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Palladium Pincer Complex Catalyzed Cross-Coupling of Vinyl Epoxides and Aziridines with Organoboronic Acids

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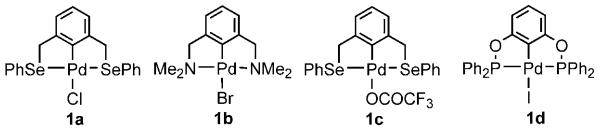
Abstract: Palladium-catalyzed cross-coupling of vinyl epoxides and aziridines with organoboronic acids was performed by using 0.5–2.5 mol% pincer-complex catalyst. The reactions proceed under mild conditions affording allyl alcohols and amines with high regioselectivity and in good to excellent yields. Under the applied reaction conditions aromatic chloro-, bromo- and iodo substituents are tolerated. Our results indicate that the mechanism of the pincer complex catalyzed and the corresponding palladium(0) catalyzed process is substantially different. It was concluded that the transformations proceed via transmetalation of the organoboronic acids to the pincer-complex catalyst followed by an S_N2'-type opening of the vinyl epoxide or aziridine substrate. In this process the palladium atom is kept in oxidation state +2 under the entire catalytic process, and therefore oxidative side reactions can be avoided.

Keywords: allylic compounds · boron · homogeneous catalysis · palladium · pincer complexes

Introduction

Palladium catalysis has become one of the most successful areas of organic synthesis due to its remarkable capacity for continuous renewal.[1–4] An important current challenge in palladium chemistry is the development of new redox reaction free catalytic systems.[5–12] In these catalytic reactions the oxidation state of palladium is usually restricted to +2; and therefore formation of palladium(0) intermediates can be avoided. It is well known that palladium(0) complexes with weakly coordinating ligands easily decompose forming amorphous palladium metal (palladium black), which is usually catalytically inactive. Furthermore, palladium(0) complexes readily undergo oxidative addition to aromatic carbon–halogen bonds, which might be undesired limiting the synthetic scope of the corresponding reaction.[1–4] We have recently found[13–18] that palladium pincer complexes,[5,6,19–22] such as **1a**–**d**[23–25] (Scheme 1), are particularly useful species to catalyze redox free synthesis and transformation of organo stannanes and silanes. Thus, we have shown that allylic and propargylic substrates undergo substitution reactions with dimetallic reagents (such as distannane and silylstannane reagents) to give allyl and propargyl stannanes and silanes.[15,16,18] In these reactions, we exploited three important features of the palladium-pincer complex catalysts: i) high redox stability of the palladium(II) central atom; ii) very strong terdentate ligand–metal bonding; and iii) presence of a σ-donating aryl ligand. Because of these features application of pincer-complex catalysts have a great potential to open new synthetic routes in palladium-catalyzed transformations.



Scheme 1. Pincer-complex catalysts employed in this study.

Recently, our interest turned to the application of pincer-complex catalysts in organoboron chemistry.[17] We have shown that potassium(allyl)trifluoroborates undergo pincer complex catalyzed allylation of sulfonyl imines under mild reaction conditions.[17] In this study we report our recent results on the palladium-pincer complex catalyzed ring opening of vinyl epoxides and aziridines (Scheme 2) with organoboronic acids. Although, palladium-catalyzed coupling of or-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: ^{13}C NMR spectra of compounds **4a**–**n**, **7a**–**p** and complex **9**.

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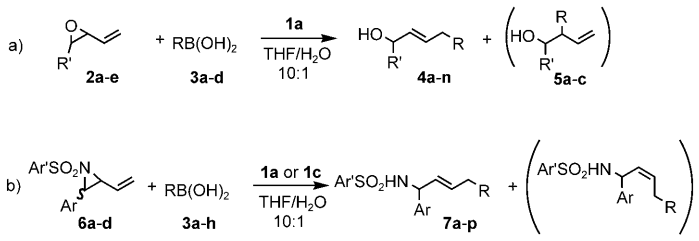


Scheme 2. Ring opening of a) vinyl epoxides and b) vinyl aziridines with organoboronic acids in the presence of catalytic amounts (0.5–2.5 mol%) of pincer complexes.

ganoboronic acids with various unsaturated substrates (Suzuki–Miyaura cross-coupling) has become one of the most important processes in synthetic organic chemistry,[26–31] the literature of palladium-catalyzed cross-coupling reactions of organoboranes with vinyl epoxides and aziridines is surprisingly scarce. Suzuki and Miyaura reported[32] a successful palladium(0)-catalyzed carbon–carbon coupling reaction of vinyl epoxides with alkenylboranes. Interestingly, by using $[Pd(PPh_3)_4]$ as catalyst source vinyl epoxides undergo carbon-oxygen coupling with arylboronic acids via (η^3-allyl)-palladium intermediates.[33] In this reaction the boronic acid derivatives react as oxygen nucleophiles instead of as carbon nucleophiles.[33,34] However, palladium-catalyzed carbon–carbon coupling of vinyl epoxides with aryl- and alkenylboronic acids has not been reported in the literature. Besides, there is a remarkable lack in the literature concerning palladium-catalyzed ring opening reactions of vinyl aziridines with organoboranes. In this study we like to demonstrate that palladium-pincer complexes **1a–c** are efficient catalysts in cross-coupling of vinyl epoxides and aziridines with organoboronic acids. In particular, we have studied the tolerance of the pincer-complex catalysts toward aromatic halogenide functionalities (chloride, bromide and iodide), which are often incompatible with palladium(0) catalysts. Furthermore, we have briefly studied the mechanistic differences between the palladium(0) and pincer-complex catalysis in ring opening of vinyl aziridines and epoxides with organoboronic acids.

Results and Discussion

Catalytic ring-opening of vinyl epoxides with organoboronic acids: Our studies have shown that vinyl epoxides **2a–e** can be efficiently coupled with arylboronic acids **3a–d** using catalytic amounts of **1a**. In these processes we have employed the typical reaction conditions of the Suzuki–Miyaura coupling reactions including the use of base and water as additives. Accordingly, in a typical procedure the appropriate epoxide (**2a–e**), the organoboronic acid derivative **3a–d** (1.2 equiv), Cs_2CO_3 (2 equiv) and catalyst **1a** (2.5 mol%) in THF/water 10:1 were stirred at 20°C for 4–9 h. Subsequently the solvent was evaporated and the product was purified by chromatography. This reaction does *not* require use of inert gas atmosphere or employment of carefully dried THF. It is also important to add that the elegant synthesis of catalyst **1a** reported by Yao and co-workers[23] is about as simple as the preparation of commonly employed palladium catalysts, such as $[Pd(PPh_3)_4]$, or $[Pd_2(dba)_3]$. Furthermore, in our experience catalyst **1a** is more stable than these classical palladium(0) catalysts, as it can be stored at ambient temperature and atmosphere without any loss of the catalytic activity.

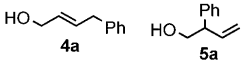
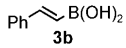
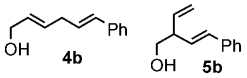
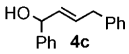
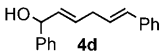
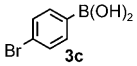
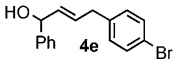
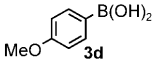
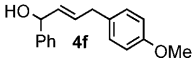
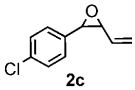
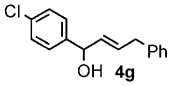
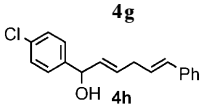
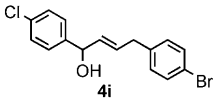
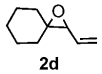
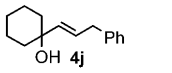
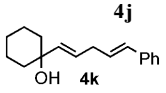
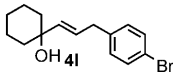
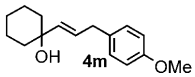
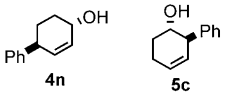
Because of the mild reaction conditions and the redox stability of the catalyst (feature i) above) halogenide (Cl and Br) substituents on the vinyl epoxide substrate (**2c**) and on the arylboronic acid component (**3c**) are tolerated. We did not observe any carbon–halogen bond cleavage in the cross-coupling reactions involving **2c** or **3c** (entries 9, 11–14 and 18). It was found that the reactivity of the acyclic epoxides **2a–d** is lower than that of cyclic epoxide **2e**, and that the parent epoxide **2a** reacted faster than its substituted analogues **2b–d**. We have briefly studied the substituent effects on the reactivity of the vinyl epoxide component. These studies indicate that phenyl- (**2b**) and cyclohexyl- (**2d**) substituted epoxides react similarly, while in the presence of an electron-withdrawing chloro substituent (**2c**) the reactivity is increased leading to about 50% faster cross-coupling reactions (compare entries 6 and 11, 8 and 13, or 9 and 14, Table 1).

