Nickel-Catalyzed Coupling Reactions of Alkyl Electrophiles, Including Unactivated Tertiary Halides, to Generate Carbon–Boron Bonds

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Supporting Information

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I. General Information

The following reagents were purchased and used as received: $NiBr_2$•diglyme (Aldrich), ligand **1** (Aldrich), *i*-Pr_2O (anhydrous; Aldrich), DMA (absolute, over molecular sieves; Aldrich), and KOEt (Strem). The secondary and tertiary alcohols (precursors to the electrophiles) were purchased (Aldrich, TCI, or Alfa Aesar) or were prepared according to literature procedures. pinB–Bpin (bis(pinacolato)diboron; Frontier Scientific) and hexB–Bhex (bis(hexylene glycolato)diboron; Frontier Scientific) were dried under vacuum at r.t.

Unless otherwise noted, reactions were conducted with stirring in oven-dried glassware under an inert atmosphere.

^{1}H and ^{13}C NMR spectra were collected on a Bruker Avance 400 spectrometer or a Bruker Avance 600 spectrometer at r.t. The carbon directly attached to the boron was not detected in the ^{13}C NMR spectra, likely due to quadropolar relaxation. GC analyses were carried out on an Agilent 6890N series system with a DB-1 column (length 30 m, internal diameter 0.25 mm).

II. Preparation of Electrophiles

The following reagents are commercially available: 1-iodo-3-phenylpropane (Aldrich), 1-bromo-3-phenylpropane (Aldrich), 4-chlorobenzyl chloride (Alfa Aesar), *trans,trans*-farnesyl chloride (Aldrich; distilled under reduced pressure before use), 2-bromoadamantane (Alfa Aesar), benzyl 4-bromopiperidine-1-carboxylate (Aldrich), 3-chlorocyclohexene (TCI; distilled under reduced pressure before use), (1-chloroethyl)benzene (TCI), 1-iodoadamantane (Aldrich; purified by flash chromatography before use), and *exo*-2-bromonorbornane (Aldrich).

The following halides were prepared according to literature procedures: (3-iodobutyl)benzene,[1] cholesteryl iodide,[2] (3-bromobutyl)benzene,[3] 4-bromo-*N*,*N*-diphenylhexanamide,[4] (2-bromo-2-methylpropyl)benzene,[5] 1-bromo-1-methylcyclohexane,[6] (3-bromo-3-methylbutyl)benzene,[7] *endo*-2-bromonorbornane (endo:exo = 96:4),[3] and 2-chlorononane.[8]

General Procedure A: Bromination of Secondary Alcohols.[3] The alcohol (neat or a solution in CH_2Cl_2) was added to a solution of Ph_3PBr_2 (1.2 equiv) and imidazole (1.2 equiv) in dry CH_2Cl_2 (0.2 M) at 0 °C. The reaction mixture was allowed to warm to r.t., and it was stirred overnight. Next, the solvent was removed on a rotary evaporator. The residue was diluted with hexanes/Et_2O (4:1), and the resulting solution was filtered and concentrated. The residue was purified by flash column chromatography with 100% hexanes or hexanes/Et_2O, or it was purified by fractional distillation under reduced pressure.

General Procedure B: Iodination of Tertiary Alcohols. $MeSO_3H$ (2.0 equiv) was added dropwise to a solution of NaI (2.0 equiv) and the tertiary alcohol in MeCN (0.2 M in the tertiary alcohol) at 0 °C. The reaction mixture was allowed to warm to r.t., and it was stirred for an additional 30 min. Next, the reaction mixture was diluted with Et_2O, washed (water, saturated $NaHCO_3$, saturated $Na_2S_2O_3$, and brine), dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by fractional distillation under reduced pressure.

General Procedure C: Bromination of Tertiary Alcohols. The alcohol (neat or a solution in a minimal amount of CH_2Cl_2) was added to a solution of LiBr (2.0 equiv) in 48 wt% aqueous HBr at 0 °C. The reaction mixture was allowed to warm to r.t., and it was stirred for 3–12 h. Next, the reaction mixture was diluted with Et_2O, washed (water, saturated $NaHCO_3$, and brine), dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by fractional distillation under reduced pressure.

General Procedure D: Bromination of Tertiary Alcohols. PBr_3 (0.42 equiv) was added dropwise to a solution of the tertiary alcohol and pyridine (0.42 equiv) in anhydrous hexanes (0.5 M in alcohol) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was allowed to warm to r.t., and it was stirred for an additional 3 h. Next, the reaction mixture was diluted with Et_2O, washed (water, saturated $NaHCO_3$, and brine), dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by fractional distillation under reduced pressure.

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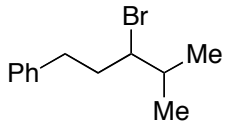
(1) Smith, S.; Fu, G. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 9334–9336.
(2) Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 510–511.
(3) González-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360–5361.
(4) Zultanski, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 15362–15364.
(5) Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232–239.
(6) Cole, S. J.; Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 103–112.
(7) Someya, H.; Yorimitsu, H.; Oshima, K. T*etrahedron* **2010**, *66*, 5993–5999.
(8) Schlenk, W., Jr. *Liebigs Ann. Chem.* **1973**, 1156–1178.

General Procedure E: Iodination of Secondary Alcohols.[9] Iodine chips (1.2 equiv) were added to a solution of Ph_3P (1.2 equiv) and imidazole (1.2 equiv) in dry CH_2Cl_2 (0.2 M) at 0 °C. The alcohol (neat or a solution in CH_2Cl_2) was added dropwise to the reaction mixture at 0 °C. The mixture was allowed to warm to r.t. and stirred overnight. Next, the solvent was removed on a rotary evaporator. The residue was diluted with hexanes/Et_2O (4:1), filtered, concentrated, and purified by flash column chromatography with hexanes.

The yields have not been optimized.



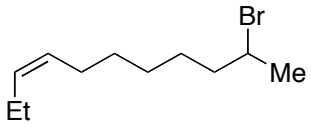
(3-Bromo-4-methylpentyl)benzene [1341946-03-9]. The bromide was prepared according to General Procedure A, using 4-methyl-1-phenylpentan-3-ol.[10] The product was distilled at 55 °C at 0.2 Torr. Colorless liquid (1.67 g, 36%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.95 (dt, J = 10.1, 3.6 Hz, 1H), 2.96-2.89 (m, 1H), 2.69 (ddd, J = 13.7, 9.1, 7.3 Hz, 1H), 2.18-2.08 (m, 1H), 2.01 (dddd, J = 14.6, 9.2, 7.2, 3.5 Hz, 1H), 1.83 (d of septets, J = 6.6, 3.7 Hz, 1H), 0.99 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 141.3, 128.74, 128.66, 126.3, 66.2, 38.5, 34.9, 34.4, 21.1, 18.3.

FT-IR (film) 3086, 3063, 3027, 2965, 2874, 1945, 1872, 1804, 1604, 1585, 1496, 1454, 1387, 1368, 1323, 1239, 1218, 1194, 1158, 1122, 1074, 1030, 973, 924, 906, 852, 793, 749, 699, 657, 618, 580, 517 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{12}H_{17}{}^{79}Br$: 240, found: 240, 242 (M^++2).



(*Z*)-10-Bromoundec-3-ene. *cis*-7-Decenal (5.00 mL, 27.3 mmol) was added dropwise to a solution of MeMgBr (3.01 M in Et_2O; 10.0 mL, 30.0 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 2 h, and then the ice bath was removed and the mixture was stirred for 1 h. Next, the reaction was quenched by the addition of saturated aqueous NH_4Cl (80 mL), and the resulting mixture was extracted with Et_2O (2 x 150 mL). The combined organic layers were washed with brine (80 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was used in the next step without purification.

The bromide was prepared according to General Procedure A, using the unpurified (*Z*)-undec-8-en-2-ol. The desired product was purified by flash chromatography with hexanes. Colorless liquid (2.96 g, 91%).

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(9) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726–14727.

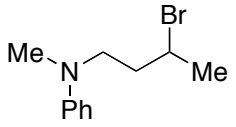
(10) Stymiest, J. L.; Dutheuil, G.; Mahmood, A.; Aggarwal, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 7491–7494.

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.37-5.25 (m, 2H), 4.10 (dqd, *J* = 8.1, 6.6, 5.2 Hz, 1H), 2.04-1.97 (m, 4H), 1.85-1.70 (m, 2H), 1.67 (d, *J* = 6.6 Hz, 3H), 1.52-1.43 (m, 1H), 1.42-1.22 (m, 5H), 0.93 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 131.9, 129.2, 52.1, 41.3, 29.7, 28.8, 27.8, 27.2, 26.7, 20.7, 14.6.

FT-IR (film) 3005, 2964, 2931, 2857, 1457, 1404, 1378, 1304, 1243, 1215, 1161, 1069, 996, 885, 793, 727, 619, 540 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{21}{}^{79}Br$: 232, found: 232, 234 (M^++2).



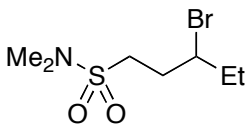
***N*-(3-Bromobutyl)-*N*-methylaniline.** The bromide was prepared according to General Procedure A, using 4-(methyl(phenyl)amino)butan-2-ol.[11] The product was purified by flash chromatography with hexanes/CH_2Cl_2 (10:1 → 5:1). Colorless oil (2.2 g, 53%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.27-7.22 (m, 2H), 6.75-6.69 (m, 3H), 4.20-4.11 (m, 1H), 3.59 (ddd, *J* = 14.8, 8.5, 4.6 Hz, 1H), 3.46 (ddd, *J* = 14.9, 8.2, 6.8 Hz, 1H), 2.96 (s, 3H), 2.13-1.95 (m, 2H), 1.75 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 148.2, 132.1, 114.1, 108.5, 51.4, 49.2, 38.9, 37.9, 27.1.

FT-IR (film) 3093, 3062, 3026, 2966, 2920, 2822, 1918, 1816, 1600, 1574, 1506, 1467, 1450, 1370, 1345, 1293, 1243, 1215, 1193, 1136, 1119, 1100, 1035, 1009, 991, 969, 943, 908, 863, 811, 749, 693, 619, 530 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{11}H_{16}{}^{79}BrN$: 241, found: 241, 243 (M^++2).



