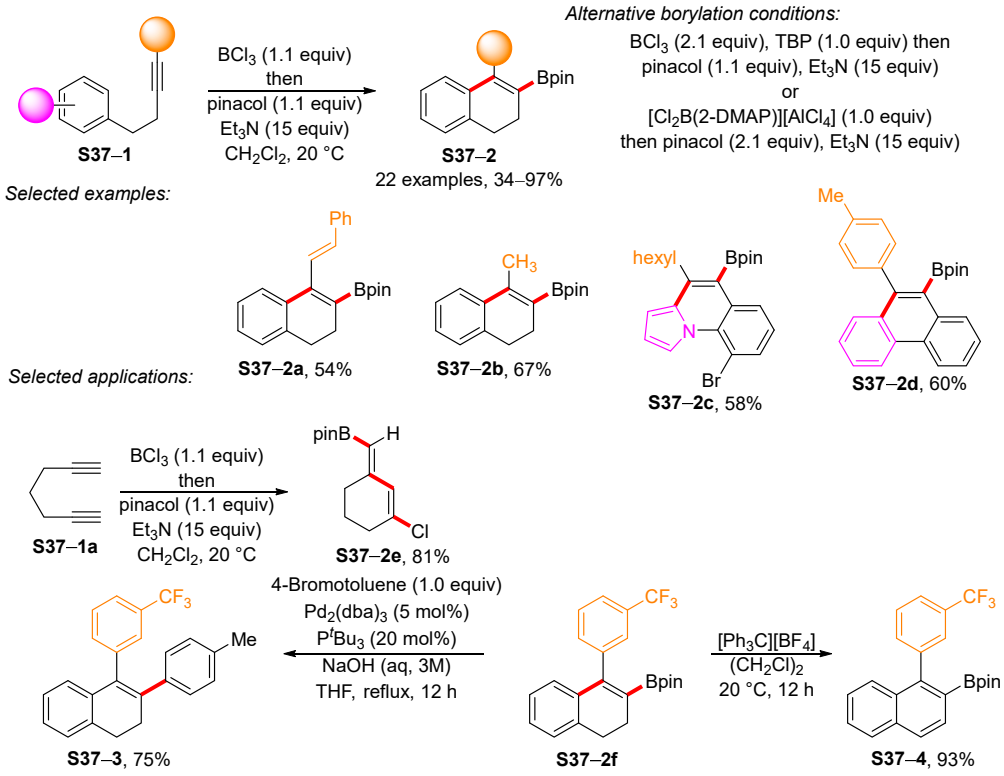
Scheme 35. Synthesis of the borylated tetrasubstituted double bond via the iron-catalyzed cross-coupling of the activated C–O bond and iridium-catalyzed C–H borylation.

Another approach for the preparation of alicyclic alkenylboronates makes use of the cyclization of acyclic precursors. An example of this approach is shown in Scheme 36 [110]. Initially, the brominated diene **S36–1** is borylated, although alkene **S36–2** cannot be isolated in its pure form, meaning that the subsequent ring-closing metathesis must be performed in a tandem reaction setup. Then, the borylated cycloalkenes **S36–3a** and **S36–3b** are obtained in high yields.



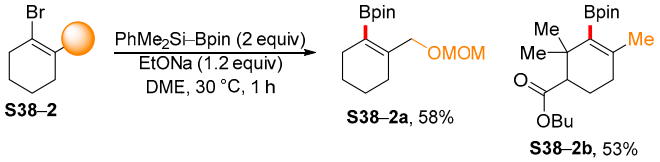
Scheme 36. Tandem Miayura borylation–RCM for the synthesis of alicyclic vinylboronates.

The preparation of the borylated dihydronaphthalene derivative **S37–2** was performed via the trans borylative cyclization of the internal alkyne **S37–1** by means of the reaction with boron trichloride and the subsequent conversion into the pinacol boronic acid ester **S37–2** under various reaction conditions (Scheme 37) [111]. The selected examples illustrate how borylative cyclization is not limited to the formation of the dihydronaphthalene derivatives **S37–2a** and **S37–2b**, as depending on the structures of the starting materials, it is possible to obtain the tricyclic compounds **S37–2c** and **S37–2d**. In addition, oxidation of the dihydronaphthalene derivative **S37–2f** can yield the boronate **S37–4**, while the Suzuki reaction of boronate **S37–2f** allows for formal access to biologically relevant nafoxidine-derived compounds.



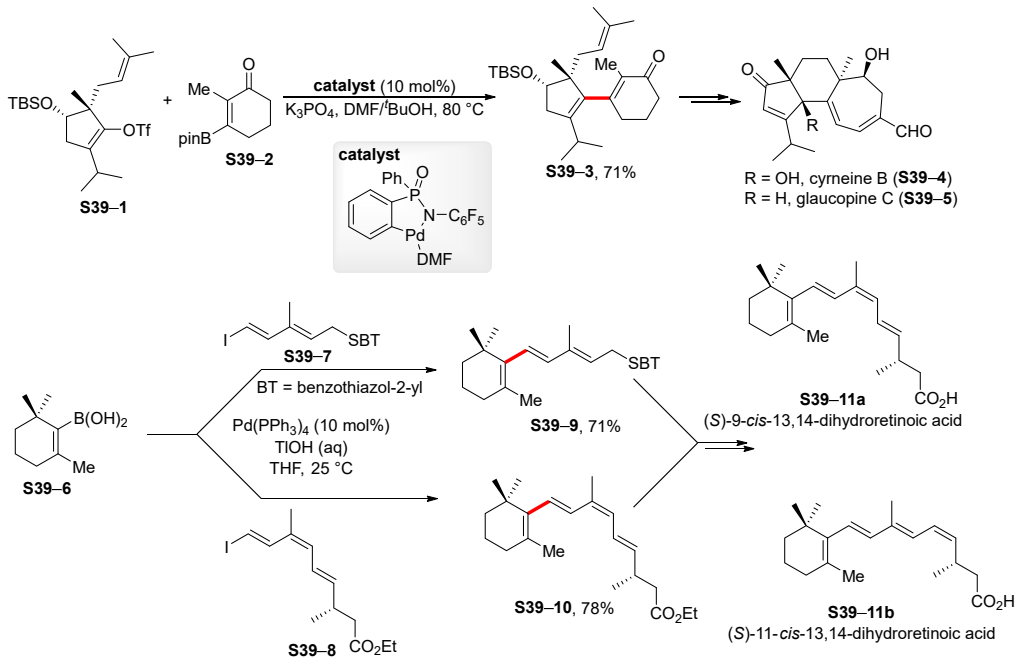
Scheme 37. Transition-metal-free trans borylative cyclization for the synthesis of dihydronaphthalene derivatives.

