Supporting Information

Visible-Light-Induced C(sp³)-H Activation for a C–C Bond Forming Reaction of 3,4-Dihydroquinoxalin-2(1H)-one with Nucleophiles Using Oxygen with a Photoredox Catalyst or in Catalyst-Free Conditions

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General Procedure. All solvents were reagent grade. Reactions were normally carried out under nitrogen atmosphere in glassware. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography. Melting points are uncorrected. ¹H NMR spectra were obtained in CDCl₃ unless otherwise noted at 400 MHz (Bruker DPX-400 or AVIII-400), or 500 MHz (Varian-Unity INOVA-500). ¹³C NMR spectra were obtained at 125 MHz or 100 MHz. The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. The UV-vis spectra were recorded with a Varian Cary® 50 UV-Vis spectrophotometer.
Scheme S1. Unless otherwise noted, the reactions were performed with 1 (1 equiv) and 2 (2 equiv) with 2 mol % of Ru(bpy)_3Cl_2•6H_2O in MeOH at ambient temperature. Percentage (%) for isolated yields after chromatography purification. Time (h) represented for the reaction to be completed. Yields in parenthesis for the reaction in the absence of Ru(bpy)_3Cl_2•6H_2O (catalyst free condition).

The light on/off experiment:

1c (50 mg, 0.21 mmol), Ru(bpy)_3Cl_2•6H_2O (2.9 mg, 0.004 mmol, 0.02 equiv), indole (48 mg, 0.40 mmol, 2.0 equiv) and CH_3OH (4.1 mL) were placed in a 10-mL two-neck flask with a magnetic stirring bar. The flask was equipped with a balloon of oxygen, and the solution was stirred at room temperature under irradiation with a 24 W white CFL (compact fluorescent light bulb, Philips, 24 W, white, Tornado, E27, 120 V, 60 Hz), located 10 cm away from the reaction vessel. After the indicated reaction time, ~50 μL of the reaction mixture aliquot was collected, diluted with CDCl_3 and analyzed by ^1^H NMR.
Fig S1. UV-visible absorption spectra of 1c at different concentrations in MeOH, and the 1:2 mixture of 1c and indole (2a) in MeOH (red line).

Fig S2. Pictures of the 1c, indole (2a), and the mixture of 1c and 2a, after 30-min CFL irradiation.

Fig S3. Conversion of 1c to 3ca in the light/dark sequence. Dark periods are shown in gray. (a) Reaction with ruthenium catalyst (blue), (b) reaction in the absence of catalyst (red).

Fig S4. The reactions were irradiated by a PHILIPS 24 W white CFL (compact fluorescent light bulb)
Preparation of 3,4-dihydroquinoxalin-2(1H)-one (1a):

To a solution of o-phenylenediamine (5 g, 46.2 mmol) in DMF (50 mL) was sequentially added ethyl 2-bromoacetate (6.1 mL, 55.0 mmol, 1.2 equiv) and triethyl amine (12.9 mL, 92.5 mmol, 2.0 equiv) at 0 °C. The resulting solution was stirred at room temperature for 16 h, followed by heating to 80 °C for 3 h. Most of DMF was removed by rotary evaporator, and the residue was partitioned between H2O (10 mL) and EtOAc (40 mL). The EtOAc layer was washed with saturated NaHCO3 (10 mL), brine (10 mL), dried over Na2SO4, and concentrated in vacuo to give the crude residue. The residue was triturated with a mixture of CH2Cl2 and hexane (1:1 v/v). The precipitate was filtered and dried in vacuo to afford 1a (5.2 g, 76% yield; Rf = 0.31 for 1a in 50% EtOAc–hexane) as a beige powder. Mp: 136–138 °C. Lit. 136–138 °C.1 Selected spectroscopic data for 1a: IR (neat): 3369, 3197, 3069, 2976, 1678, 1508, 1185, 1304, 1258, 748 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.62 (brs, 1 H), 6.89 – 6.85 (m, 1 H), 6.75 – 6.71 (m, 2 H), 6.65 (d, J = 7.5 Hz, 1 H), 3.97 (d, J = 1.5, 2 H), 3.84 (brs, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ 166.9 (C), 133.7 (C), 125.4 (C), 123.9 (CH), 119.6 (CH), 115.7 (CH), 114.0 (CH), 47.1 (CH₂);² MS (m/z, relative intensity): 149 (M⁺+1, 4), 148 (M⁺, 45), 119 (100), 118 (11), 92 (25), 91 (75), 65 (17); exact mass calculated for C₈H₈N₂O (M⁺): 148.0637, found: 148.0637.

Preparation of 4-benzoyl-3,4-dihydroquinoxalin-2(1H)-one (1b):

To a solution of 1a (200 mg, 1.35 mmol) in CH₂Cl₂ (4 mL) at 0 °C was added Et₃N (0.37 mL, 2.65 mmol, 2.0 equiv) and benzoyl chloride (0.23 mL, 1.98 mmol, 1.5 equiv). The resulting solution was stirred at room temperature for 1 h, and the reaction was quenched by the addition of water (10 ml), followed by the extraction with CH₂Cl₂ (2x10 mL). The combined organic solution was washed with saturated aqueous NaHCO₃ solution (5 mL), brine (5 mL), dried over anhydrous

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Na₂SO₄, and concentrated in vacuo to give a crude residue. The crude product was purified by flash column chromatography with 40% EtOAc–hexane (Rₓ = 0.32 for 1b in 50% EtOAc–hexane) to afford compound 1b (289 mg, 85% yield) as brown color solids. Mp: 205–206 °C, lit. 208 °C.²

Selected spectroscopic data for 1b: ¹H NMR (400 MHz, acetone-d₆): δ 9.74 (brs, 1 H), 7.50 – 7.34 (m, 5 H), 7.15 – 7.05 (m, 2 H), 6.75 (brs, 1 H); ¹³C NMR (100 MHz, acetone-d₆): δ 169.8 (C), 168.1 (C), 136.4 (C), 132.8 (C), 131.9 (CH), 129.9 (2CH), 129.5 (2CH), 129.0 (C), 127.0 (CH), 125.8 (CH), 123.1 (CH), 117.5 (CH), 48.7 (CH₂);

Preparation of 4-benzyl-3,4-dihydroquinoxalin-2(1H)-one (1c):

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\begin{array}{c}
\text{1a} \quad \text{BnCl, Na₂CO₃, EtOH} \\
85°C, 15 h; 75% \\
\rightarrow \text{1c}
\end{array}
\]

To a solution of 1a (1 g, 6.75 mmol) in EtOH (15 mL) was added Na₂CO₃ (1.43 g, 13.5 mmol, 2.0 equiv) and benzyl chloride (0.93 mL, 8.08 mmol, 1.2 equiv), and the solution was heated to reflux at 85 °C for 15 h until the completion of the reaction, as monitored by TLC. The reaction mixture was cooled to room temperature, concentrated in vacuo to give the crude residue. The crude product was dissolved in EtOAc (50 mL) and washed with water (2x20 mL). The aqueous layer was extracted with EtOAc (3x20 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (Rₓ = 0.49 for 1c in 50% EtOAc–hexane) to afford 1c (1.21 g, 75% yield) as off-white solids.³ Mp: 152–154 °C, Selected spectroscopic data for 1c: ¹H NMR (500 MHz, CDCl₃): δ 8.21 (brs, 1 H), 7.35 – 7.25 (m, 5 H), 6.95 – 6.90 (m, 1 H), 6.75 – 6.72 (m, 3 H), 4.40 (s, 2 H), 3.80 (s, 2 H); ¹³C NMR (500 MHz, CDCl₃): δ 166.7 (C), 136.2 (C), 135.3 (C), 128.8 (2CH), 127.62 (2CH), 127.59 (CH), 126.0 (C), 124.2 (CH), 119.0 (CH), 115.5 (CH), 112.3 (CH), 53.6 (CH₂), 52.3 (CH₂); MS (m/z, relative intensity): 239 (M⁺+1, 11), 238 (M⁺, 70), 194 (28), 147 (25), 119 (22), 91 (100), 65 (14); exact mass calculated for C₁₅H₁₄N₂O (M⁺): 238.1106; found: 238.1108.

Preparation of 4-(4-fluorobenzyl)-3,4-dihydroquinoxalin-2(1H)-one (1d):

![Chemical structure of 1d]

To a solution of 1a (500 mg, 3.37 mmol, 1.0 equiv) in EtOH (7.5 mL) was added Na₂CO₃ (714 mg, 6.74 mmol, 2.0 equiv) and 4-fluorobenzyl chloride (0.48 mL, 4.04 mmol, 1.2 equiv), and the solution was heated to reflux at 85 °C for 15 h until the completion of reaction, as monitored by TLC. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a crude residue. The crude residue was dissolved in EtOAc (50 mL), washed with water (2x10 mL), and the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (R_f = 0.52 for 1d in 50% EtOAc–hexane) to afford 1d (603 mg, 70% yield) as off-white solids. Mp: 182–184 °C. Selected spectroscopic data for 1d: IR (KBr): 3208, 3071, 2918, 1685, 1510, 1402, 1221, 1154, 823, 744 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.51 (s, 1 H), 7.28 – 7.24 (m, 2 H), 7.03 – 6.99 (m, 2 H), 6.95 – 6.91 (m, 1 H), 6.78 – 6.75 (m, 2 H), 6.72 (d, J = 8.0 Hz, 1 H), 4.36 (s, 2 H), 3.77 (s, 2 H), ¹³C NMR (125 MHz, CDCl₃): δ 166.9 (C), 162.2 (d, J = 244 Hz, C), 135.1 (C), 131.9 (d, J = 3 Hz, C), 129.2 (d, J = 8 Hz, 2CH), 126.2 (C), 124.2 (CH), 119.3 (CH), 115.7 (d, J = 21 Hz, 2CH), 115.6 (CH), 112.3 (CH), 52.9 (CH₂), 52.2 (CH₂); MS (m/z, relative intensity): 257 (M⁺+1, 8), 256 (M⁺, 54), 147 (17), 119 (16), 109 (100), 101 (10), 59 (20), 58 (22); exact mass calculated for C₁₅H₁₃FN₂O (M⁺): 256.1012; found: 256.1013.

Preparation of 4-(4-methylbenzyl)-3,4-dihydroquinoxalin-2(1H)-one (1e):

![Chemical structure of 1e]

To a solution of 1a (200 mg, 1.35 mmol) in EtOH (3 mL) was added Na₂CO₃ (286 mg, 2.70
mmol, 2.0 equiv) and 4-methylbenzyl chloride (0.21 mL, 1.59 mmol, 1.2 equiv), and the solution was heated to reflux at 85 °C for 15 h until the completion of reaction, as monitored by TLC. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a residue. The crude residue was dissolved in EtOAc (20 mL), and the solution was washed with water (2 x 10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo to give the crude compound. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (Rf = 0.51 for 1e in 50% EtOAc–hexane) to afford 1e (112 mg, 33% yield) as off-white solids. Mp: 146–147 °C, Selected spectroscopic data for 1e: IR (KBr): 3205, 3052, 2920, 1685, 1510, 1402, 1302, 743 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.12 (s, 1 H), 7.19 – 7.10 (m, 4 H), 6.95 – 6.90 (m, 1 H), 6.77 – 6.70 (m, 3 H), 4.35 (s, 2 H), 3.77 (s, 2 H), 2.31 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 166.8 (C), 137.3 (C), 135.4 (C), 133.1 (C), 129.5 (2CH), 127.7 (2CH), 126.0 (C), 124.2 (CH), 119.0 (CH), 115.4 (CH), 112.3 (CH), 53.3 (CH₂), 52.1 (CH₂), 21.1 (CH₃); MS (m/z, relative intensity): 253 (M⁺+1, 6), 252 (M⁺, 34), 147 (3), 146 (2), 119 (6), 106 (9), 105 (100), 92 (4), 77 (6); exact mass calculated for C₁₆H₁₆N₂O (M⁺): 252.1263; found: 252.1267.

Preparation of 4-benzyl-7-chloro-3,4-dihydroquinoxalin-2(1H)-one (1g):

To a solution of 1f (230 mg, 1.26 mmol)² in EtOH (7.5 mL) was added Na₂CO₃ (264.9 mg, 2.50 mmol, 2 equiv) and benzyl chloride (0.20 mL, 1.56 mmol, 1.2 equiv). The solution was heated to reflux at 80 °C for 15 h until the completion of reaction, as monitored by TLC. The reaction mixture was cooled to room temperature, concentrated in vacuo to give the crude residue. The crude residue was dissolved in EtOAc (20 mL), and the solution was washed with water (2 x 10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo to give the crude compound. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (Rf = 0.56 for 1g in 50% EtOAc–hexane) to afford 1g (182 mg, 53% yield) as off-white solid. Mp: 207-209 °C, Selected spectroscopic data for 1g: IR (KBr): 3206, 3062, 2924, 2855, 1690, 1586, 1511, 1397, 1296, 703 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.12 (s, 1 H), 7.36 – 7.22 (m, 5 H), 6.86 (dd, J = 8.5, 2.0 Hz, 1 H), 6.77 (d, J = 2.0 Hz, 1 H), 6.62 (d, J = 8.5 Hz, 1 H), 4.37 (s, 2 H), 3.81 (s, 2 H), ¹³C NMR (125

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MHz, CDCl3): δ 167.1 (C), 135.8 (C), 133.8 (C), 128.9 (two CH), 127.7 (CH), 127.5 (two CH), 127.1 (C), 123.77 (C), 123.73 (CH), 115.5 (CH), 113.1 (CH), 53.7 (CH2), 52.1 (CH2); MS (m/z, relative intensity): 274 (M+2, 7), 273 (M+1, 4), 272 (25), 181 (15), 153 (6), 92 (7), 91 (100), 65 (5); exact mass calculated for C15H13ClN2O (M+): 272.0716; found: 272.0715.

Preparation of 7-Fluoro-3,4-dihydroquinoxalin-2(1H)-one (1h):

![Chemical structure of 1h](image)

To a solution of 4-fluorobenzene-1,2-diamine (500 mg, 3.96 mmol) in DMF (5 mL) was added ethylbromoacetate (0.52 mL, 4.69 mmol, 1.2 equiv) and triethyl amine (1.1 mL, 7.9 mmol, 2.0 equiv) sequentially at 0 °C. The resulting solution was stirred at room temperature for 16 h, followed by heating to 80 °C for 3 h. Most of DMF was removed by rotary evaporator, and the residue was partitioned between H2O (10 mL) and EtOAc (40 mL). The EtOAc layer was washed with saturated NaHCO3 (10 ml), brine (10 mL), dried over Na2SO4, and concentrated in vacuo to give the crude residue. The crude product was purified by flash column chromatography with 40% EtOAc–hexane to afford 1h (Rf = 0.29 for 1h in 50% EtOAc-hexane) as brown color solids (341 mg, 52% yield). Mp: 245–246 °C, lit. 245–246 °C.6 Selected spectroscopic data for 1h: 1H NMR (500 MHz, acetone-d6): δ 9.35 (brs, 1 H), 6.72 (dd, J = 9.0, 5.5 Hz, 1 H), 6.66 (dd, J = 9.5, J = 2.5, 1 H), 6.59 – 6.54 (m, 1 H), 5.22 (brs, 1 H), 3.79 (s, 2 H); 13C NMR (125 MHz, acetone-d6): δ 167.2 (C), 157.2 (d, J = 232 Hz, C), 132.4 (d, J = 1.9 Hz, C), 128.7 (d, J = 10 Hz, C), 115.1 (d, J = 9 Hz, CH), 109.3 (d, J = 22.5 Hz, CH), 103.2 (d, J = 27.5 Hz, CH), 47.8 (CH2); MS (m/z, relative intensity): 166 (M+, 61), 137 (100), 110 (13), 101 (7), 83 (13); exact mass calculated for C8H7FN2O (M+): 166.0542; found: 166.0540.

