

Supporting Information

A Novel Approach to Dihydroquinolinone Derivatives *via* Cyclopropane Ring Expansion

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General considerations

All reagents were used as received. All reactions were performed under a nitrogen atmosphere in oven-dried glassware. Flash column chromatography was performed employing Wakogel® C-200. Thin-layer chromatography was performed on EM Science silica gel 60 plates with F-254 indicator (250µm thickness). Visualization was accomplished by UV light, photomolybdic acid solution or *p*-anisaldehyde acid solution. Nuclear magnetic resonance spectra (¹H, ¹³C) were recorded on a JEOL AL400 spectrometer. Mass spectra (HRMS) were recorded on a JEOL model JMS-700V. Characterization data for previously unknown compounds were determined from a single run or twice runs with isolated yields.

General procedure for the preparation of *N*-(1'-alkoxy)cyclopropyl-2-haloanilines

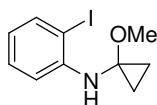
All compounds were prepared according to the following procedure: A mixture of 2-haloaniline (10.0 mmol, 0.2 M), AcOH (4.0 equiv) and (1-ethoxycyclopropoxy)trimethylsilane (1.5 ~ 2.0 equiv) in alcoholic solvent (MeOH, EtOH or *i*-PrOH, 50 mL) was refluxed for 3 ~ 20 h under nitrogen atmosphere in a 100 mL round bottomed flask equipped with a reflux condenser. Then the mixture was concentrated in vacuo with a rotary evaporator. The residue was purified by flash chromatography to give the corresponding *N*-(1'-alkoxy)cyclopropyl-2-haloaniline **1**.

General procedure for the synthesis of substituted 3,4-dihydro-2(1*H*)-quinolinones

All compounds were prepared according to the following procedure: A mixture of *N*-cyclopropyl haloaniline **1** (1.0 mmol, 0.2 M), K₂CO₃ (1.5 equiv), Pd₂(dba)₃ (1.5 mol %) and X-Phos (7.5 mol %) in DMF (5.0 mL) was stirred at 95 °C under nitrogen atmosphere in a round bottomed flask for the time specified in Table 2. The reaction mixture was then poured into aqueous 1N HCl, and the resulting mixture was extracted with AcOEt 3 times. The combined organic extracts were washed

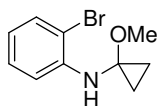
with brine 2 times. The obtained solution was dried with Na₂SO₄, and concentrated in vacuo with a rotary evaporator. The residue was purified by flash chromatography to give the corresponding 3,4-dihydro-2(*1H*)-quinolinone **3**.

Characterization data



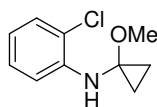
***N*-(1'-methoxy)cyclopropyl-2-iodoaniline (**1a**)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1a** as a colorless oil. *R_f* = 0.47 (*n*-heptane / ethyl acetate = 10 / 1). ¹H NMR (CDCl₃, 400 MHz) δ 7.65 (d, 1H, *J* = 8.0 Hz), 7.23-7.18 (m, 2H), 6.55-6.51 (m, 1H), 5.24 (bs, 1H), 3.28 (s, 3H), 1.18-1.15 (m, 2H), 0.96-0.93 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 144.90, 138.75, 129.15, 120.10, 114.25, 84.82, 69.67, 52.86, 14.67. IR (neat, cm⁻¹) 1585, 1489, 1447, 1420, 1306, 1221, 1061, 1009, 739. HRMS [*M*+*H*]⁺ *m/z* calcd for C₁₀H₁₂NOI+H 290.0042; Found, 290.0038.



***N*-(1'-methoxy)cyclopropyl-2-bromoaniline (**1b**)**

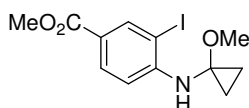
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1b** as a colorless oil. *R_f* = 0.50 (*n*-heptane / ethyl acetate = 10 / 1). ¹H NMR (CDCl₃, 400 MHz) δ 7.42 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.26-7.24 (m, 1H), 7.20 (td, 1H, *J* = 7.2, 1.2 Hz), 6.66 (ddd, 1H, *J* = 7.6, 7.2, 1.2 Hz), 5.38 (bs, 1H), 3.29 (s, 3H), 1.18-1.15 (m, 2H), 0.95-0.92 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 142.57, 132.23, 128.26, 119.31, 114.89, 109.35, 69.38, 52.89, 14.69. IR (neat, cm⁻¹) 1595, 1493, 1456, 1422, 1310, 1223, 1063, 1020, 739. HRMS [*M*+*H*]⁺ *m/z* calcd for C₁₀H₁₂NOBr+H 242.0181; Found, 242.0177.



