Supporting Information:

Enantioselective Rearrangement of Indolyl Carbonates
Catalyzed by Chiral DMAP-N-oxides

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1. General information

$^1$H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity ($s =$ singlet, $d =$ doublet; $t =$ triplet; $q =$ quartet; sext = sextet; br = broad, $m =$ multiplet), coupling constants (Hz), integration. $^{13}$C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel ADH/ODH/IE in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: $g/100$ mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Toluene and THF were freshly distilled from sodium under nitrogen prior to use. CH$_2$Cl$_2$ was distilled from CaH$_2$ under nitrogen prior to use. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. The chiral DMAP-N-oxides C$^{9a-C9f}$ and catalyst C$^{10a}$ were synthesized by the same procedure in the literature.$^1$
2. HRMS experiments

(a) C9a

\[
\text{Formula: } C_{26}H_{36}N_{4}O_{2}
\]

1a

\[
(1.1 \text{ equiv})
\]

\[
\text{Exact Mass: 557.3122} \\
\text{Found: 557.1665}
\]

\[
\text{Exact Mass: 437.2911} \\
\text{Found: 437.2889}
\]

toluene

rt, 40 min

\[
\text{Exact Mass: 557.3122} \\
\text{Found: 557.1665}
\]

\[
\text{Exact Mass: 437.2911} \\
\text{Found: 437.2889}
\]
(b) 

C9a

Formula: C26H36N4O2

1a
(1.1 equiv)

Exact Mass: 266.0823
Found: 266.0813

Exact Mass: 435.2765
Found: 435.2740

toluene
rt, 1 h

\[ \text{Exact Mass: 266.0823} \]
\[ \text{Found: 266.0813} \]

\[ \text{Exact Mass: 435.2765} \]
\[ \text{Found: 435.2740} \]
3. Substrates Synthesis

Indolyl carbonates 1a-1t were prepared according to literature precedents.\textsuperscript{2-4} Among these substrates, indolyl carbonates 1d, 1k, 1o, 1r, and 1t were new compounds and their characterization data were listed as follows.

1,1,1-Trichloro-2-methylpropan-2-yl 3-methyl-2-(((1,1,1-trichloro-2-methylpropan-2-yl)oxy)carbonyl)oxy)-1H-indole-1-carboxylate (1d)

\[
\text{A colorless solid. m.p.: 160.4-161.2 °C.}
\]

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.20 (d, \(J = 8.0\) Hz, 1H), 7.49-7.42 (m, 1H), 7.35-7.30 (m, 1H), 7.30-7.24 (m, 1H), 2.18 (s, 3H), 2.10 (s, 6H), 2.02 (s, 6H).

\textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 149.2, 148.1, 138.3, 131.5, 127.9, 124.7, 123.5, 118.9, 115.9, 105.6, 105.1, 92.4, 91.8, 21.9, 21.1, 7.0.

\textbf{HRMS:} exact mass calcd for C\textsubscript{19}H\textsubscript{19}Cl\textsubscript{6}NO\textsubscript{5}Na\textsuperscript{+} (M+Na)\textsuperscript{+} requires m/z 573.9287, found m/z 573.9284.

Phenyl 3-butyl-2-((phenoxy carbonyl)oxy)-1H-indole-1-carboxylate (1k)

\[
\text{A colorless solid. m.p.: 115.0-115.8 °C.}
\]

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.18 (d, \(J = 8.0\) Hz, 1H), 7.62-7.54 (m, 1H), 7.51-7.42 (m, 2H), 7.40-7.28 (m, 7H), 7.25-7.21 (m, 1H), 7.11 (d, \(J = 8.0\) Hz, 2H), 2.75 (d, \(J = 7.6\) Hz, 2H), 1.77-1.65 (m, 2H), 1.45 (sext, \(J = 7.6\) Hz, 2H), 0.98 (t, \(J = 7.6\) Hz, 3H).
**Phenyl 2-((phenoxy carbonyl)oxy)-3-(2-((phenoxy carbonyl)oxy)ethyl)-1H-indole-1-carboxylate (1o)**

A colorless solid. m.p.: 146.2-147.6°C.

