Regiospecific Functionalization of Methyl C-H Bonds of Alkyl Groups in Reagents with Heteroatom Functionality

Supporting Information

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General. Unless noted otherwise, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven-dried for approximately 1 h prior to use. THF and diethyl ether were obtained as HPLC grade without inhibitors; benzene, toluene, dichloromethane, and pentane were obtained as ACS reagent grade. THF, diethyl ether, benzene, toluene, dichloromethane, and pentane were degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column containing activated alumina. Cyclohexane was distilled from sodium benzophenone ketyl under nitrogen. All reagents were obtained from commercial sources and used without further purification, unless otherwise noted. *N,N*-diethyl-3-pentanamine,[1] 2-(4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ($Br(CH_2)_4Bpin$),[2] $Cp^*Rh(C_6Me_6)$,[3] $[(COD)IrCl]_2$,[4] *O,O'*-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-phenylethylphosphoramidite,[5] and $Pd(dba)_2$[6] were prepared using the reported procedures. Triethylamine, 1-ethylpiperidine, 1-butylpiperidine, and *N,N*-diethyl-3-pentanamine were dried over CaH_2 and vacuum transferred prior to use. Tributylamine was dried over CaH_2 and distilled under vacuum prior to use. Perfluorooctylethane, butyl ethyl ether, *tert*-butyl ethyl ether, and p-bromo-*tert*-butylbenzene were dried over activated alumina and filtered prior to use. 1-Fluorooctane was dried over anhydrous $CaSO_4$ and vacuum transferred prior to use. C_6D_{12} was dried over sodium benzophenone ketyl and vacuum transferred prior to use. ^1H NMR spectra were obtained at 400 or 500-MHz and recorded relative to residual protio-solvent. ^{13}C NMR spectra were obtained at 100.6 or 125.0 MHz, and chemical shifts were recorded relative to the solvent resonance. Both ^1H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{13}C NMR signals for carbon atoms α to boronate ester groups were either not observed or observed between $\delta = 20$ and 0 as broad peaks near the baseline. ^{19}F NMR spectra were obtained at 376 MHz, and chemical shifts were recorded with a C_6F_6 external standard (δ = -164.9). ^{11}B NMR spectra were obtained at 160 MHz or 80 MHz, and chemical shifts were recorded relative to $BF_3 \bullet OEt_2$ as an external standard. GC analyses were performed using a DB-1301 narrow bore column. Response factors were calculated from the ratios of pure product to added dodecahydrotriphenylene in ^1H NMR spectra and GC traces.

Representative procedure for reactions with B_2pin_2 as the limiting reagent: *N*-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl]-dibutylamine. $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and Bu_3N (256 mg, 1.38 mmol) were placed into

an NMR tube. The tube was sealed under vacuum, and the tube was heated at 150 ^{o}C for 24 h. The NMR tube was opened, and the contents were dissolved in benzene. Dodecahydrotriphenylene (11.8 mg, 0.0491 mmol) was added as an internal standard, and an aliquot was removed and analyzed by GC. The yield of boronate ester product was 75% based on the reaction of tributylamine withi B_2pin_2 to generate two equiv of the functionalized product and H_2. The compound was independently synthesized as follows: Dibutylamine (12.8 mL, 76.2 mmol) and 2-(4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.01 g, 7.62 mmol) were heated in 20 mL of MeCN at 70 ^{o}C for 4 h. The reaction mixture was cooled and added to a 10:1 mixture of pentane and toluene. Dibutylammonium bromide precipitated as a white solid. Filtration and evaporation of the solvent gave the crude product, which was nearly pure, as indicated by ^{1}H NMR spectroscopy. The product was distilled at 75-80 ^{o}C and 50 mtorr to give 740 mg (31%) of the boronate ester product. ^{1}H NMR (C_6D_6, 500 MHz) δ = 2.42 (t, 2H), 2.38 (t, 4H), 1.66 (m, 2H), 1.65 (m, 2H), 1.42 (m, 4H), 1.33 (m, 4H), 1.06 (s, 12H), 1.03 (t, 2H), 0.91 (t, 6H); ^{11}B NMR (C_6D_6, 160 MHz) δ = 34.2; ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ = 83.1, 54.9, 54.8, 30.9, 30.6, 25.3, 22.9, 21.4, 14.7. The carbon attached to boron was not observed. Anal. Calcd for $C_{18}H_{38}NBO_2$: C, 69.45; H, 12.30; N, 4.50. Found: C, 69.69; H, 12.54; N, 4.43.

