Supporting Information for:

Highly Enantioselective Insertion of Carbenoids into N-H Bonds Catalyzed by Copper Complexes of Chiral Spiro Bisoxazolines

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General. The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques. Anhydrous dichloromethane, chloroform, acetonitrile and DMSO were distilled from calcium hydride. Anhydrous benzene and THF was distilled from sodium benzophenone ketyl prior to use. The aniline and substituted anilines were purified by distillation or recrystallization before use. The bis(triflate) 5 was synthesized according to the previous method.\(^1\) CuCl and CuPF\(_6\)(MeCN)\(_4\) were prepared according to the literature

method.\(^2\) NaBARF\((\text{H}_2\text{O})_{1.5}\) was prepared according to the literatures.\(^3\) CuOTf(toluene)\(_{1/2}\), CuBr(Me\(_2\text{S}\)), CuCl\(_2\), Cu(OTf)\(_2\), Pd(OAc)\(_2\), dppp and HOBt were purchased from Aldrich or Acros company and used without further purification. NMR spectra were recorded with a Bruker or Varian spectrometer at 400 or 300 (\(^1\)H NMR), 100 or 75 (\(^13\)C NMR) MHz with CDCl\(_3\) as solvent. Chemical shifts were reported in ppm down field from internal Me\(_4\text{Si}\). HRMS were recorded on VG ZAB-HS mass spectrometer with EI resource. Optical rotations were measured using a Perkin Elmer Model 341 polarimeter. HPLC analyses were performed using a Hewlett Packard Model HP 1100 Series chromatography.

1. **Preparation of Chiral Spiro Bisoxazoline Ligands 1**

   \[
   \begin{align*}
   &\text{5} & \text{Pd(OAc)\(_2\)/dppp, CO} & \rightarrow & \text{6} & \text{30\% KOH, MeOH} \\
   & & & & & \rightarrow & \text{7} \\
   & & & & & \text{8a: R = Ph} & \text{1a: R = Ph} \\
   & & & & & \text{8b: R = Bn} & \text{1b: R = Bn} \\
   & & & & & \text{8c: R = \text{t}Bu} & \text{1c: R = \text{t}Bu} \\
   & & & & & \text{8d: R = \text{i}Pr} & \text{1d: R = \text{i}Pr} \\
   \end{align*}
   \]

**Synthesis of (S)-1,1′-spirobiindanyl-7,7′-dicarboxylic acid dimethyl ester [(S)-6]**

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A mixture of bis(triflate) (S)-5 (5.2 g 10 mmol), Pd(OAc)\textsubscript{2} (225 mg, 1.0 mmol), 1,3-bis(diphenylphosphino)propane (dppp, 412 mg, 1.0 mmol), MeOH (60 mL), DMSO (90 mL) and Et\textsubscript{3}N (24 mL) was saturated with CO and stirred under CO atmosphere at 70 °C for full conversion. After cooling to room temperature, the reaction mixture was concentrated in reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1:8) to afford product (S)-6 (2.85 g, 85%) as a white solid. Mp 118–120 °C; [α\textsubscript{2}°]D = –278 (c 1.0, CHCl\textsubscript{3}); \textsuperscript{1}H NMR δ 2.27–2.32 (m, 2H), 2.53–2.61 (m, 2H), 3.00–3.11 (m, 4H), 3.16 (s, 6H), 7.23 (t, \textit{J} = 7.6 Hz, 2H), 7.43 (d, \textit{J} = 7.2 Hz, 2H), 7.60 (d, \textit{J} = 7.6 Hz, 2H); \textsuperscript{13}C NMR δ 30.9, 38.3, 51.3, 63.3, 126.5, 126.9, 128.3, 128.7, 145.3, 149.7, 167.9; HRMS (EI) Calcd for C\textsubscript{21}H\textsubscript{20}O\textsubscript{4}: 336.1362; Found: 336.1367.

**Synthesis of (S)-1,1′-spirobiindanyl-7,7′-dicarboxylic acid [(S)-7]**

The compound (S)-6 (3.1 g, 9.2 mmol) was added to a solution of MeOH (40 mL) and 30% aqueous KOH (40 mL) and stirred at refluxing for 10 h. The resulting mixture was cooled to room temperature, diluted with water (200 mL) and adjusted pH to 4~5 with 6 M HCl, and extracted with ethyl acetate (120 mL) for three times. The combined organic layer was washed with water and saturated brine, dried over anhydrous MgSO\textsubscript{4}, and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1:1) to afford product (S)-7 (2.8 g, 97%). Further purification by recrystallization...
from toluene afforded white solid. Mp = 230–231 °C; ¹H NMR δ 2.22–2.27 (m, 2H), 2.43–2.51 (m, 2H), 2.97–3.13 (m, 4H), 7.12 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 10.8 (brs, 2H).

