Synthesis of 1,1-Organodiboronates via Rh(I)Cl-Catalyzed Sequential Regioselective Hydroboration of 1-Alkynes

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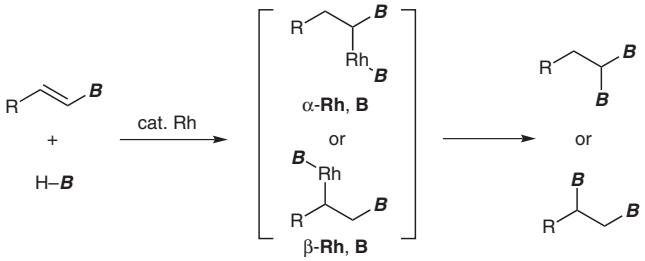
Abstract: A Rh(I)Cl–DPPB-complex-catalyzed sequential hydroboration of aryl alkynes and aliphatic alkynes was achieved. The reaction proceeded with almost perfect regioselectivity to afford 1,1-organodiboronate compounds in moderate to good yield.

Key words: rhodium, hydroborations, alkynes, regioselectivity

1,1-Organodimetallic compounds are interesting synthetic intermediates and provide unique reactivity.[1,2] We focused on the easy access to 1,1-organodiboronates, the borons of which attach to an sp^3 carbon atom, as the new approach to the preparation of 1,1-organodimetallic compounds.[3] The boronate compounds can be readily converted into alcohols, amines, and carboxylic acids, and also used for the formation of C–C bond; thus 1,1-organodiboronates would be fascinating synthetic intermediates for the further functionalization.[4] The precedents reported the formation of multiborylated compounds as a regioisomeric mixture via hydroboration or diboration.[5] Another approach is the oxidative borylation of alkenylboronates affording 1,1-organodiboronate as a side product.[6] Hiyama et al. reported the synthesis of 1,1-organodiborylated cyclopropanes and alkenes from 1,1-diboromo compounds.[4] Here describes the one-step synthesis of 1,1-organodiboronates via Rh(I)Cl-catalyzed sequential and regioselective hydroboration.

In general, the hydroboration of 1-alkynes gives alkenylboronates; the sequential regioselective hydroboration of alkenylboronates using pinacolborane providing 1,1-organodiboronates has never been reported.[7] The conventional reports concerning the hydroboration of C–C multiple bond provides a regioisomeric mixture and reduction product as well as tri- and tetraboronates; thus the control of the regioselectivity and the inhibition of overreaction via oxidative borylation are difficult to achieve. We focused on the Rh-catalyzed hydroboration, which generates Rh–C bond after the insertion of olefinic moiety into Rh–H bond (Scheme 1).

The generation of α-Rh,B intermediate is expected, which is the typical feature of the carbometalation reaction of alkenylboronates.[1] At one hand, the predominant generation of π-benzylic rhodium intermediate (β-Rh,B intermediate) derived from vinylarenes would be another regioselectivity to 1,2-organodiboronates.



Scheme 1 Regioselective Rh-catalyzed hydroboration

The numerous numbers of studies for Rh-catalyzed hydroboration of alkenes provide the efficient synthetic approaches to organoboronate compounds.[8,9] In contrast, there are a few reports concerning on Rh-catalyzed hydroboration of 1-alkynes providing alkenylboronates.[10] We hypothesized the Rh-catalyzed sequential and regioselective hydroboration of 1-alkynes to form 1,1-organodiboronates via the generation of α-Rh,B intermediate. The examination of various reaction conditions realized the regioselective formation of 1,1-organodiboronates. The reaction of **1a** and pinacolborane (HBpin, commercially available, 2.4 equiv)[11] was carried out in the presence of $[RhCl(cod)]_2$ (5 mol% Rh) and ligand (6 mol%) in DCE at room temperature (Scheme 2 and Table 1).

