Supplementary Information

Enantioselective synthesis of α-aminoboronates by NiH-catalysed asymmetric hydroamidation of alkenyl boronates

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1. Supplementary Methods

1. General Information

Solvents were either purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system or bought from the commercial sources and transferred to the glovebox without exposure to air. Other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, Aladdin, J&K, Energy Chemical, Bide Pharmatech Ltd. and were used as received. Deionized water was used after degassing. Flash chromatography was performed using glass columns with silica gel (SiliaFlash® P60, particle size 40-63 µm, Silicycle).

**NiCl₂·6H₂O** (CAS 7791-20-0, nickel(II) chloride hexahydrate, ReagentPlus®) was purchased from Sigma-Aldrich and stored under nitrogen in glovebox;

**(EtO)₃SiH** (CAS 2031-62-1, triethoxysilane) was purchased from TCI and stored under nitrogen at –20 °C in glove box;

**LiI** (CAS 10377-51-2) was purchased from Aladdin or Energy Chemical (99.9% metals basis) and stored under nitrogen in glovebox;

**DMA** (CAS 127-19-5, N,N-dimethylacetamide) was purchased from Acros (99.5%, Extra Dry, AcroSeal®) and stored under nitrogen in glovebox.

**Safety note:** MSDS indicates that **(EtO)₃SiH** is a corrosive and flammable liquid. According to the literatures¹, it may form pyrophoric gas (possibly SiH₄) during the storage or reaction. Although during our reactions, we used **(EtO)₃SiH** without incident and SiH₄ was not observed, we urge the users of these procedures to be alert to the possibility of SiH₄ formation and possible exotherms and to take suitable precautions (suitable eye protection is also required). **(MeO)₂MeSiH** could be an alternative hydride source in case of safety consideration.

**General analytical information.**

All compounds (starting materials and products) were characterized by **¹H** NMR, **¹³C** NMR, IR spectroscopy and high-resolution mass spectrometry. **¹H** NMR spectra were recorded on Bruker 500 MHz spectrometer and are referenced relative to residual
CDCl₃ proton signals at δ 7.26 ppm. ¹⁹F NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to CFCl₃ (δ 0.0 ppm). Data for ¹H and ¹⁹F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant (Hz). ¹³C NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to CDCl₃ at δ 77.16 ppm. The ¹³C NMR spectra were obtained with ¹H decoupling. Data for ¹³C NMR are reported in terms of chemical shift and multiplicity where appropriate. ¹¹B NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to BF₃·Et₂O (δ 0.0 ppm), and the broad peaks around -3 ppm were ascribed to NMR tubes. IR spectra were obtained on a Bruker Alpha or Thermo Scientific Nicolet iS10 FT-IR and was reported in terms of frequency of absorption (cm⁻¹). GC analyses were performed on Agilent 7890 or 8890 gas chromatograph with an FID detector using a J&W DB-1 column (10 m, 0.1 mm I.D.). Low Resolution Mass spectra were obtained from on an Agilent 5977A GC-MS. High Resolution Mass spectra were obtained on a Thermo Fisher Q Exactive instrument (ESI). Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. High pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel & Chiralpak columns (250 mm). Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm pathlength cell at 589 nm with [α]D values reported in degrees; concentration (c) is in g/100 mL.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No. 14-959-35C)

Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)
2. NiH-Catalyzed Asymmetric Hydroamidation of Alkenyl Boronates

**General procedure A** for NiH-catalyzed asymmetric hydroamidation of alkenyl boronates. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 1,4,2-dioxazol-5-one (0.30 mmol, 1.5 equiv) (if the olefin is a solid, it was also added at this time) and anhydrous DMA (1.0 mL, 0.20 M). The mixture was stirred for 10 min at room temperature, at which time alkenyl boronate (0.20 mmol, 1.0 equiv) (if the 1,4,2-dioxazol-5-one is a liquid, it was added at this time), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv) and (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath for up to 20 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H₂O, and the mixture was extracted with Et₂O. The organic layer was concentrated to give the crude product. n-Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by flash column chromatography (petroleum ether/EtOAc) for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated. The enantiomeric excesses (% ee) were determined by HPLC analysis using chiral stationary phases.

(R)-N-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 3, 3a). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A.
using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 71% yield (46.8 mg).

\[ ^{1}H \text{ NMR} \]

(500 MHz, CDCl₃) δ 8.47 (s, 1H), 7.80 (d, \( J = 7.4 \text{ Hz} \), 2H), 7.45 (t, \( J = 7.4 \text{ Hz} \), 1H), 7.32 (t, \( J = 7.7 \text{ Hz} \), 2H), 2.79 (t, \( J = 6.3 \text{ Hz} \), 1H), 1.75 – 1.65 (m, 1H), 1.61 – 1.52 (m, 1H), 1.49 – 1.37 (m, 2H), 1.34 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, \( J = 7.0 \text{ Hz} \), 3H);

\[ ^{13}C \text{ NMR} \]

(126 MHz, CDCl₃) δ 170.8, 133.1, 128.6, 128.2, 128.1, 81.2, 32.1, 31.3, 27.7, 25.4, 25.2, 22.7, 14.2;

\[ ^{11}B \text{ NMR} \]

(160 MHz, CDCl₃) δ 17.8;

HRMS (ESI) calcd. for C₁₉H₃₀BNaO₃ [M+Na]⁺ m/z 354.2211, found 354.2202;

IR (neat, cm⁻¹) 3079, 2925, 1608, 1530, 1127, 1099, 709;

m.p. 130 – 132 °C;

[α]D²⁵ = −35.8 (c = 1.06, CHCl₃);

HPLC analysis: the ee (95%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, \( t_R \) (major) = 6.8 min, \( t_R \) (minor) = 7.4 min.

From (Z)-1a (Figure 2, entry 15): (Z)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((Z)-1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv) were used. The title compound was prepared following the general procedure A. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 64% yield (42.6 mg).

HPLC analysis: the ee (85%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, \( t_R \) (major) = 6.9 min, \( t_R \) (minor) =
7.5 min.

(R)-N-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)benzamide (Figure 3, 3b). From (E)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (1b) (47.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 73% yield (52.5 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.80 (d, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 2H), 2.86 – 2.77 (m, 1H), 1.74 – 1.66 (m, 1H), 1.60 – 1.53 (m, 1H), 1.47 – 1.35 (m, 2H), 1.33 – 1.20 (m, 20H), 0.88 (t, $J = 6.9$ Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.9, 133.1, 128.6, 128.2, 81.2, 32.0, 31.4, 29.9, 29.4, 28.0, 25.4, 25.3, 22.8, 14.3;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 18.3;

HRMS (ESI) calcd. for C$_{21}$H$_{35}$BN$_3$O$_3$ [M+H]$^+$ m/z 360.2705, found 360.2699;

IR (neat, cm$^{-1}$) 3196, 2925, 2855, 1610, 1112, 705;

[a]$_D^{25}$ = –36.4 (c = 1.10, CHCl$_3$);

HPLC analysis: the ee (95%) was determined using a CHIRALCEL® OD-H column, 8% iPrOH in hexane, 0.5 mL/min, 254 nm UV detector, $t_R$ (minor) = 7.3 min, $t_R$ (major) = 8.0 min.

(R)-N-(5-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)
**benzamide** (Figure 3, 3c). From (E)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (1c) (54.4 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 56% yield (44.2 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (s, 1H), 7.78 (d, $J = 7.4$ Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 7.5$ Hz, 2H), 7.20 − 7.14 (m, 3H), 2.87 − 2.78 (m, 1H), 2.69 − 2.55 (m, 2H), 1.78 − 1.69 (m, 1H), 1.69 − 1.57 (m, 3H), 1.51 − 1.40 (m, 2H), 1.25 (s, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.0, 142.8, 133.2, 128.7, 128.6, 128.4, 128.2, 125.7, 81.3, 35.9, 31.6, 31.2, 27.5, 25.4, 25.3;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 18.2;

HRMS (ESI) calcd. for C$_{24}$H$_{32}$BNNaO$_3$ [M+Na]$^+$ m/z 416.2367, found 416.2358;

IR (neat, cm$^{-1}$) 3193, 2970, 2927, 1610, 1576, 1113, 698, 580;

[α]$^D_{25}$ = −32.4 (c = 0.89, CHCl$_3$);

**HPLC analysis**: the ee (96%) was determined using a CHIRALPAK® IE-3 column, 10% EtOH in hexane, 0.8 mL/min, 240 nm UV detector, $t_R$ (major) = 7.4 min, $t_R$ (minor) = 7.8 min.

(R)-N-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide (Figure 3, 3d). From (E)-4,4,5,5-tetramethyl-2-(3-methylbut-1-en-1-yl)-1,3,2-dioxaborolane (1d) (39.2 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following
the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 68% yield (43.0 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, J = 7.4 Hz, 2H), 7.64 (s, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 2.95 (t, J = 6.8 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.53 – 1.47 (m, 2H), 1.27 (s, 12H), 0.96 (d, J = 6.5 Hz, 6H);

¹³C NMR (126 MHz, CDCl₃) δ 170.9, 133.1, 128.7, 128.4, 128.0, 81.2, 40.6, 26.3, 25.3, 25.3, 23.6, 22.2;

¹¹B NMR (160 MHz, CDCl₃) δ 18.6;

HRMS (ESI) calcd. for C₁₉H₂₉BNO₃ [M+H]^+ m/z 318.2235, found 318.2231;

IR (neat, cm⁻¹) 2958, 1609, 1528, 1113, 1098, 707;

[α]D²⁵ = −37.3 (c = 0.96, CHCl₃);

HPLC analysis: the ee (92%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tₘ (minor) = 4.8 min, tₘ (major) = 5.5 min.

(R)-N-(2-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzamide (Figure 3, 3e). From (E)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e) (47.2 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash
column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 70% yield (50.0 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 – 7.76 (m, 2H), 7.71 (s, 1H), 7.50 (t, $J$ = 7.5 Hz, 1H), 7.38 (t, $J$ = 7.8 Hz, 2H), 3.00 – 2.92 (m, 1H), 1.91 – 1.81 (m, 1H), 1.76 – 1.63 (m, 4H), 1.60 – 1.51 (m, 1H), 1.51 – 1.45 (m, 1H), 1.43 – 1.36 (m, 1H), 1.27 (s, 12H), 1.22 – 1.11 (m, 3H), 1.01 – 0.84 (m, 2H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.8, 133.2, 128.7, 128.3, 128.1, 81.2, 39.1, 35.8, 34.2, 33.0, 26.8, 26.5, 26.5, 25.3, 25.3;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 18.6;

HRMS (ESI) calcd. for C$_{21}$H$_{33}$BN$_2$O$_3$ [M+H]$^+$ m/z 358.2548, found 358.2541;

IR (neat, cm$^{-1}$) 3066, 2921, 1611, 1122, 705;

$[\alpha]_{D}^25 = -41.2$ (c = 1.08, CHCl$_3$);

HPLC analysis: the ee (93%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 254 nm UV detector, $t_R$ (minor) = 6.0 min, $t_R$ (major) = 6.8 min.

(R)-N-(4-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide
(Figure 3, 3f). From (E)-2-(4-chlorobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f) (43.3 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 µL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 µL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a white solid in 59% yield (37.9 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86 (s, 1H), 7.80 (d, $J$ = 7.4 Hz, 2H), 7.46 (t, $J$ = 7.5
Hz, 1H), 7.32 (t, J = 7.7 Hz, 2H), 3.60 – 3.49 (m, 2H), 2.79 (t, J = 6.5 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.86 – 1.77 (m, 1H), 1.77 – 1.68 (m, 1H), 1.27 (s, 12H);

13C NMR (126 MHz, CDCl3) δ 171.3, 133.5, 128.7, 128.4, 127.2, 81.3, 45.3, 30.7, 28.9, 25.4, 25.3;

11B NMR (160 MHz, CDCl3) δ 16.7;

HRMS (ESI) calcd. for C17H26BClNO3 [M+H]+ m/z 338.1689, found 338.1682;

IR (neat, cm⁻¹) 3078, 2966, 1603, 1569, 1532, 1109, 712;

m.p. 53 – 55 °C;

[α]D25 = –53.3 (c = 0.51, CHCl3);

HPLC analysis: the ee (95%) was determined using a CHIRALPAK® ID-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, tR (major) = 5.1 min, tR (minor) = 5.5 min.

(R)-N-(5-Chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (Figure 3, 3g). From (E)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g) (46.1 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl2·6H2O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H2O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)3SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 55% yield (38.4 mg).

1H NMR (500 MHz, CDCl3) δ 8.52 (s, 1H), 7.80 (d, J = 7.3 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 3.59 – 3.48 (m, 2H), 2.83 – 2.75 (m, 1H), 1.83 – 1.74 (m, 2H), 1.74 – 1.66 (s, 1H), 1.64 – 1.51 (m, 3H), 1.26 (s, 12H);

13C NMR (126 MHz, CDCl3) δ 171.1, 133.3, 128.7, 128.3, 127.7, 81.2, 45.2, 32.8, 30.7,
25.5, 25.3, 25.1;

\[ ^{11} \text{B NMR} \ (160 \text{ MHz}, \text{CDCl}_3) \delta 17.6; \]

\[ \text{HRMS (ESI) calcd. for C}_{18}\text{H}_{27}\text{BClNaO}_3 [\text{M}+\text{Na}]^+ \ m/z \ 374.1665, \text{ found } 374.1656; \]

\[ \text{IR (neat, cm}^{-1}) 3193, 2971, 2929, 1610, 1576, 1111, 734; \]

\[ [\alpha]_D^{25} = -40.0 \ (c = 1.08, \text{CHCl}_3); \]

\[ \text{HPLC analysis: the ee (96\%) was determined using a CHIRALPAK® AD-H column,} \]

5\% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, \( t_R \) (minor) = 7.9 min, \( t_R \) (major) = 9.2 min.

\[(R)-N-(5-((\text{tert-Butyldimethylsilyl})oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide \ (\text{Figure 3, 3h}). \]

From (E)-\text{tert-butyldimethyl}(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (1h) (65.3 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol%), \( \text{L}^* \) (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H\(_2\)O (1.8 \( \mu \)L, 0.10 mmol, 0.50 equiv), (EtO\(_3\))\(_3\)SiH (92 \( \mu \)L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 76\% yield (68.2 mg).

\[ ^{1} \text{H NMR} \ (500 \text{ MHz}, \text{CDCl}_3) \delta 7.82 – 7.77 \ (m, 2H), 7.68 \ (s, 1H), 7.53 \ (t, J = 7.5 \text{ Hz}, 1H), 7.41 \ (t, J = 7.8 \text{ Hz}, 2H), 3.64 \ (t, J = 6.2 \text{ Hz}, 2H), 2.92 – 2.83 \ (m, 1H), 1.78 – 1.67 \ (m, 1H), 1.68 – 1.44 \ (m, 5H), 1.27 \ (s, 6H), 1.26 \ (s, 6H), 0.88 \ (s, 9H), 0.04 \ (s, 6H); \]

\[ ^{13} \text{C NMR} \ (126 \text{ MHz}, \text{CDCl}_3) \delta 170.9, 133.2, 128.8, 128.5, 128.0, 81.3, 63.3, 32.9, 31.0, 26.2, 25.4, 25.2, 24.2, 18.5, -5.1; \]

\[ ^{11} \text{B NMR} \ (160 \text{ MHz}, \text{CDCl}_3) \delta 18.9; \]

\[ \text{HRMS (ESI) calcd. for C}_{24}\text{H}_{42}\text{BNNaO}_4\text{Si} [\text{M}+\text{Na}]^+ \ m/z \ 470.2868, \text{ found } 470.2858; \]

\[ \text{IR (neat, cm}^{-1}) 3070, 2928, 2857, 1611, 1096, 706; \]
\[ [\alpha] D_{25} = -41.6 \ (c = 0.98, \text{CHCl}_3) \; ; \]

**HPLC analysis:** the ee (95%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 0.8 mL/min, 240 nm UV detector, \( t_R \) (major) = 4.9 min, \( t_R \) (minor) = 5.7 min.

\[(R)-N-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide \ (\text{Figure 3, 3i}). \] From (E)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1H) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 66% yield (55.9 mg).

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.93 (s, 1H), 7.77 (d, \( J = 7.5 \) Hz, 2H), 7.50 (t, \( J = 7.5 \) Hz, 1H), 7.36 (t, \( J = 7.8 \) Hz, 2H), 7.33 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 4.50 (s, 2H), 3.51 (t, \( J = 6.3 \) Hz, 2H), 2.90 – 2.80 (m, 1H), 1.76 – 1.57 (m, 4H), 1.57 – 1.51 (m, 2H), 1.26 (s, 12H);

\(^{13}\)C NMR (126 MHz, CDCl₃) δ 171.0, 138.6, 133.2, 128.7, 128.5, 128.1, 127.8, 127.7, 81.1, 73.1, 70.6, 30.9, 29.6, 25.4, 25.2, 24.6;

\(^{11}\)B NMR (160 MHz, CDCl₃) δ 18.3;

**HRMS** (ESI) calcd. for C₂₅H₃₄BNNaO₄ \([M + Na]^+\) m/z 446.2473, found 446.2462;

**IR** (neat, cm\(^{-1}\)) 3195, 2927, 2856, 1610, 1098, 707;

\([\alpha] D_{25} = -41.6 \ (c = 1.06, \text{CHCl}_3) \; ; \]

**HPLC analysis:** the ee (96%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, \( t_R \) (major) = 8.3 min, \( t_R \) (minor) =
(R)-6-Benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (Figure 3, 3j). From (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl benzoate (1j) (66.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 66% yield (59.7 mg).

**1H NMR** (500 MHz, CDCl₃) δ 8.06 – 7.92 (m, 3H), 7.87 (d, J = 7.3 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.44 – 7.37 (m, 4H), 4.48 – 4.39 (m, 1H), 4.32 – 4.22 (m, 1H), 2.83 (t, J = 5.9 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.78 – 1.67 (m, 2H), 1.66 – 1.57 (m, 1H), 1.56 – 1.39 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H);

**13C NMR** (126 MHz, CDCl₃) δ 171.0, 167.2, 133.3, 133.1, 130.5, 129.7, 128.8, 128.5, 128.2, 81.1, 64.7, 31.2, 29.0, 27.1, 25.7, 25.5, 25.2;

**11B NMR** (160 MHz, CDCl₃) δ 18.2;

**HRMS** (ESI) calcd. for C₂₆H₃₄BNNaO₅ [M+Na]⁺ m/z 474.2422, found 474.2413;

**IR** (neat, cm⁻¹) 3050, 2970, 2930, 1716, 1610, 1265, 1117, 734;

[α]D²⁵ = −58.1 (c = 0.98, CHCl₃);

**HPLC analysis**: the ee (95%) was determined using a CHIRALPAK® IF-3 column, 10% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, tᵣ (major) = 6.8 min, tᵣ (minor) = 7.6 min.
(R)-N-(6-((N,4-Dimethylphenyl)sulfonamido)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 3, 3k). From (E)-N,4-dimethyl-N-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)benzenesulfonamide (1k) (78.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a white solid in 57% yield (58.7 mg).

\(^1\)H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.92 (d, \(J = 7.5\) Hz, 2H), 7.63 (d, \(J = 8.2\) Hz, 2H), 7.51 (t, \(J = 7.4\) Hz, 1H), 7.39 (t, \(J = 7.7\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 3.21 – 3.11 (m, 1H), 2.93 – 2.85 (m, 1H), 2.82 – 2.73 (m, 1H), 2.68 (s, 3H), 2.42 (s, 3H), 1.72 – 1.43 (m, 7H), 1.38 – 1.31 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H);

\(^13\)C NMR (126 MHz, CDCl₃) δ 171.3, 143.5, 134.4, 133.2, 129.8, 128.7, 128.4, 127.9, 127.4, 80.8, 49.0, 34.5, 30.9, 26.4, 26.0, 25.5, 25.2, 24.8, 21.6;

\(^11\)B NMR (160 MHz, CDCl₃) δ 17.3;

HRMS (ESI) calcd. for C₂₇H₃₉BN₂NaO₅S [M+Na]^+ m/z 537.2565, found 537.2556;

IR (neat, cm⁻¹) 3050, 2929, 1610, 1156, 732;

m.p. 123 – 125 °C;

\([\alpha]_D^{25} = –25.5 (c = 1.05, CHCl₃);

HPLC analysis: the ee (97%) was determined using a CHIRALPAK® IG-3 column, 20% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, \(t_R\) (major) = 9.7 min, \(t_R\) (minor) = 12.3 min.
(R)-5-Benzamido-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (Figure 3, 3I). From (E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (11) (88.9 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 60% yield (67.9 mg).

¹H NMR (500 MHz, CDCl₃) δ 8.19 (s, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.59 (s, 1H), 4.07 (t, J = 6.1 Hz, 2H), 3.90 (t, J = 5.5 Hz, 2H), 2.83 (t, J = 6.0 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 1.79 – 1.61 (m, 7H), 1.61 – 1.53 (m, 1H), 1.53 – 1.41 (m, 2H), 1.28 (s, 6H), 1.27 (s, 6H), 1.20 (s, 6H);

¹³C NMR (126 MHz, CDCl₃) δ 178.2, 171.1, 157.0, 136.6, 133.3, 130.4, 128.6, 128.3, 127.7, 123.7, 120.8, 112.1, 81.1, 68.1, 64.5, 42.2, 37.2, 31.0, 28.9, 25.4, 25.3, 25.2, 24.1, 21.5, 15.9;

¹¹B NMR (160 MHz, CDCl₃) δ 17.9;

HRMS (ESI) calcd. for C₃₃H₄₈BNaO₆ [M+Na⁺] m/z 588.3467, found 588.3453;

IR (neat, cm⁻¹) 2925, 1725, 1610, 1151, 1127, 707;

[α]D²⁵ = –30.3 (c = 0.98, CHCl₃);

HPLC analysis: the ee (96%) was determined using a CHIRALPAK® AD-H column, 8% iPrOH in hexane, 0.8 mL/min, 240 nm UV detector, tᵣ(minor) = 7.0 min, tᵣ(major) = 8.1 min.
(R)-5-Benzamido-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 4-(N,N-dipropylsulfamoyl)benzoate (Figure 3, 3m). From (E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (1m) (95.9 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 60% yield (72.2 mg).

¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.52 (s, 1H), 7.42 (t, J = 7.7 Hz, 2H), 4.37 (t, J = 6.5 Hz, 2H), 3.13 – 3.04 (m, 4H), 2.98 – 2.88 (m, 1H), 1.89 – 1.75 (m, 3H), 1.69 – 1.49 (m, 7H), 1.26 (s, 6H), 1.26 (s, 6H), 0.86 (t, J = 7.4 Hz, 6H);

¹³C NMR (126 MHz, CDCl₃) δ 170.9, 165.6, 144.3, 133.8, 133.3, 130.3, 128.8, 128.0, 127.1, 81.5, 65.7, 50.1, 31.1, 28.9, 25.4, 25.2, 24.2, 22.1, 11.3;

¹¹B NMR (160 MHz, CDCl₃) δ 18.0;

HRMS (ESI) calcd. for C₃₁H₄₅BN₂NaO₇S [M+Na]⁺ m/z 623.2933, found 623.2923;

IR (neat, cm⁻¹) 2967, 2932, 1721, 1609, 1272, 1155, 1087, 601;

[α]D²⁵ = −30.7 (c = 1.04, CHCl₃);

HPLC analysis: the ee (96%) was determined using a CHIRALPAK® ID-3 column, 15% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, tᵣ (major) = 9.2 min, tᵣ (minor) = 13.5 min.
From \((1R,2S,5R)-2\)-isopropyl-5-methylcyclohexyl \((R)-6\)-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, 3n). From \((1R,2S,5R)-2\)-isopropyl-5-methylcyclohexyl \((E)-6-(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{hex-5-enoate (1n}) (75.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\(_2\cdot6\)H\(_2\)O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H\(_2\)O (1.8 µL, 0.10 mmol, 0.50 equiv), (EtO\(_3\))\(_3\)SiH (92 µL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 58% yield (58.1 mg).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.44 (s, 1H), 7.90 (d, \(J = 7.5\) Hz, 2H), 7.53 (t, \(J = 7.4\) Hz, 1H), 7.40 (t, \(J = 7.7\) Hz, 2H), 6.9 (td, \(J = 10.9, 4.3\) Hz, 1H), 2.93 – 2.84 (m, 1H), 2.43 – 2.22 (m, 2H), 2.00 – 1.92 (m, 1H), 1.90 – 1.80 (m, 1H), 1.78 – 1.62 (m, 5H), 1.62 – 1.54 (m, 1H), 1.54 – 1.41 (m, 3H), 1.41 – 1.32 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 1.10 – 0.92 (m, 2H), 0.89 (d, \(J = 3.9\) Hz, 3H), 0.89 – 0.81 (m, 4H), 0.76 (d, \(J = 7.0\) Hz, 3H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 174.4, 171.2, 133.3, 128.7, 128.3, 127.8, 81.0, 74.5, 47.1, 41.1, 34.4, 34.3, 31.6, 30.0, 27.1, 26.4, 25.4, 25.2, 24.0, 23.6, 22.2, 20.8, 16.4;

\(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \(\delta\) 17.2;

HRMS (ESI) calcd. for C\(_{29}\)H\(_{46}\)BNNaO\(_5\) [M+Na]\(^+\) m/z 500.3542, found 500.3531;

IR (neat, cm\(^{-1}\)) 2957, 2928, 1724, 1610, 1113;

\([\alpha]_D^{25} = -59.2\) (c = 1.01, CHCl\(_3\));

HPLC analysis: the \(dr\) (98:2) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, \(t_R\) (major) = 5.7 min, \(t_R\) (minor) = 8.6 min.
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (S)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, 3n’). From (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (1n) (75.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), ent-L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 55% yield (55.0 mg).

¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 4.71 (td, J = 10.9, 4.4 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.43 – 2.22 (m, 2H), 2.02 – 1.92 (m, 1H), 1.87 – 1.78 (m, 1H), 1.79 – 1.62 (m, 5H), 1.62 – 1.54 (m, 1H), 1.54 – 1.40 (m, 3H), 1.40 – 1.32 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.11 – 0.93 (m, 2H), 0.90 (d, J = 6.5 Hz, 3H), 0.88 – 0.81 (m, 4H), 0.73 (d, J = 6.9 Hz, 3H);

¹³C NMR (126 MHz, CDCl₃) δ 174.4, 171.2, 133.3, 128.7, 128.3, 127.8, 81.0, 74.6, 47.1, 41.1, 34.4, 34.3, 31.6, 30.0, 27.1, 26.4, 25.4, 25.1, 23.9, 23.6, 22.2, 20.9, 16.5;

¹¹B NMR (160 MHz, CDCl₃) δ 17.2;

HRMS (ESI) calcd. for C₂₉H₄₆BNNaO₅ [M+Na]⁺ m/z 500.3542, found 500.3532;

IR (neat, cm⁻¹) 2954, 2926, 1711, 1603, 1106;

[α]D²⁵ = +7.1 (c = 0.98, CHCl₃);

HPLC analysis: the dr (2:98) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tᵣ (minor) = 5.7 min, tᵣ (major) = 8.6 min.
(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (R)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, 3o). From (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (1o) (96.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 58% yield (70.3 mg).

¹H NMR (500 MHz, CDCl₃) δ 8.22 (s, 1H), 7.87 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 5.87 (d, J = 3.6 Hz, 1H), 5.30 (d, J = 2.7 Hz, 1H), 4.49 (d, J = 3.7 Hz, 1H), 4.23 – 4.14 (m, 2H), 4.10 – 4.04 (m, 1H), 4.02 – 3.96 (m, 1H), 2.92 – 2.84 (m, 1H), 2.47 – 2.32 (m, 2H), 1.80 – 1.56 (m, 4H), 1.56 – 1.41 (m, 5H), 1.34 (s, 3H), 1.30 (s, 3H), 1.29 – 1.24 (m, 15H);

¹³C NMR (126 MHz, CDCl₃) δ 173.1, 171.2, 133.4, 128.8, 128.3, 127.7, 112.4, 109.5, 105.2, 83.5, 81.1, 80.1, 76.2, 72.6, 67.4, 34.0, 30.3, 26.9, 26.9, 26.4, 25.4, 25.1, 23.9;

¹¹B NMR (160 MHz, CDCl₃) δ 17.7;

HRMS (ESI) calcd. for C₃₃H₄₆BNNaO₁₀ [M+Na]⁺ m/z 626.3107, found 626.3105;

IR (neat, cm⁻¹) 2986, 2933, 1745, 1610, 1373, 1155;
$[\alpha]_D^{25} = -46.6 \ (c = 1.00, \ CHCl_3)$;

**HPLC analysis:** the $dr \ (97:3)$ was determined using a CHIRALPAK® IF-3 column, 12% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (major) = 6.8 min, $t_R$ (minor) = 7.5 min.

![CHEMISTRY IMAGE]

(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-$d$][1,3]dioxol-6-yl]hexanoate (S)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, 3o'). From (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-$d$][1,3]dioxol-6-yl]hex-5-enoate (1o) (96.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), ent-L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 61% yield (73.4 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.24 (s, 1H), 7.87 (d, $J = 7.3$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 5.87 (d, $J = 3.7$ Hz, 1H), 5.28 (d, $J = 2.0$ Hz, 1H), 4.47 (d, $J = 3.7$ Hz, 1H), 4.24 – 4.17 (m, 2H), 4.11 – 4.05 (m, 1H), 4.04 – 3.98 (m, 1H), 2.91 – 2.82 (m, 1H), 2.49 – 2.30 (m, 2H), 1.80 – 1.56 (m, 4H), 1.55 – 1.42 (m, 5H), 1.39 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.27 (s, 6H), 1.26 (s, 6H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.2, 171.2, 133.4, 128.8, 128.3, 127.8, 112.4, 109.5,
105.2, 83.6, 81.1, 79.9, 76.3, 72.5, 67.4, 33.9, 30.2, 27.0, 27.0, 26.9, 26.4, 25.4, 25.1, 24.0;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 17.5;

HRMS (ESI) calcd. for C$_{31}$H$_{46}$BNNaO$_{10}$ [M+Na]$^+$ m/z 626.3107, found 626.3109;

IR (neat, cm$^{-1}$) 2987, 2934, 1746, 1610, 1373, 1157;

$\left[\alpha\right]_D^2 = +14.1$ (c = 1.00, CHCl$_3$);

HPLC analysis: the $dr$ (3:97) was determined using a CHIRALPAK® IF-3 column, 12% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (minor) = 6.7 min, $t_R$ (major) = 7.5 min.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (R)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, 3p). From (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (1p) (130.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 $\mu$L, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 $\mu$L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 5:2) to provide the title compound as a colorless oil in 57% yield (88.7 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.44 (s, 1H), 7.81 (d, $J$ = 7.6 Hz, 2H), 7.49 (t, $J$ = 7.4 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 2H), 2.91 – 2.82 (m, 1H), 2.73 – 2.51 (m, 4H), 2.08 (s, 3H), 2.02 – 1.84 (m, 7H), 1.84 – 1.65 (m, 5H), 1.64 – 1.47 (m, 5H), 1.45 – 1.33 (m, 4H), 1.32 – 1.18 (m, 23H), 1.17 – 1.01 (m, 6H), 0.90 – 0.79 (m, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.4, 171.2, 149.5, 140.6, 133.3, 128.7, 128.3, 127.6,
$^{11}$B NMR (160 MHz, CDCl$_3$) δ 17.2;

HRMS (ESI) calcd. for C$_{48}$H$_{76}$BNNaO$_6$ [M+Na]$^+$ m/z 796.5658, found 796.5652;

IR (neat, cm$^{-1}$) 2925, 2866, 1751, 1610, 1110;

[α]$^D_{25}$ = –19.2 (c = 1.01, CHCl$_3$);

HPLC analysis: the $dr$ (98:2) was determined using a CHIRALPAK® ID-3 column, 10% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (major) = 4.9 min, $t_R$ (minor) = 5.7 min.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (S)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, 3p'). From (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (1p) (130.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), en-t-L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 5:2) to provide the title compound as a colorless oil in 58% yield (90.5 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.52 (s, 1H), 7.81 (d, $J = 7.7$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 2H), 2.90 – 2.82 (m, 1H), 2.72 – 2.51 (m, 4H), 2.08 (s, 3H), 2.03 – 1.84 (m, 7H), 1.84 – 1.65 (m, 5H), 1.63 – 1.46 (m, 5H), 1.44 – 1.32 (m, 4H),
1.31 – 1.20 (m, 23H), 1.16 – 1.03 (m, 6H), 0.89 – 0.81 (m, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.4, 171.2, 149.5, 140.6, 133.3, 128.6, 128.3, 127.5, 126.7, 124.9, 123.1, 117.5, 80.9, 75.2, 39.5, 37.6, 37.6, 37.4, 33.9, 32.9, 32.8, 31.2, 28.1, 27.2, 25.4, 25.2, 24.9, 24.6, 24.2, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.2, 12.3, 12.0;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 17.1;

HRMS (ESI) calcd. for C$_{48}$H$_{76}$BNNaO$_6$ [M+Na]$^+$ m/z 796.5658, found 796.5654;

IR (neat, cm$^{-1}$) 2926, 2867, 1750, 1610, 1110;

$[\alpha]_D^{25} = +26.7$ (c = 1.07, CHCl$_3$);

HPLC analysis: the $dr$ (2:98) was determined using a CHIRALPAK® ID-3 column, 10% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (major) = 4.9 min, $t_R$ (minor) = 5.7 min.

(R)-4-Methoxy-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl) benzamide (Figure 4, 4b). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (2b) (57.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 $\mu$L, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 $\mu$L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a white solid in 72% yield (51.8 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.52 (s, 1H), 7.78 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 8.9$ Hz, 2H), 3.80 (s, 3H), 2.69 (t, $J = 6.6$ Hz, 1H), 1.72 – 1.63 (m, 1H), 1.58 – 1.48 (m, 1H), 1.47 – 1.36 (m, 2H), 1.35 – 1.27 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H), 0.88 (t, $J = 7.0$ Hz, 3H);
$^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.7, 163.6, 130.5, 119.4, 113.8, 80.7, 55.5, 32.2, 31.4, 27.7, 25.5, 25.3, 22.7, 14.3;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 15.8;

HRMS (ESI) calcd. for C$_{20}$H$_{33}$BN$_2$O$_4$ [M+H]$^+$ m/z 362.2497, found 362.2489;

IR (neat, cm$^{-1}$) 3064, 2925, 2854, 1609, 1497, 1260, 1108;

m.p. 166 – 168 °C;

$[\alpha]_D^{25} = -59.2$ (c = 0.98, CHCl$_3$);

**HPLC analysis:** the ee (95%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, $t_R$ (major) = 7.2 min, $t_R$ (minor) = 8.1 min.

(R)-4-(Methylthio)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 4, 4c). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-(methylthio)phenyl)-1,4,2-dioxazol-5-one (2c) (62.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), $L^*$ (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 61% yield (46.0 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.68 (s, 1H), 7.70 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 2H), 2.73 (t, $J = 6.5$ Hz, 1H), 2.47 (s, 3H), 1.74 – 1.63 (m, 1H), 1.59 – 1.49 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.27 (m, 4H), 1.27 (s, 12H), 0.88 (t, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.5, 146.2, 128.7, 124.9, 123.2, 81.0, 32.2, 31.4, 27.6, 25.4, 25.3, 22.7, 14.8, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 16.6;
HRMS (ESI) calcd. for C_{20}H_{33}BNO_{3}S [M+H]^+ m/z 378.2269, found 378.2260;
IR (neat, cm\(^{-1}\)) 3205, 2969, 2929, 1602, 1547, 1115, 733;
m.p. 166 – 167 °C;
\([\alpha]_D^{25} = -59.5\) (c = 1.16, CHCl\(_3\));
**HPLC analysis:** the ee (93%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 220 nm UV detector, \(t_R\) (major) = 9.7 min, \(t_R\) (minor) = 10.8 min.

![ tert-Butyl (R)-(4-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)phenyl)carbamate (Figure 4, 4d). From \((E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and tert-butyl (4-(5-oxo-1,4,2-dioxazol-3-yl)phenyl)carbamate (2d) (83.5 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H\(_2\)O (1.8 \(\mu\)L, 0.10 mmol, 0.50 equiv), (EtO)\(_3\)SiH (92 \(\mu\)L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 67% yield (59.8 mg).

\(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.14 (s, 1H), 7.57 (d, \(J = 8.4\) Hz, 2H), 7.40 (d, \(J = 8.6\) Hz, 2H), 2.77 – 2.67 (m, 1H), 1.76 – 1.65 (m, 1H), 1.56 – 1.38 (m, 12H), 1.36 – 1.24 (m, 16H), 0.85 (t, \(J = 6.4\) Hz, 3H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 170.5, 153.2, 143.7, 129.4, 120.3, 117.7, 81.2, 80.6, 32.1, 31.4, 28.5, 28.1, 25.5, 25.4, 22.7, 14.2;

\(^{11}\)BNMR (160 MHz, CDCl\(_3\)) \(\delta\) 15.5;

HRMS (ESI) calcd. for C\(_{24}\)H\(_{39}\)BN\(_2\)NaO\(_5\) [M+Na]^+ m/z 469.2844, found 469.2834;
IR (neat, cm\(^{-1}\)) 3224, 2929, 1733, 1605, 1520, 1154, 1096, 737;
m.p. 204 – 205 °C;
\[ \alpha \]_{D}^{25} = -37.7 (c = 1.10, CHCl \textsubscript{3});

**HPLC analysis:** the ee (94%) was determined using a CHIRALPAK® IF-3 column, 5% EtOH in hexane, 1.0 mL/min, 220 nm UV detector, \( t_{R} \) (major) = 5.7 min, \( t_{R} \) (minor) = 6.3 min.

(R)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-naphthamide

(Figure 4, 4e). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(naphthalen-1-yl)-1,4,2-dioxazol-5-one (2e) (64.0 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\textsubscript{2}·6H\textsubscript{2}O (4.8 mg, 10 mol%), \( \text{L}^* \) (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H\textsubscript{2}O (1.8 \mu\text{L}, 0.10 mmol, 0.50 equiv), (EtO\textsubscript{3})SiH (92 \mu\text{L}, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4:1) to provide the title compound as a white solid in 60% yield (45.7 mg).

**1\text{H NMR}** (500 MHz, CDCl\textsubscript{3}) \( \delta = 8.39 \) (d, \( J = 8.0 \) Hz, 1H), 7.93 (d, \( J = 8.2 \) Hz, 1H), 7.88 – 7.84 (m, 1H), 7.67 (d, \( J = 6.9 \) Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 6.88 (s, 1H), 3.17 – 3.09 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 – 1.60 (m, 1H), 1.50 – 1.39 (m, 2H), 1.39 – 1.32 (m, 4H), 1.30 (s, 12H), 0.89 (t, \( J = 7.0 \) Hz, 3H);

**13\text{C NMR}** (126 MHz, CDCl\textsubscript{3}) \( \delta = 172.1, 133.7, 132.0, 130.4, 130.0, 128.5, 127.6, 126.7, 126.4, 125.5, 124.7, 82.4, 32.0, 31.3, 27.6, 25.3, 25.2, 22.7, 14.2;

**11\text{B NMR}** (160 MHz, CDCl\textsubscript{3}) \( \delta = 23.9; \)

**HRMS** (ESI) calcd. for C\textsubscript{23}H\textsubscript{33}BNO\textsubscript{3} [M+H]\textsuperscript{+} m/z 382.2548, found 382.2542;

**IR** (neat, cm\textsuperscript{-1}) 3176, 3065, 2931, 1579, 1532, 1191, 1127, 779;

**m.p.** 53 – 55 °C

\[ \alpha \]_{D}^{25} = -34.4 (c = 0.62, CHCl\textsubscript{3});

**HPLC analysis:** the ee (84%) was determined using a CHIRALPAK® ID-3 column, 5%
EtOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (major) = 4.7 min, $t_R$ (minor) = 5.1 min.

(R)-4-Chloro-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide
(Figure 4, 4f). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (2f) (59.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 62% yield (45.7 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.57 (s, 1H), 7.74 (d, $J$ = 8.6 Hz, 2H), 7.29 (d, $J$ = 8.6 Hz, 2H), 2.85 – 2.78 (m, 1H), 1.77 – 1.64 (m, 1H), 1.62 – 1.51 (m, 1H), 1.46 – 1.36 (m, 2H), 1.35 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, $J$ = 7.0 Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 169.5, 139.6, 129.7, 128.9, 126.6, 81.7, 32.1, 31.3, 27.5, 25.3, 25.2, 22.7, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 19.1;

HRMS (ESI) calcd. for C$_{19}$H$_{29}$BCINNaO$_3$ [M+Na]$^+$ m/z 388.1821, found 388.1811;

IR (neat, cm$^{-1}$) 3066, 2969, 2927, 1606, 1485, 1092;

$[\alpha]_D^{25} = -47.6$ (c = 1.09, CHCl$_3$);

HPLC analysis: the ee (96%) was determined using a CHIRALPAK® AS-H column, 3% iPrOH in hexane, 0.4 mL/min, 254 nm UV detector, $t_R$ (minor) = 9.3 min, $t_R$ (major) = 10.3 min.
Methyl \((R)-4-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)benzoate\) (Figure 4, 4g). From \((E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane\) (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and methyl 4-(5-oxo-1,4,2-dioxazol-3-yl)benzoate (2g) (66.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), MeOH (4.0 μL, 0.10 mmol, 0.50 equiv, instead of H\(_2\)O), (EtO\(_3\))SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 62% yield (48.4 mg).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.18 (s, 1H), 7.98 (d, \(J = 8.4\) Hz, 2H), 7.85 (d, \(J = 8.5\) Hz, 2H), 3.93 (s, 3H), 3.00 – 2.91 (m, 1H), 1.77 – 1.68 (m, 1H), 1.65 – 1.53 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.24 (m, 16H), 0.88 (t, \(J = 7.0\) Hz, 3H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 169.2, 166.1, 133.8, 133.3, 129.8, 128.1, 82.1, 52.6, 32.1, 31.2, 27.4, 25.3, 25.2, 22.7, 14.2;

\(^{11}\)B NMR (160 MHz, CDCl\(_3\)) δ 21.8;

HRMS (ESI) calcd. for C\(_{21}\)H\(_{33}\)BNO\(_5\) [M+H]\(^+\) m/z 390.2446, found 390.2436;

IR (neat, cm\(^{-1}\)) 2925, 2856, 1730, 1603, 1107, 725;

m.p. 116 – 118 °C;

\([\alpha]_D^{25} = -27.8\) (c = 1.01, CHCl\(_3\));

HPLC analysis: the ee (93%) was determined using two connected CHIRALCEL\textsuperscript{®} OD-H columns, 3% iPrOH in hexane, 0.8 mL/min, 254 nm UV detector, \(t_R\) (major) = 15.7 min, \(t_R\) (minor) = 18.7 min.
\((R)\)-N-(1-(4,4,5,5\text{-}Tetramethyl\text{-}1,3,2-dioxaborolan\text{-}2\text{-}yl)hexyl)thiophene\text{-}3\text{-}carboxamide (Figure 4, 4h). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(thiophen-3-yl)-1,4,2-dioxazol-5-one (2h) (50.7 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H\(_2\)O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO\(_3\))\(_3\)SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 74% yield (49.7 mg).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.65 (s, 1H), 8.09 (dd, \(J = \) 2.9, 1.0 Hz, 1H), 7.44 (dd, \(J = \) 5.1, 1.1 Hz, 1H), 7.21 (dd, \(J = \) 5.1, 3.0 Hz, 1H), 2.76 (t, \(J = \) 5.9 Hz, 1H), 1.74 – 1.63 (m, 1H), 1.60 – 1.48 (m, 1H), 1.48 – 1.36 (m, 2H), 1.35 – 1.27 (m, 4H), 1.26 (s, 12H), 0.88 (t, \(J = \) 7.0 Hz, 3H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 166.4, 132.3, 130.5, 126.6, 126.6, 81.3, 32.1, 31.3, 27.5, 25.3, 25.2, 22.7, 14.2;

\(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \(\delta\) 17.3;

HRMS (ESI) calcd. for C\(_{17}\)H\(_{28}\)BNNaO\(_3\)S [M+Na]\(^+\) m/z 360.1775, found 360.1765;

IR (neat, cm\(^{-1}\)) 3119, 2965, 2925, 1594, 1098;

\([\alpha]_D^{25} = \) –51.0 (c = 1.01, CHCl\(_3\));

HPLC analysis: the ee (98%) was determined using a CHIRALCEL\textsuperscript{®} OD-H column, 2% iPrOH in hexane, 1.0 mL/min, 254 nm UV detector, \(t_R\) (minor) = 6.1 min, \(t_R\) (major) = 8.4 min.

