Supporting Information

Divergent C(sp²)-H Arylation of Heterocycles *via* Organic Photoredox Catalysis

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Table of Contents

1.	General Information	S2
2.	General procedure for the synthesis of starting materials	S2
3.	Typical Catalytic Procedure	
4.	Characterization of the Products	S5
5.	Gram-scale Reaction	S19
6.	Mechanism Studies	S20
7.	X-Ray Crystallographic Data of 3	
8.	References	S24
9.	Copies of NMR Spectra	S26

1. General Information

Unless otherwise noted, the reagents were purchased from commercial suppliers and used without additional purification. Melting points were measured on a microscopic apparatus and were uncorrected. X-ray analysis was performed with a single-crystal X-ray diffractometer (Gemini E) from Agilent. High resolution mass spectra (HRMS) were obtained on an Agilent LC- MSD- Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). Gas Chromatograph Mass Spectrometer (GC-MS) was performed with DSQ II from Thermo. The UV/VIS Absorption spectra were recorded using a Perkin Elmer Lambda 35 Spectrometer and a Cary 5000 UV-VIS-NIR spectrometer. The Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer in EtOH. The Cyclic voltammetry (CV) was recorded in CH₃CN by CHI660E. Silica gel was purchased from Qingdao Marine Chemical Co. Column chromatography was undertaken on silica gel (200-300 mesh) using a proper eluent system. ¹H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) spectrometer in deuterated chloroform or deuterated dimethyl sulfoxide. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet), dt (doublet and triplet), td (triplet and doublet). Coupling constants (*J*) are reported in hertz (Hz). ¹³C NMR spectra were recorded at 100 MHz on Bruker DPX-400. ¹⁹F NMR spectra were recorded using a 376 MHz spectrometer. The reactions were performed with photoreaction apparatus (SSSTECH-LAL1CV1.0) from Shanghai 3S Technology Co., Ltd. The start materials, including quinoxalin-2(1H)-ones^[1], coumarins^[2], imidazopyridines^[3] and iodonium ylides^[4] were prepared according to literatures.

2. General procedure for the synthesis of starting materials

Synthesis of quinoxalin-2(1H)-ones^[1]

Procedure A:



To a 50 mL round-bottom flask, the starting material 2-quinoxalinone (5 mmol) was added into DMF (20 mL), and then the corresponding halide (1.6 equiv.) and potassium carbonate (1.2 equiv.) were added into the reaction mixture and stirred at room temperature overnight.

When TLC analysis indicated that the 2-quinoxalinone disappeared, the water (10 mL) was added to the reaction mixture, and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water (5-9 times), dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain product **3S-15S**.

Procedure B:



A 200 mL two-necked round-bottomed flask was equipped with a magnetic stirrer bar, a rubber septum, and an argon balloon. S1 (4.0 mmol) was dissolved in Et₂O (25 mL), and NaH (60% in oil; 10.2 mmol) was added. The mixture was stirred for 1 h at room temperature, then benzoyl chloride (6.0 mmol) was added. The mixture was stirred at room temperature for 14 h. The reaction mixture was poured into H₂O and extracted CH_2Cl_2 . The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed in vacuum, and the product was purified by silica gel column chromatography.

Procedure C:



To ethanol (20 ml) suspension solution of o-arylenediamine (S3, 5 mmol) was added Ethyl 2oxoacetate (S4, 1.1 equiv.). The reaction solvent was stirred and heated to reflux for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with cooled ethanol, and finally dried to give the product 16S-17S.

Synthesis of coumarins^[2]

Procedure A:



A mixture of phenol derivatives (10.0 mmol), trifluoromethanesulfonic acid (10.0 mmol) and propiolic acid (5.0 mmol) in PhCl (25 mL) was stirred at 100 °C for 1 h. After completion of reaction as indicated by TLC, the reaction mixture was poured into H₂O, neutralized with NaHCO₃ solution and extracted CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed in vacuum, and the products were purified by silica gel column chromatography to give the desired product **20S**.

Procedure B:



A mixture of 7-hydroxycoumarin (486.4 mg, 3.0 mmol), alkyl or aryl halide (6.0 mmol), and potassium carbonate (1.24 g, 9.0 mmol) in DMF (20 mL) was stirred at various temperatures (from 30 to 85 °C) for times ranging from 1 h to overnight. The reaction mixture was extracted with ethyl acetate, and the combined extracts were washed with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue then was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to yield the products **21S-22S**.

Synthesis of imidazopyridines^[3]



An oven-dried flask was charged with 2-aminopyridines (13 mmol), the corresponding α -bromo-ketones (10 mmol), NaHCO₃ (15 mmol), and EtOH (20 mL). The mixture was stirred at 80 °C under air for 3-4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and 15 mL water was added to the mixture, then extracted by EtOAc for 3 times (3×30 mL). The combined extracts were washed with brine, dried over Na₂SO₄, and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel with petroleum ether/EtOAc (3/1) as eluent to afford pure product **238-278**.

Synthesis of iodonium ylides^[4]



To a solution of iodobenzene derivative in acetic acid was added MCPBA (1.1 equiv). The mixture was stirred at rt for 24 hours. After the reaction, water was added to the mixture, and product was extracted with chloroform. After being dried over Na₂SO₄, filtration, and removal of the solvent, diethyl ether and hexane were added to the residue to product **S10**.



Taken in a 100 mL round bottom flask fitted with a magnetic stirrer, added solution of cyclic 1,3-dione (1.0 equiv) in 30 mL methanol at room temperature added 20 mL of 10% aqueous solution of KOH followed by addition of diacetoxy iodobenzene (1.2 equiv) in 40 mL

methanol. The reaction mixture was stirred for 2 h at room temperature and then quenched with ice cold water. The resulting white precipitate was filtered and mother solution was extracted with dichloromethane, then washed with water three times, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resultant white solid was mixed with the first crop and the mixture recrystallized from DCM/Hexane the compound **38S-47S** was obtained.

3. Typical Catalytic Procedure



Under N₂ atmosphere, a Schlenk tube (15 mL) equipped with a magnetic stirrer bar was charged with quinoxalin-2(1H)-one **1a** (0.1 mmol) and iodonium ylide **2a** (0.15 mmol), EosinY (2 mol %) and K₂CO₃ in DMSO (2 mL). The reaction mixture was stirred and irradiated by the 12W blue LED at room temperature for 12 h. When the reaction was completed, the reaction mixture was added water (10 mL) and extracted with ethyl acetate (5 mL×3). The combined organic phase was dried over Na₂SO₄. The resulting crude residue was purified by column chromatography on silica gel (elute: EtOAc /petroleum ether) to give the desired product **3**.



