Supporting Information

Ru-Catalyzed Highly Diastereoselective Hydrogenation of N-tert-Butylsulfinyl Ketimines for the Synthesis of aryl glycine Derivatives

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Contents

1. General Information \hspace{1cm} S2
2. General Procedure for the Synthesis of substrates \hspace{1cm} S2
3. The absolute configuration of substrates \hspace{1cm} S9
4. Typical procedures for the Asymmetric Hydrogenation \hspace{1cm} S9
5. Synthesis of Aryl Amino Alcohol 5i \hspace{1cm} S18
6. References \hspace{1cm} S18
7. Spectral copies of \textsuperscript{1}H NMR \hspace{0.5cm}, \textsuperscript{13}C NMR \hspace{1cm} S20
8. Spectral copies of HPLC \hspace{1cm} S62
1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. Ru-MACHO catalyst was synthesized according to the reported method.\textsuperscript{1-4} \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer in CDCl\textsubscript{3} using tetramethylsilane (TMS) as the internal standard. All spectra are referenced to the CDCl\textsubscript{3} residual CHCl\textsubscript{3} peak (\textsuperscript{1}H NMR = 7.26 ppm; \textsuperscript{13}C NMR = 77.1 ppm). All coupling constants (\( J \) values) were reported in Hertz (Hz). Data are presented as follows: chemical shift in ppm and multiplicity as s = singlet, d = doublet, t = triplet, and m = multiplet. Single crystal X-ray data were collected at 100(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu K\( \alpha \) radiation (\( \lambda = 1.54178 \) Å). Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F\textsubscript{254} plates and visualization on TLC was achieved by UV light (254 nm). All chemical shifts are quoted in parts per million (ppm), measured from the center of the signal except in the case of multiplets of more than one proton, which are quoted as a range. Coupling constants are quoted to the nearest 0.1 Hz Coupling constants are quoted to the nearest 0.1 Hz. HRMS (ESI) were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

2. General Procedure for the Synthesis of \textit{N-tert-}Butanesulfinyl Ketimine Esters\textsuperscript{5}

A 250 mL, two-necked, round-bottomed flask was charged with \( \alpha \)-keto esters (20.0 mmol), THF (50 mL), \textit{tert-}butanesulfinamidine (22.0 mmol), and Ti(O\textsubscript{i}Pr)\textsubscript{4} (30.0 mmol) under nitrogen atm. The reaction mixture was then heated at reflux at 65 °C for 6 h. After completion, the reaction was allowed to cool to rt. Isopropyl acetate (50 mL) and saturated NaCl solution (50 mL) were then added and the mixture was stirred for 1 h. The solids were removed by filtration, and the filtrate was washed with water (2 \( \times \) 50 mL). The organic phase was evaporated under vacuum to dryness to obtain the crude product. The crude product was purified by flash column chromatography (silica gel, PE:EtOAc = 15:1) to afford the pure \textit{N-tert-}butanesulfinyl ketimine esters.

\textit{(S,Z)-Isopropyl 2-[(tert-butyisulfinyl)imino]-2-phenylacetate} (1a): yellow solid; 80\% yield; m.p. = 41.3-44.4 °C; \( R_f \) (PE:EtOAc = 5:1) 0.51; [\( \alpha \)]\textsubscript{D}\textsuperscript{20} = +45.0 (c = 0.1 in MeOH); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 7.77 (d, \( J = 8.0 \) Hz, 2H), 7.53-7.50 (m, 1H), 7.44 (t, \( J = 7.6 \) Hz, 2H), 5.40-5.31 (m, 1H), 1.40 (t, \( J = 7.2 \) Hz, 6H), 1.34 (s, 9H);
\[^{13}\text{C}\text{ NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 165.3, 163.6, 133.4, 132.6, 129.0, 127.9, 70.7, 59.6, 23.1, 22.0, 21.8;\ HRMS\ (ESI)\ \text{calcd\ for\ } C_{15}H_{23}NO_3S\ [M+Na]^+\ 318.1134,\ \text{found}\ 318.1136.\]

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\text{S=O}\
\\text{Et}
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\((S,Z)-\text{ethyl\ 2-[(tert-butylsulfinyl)imino]-2-phenylacetate\ (1b):\ yellow\ oil;\ 72\%\ yield;\ R_f\ (\text{PE:EtOAc}\ =\ 5:1)\ 0.40;\ [\alpha]_D^{20} = +40.0\ (c = 0.1\ in\ MeOH);\ ^1\text{H}\text{ NMR}\ (400\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 7.75\ (d, J = 8.0\ Hz, 2H), 7.49\ (t, J = 7.2\ Hz, 1H), 7.42\ (t, J = 7.6\ Hz, 2H), 4.48-4.39\ (m, 2H), 1.38\ (t, J = 7.2\ Hz, 3H), 1.31\ (s, 9H);\ ^{13}\text{C}\text{ NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 165.8, 163.3, 133.1, 132.7, 128.9, 127.9, 62.3, 59.5, 23.0, 14.0.\ HRMS\ (ESI)\ \text{calcd\ for\ } C_{14}H_{19}NO_3S\ [M+Na]^+\ 304.0978,\ \text{found}\ 304.0983.\]

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\((S,Z)-\text{Methyl\ 2-[(tert-butylsulfinyl)imino]-2-phenylacetate\ (1c):\ yellow\ solid;\ 60\%\ yield;\ m.p. = 47.5-50.1\ 0^\circ\text{C};\ R_f\ (\text{PE:EtOAc}\ =\ 5:1)\ 0.35;\ [\alpha]_D^{20} = +37.0\ (c = 0.1\ in\ MeOH);\ ^1\text{H}\text{ NMR}\ (400\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 7.76\ (d, J = 7.6\ Hz, 2H), 7.53\ (t, J = 7.2\ Hz, 1H), 7.45\ (t, J = 7.6\ Hz, 2H), 3.98\ (s, 3H), 1.35\ (s, 9H);\ ^{13}\text{C}\text{ NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 166.5, 163.2, 133.1, 132.8, 129.0, 128.0, 59.7, 52.9, 23.1.\ HRMS\ (ESI)\ \text{calcd\ for\ } C_{13}H_{17}NO_3S\ [M+Na]^+\ 290.0821,\ \text{found}\ 290.0826.\]

