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Article

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Utilization of a Trimethylsilyl Group as a Synthetic Equivalent of a Hydroxyl Group via Chemoselective C(sp^3)–H Borylation at the Methyl Group on Silicon

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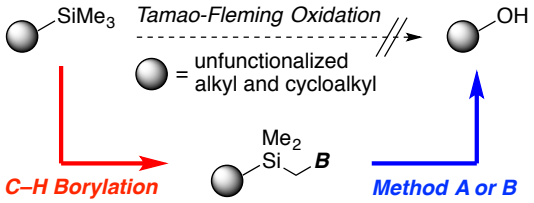
TOC graphic

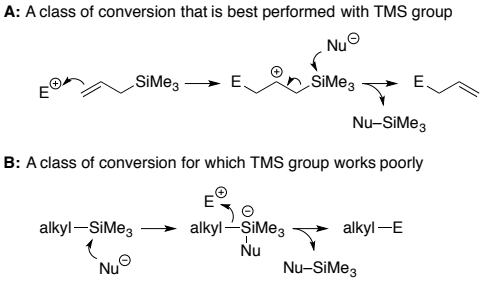


Abstract: A conversion of trimethylsilylalkanes into the corresponding alcohols is established based on an iridium-catalyzed, chemoselective C(sp^3)–H borylation of the methyl group on silicon. The (borylmethyl)silyl group formed by C(sp^3)–H borylation is treated with H_2O_2/NaOH, and the resulting (hydroxymethyl)silyl group is converted into a hydroxyl group by Brook rearrangement, followed by oxidation of the resulting methoxysilyl group under Tamao conditions. An alternative route proceeding through the formylsilyl group formed from a (hydroxymethyl)silyl group by Swern oxidation is also established. The method is applicable to substituted trimethylsilylcycloalkanes and 1,1-dimethyl-1-silacyclopentane for conversion into the corresponding stereodefined cycloalkyl alcohols and 1,4-butanediol.

Introduction

Silyl groups have been utilized as convertible yet stable handles for functionalization in synthetic organic chemistry through their conversion into halogen, oxygen, nitrogen, and carbon based functional groups. The conversions can be classified mainly into two scenarios. Halogenation of alkenyl/arylsilanes as well as the Hosomi-Sakurai reaction can be grouped into the first scenario.[1] In these cases, attack of electrophiles on the unsaturated organic groups precedes elimination of the silyl group through attack of nucleophiles on the silicon atom (Scheme 1A). This conversion is best performed with the trimethylsilyl (TMS) group because of its electron-rich, sterically less demanding nature, which promotes both the initial electrophilic and the subsequent nucleophilic steps. On the other hand, there is another class of conversions for which the TMS group works poorly. This type of conversion involves "preactivation", that is, initial formation of five-coordinated silicate species that participate in the subsequent reaction, in which the silyl group is actually converted into various functional groups (Scheme 1B).[2]

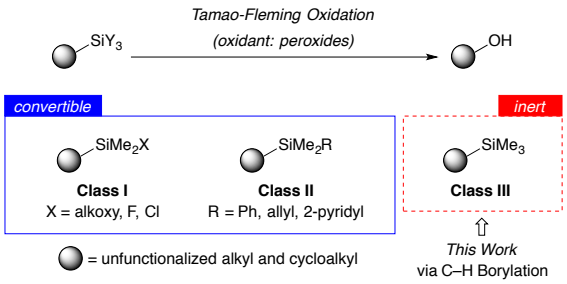
Scheme 1. Electrophilic Substitution of C–$SiMe_3$ Bond



A typical example of the latter conversion can be seen in Tamao-Fleming oxidation using peroxides as oxidants, which is widely utilized in organic synthesis (Scheme 2).[3] In this particular transformation, a base, typically fluoride, is added to activate the silyl groups before accepting a hydroperoxide as the sixth ligand on the silicon atom.[3c,3d,4] To facilitate the formation of the five-

coordinated intermediates, silyl groups that carry at least one heteroatom functional group such as alkoxy or halogen groups are utilized (**Class I**).[5] More robust, non-hydrolyzable triorganosilyl groups bearing organic groups such as phenyl, allyl, and 2-pyridyl groups, which can be easily converted into heteroatom functional groups, have also been utilized as a hydroxyl equivalent (**Class II**).[6] However, TMS groups have never been regarded as a hydroxyl equivalent, principally because of the difficulty in forming five-coordinated silicate species and of converting it into heteroatom functional groups (**Class III**).[7] It should be noted that there are reports on the conversion of the methyl group of a TMS group into heteroatom functional groups under harsh reaction conditions.[8,9,10] Indeed, Woerpel and coworkers reported oxidation of trimethylsilyldecane into decanol.[11] However, low yields as well as forcing reaction conditions involving the use of *t*-BuOOH with KH at 120 °C prevents this procedure from being adopted as a general protocol for the utilization of the TMS group in Tamao-Fleming oxidation, in spite of the fact that the TMS group shows extremely high tolerability to a range of reaction conditions and that it is easily available from inexpensive silicon sources such as $ClSiMe_3$, or by transfer hydrosilylation using $HSiMe_3$ equivalent.[12]

Scheme 2. Conversion of Silylalkanes into Alcohols



We envisioned that utilization of the TMS groups in Tamao-Fleming oxidation may become possible through the use of C–H functionalization chemistry.[13] We recently established an iridium-catalyzed C(sp^3)–H borylation system that can be used to borylate the methyl group on silicon atoms

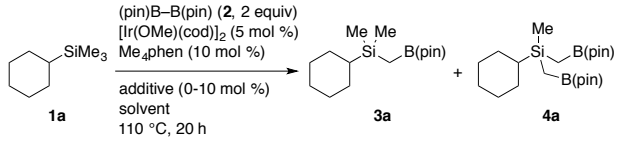
selectively over the other C(sp^3)–H bonds.[14] It was expected that this reaction would allow the conversion of a highly-stable TMS group into more reactive silyl groups that form five-coordinated silicates. Herein, we describe new protocols for conversion of the TMS groups in trimethylsilylalkanes and -cycloalkanes into hydroxyl group to give the corresponding alcohols and cycloalkyl alcohols through initial iridium-catalyzed C(sp^3)–H borylation.

Results and Discussion

Modification of Iridium-Catalyzed C(sp^3)–H Borylation. Upon conversion of trimethylsilylcyclohexane (**1a**) into cyclohexanol, we first made a modification of our original C(sp^3)–H borylation protocol, in which a large excess of silicon reagents over the diboron reagent were used.[15] We recently reported an iridium catalyst system using *t*-BuOK as an additive that accelerated the iridium-catalyzed C(sp^3)–H borylation of aliphatic compounds and a trialkoxy(methyl)silane.[14c,16,17] We applied this system to convert **1a** by using an excess of the boron source (Table 1). The reaction took place efficiently in the presence of *t*-BuOK (1.25 mol %) to give monoboryl compound **3a** and diboryl compound **4a** in 93% combined yield (**3a**:**4a** = 71:29, entry 2).[18] In sharp contrast, the borylated product was obtained only in 4% in the absence of *t*-BuOK (entry 1), indicating that significant rate acceleration was accomplished by the catalytic amount of *t*-BuOK. The amount of *t*-BuOK is important for high catalyst efficiency, as observed in the previous study (entries 2-5).[14c,16] Rate-acceleration was observed with *t*-BuOK/Ir = 0.5-0.125 (entries 2-4), whereas no acceleration was observed with *t*-BuOK/Ir = 1 (entry 5). Other additives such as MeONa, Cs_2CO_3, and CsF were equally effective in the C–H borylation of **1a** (entries 6-8). *t*-BuOMe was the optimal solvent for obtaining the borylated products with high yields (entry 2). Other ether solvents including CyOMe, THF, and 1,4-dioxane suffered from the formation of their C–H borylation products (entries 9-11).[19] The C–H borylation was slow in cyclooctane (entry 12), which could be improved by elevation of the reaction temperature (80%

combined yield at 135 °C, entry 13). Finally, we established a protocol for 1 mmol scale synthesis using reduced amount of the iridium catalyst (5 mol % Ir) and **2** (**1a**:**2** = 1:1.5), by which **3a** (71%) and **4a** (17%) were isolated after 36 h (entry 14).[20]

Table 1. Modification of Iridium-Catalyzed C(sp^3)–H Borylation[a]

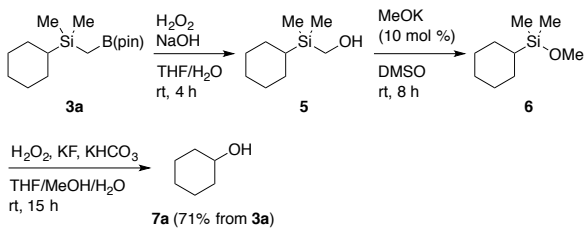


entry	additive (mol %)	additive/Ir	solvent	% yield[b] (**3a**:**4a**)[c]
1	-	0	*t*-BuOMe	4 (100:0)
2	*t*-BuOK (1.25)	0.125	*t*-BuOMe	93 (71:29)
3	*t*-BuOK (2.5)	0.25	*t*-BuOMe	90 (76:24)
4	*t*-BuOK (5.0)	0.50	*t*-BuOMe	87 (82:18)
5	*t*-BuOK (10)	1.0	*t*-BuOMe	5 (100:0)
6	MeONa (2.5)	0.25	*t*-BuOMe	87 (77:23)
7	Cs_2CO_3 (2.5)	0.25	*t*-BuOMe	76 (88:12)
8	CsF (2.5)	0.25	*t*-BuOMe	93 (80:20)
9	*t*-BuOK (2.5)	0.25	CyOMe	46 (96:4)
10	*t*-BuOK (2.5)	0.25	THF	57 (95:5)
11	*t*-BuOK (2.5)	0.25	1,4-dioxane	27 (96:4)
12	*t*-BuOK (2.5)	0.25	cyclooctane	7 (100:0)
13[d]	*t*-BuOK (2.5)	0.25	cyclooctane	80 (85:15)
14[e]	*t*-BuOK (2.5)	0.25	*t*-BuOMe	88[f] (81:19)

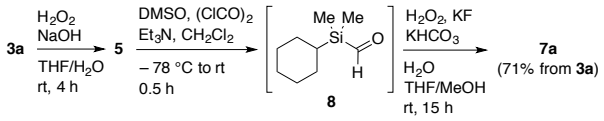
[a] **1a** (0.50 mmol), **2** (1.0 mmol), $[Ir(OMe)(cod)]_2$ (0.025 mmol), Me_4phen (0.050 mmol), and additive (0–0.050 mmol) were stirred in solvent (0.5 mL) at 110 °C for 20 h unless otherwise noted. [b] ^1H NMR yield based on **1a**. [c] Determined by ^1H NMR. [d] Reaction at 135 °C. [e] Optimized Conditions for 1 mmol scale reaction: **1a** (1.0 mmol), **2** (1.5 mmol), $[Ir(OMe)(cod)]_2$ (0.025 mmol), Me_4phen (0.050 mmol), and *t*-BuOK (0.0125 mmol) were stirred in *t*-BuOMe (0.8 mL) at 110 °C for 36 h. [f] Combined yield of isolated **3a** (71%) and **4a** (17%) based on **1a**.

Conversion of Borylmethyl Group into Hydroxyl Group. With the borylated products **3a**/**4a** in hand, we designed two oxidation methods, both of which include conversion of **3a**/**4a** into the corresponding (hydroxymethyl)silanes via oxidation with H_2O_2/NaOH. One approach was to utilize Brook rearrangement of (hydroxymethyl)dimethylsilylcyclohexane (**5**) giving methoxydimethylsilylcyclohexane (**6**), which can be oxidized to cyclohexanol (**7a**) under Tamao conditions (Method A, Scheme 3). The second approach was to oxidize **5** to formylsilanes **8**, which may undergo oxidation to **7a** upon further oxidation (Method B, Scheme 4). To demonstrate the feasibility of Method A, **5** was treated with a catalytic amount of MeOK (10 mol %) at room temperature in DMSO, giving **6** via Brook rearrangement (Scheme 3). Compound **7a** was finally obtained by application of a standard Tamao protocol with KF, $KHCO_3$, and H_2O_2 at room temperature. The total reaction yield for three steps from **3a** was calculated to be 71%. On the other hand, we found that Method B also worked efficiently. Indeed, **5** was subjected to Swern oxidation conditions to give formylsilane **8** (Scheme 4).[21] The unstable intermediate **8** was found to be oxidized directly to **7a** under standard Tamao reaction conditions. The total reaction yield for three steps from **3a** was 71%. It should be noted here that the double-borylated minor product **4a** was also converted into **7a** by Methods A and B in 78% and 67% yields, respectively (For details, see Experimental Section). We thus established that both Method A and Method B gave rise to **7a** in good yields in three steps from **3a**/**4a** (71% via Method A and 70% via Method B, entry 1, Table 2).