Among the various phosphine ligands, DPPB provided the high catalytic activity to give the desired 1,1-organodiboronate **2a** in 67% yield along with the formation of reduction product, 2-phenethylboronate, as a byproduct (entry 4). The appreciated feature of the present reaction is the almost perfect regioselectivity; the formation of α-Rh,B intermediate surpasses the formation of π-benzylic rhodium intermediate. The reaction in the presence of cationic and basic Rh complexes decreased the yield of product (entries 9 and 10).

Scheme 2 Sequential hydroboration of 1-alkyne

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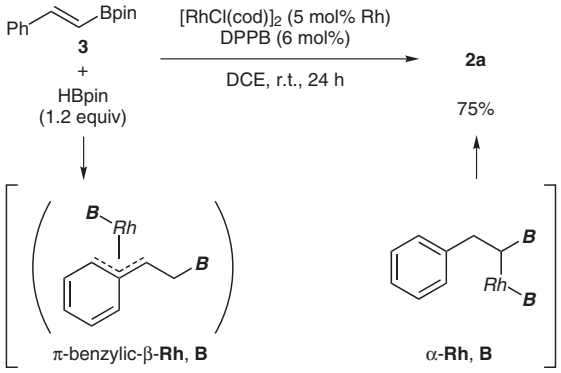
Table 1 Screening of Reaction Conditions from **1a** to **2a**

Entry	Rh complex[a]	Ligand[b]	Time (h)	Yield (%)[c]
1	$[RhCl(cod)]_2$	DPPM[d]	48	11
2	$[RhCl(cod)]_2$	DPPE[e]	24	4
3	$[RhCl(cod)]_2$	DPPP[f]	48	25
4	$[RhCl(cod)]_2$	DPPB[g]	24	67
5	$[RhCl(cod)]_2$	DPPPent[h]	30	21
6	$[RhCl(cod)]_2$	XANTPHOS[i]	24	6
7	$[RhCl(cod)]_2$	Ph_3P[j]	24	21
8	$[RhCl(cod)]_2$	$P(OPh)_3$[j]	48	40
9	$[Rh(cod)_2]BF_4$	DPPB	24	43
10	$[Rh(OH)(cod)]_2$	DPPB	24	53

[a] Amount of Rh used: 5 mol%.
[b] Amount of ligand used: 6 mol%.
[c] The yield was determined with 1,1,2,2-tetrachloroethane by the integration ratio of ^1H NMR analysis.
[d] 1,1-Bis(diphenylphosphino)methane.
[e] 1,2-Bis(diphenylphosphino)ethane.
[f] 1,3-Bis(diphenylphosphino)propane.
[g] 1,4-Bis(diphenylphosphino)butane.
[h] 1,5-Bis(diphenylphosphino)pentane.
[i] 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene.
[j] Amount of ligand used: 12 mol%.

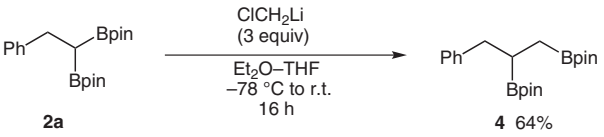
Under the optimum reaction conditions in hand, the sequential hydroboration of terminal alkynes was examined (Table 2). The reaction of phenylacetylene (**1a**) gave the desired product **2a** in 62% isolated yield (entry 1). The reaction using Rh complex (1 mol% Rh) afforded the product **2a** in 58% yield. The use of arylethynes bearing electron-donating group on benzene ring gave the similar results; *p*- and *o*-tolylacetylenes (**1b**,**c**) provided the desired products **2b** and **2c** in 57% and 75% yield, respectively (entries 2 and 3). The reaction of *p*-, *m*-, and *o*-ethynylanisoles (**1d**–**f**) afforded the diboronates **2d**–**f** in moderate yield (entries 4–6). The use of arylethyne bearing halide substituent on benzene ring decreased the yield of product; 4-bromophenylacetylene (**1g**) provided the diborylated compound **2g** in 40% yield (entry 7). The reaction of 1-ethynylnaphthalene (**1h**) gave the product **2h** in 68% yield (entry 8). 4-Ethynylbiphenyl (**1i**) provided the product **2i** in 55% yield (entry 9). The aliphatic alkynes could participate in the reaction. The reaction of **1j** gave the product **2j** in 59% yield (entry 10). Propargyl ether derivative **1k** afforded the product **2k** in 51% yield along with the formation of unidentified byproducts (entry 11). The bulky alkyne, 3,3-dimethylbut-1-yne (**1l**), decreased the yield of product **2l** (entry 12). The reaction of alkenylboronate was carried out (Scheme 3). The hydroboration of **3** with HBpin (1.2 equiv) in the presence of $[RhCl(cod)]_2$ (5 mol% Rh) and DPPB (6 mol%) gave **2a** in 75% yield. Thus, the present reaction from alkynes as substrate is considered to proceed via alkenylboronates. It is notable that the use of alkenylboronate **3** is in favor of



