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 CaH2 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 Finingan Mat TSQ-46C GC/MS/MS/DS spectrometer. Elemental analyses were performed by a Perkin-Elmer 2400 or 2400II Elemental Analyzer. 1H and 13C NMR spectra were recorded routinely in CDCl3 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 CHCl3 (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 H2O (50 mL). This was extracted with CH2Cl2 (100 mL) and the layers were separated. The organic layer washed with brine (10 mL), dried (MgSO4) and concentrated. The crude product was purified by silica gel using EtOAc/CH2Cl2 as eluent (4/1) to give 7.22 g (69%) of chiral ligand 1 as a white solid: 1H NMR (CDCl3, 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); 13C NMR (CDCl3, 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 C22H32N2O4 388.2362).

2: 1H NMR (CDCl3, 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), 1.22 (s, 6H), 0.86 (s, 6H); 13C NMR (CDCl3, 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 C26H38N2O4 442.2832).

3: 1H NMR (CDCl3, 200 MHz) δ 3.43 (dd, J = 5.2, 3.2 Hz, 2H), 2.61 (td, J = 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); 13C NMR (CDCl3, 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 C26H38N2O4 442.2832). Crystal data for 3 at 22 0C: C26H38N2O4, M = 442.59, tetragonal, P43212, a = 7.8028(13) Å, c = 40.282(4) Å, V = 2452.5 Å³, Z = 4, λ = 0.70930 Å, F(000) = 960.56, Dc = 1.199 Mg/m³, µ = 0.08 mm⁻¹, 5242 reflections, 146 parameters, R = 0.051, Rw = 0.067 for all data.

4: Dichloromethane was used as solvent for this reaction. 1H NMR (CDCl3, 200 MHz) δ 2.86 (t, J = 3.6 Hz, 1H), 2.74 (t, J = 3.8 Hz, 1H), 2.53 (td, J = 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); 13C NMR (CDCl3, 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 C20H28N2O4 360.2049). Crystal data for 4 at 22 0C: C20H28N2O4, M = 360.45, monoclinic, C2, a = 11.414(3) Å, b = 7.580(4) Å, c = 21.887(3) Å, V = 1865.4 Å³, Z = 4, λ = 0.70930 Å, F(000) = 776.48, Dc = 1.283 Mg/m³, µ = 0.09 mm⁻¹, 1812 reflections, 235 parameters, R = 0.042, Rw = 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 CH2Cl2 (3.5 mL) was added Pb(OAc)4 (0.32 g, 0.72 mmole) at room temperature under N2 atmosphere for 30 min. The reaction mixture was cooled down to 0 oC 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 CH2Cl2 (3.5 mL) dropwise. The resulting mixture was stirred for 5 min and quenched with H2O (5 mL). This was extracted with CH2Cl2 (10 mL x2) and the layers were separated. The organic layer washed with brine (10 mL), dried (MgSO4) 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 CDCl3 solution. Major N-invertomer: 1H NMR (CDCl3, 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); 13C NMR (CDCl3, 50 MHz) δ 165.04, 164.79, 153.45, 134.41, 134.41 (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 C20H15N3O5 377.1012). Crystal data for 6a at 22 0C: C20H15N3O5·1/2CH3OH, M = 393.37, monoclinic, P21/c, a = 19.745(6) Å, b = 5.258(4) Å, c = 20.316(7) Å, V = 1860.4 Å³, Z = 4, λ = 0.70930 Å, F(000) = 820.58, Dc = 1.404 Mg/m³, µ = 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 CDCl\(_3\) solution. Major \( N \)-inveromer: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta 7.81-7.67 \) (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); \(^{13}\)C NMR (CDCl\(_3\), 50 MHz) \( \delta 167.26, 164.63, 153.67, 134.34 \) (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 C\(_{14}H_{11}N_3O_5\) 301.0699); Anal. Calcd for C\(_{14}H_{11}N_3O_5\): 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 CDCl\(_3\) solution. Major \( N \)-invertomer: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta 7.76-7.62 \) (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); \(^{13}\)C NMR (CDCl\(_3\), 200 MHz) \( \delta 167.23, 164.86, 153.51, 134.02 \) (x2), 130.33, 123.02 (x2), 62.12, 45.64, 43.21, 42.94, 16.22; HRMS \( m/z \) 315.0851 (calcd for C\(_{15}H_{13}N_3O_5\) 315.0855); Anal. Calcd for C\(_{15}H_{13}N_3O_5\): C, 57.14; H, 4.16; N, 13.33. Found: C, 57.04; H, 4.05; N, 13.21. Crystal data for 6c at 22 \( ^{\circ} \)C: C\(_{15}H_{13}N_3O_5\) M\(_s\) 315.28, monoclinic, C\(_2\)/c, \( a = 19.716(5) \) Å, \( b = 10.7565(16) \) Å, \( c = 15.041(4) \) Å, \( V = 2921.0 \) Å\(^3\), \( Z = 8 \), \( \lambda = 0.70930 \) Å, \( F(000) = 1312.97 \), \( D_c = 1.434 \) Mg/m\(^3\), \( \mu = 0.11 \) 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 CDCl\(_3\) solution. Major \( N \)-invertomer: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta 7.11-7.55 \) (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); \(^{13}\)C NMR (CDCl\(_3\), 200 MHz) \( \delta 165.50, 164.68 \) (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 C\(_{17}H_{17}O_3N_5\) 343.1168). Anal. Calcd for C\(_{17}H_{17}N_3O_5\): 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 CDCl\(_3\) solution. Major \( N \)-invertomer: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta 7.78-7.64 \) (m, 4H), 7.43 (d, \( J = 8.8 \) Hz, 4H), 4.13 (t, \( J = 8.0 \) Hz, 2H), 3.31 (br, s, 1H), 2.92 (br, s, 1H), 1.24 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 50 MHz) \( \delta 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 C\(_{15}H_{13}N_3O_5\) 315.0855). Anal. Calcd for C\(_{15}H_{13}N_3O_5\): 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 CDCl\(_3\) solution. Major \( N \)-invertomer: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta 7.78-7.64 \) (m, 4H), 7.43 (d, \( J = 8.8 \) Hz, 4H), 4.13 (t, \( J = 8.0 \) Hz, 2H), 3.31 (br, s, 1H), 2.92 (br, s, 1H), 1.24 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 50 MHz) \( \delta 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 C\(_{15}H_{13}N_3O_5\) 315.0855). Anal. Calcd for C\(_{15}H_{13}N_3O_5\): 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).
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); $^1^3$C NMR (CDCl$_3$, 50 MHz) $\delta$ 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 C$_{20}$H$_{14}$ClN$_3$O$_5$ 411.0622). Anal. Calcd for C$_{20}$H$_{14}$ClN$_3$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: $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 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); $^1^3$C NMR (CDCl$_3$, 50 MHz) $\delta$ 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 C$_{16}$H$_{17}$N$_3$O$_6$ 347.1117). Crystal data for 8 at 22°C: C$_{16}$H$_{17}$N$_3$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 C$_{33}$H$_{30}$N$_4$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 C$_{28}$H$_{28}$N$_4$O$_4$ 484.2111).

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