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Selective Synthesis of Multisubstituted Olefins Utilizing *gem*- and *vic*-Diborylated Vinylsilanes Prepared by Silylborylation of an Alkynylboronate and Diborylation of Alkynylsilanes

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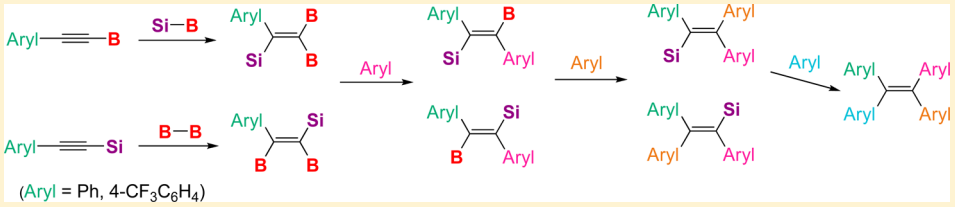
Supporting Information



ABSTRACT: The synthesis of a series of *gem*- and *vic*-diborylated vinylsilanes was accomplished via highly selective transition-metal-catalyzed *syn*-dimetalation to the alkynylmetal species. This protocol served as a general synthetic method toward regio- and stereodefined multisubstituted olefins. The key steps are the diastereoselective Suzuki−Miyaura cross-coupling reactions of *gem*- and *vic*-diborylated vinylsilanes, in which the two boron groups showed discrete reactivities to afford diverse precursors of multisubstituted olefins.

INTRODUCTION

Olefins are one of the major classes of chemical building blocks for organic synthesis. Although numerous methods exist for the preparation of olefins, the regio- and stereoselective synthesis of multisubstituted olefins still presents a challenge and is of great importance.[1] Great efforts have been made to establish a series of general methods for multisubstituted olefins such as substitution of alkenes,[2] addition across alkynes,[3] carbonyl olefination,[4] olefin metathesis,[5] etc.; in particular, the exploration of methods for tetrasubstituted olefins[6] has been well-investigated but is still a continuing important issue in organic synthesis. Because of the widespread applications of tetrasubstituted olefins in natural products,[7] pharmaceuticals,[6c,8] and functional materials,[9] there is still a high demand to explore facile, practical, and general synthetic strategies toward regio- and stereodefined tetrasubstituted olefins, in particular, those with four different substituents.

Moreover, in view of their potential use as pharmaceuticals and functional materials, extended π-system-based multisubstituted olefins such as triarylated[10] and tetraarylated olefins[11] are valuable synthetic targets. A straightforward strategy was envisaged by Itami and Yoshida[12] in which sequential installation of aryl groups (π-component) onto the C═C cores of heteroatom-substituted ethenes gave rise to unsymmetrical tetraarylated olefins selectively. Nevertheless, the participation of aryllithium and Grignard reagents limited the diversity of the introduced aryl components, as those bearing reactive functional groups were found to be incompatible with these protocols.

On the other hand, our research group has established a practical strategy that provides a series of general synthetic approaches to tetrasubstituted olefins via carbozirconation of alkynylmetal compounds bearing low-toxicity, mild, and readily available boron and silicon functionalities.[13] The sequential Pd-catalyzed cross-couplings could transform these boron and silicon groups on the C═C core into other carbon linkages, which were found to extend the diversity of multisubstituted derivatives. For example, tamoxifen-type motifs[13a] as well as tetraalkylated olefins[13c] were successfully synthesized.

Recently, considerable attention has been directed toward the potential and straightforward synthesis of dimetalated olefins in regio- and stereocontrolled manners;[14] the transition-metal-catalyzed dimetalations of alkynes using Si−Si,[15] B−B,[16] and Si−B[17,18] bond-containing compounds significantly contributed to the generation of various *vic*-dimetalated olefins. In addition, Hiyama and Shimizu reported dimetalations of lithium carbenoids with such M−M′ compounds (M, M′ = B and/or Si), yielding versatile *gem*-dimetalated olefins.[19] The discrete reactivities of the resulting carbon−boron bonds allow diastereo- and regioselective cross-couplings to serve as precursors of multisubstituted olefins and render the strategy more versatile.

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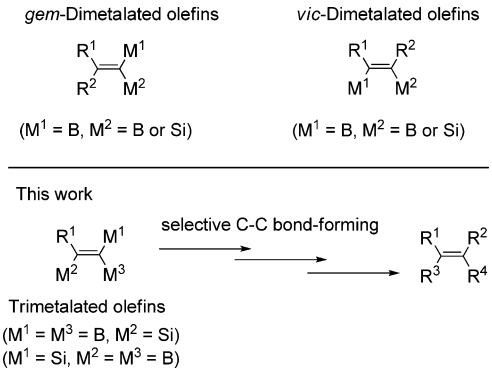
In sharp contrast, the synthesis of trimetalated olefins with several boron and silicon moieties to derive multisubstituted olefins has remained unexplored. Compared with the synthesis of dimetalated olefins, the development of trimetalated variants faces challenges in searching for suitable combinations and arrangements of metal components in the olefin framework to serve as readily available, stable, and versatile precursors of multisubstituted olefins. It is also challenging and highly demanding to investigate the selective transformation of these trimetalated olefins in diastereo- and regioselective manners by using two different metals, leading to the selective synthesis of multisubstituted olefins (Scheme 1).

Scheme 1. Trimetalated Olefins as Precursors of Tetrasubstituted Olefins



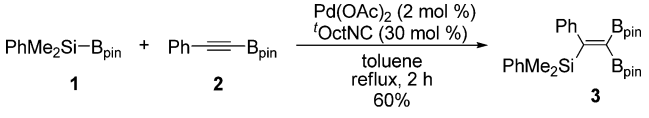
In this work, we envisaged transition-metal-catalyzed silylborylation of an alkynylboronate and diborylation of alkynylsilanes, followed by sequential diastereoselective Suzuki–Miyaura cross-coupling reactions that provide straightforward synthetic entries to hardly available unsymmetrical tetrasubstituted olefins, including an example substituted by four different aryl groups. A series of novel trimetalated olefins with boron and silicon functionalities were synthesized, and their reactivities toward the highly selective synthesis of multisubstituted olefins were investigated.[20]

RESULTS AND DISCUSSION

Synthesis of *gem*-Diborylated Vinylsilanes via Pd-Catalyzed Silylborylation of an Alkynylboronate. According to a report in 1999,[18c] in the presence of an in situ-generated palladium(0)–isonitrile complex, the reaction of silylborane **1** with alkynylboronate **2** took place in refluxing toluene. A catalytic amount of $Pd(OAc)_2$ (2 mol %) and 1,1,3,3-tetramethylbutyl isonitrile (^{t}OctNC) (30 mol %) efficiently gave rise to the silylborylation product **3** in 60% yield as a single regioisomer (Scheme 2; B_{pin} is pinacolatoboryl).

The configuration of the adduct **3** was unambiguously confirmed by X-ray crystallographic analysis (Figure S1 in the Supporting Information). Thus, silylborylation was found to take place regio- and stereoselectively with the two boryl moieties situated in the geminal position. To the best of our knowledge, this is the first example of the synthesis of a 2-silylated 1,1-diboryl-1-alkene as a unique trimetalated olefin, because it would be problematic to synthesize this compound under basic conditions.[21]

Scheme 2. Regio- and Stereoselective Silylborylation of 1 with 2



Suzuki–Miyaura Cross-Couplings of 2-Silylated *gem*-Diboryl-1-alkene 3 with Aryl Iodides 4. *gem*-Diborylated vinylsilane **3** was designed as a potential candidate to synthesize various tetrasubstituted olefins. To further test the utility of this building block, compound **3** was subsequently subjected to Suzuki–Miyaura coupling with an equimolar amount of iodobenzene (**4a**) to ascertain whether the first coupling would be diastereoselective. Screening of various palladium catalysts and ligands in diastereoselective Suzuki–Miyaura cross-couplings were conducted, and the results are listed in Table 1. A combination of $Pd(dba)_2$ with the $[HP^tBuMe_2]BF_4$ salt, which had proved to be the best catalyst for the Suzuki–Miyaura coupling reaction of alkenylboronates with alkyl bromides,[13d,22] was found to be suboptimal for the present reaction because of desilylation of **3** (entry 1). The reaction did not proceed smoothly with the $Pd(OAc)_2$ catalyst in MeOH[23] (entry 2). The participation of water in the reaction using $Pd(OAc)_2$/SPhos dramatically improved the yield of **5a**, which can be explained by the increased solubility of K_3PO_4 in toluene (entry 3 vs 4). Thus, aqueous solutions of bases were employed for further examinations instead of solid states. The better performance of KOH to facilitate faster transmetalation of the B_{pin} group is still empirical, and no general theory has been established to provide a plausible explanation (entries 7 and 8). Finally, THF was found to be the best solvent, considering its solubility and polarity to supply a homogeneous reaction system. PEPPSI-IPr[24] and $Pd_2(dba)_3{\cdot}CHCl_3/P^tBu_3$ proved more reactive and afforded relatively higher yields, albeit with reduced diastereoselectivity (entries 6 and 7). Since the palladium catalysts with monodentate ligands were not particularly efficient, several bidentate ligands with different bite angles were examined. As a result, the diastereoselectivity was obviously increased (entries 9–12). Finally, the reaction using 5 mol % $PdCl_2(dppf)$[25] at room temperature was determined as the optimal condition, affording the desired compound efficiently in satisfactory yield (85%) and diastereoselectivity (88:12) (entry 12).