**$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J$ = 8.4 Hz, 1H), 7.64 (d, $J$ = 7.8 Hz, 1H), 7.51-7.45 (m, 2H), 7.43-7.39 (m, 1H), 7.38-7.33 (m, 4H), 7.33-7.28 (m, 4H), 7.25-7.20 (m, 2H), 7.18-7.07 (m, 4H), 4.54 (t, $J$ = 7.2 Hz, 2H), 3.23 (t, $J$ = 7.2 Hz, 2H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 153.9, 151.3, 151.2, 151.0, 150.0, 148.6, 138.5, 132.5, 129.9, 129.7, 129.6, 127.2, 126.9, 126.7, 126.2, 125.6, 124.2, 121.7, 121.3, 120.9, 119.2, 115.9, 106.1, 66.9, 22.5.

**HRMS:** exact mass calcd for C$_{31}$H$_{23}$NO$_8$Na$^+$ (M+Na)$^+$ requires m/z 560.1316, found m/z 560.1317.

**Phenyl 3-benzyl-4-bromo-2-((phenoxy carbonyl)oxy)-1H-indole-1-carboxylate (1r)**

A colorless solid. m.p.: 174.2-176.3°C.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.25 (d, $J$ = 8.4 Hz, 1H), 7.49-7.44 (m, 3H), 7.37-7.29 (m, 9H), 7.24-7.19 (m, 3H), 6.96 (d, $J$ = 8.0 Hz, 2H), 4.44 (s, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.92, 150.88, 149.4, 148.3, 139.7, 139.6, 134.0, 130.0, 129.7, 129.0, 128.59, 128.56, 127.1, 126.8, 126.3, 126.1, 125.7, 121.6, 120.8, 115.0, 114.6, 109.7, 28.9.

**HRMS:** exact mass calcd for C$_{29}$H$_{20}$BrNO$_5$Na$^+$ (M+Na)$^+$ requires m/z 564.0417, found m/z 564.0415

Phenyl 6-bromo-3-methyl-2-((phenoxycarbonyl)oxy)-1H-indole-1-carboxylate (1t)

A colorless solid. m.p.: 157.1-161.3 $^\circ$C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (s, 1H), 7.50-7.45 (m, 3H), 7.40-7.29 (m, 6H), 7.26-7.23 (m, 1H), 7.11 (d, $J$ = 8.0 Hz, 2H), 2.26 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.2, 151.0, 150.0, 148.5, 137.5, 132.9, 129.9, 129.8, 127.2, 127.1, 127.0, 126.8, 121.7, 120.9, 120.5, 118.9, 118.8, 106.4, 7.2.

**HRMS:** exact mass calcd for C$_{23}$H$_{16}$BrNO$_5$Na$^+$ (M+Na)$^+$ requires m/z 488.0104, found m/z 488.0094
4. Typical procedure for the rearrangement of indolyl carbonates

In a test tube, indolyl carbonate 1 (0.05 mmol), catalyst C9a (0.6 mg, 2.5 mol%), and 3Å MS (40 mg) were added subsequently. Then, the tube was filled with N₂ gas. After that, toluene (0.5 mL) was added and the reaction was stirred at rt until reactant 1 was consumed (determined by TLC). Then, the reaction was quenched with iodomethane (0.05 mL). Subsequently, the crude mixture was purified by flash column chromatography on silica gel (gradient elution: i) pure petroleum ii) petroleum: CH₂Cl₂ = 1:10) to give the desired rearrangement product 2.
5. Gram-scale synthesis of 2a

In a 50 mL round bottom flask equipped with a magnetic stir bar, indolyl carbonate 1a (1.1640 g, 3 mmol), catalyst C9a (33 mg, 2.5 mol %), and 3Å MS (2.4000 g) were added subsequently. Then, the round bottom flask was filled with N₂ gas. After that, toluene (30 mL) was added and the reaction was stirred at rt until reactant 1a was consumed (45 h). Then, the reaction was quenched with iodomethane (3.0 mL). Subsequently, the crude mixture was extracted with EtOAc/H₂O, dried over Na₂SO₄ and concentrated in vacuo. Subsequently, the crude product was purified by flash column chromatography on silica gel (gradient elution: i) pure petroleum ii) petroleum: CH₂Cl₂ = 1:10) to give the desired rearrangement product 2a in 1.0940 g.
6. References


7. The analytical and spectral characterization data for the oxindoles

(S)-Diphenyl-3-methyl-2-oxoindoline-1,3-dicarboxylate (2a)

![Structure of 2a]

A pale yellow oil; 18.9 mg, 98% yield, 94% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 11.370 min (minor), 12.302 min (major).