Figure 1. Reactor

4. Characterization of the Products



1-methyl-3-phenylquinoxalin-2(1H)-one (3) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 89% (21.0 mg); mp: 142.5-144.7 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.32-8.29 (m, 2 H), 7.92 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.54 (t, *J* = 7.9 Hz, 1 H), 7.47 (t, *J* = 3.3 Hz, 3 H), 7.32 (m, 2 H), 3.74 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.7, 154.1, 136.1, 133.4, 133.1, 130.5, 130.3, 130.3, 129.6, 128.1, 113.6, 29.3 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₃N₂O [M+H]⁺, 237.1022. Found: m/z 237.1022.



1-ethyl-3-phenylquinoxalin-2(1H)-one (4) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 84% (21.0 mg); mp: 149.9-151.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.33-8.30 (m, 2 H), 7.96 (dd, J = 8.4 Hz, J = 1.6 Hz, 1 H), 7.57 (td, J = 8.5 Hz, J = 1.5 Hz, 1 H), 7.50-7.47 (m, 3 H), 7.38-7.34 (m, 2 H), 4.40 (q, J = 7.2 Hz, 2 H), 1.43 (t, J = 7.3 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.2, 154.2, 136.1, 133.5, 132.3, 130.8, 130.3, 129.6, 128.1, 123.5, 113.4, 37.6, 12.4 ppm; HRMS (ESI): m/z calcd for C₁₆H₁₅N₂O [M+H]⁺, 251.1179. Found: m/z 251.1179.



1-octyl-3-phenylquinoxalin-2(1H)-one (5) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 78% (26.1 mg); mp: 96.7-98.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.33-8.30 (m, 2 H), 7.95 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.47 (t, *J* = 3.5 Hz, 3 H), 7.37-7.32 (m, 2 H), 4.30 (t, *J* = 7.8 Hz, 2 H), 1.84-1.76 (m, 2 H), 1.52-1.45 (m, 2 H), 1.40-1.28 (m, 9 H), 0.88 (t, *J* = 6.5 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.4, 154.2, 136.1, 133.4, 132.6, 130.7, 130.3, 130.2, 129.6, 128.1, 123.5, 113.6, 42.7, 31.8, 29.3, 29.2, 27.3, 27.1, 22.6, 14.1 ppm; HRMS (ESI): m/z calcd for C₂₂H₂₇N₂O [M+H]⁺, 335.2118. Found: m/z 335.2119.



1-(cyclohexylmethyl)-3-phenylquinoxalin-2(1H)-one (6) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 90% (28.6 mg); mp: 99.6-101.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.32-8.29 (m, 2 H), 7.95 (d, *J* = 6.5 Hz, 1 H), 7.54 (td, *J* = 8.4 Hz, *J* = 1.4 Hz, 1 H), 7.47 (t, *J* = 3.6 Hz, 3 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 4.22 (d, *J* = 7.0 Hz, 2 H), 1.96 (s, 1 H), 1.74-1.62 (m, 6 H), 1.22-1.18 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 154.2, 136.2, 133.4, 133.1, 130.7, 130.3, 130.1, 129.6, 128.1, 123.5, 114.1, 48.3, 36.6, 31.0, 26.2, 25.9 ppm; HRMS (ESI): m/z calcd for C₂₁H₂₃N₂O [M+H]⁺, 319.1805. Found: m/z 319.1805.



1,3-diphenylquinoxalin-2(1H)-one (7) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 81% (24.1 mg); mp: 197.2-198.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.41-8.39 (m, 2 H), 8.00-7.98 (m, 1 H), 7.64 (t, *J* = 7.8 Hz, 2 H), 7.57 (t, *J* = 3.6 Hz, 1 H), 7.48-7.46 (m, 3 H), 7.36-7.34 (m, 4 H), 6.70-6.68 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.6, 154.5, 136.1, 135.8, 134.2, 133.0, 130.5, 130.3, 130.1, 130.0, 129.7, 129.4, 128.3, 128.0, 123.9, 115.4 ppm; HRMS (ESI): m/z calcd for C₂₀H₁₅N₂O [M+H]⁺, 299.1179. Found: m/z 299.1178.



1-(4-methylbenzyl)-3-phenylquinoxalin-2(1H)-one (8) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 84% (27.4 mg); mp: 107.8-109.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.37-8.35 (m, 2 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 3.5 Hz, 3 H), 7.46-7.42 (m, 1 H), 7.32 (t, *J* = 6.8 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 5.53 (s, 2 H), 2.30 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.3, 137.4, 136.1, 133.4, 132.8, 132.4, 130.6, 130.4, 130.3, 129.7, 129.6, 128.1, 127.0, 123.8, 114.4, 45.9, 21.1 ppm; HRMS (ESI): m/z calcd for C₂₂H₁₉N₂O [M+H]⁺, 327.1492. Found: m/z 327.1491.



1-(2-oxo-2-phenylethyl)-3-phenylquinoxalin-2(1H)-one (9) was purified by flash silica

chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 61% (20.7 mg); mp: 199.1-200.5 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34-8.32 (m, 2 H), 8.11 (d, *J* = 7.4 Hz, 2 H), 7.99 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.56 (t, *J* = 7.8 Hz, 2 H), 7.49-7.45 (m, 4 H), 7.36 (t, *J* = 7.3 Hz, 1 H), 6.99 (d, *J* = 8.3 Hz, 1 H), 5.80 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 191.2, 154.5, 153.9. 135.9, 134.6, 134.3, 133.3, 132.8, 130.8, 130.4, 130.4, 129.6, 129.1, 128.2, 128.1, 123.9, 113.4, 48.7 ppm; HRMS (ESI): m/z calcd for C₂₂H₁₇N₂O₂ [M+H]⁺, 341.1285. Found: m/z 341.1284.