The *Z* geometry of the major isomer of product **5a** was confirmed by X-ray crystallographic analysis (Figure 1). Furthermore, the minor product (*E*)-**5a** was distinct from (*Z*)-**5a**, as shown by comparison of its NMR data with those of an authentic sample obtained by silylborylation of diphenylethyne.[18c]

After the optimization of the reaction conditions for the diastereoselective Suzuki–Miyaura coupling of **3**, a series of aryl iodides **4** were subjected to the reaction to survey its scope. As shown in Table 2, aryl bromides such as **4a′** and **4f′** also gave the desired products in moderate to good yields. A chloride group in the substrate **4g** remained intact, and an ester group in **4h** was compatible with the reaction, with no trace of side products observed.

It is noteworthy that it is difficult to prepare compounds **5** via *anti*-silylborylation[18d] using unsymmetrical diarylated olefins because the regioselectivity of the addition would not be controllable. This protocol affords an approach to the synthesis of *trans*-stilbene derivatives **5**, although the diastereoselectivity

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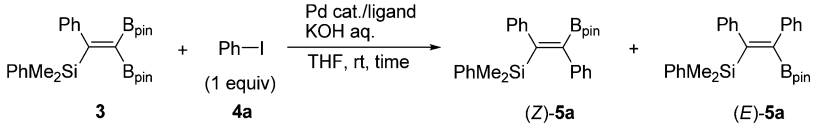
Table 1. Screening of the Optimal Conditions for the Diastereoselective Suzuki–Miyaura Coupling of 3 with Iodobenzene (4a)[a]



entry	Pd/ligand (mol %)	base (equiv)	solvent	temp	% yield (*Z*:*E*)[b]
1	$Pd(dba)_2$ (5)/$[HP^tBuMe_2]BF_4$ (20)	KOH	THF	rt	0
2	$Pd(OAc)_2$ (5)	K_2CO_3	MeOH	rt	17 (>99:1)
3	$Pd(OAc)_2$ (10)/SPhos (20)	K_3PO_4	toluene	100 °C	trace
4	$Pd(OAc)_2$ (10)/SPhos (20)	K_3PO_4 aq.	toluene	100 °C	58 (86:14)
5	$Pd(PPh_3)_4$ (20)	KOH aq.	dioxane	70 °C	24 (96:4)
6[c]	PEPPSI-IPr (10)	KOH aq.	toluene	50 °C	55 (92:8)
7[c]	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)/P^tBu_3 (20)	KOH aq.	THF	rt	76 (75:25)
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)/P^tBu_3 (20)	Cs_2CO_3 aq.	THF	rt	64 (92:8)
9	$PdCl_2(NCPh)_2$ (10)/dppe (20)	KOH aq.	THF	rt	60 (86:14)
10	$PdCl_2(NCPh)_2$ (10)/1,8-dppn(20)	KOH aq.	THF	rt	64 (85:15)
11	$PdCl_2(NCPh)_2$ (10)/dppp (20)	KOH aq.	THF	rt	89 (87:13)
12	**$PdCl_2$(dppf) (5)**	**KOH aq.**	**THF**	**rt**	**85 (88:12)**

[a]Reaction conditions: **3** (0.1 mmol), **4a** (0.1 mmol), Pd cat./ligand, base (0.3 mmol, 3 equiv) in the solvent (1 mL) for 12 h. [b]Isolated yields of the isomeric mixtures; the *Z*:*E* ratios were determined from the ^{1}H NMR spectra. [c]The reaction time was 3 h.

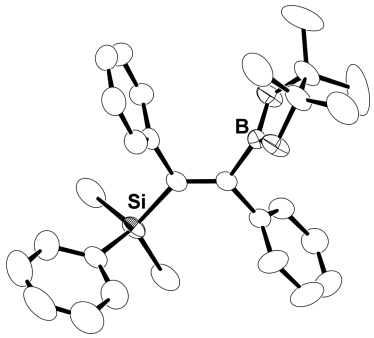


Figure 1. ORTEP drawing of **5a**.

of this Suzuki–Miyaura coupling of **3** is not perfect (up to 92%).

Highly Selective Synthesis of *vic*-Diborylated Vinylsilanes via Pt-Catalyzed Diborylation of Alkynylsilanes. Although we demonstrated that a highly selective silylborylation of an alkynylboronate could provide trimetalated olefins as precursors of diastereoselective transformations, for continuous research interests, we further explored an alternative synthetic approach to trimetalated olefins based on another combination of the boron and silicon functionalities, expecting improved diastereoselectivity of the sequential Suzuki–Miyaura coupling reaction.

The first diborylation of alkynes with bis(pinacolato)diboron (**7**) (B_2pin_2) was discovered by Suzuki and Miyaura.[26] Accordingly, diborylation of a series of alkynylsilanes **6a–c** with **7** were conducted in toluene at 80 °C for 12 h in the presence of $Pt(PPh_3)_4$ (Scheme 3). A 5 mol % loading of the platinum catalyst was sufficient to give the diborylated products **8a–c** in high yields. It is noteworthy that compound **8a** is a structural isomer of **3**.

Suzuki–Miyaura Cross-Couplings of *vic*-Diboryl-1-alkenylsilanes 8 with Aryl Iodides 4. The obtained *vic*-diborylated vinylsilanes **8** were expected to be good precursors for diastereoselective Suzuki–Miyaura couplings as variants of **3**. To further test the utility of the synthesized **8** to give multisubstituted olefins, compound **8a** was initially employed to clarify the diastereoselectivity (Scheme 4).

The reaction of **8a** with iodobenzene (**4a**) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and P^tBu_3 gave rise to a mixture of two cross-coupled products in an 86:14 ratio. The major product was confirmed to be (*Z*)-**5a** after a comparison of its spectroscopic data with that of the authentic sample. It is noteworthy that diastereoselective Suzuki–Miyaura cross-couplings of the structural isomers **8a** and **3** yielded the same compound, (*Z*)-**5a**. The authentic sample of the minor product **9a** was also readily available from **I** through the reported synthetic procedure.[21c] The ratios of major and minor products under different reaction conditions can be precisely calculated (for more details, see the Supporting Information). The results are listed in Table 3.

A 5 mol % loading of $PdCl_2$(dppf) was sufficient to afford (*Z*)-**5a** in 80% yield, and the ratio of (*Z*)-**5a** to **9a** was improved to 92:8 (entry 2). $PdCl_2$(dppp) also performed well to show a relatively higher diastereoselectivity, albeit in a lower chemical yield of 72% (entry 3). It was a delight to find that PEPPSI-IPr is the best catalyst for the synthesis of **8a** in regard to the diastereoselectivity among all of the catalysts examined. When **8b** was employed instead of **8a** (entries 5–7), $PdCl_2$(dppp) was found to be superior to PEPPSI-IPr (entry 6 vs 7).

In view of the conformational energies (*A* values) of the Ph group (2.8) and the $SiMe_2Ph$ group (2.5–2.8),[27] the diastereoselectivities of the Suzuki–Miyaura cross-couplings of **3** and **8a** cannot be explained simply by a steric effect. However, the different reactivities of the two boryl groups may possibly be attributed to the α-effect of the silicon moiety, which may facilitate the diastereoselective transmetalation at the position geminal to the silicon moiety because *vic*-diborylated alkyl aryl alkenes underwent diastereoselective Suzuki coupling at a position geminal to the aryl moiety.[28]

With the optimized reaction conditions (Table 3, entry 6) in hand, we next screened the substrate scope of diastereoselective cross-couplings of **8b** and **8c** bearing a trimethylsilyl group with various aryl iodides **4**, considering its relatively broader

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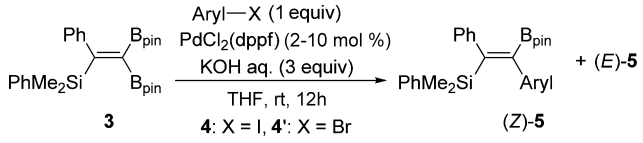
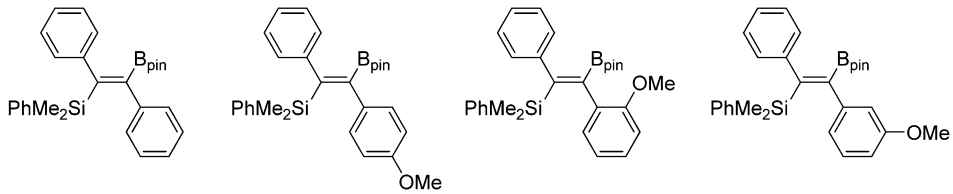
Table 2. Diastereoselective Suzuki–Miyaura Coupling of 3 with Aryl Iodides 4 or Aryl Bromides 4′[a]



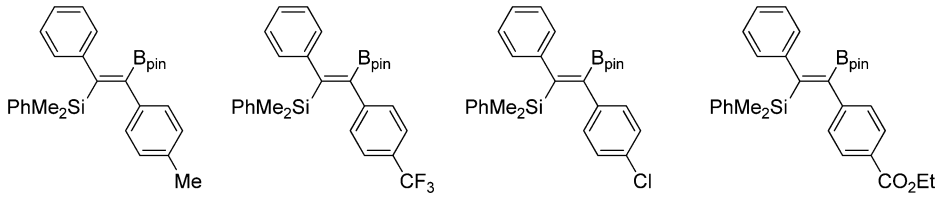


5a from **4a,** 85% (88:12) from **4a'** 78% (87:13)