***N*-(1'-methoxy)cyclopropyl-2-chloroaniline (**1c**)**

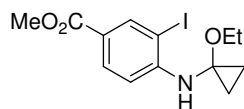
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1c** as a pale yellow oil. *R_f* = 0.48 (*n*-heptane / ethyl acetate = 10 / 1).

^1H NMR (CDCl_3 , 400 MHz) δ 7.27-7.24 (m, 2H), 7.18-7.14 (m, 1H), 6.74-6.70 (m, 1H), 5.37 (bs, 1H), 3.29 (s, 3H), 1.17-1.15 (m, 2H), 0.95-0.92 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.50, 128.96, 127.55, 118.87, 118.73, 114.72, 69.18, 52.82, 14.65. IR (neat, cm^{-1}) 1597, 1497, 1456, 1423, 1314, 1223, 1063, 1051, 1036, 739. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{10}\text{H}_{12}\text{NOCl}+\text{H}$ 198.0686; Found, 198.0682.



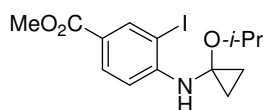
methyl 4-{N-(1'-methoxy)cyclopropyl}amino-3-iodobenzoate (1d)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **1d** as a white solid. mp = 91 °C. R_f = 0.22 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 8.35 (d, 1H, J = 1.6 Hz), 7.91 (dd, 1H, J = 8.8, 1.6 Hz), 7.18 (d, 1H, J = 8.8 Hz), 5.58 (bs, 1H), 3.87 (s, 3H), 3.29 (s, 3H), 1.22-1.19 (m, 2H), 0.97-0.94 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.67, 148.80, 140.54, 130.91, 130.88, 121.52, 112.92, 83.50, 69.46, 53.11, 53.09, 51.78, 51.77, 14.62. IR (neat, cm^{-1}) 1697, 1591, 1506, 1435, 1277, 1211, 1049, 970, 907, 745. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_3\text{I}+\text{H}$ 348.0097; Found, 348.0091.



methyl 4-{N-(1'-ethoxy)cyclopropyl}amino-3-iodobenzoate (1e)

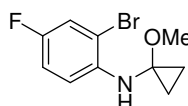
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **1e** as a white solid. mp = 95 °C. R_f = 0.27 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 8.34 (d, 1H, J = 1.6 Hz), 7.90 (dd, 1H, J = 8.4, 1.6 Hz), 7.21 (d, 1H, J = 8.4 Hz), 5.56 (bs, 1H), 3.86 (s, 3H), 3.55 (q, 2H, J = 7.2 Hz), 1.22-1.19 (m, 2H), 1.12 (t, 3H, J = 7.2 Hz), 0.96-0.93 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.89, 148.90, 140.55, 130.93, 121.47, 112.99, 83.44, 68.55, 61.43, 51.82, 15.18, 14.80. IR (neat, cm^{-1}) 1697, 1593, 1503, 1437, 1281, 1211, 1117, 1055, 762. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_3\text{I}+\text{H}$ 362.0253; Found, 362.0258.



methyl 4-{N-(1'-isopropoxy)cyclopropyl}amino-3-iodobenzoate (1f)

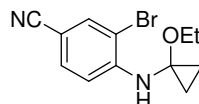
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl

acetate = 10 / 1) to afford **1f** as a pale yellow solid. mp = 103 °C. R_f = 0.29 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 8.34 (d, 1H, J = 1.6 Hz), 7.90 (dd, 1H, J = 8.4, 1.6 Hz), 7.21 (d, 1H, J = 8.4 Hz), 5.55 (bs, 1H), 3.96 (quintet, 1H, J = 6.4 Hz), 3.86 (s, 3H), 1.20-1.18 (m, 2H), 1.09 (d, 6H, J = 6.4 Hz), 0.94-0.93 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.90, 148.86, 140.48, 130.92, 121.41, 113.08, 83.34, 68.97, 67.71, 51.79, 23.22, 14.84. IR (neat, cm^{-1}) 1695, 1593, 1506, 1439, 1279, 1213, 1111, 999, 968, 760. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_3\text{I}+\text{H}$ 376.0410; Found, 376.0415.



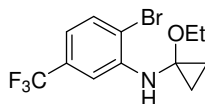
***N*-(1'-methoxy)cyclopropyl-2-bromo-4-fluoroaniline (1g)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1g** as a white solid. mp = 66 °C. R_f = 0.50 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.21-7.17 (m, 2H), 6.95 (td, 1H, J = 8.4, 2.8 Hz), 5.22 (bs, 1H), 3.27 (s, 3H), 1.16-1.13 (m, 2H), 0.93-0.90 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.56, 154.17, 139.17, 139.15, 119.14, 118.89, 115.11, 115.01, 114.93, 114.90, 108.38, 108.28, 69.64, 52.76, 14.60. IR (neat, cm^{-1}) 3351, 1503, 1454, 1217, 1059, 1049, 1009, 878, 847, 795, 777. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{10}\text{H}_{11}\text{NOFBr}+\text{H}$ 260.0086; Found, 260.0091.