1-(naphthalen-2-ylmethyl)-3-phenylquinoxalin-2(1H)-one (10) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 88% (31.8 mg); mp: 177.5-179.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.43-8.40 (m, 2 H), 8.15 (d, J = 8.4 Hz, 1 H), 8.02-7.99 (m, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.65 (td, J = 7.0 Hz, J = 1.1 Hz, 1 H), 7.58 (t, J = 7.9 Hz, 1 H), 7.50 (t, J = 3.3 Hz, 3 H), 7.34-7.32 (m, 2 H), 7.28 (t, J = 7.5 Hz, 1 H), 7.04-7.01 (m, 1 H), 6.86 (d, J = 6.8 Hz, 1 H), 6.02 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.1, 136.0, 133.9, 133.4, 132.9, 130.5, 130.5, 130.4, 129.7, 129.5, 129.2, 128.2, 128.1, 126.7, 126.1, 125.5, 123.9, 122.4, 122.2, 114.7, 44.0 ppm; HRMS (ESI): m/z calcd for C₂₅H₁₉N₂O [M+H]⁺, 363.1492. Found: m/z 363.1492.



ethyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate (11) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 83% (25.6 mg); mp: 117.8-119.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34-8.31 (m, 2 H), 7.97 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.56-7.47 (m, 4 H), 7.40-7.36 (m, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 5.09 (s, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 154.3, 153.9, 135.8, 133.2, 132.6, 130.8, 130.5, 130.5, 129.6, 128.1, 124.1, 113.0, 62.1, 43.8, 14.1 ppm; HRMS (ESI): m/z calcd for C₁₈H₁₇N₂O₃ [M+Na]⁺, 331.1053. Found: m/z 331.1053.



tert-butyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate (12) was purified by flash silica

chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 78% (26.2 mg); mp: 116.5-118.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.33-8.30 (m, 2 H), 7.96 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.55-7.47 (m, 4 H), 7.38-7.34 (m, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 5.00 (s, 2 H), 1.47 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 154.3, 154.0, 135.8, 133.2, 132.6, 130.8, 130.4, 130.4, 129.6, 128.1, 123.9, 113.1, 83.2, 44.4, 28.0 ppm; HRMS (ESI): m/z calcd for C₂₀H₂₁N₂O₃ [M+H]⁺, 337.1547. Found: m/z 337.1546.



benzyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate (13) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 74% (27.4 mg); mp: 163.7-165.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.33-8.30 (m, 2 H), 7.97 (dd, J = 8.0 Hz, J = 1.4 Hz, 1 H), 7.51-7.47 (m, 4 H), 7.39-7.29 (m, 6 H), 7.06 (d, J = 7.8 Hz, 1 H), 5.24 (s, 2 H), 5.15 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 154.3, 153.9, 135.7, 134.9, 133.2, 132.5, 130.8, 130.5, 130.5, 129.6, 128.7, 128.6, 128.4, 128.1, 124.1, 113.0, 67.7, 43.8 ppm; HRMS (ESI): m/z calcd for C₂₃H₁₉N₂O₃ [M+H]⁺, 371.1390. Found: m/z 371.1389.



1-allyl-3-phenylquinoxalin-2(1H)-one (14) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 82% (21.5 mg); mp: 68.5-70.3 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34-8.32 (m, 2 H), 7.96 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.56-7.51 (m, 1 H), 7.48 (t, *J* = 3.3 Hz, 3 H), 7.38-7.34 (m, 1 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 6.04-5.94 (m, 1 H), 5.26 (q, *J* = 10.5 Hz, 2 H), 4.99-4.97 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.3, 154.2, 136.0, 133.3, 132.6, 130.7, 130.6, 130.4, 130.2, 129.6, 128.1, 123.7, 118.2, 114.1, 44.8 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₅N₂O [M+H]⁺, 263.1179. Found: m/z 263.1179.



3-phenyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (15) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 65% (16.9 mg); mp: 142.5-144.7 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34-8.31 (m, 2 H), 7.97 (dd, J = 8.0 Hz, J = 1.3 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.51-7.48 (m, 4 H), 7.43-7.39 (m, 1 H), 5.13 (d, J = 2.5 Hz, 2 H), 2.31 (t, J = 2.5 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 153.7, 135.8, 133.3, 131.9, 130.6, 130.5, 130.4, 129.6, 128.1, 124.1, 114.0, 76.9, 73.2, 31.7 ppm;

HRMS (ESI): m/z calcd for C₁₇H₁₃N₂O [M+Na]⁺, 283.0842. Found: m/z 283.0842



1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one (16) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 81% (21.4 mg); mp: 177.6-179.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30-8.27 (m, 2 H), 7.69 (s, 1 H), 7.48-7.44 (m, 3 H), 7.09 (s, 1 H), 3.73 (s, 3 H), 2.43 (s, 3 H), 2.36 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 152.9, 140.3, 136.4, 132.7, 131.6, 131.4, 130.5, 130.0, 129.4, 128.0, 114.1, 29.2, 20.7, 19.2 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₇N₂O [M+H]⁺, 265.1335.



6,7-difluoro-1-methyl-3-phenylquinoxalin-2(1H)-one (17) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 85% (23.1 mg); mp: 173.5-174.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30-8.27 (m, 2 H), 7.76-7.72 (m, 1 H), 7.50-7.46 (m, 3 H), 7.12 (q, *J* = 7.1 Hz, 1 H), 3.71 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.4 (d, *J* = 3.6 Hz), 154.3, 151.6 (dd, *J* = 254.1 Hz, *J* = 14.5 Hz), 146.8 (dd, *J* = 247.2 Hz, *J* = 14.2 Hz), 135.5, 130.7, 130.6 (d, *J* = 10.7 Hz), 129.5, 129.3 (dd, *J* = 9.5 Hz, *J* = 2.8 Hz), 128.1, 117.9 (dd, *J* = 18.1 Hz, *J* = 2.1 Hz), 102.2 (d, *J* = 23 Hz), 29.8 ppm; ¹⁹F NMR (376 MHz, CDCl₃): -130.47 (d, *J* = 22.1 Hz), -141.94 (d, *J* = 22.4 Hz) ppm; HRMS (ESI): m/z calcd for C₁₅H₁₁F₂N₂O [M+H]⁺, 273.0834. Found: m/z 273.0834.



3-phenyl-2H-chromen-2-one (18) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 76% (16.9 mg); mp: 134.6-136.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.82 (s, 1 H), 7.72-7.70 (m, 2 H), 7.56-7.52 (m, 2 H), 7.48-7.37 (m, 4 H), 7.32-7.28 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.6, 153.6, 139.9, 134.7, 131.4, 128.9, 128.5, 128.5, 128.4, 127.9, 124.5, 119.7, 116.5 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₁O₂ [M+H]⁺, 223.0754. Found: m/z 223.0754.