Preparation of 4-benzyl-7-fluoro-3,4-dihydroquinoxalin-2(1H)-one (1i):

![Chemical structure of 1i](image)

To a solution of 1h (150 mg, 0.90 mmol) in EtOH (4 mL) was added Na₂CO₃ (191 mg, 1.8 mmol, 2.0 equiv) and benzyl chloride (0.14 mL, 1.1 mmol, 1.2 equiv). The solution was heated to reflux at 85 °C for 15 h until the completion of reaction, as monitored by TLC. The reaction mixture was cooled to room temperature, concentrated in vacuo to give the crude residue. The crude residue was dissolved in EtOAc (20 mL), and the solution was washed with water (2x10 mL). The aqueous layer was extracted with EtOAc (3x10 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo to give the crude compound. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (R_f = 0.54 for 1i in 50% EtOAc–hexane) to afford 1i (145 mg, 63% yield) as off-white solids. Mp: 131–132 °C. Selected spectroscopic data for 1i: IR (KBr): 3338, 2982, 1691, 1524, 1399, 1269, 1144, 851, 782 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.28 (s, 1 H), 7.34 – 7.23 (m, 5 H), 6.63 – 6.56 (m, 3 H), 4.34 (s, 2H), 3.75 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 167.9 (C), 156.5 (d, J = 236.5 Hz, C), 136.1 (C), 131.7 (d, J = 2 Hz, C), 128.9 (two CH), 127.68 (CH), 127.66 (two CH), 127.31 (d, J = 10 Hz, C), 113.0 (d, J = 8.6 Hz, CH), 109.8 (d, J = 22 Hz, CH), 103.3 (d, J = 26.4 Hz, CH), 54.2 (CH₂), 52.3 (CH₂); MS (m/z, relative intensity): 257 (M⁺+1, 3), 256 (M⁺, 16), 242 (9), 167 (11), 164 (18), 149 (25), 136 (19), 112 (18), 109 (13), 91 (100); exact mass calculated for C₁₅H₁₃FN₂O (M⁺): 256.1012; found: 256.1013.

Preparation of 4-propyl-3,4-dihydroquinoxalin-2(1H)-one (1j):

To a solution of 1a (200 mg, 1.35 mmol) in EtOH (4 mL) was added Na₂CO₃ (284 mg, 2.68 mmol, 2.0 equiv) and 1-bromo propane (0.17 mL, 1.6 mmol, 1.2 equiv). The solution was heated to reflux for 15 h until the completion of reaction, as monitored by TLC. The reaction mixture was cooled to room temperature, concentrated in vacuo to give the crude residue. The crude residue was dissolved in EtOAc (20 mL), and the solution was washed with water (2x10 mL). The aqueous layer was extracted with EtOAc (3x10 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo to give the crude compound. The crude product was purified by flash column chromatography with 15% EtOAc–hexane (R_f = 0.59 for 1j in 50% EtOAc–hexane) to afford 1j (109 mg, 42% yield) as off-white solids.⁷ Mp: 98–99 °C. Selected

⁷ For other preparation in literature, but without spectra data, see: Smith, R. F.; Rebel, W. J.; Beach, T. S. J. Org.
spectroscopic data for 1j: IR (KBr): 3369, 3199, 3069, 2972, 2892, 1675, 1600, 1508, 1385, 1303, 1256, 919, 823, 746 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.51 (s, 1 H), 6.97 – 6.93 (m, 1 H), 6.74 – 6.68 (m, 2 H), 6.66 (d, J = 8.0 Hz, 1 H), 3.84 (s, 2 H), 3.16 (t, J = 7.5 Hz, 2 H), 1.68 – 1.61 (m, 2 H), 0.97 (t, J = 7.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 166.9 (C), 135.1 (C), 125.9 (C), 124.2 (CH), 118.3 (CH), 115.5 (CH), 111.6 (CH), 52.2 (CH₂), 51.4 (CH₂), 18.3 (CH₂), 11.4 (CH₃); MS (m/z, relative intensity): 191 (M⁺+1, 9), 190 (M⁺, 66), 162 (30), 161 (100), 147 (25), 133 (64), 131 (32), 119 (37), 106 (8), 92 (20), 77 (12); exact mass calculated for C₁₁H₁₄N₂O (M⁺): 190.1106; found: 190.1105.

Preparation of ethyl 2-(2-hydroxyphenylamino)acetate (APS-135):

![Chemical Structure](image)

To a solution of 2-aminophenol (1 g, 9.16 mmol) and potassium fluoride (1.33 g, 22.9 mmol, 2.5 equiv) in DMF (50 mL) was added ethyl bromo acetate (6.1 mL, 55.0 mmol, 2.4 equiv). The resulting mixture was heated to 60 °C and stirred for 6 h, followed by the concentration in vacuo to give a residue. The residue was partitioned between H₂O (10 mL) and EtOAc (25 mL). The EtOAc layer was washed with saturated NaHCO₃ (2x10 ml), brine (10 mL), dried over Na₂SO₄, filtered and concentrated in vacuo to give the crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (Rf = 0.46 for APS-135 in 40% EtOAc–hexane) to afford APS-135 (1.48 g, 83% yield) as brown solid. Mp: 91–93 °C, lit. 91–93 °C;⁹ lit. 90–94 °C.¹⁰ Selected spectroscopic data for APS-135: IR (KBr): 3419, 3051, 2981, 2903, 1721, 1612, 1530, 1439, 1381, 1222, 1030, 893, 737 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 6.81 (t, J = 7.5 Hz, 1 H), 6.71 (d, J = 7.5 Hz, 1H), 6.65 (dd, J = 7.5, 7.5 Hz, 1 H), 6.57 (d, J = 7.5 Hz, 1 H), 4.23 (q, J = 7.0 Hz, 2 H), 3.91 (s, 2 H), 1.28 (t, J = 7.0 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 172.0 (C), 144.5 (C), 136.0 (C), 121.4 (CH), 119.1 (CH), 114.9 (CH), 113.1 (CH), 61.4 (CH₂), 46.6 (CH₂), 14.2 (CH₃).

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Preparation of 4-benzyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (1k):

A solution of APS-135 (200 mg, 1.02 mmol), benzaldehyde (0.12 mL, 1.2 mmol, 1.2 equiv) and glacial acetic acid (0.08 mL, 1.4 mmol, 1.4 equiv) in CH₂Cl₂ (6.3 mL) was stirred with ice bath cooling for 30 min. To this solution was added in portion of sodium triacetoxyborohydride (324 mg, 1.5 mmol, 1.5 equiv), and the reaction mixture was stirred at room temperature for 15 h. The reaction mixture was diluted with CH₂Cl₂ (10 mL), washed with saturated aqueous NaHCO₃ (10 mL), brine (10 mL), dried over Na₂SO₄, filtered and concentrated in vacuo to give the crude residue. The crude product was purified by flash column chromatography with 15% EtOAc–hexane (Rf = 0.45 for 1k in 25% EtOAc/hexane) to afford 1k (112 mg, 46% yield) as colorless oil; Selected spectroscopic data for 1k: IR (neat): 3064, 3030, 2923, 2816, 1777, 1612, 1503, 1341, 1292, 1212, 919, 746, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.38 – 7.27 (m, 5 H), 7.08 – 7.01 (m, 2 H), 6.88 – 6.83 (m, 2 H), 4.36 (s, 2 H), 3.77 (s, 2 H), ¹³C NMR (125 MHz, CDCl₃): δ 164.8 (C), 141.7 (C), 135.6 (C), 134.8 (C), 128.9 (2CH), 127.9 (CH), 127.8 (2CH), 125.2 (CH), 120.1 (CH), 117.0 (CH), 113.2 (CH), 53.5 (CH₂), 49.8 (CH₂);¹¹ MS (m/z, relative intensity): 240 (M⁺+1, 10), 239 (67), 211 (14), 120 (54), 91 (100); exact mass calculated for C₁₅H₁₃NO₂ (M⁺): 239.0946; found: 239.0947.

Preparation of 4-benzyl-3-(1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ca)

To a solution of 1c (50 mg, 0.21 mmol) and indole (48 mg, 0.4 mmol, 2.0 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 4 h. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f$ = 0.4 for 3ca in 50% EtOAc–hexane) to afford product 3ca (56.6 mg, 76% yield) as white solids; Mp: 220–222 °C. Selected spectroscopic data for 3ca: IR (KBr): 3317, 3029, 2981, 2894, 1667, 1506, 1408, 1245, 1112, 741 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.14 (brs, 1 H), 9.53 (s, 1 H), 7.55 (d, $J$ = 8.0 Hz, 1 H), 7.40 – 7.30 (m, 5 H), 7.29 – 7.24 (m, 1 H), 7.11 – 7.07 (m, 1 H), 7.03 – 6.95 (m, 3 H), 6.90 – 6.85 (m, 1 H), 6.80 – 6.75 (m, 2 H), 5.27 (s, 1 H), 4.66 (d, $J$ = 15.0 Hz, 1 H), 4.33 (d, $J$ = 15.0 Hz, 1 H), $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.9 (C), 138.9 (C), 137.6 (C), 135.9 (C), 129.5 (two CH), 128.7 (C), 128.6 (two CH), 128.1 (CH), 127.6 (C), 124.2 (CH), 124.1 (CH), 122.6 (CH), 120.5 (CH), 120.2 (CH), 119.7 (CH), 115.9 (CH), 114.0 (CH), 112.3 (CH), 112.1 (C), 60.1 (CH), 52.7 (CH$_2$) ; MS ($m/z$, relative intensity): 354 (M$^{++}$+1, 24), 353 (M$^+$, 100), 324 (36), 262 (34), 233 (22), 196 (27), 169 (11), 149 (22), 119 (45), 91 (52); exact mass calculated for C$_{23}$H$_{19}$N$_3$O (M$^+$): 353.1528; found: 353.1526.

Preparation of 3ca via catalyst-free condition:

A solution of 1c (50 mg, 0.21 mmol) and indole (48 mg, 0.4 mmol, 2.0 equiv) in CH$_3$OH was stirred under oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 14 h until the completion of reaction, as monitored by TLC and crude $^1$H NMR. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f$ = 0.4 for 3ca in 50% EtOAc–hexane) to afford product 3ca (51.2 mg, 69% yield) as white solids.
Thermal ellipsoids draw at the 50% probability level

**Figure S1.** ORTEP and Stereo plots for X-ray crystal structures of 3ca (ic18907).

CCDC 1816891 contains the supplementary crystallographic data for 3ca (ic18907). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk
Table S1. Crystal data and structure refinement for 3ca (ic18907).

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Preparation of 4-benzyl-3-(5-fluoro-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cb):

\[
1c + 2b \xrightarrow{\text{cat. Ru(bpy)}_3\text{Cl}_2\cdot6\text{H}_2\text{O}} 24\text{W CFL, O}_2 \xrightarrow{\text{CH}_3\text{OH, rt, }30\text{ h; }63\%} 3\text{cb}
\]

To a solution of 1c (50 mg, 0.21 mmol) and 5-fluoroindole (54 mg, 0.4 mmol, 2 equiv) in CH\textsubscript{3}OH (4.1 mL) was added Ru(bpy)\textsubscript{3}Cl\textsubscript{2}\cdot6H\textsubscript{2}O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 30 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane (R\textsubscript{f} = 0.39 for 3cb in 50% EtOAc–hexane) to afford product 3cb (49.3 mg, 63% yield) as white solids, Mp: 240–242 °C. Selected spectroscopic data for 3cb: IR (KBr): 3300, 3172, 3029, 2983, 1668, 1505, 1406, 1245, 1175, 1110, 929, 854, 744 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, DMSO-d\textsubscript{6}): \delta 11.1 (brs, 1 H), 10.6 (s, 1 H), 7.36 – 7.30 (m, 5 H), 7.27 – 7.22 (m, 1 H), 7.09 (dd, J = 2.5, 2.5 Hz, 1 H), 6.99 (d, J = 2.5 Hz, 1 H), 6.94 – 6.88 (m, 2 H), 6.83 – 6.79 (m, 1 H), 6.74 – 6.70 (m, 1 H), 6.62 (d, J = 8.0 Hz, 1 H), 5.20 (s, 1 H), 4.50 (d, J = 15.5 Hz, 1 H), 4.32 (d, J = 15.5 Hz, 1 H), \textsuperscript{13}C NMR (125 MHz, DMSO-d\textsubscript{6}): \delta 165.8 (C), 156.9 (d, J = 230 Hz, C), 137.8 (C), 134.0 (C), 132.8 (C), 128.4 (two CH), 127.25 (two CH), 127.16 (C), 127.0 (CH), 126.0 (d, J = 10.3 Hz, C), 125.5 (CH), 123.1 (CH), 118.4 (CH), 114.8 (CH), 112.8 (CH), 112.5 (d, J = 9.8 Hz, CH), 110.8 (d, J = 4.5 Hz, C), 109.5 (d, J = 26 Hz, CH), 103.9 (d, J = 24 Hz, CH), 59.0 (CH), 51.3 (CH\textsubscript{2}); MS (m/z, relative intensity): 373 (M\textsuperscript{+}+2, 4), 372 (M\textsuperscript{+}+1, 33), 371 (M\textsuperscript{+}, 100), 342 (40), 280 (42), 252 (28), 195 (33), 148 (19), 119 (43), 91 (53); exact mass calculated for C\textsubscript{23}H\textsubscript{18}FN\textsubscript{3}O (M\textsuperscript{+}): 371.1434; found: 371.1436.

Preparation of 4-benzyl-3-(5-chloro-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cc)

\[
1c + 2c \xrightarrow{\text{cat. Ru(bpy)}_3\text{Cl}_2\cdot6\text{H}_2\text{O}} 24\text{W CFL, O}_2 \xrightarrow{\text{CH}_3\text{OH, rt, }20\text{ h; }68\%} 3\text{cc}
\]
To a solution of 1c (50 mg, 0.21 mmol) and 5-chloroindole (61 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 20 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane (Rₛ = 0.37 for 3cc in 50% EtOAc–hexane) to afford product 3cc (55.2 mg; 68% yield) as white solids. Mp: 239–241 °C. Selected spectroscopic data for 3cc: IR (KBr): 3477, 3290, 3172, 3029, 2982, 2898, 1668, 1504, 1408, 1112, 792, 796, 734 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): 6 11.20 (s, 1 H), 10.60 (s, 1 H), 7.41 (d, J = 2.0 Hz, 1 H), 7.36 (d, J = 9.0 Hz, 1 H), 7.33 – 7.29 (m, 4 H), 7.28 – 7.22 (m, 1 H), 7.06 (dd, J = 8.5, 2.0 Hz, 1 H), 6.98 (s, 1 H), 6.90 (d, J = 7.5 Hz, 1 H), 6.82 (dd, J = 8.0, 7.5 Hz, 1 H), 6.73 (dd, J = 8.0, 7.5 Hz, 1 H), 6.64 (d, J = 8.0, 1 H), 5.22 (s, 1 H), 4.51 (d, J = 15.5 Hz, 1 H), 4.31 (d, J = 15.5 Hz, 1 H); ¹³C NMR (125 MHz, DMSO-d₆): 6 165.8 (C), 137.8 (C), 134.6 (C), 134.0 (C), 128.4 (two CH), 127.3 (two CH), 127.1 (C), 127.0 (CH), 126.9 (C), 125.2 (CH), 123.7 (C), 123.1 (CH), 121.3 (CH), 118.6 (CH), 118.5 (CH), 114.9 (CH), 113.1 (CH), 112.8 (CH), 110.4 (C), 58.8 (CH), 51.3 (CH₂); MS (m/z, relative intensity): 389 (M⁺+2, 36), 388 (M⁺+1, 45), 387 (M⁺, 100), 358 (29), 296 (39), 268 (17), 233 (15), 226 (15), 196 (35), 195 (36), 119 (52), 91 (66). Exact mass calculated for C₂₃H₁₈ClN₃O (M⁺): 387.1138; found: 387.1135.

