Notes

Synthesis of Silylboronic Esters Functionalized on Silicon

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Summary: New silylpinacolboranes bearing chloro, fluoro, alkoxy, and dialkylamino groups on silicon were synthesized in high yields via derivatization of [(diethylamino)diphenylsilyl]-pinacolborane, which was prepared by reaction of [(diethylamino)diphenylsilyl]lithium with (isopropoxy)pinacolborane, and (chlorodimethylsilyl)pinacolborane, prepared by reaction of (dimethylphenylsilyl)pinacolborane with hydrogen chloride in the presence of a catalytic amount of aluminum chloride.

Introduction

In recent years, silylboranes have received much attention in organic and organometallic chemistry. Extensive studies on silaboration of unsaturated organic molecules using transition metal catalysts have been reported.[1] Group 10 transition metal complexes have been established as efficient catalysts for silaboration of alkynes,[2] alkenes,[3] 1,3-dienes,[4] and allenes,[5] offering convenient access to organometallic compounds containing both boryl and silyl groups in regio- and stereodefined manners. Silaboration reactions that are accompanied by either C−C bond formation or cleavage have also been developed, providing new access to boron- and silicon-containing organic compounds with rather complex structures.[2b,4a,6,7] Recent studies also revealed that those catalytic reactions can be successfully applied to catalytic asymmetric synthesis, leading to new enantioenriched organoboron compounds.[4c,5d,f,g,8] Even with no transition metal catalysts, silylboranes exhibit interesting reactivities. Noncatalytic insertion reactions of isocyanides[9] and carbenoids[10] to the Si−B bond have provided new routes to organoboron compounds that are otherwise difficult to synthesize. Silylboranes have also been utilized for the generation of silyl anions,[11] silyl radicals,[12] and borylenes.[13] Further research efforts have been focused on their physical properties, including absorption and fluorescence emission in the visible region.[14]

In the course of our study on silaboration, we were interested in silylboranes bearing heteroatom substituents on silicon. Our major concern was enhancement of reactivity, which may allow us not only to make the existing reactions proceed more efficiently and selectively but also to find new reaction systems, including intramolecular reactions, in which reacting groups are introduced to the silicon atom.[3b] Such reactivity enhancement by introduction of heterosubstituents on silicon is reasonably expected from observations in catalytic hydrosilylation.[15] However, synthetic accessibility of silylboranes has not been fully exploited,[16] resulting in the lack of a practical method for the synthesis of silylboranes functionalized on silicon. Although silylboranes having various functional groups on the boron atom such as chloro, amino, and alkoxy groups have been prepared,[2c,5d,16c,d,f,g] the silyl groups are limited to triorganosilyl groups such as

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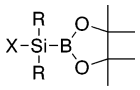
trimethylsilyl and dimethylphenylsilyl groups. Some silylboranes having heteroatom functional groups have been prepared with very bulky groups on the silicon atoms, which made it difficult to utilize them for synthetic applications.[16m] The lack of practical methods for the synthesis of silylboranes that are functionalized on the silicon atom prompted us to establish new synthetic routes to produce them. Herein, we describe a high-yield synthesis of silylboronic esters **1** bearing heteroatom substituents on silicon via derivatization of [(diethylamino)diphenylsilyl]pinacolborane, which was prepared by reaction of [(diethylamino)diphenylsilyl]-lithium with (isopropoxy)pinacolborane, and (chlorodimethylsilyl)pinacolborane, prepared by reaction of (dimethylphenylsilyl)-pinacolborane with hydrogen chloride in the presence of a catalytic amount of aluminum chloride.[17]

