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Synthesis of Stereodefined Substituted Cycloalkenes by a One-Pot Catalytic Boronation–Allylation–Metathesis Sequence

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Abstract: Stereodefined cyclohexene and cyclopentene derivatives were prepared by the coupling of allylic alcohols and other allylic precursors with unsaturated aldehydes. These reactions are based on a multicatalytic one-pot approach involving palladium pincer complex-catalyzed boronation, allylation and ring-closing metathesis reactions. This reaction sequence can be performed in an operationally simple procedure affording the cycloalkene products in high overall yields and excellent regio- and stereoselectivities. The presented procedure has a broad synthetic scope and high functional group tolerance, which allows the synthesis of bicyclic lactone and spirane skeletons and various substitution patterns including hydroxy, silyl, vinyl, allyl, and sulfonyl groups. The studied catalytic one-pot reactions involve up to three individual processes performed by up to four acid- and transition metal-catalyzed events.

Keywords: allylation; boronation; homogenous catalysis; metathesis; palladium pincer complexes; stereoselectivity

Introduction

One-pot, multi-step catalytic reactions represent one of the most important approaches for development of sustainable and cost-efficient synthetic procedures.[1–4] In this approach, the transition metal-catalyzed processes ensure a high level of atom economy,[5] while the performance of several cooperative processes sharing the same solvent and reaction vessel ensures that energy- and labor-intensive purification processes can be avoided. Our recent efforts[6–8] have been focused on the design of such one-pot, multi-step reactions involving the palladium- and iridium-catalyzed generation of organoboronates. Organoboronates[9] are often stabile compounds, however, many functionalized allylboronates are unstable and cannot be isolated without considerable purification losses.[10–12] On the other hand, allylboronates are remarkably air- and moisture-stable in solution, which allows their *in situ* application in various multi-step one-pot reactions.[6–8,13–22]

In previous studies, we have shown[6–8] that allylboronates generated *in situ* from allylic alcohols (such as **1a–f**), acetates (such as **1g**, **h**) and other precursors (such as **1i**) by palladium-catalyzed processes readily react with aldehyde, acetal, ketone and imine substrates in a one-pot sequence.

Results and Discussion

Now, we have found (Figure 1 and Table 1) that by appropriate choice of the aldehyde (**2a**) or acetal (**2b**) component, stereodefined dienes and trienes can be generated, which undergo ring-closing metathesis[23] (RCM) in a one-pot sequence with the catalytic boronation[12] and the allylation reaction. In this way, complex regio- and stereodefined cyclohexene and cyclopentene derivatives (**7a–j**) can be prepared from simple precursors in an operationally simple and efficient one-pot reaction. In this study, we disclose our results on the synthetic scope of this process, discuss the possibilities of the selective ring-closing metathesis of intermediate dienes and trienes as well as further reactions triggered by the allylation and cyclization processes.

Synthetic Scope

In a typical experiment (Figure 1), the boronation and allylation reactions were performed in a single operational step by mixing allyl precursor **1**, aldehyde **2a**, diboronate reagent **4**, catalytic amounts (5 mol%) of pincer complex catalyst **3** and *para*-toluenesulfonic