6-methyl-3-phenyl-2H-chromen-2-one (19) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 73% (17.2 mg); mp: 149.1-150.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 1 H), 7.70 (dd, J = 8.4 Hz, J = 1.5 Hz,

2 H), 7.48-7.40 (m, 3 H), 7.34 (d, J = 7.4 Hz, 2 H), 7.28 (s, 1 H), 2.43 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.3, 151.7, 139.9, 134.9, 134.2, 132.5, 128.8, 128.6, 128.5, 128.3, 127.7, 119.4, 116.2, 20.8 ppm; HRMS (ESI): m/z calcd for C₁₆H₁₃O₂ [M+H]⁺, 237.0910. Found: m/z 237.0911.



5,7-dimethyl-3-phenyl-2H-chromen-2-one (20) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 71% (17.8 mg); mp: 159.3-161.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.95 (s, 1 H), 7.70 (d, *J* = 6.9 Hz, 2 H), 7.48-7.40 (m, 3 H), 7.02 (s, 1 H), 6.95 (s, 1 H), 2.53 (s, 3 H), 2.42 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.8, 154.2, 142.4, 137.1, 135.7, 135.4, 128.6, 128.6, 128.5, 127.1, 126.4, 116.1, 114.7, 21.8, 18.3 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₅O₂ [M+Na]⁺, 273.0886. Found: m/z 273.0885.



7-((3-methylbut-2-en-1-yl)oxy)-3-phenyl-2H-chromen-2-one (21) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 64% (19.6 mg); mp: 117.8-119.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 1 H), 7.69 (d, *J* = 7.0 Hz, 2 H), 7.46-7.36 (m, 4 H), 6.89-6.89 (m, 2 H), 5.51-5.47 (m, 1 H), 4.60 (d, *J* = 6.6 Hz, 2 H), 1.82 (s, 3 H), 1.78 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 161.9, 161.0, 155.3, 140.1, 139.3, 135.1, 128.8, 128.4, 124.7, 118.7, 113.4, 113.3, 101.2, 65.5, 25.9, 18.3 ppm; HRMS (ESI): m/z calcd for C₂₀H₁₉O₃ [M+H]⁺, 307.1329. Found: m/z 307.1328.



7-(but-2-yn-1-yloxy)-3-phenyl-2H-chromen-2-one (22) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 75% (21.8 mg); mp: 119.2-121.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.77(s, 1 H), 7.69 (d, *J* = 7.0 Hz, 2 H), 7.46-7.39 (m, 4 H), 7.00 (d, *J* = 2.2 Hz, 1 H), 6.92 (dd, *J* = 8.6 Hz, *J* = 2.5 Hz, 1 H), 4.74 (d, *J* = 2.3 Hz, 2 H), 1.88 (t, *J* = 2.3 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.9, 160.7, 155.1, 140.0, 135.0, 128.8, 128.5, 128.4, 125.2, 113.7, 113.5, 101.6, 85.0, 72.9, 57.0, 3.7 ppm; HRMS (ESI): m/z calcd for C₁₉H₁₅O₃ [M+H]⁺, 291.1016. Found: m/z 291.1015.



3-phenyl-2-(p-tolyl)imidazo[1,2-a]pyridine (23) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 52% (14.8)

mg); mp: 122.5-123.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 7.0 Hz, 1 H), 7.67 (d, J = 9.1 Hz, 1 H), 7.57-7.44 (m, 7 H), 7.21-7.17 (m, 1 H), 7.09 (d, J = 8.0 Hz, 2 H), 6.72 (td, J = 6.8 Hz, J = 1.0 Hz, 1 H), 2.32 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.8, 142.5, 137.2, 131.3, 130.8, 130.1, 129.5, 129.0, 128.8, 128.0, 124.6, 123.2, 120.7, 117.5, 112.2, 21.2 ppm; HRMS (ESI): m/z calcd for C₂₀H₁₇N₂ [M+H]⁺, 285.1386. Found: m/z 285.1386.



2-(4-chlorophenyl)-3-phenylimidazo[1,2-a]pyridine (24) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 66% (20.1 mg); mp: 141.7-142.5 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 6.9 Hz, 1 H), 7.67 (d, *J* = 9.1 Hz, 1 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.56-7.50 (m, 3 H), 7.45-7.43 (m, 2 H), 7.24-7.19 (m, 3 H), 6.75 (t, *J* = 6.8 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.9, 141.3, 133.4, 132.7, 130.7, 129.7, 129.6, 129.3, 129.1, 128.5, 124.9, 123.3, 121.2, 117.6, 112.4 ppm; HRMS (ESI): m/z calcd for C₁₉H₁₄N₂Cl [M+H]⁺, 305.0840. Found: m/z 305.0842.



3-phenyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (25) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 65% (17.9 mg); mp: 97.5-98.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 7.0 Hz, 1 H), 7.66 (d, *J* = 9.1 Hz, 1 H), 7.60-7.51 (m, 5 H), 7.24-7.17 (m, 2 H), 7.09 (dd, *J* = 3.7 Hz, *J* = 1.0 Hz, 1 H), 6.94-6.92 (m, 1 H), 6.72 (td, *J* = 6.8 Hz, *J* = 1.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.7, 137.0, 137.7, 131.1, 129.6, 129.4, 129.2, 127.4, 125.2, 124.9, 124.5, 123.3, 120.0, 117.3, 112.4 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₃N₂S [M+H]⁺, 277.0794. Found: m/z 277.0794.



7-methyl-2,3-diphenylimidazo[1,2-a]pyridine (26) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 50% (14.2 mg); mp: 148.7-150.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 7.0 Hz, 1 H), 7.65 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 2 H), 7.54-7.43 (m, 6 H), 7.29-7.22 (m, 3 H), 6.56 (dd, *J* = 7.1 Hz, *J* = 1.5 Hz, 1 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 145.3, 142.1, 135.6, 134.3, 130.7, 130.1, 129.5, 128.7, 128.2, 128.0, 127.3, 122.5, 120.5, 115.9, 114.9, 21.4 ppm; HRMS (ESI): m/z calcd for C₂₀H₁₇N₂ [M+H]⁺, 285.1386. Found: m/z 285.1386.