The reaction of **2b–d** with phenyl boronic acid **3a** can also be carried out under mild conditions by using only 0.5 mol% catalyst **1a** (entries 7, 12 and 16). In these processes somewhat longer reaction times are required than with 2.5 mol% catalyst, nevertheless the high yields can be maintained. The reaction rates also depend on the substituents of the organoboronic acid component. Alkenylboronic acid **3b** reacts much faster than arylboronic acids **3a** and **3c–d**. Methoxy substitution of the arylboronic acid (**3d**) has a relatively weak effect on the rate of reaction (compare entries 6 and 10, or 15 and 19 in Table 1); however, bromo substitution of the arylboronic acid component (**3c**) clearly accelerate the cross-coupling process (see entries 6 and 9, 11 and 14 or 15 and 18).

The regioselectivity of the cross-coupling reactions involving acyclic vinyl epoxides (**2a–d**) is excellent. The reaction of the parent epoxide **2a** results in mainly 1,4-coupling products **4a** and **4b**, and traces of the 1,2-coupling products **5a** and **5b** (entries 1 and 3). The catalytic transformation of the substituted acyclic vinyl epoxides (**2b–d**) provide exclusively the 1,4-coupling products, allyl alcohols **4c–m** (entries 6–19). Cyclic epoxide **2e** reacts with a poor regioselectivity providing **4n** and **5c** in 2:1 ratio even at low temperatures (entry 20). Interestingly, however, only *trans* isomers (**4n** and **5c**) were obtained in this reaction indicating a *trans* mechanism for the epoxide opening. The related palladium(0)-catalyzed opening of **2e** with phenyltrimethylstannane reported[35] by Echavarren and Stille also proceeds with *trans* mechanism and with a relatively poor regioselectivity.

We have also tried other pincer complexes as catalysts in the cross-coupling reactions. Complex **1b**[24] displayed a high catalytic activity, however it required higher reaction tem-

Table 1. Pincer complex catalyzed cross-coupling reaction of vinyl epoxides with organoboronic acids.[a]

	Substrate	Cat.[b]	R-B(OH)$_2$	Cond.[c] [°C]/[h]	Product	Ratio[d]	Yield [%][e]
1	 **2a**	**1a**	**3a**	0/16	 **4a** **5a**	11:1	94
2	**2a**	$[Pd_2(dba)_3]$	**3a**	0/16	**4a**	**5a** 7:3	95
3	**2a**	**1a**	 **3b**	0/3	 **4b** **5b**	9:1	95
4	**2a**	**1b**	**3b**	20/4	**4b**	**5b** 7:3	95
5	**2a**	$[Pd_2(dba)_3]$	**3b**	0/3	**4b**	**5b** 3:2	94
6	 **2b**	**1a**	**3a**	20/9	 **4c**	>20:1	86
7	**2b**	**1a** (0.5%)	**3a**	20/17	**4c**	>20:1	85
8	**2b**	**1a**	**3b**	0/3	 **4d**	>20:1	95
9	**2b**	**1a**	 **3c**	20/6	 **4e**	>20:1	88
10	**2b**	**1a**	 **3d**	20/7	 **4f**	>20:1	86
11	 **2c**	**1a**	**3a**	20/5	 **4g**	>20:1	95
12	**2c**	**1a** (0.5%)	**3a**	20/17	**4g**	>20:1	81
13	**2c**	**1a**	**3b**	0/1.5	 **4h**	>20:1	95
14	**2c**	**1a**	**3c**	20/4	 **4i**	>20:1	76
15	 **2d**	**1a**	**3a**	20/9	 **4j**	>20:1	95
16	**2d**	**1a** (0.5%)	**3a**	20/17	**4j**	>20:1	91
17	**2d**	**1a**	**3b**	0/3	 **4k**	>20:1	90
18	**2d**	**1a**	**3c**	20/6	 **4l**	>20:1	75
19	**2d**	**1a**	**3d**	20/6	 **4m**	>20:1	76
20	 **2e**	**1a**	**3a**	−20/2	 **4n** **5c**	2:1	88

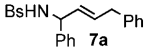
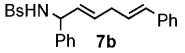
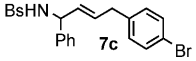
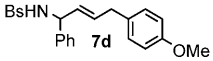
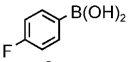
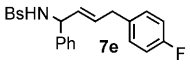
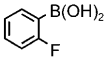
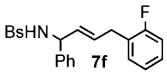
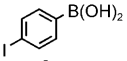
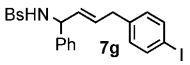
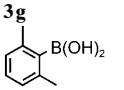
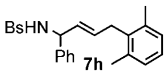
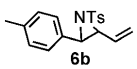
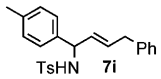
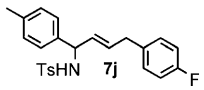
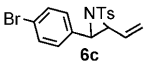
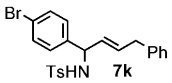
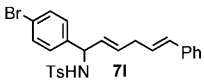
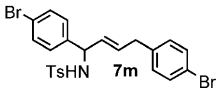
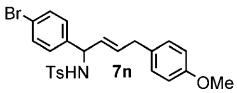
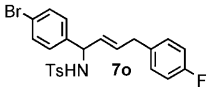
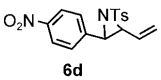
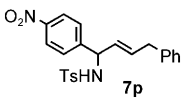
[a] The reactions were carried out by using 0.5–2.5 mol% catalyst in the presence of Cs_2CO_3 in THF/H_2O 10:1. [b] Typically 2.5 mol% catalyst was employed. The use of 0.5 mol% catalyst is indicated in parentheses. [c] Reaction temperature/reaction time. [d] Isomer ratio **4**:**5**. The >20:1 ratio indicates that isomer **5** was not detected in the crude or in the isolated product by ^{1}H NMR spectroscopy. [e] Isolated yield.

perature than **1a** (entry 4). Furthermore, the regioselectivity of the cross-coupling reaction between **2a** and **3b** is much lower with **1b** than with **1a** as catalyst (entries 3 and 4). Bedford and co-workers[25] successfully employed the trifluoroacetate salt of PCP complex **1d** for Suzuki coupling of aryl boronic acid **3a** with various aryl halogenides at elevated reaction temperature (130°C). However, we found that complex **1d**[18,25] does not display any catalytic activity under the applied mild reaction conditions. We have also attempted coupling reactions of **2a** with organoboronic acids employing commonly used palladium(0) catalysts. Catalyst $[Pd_2(dba)_3]$ displayed a high catalytic activity using **2a** with phenyl and vinyl boronic acid derivatives **3a** and **3b**. However, the regioselectivity of the $[Pd_2(dba)_3]$-catalyzed reaction is considerably lower than the corresponding process with **1a** (compare entries 1 and 2 or entries 3 and 5). Under the same reaction conditions $[Pd(PPh_3)_4]$ proved to be ineffective as the corresponding cross-coupling products **4a** and **5a** could not be observed in the reaction mixture.

