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Selective approach to N-substituted tertiary 2-pyridones

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General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Xi'an Jiao Tong University using ESI method. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Varian Mercuryplus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ¹³C NMR spectra were routinely run with broadband decoupling. High performance liquid chromatography (HPLC) was performed with FuLi (instruments) spectrometers using chiral column as noted for each compound. Optical rotations were measured on SGW[®]-1 polarimeter. Pd₂(dba)₃•CHCl₃, Ligands and 2-hydroxypyridine compounds were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Substituted vinyl cyclic carbonates were synthesized according to the previously reported procedure.^{1,2} All other chemicals were used as received from commercial resources.

General procedure for the allylic amination of vinyl cyclic carbonate 1 with 2-hydroxypyridine

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $Pd_2(dba)_3$ ·CHCl₃ (5.2 mg, 2.5 mol%), Trost's ligand (*R*,*R*)-L6 (7.8 mg, 5 mol%), vinyl cyclic carbonate 1a (25.6 mg, 0.2 mmol), and 2-hydroxypyridine (28.53 mg, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous CH₂Cl₂ (0.2 M, 1 mL) were added via syringe. The resulting mixture was stirred at 0 °C for 24 hours. The reaction mixture was warm to room temperature and the residue was purified by flash column chromatography on silica gel to afford the pure *N*-substituted 2-pyridone 3aa. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)pyridin-2(1H)-one (3aa) was prepared according to the general procedure from 1a and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 72% yield (25.8 mg). $[\alpha]^{25}_{D} = 32.8$ (c = 0.14, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 1.2, 7.2 Hz, 1H), 7.34–7.30 (m, 1H), 6.58 (dd, J = 1.2, 7.2 Hz, 1H), 6.22–6.19 (m, 1H), 6.10 (dd, J = 10.8, 17.6 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 5.31 (brt, 1H), 4.06 (dd, J = 5.2, 12.5 Hz, 1H), 3.85 (dd, J = 5.2, 12.5 Hz, 1H), 1.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 140.0, 139.1, 136.1, 122.5, 115.7, 106.9, 70.5, 68.4, 21.0; HRMS (ESI-MS): Calcd. for C₁₀H₁₃NO₂ (M + Na): 202.0839, Found: 202.0830; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, t_{minor} = 83.51 min, t_{major} = 88.53 min; 99% ee.



(S)-3-fluoro-1-(1-hydroxy-2-methylbut-3-en-2-yl)pyridin-2(1H)-one (3ab) was prepared according to the general procedure from 1a and 2b. The crude product was purified by flash

column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 76% yield (30.1 mg). $[\alpha]^{25}{}_{D} = 72.4 \ (c = 0.10, CH_2Cl_2); {}^{1}H NMR (400 MHz, CDCl_3) \delta 7.34-7.31 (m, 1H), 7.12-7.08 (m, 1H), 6.16-6.12 (m, 1H), 6.11 (dd,$ *J*= 10.8, 17.6 Hz, 1H), 5.40 (d,*J*= 10.8 Hz, 1H), 5.33 (d,*J*= 17.6 Hz, 1H), 4.66 (brs, 1H), 4.09 (dd,*J*= 5.2, 12.2 Hz, 1H), 3.94 (dd,*J* $= 7.4, 12.2 Hz, 1H), 1.64 (s, 3H); {}^{13}C NMR (100 MHz, CDCl_3) \delta 157.7, 157.6, 153.8, 152.2, 139.6, 131.2, 119.7, 119.6, 116.1, 104.4, 71.2, 68.2, 20.9; HRMS (ESI-MS): Calcd. for C₁₀H₁₂FNO₂ (M + Na): 220.0744, Found: 220.0738; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min,$ *i* $-PrOH/hexanes = 1/9, <math>t_{major} = 46.74$ min, $t_{minor} = 54.67$ min; 97% ee.



(*S*)-3-chloro-1-(1-hydroxy-2-methylbut-3-en-2-yl)pyridin-2(1H)-one (3ac) was prepared according to the general procedure from 1a and 2c. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 80% yield (34.2 mg). $[\alpha]^{25}{}_{D} = 71.5$ (c = 0.056, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.50 (m, 2H), 6.18 (t, J = 7.2 Hz, 1H), 6.13 (dd, J = 10.8, 17.6 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 4.49 (brt, 1H), 4.08 (dd, J = 5.2, 12.2 Hz, 1H), 3.97 (dd, J = 7.4, 12.2 Hz, 1H), 1.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 139.6, 137.4, 134.9, 127.5, 116.0, 105.8, 71.2, 67.9, 20.8; HRMS (ESI-MS): Calcd. for C₁₀H₁₂ClNO₂ (M + Na): 236.0449, Found: 236.0443; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 16.86 min, t_{minor} = 21.20 min; 97% ee.



(S)-4-chloro-1-(1-hydroxy-2-methylbut-3-en-2-yl)pyridin-2(1H)-one (3ad) was prepared according to the general procedure from 1a and 2d. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 79% yield (33.7 mg). $[\alpha]_{D}^{25} = 44.2$ (c = 0.032, CH₂Cl₂); ¹H NMR S4 (400 MHz, CDCl₃) δ 7.47 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.24–6.21 (m, 1H), 6.09 (dd, J = 10.8, 17.6 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.32 (d, J = 17.6 Hz, 1H), 4.73 (brt, 1H), 4.04 (dd, J = 5.2, 12.2 Hz, 1H), 3.90 (dd, J = 7.4, 12.2 Hz, 1H), 1.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 146.5, 139.6, 136.5, 120.6, 116.0, 108.3, 70.2, 67.7, 20.9; HRMS (ESI-MS): Calcd. for C₁₀H₁₂ClNO₂ (M + Na): 236.0449, Found: 236.0442; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 10.96 min, t_{minor} = 11.94 min; 90% ee.



(*S*)-5-bromo-1-(1-hydroxy-2-methylbut-3-en-2-yl)pyridin-2(1H)-one (3ae) was prepared according to the general procedure from 1a and 2e. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a white solid in 76% yield (39.2 mg). $[\alpha]^{25}_{D} = 33.8$ (c = 0.16, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 2.6 Hz, 1H), 7.34 (dd, J = 2.6, 9.5 Hz, 1H), 6.47 (d, J = 9.5 Hz, 1H), 6.10 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 17.6 Hz, 1H), 4.83 (brt, 1H), 4.04 (dd, J = 5.2, 12.2 Hz, 1H), 3.91 (dd, J = 7.4, 12.2 Hz, 1H), 1.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 142.1, 139.3, 136.1, 123.6, 116.4, 98.9, 70.8, 67.8, 20.8; HRMS (ESI-MS): Calcd. for C₁₀H₁₂BrNO₂ (M + Na): 279.9944, Found: 279.9937; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 11.91 min, t_{major} = 13.19 min; 98% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-5-iodopyridin-2(1H)-one (3af) was prepared according to the general procedure from 1a and 2f. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 75% yield (45.8 mg). $[\alpha]^{25}_{D} = 21.2$ (c = 0.13, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 2.6 Hz, 1H), 7.41 (dd, J = 2.6, 9.5 Hz, 1H), 6.37 (d, J = 9.5 Hz, 1H), 6.09 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 17.6 Hz, 1H), 4.82 (brt, 1H), 4.03 (dd, J = 5.2, 12.2 Hz, 1H), 3.90 (dd, J = 7.4, 12.2 Hz, 1H), 1.62 (s, 3H); ¹³C NMR

(100 MHz, CDCl₃) δ 162.6, 146.5, 141.1, 139.4, 124.2, 116.3, 70.7, 67.8, 65.6, 20.8; HRMS (ESI-MS): Calcd. for C₁₀H₁₂INO₂ (M + Na): 327.9805, Found: 327.9804; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 13.58 min, t_{major} = 15.02 min; 90% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-3-(trifluoromethyl)pyridin-2(1H)-one (3ag) was prepared according to the general procedure from 1a and 2g. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 81% yield (40.1 mg). $[\alpha]^{25}{}_{\rm D} = 29.4$ (c = 0.06, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.0 Hz, 2H), 6.26 (t, J = 7.2 Hz, 1H), 6.14 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 5.35 (d, J = 17.6 Hz, 1H), 4.10-3.99 (m, 3H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 140.4, 139.5, 138.7, 138.6, 116.3, 104.6, 71.0, 67.8, 20.9; HRMS (ESI-MS): Calcd. for C₁₁H₁₂F₃NO₂ (M + Na): 270.0712, Found: 270.0707; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 18.3 min, t_{minor} = 19.88 min; 98% ee.