Transition-metal-catalyzed Miyaura borylation is a popular tool for the preparation of organoboronic acid esters [112–114]. Thus far, an interesting alternative to transition-metal-catalyzed borylation has been published by Ito et al. (Scheme 38) [115]. In this work, the borylation of aryl and vinyl halides was performed with a borylating reagent in the presence of sodium ethoxide. The authors mainly used the developed procedure for the preparation of arylboronic acid esters, as well as borylated mono- and disubstituted alkenes. In addition, only two examples of borylated trisubstituted double bond **S38–2a** and **S38–2b** were synthesized to expand the scope of the developed borylation protocol.



Scheme 38. Alternative synthesis of mono- and diborylated alkenes.

Aside from the modular and asymmetric preparation of baskets [116] and starting materials for the photoelectrocyclization of bis-aryl cycloalkenones [117,118], the synthesis of substituted cyclopentenones involving the benzofuran-ring opening reaction [119], and the oxidation of nonactivated anilines [120,121], cyclohexenylboronic acid esters can be used in natural product synthesis. Selected examples are shown in Scheme 39. The tricyclic cores of cyrneine B (**S39–4**) and glaucopine C (**S39–5**) are synthesized from the diene **S39–3**, which is prepared by means of the Suzuki reaction of the cyclohexenylboronic acid ester **S39–2** with the cyclopentenyl triflate **S39–1** [122]. By contrast, the Suzuki reaction of the boronic acid **S39–6** is used to prepare the polyenes **S39–9** and **S39–10** during the preparation of the dihydroretinoic acids **S39–11a** and **S39–11b** [123].



Scheme 39. The use of borylated cyclohexenes for the synthesis of terpenoids.

5. Conclusions

In this work, we have shown how the borylated tetrasubstituted double bond has become an indispensable tool for the stereoselective preparation of tetrasubstituted alkenes. Alkenylboronic acids and alkenylboronates are the most commonly used tools for this purpose. These substances are mostly stable and easy to isolate compounds, which facilitates their use for the preparation of tetrasubstituted alkenes. In addition, a number of procedures have been developed for the stereoselective preparation of acyclic alkenylboronic acids from readily available compounds without the need for highly reactive organolithium and Grignard reagents. The situation is dramatically different for cycloalkenylboronic acids and cycloalkenylboronates. In this case, the stereoselectivity of the double bond is fixed, however, the limited stability and availability of cycloalkynes restricts their preparation to Li–B exchange reaction, Miyaura borylation, and cyclization procedures. The lack of suitable procedures for the preparation of cycloalkenylboronates is characteristic especially for the cyclization procedures. On the other hand, cyclic and acyclic vinylstannanes and

vinylsilanes are less commonly used for the stereoselective preparation of tetrasubstituted alkenes, which leaves the door open for further research in this regard.

