First Synthesis of 3,6′- and 3,7′-Biquinoline Derivatives

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Abstract: The preparation of new 3,6′- and 3,7′-biquinoline derivatives was achieved by microwave-assisted Suzuki cross-coupling between N-protected 6- or 7-bromoquinolin-2(1H)-ones and quinolin-3-ylboronic acid. Moreover, a new synthesis of 7-bromoquinolin-2(1H)-one leading solely to the 7-substituted isomer was carried out.

Keywords: quinoline, quinolinone, 6-bromoquinolin-2(1H)-one, 7-bromoquinolin-2(1H)-one, Suzuki cross-coupling

In the course of studies on new compounds with biological activity, we became interested in the synthesis of 3,6′- and 3,7′-biquinoline derivatives by the coupling of a quinoline moiety with a quinolin-2(1H)-one derivative bearing a halogen atom in the 6- or 7-position. However, only a few examples of functionalization at the 6- and 7-positions of 6- and 7-haloquinolin-2(1H)-ones have been carried out. The reported methods involved either halogen/magnesium exchange, halogen/lithium exchange, palladium-catalyzed amino carbonylation, palladium-catalyzed carboxylation, copper-catalyzed aromatic nucleophilic substitution, or Heck cross-coupling. To our knowledge, only one example of the Suzuki cross-coupling has been described with an N-unprotected 6-haloquinolin-2(1H)-one derivative and various substituted phenylboronic acids in the presence of tetrakis(triphenylphosphine)palladium, lithium chloride, and potassium carbonate.

Thus, for the preparation of 3,6′- and 3,7′-biquinoline derivatives, we decided to follow this latter method by reacting 6- or 7-bromoquinolin-2(1H)-one derivatives and quinolin-3-ylboronic acid under Suzuki cross-coupling conditions (Scheme 1).

6-Bromoquinolin-2(1H)-one (3) was prepared in three steps according to procedures already described in the literature. Iodination of 4-bromoaniline with benzyltrimethylammonium dichloroiodate in dichloromethane–methanol in the presence of calcium carbonate produced 4-bromo-2-idoaniline (1), which was reacted with methyl acrylate in the presence of palladium(II) acetate and tributylamine under microwave irradiation to give methyl (E)-3-(2-amino-5-bromophenyl)prop-2-enoate (2). The quinolinone formation to give 3 was achieved by refluxing compound 2 in ethylene glycol (Scheme 2).

While already described synthetic methods allowed the preparation of the 6-bromoquinolin-2(1H)-one (3), to our knowledge, no regioselective preparation of the corresponding 7-isomer has been reported. This compound was previously synthesized in two steps from 3-bromoaniline as an inseparable regioisomeric mixture of 5- and 7-bromoquinolin-2(1H)-ones (Scheme 3).

Therefore, a new synthesis of 7-bromoquinolin-2(1H)-one was carried out that led only to the 7-substituted isomer. We report here a convenient four-step synthesis of this heterocyclic compound in 41% overall yield starting from 4-bromo-2-nitroaniline. Diazotization of 4-bromo-2-nitroaniline followed by iodination as described by Flatt et al. afforded the corresponding aryl iodide. The reduction of the nitro group was carried out in the presence of tin(II) chloride. Literature data reported a reduction yield of 69% using four equivalents of tin(II) chloride. Under these conditions, we observed the formation of a deiodinated product. When the reaction was carried out in the presence of three equivalents of tin(II) chloride, the starting material was partially recovered. This reaction...
was optimized by using 3.5 equivalents of tin(II) chloride to obtain 6 in 90% yield. The quinolinone formation was achieved in two steps following the procedure described before for the synthesis of the 6-bromo analogue. Compound 6 was treated with methyl acrylate in the presence of palladium acetate and tributylamine under microwave irradiation to give 7 in 80% yield as well as the disubstituted analogue 8 in 9% yield. The cyclization to 9 was performed in 73% yield by refluxing 7 in ethylene glycol (Scheme 4).

