Supporting Information

One-pot synthesis of pyranoquinolin-1-ones via Rh(III)-catalysed redox annulation of 3-carboxyquinolines and alkynes

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1. General Information

Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without purification. 1,2-Dichloroethane was dried by calcium hydride. Melting point was measured on a microscopic apparatus and uncorrected. $^1$H NMR spectra were recorded on a 400 MHz spectrometer in deuterated chloroform or dimethyl sulfoxide. The chemical shifts (δ) are reported in relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet). Coupling constants (J) are reported in hertz. $^{13}$C NMR spectra were recorded using a 100 MHz spectrometer. $^{19}$F NMR spectra were recorded using a 376 MHz spectrometer. High-resolution mass spectrometry (HRMS) was performed on a Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI). Column chromatography was carried out on silica gel (230-400 mesh) from Qingdao Marine Chemical Co. X-ray analysis was performed with a single-crystal X-ray diffractometer. 1a was purchased from Bide Pharmatech Ltd., 2a, 2q, and 2u were purchased from Sigma Aldrich and used without further purification. Other alkynes$^{1,2}$ and quinoline-3-carboxylic acids$^{3,4}$ were prepared according to the literature.

2. General catalytic procedure

$[{\text{Cp}^*\text{RhCl}_2}_2]$ (0.005 mmol, 3.1 mg, 5 mol%), AgSbF$_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), quinolone-3-carboxylic acids (0.18 mmol, 1.8 equiv) and alkynes (0.1 mmol, 1.0 equiv) were weighted and placed in a dried Schlenk tube. Then 2.0 mL of DCE was added. The reaction mixture was stirred at 80 °C for 12 h (or 120 °C for 24 h). After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product.

3. Characterization of Products

**trans-3,4-Diphenyl-3,4-dihydro-1H-pyran-4,3-b]quinolin-1-one.** White solid (22.2 mg, 63% yield); m. p. 160-161 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.02 (s, 1H), 8.02 (d, $J = 8.6$ Hz, 1H), 7.96 (d, $J = 8.3$ Hz, 1H), 7.83 – 7.77 (m, 1H), 7.63 – 7.56 (m, 1H), 7.32 – 7.17 (m, 10H), 6.00 (d, $J = 5.3$ Hz, 1H), 4.97 (d, $J = 5.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.5, 157.8, 150.3, 140.3, 138.4, 137.8, 132.6, 129.3, 128.8, 128.6, 128.4, 127.5, 127.4, 127.0, 126.4, 119.0, 84.0, 52.3; HRMS (ESI)
Calcd. for C_{24}H_{17}NO_{2}: [M+H]^+, 352.1332. Found: m/z 352.1336.

**cis-3,4-Diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (10.9 mg, 31% yield); m. p. 184-186 °C. \^1H NMR (400 MHz, CDCl\textsubscript{3}) \delta 9.16 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.69 – 7.62 (m, 1H), 7.30 – 7.26 (m, 3H), 7.17 – 7.04 (m, 5H), 6.72 (d, J = 7.1 Hz, 2H), 6.11 (d, J = 3.1 Hz, 1H), 4.74 (d, J = 3.2 Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 165.4, 159.2, 150.3, 140.8, 136.1, 134.7, 133.0, 129.6, 129.4, 128.2, 128.1, 127.6, 127.4, 127.3, 126.1, 118.9, 82.1, 53.7; HRMS (ESI) Calcd. for C_{24}H_{17}NO_{2}: [M+H]^+, 352.1332. Found: m/z 352.1336.

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**trans-3,4-Bis(4-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.**
White solid (19.1 mg, 49% yield); m. p. 162-163 °C. \^1H NMR (400 MHz, CDCl\textsubscript{3}) \delta 9.04 (s, 1H), 8.00 (t, J = 9.0 Hz, 2H), 7.86 – 7.81 (m, 1H), 7.66 – 7.61 (m, 1H), 7.25 – 7.20 (m, 2H), 7.12 – 7.07 (m, 2H), 7.01 – 6.93 (m, 4H), 5.84 (d, J = 7.2 Hz, 1H), 4.86 (d, J = 7.2 Hz, 1H); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \delta -112.7, -114.5; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 164.3, 162.6 (d, J = 248.2 Hz, J\textsubscript{CF}), 162.1 (d, J = 246.0 Hz, J\textsubscript{CF}), 161.3, 160.8, 157.7, 150.2, 140.6, 133.3 (d, J = 3.4 Hz, J\textsubscript{CF}), 132.9, 130.8 (d, J = 8.0 Hz, J\textsubscript{CF}), 129.3 (d, J = 3.8 Hz, J\textsubscript{CF}), 128.5 (d, J = 8.3 Hz, J\textsubscript{CF}), 127.7, 127.0, 118.7, 115.7 (d, J = 13.5 Hz, J\textsubscript{CF}), 115.5 (d, J = 13.9 Hz, J\textsubscript{CF}), 83.6, 52.3; HRMS (ESI) Calcd. for C_{24}H_{15}F_{2}NO_{2}: [M+H]^+, 388.1144. Found: m/z 388.1145.

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**cis-3,4-Bis(4-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.**
White solid (15.8 mg, 41% yield); m. p. 183-184 °C. \^1H NMR (400 MHz, CDCl\textsubscript{3}) \delta 9.17 (s, 1H), 8.08 (dd, J = 16.2, 8.6 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.70 – 7.65 (m, 1H), 7.13 – 7.07 (m, 2H), 7.02 – 6.96 (m, 2H), 6.84 – 6.77 (m, 2H), 6.70 – 6.64 (m, 2H), 6.08 (d, J = 3.2 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \delta -113.12, -114.43; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 165.0, 163.4 (d, J = 235.8 Hz, J\textsubscript{CF}), 163.2 (d, J = 245.0 Hz, J\textsubscript{CF}), 158.6, 150.4, 141.1, 133.2, 131.1, 131.0, 129.5, 129.2, 127.9, 127.8, 127.3, 118.6, 115.4 (d, J = 4.4 Hz, J\textsubscript{CF}), 115.2 (d, J = 4.3 Hz, J\textsubscript{CF}), 81.3, 52.9; HRMS (ESI) Calcd. for C_{24}H_{15}F_{2}NO_{2}: [M+H]^+, 388.1144. Found: m/z 388.1145.
**trans-3,4-Bis(4-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (19.6 mg, 48% yield); m. p. 200 – 202 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.03 (s, 1H), 8.00 (t, $J$ = 8.7 Hz, 2H), 7.86 – 7.81 (m, 1H), 7.66 – 7.61 (m, 1H), 7.29 – 7.23 (m, 4H), 7.21 – 7.17 (m, 2H), 7.10 – 7.05 (m, 2H), 5.84 (d, $J$ = 7.2 Hz, 1H), 4.84 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 157.3, 150.2, 140.7, 135.9, 135.7, 134.6, 133.6, 132.9, 130.5, 129.3, 129.3, 129.0, 128.8, 128.0, 127.7, 127.0, 118.6, 83.3, 52.3; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Cl$_2$NO$_2$: [M+H]$^+$, 420.0553. Found: m/z 420.0555.

**cis-3,4-Bis(4-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (14.8 mg, 36% yield); m. p. 206 – 208 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.17 (s, 1H), 8.07 (dd, $J$ = 13.8, 8.6 Hz, 2H), 7.92 – 7.87 (m, 1H), 7.71 – 7.65 (m, 1H), 7.31 – 7.27 (m, 2H), 7.12 – 7.06 (m, 4H), 6.68 – 6.64 (m, 2H), 6.08 (d, $J$ = 3.2 Hz, 1H), 4.69 (d, $J$ = 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.9, 150.3, 141.2, 134.4, 134.3, 133.7, 133.3, 133.0, 130.8, 129.5, 129.2, 128.6, 128.5, 127.9, 127.4, 127.3, 118.5, 81.1, 52.9; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Cl$_2$NO$_2$: [M+H]$^+$, 420.0553. Found: m/z 420.0555.

**trans-3,4-Bis(4-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (26.2 mg, 51% yield); m. p. 182-183 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.02 (s, 1H), 7.99 (t, $J$ = 9.2 Hz, 2H), 7.83 (t, $J$ = 7.4 Hz, 1H), 7.63 (t, $J$ = 7.5 Hz, 1H), 7.41 (t, $J$ = 8.1 Hz, 4H), 7.13 (d, $J$ = 8.2 Hz, 2H), 7.02 (d, $J$ = 8.2 Hz, 2H), 5.83 (d, $J$ = 7.0 Hz, 1H), 4.82 (d, $J$ = 7.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 157.2, 150.2, 140.7, 136.5, 136.3, 132.9, 131.9, 131.8, 130.8, 129.3, 129.2, 128.6, 128.5, 127.9, 127.4, 127.3, 118.5, 83.3, 52.3; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Br$_2$NO$_2$: [M+H]$^+$, 509.9522. Found: m/z 509.9522.