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References

1. Albright, H.; Davis, A.J.; Gomez-Lopez, J.L.; Vonesh, H.L.; Quach, P.K.; Lambert, T.H.; Schindler, C.S. Carbonyl–Olefin Metathesis. *Chem. Rev.* **2021**, *121*, 9359–9406. [CrossRef] [PubMed]
2. Feng, X.; Du, H. Shi Epoxidation: A Great Shortcut to Complex Compounds. *Chin. J. Chem.* **2021**, *39*, 2016–2026. [CrossRef]
3. Kraft, S.; Ryan, K.; Kargbo, R.B. Recent Advances in Asymmetric Hydrogenation of Tetrasubstituted Olefins. *J. Am. Chem. Soc.* **2017**, *139*, 11630–11641. [CrossRef] [PubMed]
4. Wickham, L.M.; Giri, R. Transition Metal (Ni, Cu, Pd)-Catalyzed Alkene Dicarbofunctionalization Reactions. *Acc. Chem. Res.* **2021**, *54*, 3415–3437. [CrossRef]
5. Yao, H.; Hu, W.; Zhang, W. Difunctionalization of Alkenes and Alkynes via Intermolecular Radical and Nucleophilic Additions. *Molecules* **2020**, *26*, 105. [CrossRef]
6. Tandon, N.; Luxami, V.; Tandon, R.; Paul, K. Recent Advances in the Synthesis of Tamoxifen and Analogues in Medicinal Chemistry. *Asian J. Org. Chem.* **2020**, *9*, 1432–1465. [CrossRef]
7. Rajendran, S.; Swaroop, S.S.; Roy, J.; Inemai, E.; Murugan, S.; Rayala, S.K.; Venkatraman, G. p21 activated kinase-1 and tamoxifen—A deadly nexus impacting breast cancer outcomes. *BBA Rev. Cancer* **2022**, *1877*, 188668. [CrossRef]
8. Tsoi, H.; You, C.P.; Leung, M.H.; Man, E.P.S.; Khoo, U.S. Targeting Ribosome Biogenesis to Combat Tamoxifen Resistance in ER+ve Breast Cancer. *Cancers* **2022**, *14*, 1251. [CrossRef]
9. Zewdie, K.A.; Hailu, H.G.; Ayza, M.A.; Tesfaye, B.A. Antileishmanial Activity of Tamoxifen by Targeting Sphingolipid Metabolism: A Review. *Clin. Pharmacol.* **2022**, *14*, 11–17. [CrossRef]
10. Buttard, F.; Sharma, J.; Champagne, P.A. Recent advances in the stereoselective synthesis of acyclic all-carbon tetrasubstituted alkenes. *Chem. Commun.* **2021**, *57*, 4071–4088. [CrossRef]
11. Flynn, A.B.; Ogilvie, W.W. Stereocontrolled Synthesis of Tetrasubstituted Olefins. *Chem. Rev.* **2007**, *107*, 4698–4745. [CrossRef]
12. Fallis, A.G.; Forgione, P. Metal mediated carbometallation of alkynes and alkenes containing adjacent heteroatoms. *Tetrahedron* **2001**, *57*, 5899–5913. [CrossRef]
13. Ghosh, S.; Chakrabortty, R.; Ganesh, V. Dual Functionalization of Alkynes Utilizing the Redox Characteristics of Transition Metal Catalysts. *ChemCatChem* **2021**, *13*, 4262–4298. [CrossRef]
14. Gillbard, S.M.; Lam, H.W. Nickel-Catalyzed Arylative Cyclizations of Alkyne- and Allene-Tethered Electrophiles using Arylboron Reagents. *Chem. Eur. J.* **2022**, *28*, e202104230. [CrossRef]
15. Luo, Y.; Pan, X.; Yu, X.; Wu, J. Double carbometallation of alkynes: An efficient strategy for the construction of polycycles. *Chem. Soc. Rev.* **2014**, *43*, 834–846. [CrossRef]
16. Schitter, T.; Reding, A.; Werz, D.B. Cascades Involving anti-Carbopalladation Steps: From Our Initial Hypothesis to Natural Product Synthesis. *Synlett* **2019**, *30*, 1275–1288. [CrossRef]
17. Edlová, T.; Čubiňák, M.; Tobrman, T. Cross-Coupling Reactions of Double or Triple Electrophilic Templates for Alkene Synthesis. *Synthesis* **2021**, *53*, 255–266.
18. Negishi, E.-i.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. Recent Advances in Efficient and Selective Synthesis of Di-, Tri-, and Tetrasubstituted Alkenes via Pd-Catalyzed Alkenylation-Carbonyl Olefination Synergy. *Acc. Chem. Res.* **2008**, *41*, 1474–1485. [CrossRef]
19. Polák, P.; Váňová, H.; Dvořák, D.; Tobrman, T. Recent progress in transition metal-catalyzed stereoselective synthesis of acyclic all-carbon tetrasubstituted alkenes. *Tetrahedron Lett.* **2016**, *57*, 3684–3693. [CrossRef]
20. Reiser, O. Palladium-Catalyzed Coupling Reactions for the Stereoselective Synthesis of Tri- and Tetrasubstituted Alkenes. *Angew. Chem. Int. Ed.* **2006**, *45*, 2838–2840. [CrossRef]
21. Yoshida, H. Borylation and Stannylation Reactions with Tuning of Lewis Acidity. *Chem. Rec.* **2021**, *21*, 3483–3497. [CrossRef]
22. Yoshida, H. Borylation of Alkynes under Base/Coinage Metal Catalysis: Some Recent Developments. *ACS Catal.* **2016**, *6*, 1799–1811. [CrossRef]
23. Velasco, R.; Feberero, C.; Sanz, R. α-Lithiated Aryl Benzyl Ethers: Inhibition of [1,2]-Wittig Rearrangement and Application to the Synthesis of Benzo[b]furan Derivatives. *Org. Lett.* **2015**, *17*, 4416–4419. [CrossRef]

