Supporting Information

Palladium-Catalyzed Construction of Spirooxindoles by Arylative Cyclization of 3-(γ,δ-Disubstituted)allylidene-2-Oxindoles

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1. General information
All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen unless otherwise noted. Thin layer chromatography (TLC) was performed with pre-coated silica gel plates (Kieselgel 60F-254, Merck). Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with \( p \)-anisaldehyde stain followed by heating. The separations were carried out by flash column chromatography over silica gel 60 (230-400 mesh ASTM). Organic extracts were dried over anhydrous MgSO\(_4\) and the solvents were removed on a rotary evaporator under water aspirator pressure. All reagents were purchased from commercial sources and used without further treatment.

Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. \(^1\)H NMR (300 MHz) spectra were measured on a Varian Unity Plus 300. Chemical shifts are reported in ppm relative to TMS (\( \delta \) scale) used as an internal standard. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Chemical shifts of the \(^{13}\)C NMR (75 MHz) spectra were measured relative to CDCl\(_3\) (77.23 ppm). IR spectra were recorded on a Jasco FT-IR 410 spectrometer and are reported in cm\(^{-1}\). Mass spectra were obtained from the Korea Basic Science Institute (Gwangju branch) using ESI\(^+\) method. Elemental analyses (C, H, and N) were performed with a Fisons EA-1108 Elemental Analyzer machine at Korea Research Institute of Chemical Technology, Daejeon, Korea.
2. Preparation of starting materials

Typical procedure for the preparation of 3a-EE and 3a-ZE

A mixture of MBH bromide 1a (306 mg, 1.2 mmol)\textsuperscript{[1]} and PPh\textsubscript{3} (314 mg, 1.2 mmol) in CH\textsubscript{3}CN (3.0 mL) was stirred at room temperature for 4 h. The corresponding phosphonium salt, monitored by TLC, was formed quantitatively. To the reaction mixture isatin 2a (161 mg, 1.0 mmol) and K\textsubscript{2}CO\textsubscript{3} (276 mg, 2.0 mmol) were added, and the reaction mixture was stirred at room temperature for 3 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/Et\textsubscript{2}O, 3:1), compound 3a-EE (166 mg, 52\%) and 3a-ZE (134 mg, 42\%) were obtained as yellow solids. Other compounds were synthesized similarly, and the spectroscopic data of 3a-j are as follows.

(E)-Methyl 2-((E)-(1-methyl-2-oxindolin-3-ylidene)methyl)-3-phenylacrylate (3a-EE): 52\%; yellow solid, mp 112-114 °C; IR (KBr) 3056, 2950, 1711, 1610, 1469, 1254 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) δ 3.27 (s, 3H), 3.75 (s, 3H), 6.79 (d, \textit{J} = 7.5 Hz, 1H), 6.90 (t, \textit{J} = 7.5 Hz, 1H), 7.15 (d, \textit{J} = 7.5 Hz, 1H), 7.24 (t, \textit{J} = 7.5 Hz, 1H), 7.30-7.37 (m, 3H), 7.48-7.54 (m, 2H), 7.60 (d, \textit{J} = 1.5 Hz, 1H), 7.76 (d, \textit{J} = 1.8 Hz, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) δ 25.21, 52.49, 107.99, 121.33, 122.14, 123.79, 126.20, 128.71, 129.67, 129.78, 130.26, 130.52, 130.73, 134.26, 144.00, 144.06, 167.03, 167.58; ESIMS \textit{m/z} 342 [M+Na]\textsuperscript{+}. Anal. Calcd for C\textsubscript{20}H\textsubscript{17}NO\textsubscript{3}: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.19; H, 5.43; N, 4.22.

(E)-Methyl 2-((Z)-(1-methyl-2-oxindolin-3-ylidene)methyl)-3-phenylacrylate (3a-ZE): 42\%; yellow solid, mp 118-120 °C; IR (KBr) 3056, 2948, 1705, 1610, 1470, 1257 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) δ 3.23 (s, 3H), 3.83 (s, 3H), 6.83 (d, \textit{J} = 7.8 Hz, 1H), 7.05 (t, \textit{J} = 7.8 Hz, 1H), 7.21 (d, \textit{J} = 1.8 Hz, 1H), 7.32 (t, \textit{J} = 7.8 Hz, 1H), 7.39 (s, 5H), 7.47 (d, \textit{J} = 7.8 Hz, 1H), 7.76 (d, \textit{J} = 1.8 Hz, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) δ 25.84, 52.27, 108.08, 120.21, 121.93, 122.51, 128.11, 128.52, 128.94, 129.64, 129.73, 130.37, 130.75, 135.03, 142.29, 143.45, 166.21, 167.58; ESIMS \textit{m/z} 342 [M+Na]\textsuperscript{+}. Anal. Calcd for C\textsubscript{20}H\textsubscript{17}NO\textsubscript{3}: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.41; H, 5.50; N, 4.47.
(E)-Methyl 2-((E)-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3b-EE): 51%; yellow solid, mp 172-174 °C; IR (KBr) 1712, 1642, 1483, 1255, 1204, 1115 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.25 (s, 3H), 3.80 (s, 3H), 6.69 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 2.1 Hz, 1H), 7.18 (dd, J = 8.4 and 2.1 Hz, 1H), 7.30-7.36 (m, 3H), 7.45-7.50 (m, 2H), 7.60 (d, J = 1.8 Hz, 1H), 7.99 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.19, 52.67, 108.78, 122.45, 124.09, 125.70, 127.40, 128.77, 129.29, 129.34, 129.44, 130.44, 131.19, 134.16, 142.43, 144.76, 166.54, 167.22; ESIMS m/z 354 [M+H]+, 356 [M+H+2]+. Anal. Calcd for C₂₀H₁₆ClNO₃: C, 67.90; H, 4.56; N, 3.96. Found: C, 68.19; H, 4.87; N, 3.90.

(E)-Methyl 2-((Z)-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3b-ZE): 40%; yellow solid, mp 188-189 °C; IR (KBr) 1707, 1631, 1485, 1435, 1333, 1253, 1135, 1101 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.22 (s, 3H), 3.82 (s, 3H), 6.75 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 2.1 Hz, 1H), 7.28 (dd, J = 8.4 and 2.1 Hz, 1H), 7.34-7.45 (m, 6H), 7.79 (d, J = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.98, 52.33, 109.04, 120.49, 123.91, 127.48, 128.59, 128.65, 129.31, 129.49, 129.61, 129.91, 130.75, 134.87, 141.85, 141.11, 165.85, 167.35; ESIMS m/z 354 [M+H]+, 356 [M+H+2]+.

(E)-Methyl 2-((E)-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3c-EE): 49%; yellow solid, mp 158-159 °C; IR (KBr) 1707, 1595, 1490, 1435, 1253, 1185, 1115 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.26 (s, 3H), 3.70 (s, 3H), 3.79 (s, 3H), 6.70 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 8.1 and 2.4 Hz, 1H), 7.32-7.37 (m, 3H), 7.50-7.58 (m, 2H), 7.60 (d, J = 1.8 Hz, 1H), 7.97 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.13, 52.59, 55.77, 108.29, 110.41, 115.05, 122.02, 126.08, 128.73, 129.87, 130.32, 130.68, 130.77, 134.22, 137.93, 143.93, 155.44, 167.01, 167.44; ESIMS m/z 350 [M+H]+. Anal. Calcd for C₂₁H₁₉NO₄: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.32; H, 5.71; N, 3.83.

(E)-Methyl 2-((Z)-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3c-ZE): 45%; yellow solid, mp 148-150 °C; IR (KBr) 1722, 1703, 1597, 1493, 1435, 1287, 1255, 1129 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.22 (s, 3H), 3.79 (s, 3H), 3.83 (s, 3H), 6.75 (d, J = 8.7 Hz, 1H), 6.89 (dd, J = 8.7 and 2.4 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 2.1 Hz, 1H), 7.41 (s, 5H), 7.79 (d, J = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.90, 52.27, 55.95, 107.04, 108.49, 114.71, 123.40, 128.25, 128.55, 128.91, 129.65, 130.75, 130.80, 135.04, 137.49, 142.29, 155.59, 166.13, 167.58; ESIMS m/z 350 [M+H]+.
(E)-Methyl 2-((E)-(1-acetyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3d-EE): 48%; yellow solid, mp 142-144 °C; IR (KBr) 2950, 1743, 1714, 1602, 1459, 1371, 1302 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.77 (s, 3H), 3.74 (s, 3H), 7.08 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.32-7.43 (m, 3H), 7.44-7.55 (m, 2H), 7.64 (s, 1H), 8.01 (s, 1H), 8.28 (d, J = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.80, 52.65, 116.58, 122.06, 123.33, 124.82, 125.75, 128.82, 129.29, 130.26, 130.58, 130.71, 131.20, 134.12, 140.12, 144.97, 166.57, 167.76, 170.75; ESIMS m/z 370 [M+Na]⁺. Anal. Calcd for C₂₁H₁₇NO₄: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.87; H, 5.20; N, 3.94.

(E)-Methyl 2-((Z)-(1-acetyl-2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3d-ZE): 39%; yellow solid, mp 156-158 °C; IR (KBr) 1733, 1713, 1465, 1373, 1282, 1163 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.70 (s, 3H), 3.83 (s, 3H), 7.23 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 2.1 Hz, 1H), 7.36-7.45 (m, 6H), 7.55 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 2.1 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.74, 52.38, 116.88, 119.79, 123.17, 124.92, 128.40, 128.71, 129.07, 129.95, 130.12, 130.29, 130.85, 134.81, 139.58, 143.70, 166.57, 167.29, 170.82; ESIMS m/z 370 [M+Na]⁺.

