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Vinylic C–H Borylation of Cyclic Vinyl Ethers with Bis(pinacolato)diboron Catalyzed by an Iridium(I)-dtbpy Complex

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Abstract: Borylation of the vinylic C–H bond of 1,4-dioxene, 2,3-dihydrofuran, 3,4-dihydro-2H-pyran and their γ-substituted analogs was carried out in the presence of bis(pinacolato)diboron (B_2pin_2) and a catalytic amount of Ir^I-dtbpy (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) complex. The two boron atoms in B_2pin_2 participated in the coupling, thus giving two equivalents of the coupling product from one equivalent of B_2pin_2. The borylation of 1,4-dioxene in hexane resulted in 81% yield at room temperature. The borylation of 2,3-dihydrofurans at 80 °C in octane suffered from low regioselectivity, and gave a mixture of α- and β-coupling products even for hindered γ-disubstituted analogs, but γ-substituted analogs of 3,4-dihydro-2H-pyran achieved high α-selectivity, giving single coupling products. This protocol was applied to the syntheses of a key precursor of vineomycinone B2 methyl ester and other C-substituted D-glucals by borylation of protected D-glucals with B_2pin_2 to give α-boryl glucal followed by cross-coupling with haloarenes, benzyl bromide, and allyl bromide. A catalytic cycle that involves the oxidative addition of sp^2 C–H bond to iridium(III)-trisboryl intermediate as the rate-determining step has been proposed.

Keywords: boron · C–H activation · cross-coupling · iridium · regioselectivity

Introduction

Organoboron derivatives are an important class of compounds that have been utilized as synthetic intermediates, functional molecules, functional polymers, ^{10}B carriers for neutron capture therapy, and biologically active compounds.[1] Traditional methods for their synthesis are based on the reactions of trialkylborates with organo-lithium or -magnesium compounds with $B(OR)_3$.[2] Pd-catalyzed cross-coupling of aryl and vinyl halides or allyl acetates with bis(pinacolato)diboron (B_2pin_2)[3] or pinacolborane (HBpin, pin = $O_2C_2Me_4$)[4] is a milder variant for most of the functional groups. Transition metal-catalyzed C–H borylation of alkanes and arenes with HBpin or B_2pin_2, studied extensively by Hartwig,[5] Marder,[6] and Smith,[7] is highly attractive as a direct, economical, and environmentally benign process to synthesize organoboronic esters without using any halogenated starting materials. Among the catalysts developed to date, we have demonstrated the efficiency of an [Ir(OMe)(cod)]$_2$-dtbpy (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) catalyst which allowed stoichiometric borylation of arenes at room temperature[8–11] and silylation of arenes at 120 °C.[12] However, a simple extension of this protocol to vinylic C–H borylation of typical alkenes resulted in the formation of a complex mixture of boron compounds.[13] The reaction of rhodium(I) or iridium(I) complexes ([M]-X′) with catecholborane (HBcat), HBpin, or B_2pin_2 yields several species that are effective for catalyzed hydroboration of alkenes and alkynes (**2**, X = H),[14] dehydrogenative coupling with alkenes to give (*E*)-1-alkenylborates (**3**),[15] diboration of alkenes and alkynes (**2**, X = B <),[16]and C–H borylation of arenes (**4**)[5–8] [Eq. (1)]. Thus, the difficulty in achieving selective C–H coupling for alkenes can be attributed to the high ability of typical alkenes for insertion into **2** and **3** prior to the formation of a trisboryl species (**4**) required for C–H activation. Electron-rich alkenes such as vinyl ethers, which are slow towards insertion, can be used as substrates that allow selective vinylic borylation. Although simple vinyl ethers such as butyl vinyl ether resulted in around 30% of (*E*)-BuOCH=CHBpin along with several boron-containing byproducts, cyclic vinyl ethers were found to be the best substrates for achieving selective coupling at the sp^2 C–H bond.[17]

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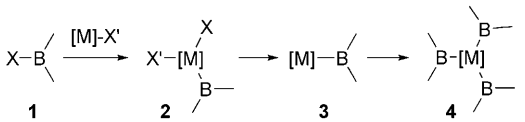
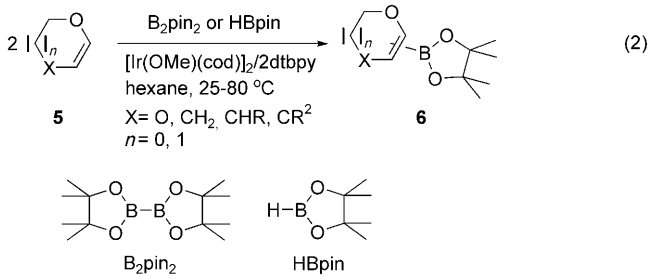


(1)

where X = H, B <; X′ = halogen, OR, alkyl; M = Rh^I, Ir^I.

Borylation of the vinylic C–H bond of five- and six-membered cyclic vinyl ethers such as 1,4-dioxene, 2,3-dihydrofurans, and 3,4-dihydro-2H-pyrans (**5**) with B_2pin_2 and HBpin selectively occurred at the vinylic C–H bond in the presence of an iridium(I)-dtbpy catalyst which gave the best results in aromatic borylation and silylation [Eq. (2)].[8–12] The two boron atoms in B_2pin_2 participated in the coupling, thus allowing the formation of two equivalents of 1-alkenylboronates (**6**) from one molar amount of B_2pin_2. Indeed, HBpin was also effective for borylation of **5**, though B_2pin_2 resulted in much higher yields than those of HBpin. In this paper, we report the effect of the catalysts, scope and limitation, and synthetic applications as well as the mechanism of the catalytic cycle.



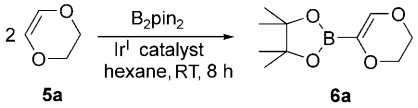
(2)

Results and Discussion

Reaction Conditions

For optimizing the conditions, the reaction between two equivalents of 1,4-dioxene (**6a**) and B_2pin_2 was carried out in hexane for 8 h at 25 °C (Table 1, [Eq. (3)]). The halide (entry 1) and cationic iridium(I) complex (entry 3) did not catalyze the reaction at room temperature, but an iridium(I) complex possessing a methoxy ligand facilitated completion of the reaction within 8 h to provide **6a** as the sole product (entry 2). The high catalyst efficiency of an (alkoxo)iridium complex even at room temperature can be attributed to its more facile conversion into a mono(boryl)iridium complex (**3**), which is the precursor of the tris(boryl)iridium(III) complex (**4**) by oxidative addition of B_2pin_2. Among the bipyridine derivatives employed, dtbpy was a better ligand than unsubstituted bpy because of its high solubility in hydrocarbons (entries 2 and 4). 3,3′-Dimethylbipyridine (**7a**), which features a twist between the two pyridyl units, was not effective (entry 5), and a 6,6′-dimethyl derivative (**7d**) did not promote the reaction at all because of the increased steric hindrance around the iridium metal center (entry 9). The electronic effect showed the superiority of the electron-rich bipyridines containing methyl, methoxy or *tert*-butyl groups at 4,4′-positions (entries 2, 6, and 10) compared to the electron-withdrawing groups (entries 11 and 12), which indicates the enhanced ability of an electron-rich catalyst for C–H oxidative addition.[18] On the other hand, the formation of **6a** in 69% yield with HBpin suggested that both B_2pin_2 and HBpin participate in the catalytic cycle.