**cis-3,4-Bis(4-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (17.8 mg, 35% yield); m. p. 206-208 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.16 (s, 1H), 8.07 (dd, $J$ = 14.1, 8.6 Hz, 2H), 7.92 – 7.86 (m, 1H), 7.71 – 7.65 (m, 1H), 7.47 – 7.42 (m, 2H), 7.25 – 7.22 (m, 2H), 7.04 (d, $J$ = 8.3 Hz, 2H), 6.64 – 6.58 (m, 2H), 6.06 (d, $J$ = 3.2 Hz, 1H), 4.68 (d, $J$ = 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 158.2, 150.3, 141.2, 134.9, 133.5, 133.3, 131.6, 131.5, 131.1, 129.5, 129.2, 127.9, 127.7, 127.3, 122.4, 121.9, 118.5, 81.1, 52.8; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Br$_2$NO$_2$: [M+H]$^+$, 509.9522. Found: m/z 509.9524.
**trans-3,4-Di-p-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (19.9 mg, 53% yield); m. p. 169-170 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.62 – 7.56 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.10 (s, 4H), 7.05 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 4.6 Hz, 1H), 4.95 (d, J = 4.6 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 158.0, 150.3, 140.2, 138.1, 137.1, 135.7, 135.0, 132.5, 129.5, 129.3, 129.3, 128.5, 127.3, 127.0, 126.3, 119.1, 83.9, 51.6, 21.1, 21.0; HRMS (ESI) Calcd. for C₂₆H₂₁NO₂: [M+H]+, 380.1645. Found: m/z 380.1649.

**cis-3,4-Di-p-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (12.6 mg, 33% yield); m. p. 175-176 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.85 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.64 (d, J = 7.8 Hz, 2H), 6.05 (d, J = 2.3 Hz, 1H), 4.68 (d, J = 2.4 Hz, 1H), 2.33 (s, 3H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 159.6, 150.3, 140.8, 137.8, 137.0, 133.1, 132.9, 131.8, 129.4, 129.4, 129.2, 128.9, 128.8, 127.5, 127.2, 126.1, 118.9, 82.2, 53.3, 21.2, 21.0; HRMS (ESI) Calcd. for C₂₆H₂₁NO₂: [M+H]+, 380.1645. Found: m/z 380.1650.

**trans-3,4-Bis(4-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (16.5 mg, 40% yield); m. p. 111-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.92 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 8.6 Hz, 1H), 7.10 (d, J = 8.6 Hz, 2H), 6.85 – 6.89 (m, 2H), 6.40 – 6.74 (m, 2H), 5.90 (d, J = 5.6 Hz, 1H), 4.90 (d, J = 5.6 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 159.4, 158.7, 158.4, 150.2, 140.3, 132.6, 130.4, 129.9, 129.9, 129.3, 127.9, 127.4, 126.9, 119.0, 83.9, 55.2, 55.2, 51.4; HRMS (ESI) Calcd. for C₂₆H₂₁NO₂: [M+H]+, 412.1543. Found: m/z 412.1545.

**cis-3,4-Bis(4-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** Pale yellow solid (12.9 mg, 31% yield); m. p. 170-171 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 7.7 Hz, 1H), 7.89 – 7.83 (m, 1H),
7.03 (d, $J = 8.6$ Hz, 2H), 6.80 (dd, $J = 6.9, 1.9$ Hz, 2H), 6.64 (s, 4H), 6.02 (d, $J = 3.2$ Hz, 1H), 4.64 (d, $J = 3.1$ Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.6, 159.6, 159.4, 158.7, 150.3, 140.8, 132.9, 130.7, 129.4, 129.2, 128.3, 127.6, 127.5, 127.2, 126.9, 118.9, 55.2, 55.1, 53.1; HRMS (ESI) Calcd. for C$_{26}$H$_{21}$NO$_4$: [M+H]$^+$, 412.1543. Found: m/z 412.1546.

trans-3,4-Bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (24.2 mg, 50% yield); m. p. 149-150 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.05 (s, 1H), 7.99 (t, $J = 8.1$ Hz, 2H), 7.84 (t, $J = 8.1$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 8.8$ Hz, 4H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 5.98 (d, $J = 6.9$ Hz, 1H), 4.97 (d, $J = 6.9$ Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.6, -62.8; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.8, 156.7, 150.2, 141.2 (d, $J_{CF} = 38.2$ Hz, $J_{CF}$), 140.8, 133.1, 131.0 (d, $J = 32.8$ Hz, $J_{CF}$), 130.0 (d, $J = 32.4$ Hz, $J_{CF}$), 129.5, 129.4, 127.9, 127.1, 127.0, 125.8 (q, $J = 3.7$ Hz, $J_{CF}$), 125.7 (q, $J = 4.5$ Hz, $J_{CF}$), 123.9 (q, $J = 274.3$ Hz, $J_{CF}$), 123.7 (q, $J = 274.3$ Hz, $J_{CF}$), 118.5, 83.0, 52.6; HRMS (ESI) Calcd. for C$_{26}$H$_{15}$F$_6$NO$_2$: [M+H]$^+$, 488.1082. Found: m/z 488.1082.

cis-3,4-Bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (18.1 mg, 37% yield); m. p. 202-203 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.19 (s, 1H), 8.08 (t, $J = 9.2$ Hz, 2H), 7.94 – 7.87 (m, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.35 (dd, $J = 11.7, 8.3$ Hz, 4H), 6.88 (d, $J = 8.1$ Hz, 2H), 6.21 (d, $J = 2.8$ Hz, 1H), 4.85 (d, $J = 3.1$ Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.6, -62.8; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.5, 157.7, 150.4, 141.3, 139.6, 138.5, 133.5, 130.7 (d, $J = 31.7$ Hz, $J_{CF}$), 130.3 (d, $J = 31.7$ Hz, $J_{CF}$), 129.8, 129.5, 129.2, 128.0, 127.3, 126.3, 125.5 (q, $J = 3.6$ Hz, $J_{CF}$), 125.3 (q, $J = 4.3$ Hz, $J_{CF}$), 123.8 (q, $J = 273.5$ Hz, $J_{CF}$), 123.7 (q, $J = 272.8$ Hz, $J_{CF}$), 118.4, 80.9, 53.0; HRMS (ESI) Calcd. for C$_{26}$H$_{15}$F$_6$NO$_2$: [M+H]$^+$, 488.1080. Found: m/z 488.1082.

trans-3,4-Bis(3-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (19.9 mg, 51% yield); m. p. 169-170 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.04 (s, 1H), 8.03 (d, $J = 8.6$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.86 – 7.81 (m, 1H),
cis-3,4-Bis(3-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (17.1 mg, 44% yield); m. p. 150-151 °C. 

1H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.71 – 7.65 (m, 1H), 7.33 – 7.28 (m, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.97 (m, 2H), 6.92 – 6.81 (m, 2H), 6.54 (d, J = 7.8 Hz, 1H), 6.46 (dt, J = 9.7, 2.1 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 4.74 (d, J = 3.3 Hz, 1H); 19F NMR (376 MHz, CDCl₃) δ -112.2, -112.5; 13C NMR (100 MHz, CDCl₃) δ 164.7, 162.7 (d, J = 246.3 Hz, J CF), 162.4 (d, J = 246.3 Hz, J CF), 158.1, 150.3, 141.2, 138.4 (d, J = 4.6 Hz, J CF), 136.9 (d, J = 7.1 Hz, J CF), 133.3, 130.0 (d, J = 8.1 Hz, J CF), 129.8 (d, J = 8.6 Hz, J CF), 129.5, 129.2, 127.9, 127.3, 125.1 (d, J = 3.0 Hz, J CF), 121.5 (d, J = 2.9 Hz, J CF), 118.5, 116.5 (d, J = 22.3 Hz, J CF), 115.4 (d, J = 21.1 Hz, J CF), 114.6 (d, J = 20.8 Hz, J CF), 113.2 (d, J = 23.2 Hz, J CF), 80.9, 53.1; HRMS (ESI) Calcd. for C₂₄H₁₅F₂NO₂: [M+H]⁺, 388.1148. Found: m/z 388.1148.

trans-3,4-Bis(3-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (21.6 mg, 52% yield); m. p. 158 – 160 °C. 

