Electro-Oxidation Induced O-S Cross-Coupling of Quinoxalinones with Sodium Sulfinates for Synthesizing 2-Sulfonyloxylated Quinoxalines

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1. General information

Chemicals and solvents were either purchased from commercial suppliers (Titan) or purified by standard techniques. The instrument for electrolysis is a DC regulated power supply (HSPY-200-01) (made in China). The anodic electrode was graphite plate (15 mm × 15 mm × 2 mm) and cathodic electrode was nickel foam (15 mm × 15 mm × 1 mm). Analytical thin-layer chromatography (TLC) was performed on silica gel plates with GF254 indicator (Yantai Jiangyou Silica gel Development Co., Ltd.) and compounds were visualized by irradiation with UV light at 254 nm. Flash chromatography was carried out utilizing silica gel 200-300 mesh (Qingdao Haiyang Chemical Co., Ltd.). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Plus-400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts were reported in ppm downfield and referenced as follows: $^1$H: TMS (0.00 ppm) or residual internal CHCl$_3$ (δ 7.26 ppm); $^{13}$C: internal CDCl$_3$ (δ 77.2 ppm). Coupling constants were quoted in Hz ($J$). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Cyclic Voltammetry were obtained on a Biologic sp300 potentiostat.

2. General procedure for the synthesis of quinoxalinones

![Quinoxaline Reaction](image)

To a solution of 1,2-phenylenediamines (5 mmol, 1.0 equiv.) in ethanol (30 mL) was added ethyl glyoxalate (6 mmol, 1.2 equiv.). The reaction system was stirred and heated to reflux at 85 °C for 1 h, then stirred at room temperature for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with ethanol (3 × 5 ml), and finally dried to give quinoxalinones.

3. General procedure for the synthesis of sodium sulfinates

![Sulfinate Reaction](image)

Sulfonyl chlorides (5.00 mmol) were added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M) and heated at 80 °C for 4 h, after cooling to room temperature the volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid.
4. General procedure for electro-oxidation induced selective O-S cross-coupling

A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), 4-Bu$_4$NBr (2.0 equiv) and 10 mL of THF/H$_2$O (8/1). The mixture was electrolyzed using constant current conditions (~13.3 mA cm$^{-2}$) at room temperature under magnetic stirring for 4 h. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of quinoxalinone), the electrodes were removed and rinsed with EtOAc and the mixture was poured into a saturated aqueous solution of NaCl and the product was then extracted with ethyl acetate (3 × 10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired pure product.

Figure S1. Reaction set-up parts

Figure S2. Assembled reaction set-up

5. Optimization of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change from standard conditions</th>
<th>Yield(%)</th>
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<tbody>
<tr>
<td>1a</td>
<td>4-MePhSO$_2$Na</td>
<td>3a</td>
</tr>
<tr>
<td>2a</td>
<td>J = 13.3 mA cm$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>TBAB, THF/H$_2$O (8/1), r.t., 4h</td>
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Table S1. Optimization of Reaction Condition$^a$
<table>
<thead>
<tr>
<th></th>
<th>Condition</th>
<th>Yield</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>without electricity</td>
<td>n.d.</td>
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<tr>
<td>3</td>
<td>without H₂O</td>
<td>trace</td>
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<tr>
<td>4</td>
<td>without TBAB</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>HOAc instead of H₂O</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>HFIP instead of H₂O</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>1,4-dioxane instead of THF</td>
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</tr>
<tr>
<td>8</td>
<td>CH₃CN instead of THF</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>KBr instead of TBAB</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>TEAB instead of TBAB</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>TMAB instead of TBAB</td>
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</tr>
<tr>
<td>12</td>
<td>20 mA, 6 h</td>
<td>62</td>
</tr>
<tr>
<td>13</td>
<td>40 mA, 3 h</td>
<td>63</td>
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<td>63</td>
</tr>
<tr>
<td>18</td>
<td>under Ar</td>
<td>81</td>
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</table>

*aReaction conditions: graphite plate anode (15 mm × 15 mm × 2 mm), nickel foam cathode (15 mm × 15 mm × 1 mm), constant current = 30 mA (J = 13.3 mA/cm²), 1a (0.50 mmol), 2a (1.00 mmol), TBAB (2.0 equiv), THF/H₂O (8/1) (10 mL), room temperature, 4 h, undivided cell; The yield of 3a was determined by ¹H NMR using 1,1,2,2-tetra-chloroethane as the internal standard; n.d. = not detected. bThe yield of the isolated product is given within the parentheses.*

6. Synthetic Application to Preparation of Bioactive Molecules

The preparation of 4a: To an oven dried two-necked flask equipped with a stirrer bar, was added 3a (0.5 mmol), PdCl₂(PPh₃)₂ (5 mol %) and CuI (10 mol %), which was dissolved in 2 mL dry THF followed by an addition of Et₃N (2 equiv) and propargyl alcohol (1.2 equiv). The reaction mixture was refluxed at 50 °C and stirred for 18 h under nitrogen atmosphere. The reaction was quenched by adding ethyl acetate/water (3/1). The layers were separated, and the aqueous layer was washed with ethyl acetate (3x20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated. The crude was purified by column chromatography.

The preparation of 4b and 4d: An oven dried screw cap glass test tube (25 mL), which was equipped with magnetic stir bar, was charged with 3a (1.0 mmol), Pd(OAc)₂ (2 mol %), BrettPhos (4 mol%), corresponding boronic acid (2.0 mmol) and K₃PO₄·H₂O (3.0 mmol). The test tube was then tightly capped with a Teflon top plastic screw cap and evacuated and back
filled with argon; this process was repeated for a total of three times. The solvent was then added by a syringe under a positive flow of argon. And then the reaction mixture was stirred at room temperature for a few seconds to create a homogeneous slurry, and then transferred to a preheated oil bath (110 °C) and allowed to stir for 2 h. After the reaction was complete, the mixture was diluted with 3-5 mL of water and ~5 mL of ethyl acetate. The organic layer was dried over Na₂SO₄, filtered, concentrated under reduced pressure, and then purified using column chromatography.

