Supporting Information

Rh(III)-catalyzed [3+3] spirocyclization of 3-aryl-3-hydroxyisoindolinones with vinylene carbonate as a three-atom unit

Hai-Shan Jin* and Cai-Cai Liang

School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, Jiangsu, China

*E-mail: hsjin@jsnu.edu.cn
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**General Methods.** Solvents and reagents were used as purchased without further purification. The reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF$_{254}$ precoated plates. Visualization of the developed plates was performed under a UV lamp. Chromatographic purification was performed with silica gel (100-200 mesh size). Melting points were uncorrected. Nuclear magnetic resonance spectra ($^1$H and $^{13}$C NMR) were recorded on Bruker DPX 400 MHz and 100 MHz spectrometers in CDCl$_3$ or DMSO-$d_6$ with the chemical shift (δ) given in parts per million (ppm). Multiplicities were indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth; the coupling constant (J) was given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on an Agilent Q-TOF mass spectrometer. 3-Aryl-3-hydroxyisoindoliones 1 were prepared according to literature procedure.¹

**General Procedure for the Synthesis of Compound 3.** To a solution of 3-aryl-3-hydroxyisoindoliones 1 (0.1 mmol) in dichloroethane (1.5 mL) was added [Cp*RhCl$_2$]$_2$ (0.0025 mmol), AgSbF$_6$ (0.01 mmol), AgOAc (0.025 mmol), and vinylene carbonate 2 (0.2 mmol). The reaction mixture was stirred at 60 °C on a heating block for 2 h. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the compound 3.

*Spiro[isochromene-1,1'-isoindolin]-3'-one (3a).* White solid (21.2 mg, 85%), petroleum ether/ethyl acetate = 5:1, mp 199-200 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.90 (s, 1H), 7.74 (d, J = 6.8 Hz, 1H), 7.67-7.60 (m, 2H), 7.51 (d, J = 6.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 5.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 168.5, 147.9, 144.5, 133.7, 131.0,
130.8, 130.4, 129.8, 128.6, 127.9, 124.6, 124.5, 123.9, 123.5, 104.9, 90.5. HRMS (ESI) m/z: [M + Na]^+ calcd for C_{16}H_{11}NO_{2}Na 272.0682; found 272.0680.

**6-Methylspiro[isochromene-1,1'-isoindolin]-3'-one (3b).** White solid (22.9 mg, 87%), petroleum ether/ethyl acetate = 5:1, mp 174-175 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.2\) Hz, 1H), 7.64-7.57 (m, 2H), 7.53 (d, \(J = 7.2\) Hz, 1H), 6.98 (s, 1H), 6.94-6.91 (m, 2H), 6.72 (d, \(J = 5.6\) Hz, 1H), 6.66 (d, \(J = 8.0\) Hz, 1H), 6.01 (d, \(J = 5.6\) Hz, 1H), 2.33 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.6, 147.1, 144.0, 139.7, 133.3, 130.6, 130.4, 129.6, 128.5, 125.2, 124.9, 124.4, 123.9, 123.8, 105.0, 90.1, 21.3. HRMS (ESI) m/z: [M + H]^+ calcd for C_{17}H_{14}NO_{2} 264.1019; found 264.1022.

**6-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (3c).** White solid (23.2 mg, 83%), petroleum ether/ethyl acetate = 5:1, mp 142-143 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.2\) Hz, 1H), 7.64-7.55 (m, 2H), 7.52 (d, \(J = 7.2\) Hz, 1H), 6.91 (s, 1H), 6.74 (d, \(J = 5.6\) Hz, 1H), 6.71-6.64 (m, 3H), 6.00 (d, \(J = 6.0\) Hz, 1H), 3.80 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.5, 160.6, 147.1, 144.4, 133.3, 131.2, 130.6, 130.4, 126.0, 123.9, 123.8, 120.3, 113.4, 109.1, 104.9, 90.2, 55.5. HRMS (ESI) m/z: [M + H]^+ calcd for C_{17}H_{14}NO_{3} 280.0968; found 280.0969.