1H NMR (400 MHz, CDCl₃) δ 9.05 (s, 1H), 8.01 (d, J = 15.4, 8.6 Hz, 2H), 7.87 – 7.81 (m, 1H), 7.67 – 7.61 (m, 1H), 7.33 (d, J = 1.7 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.25 (d, J = 1.2 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.17 (t, J = 1.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.04 (dt, J = 7.2, 1.4 Hz, 1H), 5.88 (d, J = 6.4 Hz, 1H), 4.86 (d, J = 6.4 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 164.0, 156.8, 150.2, 140.7, 139.5, 139.2, 134.7, 134.6, 133.0, 130.0, 129.8, 129.4, 129.1, 128.9, 128.0, 127.8, 127.2, 127.0, 126.7, 124.6, 118.5, 83.0, 52.3; HRMS (ESI) Calcd. for C₂₄H₁₃Cl₂NO₂: [M+H]⁺, 420.0553. Found: m/z 420.0556.
trans-3,4-Bis(3-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (28.3 mg, 56% yield); m. p. 178 – 179 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.05 (s, 1H), 8.03 (d, $J = 8.6$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.87 – 7.81 (m, 1H), 7.67 – 7.61 (m, 1H), 7.48 (s, 1H), 7.45 – 7.36 (m, 2H), 7.33 (t, $J = 1.7$ Hz, 1H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 5.1$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 1H), 5.86 (d, $J = 6.5$ Hz, 1H), 4.84 (d, $J = 6.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.9, 156.8, 150.2, 140.7, 139.8, 139.4, 133.0, 132.0, 131.8, 130.9, 130.3, 130.1, 129.6, 129.4, 129.4, 127.8, 127.7, 127.1, 125.0, 122.8, 118.5, 83.0, 52.4; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Br$_{2}$NO$_2$: [M+H]$^+$, 509.9522. Found: m/z 509.9520.

cis-3,4-Bis(3-bromophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (16.8 mg, 33% yield); m. p. 183-184 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.17 (s, 1H), 8.08 (dd, $J = 17.8$, 8.5 Hz, 2H), 7.93 – 7.86 (m, 1H), 7.68 (t, $J = 7.3$ Hz, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 12.8$ Hz, 2H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.8$ Hz, 1H), 6.99 (t, $J = 7.9$ Hz, 1H), 6.84 (s, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.06 (d, $J = 3.1$ Hz, 1H), 4.68 (d, $J = 3.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 157.9, 150.4, 141.2, 137.9, 136.7, 133.3, 132.5, 131.6, 130.8, 129.9, 129.7, 129.5, 129.3, 129.2, 128.0, 127.9, 127.3, 124.6, 122.5, 122.4, 118.5, 80.9, 53.0; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$Br$_{2}$NO$_2$: [M+H]$^+$, 509.9522. Found: m/z 509.9519.

trans-3,4-Di-m-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (22.6 mg, 60% yield); m. p. 151 – 152 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.01 (s, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.94 (dd, $J = 8.3$, 0.8 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.61 – 7.55 (m, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 3.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.08 – 6.99 (m, 2H), 5.00 (d, $J = 4.2$ Hz, 1H), 4.95 (d, $J = 4.2$ Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 157.7, 150.3, 140.1, 138.8,
cis-3,4-Di-m-tolyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (12.9 mg, 34% yield); m.p. 186 – 187 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.68 – 7.62 (m, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.00 – 6.88 (m, 4H), 6.50 (t, J = 7.3 Hz, 2H), 6.05 (d, J = 3.1 Hz, 1H), 4.68 (d, J = 3.2 Hz, 1H), 2.26 (s, 3H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 159.4, 150.3, 140.8, 137.7, 136.2, 134.6, 132.9, 130.3, 129.4, 129.2, 128.9, 128.1, 127.9, 127.9, 127.5, 127.2, 127.0, 126.7, 123.2, 119.0, 82.3, 53.6, 21.3, 21.3; HRMS (ESI) Calcd. for C₂₆H₂₁NO₂: [M+H]+, 380.1645. Found: m/z 380.1647.

trans-3,4-Bis(3-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (23.3 mg, 57% yield); m.p. 165-166 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.83 – 7.78 (m, 1H), 7.63 – 7.57 (m, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.82 – 6.73 (m, 4H), 5.98 (d, J = 4.8 Hz, 1H), 4.93 (d, J = 4.8 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 159.8, 159.7, 157.5, 150.3, 140.2, 140.0, 139.4, 132.6, 129.8, 129.6, 129.3, 129.3, 127.4, 127.0, 120.9, 119.0, 118.5, 114.9, 113.9, 112.7, 112.1, 83.6, 55.2, 52.1; HRMS (ESI) Calcd. for C₂₆H₂₁NO₄: [M+H]+, 412.1543. Found: m/z 412.1545.
trans-3,4-Bis(2-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (14.1 mg, 36% yield); m. p. 163 – 164 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.18 (s, 1H), 8.11(d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 1H), 7.88 (td, $J = 7.0$, 1.2 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.16 – 7.06 (m, 2H), 7.01 – 6.95 (m, 1H), 6.91 (t, $J = 8.2$ Hz, 2H), 6.83 – 6.70 (m, 2H), 6.41 (d, $J = 3.2$ Hz, 1H), 5.27 (d, $J = 3.3$ Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.6, -119.1; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.1, 160.6 (d, $J = 245.3$ Hz, $J_{CF}$), 159.4 (d, $J = 248.8$ Hz, $J_{CF}$), 158.0, 150.4, 140.8, 133.1, 130.5 (d, $J = 3.5$ Hz, $J_{CF}$), 129.9 (d, $J = 8.2$ Hz, $J_{CF}$), 129.4 (d, $J = 2.6$ Hz, $J_{CF}$), 129.3 (d, $J = 2.7$ Hz, $J_{CF}$), 127.7, 127.5 (d, $J = 3.2$ Hz, $J_{CF}$), 127.3, 123.9 (d, $J = 3.6$ Hz, $J_{CF}$), 123.8 (d, $J = 3.6$ Hz, $J_{CF}$), 123.3 (d, $J = 12.5$ Hz, $J_{CF}$), 122.6 (d, $J = 14.7$ Hz, $J_{CF}$), 119.1, 115.4 (d, $J = 22.9$ Hz, $J_{CF}$), 114.8 (d, $J = 20.7$ Hz, $J_{CF}$), 75.9 (d, $J = 3.1$ Hz, $J_{CF}$), 44.6; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$F$_2$NO$_2$: [M+H]$^+$, 388.1144. Found: m/z 388.1147.

cis-3,4-Bis(2-fluorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (15.0 mg, 39% yield); m. p. 173 – 174 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.09 (s, 1H), 8.03 – 7.93 (m, 2H), 7.79 (td, $J = 7.0$, 1.3 Hz, 1H), 7.61 (t, $J = 7.9$ Hz, 1H), 7.45 (td, $J = 7.6$, 1.3 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 7.06 – 6.97 (m, 2H), 6.97 – 6.89 (m, 2H), 6.25 (d, $J = 9.2$ Hz, 1H), 5.18 (d, $J = 9.2$ Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -113.8, -116.5; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 161.1 (d, $J = 245.3$ Hz, $J_{CF}$), 160.0 (d, $J = 248.8$ Hz, $J_{CF}$), 157.3, 150.1, 140.6, 132.7, 131.3 (d, $J = 4.4$ Hz, $J_{CF}$), 130.6 (d, $J = 8.5$ Hz, $J_{CF}$), 129.6, 129.5, 129.3, 128.3 (d, $J = 3.1$ Hz, $J_{CF}$), 127.5, 126.9, 124.3, 124.2 (d, $J = 3.6$ Hz, $J_{CF}$), 124.2 (d, $J = 3.7$ Hz, $J_{CF}$), 123.9 (d, $J = 13.8$ Hz, $J_{CF}$), 118.5, 115.7 (d, $J = 6.0$ Hz, $J_{CF}$), 115.5 (d, $J = 5.8$ Hz, $J_{CF}$), 48.1; HRMS (ESI) Calcd. for C$_{24}$H$_{15}$F$_2$NO$_2$: [M+H]$^+$, 388.1144. Found: m/z 388.1147.

trans-3,4-Bis(2-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. White solid (13.0 mg, 31% yield); m. p. 170 – 171 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.19 (s, 1H), 8.12 (d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.69 – 7.63 (m, 1H), 7.37 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.24 (td, $J = 7.7$, 1.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.12 – 7.04 (m, 2H), 7.03 – 6.97 (m, 1H), 6.85 – 6.78 (m, 2H), 6.50 (d, 6.50 Hz, 1H).
**cis-3,4-Bis(2-chlorophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** White solid (15.4 mg, 37% yield); m. p. 173 – 174 °C. 

\[
\begin{align*}
J = 3.3 \text{ Hz}, 1H) & \text{,} 5.66 (d, J = 3.3 \text{ Hz}, 1H); \\
{^{13}}C \text{ NMR (100 MHz, CDCl}_3 & \delta 165.3, 158.5, 150.6, 140.9, 135.7, 133.1, 133.0, 132.9, 132.5, 130.6, 129.7, 129.6, 129.4, 128.9, 128.6, 128.3, 127.7, 127.2, 126.6, 126.3, 119.1, 78.6, 45.9; \\
\text{HRMS (ESI) Calcd. for C}_{24}H_{15}Cl_2NO_2: [M+H]^+ & \text{, 420.0553. Found: m/z 420.0554.}
\end{align*}
\]

**trans-3,4-Bis(2-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** 1H NMR (400 MHz, CDCl_3) δ 9.05 (s, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.75 (td, J = 6.9, 1.2 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.28 (dd, J = 7.6, 1.2 Hz, 1H), 6.90 – 6.79 (m, 6H), 6.77 (t, J = 7.2 Hz, 1H), 6.35 (d, J = 6.6 Hz, 1H), 5.30 (d, J = 6.7 Hz, 1H), 3.68 (s, 3H), 3.62 (s, 3H).

