Preparation of Dienyl Boronates by Tandem Ene-Yne Metathesis/Dienyl Isomerization: Ready Access to Diene Building Blocks for the Synthesis of Polyenes

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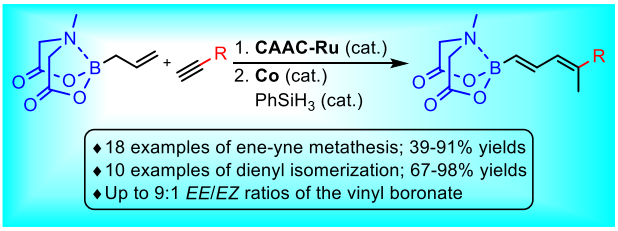
Supporting Information Placeholder



ABSTRACT: The ene-yne metathesis of alkenyl boronates with terminal alkynes is reported. These challenging metatheses were accomplished using a Grubbs catalyst bearing the cyclic alkyl amino carbene (CAAC) ligand, whereas *N*-heterocyclic carbene (NHC) derived catalysts gave lower yields. Subsequent dienyl isomerization via a cobalt-catalyzed hydrogen atom transfer (HAT) furnished the more substituted dienyl boronate with high *EE*/*EZ* ratios. Finally, the resulting dienyl boronate products were successfully used in Suzuki-Miyaura cross-coupling reactions and in a Diels-Alder cycloaddition.

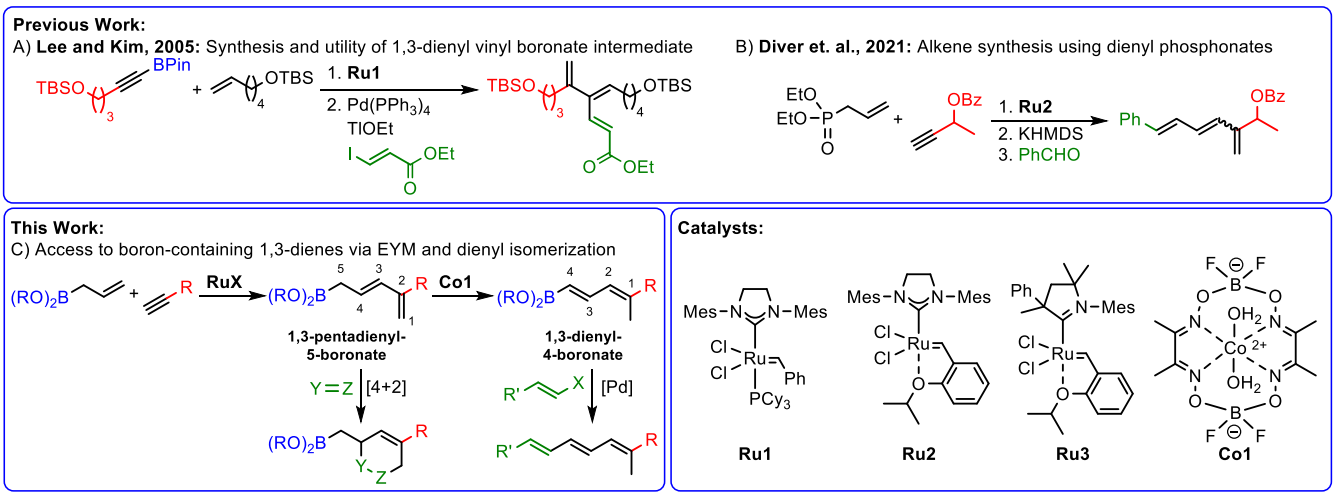
Introduction

Organoboron compounds are versatile synthetic intermediates for a variety of metal-catalyzed transformations. Most notably, the Suzuki-Miyaura reaction efficiently couples boronic acids with an electrophile to form new carbon-carbon bonds.[1] The reaction conditions are often mild, tolerant to many functional groups, chemoselective, stereoselective and generate relatively nontoxic byproducts. Due to its mild and robust nature, the Suzuki coupling is widely used in many industrial, pharmaceutical and natural product syntheses.[2] The Suzuki reaction can be used to access 1,3-diene and polyene functional groups with suitable vinyl boron or dienyl/polyenyl boron precursors. Many pharmaceuticals and natural products contain the 1,3-diene functional group or a polyene element,[3] so new synthetic methods for their stereoselective synthesis are desirable.

The venerable Suzuki-Miyaura reaction can deliver conjugated dienes and polyenes via cross coupling, however the instability of the unsaturated boronic acid is problematic.[3-4] For instance, allylic[5] and vinylic[6] boronic acids are generally unstable and require immediate use upon preparation. Decomposition of sensitive boronic acids can be managed by use of a protecting group strategy, which allows for easier use and handling as the boronate. Common boronate protecting groups include pinacol (Pin), Burke's *N*-methyliminodiacetic acid (MIDA)[7] and Molander's trifluoroborates.[8] These are well suited for sensitive boronic acids.[9] Anticipating the instability of 1,3-diene-containing boronic acids, we sought a stabilized boronate which could be used for the synthesis of alkene and polyalkene motifs.

Intermolecular ene-yne metathesis (EYM) can be used to deliver 1,3-diene-containing fragments that can be used as building blocks for the synthesis of trienes. EYM is advantageous in 1,3-diene synthesis because it uses readily-available alkene and alkyne reactants. Normally, 1,3-diene products are subject to cycloaddition or subsequent catalytic difunctionalization reactions.[10] Less often, the 1,3-diene has served as an intermediate in natural product syntheses,[11] or may appear in the natural product itself.[11c] However, there are few examples that use the 1,3-diene as a building block for the synthesis of polyalkene structures (Scheme 1).[12] Lee and Kim used the Grubbs second generation catalyst, **Ru1**, to react internal alkynyl pinacol boronates with terminal olefins to form an intermediate dienyl substituted pinacolboronate (Scheme 1A).[13] In the second step, the intermediate boronate was cross-coupled with a vinyl halide to provide the polyene product stereospecifically. More recently, we reported the ene-yne metathesis of alkenyl phosphonates with terminal alkynes to provide dienyl phosphonates, which are useful for classical Horner-Wittig alkene synthesis (Scheme 1B).[14] For more challenging cross ene-yne metatheses, we utilized a ruthenium carbene catalyst bearing a cyclic alkyl amino carbene (CAAC) ligand, **Ru3**, developed by Grubbs and Bertrand.[15] We wondered if the metathesis reactivity gains that were possible with **Ru3** could be adapted for the synthesis of dienyl boronates.

Scheme 1. Utility of 1,3-Dienes from Ene-Yne Metathesis



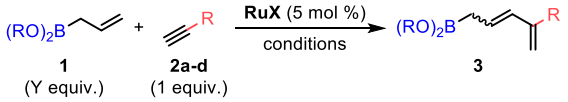
There are numerous reports of allylic[16] and vinylic[16b,16c,17] boronates undergoing cross olefin metathesis, but to the best of our knowledge, there are no examples of these unsaturated reactants being used in intermolecular ene-yne metathesis. We envisioned the metathesis of allylic boronates with terminal alkynes to form 1,3-pentadienyl-5-boronates (Scheme 1C). In the present study, these challenging metatheses were accomplished using the CAAC catalyst **Ru3** and 3 molar equivalents of alkene. Ene-yne metathesis offers unique advantages and can leverage improvements in the Grubbs catalysts for less reactive substrates. In the best cases, intermolecular EYM can be conducted at nearly 1:1 alkene:alkyne stoichiometry. Such atom economy[18] is uncommon,[14,19] but appealing due to the lack of wasted reactants. Subsequent dienyl isomerization using our recently reported cobalt-catalyzed hydrogen atom transfer (HAT) chemistry[20] smoothly furnished the 1,3-dienyl-4-boronates with good stereoselectivity.

Dienyl boronates are valuable synthetic building blocks. In this study, two types of diene-containing boronates are reported as seen in Scheme 1C. For 1,3-dienes bearing an allylic boronate, the contiguous five carbon array containing the diene subunit constitutes a 1,3-pentadienyl-5-boronate (sp^3-hybridized carbon bound to boron). In this study, the pentadienyl boronates are formed from an ene-yne metathesis step and used to access the latter unsaturated boronate, a dienyl boronate. 1,3-Dienyl-4-boronates feature a 1,3-diene conjugated with the boronate (sp^2-hybridized carbon bound to boron). Though both boron-containing 1,3-dienes have synthetic potential, we focus on 1,3-dienyl-4-boronates in order to create new sp^2-sp^2 C-C bonds, such as those found in polyenes (Scheme 1C, lower right). It is worth noting that dienyl boronates can be synthesized by alternative methods, such as the hydroboration of enyne substrates[21] or the boron-Wittig olefination of aldehydes.[22]

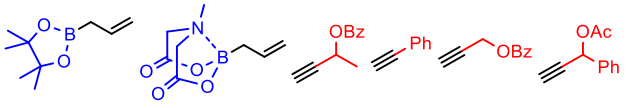
Results and Discussion

An initial study showed that allyl boronates are reactive alkene substrates in ene-yne metathesis (Table 1). Since atom economical ene-yne metathesis is a rare achievement, we were surprised to find that the electron-deficient (allyl)pinacolboronate **1a** (1 equivalent) reacted with either branched terminal alkyne **2a** or phenylacetylene **2b** (1 equivalent) to give >95% NMR yields of the expected 1,3-dienes **3** (entries 1 and 2). However, the isolated yields were lower, which we attributed to product instability on silica gel.[23] Diminished NMR yields were also observed when 3 equivalents of **1a** were used with alkyne **2c** which is unbranched at the propargylic position (entry 3). Using the Hoveyda-Grubbs catalyst **Ru2** as a faster initiating and more robust catalyst resulted in higher conversion of **2c**, but similar NMR yields were obtained, as compared to the result with **Ru1** (entry 4 vs. entry 3). Metathesis with branched alkyne **2d** resulted in appreciably higher conversion yields, but instability of **3ad** on silica gel was still a persistent problem that resulted in reasonable, albeit lower isolated yields (entries 5 and 6). To

Table 1. Initial Studies on the Ene-Yne Metathesis of Allyl Boronates with Terminal Alkynes[a]



entry	RuX	1	Y	2	3	Conv. (%)[b,c]	Yield (%)[c,d]	E/Z[e]
1	**Ru1**	**1a**	1	**2a**	**3aa**	>95	56 (>95)	3:1
2	**Ru2**	**1a**	1	**2b**	**3ab**	>95	48 (>95)	2.5:1
3	**Ru1**	**1a**	3	**2c**	**3ac**	64	- (21)	1:1
4	**Ru2**	**1a**	3	**2c**	**3ac**	89	- (27)	1:1
5	**Ru1**	**1a**	3	**2d**	**3ad**	>95	- (83)	1.6:1
6	**Ru2**	**1a**	3	**2d**	**3ad**	>95	- (84)	1.6:1
7	**Ru1**	**1b**	1	**2a**	**3ba**	>95	71 (77)	2:1
8	**Ru2**	**1b**	1	**2b**	**3bb**	>95	81 (84)	1.5:1



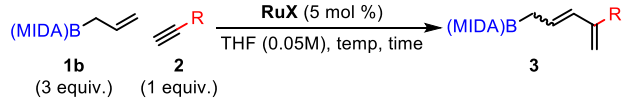
[a] Reaction conditions: solvent (0.05 – 0.10M), 60 °C, 3 h; PhH or C_6D_6 were used for **1a** and THF was used for **1b**. [b] Conversion of **2**. [c] Conversion and NMR yields based on integration vs. mesitylene as an internal standard. [d] NMR yields reported in parentheses. [e] Determined by integration of the vinylic protons.

address decomposition of **3** on silica gel, we turned our attention to chromatographically-stable allyl *N*-methyliminodiacetic acid (MIDA) boronate ester **1b**. MIDA boronates, such as **1b**, are synthetically attractive since they are robust to many chemical transformations[24] and can be hydrolyzed on demand to furnish the synthetically versatile boronic acid.[25] Using MIDA boronate **1b** as the alkene reactant with 1:1 stoichiometry to the alkyne resulted in 77-84% NMR yields (entries 7 and 8). However, unlike entries 1-2, the MIDA-containing products **3ba** and **3bb** were isolated without any notable decomposition on silica gel. Good isolated yield obtained with **1b** under conditions of atom economy is noteworthy. The slightly lower yields for **1b** compared to the allyl boronate analog **1a** may be due to the greater steric hinderance of the tetracoordinate boron atom.

Unbranched alkynes are less reactive in ene-yne metathesis and may suffer from side reactions such as alkyne oligomerization. Low NMR yields for **3ac** (entries 3 and 4 in Table 1) may be explained by the lack of branching at the propargylic position.[26] In past kinetic studies of the mechanism of ene-yne metathesis using Grubbs catalyst **Ru1**, unbranched alkynes were found to have lower reaction rates. With lower ene-yne metathesis turnover rates, the vinyl carbene intermediate, unique to ene-yne metathesis, is prone to unproductive side reactions or decomposition. Oligomerization of propargyl benzoate **2c** with **Ru2** has been previously reported,[27] which illustrates that alkynes can competitively react with the vinyl carbene intermediate in the ene-yne metathesis. In general, increased alkene equivalents or higher alkene concentration can increase the yields of 1,3-diene products in ene-yne metathesis, but we limited our studies to 3 equivalents (or less) of allylboronate **1** for a practical implementation of the reaction. A Grubbs catalyst bearing the cyclic alkyl amino carbene (CAAC) as the L-type ligand is an effective catalyst in alkene metathesis.[15] Catalyst **Ru3** was developed by Grubbs and Bertrand using a CAAC ligand rather than the N-heterocyclic carbene (NHC) which is found in earlier catalysts **Ru1** and **Ru2**. Recent mechanistic studies by Fogg, Jensen and coworkers have shown that ruthenacycles derived from CAAC carbene catalysts are less prone to decomposition via β-hydride elimination than their NHC analogs.[28] Recently, we observed a catalyst reactivity trend when using alkene-containing phosphonates with unbranched alkyne **2c** where the CAAC-containing **Ru3** proved to be the best catalyst for this ene-yne metathesis.[14] It was reasoned that **Ru3** improved chemical yields due to increased catalyst performance relative to earlier generation Grubbs catalysts.

