**Asymmetric C(sp\(^3\))-H/C(Ar) Coupling Reactions.**
**Highly Enantioenriched Indolines via Regiodivergent Reaction of a Racemic Mixture**

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**Electronic Supplementary Information**

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1.1 General Techniques and Chemicals:

Chemicals were purchased from Aldrich, Fluka, Acros, Alfa or Aesar and used without further purification.

N-alkyl-2-bromoaniline\textsuperscript{[1-2]} and methyl N-alkyl-2-bromophenyl carbamate\textsuperscript{[3]} were prepared by literature procedures. Solvents were purified by filtration on drying columns using a Solvtec\textsuperscript{©} system. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under nitrogen and glassware was further dried by heating under vacuum as necessary. F.c. (FC): silica gel 60 (40\textmu m). Molecular sieve 4Å was used without activation. Analysis with HPLC was performed using an Agilent 1100 series chromatograph with a JASCO PU–980 pump and Agilent 1100 Series detection system.

\textsuperscript{1}H, \textsuperscript{13}C-NMR spectra were recorded on Bruker AMX-500, AMX-400 or AMX-300 MHz; \textdelta- in ppm, pattern abbreviation: broad (brd), quartet (q), quintet (quint), multiplet (m). Fourier transform (FT) spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer Spectrum One photometer. HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured at 20 °C on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (\lambda = 589 nm). Melting points were determined on a Büchi M-560 apparatus and are uncorrected.

Starting Materials:

Mesitylene was distilled over CaH\textsubscript{2} under nitrogen. Dry xylenes, benzene, cesium carbonate, cesium pivalate, pivalic acid, molecular sieves 4Å, methyl-, ethyl-, benzyl-chloroformate, alkanone, (L)-(−)- and (D)-(+) norephedrine and 2-bromoaniline were purchased from Sigma-Aldrich, Fluka, Alfa Aesar or Acros. The substrates \textsuperscript{1} and N-alkylanilines were prepared by general procedure or previously reported procedure.\textsuperscript{[1-2]}

1.2 Representative procedure 1 (RP1) for N-alkyl-2-bromoaniline by reductive amination:\textsuperscript{[1]}

2-Bromoaniline (1.7 g, 10 mmol), molecular sieves 4Å (2.5 g) and alkanone (20-50 mmol, 2-5 equivs.) was dissolved in benzene (50 mL). The reaction mixture was stirred under reflux in a Dean-Stark apparatus for 4 days and then filtered through celite and washed with diethyl ether.
The filtrate was evaporated by rotary evaporator and dried under vacuum. The crude imine product was dissolved in absolute methanol (50 mL) and NaBH₄ (1.14 g, 30 mmol, 3 equivs.) was added slowly under nitrogen. The reaction mixture was stirred for 2 hours at room temperature (r.t.). 1N-KOH aq. (50 mL) was added and the mixture was extracted with dichloromethane (3×30 mL). The organic phase was dried over Na₂SO₄. After filtration and evaporation, the residue was purified by f.c. (silica gel; diethyl ether/pentane as eluent) affording N-alkyl-o-bromoaniline.

**Representative procedure 2 (RP2) for palladium-catalyzed N-arylation:**[2]

Pd₂(dba)₃ (2 mol%), rac-BINAP (6 mol%), and sodium tert-butoxide (1.4 equivs.) were sequentially filled into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry toluene, amine (1.1 equivs.) and 1,2-dibromobenzene (1 equiv.) was added under nitrogen. The resulting reaction mixture was stirred at 110 °C in a Schlenk tube behind a protection shield for 24 hours. The reaction mixture was cooled to r.t. (r.t) and diluted with ethylacetate followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl ether/pentane as eluent) to afford 2-bromo-N-alkylaniline.

2-Bromo-N-(pentan-3-yl)aniline: [1]

Synthesized by RP1, colorless oil, 26% yield, ^1^H NMR (400 MHz, CDCl₃): 1.24 (d, J = 6.4, 6H), 3.64 (oct, J = 6.4, 1H), 4.13 (d, J = 6.8 Hz, 1H), 6.51 (td, J = 7.6, 1.6 Hz, 1H), 6.63 (dd, J = 7.6, 1.6Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^1^C NMR (100 MHz): δ = 23.1, 44.5, 110.0, 112.0, 117.4, 128.6, 132.7, 144.4. IR (neat): ν = 736, 1017, 1112, 1153, 1285, 1318, 1366, 1384, 1425, 1462, 1506, 1595, 2929, 2966, 3405 cm⁻¹; HRMS calcd. for C₉H₁₂NBr 213.0153, found 213.0150.

2-Bromo-N-isopropylaniline: [3]
Synthesized by RP1, colorless oil, 32% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.92 (t, $J = 7.6$ Hz, 3H), 1.44-1.68 (m, 4H), 3.20-3.32 (m, 1H), 4.12 (d, $J = 8$ Hz, 1H), 6.49 (td, $J = 7.6$, 1.2 Hz, 1H), 6.60 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.12 (td, $J = 7.4$, 1.2 Hz, 1H), 7.39 (dd, $J = 8$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 10.3$, 26.9, 55.8, 110.0, 111.8, 117.1, 128.6, 132.7, 145.1. IR (neat): $\nu = 736$, 1016, 1163, 1286, 1321, 1381, 1427, 1459, 1507, 1594, 2875, 2931, 2963, 3410 cm$^{-1}$; HRMS calcd. for C$_{11}$H$_{16}$NBr 241.0466, found 241.0470.

2-Bromo-N-(heptan-4-yl)aniline:

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\begin{array}{c}
\text{Br} \\
\text{H} \\
\end{array}
\]

Synthesized by RP1, colorless oil, 11% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.91 (t, $J = 7.6$ Hz, 3H), 1.25-1.50 (m, 8H), 3.32-3.44 (m, 1H), 4.09 (d, $J = 8.4$ Hz, 1H), 6.48 (td, $J = 7.6$, 1.6 Hz, 1H), 6.60 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.12 (td, $J = 7.6$, 1.6 Hz, 1H), 7.38 (dd, $J = 8$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 14.4$, 19.3, 37.3, 52.8, 109.9, 111.6, 116.9, 128.6, 132.7, 145.0. MS (ESI, 70 eV): $m/z$ (%) = 270 (M+H)$^+$; IR (neat): $\nu = 1016$, 1184, 1114, 1162, 1287, 1030, 1378, 1427, 1458, 1508, 1594, 2870, 2930, 2957, 3406 cm$^{-1}$; HRMS calcd. for C$_{13}$H$_{20}$BrN 270.0851, found 270.0863.

2-Bromo-N-(1,3-diphenylpropan-2-yl)aniline:

\[
\begin{array}{c}
\text{Br} \\
\text{Ph} \\
\text{Ph} \\
\text{H} \\
\end{array}
\]

Synthesized by RP1, colorless oil, 5% yield, $^1$H NMR (400 MHz, CDCl$_3$): 2.84 (qd, $J = 14$, 6 Hz, 4H), 3.95 (quint, $J = 6$ Hz, 1H), 4.25-4.65 (brd, 1H), 6.51 (td, $J = 7.6$, 1.6 Hz, 1H), 6.67 (dd, $J = 8$, 1.2 Hz, 1H), 7.13 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.16-7.24 (m, 6H), 7.25-7.33 (m, 4H), 7.38 (dd, $J = 7.6$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 39.9$, 55.3, 110.4, 111.8, 117.7, 126.7, 128.6, 128.7, 129.7, 132.8, 138.4, 144.0. MS (ESI, 70 eV): $m/z$ (%) = 366 (M+H)$^+$; IR
(neat): $\nu = 737, 1017, 1088, 1126, 1286, 1320, 1429, 1454, 1495, 1594, 2922, 3026, 3062, 3400 \text{ cm}^{-1}$; HRMS calcd. for C$_{12}$H$_{16}$NBr 366.0851, found 366.0849

2-Bromo-N-(sec-butyl)aniline: $^[3]$

$$\text{Br}$$

Synthesized by RP1, colorless oil, 66% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.95 (t, $J = 7.6$ Hz, 1H), 1.20 (t, $J = 6.4$ Hz, 1H), 1.45-1.67 (m, 2H), 3.32-3.47 (m, 1H), 4.13 (d, $J = 6.8$ Hz, 1H), 6.50 (td, $J = 8$, 1.6 Hz, 1H), 6.61 (dd, $J = 8$, 0.8 Hz, 1H), 7.14 (td, $J = 7.6$, 0.8 Hz, 1H), 7.39 (dd, $J = 8$, 1.6 Hz, 1H).

2-Bromo-N-(pentan-2-yl)aniline:

$$\text{Br}$$

Synthesized by RP1, colorless oil, 45% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.91 (t, $J = 7.2$ Hz, 1H), 1.19 (d, $J = 6.4$ Hz, 1H), 1.31-1.65 (m, 4H), 3.40-3.56 (m, 1H), 3.95-4.35 (brd, 1H), 6.50 (td, $J = 7.6$, 1.6 Hz, 1H), 6.61 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.13 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.39 (dd, $J = 8$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 14.3, 19.5, 20.9, 39.4, 48.6, 110.0, 111.8, 117.3, 128.6, 132.7, 144.6$. MS (ESI, 70 eV): $m/z$ (%) = 242 (M+H)$^+$; IR (neat): $\nu = 739, 1018, 1048, 1112, 1166, 1286, 1321, 1378, 1426, 1459, 1508, 1595, 2871, 2930, 2960, 3408 \text{ cm}^{-1}$; ESI-HRMS calcd. for C$_{11}$H$_{17}$BrN 242.0538, found 242.0534.

2-Bromo-N-(4-methylpentan-2-yl)aniline:

$$\text{Br}$$

Synthesized by RP2, Colorless oil, 59% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.92 (t, $J = 7.2$ Hz, 1H), 1.19 (d, $J = 6$, Hz, 3H), 1.31-1.65 (m, 4H), 3.40-3.55 (m, 1H), 3.90-4.40 (brd, 1H),
6.50 (td, \( J = 7.6, 1.6 \) Hz, 1H), 6.61 (dd, \( J = 8.4, 1.6 \) Hz, 1H), 7.13 (dd, \( J = 7.6, 1.6 \) Hz, 1H), 7.39 (dd, \( J = 8, 1.6 \) Hz, 1H). \(^{13}\)C NMR (100 MHz): \( \delta = 21.2, 22.8, 23.1, 25.3, 46.9, 46.9, 110.0, 111.7, 117.2, 128.6, 132.7, 144.6. \) MS (EI, 70 eV): \( m/z \) (%) = 255 (M); IR (neat): \( \nu = 737, 1017, 1114, 1166, 1287, 1320, 1367, 1425, 1459, 1507, 1594, 2869, 2926, 2957, 3407 \) cm\(^{-1}\); EI-HRMS calcd. for \( \text{C}_{12}\text{H}_{18}\text{BrN} \) 255.0623, found 255.0621.