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\\text{OPr}
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\((S,Z)-\text{Isopropyl\ 2-[(tert-butylsulfinyl)imino]-2-(o-tolyl)acetate\ (1d):\ yellow\ solid;\ 75\%\ yield;\ m.p. = 52.7-55.2\ 0^\circ\text{C};\ R_f\ (\text{PE:EtOAc}\ =\ 5:1)\ 0.56;\ [\alpha]_D^{20} = +69.0\ (c = 0.1\ in\ MeOH);\ ^1\text{H}\text{ NMR}\ (400\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 7.53\ (d, J = 7.6\ Hz, 1H), 7.38-7.35\ (m, 1H), 7.28-7.24\ (m, 2H), 5.32-5.26\ (m, 1H), 2.56\ (s, 3H), 1.40-1.34\ (m, 15H);\ ^{13}\text{C}\text{ NMR}\ (100\ \text{MHz, CDCl}_3)\ \delta\ (\text{ppm})\ 166.2, 165.4, 138.6, 133.1, 132.2, 131.2, 129.2, 126.2, 70.7, 58.7, 23.0, 22.4, 21.8, 21.7;\ HRMS\ (ESI)\ \text{calcd\ for\ } C_{16}H_{23}NO_3S\ [M+Na]^+\ 332.1291,\ \text{found}\ 332.1286.\)
(S,Z)-Isopropyl 2-[(tert-butylsufinyl)imino]-2-(m-tolyl)acetate (1e): yellow solid; 79% yield; m.p. = 54.3-57.9 °C; Rf (PE:EtOAc = 5:1) 0.54; [α]D20 = + 31.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.57 (s, 2H), 7.33 (d, J = 5.2 Hz, 2H), 5.40-5.33 (m, 1H), 2.39 (s, 3H), 1.41 (t, J = 7.2 Hz, 6H), 1.34 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.4, 163.8, 138.8, 133.5, 133.4, 128.9, 128.4, 125.2, 70.6, 59.5, 23.2, 22.0, 21.8, 21.5; HRMS (ESI) calcd for C16H23NO3S [M+Na]+ 332.1291, found 332.1285.

(S,Z)-Isopropyl 2-[(tert-butylsufinyl)imino]-2-(p-tolyl)acetate (1f): yellow solid; 85% yield; m.p. = 55.5-58.4 °C; Rf (PE:EtOAc = 5:1) 0.50; [α]D20 = + 22.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.59 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 5.31-5.25 (m, 1H), 2.33 (s, 3H), 1.33 (t, J = 7.2 Hz, 6H), 1.26 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.4, 163.5, 143.5, 130.8, 129.7, 128.0, 120.9, 128.4, 125.2, 70.6, 59.4, 23.1, 22.0, 21.8, 21.7; HRMS (ESI) calcd for C16H23NO3S [M+Na]+ 332.1291, found 332.1283.

(S,Z)-Isopropyl 2-[(tert-butylsufinyl)imino]-2-(2-methoxyphenyl)acetate (1g): yellow solid; 68% yield; m.p. = 76.5-78.8 °C; Rf (PE:EtOAc = 5:1) 0.43; [α]D20 = + 71.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.82 (d, J = 6.8 Hz), 7.47 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 5.27-5.21 (m, 1H), 3.83 (s, 3H), 1.40 (d, J = 6.4 Hz, 6H), 1.34 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 164.6, 164.1, 158.7, 134.1, 130.6, 123.7, 121.2, 112.0, 70.2, 59.0, 55.7, 23.0, 21.9, 21.6; HRMS (ESI) calcd for C16H23NO4S [M+Na]+ 348.1240, found 348.1229.
(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(3-methoxyphenyl)acetate (1h): yellow solid; 75% yield; m.p. = 36.1-38.8 °C; Rf (PE:EtOAc = 5:1) 0.35; [α]D20 = +24.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.38-7.31 (m, 3H), 7.07 (d, J = 7.6 Hz, 1H), 5.39-5.33 (m, 1H), 3.83 (s, 3H), 1.41 (t, J = 7.2 Hz, 6H), 1.34 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.3, 163.4, 160.0, 134.7, 130.0, 120.6, 118.8, 112.7, 70.7, 59.6, 55.5, 23.2, 22.0, 21.8; HRMS (ESI) calcd for C16H23NO4S [M+Na]+ 348.1240, found 348.1232.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(4-methoxyphenyl)acetate (1i): yellow oil; 83% yield; Rf (PE:EtOAc = 5:1) 0.27; [α]D20 = +9.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.73 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.40-5.30 (m, 1H), 3.87 (s, 3H), 1.41 (t, J = 7.2 Hz, 6H), 1.32 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.5, 163.3, 163.0, 130.0, 126.2, 114.4, 70.5, 59.3, 55.6, 23.1, 22.0, 21.8; HRMS (ESI) calcd for C16H23NO4S [M+Na]+ 348.1234, found 348.1234.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(2-fluorophenyl)acetate (1j): yellow solid; 70% yield; m.p. = 45.9-49.7 °C; Rf (PE:EtOAc = 5:1) 0.51; [α]D20 = +42.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.84 (t, J = 7.6 Hz, 1H), 7.53-7.48 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 8.4 Hz, 1H), 5.35-5.27 (m, 1H), 1.40-1.36 (m, 15H); 13C NMR (100 MHz, CDCl3) δ (ppm) 164.6, 162.7, 160.3 (JCF = 45.4 Hz, 1C), 134.4 (JCF = 9.0 Hz, 1C), 130.1, 124.7, 122.3 (JCF = 9.7 Hz, 1C), 116.9 (JCF = 21.8 Hz, 1C), 70.8, 59.6, 23.1, 21.6, 21.5; HRMS (ESI) calcd for C15H20FNO3S [M+Na]+ 336.1040, found 336.1041.
(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(4-fluorophenyl)acetate (1k): yellow solid; 76% yield; m.p. = 65.4-66.9 °C; Rf (PE:EtOAc = 5:1) 0.56; [α]D^20 = + 36.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.79-7.76 (m, 2H), 7.12 (t, J = 8.4 Hz, 2H), 5.39-5.30 (m, 1H), 1.40 (t, J = 7.2 Hz, 6H), 1.33 (s, 9H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 166.7, 165.2, 163.3 (J_C-F = 182.6 Hz, 1C), 130.3 (J_C-F = 9.1 Hz, 1C), 129.8 (J_C-F = 2.9 Hz, 1C), 116.3 (J_C-F = 22.0 Hz, 1C), 70.9, 59.6, 23.1, 22.0, 21.8; HRMS (ESI) calcd for C₁₅H₂₀FNO₃S [M+Na]^+ 336.1040, found 336.1037.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(3-chlorophenyl)acetate (1l): yellow solid; 70% yield; m.p. = 68.0-74.0 °C; Rf (PE:EtOAc = 5:1) 0.57; [α]D^20 = + 55.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.77 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 5.39-5.33 (m, 1H), 1.43-1.39 (m, 6H), 1.35 (s, 9H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 164.9, 162.2, 135.2, 135.0, 132.6, 130.3, 127.8, 126.0, 71.0, 59.9, 23.2, 22.0, 21.7; HRMS (ESI) calcd for C₁₅H₂₀ClNO₃S [M+Na]^+ 352.0745, found 352.0747.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(4-chlorophenyl)acetate (1m): yellow solid; 73% yield; m.p. = 62.2-65.0 °C; Rf (PE:EtOAc = 5:1) 0.63; [α]D^20 = + 32.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.70 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 5.40-5.30 (m, 1H), 1.42-1.39 (m, 6H), 1.33 (s, 9H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 165.0, 162.4, 139.0, 131.9, 129.3, 129.2, 70.9, 59.8, 23.2, 22.0, 21.8; HRMS (ESI) calcd for C₁₅H₂₀ClNO₃S [M+Na]^+ 352.0750, found 352.0742.
(S,Z)-Isopropyl 2-(3-bromophenyl)-2-[(tert-butylsulfinyl)imino]acetate (1n): yellow solid; 68% yield; m.p. = 71.9-74.8 °C; Rf (PE:EtOAc = 5:1) 0.54; [α]D 20 = +24.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.92 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 5.39-5.33 (m, 1H), 1.43-1.39 (m, 6H), 1.34 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 164.9, 162.1, 135.5, 135.3, 130.8, 130.5, 126.5, 123.2, 71.0, 59.9, 23.2, 21.9, 21.7; HRMS (ESI) calcd for C15H20BrNO3S [M+Na]+ 396.0239, found 396.0232.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(4-bromophenyl)acetate (1o): yellow solid; 72% yield; m.p. = 66.7-70.1 °C; Rf (PE:EtOAc = 5:1) 0.56; [α]D 20 = +12.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.60 (q, J = 8.8 Hz, 4H), 5.38-5.29 (m, 1H), 1.41-1.37 (m, 6H), 1.32 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.0, 162.5, 132.3, 129.3, 127.9, 127.6, 70.9, 59.7, 23.2, 21.9, 21.7; HRMS (ESI) calcd for C15H20BrNO3S [M+Na]+ 396.0245, found 396.0232.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(3,5-dimethylphenyl)acetate (1p): yellow solid; 72% yield; m.p. = 75.8-80.0 °C; Rf (PE:EtOAc = 5:1) 0.49; [α]D 20 = +22.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.36 (s, 2H), 7.15 (s, 1H), 5.40-5.31 (m, 1H), 2.34 (s, 6H), 1.40 (t, J = 7.2 Hz, 6H), 1.33 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.5, 163.9, 138.6, 134.4, 133.4, 125.7, 70.5, 59.5, 23.2, 22.0, 21.8, 21.4; HRMS (ESI) calcd for C17H25NO3S [M+Na]+ 346.1447, found 346.1438.
(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(2,4-dimethylphenyl)acetate (1q): yellow oil; 68% yield; R<sub>f</sub> (PE:EtOAc = 5:1) 0.52; [α]<sub>D</sub><sup>20</sup> = + 53.0 (c = 0.1 in MeOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.42 (d, <i>J</i> = 7.6 Hz, 1H), 7.06 (d, <i>J</i> = 10.4 Hz, 2H), 5.31-5.26 (m, 1H), 2.53 (s, 3H), 2.34 (s, 3H), 1.39-1.32 (m, 15H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.9, 165.3, 141.8, 138.7, 133.1, 129.8, 129.4, 126.7, 70.3, 58.3, 22.8, 22.5, 21.7, 21.5, 21.2; HRMS (ESI) calcd for C<sub>17</sub>H<sub>25</sub>NO<sub>3</sub>S [M+Na]<sup>+</sup> 346.1447, found 346.1436.