Preparation of 4-benzyl-3-(5-bromo-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cd)

To a solution of 1c (50 mg, 0.21 mmol) and 5-bromoindole (78.4 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 18 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane (Rₛ = 0.38 for 3cd in 50% EtOAc–hexane) to afford product 3cd (64.1 mg; 71% yield) as white solids. Mp: 236–238 °C. Selected spectroscopic data for 3cd: IR (KBr): 3279, 3177, 3056, 3028, 2981, 2898, 2868, 1670, 1504, 1457, 1409, 1112, 884, 795, 734 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): 6 10.35 (brs, 1 H), 9.54 (s, 1 H), 7.72 (d, J = 1.5 Hz, 1
H), 7.40 – 7.31 (m, 5 H), 7.30 – 7.25 (m, 1 H), 7.20 (dd, J = 8.5, 2.0 Hz, 1 H), 7.05 – 6.98 (m, 2 H),
6.93 – 6.88 (m, 1 H), 6.83 – 6.77 (m, 2 H), 5.25 (s, 1 H), 4.70 (d, J = 15.5 Hz, 1 H), 4.34 (d, J =
15.5, 1 H), $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.6 (C), 138.8 (C), 136.3 (C), 135.7 (C), 129.5
two CH), 129.3 (C), 128.63 (two CH), 128.58 (C), 128.2 (CH), 125.6 (CH), 125.4 (CH), 124.3
(CH), 123.2 (CH), 119.9 (CH), 116.0 (CH), 114.2 (CH), 114.1 (CH), 113.2 (C), 112.0 (C), 60.0
(CH), 52.8 (CH$_2$); MS (m/z, relative intensity): 434 (M$^+$+3, 23), 433 (M$^+$+2, 100), 432 (M$^+$+1, 25),
431 (M$^+$, 98), 404 (25), 402 (24), 342 (29), 340 (30), 261 (11), 233 (39), 208 (12), 196 (42), 195
(44), 119 (56), 91 (81); exact mass calculated for C$_{23}$H$_{18}$BrN$_3$O (M$^+$): 431.0633; found: 431.0633.

Thermal ellipsoids draw at the 50% probability level

Figure S1. ORTEP and Stereo plots for X-ray crystal structures of 3cd (ic18196).

CCDC 1816892 contains the supplementary crystallographic data for 3cd (ic18196). These data can be obtained free of
charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk
Table S1. Crystal data and structure refinement for 3cd (ic18196).

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Preparation of 4-benzyl-3-(5-iodo-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ce):

To a solution of 1c (50 mg, 0.21 mmol) and 5-iodoindole (97.2 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 15 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f$ = 0.38 for 3ce in 50% EtOAc–hexane) to afford product 3ce (70 mg; 70% yield) as off-white solids. Mp: 238–240 °C. Selected spectroscopic data for 3ce: IR (KBr): 3304, 3271, 3028, 2980, 2899, 2868, 1667, 1501, 1416, 1108, 881, 797, 739 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.34 (brs, 1 H), 9.54 (s, 1 H), 7.89 (d, $J = 1.5$ Hz, 1 H), 7.40 – 7.32 (m, 5 H), 7.31 – 7.22 (m, 2 H), 7.04 – 6.97 (m, 2 H), 6.93 – 6.88 (m, 1 H), 6.83 – 6.77 (m, 2 H), 5.23 (s, 1 H), 4.69 (d, $J = 15.5$ Hz, 1 H), 4.32 (d, $J = 15.5$, 1 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.7 (C), 138.8 (C), 136.7 (C), 135.7 (C), 130.9 (CH), 130.1 (C), 129.6 (two CH), 128.7 (two CH), 128.2 (CH), 125.2 (CH), 125.1 (C), 124.3 (CH), 119.9 (CH), 116.0 (CH), 115.9 (CH), 114.6 (CH), 114.1 (CH), 111.6 (C), 83.4 (C), 59.9 (CH), 52.8 (CH$_2$) ; MS (m/z, relative intensity): 480 (M$^+$+1, 51), 479 (M$^+$, 100), 450 (33), 388 (46), 387 (30), 261 (10), 233 (37), 196 (36), 195 (35), 119 (47), 91 (75); exact mass calculated for C$_{23}$H$_{18}$IN$_3$O (M$^+$): 479.0495; found: 479.0493.

Preparation of 4-benzyl-3-(5-methyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cf):
To a solution of 1c (50 mg, 0.21 mmol) and 5-methylindole (53 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 5 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f$ = 0.39 for 3cf in 50% EtOAc–hexane) to afford product 3cf (60.2 mg; 78% yield) as white solids. Mp: 245–247 °C. Selected spectroscopic data for 3cf: IR (KBr): 3317, 3170, 3029, 2981, 2916, 1668, 1504, 1412, 1350, 1112, 738 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.84 (s, 1 H), 10.54 (s, 1 H), 7.36 – 7.29 (m, 4 H), 7.28 – 7.23 (m, 1 H), 7.22 (d, $J$ = 8.5 Hz, 1 H), 7.13 (s, 1 H), 6.93 – 6.86 (m, 2 H), 6.84 – 6.79 (m, 2 H), 6.76 – 6.70 (m, 1 H), 6.63 (d, $J$ = 8.0 Hz, 1 H), 5.13 (s, 1 H), 4.49 (d, $J$ = 15.5 Hz, 1 H), 4.24 (d, $J$ = 15.5 Hz, 1 H), 2.27 (s, 3 H); $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 166.1 (C), 137.8 (C), 134.4 (C), 133.3 (C), 128.4 (two CH), 127.4 (two CH and one C), 127.2 (C), 127.0 (CH), 126.1 (C), 123.3 (CH), 123.0 (CH), 122.9 (CH), 118.8 (CH), 118.3 (CH), 114.8 (CH), 112.8 (CH), 111.1 (CH), 109.8 (C), 58.7 (CH), 51.2 (CH$_2$), 21.2 (CH$_3$); MS (m/z, relative intensity): 368 (M$^+$+1, 32), 367 (M$^+$, 100), 338 (44), 276 (40), 247 (25), 233 (13), 196 (43), 144 (30), 119 (53), 91 (45); exact mass calculated for C$_{24}$H$_{21}$N$_3$O: 367.1685; found: 367.1684.

Preparation of 4-benzyl-3-(5-phenyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cg):

To a solution of 1c (50 mg, 0.21 mmol) and 5-phenylindole (77.2 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 15 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f$ = 0.41 for 3cg in 50% EtOAc–hexane) to afford product 3cg (64.3 mg; 71% yield) as white solids. Mp: 209–211 °C. Selected spectroscopic data for 3cg: IR (KBr): 3412, 3290, 3029, 2899, 1667, 1505, 1421, 1112, 749 cm$^{-1}$; $^1$H NMR (500 MHz,
acetone-d$_6$): $\delta$ 10.26 (brs, 1 H), 9.57 (s, 1 H), 7.72 (s, 1 H), 7.52 (d, $J = 8.0$ Hz, 2 H), 7.48 – 7.37 (m, 6 H), 7.36 – 7.32 (m, 2 H), 7.30 – 7.24 (m, 2 H), 7.10 (d, $J = 2.0$ Hz, 1 H), 7.04 (dd, $J = 7.5$, 1.5 Hz, 1 H), 6.93 – 6.88 (m, 1 H), 6.85 – 6.81 (m, 1 H), 6.78 (d, $J = 8.0$ Hz, 1 H), 5.34 (s, 1 H), 4.65 (d, $J = 15.5$ Hz, 1 H), 4.36 (d, $J = 15.5$ Hz, 1 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.9 (C), 143.3 (C), 139.0 (C), 137.3 (C), 135.9 (C), 133.4 (C), 129.5 (four CH), 128.7 (C), 128.6 (two CH), 128.1 (CH), 127.9 (two CH), 127.1 (CH), 125.5 (CH), 124.3 (CH), 122.1 (CH), 119.7 (CH), 119.1 (CH), 116.0 (CH), 113.9 (CH), 112.9 (C), 112.7 (CH), 111.0 (C), 60.4 (CH), 52.6 (CH$_2$); MS (m/z, relative intensity): 430 (M$^+$+1, 35), 429 (M$^+$, 100), 400 (32), 338 (33), 337 (16), 310 (21), 309 (22), 206 (27), 195 (24), 149 (18), 119 (27), 91 (38); exact mass calculated for C$_{29}$H$_{23}$N$_3$O: 429.1841; found: 429.1843.

Preparation of 4-benzyl-3-(6-fluoro-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ch):

To a solution of 1c (50 mg, 0.21 mmol) and 6-fluoroindole (54 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 20 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f$ = 0.38 for 3ch in 50% EtOAc–hexane) to afford product 3ch (47.1 mg; 60% yield) as white solids. Mp: 218–220 °C, Selected spectroscopic data for 3ch: IR (KBr): 3280, 3197, 3055, 2990, 2908, 1674, 1620, 1507, 1409, 1110, 836, 803, 739 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.22 (brs, 1 H), 9.52 (s, 1 H), 7.52 (dd, $J = 9.0$, 5.5 Hz, 1 H), 7.39 – 7.30 (m, 4 H), 7.29 – 7.24 (m, 1 H), 7.11 (dd, $J = 10.0$, 2.0 Hz, 1 H), 7.02 – 6.98 (m, 2 H), 6.92 – 6.87 (m, 1 H), 6.82 – 6.76 (m, 3 H), 5.25 (s, 1 H), 4.69 (d, $J = 15.5$, 1 H), 4.34 (d, $J = 15.5$ Hz, 1 H); $^{13}$C NMR (125 MHz,acetone-d$_6$): $\delta$ 166.7 (C), 160.7 (d, $J = 235$ Hz, C), 138.9 (C), 137.6 (d, $J = 12.8$ Hz, C), 135.7 (C), 129.5 (two CH), 128.6 (two CH), 128.2 (CH), 124.7 (d, $J = 3.4$ Hz, CH), 124.5 (two C), 124.3 (CH), 121.6 (d, $J = 10$ Hz, CH), 119.8 (CH), 115.9 (CH), 114.0 (CH), 112.4 (C), 108.6 (d, $J = 24.6$ Hz, CH), 98.3 (d, $J = 26$ Hz, CH), 60.1 (CH), 52.8 (CH$_2$); MS (m/z, relative intensity): 372 (M$^+$+1, 23), 371 (M$^+$, 100), 342 (29), 280 (31), 252 (19), 195 (24), 148 (13), 119 (30), 91 (37); exact mass calculated for C$_{23}$H$_{18}$FN$_3$O (M$^+$): 371.1434; found: 371.1434.
Preparation of 4-benzyl-3-(6-chloro-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ci):

![Chemical structure]

To a solution of 1c (50 mg, 0.21 mmol) and 6-chloroindole (61 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 20 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane \((R_f = 0.38\) for 3ci in 50% EtOAc–hexane) to afford product 3ci (50.4 mg; 62% yield) as white solids. Mp: 239–241 °C. Selected spectroscopic data for 3ci: IR (KBr): 3272, 3175, 3029, 2981, 2898, 1664, 1504, 1415, 1113, 1066, 803, 739 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): \(δ = 10.30\) (brs, 1 H), 9.53 (s, 1H), 7.53 (d, \(J = 9.0\) Hz, 1 H), 7.42 (d, \(J = 1.5\) Hz, 1 H), 7.41 – 7.33 (m, 4 H), 7.32 – 7.28 (m, 1 H), 7.02 – 6.96 (m, 3 H), 6.92 – 6.87 (m, 1 H), 6.81 – 6.76 (m, 2 H), 5.25 (s, 1 H), 4.68 (d, \(J = 15.0\) Hz, 1 H), 4.33 (d, \(J = 15.0\) Hz, 1 H); ¹³C NMR (125 MHz, acetone-d₆): \(δ = 166.6\) (C), 138.8 (C), 138.0 (C), 135.7 (C), 129.5 (two CH), 128.6 (two CH), 128.2 (CH), 128.1 (C), 126.3 (C), 125.1 (CH), 124.3 (CH), 121.8 (CH), 120.6 (CH), 119.8 (CH), 116.0 (CH), 115.9 (C), 114.0 (CH), 112.4 (C), 112.15 (CH), 60.0 (CH), 52.8 (CH₂); MS (m/z, relative intensity): 389 (M⁺+2, 42), 388 (M⁺+1, 32), 387 (M⁺, 100), 358 (36), 296 (42), 268 (18), 233 (12), 195 (41), 164 (17), 119 (52), 91 (57); exact mass calculated for C₂₃H₁₈ClN₃O (M⁺): 387.1138; found: 387.1136.

Preparation of 4-benzyl-3-(6-bromo-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cj)

![Chemical structure]
To a solution of 1c (50 mg, 0.21 mmol) and 6-bromoindole (78.4 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 20 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f = 0.38$ for 3ej in 50% EtOAc–hexane) to afford product 3ej (61.2 mg; 68% yield) as white solids. Mp: 251–253 °C. Selected spectroscopic data for 3cj:

**IR (KBr):** 3279, 3171, 3114, 3028, 2980, 2901, 1663, 1610, 1504, 1418, 1350, 1255, 1113, 802, 739 cm$^{-1}$; **H NMR (500 MHz, DMSO-d$_6$):** $\delta$ 11.12 (brs, 1 H), 10.60 (s, 1 H), 7.54 (d, $J = 2.0$ Hz, 1 H), 7.38 (d, $J = 8.5$ Hz, 1 H), 7.34–7.28 (m, 4 H), 7.27–7.21 (m, 1 H), 7.07 (dd, $J = 8.5, 1.5$ Hz, 1 H), 6.92 (d, $J = 2.0$ Hz, 1 H), 6.89 (dd, $J = 7.5, 1.5$ Hz, 1 H), 6.84–6.78 (m, 1 H), 6.74–6.69 (m, 1 H), 6.63 (d, $J = 8.0$ Hz, 1 H), 5.21 (s, 1 H), 4.52 (d, $J = 16.0$ Hz, 1 H), 4.30 (d, $J = 16.0$ Hz, 1 H); **C NMR (125 MHz, DMSO-d$_6$):** $\delta$ 165.7 (C), 137.8 (C), 136.9 (C), 134.0 (C), 128.4 (two CH), 127.3 (two CH), 127.1 (C), 127.0 (CH), 124.9 (C), 124.3 (CH), 123.1 (CH), 121.8 (CH), 120.9 (CH), 118.4 (CH), 114.9 (CH), 114.12 (C), 114.08 (CH), 112.8 (CH), 110.7 (C), 58.7 (CH), 51.3 (CH$_2$); **MS (m/z, relative intensity):** 434 (M$^+$+3, 51), 433 (M$^+$+2, 100), 432 (M$^+$+1, 53), 431 (M$^+$, 100), 404 (46), 402 (43), 196 (4), 195 (4) 119 (6), 91 (7); exact mass calculated for C$_{23}$H$_{18}$BrN$_3$O (M$^+$): 431.0633; found: 431.0631.