For the preparation of biquinoline derivatives, coupling between quinolin-2(1H)-ones and quinolin-3-ylboronic acid subunits was achieved by Suzuki cross-coupling (Scheme 5). Quinolin-3-ylboronic acid was prepared as previously described from 3-bromoquinoline.\textsuperscript{20} The coupling reaction was first unsuccessfully conducted on the unprotected 6-bromoquinolin-2(1H)-one (3) in the presence of tetrakis(triphenylphosphine)palladium, sodium carbonate, and lithium chloride as previously described for an N-unprotected 6-bromoquinolin-2(1H)-one derivative with phenylboronic acids.\textsuperscript{9} Despite several trials using different catalytic conditions [Pd(OAc)\textsubscript{2}/NaOMe or PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}/Na\textsubscript{2}CO\textsubscript{3}] the coupling product was not obtained using unprotected 6-bromoquinolin-2(1H)-one (3). Subsequently, the Suzuki coupling was performed using 6-bromo-1-(tert-butoxycarbonyl)quinolin-2(1H)-one (4), which was prepared by treatment of 3 with di-tert-butyl dicarbonate in the presence of sodium hydride in tetrahydrofuran (Scheme 2).

**Scheme 2**  Synthesis of 6-bromoquinolin-2(1H)-one derivatives

**Scheme 3**  Preparation of 5- and 7-bromoquinolin-2(1H)-ones as a regioisomeric mixture

**Scheme 4**  Preparation of 7-bromoquinolin-2(1H)-one
Synthesis of 3,6'- and 3,7'-Biquinoline Derivatives

Different catalytic systems were tested either in the presence of Pd(OAc)$_2$/Na$_2$CO$_3$ or PdCl$_2$(PPh$_3$)$_2$/Na$_2$CO$_3$. The best result was obtained with PdCl$_2$(PPh$_3$)$_2$/Na$_2$CO$_3$ under microwave irradiation. When the reaction was performed between 4 and quinolin-3-ylboronic acid in refluxing tetrahydrofuran using PdCl$_2$(PPh$_3$)$_2$/Na$_2$CO$_3$, the product 11 was obtained in 34% yield after four hours, while product 11 was obtained in 47% yield when the reaction was conducted for ten minutes under microwave irradiation. The same procedure applied to 7-bromo analogue 10, which was obtained in 84% yield by treating 9 with di-tert-butyl dicarbonate in the presence of sodium hydride in tetrahydrofuran (Scheme 4), afforded compound 12 in 63% yield. In this case, the use of microwave irradiation resulted in considerably shortened reaction times (Scheme 5).

Deprotection of compounds 11 and 12 with trifluoroacetic acid in dichloromethane gave the corresponding deprotected products 13 and 14 in 94% and 99% yields, respectively.

The biquinolinone derivatives 17 and 18 were obtained using a classical two-step oxidation procedure to convert the quinoline moiety into the corresponding quinolinone ring. Compounds 11 and 12 were firstly reacted with 3-chloroperoxybenzoic acid in dichloromethane to give the corresponding N-oxide derivatives 15 and 16 in 80% and 79% yields, respectively. Treatment of compounds 15 and 16 with tosyl chloride in the presence of potassium carbonate led to the biquinolinone derivatives 17 and 18 in 90% and 71% yields, respectively. The final deprotection step using trifluoroacetic acid in dichloromethane gave 3,6'-biquinoline-2,2'-dione (19) and 3,7'-biquinoline-2,2'-dione (20) in 86% and 83% yields, respectively (Scheme 5).

In conclusion, the first synthesis of pure 7-bromoquinolin-2(1H)-one (9) has been described. The preparation of new 3,6'- and 3,7'-biquinoline derivatives was achieved by microwave-assisted Suzuki cross-coupling between N-protected 6- or 7-bromoquinolin-2(1H)-ones and quinolin-3-ylboronic acid. Moreover, this is, to our knowledge, the first time that a substitution of 7-haloquinolin-2(1H)-one derivative using a Suzuki cross-coupling reaction has been reported.