**cis-3,4-Bis(2-methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.** 1H NMR (400 MHz, CDCl_3) δ 9.13 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.82 (td, J = 7.0, 1.3 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.10 – 7.04 (m, 1H), 6.68 (q, J = 6.6 Hz, 2H), 6.62 (dd, J = 7.6, 1.6 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 6.41 (d, J = 3.3 Hz, 1H), 5.42 (d, J = 3.0 Hz, 1H), 3.90 (s, 3H), 3.24 (s, 3H).

\[
\begin{align*}
{^{13}}C \text{ NMR (100 MHz, CDCl}_3 & \delta 166.1, 165.6, 160.1, 159.1, 157.4, 157.1, 156.8, 155.8, 150.2, 150.1, 140.0, 139.6, 132.5, 132.2, 130.8, 130.3, 129.5, 129.3, 129.2, 129.2, 129.2, 128.6, 128.5, 128.4, 127.6, 127.2, 127.1, 127.0, 126.9, 126.9, 126.8, 126.3, 125.0, 124.4, 120.5, 120.2, 120.1, 120.0, 119.8, 119.6, 111.0, 110.5, 110.2, 108.9, 78.5, 77.2, 77.2, 55.3, 55.3, 55.3, 54.7, 47.4; \\
\text{HRMS (ESI) Calcd. for C}_{26}H_{21}NO_4: [M+H]^+ & \text{, 412.1543. Found: m/z 412.1547.}
\end{align*}
\]
(39.4 mg, 91% yield);

**trans**-3-(P-tolyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.02 (s, 1H), 7.97 (t, \( J = 6.4 \) Hz, 1H), 7.82 – 7.78 (m, 1H), 7.62 – 7.58 (m, 1H), 7.52 (d, \( J = 9.9 \) Hz, 2H), 7.31 (d, \( J = 8.2 \) Hz, 2H), 7.16 (d, \( J = 8.1 \) Hz, 2H), 7.07 (d, \( J = 1.8 \) Hz, 2H), 5.92 (d, \( J = 6.2 \) Hz, 1H), 5.00 (d, \( J = 6.2 \) Hz, 1H), 2.27 (s, 3H).

**cis**-3-(P-tolyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.02 (s, 1H), 8.02 (t, \( J = 5.7 \) Hz, 1H), 7.85 – 7.82 (m, 1H), 7.64 – 7.62 (m, 1H), 7.55 (s, 2H), 7.40 (d, \( J = 8.3 \) Hz, 2H), 7.10 (d, \( J = 8.1 \) Hz, 2H), 7.05 (s, 2H), 5.99 (d, \( J = 6.0 \) Hz, 1H), 4.88 (d, \( J = 6.0 \) Hz, 1H), 2.32 (s, 3H).

\( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -62.56, -62.72.

\( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.1, 165.0, 158.9, 158.4, 150.4, 150.3, 141.1, 141.0, 140.2, 139.1, 138.3, 137.4, 133.2, 133.1, 132.6, 131.2, 129.9, 129.5, 129.4, 129.2, 129.2, 129.1, 129.1, 127.8, 127.7, 127.3, 127.2, 126.5, 125.8, 125.2 (q, \( J = 3.8 \) Hz, \( J_{CF} \)), 125.0 (q, \( J = 3.6 \) Hz, \( J_{CF} \)), 124.0 (q, \( J = 282.5 \) Hz, \( J_{CF} \)), 123.9 (q, \( J = 283.0 \) Hz, \( J_{CF} \)), 118.8, 118.6, 81.7, 81.4, 53.4, 53.0, 21.2, 21.0.

HRMS (ESI) Calcd. for C\(_{26}\)H\(_{18}\)F\(_3\)NO\(_2\): [M+H]\(^+\), 434.1362. Found: m/z 434.1365.

**trans**-3-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (24.3 mg, 54% yield); m. p. 166 – 168 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.04 (s, 1H), 8.00 (t, \( J = 9.1 \) Hz, 2H), 7.86 – 7.80 (m, 1H), 7.66 – 7.61 (m, 1H), 7.54 (d, \( J = 8.2 \) Hz, 2H), 7.29 (d, \( J = 8.1 \) Hz, 2H), 7.19 (d, \( J = 8.7 \) Hz, 2H), 6.78 (d, \( J = 8.8 \) Hz, 2H), 5.88 (d, \( J = 6.6 \) Hz, 1H), 4.99 (d, \( J = 6.6 \) Hz, 1H); \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -62.6; \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.3, 159.7, 157.4, 150.2, 142.1, 140.6, 132.8, 129.8, 129.5, 129.5, 129.3, 129.1, 128.0, 127.7, 127.0, 125.6 (q, \( J = 3.6 \) Hz, \( J_{CF} \)), 124.0 (q, \( J = 273.4 \) Hz, \( J_{CF} \)), 118.9, 114.0, 83.6, 55.2, 52.5; HRMS (ESI) Calcd. for C\(_{26}\)H\(_{18}\)F\(_3\)NO\(_3\): [M+H]\(^+\), 450.1312. Found: m/z 450.1314.
cis-3-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (15.1 mg, 34% yield); m. p. 175 – 176 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.17 (s, 1H), 8.07 (dd, J = 12.4, 8.5 Hz, 2H), 7.92 – 7.86 (m, 1H), 7.71 – 7.65 (m, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.10 (d, J = 3.2 Hz, 1H), 4.77 (d, J = 3.3 Hz, 1H), 3.80 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.7; ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 159.6, 158.4, 150.3, 139.1, 133.2, 130.0, 129.5, 129.2, 127.8, 127.7, 127.3, 127.3, 125.2, 125.1 (q, J = 4.2 Hz, JCF), 123.9 (q, J = 272.4 Hz, JCF), 118.8, 113.7, 81.6, 55.3, 53.5; HRMS (ESI) Calcd. for C₂₆H₁₈F₃NO₃: [M+H]⁺, 450.1312. Found: m/z 450.1316.

trans-4-Methyl-3-phenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (17.6 mg, 61% yield); m. p. 168 – 169 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.96 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.64 – 7.58 (m, 1H), 7.47 – 7.34 (m, 5H), 5.40 (d, J = 8.6 Hz, 1H), 3.75 – 3.64 (m, 1H), 1.48 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 159.8, 150.0, 140.3, 137.4, 132.6, 129.3, 129.2, 128.9, 128.7, 127.2, 127.1, 126.8, 118.4, 85.3, 40.9, 14.8; HRMS (ESI) Calcd. for C₁₉H₁₅NO₂: [M+H]⁺, 290.1176. Found: m/z 290.1181.

cis-4-Methyl-3-phenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Pale yellow solid (2.3 mg, 8% yield); m. p. 154 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.04 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.67 – 7.61 (m, 1H), 7.53 – 7.43 (m, 1H), 7.41 – 7.36 (m, 1H), 5.90 (d, J = 2.7 Hz, 1H), 3.64 – 3.55 (m, 1H), 1.17 (d, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 162.3, 149.9, 141.1, 136.5, 132.9, 129.4, 128.9, 128.6, 128.2, 127.3, 127.1, 125.6, 117.6, 81.2, 42.1, 13.4; HRMS (ESI) Calcd. for C₁₉H₁₅NO₂: [M+H]⁺, 290.1176. Found: m/z 290.1130.

trans-3,4-Di(thiophen-2-yl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Black solid (4.5 mg, 13% yield); m. p. 185 – 186 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.96 (s, 1H), 8.13 (dd, J = 8.5, 0.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.66 – 7.60 (m, 1H), 7.26 – 7.24 (m, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 6.99 (dt, J = 3.6, 1.1 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.85 (dd, J = 5.0, 3.6 Hz, 1H), 6.31 (dd, J = 2.7, 1.0 Hz, 1H), 5.27 (d, J = 2.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 156.9, 150.2,
cis-3,4-Di(thiophen-2-yl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. Black solid (4.0 mg, 11% yield); m. p. 235 – 236 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.10 (s, 1H), 8.12 (d, \(J = 8.5\) Hz, 1H), 8.02 (d, \(J = 8.2\) Hz, 1H), 7.92 – 7.85 (m, 1H), 7.69 – 7.63 (m, 1H), 7.29 (dd, \(J = 5.0, 1.2\) Hz, 1H), 7.16 (dd, \(J = 5.1, 1.0\) Hz, 1H), 7.07 (dd, \(J = 2.6, 1.0\) Hz, 1H), 6.99 (dd, \(J = 5.0, 3.6\) Hz, 1H), 6.86 (dd, \(J = 5.1, 3.6\) Hz, 1H), 6.79 (d, \(J = 3.5\) Hz, 1H), 6.33 (dd, \(J = 3.0, 0.8\) Hz, 1H), 5.09 (d, \(J = 3.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.2, 158.4, 150.0, 141.5, 138.1, 136.5, 133.2, 129.4, 129.2, 127.8, 127.3, 126.7, 126.2, 126.1, 126.0, 117.7, 78.7, 49.3; HRMS (ESI) Calcd. for C\(_{20}\)H\(_{13}\)NO\(_2\)S\(_2\): [M+H]\(^+\), 364.0460. Found: m/z 434.1365.