methyl (S)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-3-carboxylate (3ah) was prepared according to the general procedure from 1a and 2h. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 83% yield (39.4 mg). $[\alpha]^{25}_{D} = 21.7$ (c = 0.08, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, J = 2.1, 7.0 Hz, 1H), 7.79 (dd, J = 2.1, 7.0 Hz, 1H), 6.26 (t, J = 7.2 Hz, 1H), 6.16 (dd, J = 10.8, 17.6 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 5.32 (d, J = 17.6 Hz, 1H), 4.19 (brs, 1H), 4.09 (d, J = 12.2 Hz, 1H), 4.02 (d, J = 12.2 Hz, 1H), 3.89 (s, 3H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.7, 161.0, 144.3, 141.1, 139.9, 122.0, 115.8, 105.1, 70.7, 67.7, 52.4, 21.1; HRMS (ESI-MS): Calcd. for C₁₂H₁₅NO₄ (M + Na):

260.0893, Found: 260.0883; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 39.63 min, t_{minor} = 52.89 min; 93% ee.



methyl (S)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-4-carboxylate (3ai) was prepared according to the general procedure from 1a and 2i. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 80% yield (37.9 mg). $[α]^{25}_{D} = 47.1$ (c = 0.02, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.0 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 6.67 (dd, J = 2.1, 7.2 Hz, 1H), 6.11 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 4.74 (brq, 1H), 4.06 (dd, J = 5.2, 12.2 Hz, 1H), 3.92 (dd, J = 5.2, 12.2 Hz, 1H), 3.91 (s, 3H), 1.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 163.9, 140.0, 139.6, 136.7, 124.2, 116.0, 105.0, 70.6, 67.9, 52.8, 20.9; HRMS (ESI-MS): Calcd. for C₁₂H₁₅NO₄ (M + Na): 260.0893, Found: 260.0886; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 35.95 min, t_{minor} = 52.89 min; 99% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-6-oxo-1,6-dihydropyridine-3-carbaldehyde (3aj) was prepared according to the general procedure from 1a and 2j. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 84% yield (34.8 mg). $[\alpha]^{25}_{D} = 19.1$ (c = 0.08, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 9.6 (s, 1H), 8.17 (d, J = 2.1 Hz, 1H), 7.79 (dd, J = 2.1, 9.2 Hz, 1H), 6.58 (d, J = 9.2 Hz, 1H), 6.18 (dd, J = 10.8, 17.6 Hz, 1H), 5.46 (d, J = 10.8 Hz, 1H), 5.37 (d, J = 17.6 Hz, 1H), 4.10 (d, J = 12.2 Hz, 1H), 4.06 (d, J = 12.2 Hz, 1H), 3.81 (brs, 1H), 1.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 186.5, 164.1, 146.0, 138.8, 135.2, 122.6, 118.6, 116.8, 70.4, 67.3, 21.0; HRMS (ESI-MS): Calcd. for C₁₁H₁₃NO₃ (M + Na): 230.0788, Found: 230.0785; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 35.15 min, t_{minor} = 38.29 min; 98% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-5-nitropyridin-2(1H)-one (3ak) was prepared according to the general procedure from 1a and 2k. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a white solid in 78% yield (35.1 mg). $[\alpha]^{25}_{D} = 10.5$ (*c* = 0.24, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, *J* = 2.8 Hz, 1H), 8.07 (dd, *J* = 2.8, 9.8 Hz, 1H), 6.58 (d, *J* = 9.2 Hz, 1H), 6.17 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H), 5.38 (d, *J* = 17.6 Hz, 1H), 4.11 (d, *J* = 6.8 Hz, 1H), 4.07 (d, *J* = 12.2 Hz, 1H), 3.43 (brt, 1H), 1.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 138.6, 138.1, 132.7, 131.1, 121.1, 117.3, 70.8, 66.7, 21.0; HRMS (ESI-MS): Calcd. for C₁₀H₁₂N₂O₂ (M + Na): 247.0689, Found: 247.0682; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 11.89 min, t_{major} = 12.68 min; 90% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-3-methylpyridin-2(1H)-one (3al) was prepared according to the general procedure from 1a and 2l. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 62% yield (24.1 mg). $[\alpha]^{25}_{D} = 49.5$ (c = 0.09, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.35 (m, 1H), 7.22–7.20 (m, 1H), 6.13 (t, J = 4.7 Hz, 1H), 6.11 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (brq, 1H), 5.35 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 4.06 (dd, J = 4.1, 12.4 Hz, 1H), 4.85 (d, J = 4.2, 12.6 Hz, 1H), 2.14 (s, 3H), 1.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 140.4, 136.7, 133.5, 131.1, 115.3, 106.5, 70.4, 68.9, 21.1, 17.5; HRMS (ESI-MS): Calcd. for C₁₁H₁₅NO₂ (M + Na): 216.0995, Found: 216.0987; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 15.48 min, t_{minor} = 16.76 min; 99% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-4-methylpyridin-2(1H)-one (3am) was prepared according to the general procedure from 1a and 2m. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 66% yield (25.5 mg). $[\alpha]^{25}_{D} = 137.4$ (c = 0.012, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 7.4 Hz, 1H), 6.37 (s, 1H), 6.08 (dd, J = 10.8, 17.6 Hz, 1H), 6.04 (dd, J = 2.8, 6.4 Hz, 1H), 5.53 (brq, 1H), 5.36 (d, J = 10.8 Hz, 1H), 5.31 (d, J = 17.6 Hz, 1H), 4.03 (dd, J = 4.1, 12.4 Hz, 1H), 4.82 (d, J = 4.2, 12.6 Hz, 1H), 2.17 (s, 3H), 1.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 150.9, 140.2, 135.1, 120.9, 115.6, 109.5, 70.2, 68.7, 21.0, 20.6; HRMS (ESI-MS): Calcd. for C₁₁H₁₅NO₂ (M + Na): 216.0995, Found: 216.0987; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 31.51 min, t_{minor} = 33.92 min; 96% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitril e (3an) was prepared according to the general procedure from 1a and 2n. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 77% yield (36.1 mg). $[\alpha]^{25}_{D} = 4.6$ (c = 0.052, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 1H), 6.11 (dd, J = 10.8, 17.6 Hz, 1H), 6.10 (d, J = 8.2 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.34 (d, J = 17.6 Hz, 1H), 4.08–3.98 (m, 6H), 1.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 162.7, 142.2, 139.1, 116.7, 113.7, 94.2, 89.9, 70.7, 67.5, 57.1, 20.9; HRMS (ESI-MS): Calcd. for C₁₂H₁₄N₂O₃ (M + Na): 257.0897, Found: 257.0888; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 24.00 min, t_{minor} = 32.54 min; 97% ee.



(*S*)-1-(1-hydroxy-2-methylbut-3-en-2-yl)-4-methyl-3-nitropyridin-2(1H)-one (3ao) was prepared according to the general procedure from 1a and 2o. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 84% yield (40.1 mg). $[\alpha]^{25}_{D} = 36.4$ (c = 0.25, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.2 Hz, 1H), 6.13 (d, J = 8.2 Hz, 1H), 6.12 (dd, J = 10.8, 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.36 (d, J = 17.6 Hz, 1H), 4.08 (dd, J = 4.1, 12.4 Hz, 1H), 4.02 (d, J = 4.2, 12.6 Hz, 1H), 3.92 (brq, 1H), 2.24 (s, 3H), 1.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 143.3, 143.1, 139.0, 137.0, 116.8, 71.3, 67.4, 20.9, 17.3; HRMS (ESI-MS): Calcd. for C₁₁H₁₄N₂O₄ (M + Na): 261.0846, Found: 261.0837; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 22.20 min, t_{minor} = 27.50 min; 98% ee.



(*S*)-5-(1-hydroxy-2-methylbut-3-en-2-yl)furo[3,2-c]pyridin-4(5H)-one (3ap) was prepared according to the general procedure from 1a and 2p. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 78% yield (34.2 mg). $[\alpha]^{25}_{D} = 19.6 (c = 0.04, CH_2Cl_2)$; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 8.2 Hz, 1H), 6.16 (dd, J = 10.8, 17.6 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 5.32 (d, J = 17.6 Hz, 1H), 5.03 (brq, 1H), 4.13 (dd, J = 4.1, 12.4 Hz, 1H), 3.95 (d, J = 4.2, 12.6 Hz, 1H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 158.9, 143.7, 140.8, 132.9, 117.5, 115.4, 107.6, 96.5, 70.3, 68.8, 21.5; HRMS (ESI-MS): Calcd. for C₁₂H₁₃NO₃ (M + Na): 242.0788, Found: 242.0779; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 3/7, t_{major} = 10.87 min, t_{minor} = 11.72 min; 90% ee.