[α]D²⁷ = +97.5 (c = 0.46, CHCl₃). The absolute configuration of compound (S)-2a was assigned by comparison with the (S)-enantiomer reported in the literature.

**¹H NMR** (600 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.50-7.40 (m, 4H), 7.38-7.28 (m, 6H), 7.22 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.8 Hz, 2H), 1.90 (s, 3H).

(S)-Dibenzyl-3-methyl-2-oxoindoline-1,3-dicarboxylate (2b)

![Structure of 2b]

A colorless oil; 19.0 mg, 92% yield, 91% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 26.345 min (major), 31.578 min (minor).

[α]D²⁷ = 79.8 (c = 0.19, CHCl₃). The absolute configuration of compound (S)-2b was assigned by comparison with the (S)-enantiomer reported in the literature.

**¹H NMR** (400 MHz, CDCl₃) δ 7.93 (d, J = 8.4 Hz, 1H), 7.56-7.47 (m, 2H), 7.42-7.31 (m, 4H), 7.26-7.20 (m, 4H), 7.19-7.13 (m, 1H), 7.12-7.06 (m, 2H), 5.46 (s, 2H), 5.11 (s, 2H), 1.74 (s, 3H).
(S)-Dimethyl-3-methyl-2-oxoindoline-1,3-dicarboxylate (2c)

A colorless oil; 11.2 mg, 87% yield, 93% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 21.517 min (minor), 22.097 min (major).

\[ \alpha \] \(_D^{27} = +74.3 \text{ (c = 0.14, CHCl}_3) \]. The absolute configuration of compound (S)-2c was assigned by comparison with the (S)-enantiomer reported in the literature.\(^3\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.96 (d, \( J = 8.0 \text{ Hz, 1H})\), 7.41-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.23-7.17 (m, 1H), 4.04 (s, 3H), 3.67 (s, 3H), 1.73 (s, 3H).

(\(S\))-Bis(1,1,1-trichloro-2-methylpropan-2-yl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2d)

A colorless solid; 24.3 mg, 88% yield, 91% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 5.543 min (major), 6.099 min (minor).

\[ \alpha \] \(_D^{27} = +85.6 \text{ (c = 0.75, CHCl}_3) \]. The absolute configuration of the product (S)-2d was assigned by analogy.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 8.0 \text{ Hz, 1H})\), 7.39-7.32 (m, 1H), 7.41-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.22-7.16 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.85 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.4, 166.4, 148.0, 139.5, 129.6, 128.5, 125.3, 122.5, 116.1, 105.4, 105.3, 92.1, 90.2, 56.7, 21.79, 21.78, 21.3, 20.7, 18.8.

**HRMS**: exact mass calcd for C\(_{19}\)H\(_{19}\)Cl\(_6\)NO\(_5\)Na\(^+\) (M+Na\(^+\)) requires m/z 573.9287, found m/z 573.9287.
(S)-Bis(4-methoxyphenyl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2e)

A colorless solid; 19.0 mg, 86% yield, 96% ee.

**HPLC** CHIRALCEL ADH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 34.812 min (minor), 52.155 min (major).

$[\alpha]_D^{27} = +85.7$ (c = 0.62, CHCl$_3$). The absolute configuration of compound (S)-2e was assigned by comparison with the (S)-enantiomer reported in the literature.$^3$

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 8.0$ Hz, 1H), 7.47-7.38 (m, 2H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 2H), 6.98-6.91 (m, 2H), 6.90-6.80 (m, 4H), 3.83 (s, 3H), 3.77 (s, 3H), 1.88 (s, 3H).

(S)-Bis(4-fluorophenyl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2f)

A colorless oil; 19.8 mg, 94% yield, 93% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 9.338 min (minor), 10.020 min (major).