trans-3,4-Diethyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.92 (s, 1H), 8.10 (d, \(J = 3.2\) Hz, 1H), 7.95 (s, 1H), 7.61 (t, \(J = 7.9\) Hz, 2H), 4.70 - 4.65 (m, 1H), 3.13 – 3.06 (m, 1H), 2.09 – 1.93 (m, 2H), 1.82 – 1.70 (m, 2H), 1.10 – 1.01 (m, 6H).

cis-3,4-Diethyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.94 (s, 1H), 8.13 (d, \(J = 3.1\) Hz, 1H), 7.97 (s, 1H), 7.85 (td, \(J = 7.2, 1.2\) Hz, 2H), 4.65 – 4.59 (m, 1H), 3.20 – 3.13 (m, 1H), 1.93 – 1.82 (m, 2H), 1.66 – 1.55 (m, 2H), 1.12 (t, \(J = 7.4\) Hz, 3H), 0.95 (t, \(J = 7.5\) Hz, 3H).

9-Fluoro-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (16.8 mg, 46% yield); m. p. 164 – 166 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.29 (s, 1H), 7.83 (d, \(J = 8.6\) Hz, 1H), 7.78 – 7.70 (m, 1H), 7.33 – 7.22 (m, 8H), 7.19 (dd, \(J = 7.9, 1.8\) Hz, 2H), 6.01 (d, \(J = 5.4\) Hz, 1H), 4.96 (d, \(J = 5.4\) Hz, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -119.0; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.0, 158.1, 158.5 (d, \(J = 259.6\) Hz, \(J_{CF}\)), 157.3, 150.6, 138.0, 137.6, 134.1 (d, \(J = 4.5\) Hz, \(J_{CF}\)), 132.4 (d, \(J = 8.9\) Hz, \(J_{CF}\)).
9-Fluoro-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (16.8 mg, 46% yield); m. p. 196 – 198 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.45 (s, 1H), 7.90 (d, \(J = 8.6\) Hz, 1H), 7.84 – 7.77 (m, 1H), 7.34 – 7.30 (m, 1H), 7.30 – 7.26 (m, 3H), 7.17 – 7.11 (m, 3H), 6.74 – 6.69 (m, 2H), 6.11 (d, \(J = 3.2\) Hz, 1H), 4.73 (d, \(J = 3.2\) Hz, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -118.7; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.8, 160.2, 158.6 (d, \(J = 259.3\) Hz, \(J_{CF}\)), 150.6, 135.9, 134.7 (d, \(J = 4.6\) Hz, \(J_{CF}\)), 134.5, 132.9 (d, \(J = 9.1\) Hz, \(J_{CF}\)), 129.5, 128.3, 128.2 (d, \(J = 3.7\) Hz, \(J_{CF}\)), 127.5, 126.1, 125.1 (d, \(J = 4.3\) Hz, \(J_{CF}\)), 119.1, 118.6, 111.1 (d, \(J = 18.7\) Hz, \(J_{CF}\)), 82.0, 53.7; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)FNO\(_2\): [M+H]+, 370.1238. Found: m/z 370.1240.

9-Chloro-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.4 mg, 48% yield); m. p. 191 – 193 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.42 (s, 1H), 7.94 (d, \(J = 8.3\) Hz, 1H), 7.71 (t, \(J = 7.6\) Hz, 1H), 7.66 (dd, \(J = 7.5, 1.3\) Hz, 1H), 7.32 – 7.23 (m, 8H), 7.19 (dd, \(J = 7.9, 1.8\) Hz, 2H), 6.01 (d, \(J = 5.5\) Hz, 1H), 4.97 (d, \(J = 5.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.1, 158.7, 150.9, 138.0, 137.6, 137.4, 133.1, 132.2, 128.8, 128.8, 128.6, 128.5, 128.4, 127.6, 127.4, 126.4, 125.6, 119.7, 83.9, 52.3; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{19}\)ClNO\(_2\): [M+H]+, 386.0942. Found: m/z 386.0944.
mg, 50% yield); m. p. 174 – 176 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.96 (s, 1H), 8.02 (q, \(J = 5.2\) Hz, 1H), 7.61 – 7.53 (m, 2H), 7.33 – 7.22 (m, 8H), 7.18 (dd, \(J = 7.9, 1.8\) Hz, 2H), 5.99 (d, \(J = 5.6\) Hz, 1H), 4.94 (d, \(J = 5.6\) Hz, 1H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -111.3; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.3, 160.7 (d, \(J = 249.6\) Hz, \(J_{\text{CF}}\)), 157.2, 147.4, 139.5 (d, \(J = 5.6\) Hz, \(J_{\text{CF}}\)), 157.2, 147.4, 139.5 (d, \(J = 9.0\) Hz, \(J_{\text{CF}}\)), 128.8 (d, \(J = 2.1\) Hz, \(J_{\text{CF}}\)), 128.6, 128.5, 127.6, 126.4, 123.0 (d, \(J = 25.7\) Hz, \(J_{\text{CF}}\)), 119.7, 112.0 (d, \(J = 22.7\) Hz, \(J_{\text{CF}}\)), 84.1, 52.3; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)FNO\(_2\): [M+H]\(^+\), 370.1238. Found: m/z 370.1237.

8-Fluoro-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (12.6 mg, 34% yield); m. p. 216 – 218 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.11 (s, 1H), 8.10 (q, \(J = 5.2\) Hz, 1H), 7.68 – 7.59 (m, 2H), 7.30 – 7.26 (m, 3H), 7.16 – 7.04 (m, 5H), 6.70 (d, \(J = 7.1\) Hz, 2H), 6.11 (d, \(J = 3.2\) Hz, 1H), 4.72 (d, \(J = 3.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.1, 160.7 (d, \(J = 243.1\) Hz, \(J_{\text{CF}}\)), 158.5, 147.5, 140.0 (d, \(J = 5.4\) Hz, \(J_{\text{CF}}\)), 135.9, 134.6, 131.8 (d, \(J = 9.0\) Hz, \(J_{\text{CF}}\)), 129.5, 128.3, 128.2 (d, \(J = 2.1\) Hz, \(J_{\text{CF}}\)), 127.9, 127.5, 126.1, 123.4 (d, \(J = 28.6\) Hz, \(J_{\text{CF}}\)), 119.6, 112.1 (d, \(J = 24.2\) Hz, \(J_{\text{CF}}\)), 82.1, 53.5; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)FNO\(_2\): [M+H]\(^+\), 370.1238. Found: m/z 370.1237.

8-Chloro-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (18.0 mg, 47% yield); m. p. 181 – 183 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.92 (s, 1H), 7.97 (s, 1H), 7.94 (t, \(J = 3.8\) Hz, 1H), 7.35 – 7.21 (m, 8H), 7.16 – 7.04 (m, 5H), 5.98 (d, \(J = 5.7\) Hz, 1H), 4.93 (d, \(J = 5.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.1, 158.2, 148.6, 139.2, 138.0, 137.6, 133.5, 133.4, 130.9, 128.8, 128.6, 128.5, 127.6, 126.4, 119.8, 84.1, 52.4; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)ClNO\(_2\): [M+H]\(^+\), 386.0942. Found: m/z 386.0945.

8-Chloro-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. (9.8 mg, 25% yield); m. p. 202 – 203 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.07 (s, 1H), 8.04 (s, 1H), 8.01 (d, \(J = 2.4\) Hz, 1H), 7.28 (d, \(J = 2.5\) Hz, 2H), 7.16 – 7.05 (m, 6H), 6.73 – 6.68 (m, 2H), 6.10 (d, \(J = 3.2\) Hz, 1H), 4.72 (d, \(J = 3.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.9, 159.4, 148.7, 139.8, 135.9, 134.5, 133.8, 133.5, 130.8, 129.5, 128.3, 128.2, 128.2, 127.8, 127.8, 127.4, 126.1, 119.7, 82.1, 53.6; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)ClNO\(_2\): [M+H]\(^+\), 386.0942. Found: m/z 386.0945.
8-Bromo-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  (18.0 mg, 42% yield); m. p. 195 – 196 °C.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.92\) (s, 1H), 8.11 (d, \(J = 9.0\) Hz, 1H), 7.89 (d, \(J = 9.0, 2.0\) Hz, 1H), 7.32 – 7.22 (m, 8H), 7.17 (dd, \(J = 7.9, 1.8\) Hz, 2H), 5.98 (d, \(J = 5.7\) Hz, 1H), 4.93 (d, \(J = 5.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 164.1, 158.3, 148.8, 139.1, 138.0, 137.5, 136.0, 131.0, 128.8, 128.6, 128.5, 128.1, 127.6, 126.4, 121.4, 119.8, 84.0, 52.4; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)BrNO\(_2\): [M+H]\(^+\), 430.0437. Found: m/z 430.0441.