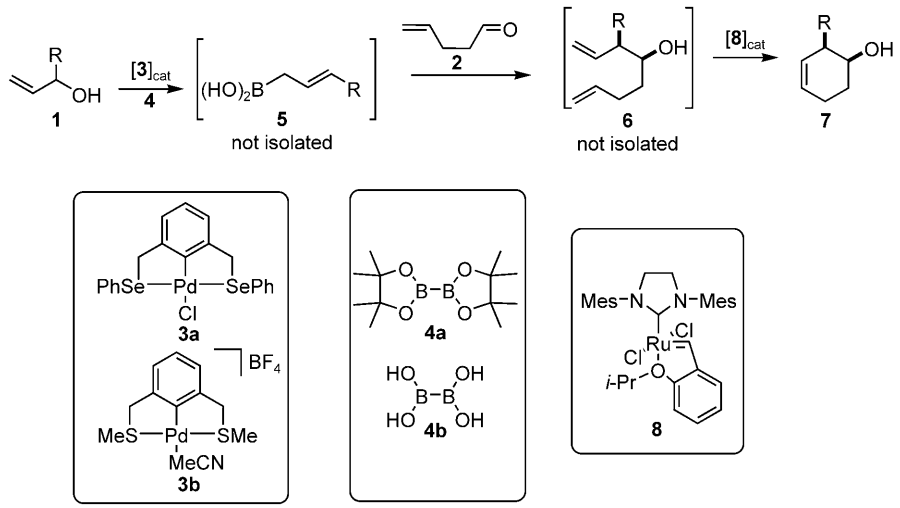


Figure 1. One-pot approach for synthesis of cycloalkenes (**7**) from allylic substrates (**1**) and aldehydes (**2**) using palladium (**3**) and ruthenium (**8**) catalysts.

acid (*p*-TsOH) in a mixture of DMSO and methanol (1:1). After the boronation reaction was completed (50 °C/16–36 h), Hoveyda–Grubbs catalyst[23,24] **8** in dichloromethane was added to the reaction mixture of the coupling reaction (without removal of the solvent) and the metathesis reaction was furnished in 20 h. Addition of **8** in the beginning of the one-pot process led to inhibition of the RCM reaction, and therefore unsatisfactory termination (**6**→**7**) of the one-pot sequence. On the other hand, the sequential treatment does not involve any inconvenience and by using it, the interference between the catalyst actions can be completely avoided.

Simple primary (**1a**) and secondary alcohols (**1b**) reacted smoothly, providing *syn*-substituted hydroxycyclohexene derivatives **7a** and **7b** as single stereoisomers (entries 1 and 2). These reactions proceeded with relatively high overall yield (68%) considering the fact that the one-pot sequence involves at least three individual chemical processes. The reaction of dienyl alcohol **1c** with **2a** or **2b** is particularly interesting from a selectivity point of view. In the coupling reaction of **1c** and **2a** (entry 3) the *in situ* formed intermediate product **6c** is a triene (Figure 2). This compound may undergo RCM to either *syn*-substituted cyclohexene derivative **7c** or *anti*-substituted cycloheptene derivative **9**. However, the RCM reaction led to exclusive formation of the six-membered ring product **7c**. It is well-known[25] that formation of six-membered rings is faster with RCM than formation of seven-membered rings, however, the *anti*-sterochemistry of the vinyl and hydroxy substituents (**9**) is expected to be thermodynamically more stabilizing than the *syn* interaction of the allyl and hydroxy groups in the six-membered ring product **7c**. Apparently, the stereoselectivity has much less influence on the rate of the RCM reaction than the ring size of the product.

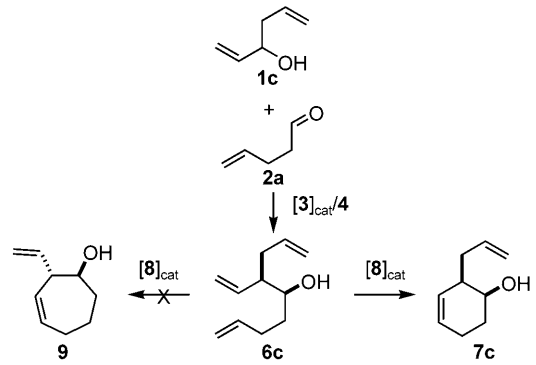
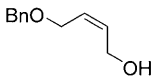
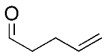
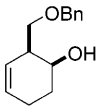
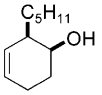
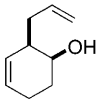
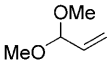
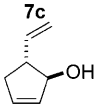
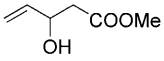
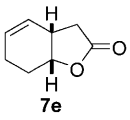
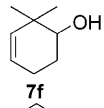
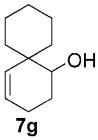
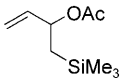
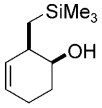
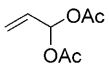
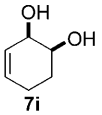
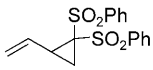
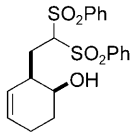


Figure 2. Selective formation of cyclohexenyl derivative **7c** *via* RCM of triene **6c**.