Synthesis of \((S_a,S,S)-7,7'\)-bis[\(N\)-(2-hydroxy-1-phenylethyl)amide]-1,1' spiropiindane \([S_a,S,S]-8a\) \(^1\)

\[
\text{HO} \quad \text{O} \quad \text{N} \quad \text{OH} \\
\text{HO} \quad \text{O} \quad \text{N} \quad \text{OH}
\]

A solution of \((S)-7\) (308 mg, 1.0 mmol), dicyclohexyl carbodiimide (870 mg, 4.2 mmol), benzotriazol-1-ol (300 mg, 2.2 mmol) and \((S)-2\)-amino-2-phenylethanol (300 mg, 2.2 mmol) in dry THF was cooled to –5 °C and stirred for 1 hour. After spontaneously warmed to room temperature the mixture was stirred for over night. The resulting mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography (ethyl acetate) to afford \((S_a,S,S)-8a\) (475 mg, 87%) as a white solid. Mp 104–107 °C; \(\left[\alpha\right]_{D}^{20} -103 \ (c \ 0.5, \ \text{CHCl}_3)\); ¹H NMR (400 MHz, CDCl₃): δ 1.22–1.30 (m, 2H), 2.23–2.29 (m, 2H), 2.44–2.50 (m, 2H), 2.86 (s, 2H), 2.94–3.02 (m, 4H), 3.50–3.61 (m, 4H), 4.42–4.46 (m, 2H), 6.91–6.99 (m, 6H), 7.14 (t, J = 7.6 Hz, 2H), 7.24–7.30 (m, 8H).

Synthesis of \((S_a,S,S)-7,7'\)-bis[\(N\)-(1-phenyl-2-hydroxyethyl)amide]-1,1' spiropiindane \([S_a,S,S]-8b\)

\[
\text{HO} \quad \text{N} \quad \text{OH} \\
\text{HO} \quad \text{N} \quad \text{OH}
\]
The compound (S<sub>a</sub>S<sub>S</sub>)<sup>-8b</sup> was synthesized from (S)-2-amino-3-phenylpropan-1-ol in 99% yield by the same procedure as that for (S<sub>a</sub>S<sub>S</sub>)<sup>-8a</sup>. White solid, mp 175–178 °C; [α]<sup>20</sup><sub>D</sub> = −106 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR: δ 2.23–2.27 (m, 2H), 2.35–2.49 (m, 6H), 2.98–3.00 (m, 6H), 3.18–3.28 (m, 4H), 3.68–3.69 (m, 2H), 6.90 (d, <i>J</i> = 7.2 Hz, 2H), 7.01 (d, <i>J</i> = 7.8 Hz, 2H), 7.08 (d, <i>J</i> = 7.2 Hz, 3H), 7.15–7.19 (m, 4H), 7.22–7.28 (m, 5H); <sup>13</sup>C NMR: δ 30.7, 26.1, 40.3, 53.9, 62.2, 63.4, 126.3, 126.7, 127.4, 128.7, 129.3, 133.9, 138.2, 145.54, 170.5; HRMS (EI) Calcd for C<sub>37</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>: 574.2832; Found: 574.2834.

**Synthesis of (S<sub>a</sub>S<sub>S</sub>)-7,7′-bis[N-(1-hydroxymethyl-2-methylpropyl)amide]-1,1′-spirobiindane [(S<sub>a</sub>S<sub>S</sub>)<sup>-8c</sup>]

\[
\text{HO} \quad \text{HN} \quad \text{O} \\
\text{NH} \quad \text{OHO} \quad \text{HNHO}
\]

The compound (S<sub>a</sub>S<sub>S</sub>)<sup>-8c</sup> was synthesized from (S)-2-amino-3-methylbutan-1-ol in 99% yield by the same procedure as that for (S<sub>a</sub>S<sub>S</sub>)<sup>-8a</sup>. White solid, mp 166–170 °C; [α]<sup>20</sup><sub>D</sub> = −126 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR: δ 0.81 (t, <i>J</i> = 6.9 Hz, 12H), 1.63–1.67 (m, 2H), 2.28–2.34 (m, 2H), 2.44–2.48 (m, 2H), 2.99–3.04 (m, 6H), 3.13–3.16 (m, 2H), 3.24–3.35 (m, 4H), 6.85 (d, 2H, <i>J</i> = 6.9 Hz), 7.17–7.32 (m, 6H); <sup>13</sup>C NMR: δ 18.9, 19.4, 28.6, 30.5, 40.1, 58.9, 63.2, 126.0, 126.3, 127.3, 134.2, 145.1, 171.0; HRMS (EI) Calcd for C<sub>29</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>: 478.2832; Found: 478.2839.