**6-Chlorospiro[isochromene-1,1'-isoindolin]-3'-one (3d).** White solid (21.3 mg, 75%), petroleum ether/ethyl acetate = 5:1, mp 201-202 °C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 9.96 (s, 1H), 7.75 (d, \(J = 6.8\) Hz, 1H), 7.68-7.61 (m, 2H), 7.52 (d, \(J = 6.8\) Hz, 1H), 7.38 (s, 1H), 7.19 (d, \(J = 8.4\) Hz, 1H), 6.95 (d, \(J = 5.6\) Hz, 1H), 6.72 (d, \(J = 8.0\) Hz, 1H), 6.16 (d, \(J = 5.6\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 168.5, 147.5, 145.9, 134.4, 133.8, 132.6, 131.2, 130.8, 127.6, 127.2, 126.7, 124.0, 123.9, 123.6, 103.9, 90.2. HRMS (ESI) m/z: [M + H]^+ calcd for C_{16}H_{11}ClNO_{2} 284.0473; found 284.0472.
6-Fluorospiro[isochromene-1,1’-isoindolin]-3’-one (3e). White solid (20.3 mg, 76%),
petroleum ether/ethyl acetate = 5:1, mp 186-187 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 7.2 Hz, 1H), 7.66-7.58 (m, 2H), 7.53 (d, $J$ = 6.8 Hz, 1H), 6.97 (s, 1H), 6.86 (d, $J$ = 9.2 Hz, 1H), 6.83-6.74 (m, 3H), 6.02 (d, $J$ = 5.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 163.5 ($J$ = 247 Hz), 146.7, 145.1, 133.5, 132.0 ($J$ = 9.1 Hz), 130.7, 130.5, 126.6 ($J$ = 8.9 Hz), 124.0, 123.8, 114.5 ($J$ = 22.2 Hz), 110.8 ($J$ = 22.6 Hz), 104.3, 89.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.8. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{16}$H$_{11}$FNO$_2$ 268.0768; found 268.0770.

7-Methylspiro[isochromene-1,1’-isoindolin]-3’-one (3h). White solid (20.5 mg, 78%),
petroleum ether/ethyl acetate = 5:1, mp 185-186 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 7.2 Hz, 1H), 7.64-7.57 (m, 2H), 7.54 (d, $J$ = 7.2 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.09 (s, 1H), 7.05 (d, $J$ = 7.6 Hz, 1H), 6.69 (d, $J$ = 5.6 Hz, 1H), 6.57 (s, 1H), 6.03 (d, $J$ = 6.0 Hz, 1H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 147.0, 143.2, 137.8, 133.3, 130.6, 130.5, 130.4, 127.9, 127.0, 124.8, 124.3, 123.9, 123.8, 104.9, 90.2, 21.4. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{14}$NO$_2$ 264.1019; found 264.1020.

7-Methoxyspiro[isochromene-1,1’-isoindolin]-3’-one (3i). White solid (20.6 mg, 74%),
petroleum ether/ethyl acetate = 5:1, mp 150-151 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 7.2 Hz, 1H), 7.64-7.56 (m, 2H), 7.55 (d, $J$ = 7.2 Hz, 1H), 7.12-7.06 (m, 1H), 6.88 (s, 1H), 6.86 (d, $J$ = 8.4 Hz, 1H), 6.74 (d, $J$ = 6.0 Hz, 1H), 6.41 (d, $J$ = 6.0 Hz, 1H), 6.36 (d, $J$ = 8.0 Hz, 1H), 3.89 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 153.3, 146.9, 143.2, 133.3, 130.7, 130.5, 128.8, 128.3, 125.7, 123.9, 119.3, 116.4, 111.0, 99.5, 90.0, 56.0. HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{17}$H$_{13}$NO$_3$Na 302.0788; found 302.0786.

7-Chlorospiro[isochromene-1,1’-isoindolin]-3’-one (3j). White solid (18.7 mg, 66%),
petroleum ether/ethyl acetate = 5:1, mp 203-204 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J$ = 7.2 Hz, 1H), 7.67-7.60 (m, 2H), 7.54 (d, $J$ = 7.2 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 1H), 7.11 (d, $J$ = 8.0 Hz, 1H), 7.01 (s, 1H), 6.75 (s, 2H), 6.04 (d, $J$ = 5.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 146.3, 144.3, 133.6, 132.9, 130.8, 130.5, 129.9, 129.5, 128.3, 125.6, 124.5, 124.1, 123.8, 104.2, 89.6. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{16}$H$_{11}$ClNO$_2$ 284.0473; found 284.0474.

