Supporting Information

Gold(I) Catalyzed Tandem Cyclization of Propargylic Esters to 4-acyloxy-1,2-dihydroquinolines

YuanMing Sun,* Peng Gu,* YuNing Gao,* Qin Xu,* and Min Shi* a,b

a Laboratory for Advanced Materials & Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China, b Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China.
mshi@mail.sioc.ac.cn

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1. **General Remarks.** Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined in a solution of CH$_2$Cl$_2$ at 20 °C by using a Perkin-Elmer-241 MC polarimeter; [α]$_D$-values are given in units of 10$^{-1}$ deg cm$^2$ g$^{-1}$. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (¹H NMR), 100 MHz (¹³C NMR) and 376 MHz (¹⁹F NMR) in CDCl$_3$, respectively. Chemical shift were reported in ppm down field from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF$_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. The optical purities of products were determined by HPLC analysis using a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, and OD-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm$^{-1}$. Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument.
2. Preparation of substrates

(a) Synthesis of 1a-1j, 1l and 1n-1z

Typical procedures:

N-protected 2-iodoanilines S1 were partially prepared according to the previous literature.[1] Propargylic alcohols S2 were prepared according to the previous literature.[2]

Sonogashira coupling:

A round bottle was filled with Pd(PPh₃)₂Cl₂ (2 mol%) and CuI (5 mol%), then a solution of S1 (10 mmol) and S2 (11 mmol) in degassed Et₃N (40 mL) was added to this bottle under argon. The reaction mixture was stirred at room temperature overnight. The reaction was filtered with a Celite and filter residue was washed with EtOAc for three times. The filtrate was combined and solvent was removed under reduced pressure. The residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1).

Synthesis of propargylic esters:

To a stirred solution of S3 (2 mmol) in DCM (20 mL) was slowly added PivCl (2.2 mmol) or AcCl (2.2 mmol) at 0 °C under argon and the mixture was allowed to be warmed to room temperature slowly. Upon consumption of the starting material, the reaction mixture was quenched with saturated NaHCO₃ aqueous solution and extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1).

(b) Synthesis of 1k.
To an anhydrous THF (20 mL) a solution of S4 (1.46 g, 10 mmol) was added NaH (60% dispersion in mineral oil, 440 mg, 11 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 30 minutes. Then PivCl (11 mmol) was added. After that, the reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was quenched with water, extracted with EtOAc, washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by a column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1) to afford S5 (1.06 g, 46% yield). S5 (2.0 mmol) was used for synthesizing 1k under the previously mentioned Sonogashira coupling conditions (160 mg, 38% yield).

(c) Synthesis of 1m.

A round bottle was filled with Pd(PPh₃)₂Cl₂ (2 mol%) and CuI (5 mol%), then Et₃N (30 mmol), trimethylsilylacetylene (11 mmol) and a solution of S1a (10 mmol) in degassed THF (40 mL) was added to this bottle under argon. The reaction mixture was stirred at room temperature overnight. The reaction was filtered with a Celite and filter residue was washed with EtOAc for three times. The filtrate was combined and solvent was removed under reduce pressure to afford the crude product. K₂CO₃ (20 mmol) was added to a solution of the crude product in MeOH (20 mL). The mixture was stirred at room temperature for three hours, and then the solvent was removed under reduce pressure. The residue was redissolved in EtOAc and water, and then extracted with EtOAc for three times. The solvent was evaporated in vacuo and the residue was purified by a column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1) to afford S6 (1.80 g, 83% yield for 2 steps).

S6 (5 mmol, 1.08 g) was dissolved in 25 mL of dry THF in a round-bottomed flask. After the mixture was cooled to -78 °C, a 2.5 M solution of BuLi in hexanes (11 mmol, 4.4 mL) was added dropwise. The temperature was maintained for 1 h with stirring. The trans-2-hexenal (5 mmol, 490
mg) was then added slowly, and stirring was continued overnight, allowing the reaction mixture to be warmed to room temperature slowly without additional cooling. After completion, the reaction was quenched with a saturated NH$_4$Cl solution and extracted with EtOAc. This was followed by isolation of the corresponding product by flash column chromatography (eluent: petroleum ether / ethyl acetate = 10:1) to afford S7 (1.23 g, 78% yield). Acylation reaction of S7 (2 mmol) was identical to the other compounds, affording 1m (694 mg, 87% yield).

3. The characterization data of substrates

3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-phenylprop-2-yn-1-yl acetate (1a): A yellow oil, 635 mg, 87% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.14 (d, $J = 8.4$ Hz, 1H), 7.61-7.59 (m, 2H), 7.45-7.37 (m, 4H), 7.32 (td, $J_1 = 1.2$ Hz, $J_2 = 8.4$ Hz, 1H), 7.23 (br, 1H), 6.95 (td, $J_1 = 1.2$ Hz, $J_2 = 8.4$ Hz, 1H), 6.68 (s, 1H), 2.15 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.8, 152.4, 140.2, 136.7, 131.9, 130.2, 129.1, 128.8, 127.7, 121.9, 117.6, 109.8, 92.5, 82.6, 80.7, 66.2, 28.2, 21.0. IR (CH$_2$Cl$_2$) $\nu$ 3405, 2978, 1733, 1579, 1449, 1368, 1305, 1305, 1222, 1155, 1043, 1022, 952, 756, 697 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{23}$NNaO$_4$$^+$ (M+Na)$^+$ requires: 388.1519, Found: 388.1516.
3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-(3-chlorophenyl)prop-2-yn-1-yl acetate (1b): A yellow oil, 694 mg, 87% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.15 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 2.4$ Hz, 1H), 7.49-7.47 (m, 1H), 7.41-7.31 (m, 4H), 7.17 (br, 1H), 6.96 (td, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz, 1H), 6.64 (s, 1H), 2.16 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.6, 152.3, 140.2, 138.6, 134.7, 132.0, 130.4, 130.1, 129.3, 127.3, 125.7, 122.0, 117.7, 109.5, 91.7, 83.1, 80.8, 65.4, 28.2, 21.0. IR (CH$_2$Cl$_2$) $\nu$ 3407, 2978, 1731, 1598, 1578, 1515, 1476, 1447, 1367, 1304, 1218, 1192, 1151, 1116, 1043, 1016, 959, 875, 831, 755, 732, 689 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{22}$NNaO$_4$Cl$^{+1}$ (M+Na)$^+$ requires: 422.1130, Found: 422.1126.
3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl acetate (1c): A yellow oil, 719 mg, 91% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.14 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.40 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.32 (td, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.23 (br, 1H), 6.97-6.92 (m, 3H), 6.63 (s, 1H), 3.83 (s, 3H), 2.13 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 160.2, 152.4, 140.2, 131.9, 130.2, 129.3, 128.9, 121.9, 117.6, 114.1, 109.9, 92.7, 82.4, 80.7, 65.9, 55.3, 28.2, 21.1. IR (CH$_2$Cl$_2$) v 3403, 2976, 1731, 1611, 1579, 1514, 1447, 1367, 1305, 1221, 1153, 1012, 943, 900, 828, 801, 755, 735, 703 cm$^{-1}$. HRMS (ESI) Calcd.
for $C_{23}H_{25}NNaO_{5}^{+1}$ (M+Na)$^+$ requires: 418.1625, Found: 418.1623.

**3-(2-(tert-Butoxycarbonyl)amino)phenyl)-1-(naphthalen-1-yl)prop-2-yn-1-yl acetate (1d):** A yellow solid, 689 mg, 83% yield, m. p. 58-60 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.26 (d, $J = 8.0$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.92-7.87 (m, 3H), 7.62-7.49 (m, 3H), 7.38 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz, 1H), 7.32-7.28 (m, 2H), 7.19 (br, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 2.16 (s, 3H), 1.50 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 152.4, 140.1, 134.0, 132.0, 131.8, 130.4, 130.2, 130.1,
129.0, 126.9, 126.6, 126.1, 125.2, 123.5, 121.9, 117.7, 109.9, 92.4, 83.1, 80.7, 64.6, 28.2, 21.0. IR (CH$_2$Cl$_2$) $\nu$ 3403, 2978, 1729, 1578, 1514, 1392, 1367, 1304, 1218, 1150, 1116, 1045, 1010, 945, 898, 858, 832, 775, 754 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{25}$NNaO$_4$ (M+Na)$^+$ requires: 438.1676, Found: 438.1672.

