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I. General Information

Commercial reagents, photocatalysts, thiol catalysts, \( p \)-toluenesulfonic acid monohydrate (TsOH), and dimethyl sulfoxide (DMSO) were purchased from Sigma–Aldrich and Acros Organics, and used directly without purification. All heteroarenes and alcohols were used directly from commercial suppliers. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. Chromatographic purification of products was accomplished by flash chromatography on silica gel (Fluka, 230-400 mesh). Thin layer chromatography (TLC) was performed on Analtech Uniplate 0.25 mm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, \( p \)-anisaldehyde, potassium permanganate, or ceric ammonium molybdate stain. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz (125 MHz) instrument, and are internally referenced to residual protio solvent signals (note: CDCl\(_3\) referenced at 7.26 and 77.0 ppm respectively; CD\(_3\)OD referenced at 3.31 and 49.0 ppm respectively). Data for \(^1\)H NMR are reported as follows: chemical shift (\( \delta \) ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz) and integration. Data for \(^{13}\)C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (\( \text{cm}^{-1} \)). High resolution mass spectra were obtained at Princeton University mass spectrometry facilities on Agilent Technologies 6220 Time-Of-Flight LC/MS with electrospray ionization method.
II. Mechanistic Studies

Fig. S1. Stern-Volmer quenching experiments of the heteroarene and thiol catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Control Conditions</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>w/o photocatalyst</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>w/o light</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>w/o acid</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>w/o thiol</td>
<td>3%</td>
</tr>
<tr>
<td>5</td>
<td>standard conditions, w/ all</td>
<td>98%</td>
</tr>
</tbody>
</table>

1H NMR yield using TsOH as the internal standard.

Fig. S2. Control experiments.
**Fig. S3. Radical quenching experiments with TEMPO and 1,1-diphenylethylene.**

<table>
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<tr>
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<th>Radical Scavenger</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>TEMPO (1.0 equiv.)</td>
<td>23%</td>
</tr>
<tr>
<td>2</td>
<td>TEMPO (2.0 equiv)</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>1,1-diphenylethylene (1.0 equiv.)</td>
<td>0%</td>
</tr>
</tbody>
</table>

$^1$H NMR yield using TsOH as the internal standard; TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy.

**Fig. S4. Light on and off experiments.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light On and Off Conditions</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>on 4 h</td>
<td>28%</td>
</tr>
<tr>
<td>2</td>
<td>on 4 h, off 16 h</td>
<td>28%</td>
</tr>
<tr>
<td>3</td>
<td>on 20 h</td>
<td>98%</td>
</tr>
</tbody>
</table>

$^1$H NMR yield using TsOH as the internal standard.

**Fig. S5. Deuterium-labeling experiments.**

**Fig. S6. Oxygen effect to the alkylation reaction.**

**Fig. S7. Radical trapping experiments with olefins and arenes.**
III. Reaction Setup

Fig. S8. Reaction setup with the magnetic stirrer, blue LED strip circled inside the glass dish (covered with aluminum foil outside), vial rack, and mini fan.

IV. Reaction optimization

$$\text{Ir(ppy)$_2$(dtbbpy)}PF_6 \text{ (1 mol%)}$$
$$\text{TFA (1 equiv.), solvent [0.5 M]}$$
$$\text{rt, 48 h, 26 W CFL}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Product</th>
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<tbody>
<tr>
<td>1</td>
<td>acetonitrile</td>
<td>16%</td>
</tr>
<tr>
<td>2</td>
<td>propionitrile</td>
<td>22%</td>
</tr>
<tr>
<td>3</td>
<td>$N,N$-dimethylacetamide</td>
<td>31%</td>
</tr>
<tr>
<td>4</td>
<td>$N,N$-dimethylformamide</td>
<td>33%</td>
</tr>
<tr>
<td>5</td>
<td>dimethyl sulfoxide (DMSO)</td>
<td>56%</td>
</tr>
<tr>
<td>6</td>
<td>dichloromethane</td>
<td>20%</td>
</tr>
<tr>
<td>7</td>
<td>1,2-dichloroethane</td>
<td>21%</td>
</tr>
<tr>
<td>8</td>
<td>chloroform</td>
<td>29%</td>
</tr>
<tr>
<td>9</td>
<td>1,2-dimethoxyethane</td>
<td>19%</td>
</tr>
<tr>
<td>10</td>
<td>ethyl acetate</td>
<td>16%</td>
</tr>
<tr>
<td>11</td>
<td>toluene</td>
<td>10%</td>
</tr>
<tr>
<td>12</td>
<td>acetone</td>
<td>13%</td>
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</tbody>
</table>

$^1$H NMR yield using 1,3-benzodioxole as the internal standard.