**Preparation of 4-benzyl-3-(7-bromo-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ck):**

![Diagram](image)

To a solution of 1c (50 mg, 0.21 mmol) and 7-bromoindole (78.4 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 18 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f = 0.38$ for 3ej in 50% EtOAc–hexane) to afford product 3ck (66.1 mg; 73% yield) as off-white solids. Mp: 228–230 °C. Selected spectroscopic data for 3ck: IR (KBr): 3267, 3065, 3034, 2910, 2852, 1668, 1500, 1430, 1253, 1110, 745, 700 cm$^{-1}$; **H NMR (500 MHz, DMSO-d$_6$):** $\delta$ 11.12 (brs, 1 H), 10.60 (s, 1 H), 7.54 (d, $J = 2.0$ Hz, 1 H), 7.38 (d, $J = 8.5$ Hz, 1 H), 7.34–7.28 (m, 4 H), 7.27–7.21 (m, 1 H), 7.07 (dd, $J = 8.5, 1.5$ Hz, 1 H), 6.92 (d, $J = 2.0$ Hz, 1 H), 6.89 (dd, $J = 7.5, 1.5$ Hz, 1 H), 6.84–6.78 (m, 1 H), 6.74–6.69 (m, 1 H), 6.63 (d, $J = 8.0$ Hz, 1 H), 5.21 (s, 1 H), 4.52 (d, $J = 16.0$ Hz, 1 H), 4.30 (d, $J = 16.0$ Hz, 1 H); **C NMR (125 MHz, DMSO-d$_6$):** $\delta$ 165.7 (C), 137.8 (C), 136.9 (C), 134.0 (C), 128.4 (two CH), 127.3 (two CH), 127.1 (C), 127.0 (CH), 124.9 (C), 124.3 (CH), 123.1 (CH), 121.8 (CH), 120.9 (CH), 118.4 (CH), 114.9 (CH), 114.12 (C), 114.08 (CH), 112.8 (CH), 110.7 (C), 58.7 (CH), 51.3 (CH$_2$); **MS (m/z, relative intensity):** 434 (M$^+$+3, 51), 433 (M$^+$+2, 100), 432 (M$^+$+1, 53), 431 (M$^+$, 100), 404 (46), 402 (43), 196 (4), 195 (4) 119 (6), 91 (7); exact mass calculated for C$_{23}$H$_{18}$BrN$_3$O (M$^+$): 431.0633; found: 431.0631.
NMR (500 MHz, acetone-d$_6$): $\delta$ 10.30 (brs, 1 H), 9.54 (s, 1 H), 7.57 (d, $J = 8.0$ Hz, 1 H), 7.39 – 7.24 (m, 6 H), 7.06 (d, $J = 2.0$ Hz, 1 H), 7.01 (dd, $J = 8.5$, 1.5 Hz, 1 H), 6.97 – 6.87 (m, 2 H), 6.83 – 6.77 (m, 2 H), 5.27 (s, 1 H), 4.69 (d, $J = 15.5$ Hz, 1 H), 4.34 (d, $J = 15.5$, 1 H), $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.5 (C), 138.8 (C), 135.9 (C), 135.7 (C), 129.5 (two CH), 129.1 (C), 128.6 (two CH), 128.2 (CH), 125.3 (CH), 125.1 (CH), 124.3 (CH), 121.6 (CH), 120.2 (CH), 119.9 (CH), 116.0 (CH), 115.9 (C), 114.1 (CH), 113.7 (C), 105.2 (C), 60.1 (CH), 52.8 (CH$_2$); MS ($m/z$, relative intensity): 434 (M$^+$+3), 433 (M$^+$+2), 432 (M$^+$+1), 431 (M$, 99$), 404 (31), 402 (30), 342 (28), 340 (29), 312 (10), 233 (24), 208 (15), 195 (45), 119 (52), 91 (58); exact mass calculated for C$_{23}$H$_{18}$BrN$_3$O: 431.0633; found: 431.0632.

Preparation of 4-benzyl-3-(2-methyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cl)

To a solution of 1c (50 mg, 0.21 mmol) and 2-methylindole (52.4 mg, 0.40 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 4 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f = 0.39$ for 3cl in 50% EtOAc–hexane) to afford product 3cl (63.1 mg; 82% yield) as light yellow solids; Mp: 234–236 °C. Selected spectroscopic data for 3cl: IR (KBr): 3283, 3194, 3059, 2977, 2892, 1656, 1507, 1426, 1302, 1252, 1228, 1154, 738, 698, 676 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.99 (s, 1 H), 10.65 (s, 1 H), 7.30 – 7.25 (m, 2 H), 7.24 – 7.18 (m, 4 H), 6.95 – 6.90 (m, 2 H), 6.82 – 6.76 (m, 2 H), 6.72 – 6.66 (m, 2 H), 6.54 (d, $J = 8.0$ Hz, 1 H), 5.28 (s, 1 H), 4.45 (d, $J = 16.5$ Hz, 1 H), 4.03 (d, $J = 16.5$ Hz, 1 H), 2.18 (s, 3 H), $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 165.8 (C), 137.7 (C), 135.2 (C), 135.0 (C), 134.3 (C), 128.4 (two CH), 127.0 (two CH), 126.8 (CH), 126.3 (C), 126.1 (C), 123.2 (CH), 120.2 (CH), 118.6 (CH), 118.3 (CH), 117.4 (CH), 114.8 (CH), 111.4 (CH), 110.5 (CH), 107.9 (C), 58.0 (CH), 50.1 (CH$_2$), 11.3 (CH$_3$); MS ($m/z$, relative intensity): 368 (M$^+$+1, 66), 367 (M$^+$, 100), 338 (42), 276 (65), 275 (44), 247 (60), 236 (77), 219 (38), 196 (70), 195 (63), 144 (82), 119 (100), 91 (89); exact mass calculated for C$_{24}$H$_{21}$N$_3$O (M$^+$): 367.1685; found: 367.1682.
Preparation of 4-benzyl-3-(2-phenyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cm)

To a solution of 1c (50 mg, 0.21 mmol) and 2-phenylindole (77.2 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 5 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f = 0.4$ for 3cm in 50% EtOAc–hexane) to afford product 3cm (71.8 mg; 80% yield) as white solid; Mp: 240–242 °C. Selected spectroscopic data for 3cm:

IR (KBr): 3386, 3189, 3053, 2985, 2900, 1673, 1506, 1397, 1447, 1307, 1231, 743, 701 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): δ 10.53 (brs, 1 H), 9.76 (s, 1 H), 7.87 (d, $J = 6.5$ Hz, 2 H), 7.47 – 7.36 (m, 4 H), 7.11 – 7.00 (m, 6 H), 6.99 – 6.95 (m, 2 H), 6.89 – 6.83 (m, 1 H), 6.82 – 6.72 (m, 2 H), 6.63 (d, $J = 8.0$ Hz, 1 H), 5.59 (s, 1 H), 4.41 (d, $J = 16.0$ Hz, 1 H), 3.82 (d, $J = 16.0$ Hz, 1 H); ¹³C NMR (125 MHz, acetone-d₆): δ 166.9 (C), 139.9 (C), 138.5 (C), 137.6 (C), 135.6 (C), 133.3 (C), 130.4 (two CH), 129.5 (two CH), 129.19 (CH), 129.17 (two CH), 128.0 (two CH), 127.64 (CH), 127.56 (C), 126.8 (C), 124.6 (CH), 122.9 (CH), 121.1 (CH), 120.4 (CH), 118.5 (CH), 116.0 (CH), 112.24 (CH), 112.21 (CH), 111.0 (C), 58.9 (CH), 51.0 (CH₂); MS (m/z, relative intensity): 430 ($M^+ + 1$, 31), 429 ($M^+$, 100), 400 (38), 338 (48), 308 (30), 236 (37), 206 (63), 204 (78), 196 (37), 119 (39), 91 (50); exact mass calculated for C₂₉H₂₃N₃O (M⁺): 429.1841; found: 429.1840.

Preparation of 4-benzyl-3-(2-(p-tolyl)-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cn):
To a solution of 1c (50 mg, 0.21 mmol) and 2-(p-tolyl)-1H-indole (82.9 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 5 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane (Rf = 0.39 for 3cn in 50% EtOAc–hexane) to afford product 3cn (74.2 mg; 80% yield) as white solid; Mp: 215–217 °C. Selected spectroscopic data for 3cn: IR (KBr): 3424, 3187, 3055, 2978, 2891, 1674, 1507, 1428, 1307, 824, 738 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): δ 10.46 (brs, 1 H), 9.74 (s, 1 H), 7.75 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 1 H), 7.24 (d, J = 7.5 Hz, 2 H), 7.11 – 7.03 (m, 5 H), 7.02 – 6.96 (m, 3 H), 6.88 – 6.82 (m, 1 H), 6.81 – 6.72 (m, 2 H), 6.60 (d, J = 8.0 Hz, 1 H), 5.59 (s, 1 H), 4.38 (d, J = 16.5 Hz, 1 H), 3.82 (d, J = 16.5 Hz, 1 H), 2.38 (s, 3 H); ¹³C NMR (125 MHz, acetone-d₆): δ 166.9 (C), 140.1 (C), 139.0 (C), 138.5 (C), 137.5 (C), 135.6 (C), 130.4 (C), 130.3 (two CH), 130.1 (two CH), 129.2 (two CH), 127.9 (two CH), 127.61 (C), 127.58 (CH), 126.9 (C), 124.6 (CH), 122.7 (CH), 121.0 (CH), 120.4 (CH), 118.5 (CH), 116.0 (CH), 112.2 (CH), 112.1 (CH), 110.8 (C), 59.0 (CH), 51.0 (CH₂), 21.4 (CH₃); MS (m/z, relative intensity): 444 (M⁺+1, 32), 443 (M⁺, 100), 414 (41), 352 (57), 322 (31), 247 (13), 236 (47), 220 (70), 218 (49), 204 (41), 196 (33), 119 (35), 91 (51); exact mass calculated for C₃₀H₂₅N₃O (M⁺): 443.1998; found: 443.1998.

Preparation of 4-benzyl-3-(1-methyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3co):

To a solution of 1c (50 mg, 0.21 mmol) and N-methylindole (52.4 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 10 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane (Rf = 0.47 for 3co in 50% EtOAc–hexane) to afford product 3co (56.1 mg; 73% yield) as white solids; Mp: 224–226 °C. Selected spectroscopic data for 3co: IR (KBr): 3182, 3045, 2976, 2913, 1678, 1501, 1391, 1225, 1147, 857, 742 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 10.60 (s, 1 H), 7.39 (dd, J = 16.5, 8.0 Hz, 2 H), 7.33 – 7.29 (m, 4 H).
7.27 – 7.22 (m, 1 H), 7.15 – 7.10 (m, 1 H), 6.98 – 6.94 (m, 1 H), 6.93 – 6.89 (m, 2 H), 6.83 – 6.78 (m, 1 H), 6.74 – 6.69 (m, 1 H), 6.61 (d, J = 8.0 Hz, 1 H), 5.22 (s, 1 H), 4.51 (d, J = 15.5 Hz, 1 H), 4.30 (d, J = 15.5 Hz, 1 H), 3.67 (s, 3 H); 13C NMR (125 MHz, DMSO-d 6): δ 165.8 (C), 137.8 (C), 136.5 (C), 133.9 (C), 128.4 (two CH), 127.6 (CH), 127.3 (two CH), 127.1 (two C), 127.0 (CH), 126.2 (C), 123.0 (CH), 121.4 (CH), 119.4 (CH), 119.1 (CH), 118.3 (CH), 114.9 (CH), 112.7 (CH), 109.7 (CH), 58.8 (CH), 51.2 (CH2), 32.4 (CH3); MS (m/z, relative intensity): 368 (M++1, 14), 367 (M+, 58), 338 (25), 276 (28), 247 (23), 236 (21), 233 (15), 219 (10), 144 (100), 91 (52); exact mass calculated for C24H21N3O (M+): 367.1685; found: 367.1685.

Preparation of 4-benzyl-3-(1-benzyl-1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cp):

To a solution of 1c (50 mg, 0.21 mmol) and N-benzylindole (83 mg, 0.40 mmol, 2 equiv) in CH3OH (4.1 mL) was added Ru(bpy)3Cl2•6H2O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 16 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane (Rf = 0.52 for 3cp in 50% EtOAc–hexane) to afford product 3cp (66.8 mg; 72% yield) as white solids; Mp: 151–153 °C. Selected spectroscopic data for 3cp: IR (KBr): 3191, 3131, 3062, 3029, 2916, 2859, 1668, 1501, 1382, 1156, 738 cm−1; 1H NMR (500 MHz, acetone-d6): δ 9.55 (s, 1 H), 7.54 (d, J = 8.0 Hz, 1 H), 7.37 – 7.29 (m, 5 H), 7.28 – 7.20 (m, 4 H), 7.11 – 7.05 (m, 4 H), 7.02 – 6.95 (m, 2 H), 6.90 – 6.85 (m, 1 H), 6.80 – 6.72 (m, 2 H), 5.31 (s, 2 H), 5.28 (s, 1 H), 4.65 (d, J = 15.5 Hz, 1 H), 4.34 (d, J = 15.5 Hz, 1 H); 13C NMR (125 MHz, acetone-d6): δ 166.8 (C), 139.0 (C), 138.9 (C), 137.6 (C), 135.7 (C), 129.50 (two CH), 129.48 (two CH), 128.63 (C), 128.59 (two CH), 128.31 (CH), 128.27 (C), 128.20 (CH), 128.1 (CH), 127.8 (two CH), 124.2 (CH), 122.7 (CH), 120.9 (CH), 120.4 (CH), 119.7 (CH), 115.9 (CH), 114.1 (CH), 111.7 (C), 111.0 (CH), 60.1 (CH), 52.8 (CH2), 50.4 (CH2); MS (m/z, relative intensity): 443 (M+, 4), 414 (2), 352 (2), 220 (6), 153 (38), 136 (42), 107 (46), 89 (58), 77 (100); exact mass calculated for C36H23N3O (M+): 443.1998; found: 443.1994.
Preparation of 4-benzyl-3-(1H-pyrrolo[2,3-b]pyridin-3-yl)-3,4-dihydroquinoxalin-2(1H)-one

To a solution of 1c (50 mg, 0.21 mmol) and 7-azaindole (47.2 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 16 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 40% EtOAc–hexane (Rf = 0.23 for 3cq in 50% EtOAc–hexane) to afford product 3cq (16.1 mg; 22% yield) as gummy compound; Selected spectroscopic data for 3cq: IR (KBr): 3059, 2922, 2851, 1683, 1387, 1258, 884, 768 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): δ 10.61 (brs, 1 H), 9.58 (s, 1 H), 8.20 (dd, J = 4.5, 1.5 Hz, 1 H), 7.80 (dd, J = 8.0, 1.5 Hz, 1 H), 7.39 – 7.31 (m, 4 H), 7.29 – 7.24 (m, 1 H), 7.16 (d, J = 2.0 Hz, 1 H), 7.03 – 6.96 (m, 2 H), 6.92 – 6.88 (m, 1 H), 6.80 (d, J = 7.5 Hz, 2 H), 5.25 (s, 1 H), 4.70 (d, J = 15.5 Hz, 1 H), 4.36 (d, J = 15.5 Hz, 1 H); ¹³C NMR (125 MHz, acetone-d₆): δ 166.6 (C), 149.6 (C), 144.3 (CH), 138.8 (C), 135.7 (C), 129.5 (two CH), 128.7 (CH), 128.6 (two CH), 128.5 (C), 128.2 (CH), 124.7 (CH), 124.4 (CH), 119.9 (CH), 119.4 (C), 116.6 (CH), 116.0 (CH), 114.0 (CH), 111.1 (C), 60.4 (CH), 52.8 (CH₂); MS (m/z, relative intensity): 355 (M⁺+1, 12), 354 (M⁺, 47), 325 (16), 263 (30), 235 (24), 195 (35), 131 (41), 119 (93), 91 (100); exact mass calculated for C₂₂H₁₈N₄O: 354.1481; found: 354.1480.