3-2-((tert-Butoxycarbonyl)amino)phenyl-1-(4-bromophenyl)prop-2-yln-yl acetate (1e): A yellow oil, 666 mg, 75% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.14 (d, $J$ = 8.0 Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 2H), 7.47 (d, $J$ = 8.0 Hz, 2H), 7.39 (d, $J$ = 7.6 Hz, 1H), 7.33 (t, $J$ = 7.6 Hz, 1H ), 7.17
(br, 1H), 6.95 (t, \(J = 7.6\) Hz, 1H), 6.62 (s, 1H), 2.15 (s, 3H), 1.53 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.6, 152.2, 140.2, 135.7, 132.0, 131.9, 130.4, 129.3, 123.2, 122.0, 117.6, 109.5, 91.9, 82.9, 80.8, 65.5, 28.2, 21.0. IR (CH\(_2\)Cl\(_2\)) v 3406, 2978, 1733, 1578, 1516, 1487, 1448, 1393, 1368, 1305, 1221, 1154, 1043, 1012, 954, 819, 756, 729 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{22}\)H\(_{22}\)BrNaO\(_4\)\(^{+}\)(M+Na)\(^{+}\) requires: 466.0624, Found: 466.0621.

3-(2-(\textit{tert}-Butoxycarbonyl)amino)-5-methylphenyl)-1-phenylprop-2-yn-1-yl acetate (1f): A
yellow oil, 652 mg, 86% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.00 (d, $J = 8.8$ Hz, 1H), 7.61-7.59 (m, 2H), 7.45-7.37 (m, 3H), 7.21 (d, $J = 1.2$ Hz, 1H), 7.14-7.12 (m, 2H), 6.67 (s, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 1.52 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.8, 152.5, 137.8, 136.8, 132.2, 131.5, 131.0, 129.1, 128.8, 127.7, 117.7, 109.8, 82.1, 82.9, 80.5, 66.2, 28.3, 21.1, 20.4. IR (CH$_2$Cl$_2$) υ 3408, 2979, 2928, 1730, 1585, 1516, 1474, 1455, 1367, 1303, 1266, 1240, 1219, 1153, 1050, 1023, 953, 898, 823, 762, 736, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{25}$NNaO$_4$+ (M+Na)$^+$ requires: 402.1676, Found: 402.1674.
3-(5-Bromo-2-((tert-butoxycarbonyl)amino)phenyl)-1-phenylprop-2-yn-1-yl acetate (1g): A yellow oil, 808 mg, 91% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.06 (d, $J = 9.2$ Hz, 1H), 7.59-7.57 (m, 2H), 7.51 (d, $J = 2.0$ Hz, 1H), 7.46-7.39 (m, 4H), 7.18 (br, 1H), 6.64 (s, 1H), 2.15 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.7, 152.1, 139.4, 136.3, 134.1, 133.1, 129.2, 128.9, 127.6, 119.1, 113.9, 111.6, 93.6, 81.2, 81.1, 66.0, 28.2, 21.0. IR (CH$_2$Cl$_2$) $\nu$ 3406, 2978, 1733, 1571, 1509, 1456, 1400, 1368, 1301, 1221, 1152, 1082, 1049, 1019, 954, 898, 823, 801, 759, 731, 697 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{22}$BrNNaO$_4$ $^{+1}$ (M+Na)$^+$ requires: 466.0624, Found: 466.0622.
3-(2-((tert-Butoxycarbonyl)amino)-5-fluorophenyl)-1-phenylprop-2-yn-1-yl acetate (1h): A yellow oil, 582 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.10 (dd, $J_1 = 1.2$ Hz, $J_2 = 8.8$ Hz, 1H), 7.60-7.58 (m, 2H), 7.46-7.38 (m, 3H), 7.12-7.01 (m, 3H), 6.65 (s, 1H), 2.11 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.7, 157.2 (d, $J = 241.3$ Hz), 152.4, 136.6 (d, $J = 2.9$ Hz), 136.3, 129.2, 128.9, 119.4 (d, $J = 8.0$ Hz), 118.0 (d, $J = 24.1$ Hz), 117.2 (d, $J = 21.9$ Hz), 111.1 (d, $J = 8.7$ Hz), 93.2, 81.5 (d, $J = 2.9$ Hz), 80.8, 66.0, 28.2, 21.0. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -120.7. IR (CH$_2$Cl$_2$) $\nu$ 3412, 2979, 1733, 1519, 1456, 1421, 1393, 1369, 1294, 1224, 1157, 1117, 1050, 1023, 958, 869, 822, 762, 738, 710, 697 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{22}$FNNaO$_4$ $^{+1}$ (M+Na)$^+$ requires: 406.1425, Found: 406.1421.
3-(2-((tert-Butoxycarbonyl)amino)-5-(trifluoromethyl)phenyl)-1-phenylprop-2-yn-1-yl acetate (II): A yellow oil, 736 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.31 (d, $J$ = 8.8 Hz, 1H), 7.65 (d, $J$ = 2.0 Hz, 1H), 7.60-7.58 (m, 2H), 7.57 (dd, $J_1$ = 1.6 Hz, $J_2$ = 8.8 Hz, 1H), 7.47-7.41 (m, 3H), 7.38 (br, 1H), 6.65 (s, 1H), 2.16 (s, 3H), 1.54 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 152.0, 143.1, 136.3, 129.3, 129.1 (q, $J$ = 3.6 Hz), 127.8, 127.7, 127.1 (q, $J$ = 3.8 Hz), 124.1 (q, $J$ = 32.9 Hz), 123.8 (q, $J$ = 269.6 Hz), 117.4, 110.0, 93.9, 81.6, 81.2, 66.1, 28.2, 21.1. $^{19}$F NMR
(376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -62.2. IR (CH$_2$Cl$_2$) $\nu$ 3402, 2980, 2933, 1739, 1619, 1587, 1527, 1474, 1457, 1425, 1394, 1369, 1334, 1310, 1256, 1224, 1154, 1124, 1078, 1022, 957, 900, 840, 811, 763, 697 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{22}$FNNaO$_4$F$_3$ $^{+1}$ (M+Na)$^+$ requires: 456.1393, Found: 456.1391.
3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-phenylprop-2-yn-1-yl pivalate (1j): A yellow oil, 732 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.16 (d, $J = 8.4$ Hz, 1H), 7.59-7.56 (m, 2H), 7.44-7.36 (m, 4H), 7.31 (td, $J_1 = 1.4$ Hz, $J_2 = 8.4$ Hz, 1H), 7.23 (br, 1H), 6.94 (td, $J_1 = 0.8$ Hz, $J_2 = 7.6$ Hz, 1H), 6.66 (s, 1H), 1.53 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.2, 152.4, 140.1, 137.0, 131.9, 130.1, 128.9, 128.7, 127.3, 121.9, 117.6, 110.0, 92.7, 82.3, 80.7, 65.9, 38.8, 28.3, 27.0. IR (CH$_2$Cl$_2$) ν 3406, 2977, 1733, 1580, 1517, 1478, 1448, 1393, 1368, 1280, 1238, 1154, 1043, 1026, 939, 755, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{29}$NNaO$_4$+$^{+}$ (M+Na)$^+$ requires: 430.1989, Found: 430.1986.
4-(2-((tert-Butyloxycarbonyl)amino)phenyl)-2-phenylbut-3-yn-2-yl pivalate (1k): A yellow solid, 160 mg, 38% yield, m. p. 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.20 (d, $J = 8.4$ Hz, 1H), 7.62-7.61 (m, 3H), 7.43-7.32 (m, 5H), 6.95 (d, $J = 7.6$ Hz, 1H), 1.99 (s, 3H), 1.50 (s, 9H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.9, 152.9, 142.8, 140.8, 131.8, 129.9, 128.4, 127.8, 124.8, 121.7, 117.8, 110.3, 95.3, 82.6, 80.3, 75.4, 39.1, 31.6, 28.3, 27.1. IR (EtOH) $\nu$ 3340, 2979, 2932, 2869, 2218, 1719, 1583, 1515, 1447, 1367, 1299, 1245, 1143, 1053, 860, 753, 745, 701 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{31}$NNaO$_4$+$^+$ (M+Na)$^+$ requires 442.2145, Found: 442.2145.
1-(2-((tert-Butoxycarbonyl)amino)phenyl)oct-1-yn-3-yl pivalate (1l): A yellow oil, 738 mg, 92% yield. $^1$H NMR (400 MHz, CDCl₃, TMS) δ 8.15 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.24 (br, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 5.57 (t, $J = 7.2$ Hz, 1H), 1.91-1.86 (m, 2H), 1.54 (m, 11H), 1.40-1.33 (m, 4H), 1.25 (s, 9H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 177.5, 152.5, 140.0, 131.8, 129.9, 121.9, 117.5, 110.2, 93.8, 80.7, 80.4, 64.3, 38.8, 34.5, 31.2, 28.3, 27.1, 24.7, 22.4, 13.9. IR (EtOH) ν 3408, 2985, 2931, 2871, 2225, 1731, 1579, 1516, 1448, 1367, 1304, 1238, 1148, 1025, 941, 896, 832, 753 cm⁻¹. HRMS (ESI) Calcd. for
C$_{24}$H$_{35}$NNaO$_4$\(^{+1}\) (M+Na)\(^+\) requires 424.2458, Found: 424.2460.

