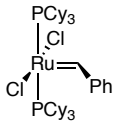
Chapter 2
Ruthenium-Catalyzed Olefin Cross-Metathesis of α-Substituted Vinyl Boronates

Introduction

The development of active, air- and moisture-stable ruthenium alkylidene catalysts (i.e., **1** and **2**) has allowed olefin metathesis to become a powerful tool in synthetic chemistry.[1] As discussed in the previous chapter, a variety of intramolecular and intermolecular reactions involving olefin metathesis can be applied to small molecule and polymer synthesis. This chapter will focus only on cross-metathesis (CM) and how substrate substitution affects the distribution of products. More specifically, the application and limitations of catalyst **2** in the synthesis of trisubstituted vinyl boronates will be discussed.



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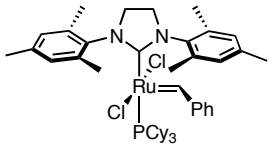

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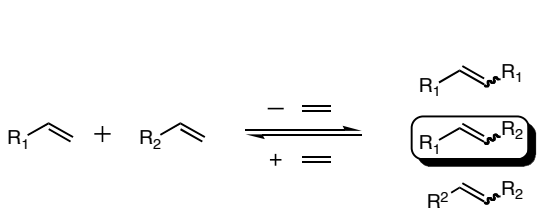
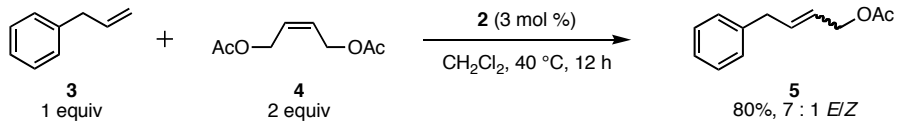
Olefin CM, at first glance, appears to be a simple approach to coupling two alkenes. Unfortunately, because the reactive functionalities are the same (two carbon–carbon double bonds), a mixture of homocoupled and heterocoupled products can be formed (Scheme 2.1).[2] This type of complication is not present when other transition metal-catalyzed reactions (i.e., coupling of an aryl halide with an arylboronic acid) are used. When a highly active complex such as **2** catalyzes the CM reaction of simple terminal alkenes, a statistical distribution of products is obtained.[3] The catalyst does not differentiate between the two olefins, and secondary metathesis continues to shuffle the

products until equilibrium is reached. Almost 10 equivalents of one olefin must be used to obtain heterocoupled product in 90% yield. One example that illustrates the lack of selectivity of CM is shown in Scheme 2.2. One equivalent of allyl benzene (**3**) reacts with two equivalents of *cis*-1,4-diacetoxy-2-butene (**4**) (equal to four equivalents of allyl acetate) to give the heterocoupled product in an 80% yield.[3a] Additionally, a mixture of olefin isomers is obtained.



$R_1 : R_2$	CM product selectivity
1 : 1	50%
2 : 1	66%
4 : 1	80%
10 : 1	91%
20 : 1	95%

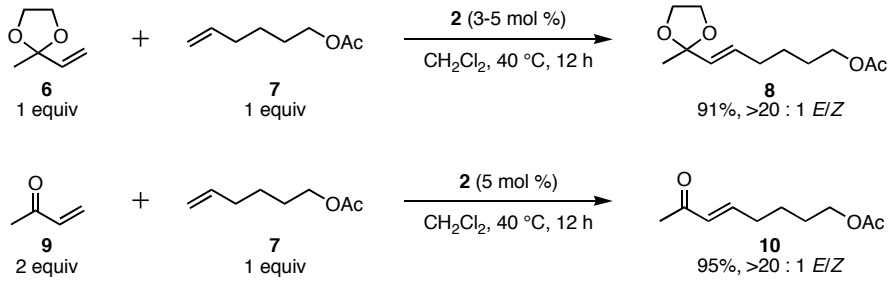
Scheme 2.1. Statistical distribution of products obtained during CM.