Cross-coupling of vinyl aziridines with organoboronic acids: The above successful studies on pincer complex catalyzed ring-opening of vinyl epoxides (**2a–e**) led us to extend the synthetic scope of the reaction to vinyl aziridine based substrates (**6a–d**) (Scheme 2b). Although the reaction conditions used for ring opening of vinyl epoxides were also suitable for aziridines, the catalytic process was rather sluggish. However, it was found that application of CsF in place of Cs_2CO_3 gave a fast reaction and high yields at 20°C (Table 2). In these cross-coupling reactions diastereomeric mixtures of *cis*- and *trans*-aziridines (**6a–d**) were employed, which were easily prepared by the method reported by Dai and co-workers.[36] The cross-coupling reaction of **6a–d** with organoboronic acids **3a–h** gave the corresponding *trans*-products **7a–p** together with trace amounts (typically 5%) of their *cis* isomers.

Most of the reactions could be carried out using pincer-complex catalyst **1a** under mild conditions with excellent yields. Similarly to the epoxide opening reactions the functional group tolerance of the reaction is very high, as aro-

Table 2. Catalytic ring opening of vinyl aziridines with organoboronic acids.[a]

	Substrate[b]	Cat.	R-B(OH)$_2$	Cond.[c] [°C]/[h]	Product	*trans*/*cis*[d]	Yield [%][e]
1	 **6a**	**1a**	**3a**	20/18	 **7a**	19:1	95
2	**6a**	**1a**	**3b**	20/3	 **7b**	19:1	95
3	**6a**	**1a**	**3c**	20/15	 **7c**	14:1	95
4	**6a**	**1a**	**3d**	20/15	 **7d**	19:1	95
5	**6a**	**1a**	 **3e**	20/15	 **7e**	14:1	93
6	**6a**	**1c**	 **3f**	20/18	 **7f**	17:1	95
7	**6a**	**1c**[f]	 **3g**	20/16	 **7g**	8:1	93
8	**6a**	$[Pd_2(dba)_3]$[f]	**3g**	20/18	**7g**	8:1	50
9	**6a**	**1c**	 **3h**	20/18	 **7h**	25:1	95
10	 **6b**	**1a**	**3a**	20/17	 **7i**	17:1	82
11	**6b**	**1a**	**3e**	20/17	 **7j**	17:1	95
12	 **6c**	**1a**	**3a**	20/16	 **7k**	10:1	86
13	**6c**	**1a**	**3b**	20/3	 **7l**	19:1	95
14	**6c**	**1a**	**3c**	20/17	 **7m**	10:1	95
15	**6c**	**1a**	**3d**	20/17	 **7n**	14:1	95
16	**6c**	**1a**	**3e**	20/16	 **7o**	10:1	95
17	 **6d**	**1a**	**3a**	20/16	 **7p**	19:1	95

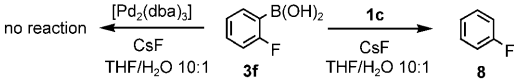
[a] The reactions were carried out by using 2.5 mol% catalyst in the presence of CsF in THF/H_2O 10:1. [b] *trans*/*cis* (about 2:1) mixture was used as substrate. Bs = benzenesulfonyl; Ts = toluenesulfonyl. [c] Reaction temperature/reaction time. [d] *trans*/*cis* ratio of the double bond geometry in the products. [e] Isolated yield. [f] 5 mol% catalyst was employed.

matic halogenides (fluoro, bromo and iodo substituents, entries 5–7 and 12–16) and nitro group (entry 17) are tolerated. Catalyst **1a** reacted slowly with iodo-derivative **3g**, and therefore the more active trifluoroacetate complex **1c** was employed to achieve a high yield (entry 7). Remarkably, product **7g** could be isolated with an intact iodo functionality. It is well known that aryliodides are usually incompatible with palladium(0) catalysts because of the rapid oxidative addition of the catalyst to the carbon-iodine bond.[1] Indeed, the reaction of **6a** and **3g** with $[Pd_2(dba)_3]$ as catalyst (entry 8) proceeds with a considerably lower yield than the corresponding reaction catalyzed by pincer complex **1c** (entry 7). The pincer complex catalyzed reactions also tolerate *ortho* substituents in the aromatic substrates (**3f** and **3h**). In these processes trifluoroacetate complex **1c** was employed as catalyst to provide high yields (entries 6 and 9). The cross-coupling reaction of **6a** and **3h** was also attempted with $[Pd_2(dba)_3]$ as catalyst. The crude reaction mixture indicated formation of **7h** together with several unidentified by-products. Unfortunately, the isolated yield could not be determined for this reaction, since we were unable to separate **7h** from the by-products even after repeated silica-gel chromatographies.

Mechanistic Aspects

In order to explore the mechanistic differences between the pincer complex (**1a** or **1c**) catalyzed and $[Pd_2(dba)_3]$-catalyzed reactions we carried out stoichiometric reactions with arylboronic acid **3f** and epoxide substrate **2a**, which was fol-

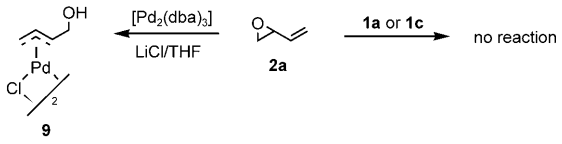
lowed by ^{19}F and ^{1}H NMR spectroscopy. It was found that **1c** reacted readily with **3f** in the presence of CsF and water in THF (Scheme 3). Monitoring the reaction at 20 °C with ^{19}F NMR spectroscopy revealed formation of fluorobenzene



Scheme 3. Stoichiometric reactions with fluoro boronic acid **3f**.

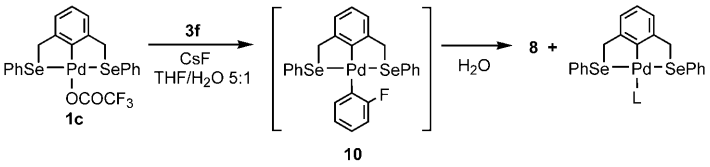
8 after 20 min. Under the same reaction conditions using $[Pd_2(dba)_3]$ instead of **1c** the fluoroboronic acid **3f** remained unchanged and formation of **8** was not observed even after several hours of reaction time. The same result was obtained without employment of any palladium sources.

We have also carried out stoichiometric experiments with the palladium catalyst and epoxide **2a** in the absence of organoboronic acids (Scheme 4). When $[Pd_2(dba)_3]$ was mixed with **2a** in $[D_8]$THF in the presence of LiCl the color of the solution rapidly turned from purple to yellow and the ^{1}H NMR spectrum showed formation of (η^3-allyl)palladium complex **9**, which could also be isolated. This reaction was also carried out with CsF in the presence of water. Although this reaction mixture also showed the above described color change, analogues of complex **9** could not be observed, only unidentified decomposition products of **2a**. This observation indicated that the application of chloride salts is necessary to form a stable complex, such as **9**, otherwise the (η^3-allyl)-palladium complex formed from **2a** and $[Pd_2(dba)_3]$ easily decomposes. Pincer complexes with chloride and triflouroacetate counterions (**1a** and **1c**) do not react with epoxide **2a** at all. This reaction mixture remained unchanged after several days.



Scheme 4. Stoichiometric reaction with epoxide **2a**.

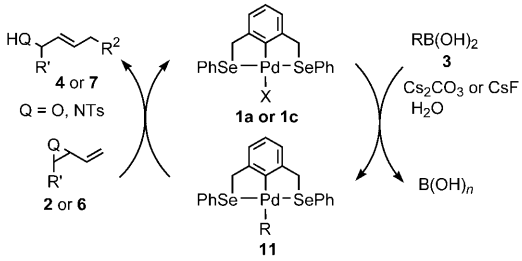
According to the above stoichiometric studies there are important mechanistic differences between the pincer complex catalyzed cross-coupling reaction and the corresponding $[Pd_2(dba)_3]$-catalyzed process. Vinyl epoxides (such as **2a**) and a palladium(0) complex readily form an (η^3-allyl)-palladium(II) complex by opening of the epoxide ring (Scheme 4).[32–34] However, in **1a** and **1c** there is only a single free coordination site available on the metal atom; and the oxidation state of palladium is restricted to +2 (features i) and ii) above), and therefore formation of an (η^3-allyl)palladium complex with a vinyl epoxide is unlikely. On the other hand **1c** reacts directly with boronic acid **3f** (Scheme 3). The relatively fast appearance of fluorobenzene **8** in this reaction mixture can be explained by transmetalation of **3f** with the pincer complex **1c** to give **10**, which undergo hydrolysis providing **8** (Scheme 5). Unfortunately, in the presence of water direct observation or isolation of **10** is prevented by this hydrolysis process. Intermediary formation



Scheme 5. Rationalization of the formation of fluorobenzene **8** in the stoichiometric reactions.

of complex **10** is also in line with our previous mechanistic results[15] on the trimethyltin transfer reactions catalyzed by **1b**. In this reaction the active catalyst is formed by transmetalation of hexamethylditin with the pincer-complex catalyst.