Fig. S9. Solvent evaluation.
Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%)  
TFA (1 equiv.), DMSO [0.5 M]  
rt, 48 h, 26 W CFL

**Fig. S10. Organocatalyst evaluation.**

<table>
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<th>Entry</th>
<th>Light Source</th>
<th>Photocatalyst</th>
<th>Product</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>26 W CFL w/ fan, 23 °C</td>
<td>1 mol%</td>
<td>51%</td>
</tr>
<tr>
<td>2</td>
<td>26 W CFL w/o fan, 29 °C</td>
<td>1 mol%</td>
<td>62%</td>
</tr>
<tr>
<td>3</td>
<td>blue LEDs w/ fan, 23 °C</td>
<td>1 mol%</td>
<td>91%</td>
</tr>
<tr>
<td>4</td>
<td>blue LEDs w/o fan, 45 °C</td>
<td>1 mol%</td>
<td>83%</td>
</tr>
<tr>
<td>5</td>
<td>2 X 34 W LED w/ fan, 40 °C</td>
<td>1 mol%</td>
<td>79%</td>
</tr>
</tbody>
</table>

$^1$H NMR yield using 1,3-benzodioxole as the internal standard.

**Fig. S11. Light source evaluation.**

<table>
<thead>
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<th>Entry</th>
<th>Acid</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TFA</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>conc. HCl</td>
<td>9%</td>
</tr>
<tr>
<td>3</td>
<td>HBF$_4$ (48 wt.% in H$_2$O)</td>
<td>73%</td>
</tr>
<tr>
<td>4</td>
<td>HClO$_4$ (70%)</td>
<td>85%</td>
</tr>
<tr>
<td>5</td>
<td>conc. H$_2$SO$_4$</td>
<td>75%</td>
</tr>
<tr>
<td>6</td>
<td>TsOH</td>
<td>89%</td>
</tr>
<tr>
<td>7</td>
<td>TsOH (1 equiv.)</td>
<td>73%</td>
</tr>
</tbody>
</table>

$^1$H NMR yield using 1,3-benzodioxole as the internal standard.

**Fig. S12. Acid evaluation.**
**Fig. S13. Organocatalyst comparisons.**

**V. Experimental Procedures and Product Characterization**

**General Procedure A for the Alkylation (Heteroarene Scope):** To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), heteroarene (0.50 mmol, 1.0 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, and added with ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. Upon reaction completion as judged by TLC and LCMS (20-48 hours), the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL), dried over Na$_2$SO$_4$, and concentrated *in vacuo*. Purification
of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

**General Procedure B for the Alkylation (Alcohol Scope):** To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), alcohol (5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, and added with methyl thioglycolate (2.5 µL, 25.0 µmol, 0.05 equiv.), then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. Upon reaction completion as judged by TLC and LCMS (20-48 hours), the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

![1-Methylisoquinoline (15)](image)

**1-Methylisoquinoline (15):** According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and
purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (65.6 mg, 92% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.39 (d, $J = 5.8$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.66 (dd, $J = 8.1, 6.8$ Hz, 1H), 7.58 (dd, $J = 8.2, 6.8$ Hz, 1H), 7.49 (d, $J = 5.8$ Hz, 1H), 2.95 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.5, 141.8, 135.8, 129.9, 127.4, 127.1, 127.0, 125.6, 119.2, 22.4; HRMS (ESI) m/z calculated for C$_{10}$H$_{10}$N [(M+H)$^+$] 144.0808, found 144.0813. IR (film) 3051, 1622, 1390, 1357, 1241, 1020, 963 cm$^{-1}$. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **52**, 6983–6987 (2013).

![1,3-Dimethylisoquinoline (16)](image)

1,3-Dimethylisoquinoline (16): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 3-methylisoquinoline (73.1 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropanoate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (71.5 mg, 91% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.60 (dd, $J = 8.2, 6.7$ Hz, 1H), 7.49 (dd, $J = 8.2, 6.7$ Hz, 1H), 7.32 (s, 1H), 2.93 (s, 3H), 2.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.0, 150.2, 136.6, 129.8, 126.6, 126.0, 125.6, 125.5, 117.1, 24.2, 22.3; HRMS (ESI) m/z calculated for C$_{11}$H$_{12}$N [(M+H)$^+$] 158.0964, found 158.0965. IR (film) 2919, 1625, 1591, 1567, 1441, 1391, 1361, 1182,
873 cm$^{-1}$. Spectra data are consistent with those reported in the literature: Tetrahedron Lett. 50, 2305–2308 (2009).