Representative procedure for reactions with the organic substrate as limiting reagent: 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and $CF_3(CF_2)_7CH_2CH_3$ (61.8 mg, 0.138 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^{o}C for 24 h. The NMR tube was opened in a drybox, and additional Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol) and B_2pin_2 (35.0 mg, 0.138 mmol) were added. The tube was again sealed under vacuum and heated for an additional 24 h at 150 ^{o}C. The NMR tube was opened, and the contents were dissolved in benzene. Dodecahydrotriphenylene (16.2 mg, 0.0674 mmol) was added as an internal standard, and an aliquot was removed and analyzed by GC. The yield for the reaction of B_2pin_2 to form the functionalized product and HBpin was 84%. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (3.4 mg, 9 μmol), B_2pin_2 (43.7 mg, 0.172 mmol), and $CF_3(CF_2)_7CH_2CH_3$ (309 mg, 0.688 mmol). The product was purified by chromatography on silica gel, eluting with pentane, to give 31 mg (31 %) of the boronate ester product. ^{1}H NMR (C_6D_6, 500 MHz) δ = 2.12 (m, 2H), 1.00 (t, 2H), 0.99 (s, 12H); ^{11}B NMR (C_6D_6, 160 MHz) δ =

33.7; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 120 to 105 (m, *C*F's), 83.9, 26.5 , 25.1, 4.5, the carbon attached to boron was not observed; ^{19}F NMR (C_6D_6, 376 MHz) δ = -82.1 (3F, t), -116.8 (2F, m), -122.7 (2F, m), -123.0 (4F, m), -123.9 (2F, m), -124.5 (2F, m), -127.3 (2F, m). Anal. Calcd for $C_{16}H_{16}BF_{17}O_2$: C, 33.47; H, 2.81. Found: C, 33.65; H, 2.64.

2-(2-*tert*-Butoxy-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The yield for the borylation of *tert*-butyl ethyl ether with B_2pin_2 as the limiting reagent was obtained by the representative procedure. Procedure for borylation with *tert*-butyl ethyl ether as limiting reagent: Cp*Rh(η^4-C_6Me_6) (5.6 mg, 14 μmol), B_2pin_2 (41.6 mg, 0.164 mmol), *tert*-butyl ethyl ether (28.2 mg, 0.276 mmol), and cyclohexane (90 μL) placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. After this time, the NMR tube was opened in a drybox, and additional Cp*Rh(η^4-C_6Me_6) (5.6 mg, 14 μmol) and B_2pin_2 (28.4 mg, 0.112 mmol) were added. The tube was again sealed under vacuum and heated for an additional 24 h at 150 ^oC. The NMR tube was opened, and the contents were dissolved in benzene. Dodecahydrotriphenylene (10.0 mg, 0.0416 mmol) was added, and an aliquot was removed and analyzed by GC. The yield of the boronate ester product was 48%, based on the reaction of B_2pin_2 to generate the functionalized product and HBpin. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (80 mg, 0.20 mmol), B_2pin_2 (1.01 g, 4.00 mmol), and *tert*-butyl ethyl ether (4.11 g, 40.0 mmol). The product was isolated by chromatography on silica, eluting with pentane:ether (10:1) to give 464 mg (51%) of the boronate ester product. ^1H NMR (C_6D_6, 500 MHz) δ = 3.63 (t, 2H), 1.36 (t, 2H); 1.14 (s, 9H), 1.06 (s, 12H); ^{11}B NMR (C_6D_6, 160 MHz) δ = 33.7; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.2, 72.4, 58.9, 28.1, 25.3. The carbon attached to boron was not observed. Anal. Calcd for $C_{12}H_{25}BO_3$: C, 63.18; H, 11.05. Found: C, 63.30; H, 11.09, N < 0.02.

2-But-3-enyl-2,4,4,5,5-pentamethyl-[1,3]dioxolane. 5-Hexen-2-one (4.91 g, 50.0 mmol), trimethylorthoformate (12.7 g, 120 mmol), *p*-toluenesulfonic acid monohydrate (95 mg, 0.50 mmol), and C_6H_6 (40 mL) were heated at reflux under nitrogen for 5 h. The red-brown solution was cooled to room temperature and neutralized with $NaHCO_3$. The solution was filtered, and the solvent was evaporated to give a red-brown liquid. The product was heated at reflux with pinacol (3.55 g, 30.0 mmol), and *p*-toluenesulfonic acid monohydrate (57.1 mg, 0.300 mmol) in $CHCl_3$ (40 mL) under nitrogen for 6 h. The solution was cooled to room temperature, neutralized with $NaHCO_3$, filtered, and the solvent was evaporated under reduced pressure. The resulting oil

