

Pd-Catalyzed Regioselective Arylboration of Vinylarenes

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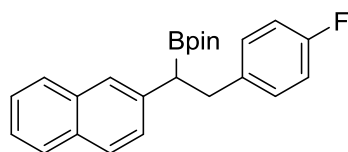
General. All experiments were conducted with a schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature using Bruker AVIII-500M spectrometers, chemical shifts (in ppm) were referenced to CDCl₃ (δ = 7.26 ppm) and DMSO-d₆ (δ = 2.50 ppm) as internal standards. ¹³C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl₃ (δ = 77.0 ppm), DMSO-d₆ (δ = 39.6 ppm). Some of vinylarenes was prepared from the corresponding aryl bromide or aryl triflates with potassium vinyltrifluoroborate according to previous literature.¹ The Aryldiazonium salts were prepared according to literature report.² Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and the most starting materials were purchased from Adamas.

¹ G. A. Molander, A. R. Brown, *J. Org. Chem.* **2006**, *71*, 9681-9686.

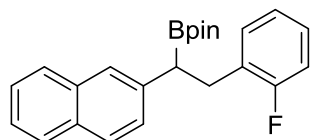
² R. Guo, H. Yang, P. Tang, *Chem. Commun.* **2015**, *51*, 8829-8832

I. General procedure A for the preparation of 1,2-arylboration product from vinylarenes and aryldiazonium tetrafluoroborates.

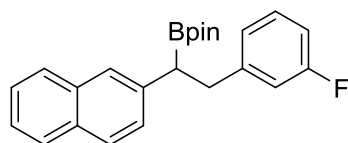
In air, a 25 mL schlenk tube was charged with aryldiazonium tetrafluoroborate (0.2 mmol, 1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), B₂pin₂ (56.0 mg, 0.22 mmol, 1.1 equiv) and K₃PO₄ (42 mg, 0.2 mmol, 1 equiv). The tube was evacuated and filled with nitrogen for three cycles. Vinylarene (0.2 mmol, 1 equiv) in 1 mL DCE was added at corresponding temperature. The reaction was allowed to stir at corresponding temperature for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 50:1-10:1) to afford the desired product.



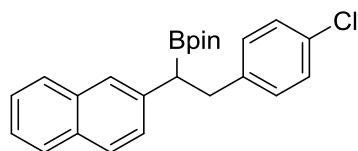
2-(2-(4-fluorophenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3aa. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 60 mg of the product as a colorless oil (80%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.73 (m, 3H), 7.65 (s, 1H), 7.46 – 7.38 (m, 3H), 7.18-7.14 (m, 2H), 6.92-6.88 (m, 2H), 3.23 (dd, *J* = 13.6, 9.5 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.81 (dd, *J* = 9.3, 7.2 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 162. (d, *J* = 241.6 Hz), 139.8, 137.26 (d, *J* = 3.1 Hz), 133.7, 131.8, 130.2 (d, *J* = 7.8 Hz), 127.8, 127.5 (d, *J* = 3.5 Hz), 127.3, 126.3, 125.7, 124.9, 114.8, 114.6, 83.5, 37.7, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰FO₂: 375.2046, found 375.2050.



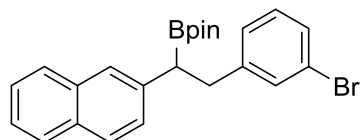
2-(2-(2-fluorophenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ab. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 2-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 47 mg of the product as a colorless oil (63%). ¹H NMR (500 MHz, CDCl₃) δ 7.80 – 7.73 (m, 3H), 7.66 (s, 1H), 7.45 – 7.37 (m, 3H), 7.19-7.15 (m, 1H), 7.14-7.08 (m, 1H), 6.98 – 6.93 (m, 2H), 3.28 (dd, *J* = 13.7, 9.2 Hz, 1H), 3.10 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.92 (dd, *J* = 8.8, 7.8 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 243.6 Hz), 139.8, 133.7, 131.8, 131.0 (d, *J* = 5.0 Hz), 128.4 (d, *J* = 15.7 Hz), 127.7, 127.5 (d, *J* = 2.3 Hz), 127.4, 126.3, 125.6, 124.9, 123.5 (d, *J* = 3.5 Hz), 115.1, 114.9, 83.5, 31.6, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰FO₂: 375.2046, found 375.2050.



2-(2-(3-fluorophenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ac. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 3-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 56mg of the product as a colorless oil (74%). ¹H NMR (500 MHz, CDCl₃) δ 7.80 – 7.74 (m, 3H), 7.66 (s, 1H), 7.46 – 7.39 (m, 4H), 7.30 – 7.26 (m, 1H), 7.13-7.06 (m, 2H), 3.23 (dd, *J* = 13.4, 10.1 Hz, 1H), 3.02 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.81 (dd, *J* = 10.0, 7.0 Hz, 1H), 1.13 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 162.7 (d, *J* = 243.2 Hz), 144.3 (d, *J* = 7.2 Hz), 139.7, 133.7, 131.8, 129.4 (d, *J* = 8.3 Hz), 127.8, 127.5 (d, *J* = 3.4 Hz), 127.2, 126.2, 125.7, 125.0, 124.5 (d, *J* = 2.6 Hz), 115.8, 115.6, 112.6 (d, *J* = 21.0 Hz), 83.6, 38.3, 24.5, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰FO₂: 375.2046, found 375.2045.