3-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide. The bromide was prepared according to General Procedure A, using 3-hydroxy-*N*,*N*-dimethylpentane-1-sulfonamide.[12] The product was purified by flash chromatography with hexanes/Et_2O (2:1 → 1:1). Colorless oil (2.16 g, 82%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 4.07-4.00 (m, 1H), 3.23-3.16 (m, 1H), 3.06-2.99 (m, 1H), 2.87 (s, 6H), 2.39-2.30 (m, 1H), 2.30-2.14 (m, 1H), 1.91-1.83 (m, 2H), 1.04 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (101 MHz; $CDCl_3$): δ 57.3, 46.5, 37.5, 32.3, 32.1, 12.0.

FT-IR (film) 2969, 1459, 1333, 1143, 959, 748, 709 cm^{-1}.

MS (ESI) *m*/*z* $[M+Na]^+$ calcd for $C_7H_{16}BrNNaO_2S$: 281.9961, found: 281.9967.

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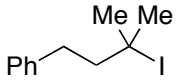
(11) Ibrahim, M. R.; Al-Awadi, N. A.; Ibrahim, Y. A.; Patel, M.; Al-Awadi, S. T*etrahedron* **2007**, *63*, 4768–4772.

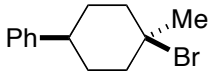
(12) Synthesized according to: Nwaukwa, S. O.; Lee, S.; Keehn, P. M. *Synth. Commun.* **1986**, *16*, 309–329.



(3-Iodo-3-methylbutyl)benzene [183726-98-9]. The iodide was prepared according to General Procedure B, using 2-methyl-4-phenylbutan-2-ol. The product was distilled at 60 °C at 0.08 Torr. Pale-orange liquid (3.5 g, 45%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.23-7.17 (m, 3H), 2.86-2.82 (m, 2H), 1.99 (s, 6H), 1.93-1.89 (m, 2H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 141.6, 128.70, 128.69, 126.2, 52.6, 51.6, 38.3, 35.4.

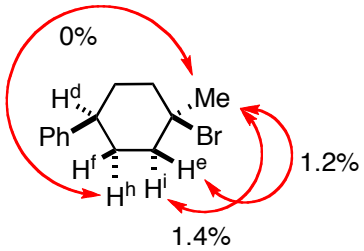


((1*s*,4*s*)-4-Bromo-4-methylcyclohexyl)benzene (cis). The bromide was prepared according to General Procedure C, using 1-methyl-4-phenylcyclohexanol (trans:cis = 45:55).[13] The product was purified by recrystallization from hexanes. White solid (5.25 g, 98%). Diastereomer ratio: >20:1.[14]

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.32-7.24 (m, 4H), 7.21-7.17 (m, 1H), 2.47 (tt, J = 12.4, 3.7 Hz, 1H^d), 2.24-2.18 (m, 2H, H^e), 2.09-1.99 (m, 2H, H^f), 1.89 (s, 3H), 1.83-1.77 (m, 2H, H^h), 1.55 (ddd, J = 14.6, 12.6, 3.8 Hz, 2H, H^i).

^{13}C NMR (101 MHz; $CDCl_3$): δ 146.7, 128.4, 127.0, 126.2, 70.8, 43.5, 43.1, 36.0, 30.9.

NOE (600 MHz, $CDCl_3$): Irradiation at s 1.89 (Me): 1.2% enhancement at H^e (2.3% for 2H), 1.4% enhancement at H^i (2.8% for 2H).

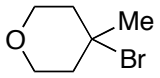


FT-IR (film) 3081, 3057, 3028, 2974, 2941, 2917, 2864, 2834, 1600, 1493, 1444, 1435, 1378, 1327, 1301, 1282, 1229, 1198, 1182, 1129, 1115, 1021, 1006, 965, 921, 900, 881, 816, 757, 701, 534, 494 cm^{-1}.

MS (EI) m/z (M$^+$) calcd for $C_{13}H_{17}{}^{79}Br$: 252, found: 252, 254 (M$^+$+2).

(13) Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 908–910.

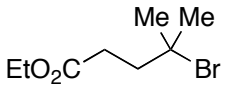
(14) For the preparation of the related compound in which there is a *t*-Bu substituent in place of the Ph substituent, see: (a) Damm, W.; Giese, B.; Hartung, J.; Hasskerl, T.; Houk, K. N.; Hüter, O.; Zipse, H. *J. Am. Chem. Soc.* **1992**, *114*, 4067–4079. (b) Pasto, D. J.; Gontarz, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6902–6908.



4-Bromo-4-methyltetrahydro-2*H*-pyran [66299-88-5]. The bromide was prepared according to General Procedure C, using 4-methyltetrahydro-2*H*-pyran-4-ol.[15] The product was distilled at 36 °C at 6 Torr. Colorless liquid (2.74 g, 71%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 3.84-3.74 (m, 4H), 1.97-1.91 (m, 2H), 1.84 (s, 3H), 1.75-1.68 (m, 2H).

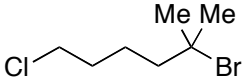
^{13}C NMR (101 MHz; $CDCl_3$): δ 66.7, 64.9, 42.3, 35.4.



Ethyl 4-bromo-4-methylpentanoate [343863-66-1]. The bromide was prepared according to General Procedure D, in the absence of pyridine, using ethyl 4-hydroxy-4-methylpentanoate.[16] The product was distilled at 35 °C at 0.25 Torr. Colorless liquid (0.58 g, 16%). The bromide should be used in the borylation reaction immediately after the distillation.

^{1}H NMR (400 MHz; $CDCl_3$): δ 4.11 (q, J = 7.1 Hz, 2H), 2.57-2.53 (m, 2H), 2.10-2.06 (m, 2H), 1.73 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 173.3, 66.4, 60.8, 42.0, 34.4, 31.9, 14.4.



5-Bromo-1-chloro-5-methylhexane. The bromide was prepared according to General Procedure D, using 6-chloro-2-methylhexan-2-ol.[17] The product was distilled at 34 °C at 0.3 Torr. Colorless liquid (4.86 g, 62%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 3.59 (t, J = 6.6 Hz, 2H), 1.87-1.80 (m, 4H), 1.79 (s, 6H), 1.74-1.66 (m, 2H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 67.7, 46.7, 44.8, 34.2, 32.5, 23.8.

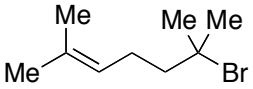
FT-IR (film) 2986, 2956, 2870, 2840, 1453, 1387, 1370, 1309, 1288, 1264, 1231, 1209, 1146, 1106, 1068, 1008, 987, 933, 885, 812, 742, 653, 601, 526, 499 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_7H_{14}{}^{79}BrCl$: 212, found: 161 (M^+–CH_3–HCl), 163 (M^++2–CH_3–HCl).

(15) Booth, H.; Khedhair, K. A.; Readshaw, S. A. T*etrahedron* **1987**, *43*, 4699–4723.

(16) Reetz, M. T.; Steinbach, R.; Westermann, J.; Peter, R. *Angew. Chem., Int. Ed.* **1980**, *19*, 1011–1012.

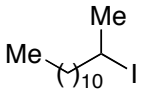
(17) Gebert, U.; Okyayuz-Baklouti, I.; Thorwart, W. Tertiary Hydroxyalkylxanthines, Medicaments Containing Them and Their Use. U.S. Patent 4,833,146, May 23, 1989.



6-Bromo-2,6-dimethylhept-2-ene [855900-58-2]. The bromide was prepared according to General Procedure D, using 2,6-dimethylhept-5-en-2-ol.[18] The product was distilled at 31 °C at 0.3 Torr. Colorless liquid (4.65 g, 62%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.12 (tdt, *J* = 7.2, 2.8, 1.4 Hz, 1H), 2.23-2.17 (m, 2H), 1.82-1.78 (m, 2H), 1.77 (s, 6H), 1.69 (d, *J* = 1.1 Hz, 3H), 1.63 (d, *J* = 0.6 Hz, 3H).

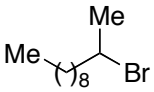
^{13}C NMR (101 MHz; $CDCl_3$): δ 132.3, 123.3, 68.2, 47.5, 34.2, 25.7, 25.2, 17.7.



2-Iodotridecane [64275-39-4]. The iodide was prepared according to General Procedure E, using 2-tridecanol. The product was purified by flash chromatography with hexanes. Colorless liquid (3.27 g, 85%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 4.16 (dqd, *J* = 8.4, 6.8, 5.2 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H), 1.81 (dddd, *J* = 14.2, 9.7, 8.6, 4.6 Hz, 1H), 1.62-1.53 (m, 1H), 1.50-1.39 (m, 1H), 1.37-1.23 (m, 17H), 0.85 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 43.2, 32.1, 31.1, 29.9, 29.83, 29.78, 29.7, 29.6, 29.1, 29.0, 22.9, 14.3.



2-Bromoundecane [39563-54-7]. The bromide was prepared according to General Procedure A, using 2-undecanol. The product was purified by flash chromatography with hexanes. Colorless liquid (3.89 g, 86%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 4.10 (dqd, *J* = 8.0, 6.6, 5.3 Hz, 1H), 1.85-1.69 (m, 2H), 1.67 (d, *J* = 6.7 Hz, 3H), 1.52-1.42 (m, 1H), 1.41-1.34 (m, 1H), 1.29-1.24 (m, 12H), 0.87-0.83 (m, 3H).

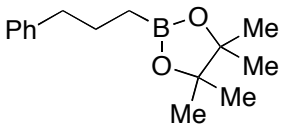
^{13}C NMR (101 MHz; $CDCl_3$): δ 52.2, 41.4, 32.1, 29.73, 29.69, 29.5, 29.2, 28.0, 26.7, 22.9, 14.3.

III. Nickel-Catalyzed Borylations of Primary and Secondary Alkyl Halides

General Procedure: KOEt (77 mg, 0.91 mmol, 1.3 equiv), pinB–Bpin (249 mg, 0.98 mmol, 1.4 equiv), and *i*-Pr_2O (3.5 mL) were added to a 4-mL vial in a nitrogen-filled glovebox (for a glovebox-free procedure, see Section IV). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1 h. The following materials were added in turn to a second 4-mL vial: $NiBr_2$•diglyme (12.3 mg, 0.035 mmol, 0.050 equiv), ligand **1** (13.9 mg,

(18) Shenoy, S. R.; Crisóstomo, F. R. P.; Iwasawa, T.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2008**, *130*, 5658–5659.

