Supporting information for:

Asymmetric Cobalt Catalysts for Hydroboration of 1,1-Disubstuted Alkenes

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I. General Information

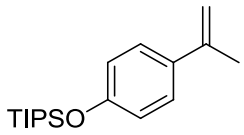
Ether, THF, and Toluene were distilled from sodium benzophenone ketyl prior to use. Pinacolborane (HBPin) (97%) was purchased from TCI and used as received. $NaHBEt_3$ (1.0 M in toluene) was purchased from Aldrich and used as received. $CoCl_2$ (99.5%) was purchased from Aldrich and used as received. (*S*)-2-Amino-3-phenylpropan-1-ol, (S)-2-amino-3,3-dimethylbutan-1-ol, (S)-2-amino-3-methylbutan-1-ol and were prepared according to a previously reported procedure.[1] The other commercial available chemicals were used as received.

NMR spectra were recorded on a Bruker-400 instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$; 1.32 ppm, CD_3CN), ^{11}B NMR chemical shifts were referenced to an external BF_3-Et_2O standard, ^{19}F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. HPLC analyses were performed on a Shimadzu SPD-20A or Agilent 1100 series. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electrospray ionization-time of flight).

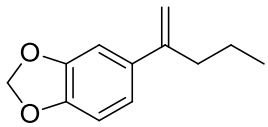
[1] McKennon, M. J.; Meyers, A. I. *J. Org. Chem.* **1993**, *58*, 3568.

II. Procedures for synthesis of starting material

All ketones were purchased from Energy and used as received. α-Methylstyrene was purchased from Energy and purified by distillation. *tert*-Butyldimethyl((4-(prop-1-en-2-yl)benzyl)oxy)silane and tert-butyldimethyl((4-phenylpent-4-en-1-yl)oxy)silane were prepared according to a previously reported procedure[3] using corresponding alcohol as starting material, which were prepared according to previously reported procedures using corresponding ester as starting material.[2] All other alkenes were prepared by Wittig olefination of the corresponding ketones according to previously reported procedures.[3,4]



Triisopropyl(4-(prop-1-en-2-yl)phenoxy)silane. Prepared according to a previously reported procedure[5] using 4-(prop-1-en-2-yl)phenol as the starting material, 92% yield, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.31 (m, 2H), 6.85-6.80 (m, 2H), 5.28 (s, 1H), 4.97 (s, 1H), 2.12 (s, 3H), 1.30-1.20 (m, 3H), 1.10 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 155.6, 142.6, 133.9, 126.5, 119.5, 110.5, 21.9, 17.9, 12.7; HRMS (EI) calculated for $[C_{18}H_{30}OSi]^+$ requires m/z 290.2066, found m/z 290.2069.



5-(Pent-1-en-2-yl)benzo[d][1,3]dioxole. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 6.93-6.86 (m, 2H), 6.79-6.74 (m, 1H), 5.94 (s, 2H), 5.22 (d, J = 1.4 Hz, 1H), 4.96 (d, *J* = 1.4 Hz, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.52-1.41 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.9, 147.6, 146.8, 135.8, 119.5, 111.3, 107.9, 106.7, 100.9, 37.6, 21.3, 13.7; HRMS (EI) calculated for

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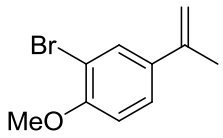
[2] da Costa, J. C. S.; Pais, K. C.; Fernandes, E. L.; de Oliveira, P. S. M.; Mendonça, J. S.; de Souza, M. V. N.; Peralta, M. A.; Vasconcelos, T. R. A. *ARKIVOC* **2006**, 128.

[3] Smith, C. R.; Zhang, A.; Mans, D. J.; RajanBabu, T. V. *Org. Synth*. **2008**, *85*, 248.

[4] Yılmaz, M. *Tetrahedron* **2011**, *67*, 8255.

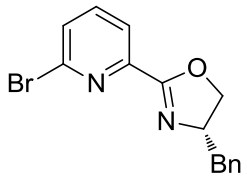
[5] Ikawa, T.; Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2004**, *60*, 6901.

$[C_{12}H_{14}O_2]^+$ requires m/z 190.0994, found m/z 190.0992.

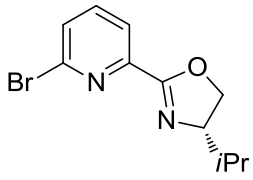


2-Bromo-1-methoxy-4-(prop-1-en-2-yl)benzene. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.66 (d, J = 2.0 Hz, 1H), 7.37 (dd, J = 8.6, 2.2 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 5.28 (s, 1H), 5.02 (s, 1H), 3.90 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.2, 141.4, 135.2, 130.5, 125.5, 111.8, 111.5, 56.3, 21.7; HRMS (EI) calculated for $[C_{10}H_{11}BrO]^+$ requires m/z 225.9993, found m/z 225.9992.

III. Procedures for Preparation of Metal Complexes



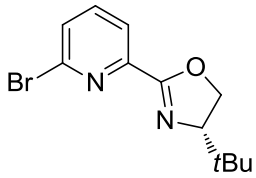
(*S*)-4-benzyl-2-(6-bromopyridin-2-yl)-4,5-dihydrooxazole (S2a). Prepared according to a previously reported procedure,[6] using 5.5051 g (30 mmol) of 6-bromopicolinonitrile, 5.0503 g (33 mmol) of (*S*)-2-amino-3-phenylpropan-1-ol, 12.0123 g (33 mmol) of $Zn(OTf)_2$, 300 mL of toluene, give 6.6612 g (21 mmol, 70% yield) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.66-7.57 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 3H), 4.67-4.62 (m, 1H), 4.45 (dd, *J* = 9.2, 8.8 Hz, 1H), 4.23 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.27 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.75 (dd, *J* = 14.0, 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 161.7, 147.4, 141.8, 138.7, 137.4, 130.2, 129.0, 128.4, 126.5, 122.7, 72.5, 67.9, 41.4; HRMS (EI) calculated for $[C_{15}H_{13}BrN_2O]^+$ requires m/z 316.0211, found m/z 316.0209.



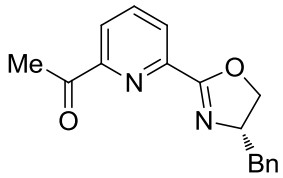
(*S*)-2-(6-bromopyridin-2-yl)-4-isopropyl-4,5-dihydrooxazole (S2b). Prepared according to a

[6] Aranda, C.; Cornejo, A.; Fraile, J. M.; Verdugo, E. G.; Gil, M. J.; Luis, S. V.; Mayoral, J. A.; Merino, V. M.; Ochoa, Z. *Green Chem.*, **2011**, *13*, 983.

previously reported procedure,[6] using 4.6476 g (26 mmol) of 6-bromopicolinonitrile, 2.90 g (28 mmol) of (S)-2-amino-3-methylbutan-1-ol, 10.22 g (28 mmol) of $Zn(OTf)_2$, 500 mL of toluene, give 6.30 g (24 mmol, 93% yield) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (dd, J = 7.2, 1.2 Hz, 1H), 7.66-7.56 (m, 2H), 4.51 (dd, J = 9.4, 8.2 Hz, 1H), 4.23 (dd, J = 8.4, 8.2 Hz, 1H), 4.20-4.11 (m, 1H), 1.93-1.84 (m, 1H), 1.04 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 161.4, 147.8, 141.9, 138.7, 130.1, 122.8, 72.9, 70.9, 32.7, 18.9, 18.1; HRMS (EI) calculated for $[C_{11}H_{13}BrN_2O]^+$ requires m/z 268.0211, found m/z 268.0213.