Considering the above, we assume that the initial step of the catalytic cycle (Scheme 6) is transmetalation of **1a** or **1c** with the corresponding organoboronic acid derivative **3**. Prior to this step the $B(OH)_2$ group is converted to a better leaving group by application of Cs_2CO_3/CsF and water.[26,29] Transmetalation of **1** with **3** results in complex **11**, from which the aryl or vinyl functionality (R) is subsequently transferred to the vinyl epoxide substrate in an S_N2' (or S_N2) type of reaction. A fast S_N2' process requires a high electron-density on the organic functionality ensured by the electron-donating SeCSe and NCN ligands, when **1a–c** are employed as catalysts. On the other hand the low catalytic activity of **1d** can be explained by the presence of π-acceptor phosphorous ligands, which decrease the electron density on the organic group. The reaction rate also depends on the electronic properties of the epoxide substrate **2**. An electron-withdrawing group on the epoxide substrate, such as a chloro functionality in **2c**, increases the electrophilicity of this substrate leading to a fast transfer of the organic group.



Scheme 6. Proposed catalytic cycle for the pincer complex (**1a**, **1c**) catalyzed reaction.

Concluding Remarks

We have shown that palladium-pincer complexes catalyze the carbon–carbon cross-coupling reaction of vinyl epoxides and aziridines with organoboronic acids. These catalytic

transformations proceed with high regioselectivity affording allyl alcohols and amines in good to excellent yields. Because of the high redox stability of the palladium(II)-pincer complex catalyst aromatic chloro-, bromo- and iodo substituents are tolerated. The applied catalysts **1a** and **1c** are easily available and the catalytic reaction does not require the use of inert gas atmosphere or application of dry solvents. It was found that $[Pd_2(dba)_3]$ also show a high catalytic activity in the presented cross-coupling reactions. However, the pincer complex catalyzed reactions proceed with higher regio- and chemoselectivity than the corresponding $[Pd_2(dba)_3]$-catalyzed processes. Our mechanistic studies indicate that the pincer complex catalyst does not undergo redox reactions; and that the oxidation state of the palladium atom is +2 under the catalytic process. It was concluded that the initial step of the reaction is transmetalation of the organoboronic acid to the pincer complex followed by an S_N2' type transfer process. The presented pincer complex catalyzed process allows cross-coupling reactions of easily accessible organoboronic acids[26–28,30] with vinyl epoxides and aziridines broadening the synthetic scope of selective palladium catalysis.

Experimental Section

The NMR spectra were recorded on Varian spectrometers. ^{1}H NMR spectra were recorded at either 300 or 400 MHz, ^{13}C NMR spectra were recorded at either 75.4 or 100.5 MHz. In these measurements $CHCl_3$ was used as internal standard ($\delta[^1H]=7.26$ ppm), $\delta[^{13}C]=77.0$ ppm). ^{19}F NMR spectra were recorded at either 282.2 or 376.3 MHz, by using α,α,α-trifluorotoluene as standard. For column chromatography silica gel (230–400 mesh) was used. MALDI-TOF spectra were recorded on a Bruker Biflex III instrument by using 2′,4′,6′-trihydroxy acetophenone (THAP) as matrix. Complex **1a** was prepared according to Yao and co-workers[23] except that the complex was purified by column chromatography by using CH_2Cl_2/Et_2O 20:1. Complex **1b** was prepared according to the procedure published by van Koten and co-workers[24] except that the final product was purified by column chromatography with CH_2Cl_2/Et_2O 20:1. Preparation of the trifluoroacetate salt of complex **1d** was first reported by Bedford and co-workers;[25] however we prepared complex **1d** by a modified procedure.[18] The vinyl epoxides and aziridines were prepared according to literature procedures.[36,37] The boronic acids are commercially available and were used as received.

General procedure for palladium-pincer complex catalyzed coupling of organoboronic acids with vinyl epoxides: Palladium-pincer complex **1a** (0.004 mmol, 2.5 mol%), vinyl epoxide (0.16 mmol), organoboronic acid (0.192 mmol, 1.2 equiv), and Cs_2CO_3 (0.32 mmol, 2 equiv) were dissolved in THF/water (10:1, 0.33 mL). This reaction mixture was stirred for the allotted reaction times and temperatures given below (see also Table 1). After completion of the reaction, the crude reaction mixture was purified by column chromatography.

General procedure for palladium-pincer complex catalyzed coupling of organoboronic acids with vinyl aziridines: Palladium-pincer complex **1a** (0.004 mmol, 2.5 mol%), vinyl aziridine (0.16 mmol), organoboronic acid (0.192 mmol, 1.2 equiv), and CsF (0.32 mmol, 2 equiv) were dissolved in THF/water (10:1, 0.33 mL). This reaction mixture was stirred for the allotted reaction times and temperatures given below (see also Table 2). After completion of the reaction, the crude reaction mixture was purified by column chromatography.

Exchange of the counterion in complex 1a to obtain TFA-complex 1c: Chloro-complex **1a** was added to $AgOCOCF_3$ (2 equiv) suspended in $CHCl_3$ at 0°C. This mixture was stirred for 1 h at 0°C and then an additional hour at 25°C in a dark reaction vessel. The AgBr precipitation was separated by centrifugation and the solvent was evaporated to yield complex **1c**, which was used without further purification. According to ^{1}H NMR, complex **1c** was formed in a diastereomeric ratio of 3:1. ^{1}H NMR: δ = 4.20 (d, ^3J(H,H) = 16.0 Hz, 2H, major diastereomer), 4.54 (d, ^3J(H,H) = 14.1 Hz, 2H, minor diastereomer), 4.66 (d, ^3J(H,H) = 14.1 Hz, 2H, minor diastereomer), 4.92 (d, ^3J(H,H) = 16.0 Hz, 2H, major diastereomer), 7.07 (d, ^3J(H,H) = 7.5 Hz, 2H), 7.18 (m, 1H), 7.30 (m, 3H), 7.41 (m, 3H), 7.56 (d, ^3J(H,H) = 7.9 Hz, 3H), 7.80 (d, ^3J(H,H) = 7.0 Hz, 1H); ^{19}F NMR: δ = −73.55 (brs).