\((R)\)-3-Methyl-N-(1-(4,4,5,5\text{-}Tetramethyl\text{-}1,3,2-dioxaborolan\text{-}2\text{-}yl)hexyl)but-2-enamide (Figure 4, 4i). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-methylprop-1-en-1-yl)-
1,4,2-dioxazol-5-one (2i) (42.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 63% yield (39.2 mg).

**¹H NMR** (500 MHz, CDCl₃) δ 8.65 (s, 1H), 5.74 (s, 1H), 2.40 – 2.33 (m, 1H), 2.18 (s, 3H), 1.87 (s, 3H), 1.60 – 1.51 (m, 1H), 1.47 – 1.39 (m, 1H), 1.36 – 1.24 (m, 6H), 1.21 (s, 6H), 1.19 (s, 6H), 0.87 (t, J = 6.9 Hz, 3H);

**¹³C NMR** (126 MHz, CDCl₃) δ 170.8, 158.2, 112.1, 80.2, 32.2, 31.5, 28.3, 28.0, 25.5, 25.1, 22.8, 21.0, 14.3;

**¹¹B NMR** (160 MHz, CDCl₃) δ 14.1;

**HRMS** (ESI) calcd. for C₁₇H₃₃BNO₃ [M+H]⁺ m/z 310.2548, found 310.2543;

**IR** (neat, cm⁻¹) 3176, 2965, 2927, 1665, 1573, 1156, 1107;

[α]D²⁵ = −79.0 (c = 1.00, CHCl₃);

**HPLC analysis**: the ee (97%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tR (major) = 5.2 min, tR (minor) = 7.2 min.

\[(R)-N-(5-(Naphthalen-2-ylmethoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)acetamide\] (Figure 4, 4j). From (E)-4,4,5,5-tetramethyl-2-(5-(naphthalen-2-ylmethoxy)pent-1-en-1-yl)-1,3,2-dioxaborolane (1t) (70.5 mg, 0.20 mmol, 1.0 equiv) and 3-methyl-1,4,2-dioxazol-5-one (2j) (30.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA

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(1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH = 10:1) to provide the title compound as a colorless oil in 47% yield (38.3 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 (s, 1H), 7.84 – 7.78 (m, 3H), 7.75 (s, 1H), 7.49 – 7.41 (m, 3H), 4.63 (s, 2H), 3.56 – 3.47 (m, 2H), 2.55 – 2.46 (m, 1H), 1.94 (s, 3H), 1.74 – 1.56 (m 3H), 1.56 – 1.37 (m, 3H), 1.17 (s, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 175.0, 136.1, 133.4, 133.1, 128.3, 128.0, 127.8, 126.6, 126.3, 126.0, 126.0, 80.7, 73.2, 70.6, 30.8, 29.6, 25.4, 25.2, 24.8, 18.1;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 16.6;

HRMS (ESI) calcd. for C$_{24}$H$_{34}$BNNaO$_4$ [M+Na]$^+$ m/z 434.2473, found 434.2461;

IR (neat, cm$^{-1}$) 3053, 2969, 2927, 1609, 1557, 1154, 1097;

$[^{[\alpha]}]D^{25} = -59.4$ (c = 1.04, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALCEL® OD-H column, 5% iPrOH in hexane, 1.0 mL/min, 254 nm UV detector, $t_R$ (minor) = 10.0 min, $t_R$ (major) = 12.1 min.

![Chemical structure](image)

(R)-N-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)octanamide (Figure 4, 4k). From (E)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborole (1i) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-heptyl-1,4,2-dioxazol-5-one (2k) (55.6 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 µL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 µL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 63% yield (56.4 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 (s, 1H), 7.35 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H),
4.48 (s, 2H), 3.53 – 3.43 (m, 2H), 2.60 – 2.52 (m, 1H), 2.27 – 2.14 (m, 2H), 1.71 – 1.52 (m, 5H), 1.52 – 1.38 (m, 3H), 1.32 – 1.22 (m, 8H), 1.20 (s, 12H), 0.87 (t, J = 7.0 Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.1, 138.6, 128.5, 127.8, 127.7, 80.8, 73.1, 70.6, 31.9, 31.7, 30.8, 29.6, 29.2, 28.9, 25.3, 25.1, 24.8, 22.7, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 16.6;

HRMS (ESI) calcd. for C$_{26}$H$_{44}$BNaO$_4$ [M+Na]$^+$ m/z 468.3256, found 468.3246;

IR (neat, cm$^{-1}$) 2963, 2925, 1603, 1155, 1099;

$[\alpha]_D^{25}$ = –50.0 (c = 1.08, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALCEL$^\circledR$ OD-H column, 8% iPrOH in hexane, 0.5 mL/min, 210 nm UV detector, $t_R$ (major) = 9.6 min, $t_R$ (minor) = 10.6 min.

(R)-3-Phenyl-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, 4l). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenethyl-1,4,2-dioxazol-5-one (2l) (57.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L$^*$ (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 $\mu$L, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 $\mu$L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 61% yield (43.9 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.43 (s, 1H), 7.30 – 7.24 (m, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.4 Hz, 2H), 2.91 (t, J = 7.8 Hz, 2H), 2.64 – 2.51 (m, 3H), 1.61 – 1.51 (m, 1H), 1.39 – 1.32 (m, 1H), 1.31 – 1.22 (m, 6H), 1.21 (s, 12H), 0.87 (t, J = 6.8 Hz, 3H);
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.3, 139.8, 128.8, 128.4, 126.7, 81.1, 34.1, 32.0, 31.2, 31.2, 27.8, 25.4, 25.2, 22.7, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 19.2;

HRMS (ESI) calcd. for C$_{21}$H$_{35}$BN$_3$O$_3$ [M+H]$^+$ m/z 360.2705, found 360.2696;

IR (neat, cm$^{-1}$) 3168, 2961, 2926, 1604, 1550, 1155, 1109;

$[\alpha]_D^{25} = -43.0$ (c = 0.91, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALCEL® OD-H column, 5% iPrOH in hexane, 1.0 mL/min, 210 nm UV detector, $t_R$ (minor) = 5.7 min, $t_R$ (major) = 6.5 min.

(R)-3-(4-Cyanophenyl)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, 4m). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-1(1H)-yl)benzonitrile (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 4-(2-(5-oxo-1,4,2-dioxazol-3-yl)ethyl)benzonitrile (2m) (64.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 $\mu$L, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 $\mu$L, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 48% yield (36.8 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 8.2 Hz, 2H), 6.41 (s, 1H), 3.02 (t, $J$ = 7.5 Hz, 2H), 2.83 – 2.74 (m, 1H), 2.62 – 2.48 (m, 2H), 1.61 – 1.51 (m, 1H), 1.44 – 1.35 (m, 1H), 1.31 – 1.24 (m, 6H), 1.23 (s, 12H), 0.87 (t, $J$ = 6.8 Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.0, 145.9, 132.5, 129.4, 119.0, 110.6, 82.2, 34.9, 31.9, 31.4, 31.1, 27.4, 25.2, 25.1, 22.7, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 23.7;
HRMS (ESI) calcd. for C_{22}H_{34}BN_{2}O_{3} [M+H]+ m/z 385.2657, found 385.2648;
IR (neat, cm^{-1}) 3173, 2964, 2927, 2229, 1606, 1155, 1109;
[a]D^{25} = -19.1 (c = 0.58, CHCl_{3});
HPLC analysis: the ee (95%) was determined using a CHIRALPAK® AD-H column, 10% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 4.1 min, t_R (minor) = 5.0 min.

(R)-3-(Furan-2-yl)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, 4n). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-(furan-2-yl)ethyl)-1,4,2-dioxazol-5-one (2n) (54.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl_{2}·6H_{2}O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_{2}O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)_{3}SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 58% yield (40.6 mg).

^1H NMR (500 MHz, CDCl_{3}) δ 7.34 – 7.26 (m, 2H), 6.26 (dd, J = 3.1, 1.9 Hz, 1H), 6.04 (d, J = 2.7 Hz, 1H), 2.95 (t, J = 7.6 Hz, 2H), 2.69 – 2.55 (m, 3H), 1.62 – 1.52 (m, 1H), 1.43 – 1.35 (m, 1H), 1.33 – 1.23 (m, 6H), 1.21 (s, 12H), 0.87 (t, J = 6.8 Hz, 3H);

^13C NMR (126 MHz, CDCl_{3}) δ 175.6, 153.3, 141.6, 110.5, 106.2, 81.3, 32.0, 31.3, 31.2, 27.7, 25.3, 25.1, 23.7, 22.7, 14.2;

^11B NMR (160 MHz, CDCl_{3}) δ 19.9;

HRMS (ESI) calcd. for C_{10}H_{34}BNO_{4} [M+H]+ m/z 350.2497, found 350.2491;
IR (neat, cm^{-1}) 3168, 2964, 2926, 1605, 1552, 1154, 1109, 729;
[a]D^{25} = -37.7 (c = 1.04, CHCl_{3});
HPLC analysis: the ee (96%) was determined using a CHIRALPAK® AD-H column,
(R)-N-(5-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)cyclopropanecarboxamide (Figure 4, 4o). From (E)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (1c) (54.4 mg, 0.20 mmol, 1.0 equiv) and 3-cyclopropyl-1,4,2-dioxazol-5-one (2o) (38.1 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 55% yield (39.3 mg).

**¹H NMR** (500 MHz, CDCl₃) δ 8.32 (s, 1H), 7.28 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 2.67 – 2.53 (m, 2H), 2.52 – 2.45 (m, 1H), 1.70 – 1.52 (m, 4H), 1.52 – 1.32 (m, 3H), 1.31 – 1.21 (m, 1H), 1.16 (s, 6H), 1.15 (s, 6H), 1.12 – 1.06 (m, 1H), 0.95 – 0.85 (m, 2H);

**¹³C NMR** (126 MHz, CDCl₃) δ 178.6, 142.8, 128.5, 128.4, 125.8, 80.5, 36.0, 31.7, 31.3, 27.9, 25.5, 25.1, 10.9, 8.6;

**¹¹B NMR** (160 MHz, CDCl₃) δ 16.2;

**HRMS** (ESI) calcd. for C₂₁H₃₃BN₂O₃ [M+H]⁺ m/z 358.2548, found 358.2538;

**IR** (neat, cm⁻¹) 3206, 3062, 2929, 1603, 1548, 1154, 1115, 734;

[α]D²⁵ = –61.3 (c = 0.97, CHCl₃);

**HPLC analysis:** the ee (98%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, tᵣ (major) = 4.3 min, tᵣ (minor) = 6.4 min.
Benzyl (R)-3-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)azetidine-1-carboxylate (Figure 4, 4p). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and benzyl 3-(5-oxo-1,4,2-dioxazol-3-yl)azetidine-1-carboxylate (2p) (82.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (CH₂Cl₂/MeOH = 30:1) to provide the title compound as a colorless oil in 47% yield (42.0 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.29 (m, 5H), 6.14 (s, 1H), 5.08 (s, 2H), 4.24 – 4.14 (m, 2H), 4.11 (t, J = 8.5 Hz, 2H), 3.29 – 3.20 (m, 1H), 3.06 – 2.96 (m, 1H), 1.67 – 1.56 (m, 1H), 1.54 – 1.42 (m, 1H), 1.33 – 1.26 (m, 6H), 1.24 (s, 6H), 1.24 (s, 6H), 0.87 (t, J = 6.6 Hz, 3H);

¹³C NMR (126 MHz, CDCl₃) δ 172.9, 156.4, 136.6, 128.6, 128.2, 128.1, 83.2, 66.9, 52.0, 32.5, 31.9, 31.0, 27.1, 25.1, 25.1, 22.6, 14.1;

¹¹B NMR (160 MHz, CDCl₃) δ 27.9;

HRMS (ESI) calcd. for C₂₄H₃₇BN₂NaO₅ [M+Na]⁺ m/z 467.2688, found 467.2678;

IR (neat, cm⁻¹) 3210, 2959, 2829, 1711, 1605, 1352, 1132;

[α]D²⁵ = −13.4 (c = 0.95, CHCl₃);

HPLC analysis: the ee (96%) was determined using a CHIRALCEL® OD-H column, 5% iPrOH in hexane, 1.0 mL/min, 210 nm UV detector, tᵣ (minor) = 9.9 min, tᵣ (major) = 11.7 min.

(R)-N-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)pentyl)carbamoyl)azetidine-1-carboxylate (Figure 4, 4p). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and benzyl 3-(5-oxo-1,4,2-dioxazol-3-yl)azetidine-1-carboxylate (2p) (82.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (CH₂Cl₂/MeOH = 30:1) to provide the title compound as a colorless oil in 47% yield (42.0 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.29 (m, 5H), 6.14 (s, 1H), 5.08 (s, 2H), 4.24 – 4.14 (m, 2H), 4.11 (t, J = 8.5 Hz, 2H), 3.29 – 3.20 (m, 1H), 3.06 – 2.96 (m, 1H), 1.67 – 1.56 (m, 1H), 1.54 – 1.42 (m, 1H), 1.33 – 1.26 (m, 6H), 1.24 (s, 6H), 1.24 (s, 6H), 0.87 (t, J = 6.6 Hz, 3H);

¹³C NMR (126 MHz, CDCl₃) δ 172.9, 156.4, 136.6, 128.6, 128.2, 128.1, 83.2, 66.9, 52.0, 32.5, 31.9, 31.0, 27.1, 25.1, 25.1, 22.6, 14.1;

¹¹B NMR (160 MHz, CDCl₃) δ 27.9;

HRMS (ESI) calcd. for C₂₄H₃₇BN₂NaO₅ [M+Na]⁺ m/z 467.2688, found 467.2678;

IR (neat, cm⁻¹) 3210, 2959, 2829, 1711, 1605, 1352, 1132;

[α]D²⁵ = −13.4 (c = 0.95, CHCl₃);

HPLC analysis: the ee (96%) was determined using a CHIRALCEL® OD-H column, 5% iPrOH in hexane, 1.0 mL/min, 210 nm UV detector, tᵣ (minor) = 9.9 min, tᵣ (major) = 11.7 min.
yl)pentyl)cyclohexanecarboxamide (Figure 4, 4q). From (E)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1i) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-cyclohexyl-1,4,2-dioxazol-5-one (2q) (50.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 65% yield (55.8 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 7.10 (s, 1H), 4.48 (s, 2H), 3.49 (t, J = 6.3 Hz, 2H), 2.59 – 2.50 (m, 1H), 2.25 – 2.15 (m, 1H), 1.89 – 1.81 (m, 2H), 1.81 – 1.71 (m, 2H), 1.70 – 1.56 (m, 4H), 1.50 – 1.39 (m, 3H), 1.39 – 1.29 (m, 2H), 1.29 – 1.21 (m, 3H), 1.19 (s, 12H);

¹³C NMR (126 MHz, CDCl₃) δ 180.9, 138.6, 128.5, 127.8, 127.7, 80.6, 73.1, 70.6, 40.5, 30.8, 29.6, 28.9, 28.8, 25.6, 25.4, 25.4, 25.1, 24.8;

¹¹B NMR (160 MHz, CDCl₃) δ 16.0;

HRMS (ESI) calcd. for C₂₅H₄₀BNaO₄ [M+Na]+ m/z 452.2943, found 452.2933;

IR (neat, cm⁻¹) 3198, 2930, 2855, 1599, 1098, 733;

[a]D²⁵ = –55.7 (c = 1.05, CHCl₃);

HPLC analysis: the ee (94%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, tR (major) = 4.6 min, tR (minor) = 8.4 min.

(R)-N-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)pivalamide (Figure 4, 4r). From (E)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1i) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-((tert-butyl)-1,4,2-dioxazol-5-one (2r) (42.9 mg, 0.30 mmol, 1.5 equiv), the title
compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 53% yield (42.4 mg).

³¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.85 (s, 1H), 4.49 (s, 2H), 3.49 (t, J = 6.3 Hz, 2H), 2.59 – 2.51 (m, 1H), 1.72 – 1.56 (m, 3H), 1.51 – 1.38 (m, 3H), 1.21 – 1.16 (m, 21H);

³¹C NMR (126 MHz, CDCl₃) δ 183.9, 138.6, 128.5, 127.8, 127.7, 80.4, 73.1, 70.5, 35.7, 30.9, 29.6, 26.9, 25.4, 25.2, 24.8;

³¹B NMR (160 MHz, CDCl₃) δ 15.8;

HRMS (ESI) calcd. for C₂₃H₃₉BN₂O₄ [M+H]+ m/z 404.2967, found 404.2956;

IR (neat, cm⁻¹) 3204, 2970, 2931, 1581, 1097, 732;

[α]D²⁵ = –49.9 (c = 0.99, CHCl₃);

HPLC analysis: the ee (83%) was determined using a CHIRALCEL® OD-H column, 5% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, tᵣ (major) = 5.3 min, tᵣ (minor) = 8.2 min.

Methyl (R)-3-((5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamoyl)bicyclo[1.1.1]pentane-1-carboxylate (Figure 4, 4s). From (E)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborane (1c) (54.4 mg, 0.20 mmol, 1.0 equiv) and methyl 3-(5-oxo-1,4,2-dioxazol-3-yl)bicyclo[1.1.1]pentane-1-carboxylate (2s) (63.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction
mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 53% yield (46.6 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 6.15 (s, 1H), 3.69 (s, 3H), 2.89 – 2.80 (m, 1H), 2.65 – 2.56 (m, 2H), 2.28 (s, 6H), 1.70 – 1.59 (m, 3H), 1.56 – 1.43 (m, 1H), 1.37 – 1.29 (m, 2H), 1.21 (s, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.5, 169.6, 142.6, 128.6, 128.4, 125.8, 82.4, 52.6, 52.0, 37.6, 37.5, 31.3, 31.0, 27.0, 25.2, 25.1;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 24.5;

HRMS (ESI) calcd. for C$_{25}$H$_{36}$BNaO$_5$ [M+Na]$^+$ m/z 464.2579, found 464.2567;

IR (neat, cm$^{-1}$) 2929, 1732, 1598, 1202, 1141;

$[\alpha]_{D}^{25} = -29.1$ (c = 0.99, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, $t_R$ (major) = 5.2 min, $t_R$ (minor) = 6.0 min.

(R)-2-(11-Oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)acetamide (Figure 4, 4t). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-((11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)methyl)-1,4,2-dioxazol-5-one (2t) (92.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 50% yield (47.6 mg).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 2.2$ Hz, 1H), 7.92 – 7.82 (m, 1H), 7.59 – 7.53 (m, 1H), 7.51 – 7.44 (m, 1H), 7.40 (dd, $J = 8.4$, 2.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 6.47 (s, 1H), 5.18 (s, 2H), 3.64 (s, 2H), 2.76 – 2.68 (m, 1H), 1.61 – 1.51 (m, 1H), 1.44 – 1.34 (m, 1H), 1.29 – 1.17 (m, 18H), 0.82 (t, $J = 6.7$ Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 190.7, 174.2, 160.9, 140.4, 136.4, 135.6, 133.1, 132.7, 129.6, 129.5, 128.0, 127.1, 125.5, 121.8, 81.8, 73.8, 39.3, 31.9, 27.4, 25.3, 25.1, 22.6, 14.1;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 22.4;

HRMS (ESI) calcd. for C$_{28}$H$_{36}$BNaO$_5$ [M+Na]$^+$ m/z 500.2579, found 500.2569;

IR (neat, cm$^{-1}$) 3055, 2927, 1660, 1613, 1265, 735;

$[\alpha]_D^{25} = -20.5$ (c = 1.01, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALPAK® AD-H column, 10% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, $t_R$ (major) = 6.3 min, $t_R$ (minor) = 7.7 min.