was purified by column chromatography on silica gel, eluting with ethyl acetate/hexane (1:6) to give 3.54 g (36%) of the the product. ^{1}H NMR (C_6D_6, 400 MHz) δ = 1.06 (s, 6H), 1.09 (s, 6H), 1.37 (s, 3H), 1.81 (m, 2H), 2.22 (m, 2H), 4.93 (ddt, 1H), 5.02 (dq, 1H), 5.81 (ddt, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ = 24.9, 25.0, 27.2, 29.9, 42.9, 82.3, 107.4, 114.2, 139.2. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.77; H, 11.10.

6-[2-(2,3-Dimethyl-2,3-butanedioxy)hexyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Yields for the catalytic borylation of 2-but-3-enyl-2,4,4,5,5-pentamethyl-[1,3]dioxolane were obtained by the representative procedures. This compound was independently synthesized as follows: 2-But-3-enyl-2,4,4,5,5-pentamethyl-[1,3]dioxolane (642 mg, 3.24 mmol), pinacolborane (498 mg, 3.89 mmol), Cp*Rh(C_2H_4)$_2$ (10 mg, 340 μmol), and CH_2Cl_2 (2 mL) were heated at reflux under nitrogen for 12 h. The brown solution was quenched with H_2O (10 mL), extracted with ether (3 x 30 mL), dried over $MgSO_4$, and reduced to an oil under vacuum. Vacuum distillation, followed by column chromatography on silica gel, eluting with ethyl acetate/hexane (1:6), gave 593 mg (80%) of the product. ^{1}H NMR (C_6D_6, 400 MHz) δ = 0.99 (t, 2H), 1.06 (s, 12H), 1.10 (s, 6H), 1.11 (s, 6H), 1.45 (s, 3H), 1.62 (m, 4H), 1.78 (t, 2H); ^{11}B NMR (C_6D_6, 80 MHz) δ = 34.0; ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ = 24.9, 25.0, 25.0, 25.1, 27.3, 28.2, 43.7, 82.1, 82.7, 107.9. The carbon attached to boron was not observed. Anal. Calcd for $C_{18}H_{35}B_1O_4$: C, 66.26; H, 10.81. Found: C, 66.33; H, 11.10.

2-(8-Fluoro-octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Yields for the catalytic reactions of 1-fluorooctane were obtained by the representative procedure. Reaction of 1-fluorooctane with B_2pin_2 for extended times occasionally formed BF_3 and octene, as determined by ^{11}B NMR and GC-MS respectively. However, this decomposition was not observed after 12 h of reaction time. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (56 mg, 140 mmol), B_2pin_2 (700. mg, 2.76 mmol), and 1-fluorooctane (2.1 g, 16 mmol). After excess 1-fluorooctane and HBpin were evaporated, the product was isolated by chromatography on silica, eluting with hexane/ethylacetate (10:1) to give 562 mg (79%). ^{1}H NMR (C_6D_6, 400 MHz) δ = 4.10 (dt, 2H), 1.61 (m, 2H), 1.45-1.30 (m, 4H), 1.26-1.10 (m, 6H), 1.08 (s, 12H), 1.01 (t, 2H); ^{11}B NMR (C_6D_6, 80 MHz) δ = 34.0; ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ = 84.0 (d, *J*=166 Hz), 83.1, 33.0, 31.1, 30.1, 29.8, 25.8, 25.3, 24.9; ^{19}F{^{1}H} NMR (C_6D_6, 376 MHz) δ = -213. Anal. Calcd for $C_{14}H_{28}BFO_2$: C, 65.13; H, 10.93. Found: C, 65.50; H, 11.03.

1-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-ethyl]-piperidine. The yield for the catalytic borylation of ethylpiperidine was obtained by the representative procedure. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6). The product mixture was treated with portions of PL-DEAM scavenger in benzene until the B_2pin_3 and pinBOBpin side products were consumed, as determined by ^{11}B NMR spectroscopy (~2 equiv). Distillation at 55-60 ^oC and 60 mtorr gave 1.12 g (46%) of the boronate ester product. ^1H NMR (C_6D_6, 500 MHz) δ = 2.59 (t, 2H), 2.33 (broad, 4H), 1.50 (m, 4H), 1.30 (m, 2H), 1.19 (t, 2H), 1.08 (s, 12H); ^{11}B NMR (C_6D_6, 80 MHz) δ = 33.8; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.1, 55.4, 54.8, 26.9, 25.5, 25.4. The carbon attached to boron was not observed. Anal. Calcd for $C_{13}H_{26}NBO_2$: C, 65.29; H, 10.96; N, 5.86. Found: C, 65.50; H, 11.07; N, 5.91.