The preparation of 4c: To a solution of 4a (0.5 mmol) in dry CH₂Cl₂ (5 mL) was slowly added BBr₃ (1.2 mmol) at -20 °C. Upon warming to room temperature, the reaction mixture was stirred overnight. 1M HCl (2 mL) was added to quench the reaction at 0 °C. The product was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried over NaSO₄, filtered and concentrated under reduced pressure. The product may be purified with a silica gel column chromatography.

7. Gram-scale experiments

A 250 mL beaker with a stir bar was charged with quinoxaline one 1a or 1k (8.0 mmol, 1.0 equiv), 4-MePhSO₂Na (2.8509 g, 16.0 mmol, 2.0 equiv) and "Bu₂NBr (3.30 g, 16.0 mmol, 2.0 equiv)
and 160 mL of THF/H₂O (8/1). Graphite plate anode (50 mm × 30 mm × 2 mm) and nickel foam cathode (50 mm × 30 mm × 1 mm) were inserted into the mixture. Then, the reaction mixture was electrolyzed under a constant current of 200 mA (J = 13.3 mA/cm²) at room temperature for 10 h. After the reaction, the electrodes were removed and rinsed with EtOAc. The mixture was poured into a saturated aqueous solution of NaCl and the product was then extracted with ethyl acetate (3 × 50 mL), dried over Na₂SO₄, and concentrated in vacuo. The solvent was concentrated in vacuo and the crude material was purified by column chromatography to furnish the desired product as a white crystal.

**Figure S3. Setup for Gram-Scale Electrolysis**

### 8. Mechanistic Experiments

**Procedure for the Mechanistic Experiment (Scheme 6, a).** A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), nBu₄NBr (2.0 equiv), 10 mL of THF/H₂O (8/1) and TEMPO (2.0 equiv), BHT (4.0 equiv), respectively. The mixture was electrolyzed using constant current conditions (~13.3 mA cm⁻²) at room temperature under magnetic stirring for 4 h. Only a tiny to trace amount of 3a was afforded.

**Procedure for the Mechanistic Experiment (Scheme 6, b).** A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfinates (1.0 mmol, 2.0 equiv), nBu₄NBr (2.0 equiv), 10 mL of THF/H₂O (8/1) and 4-tert-butyldiyrene (2.0 equiv). The mixture was electrolyzed using constant current conditions (~13.3 mA cm⁻²) at room temperature under magnetic stirring for 4 h. Vinyl sulfone 4 was produced in 18% isolated yield.

**Procedure for the Mechanistic Experiment (Scheme 6, c).** (1) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added...
quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), 4-Bu2NBr (2.0 equiv) and 10 mL of THF/H2O (8/1). The mixture was electrolyzed using constant current conditions (~13.3 mA cm−2) at room temperature under magnetic stirring for 4 h. No 3a was detected. (2) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), 4-Bu2NBr (2.0 equiv) and 10 mL of THF/H2O (8/1). Then the electrolysis system was stirred at room temperature for 4 h (electric current was zero). Still, 3a was not detected. (3) A undivided cell was equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), 4-methyl-benzenesulfonyl bromide (1.0 mmol, 2.0 equiv), Na2CO3 (1.0 equiv), 4-Bu2NBr (2.0 equiv) and 10 mL of THF/H2O (8/1). Then the electrolysis system was stirred at room temperature for 4 h (electric current was zero). 3a was obtained with 78% yield.

**Procedure for the Mechanistic Experiment (Scheme 6, d).** Several undivided cells were respectively equipped with graphite plate anode (15 mm × 15 mm × 2 mm) and nickel foam cathode (15 mm × 15 mm × 1 mm) and connected to a DC regulated power supply. To the cell was added quinoxalinone (0.5 mmol, 1.0 equiv), sodium sulfonates (1.0 mmol, 2.0 equiv), 4-Bu2NBr (2.0 equiv) and 10 mL of THF/H2O (8/1). Then the electrolysis system was stirred at room temperature for 1 h; 2 h (including turn-off 1h); 2 h; 3 h (including turn-off 1h); 3 h; 4 h (including turn-off 1h). The yield of 3a was determined by isolated yield.

**9. Cyclic voltammetry**

Cyclic voltammetry was performed in a three-electrode cell at room temperature. The working electrode was a glassy carbon and the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated KCl solution. 10 mL of THF/H2O (8/1) containing 0.1 M TBAB was poured into the electrochemical cell in all experiments. The CV of all substrates was measured at the concentration of 0.01 M. The scan rate is 50 mV/s, ranging from 0 to 2.2 V.

**10. Detail descriptions for products**

**quinoxalin-2-yl 4-methylbenzenesulfonate (3a)**

White solid, 68% yield, m.p. 90-91 °C. 1H NMR (400 MHz, CDCl3) δ 8.65 (s, 1H), 8.10 (d, J = 9.4 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 9.8 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 151.05, 146.06, 141.33, 139.84, 139.28, 133.45, 131.20, 129.90, 129.83, 129.27, 129.17, 128.60, 21.87. HRMS (ESI) Calcd for C15H12N2O3S (M+H)+: 301.0641, Found: 301.0628.