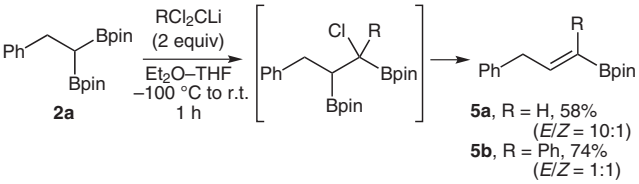
Scheme 3 Rh(I)Cl-catalyzed hydroboration of alkenylboronate

the generation of α-Rh,B intermediate rather than π-benzylic β-Rh,B intermediate.[12]

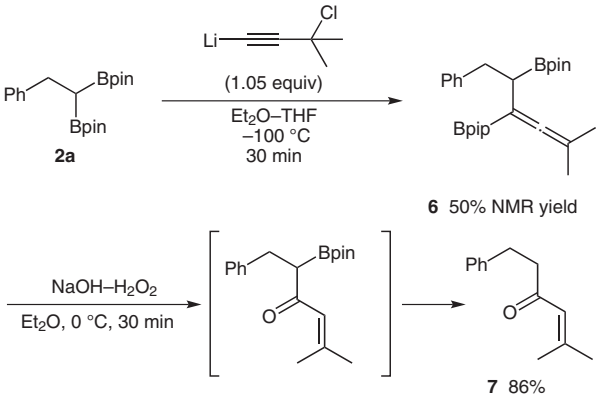
The synthetic applications were examined for the present novel type of 1,1-organodiboronate. The selective homologation reaction enables the synthesis of a wide variety of boronate compounds.[8k] The selective monohomologation of **2a** using chloromethyllithium gave the corresponding product **4** in 64% yield (Scheme 4). The reaction using dichloromethyllithium derivatives afforded the corresponding alkenylboronates **5a** and **5b**, respectively, in good yield (Scheme 5). This is the useful approach to the synthesis of multisubstituted alkenylboronates, which can participate in the Suzuki cross-coupling



Scheme 4 Homologation of **2a** using chloromethyllithium

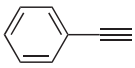
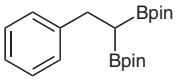
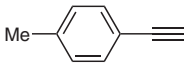
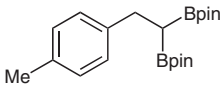
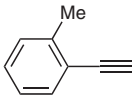
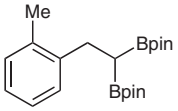
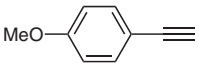
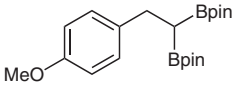
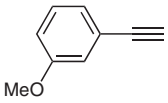
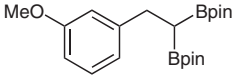
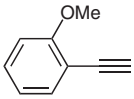
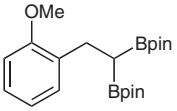
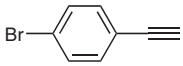
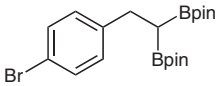
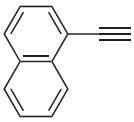
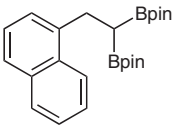
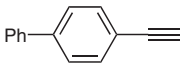
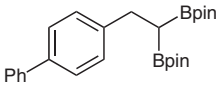
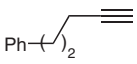
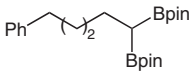
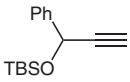
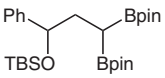
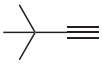
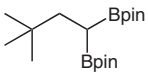


