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Synthesis of Cyclic Alkenylborates via Silaboration of Alkynes Followed by Hydrolysis for Utilization in External-Base-Free Cross Coupling

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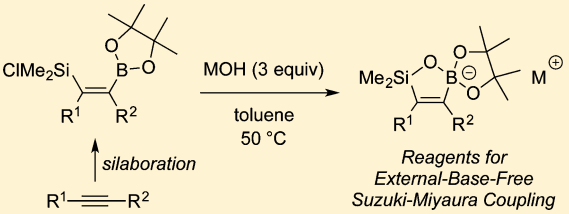
Supporting Information

ABSTRACT: Cyclic alkenylborates have been synthesized regioselectively via a palladium-catalyzed regioselective silaboration of terminal alkynes with $ClMe_2Si$–B(pin) followed by basic hydrolysis. The cyclic borates undergo cross coupling with 4-iodoanisole in the absence of an external base.



In transition-metal-catalyzed bond-forming reactions using organoboron compounds, such as Suzuki–Miyaura coupling,[1] use of isolable ate complexes of organoboron compounds has received increasing attention in recent years. For example, the organoborates **1**–**6** shown in Figure 1 have

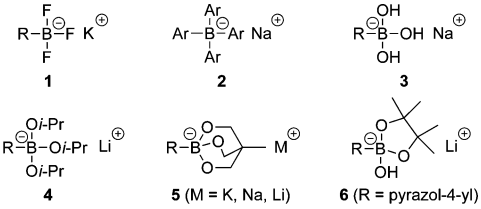
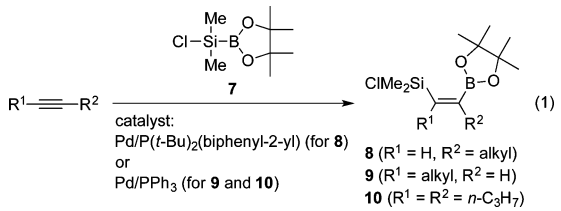


Figure 1. Isolable organoborates for Suzuki–Miyaura coupling.

been found to have advantages over tricoordinated organoboronic acids in preparation, handling, and reactivity.[2−7] In particular, the trihydroxy- and trialkoxyborates **3**–**6** show remarkably high reactivity in Suzuki–Miyaura coupling, allowing the reaction to take place even in the absence of an external base, which is essential for the coupling using organoboronic acids.[4−7] Such high reactivities of **3**–**6** are attributed to acceleration of the transmetalation step in the catalytic cycle, in which the nucleophilicity of the organic groups on the boron atoms is enhanced by formation of the four-coordinated borate structure.[1b] Use of such a reactive coupling reagent makes the cross-coupling reaction more practical through improved functional group compatibility and operational simplicity. Despite such attractive features, reactive borates are limited to trihydroxy- and trialkoxyorganoborate derivatives. For further exploration of the utility of organoborates in transition-metal-catalyzed reactions, the development of functionalized organoborate reagents is highly desirable.

We have recently established a palladium-catalyzed silaboration of alkynes using the silylboronic ester **7**, bearing a chloro group on the silicon atom (eq 1).[8,9] Complementary regiochemical control in the silaboration of terminal alkynes



was achieved by the choice of ligand on the palladium catalyst, allowing selective synthesis of regioisomeric alkenylboronic esters **8** and **9** bearing a chlorodimethylsilyl group on the β-carbon.[8a,c] It was expected that hydrolysis of the Cl–Si bond would lead to the formation of a five-membered cyclic borate via intramolecular attack of the resulting silanol oxygen on the tricoordinated boron atom. Herein, we describe the synthesis of cyclic alkenylborates **11**–**13** (Figure 2) via silaboration of alkynes followed by borate formation, which show air and water stability with interesting reactivity in Suzuki–Miyaura coupling.[10]

2-Boryl-1-silyl-1-octene **8a** was prepared by silaboration of 1-octyne with the silylboronic ester **7** using Pd/P(*t*-

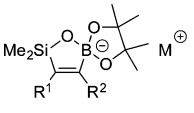


Figure 2. Cyclic alkenylborates **11**–**13** synthesized in this study.