(S,Z)-Isopropyl 2-(benzo[d][1,3]dioxol-5-yl)-2-[(tert-butylsulfinyl)imino]acetate (1r): yellow oil; 72% yield; R<sub>f</sub> (PE:EtOAc = 5:1) 0.34; [α]<sub>D</sub><sup>20</sup> = + 11.0 (c = 0.1 in MeOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.31 (s, 1H), 7.21 (d, <i>J</i> = 8.2 Hz, 1H), 6.82 (d, <i>J</i> = 8.2 Hz, 1H), 6.03 (s, 2H), 5.36-5.27 (m, 1H), 1.39 (t, <i>J</i> = 7.2 Hz, 6H), 1.30 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.3, 162.8, 151.6, 148.5, 128.0, 124.2, 108.4, 107.3, 102.0, 70.7, 59.4, 23.1, 21.9, 21.7; HRMS (ESI) calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>5</sub>S [M+Na]<sup>+</sup> 362.1033, found 362.1027.

(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)imino]-2-(naphthalen-2-yl)acetate (1s): yellow solid; 73% yield; m.p. = 54.0-57.8 °C; R<sub>f</sub> (PE:EtOAc = 5:1) 0.46; [α]<sub>D</sub><sup>20</sup> = + 61.0 (c = 0.1 in MeOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.13 (s, 1H), 7.96 (d, <i>J</i> = 8.8 Hz, 1H), 7.89-7.85 (m, 3H), 7.60-7.52 (m, 2H), 5.49-5.39 (m, 1H), 1.47-1.43 (m, 6H), 1.38 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.4, 163.6, 135.3, 132.8, 130.8, 129.7, 129.5, 128.9, 128.6, 127.9, 127.1, 123.6, 70.7, 59.7, 23.2, 22.0, 21.8; HRMS (ESI) calcd for C<sub>19</sub>H<sub>23</sub>NO<sub>3</sub>S [M+Na]<sup>+</sup> 368.1291, found 368.1281.
(S,Z)-Isopropyl 2-[(tert-butylsulfinyl)iminoo]-2-(phenanthren-9-yl)acetate (1t): yellow solid; 62% yield; m.p. = 101.8-104.0 °C; R f(PE:EtOAc = 5:1) 0.39; [α] D 20 = +50.0 (c = 0.1 in MeOH); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.82 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 7.6 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.13 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.73-7.66 (m, 3H), 7.62 (t, J = 7.6 Hz, 1H), 5.43-5.34 (m, 1H), 1.43-1.38 (m, 15H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.9, 165.0, 131.6, 131.0, 130.5, 130.2, 130.1, 129.9, 128.9, 128.7, 127.2, 126.5, 123.1, 122.7, 70.8, 59.1, 23.0, 21.8, 21.6; HRMS (ESI) calcd for C23H25NO3S [M+Na]+ 418.1453, found 418.1429.