(*S*)-1-(3-(hydroxymethyl)pent-1-en-3-yl)pyridin-2(1H)-one (3ba) was prepared according to the general procedure from 1b and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 62% yield (23.9 mg). $[\alpha]^{25}_{D} = -22.6 \ (c = 0.052, CHCl_3)$; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 1.7, 7.2 Hz, 1H), 7.34–7.31 (m, 1H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.20–6.18 (m, 1H), 6.06 (dd, J = 10.8, 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.06 (brq, 1H), 4.15 (dd, J = 4.1, 12.4 Hz, 1H), 3.95 (dd, J = 4.2, 12.6 Hz, 1H), 2.20–2.08 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 139.1, 139.1, 137.0, 122.6, 116.4, 106.4, 73.5, 67.7, 25.3, 8.2; HRMS (ESI-MS): Calcd. for C₁₁H₁₅NO₂ (M + Na): 216.0995, Found: 216.0985; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{minor} = 18.52 min, t_{major} = 21.01 min; 91% ee.



(*S*)-1-(3-(hydroxymethyl)non-1-en-3-yl)pyridin-2(1H)-one (3ca) was prepared according to the general procedure from 1c and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 82% yield (40.9 mg). $[\alpha]^{25}{}_{D} = 9.10$ (c = 0.052, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 1.7, 7.2 Hz, 1H), 7.34–7.29 (m, 1H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.20–6.17 (m, 1H), 6.06 (dd, J = 10.8, 17.6 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 5.24 (d, J = 17.6 Hz, 1H), 5.07 (brq, 1H), 4.15 (dd, J = 4.1, 12.4 Hz, 1H), 3.93 (dd, J = 4.2, 12.6 Hz, 1H), 2.14–1.97 (m, 2H), 1.33–1.20 (m, 8H), 0.85 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 139.5, 139.1, 137.0, 122.6, 116.2, 106.4, 73.2, 67.9, 33.6, 31.6, 29.5, 23.5, 22.6, 14.0; HRMS (ESI-MS): Calcd. for C₁₅H₂₃NO₂ (M + Na): 272.1621, Found: 272.1614; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 14.48 min, t_{minor} = 15.92 min; 97% ee.



(*S*)-1-(3-(hydroxymethyl)tridec-1-en-3-yl)pyridin-2(1H)-one (3da) was prepared according to the general procedure from 1d and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 79% yield (48.3 mg). $[\alpha]^{25}{}_{\rm D}$ = -10.8 (*c* = 0.24, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (dd, *J* = 1.7, 7.2 Hz, 1H), 7.34–7.29 (m, 1H), 6.57 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.20–6.17 (m, 1H), 6.06 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.40 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 17.6 Hz, 1H), 5.07 (brq, 1H), 4.15 (dd, *J* = 4.1, 12.4 Hz, 1H), 3.93 (dd, *J* = 4.2, 12.6 Hz, 1H), 2.14–1.97 (m, 2H), 1.33–1.15 (m, 16H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.5, 139.1, 137.0, 122.6, 116.2, 106.4, 73.2, 67.9, 33.6, 31.8, 29.9, 29.5, 29.4, 29.3, 23.5, 22.6, 14.1; HRMS (ESI-MS): Calcd. for C₁₉H₃₁NO₂ (M + Na): 328.2247, Found: 328.2240; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 12.11 min, t_{minor} = 13.72 min; 91% ee.



(*S*)-1-(3-(hydroxymethyl)-7-methylocta-1,6-dien-3-yl)pyridin-2(1H)-one (3ea) was prepared according to the general procedure from 1e and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 80% yield (39.5 mg). $[\alpha]^{25}_{D} = -50.4$ (c = 0.03, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, J = 1.7, 7.2 Hz, 1H), 7.33–7.29 (m, 1H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.21–6.17 (m, 1H), 6.09 (dd, J = 10.8, 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.07–5.02 (m, 2H), 4.18 (dd, J = 4.2, 12.4 Hz, 1H), 3.94 (dd, J = 4.2, 12.6 Hz, 1H), 2.12–1.91 (m, 4H), 1.64 (s, 3H), 1.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 139.4, 139.1, 136.9, 132.5, 123.0, 122.7, 116.2, 106.5, 73.0, 67.8, 33.8, 29.7, 25.6, 22.3, 17.6; HRMS (ESI-MS): Calcd. for C₁₅H₂₁NO₂ (M + Na): 270.1465, Found: 270.1459; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 14.39 min, t_{minor} = 16.23 min; 92% ee.



(*S*, *E*)-1-(3-(hydroxymethyl)-7,11-dimethyldodeca-1,6,10-trien-3-yl)pyridin-2(1H)-one (3fa) was prepared according to the general procedure from 1f and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 76% yield (47.9 mg). $[\alpha]^{25}_{D} = 16.4$ (*c* = 0.11, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 1.7, 7.2 Hz, 1H), 7.33–7.30 (m, 1H), 6.58 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.21–6.17 (m, 1H), 6.09 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.42 (d, *J* = 10.8 Hz, 1H), 5.27 (d, *J* = 17.6 Hz, 1H), 5.08–5.04 (m, 3H), 4.18 (dd, *J* = 4.2, 12.4 Hz, 1H), 3.95 (dd, *J* = 4.2, 12.6 Hz, 1H), 2.15–1.90 (m, 8H), 1.67 (s, 3H), 1.59 (s, 3H), 1.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.4, 139.1, 136.9, 136.1, 131.4, 124.2, 123.7, 122.8, 122.6, 116.2, 106.5, 73.0, 67.8, 39.6, 33.7, 26.6, 25.7, 22.2, 17.7, 16.0; HRMS (ESI-MS): Calcd. for C₂₀H₂₉NO₂ (M + Na): 338.2091, Found: 338.2083; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 9.13 min, t_{minor} = 9.87 min; 95% ee.



(*S*)-1-(6-(benzyloxy)-3-(hydroxymethyl)hex-1-en-3-yl)pyridin-2(1H)-one (3ga) was prepared according to the general procedure from 1g and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 80% yield (50.1 mg). $[\alpha]^{25}_{D} = 29.5$ (c = 0.04, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, J = 1.7, 7.2 Hz, 1H), 7.36–7.28 (m, 1H), 6.57 (dd, J = 1.2, 8.2 Hz, 1H), 6.19–6.15 (m, 1H), 6.05 (dd, J = 10.8, 17.6 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 17.6 Hz, 1H), 5.12 (brq, 1H), 4.47 (s, 2H), 4.11 (dd, J = 4.2, 12.4 Hz, 1H), 3.96 (dd, J = 4.2, 12.6 Hz, 1H), 3.47–3.44 (m, 2H), 2.26–2.16 (m, 2H), 1.63–1.53 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 139.2, 136.9, 132.4, 130.9, 128.8, 128.4, 127.6, 122.5, 116.5, 106.6, 73.0, 72.8, 68.1, 67.8, 23.7, 23.0; HRMS (ESI-MS): Calcd. for C₁₉H₂₃NO₂ (M + Na): 336.1570, Found: 336.1566; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 24.46 min, t_{minor} = 29.47 min; 96% ee.



(*S*)-1-(7-bromo-3-(hydroxymethyl)hept-1-en-3-yl)pyridin-2(1H)-one (3ha) was prepared according to the general procedure from 1h and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 68% yield (40.8 mg). $[\alpha]^{25}_{D} = 33.4$ (c = 0.06, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, J = 1.7, 7.2 Hz, 1H), 7.36–7.32 (m, 1H), 6.59 (dd, J = 1.2, 8.2 Hz, 1H), 6.22–6.19 (m, 1H), 6.04 (dd, J = 10.8, 17.6 Hz, 1H), 5.46 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 5.11 (brs, 1H), 4.10 (dd, J = 4.2, 12.4 Hz, 1H), 3.98 (d, J = 12.6 Hz, 1H), 3.41–3.35 (m, 2H), 2.20–2.05 (m, 2H), 1.88–1.75 (m, 2H), 1.53–1.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.2, 138.9, 136.9, 122.6, 116.8, 106.6, 73.0, 67.8, 32.7, 32.1, 25.3, 22.1; HRMS (ESI-MS): Calcd. for C₁₃H₁₈BrNO₂ (M + Na): 322.0413, Found: 322.0410; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 16.19 min, t_{minor} = 18.95 min; 95% ee.