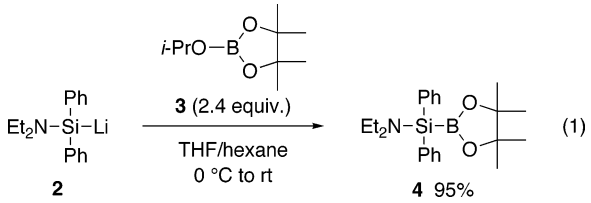


1

Results and Discussion

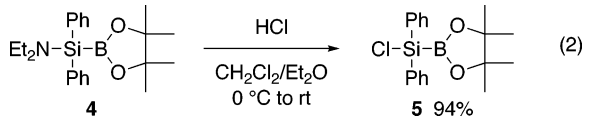
Synthesis of $XPh_2Si-B(pin)$ (X = Et_2N, Cl). Our first approach to the silylboranes having heteroatom substituents on silicon was a reaction of boron electrophiles with silyllithium that carries a dialkylamino group. Following the Si−B bond formation, the amino groups on the silicon and boron atoms could be substituted selectively by other functional groups. We initially tried a reaction of [(diethylamino)diphenylsilyl]lithium (**2**)[18] with bis(diethylamino)chloroborane and obtained the corresponding silylborane, which bore three amino groups on both the boron and silicon atoms. However, attempts using diols or acetyl chloride for selective substitution of the silicon- or boron-bound diethylamino groups all failed. We then focused on the direct preparation of [(dialkylamino)silyl]pinacolborane by the reaction of [(dialkylamino)silyl]lithiums with 2 equiv of alkoxypinacolborane.[16i]

Silyllithium **2** was reacted with 2.4 equiv of (isopropoxy)-pinacolborane (**3**)[19] in THF at 0 °C to room temperature (eq 1). The reaction proceeded cleanly to give [(diethylamino)diphenylsilyl]pinacolborane (**4**) in 95% yield. Pinacolborane [HB(pin)] could also be used as a boron electrophile for this reaction.[16i]



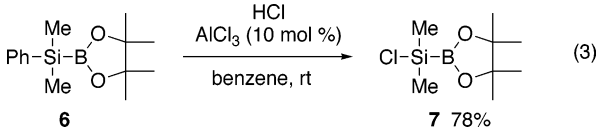
2 **3** (2.4 equiv.), THF/hexane, 0 °C to rt → **4** 95% (1)

The amino group of silylboronic ester **4** could be converted into a chloro group by the reaction with acetyl chloride or hydrogen chloride. Use of the latter was found to be practical, because in the former case removal of *N*,*N*-diethyl acetamide by distillation was not trivial. Pure **5** was isolated in 94% yield by filtration followed by distillation, when using hydrogen chloride (eq 2).



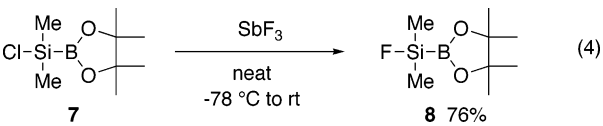
4 HCl, CH_2Cl_2/Et_2O, 0 °C to rt → **5** 94% (2)

Synthesis of $XMe_2Si-B(pin)$ (X = Cl, F, RO, R_2N). The reaction of [(dialkylamino)diphenylsilyl]lithium with boron electrophiles described above cannot be applied to the synthesis of the corresponding dimethylsilyl derivatives, because generation of [(dialkylamino)dimethylsilyl]lithium is not possible by reductive metalation. We found that reaction of (dimethylphenylsilyl)pinacolborane (**6**)[16i] with dry hydrogen chloride in the presence of a catalytic amount (10 mol %) of aluminum chloride afforded (chlorodimethylsilyl)pinacolborane (**7**), which is suitable for introduction of functional groups on the silicon atoms (eq 3).[20] It should be remarked that the chlorodephenylation occurred smoothly without cleavage of the Si−B bond, giving **7** in good yield by distillation. No reaction took place in the absence of aluminum chloride.



6 HCl, $AlCl_3$ (10 mol %), benzene, rt → **7** 78% (3)

With the (chlorosilyl)borane **7** in hand, silylboronic esters bearing other heteroatom substituents on silicon were prepared. Fluorination of **7** was successfully achieved with SbF_3 under solvent-free conditions to afford (fluorodimethylsilyl)pinacolborane (**8**) in 76% yield (eq 4).[21]



7 SbF_3, neat, -78 °C to rt → **8** 76% (4)

The reactions of **7** with alcohols proceeded cleanly in the presence of pyridine in CH_2Cl_2 (eq 5). Under these conditions, (alkoxysilyl)boranes **9a**−**d** having methoxy, ethoxy, isopropoxy, and *tert*-butoxy groups were synthesized in good yields (76−90%).