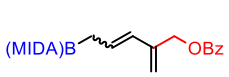
Catalyst optimization studies showed the Grubbs-Bertrand catalyst **Ru3** to be superior to the NHC-derived catalysts, **Ru1** and **Ru2** (Table 2). To tease out reactivity differences between alkynes with different propargylic substitution, we choose unbranched-**2c** and branched-**2d** as our probe substrates (for structures of alkynes **2c** and **2d**, see Table 1 above).[26-27] Cross ene-yne metathesis of **1b** with **2c** via **Ru1** or **Ru2** gave higher conversion, but the low yields of **3bc**

Table 2. Catalyst Optimization Studies

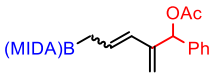


1b (3 equiv.) **2** (1 equiv.) **3**

entry	RuX	2	temp (° C), time (h)	3	Conv. (%)[a,b]	Yield (%)[b]	*E*/*Z*[c]
1	**Ru1**	**2c**	60, 3	**3bc**	>95	20	1:1
2	**Ru2**	**2c**	60, 3	**3bc**	>95	25	1:1
3	**Ru3**	**2c**	60, 3	**3bc**	>95	84	2:1
4	**Ru3**	**2c**	rt, 1	**3bc**	>95	81	1.5:1
5	**Ru1**	**2d**	60, 3	**3bd**	>95	53	1.6:1
6	**Ru2**	**2d**	60, 3	**3bd**	>95	72	1.6:1
7	**Ru3**	**2d**	60, 3	**3bd**	>95	>95	2:1
8	**Ru3**	**2d**	rt, 1	**3bd**	74	45[c]	2:1



3bc



3bd

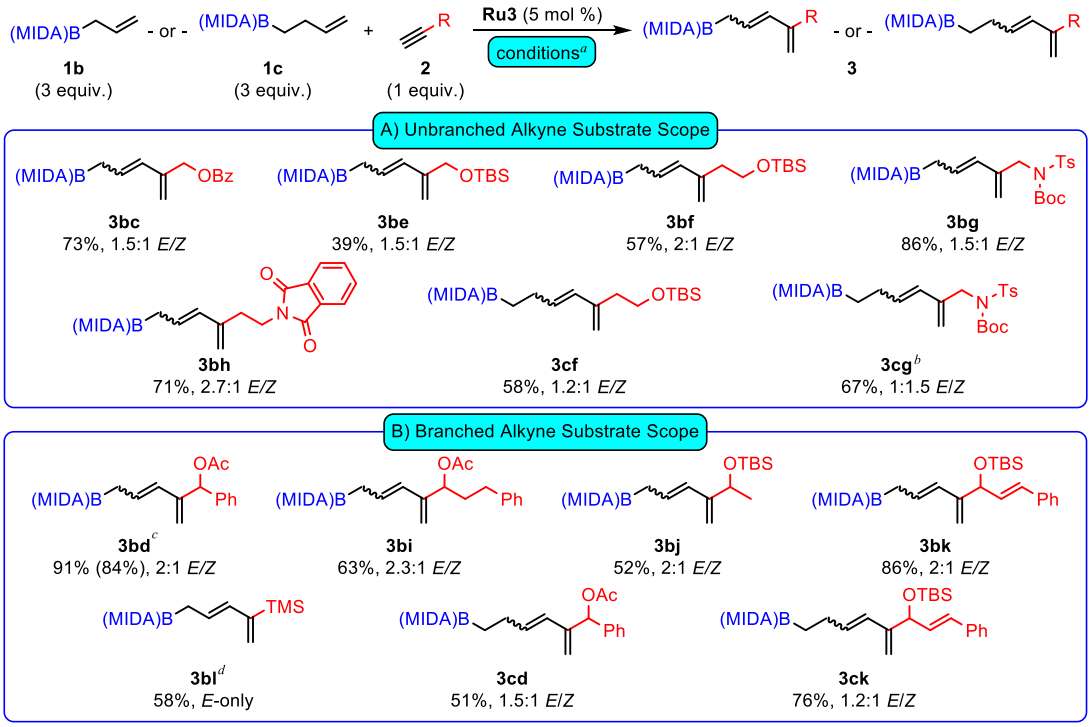
[a] Conversion of **2**. [b] Conversion and NMR yields based on integration vs. mesitylene as an internal standard. [c] Approximately 25% of 2-methylene-1-phenylbut-3-en-1-yl acetate observed.

were similar (Table 2, entries 1 and 2) to the pinacol analog **3ac** shown in Table 1. Use of CAAC-**Ru3** paralleled high conversions of entries 1 and 2, but gave significantly increased yields of diene **3bc**; similar reactivity was found at room temperature for 1 hour (entries 3 and 4). As expected, branched alkyne **2d** gave higher yields than unbranched alkyne **2c** using either **Ru1** or **Ru2** as catalysts (entries 5 and 6). However, NMR yields for **3bd** were lower than the pinacol analog, **3ad**. Yields for **3bd** improved through the use of **Ru3**, but elevated reaction temperatures were required for the highest chemical yields (entries 7 vs. 8).[29] This led us to utilize different optimized reaction conditions based on substitution at the propargylic position of the alkyne; entry 4 for unbranched alkynes and entry 7 for branched alkynes.

With optimized reaction conditions in hand, we began to examine the substrate scope for terminal alkynes (Scheme 2, panel A). Unbranched alkynes of varying functionality were successfully used in ene-yne metathesis. Alkyne **2c** with a propargylic ester furnished the diene product **3bc** in higher yields than that obtained from the corresponding silyl analog, **3be**. Extending the carbon chain by a methylene unit increased the yield and furnished diene **3bf** in moderate yield. Nitrogen functionality at the propargylic and homopropargylic site were well tolerated and furnished **3bg** and **3bh**, respectively. The allylic MIDA boronate could be replaced with its homolog, the homoallylic MIDA **1c**. Combining the homoallylic boronic acid MIDA ester **1c** with alkynes **2f** and **2g** gave the expected 1,3-dienes **3cf** and **3cg** in good yields.

Terminal alkynes with branching at the propargylic position gave good yield in the cross ene-yne metathesis using optimized conditions (Scheme 2, panel B). For these substrates, higher temperatures

Scheme 2. Substrate Scope for the Ene-Yne Metathesis of Alkenyl MIDA Boronates with Terminal Alkynes

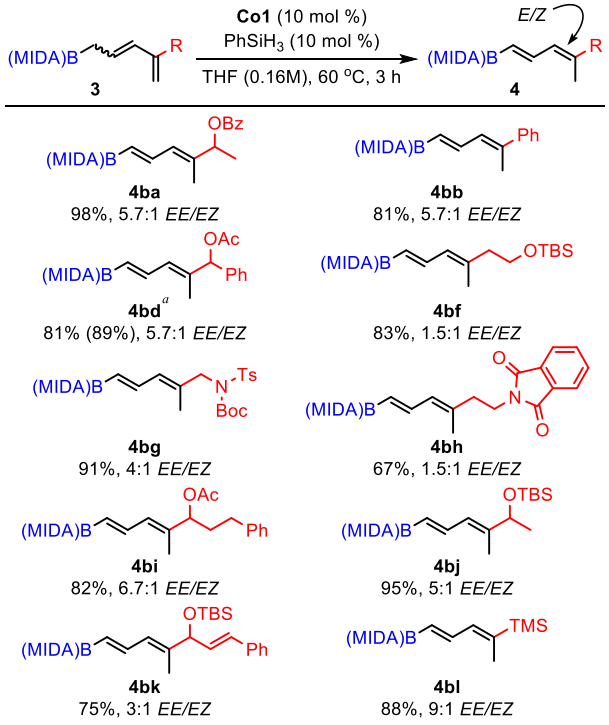


[a] Conditions: Panel A) THF (0.05M), rt, 1 h; Panel B) THF (0.05M), 60 °C, 3 h. [b] 93% NMR yield with a 1.3:1 E/Z mixture; Isolated as a 1:1.5 E/Z mixture after multiple chromatographic attempts to separate **3cg** from **1c.** [c] Yield in parentheses is representative of a 2 mmol scale reaction. [d] Performed in a thick glass-walled PTFE lined reaction tube to prevent the evaporation of low boiling **2l**.

and slightly longer reaction times resulted in better yields of the 1,3-diene products. Propargylic acetates with different propargylic sidechains gave **3bd** and **3bi** in excellent and moderate yields, respectively. Alkynes with propargylic TBS ethers afforded **3bj** and **3bk** in moderate and excellent yields, respectively, with retention of *E*-isomer of the styryl group derived from **2k**. The branched alkyne trimethylsilyl acetylene **2l** underwent ene-yne metathesis to give **3bl** as solely its *E*-isomer. The homologous MIDA boronate **1c** also underwent ene-yne metathesis with **2d** to yield **3cd**[30] and alkyne **3k** with both a silyl ether and a styrenyl sidechain, gave the expected diene **3ck**.

Next, we directly isomerized *E*/*Z* mixtures of **3** to furnish vinyl boronate **4** via our cobalt-catalyzed hydrogen atom transfer (HAT) dienyl isomerization reaction (Scheme 3).[20] In most cases, this process was stereoconvergent using *E*/*Z* mixtures of pentadienyl boronates. Initial attempts to isomerize 1,3-dienes derived from allyl pinacolboronate **1a** were unsuccessful. However, it was found that pentadienyl MIDA boronates **3** derived from **1b** furnished the 1,3-dienyl-4-boronates in high yield and with modest stereoselectivity.[31] The reactants **3** bear a variety of R sidechain substituents, derived from alkyne reactants in the previous ene-yne metathesis step. With bulkier sidechains, modest EE/EZ selectivity was found (e.g. **4ba**, **4bb**), but for those 1,3-dienes with less steric bulk, roughly equal stereoisomeric mixtures were obtained (**4bf** and **4bh**). In these latter cases, the similar size between the sidechain substituent (shown in red in Scheme 3) and the methyl group makes the energy difference between geometric isomers small.[32] The initial hydrogen atom addition is thought to occur on the terminal alkene to produce a secondary allylic radical intermediate. It is noteworthy that addition to this bond occurs for 1,3-dienes with highly branched sidechains, including those bearing both oxygen and nitrogen functionality, as shown in Scheme 3. Last, in cases where the R-

Scheme 3. Cobalt-Catalyzed Isomerization of Dienyl Boronates to Vinyl Boronates.

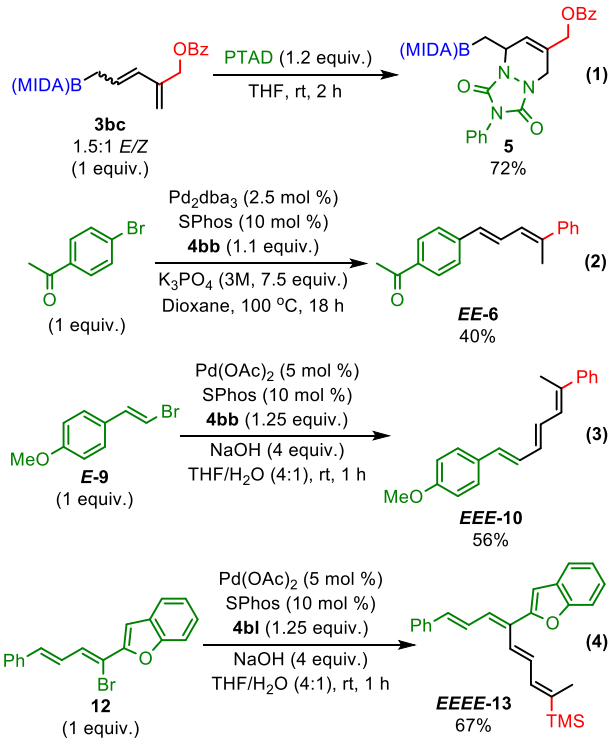


[a] Yield in parentheses is representative of a 1.14 mmol scale reaction.

sidechain bears a CH bond, there is the possibility of regiodivergent diene isomerization. However, even in these cases, isomerization towards the boron atom was observed, registering a completely regioselective dienyl isomerization, giving dienyl boronates **4**. The yields and functional group tolerance make this an attractive synthetic approach to dienylboronates **4** bearing an sp^2-hybridized carbon bound to boron. These attributes, including the ability to access a variety of R-sidechains (Scheme 3) derived from simple alkynes (through ene-yne metathesis), compare favorably to other methods for the synthesis of dienyl boronates.

The dienes produced in this study were used in further chemical transformations (Scheme 4). Classically, 1,3-dienes have proven to be versatile substrates for cycloaddition reactions. Dienes derived from ene-yne metathesis allow for the assembly of ring compounds, core units for diversity-oriented synthesis and medicinally-relevant compounds.[11a,11b] 1,3-Dienes substituted with an electropositive boron-containing group are known to undergo the Diels-Alder reaction.[33] Accordingly, diene **3bc** underwent [4+2] Diels-Alder cycloaddition with phenyl-1,3,4-triazole-2,5-dione (PTAD) at room temperature to furnish cycloadduct **5** (eq 1). Since we were interested in making new sp^2-sp^2 C-C bonds, we turned our attention to Suzuki cross coupling of dienyl boronates **4** (from Scheme 3 above). Attempts were made to deprotect the boronate prior to cross coupling, but efforts to isolate the vinyl boronic acid were unrewarded owing to product instability.[34] To overcome this problem, we elected to use Burke's slow-release strategy where a small amount of vinyl boronic acid is released *in situ*.[25a] Following this useful method, **4bb** (5.7:1 *E*/*Z* ratio) successfully coupled with 4-bromoacetophenone to furnish the cross-coupling product, **6**, solely as its *EE*-isomer (eq 2). Next, we wanted to employ dienyl boronates for the construction of polyenes.

Scheme 4. Synthetic Utility of Dienyl MIDA Boronates



First, vinyl halide ***E*-9** was prepared by the Hunsdiecker reaction[35] and subsequently cross-coupled with **4bb** to furnish triene **10** (19:1 *EEE*/*EEZ* ratio) (eq 3). Notably, the reaction was complete within 1 hour at room temperature using NaOH as base. In this case, deprotection of the MIDA boronate occured within minutes.[25b] Excess base facilitates cross coupling due to the formation of the trihydroxyboronate complex, $[R\text{-}B(OH)_3]Na$, needed for the transmetalation step in the catalytic cycle. While the vinylic boronic acid of **4bb** is unstable, trihydroxyboronate complexes are significantly more stable[9] owing to the closed valence shell at boron. The *in-situ* formation of the trihydroxyboronate complex can attenuate decomposition of sensitive vinyl boronic acids for effective cross-coupling of the dienyl boronate subunit. Adopting these mild conditions, dienyl bromide **12** was coupled with dienyl boronate **4bl** to smoothly furnish tetraene **13** (19:1 *EEEE/ZEEE* ratio) in good yield (eq 4).

Conclusions

In conclusion, a variety of boron-functionalized 1,3-dienes were prepared via the ene-yne metathesis of alkenyl boronates with terminal alkynes. Allyl pinacol boronate derivatives gave ene-yne metathesis, but a significant loss of the product was observed due to decomposition on silica gel. To minimize decomposition, MIDA boronates were used as a more chromatographically-stable alternative, allowing for improved yields of the dienyl boronates. Atom economical metatheses were observed with select alkynes, but more challenging alkynes gave efficient ene-yne metathesis by optimal use of both excess alkene and a highly active ruthenium carbene catalysts bearing a CAAC ligand. The resultant 1,3-dienes were then isomerized via a cobalt-catalyzed hydrogen atom transfer reaction, which furnished the 1,3-dienyl-4-boronates with good stereoselectivity. These resulting boron-containing 1,3-dienes successfully underwent further chemical transformations including a [4+2] Diels-Alder cycloaddition and Suzuki-Miyaura cross-couplings to access polyene products. We expect boron-containing dienes to be

useful building blocks for the synthesis of molecules containing polyene structural motifs and foresee further synthetic applications.