3 1 equiv **4** 2 equiv **5** 80%, 7 : 1 *E*/*Z*

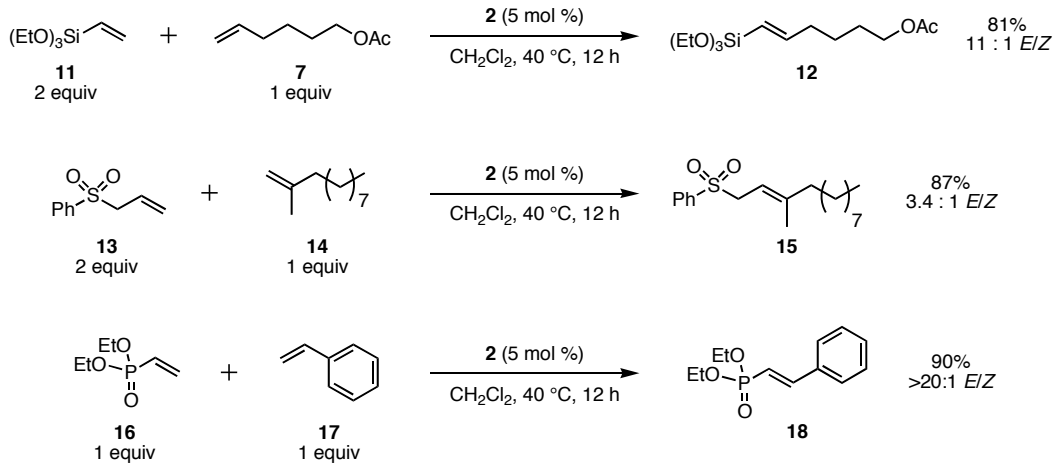
Scheme 2.2. CM of allyl benzene (**3**) and *cis*-1,4-diacetoxy-2-butene (**4**).

It was discovered that one way to promote selective CM is to introduce substitution close to the reacting alkene.[3,4] As illustrated in Scheme 2.3, bulky allylic substitution and electron-withdrawing groups in conjugation with the olefin result in a CM reaction selective for the heterocoupled product and the *E*-isomer.[3a,5] These olefins undergo homocoupling either very slowly or not at all, so the CM equilibrium is shifted toward the heterocoupled products. The relative reactivities of olefins in CM is catalyst dependent: catalysts **1** and **2** homocouple the same olefins with different efficiencies.[3] Therefore, by choosing the appropriate catalyst for a given CM reaction, high selectivity for the desired product can be achieved.



Scheme 2.3. Selective CM using one alkene that does not readily homocouple.

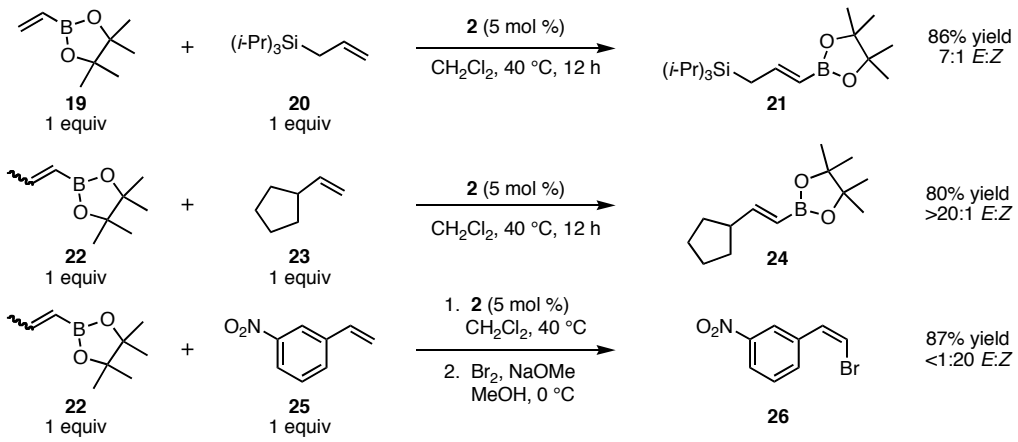
In order for CM to be a practical synthetic tool, functionalized intermediates that can undergo further manipulation must be accessible. Ruthenium benzylidene **2**, due to its high activity and tolerance of a wide variety of functionality, can catalyze the CM of olefins with allylic and vinylic substitution (Scheme 2.4).[3,6] Additionally, because the functionalized olefins typically do not homocouple readily, the reactions are selective for the heterocoupled products. The CM products can be further functionalized, sometimes even without isolation.[7]



Scheme 2.4. CM with allyl and vinyl functionalized olefins.

