Iron(II) Catalyzed Asymmetric Intramolecular Olefin Aminochlorination with Chloride Ion

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Supporting Material

A. General Information

B. Catalyst Discovery and Procedures for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination Reaction

a. Synthesis of New Nitrogen-Based Ligands and Catalyst Discovery for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination

b. Synthesis and Characterization of New Substrates

c. General Procedure for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination and Product Characterization

C. Catalyst Discovery and Procedures for the Iron-Catalyzed Asymmetric Olefin Aminochlorination Reaction

a. Catalyst Discovery for the Iron-Catalyzed Asymmetric Olefin Aminochlorination

b. Synthesis and Characterization of New Substrates

c. General Procedure for the Iron-Catalyzed Asymmetric Olefin Aminochlorination and Product Characterization
D. Mechanistic Investigation of the Iron-Catalyzed Asymmetric Olefin Aminochlorination

E. References

F. NMR Spectra
A. General Information

General Procedures. All reactions were performed in flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma–Aldrich.

Materials. Tetra-\textit{n}-butylammonium chloride (TBAC) was purchased from Sigma–Aldrich. It was further purified through recrystallization in the diethyl ether/acetone mixture and stored in a glove box under N$_2$ atmosphere. Other reagents were purchased from Sigma–Aldrich, Fluka, EM Science, and Lancaster and used directly as received. All solvents were used after being freshly distilled.

Instrumentation. Proton nuclear magnetic resonance ($^1$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on Bruker UltraShield-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak (CHCl$_3$: $\delta$ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent (CDCl$_3$: $\delta$ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants in Hertz (Hz), and integration. The mass spectroscopic data were obtained at the Georgia State University mass spectrometry facility using a Micromass Platform II single quadruple instrument. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm$^{-1}$) and absorption strength (s = strong, m = medium, w = weak).

B. Catalyst Discovery and Procedures for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination Reaction

a. Synthesis of New Nitrogen-Based Ligands and Catalyst Discovery for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination

Table S1. Catalyst discovery for the iron-catalyzed diastereoselective olefin aminochlorination reaction

<table>
<thead>
<tr>
<th>entry</th>
<th>Fe(X)2</th>
<th>ligand (mol %)</th>
<th>conversiona</th>
<th>yieldb</th>
<th>dR/cra</th>
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<tbody>
<tr>
<td>1</td>
<td>FeCl2</td>
<td>none</td>
<td>62%</td>
<td>45%</td>
<td>2:1</td>
</tr>
<tr>
<td>2</td>
<td>FeCl2</td>
<td>L1 (20)</td>
<td>&gt;95%</td>
<td>80%</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>3</td>
<td>Fe(Nttf2)</td>
<td>L1 (20)</td>
<td>&gt;95%</td>
<td>86%</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>4</td>
<td>Fe(Nttf2)</td>
<td>L2 (10)</td>
<td>&gt;95%</td>
<td>82%</td>
<td>0.83:1</td>
</tr>
<tr>
<td>5</td>
<td>Fe(Nttf2)</td>
<td>L3 (10)</td>
<td>61%</td>
<td>34%</td>
<td>0.25:1</td>
</tr>
<tr>
<td>6</td>
<td>Fe(Nttf2)</td>
<td>L4 (20)</td>
<td>&gt;95%</td>
<td>75%</td>
<td>1.8:1</td>
</tr>
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</table>

aUnless stated otherwise, the reactions were carried out under N2 atmosphere. bConversion and dR/cr are determined by 1H NMR. cIsolated yield. TBAC: tetra-n-butyrammonium chloride.

L1 was purchased from Sigma–Aldrich and used directly without further purification. L2, L3, and L4 were synthesized according to literature procedures.1-3

Procedure for Catalyst Discovery. To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added an iron catalyst (0.02 mmol) and a ligand (0.02 or 0.04 mmol). After the vial was evacuated and backfilled with N2 for three times, anhydrous CH2Cl2 (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. During this time, substrate 1 (0.2 mmol, 86 mg) and anhydrous TBAC (139 mg, 0.5 mmol) were dissolved in CH2Cl2 (4.0 mL) in a second flame-dried 3-dram vial (vial B) with a magnetic stir bar under N2 atmosphere. Both vials were degassed by brief evacuation and back filling with N2 twice. The vial B was cooled down to 0°C, and the solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at the same temperature until 1 was fully consumed
monitored by TLC. The reaction was quenched with 1 mL saturated NaHCO₃ solution and extracted with CH₂Cl₂ (1.5 mL × 3). The combined organic phase was concentrated and the residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminochlorination product 2 as a white solid. The dr was determined by ¹H NMR analysis of the crude reaction mixture.

4-(Chloro(phenyl)methyl)oxazolidin-2-one (2a): by following the general procedure under the condition described in entry 3, 2a was obtained as a white solid (36 mg, 86% yield, dr >20:1, m.p. 90–93 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.44–7.38 (m, 5H), 4.93 (s, 1H), 4.72 (d, J = 9.1 Hz, 1H), 4.62 (dd, J = 9.3, 8.1 Hz, 1H), 4.48 (dd, J = 9.4, 4.8 Hz, 1H), 4.27 (td, J = 8.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 136.6, 129.7, 129.3, 127.7, 68.6, 63.4, 58.3; IR νₘₐₓ (neat)/cm⁻¹: 3237 (m), 3139 (w), 2918 (w), 2853 (w), 1736 (s), 1715 (s), 1480 (m), 1402(m), 1237 (s), 1034 (s), 1012 (s), 931 (m), 768 (m); HRMS (ESI, m/z): calcd for C₁₀H₁₁NO₂Cl⁺ (M + H⁺), 212.0478, found 212.0485.

4-(Chloro(phenyl)methyl)oxazolidin-2-one (2b): by following the general procedure under the condition described in entry 4, 2a and 2b were obtained as a mixture (34 mg, 82% yield, dr: 0.83:1, m.p. 91–99 °C). 2b is characterized as following: ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.32 (m, 5H), 6.21 (s, 1H), 4.80 (d, J = 8.7 Hz, 1H), 4.29 (td, J = 8.4, 4.7 Hz, 1H), 4.20 (dd, J = 8.5, 1H), 4.00 (dd, J = 9.3, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 136.6, 129.7, 129.3, 127.7, 68.6, 63.4, 58.3; IR νₘₐₓ (neat)/cm⁻¹: 3230 (m), 3131 (w), 2915 (w), 2853 (w), 1734 (s), 1713 (s), 1475 (m), 1409(m), 1234 (s), 1034 (s), 1012 (s), 930 (m), 770 (m); HRMS (ESI, m/z): calcd for C₁₀H₁₁NO₂Cl⁺ (M + H⁺), 212.0478, found 212.0485.
Relative Stereochemistry Determination. The relative stereochemistry of 2 was determined by comparison of the NMR spectra of 2a and 2b with literature precedents, in which 2a and 2b were both characterized.4

<table>
<thead>
<tr>
<th>compound</th>
<th>2a</th>
<th>2-anti (literature data)4</th>
</tr>
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<tbody>
<tr>
<td><strong>1H NMR</strong></td>
<td>1H NMR (400 MHz, CDCl₃): δ 7.44–7.38 (m, 5H), 4.93 (s, 1H), 4.72 (d, $J = 9.1$ Hz, $H_a$), 4.62 (dd, $J = 9.3$, 8.1 Hz, $H_c$), 4.48 (dd, $J = 9.4$, 4.8 Hz, $H_d$), 4.27 (td, $J = 8.6$, 4.8 Hz, $H_b$).</td>
<td>1H NMR (200 MHz, CDCl₃): δ 7.70–7.40 (m, 5H), 5.90 (s, 1H), 4.89 (d, $J = 8.5$ Hz, $H_a$), 4.66 (dd, $J = 8.5$ Hz, $H_c$), 4.58 (dd, $J = 8.5$, $J = 5.0$ Hz, $H_d$), 4.40 (ddd, $J = 8.5$, $J = 5.0$ Hz, $H_b$).</td>
</tr>
<tr>
<td><strong>13C NMR</strong></td>
<td>13C NMR (100 MHz, CDCl₃): δ 158.1, 136.6, 129.7, 129.3, 127.7, 68.6, 63.4, 58.3.</td>
<td>13C NMR (50 MHz, CDCl₃): δ 158.7 (s), 136.4 (s), 129.4 (d), 129.1 (d), 127.6 (d), 68.1 (t), 63.5 (d), 58.2 (d).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>compound</th>
<th>2b</th>
<th>2-syn (literature data)4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1H NMR</strong></td>
<td>1H NMR (400 MHz, CDCl₃): δ 7.47–7.32 (m, 5H), 6.21 (s, 1H), 4.80 (d, $J = 8.7$ Hz, $H_a$), 4.29 (td, $J = 8.4$, 4.7 Hz, $H_b$), 4.20 (dd, $J = 8.5$ Hz, $H_c$), 4.00 (dd, $J = 9.3$, 4.8 Hz, $H_d$).</td>
<td>1H NMR (200 MHz, CDCl₃): δ 7.50–7.25 (m, 5H), 5.95 (s, 1H), 4.82 (d, $J = 8.5$ Hz, $H_a$), 4.34 (ddd, $J = 8.5$, 8.5, 4.7 Hz, $H_b$), 4.24 (dd, $J = 8.5$ Hz, $H_c$), 4.03 (dd, $J = 8.5$, 4.7 Hz, $H_d$).</td>
</tr>
<tr>
<td><strong>13C NMR</strong></td>
<td>13C NMR (100 MHz, CDCl₃): δ 158.4, 135.9, 129.6, 129.2, 127.6, 66.9, 65.0, 58.2.</td>
<td>13C NMR (50 MHz, CDCl₃): δ 158.9 (s), 135.9 (s), 129.4 (d), 129.0 (d), 127.5 (d), 66.9 (t), 64.8 (d), 58.6 (d).</td>
</tr>
</tbody>
</table>
Summary: the diagnostic $^1$H NMR signal to differentiate 2a (anti-addition product) and 2b (syn-addition product) is the $\delta$ H$_d$ in both compounds: $\delta$ H$_d$ in 2a is 4.49 ppm and $\delta$ H$_d$ in 2b is 4.00 ppm. The chemical shift difference between two diastereomeric compounds is consistent with a broad range of products. This stereochemistry assignment is further corroborated through X-ray crystallographic analysis of S37, a structural analogue of 2a.

b. Synthesis and Characterization of New Substrates (S1–S8)

The substrates were synthesized by following a known procedure. All new compounds have been characterized.
General procedures. To a flame-dried round bottom flask equipped with a magnetic stir bar were added hydroxyl carbamate (5.0 mmol, 1.0 equiv), 3,5-bis(trifluoromethyl)benzoic acid (5.25 mmol, 1.05 equiv) and anhydrous CH$_2$Cl$_2$ (50 mL). After stirring at -15 °C for 5 min, DCC (5.5 mmol, 1.1 equiv) in CH$_2$Cl$_2$ (10 mL) was added drop wise. The reaction was then stirred at the same temperature until all the hydroxyl carbamate was fully consumed monitored by TLC. The reaction solution was quenched by adding acetic acid (0.1 mL) and the mixture was filtered to remove N, N’-dicyclohexylurea (DCU). The filtrate was concentrated under reduced pressure, and then diethyl ether (20 mL) was added. The mixture was cooled in a refrigerator for 1 h and filtered again to remove additional DCU. The filtrate was concentrated in vacuo and the residue was purified through a gradient silica gel flash column chromatography (hexanes/EtOAc: from 20:1 to 7:1) or recrystallized directly with a hexanes/EtOAc mixture to afford the desired products (65–91% yield).