Amination of **7** was achieved by the reaction with secondary amines in the presence of triethylamine (eq 6). The reactions of diethylamine, dimethylamine, and pyrrolidine gave the corresponding (aminosilyl)boranes **10a**−**c** in high yields (71−

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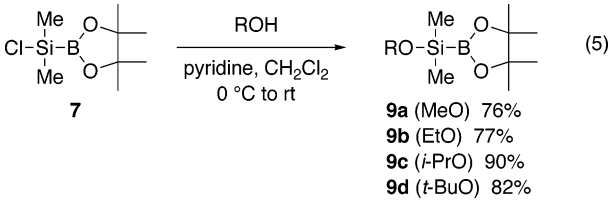
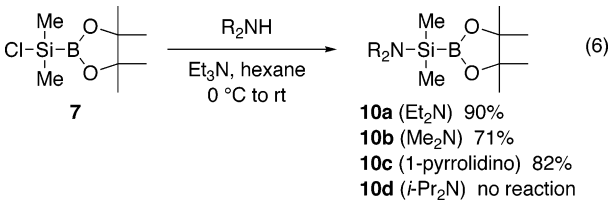


(5)

90%). However, no reaction took place when diisopropylamine was used under the same reaction conditions.



(6)

Conclusion

Practical synthetic methods for silylpinacolboranes bearing chloro, fluoro, alkoxy, and amino groups on the silicon atom were established. Functionalized diphenylsilyl derivatives were prepared from the (aminosilyl)borane **4**, which was prepared by the reaction of (aminosilyl)lithium **2** with boron electrophiles through Si−B bond formation. On the other hand, functionalized dimethylsilyl derivatives were synthesized from the (phenylsilyl)borane **6** through electrophilic aromatic *ipso*-substitution, which gave (chlorosilyl)borane **7**. Conversion of the amino group of **4** and the chloro group of **7** was achieved with the same methods as those used in the conventional conversions. It should be emphasized here that the new silylboronic esters functionalized on silicon are expected not only to show higher reactivity than the previously known triorganosilyl derivatives but also to make possible further transformation of the silyl group into other functionalities. Studies along this line are now actively being undertaken in this laboratory.

Experimental Section

General Comments. All reactions were carried out under a nitrogen or an argon atmosphere. ^{1}H NMR spectra were recorded on Varian GEMINI-2000 (300.07 MHz) or Varian Mercury-400 (400.44 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (75.45 MHz) or JEOL JNM-A500 (125.65 MHz) spectrometers. ^{11}B NMR (128.48 MHz) and ^{19}F NMR (376.87 MHz) spectra were recorded on a Varian Mercury-400 spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane (for ^{1}H and ^{13}C), BF_3·OEt_2 (for ^{11}B), and $CFCl_3$ (for ^{19}F). Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High-resolution mass spectra were recorded on a JEOL JMS-MS700 (CI) spectrometer.

Hydrogen chloride was generated by the slow addition of concentrated sulfuric acid to NH_4Cl. The gas was dried by passing through concentrated sulfuric acid prior to introduction into the reaction mixture.

Synthesis of 2-[(Diethylamino)diphenylsilyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4, eq 1). To a solution of (isopropoxy)pinacolborane (**3**, 42.6 g, 229 mmol)[19] in hexane (100 mL) was added [(diethylamino)diphenylsilyl]lithium (**2**),[18] which was prepared from (diethylamino)diphenylsilyl chloride (27.6 g, 95.3 mmol) and lithium (2.65 g, 381 mmol) in THF (90 mL), dropwise at 0 °C over 30 min. After the addition, the cooling bath was removed. The mixture was stirred for 12 h at room temperature. The volatiles were removed *in vacuo*, and then the residue was diluted with pentane. After removing the insoluble white solid by filtration under nitrogen atmosphere, the filtrate was concentrated. Recrystallization from pentane gave pure **4** (34.5 g, 95%). **4**: ^{11}B NMR (128 MHz, C_6D_6) δ 33.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.62 (m, 4H), 7.33−7.35 (m, 6H), 2.94 (q, J = 6.8 Hz, 4H), 1.28 (s, 12H), 1.00 (t, J = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 135.4, 128.8, 127.5, 83.4, 41.1, 25.0, 15.4.

Synthesis of 2-(Chlorodiphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5, eq 2). To a CH_2Cl_2 (60 mL) solution of **4** (25.1 g, 65.7 mmol) was added an Et_2O solution of hydrogen chloride (1.0 M, 145 mL, 145 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h. The white precipitate was removed by filtration under nitrogen atmosphere, and the resulting filtrate was concentrated. Bulb-to-bulb distillation under reducing pressure (190 °C/1.5 mmHg) gave **5** as white solid (21.4 g, 94%). **5**: ^{11}B NMR (128 MHz, C_6D_6) δ 32.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.73 (m, 4H), 7.36−7.47 (m, 6H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 134.0, 130.3, 128.1, 84.7, 25.0; HRMS (CI) m/z calcd for $C_{18}H_{23}BO_2ClSi$ (MH^+) 345.1249, found 345.1255.