24. Eiji, S.; Tamejiro, H. Transition Metal-Catalyzed Carbostannylation of Alkynes and Dienes. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1435–1450. [CrossRef]
25. Yoshida, H. Stannylation Reactions under Base Metal Catalysis: Some Recent Advances. *Synthesis* **2016**, *48*, 2540–2552. [CrossRef]
26. Mukai, C.; Kozaka, T.; Suzuki, Y.; Kim, I.J. New entry to the Pauson–Khand reaction: Trimethylgermyl group at the triple bond terminus as a latent functional group. *Tetrahedron* **2004**, *60*, 2497–2507. [CrossRef]
27. Mohamed, R.K.; Mondal, S.; Gold, B.; Evoniuk, C.J.; Banerjee, T.; Hanson, K.; Alabugin, I.V. Alkenes as Alkyne Equivalents in Radical Cascades Terminated by Fragmentations: Overcoming Stereoelectronic Restrictions on Ring Expansions for the Preparation of Expanded Polyaromatics. *J. Am. Chem. Soc.* **2015**, *137*, 6335–6349. [CrossRef]
28. Dalkılıç, E.; Daştan, A. Synthesis of cyclopentadiene derivatives by retro-Diels–Alder reaction of norbornadiene derivatives. *Tetrahedron* **2015**, *71*, 1966–1970. [CrossRef]
29. Shipe, W.D.; Sorensen, E.J. A Convergent Synthesis of the Tricyclic Architecture of the Guanacastepenes Featuring a Selective Ring Fragmentation. *Org. Lett.* **2002**, *4*, 2063–2066. [CrossRef]
30. Shipe, W.D.; Sorensen, E.J. Convergent, Enantioselective Syntheses of Guanacastepenes A and E Featuring a Selective Cyclobutane Fragmentation. *J. Am. Chem. Soc.* **2006**, *128*, 7025–7035. [CrossRef]
31. Masters, K.-S.; Flynn, B.L. An efficient synthesis of (±)-frondosin B using a Stille–Heck reaction sequence. *Org. Biomol. Chem.* **2010**, *8*, 1290–1292. [CrossRef] [PubMed]
32. Smith, B.J.; Qu, T.; Mulder, M.; Noetzel, M.J.; Lindsley, C.W.; Sulikowski, G.A. Synthesis and bioactivity of (±)-tetrahydrohaliclonacyclamine A. *Tetrahedron* **2010**, *66*, 4805–4810. [CrossRef]
33. Smith, B.J.; Sulikowski, G.A. Total Synthesis of (±)-Haliclonacyclamine C. *Angew. Chem. Int. Ed.* **2010**, *49*, 1599–1602. [CrossRef] [PubMed]
34. Williams, D.R.; Gladen, P.T.; Pinchman, J.R. Total Synthesis of Neodolastane Diterpenes Trichoaurantianolides C and D. *J. Org. Chem.* **2015**, *80*, 5474–5493. [CrossRef] [PubMed]
35. Zhang, Z.; Wang, J.; Li, J.; Yang, F.; Liu, G.; Tang, W.; He, W.; Fu, J.-J.; Shen, Y.-H.; Li, A.; et al. Total Synthesis and Stereochemical Assignment of Delavatine A: Rh-Catalyzed Asymmetric Hydrogenation of Indene-Type Tetrasubstituted Olefins and Kinetic Resolution through Pd-Catalyzed Triflamide-Directed C–H Olefination. *J. Am. Chem. Soc.* **2017**, *139*, 5558–5567. [CrossRef] [PubMed]
36. Braunschweig, H.; Celik, M.A.; Dellermann, T.; Frenking, G.; Hammond, K.; Hupp, F.; Kelch, H.; Krummenacher, I.; Lindl, F.; Mailänder, L.; et al. Scope of the Thermal Ring-Expansion Reaction of Boroles with Organoazides. *Chem. Eur. J.* **2017**, *23*, 8006–8013. [CrossRef] [PubMed]
37. Chaładaj, W.; Domański, S. Mild and Functional Group Tolerant Method for Tandem Palladium-Catalyzed Carbocyclization–Coupling of ε-Acetylenic β-Ketoesters with Aryl Bromides and Chlorides. *Adv. Synth. Catal.* **2016**, *358*, 1820–1825. [CrossRef]
38. Iwasaki, M.; Araki, Y.; Iino, S.; Nishihara, Y. Synthesis of Multisubstituted Triphenylenes and Phenanthrenes by Cascade Reaction of o-Iodobiphenyls or (Z)-β-Halostyrenes with o-Bromobenzyl Alcohols through Two Sequential C–C Bond Formations Catalyzed by a Palladium Complex. *J. Org. Chem.* **2015**, *80*, 9247–9263. [CrossRef]
39. Piers, E.; Romero, M.Á. Palladium-Catalyzed Intramolecular Decarboxylative Allylation of (2-Trimethylstannyl)allyl β-Oxocarboxylates. *Synthesis* **2011**, 4017–4022. [CrossRef]
40. Ruan, Y.; Wang, B.-Y.; Erb, J.M.; Chen, S.; Hadad, C.M.; Badjić, J.D. On the role of guests in enforcing the mechanism of action of gated baskets. *Org. Biomol. Chem.* **2013**, *11*, 7667–7675. [CrossRef]
41. Tanino, K.; Yamada, T.; Yoshimura, F.; Suzuki, T. Cyanoazulene-based Multistage Redox Systems Prepared from Vinylcyclopropanecarbonitrile and Cyclopentenone via Divinylcyclopropane-rearrangement Approach. *Chem. Lett.* **2014**, *43*, 607–609. [CrossRef]
42. Kats-Kagan, R.; Herzon, S.B. The Discovery of a Novel Route to Highly Substituted α-Tropolones Enables Expedient Entry to the Core of the Gukulenins. *Org. Lett.* **2015**, *17*, 2030–2033. [CrossRef]
43. Dastan, A.; Uzundumlu, E.; Balci, M.; Fabris, F.; De Lucchi, O. An Investigation on the Synthesis of New Molecular Architectures from the Cyclotrimerisation of exo- and endo-Benzotricyclo[4.2.1.02,5]nonene. *Eur. J. Org. Chem.* **2004**, 183–192. [CrossRef]
44. Shintani, R.; Kurata, H.; Nozaki, K. Intermolecular Three-Component Arylsilylation of Alkynes under Palladium/Copper Cooperative Catalysis. *J. Org. Chem.* **2016**, *81*, 3065–3069. [CrossRef]
45. Zhou, B.; Lu, A.; Shao, C.; Liang, X.; Zhang, Y. Palladium-catalyzed sequential three-component reactions to access vinylsilanes. *Chem. Commun.* **2018**, *54*, 10598–10601. [CrossRef]
46. Wisthoff, M.F.; Pawley, S.B.; Cinderella, A.P.; Watson, D.A. Stereoselective Synthesis of Cis- and Trans-Tetrasubstituted Vinyl Silanes Using a Silyl-Heck Strategy and Hiyama Conditions for Their Cross-Coupling. *J. Am. Chem. Soc.* **2020**, *142*, 12051–12055. [CrossRef]
47. Denmark, S.E.; Kallemeyn, J.M. Stereospecific Palladium-Catalyzed Cross-Coupling of (E)- and (Z)-Alkenylsilanolates with Aryl Chlorides. *J. Am. Chem. Soc.* **2006**, *128*, 15958–15959. [CrossRef]
48. Kuang, Z.; Gao, G.; Song, Q. Base-catalyzed diborylation of alkynes: Synthesis and applications of cis-1,2-bis(boryl)alkenes. *Sci. China Chem.* **2019**, *62*, 62–66. [CrossRef]
49. Ito, S.; Fukazawa, M.; Takahashi, F.; Nogi, K.; Yorimitsu, H. Sodium-Metal-Promoted Reductive 1,2-syn-Diboration of Alkynes with Reduction-Resistant Trimethoxyborane. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1171–1179. [CrossRef]

