Supporting Information

An Enantioselective Synthesis of Allylic Alcohols by the Sequential Aminoxylation-Olefinations of Aldehydes under Ambient Conditions

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Characterization, yield and *ee* data for the products 4a-h:

¹H- and ¹³C -NMR spectra were recorded on a Mercury-300 instrument (300 MHz and 75 MHz). High-resolution mass spectra were recorded on an Ion Spec Fourier Transform Mass Spectrometer.

4a, from L-proline catalysis: Yield: 74%; HPLC: Chiralpak AS column (*i*-Propanol/Hexane = 2/98, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 27.3 min, t_{major} = 34.1 min, *ee* 98%. The HPLC conditions were established by using racemic standard product, which was prepared in the same way with DL-proline as catalyst; $[\alpha]_{\text{D}} +15.4$ (c = 0.1, MeOH); ¹H-NMR (300 MHz, CDCl₃): δ 7.24 (m, 2H, ArH), 6.93 (m, 3H, ArH), 6.74 (dd, 1H, J = 16.2, 7.2 Hz, NHOCH-CH=CH-), 6.25 (d, 1H, J = 16.2 Hz, NHOCH-CH=CH-), 4.16 (t, 1H, J = 6.3 Hz, NHOCH-CH=), 2.29 (d, 3H, J 2.1 Hz, O=C-CH₃), 2.07 (m, 1H, CH(CH₃)₂), 1.07 (dd, 3H, J = 6.9, 1.8 Hz, CHCH₃), 0.98 (dd, 3H, J = 6.9, 1.9 Hz, CHCH₃); ¹³C-NMR (75 MHz, CDCl₃) δ 197.9, 148.2, 144.4, 132.7, 128.9, 122.1, 114.4, 88.2, 31.6, 27.5, 18.7, 18.3; HR-MS (MALDI-FTMS): 256.1316; C₁₄H₁₉NNaO₂⁺ (calcd 256.1313); Anal. for C₁₄H₁₉NO₂: C, 72.19; H, 8.17; N, 5.77 (calcd C, 72.07; H, 8.21; N, 6.00).

4b, from L-proline catalysis: Yield: 56%; HPLC: OD-H column (*i*-Propanol/Hexane = 4/96, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 23.9 min, t_{major} = 36.3 min, ee 98%; $[\alpha]_{\text{D}}$ +4.3 (c = 0.2, MeOH); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.25 (m, 2H, ArH), 6.98 (s, 1H, NH), 6.92 (m, 3H, ArH), 6.72 (dd, 1H, J = 16.1, 7.2 Hz, NHOCH-CH=CH-), 6.21 (d, 1H, J = 16.1 Hz, NHOCH-CH=CH-), 4.32 (m, 1H, NHOCH-CH=), 2.28 (d, 3H, J 2.0 Hz, O=C-CH_3), 1.32 (d, 3H, J = 6.4 Hz, CHCH_3); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 198.1, 148.3, 144.3, 132.5, 128.9, 122.1, 114.2, 80.1, 31.5, 15.4; HR-MS (MALDI-FTMS): 228.1003; $\text{C}_{12}\text{H}_{15}\text{NNaO}_2^+$ (calcd 228.1000); Anal. for $\text{C}_{12}\text{H}_{15}\text{NO}_2$: C, 70.29; H, 7.39; N, 6.68 (calcd C, 70.22; H, 7.37; N, 6.82).

4c, from L-proline catalysis: Yield: 70%; HPLC: AD column (*i*-Propanol/Hexane = 16/84, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 14.8 min, t_{major} = 18.5 min, ee 97%; $[\alpha]_{\text{D}}$ +13.2 (c = 0.4, MeOH); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.24 (t, 2H, J = 8.0 Hz, ArH), 6.91 (m, 3H, ArH), 6.73 (dd, 1H, J = 16.6, 7.0 Hz, NHOCH-CH=CH-), 6.23 (d, 1H, J = 16.6 Hz, NHOCH-CH=CH-), 4.35 (m, 1H, NHOCH-CH=), 2.30 (d, 3H, J = 2.0 Hz, O=C-CH_3), 1.74-1.22 (m, 4H, CH_2CH_2) 1.00 (t, 3H, J = 6.9 Hz, CH_2CH_3); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 198.0, 148.3, 144.3, 132.6, 128.9, 122.3, 114.4, 83.3, 32.2, 31.6, 19.1, 14.2; HR-MS (MALDI-FTMS): 256.1312; $\text{C}_{14}\text{H}_{19}\text{NNaO}_2^+$ (calcd 256.1313); Anal. for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C, 72.29; H, 8.18; N, 5.90 (calcd C, 72.07; H, 8.21; N, 6.00).

4d, from L-proline catalysis: Yield: 69%; HPLC: OD-H column (*i*-Propanol/Hexane = 4/96, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 22.6 min, t_{major} = 24.7 min, ee 99%; $[\alpha]_{\text{D}}$ +9.6 (c = 0.15, MeOH); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.25 (t, 2H, J = 7.9 Hz, ArH), 7.04 (s, 1H, NH), 6.93 (m, 3H, ArH), 6.71 (dd, 1H, J = 16.4, 7.0 Hz, NHOCH-CH=CH-), 6.25 (d, 1H, J = 16.4 Hz, NHOCH-CH=CH-), 4.34 (m, 1H, CHON), 2.29 (d, 3H, J = 2.1 Hz, O=C-CH_3), 1.76-1.2 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.95 (t, 3H, J = 7.2 Hz, CH_2CH_3); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 197.8, 148.3, 144.4, 132.8, 128.9, 122.3, 114.3, 83.5, 31.7, 29.4, 27.6, 22.7, 14.0; HR-MS (MALDI-FTMS): 270.1473; $\text{C}_{15}\text{H}_{21}\text{NNaO}_2^+$ (calcd 270.1470); Anal. for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C, 72.99; H, 8.57; N, 5.72 (calcd C, 72.84; H, 8.56; N, 5.66).