Synthesis of 2-(Chlorodimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7, eq 3). To a solution of **6** (9.73 g, 37.1 mmol)[16i] in benzene (40 mL) was added aluminum chloride (0.495 g, 3.71 mmol), and the mixture stirred at room temperature. Aluminum chloride was dissolved and the solution showed a pale yellow color. Hydrogen chloride was passed through the solution via a Teflon tube with vigorous stirring. The progress of the reaction was checked by GC. The starting compound was consumed after introducing ca. 30 equiv of hydrogen chloride. The reaction was quenched with acetone (5 mL), and the resulting mixture was stirred for 15 min. After removal of the volatile materials, the residue was distilled under reducing pressure (47.5−49.0 °C/2.5 mmHg) to give **7** as a colorless liquid (6.36 g, 78%). **7**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 12H), 0.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.2, 24.9, 2.1; HRMS (CI) m/z calcd for $C_8H_{19}BClO_2Si$ (MH^+) 221.0936, found 221.0934.

Synthesis of 2-(Fluorodimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8, eq 4). Antimony(III) fluoride (0.83 g. 4.6 mmol) was placed in a two-necked round-bottomed flask equipped with a magnetic stirring bar. The flask was cooled to −78 °C by acetone/dry ice bath. Then **7** (2.63 g, 11.9 mmol) was added to the flask, which immediately froze on the wall. After removal of the cooling bath, the reagents were mixed with stirring at room temperature for 3 h. The resulting dark brown solution was distilled (58−62 °C/10 mmHg) to afford **8** (1.84 g, 76%). **8**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3; ^{19}F NMR (377 MHz, $CDCl_6$) δ −176.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 12H), 0.36 (d, $^3J_{HF}$ = 8.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.8, 25.0, 0.3 (d, $^2J_{CF}$ = 14.0 Hz); HRMS (CI) m/z calcd for $C_8H_{19}BFO_2Si$ (MH^+) 205.1231, found 205.1225.

General Procedure for the Synthesis of (Alkoxysilyl)boranes 9 (eq 5). A solution of **7** in CH_2Cl_2 (1.0 M) was cooled to 0 °C. Pyridine (1.2 equiv) and an alcohol (1.1 equiv) were added to the solution in this order. The reaction mixture was warmed to room temperature and stirred for 3 h. After removal of the precipitation by filtration, the filtrates were concentrated and purified by distillation under reducing pressure.

2-(Methoxydimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a). According to the general procedure, **7** (665 mg, 3.01 mmol) was reacted with MeOH (293 mg, 3.70 mmol). The product **9a** was isolated as a colorless liquid by bulb-to-bulb distillation (90 °C/1.0 mmHg) in 76% yield (492 mg). **9a**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (s, 3H), 1.26 (s, 12H), 0.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.4, 51.1, 25.0, −1.2; HRMS (CI) m/z calcd for $C_9H_{22}BO_3Si$ (MH^+) 217.1431, found 217.1429. Anal. Calcd for $C_9H_{21}BO_3Si$: C, 50.01; H, 9.79. Found: C, 49.75; H, 9.62.

2-(Ethoxydimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b). According to the general procedure, **7** (445 mg, 2.02

mmol) was reacted with EtOH (117 mg, 2.53 mmol). The product **9b** was isolated as a colorless liquid by bulb-to-bulb distillation (90 °C/1.0 mmHg) in 77% yield (359 mg). **9b**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (q, J = 7.2 Hz, 2H), 1.25 (s, 12H), 1.21 (t, J = 7.2 Hz, 3H), 0.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.3, 59.3, 25.0, 18.5, −0.5; HRMS (CI) m/z calcd for $C_{10}H_{24}BO_3Si$ (MH^+) 231.1588, found 231.1586. Anal. Calcd for $C_{10}H_{23}BO_3Si$: C, 52.18; H, 10.07. Found: C, 51.90; H, 9.77.