(R)-3-(4,5-Diphenyloxazol-2-yl)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, 4u). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-(4,5-diphenyloxazol-2-yl)ethyl)-1,4,2-dioxazol-5-one (2u) (100.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 µL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 µL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 51% yield (51.0 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (s, 1H), 7.64 – 7.56 (m, 4H), 7.41 – 7.33 (m 6H),
3.28 – 3.18 (m, 2H), 2.97 – 2.88 (m, 2H), 2.81 – 2.73 (m, 1H), 1.63 – 1.54 (m, 1H), 1.50 – 1.39 (m, 1H), 1.34 – 1.25 (m, 4H), 1.25 – 1.20 (m, 14H), 0.84 (t, J = 6.7 Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 175.1, 162.1, 146.0, 134.6, 131.7, 129.0, 128.9, 128.8, 128.5, 128.0, 126.7, 81.5, 31.9, 31.0, 29.6, 27.8, 25.2, 25.1, 23.8, 22.6, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 20.8;

HRMS (ESI) calcd. for C$_{30}$H$_{40}$BN$_2$O$_4$ [M+H]$^+$ m/z 503.3076, found 503.3068;

IR (neat, cm$^{-1}$) 3198, 3056, 2927, 1606, 1156, 1110, 763, 693;

$[\alpha]_D^{25} = -21.1$ (c = 0.92, CHCl$_3$);

HPLC analysis: the ee (97%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 0.8 mL/min, 240 nm UV detector, $t_R$ (major) = 6.2 min, $t_R$ (minor) = 7.5 min.

(R)-2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-$1H$-indol-3-yl)-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)hexyl)acetamide (Figure 4, 4v). From (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-((1-(4-chlorobenzoyl)-5-methoxy-2-methyl-$1H$-indol-3-yl)methyl)-1,4,2-dioxazol-5-one (2v) (119.6 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure A using NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H$_2$O (1.8 μL, 0.10 mmol, 0.50 equiv), (EtO)$_3$SiH (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a light yellow solid in 46% yield (52.6 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 6.88 – 6.83 (m, 2H), 6.69 (dd, J = 9.0, 2.4 Hz, 1H), 6.37 (s, 1H), 3.81 (s, 3H), 3.74 (s, 2H),
2.73 – 2.63 (m, 1H), 2.34 (s, 3H), 1.60 – 1.49 (m, 1H), 1.41 – 1.31 (m, 1H), 1.22 (s, 12H), 1.20 – 1.11 (m, 6H), 0.80 (t, J = 6.7 Hz, 3H);

**13C NMR** (126 MHz, CDCl3) δ 173.7, 168.4, 156.5, 139.9, 136.9, 133.6, 131.3, 131.0, 130.0, 129.4, 115.3, 112.9, 111.0, 100.6, 81.7, 55.9, 31.9, 31.2, 29.0, 27.4, 25.3, 25.1, 22.6, 14.1, 13.5;

**11B NMR** (160 MHz, CDCl3) δ 21.9;

**HRMS** (ESI) calcd. for C31H40BClN2NaO5 [M+Na]+ m/z 589.2611, found 589.2596;

**IR** (neat, cm\(^{-1}\)) 3249, 2928, 1678, 1603, 1323, 1146;

**m.p.** 150 – 151 °C;

\([\alpha]_D^{25} = -34.5\) (c = 0.65, CHCl3);

**HPLC analysis:** the ee (98%) was determined using a CHIRALPAK® AD-H column, 10% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, \(t_R\) (major) = 5.7 min, \(t_R\) (minor) = 6.7 min.
3. Synthetic Application

a. Gram-Scale Experiment

\[
\begin{align*}
\text{nBu} & \quad \text{Bpin} & \quad \text{N} = \text{O} = \text{O} & \quad \text{Ph} \\
1\text{a (5.0 mmol)} & \quad 2\text{a (1.5 equiv)} & \quad 10 \text{ mol\% NiCl}_2\cdot6\text{H}_2\text{O} & \quad 12 \text{ mol\% L}\text{*} \\
& & \quad 2.5 \text{ equiv (EtO)}_3\text{SiH} & \quad 0.5 \text{ equiv LiI, 0.5 equiv H}_2\text{O} \\
& & \quad \text{DMA (0.2 M), 25 °C, 20 h} & \quad \text{Bpin} \quad \text{O} \quad \text{Ph} \\
& & & \quad 3\text{a 1.22 g, 74\% yield} \\
& & & \quad 94\% \text{ ee} \\
\end{align*}
\]

In a nitrogen-filled glove box, to an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was added NiCl$_2$·6H$_2$O (118.8 mg, 10 mol%), L$^*$ (198.9 mg, 12 mol%), LiI (334.6 mg, 2.5 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (1.224 g, 7.5 mmol, 1.5 equiv). The flask was sealed with a rubber stopper, removed from the glove box and equipped with a N$_2$ balloon, and anhydrous DMA (25 mL, 0.20 M) was added via syringe and the mixture was stirred for 10 min at 25 °C (water bath), at which time (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (1.051 g, 5.0 mmol, 1.0 equiv), H$_2$O (45 μL, 2.5 mmol, 0.50 equiv) were added via syringe and the mixture was stirred for 5 min and then (EtO)$_3$SiH (2.053 g, 12.5 mmol, 2.5 equiv) was added to the resulting mixture. The mixture was stirred at 25 °C for up to 20 h. After the reaction was complete, n-dodecane (500 μL) was added as an internal standard for GC analysis, and the reaction was quenched upon the addition of H$_2$O (150 mL). The mixture was extracted with Et$_2$O. The organic layer was concentrated. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide 3a as a white solid in 74% yield (1.220 g). The ee (94%) was determined via chiral HPLC analysis.

Supplementary Figure 1: (Left) All the reagents were added and stirred at 25 °C for 10 min.
dark green homogeneous mixture) (Center) The mixture was stirred at 25 °C for 20 h. (a light green homogeneous mixture) (Right) Purified product 3a. (A white solid (1.220 g) was obtained after purification by column chromatography.).

b. One-pot asymmetric hydroamidation w/o isolation of alkenyl boronate

\[
\begin{align*}
\text{nBu} & \quad 5 \text{ mol\% HBCy}_2 \\
1.0 \text{ equiv HBpin} & \quad \text{neat, rt, 24 h} \\
1.25 \text{ equiv} & \quad 10 \text{ mol\% NiCl}_2 \cdot 6\text{H}_2\text{O} \\
& \quad 12 \text{ mol\% L}^* \\
& \quad 1.5 \text{ equiv 2a} \\
\end{align*}
\]

\[
\begin{align*}
\text{nBu} & \quad \text{Bpin} \\
1a & \quad \text{w/o isolation} \\
& \quad 2.5 \text{ equiv (EtO)}_3\text{SiH} \\
& \quad 0.5 \text{ equiv LiI, 0.5 equiv H}_2\text{O} \\
& \quad \text{DMA, 25 °C, 20 h} \\
& \quad \text{3a 61\% yield} \\
\end{align*}
\]

The procedure was modified from the previous literature. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added freshly prepared dicyclohexylborane (3.6 mg, 5 mol%), 1-hexyne (41.1 mg, 0.5 mmol, 1.25 equiv) and pinacolborane (58 µL, 0.4 mmol, 1.0 equiv). The reaction mixture was stirred for 18 hours. Afterwards, the volatile materials were removed under reduced pressure at room temperature for 1 h. The vial was refilled with N\(_2\) and transferred to the nitrogen-filled glove box. NiCl\(_2\)·6H\(_2\)O (9.6 mg, 10 mol%), L* (16.0 mg, 12 mol%), LiI (26.8 mg, 0.20 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (97.8 mg, 0.60 mmol, 1.5 equiv) and anhydrous DMA (2.0 mL, 0.20 M) were added to the vial. The mixture was stirred for 10 min at room temperature, at which time H\(_2\)O (3.6 µL, 0.20 mmol, 0.50 equiv) and (EtO\(_3\))\(_2\)SiH (184 µL, 1.0 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath for up to 20 h (the mixture was stirred at 1000 rpm). After the reaction was complete, n-dodecane (40 µL) was added as an internal standard for GC analysis, and the reaction was quenched upon the addition of H\(_2\)O. The mixture was extracted with Et\(_2\)O. The organic layer was concentrated. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide 3a as a white solid in 61% yield (80.6 mg). The ee (94%) was determined via chiral HPLC analysis.
c. Concise Synthetic Route to Vaborbactam

![Concise Synthetic Route to Vaborbactam Diagram]

**tert-Butyl (S)-3-((tert-butyldimethylsilyl)oxy)hex-5-ynoate** (Figure 5, 5). The title compound was prepared according to the known literature method\(^2\). Spectral data match the previously reported.

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)) δ 4.29 – 4.17 (m, 1H), 2.58 (dd, \(J = 15.4, 4.8\) Hz, 1H), 2.45 (dd, \(J = 15.4, 7.1\) Hz, 1H), 2.40 (dd, \(J = 6.1, 2.7\) Hz, 2H), 1.99 (t, \(J = 2.7\) Hz, 1H), 1.45 (s, 9H), 0.87 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H);

**\(^13\)C NMR** (126 MHz, CDCl\(_3\)) δ 170.7, 81.0, 80.6, 70.6, 68.1, 43.1, 28.3, 27.5, 25.9, 18.1, -4.5, -4.7;

**HRMS** (ESI) calcd. for C\(_{16}\)H\(_{30}\)NaO\(_3\)Si [M+Na]\(^+\) m/z 321.1856, found 321.1847;

\([\alpha]\)\(_D\)\(^{25}\) = +28.9 (c = 1.02, CHCl\(_3\)), \(>99\%\) ee;

**tert-Butyl (S,E)-3-((tert-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate** (Figure 5, 6). Under N\(_2\) atmosphere, to an oven-dried round bottom flask equipped with a stir bar, Schwartz’s reagent (0.351 g, 10 mol%), CH\(_2\)Cl\(_2\) (13 mL) and tert-butyl (S)-3-((tert-butyldimethylsilyl)oxy)hex-5-ynoate (5)
(4.060 g, 13.6 mmol, 1.0 equiv) were added and stirred for 5 minutes. At 0 °C, pinacolborane (2.089 g, 16.3 mmol, 1.2 equiv) was added dropwise to the mixture. Then, the mixture was allowed to warm to rt and stirred for 48 hours. The reaction was quenched with H₂O carefully, extracted with Et₂O, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford the titled (E)-alkenyl boronate as a colorless oil in 53% yield (3.068 g).

**1H NMR** (500 MHz, CDCl₃) δ 6.57 (dt, J = 17.9, 7.0 Hz, 1H), 5.47 (d, J = 17.9 Hz, 1H), 4.22–4.13 (m, 1H), 2.40–2.32 (m, 4H), 1.43 (s, 9H), 1.25 (s, 12H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H);

**13C NMR** (126 MHz, CDCl₃) δ 171.0, 150.1, 83.2, 80.4, 68.9, 44.4, 43.7, 28.3, 26.0, 24.9, 24.9, 18.2, -4.3, -4.6;

**11B NMR** (160 MHz, CDCl₃) δ 29.9;

**HRMS** (ESI) calcd. for C₂₂H₄₃BNaO₅Si [M+Na]⁺ m/z 449.2865, found 449.2853;

**IR** (neat, cm⁻¹) 2978, 2930, 1730, 1640, 1361, 1142, 832;

[α]D²⁵ = +13.8 (c = 1.09, CHCl₃);

**HPLC analysis**: the ee (>99%) was determined using a CHIRALPAK® IF-3 column, 0.5% iPrOH in hexane, 1.0 mL/min, 220 nm UV detector, tᵣ (minor) = 6.9 min, tᵣ (major) = 8.8 min.

![Chemical Structure](image)

**tert-Butyl (3S,6R)-3-((tert-butylimidethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(2-(thiophen-2-yl)acetamido)hexanoate** (Figure 5, 7). From tert-butyl (S,E)-3-((tert-butylimidethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl 6 (85.3 mg, 0.20 mmol, 1.0 equiv) and 3-(thiophen-2-ylmethyl)-1,4,2-dioxazol-5-one (2w) (44.0 mg, 0.24 mmol, 1.2 equiv), the title compound was prepared following the general procedure A using NiCl₂·6H₂O (5.9 mg, 12.5 mol%), L* (12.0 mg, 15 mol%), TBAI (18.5 mg, 0.050 mmol, 0.25 equiv, instead
of LiI, H₂O (5.4 μL, 0.30 mmol, 1.5 equiv), (EtO)₃SiH (110 μL, 0.60 mmol, 3.0 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 50% yield (56.4 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.25 (dd, J = 5.1, 0.9 Hz, 1H), 6.98 (dd, J = 5.1, 3.5 Hz, 1H), 6.93 (d, J = 3.1 Hz, 1H), 6.58 (s, 1H), 4.08 – 3.97 (m, 1H), 3.87 (s, 2H), 2.76 – 2.66 (m, 1H), 2.39 – 2.26 (m, 2H), 1.65 – 1.55 (m, 1H), 1.55 – 1.44 (m, 3H), 1.41 (s, 9H), 1.22 (s, 12H), 0.84 (s, 9H), 0.02 (s, 3H), 0.02 (s, 3H);

¹³C NMR (126 MHz, CDCl₃) δ 173.9, 171.3, 133.9, 128.2, 127.7, 126.2, 81.7, 80.5, 68.9, 43.6, 35.0, 34.1, 28.3, 26.4, 26.0, 25.3, 25.1, 18.1, -4.4, -4.6;

¹¹B NMR (160 MHz, CDCl₃) δ 21.8;

HRMS (ESI) calcd. for C₂₈H₅₀BNaO₆SSi [M+Na]⁺ m/z 590.3113, found 590.3103;

IR (neat, cm⁻¹) 2968, 2929, 1729, 1607, 1149, 834;

[α]D²⁵ = -20.2 (c = 1.00, CHCl₃);

HPLC analysis: the dr (97:3) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tR (major) = 4.3 min, tR (minor) = 6.5 min.

2-((3R,6S)-2-Hydroxy-3-(2-(thiophen-2-yl)acetamido)-1,2-oxaborinan-6-yl)acetic acid³ (Figure 5, 8). The title compound was prepared according to a known method with a similar substrate³. To a solution of tert-butyl (3S,6R)-3-((tert-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(2-(thiophen-2-yl)acetamido)hexanoate (7) (398 mg, 0.70 mmol) in 1,4-dioxane (2 mL) was added 2 mL of 3 N HCl (aq.). The reaction mixture was heated at reflux for 2 h, after which the cooled reaction mixture was diluted with water (2 mL) and extracted with Et₂O (3 × 6 mL). The aqueous layer was concentrated to afford a sticky residue which was azeotroped with MeCN (3 × 8 mL), dissolved in 20% dioxane-water, and
lyophilized to afford a white powder (198 mg, 95%).

The crude product (150 mg) was suspended in EtOAc (3 mL). Water (0.5 mL) was added, and most of the compound appeared to go into the water layer. After sonicating for about 30 min, a white precipitate formed. The solid was collected by filtration, washed with Et₂O and hexane. The solid was dissolved in 20% dioxane-water, and lyophilized to provide the title compound as a white solid in 53% yield (79.2 mg).

**¹H NMR** (500 MHz, CD₃OD) δ 7.34 (dd, J = 5.2, 1.2 Hz, 1H), 7.09 – 7.02 (m, 1H), 7.00 (dd, J = 5.2, 3.5 Hz, 1H), 4.14 – 4.04 (m, 1H), 3.97 (s, 2H), 2.66 – 2.57 (m, 1H), 2.37 (dd, J = 15.0, 7.3 Hz, 1H), 2.25 (dd, J = 15.0, 5.8 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.68 – 1.52 (m, 2H), 1.11 – 0.97 (m, 1H);

**¹³C NMR** (126 MHz, CD₃OD) δ 177.8, 175.6, 135.2, 128.8, 128.2, 126.7, 70.5, 44.4, 32.6, 28.5, 27.6;

**¹¹B NMR** (160 MHz, CD₃OD) δ 11.7;

**HRMS (ESI)** calcd. for C₁₂H₁₅BNO₅S [M–H₂O+H]⁺ m/z 280.0809, found 280.0802;

**IR** (neat, cm⁻¹) 3511, 2941, 1718, 1607, 1225, 1183, 701;

[a]D²⁵ = −6.1 (c = 0.85, CH₃OH).
4. Mechanistic Experiments

a. Nonlinear effect study

\[ \text{Bu} \rightleftharpoons \text{Bpin} + \text{Ph} - \text{O} - \text{O} - \text{Ph} \]

1a (0.2 mmol) 2a (1.5 equiv) \[
\begin{align*}
10 \text{ mol\% NiCl}_2 \cdot 6\text{H}_2\text{O} & \quad 2.5 \text{ equiv (EtO)}_2\text{SiH} \\
12 \text{ mol\% } [\text{S}-\text{L}^* + \text{R}-\text{L}^*] & \quad 0.5 \text{ equiv LiI, 0.5 equiv H}_2\text{O} \\
\text{DMA} (0.2 \text{ M}) & \quad 25 ^\circ\text{C}, 20 \text{ h}
\end{align*}
\]

\text{Bpin} \longrightarrow \text{O} \longrightarrow \text{NH} \longrightarrow \text{Ph} \quad \text{Bn} \quad \text{Bn} \quad \text{NH}_2 \quad \text{OH}

\text{(S)-L}^* + \text{(R)-L}^*

Supplementary Table 1: Nonlinear effect study

| Entry | \( ee(\%) \) of mixed \( L^* \) | \( (S)-L^* \) (mg) | \( (R)-L^* \) (mg) | \( ee(\%) \) of 3a |
|-------|-----------------|-----------------|-----------------|-----------------|
| 1     | 20              | 4.8             | 3.2             | 17              |
| 2     | 40              | 5.6             | 2.4             | 37              |
| 3     | 60              | 6.4             | 1.6             | 52              |
| 4     | 80              | 7.2             | 0.8             | 73              |
| 5     | 99              | 8.0             | 0               | 95              |

5 parallel reactions at 0.20 mmol scale were performed following general procedure A. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol\%), specified amount of \( (S)-L^* \) and \( (R)-L^* \) (to provide the enantiomeric composition of \( L^* \)) as listed in Supplementary Table 1, LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL,
0.20 M). The mixture was stirred for 10 min at room temperature, at which time \((E)-2-(\text{hex-1-en-1-yl})-4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane (1a)}\) (42.0 mg, 0.20 mmol, 1.0 equiv), \(\text{H}_2\text{O}\) (1.8 μL, 0.10 mmol, 0.50 equiv) and \((\text{EtO})_3\text{SiH}\) (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath (the mixture was stirred at 800 rpm). The reactions were stopped at the indicated reaction time, quenched upon the addition of \(\text{H}_2\text{O}\) and extracted with \(\text{Et}_2\text{O}\). \(n\)-Dodecane (20 μL) was added as an internal standard for GC analysis. The organic layer was concentrated to give the crude product. The product was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) for each substrate. The enantiomeric excesses (% ee) were determined by HPLC analysis using chiral stationary phases.

**Note:** A linear correlation between the ee value of the ligand \(L^*\) and that of the product 3a was observed, consistent with the monomeric nature of the active catalyst.
b. Isotopic labelling experiments

Following the general procedure A, in a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl₂·dme (4.4 mg, 10 mol%), L* (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL, 0.20 M) were added, and the mixture was stirred for 10 min at 25 °C, at which time (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv), D₂O (7.2 μL, 0.40 mmol, 2.0 equiv) and (EtO)₃SiH (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C for up to 20 h (the mixture was stirred at 800 rpm). The reaction was quenched upon the addition of H₂O, and the mixture was extracted with Et₂O. The organic layer was concentrated to give the crude product. n-Dodecane (20 μL) was added as an internal standard for GC analysis. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide 3a as a colorless liquid in 57% yield (37.7 mg). The ee (96%) of 3a was determined via HPLC analysis.

**Note:** Although 2 equiv D₂O was added, no deuterium incorporation was observed in the product (3a), eliminating the possibility of a protic reagent as the hydride source.

(R)-N-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 6, 3a, no D was detected).

\(^1\)H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 2.79 (t, J = 6.5 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.61 –
1.52 (m, 1H), 1.49 – 1.37 (m, 2H), 1.34 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, J = 7.0 Hz, 3H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.9, 133.1, 128.6, 128.3, 127.9, 81.2, 32.1, 31.3, 27.6, 25.4, 25.2, 22.7, 14.2;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 17.6;

$^2$H NMR (92 MHz, CHCl$_3$) no D was detected.

Following the general procedure A, in a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl$_2$·6H$_2$O (4.8 mg, 10 mol%), $L^*$ (8.0 mg, 12 mol%), LiI (13.4 mg, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL) were added, and the mixture was stirred for 10 min at 25 °C, at which time (E)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl-2-d)-1,3,2-dioxaborolane (1b-D, 93% D) (47.8 mg, 0.20 mmol, 1.0 equiv), H$_2$O (1.8 μL, 0.50 equiv) and (EtO)$_3$SiH (92 μL, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C for up to 20 h (the mixture was stirred at 800 rpm). The reaction was quenched upon the addition of H$_2$O, and the mixture was extracted with Et$_2$O. The organic layer was concentrated to give the crude product. n-Dodecane (20 μL) was added as an internal standard for GC analysis. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide 3b-D as a colorless liquid in 70% yield (50.1 mg). The ee (96%) of 3b-D was determined via HPLC analysis.

**Note:** Diastereomerically pure 3b-D was obtained from this reaction, indicating that *syn*-hydronickellation is involved in the enantio-determining step.
\( \text{N-}((1S,2R)-1-(4,4,5,5-\text{Tetramethyl-1,3,2-dioxaborolan-2-yl})\text{octyl-2-d})\text{benzamide} \) (Figure 6, 3b-D).