8-methyl-2,3-diphenylimidazo[1,2-a]pyridine (27) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 52% (14.8 mg); mp: 96.1-98.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 7.3 Hz, 1 H), 7.65 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 2 H), 7.52-7.43 (m, 6 H), 7.29-7.27 (m, 1 H), 7.25-7.23 (m, 2 H), 6.57 (dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 1 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 145.3, 142.1, 135.6, 134.3, 130.7, 129.5, 128.7, 128.2, 128.0, 127.3, 126.0, 122.5, 120.5, 115.9, 114.9, 21.4 ppm; HRMS (ESI): m/z calcd for C₂₀H₁₇N₂ [M+H]⁺, 285.1386. Found: m/z 285.1386.



3-phenylpyrazin-2-amine (28) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 1:1), white solid, isolated yield 76% (13.0 mg); mp: 112.7-114.6 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, J = 2.7 Hz, 1 H), 7.98 (d, J = 2.7 Hz, 1 H), 7.73-7.70 (m, 2 H), 7.53-7.43 (m, 3 H), 4.78 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 140.9, 137.2, 134.6, 129.1, 129.1, 128.1 ppm; HRMS (ESI): m/z calcd for C₁₀H₁₀N₃ [M+H]⁺, 172.0869. Found: m/z 172.0867.



6-methyl-3-phenylpyrazin-2(1H)-one (29) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 2:1), white solid, isolated yield 83% (15.4 mg); mp: 209.8-211.7 °C; ¹H NMR (400 MHz, CDCl₃): δ 13.38 (s, 1 H), 8.33 (dd, J = 8.0 Hz, J = 2.0 Hz, 2 H), 7.48-7.42 (m, 4 H), 2.40 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 157.9, 149.4, 136.3, 135.9, 129.6, 128.5, 128.1, 124.2, 16.0 ppm; HRMS (ESI): m/z calcd for C₁₁H₁₁N₂O [M+H]⁺, 187.0866. Found: m/z 187.0864.



3,6-dichloro-4-phenylpyridazine (30) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 72% (16.1 mg); mp: 85.8-87.6 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.50 (m, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 154.9, 142.8, 133.2, 130.4, 129.6, 128.9, 128.9 ppm; HRMS (ESI): m/z calcd for C₁₀H₇N₂Cl₂ [M+H]⁺, 224.9981. Found: m/z 224.9977.



2-methyl-3-phenylquinoxaline (31) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 8:1), white solid, isolated yield 45% (9.9 mg); mp: 67.5-68.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.13-8.11 (m, 1 H), 8.08-8.05 (m, 1 H), 7.77-7.71 (m, 2 H), 7.67-7.65 (m, 2 H), 7.56-7.50 (m, 3 H), 2.79 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 152.6, 141.3, 141.0, 139.1, 129.8, 129.3, 129.0, 128.9, 128.6, 128.3, 24.4 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₃N₂ [M+H]⁺, 221.1073. Found: m/z 221.1072.



3-phenylquinoxalin-2-ol (32) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 84% (18.6 mg); mp: 189.6-190.7 °C; ¹H NMR (400 MHz, DMSO): δ 12.57 (s, 1 H), 8.31 (dd, J = 7.1 Hz, J = 1.5 Hz, 2 H), 7.85 (d, J = 7.9 Hz, 1 H), 7.57-7.47 (m, 4 H), 7.34 (t, J = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, DMSO): δ 155.1, 154.6, 136.1, 132.5, 132.5, 130.8, 130.7, 129.7, 129.2, 128.3, 123.9, 115.6 ppm; HRMS (ESI): m/z calcd for C₁₄H₁₁N₂O [M+H]⁺, 223.0866. Found: m/z 223.0866.



2,3-diphenyl-4H-chromen-4-one (33) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 43% (12.8 mg); mp: 129.5-131.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30 (dd, J = 8.0 Hz, J = 1.5 Hz, 1 H), 7.73-7.69 (m, 1 H), 7.54 (d, J = 8.2 Hz, 1 H), 7.46-7.40 (m, 3 H), 7.34-7.27 (m, 6 H), 7.24-7.21 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 133.7, 133.3, 132.9, 131.2, 130.1, 129.6, 128.3, 128.1, 127.6, 126.4, 125.1, 123.6, 123.0, 118.0 ppm; HRMS (ESI): m/z calcd for C₂₁H₁₅O₂ [M+H]⁺, 299.1067. Found: m/z 299.1065.



3-phenyl-2H-furo[2,3-h]chromen-2-one (34) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 55% (14.4 mg); mp: 152.4-154.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 1 H), 7.74-7.71 (m, 3 H), 7.49-7.41 (m, 5 H), 7.18 (d, J = 1.8 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.7, 157.2, 145.9, 141.1, 135.0, 130.6, 128.7, 128.5, 128.5, 126.0, 123.9, 116.6, 114.3, 109.0, 104.2 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₁O₃ [M+H]⁺, 263.0703. Found: m/z 263.0702.



7-methoxy-8-(3-methylbut-2-en-1-yl)-3-phenyl-2H-chromen-2-one (35) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 5:1), white solid, isolated yield 65% (20.8 mg); mp: 121.2-123.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.74 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.45-7.41 (m, 2 H), 7.39-7.33 (m, 2 H), 6.86 (d, *J* = 8.6 Hz, 1 H), 5.27-5.24 (m, 1 H), 3.93 (s, 3 H), 3.58 (d, *J* = 7.2 Hz, 2 H), 1.86 (s, 3 H), 1.68 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 160.9, 160.0, 151.3, 140.4, 135.3, 132.7, 128.4, 128.4, 128.3, 126.3, 124.7, 121.2, 117.6, 113.8, 107.6, 56.1, 25.8, 22.0, 18.0 ppm; HRMS (ESI): m/z calcd for C₂₁H₂₁O₃ [M+H]⁺, 321.1485. Found: m/z 321.1485.



5,6,7,8-tetramethoxy-2-(4-methoxyphenyl)-3-phenyl-4H-chromen-4-one (36) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 51% (22.8 mg); mp: 134.5-136.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.29 (m, 5 H), 7.24-7.22 (m, 2 H), 6.77 (d, *J* = 9.0 Hz, 2 H), 4.11 (s, 3 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 3.93 (s, 3 H), 3.79 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 176.3, 160.8, 159.1, 151.3, 148.6, 147.5, 144.1, 137.8, 133.3, 131.3, 131.1, 128.4, 127.5, 125.2, 122.1, 114.5, 113.6, 62.2, 62.0, 61.8, 61.7, 55.3 ppm; HRMS (ESI): m/z calcd for C₂₆H₂₅O₇ [M+H]⁺, 449.1595. Found: m/z 449.1597.