(E)-3-(p-tolyl)allyl ((3,5-bis(trifluoromethyl)benzoyl)oxy)carbamate (S1) : by following the general procedure, S1 was obtained as a white solid (82% yield, m.p. 98–100 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.55 (s, 2H), 8.43 (s, 1H), 8.14 (s, 1H), 7.29 (d, $J$ = 8.1 Hz, 2H), 7.13 (d, $J$ = 7.9 Hz, 2H), 6.68 (d, $J$ = 15.8 Hz, 1H), 6.24 (dt, $J$ = 15.8, 6.7 Hz, 1H), 4.89 (dd, $J$ = 6.7, 0.9 Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.4, 156.1, 138.4, 135.7, 133.0, 132.7 (q, $J$ = 34.4 Hz), 130.2, 129.4, 129.0, 127.8–127.4(m), 126.7, 122.6 (q, $J$ = 272.1 Hz), 120.7, 67.9, 21.2; IR $v_{max}$ (neat)/cm$^{-1}$: 3255 (m), 3085 (m), 2968 (m), 1764 (m), 1268 (s), 1134 (s), 680 (s); HRMS (ESI, m/z): calcd for C$_{29}$H$_{14}$NO$_4$F$_6$ $^-$ (M - H$^+$), 446.0921, found 446.0924.
(E)-3-(2-Chlorophenyl)allyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S2): by following the general procedure, S2 was obtained as a white solid (77% yield, m.p. 85–87 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 2H), 8.49 (s, 1H), 8.15 (s, 1H), 7.54–7.51 (m, 1H), 7.36–7.34 (m, 1H), 7.25–7.19 (m, 2H), 7.09 (d, J = 15.9 Hz, 1H), 6.28 (dt, J = 15.8, 6.3 Hz, 1H), 4.93 (d, J = 6.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 156.0, 134.0, 133.3, 132.7 (d, J = 34.4 Hz), 131.2, 130.0, 129.8, 129.3, 128.9, 127.6, 127.0, 126.9, 124.6, 122.6 (q, J = 273.0 Hz), 67.4; IR ν max (neat)/cm⁻¹: 3265 (m), 3098 (w), 2940 (w), 1756 (m), 1280 (s), 1137 (s), 681 (s); HRMS (ESI, m/z): calcd for C₁₉H₁₁NO₄F₆Cl⁻ (M - H⁻), 466.0281, found 466.0284.

(E)-3-(pyridin-3-yl)allyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S3): by following the general procedure (purification through a gradient silica gel flash column chromatography with hexanes/Acetone: from 7:1 to 2.5:1), S3 was obtained as a white solid (65% yield, m.p. 118–120 °C). ¹H NMR (400 MHz, CDCl₃): δ 9.16 (s, 1H), 8.63 (s, 1H), 8.56 (s, 2H), 8.51 (d, J = 4.5 Hz, 1H), 8.15 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.28 (dd, J = 4.8, 7.9 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 16.0, 6.2 Hz, 1H), 4.92 (d, J = 6.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 156.0, 149.2, 148.3, 133.3, 132.7 (q, J = 34.3 Hz), 131.7, 131.2, 130.1, 129.0, 127.6, 124.6, 123.6, 122.6 (q, J = 273.2 Hz), 66.9; IR ν max (neat)/cm⁻¹: 3093 (w), 2931 (w), 1750 (s), 1380 (m), 1277 (s), 1216 (s), 1137 (s), 706 (m), 682 (m); HRMS (ESI, m/z): calcd for C₁₈H₁₁NO₄F₆⁻ (M - H⁻), 433.0634, found 433.0623.
(E)-3-(naphthalen-1-yl)allyl ((3,5-bis(trifluoromethyl)benzoyl)oxy)carbamate (S4): by following the general procedure, S4 was obtained as a white solid (91% yield, m.p. 115–117 °C). 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.55 (s, 2H), 8.46 (s, 1H), 8.15 (s, 1H), 8.08 (d, $J$ = 7.8 Hz, 1H), 7.86 (d, $J$ = 8.1 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.60 (d, $J$ = 7.0 Hz, 1H), 7.56–7.42 (m, 4H), 6.34 (dt, $J$ = 13.3, 6.4 Hz, 1H), 5.02 (d, $J$ = 6.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.4, 156.1, 133.6, 133.6, 132.8, 132.7 (q, $J$ = 34.3 Hz), 131.1, 130.1 (q, $J$ = 4.2 Hz), 129.0, 128.7, 128.6, 127.7, 126.3, 125.9, 125.5, 125.0, 124.2, 123.6, 122.6 (q, $J$ = 271.0 Hz), 67.8; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3674 (m), 2988 (m), 2901 (s), 1765 (m), 1755 (m), 1381 (m), 1278 (s), 1210 (m), 1141 (s), 904 (s), 710 (s); HRMS (ESI, $m/z$): calcd for C$_{23}$H$_{15}$O$_4$NF$_6$ClNa$^+$ (M + Na$^+$), 506.0911, found 506.0910.

(E)-3-(naphthalen-2-yl)allyl ((3,5-bis(trifluoromethyl)benzoyl)oxy)carbamate (S5): by following the general procedure, S5 was obtained as a white solid (88% yield, m.p. 116–118 °C). 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.56 (s, 2H), 8.39 (s, 1H), 8.15 (s, 1H), 7.85 – 7.78 (m, 3H), 7.76 (d, $J$ = 1.6 Hz, 1H), 7.60 (dd, $J$ = 8.6, 1.8 Hz, 1H), 7.52–7.44 (m, 2H), 6.88 (d, $J$ = 15.9 Hz, 1H), 6.43 (dt, $J$ = 15.9, 6.6 Hz, 1H), 4.96 (dd, $J$ = 6.6, 1.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.4, 156.0, 135.7, 133.4, 133.3, 133.2, 132.7 (q, $J$ = 34.4 Hz), 130.1 (q, $J$ = 3.2 Hz), 129.0, 128.4, 128.1, 127.7, 127.2, 126.4, 126.3, 123.4, 122.6 (q, $J$ = 272.2 Hz), 122.1, 67.8; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3688 (m), 2988 (s), 2901 (s), 1776 (m), 1755 (m), 1380 (m), 1278 (s), 1213 (s), 1110 (m), 1076 (s), 1051 (s), 681 (m); HRMS (ESI, $m/z$): calcd for C$_{23}$H$_{15}$O$_4$NF$_6$ClNa$^+$ (M + Na$^+$), 506.0911, found 506.0914.
(E)-3-Cyclohexylallyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S6): by following the general procedure, S6 was obtained as a white solid (83% yield, m.p. 60–62 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.54 (s, 2H), 8.41 (s, 1H), 8.14 (s, 1H), 5.78 (dd, $J = 15.5$, 6.6 Hz, 1H), 5.60–5.46 (m, 1H), 4.67 (d, $J = 6.6$ Hz, 2H), 2.08–1.91 (m, 1H), 1.81–1.55 (m, 4H), 1.37–0.98 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.4, 156.1, 143.8, 132.7 (q, $J = 34.3$ Hz), 130.0, 129.0, 127.5, 122.6 (q, $J = 273.0$ Hz), 120.2, 68.2, 40.3, 32.4, 26.0, 25.9; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3070 (w), 2971 (w), 1720 (m), 1282 (m), 1211 (m), 1145 (m), 896 (m), 728 (s), 703 (s); HRMS (ESI, m/z): calcd for C$_{19}$H$_{18}$NO$_4$F$_6$ $^-$(M - H$^-$), 438.1140, found 438.1126.

![S6](image)

2-Phenylallyl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S7): by following the general procedure, S7 was obtained as a white solid (75% yield, m.p. 70–72 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.47 (s, 2H), 8.16 (s, 1H), 7.40 (d, $J = 7.2$ Hz, 2H), 7.32–7.25 (m, 3H), 5.59 (s, 1H), 5.43 (s, 1H), 5.16 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.3, 156.1, 141.6, 137.3, 132.5 (q, $J = 34.4$ Hz), 130.0, 128.9, 128.4, 128.1, 127.5, 125.9, 122.6 (q, $J = 273.1$ Hz), 116.3, 68.2; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3320 (m), 3060 (w), 1758 (m), 1281 (s), 1185 (s), 737 (s); HRMS (ESI, m/z): calcd for C$_{19}$H$_{12}$NO$_4$F$_6$ $^-$(M - H$^-$), 432.0671, found 432.0660.

![S7](image)

$(2E,4E)$-hexa-2,4-dien-1-yl (3,5-bis(trifluoromethyl)benzoyl)oxycarbamate (S8): by following the general procedure, S8 was obtained as a white solid (90% yield, m.p. 84–86 °C).

![S8](image)
\[ ^1H\ NMR\ (400\ MHz,\ CDCl_3):\ \delta\ 8.54\ (s,\ 2H),\ 8.38\ (s,\ 1H),\ 8.14\ (s,\ 1H),\ 6.30\ (dd,\ J = 15.1,\ 10.6\ Hz,\ 1H),\ 6.12–6.00\ (m,\ 1H),\ \delta\ 5.78\ (dq,\ J = 13.7,\ 6.5\ Hz,\ 1H),\ 5.63\ (dt,\ J = 14.4,\ 6.8\ Hz,\ 1H),\ 4.73\ (d,\ J = 6.7\ Hz,\ 2H),\ 1.77\ (d,\ J = 6.6\ Hz,\ 3H);\ ^{13}C\ NMR\ (100\ MHz,\ CDCl_3):\ \delta\ 163.4,\ 156.0,\ 136.3,\ 132.6\ (q,\ J = 34.3\ Hz),\ 132.4,\ 127.6,\ 122.5\ (q,\ J = 271.3\ Hz),\ 122.2,\ 67.7,\ 18.2;\ IR\ \nu_{\text{max}}\ (neat)/\text{cm}^{-1}:\ 3261\ (w),\ 3022\ (w),\ 2918\ (w),\ 2856\ (w),\ 1753\ (m),\ 1281\ (s);\ HRMS\ (ESI,\ m/z):\ \text{calcd}\ for\ C_{16}H_{12}NO_4F_6\ (M - H^+),\ 396.0671,\ \text{found}\ 396.0677.\]

c. General Procedure for the Iron-Catalyzed Diastereoselective Olefin Aminochlorination and Product Characterization

**General procedure.** To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added Fe(NTf₂)₂ (12.3 mg, 0.02 mmol, 10 mol %) and 1,10-phenanthroline (7.2 mg, 0.04 mmol, 20 mol %). After the vial was evacuated and backfilled with N₂ for three times, anhydrous CH₂Cl₂ (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. During this time, the substrate (0.2 mmol) and anhydrous TBAC (139 mg, 0.5 mmol) were dissolved in CH₂Cl₂ (4.0 mL) in a second flame-dried 3-dram vial (vial B) with a magnetic stir bar under N₂ atmosphere. Both vials were degassed by brief evacuation and back filling with N₂ twice. The vial B was cooled down to 0 °C, and the solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at the same temperature until all the starting material was fully consumed monitored by TLC. The reaction was quenched by 2 mL saturated NaHCO₃ solution. After being extracted with CH₂Cl₂ (1.5 mL × 3), the combined organic phase was concentrated and the residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminochlorination product. The \(d_r\) was determined by \(^1H\ NMR\) analysis of the crude reaction mixture.