IR Spectra were recorded on a Perkin-Elmer Paragon 500 spectrophotometer. NMR spectra were performed on a Bruker AVANCE 400 (1H: 400 MHz, 13C: 100 MHz). Mass spectra (ESI+) were determined on a high resolution Waters Micro Q-Toff apparatus. Chromatographic purifications were performed on flash silica gel Geduran SI 60 (Merck) 0.040–0.063 mm column chromatography. TLC were performed on fluorescent silica gel plates (60 F254 from Merck). Experiments under microwave irradiation were performed using a CEM Discover Benchmate microwave apparatus.

Scheme 5 Preparation of 3,6'- and 3,7'-biquinoline derivatives
6-Bromo-1-(tert-butoxycarbonyl)quinolin-2(1H)-one (4); Typical Procedure

Compound 3 (1.50 g, 6.69 mmol) was added to a suspension of NaH (60% in a mineral oil, 1.07 g, 26.8 mmol) in anhyd THF (20 mL). The mixture was stirred at 50 °C for 1 h. After cooling, a solution of (Boc)₂O (5.84 g, 26.8 mmol) in anhyd THF (10 mL) was added and the mixture was stirred at 50 °C for 2 h. After cooling, the mixture was poured into sat. aq NH₄Cl (150 mL) and extracted with EtOAc. The organic fractions were dried (MgSO₄) and evaporated. The residue was purified by flash chromatography (cyclohexane–EtOAc, 9:1) to give 4 (1.67 g, 77%) as a white solid; mp 98–99 °C.

IR (KBr): 1747, 1592, 1488, 1374, 1280, 1254, 1213, 1145 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.52 (s, 9 H, CH₃), 7.48 (d, J = 8.5 Hz, 1 H), 7.87 (d, J = 9.0 Hz, 1 H), 7.92 (dd, J₁ = 9.0 Hz, J₂ = 2.0 Hz, 1 H), 8.36 (d, J = 2.0 Hz, 1 H), 8.52 (d, J = 8.5 Hz, 1 H).

13C NMR (100 MHz, DMSO-d₆): δ = 27.2 (3 CH₃), 116.6, 130.0 (2 C), 133.5, 140.1 (CH), 84.2, 119.5, 128.1, 144.4 (C), 150.2, 156.2 (C=O).

HRMS (ES⁺): m/z [M + H]+ for C₉H₇NO₂⁺ 262.0972; found: 262.0927.

7-Bromoquinolin-2(1H)-one (9)

A soln of 7 (4.58 g, 17.9 mmol) in ethylene glycol (60 mL) was refluxed for 15 h. After cooling, the mixture was poured into H₂O (200 mL) and the solid was filtered and washed with Et₂O and CH₂Cl₂ to give 9 (2.94 g, 73%) as a brown solid; mp 270–272 °C.

IR (KBrs): 3100–2800, 1698 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 6.52 (d, J = 9.5 Hz, 1 H), 7.33 (dd, J₁ = 8.5 Hz, J₂ = 2.0 Hz, 1 H), 7.47 (d, J = 1.5 Hz, 1 H), 7.61 (d, J = 8.5 Hz, 1 H), 7.89 (d, J = 9.5 Hz, 1 H), 11.74–11.86 (br s, 1 H, NH).

13C NMR (100 MHz, DMSO-d₂): δ = 117.3, 122.4, 124.6, 129.8, 139.7 (CH), 118.1, 123.4, 139.9 (Cα-α), 161.6 (C=O).

HRMS (ES⁺): m/z [M + H]+ for C₂₇H₂₇BrNO: 523.9711; found: 523.9711.

7-Bromo-1-(tert-butoxycarbonyl)quinolin-2(1H)-one (10)

Following the typical procedure for 4 and using 9 (2.10 g, 9.4 mmol), NaH (60% in a mineral oil, 750 mg, 18.8 mmol) in anhyd THF (30 mL) and (Boc)₂O (4.10 g, 18.8 mmol) in anhyd THF (20 mL) with purification by flash chromatography (cyclohexane–EtOAc, 8:2) gave 10 (2.56 g, 84%) as a white solid; mp 95–96 °C.