Table 1. Effect of catalysts on C–H borylation of 1,4-dioxene.[a]



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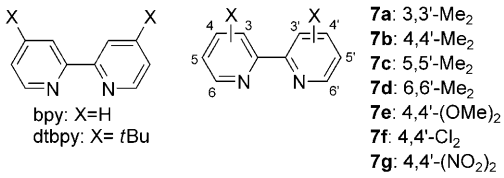


Entry	Ir complex	Ligand	Yield [%][b]
1	$[Ir(Cl)(cod)]_2$	dtbpy	0
2	$[Ir(OMe)(cod)]_2$	dtbpy	81
3	$[Ir(cod)_2]BF_4$	dtbpy	0
4	$[Ir(OMe)(cod)]_2$	bpy	50
5	$[Ir(OMe)(cod)]_2$	**7a**	0
6	$[Ir(OMe)(cod)]_2$	**7b**	75
8	$[Ir(OMe)(cod)]_2$	**7c**	55
9	$[Ir(OMe)(cod)]_2$	**7d**	0
10	$[Ir(OMe)(cod)]_2$	**7e**	71
11	$[Ir(OMe)(cod)]_2$	**7f**	0
12	$[Ir(OMe)(cod)]_2$	**7g**	0
13[c]	$[Ir(OMe)(cod)]_2$	dtbpy	69

[a] A mixture of B_2pin_2 (1 mmol), 1,4-dioxene (2 mmol), iridium complex (0.015 mmol, 3 mol%), and ligand (0.03 mmol, 3 mol%) in hexane (6 mL) was stirred for 8 h at 25 °C. [b] GC yields based on two boron atoms in B_2pin_2. [c] HBpin (1 mmol) was used in place of B_2pin_2.

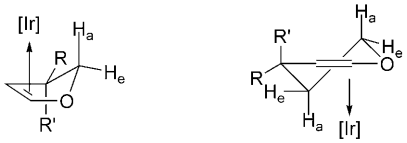
Scope and Limitation

The reactions of cyclic monoethers such as 2,3-dihydrofurans and 3,4-dihydro-2*H*-pyrans were significantly slower than 1,4-dioxene activated by two oxygen atoms. Thus, those reactions were carried out in octane at 80 °C using 3 equivalents of substrates (**5**) in the presence of one equivalent of B_2pin_2 or 1.5 equivalents of HBpin (Table 2). The borylation of dihydrofurans suffered from low regioselectivity, and gave a mixture of α- and β-coupling products even for γ-disubstituted **5d** (entries 1–3). The six-membered dihydropyr-

Abstract in Japanese:

イリジウム(I)-dtbpy触媒存在下でビス（ピナコラート）ジボロンを用いる1,4–ジオキセン、2,3–ジヒドロフラン、3,4–ジヒドロ–2H–ピランおよびこれらのγ–置換誘導体のビニルC–H結合のホウ素化を行った。室温における1,4–ジオキセンのホウ素化は81%収率で進行した。一方、80 °Cにおけるジヒドロフランのホウ素化はα–およびβ–カップリング体を与え位置選択性に欠けるが、γ–置換ジヒドロピランは選択的にα–カップリング体を与える。反応をD-グルカールのホウ素化とそれに続くクロスカップリング反応に応用し、ピネオマイシノンメチルエステルの合成前駆体を合成した。また、反応の律速段階でsp^2 C–H結合がトリス（ボリル）イリジウム（III） 中間体に酸化付加して進行する触媒サイクルを提案した。

ans were much more sensitive to steric hindrance of the substituents than the five-membered rings. Although unsubstituted dihydropyran resulted in a 75:25 selectivity, mono-substitution at the γ-carbon achieved a perfect α-selectivity (entries 4–7). Two models are shown in Equation 4. To avoid steric interaction of the axial R′ and H_a in the upper face of dihydropyrans, the double bond will coordinate from its down face to the iridium metal center in which α-carbon is less hindered than the β-carbon because of the presence of C(5)–H_a (**9**). On the other hand, steric interference at the α- and β-carbons is very small even for disubstituted dihydrofurans when the double bond coordinates from the less-hindered upper face (**8**). Thus, all attempts to improve the regioselectivity of 4-butyl-2,3-dihydrofuran (**5c**) by steric hindrance of bpy analogs were unsuccessful. The use of 1,10-phenathroline ligands possessing 2-methyl, 2-isopropyl, 2-*tert*-butyl, 2,9-dimethyl and 2,9-diisopropyl groups resulted in 61–85% α-selectivity for **5c**.



8 **9** (4)

where R = alkyl; R′ = H or alkyl.

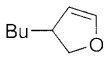
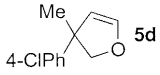
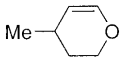
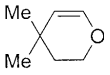
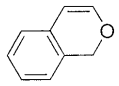
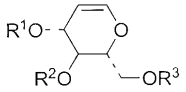
Thus, D-glucals protected by three silyl ethers (**5i** and **5j**), a silyl ether and an acetone acetal (**5k**), and cyclic silyl ether (**5l**), selectively afforded α-coupling products in high yields (entries 8–11). The reactions were carried out for 16 h at 80 °C because of the slow coupling of the greatly hindered glucals. The three substituents, namely at the 3-, 4-, and 5-carbon, will occupy all equatorial positions and thus, the model giving α-coupling products could be the same as that of **9**.