7-Fluorospiro[isochromene-1,1'-isoindolin]-3'-one (3k). White solid (13.6 mg, 51%), petroleum ether/ethyl acetate = 5:1, mp 177-178 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J$ = 7.2 Hz, 1H), 7.67-7.60 (m, 2H), 7.54 (d, $J$ = 7.2 Hz, 1H), 7.17-7.14 (m, 1H), 7.04 (t, $J$ = 8.4 Hz, 1H), 6.83 (s, 1H), 6.72 (d, $J$ = 5.6 Hz, 1H), 6.49 (d, $J$ = 8.8 Hz, 1H), 6.05 (d, $J$ = 5.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 146.3, 144.3, 133.6, 132.9, 130.8, 130.5, 129.9, 129.5, 128.3, 125.6, 124.5, 124.1, 123.8, 104.2, 90.0. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{16}$H$_{11}$FNO$_2$ 268.0768; found 268.0769.

8-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (3l). White solid (20.4 mg, 73%), petroleum ether/ethyl acetate = 5:1, mp 203-204 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J$ = 7.2 Hz, 1H), 7.57-7.49 (m, 2H), 7.41 (d, $J$ = 7.2 Hz, 1H), 7.29 (t, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 7.6 Hz, 1H), 6.73 (d, $J$ = 6.0 Hz, 1H), 6.66 (d, $J$ = 8.4 Hz, 1H), 6.62 (s, 1H), 5.93 (d, $J$ = 6.0 Hz, 1H), 3.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.3, 155.8, 150.0, 143.7, 132.6, 131.7, 130.6, 130.1, 129.3, 123.4, 122.5, 117.3, 114.7, 110.7, 103.4, 88.1, 55.5. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{14}$NO$_3$ 280.0968; found 280.0968.

5,7-Dimethylspiro[isochromene-1,1'-isoindolin]-3'-one (3m). White solid (5.8 mg, 21%),
petroleum ether/ethyl acetate = 5:1, mp 142-143 ºC. 1H NMR (400 MHz, CDCl3) δ 7.87 (d, J = 7.2 Hz, 1H), 7.65-7.56 (m, 2H), 7.55 (d, J = 5.6 Hz, 1H), 7.00 (s, 1H), 6.74 (s, 1H), 6.73 (d, J = 6.0 Hz, 2H), 6.40 (s, 1H), 6.16 (d, J = 5.6 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 168.6, 147.0, 143.0, 137.3, 134.4, 133.3, 131.9, 130.7, 130.4, 128.0, 125.4, 123.9, 123.7, 122.5, 102.2, 90.3, 21.3, 18.7. HRMS (ESI) m/z: [M + H]+ calcd for C18H16NO2 278.1176; found 278.1175.

5'-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (3n). White solid (22.3 mg, 80%), petroleum ether/ethyl acetate = 5:1, mp 186-187 ºC. 1H NMR (400 MHz, CDCl3) δ 7.78 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.17-7.12 (m, 2H), 7.08 (d, J = 8.4 Hz, 1H), 7.01 (s, 1H), 6.83 (s, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.74 (d, J = 5.6 Hz, 1H), 6.05 (d, J = 5.6 Hz, 1H), 3.84 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 168.4, 164.1, 149.2, 143.9, 129.6, 128.0, 127.7, 125.3, 124.5, 124.2, 123.0, 117.0, 108.5, 104.9, 89.6, 55.9. HRMS (ESI) m/z: [M + Na]+ calcd for C17H13NO3Na 302.0788; found 302.0788.

5'-Chlorospiro[isochromene-1,1'-isoindolin]-3'-one (3o). White solid (21.8 mg, 77%), petroleum ether/ethyl acetate = 5:1, mp 205-206 ºC. 1H NMR (400 MHz, CDCl3) δ 7.83 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.18-7.12 (m, 2H), 7.02 (s, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 5.6 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 167.1, 145.0, 143.8, 136.9, 133.4, 132.4, 129.9, 129.6, 127.9, 127.4, 125.2, 124.4, 124.3, 124.2, 105.1, 89.8. HRMS (ESI) m/z: [M + H]+ calcd for C16H11ClNO2 284.0473; found 284.0479.