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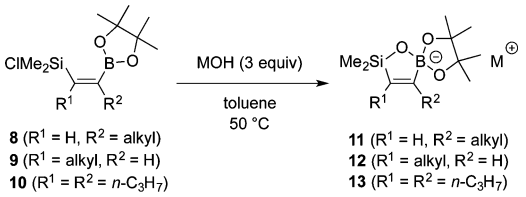
Table 1. Synthesis of Cyclic Alkenylborates 11−13[a]



8 (R^1 = H, R^2 = alkyl)
9 (R^1 = alkyl, R^2 = H)
10 (R^1 = R^2 = n-C_3H_7)

11 (R^1 = H, R^2 = alkyl)
12 (R^1 = alkyl, R^2 = H)
13 (R^1 = R^2 = n-C_3H_7)

entry	R^1	R^2		MOH	product	yield (%)[b]
1	H	n-C_6H_{13}	**8a**	KOH	**11a-K**	94
2	H	n-C_6H_{13}	**8a**	NaOH	**11a-Na**	94
3	H	n-C_6H_{13}	**8a**	CsOH•H_2O	**11a-Cs**	91
4	H	$(CH_2)_3OSiMe_2$-t-Bu	**8b**	KOH	**11b-K**	92
5	H	$(CH_2)_3Cl$	**8c**	KOH	**11c-K**	95
6	H	$(CH_2)_3CN$	**8d**	KOH	**11d-K**	87
7	H	cyclo-C_6H_{11}	**8e**	KOH	**11e-K**	84
8	n-C_6H_{13}	H	**9a**	KOH	**12a-K**	98
9	$(CH_2)_3OSiMe_2$-t-Bu	H	**9b**	NaOH	**12b-Na**	83
10	$(CH_2)_3Cl$	H	**9c**	NaOH	**12c-Na**	82
11	$(CH_2)_3CN$	H	**9d**	NaOH	**12d-Na**	87
12	cyclo-C_6H_{11}	H	**9e**	NaOH	**12e-Na**	88
13	n-C_3H_7	n-C_3H_7	**10**	KOH	**13-K**	90

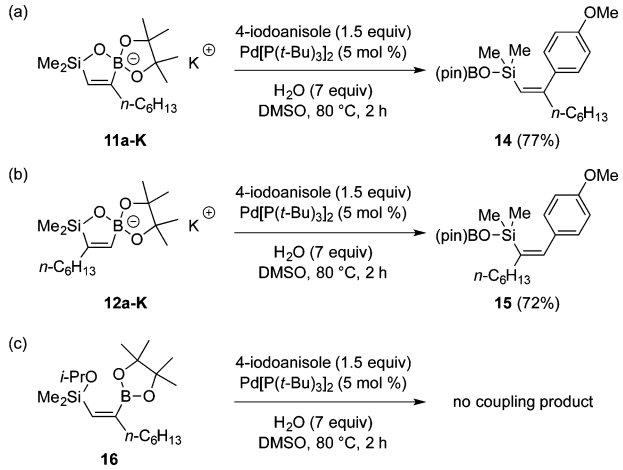
[a]Conditions: MOH (1.2 mmol) and **8**, **9**, or **10** (0.40 mmol) in toluene (0.2 mL) was stirred at 50 °C for 4 h. [b]Isolated yield.