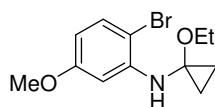
***N*-(1'-ethoxy)cyclopropyl-2-bromo-4-cyanoaniline (1h)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **1h** as a white solid. mp = 138 °C. R_f = 0.31 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.70 (d, 1H, J = 1.2 Hz), 7.48 (dd, 1H, J = 8.4, 1.2 Hz), 7.29 (d, 1H, J = 8.4 Hz), 5.74 (bs, 1H), 3.55 (q, 2H, J = 7.2 Hz), 1.23-1.20 (m, 2H), 1.13 (t, 3H, J = 7.2 Hz), 0.95-0.92 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 146.64, 135.72, 132.41, 118.65, 114.47, 108.50, 101.61, 68.16, 61.58, 15.15, 14.70. IR (neat, cm^{-1}) 3333, 2222, 1593, 1506, 1221, 1188, 1115, 957, 874, 831. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OBr}+\text{H}$ 281.0289; Found, 281.0292.



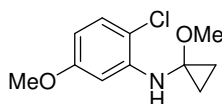
***N*-(1'-ethoxy)cyclopropyl-2-bromo-5-(trifluoromethyl)aniline (1i)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1i** as a colorless oil. R_f = 0.52 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.51 (d, 1H, J = 8.4 Hz), 7.48 (d, 1H, J = 2.0 Hz), 6.89 (dd, 1H, J = 8.4, 2.0 Hz), 5.49 (bs, 1H), 3.55 (q, 2H, J = 7.2 Hz), 1.22-1.19 (m, 2H), 1.13 (t, 3H, J = 7.2 Hz), 0.94-0.91 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 143.21, 132.51, 130.93, 130.61, 125.36, 122.65, 115.54, 115.50, 115.46, 115.42, 112.48, 112.46, 111.32, 111.28, 111.24, 111.20, 68.32, 62.12, 61.30, 15.20, 14.73, 14.19, 12.20. IR (neat, cm^{-1}) 1603, 1585, 1506, 1433, 1331, 1273, 1225, 1167, 1119, 1080, 1061, 1024, 804. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{13}\text{NOF}_3\text{Br}+\text{H}$ 324.0211; Found, 324.0211.



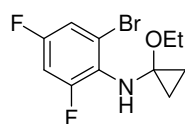
***N*-(1'-ethoxy)cyclopropyl-2-bromo-5-methoxyaniline (1j)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **1j** as a pale yellow oil. R_f = 0.35 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.28 (d, 1H, J = 8.8 Hz), 6.86 (d, 1H, J = 2.8 Hz), 6.25 (dd, 1H, J = 8.8, 2.8 Hz), 5.29 (bs, 1H), 3.78 (s, 3H), 3.55 (q, 2H, J = 6.8 Hz), 1.17-1.14 (m, 2H), 1.13 (t, 3H, J = 6.8 Hz), 0.93-0.90 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.91, 143.54, 132.24, 104.81, 101.03, 100.32, 68.36, 61.07, 55.36, 15.26, 14.80. IR (neat, cm^{-1}) 1597, 1578, 1501, 1447, 1418, 1032, 1206, 1169, 1057, 1016, 596. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2\text{Br}+\text{H}$ 286.0443; Found, 286.0450.



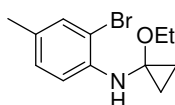
***N*-(1'-methoxy)cyclopropyl-2-chloro-5-methoxyaniline (1k)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **1k** as a white solid. mp = 85 °C. R_f = 0.30 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.13 (d, 1H, J = 8.8 Hz), 6.83 (d, 1H, J = 2.8 Hz), 6.29 (dd, 1H, J = 8.8, 2.8 Hz), 5.33 (bs, 1H), 3.78 (s, 3H), 3.29 (s, 3H), 1.17-1.14 (m, 2H), 0.95-0.92 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.29, 142.35, 129.20, 110.89, 104.14, 100.88, 69.20, 55.39, 52.89, 14.66. IR (neat, cm^{-1}) 3364, 1607, 1508, 1423, 1223, 1204, 1169, 1059, 1049, 1030, 841, 781, 758. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_2\text{Cl}+\text{H}$ 228.0791; Found, 228.0796.

