Three-Component Carboboration of Alkenes under Copper Catalysis

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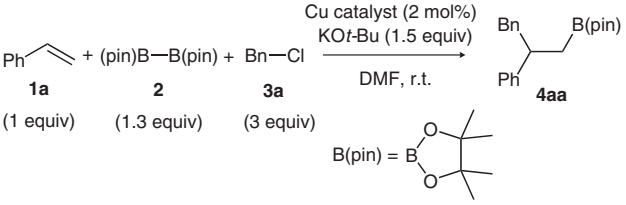
Abstract: Three-component carboboration of alkenes takes place efficiently by the reaction with a diboron compound and carbon electrophiles with the aid of a copper–NHC catalyst. The carboboration afforded diverse multisubstituted borylalkanes via the regioselective formation of carbon–boron and carbon–carbon bonds.

Key words: alkenes, carboboration, copper, equol, multicomponent reaction

The development of new synthetic routes to organoboron compounds,[1] in which the carbon–boron bonds can be transformed into various functional groups and carbon–carbon bonds through Suzuki–Miyaura cross-coupling,[2] the Petasis reaction,[3] etc., has been of great importance in modern organic synthesis. Recently, much attention has focused on unique copper catalysis for carbon–boron bond-forming reactions by the use of unsaturated hydrocarbons and organic halides,[4] and we have also reported the copper-catalyzed diborylation[5a] and borylstannylation[5b] of alkynes, in which β-borylalkenylcopper species arising from insertion of alkynes into borylcopper species[6] act as common intermediates. Furthermore, β-borylalkenylcopper species are captured by carbon electrophiles leading to the catalytic three-component carboboration of alkynes,[7–11] which provides a direct entry to multisubstituted borylalkenes through simultaneous carbon–carbon and carbon–boron bond-forming processes. In view of the high affinity of the borylcopper species for unsaturated hydrocarbons other than alkynes,[4k,12] we have also applied the carboboration protocol to simple alkenes,[13] which should lead to a direct approach to multisubstituted borylalkanes.

Initially we carried out the reaction of styrene (**1a**) with bis(pinacolato)diboron [**2**, (pin)B–B(pin)] and benzyl chloride (**3a**) in *N*,*N*-dimethylformamide at room temperature in the presence of copper(II) acetate–tricyclohexylphosphine, which produces a copper(I) complex in situ,[14] and potassium *tert*-butoxide, and observed the regioselective formation of a carbon–boron (at the terminal carbon of **1a**) and a carbon–carbon (at the internal carbon of **1a**) bond to provide 1-boryl-2,3-diphenylpropane **4aa** in 57% yield (Table 1, entry 1). Although the reaction with such a bidentate phosphine ligand as Xantphos or *rac*-BINAP proceeded in similar yield (Table 1, entries 2 and 3), the use of copper–N-heterocyclic carbene (Cu–NHC) complexes improved the efficiency of the carboboration (Table 1, entries 4–6), and chloro(1,3-dimesitylimidazolidin-2-ylidene)copper (SIMesCuCl) (Figure 1) gave the best result (77%) among the catalysts surveyed (Table 1, entry 6). A drop in basicity led to a decrease in yield: the reaction using potassium acetate or potassium carbonate afforded **4aa** in only 13% or 51% yield (Table 1, entries 7 and 8).

Table 1 Optimization of Reaction Conditions[a]



Entry	Cu Catalyst[b]	Time (h)	Yield[c] (%)
1	$Cu(OAc)_2$, Cy_3P[d]	0.5	57
2	CuI, Xantphos	0.5	53
3	CuCl, *rac*-BINAP	1	66
4	IPrCuCl	1	71
5	IMesCuCl	0.5	70
6	SIMesCuCl	0.5	77
7[e]	SIMesCuCl	7	13
8[f]	SIMesCuCl	4	51

[a] Reaction conditions: styrene (0.30 mmol), (pin)B–B(pin) (0.39 mmol), BnCl (0.90 mmol), KO*t*-Bu (0.45 mmol), Cu catalyst (6.0 μmol), DMF (0.55 mL).
[b] See also Figure 1.
[c] Determined by ^{1}H NMR.
[d] A copper(I) complex is produced in situ.[14]
[e] KOAc instead of KO*t*-Bu.
[f] K_2CO_3 instead of KO*t*-Bu.

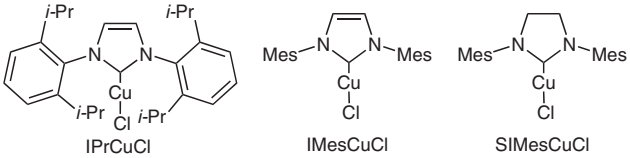


Figure 1 NHC ligands utilized

The optimized reaction was then examined using a range of monosubstituted alkenes (Table 2). The carboboration

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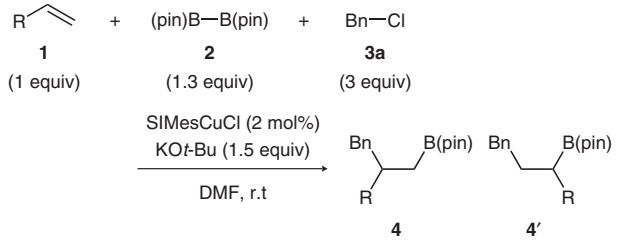
of styrene derivatives bearing an electron-donating **1b** or electron-withdrawing substituent **1c** also proceeded with high regioselectivity to afford the respective products, although the yields were lower (Table 2, entries 2 and 3).[15] The reaction was applied to 2-vinylpyridine (**1d**), vinylborane **1e**, and vinylsilanes **1f** and **1g** and gave borylalkanes **4da**–**ga** in good to high yields, in which the benzyl moiety was attached to the internal carbon of the alkene (Table 2, entries 4–7). In marked contrast, aliphatic alkenes, such as oct-1-ene (**1h**) or vinylcyclohexane (**1i**), underwent the reaction with the inverse regioselectivity to furnish **4h′** and **4i′** as the major products with the benzyl moiety at the terminal carbon of the alkene (Table 2, entries 8 and 9).