50. Nakagawa, N.; Hatakeyama, T.; Nakamura, M. Iron-Catalyzed Diboration and Carboboration of Alkynes. *Chem. Eur. J.* **2015**, *21*, 4257–4261. [CrossRef]
51. Ferrand, L.; Lyu, Y.; Rivera-Hernández, A.; Fallon, B.J.; Amatore, M.; Aubert, C.; Petit, M. Hydroboration and Diboration of Internal Alkynes Catalyzed by a Well-Defined Low-Valent Cobalt Catalyst. *Synthesis* **2017**, *49*, 3895–3904. [CrossRef]
52. Hyodo, K.; Suetsugu, M.; Nishihara, Y. Diborylation of Alkynyl MIDA Boronates and Sequential Chemoselective Suzuki–Miyaura Couplings: A Formal Carboborylation of Alkynes. *Org. Lett.* **2014**, *16*, 440–443. [CrossRef]
53. Lai, Q.; Ozerov, O.V. Dehydrogenative Diboration of Alkynes Catalyzed by Ir/CO/tBuNC System. *J. Organomet. Chem.* **2021**, *931*, 121614. [CrossRef]
54. Lee, C.-I.; Shih, W.-C.; Zhou, J.; Reibenspies, J.H.; Ozerov, O.V. Synthesis of Triborylalkenes from Terminal Alkynes by Iridium-Catalyzed Tandem C–H Borylation and Diboration. *Angew. Chem. Int. Ed.* **2015**, *54*, 14003–14007. [CrossRef]
55. Liu, X.; Ming, W.; Friedrich, A.; Kerner, F.; Marder, T.B. Copper-Catalyzed Triboration of Terminal Alkynes Using B_2pin_2: Efficient Synthesis of 1,1,2-Triborylalkenes. *Angew. Chem. Int. Ed.* **2020**, *59*, 304–309. [CrossRef]
56. Yoshii, D.; Jin, X.; Mizuno, N.; Yamaguchi, K. Selective Dehydrogenative Mono- or Diborylation of Styrenes by Supported Copper Catalysts. *ACS Catal.* **2019**, *9*, 3011–3016. [CrossRef]
57. Semba, K.; Yoshizawa, M.; Ohtagaki, Y.; Nakao, Y. Arylboration of Internal Alkynes by Cooperative Palladium/Copper Catalysis. *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1340–1343. [CrossRef]
58. Huang, Y.; Bergmann, A.M.; Brown, M.K. (Hetero)arylboration of alkynes: A strategy for the synthesis of α,α-bis(hetero)arylketones. *Org. Biomol. Chem.* **2019**, *17*, 5913–5915. [CrossRef]
59. Zhang, W.-D.; Zou, J.-Y.; Zhong, Q.; Li, S.-S.; Zhao, J. Synergistic Pd/Cu-catalysed regio- and stereoselective borylation of allenylic carbonates. *Chem. Commun.* **2022**, *58*, 1037–1040. [CrossRef]
60. Wigman, B.; Lee, W.; Wei, W.; Houk, K.N.; Nelson, H.M. Electrochemical Fluorination of Vinyl Boronates through Donor-Stabilized Vinyl Carbocation Intermediates. *Angew. Chem. Int. Ed.* **2022**, *61*, e202113972. [CrossRef]
61. Nozawa, R.; Shinokubo, H. Synthesis and Properties of meso-Arylated Corrphycenes. *Org. Lett.* **2017**, *19*, 4928–4931. [CrossRef] [PubMed]
62. La Cascia, E.; Cuenca, A.B.; Fernández, E. Opportune gem-Silylborylation of Carbonyl Compounds: A Modular and Stereocontrolled Entry to Tetrasubstituted Olefins. *Chem. Eur. J.* **2016**, *22*, 18737–18741. [CrossRef] [PubMed]
63. Cho, S.H.; Hartwig, J.F. Iridium-catalyzed diborylation of benzylic C–H bonds directed by a hydrosilyl group: Synthesis of 1,1-benzyldiboronate esters. *Chem. Sci.* **2014**, *5*, 694–698. [CrossRef]
64. Zhou, Y.; You, W.; Smith, K.B.; Brown, M.K. Copper-Catalyzed Cross-Coupling of Boronic Esters with Aryl Iodides and Application to the Carboboration of Alkynes and Allenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 3475–3479. [CrossRef] [PubMed]
65. Xu, N.; Xu, J.; Zhu, Q.; Liu, C. Synthesis of Allylboronates via Zweifel-type Deprotonative Olefination. *Adv. Synth. Catal.* **2021**, *363*, 2403–2407. [CrossRef]
66. Bin, H.-Y.; Wei, X.; Zi, J.; Zuo, Y.-J.; Wang, T.-C.; Zhong, C.-M. Substrate-Controlled Regio- and Stereoselective Synthesis of Boron-Substituted 1,4-Dienes via Copper-Catalyzed Boryl–Allylation of Alkynes with Allyl Phosphates and Bis(pinacolato)diboron. *ACS Catal.* **2015**, *5*, 6670–6679. [CrossRef]
67. Itoh, T.; Shimizu, Y.; Kanai, M. Ligand-Enabled, Copper-Catalyzed Regio- and Stereoselective Synthesis of Trialkylsubstituted Alkenylboronates from Unactivated Internal Alkynes. *J. Am. Chem. Soc.* **2016**, *138*, 7528–7531. [CrossRef]
68. Sanderson, M.D.; Kamplain, J.W.; Bielawski, C.W. Quinone-Annulated N-Heterocyclic Carbene-Transition-Metal Complexes: Observation of π-Backbonding Using FT-IR Spectroscopy and Cyclic Voltammetry. *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515. [CrossRef]
69. Kubota, K.; Iwamoto, H.; Yamamoto, E.; Ito, H. Silicon-Tethered Strategy for Copper(I)-Catalyzed Stereo- and Regioselective Alkylboration of Alkynes. *Org. Lett.* **2015**, *17*, 620–623. [CrossRef]
70. Muchnij, J.A.; Kwaramba, F.B.; Rahaim, R.J. Sterically Directed Iridium-Catalyzed Hydrosilylation of Alkenes in the Presence of Alkynes. *Org. Lett.* **2014**, *16*, 1330–1333. [CrossRef]
71. Tamao, K.; Ishida, N.; Kumada, M. (Diisopropoxymethylsilyl)methyl Grignard reagent: A new, practically useful nucleophilic hydroxymethylating agent. *J. Org. Chem.* **1983**, *48*, 2120–2122. [CrossRef]
72. Iwamoto, H.; Ozawa, Y.; Kubota, K.; Ito, H. Copper(I)-Catalyzed Regio- and Stereoselective Intramolecular Alkylboration of Propargyl Ethers and Amines. *J. Org. Chem.* **2017**, *82*, 10563–10573. [CrossRef]
73. Zhu, C.; Yang, B.; Qiu, Y.; Bäckvall, J.-E. Olefin-Directed Palladium-Catalyzed Regio- and Stereoselective Hydroboration of Allenes. *Chem. Eur. J.* **2016**, *22*, 2939–2943. [CrossRef]
74. Qiu, Y.; Yang, B.; Zhu, C.; Bäckvall, J.-E. Palladium-Catalyzed Oxidative Carbocyclization–Borylation of Enallenes to Cyclobutenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 6520–6524. [CrossRef]
75. Jin, H.; Fürstner, A. Regioselective trans-Carboboration of Propargyl Alcohols. *Org. Lett.* **2019**, *21*, 3446–3450. [CrossRef]
76. Takahashi, F.; Nogi, K.; Sasamori, T.; Yorimitsu, H. Diborative Reduction of Alkynes to 1,2-Diboryl-1,2-Dimetalloalkanes: Its Application for the Synthesis of Diverse 1,2-Bis(boronate)s. *Org. Lett.* **2019**, *21*, 4739–4744. [CrossRef]
77. Tani, T.; Takahashi, N.; Sawatsugawa, Y.; Osano, M.; Tsuchimoto, T. Stepwise Suzuki–Miyaura Cross-Coupling of Triborylalkenes Derived from Alkynyl–B(dan)s: Regioselective and Flexible Synthesis of Tetrasubstituted Alkenes. *Adv. Synth. Catal.* **2021**, *363*, 2427–2442. [CrossRef]