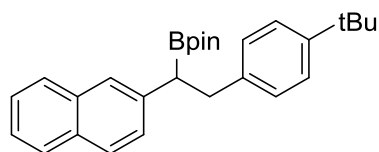


2-(2-(4-chlorophenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ad. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-chlorophenyldiazonium tetrafluoroborate (45 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 62 mg of the product as a colorless oil (79%). ¹H NMR (500 MHz, CDCl₃) δ 7.80 – 7.73 (m, 3H), 7.64 (s, 1H), 7.46 – 7.37 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.23 (dd, *J* = 13.7, 9.2 Hz, 1H), 3.03 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.81 (dd, *J* = 9.0, 7.5 Hz, 1H), 1.13 (m, 6H), 1.12 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 140.1, 139.7, 133.7, 131.8, 131.5, 130.2, 128.1, 127.8, 127.5, 127.4, 127.3, 126.3, 125.7, 125.0, 83.6, 37.9, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₆B¹⁰ClO₂: 391.1751, found 391.1750.

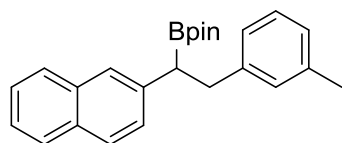


2-(2-(3-bromophenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ae. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-bromophenyldiazonium tetrafluoroborate (54 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 63 mg of the product as a light yellow oil (70%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.74 (m, 3H), 7.67 (s, 1H), 7.47 – 7.39 (m, 4H), 7.33 – 7.27 (m, 1H), 7.16 – 7.06 (m, 2H), 3.23 (dd, *J* = 13.4, 10.1 Hz, 1H), 3.02 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.81 (dd, *J* = 10.0, 6.5 Hz, 1H), 1.13 (s, 12H).

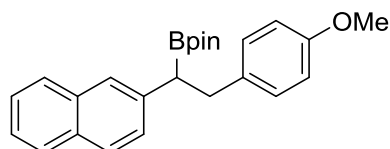
^{13}C NMR (126 MHz, CDCl_3) δ 144.1, 139.7, 133.7, 131.9, 131.8, 129.7, 128.9, 127.9, 127.6, 127.5, 127.5, 127.2, 126.2, 125.8, 125.0, 122.1, 83.6, 38.3, 24.6, 24.5. HRMS (EI) m/z calcd for $\text{C}_{24}\text{H}_{26}\text{B}^{10}\text{O}_2$: 435.1246, found 435.1242.



2-(2-(4-(tert-butyl)phenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3af. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-tert-butylphenyldiazonium tetrafluoroborate (50 mg 0.2 mmol, 1 equiv), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 5 mol%), K_3PO_4 (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 65 mg of the product as a white solid (78%). ^1H NMR (500 MHz, CDCl_3) δ 7.81-7.74 (m, 4H), 7.70 (s, 1H), 7.47 – 7.38 (m, 4H), 7.26 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 3.23 (dd, J = 13.5, 10.0 Hz, 1H), 3.07 (dd, J = 13.6, 6.7 Hz, 1H), 2.88 (dd, J = 10.0, 6.7 Hz, 1H), 1.29 (s, 9H), 1.11 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.6, 140.3, 138.5, 133.8, 131.8, 128.5, 127.7, 127.5, 127.4, 126.1, 125.6, 124.9, 124.8, 83.4, 38.0, 34.3, 31.4, 24.6, 24.4. HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{35}\text{B}^{10}\text{O}_2$: 413.2766, found 413.2758.

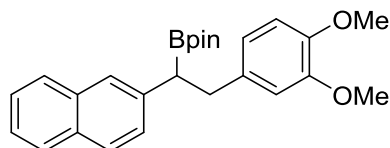


4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(m-tolyl)ethyl)-1,3,2-dioxaborolane, 3ag. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), *p*-tolyl diazonium tetrafluoroborate (41 mg, 0.2 mmol, 1 equiv), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 5 mol%), K_3PO_4 (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 53 mg of the product as a white solid (71%). ^1H NMR (500 MHz, CDCl_3) δ 7.81-7.49 (m, 3H), 7.70 (s, 1H), 7.47 – 7.38 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.09 (s, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 3.24 (dd, J = 13.4, 10.1 Hz, 1H), 3.04 (dd, J = 13.4, 6.5 Hz, 1H), 2.86 (dd, J = 10.1, 6.5 Hz, 1H), 2.30 (s, 3H), 1.12 (s, 6H), 1.11 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.6, 140.3, 137.5, 133.8, 131.8, 129.7, 128.0, 127.7, 127.5, 127.4, 126.5, 126.2, 125.9, 125.7, 124.9, 83.4, 38.6, 24.6, 24.5, 21.4. HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{29}\text{B}^{10}\text{O}_2$: 371.2297, found 371.2295.