Experimental Section

A. General Information. Unless stated otherwise, all reactions were performed in oven-dried glassware equipped with a magnetic stir bar and carried out under a nitrogen atmosphere. CH_2Cl_2, Et_2O and THF were sparged via nitrogen gas and subsequently dried by passage through an activated alumina column while under a nitrogen atmosphere via a solvent purification system. Benzene was sparged similarly and dried by passage through an activated alumina and Q5 column while under a nitrogen atmosphere via a solvent purification system. All reagents used were purchased from commercial vendors and used without further purification, unless noted otherwise. Reactions carried out at -78 °C, 0 °C and temperatures above room temperature were accomplished using a dry ice/acetone, ice water and a mineral oil (up to 80 °C)/sand bath (>80 °C), respectively. Flash column chromatography was carried out on SiliCycle 60 Å (230-400 mesh) silica gel. TLC analysis was performed on glass backed EM Sciences F254 silica plates and were visualized using a UV lamp and/or developed in a potassium permanganate stain.

The Grubbs ruthenium carbene catalysts reported herein were obtained from Umicore and used as received. The cobaloxime catalyst, **Co1**, was prepared following literature procedure.[20] Palladium catalysts were purchased from commercial vendors and used as received. Ene-yne metathesis reactions were terminated by the addition of a methanolic solution of potassium isocyanoacetate (KO_2CCH_2NC). Potassium isocyanoacetate was prepared and used as previously reported (0.20 equiv. in methanol).[36]

^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker Neo-500 MHz spectrometer with the appropriate frequency reported. ^1H and ^{13}C NMR spectra obtained in $CDCl_3$ were internally standardized via the trace solvent signals at 7.26 ppm and 77.16 ppm, respectively. ^1H and ^{13}C NMR spectra obtained in acetone-d_6 were internally standardized via the trace solvent signals at 2.05 ppm and 29.84 ppm, respectively. ^{11}B NMR spectra obtained were standardized by use of BF_3•Et_2O as an external reference set to 0.00 ppm. *E*/*Z* ratios were based on integrations in the ^1H NMR spectra. Carbon signals for the carbon directly bonded to boron are often not observed and therefore unreported in most cases herein. If the carbon signal is observed, typically as a broad singlet (bs), it is noted specifically as such. HRMS data was obtained using either a Bruker SolariXR Fourier transform-ion cyclotron resonance MS (FT-ICRMS) or a Thermo Fisher GC-Orbitrap mass spectrometer.

B. **Preparation of Alkenyl Boronates.** *2-Allyl-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**1b**).* **1b** was prepared using a modified literature procedure.[37] A 3-necked 1 L round bottomed flask was charged with trimethyl borate (29.0 mL, 260 mmol) and Et_2O (300 mL, ca. 0.87 M). The flask was then equipped with a 500 mL addition funnel, which was then charged with freshly prepared allyl magnesium bromide (ca. 0.71 M in Et_2O, 275 mL, 195 mmol). The flask was cooled to -78 °C and the Grignard reagent was added dropwise (ca. 1 h). After complete addition of the Grignard reagent, the flask was then warmed to room temperature and allowed to stir for 2 h; This resulted in a thickly precipitated rection mixture. The flask was cooled to 0 °C and a freshly prepared aqueous HCl solution (3M, 300 mL) was slowly added (ca. 10 min), which resulted in a clear biphasic mixture. The biphasic mixture was allowed to stir at 0 °C for 15 min, followed by stirring at room temperature for 30 min. The mixture was then poured into a 1 L separatory funnel and shaken vigorously. The organic layer was then removed and the aqueous layer was extracted with Et_2O (2 x 75 mL). The organic layers were combined, extracted with brine (200 mL), dried with $MgSO_4$, filtered and concentrated in a 500 mL round bottomed flask for immediate use in the next step. This furnished the crude allylic boronic acid as a clear, faint yellow oil (ca. 13.5 g, 80% crude).

The crude allylic boronic acid (crude; ca. 13.5 g, 155 mmol) was dissolved in a 4:1 mixture of toluene and DMSO (250 mL, ca. 0.63 M). *N*-Methyliminodiacetic acid (23.1 g, 157 mmol) was then added and the flask was equipped with a Dean-Stark trap and a reflux condenser. The reaction mixture was heated to reflux and allowed to stir overnight (ca. 18 h). The reaction mixture was then cooled to room temperature and poured into a 1 L separatory funnel. A 1.5:1 mixture of EtOAc and acetone (200 mL) and a 1:1 mixture of brine and water (200 mL) were added to the separatory funnel, shaken vigorously and the organic layer was removed. The aqueous layer was subsequently extracted with a 1.5:1 mixture of EtOAc and acetone (200 mL), and EtOAc (100 mL). The organic layers were combined and extracted with brine (200 mL). The organic layer was then dried with $MgSO_4$, filtered, and concentrated via rotatory evaporation under high vacuum to afford a crude faint orange solid.

The crude solid was dissolved in a minimal amount of acetone (ca. 150 mL for the first batch) and Et_2O (450 mL; 3 x the volume of acetone) was subsequently added. The mixture was then allowed to stir vigorously for 1 h. Precipitation occurs within 5 min, but was allowed to continue stirring for 1 h. The precipitate was then collected by vacuum filtration and the filtrate was concentrated to repeat this process until precipitation no longer occurred. All portions of collected precipitate were combined to afford **1b** as an off-white powdery solid (18.4 g, 60% with respect to crude boronic acid). Spectral data obtained matches literature reports.[38] ^1H NMR (500 MHz, acetone-d_6, ppm): δ 5.93 – 5.81 (m, 1H), 4.99 (d, J = 17.1 Hz, 1H), 4.89 (d, J = 10.2 Hz, 1H), 4.19 (d, J = 16.9 Hz, 2H), 3.97 (d, J = 16.9 Hz, 2H), 3.13 (s, 3H), 1.64 (d, J = 6.6 Hz, 2H).

*2-(But-3-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**1c**).* **1c** was prepared using a modified literature procedure.[37] A 3-necked 250 mL round bottomed flask was charged with trimethyl borate (5.90 mL, 58.1 mmol) and Et_2O (40 mL, ca. 1.2 M). The flask was then equipped with a 100 mL addition funnel, which was then charged with freshly prepared allyl magnesium bromide (ca. 0.54 M in Et_2O, 55.0 mL, 29.7 mmol). The flask was cooled to -78 °C and the Grignard reagent was added dropwise (ca. 1 h). After complete addition of the Grignard reagent, the flask was then warmed to room temperature and allowed to stir for 2 h; This results in a thickly precipitated rection mixture. The flask was then cooled to 0 °C and freshly prepared aqueous HCl (2M, 75 mL) was slowly added (ca. 5 min), which resulted in a clear biphasic mixture. The biphasic mixture was allowed to stir at 0 °C for 15 min, followed by stirring at room temperature for 30 min. The mixture was then poured into a 500 mL separatory funnel and shaken vigorously. The organic layer was then removed and the aqueous layer was

extracted with Et_2O (2 x 30 mL). The organic layers were combined, extracted with brine (200 mL), dried with $MgSO_4$, filtered and concentrated in a 100 mL round bottomed flask for immediate use in the next step. This furnished the crude homoallylic boronic acid as a white amorphous solid (ca. 2.29 g, 77 % crude).

The crude homoallylic boronic acid (crude; ca. 2.29 g, 22.9 mmol) was dissolved in a 4:1 mixture of toluene and DMSO (50 mL, ca. 0.46 M). *N*-Methyliminodiacetic acid (4.05 g, 27.5 mmol) was then added and the flask was equipped with a Dean-Stark trap and a reflux condenser. The reaction mixture was heated to reflux and allowed to stir overnight (ca. 18 h). The reaction mixture was then cooled to room temperature and poured into a 500 mL separatory funnel. A 1.5:1 mixture of EtOAc and acetone (100 mL) and a 1:1 mixture of brine and water (100 mL) were added to the separatory funnel, shaken vigorously and the organic layer was removed. The aqueous layer was extracted with a 1.5:1 mixture of EtOAc and acetone (100 mL), and EtOAc (50 mL). The organic layers were combined and extracted with brine (100 mL). The organic layer was then dried with $MgSO_4$, filtered, and concentrated via rotatory evaporation under high vacuum to afford an orange oily amorphous solid.

The crude oily solid was dissolved in a minimal amount of acetone (ca. 20 mL for the first batch) and Et_2O (250 mL) was subsequently added. The mixture was then allowed to stir vigorously for 1 h. Precipitation occurs within 5 min, but was allowed to continue stirring for 1 h. The precipitate was then collected by vacuum filtration to afford **1c** as a cream colored powdery solid (3.53 g, 73% with respect to crude boronic acid). Mp = 126 – 128 ˚C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 5.92 (ddt, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.87 – 4.82 (m, 1H), 4.19 (d, *J* = 16.8 Hz, 2H), 4.03 (d, *J* = 16.8 Hz, 2H), 3.10 (s, 3H), 2.13 – 2.06 (m, 2H), 0.75 – 0.68 (m, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.97. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.8, 142.6, 112.9, 62.7, 46.3, 29.2. FT-IR (ATR, cm^{-1}): 3005, 2918, 1718, 1339, 1302, 1025. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_9H_{14}BNNaO_4$ 234.0908; found 234.0906.

C. General Procedure for NMR-Tube Reactions. 1a (50 - 150 µmol), **2** (50 µmol), and mesitylene (1 drop) were added to an oven-dried 1 dram vial and dissolved in C_6D_6 (ca. 0.05M). ^{1}H NMR of the mixture was taken with a 25 s relaxation delay. At t = 0, integration of the terminal alkyne of **2** was set to 1H and the integration for the aromatic protons of mesitylene was noted for subsequent analysis. The catalyst was then added and the NMR tube was heated to 60 ºC for 3 hours. ^{1}H NMR of the reaction mixture with a 25 s relaxation delay was taken and the aromatic protons of mesitylene were integrated to the value observed at t = 0. Conversion and NMR yields were noted with respect to mesitylene.

D. General Procedure for Ene-Yne Metathesis. 1 and **2** were added to a round bottomed flask and dissolved in benzene (ca. 0.10 M) or THF (ca. 0.05 – 0.10 M) while under a nitrogen atmosphere. Upon dissolution, **RuX** (ca. 5 mol %) was added. The flask was then allowed to stir at the designated temperature for the noted period of time. The catalytic reaction was terminated by addition of a methanolic solution of potassium isocyanoacetate followed by an additional 0.5 h of stirring at room temperature. The reaction mixture was then passed through a silica gel pad (2 cm), which was washed using either Et_2O (3 x 10 mL) for derivatives of **1a** or 10% methanol in CH_2Cl_2 solution (3 x 10 mL) for derivatives of **1b** and **1c**. The filtrate was concentrated via rotatory evaporation and the crude residue was purified by flash column chromatography on silica gel to afford **3**. Reported NMR yields of **3** derived from **1b** were obtained by adding mesitylene (0.33 equiv.) after concentrating the filtrate and dissolving the crude mixture with acetone-d_6.

*3-Methylene-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-2-yl benzoate (**3aa**).* **1a** (129 mg, 0.77 mmol), **2a** (131 mg, 0.75 mmol), **Ru1** (32 mg, 38 µmol) and benzene (ca. 0.10 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3aa** after column chromatography (eluent: 4% ethyl acetate in hexanes) as a clear colorless oil with a 3:1 *E*/*Z* ratio (144 mg, 56%). Analytical TLC: R_f = 0.32 (10% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.09 – 8.03 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 6.05 (d, *J* = 16.0 Hz, 0.75H), 5.93 (dt, *J* = 16.0, 7.5 Hz, 0.75H), 5.92 (d, *J* = 11.1 Hz, 0.25 Hz), 5.82 (dt, *J* = 11.1, 8.3 Hz, 0.25H), 5.81 (q, *J* = 6.5 Hz, 0.75H), 5.55 (q, *J* = 6.5 Hz, 0.25H), 5.35 (s, 0.25H), 5.15 (s, 0.75H), 5.10 (s, 0.25H), 5.02 (s, 0.75H), 1.95 – 1.85 (m, 0.5H), 1.77 (d, *J* = 7.4 Hz, 1.5H), 1.52 (d, *J* = 6.5 Hz, 2.25H), 1.43 (d, *J* = 6.5 Hz, 0.75H), 1.23 (s, 3H), 1.21 (s, 9H). ^{11}B (160.5 MHz, $CDCl_3$, ppm): δ 32.83. ^{13}C{^{1}H} (126 MHz, $CDCl_3$, ppm): δ 165.79, 165.77, 146.5, 144.5, 132.90, 132.89, 130.83, 130.80, 129.74, 129.70, 129.3, 128.4, 127.2, 125.6, 113.8, 111.8, 83.45, 83.43, 73.8, 70.9, 24.85, 24.83, 20.5, 19.9, 17.4 (bs, **C**H_2-B), 13.9 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 2979, 2933, 1717, 1326, 1270, 711. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{20}H_{27}BNaO_4$ 365.1895; found 365.1896.

*4,4,5,5-Tetramethyl-2-(4-phenylpenta-2,4-dien-1-yl)-1,3,2-dioxaborolane (**3ab**).* **1a** (130 mg, 0.77 mmol), **2b** (85 µL, 0.77 mmol), **Ru2** (23 mg, 37 µmol) and benzene (ca. 0.10 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3ab** after column chromatography (eluent: 4% ethyl acetate in hexanes) as a clear yellow oil with a 2.5:1 *E*/*Z* ratio (100 mg, 48%). Analytical TLC: R_f = 0.27 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36 – 7.32 (m, 0.56H), 7.27 – 7.15 (m, 4.44H), 6.22 (ddt, *J* = 15.6, 1.9, 1.8 Hz, 0.72H), 6.06 (ddt, *J* = 11.4, 1.6, 1.3 Hz, 0.28H), 5.80 (dt, *J* = 11.4, 8.4 Hz, 0.28H), 5.66 (dt, *J* = 15.5, 7.8 Hz, 0.72H), 5.47 (d, *J* = 1.7, 0.28H), 5.15 – 5.12 (m, 0.28H), 5.07 – 5.05 (m, 0.72H), 1.75 (dd, *J* = 8.4, 1.2 Hz, 0.56H), 1.70 (d, *J* = 7.7 Hz, 1.44H), 1.16 (s, 8.64H), 1.16 (s, 3.36H). ^{11}B (160.5 MHz, $CDCl_3$, ppm): δ 32.84. ^{13}C{^{1}H} (126 MHz, $CDCl_3$, ppm): δ 148.3, 144.32, 141.1, 141.0, 131.9, 129.9, 129.2, 128.8, 128.4, 128.3, 128.1, 127.5, 127.3, 126.7, 114.9, 114.0, 83.41, 83.39, 24.89, 24.88, 17.0 (bs, **C**H_2-B), 13.8 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 2978, 2930, 1324, 1141. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{23}BNaO_2$ 293.1683; found 293.1680.