8-Bromo-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  (10.8 mg, 25% yield); m. p. 187 – 189 °C.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.06\) (s, 1H), 8.19 (d, \(J = 1.9\) Hz, 1H), 7.96 (d, \(J = 9.0\) Hz, 1H), 7.91 (dd, \(J = 9.0, 2.0\) Hz, 1H), 7.58 (t, \(J = 8.3\) Hz, 2H), 7.28 (d, \(J = 2.4\) Hz, 2H), 7.15 – 7.05 (m, 4H), 6.70 (d, \(J = 7.1\) Hz, 2H), 6.10 (d, \(J = 3.2\) Hz, 1H), 4.71 (d, \(J = 3.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 164.9, 159.6, 148.9, 139.7, 136.3, 135.8, 134.5, 132.6, 131.1, 130.8, 129.5, 128.3, 128.2, 127.5, 126.1, 121.6, 119.7, 82.1, 53.6; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{16}\)BrNO\(_2\): [M+H]\(^+\), 430.0437. Found: m/z 430.0438.

8-Methoxy-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.89\) (s, 1H), 7.90 (d, \(J = 9.2\) Hz, 1H), 7.43 (dd, \(J = 9.3, 2.6\) Hz, 1H), 7.32 – 7.21 (m, 7H), 7.14 – 7.03 (m, 3H), 5.96 (d, \(J = 5.4\) Hz, 1H), 4.91 (d, \(J = 5.4\) Hz, 1H), 3.93 (s, 3H).

8-Methoxy-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.02\) (s, 1H), 7.97 (d, \(J = 9.2\) Hz, 1H), 7.49 (dd, \(J = 9.2, 2.6\) Hz, 1H), 7.32 – 7.21 (m, 3H), 7.17 (d, \(J = 6.0\) Hz, 5H), 6.70 (d, \(J = 7.2\) Hz, 2H), 6.09 (d, \(J = 2.9\) Hz, 1H), 4.69 (d, \(J = 2.9\) Hz, 1H), 3.97 (s, 3H).

8-Methoxy-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.00\) (s, 1H), 7.90 (d, \(J = 9.2\) Hz, 1H), 7.43 (dd, \(J = 9.3, 2.6\) Hz, 1H), 7.32 – 7.21 (m, 3H), 7.17 (d, \(J = 6.0\) Hz, 5H), 6.70 (d, \(J = 7.2\) Hz, 2H), 6.09 (d, \(J = 2.9\) Hz, 1H), 4.69 (d, \(J = 2.9\) Hz, 1H), 3.97 (s, 3H).

8-Methoxy-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one.  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.02\) (s, 1H), 7.97 (d, \(J = 9.2\) Hz, 1H), 7.49 (dd, \(J = 9.2, 2.6\) Hz, 1H), 7.32 – 7.21 (m, 3H), 7.17 (d, \(J = 6.0\) Hz, 5H), 6.70 (d, \(J = 7.2\) Hz, 2H), 6.09 (d, \(J = 2.9\) Hz, 1H), 4.69 (d, \(J = 2.9\) Hz, 1H), 3.97 (s, 3H).

HRMS (ESI) Calcd. for C\(_{25}\)H\(_{19}\)NO\(_3\): [M+H]\(^+\), 382.1438. Found: m/z 382.1439.
7-Fluoro-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.00 (s, 1H), 8.01 – 7.93 (m, 1H), 7.65 (dd, $J = 9.9$, 2.0 Hz, 1H), 7.38 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.34 – 7.21 (m, 7H), 7.16 – 7.04 (m, 3H), 5.99 (d, $J = 5.6$ Hz, 1H), 4.94 (d, $J = 5.6$ Hz, 1H);

7-Fluoro-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.15 (s, 1H), 8.09 – 8.02 (m, 1H), 7.72 (dd, $J = 9.7$, 1.9 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.34 – 7.21 (m, 4H), 7.21 – 7.16 (m, 4H), 6.72 (d, $J = 7.2$ Hz, 2H), 6.10 (d, $J = 3.1$ Hz, 1H), 4.71 (d, $J = 3.1$ Hz, 1H);

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -102.7, -103.3.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.1 (d, $J = 234.7$ Hz, $J_{CF}$), 164.4, 164.1 (d, $J = 230.4$ Hz, $J_{CF}$), 160.4, 159.1, 151.7 (d, $J = 9.9$ Hz, $J_{CF}$), 151.5 (d, $J = 9.9$ Hz, $J_{CF}$), 140.6, 140.1, 138.1, 137.6, 135.9, 134.5, 131.8 (d, $J = 9.4$ Hz, $J_{CF}$), 131.6 (d, $J = 10.5$ Hz, $J_{CF}$), 129.5, 128.8, 128.6, 128.5, 128.3, 128.2, 127.6, 127.5, 126.4, 126.1, 124.4, 124.1, 118.5 (d, $J = 19.1$ Hz, $J_{CF}$), 118.3 (d, $J = 19.1$ Hz, $J_{CF}$), 113.3 (d, $J = 21.0$ Hz, $J_{CF}$), 113.1 (d, $J = 21.5$ Hz, $J_{CF}$), 83.9, 82.0, 53.6, 52.4.

HRMS (ESI) Calcd. for C$_{24}$H$_{16}$FNO$_2$: [M+H]$^+$, 370.1238. Found: m/z 370.1239.

7-Chloro-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.98 (s, 1H), 8.03 (d, $J = 1.5$ Hz, 1H), 7.90 (d, $J = 8.8$ Hz, 1H), 7.55 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.33 – 7.05 (m, 10H), 5.98 (d, $J = 5.8$ Hz, 1H), 4.93 (d, $J = 5.8$ Hz, 1H).

7-Chloro-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.13 (s, 1H), 8.09 (d, $J = 1.5$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 8.7$, 1.9 Hz, 1H), 7.33 – 7.05 (m, 8H), 6.71 (d, $J = 7.1$ Hz, 2H), 6.11 (d, $J = 3.2$ Hz, 1H), 4.72 (d, $J = 3.2$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 164.2, 160.4, 159.2, 150.6, 150.5, 140.5, 140.0, 139.3, 138.9, 137.9, 137.5, 135.9, 134.5, 130.5, 129.5, 128.9, 128.7, 128.6, 128.5, 128.3, 128.3, 128.2, 128.2, 127.6, 127.5, 126.4, 126.1, 125.6, 125.3, 119.1, 119.0, 83.9, 82.0, 53.6, 52.4.

HRMS (ESI) Calcd. for C$_{24}$H$_{16}$ClNO$_2$: [M+H]$^+$, 386.0942. Found: m/z 386.0941.
(34.8 mg, 81% yield)

7-Bromo-trans-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.98 (s, 1H), 8.23 (s, 1H), 7.82 (d, $J$ = 8.7 Hz, 1H), 7.68 (dd, $J$ = 8.7, 1.6 Hz, 1H), 7.34 – 7.21 (m, 7H), 7.16 – 7.04 (m, 3H), 5.98 (d, $J$ = 5.8 Hz, 1H), 4.93 (d, $J$ = 5.8 Hz, 1H).

7-Bromo-cis-3,4-diphenyl-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.12 (s, 1H), 8.29 (s, 1H), 7.90 (d, $J$ = 8.7 Hz, 1H), 7.73 (dd, $J$ = 8.7, 1.6 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.20 – 7.16 (m, 4H), 6.71 (d, $J$ = 7.2 Hz, 2H), 6.11 (d, $J$ = 3.1 Hz, 1H), 4.71 (d, $J$ = 3.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.0, 164.2, 160.3, 159.1, 150.7, 150.6, 140.6, 140.1, 137.9, 137.5, 135.8, 134.5, 131.8, 131.7, 131.3, 131.2, 130.4, 130.3, 129.5, 128.8, 128.6, 128.5, 128.3, 128.2, 128.2, 127.8, 127.6, 127.5, 127.5, 126.5, 126.1, 125.8, 125.6, 119.2, 119.2, 83.9, 81.97, 53.6, 52.4; HRMS (ESI) Calcd. for C$_{24}$H$_{16}$BrNO$_2$: [M+H]$^+$, 430.0437. Found: m/z 430.0438.

$^{3ka}$, 20% dr.