5b 87% (89:11)

5c 57% (92:8)

5d 83% (89:11)



5e 92% (88:12)

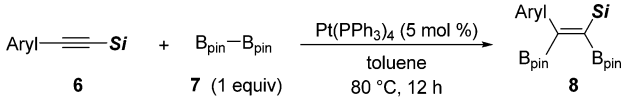
5f from **4f,** 57% (87:13) from **4f'** 59% (85:15)

5g 92% (88:12)

5h 70% (86:14)

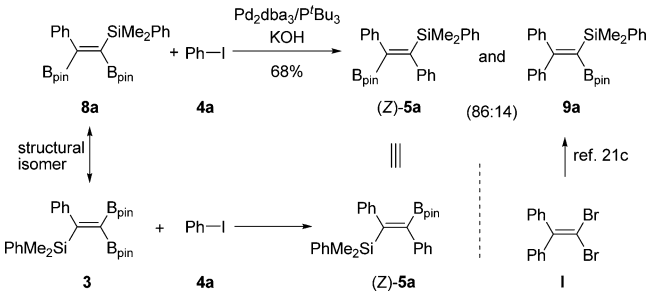
[a]Reaction conditions: **3** (0.5 mmol), **4** or **4′** (0.5 mmol), $PdCl_2$(dppf) (2–10 mol %), 3 M KOH solution (1.5 mmol) in THF (5 mL). Isolated yields after silica gel column chromatography are shown; the *Z*:*E* ratios shown in parentheses were determined from the ^{1}H NMR spectra.

Scheme 3. Diborylation of Alkynylsilanes 6 with Bis(pinacolato)diboron (7)



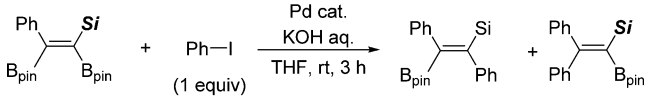
6a: Aryl = Ph, ***Si*** = $SiMe_2Ph$ — **8a**: 85%
6b: Aryl = Ph, ***Si*** = $SiMe_3$ — **8b**: 85%
6c: Aryl = 4-$CF_3C_6H_4$, ***Si*** = $SiMe_3$ — **8c**: 83%

Scheme 4. Determination of the Configurations of the Suzuki–Miyaura Coupling Products



generality compared with the $SiMe_2Ph$ group (Table 4).[4a,b,6b,29] In all cases, since the diastereoselectivity was perfect, *Z*-configured products **10** were solely obtained. A variety of aryl iodides **4** having electron-donating and -withdrawing groups were applicable to the diastereoselective coupling. For example, compounds (*Z*)-**10bb** and (*Z*)-**10bc** were formed in comparable yields. Reactive functional groups such as acetyl (**10bg**), ester (**10bh**), cyano (**10bi**), and nitro (**10bj**) groups were compatible, generating the (*Z*)-**10** series in moderate to high yields. The 4-$CF_3C_6H_4$-substituted vinylsilane **8c** also reacted with aryl iodides **4a** and **4b** to furnish (*Z*)-**10ca** and (*Z*)-**10cb**, respectively, in good yields.

Table 3. Screening of the Optimal Conditions of the Diastereoselective Suzuki–Miyaura Coupling of 8 with 4a



entry[a]	Pd cat./ligand (mol %)	% yield ((*Z*)-**5a**:**9**)[b]
1[c]	$Pd_2(dba)_3$·$CHCl_3$ (5)/P^tBu_3 (20)	68 (86:14)
2[c]	$PdCl_2$(dppf) (5)	80 (92:8)
3[c]	$PdCl_2$(dppp) (5)	72 (97:3)
4[c]	PEPPSI-IPr (10)	76 (>99:1)
5[d]	$PdCl_2$(dppf) (5)	75 (97:3)
6[d]	$PdCl_2$(dppp) (10)	78 (>99:1)
7[d]	PEPPSI-IPr (10)	36 (>99:1)

[a]Reaction conditions: **8** (0.1 mmol), **4a** (0.1 mmol), and a base (0.3 mmol) in THF (1 mL). [b]Isolated yields of the isomeric mixtures; *Z*:*E* ratios were determined from the ^{1}H NMR spectra. [c]Compound **8a** was used. [d]Compound **8b** was used.

Synthesis of Triarylated Vinylsilanes 11. With the synthesized 1,2-diarylated vinylsilanes (*Z*)-**5** and (*Z*)-**10** in hand, we successively introduced different aryl groups by Suzuki–Miyaura coupling with 1.5 equiv of aryl iodides **4** utilizing the remaining boryl moiety. As a result, various triarylated vinylsilanes **11** were successfully synthesized in the presence of $Pd_2(dba)_3$·$CHCl_3$/P^tBu_3 (Scheme 5). Compound

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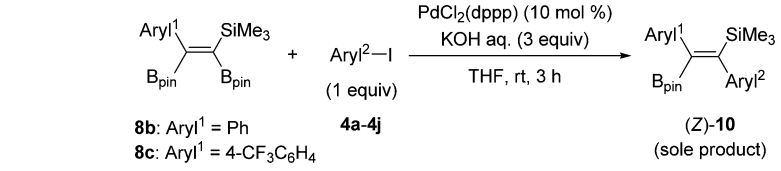
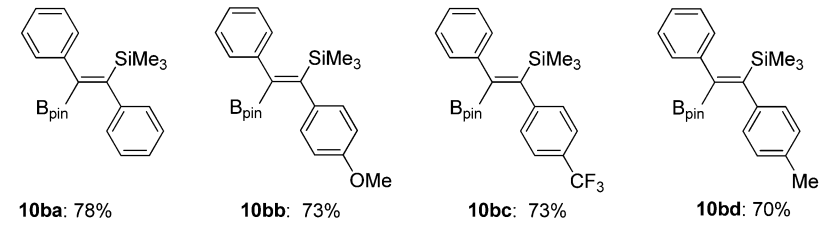
Table 4. Diastereoselective Suzuki–Miyaura Coupling of 8 with Aryl Iodides 4[a]



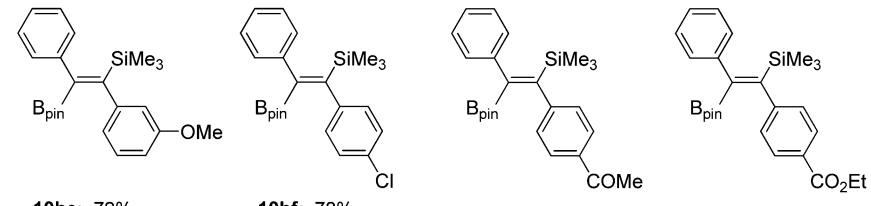
8b: $Aryl^1$ = Ph
8c: $Aryl^1$ = 4-$CF_3C_6H_4$

4a-4j

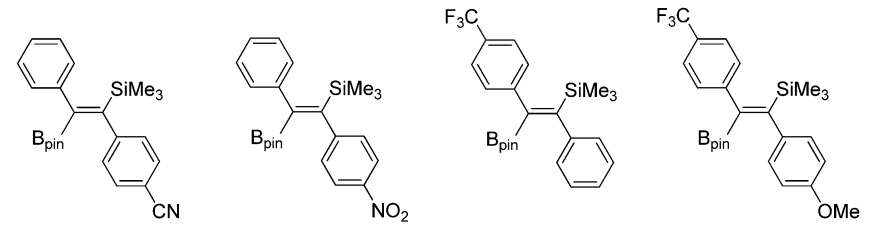
(*Z*)-**10**
(sole product)



10ba: 78% **10bb**: 73% **10bc**: 73% **10bd**: 70%



10be: 72% **10bf**: 78% **10bg**: 80% **10bh**: 71%



10bi: 56% **10bj**: 67% **10ca**: 70% **10cb**: 67%

[a]Reaction conditions: **8** (1.0 mmol), **4** (1.0 mmol), $PdCl_2$(dppp) (10 mol %), and KOH (3 M, 1 mL) in THF (10 mL). Isolated yields after silica gel column chromatography are shown.

11a was first synthesized from (*Z*)-**5b** and **4f** in 85% yield. The TMS variants were also synthesized from vinylsilanes **10** with a series of aryl iodides **4** under the same conditions. It is noteworthy that the different starting vinylsilanes **10** and sequential introduction of appropriate aryl groups in an opposite order of the first and second Suzuki–Miyaura coupling reactions afforded the corresponding triarylated vinylsilanes **11b**, **11c**, and **11d** as mutual regio- and stereoisomers. This protocol serves as a practical synthetic method for the regio- and stereodefined synthesis of the desired structural isomers of trisubstituted vinylsilanes.

Synthesis of Unsymmetrical Tetraarylated Olefin 13. Finally, the target unsymmetrical tetraarylated olefin **13** with four different aryl groups was synthesized through sequential cross-couplings of **11a** by utilizing the remaining silyl moiety, as shown in Scheme 6. With Br_2 and NaOMe in MeOH,[28e,30] the silyl group in **11a** was successfully transformed to the corresponding bromide **12** along with an inversion of the stereochemistry. A sequential Suzuki–Miyaura coupling of **12** with 4-cyanophenylboronic acid afforded the tetraarylated olefin **13** in 89% yield as the sole product, and its structure was unambiguously confirmed by X-ray diffraction (Figure S2 in the Supporting Information).