*6-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-methylenehex-4-en-2-yl benzoate (**3ba**).* **1b** (49 mg, 0.25 mmol), **2a** (44 mg, 0.25 mmol), **Ru1** (11 mg, 13 µmol) and THF (ca. 0.10 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3ba** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white amorphous solid with a 2:1 *E*/*Z* ratio (66 mg, 71%). Analytical TLC: R_f = 0.28 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 8.09 – 8.01 (m, 2H), 7.67 – 7.60 (m, 1H), 7.55 – 7.48 (m, 2H), 6.12 (d *J* = 16.1 Hz, 0.66H), 6.05 (dt, *J* = 16.0, 7.3 Hz,

0.66H), 5.95 (d, J = 11.9 Hz, 0.33H), 5.81 (dt, J = 11.9, 8.1 Hz, 0.33H), 5.80 (q, J = 6.8 Hz, 0.66H), 5.56 (q, J = 6.5 Hz, 0.33H), 5.33 (s, 0.33H), 5.22 (s, 0.33H), 5.15 (s, 0.66H), 5.01 (s, 0.66H), 4.21 (d, J = 16.9 Hz, 1.32H), 4.21 (d, J = 16.9 Hz, 0.66H), 4.02 (dd, J = 17.0, 12.5 Hz, 0.66H), 3.98 (dd, J = 16.9, 5.3 Hz, 1.32H), 3.12 (s, 2H), 3.09 (s, 1H), 1.90 – 1.78 (m, 0.66H), 1.73 (d, J = 7.2 Hz, 1.32H), 1.50 (d, J = 6.5 Hz, 2H), 1.45 (d, J = 6.5 Hz, 1H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.24. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.68, 168.66 (2C), 168.61, 165.86, 165.84, 148.1, 145.9, 133.9 (2C), 132.4, 131.6, 131.5, 130.3, 130.19, 130.15, 129.8, 129.43, 129.41, 126.1, 113.7, 111.6, 74.3, 71.2, 62.9, 62.86, 62.81, 62.8, 46.46, 46.45, 30.3, 30.1, 30.00, 29.7, 29.5, 29.4, 21.00, 20.2. FT-IR (ATR, cm^{-1}): 3007, 2995, 1765, 1714, 1275. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{19}H_{22}BNNaO_6$ 394.1432; found 394.1432.

*6-Methyl-2-(4-phenylpenta-2,4-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**3bb**).* **1b** (991 mg, 5.03 mmol), **2b** (550 µL, 5.01 mmol), **Ru2** (156 mg, 0.25 mmol) and THF (ca. 0.10 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bb** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white amorphous solid with a 1.5:1 *E*/*Z* ratio (1.21 g, 81%). Analytical TLC: R_f = 0.20 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.47 – 7.42 (m, 0.8H), 7.36 – 7.25 (m, 4.2H), 6.34 (d, J = 15.7 Hz, 0.6H), 6.16 – 6.10 (m, 0.4H), 6.87 (dt, J = 11.5, 8.2 Hz, 0.4H), 5.75 (dt, J = 15.6, 7.8 Hz, 0.6H), 5.56 (d, J = 1.8 Hz, 0.4H), 5.31 – 5.30 (m, 0.4H), 5.13 (d, J = 1.7 Hz, 0.6H), 4.98 (d, J = 1.9 Hz, 0.6H), 4.21 (d, J = 16.8 Hz, 1.2H), 4.20 (d, J = 16.9 Hz, 0.8H), 3.99 (d, J = 16.9 Hz, 0.8H), 3.98 (d, J = 16.8 Hz, 1.2H), 3.14 (s, 1.8H), 3.03 (s, 1.2H), 1.74 – 1.67 (m, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.24. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.63, 168.57, 149.5, 145.4, 141.9, 141.7, 132.8, 132.7, 131.9, 129.2, 129.1, 128.94, 128.88, 128.3, 128.2, 127.4, 115.3, 113.7, 62.90, 62.86, 46.5, 46.4. FT-IR (ATR, cm^{-1}): 3013, 2957, 1766, 1300. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{18}BNNaO_4$ 322.1227; found 322.1221.

*5-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-methylenepent-3-en-1-yl benzoate (**3bc**).* **1b** (148 mg, 0.75 mmol), **2c** (41 mg, 0.25 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bc** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white amorphous solid with a 1.5:1 *E*/*Z* ratio (66 mg, 73%). Analytical TLC: R_f = 0.20 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 8.08 – 8.02 (m, 2H), 7.67 – 7.61 (m, 1H), 7.56 – 7.48 (m, 2H), 6.19 (d, J = 16.1 Hz, 0.6H), 6.01 (dt, J = 16.1, 7.7 Hz, 0.6H), 5.91 (d, J = 11.7 Hz, 0.4H), 5.78 (dt, J = 11.8, 8.2 Hz, 0.4H), 5.37 – 5.34 (m, 0.4H), 5.29 (s, 0.4H), 5.17 (s, 0.6H), 5.10 (s, 0.6H), 5.00 (s, 1.2H), 4.88 (s, 0.8H), 4.22 (d, J = 16.9 Hz, 0.8H), 4.20 (d, J = 16.8 Hz, 1.2H), 4.03 (d, J = 16.9 Hz, 0.8H), 3.98 (d, J = 16.8 Hz, 1.2H), 3.13 (s, 1.8H), 3.11 (s, J = 1.2H), 1.86 (d, J = 8.1 Hz, 0.8H), 1.73 (d, J = 7.6 Hz, 1.2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.26. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.69, 168.67, 166.40, 166.37, 142.1, 141.4, 133.96, 133.92, 132.0, 131.1, 130.8, 130.24, 130.19 (2C), 123.0, 129.5 (2C), 127.0, 115.9, 114.7, 67.8, 65.1, 62.88, 62.83, 46.47, 46.44, 22.5 (bs, CH_2-B), 18.8 (bs, CH_2-B). FT-IR (ATR, cm^{-1}): 3009, 2959, 1760, 1717, 1274. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{20}BNNaO_6$ 380.1276; found 380.1277.

*5-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-methylene-1-phenylpent-3-en-1-yl acetate (**3bd**).* **1b** (297 mg, 1.50 mmol), **2d** (87 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bd** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white crystalline solid with a 2:1 *E*/*Z* ratio (168 mg, 91%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). Mp = 54 – 55 ˚C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.44 – 7.27 (m, 5H), 6.51 (s, 0.66H), 6.22 (s, 0.33H), 6.05 (d, J = 16.1 Hz, 0.66H), 5.83 (dt, J = 16.1, 7.8 Hz, 0.66H), 5.74 – 5.67 (m, 0.66H), 5.40 (s, 0.33H), 5.31 (2, 0.33H), 5.20 (s, 0.66H), 5.18 (s, 0.66H), 4.17 (d, J = 16.8 Hz, 0.66H), 4.04 (d, J = 16.8 Hz, 1.32H), 3.93 (d, J = 16.9 Hz, 0.33H), 3.92 (d, J = 16.9 Hz, 0.33H), 3.57 (d, J = 16.9 Hz, 0.66H), 3.52 (d, J = 16.9 Hz, 0.66H), 2.89 (s, 1H), 2.83 (s, 2H), 2.10 (s, 1H), 2.07 (s, 2H), 1.87 – 1.68 (m, 0.66H), 1.66 – 1.56 (m, 1.32H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 17.28. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.95, 169.93, 168.67, 168.66, 168.47, 168.43, 145.4, 144.3, 140.0, 139.8, 132.4, 130.7, 130.4, 129.4, 129.1, 128.9, 128.7, 128.4, 128.0, 126.2, 114.8, 113.5, 78.5, 75.5, 62.71, 62.70, 46.3, 46.1, 22.4 (bs, **C**H_2-B), 21.0, 21.0, 18.5 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 3010, 2957, 1748, 1297, 1236, 1025. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{19}H_{22}BNNaO_6$ 394.1432; found 394.1434.

2 mmol scale synthesis of 3bd Allyl boronate **1b** (1.18 g, 5.99 mmol), **2d** (348 mg, 2.00 mmol), **Ru3** (63 mg, 0.10 mmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bd** after column chromatography (eluent: 1-3% MeOH in CH_2Cl_2) as an off-white crystalline solid with a 2:1 *E*/*Z* ratio (641 mg, 84%). Spectral data matches the previously synthesized product.

*2-(4-(((tert-Butyldimethylsilyl)oxy)methyl)penta-2,4-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3be**).* **1b** (148 mg, 0.75 mmol), **2e** (41 mg, 0.24 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. This furnished diene **3be** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white amorphous solid with a 1.5:1 *E*/*Z* ratio (34 mg, 39%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.10 (d, J = 16.2 Hz, 0.6H), 5.80 (dt, J = 16.1, 7.8 Hz, 0.6H), 5.78 (d, J = 11.8 Hz, 0.4H), 5.80 – 5.75 (m, 0.4H), 5.30 – 5.27 (m, 0.4H), 5.14 – 5.10 (m, 1H), 4.91 (s, 0.6H), 4.35 – 4.32 (m, 1.2H), 4.21 (d, J = 16.9 Hz, 0.8H), 4.20 (d, J = 16.8 Hz, 1.2H), 4.20 – 4.18 (m, 0.8H), 4.01 (d, J = 16.8 Hz, 0.8H), 3.97 (d, J = 16.8 Hz, 1.2H), 3.12 (s, 1.8H), 3.11 (s, 1.2H), 1.82 (d, J = 8.1 Hz, 0.8H), 1.67 (d, J = 7.7 Hz, 1.2H), 0.92 (s, 9H), 0.09 (s, 3.6H), 0.09 (s, 2.4H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.22. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.64, 168.62, 146.2, 145.8, 131.2, 130.8, 128.1, 127.5, 112.3, 111.4, 66.5, 63.6, 62.88, 62.85, 46.40, 46.38, 26.3 (2C), 18.92, 18.89, -5.18, -5.22. FT-IR (ATR, cm^{-1}): 3009, 2955, 2929, 2886, 2857, 1748, 1102, 835. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{17}H_{30}BNNaO_5Si$ 390.1884; found 390.1882.

2-(6-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3bf**). **1b** (296 mg, 1.50 mmol), **2f** (92 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. This furnished diene **3bf** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as

a white amorphous solid with a 2:1 *E*/*Z* ratio (109 mg, 57%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.08 (d, *J* = 15.8 Hz, 0.66H), 5.83 (dt, *J* = 15.8, 7.7 Hz, 0.66H), 5.82 – 5.78 (m, 0.33H), 5.61 (dt, *J* = 11.7, 8.2 Hz, 0.33H), 5.06 (s, 0.33H), 5.02 (s, 0.33H), 4.88 – 4.87 (m, 0.66H), 4.84 (s, 0.66H), 4.20 (d, *J* = 16.8 Hz, 1.32H), 4.20 (d, *J* = 16.8 Hz, 0.66H), 4.00 (d, *J* = 16.8 Hz, 0.66H), 3.96 (d, *J* = 16.8 Hz, 1.32H), 3.73 (t, *J* = 7.1 Hz, 1.32H), 3.71 (t, *J* = 7.0 Hz, 0.66H), 3.12 (s, 2H), 3.09 (s, 1H), 2.42 (t, *J* = 7.2 Hz, 1.32H), 2.33 (t, *J* = 7.0 Hz, 0.66H), 1.81 (d, *J* = 8.1 Hz, 0.66H), 1.68 (d, *J* = 7.7 Hz, 1.32H), 0.89 (s, 6H), 0.89 (s, 3H), 0.06 (s, 4H), 0.05 (s, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.26. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.64, 168.60, 144.2, 143.2, 133.4, 130.3, 129.6, 128.3, 115.3, 114.1, 62.95, 62.88, 62.81, 62.77, 46.36, 46.34, 41.6, 36.6, 26.27, 26.26, 22.3 (bs, **C**H_2-B), 18.74, 18.73(bs, **C**H_2-B), 18.4, -5.10, -5.13. FT-IR (ATR, cm^{-1}): 2954, 2929, 2886, 2857, 1750, 1098. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{32}BNNaO_5Si$ 404.2035; found 404.2039.

*tert-Butyl-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-methylenepent-3-en-1-yl)(tosyl)carbamate (**3bg**).* **1b** (298 mg, 1.51 mmol), **2g** (155 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. This furnished diene **3bg** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as a white crystalline solid with a 1.5:1 *E*/*Z* ratio (217 mg, 86%). Analytical TLC: R_f = 0.13 (5% MeOH in CH_2Cl_2). Mp = 85 – 86 ˚C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.90 – 7.83 (m, 2H), 7.47 – 7.41 (m, 2H), 6.19 (d, *J* = 16.1 Hz, 0.6H), 5.93 (dt, *J* = 16.1, 7.7 Hz, 0.6H), 5.85 (d, *J* = 11.7 Hz, 0.4H), 5.75 (dt, *J* = 11.7, 8.1 Hz, 0.4H), 5.21 (s, 0.4H), 5.17 (s, 0.4H), 4.99 (s, 0.6H), 4.92 (s, 0.6H), 4.65 (s, 1.2H), 4.50 (s, 0.8H), 4.22 (d, *J* = 16.9 Hz, 0.8H), 4.22 (d, *J* = 16.8 Hz, 1.2H), 4.02 (d, *J* = 16.9 Hz, 0.8H), 4.00 (d, *J* = 16.8 Hz, 1.2H), 3.14 (s, 1.8H), 3.11 (s, 1.2H), 2.45 (s, 1.8H), 2.44 (s, 1.2H), 1.85 (d, *J* = 8.0 Hz, 0.8H), 1.73 (d, *J* = 7.6 Hz, 1.2H), 1.33 (s, 3.6H), 1.31 (s, 5.4H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.26. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.68, 168.64, 151.51, 151.48, 145.25, 145.24, 142.8, 142.1, 138.45, 138.43, 132.1, 131.5, 130.10, 130.09, 129.00, 128.95, 128.93, 127.3, 113.8, 111.6, 84.47, 84.40, 62.88, 62.83, 51.9, 48.8, 46.54, 46.46, 27.95, 27.92, 22.7(bs, **C**H_2-B), 21.5 (2C), 18.79 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 3004, 2981, 2973, 1762, 1729, 1290, 1250, 1155. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{23}H_{31}BN_2NaO_8S$ 529.1786; found 529.1793.

*2-(6-(1,3-Dioxoisoindolin-2-yl)-4-methylenehex-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3bh**).* **1b** (296 mg, 1.50 mmol), **2h** (99 mg, 0.50 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. This furnished diene **3bh** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as a white crystalline solid with a 2.7:1 *E*/*Z* ratio (141 mg, 71%). Analytical TLC: R_f = 0.25 (5% MeOH in CH_2Cl_2). Mp = 70 ˚C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.87 – 7.78 (m, 4H), 6.09 (d, *J* = 15.9 Hz, 0.73H), 5.99 (dt, *J* = 15.9, 7.6 Hz, 0.73H), 5.87 (d, *J* = 11.7 Hz, 0.27H), 5.67 (dt, *J* = 11.7, 8.2 Hz, 0.27H), 5.05 (s, 0.27H), 5.00 (s, 0.27H), 4.84 – 4.80 (m, 0.73H), 4.76 (s, 0.73H), 4.24 (d, *J* = 16.9 Hz, 1.46H), 4.24 (d, *J* = 16.9 Hz, 0.54H), 4.10 (d, *J* = 16.9 Hz, 1.46H), 4.05 (d, *J* = 16.8 Hz, 0.54H), 3.78 – 3.73 (m, 2H), 3.22 (s, 2.19H), 3.13 (s, 0.82H), 2.60 (t, *J* = 7.2 Hz, 1.46H), 2.53 (t, *J* = 7.4 Hz, 0.54H), 1.82 (d, *J* = 8.0 Hz, 0.54H), 1.74 (d, *J* = 7.5 Hz, 1.46H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.33. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.73, 168.70, 168.69, 168.65, 144.2, 143.3, 134.98, 134.95, 133.09, 133.06, 132.7, 130.6, 129.5, 129.0, 123.72, 123.68, 116.1, 114.8, 63.1, 62.9, 46.56, 46.48, 37.81, 37.76, 36.4, 31.8, 22.4 (bs, **C**H_2-B), 18.5 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 3008, 2955, 1767, 1709. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{20}H_{21}BN_2NaO_6$ 419.1385; found 419.1390.