Bu)$_2$(biphenyl-2-yl) catalyst[8c] and reacted with KOH (3 equiv) in toluene at 50 °C (entry 1, Table 1). After 4 h, CH_2Cl_2 was added to the resulting suspension and the insoluble precipitate was removed by filtration. The filtrate was concentrated, and the resulting solid was dried in vacuo to give a potassium salt of cyclic alkenylborate, **11a-K**, in 94% yield. Formation of **11a-K** may take place through nucleophilic substitution of the chlorine group on the silicon atom by hydroxide ion, which is followed by intramolecular attack of the silanol oxygen on the tricoordinated boron atom to form a five-membered ring. The ^{11}B NMR chemical shift of **11a-K** (δ 13 ppm in DMSO-d_6) indicates the formation of a four-coordinated boron compound.[11] Use of 3 equiv of KOH was crucial for high-yield formation of **11a-K**, whereas a lower yield of **11a-K** was observed in the reaction with 2 equiv of KOH. Borate formation did not take place at room temperature. NaOH and CsOH·H_2O could also be used for borate formation, in which cases the respective products **11a-Na** and **11a-Cs** were obtained in high yields (entries 2 and 3).

A variety of cyclic alkenylborates were synthesized by the reaction of (boryl)(silyl)alkenes with alkali-metal hydroxides in toluene at 50 °C (entries 4−13, Table 1). 2-Boryl-1-silyl-1-alkenes **8b−e** reacted with KOH to give the corresponding borates **11b−e** in high yields (entries 4−7). Functional groups such as silyloxy (entry 4), chloro (entry 5), and cyano groups (entry 6) were compatible under the reaction conditions. The protocol was applicable to the synthesis of borates **12a−e** from 1-boryl-2-silyl-1-alkenes **9a−e** (entries 8−12), which were synthesized by silaboration of 1-alkynes through a regiocomplementary reaction in which a Pd/PPh_3 catalyst was used.[8a] While the potassium borate **12a-K** was synthesized from **9a** in high yield according to the procedure described above, the corresponding potassium borates **12b−e** could not be obtained in pure form because of their insolubility in CH_2Cl_2. We found that **12b−e** could be synthesized as sodium salts, which were soluble in CH_2Cl_2, by the reaction of **9b−e** with NaOH. The potassium borate **13** was also synthesized via the reaction of KOH with alkene **10**, which was prepared by silaboration of 4-octyne (entry 13).

The potassium borates **11a-K** and **12a-K** were subjected to Suzuki−Miyaura coupling with 4-iodoanisole in DMSO in the presence of Pd[P(t-Bu)$_3$]$_2$ (5 mol %) and H_2O (7 equiv) (Scheme 1a,b). The coupling took place at 80 °C within 2 h to

Scheme 1. External-Base-Free Suzuki−Miyaura Coupling of 11a-K and 12a-K



give alkenylsilanes **14** and **15** in good yields, respectively, without adding an external base. A control reaction of alkenylboronic ester **16**, which bears an isopropoxydimethylsilyl group β to the boron atom, with 4-iodoanisole under identical conditions resulted in no coupling product (Scheme 1c),[12] indicating that the carbon−boron bonds in **11a-K** and **12a-K** are activated by the borate formation. In a previous study, we demonstrated Hiyama coupling of the related alkenylsilanes bearing an isopropoxysilyl group instead of a boryloxysilyl group in **14** and **15**.[8a]

In conclusion, we have established a synthetic route to cyclic alkenylborates via catalytic silaboration of alkynes followed by

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treatment with metal hydroxides. This method allows efficient access to the two possible regioisomers **11** and **12** on the basis of catalyst-controlled regioselective silaboration of terminal alkynes. The cyclic alkenylborates could be utilized in Suzuki–Miyaura coupling, which proceeds in the absence of an external base.

EXPERIMENTAL SECTION

General Comments. Alkenylboronic esters **8**,[8c] **9**,[8a] and **10**[8a] were synthesized by the methods reported previously. KOH and NaOH were crashed into a fine powder and dried under reducing pressure with heating (300 °C/0.5 mmHg, 12 h). CsOH·H_2O (nacalai) was used as received from commercial sources.