(E)-1-(2-((tert-Butoxycarbonyl)amino)phenyl)oct-4-en-1-yn-3-yl pivalate (1m): A yellow oil, 694mg, 87% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.16 (d, $J$ = 8.4 Hz, 1H), 7.38 (d, $J$ = 7.6 Hz, 1H), 7.31 (t, $J$ = 8.0 Hz, 1H), 7.24 (br, 1H), 6.95 (t, $J$ = 7.6 Hz, 1H), 6.07-6.02 (m, 2H), 5.64 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.8 Hz, 1H), 2.10 (q, $J$ = 7.2 Hz, 2H), 1.54 (s, 9H), 1.46 (q, $J$ = 7.2 Hz, 2H), 1.25 (s, 9H), 0.93 (t, $J$ = 7.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.2, 152.4, 140.0, 136.4, 131.9, 130.0, 124.8, 121.9, 117.5, 110.0, 92.3, 81.5, 80.7, 64.6, 38.8, 34.0, 28.3, 27.0, 21.8, 13.5. IR
(EtOH) ν 3409, 2966, 2932, 2873, 2225, 1731, 1579, 1515, 1478, 1448, 1367, 1304, 1237, 1140, 1043, 1025, 925, 898, 833, 753 cm⁻¹. HRMS (ESI) Calcd. for C₂₄H₃₃NNaO₄⁺¹ (M+Na)⁺ requires 422.2302, Found: 422.2303.

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1-(((tert-Butoxycarbonyl)amino)phenyl)ethynyl)-cyclohexyl acetate (1n): A colorless oil, 456 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.14 (d, J = 8.4 Hz, 1H), 7.65 (br, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 2.26-2.23 (m, 2H), 2.08 (s, 3H), 1.92-1.87 (m, 2H), 1.70-1.66 (m, 4H), 1.54 (s, 9H), 1.46-1.29 (m, 2H). ¹³C NMR (100 MHz, CDCl₃)
δ 169.3, 152.7, 140.5, 131.2, 129.5, 121.6, 117.5, 110.5, 95.7, 81.9, 80.1, 75.5, 36.9, 28.2, 25.0, 22.6, 21.9. IR (CH₂Cl₂) ν 3350, 2933, 2859, 1768, 1715, 1581, 1519, 1484, 1449, 1392, 1366, 1305, 1234, 1200, 1155, 1128, 1066, 1041, 1022, 978, 909, 754, 736, 702 cm⁻¹. HRMS (ESI) Calcd. for C₂₁H₂₇NNaO₄⁺¹ (M+Na)⁺ requires: 380.1832. Found: 380.1831.

3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-(p-tolyl)prop-2-yn-1-yl pivalate (1o): A yellow oil, 699 mg, 83% yield. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.15 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.23-7.21 (m, 3H), 6.94 (t, J = 7.6 Hz,
1H), 6.62 (s, 1H), 2.38 (s, 3H), 1.53 (s, 9H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.3, 152.4, 138.8, 134.1, 131.9, 130.1, 129.4, 127.3, 121.9, 117.6, 110.0, 92.9, 82.0, 80.7, 65.8, 38.8, 28.3, 27.0, 21.2. IR (EtOH) ν 3406, 2977, 2935, 2866, 2228, 1731, 1579, 1515, 1478, 1447, 1367, 1303, 1236, 1135, 1134, 1023, 929, 899, 816, 754, 725 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{31}$NNaO$_4$$^{+1}$ (M+Na)$^+$ requires 444.2145, Found: 444.2146.

3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl pivalate (1p): A yellow oil, 769 mg, 88% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.15 (d, $J = 8.4$ Hz, 1H), 7.52-
7.49 (m, 2H), 7.38 (dd, \(J_1 = 1.6\) Hz, \(J_2 = 7.6\) Hz, 1H), 7.31 (td, \(J_1 = 1.2\) Hz, \(J_2 = 8.0\) Hz, 1H), 7.23 (br, 1H), 6.97-6.92 (m, 3H), 6.61 (s, 1H), 3.83 (s, 3H), 1.53 (s, 9H), 1.23 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 177.3, 160.0, 152.4, 140.1, 131.9, 130.1, 129.2, 128.9, 121.9, 117.6, 114.1, 110.0, 93.0, 82.0, 80.7, 65.7, 55.3, 38.8, 28.3, 27.0. IR (EtOH) \(\nu\) 3406, 2977, 2927, 2873, 2224, 1729, 1579, 1514, 1478, 1367, 1304, 1237, 1136, 1030, 924, 830, 755, 704 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{26}\)H\(_{31}\)NNaO\(_5\)\(^{+1}\) (M+Na)\(^{+}\) requires 460.2094, Found: 460.2095.

1-(4-Bromophenyl)-3-(2-((\textit{tert}-butoxycarbonyl)amino)phenyl)prop-2-yn-1-yl pivalate (1q): A
yellow oil, 904 mg, 93% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.16 (d, $J$ = 8.8 Hz, 1H), 7.55 (d, $J$ = 8.8 Hz, 2H), 7.45 (d, $J$ = 8.4 Hz, 2H), 7.37 (dd, $J_1$ = 1.2 Hz, $J_2$ = 8.0 Hz, 1H), 7.33 (t, $J$ = 7.2 Hz, 1H), 7.17 (br, 1H), 6.95 (td, $J_1$ = 1.2 Hz, $J_2$ = 7.6 Hz, 1H), 6.60 (s, 1H), 1.53 (s, 9H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.1, 152.4, 140.2, 136.2, 132.0, 131.9, 130.3, 129.0, 123.0, 122.0, 117.7, 109.7, 92.1, 82.7, 80.8, 65.3, 38.8, 28.3, 27.0. IR (EtOH) ν 3408, 2976, 2932, 2866, 2227, 1731, 1578, 1515, 1448, 1367, 1304, 1237, 1132, 1043, 1012, 935, 754, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{28}$BrNNaO$_4^{+1}$ (M+Na)$^+$ requires 508.1094, Found: 508.1093.
3-(2-((tert-Butoxycarbonyl)amino)phenyl)-1-(naphthalen-1-yl)prop-2-yn-1-yl pivalate (1r): A yellow oil, 713 mg, 78% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.25 (d, $J = 8.8$ Hz, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 7.92-7.89 (m, 2H), 7.85 (d, $J = 6.8$ Hz, 1H), 7.61-7.49 (m, 3H), 7.35 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz, 1H), 7.30 (t, $J = 8.4$ Hz, 1H), 7.24 (s, 1H), 7.21 (br, 1H), 6.92 (td, $J_1 = 1.2$ Hz, $J_2 = 8.0$ Hz, 1H), 1.51 (s, 9H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.3, 152.4, 140.1, 134.0, 132.1, 132.0, 130.5, 130.1, 130.0, 128.9, 126.7, 126.3, 126.0, 125.2, 123.7, 122.0, 117.6, 110.0, 92.6, 82.9, 80.7, 64.7, 39.0, 28.3, 27.0. IR (EtOH) $\nu$ 3407, 2976, 2931, 2862, 2225, 1729, 1579, 1514, 1478, 1367, 1304, 1237, 1133, 1024, 933, 832, 754 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{29}$H$_{31}$NNaO$_4$ requires 480.2145, Found: 480.2145.
3-(2-((tert-Butoxycarbonyl)amino)-5-methylphenyl)-1-phenylprop-2-yn-1-yl pivalate (1s): A yellow oil, 783 mg, 93% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.02 (d, $J = 8.4$ Hz, 1H), 7.58-7.56 (m, 2H), 7.44-7.36 (m, 3H), 7.20 (d, $J = 1.6$ Hz, 1H), 7.13-7.11 (m, 2H), 6.65 (s, 1H), 2.25 (s, 3H), 1.52 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.3, 152.5, 137.7, 137.1, 132.1, 131.5, 130.9, 128.9, 128.8, 127.3, 117.7, 109.9, 92.3, 82.5, 80.6, 65.9, 38.8, 28.3, 27.0, 20.4. IR (EtOH) $\nu$ 3410, 2976, 2931, 2865, 2228, 1730, 1585, 1515, 1447, 1367, 1302, 1240, 1131, 1024, 937, 822, 762, 695 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{31}$NNaO$_4$$^+$ (M+Na)$^+$ requires 444.2145, Found: 444.2147.
3-(5-Bromo-2-((tert-butoxycarbonyl)amino)phenyl)-1-phenylprop-2-yn-1-yl pivalate (1t): A yellow oil, 875 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.08 (d, $J$ = 8.8 Hz, 1H), 7.55 (d, $J$ = 6.8 Hz, 2H), 7.50 (d, $J$ = 2.0 Hz, 1H), 7.45-7.39 (m, 4H), 7.18 (br, 1H), 6.63 (s, 1H), 1.52 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.2, 152.2, 139.3, 136.7, 134.1, 133.0, 129.0, 128.8, 127.2, 119.1, 113.9, 111.7, 93.9, 81.1, 80.8, 65.8, 38.8, 28.3, 27.0. IR (EtOH) $\nu$ 3406, 2976, 2926, 2866, 2225, 1731, 1571, 1507, 1456, 1367, 1299, 1236, 1150, 1021, 937, 898, 823, 764, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{28}$BrNNaO$_4^{+}$ (M+Na)$^+$ requires 508.1094, Found: 508.1094.
3-(2-((tert-Butoxycarbonyl)amino)-5-fluorophenyl)-1-phenylprop-2-yn-1-yl pivalate (1u): A yellow oil, 714 mg, 84% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.12 (dd, $J_1 = 1.2$ Hz, $J_2 = 8.0$ Hz, 1H), 7.56 ($J = 6.8$ Hz, 2H), 7.45-7.39 (m, 3H), 7.12 (br, 1H), 7.08 (dd, $J_1 = 1.2$ Hz, $J_2 = 8.4$ Hz, 1H), 7.03 (td, $J_1 = 3.2$ Hz, $J_2 = 8.4$ Hz, 1H), 6.64 (s, 1H), 1.52 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.2, 157.2 (d, $J = 241.4$ Hz), 152.5, 136.7, 136.5 (d, $J = 2.7$ Hz), 129.0, 128.8, 127.2, 119.3 (d, $J = 7.6$ Hz), 118.0 (d, $J = 24.1$ Hz), 117.2 (d, $J = 2.0$ Hz), 111.2 (d, $J = 9.2$ Hz),
93.4, 81.2 (d, \( J = 2.9 \) Hz), 80.9, 65.8, 38.8, 28.3, 27.0. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), TMS) \( \delta \) -120.8.