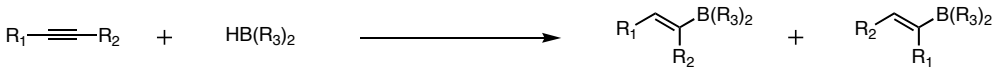
One type of functionality that is tolerated by catalyst **2** is vinyl pinacol boronates.[8] Vinyl boronates can be converted into aldehydes or ketones,[9] halides,[10] amines,[9b] and carbon containing groups[11] and are therefore valuable synthetic intermediates. Christie Morrill, a former graduate student in the group, showed that vinyl pinacol boronate (**19**)

and 1-propenyl pinacol boronate (**22**) could undergo CM selectively with many different alkenes to form 1,2-disubstituted vinyl boronates (Scheme 2.5).[8] Additionally, she illustrated that the vinyl boronate cross products could be converted to vinyl bromides in situ (two-step formation of **26**).



Scheme 2.5. CM with vinyl pinacol boronates and further functionalization.

1,2-Disubstituted vinyl boronates are typically made by the hydroboration of a terminal alkyne, which generally occurs with high regioselectivity.[9a,12] On the other hand, trisubstituted alkenes, which are made by the hydroboration of an internal alkyne, are often obtained as a mixture of isomers due to low regioselectivities (Scheme 2.6).[13] Cross-metathesis does not suffer from the same regiochemical issues that can plague hydroboration, so the synthesis of trisubstituted vinyl boronates from α-substituted vinyl pinacol boronates was explored.[14]



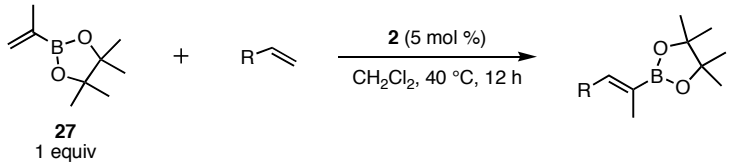
Scheme 2.6. Regioselectivity issues in the hydroboration of internal alkynes.

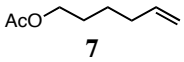
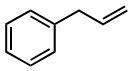
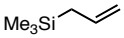
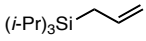
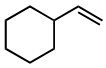
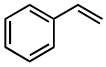
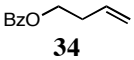
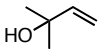
Results and Discussion

The first α-substituted vinyl pinacol boronate that was used was 2-propenyl pinacol boronate (**27**). This compound was readily synthesized from trimethyl borate, 2-propenyl magnesium chloride, and pinacol,[8] and it was stable to flash chromatography. The first reaction that was examined was the CM between **27** and 5-hexenyl acetate (**7**) (Table 2.1, entry 1), because the products were stable and separable from the starting materials by flash chromatography. The highest yield was observed when 2 equivalents of **27** were used: attempts to increase the yield using longer reaction times and higher temperatures were unsuccessful. Only the *Z*-isomer (carbon takes precedence over boron in the naming of *E* and *Z* isomers) was obtained. Unreacted vinyl boronate was always present in the reaction mixture, even after 24 h.

Cross-metathesis reactions of **27** with other olefins were explored, and, generally, the products were obtained in moderate yields, with the highest yield being 60% (Table 2.1). The *Z*:*E* selectivity was high in most reactions; the low diastereoselectivity in entry 9 may have been due to coordination of the benzoyl group to the catalyst.[15] The only trisubstituted vinyl boronates that were cleanly isolated from unreacted **27** were those obtained from reactions with **7**, **34**, and **35**; in all cases unreacted **27** remained. When polar functional groups were introduced to the allylic and homoallylic positions of the cross partners, low yields (<50%) were obtained.

Table 2.1. CM reactions of 2-propenyl pinacol boronate (**27**).