![Chemical Structure](image)

**4-(Chloro(p-tolyl)methyl)oxazolidin-2-one (S9):** by following the general procedure and carrying out reaction at -15 °C, S9 was obtained as a white solid (39 mg, 86% yield, \(d_r >20:1\), m.p. 126–129 °C). \(^1H\ NMR\ (400\ MHz,\ CDCl_3):\ \delta\ 7.27\ (d,\ J = 8.0\ Hz,\ 2H),\ 7.22\ (d,\ J = 8.1\ Hz,
2H), 4.84 (s, 1H), 4.69 (d, \( J = 9.2 \) Hz, 1H), 4.62 (dd, \( J = 9.3 \), 8.3 Hz, 1H), 4.47 (dd, \( J = 9.4 \), 4.7 Hz, 1H), 4.25 (td, \( J = 8.5 \), 5.0 Hz, 1H), 2.37 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 158.0, 139.9, 133.6, 130.0, 127.6, 68.7, 63.4, 58.3, 21.2; IR \( \nu_{\text{max}} \)(neat)/cm\(^{-1}\): 3272 (m), 3154 (w), 3037 (w), 2918 (w), 2340 (w), 1749 (s), 1404 (m), 1280 (m), 1239 (m), 1026 (m), 766 (m); HRMS (ESI, m/z): calcd for C\(_{11}\)H\(_{13}\)NO\(_2\)Cl\(^{+}\) (M + H\(^{+}\)), 226.0635, found 226.0640.

**Methyl 4-(chloro(2-oxooxazolidin-4-yl)methyl)benzoate (S10):** by following the general procedure, S10 and its diastereomer were obtained as a white solid (38 mg, 70% yield, \( dr \): 7:1, m.p. 136–139 °C). S10: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.06 (d, \( J = 8.4 \) Hz, 2H), 7.47 (d, \( J = 8.3 \) Hz, 2H), 5.58 (s, 1H), 4.79 (d, \( J = 8.6 \) Hz, 1H), 4.58 (dd, \( J = 9.5 \), 8.3 Hz, 1H), 4.45 (dd, \( J = 9.5 \), 4.7 Hz, 1H), 4.27 (td, \( J = 8.4 \), 4.7 Hz, 1H), 3.92 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.2, 158.4, 141.2, 131.3, 130.4, 127.8, 68.2, 62.8, 58.2, 52.4; its syn-diastereomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.08 (d, \( J = 8.4 \) Hz, 2H), 7.46 (d, \( J = 8.3 \) Hz, 2H), 5.62 (s, 1H), 4.85 (d, \( J = 8.3 \) Hz, 1H), 4.33 (td, \( J = 8.4 \), 5.2 Hz, 1H), 4.27 (dd, \( J = 9.1 \) Hz, 1H), 4.04 (dd, \( J = 9.2 \), 4.6 Hz, 1H ), 3.96 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.1, 157.9, 141.2, 131.4, 130.5, 127.7, 68.4, 66.8, 64.3, 62.7, 58.5, 58.1, 52.4; IR \( \nu_{\text{max}} \)(neat)/cm\(^{-1}\): 3229 (m), 3132(w), 2957 (w), 2919 (w), 2849 (w), 1731 (s), 1714 (s), 1434 (m), 1278 (s), 1243 (s), 1110 (s), 1033 (s), 1018 (s), 770 (m); HRMS (ESI, m/z): calcd for C\(_{12}\)H\(_{13}\)NO\(_4\)Cl\(^{+}\) (M + H\(^{+}\)), 270.0533, found 270.0535.

**4-(Chloro(3-chlorophenyl)methyl)oxazolidin-2-one (S11):** by following the general procedure, S11 was obtained as a white solid (33 mg, 67% yield, \( dr \): 10:1, m.p. 107–109 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.38–7.32 (m, 3H), 7.24 (s, 1H), 5.10 (s, 1H), 4.66 (d, \( J = 9.0 \) Hz, 1H), 4.59 (t, \( J = 8.8 \) Hz, 1H), 4.44 (dd, \( J = 9.7 \), 4.8 Hz, 1H), 4.21 (td, \( J = 8.8 \), 5.1 Hz, 1H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 157.7, 141.2, 131.2, 130.4, 127.7, 68.4, 66.8, 64.3, 62.7, 58.5, 58.1, 52.4; IR \( \nu_{\text{max}} \)(neat)/cm\(^{-1}\): 3272 (m), 3154 (w), 3037 (w), 2918 (w), 2340 (w), 1749 (s), 1404 (m), 1280 (m), 1239 (m), 1026 (m), 766 (m); HRMS (ESI, m/z): calcd for C\(_{12}\)H\(_{13}\)NO\(_4\)Cl\(^{+}\) (M + H\(^{+}\)), 270.0533, found 270.0535.
CDCl$_3$: $\delta$ 158.0, 138.5, 135.3, 130.6, 129.9, 127.8, 125.9, 68.4, 62.5, 58.2; IR $\nu_{\max}$ (neat)/cm$^{-1}$: 3271 (m), 2918 (w), 1749 (s), 1233 (w), 1027 (m), 700 (m); HRMS (ESI, m/z): calcd for C$_{10}$H$_{10}$NO$_2$Cl$_2$ $^+$ (M + H$^+$), 246.0089, found 246.0081.

4-(Chloro(2-chlorophenyl)methyl)oxazolidin-2-one (S12): by following the general procedure, S12 was obtained as a white solid (37 mg, 76% yield, $dr$: 10:1, m.p. 93–95 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (dd, $J = 7.5$, 2.0 Hz, 1H), 7.43 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.40–7.30 (m, 2H), 5.48 (s, 1H), 5.42 (d, $J = 8.0$ Hz, 1H), 4.55 (dd, $J = 9.3$, 8.2 Hz, 1H), 4.47 (dd, $J = 9.3$, 4.4 Hz, 1H), 4.39 (td, $J = 8.1$, 4.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.4, 134.0, 133.7, 130.6, 130.2, 129.0, 127.9, 67.9, 58.7, 57.4; IR $\nu_{\max}$ (neat)/cm$^{-1}$: 3255 (m), 3020 (w), 2982 (w), 2917 (w), 1742 (s), 1475 (m), 1402 (m), 1234 (m), 1023 (m), 736 (m), 698 (m); HRMS (ESI, m/z): calcd for C$_{10}$H$_{10}$NO$_2$Cl$_2$ $^+$ (M + H$^+$), 246.0089, found 246.0081.

4-(Chloro(pyridin-3-yl)methyl)oxazolidin-2-one (S13): by following the general procedure, S13 was obtained as a white solid (32 mg, 76% yield, $dr$: 12:1, m.p. 121–124 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (d, $J = 2.2$ Hz, 1H), 8.59 (dd, $J = 4.8$, 1.4 Hz, 1H), 7.77 (dt, $J = 7.9$, 1.9 Hz, 1H), 7.37 (dd, $J = 7.9$, 4.8 Hz, 1H), 5.64 (s, 1H), 4.77 (d, $J = 8.8$ Hz, 1H), 4.63 (dd, $J = 9.4$, 8.4 Hz, 1H), 4.47 (dd, $J = 9.5$, 4.6 Hz, 1H), 4.30 (tdd, $J = 8.6$, 4.6, 1.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.2, 150.8, 149.0, 135.4, 132.6, 124.1, 68.3, 60.8, 58.2; IR $\nu_{\max}$ (neat)/cm$^{-1}$: 3238 (m), 3133 (w), 2957 (w), 2924 (w), 2854 (w), 1742 (s), 1428 (m), 1406 (m), 1234 (m), 1026 (m), 711 (m); HRMS (ESI, m/z): calcd for C$_9$H$_{10}$N$_2$O$_2$Cl$^+$ (M + H$^+$), 213.0431, found 213.0437.
4-(Chloro(naphthalen-1-yl)methyl)oxazolidin-2-one (S14): by following the general procedure and carrying out reaction at -15 °C, S14 was obtained as a white solid (32 mg, 61% yield, $dr > 20:1$, m.p. 134–136 °C). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.24 (d, $J = 8.5$ Hz, 1H), 8.00 (t, $J = 7.6$ Hz, 2H), 7.75 (d, $J = 7.2$ Hz, 1H), 7.71–7.64 (m, 1H), 7.64–7.57 (m, 2H), 5.97 (s, 1H), 5.88 (d, $J = 7.9$ Hz, 1H), 4.76–4.68 (m, 1H), 4.61 (t, $J = 8.6$ Hz, 1H), 4.55 (dd, $J = 9.1$, 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 158.3, 134.0, 133.0, 130.9, 129.8, 129.0, 127.0, 126.3, 126.0, 125.6, 122.8, 67.7, 56.5; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3250 (m), 2923 (w), 1756 (s), 1712 (s), 1485 (m), 1416 (m), 1230 (s), 1027 (s), 760 (s); HRMS (ESI, $m/z$): calcd for C$_{14}$H$_{13}$O$_2$NCl$^+$ (M + H$^+$), 262.0629, found 262.0623.

4-(Chloro(naphthalen-2-yl)methyl)oxazolidin-2-one (S15): by following the general procedure and carrying out reaction at -15 °C, S15 was obtained as a white solid (31 mg, 59% yield, $dr > 20:1$, m.p. 136–139 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.6$ Hz, 1H), 7.86 (dt, $J = 6.4$, 3.3 Hz, 2H), 7.83 (d, $J = 1.8$ Hz, 1H), 7.56 (dt, $J = 6.2$, 3.4 Hz, 2H), 7.50 (dd, $J = 8.5$, 1.9 Hz, 1H), 4.88 (d, $J = 9.3$ Hz, 1H), 4.85 (s, 1H), 4.66 (dd, $J = 9.4$, 8.1 Hz, 1H), 4.54 (dd, $J = 9.4$, 4.7 Hz, 1H), 4.37 (td, $J = 8.8$, 5.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.9, 133.7, 133.6, 132.9, 129.7, 128.1, 127.8, 127.7, 127.3, 127.2, 124.0, 68.6, 63.8, 58.2; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3253 (m), 3144 (w), 2918 (w), 1744 (s), 1709 (s), 1479 (m), 1409 (m), 1244 (s), 1017 (s), 761 (s); HRMS (ESI, $m/z$): calcd for C$_{14}$H$_{13}$O$_2$NClH$^+$ (M + H$^+$), 262.0629, found 262.0624.
4-(1-Chloro-3-phenylprop-2-yn-1-yl)oxazolidin-2-one (S16): by following the general procedure and carrying out reaction at -15 °C, S16 and its syn-diastereomer were obtained as a white solid (44 mg, 93% yield, dr: 7:1). S16: 1H NMR (400 MHz, CDCl3): δ 7.47–7.45 (m, 2H), 7.39–7.32 (m, 3H), 5.83 (s, 1H), 4.76 (d, J = 6.4 Hz, 1H), 4.60 (dd, J = 9.5, 8.5 Hz, 1H), 4.52 (dd, J = 9.6, 4.1 Hz, 1H), 4.23 (ddd, J = 8.3, 6.4, 4.1 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 158.3, 132.0, 129.6, 128.5, 120.8, 88.9, 81.8, 67.1, 57.6, 51.0; its syn-diastereomer: 1H NMR (400 MHz, CDCl3): δ 7.50–7.43 (m, 2H), 7.40–7.31 (m, 3H), 5.79 (s, 1H), 4.73 (d, J = 6.2 Hz, 1H), 4.55–4.61 (m, 1H), 4.45 (dd, J = 9.5, 3.9 Hz, 1H), 4.30–4.25 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 158.3, 132.0, 129.6, 128.5, 120.8, 88.9, 81.8, 67.1, 57.5, 51.0; IR νmax (neat)/cm-1: 3270 (m), 3021 (w), 2980 (w), 2226 (w), 1754 (s), 1233 (s), 1039 (m), 758 (m); HRMS (ESI, m/z): calcd for C12H11NO2Cl+ (M + H+), 236.0478, found 236.0487.