Formation of a mixture of 2-(4-Butoxy-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(4-ethoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from n-butyl ethyl ether. The ratio of products from the borylation of n-butyl ethyl ether with B_2pin_2 as the limiting reagent was obtained by the representative procedure. The mixture of boronate ester products was purified by chromatography on silica gel, eluting with pentane:ether (10:1). After chromatography, the ratio of 2-(4-butoxy-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 2-(4-ethoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was greater than 6:1, and the NMR signals of the product from borylation for the ethyl group could be identified clearly. The product from borylation of the butyl group was prepared independently, as described in the following procedure. Signals due to $CH_3(CH_2)_4O(CH_2)_2Bpin$: ^1H NMR (C_6D_6, 400 MHz) δ = 3.67 (t, 2H), 3.32 (t, 2H), 1.53 (m, 2H), 1.34 (overlapping signals, m, 4H), 1.05 (s, 12H), 0.86 (t, 3H); ^{11}B NMR (C_6D_6, 160 MHz) δ = 34.0; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.3, 70.8, 68.2, 32.8, 25.3, 20.2, 14.5. The carbon attached to boron was not observed. Anal. Calcd for $C_{12}H_{25}BO_3$: C, 63.18; H, 11.05. Found: C, 63.21; H, 11.22, N < 0.02.

2-(4-Ethoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. This product was independently synthesized as follows: A solution of 2-(4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.50 g, 9.54 mmol) was treated with a solution of KOEt generated by the addition of KH (0.574 g, 14.3 mmol) to EtOH. The solution was stirred under nitrogen for 20 h. The product was isolated by chromatography on silica, eluting with pentane:ether (10:1) to give 267 mg (12%) of the boronate ester. ^1H NMR (C_6D_6, 500 MHz) δ = 3.32 (broad m, 2H), 3.27 (q, 2H),

1.71 (overlapping m, 4H), 1.10 (t, 3H), 1.04 (s, 12H), 0.98 (broad t, 2H); ^{11}B NMR (C_6D_6, 160 MHz) δ = 34.4; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.1, 71.1, 66.5, 33.3, 25.3, 21.7, 15.9. The carbon attached to boron was not observed. Anal. Calcd for $C_{12}H_{25}BO_3$: C, 63.18; H, 11.05. Found: C, 62.97; H, 10.97, N < 0.02.

Formation of a mixture of *N*,*N*-diethyl-[1-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl]-amine and Ethyl-(1-ethyl-propyl)-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-ethyl]-amine. The ratio of products from the borylation of *N*,*N*-diethyl-3-pentylamine with B_2pin_2 as the limiting reagent was obtained by the representative procedures. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (56 mg, 140 μmol), B_2pin_2 (0.700 g, 2.76 mmol), and *N*,*N*-diethyl-3-pentylamine (0.700 g, 4.89 mmol). The product mixture was treated with portions of PL-DEAM scavenger in benzene until B_2pin_3 and pinBOBpin side products were consumed, as determined by ^{11}B NMR spectroscopy (~1 equiv). The mixture was distilled at 90 ^{o}C and 50 mtorr to give 243 mg (33%) of the boronate ester products. Signals due to ethyl-(1-ethyl-propyl)-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-ethyl]-amine: ^{1}H NMR (C_6D_6, 500 MHz) δ = 2.76 (t, 2H), 2.43 (m, 1H), 2.40 (m, 2H), 1.40 (m, 4H), 1.20 (m, 2H), 1.08 (s, 12H), 1.02 (t, 3H), 0.93 (t, 6H); the signals for the other isomer are listed in the following procedure; ^{11}B NMR (C_6D_6, 80 MHz) δ = 34.0; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.1, 63.6, 45.8, 43.6, 25.4, 23.4, 15.7, 12.8. Anal. Calcd for $C_{15}H_{32}NBO_2$: C, 66.92; H, 11.98, N, 5.20. Found for the product mixture: C, 66.65; H, 11.78; N, 4.92.