(*S*)-1-(7-chloro-3-(hydroxymethyl)hept-1-en-3-yl)pyridin-2(1H)-one (3ia) was prepared according to the general procedure from 1i and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 64% yield (32.7 mg). $[\alpha]^{25}_{D} = 29.4$ (c = 0.05, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, J = 1.7, 7.2 Hz, 1H), 7.35–7.32 (m, 1H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.22–6.19 (m, 1H), 6.04 (dd, J = 10.8, 17.6 Hz, 1H), 5.45 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 17.6 Hz, 1H), 5.12 (brs, 1H), 4.11 (dd, J = 4.2, 12.4 Hz, 1H), 3.98 (d, J = 12.6 Hz, 1H), 3.54–3.48 (m, 2H), 2.20–2.05 (m, 2H), 1.80–1.75 (m, 2H), 1.52–1.44 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.3, 138.9, 136.9, 122.6, 116.8, 106.6, 73.0, 67.8, 44.5, 32.5, 32.2, 20.9; HRMS (ESI-MS): Calcd. for C₁₃H₁₈CINO₂ (M + Na): 278.0918, Found: 278.0909; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 15.85 min, t_{minor} = 18.47 min; 90% ee.



(*S*)-1-(8-bromo-3-(hydroxymethyl)oct-1-en-3-yl)pyridin-2(1H)-one (3ja) was prepared according to the general procedure from 1j and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 72% yield (45.2 mg). $[\alpha]^{25}{}_{\rm D}$ = 11.9 (*c* = 0.02, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, *J* = 1.7, 7.2 Hz, 1H), 7.35–7.30 (m, 1H), 6.58 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.22–6.18 (m, 1H), 6.05 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.43 (d, *J* = 10.8 Hz, 1H), 5.26 (d, *J* = 17.6 Hz, 1H), 5.09 (brq, 1H), 4.13 (dd, *J* = 4.2, 12.4 Hz, 1H), 3.95 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.36 (t, *J* = 6.7 Hz, 2H), 2.18–2.02 (m, 2H), 1.86–1.74 (m, 3H), 1.50–1.40 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.2, 139.1, 136.9, 122.6, 116.5, 106.6, 73.0, 67.7, 33.6, 33.3, 32.4, 28.4, 22.8; HRMS (ESI-MS): Calcd. for C₁₄H₂₀BrNO₂ (M + Na): 336.0570, Found: 336.0561; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 20.11 min, t_{minor} = 22.04 min; 93% ee.



(*S*)-1-(7-(4-bromophenoxy)-3-(hydroxymethyl)hept-1-en-3-yl)pyridin-2(1H)-one (3ka) was prepared according to the general procedure from 1k and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 80% yield (62.7 mg). $[\alpha]^{25}_{D} = 11.91$ (c = 0.36, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, J = 1.7, 7.2 Hz, 1H), 7.36–7.34 (m, 2H), 7.33–7.30 (m, 1H), 6.75–6.71 (m, 2H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.20–6.17 (m, 1H), 6.04 (dd, J = 10.8, 17.6 Hz, 1H), 5.43 (d, J = 10.8 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.13 (brq, 1H), 4.12 (dd, J = 4.2, 12.4 Hz, 1H), 3.97 (dd, J = 4.2, 12.6 Hz, 1H), 3.91–3.86 (m, 2H), 2.23–2.09 (m, 2H), 1.79–1.71 (m, 2H), 1.51–1.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 158.0, 139.2, 139.0, 136.9, 132.2, 122.6, 73.0, 67.7, 67.5, 32.8, 29.2, 20.1; HRMS (ESI-MS): Calcd. for C₁₉H₂₂BrNO₃ (M + Na): 414.0675, Found: 414.0667; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 14.42 min, t_{minor} = 17.19 min; 87% ee.



(*S*)-10-(hydroxymethyl)-10-(2-oxopyridin-1(2H)-yl)dodec-11-en-1-yl-4-methylbenzenesulfo nate (3la) was prepared according to the general procedure from 1l and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 74% yield (68.3 mg). $[\alpha]^{25}{}_{\rm D}$ = -10.82 (*c* = 0.15, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 5.4 Hz, 2H), 7.43 (dd, *J* = 1.7, 7.2 Hz, 1H), 7.35 (d, *J* = 5.4 Hz, 2H), 7.33–7.31 (m, 1H), 6.58 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.21–6.18 (m, 1H), 6.06 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.41 (d, *J* = 10.8 Hz, 1H), 5.24 (d, *J* = 17.6 Hz, 1H), 5.10 (brq, 1H), 4.13 (dd, *J* = 4.2, 12.4 Hz, 1H), 4.00 (t, *J* = 7.4 Hz, 2H), 3.93 (dd, *J* = 4.2, 12.6 Hz, 1H), 2.45 (s, 3H), 2.12–1.98 (m, 2H), 1.64–1.59 (m, 4H), 1.28–1.16 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 144.6, 139.4, 139.1, 137.0, 133.2, 129.8, 127.9, 122.6, 116.3, 106.5, 73.2, 70.7, 67.9, 33.5, 29.8, 29.2, 29.1, 28.8, 28.7, 25.2, 23.5, 21.6; HRMS (ESI-MS): Calcd. for C₂₅H₃₅NO₅S (M + Na): 484.2128, Found: 484.2122; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 5.86 min, t_{minor} = 7.93 min; 96% ee.



(*S*)-10-(hydroxymethyl)-10-(2-oxopyridin-1(2H)-yl)dodec-11-en-1-yl benzoate (3ma) was prepared according to the general procedure from 1m and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 72% yield (67.5 mg). $[\alpha]^{25}_{D} = -13.8 \ (c = 0.07, CH_2Cl_2); {}^{1}H NMR$ (400 MHz, CDCl₃) δ 8.05–8.03 (m, 2H), 7.57–7.54 (m, 1H), 7.45–7.42 (m, 3H), 7.33–7.30 (m, 1H), 6.58 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.20–6.17 (m, 1H), 6.06 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.40 (d, *J* = 10.8 Hz, 1H), 5.24 (d, *J* = 17.6 Hz, 1H), 5.09 (brq, 1H), 4.30 (t, *J* = 7.4 Hz, 2H), 4.14 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.93 (dd, *J* = 4.2, 12.6 Hz, 1H), 2.13–1.98 (m, 2H), 1.77–1.72 (m, 2H), 1.44–1.39 (m, 2H), 1.33-1.23 (m, 10H); {}^{13}C NMR (100 MHz, CDCl_3) \delta 166.7, 164.7, 139.4, 139.1, 137.0, 132.8, 130.5, 129.5, 128.3, 122.6, 116.2, 106.5, 73.2, 67.9, 65.1, 33.5, 29.8, 29.4, 29.3, 29.2, 28.7, 26.0, 23.5; HRMS (ESI-MS): Calcd. for C₂₅H₃₅NO₄ (M + Na): 434.2302,

Found: 434.2300; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, $t_{major} = 53.57$ min, $t_{minor} = 61.15$ min; 96% ee.



(*S*)-10-(hydroxymethyl)-10-(2-oxopyridin-1(2H)-yl)dodec-11-en-1-yl benzoate (3na) was prepared according to the general procedure from 1n and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 68% yield (45.6 mg). $[\alpha]^{25}_{D} = 22.7$ (c = 0.09, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 1.2, 8.2 Hz, 1H), 7.33–7.30 (m, 1H), 6.58 (dd, J = 1.2, 8.2 Hz, 1H), 6.20–6.18 (m, 1H), 6.06 (dd, J = 10.8, 17.6 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H), 5.24 (d, J = 17.6 Hz, 1H), 5.08 (brt, 1H), 4.14 (dd, J = 4.2, 12.6 Hz, 1H), 3.93 (dd, J = 4.2, 12.6 Hz, 1H), 3.66 (s, 3H), 2.28 (t, J = 7.4 Hz, 2H), 2.13–1.98 (m, 2H), 1.61–1.56 (m, 2H), 1.29–1.21 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 164.7, 139.4, 139.1, 137.0, 132.8, 130.5, 129.5, 128.3, 122.6, 116.2, 106.5, 73.2, 67.9, 65.1, 33.5, 29.8, 29.4, 29.3, 29.2, 28.7, 26.0, 23.5; HRMS (ESI-MS): Calcd. for C₁₉H₂₉NO₄ (M + Na): 358.1989, Found: 358.1984; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, t_{major} = 31.16 min, t_{minor} = 36.75 min; 94% ee.