3. The absolute configuration of substrates

In order to confirm the absolute configuration of substrates, the X-ray diffraction analysis has been carried out with one substrate 1k, the crystal can be obtained from a petroleum ether solution at -18 °C. The full crystallographic data for 1k (CCDC 1550986) can be obtained free for charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

4. Typical procedures for the Asymmetric Hydrogenation of N-tert-Butanesulfinyl Ketimine Esters

A glass liner containing a stir bar was charged with ketamine ester (0.15 mmol), Ru-MACHO (0.003 mmol, 2 mol %), CH3ONa (0.03 mmol, 20 mol %), and toluene
(0.7 mL) in that order at air. The glass liner was then placed into an autoclave followed by degassing with H₂ three times. The hydrogenation was carried out at 50 bar H₂ with stirring at 25-40 °C for 24 h. After the reaction finished, the autoclave was allowed to cool down to r.t. The hydrogen gas was then carefully released in a fume hood, and the solution transferred to a flask to evaporate under vacuum to dryness to obtain the crude product. The crude product was purified by flash column chromatography (silica gel, PE:EtOAc=5:1-2:1) to afford the corresponding product.

(R)-Isopropyl 2-[(S)-1,1-dimethylethylsulfinamido]-2-phenylacetate (2a): colorless oil; 96% yield; Rf (PE:EtOAc = 2:1) 0.62; [α]D20 = - 16.0 (c = 0.1 in MeOH); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.41 (d, J = 6.4 Hz, 2H), 7.40-7.31 (m, 3H), 5.07 (d, J = 6.0 Hz, 1H), 5.04-4.98 (m, 1H), 4.23 (d, J = 6.0 Hz, 1H), 1.25 (d, J = 6.4 Hz, 3H), 1.20 (s, 9H), 1.08 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 171.0, 137.4, 128.9, 128.6, 127.6, 69.7, 59.4, 56.9, 22.7, 21.8, 21.5; HRMS (ESI) calcd for C₁₅H₂₃NO₃S [M+Na]⁺ 320.1296, found 320.1289. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min⁻¹; column temp, 30 °C; detection, UV 220 nm; retention time (tᵣ) of (R)-2a, 27.4 min (>99.9 %).

(R)-Ethyl 2-[(S)-1,1-dimethylethylsulfinamido]-2-phenylacetate (2b): colorless oil; 92% yield; Rf (PE:EtOAc = 2:1) 0.57; [α]D20 = - 18.0 (c = 0.1 in MeOH); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43 (d, J = 6.8 Hz, 2H), 7.38-7.33 (m, 3H), 5.12 (d, J = 6.0 Hz, 1H), 4.26-4.11 (m, 1H), 3.59 (s, 2H), 1.22-1.19 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 17.5, 137.3, 129.0, 128.7, 127.7, 61.9, 59.1, 22.6, 14.1; HRMS (ESI) calcd for C₁₄H₂₁NO₃S [M+Na]⁺ 306.1134, found 306.1139. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min⁻¹; column temp, 30 °C; detection, UV 220 nm; retention time (tᵣ) of (R)-2b, 26.6 min (>99.9 %).
(R)-Methyl 2-[(S)-tert-butyulsulfinyl]amino]-2-phenylacetate (2c): colorless oil; 93% yield; $R_f$ (PE:EtOAc = 2:1) 0.40; [α]$_D^{20}$ = - 25.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.42-7.33 (m, 5H), 5.13 (d, $J$ = 6.0 Hz, 1H), 4.23 (d, $J$ = 5.6 Hz, 1H), 3.71 (s, 3H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.0, 137.2, 129.1, 128.9, 127.7, 59.0, 57.0, 52.9, 22.6; HRMS (ESI) calcd for C$_{13}$H$_{19}$NO$_3$S [M+Na]$^+$ 292.0978, found 292.0982. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time ($t_R$) of (R)-2c, 30.36 min (>99.9 %).

(R)-Isopropyl 2-(o-tolyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2d): colorless oil; 72% yield; $R_f$ (PE:EtOAc = 2:1) 0.44; [α]$_D^{20}$ = - 10.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.32 (d, $J$ = 7.2 Hz, 1H), 7.22-7.18 (m, 3H), 5.30 (d, $J$ = 4.8 Hz, 1H), 5.04-4.95 (m, 1H), 4.10 (d, $J$ = 4.4 Hz, 1H), 2.47 (s, 3H), 1.23 (d, $J$ = 6.4 Hz, 3H), 1.18 (s, 9H), 1.05 (d, $J$ = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 171.3, 136.5, 136.0, 131.0, 128.5, 127.3, 126.6, 69.6, 56.7, 55.3, 22.6, 21.8, 21.4, 19.7; HRMS (ESI) calcd for C$_{16}$H$_{25}$NO$_3$S [M+Na]$^+$ 334.1447, found 334.1443. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time ($t_R$) of (R)-2d, 18.5 min (97%); $t_R$ of (S)-2d, 34.0 min (3%).

(R)-Isopropyl 2-(m-tolyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2e): colorless oil; 95% yield; $R_f$ (PE:EtOAc = 2:1) 0.44; [α]$_D^{20}$ = - 12.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.25-7.19 (m, 3H), 7.12 (d, $J$ = 7.2 Hz, 1H), 5.05-4.98 (m, 2H), 4.14 (d, $J$ = 6.0 Hz, 1H), 2.34 (s, 3H), 1.25 (d, $J$ = 6.4 Hz, 3H), 1.21 (s, 9H), 1.09 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 171.0, 138.7, 137.3, 129.4, 128.8, 128.3, 124.6, 69.6, 59.6, 56.9, 22.6, 21.8, 21.5, 21.5; HRMS (ESI) calcd for C$_{16}$H$_{25}$NO$_3$S [M+Na]$^+$ 334.1447, found 334.1444. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time ($t_R$) of (R)-2e, 20.3 min (99.3 %); $t_R$ of (S)-2e, 28.5 min (0.7 %).
(R)-Isopropyl 2-(p-tolyl)-2-[(S)-1,1-dimethylethylsulfamido]acetate (2f): colorless oil; 96% yield; \( \text{Rf (PE:EtOAc = 2:1)} \) 0.45; [\( \alpha \)]\(_D\)\(^{20} \) = - 20.0 (c = 0.1 in MeOH); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.29 (d, \( J = 8.4 \) Hz, 2H), 7.14 (d, \( J = 8.4 \) Hz, 2H), 5.03-4.95 (m, 2H), 4.15 (d, \( J = 6.0 \) Hz, 1H), 2.32 (s, 3H), 1.24 (d, \( J = 6.4 \) Hz, 3H), 1.20 (s, 9H), 1.08 (d, \( J = 6.4 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 171.1, 138.5, 134.4, 129.6, 127.5, 69.6, 59.3, 56.8, 22.6, 21.8, 21.5, 21.3; HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)NO\(_3\)S [M+Na]\(^+\) 334.1447, found 334.1440. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL AD-H; eluent, hexane:2-propanol = 80:20; flow, 0.7 mL min\(^{-1}\); column temp, 30 °C; detection, UV 220 nm; retention time (\( t_R \)) of (R)-2f, 14.9 min (99%); \( t_R \) of (S)-2f, 17.0 min (1%).