0.046 mmol, 0.066 equiv), and DMA (1.0 mL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1–2 h (or until the solution became almost or completely homogeneous). This solution was then transferred by syringe to a 20-mL vial, and *i*-Pr_2O (4.0 mL) was added. After stirring for 5 min, the electrophile (0.70 mmol) was added. Next, the white slurry of the activated diboron reagent was added within a 1-min period, followed by an *i*-Pr_2O rinsing (0.5 mL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at r.t. for 1–7 h, until judged complete by GC analysis. Then, it was filtered through a short pad of silica gel, eluting with Et_2O (25 mL). The solvents were removed in vacuo, and the residue was purified by flash chromatography (if the products are exposed to silica gel for an extended period of time or left unpurified for >12 h, a lower yield is observed).

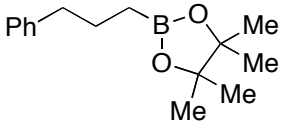


4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane [329685-40-7][19] (Table 1, Entry 1). The title compound was prepared according to the General Procedure, using 1-iodo-3-phenylpropane (172 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

First run: 123 mg (71%). Second run: 126 mg (73%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.16-7.12 (m, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.75-1.67 (m, 2H), 1.22 (s, 12H), 0.81 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 142.9, 128.8, 128.4, 125.8, 83.1, 38.8, 26.3, 25.0.



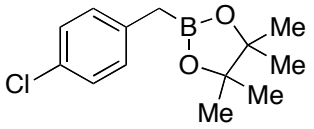
4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane [329685-40-7][19] (Table 1, Entry 2). The title compound was prepared according to the General Procedure, using 1-bromo-3-phenylpropane (139 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

First run: 122 mg (71%). Second run: 121 mg (70%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.16-7.12 (m, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.76-1.68 (m, 2H), 1.22 (s, 12H), 0.81 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 142.9, 128.8, 128.4, 125.8, 83.1, 38.8, 26.3, 25.0.

(19) (a) Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. T*etrahedron* **2004**, *60*, 10695–10700. (b) Caballero, A.; Sabo-Etienne, S. *Organometallics* **2007**, *26*, 1191–1195. (c) Lata, C. J.; Crudden, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 131–137.

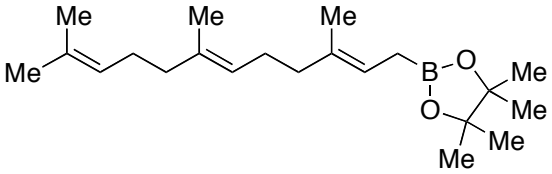


2-(4-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [517920-59-1][20] (Table 1, Entry 3). The title compound was prepared according to the General Procedure, using 4-chlorobenzyl chloride (113 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (20:1). White solid.

First run: 109 mg (61%, 75% calibrated GC). Second run: 106 mg (60%, 75% calibrated GC).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.17 (d, J = 8.4 Hz, 2H), 7.09-7.07 (m, 2H), 2.22 (s, 2H), 1.20 (s, 12H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 137.3, 130.8, 130.5, 128.5, 83.7, 24.9.



4,4,5,5-Tetramethyl-2-((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl)-1,3,2-dioxaborolane [1268820-35-4][21] (Table 1, Entry 4). The title compound was prepared according to the General Procedure, using *trans*,*trans*-farnesyl chloride (169 mg, 0.70 mmol). The reaction was complete after 4 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid.

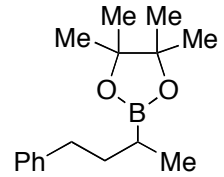
First run: 155 mg (67%, 79% calibrated GC). Second run: 154 mg (66%, 78% calibrated GC).

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.24-5.20 (m, 1H), 5.10-5.03 (m, 2H), 2.06-1.91 (m, 8H), 1.64 (d, J = 1.0 Hz, 3H), 1.56 (s, 11H), 1.21 (s, 12H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 135.4, 134.9, 131.4, 124.62, 124.58, 118.7, 83.2, 39.97, 39.94, 26.99, 26.97, 25.9, 24.9, 17.9, 16.17, 16.12.

(20) (a) Pintaric, C.; Olivero, S.; Gimbert, Y.; Chavant, P. Y.; Duñach, E. *J. Am. Chem. Soc.* **2010**, *132*, 11825–11827. (b) Ishiyama, T.; Oohashi, Z.; Ahiko, T.-a.; Miyaura, N. C*hem. Lett.* **2002**, 780–781. (c) Li, H.; Wang, L.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2943–2946.

(21) Fujiwara, Y.; Domingo, V.; Seiple, I. B.; Gianatassio, R.; Del Bel, M.; Baran, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 3292–3295.

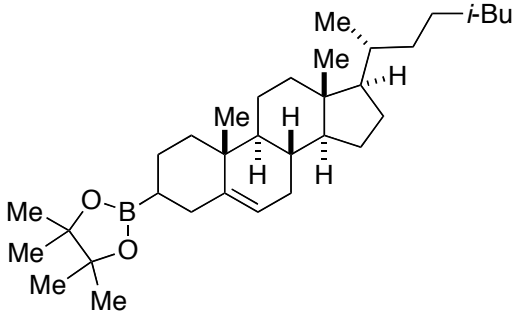


4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane [1257661-35-0][22] (Table 2, Entry 1). The title compound was prepared according to the General Procedure, using (3-iodobutyl)benzene (182 mg, 0.70 mmol). The reaction was complete after 1.5 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

First run: 143 mg (79%). Second run: 134 mg (74%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.27-7.23 (m, 2H), 7.18-7.12 (m, 3H), 2.66-2.55 (m, 2H), 1.82-1.73 (m, 1H), 1.62-1.53 (m, 1H), 1.23 (s, 12H), 1.10-1.03 (m, 1H), 1.02-1.00 (m, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.3, 128.6, 128.4, 125.7, 83.1, 35.54, 35.52, 25.02, 24.97, 15.6.



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cholest-5-ene (Table 2, Entry 2). The title compound was prepared according to the General Procedure, using cholesteryl iodide (348 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (40:1). White solid. Diastereoselectivity: 3:1 (3β:3α); assigned by comparison of the ^{1}H NMR resonances of the 3-hydroxy compound, obtained after oxidation using $NaBO_3$/THF/H_2O, with literature data.[23]

First run: 300 mg (86%). Second run: 301 mg (86%).

^{1}H NMR (400 MHz; $CDCl_3$): δ (major+minor) 5.31-5.22 (m, 1H), 2.40-2.12 (m, 1H), 2.02-1.68 (m, 5H), 1.62-1.23 (m, 12H), 1.20-1.16 (m, 12H), 1.12-0.93 (m, 13H), 0.88 (d, J = 6.6 Hz, 4H), 0.83 (dd, J = 6.6, 1.8 Hz, 6H), 0.64 (s, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ (major+minor) 144.0, 142.8, 120.0, 118.7, 83.01, 83.00, 57.08, 57.06, 56.4, 51.4, 50.8, 42.5, 41.1, 40.08, 40.06, 39.7, 39.1, 37.5, 36.4, 36.01, 35.98, 34.4, 34.0, 32.3, 32.1, 32.04, 32.02, 28.5, 28.2, 25.2, 24.96, 24.94, 24.8, 24.5, 24.3, 24.05, 23.98, 23.7, 23.03, 23.01, 22.8, 20.99, 20.95, 19.7, 19.6, 18.9, 12.1.

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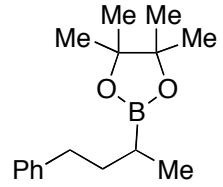
(22) (a) Larouche-Gauthier, R.; Fletcher, C. J.; Couto, I.; Aggarwal, V. K. *Chem. Commun.* **2011**, *47*, 12592–12594. (b) Larouche-Gauthier, R.; Elford, T. G.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2011**, *133*, 16794–16797.

(23) Lee, E.; Lee, Y. R.; Moon, B.; Kwon, O.; Shim, M. S.; Yun, J. S. *J. Org. Chem.* **1994**, *59*, 1444–1456.

FT-IR (film) 2934, 2868, 1467, 1412, 1384, 1313, 1267, 1234, 1214, 1146, 1110, 1026, 970, 909, 856, 799, 743 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{33}H_{57}BO_2$: 496, found: 496.

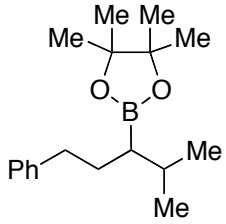


4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane [1257661-35-0][22] (Table 2, Entry 3). The title compound was prepared according to the General Procedure, using (3-bromobutyl)benzene (149 mg, 0.70 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

First run: 157 mg (86%). Second run: 159 mg (87%).

^1H NMR (400 MHz; $CDCl_3$): δ 7.26-7.21 (m, 2H), 7.18-7.11 (m, 3H), 2.66-2.54 (m, 2H), 1.81-1.72 (m, 1H), 1.61-1.52 (m, 1H), 1.23 (s, 12H), 1.09-1.02 (m, 1H), 1.00 (d, J = 6.3 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.3, 128.6, 128.4, 125.7, 83.1, 35.53, 35.51, 25.01, 24.96, 15.6.



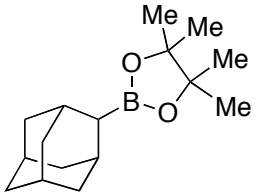
4,4,5,5-Tetramethyl-2-(4-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane [1201898-72-7][24] (Table 2, Entry 4). The title compound was prepared according to the General Procedure, using (3-bromo-4-methylpentyl)benzene (169 mg, 0.70 mmol). The reaction was complete after 4 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 30:1). Colorless liquid.

First run: 118 mg (58%). Second run: 121 mg (60%).

^1H NMR (400 MHz; $CDCl_3$): δ 7.27-7.22 (m, 2H), 7.18-7.12 (m, 3H), 2.62 (ddd, J = 13.5, 10.9, 5.2 Hz, 1H), 2.49 (ddd, J = 13.5, 10.6, 6.3 Hz, 1H), 1.79-1.60 (m, 3H), 1.26 (s, 12H), 0.93-0.87 (m, 7H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.4, 128.6, 128.4, 125.7, 83.1, 36.2, 31.6, 29.8, 25.3, 25.1, 22.5, 21.9.