2-bromo-N-(1-cyclohexylpropan-2-yl)aniline:

![Chemical structure](image)

Synthesized by RP1, colorless oil, 17% yield, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.82-1.03 (m, 2H), 1.06-1.56 (m, 6H), 1.18 (d, \( J = 6.4 \) Hz, 3H), 1.57-1.81 (m, 5H), 3.50-3.64 (m, 1H), 3.92-4.30 (brd, 1H), 6.50 (td, \( J = 7.6, 1.2 \) Hz, 1H), 6.62 (dd, \( J = 8, 1.2 \) Hz, 1H), 7.14 (d, \( J = 7.8, 1.2 \) Hz, 1H), 7.39 (dd, \( J = 8, 1.6 \) Hz, 1H). \(^{13}\)C NMR (100 MHz): \( \delta = 26.5, 26.8, 33.6, 33.8, 34.8, 45.4, 46.2, 110.1, 111.8, 117.2, 128.6, 132.7, 144.6. \) IR (neat): \( \nu = 736, 1017, 1162, 1212, 1242, 1286, 1320, 1377, 1425, 1448, 1507, 1595, 2848, 2920, 3409 \) cm\(^{-1}\); ESI-HRMS calcd. for \( \text{C}_{15}\text{H}_{23}\text{BrN} \) 296.1008, found 296.1014.

2-Bromo-N-(3-methylbutan-2-yl)aniline:

![Chemical structure](image)

Synthesized by RP2, colorless oil, 62% yield, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.93 (d, \( J = 6.8 \) Hz, 3H), 0.99 (d, \( J = 7.2 \) Hz, 3H), 1.13 (d, \( J = 6.4 \) Hz, 3H), 3.31-3.42 (m, 1H), 4.00-4.45 (brd, 1H), 6.49 (td, \( J = 7.2, 1.2 \) Hz, 1H), 6.61 (dd, \( J = 8, 1.6 \) Hz, 1H), 7.13 (td, \( J = 8, 1.6 \) Hz, 1H), 7.39 (dd, \( J = 7.6, 1.2 \) Hz, 1H). \(^{13}\)C NMR (100 MHz): \( \delta = 16.8, 17.9, 19.2, 32.4, 53.8, 110.1, 111.9, 117.1, 128.6, 132.7, 144.7. \) IR (neat): \( \nu = 736, 1016, 1107, 1163, 1242, 1284, 1322, 1388, 1373, 1427, 1458, 1506, 1594, 2873, 2961, 3412 \) cm\(^{-1}\); EI-HRMS calcd. for \( \text{C}_{11}\text{H}_{16}\text{BrN} \) 241.0466, found 241.0467.

2-Bromo-N-(3,3-dimethylbutan-2-yl)aniline:
Synthesized by RP2, colorless oil, 55% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.98 (s, 9H), 1.11 (d, $J = 6.4$ Hz, 3H), 3.19-3.32 (m, 1H), 4.26 (d, $J = 7.2$ Hz, 1H), 6.48 (td, $J = 8$, 1.6 Hz, 1H), 6.63 (dd, $J = 8$, 0.8 Hz, 1H), 7.13 (td, $J = 8$, 1.6 Hz, 1H), 7.38 (dd, $J = 7.6$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 16.0$, 27.0, 35.1, 57.5, 110.2, 111.7, 117.2, 128.7, 132.7, 145.2. IR (neat): $\nu = 735$, 1016, 1106, 1140, 1285, 1321, 1373, 1509, 1592, 2870, 2963, 3412 cm$^{-1}$; EI-HRMS calcd. for C$_{12}$H$_{18}$BrN 255.0623, found 255.0624.

2-Bromo-N-(1-methoxypropan-2-yl)aniline:

Synthesized by RP2, colorless oil, 58% yield, $^1$H NMR (400 MHz, CDCl$_3$): 1.25 (d, $J = 6.4$ Hz, 3H), 3.38 (s, 3H), 3.42 (qd, $J = 9.6$, 4.8 Hz, 2H), 3.61-3.73 (m, 1H), 4.15-4.85 (brd, 1H), 6.53 (td, $J = 8$, 1.6 Hz, 1H), 6.67 (dd, $J = 8$, 1.2 Hz, 1H), 7.14 (td, $J = 7.6$, 1.6 Hz, 1H), 7.40 (dd, $J = 8$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 18.2$, 48.7, 59.4, 110.4, 112.1, 117.9, 128.6, 132.8, 144.4. IR (neat): $\nu = 738$, 922, 986, 1018, 1100, 1166, 1198, 1239, 1284, 1319, 1369, 1388, 1428, 1457, 1504, 1595, 2829, 2879, 2926, 2977, 3403 cm$^{-1}$; ESI-HRMS calcd. for C$_{16}$H$_{15}$BrNO 244.0331, found 244.0327.

2-Bromo-N-(1-phenylpropan-2-yl)aniline:

Synthesized by RP1, colorless oil, 47% yield, $^1$H NMR (400 MHz, CDCl$_3$): 1.20 (d, $J = 6.4$ Hz, 3H), 2.71 (qd, $J = 13.2$, 4.8 Hz, 2H), 3.72-3.86 (m, 1H), 4.10-4.42 (brd, 1H), 6.54 (td, $J = 7.6$, 1.2 Hz, 1H), 6.70 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.13-7.26 (m, 4H), 7.26-7.34 (m, 2H), 7.42 (dd, $J = 7.6$, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 20.3$, 42.5, 49.8, 110.2, 112.0, 117.7, 126.6, 128.6, 128.7, 129.7, 132.8, 138.4, 144.1. IR (neat): $\nu = 737$, 1016, 1046, 1112, 1151,
1201, 1245, 1283, 1319, 1377, 1427, 1453, 1498, 1594, 2926, 2967, 3026, 3063, 3401 cm\(^{-1}\); EI-HRMS calcd. for \(\text{C}_{15}\text{H}_{16}\text{BrN} \) 289.0466, found 289.0462.

2-Bromo-\(N\)-(4-phenylbutan-2-yl)aniline:\textsuperscript{[4]}

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Synthesized by RP1, colorless oil, 43% yield, \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): 1.26 (d, \(J = 6.4\) Hz, 3H), 1.76-2.00 (m, 2H), 2.73 (t, \(J = 8\) Hz, 2H), 3.44-3.58 (m, 1H), 4.02-4.30 (brd, 1H), 6.48-6.56 (m, 2H), 7.12 (td, \(J = 7.6, 1.6\) Hz, 1H), 7.15-7.22 (m, 3H), 7.25-7.32 (m, 2H), 7.41 (dd, \(J = 8.4, 1.6\) Hz, 1H). \(^{13}\text{C}\) NMR (100 MHz): \(\delta = 21.0, 32.6, 38.9, 48.2, 110.1, 112.0, 117.5, 126.1, 128.6, 132.7, 141.9, 144.3\). IR (neat): \(\nu = 740, 1017, 1061, 1094, 1161, 1190, 1286, 1320, 1378, 1426, 1457, 1506, 1595, 2926, 2965, 3026, 3062, 3403\) cm\(^{-1}\); EI-HRMS calcd. for \(\text{C}_{16}\text{H}_{18}\text{BrN} \) 303.0623, found 303.0620.

Ethyl 4-((2-bromophenyl)amino)pentanoate:

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Synthesized by RP1, colorless oil, 8% yield, \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): 1.22 (t, \(J = 7.2\) Hz, 3H), 1.22 d, \(J = 6.4\) Hz, 3H), 1.78-2.00 (m, 2H), 2.41 (t, \(J = 7.6\) Hz, 2H), 4.11 (q, \(J = 7.2\) Hz, 1H), 6.52 (td, \(J = 8, 1.2\) Hz, 1H), 6.64 (dd, \(J = 8.4, 1.2\) Hz, 1H), 7.14 (d, \(J = 7.8, 1.2\) Hz, 1H), 7.39 (dd, \(J = 8, 1.6\) Hz, 1H). \(^{13}\text{C}\) NMR (100 MHz): \(\delta = 14.4, 20.9, 31.2, 31.9, 48.4, 60.7, 110.2, 112.0, 117.7, 128.7, 132.8, 144.3, 173.7\). IR (neat): \(\nu = 739, 1017, 1095, 1119, 1178, 1215, 1258, 1320, 1375, 1428, 1460, 1506, 1595, 1729, 2972, 3383\) cm\(^{-1}\); ESI-HRMS calcd. for \(\text{C}_{13}\text{H}_{19}\text{BrNO}_{2} \) 300.0593, found 300.0597.

2-Bromo-\(N\)-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)aniline:
Synthesized by RP1, colorless oil, 50% yield, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.03 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.21 (d, \(J = 6.4 \text{ Hz}, 3 \text{H}\)), 3.44-3.56 (m, 1H), 3.62 (t, \(J = 6 \text{ Hz}, 2 \text{H}\)), 3.98-4.32 (brd, 1H), 6.50 (td, \(J = 8, 1.6 \text{ Hz}, 1 \text{H}\)), 6.61 (dd, \(J = 8, 1.2 \text{ Hz}, 1 \text{H}\)), 7.13 (td, \(J = 7.6, 1.6 \text{ Hz}, 1 \text{H}\)), 7.38 (dd, \(J = 7.6, 1.6 \text{ Hz}, 1 \text{H}\)). \(^{13}\)C NMR (100 MHz): \(\delta = -5.1, 18.6, 21.0, 26.2, 29.5, 33.4, 48.7, 63.2, 110.0, 111.9, 117.3, 128.6, 132.7, 144.5\). IR (neat): \(\nu = 737, 833, 939, 1017, 1092, 1206, 1252, 1285, 1321, 1381, 1427, 1460, 1508, 1596, 2857, 2929, 3409 \text{ cm}^{-1}\); ESI-HRMS calcd. for C\(_{17}\)H\(_{31}\)BrNOSi 372.1335, found 372.1336.

1.3 Representative synthesis of methyl \(N\)-cycloalkyl-2-bromophenylcarbamate 1 and 6:

\(N\)-alkyl-\(o\)-bromoaniline was dissolved in methyl chloroformate (15 equivs.). The reaction mixture was refluxed for 4-24 hours and then poured into water and extracted with dichloromethane. The organic phase was dried over MgSO\(_4\) and evaporated after filtration. The filtrate was evaporated by rotary evaporator and purified by f.c. (silica gel; ethyl acetate/pentane as eluent) affording carbamate 1 or 6.