CONCLUSION

We have successfully developed selective and practical *gem*- and *vic*-diborylated vinylsilanes as the first examples of trimetalated olefins via highly selective silylborylation of an alkynylboronate and diborylation of alkynylsilanes. The obtained trimetalated olefins served as useful precursors toward the synthesis of multiarylated olefins, in particular an unsymmetrical tetraarylated olefin. Highly diastereoselective Suzuki–Miyaura cross-couplings were well-investigated to discriminate the two boryl moieties and to obtain high to perfect selectivities in introducing various aryl groups. This protocol can be compatible with a variety of functional groups on the aryl moieties, including those not compatible with the organolithium or Grignard reagents employed in previously reported approaches. The development of a more straightforward way to transform the silyl groups by C–Si bond activation/direct Hiyama cross-coupling is currently in progress to expand this protocol as a more general approach to complicated π-conjugated molecules, and further studies to clarify the reasons for the diastereoselectivity will be the subject of forthcoming papers.

EXPERIMENTAL SECTION

Regio- and Stereoselective Silylborylation of 2: Synthesis of 1-Dimethylphenylsilyl-1-phenyl-2,2-bis(4,4,5,5-tetramethyl-

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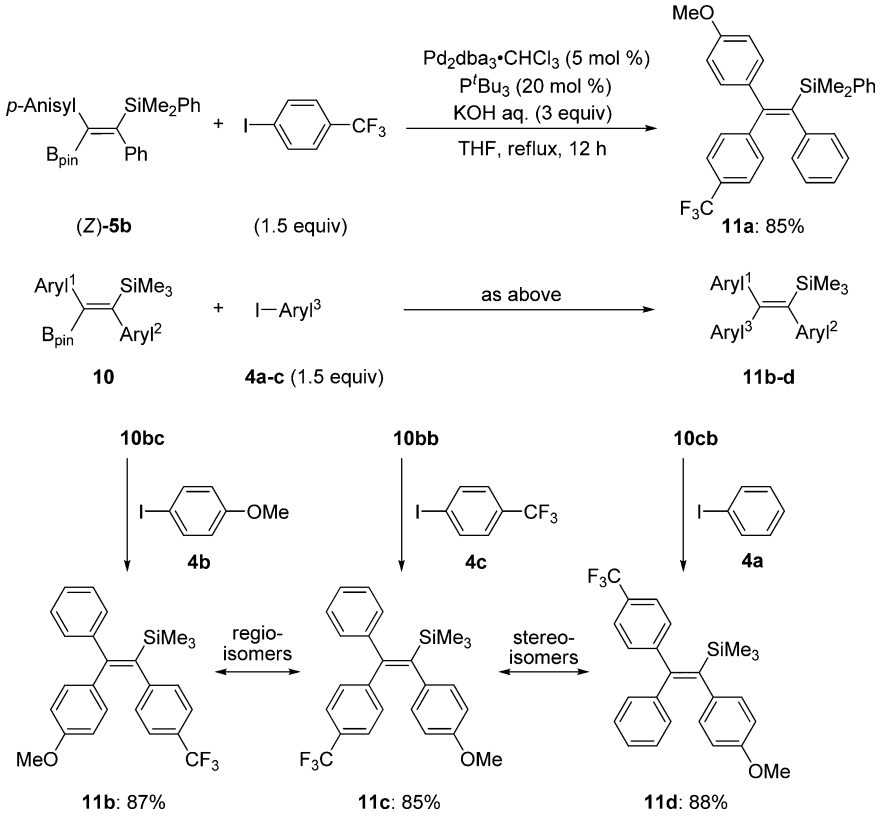
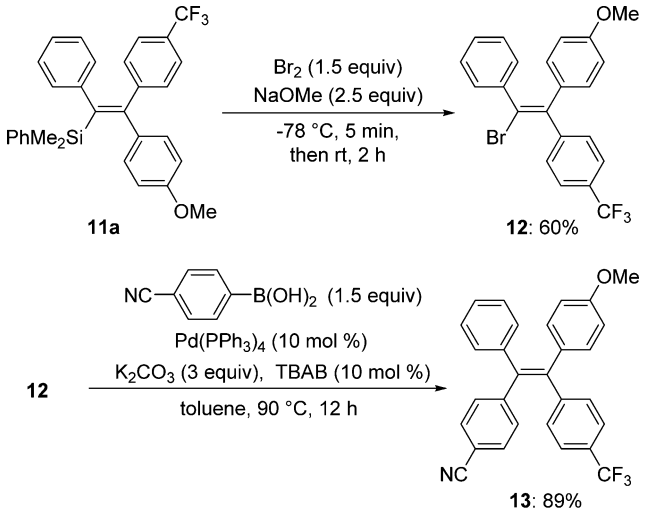
Scheme 5. Selective Synthesis of Regio- and Stereoisomers of Triarylated Vinysilanes 11



Scheme 6. Synthesis of Tetraarylated Olefin 13



1,3,2-dioxaborolan-2-yl)ethene (3). To palladium(II) acetate (9.0 mg, 0.04 mmol) in a 20 mL Schlenk tube was added liquid l,1,3,3-tetramethylbutyl isonitrile (105 μL, 0.6 mmol) with stirring at room temperature under an argon atmosphere. The color of the mixture immediately changed to a vivid red, indicating the formation of the palladium(0)−isonitrile complex. Toluene (0.5 mL), silylborane **1** (787 mg, 3 mmol), and alkynylboronate **2** (456 mg, 2 mmol) were added, and the reaction mixture was heated at reflux. The cooled reaction mixture was subjected to a short column of silica gel (hexane/ethyl acetate = 20:1) followed by recrystallization in hexane to afford the title compound **3** (588 mg, 1.2 mmol, 60%) as a white solid. Mp = 104−105 °C. R_f = 0.26 (hexane/ethyl acetate = 20:1). FT-IR (neat, cm^{-1}): 2976 (m), 2929 (m), 1330 (m), 1294 (s), 1269 (s), 1141(s), 848 (s), 700 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.27 (s, 6H), 0.95 (s, 12H), 1.06 (s, 12H), 6.97−7.00 (m, 2H), 7.08−7.19 (m, 3H), 7.24−7.27 (m, 3H), 7.52−7.56 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ −0.6, 24.3, 24.8, 83.1, 83.3, 125.4, 126.8, 127.31, 127.34, 128.4, 134.2, 139.5, 148.3, 172.3. The signal of the carbon attached to B was not observed because of low intensity. ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, rt): δ 29.9 (brs, overlapped). MS (EI) m/z (relative intensity): 490 (M^+, 1), 475 (5), 363 (4), 307(11), 135(13), 129 (6), 84 (100), 83 (29), 69 (21). Anal. Calcd for $C_{28}H_{40}SiB_2O_4$: C, 68.59; H, 8.22%. Found: C, 68.20; H, 8.40%.

The authentic sample of (*E*)-**5a** was synthesized as a white solid (612 mg, 1.39 mmol, 70%) according to the procedure above[3] using diphenylacetylene (356 mg, 2 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.39 (s, 6H), 1.09 (s, 12H), 1.06 (s, 12H), 6.75−6.78 (q, 2H), 6.78−7.07 (m, 8H), 7.37−7.39 (m, 3H) 7.68−7.71 (m, 2H).

Synthesis of (*Z*)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenylethene (5a). To a solution of $PdCl_2$(dppf) (18 mg, 0.025 mmol, 5 mol %) in THF (5 mL) as an orange suspension in a 20 mL Schlenk tube at room temperature under an Ar atmosphere was added **3** (245 mg, 0.5 mmol) followed by aryl halide **4** (0.5 mmol, 1.0 equiv). After aqueous 3 M KOH solution (1.5 mmol, 0.5 mL) was added, the reaction mixture turned deep brown immediately. The reaction mixture was stirred for 12 h at room temperature. After the reaction was complete, the reaction mixture was quenched with sat. NH_4Cl solution and then extracted with diethyl ether (20 mL × 2), and the combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration, evaporation, and silica gel chromatography (hexane/ethyl acetate = 20:1) gave the pure (*Z*)-**5a** as a white solid (164 mg, 0.37 mmol, 75% from **4a** and 150 mg, 0.34 mmol, 68% from **4a′**). Mp = 76−78 °C. R_f = 0.28 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 3068 (m), 2974 (w), 1373 (s), 1336 (s), 1141 (s), 848 (s), 700 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.03 (s, 6H), 0.97 (s, 12H), 7.21−7.34 (m, 13H), 7.40−7.43 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ −1.3, 24.2, 83.4, 125.7, 126.5, 127.3, 127.5, 127.7, 128.1, 128.4, 128.5, 133.9, 139.4, 142.0, 145.6, 153.8. The signal of the carbon attached to B was not observed because of low intensity. ^{11}B{^{1}H} NMR (192