**6-methoxyquinoxalin-2-yl 4-methylbenzenesulfonate (3b)**
White solid, 86% yield, m.p. 116-117 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.74 (m, 1H), 7.36 (m, 4H), 3.92 (s, 3H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.83, 149.61, 145.90, 143.04, 139.23, 135.53, 133.41, 129.87, 129.39, 128.96, 124.24, 106.93, 55.92, 21.81. HRMS (ESI) Calcd for C₁₆H₁₄N₂O₄S (M+H)⁺: 331.0753, Found: 331.0747.

5-methylquinoxalin-2-yl 4-methylbenzenesulfonate (3c)

White solid, 73% yield, m.p. 103-104 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.1 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 2.66 (s, 3H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.89, 145.96, 140.54, 140.11, 137.86, 137.78, 133.50, 131.07, 129.95, 129.13, 126.41, 21.84, 17.44, 17.44. HRMS (ESI) Calcd for C₁₆H₁₄N₂O₃S (M+H)⁺: 315.0798, Found: 315.0804.

8-methylquinoxalin-2-yl 4-methylbenzenesulfonate (3d)

White solid, 71% yield, m.p. 99-100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.1 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.60, 150.69 (d, J = 250.8 Hz), 146.16, 141.96 (d, J = 13.0 Hz), 140.21, 136.81, 136.80, 133.30, 130.48 (d, J = 9.9 Hz), 129.93, 129.08, 121.39 (d, J = 25.9 Hz), 113.11 (d, J = 21.9 Hz), 21.84, 19F NMR (376 MHz, CDCl₃) δ -107.86. HRMS (ESI) Calcd for C₁₆H₁₄F₃N₂O₃S (M+H)⁺: 319.0547, Found: 319.0551.

6-fluoroquinoxalin-2-yl 4-methylbenzenesulfonate (3e)

White solid, 50% yield, m.p. 67-68 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.90 (dd, J = 9.2, 5.6 Hz, 1H), 7.73 (dd, J = 8.8, 2.8 Hz, 1H), 7.60 – 7.48 (m, 1H), 7.39 (d, J = 8.1 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.60, (d, J = 250.8 Hz), 150.69 (d, J = 3.3 Hz), 146.16, 141.96 (d, J = 13.0 Hz), 140.21, 136.81, 136.80, 133.30, 130.48 (d, J = 9.9 Hz), 129.93, 129.08, 121.39 (d, J = 25.9 Hz), 113.11 (d, J = 21.9 Hz), 21.84, 19F NMR (376 MHz, CDCl₃) δ -107.86. HRMS (ESI) Calcd for C₁₅H₁₁F₂N₂O₃S (M+H)⁺: 319.0547, Found: 319.0551.

6-chloroquinoxalin-2-yl 4-methylbenzenesulfonate (3f)

White solid, 48% yield, m.p. 93-94 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 8.07 (d, J = 2.3 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 9.0 Hz, 1H), 7.68 (dd, J = 9.0, 2.3 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.13, 146.20, 141.41,
140.21, 138.29, 135.62, 132.11, 129.92, 129.67, 129.12, 128.20, 21.85. HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{11}ClN\textsubscript{2}O\textsubscript{3} (M+H): 335.0252, Found: 335.0267.

6-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3g)

![Image of 6-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3g)]

Off-white solid, 33% yield, m.p. 95-96 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.63 (s, 1H), 8.26 (d, \(J = 2.1\) Hz, 1H), 8.01 (d, \(J = 8.0\) Hz, 2H), 7.82 (dd, \(J = 8.9, 2.1\) Hz, 1H), 7.75 (d, \(J = 8.9\) Hz, 1H), 7.38 (d, \(J = 8.0\) Hz, 2H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 151.22, 146.24, 141.75, 140.21, 138.29, 131.62, 129.96, 129.80, 129.17, 21.90.

HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{11}BrN\textsubscript{2}O\textsubscript{3} (M+H): 378.9747, Found: 378.9758.

6-(trifluoromethyl)quinoxalin-2-yl 4-methylbenzenesulfonate (3h)

![Image of 6-(trifluoromethyl)quinoxalin-2-yl 4-methylbenzenesulfonate (3h)]

White solid, 33% yield, m.p. 134-135 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.75 (s, 1H), 8.23 (d, \(J = 8.7\) Hz, 1H), 8.19 (s, 1H), 8.05 (d, \(J = 8.4\) Hz, 2H), 7.92 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.42 (d, \(J = 8.0\) Hz, 2H), 2.48 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.03, 146.47, 142.21, 141.52, 139.04, 133.21, 133.09, 132.75, 130.62, 130.07, 129.28, 125.56 (q, \(J = 4.3\) Hz), 125.56 (q, \(J = 3.2\) Hz), 124.87, 122.16, 21.96. \(^{19}\)F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta\) -62.74. HRMS (ESI) Calcd for C\textsubscript{16}H\textsubscript{11}F\textsubscript{3}N\textsubscript{2}O\textsubscript{3} (M+Na): 391.0335, Found: 391.0353.

6-nitroquinoxalin-2-yl 4-methylbenzenesulfonate (3i)

![Image of 6-nitroquinoxalin-2-yl 4-methylbenzenesulfonate (3i)]

White solid, 20% yield, m.p. 145-146 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.99 (d, \(J = 2.5\) Hz, 1H), 8.05 (t, \(J = 8.8\) Hz, 3H), 7.92 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.42 (d, \(J = 8.0\) Hz, 2H), 2.48 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.93, 147.72, 146.66, 142.79, 141.62, 139.88, 133.09, 132.75, 130.07, 129.38, 124.70, 21.96. HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{11}N\textsubscript{3}O\textsubscript{5}S (M+Na): 368.0312, Found: 368.0326.