(*E*)-4-Phenyl-2-buten-1-ol (4a): The reaction mixture was stirred at 0°C for 16 h. For column chromatography pentane/Et_2O 3:2 was used, yielding **4a** (22 mg, 94%). The obtained NMR data were in agreement with the published literature values.[35]

(2*E*,5*E*)-6-Phenyl-2,5-hexadien-1-ol (4b): The reaction mixture was stirred at 0°C for 3 h. For column chromatography pentane/Et_2O 3:2 were used, yielding **4b** (27 mg, 95%). The obtained NMR data were in agreement with the published literature values.[35]

(*E*)-1,4-Diphenyl-2-buten-1-ol (4c): The reaction mixture was stirred at 20°C for 9 h. For column chromatography pentane/Et_2O 3:2 was used, yielding **4c** (33 mg, 86%). This reaction was also performed with 0.5 mol% of **1a**. In this case the reaction mixture was stirred at 20°C for 17 h yielding **4c** (32 mg, 85%). The obtained NMR data were in agreement with the published literature values.[35]

(2*E*,5*E*)-1,6-Diphenyl-2,5-hexadien-1-ol (4d): The reaction mixture was stirred at 0°C for 3 h. For column chromatography pentane/Et_2O 2:1 was used, yielding **4d** (37 mg, 92%). The obtained NMR data were in agreement with the published literature values.[35]

(*E*)-4-(4-Bromophenyl)-1-phenyl-2-buten-1-ol (4e): The reaction mixture was stirred at 20°C for 6 h. For column chromatography pentane/EtOAc 3:1 was used, yielding **4e** (45 mg, 88%). ^{1}H NMR: δ = 1.99 (brs, OH), 3.35 (d, ^3J(H,H) = 6.5 Hz, 2H), 5.2 (d, ^3J(H,H) = 6.5 Hz, 1H), 5.74 (ddt, ^3J(H,H) = 6.6, 15.3 Hz, ^4J(H,H) = 1.3 Hz, 1H), 5.88 (dt, ^3J(H,H) = 6.6, 15.2 Hz, 1H), 7.05 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.25–7.43 (m, 7H); ^{13}C NMR: δ = 37.88, 74.84, 117.19, 119.94, 126.16, 127.69, 128.55, 130.14, 130.31, 131.49, 132.35, 134.01, 138.81, 142.92.

(*E*)-4-(4-Methoxyphenyl)-1-phenyl-2-buten-1-ol (4f): The reaction mixture was stirred at 20°C for 7 h. For column chromatography pentane/Et_2O 2:1 was used, yielding **4f** (36 mg, 86%). ^{1}H NMR: δ = 2.0 (brs, 1H), 3.35 (d, ^3J(H,H) = 6.5 Hz, 2H), 3.79 (s, 3H), 5.2 (d, ^3J(H,H) = 6.6 Hz, 1H), 5.74 (ddt, ^3J(H,H) = 6.6, 15.3 Hz, ^4J(H,H) = 1.3 Hz, 1H), 5.91 (dt, ^3J(H,H) = 6.6, 15.3 Hz, 1H), 6.84 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.10 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.25–7.40 (m, 5H); ^{13}C NMR: δ = 37.66, 55.23, 74.92, 113.86, 126.17, 127.54, 128.47, 129.47, 131.38, 131.91, 133.30, 143.13, 158.00.

(E)-1-(4-Chlorophenyl)-4-phenyl-2-buten-1-ol (4g): The reaction mixture was stirred at 20°C for 5 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **4g** (41 mg, 95%). This reaction was also performed by using 0.5 mol% of **1a**. In this case the reaction mixture was stirred at 20°C for 17 h yielding **4g** (34 mg, 81%). ^{1}H NMR: δ = 1.96 (s, 1H), 3.40 (d, ^3J(H,H) = 6.7 Hz, 2H), 5.18 (d, J = 6.8, 1H), 5.70 (dd, ^3J(H,H) = 6.6, 15.1 Hz, 1H), 5.86–5.98 (m, 1H), 7.14–7.36 (m, 9H); ^{13}C NMR: δ = 38.53, 74.25, 126.21, 127.55, 128.49, 128.53, 128.58, 131.50, 133.26, 139.66, 141.47.

(2*E*,5*E*)-1-(4-Chlorophenyl)-6-phenyl-2,5-hexadien-1-ol (4h): The reaction mixture was stirred at 0°C for 1.5 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **4h** (44 mg, 95%). ^{1}H NMR: δ = 1.97 (brs, 1H), 2.98 (t, ^3J(H,H) = 6.5 Hz, 2H), 5.19 (d, ^3J(H,H) = 6.5 Hz, 1H), 5.73 (dd, ^3J(H,H) = 6.8, 14.9 Hz, 1H), 5.79–5.90 (m, 1H), 6.14–6.25 (m, 1H), 6.41 (d, ^3J(H,H) = 16.0 Hz, 1H), 7.17–7.39 (m, 9H); ^{13}C NMR: δ = 35.39, 74,37, 126.03, 127.15, 127.35, 127.55, 127.59, 128.50 128.59, 130.50 131.20, 133.19, 133.25, 137.36, 141.51.

(*E*)-4-(3-Bromophenyl)-1-(4-chlorophenyl)-2-buten-1-ol (4i): The reaction mixture was stirred at 20°C for 4 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **4I** (42 mg, 76%). ^{1}H NMR: δ = 1.95 (apps, 1H), 3.34 (d, ^3J(H,H) = 6.6 Hz, 2H), 5.17 (d, ^3J(H,H) = 6.6 Hz, 1H), 5.67 (dt, ^3J(H,H) = 6.5, 15.2 Hz, 1H), 5.81–5.93 (m, 1H), 6.98–7.46

(m, 8H); ^{13}C NMR: δ = 37.87, 74.15, 120.04, 127.53, 128.65, 130.30, 130.67, 131.55, 133.35, 133.70, 138.61, 141.36.

1-[(*E*)-3-Phenyl-1-propenyl]-1-cyclohexanol (4j): The reaction mixture was stirred at 20°C for 9 h. For column chromatography pentane/Et_2O 2:1 was used, yielding **4j** (33 mg, 95%). This reaction was also performed by using 0.5 mol% of **1a**. In this case the reaction mixture was stirred at 20°C for 17 h also yielding **4j** (32 mg, 91%). The obtained NMR data were in agreement with the literature values.[38]

1-[(1*E*,4*E*)-5-Phenyl-1,4-pentadienyl]-1-cyclohexanol (4k): The reaction mixture was stirred at 0°C for 3 h. For column chromatography pentane/Et_2O 2:1 was used, yielding **4k** (35 mg, 95%). ^{1}H NMR: δ = 1.37 (m, 11H), 2.96 (d, ^3J(H,H) = 6.2 Hz, 2H), 5.62–5.82 (m, 2H), 6.22 (dt, ^3J(H,H) = 7.0, 15.9 Hz, 1H), 6.41 (d, ^3J(H,H) = 15.9 Hz, 1H), 7.17–7.38 (m, 5H); ^{13}C NMR: δ = 22.15, 25.53, 35.60, 37.99, 71.31, 125.55, 125.99, 126.97, 128.45, 128.58, 130.62, 137.56, 139.10.

1-[(*E*)-3-(4-Bromophenyl)-1-propenyl]-1-cyclohexanol (4l): The reaction mixture was stirred at 20°C for 6 h. For column chromatography pentane/EtOAc 2:1 was used, yielding **4l** (37 mg, 75%). ^{1}H NMR: δ = 1.23–1.68 (m, 11H), 3.31 (d, ^3J(H,H) = 7.1 Hz, 2H), 5.68 (dt, ^3J(H,H) = 1.3, 15.7, 1H), 5.78 (dt, ^3J(H,H) = 6.6, 15.6 Hz, 1H), 7.04 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.40 (d, ^3J(H,H) = 8.8 Hz, 2H); ^{13}C NMR: δ = 22.10, 25.48, 37.96, 38.05, 71.30, 119.78, 126.00, 130.25, 131.41, 139.39, 139.71.

1-[(*E*)-3-(4-Methoxyphenyl)-1-propenyl]-1-cyclohexanol (4m): The reaction mixture was stirred at 20°C for 6 h. For column chromatography pentane/Et_2O 3:2 was used, yielding **4m** (30 mg, 76%). ^{1}H NMR: δ = 1.22–1.72 (m, 11H), 3.31 (d, ^3J(H,H) = 6.9 Hz, 2H), 3.79 (s, 3H), 5.63 (dt, ^3J(H,H) = 1.4, 15.7 Hz, 1H), 5.80 (dt, ^3J(H,H) = 6.8, 15.5 Hz, 1H), 6.84 (d, ^3J(H,H) = 9.1 Hz, 2H), 7.09 (d, ^3J(H,H) = 9.1 Hz, 2H); ^{13}C NMR: δ = 22.18, 25.54, 37.82, 38.00, 55.24, 71.30, 113.81, 127.08, 129.40, 132.49, 138.91, 157.92.