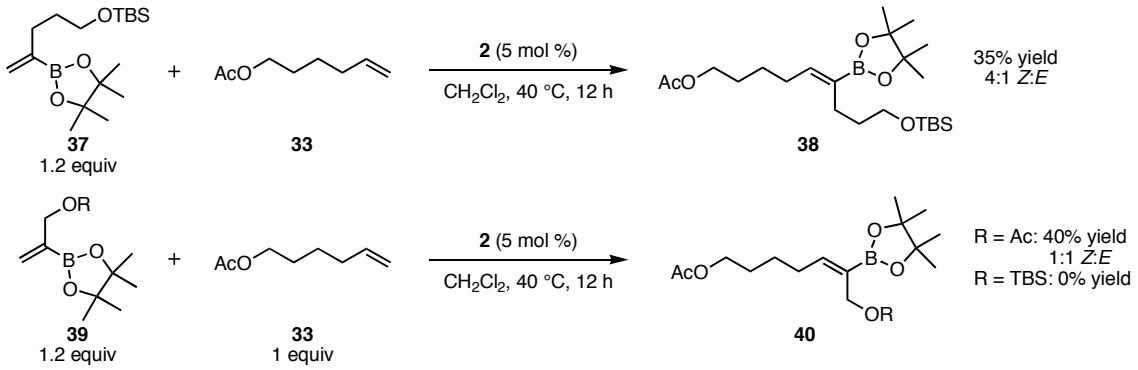
Entry	Cross Partner	Equiv	Product/1	Yield (%)[a]	*Z*:*E*
1	 **7**	0.5	–	58	>20:1
2	 **28**	2	5.5:1	59	7:1
3	 **29**	1	3.4:1	59	>20:1
4	 **30**	1	5:1	60	>20:1
5	 **31**	1	3.3:1	44	>20:1
6	 **32**	1	1:3	14	>20:1
7	 **33**	2	1.4:1	34	>20:1
8	 **34**	1	–	46	>20:1
9	 **35**	0.5	–	30	2:1
10	 **36**	1	–	0	–

[a] Yields for all entries except 1, 8, and 9 determined by ^{1}H NMR spectroscopy.

Compared to CM reactions with **19** and **22**,[8] most products were formed in much lower yield with **27**. For example, **22** reacted with 1 equiv of **30** to afford the cross product in 99% yield, which is 39% higher than the reaction in entry 4 of Table 2.1. The product derived from tertiary allylic alcohol **36** and **22** was isolated in 61% yield, but no CM was observed in the reaction of **36** with **27**. The only reaction with **27** that was similar to that with **19** or **22** was the reaction in entry 1. Vinyl boronate **19** reacted with **7**

to form the cross product in 60% yield, and the use of **27** (entry 1) only decreased the yield by 2%. It is obvious that a large difference in reactivity exists between the vinyl boronates with and without an internal methyl group.

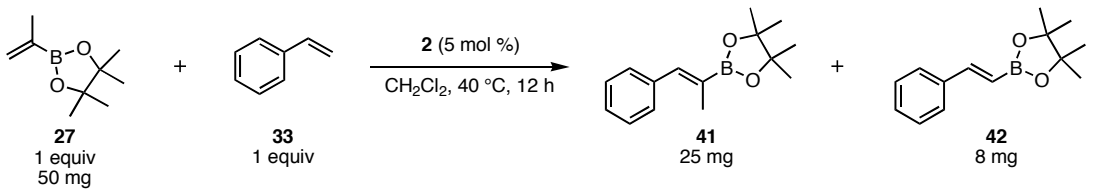
Substrates with groups larger than methyl at the α-position were synthesized by Christie Morrill and used in CM reactions (Scheme 2.7).[14,16] In those cases, yields were lower than reactions with **27**, and small changes to the starting materials often resulted in large reactivity differences. Although these compounds would be difficult to access regioselectively using internal alkyne hydroboration, the low yields and low *Z*:*E* selectivities observed in most of these reactions do not make CM a general, practical approach to synthesizing trisubstituted vinyl boronates.



Scheme 2.7. CM reactions with other α-substituted vinyl pinacol boronates.