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \( \delta \): 8.45 (s, 1H), 7.80 (d, \( J = 7.4 \text{ Hz} \), 2H), 7.46 (t, \( J = 7.4 \text{ Hz} \), 1H), 7.32 (t, \( J = 7.7 \text{ Hz} \), 2H), 2.79 (d, \( J = 6.8 \text{ Hz} \), 1H), 1.74 – 1.66 (m, 0.07H), 1.58 – 1.51 (m, 1H), 1.46 – 1.36 (m, 2H), 1.33 – 1.20 (m, 20H), 0.87 (t, \( J = 6.9 \text{ Hz} \), 3H);

\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \( \delta \): 170.9, 133.1, 128.6, 128.3, 128.0, 81.2, 32.0, 31.0 (t, \( J = 18.9 \text{ Hz} \)), 29.9, 29.4, 27.9, 25.4, 25.2, 22.8, 14.3;

\(^{11}\text{B NMR}\) (160 MHz, CDCl\(_3\)) \( \delta \): 18.0;

\(^2\text{H NMR}\) (92 MHz, CHCl\(_3\)) \( \delta \): 1.68 (corresponding to the missing 0.93H);

\text{HRMS (ESI) calcld. for \text{C}_{21}\text{H}_{33}\text{DBNNaO}_3 \ [M+Na]^+ \ m/z 383.2587, found 383.2576;}

\text{IR (neat, cm}^{-1})\): 3196, 2923, 2854, 1610, 1154, 1111, 706;

\([\alpha]_D^{25} = –38.3 \ (c = 1.00, \text{CHCl}_3)\);

\text{HPLC analysis: the ee (96\%) was determined using a CHIRALCEL® OD-H column, 8\% iPrOH in hexane, 0.5 mL/min, 254 nm UV detector, t}_R \ (\text{minor}) = 7.3 \text{ min}, t}_R \ (\text{major}) = 7.9 \text{ min} \ (\text{see Supplementary Figure 192}).
c. Capture of metal-nitrenoid intermediate

\[
\begin{array}{c}
\text{Ph-} & \text{O} \\
\text{N-} & \text{O} \\
\text{Ph-} & \text{O}
\end{array}
\quad + \quad
\begin{array}{c}
PPh_3
\end{array}
\rightarrow
\begin{array}{c}
\text{Ph-} & \text{O} \\
\text{N=} & \text{PPh}_3
\end{array}
\]

\[2a \quad \text{Ph-} & \text{O} \quad \text{PPh}_3 \Rightarrow \text{Ph-} & \text{O} \quad \text{PPh}_3 \]

10 mol% NiCl\(_2\)·6H\(_2\)O  
12 mol% L\(^*\)  
2.5 equiv (EtO\(_3\)SiH)  
0.5 equiv LiI, 0.5 equiv H\(_2\)O  
DMA (0.2 M), 25°C, 20 h  
9 81% yield (w/o Ni: <5% yield)

_N-(Triphenyl-2,5-phosphaneylidene)benzamide_ (Figure 6, 9). In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl\(_2\)·6H\(_2\)O (4.8 mg, 10 mol%), L\(^*\) (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 1,4,2-dioxazol-5-one (32.6 mg, 0.20 mmol, 1.0 equiv), PPh\(_3\) (104.9 mg, 0.40 mmol, 2.0 equiv), anhydrous DMA (1.0 mL, 0.20 M) were added and the mixture was stirred for 10 min at room temperature. H\(_2\)O (1.8 μL, 0.10 mmol, 0.50 equiv) and (EtO\(_3\)SiH (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25°C water bath for up to 20 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H\(_2\)O, and the mixture was extracted with EtOAc. The organic layer was concentrated to give the crude product. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4:1) to provide the title compound as a white solid in 81% yield (61.5 mg).

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.37 (dd, \(J = 8.0, 1.5\) Hz, 2H), 7.94 – 7.78 (m, 6H), 7.60 – 7.53 (m, 3H), 7.53 – 7.37 (m, 9H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.2, 138.6, 133.6, 133.3 (d, \(J = 9.9\) Hz), 132.4, 130.8, 129.6, 128.8 (d, \(J = 12.3\) Hz), 127.8;

\(^{31}\)P NMR (202 MHz, CDCl\(_3\)) \(\delta\) 20.7;

HRMS (ESI) calcd. for C\(_{25}\)H\(_{20}\)NNaOP [M+Na]\(^+\) m/z 404.1175, found 404.1163;

IR (neat, cm\(^{-1}\)) 3057, 1594, 1557, 1328, 1106, 719, 690, 515;

m.p. 198 – 199°C.
d. Monitoring of the Reaction Progress

Supplementary Table 2: Yield and ee of 3a as a function of time

| Entry | t (h) | yield (%) | ee (%) |
|-------|------|-----------|--------|
| 1     | 1    | 28        | 95     |
| 2     | 2    | 44        | 95     |
| 3     | 4    | 59        | 95     |
| 4     | 6.5  | 75        | 95     |
| 5     | 20   | 75        | 95     |
| 6     | 26   | 75        | 95     |
| 7     | 45   | 75        | 95     |

7 parallel reactions at 0.20 mmol scale were performed following general procedure A. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added NiCl\textsubscript{2}·6H\textsubscript{2}O (4.8 mg, 10 mol%), L\textsuperscript{*} (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (2a) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL, 0.20 M). The mixture was stirred
for 10 min at room temperature, at which time (E)-2-(hex-1-en-1-yl)-4,4,5,5-
tetramethyl-1,3,2-dioxaborolane (1a) (42.0 mg, 0.20 mmol, 1.0 equiv), H₂O (1.8 μL, 0.10 mmol, 0.50 equiv) and (EtO)₂SiH (92 μL, 0.50 mmol, 2.5 equiv) were added to
the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath (the mixture was stirred at 800 rpm). The reactions were stopped at the indicated reaction time, quenched upon the addition of H₂O and extracted with Et₂O. n-Dodecane (20 μL) was added as an internal standard for GC analysis. The organic layer was concentrated to give the crude product. The product was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) for each substrate. The enantiomeric excesses (% ee) were determined by HPLC analysis using chiral stationary phases.

Note: During the entire reaction, the ee of the product remained unchanged.
5. Determination of the Absolute Configuration

(R)-N-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide ((R)-10). To a stirred solution of (R)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-amine hydrochloride (CAS 1243174-57-3, commercial available optically pure compound) (49.9 mg, 0.20 mmol, 1.0 equiv), dimethylaminopyridine (DMAP, 2.4 mg, 0.020 mmol, 0.10 equiv) in dry CH₂Cl₂ (15 mL) at 0 °C was added Et₃N (70 μL, 0.5 mmol, 2.5 equiv). After 10 minutes, benzoyl chloride (33.7 mg, 0.24 mmol, 1.2 equiv) were added. The resulting reaction mixture was allowed to warm to rt and the stirring was continued for overnight. After the reaction was complete, the reaction was quenched upon the addition of H₂O, and the mixture was extracted with EtOAc. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound 10 as a white solid in 83% yield (52.4 mg), and the spectral data match 3d.

[α]₂⁵ = −40.9 (c = 0.94, CHCl₃);

HPLC analysis: the ee (>99%) was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tᵣ (minor) = 4.8 min, tᵣ (major) = 5.6 min, (R) configuration (see Supplementary Figure 197).

Note: The absolute configuration of 3d was determined to be (R) by comparison of the optical rotation and HPLC peak of the title compound with 3d ([α]₂⁵ = −37.3 (c = 0.96, CHCl₃); HPLC analysis: the ee (92%) of 3d was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, tᵣ (minor) = 4.8 min, tᵣ (major) = 5.5 min.).
6. Conditions Optimization

**Supplementary Table 3:** Effect of reaction parameters\(^a\).

\[
\begin{array}{llll}
\text{Entry} & \text{Variation from the standard conditions} & \text{Yield (\%)} & \text{ee (\%)} \\
1 & \text{None} & 75 (71) & 95 \\
2 & \text{w/o Ni} & 0 & - \\
3 & \text{w/o L*} & 13 & \text{nd} \\
4 & \text{NiCl}_2 \cdot \text{dme instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & 63 & 86 \\
5 & \text{NiBr}_2 \cdot 3\text{H}_2\text{O instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & 58 & 61 \\
6 & \text{NiCl}_2 \text{ instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & <5 & \text{nd} \\
7 & \text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & <5 & \text{nd} \\
8 & \text{Nil}_2 \text{ instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & 8 & \text{nd} \\
9 & \text{Nil}_2 \cdot \text{xH}_2\text{O instead of NiCl}_2 \cdot 6\text{H}_2\text{O} & 8 & \text{nd} \\
10 & \text{w/o LiI} & 46 & 97 \\
11 & \text{NaI instead of LiI} & 67 & 94 \\
12 & \text{TBAI instead of LiI} & 72 & 95 \\
13 & \text{DMMS instead of (EtO)}_3\text{SiH} & 69 & 96 \\
14 & \text{DEMS instead of (EtO)}_3\text{SiH} & 20 & 94 \\
15 & \text{(MeO)}_3\text{SiH instead of (EtO)}_3\text{SiH} & 67 & 95 \\
16 & \text{PMHS instead of (EtO)}_3\text{SiH} & <5 & \text{nd} \\
17 & \text{w/o H}_2\text{O} & 58 & 81 \\
18 & \text{MeOH instead of H}_2\text{O} & 73 & 89 \\
19 & \text{EtOH instead of H}_2\text{O} & 72 & 88 \\
20 & \text{'PrOH instead of H}_2\text{O} & 72 & 85 \\
21 & \text{'BuOH instead of H}_2\text{O} & 64 & 80 \\
22 & \text{DMF instead of DMAc} & 11 & \text{nd} \\
23 & \text{DMPU instead of DMAc} & 13 & \text{nd} \\
24 & \text{NMP instead of DMAc} & 49 & 96 \\
25 & \text{THF instead of DMAc} & 12 & \text{nd} \\
26 & \text{DCE instead of DMAc} & <5 & \text{nd} \\
27 & \text{10 °C instead of 25 °C} & 59 & 97 \\
\end{array}
\]
| temperature | condition | yield 1 | yield 2 |
|-------------|-----------|---------|---------|
| 28          | 40 °C instead of 25 °C | 74    | 85    |
| 29          | under air in a closed vial | 68    | 94    |
| 30          | 2 equiv H₂O | 70    | 96    |

[a] Yields determined by GC using n-dodecane as the internal standard, the yield in parentheses is the isolated yield (0.20 mmol scale). Enantioselectivities were determined by chiral HPLC analysis.

**Supplementary Table 4: Effect of Ligands**

\[
\begin{align*}
\alpha \text{Bu} & \rightarrow \text{Bpin} + \text{Ph} - \text{N} - \text{O} - \text{N} - \text{O} \\
1a (0.2 \text{ mmol}) & 2a (1.5 \text{ equiv}) \rightarrow \text{Bpin} \rightarrow \text{Ph} \\
& 10 \text{ mol\% NiCl₂-6H₂O} \\
& 12 \text{ mol\% } [L^*] \\
& 2.5 \text{ equiv } \text{(EtO)}₂\text{SiH} \\
& 0.5 \text{ equiv } \text{Lil}, 0.5 \text{ equiv } \text{H₂O} \\
& \text{DMA (0.2 M), 25 °C, 20 h} \\
& \text{3a}
\end{align*}
\]

![Chemical structures]

L₄, R = Ph, 18% yield, 56% ee
L₇, R = sPr, 6% yield
L₉, 18% yield, 0% ee
L₄, R = Ph, 18% yield, 56% ee
L₇, R = sPr, 6% yield
L₉, 18% yield, 0% ee
L₅, R = Bn, 74% yield, 44% ee
L₉, 18% yield, 0% ee
L₁₀, R = Ph, 6% yield
L₁₁, R = sPr, 0% yield
L₁₂, R = Ph, 67% yield, 0% ee
L₁₃, R = sPr, 80% yield, 10% ee
L₁₄, 41% yield, 7% ee
L₁₅, 16% yield, 8% ee
L₁₆, 38% yield, 8% ee
L₁₆, 38% yield, 8% ee
L₁₇, 0% yield
L₁₈, 0% yield
L₁₈, 0% yield
L₁₉, 38% yield, 75% ee
L₂₀, 51% yield, 85% ee
L₂₁, 67% yield, 93% ee
L*, 75% yield, 95% ee

[a] Yields determined by GC using n-dodecane as the internal standard, the yield in parentheses is the isolated yield (0.20 mmol scale). Enantioselectivities were determined by chiral HPLC analysis.
**Supplementary Table 5:** Effect of other olefins under standard conditions\[^{[a]}\].

| Compound | Structure | Yield | Remarks |
|----------|-----------|-------|---------|
| 1q       | ![1q_structure](image) | ![1q_structure](image) | ![1q_structure](image) | 10% yield |
| 1r       | ![1r_structure](image) | ![1r_structure](image) | ![1r_structure](image) | <5% yield |
| 1s       | ![1s_structure](image) | ![1s_structure](image) | ![1s_structure](image) | 27% yield, 2.3:1 rr |
| 3q       | ![3q_structure](image) | ![3q_structure](image) | ![3q_structure](image) | 30% yield, 75% ee\[^{[b]}\] |
| 3r       | ![3r_structure](image) | ![3r_structure](image) | ![3r_structure](image) | 18% yield |

---

\[^{[a]}\] reaction conditions were the same as **Figure 3**. \[^{[b]}\] (MeO)\(_2\)MeSiH was used instead of (EtO)\(_2\)SiH, the product was isolated as 3a after treatment with pinacol.
7. Preparation of Substrates

a. Preparation of alkenyl boronates

Compounds 1a, 1e, 1q, 1r, 1s are commercially available. Compounds (Z)-1a\(^4\), 1b\(^5\), 1c\(^7\), 1d\(^6\), 1g\(^5\), 1h\(^8\), 1i\(^9\), 1j\(^7\), 1k\(^5\), and 1b-D\(^10\) were prepared according to the previously reported procedures.

**General procedure B** for the synthesis of (E)-alkenyl boronates\(^{11}\). Under N\(_2\) atmosphere, to an oven-dried round bottom flask equipped with a stir bar, Schwartz’s reagent (10 mol%), CH\(_2\)Cl\(_2\) (2.0 M) and alkyne (1.0 equiv) were added and stirred for 5 minutes. At 0 °C, pinacolborane (1.1 equiv) was added dropwise to the mixture. Then,
the mixture was allowed to warm to 30 °C and stirred for 24 hours. The reaction was quenched with H2O, extracted with Et2O, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (petroleum ether/EtOAc) to afford the (E)-alkenyl boronates.

\[
\text{Bpin} \quad \text{Cl}
\]

**(E)-2-(4-chlorobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (Figure 3, 1f). From the 4-chlorobut-1-yne (0.89 g, 10.0 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless oil in 59% yield (1.27 g).

**\[^{1}H\text{ NMR}\]** (500 MHz, CDCl\(_3\)) \(\delta\) 6.57 (dt, \(J = 18.0, 6.4\) Hz, 1H), 5.55 (dt, \(J = 18.0, 1.4\) Hz, 1H), 3.57 (t, \(J = 7.0\) Hz, 2H), 2.65 – 2.58 (m, 2H), 1.27 (s, 12H);

**\[^{13}C\text{ NMR}\]** (126 MHz, CDCl\(_3\)) \(\delta\) 149.0, 83.4, 43.0, 38.8, 24.9;

**\[^{11}B\text{ NMR}\]** (160 MHz, CDCl\(_3\)) \(\delta\) 29.7;

**HRMS (ESI)** calcd. for C\(_{10}\)H\(_{18}\)BClNaO\(_2\) [M+Na]\(^+\) m/z 239.0981, found 239.0978;

**IR (neat, cm\(^{-1}\))** 2977, 1638, 1360, 1318, 1139, 1005.

\[
\begin{align*}
\text{HO} & \quad \text{1.0 equiv} \\
\text{Gemfibrozil} & \quad \text{1.1 equiv DEAD} \\
& \quad 1.1 \text{ equiv PPh}_{3} \\
& \quad \text{THF (0.2 M)} \\
\text{general procedure B} & \\
\text{Bpin} & \quad \text{O} \\
\end{align*}
\]

**\((E)-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl\)** 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate** (Figure 3, 1i). To an anhydrous THF (40 mL) solution of gemfibrozil (10.0 mmol, 1.0 equiv, CAS 25812-30-0), pent-4-yn-1-ol
(0.84 g, 10 mmol, 1.0 equiv) and triphenylphosphine (PPh₃, 2.89 g, 11.0 mmol, 1.1 equiv) was slowly added a THF solution (20 mL) of diethyl azodicarboxylate (DEAD, 1.92 g, 11.0 mmol, 1.1 equiv) over 30 min at 0 °C. The resulting mixture was then stirred at rt overnight. The reaction was quenched with brine and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a yellow oil in 68% yield (2.15 g).

From the resulting alkyne (1.90 g, 6.0 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 53% yield (1.41 g).

**1H NMR** (500 MHz, CDCl₃) δ 7.00 (d, \( J = 7.5 \) Hz, 1H), 6.70 – 6.54 (m, 3H), 5.47 (dt, \( J = 17.9, 1.5 \) Hz, 1H), 4.07 (t, \( J = 6.5 \) Hz, 2H), 3.96 – 3.87 (m, 2H), 2.30 (s, 3H), 2.27 – 2.19 (m, 2H), 2.30 (s, 3H), 1.80 – 1.68 (m, 6H), 1.26 (s, 12H), 1.21 (s, 6H);

**13C NMR** (126 MHz, CDCl₃) δ 177.9, 157.1, 152.9, 136.5, 130.4, 123.7, 120.8, 112.1, 83.2, 68.1, 63.9, 42.2, 37.3, 32.2, 27.4, 25.3, 24.9, 21.5, 15.9;

**11B NMR** (160 MHz, CDCl₃) δ 29.9;

**HRMS** (ESI) calcd. for C₂₆H₄₁BNaO₅ [M+Na]⁺ m/z 467.2939, found 467.2926;

**IR** (neat, cm⁻¹) 2977, 1726, 1639, 1363, 1142.
(E)-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (Figure 3, 1m). The probenecid (2.85 g, 10 mmol, 1.0 equiv, CAS 57-66-9) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.1 equiv) in CH$_2$Cl$_2$ (25 mL) at 0 °C. Pent-4-yn-1-ol (1.01 g, 12 mmol, 1.2 equiv) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH$_2$Cl$_2$ and washed with 1 M HCl (aq.), saturated NaHCO$_3$ (aq.) and brine sequentially. The organic layer was dried over anhydrous Na$_2$SO$_4$. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a yellow oil in 84% yield (2.95 g).

From the resulting alkyne (2.81 g, 8.0 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to provide the title compound as a white solid in 55% yield (2.10 g).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.14 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.6 Hz, 2H), 6.65 (dt, J = 18.0, 6.4 Hz, 1H), 5.50 (dt, J = 17.9, 1.5 Hz, 1H), 4.36 (t, J = 6.5 Hz, 2H), 3.12 – 3.06 (m, 4H), 2.37 – 2.28 (m, 2H), 1.97 – 1.87 (m, 2H), 1.60 – 1.48 (m, 4H), 1.26 (s, 12H), 0.87 (t, J = 7.4 Hz, 6H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.4, 152.5, 144.3, 133.8, 130.3, 127.1, 83.3, 65.2, 50.1, 32.2, 27.3, 24.9, 22.1, 11.3;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 30.3;

HRMS (ESI) calcd. for C$_{24}$H$_{38}$BNNaO$_6$S [M+Na]$^+$ m/z 502.2405, found 502.2392;

IR (neat, cm$^{-1}$) 2975, 1720, 1643, 1275, 1142, 601;

m.p. 63 – 65 °C.
(1R,2S,5R)-2-Isopropyl-5-methycyclohexyl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, 1n). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH₂Cl₂ (25 mL) at 0 °C. L-Menthol (1.88 g, 12 mmol, 1.2 equiv, CAS 2216-51-5) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH₂Cl₂ and washed with 1 M HCl (aq.), saturated NaHCO₃ (aq.) and brine sequentially. The organic layer was dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 80% yield (2.01 g).

From the resulting alkyne (1.88 g, 7.5 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 62% yield (1.76 g).

**1H NMR** (500 MHz, CDCl₃) δ 6.59 (dt, J = 17.9, 6.4 Hz, 1H), 5.45 (dt, J = 17.9, 1.5 Hz, 1H), 4.67 (td, J = 10.9, 4.4 Hz, 1H), 2.32 – 2.24 (m, 2H), 2.22 – 2.14 (m, 2H), 2.00 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H), 1.79 – 1.71 (m, 2H), 1.71 – 1.63 (m, 2H), 1.54 – 1.42 (m, 1H), 1.39 – 1.31 (m, 1H), 1.26 (s, 12H), 1.10 – 0.99 (m, 1H), 0.99 – 0.90 (m, 1H), 0.91 – 0.81 (m, 7H), 0.75 (d, J = 7.0 Hz, 3H);

**13C NMR** (126 MHz, CDCl₃) δ 173.2, 153.2, 83.2, 74.1, 47.2, 41.1, 35.2, 34.4, 34.3, 31.5, 26.4, 24.9, 23.8, 23.6, 22.2, 20.9, 16.4;

**11B NMR** (160 MHz, CDCl₃) δ 29.9;
HRMS (ESI) calcd. for C_{22}H_{30}BNaO_{4} [M+Na]^+ m/z 401.2834, found 401.2823;

IR (neat, cm\(^{-1}\)) 2955, 2929, 1728, 1639, 1362, 1143.