Synthesis of Cyclic Alkenylborates 11–13 (Table 1). *General Procedure.* In a glovebox, KOH, NaOH, or CsOH·H_2O (1.2 mmol) was placed in a glass tube having a PTFE stopcock (J. Young) and equipped with a magnetic stir bar. Toluene (0.8 mL) and alkenylboron compound **8**, **9**, or **10** (0.40 mmol) were added to the tube. The tube was then sealed by the stopcock and taken out from the glovebox. After 4 h at 50 °C, CH_2Cl_2 (3.0 mL) was added to the reaction mixture, and the insoluble precipitates were removed by filtration. The filtrate was concentrated in vacuo. The borates were obtained with high purity. Further purification of the products by bulb-to-bulb distillation or silica gel column chromatography met with difficulty.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(oct-1-en-1-yl-κC^2)silanolato-κO]borate (**11a-K**).* The title compound **11a-K** (128 mg, 94%) was obtained as a white solid from **8a** (128 mg, 0.39 mmol) with KOH (67 mg, 1.2 mmol). **11a-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.60 (s, 1H), 2.08 (t, J = 7.2 Hz, 2H), 1.36–1.45 (m, 2H), 1.24–1.34 (m, 6H), 1.03 (s, 6H), 0.97 (s, 6H), 0.89 (t, J = 6.8 Hz, 3H), −0.09 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 127.2, 76.5, 36.0, 31.7, 29.5, 27.9, 26.8, 26.7, 22.2, 14.0, 2.6, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 13.1; HRMS (ESI) m/z calcd for $C_{16}H_{32}BO_3Si^-$ (M − K^+) 311.2219, found 311.2231.

*Sodium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(oct-1-en-1-yl-κC^2)silanolato-κO]borate (**11a-Na**).* The title compound **11a-Na** (99 mg, 94%) was obtained as a white solid from **8a** (105 mg, 0.32 mmol) with NaOH (43 mg, 1.1 mmol). **11a-Na**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.62 (s, 1H), 2.08 (t, J = 7.2 Hz, 2H), 1.36–1.45 (m, 2H), 1.24–1.34 (m, 6H), 1.04 (s, 6H), 0.99 (s, 6H), 0.89 (t, J = 6.8 Hz, 3H), −0.08 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 127.2, 76.5, 36.0, 31.7, 29.5, 27.9, 26.8, 26.7, 22.2, 14.0, 2.7, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.3; HRMS (ESI) m/z calcd for $C_{16}H_{32}BO_3Si^-$ (M − Na^+) 311.2219, found 311.2231.