**Synthesis of (S<sub>a</sub>S<sub>S</sub>)-7,7′-bis[N-(2-hydroxy-1-tert-butylyethyl)amide]-1,1′-spirobiindane [(S<sub>a</sub>S<sub>S</sub>)<sup>-8d</sup>]

The compound (S<sub>a</sub>S<sub>S</sub>)<sup>-8d</sup> was synthesized from (S)-2-amino-3-methylbutan-1-ol in 99% yield by the same procedure as that for (S<sub>a</sub>S<sub>S</sub>)<sup>-8a</sup>. White solid, mp 175–178 °C; [α]<sup>20</sup><sub>D</sub> = −126 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR: δ 2.23–2.27 (m, 2H), 2.35–2.49 (m, 6H), 2.98–3.00 (m, 6H), 3.18–3.28 (m, 4H), 3.68–3.69 (m, 2H), 6.90 (d, <i>J</i> = 7.2 Hz, 2H), 7.01 (d, <i>J</i> = 7.8 Hz, 2H), 7.08 (d, <i>J</i> = 7.2 Hz, 3H), 7.15–7.19 (m, 4H), 7.22–7.28 (m, 5H); <sup>13</sup>C NMR: δ 30.7, 26.1, 40.3, 53.9, 62.2, 63.4, 126.3, 126.7, 127.4, 128.7, 129.3, 133.9, 138.2, 145.54, 170.5; HRMS (EI) Calcd for C<sub>37</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>: 574.2832; Found: 574.2834.
The compound (Sₐ,S,S)-8d was synthesized from (S)-2-amino-3,3-dimethylbutan-1-ol in 99% yield by the same procedure as that for (Sₐ,S,S)-8a. White solid, mp 200–203 °C, [α]²⁰ₒD = –66.4 (c 1.0, CHCl₃); ¹H NMR: δ 0.79 (s, 18H), 2.24–2.31 (m, 2H), 2.44–2.52 (m, 2H), 2.71 (brs, 2H), 2.98–3.03 (m, 4H), 3.28–3.33 (m, 4H), 3.45–3.52 (m, 2H), 6.70 (d, J = 6.8 Hz, 2H), 7.22–7.29 (m, 6H); ¹³C NMR: δ 27.1, 30.7, 33.9, 40.3, 61.5, 63.0, 126.3, 126.7, 126.5, 134.6, 145.3, 171.3; HRMS (EI) Calcd for C₃₁H₄₂N₂O₄: 506.3145; Found: 506.3136.

Synthesis of (Sₐ,S,S)-7,7’-bis[4-phenyloxazolin-2-yl]-1,1’-spirobiindane [(Sₐ,S,S)-1a]¹

A solution of (Sₐ,S,S)-8a (234 mg, 0.42 mmol), triphenylphosphine (440 mg, 1.68 mmol), triethylamine (170 mg, 1.68 mmol), tetrachloromethane (260 mg, 1.68 mmol) in dry acetonitrile was stirred overnight at room temperature. After concentrated in vacuum, the residue was dissolved in CH₂Cl₂, washed with water, dried over anhydrous magnesium sulfate, and then concentrated in vacuum. The crude product was purified by chromatography on silica gel column (ethyl acetate/petroleum ether = 1:3) to afford (Sₐ,S,S)-1a (200 mg, 93%) as a white solid. Mp 167–169°C; [α]²⁰ₒD = –321 (c 0.5, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ 2.31 (dd, J = 4.8 and 7.2 Hz, 2H), 2.60 (q, J = 10.8 Hz, 2H), 2.98–3.16 (m, 4H), 3.34–3.41 (m, 2H), 3.72 (t, J = 7.2 Hz, 2H), 4.98 (dd, J = 3.0 and 6.9 Hz, 2H), 7.05–7.08 (m, 4H), 7.18–7.28 (m, 8H), 7.36 (d, J = 6.9 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H).
Synthesis of \((S_o,S,S)-7,7′\text{-}\text{bis}(4\text{-}\text{benzyl} \text{oxazolin-2-yl})\)\(1,1′\)\text{-}\text{spirobiindane} [(\(S_o,S,S\)-1b)]

The compound \((S_o,S,S)-1c\) was synthesized from \((S_o,S,S)-8c\) in 80% yield by the same procedure as that for \((S_o,S,S)-1a\). White solid, mp 49–52 °C; \([\alpha]_{D}^{20} = –220 (c 1.0, \text{CHCl}_3)\); \(^1\)H NMR: δ 2.03 (dd, \(J = 9.6\) and 4.4 Hz, 2H), 2.24 (dd, \(J = 7.6\) and 4.4 Hz, 2H), 2.63–2.68 (m, 4H), 2.92–2.98 (m, 2H), 2.96–3.04 (m, 2H), 3.27 (t, \(J = 8.8\) Hz, 2H), 3.57 (t, \(J = 7.2\) Hz, 2H), 4.11–4.16 (m, 2H), 7.08–7.27 (m, 14H), 7.54–7.56 (d, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR: δ 30.7, 36.1, 40.3, 53.9, 62.2, 63.4, 126.3, 126.6, 126.7, 127.4, 128.7, 129.3, 133.9, 138.2, 145.5, 170.5; HRMS (EI) Calcd for \(C_{37}H_{34}N_2O_2\): 538.2620; Found: 538.2614.