(R)-Isopropyl 2-(2-methoxyphenyl)-2-[(S)-1,1-dimethylethylsulfamido]acetate (2g): colorless oil; 96% yield; \( \text{Rf (PE:EtOAc = 2:1)} \) 0.34; [\( \alpha \)]\(_D\)\(^{20} \) = - 7.0 (c = 0.1 in MeOH); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.31-7.26 (m, 2H), 6.94 (t, \( J = 7.6 \) Hz, 1H), 6.88 (d, \( J = 8.4 \) Hz, 1H), 5.22 (d, \( J = 8.4 \) Hz, 1H), 5.08-5.00 (m, 1H), 4.30 (d, \( J = 8.0 \) Hz, 1H), 3.84 (s, 3H), 1.23-1.11 (m, 12H), 1.10 (d, \( J = 6.0 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 171.2, 156.9, 129.8, 129.2, 126.7, 121.0, 111.1, 69.2, 56.9, 56.7, 55.5, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)NO\(_4\)S [M+Na]\(^+\) 350.1397, found 350.1394. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min\(^{-1}\); column temp, 30 °C; detection, UV 220 nm; retention time (\( t_R \)) of (R)-2g, 13.6 min (86%); \( t_R \) of (S)-2g, 20.0 min (14%).

(R)-Isopropyl 2-(3-methoxyphenyl)-2-[(S)-1,1-dimethylethylsulfamido]acetate (2h): colorless oil; 95% yield; \( \text{Rf (PE:EtOAc = 2:1)} \) 0.31; [\( \alpha \)]\(_D\)\(^{20} \) = - 16.0 (c = 0.1 in MeOH); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.30-7.28 (m, 1H), 7.03-6.99 (m, 2H), 6.87 (dd, \( J = 8.4, 6.0 \) Hz, 1H), 5.07-5.02 (m, 2H), 4.25 (d, \( J = 6.0 \) Hz, 1H), 3.82 (s, 3H), 1.27 (d, \( J = 6.4 \) Hz, 3H), 1.22 (s, 9H), 1.12 (d, \( J = 6.4 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 171.1, 157.6, 129.8, 129.2, 126.7, 121.0, 111.1, 69.2, 56.9, 56.7, 55.5, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C\(_{16}\)H\(_{25}\)NO\(_4\)S [M+Na]\(^+\) 350.1397, found 350.1394.
MHz, CDCl₃) δ (ppm) 170.9, 159.9, 138.8, 130.0, 119.9, 114.2, 113.1, 69.7, 59.3, 56.9, 55.4, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C₁₆H₂₅NO₄S [M+Na]⁺ 350.1397, found 350.1395. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min⁻¹; column temp, 30 °C; detection, UV 220 nm; retention time (t_R) of (R)-2h, 33.7 min (100%).

(R)-Isopropyl 2-(4-methoxyphenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2i): colorless oil; 96% yield; R_f (PE:EtOAc = 2:1) 0.50; [α]_D²⁰ = -20.0 (c = 0.1 in MeOH); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.32 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.03-4.97 (m, 2H), 4.12 (d, J = 5.6 Hz, 1H), 3.79 (s, 3H), 1.24 (d, J = 6.0 Hz, 3H), 1.20 (s, 9H), 1.08 (d, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 171.1, 159.8, 129.5, 128.9, 114.3, 69.5, 59.1, 56.8, 55.4, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C₁₆H₂₅NO₄S [M+Na]⁺ 350.1397, found 350.1391. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL AD-H; eluent, hexane:2-propanol = 80:20; flow, 0.7 mL min⁻¹; column temp, 30 °C; detection, UV 220 nm; retention time (t_R) of (R)-2i, 12.7 min (99.6%); t_R of (S)-2i, 14.3 min (0.4%).

(R)-Isopropyl 2-(2-fluorophenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2j): colorless oil; 94% yield; R_f (PE:EtOAc = 2:1) 0.49; [α]_D²⁰ = -15.0 (c = 0.1 in MeOH); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30 (t, J = 7.2 Hz, 1H), 7.27-7.20 (m, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 9.6 Hz, 1H), 5.23 (d, J = 7.6 Hz, 1H), 5.01-4.91 (m, 1H), 4.35 (d, J = 7.6 Hz, 1H), 1.18-1.12 (m, 12H), 1.01 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.4, 160.4 (J_C-F = 247.0 Hz, 1C), 130.3 (J_C-F = 8.4 Hz, 1C), 129.3 (J_C-F = 3.5 Hz, 1C), 125.4 (J_C-F = 14.1 Hz, 1C), 124.6 (J_C-F = 3.6 Hz, 1C), 116.0 (J_C-F = 21.5 Hz, 1C), 70.0, 57.0, 53.7 (J_C-F = 2.3 Hz, 1C), 22.5, 21.7, 21.4. HRMS (ESI) calcd for C₁₆H₂₅NO₄S [M+Na]⁺ 338.1197, found 338.1191. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min⁻¹; column temp, 30 °C; detection, UV 220 nm; retention time (t_R) of (R)-2j, 34.6 min (98.4 %); t_R of (S)-2j, 49.9 min (1.5 %).
(\textit{R})-Isopropyl 2-(4-fluorophenyl)-2-[(\textit{S})-1,1-dimethylethylsulfinamido]acetate (2k): colorless oil; 95\% yield; Rf (PE:EtOAc = 2:1) 0.45; [\alpha]_D^{20} = -15.0 (c = 0.1 in MeOH); \textit{^1}H NMR (400 MHz, CDCl$_3$) \( \delta \) (ppm) 7.41-7.37 (m, 2H), 7.03 (t, \( J = 8.8 \) Hz, 2H), 5.05-4.97 (m, 2H), 4.26 (d, \( J = 6.0 \) Hz, 1H), 1.24 (d, \( J = 6.4 \) Hz, 3H), 1.19 (s, 9H), 1.07 (d, \( J = 6.4 \) Hz, 3H); \textit{^{13}}C NMR (100 MHz, CDCl$_3$) \( \delta \) (ppm) 170.8, 162.8 (\( J_{C-F} = 245.9 \) Hz, 1C), 133.3 (\( J_{C-F} = 3.3 \) Hz, 1C), 129.4 (\( J_{C-F} = 8.4 \) Hz, 1C), 115.9 (\( J_{C-F} = 21.4 \) Hz, 1C), 69.9, 58.6, 56.9, 22.6, 21.8, 21.4; HRMS (ESI) calcd for C$_{15}$H$_{22}$FNO$_3$S [M+Na]$^+$ 338.1197, found 338.1188. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (\( t_R \)) of (\textit{R})-2k, 23.4 min (98.5 \%); \( t_R \) of (\textit{S})-2k, 44.4 min (1.5 \%).