(E)-Methyl 2-((E)-(2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3e-EE): 51%; yellow solid, mp 162-164 °C; IR (KBr) 3200, 1709, 1614, 1255, 1205 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.76 (s, 3H), 6.84-6.92 (m, 2H), 7.14 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.32-7.37 (m, 3H), 7.48-7.54 (m, 2H), 7.59 (d, J = 1.8 Hz, 1H), 7.98 (d, J = 1.8 Hz, 1H), 8.78 (br s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 52.61, 110.04, 121.91, 122.15, 124.12, 126.10, 128.74, 129.88, 129.97, 130.33, 130.72, 130.90, 134.24, 141.39, 144.29, 166.99, 169.43; ESIMS m/z 328 [M+Na]⁺. Anal. Calcd for C₁₉H₁₅NO₃: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.96; H, 5.07; N, 4.34.

(E)-Methyl 2-((Z)-(2-oxoindolin-3-ylidene)methyl)-3-phenylacrylate (3e-ZE): 41%; yellow solid, mp 158-160 °C; IR (KBr) 3287, 1717, 1615, 1269, 1258, 1203 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.81 (s, 3H), 6.91 (d, J = 7.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 1.8Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.41 (s, 5H), 7.47 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H), 8.52 (br s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 52.28, 110.04, 120.60, 121.99, 123.29, 128.53, 128.59, 128.80, 129.79, 129.85, 130.68, 130.81, 135.00, 140.86, 142.86, 167.68, 168.15; ESIMS m/z 328 [M+Na]⁺. Anal. Calcd for C₁₉H₁₅NO₃: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.71; H, 4.82; N, 4.41.
(E)-Methyl 2-((E)-(1-methyl-2-oxindolin-3-ylidene)methyl)-3-(naphthalen-1-yl)acrylate (3f-EE): 53%; yellow solid, mp 164-166 °C; IR (KBr) 1710, 1609, 1337, 1250, 1236, 1105 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.24 (s, 3H), 3.80 (s, 3H), 6.77 (d, J = 7.8 Hz, 1H), 6.85 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.48-7.66 (m, 4H), 7.85 (apparent t, J = 7.8 Hz, 2H), 8.12 (d, J = 8.1 Hz, 1H), 8.69 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.06, 52.62, 107.99, 121.41, 121.95, 123.73, 123.82, 125.23, 126.33, 126.98, 128.52, 128.82, 129.23, 129.63, 129.68, 130.52, 130.80, 131.07, 131.50, 133.44, 142.50, 143.99, 167.15, 167.69; ESIMS m/z 370 [M+H]⁺. Anal. Calcd for C₂₄H₁₉NO₃: C, 78.03; H, 5.18; N, 3.79. Found: C, 77.90; H, 5.37; N, 3.89.

(E)-Methyl 2-((Z)-(1-methyl-2-oxindolin-3-ylidene)methyl)-3-(naphthalen-1-yl)acrylate (3f-ZE): 42%; yellow solid, mp 146-148 °C; IR (KBr) 1722, 1704, 1630, 1470, 1335, 1249, 1130 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.26 (s, 3H), 3.90 (s, 3H), 6.83 (d, J = 7.8 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.36-7.45 (m, 2H), 7.53-7.62 (m, 2H), 7.87-7.92 (m, 2H), 8.04-8.08 (m, 1H), 8.40 (d, J = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.89, 52.35, 108.04, 120.21, 121.89, 122.65, 124.40, 125.05, 126.44, 126.94, 128.22, 128.67, 129.62, 130.04, 130.14, 130.36, 131.19, 131.62, 133.40, 140.28, 143.36, 166.39, 167.75; ESIMS m/z 370 [M+H]⁺.

(E)-Methyl 3-(3,4-dichlorophenyl)-2-((E)-(1-methyl-2-oxindolin-3-ylidene)methyl)acrylate (3g-EE): 46%; yellow solid, mp 180-182 °C; IR (KBr) 1712, 1700, 1249, 1130, 1092 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.27 (s, 3H), 3.75 (s, 3H), 6.80 (d, J = 7.8 Hz, 1H), 6.90 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.32-7.39 (m, 2H), 7.51 (d, J = 1.8 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.81 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.13, 25.87, 52.75, 108.25, 120.92, 122.21, 123.67, 128.06, 128.23, 129.07, 130.23, 130.72, 131.08, 132.46, 126.94, 128.67, 129.62, 130.04, 130.14, 130.36, 131.19, 131.62, 133.40, 140.28, 143.36, 166.39, 167.75; ESIMS m/z 388 [M+H]⁺, 390 [M+H+2]⁺, 392 [M+H+4]⁺. Anal. Calcd for C₂₀H₁₅Cl₂NO₃: C, 61.87; H, 3.89; N, 3.61. Found: C, 61.93; H, 3.49.

(E)-Methyl 3-(3,4-dichlorophenyl)-2-((Z)-(1-methyl-2-oxindolin-3-ylidene)methyl)acrylate (3g-ZE): 41%; yellow solid, mp 140-141 °C; IR (KBr) 1709, 1610, 1470, 1378, 1249, 1130 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.22 (s, 3H), 3.82 (s, 3H), 6.83 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 7.22 (dd, J = 8.4 and 2.1 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H), 7.62 (d, J = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.87, 52.42, 108.25, 120.34, 122.13, 122.15, 126.58, 129.50, 130.17, 130.51, 130.57, 131.38, 132.06, 132.90, 133.71, 134.95, 139.02, 143.65, 166.06, 167.01; ESIMS m/z 388 [M+H]⁺, 390 [M+H+2]⁺, 392 [M+H+4]⁺. Anal. Calcd for C₂₀H₁₅Cl₂NO₃: C, 61.87; H, 3.89; N, 3.61. Found: C, 62.15; H, 3.99; N, 3.72.
(E)-Methyl 3-(2,4-dichlorophenyl)-2-((E)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3h-EE): 46%; yellow solid, mp 154-155 °C; IR (KBr) 1713, 1609, 1468, 1376, 1246, 1102 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.23 (s, 3H), 3.79 (s, 3H), 6.76 (d, J = 7.8 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 7.09 (dd, J = 8.4 and 2.1 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 2.1 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.08, 52.75, 108.11, 120.85, 122.08, 123.79, 127.16, 128.15, 129.75, 130.02, 130.51, 130.57, 130.66, 131.18, 131.57, 134.95, 136.35, 139.29, 144.17, 166.35, 167.32; ESIMS m/z 388 [M+H]+, 390 [M+H+2]+, 392 [M+H+4]+.

(E)-Methyl 3-(2,4-dichlorophenyl)-2-((Z)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3h-ZE): 41%; yellow solid, mp 140-141 °C; IR (KBr) 1724, 1708, 1610, 1470, 1382, 1247, 1093 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.23 (s, 3H), 3.85 (s, 3H), 6.83 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 7.18 (dd, J = 8.4 and 1.8 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.87, 52.43, 108.20, 120.36, 122.06, 122.22, 126.70, 126.86, 129.78, 130.12, 131.27, 131.33, 131.79, 132.78, 135.51, 136.00, 143.60, 166.06, 167.04; ESIMS m/z 388 [M+H]+.

Anal. Calcd for C₂₀H₁₅Cl₂NO₃: C, 61.87; H, 3.89; N, 3.61. Found: C, 62.15; H, 4.09; N, 3.75.

(E)-Methyl 3-(3-methoxyphenyl)-2-((E)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3i-EE): 50%; yellow solid, mp 112-114 °C; IR (KBr) 1709, 1609, 1468, 1375, 1236 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.26 (s, 3H), 3.73 (s, 3H), 3.74 (s, 3H), 6.79 (d, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 7.18 (dd, J = 8.4 and 1.8 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.09, 52.56, 55.21, 108.01, 121.32, 122.12, 123.37, 123.79, 126.43, 129.67, 129.70, 129.80, 130.48, 135.49, 143.60, 144.05, 159.51, 166.99, 167.51; ESIMS m/z 350 [M+H]+.

Anal. Calcd for C₂₁H₁₉NO₄: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.01; H, 5.32; N, 4.17.

(E)-Methyl 3-(3-methoxyphenyl)-2-((Z)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3i-ZE): 39%; yellow solid, mp 110-111 °C; IR (KBr) 1707, 1610, 1470, 1336, 1240, 1092 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.23 (s, 3H), 3.75 (s, 3H), 3.83 (s, 3H), 6.83 (d, J = 7.8 Hz, 1H), 6.91-6.96 (m, 2H), 6.99 (d, J = 7.8 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.28-7.35 (m, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 25.83, 52.25, 55.21, 108.01, 115.42, 115.60, 121.32, 122.12, 123.37, 123.79, 126.43, 129.67, 129.70, 129.80, 130.48, 135.49, 143.95, 144.05, 159.51, 166.99, 167.51; ESIMS m/z 350 [M+H]+.
(E)-Methyl 3-(2,6-difluorophenyl)-2-((E)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3j-EE): 43%; yellow solid, mp 152-154 ºC; IR (KBr) 1714, 1610, 1468, 1375, 1253, 1004 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.18 (s, 3H), 3.81 (s, 3H), 6.69 (d, \(J = 7.8\) Hz, 1H), 6.75-6.84 (m, 2H), 6.88 (t, \(J = 7.8\) Hz, 1H), 7.13-7.24 (m, 3H), 7.43 (dd, \(J_{FH} = 4.2\) Hz and \(J = 2.1\) Hz, 1H), 7.84 (d, \(J = 2.1\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 26.00, 52.71, 107.86, 111.70 (dd, \(J = 22.7\) and 2.6 Hz), 112.43 (t, \(J = 18.0\) Hz), 120.79, 121.86, 123.53, 129.17 (t, \(J = 2.0\) Hz), 129.41 (t, \(J = 2.0\) Hz), 129.75, 131.19, 131.27 (t, \(J = 10.3\) Hz), 131.96 (t, \(J = 1.7\) Hz), 144.05, 159.93 (dd, \(J = 251.9\) and 6.9 Hz), 165.93, 167.49; ESIMS \(m/z\) 356 [M+H]\(^+\). Anal. Calcd for C\(_{20}\)H\(_{15}\)F\(_2\)NO\(_3\): C, 67.60; H, 4.25; N, 3.94. Found: C, 67.69; H, 4.45; N, 3.82.