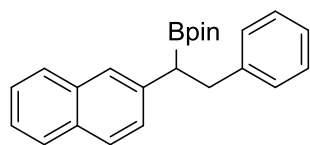


2-(2-(4-methoxyphenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ah. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-methoxyphenyldiazonium tetrafluoroborate (45 mg, 0.2 mmol, 1 equiv), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 5 mol%), K_3PO_4 (42 mg, 0.2 mmol, 1

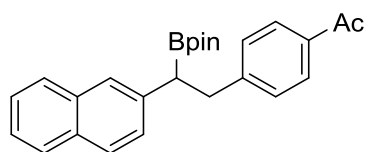
equiv), and 1 mL of DCE to afford 35 mg of the product as a white solid (45%). ¹H NMR (500 MHz, CDCl₃) δ 7.82 – 7.74 (m, 3H), 7.68 (s, 1H), 7.46 – 7.38 (m, 3H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.22 (dd, *J* = 13.6, 9.6 Hz, 1H), 3.02 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.83 (dd, *J* = 9.5, 7.0 Hz, 1H), 1.13 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 157.7, 140.2, 133.8, 133.7, 131.8, 129.8, 127.7, 127.5, 127.4, 126.3, 125.6, 124.8, 113.4, 83.4, 55.2, 37.6, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₅H₂₉B¹⁰O₃: 387.2246, found 387.2245.



2-(2-(3,4-dimethoxyphenyl)-1-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ai. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 3,4-dimethoxyphenyldiazonium tetrafluoroborate (50 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 45 mg of the product as a white solid (53%). ¹H NMR (500 MHz, CDCl₃) δ 7.79-7.74 (m, 3H), 7.66 (s, 1H), 7.44 – 7.37 (m, 3H), 6.77-6.69 (m, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.20 (dd, *J* = 13.6, 9.3 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.83 (dd, *J* = 9.1, 7.4 Hz, 1H), 1.13 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 148.3, 147.0, 140.0, 134.3, 133.7, 131.8, 127.7, 127.5, 127.4, 126.4, 125.7, 124.9, 120.7, 112.2, 110.9, 83.5, 55.8, 55.6, 38.2, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₆H₃₁B¹⁰O₄: 417.2352, found 417.2349.

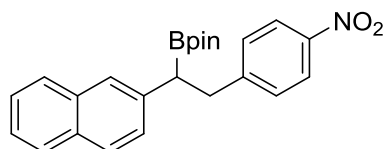


4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane, 3aj. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), phenyldiazonium tetrafluoroborate (38 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 51 mg of the product as a white solid (71%). ¹H NMR (500 MHz, CDCl₃) δ 7.82 – 7.75 (m, 3H), 7.69 (s, 1H), 7.47 – 7.39 (m, 4H), 7.25 – 7.22 (m, 3H), 7.19 – 7.12 (m, 1H), 3.28 (dd, *J* = 13.5, 9.7 Hz, 1H), 3.09 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.89 (dd, *J* = 9.6, 7.0 Hz, 1H), 1.14 (s, 6H), 1.13 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 141.6, 140.1, 133.8, 131.8, 128.8, 128.0, 127.7, 127.5, 127.4, 126.2, 125.8, 125.7, 124.9, 83.5, 38.6, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₇B¹⁰O₂: 357.2140, found 357.2147.

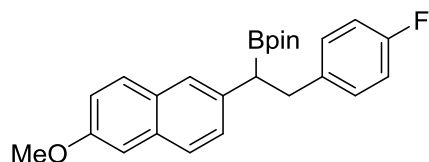


1-(4-(2-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3ak. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1

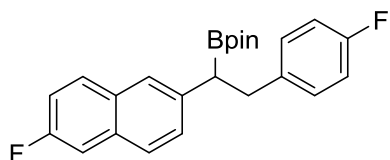
equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 55 mg of the product as a white solid (69%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.46 – 7.38 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.32 (dd, *J* = 13.6, 9.0 Hz, 1H), 3.12 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.55 (s, 3H), 1.13 (s, 6H), 1.12 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 147.6, 139.5, 134.9, 133.7, 131.8, 129.0, 128.3, 127.9, 127.5, 127.5, 127.2, 126.3, 125.7, 125.0, 83.6, 38.5, 26.5, 24.5. HRMS (EI) *m/z* calcd for C₂₆H₂₉B¹⁰O₃: 399.2246, found 399.2248.



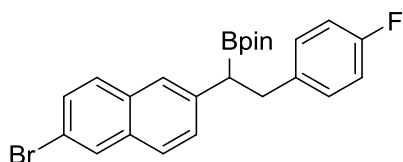
4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(4-nitrophenyl)ethyl)-1,3,2-dioxaborolane, 3al. The General procedure A was followed by using 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 52 mg of the product as a white solid (65%). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.80-7.73 (m, 3H), 7.60 (s, 1H), 7.46 – 7.39 (m, 2H), 7.36 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 3.36 (dd, *J* = 13.7, 8.6 Hz, 1H), 3.16 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.84 (t, *J* = 8.2 Hz, 1H), 1.15 (s, 6H), 1.13 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 149.7, 146.3, 138.9, 133.7, 131.9, 129.6, 128.1, 127.6, 127.5, 127.0, 126.4, 125.9, 125.2, 123.3, 83.8, 38.4, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₆B¹⁰NO₄: 402.1991, found 402.1985.