Synthetic Use

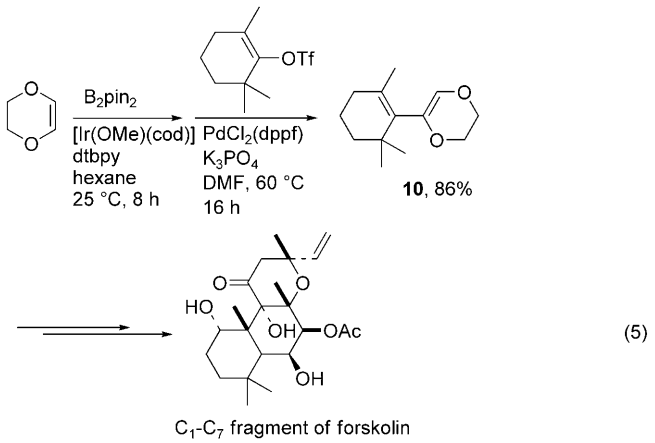
1-Alkenylboron compounds are of great value as reagents for the syntheses of biologically active compounds through C–C bond-forming reactions such as cross-coupling reaction[19] and conjugate addition reactions.[20] Pinacol esters of typical 1-alkenylboronic acids are stable for isolation by chromatography on silica gel; however, α-boryl ether (**6a**) obtained from 1,4-dioxene was very sensitive to hydrolytic protodeboronation. Thus, in situ preparation of **6a** was directly followed by cross-coupling reactions with organic halides without isolation of **6a** [Eq. (5)]. Diene **10**, the starting material previously used for the synthesis of the C1–C7 fragment of forskolin,[21] was obtained by a one-pot, two-step reaction when borylation of 1,4-dioxene (entry 2 in Table 1) was directly followed by the cross-coupling reaction. The preparation of 1.5 equivalents of **6a** toward vinyl triflate resulted in 64% yield because of competitive C–B bond cleavage, but the use of two equivalents of **6a** finally achieved 86% yield of **10**.

C-Glucals are an important class of compounds because of the frequent occurrence of these fragments in natural products.[22,23] A key skeleton (**13**) used as a precursor of vimeomycinone B2 methyl ester[23] was synthesized in 83% yield when the preparation of 1.1 equivalents of **12** was directly followed by cross-coupling reaction [Eq. (6)]. The syntheses of other C-aryl, C-benzyl, and C-allyl glucals also took place smoothly for 2-methylbromobenzene (81%), 4-bromoanisole (87%), 2-bromothiophene (87%), 1-bromocyclohexene (82%), benzyl bromide (85%), and allyl bromide (78%).

Table 2. C–H borylation of cyclic vinyl ethers [Eq. (2)].[a]

Entry	Cyclic vinyl ether	Product No.	Yield [%][b] (α/β)	Yield [%][c] (α/β)
1	 **5b**	**6b**	75 (49:51)	
2	 **5c**	**6c**	71 (86:14)	
3	 **5d**	**6d**	73 (95:5)	
4	 **5e**	**6e**	64 (75:25)	36 (69:31)
5	 **5f**	**6f**	61(100:0)	30 (100:0)
6	 **5g**	**6g**	65 (100:0)	
7	 **5h**	**6h**	81 (100:0)	55 (100:0)
8[d]	 **5i**: R^1, R^2, R^3 = TBS	**6i**	72 (100:0)	
9[d]	**5j**: R^1, R^2, R^3 = TIPS	**6j**	80 (100:0)	
10[d]	**5k**: R^1 = TIPS R^2, R^3 = CMe2	**6k**	74 (100:0)	
11[d]	**5l**: R^1 = TIPS R^2, R^3 = Si(*t*Bu)$_2$	**6l**	80 (100:0)	61 (100:0)

[a] A mixture of vinyl ether (3 mmol), $[Ir(OMe)(cod)]_2$ (0.015 mmol, 3 mol%), dtbpy (0.03 mmol, 3 mol%) and B_2pin_2 (1 mmol) or HBpin (1.5 mmol) in octane (6 mL) was stirred at 80 °C for 8 h in a sealed tube. [b] GC yields based on two boron atoms in B_2pin_2. [c] GC yields based on HBpin. [d] For 16 h.



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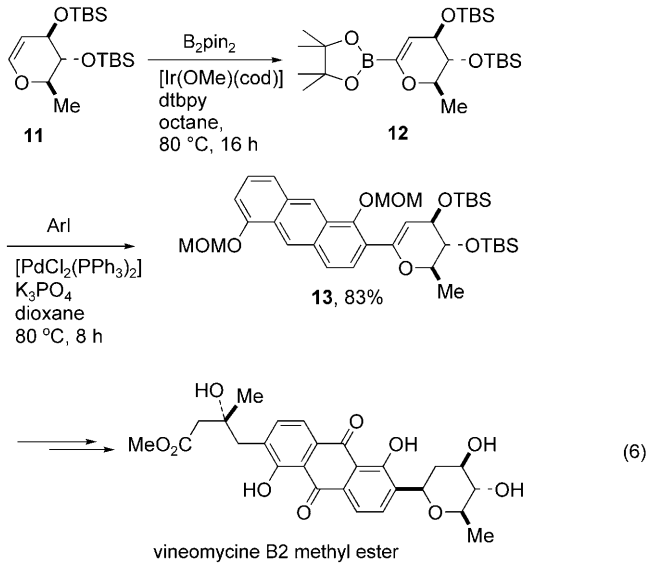


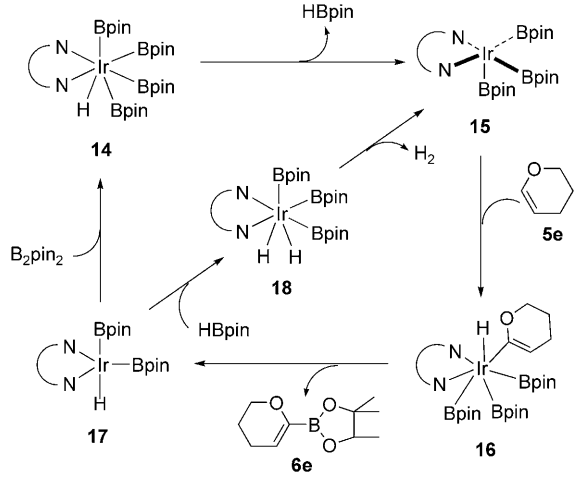
(6)

where ArI = 2-iodo-1,5-bis(methoxymethoxy)anthracene.

Catalytic Cycle

It is well-known that the catalytic cycle of C–H borylation of alkanes and arenes involve oxidative addition of a C–H bond to (boryl)metal species such as **4**, obtained from [M]-X′ and HBpin or B_2pin_2 [Eq. (1)]. The synthesis, characterization, bonding, and reactivity of these catalytically important species have been reviewed.[24] There have also been extensive theoretical studies on the M–B bond and its role in catalytic cycles.[25] The formation of monoboryl and trisboryl rhodium and iridium complexes (**2**, **3**) from interaction between [Ir(η^5-C_9H_7)(cod)] and HBpin or catecholborane,[26] or [Rh(Me)(PMe_3)$_3$] and B_2pin_2[27] was first reported by Marder. Among these iridium(I) and iridium(III) complexes, *fac*-[Ir(Bpin)$_3$(PMe_3)$_3$] was proposed by Smith as the active component involved in the catalytic cycle of C–H borylation, though both [Ir(Bpin)(PMe_3)$_4$] and *fac*-[Ir(Bpin)$_3$(PMe_3)$_3$] undergo borylation of benzene at room temperature.[7d] Mechanistic studies by Hartwig have also shown that such an Ir^{III}-tris(boryl) complex is an active component in the catalytic cycle.[8a] ^{1}H NMR spectroscopy for the reaction of B_2pin_2 in benzene at a high catalyst loading of 1/2[IrCl(cod)]$_2$/dtbpy showed the formation of a dtbpy-ligated tris(boryl)Ir^{III} complex, which was finally isolated and characterized by X-ray analysis. Thus, iridium(III)-tris(boryl) complexes (**3**) have been shown to be chemically and kinetically competent as an intermediate involved in the catalytic process, which was fully supported by the theoretical calculation of Sakaki.[25]