IR (EtOH) \( \nu \) 3411, 2978, 2931, 2869, 2226, 1731, 1571, 1516, 1478, 1420, 1367, 1292, 1235, 1153, 1134, 1021, 939, 867, 820, 761, 696 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{25}\)H\(_{28}\)BrNNaO\(_4\)\(^{+1}\) (M+Na\(^{+}\)) requires 448.1895, Found: 448.1896.
3-(2-((tert-Butoxycarbonyl)amino)-4-methylphenyl)-1-phenylprop-2-yn-1-yl pivalate (1v): A yellow oil, 741 mg, 88% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.01 (s, 1H), 7.57 ($J = 7.2$ Hz, 2H), 7.44-7.40 (m, 3H), 7.28 (s, 1H), 7.20 (br, 1H), 6.77 ($d, J = 8.0$ Hz, 1H), 6.67 (s, 1H), 2.34 (s, 3H), 1.53 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.2, 152.5, 140.8, 140.0, 137.2, 131.7, 128.8, 128.7, 127.2, 122.9, 118.1, 107.1, 92.1, 82.5, 80.7, 66.0, 38.8, 28.3, 27.0, 22.0. IR (EtOH) $\nu$ 3406, 2976, 2928, 2871, 1731, 1571, 1524, 1478, 1456, 1367, 1241, 1134, 1008, 938, 760, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{31}$NNaO$_4$$^+$ (M+Na)$^+$ requires 444.2145, Found: 444.2148.
3-(2-((tert-Butoxycarbonyl)amino)-3-fluorophenyl)-1-phenylprop-2-yn-1-yl pivalate (1w): A yellow oil, 561 mg, 66% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.57-7.55 (m, 2H), 7.43-7.37 (m, 3H), 7.25-7.22 (m, 1H), 7.12-7.09 (m, 2H), 6.66 (s, 1H), 6.23 (br, 1H), 1.48 (s, 9H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.1, 156.8 (d, $J = 249.0$ Hz), 152.7, 137.0, 128.8, 128.7, 127.9 (d, $J = 3.3$ Hz), 127.4, 127.0 (d, $J = 12.7$ Hz), 126.4 (d, $J = 8.9$ Hz), 120.1 (d, $J = 3.8$ Hz), 117.2 (d, $J = 20.9$ Hz), 92.0, 82.1 (d, $J = 4.3$ Hz), 81.0, 65.7, 38.8, 28.1, 27.0. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -118.0. IR (EtOH) $\nu$ 3426, 2976, 2925, 2863, 1725, 1696, 1497, 1473, 1457, 1367,
1246, 1137, 1067, 1023, 931, 795, 762, 696 cm\(^{-1}\). HRMS (ESI) Calcd. For C\(_{25}\)H\(_{28}\)FNNaO\(_4\)\(^{+1}\) (M+Na)\(^+\) requires 448.1896, Found: 448.1895.
3-(2-Acetamidophenyl)-1-phenylprop-2-yn-1-yl acetate (1x): A yellow oil, 571 mg, 93% yield.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.43 (d, $J = 8.0$ Hz, 1H), 8.05 (s, 1H), 7.61 (d, $J = 7.6$ Hz, 2H), 7.48-7.40 (m, 4H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.51 (s, 1H), 2.21 (s, 3H), 2.17 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 168.8, 140.2, 136.1, 131.6, 130.4, 129.3, 128.9, 127.6, 123.0, 119.3, 110.3, 92.8, 82.9, 66.8, 24.6, 21.1. IR (EtOH) $\nu$ 3364, 3058, 3033, 2929, 2227, 1733, 1578, 1516, 1447, 1368, 1300, 1219, 1160, 1043, 1013, 955, 755, 696 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{17}$NNaO$_3$ $^{+}$ (M+Na)$^+$ requires 330.1101, Found: 330.1103.
3-(2-((4-Methylphenyl)sulfonamido)phenyl)-1-phenylprop-2-yn-1-yl acetate (1y): A yellow solid, 746 mg, 89% yield, m. p. 210-213 °C. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.07 (d, J = 8.8 Hz, 1H), 7.67 (J = 8.0 Hz, 2H), 7.57 (s, 1H), 7.43-7.22 (m, 7H), 7.20-7.17 (m, 1H), 7.14 (s, 1H), 7.12 (s, 1H), 6.57 (s, 1H), 2.27 (s, 3H), 2.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 144.8, 139.5, 138.1, 137.2, 135.4, 129.6, 128.8, 128.5, 128.4, 127.9, 126.7, 124.9, 123.7, 121.0, 114.8, 111.6, 71.4, 21.4, 21.0. IR (EtOH) ν 3032, 2922, 2847, 2163, 1740, 1597, 1561, 1495, 1450, 1371, 1308, 1217, 1174, 1134, 1020, 937, 906, 810, 775, 745, 701, 663 cm⁻¹. HRMS (ESI) Calcd. for C₂₄H₂₁NNaO₄S⁺ (M+Na)⁺ requires 442.1083, Found: 442.1085.
4. General Procedure for Gold (I)-catalyzed the Cyclization Reaction:

Gold catalyzed tandem reaction of propargylic esters 1 with nonchiral monodentate phosphine ligands:

**Method A:** To a mixture of propargylic ester (0.1 mmol) in dry DCM (2 mL) was added gold (I) complex (5 mol%). The mixture was stirred at room temperature until the consumption of the starting material. Then the solvent was removed under reduced pressure and the crude product was purified by a flash chromatography (petroleum ether / ethyl acetate = 50:1). **Method B:** To a flame-dried Schlenk tube was added silver salt (5 mol%) and gold (I) complex (5 mol%) followed by the addition of dry DCM (1.0 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 15 minutes, and then a solution of propargylic ester (0.1 mmol) in DCM (1.0 mL) was added via a syringe. The mixture was stirred at room temperature until the consumption of the starting material. Then the solvent was removed under reduced pressure and the crude product was purified by a flash chromatography (petroleum ether / ethyl acetate = 50:1).

**Enantioselective Transformation of Propargylic Esters:**

To a flame-dried Schlenk pressure tube was added 4Å molecular sieves (50 mg), silver salt (10 mmol%) and chiral digold (I) complex (5 mol%) followed by the addition of solvent (1.0 mL) under argon atmosphere. The heterogeneous mixture was stirred at room temperature for 15mins, after being sonicated for 30 seconds in a commercial ultrasonic cleaner. Then a solution of propargylic ester (0.1 mmol) in solvent (1 mL) was added to the reaction mixture at the desired temperature under argon atmosphere for 24 hours. The mixture was quenched with one drop of Et3N and then...
filtered through Celite. The filter cake was washed with ethyl acetate and concentrated. Then the solvent was removed under reduced pressure and the crude product was purified by a flash chromatography (petroleum ether / ethyl acetate = 50:1).