3,5,6-triphenylpyrazin-2-ol (37) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 70% (22.7 mg); mp: 273.5-274.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 12.33 (s, 1 H), 8.51-8.48 (m, 2 H), 7.49-7.40 (m, 10 H), 7.29-7.27 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.3, 149.4, 137.3, 135.6, 135.1, 133.1, 132.5, 129.9, 129.8, 129.6, 129.0, 128.9, 128.1, 128.0, 127.6 ppm; HRMS (ESI): m/z calcd for C₂₂H₁₇N₂O [M+H]⁺, 325.1335. Found: m/z 325.1330.



1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (38) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 75% (18.8 mg); mp: 159.1-162.3 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 8.2 Hz, 2 H), 7.93 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.55 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1 H), 7.38-7.28 (m, 4 H), 3.77 (s, 3 H), 2.42 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.1, 140.6, 133.3, 133.3, 133.2, 130.4, 130.1, 129.5, 128.8, 123.7, 113.5 ppm; HRMS (ESI): m/z calcd for C₁₆H₁₅N₂O [M+H]⁺, 251.1179. Found: m/z 251.1180.



3-(4-ethylphenyl)-1-methylquinoxalin-2(1H)-one (39) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 87% (23.0 mg); mp: 139.5-141.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 8.3 Hz, 2 H), 7.93 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 1 H), 7.55 (td, *J* = 8.6 Hz, *J* = 1.5 Hz, 1 H), 7.38-7.30 (m, 4 H), 3.77 (s, 3 H), 2.72 (q, *J* = 7.6 Hz, 2 H), 1.27 (t, *J* = 7.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.2, 146.9, 133.6, 133.3, 133.2, 130.4, 130.1, 129.6, 127.7, 123.7, 113.6, 29.3, 28.9, 15.5 ppm; HRMS (ESI): m/z calcd for C₁₇H₁₇N₂O [M+H]⁺, 265.1335. Found: m/z 265.1335.



3-(4-(tert-butyl)phenyl)-1-methylquinoxalin-2(1H)-one (40) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 80% (23.4 mg); mp: 89.5-91.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, *J* = 8.6 Hz, 2 H), 7.94 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.56 (td, *J* = 8.6 Hz, *J* = 1.4 Hz, 1 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 7.35 (q, *J* = 7.9 Hz, 2 H), 3.77 (s, 3 H), 1.36 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.3, 153.6, 133.3, 133.2, 130.4, 130.1, 129.3, 125.2, 123.7, 113.6, 34.9, 31.2, 29.3 ppm; HRMS (ESI): m/z calcd for C₁₉H₂₁N₂O [M+H]⁺, 293.1648. Found: m/z 293.1647.



1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (41) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 67% (20.4 mg); mp: 103.7-105.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 8.1 Hz, 2 H), 7.96

(dd, J = 8.0 Hz, J = 1.3 Hz, 1 H), 7.73 (d, J = 8.3 Hz, 2 H), 7.62 (td, J = 8.6 Hz, J = 1.4 Hz, 1 H), 7.43-7.36 (m, 2 H), 3.78 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.6, 152.6, 139.3, 133.5, 133.0, 131.8 (d, J = 32.1 Hz), 130.9 (d, J = 32.5 Hz), 129.9, 124.1 (d, J = 272.2 Hz), 125.0 (q, J = 3.7 Hz), 124.0, 113.7, 29.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃): -62.80 (s) ppm; HRMS (ESI): m/z calcd for C₁₆H₁₂F₃N₂O [M+H]⁺, 305.0896. Found: m/z 305.0894.



3-(4-fluorophenyl)-1-methylquinoxalin-2(1H)-one (42) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 74% (18.8 mg); mp: 149.3-151.6 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.41-8.37 (m, 2 H), 7.94 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.59 (td, *J* = 8.6 Hz, *J* = 1.4 Hz, 1 H), 7.38 (q, *J* = 9.5 Hz, 2 H), 7.16 (t, *J* = 8.8 Hz, 2 H), 3.78 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 164.2 (d, *J* = 251.0 Hz), 154.7, 152.8, 133.3, 133.0, 132.2 (d, *J* = 3.1 Hz), 131.9, 131.8, 130.4, 123.9, 115.1 (d, *J* = 21.5 Hz), 113.6, 29.4 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₂FN₂O [M+H]⁺, 255.0928. Found: m/z 255.0927.



3-(4-chlorophenyl)-1-methylquinoxalin-2(1H)-one (43) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 81% (21.6 mg); mp: 182.3-183.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 8.7 Hz, 2 H), 7.94 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.59 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1 H), 7.46-7.44 (m, 2 H), 7.41-7.34 (m, 2 H), 3.78 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.6, 152.7, 136.6,134.4, 133.4, 133.0, 131.0, 130.6, 130.5, 128.3, 123.9, 113.7, 29.4 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₂ClN₂O [M+H]⁺, 271.0633. Found: m/z 271.0631.



3-(4-bromophenyl)-1-methylquinoxalin-2(1H)-one (44) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 72% (22.6 mg); mp: 176.5-178.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.6 Hz, 2 H), 7.94 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H), 7.63-7.57 (m, 3 H), 7.41-7.34 (m, 2 H), 3.77 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.6, 152.8, 134.9, 133.4, 133.0, 131.3, 131.2, 130.6, 130.5, 125.1, 123.9, 113.7, 29.4 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₂BrN₂O [M+H]⁺, 315.0128. Found: m/z 315.0125.



1-methyl-3-(m-tolyl)quinoxalin-2(1H)-one (45) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 55% (13.8 mg); mp: 107.5-109.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.08 (m, 2 H), 7.96 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 1 H), 7.60-7.55 (m, 1 H), 7.40-7.36 (m, 3 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 3.78 (s, 3 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 154.5, 137.7, 136.0, 133.4, 133.1, 131.2, 130.4, 130.3, 130.0, 128.0, 126.7, 123.8, 113.6, 29.3, 21.6 ppm; HRMS (ESI): m/z calcd for C₁₆H₁₄N₂ONa [M+Na]⁺, 273.0998. Found: m/z 273.0997.



