Supporting information for

Asymmetric Syntheses of
Spiro[benzofuro-cyclopenta[1,2-b]indole-indoline]
Scaffolds via Consecutive Cyclization

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General Information

All reagents were used without purification. All solvents were purified and dried according to standard methods. The reaction products were purified by flash column chromatography on 200-300 mesh silica gel. The melting point was recorded on a melting point apparatus (MPA100, Stanford Research Systems, Inc.). Optical rotations were measured with a Jasco-P-2000 digital polarimeter at 20 or 25 °C and concentrations (c) are given in g×(100 mL)^{-1}. \(^1\)H and \(^{13}\)C NMR spectra were recorded with Bruker 400 MHz spectrometers (400 MHz for \(^1\)H NMR, 101 MHz for \(^{13}\)C NMR); chemical shifts (δ) are given in ppm. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. Analytical HPLC was recorded on a HPLC machine equipped with Elite P1201 series or Ichrom 5100 series quaternary pump with a UV diode array detector. Enantiomeric excess values were measured by analytical HPLC with Daicel ChiralPak AD-H column.

General Procedure for Enantioselective Cyclization

In a 10 mL tube, a mixture of 1 (0.12 mmol), BINOL-type imidodip-hosphoric acid 6b (0.005 mmol), 4Å molecular sieves (50 mg) and chloroform (2 mL) was stirred at 20 °C for 10 min. Then (E)-1-styrylnaphthols 2 (0.1 mmol) was added. After the reaction completed, the mixture was purified by silicagel chromatography (petroleumether/ethyl acetate = 10:1) directly to afford the product 3. (R_f=0.4 in petroleumether/ ethyl acetate=10:1).
Table S1. Optimization of the reaction conditions for the consecutive cyclization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Yield</th>
<th>ee</th>
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<tr>
<td>1</td>
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<td>15</td>
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<tr>
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<td>6b(2)</td>
<td>4Å MS</td>
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<td>98</td>
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</table>

*Reaction condition: 1a (0.12 mmol), 2a (0.1 mmol), catalyst (4, 5 or 6) in solvent (2 mL), 20 °C, the amount of additive was 50 mg, reaction time was 24 h. *Isolated yields. *ee value was determined by HPLC analysis on a Chiralcel AD-H column, and the d.r. was determined by ¹H NMR of isolated product, d.r. > 19:1. *the reaction time was extended to 48 h. *BINOL is behalf of 1,1'-Bi-2-naphthol skeleton.

After product 3aa structure was confirmed, various phosphoric acids were used to attempt to catalyze this reaction (Table 1). When H₈-BINOL-type CPAs were used to catalyze the reaction, moderate yield (81% yield) and ee values (79% ee) were obtained (Entry 2, Table 1). Subsequently H₈-BINOL-type imidodiphosphoric acids were screened, 1-naphthyl substituted H₈-BINOL imidodiphosphoric acid catalyst (5a) gave the 87% ee value and 66% yield (Entry 5, Table 1). The ee value increased obviously
owing to stronger chiral control ability and the yield decreased because of weaker acidity compared with CPAs. Thus, BINOL-type imidodi-phosphoric acids possessing outstanding chiral control ability and stronger acidity meanwhile led to excellent results as expected. On this occasion, 2-naphthyl group substituted BINOL imidodiphosphoric acid catalyst (6b) afforded 3aa with excellent enantioselectivity (91% ee), diastereoselectivity (d.r. > 19:1) and yield (82%) at 20 °C (Entry 10, Table 1). When the solvents were screened, alkyl halide solvent provided with better outcome than toluene in term of ee values (Entry 12-14, Table 1) and the reaction couldn’t occur in THF (Entry 15, Table 1). The solvent CHCl₃ gave the best result (97% ee, 88% yield, Entry 14, Table 1). When 50 mg 4Å molecular sieves were added into the reaction, the yield and ee value (99% ee, 92% yield, Entry 17, Table 1) have increased slightly at the same time. When attempted to reduce the catalyst loading to 2 mol%, the reaction could still go on smoothly and there were no significant changes in yield and ee value despite prolonged reaction time (48 h, 98% ee, 90% yield, Entry 19, Table 1). Thus, the optimal reaction condition has been established as catalyst 6b (5 mol %), 1a (0.12 mmol), 2a (0.10 mmol), 4Å molecular sieves (50 mg) in CHCl₃ (2 mL) at 20 °C.
Characterization data for compounds 3aa-3am.

3aa:

(3R,6c'S,7'S,8a'R,13a'R)-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3';1,5]cyclopenta[1,2-b]indol]-2-one:  white solid, mp 198 - 200 °C, 46.6 mg, 92% yield, 99% ee, >19:1 d.r. [α]D 20 = +298.7 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.73 (t, J = 8.9 Hz, 2H), 7.45 (d, J = 7.3 Hz, 1H), 7.25 – 7.05 (m, 10H), 6.93 (t, J = 7.6 Hz, 1H), 6.71 (dd, J = 16.7, 8.2 Hz, 2H), 6.62 – 6.54 (m, 2H), 6.45 (d, J = 7.3 Hz, 1H), 5.26 (d, J = 11.2 Hz, 1H), 4.42 (s, 1H), 3.68 (d, J = 11.2 Hz, 1H), 2.72 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 175.1, 155.3, 149.6, 143.9, 136.1, 130.6, 129.9, 129.4, 129.1, 129.0, 128.4, 128.4, 128.2, 127.6, 126.2, 125.1, 123.9, 122.9, 122.7, 122.5, 122.1, 121.0, 118.9, 115.3, 112.3, 109.1, 107.7, 66.7, 64.9, 63.4, 56.5, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 20.251 min, t_minor = 9.036 min. HRMS (ESI): calcd for C35H26N2O2 [M + H]+, 507.2067; found, 507.2065.
3ba:

(3R,6c'S,7'S,8a' R,13a'R)-1,10'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 186 - 188 °C, 47.0 mg, 90% yield, 95% ee, >19:1 d.r. [α]D^20 = +276.2 (c = 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 8.8 Hz, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.25 - 7.07 (m, 9H), 6.92 (t, J = 7.1 Hz, 2H), 6.71 - 6.63 (m, 2H), 6.58 (d, J = 7.7 Hz, 1H), 6.27 (s, 1H), 5.24 (d, J = 11.2 Hz, 1H), 5.19 (s, 1H), 4.40 (s, 1H), 3.66 (d, J = 11.2 Hz, 1H), 2.73 (s, 3H), 2.11 (s, 3H). ^13C NMR (101 MHz, CDCl₃) δ 175.1, 155.3, 147.4, 143.9, 136.1, 130.6, 129.9, 129.5, 129.4, 129.1, 128.9, 128.4, 128.3, 128.2, 127.6, 126.2, 125.5, 123.9, 123.5, 122.7, 122.5, 122.0, 121.0, 115.8, 112.3, 109.2, 107.7, 66.6, 65.1, 63.4, 56.4, 25.5, 20.7. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 18.243 min, t_minor = 8.745 min. HRMS (ESI): calcd for C₃₆H₂₈N₂O₂ [M + H]^+ 521.2224; found, 521.2230.
3ca:

\[
(3R,6c'S,7S,8a'R,13a'R)-10'-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5''']furo[2',3':1,5']cyclohepta[1,2-b]indol]-2-one: \text{white solid, mp 169 - 170°C, 45.2 mg, 86% yield, >19:1 d.r. } [\alpha]_D^{20} = +302.1 \text{ (c = 1.0, CHCl}_3); \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.73 (t, J = 8.2 Hz, 2H), 7.43 (d, J = 7.3 Hz, 1H), 7.25 - 7.06 (m, 9H), 6.94 (t, J = 7.6 Hz, 1H), 6.86 - 6.78 (m, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.65 - 6.54 (m, 2H), 6.21 (dd, J = 8.0, 1.9 Hz, 1H), 5.23 (d, J = 11.1 Hz, 2H), 4.40 (s, 1H), 3.67 (d, J = 11.2 Hz, 1H), 2.75 (s, 3H). \text{ } ^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 175.0, 157.0 (d, J = 235 Hz), 155.2, 145.9, 143.7, 135.8, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.6 (d, J = 8 Hz), 126.3, 123.8, 122.8 (d, J = 10 Hz), 122.0, 120.9, 116.0, 115.3 (d, J = 23 Hz), 112.3, 110.3 (d, J = 24 Hz), 109.7 (d, J = 7 Hz), 108.0, 66.6, 65.0, 63.3, 56.5, 25.6. \text{HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, } \lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 31.778 \text{ min, } t_{\text{minor}} = 10.131 \text{ min. HRMS (ESI): calcd for C}_{35}H_{25}FN_2O_2 \ [M + H]^+ \text{, 525.1973; found, 525.1971.}
3da: 