60:40

trans-7,8-Diphenyl-7,8-dihydro-5H-pyrano[4,3-b]pyridin-5-one. White solid (3.6 mg, 12% yield); m. p. 159 – 160 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.74 (dd, $J$ = 4.74, 1.60 Hz, 1H), 8.46 (dd, $J$ = 7.89, 1.69 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 7.30 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 7.11 – 7.02 (m, 2H), 5.81 (d, $J$ = 7.68 Hz, 1H), 4.74 (d, $J$ = 7.38 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.2, 160.2, 154.7, 137.9, 137.6, 137.3, 129.3, 129.1, 128.8, 128.5, 128.4, 127.7, 126.7, 123.2, 84.6, 52.5; HRMS (ESI) Calcd. for C$_{20}$H$_{15}$NO$_2$: [M+H]$^+$, 302.1176. Found: m/z 302.1174.

cis-7,8-Diphenyl-7,8-dihydro-5H-pyrano[4,3-b]pyridin-5-one. White solid (2.4 mg, 8% yield); m. p. 186 – 187 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (dd, $J$ = 4.79, 1.58 Hz, 1H), 8.56 (dd, $J$ = 7.87, 1.62, 1H), 7.48 (q, $J$ = 4.87 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.16 – 7.05 (m, 5H), 6.72 – 6.67 (m, 2H), 6.05 (d, $J$ = 3.52 Hz, 1H), 4.55 (d, $J$ = 3.52 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.1, 161.2, 154.9, 138.2, 136.0, 134.3, 129.4, 128.2, 128.2, 128.1, 127.5, 126.1, 123.6, 121.2, 82.1, 53.0; HRMS (ESI) Calcd. for C$_{20}$H$_{15}$NO$_2$: [M+H]$^+$, 302.1176. Found: m/z 302.1172.
4. Control experiments

(a) Under no O\(_2\) and H\(_2\)O reaction conditions

\[
\text{Ph-} + \text{Ph} \quad [\text{Cp*RhCl}_2]^2 (5 \text{ mol\%}) \quad \text{AgSbF}_6 (20 \text{ mol\%}) \quad \text{KOAc (0.5 equiv)} \quad \text{DCE, N}_2, 80 ^\circ \text{C, 12 h}
\]

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
\text{2a} & \quad 3aa, 94\%
\end{align*}
\]

\([\text{Cp*RhCl}_2]^2 (0.005 \text{ mmol, 3.1 mg, 5 mol\%}), \text{AgSbF}_6 (0.02 \text{ mmol, 6.9 mg, 20 mol\%}), \text{KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), 1a} (0.18 \text{ mmol, 1.8 equiv}) \text{ and 2a} (0.1 \text{ mmol, 1.0 equiv}) \text{ were weighted and placed in a dried Schlenk tube. Then} 2.0 \text{ mL of anhydrous DCE was added. The reaction mixture was stirred at} 80 ^\circ \text{C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product 3aa was obtained in 94\% yield, indicating that external oxygen and water are no necessary for this reaction.}

(b) \(d\)-Incorporation reaction

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{1a, 0.09 mmol} & \quad \text{1a-}d_2, 0.09 \text{ mmol} & \quad \text{2a, 0.1 mmol}
\end{align*}
\]

\[
\begin{align*}
\text{trans-}d-3aa, 24\% & + \quad \text{cis-}d-3aa, 13\% \\
\text{D} & \quad \text{D} & \quad \text{D} & \quad \text{D}
\end{align*}
\]

\([\text{Cp*RhCl}_2]^2 (0.005 \text{ mmol, 3.1 mg, 5 mol\%}), \text{AgSbF}_6 (0.02 \text{ mmol, 6.9 mg, 20 mol\%}), \text{KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), 1a-}d_2 (0.09 \text{ mmol, 0.9 equiv}), \text{1a} (0.09 \text{ mmol, 0.9 equiv}) \text{ and 2a} (0.1 \text{ mmol, 1.0 equiv}) \text{ were weighted and placed in same dried Schlenk tube. Then} 2.0 \text{ mL of anhydrous DCE was added. The reaction mixture was stirred at} 80 ^\circ \text{C for 4 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford \(d\)-3aa (trans) and \(d\)-3aa (cis) in 24\% and 13\% yield, and \(d\)-incorporation occurred at the two C\(_{sp3}\)-H, suggesting that two C\(_{sp3}\)-H in the products are partially derived from the ortho C-H of the carboxylic acid. The \(d\)-incorporation was calculated from \(^1\text{H NMR spectrum\)}. (see the following \(^1\text{H NMR spectrum\)}. \)
$^1$H NMR spectrum of compound 3aa (trans)

$^1$H NMR spectrum of compound 3aa (cis)
(c) $d$-Incorporation reaction

$$\text{[Cp}^*\text{RhCl}_2]_2 (0.005 \text{ mmol, 3.1 mg, 5 mol\%}), \text{ AgSbF}_6 (0.02 \text{ mmol, 6.9 mg, 20 mol\%}), \text{ KOAc (0.05 mmol, 4.9 mg, 0.5 equiv)}, 1a-d (0.18 \text{ mmol, 1.8 equiv}) \text{ and } 2a (0.1 \text{ mmol, 1.0 equiv}) \text{ were weighted and placed in a dried Schlenk tube. Then 2.0 mL of anhydrous DCE was added. The reaction mixture was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford $d$-incorporation on the three positions of $d$-3aa (trans) and $d$-3aa (cis), indicates that two C$_{sp3}$-H in the products are partially derived from carboxylic acid. The $d$-incorporation was calculated from $^1\text{H NMR}$ spectrum (see the following $^1\text{H NMR}$ spectrum).}

$^1\text{H NMR}$ spectrum of compound 3aa (trans)
(d) Under the reaction conditions of 1,2-dichloroethane–$d_4$ as solvent

\[
\begin{array}{c}
\text{1a} & + & \text{2a} \\
\text{[Cp*RhCl}_2\text{]} & (0.005 \text{ mmol, 3.1 mg, 5 mol\%}) & \text{AgSbF}_6 & (0.02 \text{ mmol, 6.9 mg, 20 mol\%}) & \text{KOAc} & (0.05 \text{ mmol, 4.9 mg, 0.5 equiv}), \ \text{1a} & (0.18 \text{ mmol, 1.8 equiv}) & \text{and} & \text{2a} & (0.1 \text{ mmol, 1.0 equiv})
\end{array}
\]

were weighted and placed in a dried Schlenk tube. Then 0.77 mL of 1,2-dichloroethane–$d_4$ was added. The reaction mixture was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (PE/EA/DCM = 100/20/3 mL) to afford the desired product 3aa was obtained in 62% yield, and no $d$-incorporation occurred at the two C$_{sp3}$-H.

5. Mechanistic studies

Possible intermediate detection in reaction system

To a dried Schlenk tube was added [Cp*RhCl$_2$]$_2$ (0.005 mmol, 3.1 mg, 5 mol%), AgSbF$_6$ (0.02 mmol, 6.9 mg, 20 mol%), KOAc (0.05 mmol, 4.9 mg, 0.5 equiv), quinolone-3-carboxylic acids (0.18 mmol, 1.8 equiv), alkynes (0.1 mmol, 1.0 equiv) in DCE (2.0 mL) under air. The reaction mixture was stirred at 80 °C for 4 h, and then
cooled down to room temperature. The reaction solution is detected by high resolution mass spectrometry. Calculated Mass for C_{24}H_{17}NO_{2}: 351.1259. Found Mass in HRMS-ESI: 350.1186 [M-H⁺] (see the following HRMS spectrum).

6. X-Ray Crystallographic Data of 3aa and 3ap

X-Ray Crystallographic Data of 3aa (trans)
**Single-crystal X-Ray Molecular Structure of 3aa (trans)**

The structure of 3aa (trans) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850247.

**Table S1 Crystal data and structure refinement for 3aa (trans).**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
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</tr>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{17}NO_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>351.38</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
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<tr>
<td>Space group</td>
<td>P-1</td>
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<tr>
<td>a/Å</td>
<td>11.0804(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.2799(5)</td>
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<tr>
<td>c/Å</td>
<td>13.6018(4)</td>
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<td>β/°</td>
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<td>γ/°</td>
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<td>Volume/Å³</td>
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<td>F(000)</td>
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<td>Crystal size/mm³</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å⁻³</td>
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X-Ray Crystallographic Data of 3aa (cis)

The structure of 3aa (cis) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850250.

Table S2 Crystal data and structure refinement for 3aa (cis).

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<tr>
<th>Identification code</th>
<th>3aa (cis)</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{17}NO_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>351.38</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2_{1}/c</td>
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<td>a/Å</td>
<td>8.5534(8)</td>
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<td>c/Å</td>
<td>37.5979(18)</td>
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<td>α/°</td>
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<td>Volume/Å³</td>
<td>1763.7(2)</td>
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<td>Z</td>
<td>4</td>
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X-Ray Crystallographic Data of 3ap (trans)

The structure of 3ap (trans) was determined by the X-ray diffraction. Recrystallized from chloroform/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1850256.
Table S3 Crystal data and structure refinement for 3ap (trans).