In addition to unreacted starting materials, homocoupled cross partners, and the desired trisubstituted vinyl boronates, 1,2-disubstituted vinyl boronates were often formed during the course of the CM reactions described above. For example, in the reaction between **27** and styrene (**33**), a small amount of 1,2-disubstituted vinyl boronate **42** was present (Scheme 2.8). Upon closer inspection of the ^{1}H NMR spectrum and GC-MS of **27**, there was approximately 5% of **22** contaminating **27**. Assuming 5% contamination of **27** with **22**, the maximum yield of **42** was 3.4 mg in the reaction in

Scheme 2.8, but more than twice that amount was present. Was this due to a lack of quantitative accuracy in determining the amount of **22** in **27**, or was there an isomerization that shifted the methyl group from the internal position to the terminal position of the olefin prior to CM?



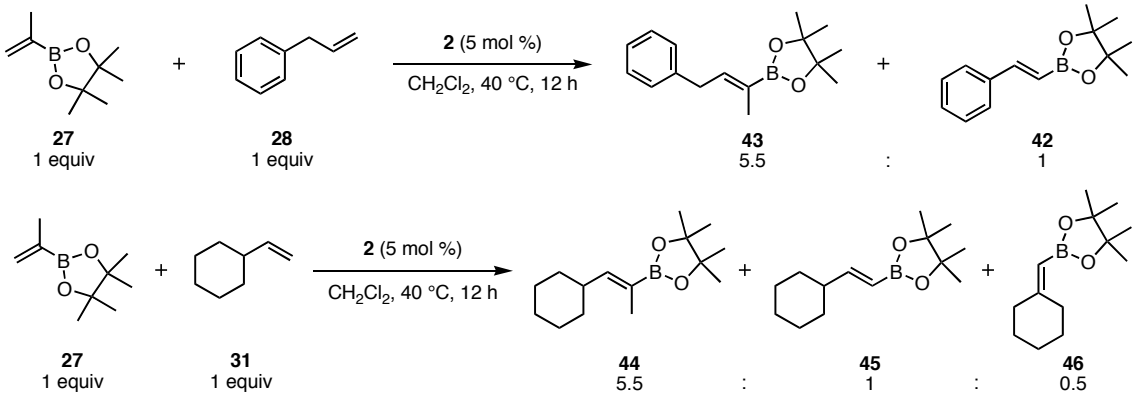
Scheme 2.8. Possible isomerization of **27** during CM.

The presence of a demethylated product was not unique to the reaction shown in Scheme 2.8. 1,2-Disubstituted vinyl boronates were observed in the CM reactions with allylbenzene (**28**), allyltrimethylsilane (**29**), allyltriisopropylsilane (**30**), vinylcyclohexane (**31**), and vinylcyclopentane (**32**). In all of these cases only small amounts of the 1,2-disubstituted products were present, but it was often greater than 100% yield based on the amount of **22** contaminating **27**, suggesting a methyl group shift was occurring. Unfortunately, the 1,2-disubstituted products were never separated from other byproducts due to the similarities in polarity, so isolated yields were never obtained. Although 1,2-disubstituted vinyl boronates were not formed by CM when groups larger than methyl were in the α-position, migration of the alkyl group from the α-position to the β-position was observed in up to 20% yield.[16] That observation supports an isomerization pathway leading to the impurities, but the mechanism by which the alkyl group migrates is not known.

In an attempt to discover whether **27** was undergoing a methyl group loss (to form **19**) or migration (to form **22**), it was exposed to catalyst **2** under the normal reaction

conditions. After 12 h, the major component of the reaction mixture was **27**. Only 3% of **22** was present, and no **19** was observed. Interestingly, compound **42** was present in 5% relative to **27**, but no **41** had formed. Presumably **42** originates from the reaction of either **22** or **19** with the benzylidene on catalyst **2**. The fact that no **41** was formed suggests that catalyst **2** reacts much more readily with terminal or 1,2-disubstituted vinyl boronates than with 1,1-disubstituted vinyl boronates. The small amount of **22** and **42** in this reaction (8%, more than the expected 5% based on the contamination of **27**) suggests that methyl group migration can occur and is dependent on the cross partner.