7-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3j)

![Image of 7-bromoquinoxalin-2-yl 4-methylbenzenesulfonate (3j)]

White solid, 47% yield, m.p. 128-129 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.64 (s, 1H), 8.12 – 7.99 (m, 3H), 7.96 (d, \(J = 8.9\) Hz, 1H), 7.86 – 7.77 (m, 1H), 7.41 (d, \(J = 8.0\) Hz, 2H), 2.48 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 151.69, 146.27, 140.49, 140.03, 139.56, 133.40, 130.88, 130.54, 130.00, 129.25, 125.48, 21.95. HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{11}BrN\textsubscript{2}O\textsubscript{3} (M+H): 378.9747, Found: 378.9736.

6,7-difluoroquinoxalin-2-yl 4-methylbenzenesulfonate (3k)

![Image of 6,7-difluoroquinoxalin-2-yl 4-methylbenzenesulfonate (3k)]

White solid, 33% yield, m.p. 95-96 °C. \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.63 (s, 1H), 8.26 (d, \(J = 2.1\) Hz, 1H), 8.01 (d, \(J = 8.0\) Hz, 2H), 7.82 (dd, \(J = 8.9, 2.1\) Hz, 1H), 7.75 (d, \(J = 8.9\) Hz, 1H), 7.38 (d, \(J = 8.0\) Hz, 2H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 151.22, 146.24, 141.75, 140.21, 138.29, 131.62, 129.96, 129.80, 129.17, 123.69, 21.90. HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{11}BrN\textsubscript{2}O\textsubscript{3} (M+H): 335.0252, Found: 335.0267.
White solid, 50% yield, m.p. 133-134 °C. 1H NMR (400 MHz, CDCl3) δ 8.62 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.85 (dd, J = 10.2, 8.1 Hz, 1H), 7.64 (dd, J = 10.3, 7.9 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 153.19 (dd, J = 257.0, 15.8 Hz), 152.16 (dd, J = 255.4, 15.7 Hz), 151.49 (d, J = 3.1 Hz), 146.32, 139.47 (d, J = 3.5 Hz), 138.52 (dd, J = 10.7, 1.6 Hz), 137.27 (dd, J = 11.2, 1.4 Hz), 133.29, 130.00, 129.14, 115.29 (dd, J = 17.7, 2.1 Hz), 114.48 (dd, J = 18.0, 1.8 Hz), 21.90. 19F NMR (376 MHz, CDCl3) δ -127.58 – -127.73 (m), -129.78 (m). HRMS (ESI) Calcd for C15H10Cl2N2O3S (M+Na)+: 359.0272, Found: 359.0289.

6,7-dichloroquinoxalin-2-yl 4-methylbenzenesulfonate (3l)

White solid, 67% yield, m.p. 157-158 °C. 1H NMR (400 MHz, CDCl3) δ 8.62 (s, 1H), 8.20 (s, 1H), 8.08 – 7.94 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 151.80, 146.39, 140.40, 139.88, 138.60, 136.09, 133.25, 130.03, 129.92, 129.23, 129.11, 21.94. HRMS (ESI) Calcd for C15H10Cl2N2O3S (M+Na)+: 390.9681, Found: 390.9685.

6,7-dibromoquinoxalin-2-yl 4-methylbenzenesulfonate (3m)

Off-white solid, 78% yield, m.p. 183-184 °C. 1H NMR (400 MHz, CDCl3) δ 8.63 (s, 1H), 8.40 (s, 1H), 8.19 (s, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 151.80, 146.39, 140.40, 139.88, 138.60, 136.09, 134.50, 133.25, 130.05, 129.11, 21.94. HRMS (ESI) Calcd for C15H16Br2N2O3S (M+Na)+: 478.8671, Found: 478.8691.

6,7-dimethylquinoxalin-2-yl 4-methylbenzenesulfonate (3n)

White solid, 80% yield, m.p. 115-116 °C. 1H NMR (400 MHz, CDCl3) δ 8.54 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.83 (s, 1H), 7.64 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 150.74, 145.89, 142.03, 140.50, 140.42, 138.72, 138.17, 133.59, 129.90, 129.10, 128.33, 127.74, 21.89, 20.48, 20.37. HRMS (ESI) Calcd for C17H16N2O3S (M+Na)+: 351.0774, Found: 351.0785.

quinazolin-4-yl 4-methylbenzenesulfonate (3o)

White solid, 60% yield, m.p. 185-186 °C. 1H NMR (400 MHz, CDCl3) δ 8.77 (s, 1H), 8.14 (d, J = 9.1 Hz, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.78 – 7.70 (m, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 158.62,
146.77, 140.54, 135.65, 133.50, 129.83, 128.33, 128.00, 127.19, 122.08, 21.85. HRMS (ESI) Calcd for C₁₅H₁₅N₂O₃S (M+H)⁺: 301.0641, Found: 301.0652.

**benzo[g]quinoxalin-2-yl 4-methylbenzenesulfonate (3p)**

![benzo[g]quinoxalin-2-yl 4-methylbenzenesulfonate](image)

Yellow solid, 11% yield, m.p. 166-167 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.62 (s, 1H), 8.41 (s, 1H), 8.17 – 7.97 (m, 4H), 7.65 – 7.51 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.44, 146.12, 140.54, 137.69, 135.98, 134.40, 133.50, 129.92, 129.33, 128.75, 128.21, 128.13, 127.65, 127.08, 126.79, 21.90.