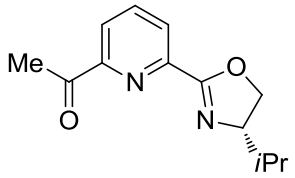


(*S*)-2-(6-bromopyridin-2-yl)-4-(tert-butyl)-4,5-dihydrooxazole (S2c). Prepared according to a previously reported procedure,[6] using 10.51 g (57 mmol) of 6-bromopicolinonitrile, 7.37 g (63 mmol) of (S)-2-amino-3,3-dimethylbutan-1-ol, 22.91 g (63 mmol) of $Zn(OTf)_2$, 1000 mL of toluene, give 12.4559 g (44 mmol, 77% yield) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (dd, J = 7.2, 1.2 Hz, 1H), 7.65-7.55 (m, 2H), 4.45 (dd, J = 10.2, 9.0 Hz, 1H), 4.32 (dd, J = 8.8, 8.6 Hz, 1H), 4.11 (dd, J = 10.2, 8.6 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 161.3, 147.9, 141.8, 138.6, 130.1, 122.9, 77.3, 77.0, 76.7, 76.5, 69.5, 34.0, 25.9; HRMS (EI) calculated for $[C_{12}H_{15}BrN_2O]^+$ requires m/z 282.0368, found m/z 282.0370.

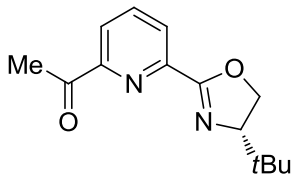


(*S*)-1-(6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethanone (S3a). To a 100 mL round-bottom flask with 1.8960 g (6.0 mmol) of S2a and 50 mL of dry ether under nitrogen atmosphere at -78 ^{o}C, a solution of *n*-BuLi (2.4 mL, 2.5 M in hexane, 6.0 mmol) in 10 mL of ether was added dropwise over 20 min. The mixture was stirred for 1 h, then added with 1.2 mL (12 mmol, 0.94 g/mL) of DMA. After 2 h, the resulting mixture was allowed to warm to room temperature and treated with water (20 mL). The separated organic phase was washed with brine

(20 mL x 3) and dried over Na_2SO_4, flitered, and concentrated. The residue was purified by flash column chromatography using 5:1 PE/EtOAc as the eluent to give 0.6515 g (2.3 mmol, 39% yield) of the title compound as a yellow oil. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.23 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.13 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.92 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.35-7.21 (m, 5H), 4.74-4.64 (m, 1H), 4.48 (dd, *J* = 9.4, 8.8 Hz, 1H), 4.27 (dd, *J* = 8.4, 7.8 Hz, 1H), 3.30 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.83-2.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 199.3, 162.4, 153.2, 146.1, 137.4, 137.3, 129.0, 128.4, 127.1, 126.4, 123.1, 72.3, 67.9, 41.4, 25.5; HRMS (EI) calculated for $[C_{17}H_{16}N_2O_2]^+$ requires m/z 280.1212, found m/z 280.1208.

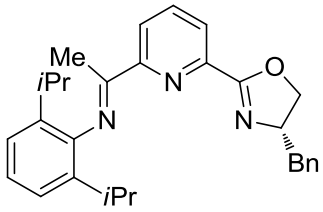


(*S*)-1-(6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethanone (S3b). Prepared according to the procedure of S3a, using 0.5365 g (2.0 mmol) of S2b, 0.80 mL (2.0 mmol, 2.5 M in hexane) of *n*-BuLi, 240 μL (2.4 mmol, 0.94 g/mL) of DMA, and 20 mL of ether, give 0.1622 g (0.70 mmol, 35% yield) of the title compound as a yellow oil. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.30-8.22 (m, 1H), 8.16-8.08 (m, 1H), 7.93 (dd, J = 8.0, 7.8 Hz, 1H), 4.61-4.52 (m, 1H), 4.31-4.23 (m, 1H), 4.23-4.14 (m, 1H), 2.80 (s, 3H), 1.98-1.84 (m, 1H), 1.08 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 199.5, 162.0, 153.3, 146.4, 137.3, 127.3, 123.1, 72.8, 70.8, 32.7, 25.6, 18.9, 18.1; HRMS (EI) calculated for $[C_{13}H_{16}N_2O_2]^+$ requires m/z 232.1212, found m/z 232.1211.

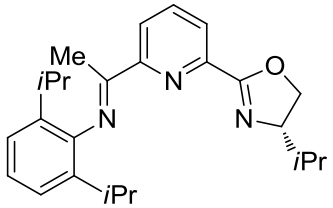


(*S*)-1-(6-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethanone (S3c). Prepared according to the procedure of S3a, using 0.8413 g (3.0 mmol) of S2c, 1.2 mL (3.0 mmol, 2.5 M in hexane) of *n*-BuLi, 360 μL (3.6 mmol, 0.94 g/mL) of DMA, and 30 mL of ether, give 0.2955 g (1.2 mmol, 40% yield) of the title compound as a yellow oil. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.30 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.92 (dd, J = 7.8, 7.8 Hz, 1H), 4.55-4.45 (m, 1H),

4.41-4.29 (m, 1H), 4.21-4.08 (m, 1H), 2.80 (s, 3H), 0.99 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 199.7, 162.0, 153.3, 146.5, 137.4, 127.4, 123.1, 76.4, 69.5, 33.9, 25.9, 25.6; HRMS (EI) calculated for $[C_{14}H_{18}N_2O_2]^+$ requires m/z 246.1368, found m/z 246.1366.

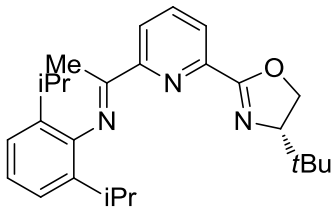


(*S*)-(-)-*N*-(1-(6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylanili ne (1a). A 100 mL Schlenk flask was charged with 1.20 g (4.3 mmol) of S3a, 45 mL of MeOH, 0.9 mL (4.8 mmol, 0.94 g/mL) of 2,6-diisopropylaniline and 45 μL of HCOOH in nitrogen atmosphere, then the mixture was refluxed for 24 h. The resulting mixture was concentrated, and purified by flash column chromatography using 3:1 PE/EtOAc as the eluent to give 0.78 g (1.8 mmol, 41% yield) of the title compound as a pale yellow solid. Optical Rotation: $[\alpha]^{20}_D$ = -1.5 (c 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.35-7.21 (m, 5H), 7.19-7.13 (m, 2H), 7.12-7.06 (m, 1H), 4.74-4.64 (m, 1H), 4.47 (dd, *J* = 9.4, 8.6 Hz, 1H), 4.27 (dd, *J* = 8.6, 8.0 Hz, 1H), 3.33 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.83-2.67 (m, 3H), 2.30 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 166.7, 163.2, 156.2, 146.3, 145.9, 137.7, 137.0, 135.6, 129.2, 128.6, 126.6, 125.3, 123.6, 123.2, 122.9, 72.5, 68.2, 41.7, 28.2, 23.2, 22.8, 17.2; HRMS (EI) calculated for $[C_{29}H_{33}N_3O]^+$ requires m/z 439.2624, found m/z 439.2621.