Scheme 3. Conversion of (Borylmethyl)silyl Group into Hydroxyl Group via Brook Rearrangement (Method A)

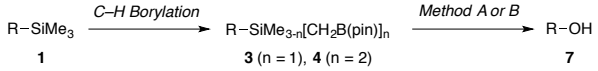


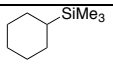
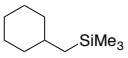
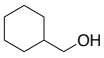
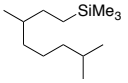
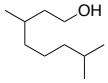
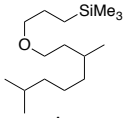
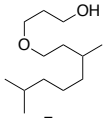
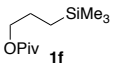
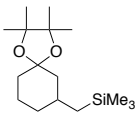
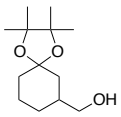
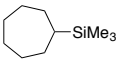
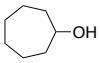
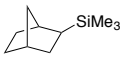
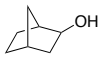
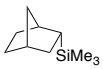
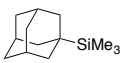
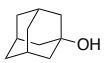
Scheme 4. Conversion of (Borylmethyl)silyl Group into Hydroxyl Group via Swern Oxidation (Method B)



Synthesis of Alcohols from Trimethylsilylalkanes. A range of trimethylsilylalkanes and -cycloalkanes were subjected to the modified C(sp^3)–H borylation and following conversion into alcohols (Table 2). Primary alkyl-substituted compounds **1b**–**g** underwent C(sp^3)–H borylation in *t*-BuOMe at 110 °C using **2** (1.5 equiv) in the presence of Ir-Me_4phen catalyst (5 mol %) with *t*-BuOK (1.25 mol %), giving the corresponding (borylmethyl)silanes **3b**–**g** and bis(borylmethyl)silane **4b**–**g** in 71-89% combined yields, respectively (entries 2-7). In the reaction of trimethylsilyloctane (**1d**), C(sp^3)–H borylation at the octyl terminus also took place to give (borylmethyl)(8-boryloctyl)dimethylsilane **9** in 7% yield, therby resulting in a slight decrease of the combined yield of **3d**/**4d** (71%, entry 4). Alkyl ether (entry 5), pivalate (entry 6), and pinacol-derived acetal (entry 7) were tolerant under the conditions using Ir/*t*-BuOK, although 3-[(trimethylsilyl)methyl]cyclohexan-1-one did not give the corresponding **3** and **4**.[22] Following three-step conversion of the borylated compounds using Method A resulted in the formation of the corresponding alcohols **7b**–**g** with reasonable yields, except for pivalate **7f** (entries 2-7). For conversion of **3f**/**4f** into **7f**, Method B gave a significantly better yield than Method A (63% vs. 41%, entry 6).

Table 2. Alcohol Synthesis from Trimethylsilylalkanes[a]



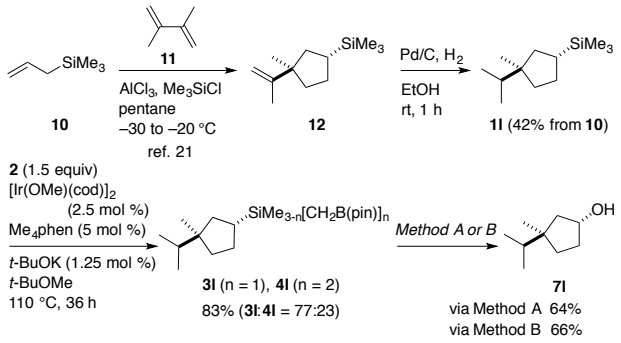
entry	substrate	% yield[b] (**3**:**4**)	alcohol	Method: % yield[c]
1	 **1a**	88 (81:19)	 **7a**	A: 71; B: 70
2	 **1b**	89 (73:27)	 **7b**	A: 62
3	 **1c**	77 (69:31)	 **7c**	A: 70; B: 71
4	 **1d**	71 (72:28)[d]	 **7d**	A: 65
5	 **1e**	81 (68:32)	 **7e**	A: 69; B: 76
6	 **1f**	74 (76:24)	 **7f**	A: 41; B: 63
7	 **1g**	86 (76:24)	 **7g**	A: 73
8	 **1h**	87 (80:20)	 **7h**	A: 61; B: 60
9[e]	 **1i**	89 (80:20)	 **7i**	A: 58[f]
10[g]	 **1j**	88 (83:17)	 **7j**	A: 56[g]
11	 **1k**	78 (92:8)	 **7k**	A: 65[h]; B: 29[h]

[a] C–H Borylation: **1** (1.0 mmol), **2** (1.5 mmol), $[Ir(OMe)(cod)]_2$ (0.025 mmol), Me_4phen (0.050 mmol), and *t*-BuOK (0.0125 mmol) were stirred in *t*-BuOMe (0.8 mL) at 110 °C for 36 h. Method A: 1) H_2O_2, NaOH, THF/H_2O, rt, 4 h; 2) MeOK (10 mol %), DMSO, rt, 8 h; 3) H_2O_2, KF, $KHCO_3$, THF/MeOH/H_2O, rt, 15 h. Method B: 1) H_2O_2, NaOH, THF/H_2O, rt, 4 h; 2) DMSO, $(ClCO)_2$, Et_3N, CH_2Cl_2, –78 °C to rt,; 3) H_2O_2, KF, $KHCO_3$, THF/MeOH/H_2O, rt, 15 h. [b] Combined yield of isolated **3** and **4** based on **1**. [c] Isolated yield from **3**/**4** (3 steps). [d] (pin)B$(CH_2)_8$SiMe_2(CH_2B(pin)) (**9**) was also formed in 7% yield. [e] exo:endo = 94:6. [f] exo:endo = 95:5. [g] only endo. [h] 40 h for the 3rd step (oxidation).

Secondary alkyl-substituted compounds **1h–j** were converted efficiently into **3h–j**/**4h–j** under the modified C(sp^3)–H borylation conditions (entries 8-10, Table 2). The reaction of sterically more demanding **1k** also gave **3k** and **4k** in good combined yield with higher selectivity for the formation of monoborylated product **3k** (entry 11). Treatment of **3h–k**/**4h–k** under the conditions of Method A afforded **7h-k** in 56–65% yields (entries 8–11). Although Methods A and B were comparably effective, the yield of **7k** dropped significantly in the conversion of **3k**/**4k** using Method B, in which oxidation of the formylsilanes was rather slow (entry 11). The stereochemistry of **1i** and **1j** was retained during the C–H borylation and following oxidation (entries 9 and 10).

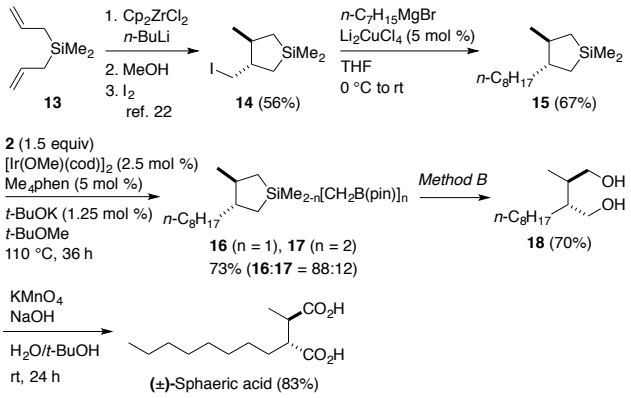
Application to the Synthesis of a Stereodefined Cyclopentanol Derivative. The present C–H borylation-based conversion of trimethylsilylalkanes was applied to the synthesis of stereodefined organic compounds starting from readily available TMS-based reagents, such as allyltrimethylsilane (**10**) and diallyldimethylsilane (**13**) (Schemes 5 and 6). Jung and coworkers reported an $AlCl_3$/Me_3SiCl-mediated reaction of **10** with 2,3-dimethyl-1,3-butadiene (**11**), which gives [3+2] cycloaddition product **12** diastereoselectively (Scheme 5).[23] We focused on the potential usefulness of the stereodefined five-membered ring. Compound **1l** was obtained by hydrogenation of **12** and subjected to the C(sp^3)–H borylation, which was followed by conversion into alcohol **7l**. C–H borylation of **1l** took place chemoselectively at the methyl group on silicon to afford **3l** and **4l** in 83% yield (**3l**:**4l** = 77:23). Alcohol **7l** was obtained in 66–64% yield by the following conversions using either Method A or B.

Scheme 5. Synthesis of a Stereodefined Cyclopentanol Derivative Starting from Allyltrimethylsilane (**10**)

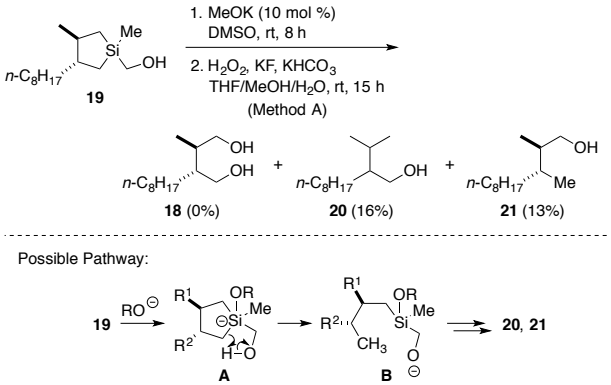


Application to the Synthesis of (±)-Sphaeric acid. The present method was extended to conversion of 1,1-dimethyl-1-silacyclopentane into 1,4-diol via double oxidative cleavage of Si–C bonds, leading to the synthesis of (±)-Sphaeric acid (Scheme 6). Takahashi and coworkers reported the stereoselective synthesis of silacyclopentane **14** via formation of zirconacyclopentane from **13**, followed by treatment with MeOH and I_2.[24] Copper-catalyzed alkylation of **14** with heptylmagnesium bromide gave **15**, which was then subjected to the modified iridium-catalyzed C(sp^3)–H borylation. The reaction took place selectively at the methyl group on the silicon atom to give **16** and **17** in 73% combined yield (**16**:**17** = 88:12).[25] Conversion of **16**/**17** according to Method B resulted in the formation of diol **18** in 70% yield. Finally, oxidation of **18** with $KMnO_4$ under basic conditions afforded (±)-Sphaeric acid.[26] It is interesting to note that the use of Method A in the conversion of **19** never led to the formation of **18** (Scheme 7). Instead, mono-ols **20** and **21** were obtained, albeit in low yields. **20** and **21** were probably formed through ring opening of **19** to form acyclic alkylsilanes in the presence of MeOK. A possible mechanism is that an alkoxide attacks to the silicon center of **19** to form silicate **A**, which undergoes protonation by the hydroxyl group accompanied with opening of the five-membered ring to give **B**.[27]

Scheme 6. Synthesis of (±)-Sphaeric Acid Starting from Diallyldimethylsilane (**13**)



Scheme 7. Attempted Conversion of **19** through Method A



Conclusion

We have established a new method to utilize unreactive alkylsilanes in organic synthesis. The trimethylsilyl group of trimethylsilylalkanes and -cycloalkanes could be converted into hydroxyl group to give alcohols. The conversion is based on iridium-catalyzed chemoselective C(sp^3)–H borylation of the methyl group on silicon for the conversion into (borylmethyl)silanes, which are further converted into (hydroxymethyl)silanes via H_2O_2 oxidation. Two complementary oxidation protocols have been established: Method A involves formation of methoxysilanes via Brook rearrangement, and Method B involves formation of formylsilanes via Swern oxidation. Both protocols are finalized by application of

Tamao-Fleming oxidation to give the corresponding alcohols. These protocols have enabled the use of stereodefined TMS-substituted cycloalkanes, which has not been commonly employed in synthetic applications.

Experimental Section

General: All iridium-catalyzed reactions were performed in Glove Box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Other reactions were also carried out under an atmosphere of nitrogen unless otherwise noted. Materials were weighted by an electric balance (readability: 0.01 mg). Gas chromatography (GC) was performed on a FID detector with a column (100% dimethylpolysiloxane, ϕ 0.32 mm x 15 m). Column chromatography was performed with silica gel (pH 7.0, 40-63 μm, 60 Å). Gel Permeation Chromatography (GPC) was performed with series-connected a column for exclusion limit of 1000 (ϕ 20 mm x 600 mm) and a column for exclusion limit of 5000 (ϕ 20 mm x 600 mm). ^{1}H NMR (399.89 MHz), ^{13}C NMR (100.55 MHz), and ^{11}B NMR (128.30 MHz) spectra were recorded at ambient temperature using $CDCl_3$ as a solvent. For ^{1}H and ^{13}C NMR, chemical shifts (δ) in parts per million (ppm) were referenced to the solvent residual peak as an internal standard: $CHCl_3$ for ^{1}H NMR (δ 7.26) and $CDCl_3$ for ^{13}C NMR (δ 77.0). For ^{11}B NMR, chemical shifts (δ) in ppm were referenced to $BF_3{\cdot}OEt_2$ as an external standard. ^{1}H NMR data were reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (J), and integration. High resolution mass spectra were recorded on a magnetic sector mass spectrometer (EI) and a Fourier-transform mass spectrometer (ESI, APCI, DART). Infrared spectra were recorded on a FT-IR spectrometer attached a single-reflection horizontal attenuated total reflection attachment.

Solvents and reagents: *t*-BuOMe, CyOMe, cyclooctane, and DMSO were distilled over calcium hydride and degassed. THF and 1,4-dioxane were dried and degassed by benzophenone ketyl. Dry

CH_2Cl_2 was purchased and used as received. Bis(pinacolato)diboron (**2**) was purchased and purified by recrystallization (pentane) before use. Other reagents were used as received from commercial sources.

Catalysts and a ligand: $[Ir(OMe)(cod)]_2$[28] was synthesized by the method reported previously. 3,4,7,8-Tetramethyl-1,10-phenanthroline (Me_4phen) was used as received from commercial source. *t*-BuOK, MeONa, Cs_2CO_3, CsF, and KOMe were purchased and dried in vacuo (150 ºC, 12 h) before use.

Preparation of Substrates: Trimethylsilylalkanes **1a-k** were synthesized as follows.

Trimethylsilylcyclohexane (1a)[14b]**:** In a 200 mL three neck flask, a solution of methylmagnesium iodide was prepared from iodomethane (3.1 g, 22 mmol) with magnesium turnings (0.54 g, 22 mmol) in Et_2O (25 mL). The solution was cooled to 0 °C by ice-water bath. Cyclohexyldimethylsilyl chloride (3.5 g, 20 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring for 8 h, excess amount of sat. NH_4Cl aq. was added. The organic layer was separated, and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic portions were washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (48.5-49.0 °C/9 mmHg) to afford **1a** (2.5 g, 16 mmol, 81%) as a colorless oil. **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.76 (m, 5H), 0.98-1.28 (m, 5H), 0.53 (tt, J = 12.8, 3.2 Hz, 1H), –0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.1, 27.4, 27.0, 26.2, –3.6.