Reaction of 2e with 3a to obtain 4n and 5c: The reaction mixture was stirred at −20°C for 2 h. For column chromatography pentane/EtOAc 2:1 were used to separate the regioisomers **4n** and **5c** to yield 4-phenyl-2-cyclohexen-1-ol (**4n**; 39 mg, 78%) and 2-phenyl-3-cyclohexen-1-ol (**5c**; 8.4 mg, 10%). The NMR data obtained were in agreement with the literature values.[35]

***N*^{1}-[(*E*)-1,4-Diphenyl-2-butenyl]-1-benzenesulfonamide (7a)**: The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7a** (56 mg, 95%). ^{1}H NMR: δ = 3.25 (d, ^3J(H,H) = 6.6 Hz, 2H), 4.97 (t, ^3J(H,H) = 7.1 Hz, 1H), 5.03 (d, ^3J(H,H) = 7.3 Hz, 1H), 5.51 (dd, ^3J(H,H) = 6.3, 15.1 Hz, 1H), 5.63 (dt, ^3J(H,H) = 6.5, 15.2 Hz, 1H), 7.04 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.1–7.3 (m, 8H), 7.34 (t, ^3J(H,H) = 7.8 Hz, 2H), 7.46 (t, ^3J(H,H) = 7.5 Hz, 1H), 7.72 (d, ^3J(H,H) = 7.4 Hz, 2H); ^{13}C NMR: δ = 38.36, 59.41, 126.16, 126.94, 127.1, 127.68, 128.42, 128.49, 128.58, 128.73, 130.15, 132.29, 132.32, 139.35, 139.77, 140.66; MS (MALDI-TOF): *m*/*z*: 386.1 [*M*+Na]$^+$, 402.08 [*M*+K]$^+$.

***N*^{1}-[(2*E*,5*E*)-1,6-Diphenyl-2,5-hexadienyl]-1-benzenesulfonamide (7b)**: The reaction mixture was stirred at 20°C for 3 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7b** (59 mg, 95%). ^{1}H NMR: δ = 2.81 (t, *J* = 6.0 Hz, 2H), 5.00 (br t, *J* = 6.6 Hz, 1H), 5.27 (br d, *J* = 7.4 Hz, 1H), 5.54 (m, 2H), 6.01 (dt, *J* = 15.9 Hz, 6.8 Hz, 1H), 6.30 (dt, *J* = 15.9 Hz, 1.3 Hz, 1H), 7.13–7.39 (m, 12H), 7.41–7.47 (m, 1H), 7.75–7.78 (m, 2H); ^{13}C NMR: δ = 35.2, 59.5, 126.0, 126.9, 127.1, 127.1, 127.3, 127.6, 128.4, 128.5, 128.7, 130.0, 131.1, 131.3, 132.3, 137.3, 139.8, 140.7; MS (MALDI-TOF): *m*/*z*: 389.07 [*M*+H]$^+$, 413.25 [*M*+Na]$^+$, 428.23 [*M*+K]$^+$.

***N*^{1}-[(*E*)-4-(4-Bromophenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7c)**: The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7c** (67 mg, 95%). ^{1}H NMR: δ = 3.18 (d, ^3J(H,H) = 6.3 Hz, 2H), 4.96 (t, ^3J(H,H) = 6.7 Hz, 1H), 5.18 (d, ^3J(H,H) = 7.3 Hz, 1H), 5.49 (dd, ^3J(H,H) = 6.0, 15.1 Hz, 1H), 5.6 (dt, ^3J(H,H) = 6.3, 15.4 Hz, 1H), 6.9 (d, ^3J(H,H) = 8.3 Hz, 2H), 7.07–7.24 (m, 5H), 7.31–7.38 (m, 4H), 7.47 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.72 (d, ^3J(H,H) = 7.5 Hz, 2H); ^{13}C NMR: δ = 37.68, 59.34, 119.95, 126.91, 127.05, 127.74, 128.61, 128.74, 130.25, 130.69, 131.45, 131.47, 132.35, 138.32, 139.61, 140.63; MS (MALDI-TOF): *m*/*z*: 465.09/467.08 [*M*+Na]$^+$, 481.09/483.08 [*M*+K]$^+$.

***N*^{1}-[(*E*)-4-(4-Methoxyphenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7d)**: The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7d** (58 mg, 95%). ^{1}H NMR: δ = 3.17 (d, ^3J(H,H) = 6.5 Hz, 2H), 3.78 (s, 3H), 4.97 (t, ^3J(H,H) = 6.8 Hz, 1H), 5.35 (d, ^3J(H,H) = 7.3 Hz, 1H), 5.48 (dd, ^3J(H,H) = 6.4, 15.2 Hz, 1H), 5.61 (dt, ^3J(H,H) = 6.6, 15.3 Hz, 1H), 6.8 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.95 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.11–7.23 (m, 5H), 7.34 (t, ^3J(H,H) = 7.9 Hz, 2H), 7.46 (t, ^3J(H,H) = 7.5 Hz, 1H), 7.74 (d, ^3J(H,H) = 7.9 Hz, 2H); ^{13}C NMR: δ = 37.39, 55.17, 59.38, 113.78, 126.9, 127.04, 127.53, 128.47, 128.66, 129.38, 129.81, 131.36, 132.21, 132.57, 139.81, 140.65, 157.92; MS (MALDI-TOF): *m*/*z*: 416.18 [*M*+Na]$^+$, 432.17 [*M*+K]$^+$.

***N*^{1}-[(*E*)-4-(4-Fluorophenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7e)**: The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7e** (57 mg, 93%). ^{1}H NMR: δ = 3.21 (d, ^3J(H,H) = 6.45 Hz, 2H), 4.96 (t, ^3J(H,H) = 6.9 Hz, 1H), 5.1 (d, ^3J(H,H) = 7.3 Hz, 1H), 5.49 (dd, ^3J(H,H) = 6.3, 15.2 Hz, 1H), 5.63 (dt, ^3J(H,H) = 6.6, 15.4 Hz, 1H), 6.9–7.24 (m, 9H), 7.35 (t, ^3J(H,H) = 7.5 Hz, 2H), 7.47 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.72 (d, ^3J(H,H) = 7.5 Hz, 2H); ^{13}C NMR: δ = 37.5, 59.38, 115.28, 115.06, 127.0 (d, *J*(C,F) = 16.4 Hz), 127.74, 128.68 (d, *J*(C,F) = 12.7 Hz), 129.88 (d, *J*(C,F) = 8.4 Hz), 130.4, 132.04, 132.35, 134.97 (d, *J*(C,F) = 3.8 Hz), 139.7, 140.67, 160.21, 162.63; MS (MALDI-TOF): *m*/*z*: 404.13 [*M*+Na]$^+$, 420.12 [*M*+K]$^+$.

***N*^{1}-[(*E*)-4-(2-Fluorophenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7f)**: In this reaction 2.5 mol% of complex **1c** was used as catalyst. The reaction mixture was stirred at 0°C for 1 h and an additional 15 h at 20°C. For column chromatography pentane/EtOAc 5:1 was used, yielding **7f** (58 mg, 95%). ^{1}H NMR: δ = 3.25 (d, ^3J(H,H) = 6.1 Hz, 2H), 4.97 (t, ^3J(H,H) = 7.0 Hz, 1H), 5.13 (d, ^3J(H,H) = 7.5 Hz, 1H), 5.50 (dd, ^3J(H,H) = 6.3, 15.5 Hz, 1H), 5.60 (dt, ^3J(H,H) = 6.3, 15.2 Hz, 1H), 6.95–7.06 (m, 3H), 7.10–7.24 (m, 6H), 7.33 (t, ^3J(H,H) = 7.7 Hz, 2H), 7.45 (t, ^3J(H,H) = 7.3 Hz, 1H), 7.72 (d, ^3J(H,H) = 7.6 Hz, 2H); ^{13}C NMR: δ = 31.38 (d, *J*(C,F) = 3.1 Hz), 59.25, 115.20 (d, *J*(C,F) = 21.8 Hz), 124.03 (d, *J*(C,F) = 3.8 Hz), 126.27 (d, *J*(C,F) = 16 Hz), 126.76, 127.01 (d, *J*(C,F) = 11.8 Hz), 127.14, 127.67, 127.95 (d, *J*(C,F) = 7.9 Hz), 128.63 (d, *J*(C,F) = 14.4 Hz), 130.39, 130.53 (d, *J*(C,F) = 4.7 Hz), 130.64, 132.31, 139.7, 140.62, 159.58, 162.02; MS (MALDI-TOF): *m*/*z*: 404.1 [*M*+Na]$^+$, 420.08 [*M*+K]$^+$.