4-(1-Chloro-1-phenylethyl)oxazolidin-2-one (S17a) : by following the general procedure, S17a was obtained as a white solid (22 mg, 50% yield, dr >20:1, m.p. 75–77 °C). Its relative chemistry was determined by comparison of the 1H NMR data with the literature data.1 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 7.9 Hz, 2H), 7.47–7.31 (m, 3H), 5.18 (s, 1H), 4.46 (dd, J = 6.3, 1.9 Hz, 2H), 4.33 (t, J = 6.5 Hz, 1H), 1.98 (d, J = 1.9 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 158.7, 140.5, 128.9, 128.8, 126.6, 72.3, 66.8, 62.2, 24.7; IR νmax (neat)/cm-1: 3260 (m), 3120 (w), 2996 (w), 2915 (w), 1730(s), 1035 (w), 1232 (m), 1040 (m), 709 (m); HRMS (ESI, m/z): calcd for C11H13NO2Cl+ (M + H+), 226.0635, found 226.0640.

4-(2-Chloropropan-2-yl)oxazolidin-2-one (S18) : by following the general procedure, S18 was obtained as a white solid (25 mg, 76% yield, m.p. 53–56 °C). 1H NMR (400 MHz, CDCl3): δ
6.58 (s, 1H), 4.47 (t, \( J = 9.2 \) Hz, 1H), 4.35 (dd, \( J = 9.5, 4.6 \) Hz, 1H), 3.98 (dd, \( J = 8.9, 4.6 \) Hz, 1H), 1.56 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)):\( \delta \) 159.6, 69.4, 66.7, 61.8, 27.8, 26.8; IR \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \): 2923 (s), 2860(s), 1763 (s), 1481 (w), 1340 (m), 1220(s), 1049(s), 809 (s); HRMS (ESI, \( m/z \)): calcd for C\(_6\)H\(_{11}\)NO\(_2\)Cl\(^+\) (M + H\(^+\)), 164.0422, found 164.0417.

\( \pm \)-4-(Chloro(cyclohexyl)methyl)oxazolidin-2-one (S19): by following the general procedure and carrying out the reaction for 5 h, S19 was obtained as a white solid (30 mg, 69% yield, \( d_r >20:1 \), m.p. 115–118 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.16 (s, 1H), 4.52 (t, \( J = 8.8 \) Hz, 1H), 4.34 (dd, \( J = 9.1, 5.4 \) Hz, 1H), 4.11 (td, \( J = 8.4, 5.4 \) Hz, 1H), 3.77 (dd, \( J = 8.4, 3.4 \) Hz, 1H), 1.84–1.62 (m, 6H), 1.51–1.01 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)):\( \delta \) 160.1, 69.7, 68.9, 54.5, 39.8, 30.7, 26.2, 26.0, 25.9, 25.5; IR \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \): 2925 (s), 2851(s), 1759 (s), 1482 (w), 1375 (m), 1227(s), 1149(s), 1035 (s), 820 (s); HRMS (ESI, \( m/z \)): calcd for C\(_{10}\)H\(_{17}\)O\(_2\)NCl\(^+\) (M + H\(^+\)), 218.0942, found 218.0937.

4-(Chloromethyl)-4-phenyloxazolidin-2-one (S20): by following the general procedure and carrying out the reaction for 12 h, S20 was obtained as a white solid (32 mg, 77% yield, m.p. 109–112 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.46–7.42 (m, 2H), 7.39–7.36 (m, 1H), 7.32–7.30 (m, 2H), 6.50 (s, 1H), 4.66 (d, \( J = 8.9 \) Hz, 1H), 4.44 (d, \( J = 8.9 \) Hz, 1H), 3.93 (d, \( J = 11.7 \) Hz, 1H), 3.88 (d, \( J = 11.7 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)):\( \delta \) 158.9, 139.6, 129.3, 128.7, 124.9, 74.1, 64.1, 51.3; IR \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \): 3266 (m), 2912 (w), 2853 (w), 1753 (s), 1396 (w), 1094 (s), 1052 (w); HRMS (ESI, \( m/z \)): calcd for C\(_{10}\)H\(_{11}\)NO\(_2\)Cl\(^+\) (M + H\(^+\)), 212.0478, found 212.0479.
4-(E-1-chlorobut-2-en-1-yl)oxazolidin-2-one (S21): by following the general procedure, S21 and its syn-diastereomer were obtained as white solids (31 mg, 88% yield, dr: 1.5:1). S21: 1H NMR (400 MHz, CDCl₃): δ 6.15 (s, 1H), 5.88 (dd, J = 12.5, 6.0 Hz, 1H), 5.50–5.39 (m, 1H), 4.50 (t, J = 8.9 Hz, 1H), 4.32 (dd, J = 9.2, 4.9 Hz, 1H), 4.24 (dd, J = 17.6, 9.4 Hz, 1H), 4.04–3.95 (m, 1H), 1.77 (d, J = 5.1 Hz, 3H); 13C NMR (100 MHz, CDCl₃): δ 159.1, 133.9, 126.4, 67.8, 63.5, 57.1, 17.8; its syn-diastereomer: 1H NMR (400 MHz, CDCl₃): δ 6.26 (s, 1H), 5.93 (dd, J = 11.7, 6.4 Hz, 1H), 5.50–5.39 (m, 1H), 4.41 (t, J = 9.0 Hz, 1H), 4.21–4.16 (m, 1H), 4.04–3.95 (m, 1H), 1.75–1.73 (d, J = 5.0 Hz, 3H); 13C NMR (100 MHz, CDCl₃): δ 158.9, 133.9, 125.7, 66.9, 64.3, 57.3, 17.8; IR νmax (neat)/cm⁻¹: 3238 (m), 3135 (w), 2972 (w), 2925 (m), 1760(s), 1667 (m), 1403 (m), 1234 (s), 1004 (m), 966 (s), 1027(s), 742 (s); HRMS (ESI, m/z): calcd for C₇H₁₀NO₂NaCl⁺ (M + Na⁺), 198.0298, found 198.0304.

4-Chlorohexahydrobenzo[d]oxazol-2(3H)-one (S22): by following the general procedure, S22 was obtained as a white solid (22 mg, 64% yield, dr >20:1, m.p. 112–114 °C). 1H NMR (400 MHz, CDCl₃): δ 5.63 (s, 1H), 4.71 (dt, J = 6.3, 3.2 Hz, 1H), 3.80 (ddd, J = 12.2, 8.6, 4.3 Hz, 1H), 3.62 (dd, J = 8.5, 6.1 Hz, 1H), 2.32-2.09 (m, 2H), 1.76–1.52 (m, 4H); 13C NMR (100 MHz, CDCl₃): δ 159.1, 77.0, 62.2, 60.6, 31.8, 25.9, 19.7; IR νmax (neat)/cm⁻¹: 3272 (m), 3135 (w), 2972 (w), 2925 (m), 2852 (w), 1760(s), 1667 (m), 1403 (m), 1234 (s), 1004 (m), 966 (s), 1027(s), 742 (s); HRMS (ESI, m/z): calcd for C₇H₁₁NO₂Cl⁺ (M + H⁺), 176.0478, found 176.0480.

C. Catalyst Discovery and Procedures for the Iron-Catalyzed Asymmetric Olefin Aminochlorination Reaction
a. Catalyst Discovery for the Iron-Catalyzed Asymmetric Olefin Aminochlorination

Chiral ligands L5–L9 were synthesized by following literature procedures.2, 5-7

**Procedure for the Catalyst Discovery.** To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added Fe(NTf₂)₂ (9.2 mg, 0.015 mmol) and a chiral ligand (0.015 mmol). After the vial was evacuated and backfilled with N₂ for three times, re-distilled and anhydrous CHCl₃ (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. During this time, substrate (0.1 mmol) and anhydrous TBAC (69.5 mg, 0.25 mmol) were dissolved in CHCl₃ (3.0 mL, re-distilled and anhydrous) in a second flame-dried 2-dram vial (vial B) with a magnetic stir bar and freshly activated 4 Å molecular sieves under N₂ atmosphere. Both vials were degassed by brief evacuation and back filling with N₂ twice. The vial B was cooled down to -60 °C, and the solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at the same temperature for 12 h and quenched with 1 mL saturated NaHCO₃ solution. The reaction mixture was extracted with CH₂Cl₂ (1.5 mL × 3), and the combined organic phase was concentrated *in vacuo*. The residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford

**Table S2.** Catalyst discovery for the iron-catalyzed asymmetric olefin aminochlorination reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Ligand</th>
<th>Conversion[^b]</th>
<th>Yield[^c]</th>
<th>dₜ[^b]  (and[^e]; 3 atm)</th>
<th>ee[^d] (and[^e]; 3 atm)</th>
<th>ee[^d] (and[^e]; 3 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L5</td>
<td>&gt;95%</td>
<td>53%</td>
<td>9:1</td>
<td>84%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>2</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L6</td>
<td>&gt;95%</td>
<td>68%</td>
<td>0:48:1</td>
<td>24%</td>
<td>79%</td>
</tr>
<tr>
<td>3</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L7</td>
<td>88%</td>
<td>61%</td>
<td>1:7:4</td>
<td>&lt;5%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>4</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L8</td>
<td>&gt;95%</td>
<td>32%</td>
<td>2:45:1</td>
<td>47%</td>
<td>30%</td>
</tr>
<tr>
<td>5</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L9</td>
<td>&gt;95%</td>
<td>82%</td>
<td>0:5:1</td>
<td>8%</td>
<td>24%</td>
</tr>
<tr>
<td>6[^a]</td>
<td>3,5-(CF₃)₂-b-Ph</td>
<td>L5</td>
<td>&gt;95%</td>
<td>51%</td>
<td>10:5:1</td>
<td>90%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>7[^a]</td>
<td>CH₃</td>
<td>L5</td>
<td>&gt;95%</td>
<td>42%</td>
<td>1:1:1</td>
<td>97%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>8[^a]</td>
<td>CH₂Cl</td>
<td>L5</td>
<td>&gt;95%</td>
<td>67%</td>
<td>9:6:1</td>
<td>89%</td>
<td>&lt;5%</td>
</tr>
</tbody>
</table>
the aminochlorination product as a white solid. The \( dr \) was determined by \(^1\)H NMR analysis and the \( ee \) was measured by chiral HPLC analysis. The results are listed in the table (Table S2). The absolute stereochemistry was determined by X-ray crystallographic analysis of a structural analog of 2a with heavy atoms.

The racemic products with low \( dr \) (for HPLC assay purposes) were obtained by following the general procedure of the iron-catalyzed diastereoselective olefin aminochlorination under the ligand-free condition (Table S1, entry 1).

\[
\text{(S)-4-[(R)-chloro(phenyl)methyl]oxazolidin-2-one (2a): by following the general procedure under the condition described in entry 8, the product 2a obtained as a white solid (15 mg, 67\% yield, \( dr \): 9.6:1). [\alpha]_D^{20} = + 56.4^\circ (c 1.0, \text{CH}_2\text{Cl}_2). The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10\% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer (2a): \( t_r \) (minor) = 19.5 min, \( t_r \) (major) = 22.4 min, 89\% \( ee \); the syn-diastereomer (2b): \( t_r \) (minor) = 23.8 min, \( t_r \) (major) = 30.9 min, <5\% \( ee \).}
\]

\textit{Racemic sample}
Enantio-enriched sample (anti-diastereomer, 2a, 89% ee)

Enantio-enriched sample (syn-diastereomer, 2b, <5% ee)
b. Synthesis and Characterization of New Substrates (S23–S34)

Chloroacetoxyl carbamates were synthesized by following a known procedure.¹

General Procedure. To a flame-dried round bottom flask equipped with a magnetic stir bar were added a hydroxyl carbamate (5.0 mmol, 1.0 equiv), chloroacetic acid (5.25 mmol, 1.05 equiv) and anhydrous CH₂Cl₂ (50 mL). After stirring at -15 °C for 2 min, DCC (5.5 mmol, 1.1 equiv) and DMAP (0.5 mmol, 0.1 equiv) in CH₂Cl₂ (10 mL) was added drop wise. The reaction mixture was stirred at the same temperature until all the hydroxyl carbamate was fully consumed monitored by TLC. The reaction mixture was filtered to remove N, N’-dicyclohexylurea (DCU). The filtrate was concentrated in vacuo, and then diethyl ether (20 mL) was added. The mixture was cooled in a refrigerator for 0.5 h and filtered again to remove the additional DCU. The filtrate was concentrated in vacuo and the residue was purified through a rapid gradient silica gel flash column chromatography (hexanes/acetone: from 10:1 to 3:1) and further recrystallization from a mixture of hexanes/EtOAc to afford the desired products (59–86% yield).