Synthesis of \((S_o,S,S)-7,7′\text{-}\text{bis}(4\text{-}\text{isopropyl} \text{oxazolin-2-yl})\)\(1,1′\)\text{-}\text{spirobiindane} [(\(S_o,S,S\)-1c)]

The compound \((S_o,S,S)-1c\) was synthesized from \((S_o,S,S)-8c\) in 73% yield by the same procedure as that for \((S_o,S,S)-1a\). White solid, mp = 64–66 °C; \([\alpha]_{D}^{20} = –353 (c 1.0, \text{CHCl}_3)\); \(^1\)H NMR: δ 0.67 (d, \(J = 6.9\) Hz, 6H), 0.77 (d, \(J = 6.6\) Hz, 6H), 1.11–1.20 (m, 2H), 2.23 (dd, \(J = 7.2\) and 4.5 Hz, 2H), 2.62–2.72 (m, 2H), 2.91–3.07 (m, 6H), 3.33 (dd, \(J = 7.8\) and 1.5 Hz, 2H), 3.48–3.62 (m, 4H), 7.15 (t, \(J = 7.5\) Hz, 2H), 7.30 (d, \(J = 7.2\) Hz, 2H), 7.54 (d, \(J = 7.8\) Hz, 2H); \(^{13}\)C NMR: δ 17.8, 19.6, 30.6, 32.4, 38.4, 69.6, 72.3, 125.8, 126.4, 127.8, 145.1, 148.5, 163.4; HRMS (EI) Calcd for \(C_{29}H_{34}N_2O_2\): 442.2620; Found: 442.2633.
Synthesis of (S,S,S)-7,7′-bis(4-tert-butyloxazolin-2-yl)-1,1′-spirobiindane [(S,S,S)-1d]

The compound (S,S,S)-1d was synthesized from (S,S,S)-8d in 25% yield by the same procedure as that for (S,S,S)-1a. White solid, mp 149–152 °C; [α]$_{20}^{D}$ = –395 (c 1.0, CHCl$_3$);

$^1$H NMR: δ 0.75 (s, 18H), 2.19–2.25 (m, 2H), 2.46–2.57 (m, 2H), 2.91–3.07 (m, 6H), 3.58–3.64 (m, 4H), 7.16 (t, $J$ = 7.5 Hz, 2H), 7.33 (d, $J$ = 7.5 Hz, 2H), 7.71 (d, $J$ = 7.5 Hz, 2H);

$^{13}$C NMR: δ 25.8, 30.6, 33.7, 38.7, 68.1, 74.9, 124.2, 125.9, 126.5, 128.7, 144.9, 149.0, 164.1;

HRMS (EI) Calcd for C$_{31}$H$_{38}$N$_2$O$_2$: 470.2933; Found: 470.2922.

2. General Procedure for Cu-Catalyzed Asymmetric Insertion of Carbenoid into Anilines

The CuCl (1.0 mg, 0.01 mmol, 5 mol%), (S,S,S)-1a (6.1 mg, 0.012 mmol, 6 mol%) and NaBARF.(H$_2$O)$_{1.5}$ (11.3 mg, 0.012 mmol, 6 mol%) were introduced into an oven-dried Schlenk tube in argon-filled glovebox. CH$_2$Cl$_2$ (2 mL) was injected and the solution was stirred at room temperature under the argon atmosphere for 2 h, followed by additions of aniline (19 mg, 0.2 mmol) and ethyl $\alpha$-diazopropionate (26 mg, 0.2 mmol). The resulting mixture was stirred for 2 h and the product was purified by flash chromatography (ethyl acetate/petroleum ether = 1:10).
3. Analytical Data for N-H Insertion Products

(R)-(+)Ethyl 2-(phenylamino)propionate (4a) ⁴

\[
\text{Colorless oil, 94% yield, } ^1\text{H NMR: } \delta 1.25 (t, J = 7.2 \text{ Hz, 3H}), 1.47 (d, J = 6.4 \text{ Hz, 3H}), 4.09-4.21 (m, 4H), 6.61 (d, J = 8.4 \text{ Hz, 2H}), 6.74 (t, J = 7.2 \text{ Hz, 1H}), 7.17 (t, J = 7.6 \text{ Hz, 2H}); 98\% \text{ ee [HPLC condition: Chiralpak AS column, } n-\text{Hexane}/2-\text{PrOH} = 98:2, \text{ flow rate} = 1.0 \text{ mL/min, wavelength} = 254 \text{ nm, } t_R = 5.65 \text{ min for major isomer, } t_R = 6.26 \text{ min for minor isomer]; } [\alpha]^{20}_D = +98.8 (c 1.0, \text{EtOH}) \text{ and } [\alpha]^{20}_D = +58.7 (c 1.0, \text{CHCl}_3). \text{ [lit } ⁵\text{]: } [\alpha]_D = +5.9 (c 0.09, \text{CHCl}_3) \text{ for } >75\% \text{ ee, (R)}.\]