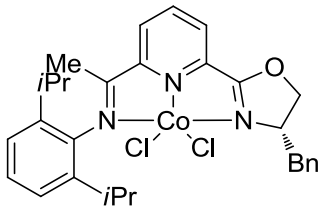


(*S*,*E*)-2,6-diisopropyl-N-(1-(6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)ani

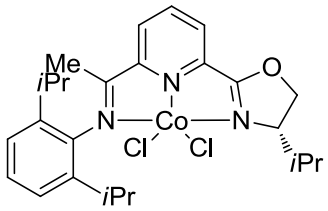
line (1b). Prepared according to the procedure of 1a, using 1.03 g (4.2 mmol) of S3b, 42 mL of MeOH, 0.9 mL (4.8 mmol, 0.94 g/mL) of 2,6-diisopropylaniline and 42 μL of HCOOH, give 0.6495 g (1.7 mmol, 40% yield) of the title compound as a pale yellow solid. Optical Rotation: $[\alpha]^{20}_{D}$ = -53.7 (c 1.03, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.51 (dd, *J* = 7.8, 0.8 Hz, 1H), 8.19 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.20-7.13 (m, 2H), 7.13-7.06 (m, 1H), 4.60-4.51 (m, 1H), 4.25 (dd, *J* = 8.4, 8.2 Hz, 1H), 4.23-4.15 (m, 1H), 2.79-2.67 (m, 2H), 2.29 (s, 3H), 1.96-1.87 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.7, 162.6, 156.2, 146.3, 146.1, 136.9, 135.7, 125.3, 123.6, 123.1, 123.0, 72.9, 70.9, 32.8, 28.2, 23.2, 22.8, 19.1, 18.2, 17.2. HRMS (EI) calculated for $[C_{25}H_{33}N_3O]^+$ requires m/z 391.2624, found m/z 391.2626.



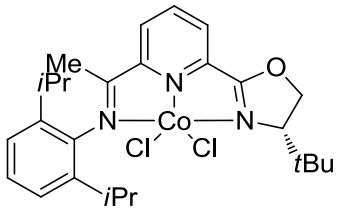
(*S*,*E*)-N-(1-(6-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline (1c). Prepared according to the procedure of 1a, using 0.55 g (2.2 mmol) of S3c, 22 mL of MeOH, 0.45 mL (2.4 mmol, 0.94 g/mL) of 2,6-diisopropylaniline and 22 μL of HCOOH, give 0.2856 g (0.71 mmol, 32% yield) of the title compound as a pale yellow solid. Optical Rotation: $[\alpha]^{20}_{D}$ = -67.0 (c 1.0, $CHCl_3$); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 8.50 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.19-7.13 (m, 2H), 7.12-7.06 (m, 1H), 4.50 (dd, *J* = 10.2, 8.8 Hz, 1H), 4.35 (dd, *J* = 8.4, 8.8 Hz, 1H), 4.15 (dd, *J* = 10.2, 8.4 Hz, 1H), 2.79-2.66 (m, 2H), 2.28 (s, 3H), 1.17-1.10 (m, 12H), 0.99 (s, 9H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 166.7, 162.6, 156.1, 146.3, 146.1, 136.9, 135.7, 125.4, 123.6, 123.03, 122.95, 76.4, 69.4, 34.0, 28.20, 28.18, 25.9, 23.2, 22.8, 17.2; HRMS (EI) calculated for $[C_{26}H_{35}N_3O]^+$ requires m/z 405.2780, found m/z 405.2785.



2a. Prepared according to a previously reported procedure,[7] A 100 mL Schlenk flask was charged with 0.9018 g (2.1 mmol) of 1a, 21 mL of THF and 0.2532 g (3.0 mmol) of $CoCl_2$ in nitrogen atmosphere, then the mixture was stirred at room temperature for 5 h, then 11 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air, washed with ether and dried *in vacuo* to yield 1.0532 g (1.85 mmol, 95% yield) of green powder. Anal. Calcd for $C_{29}H_{33}Cl_2CoN_3O$: C, 61.17; H, 5.84, N, 7.38; Found: C, 60.92; H, 5.69; N, 7.37.



2b. Prepared according to a previously reported procedure,[7] A 100 mL Schlenk flask was charged with 0.3922 g (1.0 mmol) of 1b, 10 mL of THF and 0.1208 g (0.95 mmol) of $CoCl_2$ in nitrogen atmosphere, then the mixture was stirred at room temperature for 5 h, then 5 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air, washed with ether and dried *in vacuo* to yield 0.4259 g (0.82 mmol, 86% yield) of green powder. Anal. Calcd for $C_{25}H_{33}Cl_2CoN_3O$: C, 57.59; H, 6.38, N, 8.06; Found: C, 57.96; H, 6.81; N, 7.86.



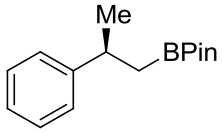
2c. Prepared according to a previously reported procedure,[7] A 100 mL Schlenk flask was charged with 1.2230 g (3.0 mmol) of 1c, 40 mL of THF, and 0.3681 g (2.9 mmol) of $CoCl_2$ in nitrogen atmosphere, then the mixture was stirred at room temperature for 5 h, then 15 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air, washed with ether and dried *in vacuo* to yield 1.3296 g (2.49 mmol, 88% yield) of green powder. Anal. Calcd for $C_{26}H_{35}Cl_2CoN_3O$: C, 58.32; H, 6.59, N, 7.85; Found: C, 58.11; H, 6.72; N, 7.38.

IV. Asymmetric Hydroboration of Alkenes

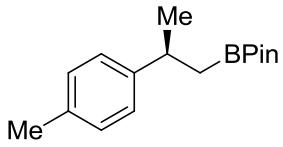
General procedure for Asymmetric *anti*-Markovnikov alkene Hydroboration: To a 25 mL

[7] Small, B. L.; Brookhart, B.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.

flame-dried Schlenk flask cooled under argon, 2c (0.0125 mmol), toluene (0.5 mL) or neat, alkene (2.5 mmol), and HBPin (375 μL, 97%, 2.5 mmol) were added insequence. The mixture was placed at -20 ^{o}C and was injected with $NaBHEt_3$ (1 M) (37.5μL, 0.038 mmol) by dropwise and then stirred at room temperature (20-30 ^{o}C) for 1 h. The resulting solution was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give the corresponding product.



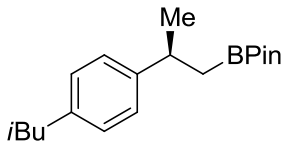
(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (7a).[8] Prepared according to the general procedure using 325 μL (0.91 g/mL, 2.5 mmol) of α-Methylstyrene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0068 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5866 g (2.4 mmol, 96% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +22.2 (c 0.99, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_{D}$ = +16.6 (c 1.0, $CHCl_3$), 87% ee); 98.1% ee, determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.25 mL/min, *n* = 254 nm, t_r 16.8 (minor), 18.1 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.29-7.20 (m, 4H), 7.17-7.10 (m, 1H), 3.09-2.96 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.19-1.10 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 128.1, 126.5, 125.6, 82.8, 35.7, 24.8, 24.7, 24.6, 21.1. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; HRMS (EI) calculated for $[C_{15}H_{23}BO_2]^{+}$ requires m/z 246.1791, found m/z 246.1791.



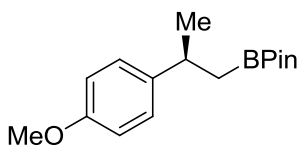
(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane (7b).[8] Prepared according to the general procedure using 365 μL (0.91 g/mL, 2.5 mmol) of 1-Methyl-4-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0072 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give

[8] Corberán, R.; Mszar, N. W.; Hoveyda A. H. *Angew. Chem. Int. Ed.* **2011**, *50*, 7079.