Note: Most chloroacetoxyl carbamates must be purified rapidly by flash columns (flash rate: ca. 50 mL/min) because they tend to undergo hydrolysis upon exposure to silica gel for an extended period of time.

E-Cinnamyl (2-chloroacetoxycarbamate) (S23): by following the general procedure, S23 was obtained as a white solid (79% yield, m.p. 50–51 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.48 (s, 1H), 7.40–7.38 (m, 2H), 7.35–7.28 (m, 3H), 6.68 (d, J = 15.9 Hz, 1H), 6.26 (dt, J = 15.9, 6.5 Hz, 1H), 4.85 (dd, J = 6.5, 1.1 Hz, 2H), 4.21 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 156.1, 135.9, 135.4, 128.7, 128.4, 126.8, 121.9, 67.6, 38.6; IR v_max (neat)/cm⁻¹: 3257 (m), 3027 (w),
2955 (w), 1793 (m), 1733 (s), 1448 (s), 1244 (m), 1214 (m), 1050 (s), 1025 (m), 804 (m), 770 (s), 698 (s); HRMS (ESI, m/z): calcd for C_{12}H_{12}O_{4}NClNa^{+} (M + Na^{+}), 292.0347, found 292.0339.

\[\text{(E)}-3-(p\text{-tolyl})\text{allyl (2-chloroacetoxy)carbamate (S24): by following the general procedure,} \]
\[\text{S24 was obtained as a white solid (82\% yield, m.p. 72--74 °C).} \]
\[\text{}^{1}\text{H NMR (400 MHz, CDCl}_{3}\text{):} \]
\[\delta 8.19 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.7 Hz, 2H), 6.66 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 6.6 Hz, 1H), 4.84 (d, J = 6.6 Hz, 2H), 4.22 (s, 2H), 2.34 (s, 3H); \]
\[\text{13C NMR (100 MHz, CDCl}_{3}\text{):} \]
\[\delta 166.7, 155.9, 138.4, 135.6, 133.0, 129.4, 126.7, 120.7, 67.8, 38.5, 21.3; IR } \nu_{\text{max}} \text{(neat)/cm}^{-1} : 3212 (m), 3007 (w), 2958 (w), 1807 (m), 1741 (m), 1716 (s), 1481 (s), 1268 (m), 1110 (s), 978 (m), 817 (m), 794 (m); \]
\[\text{HRMS (ESI, } m/z\text{): calcd for C}_{13}\text{H}_{14}\text{O}_{4}\text{NClNa}^{+} (M + Na^{+}), 306.0504, \text{found 306.0496.} \]

\[\text{Methyl (E)-4-(((2-chloroacetoxy)carbamoyl)oxy)prop-1-en-1-yl)benzoate (S25): by following the general procedure,} \]
\[\text{S25 was obtained as a white solid (68\% yield, m.p. 72--75 °C).} \]
\[\text{}^{1}\text{H NMR (400 MHz, CDCl}_{3}\text{):} \]
\[\delta 8.20 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.9, 6.3 Hz, 1H), 4.90 (dd, J = 6.3, 1.4 Hz, 2H), 4.25 (s, 2H), 3.94 (s, 3H); \]
\[\text{13C NMR (100 MHz, CDCl}_{3}\text{):} \]
\[\delta 166.8, 156.0, 136.7, 135.8, 134.6, 128.7, 128.0, 127.3, 126.6, 125.4, 67.4, 38.6; IR } \nu_{\text{max}} \text{(neat)/cm}^{-1} : 3262 (m), 3015 (w), 2954 (w), 1793 (w), 1747 (m), 1696 (s), 1435 (m), 1280 (s), 1252 (s), 1130 (s), 960 (m), 750 (s); \]
\[\text{HRMS (ESI, } m/z\text{): calcd for C}_{14}\text{H}_{14}\text{O}_{6}\text{NClNa}^{+} (M + Na^{+}), 350.0402, \text{found 350.0391.} \]
(E)-3-(4-fluorophenyl)allyl (2-chloroacetoxy)carbamate (S26): by following the general procedure, S26 was obtained as a white solid (86% yield, m.p. 68–70 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.40 (s, 1H), 7.37 (dd, $J = 8.4, 5.3$ Hz, 2H), 7.03 (t, $J = 8.5$ Hz, 2H), 6.66 (d, $J = 15.8$ Hz, 1H), 6.20 (dt, $J = 15.9, 6.6$ Hz, 1H), 4.85 (d, $J = 6.6$ Hz, 2H), 4.24 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.8, 162.7 (d, $J = 247.9$ Hz), 155.9, 134.2, 132.0 (d, $J = 3.3$ Hz), 128.4 (d, $J = 8.1$ Hz), 121.6 (d, $J = 2.3$ Hz), 115.6 (d, $J = 21.7$ Hz), 67.5, 38.5; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -113.2 (tt, $J = 9.0, 5.1$ Hz); IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3199 (m), 3006 (w), 2957 (w), 1805 (s), 1739 (s), 1715 (s), 1507 (s), 1481(s), 1266 (s), 1226 (s), 1115 (s), 982 (s), 821 (m), 763 (m); HRMS (ESI, m/z): calcd for C$_{12}$H$_{11}$O$_4$NClFNa$^+$ (M + Na$^+$), 310.0253, found 310.0244.

(E)-3-(4-chlorophenyl)allyl (2-chloroacetoxy)carbamate (S27): by following the general procedure, S27 was obtained as a white solid (76% yield, m.p. 80–82 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (s, 1H), 7.33–7.28 (m, 4H), 6.64 (d, $J = 15.9$ Hz, 1H), 6.24 (dt, $J = 15.9, 6.5$ Hz, 1H), 4.85 (dd, $J = 6.5, 1.3$ Hz, 2H), 4.23 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.8, 155.8, 134.3, 134.1, 128.9, 127.9, 122.5, 67.4, 38.5; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3200 (s), 3007 (w), 2941 (w), 1805 (s), 1739 (m), 1714 (s), 1481(s), 1405 (m), 1264 (s), 1115 (s), 1089 (s), 978 (s), 799 (s); HRMS (ESI, m/z): calcd for C$_{12}$H$_{11}$O$_4$NCl$_2$Na$^+$ (M + Na$^+$), 325.9957, found 325.9948.

(E)-3-(4-bromophenyl)allyl (2-chloroacetoxy)carbamate (S28): by following the general procedure, S28 was obtained as a white solid (82% yield, m.p. 99–100 °C). $^1$H NMR (400 MHz,
CDCl₃): δ 8.18 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.9, 6.4 Hz, 1H), 4.84 (dd, J = 6.4, 1.3 Hz, 2H), 4.22 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 155.8, 134.8, 134.1, 131.8, 128.2, 122.7, 122.3, 67.3, 38.5; IR ʋmax (neat)/cm⁻¹: 3675 (m), 3205 (w), 2988 (s), 2901 (s), 1804 (m), 1716 (s), 1483 (m), 1265 (s), 1117 (s), 1027 (s), 797 (s); HRMS (ESI, m/z): calcd for C₁₂H₁₁O₄NBrClNa⁺ (M + Na⁺), 369.9601, found 369.9596.

(E)-3-(m-tolyl)allyl (2-chloroacetoxy)carbamate (S₂₉): by following the general procedure, S₂₉ was obtained as a white solid (81% yield, m.p. 51–53 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 7.24–7.18 (m, 3H), 7.13–7.06 (m, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.25 (dt, J = 15.8, 6.6 Hz, 1H), 4.84 (dd, J = 6.6, 1.2 Hz, 2H), 4.21 (s, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 156.1, 138.3, 135.8, 135.6, 129.2, 128.6, 127.5, 123.9, 121.6, 67.7, 38.6, 21.4; IR ʋmax (neat)/cm⁻¹: 3206 (m), 3006 (w), 2960 (w), 1800 (m), 1744 (m), 1719 (s), 1480 (s), 1266 (m), 1112 (s), 975 (m), 819 (m), 791 (m); HRMS (ESI, m/z): calcd for C₁₃H₁₄O₄NClNa⁺ (M + Na⁺), 306.0504, found 306.0496.

(E)-3-(3-chlorophenyl)allyl (2-chloroacetoxy)carbamate (S₃₀): by following the general procedure, S₃₀ was obtained as a white solid (77% yield, m.p. 49–51 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.29 (s, 1H), 7.37 (s, 1H), 7.28–7.22 (m, 3H), 6.62 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 15.8, 6.4 Hz, 1H), 4.85 (dd, J = 6.4, 1.2 Hz, 2H), 4.23 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 155.8, 137.7, 134.6, 133.7, 129.9, 128.3, 126.3, 125.0, 123.5, 67.2, 38.5; IR ʋmax (neat)/cm⁻¹: 3206 (m), 2956 (w), 1778 (s), 1752 (s), 1722 (s), 1594 (m), 1565(m), 1460 (m), 1244
(s), 1215 (s), 1112 (s), 965 (s), 773 (s); HRMS (ESI, \textit{m/z}): calcd for C\textsubscript{12}H\textsubscript{11}O\textsubscript{4}NCl\textsubscript{2}Na\textsuperscript{+} (M + Na\textsuperscript{+}), 325.9957, found 325.9947.

![S31](image)

\textbf{(E)-3-(3-bromophenyl)allyl (2-chloroacetoxy)carbamate (S31):} by following the general procedure, S31 was obtained as a white solid (76\% yield, m.p. 64–67 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{δ} 8.28 (s, 1H), 7.53 (s, 1H), 7.40 (d, \textit{J} = 7.8 Hz, 1H), 7.30 (d, \textit{J} = 7.8 Hz, 1H), 7.20 (t, \textit{J} = 7.8 Hz, 1H), 6.61 (d, \textit{J} = 16.0 Hz, 1H), 6.27 (dt, \textit{J} = 15.9, 6.4 Hz, 1H), 4.85 (dd, \textit{J} = 6.4, 1.4 Hz, 2H), 4.22 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{δ} 166.7, 155.8, 138.0, 133.6, 131.2, 130.2, 129.6, 125.4, 123.5, 122.8, 67.1, 38.5; IR \textit{ν}\textsubscript{\textit{max}} (neat)/cm\textsuperscript{-1}: 3206 (m), 3032 (w), 2971 (w), 2955 (w), 1777 (s), 1750(s), 1563 (m), 1238 (s), 1136 (s), 966 (s), 799 (s); HRMS (ESI, \textit{m/z}): calcd for C\textsubscript{12}H\textsubscript{11}O\textsubscript{4}NBrClNa\textsuperscript{+} (M + Na\textsuperscript{+}), 369.9601, found 369.9596.