\((3R,6c'S,7'S,8a'R,13a'R)-10'-chloro-1-methyl-7'-phenyl-6c',7',8a',
13'-tetrahydrosso[p]indoline-3,8'-naphtho[1'',2':4',5']furo[2',3':1,5]
cyclopenta[1,2-b]indol]-2-one: white solid, mp 188 - 190°C,
46.0 mg, 85% yield, 98% ee, >19:1 d.r. \([\alpha]_D^{20} = +274.1 \ (c = 1.0,
CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta 7.72 \ (t, J = 8.7 \ Hz, 2H),
7.43 \ (d, J = 7.4 \ Hz, 1H), 7.24 - 7.05 \ (m, 10H), 6.93 \ (t, J = 7.4 \ Hz,
1H), 6.67 \ (d, J = 8.4 \ Hz, 1H), 6.61 \ (dd, J = 9.9, 8.4 \ Hz, 2H), 6.43
(d, J = 1.4 \ Hz, 1H), 5.35 \ (s, 1H), 5.23 \ (d, J = 11.2 \ Hz, 1H), 4.39 \ (s, 1H), 3.64 \ (d, J = 11.2 \ Hz, 1H), 2.76
(s, 3H). \(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta 175.0, 155.1, 148.3, 143.7, 135.7, 130.5, 130.1, 129.4, 129.0,
128.8, 128.6, 128.4, 128.2, 127.7, 126.9, 126.4, 123.9, 123.3, 123.0, 122.9, 122.8, 122.0, 120.9,
115.6, 112.2, 109.8, 108.1, 66.6, 65.0, 62.8, 56.3, 25.6. HPLC analysis: Daicel Chiralcel AD-H
column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, \(\lambda = 254 \ nm\), retention time: \(t_{major} = 39.671
\) min, \(t_{minor} = 8.362 \) min. HRMS (ESI): calcd for C\(_{35}\)H\(_{25}\)ClN\(_2\)O\(_2\) \([M + H]^+\), 541.1677; found, 541.1680.
3ea: 

(3R,6c'S,7S,8a'R,13a'R)-10'-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5']cyclopenta[1,2-b]indol]-2-one: white solid, mp 156 - 158 °C, 49.2 mg, 84% yield, 98% ee, >19:1 d.r. [α]D 20 = +263.1 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.74 – 7.67 (m, 2H), 7.41 (d, J = 6.9 Hz, 1H), 7.23 – 7.04 (m, 10H), 6.91 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.61 – 6.49 (m, 3H), 5.32 (s, 1H), 5.21 (d, J = 11.2 Hz, 1H), 4.37 (s, 1H), 3.62 (d, J = 11.3 Hz, 1H), 2.74 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 175.0, 155.1, 148.7, 143.7, 135.7, 131.8, 130.5, 130.1, 129.4, 128.8, 128.8, 128.6, 128.4, 128.2, 127.7, 127.3, 126.4, 125.8, 123.9, 122.9, 122.8, 122.0, 120.8, 115.4, 112.2, 110.3, 108.1, 66.7, 65.0, 62.7, 56.29, 25.64. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 42.040 min, t_minor = 8.626 min. HRMS (ESI): calcd for C35H25BrN2O2 [M + H]⁺, 585.1172; found, 585.1171.
3fa: (1S,2R,3R)-3-(2-hydroxynaphthalen-1-yl)-l'-methyl-2'-oxo-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indoline]-7-carbonitrile: white solid, mp 171 – 173 °C, 45.3 mg, 85% yield, 55% ee, >19:1 d.r. [α]D 20 = +256.6 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.73 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 8.4 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.21 – 7.07 (m, 8H), 6.96 (t, J = 7.2 Hz, 1H), 6.75 – 6.62 (m, 4H), 5.89 (s, 1H), 5.25 (d, J = 11.3 Hz, 1H), 4.40 (s, 1H), 3.66 (d, J = 11.3 Hz, 1H), 2.78 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 174.9, 155.0, 152.9, 143.5, 135.3, 134.6, 130.4, 130.3, 129.5, 129.0, 128.7, 128.5, 128.3, 128.1, 127.9, 126.6, 126.6, 125.6, 123.8, 123.1, 123.0, 122.0, 120.6, 120.3, 114.7, 112.0, 108.3, 108.1, 100.2, 66.6, 64.9, 61.6, 56.0, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tmajor = 53.480 min, tminor = 6.760 min. HRMS (ESI): calcd for C36H25N3O2 [M + H]+, 532.2020; found, 532.2022
3ga:

\[(3R,6c'S,7'S,8a'R,13a'R)-10'-methoxy-1-methyl-7'-phenyl-6c',7,8 \ a',13'-tetrahydrospiro[indoline-3,8'-napththo[1''',2''':4',5']furo[2',3':1 ,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 169 - 171 °C, 48.4 mg, 90% yield, 55% ee, >19:1 d.r. [\(\alpha\)D]20 = +274.1 (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (t, \(J = 9.0 \text{ Hz}, 2\text{H})", 7.46 (d, \(J = 7.0 \text{ Hz}, 1\text{H})", 7.25 - 7.07 (m, 9H), 6.95 (t, \(J = 8.4 \text{ Hz}, 2\text{H})", 6.76 - 6.67 (m, 3H), 6.58 (d, \(J = 7.7 \text{ Hz}, 1\text{H})", 6.12 (s, 1H), 5.26 (d, \(J = 11.2 \text{ Hz}, 1\text{H})", 5.12 (s, 1H), 4.42 (s, 1H), 3.69 (d, \(J = 11.2 \text{ Hz}, 1\text{H})", 3.62 (s, 3H), 2.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.1, 155.3, 153.7, 143.9, 143.8, 136.0, 130.5, 129.9, 129.4, 128.9, 128.9, 128.5, 128.4, 128.2, 127.6, 127.0, 126.2, 123.9, 122.7, 122.6, 122.0, 121.0, 116.2, 113.8, 112.4, 110.2, 110.1, 107.8, 66.6, 65.1, 63.6, 56.5, 55.9, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, \(\lambda = 254 \text{ nm}, retention time: \(t_{\text{major}} = 26.356 \text{ min, } t_{\text{minor}} = 12.375 \text{ min. HRMS (ESI)}: \text{calcd for } C_{36}H_{28}N_{2}O_{3} \ [M + H]^+ , 537.2173; found, 537.2174.} \]
3ha:

\((3R,6c'S,7'S,8a'R,13a'R)-1,11\text{-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2',4',5']fur}[2',3':1,5]cyclopenta[1,2-b][indol]-2-one\): white solid, mp 187 - 189 °C, 44.8 mg, 86% yield, 99% ee, >19:1 d.r. \([\alpha]_D^{20} = +278.6 \text{ (c = 1.0, CHCl}_3\text{)}\); \(^1\text{H NMR (400 MHz, CDCl}_3\text{)}\) \(\delta 7.74 \text{ (t, } J = 8.0 \text{ Hz, 2H), 7.46 (d, } J = 7.3 \text{ Hz, 1H), 7.27 - 7.08 \text{ (m, 9H), 6.96 (t, } J = 7.4 \text{ Hz, 1H), 6.72 (d, } J = 8.4 \text{ Hz, 1H), 6.63 - 6.55 \text{ (m, 2H), 6.41 (dd, } J = 23.2, 7.3 \text{ Hz, 2H), 5.28 (d, } J = 10.9 \text{ Hz, 1H), 4.43 (s, 1H), 3.70 (d, } J = 11.2 \text{ Hz, 1H), 2.77 (s, 3H), 2.29 (s, 3H). \(^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}\) \(\delta 175.2, 155.3, 149.8, 149.8, 143.9, 139.0, 136.2, 129.9, 129.4, 129.2, 129.0, 128.4, 128.4, 128.2, 127.5, 126.2, 123.9, 122.7, 122.6, 122.5, 122.2, 122.1, 121.1, 119.7, 115.7, 112.3, 110.0, 107.7, 66.6, 64.9, 63.2, 56.4, 25.5, 21.8. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, \(\lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 32.002 \text{ min, } t_{\text{minor}} = 11.986 \text{ min. HRMS (ESI): calcd for C}_{36}\text{H}_{28}\text{N}_2\text{O}_2 [M + H]^+, 521.2224; found, 521.2227.}
3ia:

(3R,6c'S,7'S,8a'R,13a'R)-11'-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetracyclospiro[indoline-3,8'-naphtho[1',2'-b]indol]-2-one: white solid, mp 183 - 185 °C, 47.7 mg, 91% yield, 98% ee, >19:1 d.r. [α]_D^20 = +293.2 (c = 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 7.3 Hz, 1H), 7.24 – 7.06 (m, 9H), 6.94 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 7.7 Hz, 1H), 6.40 – 6.33 (m, 2H), 6.29 – 6.21 (m, 1H), 5.46 (s, 1H), 5.26 (d, J = 11.2 Hz, 1H), 4.34 (d, J = 11.9 Hz, 1H), 3.66 (d, J = 11.2 Hz, 1H), 2.76 (s, 3H). ^13C NMR (101 MHz, CDCl₃) δ 175.1, 164.2 (d, J = 242 Hz), 155.2, 151.0, 150.9, 143.8, 136.0, 130.5, 129.4, 128.9, 128.9, 128.8, 128.6, 128.4, 128.2, 127.6, 126.4, 123.9, 123.5 (d, J = 11 Hz), 122.8 (d, J = 21 Hz), 122.1, 120.9, 120.5 (d, J = 23 Hz), 115.8, 112.2, 107.8, 104.9 (d, J = 23 Hz), 96.8 (d, J = 27 Hz), 66.7, 64.7, 62.5, 56.3, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 30.519 min, t_minor = 10.231 min. HRMS (ESI): calcd for C₉₈H₇₅F₂N₂O₂ [M + H]^+: 525.1973; found, 525.1980.
3ja:

\[ (3R,6c'S,7'S,8a'R,13a'R)-11'-chloro-1-methyl-7'-phenyl-6c',7',8a',1 \\
3'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5] \\
cyclopenta[1,2-b]indol]-2-one \] white solid, mp 175 - 177 °C, 43.3 \\
mg, 80% yield, 99% ee, >19:1 d.r. \( [\alpha]_D^{20} = +301.3 \) (c = 1.0, CHCl₃); \\
\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.71 (d, \( J = 8.9 \) Hz, 2H), 7.42 (d, \( J = \\
7.3 \) Hz, 1H), 7.25 - 7.05 (m, 9H), 6.94 (t, \( J = 7.6 \) Hz, 1H), 6.71 - 6.64 \\
(m, 2H), 6.60 - 6.51 (m, 2H), 6.35 (d, \( J = 7.8 \) Hz, 1H), 5.39 (s, 1H), \\
5.24 (d, \( J = 11.2 \) Hz, 1H), 4.36 (s, 1H), 3.66 (d, \( J = 11.2 \) Hz, 1H), 2.76 (s, 3H). \(^1\)C NMR (101 MHz, \\
CDCl₃) \( \delta \) 174.9, 155.1, 150.6, 143.8, 135.8, 134.7, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, \\
128.2, 127.7, 126.4, 123.9, 123.6, 123.5, 122.9, 122.7, 122.1, 120.9, 118.6, 115.5, 112.2, 109.1, 107.9, \\
66.6, 64.9, 62.5, 56.3, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = \\
70/30, flow rate = 1.0 mL/min, \( \lambda = 254 \) nm, retention time: \( t_{major} = 29.043 \) min, \( t_{minor} = 9.878 \) min. \\
HRMS (ESI): calcd for C₃₅H₂₅ClN₂O₂ \( [M + H]^+ \), 541.1677; found, 541.1680.
3ka: (3R,6c'S,7'S,8a'R,13a'R)-11'bromo-1-methyl-7'-phenyl-6c',7',8a',13' tetrahydrospiro[indoline-3,8'-naphtho[1'',2':4',5'']furo[2',3':1,5]cycloptenta[1,2-b]indol]-2-one: white solid, mp 173 - 175 °C, 50.3 mg, 86% yield, 99% ee, >19:1 d.r. [α]20 = +294.3 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.3 Hz, 1H), 7.24 – 7.05 (m, 9H), 6.94 (t, J = 7.6 Hz, 1H), 6.79 (s, 1H), 6.69 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 7.7 Hz, 1H), 6.30 (d, J = 7.8 Hz, 1H), 5.40 (s, 1H), 5.23 (d, J = 11.2 Hz, 1H), 4.35 (s, 1H), 3.66 (d, J = 11.2 Hz, 1H), 2.76 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 174.9, 155.1, 150.8, 143.8, 135.8, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, 128.3, 127.7, 126.4, 124.0, 123.9, 122.9, 122.8, 122.7, 122.1, 121.4, 120.9, 115.4, 112.2, 111.9, 107.9, 66.5, 64.9, 62.5, 56.2, 25.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 27.169 min, t_minor = 9.430 min. HRMS (ESI): calcd for C35H25BrN2O2 [M + H]+, 585.1172; found, 585.1170.
3la:

\[
(3R,6c'S,7'S,8a'R,13a'R)-1,12'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2''-4',5']furo[2',3',1,5]cyclopenta[1,2-b]indol]-2-one: \]
white solid, mp 174 - 176 °C, 47.9 mg, 92% yield, 97% ee, >19:1 d.r. \([\alpha]_D^{20} = +258.1 (c = 1.0, \text{CHCl}_3); \]
\[^1\text{H} \text{NMR (400 MHz, CDCl}_3) \delta 7.74 (t, J = 9.4 \text{ Hz, 2H}), 7.45 (d, J = 7.3 \text{ Hz, 1H}), 7.26 – 7.06 (m, 9H), 6.95 (t, J = 8.7 \text{ Hz, 2H}), 6.73 (d, J = 8.4 \text{ Hz, 1H}), 6.55 (t, J = 7.9 \text{ Hz, 2H}), 6.33 (d, J = 7.3 \text{ Hz, 1H}), 5.31 (d, J = 11.2 \text{ Hz, 1H}), 5.18 (s, 1H), 4.48 (s, 1H), 3.69 (d, J = 11.2 \text{ Hz, 1H}), 2.73 (s, 3H), 2.21 (s, 3H). \]
\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3) \delta 175.2, 155.4, 148.5, 143.9, 136.2, 130.6, 130.0, 129.4, 129.1, 129.0, 128.4, 128.2, 127.6, 126.3, 124.5, 123.9, 122.7, 122.6, 122.1, 121.1, 120.3, 119.2, 118.5, 115.2, 112.4, 107.8, 66.8, 64.9, 63.7, 56.7, 25.5, 17.0. \]
Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, \(\lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 17.915 \text{ min}, t_{\text{minor}} = 6.015 \text{ min. HRMS (ESI): calcd for C}_{36}H_{28}N_{2}O_{2} \ [M + H]^+; 521.2224; \text{found, 521.2226.}}\]
3ma: 

(3R,6c'S,7'S,8a'R,13a'R)-12'-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2''-4',5']furo[2',3':1,5]cyclo penta[1,2-b]indol]-2-one: white solid, mp 152 - 154 °C, 50.9 mg, 87% yield, 97% ee, >19:1 d.r. \([\alpha]_D^{20} = +284.1 \text{ (c} = 1.0, \text{ CHCl}_3)\).

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.47 (d, \(J = 7.3\) Hz, 1H), 7.29 (t, \(J = 3.7\) Hz, 2H), 7.17 (m, 8H), 6.97 (t, \(J = 7.6\) Hz, 1H), 6.74 (d, \(J = 8.4\) Hz, 1H), 6.59 (d, \(J = 7.7\) Hz, 1H), 6.48 (t, \(J = 7.6\) Hz, 1H), 6.42 (d, \(J = 7.2\) Hz, 1H), 5.59 (s, 1H), 5.35 (d, \(J = 11.3\) Hz, 1H), 4.56 (s, 1H), 3.68 (d, \(J = 11.3\) Hz, 1H), 2.76 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) \(\delta\) 174.9, 155.2, 148.2, 143.8, 135.7, 131.5, 130.5, 130.1, 129.5, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.3, 126.1, 123.9, 122.9, 122.6, 122.1, 121.7, 120.8, 119.7, 114.2, 112.2, 107.8, 102.0, 66.7, 64.9, 63.9, 56.4, 25.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: \(t_{\text{major}} = 29.163\) min, \(t_{\text{minor}} = 6.166\) min. HRMS (ESI): calcd for C$_{35}$H$_{25}$BrN$_2$O$_2$ \([M + H]^+)\, 585.1172; found, 585.1170.
3na:

(3R,6c'S,7'S,8a'R,13α'R)-1,5-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2'':4',5']furo[2',3':1,5]cyclopanta[1,2-b]indol]-2-one: white solid, mp 188 - 190 °C, 46.9 mg, 90% yield, 98% ee, >19:1 d.r. [α]_D^20 = +282.1 (c = 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 8.2 Hz, 2H), 7.28 (s, 1H), 7.18 (m, 8H), 7.00 (d, J = 7.7 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.70 (dd, J = 15.4, 8.2 Hz, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.50 - 6.47 (m, 2H), 5.33 (s, 0H), 5.26 (d, J = 11.2 Hz, 1H), 4.42 (s, 1H), 3.67 (d, J = 11.2 Hz, 1H), 2.70 (s, 3H), 2.36 (s, 3H). ^13C NMR (101 MHz, CDCl₃) δ 175.1, 155.3, 149.6, 141.5, 136.3, 132.0, 130.6, 129.9, 129.4, 129.1, 129.0, 128.7, 128.4, 128.2, 127.5, 126.2, 125.2, 123.9, 122.9, 122.7, 121.1, 118.8, 115.3, 112.3, 109.1, 107.5, 66.7, 64.8, 63.5, 56.6, 25.5, 21.3. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 14.796 min, t_minor = 7.902 min. HRMS (ESI): calcd for C₃₆H₂₈N₂O₂ [M + H]+, 521.2224; found, 521.2227.
3oa:

(3R,6c'S,7'S,8a'R,13a'R)-5-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5']cy
clopena[1,2-b]indol]-2-one: white solid, mp 168 - 170 °C, 48.3 mg, 92% yield, 98% ee, >19:1 d.r. [α]D20 = +268.4 (c = 1.0, CHCl3);