Preparation of 4-benzyl-3-(2-hydroxynaphthalen-1-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cr):

To a solution of 1c (50 mg, 0.21 mmol) and naphthalen-2-ol (288.3 mg, 2.0 mmol, 9.5 equiv)
in CH$_2$Cl$_2$ (3.9 mL) was added Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 48 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 40% EtOAc–hexane ($R_f = 0.37$ for 3cr in 50% EtOAc–hexane) to afford product 3cr (40.2 mg; 50% yield) as white solids and 5 ($R_f = 0.30$ for 5 in 50% EtOAc–hexane, 12.1 mg, 23% yield). For 3cr: mp, 202–203 °C; elected spectroscopic data for 3cr: IR (KBr): 3299, 3191, 3114, 3027, 2918, 1651, 1507, 1433, 1273, 973, 814, 745 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.63 (s, 1 H), 10.01 (s, 1 H), 8.05 (d, $J = 8.5$ Hz, 1 H), 7.78 (d, $J = 8.5$ Hz, 1 H), 7.73 (d, $J = 8.5$ Hz, 1 H), 7.38 – 7.33 (m, 1 H), 7.27 – 7.22 (m, 1 H), 7.16 – 7.06 (m, 6 H), 6.87 (d, $J = 7.5$ Hz, 1 H), 6.70 (dd, $J = 7.5, 7.5$ Hz 1 H), 6.61 (dd, $J = 7.5, 7.0$ Hz, 1 H), 6.38 (d, $J = 8.0$ Hz, 1 H), 6.23 (s, 1 H), 4.32 (d, $J = 17.0$ Hz, 1 H), 4.06 (d, $J = 17.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 166.5 (C), 154.7 (C), 138.2 (C), 134.4 (C), 129.8 (CH), 128.6 (CH), 128.1 (four CH), 126.35 (CH), 126.32 (four CH), 125.7 (C), 122.9 (CH), 122.3 (CH), 117.9 (CH), 114.6 (CH), 57.5 (CH), 50.6 (CH$_2$), *few aryl carbons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS ($m/z$, relative intensity): 380 (M$^+$, 10), 378 (M$^+$–2, 6), 361 (5), 289 (10), 252 (10), 224 (28), 205 (23), 144 (22), 115 (15), 91 (100); exact mass calculated for C$_{25}$H$_{20}$N$_2$O$_2$: 380.1525; found: 380.1527.

For 5: mp, 137–138 °C; IR (KBr): 3304, 3187, 3039, 2922, 1664, 1510, 1385, 1312, 994, 965, 746, 700 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 9.60 (brs, 1 H), 7.41 (d, $J = 8.0$ Hz, 2 H), 7.33 (dd, $J = 7.5, 7.5$ Hz, 2 H), 7.26 (dd, $J = 7.5, 7.5$ Hz, 1 H), 7.00 (dd, $J = 8.0, 1.5$ Hz, 1 H), 6.89 – 6.84 (m, 1 H), 6.82 – 6.77 (m, 2 H), 5.53 (d, $J = 6.5$ Hz, 1 H), 5.16 (d, $J = 6.5$ Hz, 1 H), 4.81 (d, $J = 15.0$ Hz, 1 H), 4.59 (d, $J = 15.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 164.4 (C), 138.7 (C), 133.0 (C), 129.4, (two CH), 128.6 (two CH), 128.1 (CH), 127.8 (C), 123.7 (CH), 120.3 (CH), 115.9 (CH), 114.9 (CH), 82.1 (CH), 52.5 (CH$_2$); MS ($m/z$, relative intensity): 253 (M$^+$–1, 1), 238 (1), 221 (2), 208 (2), 178 (3), 167 (4), 153 (10), 149 (15), 136 (14), 105 (41), 101 (28), 89 (27), 77 (62), 58 (100); exact mass calculated for C$_{15}$H$_{14}$N$_2$O$_2$: 254.1055; found: 254.1058.
Preparation of 3-(1H-benzo[g]indol-3-yl)-4-benzyl-3,4-dihydroquinoxalin-2(1H)-one (3cs):

To a solution of 1c (50 mg, 0.21 mmol) and 1H-benzo[g]indole (66.8 mg, 0.40 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 5 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f = 0.4$ for 3cs in 50% EtOAc–hexane) to afford product 3cs (66.4 mg; 78% yield) as off-white solids. Mp: 241–243 °C. Selected spectroscopic data for 3cs: IR (KBr): 3306, 3061, 2952, 2920, 2851, 1667, 1506, 1392, 1252, 1222, 1109, 800, 746, 697 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 11.93 (s, 1 H), 10.62 (s, 1 H), 8.28 (d, $J = 8.5$ Hz, 1 H), 7.89 (d, $J = 8.5$ Hz, 1 H), 7.58 – 7.49 (m, 2 H), 7.43 – 7.37 (m, 2 H), 7.34 – 7.30 (m, 4 H), 7.28 – 7.22 (1 H), 6.95 – 6.92 (m, 2 H), 6.85 – 6.80 (m, 1 H), 6.78 – 6.72 (m, 1 H), 6.65 (d, $J = 8.0$ Hz, 1 H), 5.30 (s, 1 H), 4.53 (d, $J = 15.0$ Hz, 1 H), 4.33 (d, $J = 15.5$ Hz, 1 H); ¹³C NMR (125 MHz, DMSO-d₆): δ 166.1 (C), 137.8 (C), 134.2 (C), 130.6 (C), 129.6 (C), 128.4 (two CH), 128.2 (CH), 127.36 (two CH), 127.33 (C), 127.0 (CH), 125.3 (CH), 123.7 (CH), 123.1 (CH), 121.8 (CH), 121.7 (C), 121.3 (C), 120.4 (CH), 119.7 (CH), 119.4 (CH), 118.5 (CH), 114.8 (CH), 112.9 (CH), 112.4 (C), 58.8 (CH), 51.3 (CH₂); MS ($m/z$, relative intensity): 404 (M⁺+1, 29), 403 (M⁺, 100), 374 (38), 312 (35), 283 (21), 196 (28), 180 (29), 119 (30), 97 (32), 91 (29); exact mass calculated for C₂₇H₂₁N₃O (M⁺): 403.1685; found: 403.1685.

Preparation of 4-benzyl-3-(1H-pyrrol-2-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ct):

Preparation of 4-benzyl-3-(1H-pyrrol-2-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ct):
To a solution of 1c (50 mg, 0.21 mmol) and pyrrole (28 mg, 0.42 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 24 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane (Rᵢ = 0.47 for 3ct in 50% EtOAc–hexane) to afford product 3ct (39.1 mg; 61% yield) as yellow solids. Mp: 213–214 °C. Selected spectroscopic data for 3ct: IR (KBr): 3335, 3059, 2910, 1674, 1504, 1397, 1225, 1111, 1026, 975, 885, 739, 702 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): δ 9.83 (brs, 1 H), 9.54 (s, 1 H), 7.39 – 7.30 (m, 4 H), 7.29 – 7.23 (m, 1 H), 6.96 (dd, J = 8.0, 1.5 Hz, 1 H), 6.89 – 6.85 (m, 1 H), 6.78 – 6.74 (m, 2 H), 6.70 – 6.67 (m, 1 H), 5.93 (dd, J = 6.0, 2.5 Hz, 1 H), 5.74 (m, 1 H), 4.93 (s, 1 H), 4.66 (d, J = 15.5 Hz, 1 H), 4.27 (d, J = 15.5, 1 H); ¹³C NMR (125 MHz, acetone-d₆): δ 166.3 (C), 138.7 (C), 135.4 (C), 129.5 (two CH), 128.6 (two CH), 128.3 (C), 128.2 (CH), 127.3 (C), 124.2 (CH), 119.9 (CH), 119.0 (CH), 116.0 (CH), 114.2 (CH), 108.8 (CH), 107.4 (CH), 61.1 (CH), 52.8 (CH₂); MS (m/z, relative intensity): 304 (M⁺+1, 20), 303 (M⁺, 100), 275 (10), 274 (15), 212 (47), 196 (34), 195 (43), 184 (15), 169 (16), 119 (62), 91 (76); exact mass calculated for C₁₉H₁₇N₃O: 303.1372; found: 303.1369.

**Preparation of 3cu-p and 3cu-o.**

To a solution of 1c (50 mg, 0.21 mmol) and phenol (190 mg, 2.02 mmol, 10 equiv) in CH₂Cl₂ (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 72 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 20% to 40% EtOAc–hexane (Rᵢ = 0.54 for 3cu-o in 50% EtOAc–hexane) to afford product 3cu-o (19.2 mg; 28% yield) as white solids and 3cu-p (Rᵢ = 0.27 for 3cu-p in 50% EtOAc–hexane, 22.1 mg, 32% yield) as white solids. For 3cu-p: mp: 205–207 °C; IR (KBr): 3266, 3174, 3028, 2980, 2913, 1661, 1504, 1423, 1384, 1256, 739 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 10.60 (s, 1 H), 9.47 (s, 1 H), 7.35 – 7.21 (m, 5 H), 6.92 (d, J = 8.5 Hz, 2 H), 6.84 (dd, J = 8.0, 1.5 Hz, 1 H), 6.81 – 6.76 (m, 1 H), 6.69 – 6.64 (m, 3 H), 6.62 (d, J = 8.0 Hz, 1 H), 4.84 (s, 1 H), 4.52 (d,
\[ J = 16.0 \text{ Hz}, 1 \text{ H}, \] 4.20 (d, \( J = 16.0 \text{ Hz}, 1 \text{ H} \)), 13C NMR (125 MHz, DMSO-d6): \( \delta \) 165.9 (C), 157.3 (C), 137.6 (C), 133.5 (C), 128.5 (two CH), 128.0 (two CH), 127.8 (C), 127.3 (two CH), 127.0 (CH), 126.5 (C), 123.1 (CH), 118.1 (CH), 115.3 (two CH), 114.8 (CH), 112.3 (CH), 64.7 (CH), 51.1 (CH2); MS (m/z, relative intensity): 331 (M\(^{+}\)+1, 42), 330 (M\(^{+}\), 100), 301 (10), 239 (49), 209 (62), 195 (18), 91 (5); exact mass calculated for C\(_{21}\)H\(_{18}\)N\(_{2}\)O\(_{2}\): 330.1368; found: 330.1369.

For 3cu-o: mp, 183–184 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.83 (s, 1 H), 8.51 (s, 1 H), 7.33 – 7.13 (m, 6 H), 7.04 – 6.91 (m, 3 H), 6.85 (d, \( J = 8.5 \text{ Hz}, 1 \text{ H} \)), 6.80 – 6.70 (m, 3 H), 5.36 (s, 1 H), 4.83 (d, \( J = 15.5 \text{ Hz}, 1 \text{ H} \)), 4.17 (d, \( J = 15.5 \text{ Hz}, 1 \text{ H} \)); \(^1\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 168.0 (C), 154.9 (C), 135.9 (C), 134.2 (C), 129.7 (CH), 128.9 (two CH), 127.8 (CH), 127.4 (two CH), 126.0 (CH), 125.5 (CH), 124.0 (C), 123.5 (C), 120.5 (CH), 119.0 (CH), 118.7 (CH), 116.0 (CH), 112.2 (CH), 60.7 (CH), 52.1 (CH2); MS (m/z, relative intensity): 331 (M\(^{+}\)+1, 15), 330 (M\(^{+}\), 69), 301 (5), 239 (65), 209 (33), 195 (6), 119 (19), 91 (100), 65 (20); exact mass calculated for C\(_{21}\)H\(_{18}\)N\(_{2}\)O\(_{2}\): 330.1368; found: 330.1366.

**Preparation of 3cv-1 and 3cv-2:**

![Chemical reaction diagram](image_url)

To a solution of \( 1c \) (50 mg, 0.21 mmol) and (cyclohex-1-en-1-yloxy)trimethylsilane (70 mg, 0.41 mmol, 2 equiv) in CH\(_3\)OH (4.1 mL) was added Ru(bpy)\(_3\)Cl\(_2\)•6H\(_2\)O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 7 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (\( R_f = 0.45 \) for 3cv-1; \( R_f = 0.44 \) for 3cv-2 in 40% EtOAc–hexane, developed twice) to afford pure product 3cv-1 and 3cv-2 mixtures (58.2 mg; 83% yield, in a ratio of 80:20, determined by \(^1\)H NMR). The mixture was further purified by flash column chromatography to give the pure 3cv-1 and pure 3cv-2 for spectra analysis. Both of them are colorless gummy compounds.

Selected spectroscopic data for 3cv-1: IR (neat): 3208, 3062, 2937, 2864, 1680, 1507, 1379, 1260, 1126, 1027, 744, 700 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.87 (s, 1 H), 7.26 – 7.14 (m, 5 H), 6.92 – 6.85 (m, 1 H), 6.77 (d, \( J = 4.0 \text{ Hz}, 2 \text{ H} \)), 6.70 (d, \( J = 8.0 \text{ Hz}, 1 \text{ H} \)), 4.60 – 4.48 (m, 3 H), 2.54 – 2.46 (m, 1 H), 2.42 – 2.35 (m, 1 H), 2.28 – 2.17 (m, 1 H), 1.99 – 1.84 (m, 2 H), 1.83 – 1.74
(m, 1 H), 1.68 – 1.44 (m, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 210.3 (C), 165.8 (C), 137.7 (C), 133.4 (C), 128.5 (two CH), 127.4 (two CH), 127.3 (CH), 126.9 (C), 124.1 (CH), 119.5 (CH), 115.9 (CH), 115.6 (CH), 61.1 (CH), 55.1 (CH$_2$), 50.9 (CH), 42.1 (CH$_2$), 30.5 (CH$_2$), 27.7 (CH$_2$), 24.5 (CH$_2$); MS (m/z, relative intensity): 334 (M$^+$, 8), 244 (10), 243 (71), 237 (30), 194 (15), 129 (5), 92 (14), 91 (100); exact mass calculated for C$_{21}$H$_{22}$N$_2$O$_2$: 334.1681; found: 334.1678.

Selected spectroscopic data for 3cv-2: $^1$H NMR (500 MHz, CDCl$_3$): δ 8.49 (s, 1 H), 7.28 – 7.16 (m, 5 H), 6.88 – 6.82 (m, 1 H), 6.70 – 6.63 (m, 3 H), 4.78 (d, J = 3.0 Hz, 1 H), 4.61 (s, 2 H), 2.83 – 2.77 (m, 1 H), 2.47 – 2.40 (m, 1 H), 2.27 – 2.18 (m, 1 H), 1.98 – 1.91 (m, 1 H), 1.89 – 1.82 (m, 1 H), 1.78 – 1.71 (m, 1 H), 1.67 – 1.47 (m, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 209.6 (C), 168.1 (C), 137.8 (C), 134.5 (C), 128.6 (two CH), 127.4 (CH), 127.2 (two CH), 126.1 (C), 124.3 (CH), 118.9 (CH), 115.2 (CH), 114.5 (CH), 60.4 (CH), 55.9 (CH), 55.2 (CH$_2$), 41.7 (CH$_2$), 28.9 (CH$_2$), 26.7 (CH$_2$), 24.4 (CH$_2$).