5'-Bromospiro[isochromene-1,1'-isoindolin]-3'-one (3p). White solid (24.9 mg, 76%), petroleum ether/ethyl acetate = 5:1, mp 200-201 ºC. 1H NMR (400 MHz, CDCl3) δ 8.00 (s, 1H),
7.74 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.18-7.12 (m, 2H), 6.88 (s, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 5.6 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H).

13C NMR (100 MHz, CDCl3) δ 166.9, 145.5, 143.8, 136.3, 132.6, 129.9, 129.6, 127.9, 127.3, 127.2, 125.5, 124.8, 124.5, 124.3, 105.1, 89.9.

HRMS (ESI) m/z: [M + H]+ calcd for C16H11BrNO2 327.9968; found 327.9970.

5',6'-Dichlorospiro[isochromene-1,1'-isoindolin]-3'-one (3q). White solid (20.9 mg, 66%), petroleum ether/ethyl acetate = 5:1, mp 210-211 °C. 1H NMR (400 MHz, CDCl3) δ 7.92 (s, 1H), 7.64 (s, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.19-7.12 (m, 2H), 7.08 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 5.6 Hz, 1H), 6.07 (d, J = 5.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 166.4, 146.1, 143.6, 137.8, 135.5, 130.2, 130.1, 129.6, 128.1, 126.4, 124.5, 124.2, 105.2, 89.6.

HRMS (ESI) m/z: [M + H]+ calcd for C16H11Cl2NO2 318.0083; found 318.0091.

4',5',6',7'-Tetrahydrospiro[isochromene-1,1'-isoindol]-3'(2'H)-one (3r). White solid (15.7 mg, 62%), petroleum ether/ethyl acetate = 5:1, mp 127-128 °C. 1H NMR (400 MHz, CDCl3) δ 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 5.6 Hz, 1H), 6.46 (s, 1H), 5.90 (d, J = 6.0 Hz, 1H), 2.36-2.26 (m, 3H), 2.11-2.06 (m, 1H), 1.81-1.70 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 172.1, 156.0, 144.1, 132.9, 129.9, 129.5, 127.8, 126.7, 124.3, 123.8, 104.1, 90.6, 21.9, 21.8, 21.7, 19.9. HRMS (ESI) m/z: [M + Na]+ calcd for C16H15NO2Na 276.0995; found 276.0994.

5'-Chloro-6-methylspiro[isochromene-1,1'-isoindolin]-3'-one (3t). White solid (20.2 mg, 68%), petroleum ether/ethyl acetate = 5:1, mp 189-190 °C. 1H NMR (400 MHz, CDCl3) δ 7.81 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 6.98 (s, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 6.0 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.01 (d, J = 6.0 Hz, 1H), 2.33
s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 145.2, 143.8, 139.9, 136.8, 133.4, 132.4, 129.5, 128.6, 125.1, 125.0, 124.6, 124.2, 124.1, 105.1, 89.9, 21.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{13}$ClNO$_2$ 298.0629; found 298.0632.

5'-Bromo-6-methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (3u). White solid (24 mg, 67%), petroleum ether/ethyl acetate = 5:1, mp 188-189 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (s, 1H), 7.70 (d, $J$ = 8.8 Hz, 1H), 7.39 (d, $J$ = 8.0 Hz, 1H), 7.25 (s, 1H), 6.72-6.63 (m, 4H), 5.99 (d, $J$ = 5.6 Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 160.7, 145.8, 144.3, 136.2, 132.6, 131.1, 127.1, 125.8, 125.4, 124.6, 119.6, 113.5, 109.2, 105.0, 90.1, 55.5. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{13}$BrNO$_3$ 358.0073; found 358.0073.

5'-Bromo-7-methylspiro[isochromene-1,1'-isoindolin]-3'-one (3v). White solid (20.8 mg, 61%), petroleum ether/ethyl acetate = 5:1, mp 152-153 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (s, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.41 (d, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 7.6 Hz, 1H), 7.10 (s, 1H), 7.06 (d, $J$ = 8.0 Hz, 1H), 6.67 (d, $J$ = 5.6 Hz, 1H), 6.56 (s, 1H), 6.03 (d, $J$ = 5.6 Hz, 1H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 145.7, 143.0, 138.0, 136.3, 132.6, 130.6, 127.3, 127.1, 126.9, 125.5, 124.7, 124.6, 124.4, 105.0, 90.0, 21.4. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{13}$BrNO$_3$ 342.0124; found 342.0122.