For the through-space coupling between the fluoride atom and the vinyl proton, see: J.-C. Hierso, *Chem. Rev.* 2014, 114, 4838-4867.

(E)-Methyl 3-(2,6-difluorophenyl)-2-((Z)-(1-methyl-2-oxoindolin-3-ylidene)methyl)acrylate (3j-ZE): 40%; yellow solid, mp 70-72 ºC; IR (KBr) 1707, 1611, 1462, 1257, 1093, 1002 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.18 (s, 3H), 3.85 (s, 3H), 6.77 (d, \(J = 7.8\) Hz, 1H), 6.87-6.95 (m, 2H), 6.96-7.03 (m, 2H), 7.25-7.35 (m, 2H), 7.39 (d, \(J = 7.2\) Hz, 1H), 7.56 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 25.80, 52.41, 108.01, 111.61 (dd, \(J = 22.9\) and 2.3 Hz), 112.58 (t, \(J = 18.3\) Hz), 120.23, 121.83, 122.53, 126.97 (t, \(J = 1.7\) Hz), 129.46, 129.89, 130.09, 131.09 (t, \(J = 10.4\) Hz), 133.35, 143.63, 161.16 (dd, \(J = 252.5\) and 6.9 Hz), 165.80, 166.56; ESIMS \(m/z\) 356 [M+H]\(^+\). Anal. Calcd for C\(_{20}\)H\(_{15}\)F\(_2\)NO\(_3\): C, 67.60; H, 4.25; N, 3.94. Found: C, 67.92; H, 4.50; N, 4.15.
A mixture of MBH bromide 1f (299 mg, 1.2 mmol) and PPh₃ (314 mg, 1.2 mmol) in CH₃CN (3.0 mL) was stirred at room temperature for 2 h. The corresponding phosphonium salt, monitored by TLC, was formed quantitatively. To the reaction mixture isatin 2a (161 mg, 1.0 mmol) and K₂CO₃ (322 mg, 2.0 mmol) were added, and the reaction mixture was stirred at room temperature for 8 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/Et₂O, 3:1), compound 3k-EE (119 mg, 38%) was obtained as yellow oil. This compound 3k-EE was contaminated with unidentified impurity (ca.10%, based on ¹H NMR), and the spectroscopic data of crude 3k-EE are as follows. Although 3k-EE was somewhat impure the palladium-catalyzed arylative cyclization was examined in benzene; however, a severe decomposition was observed.

(E)-Methyl 2-(((E)-(1-methyl-2-oxoindolin-3-ylidene)methyl)oct-2-enoate (3k-EE): 38%; yellow oil; IR (film) 2954, 1601, 1610, 1469, 1336, 1249 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.82 (t, J = 6.9 Hz, 3H), 1.18-1.24 (m, 4H), 1.40-1.45 (m, 2H), 2.15 (apparent q, J = 7.8 Hz, 2H), 3.25 (s, 3H), 3.73 (s, 3H), 6.80 (d, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 7.15 (td, J = 7.8 and 1.5 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H); ESIMS m/z 314 [M+H]⁺.
3. Optimization of Pd-catalyzed arylative cyclization of 3a-ZE

We selected 3a-ZE as a model compound and examined the palladium-catalyzed synthesis of spirooxindole 4a by arylative cyclization with benzene and iodobenzene, as shown in Table 1. The reaction of 3a-ZE and benzene (50 equiv) in the presence of Pd(OAc)$_2$ (5 mol%)/AgOAc (2.0 equiv)/PivOH (6.0 equiv) afforded a low yield (28%) of product 4a (entry 1). The use of an excess amount of AgOAc (4.0 equiv) gave 4a in an improved yield (65%, entry 2) along with 5a (11%). The yield of 4a decreased to 40% (entry 3) in the presence of lesser amount of benzene (30 equiv). The use of Pd(TFA)$_2$ as a catalyst (entry 4) was equally effective as compared to that of Pd(OAc)$_2$. The use of Ag$_2$CO$_3$ (entry 5) and AcOH (entry 6) were less effective. In order to compare the reactivity under the typical Mizoroki–Heck conditions, the reaction with iodobenzene was examined (entry 7).[2a] However, compound 4a was not formed in any trace amount. In addition, the reaction under the conditions of Chen and co-workers employing AgOAc in acetic acid (entry 8) was not effective.[2b] Thus, we selected the condition of entry 2 as an optimized one.

![Reaction scheme](https://example.com/react_scheme.png)

**Table 1. Optimization of Pd-catalyzed arylative cyclization of 3a-ZE.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>4a (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>Pd(OAc)$_2$ (5 mol%), AgOAc (2.0 equiv), PivOH (6.0 equiv), benzene (50 equiv), reflux, 30 h</td>
<td>28$^a$</td>
</tr>
<tr>
<td>2$^a$</td>
<td>Pd(OAc)$_2$ (5 mol%), AgOAc (4.0 equiv), PivOH (6.0 equiv), benzene (50 equiv), reflux, 30 h</td>
<td>65</td>
</tr>
<tr>
<td>3$^a$</td>
<td>Pd(OAc)$_2$ (5 mol%), AgOAc (4.0 equiv), PivOH (6.0 equiv), benzene (30 equiv), reflux, 30 h</td>
<td>40$^a$</td>
</tr>
<tr>
<td>4$^a$</td>
<td>Pd(TFA)$_2$ (5 mol%), AgOAc (4.0 equiv), PivOH (6.0 equiv), benzene (50 equiv), reflux, 30 h</td>
<td>66$^a$</td>
</tr>
<tr>
<td>5$^a$</td>
<td>Pd(OAc)$_2$ (5 mol%), Ag$_2$CO$_3$ (4.0 equiv), PivOH (6.0 equiv), benzene (50 equiv), reflux, 30 h</td>
<td>21$^a$</td>
</tr>
<tr>
<td>6$^a$</td>
<td>Pd(OAc)$_2$ (5 mol%), AgOAc (4.0 equiv), AcOH (6.0 equiv), benzene (50 equiv), reflux, 30 h</td>
<td>52$^a$</td>
</tr>
<tr>
<td>7$^a$</td>
<td>Pd(OAc)$_2$ (10 mol%), P(o-tol)$_3$, NaHCO$_3$ (2.5 equiv), TBAB (1.0 equiv), PhI (3.0 equiv), DMF, 130 °C, 20 h</td>
<td>0$^e$</td>
</tr>
<tr>
<td>8$^a$</td>
<td>Pd(OAc)$_2$ (20 mol%), AgOAc (4.0 equiv), PhI (3.0 equiv), AcOH (50 equiv), 120 °C, 60 h</td>
<td>&lt;10$^f$</td>
</tr>
</tbody>
</table>

$^a$ Substrate 3a-ZE (0.3 mmol) was used.
$^b$ Isolated yield.
$^c$ 5a was not isolated.
$^d$ Substrate 3a-EE (0.3 mmol) was used.
$^e$ Severe decomposition.
$^f$ Estimated roughly based on TLC observation.
4. Isomerization of C<sub>a</sub>=C<sub>b</sub> double bond of 3a

We examined the isomerization between 3a-EE and 3a-ZE under various conditions (Table 2). The double bond stereochemistry of 3a-EE and 3a-ZE in refluxing benzene even in the presence of AgOAc (entries 1-4) was not isomerized. The isomerization proceeded slowly in the presence of PivOH (entries 5 and 6). The isomerization progress was monitored by 1H NMR with 3a-EE and 3a-ZE in benzene-d<sub>6</sub> (entries 7-10) in the presence of Pd(OAc)<sub>2</sub> (5 mol%). 3a-EE was changed to a 3:1 (3a-EE/3a-ZE) mixture after 18 h (entry 8). Similarly, 3a-ZE was also changed to a 3:1 (3a-EE/3a-ZE) mixture after 18 h (entry 10). Actually, the isomerization of 3a-ZE was faster than that of 3a-EE (entry 7 versus entry 9). It is interesting to note that the isomerization was faster under the standard palladium-catalyzed arylative cyclization condition employing Pd(OAc)<sub>2</sub>/AgOAc/PivOH (entries 11 and 12), as compared to the isomerization in the presence of Pd(OAc)<sub>2</sub> only (entries 7-10). The spectra of the isomerization progress in benzene-d<sub>6</sub> in the presence of Pd(OAc)<sub>2</sub> over time are shown in the next page.