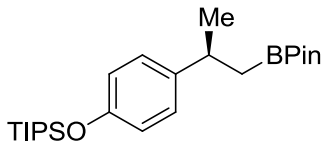
0.5939 g (2.3 mmol, 91% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +24.9 (c 0.97, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_{D}$ = +16.2 (c 1.0, $CHCl_3$), 74% ee); 98.3% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 23.2 (major), 25.3 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.13 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 3.06-2.94 (m, 1H), 2.30 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.21-1.09 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 146.2, 134.9, 128.8, 126.4, 82.9, 35.3, 24.8, 24.7, 24.6, 21.4, 20.9; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; HRMS (EI) calculated for $[C_{16}H_{25}BO_2]^+$ requires m/z 260.1948, found m/z 260.1951.



(*S*)-2-(2-(4-isobutylphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7c). Prepared according to the general procedure using 504 μL (0.87 g/mL, 2.5 mmol) of 1-isobutyl-4-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 0.50 mmol) of HBPin, 0.0071 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5830 g (1.9 mmol, 77% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +19.1 (c 1.0, $CHCl_3$); 98.9% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel OJ-H x 3, *n*-hexane/*i*-PrOH = 98/2, 0.75 mL/min, *n* = 220 nm, t_r 31.3 (major), 32.4(minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.13 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 3.00 (m, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.89-1.75 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.20-1.08 (m, 14H), 0.88 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) : δ 146.3, 138.9, 128.9, 126.3, 82.9, 45.0, 35.4, 30.2, 25.0, 24.7, 24.6, 22.4, 22.3, 21.1; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.7; HRMS (EI) calculated for $[C_{19}H_{31}BO_2]^+$ requires m/z 302.2417, found m/z 302.2422.



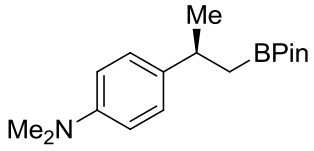
(*S*)-(+)-2-(2-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7d). [9] Prepared according to the general procedure using 0.3724 g (2.5 mmol) of 1-Methoxy-4-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0069 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6150 g (2.2 mmol, 89% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +22.7 (c 0.98, $CHCl_3$) (Lit.[9] $[\alpha]^{23}_D$ = -11.2, (c 1.0, CH_2Cl_2), 32% ee), 96.1% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 35.6 (minor), 38.6 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.99 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.20-1.08 (m, 14H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.5, 141.4, 127.4, 113.5, 82.9, 55.1, 34.9, 25.1, 24.7, 24.6, 21.4; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.9; HRMS (EI) calculated for $[C_{16}H_{25}BO_3]^+$ requires m/z 276.1897, found m/z 276.1890.



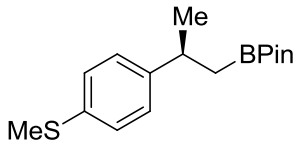
(*S*)-(+)-triisopropyl(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenoxy)silane (7e). Prepared according to the general procedure using 0.7254 g (2.5 mmol) of Triisopropyl(4-(prop-1-en-2-yl)phenoxy)silane, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0271 g (0.051 mmol) of 2c, 150 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.9058 g (2.2 mmol, 87% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +20.0 (c 0.97, $CHCl_3$), >99% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC

[9] Mazet, C.; Gérard, D. *Chem. Commun.*, **2011**, *47*, 298.

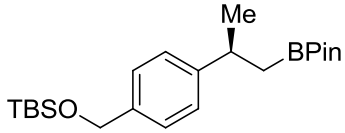
conditions: Chiralcel AD-H x 3, *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, *n* = 220 nm, t_r 31.2 (major), 33.4 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.04-2.91 (m, 1H), 1.29-1.20 (m, 6H), 1.14 (d, *J* = 1.8 Hz, 12H), 1.12-1.05 (m, 20H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.8, 141.6, 127.3, 119.4, 82.9, 35.1, 25.4, 24.7, 21.4, 17.9, 12.7; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; HRMS (EI) calculated for $[C_{24}H_{43}BO_4Si]^+$ requires m/z 418.3075, found m/z 418.3074.



(*S*)-(+)-*N*,*N*-dimethyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)aniline (7f). Prepared according to the general procedure using 0.4066 g (1.0 mmol) of *N*,*N*-Dimethyl-4-(prop-1-en-2-yl)aniline, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0070 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.4908 g (1.9 mmol, 75% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +28.9 (c 0.98, $CHCl_3$), 95.9% ee, determined by HPLC after conversion to the corresponding acetate according to a previous report,[8] HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 33.6 (minor), 35.9 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.12 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 3.01-2.84 (m, 7H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.18 (s, 12H), 1.15-1.07 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.0, 137.9, 127.1, 113.0, 82.9, 41.0, 34.7, 25.0, 24.8, 24.7, 21.3; ^{11}B NMR (CDCl3, 128 MHz): δ 34.0; HRMS (EI) calculated for $[C_{17}H_{28}BNO_2]^+$ requires m/z 289.2213, found m/z 289.2219.

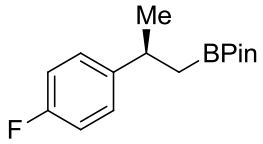


(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-(4-(methylthio)phenyl)propyl)-1,3,2-dioxaborolane (7g). Prepared according to the general procedure using 0.4177 g (2.5 mmol) of Methyl(4-(prop-1-en-2-yl)phenyl)sulfane, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0068 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$, and 0.5 mL of toluene. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6595 g (2.3 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +34.5 (c 1.0, $CHCl_3$), 97.7% ee, determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99/1, 0.25 mL/min, *n* = 254 nm, t_r 38.8 (major), 42.2 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.22-7.13 (m, 4H), 3.05-2.94 (m, 1H), 2.45 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.19-1.10 (m, 14H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 146.6, 134.9, 127.23, 127.17, 83.0, 35.3, 24.74, 24.67, 20.9, 16.5; ^{11}B NMR (CDCl3, 128 MHz): δ 33.6; HRMS (EI) calculated for $[C_{16}H_{25}BO_2S]^+$ requires m/z 292.1668, found m/z 292.1672.



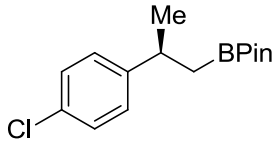
(*S*)-(+)-tert-butyldimethyl((4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzyl)oxy)silane (7h). Prepared according to the general procedure using 0.7233 g (2.5 mmol) of *tert*-Butyldimethyl((4-(prop-1-en-2-yl)benzyl)oxy)silane, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0066 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.8801 g (2.3 mmol, 90% yield) of the title compound as a colorless oil. Optical

Rotation: $[\alpha]^{20}_D$ = +19.1 (c 0.99, $CHCl_3$), 95.1% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, *n* = 254 nm, t_r 16.2 (minor), 17.6 (major); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.15 (m, 4H), 4.69 (s, 2H), 3.08-2.95 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.21-1.10 (m, 14H), 0.93 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.9, 138.7, 126.4, 126.0, 83.0, 64.9, 35.5, 26.0, 24.9, 24.8, 24.7, 21.3, 18.4, -5.2; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.0; HRMS (EI) calculated for $[C_{22}H_{39}BO_3Si]^+$ requires m/z 390.2762, found m/z 390.2763.