$[\alpha]_D^{27} = 95.4$ (c = 0.23, CHCl$_3$). The absolute configuration of compound (S)-2f was assigned by comparison with the (S)-enantiomer reported in the literature.$^3$

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.50-7.39 (m, 2H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 2H), 6.98-6.91 (m, 2H), 6.90-6.80 (m, 4H), 3.83 (s, 3H), 3.77 (s, 3H), 1.88 (s, 3H).
(S)-Phenyl -1-(4-methoxyphenyl)-3-methyl-2-oxoindoline-3-carboxylate (2g)

![Chemical Structure](image)

A colorless oil; 18.3 mg, 98% yield, 88% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 41.653 min (major), 50.765 min (minor).

\[ \alpha_D^{27} = -175 \ (c = 0.504, \ CHCl_3) \]. The absolute configuration of compound (S)-2g was assigned by analogy.

**1H NMR** (400 MHz, CDCl₃) \( \delta \) 7.43-7.27 (m, 6H), 7.20 (t, \( J = 7.6 \ Hz, 1H) \), 7.15 (t, \( J = 7.6 \ Hz, 1H \)), 7.08-7.02 (m, 2H), 7.02-6.96 (m, 2H), 6.82 (d, \( J = 8.0 \ Hz, 1H \)), 3.87 (s, 3H), 1.88 (s, 3H).

(S)-Phenyl -1-allyl-3-methyl-2-oxoindoline-3-carboxylate (2h)

![Chemical Structure](image)

A colorless oil; 14.5 mg, 95% yield, 81% ee.

**HPLC** CHIRALCEL ADH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 9.665 min (minor), 12.630 min (major).

\[ \alpha_D^{27} = 66.48 \ (c = 0.307, \ CHCl_3) \]. The absolute configuration of compound (S)-2h was assigned by analogy.

**1H NMR** (400 MHz, CDCl₃) \( \delta \) 7.37-7.29 (m, 4H), 7.19 (t, \( J = 7.6 \ Hz, 1H) \), 7.12 (t, \( J = 7.6 \ Hz, 1H \)), 6.95 (d, \( J = 8.4 \ Hz, 2H \)), 6.89 (d, \( J = 8.0 \ Hz, 1H \)), 5.91-5.82 (m, 1H), 5.28-5.19 (m, 2H), 4.54-4.45 (m, 1H), 4.40-4.28 (m, 1H), 1.79 (s, 3H).
(\(S\))-Phenyl-1,3-dimethyl-2-oxoindoline-3-carboxylate (2i)

![Chemical Structure](image)

A colorless oil; 12.8 mg, 91% yield, 50% ee.

**HPLC** CHIRALCEL OD(H), \(n\)-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, \(\lambda = 256\) nm, retention time: 13.400 min (minor), 15.830 min (major).

\([\alpha]_{D}^{27} = 30.9\) (c = 0.204, CHCl\(_3\)). The absolute configuration of compound (\(S\))-2i was assigned by analogy.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39-7.35 (m, 2H), 7.33-7.27 (m, 2H), 7.20-7.17 (m, 1H), 7.13 (t, \(J = 7.6\) Hz, 1H), 6.96-6.90 (m, 3H), 3.30 (s, 3H), 1.78 (s, 3H).

(\(S\))-Diphenyl-3-ethyl-2-oxoindoline-1,3-dicarboxylate (2j)

![Chemical Structure](image)

A colorless solid; 18.4 mg, 92% yield, 96% ee.

**HPLC** CHIRALCEL ADH, \(n\)-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, \(\lambda = 256\) nm, retention time: 12.400 min (minor), 14.880 min (major).

\([\alpha]_{D}^{27} = +90.0\) (c = 0.32, CHCl\(_3\)). The absolute configuration of compound (\(S\))-2j was assigned by comparison with the (\(S\))-enantiomer reported in the literature.\(^3\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 8.0\) Hz, 1H), 7.49-7.39 (m, 4H), 7.38-7.28 (m, 6H), 7.25-7.18 (m, 1H), 7.02-6.95 (m, 2H), 2.56 (dq, \(J = 14.0, 7.2\) Hz, 1H), 2.42 (dq, \(J = 14.0, 7.2\) Hz, 1H), 0.86 (t, \(J = 7.2\) Hz, 3H).
(S)-Diphenyl-3-butyl-2-oxoindoline-1,3-dicarboxylate (2k)

A colorless solid; 19.4 mg, 92% yield, 96% ee.