Using **2b** as aldehyde precursor, another cyclic diene (**7d**) can be prepared *via* triene **6d** (entry 4). In this process, highly reactive acrylaldehyde was used as the coupling component. This aldehyde was generated *in situ* from acetal **2b**, which was added after completion of boronation of **1c**. Acetal **2b** was smoothly hydrolyzed[8] in the reaction mixture in the presence of catalytic amounts of *p*-TsOH and water. Thus, the overall reaction is a quadruple catalytic system, in which *p*-TsOH catalyzes two reactions: hydrolysis of **2b** and the boronation[12] of allylic alcohol **1c**, while palladium pincer complex **3** catalyzes the boronation process[12] and ruthenium catalyst **8** the RCM reaction. There is a theoretical possibility that triene **6d** cyclizes to the cyclobutene derivative **10**, however, the expected product in this process is *anti*-substituted cyclopentene derivative **7d**, which was obtained in 63% overall yield as the only product (Figure 3). The above methods represent a useful alternative (entry 3) or a complementary (entry 4) approach to

Table 1. Coupling of allylic substrates with aldehyde **2a** and acetal **2b** followed by ring closing metathesis in a one-pot sequence.[a]

Entry	Substrates	Product	Yield [%][b]
1	 **1a** +  **2a**	 **7a**	68
2	 **1b** + **2a**	 **7b**	68
3[c]	 **1c** + **2a**	 **7c**	78
4[c,d]	**1c** +  **2b**	 **7d**	63
5	 **1d** + **2a**	 **7e**	68
6	 **1e** + **2a**	 **7f**	82
7	 **1f** + **2a**	 **7g**	72
8[e]	 **1g** + **2a**	 **7h**	63
9[e,f]	 **1h** + **2a**	 **7i**	69
10	 **1i** + **2a**	 **7j**	80

[a] Unless otherwise stated, substrate **1** and **2a** were dissolved in a DMSO/MeOH mixture in the presence of the diboronic reagent **4a** (1.2 equiv.), palladium catalyst **3a** (5 mol%), *p*-TsOH (10 mol%) and water (8.0 equiv.). After stirring at 50 °C for 16–36 h, a DCM solution of ruthenium catalyst **8** (5 mol%) was added and the solution was refluxed for another 20 h.

[b] Isolated yield of the overall process.

[c] RCM was performed in only 2–4 h.

[d] Acetal **2b** was added after 16 h.

[e] The boronation reaction was conducted without addition of *p*-TsOH and water.

[f] This product was obtained after hydrolysis.

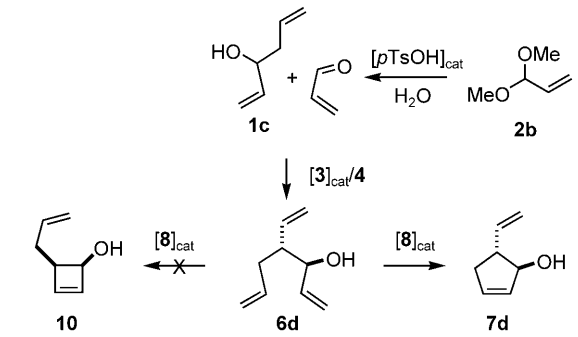


Figure 3. One-pot, multi-step synthesis of cylopentene derivative **7d** *via* RCM of triene **6d**.

the carbometallation procedure of cyclic dienes reported by Singleton and co-workers.[26,27]

Carboxy functionalized allylic alcohol **1d** (entry 5) undergoes boronation and coupling reaction to form **6e**, which is followed by immediate lactonization providing **6e′**. The RCM process of **6e′** can be smoothly performed affording bicyclic lactone **7e**, which is a useful building block in natural product synthesis.[28,29] Together with the lactonization, this one-pot procedure (**1d**→**7e**) involves four discrete reactions (Figure 4).