Table 2 Copper-Catalyzed Carboboration of Monosubstituted Alkenes[a]



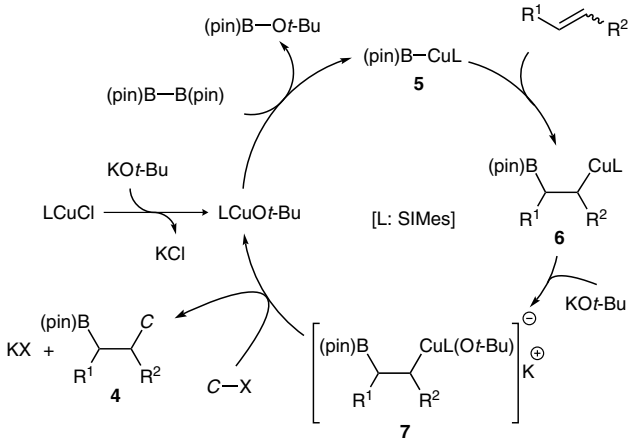
Entry	Alkene	R	Time (h)	Product	Yield[b] (%)	Ratio[c] (**4**/**4′**)
1	**1a**	Ph	1	**4aa**	65	>99:1
2	**1b**	4-MeOC$_6$H$_4$	1	**4ba**, **4ba′**	47	88:12
3	**1c**	4-ClC$_6$H$_4$	1	**4ca**	12	>99:1
4	**1d**	2-pyridyl	1	**4da**, **4da′**	52	91:9
5	**1e**	B(pin)	7	**4ea**, **4ea′**	68	98:2
6	**1f**	SiMe$_2$Ph	8	**4fa**, **4fa′**	85	94:6
7	**1g**	TMS	1	**4ga**, **4ga′**	82	93:7
8	**1h**	(CH$_2$)$_5$Me	1	**4ha**, **4ha′**	45	2:98
9	**1i**	Cy	1	**4ia**, **4ia′**	38	17:83

[a] Reaction conditions: alkene (0.30 mmol), (pin)B–B(pin) (0.39 mmol), BnCl (0.90 mmol), KO*t*-Bu (0.45 mmol), SIMesCuCl (6.0 μmol), DMF (0.55 mL).
[b] Yield of isolated **4** and **4′**.
[c] Determined by ^{1}H NMR.

As shown in Table 3, disubstituted alkenes could also participate in the carboboration; perfect regioselectivity was observed in the reaction of 1,1-disubstituted alkenes **1j**–**l** (Table 3, entries 1–3), but a mixture of stereoisomers[16] was formed with 1,2-disubstituted alkenes *cis*-stilbene (**1m**) or norbornene (**1n**) (Table 3, entries 4 and 5). However, boryl and benzyl moieties were introduced into 1,2-dihydronaphthalene (**1o**) regio- and stereoselectively affording *syn*-adduct **4oa** in 75% yield (Table 3, entry 6).

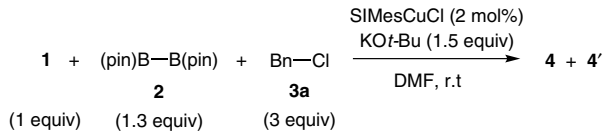
The versatility of the carboboration was further expanded by employing various carbon electrophiles (Table 4). The reaction of *para*- or *ortho*-substituted benzyl chlorides **3b**–**g** with vinylsilane **1f** and diboron **2** furnished high yields of the respective products (Table 4, entries 1–6), irrespective of the electronic character of the substituents, and sterically congested 2,4,6-triisopropylbenzyl chloride (**3h**), 2,4,6-trimethylbenzyl chloride (**3i**), and 1-naphthylmethyl chloride (**3j**) could also act as a carbon electrophile (Table 4, entries 7–9). In addition to benzyl chlorides, the present reaction was applied to butyl bromide (**3k**) and methyl iodide (**3l**) to provide the alkylboration products in 70% and 50% yield, respectively (Table 4, entries 10 and 11). The sole formation of the cyclopropylmethylated product **4fm** in the reaction with **3m** suggested that a radical pathway is not operating in the carboboration (Table 4, entry 12),[17] and moreover chemoselective reaction with 1,5-dibromopentane (**3n**) or ethyl 4-bromobutanoate (**3o**) occurred, leaving the reactive functional groups (C–Br and ester moieties) intact (Table 4, entries 13 and 14).

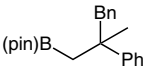
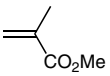
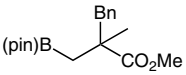
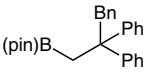
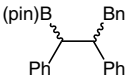
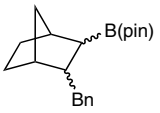
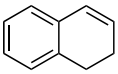
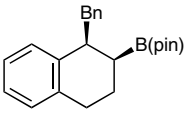
As was the case with the previous copper-catalyzed carboboration of alkynes,[11] a β-borylalkylcopper species **6**, generated by the addition of a borylcopper species **5** to an alkene,[4h,12b,18] should also serve as a key intermediate in the present reaction (Scheme 1). Subsequent reaction of **6** with potassium *tert*-butoxide produces cuprate **7**, which is then captured by a carbon electrophile to provide a carboboration product and copper(I) *tert*-butoxide.[19] The observed regioselectivity in the reaction of aryl-, boryl-, and silylalkenes should be ascribed to the selective formation of the carbon–copper bond at the α position of these substituents in the borylcupration **5** to **6**, induced by the electronic-directing effect of the substituents.



Scheme 1 A plausible catalytic cycle for carboboration

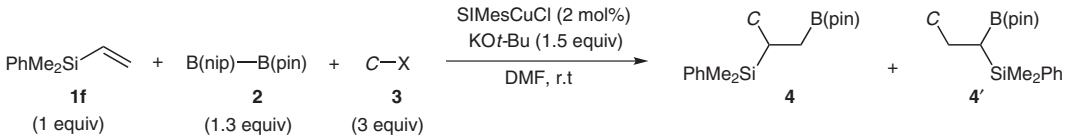
Table 3 Copper-Catalyzed Carboboration of Disubstituted Alkenes[a]



Entry	Alkene		Time (h)	Product		Yield[b] (%)	Ratio[c] (**4**/**4′**)
1	**1j**		1	**4ja**		34	>99:1
2	**1k**		1	**4ka**		40	>99:1
3	**1l**		0.5	**4la**		35	>99:1
4	**1m**		4	**4ma**, **4ma′**		40	77:23[d]
5	**1n**		0.5	**4na**, **4na′**		60	62:38[d]
6	**1o**		0.5	**4oa**		75	>99:1[d]

[a] Reaction conditions: alkene (0.30 mmol), (pin)B–B(pin) (0.39 mmol), BnCl (0.90 mmol), KO*t*-Bu (0.45 mmol), SIMesCuCl (6.0 μmol), DMF (0.55 mL).
[b] Yield of isolated **4** and **4′**.
[c] Determined by ^{1}H NMR.
[d] Ratio of stereoisomers.