Methyl (2-bromophenyl)(isopropyl)carbamate 1a: \([3]\)

White solid, 77% yield, M.p. 47 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.01 (d, \(J = 7.2 \text{ Hz}, 3 \text{H}\)), 1.30 (d, \(J = 6.4 \text{ Hz}, 3 \text{H}\)), 3.61 (s, 3H), 4.36-4.42 (m, 1H), 7.15 (dd, \(J = 7.6, 1.6 \text{ Hz}, 1 \text{H}\)), 7.17 (d, \(J = 7.6 \text{ Hz}, 1 \text{H}\)), 7.30 (td, \(J = 7.6, 1.6 \text{ Hz}, 1 \text{H}\)), 7.62 (d, \(J = 7.6, 1.2 \text{ Hz}, 1 \text{H}\)). \(^{13}\)C NMR (100 MHz): \(\delta = 19.8, 22.8, 50.5, 53.0, 126.1, 128.0, 129.1, 130.8, 133.6, 138.6, 155.4\). MS (ESI, 70 eV): \(m/z \% = 253 \text{ (M)}^+\); IR (neat): \(\nu = 726, 755, 785, 861, 955, 980, 1051, 1095, 1134, 1194, 1249, 1265, 1276, 1319, 1368, 1390, 1441, 1477, 1586, 1706, 2977 \text{ cm}^{-1}\); ESI-HRMS calcd. for C\(_{11}\)H\(_{14}\)NNaO\(_2\)Br 294.0100, found 253.0099.
Methyl (2-bromophenyl)(pentan-3-yl)carbamate 1b:
White solid, 93% yield, M.p. 36 °C, $^1$H NMR (400 MHz, CDCl$_3$): 1.16-1.46 (m, 5H), 1.58-1.69 (m, 1H), 1.70-1.82 (m, 2H), 1.96-2.10 (m, 2H), 3.22-3.36 (m, 1H), 4.22 (d, $J = 7.6$ Hz, 1H), 6.50 (td, $J = 8$, 1.2 Hz, 1H), 6.63 (dd, $J = 8$ Hz, 1H), 7.13 (d, $J = 8$, 1.2 Hz, 1H), 7.39 (dd, $J = 8$, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz): δ = 25.6, 26.1, 30.4, 33.1, 53.0, 58.4, 126.2, 127.9, 129.0, 131.1, 133.5, 138.8, 155.5. MS (ESI, 70 eV): $m/z$ (%) = 253 (M)$^+$; IR (neat): $\tilde{\nu}$ = 736, 853, 888, 923, 1016, 1096, 1126, 1148, 1231, 1253, 1285, 1319, 1366, 1429, 1451, 1505, 1592, 2852, 2927, 3404 cm$^{-1}$; HRMS calcd. for C$_{12}$H$_{16}$NBr 253.0466, found 253.0466.
Methyl (2-bromophenyl)(heptan-4-yl)carbamate 1c:

White solid, 97% yield, M.p. 41 °C, $^1$H NMR (400 MHz, CDCl$_3$): 0.84 (t, $J = 7.2$ Hz, 1H), 0.95 (t, $J = 7.2$ Hz, 1H), 1.03-1.18 (m, 1H), 1.20-1.72 (m, 7H), 3.61 (s, 3H), 4.04-4.34 (m, 1H), 7.08-7.18 (m, 2H), 7.30 (td, $J = 7.6, 1.2$ Hz, 1H), 7.61 (dd, $J = 8.8, 1.6$ Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 14.3, 14.4, 20.1, 20.7, 34.4, 36.8, 53.1, 59.8, 53.1, 59.8, 126.0, 128.1, 128.6, 130.1, 139.4, 156.0. MS (ESI, 70 eV): m/z (%) = 328 (M+H)$^+$; IR (neat): $\nu = 744, 763, 905, 930, 1001, 1031, 1058, 1108, 1191, 1264, 1289, 1318, 1389, 1440, 1473, 1585, 1707, 2871, 2957$ cm$^{-1}$; HRMS calcd. for C$_{15}$H$_{23}$BrNO$_2$ 328.0906, found 328.0904.
Methyl (2-bromophenyl)(1,3-diphenylpropan-2-yl)carbamate 1d:
White solid, M.p. 77 °C, 88% yield, $^1$H NMR (400 MHz, CDCl$_3$): 2.60 (dd, $J = 14$, 6 Hz, 1H), 3.40 (d, $J = 8$ Hz, 2H), 3.42-3.51 (m, 1H), 3.66 (s, 3H), 4.00-4.15 (m, 1H), 5.93 (d, $J = 7.2$ Hz, 1H), 6.15-6.39 (brd, 0.1H), 6.96-7.11 (m, 4H), 7.15-7.36 (m, 8H), 7.54 (d, $J = 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 37.0$, 40.1, 53.1, 66.8, 124.6, 126.5, 126.6, 128.3, 128.6, 128.7, 129.4, 129.7, 130.0, 133.4, 139.4, 139.7, 141.5, 155.3. MS (ESI, 70 eV): $m/z$ (%) = 424 (M+H)$^+$; IR (neat): $\nu = 699$, 720, 750, 789, 917, 943, 994, 1029, 1061, 1129, 1155, 1191, 1217, 1265, 1293, 1401, 1441, 1474, 1495, 1584, 1602, 1707, 2951, 3027 cm$^{-1}$; ESI-HRMS calcd. for C$_{23}$H$_{23}$NOBr 424.0906, found 424.0897.
Methyl (2-bromophenyl)(sec-butyl)carbamate 6a: [3]

Colorless oil, 98% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.87 (t, $J = 7.6$ Hz, 1H), 0.96 (d, $J = 6.8$ Hz, 2H), 0.98 (t, $J = 7.6$ Hz, 2H), 1.32 (d, $J = 6.4$ Hz, 1H), 1.45-1.60 (m, 0.8H), 1.66-1.84 (m, 1.2H), 3.61 (s, 3H), 4.01-4.13 (m, 0.5H), 4.22-4.44 (m, 0.5H), 7.09-7.22 (m, 2H), 7.25-7.33 (m, 1H), 7.54-7.66 (m, 1H). $^{13}$C NMR (100 MHz): $\delta = 11.3, 11.8, 16.8, 19.3, 26.9, 29.9, 52.9, 53.0, 55.9, 57.5, 125.7, 126.3, 128.0, 128.8, 128.9, 130.5, 133.5, 138.4, 139.6, 155.2, 155.8. MS (ESI, 70 eV): $m/z$ (%) = 286 (M+H)+; IR (neat): $\nu = 730, 753, 840, 935, 953, 998, 1028, 1052, 1093, 1120, 1191, 1244, 1266, 1295, 1310, 1325, 1389, 1439, 1475, 1585, 1706, 2877, 2968 cm$^{-1}$; ESI-HRMS calcd. for C$_{12}$H$_{17}$BrN 286.0437, found 286.0432.
Methyl (2-bromophenyl)(pentan-2-yl)carbamate 6b:
Colorless oil, 99% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.85 (t, $J = 7.2$ Hz, 1.2H), 0.91-1.00 (m, 4H), 1.07-1.53 (m, 3.8H), 1.61-1.77 (m, 1H), 3.61 (s, 3H), 4.10-4.24 (m, 0.4H), 4.30-4.55 (m, 0.6H), 7.10-7.22 (m, 2H), 7.26-7.34 (m, 1H), 7.38 (d, $J = 8$, 1H). $^{13}$C NMR (100 MHz): $\delta$ = 14.2, 14.2, 17.3, 20.0, 20.4, 52.9, 53.0, 54.3, 55.7, 125.8, 126.3, 128.0, 128.8, 128.9, 130.5, 138.4, 139.6, 155.3, 155.7. MS (ESI, 70 eV): $m/z$ (%) = 300 (M+H)$^+$. IR (neat): $\nu =$ 728, 746, 761, 785, 869, 911, 951, 1028, 1056, 1301, 1191, 1264, 1319, 1390, 1440, 1475, 1585, 1605, 2872, 2957 cm$^{-1}$; ESI-HRMS calcd. for C$_{13}$H$_{19}$BrNO$_2$ 300.0593, found 300.0604.
Methyl (2-bromophenyl)(4-phenylbutan-2-yl)carbamate 6c:

White solid, 88% yield, M.p. 61 °C, $^1$H NMR (400 MHz, CDCl$_3$): 1.12 (d, $J = 6.8$ Hz, 1.9H), 1.48 (d, $J = 6.8$ Hz, 1.1H), 1.55-1.67 (m, 0.4H), 1.82-1.99 (m, 0.6H), 2.08-2.26 (m, 1H), 2.70 (d, $J = 8.4$ Hz, 0.7H), 2.81 (t, $J = 8.4$ Hz, 1.3H), 3.71 (s, 3H), 4.23-4.39 (m, 0.4H), 4.49-4.67 (m, 0.6H), 7.15-7.45 (m, 8H), 7.70 (td, $J = 8.4$, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ = 17.3, 20.2, 33.3, 33.6, 35.9, 39.0, 53.0, 53.1, 54.5, 55.7, 125.7, 126.1, 126.1, 126.3, 128.2, 128.5, 128.6, 128.9, 129.1, 133.7, 138.5, 141.8, 142.0, 155.4, 155.8. MS (ESI, 70 eV): $m/z$ (%) = 278 (M+H)$^+$; IR (neat): $\nu$ = 724, 750, 783, 952, 1029, 1043, 1060, 1117, 1190, 1317, 1389, 1440, 1475, 1585, 1705, 2950, 3026 cm$^{-1}$; ESI-HRMS calcd. for C$_{15}$H$_{20}$NO$_4$ 278.1386, found 278.1390.
Methyl (2-bromophenyl)(5-(tert-butyldimethylsilyl)oxy)pentan-2-yl)carbamate 6d:
Colorless oil, 29% yield, $^1$H NMR (400 MHz, CDCl$_3$): -0.04 (s, 1H), -0.03 (s, 1H), 0.04 (s, 3.8H), 0.08 (s, 0.8H), 0.82 (s, 3.2H), , 0.88 (d $J = 6.8$ Hz, 1.1H), 0.89 (s, 5H), 0.98 (d $J = 6.8$ Hz, 1.9H), , 1.34 (d $J = 6.8$ Hz, 1.1H), 1.44-1.85 (m, 4H), 3.47-3.74 (m, 2H), 3.61 (s, 3H), 4.08-4.28 (m, 0.4H), 4.40-4.58 (m, 0.6H) 7.10-7.23 (m, 2H), 7.29 (td, $J = 8$, 1.2 Hz, 1H), 7.14 (d, $J = 8$, 1.2 Hz, 1H), 7.38 (dd, $J = 8$, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = -5.2$, -5.1, 15.5, 17.6, 18.5, 18.6, 20.1, 26.2, 26.2, 30.0, 30.5, 33.4, 53.0, 53.1, 54.2, 55.8, 63.1, 125.8, 126.4, 128.1, 128.9, 129.0, 130.6, 130.7, 138.2, 155.9. MS (ESI, 70 eV): $m/z$ (%) = 430 (M+H)$^+$; IR (neat): $\nu = 729, 774, 833, 939, 1006, 1030, 1090, 1192, 1252, 1321, 1390, 1441, 1475, 1586, 1711, 2857, 2952$ cm$^{-1}$; ESI-HRMS calcd. for $\text{C}_{19}\text{H}_{33}\text{BrNO}_3\text{Si}$ 430.1407, found 430.1406.
Ethyl 4-((2-bromophenyl)(methoxycarbonyl)amino)pentanoate 6e:

![Chemical Structure](image)

Colorless oil, >99% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.99 (d, $J = 6.8$ Hz, 2H), 1.45-1.28 (m, 3.2H), 1.34 (d, $J = 6.8$ Hz, 1H), 1.54-1.68 (m, 0.8H), 1.68-1.81 (m, 2H), 1.77-1.91 (m, 0.7H), 1.97-2.14 (m, 1H), 2.36 (t, $J = 7.6$ Hz, 0.7H), 2.45 (t, $J = 7.6$ Hz, 1.3H), 3.61 (s, 3H), 4.02-4.20 (m, 2.3H), 4.30-4.56 (m, 0.7H), 7.11-7.23 (m, 2H), 7.26-7.35 (m, 1H), 7.62 (d, $J = 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz): $\delta = 14.4, 17.4, 19.9, 29.3, 31.8, 32.1, 53.0, 53.2, 53.8, 55.7, 60.6, 60.7, 125.5, 126.3, 128.2, 128.2, 129.0, 129.1, 130.5, 130.6, 133.7, 133.8, 138.2, 139.5, 155.8. MS (ESI, 70 eV): $m/z$ (%) = 358 (M+H)$^+$; IR (neat): $\nu$ = 758, 785, 856, 946, 1029, 1076, 1119, 1129, 1319, 1390, 1441, 1475, 1586, 1706, 2980 cm$^{-1}$; ESI-HRMS calcd. for C$_{15}$H$_{21}$BrNO$_4$ 358.0648, found 358.0640.
Methyl (2-bromophenyl)(1-methoxypropan-2-yl)carbamate 6f:
White solid, 87% yield, M.p. 39 ºC; $^1$H NMR (400 MHz, CDCl$_3$): 0.98 (d, $J$ = 6.8 Hz, 2H), 1.39 (d, $J$ = 6.8 Hz, 1H), 3.27 (s, 1.3H), 3.39 (s, 1.7H), 3.42 (d, $J$ = 6.4 Hz, 2H), 3.61 (s, 2.4H), 3.74-3.85 (m, 0.6H), 4.00-4.12 (m, 0.3H), 4.40-4.80 (m, 0.7H), 7.25-7.34 (m, 2H), 7.60 (t, $J$ = 7.6 Hz, 1H). $^{13}$C NMR (100 MHz): $\delta$ = 14.4, 16.7, 52.7, 52.9, 53.1, 73.9, 74.8, 124.9, 126.2, 128.0, 128.1, 128.7, 129.1, 130.9, 131.4, 133.3, 133.3, 155.0, 155.8. MS (ESI, 70 eV): $m/z$ (%) = 302 (M+H)$^+$; IR (neat): $\nu$ = 728, 759, 786, 928, 958, 982, 1045, 1029, 1073, 1103, 1154, 1194, 1268, 1298, 1318, 1375, 1441, 1475, 1586, 1706, 2582, 2951 cm$^{-1}$; HRMS calcd. for C$_{12}$H$_{17}$BrNO$_3$ 302.0386, found 302.0390.
Methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate 6g:

![Structural formula of the compound]

White solid, 97% yield, M.p. 102 °C, $^1$H NMR (400 MHz, CDCl$_3$): 0.90 (d, $J = 6.8$ Hz, 1.7H), 0.83 (d, $J = 6.8$ Hz, 1.3H), 2.44 (dd, $J = 12.8$, 9.2 Hz, 0.4H), 2.78 (dd, $J = 12.8$, 10 Hz, 0.6H), 3.27 (dd, $J = 12.8$, 8.4 Hz, 0.6H), 3.33-3.43 (m, 0.4H), 3.65 (s, 3H), 4.10-4.26 (m, 0.4H), 4.34-4.64 (m, 0.6H), 6.70 (d, $J = 7.2$ Hz, 0.4H), 7.05-7.37 (m, 7.6H), 7.56-7.66 (m, 1H). $^{13}$C NMR (100 MHz): $\delta$ = 16.3, 19.3, 40.8, 43.3, 53.0, 53.1, 56.3, 59.2, 125.3, 126.2, 126.6, 128.2, 128.6, 128.9, 129.2, 129.6, 130.6, 130.7, 133.6, 138.9, 139.5, 140.3, 155.2, 155.6. MS (ESI, 70 eV): $m/z$ (%) = 348 (M+H)$^+$; IR (neat): $\nu$ = 700, 729, 744, 761, 830, 860, 915, 951, 983, 1029, 1069, 1167, 1191, 1293, 1325, 1388, 1440, 1475, 1585, 1704, 2951, 2978, 3027, 3062 cm$^{-1}$; HRMS calcd. for C$_{17}$H$_{19}$BrNO$_2$ 348.0593, found 348.0589.
Methyl (2-bromophenyl)(4-methylpentan-2-yl)carbamate \textbf{6h}:
White solid, 91% yield, M.p. 51 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.82-0.88 (m, 2.2H), 0.91-1.01 (m, 5.8H), 1.05-1.18 (m, 0.4H), 1.26-1.41 (m, 0.4H), 1.41-1.50 (m, 0.4H), 1.51-1.72 (m, 1.4H), 3.60 (s, 2.6H), 3.78 (s, 0.4H), 4.18-4.36 (brd, 0.4H), 4.44-4.60 (m, 0.6H), 7.10-7.20 (m, 2H), 7.26-7.34 (m, 1H), 7.62 (dt, \(J = 8, 1.6\) Hz, 1H). \(^{13}\)C NMR (100 MHz): \(\delta =^{13}\)C NMR (100 MHz): \(\delta = 17.4, 20.2, 21.7, 22.3, 23.5, 23.8, 25.3, 25.4, 43.1, 46.2, 52.6, 52.9, 53.0, 53.9, 125.8, 126.4, 128.0, 128.8, 128.9, 130.5, 130.6, 133.6, 138.4, 139.5, 155.4, 155.7. MS (ESI, 70 eV): \(m/z\) (%) = 314 (M+H); IR (neat): \(\nu = 728, 757, 784, 950, 1030, 1061, 1108, 1168, 1191, 1264, 1290, 1317, 1366, 1389, 1400, 1474, 1585, 1705, 2954\) cm\(^{-1}\); ESI-HRMS calcd. for C\(_{14}\)H\(_{21}\)BrNO 314.0750, found 314.0748.
Methyl (2-bromophenyl)(1-cyclohexylpropan-2-yl)carbamate 6i:

White solid, 94% yield, M.p. 59 °C, $^1$H NMR (400 MHz, CDCl$_3$): 0.75-1.40 (m, 11.1H), 1.44-1.87 (m, 5.9H), 3.60 (s, 3H), 4.21-4.36 (m, 0.4H), 4.42-4.64 (m, 0.6H), 7.08-7.21 (m, 2H), 7.25-7.33 (m, 1H), 7.56-7.66 (m, 1H). $^{13}$C NMR (100 MHz): $\delta$ = 17.6, 20.4, 26.4, 26.5, 26.6, 26.8, 41.6, 44.8, 52.1, 53.0, 53.3, 125.8, 126.4, 128.0, 128.8, 128.9, 130.4, 130.6, 133.6, 139.6, 155.4, 155.6. MS (ESI, 70 eV): $m/z$ (%) = 354 (M+H)$^+$; IR (neat): $\nu$ = 728, 755, 843, 877, 950, 1030, 1068, 1115, 1190, 1264, 1314, 1370, 1391, 1440, 1475, 1586, 1606, 2850, 2921 cm$^{-1}$; ESI-HRMS calcd. for C$_{17}$H$_{25}$BrNO$_2$ 354.1063, found 354.1054.
Methyl (2-bromophenyl)(3-methylbutan-2-yl)carbamate 6j:
Colorless oil, 88% yield, $^1$H NMR (400 MHz, CDCl$_3$): 0.80 (d, $J = 6.8$ Hz, 0.7H), 0.92 (d, $J = 6.8$ Hz, 2.3H), 0.93 (d, $J = 6.4$ Hz, 2.3H), 1.03 (d, $J = 7.6$ Hz, 0.7H), 1.10 (d, $J = 6.8$ Hz, 1H), 1.74-1.90 (m, 0.8H), 2.20-2.42 (m, 0.2H), 3.38-3.48 (m, 0.3 H), 3.62 (s, 3H), 4.14-4.32 (m, 0.7H), 7.08-7.23 (m, 2H), 7.30 (td, $J = 7.6, 1.2$ Hz, 1H), 7.56-7.66 (m, 1H). $^{13}$C NMR (100 MHz): $\delta$ 14.9, 16.8, 19.7, 19.8, 20.3, 22.1, 31.2, 34.0, 52.8, 53.1, 59.9, 65.2, 124.8, 126.6, 128.0, 128.2, 128.4, 128.8, 130.1, 130.2, 133.6, 133.7, 138.6, 141.9, 155.1, 156.3. MS (ESI, 70 eV): $m/z$ (%) = 300 (M+H)$^+$; IR (neat): $\nu$ = 731, 755, 900, 949, 986, 1031, 1054, 1092, 1109, 1160, 1191, 1262, 1306, 1383, 1440, 1474, 1585, 1706, 2875, 2964 cm$^{-1}$; ESI-HRMS calcd. for C$_{13}$H$_{19}$BrNO$_2$ 300.0593, found 300.0583.
Methyl (2-bromophenyl)(3,3-dimethylbutan-2-yl)carbamate 6k:

![NMR spectrum](image)

White solid, 48% yield, M.p. 67 °C, $^1$H NMR (400 MHz, CDCl$_3$): 0.92-1.06 (m, 11.6H), 1.52 (d, $J = 7.2$ Hz, 0.6H), 3.59 (s, 3H), 3.71-3.91 (m, 0.2H), 4.20-4.60 (m, 0.8H), 7.06-7.17 (m, 1H), 7.23-7.41 (m, 2H), 7.55-7.62 (m, 1H). $^{13}$C NMR (100 MHz): $\delta = 12.6, 16.4, 27.8, 28.5, 36.6, 36.9, 53.0, 53.2, 57.0, 58.9, 62.1, 66.4, 126.7, 127.6, 127.8, 128.3, 128.7, 131.3, 133.5, 134.1, 140.2, 142.6, 156.0. MS (ESI, 70 eV): $m/z$ (%) = 314 (M+H)$^+$; IR (neat): $\nu = 731, 755, 900, 949, 986, 1031, 1054, 1092, 1109, 1160, 1191, 1261, 1306, 1283, 1440, 1474, 1585, 1706, 2875, 2964$ cm$^{-1}$; ESI-HRMS calcd. for C$_{14}$H$_{21}$BrNO$_2$ 314.0750, found 314.0752.
1.4 Representative racemic synthesis of indolines 2 and 7:

Carbamate (0.2 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), pivalic acid (6.1 mg, 0.06 mmol), cecium carbonate (97.5 mg, 0.3 mmol), and PCy$_3$·HBF$_4$ (14.7 mg, 0.04 mmol) were sequentially filled into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes were added under nitrogen and the resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield overnight (17-24 h). The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the racemic indoline.

1.5 Racemic synthesis of indoline 7a using PCy$_3$·HBF$_4$ as a ligand:

Substrate 6a (57.2 mg, 0.2 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), pivalic acid (6.1 mg, 0.06 mmol), cecium carbonate (97.5 mg, 0.3 mmol), and PCy$_3$·HBF$_4$ (14.7 mg, 0.04 mmol) were placed into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes 2 mL were added under nitrogen and the resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was
cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the racemic indoline 7a in 91% yield (37.3 mg).

**Racemic synthesis of indoline 7a using IPr·HCl as a ligand:**

Substrate 6a (57.2 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]2 (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and IPr·HCl (8.5 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylene (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline 7a in 91% yield (37.5 mg).

**1.6 Representative procedure for the asymmetric NHC-palladium catalyzed C-H activation:**

Carbamate 1a (62.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]2 (2.6 mg, 0.005 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and NHC-HI (0.01 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry mesitylene (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 160 °C in the Schlenk tube behind a protective shield for 3 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline methyl carbamate 2a.
1.7 Synthesis, spectra, analysis of substrates 2a-d and 7a-h, and 8a-h

(S)-methyl 2-methylindoline-1-carboxylate 2a: \[^3\]

![Chemical structure of 2a](image)

Colorless oil, 84% yield (32.1 mg), 90\% ee, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.27 (d, \(J = 7.2\) Hz, 1H), 2.62 (dd, \(J = 16, 2\) Hz, 1H), 3.35 (dd, \(J = 16, 9.6\) Hz, 1H), 3.83 (s, 3H), 4.40-4.65 (m, 1H), 6.57 (t, \(J = 7.2\) Hz, 1H), 7.14 (d, \(J = 7.6\) Hz, 1H), 7.17 (t, \(J = 7.6\) Hz, 1H), 7.44-8.10 (brd, 1H).

The enantiomer ratio was determined by HPLC: (chiral column: AS-H, \(n\)-hexane/\(i\)-propanol = 99 : 1, 0.5 mL/min, 254 nm); \(t_R = 11.7\) min [minor] and 13.6 min [major]. \([\alpha]_D^{20} = +52.0\) (\(c = 0.5\) in CH\(_2\)Cl\(_2\)).
(2S,3R)-methyl 2-ethyl-3-methylindoline-1-carboxylate 2b:

$$\text{HO}_2$$

Colorless oil, 92% yield (40.3 mg), 97% ee, $^1$H NMR (400 MHz, CDCl$_3$): 0.87 (t, $J = 7.6$ Hz, 3H), 1.23 (d, $J = 6.8$ Hz, 3H), 1.46-1.61 (m, 1H), 1.70-1.82 (m, 1H), 2.96 (qd, $J = 6.8$, 1.6 Hz, 1H), 3.82 (s, 3H), 3.78-3.98 (m, 1H), 7.03 (s, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.34-8.12 (brd, 1H). $^{13}$C NMR (100 MHz): $\delta = 9.2$, 22.8, 27.1, 40.2, 52.7, 66.9, 115.4, 123.0, 124.4, 127.8, 136.2, 136.4, 154.2. MS (ESI, 70 eV): $m/z$ (%) = 220 (M+H)$^+$; IR (neat): $\nu = 753$, 820, 1019, 1065, 1137, 1192, 1216, 1284, 1312, 1335, 1391, 1441, 1485, 1602, 1706, 2963 cm$^{-1}$; ESI-HRMS calcd. for C$_{13}$H$_{18}$NO$_2$ 220.1332, found 220.1332.
The ratio of enantiomers was determined by HPLC: (chiral column: AS-H, n-hexane/ i-propanol = 99 : 1, 0.5 mL/min, 254 nm); $t_R = 8.7$ min [minor] and 9.6 min [major]. $[\alpha]_D^{20} = +6.3$ ($c = 1.0$ in CH$_2$Cl$_2$).

CD spectrum: 0.000023 M in n-hexane at 20 °C

(2S,3R)-methyl 3-ethyl-2-propyldoline-1-carboxylate 2c:
Colorless oil, 92% yield (45.4 mg), 97% ee, $^1$H NMR (400 MHz, CDCl$_3$): 0.81-0.98 (m, 6H), 1.18-1.78 (m, 6H), 2.76 (t, $J = 6.4$ Hz, 1H), 3.83 (s, 3H), 3.95-4.18 (m, 1H), 6.95 (td, $J = 7.6$, 0.8 Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.46-8.10 (m, 1H). $^{13}$C NMR (100 MHz): δ = 11.3, 14.2, 18.2, 29.5, 31.1, 36.4, 36.8, 47.2, 47.6, 52.6, 65.0, 115.5, 122.8, 124.9, 125.2, 127.8, 134.7, 135.4, 140.8, 141.9, 153.9, 154.2. MS (ESI, 70 eV): m/z (%) = 248 (M+H)$^+$; IR (neat): ν = 748, 794, 869, 931, 1022, 1064, 1116, 1135, 1190, 1209, 1269, 1284, 1306, 1332, 1389, 1441, 1461, 1483, 1602, 1703, 2873, 2931, 2958 cm$^{-1}$; ESI-HRMS calcd. for C$_{15}$H$_{22}$NO$_2$ 248.1645, found 248.1642.
The enantiomer ratio was determined by HPLC: (chiral column: (R,R)-Whelk-O1, n-hexane/i-propanol = 99.05 : 0.5, 1.0 mL/min, 254 nm); \( t_R = \text{8.2 min [minor]} \) and \( 9.3 \text{ min [major]} \). \( [\alpha]_D^{20} = +9.0 \) (c = 2.0 in CH₂Cl₂).
The CD spectrum of the compound 2d is shown in the image. The spectrum was recorded in n-hexane at 20 °C.

**2d:**

White solid, 82% yield (56.3 mg), M.p. 75 °C, 98% ee. 

**1H NMR (400 MHz, CDCl3):** 2.70 (dd, J = 12.8, 10.8 Hz, 1H), 3.20-3.50 (brd, 1H), 3.79 (s, 3H), 4.15 (s, 1H), 4.40-4.60 (m, 1H), 6.50-6.62 (m, 2H), 6.96-7.14 (m, 5H), 7.18-7.41 (m, 6H), 8.44-8.20 (brd, 1H).

**13C NMR (100 MHz):** δ = 40.6, 50.4, 52.8, 69.9, 115.7, 123.5, 126.3, 126.8, 126.9, 127.2, 128.6, 128.8, 129.9, 132.9, 137.4, 144.1, 153.7.

**MS (ESI, 70 eV):** m/z (%) = 344 (M+H)+; IR (neat): ν = 698, 733, 757, 792, 849, 878, 919, 1057, 1079, 1136, 1157, 1193, 1246, 1278, 1304, 1342, 1390, 1441, 1484, 1598, 1711, 2952, 3027 cm⁻¹; ESI-HRMS calcd. for C_{23}H_{22}NO_{2} 344.1645, found 344.1648.
The ratio of enantiomers was determined by HPLC: (chiral column: OD-H, \( n \)-hexane/ \( i \)-propanol = 99 : 1, 1.0 mL/min, 254 nm); \( t_R = 10.1 \) min [minor] and \( 13.2 \) min [major]. \([\alpha]_D^{20} = +107.8 \) (\( c = 1.0 \) in \( \text{CH}_2\text{Cl}_2 \)).

CD spectrum: 0.000052 M in \( n \)-hexane at 20 °C

\((R)\)-methyl 2-ethylindoline-1-carboxylate \( 7a \); \((S,S)\)-NHCHI (3) was used.
Colorless oil, 57% yield calcd. by NMR (23.2 mg), 77% ee, $^1$H NMR (400 MHz, CDCl$_3$): 0.86 (t, $J$ = 7.6 Hz, 3H), 1.49-1.63 (m, 1H), 1.67-1.87 (m, 1H), 2.74 (dd, $J$ = 16, 2.4 Hz, 1H), 3.27 (dd, $J$ = 16, 9.6 Hz, 1H), 3.82 (s, 3H), 4.28-4.46 (m, 1H), 6.94 (td, $J$ = 7.2, 0.8 Hz, 1H), 7.12 (d, $J$ = 7.6 Hz, 1H), 7.15 (t, $J$ = 7.6 Hz, 1H), 7.34-8.10 (m, 1H).
76% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \(t_R = 21.44\) min. (major) and 26.68 (minor)].

(R)-methyl 2-ethylindoline-1-carboxylate 7a and (2R,3S)-methyl 2,3-dimethylindoline-1-carboxylate 8a; (S,S)-NHC. (3) was used.