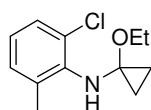


***N*-(1'-ethoxy)cyclopropyl-2-bromo-4,6-difluoroaniline (1l)**

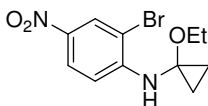
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1l** as a colorless oil. R_f = 0.47 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.07-7.04 (m, 1H), 6.86-6.80 (m, 1H), 5.09 (bs, 1H), 3.54 (q, 2H, J = 7.2 Hz), 1.14-1.10 (m, 2H), 1.08 (t, 3H, J = 7.2 Hz), 1.01-0.98 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.70, 154.28, 154.16, 153.87, 153.75, 151.36, 151.23, 128.35, 115.03, 114.99, 114.78, 114.74, 112.85, 112.78, 105.15, 104.89, 104.64, 71.07, 71.04, 61.27, 16.15, 16.09, 15.23. IR (neat, cm^{-1}) 1595, 1485, 1416, 1225, 1113, 1061, 845, 829. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{11}\text{H}_{12}\text{NOF}_2\text{Br}+\text{H}$ 292.0149; Found, 292.0154.

***N*-(1'-ethoxy)cyclopropyl-2-bromo-4-methylaniline (1m)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1m** as a pale yellow oil. R_f = 0.44 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.25 (d, 1H, J = 1.6 Hz), 7.18 (d, 1H, J = 8.4 Hz), 7.01 (dd, 1H, J = 8.4, 1.6 Hz), 5.23 (bs, 1H), 3.55 (q, 2H, J = 7.2 Hz), 2.24 (s, 3H), 1.15-1.13 (m, 2H), 1.12 (t, 3H, J = 7.2 Hz), 0.93-0.90 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.23, 132.38, 128.83, 128.64, 114.78, 109.03, 68.50, 60.93, 20.05, 15.25, 14.77. IR (neat, cm^{-1}) 1611, 1506, 1314, 1221, 1061, 1040, 959, 810. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{16}\text{NOBr}+\text{H}$ 270.0494; Found, 270.0499.

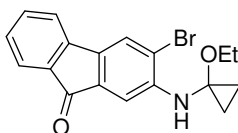
***N*-(1'-ethoxy)cyclopropyl-2-chloro-6-methylaniline (1n)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 20 / 1) to afford **1n** as a yellow oil. R_f = 0.54 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.13 (dd, 1H, J = 7.6, 0.8 Hz), 7.02 (dd, 1H, J = 7.6, 0.8 Hz), 6.74 (t, 1H, J = 7.6 Hz), 5.13 (bs, 1H), 3.65 (q, 2H, J = 7.2 Hz), 2.48 (s, 3H), 1.12 (t, 3H, J = 7.2 Hz), 1.11-1.07 (m, 2H), 0.87-0.84 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.78, 130.46, 130.42, 126.50, 124.26, 121.12, 71.22, 61.18, 20.95, 16.57, 15.29. IR (neat, cm^{-1}) 1466, 1306, 1229, 1061, 1015, 760, 721. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{16}\text{NOCl}+\text{H}$ 226.0999; Found, 226.1003.



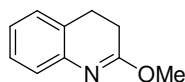
***N*-(1'-ethoxy)cyclopropyl-2-bromo-4-nitroaniline (1o)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 5 / 1) to afford **1o** as a pale yellow solid. mp = 139 °C. R_f = 0.24 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 8.38 (d, 1H, J = 2.4 Hz), 8.13 (dd, 1H, J = 9.2, 2.4 Hz), 7.31 (d, 1H, J = 9.2 Hz), 5.90 (bs, 1H), 3.57 (q, 2H, J = 7.2 Hz), 1.26-1.24 (m, 2H), 1.14 (t, 3H, J = 7.2 Hz), 0.98-0.96 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.49, 139.29, 128.49, 124.63, 113.24, 107.80, 68.33, 61.77, 15.16, 14.74. IR (neat, cm^{-1}) 3352, 1591, 1504, 1325, 1306, 1221, 1115, 1057, 1013, 745, 492. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_3\text{Br}+\text{H}$ 301.0188; Found, 301.0183.