Table 4 Copper-Catalyzed Carboboration with Various Carbon Electrophiles[a]



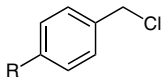
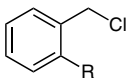
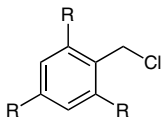
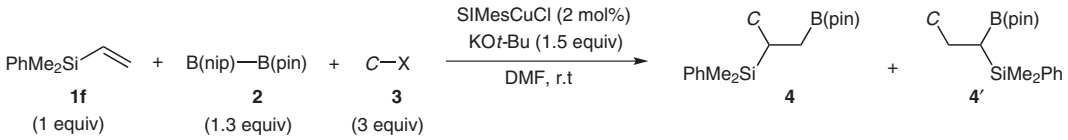
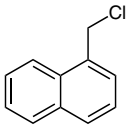
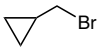
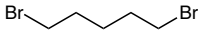
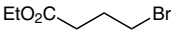
Entry	C–X	R	**3**	Time (h)	Product	Yield[b] (%)	Ratio[c] (**4**/**4′**)[c]
1		*i*-Pr	**3b**	4	**4fb**, **4fb′**	90	92:8
2		Me	**3c**	3	**4fc**, **4fc′**	88	95:5
3		Cl	**3d**	3	**4fd**, **4fd′**	85	95:5
4		OMe	**3e**	3	**4fe**, **4fe′**	90	97:3
5		Me	**3f**	4	**4ff**, **4ff′**	90	96:4
6		Cl	**3g**	4	**4fg**, **4fg′**	73	98:2
7		*i*-Pr	**3h**	2	**4fh**, **4fh′**	46	88:12
8		Me	**3i**	2	**4fi**, **4fi′**	58	91:9

Table 4 Copper-Catalyzed Carboboration with Various Carbon Electrophiles[a] (continued)

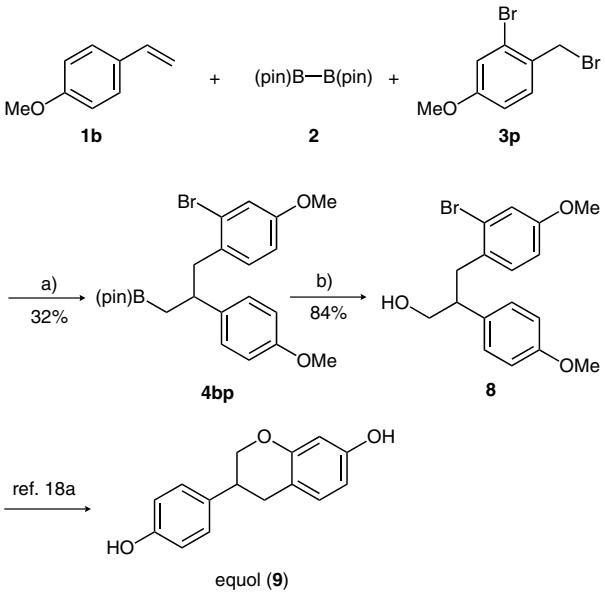


Entry	C–X	R	3	Time (h)	Product	Yield[b] (%)	Ratio[c] (**4**/**4′**)[c]
9			**3j**	7	**4fj**, **4fj′**	72	97:3
10	BuBr		**3k**	10	**4fk**, **4fk′**	70	97:3
11	MeI		**3l**	3	**4fl**	50	>99:1
12			**3m**	7	**4fm**	85	>99:1
13			**3n**	7	**4fn**, **4fn′**	70	98:2
14			**3o**	7	**4fo**, **4fo′**	37	96:4

[a] Reaction conditions: dimethyl(phenyl)vinylsilane (0.30 mmol), (pin)B–B(pin) (0.39 mmol), carbon electrophile (0.90 mmol), KO*t*-Bu (0.45 mmol), SIMesCuCl (6.0 μmol), DMF (0.55 mL).
[b] Yield of isolated **4** and **4′**.
[c] Determined by ^{1}H NMR.

Finally, the synthetic utility of the carboboration product was demonstrated by the formal total synthesis (Scheme 2) of equol, which has potential anti-osteoporosis and anti-breast cancer activity with its estrogen-like effects.[20,21] Thus, the carboboration using 4-methoxystyrene (**1b**), diboron **2**, and 2-bromo-4-methoxybenzyl bromide (**3p**) afforded the borylalkane **4bp**, in which the C–B bond was readily converted into a C–OH bond by oxidation with hydrogen peroxide. The resulting alcohol **8** has previously been transformed into equol (**9**) by a palladium-catalyzed intramolecular C–O bond-forming reaction and demethylation of the methoxy moieties.[21a]

In conclusion, we have demonstrated that the three-component carboboration of alkenes with a diboron compound and carbon electrophiles proceeds efficiently with the aid of a catalytic amount of a Cu–NHC complex in a straightforward approach to diverse multisubstituted borylalkanes. Moreover, the synthetic utility of the carboboration is shown by the formal total synthesis of biologically significant equol. Further studies on catalytic three-component borylation reactions using other electrophiles are in progress.



Scheme 2 Formal total synthesis of equol. *Reagents and conditions*: (a) 4-methoxystyrene (1 equiv), **2** (1.3 equiv), 2-bromo-4-methoxybenzyl bromide (3 equiv), KO*t*-Bu (1.5 equiv), SIMesCuCl (2 mol%), DMF, r.t., 13 h; (b) 32 wt% H_2O_2 (5 equiv), NaOH (5 equiv), THF, 0 °C, 0.5 h.

All manipulations of O_2- and moisture-sensitive materials were conducted with standard Schlenk techniques under a purified argon atmosphere. NMR spectra were taken on a Varian 400-MR (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer or a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer using residual $CHCl_3$ (^{1}H, δ = 7.26 ppm) or $CDCl_3$ (^{13}C, δ = 77.0 ppm) as an internal standard. HRMS were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL. Preparative recycling gel permeation chromatography was performed with Jai LC-908 or Jai LC-9201 equipped with Jai GEL-1H and 2H columns ($CHCl_3$). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. DMF was distilled from CaH_2. 2-Bromo-4-methoxybenzyl bromide (**3p**) was prepared according to a literature procedure.[21a] IPrCuCl, IMesCuCl, and SIMesCuCl were prepared according to literature procedures.[22]

Copper-Catalyzed Carboboration of Alkenes; General Procedure

A Schlenk tube equipped with a magnetic stirring bar was charged with SIMesCuCl (6.0 μmol), alkene 0.30 mmol), bis(pinacolato)diboron (0.39 mmol), a carbon electrophile (0.90 mmol), 1 M KO*t*-Bu in THF (0.45 mmol), and DMF (0.55 mL). The mixture was stirred at r.t. for the period specified in Tables 2–4, and diluted with EtOAc before filtration through a Celite plug. The organic solution was washed with brine (2 ×) and dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography (silica gel, hexane–EtOAc or hexane–CH_2Cl_2) or gel-permeation chromatography ($CHCl_3$) gave the product.

In the ^{13}C NMR spectra, boron-bound carbons were not detected because of quadrupolar relaxation.

2-(2,3-Diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa)

Pale yellow oil; yield: 62.8 mg (0.195 mmol, 65%).

^1H NMR ($CDCl_3$): δ = 1.06 (s, 6 H), 1.08 (s, 6 H), 1.15–1.25 (m, 2 H), 2.84–2.93 (m, 2 H), 3.11–3.18 (m, 1 H), 7.05 (d, *J* = 7.0 Hz, 2 H), 7.12–7.24 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 24.53, 24.65, 43.57, 46.17, 82.89, 125.68, 125.84, 127.50, 127.90, 127.94, 129.31, 140.69, 146.41.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{27}O_2BNa$: 345.19963; found: 345.19992.

2-[2-(4-Methoxyphenyl)-3-phenylpropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ba)

Pale yellow oil; yield: 49.7 mg (0.141 mmol, 47%).