Cyclohexene derivatives with quaternary carbons are important synthetic intermediates in the preparation of steroids and related bioactive species.[30] Starting from allylic alcohols **1e**, **f** (entries 6 and 7), these structural motifs can easily be created by the presented one-pot reaction (Figure 1). The presence of a quaternary carbon does not affect the regiochemistry of the allylation reaction, which affords the branched product selectively. The RCM reaction also proceeds smoothly in the presence of the quaternary carbon to give dimethylcyclohexenol **7f** and bicyclic spirane **7g**.

Usually, the preferred substrates of the catalytic boronation reactions are inexpensive allylic alcohols.[6,12] However, there are a few exceptions, when the allylic alcohols are unstable under the applied reaction conditions (entries 8 and 9) or when the requisite alcohols are more difficult to access than other derivatives (entry 10). Compound **1g** (and the corre-

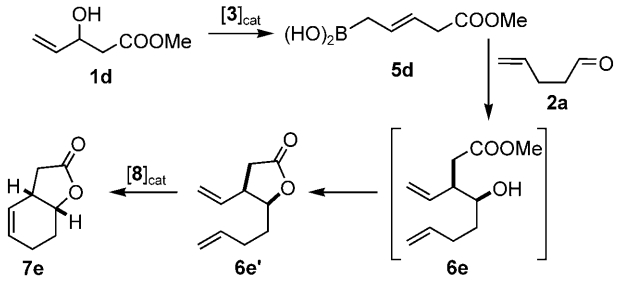


Figure 4. Synthesis of bicyclic lactone **7e** in a one-pot sequence.

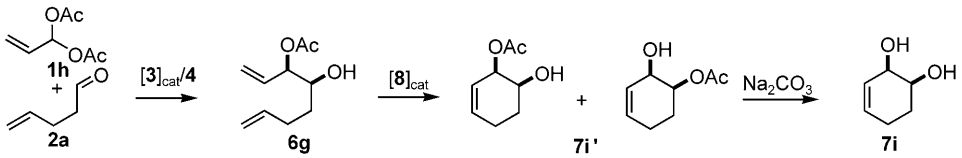


Figure 5. Efficient synthesis of dihydroxycyclohexene derivative **7i** from **1h** and **2a**.

sponding allylic alcohol) is highly unstable under acidic conditions. Even in the presence of 5 mol% of *p*-TsOH, **1g** undergoes rapid Peterson elimination to give butadiene. Therefore, the boronation had to be carried out under neutral conditions to obtain the corresponding silylated allylboronate,[10] which readily reacted with **2a** under one-pot conditions. Subsequent addition of catalytic amounts of **8** to the reaction mixture of the coupling reaction resulted in **7h**. Because of the mild, neutral reaction conditions of this one-pot reaction of three discrete processes, the desilylation reaction could be completely avoided.

Dihydroxycyclohexene derivative **7i** is an important intermediate in synthesis of carbosugars and sugar mimics.[31–34] A straightforward stereoselective synthesis of **7i** can easily be performed using the presented one-pot procedure (entry 9, Figure 5). The synthesis can be achieved using easily available diacetate **1h**, which is first boronated and then coupled with **2a** affording coupling product **6g**. In **6g**, the acetate functionality is located on the allylic hydroxy group. However, after one-pot RCM reaction of **6g**, in the cyclized product (**7i′**) the acetate group has partially migrated to the homoallylic hydroxy group. One possible reason for the acetate migration can be the close vicinity of the *syn* hydroxy groups in **7i′**, which is imposed by the six-membered ring framework. This close vicinity is probably not realized in the acyclic precursor **6g** because of free rotation of the carbon-carbon bonds. The final product **7i** was isolated after acetate hydrolysis of **7i′**.

The one-pot reactions do not necessarily require allylic alcohol and acetate precursors. For example, activated vinylcyclopropane derivative **1i** readily underwent the boronation, allylation followed by RCM reaction providing **7j**. The excellent selectivity of the cooperative processes ensures that the bulky sulfone substituent and the hydroxy group have a *syn* geometry in the single diastereomeric product (**7j**) of the reaction sequence.