![Diagram](https://via.placeholder.com/150)

**Table 2. Isomerization of C<sub>a</sub>=C<sub>b</sub> double bond of 3a.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Ratio (3a-EE:3a-ZE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a-EE, benzene, 80 °C, 12 h</td>
<td>(100:0)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>3a-ZE, benzene, 80 °C, 12 h</td>
<td>(0:100)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>3a-EE, AgOAc (4.0 equiv), benzene, 80 °C, 12 h</td>
<td>(100:0)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>3a-ZE, AgOAc (4.0 equiv), benzene, 80 °C, 12 h</td>
<td>(0:100)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>3a-EE, PivOH (6.0 equiv), benzene, 80 °C, 12 h</td>
<td>(20:1)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>3a-ZE, PivOH (6.0 equiv), benzene, 80 °C, 12 h</td>
<td>(1:10)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>3a-EE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), benzene-d&lt;sub&gt;6&lt;/sub&gt;, 80 °C, 8 h</td>
<td>(5:1)&lt;sup&gt;[b]&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>3a-EE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), benzene-d&lt;sub&gt;6&lt;/sub&gt;, 80 °C, 18 h</td>
<td>(3:1)&lt;sup&gt;[b]&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>3a-ZE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), benzene-d&lt;sub&gt;6&lt;/sub&gt;, 80 °C, 8 h</td>
<td>(1:1)&lt;sup&gt;[b]&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>3a-ZE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), benzene-d&lt;sub&gt;6&lt;/sub&gt;, 80 °C, 18 h</td>
<td>(3:1)&lt;sup&gt;[b]&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>3a-EE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), AgOAc (4.0 equiv) PivOH (6.0 equiv), benzene, 80 °C, 1 h</td>
<td>(3:1)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>3a-ZE, Pd(OAc)&lt;sub&gt;2&lt;/sub&gt; (5 mol%), AgOAc (4.0 equiv) PivOH (6.0 equiv), benzene, 80 °C, 1 h</td>
<td>(3:1)&lt;sup&gt;[a]&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>[a]</sup> Estimated roughly based on TLC observation.  
<sup>[b]</sup> Determined by 1H NMR.
5. Pd-catalyzed isomerization of 3a-EE and 3a-ZE (Entries 7-10 in Table 2)

Conditions (ii-v): Pd(OAc)$_2$ (5 mol%), benzene-$d_6$, 80 °C.
(i) 3a-EE (300 MHz), (ii) 3a-EE, 8 h (600 MHz), (iii) 3a-EE, 18 h (600 MHz), (iv) 3a-ZE, 18 h (600 MHz), (v) 3a-ZE, 8 h (600 MHz), (vi) 3a-ZE (300 MHz).

(i)

(ii)

3a-EE:3a-ZE = 5:1

(iii)

3a-EE:3a-ZE = 3:1

(iv)

3a-EE:3a-ZE = 3:1

(v)

3a-EE:3a-ZE = 1:1

(vi)
6. Synthesis of spirooxindoles

Typical procedure for the synthesis of spirooxindoles 4a and 5a

A mixture of 3a-EE (96 mg, 0.3 mmol), Pd(OAc)$_2$ (3 mg, 5 mol%), AgOAc (201 mg, 4.0 equiv), and PivOH (184 mg, 6.0 equiv) in benzene (1.17 g, 50 equiv) was heated to reflux for 30 h under N$_2$ balloon atmosphere. After the usual aqueous extractive workup with EtOAc and column chromatographic purification process (hexanes/Et$_2$O, 4:1), the spirooxindoles 4a (76 mg, 64%) and 5a (12 mg, 10%) were isolated as white solids. Other compounds were synthesized similarly, and the spectroscopic data of 4a-o, 4c'-n' and 5a-j are as follows.

(1'S,4'S)-Methyl 1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4a): 64%; white solid, mp 200-201 °C; IR (KBr) 1718, 1609, 1491, 1342, 1285, 1079 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 3.37 (s, 3H), 3.62 (s, 3H), 5.27 (s, 1H), 6.55 (dd, $J$ = 7.8 and 0.9 Hz, 1H), 6.69 (d, $J$ = 1.2 Hz, 1H), 6.95-7.20 (m, 7H), 7.28-7.35 (m, 2H), 7.38 (td, $J$ = 7.8 and 1.2 Hz, 1H), 7.75 (dd, $J$ = 8.4 and 1.2 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 26.93, 45.10, 51.79, 55.44, 108.36, 123.58, 125.06, 126.47, 126.88, 126.95, 128.07, 128.37, 129.07, 129.53, 129.98, 131.05, 133.33, 133.60, 135.10, 137.92, 143.48, 143.56, 166.21, 176.32; ESIMS $m/z$ 396 [M+H]$^+$. Anal. Calcd for C$_{26}$H$_{21}$NO$_3$: C, 78.97; H, 5.35; N, 3.54. Found: C, 79.11; H, 5.39; N, 3.20.

(1'S,4'R)-Methyl 1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (5a): 10%; white solid, mp 150-152 °C; IR (KBr) 1721, 1608, 1491, 1284, 1079 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 3.35 (s, 3H), 3.59 (s, 3H), 5.33 (s, 1H), 6.61 (dd, $J$ = 7.8 and 1.2 Hz, 1H), 6.73 (d, $J$ = 1.8 Hz, 1H), 6.99-7.04 (m, 2H), 7.09-7.25 (m, 5H), 7.30-7.43 (m, 5H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 26.91, 44.19, 51.73, 55.54, 108.60, 123.58, 125.06, 126.47, 126.88, 126.95, 128.37, 129.07, 129.53, 129.98, 131.05, 133.33, 133.60, 135.10, 137.92, 143.48, 143.56, 166.21, 176.32; ESIMS $m/z$ 396 [M+H]$^+$. Anal. Calcd for C$_{26}$H$_{21}$NO$_3$: C, 78.97; H, 5.35; N, 3.54. Found: C, 78.84; H, 5.52; N, 3.40.
(1'S,4'R)-Methyl 4'-[(3,5-dimethylphenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4b): 55%; white solid, mp 205-206 °C; IR (KBr) 1721, 1609, 1470, 1341, 1227, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.31 (s, 6H), 3.37 (s, 3H), 3.63 (s, 3H), 5.18 (s, 1H), 6.54 (dd, J = 7.8 and 1.2 Hz, 1H), 6.68 (d, J = 1.2 Hz, 1H), 6.82 (s, 1H), 6.93-7.01 (m, 3H), 7.06 (td, J = 7.5 and 0.9 Hz, 1H), 7.11 (td, J = 7.2 and 1.2 Hz, 1H), 7.18-7.21 (m, 1H), 7.36 (s, 2H), 7.37 (td, J = 7.8 and 1.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 21.39, 26.96, 44.90, 51.77, 55.43, 108.30, 109.72, 123.52, 125.06, 126.75, 126.97, 127.33, 128.01, 128.27, 128.99, 129.87, 130.93, 133.36, 135.29, 137.60, 138.12, 143.38, 143.46, 166.29, 176.34; ESIMS m/z 424 [M+H]⁺. Anal. Calcd for C₂₈H₂₅NO₃: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.45; H, 6.27; N, 3.18.

(1'S,4'R)-Methyl 4'-[(3,5-dimethylphenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (5b): 16%; white solid, mp 178-179 °C; IR (KBr) 1722, 1608, 1469, 1342, 1283, 1228, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.31 (s, 6H), 3.35 (s, 3H), 3.61 (s, 3H), 5.24 (s, 1H), 6.59 (dd, J = 7.8 and 1.5 Hz, 1H), 6.74 (d, J = 1.5 Hz, 1H), 6.85 (s, 1H), 6.98 (s, 2H), 6.99-7.04 (m, 2H), 7.18-7.23 (m, 2H), 7.39 (td, J = 7.8 and 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 21.39, 26.90, 44.04, 51.76, 55.60, 108.60, 123.52, 125.11, 126.43, 126.60, 127.03, 128.00, 128.40, 129.09, 130.18, 130.78, 133.45, 133.77, 133.96, 137.81, 143.74, 143.97, 166.23, 177.18, one carbon was overlapped; ESIMS m/z 424 [M+H]⁺.

(1'S,4'R)-Methyl 1,6',7'-trimethyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4c): 45%; white solid, mp 228-229 °C; IR (KBr) 1720, 1657, 1469, 1341, 1285, 1232 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.00 (s, 3H), 2.07 (s, 3H), 3.37 (s, 3H), 3.61 (s, 3H), 5.19 (s, 1H), 6.28 (s, 1H), 6.66 (d, J = 1.2 Hz, 1H), 6.92 (s, 1H), 6.94-6.98 (m, 1H), 7.00 (d, J = 7.8 Hz, 1H), 7.07 (td, J = 7.5 and 0.9 Hz, 1H), 7.15-7.20 (m, 1H), 7.28-7.34 (m, 2H), 7.38 (td, J = 7.8 and 1.5 Hz, 1H), 7.75 (dd, J = 7.8 and 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 19.32, 19.49, 26.92, 44.74, 51.73, 55.20, 108.30, 123.52, 125.05, 126.32, 127.43, 128.28, 128.33, 128.91, 129.48, 130.72, 133.46, 133.83, 135.18, 135.35, 135.48, 136.79, 143.48, 143.84, 166.34, 176.58; ESIMS m/z 424 [M+H]⁺. Anal. Calcd for C₂₈H₂₅NO₃: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.68; H, 6.24; N, 3.17.
(1'S,4'S)-Methyl 4'- (3,4-dimethylphenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4c'): 24%; white solid, mp 208-209 °C; IR (KBr) 1721, 1610, 1490, 1341, 1284, 1225, 1078 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.20 (s, 3H), 2.25 (s, 3H), 3.37 (s, 3H), 3.63 (s, 3H), 5.20 (s, 1H), 6.54 (dd, J = 7.8 and 1.2 Hz, 1H), 6.67 (d, J = 1.2 Hz, 1H), 6.94-7.01 (m, 3H), 7.03-7.09 (m, 2H), 7.11 (dt, J = 7.2 and 1.5 Hz, 1H), 7.19 (dt, J = 7.8 and 0.9 Hz, 1H), 7.37 (td, J = 7.5 and 1.2 Hz, 1H), 7.46 (dd, J = 7.8 and 1.8 Hz, 1H), 7.53 (s, 1H), ¹³C NMR (CDCl₃, 125 MHz) δ 19.40, 19.90, 26.94, 44.66, 51.77, 55.44, 108.30, 123.53, 125.07, 126.71, 126.81, 126.95, 128.05, 128.99, 129.58, 129.88, 130.71, 130.99, 133.31, 133.49, 134.59, 135.28, 136.42, 138.29, 141.02, 143.48, 166.32, 176.32; ESIMS m/z 424 [M+H]⁺. Anal. Calcd for C₂₈H₂₅NO₃: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.57; H, 5.75; N, 3.02.