4e, from L-proline catalysis: Yield: 81%; HPLC: OD-H column (*i*-Propanol/Hexane = 8/92, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 31.2 min, t_{major} = 38.4 min, ee 97%; $[\alpha]_{\text{D}}$ +29.1 (c = 0.1, MeOH); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.35-7.18 (m, 7H, ArH), 6.93 (t, 1H, J = 7.6 Hz, ArH), 6.80 (m, 2H, ArH), 6.73 (dd, 1H, J = 16.2, 7.3 Hz, NHOCH-CH=CH-), 6.23 (d, 1H, J = 16.2 Hz, NHOCH-CH=CH-), 4.50 (m, 1H, CHON), 3.09 (dd, 1H, J = 13.5, 6.6 Hz, CH_2Ar), 2.88 (dd, 1H, J = 13.5, 6.5 Hz, CH_2Ar), 2.30 (d, 3H, J = 2.0 Hz, O=C-CH_3); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 198.3, 148.1, 144.3, 137.5, 132.7, 129.3, 128.8, 128.4, 126.3, 122.0, 114.1, 84.6, 36.1, 31.2; HR-MS (MALDI-FTMS): 282.1491; $\text{C}_{18}\text{H}_{20}\text{NO}_2^+$ (calcd 282.1494); Anal. for $\text{C}_{18}\text{H}_{19}\text{NO}_2$: C, 76.92; H, 6.85; N, 5.14 (calcd C, 76.84; H, 6.81; N, 4.98).

4f, from L-proline catalysis: Yield: 71%; HPLC: AD column (*i*-Propanol/Hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 21.6 min, t_{major} = 25.3 min, ee 98%; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.23 (m, 2H, ArH), 6.92 (m, 3H, ArH), 6.74 (dd, 1H, J = 16.2, 7.5 Hz, NHOCH-CH=CH-), 6.22 (d, 1H, J = 16.2 Hz, NHOCH-CH=CH-), 5.81 (m, 1H, CH=CH_2), 5.03 (d, 1H, J = 17.4 Hz, trans-CH=CH_2), 4.92 (d, 1H, J = 10.1 Hz, cis-CH=CH_2), 4.36 (dq, 1H, J = 6.3, 2.6 Hz, CHON), 2.31 (s, 3H, O=C-CH_3), 2.25 (m, 2H, $\text{CH}_2\text{CH=CH}_2$), 1.85 (m, 1H, CH_2CHO), 1.68 (m, 1H, CH_2CHO); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 198.0, 148.1, 144.2, 137.6, 132.6, 128.9, 122.1, 114.6, 114.3, 83.0, 31.5, 29.7, 28.9; HR-MS (MALDI-FTMS): 246.1490; $\text{C}_{15}\text{H}_{20}\text{NO}_2^+$ (calcd 246.1494); Anal. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.48; H, 7.79; N, 5.67 (calcd C, 73.44; H, 7.81; N, 5.71).

4g, from L-proline catalysis: Yield: 64%; HPLC: AS column (*i*-Propanol/Hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm), t_{minor} = 28.4 min, t_{major} = 31.5 min, ee 99%; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.33 (m, 5H, CH_2ArH), 7.25 (m, 2H, NHArH), 6.92 (m, 3H, NHArH), 6.73 (dd, 1H, J = 16.0, 7.2 Hz, NHOCH-CH=CH-), 6.24 (d, 1H, J = 16.0 Hz, NHOCH-CH=CH-), 4.59 (s, 2H, PhCH_2O), 4.49 (m, 1H, CHON), 3.95 (m, 2H, BnOCH_2), 2.32 (d, 3H, J = 2.0 Hz, O=C-CH_3); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 198.0, 148.3, 144.3, 137.7, 132.7, 128.9, 128.3, 127.5, 127.4, 122.0,

114.1, 82.1, 73.1, 69.0, 31.9; HR-MS (MALDI-FTMS): 334.1422; $C_{19}H_{21}NNaO_3^+$ (calcd 334.1419); Anal. for $C_{19}H_{21}NO_3$: C, 73.22; H, 6.77; N, 4.31 (calcd C, 73.29; H, 6.80; N, 4.50).

4h, from L-proline catalysis: Yield: 52%; HPLC: OD-H column (*i*-Propanol/Hexane = 16/84, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_{\text{minor}} = 22.7$ min, $t_{\text{major}} = 25.4$ min, ee 95%; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.24 (m, 2H, ArH), 6.93 (m, 3H, ArH), 6.71 (dd, 1H, $J = 16.1, 7.1$ Hz, NHOCH-CH=CH-), 6.24 (d, 1H, $J = 16.1$ Hz, NHOCH-CH=CH-), 4.55 (s, br, 1H, BOCNH), 4.33 (m, 1H, CHON), 3.18 (m, 2H, NHCH_2), 2.30 (d, 3H, $J = 2.0$ Hz, O=C-CH_3), 1.81-1.37 (m, 6H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.44 (s, 9H, $3\times\text{CH}_3$); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 198.1, 167.2, 148.3, 144.4, 132.6, 128.8, 122.1, 114.3, 83.3, 70.3, 44.0, 31.5, 30.1, 29.1, 28.3, 22.5; HR-MS (MALDI-FTMS): 385.2101; $C_{20}H_{30}N_2NaO_4^+$ (calcd 385.2103); Anal. for $C_{20}H_{30}N_2O_4$: C, 65.99; H, 8.27; N, 7.49 (calcd C, 66.27; H, 8.34; N, 7.73).