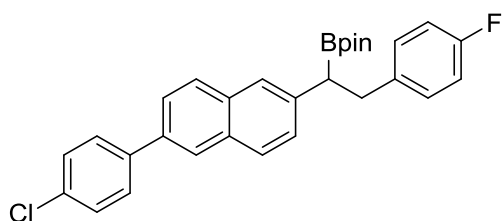
2-(2-(4-fluorophenyl)-1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ba. The General procedure A was followed by using 2-methoxy-6-vinylnaphthalene (36 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 45 mg of the product as a white solid (56%). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (dd, *J* = 8.5, 4.1 Hz, 2H), 7.57 (s, 1H), 7.36 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.17 – 7.09 (m, 4H), 6.93 – 6.87 (m, 2H), 3.91 (s, 3H), 3.20 (dd, *J* = 13.6, 9.5 Hz, 1H), 3.01 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.76 (dd, *J* = 9.4, 7.2 Hz, 1H), 1.11 (s, 6H), 1.11 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 162.1 (d, *J* = 241.6 Hz), 157.0, 137.4 (d, *J* = 7.6 Hz), 132.8, 130.2 (d, *J* = 7.8 Hz), 129.2, 129.0, 127.8, 126.7, 126.2, 118.5, 114.7 (d, *J* = 20.7 Hz), 105.5, 83.5, 55.3, 37.9, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₅H₂₈B¹⁰FO₃: 405.2152, found 405.2162.



2-(1-(6-fluoronaphthalen-2-yl)-2-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ca. The General procedure A was followed by using 2-fluoro-6-vinylnaphthalene (34 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), K₃PO₄ (42 mg, 0.2 mmol, 1 equiv), and 1 mL of DCE to afford 57 mg of the product as a white solid (72%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (dd, *J* = 9.0, 5.6 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 7.44 – 7.36 (m, 2H), 7.21 (td, *J* = 8.8, 2.6 Hz, 1H), 7.14 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 2H), 3.21 (dd, *J* = 13.6, 9.4 Hz, 1H), 3.01 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.79 (dd, *J* = 9.2, 7.4 Hz, 1H), 1.12 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 241.7 Hz), 161.1 (d, *J* = 243.0 Hz), 139.0 (d, *J* = 2.6 Hz), 137.1 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 9.1 Hz), 130.7, 130.2 (d, *J* = 7.8 Hz), 129.7 (d, *J* = 8.9 Hz), 128.3, 127.2 (d, *J* = 5.3 Hz), 126.3, 116.0 (d, *J* = 25.1 Hz), 114.7 (d, *J* = 20.8 Hz), 110.5 (d, *J* = 20.1 Hz), 83.6, 37.8, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰F₂O₂: 393.1952, found 393.1962.



2-(1-(6-bromonaphthalen-2-yl)-2-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3da. The General procedure A was followed by using 2-bromo-6-vinylnaphthalene (46 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), and K₃PO₄ (162 mg, 2.5 eq), and 1 mL of DCE to afford 55 mg of the product as a white solid (61%). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.63 (dd, *J* = 17.8, 8.6 Hz, 2H), 7.59 (s, 1H), 7.49 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.90 – 6.87 (m, 2H), 3.21 (dd, *J* = 13.6, 9.3 Hz, 1H), 3.01 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.79 (dd, *J* = 9.1, 7.4 Hz, 1H), 1.12 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 162.1 (d, *J* = 241.8 Hz), 140.4, 137.0 (d, *J* = 3.2 Hz), 132.9, 132.1, 130.2 (d, *J* = 7.8 Hz), 129.5, 129.1 (d, *J* = 11.8 Hz), 128.3, 126.9, 126.3, 118.8, 114.8 (d, *J* = 20.8 Hz), 83.6, 37.6, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰BrFO₂: 453.1151, found 453.1154.

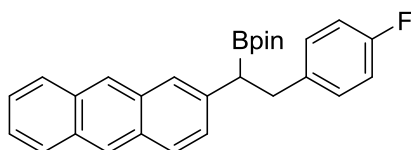


2-(1-(6-(4-chlorophenyl)naphthalen-2-yl)-2-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ea. The General procedure A was followed by using 2-(4-chlorophenyl)-6-vinylnaphthalene (53 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium

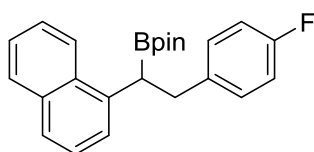
tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), and K₃PO₄ (162 mg, 2.5 eq), and 1 mL of DCE to afford 67 mg of the product as a white solid (68%).

¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 0.8 Hz, 1H), 7.82 (dd, *J* = 14.3, 8.5 Hz, 2H), 7.67 – 7.62 (m, 4H), 7.46 – 7.42 (m, 3H), 7.17 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 3.25 (dd, *J* = 13.6, 9.3 Hz, 1H), 3.05 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.84 (dd, *J* = 9.1, 7.5 Hz, 1H), 1.14 (s, 6H), 1.13 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 241.7 Hz), 140.3, 139.7, 137.22 (d, *J* = 3.1 Hz), 136.4, 133.2, 133.0, 132.0, 130.2 (d, *J* = 7.8 Hz), 128.9, 128.5, 128.2, 128.1, 128.0, 126.1, 125.4, 125.1, 114.9, 114.7, 83.6, 37.7, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₃₀H₂₉B¹⁰ClFO₂: 485.1969, found 485.1970.