(1'S,4'S)-Methyl 6',7'-dichloro-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4d): 44%; white solid, mp 234-236 °C; IR (KBr) 1720, 1609, 1470, 1341, 1222, 1083 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.62 (s, 3H), 5.19 (s, 1H), 6.63 (d, J = 1.2 Hz, 1H), 6.93-6.96 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.10 (td, J = 7.5 and 0.9 Hz, 1H), 7.19-7.25 (m, 1H), 7.26 (s, 1H), 7.31-7.38 (m, 2H), 7.42 (td, J = 7.8 and 1.2 Hz, 1H), 7.72 (dd, J = 8.1 and 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.09, 44.61, 51.94, 54.91, 108.77, 123.92, 125.02, 126.98, 128.67, 128.70, 129.42, 129.63, 131.01, 131.39, 131.62, 132.23, 132.78, 133.10, 133.94, 138.32, 142.33, 143.31, 165.78, 175.39; ESIMS m/z 464 [M+H]⁺, 466 [M+H+2]⁺, 468 [M+H+4]⁺. Anal. Calcd for C₂₆H₁₉Cl₂NO₃: C, 67.25; H, 4.12; N, 3.02. Found: C, 67.58; H, 4.40; N, 2.71.

(1'S,4'S)-Methyl 4'- (3,4-dichlorophenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4d'): 48%; white solid, mp 246-248 °C; IR (KBr) 1720, 1610, 1489, 1343, 1284, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.66 (s, 3H), 5.22 (s, 1H), 6.55 (d, J = 7.5 Hz, 1H), 6.74 (s, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.99-7.18 (m, 5H), 7.37 (d, J = 8.1 Hz, 1H), 7.40 (td, J = 7.8 and 1.5 Hz, 1H), 7.65 (dd, J = 8.1 and 2.4 Hz, 1H), 7.97 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 27.05, 44.34, 51.97, 55.47, 108.49, 123.70, 125.05, 127.22, 127.35, 128.29, 129.01, 129.25, 129.77, 130.59, 131.22, 131.65, 132.24, 132.49, 134.71, 134.74, 136.78, 143.52, 143.86, 165.83, 176.02; ESIMS m/z 464 [M+H]⁺, 466 [M+H+2]⁺, 468 [M+H+4]⁺. Anal. Calcd for C₂₆H₁₀Cl₂NO₃: C, 67.25; H, 4.12; N, 3.02. Found: C, 67.19; H, 4.01; N, 3.18.
(1'S,4'S)-Methyl 6',7'-dibromo-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4e): 46%; white solid, mp 236-238 °C; IR (KBr) 1720, 1609, 1469, 1339, 1221, 1081 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.61 (s, 3H), 5.17 (s, 1H), 6.64 (d, J = 0.9 Hz, 1H), 6.78 (s, 1H), 6.95 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.31-7.44 (m, 4H), 7.72 (dd, J = 8.4 and 1.5 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.10, 44.58, 51.93, 54.89, 108.78, 123.13, 123.94, 124.47, 125.02, 126.98, 128.67, 129.43, 129.63, 131.88, 132.31, 132.72, 133.13, 133.88, 134.86, 135.74, 143.31, 165.74, 175.31; ESIMS m/z 552 [M+H]+, 554 [M+H+2]+, 556 [M+H+4]+. Anal. Calcd for C₂₆H₁₉Br₂NO₃: C, 56.45; H, 3.46; N, 2.53. Found: C, 56.80; H, 3.69; N, 2.41.

(1'S,4'S)-Methyl 4'-(3,4-dibromophenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4e'): 24%; white solid, mp 242-244 °C; IR (KBr) 1720, 1610, 1469, 1343, 1285, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.66 (s, 3H), 5.20 (s, 1H), 6.55 (d, J = 8.1 Hz, 1H), 6.74 (s, J = 0.9 Hz, 1H), 6.99-7.18 (m, 5H), 7.39 (td, J = 7.8 and 1.5 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.63 (dd, J = 8.4 and 2.4 Hz, 1H), 8.13 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.07, 44.32, 51.98, 55.48, 108.49, 122.82, 123.69, 124.59, 125.05, 127.25, 127.37, 128.30, 129.25, 129.79, 129.91, 131.23, 132.44, 133.56, 134.76, 134.87, 136.72, 144.66, 165.82, 175.97; one carbon was overlapped; ESIMS m/z 552 [M+H]+, 554 [M+H+2]+, 556 [M+H+4]+. Anal. Calcd for C₂₆H₁₉Br₂NO₃: C, 56.45; H, 3.46; N, 2.53. Found: C, 56.73; H, 3.68; N, 2.70.

(1'S,4'S)-Methyl 4'-(3,5-dichlorophenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4f): 37%; white solid, mp 234-235 °C; IR (KBr) 1720, 1610, 1433, 1343, 1287, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.67 (s, 3H), 5.21 (s, 1H), 6.56 (d, J = 7.5 Hz, 1H), 6.76 (d, J = 0.9 Hz, 1H), 6.94 (dd, J = 7.5 and 0.9 Hz, 1H), 6.99-7.10 (m, 3H), 7.14-7.19 (m, 3H), 7.40 (td, J = 7.8 and 1.2 Hz, 1H), 7.78 (d, J = 2.1 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.10, 44.65, 51.99, 55.46, 108.48, 123.66, 125.03, 126.85, 127.33, 127.43, 128.20, 128.30, 129.25, 129.72, 131.25, 132.23, 134.68, 134.71, 135.06, 136.45, 143.54, 146.85, 165.72, 175.86; ESIMS m/z 464 [M+H]+, 466 [M+H+2]+, 468 [M+H+4]+. Anal. Calcd for C₂₆H₁₉Cl₂NO₃: C, 67.25; H, 4.12; N, 3.02. Found: C, 67.49; H, 4.30; N, 3.03.
(1'S,4'S)-Methyl 5-chloro-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4h): 62%; white solid, mp 210-211 °C; IR (KBr) 1721, 1607, 1490, 1337, 1285, 1073 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.36 (s, 3H), 3.65 (s, 3H), 5.27 (s, 1H), 6.56 (dd, \(J = 7.8\) and 1.2 Hz, 1H), 6.67 (d, \(J = 1.5\) Hz, 1H), 6.94 (d, \(J = 8.4\) Hz, 1H), 6.96 (d, \(J = 1.8\) Hz, 1H), 7.03 (td, \(J = 8.1\) and 1.5 Hz, 1H), 7.12-7.22 (m, 3H), 7.29-7.38 (m, 3H), 7.74 (dd, \(J = 8.4\) and 1.2 Hz, 2H); \(^1^3\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 27.06, 45.05, 51.89, 55.47, 109.35, 125.54, 126.56, 126.84, 127.03, 128.34, 128.42, 128.91, 129.09, 129.51, 130.13, 130.33, 132.68, 133.84, 136.52, 137.91, 142.07, 143.31, 166.02, 175.88; ESIMS m/z 430 [M+H]\(^+\), 432 [M+H+2]\(^+\). Anal. Calcd for C\(_{26}\)H\(_{20}\)ClNO\(_3\): C, 72.64; H, 4.69; N, 3.26. Found: C, 72.51; H, 4.43; N, 3.39.

(1'S,4'R)-Methyl 5-chloro-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (5h): 17%; white solid, mp 164-165 °C; IR (KBr) 1724, 1606, 1489, 1337, 1285, 1228, 1072 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.34 (s, 3H), 3.61 (s, 3H), 5.33 (d, \(J = 1.5\) Hz, 1H), 6.60 (dd, \(J = 7.5\) and 1.2 Hz, 1H), 6.70 (d, \(J = 1.5\) Hz, 1H), 6.95 (d, \(J = 8.4\) Hz, 1H), 7.02-7.08 (m, 1H), 7.12-7.18 (m, 3H), 7.20-7.26 (m, 1H), 7.32-7.40 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 27.05, 44.16, 51.83, 55.58, 109.55, 125.64, 126.51, 126.78, 127.30, 128.29, 128.63, 128.69, 128.88, 128.91, 129.15, 130.30, 130.50, 132.62, 134.45, 135.32, 137.63, 142.31, 143.92, 166.08, 176.52; ESIMS m/z 430 [M+H]\(^+\), 432 [M+H+2]\(^+\).