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(R)-Isopropyl 2-[(\textit{S})-1,1-dimethylethylsulfinamido]-2-(3-chlorophenyl)acetate (2l): colorless oil; 95\% yield; Rf (PE:EtOAc = 2:1) 0.46; [\alpha]_D^{20} = -15.0 (c = 0.1 in MeOH); \textit{^1}H NMR (400 MHz, CDCl$_3$) \( \delta \) (ppm) 7.42 (s, 1H), 7.33-7.29 (m, 3H), 5.06-4.99 (m, 2H), 4.34 (d, \( J = 6.4 \) Hz, 1H), 1.27 (d, \( J = 6.0 \) Hz, 3H), 1.20 (s, 9H), 1.11 (d, \( J = 6.4 \) Hz, 3H); \textit{^{13}}C NMR (100 MHz, CDCl$_3$) \( \delta \) (ppm) 170.5, 139.4, 134.8, 130.2, 128.9, 127.8, 125.9, 70.2, 58.4, 57.1, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C$_{15}$H$_{22}$ClNO$_3$S [M+Na]$^+$ 354.0901, found 354.0895. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (\( t_R \)) of (\textit{R})-2l, 15.9 min (97\%); \( t_R \) of (\textit{S})-2l, 23.7 min (3\%).

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(R)-Isopropyl 2-(4-chlorophenyl)-2-[(\textit{S})-1,1-dimethylethylsulfinamido]acetate (2m): colorless oil; 93\% yield; Rf (PE:EtOAc = 2:1) 0.52; [\alpha]_D^{20} = -20.0 (c = 0.1 in MeOH); \textit{^1}H NMR (400 MHz, CDCl$_3$) \( \delta \) (ppm) 7.38-7.32 (m, 4H), 5.06-4.98 (m, 2H), 4.32 (d, \( J = 6.4 \) Hz, 1H), 1.25 (d, \( J = 6.0 \) Hz, 3H), 1.19 (s, 9H), 1.09 (d, \( J = 6.4 \) Hz,
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.6, 136.0, 134.6, 129.2, 129.0, 70.1, 58.4, 57.0, 22.6, 21.8, 21.5. HRMS (ESI) calcd for C$_{15}$H$_{22}$ClNO$_3$S [M+Na]$^+$ 354.0901, found 354.0897. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2m, 22.4 min (>99.9 %).

(R)-Isopropyl 2-(3-bromophenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2n): colorless oil; 97% yield; R$_R$(PE:EtOAc = 2:1) 0.51; $[\alpha]_D^{20}$ = -15.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.57 (s, 1H), 7.45 (d, $J$ = 8.0 Hz, 1H), 7.37 (d, $J$ = 8.0 Hz, 1H), 7.26-7.21 (m, 1H), 5.05-4.99 (m, 2H), 4.33 (d, $J$ = 6.4 Hz, 1H), 1.26 (d, $J$ = 6.0 Hz, 3H), 1.19 (s, 9H), 1.10 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.5, 139.6, 131.8, 130.6, 130.5, 126.3, 122.9, 58.3, 57.1, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C$_{15}$H$_{22}$BrNO$_3$S [M+Na]$^+$ 398.0396, found 398.0377. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2n, 17.0 min (95.5 %); t$_R$ of (S)-2n, 24.2 min (4.5 %).

(R)-Isopropyl 2-(4-bromophenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2o): colorless oil; 92% yield; R$_R$(PE:EtOAc = 2:1) 0.62; $[\alpha]_D^{20}$ = -22.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.47 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 5.03-4.96 (m, 2H), 4.33 (d, $J$ = 6.0 Hz, 1H), 1.24 (d, $J$ = 6.0 Hz, 3H), 1.17 (s, 9H), 1.07 (d, $J$ = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 170.5, 136.5, 132.1, 129.3, 122.8, 70.0, 58.4, 57.0, 22.6, 21.8, 21.4; HRMS (ESI) calcd for C$_{15}$H$_{22}$BrNO$_3$S [M+Na]$^+$ 398.0396, found 398.0381. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2o, 26.1 min (99%); t$_R$ of (S)-2o, 49.9 min (1%).
(R)-Isopropyl-2-(3,5-dimethylphenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2p): colorless oil; 94% yield; R_f (PE:EtOAc = 2:1) 0.57; [α]_D^{20} = -20.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.00 (s, 2H), 6.94 (s, 1H), 5.07-4.97 (m, 2H), 4.06 (d, J = 5.6 Hz, 1H), 2.29 (s, 6H), 1.25 (s, 6H), 1.22 (s, 9H), 1.11 (d, J = 6.4 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ (ppm) 171.1, 138.5, 137.1, 130.4, 125.3, 69.5, 59.9, 56.8, 22.6, 21.8, 21.5, 21.4; HRMS (ESI) calcd for C_{17}H_{27}NO_3S [M+Na]^+ 348.1604, found 348.1598. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL AD-H; eluent, hexane:2-propanol = 80:20; flow, 0.7 mL min^{-1}; column temp, 30 °C; detection, UV 220 nm; retention time (t_R) of (R)-2p, 16.4 min (97%); t_R of (S)-2p, 23.9 min (3%).

(R)-Isopropyl-2-(2,4-dimethylphenyl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2q): colorless oil; 76% yield; R_f (PE:EtOAc = 2:1) 0.55; [α]_D^{20} = -23.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.20 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 6.4 Hz, 2H), 5.26 (d, J = 4.4 Hz, 1H), 5.03-4.97 (m, 1H), 4.01 (d, J = 4.4 Hz, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 1.24-1.20 (m, 12H), 1.07 (d, J = 6.0 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ (ppm) 171.5, 138.3, 136.3, 133.0, 131.8, 127.3, 127.2, 69.5, 56.7, 55.4, 22.6, 21.8, 21.5, 21.2, 19.6. HRMS (ESI) calcd for C_{17}H_{27}NO_3S [M+Na]^+ 348.1604, found 348.1595. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min^{-1}; column temp, 30 °C; detection, UV 220 nm; retention time (t_R) of (R)-2q, 18.4 min (>99.9 %).

