Supporting Information

Concise construction of 12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-ones via an unusual TBHP/Na₂CO₃ promoted cascade oxidative cyclization and interrupted Dimroth rearrangement

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1. General

All chemicals were used as received without further purification unless stated otherwise. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm⁻¹. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300, 400 or 600 MHz spectrometer. Chemical shifts of ¹H NMR are reported in ppm, relative to the internal standard of tetramethylsilane (TMS, δ = 0.00 ppm). Chemical shifts of ¹³C NMR were reported in ppm with the solvent as the internal standard (CDCl₃: δ = 77.0 ppm, DMSO-d₆: δ = 39.52 ppm). HRMS were obtained on an Apex-Ultra MS equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected. Compound 4a was synthesized according to a known process.¹

2. Experimental procedures.

2.1. General procedure for preparation of 3a–3u (3a as an example).

**General procedure:** To a sealed tube charged with isatin 1a (74 mg, 0.5 mmol), 1-fluoro-2-isothiocyanatobenzene 2a (77 mg, 0.5 mmol), sodium carbonate (159 mg, 1.5 mmol) in DMSO (3 mL) was added TBHP (tert-butyl hydroperoxide, 5.5M in decane, 110 mg, 0.75 mmol) at room temperature. The resulting mixture was stirred at 100°C in a sealed vessel under air, after disappearance of the reactant (monitored by TLC), the mixture was quenched with water (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to yield the desired product 3aa as white solid (82% yield).

2.2. Experimental procedure for preparation of 6, 7, 8.

![Diagram](image)

2-((2-fluorophenyl)amino)-4H-benzo[d][1,3]thiazin-4-one(5): To a sealed tube charged with isatin 1a (74 mg, 0.5 mmol), 1-fluoro-2-isothiocyanatobenzene 2a (77 mg, 0.5 mmol), sodium carbonate (159 mg, 1.5 mmol) in DMSO (3 mL) was added TBHP (5.5 M in decane, 110 mg, 0.75 mmol) at room temperature. The resulting mixture was stirred at 100°C in a sealed vessel under air for 3 min, then quenched with water (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the target molecule 5 as yellow solid (78% yield).
2-(phenylamino)-4H-benzo[d][1,3]thiazin-4-one(7): Following the procedure for 5, isatin 1a (74 mg, 0.5 mmol), 2-isothiocyanatobenzene (77 mg, 0.5 mmol), sodium carbonate (159 mg, 1.5 mmol), TBHP (5.5 M in decane, 110 mg, 0.75 mmol) in DMSO (3 mL) yielded 7 as yellow solid (75% yield).

3-phenyl-2-thioxo-2,3-dihydroquinazolin-4(1H)-one(8): To a sealed tube charged with 6 (127 mg, 0.5 mmol) and sodium carbonate (159 mg, 1.5 mmol) was added DMSO (3 mL) at room temperature. The resulting mixture was stirred at 100°C in a sealed vessel under air, after disappearance of the reactant (monitored by TLC), the mixture was quenched with water (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was recrystallized from ethanol to yield the target molecule 8 as white solid (75% yield).

3. Crystallographic data and molecular structure of 3f

CCDC 1511240 (3f) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif/
4. Spectral data of compound 3a–3u, 6, 7, 8.

**12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3a)**: white solid; yield: 82% (X = F, 104 mg), 66% (X = Cl, 84 mg), 77% (X = Br, 97 mg), 75% (X = I, 95 mg); m.p. 193–195 °C; IR (KBr): 1689, 1591, 1554, 1468, 1305 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.96 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃): δ = 160.6, 156.9, 147.0, 136.0, 134.8, 127.1, 126.7, 126.6, 125.8, 125.8, 123.6, 121.7, 119.2, 118.5. MS (EI): m/z = 253.05 [M⁺].

**2-methyl-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3b)**: white solid; yield: 83% (110 mg); m.p. 209–210 °C; IR (KBr): 1731, 1619, 1542, 1485, 1303 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.92 (d, J = 8.4 Hz, 1H), 8.10 (s, 1H), 7.55–7.46 (m, 3H), 7.40 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ = 160.5, 155.8, 145.0, 136.2, 135.9, 135.8, 126.5, 126.4, 126.2, 125.5, 123.6, 121.6, 119.1, 118.1, 21.2. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₅H₁₈N₂NaOS: 289.0406; found: 289.0404.

**2-methoxy-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3c)**: white solid; yield: 88% (X = F, 124 mg), 80% (X = Br, 113 mg); m.p. 189–190 °C; IR (KBr): 1716, 1614, 1579, 1487, 1363, 1272, 1030 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.95 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.58–7.50 (m, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.34–7.30 (m, 1H), 3.90 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ = 160.4, 157.5, 154.2, 141.8, 135.9, 127.3, 126.5, 126.5, 125.2, 123.8, 121.6, 119.1, 119.1, 106.0, 55.7. HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₁N₂O₂S: 283.0536; found: 283.0540.