![Chemical structure](image)

Especially, L4(AuCl)2 was synthesized according to the previous reported work.[3]

5. The characterization data of products

![Chemical structure](image)

**tert-Butyl 4-acetoxy-2-phenylquinoline-1(2H)-carboxylate (2a):** A yellow oil, 35 mg, 96% yield.

\[ ^1\text{H NMR (400 MHz, CDCl}_3, \text{TMS)} \delta 7.51 (d, J = 7.2 \text{ Hz}, 1\text{H}), 7.36 (d, J = 6.8 \text{ Hz}, 2\text{H}), 7.26-7.17 \text{ (m, 5H)}, 7.04 (t, J = 7.2 \text{ Hz}, 1\text{H}), 6.29 (d, J = 6.4 \text{ Hz}, 1\text{H}), 5.96 (d, J = 6.4 \text{ Hz}, 1\text{H}), 2.34 (s, 3\text{H}), 1.55 (s, 9\text{H}). \]

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 168.8, 153.1, 143.5, 139.5, 135.6, 128.5, 128.4, 127.8, 127.2, 124.9, 123.6, 123.2, 121.1, 115.5, 81.9, 54.8, 28.3, 20.9. \]

IR (CH\(_2\)Cl\(_2\)) \( \nu 2976, 2929, 1767, 1696, 1489, 1455, 1369, 1331, 1308, 1254, 1200, 1162, 1146, 1128, 1044, 1031, 902, 873, 763, 698 \text{ cm}^{-1}. \)

tert-Butyl 4-acetoxy-2-(3-chlorophenyl)quinoline-1(2H)-carboxylate (2b): A colorless oil, 34 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.52-7.50 (m, 1H), 7.37 (s, 1H), 7.25-7.15 (m, 5H), 7.06 (td, $J_1$ = 1.2 Hz, $J_2$ = 7.2 Hz, 1H), 6.28 (d, $J$ = 6.8 Hz, 1H), 5.94 (d, $J$ = 6.8 Hz, 1H), 2.36 (s, 3H), 1.56 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 153.0, 143.9, 141.6, 135.4, 134.3, 129.8, 128.6, 128.0, 127.5, 125.4, 124.9, 123.8, 123.0, 121.3, 114.6, 82.2, 54.2, 28.3, 20.9. IR (CH$_2$Cl$_2$) $\nu$ 2978, 2928, 2846, 1768, 1697, 1595, 1572, 1489, 1475, 1456, 1370, 1332, 1309, 1253, 1199, 1161,
1147, 1129, 1084, 1044, 1031, 765, 705 cm\(^{-1}\). HRMS (ESI) Calcd. For C\(_{22}\)H\(_{26}\)ClN\(_2\)O\(_4\)\(^{+1}\) (M+NH\(_4\))\(^{+}\) requires: 417.1576, Found: 417.1574.

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**tert-Butyl 4-acetoxy-2-(4-methoxyphenyl)quinoline-1(2H)-carboxylate (2c):** A colorless oil, 39 mg, 99% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) 7.48 (dd, \(J_1 = 3.2\) Hz, \(J_2 = 6.8\) Hz, 1H), 7.31-7.26 (m, 2H), 7.20-7.16 (m, 2H), 7.04 (t, \(J = 7.6\) Hz, 1H), 6.78-6.75 (m, 2H), 6.25 (d, \(J = 6.4\) Hz, 2H).
1H), 5.91 (d, J = 6.4 Hz, 1H), 3.73 (s, 3H), 2.34 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.9, 159.2, 153.0, 143.4, 135.4, 131.5, 128.7, 128.3, 124.9, 123.5, 123.1, 121.0, 115.8, 113.8, 81.8, 55.1, 54.3, 28.3, 20.9. IR (CH$_2$Cl$_2$) ν 2964, 2930, 1764, 1694, 1608, 1510, 1488, 1455, 1368, 1331, 1259, 1198, 1174, 1161, 1143, 1030, 987, 903, 796, 761, 736, 702 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{29}$N$_2$O$_5$$^{+}$ (M+NH$_4^+$) requires: 413.2071, Found: 413.2070.

**tert-Butyl 4-acetoxy-2-(naphthalen-1-yl)quinoline-1(2H)-carboxylate (2d):** A yellow oil, 38 mg,
92% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 8.52 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.52-7.45 (m, 3H), 7.27-7.18 (m, 3H), 7.11-7.07 (m, 2H), 6.06 (d, $J = 6.8$ Hz, 1H), 2.33 (s, 3H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.9, 153.2, 143.7, 141.1, 136.2, 134.0, 130.4, 128.8, 128.5, 128.3, 127.9, 126.3, 125.7, 125.4, 125.3, 124.1, 123.7, 123.6, 121.1, 116.3, 82.0, 52.0, 28.2, 20.9. IR (CH$_2$Cl$_2$) $\nu$ 2973, 2928, 1769, 1701, 1483, 1455, 1369, 1342, 1320, 1306, 1258, 1195, 1165, 1149, 1093, 1043, 1031, 902, 815, 763, 740, 699 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{29}$N$_2$O$_4$+1 (M+NH$_4$)$^+$ requires: 433.2122, Found: 433.2121.
**tert-Butyl 4-acetoxy-2-(4-bromophenyl)quinoline-1(2H)-carboxylate (2e):** A colorless oil, 41 mg, 91% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.47 (br, 1H), 7.36 (d, $J$ = 8.8 Hz, 2H), 7.26-7.17 (m, 4H), 7.05 (t, $J$ = 7.6 Hz, 1H), 6.25 (d, $J$ = 6.4 Hz, 1H), 5.93 (d, $J$ = 6.8 Hz, 1H), 2.35 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 153.0, 143.8, 138.4, 135.3, 131.6, 129.1, 128.5, 124.8, 123.8, 122.9, 121.9, 121.2, 114.9, 82.1, 54.1, 28.3, 20.9. IR (CH$_2$Cl$_2$) $\nu$ 2978, 2931, 1766, 1735, 1698, 1579, 1518, 1488, 1449, 1393, 1369, 1332, 1306, 1238, 1222, 1201, 1157, 1044, 1012, 953, 756, 667 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{26}$BrN$_2$O$_4$+1 (M+NH$_4$)$^+$ requires: 461.1070, Found: 461.1066.
**tert-Butyl 4-acetoxy-6-methyl-2-phenylquinoline-1(2H)-carboxylate (2f):** A colorless oil, 37 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.36-7.35 (m, 3H), 7.26-7.20 (m, 3H), 6.99 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 6.28 (d, J = 5.6 Hz, 1H), 5.94 (d, J = 6.4 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 1.54 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 153.1, 143.6, 139.6, 133.11, 133.07, 129.1, 128.4, 127.7, 127.2, 124.8, 122.9, 121.4, 115.5, 81.7, 54.7, 29.7, 28.3, 21.0. IR (CH₂Cl₂) ν 2974, 2928, 1766, 1694, 1494, 1455, 1368, 1327, 1308, 1257, 1207, 1189, 1162, 1150, 1083, 1042, 1031, 1008, 913, 873, 800, 763, 739, 698 cm⁻¹. HRMS (ESI) Calcd. for C₂₃H₂₉N₂O₄⁺¹ (M+NH₄)⁺ requires: 397.2122, Found: 397.2121.
**tert-Butyl 4-acetoxy-6-bromo-2-phenylquinoline-1(2H)-carboxylate (2g):** A colorless oil, 41 mg, 92% yield. 

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.40 (br, 1H), 7.34-7.21 (m, 7H), 6.29 (d, $J = 6.4$ Hz), 6.01 (d, $J = 6.8$ Hz, 1H), 2.36 (s, 3H), 1.55 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.6, 152.8, 142.3, 139.1, 134.7, 131.2, 128.6, 128.0, 127.2, 126.5, 125.1, 124.0, 116.71, 116.65, 82.4, 54.9, 28.3, 21.0. IR (CH$_2$Cl$_2$) ν 2964, 2928, 1766, 1694, 1599, 1511, 1488, 1455, 1393, 1368, 1327,
1259, 1198, 1159, 1141, 1088, 1044, 1031, 1017, 797, 775, 676 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{22}\)H\(_{26}\)BrN\(_2\)O\(_4\)\(^+\) (M+NH\(_4\))\(^+\) requires: 461.1070, Found: 461.1069.