(Trimethylsilylmethyl)cyclohexane (1b)[12]**:** In a 300 mL three neck flask, a solution of (cyclohexylmethyl)magnesium bromide was prepared from bromomethylcyclohexane (18 g, 100 mmol) with magnesium turnings (2.7 g, 110 mmol) in THF (100 mL). Trimethylsilyl chloride (13 g, 120 mmol) was then added to the solution slowly, and the reaction mixture was refluxed for 12 h. The reaction was quenched by sat. NH_4Cl aq., and hexane (300 mL) was added. The organic layer was

washed with water (100 mL x 3), washed with brine (100 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (81.0-82.0 °C/22 mmHg) to afford **1b** (12 g, 73 mmol, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56-1.72 (m, 5H), 1.31-1.42 (m, 1H), 1.05-1.29 (m, 3H), 0.85-0.98 (m, 2H), 0.48 (d, J = 6.8 Hz, 2H), –0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.9, 34.4, 26.6, 26.3, 25.8, –0.5.

1-(Trimethylsilyl)-3,7-dimethyloctane (1c): In a 100 mL two neck flask, a solution of (3,7-dimethyloctyl)magnesium bromide was prepared from 1-bromo-3,7-dimethyloctane (4.4 g, 20 mmol) with magnesium turnings (0.53 g, 22 mmol) in THF (20 mL). Trimethylsilyl chloride (2.6 g, 24 mmol) was then added to the solution slowly, and the reaction mixture was refluxed for 12 h. The reaction was quenched by sat. NH_4Cl aq., and hexane (50 mL) was added. The organic layer was washed with water (20 mL x 3), washed with brine (20 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (89.0-90.0 °C/4 mmHg) to afford **1c** (3.0 g, 14 mmol, 68%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (septet, J = 6.4 Hz, 1H), 0.98-1.36 (m, 9H), 0.869 (d, J = 6.4 Hz, 3H), 0.867 (d, J = 6.4 Hz, 3H), 0.84 (d, J = 6.4 Hz, 3H), 0.36-0.54 (m, 2H), –0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 39.4, 36.7, 35.6, 30.9, 28.0, 24.8, 22.7, 22.6, 19.3, 13.4, –1.7. HRMS (EI) *m/z* calcd for $C_{13}H_{30}Si^+$ $[M]^+$: 214.2111, found: 214.2115.

Trimethylsilyloctane (1d)[14b]**:** In a 200 mL three neck flask, a solution of octylmagnesium bromide was prepared from 1-bromooctane (3.9 g, 20 mmol) with magnesium turnings (0.49 g, 20 mmol) in THF (20 mL). The solution was cooled to 0 °C by ice-water bath. Trimethylsilyl chloride (2.4 g, 22 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was refluxed for 6 h. The reaction was quenched by sat. NH_4Cl aq., and hexane (50 mL) was added. The organic layer was washed with water (20 mL x 3), washed with brine (10 mL x 1), and dried

over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (70.0-71.0 °C/13 mmHg) to afford **1d** (2.9 g, 15 mmol, 77%) as a colorless oil. **1d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23-1.34 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H), 0.45-0.51 (m, 2H), –0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 33.7, 32.0, 29.4, 29.3, 23.9, 22.7, 16.7, 14.1, –1.6.

3,7-Dimethyloctyl 3-trimethylsilylpropyl ether (1e): In a 100 mL two neck flask was charged with NaH (in oil, 50~72%, 0.99 g, 21~30 mmol), THF (25 mL) and 1-bromo-3,7-dimethyloctane (5.3 g, 24 mmol). The flask was cooled to 0 ºC by ice-water bath, and 3-trimethylsilylpropanol (2.7 g, 20 mmol) was added dropwise. After stirring at 0 ºC for 1 h, the cooling bath was removed and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by water, and diethyl ether (50 mL) was added. The organic layer was washed with water (20 mL x 2), washed with brine (20 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane:Et_2O = 20:1). **1e** (3.6 g, 13 mmol, 66%) was obtained as a colorless oil. **1e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39-3.48 (m, 2H), 3.36 (t, J = 6.8 Hz, 2H), 1.46-1.66 (m, 5H), 1.19-1.43 (m, 4H), 1.04-1.19 (m, 3H), 0.88 (d, J =7.2 Hz, 3H), 0.86 (d, J =6.8 Hz, 6H), 0.45-0.50 (m, 2H), –0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 73.9, 69.2, 39.3, 37.4, 36.8, 29.9, 28.0, 24.7, 24.2, 22.7, 22.6, 19.7, 12.6, –1.7. HRMS (EI) *m/z* calcd for $C_{16}H_{35}OSi^{+}$ $[M - H]^{+}$: 271.2452, found: 271.2452.

3-(Trimethylsilyl)propyl pivalate (1f): In a 100 mL two neck flask was charged with 3-trimethylsilylpropanol (2.6 g, 20 mmol), 4-(dimethylamino)pyridine (0.24 g, 2 mmol), triethylamine (4.0 g, 40 mmol) and CH_2Cl_2 (20 mL). Pivalic anhydride (5.6 g, 30 mmol) was added and the reaction mixture was stirred at room temperature. After 24 h, water (10 mL) was added, and the aqueous layer was extracted with dichloromethane (10 mL x 2). The organic layer was collected, and the combined organic portions were washed with brine (10 mL x 1), and dried over anhydrous sodium sulfate. After

removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane:Et_2O = 20:1). **1f** (2.2 g, 10 mmol, 51%) was obtained as a colorless oil. **1f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (t, J = 6.8 Hz, 2H), 1.56-1.65 (m, 2H), 1.20 (s, 9H), 0.46-0.53 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 66.9, 38.7, 27.2, 23.3, 12.4, –1.8. HRMS (APCI) *m/z* calcd for $C_{11}H_{25}O_2Si^+$ $[M + H]^+$: 217.1618, found: 217.1618.

2,2,3,3-Tetramethyl-7-trimethylsilylmethyl-1,4-dioxaspiro[4.5]decane (1g): The 1,4-addition of Grignard reagent was performed in accordance with a reported procedure.[29] In a 500 mL three neck flask, a solution of (trimethylsilylmethyl)magnesium chloride was prepared from (chloromethyl)trimethylsilane (8.6 g, 70 mmol) with magnesium turnings (1.9 g, 77 mmol) in diethyl ether (70 mL). CuBr (0.39 g, 2.7 mmol) was added, and the reaction mixture was cooled to 0 ºC by ice-water bath. 2-Cyclohexen-1-one (5.8 g, 60 mmol) in diethyl ether (45 mL, rinsed 5 mL x 2) was added dropwise to the reaction mixture over 15 min. The cooling bath was removed, and the resulting mixture was stirred at room temperature for 30 min. The reaction was quenched by water (90 mL) at 0 ºC and the organic layer was washed with water (150 mL x 3), washed with brine (150 mL x 1), and dried over anhydrous sodium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was purified by Kugelrohr distillation (80 °C/0.4 mmHg) to afford 3-[(trimethylsilyl)methyl]cyclohexan-1-one (9.4 g, 51 mmol, 85%) as a colorless oil.

In a 200 mL flask, pinacol (12 g, 100 mmol), *p*-TsOH·H_2O (0.39 g, 2 mmol) and 3-[(trimethylsilyl)methyl]cyclohexan-1-one (3.7 g, 20 mmol) were dissolved in toluene (80 mL). The resulting mixture was refluxed with removing water using Dean-Stark apparatus for 24 h. After cooling to room temperature, sat. $NaHCO_3$ aq. was added to the reaction mixture and the organic layer was washed with water (20 mL x 2). The aqueous layer was extracted with diethyl ether (20 mL x 2). The organic layer was collected, and the combined organic portions were washed with brine (20 mL x 1), and dried over anhydrous sodium sulfate. After removal of the volatiles by a rotary evaporator, the

resulting crude product was purified by column chromatography on silica gel (hexane:Et_2O = 20:1). **1g** (2.6 g, 9.2 mmol, 46%) was obtained as a colorless oil. **1g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.88 (m, 3H), 1.47-1.67 (m, 3H), 1.38 (td, J = 12.8, 4.4 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.17 (t, J = 12.4 Hz, 1H), 0.77-0.89 (m, 1H), 0.52 [dd (AB pattern), J = 14.8, 6.4 Hz, 1H], 0.45 [dd (AB pattern), J = 14.8, 7.6 Hz, 1H], 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.0, 82.4, 81.6, 48.9, 38.4, 35.6, 32.0, 25.4, 24.90 (2C), 24.88, 24.7, 23.5, –0.5. HRMS (EI) *m/z* calcd for $C_{16}H_{32}O_2Si^+$ $[M]^+$: 284.2166, found: 284.2165.

Trimethylsilylcycloheptane (1h)[12]: In a 200 mL three neck flask, a solution of (cycloheptyl)magnesium bromide was prepared from bromocycloheptane (8.9 g, 50 mmol) with magnesium turnings (1.3 g, 55 mmol) in THF (50 mL). Dimethylsilyl chloride (5.7 g, 60 mmol) was then added to the solution slowly, and the reaction mixture was stirred at room temperature for 2 h. After removal of the volatiles under reduced pressure, hexane was added and filtered through a pad of Celite and the resulting solution was concentrated to afford crude cycloheptyldimethylsilane. The crude cycloheptyldimethylsilane was collected to a 200 mL three neck flask. THF (50 mL) was added to the flask. The flask was cooled to –78 °C by dry ice-acetone bath and MeLi (3.0 M in diethoxymethane, 17 mL, 51 mmol) was added to the reaction mixture. After stirring for 1 h, the cooling-bath was removed, and slowly warmed to room temperature. The resulting mixture was pored into hexane (200 mL) and quenched by water. The organic layer was washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (79.0-80.5 °C/14 mmHg) to afford **1h** (2.0 g, 12 mmol, 24%) as a colorless oil. **1h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65-1.80 (m, 4H), 1.52-1.65 (m, 2H), 1.34-1.52 (m, 4H), 1.14-1.28 (m, 2H), 0.60 (tt, J = 11.2, 3.2 Hz, 1H), –0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 30.1, 28.8, 28.4, 26.7, –3.3.

(1*S,2*S**,4*R**)-2-Trimethylsilylbicyclo[2.2.1]heptane (1i)**[12]: The hydrosilylation was performed in accordance with a reported procedure.[30] To a 200 mL three neck flask, norbornene (5.7 g, 60 mmol), $PtCl_2$(cod) (0.23 g, 0.60 mmol), toluene (60 mL) and dimethylchlorosilane (8.5 g, 90 mmol) were added. The reaction mixture was stirred for 4 h at 80 ºC. After removal of the volatiles, the crude product was distilled under reduced pressure (101.0-102.0 °C/22 mmHg) to afford *exo*-bicyclo[2.2.1]heptan-2-ylchlorodimethylsilane (8.8 g, 47 mmol, 78%) as a colorless oil.

To a 100 mL three neck flask, *exo*-bicyclo[2.2.1]heptan-2-ylchlorodimethylsilane (3.8 g, 20 mmol) and THF (20 mL) were added. The flask was cooled to –78 °C by dry ice-acetone bath and MeLi (3.0 M in diethoxymethane, 7 mL, 21 mmol) was added to the reaction mixture over 10 min. The reaction mixture was stirred for 1 h. The cooling-bath was removed, and after stirring at room temperature for 1 h, the reaction was quenched by water, and hexane (50 mL) was added. The organic layer was washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (87.0-88.0 °C/25 mmHg) to afford **1i** (2.8 g, 17 mmol, 84%) as a colorless oil. **1i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (broad, 1H), 2.15 (broad, 1H), 1.47-1.57 (m, 2H), 1.33-1.39 (m, 2H), 1.06-1.25 (m, 4H), 0.50 (dt, J = 8.8, 1.6 Hz, 1H), –0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.79, 37.75, 36.9, 34.3, 32.5, 29.4, 28.9, –2.7.

(1*S,2*R**,4*R**)-2-Trimethylsilylbicyclo[2.2.1]heptane (1j)**[31]**:** The deprotonation of norbornene was performed in accordance with a reported procedure.[32] To a 100 mL two neck flask, potassium *tert*-butoxide (1.8 g, 16 mmol) and THF (9 mL) were added. The flask was cooled to –78 °C by dry ice-acetone bath and THF solution of norbornene (5.6 g, 59 mmol, in THF 8 mL, rinsed twice with 0.5 mL) was added. *n*-BuLi (1.6 M in hexane, 10 mL, 16 mmol) was added to the reaction mixture over 45 min. The reaction mixture was slowly warmed to –40 ºC and stirred for 90 min, then re-cooled to –78 ºC. Trimethylsilyl chloride (3.7 g, 34 mmol) was then added to the solution slowly, and the reaction mixture

was stirred for 1 h. The cooling-bath was removed, and after stirring at room temperature for 1 h, the reaction was quenched by sat. NH_4Cl aq., and hexane (50 mL) was added. The organic layer was washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (81.0-82.0 °C/30 mmHg) to afford 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (1.3 g, 8 mmol, 49%) as a colorless oil.