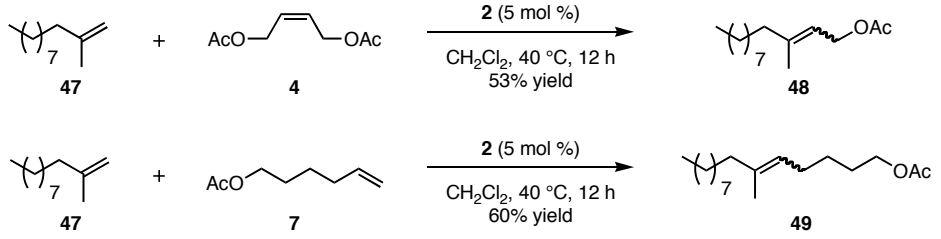
In addition to methyl and alkyl group migrations, olefin isomerization was also observed. For example, when both allylbenzene (**28**) and vinylcyclohexane (**31**) were used as cross partners, products arising from alkene-isomerization and/or methyl migration CM were observed (Scheme 2.9). In the reaction of vinylcyclopentane (**32**) with **27**, a mixture of products analogous to those obtained with vinylcyclohexane (**31**) was formed. A ruthenium hydride, formed by catalyst decomposition, could have caused the olefin isomerizations.[17]



Scheme 2.9. Complex product mixture arising from olefin isomerizations and methyl migrations.

It was not completely surprising that these reactions were plagued by low yields and complications. Although catalyst **2** is one of the most reactive, ruthenium-based,

olefin metathesis catalysts known, it does not readily catalyze the synthesis of trisubstituted alkenes by CM. In cases where trisubstituted olefins are formed, at least one of the substituents on the 1,1-disubstituted alkene is a methyl group (Scheme 2.10).[18] There are certain examples where trisubstituted olefins are formed in yields ≥80%, but typically it is not a reliable reaction and has not found widespread use in synthetic organic chemistry. In order for this reaction to become practical, a more active olefin metathesis catalyst is needed.



Scheme 2.10. CM reactions to form trisubstituted olefins.

Conclusion

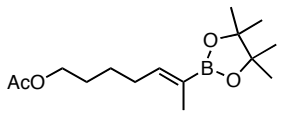
Vinyl boronates are versatile functional groups that can take part in many powerful synthetic transformations, and cross-metathesis (CM) is a mild, efficient way to make 1,2-disubstituted vinyl boronates. Because current approaches to the formation of trisubstituted vinyl boronates suffer from regioselectivity issues, CM with 1,1-disubstituted vinyl boronates was explored as an alternative route. In some instances the desired products were formed in 58%–60% yield, but many reactions were plagued by low yields and complicated product mixtures, including alkyl group migrations and olefin isomerizations. The lack of success found here illustrates the need for a more active olefin metathesis catalyst that can form trisubstituted alkenes efficiently.

Experimental

General Experimental. NMR spectra were recorded on an Oxford 300 MHz NMR spectrometer running Varian VNMR software. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext), multiplet (m), and broad (br). Spectroscopic data are provided for the major olefin isomer. For all vinylboronates reported the ^{13}C peak of the α-carbon is not observed due to the large quadrupolar effect of the attached boron nucleus.

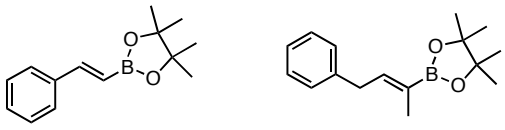
Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed with standard potassium permanganate stain or UV light. Flash column chromatography was performed using silica gel 60 (230–400 mesh). All glassware was either oven dried or flame dried, and reactions were done under an atmosphere of argon. All commercial chemicals were used as obtained except 1,4-diacetoxy-*cis*-2-butene (**4**), which was distilled from CaH_2. Benzene, methylene chloride, diethyl ether, and THF were dried by passage through solvent columns containing activated alumina.

General Cross-metathesis Procedure. To a solution of **2** (5 mol %) in CH_2Cl_2 (0.2 M in substrate) was added **27** (1 equiv) and cross partner (0.5–2 equiv), and the reaction stirred at 40 °C for 12 h. After rotary evaporation of the solvent, the remaining residue was purified by flash chromatography to afford the desired product (often as a mixture with other compounds).