(24) Bagutski, V.; Ros, A.; Aggarwal, V. K. T*etrahedron* **2009**, *65*, 9956–9960.



2-Adamantan-2-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 5). The title compound was prepared according to the General Procedure, using 2-bromoadamantane (151 mg, 0.70 mmol). The reaction was complete after 7 h. Solvent used for chromatography: hexanes/Et_2O (40:1). White solid.

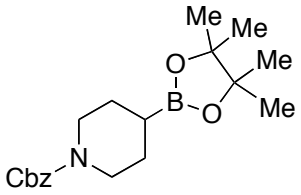
First run: 120 mg (65%, 70% calibrated GC). Second run: 121 mg (66%, 69% calibrated GC).

^{1}H NMR (400 MHz; $CDCl_3$): δ 2.02 (br d, J = 1.2 Hz, 2H), 1.85-1.64 (m, 12H), 1.33 (br s, 1H), 1.22 (s, 12H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.9, 39.5, 37.9, 36.5, 29.5, 28.4, 28.3, 25.0.

FT-IR (film) 2977, 2902, 2846, 2648, 1450, 1407, 1380, 1364, 1351, 1306, 1287, 1272, 1214, 1166, 1145, 1111, 1098, 1057, 1044, 980, 963, 876, 850, 806, 739, 669, 639, 556 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{16}H_{27}BO_2$: 262, found: 262.



Benzyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (Table 2, Entry 6). The title compound was prepared according to the General Procedure, using benzyl 4-bromopiperidine-1-carboxylate (209 mg, 0.70 mmol). The reaction was complete after 6 h. Solvent used for chromatography: hexanes/Et_2O (5:1 → 3:1). The product was washed with a 1 M solution of Na_2CO_3 to remove traces of excess pinB–Bpin. White solid.

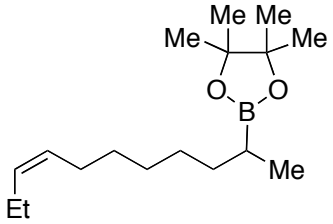
First run: 187 mg (77%). Second run: 199 mg (82%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35-7.30 (m, 4H), 7.30-7.24 (m, 1H), 5.08 (s, 2H), 3.85-3.79 (m, 2H), 3.01-2.96 (m, 2H), 1.64-1.55 (m, 2H), 1.55-1.42 (m, 2H), 1.20 (s, 12H), 1.10 (tt, J = 10.4, 3.9 Hz, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 155.5, 137.3, 128.6, 128.02, 127.96, 83.4, 67.0, 45.3, 27.1 (broad, low intensity), 25.0.

FT-IR (film) 2978, 2935, 2853, 1701, 1498, 1469, 1431, 1381, 1335, 1276, 1263, 1241, 1180, 1145, 1101, 1067, 1022, 968, 950, 912, 852, 764, 738, 698, 670, 603, 554 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{19}H_{28}BNO_4$: 345, found: 345.



(*Z*)-4,4,5,5-Tetramethyl-2-(undec-8-en-2-yl)-1,3,2-dioxaborolane (Table 2, Entry 7). The title compound was prepared according to the General Procedure, using (*Z*)-10-bromoundec-3-ene (97:3 *Z*:*E*) (163 mg, 0.70 mmol). The reaction was complete after 2.5 h. Solvent used for chromatography: hexanes/Et_2O (40:1). Colorless liquid. 95:5 *Z*:*E*.

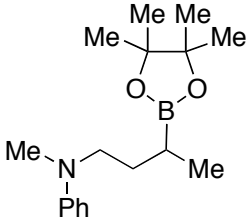
First run: 166 mg (85%). Second run: 164 mg (83%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.34-5.25 (m, 2H), 2.03-1.92 (m, 4H), 1.44-1.36 (m, 1H), 1.31-1.23 (m, 7H), 1.20 (s, 12H), 0.99-0.89 (m, 7H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 131.6, 129.6, 82.9, 33.4, 30.0, 29.7, 29.0, 27.3, 24.94, 24.91, 20.7, 15.7, 14.6.

FT-IR (film) 2977, 2927, 2855, 1654, 1464, 1405, 1387, 1371, 1315, 1274, 1239, 1215, 1146, 1112, 1069, 1005, 968, 861, 794, 688, 670, 579, 521 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{17}H_{33}BO_2$: 280, found: 280.



***N*-Methyl-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)aniline (Table 2, Entry 8).** The title compound was prepared according to the General Procedure, using *N*-(3-bromobutyl)-*N*-methylaniline (170 mg, 0.70 mmol). The reaction was complete after 4 h. Solvent used for chromatography: hexanes/Et_2O (20:1 → 10:1). Colorless oil.

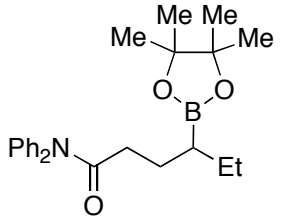
First run: 140 mg (69%). Second run: 138 mg (68%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.22-7.16 (m, 2H), 6.72 (dt, *J* = 9.0, 1.6 Hz, 2H), 6.64 (tt, *J* = 7.2, 0.9 Hz, 1H), 3.36-3.23 (m, 2H), 2.89 (s, 3H), 1.74-1.66 (m, 1H), 1.58-1.50 (m, 1H), 1.23 (s, 12H), 1.04-0.97 (m, 4H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 149.6, 129.2, 115.9, 112.3, 83.2, 52.6, 38.3, 30.0, 25.05, 24.99, 15.9.

FT-IR (film) 3094, 3061, 3026, 2977, 2871, 1600, 1575, 1508, 1464, 1371, 1319, 1235, 1215, 1144, 1113, 1035, 990, 967, 862, 837, 747, 692, 671, 579, 517 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{17}H_{28}BNO_2$: 289, found: 289.



***N,N*-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (Table 2, Entry 9).** The title compound was prepared according to the General Procedure, using 4-bromo-*N,N*-diphenylhexanamide (242 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for the first chromatography: hexanes/Et_2O (2:1); solvent used for the second chromatography: CH_2Cl_2/Et_2O (15:1). White solid.

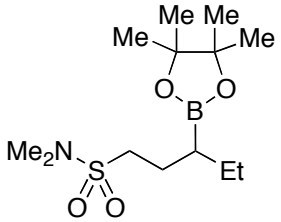
First run: 173 mg (63%). Second run: 177 mg (64%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.47-7.08 (br m, 10H), 2.37-2.20 (m, 2H), 1.86-1.69 (m, 2H), 1.45-1.29 (m, 2H), 1.14 (d, J = 2.4 Hz, 12H), 0.90-0.82 (m, 4H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 173.5, 143.3, 126.6-129.3 (br; two resonances), 83.1, 35.3, 27.1, 24.99, 24.94, 24.4, 13.7.

FT-IR (film) 3063, 2976, 2930, 2871, 1676, 1594, 1493, 1453, 1372, 1315, 1269, 1215, 1144, 1111, 1075, 1031, 1005, 966, 901, 855, 757, 702, 622, 579, 521 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{24}H_{32}BNO_3$: 393, found: 393.



***N,N*-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentane-1-sulfonamide (Table 2, Entry 10).** The title compound was prepared according to the General Procedure, using 3-bromo-*N,N*-dimethylpentane-1-sulfonamide (181 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for the first chromatography: hexanes/Et_2O (2:1); solvent used for the second chromatography: CH_2Cl_2/Et_2O (100:0 → 15:1). Colorless oil.

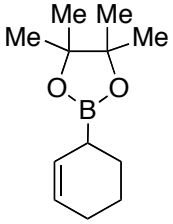
First run: 149 mg (70%). Second run: 148 mg (69%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 3.03-2.87 (m, 2H), 2.84 (s, 6H), 1.88-1.74 (m, 2H), 1.41 (m, 2H), 1.20 (s, 12H), 0.95 (ddd, J = 14.1, 7.8, 5.9 Hz, 1H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 83.5, 48.3, 37.7, 25.06, 24.96, 24.2, 23.9, 13.4.

FT-IR (film) 2976, 2945, 2875, 1462, 1389, 1335, 1270, 1214, 1145, 1057, 963, 894, 854, 793, 747, 709, 670, 558, 498, 484 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{13}H_{28}BNO_4S$: 305, found: 305.

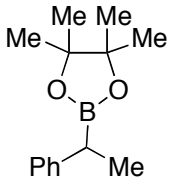


2-(Cyclohex-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [167773-14-0][25] (Table 2, Entry 11). The title compound was prepared according to the General Procedure, using 3-chlorocyclohexene (82 mg, 0.70 mmol). The reaction was complete after 4 h. Due to the volatility of the product, the DMA was not evaporated from the crude reaction mixture. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid.

First run: 86 mg (59%). Second run: 89 mg (61%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.71-5.60 (m, 2H), 2.07-1.93 (m, 2H), 1.77-1.52 (m, 5H), 1.21 (s, 12H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 127.8, 126.2, 83.3, 25.2, 25.0, 24.8, 24.3, 22.7.



4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane [174090-36-9][20a,26] (Table 2, Entry 12). The title compound was prepared according to the General Procedure for tertiary alkyl halides (see below), using (1-chloroethyl)benzene (98 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

First run: 120 mg (74%). Second run: 118 mg (73%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.19 (m, 4H), 7.11 (tt, J = 7.0, 1.7 Hz, 1H), 2.42 (q, J = 7.5 Hz, 1H), 1.31 (d, J = 7.5 Hz, 3H), 1.19 (s, 6H), 1.18 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 145.2, 128.5, 128.0, 125.3, 83.5, 24.83, 24.79, 17.3.

IV. Nickel-Catalyzed Borylations of Tertiary Alkyl Halides

General Procedure: KOEt (82 mg, 0.98 mmol, 1.4 equiv), pinB–Bpin (267 mg, 1.05 mmol, 1.5 equiv), and *i*-Pr_2O (3.5 mL) were added to a 4-mL vial in a nitrogen-filled glovebox (for a

(25) (a) Yang, C.-T.; Zhang, Z.-Q.; Tajuddin, H.; Wu, C.-C.; Liang, J.; Liu, J.-H.; Fu, Y.; Czyzewska, M.; Steel, P. G.; Marder, T. B.; Liu, L. *Angew. Chem., Int. Ed.* **2012**, *51*, 528–532. (b) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915–12917. (c) Dutheuil, G.; Selander, N.; Szabó, K. J.; Aggarwal, V. K. *Synthesis* **2008**, 2293–2297. (d) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034–16035. (e) Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534–2535.