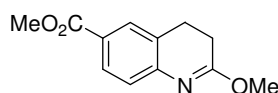
2-{*N*-(1'-ethoxy)cyclopropyl}amino-3-bromo-9-fluorenone (1p)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 5 / 1) to afford **1p** as a red solid. mp = 155 °C. R_f = 0.20 (*n*-heptane / ethyl acetate = 10 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.60 (d, 1H, J = 7.2 Hz), 7.60 (s, 1H), 7.56 (s, 1H), 7.42 (t, 1H, J = 7.6 Hz), 7.33 (d, 1H, J = 7.6 Hz), 7.18 (t, 1H, J = 7.2 Hz), 5.54 (bs, 1H), 3.55 (q, 2H, J = 7.2 Hz), 1.23-1.20 (m, 2H), 1.12 (t, 3H, 7.2 Hz), 0.96-0.93 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.46, 144.43, 143.83, 134.79, 134.74, 134.69, 134.08, 127.80, 124.41, 124.34, 119.21, 114.53, 110.97, 68.35, 61.31, 15.24, 14.79. IR (neat, cm^{-1}) 1703, 1595, 1489, 1456, 1418, 1314, 1217, 1057, 955, 758, 731. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{18}\text{H}_{16}\text{NOBr}_2+\text{H}$ 358.0443; Found, 358.0448.



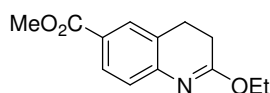
2-methoxy-3,4-dihydroquinoline (2a)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **2a** as a pale yellow oil. R_f = 0.54 (*n*-heptane / ethyl acetate = 5 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.21-7.18 (m, 1H), 7.16-7.14 (m, 1H), 7.10 (d, 1H, J = 7.2 Hz), 7.02 (td, 1H, J = 7.2, 1.6 Hz), 3.90 (s, 3H), 2.86 (t, 2H, J = 8.0 Hz), 2.45 (t, 2H, J = 8.0 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.21, 144.19, 127.39, 127.28, 126.47, 124.73, 124.42, 53.28, 25.45, 25.11. IR (neat, cm^{-1}) 1636, 1601, 1479, 1437, 1358, 1265, 1240, 1188, 1016, 760, 673. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{10}\text{H}_{11}\text{NO}+\text{H}$ 162.0919; Found, 162.0918.



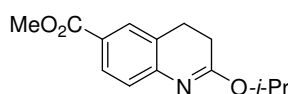
***O*-methyl-6-quinolinecarboxylic acid, 1,2,3,4-tetrahydro-2-oxo-, methyl ester (2b)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **2b** as a white solid. mp = 106 °C. R_f = 0.38 (*n*-heptane / ethyl acetate = 5 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.88 (d, 1H, J = 8.4 Hz), 7.81 (s, 1H), 7.18 (d, 1H, J = 8.4 Hz), 3.93 (s, 3H), 3.89 (s, 3H), 2.90 (t, 2H, J = 8.4 Hz), 2.47 (t, 2H, J = 8.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.06, 167.07, 148.60, 129.22, 128.74, 126.40, 125.88, 124.54, 53.62, 51.92, 25.15, 25.00. IR (neat, cm^{-1}) 1707, 1636, 1595, 1431, 1360, 1290, 1246, 1194, 1094, 1016, 849, 764. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3+\text{H}$ 220.0974; Found, 220.0979.



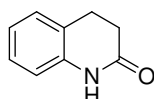
***O*-ethyl-6-quinolinecarboxylic acid, 1,2,3,4-tetrahydro-2-oxo-, methyl ester (2c)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **2c** as a white solid. mp = 82 °C. R_f = 0.43 (*n*-heptane / ethyl acetate = 5 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.87 (d, 1H, J = 8.0 Hz), 7.80 (s, 1H), 7.15 (d, 1H, J = 8.0 Hz), 4.38 (q, 2H, J = 7.2 Hz), 3.89 (s, 3H), 2.89 (t, 2H, J = 8.4 Hz), 2.46 (t, 2H, J = 8.4 Hz), 1.37 (t, 3H, J = 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.65, 167.08, 148.82, 129.18, 128.71, 126.41, 125.69, 124.43, 62.16, 51.92, 25.26, 25.13, 14.25. IR (neat, cm^{-1}) 1715, 1628, 1591, 1570, 1435, 1377, 1346, 1240, 1188, 1036. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3+\text{H}$ 234.1130; Found, 234.1128.



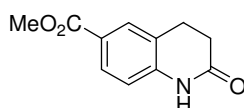
***O*-isopropyl-6-quinolinecarboxylic acid, 1,2,3,4-tetrahydro-2-oxo-, methyl ester (2d)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 10 / 1) to afford **2d** as an off-white solid. mp = 64 °C. R_f = 0.50 (*n*-heptane / ethyl acetate = 5 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.87 (d, 1H, J = 8.0 Hz), 7.79 (s, 1H), 7.13 (d, 1H, J = 8.0 Hz), 5.42 (septet, 1H, J = 6.0 Hz), 3.89 (s, 3H), 2.88 (t, 2H, J = 8.0 Hz), 2.42 (t, 2H, J = 8.0 Hz), 1.33 (d, 6H, J = 6.0 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.00, 167.13, 149.08, 129.14, 128.68, 126.35, 125.48, 124.35, 68.69, 51.88, 25.60, 25.13, 21.84. IR (neat, cm^{-1}) 1707, 1626, 1593, 1435, 1373, 1254, 1240, 1192, 1092, 1005, 762. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3+\text{H}$ 248.1287; Found, 248.1290.