1H NMR (400 MHz, CDCl3) δ 7.72 (t, J = 7.9 Hz, 2H), 7.25 – 7.07 (m, 9H), 6.93 (dd, J = 16.1, 8.3 Hz, 2H), 6.69 (t, J = 8.9 Hz, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.48 (t, J = 6.3 Hz, 2H), 5.35 (s, 1H), 5.25 (d, J = 11.2 Hz, 1H), 4.40 (s, 1H), 3.64 (d, J = 11.1 Hz, 1H), 2.72 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 174.8, 159.3 (d, J = 239 Hz), 155.3, 149.6, 139.8, 135.9, 130.9 (d, J = 8 Hz), 130.5, 130.1, 129.4, 129.2, 128.9, 128.4, 128.3, 127.7, 126.3, 124.7, 123.8, 122.8 (d, J = 5 Hz), 120.9, 118.9, 115.2, 114.8 (d, J = 23 Hz), 112.3, 110.3 (d, J = 25 Hz), 109.2, 108.3 (d, J = 7 Hz), 67.0, 64.9, 63.5, 56.5, 56.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tmajor = 14.169 min, tminor = 10.485 min. HRMS (ESI): calcd for C35H25FN2O2 [M + H]+, 525.1973; found, 525.1981.
3pa:

(3R,6c'S,7'S,8a'R,13a'R)-5-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5'']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 176 - 178 °C, 48.2 mg, 89% yield, 99% ee, >19:1 d.r. \([\alpha]_D^{20} = +283.2\) (c = 1.0, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) δ 7.73 (t, \(J = 9.4\) Hz, 2H), 7.45 (d, \(J = 1.8\) Hz, 1H), 7.24 – 7.09 (m, 9H), 6.92 (t, \(J = 7.6\) Hz, 1H), 6.72 (d, \(J = 7.9\) Hz, 1H), 6.68 – 6.56 (m, 2H), 6.48 (t, \(J = 8.2\) Hz, 1H), 5.29 (s, 1H), 5.23 (d, \(J = 11.2\) Hz, 1H), 4.40 (s, 1H), 3.64 (d, \(J = 11.2\) Hz, 1H), 2.70 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ 174.7, 155.3, 149.6, 142.5, 135.8, 131.0, 130.5, 130.1, 129.4, 129.3, 128.9, 128.5, 128.4, 127.9, 127.8, 126.3, 124.6, 123.8, 122.8, 122.6, 120.8, 118.9, 115.2, 112.3, 109.1, 108.8, 66.8, 64.9, 63.5, 56.5, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: \(t_{major} = 13.730\) min, \(t_{minor} = 8.310\) min. HRMS (ESI): calcd for C₃₅H₂₅ClN₂O₂ [M + H]⁺, 541.1677; found, 541.1678.
3qa: 

\[
(3R,6c'S,7'S,8a'R,13a'R)-5\text{-bromo}\text{-1-methyl}\text{-7}'\text{-phenyl}\text{-6c',7',8a',13}
\text{'-tetrahydrospiro[indoline-3,8'-naphtho[1',2''\text{a}',4',5']furo[2',3':1,5]}
\text{cyclopenta[1,2-b]indol]}\text{-2-one}: \text{white solid, mp} \ 195 - 197 ^\circ\text{C, 50.9 mg, 87% yield, 92% ee, } > 19:1 \ d.r. \ [\alpha]_D ^{20} = +283.2 \ (c = 1.0, \text{CHCl}_3);
\]

\[\text{^1H NMR (400 MHz, CDCl}_3) \ \delta \ 7.73 \ (t, J = 9.4 \text{ Hz, 2H}), \ 7.58 \ (d, J = 1.7 \text{ Hz, 1H}), \ 7.33 \ (dd, J = 8.2, 1.8 \text{ Hz, 1H}), \ 7.25 - 7.08 \ (8 \text{H}), \ 6.92 \ (t, J = 7.6 \text{ Hz, 1H}), \ 6.72 \ (d, J = 7.9 \text{ Hz, 1H}), \ 6.65 \ (d, J = 8.5 \text{ Hz, 1H}), \ 6.60 \ (t, J = 7.4 \text{ Hz, 1H}), \ 6.50 - 6.42 \ (m, 2H), \ 5.29 \ (s, 1H), \ 5.23 \ (d, J = 11.2 \text{ Hz, 1H}), \ 4.40 \ (s, 1H), \ 3.63 \ (d, J = 11.2 \text{ Hz, 1H}), \ 2.70 \ (s, 3H). \ \text{^13C NMR (101 MHz, CDCl}_3) \ \delta \ 174.6, 155.3, 149.6, 142.9, 135.8, 131.4, 131.3, 130.5, 130.1, 129.4, 129.3, 128.9, 128.5, 128.4, 127.8, 126.3, 125.4, 124.6, 123.8, 122.9, 122.8, 120.8, 118.9, 115.2, 115.1, 112.3, 109.3, 109.1, 66.8, 64.9, 63.5, 56.5, 25.6. \ \text{HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-ProH = 70/30, flow rate = 1.0 mL/min, } \lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 15.097 \text{ min, } t_{\text{minor}} = 8.741 \text{ min. HRMS (ESI): calcd for } \text{C}_{35}\text{H}_{25}\text{BrN}_2\text{O}_2 \ [M + H]^+, 585.1172; \text{found, 585.1174.} \]
3ra:

(3R,6c'S,7'S,8a'R,13a'R)-5-methoxy-1-methyl-7'-phenyl-6c',7',8 a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'';4',5']furo[2', 3';1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 182 - 184 °C, 48.3 mg, 90% yield, 79% ee, 11:1 d.r. [α]D = +274.5 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.76 (t, J = 8.2 Hz, 2H), 7.27 – 7.09 (m, 8H), 7.07 – 6.93 (m, 2H), 6.77 – 6.70 (m, 3H), 6.62 (t, J = 7.4 Hz, 1H), 6.50 (t, J = 7.6 Hz, 2H), 5.28 (d, J = 11.2 Hz, 1H), 4.43 (s, 1H), 3.82 (s, 3H), 3.68 (d, J = 11.2 Hz, 1H), 2.83 (s, 0H), 2.71 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 174.8, 156.0, 155.3, 149.6, 137.4, 136.2, 130.6, 130.4, 130.0, 129.4, 129.1, 129.0, 128.4, 128.3, 127.6, 126.3, 125.0, 123.9, 122.9, 122.8, 121.1, 118.8, 115.3, 112.8, 112.3, 109.3, 109.2, 108.2, 67.1, 64.9, 63.7, 56.5, 55.8, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 63.727 min, t_minor = 13.385 min. HRMS (ESI): calcd for C36H32N2O3 [M + H]+, 537.2173; found, 537.2175.
3sa:

\[
(3R,6c'S,7'S,8a'R,13a'R)-6-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'
tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5]
cyclopenta[1,2-b]indol]-2-one: \text{white solid, mp 136 - 138 °C, 45.1 mg, 86% yield, 99% ee, 10:1 d.r.} \quad \left[\alpha\right]_D^{20} = +276.3 \text{ (c = 1.0, CHCl}_3)\text{; } ^1H\text{ NMR (400 MHz, CDCl}_3) \delta 7.70 (t, J = 7.8 Hz, 2H), 7.37 – 6.31 (m, 1H), 7.21 – 7.06 (m, 8H), 6.95 – 6.86 (m, 1H), 6.79 – 6.62 (m, 3H), 6.58 (t, J = 7.3 Hz, 1H), 6.30 (dd, J = 8.8, 2.3 Hz, 1H), 5.27 (s, 1H), 5.21 (d, J = 4.0, 1H), 4.37 (s, 1H), 3.62 (d, J = 11.2 Hz, 1H), 2.67 (s, 4H). ^{13}\text{C NMR (101 MHz, CDCl}_3) \delta 175.4, 163.1 (d, J = 243 Hz), 155.2, 149.5, 145.4 (d, J = 12 Hz), 135.9, 130.5, 129.4, 129.2, 128.9, 128.4, 128.3, 127.7, 126.3, 124.8, 124.3, 124.3, 123.8, 123.2 (d, J = 10 Hz), 122.8 (d, J = 3 Hz), 120.8, 119.0, 115.1, 112.3, 109.1, 108.6 (d, J = 22 Hz), 96.7 (d, J = 28 Hz), 66.4, 64.9, 63.3, 56.3, 25.6. \text{HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, } \lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 20.451 \text{ min, } t_{\text{minor}} = 9.309 \text{ min. HRMS (ESI): calcd for } C_{35}H_{25}FN_{2}O_{2}^{+} [M + H]^+, 525.1973; \text{found, } 525.1970.\]
3ta:

(3R,6c'S,7'S,8a'R,13a'R)-6-chloro-1-methyl-7'-phenyl-6c',7',8a',13'tetrahydrospiro[indoline-3,8'-naphtha[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 129 - 131 °C, 47.6 mg, 88% yield, 99% ee, >19:1 d.r. [α]_D^{20} = +284.2 (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 9.2 Hz, 2H), 7.36 (t, J = 7.1 Hz, 1H), 7.22 – 7.05 (m, 9H), 6.92 (t, J = 7.2 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.68 – 6.56 (m, 3H), 6.47 (d, J = 7.3 Hz, 1H), 5.30 (s, 1H), 5.24 (d, J = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, J = 11.2 Hz, 1H), 2.70 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.0, 155.2, 149.5, 145.0, 135.8, 134.2, 130.5, 130.0, 129.4, 129.2, 128.9, 128.4, 128.3, 127.8, 127.5, 126.3, 124.7, 123.8, 123.1, 122.8, 122.4, 120.8, 119.0, 115.1, 112.3, 109.1, 108.61, 66.4, 64.8, 63.4, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 17.028 min, t_minor = 9.111 min. HRMS (ESI): calcd for C₃₅H₂₅ClN₂O₂ [M + H]⁺, 541.1677; found, 541.1679.