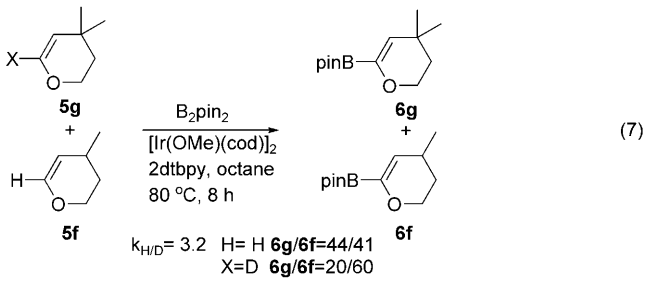
A proposed catalytic cycle analogous to that of aliphatic and aromatic C–H borylation[7d,8f] is shown in Scheme 1. A



Scheme 1. Proposed catalytic cycle.

tris(boryl)Ir^{III} intermediate (**15**) can be first produced by oxidative addition of B_2pin_2 to Ir(Bpin)(dtbpy) generated by oxidative addition/reductive elimination between B_2pin_2 and Ir(OMe)(dtbpy). [Ir(OMe)(cod)]$_2$ is a better precursor than [IrCl(cod)]$_2$, since it smoothly yields Ir(Bpin)(dtbpy) at room temperature because of the higher bond energy of the resulting B–O bond than that of the B–Cl bond. Thus, the catalyst activity parallels the order of basic strength of the anionic ligand on the iridium(I) precursor: MeO > HO > PhO > AcO ≫ Cl.[8c] Oxidative addition of a vinyl ether, such as dihydropyran (**5e**), yields an Ir^V species (**16**) that reductively eliminates a vinylboronate (**6e**). Oxidative addition of B_2pin_2 to **17** can be followed by reductive elimination of HBpin to regenerate **15**. The resulting HBpin may participate in the catalytic cycle through a sequence of oxidative addition to **17** and reductive elimination of **15** and H_2 from an 18-electron Ir^V intermediate (**18**). Along this catalytic cycle, electron donation to the metal center by two nitrogen atoms of a bipyridine ligand, as well as small steric hindrance by a planar bipyridine ligand, three Bpin rings, and an sp^2 C–H bond of **5**, can be crucial for the formation of such sterically hindered hepta-coordinated Ir^V intermediates (**16**) under mild conditions.[8c]

Competitive reactions of an equimolar amount of **5g** (X = H, D) and **5f** suggested the rate-determining role of C–H oxidative addition among the four processes involved in the catalytic cycle [Eq. (7)]. The isotope effect, determined from the yields of **5g** (X = H) and **5g** (X = D), was 3.2, which is similar to the value of 3.6 previously observed in aromatic C–H borylation.[8a] The reaction rate is first-order toward alkene substrates. There was a linear dependency between the concentration of **5g** and the yield of **6g** [Eq. (8)].



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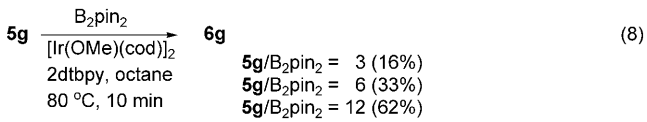
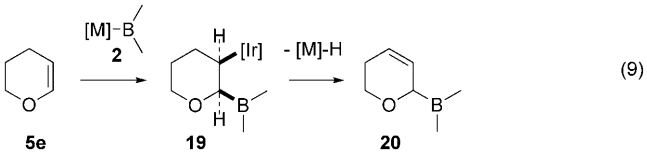


(8)

Another probable catalytic cycle is a sequence that proceeds through insertion of [Ir]-B species (**3**) to the C=C followed by β-hydride elimination. This cycle, which is analogous to Heck coupling, has been used for rhodium-catalyzed borylation of alkenes[15] with HBpin or HBcat [Eq. (9)]. However, this route should be ruled out because of the presence of isotropic effect for **5g** and no formation of **20** for **5e** [Eq. (9)].



(9)

Conclusions

In conclusion, we have demonstrated that one-step borylation of a vinylic C–H bond provides simple access to α-boryl cyclic vinyl ethers including α-boryl glucals, which have traditionally been prepared by transmetalation between lithium reagents and trialkyl borates.[28] Because of the simple experimental procedure under mild conditions, extension of this protocol to other substrates will be the topic of further accounts from this laboratory.

Experimental Section

General Methods

All the experiments were carried out under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded as a $CDCl_3$ solution on a JEOL EX-400 spectrometer (400 or 100 MHz) and Me_4Si or residual protiated solvent was used as the internal standard. High-resolution mass spectra were recorded on a JEOL JMS-DX303 spectrometer. GC analysis was performed on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m).

Materials

Methoxo-1,5-cyclooctadiene iridium(I) dimer,[29a] chloro-1,5-cyclooctadiene iridium(I) dimer,[29b] bis(1,5-cyclooctadiene) iridium(I) tetrafluoroborate,[29c] dichloro [1,1′-bis(diphenylphosphino)ferrocene] palladium,[30a] and dichloro bis(triphenylphosphine) palladium[30b] were prepared by the literature procedure. The preparation of bis(pinacolato)diboron[31a] and pinacolborane[31b] were reported previously. 2,2′-Bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine, 6,6′-dimethyl-2,2′-bipyridine, 4,4′-di-*tert*-butyl-2,2′-bipyridine, and 2,9-dimethylphenanthroline were commercially available. 3,3′-Dimethyl-2,2′-bipyridine,[32a] 4,4′-dimethoxy-2,2′-bipyridine,[32b] 4,4′-dichloro-2,2′-bipyridine,[32b] 4,4′-dinitro-2,2′-bipyridine,[32c] 2-methyl-1,10-phenanthroline,[32d] 2-isopropyl-1,10-phenanthroline,[32d] 2-*tert*-butyl-1,10-phenanthroline,[32d] and 2,9-diisopropyl-1,10-phenanthroline[12c] were prepared by the literature procedure. Hexane, octane, and dioxane were distilled from sodium, and DMF was distilled from molecular sieves before use. 2-methylbromobenzene, 4-bromoanisole, 2-bromothiophen, benzyl bromide, and allyl bromide were commercially available. 1-bromocylohexene,[33a] vinyltriflate,[33b] and aryliodide[33c] were prepared by the literature procedure.1,4-Dioxene, dihydropyran, and dihydrofuran were commercially available. Noncommercially available vinyl ethers[34] and D-glucals[35] were prepared according to literature procedure.