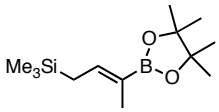
50

(*Z*)-6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-enyl acetate (50). Following the general procedure, **27** (100 mg, 0.60 mmol), **7** (48 μL, 42 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 49 mg (58% yield, >20:1 *Z*:*E*) of **50** (5% ethyl acetate in hexanes) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.28 (dt, J = 7.0, 1.6 Hz, 1H), 4.05 (t, J = 6.6 Hz, 2H), 2.14 (q, J = 7.4 Hz, 2H), 2.03 (s, 3H), 1.59–1.69 (m, 2H), 1.66 (s, 3H), 1.43–1.51 (m, 2H), 1.25 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.4, 145.8, 83.3, 64.6, 28.5, 28.3, 25.3, 25.0, 21.2, 14.1.



42 **43**

(*Z*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (43). Following the general procedure, **27** (50 mg, 0.30 mmol), **28** (79 μL, 70 mg, 0.60 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 45 mg (59% yield, 7:1 *Z*:*E*) of **43** (3% ethyl acetate in hexanes) as a mixture with unreacted **27** and **42** (**43**:**27**:**42** = 5.5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): (*Z*-isomer δ 7.17–7.32 (m, 5H), 6.49 (dt, J = 6.9, 1.6 Hz, 1H), 3.49 (d, J = 7.1 Hz, 2H), 1.82 (d, J = 0.8 Hz, 3H), 1.26 (s, 12H); **42**: 6.18 (d, J = 18.6, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 144.4, 140.7, 128.9, 128.6, 126.1, 83.4, 35.3, 25.0, 14.2.



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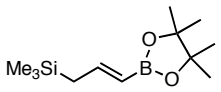
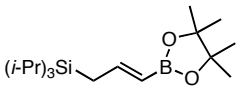
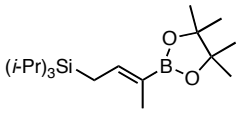


52

(*Z*)-Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enyl)silane (51). Following the general procedure, **27** (50 mg, 0.30 mmol), **29** (47 μL, 34 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1 mL CH_2Cl_2 afforded 45 mg (59% yield, >20:1 *Z*:*E*) of **51** (2% ethyl acetate in hexanes) as a mixture with unreacted **27** and **52** (**51**:**27**:**52** = 3.4:1:0.4). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.44 (tq, J = 8.8, 1.6 Hz, 1H), 1.66 (d, J = 8.8 Hz, 2H), 1.62–1.63 (m, 3H), 1.25 (s, 12H), 0.02 (s, 9H); **52**: 6.66 (dt, J = 18.0, 8.1 Hz, 1H).

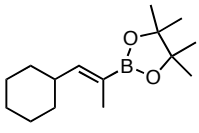


21

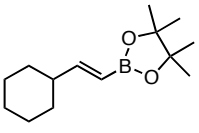


53

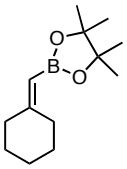
(*Z*)-Triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enyl)silane (53). Following the general procedure, **27** (50 mg, 0.30 mmol), **30** (72 μL, 59 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 60 mg (60% yield, >20:1 *Z*:*E*) of **53** (2.5% ethyl acetate in hexanes) as a mixture with unreacted **27** and **21** (**53**:**27**:**21** = 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.53 (tq, J = 8.8, 1.6 Hz, 1H). 1.72 (d, J = 8.9 Hz, 2H), 1.69 (d, J = 1.6 Hz, 3H), 1.23 (s, 12H), 1.04 (s, 18H); **21**: 6.75 (dt, J = 17.9, 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 144.6, 83.0, 24.9, 18.9, 14.0, 13.9, 11.5.



44

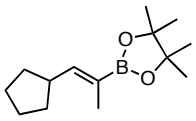


45

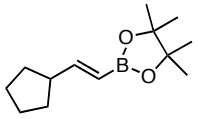


46

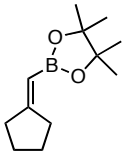
(*Z*)-2-(1-Cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (44). Following the general procedure, **27** (50 mg, 0.30 mmol), **31** (41 μL, 33 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 33 mg (44% yield, >20:1 *Z*:*E*) of **44** (2% ethyl acetate in hexanes) as a mixture with unreacted **27**, **45**, and **46** (**44**:**27**:**45**:**46** = 3.3:1:0.8:0.2). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.12 (dd, J = 8.8, 1.6 Hz, 1H), 1.68 (d, J = 1.6, 3H), 1.58–1.74 (m) 1.03–1.34 (m), 1.26 (s, 12H); **45**: 6.58 (dd, J = 18.1, 6.6 Hz, 1H); **46**: 5.01 (s, 1H).