HPLC Chromatogram
3ua: (3R,6c’S,7’S,8a’R,13a’R)-6-bromo-1-methyl-7’-phenyl-6c’,7’,8a’,13’-tetrahydrospiro[indoline-3,8’-naptho[1’',2’’;4’,5’’]furo[2’,3’;1,5]cyclopenta[1,2-b]indol]-2-one; white solid, mp 136 - 138 °C, 49.7 mg, 85% yield, 94% ee, >19:1 d.r. [α]D = +264.3 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.73 (t, J = 8.8 Hz, 2H), 7.31 (d, J = 7.9 Hz, 1H), 7.26 – 7.09 (m, 9H), 6.93 (t, J = 7.3 Hz, 1H), 6.74 – 6.57 (m, 4H), 6.48 (d, J = 7.3 Hz, 1H), 5.29 (s, 1H), 5.23 (d, J = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, J = 11.2 Hz, 1H), 2.70 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 174.9, 155.2, 149.5, 145.2, 135.8, 130.1, 129.4, 129.3, 128.9, 128.4, 128.4, 128.1, 127.8, 126.3, 125.3, 124.6, 123.8, 123.4, 122.8, 122.0, 120.8, 119.0, 115.1, 112.3, 111.3, 109.1, 66.5, 64.7, 63.3, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tmajor = 16.470 min, tminor = 9.430 min. HRMS (ESI): calcd for C35H28BrN2O2 [M + H]+, 585.1172; found, 585.1170.
3va:

(3R,6c’S,7’S,8a’R,13a’R)-7-fluoro-1-methyl-7’-phenyl-6c’,7’,8a’,13’tetrahydrospiro[indoline-3,8’-naphtho[1″,2″:4′,5′]furo[2′,3′:1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 185 - 187 °C, 45.6 mg, 87% yield, 98% ee, >19:1 d.r. [α]D 20 = +264.8 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.75 (t, J = 7.7 Hz, 2H), 7.28 – 7.13 (m, 9H), 7.09 – 7.01 (m, 1H), 7.00 – 6.93 (m, 2H), 6.78 – 6.63 (m, 3H), 6.54 (d, J = 7.3 Hz, 1H), 5.35 (s, 1H), 5.27 (d, J = 11.2 Hz, 1H), 4.43 (s, 1H), 3.68 (d, J = 11.2 Hz, 1H), 2.97 (d, J = 4 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 174.8, 155.3, 149.6, 147.1 (d, J = 243 Hz), 135.8, 132.1 (d, J = 4 Hz), 130.5, 130.5, 130.4, 130.0, 129.4, 129.3, 128.9, 128.4, 128.3, 127.8, 126.3, 124.7, 123.8, 123.1 (d, J = 6 Hz), 122.8 (d, J = 6 Hz), 120.9, 119.0, 118.0 (d, J = 3 Hz), 116.5 (d, J = 19 Hz), 115.3, 112.3, 109.2, 67.0 (d, J = 2 Hz), 65.1, 63.6, 56.4, 28.0 (d, J = 6 Hz). HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 26.095 min, t_minor = 9.002 min. HRMS (ESI): calcd for C35H25FN2O2 [M + H]+, 525.1973; found, 525.1977.
3wa:

(3R,6c'S,7'S,8a'R,13a'R)-7-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetracyclospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 170 - 172 °C, 46.5 mg, 86% yield, 99% ee, >19:1 d.r. [α]D = +272.1 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.73 (t, J = 8.9 Hz, 2H), 7.35 (d, J = 7.3 Hz, 1H), 7.24 - 7.09 (m, 9H), 7.00 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.73 (t, J = 7.8 Hz, 1H), 6.64 (t, J = 8.3 Hz, 2H), 6.51 (d, J = 7.3 Hz, 1H), 5.30 (s, 1H), 5.24 (d, J = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, J = 11.2 Hz, 1H), 3.08 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 175.4, 155.2, 149.5, 139.8, 135.7, 131.9, 130.8, 130.5, 130.0, 129.4, 129.3, 128.9, 128.4, 128.1, 127.9, 126.3, 124.6, 123.8, 123.3, 122.9, 122.8, 120.8, 120.7, 119.1, 115.1, 115.1, 112.3, 109.2, 66.4, 65.2, 63.8, 56.4, 28.8. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 29.920 min, t_minor = 9.835 min. HRMS (ESI): calcd for C35H25ClN2O2 [M + H]+, 541.1677; found, 541.1682.
3xa:

(3R,6c’S,7’S,8a’R,13a’R)-7-bromo-1-methyl-7’-phenyl-6c’,7’,8a’,13’tetrahydrospiro[indoline-3,8’-naphtho[1″,2″:4′,5′]furo[2′,3′:1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 158 - 160 °C, 50.3 mg, 86% yield, 97% ee, >19:1 d.r. $[\alpha]_D^{20} = +281.3 \ (c = 1.0, \ CHCl_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (t, $J = 9.4$ Hz, 2H), 7.39 (d, $J = 7.3$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.23 – 7.10 (m, 8H), 6.97 – 6.89 (m, 2H), 6.74 (d, $J = 7.9$ Hz, 1H), 6.66 – 6.61 (m, 2H), 6.50 (d, $J = 7.3$ Hz, 1H), 5.28 (s, 1H), 5.24 (d, $J = 11.2$ Hz, 1H), 4.37 (s, 1H), 3.62 (d, $J = 11.2$ Hz, 1H), 3.08 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.5, 155.2, 149.5, 141.2, 135.7, 134.1, 132.2, 130.5, 130.0, 129.4, 129.3, 128.8, 128.4, 127.9, 126.3, 124.6, 123.8, 123.7, 122.9, 122.8, 121.2, 120.8, 119.1, 115.1, 112.3, 109.2, 102.1, 66.4, 65.2, 63.8, 56.5, 29.0. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_{\text{major}} = 32.498$ min, $t_{\text{minor}} = 10.311$ min. HRMS (ESI): calcd for C$_{35}$H$_{25}$BrN$_2$O$_2$ \([M + H]^+\), 585.1172; found, 585.1180.
3ab: (3R,6c’S,7’S,8a’R,13a’R)-7-bromo-1-methyl-7’-(o-tolyl)-6c’,7’,8a’,13 1-tetrahydrospiro[indoline-3,8’-naphtho[1’’,2’’:4’,5’]furo[2’,3’:1,5]cy clopent[a]b]indol]-2-one: white solid, mp 197-199 °C, 45.8 mg, 88% yield, 99% ee, [α]D = 276.3 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.04 (d, J = 7.5 Hz, 1H), 7.72 (t, J = 8.0 Hz, 2H), 7.49 (d, J = 7.0 Hz, 1H), 7.24 – 7.01 (m, 7H), 6.87 (t, J = 7.2 Hz, 1H), 6.81 – 6.69 (m, 2H), 6.65 – 6.55 (m, 2H), 6.40 (dd, J = 19.7, 7.6 Hz, 2H), 5.33 (s, 1H), 5.13 (d, J = 11.1 Hz, 1H), 4.47 (s, 1H), 4.20 (d, J = 11.1 Hz, 1H), 2.83 (s, 3H), 1.58 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 175.7, 155.1, 149.7, 143.9, 137.2, 135.5, 130.4, 129.9, 129.3, 129.1, 129.0, 128.6, 128.2, 127.8, 127.1, 126.3, 126.1, 125.0, 123.4, 122.8, 122.7, 122.4, 122.2, 121.0, 118.9, 115.1, 112.2, 109.1, 107.9, 99.9, 66.2, 63.8, 58.3, 58.1, 25.6, 20.1. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 19.540 min, t_minor = 7.400 min. HRMS (ESI): calcd for C36H28N2O2 [M + H]+, 521.2224; found, 521.2225.
3ac:

(3R,6c’S,7’S,8a’R,13a’R)-1-methyl-7’-(m-tolyl)-6c’,7’,8a’,13’-tetrahyd rospiro[indoline-3,8’-naphtho[1”,2”-4’,5’]furo[2’,3’:1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 157 - 159 °C, 45.4 mg, 87% yield, 99% ee, >19:1 d.r. [α]_D^{20} = +269.6 (c = 1.0, CHCl₃); H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 7.7 Hz, 2H), 7.44 (d, J = 7.0 Hz, 1H), 7.24 – 6.90 (m, 10H), 6.72 (t, J = 7.9 Hz, 2H), 6.58 (t, J = 7.4 Hz, 2H), 6.45 (d, J = 6.9 Hz, 1H), 5.32 (s, 1H), 5.25 (d, J = 11.1 Hz, 1H), 4.42 (s, 1H), 3.65 (d, J = 11.1 Hz, 1H), 2.73 (s, 3H), 2.15 (s, 3H). C NMR (101 MHz, CDCl₃) δ 175.1, 155.3, 149.6, 143.9, 137.6, 136.0, 130.6, 129.9, 129.8, 129.4, 129.1, 128.4, 128.3, 128.2, 128.0, 126.2, 125.9, 125.1, 124.0, 122.9, 122.7, 122.5, 122.1, 121.1, 118.9, 115.3, 112.3, 109.1, 107.7, 66.7, 64.8, 63.4, 56.5, 25.4, 21.2. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 13.736 min, t_minor = 6.495 min. HRMS (ESI): calcd for C₃₆H₂₈N₂O₂ [M + H]^+ 521.2224; found, 521.2221. H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 8.5 Hz, 2H), 7.44 (d, J = 7.3 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.17 – 7.06 (m, 3H), 7.05 – 6.92 (m, 5H), 6.72 (dd, J = 10.4, 8.5 Hz, 2H), 6.58 (t, J = 7.4 Hz, 2H), 6.45 (d, J = 7.3 Hz, 1H), 5.24 (d, J = 11.2 Hz, 1H), 4.41 (s, 1H), 3.64 (d, J = 11.2 Hz, 1H), 2.72 (s, 3H), 2.14 (s, 3H).
3ad:

$\text{(3R,6c'S,7'S,8a'R,13a'R)-1-methyl-7'-}(p\text{-tolyl})\text{-6c',7',8a',13'-tetrahydrop}$

ospiro[indoline-3,8'-naphtho[1'',2''-4',5']furo[2',3':1,5]cyclopenta[1, 2-b]indol]-2-one: white solid, mp 147 - 149 °C, 45.8 mg, 88% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20} = +295.1$ (c = 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (t, $J = 7.5$ Hz, 2H), 7.43 (d, $J = 7.3$ Hz, 1H), 7.24 – 7.05 (m, 7H), 6.98 – 6.86 (m, 3H), 6.72 (d, $J = 8.0$ Hz, 2H), 6.59 (t, $J = 7.1$ Hz, 2H), 6.45 (d, $J = 7.3$ Hz, 1H), 5.36 (s, 1H), 5.25 (d, $J = 11.2$ Hz, 1H), 4.41 (s, 1H), 3.66 (d, $J = 11.1$ Hz, 1H), 2.73 (s, 3H), 2.24 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.2, 155.3, 149.6, 143.9, 137.1, 133.0, 130.6, 129.9, 129.4, 129.2, 129.1, 128.9, 128.8, 128.4, 126.2, 125.1, 124.0, 122.9, 122.7, 122.5, 122.1, 121.2, 118.9, 115.2, 112.3, 109.2, 107.8, 66.7, 64.5, 63.5, 56.5, 25.5, 21.1. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_{\text{major}} = 11.801$ min, $t_{\text{minor}} = 7.610$ min. HRMS (ESI): calcd for C$_{36}$H$_{28}$N$_2$O$_2$ $[M + H]^+$, 521.2224; found, 521.2222.
3ae:

\((3R,6c'S,7'R,8a'R,13a'R)-7'-(2-chlorophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclpentena[1,2-b]indol]-2-one\): white solid, mp 185 - 187 °C, 46.5 mg, 86% yield, 99% ee, >19:1 d.r. \([\alpha]_D^{20} = +286.3\) (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, \(J = 7.9\) Hz, 2H), 7.78 – 7.70 (m, 2H), 7.59 (d, \(J = 7.4\) Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.05 (m, 6H), 7.00 (d, \(J = 7.9\) Hz, 1H), 6.92 (t, \(J = 7.6\) Hz, 1H), 6.71 (d, \(J = 7.9\) Hz, 1H), 6.66 – 6.55 (m, 2H), 6.42 (t, \(J = 6.8\) Hz, 2H), 5.17 (d, \(J = 11.3\) Hz, 1H), 4.67 (d, \(J = 11.3\) Hz, 1H), 4.47 (s, 1H), 2.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.4, 155.2, 149.7, 143.7, 135.3, 134.8, 130.5, 130.1, 129.7, 129.4, 129.2, 128.6, 128.5, 128.1, 127.1, 126.2, 124.7, 123.6, 123.1, 122.9, 122.7, 122.5, 120.5, 118.8, 114.9, 112.3, 109.1, 107.7, 66.4, 64.3, 57.7, 57.0, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: \(t_{\text{major}} = 28.685\) min, \(t_{\text{minor}} = 9.700\). HRMS (ESI): calcd for C₃₅H₂₅ClN₂O₂ \([M + H]^+\), 541.1677; found, 541.1672.
3af:

\[((3R,6c'S,7'S,8a'R,13a'R)-7'-\text{[3-chlorophenyl]}-1\text{-methyl-6c',7',8a',13'\text{tetrahydrospiro[indoline-3,8'-naphtho[1''2':4',5'furo[2',3':1,5]cy clopenta[1,2-b]indol]-2-one}}: \text{white solid, mp} 161 - 163 \degree\text{C}, 48.2 \text{mg, 89\% yield, 98\% ee, } >\text{19:1 d.r.} \ \left[\alpha\right]_D^{20} = +276.5 \text{ (c = 1.0, CHCl}_3\right); \text{ }^1\text{H NMR} \text{ (400 MHz, CDCl}_3\right) \delta 7.73 \text{ (t, } J = 7.8 \text{ Hz, 2H)}, 7.41 \text{ (d, } J = 7.0 \text{ Hz, 1H)}, 7.23 - 6.94 \text{ (m, 11H)}, 6.73 - 6.64 \text{ (m, 2H)}, 6.62 - 6.53 \text{ (m, 2H)}, 6.42 \text{ (d, } J = 7.3 \text{ Hz, 1H)}, 5.20 \text{ (d, } J = 11.1 \text{ Hz, 1H)}, 4.40 \text{ (s, 1H)}, 3.61 \text{ (d, } J = 11.2 \text{ Hz, 1H)}, 2.72 \text{ (s, 3H).} \text{ }^{13}\text{C NMR} \text{ (101 MHz, CDCl}_3\right) \delta 174.9, 155.3, 149.6, 143.8, 138.5, 134.0, 130.5, 130.2, 129.5, 129.4, 129.2, 129.1, 128.7, 128.6, 128.6, 127.8, 127.1, 126.5, 124.8, 123.7, 122.9, 122.8, 122.1, 120.6, 118.9, 115.2, 112.4, 109.1, 107.9, 66.6, 64.2, 63.4, 56.4, 25.5. \text{HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH } = 70/30, \text{flow rate } = 1.0 \text{ mL/min, } \lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 15.241 \text{ min, } t_{\text{minor}} = 7.690. \text{HRMS (ESI): calcd for C}_{35}\text{H}_{25}\text{ClN}_2\text{O}_2 \text{ [M + H]}^+, 541.1677; \text{found, 541.1671.}
3ag:

\((3R,6c'S,7'S,8a'R,13a'R)-7'-(4-chlorophenyl)-1-methyl-6c',7',8a',13'\)-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'';4',5'\]furo[2',3';1,5\]cy clopenta[1,2-b]indol]-2-one: white solid, mp 194 - 196 °C, 47.0 mg, 87% yield, 99% ee. >19:1 d.r. \([\alpha]_D^{20} = +267.3 (c = 1.0, \text{CHCl}_3)\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.76 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.45 (d, J = 7.1 \text{ Hz}, 1\text{H}), 7.27 - 7.00 (m, 10\text{H}), 6.73 (t, J = 8.8 \text{ Hz}, 2\text{H}), 6.66 - 6.55 (m, 2\text{H}), 6.47 (d, J = 7.1 \text{ Hz}, 1\text{H}), 5.38 (s, 1\text{H}), 5.25 (d, J = 11.1 \text{ Hz}, 1\text{H}), 4.44 (s, 1\text{H}), 3.69 (d, J = 11.1 \text{ Hz}, 1\text{H}), 2.78 (s, 3\text{H}).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 175.0, 155.3, 149.5, 143.8, 134.9, 133.4, 130.5, 130.2, 130.1, 129.4, 129.2, 128.7, 128.6, 128.4, 126.5, 124.8, 123.7, 122.9, 122.7, 122.0, 120.7, 118.9, 115.2, 112.4, 109.1, 108.0, 66.7, 64.0, 63.5, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, \(\lambda = 254 \text{ nm}, \text{retention time: } t_{\text{major}} = 40.441 \text{ min}, t_{\text{minor}} = 37.019. \text{HRMS (ESI): calcd for } \text{C}_{35}\text{H}_{25}\text{ClN}_2\text{O}_2 \ [M + H]^+; 541.1677; \text{found, 541.1674.} \)
3ah:

(3R,6c’S,7’S,8a’R,13a’R)-7’-(4-fluorophenyl)-1-methyl-6c’,7’,8a’,13’-tetrahydrospiro[indoline-3,8’-naphtho[1’,2’:4’,5’]furo[2’,3’:1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 185-187 °C, 45.2 mg, 86% yield, 98% ee, 12:1 d.r. $[\alpha]_D^{20} = +344.3$ (c = 1.0, CHCl$_3$);

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 6.0 Hz, 2H), 7.43 (d, $J$ = 6.8 Hz, 1H), 7.24 – 7.06 (m, 7H), 7.04 – 6.96 (m, 1H), 6.81 (t, $J$ = 7.5 Hz, 2H), 6.70 (t, $J$ = 8.0 Hz, 2H), 6.64 – 6.54 (m, 2H), 6.45 (d, $J$ = 6.6 Hz, 1H), 5.35 (s, 1H), 5.20 (d, $J$ = 11.2 Hz, 1H), 4.42 (s, 1H), 3.66 (d, $J$ = 10.9 Hz, 1H), 2.74 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.1, 162.3 (d, $J$ = 245 Hz), 155.3, 149.5, 143.8, 132.0 (d, $J$ = 3 Hz), 130.5, 130.4, 130.1, 129.5, 129.1, 128.9, 128.6 (d, $J$ = 7 Hz), 126.4, 124.9, 123.7, 122.8 (d, $J$ = 6 Hz), 122.7, 122.0, 120.8, 118.9, 115.2, 115.0, 112.3, 109.1, 107.9, 66.7, 64.0, 63.3, 56.5, 25.57. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda$ = 254 nm, retention time: $t_{\text{major}} = 19.433$ min, $t_{\text{minor}} = 24.662$ min. HRMS (ESI): calcd for C$_{35}$H$_{25}$FN$_2$O$_2$ [M + H]$^+$, 525.1973; found, 525.1970.
3ai:

\( (3R,6c'S,7'S,8a'R,13a'R)-7'-(4\text{-bromophenyl})-1\text{-methyl-6c',7',8a',13't} \)

tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2',3':1,5]cyclo

tenta[1,2-b]indol]-2-one: \) white solid, mp 163 - 165 °C, 49.7 mg, 85% yield, 98% ee, >19:1 d.r. \([\alpha]_D^{20} = +269.8 \) (c = 1.0, CHCl\(_3\))

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.74 (d, \( J = 7.9 \) Hz, 2H), 7.41 (d, \( J = 6.4 \) Hz, 1H), 7.25 - 6.97 (m, \( J = 33.2, 23.8, 7.4 \) Hz, 10H), 6.76 - 6.66 (m, 2H), 6.64 - 6.54 (m, 2H), 6.45 (d, \( J = 6.1 \) Hz, 1H), 5.37 (s, 1H), 5.22 (d, \( J = 10.7 \) Hz, 1H), 4.42 (s, 1H), 3.65 (d, \( J = 10.8 \) Hz, 1H), 2.75 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 175.0, 155.3, 149.5, 143.8, 135.4, 131.4, 130.6, 130.5, 130.2, 129.4, 129.2, 128.7, 128.6, 126.6, 124.8, 123.7, 122.9, 122.7, 122.0, 121.7, 120.7, 118.9, 115.2, 112.4, 109.1, 108.0, 99.9, 66.6, 64.0, 63.6, 56.4, 25.6.

HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, \( \lambda = 254 \) nm, retention time: \( t_{\text{major}} = 21.043 \) min, \( t_{\text{minor}} = 17.755 \) min. HRMS (ESI): calc'd for C\(_{35}\)H\(_{25}\)BrN\(_2\)O\(_2\) \([\text{M} + \text{H}]^+\), 585.1172; found, 585.1174.
3aj:

\[
(3R,6c'S,7'S,8a'R,13a'R)-1\text{-methyl-7'}-(4\text{-trifluoromethyl}phenyl)-6c' ,7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1''',2''':4',5']furo[2' ,3':1,5']cyclopenta[1,2-b]indol]-2\text{-one}: \text{white solid, mp 133 - 135 } ^\circ\text{C, 49.5 mg, 86% yield, 98% ee, } >19:1 \text{ d.r. } [\alpha]_D^{20} = +351.7 \text{ (c = 1.0, CHCl}_3); ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.80 - 7.68 \text{ (m, 2H), 7.45 (d, } J = 7.0 \text{ Hz, 1H), 7.36 (s, 4H), 7.19 (m, 5H), 6.95 (t, } J = 7.3 \text{ Hz, 1H), 6.69 (d, } J = 7.7 \text{ Hz, 1H), 6.60 (t, } J = 8.8 \text{ Hz, 3H), 6.45 (d, } J = 7.0 \text{ Hz, 1H), 5.39 (s, 1H), 5.28 (d, } J = 11.0 \text{ Hz, 1H), 4.45 (s, 1H), 3.75 (d, } J = 11.0 \text{ Hz, 1H), 2.75 (s, 3H). ^{13}\text{C NMR (101 MHz, CDCl}_3) \delta 174.9, 155.3, 149.5, 143.7, 140.6, 130.4, 130.2, 129.4, 129.3, 128.8, 128.6, 128.5, 126.5, 125.2 (q, } J = 4.0 \text{ Hz), 124.6, 123.5, 122.9, 122.9, 122.8, 122.1, 120.5, 118.9, 115.2, 112.4, 109.2, 108.1, 66.7, 64.2, 63.8, 56.6, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, } \lambda = 254 \text{ nm, retention time: } t_{\text{major}} = 11.440 \text{ min, } t_{\text{minor}} = 14.316 \text{ min. HRMS (ESI): calcd for C}_{36}H_{25}F_3N_2O_2 \text{ [M + H] }^+, 575.1941; \text{ found, 575.1947.} \]
3ak: methyl-4-[(3R,6c'S,7'S,8a'R,13a'R)-1-methyl-2-oxo-6c',7',8a',
13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2':4',5']furo[2',
3':1,5]cyclopenta[1,2-b]indol]-7'-yl]benzoate: white solid, mp
200 - 202 °C, 46.6 mg, 87% yield, 98% ee, >19:1 d.r. [α]_D
20 = +287.3 (c = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d,
J = 24.7 Hz, 4H), 7.43 (s, 1H), 7.29 (s, 2H), 7.24 – 7.03 (m, 5H),
6.94 (s, 1H), 6.70 (d, J = 6.1 Hz, 2H), 6.58 (s, 1H), 6.45 (s, 1H),
5.38 (s, 1H), 5.29 (d, J = 10.0 Hz, 1H), 4.44 (s, 1H), 3.86 (s, 3H),
3.74 (d, J = 10.0 Hz, 1H), 2.71 (s, 3H). ^13C NMR (101 MHz, CDCl_3) δ 174.8, 166.9, 155.3, 149.6,
143.7, 141.6, 130.4, 130.2, 129.5, 129.3, 129.0, 128.7, 126.5, 124.8, 123.6, 122.9, 122.9,
122.8, 122.7, 122.1, 120.6, 118.9, 115.4, 112.3, 109.1, 107.9, 66.8, 64.6, 63.5, 56.2, 52.0, 25.5.
HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_major = 39.309 min, t_minor = 31.456 min. HRMS (ESI): calcd for C_{37}H_{28}BrN_{2}O_{4} [M + H]^+; 565.2122; found, 565.2124.
3al: (3R,6c'S,7'S,8a'R,13a'R)-1-methyl-7'-{(4-nitrophenyl)-6c',7',8a',13' -tetrahydrospiro[indoline-3,8'-naphtho[1',2'':4',5']furo[2',3':1,5] cyploenta[1,2-b]indol]-2-one: white solid, mp 181 - 183 °C, 45.3 mg, 82% yield, 98% ee, >19:1 d.r. \([\alpha]_D^{20} = +275.3\) (c = 1.0, CHCl₃);

$^1$H NMR (400 MHz, CDCl₃) δ 7.97 (d, \(J = 8.5\) Hz, 2H), 7.75 (t, \(J = 8.2\) Hz, 2H), 7.46 (d, \(J = 7.3\) Hz, 1H), 7.41 (d, \(J = 7.8\) Hz, 2H), 7.26 (t, \(J = 7.6\) Hz, 1H), 7.22 – 7.09 (m, 4H), 6.96 (t, \(J = 7.6\) Hz, 1H), 6.71 (d, \(J = 7.8\) Hz, 1H), 6.67 – 6.55 (m, 3H), 6.43 (d, \(J = 7.3\) Hz, 1H), 5.39 – 5.27 (m, 1H), 4.44 (s, 2H), 3.78 (d, \(J = 11.1\) Hz, 1H), 2.73 (s, 3H), $^{13}$C NMR (101 MHz, CDCl₃) δ 174.6, 155.4, 149.4, 147.4, 144.1, 143.6, 130.4, 130.3, 129.8, 129.5, 129.3, 129.0, 128.8, 128.1, 126.7, 124.4, 123.3, 123.1, 122.9, 122.9, 122.8, 122.0, 120.2, 119.0, 115.2, 112.4, 109.1, 108.1, 66.8, 64.1, 63.7, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: \(t_{major} = 39.309\) min, \(t_{minor} = 31.456\) min. HRMS (ESI): calcd for C₃₅H₂₅N₃O₄ [M + H]+, 552.1918; found, 552.1920.