*7-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-methylene-1-phenylhept-5-en-3-yl acetate (**3bi**).* **1b** (296 mg, 1.50 mmol), **2i** (102 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bi** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as a white amorphous solid with a 2.3:1 *E*/*Z* ratio (126 mg, 63%). Analytical TLC: R_f = 0.13 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.33 – 7.25 (m, 2H), 7.25 – 7.19 (m, 2H), 7.19 – 7.14 (m, 1H), 6.05 (d, *J* = 16.1 Hz, 0.7H), 5.90 (dt, *J* = 16.1, 7.7 Hz, 0.7H), 5.85 (d, *J* = 11.7 Hz, 0.3H), 5.80 (ddd, *J* = 11.7, 7.9, 7.6 Hz, 0.3H), 5.43 (dd, *J* = 8.2, 4.5 Hz, 0.7H), 5.24 – 5.20 (m, 0.3H), 5.22 (s, 0.7H), 5.01 (s, 0.7H), 4.99 (s, 0.7H), 4.21 (d, *J* = 16.9, 0.6H), 4.21 (d, *J* = 16.9 Hz, 1.4H), 4.02 (dd, *J* = 16.9, 6.7 Hz, 0.6H), 3.96 (dd, *J* = 16.9, 10.8 Hz, 1.4H), 3.10 (s, 2.1H), 3.09 (s, 0.9H), 2.73 – 2.58 (m, 2H), 2.04 (s, 2.1H), 2.04 (s, 0.9H), 2.03 – 1.90 (m, 2H), 1.87 – 1.76 (m, 0.6H), 1.68 (d, *J* = 7.7 Hz, 1.4H), ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.29. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 170.30, 170.25, 168.68, 168.67, 168.64, 168.60, 146.8, 144.6, 142.5, 142.3, 132.3, 130.3, 129.6, 129.26, 129.21, 129.19, 129.15, 126.65, 126.62, 126.1, 114.5, 112.0, 76.6, 73.4, 62.87, 62.83, 62.78, 62.75, 46.44, 46.36, 36.8, 36.0, 32.5, 32.3, 22.6 (bs, **C**H_2-B), 21.04, 21.01, 18.60 (bs, **C**H_2-B). FT-IR (ATR, cm^{-1}): 3025, 2955, 1745, 1242, 1024. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{26}BNNaO_6$ 422.1745; found 422.1754.

*2-(5-((tert-Butyldimethylsilyl)oxy)-4-methylenehex-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3bj**).* **1b** (178 mg, 0.90 mmol), **2j** (54 mg, 0.29 mmol), **Ru3** (10 mg, 16 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bj** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as a white amorphous solid with a 2:1 *E*/*Z* ratio (58 mg, 52%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.05 (d, *J* = 16.0 Hz, 0.66H), 5.90 (dt, *J* = 16.0, 7.7 Hz, 0.66H), 5.87 – 5.82 (m, 0.33H), 5.73 (dt, *J* = 11.8, 8.0 Hz, 0.33H), 5.27 – 5.22 (m, 0.33H), 5.08 (bs, 1H), 4.88 (d, *J* = 2.2 Hz), 4.58 (q, *J* = 6.3 Hz, 0.66H), 4.32 (q, *J* = 6.3 Hz, 0.33H), 4.21 (d, *J* = 16.9 Hz, 2H), 4.03 (dd, *J* = 16.9, 5.9 Hz, 0.66H), 3.95 (dd, *J* = 16.9, 6.5 Hz, 1.32H), 3.12 (s, 2H), 3.11 (s, 1H), 1.87 – 1.72 (m, 0.66H), 1.68 (d, *J* = 7.6 Hz, 1.32H), 0.91 (s, 3H), 0.90 (s, 6H), 0.08 (s, 1H), 0.07 (s, 2H), 0.05 (s, 1H), 0.04 (s, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.22. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.65, 168.64, 168.59, 168.56, 152.0, 149.9, 131.0, 130.7, 128.7, 127.0, 111.6, 110.2, 72.6, 69.6, 62.88, 62.87, 62.83, 62.82, 46.42, 26.24, 26.23, 25.44, 24.4, 18.79, 18.76, -4.63, -4.71, -4.77, -4.79. FT-IR (ATR, cm^{-1}): 2958, 2929, 2857, 1765, 1253, 1005. HRMS (ESI – FT-ICRMS) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{32}BNNaO_5Si$ 404.2040; found 404.2041.

2-((6E)-5-((tert-Butyldimethylsilyl)oxy)-4-methylene-7-phenylhepta-2,6-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3bk**). **1b** (147 mg, 0.75 mmol), **2k** (70 mg, 0.26 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3bk** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange amorphous solid with a 2:1 E/Z ratio (104 mg, 86%). Analytical TLC: R_f = 0.29 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.39 – 7.35 (m, 1.32H), 7.35 – 7.29 (m, 2.66H), 7.25 – 7.21 (m, 1H), 6.54 (d, J = 15.9 Hz, 0.66H), 6.52 (d, J = 15.9 Hz, 0.33H), 6.16 (dd, J = 15.9, 5.8 Hz, 0.66H), 6.07 (dd, J = 15.9, 6.2 Hz, 0.33H), 6.01 (d, J = 16.1 Hz, 0.66H), 5.95 (dt, J = 16.1, 6.9 Hz, 0.66H), 5.90 (d, J = 12.1 Hz, 0.33H), 5.71 – 5.63 (m, 0.33H), 3.68 – 3.50 (m, 2H), 3.47 (d, J = 16.4 Hz, 0.33H), 3.46 (d, J = 16.4 Hz, 0.66H), 3.43 (d, J = 16.3 Hz, 0.33H), 3.40 (d, J = 16.4 Hz, 0.66H), 2.71 (s, 2H), 2.58 (s, 1H), 1.87 (d, J = 7.3 Hz, 0.66H), 1.79 – 1.65 (m, 1.32H), 0.93 (s, 3H), 0.92 (s, 6H), 0.09 (s, 2H), 0.08 (s, 2H), 0.08 (s, 2H). ^{11}B (160.5 MHz, $CDCl_3$, ppm): δ 12.67. ^{13}C{^{1}H} (126 MHz, $CDCl_3$, ppm): δ 166.73, 166.72, 166.66, 166.61, 147.4, 146.0, 136.9, 136.7, 133.0, 132.3, 130.4, 122.5, 129.3, 129.2, 128.92, 128.89, 127.91, 127.86, 127.0, 126.6, 126.4, 113.4, 112.9, 76.9, 74.6, 62.3, 62.2, 62.13, 62.06, 45.34, 45.25, 26.0, 25.8, 18.5, -4.54, -4.58, -4.63, -4.66. FT-IR (ATR, cm^{-1}): 3024, 2955, 2929, 2886, 2857, 1764, 1251. HRMS (ESI – FT-ICRMS) m/z: [M + Na]$^+$ calcd for $C_{25}H_{36}BNNaO_5Si$ 492.2348; found 492.2352.

*(E)-6-Methyl-2-(4-(trimethylsilyl)penta-2,4-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**3bl**).* **1b** (302 mg, 1.53 mmol), **2l** (72.5 µL, 0.51 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h, except with a thick walled, PTFE lined reaction tube as the reaction vessel to prevent evaporation of **2l**. This furnished diene **3bl** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as white crystalline solid as solely the *E*-isomer (87 mg, 58%). Analytical TLC: R_f = 0.29 (5% MeOH in CH_2Cl_2). Mp = 136 ˚C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.19 (d, *J* = 15.9 Hz, 1H), 5.84 (dt, *J* = 15.9, 7.7 Hz, 1H), 5.56 (d, *J* = 3.4 Hz, 1H), 5.26 (d, *J* = 3.4 Hz, 1H), 4.21 (d, *J* = 16.8 Hz, 2H), 3.94 (d, *J* = 16.9 Hz, 2H), 3.11 (s, 3H), 1.69 (d, *J* = 7.6 Hz, 2H), 0.15 (9H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.21. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.6, 150.1, 136.4, 131.0, 125.6, 62.9, 46.4, 22.7 (bs, **C**H_2-B), -0.7. FT-IR (ATR, cm^{-1}): 3001, 2952, 1760, 1736, 1248, 1086. HRMS (ESI – FT-ICRMS) *m/z*: [M + Na]$^+$ calcd for $C_{13}H_{22}BNNaO_4Si$ 318.1303; found 318.1306.

*6-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-methylene-1-phenylhex-3-en-1-yl acetate (**3cd**).* **1c** (318 mg, 1.51 mmol), **2d** (87 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3cd** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as an orange oil with a 1.5:1 *E*/*Z* ratio (98 mg, 51%). Analytical TLC: R_f = 0.21 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.44 – 7.41 (m, 1H), 7.44 – 7.30 (m, 3H), 7.33 – 7.27 (m, 1H), 6.50 (s, 0.6H), 6.21 (s, 0.4H), 6.04 (d, *J* = 16.0 Hz, 0.6H), 5.90 (dt, *J* = 16.0, 6.7 Hz, 0.6H), 5.67 – 5.59 (m, 0.8H), 5.40 (s, 0.4H), 5.21 (s, 0.6H), 5.19 (s, 0.6H), 5.13 (s, 0.4H), 4.17 (d, *J* = 16.8 Hz, 0.8H), 4.17 (d, *J* = 16.9 Hz, 1.2H), 3.99 (d, *J* = 16.9 Hz, 0.8H), 3.99 (d, *J* = 16.9 Hz, 1.2H), 3.04 (s, 1.8H), 3.04 (s, 1.2H), 2.25 – 2.18 (m, 0.8H), 2.11 – 2.06 (m, 1.2H), 2.09 (s, 1.2H), 2.07 (s, 1.8H), 0.69 – 0.63 (m, 1.2H), 0.63 – 0.56 (m, 0.8H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.92. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.9, 168.77, 168.76, 168.75, 145.7, 144.4, 139.9, 139.8, 138.6, 135.9, 129.16, 129.12, 128.8, 128.7, 128.47, 128.2, 128.0, 125.1, 114.8, 113.9, 78.2, 75.4, 62.67, 62.65, 4628, 46.27, 28.5, 24.2, 21.0 (2C). FT-IR (ATR, cm^{-1}): 3014, 2936, 2890, 1745, 1238, 1025. HRMS (ESI – FT-ICRMS) *m/z*: [M + Na]$^+$ calcd for $C_{20}H_{24}BNNaO_6$ 408.1589; found 408.1588.

*2-(7-((tert-Butyldimethylsilyl)oxy)-5-methylenehept-3-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3cf**).* **1c** (317 mg, 1.50 mmol), **2f** (93 mg, 0.50 mmol), **Ru3** (16 mg, 26 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. This furnished diene **3cf** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as an orange oil with a 1.2:1 *E*/*Z* ratio (115 mg, 58%). Analytical TLC: R_f = 0.29 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.07 (d, *J* = 15.8 Hz, 0.55H), 5.86 (dt, *J* = 15.7, 6.7 Hz, 0.55H), 5.74 (d, *J* = 11.7 Hz, 0.45H), 5.57 (dt, *J* = 11.7, 7.3 Hz, 0.45H), 5.02 (d, *J* = 0.45H), 4.92 (bs, 1H), 4.88 (s, 0.55H), 4.18 (d, *J* = 16.9 Hz, 1.1H), 4.17 (d, *J* = 16.9 Hz, 0.9H), 4.02 (d, *J* = 16.9 Hz, 1.1H), 4.00 (d, *J* = 16.9 Hz, 0.9H), 3.75 (t, *J* = 7.1 Hz, 1.1H), 3.70 (t, *J* = 7.0 Hz, 0.9H), 3.10 (s, 1.65H), 3.09 (s, 1.35H), 2.43 (t, *J* = 7.1 Hz, 1.1H), 2.33 – 2.26 (m, 0.9H), 2.31 (t, *J* = 7.0 Hz, 0.9H), 2.20 – 2.13 (m, 1.1H), 0.89 (s, 4.95H), 0.89 (s, 4.05H), 0.77 – 0.70 (m, 2H), 0.05 (s, 2.7H), 0.05 (s, 3.3H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.93. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.77, 168.75, 144.1, 143.3, 136.2, 133.9, 131.3, 129.0, 115.3, 114.8, 63.0, 62.9, 62.62, 62.58, 46.24, 46.22, 41.6, 36.7, 28.2, 26.3 (2C), 24.2, 18.75, 18.74, 17.4 (bs, **C**H_2-B), 16.6 (bs, **C**H_2-B), -5.11, -5.14. FT-IR (ATR, cm^{-1}): 2999, 2954, 2929, 2896, 2858, 1761, 1743, 1095. HRMS (ESI – FT-ICRMS) *m/z*: [M + Na]$^+$ calcd for $C_{19}H_{34}BNNaO_5Si$ 418.2192; found 418.2194.

*tert-Butyl (6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-methylenehex-3-en-1-yl)(tosyl)carbamate (**3cg**).* **1c** (159 mg, 0.75 mmol), **2g** (77 mg, 0.50 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at room temperature for 1 h. **3cg** was observed in 93% NMR yield with a 1.3:1 *E*/*Z* ratio. **(*E*)-3cg** overlaps with **1c** via TLC and required three chromatographic (eluent: 1-2% MeOH in CH_2Cl_2) attempts isolate a sufficiently pure sample of **3cg** as a white amorphous solid with a 1:1.5 *E*/*Z* ratio (87 mg, 67%). Analytical TLC: R_f = 0.26 (*Z*) and 0.23 (*E*) (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.90 – 7.83 (m, 2H), 7.47 – 7.42 (m, 2H), 6.19 (d, *J* = 16.1 Hz, 0.4H), 5.96 (dt, *J* = 16.1, 6.6 Hz, 0.4H), 5.78 (d, *J* = 11.8 Hz, 0.6H), 5.71 (dt, *J* = 11.7, 7.2 Hz, 0.6H), 5.15 (s, 0.6H), 5.06 (s, 0.6H), 5.04 (s, 0.6H), 4.94 (s, 0.4H), 4.66 (s, 0.8H), 4.49 (s, 1.2H), 4.21 (d, *J* = 16.8 Hz, 0.8H), 4.20 (d, *J* = 16.8 Hz, 1.2H), 4.04 (d, *J* = 16.9 Hz, 0.8H), 4.03 (d, *J* = 16.9 Hz, 1.2H), 3.12 (s, 1.2H), 3.11 (s, 1.8H), 2.45 (s, 1.2H), 2.45 (s,1.8H), 2.36 – 2.99 (m 1.2H), 2.22 – 2.15 (m, 0.8H), 1.34 (s, 5.4H), 1.32 (s, 3.6H), 0.80 – 0.74 (m, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.90. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.8 (2C), 151.53, 151.51, 145.31, 145.25, 142.6, 142.3, 138.48, 138.42, 138.2, 134.5, 130.1 (2C), 129.3, 129.02, 128.98, 126.3, 114.0, 112.2, 84.47, 84.43, 62.71, 62.68, 51.7, 48.9, 46.33, 46.32, 28.6, 17.97, 27.93, 24.5, 21.5 (2C). FT-IR (ATR, cm^{-1}): 3003, 2982, 2927, 1756, 1728, 1152.

HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{33}BN_2NaO_8S$ 543.1943; found 543.1947.

2-((7E)-6-((tert-Butyldimethylsilyl)oxy)-5-methylene-8-phenylocta-3,7-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3ck**). **1c** (158 mg, 0.75 mmol), **2k** (67 mg, 0.25 mmol), **Ru3** (8 mg, 13 µmol) and THF (ca. 0.05 M) were used in following the general procedure at 60 ºC for 3 h. This furnished diene **3ck** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange oil with a 1.2:1 E/Z ratio (90 mg, 76%). Analytical TLC: R_f = 0.23 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.45 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 6.70 (d, J = 15.8 Hz, 0.55H), 6.64 (d, J = 15.9 Hz, 0.45H), 6.30 (dd, J = 15.8, 5.9 Hz, 0.55H), 6.22 (dd, J = 15.9, 6.0 Hz, 0.45H), 6.15 (dt, J = 16.0, 6.5 Hz, 0.55H), 6.06 (d, J = 16.1 Hz, 0.55H), 5.83 (d, J = 11.7 Hz, 0.45H), 5.69 (dt, J = 11.7, 7.2 Hz, 0.45H), 5.39 (s, 0.45H), 5.23 (s, 0.55H), 5.10 (d, J = 5.9 Hz, 0.55H), 5.06 (s, 0.55H), 5.03 (s, 0.45H), 4.85 (d, J = 5.9 Hz, 0.45H), 4.18 (d, J = 16.8 Hz, 0.9H), 4.16 (d, J = 16.9 Hz, 1.1H), 4.00 (d, J = 16.8 Hz, 1.1H), 3.95 (d, J = 16.9 Hz, 0.9H), 3.06 (s, 1.65H), 2.99 (s, 1.35H), 2.30 (dt, J = 8.1, 7.4 Hz, 0.9H), 2.16 (dt, J = 9.4, 6.7 Hz, 1.1H), 0.95 (s, 9H), 0.77 – 0.71 (m, 1.1H), 0.71 – 0.66 (m, 0.9H), 0.13 – 0.09 (m, 6H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.95. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 168.76, 168.73, 149.2, 147.6, 138.02, 137.97, 137.8, 135.2, 133.0, 132.7, 130.08, 130.03, 129.42, 129.38, 128.20, 128.17, 128.0, 127.25, 127.21, 125.5, 113.1, 112.0, 77.6, 74.9, 62.7, 62.6, 46.2, 46.2, 28.7, 26.3, 24.4, 18.9, 17.4 (bs, **C**H_2-B), 16.6 (bs, **C**H_2-B), -4.48, -4.58, -4.62. FT-IR (ATR, cm^{-1}): 3024, 2955, 2929, 2856, 1762. HRMS (ESI – FT-ICRMS) m/z: $[M + Na]^+$ calcd for $C_{26}H_{38}BNNaO_5Si$ 506.2505; found 506.2508.

E. General Procedure for Dienyl Isomerization. 3 was added to either a 1 dram or 20 mL scintillation vial, which was brought into a nitrogen filled glovebox and subsequently dissolved in THF (ca. 0.16M). **Co1** (ca. 10 mol %) and phenylsilane (ca. 10 mol %) were then added and the vial was allowed to stir at 60 ºC for 3 h. The reaction was then cooled to room temperature, brought out of the glovebox and filtered through a 0.45 µm PTFE membrane. The filtrate was concentrated via rotatory evaporation and the crude residue was purified by flash column chromatography on silica gel to furnish **4**.

*3-Methyl-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hexa-3,5-dien-2-yl benzoate (**4ba**).* **3ba** (61 mg, 0.16 mmol), **Co1** (7.0 mg, 17 µmol) and phenylsilane (2.0 µl, 16 µmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4ba** after column chromatography (eluent: 4% MeOH in CH_2Cl_2) as a white amorphous solid with a 5.7:1 *EE*/*EZ* ratio (60 mg, 98%). Analytical TLC: R_f = 0.24 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 8.08 – 8.01 (m, 2H), 7.67 – 7.61 (m, 1H), 7.55 – 7.48 (m, 2H), 7.09 (dd, *J* = 17.2, 11.0 Hz, 0.15H), 6.87 (dd, *J* = 17.3, 10.7 Hz, 0.85H), 6.25 (d, *J* = 10.8 Hz, 0.85H), 6.12 (q, *J* = 6.6 Hz, 0.15H), 6.01 (d, *J* = 11 Hz, 0.15H), 5.73 (d, *J* = 17.3 Hz, 0.85H), 5.64 (d, *J* = 17.2 Hz, 0.15H), 5.54 (q, *J* = 6.6 Hz, 0.85H), 4.24 – 4.17 (m, 2H), 4.04 (d, *J* = 17.0 Hz, 1.7H), 3.99 (d, *J* = 16.9 Hz, 0.3H), 2.99 (s, 2.55H), 2.97 (s, 0.45H), 1.90 (s, 2.55H), 1.89 (s, 0.45H), 1.47 (d, *J* = 6.6 Hz, 0.45H), 1.46 (d, *J* = 6.6 Hz, 2.55H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.76. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.10, 169.07, 169.04, 169.01, 165.84, 165.82, 138.45, 138.37, 138.2, 137.9, 133.86, 133.85, 131.6, 131.5, 130.18, 130.16, 129.44, 129.42, 129.0 (2C), 76.1, 70.6, 62.36, 62.33, 62.32, 62.30, 47.43, 47.38, 19.46, 19.40, 18.8, 13.0. FT-IR (ATR, cm^{-1}): 2951, 2923, 2854, 1763, 1711, 1272, 1026. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{22}BNNaO_6$ 394.1432; found 394.1432.

*6-Methyl-2-(4-phenylpenta-1,3-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4bb**).* **3bb** (49 mg, 0.16 mmol), **Co1** (7.0 mg, 17 µmol) and phenylsilane (2.0 µl, 16 µmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bb** after column chromatography (eluent: 4% MeOH in CH_2Cl_2) as a white solid with a 5.7:1 *EE*/*EZ* ratio (60 mg, 98%). Analytical TLC: R_f = 0.24 (5% MeOH in CH_2Cl_2). Mp = 161 – 163 °C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.53 – 7.48 (m, 1.7H), 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1.3H), 7.05 (dd, *J* = 17.2, 10.8 Hz, 0.85H), 6.69 (dd, *J* = 17.3, 10.8 Hz, 0.15H), 6.58 (d, *J* = 10.8 Hz, 0.85H), 6.24 (d, *J* = 10.8 Hz, 0.15H), 5.84 (d, *J* = 17.2 Hz, 0.85H), 5.67 (d, *J* = 17.3 Hz, 0.15H), 4.23 (d, *J* = 16.9 Hz, 1.7H), 4.16 (d, *J* = 16.9 Hz, 0.3H), 4.06 (d, *J* = 16.9 Hz, 1.7H), 3.97 (d, *J* = 16.9 Hz, 0.3H), 3.04 (s, 2.55H), 2.98 (s, 0.45H), 2.20 (s, 2.55H), 2.12 (s, 0.45H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.76. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.1, 169.0, 143.8, 142.2, 140.4, 140.0, 139.5, 137.3, 130.6, 130.1, 129.2, 129.1, 129.0, 128.1, 128.0, 126.4, 62.4, 62.3, 47.5, 47.3, 25.6, 16.1. FT-IR (ATR, cm^{-1}): 3018, 2957, 2930, 2856, 1762, 1748, 1288. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{18}BNNaO_4$ 322.1221; found 322.1222.

*2-Methyl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylpenta-2,4-dien-1-yl acetate (**4bd**).* **3bd** (92 mg, 0.25 mmol), **Co1** (11 mg, 26 µmol) and phenylsilane (3.1 µl, 25 µmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bd** after column chromatography (eluent: 2 – 3% MeOH in CH_2Cl_2) as an orange solid with a 5.7:1 *EE*/*EZ* ratio (75 mg, 81%). Analytical TLC: R_f = 0.18 (5% MeOH in CH_2Cl_2). Mp = 87 – 88 °C. ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.41 – 7.28 (m, 5H), 7.24 (dd, *J* = 17.2, 10.9 Hz, 0.15H), 6.93 (s, 0.15H), 6.86 (dd, *J* = 17.3, 10.7 Hz, 0.85H), 6.32 (d, *J* = 10.7 Hz, 0.85H), 6.21 (s, 0.85H), 6.14 (d, *J* = 10.7 Hz, 0.15H), 5.78 (d, *J* = 17.3 Hz, 0.85H), 5.75 (d, *J* = 17.2 Hz, 0.15H), 4.22 (d, *J* = 16.9 Hz, 0.3H), 4.21 (d, *J* = 16.9 Hz, 1.7H), 4.04 (d, *J* = 16.9 Hz, 1.7H), 4.03 (d, *J* = 16.9 Hz, 0.15H), 4.03 (d, *J* = 16.9 Hz, 0.15H), 3.01 (s, 0.45H), 3.00 (s, 2.55H), 2.14 (s, 0.45H), 2.12 (s, 2.55H), 1.69 (s, 2.55H), 1.68 (s, 0.45H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.71. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 170.1, 169.9, 169.09, 169.07, 169.06, 169.02, 139.9, 139.3, 138.4, 138.0, 138.1, 136.5, 132.2, 130.0, 129.20, 129.16, 128.6, 128.3, 127.9, 127.5, 126.5, 80.1, 73.6, 62.34, 62.33, 62.30, 47.5, 47.4, 21.0, 20.9, 18.7, 13.4. FT-IR (ATR, cm^{-1}): 3010, 2957, 1764, 1742, 1026. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{22}BNNaO_6$ 394.1432; found 394.1437.

1.14 mmol scale synthesis of 4bd Diene **3bd** (423 mg, 1.14 mmol), **Co1** (47 mg, 0.11 mmol) and phenylsilane (14 µl, 0.11 mmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bd** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange solid with a 5.7:1 *EE*/*EZ* ratio (378 mg, 89%). Spectral data matches the previously synthesized product.

*2-(6-((tert-Butyldimethylsilyl)oxy)-4-methylhexa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4bf**).* **3bf** (83

mg, 0.22 mmol), **Co1** (10 mg, 24 μmol) and phenyl silane (2.7 μl, 22 μmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bf** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange amorphous solid with a 1.5:1 *EE*/*EZ* ratio (69 mg, 83%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.85 (dd, *J* = 17.3, 10.8 Hz, 0.4H), 6.84 (dd, *J* = 17.2, 10.7 Hz. 0.6H), 5.98 (d, *J* = 10.8 Hz, 0.4H), 5.96 (d, *J* = 10.8 Hz, 0.6H), 5.54 (d, *J* = 17.3 Hz, 0.6H), 5.53 (d, *J* = 17.2 Hz, 0.4H), 4.19 (d, *J* = 16.9 Hz, 1.2H), 4.19 (d, *J* = 16.8 Hz, 0.8H), 4.01 (d, *J* = 16.9 Hz, 1.2H), 3.99 (d, *J* = 16.8 Hz, 0.8H), 3.74 (t, *J* = 6.7 Hz, 1.2H), 3.72 (t, *J* = 6.9 Hz, 0.8H), 2.98 (s, 1.8H), 2.98 (s, 1.2H), 2.44 (t, *J* = 6.9 Hz, 0.8H), 2.26 (t, *J* = 6.7 Hz, 1.2H), 1.83 – 1.80 (m, 3H), 0.89 (s, 3.6H), 0.88 (s, 5.6H), 0.06 (s, 2.4H), 0.05 (s, 3.6H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.89. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.1, 169.0, 139.4, 139.3, 137.7, 137.4, 130.4, 130.0, 62.53, 62.50, 62.26, 62.23, 47.36, 47.34, 43.8, 36.6, 26.29, 26.25, 24.6, 18.77, 18.76, 17.3, -5.15, -5.17. FT-IR (ATR, cm^{-1}): 3011, 2955, 2929, 2857, 1763, 1254, 1024. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{18}H_{32}BNNaO_5Si$ 404.2035; found 404.2041.

*tert-Butyl (2-methyl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)penta-2,4-dien-1-yl)(tosyl)carbamate (**4bg**).* **3bg** (131 mg, 0.26 mmol), **Co1** (11 mg, 26 μmol) and phenyl silane (3.2 μl, 26 μmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bg** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as an orange amorphous solid with a 4:1 *EE*/*EZ* ratio (119 mg, 91%). Analytical TLC: R_f = 0.19 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.86 – 7.81 (m, 2H), 7.46 – 7.40 (m, 2H), 7.03 (dd, *J* = 17.2, 10.9 Hz, 0.2H), 6.88 (dd, *J* = 17.2, 10.7 Hz, 0.8H), 6.09 (d, *J* = 10.8 Hz, 0.2H), 6.05 (d, *J* = 10.7 Hz, 0.8H), 5.65 (d, *J* = 17.2 Hz, 0.2H), 5.62 (d, *J* = 17.2 Hz, 0.8H), 4.74 (s, 0.4H), 4.47 (s, 1.6H), 4.21 (d, *J* = 16.9 Hz, 1.6H), 4.20 (d, *J* = 16.8 Hz, 0.4H), 4.05 (d, *J* = 16.9 Hz, 1.6H), 4.00 (d, *J* = 16.8 Hz, 0.4H), 3.01 (s, 2.4H), 2.97 (s, 0.6H), 2.44 (bs, 3H), 1.79 (s, 2.4H), 1.76 (d, 0.6H), 1.33 (s, 9H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.95. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.09, 169.08, 151.9, 151.7, 145.27, 145.23, 138.6, 138.4, 138.30, 138.26, 134.9, 134.8, 131.5, 130.13, 130.08, 129.03, 128.95, 128.8, 84.6, 84.5, 62.4, 32.2, 53.7, 47.8, 47.38, 47.37, 27.99, 27.94, 21.5 (2C), 21.4, 14.9. FT-IR (ATR, cm^{-1}): 2980, 2963, 1764, 1729, 1351, 1289, 1255, 1152. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{23}H_{31}BN_2NaO_8S$ 529.1786; found 529.1796.