***N*,*N*-diethyl-[1-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl]-amine.**[7] This product was independently synthesized as follows: A mixture of $[(COD)IrCl]_2$ (129 mg, 0.096 mmol), *O,O'*-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-phenylethylphosphoramidite (104 mg, 0.192 mmol) and Et_2NH (456 mg, 6.24 mmol) in THF (2 mL) was heated at 80 ^{o}C for 15 min. The mixture was cooled to 0 ^{o}C, and methyl *trans*-pent-2-enyl carbonate (692 mg, 4.80 mmol) was added. The reaction mixture was allowed to warm to room temperature over 3 h. After an additional 9 h, the solvent was evaporated, and the resulting liquid was purified by bulb-to-bulb distillation under vacuum, to give 260 mg (38%) of a 1:1 mixture of terminal and internal alkenes, as indicated by the ^{1}H NMR spectrum. HBpin (471 mg, 3.68 mmol) was added to the mixture of isomers, and the mixture was sealed under vacuum in an NMR tube and heated at 150 ^{o}C for 24 h. After this time, ^{11}B NMR indicated formation of the alkylboronate ester(s), along

with pinBOBpin, B_2pin_3, or both. The reaction mixture was concentrated to an oil under vacuum, dissolved in benzene, and treated with PL-DEAM scavenger until the ^{11}B NMR spectrum indicated that all the pinBOBpin and B_2pin_3 had been consumed (~2 equiv total, 48 h total). The product was distilled at 65 ^oC and 20 mtorr to give 20 mg (4%, 1.5% for two steps) of the boronate ester product. ^1H NMR (C_6D_6, 400 MHz) δ = 2.45 (m, 1H), 2.41 (m, 4H), 1.62 (m, 2H), 1.32 (m, 2H), 1.07 (s, 12H), 1.04 (t, 2H), 1.02 (t, 6H), 0.96 (t, 3H); ^{11}B NMR (C_6D_6, 80 MHz) δ = 33.4; $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 83.0, 64.0, 44.0, 25.4, 25.1, 23.5, 15.8, 12.8. The carbon attached to boron was not observed. Anal. Calcd for $C_{15}H_{32}NBO_2$: C, 66.92; H, 11.98, N, 5.20. Found: C, 66.65; H, 12.21; N, 5.26.

Formation of a mixture of 2-(4-ethoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-Butoxy-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(4-butoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), butyl ethyl ether (70.5 mg, 0.690 mmol), and dibutyl ether (89.9 mg, 0.690 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. The NMR tube was opened, and the contents were dissolved in benzene. Dodecahydrotriphenylene (23.5, 0.0978 mmol) was added, and an aliquot was removed and analyzed by GC. The ratio of 2-(4-butoxy-ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 2-(4-ethoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 2-(4-butoxy-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was determined to be 4:1:2, after correction for response factors

Formation of a mixture of 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 2-octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Cp*Rh(η^4-C_6Me_6) (1.5 mg, 4.0 μmol), B_2pin_2 (20.5 mg, 0.0807 mmol), (perfluoro-n-octyl)ethane (77.0 mg, 1.72 mmol), and octane (9.8 mg, 0.0859 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. The NMR tube was opened, and the contents were dissolved in benzene. Dodecahydrotriphenylene (19.8 mg, 0.0824 mmol) was added, and an aliquot was removed and analyzed by GC. The ratio of 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 2-octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was determined to be 94:6, after correction for response factors.

1-(2-*tert*-Butoxy-ethyl)-4-*tert*-butyl-benzene (Table 2, Entry 1). Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and *tert*-butyl ethyl ether (141 mg, 1.38 mmol)

were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 °C for 24 h. The NMR tube was opened in a drybox, and the contents were dissolved in toluene (0.4 mL) and transferred to a vial containing *p*-bromo-*tert*-butylbenzene (70.6 mg, 0.331 mmol), $CsOH{\cdot}H_2O$ (139 mg, 0.820 mmol), $Pd(dba)_2$ (7.9 mg, 14 μmol), and 1,1'-bis(diisopropylphosphino)ferrocene (5.8 mg, 14 μmol). The vial was sealed with a PTFE lined screw-cap, and was heated for 24 h at 100 °C. The vial was then opened, and the contents were diluted with benzene. Dodecahydrotriphenylene (12.9 mg, 0.0532 mmol) was added as an internal standard, and an aliquot was removed and analyzed by GC. The yield of the *tert*-butoxyalkylarene was 87%, based on the reaction of the ether and B_2pin_2 to form the functionalized product and HBpin. The alkylarene product was independently synthesized as follows: Isobutylene was bubbled through a solution of 2-(4-tert-butylphenyl)ethanol (1.10 g, 6.17 mmol) in 20 mL of hexane containing Amberlyst 15 (300 mg) with rapid stirring for 5 h. The solution was filtered through Celite, and the solvent was evaporated to give 788 mg (54%) of the alkylarene. ^{1}H NMR (C_6D_6, 400 MHz) δ = 7.52 (d, 2H), 7.12 (d, 2H), 3.37 (t, 2H), 2.78 (t, 2H), 1.12 (s, 9H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 149.2, 137.4, 129.5, 125.7, 72.7, 63.7, 37.8, 34.7, 31.9, 28.0. Anal. Calcd for $C_{17}H_{30}O$: C, 81.99; H, 11.18. Found: C, 81.70; H, 11.25, N < 0.02.