In a two neck Schlenk tube was charged with Rh/C (5 wt%, 0.83 g, 0.40 mmol). The tube was evacuated and backfilled with H_2. Ethanol (8 mL) was added to the tube and the mixture was stirred for 10 min. 2-Trimethylsilylbicyclo[2.2.1]hept-2-ene (0.67 g, 4.0 mmol) was added, and the resulting mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through celite. The solution was concentrated by using a rotary evaporator, and the resulting crude product was purified by Kugelrohr distillation (60 ºC, 0.3 mmHg). **1j** (0.59 g, 87%) was obtained as a colorless oil. **1j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (broad, 1H), 2.25 (broad, 1H), 1.62-1.73 (m, 1H), 1.40-1.54 (m, 1H), 1.32-1.40 (m, 2H), 1.20-1.32 (m, 2H), 1.03-1.12 (m, 2H), 0.85-0.95 (m, 1H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 41.8, 39.4, 37.2, 31.5, 29.9, 28.9, 27.3, –1.5.

1-Trimethylsilyladamantane (1k)[33]: Synthesis of **1k** was performed in accordance with a reported procedure.[33] To a 100 mL two neck flask, HMPA (10 mL) and hexamethyldisilane (2.5 mL, 12.5 mmol) were added. The solution was cooled to 0 °C by ice-water bath and MeLi (1.0 M in diethyl ether, 10 mL, 10 mmol) was added and the reaction mixture was stirred for 15 min. The reaction mixture was frozen at –78 ºC. 1-Bromoadamantane (1.6 g, 7.4 mmol) in diethyl ether 10 mL was added over 1 min. The cooling-bath was removed, and slowly warmed to 10 ºC (internal temp.). The reaction mixture was poured into hexane (300 mL), and washed with water (100 mL x 3) and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the remained starting material was removed by silica gel column chromatography (hexane). Pure **1k** (0.45 g, 2.1

mmol, 29%) was obtained by purification using GPC (eluent: $CHCl_3$). **1k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (broad, 3H), 1.68-1.81 (m, 6H), 1.63 (broad, 6H), –0.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.7, 37.1, 27.7, 21.0, –5.6.

Modification of Iridium-Catalyzed C(sp^3)–H Borylation (Table 1): Reaction conditions for C(sp^3)–H borylation of **1a** were screened using excess amount of **2**. In a glove box, a glass tube having PTFE stopcock, equipped with a magnetic stirring bar, was charged with $[Ir(OMe)(cod)]_2$ (17 mg, 0.025 mmol), Me_4phen (12 mg, 0.05 mmol), bis(pinacolato)diboron (**2**) (254 mg, 1.0 mmol), *t*-BuOK (0-0.10 mmol), a solvent (0.5 mL), and trimethylsilylcyclohexane (**1a**) (78 mg, 0.5 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110 or 135 °C with stirring for 20 h. After cooling to room temperature, undecane (39 mg, 0.25 mmol) was added, and the resulting mixture was analyzed by GC to determine the yields of **3a** and **4a**.

Modified Procedure for C(sp^3)–H Borylation of 1a (entry 14, Table 1): In a glove box, a glass tube having PTFE stopcock, equipped with a magnetic stirring bar, was charged with $[Ir(OMe)(cod)]_2$ (17 mg, 0.025 mmol), Me_4phen (12 mg, 0.05 mmol), bis(pinacolato)diboron (**2**) (381 mg, 1.5 mmol), *t*-BuOK (1.4 mg, 0.013 mmol), *t*-BuOMe (0.8 mL), and trimethylcyclohexane (**1a**) (156 mg, 1.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110 °C with stirring for 36 h. After cooling the solution to room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was purified by column chromatography on silica gel to afford **3a** (200 mg, 0.71 mmol, 71%; eluent: hexane:Et_2O = 20:1) and **4a** (70 mg, 0.17 mmol, 17%; eluent: hexane:Et_2O = 10:1). **Cyclohexyldimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61-1.78 (m, 5H), 1.23 (s, 12H), 1.12-1.26 (m, 3H), 0.90-1.12 (m, 2H), 0.55 (tt, J = 12.8, 3.2 Hz, 1H), 0.04 (s, 2H), 0.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 28.1, 27.2, 27.0, 26.6, 24.9, –3.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.7. HRMS (APCI) *m/z* calcd

for $C_{15}H_{32}BO_2Si^+$ $[M + H]^+$: 283.2259, found: 283.2254. **Cyclohexylmethylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.77 (m, 5H), 1.20-1.28 (m, 5H), 1.22 (s, 24H), 0.61 (tt, J = 12.0, 2.4 Hz, 1H), 0.11 [d (AB pattern), J = 12.4 Hz, 2H], 0.07 [d (AB pattern), J = 12.4 Hz, 2H], 0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 28.1, 27.2, 27.0, 26.9, 25.0, –2.3 (*C*–B, broad), –3.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4. HRMS (APCI) *m/z* calcd for $C_{21}H_{43}B_2O_4Si^+$ $[M + H]^+$: 409.3111, found: 409.3103.

Conversion of (Borylmethyl)silyl Group into Hydroxyl Group via Brook Rearrangement (Method A) (Scheme 3): To a 50 mL flask, **3a** (0.28 g, 1.0 mmol), THF (2 mL), NaOH (5 N aqueous solution, 0.80 mL) and H_2O_2 (30% aqueous solution, 0.40 mL) were added in this order. The resulting mixture was stirred for 4 h at room temperature under air. After cooling the solution to 0 °C by ice-water bath, a saturated aqueous solution of $Na_2S_2O_3$ (ca. 5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, pinacol was removed by Kugelrohr distillation (50 °C/1 mmHg) to give **5** (0.16 g, 0.94 mmol, 94%) as a colorless oil. **Cyclohexyl(hydroxymethyl)dimethylsilane (5):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (s, 2H), 1.64-1.78 (m, 5H), 1.07-1.29 (m, 5H), 0.87 (broad s, O*H*, 1H), 0.73 (tt, J = 12.0, 3.2 Hz, 1H), 0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.5, 28.0, 27.4, 26.9, 24.0, –7.0. HRMS (APCI) *m/z* calcd for $C_9H_{21}OSi^+$ $[M + H]^+$: 173.1356, found: 173.1355. IR (neat) 3296 cm^{-1} (ν_{OH}).

To a 5 mL Schlenk tube, **5** (35 mg, 0.20 mmol), KOMe (1.4 mg, 0.020 mmol) and DMSO (0.8 mL) were added. The resulting mixture was stirred at room temperature under nitrogen atmosphere. After 8 h, KF (29 mg, 0.50 mmol), $KHCO_3$ (60 mg, 0.60 mmol), THF/MeOH (v/v = 1/1, 1 mL) and H_2O_2 (30% aqueous solution, 120 μL) were added, and the resulting mixture was stirred for 15 h at room temperature under air. After cooling the solution to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (ca. 5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (ca. 10 mL x

3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Undecane (31 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. **7a** was formed in 76% yield from **5** (71% yield from **3a**). **7a** was assigned by comparison with GC and ^{1}H NMR data of authentic sample.

Conversion of Bis(borylmethyl)silyl Group of 4a into Hydroxyl Group via Method A: To a 50 mL flask, **4a** (0.20 g, 0.5 mmol), THF (2 mL), NaOH (5 N aqueous solution, 0.80 mL) and H_2O_2 (30% aqueous solution, 0.40 mL) were added in this order. The resulting mixture was stirred for 4 h at room temperature under air. After cooling the solution to 0 °C by ice-water bath, a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, pinacol was removed by Kugelrohr distillation (50 °C/1 mmHg) to give cyclohexylbis(hydroxymethyl)methylsilane (**22**) (86 mg, 0.46 mmol, 91%) as a white solid. **Cyclohexylbis(hydroxymethyl)methylsilane (22):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 [d (AB pattern), J = 14.0 Hz, 2H], 3.57 [d (AB pattern), J = 14.0 Hz, 2H], 2.03-2.20 (broad, O*H*, 2H), 1.62-1.78 (m, 5H), 1.10-1.30 (m, 5H), 0.88 (tt, J = 12.0, 2.8 Hz, 1H), 0.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 53.8, 27.8, 27.4, 26.8, 22.3, –9.8. HRMS (ESI) *m/z* calcd for $C_9H_{21}O_2Si^+$ $[M + H]^+$: 189.1305, found: 189.1304. IR (neat) 3221 cm^{-1} (ν_{OH}).

To a 5 mL Schlenk tube, **22** (38 mg, 0.20 mmol), KOMe (1.4 mg, 0.020 mmol) and DMSO (0.8 mL) were added. The resulting mixture was stirred at room temperature under nitrogen atmosphere. After 8 h, KF (29 mg, 0.50 mmol), $KHCO_3$ (60 mg, 0.60 mmol), THF/MeOH (v/v = 1/1, 1.0 mL) and H_2O_2 (30% aqueous solution, 120 μL) were added, and the resulting mixture was stirred for 15 h at room temperature under air. After cooling the solution to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Undecane

(31 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. **7a** was formed in 79% yield from **22** (72% yield from **4a**).

Conversion of (Borylmethyl)silyl Group into Hydroxyl Group via Swern Oxidation (Method B) (Scheme 4): A procedure for conversion of **3a** to **5** (94% yield) is same as described above. To a 5 mL Schlenk tube, oxalyl chloride (78 mg, 0.61 mmol) and CH_2Cl_2 (0.75 mL) were added. The tube was cooled to –78 ºC by dry ice-acetone bath, and a CH_2Cl_2 (0.75 mL) solution of DMSO (43 mg, 0.55 mmol) was added. After 5 min, and a CH_2Cl_2 (0.75 mL) solution of **5** (86 mg, 0.5 mmol) was added, and the resulting mixture was stirred at –78 ºC for 15 min. Et_3N (0.25 g, 2.5 mmol) was added and the cooling bath was removed. KF (77 mg, 1.3 mmol), $KHCO_3$ (150 mg, 1.5 mmol), THF/MeOH (v/v = 1/1, 2.5 mL) and H_2O_2 (30% aqueous solution, 300 μL) were added, and the resulting mixture was stirred for 15 h at room temperature under air. After cooling the solution to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Undecane (78 mg, 0.50 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. **7a** was formed in 75% yield from **5** (71% yield from **3a**).

Conversion of Bis(borylmethyl)silyl Group of 4a into Hydroxyl Group via Method B: A procedure for conversion of **4a** to **22** (91% yield) is same as described above. To a 5 mL Schlenk tube, oxalyl chloride (78 mg, 0.61 mmol) and CH_2Cl_2 (0.75 mL) were added. The tube was cooled to –78 ºC by dry ice-acetone bath, and a CH_2Cl_2 (0.75 mL) solution of DMSO (43 mg, 0.55 mmol) was added. After 5 min, a CH_2Cl_2 (0.75 mL) solution of **22** (47 mg, 0.25 mmol) was added, and the resulting mixture was stirred at –78 ºC for 15 min. Et_3N (0.25 g, 2.5 mmol) was added and the cooling bath was removed. KF (36 mg, 0.63 mmol), $KHCO_3$ (75 mg, 0.75 mmol), THF/MeOH (v/v = 1/1, 1.3 mL) and H_2O_2 (30% aqueous solution, 150 μL) were added, and the resulting mixture was stirred for 15 h at room temperature under air. After cooling the solution using ice-water bath, a saturated solution of

$Na_2S_2O_3$ (5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Undecane (39 mg, 0.25 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. **7a** was formed in 74% yield from **22** (67% yield from **4a**).

Alcohol Synthesis from Trimethylsilylalkanes (Table 2): *General Procedure for the Conversion of Alkyl–SiMe$_3$ (**1**) to Alkyl–OH (**7**):* A procedure that is suitable for sequential operation is given as follows. *C–H Borylation:* In a glove box, a glass tube having PTFE stopcock, equipped with a magnetic stirring bar, was charged with $[Ir(OMe)(cod)]_2$ (17 mg, 0.025 mmol), Me_4phen (12 mg, 0.050 mmol), bis(pinacolato)diboron (**2**) (381 mg, 1.5 mmol), *t*-BuOK (1.4 mg, 0.013 mmol), *t*-BuOMe (0.8 mL), and Alkyl–SiMe$_3$ (**1**) (1.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110 °C with stirring for 36 h. After cooling the solution to room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was purified by column chromatography on silica gel to afford **3** and **4**. Although **3** and **4** were generally separable, these were subjected to the next step together.

*Brook Rearrangement-Based Conversion of **3** and **4** (Method A):* A 50 mL flask was charged with **3** and **4**. To the flask, THF (2 mL), NaOH (5 N aqueous solution, 0.80 mL) and H_2O_2 (30% aqueous solution, 0.40 mL) were added in this order. The resulting mixture was stirred for 4 h at room temperature under air. After cooling the solution to 0 °C by ice-water bath, a saturated aqueous solution of $Na_2S_2O_3$ (ca. 5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, pinacol was removed by Kugelrohr distillation (50 °C/1 mmHg). The obtained (hydroxylmethyl)silanes were subjected to Brook rearrangement without further purification.

The obtained (hydroxylmethyl)silanes were combined to a 20 mL Schlenk tube. To the Schlenk tube, KOMe (7.0 mg, 0.10 mmol) and DMSO (4.0 mL) were added. The resulting mixture was stirred at room temperature under nitrogen atmosphere. After 8 h, KF (145 mg, 2.5 mmol), $KHCO_3$ (300 mg, 3.0 mmol), THF/MeOH (v/v = 1/1, 5.0 mL) and H_2O_2 (30% aqueous solution, 0.60 mL) were added, and the resulting mixture was stirred for 15 h at room temperature under air. After cooling the solution to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (10 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (15 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Pure **7** was obtained after purification with column chromatography on silica gel.

*Swern Oxidation-Based Conversion of **3** and **4** (Method B):* A 50 mL flask was charged with **3** and **4**. To the flask, THF (2 mL), NaOH (5 N aqueous solution, 0.80 mL) and H_2O_2 (30% aqueous solution, 0.40 mL) were added in this order. The resulting mixture was stirred for 4 h at room temperature under air. After cooling the solution to 0 °C by ice-water bath, a saturated aqueous solution of $Na_2S_2O_3$ (ca. 5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, pinacol was removed by Kugelrohr distillation (50 °C/1 mmHg). The obtained (hydroxylmethyl)silanes were subjected to Swern oxidation without further purification.