(*R*)-1-(12-hydroxy-3-(hydroxymethyl)dodec-1-en-3-yl)pyridin-2(1H)-one (3oa) was prepared according to the general procedure from 1o and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 42% yield (20.3 mg). $[\alpha]^{25}_{D} = 51.6$ (c = 0.02, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.32 (m, 4H), 7.19–7.19 (m, 2H), 7.16 (dd, J = 1.6, 9.2 Hz, 1H), 6.42 (dd, J = 10.8, 17.6 Hz, 1H), 6.15–6.12 (m, 1H), 5.52 (brq, 1H), 5.49 (d, J = 10.8 Hz, 1H), 4.80 (d, J = 17.6 Hz, 1H), 4.50 (dd, J = 5.6, 12.8 Hz, 1H), 4.03 (dd, J = 5.6, 12.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 140.6, 139.4, 138.5, 137.8, 128.9, 128.0, 126.6, 122.8, 117.7, 106.3, 69.9, 68.9; HRMS (ESI-MS): Calcd. for C₁₅H₁₅NO₂ (M + Na): 264.0995, Found: 264.0987;

HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, $t_{major} = 30.37$ min, $t_{minor} = 36.69$ min; 89% ee.



(*R*)-1-(1-hydroxy-2-(4-methoxyphenyl)but-3-en-2-yl)pyridin-2(1H)-one (3pa) was prepared according to the general procedure from 1p and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 38% yield (22.1 mg). $[\alpha]^{25}_{D} = 79.7$ (c = 0.01, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.81 (m, 3H), 7.69 (d, J = 1.5 Hz, 1H), 7.54–7.50 (m, 2H), 7.40–7.35 (m, 2H), 7.17 (dd, J = 1.8, 7.2 Hz, 1H), 6.69 (dd, J = 1.8, 7.2 Hz, 1H), 6.42 (dd, J = 10.8, 17.6 Hz, 1H), 6.13–6.10 (m, 1H), 5.68 (brq, 1H), 5.55 (d, J = 10.8 Hz, 1H), 4.84 (d, J = 17.6 Hz, 1H), 4.63 (dd, J = 5.4, 12.8 Hz, 1H), 4.10 (dd, J = 5.4, 12.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 139.5, 138.5, 137.6, 133.1, 132.7, 129.0, 128.3, 127.6, 126.7, 126.6, 125.8, 124.4, 122.8, 117.8, 115.0, 106.3, 73.1, 68.9; HRMS (ESI-MS): Calcd. for C₁₉H₁₇NO₂ (M + Na): 314.1152, Found: 314.1147; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, t_{minor} = 10.83 min, t_{major} = 12.00 min; 82% ee.



(*S*)-1-(1-hydroxy-2-(thiophen-2-yl)but-3-en-2-yl)pyridin-2(1H)-one (3qa) was prepared according to the general procedure from 1q and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 2:1) on silica gel to provide the title compound as a colorless oil in 44% yield (21.8 mg). $[\alpha]^{25}_{D} = 72.7$ (c = 0.07, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.33 (m, 2H), 7.13 (dd, J = 1.8, 7.4 Hz, 1H), 7.03 (dd, J = 3.6, 7.4 Hz, 1H), 7.00 (dd, J = 1.8, 7.4 Hz, 1H), 6.63 (dd, J = 1.6, 7.4 Hz, 1H), 6.40 (dd, J = 10.8, 17.6 Hz, 1H), 6.14–6.12 (m, 1H), 5.57 (brq, 1H), 5.48 (d, J = 10.8 Hz, 1H), 4.87 (d, J = 17.6 Hz, 1H), 4.48 (dd, J = 5.6, 12.8 Hz, 1H), 4.23 (dd, J = 5.6, 12.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 144.2, 139.5, 137.8, 137.2, 126.9, 126.7, 126.5, 122.7, 117.3, 106.4, 74.9, 69.5; HRMS

(ESI-MS): Calcd. for C₁₃H₁₃NO₂S (M + Na): 270.0559, Found: 270.0552; HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, t_{major} = 16.94 min, t_{minor} = 24.92 min; 80% ee.

Gram-scale synthesis and further transformation for Figure 2



Scale-up Experiment: In a 100 mL round-bottom flask equipped with a magnetic stir bar, $Pd_2(dba)_3$ ·CHCl₃ (65.0 mg, 1.25 mol%), Trost's ligand (*R*,*R*)-L6 (98 mg, 2.5 mol%), vinyl cyclic carbonate 1a (640.6 mg, 5.0 mmol), and 2-hydroxypyridine (1.23 g, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous CH₂Cl₂ (0.2 M, 50 mL) were added via syringe. The resulting mixture was stirred at 0 °C for 48 hours. The reaction mixture was warm to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography on silica gel to afford the title compound 3aa in 85% isolated yield without any lose in enantiomeric excess.

Procedure for the synthesis of 5:



Pd(dppf)Cl₂ (10 mol%) 2-PyB(OH)₂ (2.5 equiv)

Et₃N (3 equiv) dioxane/H₂O, 80 °C



5 68% yield, 95.4% ee

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **3ae** (51.6 mg, 0.2 mmol, 98% ee), Pd(dppf)Cl₂ (10 mol%), 2-PyB(OH)₂ (61.5 mg, 0.5 mmol), and Et₃N (83.2 μ ml, 0.6 mmol). The flask was evacuated and backfilled with nitrogen and placed under nitrogen atmosphere. To the flask was added freshly distilled dioxane (2.0 mL) and deionized water (0.2 mL). The reaction mixture was stirred at 80 °C for 24 h. The reac-

tion mixture was cooled and concentrated and the residue was purified by silica gel column chromatography (PE/EA = 5/1) to afford the desired product **5** as a yellow oil in 68% yield. HPLC conditions: Chiralcel IC column, 254 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/5, $t_{minor} = 67.07 \text{ min}$, $t_{minor} = 79.31 \text{ min}$; 95.4% ee. $[\alpha]^{25}_{D} = 18.5$ (c = 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.59–8.57 (m, 1H), 8.38 (d, J = 3.6 Hz, 1H), 7.75–7.70 (m, 1H), 7.47 (d, J = 12.0 Hz, 1H), 7.39–7.32 (m, 1H), 7.21–7.17 (m, 1H), 6.64 (d, J = 12.2 Hz, 1H), 6.22 (dd, J = 10.8, 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.36 (d, J = 17.6 Hz, 1H), 5.18 (brs, 1H), 4.13 (d, J = 18.6 Hz, 1H), 3.96 (d, J = 18.6 Hz, 1H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 153.5, 149.6, 139.7, 137.4, 137.0, 135.7, 121.9, 121.8, 119.1, 118.6, 115.8, 70.7, 68.1, 21.2; HRMS (ESI-MS): Calcd. for C₁₅H₁₆N₂O₂ (M + Na): 257.1285, Found: 257.1276.

Mechanistic studies:

(1) Preparation and exclusion of the possible linear O-allyl intermediate



Compound 7ab prepared according the reported literature.³ was to (Z)-2-methylbut-2-ene-1,4-diol⁴ (204.3 mg, 2 mmol, 1.0 equiv) was added dropwise to a stirred suspension of NaH (58 mg, 1.0 equiv) in THF (10 ml) at 0 °C. After stirring for 15 minutes, a solution of 2-fluoropyridine (194.0 mg, 2.4 mmol, 1.2 equiv) in 5 ml THF was added dropwise. The resulting mixture was stirred at room temperature for 15 hours. The reaction was quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure and the crude product was purified with column chromatography (petroleum ether: ethyl acetate = 20: 1) to obtain a colorless oil (53.8 mg, 15 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, J = 1.8, 5.0 Hz, 1H), 7.51-7.42 (m, 1H), 6.82 (dd, J = 5.0, 7.2 Hz, 1H), 6.76 (dd, J = 1.8, 7.2 Hz, 1H), 5.69 (t, J = 6.4Hz, 1H), 4.60 (d, J = 6.5 Hz, 1H), 4.22 (s, 2H), 1.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 143.8, 141.6, 138.4, 121.0, 114.8, 107.7, 64.0, 61.0, 18.6; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M + Na): 202.0844, Found: 202.0836.



To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $Pd_2(dba)_3$ ·CHCl₃ (5.2 mg, 2.5 mol%), Trost's ligand (*R*,*R*)-**L6** (7.8 mg, 5 mol%), compound **7ab** (35.84 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous CH₂Cl₂ (0.2 M, 1 mL) were added via syringe. The resulting mixture was stirred at 0 °C for 24 hours. The reaction mixture was warm to room temperature and the solvent was removed under reduced pressure. The ¹H NMR of the crude reaction mixture indicated no conversion of the starting material at all.