(1'S,4'S)-Methyl 5-methoxy-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4i): 67%; white solid, mp 118-120 °C; IR (KBr) 1715, 1601, 1496, 1347, 1284, 1230 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.34 (s, 3H), 3.63 (s, 3H), 3.73 (s, 3H), 5.27 (s, 1H), 6.57 (t, \(J = 1.5\) Hz, 1H), 6.58 (dd, \(J = 7.5\) and 1.2 Hz, 1H), 6.70 (d, \(J = 1.2\) Hz, 1H), 6.91 (apparent d, \(J = 1.5\) Hz, 2H), 7.00 (td, \(J = 8.1\) and 1.5 Hz, 1H), 7.12 (td, \(J = 7.8\) and 1.5 Hz, 1H), 7.15-7.21 (m, 2H), 7.29-7.34 (m, 2H), 7.77 (dd, \(J = 8.1\) and 1.2 Hz, 2H); \(^1^3\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 26.99, 45.09, 51.79, 55.76, 55.86, 108.81, 111.79, 113.86, 126.46, 126.90, 126.98, 128.06, 128.36, 129.55, 129.94, 131.03, 133.32, 133.62, 136.21, 136.89, 137.85, 143.53, 156.69, 166.21, 176.00; ESIMS m/z 426 [M+H]\(^+\). Anal. Calcd for C\(_{27}\)H\(_{23}\)NO\(_4\): C, 76.22; H, 5.45; N, 3.29. Found: C, 76.51; H, 5.64; N, 3.10.
(1'S,4'R)-Methyl 5-methoxy-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (5i): 14%; white solid, mp 156-158 °C; IR (KBr) 1721, 1600, 1497, 1347, 1284, 1230 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.32 (s, 3H), 3.60 (s, 3H), 3.74 (s, 3H), 5.34 (s, 1H), 6.63 (dd, \(J = 7.8\) and 1.5 Hz, 1H), 6.75 (d, \(J = 1.5\) Hz, 1H), 6.77 (t, \(J = 1.5\) Hz, 1H), 6.91 (apparent d, \(J = 1.5\) Hz, 2H), 7.00-7.06 (m, 1H), 7.13 (td, \(J = 7.8\) and 1.2 Hz, 1H), 7.16-7.24 (m, 2H), 7.28-7.39 (m, 4H); 13C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 26.99, 44.16, 51.76, 55.69, 55.97, 108.98, 112.19, 113.64, 126.63, 126.68, 127.19, 128.02, 128.52, 128.66, 130.29, 131.06, 133.71, 133.80, 135.02, 137.11, 137.52, 144.27, 156.62, 166.21, 176.73; ESIMS \(m/z\) 426 [M+H]\(^+\). Anal. Calcd for C\(_{27}\)H\(_{23}\)NO\(_4\): C, 76.22; H, 5.45; N, 3.29. Found: C, 76.19; H, 5.70; N, 3.25.

(1'S,4'R)-Methyl 1-acetyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4j): 71%; white solid, mp 200-201 °C; IR (KBr) 1762, 1719, 1475, 1269, 1229, 1163 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 2.74 (s, 3H), 3.65 (s, 3H), 5.30 (d, \(J = 1.2\) Hz, 1H), 6.62 (dd, \(J = 7.8\) and 1.5 Hz, 1H), 6.76 (d, \(J = 1.2\) Hz, 1H), 6.96 (dd, \(J = 7.5\) and 1.5 Hz, 1H), 7.02-7.07 (m, 1H), 7.13-7.24 (m, 4H), 7.38-7.37 (m, 2H), 7.44 (td, \(J = 7.8\) and 1.5 Hz, 1H), 7.68 (dd, \(J = 8.4\) and 0.9 Hz, 2H), 8.38 (dd, \(J = 8.4\) and 0.9 Hz, 1H); 13C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 26.74, 44.99, 51.97, 55.86, 116.79, 124.92, 126.20, 126.71, 127.11, 127.26, 128.50 (2C), 129.38, 129.39, 130.14, 131.09, 132.55, 133.82, 133.91, 137.65, 139.77, 143.21, 166.01, 171.15, 176.73; ESIMS \(m/z\) 424 [M+H]\(^+\). Anal. Calcd for C\(_{27}\)H\(_{21}\)NO\(_4\): C, 76.58; H, 5.00; N, 3.31. Found: C, 76.86; H, 5.24; N, 3.15.

(1'S,4'R)-Methyl 1-acetyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (5j): 4%; white solid, mp 184-185 °C; IR (KBr) 1763, 1719, 1462, 1269, 1231, 1163 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 2.69 (s, 3H), 3.61 (s, 3H), 5.32 (d, \(J = 1.8\) Hz, 1H), 6.65 (d, \(J = 1.8\) Hz, 1H), 6.78 (d, \(J = 1.8\) Hz, 1H), 7.03-7.09 (m, 1H), 7.15-7.17 (m, 2H), 7.42-7.48 (m, 1H), 8.40 (d, \(J = 8.4\) Hz, 1H); 13C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 26.66, 44.16, 51.89, 56.02, 116.96, 124.93, 126.23, 126.73, 126.80, 127.43, 128.43, 128.62, 128.76, 129.48, 130.59, 130.85, 132.29, 132.68, 134.51, 137.48, 140.09, 143.82, 166.02, 171.04, 177.23; ESIMS \(m/z\) 424 [M+H]\(^+\). Anal. Calcd for C\(_{27}\)H\(_{21}\)NO\(_4\): C, 76.58; H, 5.00; N, 3.31. Found: C, 76.86; H, 5.24; N, 3.15.

(1'S,4'S)-Methyl 1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-phenanthrene]-3'-carboxylate (4l): 57%; white solid, mp 221-222 °C; IR (KBr) 1715, 1609, 1470, 1343, 1252, 1078 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.41 (s, 3H), 3.46 (s, 3H), 5.32 (br s, 1H), 6.57-6.60 (m, 1H), 6.82 (s, 1H), 6.96-7.12 (m, 6H), 7.40 (t, \(J = 7.5\) Hz, 1H), 7.47 (t, \(J = 7.8\) Hz, 1H), 7.53 (t, \(J = 7.5\) Hz, 1H), 7.66-7.76 (m, 2H), 7.89 (d, \(J = 8.1\) Hz, 1H), 8.12 (d, \(J = 6.6\) Hz, 1H), 8.76 (d, \(J = 8.7\) Hz, 1H); 13C NMR (DMSO-d\(_6\), 75 MHz) \(\delta\) 26.87, 37.04, 51.67, 54.82, 109.39, 123.32, 124.29, 124.43, 125.56, 125.65, 126.47, 126.85, 126.97, 127.14, 127.87, 128.56, 129.23, 130.81, 131.65, 133.20, 133.62, 134.70, 134.70, 134.82, 166.02, 171.04, 177.23; ESIMS \(m/z\) 446 [M+H]+. Anal. Calcd for C\(_{30}\)H\(_{23}\)NO\(_3\): C, 80.88; H, 5.20; N, 3.14. Found: C, 80.63; H, 5.39; N, 3.02.
(1'S,4'S)-Methyl 1-methyl-4'-(naphthalen-1-yl)-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4I'): 14%; white solid, mp 215-217 °C; IR (KBr) 1720, 1609, 1469, 1343, 1285, 1228, 1078 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 3.28 (s, 3H), 3.36 (s, 3H), 6.19 (br s, 1H), 6.54-6.59 (m, 1H), 6.75 (d, J = 1.2 Hz, 1H), 6.91-6.95 (m, 1H), 6.97-7.03 (m, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.25-7.38 (m, 3H), 7.45-7.53 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 6.9 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 8.78 (br s, 1H); ¹³C NMR (DMSO-d₆, 80 °C, 125 MHz) δ 26.36, 38.21, 50.98, 54.76, 108.99, 122.97, 123.84, 123.99, 125.25, 125.27, 125.95, 126.15, 126.35, 126.65, 126.74, 127.34, 128.21, 128.32, 128.94, 130.55, 131.32, 133.09, 133.37, 133.50, 133.65, 137.86, 140.63, 143.69, 175.38; ESIMS m/z 446 [M+H]+. Anal. Calcd for C₃₀H₂₃NO₃: C, 80.88; H, 5.20; N, 3.14. Found: C, 81.05; H, 5.43; N, 3.27.

(1'S,4'S)-Methyl 4'-(2,4-dichlorophenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4m): 59%; white solid, mp 206-208 °C; IR (KBr) 1720, 1610, 1472, 1343, 1285, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.37 (s, 3H), 3.64 (s, 3H), 5.96 (s, 1H), 6.55 (dd, J = 7.8 and 1.2 Hz, 1H), 6.82 (d, J = 1.2 Hz, 1H), 6.95-7.04 (m, 3H), 7.08 (td, J = 7.5 and 0.9 Hz, 1H), 7.14 (dt, J = 7.2 and 1.5 Hz, 1H), 7.19 (dd, J = 8.7 and 2.1 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.40 (dt, J = 7.8 and 1.5 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.98, 39.46, 51.98, 55.36, 108.50, 123.77, 125.08, 127.08, 127.42, 128.05, 128.41, 128.89, 129.17, 129.23, 130.81, 132.27, 132.51, 132.57, 134.18, 134.74, 135.29, 137.18, 140.53, 143.41, 165.74, 176.33; ESIMS m/z 464 [M+H]+, 466 [M+H+2]+, 468 [M+H+4]+. Anal. Calcd for C₂₆H₁₉Cl₂NO₃: C, 67.25; H, 4.12; N, 3.02. Found: C, 67.24; H, 4.39; N, 3.17.