IR (KBr): 1766, 1610, 1489, 1261, 1214, 1148–1118 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.52 (s, 9 H, CH₃), 7.47 (d, J = 8.5 Hz, 1 H), 7.80 (dd, J₁ = 8.5 Hz, J₂ = 2.0 Hz, 1 H), 8.03 (d, J = 8.5 Hz, 1 H), 8.16 (d, J = 2.0 Hz, 1 H), 8.57 (d, J = 8.5 Hz, 1 H).

13C NMR (100 MHz, DMSO-d₂): δ = 27.2 (3 CH₃), 116.1, 129.8, 129.9 (2 C), 141.1 (CH), 84.3, 123.9, 125.7, 146.4 (C), 150.2, 156.7 (C=O).

HRMS (ES⁺): m/z [M + Na]+ for C₂₇H₂₇BrNaNO₂: 346.0055; found: 346.0058.

1-(tert-Butoxycarbonyl)-3,6-biquinolin-2(1H)-one (11); Typical Procedure

To a soln of 4 (200 mg, 0.62 mmol) in THF (7 mL) were added PdCl₂(PPh₃)₂ (21.7 mg, 0.031 mmol), aq 2 M Na₂CO₃ (1.54 mL, 3.08 mmol) and quinolin-3-ylboronic acid (160 mg, 0.92 mmol). The mixture was stirred under microwave irradiation (64 °C, 50 W, P atm) for 10 min then poured into H₂O (20 mL) and extracted with EtOAc. The organic fractions were dried (MgSO₄) and evaporated. The residue was purified by flash chromatography (cyclohexane–EtOAc, 8:2) to give 11 (0.69 mg, 47%) as a white solid; mp 143–144 °C.

IR (KBr): 1758, 1213, 1145 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.54 (s, 9 H, CH₃), 7.49 (d, J = 8.5 Hz, 1 H), 7.68 (dd, J₁ = 8.0 Hz, J₂ = 7.0 Hz, 1 H), 7.81 (dd, J₁ = 8.0 Hz, J₂ = 1.0 Hz, 1 H), 8.07–8.18 (m, 3 H), 8.35 (dd, J₁ = 9.0 Hz, J₂ = 2.0 Hz, 1 H), 8.60–8.65 (m, 2 H), 8.83 (d, J = 2.0 Hz, 1 H), 9.42 (d, J = 2.0 Hz, 1 H).

13C NMR (100 MHz, DMSO-d₂): δ = 27.2 (3 CH₃), 116.2, 126.1, 127.2, 128.5, 128.7, 129.8, 129.9, 133.5, 141.2, 149.5 (CH), 84.1, 127.2, 127.6, 131.8, 135.1, 145.4, 147.0 (C), 150.4, 156.2 (C=O).

HRMS (ES⁺): m/z [M + H]+ for C₂₉H₂₉BrNO₂: 573.1552; found: 573.1561.

1-(tert-Butoxycarbonyl)-3,7-biquinolin-2(1H)-one (12)

Following the typical procedure for 11 using 10 (100 mg, 0.308 mmol) in THF (5 mL), PdCl₂(PPh₃)₂ (10.8 mg, 0.015 mmol), aq 2 M Na₂CO₃ (0.77 mL, 1.54 mmol), and quinolin-3-ylboronic acid (80.0 mg, 0.46 mmol) with microwave irradiation (64 °C, 50 W, P atm) for 5 min. Work up used H₂O (10 mL) and purification was by flash chromatography (cyclohexane–EtOAc, 8:2 then 7:3) to give 12 (72.6 mg, 63%) as a white solid; mp 145–146 °C.
IR (KBr): 1763, 1652, 1219, 1143 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.54 (s, 9 H, CH₃), 7.45 (d, J = 8.5 Hz, 1 H), 7.68 (dd, J₁ = 8.0 Hz, J₂ = 7.0 Hz, J₃ = 1.0 Hz, 1 H), 7.82 (dd, J₁ = 8.5 Hz, J₂ = 7.0 Hz, J₃ = 1.5 Hz, 1 H), 8.07–8.13 (m, 2 H), 8.20 (dd, J₁ = 8.5 Hz, J₂ = 1.5 Hz, 1 H), 8.24 (d, J = 8.5 Hz, 1 H), 8.45–8.46 (m, 1 H), 8.61 (d, J = 8.5 Hz, 1 H), 8.89 (d, J = 2.0 Hz, 1 H), 9.45 (d, J = 2.5 Hz, 1 H).

