Enantioselective Aziridination of Alkenes with *N*-Aminophthalimide in the Presence of Lead Tetraacetate-Mediated Chiral Ligand

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Supporting Information

General Methods. All reactions were carried out in flame or oven-dried glassware under a positive pressure of nitrogen. Air- and moisture- sensitive compounds were introduced by the use of cannula through a rubber septum. Most reagents were commercially available and of synthetic grade. Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Dichloromethane and toluene were dried over CaH_2 and distilled before use. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash column chromatography by the use of E. Merck silica gel 60 (230-400 mesh). HRMS values were measured by Finigan Mat TSQ-46C GC/MS/MS/DS spectrometer. Elemental analyses were performed by a Perkin-Elmer 2400 or 2400II Elemental Analyzer. ^1H and ^{13}C NMR spectra were recorded routinely in CDCl_3 on a Varian Gemini 2000 spectrometer. Enantiomeric ratios were determined using a Daicel Chiralcel chiral OD and chiralpak AD columns via HPLC analysis.

General procedure for the preparation of diimine chiral ligands 1-4. To a solution of ketopinic acid (10 g, 54.9 mmol) in CHCl_3 (100 mL) was added ethylenediamine (1.64 g, 27.4 mmol) and acetic acid (0.1 mL) at room temperature. The resulting mixture was brought to reflux for 36 h and quenched with H_2O (50 mL). This was extracted with CH_2Cl_2 (100 mL) and the layers were separated. The organic layer washed with brine (10 mL), dried (MgSO_4) and concentrated. The crude product was purified by silica gel using $\text{EtOAc}/\text{CH}_2\text{Cl}_2$ as eluent (4/1) to give 7.22 g (69%) of chiral ligand **1** as a white solid: ^1H NMR (CDCl_3 , 200 MHz) δ 3.65 (dd, $J = 15.0, 3.8$ Hz, 4H), 2.56 (dd, $J = 18.2, 3.6$ Hz, 2H), 2.40 (td, $J = 12.2, 3.6$ Hz, 2H), 2.15-1.97 (m, 6H), 1.68 (td, $J = 12.8, 4.0$ Hz, 2H), 1.43-1.30 (m, 2H), 1.25 (s, 6H), 0.87 (s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 185.09, 173.21, 60.68, 50.78, 50.30, 43.86, 35.40, 31.62, 27.84, 20.07, 19.85; HRMS m/z 388.2336 (calcd for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_4$ 388.2362).

2: ^1H NMR (CDCl_3 , 200 MHz) δ 3.45 (m, 2H), 2.52 (m, 2H), 2.36 (m, 2H), 2.11-1.98 (m,

6H), 1.81-1.67 (m, 4H), 1.60-1.24 (m, 6H), 1.22 (s, 6H), 0.86(s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 183.34, 173.13, 64.38, 60.19, 50.37, 43.68, 34.99, 31.77, 30.54, 27.84, 23.76, 20.04, 19.57; HRMS m/z 442.2834 (calcd for $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_4$ 442.2832).

3: ^1H NMR (CDCl_3 , 200 MHz) δ 3.43 (dd, $J = 5.2, 3.2$ Hz, 2H), 2.61 (t, $J = 3.0$ Hz, 1H), 2.54 (t, $J = 3.8$ Hz, 1H), 2.35 (td, $J = 12.1, 4.6$ Hz, 2H), 2.11-1.92 (m, 6H), 1.83 (d, $J = 6.6$ Hz, 2H), 1.65-1.27 (m, 10H), 1.25-1.24 (m, 2H), 1.23 (s, 6H), 0.83 (s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 183.24, 173.10, 64.33, 60.55, 49.31, 43.93, 34.93, 32.41, 31.07, 27.90, 23.85, 20.17, 20.06; HRMS m/z 442.2833 (calcd for $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_4$ 442.2832). Crystal data for **3** at 22 $^\circ\text{C}$: $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_4$ M 442.59, tetragonal, $P4_32_12$, $a = 7.8028(13)$ Å, $c = 40.282(4)$ Å, $V = 2452.5$ Å 3 , $Z = 4$, $\lambda = 0.70930$ Å, $F(000) = 960.56$, $D_c = 1.199$ Mg/m 3 , $\mu = 0.08$ mm $^{-1}$, 5242 reflections, 146 parameters, $R = 0.051$, $R_w = 0.067$ for all data.