*2-((1E,3E)-6-(1,3-Dioxoisoindolin-2-yl)-4-methylhexa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4bh**).* **3bh** (92 mg, 0.23 mmol), **Co1** (10 mg, 24 μmol) and phenyl silane (2.9 μl, 24 μmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bh** after column chromatography (eluent: 2 – 3% MeOH in CH_2Cl_2) as an orange amorphous solid with a 1.5:1 *EE*/*EZ* ratio (62 mg, 67%). Analytical TLC: R_f = 0.25 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.86 – 7.80 (m, 4H), 6.76 (dd, *J* = 17.3, 10.6 Hz, 0.66H), 6.70 (dd, *J* = 17.2, 10.7 Hz, 0.33H), 5.93 (d, *J* = 10.7 Hz, 0.33H), 5.84 (d, *J* = 10.6 Hz, 0.66H), 5.44 (d, *J* = 17.3 Hz, 0.66H), 5.41 (d, *J* = 17.3 Hz, 0.33H), 4.17 (d, *J* = 16.8 Hz, 1.32H), 4.14 (d, *J* = 16.8 Hz, 0.66H), 3.97 (d, *J* = 16.8 Hz, 1.32H), 3.88 (d, *J* = 16.8 Hz, 0.66H), 3.79 (t, *J* = 6.8 Hz, 0.66H), 3.79 (t, *J* = 7.0 Hz, 1.32H), 2.88 (s, 2H), 2.70 (s, 1H), 2.62 (t, *J* = 6.8 Hz, 0.66H), 2.43 (t, *J* = 7.0 Hz, 1.32H), 1.87 (s, 1H), 1.87 (s, 2H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.14, 10.71. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.0, 168.9, 168.61, 168.60, 139.0, 138.5, 136.68, 136.61, 134.96, 134.95, 133.04, 133.02, 131.6, 130.4, 123.8, 123.7, 62.3, 62.2, 47.4, 47.2, 39.1, 36.9, 36.6, 31.6, 23.6, 16.6. FT-IR (ATR, cm^{-1}): 3012, 2956, 1764, 1707, 1249, 1154, 1026. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{21}BN_2NaO_6$ 419.1385; found 419.1388. Note: Resubjecting **4bh** to the reaction conditions for dienyl isomerization resulted in a negligible change from 1.5:1 *EE*/*EZ* to 1.6:1 *EE*/*EZ* ratio, as determined by ^{1}H NMR spectroscopy: integration of 5.93 ppm (0.62H, E-isomer) vs. 5.84 ppm (0.38H, Z-isomer).

*4-Methyl-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylhepta-4,6-dien-3-yl acetate (**4bi**).* **3bi** (77 mg, 0.19 mmol), **Co1** (8.0 mg, 19 μmol) and phenyl silane (2.4 μl, 20 μmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bi** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as a pale yellow amorphous solid with a 6.7:1 *EE*/*EZ* ratio (63 mg, 82%). Analytical TLC: R_f = 0.34 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 7.29 – 7.25 (m, 2H), 7.23 – 7.19 (m, 2H), 7.19 – 7.15 (m, 1H), 6.98 (dd, *J* = 17.2, 10.9 Hz, 0.13H), 6.84 (dd, *J* = 17.3, 10.3 Hz, 0.87H), 6.12 (d, *J* = 10.8 Hz, 0.87H), 6.03 (d, *J* = 10.9 Hz, 0.13H), 5.79 (dd, *J* = 7.9, 6.4 Hz, 0.13H), 5.72 (d, *J* = 17.3 Hz, 0.87H), 5.61 (d, *J* = 17.2 Hz, 0.13H), 5.16 (dd, *J* = 7.7, 6.0 Hz, 0.87H), 4.21 (d, *J* = 16.9 Hz, 1.74H), 4.21 (d, *J* = 16.9 Hz, 0.26H), 4.03 (d, *J* = 16.9 Hz, 1.74H), 3.99 (d, *J* = 16.9 Hz, 0.13H), 3.98 (d, *J* = 16.9 Hz, 0.13H), 2.99 (s, 2.61H), 2.86 (s, 0.39H), 2.68 – 2.54 (m, 2H), 2.02 (s, 2.61H), 2.02 – 1.91 (m, 2H), 2.00 (s, 0.39H), 1.80 (d, *J* = 1.2 Hz, 2.61H), 1.78 (s, 0.39H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.77. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 170.30, 170.25, 169.08, 169.06, 169.00, 168.98, 142.4, 142.3, 138.4, 138.1, 137.1, 136.9, 131.7, 130.1, 129.28, 129.20, 129.18, 129.13, 126.74, 126.69, 78.7, 72.7, 62.39, 62.30, 62.29, 62.26, 47.40, 47.37, 35.30, 35.29, 32.39, 32.33, 21.0, 30.9, 18.7, 12.8. FT-IR (ATR, cm^{-1}): 3024, 2954, 2863, 1763, 1242, 1025. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{21}H_{26}BNNaO_6$ 422.1745; found 422.1738.

*2-(5-((tert-Butyldimethylsilyl)oxy)-4-methylhexa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4bj**).* **3bj** (58 mg, 0.15 mmol), **Co1** (7.0 mg, 17 μmol) and phenyl silane (1.9 μl, 15 μmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bj** after column chromatography (eluent: 2% MeOH in CH_2Cl_2) as a pale yellow amorphous solid with a 5:1 *EE*/*EZ* ratio (55 mg, 95%). Analytical TLC: R_f = 0.26 (5% MeOH in CH_2Cl_2). ^{1}H NMR (500 MHz, acetone-d_6, ppm): δ 6.95 (dd, *J* = 17.1, 11.0 Hz, 0.17H), 6.85 (dd, *J* = 17.3, 10.8 Hz, 0.83H), 6.14 (d, *J* = 10.8 Hz, 0.83H), 5.86 (d, *J* = 11.0 Hz, 0.17H), 5.64 (d, *J* = 17.3 Hz, 0.83H), 5.57 (d, *J* = 17.1 Hz, 0.17H), 5.04 (q, *J* = 6.4 Hz, 0.17H), 4.29 (q, *J* = 6.3 Hz, 0.83H), 4.20 (d, *J* = 16.9 Hz, 0.34H), 4.20 (d, *J* = 16.9 Hz, 1.66H), 4.03 (d, *J* = 16.9 Hz, 0.83H), 4.03 (d, *J* = 16.9 Hz, 0.83H), 4.00 (d, *J* = 16.9 Hz, 0.17H), 3.96 (d, *J* = 16.9 Hz, 0.17H), 3.00 (s, 2.49H), 2.98 (s, 0.51H), 1.78 – 1.75 (m, 3H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.90 (s, 7.47H), 0.88 (s, 1.53H), 0.07 (s, 3H), 0.03 (s, 2.17H), 0.02 (s, 0.83H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.20, 10.84. ^{13}C{^{1}H} (126 MHz, acetone-d_6, ppm): δ 169.09, 169.07,

169.05, 168.97, 143.3, 143.2, 139.1, 137.9, 128.0, 126.6, 74.2, 67.3, 62.32, 62.31, 62.25, 62.23, 47.4, 26.20, 26.18, 23.6, 23.2, 18.7, 17.9, 12.5, -4.61, -4.68, -4.71, -4.75. FT-IR (ATR, cm^{-1}): 3043, 2956, 2929, 2887, 2857, 1762, 1252, 1025. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{32}BNNaO_5Si$ 404.2035; found 404.2037.

2-((6E)-5-((tert-Butyldimethylsilyl)oxy)-4-methyl-7-phenylhepta-1,3,6-trien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4bk**). **3bk** (80 mg, 0.17 mmol), **Co1** (7.0 mg, 17 µmol) and phenyl silane (2.2 µl, 18 µmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bk** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange amorphous solid with a 3:1 EE/EZ ratio (60 mg, 75%). Analytical TLC: R_f = 0.27 (5% MeOH in CH_2Cl_2). ^1H NMR (500 MHz, acetone-d_6, ppm): δ 7.46 – 7.41 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.20 (m, 1H), 7.09 (dd, J = 17.1, 11.0 Hz, 0.25H), 6.88 (dd, J = 17.3, 10.8 Hz, 0.75H), 6.69 (d, J = 16.0 Hz, 0.25H), 6.69 (d, J = 15.8 Hz, 0.75H), 6.31 – 6.26 (m, 1H), 6.23 (dd, J = 15.8, 6.0 Hz, 0.75H), 6.00 (d, J = 11.0 Hz, 0.25H), 5.70 (d, J = 17.3 Hz, 0.75H), 5.67 (d, J = 17.1 Hz, 0.25H), 5.57 (d, J = 5.0 Hz, 0.25H), 4.82 (d, J = 6.0 Hz, 0.75H), 4.22 (d, J = 16.9 Hz, 0.25H), 4.22 (d, J = 16.9 Hz, 0.25H), 4.21 (d, J = 16.9 Hz, 1.5H), 4.04 (d, J = 16.9 Hz, 0.75H), 4.04 (d, J = 16.9 Hz, 0.75H), 4.00 (d, J = 16.9 Hz, 0.25H), 3.97 (d, J = 16.9 Hz, 0.25H), 3.01 (s, 2.25H), 3.00 (s, 0.75H), 1.81 – 1.77 (m, 3H), 0.95 (bs, 9H), 0.13 – 0.09 (m, 6H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.94. $^{13}C\{^1H\}$ (125 MHz, acetone-d_6, ppm): δ 169.08, 169.06 (2C), 168.98, 140.8, 140.7, 139.0, 137.97, 137.94, 137.92, 132.2, 131.7, 130.4, 129.7, 129.44, 129.41, 129.3, 129.1, 128.3, 128.2, 127.9, 127.3, 79.2, 71.9, 62.4 (2C), 62.31, 62.28, 47.4 (2C), 26.25, 26.24, 18.89, 18.88, 18.2, 12.9, -4.44, -4.48, -4.62, -4.66. FT-IR (ATR, cm^{-1}): 3025, 2954, 2929, 2886, 2856, 1762, 1251, 1027. HRMS (ESI – FT-ICRMS) m/z: $[M + Na]^+$ calcd for $C_{25}H_{36}BNNaO_5Si$ 492.2348; found 492.2349.

*6-Methyl-2-(4-(trimethylsilyl)penta-1,3-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4bl**)*. **3bl** (56 mg, 0.19 mmol), **Co1** (8.0 mg, 19 µmol) and phenyl silane (2.3 µl, 19 µmol) were used in following the general procedure for dienyl isomerization. This furnished diene **4bl** after column chromatography (eluent: 3% MeOH in CH_2Cl_2) as an orange solid with a 9:1 *EE*/*EZ* ratio (49 mg, 88%). Analytical TLC: R_f = 0.25 (5% MeOH in CH_2Cl_2). Mp = 201 – 203 °C. ^1H NMR (500 MHz, acetone-d_6, ppm): δ 7.00 (dd, *J* = 17.2, 10.5 Hz, 0.9H), 6.90 (dd, *J* = 17.1, 11.0 Hz, 0.1H), 6.63 (d, *J* = 10.9 Hz, 0.1H), 6.39 (d, *J* = 10.5 Hz, 0.9H), 5.72 (d, *J* = 17.2 Hz, 0.9H), 5.59 (d, *J* = 17.1 Hz, 0.1H), 4.23 (d, *J* = 16.9 Hz, 0.2H), 4.22 (d, *J* = 16.9 Hz, 1.8H), 4.04 (d, *J* = 16.9 Hz, 1.8H), 3.99 (d, *J* = 16.8 Hz, 0.2H), 3.01 (s, 2.7H), 2.99 (s, 0.3H), 1.87 – 1.83 (m, 3H), 0.17 (s, 0.9H), 0.09 (s, 8.1H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 10.79. $^{13}C\{^1H\}$ (126 MHz, acetone-d_6, ppm): δ 169.07, 169.01, 144.4, 142.6, 142.2, 140.6, 140.0, 138.3, 62.3, 62.1, 47.4, 47.2, 25.0, 15.3, 0.1, -2.1. FT-IR (ATR, cm^{-1}): 3015, 2955, 2855, 1747, 1246, 1020, 1001, 834. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{22}BNNaO_4Si$ 318.1303; found 318.1306.

(8-((6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-1,3-dioxo-2-phenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a]pyridazin-6-yl)methyl benzoate (**5**). **3bc** (119 mg, 0.33 mmol) was added to a 25 mL round bottomed flask and dissolved in THF (ca. 0.07M). 4-Phenyl-1,2,4-triazole-3,5-dione (PTAD, 70 mg, 0.40 mmol) was then added and the reaction mixture was allowed to stir for 2 h at room temperature. The reaction mixture was then concentrated and purified by flash column chromatography on silica gel (eluent: 4% MeOH in CH_2Cl_2) to furnish the Diels-Alder adduct **5** as a white solid (127 mg, 72%). Analytical TLC: R_f = 0.16 (5% MeOH in CH_2Cl_2). Mp = 128 – 130 °C. ^1H NMR (500 MHz, acetone-d_6, ppm): δ 8.15 – 8.09 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.45 (m, 2H), 7.51 – 7.36 (m, 1H), 7.43 – 7.37 (m, 1H), 6.41 – 6.37 (m, 1H), 5.00 (d, J = 13.0 Hz, 1H), 4.96 (d, J = 12.9 Hz, 1H), 4.37 (d, J = 16.0 Hz, 1H), 4.24 (d, J = 17.0 Hz, 1H), 4.24 (d, J = 16.9 Hz, 1H), 4.16 – 4.11 (m, 1H), 4.14 (d, J = 16.9 Hz, 1H), 4.06 (d, J = 17.0 Hz, 1H), 3.14 (s, 3H), 1.50 (dd, J = 13.4, 3.3 Hz, 1H), 1.09 (dd, J = 13.4, 11.4 Hz, 1H). ^{11}B (160.5 MHz, acetone-d_6, ppm): δ 12.13. $^{13}C\{^1H\}$ (126 MHz, acetone-d_6, ppm): δ 168.7, 168.6, 166.5, 154.1, 152.3, 134.1, 133.1, 130.8, 130.4, 129.5, 129.48, 128.47, 127.9, 127.3, 126.5, 66.1, 62.64, 62.58, 52.9, 46.5, 45.2, 20.1 (CH_2-B). FT-IR (ATR, cm^{-1}): 3009, 2956, 1763, 1697, 1418, 1268, 1248, 1024. HRMS (ESI – FT-ICRMS) m/z: $[M + Na]^+$ calcd for $C_{26}H_{25}BN_4NaO_8$ 555.1658; found 555.1659.

*1-(4-((1E,3E)-4-Phenylpenta-1,3-dien-1-yl)phenyl)ethan-1-one (**6**)*. **6** was prepared following a modified literature procedure for the slow *in-situ* deprotection of MIDA boronates.[25a] Pd_2dba_3 (5 mg, 5 µmol) and SPhos (8 mg, 20 µmol) were added to a 25 mL Schlenk tube and dissolved in degassed 1,4-dioxane (2.5 mL). This mixture was allowed to stir for 10 min at room temperature to allow for phosphine ligation onto palladium. Freshly recrystallized 4'-bromobenzophenone (40 mg, 0.20 mmol), **4bb** (5.7:1 *EE*/*EZ*; 66 mg, 0.22 mmol) and a degassed aqueous solution of K_3PO_4 (3M; 0.50 mL, 1.50 mmol) were then added. The Schlenk tube was then equipped with a cold-finger condenser, heated to reflux and allowed to stir for 18 h.