1-[(*E*)-4-(4-Iodophenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7g): In this reaction three equivalents of 4-iodo phenyl boronic acid (**3g**) and CsF was employed in the presence of 5 mol% of complex **1c**. The reaction mixture was stirred at 20°C for 16 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7g** (75 mg, 93%). ^{1}H NMR: δ = 3.17 (d, ^3J(H,H) = 6.5 Hz, 2H), 4.96 (t, ^3J(H,H) = 7.0 Hz, 1H), 5.27 (d, ^3J(H,H) = 7.0 Hz, 1H), 5.49 (dd, ^3J(H,H) = 6.3, 15.6 Hz, 1H), 5.60 (dt, ^3J(H,H) = 6.3, 15.6 Hz, 1H), 6.75–7.82 (m, 14H); ^{13}C NMR: δ = 37.77, 59.32, 91.29, 126.89, 127.03, 127.07, 127.70, 128.59, 128.73, 128.78, 130.59, 130.69, 131.38, 132.33, 137.41, 139.00, 139.60, 140.60; MS (MALDI-TOF): *m*/*z*: 512.33 [*M*+Na]$^+$, 528.32 [*M*+K]$^+$.

***N*^{1}-[(*E*)-4-(2,6-Dimethylphenyl)-1-phenyl-2-butenyl]-1-benzenesulfonamide (7h)**: In this reaction 2.5 mol% of complex **1c** was used as catalyst. The reaction mixture was stirred at 0°C for 1 h and an additional 17 h at 20°C. For column chromatography pentane/CH_2Cl_2 1:1 was used, yielding **7h** (59 mg, 95%). ^{1}H NMR: δ = 2.17 (s, 6H), 3.24 (d, ^3J(H,H) = 5.7 Hz, 2H), 4.93 (t, ^3J(H,H) = 7 Hz, 1H), 5.11 (d, ^3J(H,H) = 7.7 Hz, 1H), 5.30 (dd, ^3J(H,H) = 6.3, 15.4 Hz, 1H), 5.53 (dt, ^3J(H,H) = 5.7, 15.3 Hz, 1H), 6.95–7.24 (m, 8H), 7.31 (t, ^3J(H,H) = 7.2 Hz, 2H), 7.44 (t, ^3J(H,H) = 7.5 Hz, 1H), 7.71 (d, ^3J(H,H) = 7.4 Hz, 2H); ^{13}C NMR: δ = 19.78, 32.01, 59.24, 126.10, 126.88, 126.97, 127.54, 128.01, 128.47, 128.65, 129.01, 130.17, 132.26, 135.54, 136.42, 139.90, 140.61; MS (MALDI-TOF): *m*/*z*: 414.13 [*M*+Na]$^+$, 430.11 [*M*+K]$^+$.

***N*^{1}-[(*E*)-1-(4-Methylphenyl)-4-phenyl-2-butenyl]-4-methyl-1-benzenesulfonamide (7i)**: The reaction mixture was stirred at 20°C for 17 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7i** (51 mg, 82%). ^{1}H NMR: δ = 2.29 (s, 3H), 2.39 (s, 3H), 3.25 (d, ^3J(H,H) = 6.3 Hz, 2H), 4.90 (t, ^3J(H,H) = 6.8 Hz, 1H), 4.99 (d, ^3J(H,H) =

6.8 Hz, 1H), 5.50 (dd, ^3J(H,H) = 6.2, 15.4 Hz, 1H), 5.64 (dt, ^3J(H,H) = 6.1, 15.1 Hz, 1H), 7.00–7.32 (m, 11H), 7.62 (d, ^3J(H,H) = 8.3 Hz, 2H); ^{13}C NMR: δ = 20.97, 21.44, 38.35, 59.14, 126.08, 126.86, 127.20, 128.36, 128.48, 129.19, 129.28, 129.35, 130.46, 131.80, 137.02, 137.32, 137.75, 139.47, 142.96; MS (MALDI-TOF): *m/z*: 414.35 $[M+Na]^+$, 430.36 $[M+K]^+$.

N^1-[(*E*)-4-(4-Fluorophenyl)-1-(4-methylphenyl)-2-butenyl]-4-methyl-1-benzenesulfonamide (7j): The reaction mixture was stirred at 20°C for 17 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7j** (65 mg, 95%). ^{1}H NMR: δ = 2.29 (s, 3H), 2.38 (s, 3H), 3.21 (d, ^3J(H,H) = 6.3 Hz, 2H), 4.88 (t, ^3J(H,H) = 6.4 Hz, 1H), 5.09 (d, ^3J(H,H) = 6.4 Hz, 1H), 5.49 (dd, ^3J(H,H) = 5.7, 15.6 Hz, 1H), 5.62 (dt, ^3J(H,H) = 6.2, 15.6 Hz, 1H), 6.87–7.06 (m, 8H), 7.14 (d, ^3J(H,H) = 8.0 Hz, 2H), 7.61 (d, ^3J(H,H) = 7.7 Hz, 2H); ^{13}C NMR: δ = 20.97, 21.42, 37.45, 59.11, 115.07 (d, *J*(C,F) = 21.5 Hz), 126.84, 127.18, 129.22, 129.28, 129.92, 130.71, 131.59, 135.09 (d, *J*(C,F) = 3.2 Hz), 136.94, 137.74, 143.01, 159.75, 162.99; ^{19}F NMR: δ = −117.59 (m); MS (MALDI-TOF): *m/z*: 432.36 $[M+Na]^+$, 448.36 $[M+K]^+$.

N^1-[(*E*)-1-(4-Bromophenyl)-4-phenyl-2-butenyl]-4-methyl-1-benzenesulfonamide (7k): The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7k** (68 mg, 93%). ^{1}H NMR: δ = 2.39 (s, 3H), 3.23 (d, ^3J(H,H) = 6.5 Hz, 2H), 4.89 (t, ^3J(H,H) = 6.6 Hz, 1H), 5.34 (d, ^3J(H,H) = 7.9 Hz, 1H), 5.45 (dd, ^3J(H,H) = 6.1, 16.0 Hz, 1H), 5.60 (dt, ^3J(H,H) = 6.6, 15.1 Hz, 1H), 6.97–7.61 (m, 13H); ^{13}C NMR: δ = 21.46, 38.32, 58.74, 121.46, 126.18, 127.11, 128.41, 128.44, 128.77, 129.35, 129.56, 131.50, 132.71, 137.46, 138.92, 139.15, 143.26; MS (MALDI-TOF): *m/z*: 478.30/480.30 $[M+Na]^+$, 494.30/496.29 $[M+K]^+$.

N^1-[(2*E*,5*E*)-1-(4-Bromophenyl)-6-phenyl-2,5-hexadienyl]-4-methyl-1-benzenesulfonamide (7l): The reaction mixture was stirred at 20°C for 3 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7l** (73 mg, 95%). ^{1}H NMR: δ = 2.35 (s, 3H), 2.81 (t, *J* = 6.2 Hz, 2H), 4.91 (br t, *J* = 6.8 Hz, 1H), 5.18 (br d, *J* = 7.1 Hz, 1H), 5.42–5.59 (m, 2H), 6.01 (dt, *J* = 15.7 Hz, 6.7 Hz, 1H), 6.29 (d, *J* = 15.7 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.19–7.35 (m, 7H), 7.59 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR: δ = 21.4, 35.2, 58.9, 121.5, 126.0, 127.1, 127.2, 128.5, 128.8, 129.4, 129.6, 131.3, 131.6, 131.9, 137.3, 137.6, 138.9, 143.3; MS (MALDI-TOF): *m/z*: 504.05/506.04 $[M+Na]^+$, 520.06/522.05 $[M+K]^+$.