Scheme 5 Homologation of **2a** using dichloromethyllithium derivatives



Scheme 6 Homologation of **2a** for allenylboronate synthesis and sequential oxidation

Table 2 Synthesis of Various 1,1-Organodiboronates[a]

Entry	1-Alkyne		Product		Yield (%)[b]
1	**1a**		**2a**		62, 58[c] (17, 16[c])
2	**1b**		**2b**		57 (24)
3	**1c**		**2c**		75 (16)
4	**1d**		**2d**		61 (23)
5	**1e**		**2e**		63 (19)
6	**1f**		**2f**		64 (18)
7	**1g**		**2g**		40 (24)
8	**1h**		**2h**		68 (14)
9	**1i**		**2i**		55 (20)
10	**1j**		**2j**		59 (12)
11[d]	**1k**		**2k**		51
12[d]	**1l**		**2l**		26

[a] The reaction of alkyne and HBpin (2.4 equiv) was carried out in the presence of $[RhCl(cod)]_2$ (5 mol% Rh) and DPPB (6 mol%) in DCE at r.t. for 24 h.
[b] The isolated yields are described. The yields of the reduction product of alkenylboronate are described in parentheses.
[c] The yield using $[RhCl(cod)]_2$ (1 mol% Rh) and DPPB (1.2 mol%) is described.
[d] Unidentified side products were obtained.

reaction. The reaction using 3-chloro-3-methylbut-1-ynyllithium provided the allenylboronate **6** in moderate yield (Scheme 6).[4d] The allenylboronate **6** bearing an additional boryl group alpha to the C–C double bond was successively oxidized under the typical conditions to give the enone derivative **7**. This result suggested that the predominant oxidation of allenylboronate moiety proceeded to form enone bearing boronate moiety at α-carbon and subsequent isomerization and protonation took place to furnish enone **7** in 86% yield.

In conclusion, we succeeded in the sequential regioselective hydroboration of terminal alkynes for the facile synthesis of 1,1-organodiboronates in the presence of $[RhCl(cod)]_2$ and DPPB. The formation of α-Rh,B intermediate surpasses the formation of β-Rh,B intermediate which is the favorable regioselectivity of the Rh-catalyzed hydroboration of vinylarenes. The demonstration of synthetic utility of 1,1-organodiboronate showed the homologation reaction for the synthesis of 1,2-organodiboronate, di- and trisubstituted alkenylboronates, and allenylboro-

nate. The continuous studies are in progress, and the synthetic applications are in due course in our laboratory.

Typical Procedure of Rh(I)-Catalyzed Sequential Hydroboration

To a mixture of $[RhCl(cod)]_2$ (12.3 mg, 0.025 mmol, 5 mol% Rh), DPPB (25.6 mg, 0.06 mmol, 6 mol%) in DCE (1 mL) were added phenylacetylene (**1a**, 1.0 mmol, 102 mg) and pinacolborane (2.4 mmol, 308 mg, 2.4 equiv) at r.t. The reaction mixture was stirred at r.t. for 24 h and passed through a pad of SiO_2 with Et_2O (50 mL). The crude mixture was concentrated to dryness. The purification by SiO_2 column chromatography (5% EtOAc in hexane as eluent) gave the product **2a** in 62% yield (0.62 mmol) as colorless oil.