1-*tert*-Butyl-4-(8-fluoro-octyl)-benzene (Table 2, Entry 2). $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and 1-fluorooctane (182 mg, 1.38 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 °C for 12 h. The NMR tube was opened in a drybox, and the contents were dissolved in DMF (0.5 mL) and transferred to a vial containing *p*-bromo-*tert*-butylbenzene (58.8 mg, 0.276 mmol), CsF (83.8 mg, 0.552 mmol), $Pd(dba)_2$ (7.9 mg, 14 μmol), and 1,1'-bis(diisopropylphosphino)ferrocene (5.8 mg, 14 μmol). The vial was sealed with a PTFE-lined screw-cap and heated for 24 h at 100 °C. The vial was then opened, and the contents were diluted with benzene. Dodecahydrotriphenylene (19.6 mg, 0.0815 mmol) was added as an internal standard, and an aliquot was removed and analyzed by GC. The yield of the 8-fluorooctylarene product was 29%, based on the reaction of the fluorooctane with B_2pin_2 to form the functionalized product and HBpin. To obtain isolated material for spectral and analytical data, 2-(8-fluoro-octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122 mg, 0.473 mmol), *p*-bromo-*tert*-butylbenzene (142 mg, 0.662 mmol), $CsOH{\cdot}H_2O$ (278 mg, 1.64 mmol), $Pd(dba)_2$ (15.8 mg, 28 μmol), 1,1'-

bis(diisopropylphosphino)ferrocene (11.2 mg, 28 μmol) and toluene (0.8 mL) were placed in a vial. The vial was sealed with a PTFE lined screw-cap, and heated for 24 h at 100 ^{o}C. The product was purified by thin -layer chromatography on supported silica gel, eluting with hexanes followed by extraction with dichloromethane to give 30 mg (24%) of the fluoroalkylarene product. ^{1}H NMR (C_6D_6, 500 MHz) δ = 7.20 (d, 2H), 7.02 (d, 2H), 4.33 (dt, 2H), 2.47 (t, 2H), 1.53 (overlapping signals, m, 4H), 1.24 (overlapping signals, m, 8H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ = 148.6, 140.0, 128.2, 125.3, 84.4 (d, *J*=164 Hz), 35.6, 34.5, 31.7, 30.7, 30.6, 29.6, 29.5, 25.4 (d, J=5.6 Hz) (d). Anal. Calcd for $C_{17}H_{27}F$: C, 81.54; H, 10.87. Found: C, 81.62; H, 10.92 N < 0.02.

1-*tert*-Butyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl)-benzene (Table 2, Entry 3). Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and $CF_3(CF_2)_7CH_2CH_3$ (274 mg, 0.552 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^{o}C for 24 h. The NMR tube was opened in a drybox, and the contents were dissolved in toluene (0.4 mL) and transferred to a vial containing *p*-bromo-*tert*-butylbenzene (70.6 mg, 0.331 mmol), $CsOH{\cdot}H_2O$ (139 mg, 0.820 mmol), $Pd(dba)_2$ (7.9 mg, 14 μmol), and 1,1'-bis(diisopropylphosphino)ferrocene (5.8 mg, 14 μmol). The vial was sealed with a PTFE lined screw-cap and heated for 24 h at 100 ^{o}C. The vial was then opened, and the contents were diluted with benzene. Dodecahydrotriphenylene (22.8 mg, 0.0948 mmol) was added as an internal standard, and an aliquot was removed and analyzed by GC. The yield of fluoroalkylarene was 64%, based on the reaction of B_2pin_2 to form the functionalized product and HBpin. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (5.6 mg, 14 μmol), B_2pin_2 (70.0 mg, 0.276 mmol), and $CF_3(CF_2)_7CH_2CH_3$ (589 mg, 1.10 mmol) and the coupling reaction was conducted with *p*-bromo-*tert*-butylbenzene (142 mg, 0.662 mmol), $CsOH{\cdot}H_2O$ (278 mg, 1.64 mmol), $Pd(dba)_2$ (15.8 mg, 28 μmol), 1,1'-bis(diisopropylphosphino)ferrocene (11.2 mg, 28 μmol). The product was isolated by chromatography on silica gel, eluting with hexane to give 28 mg (18 %) of the fluoroalkylarene product. ^{1}H NMR (C_6D_6, 500 MHz) δ = 7.21 (d, 2H), 6.81 (d, 2H), 2.63 (m, 2H), 2.07 (m, 2H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ = 149.9, 136.3, 128.2, 125.9, 120 to 105 (m, *C*F's), 34.7, 33.3, 31.5, 26.1. ^{19}F NMR (C_6D_6, 376 MHz) δ = -82.1 (3F, m), -115.5 (2F, m), -122.7 (2F, m), -123.0 (4F, m), -123.8 (2F, m), -124.4 (2F, m), -127.3 (2F, m). Anal. Calcd for $C_{20}H_{17}F_{17}$: C, 41.39; H, 2.95. Found: C, 41.62; H, 2.77, N < 0.02.