![S32](image)

\textbf{(E)-3-(\textit{o}-tolyl)allyl (2-chloroacetoxy)carbamate (S32):} by following the general procedure, S32 was obtained as a white solid (64\% yield, m.p. 70–72 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{δ} 8.24 (s, 1H), 7.45–7.42 (m, 1H), 7.21–7.14 (m, 3H), 6.92 (d, \textit{J} = 15.7 Hz, 1H), 6.16 (dt, \textit{J} = 15.7, 6.6 Hz, 1H), 4.87 (dd, \textit{J} = 6.5, 1.0 Hz, 2H), 4.22 (s, 2H), 2.35 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{δ} 166.7, 155.9, 135.8, 135.0, 133.4, 130.4, 128.2, 126.2, 125.9, 123.1, 67.8, 38.5, 19.7; IR \textit{ν}\textsubscript{\textit{max}} (neat)/cm\textsuperscript{-1}: 3210 (m), 3004 (w), 2956 (w), 1807 (m), 1742 (m), 1715 (s), 1480 (s), 1272 (m), 1102 (s), 976 (m), 820 (m), 790 (m); HRMS (ESI, \textit{m/z}): calcd for C\textsubscript{13}H\textsubscript{14}O\textsubscript{4}NCINa\textsuperscript{+} (M + Na\textsuperscript{+}), 306.0504, found 306.0494.
(E)-3-(2-chlorophenyl)allyl (2-chloroacetoxy)carbamate (S33): by following the general procedure, S33 was obtained as a white solid (69% yield, m.p. 78–80 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.16 (s, 1H), 7.58–7.47 (m, 1H), 7.42–7.31 (m, 1H), 7.25–7.18 (m, 2H), 7.08 (dt, $J$ = 15.9, 1.4 Hz, 1H), 6.26 (dt, $J$ = 15.8, 6.4 Hz, 1H), 4.90 (dd, $J$ = 6.4, 1.4 Hz, 2H), 4.23 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 155.7, 134.0, 133.4, 131.2, 129.8, 129.3, 127.1, 127.0, 124.7, 67.4, 38.5; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3200 (m), 3029 (w), 2973 (w), 2929 (w), 1777 (s), 1754 (s), 1455 (m), 1235 (s), 1133 (s), 969 (s), 804 (m), 726 (s); HRMS (ESI, m/z): calcd for C$_{12}$H$_{11}$O$_4$NCl$_2$Na$^+$ (M + Na$^+$), 325.9957, found 325.9948.

(E)-3-(pyridin-3-yl)allyl (2-chloroacetoxy)carbamate (S34): by following the general procedure, S34 was obtained as a white solid (55% yield, m.p. 69–71 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.03 (s, 1H), 8.61 (d, $J$ = 2.2 Hz, 1H), 8.50 (dd, $J$ = 4.8, 1.6 Hz, 1H), 7.72 (dt, $J$ = 8.0, 2.0 Hz, 1H), 7.30–7.27 (m, 1H), 6.67 (d, $J$ = 16.0 Hz, 1H), 6.34 (dt, $J$ = 16.0, 6.2 Hz, 1H), 4.87 (dd, $J$ = 6.2, 1.4 Hz, 2H), 4.23 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 155.9, 149.1, 148.3, 133.4, 131.7, 131.1, 124.6, 123.6, 66.8, 38.5; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3225 (m), 3026 (w), 3006 (w), 2959 (w), 1750 (m), 1726 (s), 1460 (s), 1208 (m), 1112 (s), 960 (m), 820 (m), 790 (m); HRMS (ESI, m/z): calcd for C$_{11}$H$_{11}$O$_4$N$_2$ClNa$^+$ (M + Na$^+$), 293.0402, found 293.0410.

c. General Procedure for the Iron-Catalyzed Asymmetric Olefin Aminochlorination and Product Characterization

**General Procedure.** To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added Fe(NTf$_2$)$_2$ (9.2 mg, 0.015 mmol, 15 mol %) and ligand L5 (7.3 mg, 0.015 mmol, 15 mol %). After the vial was evacuated and backfilled with N$_2$ for three times, CHCl$_3$
(1.0 mL, re-distilled and anhydrous) was added and the mixture was stirred at room temperature for 20 min. Meanwhile, a second flame-dried and N₂-protected 2-dram vial (vial B) with a magnetic stir bar was charged with the substrate (0.1 mmol), anhydrous TBAC (69.5 mg, 0.25 mmol), freshly activated 4 Å molecular sieves and CHCl₃ (3.0 mL, re-distilled and anhydrous). Both vials were degassed by brief evacuation and back filling with N₂ twice. Vial B was cooled down to -60 °C, and the catalyst solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at this temperature for 12 h and then gradually warmed to room temperature. The reaction was quenched with 1 mL saturated NaHCO₃ solution. The reaction mixture was extracted with CH₂Cl₂ (1.5 mL × 3), and the combined organic phase was concentrated in vacuo. The residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminochlorination product. The dr was determined by ¹H NMR analysis and the ee was measured by chiral HPLC analysis. The assignment of diastereomers on HPLC traces was based on ¹H NMR analysis.

(R)-4-((R)-chloro(p-tolyl)methyl)dihydrofuran-2(3H)-one (S9) : by following the general procedure, the product S9 was obtained as a white solid (14 mg, 65% yield, dr: 15:1). The ee was determined by chiral HPLC analysis (Chiral OD-H column, 7% EtOH in hexanes, flow rate = 0.9 mL/min, UV detection at 230 nm). The anti-diastereomer: tᵣ (minor) = 35.1 min, tᵣ (major) = 32.3 min, 91% ee; the syn-diastereomer: tᵣ (minor) = 39.0 min, tᵣ (major) = 36.7 min, <5% ee.

Racemic sample
Enantio-enriched sample (91% ee): it was obtained by using chiral ligand ent-L\textsubscript{5}

\[
\text{Methyl } 4-((S)\text{-chloro}(R)-2\text{-oxooxazolidin-4-yl})\text{methyl} \text{benzoate (S10): by following the general procedure, the product S10 was obtained as a white solid (19 mg, 69\% yield, } dr: 5.2:1). \text{ The } ee \text{ was determined by chiral HPLC analysis (Chiral OD-H column, 10\% EtOH in hexanes, flow rate } = 1.0 \text{ mL/min, UV detection at 205 nm). The } anti\text{-diastereomer: } t_r\text{(minor)} = 34.4 \text{ min, } t_r\text{(major)} = 38.6 \text{ min, 86\% ee; the } syn\text{-diastereomer: } t_r\text{(minor)} = 42.2 \text{ min, } t_r\text{(major)} = 45.1 \text{ min, <5\% ee.}
\]

Racemic sample
Enantio-enriched sample (86% ee)

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(R)-4-((S)-chloro(4-fluorophenyl)methyl)oxazolidin-2-one (S35): by following the general procedure, the product S35 was obtained as a white solid (20 mg, 84% yield, dr: 12:1, m.p. 109–111 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.42–7.35 (m, 2H), 7.15–7.08 (m, 2H), 5.28 (s, 1H), 4.73 (d, J = 8.8 Hz, 1H), 4.60 (dd, J = 9.4, 8.2 Hz, 1H), 4.45 (dd, J = 9.5, 4.8 Hz, 1H), 4.24 (ddd, J = 8.7, 8.2, 5.3 Hz, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): δ 163.2 (d, J = 249.8 Hz), 158.2, 132.5 (d, J = 3.6 Hz), 129.6 (d, J = 8.5 Hz), 116.4 (d, J = 21.7 Hz), 68.4, 62.7, 58.3; \(^1\)F NMR (376 MHz, CDCl\(_3\)) δ -110.89 (td, J = 8.2, 4.4 Hz); IR \(\nu_{\text{max}}\) (neat)/cm\(^{-1}\): 3236 (m), 3131 (w), 2929 (w), 2850 (w), 1727 (s), 1605 (m), 1510 (s), 1409 (m), 1394 (m), 1232 (s), 1023 (s), 838 (m); HRMS (ESI, \(m/z\)): calcd for C\(_{10}\)H\(_{10}\)O\(_2\)NClFH\(^+\) (M + H\(^+\)), 230.0379, found 230.0374; The \(ee\) was determined by Chiral HPLC analysis (Chiral S, S, Whelk column, 5% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: \(t_r\) (minor) = 37.0 min, \(t_r\) (major) = 39.0 min, 90% \(ee\); the syn-diastereomer: \(t_r\) (minor) = 41.8 min, \(t_r\) (major) = 43.6 min, <5% \(ee\).

**Racemic sample**

![Graph](image-url)

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Totals: 1.49341e5 2272.53760
Enantio-enriched sample (90% ee)

(R)-4-(S)-chloro(4-chlorophenyl)methyl)oxazolidin-2-one (S36): by following the general procedure, the product S36 was obtained as a white solid (15 mg, 62% yield, dr: 11:1, m.p. 123–126 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 5.07 (s, 1H), 4.71 (d, $J = 8.9$ Hz, 1H), 4.61 (dd, $J = 9.5, 8.2$ Hz, 1H), 4.45 (dd, $J = 9.5, 4.8$ Hz, 1H), 4.27–4.17 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.0, 135.7, 135.0, 129.5, 129.1, 68.4, 62.6, 58.2; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3259 (m), 3012 (w), 2986 (w), 1765 (s), 1472 (m), 1239 (m), 1018 (m), 755 (m), 500 (s); HRMS (ESI, m/z): calcd for C$_{10}$H$_{10}$NO$_2$Cl$_2$+$^+$ (M + H$^+$), 246.0089, found 246.0084. The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 230 nm). The anti-diastereomer: $t_r$(minor) = 20.1 min, $t_r$(major) = 18.7 min, 88% ee; the syn-diastereomer: $t_r$(minor) = 26.7 min, $t_r$(major) = 28.5 min, <5% ee.
Racemic sample

Enantio-enriched sample (88% ee)
(R)-4-((S)-chboro(4-bromophenyl)methyl)oxazolidin-2-one \((S37)\): by following the general procedure, the product \(S37\) was obtained as a white solid (21 mg, 71% yield, \(dr\): 11:1, m.p. 139–141°C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56 (d, \(J = 8.4\) Hz, 2H), 7.27 (d, \(J = 8.4\) Hz, 2H), 5.33 (s, 1H), 4.70 (d, \(J = 8.7\) Hz, 1H), 4.58 (t, \(J = 8.8\) Hz, 1H), 4.44 (dd, \(J = 9.4, 4.8\) Hz, 1H), 4.23 (td, \(J = 8.6, 4.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.2, 135.6, 132.5, 129.3, 123.8, 68.3, 62.7, 58.2; IR \(\nu_{\text{max}}\) (neat)/cm\(^{-1}\): 3274 (m), 2923 (w), 2851 (w), 1757 (s), 1488 (m), 1405 (m), 1239 (m), 1010 (m); HRMS (ESI, \(m/z\)): calcd for C\(_{10}\)H\(_{10}\)O\(_2\)NBrCl\(^+\) (M + H\(^+\)), 289.9578, found 289.9574. \([\alpha]_D^{20} = +11.4^\circ\) (c 1.0, CH\(_2\)Cl\(_2\)). The \(ee\) was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The \(anti\)-diastereomer: \(t_r\) (minor) = 21.9 min, \(t_r\) (major) = 19.6 min, 86% \(ee\); the \(syn\)-diastereomer: \(t_r\) (minor) = 26.6 min, \(t_r\) (major) = 29.6 min, <5% \(ee\).

Racemic sample
Enantio-enriched sample (86% ee)

The absolute stereochemistry of S37 was determined by X-ray crystallographic analysis. The crystal structure has been deposited in The Cambridge Crystallographic Data Centre as CCDC 1041826.