^1H NMR ($CDCl_3$): δ = 106 (s, 6 H), 1.07 (s, 6 H), 1.24–1.37 (m, 2 H), 2.83 (d, *J* = 7.4 Hz, 2 H), 3.04–3.12 (m, 1 H), 3.76 (s, 3 H), 6.76 (d, *J* = 8.5 Hz, 2 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 7.06 (d, *J* = 8.5 Hz, 2 H), 7.13 (t, *J* = 7.1 Hz, 1 H), 7.19 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 24.57, 24.71, 42.74, 46.38, 55.20, 82.89, 113.28, 125.63, 128.36, 129.34, 138.60, 140.80, 157.66.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{29}O_3BNa$: 357.21020; found: 375.21027.

2-[2-(4-Chlorophenyl)-3-phenylpropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ca)

Pale yellow oil; yield: 12.8 mg (0.036 mmol, 12%).

^1H NMR ($CDCl_3$): δ = 1.06 (s, 6 H), 1.09 (s, 6 H), 1.13 (dd, *J* = 16.0, 9.5 Hz, 1 H), 1.21 (dd, *J* = 15.7, 6.5 Hz, 1 H), 2.81 (dd, *J* = 13.1, 8.1 Hz, 1 H), 2.86 (dd, *J* = 13.8, 7.4 Hz, 1 H), 3.11 (tdd, *J* = 7.7, 7.7, 7.7 Hz, 1 H), 6.99 (d, *J* = 7.7 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.12–7.21 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 24.56, 24.70, 43.03, 46.01, 83.03, 125.83, 127.99, 128.02, 128.90, 129.26, 131.38, 140.24, 144.85.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{26}O_2BClNa$: 356.17144; found: 356.17219.

2-[1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]pyridine (4da)

Pale yellow oil; yield: 50.4 mg (0.156 mmol, 52%).

^1H NMR ($CDCl_3$): δ = 0.86–0.92(m, 1 H), 1.05–1.09 (m, 1 H), 1.16 (s, 6 H), 1.93 (s, 6 H), 2.83 (dd, *J* = 13.3, 8.2 Hz, 1 H), 3.14 (dd, *J* = 13.5, 6.8 Hz, 1 H), 3.45 (m, *J* = 7.5 Hz, 1 H), 7.15–7.20 (m, 4 H), 7.22–7.26 (m, 3 H), 7.68 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1 H), 8.59 (ddd, *J* = 5.1, 1.4, 1.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 25.33, 25.59, 43.18, 44.47, 80.85, 121.99, 122.52, 125.91, 128.15, 129.20, 138.42, 140.36, 144.78, 165.51.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{27}O_2NB$: 324.21294; found: 324.21558.

2,2′-(3-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4ea)

Pale yellow oil; yield: 75.9 mg (0.204 mmol, 68%).

^1H NMR ($CDCl_3$): δ = 0.82 (d, *J* = 7.9, 2 H), 1.16 (s, 6 H), 1.19 (s, 6 H), 1.22 (s, 12 H), 1.46 (m, *J* = 7.9 Hz, 1 H), 2.60 (dd, *J* = 13.4, 8.5 Hz, 1 H), 2.79 (dd, *J* = 13.7, 7.4 Hz, 1 H), 7.13 (t, *J* = 7.0 Hz, 1 H), 7.18–7.24 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 24.74, 24.77, 24.82, 24.89, 39.48, 82.86, 82.93, 125.45, 127.91, 129.09, 142.31.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{34}O_4B_2Na$: 395.25354; found: 395.25458.

Dimethyl(phenyl)[1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]silane (4fa)

Pale yellow oil; yield: 97.0 mg (0.255 mmol, 85%).

^1H NMR ($CDCl_3$): δ = 0.23 (s, 3 H), 0.23 (s, 3 H), 0.75 (dd, *J* = 16.3, 7.4 Hz, 1 H), 0.89 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.14 (s, 6 H), 1.16 (s, 6 H), 1.52–1.57 (m, 1 H), 2.49 (dd, *J* = 13.8, 9.8 Hz, 1 H), 2.76 (dd, *J* = 13.9, 5.7 Hz, 1 H), 7.12–7.16 (m, 3 H), 7.21–7.24 (m, 2 H), 7.33–7.35 (m, 3 H), 7.52–7.54 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.27, –4.21, 22.10, 24.79, 24.96, 38.45, 82.79, 82.87, 125.53, 127.57, 127.98, 128.68, 129.10, 134.10, 138.60, 142.42.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{33}O_2BNaSi$: 403.22351; found: 403.22391.

Trimethyl[1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]silane (4ga)

Pale yellow oil; yield: 78.3 mg (0.246 mmol, 82%).

^1H NMR ($CDCl_3$): δ = –0.07 (s, 9 H), 0.73 (dd, *J* = 16.5, 4.5 Hz, 1 H), 0.83 (dd, *J* = 16.5, 6.6 Hz, 1 H), 1.18 (s, 6 H), 1.19 (s, 6 H), 1.24–1.27 (m, 1 H), 2.51 (dd, *J* = 14.0, 9.6 Hz, 1 H), 2.74 (dd, *J* = 13.8, 6.2 Hz, 1 H), 7.15 (tt, *J* = 6.9, 1.3 Hz, 1 H), 7.19–7.27 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = –2.71, 22.68, 24.73, 24.84, 25.02, 38.67, 39.65, 82.86, 125.51, 128.01, 129.11, 142.72.

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{31}O_2BNaSi$: 341.20786; found: 341.20831.

4,4,5,5-Tetramethyl-2-(1-phenylnonan-3-yl)-1,3,2-dioxaborolane (4ha′)

Pale yellow oil; yield: 44.6 mg (0.135 mmol, 45%).

^1H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3 H), 1.00–1.08 (m, 1 H), 1.23–1.31 (m, 20 H), 1.34–1.48 (m, 3 H), 1.59–1.68 (m, 1 H), 1.69–1.79 (m, 1 H), 2.59 (dt, *J* = 10.1, 6.4 Hz, 2 H), 7.16 (tt, *J* = 7.1, 2.3 Hz, 1 H), 7.18 (d, *J* = 7.1 Hz, 2 H), 7.26 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.11, 22.62, 24.80, 24.86, 29.15, 29.59, 31.26, 31.82, 33.55, 35.68, 82.89, 125.50, 128.19, 128.38, 143.12.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{36}O_2B$: 331.28029; found: 331.28006.

2-(2-Cyclohexyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ia) and 2-(1-Cyclohexyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ia′)

Pale yellow oil; yield: 37.4 mg (0.114 mmol, 38%).

^1H NMR ($CDCl_3$): δ = 0.69 (dd, *J* = 15.5, 7.7 Hz, 0.2 H), 0.78 (dd, *J* = 15.6, 6.5 Hz, 0.2 H), 0.91–1.24 (m, 10.4 H), 1.28 (s, 12 H), 1.37–1.45 (m, 1.3 H), 1.62–1.64 (m, 8.3 H), 1.67–1.71 (m, 4.1 H), 1.72–1.78 (m, 2.6 H), 1.81–1.86 (m, 0.3 H), 2.42 (dd, *J* = 13.2, 8.3 Hz, 0.2 H), 2.49 (ddd, *J* = 13.4, 10.7, 6.1 Hz, 1 H), 2.63 (ddd, *J* = 13.7, 11.1, 5.2 Hz, 1 H), 2.68 (dd, *J* = 13.4, 6.6 Hz, 0.2 H), 7.16 (tt, *J* = 7.5, 1.3 Hz, 1.1 H), 7.18 (d, *J* = 7.1 Hz, 2.5 H), 7.26 (t, *J* = 7.6 Hz, 2.1 H).