To a 20 mL Schlenk tube, oxalyl chloride (152 mg, 1.2 mmol) and CH_2Cl_2 (1.5 mL) were added. The tube was cooled to –78 ºC by dry ice-acetone bath, and a CH_2Cl_2 (1.5 mL) solution of DMSO (86 mg, 1.1 mmol) was added. After 5 min, a CH_2Cl_2 (0.75 mL) solution of (hydroxymethyl)silanes was added, and the resulting mixture was stirred at –78 ºC for 15 min. Et_3N (0.25 g, 2.5 mmol) was added and the cooling bath was removed. KF (145 mg, 2.5 mmol), $KHCO_3$ (300 mg, 3.0 mmol), THF/MeOH (v/v = 1/1, 5.0 mL) and H_2O_2 (30% aqueous solution, 0.60 mL) were added, and the resulting mixture

was stirred for 15 h at room temperature under air. After cooling the solution using ice-water bath, a saturated solution of $Na_2S_2O_3$ (10 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (15 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Pure **7** was obtained after purification with column chromatography on silica gel.

Synthesis of 7a from 1a (entry 1): See above.

Synthesis of 7b from 1b (entry 2): According to the *General Procedure*, C–H borylation of **1b** (170 mg, 1.0 mmol) was carried out. **3b** (193 mg, 0.65 mmol, 65%) and **4b** (101 mg, 0.24 mmol, 24%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3b**; hexane:Et_2O = 10:1 for **4b**). **(Cyclohexylmethyl)dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55-1.72 (m, 5H), 1.34-1.45 (m, 1H), 1.04-1.28 (m, 3H), 1.23 (s, 12H), 0.85-0.97 (m, 2H), 0.52 (d, J = 7.2 Hz, 2H), 0.09 (s, 2H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 36.8, 34.2, 26.6, 26.3, 26.1, 24.9, 0.3 (*C*–B, broad), –0.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3. HRMS (APCI) *m/z* calcd for $C_{16}H_{34}BO_2Si^+$ $[M + H]^+$: 297.2416, found: 297.2413. **(Cyclohexylmethyl)(methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54-1.74 (m, 5H), 1.39-1.50 (m, 1H), 1.04-1.29 (m, 3H), 1.23 (s, 24H), 0.84-0.98 (m, 2H), 0.57 (d, J = 6.8 Hz, 2H), 0.14 (s, 4H), 0.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 36.9, 34.0, 26.6, 26.3, 26.1, 25.0 [*C*H_3 of B(pin), 4C], 24.9 [*C*H_3 of B(pin), 4C], 0.7 (*C*–B, broad), –0.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS (ESI) *m/z* calcd for $C_{22}H_{45}B_2O_4Si^+$ $[M + H]^+$: 423.3268, found: 423.3260. The borylalkanes **3b** and **4b** (0.89 mmol total) were subjected to Method A. An alcohol **7b** (63 mg, 0.55 mmol, 62%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **Cyclohexylmethanol (7b)**[34]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (d, J = 6.4 Hz, 2H), 1.64-1.79 (m, 5H), 1.42-1.54 (m, 1H), 1.38 (s, 1H, O*H*), 1.10-1.32 (m, 3H), 0.88-1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.8, 40.5, 29.5, 26.6, 25.8. IR (neat) 3287 cm^{-1} (ν_{OH}).

Synthesis of 7c from 1c (entry 3): According to the *General Procedure*, C–H borylation of **1c** (215 mg, 1.0 mmol) was carried out. **3c** (180 mg, 0.53 mmol, 53%) and **4c** (112 mg, 0.24 mmol, 24%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3c**; hexane:Et_2O = 10:1 for **4c**). **(3,7-Dimethyloctyl)dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3c):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (septet, J = 6.4 Hz, 1H), 1.18-1.35 (m, 4H), 0.98-1.18 (m, 5H), 1.23 (s, 12H), 0.86 (d, J = 6.4 Hz, 6H), 0.83 (d, J = 6.0 Hz, 3H), 0.40-0.57 (m, 2H), 0.08 (s, 2H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 39.4, 36.6, 35.6, 30.7, 28.0, 24.9, 24.8, 22.7 [*C*H_3 of –CH(CH_3)$_2$, 1C], 22.6 [*C*H_3 of –CH(CH_3)$_2$, 1C], 19.2, 13.8, –0.6 (*C*–B, broad), –1.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.9. HRMS (APCI) *m/z* calcd for $C_{19}H_{42}BO_2Si^+$ $[M + H]^+$: 341.3042, found: 341.3037. **(3,7-Dimethyloctyl)(methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4c):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (septet, J = 6.8 Hz, 1H), 1.00-1.39 (m, 9H), 1.23 (s, 24H), 0.86 (d, J = 6.8 Hz, 6H), 0.84 (d, J = 6.4 Hz, 3H), 0.46-0.62 (m, 2H), 0.13 (s, 4H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 39.4, 36.6, 35.7, 30.6, 28.0, 25.0 [*C*H_3 of B(pin), 4C], 24.94 [*C*H_3 of B(pin), 4C], 24.86, 22.7 [*C*H_3 of –CH(CH_3)$_2$, 1C], 22.6 [*C*H_3 of –CH(CH_3)$_2$, 1C], 19.2, 14.0, –0.2 (*C*–B, broad), –1.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (ESI) *m/z* calcd for $C_{25}H_{53}B_2O_4Si^+$ $[M + H]^+$: 467.3894, found: 467.3888. The borylalkanes **3c** and **4c** (0.77 mmol total) were subjected to either Method A or Method B. An alcohol **7c** (85 mg, 0.54 mmol, 70% by Method A; 87 mg, 0.55 mmol, 71% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **3,7-Dimethyl-1-octanol (7c)**[35]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63-3.73 (m, 2H), 1.47-1.65 (m, 2H), 1.52 (septet, J = 6.8 Hz, 1H), 1.20-1.43 (m, 4H), 1.26 (s, 1H, O*H*), 1.08-1.20 (m, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 61.3, 40.0, 39.3, 37.4, 29.5, 28.0, 24.7, 22.7 [*C*H_3 of –CH(CH_3)$_2$, 1C], 22.6 [*C*H_3 of –CH(CH_3)$_2$, 1C], 19.6. IR (neat) 3300 cm^{-1} (ν_{OH}).

Synthesis of 7d from 1d (entry 4): According to the *General Procedure*, C–H borylation of **1d** (187 mg, 1.0 mmol) was carried out. **3d** (159 mg, 0.51 mmol, 51%), **4d** (88 mg, 0.20 mmol, 20%) and **9** (31 mg, 0.07 mmol, 7%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3d**; hexane:Et_2O = 10:1 for **4d** and **9**). **Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl](octyl)silane** (**3d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.33 (m, 12H), 1.23 (s, 12H), 0.88 (t, J = 6.8 Hz, 3H), 0.48-0.55 (m, 2H), 0.08 (s, 2H), 0.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 33.6, 32.0, 29.32, 29.28, 24.9, 23.8, 22.7, 17.1, 14.1, –0.6 (*C*–B, broad), –1.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5. HRMS (APCI, negative) *m/z* calcd for $C_{17}H_{36}BO_2Si^-$ $[M - H]^-$: 311.2583, found: 311.2585. **Methyl(octyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4d):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18-1.37 (m, 12H), 1.22 (s, 24H), 0.88 (t, J = 7.2 Hz, 3H), 0.54-0.59 (m, 2H), 0.13 (s, 4H), 0.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 33.7, 32.0, 29.3 (two non-equivalent carbons were overlapped), 25.0 [*C*H_3 of B(pin), 4C], 24.9 [*C*H_3 of B(pin), 4C], 23.6, 22.7, 17.3, 14.1, –0.2 (*C*–B, broad), –1.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS (ESI) *m/z* calcd for $C_{23}H_{49}B_2O_4Si^+$ $[M + H]^+$: 439.3581, found: 439.3579. **Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl][8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl]silane (9):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.44 (m, 2H), 1.14-1.34 (m, 10H), 1.24 (s, 12H), 1.23 (s, 12H), 0.76 (t, J = 8.0 Hz, 2H), 0.46-0.56 (m, 2H), 0.07 (s, 2H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.8, 82.7, 33.6, 32.5, 29.4, 29.3, 24.9, 24.8, 24.0, 23.8, 17.1, 11.2 (*C*–B, broad), –0.7 (*C*–B, broad), –1.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6. HRMS (ESI) *m/z* calcd for $C_{23}H_{49}B_2O_4Si^+$ $[M + H]^+$: 439.3581, found: 439.3578. The borylalkanes **3d** and **4d** (0.71 mmol total) were subjected to Method A. 1-Octanol (**7d**, 60 mg, 0.46 mmol, 65%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **7d** was assigned by comparison with GC and ^{1}H NMR data of authentic sample.

Synthesis of 7e from 1e (entry 5): According to the *General Procedure*, C–H borylation of **1e** (273 mg, 1.0 mmol) was carried out. **3e** (220 mg, 0.55 mmol, 55%) and **4e** (136 mg, 0.26 mmol, 26%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 10:1 for **3e**; hexane:Et_2O = 5:1 for **4e**). **[3-[(3,7-Dimethyloctyl)oxy]propyl]dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39-3.47 (m, 2H), 3.36 (t, J = 6.8 Hz, 2H), 1.46-1.65 (m, 5H), 1.19-1.41 (m, 4H), 1.23 (s, 12H), 1.05-1.17 (m, 3H), 0.87 (d, J = 6.4 Hz, 3H), 0.86 (d, J = 6.8 Hz, 6H), 0.49-0.55 (m, 2H), 0.09 (s, 2H), 0.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 73.7, 69.1, 39.3, 37.4, 36.8, 29.9, 28.0, 24.9, 24.7, 24.0, 22.7 [*C*H_3 of –CH(CH_3)$_2$, 1C], 22.6 [*C*H_3 of –CH(CH_3)$_2$, 1C], 19.7, 13.1, –0.6 (*C*–B, broad), –1.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (APCI) *m/z* calcd for $C_{22}H_{48}BO_3Si^+$ $[M + H]^+$: 399.3460, found: 399.3454. **[3-[(3,7-Dimethyloctyl)oxy]propyl](methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38-3.47 (m, 2H), 3.36 (t, J = 6.8 Hz, 2H), 1.46-1.66 (m, 5H), 1.17-1.40 (m, 4H), 1.22 (s, 24H), 1.05-1.17 (m, 3H), 0.87 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 6H), 0.54-0.59 (m, 2H), 0.14 (s, 4H), 0.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 73.9, 69.0, 39.3, 37.4, 36.9, 29.9, 28.0, 25.0 [*C*H_3 of B(pin), 4C], 24.9 [*C*H_3 of B(pin), 4C], 24.7, 23.9, 22.7 [*C*H_3 of –CH(CH_3)$_2$, 1C], 22.6 [*C*H_3 of –CH(CH_3)$_2$, 1C], 19.7, 13.2, –0.5 (*C*–B, broad), –1.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS (APCI) *m/z* calcd for $C_{28}H_{59}B_2O_5Si^+$ $[M + H]^+$: 525.4312, found: 525.4306. The borylalkanes **3e** and **4e** (0.81 mmol total) were subjected to either Method A or Method B. An alcohol **7e** (121 mg, 0.56 mmol, 69% by Method A; 133 mg, 0.61 mmol, 76% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **3-[(3,7-Dimethyloctyl)oxy]propan-1-ol (7e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (t, J = 5.6 Hz, 2H), 3.57-3.66 (m, 2H), 3.41-3.51 (m, 2H), 2.31 (broad s, 1H, O*H*), 1.83 (quintet, J = 5.6 Hz, 2H), 1.56-1.67 (m, 1H), 1.45-1.56 (m, 2H), 1.19-1.42 (m, 4H), 1.05-1.19 (m, 3H), 0.88 (d, J = 6.4 Hz, 3H), 0.86 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.5, 69.8, 62.5, 39.3, 37.4, 36.7, 32.0, 29.9, 28.0, 24.7, 22.7 [*C*H_3

of –$CH(CH_3)_2$, 1C], 22.6 [CH_3 of –$CH(CH_3)_2$, 1C], 19.7. HRMS (APCI) *m/z* calcd for $C_{13}H_{29}O_2^+$ [M + H]$^+$: 217.2162, found: 217.2154. IR (neat) 3331 cm^{-1} (ν_{OH}).

Synthesis of 7f from 1f (entry 6): According to the *General Procedure*, C–H borylation of **1f** (216 mg, 1.0 mmol) was carried out. **3f** (193 mg, 0.56 mmol, 56%) and **4f** (83 mg, 0.18 mmol, 18%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 10:1 for **3f**; hexane:Et_2O = 5:1 for **4f**). **3-[Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silyl]propyl pivalate (3f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, J = 6.8 Hz, 2H), 1.58-1.67 (m, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.50-0.58 (m, 2H), 0.09 (s, 2H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 82.7, 66.9, 38.7, 27.2, 24.9, 23.1, 12.8, –0.8 (*C*–B, broad), –1.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3. HRMS (ESI) *m/z* calcd for $C_{17}H_{36}BO_4Si^+$ [M + H]$^+$: 343.2470, found: 343.2464. **3-[Methylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silyl]propyl pivalate (4f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, J = 6.8 Hz, 2H), 1.62-1.72 (m, 2H), 1.22 (s, 24H), 1.19 (s, 9H), 0.56-0.63 (m, 2H), 0.14 (s, 4H), 0.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 82.7, 67.1, 38.7, 27.2, 25.0 [CH_3 of B(pin), 4C], 24.9 [CH_3 of B(pin), 4C], 23.1, 13.0, –0.4 (*C*–B, broad), –1.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS (ESI) *m/z* calcd for $C_{23}H_{47}B_2O_6Si^+$ [M + H]$^+$: 469.3323, found: 469.3316. The borylalkanes **3f** and **4f** (0.74 mmol total) were subjected to either Method A or Method B. An alcohol **7f** (49 mg, 0.30 mmol, 41% by Method A; 75 mg, 0.47 mmol, 63% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **3-Hydroxypropyl pivalate (7f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (t, J = 6.0 Hz, 2H), 3.68 (t, J = 6.0 Hz, 2H), 1.88 (broad s, 1H, O*H*), 1.87 (quintet, J = 6.0 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 61.2, 59.2, 38.8, 31.9, 27.2. HRMS (ESI) *m/z* calcd for $C_8H_{17}O_3^+$ [M + H]$^+$: 161.1172, found: 161.1170. IR (neat) 3435 (ν_{OH}), 1728 (ν_{CO}) cm^{-1}.