(2) Preparation and exclusion of the possible branched O-allyl intermediate



Compound **6ab** was prepared according to the reported literature.³ 2-methylbut-3-ene-1,2-diol (510.7 mg, 5 mmol, 1.0 equiv) was added dropwise to a stirred suspension of NaH (144 mg, 1.2 equiv) in THF (10 ml) at 0 °C. After stirring for 15 minutes, a solution of 2-fluoropyridine (485.5 mg, 2 mmol, 1 equiv) in 10 ml THF was added dropwise. The resulting mixture was stirred at room temperature for 15 hours. The reaction was quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layer was dried with Na₂SO₄ and the solvent was removed under reduced pressure and the crude product was purified with column chromatography (petroleum ether: ethyl acetate = 20: 1) to obtain a colorless oil (89.6 mg, 10 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 4.8 Hz, 1H), 7.51–7.58 (m, 1H), 6.83 (t, *J* = 6.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.03 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.6 Hz, 1H), 4.01 (d, *J* = 11.2 Hz, 1H), 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 1H), 2.15 (brs, 1H), 1.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 146.8, 140.4, 138.5, 116.8, 115.3, 111.7, 82.0, 70.0, 19.0; HRMS (ESI-MS): Calcd. for C₁₀H₁₃NO₂ (M + Na): 202.0844, Found: 202.0837.



10% conversion with 1:10 b/l regioselectivity

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $Pd_2(dba)_3$ ·CHCl₃ (5.2 mg, 2.5 mol%), Trost's ligand (*R*,*R*)-**L6** (7.8 mg, 5 mol%), compound **6ab** (35.84 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen. Anhydrous CH₂Cl₂ (0.2 M, 1 mL) were added via syringe. The resulting mixture was stirred at 0 °C for 48 hours. The reaction mixture was warm to room temperature and the solvent was removed under reduced pressure. The ¹H NMR of the crude reaction mixture indicated only about 10% conversion of the starting material and 1/10 branched to linear ratio were determined by the ¹H NMR of the crude reaction mixture. In the meantime, **3aa** was not enough for further analysis.

X-ray crystallography of 3ak

A single-crystal of **3ak** was obtained from dichloromethane/hexane solvent system at room temperature. Diffraction data were collected on a Bruker SMART Apex-II CCD-based X-ray diffractometer with Cu-K α radiation. The empirical absorption correction was applied by using the SADABS program. The structure was solved using direct method, and refined by full-matrix least-squares on F^2 (G.M. Sheldrick, SHELXTL2008, program of crystal structure refinement, University of Göttingen, Germany, 1997). H-atoms were refined isotopically, while all other atoms were refined anisotropically. The crystallographic data is summarized in Table F1 and the diagram is shown in Figure F1.

 Table F1. Crystal data and structure refinement for 3ak.

Identification code	А
Empirical formula	C10 H12 N2 O4
Formula weight	224.22
Temperature/K	173.00
Wavelength	0.71073 Å
Crystal system	monoclinic
space group	P2

Unit cell dimensions	
Volume	
7	
Calculated density	
Calculated defisity	
Absorption coefficient	
F(000)	
Crystal size	
Theta range for data collection	
Index range	
Reflections collected	
Independent reflections	
Completeness to theta	
Theta (max)	
Absorption correction	
Refinement method	
Data / restraints / parameters	
Goodness-of-fit on F ²	
Final R indices [I>2sigma(I)]	
R indices (all data)	
Absolute structure parameter	
Largest diff, peak and hole	

a = 10.9511(8) Å alpha = 90 deg.b = 7.5328(6) Åbeta = 99.332 deg. c = 12.7907(9) Agamma = 90 deg.1041.17(13) Å³ 4 1.430 mg/m^3 0.112 mm⁻¹ 472.0 0.13 x 0.12 x 0.1mm³ 4.548 to 61.052 deg. -15≤h≤15, -10≤k≤8, -18≤l≤17 12389 5296 [$R_{int} = 0.0318$, $R_{sigma} = 0.0452$] 1.56/0.83 30.526 MULTI-SCAN Full-matrix least-squares on F^2 5296 / 1 / 305 1.042 $R_1 = 0.0489, wR2 = 0.1116$ R1 = 0.0677, wR2 = 0.1234-1.1 (9) 0.32/-0.22 e.Å⁻³



Figure F1. X-ray of 3ak

References:

- 1. M. Salman, Y. Xu, S. Khan, J. Zhang and A. Khan, Chem. Sci., 2020, 11, 5481.
- (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem. Int. Ed.* 2014, 53, 6439;
 (b) A. Khan, L. Yang, J. Xu, L. Y. Jin and Y. J. Zhang, *Angew. Chem. Int. Ed.* 2014, 53, 11257.
- (a) Rodrigues, E. E. Lee, R. A. Batey, Org. Lett. 2010, 12, 260; (b) C. Li, M. Kähny, B. Breit, Angew. Chem. Int. Ed., 2014, 53, 13780.
- E. Jecs, E. J. Miller, R. J. Wilson, H. H. Nguyen, Y. A. Tahirovic, B. M. Katzman, V. M. Truax, M. B. Kim, K. M. Kuo, T. Wang, C. S. Sum, M. E. Cvijic, G. M. Schroeder, L. J. Wilson and D. C. Liotta, ACS Med. Lett. 2018, 9, 89.











S29







S32


















S40











3da



















S47





























Inject Time: 2019-07-27 14:33:12 Stop Time: 2019-07-27 16:13:12 Comment:



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		83.428	18671.3	2294775.3	50.7282	50.7282	+ BB
2		88.060	15139.8	2228891.5	49.2718	49.2718	+ BB
	Total:		33811.1	4523666.9	100.0000	100.0000	

Inject Time: 2019-07-27 16:14:05 Comment:

Stop Time: 2019-07-27 17:54:05



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		83.507	24.0	2152.1	0.1711	0.1711	+NBB
2		88.534	9476.5	1255874.9	99.8289	99.8289	+ BB
	Total:		9500.5	1258027.0	100.0000	100.0000	



Inject Time: 2019-08-15 10:57:27 Comment:

Stop Time: 2019-08-15 12:02:26



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		45.969	8530.8	489358.8	51.8443	51.8443	+ BB
2		54.676	6747.8	454541.4	48.1557	48.1557	+ BB
	Total:		15278.6	943900.2	100.0000	100.0000	



Stop Time: 2019-08-15 15:04:57



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		46.740	21368.7	1352182.1	98.3735	98.3735	+ BB
2		54.670	298.0	22356.5	1.6265	1.6265	+ BB
	Total:		21666.7	1374538.7	100.0000	100.0000	



Inject Time: 2019-08-08 11:06:48 Comment:

Stop Time: 2019-08-08 11:36:47



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.748	87453.2	2351149.2	50.0243	50.0243	BB
2		20.901	67763.7	2348867.6	49.9757	49.9757	BB
	Total:		155216.9	4700016.8	100.0000	100.0000	



Stop Time: 2019-08-08 10:25:08



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.858	29462.2	780370.8	98.5417	98.5417	BB
2		21.195	334.6	11548.3	1.4583	1.4583	BB
	Total:		29796.8	791919.1	100.0000	100.0000	



Inject Time: 2019-08-22 09:21:22 Comment:

Stop Time: 2019-08-22 10:11:22



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		10.928	53266.0	875172.6	49.9358	49.9358	+ BB
2		12.044	47734.9	877423.9	50.0642	50.0642	+ BB
	Total:		101000.9	1752596.4	100.0000	100.0000	

Inject Time: 2019-08-22 11:53:57 Comment:

Stop Time: 2019-08-22 12:13:57



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		10.957	65705.0	1088319.1	95.1966	95.1966	+ BB
2		11.937	4649.6	54913.6	4.8034	4.8034	+ BB
	Total:		70354.6	1143232.7	100.0000	100.0000	







Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		12.589	304187.2	5891089.7	49.5211	49.5211	+ BB
2		13.939	270385.7	6005036.4	50.4789	50.4789	+ BB
	Total:		574572.9	11896126.1	100.0000	100.0000	

Inject Time: 2019-08-17 11:27:23 Comment:

Stop Time: 2019-08-17 11:47:23



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		11.909	5699.7	103568.0	1.0811	1.0811	+ BB
2		13.191	382382.9	9476423.3	98.9189	98.9189	+ BB
	Total:		388082.6	9579991.3	100.0000	100.0000	



Inject Time: 2019-08-29 10:34:11 Comment:

Stop Time: 2019-08-29 11:24:11



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		13.553	123499.2	2818614.4	49.9065	49.9065	+ BB
2		15.024	110324.6	2829174.0	50.0935	50.0935	+ BB
	Total:		233823.8	5647788.4	100.0000	100.0000	

Inject Time: 2019-08-29 11:28:50 Comment:

Stop Time: 2019-08-29 11:48:49



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		13.585	21780.7	443963.9	4.9859	4.9859	+ BB
2		15.017	319290.8	8460360.0	95.0141	95.0141	+ BB
	Total:		341071.5	8904324.0	100.0000	100.0000	



Inject Time: 2019-08-17 10:14:11 Comment:

Stop Time: 2019-08-17 10:39:11



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		18.190	36146.3	1069852.7	50.8316	50.8316	+ BB
2		19.723	32498.1	1034845.8	49.1684	49.1684	+ BB
	Total:		68644.4	2104698.5	100.0000	100.0000	

Inject Time: 2019-08-17 09:48:18 Comment:

Stop Time: 2019-08-17 10:13:18



Analysis Re	esults
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No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		18.300	8663.3	263549.3	98.7801	98.7801	+ BB
2		19.877	130.3	3254.8	1.2199	1.2199	+ BB
	Total:		8793.6	266804.0	100.0000	100.0000	



Inject Time: 2019-09-02 09:53:06 Comment:

Stop Time: 2019-09-02 10:53:05



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		39.590	12043.1	973281.9	51.1114	51.1114	+ BB
2		52.480	8863.9	930956.0	48.8886	48.8886	+ BB
	Total:		20907.0	1904237.9	100.0000	100.0000	

Inject Time: 2019-09-02 10:53:58 Comment:

Stop Time: 2019-09-02 11:53:58



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		39.633	7038.5	558073.0	96.6524	96.6524	+ BB
2		52.888	286.7	19329.2	3.3476	3.3476	+ BB
	Total:		7325.2	577402.2	100.0000	100.0000	



Inject Time: 2019-08-22 16:11:01 Comment:

Stop Time: 2019-08-22 17:11:01



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		36.188	1434.8	95208.0	49.8162	49.8162	BB
2		52.980	960.7	95910.4	50.1838	50.1838	BB
	Total:		2395.5	191118.4	100.0000	100.0000	

Inject Time: 2019-08-22 15:10:10 Comment:

Stop Time: 2019-08-22 16:10:09



	Ana	lysis	Res	ults
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No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		35.947	16396.0	1107434.5	99.3637	99.3637	+ BB
2		52.891	88.1	7092.3	0.6363	0.6363	BB
	Total:		16484.1	1114526.7	100.0000	100.0000	



Inject Time: 2019-08-22 10:12:14 Comment:

Stop Time: 2019-08-22 11:02:13



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		34.619	316005.2	19940044.7	49.9233	49.9233	+ BB
2		38.575	281919.7	20001274.9	50.0767	50.0767	+ BB
	Total:		597924.9	39941319.6	100.0000	100.0000	

Inject Time: 2019-08-22 12:14:46 Comment:

Stop Time: 2019-08-22 13:04:46



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		35.148	2087.3	108778.4	1.0771	1.0771	+ BB
2		38.290	144937.9	9990637.5	98.9229	98.9229	+ BB
	Total:		147025.2	10099415.9	100.0000	100.0000	



Inject Time: 2019-08-29 11:49:43 Comment:

Stop Time: 2019-08-29 12:09:43



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		11.679	232876.6	4642570.4	51.6079	51.6079	+ BB
2		12.534	208859.8	4353288.3	48.3921	48.3921	+ BB
	Total:		441736.4	8995858.7	100.0000	100.0000	

Inject Time: 2019-08-22 17:11:53 Comment:

Stop Time: 2019-08-22 17:56:53



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		11.891	22374.0	413738.0	4.8201	4.8201	+ BB
2		12.684	370242.2	8169892.9	95.1799	95.1799	+ BB
	Total:		392616.2	8583630.9	100.0000	100.0000	



Inject Time: 2019-08-09 16:11:45 Stop Time: 2019-08-09 17:01:45 Comment:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		15.815	10455.2	236390.3	49.9974	49.9974	+ BB
2		17.002	9569.6	236415.0	50.0026	50.0026	+ BB
	Total:		20024.8	472805.3	100.0000	100.0000	

Inject Time: 2019-08-09 17:02:37 Comment:

Stop Time: 2019-08-09 17:51:37



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		15.484	33844.3	783531.8	99.3219	99.3219	+ BB
2		16.763	249.4	5349.6	0.6781	0.6781	+ BB
	Total:		34093.7	788881.4	100.0000	100.0000	



Inject Time: 2019-08-09 11:13:47 Comment:

Stop Time: 2019-08-09 11:53:46



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		31.296	22886.3	1096193.5	49.9958	49.9958	BV
2		33.608	20537.2	1096378.6	50.0042	50.0042	VB
	Total:		43423.5	2192572.1	100.0000	100.0000	

Inject Time: 2019-08-09 11:54:37 Comment: Stop Time: 2019-08-09 12:34:36



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		31.507	4283.5	206960.3	98.0372	98.0372	VV
2		33.923	79.8	4143.6	1.9628	1.9628	VV
	Total:		4363.3	211103.8	100.0000	100.0000	


Inject Time: 2019-08-29 14:40:03 Comment:

Stop Time: 2019-08-29 15:20:02



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		24.230	47771.9	2815780.0	50.3985	50.3985	BB
2		32.214	33261.2	2771251.6	49.6015	49.6015	BB
	Total:		81033.1	5587031.6	100.0000	100.0000	

Inject Time: 2019-08-29 13:06:58 Comment:

Stop Time: 2019-08-29 13:46:58



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		23.998	68244.8	5990921.4	98.3994	98.3994	+ BB
2		32.546	1401.0	97449.7	1.6006	1.6006	+ BB
	Total:		69645.8	6088371.1	100.0000	100.0000	



Inject Time: 2019-08-16 12:51:21 Comment:

Stop Time: 2019-08-16 13:41:21



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		22.378	11306.9	390816.1	50.0480	50.0480	BB
2		27.562	9018.8	390067.1	49.9520	49.9520	BB
	Total:		20325.7	780883.2	100.0000	100.0000	

Inject Time: 2019-08-16 13:42:12 Comment:

Stop Time: 2019-08-16 14:32:12



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		22.208	44326.4	1535622.4	98.9034	98.9034	+ BB
2		27.503	400.5	17027.0	1.0966	1.0966	+ BB
	Total:		44726.9	1552649.4	100.0000	100.0000	



Inject Time: 2019-08-28 17:17:49 Comment:

Stop Time: 2019-08-28 18:17:49



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		10.803	1605648.1	27623633.6	50.1729	50.1729	+ BB
2		11.623	1438798.2	27433274.8	49.8271	49.8271	+ BB
	Total:		3044446.3	55056908.4	100.0000	100.0000	

Inject Time: 2019-08-29 09:17:27 Comment:

Stop Time: 2019-08-29 09:32:27



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		10.870	192886.5	3358015.3	95.1633	95.1633	+ BB
2		11.719	11570.9	170670.5	4.8367	4.8367	+ BB
	Total:		204457.4	3528685.8	100.0000	100.0000	



Inject Time: 2019-08-30 16:31:57 Comment:

Stop Time: 2019-08-30 17:06:57



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		18.702	65535.2	2065017.5	49.9496	49.9496	+ BB
2		21.042	55417.1	2069186.8	50.0504	50.0504	+ BB
	Total:		120952.3	4134204.4	100.0000	100.0000	

Inject Time: 2019-08-31 13:53:50 Comment:

Stop Time: 2019-08-31 14:43:50



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		18.523	2174.8	55031.9	4.4389	4.4389	+ BB
2		21.007	6608.9	1184729.7	95.5611	95.5611	+ BB
	Total:		8783.7	1239761.6	100.0000	100.0000	



Inject Time: 2019-09-02 12:54:52 Comment:





Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.465	4558.8	114789.2	49.7967	49.7967	+ BB
2		15.901	4043.8	115726.3	50.2033	50.2033	+ BB
	Total:		8602.6	230515.5	100.0000	100.0000	

Inject Time: 2019-09-02 12:04:01 Comment:

Stop Time: 2019-09-02 12:54:01



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.478	3164.1	86139.4	98.5322	98.5322	+ BB
2		15.922	65.3	1283.2	1.4678	1.4678	+ BB
	Total:		3229.4	87422.5	100.0000	100.0000	



Inject Time: 2019-09-04 09:54:06 Comment:

Stop Time: 2019-09-04 10:14:06



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		12.947	7742.5	176522.2	50.2439	50.2439	+ BB
2		14.514	6596.5	174808.2	49.7561	49.7561	+ BB
	Total:		14339.0	351330.4	100.0000	100.0000	

Inject Time: 2019-09-04 10:14:58 Comment:

Stop Time: 2019-09-04 10:34:58



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		12.115	2101.7	49143.2	95.7011	95.7011	+ BB
2		13.725	137.3	2207.5	4.2989	4.2989	+ BB
	Total:		2239.0	51350.7	100.0000	100.0000	