Preparation of 4-benzyl-3-(2-oxobut-3-en-1-yl)-3,4-dihydroquinoxalin-2(1H)-one (3cw):

To a solution of 1c (50 mg, 0.21 mmol) and 2-trimethylsilyloxy-1,3-butadiene (65 mg, 0.46 mmol, 2 equiv) in CH$_3$OH (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 4 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f = 0.48$ for 3cw in 50% EtOAc–hexane) to afford product 3cw (51 mg; 79% yield) as colorless gummy compound. Selected spectroscopic data for 3cw: IR (neat): 3208, 3062, 2964, 2922, 1684, 1507, 1401, 1261, 1092, 1027, 800, 744, 700 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.05 (s, 1 H), 7.37 – 7.11 (m, 5 H), 6.93 – 6.86 (m, 1 H), 6.82 – 6.71 (m, 2 H), 6.64 (d, J = 8.0 Hz, 1 H), 6.32 – 6.20 (m, 1 H), 6.05 (d, J = 17.6 Hz, 1 H), 5.77 (d, J = 10.4 Hz, 1 H), 4.58 – 4.46 (m, 2 H), 4.36 (d, J = 15.6 Hz, 2 H), 2.98 – 2.87 (m, 1 H), 2.82 – 2.74 (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.3 (C), 167.8 (C), 137.0 (C), 136.2 (CH), 133.1 (C), 129.2 (CH$_2$), 128.7 (two CH), 127.4 (CH), 127.3 (two CH), 126.2 (C), 124.3 (CH), 119.6 (CH), 115.6 (CH), 114.7 (CH), 58.7 (CH), 53.6 (CH$_2$), 39.7 (CH$_2$); MS (m/z, relative intensity): 306 (M$^+$, 8), 237 (6), 215 (85), 187 (37), 161 (9), 131 (5), 91 (100); exact mass calculated for C$_{19}$H$_{18}$N$_2$O$_2$: 306.1368; found: 306.1377.
Preparation of 1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxaline-2-carbonitrile (3cx)

To a solution of 1c (50 mg, 0.21 mmol) and trimethylsilyl cyanide (42 mg, 0.42 mmol, 2 equiv) in CH₃OH (4.1 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 7 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane (Rₚ = 0.52 for 3cx in 50% EtOAc–hexane) to afford product 3cx (41 mg; 74% yield) as white solids. Mp: 161–162 °C. Selected spectroscopic data for 3cx: IR (neat): 3206, 3066, 2961, 2923, 2855, 1702, 1504, 1260, 1021, 802, 746, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.40 (s, 1 H), 7.43 – 7.34 (m, 5 H), 7.14 – 7.07 (m, 1 H), 7.02 – 6.89 (m, 3 H), 4.80 (d, J = 13.5 Hz, 1 H), 4.56 (s, 1 H), 4.07 (d, J = 13.5 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 159.7 (C), 133.8 (C), 132.4 (C), 129.3 (two CH), 128.8 (three CH), 125.8 (C), 125.2 (CH), 122.10 (CH), 116.5 (CH), 114.4 (CH), 112.8 (C), 52.1 (CH₂), 51.9 (CH); MS (m/z, relative intensity): 264 (M⁺+1, 3), 263 (M⁺, 20), 172 (1), 146 (19), 118 (3), 91 (100); exact mass calculated for C₁₆H₁₃N₃O: 263.1059; found: 263.1059.

Preparation of 4-benzyl-7-chloro-3-(1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ga):

To a solution of 1g (50 mg, 0.18 mmol) and indole (42.1 mg, 0.36 mmol, 2 equiv) in CH₃OH (3.6 mL) was added Ru(bpy)₃Cl₂•6H₂O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact
florescence lamp (24 W) for 12 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane (R_f = 0.48 for 3ga in 50% EtOAc–hexane) to afford product 3ga (51.5 mg; 72% yield) as white solids. Mp: 200–201 °C. Selected spectroscopic data for 3ga: IR (KBr): 3292, 3066, 2960, 1662, 1582, 1504, 1393, 1227, 948, 804, 740, 709 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆): δ 10.20 (brs, 1 H), 9.66 (s, 1 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.40 – 7.25 (m, 6 H), 7.13 – 7.08 (m, 1 H), 7.06 – 6.97 (m, 3 H), 6.88 (dd, J = 8.5, 2.5 Hz, 1 H), 6.73 (d, J = 8.5 Hz, 1 H), 5.31 (s, 1 H), 4.64 (d, J = 15.5 Hz, 1 H), 4.38 (d, J = 15.5 Hz, 1 H); ¹³C NMR (125 MHz, acetone-d₆): δ 166.7 (C), 138.5 (C), 137.6 (C), 134.7 (C), 129.9 (C), 129.5 (two CH), 128.5 (two CH), 128.2 (CH), 127.5 (C), 124.1 (CH), 123.8 (C), 123.5 (CH), 122.8 (CH), 120.4 (CH), 120.3 (CH), 115.5 (CH), 115.1 (CH), 112.4 (CH), 111.8 (C), 60.0 (CH), 52.9 (CH₂); MS (m/z, relative intensity): 389 (M⁺+2, 34), 388 (M⁺+1, 25), 387 (100), 358 (26), 296 (35), 268 (19), 230 (39), 153 (36), 130 (40), 91 (59); exact mass calculated for C₂₃H₁₈ClN₃O: 387.1138; found: 387.1136.

Thermal ellipsoids draw at the 50% probability level

Figure S1. ORTEP and Stereo plots for X-ray crystal structures of 3ga (ic18529_sq).

CCDC 1816893 contains the supplementary crystallographic data for 3ga (ic18529_sq). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk
Table S1. Crystal data and structure refinement for 3ga (ic 18529_sq).

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Preparation of 4-benzyl-7-fluoro-3-(1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3ia):

```
\[
\begin{align*}
1i \quad & + \quad \text{cat. Ru(bpy)_3Cl_2 \cdot 6H_2O} \\
& \quad \text{CFL, O}_2 \\
& \quad \text{CH}_3\text{OH, rt, 15 h; 64%} \\
\rightarrow
\end{align*}
\]
```

To a solution of 1i (50 mg, 0.19 mmol) and indole (44.5 mg, 0.38 mmol, 2 equiv) in CH$_3$OH (3.8 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact fluorescence lamp (24 W) for 15 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f = 0.46$ for 3ia in 50% EtOAc–hexane) to afford product 3ia (46.2 mg; 64% yield) as white solids. Mp: 211–212 °C. Selected spectroscopic data for 3ia: IR (KBr): 3287, 3189, 3059, 3027, 2977, 2925, 2885, 1661, 1603, 1521, 1408, 1225, 1153, 963, 844, 790, 736, 697 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.18 (brs, 1 H), 9.64 (s, 1 H), 7.56 (d, $J = 8.0$ Hz, 1 H), 7.40 – 7.31 (m, 5 H), 7.30 – 7.24 (m, 1 H), 7.12 – 7.08 (m, 1 H), 7.02 – 6.97 (m, 2 H), 6.84 (dd, $J = 9.5$, 3.0 Hz, 1 H), 6.73 – 6.69 (m, 1 H), 6.67 – 6.62 (m, 1 H), 5.27 (s, 1 H), 4.60 (d, $J = 15.0$ Hz, 1 H), 4.35 (d, $J = 15.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 167.2 (C), 157.5 (d, $J = 234.4$ Hz, C), 138.7 (C), 137.5 (C), 132.3 (d, $J = 2.3$ Hz, C), 130.0 (d, $J = 10.5$ Hz, C), 129.5 (two CH), 128.6 (two CH), 128.2 (CH), 127.6 (C), 124.0 (CH), 122.7 (CH), 120.3 (CH), 120.2 (CH), 114.8 (d, $J = 8.8$ Hz, CH), 112.4 (CH), 111.6 (C), 109.4 (d, $J = 22.1$ Hz, CH), 103.3 (d, $J = 26.3$ Hz, CH), 60.0 (CH), 53.3 (CH$_2$); MS ($m$/z, relative intensity): 372 (M$^+$+1, 35), 371 (M$^+$, 100), 343 (15), 342 (35), 280 (44), 252 (36), 251 (28), 214 (42), 213 (32), 137 (50), 130 (46), 91 (76); exact mass calculated for C$_{23}$H$_{18}$FN$_3$O: 371.1434; found: 371.1437.

Preparation of 3-(1H-indol-3-yl)-4-propyl-3,4-dihydroquinoxalin-2(1H)-one (3ja):

```
\[
\begin{align*}
1j \quad & + \quad \text{cat. Ru(bpy)_3Cl_2 \cdot 6H_2O} \\
& \quad \text{CFL, O}_2 \\
& \quad \text{CH}_3\text{OH, rt, 16 h; 50%} \\
\rightarrow
\end{align*}
\]
```
To a solution of 1i (50 mg, 0.26 mmol) and indole (60.9 mg, 0.52 mmol, 2 equiv) in CH$_3$OH (5.2 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 16 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane ($R_f$ = 0.46 for 3ja in 40% EtOAc–hexane) to afford product 3ja (40.5 mg; 50% yield) as pale yellow solids. Mp: 189–190 °C. Selected spectroscopic data for 3ja: IR (KBr): 3290, 3184, 3056, 2960, 2926, 2869, 1660, 1507, 1430, 1245, 1099, 739 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.09 (brs, 1 H), 9.42 (s, 1 H), 7.68 ($J$ = 8.0 Hz, 1 H), 7.35 ($d$, $J$ = 8.0 Hz, 1 H), 7.08 (dd, $J$ = 8.0, 7.0 Hz, 1 H), 7.01 – 6.93 (m, 4 H), 6.81 ($d$, $J$ = 8.0 Hz, 1 H), 6.77 – 6.72 (m, 1 H), 5.27 (s, 1 H), 3.50 – 3.42 (m, 1 H), 3.16 – 3.08 (m, 1 H), 1.76 – 1.56 (m, 2 H), 0.94 ($t$, $J$ = 7.5 Hz, 3 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.6 (C), 137.6 (C), 135.9 (C), 128.3 (C), 127.5 (C), 124.3 (CH), 123.9 (CH), 123.7 (C), 122.6 (CH), 120.6 (CH), 120.1 (CH), 118.9 (CH), 115.9 (CH), 112.9 (CH), 112.2 (CH), 60.4 (CH), 51.0 (CH$_2$), 21.1 (CH$_2$), 11.7 (CH$_3$); MS (m/z, relative intensity): 306 (M$^+$+1, 23), 305 (M$, 100), 277 (29), 276 (87), 262 (17), 248 (24), 234 (16), 161 (13), 130 (52), 119 (64); exact mass calculated for C$_{19}$H$_{19}$N$_3$O: 305.1528; found: 305.1526.

Preparation of 4-(4-fluorobenzyl)-3-(1H-indol-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (3da):

$$\text{F} \quad \text{N} \quad \text{H} \quad \text{K} \quad \text{O}$$

$\text{1d}$  +  $\text{cat. Ru(bpy)$_3$Cl$_2$•6H$_2$O}$

$\text{CFL, O$_2$}$

$\text{CH}_3$OH, rt, 10 h; 71%

To a solution of 1d (50 mg, 0.19 mmol) and indole (46.8 mg, 0.4 mmol, 2 equiv) in CH$_3$OH (3.9 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 10 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 25% EtOAc–hexane ($R_f$ = 0.44 for 3da in 50% EtOAc–hexane) to afford product 3da (51.5 mg; 71% yield) as white solids. Mp: 227–228 °C. Selected spectroscopic data for 3da: IR (KBr): 3441, 3331, 3185, 3066, 2987, 2922, 2828, 1683, 1507, 1374, 1224, 1151, 1102, 828, 742 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 10.15 (brs, 1 H), 9.53 (s, 1 H), 7.56 ($d$, $J$ = 8.0 Hz, 1 H), 7.35 ($d$, $J$ = 8.0 Hz, 1 H), 7.08 (dd, $J$ = 8.0, 7.0 Hz, 1 H), 7.01 – 6.93 (m, 4 H), 6.81 ($d$, $J$ = 8.0 Hz, 1 H), 6.77 – 6.72 (m, 1 H), 5.27 (s, 1 H), 3.50 – 3.42 (m, 1 H), 3.16 – 3.08 (m, 1 H), 1.76 – 1.56 (m, 2 H), 0.94 ($t$, $J$ = 7.5 Hz, 3 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 166.6 (C), 137.6 (C), 135.9 (C), 128.3 (C), 127.5 (C), 124.3 (CH), 123.9 (CH), 123.7 (C), 122.6 (CH), 120.6 (CH), 120.1 (CH), 118.9 (CH), 115.9 (CH), 112.9 (CH), 112.2 (CH), 60.4 (CH), 51.0 (CH$_2$), 21.1 (CH$_2$), 11.7 (CH$_3$); MS (m/z, relative intensity): 306 (M$^+$+1, 23), 305 (M$, 100), 277 (29), 276 (87), 262 (17), 248 (24), 234 (16), 161 (13), 130 (52), 119 (64); exact mass calculated for C$_{19}$H$_{19}$N$_3$O: 305.1528; found: 305.1526.
Hz, 1 H), 7.43 – 7.36 (m, 3 H), 7.12 – 7.06 (m, 3 H), 7.02 – 6.95 (m, 3 H), 6.91 – 6.86 (m, 1 H),
6.81 – 6.77 (m, 1 H), 6.74 (d, J = 8.0 Hz, 1 H), 5.27 (s, 1 H), 4.64 (d, J = 15.0 Hz, 1 H), 4.34 (d, J =
15.0 Hz, 1 H); $^{13}$C NMR (125 MHz, acetone-$d_6$): $\delta$166.9 (C), 163.0 (d, J = 243.2 Hz, C), 137.6 (C),
135.6 (C), 135.0 (d, J = 3.1 Hz, C), 130.4 (d, J = 8.1 Hz, two CH), 128.8 (C), 127.6 (C), 124.2 (CH),
124.1 (CH), 122.7 (CH), 120.5 (CH), 120.2 (CH), 119.8 (CH), 116.1 (d, J = 21.5 Hz, two CH),
115.9 (CH), 114.0 (CH), 112.3 (CH), 112.0 (C), 60.2 (CH), 52.1 (CH$_2$); MS (m/z, relative intensity):
373 (M$^+$+2, 5), 372 (M$^+$+1, 37), 371 (M$^+$, 100), 342 (47), 262 (53), 234 (31), 233 (25), 214 (50),
213 (39), 130 (41), 119 (46), 109 (82), 92 (16); exact mass calculated for C$_{23}$H$_{18}$FN$_3$O: 371.1434; found: 371.1434.