**quinolin-2-yl 4-methylbenzenesulfonate (3q)**

![quinolin-2-yl 4-methylbenzenesulfonate](image)

White solid, 58% yield, m.p. 62-63 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.7 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.67 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.50 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 8.7 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.32, 146.06, 145.40, 140.74, 134.08, 130.46, 129.64, 129.07, 128.57, 127.58, 127.11, 126.79, 114.27, 21.78.

**isoquinolin-1-yl 4-methylbenzenesulfonate (3r)**

![isoquinolin-1-yl 4-methylbenzenesulfonate](image)

White solid, 67% yield, m.p. 144-145 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.65 (ddd, J = 8.2, 7.2, 1.4 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.61, 145.89, 136.80, 134.42, 134.00, 129.64, 129.62, 128.44, 127.88, 126.64, 126.38, 125.50, 107.46, 21.86. HRMS (ESI) Calcd for C₁₆H₁₄NO₃S (M+H)⁺: 300.0689, Found: 300.0701.

**pyrazin-2-yl 4-methylbenzenesulfonate (3s)**

![pyrazin-2-yl 4-methylbenzenesulfonate](image)

White solid, 40% yield, m.p. 60-61 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 12.1 Hz, 2H), 8.24 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 154.15, 146.06, 143.04, 142.19, 138.64, 133.28, 130.04, 128.82, 21.90. HRMS (ESI) Calcd for C₁₆H₁₃NO₃S (M+H)⁺: 251.0485, Found: 251.0493.

**pyridin-2-yl 4-methylbenzenesulfonate (3u)**

![pyridin-2-yl 4-methylbenzenesulfonate](image)
Off-white oil, 72% yield. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.28 – 8.21 (m, 1H), 7.88 (d, \( J = 8.4 \) Hz, 2H), 7.76 (ddd, \( J = 8.3, 7.3, 2.0 \) Hz, 1H), 7.33 (d, \( J = 7.9 \) Hz, 2H), 7.20 (ddd, \( J = 7.3, 4.9, 1.0 \) Hz, 1H), 7.09 (d, \( J = 8.2 \) Hz, 1H), 2.43 (s, 3H). \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 157.02, 148.36, 145.37, 140.15, 133.74, 129.76, 128.60, 122.70, 115.95, 21.75. HRMS (ESI) Calcd for \( \text{C}_{12}\text{H}_{11}\text{NO}_3\text{S} \): 250.0532, Found: 250.0539.

\textit{Quinoxalin-2-yl benzenesulfonate (3v)}

![Chemical structure](image)

White solid, 60% yield, m.p. 83-84 °C. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.66 (s, 1H), 8.15 (d, \( J = 8.0 \) Hz, 2H), 8.09 (dd, \( J = 7.8, 2.3 \) Hz, 1H), 7.90 – 7.83 (m, 1H), 7.77 – 7.67 (m, 3H), 7.63 – 7.56 (m, 2H). \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 150.89, 141.28, 139.69, 139.12, 136.43, 134.70, 131.20, 129.84, 129.22, 129.19, 129.02, 128.47. HRMS (ESI) Calcd for \( \text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_3\text{S} \): 287.0485, Found: 287.0471.

\textit{Quinoxalin-2-yl 4-methoxybenzenesulfonate (3w)}

![Chemical structure](image)

Off-white solid, 61% yield, m.p. 76-78 °C. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.65 (s, 1H), 8.15 – 8.01 (m, 3H), 7.93 – 7.84 (m, 1H), 7.80 – 7.67 (m, 2H), 7.03 (d, \( J = 8.0 \) Hz, 2H), 3.88 (s, 3H). \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 164.56, 151.02, 141.17, 139.72, 139.21, 131.46, 131.11, 129.70, 129.15, 128.47, 127.40, 114.41, 55.83. HRMS (ESI) Calcd for \( \text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4\text{S} \): 339.0410, Found: 339.0410.

\textit{Quinoxalin-2-yl [1,1'-biphenyl]-4-sulfonate (3y)}

![Chemical structure](image)

White solid, 58% yield, m.p. 84-85 °C. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.67 (s, 1H), 8.08 (d, \( J = 8.7 \) Hz, 3H), 7.95 – 7.85 (m, 1H), 7.82 – 7.67 (m, 2H), 7.61 (d, \( J = 8.7 \) Hz, 2H), 1.35 (s, 9H). \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 158.91, 150.99, 147.60, 141.28, 139.80, 139.24, 133.29, 131.14, 129.76, 129.19, 128.96, 128.54, 126.28, 35.46, 31.04. HRMS (ESI) Calcd for \( \text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{S} \): 343.1111, Found: 343.1096.

\textit{Quinoxalin-2-yl [1,1'-biphenyl]-4-sulfonate (3y)}

![Chemical structure](image)

White solid, 56% yield, m.p. 96-97 °C. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.69 (s, 1H), 8.22 (d, \( J = 8.0 \) Hz, 2H), 8.14 – 8.05 (m, 1H), 7.95 – 7.85 (m, 1H), 7.84 – 7.68 (m, 4H), 7.61 (d, \( J = 7.2 \) Hz, 2H), 7.52 – 7.38 (m, 3H). \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 150.97, 147.60, 141.28, 139.71,
139.15, 138.79, 134.82, 131.19, 129.81, 129.20, 129.16, 128.94, 128.48, 127.72, 127.42. HRMS (ESI) Calcd for C_{20}H_{14}N_{2}O_{3}S (M+Na)^+: 385.0617, Found: 385.0636.