[Image of 3al molecule]
3am:

(4bR,5R,6S,6aS,11aR)-1'-methyl-6-phenyl-4b,6,6a,12-tetrahydrospiroo[benzofuro[2',3':1,5]cyclopenta[1,2-b]indole-5,3'-indolin]-2'-one: white solid, mp 132 - 134 °C, 45.3 mg, 62% yield, 81% ee, >19:1 d.r. 

[$\alpha$]$_D$$^{20} = +212.3$ (c = 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J$ = 7.5 Hz, 1H), 7.24 - 7.18 (m, 1H), 7.12 - 6.92 (m, 7H), 6.88 (d, $J$=8.1 Hz) 6.80 - 6.71 (m, 3H), 6.67 - 6.58 (m, 2H), 6.51 - 6.41 (m, 2H), 5.10 (s, 1H), 4.66 (s, 1H), 4.50 (d, $J$ = 11.9 Hz, 1H), 3.88 (d, $J$ = 11.9 Hz, 1H), 3.06 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.9, 157.9, 149.0, 143.1, 134.8, 129.0, 128.5, 128.2, 128.1, 128.0, 127.8, 127.3, 126.4, 125.3, 125.1, 123.9, 123.8, 121.8, 120.7, 119.4, 115.5, 109.9, 108.5, 107.6, 65.8, 64.0, 62.1, 55.3, 26.3. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda$ = 254 nm, retention time: $t_{major} = 16.285$ min, $t_{minor} = 14.066$ min. HRMS (ESI): calcd for C$_{31}$H$_{24}$N$_2$O$_2$ [M + H]$^+$, 457.1911; found, 457.1918.
HPLC spectra of racemic and enantioenriched products.

3aa

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### Peak 1

- **RT (min):** 9.878
- **Height (mV):** 2.15
- **Area (mV*s):** 77.14
- **Area (%):** 0.4118

### Peak 2

- **RT (min):** 29.043
- **Height (mV):** 152.92
- **Area (mV*s):** 18654.53
- **Area (%):** 99.5882

---

**Diagram 1:**

![Diagram of compound 3ja](image1.png)

**Diagram 2:**

![Diagram of compound 3ja](image2.png)
### 3ka

<table>
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![Graph 1](image1)

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![Graph](image1)

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![Graph](image2)
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### 3wa (alternative)

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Intermediate data

7an:

3-(5-fluoro-2-hydroxyphenyl)-1'-methyl-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one: white solid, mp 113 - 115 °C, 30mg, 63% yield. 1H NMR (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 7.16 (d, $J = 8.1$ Hz, 1H), 7.13 - 7.02 (m, 7H), 7.02 - 6.90 (m, 4H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 5.6$ Hz, 2H), 5.51 (d, $J = 9.0$ Hz, 1H), 4.87 (d, $J = 9.0$ Hz, 1H), 3.32 (s, 3H) $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.1, 155.5 (d, $J = 236$ Hz), 150.4, 145.7, 142.3, 140.5, 136.5, 130.4, 128.2, 127.8, 127.8 (d, $J = 7$ Hz), 125.3, 122.5 (d, $J = 12$ Hz), 121.6, 120.0, 117.7 (d, $J = 49$ Hz), 117.5, 115.5 (d, $J = 23$ Hz), 114.5 (d, $J = 23$ Hz), 111.9, 107.8, 67.6, 60.3, 43.0, 26.7. HRMS (ESI): calcd for C$_{31}$H$_{23}$FN$_2$O$_2$ [M + H]$^+$, 475.1816; found 475.1813.
7ao:

3-(5-chloro-2-hydroxyphenyl)-1'-methyl-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one: white solid, mp 121 - 123 °C, 32 mg, 65% yield. 15:1 d.r., $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 7.16 (d, $J = 8.1$ Hz, 1H), 7.14 – 6.91 (m, 11H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 5.6$ Hz, 2H), 5.51 (d, $J = 9.0$ Hz, 1H), 4.87 (d, $J = 9.0$ Hz, 1H), 3.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.3, 153.2, 145.6, 142.4, 140.6, 136.6, 130.4, 129.1, 128.3, 128.2, 128.1, 127.9, 127.1, 125.4, 125.4, 122.6, 122.4, 121.7, 120.0, 118.2, 117.9, 117.4, 112.0, 107.9, 67.6, 60.3, 43.5, 26.7. HRMS (ESI): calcd for C$_{31}$H$_{23}$ClN$_2$O$_2$ [M + H]$^+$, 491.1521; found 491.1526.
Control experiment data

3wa

(3R,6c'S,7'S,8a'R,13a'R)-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indolin-3,8']-naphtho[1''''',2'''':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 99 - 101 °C, 35.0 mg, 71% yield, 93% ee, >19:1 d.r. [α]D20 = +268.6 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.74 (t, J = 8.4 Hz, 2H), 7.57 (s, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.24 – 6.97 (m, 10H), 6.94 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 7.6 Hz, 2H), 6.59 (d, J = 7.6 Hz, 1H), 6.56 – 6.49 (m, 2H), 5.38 (s, 1H), 4.41 (s, 1H), 3.70 (d, J = 11.2 Hz, 1H), 13C NMR (101 MHz, CDCl3) δ 177.5, 155.2, 149.5, 141.00, 136.1, 130.6, 130.0, 129.8, 129.4, 129.1, 129.0, 128.4, 128.4, 128.4, 128.3, 127.7, 126.3, 124.9, 124.0, 123.1, 122.8, 122.5, 122.4, 121.0, 119.0, 115.3, 112.3, 109.7, 109.0, 67.0, 64.9, 63.8, 56.3. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tmajor = 22.127 min, tminor = 11.733 min. HRMS (ESI): calcd for C34H32N2O2 [M + H]+, 493.1911; found, 493.1906.
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1 | 13.704 | 52.89 | 2672.75 | 30.7834  
2 | 22.137 | 35.99 | 2514.72 | 28.9633  
3 | 24.879 | 19.80 | 1547.11 | 17.8189  
4 | 39.145 | 13.24 | 1947.86 | 22.4345  

Peak | RT [min] | Height [mV] | Area [mV*s] | Area%  
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1 | 13.733 | 11.41 | 538.46 | 3.4493  
2 | 22.127 | 196.01 | 15072.51 | 96.5507  

120
(3R,6c'S,7'S,8a'R,13a'R)-1,13'-dimethyl-7'-phenyl-6c',7,8a',13'-tetrahyd rospiro[indoline-3,8'-naptho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b] indol]-2-one: white solid, mp 141 - 143 °C, 13.0 mg, 25% yield, 21:1 d.r.; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (t, $J = 8.9$ Hz, 2H), 7.44 (d, $J = 7.2$ Hz, 1H), 7.25 - 7.02 (m, 10H), 6.95 (t, $J = 8.0$, 3.9 Hz, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 6.57 (d, $J = 4.0$ Hz, 1H), 6.53 - 6.38 (m, 3H), 5.29 (d, $J = 11.1$ Hz, 1H), 4.37 (s, 1H), 3.71 (d, $J = 11.1$ Hz, 1H), 2.97 (s, 3H), 2.71 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.0, 156.1, 151.0, 144.0, 136.4, 130.5, 130.0, 129.3, 129.2, 129.0, 128.4, 128.2, 127.6, 126.2, 124.2, 124.0, 122.6, 122.5, 122.1, 121.1, 117.7, 116.8, 112.0, 107.7, 104.8, 66.5, 64.8, 62.3, 53.2, 77.2, 27.7, 25.4. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_1 = 5.346$ min, $t_2 = 9.795$ min. HRMS (ESI): calcd for C$_{35}$H$_{26}$N$_2$O$_2$ [M + H]$^+$, 521.2224; found, 521.2216.
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Figure 1. X-Ray Structure of 3ca:

X-ray crystallographic analysis has been established. The enantioenriched spiro[benzofuro-cyclopenta[1,2-b]indole-indoline] structure 3ca (32 mg, 98% ee) was dissolved by 3 mL prepared solvents (ethanol:n-hexane=2:1) and transferred into a test tube. The tube was placed in dry and avoid light position for 2 days. The crystals were separated out by filtrating. The absolute configuration of 3ca was established by X-ray crystallographic analysis. In Figure 1, the C36, C37 and O3 come from solvent ethanol. The result of X-ray crystallographic analysis shows chiral spiro[benzofuro-cyclopenta[1,2-b]indole-indoline] structure 3ca is (7R, 8R, 9S, 20S, 27R) configuration as shown in Figure 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.