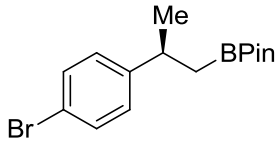


(*S*)-(+)-2-(2-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7i).[8] Prepared according to the general procedure using 338 μL (1.01 g/mL, 2.5 mmol) of 1-Fluoro-4-(prop-1-en-2-yl)benzene, 375 μL (1.0 g/mL, 97%, 2.5 mmol) of HBPin, 0.0069 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6300 g (2.4 mmol, 95% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +21.8 (c 1.0, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = +20.9 (c 0.98, $CHCl_3$), 93.2% ee), 95.3% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 220 nm, t_r 21.7 (minor), 22.8 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.22-7.14 (m, 2H), 6.98-6.89 (m, 2H), 3.08-2.95 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.20-1.06 (m, 14H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 161.0 (d, *J* = 241.4 Hz), 144.7 (d, *J* = 2.9 Hz), 127.9 (d, *J* = 8.0 Hz),

114.7 (d, J = 20.4 Hz), 83.0, 35.1, 25.1, 24.7, 24.6, 21.3; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.8; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -118.2; HRMS (EI) calculated for $[C_{15}H_{22}BFO_2]^+$ requires m/z 264.1697, found m/z 264.1693.

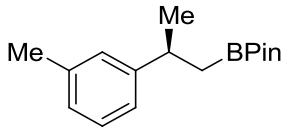


(S)-2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7j).[9] Prepared according to the general procedure using 355 μL (1.1 g/mL, 2.5 mmol) of 1-Fluoro-4-(prop-1-en-2-yl)benzene, 375 μL (1.0 g/mL, 97%, 2.5 mmol) of HBPin, 0.0142 g (0.027 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5900 g (2.1 mmol, 84% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +26.9 (c 0.99, $CHCl_3$) (Lit.[9] $[\alpha]^{23}_D$ = -17.9 (c 1.0, CH_2Cl_2), 77% ee), 94.9% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 21.7 (minor), 23.1 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.22 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 3.07-2.94 (m, 1H), 1.24 (d, J = 6.8 Hz, 3H), 1.20-1.08 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 147.6, 131.1, 128.2, 128.0, 83.0, 35.2, 24.8, 24.71, 24.67, 20.8; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.3; HRMS (EI) calculated for $[C_{15}H_{22}BClO_2]^+$ requires m/z 280.1401, found m/z 280.1399;



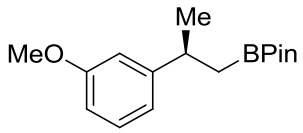
(*S*)-2-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7k).[9] Prepared

according to the general procedure using 375 μL (1.4 g/mL, 2.5 mmol) of 1-Bromo-4-(prop-1-en-2-yl)benzene, 375 μL (1.0 g/mL, 97%, 2.5 mmol) of HBPin, 0.0687 g (0.13 mmol) of 2c, 375 μL (1 M in THF, 0.38 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.3664 g (1.1 mmol, 45% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +27.5 (c 0.99, $CHCl_3$) (Lit.[9] $[\alpha]^{23}_D$ = -18.4 (c 1.0, CH_2Cl_2), 80% ee), 94.9% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[9] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 23.7 (minor), 25.0 (major); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.06-2.93 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21-1.09 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 148.2, 131.1, 128.4, 119.2, 83.0, 77.3, 77.0, 76.7, 35.3, 24.7, 24.7, 24.7, 21.0; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.6; HRMS (EI) calculated for $[C_{15}H_{22}BBrO_2]^+$ requires m/z 324.0896, found m/z 324.0900.



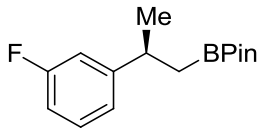
(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-(m-tolyl)propyl)-1,3,2-dioxaborolane (7l).[8] Prepared according to the general procedure using 365 μL (0.91 g/mL, 2.5 mmol) of 1-Methyl-3-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0067 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5823 g (2.2 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +19.1 (c 1.0, $CHCl_3$) (Lit. $[\alpha]^{20}_D$ = +14.0 (c 1.0, $CHCl_3$), 87% ee), 97.7% ee, determined by HPLC,

HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99/1, 0.25 mL/min, *n* = 254 nm, t_r 20.0 (minor), 22.0 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.15 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.08-7.00 (m, 2H), 6.96 (d, *J* = 7.4 Hz, 1H), 3.05-2.94 (m, 1H), 2.31 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.20-1.09 (m, 14H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 149.1, 137.5, 128.0, 127.4, 126.3, 123.5, 82.9, 35.7, 24.7, 24.6, 21.4, 21.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.9; HRMS (EI) calculated for $[C_{16}H_{25}BO_2]^+$ requires m/z 246.1948, found m/z 246.1951.

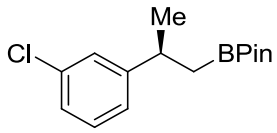


(*S*)-(+)-2-(2-(3-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7m).[8]

Prepared according to the general procedure using 480 μL (0.87 g/mL, 2.5 mmol) of 1-methoxy-3-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 0.50 mmol) of HBPin, 0.0069 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5492 g (2.0 mmol, 80% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +18.9 (c 0.99, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = +13.2 (c 1.0, $CHCl_3$), 83% ee), 98.7% ee, determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.25 mL/min, *n* = 254 nm, t_r 20.6 (minor), 21.6 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.18 (dd, *J* = 8.0, 7.8 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.79 (s, 1H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.79 (s, 3H), 3.07-2.94 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.21-1.09 (m, 14H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 159.5, 151.0, 129.1, 119.0, 112.4, 110.9, 82.9, 55.1, 35.8, 24.75, 24.65, 21.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; HRMS (EI) calculated for $[C_{16}H_{25}BO_3]^+$ requires m/z 276.1897, found m/z 276.1902.

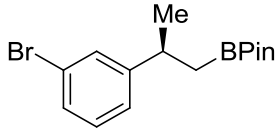


(*S*)-(+)-2-(2-(3-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7n).[8] Prepared according to the general procedure using 350 μL (0.98 g/mL, 2.5 mmol) of 1-Fluoro-3-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0067 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5337 g (2.0 mmol, 81% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +20.7 (c 0.99, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = +12.1 (c 1.0, $CHCl_3$), 75% ee), 98.1%, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 17.7 (minor), 21.0 (major); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.16 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 10.4 Hz, 1H), 6.83 (dt, *J* = 8.4, 2.0 Hz, 1H), 3.09-2.97 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.20-1.09 (m, 14H); ^{13}C NMR (CDCl3, 100 MHz): δ 162.9 (d, *J* = 242.8), 152.0 (d, *J* = 6.6 Hz), 129.5 (d, *J* = 8.1 Hz), 122.3 (d, *J* = 2.2 Hz), 113.5 (d, *J* = 20.4 Hz), 112.4 (d, *J* = 21.2 Hz), 83.0, 35.6, 24.73, 24.68, 24.6, 20.9; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -114.1; HRMS (EI) calculated for $[C_{15}H_{22}BFO_2]^+$ requires m/z 264.1697, found m/z 264.1701.



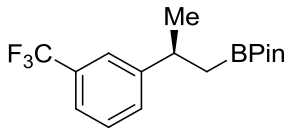
(*S*)-(+)-2-(2-(3-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7o). Prepared according to the general procedure using 375 μL (1.0 g/mL, 2.5 mmol) of

1-Chloro-3-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0067 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5106 g (1.8 mmol, 72% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +20.4 (c 1.0, $CHCl_3$), 97.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 32.1 (minor), 34.6 (major); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.15 (m, 2H), 7.14-7.08 (m, 2H), 3.06-2.95 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.20-1.08 (m, 14H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 151.3, 133.8, 129.4, 127.0, 125.8, 124.8, 83.1, 35.6, 24.73, 24.69, 24.5, 21.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.6; HRMS (EI) calculated for $[C_{15}H_{22}BClO_2]^+$ requires m/z 280.1401, found m/z 280.1405.