(+)-Ethyl 2-(p-toluidino)propionate (4b) ⁴

\[
\text{Colorless oil, 94% yield, } ^1\text{H NMR: } \delta 1.24 (t, J = 7.2 \text{ Hz, 3H}), 1.44 (d, J = 6.8 \text{ Hz, 3H}), 2.23 (s, 3H), 4.01-4.20 (m, 4H), 6.54 (d, J = 8.4 \text{ Hz, 2H}), 6.98 (d, J = 8.4 \text{ Hz, 2H}); 91\% \text{ ee [HPLC condition: Chiralpak AS column, } n-\text{Hexane}/2-\text{PrOH} = 98:2, \text{ flow rate} = 1.0 \text{ mL/min, wavelength} = 254 \text{ nm, } t_R = 8.17 \text{ min for major isomer, } t_R = 9.48 \text{ min for minor isomer]; } [\alpha]^{20}_D = +59.8 (c 0.9, \text{EtOH}).\]

(+)-Ethyl 2-($\rho$-methoxyphenylamino)propionate (4c)

Colorless oil, 96% yield, $^1$H NMR: $\delta$ 1.23 (t, $J = 6.8$ Hz, 3H), 1.44 (d, $J = 6.8$ Hz, 3H), 3.73 (s, 3H), 3.87 (s, 1H), 4.04 (q, $J = 6.8$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 6.59 (d, $J = 8.8$ Hz, 2H), 6.76 (d, $J = 8.8$ Hz, 2H); 85% ee [HPLC condition: Chiralpak AS column, $n$-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R$ = 21.75 min for minor isomer, $t_R$ = 23.36 min for major isomer]; $[\alpha]_D^{20} = +41.8$ (c 1.0, EtOH).

(+)-Ethyl 2-($\rho$-chlorophenylamino)propionate (4d)

Colorless oil, 92% yield, $^1$H NMR: $\delta$ 1.24 (t, $J = 7.2$ Hz, 3H), 1.43 (d, $J = 6.8$ Hz, 3H), 4.05 (q, $J = 6.8$ Hz, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 6.50 (d, $J = 8.8$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR: $\delta$ 14.4, 18.9, 52.3, 61.4, 114.7, 123.0, 129.3, 145.5, 174.5; HRMS (EI) Calcd for C$_{11}$H$_{14}$NO$_2$Cl: 227.0713, Found: 227.0716; 98% ee [HPLC condition: Chiralpak AS column, $n$-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R$ = 9.40 min for minor isomer, $t_R$ = 10.05 min for major isomer]; $[\alpha]_D^{20} = +101$ (c 1.0, EtOH).

(+)-Ethyl 2-($\rho$-bromophenylamino)propionate (4e)
Colorless oil, 95% yield, $^1$H NMR: $\delta$ 1.24 (t, $J = 7.2$ Hz, 3H), 1.44 (d, $J = 6.8$ Hz, 3H), 4.02–4.09 (m, 1H), 4.15–4.24 (m, 3H), 6.46 (d, $J = 9.2$ Hz, 2H), 7.23 (d, $J = 9.2$ Hz, 2H); $^{13}$C NMR: $\delta$ 14.4, 18.9, 52.2, 61.5, 110.1, 115.2, 132.2, 145.9, 174.4; HRMS (EI) Calcd for C$_{11}$H$_{14}$NO$_2$Br: 271.0208, Found: 271.0211; 98% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 10.13$ min for minor isomer, $t_R = 12.21$ min for major isomer]; $[\alpha]^{20}_D = +78.9$ (c 1.0, EtOH).

(+)-Ethyl 2-(m-toluidino)propionate (4f)

Colorless oil, 92% yield, $^1$H NMR: $\delta$ 1.25 (t, $J = 7.2$ Hz, 3H), 1.46 (d, $J = 6.4$ Hz, 3H), 2.26 (s, 3H), 4.10–4.14 (m, 2H), 4.15–4.21 (m, 2H), 6.41–6.43 (m, 2H), 6.56 (d, $J = 7.6$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H); $^{13}$C NMR: $\delta$ 14.4, 19.2, 21.7, 52.3, 61.2, 110.7, 114.5, 119.4, 129.3, 139.3, 146.9, 174.8; HRMS (EI) Calcd for C$_{12}$H$_{17}$NO$_2$: 207.1259; Found: 207.1263; 96% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.10$ min for major isomer, $t_R = 6.60$ min for minor isomer]; $[\alpha]^{20}_D = +72.2$ (c 0.8, EtOH).