78. Tani, T.; Sawatsugawa, Y.; Sano, Y.; Hirataka, Y.; Takahashi, N.; Hashimoto, S.; Sugiura, T.; Tsuchimoto, T. Alkynyl–B(dan)s in Various Palladium-Catalyzed Carbon–Carbon Bond-Forming Reactions Leading to Internal Alkynes, 1,4-Enynes, Ynones, and Multiply Substituted Alkenes. *Adv. Synth. Catal.* **2019**, *361*, 1815–1834. [CrossRef]
79. Tsuchimoto, T.; Utsugi, H.; Sugiura, T.; Horio, S. Alkynylboranes: A Practical Approach by Zinc-Catalyzed Dehydrogenative Coupling of Terminal Alkynes with 1,8-Naphthalenediaminatoborane. *Adv. Synth. Catal.* **2015**, *357*, 77–82. [CrossRef]
80. Zhang, M.; Yao, Y.; Stang, P.J.; Zhao, W. Divergent and Stereoselective Synthesis of Tetraarylethylenes from Vinylboronates. *Angew. Chem. Int. Ed.* **2020**, *59*, 20090–20098. [CrossRef]
81. Biswas, S.; Jana, D.; Kumar, G.S.; Maji, S.; Kundu, P.; Ghorai, U.K.; Giri, R.P.; Das, B.; Chattopadhyay, N.; Ghorai, B.K.; et al. Supramolecular Aggregates of Tetraphenylethene-Cored AIEgen toward Mechanoluminescent and Electroluminescent Devices. *ACS Appl. Mater. Interfaces* **2018**, *10*, 17409–17418. [CrossRef]
82. Wang, L.; Li, W.; Wang, Z.; Luo, Q. Triptycene-scaffolded tetraphenylethylenes with irregular temperature-dependence AIE. *Tetrahedron Lett.* **2019**, *60*, 439–443. [CrossRef]
83. Liu, Y.; Bai, Q.; Li, J.; Zhang, S.; Zhang, C.; Lu, F.; Yang, B.; Lu, P. Efficient pyrene-imidazole derivatives for organic light-emitting diodes. *RSC Adv.* **2016**, *6*, 17239–17245. [CrossRef]
84. Dong, Y.; Shen, J.; Li, W.; Zhao, R.; Pan, Y.; Song, Q.; Zhang, C. Opposite ESIPT characteristic of two AIE-active isomers with different linkage sites. *Tetrahedron* **2019**, *75*, 2670–2675. [CrossRef]
85. Huang, W.; Zhang, H.; Ma, J.; Chen, M.; Zhu, H.; Wang, W. Ladder-type conjugated oligomers prepared by the Scholl oxidative cyclodehydrogenation reaction: Synthesis, characterization and application in field effect transistors. *J. Mater. Chem. C* **2015**, *3*, 6200–6208. [CrossRef]
86. Huang, Y.; Huang, W.; Yang, J.; Ma, J.; Chen, M.; Zhu, H.; Wang, W. The synthesis, characterization and flexible OFET application of three (Z)-1,2-bis(4-(tert-butyl)phenyl)ethane based copolymers. *Polym. Chem.* **2016**, *7*, 538–545. [CrossRef]
87. Yang, J.; Huang, W.; Lin, T.; Pan, X.; Zhu, H.; Huang, Y.; Wang, W. Intramolecular oxidative cyclodehydrogenation route for the synthesis of strap-like conjugated polymers. *RSC Adv.* **2017**, *7*, 10763–10773. [CrossRef]
88. Yang, L.; Zhang, Y.; Zhang, X.; Li, N.; Quan, Y.; Cheng, Y. Doping-free circularly polarized electroluminescence of AIE-active chiral binaphthyl-based polymers. *Chem. Commun.* **2018**, *54*, 9663–9666. [CrossRef]
89. Bijesh, S.; Misra, R. Triphenylamine Functionalized Unsymmetrical Quinoxalines. *Asian J. Org. Chem.* **2018**, *7*, 1882–1892. [CrossRef]
90. Li, Y.; Liu, K.; Li, X.; Quan, Y.; Cheng, Y. The amplified circularly polarized luminescence regulated from D–A type AIE-active chiral emitters via liquid crystals system. *Chem. Commun.* **2020**, *56*, 1117–1120. [CrossRef]