Mechanistic Aspects

The overall one-pot reaction is based on the cooperative action of palladium-catalyzed borylation, subsequent allylation and ruthenium-catalyzed metathesis reaction (Figure 6). The optimized conditions of the boronation reactions involve application of pincer complex catalysts **3a** or **3b**, boronate source **4a** or **4b** in a mixture of DMSO and methanol.[6,10,12] The boronation reaction is accelerated by application of *p*-TsOH (5 mol%),[12] however, the reaction can also be carried out under neutral conditions (e.g., entry 8)[10] when diboronic acid **4b** is used as boronate source. On the other hand, when **4a** is used as a boronate

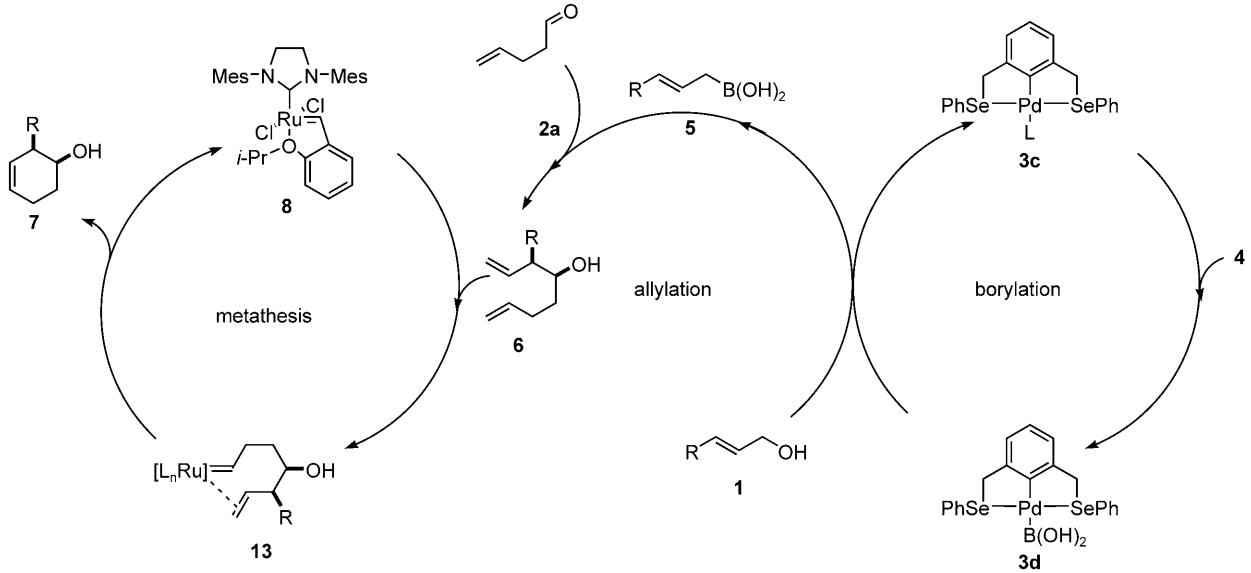


Figure 6. Mechanistic overview of the one-pot sequence.

source, addition of *p*-TsOH is required for the efficient boronation process. As **4a** is less expensive and more accessible, than **4b**, we used this boronate source whenever it was possible together with catalytic amounts of *p*-TsOH.

The coupling reaction between allylboronate **5** and aldehyde **2**, providing **6** proceeds smoothly under the reaction conditions of the boronation. The high diastereoselectivity of the allylation arises from the compact, highly ordered, six-membered ring TS of the process.[35] The allylation process is probably also facilitated in the presence of catalytic amounts of a Brønsted acid, such as *p*-TsOH.[36,37] Most importantly, the metathesis reaction performed by addition of **8** in dichloromethane could be performed smoothly in the presence of the solvents (DMSO, MeOH), catalysts (**3** and *p*-TsOH) and waste products (water, boric acid and its esters) of the boronation reaction. This is due to the exceptional robustness of catalyst **8**, which allows performance of RCM reactions as the terminating catalytic step of one-pot multi-step reactions.[38] The overall one-pot procedure involves typically three individual reactions (borylation, allylation and metathesis) incorporating three catalytic events: palladium (**3**) and a sulfonic acid (*p*-TsOH) catalyzed boronation and ruthenium (**8**) catalyzed RCM reaction.