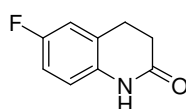
3,4-dihydro-2(1H)-quinolinone (3a)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3a** as a white solid. mp = 165 °C. R_f = 0.50 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 8.39 (bs, 1H), 7.19-7.16 (m, 2H), 6.99 (t, 1H, J = 7.2 Hz), 6.79 (d, 1H, J = 7.2 Hz), 2.98 (t, 2H, J = 7.6 Hz), 2.65 (t, 2H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.34, 137.31, 127.82, 127.46, 123.54, 122.99, 115.55, 30.66, 25.26. IR (neat, cm^{-1}) 1674, 1591, 1489, 1431, 1383, 1281, 1246, 1198, 812, 743, 681.



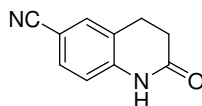
6-quinolinecarboxylic acid, 1,2,3,4-tetrahydro-2-oxo-, methyl ester (3b)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3b** as an off-white solid. mp = 185 °C. R_f = 0.47 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.96 (bs, 1H), 7.89-7.87 (m, 2H), 6.78 (d, 1H, J = 8.8 Hz), 3.90 (s, 3H), 3.03 (t, 2H, J = 7.6 Hz), 2.68 (t, 2H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.96, 166.58, 141.26, 129.57, 129.52, 124.83, 123.31, 115.17, 52.04, 30.43, 25.06. IR (neat, cm^{-1}) 1711, 1668, 1614, 1373, 1285, 1246, 1186, 764.

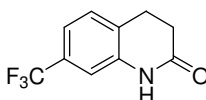


6-fluoro-3,4-dihydro-2(1H)-quinolinone (3c)

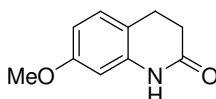
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3c** as a white solid. mp = 181 °C. R_f = 0.46 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 10.09 (bs, 1H), 7.05 (dd, 1H, J = 9.2, 2.8 Hz), 6.97 (td, 1H, J = 8.8, 2.8 Hz), 6.84 (dd, 1H, J = 9.2, 8.8 Hz), 2.87 (t, 2H, J = 7.6 Hz), 2.43 (t, 2H, J = 7.6 Hz). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ 169.88, 158.56, 156.19, 134.77, 134.75, 125.71, 125.63, 116.06, 115.97, 114.57, 114.34, 113.51, 113.29, 29.93, 24.75, 24.73. IR (neat, cm^{-1}) 1663, 1495, 1381, 1227, 947, 864, 650, 579, 527.

**6-cyano-3,4-dihydro-2(1H)-quinolinone (3d)**

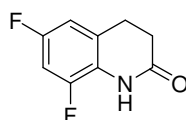
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 2) to afford **3d** as a yellow solid. mp = >250 °C. R_f = 0.39 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (DMSO- d_6 , 400 MHz) δ 10.50 (bs, 1H), 7.66 (s, 1H), 7.60 (d, 1H, J = 8.0 Hz), 6.97 (d, 1H, J = 8.0 Hz), 2.92 (t, 2H, J = 7.6 Hz), 2.50 (t, 2H, J = 7.6 Hz). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 170.28, 142.62, 131.67, 131.55, 124.73, 119.22, 115.53, 103.60, 29.69, 24.15. IR (neat, cm^{-1}) 2222, 1670, 1499, 1368, 1323, 1204, 912, 826, 642.

**7-trifluoromethyl-3,4-dihydro-2(1H)-quinolinone (3e)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3e** as an off-white solid. mp = 176 °C. R_f = 0.60 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 8.69 (bs, 1H), 7.30-7.26 (m, 2H), 7.03 (s, 1H), 3.04 (t, 2H, J = 7.6 Hz), 2.68 (t, 2H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.10, 137.88, 130.28, 129.96, 128.38, 127.47, 122.45, 119.83, 119.79, 119.75, 112.25, 30.20, 25.27. IR (neat, cm^{-1}) 1680, 1489, 1408, 1329, 1163, 1119, 1070, 887, 826, 694. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{10}\text{H}_8\text{NOF}_3+\text{H}$ 216.0636; Found, 216.0639.