(1'S,4'R)-Methyl 5',7'-dichloro-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4m'): 8%; white solid, mp 252-253 °C; IR (KBr) 1721, 1608, 1491, 1342, 1275, 1075 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.36 (s, 3H), 3.64 (s, 3H), 5.47 (s, 1H), 5.62 (s, 1H), 6.53 (d, J = 0.9 Hz, 1H), 6.89 (dd, J = 7.5 and 0.9 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 7.09 (td, J = 7.5 and 0.9 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 1.8 Hz, 1H), 7.26-7.32 (m, 2H), 7.40 (td, J = 7.8 and 1.2 Hz, 1H), 7.80 (dd, J = 8.4 and 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 27.12, 42.99, 51.96, 55.87, 108.76, 123.97, 125.02, 125.98, 126.58, 127.79, 129.60, 129.83, 130.96, 131.71, 133.14, 133.84, 134.45, 134.75, 135.74, 135.83, 140.07, 143.03, 165.72, 175.41; ESIMS m/z 464 [M+H]+, 466 [M+H+2]+, 468 [M+H+4]+. Anal. Calcd for C₂₆H₁₉Cl₂NO₃: C, 67.25; H, 4.12; N, 3.02. Found: C, 67.29; H, 4.38; N, 2.75.
(1'S,4'S)-Methyl 4'-(3-methoxyphenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4n): 60%; white solid, mp 149-151 °C; IR (KBr) 1720, 1608, 1490, 1342, 1257, 1079 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.36 (s, 3H), 3.64 (s, 3H), 3.80 (s, 3H), 5.25 (s, 1H), 6.55 (dd, J = 8.1 and 1.2 Hz, 1H), 6.70 (d, J = 1.2 Hz, 1H), 6.73 (dd, J = 8.4, 2.4 and 0.9 Hz, 1H), 6.93-7.02 (m, 3H), 7.03 (m, 2H), 7.33 (d, J = 7.5 Hz, 1H), 7.38 (td, J = 7.8 and 1.2 Hz, 1H), 7.42 (t, J = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.94, 45.10, 51.80, 55.34, 55.42, 108.31, 112.68, 114.58, 121.95, 123.53, 125.05, 126.87, 126.98, 128.04, 129.04 (2C), 129.82, 131.04, 133.22, 133.70, 135.11, 137.79, 143.51, 145.07, 159.80, 166.21, 176.19; ESIMS m/z 426 [M+H]⁺. Anal. Calcd for C₂₇H₂₃NO₄: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.29; H, 5.73; N, 3.11.

(1'S,4'S)-Methyl 6'-methoxy-1-methyl-2-oxo-4'-phenyl-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4n'): 16%; white solid, mp 170-172 °C; IR (KBr) 1720, 1609, 1502, 1340, 1254, 1078 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.36 (s, 3H), 3.61 (s, 3H), 3.64 (s, 3H), 5.22 (s, 1H), 6.47 (d, J = 9.0 Hz, 1H), 6.58 (dd, J = 8.7 and 2.7 Hz, 1H), 6.66 (d, J = 2.7 Hz, 1H), 6.69 (d, J = 0.9 Hz, 1H), 6.95 (dd, J = 7.5 and 0.9 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 7.06 (td, J = 7.5 and 0.9 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.29-7.34 (m, 2H), 7.37 (td, J = 7.8 and 1.2 Hz, 1H), 7.76 (dd, J = 8.4 and 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.92, 45.47, 51.78, 55.02, 55.11, 108.33, 113.83, 114.00, 123.48, 123.54, 125.01, 126.50, 128.14, 128.43, 128.99, 129.43, 133.19, 133.87, 135.15, 139.33, 143.44, 158.95, 166.24, 176.50, one carbon was overlapped; ESIMS m/z 426 [M+H]⁺. Anal. Calcd for C₂₇H₂₃NO₄: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.29; H, 5.72; N, 3.25.

(1'S,4'S)-Methyl 4'-(2,6-difluorophenyl)-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (4o): 57%; white solid, mp 231-233 °C; IR (KBr) 1723, 1608, 1469, 1283, 1231, 1081 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.38 (s, 3H), 3.61 (s, 3H), 5.67 (d, J = 1.8 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H), 6.84 (d, J = 1.8 Hz, 1H), 6.85-6.92 (m, 3H), 6.97 (d, J = 7.8 Hz, 1H), 7.00 (dd, J = 7.8 and 1.2 Hz, 1H), 7.02-7.24 (m, 4H), 7.33 (td, J = 7.8 and 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 26.77, 33.39, 51.80, 55.37, 108.37, 111.46 (dd, J = 21.9 and 3.5 Hz), 120.09 (t, J = 16.4 Hz), 123.40, 124.97, 126.92, 127.60, 128.00, 128.62 (t, J = 10.1 Hz), 128.97, 129.08, 130.28, 131.68, 134.94, 135.33, 143.07, 161.35 (dd, J = 248.9 and 7.5 Hz), 165.91, 176.25, one carbon was overlapped; ESIMS m/z 432 [M+H]⁺. Anal. Calcd for C₂₆H₁₉F₂NO₃: C, 72.38; H, 4.44; N, 3.25. Found: C, 72.60; H, 4.71; N, 3.04.
Typical procedure for the synthesis of spirooxindoles 4g/4g’

A mixture of 3a-EE (96 mg, 0.3 mmol), Pd(OAc)_2 (3 mg, 5 mol%), AgOAc (201 mg, 4.0 equiv), and PivOH (184 mg, 6.0 equiv) in benzene-d_6 (1.26 g, 50 equiv) was heated to reflux for 72 h under N_2 balloon atmosphere. After the usual aqueous extractive workup with EtOAc and column chromatographic purification process (hexanes/Et_2O, 4:1), the spirooxindole 4g/4g’ was isolated as an inseparable mixture (80 mg, 67%). The ratio of 4g/4g’ was determined as 55:45 based on its ^1H NMR spectrum.

4g/4g’ (55:45 mixture): 67%; white solid; ^1H NMR (CDCl_3, 300 MHz) δ 3.37 (s, 3H), 3.62 (s, 3H), 5.27 (d, J = 1.2 Hz, 1H), 6.56 (dd, J = 7.8 and 1.2 Hz, 0.46H, 4g’-H_b), 6.70 (d, J = 1.2 Hz, 1H), 6.95-7.21 (m, 5H), 7.32 (t, J = 7.8 Hz, 1H), 7.38 (td, J = 7.8 and 1.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1.27H, 4g-H_a).

The ortho-protons (H_a) of the phenyl group at the 4’-position of 4g appeared at downfield (δ = 7.76 ppm) due to the anisotropy of the carbonyl group of ester. The proton (H_b) at the 5’-position of 4g’ appeared at quite upfield (δ = 6.56 ppm) due to the anisotropy of the phenyl ring at the 4’-position. These two characteristic peaks provided the information for the structure assignment.
A mixture of 8-EE (104 mg, 0.4 mmol), Pd(OAc)$_2$ (4 mg, 5 mol%), AgOAc (266 mg, 4.0 equiv), and PivOH (244 mg, 6.0 equiv) in benzene (1.55 g, 50 equiv) was heated to reflux for 40 h under N$_2$ balloon atmosphere. After the usual aqueous extractive workup with EtOAc and column chromatographic purification process (hexanes/Et$_2$O, 5:1), compound 9-E (28 mg, 21%), compound 9-Z (52 mg, 39%) and compound 10 (19 mg, 14%) were isolated as yellow solids, and the spectroscopic data of 9 and 10 as follows.

(E)-3-(3,3-Diphenylallylidene)-1-methylindolin-2-one (9-E): 21%; yellow solid, mp 166-168 °C; IR (KBr) 1699, 1602, 1468, 1375, 1335, 1103 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 3.24 (s, 3H), 6.84 (d, $J = 7.8$ Hz, 1H), 7.06 (td, $J = 7.8$ and 1.2 Hz, 1H), 7.25-7.32 (m, 3H), 7.36-7.48 (m, 9H), 7.53 (d, $J = 12.3$ Hz, 1H), 7.72 (d, $J = 7.2$ Hz, 1H); $^1$C NMR (CDCl$_3$, 75 MHz) δ 26.01, 108.04, 121.93, 122.41, 122.66, 123.60, 126.19, 128.40, 128.49, 128.68, 128.76, 128.86, 129.07, 130.91, 133.62, 138.09, 141.79, 143.63, 154.45, 168.60; ESIMS $m/z$ 338 [M+H]$^+$. 

(Z)-3-(3,3-Diphenylallylidene)-1-methylindolin-2-one (9-Z): 39%; yellow solid, mp 165-167 °C; IR (KBr) 1690, 1613, 1470, 1381, 1335, 1090 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 3.34 (s, 3H), 6.85 (d, $J = 7.8$ Hz, 1H), 7.00 (t, $J = 7.8$ Hz, 1H), 7.26-7.34 (m, 3H), 7.35-7.45 (m, 9H), 7.46-7.60 (m, 5H), 8.70 (d, $J = 12.0$ Hz, 1H); $^1$C NMR (CDCl$_3$, 75 MHz) δ 25.67, 107.78, 119.26, 121.58, 122.66, 123.60, 126.19, 128.40, 128.49, 128.68, 128.76, 128.86, 129.07, 130.91, 133.42, 138.49, 141.28, 142.31, 152.80, 167.50; ESIMS $m/z$ 338 [M+H]$^+$. 