Synthesis of 7g from 1g (entry 7): According to the *General Procedure*, C–H borylation of **1g** (285 mg, 1.0 mmol) was carried out. **3g** (267 mg, 0.65 mmol, 65%) and **4g** (113 mg, 0.21 mmol, 21%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 5:1 for **3g**; hexane:Et_2O = 2:1 for **4g**) and Kugelrohr distillation (80 ºC/0.3 mmHg to remove low b.p. material, for **4g**). **Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl][(2,2,3,3-tetramethyl-1,4-dioxaspiro[4.5]decan-7-yl)methyl]silane (3g):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69-1.87 (m, 3H), 1.47-1.68 (m, 3H), 1.38 (td, J = 12.8, 4.4 Hz, 1H), 1.23 (s, 12H), 1.224 (s, 3H), 1.217 (s, 3H), 1.213 (s, 6H), 1.18 (t, J = 12.4 Hz, 1H), 0.83 (qd, J = 12.0, 4.0 Hz, 1H), 0.56 [dd (AB pattern), J = 14.8, 6.4 Hz, 1H], 0.50 [dd (AB pattern), J = 14.8, 7.2 Hz, 1H], 0.08 (s, 2H), 0.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.0, 82.6, 82.3, 81.6, 49.0, 38.4, 35.4, 31.9, 25.7, 24.95, [*C*H_3 of C(pin), 2C], 24.93 [*C*H_3 of B(pin), 4C], 24.88 [*C*H_3 of C(pin), 1C], 24.7 [*C*H_3 of C(pin), 1C], 23.5, 0.3 (*C*–B, broad), –0.1 (Si*C*H_3), –0.5 (Si*C*H_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{43}BO_4SiNa^+$ $[M + Na]^+$: 433.2916, found: 433.2902. **Methylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl][(2,2,3,3-tetramethyl-1,4-dioxaspiro[4.5]decan-7-yl)methyl]silane (4g):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71-1.87 (m, 3H), 1.46-1.71 (m, 3H), 1.37 (td, J = 12.8, 4.8 Hz, 1H), 1.22 (s, 24H), 1.18-1.23 (m, 13H), 0.83 (qd, J = 12.2, 4.4 Hz, 1H), 0.58 (d, J = 6.8 Hz, 2H), 0.14 (s, 4H), 0.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.0, 82.6, 82.3, 81.5, 49.2, 38.5, 35.2, 31.7, 25.6, 25.0 [*C*H_3 of C(pin), 1C] 24.98 [*C*H_3 of C(pin), 1C], 24.96 [*C*H_3 of B(pin), 4C], 24.94 [*C*H_3 of B(pin), 4C], 24.89 [*C*H_3 of C(pin), 1C], 24.75 [*C*H_3 of C(pin), 1C], 23.5, 0.6 (*C*–B, broad), –0.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{54}B_2O_6SiNa^+$ $[M + Na]^+$: 559.3768, found: 559.3759. The borylalkanes **3g** and **4g** (0.86 mmol total) were subjected to Method A. An alcohol **7g** (144 mg, 0.63 mmol, 73%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:2). **(2,2,3,3-Tetramethyl-1,4-dioxaspiro[4.5]decan-7-yl)methanol (7g):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (d, J = 6.0 Hz, 2H), 1.76-1.92, (m, 3H), 1.51-1.76 (m, 3H), 1.46 (td, J = 12.8, 4.0 Hz,

1H), 1.40 (s, 1H, O*H*), 1.26 (t, *J* = 13.2 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 0.86-0.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 106.7, 82.5, 81.9, 68.2, 41.9, 38.9, 38.4, 28.0, 25.0, 24.83, 24.77, 24.75, 22.8. HRMS (EI) *m/z* calcd for $C_{13}H_{24}O_3^+$ $[M]^+$: 228.1720, found: 228.1725. IR (neat) 3410 cm^{-1} (ν_{OH}).

Synthesis of 7h from 1h (entry 8): According to the *General Procedure*, C–H borylation of **1h** (170 mg, 1.0 mmol) was carried out. **3h** (207 mg, 0.70 mmol, 70%) and **4h** (72 mg, 0.17 mmol, 17%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3h**; hexane:Et_2O = 10:1 for **4h**). **Cycloheptyldimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3h):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66-1.79 (m, 4H), 1.52-1.63 (m, 2H), 1.35-1.52 (m, 4H), 1.14-1.30 (m, 2H), 1.23 (s, 12H), 0.62 (tt, *J* = 11.2, 3.2 Hz, 1H), 0.06 (s, 2H), 0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 30.0, 28.7, 28.4, 27.1, 24.9, –2.4 (*C*–B, broad), –3.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3. HRMS (APCI) *m/z* calcd for $C_{16}H_{34}BO_2Si^+$ $[M + H]^+$: 297.2416, found: 297.2413. **Cycloheptyl(methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4h):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66-1.82 (m, 4H), 1.52-1.62 (m, 2H), 1.35-1.52 (m, 4H), 1.10-1.32 (m, 2H), 1.22 (s, 24H), 0.67 (tt, *J* = 11.2, 3.2 Hz, 1H), 0.13 [d (AB pattern), *J* = 12.4 Hz, 2H], 0.08 [d (AB pattern), *J* = 12.4 Hz, 2H], 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 30.0, 28.7, 28.3, 27.2, 24.99 [*C*H_3 of B(pin), 4C], 24.96 [*C*H_3 of B(pin), 4C], –2.0 (*C*–B, broad), –2.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{45}B_2O_4Si^+$ $[M + H]^+$: 423.3268, found: 423.3259. The borylalkanes **3h** and **4h** (0.87 mmol total) were subjected to either Method A or Method B. An alcohol **7h** (61 mg, 0.53 mmol, 61% by Method A; 60 mg, 0.52 mmol, 60% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **Cycloheptanol (7h)**[36]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (septet, *J* = 4.0 Hz, 1H), 1.86-1.96 (m, 2H), 1.59-1.70 (m, 2H), 1.50-1.59 (m, 6H), 1.32-1.45 (m, 2H), 1.41 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.8, 37.6, 28.1, 22.6. IR (neat) 3331 cm^{-1} (ν_{OH}).

Synthesis of 7i from 1i (entry 9): According to the *General Procedure*, C–H Borylation of **1i** (168 mg, 1.0 mmol) was carried out. **3i** (210 mg, 0.71 mmol, 71%) and **4i** (75 mg, 0.18 mmol, 18%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3i**; hexane:Et_2O = 10:1 for **4i**). **[(1*S**,2*S**,4*R**)-Bicyclo[2.2.1]heptan-2-yl]dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3i):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (broad s, 1H), 2.18 (broad s, 1H), 1.45-1.57 (m, 2H), 1.34-1.40 (m, 2H), 1.12-1.28 (m, 3H), 1.23 (s, 12H), 1.04-1.12 (m, 1H), 0.54 (t, J = 8.8 Hz, 1H), 0.05 (s, 2H), 0.00 (s, 3H), –0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 37.8, 37.7, 36.9, 34.3, 32.5, 29.8, 28.8, 25.0 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], –1.7 (*C*–B, broad), –2.5 (Si*C*H_3), –2.6 (Si*C*H_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5. HRMS (APCI) *m/z* calcd for $C_{16}H_{32}BO_2Si^+$ $[M + H]^+$: 295.2259, found: 295.2251. **[(1*S**,2*S**,4*R**)-Bicyclo[2.2.1]heptan-2-yl](methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4i):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (broad s, 1H), 2.21 (broad s, 1H), 1.44-1.58 (m, 2H), 1.34-1.44 (m, 2H), 1.11-1.30 (m, 3H), 1.22 (s, 24H), 1.02-1.13 (m, 1H), 0.61 (t, J = 8.8 Hz, 1H), 0.07-0.15 (m, 4H), 0.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 37.8, 37.7, 36.9, 34.3, 32.7, 30.1, 28.8, 25.03 [*C*H_3 of B(pin), 2C], 24.98 [*C*H_3 of B(pin), 2C], 24.96 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], –1.3 (*C*–B, broad), –2.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{43}B_2O_4Si^+$ $[M + H]^+$: 421.3111, found: 421.3101. The borylalkanes **3i** and **4i** (0.89 mmol total) were subjected to Method A. An alcohol **7i** (58 mg, 0.52 mmol, 58%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1) and Kugelrohr distillation to remove remained solvent. ***exo*-Norborneol (7i)**[37]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (d, J = 6.8 Hz, 1H), 2.25 (s, 1H), 2.14 (d, J = 4.4 Hz, 1H), 1.66 (ddd, J = 13.2, 6.8, 2.4 Hz, 1H), 1.56 (d, J = 10.0 Hz, 1H), 1.24-1.53 (m, 4H), 1.12 (d, J = 10.0 Hz, 1H), 0.95-1.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.0, 44.3, 42.4, 35.4, 34.4, 28.1, 24.4. IR (neat) 3296 cm^{-1} (ν_{OH}).

Synthesis of 7j from 1j (entry 10): According to the *General Procedure*, C–H borylation of **1j** (168 mg, 1.0 mmol) was carried out. **3j** (215 mg, 0.73 mmol, 73%) and **4i** (63 mg, 0.15 mmol, 15%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3j**; hexane:Et_2O = 10:1 for **4j**). **[(1*R**,2*S**,4*S**)-bicyclo[2.2.1]heptan-2-yl]dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3j):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (broad s, 1H), 2.24 (broad t, J = 4.0 Hz, 1H), 1.64-1.74 (m, 1H), 1.40-1.51 (m, 1H), 1.33-1.40 (m, 2H), 1.18-1.30 (m, 2H), 1.23 (s, 12H), 1.02-1.11 (m, 2H), 0.90-0.98 (m, 1H), 0.12 [d (AB pattern), J = 12.4 Hz, 1H], 0.08 [d (AB pattern), J = 12.4 Hz, 1H], 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 41.8, 39.4, 37.2, 31.6, 29.9, 29.4, 27.3, 25.0 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], –0.4 (*C*–B, broad), –1.4 (Si*C*H_3), –1.6 (Si*C*H_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4. HRMS (APCI) *m/z* calcd for $C_{16}H_{32}BO_2Si^+$ [M + H]$^+$: 295.2259, found: 295.2254. **[(1*R*,2*S*,4*S*)-Bicyclo[2.2.1]heptan-2-yl](methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4j):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (broad s, 1H), 2.23 (broad s, 1H), 1.66-1.76 (m, 1H), 1.33-1.50 (m, 3H), 1.13-1.33 (m, 2H), 1.22 (s, 24H), 0.94-1.13 (m, 3H), 0.09-0.21 (m, 4H), 0.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.61[O*C* of B(pin), 2C], 82.58 [O*C* of B(pin), 2C], 41.8, 39.4, 37.2, 31.7, 29.9, 29.8, 27.3, 25.1 [*C*H_3 of B(pin), 2C], 25.02 [*C*H_3 of B(pin), 2C], 24.96 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], –0.1 (*C*–B, broad), –1.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6. HRMS (ESI) *m/z* calcd for $C_{22}H_{43}B_2O_4Si^+$ [M + H]$^+$: 421.3111, found: 421.3100. The borylalkanes **3j** and **4j** (0.88 mmol total) were subjected to Method A. An alcohol **7j** (55 mg, 0.49 mmol, 56%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1) and Kugelrohr distillation to remove remained solvent. ***endo*-Norborneol (7j)**[37]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19-4.26 (m, 1H), 2.25 (broad t, J = 4.0 Hz, 1H), 2.16 (broad t, J = 4.0 Hz, 1H), 1.83-1.99 (m, 2H), 1.51-1.62 (m, 1H), 1.43 (s, 1H, O*H*),

1.26-1.41 (m, 4H), 0.84 (dt, J = 12.8, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 73.1, 42.5, 39.6, 37.6, 37.2, 29.8, 19.9. IR (neat) 3287 cm^{-1} (ν_{OH}).