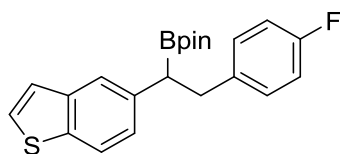
2-(1-(anthracen-2-yl)-2-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3fa. The General procedure A was followed by using 2-vinylanthracene (40 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), and K₃PO₄ (162 mg, 2.5 eq), and 1 mL of DCE to afford 66 mg of the product as a white solid (78%). ¹H NMR (500 MHz, CDCl₃) δ 8.37 (s, 1H), 8.33 (s, 1H), 7.98 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.78 (s, 1H), 7.48 – 7.39 (m, 3H), 7.18 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 3.27 (dd, *J* = 13.6, 9.4 Hz, 1H), 3.09 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.86 (dd, *J* = 9.0, 7.4 Hz, 1H), 1.15 (s, 6H), 1.14 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 241.7 Hz), 139.2, 137.2 (d, *J* = 3.1 Hz), 132.0, 131.7, 131.2, 130.5, 130.2 (d, *J* = 7.8 Hz), 128.1, 128.0, 128.0, 127.4, 125.8 (d, *J* = 8.8 Hz), 125.4, 125.2, 124.9, 114.9, 114.7, 83.6, 37.4, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₈H₂₈B¹⁰FO₂: 425.2203, found 425.2214.



2-(2-(4-fluorophenyl)-1-(naphthalen-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ga, The General procedure A was followed by using 1-vinylnaphthalene (40 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (31 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), and K₃PO₄ (162 mg, 2.5 eq), and 1 mL of DCE to afford 33 mg of the product as a colorless oil 43%).

¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.71 – 7.67 (m, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.37 (m, 2H), 7.17 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 3.37 (dd, *J* = 9.5, 6.3 Hz, 1H), 3.28 (dd, *J* = 13.3, 9.6 Hz, 1H), 3.09 (dd, *J* = 13.3, 6.3 Hz, 1H), 1.13 (s, 6H), 1.11 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 241.8 Hz), 138.8, 137.5, 134.0, 131.9, 130.2 (d, *J* = 7.7 Hz), 128.8, 126.2, 125.8, 125.6, 125.5, 125.5, 125.3, 123.9, 114.7 (d, *J* = 20.8 Hz), 83.6, 37.5, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₄H₂₅B¹⁰FO₂: 375.2046, found 375.2040.

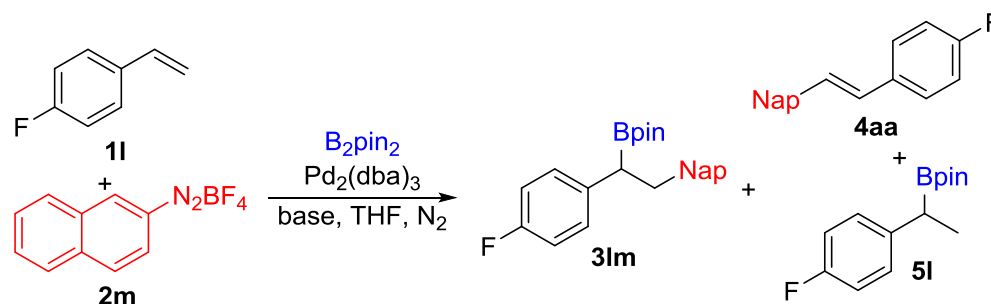


2-(1-(benzo[b]thiophen-5-yl)-2-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ha, The General procedure A was followed by using 5-vinylbenzo[b]thiophene (32 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (31 mg 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), and K₃PO₄ (162 mg, 2.5 eq), and 1 mL of DCE to afford 45 mg of the product as a white solid (59%).

¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.17 – 7.11 (m, 2H), 6.90 (t, *J* = 8.8 Hz, 2H), 3.18 (dd, *J* = 13.6, 9.5 Hz, 1H), 2.98 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.75 (dd, *J* = 9.4, 7.2 Hz, 1H), 1.12 (s, 6H), 1.12 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 161.2 (d, *J* = 241.0 Hz), 140.0, 138.4, 137.3 (d, *J* = 3.1 Hz), 137.0, 130.2 (d, *J* = 7.8 Hz), 126.2, 125.3, 123.8, 123.0, 122.2, 114.7 (d, *J* = 20.8 Hz), 83.5, 38.3, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₂H₂₄B¹⁰FO₂S: 381.1610, found 381.1603.

Table S1. Condition screening.^a

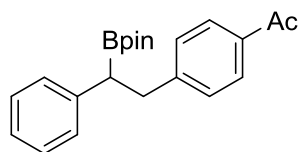


entry	base	temp (°C)	3Im (%) ^b	4aa (%) ^b	5I (%) ^b
1	Na ₂ CO ₃	rt	35	30	30
2	K ₂ CO ₃	rt	30	34	34
3	Cs ₂ CO ₃	rt	28	21	21
4	KOAc	rt	32	25	25
5	K ₃ PO ₄	rt	32	33	33
6	K ₂ HPO ₄	rt	29	31	31
7	NaHCO ₃	rt	34	29	29
8	Na ₂ CO ₃	0	40	26	26
9 ^c	Na ₂ CO ₃	0	53	21	21
10 ^d	Na ₂ CO ₃	0	68	14	14

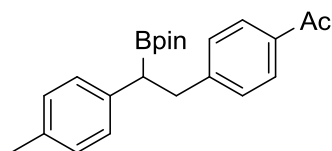
^a Reaction conditions: 1-fluoro-4-vinylbenzene **1I** (0.2 mmol), aryldiazonium salt **2m** (1 equiv), Pd₂(dba)₃ (5 mol %), B₂pin₂ (1.1 equiv), base (1 equiv), THF (1 mL), N₂, 24 h; ^b GC yield; ^c Pd₂(dba)₃ (10 mol %); ^d Pd₂(dba)₃ (15 mol %). The products of **3Im** and **5I** did not get the clean NMR.