**tert-Butyl 4-acetoxy-6-fluoro-2-phenylquinoline-1(2H)-carboxylate (2h):** A yellow oil, 33mg, 86% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) 7.47 (br s, 1H), 7.35-7.22 (m, 5H), 6.90-6.87 (m, 2H), 6.31 (d, \(J = 6.0\) Hz, 1H), 6.05 (d, \(J = 6.4\) Hz, 1H), 2.35 (s, 3H), 1.55 (s, 9H). \(^{13}\)C NMR (100 MHz,
$\text{CDCl}_3$ $\delta$ 168.6, 158.9 (d, $J = 241.4$ Hz), 153.0, 142.7 (d, $J = 2.2$ Hz), 139.1, 131.4 (d, $J = 2.9$ Hz), 128.5, 128.0, 127.2, 126.6 (d, $J = 6.6$ Hz), 125.0 (d, $J = 8.0$ Hz), 116.8, 115.0 (d, $J = 22.6$ Hz), 108.0 (d, $J = 24.8$ Hz), 82.1, 54.7, 28.3, 20.9. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -118.4. IR (CH$_2$Cl$_2$) $\nu$ 2976, 1768, 1697, 1614, 1586, 1490, 1455, 1437, 1368, 1322, 1307, 1290, 1251, 1225, 1196, 1079, 1030, 1008, 932, 900, 868, 805, 763, 738, 698 cm$^{-1}$. HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{26}\text{FN}_2\text{O}_4^{+1} (\text{M}+\text{NH}_4)^+$ requires: 401.1871, Found: 401.1870.
**tert-Butyl 4-acetoxy-2-phenyl-6-(trifluoromethyl)quinoline-1(2H)-carboxylate (2i):** A colorless oil, 37 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.67 (d, $J$ = 8.4 Hz, 1H), 7.45-7.43 (m, 2H), 7.34-7.32 (m, 2H), 7.29-7.24 (m, 3H), 6.32 (d, $J$ = 6.8 Hz, 1H), 6.07 (d, $J$ = 6.8 Hz, 1H), 2.37 (s, 3H), 1.56 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.6, 152.6, 142.3, 139.1, 138.6, 128.6, 128.2, 127.1, 125.3 (q, $J$ = 4.1 Hz), 125.2 (q, $J$ = 3.6 Hz), 124.9, 124.1 (q, $J$ = 287 Hz), 123.4, 118.3 (q, $J$ = 3.5 Hz), 116.8, 82.8, 55.1, 28.3, 21.0. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -62.2. IR (CH$_2$Cl$_2$) v 2978, 2935, 1771, 1499, 1456, 1441, 1370, 1358, 1315, 1274, 1251, 1195, 1162, 1124, 1088, 1044, 897, 827, 764, 735, 698 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{26}$F$_3$N$_2$O$_4$$^{+}$ (M+NH$_4$)$^+$ requires: 451.1839, Found: 451.1838.
**tert-Butyl (S)-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2j):** A yellow oil, 1.92 g, 96% yield. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.50 (d, J = 6.4 Hz, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.27-7.14 (m, 5H), 7.04 (td, J₁ = 1.2 Hz, J₂ = 8.0 Hz, 1H), 6.30 (d, J = 6.4 Hz, 1H), 5.93 (d, J = 6.8 Hz, 1H), 1.55 (s, 9H), 1.40 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 153.1, 143.7, 139.6, 135.6, 128.5, 128.3, 127.8, 127.3, 125.0, 123.64, 123.59, 121.0, 115.3, 81.8, 54.8, 39.4, 28.3, 27.3. IR (CH₂Cl₂) ν 2975, 2931, 1755, 1698, 1602, 1490, 1455, 1369, 1330, 1307, 1273, 1255, 1211, 1163, 1146, 1114, 1043, 1029, 987, 899, 753, 698 cm⁻¹. HRMS (ESI) Calcd. for C₂₅H₃₃N₂O₄⁺ (M+NH₄)⁺ requires: 425.2435, Found: 425.2434.

Compound 2j: A yellow oil, 36 mg, 88% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; tₘᵣᵢₐᵢᵦ = 49.49 min, tₘᵢₐᵢᵦ = 43.50 min; ee% = 96%; [α]²⁰_D = -43.5 (c 1.00, CH₂Cl₂)].
Translation: Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; t\textsubscript{minor} = 49.49 min, t\textsubscript{major} = 43.50 min; ee% = 96%].

![Chemical Structure](image)
**tert-Butyl (S)-2-methyl-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2k):** A white solid, 34 mg, 80% yield, m. p. 153-155 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.56 (d, $J$ = 7.6 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.23-7.16 (m, 2H), 7.06 (d, $J$ = 7.6 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 5.23 (s, 1H), 1.97 (s, 3H), 1.34 (s, 9H), 1.14 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.2, 153.7, 147.7, 139.3, 137.5, 128.7, 128.3, 126.6, 125.9, 121.9, 121.1, 120.7, 120.6, 81.6, 63.3, 39.3, 27.5, 27.2, 24.4. IR (EtOH) $\nu$ 2976, 2921, 2869, 1752, 1701, 1494, 1323, 1164, 1108, 750, 699 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{35}$N$_2$O$_4$+ (M+NH$_4$)$^+$ requires 439.2591, Found: 439.2593.

**Compound 2k:** A white solid, 29 mg, 69% yield, m. p. 120-122 °C. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column [$\lambda$ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.5 mL/min; $t_{\text{minor}}$ = 6.03 min, $t_{\text{major}}$ = 6.46 min; ee% = 72%; $\lbrack \alpha \rbrack$$_{20}^{\text{D}}$ = -38.1 (c 1.00, CH$_2$Cl$_2$)].
Translation: Chiralcel OD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate:
0.5 mL/min; \( t_{\text{minor}} = 6.03 \text{ min}, t_{\text{major}} = 6.46 \text{ min}; \text{ee}\% = 72\% \). 

\( \text{tert-Butyl (R,E)-2-(pent-1-en-1-yl)-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2m)}: \) A yellow oil, 38 mg, 95% yield. \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\), TMS) \( \delta 7.61 \text{ (br, 1H)}, 7.22 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 7.12 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 7.03 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 5.71-5.65 \text{ (m, 2H)}, 5.56 \text{ (t, } J = 6.4 \text{ Hz, 1H)}, 5.35 \text{ (dd, } J_1 = 6.4 \text{ Hz, } J_2 = 15.2 \text{ Hz, 1H}), 1.90 \text{ (q, } J = 7.6 \text{ Hz, 2H)}, 1.52 \text{ (s, 9H)}, 1.38 \text{ (s, 9H)}, 1.29 \text{ (q, } J = 7.6 \text{ Hz, 2H)}, 0.76 \text{ (t, } J = 7.2 \text{ Hz, 3H)}. \) \( ^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta 176.4, 152.7, 143.0, 135.7, 133.5, 128.1, 125.9, 124.5, 123.4, 123.3, 120.9, 114.9, 81.4, 53.5, 39.3, 34.1, 28.3, 27.2, 22.1, 13.4. \) IR (EtOH) \( \nu \) 2971, 2931, 2873, 1755, 1698, 1488, 1368, 1330, 1144, 1163, 1112, 1043, 963, 753 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{24}\)H\(_{37}\)N\(_2\)O\(_4\)\(^{+1}\) (M+NH\(_4\))^+ requires 417.2748, Found: 417.2750.

Compound 2m: A yellow oil, 33 mg, 83% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column \( [\lambda = 230 \text{ nm}]; \text{eluent: Hexane/Isopropanol = 99/1}; \text{Flow rate: 0.3 mL/min}; t_{\text{minor}} = 27.66 \text{ min}, t_{\text{major}} = 23.21 \text{ min}; \text{ee}\% = 91\%; [\alpha]^{20}_D = -118.3 (c 1.00, CH\(_2\)Cl\(_2\))] \).
Translation: Chiralcel AD-H column [\( \lambda = 230 \) nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; \( t_{\text{minor}} = 27.66 \) min, \( t_{\text{major}} = 23.21 \) min; ee% = 91%].
**tert-Butyl 4'-acetoxy-1'H-spiro[cyclohexane-1,2'-quinoline]-1'-carboxylate (2n):** A yellow oil, 30 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.23-7.16 (m, 2H), 7.12-7.11 (m, 1H), 7.08-7.04 (m, 1H), 5.89 (s, 1H), 2.34-2.29 (m, 5H), 1.77-1.73 (m, 2H), 1.68-1.65 (m, 2H), 1.51-1.41 (m, 13H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 153.6, 142.7, 138.9, 127.6, 126.2, 124.4, 123.8, 122.1, 120.8, 80.8, 59.8, 34.6, 28.1, 25.3, 22.5, 21.0. IR (CH$_2$Cl$_2$) $\nu$ 2935, 2860, 1725, 1580, 1518, 1447, 1392, 1366, 1304, 1282, 1229, 1153, 1041, 1022, 977, 958, 913, 840, 803, 753, 703 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{21}$H$_{31}$N$_2$O$_4$ ($\text{M+NH}_4^+$) requires: 375.2278, Found: 375.2278.
**tert-Butyl (S)-4-(pivaloyloxy)-2-(p-tolyl)quinoline-1(2H)-carboxylate (2o):** A yellow oil, 36 mg, 86% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.49 (d, $J$ = 6.0 Hz, 1H), 7.27-7.25 (m, 2H), 7.20-7.14 (m, 2H), 7.06-7.01 (m, 3H), 6.26 (d, $J$ = 7.2 Hz, 1H), 5.90 (d, $J$ = 6.8 Hz, 1H), 2.26 (s, 3H), 1.54 (s, 9H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.5, 153.0, 143.5, 137.5, 136.6, 135.6, 129.1, 128.2, 127.2, 125.0, 123.57, 123.55, 120.9, 115.5, 81.7, 54.6, 39.3, 28.3, 27.2, 21.1. IR (EtOH) ν 2975, 2931, 2866, 1754, 1696, 1512, 1488, 1368, 1328, 1272, 1161, 1110, 1042, 1030, 899, 754, 731 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{35}$N$_2$O$_4$$^{+1}$ (M+NH$_4$)$^+$ requires 439.2591, Found: 439.2593.