**quinoxalin-2-yl 4-acetamidobenzenesulfonate (3z)**

![Diagram of quinoxalin-2-yl 4-acetamidobenzenesulfonate]

White solid, 60% yield, m.p. 42-43 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.34 (s, 1H), 8.12 – 8.01 (m, 3H), 7.89 – 7.82 (m, 1H), 7.82 – 7.70 (m, 2H), 7.33 – 7.23 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.34, 150.94, 144.17, 141.25, 139.69, 139.03, 131.36, 130.54, 130.19, 129.96, 129.21, 128.44, 119.17, 24.78. HRMS (ESI) Calcd for C_{16}H_{13}N_{3}O_{4}S (M+H)^+: 344.0700, Found: 344.0710.

**quinoxalin-2-yl 4-fluorobenzenesulfonate (3aa)**

![Diagram of quinoxalin-2-yl 4-fluorobenzenesulfonate]

White solid, 73% yield, m.p. 100-101 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.26 – 8.15 (m, 2H), 8.14 – 8.05 (m, 1H), 7.92 – 7.82 (m, 1H), 7.80 – 7.70 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 166.31 (d, J = 256.4 Hz), 150.89, 141.31, 139.57, 139.05, 132.45 (d, J = 3.4 Hz), 132.16 (d, J = 9.7 Hz), 131.28, 129.90, 129.25, 128.38, 116.60 (d, J = 22.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -101.38 (m). HRMS (ESI) Calcd for C_{14}H_{9}FN_{2}O_{3}S (M+H)^+: 305.0390, Found: 305.0396.

**quinoxalin-2-yl 4-chlorobenzenesulfonate (3ab)**

![Diagram of quinoxalin-2-yl 4-chlorobenzenesulfonate]

White solid, 61% yield, m.p. 98-99 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.16 – 8.05 (m, 3H), 7.90 – 7.82 (m, 1H), 7.76 (td, J = 6.4, 3.4 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.86, 141.48, 141.34, 139.55, 139.00, 134.97, 131.32, 130.60, 129.95, 129.54, 129.27, 128.39. HRMS (ESI) Calcd for C_{14}H_{9}ClN_{2}O_{3}S (M+H)^+: 321.0095, Found: 321.0079.

**quinoxalin-2-yl 4-iodobenzenesulfonate (3ac)**

![Diagram of quinoxalin-2-yl 4-iodobenzenesulfonate]

White solid, 50% yield, m.p. 121-122 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.15 – 8.07 (m, 1H), 7.96 (d, J = 8.6 Hz, 2H), 7.91 – 7.83 (m, 3H), 7.81 – 7.72 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.90, 141.40, 139.62, 139.04, 138.56, 136.26, 131.36, 130.37, 129.99, 129.33, 128.48, 102.94. HRMS (ESI) Calcd for C_{14}H_{9}I_{2}N_{2}O_{3}S (M+H)^+: 412.9451, Found: 412.9466.

**quinoxalin-2-yl 2-bromobenzenesulfonate (3ad)**

![Diagram of quinoxalin-2-yl 2-bromobenzenesulfonate]
White solid, 82% yield, m.p. 98-99 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.73 (s, 1H), 8.27 (dt, J = 7.3, 1.7 Hz, 1H), 7.79 (dt, J = 7.8, 1.4 Hz, 1H), 7.77 – 7.67 (m, 3H), 7.58 – 7.47 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.68, 141.19, 139.42, 138.66, 136.75, 135.60, 135.27, 132.72, 131.15, 129.83, 129.07, 128.35, 127.66, 120.96. HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$O$_3$S (M+H)$^+$: 364.9590, Found: 364.9572.

**quinoxalin-2-yl 3-bromobenzenesulfonate (3ae)**

![quinoxalin-2-yl 3-bromobenzenesulfonate (3ae)](image)

Off-white solid, 55% yield, m.p. 62-63 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.37 (s, 1H), 8.15 – 8.04 (m, 2H), 7.91 – 7.84 (m, 1H), 7.84 – 7.72 (m, 3H), 7.48 (t, J = 8.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.85, 141.37, 139.50, 138.85, 138.28, 137.66, 132.27, 131.39, 130.63, 129.98, 129.28, 128.41, 127.62, 122.93. HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$O$_3$S (M+H)$^+$: 364.9590, Found: 364.9573.

**quinoxalin-2-yl 4-bromobenzenesulfonate (3af)**

![quinoxalin-2-yl 4-bromobenzenesulfonate (3af)](image)

White solid, 63% yield, m.p. 118-119 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.12 – 8.06 (m, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.91 – 7.81 (m, 1H), 7.74 (dd, J = 8.5, 5.8 Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.80, 141.27, 139.48, 138.93, 135.48, 132.49, 131.27, 130.56, 130.07, 129.89, 129.21, 128.34. HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$O$_3$S (M+H)$^+$: 364.9590, Found: 364.9573.

**quinoxalin-2-yl 4-(trifluoromethyl)benzenesulfonate (3ag)**

![quinoxalin-2-yl 4-(trifluoromethyl)benzenesulfonate (3ag)](image)

White solid, 41% yield, m.p. 108-109 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.64 (s, 1H), 8.25 (d, J = 8.2 Hz, 2H), 8.12 – 8.01 (m, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.80 – 7.75 (m, 1H), 7.75 – 7.67 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.90, 141.43, 140.22, 139.60, 138.97, 137.04 – 135.25 (q, J = 33.0 Hz), 131.59, 130.25, 129.86, 129.36, 128.47, 126.44 (q, J = 3.7 Hz), 124.46, 121.74. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.36. HRMS (ESI) Calcd for C$_{15}$H$_9$F$_3$N$_2$O$_3$S (M+H)$^+$: 355.0359, Found: 355.0349.