II. General procedure B for the preparation of 1,2-arylboration product from styrenes and aryldiazonium tetrafluoroborates.

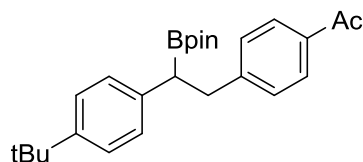
In air, a 25 mL schlenk tube was charged with aryldiazonium tetrafluoroborate (0.2 mmol, 1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), B₂pin₂ (56.0 mg, 0.22 mmol, 1.1 equiv) and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. Styrene (0.2 mmol, 1 equiv) of 1 mL THF was added at 0°C. The reaction was allowed to stir at 0°C for 24 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 10:1) to afford the desired product.



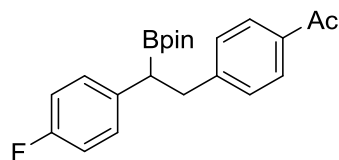
1-(4-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3ik. The General procedure B was followed by using styrene (21 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 41mg of the product as a white solid (58%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.21-7.19 (m, 2H), 7.17 – 7.12 (m, 1H), 3.21 (dd, *J* = 13.6, 9.1 Hz, 1H), 3.00 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.67 (dd, *J* = 8.9, 7.6 Hz, 1H), 2.56 (s, 3H), 1.13 (s, 6H), 1.12 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 147.7, 141.9, 134.9, 129.0, 128.4, 128.3, 125.6, 83.5, 38.7, 26.5, 24.5. HRMS (EI) *m/z* calcd for C₂₂H₂₇B¹⁰O₃: 349.2090, found 349.2097.



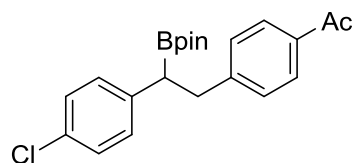
1-(4-(2-(4-methylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3jk. The General procedure B was followed by using 1-methyl-4-vinylbenzene (24 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 38 mg of the product as a white solid (53%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.18 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.97 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.63 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.56 (s, 3H), 2.29 (s, 3H), 1.12 (s, 6H), 1.11 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 147.8, 138.7, 134.9, 134.9, 129.1, 129.0, 128.2, 83.5, 38.9, 26.5, 24.6, 24.5, 21.0. HRMS (EI) *m/z* calcd for C₂₃H₂₉B¹⁰O₃: 363.2246, found 363.2253.



1-(4-(2-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3kk. The General procedure B was followed by using 1-(tert-butyl)-4-vinylbenzene (32 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 41 mg of the product as a white solid (50%). ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.28-7.26 (m, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 3.18 (dd, *J* = 13.5, 9.9 Hz, 1H), 2.99 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.66 (d, *J* = 6.7 Hz, 1H), 2.57 (s, 3H), 1.30 (s, 9H), 1.11 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 148.3, 147.9, 138.8, 134.9, 129.1, 128.2, 127.9, 125.3, 83.5, 39.0, 34.3, 31.4, 26.6, 24.6, 24.5. HRMS (EI) *m/z* calcd for C₂₆H₃₅B¹⁰O₃: 405.2716, found 405.2711.

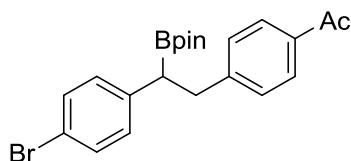


1-(4-(2-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3lk. The General procedure B was followed by using 1-fluoro-4-vinylbenzene (24 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 42 mg of the product as a white solid (57%). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 8.7, 5.4 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 3.17 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.95 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.64 (t, *J* = 8.2 Hz, 1H), 2.56 (s, 3H), 1.13 (s, 6H), 1.12 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 197.9, 161(d, *J* = 241.7 Hz), 147.3, 137.4 (d, *J* = 3.2 Hz), 135.0, 129.7 (d, *J* = 7.8 Hz), 129.0, 128.2, 115.1(d, *J* = 20.8 Hz), 83.6, 38.8, 26.5, 24.5. HRMS (EI) *m/z* calcd for C₂₂H₂₆B¹⁰FO₃: 367.1995, found 367.2001.

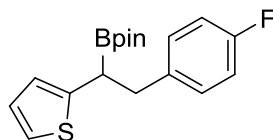


1-(4-(2-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3mk. The General procedure B was followed by using 1-chloro-4-vinylbenzene (27 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv), Pd₂(dba)₃ (27.5 mg, 15 mol%), and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 41 mg of the product as a white solid (54%). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.20 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.98 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.66 (t, *J* = 8.7 Hz, 1H), 2.58 (s, 3H), 1.16 (s, 6H), 1.15 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 197.9, 147.2,

140.4, 135.0, 131.3, 129.7, 129.0, 128.5, 128.3, 83.7, 38.5, 26.5, 24.5. HRMS (EI) m/z calcd for $C_{22}H_{26}B^{10}ClO_3$: 383.1700, found 383.1698.