Synthesis of 7k from 1k (entry 11): According to the *General Procedure*, C–H borylation of **1k** (208 mg, 1.0 mmol) was carried out. **3k** (241 mg, 0.72 mmol, 72%) and **4k** (28 mg, 0.06 mmol, 6%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3k**; hexane:Et_2O = 10:1 for **4k**). **(1-Adamantyl)dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3k):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.88 (m, 3H), 1.69-1.80 (m, 6H), 1.63 (d, J = 2.8 Hz, 6H), 1.24 (s, 12H), 0.01 (s, 2H), –0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 37.6, 36.9, 27.7, 25.0, 21.5, –5.1 (*C*–B, broad), –5.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6. HRMS (EI) *m/z* calcd for $C_{19}H_{35}BO_2Si^+$ $[M]^+$: 334.2494, found: 334.2499. **(1-Adamantyl)(methyl)bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4k):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (broad, 3H), 1.73 (broad, 6H), 1.67 (d, J = 2.4 Hz, 6H), 1.22 (s, 24H), 0.07 [d (AB pattern), J = 12.8 Hz, 2H], 0.024 [d (AB pattern), J = 12.8 Hz, 2H], 0.016 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 37.6, 36.9, 27.7, 25.03 [*C*H_3 of B(pin), 4C], 25.02 [*C*H_3 of B(pin), 4C], 22.2, –4.2 (*C*–B, broad), –5.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3. HRMS (ESI) *m/z* calcd for $C_{25}H_{47}B_2O_4Si^+$ $[M + H]^+$: 461.3424, found: 461.3416. The borylalkanes **3k** and **4k** (0.78 mmol total) were subjected to either modified Method A or Method B (Tamao-Fleming oxidation step: for 40 h). An alcohol **7k** (78 mg, 0.51 mmol, 65% by Method A; 34 mg, 0.23 mmol, 29% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 5:1). **1-Adamantanol (7k)**[37]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (broad, 3H), 1.71 (d, J = 2.4 Hz, 6H), 1.54-1.67 (m, 6H), 1.36 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.2, 45.4, 36.1, 30.7. IR (neat) 3279 cm^{-1} (ν_{OH}).

An Attempt on C(sp^3)–H Borylation of [(Trimethylsilyl)methyl]cyclohexan-1-one: C–H borylation of [(trimethylsilyl)methyl]cyclohexan-1-one (185 mg, 1.0 mmol) was examined according to

the *General Procedure*. However, formation of the corresponding **3** and **4** were not observed by GC analysis.

The Robustness Test According to the Glorius' Procedure:[22] In a glove box, a glass tube having PTFE stopcock, equipped with a magnetic stirring bar, was charged with $[Ir(OMe)(cod)]_2$ (17 mg, 0.025 mmol), Me_4phen (12 mg, 0.050 mmol), bis(pinacolato)diboron (**2**) (381 mg, 1.5 mmol), *t*-BuOK (1.4 mg, 0.013 mmol), *t*-BuOMe (0.8 mL), an additive (1.0 mmol), and **1a** (1.0 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110 °C with stirring for 36 h. After cooling to room temperature, undecane (78 mg, 0.50 mmol) was added, and the resulting mixture was analyzed by GC.

The borylation of **1a** to form **3a** and **4a** was completely suppressed in the presence of 1 equiv of *N*-methylacetamide, acetonitrile, or nitromethane. In the presence of 1 equiv of benzene, formation of 1,3- and 1,4-diborylbenzene (30 and 10% yields, respectively) and 1,3,5-triborylbenzene (57% yield) took place, indicating that $C(sp^2)$–H bond is much more reactive than $C(sp^3)$–H bond under the Ir/*t*-BuOK catalyst system.

Synthesis of a Stereodefined Cyclopentanol Starting from Allyltrimethylsilane (10) (Scheme 5): Compound **12** was prepared according to the procedure reported previously.[23a] To a 100 mL two neck flask, $AlCl_3$ (1.2 g, 9 mmol) and pentane (6.2 mL) were added. The flask was cooled to –30 °C, then Me_3SiCl (9.8 g, 90 mmol) and allyltrimethylsilane (**10**, 2.1 g, 18 mmol) were added. 2,3-Dimethyl-1,3-butadiene (**11**, 2.1 mL, 19 mmol) was added over a period of 1 h to the mixture using syringe pump at –30 to –20 °C. Then resulting mixture was stirred at that temperature for another 2 h. The reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$. The organic layer was separated, washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles under reduced pressure, the product **12** (1.7 g, 8.7

mmol) was obtained as a colorless liquid after purification by Kugelrohr distillation (0.4 mmHg, 70 ºC) and column chromatography on silica gel (hexane).

A suspension of **12** (1.7 g) and Pd/C (10 wt. %, 0.85 g, 10 mol %) in EtOH (16 mL) was stirred for 1 h under H_2 atmosphere. The mixture was filtered through a pad of Celite and the resulting solution was concentrated. Compound **1l** (1.5 g, 7.6 mmol, 42%) was obtained by column chromatography on silica gel (hexane). **(1*R**,3*R**)-3-Isopropyl-3-methyl-1-trimethylsilylcyclopentane (1l)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.71 (m, 2H), 1.49 (septet, J = 6.8 Hz, 1H), 1.29-1.42 (m, 3H), 0.92-1.07 (m, 2H), 0.85 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), 0.78 (s, 3H), –0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 45.9, 41.1, 40.1, 37.2, 27.7, 26.4, 22.2, 18.7 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], 18.3 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], –3.1. HRMS (EI) *m/z* calcd for $C_{12}H_{26}Si^+$ $[M]^+$: 198.1798, found: 198.1804.

*Synthesis of **7l** from **1l**:* According to the *General Procedure* given for Table 2, C–H borylation was carried out using **1l** (198 mg, 1.0 mmol). **3l** (208 mg, 0.64 mmol, 64%) and **4l** (86 mg, 0.19 mmol, 19%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **3l**; hexane:Et_2O = 10:1 for **4l**). **[(1*R**,3*R**)-3-Isopropyl-3-methylcyclopentyl]dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3l):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.74 (m, 2H), 1.48 (septet, J = 6.8 Hz, 1H), 1.30-1.42 (m, 3H), 1.23 (s, 12H), 0.98-1.08 (m, 2H), 0.84 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H), 0.78 (s, 3H), 0.07 (s, 2H), 0.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 45.9, 40.9, 40.0, 37.2, 27.7, 27.0, 25.0 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], 22.3, 18.7 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], 18.3 [*C*H_3 of –CH(CH$_3$)$_2$, 1C] –1.9 (*C*–B, broad), –2.96 (Si*C*H_3), –2.99 (Si*C*H_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.5. HRMS (APCI) *m/z* calcd for $C_{18}H_{38}BO_2Si^+$ $[M + H]^+$: 325.2729, found: 325.2722. **[(1*R**,3*R**)-3-Isopropyl-3-methylcyclopentyl]methylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (4l):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66-1.80 (m, 2H), 1.48 (septet, J = 6.8 Hz, 1H), 1.30-1.42 (m, 3H), 1.22 (s, 24H), 1.00-1.12 (m, 2H), 0.84 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H), 0.79 (s, 3H), 0.11 (s, 4H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 82.6, 45.9, 40.8, 40.1, 37.0, 27.8, 27.5, 25.03 [*C*H_3 of B(pin), 2C], 24.99 [*C*H_3 of B(pin), 2C], 24.96 [*C*H_3 of B(pin), 2C], 24.9 [*C*H_3 of B(pin), 2C], 22.5, 18.7 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], 18.3 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], –1.6 (*C*–B, broad), –2.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS (APCI) *m/z* calcd for $C_{24}H_{49}B_2O_4Si^+$ $[M + H]^+$: 451.3581, found: 451.3576. The borylalkanes **3l** and **4l** (0.77 mmol total) were subjected to either Method A or Method B. An alcohol **7l** (76 mg, 0.53 mmol, 64% by Method A, 78 mg, 0.55 mmol, 66% by Method B) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **(1*R**,3*R**)-3-Isopropyl-3-methylcyclopentan-1-ol (7l):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27-4.34 (m, 1H), 1.91-2.00 (m, 1H), 1.83 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.62-1.72 (m, 1H), 1.46 (s, 1H, O*H*), 1.36-1.55 (m, 3H), 1.32 (dd, *J* = 14.0, 4.0 Hz, 1H), 1.00 (s, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 74.3, 47.7, 44.3, 37.9, 36.6, 35.2, 23.1, 18.3 [*C*H_3 of –CH(CH$_3$)$_2$, 1C], 18.0 [*C*H_3 of –CH(CH$_3$)$_2$, 1C]. HRMS (ESI) *m/z* calcd for $C_9H_{18}ONa^+$ $[M + Na]^+$: 165.1250, found: 165.1246. IR (neat) 3319 cm^{-1} (ν_{OH}).

Synthesis of (±)-Sphaeric Acid Starting from Diallyldimethylsilane (13) (Scheme 6): Compound **14** was prepared according to the procedure reported previously.[24] To a 500 mL three neck flask, Cp_2ZrCl_2 (7.0 g, 24 mmol) and THF (120 mL) were added. The flask was cooled to –78 °C by dry ice-acetone bath and *n*-BuLi (1.6 M in hexane, 30 mL, 48 mmol) was added to the reaction mixture. After 1 h, diallyldimethylsilane (**13**, 3.4 g, 24 mmol) was added and the cooling bath was removed. The reaction mixture was stirred at room temperature for 1 h. MeOH (0.77 g, 24 mmol) was added and stirred at room temperature for 1 h. The reaction mixture was cooled to 0 ºC by ice-water bath and I_2 (6.1 g, 24 mmol) was added. After 1 h, the cooling bath was removed and stirred at room temperature for 1 h. The volatiles were removed by a rotary evaporator, hexane (150 mL) was added. The organic layer was collected (rinsed with hexane 100 mL), washed with brine (100 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude

product was purified by column chromatography on silica gel (hexane). **14** (3.6 g, 13 mmol, 56%) was obtained.

To a 300 mL three neck flask, **14** (0.80 g, 3 mmol), THF (5 mL) and Li_2CuCl_4 (0.1 M in THF, 1.5 mL, 0.15 mmol) were added. The flask was cooled to 0 ºC by ice-water bath and heptylmagnesium bromide, which was prepared from 1-bromoheptane (2.7 g, 15 mmol) with magnesium turnings (0.40 g, 17 mmol) in THF (15 mL), was added. After stirring at 0 ºC for 2 h, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched by sat. NH_4Cl aq. at 0 ºC, and hexane (100 mL) was added. The organic layer was washed with water (20 mL x 3), washed with brine (20 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane) to give a mixture of **15** and tetradecane, which was formed by dimerization of heptylmagnesium bromide. Finally, compound **15** (0.48 g, 2.0 mmol, 67%) was obtained as a colorless oil by purification using GPC ($CHCl_3$). **(3*R**,4*R**)-1,1,3-trimethyl-4-octylsilolane (15)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52-1.63 (m, 1H), 1.17-1.44 (m, 14H), 1.06-1.17 (m, 1H), 0.83-1.01 (m, 8H), 0.19 (dd, J = 14.4, 11.2 Hz, 1H), 0.11 (dd, J = 14.4, 10.8 Hz, 1H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.0, 40.2, 35.8, 31.9, 30.0, 29.7, 29.4, 27.7, 23.6, 22.7, 22.0, 19.8, 14.1, –1.00, –1.02. HRMS (EI) *m/z* calcd for $C_{15}H_{32}Si^+$ $[M]^+$: 240.2268, found: 240.2264.

*Synthesis of (±)-Spaeric acid from **13**:* According to the *General Procedure* described in *Section 7*, C–H borylation was carried out using **13** (241 mg, 1.0 mmol). **16** (234 mg, 0.64 mmol, 64%, d.r. = ca. 1:1) and **17** (44 mg, 0.09 mmol, 9%) were obtained after purification by column chromatography on silica gel (hexane:Et_2O = 20:1 for **16**; hexane:Et_2O = 10:1 for **17**). **(3*R**,4*R**)-1,3-Dimethyl-4-octyl-1-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silolane (16):** Characterization data were given for a mixture of diastereomer A and B (ca. 1:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53-1.64 (m, diastereomer A and B, 2H), 1.23 (s, diastereomer A and B, 24H), 1.04-1.42 (m, diastereomer A and B,

30H), 0.84-1.04 (m, diastereomer A and B, 16H), 0.32 (dd, J = 14.4, 11.6 Hz, diastereomer A or B, 1H, SiCH_2C), 0.22 (dd, J = 14.4, 11.6 Hz, diastereomer A or B, 1H, SiCH_2C), 0.20 [d (AB pattern), J = 13.6 Hz, diastereomer A and B, 2H, SiCH_2B], 0.16 [d (AB pattern), J = 13.6 Hz, diastereomer A and B, 2H, SiCH_2B], 0.11-0.21 (overlapped, diastereomer A or B, 1H), 0.13 (s, diastereomer A or B, 3H, SiCH_3), 0.12 (s, diastereomer A or B, 3H, SiCH_3), 0.09 (dd, J = 14.4, 10.8 Hz, diastereomer A or B, 1H, SiCH_2C)]. ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 46.9, 40.2, 40.1, 35.8, 35.7, 31.9, 30.0, 29.7, 29.38, 29.37, 27.70, 27.67, 24.95, 24.93, 24.90, 23.96, 23.84, 22.7, 21.9, 20.1, 20.0, 14.1, –0.3 (*C*–B, broad), –0.6, –0.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (EI) *m/z* calcd for $C_{21}H_{43}BO_2Si^+$ $[M]^+$: 366.3120, found: 366.3113. **(3*R**,4*R**)-3-Methyl-4-octyl-1,1-bis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silolane (17):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55-1.64 (m, 1H), 1.22 (s, 24H), 1.16-1.43 (m, 14H), 0.97 (d, J = 6.8 Hz, 3H), 0.90-1.12 (m, 3H), 0.87 (t, J = 6.8 Hz, 3H), 0.32 (dd, J = 14.4, 12.0 Hz, 1H), 0.22 (s, 2H), 0.22 (dd, J = 14.4, 10.4 Hz, 1H), 0.21 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 46.8, 40.2, 35.6, 31.9, 30.0, 29.7, 29.4, 27.6, 25.04 [*C*H_3 of B(pin), 2C], 25.01 [*C*H_3 of B(pin), 2C], 24.99 [*C*H_3 of B(pin), 2C], 24.97 [*C*H_3 of B(pin), 2C], 24.0, 22.7, 21.7, 20.1, 14.1, 0.2 (*C*–B, broad). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS (ESI) *m/z* calcd for $C_{27}H_{55}B_2O_4Si^+$ $[M + H]^+$: 493.4050, found: 493.4055. The borylalkanes **16** and **17** (0.73 mmol total) were subjected to Method B. An alcohol **18** (111 mg, 0.51 mmol, 70%) was obtained after purification by column chromatography on silica gel (hexane:Et_2O = 1:1). **(2*R**,3*R**)-2-Methyl-3-octylbutane-1,4-diol (18)**[26a]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (dd, J = 11.2, 2.8 Hz, 1H), 3.71 (dd, J = 11.2, 3.6 Hz, 1H), 3.58 (dd, J = 11.2, 5.6 Hz, 1H), 3.53 (dd, J = 11.2, 5.6 Hz, 1H), 2.56 (broad, 2H, O*H*), 1.72-1.82 (m, 1H), 1.18-1.50 (m, 15H), 0.99 (d, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.9, 62.3, 43.8, 37.1, 31.9, 30.0, 29.6, 29.3, 29.1, 27.7, 22.7, 15.2, 14.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{29}O_2^+$ $[M + H]^+$: 217.2162, found: 217.2158. IR (neat) 3308 cm^{-1} (ν_{OH}). In a Schlenk tube, **18** (43 mg, 0.20 mmol), *t*-BuOH (2 mL), NaOH (0.5 N aqueous solution, 4 mL), and $KMnO_4$ (0.33 N aqueous solution, 6 mL) were added and