Conclusions

In this study, we have shown that allylic alcohols and other allylic substrates can be transformed to stereodefined functionalized cyclohexene and cyclopentene derivatives in a multicatalytic one-pot sequence. This transformation is based on palladium pincer complex based boronation of the allylic precursors, which is followed by highly diastereoselective coupling with unsaturated aldehydes and terminated by ring-closing metathesis. The procedure is operationally simple, providing the corresponding products in a high overall yield (63–82%) with excellent diastereo- and regioselectivity. The presented method has a broad synthetic scope including functionalized allylic alcohols, acetates and vinylcyclopropane substrates. The overall process may involve up to four individual reactions (entries 4 and 5), in which three or four catalytic events take place. The products are useful building blocks in advanced organic synthesis and natural product synthesis.[26–34,39–41]

Experimental Section

The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C) at room temperature using a 400 MHz NMR spectrometer. High resolution mass data were obtained using the ESI technique. The applied chemicals were obtained from commercial sources or synthesized according to literature procedures: **1d**,[42] **1g**,[43] **1i**,[44] **3a**[6] and **3b**.[45]

General Procedure

Substrates **1** (0.15 mmol) and **2a** (2.0 equiv.) were dissolved in a DMSO/MeOH (0.2/0.2 mL) mixture followed by addition of the diboronic reagent **4a** (1.2 equiv.), palladium catalyst **3a** (5 mol%), *p*-toluenesulfonic acid (10 mol%) and water (8.0 equiv.). The mixture was stirred at 50 °C for 20 h. Subsequently, ruthenium catalyst **8** (5 mol%) in dichloromethane (20 mL) was added, and this mixture was refluxed under argon for 20 h. Thereafter, the reaction mixture was quenched by water and the phases separated. After evaporation of the organic phase, product **7** was purified by silica gel chromatography.

2-[(Benzyloxy)methyl]-3-cyclohexen-1-ol (7a): This compound was prepared according to the above general procedure from **1a** and **2a**, affording **7a** in 68% yield. The NMR data obtained for **7a** are in agreement with the previously reported[6] values. ^{1}H NMR ($CDCl_3$): $\delta = 7.32$ (m, 5H), 5.78 (m, 1H), 5.43 (m, 1H), 4.55 (s, 2H), 4.15 (m, 1H), 3.62 (m, 2H), 2.99 (d, $J = 5.0$ Hz, 1H), 2.65 (m, 1H), 2.21 (m, 1H), 2.05 (m, 1H), 1.79 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 137.8$, 129.0, 128.5, 127.8, 127.7, 124.8, 73.4, 71.5, 68.1, 40.2, 27.9, 22.4; HR-MS (ESI): $m/z = 241.1202$, calcd. for $[C_{14}H_{18}O_2+Na]^+$: 241.1199.

2-Pentyl-3-cyclohexen-1-ol (7b): This compound was prepared according to the above general procedure from **1b** and **2a** except that the borylation based allylation was conducted for 36 h, affording **7b** in 68% yield. The NMR data obtained for **7b** are in agreement with the previously reported[6] values. ^{1}H NMR ($CDCl_3$): $\delta = 5.69$ (m, 1H), 5.47 (m, 1H), 4.00 (m, 1H), 2.17 (m, 2H), 2.05 (m, 1H), 1.89 (m, 1H), 1.68 (m, 1H), 1.54 (m, 1H), 1.35 (m, 8H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 128.9$, 126.5, 67.6, 40.1, 32.1, 31.0, 28.5, 26.7, 22.6, 21.4, 14.1; HR-MS (ESI): $m/z = 191.1405$, calcd. for $[C_{11}H_{20}O+Na]^+$: 191.1406.