(R)-Isopropyl 2-(benzo[d][1,3]dioxol-5-yl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2r): colorless oil; 93% yield; R_f (PE:EtOAc = 2:1) 0.34; [α]_D^{20} = -17.0 (c = 0.1 in MeOH); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 6.88 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 7.6 Hz, 1H), 5.95 (s, 2H), 5.03-4.95 (m, 2H), 4.14 (d, J = 5.6 Hz, 1H), 1.24 (d, J =
6.4 Hz, 3H), 1.20 (s, 9H), 1.10 (d, J = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 170.9, 148.1, 147.9, 131.2, 121.4, 108.5, 107.9, 101.4, 69.7, 59.2, 56.9, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C$_{16}$H$_{23}$NO$_5$S [M+Na]$^+$ 364.1189, found 364.1178.

The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL AD-H; eluent, hexane:2-propanol = 80:20; flow, 0.7 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2r, 16.8 min (98%); t$_R$ of (S)-2r, 21.4 min (2%).

(R)-Isopropyl 2-[(S)-1,1-dimethylethylsulfinamido]-2-(naphthalen-2-yl)acetate (2s): colorless oil; 90% yield; $R_f$ (PE:EtOAc = 2:1) 0.41; [α]$_D^{20}$ = - 19.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.89 (s, 1H), 7.85-7.82 (m, 3H), 7.54-7.48 (m, 3H), 5.25 (d, J = 6.0 Hz, 1H), 5.06-5.00 (m, 1H), 4.38 (d, J = 6.0 Hz, 1H), 1.27-1.22 (m, 12H), 1.06 (d, J = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 171.0, 134.8, 133.3, 128.8, 128.2, 127.8, 127.0, 126.6, 126.5, 125.1, 69.8, 59.2, 56.9, 22.6, 21.8, 21.5; HRMS (ESI) calcd for C$_{19}$H$_{25}$NO$_3$S [M+Na]$^+$ 370.1447, found 370.1447. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL OD-H; eluent, hexane:2-propanol = 98:2; flow, 1.0 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2s, 13.0 min (95%); t$_R$ of (S)-2s, 13.7 min (5%).

(R)-Isopropyl 2-(phenanthren-9-yl)-2-[(S)-1,1-dimethylethylsulfinamido]acetate (2t): colorless oil; 85% yield; $R_f$ (PE:EtOAc = 2:1) 0.36; [α]$_D^{20}$ = - 18.0 (c = 0.1 in MeOH); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.75 (d, J = 8.8 Hz, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.34-8.32 (m, 1H), 7.90-7.86 (m, 2H), 7.69-7.59 (m, 4H), 5.84 (d, J = 4.0 Hz, 1H), 5.10-5.03 (m, 1H), 4.25 (d, J = 3.6 Hz, 1H), 1.23-1.21 (m, 12H), 0.98 (d, J = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 171.4, 131.8, 131.2, 131.1, 130.7, 129.6, 129.1, 128.1, 127.5, 127.2, 127.1, 126.9, 124.6, 123.4, 122.6, 69.9, 56.9, 56.8, 22.7, 21.8, 21.4; HRMS (ESI) calcd for C$_{23}$H$_{27}$NO$_5$S [M+Na]$^+$ 420.1589, found 420.1589. The diastereomeric ratio was determined by HPLC analysis. Column, CHIRALCEL AD-H; eluent, hexane:2-propanol = 80:20; flow, 0.7 mL min$^{-1}$; column temp, 30 °C; detection, UV 220 nm; retention time (t$_R$) of (R)-2t, 16.5 min (>99.9 %).
5. Synthesis of Aryl Amino Alcohol 5i

According to our method, 1 g substrate 1i was used for a gram scale reaction. 0.996 g product 2i was obtained with 96% isolated yield and more than 98:2 d.r. value. The N-sulfinyl aryglycine derivative 2i (996 mg, 3.0 mmol) was taken up in MeOH (10.0 mL) and was treated with 4.0 M HCl in dioxane (4.0 mL) at room temperature for 1 h. The reaction mixture was concentrated under vacuum, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the amine hydrochloride (4i). In a two-neck round-bottomed flask, LiAlH₄ (2 eq.) was added cautious to a solution of amine hydrochloride (1.0 eq) in THF(10 mL) at 0 °C. After addition, the solution was heated to reflux for 3 h. NaOH (15 ml, 1M) was added and liquid layer separated from the solid, the solid washed with EA. The combined organic phases washed by saturated NaCl and dried with NaSO₄, concentrated in vacuo to give aryl amino alcohol 5i (0.463 g, 94%) as a white solid.

(R)-2-isoproxy-1-(4-methoxyphenyl)-2-oxoethan-1-aminium chloride (4i): White solid; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.05 (brs, 3H), 7.43 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.04-4.99 (m, 2H), 3.80 (s, 3H), 1.23 (d, J = 6.4 Hz, 3H), 1.10 (d, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 168.3, 160.9, 130.2, 124.1, 114.7, 71.2, 56.7, 55.6, 21.7, 21.4.

(R)-2-amino-2-(4-methoxyphenyl)ethan-1-ol (5i): White solid; > 96 % ee; [α]D²⁰ = -25.0 (c = 1.0 in EtOH) (lit. [α]D = -21.9 (c = 1.0 in EtOH), 96% e.e.); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.18 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 3.93 (q, J = 4.4 Hz, 1H), 3.73 (s, 3H), 3.63 (dd, J = 10, 4.4 Hz, 1H), 3.48-3.43 (m, 1H), 1.95 (br, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 159.1, 134.9, 127.7, 114.1, 68.2, 56.8, 55.4; HRMS (ESI) calcd for C₉H₁₃NO₂ [M+H]⁺ 168.1019, found 168.1026.