2-Phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2a)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 (m, 2 H), 7.14 (m, 2 H), 7.03 (m, 1 H), 3.24 (d, *J* = 8.3 Hz, 2 H), 1.51 (t, *J* = 8.3 Hz, 1 H), 1.04 (s, 24 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 145.1, 128.8, 125.7, 82.9, 32.1, 24.9, 24.7. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.2. IR (neat): 2978, 1454, 1319, 1139, 971, 851 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{20}H_{33}B_2O_4^+$: 359.2559 [M + H]$^+$; found: 359.2567 [M + H]$^+$.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-*p*-tolylethane (2b)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.98 (m, 2 H), 6.70 (m, 2 H), 2.97 (d, *J* = 8.0 Hz, 2 H), 1.84 (s, 3 H), 1.25 (t, *J* = 8.0 Hz, 1 H), 0.77 (s, 24 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 124.1, 134.6, 129.0, 128.7, 82.9, 31.7, 27.7, 24.6, 21.0. ^{11}B NMR (128 MHz, C_6D_6): δ = 33.7. IR (neat): 2978, 1379, 1319, 1140, 970, 854 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{21}H_{34}B_2O_4$: 372.2643; found: 372.2629.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-*o*-tolylethane (2c)

Pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.21 (m, 1 H), 6.77 (m, 3 H), 2.93 (d, *J* = 8.5 Hz, 2 H), 1.95 (s, 3 H), 1.26 (t, *J* = 8.5 Hz, 1 H), 0.78 (s, 24 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 142.9, 136.2, 130.2, 128.7, 125.9, 125.8, 82.9, 29.0, 24.8, 19.5. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.5. IR (neat): 2978, 1464, 1315, 1141, 971, 852 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{21}H_{35}B_2O_4^+$: 373.2716 [M + H]$^+$; found: 373.2733 [M + H]$^+$.

2-*p*-Methoxyphenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2d)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.24 (m, 2 H), 6.77 (m, 2 H), 3.33 (s, 3 H), 3.22 (d, *J* = 8.4 Hz, 2 H), 1.50 (t, *J* = 8.4 Hz, 1 H), 1.07 (s, 12 H), 1.06 (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 158.3, 137.2, 129.6, 113.9, 82.9, 54.8, 31.3, 24.9, 24.8. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.0. IR (neat): 2978, 1463, 1301, 1140, 972, 854 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{21}H_{34}B_2O_5$: 388.2592; found: 388.2552.

2-*m*-Methoxyphenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2e)

Pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.81 (m, 1 H), 6.70 (m, 2 H), 6.41 (m, 1 H), 3.08 (s, 3 H), 2.97 (d, *J* = 8.4 Hz, 2 H), 1.75 (t, *J* = 8.4 Hz, 1 H), 0.79 (s, 12 H), 0.78 (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 160.2, 146.7, 129.3, 121.1, 114.2, 111.6, 82.9, 54.6, 32.3, 24.9, 24.8. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.0. IR (neat): 2978, 1489, 1317, 1140, 972, 850 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{21}H_{34}B_2O_5$: 388.2592; found: 388.2554.

2-*o*-Methoxyphenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2f)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.99 (m, 1 H), 6.54 (m, 1 H), 6.27 (m, 1 H), 5.99 (m, 1 H), 2.91 (d, *J* = 8.0 Hz, 2 H), 2.75 (s, 3 H), 1.28 (t, *J* = 8.0 Hz, 1 H), 0.55 (s, 12 H), 0.54 (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 158.1, 133.2,130.0, 126.9, 120.2, 110.2, 82.8, 54.6, 26.9, 24.9, 24.8. ^{11}B NMR (128 MHz, C_6D_6): δ = 33.8; IR (neat): 2978, 1493, 1317, 1140, 972, 852 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{21}H_{34}B_2O_5$: 388.2592; found: 388.2594.

2-*p*-Bromophenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2g)

Pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.27 (m, 2 H), 6.93 (m, 2 H), 3.03 (d, *J* = 8.4 Hz, 2 H), 1.35 (t, *J* = 8.4 Hz, 1 H), 1.02 (s, 24 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 144.0, 131.3, 130.6, 119.5, 83.0, 31.4, 24.9, 24.7. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.4. IR (neat): 2978, 1486, 1317, 1072, 971, 852 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{20}H_{32}B_2BrO_4^+$: 437.1665 [M + H]$^+$; found: 437.1678 [M + H]$^+$.