Compound 2o: A yellow oil, 32 mg, 76% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; $t_{\text{minor}}$ = 44.56 min, $t_{\text{major}}$ = 54.53 min; ee% = 94%; [α]$^{20}_D$ = -64.1 (c 1.00, CH$_2$Cl$_2$)].
Translation: Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; t_{minor} = 44.56 min, t_{major} = 54.53 min; ee% = 94%].
**tert-Butyl (S)-2-(4-methoxyphenyl)-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2p):** A brown oil, 43 mg, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.47 (d, $J = 6.0$ Hz, 1H), 7.32 (d, $J = 8.8$ Hz, 2H), 7.20-7.14 (m, 2H), 7.03 (td, $J_1 = 0.8$ Hz, $J_2 = 7.6$ Hz, 1H), 6.79-6.76 (m, 2H), 6.26 (d, $J = 6.8$ Hz, 1H), 5.87 ($J = 6.8$ Hz, 1H), 3.72 (s, 3H), 1.55 (s, 9H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.7, 159.2, 153.0, 143.6, 135.5, 131.6, 128.7, 128.2, 125.0, 123.6, 123.5, 120.9, 115.5, 113.8, 81.7, 55.1, 54.3, 39.3, 28.3, 27.2. IR (EtOH) $\nu$ 3072, 2975, 2932, 2876, 2833, 1753, 1695, 1510, 1368, 1330, 1247, 1161, 1110, 1030, 834, 756, 735 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{26}$H$_{35}$N$_2$O$_5$ + (M+NH$_4$)$^+$ requires 455.2540, Found: 455.2541.

Compound 2p: A yellow oil, 35 mg, 80% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [$\lambda = 230$ nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; $t_{\text{minor}} = 26.10$ min, $t_{\text{major}} = 46.06$ min; ee$\% = 96\%$; $[\alpha]^2_0$ = -56.5 (c 1.00, CH$_2$Cl$_2$)].
Translation: Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; t\textsubscript{minor} = 26.10 min, t\textsubscript{major} = 46.06 min; ee% = 96%].
tert-Butyl (S)-2-(4-bromophenyl)-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2q): A white solid, 44 mg, 91% yield, m. p. 126-130 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.46 (d, $J$ = 6.4 Hz, 1H), 7.36 (d, $J$ = 8.8 Hz, 2H), 7.28-7.26 (m, 2H), 7.21-7.14 (m, 2H), 7.05 (td, $J_1$ = 0.8 Hz, $J_2$ = 7.6 Hz), 6.26 (d, $J$ = 6.4 Hz, 1H), 5.89 (d, $J$ = 6.8 Hz, 1H), 1.54 (s, 9H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.6, 153.0, 144.0, 138.5, 135.3, 131.6, 129.1, 128.4, 125.0, 123.8, 123.4, 121.9, 121.1, 114.6, 82.1, 54.1, 39.4, 28.3, 27.2. IR (EtOH) $\nu$ 3638, 3547, 3391, 3189, 2976, 2920, 2849, 1740, 1699, 1491, 1367, 1334, 1274, 1161, 1136, 1118, 1030, 866, 831, 753 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{32}$N$_2$O$_4^{+}$ (M+NH$_4$)$^+$ requires 503.1540, Found: 503.1539.

Compound 2q: A white solid, 42 mg, 86% yield, m. p. 100-102 °C. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [$\lambda$ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; $t_{\text{minor}}$ = 54.38 min, $t_{\text{major}}$ = 50.25 min; ee% = 96%; $[\alpha]^{20}\text{D}$ = -111.1 (c 1.00, CH$_2$Cl$_2$)].
Translation: Chiracel AD-H column [$\lambda = 230$ nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; $t_{\text{minor}} = 54.38$ min, $t_{\text{major}} = 50.25$ min; ee% = 96%].
**tert-Butyl (S)-2-(naphthalen-1-yl)-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2r):** A yellow solid, 42 mg, 92% yield, m. p. 184-188 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 8.54 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.61-7.43 (m, 4H), 7.27-7.25 (m, 1H), 7.19-7.18 (m, 2H), 7.12-7.08 (m, 2H), 6.02 (d, $J = 6.4$ Hz, 1H), 1.49 (s, 9H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$, δ 176.7, 153.2, 143.9, 136.2, 134.8, 134.0, 130.4, 128.8, 128.5, 128.2, 126.3, 125.8, 125.54, 125.46, 125.4, 124.2, 124.0, 123.7, 121.0, 116.1, 81.9, 51.9, 39.3, 28.2, 27.3. IR (EtOH) ν 3394, 2966, 2921, 2849, 1753, 1699, 1488, 1327, 1111, 1025, 937, 766, 659 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{29}$H$_{35}$N$_2$O$_4$ (M+NH$_4$)$^+$ requires 475.2591, Found: 475.2592.

**Compound 2r:** A yellow oil, 38 mg, 83% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [$\lambda = 230$ nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.30 mL/min; $t_{\text{minor}} = 18.62$ min, $t_{\text{major}} = 36.40$ min; ee% = 90%; [α]$^\text{D} = -81.3$ (c 1.00, CH$_2$Cl$_2$)].
Translation: Chiralcel AD-H column \([\lambda = 230 \text{ nm}]\); eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.30 mL/min; \(t_{\text{minor}} = 18.62 \text{ min}, t_{\text{major}} = 36.40 \text{ min}; \text{ee}\% = 90\%\).

**tert-Butyl 6-methyl-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2s):** A brown oil, 41 mg, 97% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta 7.38-7.37 (m, 3H), 7.26-7.19 (m, 3H), 6.99 (d, J = 8.4 \text{ Hz}, 1H), 6.93 (s, 1H), 6.28 (d, J = 6.4 \text{ Hz}, 1H), 5.90 (d, J = 6.4 \text{ Hz}, 1H), 2.27 (s, 3H), 1.54 (s, 9H), 1.41 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 176.6, 153.2, 143.8, 139.6, 133.11, 133.06, 129.0, 128.4, 127.7, 127.3, 124.9, 123.3, 121.4, 115.2, 81.6, 54.7, 39.3, 28.3, 27.2, 21.0. IR (EtOH) \(\nu\) 3065, 2971, 2923, 2866, 1751, 1693, 1493, 1367, 1325, 1250, 1150, 1117, 1042, 914, 877, 807, 743, 703 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{26}\)H\(_{35}\)N\(_2\)O\(_4\)\(^{+1}\) (M+NH\(_4\))\(^+\) requires 439.2591, Found: 439.2593.
**tert-Butyl 6-bromo-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2t):** A yellow oil, 45 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.38-7.34 (m, 3H), 7.29-7.22 (m, 5H), 6.30 (d, J = 6.0 Hz, 1H), 5.97 (d, J = 6.4 Hz, 1H), 1.54 (s, 9H), 1.40 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 176.4, 152.7, 142.5, 139.1, 134.6, 131.0, 128.6, 128.0, 127.2, 126.6, 125.4, 124.0, 116.6, 116.5, 82.3, 54.8, 39.4, 28.3, 27.2. IR (EtOH) ν 2975, 2934, 2865, 2250, 1752, 1696, 1481, 1320, 1147, 1113, 1028, 910, 731, 697 cm⁻¹. HRMS (ESI) Calcd. for C₂₅H₂₃N₂O₄⁺ (M+NH₄)⁺ requires 503.1540, Found: 503.1540.
tert-Butyl (S)-6-fluoro-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2u): A yellow oil, 41 mg, 96% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 7.46 (br, 1H), 7.36 (d, $J$ = 6.8 Hz, 2H), 7.28-7.20 (m, 3H), 6.90-6.83 (m, 2H), 6.32 (d, $J$ = 6.0 Hz, 1H), 6.01 (d, $J$ = 6.4 Hz, 1H), 1.54 (s, 9H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.4, 158.9 (d, $J$ = 241.4 Hz), 153.0, 142.9 (d, $J$ = 2.5 Hz), 139.1, 131.5 (d, $J$ = 2.3 Hz), 128.5, 127.9, 127.2, 126.7 (d, $J$ = 6.8 Hz), 125.3 (d, $J$ = 7.8 Hz), 116.6, 114.9 (d, $J$ = 22.4 Hz), 107.8 (d, $J$ = 23.9 Hz), 82.0, 54.7, 39.4, 28.3, 27.0. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) δ -118.1. IR (EtOH) ν 2977, 2935, 2869, 2257, 1753, 1695, 1488, 1368,
1322, 1250, 1157, 1029, 911, 867, 733, 698 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{25}\)H\(_{32}\)N\(_2\)O\(_4\)\(^{+1}\) (M+NH\(_4\))\(^+\) requires 443.2341, Found: 443.2344.