4-(2,4,4,5,5-Pentamethyl-[1,3]dioxolan-2-yl)-butan-1-ol (Table 2, Entry 4).[8] Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and 2-butyl-2,4,4,5,5-pentamethyl-[1,3]dioxolane (140 mg, 1.38 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. The NMR tube was opened, and the contents were dissolved in THF (3 mL). This solution was treated dropwise with aqueous KOH (2 mL, 2 M) and H_2O_2 (2 mL, 30%) at 0 ^oC and then allowed to warm to room temperature. After 2 h, the aqueous solution was extracted with diethyl ether. The ether solution was dried over $MgSO_4$ and concentrated to an oil under vacuum. A solution of 1,3,5-trimethoxybenzene (10.1 mg, 60. μmol) in CD_3OD was added to the oil and comparison of the integrations of the ^1H NMR resonances of the product versus the integrations of the methyl resonance of 1,3,5-trimethoxybenzene indicated that the yield of alcohol was 68%, based on the reaction of the dioxolane and B_2pin_2 to the boronate ester and HBpin. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (83 mg, 0.21 mmol), B_2pin_2 (754 mg, 2.97 mmol), and 2-butyl-2,4,4,5,5-pentamethyl-[1,3]dioxolane (2.0 g, 11.9 mmol) and the crude product was converted to the alcohol with aqueous KOH (2 mL, 2 M) and H_2O_2 (2 mL, 30%). Analytically pure product (43 mg, 8%) was obtained by column chromatography on silica gel, eluting with ethyl acetate/hexane (1:10) and then with ethyl acetate/hexane (2:1), followed by distillation at 60 ^oC and 20 mtorr. ^1H NMR (C_6D_6, 400 MHz) δ = 3.38 (t, 2H), 1.71 (t, 2H), 1.54 (m, 4H), 1.43 (s, 3H), 1.11 (s, 6H), 1.10 (s, 6H), 1.05 (broad, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ = 108.2, 82.7, 62.9, 43.8, 33.9, 27.5, 25.3, 25.2, 22.2. The carbon attached to boron was not observed. Anal. Calcd for $C_{12}H_{24}O_5$: C, 66.63; H, 11.18. Found: C, 66.46; H, 10.93, N < 0.02.

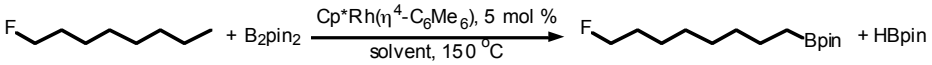
Potassium 2-(*tert*-butoxy)ethyltrifluoroborate (Table 2, Entry 5).[9] Cp*Rh(η^4-C_6Me_6) (2.8 mg, 7.0 μmol), B_2pin_2 (35.0 mg, 0.138 mmol), and *tert*-butyl ethyl ether (141 mg, 1.38 mmol) were placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. The NMR tube was opened, the contents were dissolved in methanol, and the resulting solution was rapidly stirred with solid KHF_2 (100 mg, 1.28 mmol) for 2 h. Filtration and evaporation of the solvent gave an oily solid. A solution of 1,3,5-trimethoxybenzene (19.8 mg, 0.118 mmol) in CD_3OD was added to this material, and comparison of the integrations of the ^1H NMR resonances of the product versus the integrations of the methyl resonance of 1,3,5-trimethoxybenzene indicated that the yield of the *tert*-butoxyalkyl trifluoroborate was 86% yield