*Cesium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(oct-1-en-1-yl-κC^2)silanolato-κO]borate (**11a-Cs**).* The title compound **11a-Cs** (165 mg, 91%) was obtained as a white solid from **8a** (135 mg, 0.41 mmol) with CsOH·H_2O (186 mg, 1.1 mmol). **11a-Cs**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.59 (s, 1H), 2.07 (t, J = 7.2 Hz, 2H), 1.36–1.44 (m, 2H), 1.25–1.34 (m, 6H), 1.03 (s, 6H), 0.97 (s, 6H), 0.89 (t, J = 6.8 Hz, 3H), −0.10 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 127.1, 76.4, 36.1, 31.7, 29.5, 27.9, 26.9, 26.7, 22.2, 14.0, 2.9, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.7; HRMS (ESI) m/z calcd for $C_{16}H_{32}BO_3Si^-$ (M − Cs^+) 311.2219, found 311.2232.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-{5-(tert-butyldimethylsilyloxy)pent-1-en-1-yl-κC^2}silanolato-κO]borate (**11b-K**).* The title compound **11b-K** (111 mg, 92%) was obtained as a white solid from **8b** (115 mg, 0.27 mmol) with KOH (46 mg, 0.82 mmol). **11b-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.60 (s, 1H), 3.59 (t, J = 7.2 Hz, 2H), 2.10 (t, J = 7.2 Hz, 2H), 1.61 (quintet, J = 7.2 Hz, 2H), 1.03 (s, 6H), 0.97 (s, 6H), 0.90 (s, 9H), 0.05 (s, 6H), −0.09 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 127.1, 76.4, 63.6, 32.0, 31.3, 27.0, 26.7, 25.9, 18.0, 2.8, −5.2, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 13.1; HRMS (ESI) m/z calcd for $C_{19}H_{40}BO_4Si_2^-$ (M − K^+) 399.2564, found 399.2570.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(5-chloropent-1-en-1-yl-κC^2)silanolato-κO]borate (**11c-K**).* The title compound **11c-K** (98 mg, 95%) was obtained as a white solid from **8c** (98 mg, 0.30 mmol) with KOH (53 mg, 0.95 mmol). **11c-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.61 (s, 1H), 3.60 (t, J = 7.2 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 1.90 (quintet, J = 7.2 Hz, 2H), 1.03 (s, 6H), 0.97 (s, 6H), −0.096 (s, 3H), −0.100 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 128.9, 76.5, 46.3, 33.3, 31.3, 27.0, 26.7, 2.8, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.6; HRMS (ESI) m/z calcd for $C_{13}H_{25}BClO_3Si^-$ (M − K^+) 303.1360, found 303.1369.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(5-cyanopent-1-en-1-yl-κC^2)silanolato-κO]borate (**11d-K**).* The title compound **11d-K** (111 mg, 87%) was obtained as a white solid from **8d** (120 mg, 0.38 mmol) with KOH (65 mg, 1.2 mmol). **11d-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.62 (s, 1H), 2.39 (t, J = 7.2 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 1.75 (quintet, J = 7.2 Hz, 2H), 1.03 (s, 6H), 0.97 (s, 6H), −0.09 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 129.7, 121.2, 76.5, 35.2, 27.0, 26.7, 23.8, 16.1, 2.8, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.6; HRMS (ESI) m/z calcd for $C_{14}H_{25}BNO_3Si^-$ (M − K^+) 294.1702, found 294.1708.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(2-cyclohexylethen-1-yl-κC^2)silanolato-κO]borate (**11e-K**).* The title compound **11e-K** (97 mg, 84%) was obtained as a white solid from **8e** (109 mg, 0.33 mmol) with KOH (59 mg, 1.1 mmol). **11e-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.59 (s, 1H), 2.10–2.19 (m, 1H), 1.60–1.78 (m, 4H), 1.10–1.34 (m, 6H), 1.04 (s, 6H), 0.98 (s, 6H), −0.11 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 124.2, 76.4, 41.9, 33.0, 27.0, 26.9, 26.8, 26.6, 2.9, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 13.1; HRMS (ESI) m/z calcd for $C_{16}H_{30}BO_3Si^-$ (M − K^+) 309.2063, found 309.2074.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(oct-1-en-2-yl-κC^1)silanolato-κO]borate (**12a-K**).* The title compound **12a-K** (132 mg, 98%) was obtained as a white solid from **9a** (126 mg, 0.38 mmol) with KOH (66 mg, 1.2 mmol). **12a-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.32 (s, 1H), 2.07 (t, J = 6.8 Hz, 2H), 1.21–1.39 (m, 8H), 0.99 (s, 6H), 0.96 (s, 6H), 0.89 (t, J = 6.8 Hz, 3H), −0.05 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.5, 76.2, 35.3, 31.4, 29.6, 29.0, 26.1, 25.9, 22.1, 14.0, 2.1, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.5; HRMS (ESI) m/z calcd for $C_{16}H_{32}BO_3Si^-$ (M − K^+) 311.2219, found 311.2230.