6. References

7. Spectral copies of $^1$H NMR 、$^{13}$C NMR

$^1$H NMR (CDCl$_3$) of 1a

$^{13}$C NMR (CDCl$_3$) of 1a
$^1$H NMR (CDCl$_3$) of 1b

$^{13}$C NMR (CDCl$_3$) of 1b
$^1$H NMR (CDCl$_3$) of 1c

$^{13}$C NMR (CDCl$_3$) of 1c
$^1$H NMR (CDCl$_3$) of 1d

$^{13}$C NMR (CDCl$_3$) of 1d
$^1$H NMR (CDCl$_3$) of 1e

$^{13}$C NMR (CDCl$_3$) of 1e
$^1$H NMR (CDCl$_3$) of 1f

![NMR spectrum of 1f](image)

$^{13}$C NMR (CDCl$_3$) of 1f

![C NMR spectrum of 1f](image)
$^1$H NMR (CDCl$_3$) of 1g

$^{13}$C NMR (CDCl$_3$) of 1g
$^1$H NMR (CDCl$_3$) of 1h

13C NMR (CDCl$_3$) of 1h
$^1$H NMR (CDCl$_3$) of 1i

\[
\begin{array}{c}
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\]

$^{13}$C NMR (CDCl$_3$) of 1i

\[
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$^{13}$C NMR (CDCl$_3$) of 1j
$^1$H NMR (CDCl$_3$) of 1k

$^{13}$C NMR (CDCl$_3$) of 1k
$^1$H NMR (CDCl$_3$) of 11

$^{13}$C NMR (CDCl$_3$) of 11
$^1$H NMR (CDCl$_3$) of 1m

$^{13}$C NMR (CDCl$_3$) of 1m
$^1$H NMR (CDCl$_3$) of 1n

$^{13}$C NMR (CDCl$_3$) of 1n
$^1$H NMR (CDCl$_3$) of 1o

$^{13}$C NMR (CDCl$_3$) of 1o
$^1$H NMR (CDCl$_3$) of 1p

\[ \text{NMR Data} \]

$^1$C NMR (CDCl$_3$) of 1p

\[ \text{NMR Data} \]
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$^{1}$H NMR (CDCl$_3$) of 1r

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$^{13}$C NMR (CDCl$_3$) of 2e
$^1$H NMR (CDCl$_3$) of 2f

$^{13}$C NMR (CDCl$_3$) of 2f
$^1$H NMR (CDCl$_3$) of 2g

$^{13}$C NMR (CDCl$_3$) of 2g
$^1$H NMR (CDCl$_3$) of 2h

$^{13}$C NMR (CDCl$_3$) of 2h
$^1$H NMR (CDCl$_3$) of 2i

![NMR spectrum of 2i](image)

$^{13}$C NMR (CDCl$_3$) of 2i

![NMR spectrum of 2i](image)
$^1$H NMR (CDCl$_3$) of 2j

$^{13}$C NMR (CDCl$_3$) of 2j
$^1$H NMR (CDCl$_3$) of 2k

$^{13}$C NMR (CDCl$_3$) of 2k
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$^{13}$C NMR (CDCl$_3$) of 2l
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$^{13}$C NMR (CDCl$_3$) of 2m
$^1$H NMR (CDCl$_3$) of 2n

$^{13}$C NMR (CDCl$_3$) of 2n
$^1$H NMR (CDCl$_3$) of 2o

\[
\begin{align*}
\text{HN} & \quad \text{S=O} \\
\text{Br} & \quad \text{O/Pr} \\
\end{align*}
\]

$^{13}$C NMR (CDCl$_3$) of 2o

\[
\begin{align*}
\text{HN} & \quad \text{S=O} \\
\text{Br} & \quad \text{O/Pr} \\
\end{align*}
\]
$^1$H NMR (CDCl$_3$) of 2p

$^{13}$C NMR (CDCl$_3$) of 2p
$^1$H NMR (CDCl$_3$) of 2q

$^{13}$C NMR (CDCl$_3$) of 2q
$^1$H NMR (CDCl$_3$) of 2r

$^{13}$C NMR (CDCl$_3$) of 2r
$^1$H NMR (CDCl$_3$) of 2s

$^{13}$C NMR (CDCl$_3$) of 2s
$^1$H NMR (CDCl$_3$) of 2t

![NMR spectrum of 2t](image)

$^{13}$C NMR (CDCl$_3$) of 2t

![NMR spectrum of 2t](image)
$^{1}H$ NMR (CDCl$_3$) of 4i

$^{13}C$ NMR (CDCl$_3$) of 4i
$^1$H NMR (CDCl$_3$) of 5i

$^{13}$C NMR (CDCl$_3$) of 5i
7. Spectral copies of HPLC

Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1a using Pd/C

![Graph of Hydrogenation of 1a using Pd/C](image)

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Hydrogenation of 1a using Ru-MACHO

![Graph of Hydrogenation of 1a using Ru-MACHO](image)

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Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1b using Pd/C

Hydrogenation of 1b using Ru-MACHO

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Hydrogenation of 1c using Pd/C

Hydrogenation of 1c using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1d using Pd/C

Hydrogenation of 1d using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1e using Pd/C

Hydrogenation of 1e using Ru-MACHO
Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1f using Pd/C

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Hydrogenation of 1f using Ru-MACHO

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Hydrogenation of 1g using Pd/C

Hydrogenation of 1g using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of **1h** using **Pd/C**

Hydrogenation of **1h** using **Ru-MACHO**
Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1i using Pd/C

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Hydrogenation of 1i using Ru-MACHO

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Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1j using Pd/C

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Hydrogenation of 1j using Ru-MACHO

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Hydrogenation of 1k using Pd/C

Hydrogenation of 1k using Ru-MACHO

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Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 11 using Pd/C

Hydrogenation of 11 using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1m using Pd/C

Hydrogenation of 1m using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30°C)

Hydrogenation of \textbf{1n} using Pd/C

Hydrogenation of \textbf{1n} using Ru-MACHO
Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1o using Pd/C

Hydrogenation of 1o using Ru-MACHO

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Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1p using Pd/C

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Hydrogenation of 1p using Ru-MACHO

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Chiral HPLC Charts for Reduction Product (OD-H, Hexane/2-PrOH=98:2, F=1.0 mL/min, 220 nm, 30 °C)

Hydrogenation of 1q using Pd/C

![HPLC Chart for Hydrogenation of 1q using Pd/C](image)

### Peak Table

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Hydrogenation of 1q using Ru-MACHO

![HPLC Chart for Hydrogenation of 1q using Ru-MACHO](image)

### Peak Table

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<thead>
<tr>
<th>Peak</th>
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78
Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F = 0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1r using Pd/C

Hydrogenation of 1r using Ru-MACHO
Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1s using Pd/C

Hydrogenation of 1s using Ru-MACHO
Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1t using Pd/C

Hydrogenation of 1t using Ru-MACHO

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Chiral HPLC Charts for Reduction Product (AD-H, Hexane/2-PrOH=80:20, F=0.7 mL/min, 220 nm, 30 °C)

Hydrogenation of 1i using Pd/C

Hydrogenation of 1i in a gram scale using Ru-MACHO