13C NMR (100 MHz, DMSO-d₆): δ = 27.2 (3 CH₃), 115.8, 125.8 (2 C), 121.7, 126.2 (2 C), 128.9, 129, 133.9, 140.7, 149.5 (CH), 84.0, 126.4, 126.7, 131.7, 139.0, 146.1, 147.1 (C), 150.4, 156.4 (C=O).

HRMS (ES+): m/z [M + H]+ for C₃₂H₂₆N₈O₇: 373.552; found: 373.571.

3,6'-Biquinolin-2(1'H)-one (13); Typical Procedure
To a soln of 11 (191 mg, 0.51 mmol) in anhyd CH₂Cl₂ (5 mL) was added TFA (0.38 mL, 5.12 mmol). The mixture was stirred at r.t. for 2 h then basified with sat. aq NaHCO₃. The solid was filtered and thoroughly washed with H₂O then with Et₂O to give 13 (131 mg, 94%) as a white solid; mp 225 °C.

IR (KBr): 3625–3000, 1675, 1565, 1430 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 6.58 (d, J = 9.5 Hz, 1 H), 7.47 (d, J = 8.5 Hz, 1 H), 7.65 (t, J = 7.5 Hz, 1 H), 7.77 (t, J = 7.5 Hz, 1 H), 8.01 (d, J = 9.5 Hz, 1 H), 8.03–8.08 (m, 3 H), 8.24 (s, 1 H), 8.67 (s, 1 H), 9.30 (d, J = 2.0 Hz, 1 H), 11.69–12.12 (br s, 1 H, NH).

13C NMR (100 MHz, DMSO-d₆): δ = 116.1, 122.6, 126.3, 127.1, 128.3, 1287, 129.2, 129.4, 132.3, 140.3, 149.3 (CH), 197.9, 197.7, 130.4, 130.2, 138.0, 146.7 (C=O).


3,7'-Biquinolin-2(1'H)-one (14)
Following the typical procedure for 13 using 12 (600 mg, 1.61 mmol) in anhyd CH₂Cl₂ (20 mL) and TFA (0.60 mL, 921 mg, 8.1 mmol) gave 14 (437 mg, 99%) as a pale yellow solid; mp ≥ 241 °C.

IR (KBr): 3388, 1678 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 6.56 (d, J = 9.5 Hz, 1 H), 7.68–7.73 (m, 3 H), 7.83 (dd, J₁ = 8.5 Hz, J₂ = 7.0 Hz, J₃ = 1.5 Hz, 1 H), 7.85 (d, J = 8.0 Hz, 1 H), 7.99 (d, J = 9.5 Hz, 1 H), 8.10 (d, J = 8.5 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 8.72 (d, J = 2.0 Hz, 1 H), 9.25 (d, J = 2.5 Hz, 1 H), 11.87 (s, 1 H, NH).

13C NMR (100 MHz, DMSO-d₆): δ = 113.4, 121.0, 122.4, 127.4, 128.3, 128.6, 128.8, 130.2, 133.9, 139.9, 149.0 (CH), 118.9, 127.6, 132.2, 138.8, 139.5, 146.5 (C=O)...


1-(tert-Benzoxycarbonyl)-1-oxido-3,6'-biquinolin-2(1'H)-one (20);

To a soln of 15 (250 mg, 0.77 mmol) in CH₂Cl₂ (3 mL) was added 10% w/v aq K₂CO₃ (4 mL) and TsCl (177 mg, 0.93 mmol). The mixture was stirred at r.t. for 4 h. After decantation, the aqeous layer was extracted with EtOAc. The organic fractions were dried (MgSO₄) and evaporated. The residue was washed with CH₂Cl₂ to give 17 (270 mg, 90%) as a white solid; mp 284 °C.