(3aR,5R,6S,6aR)-5-[(R)-2,2-dimethyl-1,3-dioxolan-4-yl]-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, 1o). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH\(_2\)Cl\(_2\) (25 mL) at 0 °C. Diacetone-D-glucose (3.12 g, 12 mmol, 1.2 equiv, CAS 582-52-5) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH\(_2\)Cl\(_2\) and washed with 1 M HCl (aq.), saturated NaHCO\(_3\) (aq.) and brine sequentially. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\). After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 86% yield (3.05 g).

From the resulting alkyne (3.01 g, 8.5 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column
chromatography (petroleum ether/EtOAc = 5:1) to provide the title compound as a colorless oil in 57% yield (2.33 g).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.57 (dt, $J = 18.0, 6.4$ Hz, 1H), 5.86 (d, $J = 3.7$ Hz, 1H), 5.45 (dt, $J = 17.9, 1.5$ Hz, 1H), 5.26 (d, $J = 1.9$ Hz, 1H), 4.46 (d, $J = 3.7$ Hz, 1H), 4.23 – 4.16 (m, 2H), 4.11 – 4.05 (m, 1H), 4.03 – 3.98 (m, 1H), 2.41 – 2.30 (m, 2H), 2.24 – 2.15 (m, 2H), 1.82 – 1.73 (m, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 1.32 – 1.29 (m, 6H), 1.26 (s, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.1, 152.8, 112.4, 109.5, 105.2, 83.5, 83.3, 80.0, 76.1, 72.6, 67.5, 34.9, 33.7, 27.0, 26.9, 26.4, 25.4, 24.9, 23.4;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 30.0;

HRMS (ESI) calcd. for C$_{24}$H$_{39}$BNaO$_9$ [M+Na]$^+$ m/z 505.2579, found 505.2577;

IR (neat, cm$^{-1}$) 2981, 2936, 1745, 1638, 1363, 1142, 1073.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, 1p). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH$_2$Cl$_2$ (25 mL) at 0 °C. (+)-α-Tocopherol (5.16 g, 12 mmol, 1.2 equiv, CAS 59-02-9) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH$_2$Cl$_2$ and washed with 1 M HCl (aq.), saturated NaHCO$_3$ (aq.) and brine.
sequentially. The organic layer was dried over anhydrous Na$_2$SO$_4$. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 87% yield (4.57 g).

From the resulting alkyne (4.46 g, 8.5 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless oil in 68% yield (3.78 g).

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.64 (dt, $J = 17.9, 6.5$ Hz, 1H), 5.50 (dt, $J = 17.9, 1.4$ Hz, 1H), 2.64 – 2.55 (m, 4H), 2.35 – 2.27 (m, 2H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 – 1.89 (m, 5H), 1.85 – 1.70 (m, 2H), 1.58 – 1.48 (m, 3H), 1.46 – 1.32 (m, 4H), 1.33 – 1.21 (s, 23H), 1.17 – 1.02 (m, 6H), 0.90 – 0.82 (m, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 172.2, 153.0, 149.5, 140.6, 126.8, 125.0, 123.1, 117.5, 83.3, 75.2, 39.5, 37.6, 37.4, 35.3, 33.7, 33.0, 32.9, 31.3, 28.1, 25.0, 24.9, 24.6, 23.9, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.1, 12.3, 12.0;

$^{11}$B NMR (160 MHz, CDCl$_3$) δ 29.9;

HRMS (ESI) calcd. for C$_{41}$H$_{69}$BNaO$_5$ [M+Na]$^+$ m/z 675.5130, found 675.5128;

IR (neat, cm$^{-1}$) 2926, 2868, 1753, 1638, 1362, 1133.

(E)-4,4,5,5-Tetramethyl-2-(5-(naphthalen-2-ylmethoxy)pent-1-en-1-yl)-1,3,2-dioxaborolane (Figure 4, 1t). From 2-((pent-4-yn-1-loxy)methyl)naphthalene (1.35 g, 6.0 mmol), the title compound was prepared following the general procedure B. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 64% yield (1.35 g).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.83 (d, $J = 9.1$ Hz, 3H), 7.77 (s, 1H), 7.49 – 7.43 (m, 3H), 6.65 (dt, $J = 17.9, 6.4$ Hz, 1H), 5.47 (dt, $J = 17.9, 1.5$ Hz, 1H), 4.66 (s, 2H), 3.53 (t, $J = 6.5$ Hz, 2H), 2.32 – 2.23 (m, 2H), 1.82 – 1.74 (m, 2H), 1.26 (s, 12H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 153.9, 136.2, 133.4, 133.1, 128.3, 128.0, 127.8, 126.4,
126.2, 125.9, 83.2, 73.1, 69.9, 32.5, 28.4, 24.9;

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 30.0;

HRMS (ESI) calcd. for C$_{22}$H$_{29}$BNaO$_3$ [M+Na]$^+$ m/z 375.2102, found 375.2093;

IR (neat, cm$^{-1}$) 2978, 2935, 2856, 1639, 1362, 1143.
b. Preparation of 1,4,2-dioxazol-5-ones

Compounds 2a, 2b, 2f, 2k, 2l, 2s, 2t and 2v were prepared according to reference 12. Compounds 2g, 2j, 2o, 2q and 2r were prepared according to reference 13.

![Chemical structures of compounds 2a to 2v.]

**General procedure C** for the synthesis of 1,4,2-dioxazol-5-ones\textsuperscript{12-14}. 1,1'-Carbonyldiimidazole (CDI, 1.5 equiv) was added to a mixture of carboxylic acid (1.0 equiv.) in dry tetrahydrofuran (THF, 1.0 M) at rt. The reaction mixture was stirred for 2 hours. Afterward, hydroxylamine hydrochloride (2.0 equiv) was added. The resulting mixture was stirred overnight. The reaction mixture was diluted with 5% KHSO\textsubscript{4} (aq) and extracted with EtOAc. The combined organic layer was washed with water and
brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude hydroxamic acid was used for next step without further purification.

To a stirred solution of hydroxamic acid (1.0 equiv) in freshly distilled dichloromethane, 1,1′-carbonyldiimidazole (1.0 equiv) was added in one portion at rt. After being stirred for 2 hours, the reaction mixture was quenched with 1 N HCl (aq.), and extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The resulting residue was purified quickly by short silica pad (PE/EA = 10:1 ~ 5:1) to give the desired 1,4,2-dioxazol-5-ones.

![3-(4-(Methylthio)phenyl)-1,4,2-dioxazol-5-one](image)

**3-(4-(Methylthio)phenyl)-1,4,2-dioxazol-5-one** (Figure 4, 2c). From 4-(methylthio)benzoic acid (1.68 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 10:1) to provide the title compound as a white solid in 58% yield (1.21 g).

**¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 2.54 (s, 3H);

**¹³C NMR** (101 MHz, CDCl₃) δ 163.5, 154.0, 147.4, 126.8, 125.8, 115.9, 14.9;

**HRMS** (ESI) calcd. for C₈H₇NNaOS [M–CO₂+Na]⁺ m/z 116.0321, found 116.0317;

**IR** (neat, cm⁻¹) 1824, 1605, 1360, 1097, 996, 750;

**m.p.** 115 – 116 °C.

![tert-Butyl (4-(5-oxo-1,4,2-dioxazol-3-yl)phenyl)carbamate](image)

**tert-Butyl (4-(5-oxo-1,4,2-dioxazol-3-yl)phenyl)carbamate** (Figure 4, 2d). From 4-(((tert-butoxycarbonyl)amino)benzoic acid (2.37 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a
white solid in 47% yield (1.31 g).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, $J = 8.9$ Hz, 2H), 7.55 (d, $J = 8.9$ Hz, 2H), 6.77 (s, 1H), 1.53 (s, 9H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.4, 154.1, 152.1, 143.7, 128.0, 118.4, 114.0, 81.9, 28.4;

HRMS (ESI) calcd. for C$_{12}$H$_{14}$N$_2$NaO$_3$ [M–CO$_2$+Na]$^+$ m/z 257.0897, found 257.0893;

IR (neat, cm$^{-1}$) 3355, 1860, 1698, 1613, 1502, 1155, 757;

m.p. 159 – 160 ºC.

3-(naphthalen-1-yl)-1,4,2-dioxazol-5-one (Figure 4, 2e). From 1-naphthoic acid (3.44 g, 20 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a white solid in 27% yield (1.15 g).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.79 – 8.71 (m, 1H), 8.13 (d, $J = 8.3$ Hz, 1H), 8.06 (dd, $J = 7.3$, 1.2 Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.74 – 7.68 (m, 1H), 7.67 – 7.56 (m, 2H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.1, 153.6, 134.9, 133.9, 129.6, 129.5, 129.3, 129.1, 127.4, 125.5, 124.9, 116.7;

HRMS (ESI) calcd. for C$_{11}$H$_8$NO [M–CO$_2$+H]$^+$ m/z 170.0601, found 170.0596;

IR (neat, cm$^{-1}$) 1809, 1321, 1002, 759;

m.p. 53 – 54 ºC.

3-(Thiophen-3-yl)-1,4,2-dioxazol-5-one (Figure 4, 2h). From thiophene-3-carboxylic acid (1.28 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a white solid in 72% yield (1.22
g). Spectral data match those previously reported\textsuperscript{15}.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.07 – 7.99 (m, 1H), 7.56 – 7.45 (m, 2H);

\textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 160.5, 153.7, 130.6, 128.7, 124.8, 121.1.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{3-(2-Methylprop-1-en-1-yl)-1,4,2-dioxazol-5-one (Figure 4, 2i). From 3-methylbut-2-enoic acid (1.00 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 10:1) to provide the title compound as a yellow liquid in 55\% yield (0.78 g).
\textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 5.83 – 5.74 (m, 1H), 2.13 (d, \(J = 0.9\) Hz, 3H), 2.04 (d, \(J = 1.3\) Hz, 3H);
\textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\textsubscript{3}) \(\delta\) 163.0, 156.6, 154.0, 104.8, 27.8, 21.8;
\textbf{HRMS} (ESI) calcd. for C\textsubscript{5}H\textsubscript{8}NO \([\text{M–CO}_2+\text{H}]^+\) m/z 98.0601, found 98.0602;
\textbf{IR} (neat, cm\textsuperscript{-1}) 1830, 1656, 1284, 1154, 984, 761.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{4-(2-(5-Oxo-1,4,2-dioxazol-3-yl)ethyl)benzonitrile (Figure 4, 2m). From 3-(4-cyanophenyl)propanoic acid (1.75 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 5:1) to provide the title compound as a white solid in 79\% yield (1.71 g).
\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.64 (d, \(J = 8.3\) Hz, 2H), 7.34 (d, \(J = 8.3\) Hz, 2H), 3.12 (t, \(J = 7.6\) Hz, 2H), 3.02 – 2.93 (m, 2H);
\textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 165.3, 153.8, 143.4, 132.9, 129.2, 118.6, 111.5, 30.4, 26.2;
\textbf{HRMS} (ESI) calcd. for C\textsubscript{10}H\textsubscript{8}N\textsubscript{2}NaO \([\text{M–CO}_2+\text{Na}]^+\) m/z 195.0529, found 195.0524;

73}
IR (neat, cm$^{-1}$) 2231, 1826, 1637, 1148, 989, 756, 558;
m.p. 82 – 83 °C.

3-(2-(Furan-2-yl)ethyl)-1,4,2-dioxazol-5-one (Figure 4, 2n). From 3-(furan-2-
yl)propanoic acid (1.40 g, 10 mmol), the title compound was prepared following the
general procedure C. The crude material was purified quickly by short silica pad
(petroleum ether/EtOAc = 5:1) to provide the title compound as a white solid in 72% yield
(1.30 g).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34 (dd, $J = 1.8, 0.6$ Hz, 1H), 6.30 (dd, $J = 3.2, 1.9$ Hz,
1H), 6.15 – 6.06 (m, 1H), 3.08 (t, $J = 7.3$ Hz, 2H), 3.03 – 2.94 (m, 2H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.7, 154.1, 151.4, 142.2, 110.6, 106.8, 24.1, 23.3;

HRMS (ESI) calcd. for C$_7$H$_7$NNaO$_2$ [M–CO$_2$+Na]$^+$ m/z 160.0369, found 160.0365;
IR (neat, cm$^{-1}$) 1819, 1641, 1152, 983, 758;
m.p. 50 – 51 °C.

Benzyl 3-(5-oxo-1,4,2-dioxazol-3-yl)azetidine-1-carboxylate (Figure 4, 2p). From 1-
((benzyloxy)carbonyl)azetidine-3-carboxylic acid (2.35 g, 10 mmol), the title
compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 3:1) to provide the title compound as a white solid in 63% yield (1.74 g).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 – 7.29 (m, 5H), 5.12 (s, 2H), 4.37 (t, $J = 9.0$ Hz,
2H), 4.26 (dd, $J = 9.1, 6.0$ Hz, 2H), 3.84 – 3.73 (m, 1H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.6, 156.0, 153.6, 136.1, 128.7, 128.5, 128.3, 67.4,
51.3, 24.7;

HRMS (ESI) calcd. for C$_{12}$H$_{12}$N$_2$NaO$_3$ [M–CO$_2$+Na]$^+$ m/z 255.0740, found 255.0733;
IR (neat, cm\(^{-1}\)) 1820, 1708, 1356, 1131, 990, 760, 732;
m.p. 110 – 111 °C.

3-(2-(4,5-Diphenyloxazol-2-yl)ethyl)-1,4,2-dioxazol-5-one (Figure 4, 2u). From 3-(4,5-diphenyloxazol-2-yl)propanoic acid (2.93 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 81% yield (2.71 g).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.66 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.41 – 7.31 (m, 6H), 3.35 – 3.21 (m, 4H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 165.4, 159.5, 154.0, 146.2, 135.4, 132.1, 128.9, 128.9, 128.8, 128.7, 128.4, 128.0, 126.7, 23.1, 22.5;

HRMS (ESI) calcd. for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_2\)[M–CO\(_2\)+Na\(^+\)] m/z 313.0948, found 313.0941;

IR (neat, cm\(^{-1}\)) 1869, 1829, 1157, 991, 757, 694;
m.p. 76 – 77 °C.

3-(Thiophen-2-ylmethyl)-1,4,2-dioxazol-5-one (Figure 5, 2w). From 2-(thiophen-2-yl)acetic acid (1.42 g, 10 mmol), the title compound was prepared following the general procedure C. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as an orange solid in 62% yield (1.14 g).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 (dd, \(J = 5.1, 1.2\) Hz, 1H), 7.08 – 6.97 (m, 2H), 4.17 (s, 2H);

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 164.5, 153.8, 131.0, 128.4, 127.7, 126.6, 25.7;

HRMS (ESI) calcd. for C\(_6\)H\(_6\)NOS [M–CO\(_2\)+H\(^+\)] m/z 140.0165, found 140.0161;
IR (neat, cm\(^{-1}\)) 1817, 1632, 1341, 1150, 988, 712;
m.p. 51 – 52 °C.

c. Preparation of \(\text{L}^*\)

\[
\begin{array}{c}
\text{BocHN} \\
\text{Me}
\end{array} \quad \text{BnMgBr} \quad \frac{\text{THF, rt}}{\text{BnHN}} \quad \text{CF}_3\text{COOH} \quad \frac{\text{CH}_2\text{Cl}_2, \text{rt}}{\text{H}_2\text{N}}
\]

\((S)-3\text{-Amino-2-benzyl-1,4-diphenylbutan-2-ol (L\(^*\))}\).

Under \(\text{N}_2\) atmosphere, methyl (\text{tert}-butoxycarbonyl)-\text{L}-phenylalaninate (2.23 g, 8.0 mmol, 1.0 equiv) was dissolved in \(\text{THF}\) (10 mL). The solution was cooled to 0 °C, and benzylmagnesium chloride (40 mL, 1.0 M in \(\text{THF}\), 5.0 equiv) was added dropwise over 15 min. The resulting mixture was warmed to rt and stirred for 24 h at rt. Completion of the reaction was monitored by TLC. The solution was cooled to 0 °C again and carefully quenched with a saturated aqueous solution of \(\text{NH}_4\text{Cl}\). The mixture was extracted with \(\text{Et}_2\text{O}\) and washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated under reduced pressure to give the crude product. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide \text{tert}-butyl \((S)-(3\text{-benzyl-3-hydroxy-1,4-diphenylbutan-2-yl})\text{carbamate as a sticky oil or white solid in 38\% yield (1.31 g).}\)

\(\text{CF}_3\text{COOH (2.0 mL) was added to a solution of \text{tert}-butyl (S)-(3-benzyl-3-hydroxy-1,4-diphenylbutan-2-yl)carbamate (1.31 g, 3.0 mmol, 1.0 equiv) in \text{CH}_2\text{Cl}_2 (10 mL), and the mixture was stirred at rt. Completion of the reaction was monitored by TLC. The solution was cooled to 0 °C, and saturated aqueous \text{NaHCO}_3 was added carefully. The mixture was extracted with \text{Et}_2\text{O and washed with saturated aqueous K}_2\text{CO}_3, \text{brine, dried over Na}_2\text{SO}_4, filtered, and concentrated under reduced pressure to give the crude product. After recrystallization (petroleum ether/EtOAc), (S)-3\text{-amino-2-benzyl-1,4-diphenylbutan-2-ol was obtained as a white solid in 85\% yield (0.85 g).}\)}

\(^1\text{H NMR (500 MHz, CD}_3\text{CN)) \delta 7.40 – 7.14 (m, 13H), 7.09 – 7.03 (m, 2H), 3.90 (s, 1H),}\)
3.23 (d, $J = 12.5$ Hz, 1H), 2.95 (d, $J = 13.3$ Hz, 1H), 2.90 – 2.78 (m, 2H), 2.68 (d, $J = 13.3$ Hz, 1H), 2.52 – 2.38 (m, 2H), 1.04 (s, 2H);

$^{13}$C NMR (126 MHz, CD$_3$CN) $\delta$ 141.6, 139.4, 139.3, 132.2, 131.9, 130.1, 129.3, 128.8, 128.7, 127.1, 127.0, 126.9, 76.2, 59.4, 42.4, 42.3, 39.6;

HRMS (ESI) calcd. for C$_{23}$H$_{26}$NO [M+H]$^+$ m/z 332.2009, found 332.2000;

IR (neat, cm$^{-1}$) 3377, 3317, 3026, 2937, 1493, 752, 696;

m.p. 133 – 135 °C;

$[\alpha]_D^{23} = +17.1$ (c = 0.79, CHCl$_3$).
II. Supplementary Figures
1. NMR Spectroscopic Data

Supplementary Figure 2: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3a.

Supplementary Figure 2: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3a.
Supplementary Figure 3: $^{13}$C NMR (126 MHz, CDCl₃) spectrum of 3a.
Supplementary Figure 4: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3a.
Supplementary Figure 5: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3b.
Supplementary Figure 6: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3b.
Supplementary Figure 7: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3b.
Supplementary Figure 8: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3c.
Supplementary Figure 9: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3c.
Supplementary Figure 10: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3c.
Supplementary Figure 11: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3d.
Supplementary Figure 12: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3d.
Supplementary Figure 13: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3d.
Supplementary Figure 14: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3e.
Supplementary Figure 15: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3e.
Supplementary Figure 16: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3e.
Supplementary Figure 17: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3f.
Supplementary Figure 18: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3f.
Supplementary Figure 19: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3f.
Supplementary Figure 20: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3g.
Supplementary Figure 21: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3g.
Supplementary Figure 22: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3g.
Supplementary Figure 23: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3h.
Supplementary Figure 24: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3h.
Supplementary Figure 25: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3h.
Supplementary Figure 26: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3i.
Supplementary Figure 27: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3i.
**Supplementary Figure 28:** $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3i.
Supplementary Figure 29: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3j.
Supplementary Figure 30: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3j.
Supplementary Figure 31: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3j.
**Supplementary Figure 32:** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3k.
Supplementary Figure 33: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3k.
Supplementary Figure 34: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3k.
Supplementary Figure 35: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3l.
Supplementary Figure 36: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3l.
Supplementary Figure 37: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3l.
Supplementary Figure 38: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3m.
Supplementary Figure 39: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3m.
Supplementary Figure 40: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3m.
Supplementary Figure 41: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3n.
Supplementary Figure 42: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3n.
Supplementary Figure 43: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3n.
Supplementary Figure 44: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3n'.
Supplementary Figure 45: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3n$'$.
Supplementary Figure 46: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3n'.

$\text{3n'}$

$^{11}$B NMR (160 MHz, CDCl$_3$)
**Supplementary Figure 47:** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3o.
Supplementary Figure 48: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3o.
Supplementary Figure 49: $^{11}B$ NMR (160 MHz, CDCl$_3$) spectrum of 3o.
Supplementary Figure 50: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3o'.
Supplementary Figure 51: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3o'.

3o'
Supplementary Figure 52: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3o'.
Supplementary Figure 53: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3p.
Supplementary Figure 54: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3p.
Supplementary Figure 55: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3p.
Supplementary Figure 56: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3p$^\prime$. 

$^1$H NMR (500 MHz, CDCl$_3$)

3p$^\prime$
Supplementary Figure 57: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of $3p'$. 