Colorless oil, 8a: 38% yield calcd. by NMR (15.5 mg), 7a + 8a: \(^1\)H NMR (400 MHz, CDCl\(_3\)):
\[\delta 0.88 (t, J = 7.4 \text{ Hz}, 4\text{H}), 1.23 (d, J = 7.0 \text{ Hz}, 2\text{H}), 1.29 (d, J = 6.3 \text{ Hz}, 2\text{H}), 1.52-1.63 (m, \text{m})\]
1.4H), 1.77 (brd, 1H), 2.76 (d, \( J = 16.0 \) Hz, 1H), 2.85 (q, \( J = 6.8 \) Hz, 0.65H), 3.28 (dd, \( J = 16.0, 9.6 \) Hz, 1H), 3.83 (s, 5H), 4.05 (brd, 0.65H), 4.38 (brd, 1H), 6.93-7.00 (m, 1.65H), 7.13-7.21 (m, 3.5H), 7.77 (brd, 1.65H). \( 7a + 8a \): \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 9.1, 20.5, 21.8, 27.3, 32.90, 32.97, 43.0, 52.4, 60.6, 63.4, 115.2, 115.3, 122.7, 122.8, 124.3, 124.8, 127.3, 127.7, 153.8.

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8a: >99% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \( t_R = 15.19 \) min. (major)]

\((R)\)-methyl 2-propylindoline-1-carboxylate 7b; \((S,S)\)-NHC\(\text{HI}\) (3) was used.

68% yield calcd. by NMR (29.7 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.90 (t, \( J = 7.6 \) Hz, 3H), 1.22-1.39 (m, 2H), 1.22-1.39 (m, 2H), 1.45-1.56 (m, 1H), 2.73 (dd, \( J = 16, 2 \) Hz, 1H), 3.27 (dd, \( J = 16, 9.6 \) Hz, 1H), 3.82 (s, 3H), 4.34-4.56 (brd, 1H), 6.94 (td, \( J = 7.6, 1.2 \) Hz, 1H), 7.12(d, \( J = 8 \) Hz, 1H), 7.16 (t, \( J = 7.6 \) Hz, 1H), 7.26-8.40 (brd, 1H). \(^{13}\)C NMR (100 MHz): \( \delta = \)}
14.2, 18.3, 33.6, 37.0, 52.6, 59.5, 115.5, 122.9, 125.0, 127.5, 130.6, 154.0. MS (ESI, 70 eV): 
$m/z$ (%) = 220 (M+H)$^+$; IR (neat): $\nu = 751, 1022, 1059, 1135, 1193, 1221, 1239, 1270, 1290, 1330, 1390, 1441, 1485, 1603, 1702, 2871, 2957$ cm$^{-1}$; ESI-HRMS calcd. for $C_{13}H_{18}NO_2$ 220.1332, found 220.1320.
61% ee [chiral column: AS-H, n-hexane/i-PrOH = 100 : 0, 0.5 mL/min, 254 nm; $t_R = 22.79$ min. (major) and 29.39 (minor)].

(R)-methyl 2-propylindoline-1-carboxylate $7b$ and (2R,3S)-methyl 3-ethyl-2-methylindoline-1-carboxylate $8b$; (S,S)-NHC$_2$HI (3) was used.

Colorless oil $8b$: 22% yield calcd. by NMR (9.6 mg), $7b + 8b$: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.90-0.95 (m, 4.7H), 1.27-1.36 (m, 4H), 1.48-1.59 (m, 2H), 1.72 (brd, 1.4H), 2.67 (t, $J = 6.4$ Hz, 2H), 3.57 (m, 1H), 6.89 (s, 1H), 7.39 (brd, 1H).
Hz, 0.5H), 2.74 (dd, $J = 16.0, 1.8$ Hz, 1H), 3.28 (dd, $J = 16.0, 9.6$ Hz, 1H), 3.84 (s, 4.5H), 4.18 (brd, 0.5H), 4.44 (brd, 1H), 6.93-7.00 (m, 1.5H), 7.13-7.22 (m, 3H), 7.65 (brd, 1.5H). 7b + 8b: $^{13}$C NMR (100 MHz, CDCl$_3$): 11.1, 14.0, 18.1, 29.0, 33.4, 36.7, 49.9, 52.4, 59.3, 61.0, 115.3, 122.6, 122.7, 124.8, 127.3, 127.7, 153.5, 153.7.
8b: 96% ee [chiral column: AS-H, n-hexane/i-PrOH = 100 : 0, 0.5 mL/min, 254 nm; \( t_R = 17.81 \) min. (major) and 19.87 (minor)].

(R)-methyl 2-phenethylindoline-1-carboxylate 7c; (S,S)-NHCHI (4) was used.

Colorless oil, 62% yield (34.8 mg), \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.80-1.96 (m, 1H), 2.00-2.18 (m, 1H), 2.52-2.72 (m, 2H), 2.82 (dd, \( J = 16, 2 \) Hz, 1H), 3.32 (dd, \( J = 16, 9.6 \) Hz, 1H), 3.81 (s, 3H), 4.34-4.60 (brd, 1H), 6.96 (t, \( J = 7.2, 0.8 \) Hz, 1H), 7.10-7.22 (m, 5H), 7.26-7.30
(m, 2H), 7.40-8.10 (brd, 1H). $^{13}$C NMR (125 MHz): $\delta$ = 15.5, 31.3, 33.6, 36.2, 52.7, 59.3, 66.0, 115.6, 123.0, 125.1, 126.1, 127.6, 128.5, 130.3, 141.5, 142.1, 153.9. MS (ESI, 70 eV): $m/z$ (%) = 282 (M+H)$^+$; IR (neat): $\nu$ = 749, 840, 942, 1056, 1130, 1191, 1225, 1289, 1330, 1389, 1440, 1484, 1602, 1701, 2858, 2952, 3027 cm$^{-1}$; ESI-HRMS calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_2$: 282.1488, found 282.1480.
\[ \alpha \] D²⁰ = -19.4 (c = 1.0 in CH₂Cl₂), 47% ee, [chiral column: (R,R)-Whelk-O1, n-hexane/i-PrOH = 99:1, 0.5 mL/min, 254 nm; \( t_R = 28.26 \) min. (major) and 47.58 min. (minor)].
CD spectrum: 0.0001 M in n-hexane at 20 °C.

(2R,3S)-methyl 3-benzyl-2-methylindoline-1-carboxylate 8c; (S,S)-NHC\textsubscript{H}I (4) was used.

\[
\begin{array}{c}
\text{H} \quad \text{Ph} \\
\text{N} \quad \text{H} \\
\text{CO}_2\text{Me}
\end{array}
\]

Colorless oil, 32% yield (17.9 mg), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 1.12 (d, \(J = 6.4\) Hz, 3H), 2.69-2.82 (m, 2H), 3.02 (t, \(J = 14.9\) Hz, 1H), 3.78 (s, 3H), 4.18 (brd, 1H), 6.85-6.93 (m, 2H), 7.08 (d, \(J = 6.9\) Hz, 2H), 7.13-7.27 (m, 4H), 7.59 (brd, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 20.9, 42.4, 49.9, 52.6, 60.8, 115.6, 122.7, 125.3, 126.6, 128.2, 128.6, 129.4, 139.0. IR (neat, cm\textsuperscript{-1}): 2947, 1701, 1601, 1482, 1439, 1387, 1280, 1190, 1059, 748, 698. EI-HRMS: calcd. for C\textsubscript{18}H\textsubscript{20}NO\textsubscript{2}: 282.1488, found: 282.1479.
\[ \alpha_D^{25} = +15.4 \] (\( c = 0.5 \) in CH\(_2\)Cl\(_2\)), \( >99\% \) ee, [chiral column: (\( R,R \))-Whelk-O1, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \( t_R = 19.86 \) min. (major)].
CD spectrum: 0.0001 M in n-hexane at 20 °C.

(R)-methyl 2-(3-((tert-butyldimethylsilyl)oxy)propyl)indole-1-carboxylate 7d; (S,S)-NHCHI (3) was used.

Colorless oil, 68% yield (47.4 mg), \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.00 (s, 3H), 0.01 (s, 3H), 0.86 (s, 9H), 1.41-1.67 (m, 3H), 1.70-1.84 (m, 1H), 2.75 (dd, \(J = 16\), 2 Hz, 1H), 3.28 (dd, \(J = 16\), 9.6 Hz, 1H), 3.58 (t, \(J = 6.4\) Hz, 2H), 3.81 (s, 3H), 4.30-4.60 (brd, 1H), 6.94 (td, \(J = 7.2\), 0.8 Hz, 1H), 7.12 (d, \(J = 7.2\) Hz, 1H), 7.16 (t, \(J = 7.6\) Hz, 1H), 7.40-8.20 (brd, 1H). \(^{13}\)C NMR (125 MHz): \(\delta = 18.5, 26.1, 28.3, 31.2, 33.6, 52.6, 59.5, 63.1, 115.5, 122.9, 125.0, 127.6, 130.5, 154.0\). MS (ESI, 70 eV): \(m/z\) (%) = 350 (M+H); IR (neat): \(\nu = 751, 833, 938, 1022, 1059, 1093, 1132, 1191, 1227, 1251, 1284, 1307, 1330, 1390, 1441, 1463, 1486, 1603, 1705, 2857, 2930, 2952 cm\(^{-1}\)); EI-HRMS calcd. for C\(_{19}\)H\(_{32}\)NO\(_3\)Si 350.2145, found 350.2150.
$[\alpha]_{D}^{25} = -18.8 \ (c = 1.0 \text{ in CH}_2\text{Cl}_2), \ 55\% \ ee, \ [\text{chiral column: (R,R)-Whelk-O1, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; } t_{R} = 18.65 \text{ min. (major) and 24.72 min. (minor)}].$

CD spectrum: 0.0001 M in n-hexane at 20 °C.
(2R,3S)-methyl 3-2-tert-butyldimethylsilyloxethyl-2-methylindoline-1-carboxylate 8d; (S,S)-NHCHHI (3) was used.