4: Dichloromethane was used as solvent for this reaction. ^1H NMR (CDCl_3 , 200 MHz) δ 2.86 (t, $J = 3.6$ Hz, 1H), 2.74 (t, $J = 3.8$ Hz, 1H), 2.53 (td, $J = 12.6, 4.8$ Hz, 2H), 2.32-2.04 (m, 6H), 1.82 (td, $J = 9.0, 4.2$ Hz, 2H), 1.45 (m, 2H), 1.29 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 181.90, 171.84, 60.99, 51.74, 44.03, 35.63, 31.65, 27.69, 20.01, 19.89; HRMS m/z 360.2011 (calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_4$ 360.2049). Crystal data for **4** at 22 $^\circ\text{C}$: $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_4$ M 360.45, monoclinic, $C2$, $a = 11.414(3)$ Å, $b = 7.580(4)$ Å, $c = 21.887(3)$ Å, $V = 1865.4$ Å 3 , $Z = 4$, $\lambda = 0.70930$ Å, $F(000) = 776.48$, $D_c = 1.283$ Mg/m 3 , $\mu = 0.09$ mm $^{-1}$, 1812 reflections, 235 parameters, $R = 0.042$, $R_w = 0.079$ for all data.

General Procedure for the Preparation of Optically Enriched Aziridines 6a-f. To a solution of chiral ligand **4** (0.26 g, 0.72 mmole) in CH_2Cl_2 (3.5 mL) was added $\text{Pb}(\text{OAc})_4$ (0.32 g, 0.72 mmole) at room temperature under N_2 atmosphere for 30 min. The reaction mixture was cooled down to 0 $^\circ\text{C}$ and was added a solution of *N*-aminophthalimide (0.11 g, 0.68 mmol) and 3-((*E*)-3-phenyl-2-propenoyl)-1,3-oxazolidin-2-one **5a** (0.10 g, 0.46 mmol) in CH_2Cl_2 (3.5 mL) dropwise. The resulting mixture was stirred for 5 min and quenched with H_2O (5 mL). This was extracted with CH_2Cl_2 (10 mL x2) and the layers were separated. The organic layer washed with brine (10 mL), dried (MgSO_4) and concentrated. The crude product was purified by silica gel using hexane/EtOAc as eluent (1/1) to give 0.15 g (83%) of **6a** as a white solid. Exists as two *N*-invertomers in a ratio of *ca.* 9:1 in CDCl_3 solution. Major *N*-invertomer: ^1H NMR (CDCl_3 , 200 MHz) δ 7.79-7.76 (m, 2H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.69-7.66 (m, 2H), 7.53-7.50 (m, 2H), 7.48-7.38 (m, 2H), 5.17 (d, $J = 5.2$ Hz, 1H), 4.50 (d, $J = 5.2$ Hz, 1H), 4.54-4.42 (m, 2H), 4.02-3.91 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 165.04, 164.79, 153.45, 134.41, 134.15 (x2), 130.32, 128.75, 128.71 (x2), 127.55 (x2), 123.17 (x2), 62.18, 50.59, 43.96, 43.00; HRMS m/z 377.1020 (calcd for $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_5$ 377.1012). Crystal data for **6a** at 22 $^\circ\text{C}$: $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_5 \cdot 1/2\text{CH}_3\text{OH}$, M 393.37, monoclinic, $P2_1/c$, $a = 19.745(6)$ Å, $b = 5.258(4)$ Å, $c = 20.316(7)$ Å, $V = 1860.4$ Å 3 , $Z = 4$, $\lambda = 0.70930$ Å, $F(000) = 820.58$, $D_c = 1.404$ Mg/m 3 , $\mu = 0.10$ mm $^{-1}$, 3370 reflections, 249 parameters, $R =$

0.117, $R_w = 0.083$ for all data. HPLC conditions: Daicel Chiralcel chiralpak AD, 2-propanol:hexane = 60:40 (0.65 mL/min), $t_R = 28.38$ min (*S*, *R*) and 61.68 min (*R*, *S*).