**quinoxalin-2-yl 4-cyanobenzenesulfonate (3ah)**

![quinoxalin-2-yl 4-cyanobenzenesulfonate (3ah)](image)
White solid, 61% yield, m.p. 135-136 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 1H), 8.31 (d, $J = 8.4$ Hz, 2H), 8.18 – 8.06 (m, 1H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.87 – 7.72 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.69, 141.45, 140.76, 139.35, 138.78, 132.91, 131.51, 130.18, 129.77, 129.32, 128.26, 118.26, 116.97. HRMS (ESI) Calcd for C$_{13}$H$_9$N$_3$O$_3$S (M+Na)$^+$: 334.0257, Found: 334.0268.

**methyl 4-((quinoxalin-2-ylxy)sulfonyl)benzoate (3ai)**

White solid, 36% yield, m.p. 104-105 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.23 (s, 4H), 8.14 – 8.07 (m, 1H), 7.83 (ddd, $J = 7.9$, 3.1, 1.4 Hz, 1H), 7.75 (dd, $J = 5.4$, 4.7, 3.3 Hz, 2H), 3.96 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.37, 150.88, 141.46, 140.45, 139.62, 139.02, 135.63, 131.40, 130.33, 130.07, 129.34, 128.48, 52.92. HRMS (ESI) Calcd for C$_{16}$H$_{12}$N$_2$O$_5$S (M+Na)$^+$: 367.0359, Found: 367.0376.

**quinoxalin-2-yl naphthalene-2-sulfonate (3ak)**

White solid, 66% yield, m.p. 77-78 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 1H), 8.67 (s, 1H), 8.11 (dd, $J = 8.7$, 1.9 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.98 (dd, $J = 11.4$, 8.4 Hz, 2H), 7.89 (dd, $J = 8.1$, 1.3 Hz, 1H), 7.73 – 7.56 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.94, 141.22, 139.65, 139.09, 135.64, 133.18, 131.84, 131.30, 131.14, 129.84, 129.76, 129.50, 129.45, 129.14, 128.42, 128.03, 127.92, 123.23. HRMS (ESI) Calcd for C$_{18}$H$_{12}$N$_2$O$_3$S (M+Na)$^+$: 359.0461, Found: 359.0460.

**quinoxalin-2-yl naphthalene-1-sulfonate (3al)**

White solid, 50% yield, m.p. 119-120 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, $J = 8.7$ Hz, 1H), 8.61 (s, 1H), 8.43 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.07 – 7.99 (m, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.79 – 7.53 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.94, 141.28, 139.76, 138.95, 136.21, 134.16, 132.17, 131.58, 131.11, 129.82, 129.17, 129.12, 128.60, 128.56, 127.43, 124.74, 124.07. HRMS (ESI) Calcd for C$_{18}$H$_{12}$N$_2$O$_3$S (M+H)$^+$: 337.0641, Found: 337.0646.

**quinoxalin-2-yl 2,3-dihydrobenzo[b][1,4]dioxine-6-sulfonate (3am)**

White solid, 61% yield, m.p. 135-136 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 1H), 8.31 (d, $J = 8.4$ Hz, 2H), 8.18 – 8.06 (m, 1H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.87 – 7.72 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.69, 141.45, 140.76, 139.35, 138.78, 132.91, 131.51, 130.18, 129.77, 129.32, 128.26, 118.26, 116.97. HRMS (ESI) Calcd for C$_{13}$H$_9$N$_3$O$_3$S (M+Na)$^+$: 334.0257, Found: 334.0268.
White solid, 50% yield, m.p. 110-111 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.13 – 8.04 (m, 1H), 7.95 – 7.86 (m, 1H), 7.74 (tt, J = 7.0, 5.1 Hz, 2H), 7.67 (d, J = 2.3 Hz, 1H), 7.60 (dd, J = 8.6, 2.3 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 4.35 – 4.25 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 151.02, 149.28, 143.69, 141.25, 139.82, 139.21, 131.19, 129.78, 129.20, 128.58, 128.12, 123.03, 118.85, 117.88, 64.75, 64.17. HRMS (ESI) Calcd for C₁₆H₁₂N₂O₅S (M+H): 345.0540, Found: 345.0549.

quinoxalin-2-yl thiophene-2-sulfonate (3an)

White solid, 70% yield, m.p. 117-118 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.18 – 8.09 (m, 1H), 8.03 – 7.93 (m, 2H), 7.85 – 7.73 (m, 3H), 7.17 (dd, J = 5.0, 3.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.05, 141.47, 139.77, 139.07, 136.67, 135.73, 135.62, 131.37, 130.02, 129.38, 128.61, 127.65. HRMS (ESI) Calcd for C₁₂H₈N₂O₃S₂ (M+Na): 314.9869, Found: 314.9883.

quinoxalin-2-yl pyridine-3-sulfonate (3ao)

White solid, 60% yield, m.p. 74-75 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 1H), 8.93 (dd, J = 4.9, 1.6 Hz, 1H), 8.71 (s, 1H), 8.48 (dt, J = 8.2, 1.9 Hz, 1H), 8.19 – 8.07 (m, 1H), 7.86 (dt, J = 8.1, 2.8 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.58 (dd, J = 8.1, 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.92, 150.94, 150.09, 141.49, 139.46, 138.83, 136.89, 133.79, 131.51, 130.13, 129.38, 128.42, 123.75. HRMS (ESI) Calcd for C₁₂H₈N₂O₃S (M+Na): 310.0257, Found: 310.0256.

quinoxalin-2-yl ethanesulfonate (3ap)

White solid, 12% yield, m.p. 76-77 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 8.16 (d, J = 9.4 Hz, 1H), 7.99 (d, J = 9.7 Hz, 1H), 7.87 – 7.74 (m, 2H), 3.83 (q, J = 7.4 Hz, 2H), 1.64 (d, J = 14.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.06, 142.08, 141.17, 138.93, 3.83 (q, J = 7.4 Hz, 2H), 1.64 (d, J = 14.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.22, 151.50, 141.50, 139.72, 139.53, 131.41, 130.03, 129.39, 128.52, 48.84, 8.37. HRMS (ESI) Calcd for C₁₀H₁₀N₂O₃ (M+H): 239.0485, Found: 239.0496.