General Procedure for Reaction using Nitrogen Bubbler

A 25 mL-flask equipped with a magnetic stirring bar, a septum inlet, and a condenser connected to a nitrogen bubbler was charged with $[Ir(OMe)(cod)]_2$ (3 mol%, 0.015 mmol), dtbpy (3 mol%, 0.030 mmol), and B_2pin_2 (1.0 mmol) and then flushed with nitrogen. Hexane or octane (6 mL) and substrate (2.0–3.0 mmol) were added, and the mixture was stirred at 80 °C (25 °C for **5a**) for 8–16 h. The product was isolated by kugelrohr distillation to give an analytically pure sample.

The following vinylboranes were prepared by the above general procedure.

6a: 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1,4-dioxine: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.57$ (s, 1H), 4.13–4.10 (m, 2H), 4.07–4.04 (m, 2H), 1.28 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 138.73, 83.74, 65.06, 63.95, 24.60 ppm; MS (EI): *m/z* (%): 212(100) $[M]^+$, 169(17), 126(13); HRMS (EI): *m/z* calcd for $[C_{10}H_{17}BO_4]$: 212.1220; found: 212.1223.

6i: 1,5-Anhydro-2-deoxy-3,4,6-tris-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-*C*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.46$ (dd, $J = 4.3$ Hz, $J = 1.6$ Hz, 1H), 4.07–4.01 (m, 1H), 3.89–3.83 (m, 3H), 3.77 (dd, $J = 11.1$ Hz, $J = 5.0$ Hz, 1H), 1.27 (s, 12H), 0.879 (s, 9H), 0.873 (s, 9H), 0.857 (s, 9H), 0.0841 (s, 3H), 0.0753 (s, 3H), 0.0676 (s, 3H), 0.0637 (s, 3H), 0.044 (s, 3H), 0.0170 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 114.69$, 84.03, 79.10, 69.62, 66.38, 61.06, 26.00, 25.88, 24.75, 24.63, 18.34, 18.08, 18.02, −4.25, −4.40, −4.45, −4.64, −5.21, −5.25 ppm; MS (EI): *m/z* (%): 599-(0.3) $[M-CH_3]^+$, 557(5), 501(2), 425(3), 337(3), 301(22), 171(24), 147(21), 73(100); HRMS (FAB): *m/z* calcd for $[C_{30}H_{63}BO_6Si_3+Na]$: 637.3923; found: 637.3929.

6j: 1,5-Anhydro-2-deoxy-3,4,6-tris-*O*-(triisopropylsilyl)-1-*C*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.58$ (dd, $J = 5.4$ Hz, $J = 1.7$ Hz, 1H), 4.31 (ddd, $J = 7.3$ Hz, $J = 7.3$ Hz, $J = 1.7$ Hz, 1H), 4.13 (d, $J = 1.7$ Hz, 1H), 3.95 (dd, $J = 8.3$ Hz, $J = 8.3$ Hz, 1H), 3.94 (d, $J = 7.3$ Hz, 1H), 3.86 (dd, $J = 10.7$ Hz,

J=5.6 Hz, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 1.10–1.00 ppm (m, 63H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=113.85, 83.93, 79.57, 69.71, 64.93, 61.58, 24.88, 14.17, 18.18, 18.10, 18.09, 18.05, 12.51, 12.37, 11.97 ppm; HRMS (FAB): m/z calcd for $[C_{39}H_{81}BO_6Si_3+Na]$: 763.5332; found: 763.5323.

6k: 1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-(1-methylethylidene)-1-*C*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.45 (d, J=2.0 Hz, 1H), 4.43 (dd, J=7.3 Hz, J=1.9 Hz, 1H), 4.02 (dd, J=11.4 Hz, J=5.9 Hz, 1H), 3.87 (dd, J=11.4 Hz, J=10.2 Hz, 1H), 3.81 (dd, J=10.3 Hz, J=7.8 Hz, 1H), 3.67 (ddd, J=10.8 Hz, J=10.2 Hz, J=5.9 Hz, 1H), 1.48 (s, 3H), 1.38 (s, 3H), 1.27 (s, 12H), 1.14–1.06 ppm (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=119.55, 99.33, 84.36, 72.89, 69.76, 68.30, 62.01, 28.96, 24.68, 24.66, 18.87, 18.06, 17.99, 12.33 ppm; MS (EI): m/z (%): 453(2) $[M-CH_3]^+$, 425(76), 367(74), 311(53), 239(28), 155(27), 101(27), 83(100); HRMS (FAB): m/z calcd for $[C_{24}H_{45}BO_6Si+Na]$: 491.2976; found: 491.2992.

6l: 1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.45 (d, J=2.2 Hz, 1H), 4.42 (dd, J=7.1 Hz, J=2.2 Hz, 1H), 4.26 (dd, J=10.4 Hz, J=4.9 Hz, 1H), 4.00 (dd, J=10.5 Hz, J=10.4 Hz, 1H), 3.99 (dd, J=10.4 Hz, J=7.1 Hz, 1H), 3.77 (ddd, J=10.3, J=10.2 Hz, J=4.8 Hz, 1H), 1.26 (s, 12H), 1.15–1.08 (m, 21H), 1.04 (s, 9H), 0.97 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=119.26, 84.27, 77.20, 72.86, 71.29, 66.23, 27.41, 26.90, 24.67, 24.61, 22.71, 19.80, 18.20, 18.17, 12.49 ppm; MS (EI): m/z (%): 568(0.1) $[M]^+$, 525(2), 355(6), 317(4), 207(100); HRMS (EI): m/z calcd for $[C_{29}H_{57}BO_6Si_2]$: 568.3787; found: 568.3798.

12:1,5-anhydro-2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-*C*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.43 (d, J=2.9 Hz, 1H), 4.10 (ddd, J=5.4 Hz, J=3.4 Hz, J=1.0 Hz, 1H), 3.88 (dq, J=6.8 Hz, J=6.3 Hz, 1H), 3.53 (dd, J=7.3 Hz, J=5.4 Hz, 1H), 1.32 (d, J=6.8 Hz, 3H), 1.28 (s, 6H), 1.27 (s, 6H), 0.91 (s, 9H), 0.88 (s, 9H), 0.12 (s, 3H), 0.096 (s, 3H), 0.094 (s, 3H), 0.073 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=117.12, 84.12, 75.03, 74.74, 70.19, 26.12, 25.98, 24.83, 24.54, 18.20, 18.07, 17.32, −3.58, −3.77, −4.09, −4.19 ppm; MS (EI): m/z (%): 484(0.3) $[M]^+$, 427(54), 313(100), 255(24), 159(20), 147(18.4), 115(33); HRMS (EI): m/z calcd for $[C_{24}H_{49}BO_5Si_2]$: 484.3211; found: 484.3224.