(26) Noh, D.; Chea, H.; Ju, J.; Yun, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6062–6064.

glovebox-free procedure, see below). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1 h. The following materials were added in turn to a second 4-mL vial: $NiBr_2$•diglyme (24.7 mg, 0.070 mmol, 0.10 equiv), ligand **1** (27.4 mg, 0.091 mmol, 0.13 equiv), and DMA (1.0 mL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1–2 h (or until the solution became almost or completely homogeneous). This solution was then transferred by syringe to a 20-mL vial, and *i*-Pr_2O (12.0 mL) was added. After stirring for 5 min, the electrophile (0.70 mmol) was added. Next, the white slurry of the activated diboron reagent was added within a 1-min period, followed by an *i*-Pr_2O rinsing (1.0 mL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at r.t. for 1–6 h, until judged complete by GC analysis. Then, it was filtered through a short pad of silica gel, eluting with Et_2O (25 mL). The solvents were removed in vacuo, and the residue was purified by flash chromatography (if the products are exposed to silica gel for an extended period of time or left unpurified for >12 h, a lower yield is observed).

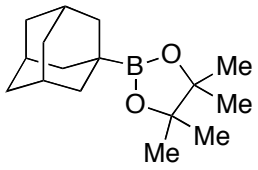
Glovebox-free procedure A (using KOEt): All glassware was dried in a vacuum oven and then cooled to r.t. under an atmosphere of nitrogen. Under a flow of argon, pinB–Bpin (267 mg, 1.05 mmol, 1.5 equiv) and KOEt (82 mg, 0.98 mmol, 1.4 equiv) were added quickly to a 4-mL vial, and the vial was sealed with a teflon-lined septum cap. The vial was evacuated and backfilled with nitrogen three times, and then *i*-Pr_2O (3.5 mL) was added via syringe. The resulting mixture was stirred vigorously at r.t. for 1 h under an atmosphere of nitrogen. In the air, the following materials were added in turn to a second 4-mL vial: $NiBr_2$•diglyme (24.7 mg, 0.070 mmol, 0.10 equiv) and ligand **1** (27.4 mg, 0.091 mmol, 0.13 equiv). The vial was sealed with a teflon-lined septum cap, and then the vial was evacuated and backfilled with nitrogen three times. Next, DMA (1.0 mL) was added via syringe. The resulting mixture was stirred vigorously at r.t. for 1–2 h (or until the solution became almost or completely homogeneous). A 20-mL vial, sealed with a teflon-lined septum cap, was evacuated and backfilled with nitrogen three times, and then *i*-Pr_2O (12.0 mL) was added via syringe. The solution of nickel/ligand in DMA was transferred by syringe to the 20-mL vial. The solution was stirred for 5 min, and then the electrophile (0.70 mmol) was added. Next, the white slurry of the activated diboron reagent was added via syringe within a 1-min period to the 20-mL vial, followed by an *i*-Pr_2O rinsing (1.0 mL). The reaction mixture was stirred at r.t. for 1–6 h under an atmosphere of nitrogen, until judged complete by GC analysis. Then, it was filtered through a short pad of silica gel, eluting with Et_2O (25 mL). The solvents were removed in vacuo, and the residue was purified by flash chromatography (if the products are exposed to silica gel for an extended period of time or left unpurified for >12 h, a lower yield is observed).

When employed for the borylation illustrated in Entry 6 of Table 3 (reaction time: 2 h), the desired product was isolated in 72% yield (130 mg).

Glovebox-free procedure B (using KO*t*-Bu and EtOH): All glassware was dried in a vacuum oven and then cooled to r.t. under an atmosphere of nitrogen. In the air, pinB–Bpin (267 mg, 1.05 mmol, 1.5 equiv) was added to a 4-mL vial, and the vial was sealed with a teflon-lined septum cap. The vial was evacuated and backfilled with nitrogen three times, and then *i*-Pr_2O (2.5 mL) was added via syringe. In the air, KO*t*-Bu (110 mg, 0.98 mmol, 1.4 equiv) was added to a second 4-mL vial, and the vial was sealed with a teflon-lined septum cap. The vial was evacuated and backfilled with nitrogen three times, and then *i*-Pr_2O (1.0 mL) and

anhydrous EtOH (57 μL, 0.98 mmol, 1.4 equiv) were added via syringe. The resulting mixture was stirred vigorously at r.t. for 20 min under an atmosphere of nitrogen, and then the solution of pinB–Bpin was added via cannula. The resulting mixture was stirred vigorously at r.t. for 1 h under an atmosphere of nitrogen. In the air, the following materials were added in turn to a third 4-mL vial: $NiBr_2$•diglyme (24.7 mg, 0.070 mmol, 0.10 equiv) and ligand **1** (27.4 mg, 0.091 mmol, 0.13 equiv), and the vial was sealed with a teflon-lined septum cap. The vial was evacuated and backfilled with nitrogen three times, and then DMA (1.0 mL) was added via syringe. The resulting mixture was stirred vigorously at r.t. for 1–2 h (or until the solution became almost or completely homogeneous). A 20-mL vial, sealed with a teflon-lined septum cap, was evacuated and backfilled with nitrogen three times, and then *i*-Pr_2O (12.0 mL) was added via syringe. The solution of nickel/ligand in DMA was transferred by syringe to the 20-mL vial. The mixture was stirred for 5 min, and then the electrophile (0.70 mmol) was added. Next, the white slurry of the activated diboron reagent was added via syringe within a 1-min period to the 20-mL vial, followed by an *i*-Pr_2O rinsing (1.0 mL). The reaction mixture was stirred at r.t. for 1–6 h under an atmosphere of nitrogen, until judged complete by GC analysis. Then, it was filtered through a short pad of silica gel, eluting with Et_2O (25 mL). The solvents were removed in vacuo, and the residue was purified by flash chromatography (if the products are exposed to silica gel for an extended period of time or left unpurified for >12 h, a lower yield is observed).

When employed for the borylation illustrated in Entry 6 of Table 3 (reaction time: 2 h), the desired product was isolated in 74% yield (135 mg).



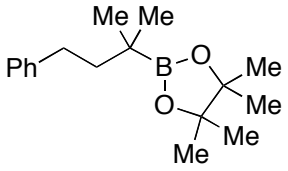
2-Adamantan-1-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [1357000-33-9][27] (Table 3, Entry 1). The title compound was prepared according to the General Procedure, using 1-iodoadamantane (184 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). White semi-solid.

First run: 139 mg (75%). Second run: 132 mg (72%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.81 (br s, 3H), 1.72 (br t, J = 3.1 Hz, 12H), 1.17 (s, 12H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.8, 38.2, 37.7, 27.8, 24.8.

(27) Ito, H.; Kubota, K. *Org. Lett.* **2012**, *14*, 890–893.



4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane (Table 3, Entry 2). The title compound was prepared according to the General Procedure, using (3-iodo-3-methylbutyl)benzene (192 mg, 0.70 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). White/colorless needles.

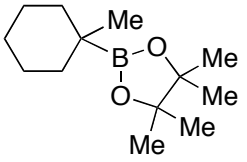
First run: 75 mg (39%). Second run: 79 mg (41%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.18-7.11 (m, 3H), 2.56-2.51 (m, 2H), 1.58-1.54 (m, 2H), 1.23 (s, 12H), 0.97 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.9, 128.5, 128.4, 125.6, 83.2, 43.7, 33.3, 24.98, 24.96.

FT-IR (film) 3086, 3063, 3027, 2977, 2936, 2862, 1605, 1497, 1475, 1455, 1389, 1371, 1310, 1267, 1194, 1166, 1137, 1070, 1031, 1005, 966, 855, 767, 746, 717, 699, 671, 580, 521, 498, 467 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{17}H_{27}BO_2$: 274, found: 274.



4,4,5,5-Tetramethyl-2-(1-methylcyclohexyl)-1,3,2-dioxaborolane [255041-54-4] (Table 3, Entry 3). The title compound was prepared according to the General Procedure, using 1-bromo-1-methylcyclohexane (124 mg, 0.70 mmol). The reaction was complete after 3 h. Due to the volatility of the product, the DMA was not evaporated from the crude reaction mixture, but it was washed out via extraction with water. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid.

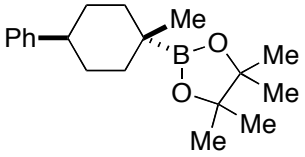
First run: 104 mg (66%). Second run: 106 mg (68%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.81-1.76 (m, 2H), 1.62-1.53 (m, 3H), 1.28-1.15 (m, 14H), 1.15-1.04 (m, 1H), 0.90-0.83 (m, 5H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.8, 37.0, 26.4, 25.9, 25.5, 24.7.

FT-IR (film) 2978, 2924, 2854, 2671, 1465, 1388, 1336, 1317, 1303, 1263, 1233, 1215, 1165, 1145, 1109, 1083, 1042, 1020, 968, 932, 895, 859, 847, 828, 715, 691, 670, 580, 550, 470 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{13}H_{25}BO_2$: 224, found: 224.



4,4,5,5-Tetramethyl-2-((1*s*,4*s*)-1-methyl-4-phenylcyclohexyl)-1,3,2-dioxaborolane (cis) (Table 3, Entry 4). The title compound was prepared according to the General Procedure, using ((1*s*,4*s*)-4-bromo-4-methylcyclohexyl)benzene (cis) (177 mg, 0.70 mmol). The reaction was

complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 30:1). Colorless viscous oil. Diastereoselectivity: 11:1 (cis:trans; not separated).

First run: 143 mg (68%). Second run: 153 mg (73%).