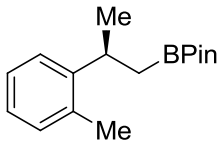


(*S*)-2-(2-(3-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7p).[8] Prepared according to the general procedure using 360 μL (1.4 g/mL, 2.5 mmol) of 1-bromo-3-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0141 g (0.025 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6304 g (2.0 mmol, 78% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +15.0 (c 1.0, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = +14.2 (c 1.0, $CHCl_3$), 79% ee), 98.1% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0

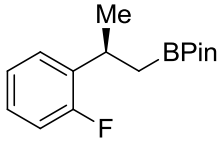
mL/min, *n* = 254 nm, t_r 16.6 (minor), 17.9 (major); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.30-7.24 (m, 1H), 7.19-7.09 (m, 2H), 3.05-2.94 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.20-1.06 (m, 14H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 151.6, 130.0, 129.8, 128.7, 125.3, 122.2, 83.1, 35.6, 24.74, 24.70, 24.5, 21.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.8; HRMS (EI) calculated for $[C_{15}H_{22}BBrO_2]^+$ requires m/z 324.0896, found m/z 324.0901.



(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-(3-(trifluoromethyl)phenyl)propyl)-1,3,2-dioxaborolane (7q).[8] Prepared according to the general procedure using 410 μL (1.1 g/mL, 2.5 mmol) of 1-(Prop-1-en-2-yl)-3-(trifluoromethyl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0139 g (0.026 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6824 g (2.2 mmol, 87% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +17.6 (c 1.0, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = +12.0 (c 1.0, $CHCl_3$), 61% ee), 96.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 0.8 mL/min, *n* = 254 nm, t_r 24.8 (minor), 26.0 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.50 (s, 1H), 7.45-7.33 (m, 3H), 3.15-3.04 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.20-1.08 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.0, 130.3 (q, *J* = 31.6 Hz), 130.0, 128.6, 124.4 (q, *J* = 270.5 Hz), 123.7 (q, *J* = 3.7 Hz), 122.5 (q, *J* = 4.2 Hz), 83.1, 35.7, 24.7, 24.6, 20.9; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.5; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.5; HRMS (EI) calculated for $[C_{16}H_{22}BF_3O_2]^+$ requires m/z 314.1665, found m/z 314.1664.

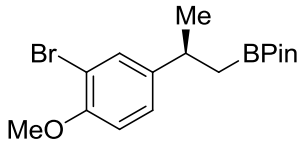


(*S*)-4,4,5,5-tetramethyl-2-(2-(o-tolyl)propyl)-1,3,2-dioxaborolane (7r).[9] Prepared according to the general procedure using 375 μL (0.88 g/mL, 2.5 mmol) of 1-methyl-2-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0267 g (0.050 mmol) of 2c, 150 μL (1 M in THF, 0.15 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6268 g (2.4 mmol, 96% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +9.7 (c 1.01, $CHCl_3$), 65.7% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 220 nm, t_r 21.6 (major), 23.8 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.11-7.00 (m, 2H), 3.34-3.21 (m, 1H), 2.36 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.20-1.07 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 147.2, 134.9, 129.9, 126.0, 125.3, 125.2, 82.9, 30.6, 24.7, 24.6, 24.2, 20.5, 19.5; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.4; HRMS (EI) calculated for $[C_{16}H_{25}BO_2]^+$ requires m/z 260.1948, found m/z 260.1942.



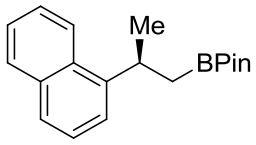
(*S*)-(+)-2-(2-(2-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7s). Prepared according to the general procedure using 350 μL (0.98 g/mL, 2.5 mmol) of 1-fluoro-2-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 0.5 mmol) of HBPin, 0.0066 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction

mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.4899 g (1.9 mmol, 74% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +13.4 (c 1.0, $CHCl_3$), 83.9% ee, determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.25 mL/min, *n* = 254 nm, t_r 16.1 (minor), 17.5 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.29-7.21 (m, 1H), 7.16-7.09 (m, 1H), 7.05 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.00-6.92 (m, 1H), 3.41-3.30 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.21-1.09 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.5 (d, *J* = 242.8 Hz), 135.6 (d, *J* = 14.6 Hz), 127.7 (d, *J* = 5.1 Hz), 127.0 (d, *J* = 8.1 Hz), 123.8 (d, *J* = 2.9 Hz), 115.1 (d, *J* = 22.6 Hz), 83.0, 28.8, 24.7, 24.6, 23.5, 19.5; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -118.7; HRMS (EI) calculated for $[C_{15}H_{22}BFO_2]^+$ requires m/z 264.1697, found m/z 264.1695.

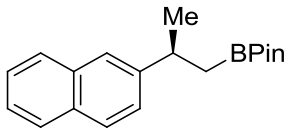


(*S*)-2-(2-(3-bromo-4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7t). Prepared according to the general procedure using 0.5687 g (2.5 mmol) of 2-bromo-1-methoxy-4-(prop-1-en-2-yl)benzene, 375 μL (0.89 g/mL, 97%, 0.5 mmol) of HBPin, 0.0142 g (0.025 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$, 0.5 mL of toluene. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.7462 g (2.1 mmol, 85% yield) of the title compound as a white solid. Optical Rotation: $[\alpha]^{20}_{D}$ = +21.6 (c 0.98, $CHCl_3$), 96.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 220 nm, t_r 24.6 (minor), 26.3 (major); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 7.42 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.4,

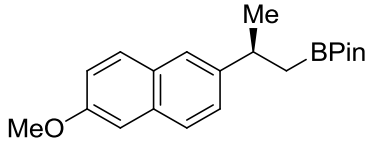
2.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.03-2.91 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21-1.07 (m, 14H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 153.8, 143.0, 131.7, 126.4, 111.8, 111.2, 83.0, 56.3, 34.8,24.76, 24.74, 24.72, 21.3; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.8; HRMS (EI) calculated for $[C_{16}H_{24}BBrO_3]^+$ requires m/z 354.1002, found m/z 354.1004.



(*S*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (7u).[8] Prepared according to the general procedure using 411 μL (1.0 g/mL, 2.5 mmol) of 1-(prop-1-en-2-yl)naphthalene, 375 μL (0.89 g/mL, 97%, 0.5 mmol) of HBPin, 0.0142 g (0.025 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6640 g (2.3 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = -1.7 (c 1.0, $CHCl_3$) (Lit.[8] $[\alpha]^{20}_D$ = -1.4 (c 1.0, $CHCl_3$), 92% ee), 52.8% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 29.8 (minor), 23.7 (major); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.70-7.63 (m, 1H), 7.53-7.39 (m, 4H), 3.97-3.85 (m, 1H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.38-1.23 (m, 2H), 1.14 (s, 6H), 1.10 (s, 6H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 145.3, 133.8, 131.3, 128.7, 126.1, 125.6, 125.4, 125.1, 123.6, 122.1, 83.0, 30.0, 24.7, 24.6, 24.4, 20.7; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.9; HRMS (EI) calculated for $[C_{19}H_{25}BO_2]^+$ requires m/z 354.1002, found m/z 354.1004.