General Procedure for Reaction using Resealable Schlenk Tube

A resealable Schlenk tube containing $[Ir(OMe)(cod)]_2$ (3 mol%, 0.015 mmol), dtbpy (3 mol%, 0.030 mmol), and B_2pin_2 (1.0 mmol) was flushed with nitrogen and then charged with octane (6 mL) and substrate (3.0 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 80 °C for 8 h. The product was isolated by kugelrohr distillation to give an analytically pure sample.

The following vinylboranes were prepared by the above general procedure.

6b: 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-furan: ^{1}H NMR (400 MHz, $CDCl_3$): (α-boryl isomer) δ=5.73 (t, J=2.9 Hz, 1H), 4.32 (t, J=9.8 Hz, 2H), 2.65 (dt, J=10.2 Hz, J=2.9 Hz, 2H), 1.29 ppm (s, 12H); (β-boryl isomer) δ=6.84 (t, J=1.9 Hz, 1H), 4.36 (t, J=9.5 Hz, 2H), 2.68 (dt, J=9.8 Hz, J=2.0 Hz, 2H), 1.26 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (α-boryl isomer) δ=116.55, 84.16, 69.89, 30.85, 24.73 ppm; (β-boryl isomer) δ=158.40, 82.87, 71.54, 30.10, 24.73 ppm. MS (EI): (α-boryl isomer) m/z (%): 196(100) $[M]^+$, 181(21), 151(22), 123(21), 110(16); (β-boryl isomer) m/z (%): 196(100) $[M]^+$, 181(35), 139(29), 123(17), 96(32); HRMS (EI): m/z calcd for $[C_{10}H_{17}BO_3]$: 196.1271; found: 196.1273.

6c: 3-Butyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-furan: ^{1}H NMR (400 MHz, $CDCl_3$): (α-boryl isomer) δ=5.71 (d, J=2.68 Hz, 1H), 4.36 (dd, J=10.0 Hz, J=9.0 Hz, 1H), 3.93 (dd, J=8.8 Hz, J=7.3 Hz, 1H), 3.01–2.91 (m, 1H), 1.46–1.31 (m, 6H), 1.28 (s, 12H), 0.87 ppm (t, J=6.8 Hz, 3H); (β-boryl isomer) δ=6.82 (d, J=1.5 Hz, 1H), 4.33 (t, J=9.3 Hz, 1H), 4.08 (dd, J=8.8 Hz, J=5.6 Hz, 1H), 3.01–2.91 (m, 1H), 1.46–1.31 (m, 6H), 1.25 (s, 12H), 0.87 ppm (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (α-boryl isomer) δ=121.30, 84.19, 75.65, 43.87, 34.66, 29.66, 24.75, 24.66, 22.68, 14.00 ppm; (β-boryl isomer) δ=158.00, 82.64, 66.98, 43.05, 34.75, 29.96, 24.55, 22.85, 14.06 ppm. MS (EI): (α-boryl isomer) m/z (%): 253(56) $[M+1]^+$, 195(71), 151(35), 101(24), 83(100); (β-boryl isomer) m/z (%): 252(100) $[M]^+$, 195(45), 151(21), 83(40); HRMS (EI): m/z calcd for $[C_{14}H_{25}BO_3]$: 252.1897; found: 252.1893.

6d: 3-(4-Chlorophenyl)-3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-furan: ^{1}H NMR (400 MHz, $CDCl_3$): (α-boryl isomer) δ=7.29–7.22 (m, 4H), 5.83 (s, 1H), 4.33–4.23 (m, 2H), 1.51 (s, 3H), 1.33 ppm (s, 12H); (β-boryl isomer) δ=6.97 (s, 1H), 4.01 (t, J=5.4 Hz, 2H), 7.29–7.22 (m, 4H), 6.95 (s, 1H), 4.33–4.23 (m, 2H), 1.61 (s, 3H), 1.27 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (α-boryl isomer) δ=145.42, 132.00, 128.33, 125.38, 84.36, 83.85, 51.28, 26.77, 24.68; (β-boryl isomer) not assigned. MS (EI): (α-boryl isomer) m/z (%): 320(13) $[M]^+$, 305(61), 205(69), 170(35), 141(63), 128(45), 115(100), 89(32); (β-boryl isomer) m/z (%): 320(21) $[M]^+$, 305(100), 205(79), 179(11), 141(10), 115(13), 83(26); HRMS (EI): m/z calcd for $[C_{17}H_{22}BClO_3]$: 320.1351; found: 320.1349.

6e: 6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydro-2*H*-pyran: ^{1}H NMR (400 MHz, $CDCl_3$): (α-boryl isomer) δ=5.58 (t, J=3.9 Hz, 1H), 3.99 (t, J=5.4 Hz, 2H), 2.08–2.03 (m, 2H), 1.98–1.85 (m, 2H), 1.28 ppm (s, 12H); (β-boryl isomer) δ=6.97 (s, 1H), 4.01 (t, J=5.4 Hz, 2H), 2.08–2.03 (m, 2H), 1.98–1.85 (m, 2H), 1.24 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (α-boryl isomer) δ=116.42, 83.91, 65.58, 24.68, 22.11, 20.66 ppm; (β-boryl isomer) δ=155.06, 82.63, 66.19, 24.68, 22.20, 20.11. MS (EI): (α-boryl isomer) m/z (%): 211(100) $[M+1]^+$, 193-(0.8), 167(15), 153(16), 137(0.7), 109(10), 83(16); (β-boryl isomer) m/z (%): 210(100) $[M]^+$, 195(16), 151(11), 137(13), 124(41), 109(30), 83(18); HRMS (EI): m/z calcd for $[C_{11}H_{19}BO_3]$: 210.1427; found: 210.1410.

6f: 4-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydro-2*H*-pyran: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.47 (d, J=2.7 Hz, 1H), 4.03 (ddd, J=10.9 Hz, J=6.0 Hz, J=3.2 Hz, 1H), 3.92 (ddd, J=10.9 Hz, J=8.7 Hz, J=2.5 Hz, 1H), 2.33–2.26 (m, 1H), 1.92–1.84 (m, 1H), 1.53–1.43 (m, 1H), 1.28 (s, 12H), 1.01 ppm (d, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=122.53, 83.99, 64.30, 30.49, 25.96, 24.80, 24.64, 21.38 ppm; MS (EI): m/z (%): 224(47) $[M]^+$, 209(100), 124(35), 83(45); HRMS (EI): m/z calcd for $[C_{12}H_{21}BO_3]$: 224.1584; found: 224.1583.