the resulting solution was stirred at room temperature. After 24 h, the reaction was quenched by sat. Na_2SO_3 aq. and the resulting mixture was filtered through celite. The resulting aqueous layer was washed with Et_2O (5 mL). The solution was acidified by 1 N HCl aq. to pH = 2, and the organic materials was extracted with CH_2Cl_2 (20 mL x 5), washed with brine (10 mL) and dried over anhydrous sodium sulfate. Pure Sphaeric acid (41 mg, 0.17 mmol, 83 %) was obtained after removal of the volatiles by a rotary evaporator. **(±)-Sphaeric acid**[26]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.5 (broad s, 2H, COO*H*), 2.73 (dq, J = 10.4, 7.2 Hz, 1H), 2.58 (ddd, J =10.4, 8.8, 4.0 Hz, 1H), 1.65-1.76 (m, 1H), 1.50-1.62 (m, 1H), 1.18-1.46 (m, 15H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 182.2, 47.6, 40.9, 31.8, 29.6, 29.3, 29.2 (two non-equivalent carbons were overlapped), 26.2, 22.6, 15.3, 14.1. HRMS (ESI, negative) *m/z* calcd for $C_{13}H_{23}O_4^-$ $[M - H]^-$: 243.1602, found: 243.1598. IR (neat) 1703 cm^{-1} (ν_{CO}).

Attempted Conversion of 19 through Method A (Scheme 7): *Preparation of **19**:* To a 50 mL flask, **16** (0.37 g, 1.0 mmol), THF (2 mL), NaOH (5 N aqueous solution, 0.80 mL) and H_2O_2 (30% aqueous solution, 0.40 mL) were added in this order. The resulting mixture was stirred for 4 h at room temperature under air. After cooling the solution to 0 °C by ice-water bath, a saturated aqueous solution of $Na_2S_2O_3$ (ca. 5 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Pure **19** (0.24 g, 0.95 mmol, 95%) was obtained as a colorless oil after purification by column chromatography on silica gel (hexane:Et_2O = 2:1). **(3*R**,4*R**)-1-Methyl-4-octyl-1-(hydroxymethyl)silolane (19)**: Characterization data were given for a mixture of diastereomer A and B (ca. 1:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.471 (d, J = 4.0 Hz, diastereomer A or B, 2H), 3.466 (d, J = 4.0 Hz, diastereomer A or B, 2H), 1.54-1.65 (m, diastereomer A and B, 2H), 1.09-1.45 (m, diastereomer A and B, 30H), 0.90-1.09 (m, diastereomer A and B, 6H), 1.009 (d, J = 6.4 Hz, diastereomer A or B, 3H), 1.006 (d, J = 6.4 Hz, diastereomer A or B, 3H), 0.88 (t, J = 6.4 Hz, diastereomer A and B, 6H),

0.35 (dd, J = 14.4, 11.2 Hz, diastereomer A or B, 1H, SiCH_2C), 0.27 (dd, J = 14.8, 11.2 Hz, diastereomer A or B, 1H, SiCH_2C), 0.22 (dd, J = 15.2, 11.2 Hz, diastereomer A or B, 1H, SiCH_2C), 0.152 (s, diastereomer A or B, 3H), 0.145 (s, diastereomer A or B, 3H), 0.10-0.18 (overlapped, diastereomer A or B, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.4, 47.2, 46.7, 40.5, 40.0, 35.8, 35.7, 31.9, 30.01, 29.98, 29.7, 29.4, 27.69, 27.67, 22.7, 22.0, 21.9, 21.0, 20.3, 17.2, 16.6, 14.1, –4.8. HRMS (DART) *m/z* calcd for $C_{15}H_{33}OSi^+$ $[M + H]^+$: 257.2295, found: 257.2289. IR (neat) 3333 cm^{-1} (ν_{OH}).

*Conversion of **19** by Method A:* To a 4 mL vial, **19** (24 mg, 0.10 mmol), KOMe (0.70 mg, 0.010 mmol) and DMSO (0.4 mL) were added. The resulting mixture was stirred at room temperature under nitrogen atmosphere. After 8 h, KF (15 mg, 0.25 mmol), $KHCO_3$ (30 mg, 0.30 mmol), THF/MeOH (v/v = 1/1, 0.5 mL) and H_2O_2 (30% aqueous solution, 60 μL) were added, and the resulting mixture was stirred at room temperature for 15 h under air. After cooling to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (ca. 2 mL) was added slowly. The organic materials were extracted with CH_2Cl_2 (5 mL x 4), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Undecane (7.3 mg, 0.05 mmol, internal standard) was added, and GC analysis of the resulting mixture indicates the yield of **20** is 16% and the yield of **21** is 13%. The structures of **20** and **21** were confirmed by comparison with GC and ^{1}H NMR data of authentic samples, which were prepared through the following conversions.

*Synthesis of Authentic Sample of **20**:* In a 100 mL flask, 3-methylbutanal (0.86 g, 10 mmol), cyclohexylamine (0.99 g, 10 mmol) and *p*-TsOH·H_2O (95 mg, 0.5 mmol) were dissolved in benzene (30 mL). The resulting mixture was refluxed with removing water using Dean-Stark apparatus for 1.5 h. Solvent was removed and the obtained imine was dissolved in THF (8 mL). This solution was added dropwise to a solution of LDA, which was prepared from *N*,*N*-diisopropylamine (1.2 g, 12 mmol) with *n*-BuLi (1.6 M in hexane, 7.5 mL, 12 mmol) in THF (4 mL), at –78 ºC. After stirring for 2.5 h, 1-bromooctane (3.9 g, 20 mmol) was added, and slowly warmed to room temperature. After 40 h, the

reaction was quenched with 0.5 N HCl aq. (pH 2~3), and the organic materials was extracted with diethyl ether and dried over anhydrous sodium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane:CH_2Cl_2 = 2:1) to afford 2-isopropyldecanal (**23**, 1.4 g, 7.2 mmol, 72%). **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 3.6 Hz, 1H), 1.98-2.06 (m, 1H), 1.97 (septet, J = 6.8 Hz, 1H), 1.56-1.69 (m, 1H), 1.38-1.50 (m, 1H), 1.13-1.35 (m, 12H), 0.96 (d, J = 6.8 Hz, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 58.4, 31.8, 29.7, 29.4, 29.2, 28.3, 27.6, 26.1, 22.6, 20.3, 19.8. 14.1. HRMS (APCI) *m/z* calcd for $C_{13}H_{27}O^+$ $[M + H]^+$: 199.2056, found: 199.2054.

To a 100 mL three neck flask, $NaBH_4$ (76 mg, 2 mmol) and EtOH (4 mL) were added. **23** (0.40 g, 2 mmol) was slowly added to the mixture. After stirring at room temperature for 1 h, the reaction was quenched with 1 N HCl aq. and the organic materials was extracted with diethyl ether (10 mL x 2), washed with brine (10 mL) and dried over anhydrous sodium sulfate. After removal of the volatiles by a rotary evaporator, **20** (0.38 g, 1.9 mmol, 94%) was obtained. **2-Isopropyldecan-1-ol (20)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54-3.65 (m, 2H), 1.75-1.87 (m, 1H), 1.04-1.38 (m, 16H), 0.90 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.8, 46.6, 31.9, 30.1, 29.6, 29.3, 27.9, 27.8, 27.7, 22.7, 19.8. 19.2, 14.1. HRMS (EI) *m/z* calcd for $C_{13}H_{26}^+$ $[M - H_2O]^+$: 182.2029, found: 182.2029. IR (neat) 3341 cm^{-1} (ν_{OH}).

*Synthesis of Authentic Sample of **21**:* Synthesis of (*Z*)-3-methylundec-2-ene (**24**) was performed in accordance with a reported procedure.[38] To a 100 mL two neck flask, 1-octene (1.1 g, 10 mmol) and THF (5 mL) were added and the flask was cooled to 0 ºC by ice-water bath. 9-Borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF, 20 mL, 10 mmol) was added to the flask and stirred for 2 h at 0 ºC. After warming to room temperature, $PdCl_2$(dppf) (0.21 g, 0.3 mmol), (*Z*)-2-bromo-2-butene (1.3 g, 9.5 mmol) and 3N NaOH aq, (10 mL) was added. The reaction mixture was refluxed for 14 h. Hexane (40 mL) was added and the reaction was quenched by 30% H_2O_2 aq. (5 mL). The organic layer was separated, and

aqueous layer was extracted with hexane (20 mL x 2). Organic layer was collected and washed with brine (30 mL) and dried over anhydrous sodium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane) to afford **24** (1.5 g, 8.6 mmol, 91%). **(*Z*)-3-Methylundec-2-ene (24)**[38]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (q, J = 6.4 Hz, 1H), 2.01 (t, J = 7.2 Hz, 2H), 1.64-1.68 (m, 3H), 1.53-1.58 (m, 3H), 1.20-1.41 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 118.6, 31.9, 31.4, 29.6 (two non-equivalent carbons were overlapped), 29.3, 27.8, 23.4, 22.7, 14.1, 13.2. Geometry of the double bond was confirmed by NOE.

A 100 mL two neck flask, $BH_3{\cdot}SMe_2$ (1.6 mL, 16 mmol) and THF (8 mL) were added and the flask was cooled to –20 ºC. **24** (0.67 g, 4 mmol, in THF 8 mL) was added to the flask and warmed to 0 ºC over 2 h. The flask was re-cooled to –20 ºC, and pinacol (3.8 g, 32 mmol, in THF 20 mL) was added. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 6 h. The resulting mixture was poured into ice water (20 mL) and hexane (100 mL) was added. The organic layer was washed with water (100 mL x2), washed with brine (50 mL) and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was purified by column chromatography on silica gel (hexane:Et_2O = 20:1). (2*R**,3*R**)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylundecane (**25**, 0.30 g, 1.0 mmol, 26%) was obtained as a colorless oil. **25**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44-1.58 (m, 1H), 1.06-1.40 (m, 14H), 1.24 (s, 12H), 0.82-1.02 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 35.51, 35.46, 31.9, 30.0, 29.7, 29.4, 27.3, 24.8 [*C*H_3 of B(pin), 2C], 24.7 [*C*H_3 of B(pin), 2C], 22.7, 18.7, 14.1, 12.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6. HRMS (EI) *m/z* calcd for $C_{18}H_{37}BO_2^+$ $[M]^+$: 296.2881, found: 296.2882.

To a 5 mL Schlenk tube, **25** (0.15 g, 0.50 mmol), bromochloromethane (0.13 g, 1.0 mmol), and THF (1.5 mL) were added and the flask was cooled to –78 ºC by dry ice-acetone bath. *n*-BuLi (1.6 M in

hexane, 0.62 mL, 1.0 mmol) was added to the flask over 10 min and stirred for 30 min at –78 ºC. The cooling bath was removed and the reaction mixture was stirred for 5 h at room temperature. The reaction was quenched by water and hexane (40 mL) was added. The organic layer was washed with water (10 mL x 2), washed with brine (10 mL) and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the resulting crude product was collected to a Schlenk tube. To the tube, THF (1 mL), NaOH (5 N aqueous solution, 400 μL) and H_2O_2 (30% aqueous solution, 200 μL) were added, and the resulting mixture was stirred at room temperature for 4 h under air. After cooling to 0 ºC by ice-water bath, a saturated solution of $Na_2S_2O_3$ (2 mL) was added slowly. The organic materials were extracted with EtOAc (15 mL x 3), and the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, the crude mixture was purified by column chromatography on silica gel (hexane:Et_2O = 4:1). **21** (83 mg, 0.41 mmol, 82%) was obtained as a colorless oil. **(2*R**,3*R**)-2,3-dimethylundecan-1-ol (21)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (dd, J = 10.4, 5.2 Hz, 1H), 3.44 (dd, J = 10.4, 7.2 Hz, 1H), 1.41 (s, 1H, O*H*), 1.00-1.68 (m, 16H), 0.89 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.1, 40.7, 34.6, 32.8, 31.9, 30.0, 29.7, 29.3, 27.5, 22.7, 17.0, 14.1, 13.6. HRMS (EI) *m/z* calcd for $C_{13}H_{27}O^+$ $[M - H]^+$: 199.2056, found: 199.2054. IR (neat) 3337 cm^{-1} (ν_{OH}).

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Supporting Information: ^{1}H and ^{13}C NMR spectra of new products and known key compounds. This material is available free of charge via Internet at http://pubs.acs.org.

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