**3-methoxy-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3d)**: white solid, m.p. 223–225 °C; IR (KBr): 1679, 1610, 1589, 1511, 1486, 1360, 1302, 1162 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.89 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.41–7.29 (m, 2H), 6.97–6.88 (m, 2H), 3.91–3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 164.6, 159.8, 157.4, 149.1, 135.9, 128.3, 126.5, 126.2, 123.3, 121.4, 118.9, 115.8, 111.8, 106.2, 55.6. HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₁N₂O₂S: 283.0536; found: 283.0539.

**1-chloro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3e)**: white solid; yield: 75% (107 mg); m.p. 221–222 °C; IR (KBr): 1683, 1588, 1538, 1455, 1304 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.99 (d, J = 8.4Hz, 1H), 7.60 (t, J = 8.4Hz, 2H), 7.53 (d, J = 7.8Hz, 1H), 7.48–7.40 (m, 3H). ¹³C NMR (150
1-bromo-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3f): white solid, yield: 63%; m.p. 218–220 °C; IR (KBr): 1686, 1573, 1533, 1449, 1300 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 9.01\) (d, \(J = 8.4\) Hz, 1H), 7.71 (d, \(J = 7.8\) Hz, 1H), 7.60 (t, \(J = 8.4\) Hz, 2H), 7.54–7.41 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 158.8, 157.4, 149.4, 134.3, 132.5, 126.9, 126.9, 126.0, 123.7, 121.9, 121.8, 119.5, 116.5\). HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{14}\)H\(_7\)ClN\(_2\)NaOS: 308.9860; found: 308.9854.

2-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3g): white solid, yield: 78% (105 mg); m.p. 230–232 °C; IR (KBr): 1688, 1591, 1559, 1481, 1202 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.96\) (d, \(J = 7.8\) Hz, 1H), 8.01 (d, \(J = 7.2\) Hz, 1H), 7.68–7.63 (m, 1H), 7.61 (d, \(J = 7.2\) Hz, 1H), 7.52–7.45 (m, 2H), 7.45–7.40 (m, 1H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 160.8, 159.9, 159.2, 156.2, 143.8, 135.7, 128.2, 128.1, 126.9, 126.8, 123.7, 123.4, 121.8, 119.6, 119.2, 111.8, 111.7\). HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{14}\)H\(_7\)F3NaOS: 293.0155; found: 293.0160.

2-chloro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3h): yellow solid; yield: 71% (X = F, 94 mg); 65% (X = Br, 86 mg); m.p. 223–224 °C; IR (KBr): 1688, 1567, 1466, 1330, 1267 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.91\) (d, \(J = 8.0\) Hz, 1H), 8.33–8.21 (m, 1H), 7.67–7.62 (m, 1H), 7.58–7.51 (m, 2H), 7.46–7.37 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 159.6, 157.2, 145.7, 135.8, 135.2, 131.4, 127.5, 127.0, 126.9, 126.4, 123.7, 121.8, 119.5, 119.3\). HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{14}\)H\(_7\)ClN\(_2\)NaOS: 308.9860; found: 308.9864.

2-bromo-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3i): yellow solid; yield: 58% (96 mg); m.p. 225–226 °C; IR (KBr): 1686, 1588, 1545, 1450, 1302 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.92\) (d, \(J = 8.0\) Hz, 1H), 8.51–8.42 (m, 1H), 7.85–7.75 (m, 1H), 7.59 (d, \(J = 7.6\) Hz, 1H), 7.53–7.31 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 159.5, 157.4, 146.0, 138.0, 135.9, 129.6, 127.7, 127.0, 127.0, 127.3, 121.9, 119.9, 119.3, 119.0\). HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{14}\)H\(_7\)BrN\(_2\)NaOS: 352.9355; found: 352.9345.

3-chloro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3j): white solid; yield: 68% (97 mg); m.p. 218–220 °C; IR (KBr): 1691, 1572, 1546, 1463, 1300, 1239 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.96\) (d, \(J = 8.4\) Hz, 1H), 8.31 (d, \(J = 8.4\) Hz, 1H), 7.66–7.57 (m, 2H), 7.48 (t, \(J = 7.8\) Hz, 1H), 7.43 (t, \(J = 7.8\) Hz, 1H), 7.39 (d, \(J = 8.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 160.0, 158.4, 148.0, 141.1, 135.8, 128.5, 126.9, 126.9, 126.4, 125.4, 123.6, 121.8, 119.2, 116.9\). HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{14}\)H\(_7\)ClN\(_2\)NaOS: 308.9860; found: 308.9862.
3-bromo-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3k): yellow solid; yield: 55% (91 mg); m.p. 239–240 °C; IR (KBr): 1689, 1587, 1463, 1330, 1239 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.93 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.81–7.72 (m, 1H), 7.63–7.55 (m, 1H), 7.50–7.53 (m, 1H), 7.49–7.36 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.2, 158.3, 148.0, 135.9, 129.7, 129.2, 128.6, 128.5, 127.0, 126.9, 123.6, 121.8, 119.3, 117.3. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₉BrN₂O₂S: 352.9355; found: 352.9348.