6g: 4,4-Dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydro-2*H*-pyran: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.40 (s, 1H), 3.97 (ddd, J=5.4 Hz, J=4.2 Hz, J=1.5 Hz, 2H), 1.62 (ddd, J=5.6 Hz, J=5.4 Hz, J=1.0 Hz, 2H), 1.29 (s, 12H), 1.05 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=126.84, 83.99, 62.89, 36.84, 29.99, 28.31, 24.73 ppm; MS (EI): m/z (%): 238(12) $[M]^+$, 223(100), 141(20); HRMS (EI): m/z calcd for $[C_{13}H_{23}BO_3]$: 238.1740; found: 238.1737.

6h: 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-isochromene: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.21 (dd, J=5.8 Hz, J=2.4 Hz, 1H), 7.20 (dd, J=5.9 Hz, J=2.2 Hz, 1H), 7.04–6.98 (m, 2H), 6.57 (s, 1H), 5.05 (s, 2H), 1.33 ppm (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=129.63, 129.41, 128.04, 127.87, 123.99, 123.72, 118.50, 84.40, 67.58, 24.73 ppm; MS (EI): m/z (%): 258(100) $[M]^+$, 201(13), 175(16), 157(16), 129(32); HRMS (EI): m/z calcd for $[C_{15}H_{19}BO_3]$: 258.1427; found: 258.1421.

Competition Experiments

A resealable Schlenk tube containing $[Ir(OMe)(cod)]_2$ (3 mol%, 0.015 mmol), dtbpy (3 mol%, 0.030 mmol), and B_2pin_2 (1.0 mmol) was flushed with nitrogen and then charged with octane (6 mL), **5g** (X=H or D, 10.0 mmol), and **5f** (10.0 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 80 °C for 8 h. Volatile materials were removed under reduced pressure and mesitylene (0.33 mmol) was added as an internal standard. The resulting mixture was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$.

Reaction Order Experiments

A resealable Schlenk tube containing $[Ir(OMe)(cod)]_2$ (3 mol%, 0.015 mmol), dtbpy (3 mol%, 0.030 mmol), and B_2pin_2 (1.0 mmol) was flushed with nitrogen and then charged with octane (6 mL) and **5g** (3.0–12.0 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 80 °C for 10 min. Tridecane (100 μL) was then added to the resulting mixture as an internal standard, and analyzed by GC.

One-pot Synthesis of Conjugated Dienyl Ether

A 25 mL-flask equipped with a magnetic stirring bar, a septum inlet, and a condenser connected to a nitrogen bubbler was charged with [Ir(OMe)(cod)]$_2$ (3 mol%, 0.018 mmol), dtbpy (3 mol%, 0.036 mmol), and B_2pin_2 (1.2 mmol) and then flushed with nitrogen. Hexane (2 mL) and 1,4-dioxene (2.4 mmol) were added, and the mixture was stirred at 25°C for 8 h to give a solution of the corresponding boronate. To this solution $PdCl_2$(dppf) (3 mol%, 0.03 mmol), K_3PO_4 (3.0 mmol), DMF (4 mL), and triflate (1.0 mmol) were added. The resulting mixture was then stirred at 60°C for 16 h. The product was extracted by ether, washed with water, and dried over $MgSO_4$. Column chromatography over silica gel provided analytically pure sample.

One-pot Synthesis of C-Aryl Glucal

A 25 mL-flask equipped with a magnetic stirring bar, a septum inlet, and a condenser connected to a nitrogen bubbler was charged with [Ir(OMe)(cod)]$_2$ (3 mol%, 0.011 mmol), dtbpy (3 mol%, 0.022 mmol), and B_2pin_2 (0.72 mmol) and then flushed with nitrogen. Octane (2 mL) and **11** (2.2 mmol) were added, and the mixture was stirred at 80°C for 16 h to give a solution of corresponding boronate. To this solution $PdCl_2(PPh_3)$ (3 mol%, 0.03 mmol), K_3PO_4 (3.0 mmol), dioxane (4 mL), and iodide (1.0 mmol) were added. The resulting mixture was then stirred at 80°C for 8 h. The product was extracted by ether, washed with water, and dried over $MgSO_4$. Column chromatography over silica gel provided analytically pure sample.

General Procedure for One-pot Synthesis of C-Aryl Glucals with Various Bromides.

A 25 mL-flask equipped with a magnetic stirring bar, a septum inlet, and a condenser connected to a nitrogen bubbler was charged with [Ir(OMe)(cod)]$_2$ (3 mol%, 0.010 mmol), dtbpy (3 mol%, 0.020 mmol), and B_2pin_2 (0.69 mmol) and then flushed with nitrogen. Octane (2 mL) and **51** (2.1 mmol) were added, and the mixture was stirred at 80°C for 16 h to give a solution of the corresponding boronate. To this solution $PdCl_2(PPh_3)$ (3 mol%, 0.03 mmol), K_3PO_4 (3.0 mmol), dioxane (4 mL), and bromide (1.0 mmol) were added. Resulting mixture was then stirred at 80°C for 8 h. The product was isolated by kugelrohr distillation to give an analytically pure sample.