$^{13}$C NMR (126 MHz, CDCl$_3$)
Supplementary Figure 58: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3p'.
Supplementary Figure 59: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4b.
Supplementary Figure 60: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4b.
Supplementary Figure 61: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4b.
**Supplementary Figure 62:** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4c.
Supplementary Figure 63: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4c.
Supplementary Figure 64: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4c.
Supplementary Figure 65: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4d.
Supplementary Figure 66: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4d.
Supplementary Figure 67: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4d.
Supplementary Figure 68: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4e.
Supplementary Figure 69: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4e.
Supplementary Figure 70: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4e.
Supplementary Figure 71: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4f.
Supplementary Figure 72: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4f.
Supplementary Figure 73: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4f.
Supplementary Figure 74: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4g.
Supplementary Figure 75: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4g.
Supplementary Figure 76: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4g.
Supplementary Figure 77: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4h.
Supplementary Figure 78: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4h.
Supplementary Figure 79: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4h.
**Supplementary Figure 80:** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4i.
Supplementary Figure 81: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4i.
Supplementary Figure 82: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4i.
Supplementary Figure 83: $^1\text{H}$ NMR (500 MHz, CDCl$_3$) spectrum of 4j.
Supplementary Figure 84: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4j.
Supplementary Figure 85: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4j.
Supplementary Figure 86: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4k.
Supplementary Figure 87: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4k.
Supplementary Figure 88: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4k.
Supplementary Figure 89: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4l.
Supplementary Figure 90: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4l.
Supplementary Figure 91: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4l.
Supplementary Figure 92: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4m.
Supplementary Figure 93: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4m.
**Supplementary Figure 94:** $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4m.
Supplementary Figure 95: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4n.
Supplementary Figure 96: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4n.
Supplementary Figure 97: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4n.
Supplementary Figure 98: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of $4o$. 
Supplementary Figure 99: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 40.
Supplementary Figure 100: $^{11}$B NMR (160 MHz, CDCl₃) spectrum of 4o.
Supplementary Figure 101: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4p.
Supplementary Figure 102: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4p.
**Supplementary Figure 103:** $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of $4p$. 

$^{11}$B NMR (160 MHz, CDCl$_3$)
Supplementary Figure 104: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4q.
Supplementary Figure 105: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4q.
Supplementary Figure 106: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4q.
Supplementary Figure 107: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4r.
Supplementary Figure 108: $^{13}\text{C}$ NMR (126 MHz, CDCl$_3$) spectrum of 4r.
Supplementary Figure 109: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4r.
Supplementary Figure 110: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4s.
Supplementary Figure 111: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4s.
Supplementary Figure 112: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4s.
Supplementary Figure 113: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4t.
Supplementary Figure 114: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4t.
Supplementary Figure 115: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4t.
**Supplementary Figure 116:** $^{1}$H NMR (500 MHz, CDCl$_3$) spectrum of **4u**.
Supplementary Figure 117: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4u.
Supplementary Figure 118: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4u.
Supplementary Figure 119: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4v.
Supplementary Figure 120: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of $4v$. 
Supplementary Figure 121: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 4v.
Supplementary Figure 122: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 5.
Supplementary Figure 123: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 5.
1H NMR (500 MHz, CDCl₃) spectrum of 6.

Supplementary Figure 124: 1H NMR (500 MHz, CDCl₃) spectrum of 6.
Supplementary Figure 125: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 6.
Supplementary Figure 126: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 6.
Supplementary Figure 127: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 7.
Supplementary Figure 128: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 7.
Supplementary Figure 129: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 7.
Supplementary Figure 130: $^1$H NMR (500 MHz, CD$_3$OD) spectrum of 8.
Supplementary Figure 131: $^{13}$C NMR (126 MHz, CD$_3$OD) spectrum of 8.
Supplementary Figure 132: $^{11}$B NMR (160 MHz, CD$_3$OD) spectrum of 8.
Supplementary Figure 133: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3a (no D was detected).
Supplementary Figure 134: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3a (no D was detected).
Supplementary Figure 135: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3a (no D was detected).
Supplementary Figure 136: $^2$H NMR (92 MHz, CHCl$_3$) spectrum of 3a (no D was detected).
**Supplementary Figure 137**: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3b-D.
Supplementary Figure 138: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 3b-D.
Supplementary Figure 139: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 3b-D.
Supplementary Figure 140: $^2$H NMR (92 MHz, CHCl$_3$) spectrum of 3b-D.
Supplementary Figure 141: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9.
Supplementary Figure 142: $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 9.
Supplementary Figure 143: $^{31}$P NMR (202 MHz, CDCl$_3$) spectrum of 9.
Supplementary Figure 144: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1f.
Supplementary Figure 145: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 1f.
Supplementary Figure 146: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1f.
Supplementary Figure 147: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 11.
Supplementary Figure 148: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 11.
Supplementary Figure 149: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 11.
Supplementary Figure 150: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1m.
Supplementary Figure 151: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 1m.
Supplementary Figure 152: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1m.
Supplementary Figure 153: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1n.
Supplementary Figure 154: $^{13}\text{C}$ NMR (126 MHz, CDCl$_3$) spectrum of 1n.
Supplementary Figure 155: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1n.
Supplementary Figure 156: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1o.
Supplementary Figure 157: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 10.
Supplementary Figure 158: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1o.
Supplementary Figure 159: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1p.
Supplementary Figure 160: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 1p.
Supplementary Figure 161: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1p.
Supplementary Figure 162: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1t.
Supplementary Figure 163: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 1t.

$^{13}$C NMR (126 MHz, CDCl$_3$)
Supplementary Figure 164: $^{11}$B NMR (160 MHz, CDCl$_3$) spectrum of 1t.

1t

$^{11}$B NMR (160 MHz, CDCl$_3$)
Supplementary Figure 165: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2c.
Supplementary Figure 166: $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2c.
Supplementary Figure 167: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2d.
Supplementary Figure 168: $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2d.
Supplementary Figure 169: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 2e.
Supplementary Figure 170: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 2e.
Supplementary Figure 171: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2h.
Supplementary Figure 172: $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2h.
Supplementary Figure 173: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 2i.
Supplementary Figure 174: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 2i.
Supplementary Figure 175: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2m.
Supplementary Figure 176: $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2m.
Supplementary Figure 177: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 2n.
Supplementary Figure 178: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 2n.
Supplementary Figure 179: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of $2p$. 
Supplementary Figure 180: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 2p.
Supplementary Figure 181: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 2u.
Supplementary Figure 182: $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 2u.
Supplementary Figure 183: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 2w.
Supplementary Figure 184: \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) spectrum of 2w.
Supplementary Figure 185: $^1$H NMR (500 MHz, CD$_3$CN) spectrum of L*.
Supplementary Figure 186: $^{13}$C NMR (126 MHz, CD$_3$CN) spectrum of L*.
2. HPLC Trace

Data File: H:\ORIGINAL DATA\ZY-09-146-10-RAC.D
Sample Name: ZY-09-146-10-IE

--------------------------------------------------
Acq. Operator : 系统   Seq. Line :  3
Acq. Instrument : HPLC-1260   Location :  61
Injection Date  : 1/29/2022 5:06:07 PM   Inj :  1

Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl

Acq. Method : D:\zy\20220124\YH 2022-01-29 16-32-07\5EtOH10_10-1-6-240.M
Last changed   : 1/29/2022 4:32:31 PM by 系统

Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\3IPA_30_8_2.-SFT.M (Sequence Method)
Last changed   : 3/28/2022 10:48:30 PM by SYSTEM
(modified after loading)

--------------------------------------------------

Area Percent Report

--------------------------------------------------
Sorted By : Signal
Multiplier :  1.0000
Dilution :  1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| #  | RetTime | Type | Width | Area    | Height | Area % |
|----|---------|------|-------|---------|--------|--------|
| 1  | 6.831   | VB   | 0.113 | 3366.24365 | 454.14883 | 50.1751 |
| 2  | 7.422   | BB   | 0.125 | 3342.75000 | 406.73416 | 49.8249 |

Totals : 6708.99365 860.88300

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*** End of Report ***

Supplementary Figure 187: HPLC spectrum of (±)-3a.
Supplementary Figure 188: HPLC spectrum of 3a.
Supplementary Figure 189: HPLC spectrum of 3a (from (Z)-1a).
Supplementary Figure 190: HPLC spectrum of (±)-3b.
Supplementary Figure 191: HPLC spectrum of 3b.
Data File E:\DATA\20220317\LC 2022-03-21 09-08-37\1FA-0301--004.D
Sample Name: ZY-10-57-1-EE

=====================================================================
Acq. Operator : SYSTEM      Seq. Line :  4
Acq. Instrument : HPLC1260    Location : P1-F1
Injection Date  : 3/21/2022 9:53:03 AM      Inj :  1
                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0_5_1-254.M
Last changed    : 3/21/2022 9:08:37 AM by SYSTEM
Analysis Method : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0_5_1-254.M (Sequence Method)
Last changed    : 3/21/2022 12:17:47 PM by SYSTEM
(modified after loading)

VWD1 A, Wavelength=254 nm (E:\DATA\20220317\LC 2022-03-21 09-08-37\1FA-0301--004.D)

Area Percent Report

Sorted By        :      Signal
Multiplier       :      1.0000
Dilution         :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| #  | Peak RetTime | Type | Width | Area     | Height | Area % |
|----|-------------|------|-------|----------|--------|--------|
| 1  | 7.280       | BV E | 0.1991| 85.09237 | 6.39980| 1.9985 |
| 2  | 7.917       | VB R | 0.2023| 4172.81006| 313.51718| 98.0015|

Totals : 4257.90243 319.91699

=====================================================================

*** End of Report ***

Supplementary Figure 192: HPLC spectrum of 3b-D.
Supplementary Figure 193: HPLC spectrum of (±)-3c.

HPLC1260 3/29/2022 9:27:31 AM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-187-2-EE.D
Sample Name: ZY-09-187-2-EE

---------------------------------------------------------------------
Acq. Operator       : 系统               Seq. Line :  4
Acq. Instrument     : HPLC-1260             Location :  43
Injection Date      : 12/23/2021 9:54:02 AM   Inj :  1
Inj Volume          : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method         : D:\zy\20211219\YH 2021-12-23 09-03-54\10EtOH-15-0.8-1-6-240.M
Last changed        : 12/23/2021 9:03:56 AM by 系统
Analysis Method     : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence Method)
Last changed        : 3/29/2022 9:27:03 AM by SYSTEM (modified after loading)

Area Percent Report

Sorted By :      Signal
Multiplier :  1.0000
Dilution :  1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| # | RetTime [min] | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|--------------|-------------|--------------|--------------|---------|
| 1 | 7.410        | 0.1140      | 2207.72168   | 294.35645    | 97.8049 |
| 2 | 7.787        | 0.1295      | 49.54852     | 5.61053      | 2.1951  |

Totals : 2257.27020  299.96697

---------------------------------------------------------------------

*** End of Report ***

Supplementary Figure 194: HPLC spectrum of 3c.
Supplementary Figure 195: HPLC spectrum of (±)-3d.
Supplementary Figure 196: HPLC spectrum of 3d.
Supplementary Figure 197: HPLC spectrum of (R)-10.
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-RAC.D
Sample Name: ZY-09-186-2-RAC

---

Acq. Operator : 系统
Acq. Instrument : HPLC-1260
Injection Date : 12/15/2021 11:47:34 AM

Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl

---

Area Percent Report
---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| #  | RetTime | Width  | Area     | Height   | Area % |
|----|---------|--------|----------|----------|--------|
| 1  | 5.944   | 0.2142 | 3801.18140 | 266.80502 | 49.7416 |
| 2  | 6.843   | 0.2460 | 3840.67212 | 230.42453 | 50.2584 |

Totals : 7641.85352 497.22955

---

*** End of Report ***

Supplementary Figure 198: HPLC spectrum of (±)-3e.
Data File: F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-EE.D
Sample Name: ZY-09-186-2-EE

| Acq. Operator     | 系统   | Seq. Line: 9 |
|-------------------|--------|--------------|
| Acq. Instrument   | HPLC-1260 | Location: 13 |
| Injection Date    | 12/15/2021 11:31:08 AM | Inj: 1 |

Different Inj Volume from Sample Entry! Actual Inj Volume: 1.200 µl

| Acq. Method       | D:\zy\20211129\YH 2021-12-15 09-26-25\5IPA-15-1.0-1-6-254-ZH.M |
|-------------------|------------------------------------------------------------------|
| Last changed      | 12/15/2021 11:14:11 AM by 系统                                   |

Analysis Method: E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence Method)

Last changed: 3/29/2022 9:24:40 AM by SYSTEM (modified after loading)

Additional Info: Peak(s) manually integrated

---

VWD1A, Wavelength=254 nm (F:ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-EE.D)

|         | Cy | Bpin- | O | Ph |
|---------|----|-------|---|----|
| Signal 1| VWD1 A, Wavelength=254 nm (F:ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-EE.D) |

---

Area Percent Report

| Sorted By | Signal |
|-----------|--------|
| Multiplier| 1.0000 |
| Dilution  | 1.0000 |

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| # | RetTime | Type | Width | Area  | Height | Area % |
|---|---------|------|-------|-------|--------|--------|
| 1 | 5.955   | BB   | 0.2016| 174.05440 | 12.64594 | 3.7263 |
| 2 | 6.839   | BB   | 0.2464| 4496.94629 | 272.66776 | 96.2737 |

Totals: 4671.00069 285.31369

---

** Supplementary Figure 199: HPLC spectrum of 3e.**

HPLC1260 3/29/2022 9:24:42 AM SYSTEM
Supplementary Figure 200: HPLC spectrum of (±)-3f.
Supplementary Figure 201: HPLC spectrum of 3f.

Data File H:\DATA2\ZY-10-64-2-EE.D
Sample Name: ZY-10-64-2-EE

Acq. Operator: 系统
Acq. Instrument: HPLC-1260
Injection Date: 5/24/2022 7:15:09 PM
Inj Volume: 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume: 0.300 µl
Acq. Method: D:\zy\20220524\YH 2022-05-24 18-17-05\5EtOH15_10-1-2-240.M
Analysis Method: E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence Method)
Last changed: 5/24/2022 7:13:28 PM by 系统
Last changed: 6/7/2022 10:10:23 AM by SYSTEM (modified after loading)
Additional Info: Peak(s) manually integrated

Area Percent Report

| # | RetTime | Type | Width | Area   | Height  | Area % |
|---|---------|------|-------|--------|---------|--------|
| 1 | 5.117   | MF   | 0.0856| 2629.60010 | 512.06506 | 97.4649 |
| 2 | 5.524   | MF   | 0.1180| 68.39656 | 9.66246  | 2.5351  |

Totals: 2697.99666 521.72753

*** End of Report ***
Data File H:\1\ZY-09-186-6-RAC.D
Sample Name: ZY-09-186-6-RAC

Acq. Operator: 系统
Acq. Instrument: HPLC-1260
Injection Date: 8/20/2022 5:00:51 PM
Injection Volume: 3.000 µl

Different Inj Volume from Sample Entry! Actual Inj Volume: 1.600 µl

Acq. Method: D:\zy\20220803\YH 2022-08-20 08-41-06\SIPA20_10-1-2-240.M
Last changed: 8/20/2022 1:41:14 PM by 系统

Analysis Method: E:\DATA\20220317\LC 2022-08-22 08-37-45\SIAPA-40-1.0-1-220-QDY.M (Sequence Method)
Last changed: 8/22/2022 7:02:33 PM by SYSTEM (modified after loading)

Additional Info: Peak(s) manually integrated

Supplementary Figure 202: HPLC spectrum of (±)-3g.
Supplementary Figure 203: HPLC spectrum of 3g.
Supplementary Figure 204: HPLC spectrum of (±)-3h.
Supplementary Figure 205: HPLC spectrum of 3h.

HPLC1260 3/29/2022 9:28:55 AM SYSTEM
Data File E:\DATA\20210920\LC 2021-12-06 14-33-37\OnlineEdited--061.D
Sample Name: ZY-09-168-5-RAC

Supplementary Figure 206: HPLC spectrum of (±)-3i.
Supplementary Figure 207: HPLC spectrum of 3i.

HPLC1260 12/7/2021 9:56:18 PM SYSTEM
Supplementary Figure 208: HPLC spectrum of (±)-3j.

HPLC1260 8/22/2022 7:14:38 PM SYSTEM
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| #  | RetTime Type | Width | Area    | Height  | Area  |
|----|--------------|-------|---------|---------|-------|
|    | [min]        | [min] | [mAU*s] | [mAU]   | %     |
|----|--------------|-------|---------|---------|-------|
| 1  | 6.759 MM     | 0.1347| 2771.72 | 342.95  | 97.68 |
| 2  | 7.620 MM     | 0.2110| 65.57   | 5.18    | 2.31  |

Totals : 2837.29167 348.13124

*** End of Report ***
Data File: H:\ZY-10-115-5-RAC.D
Sample Name: ZY-10-115-6-12

---

Acq. Operator : 系统
Seq. Line : 27
Acq. Instrument : HPLC-1260
Location : 54
Injection Date : 8/19/2022 10:13:31 PM
Inj : 1

Different Inj Volume from Sample Entry! Actual Inj Volume : 4.000 µl

Acq. Method : D:\zy\20220803\YH 2022-08-19 14-14-07\20EtOH20_10-1-2-254.M

Last changed : 8/19/2022 2:14:07 PM by 系统

Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence Method)

Last changed : 8/22/2022 7:33:29 PM by SYSTEM (modified after loading)

Additional Info : Peak(s) manually integrated

---

Area Percent Report

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm (H:\ZY-10-115-5-RAC.D)

| # | RetTime [min] | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|--------------|-------------|--------------|-------------|--------|
| 1 | 9.756 BB     | 0.4317      | 1.09960e+04 | 387.94690   | 50.3217|
| 2 | 11.753 BB    | 0.5502      | 1.08554e+04 | 288.05551   | 49.6783|

Totals : 2.18514e+04 676.00241

---

*** End of Report ***

---

Supplementary Figure 210: HPLC spectrum of (±)-3k.

---

HPLC1260 8/22/2022 7:33:32 PM SYSTEM
Data File H:\OnlineEdited--024.D
Sample Name: ZY-10-115-5-13

-----------------------------------------------------------------------------------
Acq. Operator : 系统  Seq. Line : 24
Acq. Instrument : HPLC-1260  Location : 75
Injection Date : 8/19/2022 9:19:43 PM  Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 3.200 µl
Acq. Method : D:\zy\20220803\YH 2022-08-19 14-14-07\20EtOH20_10-1-2-254.M
Last changed : 8/19/2022 2:14:07 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-19 14-05-28\10IPA_10_8_3.M (Sequence Method)
Last changed : 8/19/2022 10:26:56 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| # | RetTime | Width | Area      | Height | %    |
|---|---------|-------|-----------|--------|------|
| 1 | 9.715   | BB    | 0.4357    | 9538.70508 | 339.05954 | 98.3459 |
| 2 | 12.346  | MM    | 0.5951    | 160.43559 | 4.49287  | 1.6541  |

Totals : 9699.14067 343.55241

================================================================================

*** End of Report ***

Supplementary Figure 211: HPLC spectrum of 3k.
Supplementary Figure 212: HPLC spectrum of (±)-3l.

HPLC1260 3/29/2022 9:59:20 AM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-12-12-EE.D
Sample Name: ZY-10-12-12-EE

Acq. Operator : 系统   Seq. Line : 8
Acq. Instrument : HPLC-1260   Location : 82
Injection Date : 3/14/2022 7:52:12 PM   Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method : D:\zy\20220302\YH 2022-03-14 18-14-35\8IPA20_8-1-2-240.M
Last changed : 3/14/2022 7:50:44 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed : 3/29/2022 9:59:57 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| #  | RetTime | Type | Width  | Area   | Height  | Area % |
|----|---------|------|--------|--------|---------|--------|
| 1  | 6.983   | BB   | 0.2180 | 115.32585 | 7.70988 | 1.8705 |
| 2  | 8.145   | BB   | 0.2674 | 6050.16260 | 333.05563 | 98.1295 |

Totals : 6165.48845 340.76552

*** End of Report ***

Supplementary Figure 213: HPLC spectrum of 3I.
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-5-RAC.D
Sample Name: ZY-10-24-5-RAC

Acq. Operator : 系统               Seq. Line :  27
Acq. Instrument : HPLC-1260         Location :   71
Injection Date : 2/14/2022 10:13:51 PM  Inj :   1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\15EtOH30_10-1-2-254.M
Last changed    : 2/14/2022 9:50:04 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed    : 3/29/2022 10:02:54 AM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm (F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-5-RAC.D)

| Peak RetTime Type | Width   | Area     | Height   | Area % |
|------------------|---------|----------|----------|--------|
| #    | [min]  | [min]    | [mAU*s]  | [mAU]  | %     |
|------|--------|----------|----------|--------|-------|
| 1    | 9.201  | 0.2237   | 4765.29834 | 317.25735 | 50.2247 |
| 2    | 13.302 | 0.4520   | 4722.66553 | 153.67970 | 49.7753 |

Totals : 9487.96387  470.93706

Supplementary Figure 214: HPLC spectrum of (±)-3m.
Data File: F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-5-EE.D
Sample Name: ZY-10-24-5-EE

---------------------------------------------------------------------
Acq. Operator : 系统          Seq. Line : 26
Acq. Instrument : HPLC-1260     Location : 72
Injection Date : 2/14/2022 9:51:27 PM     Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.600 µl
Acq. Method : D:\zy\20220201\YH 2022-02-14 12-55-19\15EtOH30_10-1-2-254.M
Last changed : 2/14/2022 9:50:04 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed : 3/29/2022 10:02:54 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

---|-------|----|-------|----------|----------|--------|
1   9.204 BB    0.2267 4723.18945  311.85480  98.1437
2  13.512 BB    0.3615   89.33582    2.91907   1.8563
Totals : 4812.52527  314.77387
---

Supplementary Figure 215: HPLC spectrum of 3m.