After 18 h, the reaction mixture was cooled to room temperature and transferred to a 60 mL separatory funnel. The mixture was then diluted with an aqueous solution of NaOH (0.50M, 10 mL) and Et_2O (10 mL). The biphasic mixture was vigorously shaken, and the organic layer was removed. The aqueous layer was then extracted with additional Et_2O (2 x 10 mL). The organic layers were then combined, extracted with brine (20 mL), dried with $MgSO_4$, filtered and concentrated via rotatory evaporation. The crude residue was then dry loaded onto silica gel, packed on a silica gel column and purified by flash column chromatography (eluent: 5% ethyl acetate in hexanes). This furnished diene **6** as a yellow solid solely as the *EE*-isomer (21 mg, 40%). Analytical TLC: R_f = 0.13 (5% ethyl acetate in hexanes). Mp = 146 – 147 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 6.69 (d, *J* = 15.4 Hz, 1H), 6.67 (d, *J* = 11.0 Hz, 1H), 2.60 (s, 3H), 2.31 (s, 3H). $^{13}C\{^1H\}$ (126 MHz, $CDCl_3$, ppm): δ 197.6, 142.8, 142.6, 139.1, 135.8, 131.6, 129.0, 128.5, 127.7, 127.1, 126.4, 125.8, 26.7, 16.5. FT-IR (ATR, cm^{-1}): 3047, 2919, 2850, 1672, 1596, 1269, 961. HRMS (ESI – FT-ICRMS) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{18}NaO$ 285.1250; found 285.1254.

*Ethyl (E)-3-(4-methoxyphenyl)acrylate (**7**)*. NaH (60% dispersion in oil; 1.45 g, 36.3 mmol) was added to a 250 mL round bottomed flask, suspended in THF (100 mL) and cooled to 0 °C. Triethyl phosphonoacetate (7.20 mL, 36.0 mmol) was then added dropwise and the mixture was allowed to stir for 0.5 h at

0 ºC; This resulted in a pale yellow solution. *p*-Anisaldehyde (3.60 mL, 29.6 mmol) was then added and the reaction mixture was allowed to warm to room temperature and stir for 2.5 h.

The reaction was quenched with a saturated aqueous solution of NH_4Cl (50 mL) and the organic layer was removed. The aqueous layer was then extracted with Et_2O (3 x 20 mL). The organic layers were combined and then extracted with water (50 mL) and brine (50 mL). The organic layer was then dried with $MgSO_4$, filtered and concentrated. The crude oil was then passed through a silica gel plug (eluent: 10% ethyl acetate in hexanes), which furnished ester **7** as a clear yellow oil (5.84 g, 96%). Spectral data obtained matched literature reports.[39] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

*(E)-3-(4-Methoxyphenyl)acrylic acid (**8**).* **7** (5.78 g, 28.0 mmol) was add to a 250 mL round bottomed flask and dissolved in ethanol (50 mL). An aqueous solution of NaOH (1M; 56 mL, 56.0 mmol) was then added and the reaction mixture was vigorously stirred at 60 ºC for 1 h. The solution was the acidified with HCl (2M, 40 mL), which precipitated a white solid. The precipitate was collected by vacuum filtration and washed thoroughly with cold ethanol. The crude solid was then recrystallized using a minimal amount of a boiling mixture of 5% ethanol in benzene. Cooling of this solution furnished **8** as a white crystalline solid, which was collected by vacuum filtration (4.23 g, 85%). Spectral data obtained matched literature reports.[39] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 11.63 (bs, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 HZ, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H).

*(E)-1-(2-Bromovinyl)-4-methoxybenzene (**9**).* **9** was prepared following a modified literature procedure.[40] **8** (891 mg, 5.00 mmol) was added to a 50 mL round bottomed flask and suspended in a 9:1 mixture of acetonitrile:water (ca. 0.20M). Et_3N (35 μL, 0.25 mmol) was added and the mixture was allowed to stir for 5 minutes; the suspension dissolved shortly after adding Et_3N. Freshly recrystallized *N*-bromosuccinimide (1.04 g, 6.01 mmol) was then added in one portion and the reaction mixture was allowed to stir for 1 hour at room temperature.

The reaction mixture was transferred to a 125 mL separatory funnel, diluted with Et_2O (20 mL) and extracted with water (20 mL). The organic layer was removed and the aqueous layer was extracted with additional Et_2O (2 x 20 mL). The organic layers were then combined, extracted with brine (40 mL), dried with $MgSO_4$, filtered and concentrated. The crude oily solid was then purified by flash column chromatography on silica gel (eluent: 2% Et_2O in hexanes) to furnish **9** as an off-white crystalline solid (811 mg, 76%). Analytical TLC: R_f = 0.45 (2% Et_2O in hexanes). Spectral data obtained matches literature reports.[41] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.23 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 14.0 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 14.0 Hz, 1H), 3.81 (s, 3H).

*1-Methoxy-4-((1E,3E,5E)-6-phenylhepta-1,3,5-trien-1-yl)benzene (**10**).* **4bb** (6.7:1 *E*/*Z*; 74 mg, 0.25 mmol), **9** (43 mg, 0.20 mmol), NaOH (33 mg, 0.83 mmol), $Pd(OAc)_2$ (2.3 mg, 10 μmol) and SPhos (8.4 mg, 21 μmol) were added to a 10 mL round bottomed flask and dissolved in a 4:1 degassed mixture of THF:H_2O (ca. 0.07M). The reaction mixture was then allowed to stir at room temperature for 1 h.

The reaction mixture was then transferred to a 60 mL separatory funnel and diluted with water (10 mL) and Et_2O (10 mL). The organic layer was removed and the aqueous layer was extracted with additional Et_2O (2 x 10 mL). The organic layers were then combined, extracted with brine (30 mL), dried with $MgSO_4$, filtered and concentrated. The crude residue was then dry loaded onto silica gel, packed on a silica gel column and purified by flash column chromatography (eluent: 3% ethyl acetate in hexanes). This furnished triene **10** as a yellow amorphous solid (31 mg, 56%) with a 19:1 1*E,3E,5E*/1*E,3E,5Z* ratio. Analytical TLC: R_f = 0.25 (5% ethyl acetate in hexanes). Note: Trace amounts of the 1*E*,3*E*,5*Z*-**10** isomer observed, derived from 1*E*,3*Z*-**3bb**. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.51 – 7.47 (m, 2H), 7.39 – 7.33 (m, 4H), 7.28 – 7.23 (m, 1H), 6.91 – 6.86 (m, 2H), 6.83 (dd, *J* = 15.5, 10.8 Hz, 1H), 6.73 (dd, *J* = 14.5, 11.3 Hz, 1H), 6.60 (d, *J* = 11.2 Hz, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.51 (dd, *J* = 14.4, 10.7 Hz, 1H), 3.83 (s, 3H), 2.23 (d, *J* = 0.8H, 3H). $^{13}C\{^1H\}$ (126 MHz, $CDCl_3$, ppm): δ 159.4, 143.1, 136.1, 134.1, 132.0, 130.5, 129.4, 128.5, 127.72, 127.69, 127.55, 127.2, 125.7, 114.3, 55.5, 16.2. FT-IR (ATR, cm^{-1}): 3028, 2953, 2930, 1508, 1246, 1174, 1033, 981. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{20}NaO$ 299.1406; found 299.1407.

*(E)-(4,4-Dibromobuta-1,3-dien-1-yl)benzene (**11**).* CBr_4 (10.12 g, 30.5 mmol) was added to a 250 mL round bottomed flask, dissolved in CH_2Cl_2 (75 mL) and cooled to 0 ºC. PPh_3 (15.80 g, 60.2 mmol) was added to a 100 mL round bottomed flask and dissolved in CH_2Cl_2 (50 mL). The PPh_3 solution was then added to the solution of CBr_4 via canula over the course of 1 hour while maintaining 0 ºC; This resulted in a dark red solution upon complete addition. *trans*-Cinnamaldehyde (2.00 mL, 15.9 mmol) in THF (10 mL) was then added and the reaction mixture was allowed to warm to room temperature and stir overnight (ca. 18 h).

The reaction mixture was transferred to a 500 mL separatory funnel and was extracted with water (50 mL). The organic layer was removed and the aqueous layer was extracted with additional CH_2Cl_2 (2 x 20 mL). The organic layers were combined and then extracted with brine (100 mL), dried with $MgSO_4$, filtered and concentrated via rotatory evaporation. The red oily solid was then dissolved in CH_2Cl_2 (ca. 50 mL) and diluted with Et_2O (150 mL), which precipitated a pale yellow solid. The pale yellow solid was removed via filtration and the desired filtrate was concentrated via rotatory evaporation to furnish an oily solid. The oily solid was then dissolved in a minimal amount of CH_2Cl_2 (ca. 20 mL) and was diluted with petroleum ether (ca. 100 mL), which precipitated a white solid. The white solid was removed by filtration and the desired filtrate was dry loaded on celite (ca. 10 g). The celite was then packed on a silica gel column and purified by flash column chromatography (eluent: 1% ethyl acetate in hexanes). This furnished **11** as a white solid (3.31 g, 72%). Analytical TLC: R_f = 0.43 (1% ethyl acetate in hexanes). Spectral data obtained matches literature reports.[42] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.47 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.10 (d, *J* = 9.8 Hz, 1H), 6.79 (dd, *J* = 15.7, 9.8 Hz, 1H), 6.72 (d, *J* = 15.7 Hz, 1H).

*2-((1Z,3E)-1-Bromo-4-phenylbuta-1,3-dien-1-yl)benzofuran (**12**).* **11** (216 mg, 0.75 mmol), 2-benzofuranylboronic acid (122 mg, 0.75 mmol), Cs_2CO_3 (733 mg, 2.25 mmol), and $Pd(PPh_3)_4$ (61 mg, 53 μmol) were added to a 25 mL round bottomed flask

and dissolved in a 4:1 degassed mixture of THF:H_2O (0.10M). The reaction mixture was allowed to stir for 18 h at room temperature. Due to incomplete conversion of the boronic acid, an additional portion of $Pd(PPh_3)_4$ (20 mg, 17 μmol) was added and the reaction mixture was allowed to stir for an additional 1 h. Once full conversion was observed, the reaction mixture was transferred to a separatory funnel and diluted with water (10 mL) and ethyl acetate (10 mL). The organic layer was removed and the aqueous layer was extracted with additional ethyl acetate (2 x 15 mL). The organic layers were combined, extracted with brine (25 mL), dried with $MgSO_4$, filtered and dry loaded onto silica gel (ca. 1 g). The dry loaded silica gel was then packed on a silica gel column and purified by flash column chromatography (eluent: 1% ethyl acetate in hexanes). This furnished **12** as a yellow solid (103 mg, 42%). Analytical TLC: R_f = 0.17 (1% ethyl acetate in hexanes). Note: Trace amounts of the 1*E*,3*E*-**12** isomer was observed. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.47 (d, *J* = 10.5 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 6.99 (s, 1H), 6.91 (d, *J* = 15.6 Hz, 1H). ^{13}C{^{1}H}9 (126 MHz, $CDCl_3$, ppm): δ 155.6. 153.8. 137.8. 136.9, 129.1, 128.9, 128.8, 128.7, 127.1, 126.2, 125.5, 123.3, 121.5, 112.1, 111.1, 107.7. FT-IR (ATR, cm^{-1}): 3082, 3069, 3036, 3016, 1447, 1256, 966, 747, 688. HRMS (FTMS + p EI – GC-Orbitrap) *m*/*z*: $[M]^+$ calcd for $C_{18}H_{13}OBr$ 324.0150; found 324.0144.

*((2E,4E,6E,8E)-6-(Benzofuran-2-yl)-9-phenylnona-2,4,6,8-tetraen-2-yl)trimethylsilane (**13**).* **4bl** (9:1 *E*/*Z*; 105 mg, 0.32 mmol), **12** (86 mg, 0.27 mmol), NaOH (49 mg, 1.2 mmol), $Pd(OAc)_2$ (3.4 mg, 15 μmol) and SPhos (13 mg, 31 μmol) were added to a 25 mL round bottomed flask and dissolved in a 4:1 mixture of THF:water (4.5 mL). The reaction mixture was allowed to stir for 1 h at room temperature and was transferred to a separatory funnel. The reaction mixture was then diluted with water (10 mL) and Et_2O (10 mL), and the organic layer was removed. The aqueous layer was extracted with additional Et_2O (2 x 10 mL). The organic layers were combined, extracted with brine (30 mL), dried with $MgSO_4$, filtered and concentrated onto silica gel (ca. 1 g). The dry loaded silica gel was then packed on a silica gel column and purified by flash column chromatography (eluent: 1-2% ethyl acetate in hexanes). This gave tetraene **13** as a vibrant yellow oil (68 mg, 67%) with a 19:1 2*E*,4*E*,6*E*,8*E*/2*Z*,4*E*,6*E*,8*E* ratio. Analytical TLC: R_f = 0.19 (2% ethyl acetate in hexanes). Note: Trace amounts of the 2*Z*,4*E*,6*E*,8*E*-**13** isomer was observed, derived from the 1*E*,3*Z*-**4bl** isomer. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.58 – 7.53 (m, 1H), 7.52 – 7.47 (m, 3H), 7.38 – 7.33 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.12 (dd, *J* = 15.4, 10.8 Hz, 1H), 7.05 (d, *J* = 11.6 Hz, 1H), 6.83 (d, *J* = 15.3 Hz, 1H), 6.83 (s, 1H), 6.79 (d, *J* = 15.4 Hz, 1H), 6.56 (d, *J* = 10.8 Hz, 1H), 1.89 (s, 3H), 0.16 (s, 9H). ^{13}C{^{1}H} (126 MHz, $CDCl_3$, ppm): δ 156.3, 154.8, 143.1, 137.5, 137.0, 135.9, 130.5, 129.8, 129.2, 128.9, 128.7, 128.1, 126.9, 126.5, 125.0, 124.6, 123.0, 121.0, 111.1, 104.9, 15.7, -2.0. FT-IR (ATR, cm^{-1}): 3083, 3064, 3002, 2954, 2897, 1452, 1258, 1247, 962, 838, 748, 690. HRMS (ESI – FT-ICRMS) *m*/*z*: $[M + Na]^+$ calcd for $C_{26}H_{28}NaOSi$ 407.1802; found 407.1807.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Product summary and NMR spectra of new compounds (PDF).

FAIR data, including the primary NMR FID files, for compounds (ZIP).

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Notes

The authors declare no competing financial interest.

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formed a ruthenium methylidene intermediate, which cross-metathesized with **2d**. This results in the formation of 2-methylene-1-phenylbut-3-en-1-yl acetate.

(30) The lower than expected yield of **3cd** could be explained by significiant alkene homodimer that formed through competing intermolecular alkene-alkene metathesis of homoallylboronate **1c**.

(31) Attempts were made to isomerize dienes **3bc** and **3bf**, but failed to solely furnish **4**. Instead, we observed an inseperable mixture of **4** and of an isomerization product favoring isomerization toward the R-substituent derived from the alkyne. A similar isomerization product was previously observed; refer to Ref. 21.

(32) Resubjecting diene **4bh** to the reaction conditions of Scheme 3 resulted in a negligible change from 1.5:1 *EE*/*EZ* to 1.6:1 *EE*/*EZ* ratio.

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(34) Many attempts were made to either isolate the boronic acid or prepare it as a solution in THF after extractive work-up post-deprotection. However, the boronic acid was noticeably unstable and decomposed prior to a successful cross-coupling, typically affording low yielding cross-products (ca. 20%). Vinyl boronic acids are well known for their instability; refer to Ref. 6.

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