91. Maragani, R.; Sharma, R.; Misra, R. Donor-Acceptor Triphenylvinyl and Tetraphenyl Conjugates: Synthesis, Aggregation and Computational Studies. *ChemistrySelect* **2017**, *2*, 10033–10037. [CrossRef]
92. Qi, J.; Duan, X.; Cai, Y.; Jia, S.; Chen, C.; Zhao, Z.; Li, Y.; Peng, H.-Q.; Kwok, R.T.K.; Lam, J.W.Y.; et al. Simultaneously boosting the conjugation, brightness and solubility of organic fluorophores by using AIEgens. *Chem. Sci.* **2020**, *11*, 8438–8447. [CrossRef] [PubMed]
93. Blomquist, A.T.; Liu, L.H. Many-membered Carbon Rings. VII. Cycloöctyne. *J. Am. Chem. Soc.* **1953**, *75*, 2153–2154. [CrossRef]
94. Green, J.R. Cycloheptyne–cobalt complexes via allylation of stabilized γ-carbonyl cations. *Chem. Commun.* **1998**, 1751–1752. [CrossRef]
95. Farmer, M.E.; Ehehalt, L.E.; Pabst, T.P.; Tudge, M.T.; Chirik, P.J. Well-Defined Cationic Cobalt(I) Precatalyst for Olefin-Alkyne [2 + 2] Cycloaddition and Olefin-Diene Hydrovinylation Reactions: Experimental Evidence for Metallacycle Intermediates. *Organometallics* **2021**, *40*, 3599–3607. [CrossRef]
96. Polák, P.; Tobrman, T. Novel Selective Approach to Terminally Substituted [n]Dendralenes. *Eur. J. Org. Chem.* **2019**, *2019*, 957–968. [CrossRef]
97. Nowikow, C.; Fuerst, R.; Kauderer, M.; Dank, C.; Schmid, W.; Hajduch, M.; Rehulka, J.; Gurska, S.; Mokshyna, O.; Polishchuk, P.; et al. Synthesis and biological evaluation of cis-restrained carbocyclic combretastatin A-4 analogs: Influence of the ring size and saturation on cytotoxic properties. *Bioorg. Med. Chem.* **2019**, *27*, 115032. [CrossRef]
98. León, T.; Fernández, E. The Pauson–Khand reaction using alkynylboronic esters: Solving a long-standing regioselectivity issue. *Chem. Commun.* **2016**, *52*, 9363–9366. [CrossRef]
99. Albarghouti, G.; Rayyan, S. General Method for the Synthesis of Substituted Cyclopentenones via α-Borylzirconacyclopentene Intermediates. *Org. Prep. Proced. Int.* **2020**, *52*, 1–8. [CrossRef]
100. Sarter, C.; Dey, S.; Jäschke, A. Photoswitchable Oligonucleotides Containing Different Diarylethene-Modified Nucleotides. *ACS Omega* **2019**, *4*, 12125–12129. [CrossRef]
101. Buckup, T.; Sarter, C.; Volpp, H.-R.; Jäschke, A.; Motzkus, M. Ultrafast Time-Resolved Spectroscopy of Diarylethene-Based Photoswitchable Deoxyuridine Nucleosides. *J. Phys. Chem. Lett.* **2015**, *6*, 4717–4721. [CrossRef]
102. Kellis, D.L.; Sarter, C.; Cannon, B.L.; Davis, P.H.; Graugnard, E.; Lee, J.; Pensack, R.D.; Kolmar, T.; Jäschke, A.; Yurke, B.; et al. An All-Optical Excitonic Switch Operated in the Liquid and Solid Phases. *ACS Nano* **2019**, *13*, 2986–2994. [CrossRef]
103. Altenhofer, E.; Harmata, M. Radical isomerization of borylated allylic sulfones. *Tetrahedron Lett.* **2015**, *56*, 3176–3178. [CrossRef]
104. Altenhofer, E.F.; Harmata, M. Suzuki–Miyaura Coupling Reactions of Conjunctive Reagents: 2-Borylated Allylic Sulfones. *J. Org. Chem.* **2015**, *80*, 8168–8174. [CrossRef]