Colorless oil, 21% yield (14.6 mg), \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.06 (d, \(J = 3.4\) Hz, 6H), 0.91 (s, 9H), 1.26 (d, \(J = 6.4\) Hz, 3H), 1.69-1.74 (m, 2H), 2.96 (t, \(J = 6.7\) Hz, 1H), 3.71 (d, \(J = 6.0\) Hz, 2H), 3.83 (s, 3H), 4.26-4.30 (m, 1H), 6.97 (td, \(J = 7.4, 0.9\) Hz, 1H), 7.15-7.21 (m, 2H), 7.61 (brd, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): 5.0, 1.2, 18.4, 20.6, 26.1, 39.0, 45.1, 52.6, 60.6, 61.3, 115.6, 122.8, 125.0, 127.9, 134.4. IR (neat, cm\(^{-1}\)): 2926, 2854, 1705, 1602, 1485, 1440, 1389, 1250, 1094, 1054, 938, 832, 749. EI-HRMS: calcd. for C\(_{19}\)H\(_{32}\)NO\(_3\)Si [M+H]\(^+\): 350.2145, found: 350.2137.
$[\alpha]_D^{25} = +6.6 \ (c = 0.5 \text{ in } \text{CH}_2\text{Cl}_2), >99\% \text{ ee, [chiral column: (R,R)-Whelk-O1, } n\text{-hexane/i-PrOH} = 99 : 1, 0.5 \text{ mL/min, 254 nm; } t_R = 14.03 \text{ min. (major)}.\$ 

CD spectrum: 0.0001 M in $n$-hexane at 20 °C.
(R)-methyl 2-(3-ethoxy-3-oxopropyl)indoline-1-carboxylate 7e; (S,S)-NHC\'Hl (3) was used.

Colorless oil, 63% yield (55.4 mg), \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): 1.21 (t, \(J = 7.2\) Hz, 3H), 1.88-2.79 (m, 1H), 2.21-2.38 (m, 2H), 2.71 (dd, \(J = 16.4, 2.4\) Hz, 1H), 3.32 (dd, \(J = 16, 9.6\) Hz, 1H), 3.82 (s, 3H), 4.09 (q, \(J = 7.2\) Hz, 2H), 4.44-4.63 (brd, 1H), 6.95 (td, \(J = 7.6, 0.8\) Hz, 1H), 7.12 (d, \(J = 7.2\) Hz, 1H), 7.16 (t, \(J = 7.6\) Hz, 1H), 7.48-7.80 (brd, 1H). \(^{13}\)C NMR (100 MHz): \(\delta = 14.4, 30.1, 30.2, 52.8, 58.6, 60.7, 115.8, 123.2, 125.0, 127.7, 130.1, 153.9, 173.2.

MS (ESI, 70 eV): \(m/\text{z (\%)} = 300\text{ (M+Na)}^{+}\); IR (neat): \(\nu = 753, 859, 941, 1023, 1057, 1089, 1130, 1186, 1225, 1285, 1330, 1389, 1441, 1435, 1503, 2956\text{ cm}^{-1}\); EI-HRMS calcd. for \(\text{C}_{15}\text{H}_{19}\text{NO}_{4}\text{Na}\) 300.1206, found 300.1206.
\([\alpha]_D^{20} = -31.78\ (c = 1.0\ \text{in CH}_2\text{Cl}_2), 69\%\ e.e, [\text{chiral column: OD-H, } n\text{-hexane/}\text{i-PrOH} = 99:1, \ 0.5\ \text{mL/min}, 254\ \text{nm}; t_R = 20.54\ \text{min. (major) and 25.08 (minor)}].\)
CD spectrum: 0.0001 M in n-hexane at 20 °C.

(2R,3S)-methyl 3-(2-ethoxy-2-oxoethyl)-2-methylindoline-1-carboxylate 8e; (S,S)-NHC=HI (3) was used.

![Chemical Structure]

Colorless oil, 36% yield (19.9 mg), ¹H NMR (400 MHz, CDCl₃): δ 1.31 (t, J = 7.1 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.56-2.58 (m, 2H), 3.30 (t, J = 7.4 Hz, 1H), 3.89 (s, 3H), 4.22 (qd, J = 7.2, 1.7 Hz, 2H), 4.27 (brd, 1H), 7.03 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.47-7.88 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): 14.2, 20.4, 28.4, 29.7, 40.6, 44.2, 52.5, 60.7, 61.5, 115.5, 122.9, 124.8, 128.3, 171.7. IR (neat, cm⁻¹): 2958, 1704, 1602, 1484, 1440, 1336, 1281, 1170, 1059, 1023, 752. EI-HRMS: calcd. for C₁₅H₂₀NO₄: 278.1386, found: 278.1380.
\([\alpha]_D^{20} = -8.43\ (c = 0.5\ in\ CH_2Cl_2)\). 98% ee, [chiral column: AS-H, \(n\)-hexane/\(i\)-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \(t_R = 17.04\ min\) (major) and 19.01 (minor)].

(S)-methyl 2-(methoxymethyl)indoline-1-carboxylate 7f; (S,S)-NHC\(\text{H}\)I (3) was used.

Colorless oil, 62% yield, calcd. by NMR (27.4 mg), \(^1\)H NMR (400 MHz, CDCl\(_3\)): 3.01 (dd, \(J = 16.4, 2.4\ Hz, 1H\)), 3.25 (dd, \(J = 16, 9.6\ Hz, 1H\)), 3.58 (dd, \(J = 9.2, 4\ Hz, 1H\)), 3.83 (s, 3H), 4.50-4.70 (m, 1H), 7.14 (d, \(J = 7.6\ Hz, 1H\)), 7.15 (t, \(J = 8.4\ Hz, 1H\)), 7.32-8.00 (brd, 1H). \(^13\)C NMR (125 MHz): \(\delta = 31.3, 52.5, 58.1, 59.0, 72.9, 115.2, 122.9, 124.9, 127.2, 130.1, 141.8,\)
153.6. MS (ESI, 70 eV): $m/z$ (%) = 244 (M+H)$^+$; IR (neat): $\nu = 712, 752, 833, 860, 939, 972, 1021, 1055, 1116, 1137, 1192, 1225, 1282, 11308, 1332, 1379, 1440, 1462, 1484, 1602, 1702, 2926 \text{ cm}^{-1}$; ESI-HRMS calcd. for C$_{12}$H$_{15}$NO$_3$Na 244.0944, found 244.0944.
7f: 67% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 29.45$ min. (major) and 34.67 (minor)].

(S)-methyl 2-(methoxymethyl)indoline-1-carboxylate 7f and (2R,3S)-methyl 3-methoxy-2-methylindoline-1-carboxylate 8f, (S,S)-NHC-HI (3) was used.

Colorless oil, 24% yield calc'd. by NMR (10.6 mg), 7f + 8f: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.26 (d, $J = 7.0$ Hz, 1H), 3.03 (dd, $J = 16.2$, 2.1 Hz., 1H), 3.27 (dd, $J = 16.4, 9.7$ Hz, 1H), 3.33 (s, 1.5H), 3.34 (s, 3H), 3.60 (dd, $J = 9.0, 3.9$ Hz, 1H), 3.84 (s, 4.5H), 4.29 (brd, 0.5H),
4.39 (brd, 0.5H), 4.61 (brd, 1H), 6.96 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.4 Hz, 0.5H), 7.14-7.18 (m, 2H), 7.33-7.39 (m, 1H), 7.70 (brd, 1.5H). **7f + 8f**: $^{13}$C NMR (100 MHz, CDCl$_3$): 14.3, 18.5, 28.4, 31.4, 52.6, 53.0, 55.1, 58.2, 58.7, 59.1, 61.0, 72.9, 74.7, 84.7, 115.3, 115.9, 122.6, 123.0, 125.0, 127.3, 127.9, 128.0, 128.9, 130.4, 131.2, 133.2, 155.7.
8f: >99% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \( t_R = 27.67 \) min. (major)].

\((R)\)-methyl 2-benzylindoline-1-carboxylate 7g; \((S,S)\)-NHCHI (4) was used.

Colorless oil, 49% yield (26.2 mg), 95% ee, \(^1\)H NMR (400 MHz, CDCl\(_3\)): 2.61 (dd, \( J = 12.8, 10 \) Hz, 1H), 2.80 (dd, \( J = 16, 1.6 \) Hz, 1H), 3.13 (dd, \( J = 16.4, 9.6 \) Hz, 1H), 3.00-3.42 (m, 1H), 3.84 (s, 3H), 4.60-4.80 (m, 1H), 6.98 (t, \( J = 7.2 \) Hz, 1H), 7.15 (d, \( J = 7.6 \) Hz, 1H), 7.17-7.28
(m, 4H), 7.28-7.36 (m, 2H), 7.38-8.30 (brd, 1H). $^{13}$C NMR (125 MHz): $\delta = 32.7, 40.3, 52.5, 60.6, 115.3, 122.8, 125.1, 126.5, 127.0, 127.5, 128.4, 128.7, 129.5, 137.7, 141.6, 153.6. MS (ESI, 70 eV): $m/z$ (%) = 268 (M+H)$^+$. IR (neat): $\nu = 698, 725, 759, 845, 870, 894, 918, 936, 1020, 1058, 1087, 1128, 1145, 1191, 1232, 1275, 1309, 1359, 1391, 1441, 1484, 1602, 1703, 2855, 2913, 2948, 3029, 3064 \text{ cm}^{-1}$; ESI-HRMS calcd. for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ 268.1332, found 268.1338.
\([\alpha]_D^{25} = -21.25 \ (c = 1.0 \ \text{in CH}_2\text{Cl}_2), \ 95\% \ ee, \ [\text{chiral column: AD-H, } n\text{-hexane/}i\text{-PrOH} = 99 : 1, \ 0.5 \ \text{mL/min, 254 nm; } t_R = 36.14 \ \text{min. (major) and 40.37 (minor)}].

\[ \text{CD spectrum: 0.0001 M in } n\text{-hexane at 20 °C.} \]
(2R,3S)-methyl 2-methyl-3-phenylindoline-1-carboxylate 8g; (S,S)-NHC\(\text{HI} (4)\) was used.

Colorless oil, 44% yield (23.5 mg), \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.46 (d, \(J = 6.1\) Hz, 3H), 3.85 (s, 3H), 3.98 (d, \(J = 1.8\) Hz, 1H), 4.39 (brd, 1H), 6.99 (t, \(J = 7.3\) Hz, 1H), 7.03-7.06 (m, 3H), 7.20-7.29 (m, 4H), 7.81 (brd, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 21.5, 52.7, 54.5, 64.8, 115.6, 123.3, 126.0, 127.1, 127.3, 128.4, 128.9, 144.2, 153.8. IR (neat, cm\(^{-1}\)): EI-HRMS: calcd. for C\(_{17}\)H\(_{18}\)NO\(_2\): 268.1332, found: 268.1332.
\([\alpha]_D^{20} = +110.15 (c = 1.0 \text{ in CH}_2\text{Cl}_2), >99\% \text{ ee} \) [chiral column: AD-H, \(n\)-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \(t_R = 31.89 \text{ min.} \) (major)].
CD spectrum: 0.0001 M in $n$-hexane at 20 °C.