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MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 440 (M^+, 22), 425 (35), 356 (28), 265 (21), 247 (18), 178 (39), 135 (100), 84 (58), 83 (27), 69 (14). Anal. Calcd for $C_{28}H_{33}SiBO_2$: C, 76.35; H, 7.55%. Found: C, 76.52; H, 7.61%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5b**).* White solid (182 mg, 0.39 mmol, 77%). Mp = 122−123 °C. R_f = 0.13 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 3068 (m), 2980 (m), 1602 (m), 1508 (s), 1340 (s), 1298 (s), 1246 (s), 1143 (s), 852 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ −0.03 (s, 6H), 0.90 (s, 12H), 3.79 (s, 3H), 6.73 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 7.14−7.19 (m, 3H), 7.22−7.28 (m, 5H), 7.35−7.38 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.1, 24.3, 55.1, 83.4, 113.2, 125.6, 127.3, 127.5, 128.4, 128.5, 129.2, 133.9, 134.5, 139.7, 145.7, 153.4, 158.4. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 470 (M^+, 67), 455 (31), 386 (49), 295 (18), 227 (24), 208 (48), 135 (100), 84 (24), 83 (32). Anal. Calcd for $C_{29}H_{35}SiBO_3$: C, 74.03; H, 7.50%. Found: C, 74.43; H, 7.48%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(2-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5c**).* White solid (123 mg, 0.26 mmol, 52%). Mp = 95−96 °C. R_f = 0.19 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2980 (m), 2980 (m), 1456 (m), 1338 (s), 1303 (s), 1242 (m), 1141 (s), 1111 (s), 813 (m), 700 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.00 (s, 6H), 0.89 (s, 12H), 3.75 (s, 3H), 6.69 (dd, J = 8.4, 0.6 Hz, 1H), 6.77 (td, J = 7.5, 1.5 Hz, 1H), 7.05 (dd, J = 7.5, 1.5 Hz, 1H), 7.12−7.31 (m, 11H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.3, 24.2, 55.0, 83.0, 109.5, 120.0, 125.5, 127.2 (overlapped), 128.2, 128.3, 129.0, 130.9, 132.0, 133.8, 139.7, 145.7, 155.7, 156.7. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.6. MS (EI) m/z (relative intensity): 470 (M^+, 35), 455 (43), 356 (31), 355 (88), 354 (23), 277 (23), 251 (18), 208 (19), 135 (100), 84 (15), 83 (21). Anal. Calcd for $C_{29}H_{35}SiBO_3$: C, 74.03; H, 7.50%. Found: C, 73.73; H, 7.40%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(3-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5d**).* White solid (173 mg, 0.37 mmol, 74%). Mp = 90−91 °C. R_f = 0.14 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2974 (m), 2929 (w), 1456 (m), 1338 (s), 1305 (s), 1263 (s), 1141 (s), 845 (s), 816 (m), 702 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ −0.02 (s, 6H), 0.91 (s, 12H), 3.58 (s, 3H), 6.70−6.74 (m, 2H), 6.80−6.83 (m, 1H), 7.12 (t, J = 7.8 Hz, 1H), 7.17−7.19 (m, 3H), 7.23−7.26 (m, 5H), 7.37−7.40 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.2, 24.2, 54.9, 83.4 112.6, 113.3, 120.6, 125.7, 127.4, 127.5, 128.4, 128.5, 128.8, 133.9, 139.7, 143.3, 145.6, 153.6, 159.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.5. MS (EI) m/z (relative intensity): 470 (M^+, 20), 455 (40), 386 (29), 295 (18), 277 (23), 277 (23), 208 (42), 135 (100), 84 (39), 83 (38). Anal. Calcd for $C_{29}H_{35}SiBO_3$: C, 74.03; H, 7.50%. Found: C, 73.63; H, 7.59%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-methylphenyl)ethene (**5e**).* White solid (192 mg, 0.42 mmol, 81%). Mp = 83−84 °C. R_f = 0.27 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2980 (m), 1342 (s), 1305 (m), 1141 (s), 1111 (m), 850 (m), 700 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ −0.05 (s, 6H), 0.89 (s, 12H), 2.31 (s, 3H), 6.97−7.00 (m, 2H), 7.05−7.07 (m, 2H), 7.12−7.17 (m, 3H), 7.20−7.26 (m, 5H), 7.32−7.35 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.2, 21.1, 24.2, 83.3, 125.6, 127.3, 127.4, 128.0, 128.3, 128.4, 128.5, 133.9, 136.0, 139.1, 139.5, 145.7, 153.5. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 454 (M^+, 37), 439 (31), 370 (33), 279 (21), 261 (24), 192 (59), 135 (100), 84 (47), 83 (39). Anal. Calcd for $C_{29}H_{35}SiBO_2$: C, 76.64; H, 7.76%. Found: C, 76.56; H, 7.60%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4-trifluoromethylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5f**).* White solid isolated in 50% yield (126 mg, 0.25 mmol) from *p*-iodo(trifluoromethyl)benzene (**4f**) and 50% yield (127 mg, 0.26 mmol) from *p*-bromo(trifluoromethyl)benzene (**4f′**). Mp = 104−105 °C. R_f = 0.12 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2981 (w), 1348 (m), 1323 (s), 1159 (s), 1141 (s), 1116 (s), 1107 (s), 1064 (s), 702 (m). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.01 (s, 6H), 0.89 (s, 12H), 7.15−7.30 (m, 12H), 7.37 (d, J = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ −1.2, 24.2, 83.6, 124.3 (q, J_{C-F} = 272.2 Hz), 124.6 (q, J_{C-F} = 3.3 Hz), 126.0, 127.5, 127.7, 128.2, 128.4, 128.5 (q, J_{C-F} = 32 Hz), 128.6, 133.7, 138.6, 145.3, 145.7, 155.8. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.1. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ −62.8. MS (EI) m/z (relative intensity): 508 (M^+, 19), 493 (35), 431 (14), 354 (32), 227 (17), 135 (100), 84 (71), 83 (31). Anal. Calcd for $C_{29}H_{32}SiBO_2F_3$: C, 68.50; H, 6.34%. Found: C, 68.49; H, 6.05%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5g**).* White solid (192 mg, 0.40 mmol, 81%). Mp = 105−106 °C. R_f = 0.16 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2983 (m), 1489 (m), 1338 (s), 1303 (s), 1141 (s), 1111 (m), 840 (s), 773 (m), 702 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.00 (s, 6H), 0.90 (s, 12H), 7.03−7.08 (m, 2H), 7.10−7.18 (m, 5H), 7.19−7.32 (m, 7H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.2, 24.2, 83.5, 125.8, 127.4, 127.6, 127.8, 128.3, 128.5, 129.5, 132.4, 133.8, 139.0, 140.5, 145.4, 155.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.2. MS (EI) m/z (relative intensity): 474 (M^+, 14), 459 (18), 390 (13), 211 (16), 135 (100), 84 (47), 83 (23). Anal. Calcd for $C_{28}H_{32}SiBO_2Cl$: C, 70.82; H, 6.79%. Found: C, 70.99; H, 6.70%.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4-ethoxycarbonylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**5h**).* White solid (154 mg, 0.30 mmol, 60%). Mp = 91−92 °C. R_f = 0.27 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2983 (m), 1489 (m), 1338 (s), 1303 (s), 1141 (s), 1111 (m), 840 (s), 773 (m), 702 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ −0.03 (s, 6H), 0.88 (s, 12H), 1.40 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 7.13−7.33 (m, 12H), 7.87 (d, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ −1.2, 14.3, 24.2, 60.8, 83.6, 125.9, 127.4, 127.6, 128.1, 128.2, 128.51, 128.58, 129.1, 133.8, 138.8, 145.3, 147.0, 155.1, 166.6. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 28.6. MS (EI) m/z (relative intensity): 512 (M^+, 21), 468 (17), 397 (21), 355 (40), 337 (32), 250 (37), 206 (33), 205 (59), 204 (20), 135 (100), 107 (16), 105 (24). Anal. Calcd for $C_{31}H_{37}SiBO_4$: C, 72.65; H, 7.28%. Found: C, 72.55; H, 7.10%.

General Procedure for the Synthesis of (*Z*)-1,2-Diboryl-1-silylated Stilbenes 8 by Highly Selective Diborylation of 6. A 100-mL flask equipped with a magnetic stirring bar and reflux condenser was charged with $Pt(PPh_3)_4$ (311 mg, 0.25 mmol, 5 mol %) and bis(pinacolato)diboron (**7**) (1.27 g, 5 mmol, 1.0 equiv) under an Ar atmosphere. Toluene (50 mL) and 1-alkynylsilane **6** (5 mmol) were added, affording a yellow solution. After the reaction reached completion overnight at 80 °C, the reaction mixture was cooled to room temperature. Toluene was removed via a rotary evaporator to yield a yellow residue, which was subjected to a short column chromatography on neutral silica gel with hexanes/EtOAc = 20:1 as the eluent to afford an off-white solid. Further recrystallization with CH_2Cl_2/hexane gave analytically pure white crystals of **8**.

*(Z)-1-(Dimethylphenylsilyl)-2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**8a**).* White crystals (2.08 g, 4.25 mmol, 85%). Mp = 127−128 °C. FT-IR (neat, cm^{-1}): 2974 (m), 1369 (m), 1339 (m), 1321 (s), 1300 (s), 1202 (m), 1146 (s), 1111 (w), 843 (m), 772 (w), 704 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 0.09 (s, 6H), 1.34 (s, 12H), 1.35 (s, 12H), 7.10−7.12 (m, 2H), 7.25−7.26 (m, 3H), 7.38−7.39 (m, 3H), 7.58−7.59 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ −0.7, 24.7, 25.3, 83.6, 83.9, 126.3, 127.3, 127.4, 127.8, 128.2, 134.2, 140.9, 145.4. The signals of the two carbons attached to B were not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.2 (brs, overlapped). MS (EI) m/z (relative intensity): 490 (M^+, 2), 475 (3), 363 (6), 307 (14), 271 (7),

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221 (7), 135 (13), 119 (21), 84 (100), 83 (27), 69 (24). Anal. Calcd for $C_{28}H_{40}B_2O_4Si$: C, 68.59; H, 8.22%. Found: C, 68.61; H, 8.06%.