IR (KBr): 3650–3175, 1752, 1144 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.54 (s, 9 H, CH₃), 7.23 (ddd, J₁ = 8.0 Hz, J₂ = 7.0 Hz, J₃ = 1.0 Hz, 1 H), 7.38 (d, J = 8.0 Hz, 1 H), 7.43 (d, J = 8.5 Hz, 1 H), 7.54 (ddd, J₁ = 8.5 Hz, J₂ = 7.0 Hz, J₃ = 1.5 Hz, 1 H), 7.78 (dd, J₁ = 8.0 Hz, J₂ = 1.0 Hz, 1 H), 7.97 (d, J = 9.0 Hz, 1 H), 8.21 (dd, J₁ = 9.0 Hz, J₂ = 2.0 Hz, 1 H), 8.32 (s, 1 H), 8.50 (d, J = 2.0 Hz, 1 H), 8.59 (d, J = 8.5 Hz, 1 H), 11.99–12.17 (br s, 1 H, NH).

13C NMR (100 MHz, DMSO-d₆): δ = 27.3 (3 CH₃), 114.8, 115.7, 121.2, 127.2, 127.6, 130.5, 131.4, 134.8, 141.1 (CH), 84.0, 119.5, 126.6, 130.4, 134.6, 138.6, 145.2 (C), 150.4, 156.1, 161.0 (C=O).

HRMS (ES+): m/z [M + H]– CO₂ – C₆H₄NO₃ for C₁₃H₈N₂O₇: 289.0977; found: 289.0984.

1-(tert-Benzoxycarbonyl)-3,7'-biquinoline-2,2'(1'H,1'H)-dione (18)

To a soln of 16 (200 mg, 0.515 mmol) in CH₂Cl₂ (5 mL) were added 10% w/v aq K₂CO₃ (4 mL) and TsCl (118 mg, 0.62 mmol). The mixture was stirred at r.t. for 3 h. The solid was washed with Et₂O to give 18 (142 mg, 71%) as a white solid; mp 280 °C.

IR (KBr): 3650–3000, 1763, 1660, 1567, 1430, 1213, 1152 cm⁻¹.

1H NMR (400 MHz, DMSO-d₆): δ = 1.53 (s, 9 H, CH₃), 7.23 (t, J = 7.5 Hz, 1 H), 7.37–7.44 (m, 2 H), 7.54 (t, J = 7.5 Hz, 1 H), 7.79
(d, J = 7.5 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 8.09 (d, J = 8.5 Hz, 1 H), 8.38 (s, 1 H), 8.39 (s, 1 H), 8.55 (d, J = 8.5 Hz, 1 H), 12.00–12.40 (br s, 1 H, NH).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 27.3 (2 CH), 114.8, 115.5, 122.0, 127.2, 127.4 (2 C), 128.4, 130.7, 139.0, 140.5 (CH), 84.0, 119.5, 126.3, 130.3, 138.4, 138.7, 145.6, 150.5 (C), 156.1, 161.0 (C=O).

HRMS (ES$^+$): [M + H – CO$_2$ – C$_4$H$_8$]$^+$ for C$_{18}$H$_{13}$N$_2$O$_2$: 289.0977; found: 289.0992.

3.6′-Biquinoline-2,2′(1H,1′H)-dione (19)
Following the typical procedure for 13 using 17 (253 mg, 0.65 mmol) in anhyd CH$_2$Cl$_2$ (10 mL) and TFA (0.10 mL, 154 mg, 1.35 mmol) with stirring for 2 h gave 19 (161 mg, 86%) as a beige solid; mp 291 °C.

IR (KBr): 3650–3200, 1662 cm$^{-1}$.

3.7′-Biquinoline-2,2′(1H,1′H)-dione (20)
Following the typical procedure for 13 using 18 (90 mg, 0.232 mmol) in anhyd CH$_2$Cl$_2$ (4 mL) and TFA (86 µL, 132 mg, 1.16 mmol) with stirring at r.t. for 3 h gave 20 (55.3 mg, 83%) as a pale yellow solid; mp 289 °C.

IR (KBr): 3650–3200, 1662 cm$^{-1}$.

HRMS (ES$^+$): [M + H]$^+$ for C$_{18}$H$_{13}$N$_2$O$_2$: 289.0977; found: 289.0993.

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