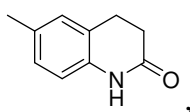
**7-methoxy-3,4-dihydro-2(1H)-quinolinone (3f)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 2) to afford **3f** as a yellow solid. mp = 147 °C. R_f = 0.44 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (bs, 1H), 7.06 (d, 1H, J = 8.4 Hz), 6.54 (dd, 1H, J = 8.4, 2.8 Hz), 6.31-6.29 (m, 1H), 3.78 (s, 3H), 2.90 (t, 2H, J = 7.6 Hz), 2.62 (t, 2H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.49, 159.25, 138.33, 128.59, 115.74, 108.29, 101.69, 55.45, 31.06, 24.56. IR (neat, cm^{-1}) 1672, 1622, 1591, 1379, 1269, 1161, 1036, 851, 797.

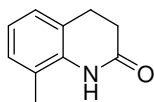


6,8-difluoro-3,4-dihydro-2(1H)-quinolinone (3g)

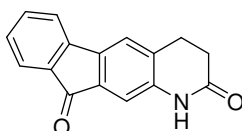
The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3g** as a yellow solid. mp = 195 °C. R_f = 0.55 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (bs, 1H), 6.80-6.73 (m, 2H), 3.00 (t, 2H, J = 7.6 Hz), 2.66 (t, 2H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.10, 158.97, 158.85, 156.53, 156.41, 150.73, 150.61, 148.29, 148.16, 126.87, 126.84, 126.78, 126.75, 122.25, 122.21, 122.12, 122.09, 110.52, 110.48, 110.29, 110.25, 102.65, 102.43, 102.39, 102.17, 30.31, 25.60, 25.57, 25.55. IR (neat, cm^{-1}) 1697, 1506, 1429, 1366, 1250, 1113, 1011, 966, 835, 797, 586, 513. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_9\text{H}_7\text{NOF}_2+\text{H}$ 184.0574; Found, 184.0575

**6-methyl-3,4-dihydro-2(1H)-quinolinone (3h)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3h** as an off-white solid. mp = 137 °C. R_f = 0.50 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 8.26 (bs, 1H), 6.98-6.96 (m, 2H), 6.69-6.66 (m, 1H), 2.93 (t, 2H, J = 7.6 Hz), 2.62 (t, 2H, J = 7.6 Hz), 2.29 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.14, 134.84, 132.53, 128.51, 127.88, 123.47, 115.38, 115.30, 30.77, 25.31, 20.70. IR (neat, cm^{-1}) 1667, 1505, 1379, 1254, 1192, 827, 525, 463.

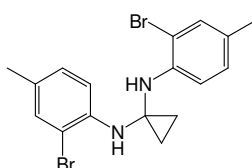
**8-methyl-3,4-dihydro-2(1H)-quinolinone (3i)**

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3i** as an off-white solid. mp = 134 °C. R_f = 0.60 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.73 (bs, 1H), 6.98 (s, 1H), 6.98 (d, 1H, J = 8.8 Hz), 6.64 (d, 1H, J = 8.8 Hz), 2.93 (t, 2H, J = 7.6 Hz), 2.62 (t, 2H, J = 7.6 Hz), 2.29 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.45, 135.52, 129.01, 125.75, 123.71, 122.65, 30.75, 25.66, 16.70. IR (neat, cm^{-1}) 1655, 1597, 1470, 1383, 1260, 1192, 1028, 758, 731, 525.

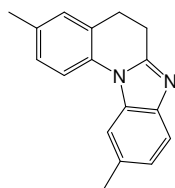


3,4-dihydro-1*H*-indeno[1,2-*g*]quinoline-2,10-dione (3j)

The general procedure was followed. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 1) to afford **3j** as an orange solid. mp = >250 °C. R_f = 0.38 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 8.38 (bs, 1H), 7.62 (d, 1H, J = 7.2 Hz), 7.45 (qd, 1H, J = 7.2, 1.2 Hz), 7.42 (t, 1H, J = 7.2 Hz), 7.31 (s, 1H), 7.26 (s, 1H), 7.24 (td, 1H, J = 7.2, 1.2 Hz), 3.05 (t, 2H, J = 7.6 Hz), 2.69 (t, 2H, J = 7.6 Hz). ^{13}C NMR (DMSO-d^6 , 100 MHz) δ 192.63, 169.84, 144.12, 139.30, 137.63, 135.25, 133.30, 132.67, 130.64, 128.31, 123.68, 120.85, 120.19, 110.54, 29.62, 25.34. IR (neat, cm^{-1}) 1705, 1668, 1597, 1456, 1412, 1373, 1327, 839, 762, 669. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{11}\text{NO}_2+\text{H}$ 250.0868; Found, 250.0869.