54

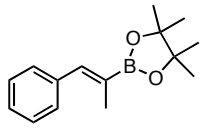


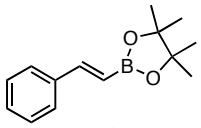
55



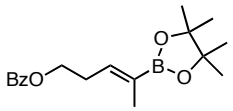
56

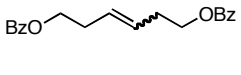
(*Z*)-2-(1-Cyclopentylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (54). Following the general procedure, **27** (50 mg, 0.30 mmol), **32** (41 μL, 29 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 10 mg (14% yield, >20:1 *Z*:*E*) of **54** (2% ethyl acetate in hexanes) as a mixture with unreacted **27**, **55**, and **56** (**54**:**27**:**55**:**56** = 1:3:0.4:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.24 (tq, J = 8.8, 1.6 Hz, 1H), 1.70 (d, J = 1.6 Hz, 3H), 1.50–1.80 (m), 1.20–1.28 (m), 1.25 (s, 12H); **55**: 6.61 (dd, J = 18.1, 7.1 Hz, 1H); **56**: 5.27 (quint, J = 1.6 Hz, 1H).


41

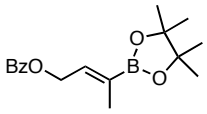

42

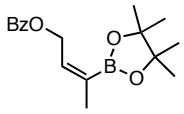
(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (41). Following the general procedure, **27** (50 mg, 0.30 mmol), **33** (68 μL, 62 mg, 0.60 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 25 mg (34% yield, >20:1 *Z*:*E*) of **41** (2% ethyl acetate in hexanes) as a mixture with unreacted **27** and **42** (**41**:**27**:**42** = 1.4:1:0.5). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.21–7.40 (m, 6H), 2.00 (d, J = 1.6 Hz, 3H), 1.28 (s, 12H); **42**: 6.17 (d, J = 18.4 Hz, 1H).


57


58

(*Z*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enyl benzoate (57). Following the general procedure, **27** (50 mg, 0.30 mmol), **34** (50 μL, 52 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded 43 mg (46% yield, >20:1 *Z*:*E*) of **57** (5% ethyl acetate in hexanes) as a mixture with **58** (**57**:**58** = 1:0.24). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.00–8.06 (m, 2H), 7.51–7.58 (m, 1H), 7.39–7.46 (m, 2H), 6.36 (tq, J = 7.1 Hz, 1.6 Hz, 1H), 4.36 (d, J = 7.1 Hz, 2H), 2.62 (observed q (actually a dt), J = 7.1 Hz, 2H), 1.75 (br s, 3H), 1.26 (s, 12H); **58**: 5.64–5.66 (m, 2H).


Z-59


E-59

(*Z* and *E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enyl benzoate (*Z*-59) and (*E*-59). Following the general procedure, **27** (100 mg, 0.60 mmol), **35** (88 mg, 0.30 mmol), and **2** (12.6 mg, 0.015 mmol) in 1.5 mL CH_2Cl_2 afforded a total of 46 mg

(30% yield, 2:1 *Z*:*E*) of ***Z*-59** and ***E*-59** (4% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) ***Z*-59**: δ 8.05–8.08 (m, 2H), 7.53–7.59 (m, 1H), 7.41–7.46 (m, 2H), 6.47 (tq, J = 5.9, 1.8 Hz, 1H), 4.98 (dd, J = 5.9, 0.9 Hz, 2H), 1.81 (dd, J = 1.8, 0.9 Hz, 3H), 1.28 (s, 12H); ***E*-59**: 8.05–8.08 (m, 2H), 7.52–7.57 (m, 1H), 7.41–7.46 (m, 2H), 6.26 (t, J = 5.9 Hz, 1H), 5.13 (dd, J = 6.4, 1.4 Hz, 2H), 1.86 (d, J = 1.4 Hz, 3H), 1.30 (s, 12H).

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