4-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3l): yellow solid; yield: 33% (45 mg) m.p. 215–216 °C; IR (KBr): 1695, 1615, 1590, 1448, 1255, 1195 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.92 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.51–7.31 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ = 159.7, 159.7, 157.9, 157.5, 154.1, 136.8, 136.7, 135.7, 126.9, 126.9, 125.6, 125.5, 123.8, 122.6, 122.5, 121.8, 120.4, 120.1, 119.9, 119.3. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₀FN₂NaOS: 293.0155; found: 293.0150.

8-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3m): white solid; yield: 72% (194 mg) m.p. 225–226 °C; IR (KBr): 1688, 1585, 1550, 1469, 1294, 1185 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.98–8.94 (m, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.34–7.26 (m, 1H), 7.20–7.09 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 161.9, 160.5, 159.4, 156.5, 147.1, 135.0, 132.4, 127.1, 126.1, 126.0, 125.5, 125.4, 120.6, 120.5, 118.5, 114.2, 114.0, 109.2, 109.0. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₂FN₂NaOS: 293.0155; found: 293.0155.

10-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3n): white solid; yield: 75% (101.25 mg) m.p. 163–165 °C; IR (KBr): 1718, 1583, 1555, 1464, 1281, 1252, 1175 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (d, J = 8.0 Hz, 1H), 7.74–7.66 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.43–7.29 (m, 3H), 7.23–7.12 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 158.5, 156.2, 152.0, 149.4, 146.8, 134.8, 128.1, 128.0, 127.4, 126.8, 126.8, 125.9, 125.4, 122.6, 122.4, 118.8, 118.8, 117.6, 117.6, 116.0, 115.8. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₄FN₂NaOS: 293.0155; found: 293.0152.

7-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one (3o): white solid; yield: 81% (109 mg) m.p. 182–183 °C; IR (KBr): 1699, 1599, 1466, 1250, 1206, 1117 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.45–7.31 (m, 2H), 7.10 (t, J = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.5, 157.5, 156.4, 155.0, 146.9, 137.8, 137.8, 135.1, 128.3, 128.2, 127.1, 126.1, 126.0, 118.4, 115.0, 114.9, 113.2, 113.0, 111.4, 111.1. HRMS (ESI): m/z [M + H]⁺ calcd for C₁₄H₁₃FN₂NaOS: 293.0155; found: 293.0150.

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8-methoxy-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3p): white solid; yield: 61% (86 mg); m.p. 208–210 °C; IR (KBr): 1678, 1583, 1553, 1479, 1261, 1179 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.87 (d, J = 8.8 Hz, 1H), 8.38 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.08 (s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 160.4, 158.3, 147.2, 134.6, 129.8, 127.0, 125.9, 125.8, 125.1, 120.1, 118.6, 112.9, 106.7, 55.7. HRMS (ESI): m/z [M + H]+ calcld for C₁₅H₁₁N₂O₃S: 283.0536; found: 283.0530.

8-methyl-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3q): white solid; yield: 75% (100 mg); m.p. 238–240 °C; IR (KBr): 1647, 1581, 1450, 1287, 1038 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.76 (d, J = 8.8 Hz, 1H), 8.36–8.30 (m, 1H), 7.75–7.67 (m, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.32 (s, 1H), 7.18 (d, J = 8.8 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.5, 157.0, 147.1, 137.0, 134.7, 133.8, 127.6, 127.0, 125.8, 125.7, 123.6, 121.9, 118.8, 118.5, 21.3. HRMS (ESI): m/z [M + Na]+ calcld for C₁₅H₁₀N₂NaOS: 289.0406; found: 289.0400.

9-methyl-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3r): white solid, yield: 68% (90 mg); m.p. 213–214 °C; IR (KBr): 1688, 1579, 1550, 1463, 1306 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.76 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.46–7.33 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 160.7, 157.4, 147.1, 137.1, 136.0, 134.7, 127.6, 127.0, 125.8, 125.6, 121.2, 120.2, 119.6, 118.5, 21.7. HRMS (ESI): m/z [M + Na]+ calcld for C₁₅H₁₀N₂NaOS: 289.0406; found: 289.0403.