N^1-[(*E*)-1,4-di(4-Bromophenyl)-2-butenyl]-4-methyl-1-benzenesulfonamide (7m): The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7m** (82 mg, 95%). ^{1}H NMR: δ = 2.39 (s, 3H), 3.18 (d, ^3J(H,H) = 6.2 Hz, 2H), 4.88 (t, ^3J(H,H) = 6.8 Hz, 1H), 5.22 (d, ^3J(H,H) = 7.3 Hz, 1H), 5.44 (dd, ^3J(H,H) = 6.2, 15.6 Hz, 1H), 5.57 (dt, ^3J(H,H) = 6.7, 15.3 Hz, 1H), 6.89 (d, ^3J(H,H) = 8.1 Hz, 2H), 6.97 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.13 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.30 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.35 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.55 (d, ^3J(H,H) = 8.2 Hz, 2H); ^{13}C NMR: δ = 21.45, 37.47, 58.76, 115.03, 115.11, 115.31, 121.54, 127.11. 128.53, 128.75, 129.37, 129.44, 129.59, 129.80, 129.91, 131.56, 131.68, 132.51, 134.75, 134.79, 137.48, 138.82, 143.34, 159.79, 163.03; MS (MALDI-TOF): *m/z*: 556.40, 558.40, 560.38 $[M+Na]^+$, 572.39, 574.40, 576.38 $[M+K]^+$.

N^1-[(*E*)-1-(4-Bromophenyl)-4-(4-methoxyphenyl)-2-butenyl]-4-methyl-1-benzenesulfonamide (7n): The reaction mixture was stirred at 20°C for 16 h. For column chromatography pentane/EtOAc 5:1 was used, yielding **7n** (75 mg, 95%). ^{1}H NMR: δ = 2.39 (s, 3H), 3.17 (d, ^3J(H,H) = 6.8 Hz, 2H), 3.78 (s, 3H), 4.88 (t, ^3J(H,H) = 8.4 Hz, 1H), 5.18 (d, ^3J(H,H) = 8.7 Hz, 1H), 5.42 (dd, ^3J(H,H) = 6.5, 15.6 Hz, 1H), 5.57 (dt, ^3J(H,H) = 6.3, 15.3 Hz, 1H), 6.75–7.64 (m, 12H); ^{13}C NMR: δ = 21.46, 37.44, 55.22, 58.81, 113.85, 121.48, 127.13, 128.77, 129.36, 129.39, 131.15, 131.51, 133.25, 137.49, 138.94, 143.28, 158.03; MS (MALDI-TOF): *m/z*: 484.35/486.35 $[M+H]^+$, 508.37/509.37 $[M+Na]^+$, 524.36/526.36 $[M+K]^+$.

N^1-[(*E*)-1-(4-Bromophenyl)-4-(4-fluorophenyl)-2-butenyl]-4-methyl-1-benzenesulfonamide (7o): The reaction mixture was stirred at 20°C for 15 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7o** (73 mg, 95%). ^{1}H NMR: δ = 2.39 (s, 3H), 3.20 (d, ^3J(H,H) = 6.5 Hz, 2H), 4.88 (t, ^3J(H,H) = 6.8 Hz, 1H), 5.33 (d, ^3J(H,H) = 8.2 Hz, 1H), 5.43 (dd, ^3J(H,H) = 6.5, 15.3 Hz, 1H), 5.58 (dt, ^3J(H,H) = 6.3, 15.8 Hz, 1H), 6.87–7.01 (m, 5H), 7.13 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.30 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.56 (d, ^3J(H,H) = 8.3 Hz, 2H); ^{13}C NMR: δ = 21.45, 37.47, 58.76, 115.16 (d, *J*(C,F) = 22.2 Hz), 121.54, 127.11, 128.75, 129.37, 129.91, 131.56, 132.51, 134.77 (d, *J*(C,F) = 3.2 Hz), 137.47, 138.82, 143.34, 159.79, 163.03; ^{19}F NMR: δ = −117.43 (m); MS (MALDI-TOF): *m/z*: 496.34/498.34 $[M+Na]^+$, 512.35/514.36 $[M+K]^+$.

N^1-[(*E*)-1-(4-Nitrophenyl)-4-phenyl-2-butenyl]-4-methyl-1-benzenesulfonamide (7p): The reaction mixture was stirred at 20°C for 16 h. For column chromatography pentane/EtOAc 4:1 was used, yielding **7p** (64 mg, 95%). ^{1}H NMR: δ = 2.37 (s, 3H), 3.23 (d, ^3J(H,H) = 6.6 Hz, 2H), 5.0 (t, ^3J(H,H) = 6.8 Hz, 1H), 5.44 (dd, ^3J(H,H) = 6.8, 13.7 Hz, 2H), 5.6 (dt, ^3J(H,H) = 7.3, 15.7 Hz, 1H), 7.01 (d, ^3J(H,H) = 7 Hz, 2H), 7.10–7.36 (m, 7H), 7.59 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.03 (d, ^3J(H,H) = 8.5 Hz, 2H); ^{13}C NMR: δ = 21.43, 38.34, 58.80, 123.63, 126.34, 127.11, 127.93, 128.42, 128.49, 128.75, 129.49, 133.95, 137.16, 138.77, 143.69, 147.12, 147.19; MS (MALDI-TOF): *m/z*: 445.07 $[M+Na]^+$, 461.06 $[M+K]^+$.

Stoichiometric reaction of complex 1c and boronic acid 3f: Complex **1c** (prepared from 2.2 mg chloro complex **1a**, 0.004 mmol) was mixed with 2-fluorophenyl boronic acid **3f** (0.008 mmol, 1.1 mg, 2 equiv) in [D$_8$]THF (0.5 mL) and water (0.05 mL). To this mixture was added CsF (0.02 mmol, 3.0 mg, 5 equiv). The progress of the reaction was monitored by an array experiment using ^{1}H NMR spectroscopy.

Stoichiometric reaction of [Pd$_2$dba$_3$] and boronic acid 3f: [Pd$_2$(dba)$_3$] (3.7 mg, 0.004 mmol) was mixed with 2-fluorophenyl boronic acid **3f** (0.008 mmol, 1.1 mg, 2 equiv) in [D$_8$]THF (0.5 mL) and water (0.05 mL). To this mixture was added CsF (0.020 mmol, 3.0 mg, 5 equiv). The progress of the reaction was monitored by an array experiment using ^{1}H NMR spectroscopy.

Stoichiometric reaction of [Pd$_2$(dba)$_3$] and vinyl epoxide 2a affording complex 9: [Pd$_2$dba$_3$] (3.8 mg, 0.004 mmol) was mixed with vinyl epoxide **2a** (0.008 mmol, 0.56 mg, 2 equiv) and LiCl (0.020 mmol, 0.56 mg, 5 equiv) in THF (0.5 mL). The progress of the reaction was followed by ^{1}H NMR spectroscopy. After 60 min the product was purified by column chromatography by using CH_2Cl_2 until all dibenzylidene acetone was eluted and then CH_2Cl_2/Et$_2$O 1:1 to get pure complex **9**. ^{1}H NMR: δ = 3.00 (d, ^3J(H,H) = 12 Hz, 1H), 3.57 (ddd, *J*(H,H) = 4.31 Hz, 7.0 Hz, 14.75 Hz, 1H), 3.81 (ddd, *J*(H,H) = 3.4, 6.4, 14.8 Hz, 1H), 3.96 (dt, ^3J(H,H) = 4.2, 10.9 Hz, 1H), 4.06 (d, ^3J(H,H) = 6.7 Hz, 1H), 5.59 (dt, ^3J(H,H) = 6.7, 11.6 Hz, 1H); ^{13}C NMR: δ = 60.54, 61.79, 85.99, 107.67.

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