^{13}C NMR ($CDCl_3$): δ = 24.79, 24.83, 24.86, 25.10, 26.74, 26.77, 26.78, 26.85, 28.92, 30.33, 31.05, 32.42, 32.80, 36.06, 39.66, 39.92,

41.46, 41.89, 82.79, 82.91, 125.40, 125.49, 128.02, 128.18, 128.34, 129.33, 142.24, 143.19.

HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{34}O_2B$: 329.26464; found: 329.26447.

4,4,5,5-Tetramethyl-2-(2-methyl-2,3-diphenylpropyl)-1,3,2-dioxaborolane (4ja)
Pale yellow oil; yield: 34.3 mg (0.102 mmol, 34%).

^{1}H NMR ($CDCl_3$): δ = 1.12 (s, 6 H), 1.06 (s, 6 H), 1.11 (d, *J* = 15.4 Hz, 1 H), 1.42 (s, 3 H), 1.45 (d, *J* = 15.0 Hz, 1 H), 2.94 (q, *J* = 12.4 Hz, 2 H), 6.80 (dd, *J* = 6.3, 3.2 Hz, 2 H), 7.10–7.11 (m, 3 H), 7.14 (tt, *J* = 7.0, 1.5 Hz, 1 H), 7.23–7.29 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 24.46, 24.70, 26.37, 40.38, 52.21, 82.67, 125.40, 125.72, 126.54, 127.30, 127.61, 130.60, 138.95, 148.84.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{22}H_{29}O_2BNa$: 359.21528; found: 359.21536.

Methyl 2-Benzyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (4ka)
Pale yellow oil; yield: 38.2 mg (0.12 mmol, 40%).

^{1}H NMR ($CDCl_3$): δ = 0.87 (d, *J* = 15.4 Hz, 1 H), 1.19 (d, *J* = 15.5 Hz, 1 H), 1.22 (s, 6 H), 1.23 (s, 6 H), 1.24 (s, 3 H), 2.91 (s, 2 H), 3.63 (s, 3 H), 7.11 (d, *J* = 7.6 Hz, 2 H), 7.19 (tt, *J* = 7.1, 2.0 Hz, 1 H), 7.22–7.25 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 24.41, 24.72, 24.84, 45.26, 46.89, 51.51, 82.96, 126.30, 127.84, 130.34, 138.87, 178.04.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{27}O_4BNa$: 341.18946; found: 341.19022.

4,4,5,5-Tetramethyl-2-(2,2,3-triphenylpropyl)-1,3,2-dioxaborolane (4la)
Pale yellow solid; yield: 41.8 mg (0.105 mmol, 35%); mp 139.7–141.0 °C.

^{1}H NMR ($CDCl_3$): δ = 1.02 (s, 12 H), 1.54 (s, 2 H), 3.63 (s, 2 H), 6.61 (dd, *J* = 7.9, 1.5 Hz, 2 H), 7.04 (tt, *J* = 7.2, 1.3 Hz, 2 H), 7.09 (tt, *J* = 7.2, 1.7 Hz, 1 H), 7.13–7.16 (m, 6 H), 7.21 (t, *J* = 7.4 Hz, 4 H).

^{13}C NMR ($CDCl_3$): δ = 24.64, 45.13, 48.37, 82.76, 125.49, 125.67, 127.04, 127.51, 128.08, 131.03, 138.65, 149.89.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{27}H_{31}O_2BNa$: 421.23093; found: 421.23099.

4,4,5,5-Tetramethyl-2-(1,2,3-triphenylpropyl)-1,3,2-dioxaborolane (4ma, 4ma′)
Pale yellow solid; yield: 47.8 mg (0.12 mmol, 40%); mp 74.4–76.5 °C.

^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 6 H), 0.84 (s, 6 H), 1.25 (s, 1.3 H), 1.28 (s, 1.3 H), 2.50 (dd, *J* = 13.4, 11.2 Hz, 1 H), 2.78 (d, *J* = 12.1 Hz, 1 H), 2.82 (d, *J* = 12.7 Hz, 0.3 H), 2.87 (dd, *J* = 13.4, 11.3 Hz, 0.3 H), 2.89 (dd, *J* = 13.3, 3.2 Hz, 1 H), 3.16 (dd, *J* = 13.1, 3.1 Hz, 0.3 H), 3.32 (td, *J* = 11.4, 3.0 Hz, 1 H), 3.44 (td, *J* = 11.3, 3.4 Hz, 0.4 H), 6.68 (dd, *J* = 7.4, 1.6 Hz, 2 H), 6.82 (dd, *J* = 7.9, 1.4 Hz, 0.6 H), 6.91–7.11 (m, 10.3 H), 7.17 (t, *J* = 8.0 Hz, 2.1 H), 7.22 (tt, *J* = 7.2, 1.0 Hz, 1.3 H), 7.36 (tt, *J* = 7.7, 1.1 Hz, 2.2 H), 7.45 (dd, *J* = 8.2, 0.9 Hz, 2.2 H).

^{13}C NMR ($CDCl_3$): δ = 23.99, 24.31, 24.60, 24.75, 41.82, 43.85, 50.64, 50.71, 83.06, 83.57, 124.99, 125.32, 125.49, 125.60, 125.64, 126.05, 127.45, 127.57, 127.76, 127.80, 128.34, 128.49, 128.65, 129.06, 129.11, 129.19, 129.27, 140.50, 140.57, 141.22, 144.04.

HRMS: *m/z* [M + H]$^+$ calcd for $C_{27}H_{32}O_2B$: 399.24899; found: 399.24899.

2-(3-Benzylbicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4na, 4na′)
Pale yellow solid; yield: 56.2 mg (0.18 mmol, 60%); mp 78.7–79.7 °C.

^{1}H NMR ($CDCl_3$): δ = 1.02–1.09 (m, 2 H), 1.10 (s, 4.2 H), 1.10 (s, 4.2 H), 1.14–1.20 (m, 1.9 H), 1.23 (s, 6 H), 1.24 (s, 6 H), 1.33–1.57 (m, 5 H), 1.68 (d, *J* = 9.5 Hz, 1.7 H), 1.92 (d, *J* = 3.9 Hz, 1 H), 2.01 (ddd, *J* = 12.6, 9.1, 3.4 Hz, 1 H), 2.08 (t, *J* = 2.08 Hz, 0.7 H), 2.16–2.21 (m, 1.3 H), 2.27 (d, *J* = 2.9 Hz, 1 H), 2.33 (dd, *J* = 13.7, 11.6 Hz, 1 H), 2.58 (dd, *J* = 13.2, 7.9 Hz, 0.7 H), 2.65 (dd, *J* = 13.4, 7.3 Hz, 0.7 H), 2.77 (dd, *J* = 13.5, 4.5 Hz, 1 H), 7.13 (t, *J* = 7.1 Hz, 1 H), 7.17 (d, *J* = 7.2 Hz, 3.6 H), 7.23 (t, *J* = 7.5 Hz, 1.4 H), 7.27 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 22.14, 24.54, 24.58, 24.84, 25.01, 29.91, 31.55, 32.93, 34.89, 38.84, 39.11, 39.38, 39.70, 40.31, 40.66, 45.32, 46.75, 82.63, 82.87, 125.36, 125.49, 128.07, 128.09, 128.86, 129.01, 142.40, 142.55.

HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{30}O_2B$: 313.23334; found: 313.23334.

2-(1-Benzyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4oa)
Pale yellow solid; yield: 78.4 mg (0.225 mmol, 75%); mp 71.4–73.5 °C.

^{1}H NMR ($CDCl_3$): δ = 1.31 (s, 12 H), 1.53 (m, *J* = 4.0 Hz, 1 H), 1.70–2.02 (m, 2 H), 2.68 (dd, *J* = 12.8, 10.1 Hz, 1 H), 2.83 (m, *J* = 8.7 Hz, 1 H), 2.90 (t, *J* = 4.6 Hz, 1 H), 2.96 (dd, *J* = 12.9, 3.5 Hz, 1 H), 3.21 (dt, *J* = 10.2, 3.7 Hz, 1 H), 6.24 (d, *J* = 7.6 Hz, 1 H), 6.79 (td, *J* = 7.3, 1.1 Hz, 1 H), 7.03–7.08 (m, 4 H), 7.19 (t, *J* = 7.2, 1.8 Hz, 1 H), 7.24 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 19.71, 24.80, 25.16, 29.02, 42.24, 42.33, 83.22, 124.07, 125.70, 127.93, 129.14, 129.17, 129.77, 135.94, 140.62, 141.46.

HRMS: *m/z* [M + H]$^+$ calcd for $C_{23}H_{30}O_2B$: 349.23334; found: 349.23343.

[1-(4-Isopropylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fb)
Pale yellow oil; yield: 114.1 mg (0.27 mmol, 90%).

^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 3 H), 0.22 (s, 3 H), 0.73 (dd, *J* = 16.2, 7.7 Hz, 1 H), 0.89 (dd, *J* = 16.3, 5.7 Hz, 1 H), 1.12 (s, 6 H), 1.13 (s, 6 H), 1.22 (d, *J* = 6.8 Hz, 6 H), 1.50–1.56 (m, 1 H), 2.44 (dd, *J* = 13.8, 9.9 Hz, 1 H), 2.73 (dd, *J* = 14.2, 5.8, 1 H), 2.84 (m, *J* = 6.9 Hz, 1 H), 7.07 (s, 4 H), 7.31–7.33 (m, 3 H), 7.44–7.52 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.38, –4.26, 21.97, 24.07, 24.79, 24.94, 33.65, 36.45, 38.02, 82.82, 125.99, 127.51, 128.61, 128.96, 134.08, 138.68, 139.61, 145.97.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{26}H_{39}O_2BNaSi$: 445.27046; found: 445.27017.

Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-tolyl)propan-2-yl]silane (4fc)
Pale yellow oil; yield: 104.1 mg (0.264 mmol, 88%).

^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 3 H), 0.22 (s, 3 H), 0.73 (dd, *J* = 16.0, 7.3 Hz, 1 H), 0.86 (dd, *J* = 16.0, 6.4 Hz, 1 H), 1.13 (s, 6 H), 1.15 (s, 6 H), 1.48–1.54 (m, 1 H), 2.29 (s, 3 H), 2.44 (dd, *J* = 13.8, 9.8 Hz, 1 H), 2.71 (dd, *J* = 14.1, 6.1 Hz, 1 H), 7.23 (s, 4 H), 7.32–7.34 (m, 3 H), 7.51–7.52 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.24, –4.18, 20.98, 22.09, 24.79, 24.96, 37.97, 82.85, 127.54, 128.63, 128.67, 128.96, 134.12, 134.86, 138.69, 139.22.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{24}H_{35}O_2BNaSi$: 417.23916; found: 417.23886.

[1-(4-Chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fd)
Pale yellow oil; yield: 105.8 mg (0.255 mmol, 85%).

^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 3 H), 0.24 (s, 3 H), 0.70 (dd, *J* = 16.4, 7.2 Hz, 1 H), 0.87 (dd, *J* = 16.4, 6.0 Hz, 1 H), 1.14 (s, 6 H), 1.15 (s, 6 H), 1.44–1.50 (m, 1 H), 2.42 (dd, *J* = 13.8, 10.1 Hz, 1 H), 2.70 (dd,

J = 14.0, 5.6 Hz, 1 H), 7.05 (d, J = 8.4 Hz, 2 H), 7.16 (d, J = 8.3 Hz, 2 H), 7.33–7.34 (m, 3 H), 7.49–7.51 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.49, –4.08, 22.16, 24.80, 24.94, 37.80, 82.95, 127.62, 128.03, 128.76, 130.42, 131.19, 134.04, 138.32, 140.89.

HRMS: m/z [M + Na]$^+$ calcd for $C_{23}H_{32}O_2BClNaSi$: 437.18454; found: 437.18442.

[1-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fe)
Pale yellow oil; yield: 110.8 mg (0.27 mmol, 90%).

^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3 H), 0.21 (s, 3 H), 0.73 (dd, J = 16.2, 7.4 Hz, 1 H), 0.86 (dd, J = 16.4, 6.2 Hz, 1 H), 1.14 (s, 6 H), 1.15 (s, 6 H), 1.45–1.51 (m, 1 H), 2.42 (dd, J = 13.8, 9.7 Hz, 1 H), 2.69 (dd, J = 13.8, 5.7 Hz, 1 H), 3.77 (s, 3 H), 6.76 (d, 8.6 Hz, 2 H), 7.05 (d, J = 8.6 Hz, 2 H), 7.32–7.34 (m, 3 H), 7.50–7.52 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.28, –4.15, 22.31, 24.80, 24.98, 37.55, 55.20, 82.86, 113.44, 127.54, 128.63, 129.93, 134.10, 134.43, 138.68, 157.60.

HRMS: m/z [M + Na]$^+$ calcd for $C_{24}H_{35}O_3BNaSi$: 433.23407; found: 433.23407.

Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2-tolyl)propan-2-yl]silane (4ff)
Pale yellow oil; yield: 106.5 mg (0.27 mmol, 90%).

^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 3 H), 0.28 (s, 3 H), 0.75 (dd, J = 16.4, 6.8, Hz, 1 H), 0.88 (dd, J = 16.6, 6.4 Hz, 1 H), 1.10 (s, 6 H), 1.12 (s, 6 H), 1.51–1.56 (m, 1 H), 2.20 (s, 3 H), 2.43 (dd, J = 13.9, 10.7 Hz, 1 H), 2.76 (dd, J = 13.9, 5.0 Hz, 1 H), 7.05–7.06 (m, 3 H), 7.08–7.10 (m, 1 H), 7.33–7.34 (m, 3 H), 7.54–7.55 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.44, –4.25, 19.42, 20.10, 24.75, 24.83, 24.93, 35.78, 82.82, 125.37, 125.64, 127.56, 128.71, 129.87, 130.10, 134.10, 136.56, 138.63, 140.22.