105. Palani, V.; Hugelshofer, C.L.; Kevlishvili, I.; Liu, P.; Sarpong, R. A Short Synthesis of Delavatine A Unveils New Insights into Site-Selective Cross-Coupling of 3,5-Dibromo-2-pyrone. *J. Am. Chem. Soc.* **2019**, *141*, 2652–2660. [CrossRef]
106. Palani, V.; Hugelshofer, C.L.; Sarpong, R. A Unified Strategy for the Enantiospecific Total Synthesis of Delavatine A and Formal Synthesis of Incarviatone A. *J. Am. Chem. Soc.* **2019**, *141*, 14421–14432. [CrossRef]
107. Hong, B.; Li, C.; Wang, Z.; Chen, J.; Li, H.; Lei, X. Enantioselective Total Synthesis of (−)-Incarviatone A. *J. Am. Chem. Soc.* **2015**, *137*, 11946–11949. [CrossRef]
108. Geng, S.; Zhang, J.; Chen, S.; Liu, Z.; Zeng, X.; He, Y.; Feng, Z. Development and Mechanistic Studies of Iron-Catalyzed Construction of Csp2–B Bonds via C–O Bond Activation. *Org. Lett.* **2020**, *22*, 5582–5588. [CrossRef]
109. Sasaki, I.; Taguchi, J.; Doi, H.; Ito, H.; Ishiyama, T. Iridium(I)-catalyzed C–H Borylation of α,β-Unsaturated Esters with Bis(pinacolato)diboron. *Chem. Asian J.* **2016**, *11*, 1400–1405. [CrossRef]
110. Heinrich, C.F.; Durand, D.; Starck, J.; Michelet, V. Ruthenium Metathesis: A Key Step To Access a New Cyclic Tetrasubstituted Olefin Platform. *Org. Lett.* **2020**, *22*, 7064–7067. [CrossRef]
111. Warner, A.J.; Lawson, J.R.; Fasano, V.; Ingleson, M.J. Formation of C(sp^2)–Boronate Esters by Borylative Cyclization of Alkynes Using BCl_3. *Angew. Chem. Int. Ed.* **2015**, *54*, 11245–11249. [CrossRef] [PubMed]
112. Kamio, S.; Yoshida, H. Synthetic Chemistry with Lewis Acidity-Diminished B(aam) and B(dan) Groups: Borylation Reactions and Direct Cross-Couplings. *Adv. Synth. Catal.* **2021**, *363*, 2310–2324. [CrossRef]
113. Kubota, K.; Iwamoto, H.; Ito, H. Formal nucleophilic borylation and borylative cyclization of organic halides. *Org. Biomol. Chem.* **2017**, *15*, 285–300. [CrossRef] [PubMed]
114. Steven, A. Micelle-Mediated Chemistry in Water for the Synthesis of Drug Candidates. *Synthesis* **2019**, *51*, 2632–2647. [CrossRef]
115. Yamamoto, E.; Ukigai, S.; Ito, H. Boryl substitution of functionalized aryl-, heteroaryl- and alkenyl halides with silylborane and an alkoxy base: Expanded scope and mechanistic studies. *Chem. Sci.* **2015**, *6*, 2943–2951. [CrossRef]
116. Gunther, M.J.; Pavlović, R.Z.; Finnegan, T.J.; Wang, X.; Badjić, J.D. Enantioselective Construction of Modular and Asymmetric Baskets. *Angew. Chem. Int. Ed.* **2021**, *60*, 25075–25081. [CrossRef]
117. Zhao, X.; Song, C.; Rainier, J.D. Stereodivergent Photoelectrocyclization Reactions of Bis-aryl Cycloalkenones: Intercepting Photoelectrocyclization Intermediates with Acid. *Org. Lett.* **2019**, *21*, 8611–8614. [CrossRef]
118. Zhao, X.; Song, C.; Rainier, J.D. Photoelectrocyclization Reactions of Conjugated Cycloalkenones: Scope and Reactivity. *J. Org. Chem.* **2020**, *85*, 5449–5463. [CrossRef]
119. Wang, K.; Jiang, C.; Zhang, Z.; Han, C.; Wang, X.; Li, Y.; Chen, K.; Zhao, J. Cut and sew: Benzofuran-ring-opening enabled cyclopentenone ring formation. *Chem. Commun.* **2020**, *56*, 12817–12820. [CrossRef]
120. Deng, T.; Mazumdar, W.; Ford, R.L.; Jana, N.; Izar, R.; Wink, D.J.; Driver, T.G. Oxidation of Nonactivated Anilines to Generate N-Aryl Nitrenoids. *J. Am. Chem. Soc.* **2020**, *142*, 4456–4463. [CrossRef]
121. Deng, T.; Shi, E.; Thomas, E.; Driver, T.G. I(III)-Catalyzed Oxidative Cyclization–Migration Tandem Reactions of Unactivated Anilines. *Org. Lett.* **2020**, *22*, 9102–9106. [CrossRef]
122. Wu, G.-J.; Han, X. An improved synthesis of the [5.6.7]-tricyclic core of cyrneine B and glaucopine C. *Org. Chem. Front.* **2020**, *7*, 2960–2964. [CrossRef]
123. Vaz, B.; Alvarez, R.; de Lera, A.R. Stereocontrolled synthesis of (S)-9-*cis*- and (*S*)-11-*cis*-13,14-dihydroretinoic acid. *Tetrahedron* **2016**, *72*, 3898–3904. [CrossRef]