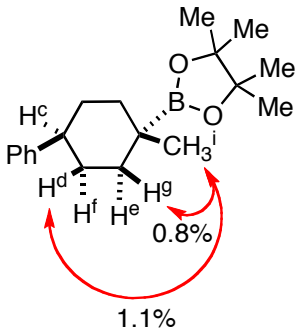
^{1}H NMR (400 MHz; $CDCl_3$): δ (major, cis) 7.29-7.24 (m, 2H), 7.22-7.20 (m, 2H), 7.17-7.13 (m, 1H), 2.51-2.43 (m, 1H), 1.77-1.60 (m, 6H), 1.57-1.51 (m, 2H), 1.23 (s, 12H), 1.06 (s, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ (major, cis) 148.0, 128.3, 126.9, 125.7, 82.8, 44.1, 32.9, 28.0, 24.7, 18.6.

^{1}H NMR (600 MHz; $(CD_3)_2CO$): δ (major, cis) 7.31-7.27 (m, 4H), 7.17 (tt, J = 6.6, 1.9 Hz, 1H), 2.50 (tt, J = 11.4, 3.7 Hz, 1H, H^c), 1.78 (qd, J = 12.2, 2.8 Hz, 2H, H^d), 1.70 (td, J = 12.8, 3.1 Hz, 2H, H^e), 1.62-1.59 (m, 2H, H^f), 1.54 (br d, J = 13.2 Hz, 2H, H^g), 1.25 (s, 12H), 1.08 (s, 3H, CH_3, H^i).

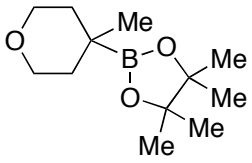
^{13}C NMR (151 MHz; $(CD_3)_2CO$): δ (major, cis) 148.0, 128.4, 127.0, 125.8, 82.8, 44.3, 33.0, 28.2, 24.3, 18.5.

NOE (600 MHz, $(CD_3)_2CO$) Irradiation at s 1.08 (CH_3, H^i): 0.8% enhancement at H^g (1.5% for 2H), 1.1% enhancement at H^d (2.1% for 2H).



FT-IR (film) 3061, 3027, 2977, 2924, 2858, 1602, 1493, 1467, 1400, 1379, 1338, 1308, 1257, 1216, 1166, 1150, 1131, 1097, 1020, 971, 850, 756, 699, 671, 580, 531 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{19}H_{29}BO_2$: 300, found: 300.



4,4,5,5-Tetramethyl-2-(4-methyltetrahydro-2*H*-pyran-4-yl)-1,3,2-dioxaborolane (Table 3, Entry 5). The title compound was prepared according to the General Procedure, using 4-bromo-4-methyltetrahydro-2*H*-pyran (125 mg, 0.70 mmol). The reaction was complete after 4 h. Due to the volatility of the product, the DMA was not evaporated from the crude reaction mixture, but it was washed out via extraction with water. Solvent used for chromatography: hexanes/Et_2O (10:1 → 7:1). Colorless liquid.

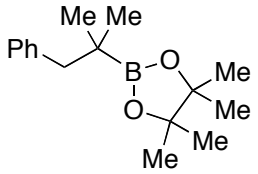
First run: 115 mg (72%). Second run: 113 mg (72%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 3.85-3.80 (m, 2H), 3.34 (td, J = 11.8, 2.2 Hz, 2H), 1.72 (dq, J = 13.1, 2.1 Hz, 2H), 1.26-1.15 (m, 14H), 0.92 (s, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 83.4, 67.6, 36.9, 25.7, 24.9.

FT-IR (film) 3051, 2979, 2952, 2838, 2752, 2692, 1460, 1437, 1380, 1323, 1308, 1274, 1247, 1235, 1214, 1199, 1165, 1143, 1103, 1086, 1034, 1014, 984, 966, 885, 855, 837, 739, 716, 694, 670, 604, 579 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{12}H_{23}BO_3$: 226, found: 226.



4,4,5,5-Tetramethyl-2-(2-methyl-1-phenylpropan-2-yl)-1,3,2-dioxaborolane (Table 3, Entry 6; gram-scale reaction). The title compound was prepared according to the General Procedure, using (2-bromo-2-methylpropyl)benzene (149 mg, 0.70 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 30:1). White solid.

First run: 129 mg (71%). Second run: 127 mg (70%).

^1H NMR (400 MHz; $CDCl_3$): δ 7.23-7.17 (m, 4H), 7.15-7.11 (m, 1H), 2.60 (s, 2H), 1.19 (s, 12H), 0.93 (s, 6H).

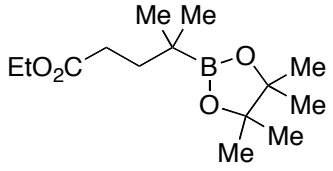
^{13}C NMR (101 MHz; $CDCl_3$): δ 140.6, 130.4, 127.8, 125.8, 83.3, 46.6, 25.0 (6 CH_3, confirmed by gHMQC).

FT-IR (film) 3085, 3063, 3028, 2978, 2954, 2935, 2862, 1605, 1495, 1474, 1454, 1388, 1371, 1356, 1309, 1274, 1214, 1166, 1135, 1110, 1032, 968, 908, 875, 851, 741, 703, 690, 669, 596, 579, 553, 486, 457 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{16}H_{25}BO_2$: 260, found: 260.

The reaction was conducted on a gram-scale according to the General Procedure, using (2-bromo-2-methylpropyl)benzene (1.49 g, 7.0 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 30:1). White solid (1.28 g, 70%).

When the same reaction was conducted with half of the standard catalyst loading (5% $NiBr_2$•diglyme, 6.6% ligand **1**), the purified product was generated in 56% yield (1.03 g).



Ethyl 4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (Table 3, Entry 7). The title compound was prepared according to the General Procedure, using ethyl 4-bromo-4-methylpentanoate (156 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 10:1). Colorless liquid.

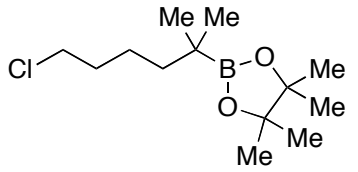
First run: 99 mg (53%). Second run: 98 mg (52%).

^1H NMR (400 MHz; $CDCl_3$): δ 4.13 (q, J = 7.1 Hz, 2H), 2.32-2.28 (m, 2H), 1.65-1.61 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.24 (s, 12H), 0.95 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 174.3, 83.0, 60.1, 35.5, 31.4, 24.7, 24.5, 14.2.

FT-IR (film) 2979, 2939, 2864, 1737, 1477, 1391, 1372, 1311, 1246, 1168, 1137, 1029, 967, 853, 777, 717, 692, 671, 580 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{14}H_{27}BO_4$: 270, found: 255 (M^+–CH_3).



2-(6-Chloro-2-methylhexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, Entry 8). The title compound was prepared according to the General Procedure, using 5-bromo-1-chloro-5-methylhexane (150 mg, 0.70 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid.

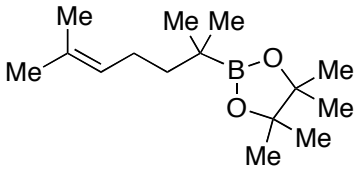
First run: 113 mg (62%). Second run: 115 mg (63%).

^1H NMR (400 MHz; $CDCl_3$): δ 3.50 (t, J = 6.8 Hz, 2H), 1.71 (pentet, J = 7.1 Hz, 2H), 1.39-1.30 (m, 2H), 1.26-1.21 (m, 2H), 1.19 (s, 12H), 0.87 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 83.1, 45.4, 40.5, 33.7, 25.0, 24.9, 24.0.

FT-IR (film) 2967, 2937, 2863, 1476, 1390, 1371, 1308, 1214, 1144, 1112, 1066, 967, 853, 741, 717, 693, 670, 653, 580 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{13}H_{26}BClO_2$: 260, found: 245 (M^+–CH_3).



2-(2,6-Dimethylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, Entry 9). The title compound was prepared according to the General Procedure, using 6-bromo-2,6-dimethylhept-2-ene (144 mg, 0.70 mmol). The reaction was complete after 2 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid.

First run: 116 mg (66%). Second run: 117 mg (66%).

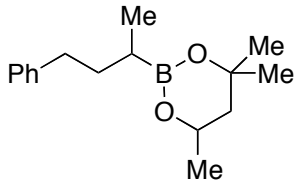
^1H NMR (400 MHz; $CDCl_3$): δ 5.12-5.06 (m, 1H), 1.92-1.86 (m, 2H), 1.64 (d, J = 1.1 Hz, 3H), 1.57 (d, J = 0.7 Hz, 3H), 1.27-1.22 (m, 2H), 1.20 (s, 12H), 0.90 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 130.9, 125.6, 83.0, 41.5, 25.9, 25.4, 25.0, 24.9, 17.7.

FT-IR (film) 2978, 2932, 2862, 1475, 1389, 1370, 1307, 1215, 1187, 1139, 967, 932, 856, 836, 743, 717, 693, 671, 580 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{15}H_{29}BO_2$: 252, found: 252.

V. Nickel-Catalyzed Borylations (eq 2–4; Figures 1, 2, and 4)



4,4,6-Trimethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborinane (eq 2). The title compound was prepared according to the General Procedure, using (3-bromobutyl)benzene (149 mg, 0.70 mmol) and bis(hexylene glycolato)diboron instead of bis(pinacolato)diboron. The reaction was complete after 12 h. Solvent used for chromatography: hexanes/Et_2O (40:1 → 20:1). Colorless liquid.

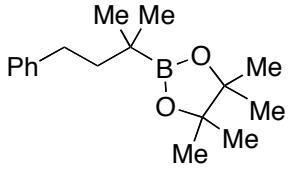
First run: 126 mg (69%). Second run: 128 mg (70%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.18-7.11 (m, 3H), 4.16-4.07 (m, 1H), 2.63-2.50 (m, 2H), 1.76-1.67 (m, 2H), 1.54-1.45 (m, 1H), 1.40-1.33 (m, 1H), 1.25-1.23 (m, 6H), 1.21 (d, J = 6.2 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.91-0.84 (m, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.9, 128.7, 128.3, 125.5, 70.4, 64.63, 64.62, 46.2, 35.93, 35.86, 35.74, 35.67, 31.5, 28.31, 28.27, 23.5, 16.12, 16.04.

FT-IR (film) 3085, 3062, 3026, 2973, 2931, 2868, 1604, 1496, 1455, 1415, 1390, 1344, 1303, 1273, 1251, 1211, 1171, 1111, 1056, 1030, 896, 819, 769, 747, 699, 681 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{16}H_{25}BO_2$: 260, found: 260.