3-(3-bromophenyl)-1-methylquinoxalin-2(1H)-one (46) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 74% (23.2 mg); mp: 113.7-115.6 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1 H), 8.32 (d, *J* = 7.9 Hz, 1 H), 7.95 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1 H), 7.60 (t, *J* = 8.1 Hz, 2 H), 7.41-7.33 (m, 3 H), 3.77 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 152.3, 137.9, 133.4, 133.2, 132.9, 132.4, 130.8, 130.6, 129.6, 128.3, 123.9, 122.3, 113.7, 29.4 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₂BrN₂O [M+H]⁺, 315.0128. Found: m/z 315.0123.



1-methyl-3-(o-tolyl)quinoxalin-2(1H)-one (47) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 68% (17.0 mg); mp: 105.7-106.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.93 (dd, J = 8.6 Hz, J = 1.6 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.47-7.45 (m, 1 H), 7.41-7.33 (m, 3 H), 7.31-7.27 (m, 2 H), 3.78 (s, 3 H), 2.34 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 154.6, 136.8, 136.1, 133.6, 132.9, 130.6, 130.5, 129.4, 129.2, 125.6, 123.8, 113.7, 29.4, 20.0 ppm; HRMS (ESI): m/z calcd for C₁₆H₁₅N₂O [M+H]⁺, 251.1179. Found: m/z 251.1178.



3-(4-(tert-butyl)phenyl)quinoxalin-2-ol (48) was purified by flash silica chromatography

(pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 82% (22.8 mg); mp: 214.5-215.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 8.4 Hz, 2 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 7.57-7.49 (m, 3 H), 7.39-7.35 (m, 2 H), 1.39 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.6, 154.4, 153.9, 133.4, 132.9, 131.1, 130.2, 129.4, 129.3, 125.3, 124.3, 115.5, 34.9, 31.3 ppm; HRMS (ESI): m/z calcd for C₁₈H₁₉N₂O [M+H]⁺, 279.1492. Found: m/z 279.1490.



3-(4-bromophenyl)-6,7-dichloro-1-methylquinoxalin-2(1H)-one (49) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 53% (20.2 mg); mp: 236.7-237.9 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, *J* = 8.7 Hz, 2 H), 8.02 (s, 1 H), 7.62 (d, *J* = 8.7 Hz, 2 H), 7.43 (s, 1 H), 3.73 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 153.8, 134.7, 134.2, 132.7, 132.0, 131.4, 131.3, 131.1, 127.8, 125.9, 115.2, 29.6 ppm; HRMS (ESI): m/z calcd for C₁₅H₁₂BrCl₂N₂O [M+H+2]⁺, 284.9328. Found: m/z 284.9323.



3-(4-chlorophenyl)-6-methylpyrazin-2(1H)-one (50) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), white solid, isolated yield 68% (15.0 mg); mp: 252.1-253.6 °C; ¹H NMR (400 MHz, DMSO): δ 12.63 (s, 1 H), 8.35 (d, *J* = 8.7 Hz, 2 H), 7.50-7.47 (m, 2 H), 7.35 (s, 1 H), 2.22 (s, 3 H); ¹³C NMR (100 MHz, DMSO): δ 160.9, 140.2, 138.9, 134.9, 133.1, 127.3, 20.8 ppm; HRMS (ESI): m/z calcd for C₁₁H₁₀ClN₂O [M+H]⁺, 221.0476. Found: m/z 221.0473.



3-(4-ethylphenyl)-5,6-diphenylpyrazin-2-ol (51) was purified by flash silica chromatography (pertroleum ether/ethyl acetate = 3:1), yellow solid, isolated yield 78% (27.5 mg); mp: 258.4-259.7 °C; ¹H NMR (400 MHz, CDCl₃): δ 12.55 (s, 1 H), 8.42 (d, *J* = 8.3 Hz, 2 H), 7.51-7.47 (m, 3 H), 7.44-7.40 (m, 4 H), 7.27 (s, 2 H), 7.26-7.25 (s, 3 H), 2.73 (q, *J* = 7.6 Hz, 2 H), 1.29 (t, *J* = 7.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.5, 149.4, 146.4, 137.5, 134.7, 133.2, 133.0, 132.6, 129.7, 129.7, 129.6, 129.1, 128.8, 128.1, 127.6, 127.5, 28.9, 15.6 ppm; HRMS (ESI): m/z calcd for C₂₄H₂₁N₂O [M+Na]⁺, 375.1468. Found: m/z 375.1463.

5. Gram-scale Reaction



A mixture of quinoxalin-2(1H)-one **1a** (3 mmol, 0.48 g, 1 equiv) and iodonium ylide **2a** (4.5 mmol, 1.54 g, 1.5 equiv), EosinY (2 mol %, 0.0390 g) and K_2CO_3 (3 mmol, 0.4140 g, 1equiv) was added in a dry round-bottomed flask under N₂ atmosphere. To the mixture, DMSO (10 mL) was added *via* a syringe and the reaction mixture was stirred and irradiated by the 12W blue LED at room temperature for 24 h, which was monitored with TLC. After completion of the reaction, the reaction mixture was added water and extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄. The resulting crude residue was purified by column chromatography on silica gel (elute: EtOAc /petroleum ether) to give the desired product **3** (0.50 g, 71%).

6. Mechanism Studies Radical trapping experiment



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with quinoxalin-2(1H)-one **1a** (0.1 mmol) and iodonium ylide **2a** (0.15 mmol), EosinY (2 mol %), K_2CO_3 (1equiv) and DMSO (2 mL). The reaction mixture was then stirred and irradiation with a 12 W blue LED at room temperature for 12 h under N₂ atmosphere. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na₂SO₄ and filtered. The filtrate was concentrated in vacuo. The adduct **52** could be detected by GC-MS (m/z, relative intensity): 256.1.



Figure 2. GC-MS spectrum of compound 52

UV/VIS Absorption spectra

The UV/VIS Absorption spectra were recorded in EtOH of a 0.05 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.



Figure 3. The UV/Vis absorption spectra of 1a, 2a, 3, Eosin Y in EtOH (0.05 mM) Stern-Volmer Quenching Experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared 0.05 Mm solution of Eosin Y in EtOH and was added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature.



Figure 4. Luminescence quenching experiments of Eosin Y with 1a



Figure 5. Luminescence quenching experiments of Eosin Y with 2a



Figure 6. Luminescence quenching experiments of Eosin Y with reactants

Cyclic Voltammetry

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M TBAPF 6 in CH₃CN).