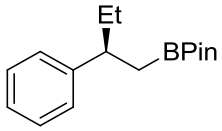


(*S*)-(+)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (7v).[8] Prepared according to the general procedure using 0.4350 g (2.5 mmol) of 2-(Prop-1-en-2-yl)naphthalene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0069 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$, and 0.5 mL of toluene. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6721 g (2.3 mmol, 91% yield) of the title compound as a colorless oil. Optical Rotation: (Lit.[8] $[\alpha]^{20}_D$ = +26.5 (c 1.0, $CHCl_3$), 97.9% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 254 nm, t_r 53.2 (major), 57.8 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.81-7.73 (m, 3H), 7.65 (s, 1H), 7.45-7.35 (m, 3H), 3.27-3.14 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.29-1.20 (m, 2H), 1.14 (s, 12H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 146.7, 133.6, 132.1, 127.7, 127.54, 127.49, 125.8, 125.6, 124.9, 124.4, 83.0, 35.8, 24.73, 24.71, 24.68, 20.9; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.6; HRMS (EI) calculated for $[C_{19}H_{25}BO_2]^+$ requires m/z 296.1948, found m/z 296.1959.



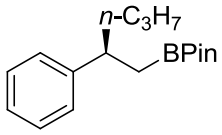
(*S*)-2-(2-(6-methoxynaphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7w). Prepared according to the general procedure using 0.4977 g (2.5 mmol) of 2-methoxy-6-(prop-1-en-2-yl)naphthalene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0141 g (0.025 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$, and 0.5 mL of toluene.

After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.7452 g (2.3 mmol, 91% yield) of the title compound as a white solid. Optical Rotation: $[\alpha]^{20}_{D}$ = +32.7 (c 1.05, $CHCl_3$), 97.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 37.1 (major), 39.8 (minor); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 7.70-7.62 (m, 2H), 7.58 (s, sH), 7.36 (d, *J* = 8.4 Hz, 1H), 7.15-7.05 (m, 2H), 3.88 (s, 3H), 3.24-3.11 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.26-1.19 (m, 2H), 1.13 (s, 12H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 157.0, 144.4, 133.0, 129.0 (2C), 126.6, 126.3, 124.3, 118.4, 105.6, 83.0, 55.2, 35.7, 24.8, 24.74, 24.68, 21.0; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.7; HRMS (EI) calculated for $[C_{20}H_{27}BO_3]^+$ requires m/z 326.2053, found m/z 326.2052.



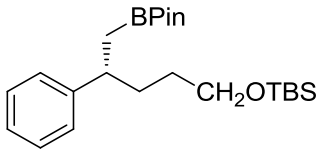
(*R*)-(+)-4,4,5,5-tetramethyl-2-(2-phenylbutyl)-1,3,2-dioxaborolane (7x).[8] Prepared according to the general procedure using 368 μL (0.85 g/mL, 2.5 mmol) of But-1-en-2-ylbenzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0146 g (0.026 mmol) of 2c, 75 μL (1 M in THF, 0.075 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5243 g (2.0 mmol, 81% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +13.9 (c 0.97, $CHCl_3$) (Lit. Lit.[8] $[\alpha]^{20}_{D}$ = +7.2 (c 1.1, $CHCl_3$), 90% ee); 98.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.9 mL/min, *n* = 254 nm, t_r 28.8 (major), 36.7 (major); ^{1}H NMR

($CDCl_3$, 400.1 MHz): δ 7.25 (dd, *J* = 7.2, 6.8 Hz, 2H), 7.21-7.16 (m, 2H), 7.16-7.10 (m, 1H), 2.79-2.65 (m, 1H), 1.69-1.51 (m, 2H), 1.26-1.16 (m, 1H), 1.15-0.99 (m, 13H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 147.2, 128.0, 127.5, 125.6, 82.8, 43.2, 32.2, 24.63, 24.60, 19.2, 12.2; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.8; HRMS (EI) calculated for $[C_{16}H_{25}BO_2]^+$ requires m/z 260.1948, found m/z 260.1954.

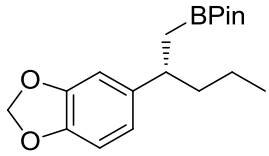


(*R*)-(+)-4,4,5,5-tetramethyl-2-(2-phenylpentyl)-1,3,2-dioxaborolane (7y).[10] Prepared according to the general procedure using 484 μL (0.87 g/mL, 2.5 mmol) of Pent-1-en-2-ylbenzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0072 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.5305 g (1.9 mmol, 72% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +11.8 (c 1.0, $CHCl_3$), 98.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 220 nm, t_r 14.3 (minor), 15.1 (major); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.24 (dd, *J* = 7.4, 7.2 Hz, 2H), 7.21-7.17 (m, 2H), 7.13 (dd, *J* = 7.4, 7.2 Hz, 1H), 2.90-2.77 (m, 1H), 1.62-1.53 (m, 2H), 1.25-1.04 (m, 16H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.5, 128.0, 127.4, 125.6, 82.9, 41.8, 41.2, 24.6, 20.7, 19.7, 14.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.6; HRMS (EI) calculated for $[C_{18}H_{29}BO_2]^+$ requires m/z 274.2104, found m/z 274.2108.

[10]Cho, S. H.; Hartwig, J. H. *J. Am. Chem. Soc.* **2013**, *135*, 8157.

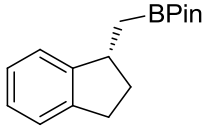


(*R*)-tert-butyldimethyl((4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane (7z). Prepared according to the general procedure using 0.6872 g (2.5 mmol) of tert-butyldimethyl((4-phenylpent-4-en-1-yl)oxy)silane, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0662 g (0.13 mmol) of 2c, 375 μL (1 M in THF, 0.38 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.6269 g (1.6 mmol, 62% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +4.8 (c 0.96, $CHCl_3$), 96.5% ee, determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AD-H x 3, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, *n* = 220 nm, t_r 30.4 (major), 32.3 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.39 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.37-7.32 (m, 2H), 7.31-7.25 (m, 1H), 3.68 (t, *J* = 6.6 Hz, 2H), 3.02-2.91 (m, 1H), 1.89-1.67 (m, 2H), 1.65-1.43 (m, 2H), 1.43-1.19 (m, 14H), 1.02 (s, 9H), 0.15 (d, *J* = 2.0 Hz, 6H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) : δ 147.2, 128.0, 127.4, 125.7, 82.9, 63.3, 41.4, 35.6, 31.0, 26.0, 24.6, 19.9, 18.3, -5.3; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.7. HRMS (EI) calculated for $[C23H41BO_3Si]^+$ requires m/z 404.2918, found m/z 404.2921.



(*R*)-2-(2-(benzo[d][1,3]dioxol-5-yl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7aa). Prepared according to the general procedure using 0.4852 g (2.5 mmol) of 5-(pent-1-en-2-yl)benzo[d][1,3]dioxole, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0662 g (0.13 mmol) of 2c, 375 μL (1 M in THF, 0.38 mmol) of $NaBHEt_3$. After 1 h, the crude reaction

mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.7153 g (2.2 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = +15.5 (c 1.03, $CHCl_3$), 93.9% ee, determined by HPLC determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 22.7 (major), 26.0 (minor); ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 6.73-6.67 (m, 2H), 6.67-6.61 (m, 1H), 5.89 (s, 2H), 2.83-2.69 (m, 1H), 1.56-1.46 (m, 2H), 1.21-1.10 (m, 16H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) : δ 147.3, 145.3, 141.6, 120.3, 107.7, 107.6, 100.5, 82.9, 41.8, 41.0, 24.6 (2C), 20.7, 19.9, 14.0; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 33.8; HRMS (EI) calculated for $[C_{18}H_{27}BO_4]^+$ requires m/z 318.2002, found m/z 318.2004.