2-(Naphthalen-1-yl)-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2h)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.12 (m, 1 H), 7.58 (m, 2 H), 7.47 (m, 1 H), 7.23 (m, 1 H), 7.15 (m, 2 H), 3.63 (d, *J* = 8.0 Hz, 2 H), 1.64 (t, *J* = 8.0 Hz, 1 H), 0.98 (s, 12 H), 0.97 (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 140.9, 134.4, 132.6, 128.8, 126.7, 125.8, 125.6, 125.5, 125.4, 124.5, 83.0, 28.9, 24.9, 24.8. ^{11}B NMR (128 MHz, C_6D_6): δ = 33.8. IR (neat): 2978, 1378, 1323, 1140, 972, 849 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{24}H_{34}B_2O_4$: 408.2643; found: 408.2614.

2-*p*-Biphenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (2i)

Pale yellow solid; mp 87 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.43 (m, 6 H), 7.15 (m, 3 H), 3.29 (d, *J* = 8.3 Hz, 2 H), 1.56 (t, *J* = 8.3 Hz, 1 H), 1.07 (s, 12 H), 1.06 (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 144.3, 141.9, 138.8, 129.2, 128.9, 127.3, 127.1, 127.0, 83.0, 31.8, 24.9, 24.7. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.1. IR (neat): 2977, 1486, 1319, 971, 842 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{26}H_{36}B_2O_4$: 434.2800; found: 434.2795.

5-Phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentane (2j)

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.27 (m, 2 H), 7.14 (m, 3 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 1.60 (m, 4 H), 1.32 (m, 2 H), 1.21 (s, 24 H), 0.72 (t, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 142.9, 128.4, 128.1, 125.4, 82.9, 36.7, 32.1, 31.3, 25.5, 24.8, 24.5. ^{11}B NMR (128 MHz, C_6D_6): δ = 33.9. IR (neat): 2978, 1371, 1315, 1142, 970, 850 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{23}H_{38}B_2O_4$: 400.2956; found: 400.2942.

3-(*tert*-Butyldimethylsiloxy)-3-phenyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane (2k)

Pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.51 (m, 2 H), 7.17 (m, 2 H), 7.04 (m, 1 H), 4.87 (t, *J* = 7.6 Hz, 1 H), 2.47 (m, 1 H), 2.34 (m, 1 H), 1.30 (t, *J* = 7.6 Hz, 1 H), 1.08 (m, 24 H), 0.99 (s, 9 H), 0.19 (s, 3 H), 0.00 (m, 3 H). ^{13}C NMR (100 MHz, C_6D_6): δ = 146.4, 128.3, 127.2, 126.6, 84.84, 84.82, 77.6, 38.1, 26.2, 25.1, 24.9, 24.8, 24.7, 18.5, –4.3, –4.5. ^{11}B NMR (128 MHz, C_6D_6): δ = 34.0. IR (neat): 2978, 1389, 1319, 1092, 970, 849 cm^{-1}. HRMS–FAB (+): *m/z* calcd for $C_{27}H_{47}B_2O_5^+$: 501.3373 [M – 1]$^+$; found: 501.3397 [M – 1]$^+$.

3,3-Dimethyl-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane (2l)

White solid; mp 67 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.53 (d, *J* = 6.8 Hz, 2 H), 1.23 (s, 24 H), 0.84 (s, 9 H), 0.74 (t, *J* = 6.8 Hz, 1

H). ^{13}C NMR (100 MHz, C_6D_6): δ = 82.3, 39.2, 31.5, 29.1, 24.7, 24.6. ^{11}B NMR (128 MHz, C_6D_6): δ = 33.9. IR (neat): 2978, 1389, 1309, 1144, 968, 866 cm^{-1}. ESI-HRMS (+): *m/z* calcd for $C_{18}H_{36}B_2NaO_4^+$: 361.2692 [M + Na]$^+$; found: 361.2686 [M + Na]$^+$.

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