of the alkyltrifluoroborate based on the reaction of the ether and B_2pin_2 to form the functionalized product and HBpin. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (40 mg, 0.10 mmol), B_2pin_2 (520 mg, 2.05 mmol), and *tert*-butyl ethyl ether (2.10 g, 20 mmol). The borylated *tert*-butyl ethyl ether was purified by passing the mixture through a plug of silica gel, eluting with a 1:1 mixture of pentane and diethyl ether and was converted to the alkyltrifluoroborate by treatment of the oil resulting from evaporation of solvent with KHF_2 in methanol. Analytically pure alkoxyalkylfluoroborate (120 mg, 28%) was obtained by precipitating the product three times from MeCN with Et_2O. ^{1}H NMR (CD_3OD, 500 MHz) δ = 3.46 (m, 2H), 1.19 (s, 9H), 0.55 (broad m, 2H); $^{13}C\{^1H\}$ NMR (CD_3OD, 126 MHz) δ = 73.9, 62.8, 28.2, the carbon attached to boron was not observed; $^{19}F\{^1H\}$ NMR (CD_3OD, 376 MHz) δ = -143. Anal. Calcd for $C_6H_{13}BF_3KO$: C, 34.63; H, 6.30. Found: C, 34.29; H, 6.22, N < 0.02.

Potassium 2-(1-piperidino)ethyltrifluoroborate (Table 2, Entry 6). Cp*Rh(η^4-C_6Me_6) (5.6 mg, 14 μmol), B_2pin_2 (70.0 mg, 0.276 mmol), and 1-ethylpiperidine (312 mg, 2.76 mmol) were placed into an NMR tube. The tube was placed into an NMR tube and sealed under vacuum. The tube was heated at 150 ^oC for 24 h. The NMR tube was opened, the contents were dissolved in methanol, and the resulting solution was rapidly stirred with solid KHF_2 (216 mg, 2.76 mmol) for 2 h. Filtration and evaporation of the solvent gave an oily solid. A solution of 1,3,5-trimethoxybenzene (38.9 mg, 0.231 mmol) in CD_3OD was added to this material, and comparison of the integrations of the ^{1}H NMR resonances of the product versus the integrations of the methyl resonance of 1,3,5-trimethoxybenzene indicated that the yield of the aminoalkyl trifluoroborate was 69% yield, based on the reaction of amine and B_2pin_2 to form two equiv of the functionalized product and H_2. To obtain isolated material for spectral and analytical data, the borylation reaction was conducted with Cp*Rh(η^4-C_6Me_6) (78.8 mg, 0.197 mmol), B_2pin_2 (1.00 g, 3.94 mmol), and 1-ethylpiperidine (4.5 g, 39 mmol). The borylated product was isolated by treatment with PL-DEAM scavenger in benzene and distilled. The distillate was diluted with MeOH and converted to the fluoroborate by addition of solid KHF_2 (2.3 g, 29 mmol) for 2 h. An analytically pure sample (252 mg, 15%) of the product was obtained by precipitating the product three times from MeCN with Et_2O. ^{1}H NMR (CD_3OD, 500 MHz) δ = 3.51 (m, 2H), 3.04 (m, 2H), 2.80 (m, 2H), 1.95 (m, 2H), 1.83 (m, 1H), 1.71 (m, 2H), 1.51 (m, 1H), 0.61 (broad m, 2H); ^{11}B NMR (C_6D_6, 160 MHz) δ = 5.2; $^{13}C\{^1H\}$ NMR (CD_3OD, 126 MHz) δ = 58.9, 53.5, 24.6,

23.1, the carbon attached to boron was not observed; $^{19}F\{^{1}H\}$ NMR (CD_3OD, 376 MHz) δ = -142.8. Anal. Calcd for $C_7H_{14}NBO_2$: C, 38.37; H, 6.44; N, 6.39. Found: C, 38.61; H, 6.56; N, 6.20.

Table S1. Yields by GC of the borylation of fluorooctane as a function of the ratio of 1-fluorooctane:B_2pin_2:solvent.



Solvent = cyclohexane 1-fluorooctane:B_2pin_2:cyclohexane	Yield(%)	Solvent = cyclooctane 1-fluorooctane:B_2pin_2:cyclooctane	Yield(%)
10:1:10	55	10:1:10	61
1:1:3	39	1:1:3	32
1:2:3	40	1:2:3	18
10:1:0	83		
1:2:0	46		

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