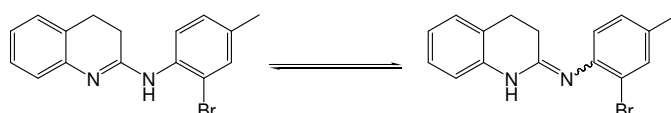
**1,1-di(2-bromo-4-methylanilino)cyclopropane (5)**

The compound **5** was obtained as a byproduct during the course of the preparation of **1m**. Pure white solid **5** was separated out from the extract. mp = 127 °C. R_f = 0.65 (*n*-heptane / ethyl acetate = 5 / 1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.19 (s, 2H), 7.05-7.03 (m, 4H), 5.36 (bs, 2H), 2.21 (s, 6H), 1.24 (s, 4H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.29, 132.99, 128.84, 128.58, 113.37, 110.07, 45.58, 20.02, 16.63. IR (neat, cm^{-1}) 1606, 1500, 1302, 1278, 1259, 1231, 1030, 863, 801, 670. HRMS was not detected due to decomposition of the compound. Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{Br}_2$: C, 49.78; H, 4.42; N, 6.83. Found: C, 49.83; H, 4.43; N, 6.72.

**3,10-dimethyl-5,6-dihydrobenzimidazo[1,2-*a*]quinoline (6)**

A mixture of 1,1-dianilino-cyclopropane **5** (1.0 mmol, 0.2 M), K_2CO_3 (2.0 equiv), $\text{Pd}_2(\text{dba})_3$ (3.0 mol %) and X-Phos (15.0 mol %) in DMF (5.0 mL) was stirred at 95 °C under nitrogen atmosphere in a round bottomed flask for 30 h. The reaction mixture was then poured into 0.5N HCl aq., and the resulting mixture was extracted with AcOEt 3 times. The combined organic extracts were washed with brine 2 times. The obtained solution was dried with Na_2SO_4 , and concentrated in vacuo with a rotary evaporator. The residue was purified by flash chromatography (*n*-heptane / ethyl acetate = 1 / 2) to give the corresponding 5,6-dihydrobenzimidazo[1,2-*a*]quinoline **6** as an

off-white solid. mp = 114 °C. R_f = 0.27 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.72 (d, 1H, J = 8.0 Hz), 7.66 (s, 1H), 7.65 (d, 1H, J = 8.0 Hz), 7.22 (d, 1H, J = 8.0 Hz), 7.18 (s, 1H), 7.13 (d, 1H, J = 8.0 Hz), 3.20 (t, 2H, J = 6.8 Hz), 2.99 (t, 2H, J = 6.8 Hz), 2.54 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.15, 141.73, 134.60, 133.53, 132.84, 132.15, 129.70, 128.43, 128.11, 123.99, 119.27, 116.36, 111.31, 26.59, 24.63, 21.97, 20.89. IR (neat, cm^{-1}) 1539, 1506, 1479, 1379, 1248, 1190, 802, 741, 599, 545. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2+\text{H}$ 249.1392; Found, 249.1387.



***N*-(2-bromo-4-methylphenyl)-3,4-dihydro-2(1*H*)-quinolinamine (7 and 8)**

The compound **7** and **8** were obtained as byproducts during the reaction of **5**. The crude material was purified on silica gel (*n*-heptane / ethyl acetate = 1 / 2) to afford **7** and **8** as an off-white solid. mp = 197~199 °C. R_f = 0.64 (*n*-heptane / ethyl acetate = 1 / 2). ^1H NMR (CDCl_3 , 400 MHz) δ 7.44 (s, 0.5 H), 7.38 (s, 0.5 H), 7.11 (d, 0.5H, J = 8.8 Hz), 7.05 (d, 0.5H, J = 6.8 Hz), 6.95-6.90 (m, 2H), 6.88-6.85 (m, 0.5H), 6.69 (bs, 0.5H), 6.43 (d, 0.5H, J = 8.0 Hz), 6.34 (bs, 0.5H), 2.95-2.91 (m, 1H), 2.84-2.77 (m, 2H), 2.43 (t, 1H, J = 7.6 Hz), 2.33 (s, 1.5H), 2.30 (s, 1.5H), 2.28 (s, 1.5H), 2.26 (s, 1.5H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 157.21, 153.48, 144.02, 135.12, 134.35, 133.82, 133.64, 132.93, 131.42, 130.96, 129.40, 128.80, 128.75, 128.31, 127.85, 127.76, 124.05, 123.58, 123.11, 122.99, 116.10, 114.52, 30.21, 25.55, 25.14, 25.06, 20.70, 20.64, 20.48, 20.43. IR (neat, cm^{-1}) 1649, 1593, 1504, 1377, 1334, 1255, 1222, 1046, 840, 818, 673, 536, 448. HRMS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{Br}+\text{H}$ 329.0653; Found, 329.0650.