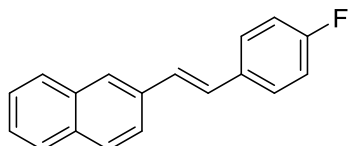


1-(4-(2-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one, 3nk. The General procedure B was followed by using 1-bromo-4-vinylbenzene (36 mg, 0.2 mmol, 1 equiv), 4-acetylphenyldiazonium tetrafluoroborate (47 mg, 0.2 mmol, 1 equiv), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (27.5 mg, 15 mol%), and Na_2CO_3 (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 41 mg of the product as a white solid (48%). 1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.18 (dd, J = 13.6, 8.6 Hz, 1H), 2.95 (dd, J = 13.6, 7.9 Hz, 1H), 2.62 (t, J = 8.2 Hz, 1H), 2.56 (s, 3H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 147.1, 140.9, 135.0, 131.4, 130.1, 129.0, 128.3, 119.3, 83.7, 38.5, 26.5, 24.5. HRMS (EI) m/z calcd for $C_{22}H_{26}B^{10}BrO_3$: 427.1195, found 427.1200.



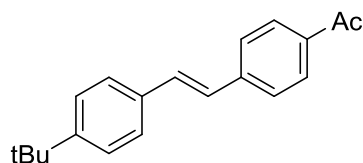
2-(2-(4-fluorophenyl)-1-(thiophen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3ol. The General procedure B was followed by using 1-bromo-4-vinylbenzene (36 mg, 0.2 mmol, 1 equiv), 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (27.5 mg, 15 mol%), and Na_2CO_3 (23 mg, 0.2 mmol, 1 equiv), and 1 mL of THF to afford 47 mg of the product as a light yellow oil (71%). 1H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 2H), 7.08 (dd, J = 5.1, 0.9 Hz, 1H), 6.94 – 6.88 (m, 3H), 6.78 (d, J = 3.4 Hz, 1H), 3.09 (dd, J = 13.4, 9.6 Hz, 1H), 3.00 (dd, J = 13.4, 6.9 Hz, 1H), 2.94 (dd, J = 9.4, 7.0 Hz, 1H), 1.15 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3(d, J = 242.0 Hz), 145.0, 136.7 (d, J = 3.2 Hz), 130.2 (d, J = 7.8 Hz), 126.7, 124.1, 122.9, 114.7(d, J = 21.0 Hz), 83.8, 39.0, 24.6, 24.5. HRMS (EI) m/z calcd for $C_{18}H_{22}B^{10}FO_2S$: 331.1454, found 331.1462.

III. Byproducts from Heck reaction or hydroboration reaction.

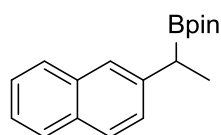


(E)-2-(4-fluorostyryl)naphthalene, 4aa. In air, a 25 mL schlenk tube was charged with 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 5 mol%), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv) and Cs_2CO_3 (66 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. 2-vinylnaphthalene (31 mg, 0.2 mmol, 1 equiv) of 1 mL *t*-Amyl-OH was added at room temperature. The reaction was allowed to stir at 60 °C for 12 hours. Upon completion, the reaction mixture was diluted with

ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford 7.2 mg of the product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.87 – 7.81 (m, 4H), 7.73 (dd, J = 8.6, 1.7 Hz, 1H), 7.54-7.45 (m, 4H), 7.20 (s, 2H), 7.12 – 7.05 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.3 (d, J = 245.8 Hz), 134.6, 133.7, 133.5 (d, J = 3.4 Hz), 133.0, 128.5 (d, J = 2.4 Hz), 128.3, 128.0, 127.9, 127.7 (d, J = 9.2 Hz), 126.6, 126.4, 125.9, 123.4, 115.7, 115.6. The analytical data for this compound was in agreement with the reported data.³



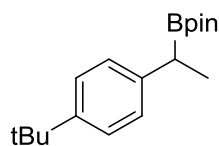
(E)-1-(4-(4-(tert-butyl)styryl)phenyl)ethan-1-one, 4kk. In air, a 25 mL schlenk tube was charged with 4-acetylphenyldiazonium tetrafluoroborate (47 mg 0.2 mmol, 1 equiv), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 5 mol%), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv) and Na_2CO_3 (23 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. 4-tert-Butylstyrene (32 mg, 0.2 mmol, 1 equiv) of 1 mL THF was added at room temperature. The reaction was allowed to stir at 70 °C for 6 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford 7.2 mg of the product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 16.3 Hz, 1H), 7.10 (d, J = 16.4 Hz, 1H), 2.61 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.5, 151.60, 142.2, 135.7, 133.9, 131.3, 128.8, 126.6, 126.5, 126.4, 125.7, 34.7, 31.2, 26.6. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: 278.1671, found 278.1675.



4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane, 5a. In air, a 25 mL schlenk tube was charged with 4-fluorophenyldiazonium tetrafluoroborate (42 mg 0.2 mmol, 1 equiv), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 5 mol%), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv) and Cs_2CO_3 (26 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. 2-vinylnaphthalene (31 mg, 0.2 mmol, 1 equiv) of 1 mL *t*-Amyl-OH was added at room temperature. The reaction was allowed to stir at 60 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford 12 mg of the product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.74 (m, 3H), 7.65 (d, J = 0.7 Hz, 1H), 7.45-7.38 (m, 3H), 2.63 (q, J = 7.4 Hz, 1H), 1.44 (d, J = 7.5 Hz, 3H), 1.22 (d, J = 7.7 Hz, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.5, 133.8, 131.9, 127.6,

³ A. R. Ehle, Q. Zhou, M. P. Watson, *Org. Lett.* **2012**, *14*, 1202-1205.