6b: Exists as two *N*-invertomers in a ratio of *ca.* 9:1 in CDCl₃ solution. Major *N*-invertomer: ¹H NMR (CDCl₃, 200 MHz) δ 7.81-7.67 (m, 4H), 4.62-4.40 (m, 2H), 4.51 (dd, $J = 7.6, 4.8$ Hz, 1H), 4.20-4.11 (m, 2H), 3.06 (d, $J = 7.6$ Hz, 1H), 2.93 (d, $J = 4.8$ Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 167.26, 164.63, 153.67, 134.34 (x2), 134.09, 130.07, 123.37 (x2), 123.08, 62.60, 42.65, 39.09, 37.36; HRMS m/z 301.0709 (calcd for C₁₄H₁₁N₃O₅ 301.0699); Anal. Calcd for C₁₄H₁₁N₃O₅: C, 55.82; H, 3.68; N, 13.95. Found: C, 55.74; H, 3.53; N, 13.82; HPLC conditions: Daicel Chiralcel OD, 2-propanol:hexane = 40:60 (0.75 mL/min), $t_R = 43.5$ min (*R*) and 63.5 min (*S*).

6c: Exists as two *N*-invertomers in a ratio of *ca.* 2.8:1 in CDCl₃ solution. Major *N*-invertomer: ¹H NMR (CDCl₃, 200 MHz) δ 7.76-7.62 (m, 4H), 4.63 (d, $J = 5.0$ Hz, 1H), 4.55-4.40 (m, 2H), 4.01-3.78 (m, 2H), 3.44 (qd, $J = 5.8, 5.0$ Hz, 1H), 1.54 (d, $J = 5.8$ Hz, 3H); ¹³C NMR (CDCl₃, 200 MHz) δ 167.23, 165.67, 164.86, 153.51, 134.02 (x2), 130.33, 123.02 (x2), 62.12, 45.64, 43.21, 42.94, 16.22; HRMS m/z 315.0851 (calcd for C₁₅H₁₃N₃O₅ 315.0855); Anal. Calcd for C₁₅H₁₃N₃O₅: C, 57.14; H, 4.16; N, 13.33. Found: C, 57.04; H, 3.95; N, 13.21. Crystal data for **6c** at 22 °C: C₁₅H₁₃N₃O₅ M 315.28, monoclinic, C2/c, $a = 19.716(5)$ Å, $b = 10.7565(16)$ Å, $c = 15.041(4)$ Å, $V = 2921.0$ Å³, $Z = 8$, $\lambda = 0.70930$ Å, $F(000) = 1312.97$, $D_c = 1.434$ Mg/m³, $\mu = 0.11$ mm⁻¹, 3317 reflections, 209 parameters, $R = 0.088$, $R_w = 0.115$ for all data.

6d: Exists as two *N*-invertomers in a ratio of *ca.* 5.7:1 in CDCl₃ solution. Major *N*-invertomer: ¹H NMR (CDCl₃, 200 MHz) δ 7.11-7.55 (m, 4H), 4.56 (d, $J = 5.2$ Hz, 1H), 4.43-4.34 (m, 2H), 3.92-3.75 (m, 2H), 3.43 (q, $J = 5.6$ Hz, 1H), 1.72-1.62 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 165.50, 164.68 (x2), 153.39, 133.85 (x2), 129.97 (x2), 122.73 (x2), 62.01, 49.37, 42.73, 42.01, 32.90, 19.19, 13.57; HRMS m/z 343.1177 (calcd for C₁₇H₁₇O₃N₅ 343.1168). Anal. Calcd for C₁₇H₁₇N₅O₃: C, 59.47; H, 4.99; N, 12.24 Found: C, 59.54; H, 4.66; N, 12.17. HPLC conditions: Daicel Chiralcel chiralpak AD, 2-propanol:hexane = 40:60 (0.65 mL/min), $t_R = 24.30$ min (*R*, *S*) and 33.21 min (*S*, *R*).