The following vinylboranes were prepared by the above general procedure.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-(2-methlphenyl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.31 (dd, J=6.4 Hz, J=2.0 Hz, 1H), 7.23 (ddd, J=7.8 Hz, J=6.3 Hz, J=2.0 Hz, 1H), 7.16 (d, J=7.3 Hz, 1H), 7.15 (dd, J=7.3 Hz, J=6.3 Hz, 1H), 4.82 (d, J=2.4 Hz, 1H), 4.57 (dd, J=6.8 Hz, J=2.4 Hz, 1H), 4.22 (dd, J=9.3 Hz, J=3.9 Hz, 1H), 4.13 (dd, J=9.8 Hz, J=6.8 Hz, 1H), 4.04 (dd, J=10.2 Hz, J=8.8 Hz, 1H), 3.99 (ddd, J=10.3 Hz, J=9.8 Hz, J=4.4 Hz, 1H), 2.35 (s, 3H), 1.20–1.10 (m, 21H), 1.09 (s, 9H), 1.02 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.85, 136.56, 134.89, 130.40, 129.00, 128.74, 125.58, 104.92, 77.63, 73.08, 71.73, 66.12, 27.50, 26.99, 22.78, 20.25, 19.87, 18.18, 12.47 ppm; MS (EI): *m*/*z* (%): 532(0.7) $[M]^+$, 489(10), 319(22), 171(100); HRMS (EI): *m*/*z* calcd for $[C_{30}H_{52}O_4Si_2]$: 532.3404; found: 532.3414.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] −1-*C*-(4-methoxyphenyl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45 (d, J=8.3 Hz, 2H), 6.85 (d, J=8.8 Hz, 2H), 5.12 (d, J=2.0 Hz, 1H), 4.58 (dd, J=6.8 Hz, J=2.0 Hz, 1H), 4.31 (dd, J=10.2 Hz, J=4.9 Hz, 1H), 4.10 (dd, J=10.2 Hz, J=9.8 Hz, 1H), 4.09 (dd, J=10.6 Hz, J=6.8 Hz, 1H), 3.97 (ddd, J=10.6 Hz, J=10.2 Hz, J=4.9 Hz, 1H), 3.81 (s, 3H), 1.21–1.13 (m, 21H), 1.08 (s, 9H), 1.02 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.95, 150.86, 126.83, 113.53, 99.63, 77.60, 72.89, 71.81, 66.14, 55.26, 27.46, 26.95, 22.76, 19.87, 18.20, 18.18, 12.50 ppm; MS (EI): *m*/*z* (%): 548(5) $[M]^+$, 539(11), 521(13), 505(9), 399(11), 375(16), 335(32), 291(20), 187(53), 135(100); HRMS (EI): *m*/*z* calcd for $[C_{30}H_{52}O_5Si_2]$: 548.3353; found: 548.3343.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-(2-thiophenyl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.21 (dd, J=4.9 Hz, J=1.0 Hz, 1H), 7.16 (dd, J=3.9 Hz, J=1.0 Hz, 1H), 6.97 (dd, J=5.4 Hz, J=3.8 Hz, 1H), 5.17 (d, J=2.4 Hz, 1H), 4.55 (dd, J=6.8 Hz, J=2.4 Hz, 1H), 4.29 (dd, J=10.3 Hz, J=4.9 Hz, 1H), 4.10 (dd, J=10.3 Hz, J=6.8 Hz, 1H), 4.09 (dd, J=10.2 Hz, J=9.8 Hz, 1H), 3.99 (ddd, J=10.3 Hz, J=10.2 Hz, J=4.4 Hz, 1H), 1.19–1.11 (m, 21H), 1.08 (s, 9H), 1.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.82, 137.89, 127.21, 125.35, 124.12, 100.63, 77.45, 73.15, 71.50, 65.98, 27.45, 26.94, 22.76, 19.87, 18.17, 18.14, 12.47 ppm; MS (EI): *m*/*z* (%): 524() $[M]^+$, 499(12), 481(23), 351(17), 311(49), 201(17), 163(100), 111(81); HRMS (EI): *m*/*z* calcd for $[C_{27}H_{48}SO_4Si_2]$: 524.2812; found: 524.2798.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-(1-cyclohexenyl)-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.19 (t, J=3.9 Hz, 1H), 4.73 (d, J=2.0 Hz, 1H), 4.48 (dd, J=6.8 Hz, J=1.7 Hz, 1H), 4.22 (dd, J=10.2 Hz, J=4.9 Hz, 1H), 4.03 (dd, J=10.3 Hz, J=10.2 Hz, 1H), 3.99 (dd, J=10.2 Hz, J=7.3 Hz, 1H), 3.82 (ddd, J=10.3 Hz, J=10.2 Hz, J=4.9 Hz, 1H), 2.16–2.06 (m, 4H), 1.72–1.62 (m, 2H), 1.62–1.52 (m, 2H), 1.17–1.09 (m, 21H), 1.06 (s, 9H), 0.98 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.47, 129.90, 125.77, 99.90, 77.68, 72.48, 71.92, 66.17, 27.43, 26.93, 25.35, 24.45, 22.73, 22.59, 22.03, 19.85, 18.16, 18.13, 12.46 ppm; MS (EI): *m*/*z* (%): 522(4) $[M]^+$, 495(10), 479(8), 399(9), 177(27), 161(100); HRMS (EI): *m*/*z* calcd for $[C_{29}H_{54}O_4Si_2]$: 522.3560; found: 522.3564.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-benzyl-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.28 (dd, J=7.8 Hz, J=7.3 Hz, 2H), 7.22 (d, J=7.8 Hz, 1H), 7.21 (d, J=8.2 Hz, 2H), 4.41 (d, J=1.0 Hz, 1H), 4.38 (dd, J=6.8 Hz, J=1.0 Hz, 1H), 4.13 (dd, J=10.2 Hz, J=4.9 Hz, 1H), 3.98 (dd, J=10.7 Hz, J=6.8 Hz, 1H), 3.94 (dd, J=10.8 Hz, J=10.2 Hz, 1H), 3.77 (ddd, J=10.3 Hz, J=10.2 Hz, J=4.9 Hz, 1H), 3.28 (s, 2H), 1.10–1.03 (m, 21H), 1.05 (s, 9H), 0.97 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.33, 137.53, 128.95, 126.42, 102.22, 77.59, 72.85, 71.43, 66.11, 39.49, 27.46, 26.93, 22.72, 19.82, 18.10, 18.08, 12.38 ppm; MS (EI): *m*/*z* (%): 532(1) $[M]^+$, 489(7), 319(15), 171(100); HRMS (EI): *m*/*z* calcd for $[C_{30}H_{52}O_4Si_2]$: 532.3404; found: 532.3403.

1,5-Anhydro-2-deoxy-3-*O*-(triisopropylsilyl)-4,6-*O*-[bis(1,1-dimethylethyl)silylene] -1-*C*-allyl-D-arabino-hex-1-enitol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.79 (dddd, J=17.1 Hz, J=10.24 Hz, J=6.8 Hz, J=6.8 Hz, 1H), 5.09 (dddd, J=17.1 Hz, J=2.0 Hz, J=1.5 Hz, J=1.5 Hz, 1H), 5.07 (dddd, J=8.3 Hz, J=1.5 Hz, J=1.5 Hz, J=1.4 Hz, 1H), 4.48 (d, J=2.0 Hz, 1H), 4.40 (dddd, J=6.8 Hz, J=2.0 Hz, J=1.5 Hz, J=1.4 Hz, 1H), 4.16 (dd, J=10.2 Hz, J=5.4 Hz, 1H), 3.97 (dd, J=10.2 Hz, J=6.8 Hz, 1H), 3.96 (dd, J=10.7 Hz, J=10.3 Hz, 1H), 2.76–2.70 (m, 2H), 1.14–1.08 (m, 21H), 1.06 (s, 9H), 0.98 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.64, 133.61, 117.09, 101.01, 77.63, 72.79, 71.45, 66.14, 37.41, 27.46, 22.73, 19.85, 18.16, 18.14, 12.45 ppm; MS (EI): *m*/*z* (%): 482(0.7) $[M]^+$, 457(1), 439(11), 269(14), 121(100); HRMS (EI): *m*/*z* calcd for $[C_{26}H_{50}O_4Si_2]$: 482.3247; found: 482.3250.

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