Structure Plots
Crystal Data and Experimental

Experimental. Single colorless prism-shaped crystals of (cruz-parabrac) were recrystallized from DCM by slow evaporation. A suitable crystal (0.32 × 0.20 × 0.14 mm$^3$) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was cooled to $T = 110(2)$ K during data collection. The structure was solved with the ShelXD (Sheldrick, 2008) structure solution program using Olex2 (Dolomanov et al., 2009), using the Dual Space solution method. The structure was refined with version 2013-4 of ShelXL-97 (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. C$_{18}$H$_8$BrClNO$_2$. $M_r = 290.54$, monoclinic, P2$_1$ (No. 4), $a = 5.9280(4)$ Å, $b = 7.6682(5)$ Å, $c = 11.3533(8)$ Å, $\beta = 95.944(3)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 513.31(6)$ Å$^3$, $T = 110(2)$ K, $Z = 2$, $Z' = 1$, $\mu$ (MoK$_\alpha$) = 4.240, 5260 reflections measured, 2561 unique ($R$_{int} = 0.0271) which were used in all calculations. The final $wrR_2$ was 0.0544 (all data) and $R_I$ was 0.0264 (1 > 2(I)).

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(R)-4-((S)-chloro(m-tolyl)methyl)oxazolidin-2-one (S38): by following the general procedure, the product S38 was obtained as a white solid (17 mg, 75% yield, dr: 12:1, m.p.126–129 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33–7.29 (m, 1H), 7.21–7.17 (m, 3H), 4.83 (s, 1H), 4.67 (d, $J = 9.3$ Hz, 1H), 4.62 (dd, $J = 9.3$, 8.3 Hz, 1H), 4.48 (dd, $J = 9.4$, 4.8 Hz, 1H), 4.26 (td, $J = 8.4$, 4.8 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.3, 139.2, 136.5, 130.4, 129.2, 128.3, 124.7, 68.5, 63.6, 58.2, 21.4; IR $\nu_{max}$ (neat)/cm$^{-1}$: 3270 (m), 3144 (w), 3041 (w), 2928 (w), 2341 (w), 1752 (s), 1679 (w), 1631 (s), 1586 (s), 1504 (s), 1498 (s), 1402 (m), 1276 (m), 1239 (m), 1028 (m), 760 (m); HRMS (ESI, m/z): calcd for C$_{11}$H$_{13}$NO$_2$Cl$^-$ (M + H$^+$), 226.0635, found 226.0640. The ee was determined by Chiral HPLC analysis (Chiral S, S, Whelk column, 5% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: $t_r$ (minor) = 18.0 min, $t_r$ (major) = 15.4 min, 87% ee; the syn-diastereomer: $t_r$ (minor) = 19.8 min, $t_r$ (major) = 22.5 min, <5% ee.

Racemic sample

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Totals: 1.21708e4 355.26514
Enantio-enriched sample (87% ee): it was obtained by using ent-L5 ligand.

(R)-4-((S)-chloro(3-chlorophenyl)methyl)oxazolidin-2-one (S11): by following the general procedure, the product S11 was obtained as a white solid (16 mg, 63% yield, dr: 10:1). The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: t_r (minor) = 24.2 min, t_r (major) = 20.4 min, 80% ee; the syn-diastereomer: t_r (minor) = 25.2 min, t_r (major) = 35.2 min, <5% ee.

Racemic sample
Enantio-enriched sample (80% ee): it was obtained by using ent-L5 ligand.

(R)-4-((S)-chloro(3-bromophenyl)methyl)oxazolidin-2-one (S39): by following the general procedure under the condition described in entry 8, the product S39 was obtained as a white solid (21 mg, 71% yield, $dr$: 15:1, m.p. 113–115 °C ). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58–7.51 (m, 2H), 7.34–7.28 (m, 1H), 7.32 (s, 1H), 5.05 (s, 1H), 4.67 (d, $J = 9.1$ Hz, 1H), 4.62 (dd, $J = 9.5, 8.2$ Hz, 1H).
Hz, 1H), 4.47 (dd, J = 9.5, 4.7 Hz, 1H), 4.24 (ddd, J = 8.7, 8.1, 4.7 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.0, 138.8, 132.9, 130.8, 130.7, 126.4, 123.3, 68.4, 62.4, 58.2; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3272 (m), 2923 (w), 2952 (w), 1747 (s), 1476 (m), 1428 (m), 1237(m), 1025(m), 732 (m); HRMS (ESI, m/z): calcd for C$_{10}$H$_{10}$O$_2$NBrCl$^-$ (M + H$^+$), 289.9578, found 289.9573. The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: $t_r$ (minor) = 21.9 min, $t_r$ (major) = 25.6 min, 80% ee; the syn-diastereomer: $t_r$ (minor) = 26.9 min, $t_r$ (major) = 39.5 min, <5% ee.

**Racemic sample**

![Chromatogram of racemic sample](image)

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Totals: 8.48081e4 1909.57901

**Enantio-enriched sample (80% ee)** it was obtained by using _ent-L5_ ligand.

![Chromatogram of enantio-enriched sample](image)
(R)-4-((S)-chloro(o-tolyl)methyl)oxazolidin-2-one (S40): by following the general procedure under the condition described in entry 8, the product S40 was obtained as a white solid (18 mg, 78% yield, dr: 4.5:1, m.p.114–116 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32–7.28 (m, 1H), 7.21–7.17 (m, 3H), 7.23–7.20 (m, 1H), 5.01 (s, 1H), 4.68 (d, $J$ = 9.2 Hz, 1H), 4.61 (dd, $J$ = 9.4, 8.2 Hz, 1H), 4.48 (dd, $J$ = 9.4, 4.8 Hz, 1H), 4.29–4.23(m, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.4, 136.7, 131.3, 129.4, 127.2, 126.6, 68.8, 59.1, 57.5, 19.4; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3269 (m), 3144 (w), 3035 (w), 2922 (w), 2340 (w), 1750 (s), 1510 (w), 1460 (m), 1300 (m), 1021 (m), 765 (m); HRMS (ESI, m/z): calcd for C$_{11}$H$_{13}$NO$_2$Cl$^+$ (M + H$^+$), 226.0635, found 226.0640. The ee was determined by Chiral HPLC analysis (Chiral $S$, $S$, Whelk column, 5% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: $t_r$ (minor) = 37.8 min, $t_r$ (major) = 34.9 min, 77% ee; the syn-diastereomer: $t_r$ (minor) = 47.3 min, $t_r$ (major) = 52.5 min, <5% ee.

**Racemic sample**
Enantio-enriched sample (77 % ee): it was obtained by using ent-L5 ligand.

\[
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\text{Peak} & \text{RetTime} & \text{Type} & \text{Width} & \text{Height} & \text{Area} \\
\# & [\text{min}] & [\text{min}] & [\text{mAU}*] & [\text{mAU}] & \% \\
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1 & 35.63 & BV & 0.7489 & 1.3527e4 & 252.55251 & 6.6802 \\
2 & 36.855 & VB & 0.8558 & 1.3922e4 & 236.16118 & 6.8750 \\
3 & 47.263 & BB & 1.0879 & 8.7084e6 & 1154.61365 & 43.0037 \\
4 & 52.453 & BB & 1.2384 & 8.7970e5 & 1011.78650 & 43.4411 \\
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\text{Totals:} & & & 2.02505e5 & 2655.11383 & \\
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\((R)-4-((S)\text{-chloro}(2\text{-chlorophenyl})\text{methyl})\text{oxazolidin-2-one}\) (S12): by following the general procedure, the product S1 was obtained as a white solid (14 mg, 55% yield, \textit{dr:} 12:1). The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 225 nm). The \textit{anti}-diastereomer: \textit{t}_r (minor) = 19.2 min, \textit{t}_r (major) = 17.1 min, 79% ee; the \textit{syn}-diastereomer: \textit{t}_r (minor) = 23.3 min, \textit{t}_r (major) = 24.4 min, <5% ee.
Racemic sample

Enantio-enriched sample (79% ee): it was obtained by using \textit{ent-L5} ligand.
(R)-4-((S)-chloro(naphthalen-1-yl)methyl)oxazolidin-2-one (S14): by following the general procedure, the product S14 was obtained as a white solid (17 mg, 63% yield, \( dr: 10:1 \)). The ee was determined by Chiral HPLC analysis (Chiral \( S, S \), column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: \( t_c \) (minor) = 36.8 min, \( t_c \) (major) = 33.1 min, 92% ee; the syn-diastereomer: \( t_c \) (minor) = 41.5 min, \( t_c \) (major) = 40.5 min, 26% ee.

Racemic sample

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Enantio-enriched sample (92% ee)

(R)-4-((S)-chloro(naphthalen-2-yl)methyl)oxazolidin-2-one (S15): by following the general procedure under the condition described in entry 8, the product S15 was obtained as a white solid (14 mg, 53% yield, dr: 4.5:1). The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 15% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 225 nm). The anti-diastereomer: t_r (minor) = 21.7 min, t_r (major) = 24.8 min, 89% ee; the syn-diastereomer: t_r (minor) = 28.5 min, t_r (major) = 32.0 min, <5% ee.
Racemic sample

Enantio-enriched sample (89% ee): it was obtained by using *ent*-L5 ligand.

---

**Table 1: Peak RetTime Type Width Area Height Area %**

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**Total:** 6.93910e4 1574.40724

S46
(R)-4-((S)-chloro(pyridin-3-yl)methyl)oxazolidin-2-one (S13): by following the general procedure, the product S13 and its diastereomer were obtained as a white solid (11 mg, 51% yield, $dr: 1.8:1$). Its syn-diastereomer: $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (d, $J = 22.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.35 (t, $J = 6.2$ Hz, 1H), 6.04 (s, 1H), 4.88 (d, $J = 7.6$ Hz, 1H), 4.38 (td, $J = 8.4$, 4.2 Hz, 1H), 4.31 (dd, $J = 8.4$, 8.4 Hz, 1H), 4.06 (dd, $J = 8.6$, 4.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 150.9, 148.8, 135.3, 132.6, 124.1, 66.7, 62.1, 58.5. The ee was determined by Chiral HPLC analysis (Chiral AS-H column, 25% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: $t_c$ (minor) = 42.6 min, $t_c$ (major) = 34.0 min, 70% ee; the syn-diastereomer: $t_c$ (minor) = 23.1 min, $t_c$ (major) = 25.9 min, <5% ee.

Racemic sample

Enantio-enriched sample (70% ee): it was obtained by using ent-L5 ligand.
(R)-4-((S)-chloro(o-tolyl)methyl)oxazolidin-2-one (S19a): by following the general procedure, the product S19a and its diastereomer were obtained as a white solid (18 mg, 78% yield, dr: 2.0:1). The ee was determined by Chiral HPLC analysis after benzylation (Chiral OD-H column, 10% isopropanol in hexanes, flow rate = 1.0 mL/min, UV detection at 254 nm). The anti-diastereomer: t_r (minor) = 26.7 min, t_r (major) = 24.9 min, 54% ee.
Racemic sample of the $S19c$ 

Enantio-enriched sample of $S19c$ (54% ee)
**S19b**

(R)-4-((R)-chloro(o-tolyl)methyl)oxazolidin-2-one (S19b, separable from S19a): $^1$H NMR (400 MHz, CDCl$_3$): δ 6.04 (s, 1H), 4.55 – 4.39 (m, 1H), 4.21 (q, $J = 5.4$, 5.0 Hz, 2H), 3.73 (t, $J = 5.6$ Hz, 1H), 1.86–1.71 (m, 3H), 1.72–1.51 (m, 3H), 1.24 (dddd, $J = 31.7$, 20.2, 8.0, 3.2 Hz, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.9, 70.5, 67.6, 55.0, 40.6, 30.7, 27.9, 25.9, 25.8, 25.7; IR $\nu_{\text{max}}$(neat)/cm$^{-1}$: 2920 (s), 2857(s), 1765 (s), 1434 (w), 1352 (m), 1245(s), 1130(s), 1030 (s), 824 (s); HRMS (ESI, $m/z$): calcd for C$_{10}$H$_{17}$O$_2$NCl$^+$ (M + H$^+$), 218.0942, found 218.0937. The ee was determined by Chiral HPLC analysis after benzylation (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 254 nm). The anti-diastereomer: $t_c$(minor) = 12.0 min, $t_c$(major) = 21.3 min, 10% ee.