*(Z)-1-(Trimethylsilyl)-2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**8b**).* White crystals (1.82 g, 4.25 mmol, 85%). Mp = 169−170 °C. FT-IR (neat, cm^{-1}): 2980 (m), 1371 (w), 1317 (s), 1296 (s), 1269 (m), 1146 (s), 845 (s), 704 (w). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.19 (s, 9H), 1.22 (s, 12H), 1.37 (s, 12H), 7.10−7.12 (m, 2H), 7.19−7.20 (m, 1H), 7.22−7.25 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.8, 24.7, 25.5, 83.6, 83.9, 126.2, 127.4, 127.8, 145.8. The signals of the two carbons attached to B were not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.2, 30.9. MS (EI) m/z (relative intensity): 429 (M^+, 0.01), 413 (7), 287 (13), 286 (6), 231 (5), 129 (4), 84 (100), 69 (30). Anal. Calcd for $C_{23}H_{38}B_2O_4Si$: C, 64.51; H, 8.94%. Found: C, 64.49; H, 8.97%.

*(Z)-1-(Trimethylsilyl)-2-(4-trifluoromethylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**8c**).* White needlelike crystals (2.06 g, 4.15 mmol, 83%). Mp = 170 °C. FT-IR (neat, cm^{-1}): 2984 (w), 1310 (s), 1204 (w), 1119 (m), 1064 (m), 1018 (w), 851 (s), 604 (w). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.19 (s, 9H), 1.23 (s, 12H), 1.38 (s, 12H), 7.21 (d, J = 9 Hz, 2H), 7.50 (d, J = 9 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.8, 24.7, 25.6, 83.8, 84.2, 124.4 (q, J_{C-F} = 270.5 Hz), 124.4 (q, J_{C-F} = 3.5 Hz), 128.1, 128.3 (q, J_{C-F} = 32 Hz), 149.6. The signals of the two carbons attached to B were not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 28.8 (brs, overlapped). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, rt): δ −62.5. MS (EI) m/z (relative intensity): 496 (M^+, 0), 481 (3), 438 (4), 355 (16), 84 (100), 83 (29), 69 (25). Anal. Calcd for $C_{24}H_{37}B_2F_3O_4Si$: C, 58.09; H, 7.51%. Found: C, 58.23; H, 7.11%.

Diastereoselective Suzuki−Miyaura Cross-Coupling of 8 with Aryl Iodide 4a and Determination of the Ratio of the Two Regioisomers. To a THF solution of the palladium catalyst and the ligand in a 20 mL Schlenk tube under an Ar atmosphere was added **8a** (49 mg, 0.1 mmol). To the reaction mixture were then added iodobenzene **4a** (11.2 μL, 20.4 mg, 0.1 mmol) and the base (3.0 equiv). After being stirred at room temperature for 3 h, the reaction mixture was quenched with sat. NH_4Cl solution and then extracted with diethyl ether (10 mL × 2). The combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration, evaporation, and preparative TLC gave a mixture of regioisomers of the target products (*Z*)-**5a** and **9a** in 68% combined yield. The (*Z*)-**5a**:**9a** ratio (86:14) was determined from the ^1H NMR spectrum using different protons assigned to the methyl groups of −$SiMe_2Ph$ as the references (see the ^1H NMR spectrum shown in Figure S3 in the Supporting Information).

General Procedure for the Synthesis of (*Z*)-1-(Trimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diarylethenes. To a solution of $PdCl_2$(dppp) (29 mg, 0.025 mmol, 10 mol %) in THF (5 mL) as an off-white suspension in a 20 mL Schlenk tube at room temperature under an Ar atmosphere were added **8** (0.5 mmol) and aryl halide **4** (0.5 mmol, 1.0 equiv). When aqueous 3 M KOH solution (1.5 mmol, 0.5 mL) was added, the reaction mixture immediately turned deep brown. The reaction mixture was stirred for an additional 3 h at room temperature. After the reaction was complete, the reaction mixture was quenched with sat. NH_4Cl solution and then extracted with diethyl ether (20 mL × 2). The combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration, evaporation, and column chromatography on silica gel gave the analytically pure (*Z*)-**10**.

*(Z)-1-(Trimethylsilyl)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10ba**).* White solid (147 mg, 0.39 mmol, 78%). Mp = 72−73 °C. R_f = 0.38 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2978 (m), 1344 (s), 1310 (s), 1246 (m), 1144 (s), 852 (s), 837 (s), 700 (s). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.25 (s, 9H), 0.90 (s, 12H), 7.15−7.18 (m, 3H), 7.23−7.27 (m, 3H), 7.30−7.31 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 24.3, 83.4, 125.6, 126.5, 127.6, 127.9, 128.0, 128.1, 142.6, 146.0, 156.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.3. MS (EI) m/z (relative intensity): 378 (M^+, 71), 363 (58), 263 (52), 221 (41), 178 (85), 135 (28), 101 (22), 84 (100), 73 (64), 69 (22). Anal. Calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26%. Found: C, 73.05; H, 8.25%.

*(Z)-1-(Trimethylsilyl)-1-(4-methoxyphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bb**).* White solid (148 mg, 0.36 mmol, 73%). Mp = 106−107 °C. R_f = 0.21 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2980 (m), 1506 (m), 1342 (m), 1302 (m), 1246 (s), 1142 (m), 849 (s), 708 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.25 (s, 9H), 0.93 (s, 12H), 3.80 (s, 3H), 6.83 (d, J = 9 Hz, 2H), 7.08 (d, J = 9 Hz, 2H), 7.23−7.24 (m, 1H), 7.28−7.30 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 24.3, 55.3, 83.3, 113.0, 126.4, 127.8, 128.1, 129.1, 138.4, 142.6, 155.5, 157.9. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.5. MS (EI) m/z (relative intensity): 408 (M^+, 100), 393 (65), 293 (30), 251 (47), 208 (81), 165 (29), 135 (16), 84 (26), 83 (41), 73 (45). Anal. Calcd for $C_{24}H_{33}BO_3Si$: C, 70.58; H, 8.14%. Found: C, 70.43; H, 8.14%.

*(Z)-1-(Trimethylsilyl)-1-(4-trifluoromethylphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bc**).* White solid (163 mg, 0.37 mmol, 73%). Mp = 107−108 °C. R_f = 0.37 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2990 (w), 2978 (w), 1341 (s), 1329 (s), 1315 (m), 1248 (w), 1155 (m), 1121 (m), 1069 (m), 851 (s). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.24 (s, 9H), 0.89 (s, 12H), 7.27−7.29 (m, 5H), 7.31−7.34 (m, 2H), 7.54 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.1, 24.2, 83.6, 124.47 (q, J_{C-F} = 270.2 Hz), 124.50 (q, J_{C-F} = 3.5 Hz), 126.8, 127.98, 127.99 (q, J_{C-F} = 21.6 Hz), 128.0, 128.4, 142.2, 150.1, 155.3. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, rt): δ −62.6. MS (EI) m/z (relative intensity): 446 (M^+, 37), 431 (46), 354 (19), 289 (13), 227 (16), 135 (11), 101 (53), 84 (100), 73 (53). Anal. Calcd for $C_{24}H_{30}BO_2SiF_3$: C, 64.58; H, 6.77%. Found: C, 64.60; H, 6.42%.

*(Z)-1-(Trimethylsilyl)-1-(4-methylphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bd**).* White solid (137 mg, 0.35 mmol, 70%). Mp = 102−103 °C. R_f = 0.37 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2980 (m), 2953 (w), 1506 (w), 1340 (s), 1304 (s), 1246 (m), 1142 (s), 984 (m), 845 (s), 706 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.25 (s, 9H), 0.91 (s, 12H), 2.32 (s, 3H), 7.04 (d, J = 8 Hz, 2H), 7.08 (d, J = 8 Hz, 2H), 7.23−7.25 (m, 1H), 7.28−7.32 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 21.0, 24.3, 83.3, 126.4, 127.8, 127.9, 128.1, 128.2, 135.0, 142.7, 142.9, 156.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.3. MS (EI) m/z (relative intensity): 392 (M^+, 82), 377 (52), 295 (15), 277 (48), 235 (41), 193 (20), 192 (100), 84 (53), 83 (37), 73 (47). Anal. Calcd for $C_{24}H_{33}BO_2Si$: C, 73.46; H, 8.48%. Found: C, 73.26; H, 8.47%.

*(Z)-1-(Trimethylsilyl)-1-(3-methoxyphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10be**).* White solid (147 mg, 0.36 mmol, 72%). Mp = 90 °C. R_f = 0.25 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2978 (m), 1585 (m), 1508 (s), 1489 (m), 1341 (s), 1304 (s), 1167 (m), 839 (s), 708 (m), 852 (s). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.23 (s, 9H), 0.93 (s, 12H), 3.82 (s, 3H), 6.72−6.77 (m, 3H), 7.17 (t, J = 8 Hz, 1H), 7.22−7.26 (m, 1H), 7.29−7.32 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.3, 24.3, 55.2, 83.4, 111.7, 113.1, 120.6, 126.5, 127.9, 128.1, 128.6, 142.5, 147.4, 155.8, 159.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 408 (M^+, 85), 393 (82), 294 (25), 293 (100), 292 (32), 251 (43), 208 (90), 135 (20), 84 (50), 83 (50), 73 (65). Anal. Calcd for $C_{24}H_{33}BO_3Si$: C, 70.58; H, 8.14%. Found: C, 70.78; H, 8.34%.