3-(quinoxalin-2-yl)prop-2-yn-1-ol (4a)

The title compound was known.[3] White solid, 65% yield (2 steps). ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.15 – 8.01 (m, 2H), 7.86 – 7.72 (m, 2H), 4.64 (s, 2H), 3.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 147.06, 142.08, 141.17, 138.93, 131.00, 130.87, 129.29, 129.22, 92.52, 83.05, 51.39. HRMS (ESI) Calcd for C₁₁H₈N₂O (M+H): 185.0709, Found: 185.0717.
2-(3,4-dimethoxyphenyl)-6,7-dimethylquinoxaline (4b)

\[ \text{Me} \quad \text{N} \quad \text{OMe} \quad \text{Me} \]

The title compound was known.\[^{[5]}\] White solid, 52% yield (2 steps). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.19 (s, 1H), 7.89 (s, 1H), 7.83 (s, 2H), 7.69 (dd, $J$ = 8.4, 2.1 Hz, 1H), 7.01 (d, $J$ = 8.4 Hz, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 2.50 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.02, 150.61, 149.82, 142.16, 141.22, 140.86, 140.24, 139.81, 130.01, 128.53, 128.20, 120.31, 111.33, 110.26, 56.20, 56.14, 20.46, 20.40. HRMS (ESI) Calcd for C$_{18}$H$_{18}$N$_2$O$_2$ (M+Na)$^+$: 317.1261, Found: 317.1276.

4-(6,7-dimethylquinoxalin-2-yl)benzene-1,2-diol (4c)

\[ \text{Me} \quad \text{N} \quad \text{OH} \]

The title compound was known.\[^{[5]}\] Orange solid, 49% yield (3 steps). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.29 (s, 1H), 7.80 (s, 2H), 7.75 (s, 1H), 7.62 (d, $J$ = 8.3 Hz, 1H), 6.90 (d, $J$ = 8.3 Hz, 1H), 2.46 (s, 6H). $^{13}$C NMR (100 MHz, DMSO) δ 150.29, 148.78, 146.30, 142.14, 140.93, 138.92, 138.75, 137.51, 137.10, 127.56, 127.48, 127.10, 118.95, 115.89, 113.95, 19.78, 19.65. HRMS (ESI) Calcd for C$_{16}$H$_{14}$N$_2$O$_2$ (M+H)$^+$: 267.1128, Found: 267.1128.

6,7-dimethyl-2-phenylquinoxaline (4d)

\[ \text{Me} \quad \text{N} \quad \text{Me} \]

The title compound was known.\[^{[6]}\] White solid, 52% yield (2 steps). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.17 (s, 1H), 8.16 – 8.09 (m, 2H), 7.82 (d, $J$ = 12.2 Hz, 2H), 7.54 – 7.41 (m, 3H), 2.44 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.93, 142.04, 140.74, 140.47, 140.08, 137.11, 129.84, 129.05, 128.69, 128.12, 127.38, 20.35, 20.34, 20.32. HRMS (ESI) Calcd for C$_{16}$H$_{14}$N$_2$ (M+H)$^+$: 235.1230, Found: 235.1237.

(E)-1-(tert-butyl)-4-(2-tosylvinyl)benzene (5)

\[ \text{4-PhMe-4} \]

The title compound was known.\[^{[7]}\] White solid, 18% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 8.5 Hz, 2H), 7.64 (d, $J$ = 15.4 Hz, 1H), 7.41 (s, 4H), 7.36 – 7.28 (m, 2H), 6.81 (d, $J$ = 15.5 Hz, 1H), 2.42 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.96, 144.33, 142.04, 138.14, 130.02, 129.83, 128.51, 127.75, 126.78, 126.16, 35.09, 31.21, 21.71. HRMS (ESI) Calcd for C$_{19}$H$_{23}$O$_2$S (M+Na)$^+$: 337.1233, Found: 337.1240.

4,4'-Dimethyldiphenyl disulfone (7)

\[ \text{PhMe-4} \]

The title compound was known.\[^{[1]}\] White solid, 18% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 8.5 Hz, 2H), 7.64 (d, $J$ = 15.4 Hz, 1H), 7.41 (s, 4H), 7.36 – 7.28 (m, 2H), 6.81 (d, $J$ = 15.5 Hz, 1H), 2.42 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.96, 144.33, 142.04, 138.14, 130.02, 129.83, 128.51, 127.75, 126.78, 126.16, 35.09, 31.21, 21.71. HRMS (ESI) Calcd for C$_{19}$H$_{23}$O$_2$S (M+Na)$^+$: 337.1233, Found: 337.1240.
The title compound was known.[8] White solid, 4% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 8.4\) Hz, 4H), 7.43 (d, \(J = 8.4\) Hz, 4H), 2.51 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.29, 131.65, 130.56, 128.02, 22.19. HRMS (ESI) Calcd for C\(_{14}\)H\(_{14}\)O\(_2\)S\(_2\) (M+Na): 333.0231, Found: 333.0227.

11. References


12. X-ray Crystal Structure of Compound 3n

![X-ray Crystal Structure of Compound 3n](image)

**Table 1.** Crystal data and structure refinement for CCDC 2162074.

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13. Copies of product NMR Spectra