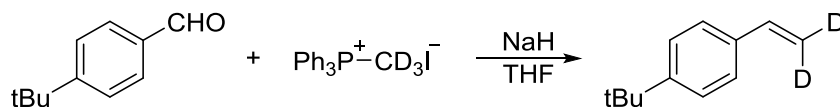
127.5, 127.4, 127.2, 125.6, 125.2, 124.7, 83.4, 24.6, 24.6, 16.8. The analytical data for this compound was in agreement with the reported data.⁴



2-(1-(4-(tert-butyl)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 5k. In air, a 25 mL schlenk tube was charged with 4-acetylphenyldiazonium tetrafluoroborate (47 mg 0.2 mmol, 1 equiv), Pd₂(dba)₃ (9.2 mg, 5 mol%), B₂pin₂ (56 mg, 0.22 mmol, 1.1 equiv) and Na₂CO₃ (23 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. 4-tert-Butylstyrene (32 mg, 0.2 mmol, 1 equiv) of 1 mL THF was added at room temperature. The reaction was allowed to stir at 70 °C for 6 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford 8.0 mg of the product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.41 (q, *J* = 7.5 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 9H), 1.22 (d, *J* = 6.0 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 147.6, 141.7, 127.3, 125.2, 83.2, 34.2, 31.4, 24.6, 24.6, 17.2. HRMS (EI) *m/z* calcd for C₁₈H₂₉B¹⁰O₂: 287.2297, found 287.2294.

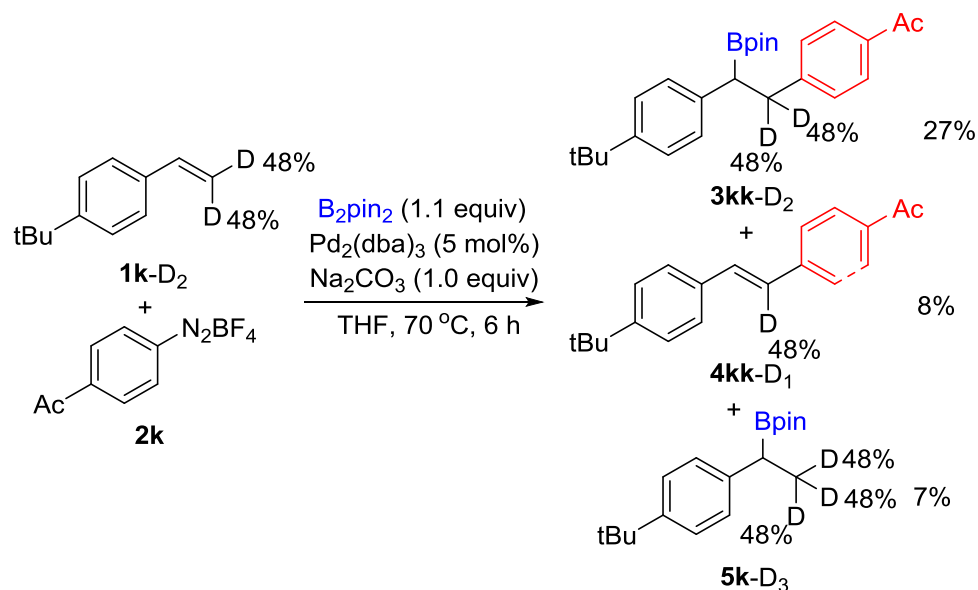
IV. Mechanistic experiments.

1. Synthesis of 4-tert-Butylstyrene-β,β-d₂



To a suspension of methyl-d₃-triphenylphosphonium iodide (0.41 g, 1 mmol) and 4-tert-Butylbenzaldehyde (130 mg, 0.8 mmol) in dry THF (4 mL) was added NaH (40%) (120 mg, 3 mmol) at 0 °C. The reaction was stirred at r.t. overnight. The mixture was diluted with CH₂Cl₂, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude reaction mixture was purified on silica gel (pentane: ethyl acetate = 200:1) to afford the desired product as colorless oil. (yield 68%, deuterated ratio 48%). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.35 (m, 4H), 6.73 – 6.68 (m, 1H), 5.74 – 5.68 (m, 0.52H), 5.21 – 5.18 (m, 0.52H), 1.33 (s, 9H).

⁴ C. Zarate, R. Manzano, R. Martin, *J. Am. Chem. Soc.* **2015**, *137*, 6754-6757.



2. General procedure C for isotope labelled experiment

In air, a 25 mL schlenk tube was charged with 4-acetylphenyldiazonium tetrafluoroborate (47 mg 0.2 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 5 mol%), B_2pin_2 (56 mg, 0.22 mmol, 1.1 equiv) and Na_2CO_3 (23 mg, 0.2 mmol, 1 equiv). The flask was evacuated and filled with nitrogen for three cycles. 4-tert-Butylstyrene- β,β - d_2 (32 mg, 0.2 mmol, 1 equiv) of 1 mL THF was added at room temperature. The reaction was allowed to stir at 70 °C for 6 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

V. NMR Spectroscopic Data