*(Z)-1-(Trimethylsilyl)-1-(4-chlorophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bf**).* White solid (161 mg, 0.39 mmol, 78%). Mp = 141−142 °C. R_f = 0.20 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2976 (w), 1489 (m), 1371 (m), 1337 (s), 1302 (s), 1140 (s), 1011 (w), 849 (s), 702 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.26 (s, 9H), 0.93 (s, 12H), 7.09 (d, J = 8 Hz, 2H), 7.24−7.32 (m, 7H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.1, 24.3, 83.5, 126.7, 127.6, 127.9, 128.0, 129.4, 131.5, 142.3, 144.5,

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155.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 412 (M^+, 47), 397 (37), 255 (17), 212 (43), 101 (45), 84 (100), 83 (40), 73 (68), 69 (19). Anal. Calcd for $C_{23}H_{30}BClO_2Si$: C, 66.92; H, 7.32%. Found: C, 66.52; H, 7.03%.

*(Z)-1-(Trimethylsilyl)-1-(4-acetylphenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bg**).* White solid (168 mg, 0.40 mmol, 80%). Mp = 132−133 °C. R_f = 0.18 (hexane/ethyl acetate = 10:1). FT-IR (KBr, cm^{-1}): 2980 (w), 2959 (w), 1678 (s), 1601 (m), 1341 (m), 1317 (m), 1267 (m), 1142 (m), 851 (s). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.28 (s, 9H), 0.85 (s, 12H), 2.57 (s, 3H), 7.22−7.30 (m, 7H), 7.86 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 24.2, 26.6, 83.5, 126.7, 127.8, 127.9, 128.0, 128.2, 134.7, 142.2, 151.7, 155.6, 198.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.1. MS (EI) m/z (relative intensity): 420 (M^+, 68), 405 (22), 305 (24), 205 (29), 204 (100), 84 (51), 73 (65). Anal. Calcd for $C_{25}H_{33}BO_3Si$: C, 71.42; H, 7.91%. Found: C, 71.53; H, 7.59%.

*4-[(1Z)-1-(Trimethylsilyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzoic Acid Ethyl Ester (**10bh**).* White solid (159 mg, 0.35 mmol, 71%). Mp = 97−98 °C. R_f = 0.11 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2980 (m), 1717 (s), 1605 (m), 1341 (m), 1271 (s), 1142 (m), 851 (m), 700 (w). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.26 (s, 9H), 0.90 (s, 12H), 1.41 (t, J = 7 Hz, 3H), 4.38 (q, J = 7 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 7.25−7.26 (m, 1H), 7.29−7.32 (m, 4H), 7.97 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 14.3, 24.2, 60.8, 83.5, 126.7, 127.7, 127.9, 127.99, 128.01, 129.0, 142.2, 151.3, 155.6, 166.8. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.2. MS (EI) m/z (relative intensity): 450 (M^+, 48), 435 (17), 289 (19), 205 (100), 84 (29), 73 (32). Anal. Calcd for $C_{26}H_{35}BO_4Si$: C, 69.33; H, 7.83%. Found: C, 68.93; H, 7.76%.

*(Z)-1-(Trimethylsilyl)-1-(4-cyanophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bi**).* Off-white solid (113 mg, 0.28 mmol, 56%). Mp = 214 °C. R_f = 0.11 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2978 (m), 2956 (m), 2224 (m), 1601 (w), 1327 (s), 1302 (s), 1140 (s), 982 (w), 849 (s), 708 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.25 (s, 9H), 0.91 (s, 12H), 7.26−7.28 (m, 5H), 7.31−7.34 (m, 2H), 7.59 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.1, 24.2, 83.6, 109.3, 119.3, 126.9, 127.9, 128.0, 128.8, 131.4, 141.9, 151.6, 155.1. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.2. MS (EI) m/z (relative intensity): 403 (M^+, 589), 402 (28), 388 (40), 263 (52), 175 (20), 101 (49), 84 (96), 83 (27), 73 (100). Anal. Calcd for $C_{24}H_{30}BNO_2Si$: C, 71.46; H, 7.50; N, 3.47%. Found: C, 71.49; H, 7.43; N, 3.43%.

*(Z)-1-(Trimethylsilyl)-1-(4-nitrophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10bj**).* White solid (142 mg, 0.34 mmol, 67%). Mp = 204 °C. R_f = 0.13 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2976 (w), 1589 (w), 1512 (m), 1344 (s), 1140 (m), 986 (w), 849 (m), 712 (w). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.24 (s, 9H), 0.91 (s, 12H), 7.27−7.29 (m, 3H), 7.32−7.34 (m, 4H), 8.17 (d, J = 9 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.1, 24.2, 83.7, 122.9, 127.0, 127.9, 128.0, 128.8, 141.9, 146.1, 153.9, 155.0. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. MS (EI) m/z (relative intensity): 423 (M^+, 37), 408 (45), 280 (68), 101 (52), 84 (100), 83 (38), 73 (86). Anal. Calcd for $C_{23}H_{30}BNO_4Si$: C, 65.25; H, 7.14; N, 3.31%. Found: C, 65.10; H, 6.75; N, 3.23%.

*(Z)-1-(Trimethylsilyl)-1-phenyl-2-(4-trifluoromethylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10ca**).* White solid (156 mg, 0.35 mmol, 70%). Mp = 103−104 °C. R_f = 0.32 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2978 (m), 1612 (w), 1312 (s), 1269 (w), 1151 (s), 1124 (s), 1066 (m), 986 (w), 845 (s), 708 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.26 (s, 9H), 0.89 (s, 12H), 7.13 (d, J = 7 Hz, 2H), 7.17−7.19 (m, 1H), 7.24−7.27 (m, 2H), 7.41 (d, J = 7 Hz, 2H), 7.57 (d, J = 7 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 24.2, 83.6, 124.4 (q, J_{C-F} = 270.4 Hz), 124.8 (q, J_{C-F} = 3.7 Hz), 125.8, 127.7, 127.8, 128.4, 128.9 (q, J_{C-F} = 31.8 Hz), 145.5, 146.5, 157.7. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.3. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, rt): δ −62.6. MS (EI) m/z (relative intensity): 446 (M^+, 27), 431 (34), 354 (15), 289 (14), 227 (14), 101 (21), 84 (100), 73 (47), 69 (16). Anal. Calcd for $C_{24}H_{30}BF_3O_2Si$: C, 64.58; H, 6.77%. Found: C, 64.49; H, 6.42%.

*(Z)-1-(Trimethylsilyl)-1-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**10cb**).* White solid (160 mg, 0.34 mmol, 67%). Mp = 148 °C. R_f = 0.19 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2981 (w), 1612 (w), 1506 (m), 1373 (w), 1325 (s), 1284 (w), 1244 (m), 1064 (m), 848 (s). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.25 (s, 9H), 0.93 (s, 12H), 3.80 (s, 3H), 6.83 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.57 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.2, 24.3, 55.3, 83.6, 113.1, 124.4 (q, J_{C-F} = 270.5 Hz), 124.8 (q, J_{C-F} = 3.7 Hz), 128.4, 128.7 (q, J_{C-F} = 32.1 Hz), 128.9, 138.0, 146.5, 157.3, 158.1. The signal of the carbon attached to B was not observed because of low intensity. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, rt): δ 29.4. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, rt): δ −62.6. MS (EI) m/z (relative intensity): 476 (M^+, 81), 475 (18), 462 (30), 461 (100), 460 (22), 361 (20), 319 (43), 276 (68), 165 (22), 84 (59), 83 (65), 73 (63). Anal. Calcd for $C_{25}H_{32}BF_3O_3Si$: C, 63.03; H, 6.77%. Found: C, 63.00; H, 6.40%.

Suzuki−Miyaura Cross-Coupling of 5b or 10 with 4: Synthesis of 11. To a deep-purple solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.025 mmol, 5 mol %) and P^tBu_3 (20 mg, 0.1 mmol, 20 mol %) in THF (5 mL) in a 20 mL Schlenk tube were added **5b** or **10** (0.5 mmol) and **4** (0.75 mmol, 1.5 equiv) at room temperature under an Ar atmosphere. After aqueous 3 M KOH solution (1.5 mmol, 0.5 mL) was added, the reaction mixture turned deep brown immediately. The reaction mixture was heated to reflux and stirred for 12 h. After the reaction was complete, the reaction mixture was quenched with sat. NH_4Cl solution and then extracted with diethyl ether (20 mL × 2), and the combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration, evaporation, and silica gel chromatography (hexane/ethyl acetate = 20:1) gave the title compound **11**.

*(Z)-1-(Dimethylphenylsilyl)-1-phenyl-2-(4-trifluoromethylphenyl)-2-(4-methoxyphenyl)ethene (**11a**).* Colorless viscous oil (207 mg, 0.42 mmol, 85%). R_f = 0.41 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 3068 (w), 1608 (m), 1506 (s), 1325 (s), 1247 (s), 1165 (s), 1122 (m), 1111 (s), 854 (s), 702 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.09 (s, 6H), 3.84 (s, 3H), 6.78 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 7.05−7.10 (m, 5H), 7.13−7.18 (m, 2H), 7.29−7.39 (m, 7H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ −0.8, 55.2, 113.3, 124.1 (q, J_{C-F} = 272.1 Hz), 124.2 (q, J_{C-F} = 3.5 Hz), 125.3, 127.5, 127.6, 128.8 (q, J_{C-F} = 32.6 Hz), 128.6, 129.5, 129.7, 130.8, 133.8, 135.6, 139.8, 143.3, 144.2, 147.1, 153.2, 159.0. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, rt): δ −62.8. MS (EI) m/z (relative intensity): 488 (M^+, 77), 473 (21), 334 (20), 265 (20), 227 (66), 135 (100). Anal. Calcd for $C_{30}H_{27}SiOF_3$: C, 73.74; H, 5.57%. Found: C, 73.78; H, 5.74%.