2-(Isopropoxydimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9c). According to the general procedure, **7** (1.02 g, 4.62 mmol) was reacted with *i*-PrOH (307 mg, 5.01 mmol). The product **9c** was isolated as a colorless liquid by bulb-to-bulb distillation (100 °C/1.5 mmHg) in 90% yield (1.01 g). **9c**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (septet, J = 6.0 Hz, 1H), 1.25 (s, 12H), 1.17 (d, J = 6.0 Hz, 6H), 0.22 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.2, 66.1, 25.6, 25.0, 0.06; HRMS (CI) m/z calcd for $C_{11}H_{26}BO_3Si$ (MH^+) 245.1744, found 245.1737. Anal. Calcd for $C_{11}H_{25}BO_3Si$: C, 54.10; H, 10.32. Found: C, 54.34; H, 10.07.

2-(*tert*-Butoxydimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9d). According to the general procedure, **7** (468 mg, 2.12 mmol) was reacted with *t*-BuOH (206 mg, 2.78 mmol). The product **9d** was isolated as a colorless liquid by bulb-to-bulb distillation (110 °C/1.0 mmHg) in 82% yield (447 mg). **9d**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 9H), 1.25 (s, 12H), 0.21 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.1, 72.1, 31.8, 24.9, 2.1; HRMS (CI) m/z calcd for $C_{12}H_{26}BO_3Si$ [$(M - H)^+$] 257.1744, found 257.1739. Anal. Calcd for $C_{12}H_{27}BO_3Si$: C, 55.81; H, 10.54. Found: C, 55.77; H, 10.66.

General Procedure for the Synthesis of (Aminosilyl)boranes 10 (eq 6). A solution of **7** in hexane (0.50 M) was cooled to 0 °C. Triethylamine (1.2 equiv) and dialkylamine (1.1 equiv) were added to the solution in this order. The reaction mixture was warmed to room temperature and stirred for 24 h. After removal of the precipitation by filtration, the filtrates were treated with triethylamine (1.2 equiv) and dialkylamine (1.1 equiv) again, since a small amount of unreacted **7** was contained in the product of the first reaction (checked by ^{1}H NMR analysis). After filtration to remove precipitates, the filtrates were concentrated and purified by distillation under reducing pressure.

2-[(Diethylamino)dimethylsilyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10a). According to the general procedure, **7** (3.43 g, 15.6 mmol) was reacted with Et_2NH (1.25 g, 17.8 mmol) twice (85% conversion after first reaction and 100% conversion after second reaction). The product **10a** was isolated as a colorless liquid by bulb-to-bulb distillation (115 °C/1.5 mmHg) in 90% yield (3.62 g). **10a**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (q, J = 7.2 Hz, 4H), 1.24 (s, 12H), 0.99 (t, J = 7.2 Hz, 6H), 0.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 82.9, 41.2, 25.0, 15.8, −0.7. Anal. Calcd for $C_{12}H_{28}BNO_2Si$: C, 56.03; H, 10.97; N, 5.44. Found: C, 55.82; H, 10.69; N, 5.48.

2-[(Dimethylamino)dimethylsilyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b). According to the general procedure, **7** (1.11 g, 5.04 mmol) was reacted with Me_2NH (2.0 M THF solution, 2.77 mL, 5.54 mmol) twice. The product **10b** was isolated as a colorless liquid by bulb-to-bulb distillation (110 °C/2.5 mmHg) in 71% yield (824 mg). **10b**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 6H), 1.24 (s, 12H), 0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.1, 38.9, 25.0, −2.6. Anal. Calcd for $C_{10}H_{24}BNO_2Si$: C, 52.40; H, 10.55; N, 6.11. Found: C, 52.13; H, 10.26; N, 5.82.

2-(Dimethylpyrrolidinosilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10c). According to the general procedure, **7** (1.12 g, 5.09 mmol) was reacted with pyrrolidine (407 mg, 5.73 mmol). The product **10c** was isolated as a colorless liquid by bulb-to-bulb distillation (110 °C/0.6 mmHg) in 82% yield (1.06 g). **10c**: ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90−2.93 (m, 4H), 1.69−1.72 (m, 4H), 1.23 (s, 12H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.0, 47.6, 26.7, 25.0, −2.4. Anal. Calcd for $C_{12}H_{26}BNO_2Si$: C, 56.47; H, 10.27. Found: C, 56.68; H, 10.01.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new silylboronic esters. This material is available free of charge via the Internet at http://pubs.acs.org.

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