6e: Exists as two *N*-invertomers in a ratio of *ca.* 9:1 in CDCl₃ solution. Major *N*-invertomer: ¹H NMR (CDCl₃, 200 MHz) δ 7.82-7.68 (m, 4H), 4.54 (t, $J = 8.0$ Hz, 2H), 4.13 (t, $J = 8.0$, 2H), 3.31 (br. s, 1H), 2.92 (br. s, 1H), 1.24 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 166.65, 165.33, 164.28, 150.99, 132.58, 128.79, 121.57, 61.11, 45.97, 41.00, 39.96, 13.54; HRMS m/z 315.0868 (calcd for C₁₅H₁₃N₃O₅ 315.0855). Anal. Calcd for C₁₅H₁₃N₃O₅: C, 57.14; H, 4.16; N, 13.33. Found: C, 56.93; H, 3.99; N, 13.58; HPLC conditions: Daicel Chiralcel chiralpak AD, 2-propanol:hexane = 70:30 (0.70 mL/min), $t_R = 37.66$ min (*R*) and 69.37 min (*S*).

6f: Exists as two *N*-invertomers in a ratio of *ca.* 9:1 in CDCl₃ solution. Major *N*-invertomer: ¹H NMR (CDCl₃, 200 MHz) δ 7.78-7.64 (m, 4H), 7.43 (d, $J = 8.8$ Hz, 4H),

5.11 (d, $J = 5.0$ Hz, 1H), 4.44 (d, $J = 5.0$ Hz, 1H), 4.54-4.43 (m, 2H), 4.02-3.90 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 164.74, 164.70, 153.45, 134.65, 134.18 (x2), 133.00, 130.21, 128.92 (x2), 128.87, 123.18 (x2), 62.22, 49.77, 43.93, 42.95; HRMS m/z 411.0617 (calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}_3\text{O}_5$ 411.0622). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}_3\text{O}_5$: C, 58.33; H, 3.43; N, 10.20. Found: C, 58.28; H, 3.09; N, 10.40; HPLC conditions: Daicel Chiralcel chiralpak AD, 2-propanol:hexane = 60:40 (0.65 mL/min), $t_R = 38.29$ min (*S*, *R*) and 88.78 min (*R*, *S*).

8: ^1H NMR (CDCl_3 , 200 MHz) δ 7.86-7.72 (m, 4H), 5.61 (d, $J = 2.0$ Hz, 1H), 4.04 (t, $J = 5.2$ Hz, 2H), 4.03 (s, 1H), 3.83 (t, $J = 5.2$ Hz, 2H), 2.20 (br. 1H), 1.57 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 168.32, 166.62, 150.34, 134.73 (x2), 129.81, 123.78 (x2), 81.76, 64.39, 60.11, 44.61, 25.95, 20.50; HRMS m/z 347.1092 (calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6$ 347.1117). Crystal data for **8** at 22 $^\circ\text{C}$: $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6$ M 347.32, triclinic, P1, $a = 7.8713(16)$ Å, $b = 9.937(4)$ Å, $c = 11.143(4)$ Å, $V = 793.0$ Å 3 , $Z = 2$, $\lambda = 0.70930$ Å, $F(000) = 364.27$, $D_c = 1.455$ Mg/m 3 , $\mu = 0.11$ mm $^{-1}$, 3279 reflections, 227 parameters, $R = 0.038$, $R_w = 0.047$ for all data. HPLC conditions: Daicel Chiralcel OD, 2-propanol:hexane = 20:80 (0.90 mL/min), $t_R = 38.57$ min (*R*) and 53.24 min (*S*).

7a: $[\alpha]_D = -86.1$ ($c=1$, CHCl_3), previous prepared 1 : $[\alpha]_D = -88.0$ ($c = 1$, CHCl_3); HRMS m/z 546.2200 (calcd for $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_4$ 546.2267).

7c: $[\alpha]_D = -102.2$ ($c=1$, CHCl_3), previous prepared 1 : $[\alpha]_D = -105.4$ ($c = 1$, CHCl_3); HRMS m/z 484.2115 (calcd for $\text{C}_{28}\text{H}_{28}\text{N}_4\text{O}_4$ 484.2111).

Ref:

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