(*R*)-2-((2,3-dihydro-1H-inden-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ab).[11] Prepared according to the general procedure using 332 μL (0.98 g/mL, 2.5 mmol) of 1-methylene-2,3-dihydro-1H-indene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0069 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.3194 g (1.2 mmol, 50% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_{D}$ = -13.0 (c 0.99, $CHCl_3$), 95.3% ee, determined by HPLC determined by HPLC after conversion to the corresponding alcohol which was prepared according to a previously reported procedure,[8] HPLC conditions: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 16.2 (minor), 17.6 (major); ^{1}H NMR: (400.1 MHz, $CDCl_3$): δ 7.26-7.07 (m, 4H), 3.36-3.24 (m, 1H), 2.95-2.75 (m, 2H), 2.41-2.29 (m, 1H), 1.70-1.55 (m, 1H), 1.40-1.32 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.02-0.92 (m, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ 149.1, 143.7, 126.0, 125.9, 124.2, 123.3, 83.1, 40.7, 34.8, 31.4, 24.9, 24.7, 17.3; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 34.2; HRMS (EI) calculated for $[C_{16}H_{23}BO_2]^+$ requires m/z 258.1791, found m/z 258.1790.

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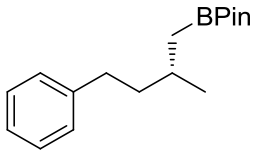
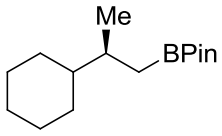
[11] Bose, S. K.; Marder, T. B. *Org. Lett.* **2014**, *16*, 4562.

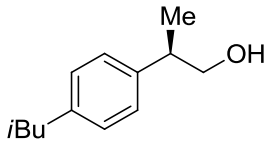


(*S*)-4,4,5,5-tetramethyl-2-(2-methyl-4-phenylbutyl)-1,3,2-dioxaborolane (7ac).[9] Prepared according to the general procedure using 413 μL (0.88 g/mL, 2.5 mmol) of (3-methylbut-3-en-1-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0070 g (0.013 mmol) of 2c, 37.5 μL (1 M in THF, 0.038 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.4908 g (1.8 mmol, 72% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = -3.0 (c 1.0, $CHCl_3$), 33.7% ee, determined by HPLC after conversion to the corresponding acetate which was prepared according to a previously reported procedure,[9] HPLC conditions: Chiralcel OJ-H x 3, *n*-hexane/*i*-PrOH = 98/2, 0.75 mL/min, *n* = 254 nm, t_r 33.5 (major), 35.9 (minor); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.31-7.22 (m, 2H), 7.22-7.12 (m, 3H), 2.69-2.53 (m, 2H), 1.85-1.72 (m, 1H), 1.65-1.45 (m, 2H), 1.24 (s, 12H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.94-0.86 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.2, 128.3, 128.2, 125.4, 82.8, 41.5, 33.7, 29.4, 24.8, 24.8, 24.5, 22.2, 19.5; ^{11}B NMR: (128 MHz, $CDCl_3$): δ 34.3; HRMS (EI) calculated for $[C_{17}H_{27}BO_2]^+$ requires m/z 274.2104, found m/z 274.2101.

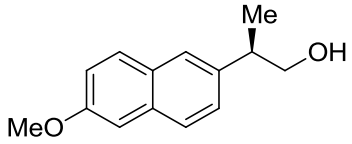


(*S*)-2-(2-cyclohexylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ad).[9] Prepared according to the general procedure using 373 μL (0.83 g/mL, 2.5 mmol) of (3-methylbut-3-en-1-yl)benzene, 375 μL (0.89 g/mL, 97%, 2.5 mmol) of HBPin, 0.0668 g (0.13 mmol) of 2c, 375 μL (1 M in THF, 0.38 mmol) of $NaBHEt_3$. After 1 h, the crude reaction mixture was purified by flash column chromatography using 20:1 PE/EtOAc as the eluent to give 0.4045 g (1.8 mmol, 72% yield) of the title compound as a colorless oil.Optical Rotation: $[\alpha]^{20}_D$ = +3.3 (c 0.95, $CHCl_3$), 70.1% ee, determined by HPLC after conversion to the corresponding 2-Naphthoic acid ester which was prepared according to a previously reported procedure,[9] HPLC conditions: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r 5.5 (major), 6.1 (minor); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.82-1.52 (m, 7H), 1.25 (s, 12H), 1.20-1.04 (m, 4H), 1.02-0.80 (m, 6H); ^{13}C

NMR (100.6 MHz, $CDCl_3$): δ 82.8, 44.8, 34.5, 30.3, 29.2, 26.9, 26.8, 24.9, 24.7, 19.1, 16.7; ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.4; HRMS (EI) calculated for $[C_{15}H_{29}BO_2]^+$ requires m/z 225.2261, found m/z 225.2265.



(R)-2-(4-isobutylphenyl)propan-1-ol (8c).[12] Prepared according to a previously reported procedure,[8] using 0.1462 g (0.48 mmol) of **7c**, 4 mL of ether, 4 mL (3 M) of NaOH and 3 mL (30%) of H_2O_2, the mixture was stirred at room temperature for 3 h, the crude reaction mixture was then extracted with Et_2O (5 mL x 3), the organic layer was then dried over anhydrous Na_2SO_4. Evaporation and purified by flash column chromatography using 10:1 PE/EtOAc as the eluent to give 0.0886 g (0.46 mmol, 96% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]^{20}_D$ = +14.6 (c 0.98, $CHCl_3$) (Lit.[12] $[\alpha]^{20}_D$ = -13.0 (c 1.0, $CHCl_3$), 89% ee), 98.9% ee; ^1H NMR (400.1 MHz, $CDCl_3$): δ 7.20-7.07 (m, 4H), 3.67 (s, 2H), 2.99-2.86 (m, 1H), 2.45 (d, J = 6.8 Hz, 2H), 1.94-1.79 (m, 1H), 1.47 (br, s, 1H), 1.26 (d, J = 7.0 Hz, 3H), 0.96-0.87 (m, 6H).



(R)-2-(6-methoxynaphthalen-2-yl)propan-1-ol (8w).[13] Prepared according to a previously reported procedure,[8] using 0.6983 g (2.1 mmol) of **7w**, 17 mL of ether, 17 mL (3 M) of NaOH and 13 mL (30%) of H_2O_2, the mixture was stirred at room temperature for 3 h, the crude reaction mixture was then extracted with Et_2O (20 mL x 3), the organic layer was then dried over anhydrous Na_2SO_4. Evaporation and purified by flash column chromatography using 10:1 PE/EtOAc as the eluent to give 0.4480 g (2.1 mmol, 97% yield) of the title compound as a white solid; $[\alpha]^{20}_D$ = +16.7 (c 0.9, $CHCl_3$) (Lit.[13] $[\alpha]^{20}_D$ = +17.5 (c 1.0, $CHCl_3$), 99% ee), 97.5% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, *n* = 254 nm, t_r

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[12] Basak, A.; Nag, A.; Bhattacharya, G.; Mandal, S.; Nag, S. *Tetrahedron: Asymmetry* **2000**, 11, 2403.

[13] Koul, S.; Koul, J. L.; Singh, B.; Kapoor, M.; Parshad, R.; Manhas, K. S.; Taneja, S. C.; Qazi, G. N. *Tetrahedron: Asymmetry* **2005**, *16*, 2575.

37.1 (major), 39.8 (minor); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.8, 7.6 Hz, 2H), 7.61 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.18-7.09 (m, 2H), 3.92 (s, 3H), 3.78 (dd, *J* = 6.4, 6.2 Hz, 2H), 3.15-3.04 (m, 1H), 1.41-1.30 (m, 4H).