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<tbody>
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<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>c/Å</td>
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<td>α/°</td>
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<td>85.566(5)</td>
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<td>γ/°</td>
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<td>Volume/Å^{3}</td>
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<td>F(000)</td>
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<td>Crystal size/mm^{3}</td>
<td>0.12 \times 0.11 \times 0.09</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
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<tr>
<td>2Θ range for data collection/°</td>
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<td>Index ranges</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Goodness-of-fit on F^{2}</td>
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<td>Final R indexes [I \geq 2σ (I)]</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å^{-3}</td>
<td>0.39/-0.38</td>
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</table>

7. References


8. NMR spectra of the substrates and products

$^1$H NMR spectrum of compound 1b

$^{19}$F NMR spectrum of compound 1b
\( ^{13}\text{C} \) NMR spectrum of compound 1b

\( ^{1}\text{H} \) NMR spectrum of compound 1c
$^{13}$C NMR spectrum of compound 1c

$^1$H NMR spectrum of compound 1d
$^{19}$F NMR spectrum of compound 1d

$^{13}$C NMR spectrum of compound 1d
$^1$H NMR spectrum of compound 1e

$^{13}$C NMR spectrum of compound 1e
$^1$H NMR spectrum of compound 1f

$^{13}$C NMR spectrum of compound 1f
$^1$H NMR spectrum of compound 1g

$^{13}$C NMR spectrum of compound 1g
$^1$H NMR spectrum of compound 1h

$^{19}$F NMR spectrum of compound 1h
$^{13}$C NMR spectrum of compound 1h

$^1$H NMR spectrum of compound 1i
$^{13}$C NMR spectrum of compound 1i

$^1$H NMR spectrum of compound 1j
$^{13}$C NMR spectrum of compound 1j

$^1$H NMR spectrum of compound 3aa (trans)
\[ ^{13}\text{C} \text{NMR spectrum of compound 3aa (trans)} \]

\[ ^{1}\text{H} \text{NMR spectrum of compound 3aa (cis)} \]
$^{13}$C NMR spectrum of compound 3aa (cis)

$^1$H NMR spectrum of compound 3ab (trans)
$^{19}$F NMR spectrum of compound 3ab (trans)

$^{13}$C NMR spectrum of compound 3ab (trans)
$^1$H NMR spectrum of compound 3ab (cis)

$^{19}$F NMR spectrum of compound 3ab (cis)
$^{13}$C NMR spectrum of compound 3ab (cis)

$^1$H NMR spectrum of compound 3ac (trans)
$^{13}$C NMR spectrum of compound 3ac (trans)

$^1$H NMR spectrum of compound 3ac (cis)
\[ ^{13}\text{C} \text{NMR spectrum of compound 3ac (cis)} \]

\[ ^{1}\text{H} \text{NMR spectrum of compound 3ad (trans)} \]
$^{13}$C NMR spectrum of compound 3ad (trans)

$^1$H NMR spectrum of compound 3ad (cis)
$^{13}$C NMR spectrum of compound 3ad (cis)

$^1$H NMR spectrum of compound 3ae (trans)
$^{13}$C NMR spectrum of compound 3ae (trans)

$^1$H NMR spectrum of compound 3ae (cis)
$^{13}$C NMR spectrum of compound 3ae (cis)

$^1$H NMR spectrum of compound 3af (trans)
$^{13}$C NMR spectrum of compound 3af (trans)

$^1$H NMR spectrum of compound 3af (cis)
$^{13}$C NMR spectrum of compound 3af (cis)

$^1$H NMR spectrum of compound 3ag (trans)
$^{19}$F NMR spectrum of compound 3ag (trans)

$^{13}$C NMR spectrum of compound 3ag (trans)
$^1$H NMR spectrum of compound 3ag (cis)

$^{19}$F NMR spectrum of compound 3ag (cis)
$^{13}$C NMR spectrum of compound 3ag (cis)

$^1$H NMR spectrum of compound 3ah (trans)
$^{19}$F NMR spectrum of compound 3ah (trans)

$^{13}$C NMR spectrum of compound 3ah (trans)
$^1$H NMR spectrum of compound 3ah (cis)

$^{19}$F NMR spectrum of compound 3ah (cis)
$^{13}$C NMR spectrum of compound 3ah (cis)

$^1$H NMR spectrum of compound 3ai (trans)
$^{13}$C NMR spectrum of compound 3ai (trans)

$^1$H NMR spectrum of compound 3ai (cis)
$^{13}$C NMR spectrum of compound 3ai (cis)

$^1$H NMR spectrum of compound 3aj (trans)
$^{13}$C NMR spectrum of compound 3aj (trans)

$^1$H NMR spectrum of compound 3aj (cis)
$^{13}$C NMR spectrum of compound 3aj (cis)

$^1$H NMR spectrum of compound 3ak (trans)
$^{13}$C NMR spectrum of compound 3ak (trans)

$^1$H NMR spectrum of compound 3ak (cis)
$^{13}$C NMR spectrum of compound 3ak (cis)

$^1$H NMR spectrum of compound 3al (trans)
$^{13}\text{C}$ NMR spectrum of compound 3al (trans)

$^{1}\text{H}$ NMR spectrum of compound 3al (cis)
$^{13}$C NMR spectrum of compound 3al (cis)

$^1$H NMR spectrum of compound 3am (trans)
$^{19}$F NMR spectrum of compound 3am (trans)

$^{13}$C NMR spectrum of compound 3am (trans)
\(^1\)H NMR spectrum of compound 3am (cis)

\(^19\)F NMR spectrum of compound 3am (cis)
$^{13}$C NMR spectrum of compound 3am (cis)

$^1$H NMR spectrum of compound 3an (trans)
$^{13}$C NMR spectrum of compound 3an (trans)

$^1$H NMR spectrum of compound 3an (cis)
$^{13}$C NMR spectrum of compound 3an (cis)

$^1$H NMR spectrum of compound 3ao
$^{13}$C NMR spectrum of compound 3ao

$^1$H NMR spectrum of compound 3ap
$^{19}$F NMR spectrum of compound 3ap

$^{13}$C NMR spectrum of compound 3ap
$^1$H NMR spectrum of compound 3aq (trans)

$^{19}$F NMR spectrum of compound 3aq (trans)
$^{13}$C NMR spectrum of compound 3aq (trans)

$^1$H NMR spectrum of compound 3aq (cis)
$^{19}\text{F NMR}$ spectrum of compound 3aq (cis)

$^{13}\text{C NMR}$ spectrum of compound 3aq (cis)
$^1$H NMR spectrum of compound 3ar (trans)

$^{13}$C NMR spectrum of compound 3ar (trans)
$^{1}H$ NMR spectrum of compound 3ar (cis)

$^{13}C$ NMR spectrum of compound 3ar (cis)
$^1$H NMR spectrum of compound 3as (trans)

$^{13}$C NMR spectrum of compound 3as (trans)
$^1$H NMR spectrum of compound 3as (cis)

$^{13}$C NMR spectrum of compound 3as (cis)
$^1$H NMR spectrum of compound 3at

$^{13}$C NMR spectrum of compound 3at
\[ ^1H \text{ NMR spectrum of compound 3ba (trans)} \]

\[ ^19F \text{ NMR spectrum of compound 3ba (trans)} \]
$^{13}$C NMR spectrum of compound 3ba (trans)

$^1$H NMR spectrum of compound 3ba (cis)
$^{19}$F NMR spectrum of compound 3ba (cis)

$^{13}$C NMR spectrum of compound 3ba (cis)
$^1$H NMR spectrum of compound 3ca (trans)

$^{13}$C NMR spectrum of compound 3ca (trans)
$^1$H NMR spectrum of compound 3ca (cis)

$^{13}$C NMR spectrum of compound 3ca (cis)
$^1$H NMR spectrum of compound 3da (trans)

$^{19}$F NMR spectrum of compound 3da (trans)
$^{13}$C NMR spectrum of compound 3da (trans)

$^1$H NMR spectrum of compound 3da (cis)
$^1$H NMR spectrum of compound 3da (cis)

$^1$C NMR spectrum of compound 3da (cis)
$^1$H NMR spectrum of compound 3ea (trans)

$^{13}$C NMR spectrum of compound 3ea (trans)
$^1$H NMR spectrum of compound 3ea (cis)

$^{13}$C NMR spectrum of compound 3ea (cis)
$^1$H NMR spectrum of compound 3fa (trans)

$^{13}$C NMR spectrum of compound 3fa (trans)
\(^1\text{H NMR spectrum of compound 3fa (cis)}\)

\(^{13}\text{C NMR spectrum of compound 3fa (cis)}\)
\(^1\)H NMR spectrum of compound 3ga

\(^{13}\)C NMR spectrum of compound 3ga
$^1$H NMR spectrum of compound 3ha

$^{19}$F NMR spectrum of compound 3ha
$^{13}\text{C}$ NMR spectrum of compound 3ha

$^{1}\text{H}$ NMR spectrum of compound 3ia
\(^{13}\)C NMR spectrum of compound 3ia

\(^{1}\)H NMR spectrum of compound 3ja
$^{13}$C NMR spectrum of compound 3ja

$^1$H NMR spectrum of compound 3ka (trans)
$^{13}$C NMR spectrum of compound 3ka (trans)

$^1$H NMR spectrum of compound 3ka (cis)
$^{13}$C NMR spectrum of compound 3ka (cis)