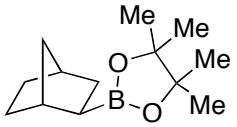


4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane (eq 3). The title compound was prepared according to the General Procedure, using (3-bromo-3-methylbutyl)benzene (159 mg, 0.70 mmol). The activated diboron reagent was added at –10 °C. The reaction was complete after 72 h at –10 °C. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). White needles.

First run: 153 mg (80%). Second run: 155 mg (81%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.18-7.11 (m, 3H), 2.56-2.52 (m, 2H), 1.59-1.54 (m, 2H), 1.24 (s, 12H), 0.98 (s, 6H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 143.9, 128.5, 128.4, 125.6, 83.2, 43.7, 33.3, 24.98, 24.97.

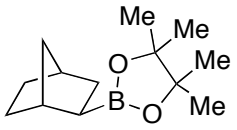


***exo*-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [141091-39-6][19a,25a,28] (eq 4).** The title compound was prepared according to the General Procedure, using *exo*-2-bromonorbornane (123 mg, 0.70 mmol). The reaction was complete after 4 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid. Diastereoselectivity: *exo* only.

First run: 118 mg (76%). Second run: 125 mg (81%).

^1H NMR (400 MHz; $CDCl_3$): δ 2.25-2.23 (m, 1H), 2.20-2.16 (m, 1H), 1.53-1.40 (m, 3H), 1.34-1.28 (m, 1H), 1.22-1.17 (m, 14H), 1.16-1.10 (m, 2H), 0.86-0.82 (m, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 83.0, 38.9, 38.3, 36.8, 32.42, 32.38, 29.5, 24.9.



***exo*-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [141091-39-6][19a,25a,28] (eq 4).** The title compound was prepared according to the General Procedure, using *endo*-2-bromonorbornane (123 mg, 0.70 mmol). The reaction was complete after 4 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless liquid. Diastereoselectivity: *exo* only.

First run: 120 mg (77%). Second run: 118 mg (76%).

^1H NMR (400 MHz; $CDCl_3$): δ 2.26-2.23 (m, 1H), 2.20-2.17 (m, 1H), 1.53-1.40 (m, 3H), 1.34-1.28 (m, 1H), 1.24-1.17 (m, 14H), 1.16-1.10 (m, 2H), 0.86-0.82 (m, 1H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 83.0, 38.9, 38.3, 36.8, 32.42, 32.38, 29.5, 24.9.

Procedure for Figures 1 and 4: KOEt (4.2 mg, 0.050 mmol, 0.25 equiv), pinB–Bpin (13.7 mg, 0.054 mmol, 0.27 equiv), and *i*-Pr_2O (1.0 mL) were added to a 4-mL vial in a nitrogen-filled glovebox. The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1 h. The following materials were added in turn to a second 4-mL vial: $NiBr_2$•diglyme (3.5 mg, 0.010 mmol, 0.050 equiv), ligand **1** (4.0 mg, 0.013 mmol, 0.066 equiv), and DMA (290 μL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 1–2 h (or until the solution became almost or completely homogeneous). Next, *i*-Pr_2O (1.0 mL) and the pair of alkyl halides (0.20 mmol each; see Figures 1 and 4) were added to this solution. After stirring for 5 min, the white slurry of the activated diboron reagent was added within a 1-min period, followed by an *i*-Pr_2O rinsing (0.3 mL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at r.t. for 1 h. Next, *n*-dodecane (20.0 μL) was added to the vial as an internal standard, and the reaction mixture was analyzed by GC.

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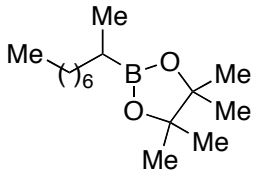
(28) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909–910.

Procedure for Figure 2:[9] $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 0.040 equiv), ligand **5** (6.6 mg, 0.020 mmol, 0.080 equiv), and DMA (400 μL) were added to a 4-mL vial in a nitrogen-filled glovebox. The vial was sealed with a teflon-lined septum cap, and the mixture was stirred vigorously at r.t. for 20 min, resulting in a deep-blue solution. The following materials were added in turn to a second 4-mL vial: the pair of alkyl bromides (0.25 mmol each; see Figure 2) and DMA (300 μL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred for 1 min. Next, the solution of $Ni(cod)_2$/ligand **5** in the first vial was treated with a solution of *n*-hexylzinc iodide (0.84 M in DMA; 80 μL, 0.068 mmol, 0.27 equiv). The mixture was stirred for 1 min, and then the solution of alkyl bromides in DMA was added, followed by a DMA rinsing (100 μL). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at r.t. for 20 h. Next, the reaction was quenched with ethanol (0.50 mL), *n*-dodecane (25.0 μL) was added to the vial as an internal standard, and the reaction mixture was analyzed by GC.



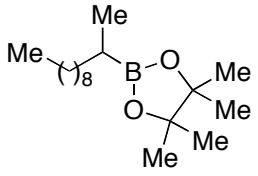
4,4,5,5-Tetramethyl-2-(nonan-2-yl)-1,3,2-dioxaborolane (for Figure 4). The title compound was prepared according to the General Procedure, using 2-bromononane (145 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless oil (150 mg, 84%).

^1H NMR (400 MHz; $CDCl_3$): δ 1.43-1.36 (m, 1H), 1.30-1.23 (m, 11H), 1.20 (s, 12H), 0.99-0.90 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.9, 33.4, 32.1, 30.0, 29.5, 29.2, 24.94, 24.91, 22.9, 15.7, 14.3.

FT-IR (film) 2978, 2957, 2925, 2855, 1465, 1406, 1387, 1315, 1274, 1244, 1215, 1146, 1112, 1007, 968, 861, 688, 669, 579 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{15}H_{31}BO_2$: 254, found: 254.



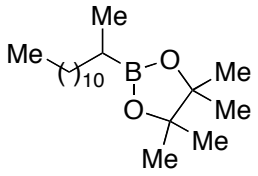
4,4,5,5-Tetramethyl-2-(undecan-2-yl)-1,3,2-dioxaborolane (for Figure 4). The title compound was prepared according to the General Procedure, using 2-bromoundecane (165 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless oil (171 mg, 86%).

^1H NMR (400 MHz; $CDCl_3$): δ 1.45-1.34 (m, 1H), 1.30-1.22 (m, 15H), 1.20 (s, 12H), 1.00-0.91 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.9, 33.5, 32.1, 30.1, 29.85, 29.81, 29.5, 29.2, 24.94, 24.91, 22.9, 15.7, 14.3.

FT-IR (film) 2978, 2957, 2925, 2854, 1466, 1406, 1387, 1371, 1315, 1270, 1215, 1146, 1111, 1006, 968, 861, 688, 670, 579 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{17}H_{35}BO_2$: 282, found: 282.



4,4,5,5-Tetramethyl-2-(tridecan-2-yl)-1,3,2-dioxaborolane (for Figure 4). The title compound was prepared according to the General Procedure, using 2-iodotridecane (217 mg, 0.70 mmol). The reaction was complete after 3 h. Solvent used for chromatography: hexanes/Et_2O (1:0 → 40:1). Colorless oil (184 mg, 84%).

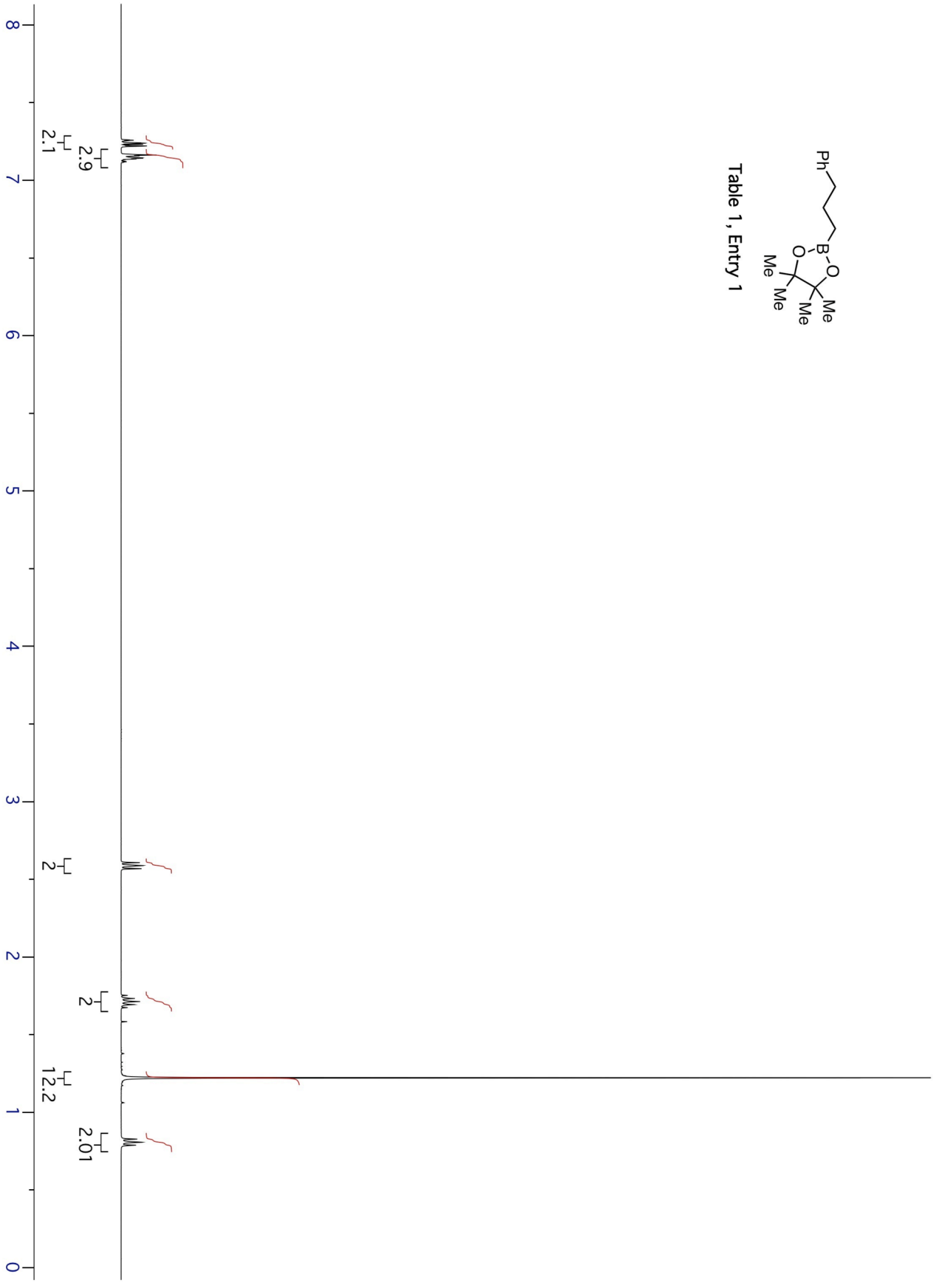
^1H NMR (400 MHz; $CDCl_3$): δ 1.43-1.36 (m, 1H), 1.30-1.22 (m, 19H), 1.20 (s, 12H), 0.99-0.90 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 82.9, 33.5, 32.1, 30.1, 29.88, 29.85, 29.84, 29.6, 29.2, 24.94, 24.91, 22.9, 15.7, 14.3.