*Potassium (2,3-Dimethyl-2,3-butanediolato-κO,κO′)[1,1-dimethyl-1-(oct-4-en-4-yl-κC^5)silanolato-κO]borate (**13-K**).* The title compound **13-K** (93 mg, 90%) was obtained as a white solid from **10** (98 mg, 0.30 mmol) with KOH (50 mg, 0.89 mmol). **13-K**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.96–2.05 (m, 4H), 1.40 (sextet, J = 7.2 Hz, 2H), 1.32 (sextet, J = 7.2 Hz, 2H), 1.03 (s, 6H), 0.96 (s, 6H), 0.87 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H), −0.10 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.5, 76.3, 32.2, 31.1, 27.0, 26.9, 23.6, 22.6, 15.1, 14.7, 2.9, the boron-bound carbon was not detected due to quadrupolar relaxation; ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.6; HRMS (ESI) m/z calcd for $C_{16}H_{32}BO_3Si^-$ (M − K^+) 311.2219, found 311.2231.

External-Base-Free Suzuki–Miyaura Coupling of 11a-K and 12a-K (Scheme 1). *General Procedure.* In a glovebox, Pd[P(*t*-Bu)$_3$]$_2$ (5.1 mg, 10 μmol), 4-iodoanisole (70 mg, 0.30 mmol), and **11a-K** or **12a-K** (66 mg, 0.20 mmol) were placed in a glass tube having a PTFE stopcock (J. Young) with a magnetic stir bar. After addition of DMSO (0.4 mL), the tube was sealed by the stopcock and taken out from the glovebox. H_2O (25 mg, 1.4 mmol) was added to the mixture under an atmosphere of nitrogen. The tube was sealed by the stopcock again and heated at 80 °C for 2 h with stirring. After it was cooled to room temperature, the mixture was filtered through a pad of Celite and the resulting solution was dried over anhydrous $MgSO_4$. The coupling product was isolated by bulb-to-bulb distillation (140 °C/0.6 mmHg).

*1-Dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)silyl-2-(4-methoxyphenyl)-1-octene (**14**).* The title compound **14** (65 mg,

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77%) was obtained from **11a-K** (71 mg, 0.22 mmol) with 4-iodoanisole (68 mg, 0.29 mmol). **14**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.14−7.19 (m, 2H), 6.85−6.90 (m, 2H), 5.51 (s, 1H), 3.75 (s, 3H), 2.38 (t, J = 6.8 Hz, 2H), 1.18−1.33 (m, 8H), 1.17 (s, 12H), 0.82 (t, J = 6.8 Hz, 3H), −0.25 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.8, 158.6, 135.5, 128.9, 126.9, 113.2, 73.8, 55.1, 41.8, 31.2, 27.6, 25.0, 24.6, 22.2, 14.0, 1.9. ^{11}B NMR (128 MHz, C_6D_6) δ 22.4; HRMS (ESI) m/z calcd for $C_{23}H_{40}BO_4Si^+$ (M + H$^+$) 419.2783, found 419.2801.

2-Dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)silyl-1-(4-methoxyphenyl)-1-octene (15). The title compound **15** (103 mg, 72%) was obtained from **12a-K** (120 mg, 0.34 mmol) with 4-iodoanisole (111 mg, 0.47 mmol). **15**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H), 6.87 (d, J = 8.4 Hz, 2H), 3.76 (s, 3H), 2.26 (t, J = 7.2 Hz, 2H), 1.40−1.49 (m, 2H), 1.25−1.36 (m, 6H), 1.18 (s, 12H), 0.90 (t, J = 7.2 Hz, 1H), −0.04 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.3, 143.2, 141.2, 132.1, 129.8, 113.2, 73.7, 55.1, 38.8, 31.3, 28.7, 25.0, 24.6, 22.2, 14.1, 2.1. ^{11}B NMR (128 MHz, C_6D_6) δ 22.0; HRMS (ESI) m/z calcd for $C_{23}H_{40}BO_4Si^+$ (M + H$^+$) 419.2783, found 419.2803.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving additional general comments, characterization data of **12b-Na**, **12c-Na**, **12d-Na**, and **12e-Na**, and ^{1}H and ^{13}C NMR spectra of new compounds. 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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