8-bromo-2-methoxy-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3s): white solid; yield: 80% (144 mg); m.p. 232–234 °C; IR (KBr): 1674, 1616, 1585, 1552, 1485, 1457, 1361, 1295 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.83 (d, J = 8.8 Hz, 1H), 7.73–7.65 (m, 2H), 7.57–7.53 (m, 2H), 7.37–7.34 (m, 1H), 3.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.4, 157.8, 153.5, 141.8, 134.9, 129.8, 127.6, 125.9, 125.5, 124.4, 120.3, 119.8, 119.1, 106.1, 55.8. HRMS (ESI): m/z [M + H]+ calcld for C₁₅H₁₀BrN₂O₃S: 360.9641; found: 360.9646.

8-chloro-3-methoxy-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3t): light yellow solid; yield: 71% (112 mg); m.p. 229–231 °C; IR (KBr): 1685, 1586, 1551, 1483, 1443, 1357, 1246, 1213 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 9.00 (s, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.05–6.93 (m, 2H), 3.91 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 165.3, 160.1, 157.6, 149.3, 136.9, 133.0, 128.8, 126.8, 122.4, 121.9, 119.5, 116.4, 111.9, 106.7, 55.8. HRMS (ESI): m/z [M + H]+ calcld for C₁₅H₁₀ClN₂O₃S: 317.0146; found:317.0150.
3-chloro-7-fluoro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3v): white solid, yield: 66% (100 mg); m.p. 201–202 °C; IR (KBr): 1692, 1578, 1545, 1459, 1421, 1269, 1241, 1199, 1111 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.70 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.67–7.53 (m, 1H), 7.47–7.37 (m, 2H), 7.17 (t, J = 8.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 159.9, 157.9, 157.5, 155.1, 147.9, 149.1, 141.4, 137.7, 137.6, 128.6, 128.5, 125.6, 116.9, 115.1, 115.0, 113.4, 113.2, 111.4, 111.2. HRMS (ESI): m/z [M + H]+ calcd for C₁₄H₁₀ClFN₂OS: 304.9946; found: 304.9951.

2-((2-fluorophenyl)amino)-4H-benzo[d][1,3]thiazin-4-one(6): yellow solid; yield: 78% (106 mg); m.p. 149–150 °C; IR (KBr): 3330, 1647, 1600, 1546, 1460, 1332, 1148 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.36 (t, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.69–7.59 (m, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.20–7.04 (m, 3H), 5.27 (br, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 183.0, 154.5, 152.1, 152.0, 149.1, 136.0, 128.5, 126.8, 126.7, 125.3, 125.2, 125.0, 124.9, 124.6, 124.5, 123.2, 118.0, 115.3, 115.1, 105.1. HRMS (ESI): m/z [M + H]+ calcd for C₁₄H₁₀F₂O₂S: 273.0492; found: 273.0508.

2-(phenylamino)-4H-benzo[d][1,3]thiazin-4-one(7): yellow solid; yield: 75% (95 mg). m.p. 147–148 °C; IR (KBr): 3334, 1643, 1599, 1542, 1455 cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ = 10.21 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.88–7.77 (m, 2H), 7.75–7.71 (m, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 183.1, 151.2, 149.3, 139.2, 135.9, 128.5, 128.1, 124.3, 124.1, 123.2, 117.1. HRMS (ESI): m/z [M + H]+ calcd for C₁₄H₁₃N₃O₂S: 255.0587; found: 255.0587.

3-phenyl-2-thioxo-2,3-dihydroquinazolin-4(1H)-one(8): white solid; yield: 75% (95 mg); m.p. > 300 °C; IR (KBr): 3450, 1662, 1626, 1528, 1196 cm⁻¹; ¹H NMR(600MHz, DMSO-d₆): δ = 13.06 (s, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.82–7.73 (m, 1H), 7.55–7.44 (m, 3H), 7.44–7.39 (m, 1H), 7.38–7.24 (m, 3H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 176.1, 159.8, 139.6, 139.3, 135.6, 129.0, 128.9, 128.1, 127.4, 124.3, 116.2, 115.7. MS (EI): m/z = 253.03 {[M]+}.

Note: Target products such as 8-bromo-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3v), 8-chloro-12H-benzo[4,5]thiazolo[2,3-b]quinazolin-12-one(3w), etc. could be obtained by this method in high yields, but we cannot obtain their ¹³C NMR spectra due to their poor solubility in most solvents.
5. Reference
6. Appendix: spectral copies of $^1$H NMR, and $^{13}$C NMR

3a CDCl$_3$

600 MHz

3a CDCl$_3$

150 MHz
3c CDCl$_3$
600 MHz

3c CDCl$_3$
150 MHz

-S12-
$3f$ CDCl$_3$

600 MHz

$3f$ CDCl$_3$

100 MHz
3h CDCl₃
400 MHz

3h CDCl₃
100 MHz
$\text{3m CDCl}_3$
$400 \text{ MHz}$