FT-IR (film) 2925, 2854, 1466, 1406, 1386, 1315, 1272, 1216, 1146, 1111, 1006, 968, 861, 721, 688, 671, 579, 522 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{19}H_{39}BO_2$: 310, found: 310.

VI. ^{1}H NMR Spectra



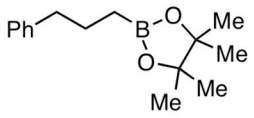


Table 1, Entry 2

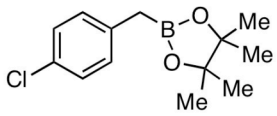


Table 1, Entry 3

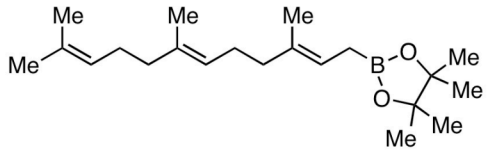


Table 1, Entry 4

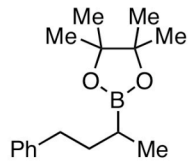
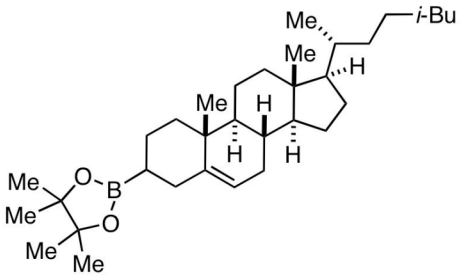


Table 2, Entry 1



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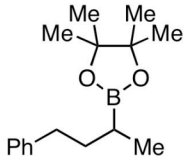


Table 2, Entry 3

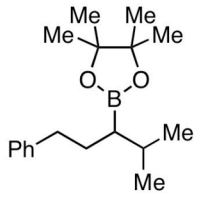
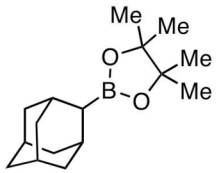


Table 2, Entry 4



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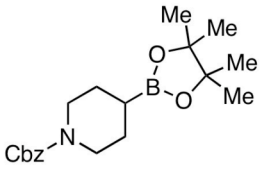


Table 2, Entry 6

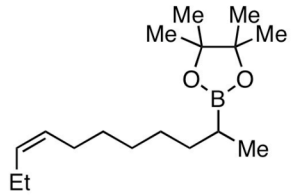


Table 2, Entry 7

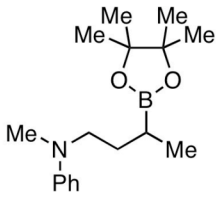


Table 2, Entry 8

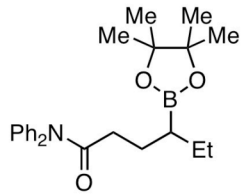
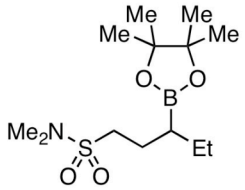


Table 2, Entry 9



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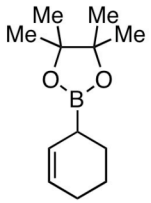

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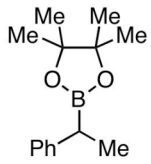
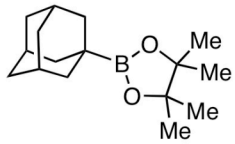


Table 2, Entry 12



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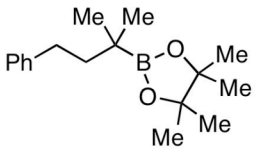

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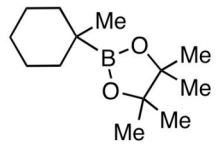

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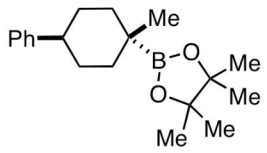

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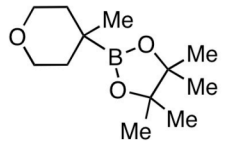

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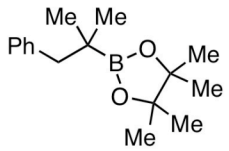

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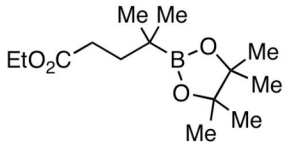

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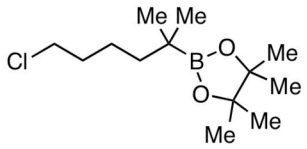

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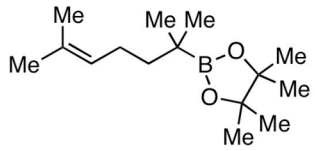

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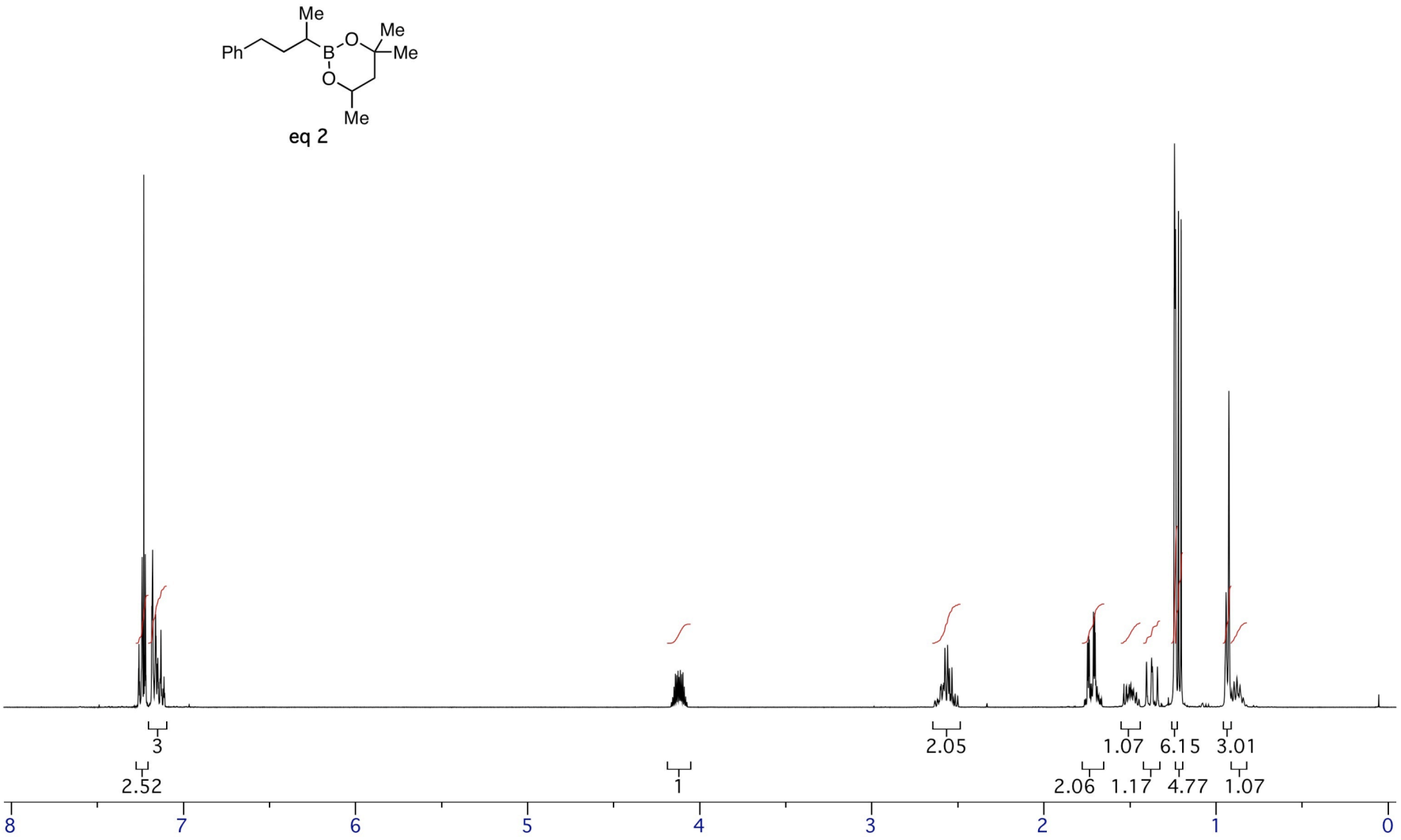
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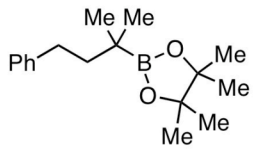

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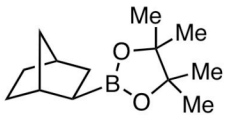

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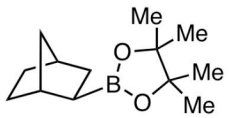

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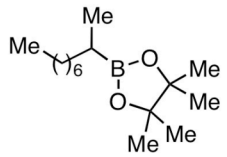

Figure 4

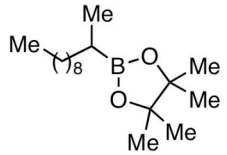

Figure 4

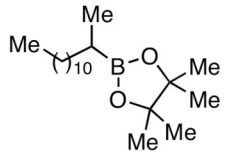

Figure 4