**HPLC** CHIRALCEL ADH, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 19.597 min (major), 22.448 min (minor).

$[\alpha]_D^{27} = +31.4$ (c = 0.78, CHCl$_3$). The absolute configuration of the product (S)-2h was assigned by analogy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.0$ Hz, 1H), 7.48-7.40 (m, 4H), 7.36-7.28 (m, 6H), 7.25-7.19 (m, 1H), 7.01-6.95 (m, 2H), 2.54-2.44 (m, 1H), 2.42-2.32 (m, 1H), 1.39-1.29 (m, 2H), 1.27-1.20 (m, 1H), 1.12-1.00 (m 1H), 0.86 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.9, 167.5, 150.4, 150.2, 149.4, 139.9, 129.9, 129.8, 129.6, 127.0, 126.7, 126.5, 125.8, 123.3, 121.7, 121.3, 115.9, 60.4, 34.8, 25.9, 22.8, 13.9.

**HRMS:** exact mass calcd for C$_{26}$H$_{23}$NO$_5$Na$^+$ (M+Na)$^+$ requires m/z 452.1468, found m/z 452.1472.

(S)-Diphenyl-3-benzyl-2-oxoindoline-1,3-dicarboxylate (2l)

A colorless solid; 22.6 mg, 98% yield, 92% ee.

**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 8.145 min (major), 9.283 min (minor).

$[\alpha]_D^{27} = +33.1$ (c = 0.24, CHCl$_3$). The absolute configuration of compound (S)-2i was assigned by comparison with the (S)-enantiomer reported in the literature.$^3$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.6$ Hz, 1H), 7.52 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.45-7.08 (m, 13H), 7.06-7.00 (m, 2H), 6.96-6.90 (m, 2H), 3.78 (d, $J = 13.2$ Hz, 1H), 3.68 (d, $J = 13.2$ Hz, 1H).

**(S)-Diphenyl-3-allyl-2-oxoindoline-1,3-dicarboxylate (2m)**

![Chemical Structure](image)

A colorless solid; 18.3 mg, 89% yield, 84% ee.

HPLC CHIRALCEL IE, $n$-hexane/2-propanol = 50/50, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 6.277 min (minor), 6.767 min (major).

$[\alpha]_D^{27} = +77.5$ (c = 0.60, CHCl$_3$). The absolute configuration of compound (S)-2j was assigned by comparison with the (S)-enantiomer reported in the literature.$^3$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 8.4$ Hz, 1H), 7.50-7.40 (m, 4H), 7.38-7.27 (m, 6H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 5.58-5.47 (m, 1H), 5.18 (d, $J = 16.8$ Hz, 1H), 5.09 (d, $J = 10.2$ Hz, 1H), 3.18 (d, $J = 7.2$ Hz, 2H).

**(S)-Diphenyl-3-(cyanomethyl)-2-oxoindoline-1,3-dicarboxylate (2n)**

![Chemical Structure](image)

A pale yellow solid; 20.0 mg, 98% yield, 85% ee.

HPLC CHIRALCEL IE, $n$-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, $\lambda = 256$ nm, retention time: 20.940 min (minor), 28.458 min (major).

$[\alpha]_D^{27} = +70.4$ (c = 0.12, CHCl$_3$). The absolute configuration of compound (S)-2k was assigned by comparison with the (S)-enantiomer reported in the literature.$^3$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17-8.08 (m, 1H), 7.60-7.52 (m, 2H), 7.50-7.43 (m, 2H), 7.42-7.30 (m, 6H), 7.28-7.23 (m, 1H), 7.03-6.93 (m, 2H), 3.51 (d, $J$ = 16.8 Hz, 1H), 3.31 (d, $J$ = 16.8 Hz, 1H).

(S)-Diphenyl-2-oxo-3-(2-((phenoxy carbonyl)oxy)ethyl)indoline-1,3-dicarboxylate (2o)

![Chemical Structure](image)

A colorless oil; 25.2 mg, 94 % yield, 95% ee.