Compound 2u: A yellow oil, 30 mg, 70% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [\(\lambda = 230\) nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; \(t_{\text{minor}} = 14.10\) min, \(t_{\text{major}} = 22.08\) min; ee\% = 91%; \([\alpha]\)^{20}_D = -68.0 (c 1.00, CH\(_2\)Cl\(_2\))].
Translation: Chiralcel AD-H column [\(\lambda = 230\) nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; \(t_{\text{minor}} = 14.10\) min, \(t_{\text{major}} = 22.08\) min; ee\% = 91\%].
tert-Butyl (S)-7-methyl-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2v): A white solid. 39 mg, 93% yield, m. p. 103-105 °C. 1H NMR (400 MHz, CDCl3, TMS) δ 7.40-7.35 (m, 3H), 7.25-7.19 (m, 3H), 7.03 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.28 (d, J = 6.4 Hz, 1H), 5.85 (d, J = 6.4 Hz, 1H), 2.28 (s, 3H), 1.55 (s, 9H), 1.39 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 176.6, 153.1, 143.9, 139.8, 138.4, 135.5, 128.5, 127.7, 127.3, 125.6, 124.4, 121.0, 120.8, 114.0, 81.7, 54.9, 39.3, 28.3, 27.3, 21.6. IR (EtOH) ν 2977, 2925, 2867, 2257, 1744, 1702, 1504, 1376, 1306, 1140, 1119, 1029, 896, 816, 747, 702 cm⁻¹. HRMS (ESI) Calcd. for C26H35N2O4⁺1 (M+NH4)⁺ requires 439.2591, Found: 439.2594.

Compound 2v: A yellow oil, 28 mg, 67% yield. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; t_minor = 33.00 min, t_major = 39.90 min; ee% = 93%; [α]²⁰_D = -79.1 (c 1.00, CH₂Cl₂)].
Translation: Chiralcel AD-H column [$\lambda = 230$ nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.3 mL/min; $t_{\text{minor}} = 33.00$ min, $t_{\text{major}} = 39.90$ min; ee% = 93%].

 tert-Butyl 8-fluoro-2-phenyl-4-(pivaloyloxy)quinoline-1(2H)-carboxylate (2w): A yellow oil, 36 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$. 7.41 (d, $J = 7.6$ Hz, 2H), 7.27-7.18 (m, 3H), 7.05-7.02 (m, 2H), 6.96-6.91 (m, 2H), 6.29 (br, 1H), 6.11 (d, $J = 6.8$ Hz, 1H), 1.50 (s, 9H), 1.41 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 155.9 ($J = 249.3$ Hz), 153.3, 143.4 ($J = 3.1$ Hz), 138.8, 128.4, 127.7, 127.1, 126.6, 125.4 ($J = 8.9$ Hz), 123.6 ($J = 9.5$ Hz), 117.4, 116.6 ($J = 2.7$ Hz), 116.1 ($J = 21.4$ Hz), 82.0, 54.3, 39.4, 27.9, 27.2. $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$) $\delta$ -116.9. IR (EtOH) v 3072, 2980, 2930, 2865, 1759, 1701, 1477, 1377, 1296, 1249, 1147, 1122, 1102, 1024, 911, 898, 777, 740, 704 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{32}$FN$_2$O$_4$H$^+$ (M+NH$_4$)$^+$ requires 443.2341, Found: 443.2344.
443.2343.

N-(2-cinnamoylphenyl)acetamide (3x): It is a known product, 24.9 mg, 94% yield.[4]

6. Reduction of product 2j
A solution of 2j (0.1 mmol) in THF was cold down to -0 °C, and then LiAlH$_4$ (0.4 mmol) was added into the solution for three times. The resulting mixture was stirred at room temperature for 2 h. After the reaction completed, the mixture was purified by a silica gel column chromatography (elution with PE/EtOAc = 4/1) to obtain the desired product 4j (26 mg, 80% yield). X-ray crystallographic analysis was used to determine the relative and absolute configuration of 4j.

**tert-Butyl (2S,4S)-4-hydroxy-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (4j):** A white solid, 26 mg, 80% yield, m. p. 200-204 °C. $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 7.72 (d, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.32 (td, $J_1$ = 1.2 Hz, $J_2$ = 7.6 Hz, 1H), 7.28-7.24 (m, 2H), 7.20-7.15 (m, 4H), 5.27 (dd, $J_1$ = 7.6 Hz, $J_2$ = 10.0 Hz, 1H), 4.54-4.52 (m, 1H), 2.68-2.62 (m, 1H), 2.19 (br, 1H), 1.85-1.76 (m, 1H), 1.36 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.7, 144.2, 136.3, 136.0, 128.4, 127.2, 126.7, 125.7, 124.9, 124.0, 122.7, 81.3, 65.9, 56.5, 43.8, 28.1. IR (EtOH) $\nu$ 3475, 2965, 2922, 2851, 1488, 1454, 1392, 1257, 1158, 1127, 1063, 1024, 967, 858, 758, 745 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{20}$H$_{23}$NNaO$_3$ $^{+1}$ (M+Na)$^+$ requires 348.1570, Found: 348.1570. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [$\lambda$ = 230 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.5 mL/min; $t_{\text{minor}}$ = 38.15 min, $t_{\text{major}}$ = 28.27 min; ee% = 96%; [$\alpha$]$^D$ = +34.2 (c 1.00, CH$_2$Cl$_2$)].
7. Synthesis of aromatase inhibitor 6j

Translation: Chiracel AD-H column \([\lambda = 230 \text{ nm}; \text{ eluent: Hexane/Isopropanol} = 85/15; \text{ Flow rate: 0.5 mL/min; } t_{\text{minor}} = 38.15 \text{ min, } t_{\text{major}} = 28.27 \text{ min; ee}\% = 96\%].\)
Compound **2j** (0.5 mmol, 204mg) was dissolved in a mixture of THF (5 mL), MeOH (5 mL) and 2M HCl (5 mL). The solution was stirred at 60 °C for 2 h. The reaction solution was concentrated under reduced pressure and was added saturated Na₂CO₃ aqueous solution to adjust pH to 7, extracted with EtOAc and dried over anhydrous Na₂SO₄. The mixture was purified by a silica gel column chromatography (elution with PE/EtOAc = 4/1) to obtain the desired product **S8** (67 mg, 60% yield). Reduction of **S8** to afford crude product **5j** and the relative configuration of **5j** has been reported. Then, aromatase inhibitor **6j** (46 mg, 84% yield for two steps) was prepared according to another previously reported work and the relative configuration of **6j** was confirmed by Nuclear Overhauser Effect Spectroscopy (NOESY).

**(2S,4S)-4-(1H-imidazol-1-yl)-2-phenyl-1,2,3,4-tetrahydroquinoline (6j):** A white solid, 46 mg, 50% yield for three steps, m. p. 192-193 °C. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.39 (s, 1H), 7.36-7.29 (m, 5H), 7.18 (t, J = 8.0 Hz, 1H), 7.08 (s, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.72-6.67 (m, 2H), 5.27 (t, J = 4.0 Hz, 1H), 4.44 (br, 1H), 4.24 (t, J = 7.6 Hz, 1H), 2.31-2.29 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 142.4, 136.9, 130.4, 130.0, 129.3, 128.8, 128.0, 126.6, 118.3, 117.8, 115.8, 114.8, 53.0, 51.5, 38.9. IR (EtOH) ν 3241, 3106, 3024, 2989, 2850, 1610, 1497, 1445, 1323, 1293, 1256, 1076, 921, 834, 748, 700, 662 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₁₈N₃⁺ (M+H)⁺ requires 276.1495, Found: 276.1496. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; tₘᵢₙᵢᵢᵠ = 20.90 min, tₘᵢₐᵢᵢᵠ = 22.84 min; ee% = 96%; [α] vbCrLf = +37.3 (c 1.00, CH₂Cl₂)].
Translation: Chiralcel AD-H column [$\lambda = 230$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; $t_{\text{minor}} = 20.90$ min, $t_{\text{major}} = 22.84$ min; ee% = 96%].

Nuclear Overhauser Effect Spectroscopy (NOESY)

8. X-ray Data of 4j
The crystal data of 4j have been deposited in CCDC with number 1435436. Empirical Formula: C_{20}H_{23}NO_{3}; Formula Weight: 325.39; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.160 x 0.110 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 8.6053(10)Å, b = 11.6403(14)Å, c = 17.468(2)Å, α = 90°, β = 90°, γ = 90°, V = 1749.7(4)Å^3; Space group: P 21 21 21; Z = 4; D_{calc}= 1.235 g/cm^3; F_{000} = 696; Final R indices [I>2sigma(I)] R1 = 0.0385, wR2 = 0.1014.

9. References