(+)-Ethyl 2-(m-chlorophenylamino)propionate (4g) 6

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Colorless oil, 95% yield, $^1$H NMR: $\delta$ 1.26 (t, $J = 7.2$ Hz, 3H), 1.46 (d, $J = 6.8$ Hz, 3H), 4.07–4.27 (m, 4H), 6.46 (dd, $J = 8.4$ and 2.4 Hz, 1H), 6.56–6.57 (m, 1H), 6.68–6.70 (m, 1H), 7.6 (t, $J = 8.0$ Hz, 1H); 97% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.59$ min for major isomer, $t_R = 8.27$ min for minor isomer]; $[\alpha]^{20}_D = +82.6$ (c 1.2, EtOH).

(+)-Ethyl 2-($m$-bromophenylamino)propionate (4h)

Colorless oil, 96% yield, $^1$H NMR: $\delta$ 1.19 (t, $J = 6.9$ Hz, 3H), 1.38 (d, $J = 6.9$ Hz, 3H), 3.96–4.06 (m, 1H), 4.10–4.18 (m, 3H), 6.42–6.45 (m, 1H), 6.66–6.67 (m, 1H), 6.75–6.78 (m, 1H), 6.93 (t, $J = 8.1$ Hz, 1H); $^{13}$C NMR: $\delta$ 14.2, 18.7, 51.8, 61.3, 112.1, 116.0, 121.0, 123.3, 130.5, 147.9, 174.1; HRMS (EI) Calcd for C$_{13}$H$_{14}$NO$_2$Br: 271.0208. Found: 271.0206; 98% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 7.11$ min for major isomer, $t_R = 8.54$ min for minor isomer]; $[\alpha]^{20}_D = +71.7$ (c 1.0, EtOH).

(+)-Ethyl 2-($o$-toluidino)propionate (4i)
Colorless oil, 95% yield, $^1$H NMR: $\delta$ 1.26 (t, $J = 7.2$ Hz, 3H), 1.51 (d, $J = 6.8$ Hz, 3H), 2.21 (s, 3H), 4.07–4.09 (m, 1H), 4.16–4.23 (m, 3H), 6.54 (d, $J = 8.0$ Hz, 1H), 6.67–6.71 (m, 1H), 7.06–7.11 (m, 2H); $^{13}$C NMR: $\delta$ 14.4, 17.6, 19.3, 52.2, 61.3, 110.6, 118.0, 122.8, 127.3, 130.6, 144.9, 174.9; HRMS (EI) Caled for C$_{12}$H$_{17}$NO$_2$: 207.1259; Found: 207.1254; 98% ee [HPLC condition: Chiralpak AD-H column, n-Hexane/2-PrOH = 99:1, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 13.01$ min for major isomer, $t_R = 15.71$ min for minor isomer]; $[\alpha]^{20}_D = +31.9$ (c 1.0, EtOH).

(+)-Ethyl 2-(o-methoxyphenylamino)propionate (4j)

\[
\begin{align*}
&\text{OMe} \\
&\text{N} \\
&\text{O} \\
&\text{O}
\end{align*}
\]

Colorless oil, 86% yield, $^1$H NMR: $\delta$ 1.24 (t, $J = 7.0$ Hz, 3H), 1.50 (d, $J = 6.4$ Hz, 3H), 3.85 (s, 3H), 4.11–4.21 (m, 3H), 4.70 (d, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.68–6.71 (m, 1H), 6.77–6.84 (m, 2H); 98% ee [HPLC condition: Chiralpak AD-H column, n-Hexane/2-PrOH = 99:1, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 21.56$ min for major isomer, $t_R = 25.66$ min for minor isomer]; $[\alpha]^{20}_D = +23.7$ (c 1.1, EtOH).

(+)-Ethyl 2-(o-chlorophenylamino)propanoate (4k)

\[
\begin{align*}
&\text{Cl} \\
&\text{N} \\
&\text{O} \\
&\text{O}
\end{align*}
\]

Colorless oil, 95% yield, $^1$H NMR: $\delta$ 1.25 (t, $J = 7.2$ Hz, 3H), 1.52 (d, $J = 7.2$ Hz, 3H), 4.13–4.22 (m, 3H), 4.80 (d, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 8.4$ Hz, 1H), 6.64–6.68 (m, 1H), 7.09–7.13 (m, 1H), 7.25–7.27(m, 1H); $^{13}$C NMR $\delta$ 14.37, 19.01, 52.08, 61.48, 111.83, 118.31,
119.91, 127.95, 129.61, 142.85, 174.10; HRMS (EI) Calcd for C_{11}H_{14}NO_{2}Cl: 227.0713, Found: 227.0710; 88% ee [HPLC condition: Chiralcel OD-H column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, \( t_R = 7.00 \) min for major isomer, \( t_R = 22.99 \) min for minor isomer]; \([\alpha]^{20}_D = +9.8 \) (c 1.1, EtOH).