**HPLC** CHIRALCEL IE, $n$-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, $\lambda$ = 256 nm, retention time: 24.280 min (minor), 28.282 min (major).

$[\alpha]_D^{27} = +46.0$ (c = 0.57, CHCl$_3$). The absolute configuration of the product (S)-2l was assigned by analogy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (d, $J$ = 8.0 Hz, 1H), 7.55-7.47 (m, 1H), 7.46-7.41 (m, 1H), 7.38-7.28 (m, 7H), 7.25-7.17 (m, 5H), 7.15-7.08 (m, 2H), 7.02-6.95 (m, 2H), 4.45 (ddd, $J$ = 9.2, 5.6, 3.6 Hz, 1H), 4.01 (td, $J$ = 10.8, 4.4 Hz, 1H), 3.15 (ddd, $J$ = 15.2, 10.8, 6.0 Hz, 1H), 2.85 (dt, $J$ = 14.8, 4.0 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.7, 167.1, 153.2, 151.0, 150.3, 150.2, 149.6, 140.3, 130.6, 129.64, 129.61, 129.59, 126.68, 126.58, 126.3, 125.9, 125.1, 123.4, 121.6, 121.2, 116.5, 64.1, 58.5, 33.0.

**HRMS:** exact mass calcd for C$_{31}$H$_{23}$NO$_8$Na$^+$ (M+Na)$^+$ requires m/z 560.1316, found m/z 560.1299.

(S)-Diphenyl-3-(2-((methoxycarbonyl)amino)ethyl)-2-oxoindoline-1,3-dicarboxylate (2p)

![Chemical Structure](image)
A colorless oil; 22.8 mg, 96% yield, 88% ee.

**HPLC CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, \( \lambda = 256 \text{ nm} \), retention time: 42.518 min (major), 49.835 min (minor).

\([\alpha]_D^{27} = +73.5 \ (c = 0.55, \text{CHCl}_3) \). The absolute configuration of compound (S)-2m was assigned by comparison with the (S)-enantiomer reported in the literature.3

**H NMR (400 MHz, CDCl3)** \( \delta \ 8.05 \ (d, \ J = 8.4 \text{ Hz, 1H}), 7.50-7.40 \ (m, 4H), 7.37-7.28 \ (m, 6H), 7.22 \ (t, \ J = 7.6 \text{ Hz, 1H}), 7.01-6.92 \ (m, 2H), 4.75 \ (br, 1H), 3.58 \ (s, 3H), 3.36-3.12 \ (m, 2H), 2.81 \ (dt, \ J = 14.4, 7.6 \text{ Hz, 1H}), 2.68-2.53 \ (m, 1H).**

*(S)-Diphenyl-2-oxo-3-phenylindoline-1,3-dicarboxylate (2q)*

![Structure of 2q]

A colorless solid; 22.0 mg, 98% yield, 92% ee.

**HPLC CHIRALCEL ADH, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, \( \lambda = 256 \text{ nm} \), retention time: 15.922 min (minor), 23.277 min (major).

\([\alpha]_D^{27} = +70.3 \ (c = 0.64, \text{CHCl}_3) \). The absolute configuration of compound (S)-2n was assigned by comparison with the (S)-enantiomer reported in the literature.2

**H NMR (400 MHz, CDCl3)** \( \delta \ 8.16 \ (d, \ J = 8.0 \text{ Hz, 1H}), 7.65 \ (dd, \ J = 7.6, 1.2 \text{ Hz, 1H}), 7.56 \ (td, \ J = 7.6, 1.2 \text{ Hz, 1H}), 7.48-7.20 \ (m, 14H), 7.11-7.00 \ (m, 2H).**

*(S)-Diphenyl-3-benzyl-4-bromo-2-oxoindoline-1,3-dicarboxylate (2r)*

![Structure of 2r]

A colorless oil; 23.5 mg, 87 % yield, 92% ee.