Preparation of 3-(1H-indol-3-yl)-4-(4-methylbenzyl)-3,4-dihydroquinoxalin-2(1H)-one (3ea):

To a solution of 1e (50 mg, 0.20 mmol) and indole (44.5 mg, 0.4 mmol, 2 equiv) in CH$_3$OH
(3.8 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred
under an oxygen atmosphere at room temperature and irradiated with a household compact
florescence lamp (24 W) for 10 h until the completion of the reaction. The reaction mixture was
concentrated in vacuo to give a residue. The crude product was purified by flash column
chromatography with 25% EtOAc–hexane ($R_f$ = 0.40 for 3ea in 50% EtOAc–hexane) to afford
product 3ea (56.2 mg; 77% yield) as white solids. Mp: 218–220 °C. Selected spectroscopic data for
3ea: IR (KBr): 3254, 3179, 3038, 2974, 2897, 2851, 1655, 1503, 1415, 1415, 1195, 1109, 738 cm$^{-1}$;
$^1$H NMR (500 MHz, acetone-$d_6$): $\delta$ 10.14 (brs, 1 H), 9.51 (s, 1 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.37 (d,
J = 8.0 Hz, 1 H), 7.24 (d, J = 7.5 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.11 – 7.07 (m, 1 H), 7.01 –
6.95 (m, 3 H), 6.91 – 6.87 (m, 1 H), 6.80 – 6.75 (m, 2 H), 5.25 (s, 1 H), 4.62 (d, J = 15.5, 1 H), 4.27
(d, J = 15.5, 1 H), 2.31 (s, 3 H); $^{13}$C NMR (125 MHz, acetone-$d_6$): $\delta$ 166.9 (C), 137.6 (C), 137.5 (C),
136.0 (C), 135.7 (C), 130.1 (two CH), 128.7 (C), 128.6 (two CH), 127.6 (C), 124.2 (CH), 124.0 (CH),
122.6 (CH), 120.5 (CH), 120.1 (CH), 119.6 (CH), 115.9 (CH), 114.0 (CH), 112.3 (CH), 112.1 (C),
59.9 (CH), 52.4 (CH$_2$), 21.2 (CH$_3$); MS (m/z, relative intensity): 368 (M$^+$+1, 7), 367 (M$^+$, 26),
338 (6), 262 (10), 234 (8), 210 (8), 209 (9), 171 (43), 170 (100), 169 (55), 168 (23), 144 (22), 105
(24), 85 (19); exact mass calculated for C$_{24}$H$_{21}$N$_3$O: 367.1685; found: 367.1685.
Preparation of 4-benzyl-3-(1H-indol-3-yl)-3,4-dihydro-2H-benzo[b] [1,4]oxazin-2-one (3ka) and 9

To a solution of 1k (50 mg, 0.209 mmol) and indole (48 mg, 0.4 mmol, 2 equiv) in CH$_3$CN (4.1 mL) was added Ru(bpy)$_3$Cl$_2$•6H$_2$O (2.9 mg, 0.004 mmol, 0.02 equiv). The solution was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 48 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 15% EtOAc–hexane ($R_f$ = 0.38 for 3ka in 25% EtOAc–hexane) to afford product 3ka (32.6 mg; 44% yield) as gummy compound and 9 (10.5 mg; 20% yield; $R_f$ = 0.26 for 9 in 25% EtOAc–hexane) as brown color gummy compound.

Selected spectroscopic data for 3ka: IR (neat): 3416, 2963, 1748, 1613, 1501, 1260, 1095, 1020, 800, 744 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.08 (s, 1 H), 7.48 (d, $J = 8.0$ Hz, 1 H), 7.36 – 7.24 (m, 6 H), 7.18 (dd, $J = 7.5$, 7.5 Hz, 1 H), 7.10 (dd, $J = 7.5$, 7.5 Hz, 2 H), 7.05 (dd, $J = 8.0$, 7.5 Hz, 1 H), 6.89 (dd, $J = 8.0$, 7.5 Hz, 1 H), 6.80 (d, $J = 8.0$ Hz, 1 H), 6.71 (d, $J = 2.5$, 1 H), 5.38 (s, 1 H), 4.60 (d, $J = 14.5$ Hz, 1 H), 4.14 (d, $J = 14.5$ Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 164.5 (C), 141.9 (C), 136.1 (C), 135.8 (C), 134.2 (C), 128.8 (two CH), 127.80 (two CH), 127.78 (CH), 126.1 (C), 125.4 (CH), 122.8 (two CH), 120.5 (CH), 119.9 (CH), 119.2 (CH), 116.6 (CH), 113.9 (CH), 111.2 (CH), 108.8 (C), 55.9 (CH), 51.6 (CH$_2$); $^{12}$ MS ($m/z$, relative intensity): 355 (M$^+$+1, 9), 354 (M$^+$, 34), 338 (19), 326 (51), 276 (17), 235 (100), 196 (28), 157 (19), 129 (30), 119 (25), 91 (61); exact mass calculated for C$_{23}$H$_{18}$N$_2$O$_2$: 354.1368; found: 354.1371.

Selected spectroscopic data for 9: IR (neat): 3323, 2925, 2854, 1671, 1500, 1242, 1035, 753 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34 – 7.27 (m, 2 H), 7.26 – 7.21 (m, 3 H), 7.07 (dd, $J = 8.0$, 1.0 Hz, 1 H), 7.04 – 6.98 (m, 1 H), 6.97 – 6.89 (m, 2 H), 5.73 (s, 1 H), 5.27 (d, $J = 16.0$ Hz, 1 H), 5.06 (d, $J = 16.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.0 (C), 142.0 (C), 135.4 (C), 128.9 (two CH), 128.0 (C), 127.6 (CH), 126.5 (two CH), 124.5 (CH), 123.3 (CH), 118.2 (CH), 115.7 (CH), 90.6 (CH), 45.6 (CH$_2$); MS ($m/z$, relative intensity): 255 (M$^+$, 7), 226 (19), 148 (3), 136 (2), 111 (2), 91 (100); exact mass calculated for C$_{13}$H$_{13}$NO$_3$: 255.0895; found: 255.0893.

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Preparation of natural product cephalandole A (4ka):

To a solution of 3ka (50 mg, 0.14 mmol) in dry THF (1 mL) 10% Pd/C (10 mg) was added and
the reaction mixture was stirred under hydrogen atmosphere for 16 h, diluted with THF (1 mL)
added DDQ (32 mg, 0.14 mmol, 1.0 equiv) and stirred for 1 h under nitrogen atmosphere. The
reaction mixture was filtered through celite. The organic layer was concentrated in vacuo to give the
 crude residue. The crude product was purified by flash column chromatography with 10%
EtOAc–hexane (Rf = 0.45 for 4ka in 25% EtOAc–hexane) to afford compound 4ka (22.5 mg, 61%
yield) as yellow solid; Mp: 247–248 °C. Selected spectroscopic data for 4ka: IR (neat): 3297, 3052,
2959, 2923, 1718, 1605, 1531, 1238, 1103, 940, 742 cm\(^{-1}\); \(^1\)H NMR (500 MHz, acetone-d\(_6\)): δ
11.04 (brs, 1 H), 8.91 – 8.87 (m, 1 H), 8.82 (d, J = 3.5 Hz, 1 H), 7.88 (dd, J = 8.0, 1.5 Hz, 1 H),
7.59 – 7.55 (m, 1 H), 7.51 – 7.46 (m, 1 H), 7.45 – 7.40 (m, 1 H), 7.35 – 7.33 (m, 1 H), 7.31 – 7.25
(m, 2 H); \(^13\)C NMR (125 MHz, acetone-d\(_6\)): δ 153.1 (C), 149.1 (C), 146.3 (C), 138.0 (C), 134.7
(CH), 133.3 (C), 129.7 (CH), 129.0 (CH), 127.5 (C), 126.2 (CH), 124.3 (CH), 124.2 (CH), 122.6
(CH), 116.8 (CH), 112.8 (CH), 112.5 (C);\(^{13}\) MS (m/z, relative intensity): 263 (M\(^+\)+1, 9), 262 (M\(^+\),
52), 235 (17), 234 (100), 205 (13), 142 (15), 117 (7), 115 (11), 103 (4); exact mass calculated for
C\(_{16}\)H\(_{10}\)N\(_2\)O\(_2\): 262.0742; found: 262.0745.

Preparation of 5, 6 and 7

A solution of 1c (50 mg, 0.21 mmol) and Ru(bpy)\(_3\)Cl\(_2\)•6H\(_2\)O (2.9 mg, 0.004 mmol, 0.02 equiv)
in CH\(_3\)OH (4.1 mL) was stirred under an oxygen atmosphere at room temperature and irradiated

\(^{13}\) (a) Huo, C.; Dong, J.; Su, Y.; Tang, J.; Chen, F. Chem. Commun. 2016, 52, 13341–13344. (b) Mason, J. J.; Bergman,
with a household compact florescence lamp (24 W) for 5 h until the completion of the reaction. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f = 0.30$ for 5, and $R_f = 0.32$ for 6 in 50% EtOAc–hexane) to afford mixture of compounds 5 (14.1 mg; 26% yield) and 6 (30.1 mg, 53% yield) and 7 (7.1 mg, 13% yield; $R_f = 0.23$ in 50% EtOAc–hexane) as white solids.

For 5: mp, 137–138 °C; IR (KBr): 3304, 3187, 3039, 2922, 2854, 1664, 1510, 1385, 1312, 994, 964, 746, 700 cm$^{-1}$; $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ 9.60 (brs, 1 H), 7.41 (d, $J = 8.0$ Hz, 2 H), 7.33 (dd, $J = 7.5$, 7.5 Hz, 2 H), 7.26 (dd, $J = 7.5$, 7.5 Hz, 1 H), 7.00 (dd, $J = 8.0$, 1.5 Hz, 1 H), 6.89 – 6.84 (m, 1 H), 6.82 – 6.77 (m, 2 H), 5.53 (d, $J = 6.5$ Hz, 1 H), 5.16 (d, $J = 6.5$ Hz, 1 H), 4.81 (d, $J = 15.0$ Hz, 1 H), 4.59 (d, $J = 15.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 164.4 (C), 138.7 (C), 133.0 (C), 129.4, (two CH), 128.6 (two CH), 128.1 (CH), 127.8 (C), 123.7 (CH), 120.3 (CH), 115.9 (CH), 114.9 (CH), 82.1 (CH), 52.5 (CH$_2$); MS ($m/z$, relative intensity): 253 (M$^+$–1, 1), 238 (1), 208 (2), 178 (3), 167 (4), 149 (15), 136 (14), 105 (41), 101 (28), 77 (62), 58 (100); exact mass calculated for C$_{13}$H$_{14}$N$_2$O$_2$: 254.1055; found: 254.1058.

![Figure S1. ORTEP and Stereo plots for X-ray crystal structures of 5 (ic18595).](image)

CCDC 1816894 contains the supplementary crystallographic data for 5 (ic18595). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk
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For 6: yellow gummy compound; IR (neat): 3211, 3062, 2924, 2855, 1687, 1508, 1384, 1054, 922, 742, 697 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.76 (brs, 1 H), 7.37 – 7.21 (m, 5 H), 6.98 – 6.91 (m, 1 H), 6.87 – 6.77 (m, 3 H), 4.80 (d, \(J = 15.0\) Hz, 1 H), 4.74 (s, 1 H), 4.52 (d, \(J = 14.5\) Hz, 1 H), 3.37 (s, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 162.2 (C), 136.1 (C), 131.7 (C), 128.8 (two CH), 127.8 (two CH), 127.7 (CH), 124.9 (C), 124.1 (CH), 120.1 (CH), 115.5 (CH), 113.5 (CH), 87.9 (CH\(_3\)), 56.5 (CH), 52.6 (CH\(_2\)); MS (m/z, relative intensity): 269 (M\(^{+}\) + 1, 3), 268 (M\(^{+}\), 13), 237 (9), 209 (24), 208 (16), 146 (11), 118 (11), 91 (100); exact mass calculated for C\(_{16}\)H\(_{16}\)N\(_2\)O\(_2\): 268.1212; found: 268.1212.

For 7: mp: 268–269 °C; IR (neat): 3189, 3052, 2997, 2913, 2869, 2776, 1684, 1503, 1387, 1259, 882, 766 cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \(\delta\) 12.10 (brs, 1 H), 7.34 – 7.23 (m, 5 H), 7.21 – 7.16 (m, 2 H), 7.15 – 7.10 (m, 1 H), 7.08 – 7.04 (m, 1 H), 5.38 (s, 2 H); \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)): \(\delta\) 155.7 (C), 153.6 (C), 135.7 (C), 128.6 (two CH), 127.2 (CH), 126.6 (two CH), 126.3 (C), 125.9 (C), 123.6 (CH), 123.0 (CH), 115.7 (CH), 115.4 (CH), 45.5 (CH\(_2\)); MS (m/z, relative intensity): 253 (M\(^{+}\) + 1, 8), 252 (M\(^{+}\), 47), 235 (2), 224 (2), 195 (2), 161 (2), 146 (3), 133 (6), 119 (3), 106 (3), 92 (10), 91 (100); exact mass calculated for C\(_{15}\)H\(_{12}\)N\(_2\)O\(_2\): 252.0899; found: 252.0898.

**Figure S1.** ORTEP and Stereo plots for X-ray crystal structures of 7 (ic18614).

CCDC 1816895 contains the supplementary crystallographic data for 7 (ic18614). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

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Table S1. Crystal data and structure refinement for 7 (ic18614).

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Preparation of 3-(1H-indol-3-yl)quinoxalin-2(1H)-one

A solution of 1a (50 mg, 0.338 mmol), indole (77.3 mg, 0.66 mmol, 2 equiv) and Ru(bpy)₃Cl₂•6H₂O (4.5 mg, 0.007 mmol, 0.02 equiv) in CH₃OH (6.7 mL) was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp (24 W) for 2 until the completion of the reaction, as monitored by TLC. 1a was completely converted into 8 with trace amounts of 4aa, determined by crude ¹H-NMR of reaction mixture. The reaction was continued to for 5 days until 8 was converted into 4aa monitored by the TLC. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane (Rf = 0.33 for 4aa in 50% EtOAc–hexane) to afford compound 4aa (57.3 mg, 65% yield) as yellow solids. Mp: 332–334 °C. Selected spectroscopic data for 4aa: ¹H NMR (500 MHz, DMSO-d₆): δ 12.39 (brs, 1 H), 11.77 (brs, 1 H), 8.94 (s, 1 H), 8.89 – 8.85 (m, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.53 – 7.49 (m, 1 H), 7.45 – 7.40 (m, 1 H), 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2 H), ¹³C NMR (125 MHz, DMSO-d₆): δ 154.4 (C), 151.9 (C), 136.2 (C), 133.0 (CH), 132.6 (C), 130.1 (C), 127.9 (CH), 127.5 (CH), 126.1 (C), 123.2 (CH), 122.9 (CH), 122.5 (CH), 120.9 (CH), 114.9 (CH), 111.8 (CH), 111.3 (C).¹⁵

Preparation of quinoxalin-2(1H)-one (8)

A solution of 1a (50 mg, 0.338 mmol), indole (77.3 mg, 0.66 mmol, 2 equiv) and Ru(bpy)₃Cl₂•6H₂O (4.5 mg, 0.007 mmol, 0.02 equiv) in CH₃OH (6.7 mL) was stirred under an oxygen atmosphere at room temperature and irradiated with a household compact florescence lamp

(24 W) for 2 until the completion of the reaction, as monitored by TLC. The reaction mixture was concentrated in vacuo to give a residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane ($R_f = 0.31$ for $8$ in 50% EtOAc–hexane) to afford compound $8$ (34.9 mg, 71% yield) as yellow solids and trace amount of $4aa$ (around 1 mg). For $8$: mp, 261–263 °C; $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 12.41 (brs, 1 H), 8.16 (s, 1 H), 7.77 (d, $J = 7.5$ Hz, 1 H), 7.56 – 7.52 (m, 1 H), 7.32 – 7.27 (m, 2 H), $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 154.9 (C), 151.6 (CH), 132.0 (C), 131.8 (C), 130.7 (CH), 128.7 (CH), 123.2 (CH), 115.7 (CH).$^{16}$