1.8. Preparation of (S)- and (R)-1-phenylpropan-2-amine: \[5\]

To a solution of (L)-(-)-norephedrine (4.0 g, 26.5 mmol, 1 eq.) in toluene (40 mL), thionyl chloride (4.0 g, 33.6 mmol, 1.26 eq.) was slowly added and the reaction mixture stirred at 60 °C for 6 hours. After cooling the reaction mixture to 10 °C, the product started to precipitate. The solid was collected by filtration, washed with toluene (20 mL) and dried in vacuo to afford the crude (L)-(-)-chloroamphetamine hydrochloride (5.1 g, 95%).

A two neck round bottom flask (100 mL) with a magnetic stirring bar was charged with (L)-(-)-chloroamphetamine hydrochloride (5.0 g, 24.2 mmol), water (12 mL) and activated charcoal (5 g). Then 0.31 g of Pd/C (50 wt% water wet) was added along with sodium acetate (4.5 g, 54 mmol), and acetic acid (11.0 g, 183 mmol). The flask was put under a H$_2$ atmosphere (H$_2$ filled balloon) and stirred at 20 °C for 24 hours. The reaction mixture was filtered through a pad of celite and washed with water. The pH of the filtrate was adjusted to pH 12 with sodium hydroxide. The crude product was extracted with ethyl acetate, washed with brine and dried over MgSO$_4$. After filtration, volatiles were removed by rotary evaporator affording (S)-1-phenylpropan-2-amine in (3.2 g, 98%).

(S)-1-Phenylpropan-2-amine:
Colorless oil, $[\alpha]_D^{25} = +23.1$ ($c = 1.0$ in CH$_2$Cl$_2$), >99% ee, [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 29.56$ min. (major)].
(R)-1-phenylpropan-2-amine: Colorless oil, $[\alpha]_D^{25} = -24.15$ ($c = 1.0$ in CH$_2$Cl$_2$), >99% ee [chiral column: AD-H, $n$-hexane/$i$-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 32.24$ min. (major)].
1.9 Preparation of enantio-pure \((R)\)- and \((S)\)-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate 6g:

\[(R)\]-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate 6g:
\[
\begin{align*}
\text{[\(\alpha\)]D}^{25} & = -29.15 \ (c = 1.0 \text{ in CH}_2\text{Cl}_2), 99\% \text{ ee}, \ [	ext{chiral column: AD-H, } n\text{-hexane/i-PrOH} = 99 : 1, \ 0.5 \text{ mL/min, 254 nm; } t_R = 34.56 \text{ min. (minor) and 52.62 min. (major)}.}
\end{align*}
\]
(S)-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate 6g:

$[\alpha]_D^{25} = +30.8 \ (c = 1.0 \ \text{in CH}_2\text{Cl}_2)$, >99% ee, [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 34.39 \ \text{min. (major)}$.]
1.10 Synthesis of (S)-methyl 2-(methoxymethyl)indoline-1-carboxylate 7f:

![Chemical Structure](image)

Carbamate (S)-6f \[^{[6]}\] (60.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(\(\pi\)-cinnamyl)Cl] \(_2\) (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and (S,S)-NHC-HI (3) (11.8 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The
reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline methyl carbamate (R)-7f in 97% yield (42.8 mg) and >99% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 28.44$ min. (major)].
1.11 Synthesis of (2S,3R)-methyl 3-methoxy-2-methylindoline-1-carboxylate 8f:

Carbamate [(S)-6f (60.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]2 (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and (R,R)-NHC-HI (3) (11.8 mg, 0.02 mmol)] were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by
filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the mixture of indolines \((R)-\text{7f} (>99\% \text{ ee})\) in 54.1 \% yield (25.2 mg; yield calcd. by NMR) and \((2S,3R)-\text{8f} (>99\% \text{ ee})\) in 40.8 \% yield (18.1 mg; yield calcd. by NMR).

\textbf{7f}: >99\% ee [chiral column: AD-H, \(n\)-hexane/\(i\)-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \(t_R = 28.70 \text{ min. (major)}\)].
8f: >99% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; $t_R = 26.17$ min. (major)].
1.12 Synthesis of (R)-methyl 2-benzylindoline-1-carboxylate 7g:

The same procedure as for (S)-7f applied to the synthesis of (R)-7g. Carbamate (S)-6g was used. (R)-7g formed in 96% yield (51.2 mg), >99% ee [chiral column: AD-H, n-hexane/i-PrOH = 99 : 1, 0.5 mL/min, 254 nm; \( t_R = 36.51 \) min (major)].
Area Percent Report

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*** End of Report ***
1.13 Synthesis of (2R,3S)-methyl 2-methyl-3-phenylindoline-1-carboxylate 8g:

The same procedure as for (2S,3R)-8f applied to the synthesis of (2R,3S)-8g. Carbamate (R)-6g was used. (2R,3S)-8g formed in 97% yield (51.8 mg), >99% ee [chiral column: AD-H, n-hexane/i-ProH = 99 : 1, 0.5 mL/min, 254 nm; \( t_R = 31.71 \) min. (major)].
**Area Percent Report**

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***End of Report***
(2R,3S)-2-methyl-3-phenylindoline (9):

To a solution of (2R,3S)-8g (53.4 mg, 0.2 mmol, 1 equiv.) in THF/MeOH (2.5 mL/ 5 mL) was added 5N-NaOH aq. (2 mL, 10 mmol, 50 equivs). This mixture was refluxed for 24 hours. After cooling to r.t. it was extracted with CH2Cl2. The combined organic phases were dried over Na2SO4. After filtration and evaporation the crude residue was purified by flash column chromatography (silica gel; eluent: ethyl acetate:pentane = 1:20) affording indoline 9 as a colorless oil in 92% yield (38.4 mg, [α]D 20 = +35.0 (c = 0.5 in CH2Cl2). >99% ee, [chiral column, AD-H, n-hexane/i-PrOH = 99:1, 0.5 mL/min, 254 nm, tR = 20.36 min. (major)]. 1H NMR (400 MHz, CDCl3): 1.31 (d, J = 6.0 Hz, 3H), 3.84 (q, J = 5.9 Hz, 1H), 3.92 (d, J = 9.6 Hz, 1H), 6.65-6.69 (m, 2H), 6.79-6.82 (m, 2H), 7.70 (tt, J = 7.6, 1.0 Hz, 1H), 7.22-7.26 (m, 2H), 7.29-7.33 (m, 2H). 13C NMR (100 MHz) δ 20.5, 57.2, 65.6, 109.5, 119.2, 125.1, 127.0, 127.9, 128.7, 128.9, 132.6, 142.8, 151.0. IR (neat, cm−1): 3364, 3028, 2963, 2854, 1732, 1605, 1482, 1464, 1375, 1245, 1214, 1017, 746, 698. HRMS (EI): calcd. for C18H19N2O ([M+H]+): 210.1277, found: 210.1280.
**Area Percent Report**

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*** End of Report ***
1.15 IR and vibrational circular dichroism (VCD) spectra:

IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm⁻¹) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Solutions of ca. 10 mg in 500 µl CD₂Cl₂ were prepared and measured in a cell equipped with CaF₂ windows and a 130 µm spacer. The neat solvent served as the reference. For both the sample and reference 8400 scans at 4 cm⁻¹ resolution were averaged.

Computational methods. Density functional theory (DFT) as implemented in Gaussian03 was used to study the structure of 2a and 8g and to calculate the corresponding IR and VCD spectra.(ref Gaussian) The calculations were performed using the b3lyp functional (ref A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652, C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.) and a 6-31G(d) basis set.(ref: R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54 (1971) 724). Prior to the calculation of the spectra all degrees of freedom were completely relaxed. IR and VCD spectra were constructed from calculated dipole and rotational strengths using the GaussView program.[7]

Discussion of results:

VCD spectroscopy was used to determine the stereochemistry of the indolines 2a and 8g. For both compounds four isomers are possible, corresponding to the cis and trans arrangement of the two substituents and the corresponding enantiomers. In addition one has to consider conformational freedom. For the phenyl-methyl compound two conformers are possible corresponding to the arrangement of the ester group. For the methyl-ethyl compound
additionally three positions are feasible for the ethyl group leading to a total of six conformers for each stereoisomer. All the conformers were calculated. The discussion presented here is however based only on the most stable conformer of the corresponding compound. A more detailed discussion will be given elsewhere.

Indoline 2a:

The IR and VCD spectra of the cis and trans compound are quite similar, particularly for the carbonyl vibration, the weak band measure around 1600 cm\(^{-1}\) and the group of bands slightly below 1500 cm\(^{-1}\) (calculated slightly above 1500 cm\(^{-1}\)). A clear distinction is possible based on the strong band measure at around 1400 cm\(^{-1}\) (calculated at 1460 cm\(^{-1}\)). For the cis compound this band is calculated positive in the VCD and has opposite phase as the carbonyl band. For the trans this band is calculated strongly negative and has the same phase as the carbonyl band, as is observed in the experiment. In the experiment there is a positive band at 1460, which is due to another conformer.

Conclusion: Analysis of the VCD spectra strongly indicates that the measured compound corresponds to the trans compound and the enantiomer corresponds to the one considered in the calculation.

Indoline 8g:

The IR and VCD spectra of the cis and trans compound are again quite similar. Also in this case the region around the strong band measure slightly below 1400 cm\(^{-1}\) (calculated slightly above 1400 cm\(^{-1}\)) is most conclusive. For the cis there are positive and negative bands, whereas for the trans only strong negative bands are calculated. The experiment reveals two strong positive bands, where the stronger one corresponds to a relatively weak band in the IR. This is a strong indication for the trans configuration. Furthermore, for the cis a relatively strong carbonyl band in the VCD is predicted, in contrast to the experiment. The
bands calculated for the trans have opposite sign compared to the measured spectrum, which shows that the enantiomer considered in the calculation has opposite absolute configuration with respect to the measured compound.

Conclusion: Analysis of the VCD spectra strongly indicates that the measured compound corresponds to the trans compound and the enantiomer measured has opposite absolute configuration with respect to the one calculated.
Indoline 2a:
Experimental spectra
(2S,3R)-methyl 2-ethyl-3-methylindoline-1-carboxylate 2a:
(2S,3S)-methyl 2-ethyl-3-methylindoline-1-carboxylate 2a:
Indoline 8g:
Experimental spectra
(2S,3R)-methyl 2-methyl-3-phenylindoline-1-carboxylate 8g:
(2R,3R)-methyl 2-methyl-3-phenylindoline-1-carboxylate 8g:
1.16 References:


[6] Carbamate (S)-6f synthesized by similar procedure as for rac-6f starting from enantiopure commercially available (S)-1-methoxypropan-2-amine.