Inject Time: 2019-09-02 15:50:09 Stop Time: 2019-09-02 16:20:09 Comment:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.391	5645.6	145750.0	49.8727	49.8727	+ BB
2		16.185	4851.7	146493.8	50.1273	50.1273	+ BB
	Total:		10497.3	292243.8	100.0000	100.0000	

Inject Time: 2019-09-02 16:21:02 Comment:

Stop Time: 2019-09-02 16:46:02



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.392	2122.4	54186.6	96.0403	96.0403	+ BB
2		16.231	93.4	2234.1	3.9597	3.9597	+ BB
	Total:		2215.8	56420.7	100.0000	100.0000	



Inject Time: 2019-09-20 08:53:27 Comment:

Stop Time: 2019-09-20 09:43:26



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		9.139	22550.8	442245.4	50.3259	50.3259	+ BB
2		9.867	22739.4	436517.9	49.6741	49.6741	+ BB
	Total:		45290.2	878763.3	100.0000	100.0000	

Inject Time: 2019-09-20 11:46:09 Comment:

Stop Time: 2019-09-20 12:16:08



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		9.134	9871.8	200027.0	97.5830	97.5830	+ BB
2		9.875	329.6	4954.4	2.4170	2.4170	+ BB
	Total:		10201.4	204981.5	100.0000	100.0000	





Stop Time: 2019-09-05 17:33:41



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		24.152	4097.3	193197.7	50.1858	50.1858	+ BB
2		29.120	3275.9	191767.5	49.8142	49.8142	+ BB
	Total:		7373.2	384965.3	100.0000	100.0000	

Inject Time: 2019-09-05 17:34:35 Comment:

Stop Time: 2019-09-05 18:09:35



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		24.456	4093.6	184914.1	97.8676	97.8676	+ BB
2		29.474	84.6	4029.0	2.1324	2.1324	+ BB
	Total:		4178.2	188943.1	100.0000	100.0000	



Inject Time: 2019-09-16 10:43:37 Stop Time: 2019-09-16 11:23:37 Comment:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.135	17662.5	689043.0	51.3357	51.3357	+ BB
2		18.859	12940.7	653186.2	48.6643	48.6643	+ BB
	Total:		30603.2	1342229.2	100.0000	100.0000	

Inject Time: 2019-09-17 09:09:59 Comment:

Stop Time: 2019-09-17 09:39:58



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.190	6926.6	266739.8	97.6892	97.6892	+ BB
2		18.957	225.3	6309.7	2.3108	2.3108	+ BB
	Total:		7151.9	273049.6	100.0000	100.0000	



Inject Time: 2019-09-16 09:52:46 Comment:

Stop Time: 2019-09-16 10:42:46



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		15.815	19132.4	547063.7	50.0956	50.0956	+ BB
2		18.358	15690.2	544975.6	49.9044	49.9044	+ BB
	Total:		34822.6	1092039.2	100.0000	100.0000	

Inject Time: 2019-09-17 09:40:52 Comment:

Stop Time: 2019-09-17 10:07:51



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		15.857	5123.0	168135.4	94.9894	94.9894	+ BB
2		18.468	327.6	8868.9	5.0106	5.0106	+ BB
	Total:		5450.6	177004.3	100.0000	100.0000	



Inject Time: 2019-09-16 08:45:58 Comment:





Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		20.123	6038.6	263503.3	49.9550	49.9550	+ BB
2		22.306	5504.7	263978.0	50.0450	50.0450	+ BB
	Total:		11543.3	527481.2	100.0000	100.0000	

Inject Time: 2019-09-16 11:27:11 Comment:

Stop Time: 2019-09-16 12:17:12



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		20.110	1331.3	152924.7	96.4882	96.4882	+ BB
2		24.047	166.8	5565.9	3.5118	3.5118	+ BB
	Total:		1498.1	158490.5	100.0000	100.0000	



Inject Time: 2019-09-17 15:33:00 Comment:

Stop Time: 2019-09-17 16:18:00



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.461	34072.3	1026635.7	49.7113	49.7113	+ BB
2		17.165	27375.2	1038558.3	50.2887	50.2887	+ BB
	Total:		61447.5	2065194.0	100.0000	100.0000	

Inject Time: 2019-09-17 16:18:54 Comment:

Stop Time: 2019-09-17 16:43:54



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		14.418	22515.9	673048.2	93.4947	93.4947	+ BB
2		17.192	1783.7	46830.4	6.5053	6.5053	+ BB
	Total:		24299.6	719878.5	100.0000	100.0000	



Inject Time: 2019-10-08 13:36:34 Comment:





No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		5.797	82307.7	2327487.9	48.0406	48.0406	+ BB
2		7.776	80235.9	2517347.5	51.9594	51.9594	+ BB
	Total:		162543.6	4844835.4	100.0000	100.0000	

Inject Time: 2019-10-08 14:27:28 Comment:

Stop Time: 2019-10-08 14:44:51



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		5.866	8174.5	123682.8	98.0304	98.0304	+ BB
2		7.930	283.1	2484.9	1.9696	1.9696	+ BB
	Total:		8457.6	126167.7	100.0000	100.0000	



Inject Time: 2019-09-17 10:15:08 Comment:

Stop Time: 2019-09-17 11:30:08



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		53.180	7411.5	835076.9	50.2650	50.2650	+ BB
2		60.828	6153.2	826270.3	49.7350	49.7350	+ BB
	Total:		13564.7	1661347.2	100.0000	100.0000	

Inject Time: 2019-09-17 11:31:01 Comment:

Stop Time: 2019-09-17 12:46:01



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		53.578	1946.0	215708.2	98.0308	98.0308	+ BB
2		61.153	52.8	4333.0	1.9692	1.9692	+ BB
	Total:		1998.8	220041.2	100.0000	100.0000	



Inject Time: 2019-09-20 10:45:15 Comment:





No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		31.477	3921.8	265460.3	49.8293	49.8293	+ BB
2		36.840	3274.3	267278.7	50.1707	50.1707	+ BB
	Total:		7196.1	532739.0	100.0000	100.0000	

Inject Time: 2019-09-20 13:46:36 Comment:

Stop Time: 2019-09-20 14:36:35



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		31.160	8203.1	630527.9	97.0155	97.0155	+ BB
2		36.749	362.6	19397.3	2.9845	2.9845	+ BB
	Total:		8565.7	649925.2	100.0000	100.0000	



Comment:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		30.230	47771.9	2815780.0	50.3985	50.3985	BB
2		36.214	33261.2	2771251.6	49.6015	49.6015	BB
	Total:		81033.1	5587031.6	100.0000	100.0000	



Comment:

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		30.375	751.3	68967.7	94.5211	94.5211	BB
2		36.686	91.1	3997.7	5.4789	5.4789	+ BB
	Total:		842.4	72965.4	100.0000	100.0000	



Inject Time: 2019-08-16 16:09:08 Comment:

Stop Time: 2019-08-16 16:59:09



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		20.112	544.3	12966.6	49.4911	49.4911	+ BB
2		21.561	503.8	13233.3	50.5089	50.5089	+ BB
	Total:		1048.1	26199.8	100.0000	100.0000	

Inject Time: 2019-08-16 14:33:03 Comment:

Stop Time: 2019-08-16 15:13:03



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		20.352	112.7	2958.9	2.3364	2.3364	+ BB
2		21.852	3900.1	123683.5	97.6636	97.6636	+ BB
	Total:		4012.8	126642.4	100.0000	100.0000	



Inject Time: 2019-10-08 17:08:28 Comment:

Stop Time: 2019-10-08 17:38:28



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.097	19132.4	547063.7	50.0956	50.8397	+ BB
2		25.314	15690.2	544975.6	49.9044	49.1603	+ BB
	Total:		34822.6	1092039.2	100.0000	100.0000	



Comment:

No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		16.941	6224.0	164600.6	90.2115	90.2115	+ BB
2		24.922	584.8	17860.2	9.7885	9.7885	+ BB
	Total:		6808.8	182460.8	100.0000	100.0000	



Inject Time: 2019-09-14 10:29:57 Comment:

Stop Time: 2019-09-14 11:59:57



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		65.932	143463.5	17491493.2	49.9319	49.9319	+ BB
2		79.204	117415.2	17539217.4	50.0681	50.0681	+ BB
	Total:		260878.7	35030710.5	100.0000	100.0000	

Inject Time: 2019-09-14 12:08:31 Comment:

Stop Time: 2019-09-14 13:38:31



No.	Compound	R.Time	Height	Area	Area%	Conc.	Туре
1		67.071	3325.7	336802.9	2.2800	2.2800	+ BB
2		79.308	102692.7	14435132.8	97.7200	97.7200	+ BB
	Total:		106018.4	14771935.8	100.0000	100.0000	