**HPLC CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, \( \lambda = 256 \text{ nm} \), retention time:12.035 min (minor), 15.068 min (major).**
$\lbrack \alpha \rbrack_D^{27} = -765$ (c = 0.200, CHCl$_3$). The absolute configuration of the product (S)-2r was assigned by analogy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J$ = 8.4 Hz, 1H), 7.49-7.35 (m, 5H), 7.31 (t, $J$ = 7.6 Hz, 1H), 7.28-7.23 (m, 1H), 7.23-7.16 (m, 3H), 7.16-7.06 (m, 5H), 6.95 (d, $J$ = 7.2 Hz, 2H), 4.06 (d, $J$ = 13.6 Hz, 1H), 3.80 (d, $J$ = 13.2 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.5, 165.6, 150.5, 150.0, 148.5, 141.6, 133.5, 131.1, 129.8, 129.74, 129.65, 129.1, 128.2, 127.6, 126.8, 126.6, 126.3, 121.6, 121.5, 118.9, 114.5, 63.6, 38.3.

HRMS: exact mass calcd for C$_{29}$H$_{20}$BrNO$_5$Na$^+$ (M+Na)$^+$ requires m/z 564.0417, found m/z 564.0417

(S)-Diphenyl-5-bromo-3-methyl-2-oxoindoline-1,3-dicarboxylate (2s)

![2s]

A colorless solid; 22.8 mg, 98% yield, 92% ee.

HPLC CHIRALCEL IE, $n$-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, $\lambda$ = 256 nm, retention time: 9.515 min (minor), 10.178 min (major).

$[\alpha]_D^{27} = +6.5$ (c = 0.42, CHCl$_3$). The absolute configuration of compound (S)-2o was assigned by comparison with the (S)-enantiomer reported in the literature.$^2$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 8.8 Hz, 1H), 7.60-7.54 (m, 2H), 7.49-7.41 (m, 2H), 7.39-7.21 (m, 6H), 7.04-6.98 (m, 2H), 1.90 (s, 3H).

(S)-Diphenyl-6-bromo-3-methyl-2-oxoindoline-1,3-dicarboxylate (2t)

![2t]

A colorless oil; 21.6 mg, 93% yield, 93% ee.

S20
**HPLC** CHIRALCEL IE, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 9.253 min (minor), 10.567 min (major).

\[ [\alpha]_D^{27} = -162.62 \text{ (c = 0.610, CHCl}_3) \]. The absolute configuration of the product (S)-2t was assigned by analogy.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 8.28 (s, 1H), 7.50-7.42 (m, 3H), 7.39-7.28 (m, 6H), 7.26-7.21 (m, 1H), 6.98 (d, \( J = 8.4 \) Hz, 2H), 1.89 (s, 3H).

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 171.9, 167.2, 150.3, 150.1, 149.3, 140.2, 129.8, 129.7, 128.9, 127.6, 126.9, 126.7, 124.3, 123.7, 121.5, 121.2, 119.6, 55.8, 20.9.

**HRMS:** exact mass calcd for C\(_{23}\)H\(_{16}\)BrNO\(_3\)Na\(^+\) (M+Na\(^+\)) requires m/z 488.0104, found m/z 488.0103.
8. Copies of NMR spectra

$^1$H NMR of 1d

$^{13}$C NMR of 1d
$^1$H NMR of 1l

13C NMR of 1l
$^1$H NMR of 1t

$^{13}$C NMR of 1t
$^{1}H$ NMR of 2a

$^{1}H$ NMR of 2b
$^{13}$C NMR of 2d

$^1$H NMR of 2e
$^1$H NMR of 2h

$^1$H NMR of 2i
$^1$H NMR of 2j

$^1$H NMR of 2k

S32
$^{13}$C NMR of 2k

1H NMR of 2l
$^{13}$C NMR of 2t

![13C NMR spectrum of 2t with chemical shifts]

Chemical shifts (ppm):
- 171.86
- 167.71
- 150.29
- 149.26
- 149.18
- 129.82
- 129.67
- 128.91
- 128.61
- 126.89
- 124.33
- 123.74
- 121.19
- 119.58
- 77.48
- 77.16
- 76.84
- 55.78
- 20.90

Compound: 2t

Structural formula:

![Structural formula of 2t]


decription...
9. Copies of HPLC Spectra

[Graph showing HPLC spectra with peaks and retention times]

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**积分结果**

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3 mmol scale