5',6'-Dichloro-6-methylspiro[isochromene-1,1'-isoindolin]-3'-one (3w). White solid (13.2 mg, 40%), petroleum ether/ethyl acetate = 5:1, mp 203-204 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (s, 1H), 7.62 (s, 1H), 7.21 (s, 1H), 6.98 (s, 1H), 6.97 (d, $J$ = 9.2 Hz, 1H), 6.70 (d, $J$ = 8.4 Hz, 1H), 6.69 (d, $J$ = 6.0 Hz, 1H), 6.01 (d, $J$ = 6.0 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 146.3, 143.6, 140.2, 137.8, 135.3, 130.2, 129.5, 128.8, 126.0, 125.8, 125.2, 124.2, 124.1, 105.1, 89.7, 21.3. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{17}$H$_{12}$Cl$_2$NO$_2$ 332.0240;
1.0 mmol Scale Synthesis of 3a. To a solution of 3-hydroxy-3-phenylisoindolinone 1a (225 mg, 1.0 mmol) in dichloroethane (10 mL) was added \([\text{Cp}^*\text{RhCl}_2]\) (15.5 mg, 0.025 mmol), AgSbF$_6$ (34 mg, 0.1 mmol), AgOAc (42 mg, 0.25 mmol), and vinylene carbonate 2 (130 μL, 2.0 mmol). The reaction mixture was stirred at 60 °C on a heating block for 2 h. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the compound 3a as a white solid (213 mg, 86%).

Procedure for the Synthesis of Compound 5. To a solution of compound 3a (25 mg, 0.1 mmol) in THF (2 mL) was added NaH (60% oil dispersion) (6 mg, 0.15 mmol). After stirring at 0 °C for 40 min, prenyl bromide (20 μL, 0.15 mmol) was added at 0 °C and the reaction mixture was warmed slowly to room temperature and stirred for additional 1 h. Then, the resulting mixture was quenched by water and extracted with DCM. The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography to afford the compound 5.

2′-(3-Methylbut-2-en-1-yl) spiro[isochromene-1,1′-isooindolin]-3′-one (5). White solid (15.9 mg, 50%), petroleum ether/ethyl acetate = 5:1, mp 83-84 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85-7.83 (m, 1H), 7.54-7.49 (m, 2H), 7.42-7.38 (m, 1H), 7.29-7.26 (m, 1H), 7.11-7.04 (m, 2H), 6.72 (d, $J$ = 5.6 Hz, 1H), 6.59 (d, $J$ = 7.6 Hz, 1H), 5.87 (d, $J$ = 6.0 Hz, 1H), 5.04 (t, $J$ = 6.4 Hz, 1H), 4.15 (dd, $J$ = 15.6, 7.2 Hz, 1H), 3.82 (dd, $J$ = 15.6, 6.4 Hz, 1H), 1.55 (s, 3H), 1.52 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.0, 148.2, 144.1, 134.8, 132.8, 130.7, 130.3, 130.1, 129.5, 127.4, 126.6, 126.0, 124.2, 123.3, 123.3, 120.1, 102.4, 93.7, 38.2, 25.7, 17.7. HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{21}$H$_{19}$NO$_2$Na 340.1308; found 340.1308.
Mechanistic Studies.

(a) H/D exchange experiment. To a solution of 1a-d$_5$ (23 mg, 0.1 mmol) in DCE (1.5 mL) was added [Cp*RhCl$_2$]$_2$ (1.6 mg, 0.0025 mmol), AgSbF$_6$ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and H$_2$O (9 µL, 0.5 mmol). The reaction mixture was stirred at 60 °C on a heating block for 10 min. Then, the solvent was removed and the residue was purified to recover the compound 1a in 85% yield (19.6 mg). And H/D exchanges at the ortho-position (50% H) of the phenyl ring were observed by $^1$H NMR analysis.
(b) KIE study (competition experiment). To a mixture of 1a (22.5 mg, 0.1 mmol) and 1a-d5 (23 mg, 0.1 mmol) in DCE (1.5 mL) was added [Cp*RhCl₂]₂ (1.6 mg, 0.0025 mmol), AgSbF₆ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate 2 (13 μL, 0.2 mmol). The reaction mixture was stirred at 60 °C on a heating block for 20 min. Then, the solvent was removed and the residue was purified to afford a mixture of 3a and 3a-d₄. ¹H NMR analysis of the product mixture gave a 3a:3a-d₄ ratio of 2.33.