Figure 7. CV of Reaction reagents (5 mM in CH₃CN)

Light ON-OFF experiment



Figure 8. Light ON-OFF experiment

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with quinoxalin-2(1H)-one **1a** (0.1 mmol) and iodonium ylide **2a** (0.15 mmol), EosinY (2 mol %), K_2CO_3 (1equiv) and DMSO (2 mL). The reaction mixture was then stirred and irradiation with a 12 W blue LED at room temperature under N₂ atmosphere. After 2 h, the blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the blue LED was turned back on to irradiate the remaining two reaction mixtures. After an additional 2 h of irradiation, the blue LED was turned off, and one vial was removed for analysis. The remaining vial was removed for analysis. The remaining three vials were stirle and additional 2 h of irradiation. The blue LED was turned off, and one vial was removed for analysis. The remaining two reaction mixtures. After an additional 2 h of irradiation, the blue LED was turned off, and one vial was removed for analysis. The remaining vial was stirred in the absence of light for an additional 2 h. Then, the last vial was removed for analysis. The yield of the product was isolated yield.

7. X-Ray Crystallographic Data of 3



Figure 4. Single-crystal X-ray Molecular Structure of 3

The structure of **3** (containing little solvent) was determined by the X-ray diffraction. Recrystallized from ethyl acetate/petroleum ether. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data and assigned as **CCDC: 2106532**. ORTEP view of complex Ellipsoids are represented at the 50% probability level.

e e	
Identification code	3
Empirical formula	$C_{15}H_{12}N_2O$
Formula weight	236.27
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.3920(6)
b/Å	7.1332(4)
c/Å	20.1084(8)
$\alpha/^{\circ}$	90
β/°	95.662(4)
$\gamma/^{\circ}$	90
Volume/Å ³	2339.77(18)
Z	8
$ ho_{calc}g/cm^3$	1.341
μ/mm^{-1}	0.686
F(000)	992.0
Crystal size/mm ³	0.16 imes 0.13 imes 0.1
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^{\circ}$	6.644 to 134.146
Index ranges	$\text{-19} \le h \le 19, \text{-7} \le k \le 8, \text{-16} \le l \le 24$
Reflections collected	8634
Independent reflections	4191 [$R_{int} = 0.0235, R_{sigma} = 0.0363$]
Data/restraints/parameters	4191/0/327
Goodness-of-fit on F ²	1.045
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0497, wR_2 = 0.1265$
Final R indexes [all data]	$R_1 = 0.0687, wR_2 = 0.1434$
Largest diff. peak/hole / e Å-3	.19/-0.21

Table 1 Crystal data and structure refinement for 3.

8. References

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9. Copies of NMR Spectra



¹H NMR (400 MHz, CDCl₃) spectrum of compound 3



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 3



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 5



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 6



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 7



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 8



¹H NMR (400 MHz, CDCl₃) spectrum of compound 9



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 9





ppm



¹H NMR (400 MHz, CDCl₃) spectrum of compound 11



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 11



¹H NMR (400 MHz, CDCl₃) spectrum of compound 12



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 12



¹H NMR (400 MHz, CDCl₃) spectrum of compound 13



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 13


¹H NMR (400 MHz, CDCl₃) spectrum of compound 14



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 14



¹H NMR (400 MHz, CDCl₃) spectrum of compound 15



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 15



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 16

0 ppm



¹H NMR (400 MHz, CDCl₃) spectrum of compound 17



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 17



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 17



¹H NMR (400 MHz, CDCl₃) spectrum of compound 18



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 18



¹H NMR (400 MHz, CDCl₃) spectrum of compound 19



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 19



¹H NMR (400 MHz, CDCl₃) spectrum of compound 20



¹H NMR (400 MHz, CDCl₃) spectrum of compound 21



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 21



¹H NMR (400 MHz, CDCl₃) spectrum of compound 22



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 22



¹H NMR (400 MHz, CDCl₃) spectrum of compound 23



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 23



¹H NMR (400 MHz, CDCl₃) spectrum of compound 24



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 24



¹H NMR (400 MHz, CDCl₃) spectrum of compound 25



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 25



¹H NMR (400 MHz, CDCl₃) spectrum of compound 26



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 26



¹H NMR (400 MHz, CDCl₃) spectrum of compound 27



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 27



¹H NMR (400 MHz, CDCl₃) spectrum of compound 28



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 28



¹H NMR (400 MHz, CDCl₃) spectrum of compound 29



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 29



¹H NMR (400 MHz, CDCl₃) spectrum of compound 30



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 30



¹H NMR (400 MHz, CDCl₃) spectrum of compound 31



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 31



¹H NMR (400 MHz, DMSO) spectrum of compound 32



¹³C NMR (100 MHz, DMSO) spectrum of compound 32



¹H NMR (400 MHz, CDCl₃) spectrum of compound 33



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 33



¹H NMR (400 MHz, CDCl₃) spectrum of compound 34



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 34



¹H NMR (400 MHz, CDCl₃) spectrum of compound 35







¹H NMR (400 MHz, CDCl₃) spectrum of compound 36



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 36



¹H NMR (400 MHz, CDCl₃) spectrum of compound 37



¹H NMR (400 MHz, CDCl₃) spectrum of compound 38



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 38



¹H NMR (400 MHz, CDCl₃) spectrum of compound 39



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 39



¹H NMR (400 MHz, CDCl₃) spectrum of compound 40



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 40



¹H NMR (400 MHz, CDCl₃) spectrum of compound 41



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 41



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 41



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 42



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 42



¹H NMR (400 MHz, CDCl₃) spectrum of compound 43



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 43



¹H NMR (400 MHz, CDCl₃) spectrum of compound 44



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 44



¹H NMR (400 MHz, CDCl₃) spectrum of compound 45



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 45



¹H NMR (400 MHz, CDCl₃) spectrum of compound 46



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 46



¹H NMR (400 MHz, CDCl₃) spectrum of compound 47



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 47



¹H NMR (400 MHz, CDCl₃) spectrum of compound 48


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 48



¹H NMR (400 MHz, CDCl₃) spectrum of compound 49



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 49



¹H NMR (400 MHz, DMSO) spectrum of compound 50



¹³C NMR (100 MHz, DMSO) spectrum of compound 50



¹H NMR (400 MHz, CDCl₃) spectrum of compound 51



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 51