3-(2,3-Diphenylallylidene)-1-methylindolin-2-one (10): 14%; yellow solid, mp 180-182 °C; IR (KBr) 1707, 1608, 1469, 1373, 1335, 1102 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 3.28 (s, 3H), 6.36 (d, $J = 7.5$ Hz, 1H), 6.61 (td, $J = 7.8$ and 1.2 Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 7.12 (td, $J = 7.8$ and 1.2 Hz, 1H), 7.21 (d, $J = 1.8$ Hz, 1H), 7.26-7.40 (m, 6H), 7.41-7.46 (m, 2H), 7.47-7.53 (m, 2H), 7.86 (d, $J = 1.8$ Hz, 1H); $^1$C NMR (CDCl$_3$, 75 MHz) δ 26.11, 107.59, 120.87, 121.66, 125.32, 127.62, 128.02, 128.39, 128.47, 128.89, 129.04, 130.04, 134.60, 136.51, 136.66, 136.74, 140.59, 143.92, 168.50, one carbon was overlapped; ESIMS $m/z$ 338 [M+H]$^+$. 

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7. Pd-catalyzed oxidative arylation of 8-EE

A mixture of 8-EE (104 mg, 0.4 mmol), Pd(OAc)$_2$ (4 mg, 5 mol%), AgOAc (266 mg, 4.0 equiv), and PivOH (244 mg, 6.0 equiv) in benzene (1.55 g, 50 equiv) was heated to reflux for 40 h under N$_2$ balloon atmosphere. After the usual aqueous extractive workup with EtOAc and column chromatographic purification process (hexanes/Et$_2$O, 5:1), compound 9-E (28 mg, 21%), compound 9-Z (52 mg, 39%) and compound 10 (19 mg, 14%) were isolated as yellow solids, and the spectroscopic data of 9 and 10 as follows.
8. Synthesis of 9-\textit{E} and 9-\textit{Z} by Knoevenagel condensation

\[
\text{N-methyloxindole (74 mg, 0.5 mmol) + \beta-phenylcinnamaldehyde (106 mg, 1.5 equiv) in aq. EtOH (1:1, 2 mL) + NaOH (27 mg, 2.0 equiv) \rightarrow 9-\textit{E} (66 mg, 58\%) + 9-\textit{Z} (42 mg, 37\%)}
\]

To a stirred solution of \textit{N}-methyloxindole (74 mg, 0.5 mmol) and \β-phenylcinnamaldehyde (106 mg, 1.5 equiv) in aq. EtOH (1:1, 2 mL) was added NaOH (27 mg, 2.0 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After the usual aqueous extractive workup with EtOAc and column chromatographic purification process (hexanes/EtO, 5:1), compound \textit{9-\textit{E}} (66 mg, 58\%) and compound \textit{9-\textit{Z}} (42 mg, 37\%) were isolated as yellow solids. These compounds \textit{9-\textit{E}} and \textit{9-\textit{Z}} were identical with the compounds obtained by the Pd-catalyzed arylation of \textit{8-EE}.

9. Thionation of \textit{4a}

\[
\text{4a + Lawesson's reagent (2.5 equiv) \rightarrow 11 (74 mg, 90\%)}
\]

To a stirred solution of \textit{4a} (79 mg, 0.2 mmol) in toluene (2.0 mL) was added Lawesson’s reagent (202 mg, 2.5 equiv) at room temperature, and the reaction mixture was heated to 100 °C for 24 h. After removal of toluene and column chromatographic purification process (hexanes/EtO, 3:1) compounds \textit{11} (74 mg, 90\%) was obtained as a white solid, and the spectroscopic data of \textit{11} are as follows.

(1'S,4'S)-Methyl 1-methyl-4'-phenyl-2-thioxo-4'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (\textit{11}): 90\%; white solid, mp 264-265 °C; IR (KBr) 1721, 1599, 1433, 1365, 1282, 1225, 1082 cm\textsuperscript{-1}; \textit{1}H NMR (CDCl\textsubscript{3}, 300 MHz) δ 3.59 (s, 3H), 3.79 (s, 3H), 5.23 (s, 1H), 6.47 (d, \textit{J} = 8.1 Hz, 1H), 6.54 (d, \textit{J} = 1.5 Hz, 1H), 6.93-7.00 (m, 2H), 7.06-7.24 (m, 5H), 7.29-7.35 (m, 2H), 7.39 (td, \textit{J} = 7.8 and 1.2 Hz, 1H), 7.82 (dd, \textit{J} = 8.4 and 1.2 Hz, 2H); \textit{13}C NMR (CDCl\textsubscript{3}, 75 MHz) δ 31.95, 44.45, 51.73, 64.91, 109.62, 125.08, 125.24, 126.50, 126.97, 127.14, 127.82, 128.27, 129.04, 129.85, 130.10, 131.78, 132.68, 133.81, 137.19, 139.25, 143.88, 144.47, 166.53, 207.05; ESIMS \textit{m/z} 412 [M+H]\textsuperscript{+}. Anal. Calcd for C\textsubscript{26}H\textsubscript{21}NO\textsubscript{2}S: C, 75.88; H, 5.14; N, 3.40. Found: C, 76.07; H, 5.36; N, 3.21.

23
10. Synthesis of 12 and 13

Typical procedure for the synthesis of 12

To a stirred solution of 4a (119 mg, 0.3 mmol) in aq. MeOH (1:1, 2.0 mL) was added KOH (25 mg, 1.5 equiv) at 0 °C, and the reaction mixture was heated to reflux for 5 h. The aqueous solution was then acidified using aqueous HCl (2 M) to pH 2 and extracted with CH2Cl2, dried over MgSO4, and concentrated under reduced pressure to obtain the corresponding carboxylic acid derivative. A mixture of this crude carboxylic acid derivative and PPA (0.5 mL) was heated to 60 °C for 6 h. The reaction mixture was allowed to cool to room temperature, quenched with water (20 mL), basified to pH 7 with aqueous NaHCO3, and extracted with CH2Cl2 (20 mL × 3). The combined organic layers were washed with brine, dried over MgSO4, and column chromatographic purification process (hexanes/Et2O, 2:1) afforded the spirooxindole 12 (92 mg, 84%) as a white solid, and the spectroscopic data of 12 are as follows.

**(1'S,11bR)-1'-Methylspiro[benzo[c]fluorene-5,3'-indoline]-2',7(11bH)-dione (12):** 84%; white solid, mp 200-201 °C; IR (KBr) 1712, 1665, 1607, 1489, 1348 cm⁻¹; ¹H NMR (CDCl3, 300 MHz) δ 3.42 (s, 3H), 5.25 (s, 1H), 6.95 (td, J = 7.8 and 1.2 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 7.00 (dd, J = 7.8 and 1.2 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 2.7 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.29 (td, J = 7.8 and 1.2 Hz, 1H), 7.36 (td, J = 7.8 and 1.2 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.79 (td, J = 7.5 and 1.2 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H); ¹³C NMR (CDCl3, 75 MHz) δ 26.80, 41.81, 56.60, 108.91, 123.43, 124.03, 124.03, 124.99, 142.17, 142.99, 149.33, 177.90, 190.28; ESIMS m/z 364 [M+H]⁺. Anal. Calcd for C25H17NO2: C, 82.63; H, 4.72; N, 3.85. Found: C, 82.54; H, 4.97; N, 3.64.
Typical procedure for the synthesis of 13

A mixture of 4a (119 mg, 0.3 mmol) and PPA (0.5 mL) was heated to 100 °C for 6 h. The reaction mixture was allowed to cool to room temperature, quenched with water (20 mL), basified to pH 7 with aqueous NaHCO₃, and extracted with CH₂Cl₂ (20 mL × 3). The combined organic layers were washed with brine, dried over MgSO₄, and column chromatographic purification process (hexanes/Et₂O, 2:1) gave the polycyclic compound 13 (52 mg, 48%) as a red solid, and the spectroscopic data of 13 are as follows.

2-Methyl-1H-benzo[k]indenо[2,1-i]phenanthridine-1,15(2H)-dione (13): 48%; red solid, mp 220-221 °C; IR (KBr) 1718, 1651, 1600, 1477, 1396, 1286 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.83 (s, 3H), 7.27-7.38 (m, 2H), 7.44-7.60 (m, 3H), 7.70-7.82 (m, 3H), 8.07 (d, J = 7.8 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.69-8.77 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 30.19, 114.80, 118.81, 120.92, 121.87, 122.94, 124.30, 125.11, 128.88, 129.07, 129.14, 129.23, 129.45, 130.31, 130.52, 131.71, 133.68, 134.80, 136.03, 138.78, 141.98, 145.13, 158.47, 190.47, one carbon was overlapped; ESIMS m/z 362 [M+H]+. Anal. Calcd for C₂₅H₁₅NO₂: C, 83.09; H, 4.18; N, 3.88. Found: C, 82.91; H, 4.40; N, 3.71.

11. References


12. X-Ray crystal data of compound 4a

Crystal data of compound 4a: solvent of crystal growth (hexane/CH$_2$Cl$_2$); empirical formula C$_{26}$H$_{21}$NO$_3$, Fw = 395.4, crystal dimensions 0.20 x 0.12 x 0.11 mm$^3$, Monoclinic, space group $P2_1/n$, $a = 8.1600(10)$ Å, $b = 8.2904(8)$ Å, $c = 28.866(2)$ Å, $\alpha = 90.00^\circ$, $\beta = 90.048(7)^\circ$, $\gamma = 90.00^\circ$, $V = 1952.8(3)$ Å$^3$, $Z = 4$, $D_{calc} = 1.345$ mg/m$^3$, $F_{000} = 832$, MoK$\alpha$ ($\lambda = 0.71073$ Å), $R_I = 0.2428$, $wR_2 = 0.5360$, GOF = 1.075 ($I > 2\sigma(I)$). The X-ray data have been deposited in CCDC with number 1013580.
13. Scanned $^1$H and $^{13}$C NMR spectra
4e'