2-Allyl-3-cyclohexen-1-ol (7c): This compound was prepared according to the above general procedure from **1c** and **2a**, except that the ring-closing metathesis was conducted for 2 h, affording **7c** in 78% yield. The NMR data obtained for **7c** are in agreement with the previously reported[26] values. ^{1}H NMR ($CDCl_3$): $\delta = 5.88$ (dddd, $J = 7.0$, 7.0, 10.3, 17.0 Hz, 1H), 5.72 (m, 1H), 5.47 (m, 1H), 5.11 (d, $J = 17.0$ Hz, 1H), 5.06 (d, $J = 10.3$ Hz, 1H), 4.01 (m, 1H), 2.17 (m, 5H), 1.79 (m, 2H), 1.51 (br, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 137.0$, 128.0, 126.9, 116.3, 67.6, 40.0, 35.6, 28.4, 21.3; HR-MS (ESI): $m/z = 161.0937$, calcd. for $[C_9H_{14}O+Na]^+$: 161.0929.

5-Vinyl-2-cyclopenten-1-ol (7d): This compound was prepared according to the above general procedure from **1c** and **2b**, except that **2b** was added after 16 h. The mixture was thereafter stirred for another 6 h. The ring-closing metathesis was conducted for 4 h, affording **7d** in 63% yield. ^{1}H NMR ($CDCl_3$): $\delta = 5.88$ (m, 1H), 5.86 (ddd, $J = 7.9$, 10.3, 17.3 Hz, 1H), 5.76 (m, 1H), 5.11 (d, $J = 17.3$ Hz, 1H), 5.02 (d, $J = 10.3$ Hz, 1H), 4.59 (m, 1H), 2.62 (m, 2H), 2.15 (m, 1H), 2.03 (br, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 140.2$, 133.1,

133.0, 114.7, 82.8, 52.9, 37.3; HR-MS (ESI): $m/z = 133.0620$, calcd. for $[C_7H_{10}O+Na]^+$: 133.0624.

7-Oxabicyclo[4.3.0]-2-nonen-8-one (7e): This compound was prepared according to the above general procedure from **1d** and **2a**, except that instead of **3a**, catalyst **3b** was used, affording **7e** in 68% yield. The NMR data obtained for **7e** are in agreement with the previously reported[28] values. ^{1}H NMR ($CDCl_3$): $\delta = 5.88$ (m, 1H), 5.47 (m, 1H), 4.76 (ddd, $J = 2.7$, 5.6, 5.6 Hz, 1H), 3.00 (m, 1H), 2.76 (m, 1H), 2.30 (m, 1H), 2.10 (m, 3H), 1.78 (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 176.8$, 128.8, 125.6, 78.1, 35.8, 34.5, 24.6, 19.2; HR-MS (ESI): $m/z = 161.0574$, calcd. for $[C_8H_{10}O_2+Na]^+$: 161.0573.

2,2-Dimethyl-3-cyclohexen-1-ol (7f): This compound was prepared according to the above general procedure from **1e** and **2a**, affording **7f** in 82% yield. ^{1}H NMR ($CDCl_3$): $\delta =$ 5.51 (m, 1H), 5.36 (m, 1H), 3.57 (m, 1H), 2.10 (m, 2H), 1.73 (m, 2H), 1.44 (br, 1H), 1.05 (s, 3H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 136.2$, 124.0, 75.2, 36.7, 28.1, 26.9, 23.8, 22.7; HR-MS (ESI): $m/z = 149.0936$, calcd. for $[C_8H_{14}O+Na]^+$: 149.0937.