KIE study (parallel experiment). To a mixture of 1a (22.5 mg, 0.1 mmol) or 1a-d₅ (23 mg, 0.1 mmol) in DCE (1.5 mL) was added [Cp*RhCl₂]₂ (1.6 mg, 0.0025 mmol), AgSbF₆ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate 2 (13 μL, 0.2 mmol). The resulting mixtures were stirred separately at 60 °C on a heating block for 20 min. Then,
these two reaction mixtures were combined, and the solvent was removed and the residue was purified to afford a mixture of 3a and 3a-<i>d<sub>4</sub></i>. <sup>1</sup>H NMR analysis of the product mixture gave a 3a:3a-<i>d<sub>4</sub></i> ratio of 1.94.

(c) **Intermolecular Competition Experiment between 1c and 1e**. To a solution of 1c (25.5 mg, 0.1 mmol) and compound 1e (24.3 mg, 0.1 mmol) in dichloroethane (1.5 mL) was added [Cp*RhCl]<sub>2</sub> (1.6 mg, 0.0025 mmol), AgSbF<sub>6</sub> (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate 2 (13 μL, 0.2 mmol). The reaction mixture was stirred at 60 °C on a heating block for 2 h. After completion of the reaction, the solvent was removed and the residue was purified to afford 3c (12.7 mg, 0.046 mmol) and 3e (8.1 mg, 0.03 mmol). The molar ratio of 3c and 3e was thus calculated as 1.5:1.
References

$^1$H NMR Spectrum (400 MHz, DMSO-$d_6$) of Compound 3a

$^{13}$C NMR Spectrum (100 MHz, DMSO-$d_6$) of Compound 3a

S15
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3b

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3b
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3c

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3c
$^1$H NMR Spectrum (400 MHz, DMSO-$d_6$) of Compound 3d

$^{13}$C NMR Spectrum (100 MHz, DMSO-$d_6$) of Compound 3d
**H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3e**

**C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3e**
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3h

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3h
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3i

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3i
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3j

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3j
**H NMR Spectrum (400 MHz, CDCl₃) of Compound 3k**

**C NMR Spectrum (100 MHz, CDCl₃) of Compound 3k**
H NMR Spectrum (400 MHz, CDCl₃) of Compound 3l

C NMR Spectrum (100 MHz, CDCl₃) of Compound 3l
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3m

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3m
\textsuperscript{1}H NMR Spectrum (400 MHz, CDCl\textsubscript{3}) of Compound 3n

\textsuperscript{13}C NMR Spectrum (100 MHz, CDCl\textsubscript{3}) of Compound 3n
\[ \text{H NMR Spectrum (400 MHz, CDCl}_3\text{) of Compound 3o} \]

\[ \text{C NMR Spectrum (100 MHz, CDCl}_3\text{) of Compound 3o} \]
H NMR Spectrum (400 MHz, CDCl₃) of Compound 3p

1³C NMR Spectrum (100 MHz, CDCl₃) of Compound 3p
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3q

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3q
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3r

$^1$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3r
H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3t

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3t

$^1$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3t
\[ \text{H NMR Spectrum (400 MHz, CDCl}_3\text{) of Compound 3u} \]

\[ \text{\textsuperscript{13}C NMR Spectrum (100 MHz, CDCl}_3\text{) of Compound 3u} \]
H NMR Spectrum (400 MHz, CDCl₃) of Compound 3v

13C NMR Spectrum (100 MHz, CDCl₃) of Compound 3v
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3w

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3w
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 5

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 5
$^{19}$F NMR Spectrum (376 MHz, CDCl$_3$) of Compound 3e

$^{19}$F NMR Spectrum (376 MHz, CDCl$_3$) of Compound 3k