*(E)-1-(Trimethylsilyl)-1-(4-trifluoromethylphenyl)-2-phenyl-2-(4-methoxyphenyl)ethene (**11b**).* White solid (185 mg, 0.43 mmol, 87%). Mp = 74−75 °C. R_f = 0.42 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2955 (w), 1609 (m), 1506 (m), 1321 (s), 1113 (s), 1065 (m), 868 (m), 829 (m), 704 (m). ^1H NMR (600 MHz, $CDCl_3$, rt): δ −0.19 (s, 9H), 3.66 (s, 3H), 6.56 (d, J = 8 Hz, 2H), 6.85 (d, J = 8 Hz, 2H), 7.13 (d, J = 8 Hz, 2H), 7.31−7.33 (m, 3H), 7.34−7.38 (m, 2H), 7.44 (d, J = 8 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 0.4, 54.9, 112.8, 124.5 (q, J_{C-F} = 270.5 Hz), 124.5 (q, J_{C-F} = 3.5 Hz), 127.1 (q, J_{C-F} = 32 Hz), 127.3, 128.0, 129.4, 129.6, 130.7, 135.1, 142.3, 144.2, 148.5, 154.0, 157.9. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, rt): δ −62.4. MS (EI) m/z (relative intensity): 426 (M^+, 100), 411 (28), 257 (54), 227 (62), 165 (52), 135 (51), 73 (81). HRMS (FAB) Calcd for $C_{25}H_{25}F_3OSi$: 426.1627. Found: 426.1611.

*(E)-1-(Trimethylsilyl)-1-(4-methoxyphenyl)-2-phenyl-2-(4-trifluoromethylphenyl)ethene (**11c**).* White solid (182 mg, 0.43 mmol, 85%). Mp = 88−89 °C. R_f = 0.44 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2958 (w), 1506 (m), 1321 (s), 1286 (w),

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1242 (s), 1122 (s), 1109 (m), 837 (s), 700 (m). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ −0.19 (s, 9H), 3.74 (s, 3H), 6.70 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 7.29−7.32 (m, 3H), 7.34−7.36 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 0.3, 55.0, 113.1, 124.2 (q, J_{C-F} = 270.5 Hz), 124.3 (q, J_{C-F} = 3.7 Hz), 127.4, 127.7 (q, J_{C-F} = 32.1 Hz), 128.1, 129.5, 129.6, 130.1, 135.5, 143.6, 145.7, 147.0, 152.4, 157.3. ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$, rt): δ −62.7. MS (EI) m/z (relative intensity): 426 (M^+, 100), 412 (25), 411 (78), 257 (26), 227 (22), 203 (16), 165 (29), 135 (28), 73 (93). HRMS (FAB) Calcd for $C_{25}H_{25}F_3OSi$: 426.1627. Found: 426.1628.

(Z)-1-(Trimethylsilyl)-1-(4-methoxyphenyl)-2-phenyl-2-(4-trifluoromethylphenyl)ethene (11d). White solid (188 mg, 0.44 mmol, 88%). Mp = 117−118 °C. R_f = 0.42 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 2955 (w), 1504 (m), 1325 (s), 1244 (m), 1122 (m), 1064 (m), 867 (m), 840 (m). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ −0.20 (s, 9H), 3.73 (s, 3H), 6.69 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 6.91−6.92 (m, 2H), 6.97−6.98 (m, 1H), 7.02 (t, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 0.4, 54.9, 113.0, 124.2 (q, J_{C-F} = 270.4 Hz), 124.9 (q, J_{C-F} = 3.5 Hz), 126.2, 127.5, 129.29 (q, J_{C-F} = 32.1 Hz), 129.3, 129.8, 130.1, 135.6, 142.6, 145.1, 148.1, 152.4, 157.2. ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$, rt): δ −62.6. MS (EI) m/z (relative intensity): 426 (M^+, 100), 412 (25), 411 (77), 257 (24), 227 (20), 203 (18), 165 (27), 135 (24), 73 (51). HRMS (FAB) Calcd for $C_{25}H_{25}F_3OSi$: 426.1627. Found: 426.1607.

Desilylbromination of 11a: Synthesis of (*E*)-1-Bromo-1-phenyl-2-(4-trifluoromethylphenyl)-2-(4-methoxyphenyl)-ethene (12). To a solution of **11a** (212 mg, 0.43 mmol) in a 20 mL Schlenk tube was added Br_2 (0.64 mL, 0.64 mmol, 1.5 equiv, 1.0 M CH_2Cl_2 solution) at −78 °C, followed by NaOMe (1.1 mL, 1.1 mmol, 1.0 M MeOH solution). After being stirred for 5 min at −78 °C, the reaction mixture was allowed to warm slowly to room temperature, stirred for another 2 h, quenched with H_2O, and extracted with Et_2O (10 mL × 2). Evaporation and column chromatography (hexane/ethyl acetate = 20:1) yielded a viscous oil. Recrystallization from Et_2O/hexane afforded the title compound **12** (112 mg, 0.26 mmol, 60%) as a white solid. Mp = 97−98 °C. R_f = 0.30 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 833 (m), 1066 (m), 1122 (s), 1165 (m), 1250 (s), 1327 (s), 1510 (m), 1605 (m). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 3.71 (s, 3H), 6.62 (d, J = 9 Hz, 2H), 6.84 (d, J = 9 Hz, 2H), 7.20−7.25 (m, 3H), 7.33−7.36 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 55.1, 113.4, 122.1, 124.1 (q, J_{C-F} = 272.1 Hz), 125.2 (q, J_{C-F} = 3.3 Hz), 128.09, 128.12, 129.4 (q, J_{C-F} = 32.6 Hz), 130.0, 130.2, 131.6, 132.6, 140.8, 141.8, 147.5, 158.7. ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, rt): δ −62.9. MS (EI) m/z (relative intensity): 434 (M^+, 60), 432 (59), 354 (25), 353 (100), 252 (18), 239 (21). Anal. Calcd for $C_{22}H_{16}BrF_3O$: C, 60.99; H, 3.72%. Found: C, 60.87; H, 3.48%.

Suzuki−Miyaura Cross-Coupling Reaction of 12 with 4-Cyanophenylboronic Acid: Synthesis of (*E*)-1-(4-Cyanophenyl)-1-phenyl-2-(4-trifluoromethylphenyl)-2-(4-methoxyphenyl)-ethene (13). To a yellow solution of $Pd(PPh_3)_4$ (5 mg, 0.004 mmol, 2 mol %) in toluene (2 mL) in a 20 mL Schlenk tube were added **12** (86 mg, 0.2 mmol), 4-cyanophenylboronic acid (44 mg, 0.3 mmol, 1.5 equiv), tetrabutylammonium bromide (TBAB) (6 mg, 0.02 mmol, 10 mol %), and 2 M K_2CO_3 aqueous solution (0.3 mL, 0.6 mmol, 3 equiv) at room temperature under an Ar atmosphere. The reaction mixture was heated to 90 °C and stirred for 12 h. After the reaction was complete, the reaction mixture was quenched with sat. NH_4Cl solution and then extracted with diethyl ether (20 mL × 2). The combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration, evaporation, and silica gel chromatography (hexane/ethyl acetate = 20:1) gave **13** (81 mg, 0.18 mmol, 89%) as a pale-yellow fluffy solid. Mp = 135−136 °C. R_f = 0.18 (hexane/ethyl acetate = 20:1). FT-IR (KBr, cm^{-1}): 833 (m), 1066 (m), 1126 (s), 1165 (m), 1247 (s), 1323 (s), 1506 (m), 1602 (m), 2227 (w). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 3.75 (s, 3H), 6.67 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 6.99−7.03 (m, 2H), 7.09−7.19 (m, 7H), 7.40 (d, J = 8.1 Hz, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 55.1, 110.2, 113.3, 118.8, 124.0 (q, J_{C-F} = 272.1 Hz), 124.9 (q, J_{C-F} = 3.5 Hz), 127.1, 128.1, 129.0 (q, J_{C-F} = 32 Hz), 131.1, 131.5, 131.6, 131.9, 132.4, 134.4, 139.6, 141.3, 142.4, 146.8, 148.3, 158.7. ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, rt): δ −62.9. MS (EI) m/z (relative intensity): 456 (M^+, 33), 455 (100), 436 (2), 353 (2), 278 (3), 277 (3), 266 (3), 264 (3), 239 (3), 218 (2). Anal. Calcd for $C_{29}H_{20}NF_3O$: C, 76.47; H, 4.43; N, 3.08%. Found: C, 76.53; H, 4.35, N, 3.02%.

X-ray Structural Analysis of 3, (*Z*)-5a, and 13. CCDC-931441 (**3**), CCDC-931442 [(*Z*)-**5a**], and CCDC-931443 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336-033.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; characterization data for all of the compounds; and X-ray data for **3**, (*Z*)-**5a**, and **13**, including CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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