**Racemic sample of the S19d**

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Enantio-enriched sample of S19d (10% ee)

(R)-4-((S)-1-chloro-1-phenylethyl)oxazolidin-2-one (S17b): by following the general procedure with ligand L6 and carrying out reaction at -40 °C, the product S17b and its syn-diastereomer S17a were obtained as a white solid (10 mg, 45% yield, dr: 2.3:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57–7.49 (m, 2H), 7.44–7.32 (m, 3H), 4.41 (dd, $J = 9.0$, 4.3 Hz, 1H), 4.26 (t, $J = 9.2$ Hz, 1H), 4.09 (dd, $J = 9.6$, 4.3 Hz, 1H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.5, 140.1, 129.0, 128.9, 126.5, 73.6, 66.2, 62.6, 29.7, 24.3; IR $v_{\text{max}}$ (neat)/cm$^{-1}$: 3260 (m), 3136 (w), 2984 (w), 2921 (w), 1749(s), 1040 (w), 1236 (m), 1046 (m), 701 (m); HRMS (ESI, $m$/z): calcd for C$_{11}$H$_{13}$NO$_2$Cl$^+$ (M + H$^+$), 226.0635, found 226.0640. The ee was determined by Chiral HPLC analysis (Chiral OD-H column, 10% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The anti-diastereomer: $t_s$ (minor) = 18.3 min, $t_r$ (major) = 25.8 min, 86% ee; the syn-diastereomer: $t_s$ (minor) = 23.0 min, $t_r$ (major) = 20.8 min, 50% ee. 
Racemic sample

Enantio-enriched sample S17b (86% ee): it was obtained by using L6 ligand.

Enantio-enriched sample S17a (50 % ee): it was obtained by using L6 ligand.
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**tert-Butyl ((1S,2R)-1-chloro-3-hydroxy-1-phenylpropan-2-yl)carbamate (4):** by following a literature procedure, 4 was obtained from 2a (87% yield for two steps). At room temperature, to a round bottom flask equipped with a magnetic stir bar were added 2a (0.2 mmol, 1.0 equiv), anhydrous CH$_2$Cl$_2$ (3 mL), Et$_3$N (0.24 mmol, 1.2 equiv), DMAP (0.02 mmol, 0.1 equiv) and Boc$_2$O (0.3 mmol, 1.5 equiv). The reaction mixture was then stirred at room temperature until 2a was fully consumed monitored by TLC. After evaporating the solvent, the residue was purified through gradient silica gel flash column chromatography (hexanes/EtOAc: from 6:1 to 2:1) to afford the N-Boc-protected intermediate (61 mg, 99% yield). The obtained N-Boc-protected intermediate (0.2 mmol, 1.0 equiv) was dissolved in MeOH (2 mL); Cs$_2$CO$_3$ (0.02 mmol) was added and the mixture was stirred at room temperature until all the starting material was consumed. The reaction was quenched with saturated NH$_4$Cl solution. After removal of MeOH, the aqueous phase was extracted with CH$_2$Cl$_2$ (4 × 5 mL) and then dried over anhydrous Na$_2$SO$_4$. After evaporating the solvent, the residue was purified through gradient silica gel flash column chromatography (hexanes/EtOAc: from 6:1 to 3:1) to afford chloro amino alcohol 4 (51 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.40–7.27 (m, 3H), 5.15 (d, $J = 5.5$ Hz, 1H), 4.96 (d, $J = 8.8$ Hz, 1H), 4.15–4.09 (m, 1H), 4.04 (dd, $J = 11.3$, 4.7 Hz, 1H), 3.75 (dd, $J = 11.3$, 3.6 Hz, 1H), 2.04 (s, 1H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.4, 138.0, 128.5, 128.5, 127.9, 80.0, 62.2, 61.9, 57.6, 28.2; IR $\nu_{	ext{max}}$ (neat)/cm$^{-1}$: 3316 (br), 2977 (m), 2970 (w), 1744 (s), 1691(s), 1498 (m), 1455 (m), 1392 (m), 1367 (m), 1250 (m), 1168 (s), 1052 (m), 698 (m); HRMS (ESI, m/z): calcd for C$_{14}$H$_{21}$NO$_3$Cl$^+$ (M + H$^+$), 286.1192, found 286.1195.
The enantio-enriched 4 was obtained from enantio-enriched 2a (obtained by using \textit{ent-}L5 ligand) by following the above procedure. \textit{(dr: 15:1, 85\% yield over two steps). \([\alpha]_D^{20} = -31^\circ \text{ c 1.0, CH}_2\text{Cl}_2\). The \textit{ee} was determined by Chiral HPLC analysis (Chiral OD-H column, 5\% EtOH in hexanes, flow rate = 1.0 mL/min, UV detection at 215 nm): \(t_r\) (minor) = 9.9 min, \(t_r\) (major) = 7.1 min, 88\% \textit{ee}.}

\textit{Racemic sample of 4 (dr: 1:1)}

\begin{tabular}{cccccc}
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\textbf{Peak} & \textbf{Ret Time} & \textbf{Type} & \textbf{Width} & \textbf{Area} & \textbf{Height} & \textbf{Area} \\
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1 & 7.132 VB & & 0.3206 & 758.65222 & 34.76191 & 25.0030 \\
2 & 8.839 BV & & 0.5054 & 1514.52441 & 49.99388 & 49.9144 \\
3 & 9.882 VB & & 0.4009 & 761.06787 & 29.70838 & 25.0826 \\
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\end{tabular}

\textit{Totals}:

3034.24451 114.46416

\textit{Racemic sample of 4 (dr >20:1)}

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2 & 9.755 MM & & 0.4151 & 1.01035e4 & 405.66406 & 49.9936 \\
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\textit{Totals}:

2.02095e4 895.14240
Enantio-enriched sample of 4 (dr: 15:1, 88% ee.)

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Totals: 5.32541e4 2172.01236
D. Mechanistic Investigation of the Iron-Catalyzed Asymmetric Olefin Aminochlorination

a. Fe(NTf₂)₂-Catalyzed Asymmetric Aminochlorination and Aminohydroxylation with Isomeric Olefins

**Procedure.** To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added Fe(NTf₂)₂ (9.2 mg, 0.015 mmol, 15 mol %) and ligand L5 (7.3 mg, 0.015 mmol, 15 mol %). After the vial was evacuated and backfilled with N₂ for three times, CHCl₃ (1.0 mL, re-distilled and anhydrous) was added and the mixture was stirred at room temperature for 20 min. Meanwhile, a second flame-dried and N₂-protected 2-dram vial (vial B) with a magnetic stir bar was charged with the substrate (1 or 1′, 0.1 mmol), anhydrous TBAC (69.5 mg, 0.25 mmol), freshly activated 4 Å molecular sieves and CHCl₃ (3.0 mL, re-distilled and anhydrous). Both vials were degassed by brief evacuation and back filling with N₂ twice. Vial B was cooled down to -60 °C, and the catalyst solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at this temperature for 12 h and then quenched with 1 mL saturated NaHCO₃ solution. The reaction mixture was extracted with CH₂Cl₂ (1.5 mL × 3), and the combined organic phase was concentrated *in vacuo*. The residue was purified through a gradient
silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford both the aminochlorination product $2a/b$ and the aminohydroxylation product $5a/b$. The $dr$ was determined by $^1$H NMR analysis and the $ee$ of $2a/b$ was directly measured by chiral HPLC analysis. The $ee$ of $5a/b$ was measured after the hydrolysis.\(^1\)

b. Rate Acceleration Effect of External Chloride Ion

Procedure. These experiments were carried out under the condition described above, except in the absence of TBAC. Under this condition, both $1$ and $1'$ were fully recovered.

c. FeCl$_2$-Catalyzed and Mediated Asymmetric Olefin Aminochlorination Reactions

Procedure. To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added FeCl$_2$ (0.015 mmol, 15 mol %) and ligand L5 (7.3 mg, 0.015 mmol, 15 mol %). After the vial was evacuated and backfilled with N$_2$ for three times, CHCl$_3$ (1.0 mL, re-distilled and anhydrous) was added and the mixture was stirred at room temperature for 20 min. Meanwhile, a second flame-dried and N$_2$-protected 2-dram vial (vial B) with a magnetic stir bar was charged with $1$ (0.1 mmol), anhydrous TBAC (69.5 mg, 0.25 mmol), freshly activated 4 Å molecular sieves and CHCl$_3$ (3.0 mL, re-distilled and anhydrous). Both vials were degassed by brief evacuation and back filling with N$_2$ twice. Vial B was cooled down to -60 °C, and the catalyst solution in vial A was added to vial B drop wise via a syringe. The resulting solution
was stirred at this temperature for 12 h and then quenched with 1 mL saturated NaHCO₃ solution. The reaction mixture was extracted with CH₂Cl₂ (1.5 mL × 3), and the combined organic phase was concentrated in vacuo. The residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford both the aminochlorination product 2a/b and the aminohydroxylation product 5a/b. The dr was determined by ¹H NMR analysis and the ee of 2a/b was directly measured by chiral HPLC analysis. The ee of 5a/b was measured after the hydrolysis.

**Procedure.** To a flame-dried sealable 2-dram vial (vial A) equipped with a magnetic stir bar were added FeCl₂ (0.1 mmol, 100 mol %) and ligand L₅ (0.1 mmol, 100 mol %). After the vial was evacuated and backfilled with N₂ three times, CHCl₃ (1.0 mL, re-distilled and anhydrous) was added and the mixture was stirred at room temperature for 20 min. Meanwhile, a second flame-dried and N₂-protected 2-dram vial (vial B) with a magnetic stir bar was charged with 1 (0.1 mmol), freshly activated 4 Å molecular sieves and CHCl₃ (3.0 mL, re-distilled and anhydrous). Both vials were degassed by brief evacuation and back filling with N₂ twice. Vial B was cooled down to -60 °C, and the catalyst solution in vial A was added to vial B drop wise via a syringe. The resulting solution was stirred at this temperature for 12 h and then quenched with 1 mL saturated NaHCO₃ solution. The reaction mixture was extracted with CH₂Cl₂ (1.5 mL × 3), and the combined organic phase was concentrated in vacuo. The residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford both the aminochlorination product 2a/b, the aminohydroxylation product 5a, and the aziridine 6. The dr was determined by ¹H NMR analysis and the ee of 2a/b and 6 was directly measured by chiral HPLC analysis. The ee of 5a was measured after the hydrolysis.
E. References

F. NMR Spectra

(CDC13, 400 MHz)
$dr > 20:1$

(CDC13, 100 MHz)
$dr > 20:1$
S10
(CDCl₃, 400 MHz)
dr > 20:1

S10
(CDCl₃, 100 MHz)
dr > 20:1
S11
(CDC\textsubscript{3}, 400 MHz)
\(d_r > 20:1\)

S11
(CDC\textsubscript{3}, 100 MHz)
\(d_r > 20:1\)
(CDCl₃, 400 MHz)  

\( dr = 12:1 \)

(CDCl₃, 100 MHz)  

\( dr = 12:1 \)
(CD$_3$CN, 400 MHz)
$dr > 20:1$

$S14$

$S14$

(100 MHz)
$dr > 20:1$

$S14$
Minor diastereomer
S19a
(CDCls, 400 MHz)

S19a
(CDCls, 100 MHz)
minor diastereomer

major diastereomer
S22
(CDCl₃, 400 MHz)
dr > 20:1

S22
(CDCl₃, 100 MHz)
dr > 20:1
S33
(CDCl₃, 400 MHz)

S33
(CDCl₃, 100 MHz)
(CDCl₃, 400 MHz) δr > 20:1

(CDCl₃, 100 MHz) δr > 20:1
Minor diastereomer