(-)-Ethyl 2-(naphthalen-1-ylamino)propionate (4l) \(^4\)

\[
\text{O} \quad \text{HN} \quad \text{O}
\]

Colorless oil, 89% yield, \(^1\)H NMR: \( \delta 1.28 \) (t, \( J = 7.2 \) Hz, 3H), 1.61 (d, \( J = 6.8 \) Hz, 3H), 4.20–4.34 (m, 3H), 4.96 (d, \( J = 4.0 \) Hz, 1H), 6.54 (d, \( J = 7.2 \) Hz, 1H), 7.26–7.34 (m, 2H), 7.45–7.47 (m, 2H), 7.78–7.80 (m, 1H), 7.90–7.92 (m, 1H); 98% ee [HPLC condition: Chiralpak AD-H column, n-Hexane/2-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, \( t_R = 7.81 \) min for major isomer, \( t_R = 10.18 \) min for minor isomer]; \([\alpha]^{20}_D = -23.9 \) (c 1.1, EtOH).

(+)-Ethyl 2-(naphthalen-2-ylamino)propionate (4m)

\[
\text{O} \quad \text{HN} \quad \text{O}
\]

White solid, 91% yield, mp = 80–82 °C, \(^1\)H NMR: \( \delta 1.27 \) (t, \( J = 7.2 \) Hz, 3H), 1.54 (d, \( J = 6.8 \) Hz, 3H), 4.17–4.36 (m, 4H), 6.78 (s, 1H), 6.90–6.93 (m, 1H), 7.21 (t, \( J = 6.8 \) Hz, 1H), 7.36 (t, \( J = 8.0 \) Hz, 1H), 7.59–7.68 (m, 3H); \(^{13}\)C NMR: \( \delta 14.2, 18.8, 52.1, 61.2, 105.4, 118.1, 122.4, 126.1, 126.3, 127.6, 129.1, 135.0, 144.3, 174.5 \); HRMS (EI) Calcd for C_{15}H_{17}NO_{2}: 243.1259. Found: 243.1266; 98% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, \( t_R = 9.20 \) min for major isomer, \( t_R = 11.26 \)
min for minor isomer]; $[\alpha]^{20}_D = +173$ (c 1.0, EtOH).

(+)-Methyl 2-(phenylamino)propionate (4n) 7

![Image of (+)-Methyl 2-(phenylamino)propionate](image)

Colorless oil, 78% yield, $^1$H NMR: δ 1.48 (d, $J = 5.6$ Hz, 3H), 3.73 (s, 3H), 4.15 (brs, 2H), 6.61 (d, $J = 8.4$ Hz, 2H), 6.75 (t, $J = 7.2$ Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 2H); 96% ee [HPLC condition: Chiralpak AS column, $n$-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.79$ min for major isomer, $t_R = 10.94$ min for minor isomer]; $[\alpha]^{20}_D = +111$ (c 1.0, EtOH).

(+)-tert-Butyl 2-(phenylamino)propionate (4o) 4

![Image of (+)-tert-Butyl 2-(phenylamino)propionate](image)

Colorless oil, 93% yield, $^1$H NMR: δ 1.43 (s, 9H), 4.01 (q, $J = 6.8$ Hz, 1H), 4.14 (brs, 1H), 6.60 (d, $J = 8.0$ Hz, 2H), 6.72 (t, $J = 7.2$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 2H); 96% ee [HPLC condition: Chiralpak AS column, $n$-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.51$ min for major isomer, $t_R = 8.60$ min for minor isomer]; $[\alpha]^{20}_D = +43.3$ (c 1.0, EtOH).

(+)-Ethyl 2-(phenylamino)butyrate (4p)

---

Colorless oil, 51% yield, $^1$H NMR: δ 1.00 (t, $J = 7.6$ Hz, 3H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.77–1.93 (m, 2H), 4.02 (t, $J = 6.4$ Hz, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 6.62 (d, $J = 7.6$ Hz, 2H), 6.72 (t, $J = 7.6$ Hz, 1H), 7.17 (t, $J = 8.0$ Hz, 2H); $^{13}$C NMR: δ 10.1, 14.5, 26.3, 58.0, 61.2, 113.6, 118.4, 129.5, 147.1, 174.2; HRMS (EI) Calcd for C$_{12}$H$_{17}$NO$_2$: 207.1259; Found: 207.1266; 94% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R$ = 6.41 min for major isomer, $t_R$ = 7.31 min for minor isomer]; $[\alpha]^{20}_D = +100$ (c 1.0, EtOH).

(+)-Methyl 2-phenyl-2-(phenylamino)acetate (4q) 4

White solid, 85% yield, mp = 76–78 °C; $^1$H NMR: δ 3.73 (s, 3H), 4.96 (s, 1H), 5.01 (s, 1H), 6.55 (d, $J = 8.0$ Hz, 2H), 6.69 (t, $J = 7.2$ Hz, 1H), 7.12 (t, $J = 8.0$ Hz, 2H), 7.30–7.37 (m, 3H), 7.49 (d, $J = 7.2$ Hz, 2H); 8% ee [HPLC condition: Chiralpak AS column, n-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R$ = 6.18 min for major isomer, $t_R$ = 8.68 min for minor isomer, $t_R$ = 10.29 min for minor isomer]; $[\alpha]^{20}_D = -7.3$ (c 1.0, EtOH).