Spiro[5.5]undec-4-en-1-ol (7g): This compound was prepared according to the above general procedure from **1f** and **2a**, affording **7g** in 72% yield. ^{1}H NMR ($CDCl_3$): $\delta = 5.71$ (d, $J = 10.3$ Hz, 1H), 5.62 (ddd, $J = 3.4$, 3.4, 10.3 Hz, 1H), 3.65 (m, 1H), 2.11 (m, 2H), 1.79 (m, 2H), 1.43 (m, 11H); ^{13}C NMR ($CDCl_3$): $\delta = 132.5$, 125.1, 73.2, 38.7, 36.4, 32.2, 26.2, 25.4, 22.3, 21.6, 21.3; HR-MS (ESI): $m/z = 189.1251$, calcd. for $[C_{11}H_{18}O+Na]^+$: 189.1250.

2-[(1,1,1-Trimethylsilyl)methyl]-3-cyclohexen-1-ol (7h): This compound was prepared according to the above general procedure from **1g** and **2a**, except that **3b** was used as catalyst and **4b** was employed as boronate source. In addition, this reaction was performed in the absence of *p*-TsOH and added water conducting the boronation step for 16 h, affording **7h** in 63% yield. ^{1}H NMR ($CDCl_3$): $\delta = 5.62$ (m, 1H), 5.47 (m, 1H), 3.86 (m, 1H), 2.37 (m, 1H), 2.10 (m, 2H), 1.76 (m, 2H), 1.51 (br, 1H), 0.66 (m, 2H), 0.05 (s, 9H); ^{13}C NMR ($CDCl_3$): $\delta = 130.6$, 125.9, 69.6, 36.7, 27.8, 21.9, 17.8, −0.7; HR-MS (ESI): $m/z = 207.1176$, calcd. for $[C_{10}H_{20}OSi+Na]^+$: 207.1176.

3-Cyclohexen-1,2-diol (7i): This compound was prepared by a modified version of the above general procedure. Thus, **1h** (0.15 mmol) was stirred with diboronic reagent **4b** (1.2 equiv.), molecular sieves (4 Å, 15 mg) and palladium catalyst **3b** (5 mol%), in DMSO (0.4 mL) for 36 h at 40 °C.[10] Thereafter, aldehyde **2a** was added and the stirring continued for another 24 h. To this mixture ruthenium catalyst **8** (5 mol%) in dichloromethane (20 mL) was added and refluxed under argon for 20 h. Thereafter, the reaction mixture was quenched by water and the phases separated. After evaporation of the organic phase **7i′** was purified by silica gel chromatography. After hydrolysis of **7i′** (by 20 mol% Na_2CO_3 in MeOH at room temperature for 4 h followed by filtration through a plug of silica), diol **7i** was obtained in 69% yield. The NMR data obtained for **7i** are in agreement with the previously reported[32] values. ^{1}H NMR ($CDCl_3$): $\delta = 5.89$ (m, 1H), 5.74 (m, 1H), 4.14 (m, 1H), 3.83 (m, 1H), 2.28 (br, 2H), 2.14 (m, 2H), 1.76 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 131.5$, 126.9, 68.8, 66.5, 25.9, 23.5; HR-MS (ESI): $m/z = 137.0571$, calcd. for $[C_6H_{10}O_2+Na]^+$: 137.0573.

2-[2,2-Di(phenylsulfonyl)ethyl]-3-cyclohexen-1-ol (7j): This compound was prepared according to the above general procedure from **1i** and **2a**, except that instead of **3a**, catalyst **3b** was used, affording **7j** in 80% yield. ^{1}H NMR ($CDCl_3$): $\delta = 7.96$ (m, 4H), 7.70 (m, 2H), 7.58 (m, 4H), 5.68 (m, 1H), 5.33 (m, 1H), 4.98 (dd, $J = 3.6$, 7.3 Hz, 1H), 4.02 (m, 1H), 2.63 (m, 1H), 2.43 (m, 1H), 2.09 (m, 3H), 1.95 (d, $J = 6.0$ Hz, 1H), 1.70 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 137.8$, 137.6, 134.6, 134.5, 129.7, 129.6, 129.1, 129.0, 128.1, 126.8, 81.5, 67.8, 38.0, 27.3, 26.6, 22.6; HR-MS (ESI): $m/z =$ 429.0798, calcd. for $[C_{20}H_{22}O_5S_2+Na]^+$: 429.0801.

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