HPLC1260 3/29/2022 10:03:22 AM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-25-RAC.D
Sample Name: ZY-10-25-RAC

===================================================================
Acq. Operator: 系统   Seq. Line: 35
Acq. Instrument: HPLC-1260   Location: 81
Injection Date: 2/15/2022 12:45:00 AM   Inj: 1
   Inj Volume: 3.000 µl
Different Inj Volume from Sample Entry!   Actual Inj Volume: 1.000 µl
Acq. Method: D:\zy\20220201\YH 2022-02-14 12-55-19\SIPA15_10-1-6-240.M
Last changed: 2/14/2022 9:25:27 PM by 系统
Analysis Method: E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed: 3/29/2022 10:04:39 AM by SYSTEM (modified after loading)

VWD1 A, Wavelength=240 nm (F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-25-RAC.D)

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
-----|-------|----|-------|----------------|--------|
1   5.713 BB 0.2128 4071.67749 284.85623 49.0033
2   8.616 BB 0.3652 4237.30811 174.26460 50.9967
Totals: 8308.98560 459.12083

===================================================================

*** End of Report ***

Supplementary Figure 216: HPLC spectrum of (±)-3n.
Supplementary Figure 217: HPLC spectrum of 3n.
**Supplementary Figure 218**: HPLC spectrum of 3n'.

HPLC1260 3/29/2022 10:05:25 AM SYSTEM
Acq. Operator : 系统       Seq. Line : 5
Acq. Instrument : HPLC-1260    Location : 81
Injection Date : 6/26/2022 3:12:35 PM    Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 0.600 µl
Acq. Method : D:\zy\20220624\YH 2022-06-26 14-05-25\12EtOH20_10-1-2-240.M
Last changed : 6/26/2022 2:05:25 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M
             (Sequence Method)
Last changed : 8/9/2022 9:05:21 AM by SYSTEM
             (modified after loading)

--- Area Percent Report ---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| # | RetTime | Width | Area    | Height  | Area percentage |
|---|---------|-------|---------|---------|----------------|
| 1 | 6.754   | BV    | 0.1230  | 2800.11133 | 347.39279 | 46.7353 |
| 2 | 7.505   | VB    | 0.1456  | 3191.31055 | 330.62488 | 53.2647 |

Totals : 5991.42188 678.01767

--- *** End of Report *** ---

**Supplementary Figure 219:** HPLC spectrum of (±)-3o.
Data File H:\A\ZY-10-91-2-EE.D
Sample Name: ZY-10-91-2-EE

Acq. Operator : 系统   Seq. Line :   3
Acq. Instrument : HPLC-1260   Location :   82
Injection Date  : 6/26/2022 2:29:40 PM   Inj :   1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220624\YH 2022-06-26 14-05-25\12EtOH20_10-1-2-240.M
Last changed    : 6/26/2022 2:05:25 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence Method)
Last changed    : 8/9/2022 9:03:39 AM by SYSTEM  (modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| # | RetTime | Type | Width | Area     | Height | Area   | %     |
|---|---------|------|-------|----------|--------|--------|-------|
| 1 | 6.781   | BV   | R     | 0.1229   | 3513.69751 | 436.44815 | 97.4507 |
| 2 | 7.545   | VB   | E     | 0.1465   | 91.91974   | 9.48676  | 2.5493 |

Totals : 3605.61725 445.93491

*** End of Report ***

Supplementary Figure 220: HPLC spectrum of 3o.

HPLC1260 8/9/2022 9:03:41 AM SYSTEM
Supplementary Figure 221: HPLC spectrum of 3o'.

HPLC1260 8/9/2022 9:04:44 AM SYSTEM
Supplementary Figure 222: HPLC spectrum of (±)-3p.

HPLC1260 8/9/2022 9:10:31 AM SYSTEM
Supplementary Figure 223: HPLC spectrum of 3p.
Data File: H:\A\ZY-10-101-6-EE.D
Sample Name: ZY-10-101-6-EE

---

Acq. Operator: 系统  Seq. Line: 32
Acq. Instrument: HPLC-1260  Location: 63
Injection Date: 7/5/2022 1:09:09 AM  Inj: 1

Different Inj Volume from Sample Entry! Actual Inj Volume: 0.300 µl

Acq. Method: D:\zy\20220624\YH 2022-07-04 14-04-41\18EtOH15_10-1-6-240.M

Last changed: 7/4/2022 7:42:02 PM by 系统
Analysis Method: E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence Method)
Last changed: 8/9/2022 9:09:12 AM by SYSTEM (modified after loading)

Additional Info: Peak(s) manually integrated

---

Area Percent Report
---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|--------------|------|-------------|--------------|-------------|---------|
| 1 | 4.921        | BB   | 0.0754      | 58.30293     | 11.65547    | 2.2584  |
| 2 | 5.660        | VB R | 0.0991      | 2523.31274   | 384.16348   | 97.7416 |

Totals: 2581.61567 395.81895

---

*** End of Report ***

Supplementary Figure 224: HPLC spectrum of 3p'.
Supplementary Figure 225: HPLC spectrum of (±)-4b.

HPLC1260 3/28/2022 11:08:27 PM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-3-EE.D
Sample Name: ZY-09-161-3-EE

Supplementary Figure 226: HPLC spectrum of 4b.
Supplementary Figure 227: HPLC spectrum of (±)-4c.

HPLC1260 8/23/2022 3:25:29 PM SYSTEM
Data File: H:\1\ZY-09-189-2-EE.D
Sample Name: ZY-09-189-2-EE

Supplementary Figure 228: HPLC spectrum of 4c.
Supplementary Figure 229: HPLC spectrum of (±)-4d.
Supplementary Figure 230: HPLC spectrum of 4d.
Supplementary Figure 231: HPLC spectrum of (±)-4e.
Data File H:\DATA2\ZY-10-69-6-EE.D
Sample Name: ZY-10-69-6-EE

=====================================================================
Acq. Operator : 系统 Seq. Line : 4
Acq. Instrument : HPLC-1260 Location : 42
Injection Date : 5/29/2022 8:55:45 PM Inj : 1

Inj Volume : 3.000 µl

Different Inj Volume from Sample Entry! Actual Inj Volume : 0.100 µl

Acq. Method : D:\zy\20220328\YH 2022-05-29 20-09-39\SEtOH15_10-1-2-240.M
Last changed : 5/29/2022 8:09:40 PM by 系统

Analysis Method : E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence Method)
Last changed : 6/7/2022 10:13:51 AM by SYSTEM (modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm (H:\DATA2\ZY-10-69-6-EE.D)

| Peak RetTime Type | Width  | Area      | Height | Area % |
|-------------------|--------|-----------|--------|--------|
| #                 | [min]  | [min]     | [mAU*s]| [mAU]  |
| 1                 | 4.747  | BV        | 0.0710 | 1203.43774 | 257.80865 | 92.1441 |
| 2                 | 5.134  | VB        | 0.0789 | 102.60114   | 19.82286   | 7.8559 |

Totals : 1306.03889 277.63151

=====================================================================

*** End of Report ***

Supplementary Figure 232: HPLC spectrum of 4e.
Data File E:\DATA\20210920\LC 2021-11-30 09-32-52\OnlineEdited--053.D
Sample Name: ZY-09-164-5-RAC

Supplementary Figure 233: HPLC spectrum of (±)-4f.

HPLC1260 12/1/2021 12:28:02 PM SYSTEM
Supplementary Figure 234: HPLC spectrum of 4f.

HPLC1260 12/1/2021 12:28:56 PM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-8-RAC.D
Sample Name: ZY-09-161-8-RAC

Supplementary Figure 235: HPLC spectrum of (±)-4g.
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] %
1 15.710 BB 0.4667 8486.95020 274.90009 96.3010
2 18.658 BB 0.5090 325.99210 7.82603 3.6990

Totals : 8812.94229 282.72612

*** End of Report ***

Supplementary Figure 236: HPLC spectrum of 4g.

HPLC1260 3/28/2022 11:09:40 PM SYSTEM
Supplementary Figure 237: HPLC spectrum of (±)-4h.

HPLC1260 12/1/2021 12:30:23 PM SYSTEM  Page 1 of 1
Supplementary Figure 238: HPLC spectrum of 4h.

HPLC1260 12/1/2021 12:30:54 PM SYSTEM
Data File: E:\DATA\20211222\LC 2021-12-22 14-06-06\1CB-0401.D
Sample Name: ZY-09-167-6-RAC

Acq. Operator: SYSTEM
Seq. Line: 4
Acq. Instrument: HPLC1260
Location: P1-C2
Injection Date: 12/22/2021 2:55:43 PM
Inj: 1

Inj Volume: 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume: 0.500 µl
Acq. Method: E:\DATA\20211222\LC 2021-12-22 14-06-06\SIPA15_10_3-240.M
Last changed: 12/22/2021 2:06:06 PM by SYSTEM

Analysis Method: E:\DATA\20211222\LC 2021-12-22 14-06-06\SIPA15_10_3-240.M (Sequence Method)
Last changed: 12/22/2021 3:19:21 PM by SYSTEM (modified after loading)

Additional Info: Peak(s) manually integrated

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Area Percent Report
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Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm (E:\DATA\20211222\LC 2021-12-22 14-06-06\1CB-0401.D)

| # | Ret Time [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---------------|------|-------------|-------------|-------------|-------|
| 1 | 5.275         | BB   | 0.1542      | 2320.10425  | 228.95290   | 50.1665 |
| 2 | 7.198         | BB   | 0.2309      | 2304.70605  | 152.02585   | 49.8335 |

Totals: 4624.81030 380.97874

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*** End of Report ***

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Supplementary Figure 239: HPLC spectrum of (±)-4i.

HPLC1260 12/22/2021 3:19:33 PM SYSTEM
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
#   [min]  [min]    [mAU*s]  [mAU]     %
----|-------|-------|----------|----------|--------|
1   5.237 BB    0.1545 2407.39844  236.98210  98.3816
2   7.166 BB    0.2291   39.60282    2.63921   1.6184

Totals : 2447.00126  239.62132

*** End of Report ***

Supplementary Figure 240: HPLC spectrum of 4i.
Data File H:\ORIGINAL DATA\ZY-09-160-1-RAC.D
Sample Name: ZY-09-160-1-RAC

Supplementary Figure 241: HPLC spectrum of (±)-4j.

HPLC1260 3/28/2022 11:00:17 PM SYSTEM
Data File H:\ORIGINAL DATA\ZY-09-160-2-EE.D
Sample Name: ZY-09-160-2-EE

=====================================================================
Acq. Operator : 系统 Seq. Line : 7
Acq. Instrument : HPLC-1260 Location : 32
Injection Date : 11/20/2021 11:29:33 AM Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 5.000 µl
Acq. Method : D:\zy\20211023\YH 2021-11-20 09-04-54\SIPA20_10-1-6-254.M
Last changed : 11/20/2021 9:33:00 AM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\0.2IPA-40-0.5-1-XYH.M (Sequence Method)
Last changed : 3/28/2022 10:59:28 PM by 系统 (modified after loading)
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| # | RetTime Type | Width | Area     | Height | Area   | %       |
|---|--------------|-------|----------|--------|--------|---------|
| 1 | 9.999 MM     | 0.9422| 137.99254| 2.44099| 1.5152 |         |
| 2 | 12.136 BB    | 0.6388| 8969.10059| 208.12076| 98.4848|         |

Totals : 9107.09312 210.56175

*** End of Report ***

Supplementary Figure 242: HPLC spectrum of 4j.

HPLC1260 3/28/2022 10:59:30 PM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-166-5-RAC.D
Sample Name: ZY-09-166-7-0D

=====================================================================
Acq. Operator : 系统     Seq. Line :  13
Acq. Instrument : HPLC-1260     Location :   31
Injection Date : 12/4/2021 12:57:37 PM     Inj :   1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-04 09-05-16\8IPA20_5-1-2-210.M
Last changed    : 12/4/2021 9:13:44 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed    : 3/28/2022 11:23:29 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated

=====================================================================
Area Percent Report
=====================================================================
Sorted By              :      Signal
Multiplier             :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

| #  | RetTime Type | Width | Area   | Height | Area  |
|----|--------------|-------|--------|--------|-------|
|    | [min]        | [min] | [mAU*s]| [mAU]  | %     |
|----|--------------|-------|--------|--------|-------|
| 1  | 9.563 BV     | 0.2638| 4313.62402| 250.64847| 49.6492|
| 2  | 10.598 VB    | 0.3083| 4374.57373| 217.81007| 50.3508|

Totals : 8688.19775 468.45854

=====================================================================
*** End of Report ***

Supplementary Figure 243: HPLC spectrum of (±)-4k.

HPLC1260 3/28/2022 11:23:31 PM SYSTEM
Supplementary Figure 244: HPLC spectrum of 4k.

HPLC1260 3/28/2022 11:22:42 PM SYSTEM
Supplementary Figure 245: HPLC spectrum of (±)-4l.
Supplementary Figure 246: HPLC spectrum of 4l.
**Area Percent Report**

```
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

| Peak RetTime Type | Width | Area    | Height   | Area   | %     |
|-------------------|-------|---------|----------|--------|-------|
| #                 | [min] | [min]   | [mAU*s]  | [mAU]  | %     |
| 1                 | 4.047 | BV R    | 0.1112   | 2139.70337 | 291.44876 | 50.2747 |
| 2                 | 4.972 | BB      | 0.1464   | 2116.31763 | 218.64890 | 49.7253 |

Totals : 4256.02100 510.09766
```

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**Supplementary Figure 247: HPLC spectrum of (±)-4m.**

HPLC1260 3/29/2022 9:32:28 AM SYSTEM  
Page 1 of 1
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-1-EE.D
Sample Name: ZY-09-188-1-EE

---

Acq. Operator: system
Acq. Instrument: HPLC-1260
Injection Date: 12/19/2021 4:33:36 PM

Different Inj Volume from Sample Entry! Actual Inj Volume: 0.400 µl

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Area Percent Report
---

Signal: VWD1 A, Wavelength=220 nm
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: VWD1 A, Wavelength=220 nm

| #   | RetTime Type | Width  | Area      | Height     | Area % |
|-----|--------------|--------|-----------|------------|--------|
| 1   | 4.054 VV R   | 0.1098 | 1915.36646| 261.94006  | 97.7296|
| 2   | 4.982 VB     | 0.1468 | 44.49722  | 4.54354    | 2.2704 |

Totals: 1959.86367 266.48360

---

Supplementary Figure 248: HPLC spectrum of 4m.
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-6-RAC.D
Sample Name: ZY-09-188-6-RAC

Acq. Operator: 系统
Acq. Instrument: HPLC-1260
Injection Date: 12/19/2021 3:00:44 AM
Inj Volume: 3.000 µl

Different Inj Volume from Sample Entry! Actual Inj Volume: 0.400 µl

Acq. Method: D:\zy\20211129\YH 2021-12-18 15-56-07\5IPA15_8-1-6-220.M

Analysis Method: E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence Method)

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

| # | RetTime | Type | Width | Area     | Height   | Area % |
|---|---------|------|-------|----------|----------|--------|
| 1 | 5.591   | BV R | 0.1505| 4951.50684| 499.95935| 50.0940|
| 2 | 7.468   | BB   | 0.2189| 4932.93262| 342.67126| 49.9060|

Totals: 9884.43945 842.63062

*** End of Report ***

Supplementary Figure 249: HPLC spectrum of (±)-4n.
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

| # | RetTime [min] | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|--------------|-------------|--------------|--------------|---------|
| 1 | 5.597 MF     | 0.1660      | 3363.61768   | 337.73022    | 98.0657 |
| 2 | 7.474 BB     | 0.2115      | 66.34515     | 4.51200      | 1.9343  |

Totals : 3429.96283 342.24223

*** End of Report ***

Supplementary Figure 250: HPLC spectrum of 4n.
Data File: F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-195-5-RAC.D
Sample Name: ZY-09-195-5-RAC

Acq. Operator: 系统
Acq. Instrument: HPLC-1260
Injection Date: 12/31/2021 6:45:20 PM
Inj Volume: 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume: 1.000 µl

Injection Date: 12/31/2021 5:46:49 PM by 系统
Last changed: 3/29/2022 9:53:44 AM by SYSTEM (modified after loading)
Analysis Method: E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed: 3/29/2022 9:53:44 AM by SYSTEM

Additional Info: Peak(s) manually integrated

Supplementary Figure 251: HPLC spectrum of (±)-4o.

HPLC1260 3/29/2022 9:53:46 AM SYSTEM
Supplementary Figure 252: HPLC spectrum of 4o.
Supplementary Figure 253: HPLC spectrum of (±)-4p.
Supplementary Figure 254: HPLC spectrum of 4p.

HPLC1260 3/29/2022 10:01:39 AM SYSTEM
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

| # | RetTime | Type | Width | Area    | Height | Area % |
|---|---------|------|-------|---------|--------|--------|
| 1 | 4.563   | VB R | 0.1617| 2529.77661| 231.13509| 49.2039 |
| 2 | 8.347   | BB   | 0.3129| 2611.63428| 123.91994| 50.7961 |

Totals: 5141.41089 355.05503

*** End of Report ***

Supplementary Figure 255: HPLC spectrum of (±)-4q.
Supplementary Figure 256: HPLC spectrum of 4q.
Supplementary Figure 257: HPLC spectrum of (±)-4r.
Supplementary Figure 258: HPLC spectrum of 4r.
Supplementary Figure 259: HPLC spectrum of (±)-4s.

HPLC1260 3/29/2022 9:49:39 AM SYSTEM
### Supplementary Figure 260: HPLC spectrum of 4s.

HPLC1260 3/29/2022 9:49:17 AM SYSTEM

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**Data File**: F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-194-5-EE.D

**Sample Name**: ZY-09-194-5-EE

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**Acq. Operator**: 系统  
**Seq. Line**: 6  
**Acq. Instrument**: HPLC-1260  
**Location**: 21  
**Injection Date**: 1/3/2022 10:36:44 AM  
**Inj**: 1  
**Inj Volume**: 3.000 µl  
**Different Inj Volume from Sample Entry! Actual Inj Volume**: 0.800 µl  
**Acq. Method**: D:\zy\20211226\YH 2022-01-03 09-22-34\SIIPA-15-1.0-1-1-2-220.M  
**Last changed**: 1/3/2022 10:03:22 AM by 系统  
**Analysis Method**: E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)  
**Last changed**: 3/29/2022 9:49:15 AM by SYSTEM (modified after loading)  
**Additional Info**: Peak(s) manually integrated

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**Area Percent Report**

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**Sorted By**: Signal  
**Multiplier**: 1.0000  
**Dilution**: 1.0000  
**Do not use Multiplier & Dilution Factor with ISTDs**

**Signal 1**: VWD1 A, Wavelength=220 nm  

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|---------------|------|-------------|--------------|--------------|----------|
| 1 | 5.215         | BV   | 0.1852      | 3155.59595   | 247.50763    | 98.5435  |
| 2 | 6.045         | VB   | 0.2622      | 46.64185     | 2.39526      | 1.4565   |

**Totals**: 3202.23780 249.90289

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*** End of Report ***
**Supplementary Figure 261:** HPLC spectrum of (±)-4t.

HPLC1260 3/28/2022 11:11:48 PM SYSTEM
Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-165-5-EE.D
Sample Name: ZY-09-165-5-EE

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Acq. Operator : 系统   Seq. Line : 9
Acq. Instrument : HPLC-1260   Location : 51
Injection Date : 12/27/2021 10:58:49 AM   Inj : 1
Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 1.300 µl
Acq. Method : D:\zy\20211226\YH 2021-12-27 08-56-44\10IPA15_1-1-2-240.M
Last changed : 12/27/2021 8:56:44 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed : 3/28/2022 11:11:10 PM by SYSTEM
(modified after loading)

Area Percent Report

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=240 nm

| #  | Peak RetTime | Type | Width  | Area      | Height | Area % |
|----|--------------|------|--------|-----------|--------|--------|
| 1  | 6.297        | BV   | 0.2116 | 3430.65576| 247.72098| 98.5969 |
| 2  | 7.662        | VB   | 0.2450 | 48.82105  | 2.81994 | 1.4031 |

Totals : 3479.47681 250.54092

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*** End of Report ***

Supplementary Figure 262: HPLC spectrum of 4t.
Supplementary Figure 263: HPLC spectrum of (±)-4u.
**Supplementary Figure 264:** HPLC spectrum of 4u.

HPLC1260 3/29/2022 9:58:16 AM SYSTEM
Supplementary Figure 265: HPLC spectrum of (±)-4v.

HPLC1260 3/29/2022 9:56:19 AM SYSTEM
Supplementary Figure 266: HPLC spectrum of 4v.
Supplementary Figure 267: HPLC spectrum of (±)-6.
Data File: F:/ZY\AMIDE\ORIGINAL DATA\ZY-10-41-EE.D
Sample Name: ZY-10-41-EE

Acq. Operator: 系统
Acq. Instrument: HPLC-1260
Injection Date: 3/2/2022 9:44:50 PM
Injection Volume: 3.000 µl

Different Injection Volume from Sample Entry! Actual Injection Volume: 1.500 µl

Acq. Method: D:\zy\20220302\YH 2022-03-02 20-49-54\0.5IPA-15-1.0-1-2-220-SFT.M
Last changed: 3/2/2022 9:25:44 PM by 系统

Analysis Method: E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence Method)
Last changed: 3/29/2022 10:06:28 AM by SYSTEM
(modified after loading)

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
1 8.756 BB 0.3500 5931.49121 248.95393 100.0000

Totals: 5931.49121 248.95393

*** End of Report ***

Supplementary Figure 268: HPLC spectrum of 6.
Supplementary Figure 269: HPLC spectrum of (+)-7.

HPLC1260 3/29/2022 10:11:08 AM SYSTEM
Supplementary Figure 270: HPLC spectrum of 7.
III. Supplementary References

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