Ethyl 2-(methyl(phenyl)amino)propionate (4r) 4

-[S16]-
Colorless oil, 93% yield, $^1$H NMR: δ 1.22 (t, $J = 6.9$ Hz, 3H), 1.47 (d, $J = 7.2$ Hz, 3H), 2.89 (s, 3H), 4.14–4.17 (m, 2H), 4.47–4.54 (m, 1H), 6.75–6.80 (m, 3H), 7.21–7.26 (m, 2H); rac. [HPLC condition: Chiralpak AD-H column, $n$-Hexane/2-PrOH = 98:2, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.67$ min, $t_R = 7.04$ min].

**Ethyl 2-benzamidopropionate (4s)**  

![Chemical structure](image)

White solid, 55% yield, mp = 74–76 °C; $^1$H NMR: δ 1.31 (t, $J = 7.2$ Hz, 3H), 1.52 (d, $J = 7.2$ Hz, 3H), 4.21–4.27 (m, 2H), 4.74–4.79 (m, 1H), 6.76 (m, 1H), 7.42–7.45 (m, 2H), 7.51–7.56 (m, 3H); rac. [HPLC condition: Chiralcel OB column, $n$-Hexane/2-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 235 nm, $t_R = 21.22$ min, $t_R = 27.98$ min].

---

4. NMR Spectra for New Ligands and Intermediates

(S)-1,1′-Spirobiindanyl-7,7'-dicarboxylic acid dimethyl ester
(S_19,S_19)-7,7\textsuperscript{'}-Bis[N-(1-benzyl-2-hydroxyethyl)amide]-1,1\textsuperscript{'}-spirobiindane
(S\textsubscript{m},S,S)-7,7'-Bis[N-(1-hydroxymethyl-2-methylpropyl)amide]-1,1'-spirobiindane
(S<sub>m</sub>,S,S)-7,7′-Bis[N-(2-hydroxy-1-tert-butylethyl)amide]-1,1′-spirobiindane
(S<sub>en</sub>,S,S)-7,7′-Bis(4-benzyloxazolin-2-yl)-1,1′-spirobiindane
(Sₚ,S,S)-7,7′-Bis(4-isopropylloxazolin-2-yl)-1,1′-spirobiindane
(S<sub>m</sub>,S,S)-7,7′-Bis (4-tert-butyloxazolin-2-yl)-1,1′-spirobiindane
5. NMR Spectra for New N-H Insertion Products

(+)-Ethyl 2-(p-chlorophenylamino)propionate (4d)
(+)-Ethyl 2-(ρ-bromophenylamino)propionate (4e)
(+)-Ethyl 2-(m-toluidino)propionate (4f)
(+)-Ethyl 2-(m-bromophenylamino)propionate (4h)
(+)-Ethyl 2-((o-toluidino)propionate (4i)
(+) - Ethyl 2- (o-chlorophenylamino) propionate (4k)
(+) - Ethyl 2-(naphthalen-2-ylamino)propionate (4m)
(+)-Ethyl 2-(phenylamino)butyrate (4p)
6. HPLC Charts for N-H Insertion Products

(+)-Ethyl 2-(phenylamino)propionate (4a)

![HPLC Chart 1](image1)

![HPLC Chart 2](image2)

**Signal 1: VWD1 A, Wavelength=254 nm**

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(+)-Ethyl 2-(p-toluidino)propionate (4b)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-(4-methoxyphenylamino)propionate (4c)
(+)-Ethyl 2-((p-chlorophenylamino)propionate (4d)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-(p-bromophenylamino)propionate (4e)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-(m-toluidino)propionate (4f)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-((m-chlorophenylamino)propionate (4g)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-\((m\)-bromophenylamino)propionate (4h)
(±)-Ethyl 2-(o-toluidino)propionate (4i)

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Signal 1: VWD 1 A, Wavelength=254 nm

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(+)-Ethyl 2-((o-methoxyphenylamino)propionate (4j)

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(+)-Ethyl 2-(o-fluorophenylamino)propionate (4k)

Signal 1: VWD1 A, Wavelength=254 nm

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(-)-Ethyl 2-(naphthalen-1-ylamino)propionate (4l)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-(naphthalen-2-ylamino)propionate (4m)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Methyl 2-(phenylamino)propionate (4n)

Signal 1: VWD1 A, Wavelength=254 nm

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(±)-tert-Butyl 2-(phenylamino)propionate (4o)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)-Ethyl 2-(phenylamino)butyrate (4p)

Signal 1: VWD1 A, Wavelength=254 nm

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(+)‐Methyl 2‐phenyl‐2‐(phenylamino)acetate (4q)

![Chemical Structure](image1)

### HPLC Data

**Signal 1: VWD 1 A, Wavelength=254 nm**

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