Fig S48. 1H NMR (CDCl₃, 500 MHz) of compound 1a
Fig S49. 13C NMR (CDCl3, 125 MHz) of compound 1a
Fig S50. DEPT of compound 1a
Fig S51. 1H NMR (acetone-d6, 400 MHz) of compound 1b

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Fig S52. 13C NMR (acetone-d6, 100 MHz) of compound 1b
Fig S53. DEPT of compound 1b

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Fig S54. 1H NMR (CDCl3, 500 MHz) of compound 1c
Fig S55. 13C NMR (CDCl3, 125 MHz) of compound 1c
Fig S56. DEPT of compound 1c
Fig S57. 1H NMR (CDCl3, 500 MHz) of compound 1d
Fig S58. 1H NMR (CDCl3, 125 MHz) of compound 1d
Fig S59. DEPT of compound 1d

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Fig S60. 1H NMR (CDCl3, 500 MHz) of compound 1e
Fig S61. 13C NMR (CDCl3, 500 MHz) of compound 1e
Fig S62. DEPT of compound 1e
Fig S63. 1H NMR (acetone-d6, 500 MHz) of compound 1f
Fig S64. 1H NMR (CDCl3, 500 MHz) of compound 1g
Fig S65. 13C NMR (CDCl3, 125 MHz) of compound 1g
Fig S66. DEPT of compound 1g
Fig S67. 1H NMR (acetone-d6, 500 MHz) of compound 1h
Fig S68. 13C NMR (acetone-d6, 125 MHz) of compound 1h
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**Fig S69. DEPT of compound 1h**

![NMR spectrum graph](graph.png)
Fig S70. 1H NMR (CDCl3, 500 MHz) of compound 1i
Fig S73. 1H NMR (CDCl3, 500 MHz) of compound 1j
Fig S74. 13C NMR (CDCl3, 125 MHz) of compound 1j
Fig S75. DEPT of compound 1j
Fig S76. 1H NMR (CDCl3, 500 MHz) of compound 1k
Fig S77. 13C NMR (CDCl3, 125 MHz) of compound 1k
Fig S78. DEPT of compound 1k
Fig S79. 1H NMR (acetone-d6, 500 MHz) of compound 3ca
Fig S80. 13C NMR (acetone-d6, 125 MHz) of compound 3ca
Fig S81. DEPT of compound 3ca
Fig S82. 1H NMR (DMSO-d6, 500 MHz) of compound 3cb
Fig S83. 13C NMR (DMSO-d6, 125 MHz) of compound 3cb
Fig S84, DEPT of compound 3cb
Fig S85. 1H NMR (DMSO-d6, 500 MHz) of compound 3cc
Fig S86. 13C NMR (DMSO-d6, 125 MHz) of compound 3cc
Fig S87. DEPT of compound 3cc

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Fig S88. 1H NMR (acetone-d6, 500 MHz) of compound 3cd
Fig S89. 13C NMR (acetone-d6, 125 MHz) of compound 3cd
Fig S90. DEPT of compound 3cd
Fig S91. HSQC of compound 3cd
Fig S92. COSY of compound 3cd
Fig S93. NOESY of compound 3cd
Fig S94. 1H NMR (acetone-d6, 500 MHz) of compound 3ce
Fig S95. 13C NMR (acetone-d6 125 MHz) of compound 3ce
Fig S96. DEPT of compound 3ce
Fig S97. 1H NMR (DMSO-d6, 500 MHz) of compound 3cf
Fig S98. 13C NMR (DMSO-d6, 125 MHz) of compound 3cf
Fig S99. DEPT of compound 3cf
Fig S100. HSQC of compound 3cf
Fig S101. COSY of compound 3cf
Fig S102. NOESY of compound 3cf
Fig S103. 1H NMR (acetone-d6, 500 MHz) of compound 3cg
Fig S104. 13C NMR (acetone-d6, 125 MHz) of compound 3cg
Fig S105. DEPT of compound 3cg
Fig S106. HSQC of compound 3cg
Fig S107. COSY of compound 3cg
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Fig S108. NOESY of compound 3cg
Fig S109. 1H NMR (acetone-d6, 500 MHz) of compound 3ch
Fig S110. 13C NMR (acetone-d6, 125 MHz) of compound 3ch
Fig S111. DEPT of compound 3ch
Fig S112. 1H NMR (acetone-d6, 500 MHz) of compound 3ci
Fig S113. 13C NMR (acetone-d6, 125 MHz) of compound 3ci
Fig S114. DEPT of compound 3ci
Fig S115. HSQC of compound 3ci
Fig S116. COSY of compound 3ci
Fig S117. NOESY of compound 3ci
Fig S118. 1H NMR (DMSO-d6, 500 MHz) of compound 3cj
Fig S119. 13C NMR (DMSO-d6, 125 MHz) of compound 3cj
Fig S120. DEPT of compound 3cj
Fig S121. 1H NMR (acetone-d6, 500 MHz) of compound 3ck
Fig S122. 13C NMR (acetone-d6, 125 MHz) of compound 3ck
Fig S123. DEPT of compound 3ck
Fig S124. 1H NMR (DMSO-d6, 500 MHz) of compound 3cl
Fig S125. 13C NMR (DMSO-d6, 125 MHz) of compound 3cl
Fig S126. DEPT of compound 3cl
Fig S127. 1H NMR (acetone-d6, 500 MHz) of compound 3cm
**Fig S128.** 13C NMR (acetone-d6, 125 MHz) of compound 3cm
Fig S129. DEPT of compound 3cm
Fig S130. 1H NMR (acetone-d6, 500 MHz) of compound 3cn
Fig S131. 13C NMR (acetone-d6, 125 MHz) of compound 3cn
Fig S132. DEPT of compound 3cn
Fig S133. HSQC of compound 3cn
Fig S134. COSY of compound 3cn
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Fig S136. 1H NMR (DMSO-d6, 500 MHz) of compound 3co
Fig S137. 13C NMR (DMSO-d6, 125 MHz) of compound 3co
Fig S138. DEPT of compound 3co
Fig S139. HSQC of compound 3co
Fig S140. COSY of compound 3co
Fig S141. NOESY of compound 3co
Fig S142. 1H NMR (acetone-d6, 500 MHz) of compound 3cp
Fig S143. 13C NMR (acetone-d6, 125 MHz) of compound 3cp
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Fig S145. HSQC of compound 3cp
Fig S146. COSY of compound 3cp
Fig S147. NOESY of compound 3cp
Fig S148. 1H NMR (acetone-d6, 500 MHz) of compound 3cq
Fig S149. 13C NMR (acetone-d6, 125 MHz) of compound 3cq
Fig S150. DEPT of compound 3cq
Fig S151. 1H NMR (DMSO-d6, 500 MHz) of compound 3cr
Fig S152. 13C NMR (DMSO-d6, 125 MHz) of compound 3cr
Fig S153. DEPT of compound 3cr
Fig S154. 1H NMR (DMSO-d6, 500 MHz) of compound 3cs
Fig S155. 13C NMR (DMSO-d6, 125 MHz) of compound 3cs
Fig S156. DEPT of compound 3cs
Fig S157. HSQC of compound 3cs
Fig S158. COSY of compound 3cs
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Fig S160. 1H NMR (acetone-d6, 500 MHz) of compound 3ct
Fig S161. 13C NMR (acetone-d6, 125 MHz) of compound 3ct
Fig S162. DEPT of compound 3ct
Fig S163. 1H NMR (CDCl3, 500 MHz) of compound 3cu-o
Fig S164. 13C NMR (CDCl3, 125 MHz) of compound 3cu-o
Fig S165. DEPT of compound 3cu-o
Fig S166. 1H NMR (DMSO-d6, 500 MHz) of compound 3cu-p
Fig S167. 13C NMR (DMSO-d6, 125 MHz) of compound 3cu-p
Fig S168. DEPT of compound 3cu-p
Fig S169. HSQC of compound 3cu-p
Fig S170. COSY of compound 3cu-p
Fig S171. NOESY of compound 3cu-p
Fig S172. 1H NMR (CDCl3, 500 MHz) of compound 3cv-1
Fig S173. 13C NMR (CDCl3, 125 MHz) of compound 3cv-1
Fig S174. DEPT of compound 3cv-1
Fig S175. HSQC of compound 3cv-1
Fig S176. COSY of compound 3cv-1
Fig S177. NOESY of compound 3cv-1
Fig S178. 1H NMR (CDCl3, 500 MHz) of compound 3cv-2
Fig S179. 13C NMR (CDCl3, 125 MHz) of compound 3cv-2
Fig S180. DEPT of compound 3cv-2
Fig S181. HSQC of compound 3cv-2
Fig S182. COSY of compound 3cv-2
Fig S183. NOESY of compound 3cv-2
Fig S184. 1H NMR (CDCl₃, 400 MHz) of compound 3cw

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SP01  400.1324008 MHz
NUC1  1H
P1  14.50 usec
PLW1  12.50000000 W

F2 - Processing parameters
SI  16384
SF  400.1300241 MHz
WDW  EM
SSB  0
LB  0 Hz
GB  0
PC  1.00
Fig S185. 13C NMR (CDCl3, 100 MHz) of compound 3cw

Current Data Parameters
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EXPNO 2
PROCNO 1

FZ - Acquisition Parameters
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Time_ 16:16
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PULPROG zgq90
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SOLVENT CDCl3
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FIDRES 0.383387 Hz
AQ 1.3042164 sec
AG 256
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DE 6.50 usec
TE 300.0 K
DI 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

************ CHANNEL f1 ************
NUC1 13C
P1 10.20 usec
PL1 0.00 dB
SF01 100.627995 MHz

************ CHANNEL f2 ************
CPU6216
NUC2 1H
PCP02 90.00 usec
PL2 -3.00 dB
PL12 14.50 dB
PL13 17.50 dB
SF02 400.132608 MHz

F2 - Processing parameters
SI 32768
SF 100.6127723 MHz
WDM EM
SSB 0
LB 0.30 Hz
GB 0
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ID NMR plot parameters
C1 20.00 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P 0.000 ppm
F2 0.00 Hz
PRMCM 11.00000 ppm/cm
HZCM 1106.74048 Hz/cm
Fig S186. DEPT of compound 3cw

Current Data Parameters
NAME APS-01-201
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170315
Time 16:16
INSTRUM spect
PROB HD 5 mm QNP 1H
FULLPROG 2pg30
TD 65536
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NS 376
DS 4
SMH 25125.629 Hz
FIDRES 0.383387 Hz
AG 1.3042164 sec
AG 256
DM 19.900 usec
DE 6.50 usec
TE 360.0 x
D1 2.00000000 sec
d11 0.30000000 sec
d12 0.00000000 sec

********** CHANNEL 11 **********
NUC1 13C
P1 10.20 usec
PL1 0.00 dB
SF01 100.6237959 MHz

********** CHANNEL 12 **********
CPDPRG2 waltz16
NUC2 1H
PSD02 30.00 usec
PL2 -3.00 dB
PL12 14.50 dB
PL13 17.50 dB
SF02 400.1326008 MHz

F2 - Processing parameters
S1 32768
SF 100.6127723 MHz
WDW DM
SSB 0
LB 0.30 Hz
OB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FIP 220.000 ppm
F1 22134.81 Hz
F2P 0.00 ppm
F2 0.00 Hz
PPMC 11.00000 ppm/cm
HZCM 1106.7404B Hz/cm
Fig S187. 1H NMR (CDCl3, 400 MHz) of compound 3cx
Fig S188. 13C NMR (CDCl3, 100 MHz) of compound 3cx

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| ************** CHANNEL f1 ************** |
| NUC1                      | 13C                      |
| P1                        | 10.20 usec               |
| PL1                       | 0.00 dB                  |
| SF01                      | 100.6237952 MHz          |

| ************** CHANNEL f2 ************** |
| COPROG2                   | watt;16                  |
| NUC2                      | 1H                      |
| PCP02                     | 90.00 usec               |
| PL2                       | -3.00 dB                 |
| PL12                      | 14.50 dB                 |
| PL13                      | 17.50 dB                 |
| SF02                      | 400.1326008 MHz          |

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Fig S190. 1H NMR (acetone-d6, 500 MHz) of compound 3da
Fig S191. 13C NMR (acetone-d6, 125 MHz) of compound 3da
Fig S192. DEPT of compound 3da
Fig S193. 1H NMR (acetone-d6, 500 MHz) of compound 3ea
Fig S194. 13C NMR (acetone-d6, 125 MHz) of compound 3ea
Fig S196. HSQC of compound 3ea
Fig S197. COSY of compound 3ea
Fig S198. NOESY of compound 3ea
Fig S199. 1H NMR (acetone-d₆, 500 MHz) of compound 3ga
Fig S200. 13C NMR (acetone-d6, 125 MHz) of compound 3ga
Fig S201. DEPT of compound 3ga
Fig S202. 1H NMR (acetone-d6, 500 MHz) of compound 3ia
Fig S203. 13C NMR (acetone-d6, 125 MHz) of compound 3ia
Fig S204. DEPT of compound 3ia
Fig S205. 1H NMR (acetone-d6, 500 MHz) of compound 3ja
Fig S206. 13C NMR (acetone-d6, 125 MHz) of compound 3ja
Fig S207. DEPT of compound 3ja
Fig S208. 1H NMR (CDCl₃, 500 MHz) of compound 3ka
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<th>13C NMR (CDCl3, 125 MHz) of compound 3ka</th>
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Figure S209: 13C NMR (CDCl3, 125 MHz) of compound 3ka
Fig S210. DEPT of compound 3ka
Fig S211. HSQC of compound 3ka
Fig S212. COSY of compound 3ka
Fig S213. NOESY of compound 3ka
Fig S214. 1H NMR (DMSO-d6, 500 MHz) of compound 4aa
Fig S215. 13C NMR (DMSO-d6, 125 MHz) of compound 4aa
Fig S217. HSQC of compound 4aa
Fig S218. COSY of compound 4aa
Fig S219. NOESY of compound 4aa
Fig S220. 1H NMR (acetone-d6, 500 MHz) of compound 4ka
Fig. S221. 13C NMR (acetone-d6, 125 MHz) of compound 4ka
Fig S222. DEPT of compound 4ka
Fig S223. HSQC of compound 4ka
Fig S224. COSY of compound 4ka
Fig S225. NOESY of compound 4ka
Fig S226. 1H NMR (acetone-d6, 500 MHz) of compound 5
Fig S227. 13C NMR (acetone-d6, 125 MHz) of compound 5
Fig S228. DEPT of compound 5
Fig S229. 1H NMR (CDCl3, 500 MHz) of compound 6
Fig S230. 13C NMR (CDCl3, 125 MHz) of compound 6
Fig S231. DEPT of compound 6
Fig S232. 1H NMR (DMSO-d6, 500 MHz) of compound 7
Fig S233. 13C NMR (DMSO-d6, 125 MHz) of compound 7
Fig S234. DEPT of compound 7
Fig S235. HSQC of compound 7
Fig S236. COSY of compound 7
Fig S237. NOESY of compound 7
Fig S238. 1H NMR (DMSO-d6, 500 MHz) of compound 8
Fig S239. 13C NMR (DMSO-d6, 125 MHz) of compound 8
Fig S240. DEPT of compound 8
Fig S241. 1H NMR (CDCl₃, 500 MHz) of compound 9
Fig S242. 13C NMR (CDCl3, 125 MHz) of compound 9
Fig S243. DEPT of compound 9
Fig S244. 1H NMR (CDCl₃, 500 MHz) of compound APS-135
Fig S245. 13C NMR (CDCl3, 125 MHz) of compound APS-135
Fig S246. DEPT of compound APS-135