HRMS: m/z [M + Na]$^+$ calcd for $C_{24}H_{35}O_2BNaSi$: 417.23916; found: 417.23914.

[1-(2-Chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fg)
Pale yellow oil; yield: 90.9 mg (0.219 mmol, 73%).

^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 3 H), 0.30 (s, 3 H), 0.73 (dd, J = 16.4, 6.8 Hz, 1 H), 0.88 (dd, J = 16.6, 6.5 Hz, 1 H), 1.11 (s, 6 H), 1.13 (s, 6 H), 1.66 (tdd, J = 6.4, 4.7, 11.0 Hz, 1 H), 2.53 (dd, J = 13.8, 10.7 Hz, 1 H), 2.93 (dd, J = 13.9, 5.0 Hz, 1 H), 7.07 (td, J = 7.4, 1.9 Hz, 1 H), 7.10 (td, J = 7.3, 1.6 Hz, 1 H), 7.18 (dd, J = 7.4, 1.9 Hz, 1 H), 7.26 (dd, 7.6, 1.6 Hz, 1 H), 7.32–7.34 (m, 3 H), 7.54–7.56 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.37, –4.27, 20.02, 24.82, 24.93, 35.95, 82.85, 126.19, 126.97, 127.54, 128.72, 129.39, 131.26, 134.13, 134.38, 138.43, 139.56.

HRMS: m/z [M + Na]$^+$ calcd for $C_{23}H_{32}O_2BClNaSi$: 437.18454; found: 437.18430.

Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2,4,6-triisopropylphenyl)propan-2-yl]silane (4fh) and Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2,4,6-triisopropylphenyl)propyl]silane (4fh′)
Pale yellow oil; yield: 69.9 mg (0.138 mmol, 46%).

^{1}H NMR ($CDCl_3$): δ = 0.30 (s, 0.4 H), 0.32 (s, 0.4 H), 0.34 (s, 3 H), 0.35 (s, 3 H), 0.72 (dd, J = 16.7, 6.6 Hz, 1 H), 0.82 (dd, J = 16.7, 7.1 Hz, 1 H), 1.02 (s, 6 H), 1.07 (s, 6 H), 1.11 (d, J = 6.8 Hz, 12 H), 1.15 (d, J = 5.2 Hz, 2.2 H), 1.21 (d, J = 6.9 Hz, 6 H), 1.23–1.27 (m, 2.2 H), 1.42–1.49 (m, 1 H), 2.43 (dd, J = 13.8, 9.7 Hz, 0.4 H), 2.56 (dd, J = 14.4, 12.1 Hz, 1 H), 2.65 (dd, J = 14.4, 4.4 Hz, 1 H), 2.81 (sept, J = 6.9 Hz, 1.2 H), 2.98 (sept, J = 6.8 Hz, 2 H), 3.10 (sept, J = 6.9 Hz, 0.4 H), 6.88 (s, 2 H), 6.92 (s, 0.3 H), 7.31–7.34 (m, 0.7 H), 7.36–7.38 (m, 3 H), 7.50–7.53 (m, 0.4 H), 7.58–7.60 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –5.08, –4.27, –4.15, –4.01, 21.70, 22.31, 23.76, 24.04, 24.07, 24.41, 24.55, 24.62, 24.83, 24.96, 25.12, 28.39, 28.70, 29.06, 33.90, 37.55, 82.69, 82.77, 113.39, 120.64, 120.71, 127.55, 128.64, 128.73, 129.94, 132.92, 133.66, 134.07, 138.86, 145.67, 146.42, 147.32.

HRMS: m/z [M + Na]$^+$ calcd for $C_{32}H_{51}O_2BNaSi$: 529.36436; found: 529.36395.

[1-Mesityl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fi) and [3-Mesityl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]dimethyl(phenyl)silane (4fi′)
Pale yellow oil; yield: 73.5 mg (0.174 mmol, 58%).

^{1}H NMR ($CDCl_3$): δ = 0.30 (s, 0.2 H), 0.31 (s, 0.2 H), 0.33 (s, 3 H), 0.34 (s, 3 H), 0.68 (dd, J = 16.6, 6.9 Hz, 1 H), 0.81 (dd, J = 16.2, 7.5 Hz, 1 H), 1.05 (s, 6 H), 1.06 (s, 6 H), 1.54–1.60 (m, 1 H), 2.16 (s, 6 H), 2.18 (s, 0.5 H), 2.20 (s, 3 H), 2.22 (s, 0.2 H), 2.51 (dd, J = 14.0, 12.4 Hz, 1 H), 2.63 (dd, J = 14.2, 4.6 Hz, 1 H), 6.74 (s, 2 H), 6.78 (s, 0.2 H), 7.30–7.32 (m, 0.3 H), 7.32–7.35 (m, 3 H), 7.50–7.52 (m, 0.2 H), 7.56–7.58 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.69, –4.08, 19.53, 19.57, 20.44, 20.71, 24.78, 24.87, 24.91, 30.84, 82.71, 127.54, 128.63, 128.70, 128.84, 133.72, 134.12, 134.47, 135.52, 136.95, 138.71.

HRMS: m/z [M + Na]$^+$ calcd for $C_{26}H_{39}O_2BNaSi$: 445.27046; found: 445.27042.

Dimethyl[1-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl](phenyl)silane (4fj)
Pale yellow solid; yield: 93.0 mg (0.216 mmol, 72%); mp 87.9–89.2 °C.

^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 3 H), 0.26 (s, 3 H), 0.82 (dd, J = 16.7, 7.4 Hz, 1 H), 0.94 (dd, J = 16.5, 6.1 Hz, 1 H), 1.06 (s, 6 H), 1.12 (s, 6 H), 1.68–1.74 (m, 1 H), 2.90 (dd, J = 26.5, 16.1 Hz, 1 H), 3.20 (dd, J = 14.0, 5.7 Hz, 1 H), 7.24 (d, J = 7.3 Hz, 1 H), 7.30 (t, J = 7.7 Hz, 1 H), 7.33–7.36 (m, 3 H), 7.37–7.43 (m, 2 H), 7.55 (dd, J = 7.1, 2.6 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 1 H), 7.78 (d, J = 8.3 Hz, 1 H), 7.91 (d, J = 8.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = –4.47, –4.17, 21.49, 24.82, 24.89, 35.97, 82.85, 124.41, 125.12, 125.14, 125.32, 126.48, 127.00, 127.59, 128.50, 128.76, 132.32, 133.95, 134.14, 138.22, 138.65.

HRMS: m/z [M + Na]$^+$ calcd for $C_{27}H_{35}O_2BNaSi$: 453.23916; found: 453.23880.

Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl]silane (4fk)
Pale yellow oil; yield: 72.7 mg (0.21 mmol, 70%).

^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6 H), 0.69 (dd, J = 16.1, 8.7 Hz, 1 H), 0.82 (t, J = 7.0 Hz, 3 H), 0.89 (dd, J = 15.9, 5.4 Hz, 1 H), 1.07–1.13 (m, 1 H), 1.16–1.31 (m, 17 H), 1.43–1.48 (m, 1 H), 7.31–7.36 (m, 3 H), 7.51 (dd, J = 6.3, 2.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.42, –4.04, 14.02, 20.00, 22.98, 24.76, 24.97, 31.36, 32.15, 82.88, 127.49, 128.54, 134.05, 139.17.

HRMS: m/z [M + Na]$^+$ calcd for $C_{20}H_{35}O_2BNaSi$: 369.23916; found: 369.23938.

Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]silane (4fl)
Pale yellow oil; yield: 45.6 mg (0.15 mmol, 50%).

^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 6 H), 0.57 (dd, J = 15.8, 11.4 Hz, 1 H), 0.94 (dd, J = 15.8, 3.9 Hz, 1 H), 0.95 (d, J = 7.4 Hz, 3 H), 1.07–1.16 (m, 1 H), 1.22 (s, 6 H), 1.23 (s, 6 H), 7.31–7.32 (m, 1 H), 7.33 (d, J = 2.6 Hz, 2 H), 7.50 (dd, J = 6.8, 2.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = –5.45, –5.11, 14.60, 16.90, 24.68, 25.04, 82.94, 127.52, 128.66, 134.07, 138.48.

HRMS: m/z [M + Na]$^+$ calcd for $C_{17}H_{29}O_2BNaSi$: 327.19221; found: 327.19223.

[1-Cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]dimethyl(phenyl)silane (4fm)
Pale yellow oil; yield: 87.8 mg (0.255 mmol, 85%).

^{1}H NMR ($CDCl_3$): δ = –0.10 (m, *J* = 4.6 Hz, 1 H), –0.01 (m, 4.6 Hz, 1 H), 0.26 (s, 3 H), 0.27 (s, 3 H), 0.30–0.38 (m, 2 H), 0.59–0.67 (m, 1 H), 0.83 (dd, *J* = 16.2, 8.8 Hz, 1 H), 0.94 (dd, *J* = 16.1, 5.3 Hz, 1 H), 1.10–1.12 (m, 1 H), 1.21 (s, 6 H), 1.21 (s, 6 H), 1.26–1.31 (m, 1 H), 1.36 (td, *J* = 6.3, 13.2 Hz, 1 H), 7.31–7.33 (m, 3 H), 7.52 (dd, *J* = 6.5, 2.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.41, –3.92, 4.83, 5.52, 10.69, 20.92, 24.78, 25.01, 37.72, 82.86, 127.48, 128.54, 134.04, 139.15.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{33}O_2BNaSi$: 367.22351; found: 367.22372.

[7-Bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-yl]dimethyl(phenyl)silane (4fn)
Pale yellow oil; yield: 92.3 mg (0.21 mmol, 70%).

^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6 H), 0.69 (dd, *J* = 16.2, 8.7 Hz, 1 H), 0.90 (dd, *J* = 16.1, 5.5 Hz, 1 H), 1.07–1.12 (m, 1 H), 1.16–1.26 (m, 14 H), 1.28–1.37 (m, 3 H), 1.41–1.47 (m, 1 H), 1.76 (m, *J* = 7.1 Hz, 2 H), 3.33 (t, *J* = 6.9 Hz, 2 H), 7.31–7.34 (m, 3 H), 7.51 (dd, *J* = 6.6, 2.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.60, –3.96, 19.97, 24.77, 24.99, 28.13, 28.40, 32.25, 32.68, 33.99, 82.93, 127.54, 128.63, 134.00, 138.99.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{36}O_2BBrNaSi$: 461.16532; found: 461.16519.

Ethyl 5-(Dimethylphenylsilyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (4fo)
Pale yellow oil; yield: 44.9 mg (0.111 mmol, 37%).

^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6 H), 0.69 (dd, *J* = 16.2, 8.5 Hz, 1 H), 0.90 (dd, *J* = 16.3, 5.3 Hz, 1 H), 1.07–1.13 (m, 1 H), 1.18–1.25 (m, 16 H), 1.42–1.55 (m, 2 H), 1.62–1.72 (m, 1 H), 2.17 (ddd, *J* = 15.2, 8.7, 6.5 Hz, 1 H), 2.23 (ddd, *J* = 15.2, 8.7, 6.5 Hz, 1 H), 4.07 (q, *J* = 6.8 Hz, 2 H), 7.31–7.34 (m, 3 H), 7.5 (dd, *J* = 6.4, 3.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.63, 4.10, 14.23, 19.69, 24.47, 24.78, 24.95, 32.02, 34.61, 60.06, 82.97, 127.57, 128.67, 134.03, 138.76, 173.73.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{37}O_4BNaSi$: 427.24464; found: 427.24432.

2-[3-(2-Bromo-4-methoxyphenyl)-2-(4-methoxyphenyl)propyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4bp)
Pale yellow oil; yield: 147.6 mg (0.32 mmol, 32%).

^{1}H NMR ($CDCl_3$): δ = 1.02 (s, 6 H), 1.05 (s, 6 H), 1.17 (d, *J* = 8.1 Hz, 2 H), 2.87 (dd, *J* = 13.5, 7.4 Hz, 1 H), 2.90 (dd, *J* = 13.4, 7.4 Hz, 2 H), 3.15 (quint, *J* = 7.7 Hz, 1 H), 3.74 (s, 3 H), 3.76 (s, 3 H), 6.66 (dd, *J* = 8.6, 2.7 Hz, 1 H), 6.76 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 2.6 Hz, 1 H), 7.09 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 24.49, 24.76, 40.94, 45.40, 55.22, 55.42, 82.89, 113.07, 113.33, 117.60, 124.90, 128.38, 131.85, 132.14, 138.51, 157.75, 158.15.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{30}O_4BBrNa$: 483.13127; found: 483.13126.

3-(2-Bromo-4-methoxyphenyl)-2-(4-methoxyphenyl)propan-1-ol (8)
Pale yellow oil; yield: 62.0 mg (0.176 mmol, 84%).

^{1}H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 6.3 Hz, 1 H), 2.82–2.90 (m, 1 H), 3.10 (dd, *J* = 14.4, 7.3 Hz, 1 H), 3.13 (dd, *J* = 14.0, 7.1 Hz, 1 H), 3.75 (s, 3 H), 3.76–3.81 (m, 1 H), 3.79 (s, 3 H), 6.67 (dd, *J* = 8.5, 2.7 Hz, 1 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 1 H), 7.07 (d, *J* = 2.7 Hz, 1 H), 7.14 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 38.12, 47.66, 55.21, 55.44, 66.21, 113.29, 114.03, 117.82, 124.70, 129.02, 131.15, 11.56, 133.50, 158.36, 158.44.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{19}O_3BrNa$: 373.04098; found: 373.04126.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000084.

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