**Methyl 1-Methylisoquinoline-3-carboxylate (17):** According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 3-isoquinolinecarboxylate (95.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (98.5 mg, 98% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.43 (s, 1H), 8.15 (d, $J$ = 8.3 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.72 (m, 2H), 4.02 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 166.4, 159.3, 140.3, 135.4, 130.6, 129.3, 128.9, 128.6, 125.7, 122.9, 52.8, 22.6; HRMS (ESI) m/z calculated for C$_{12}$H$_{12}$NO$_2$ [(M+H)$^+$] 202.0863, found 202.0866. IR (film) 2950, 1712, 1286, 1239, 1149, 1108, 1001, 902 cm$^{-1}$. Spectra data are consistent with those reported in the literature: J. Org. Chem. 79, 7041–7050 (2014).
5-Bromo-1-methylisoquinoline (18): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 5-bromoisoquinoline (105.1 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (94.3 mg, 85% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.48 (d, $J = 6.0$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 6.0$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 2.97 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.0, 143.2, 135.1, 133.7, 128.5, 127.3, 125.3, 122.3, 118.1, 22.6; HRMS (ESI) m/z calculated for C$_{10}$H$_9$BrN [(M+H)$^+$] 221.9913, found 221.9912. IR (film) 3038, 1575, 1485, 1401, 1342, 1220, 1076, 829 cm$^{-1}$.

![19a and 19b](image)

2-Methylquinoline (19a) and 4-Methylquinoline (19b): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), quinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (30.8 mg, 43% yield for 19a; 15.8 mg, 22% yield for 19b). Compound 19a: $^1$H NMR (500 MHz,
CDCl₃): δ 8.04 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 2.75 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 159.0, 147.8, 136.1, 129.4, 128.6, 127.5, 126.4, 125.6, 122.0, 25.4; HRMS (ESI) m/z calculated for C₁₀H₁₀N [(M+H)⁺] 144.0808, found 144.0813. IR (film) 3055, 1601, 1506, 1423, 1220, 1116, 1009, 819 cm⁻¹. Compound 19b: ¹H NMR (500 MHz, CDCl₃): δ 8.78 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.71 (dd, J = 8.4, 6.6 Hz, 1H), 7.57 (dd, J = 8.2, 6.8 Hz, 1H), 7.24 (d, J = 4.3 Hz, 1H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 150.2, 148.0, 144.3, 130.0, 129.1, 128.3, 126.3, 123.8, 121.9, 18.7; HRMS (ESI) m/z calculated for C₁₀H₁₀N [(M+H)⁺] 144.0808, found 144.0812. IR (film) 2925, 1595, 1508, 1454, 1391, 1305, 1138, 838 cm⁻¹. Spectra data are consistent with those reported in the literature: J. Am. Chem. Soc. 136, 11910–11913 (2014).

2,4-Dimethylquinoline (20): According to the general procedure A, Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-methylquinoline (67.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (74.6 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.66 (dd, J = 8.4, 6.8 Hz, 1H), 7.49
(dd, $J = 8.3, 6.8$ Hz, 1H), 7.13 (s, 1H), 2.69 (s, 3H), 2.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.6, 147.6, 144.1, 129.1, 129.0, 126.5, 125.3, 123.5, 122.6, 25.2, 18.5; HRMS (ESI) m/z calculated for C$_{11}$H$_{12}$N [(M+H)$^+$] 158.0964, found 158.0967. IR (film) 2920, 1602, 1562, 1446, 1372, 1192, 1025, 858 cm$^{-1}$. Spectra data are consistent with those reported in the literature: Org. Lett. 10, 173–175 (2008).

$\text{2,4-Dimethylquinoline (21)}$: According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-methylquinoline (66.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (73.1 mg, 93% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.66 (dd, $J = 8.5, 6.8$ Hz, 1H), 7.48 (dd, $J = 8.3, 6.8$ Hz, 1H), 7.11 (s, 1H), 2.68 (s, 3H), 2.64 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.6, 147.7, 144.1, 129.1, 129.0, 126.5, 125.3, 123.5, 122.7, 25.2, 18.5; HRMS (ESI) m/z calculated for C$_{11}$H$_{12}$N [(M+H)$^+$] 158.0964, found 158.0964. IR (film) 2919, 1602, 1562, 1445, 1372, 1192, 1035, 858 cm$^{-1}$. Spectra data are consistent with those reported in the literature: Org. Lett. 10, 173–175 (2008).
4-Methyl-2-phenylquinoline (22): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-phenylquinoline (103.7 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (99.9 mg, 91% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J$ = 8.3 Hz, 1H), 8.17 (m, 2H), 7.99 (d, $J$ = 8.3 Hz, 1H), 7.73 (t, $J$ = 7.0 Hz, 1H), 7.71 (s, 1H), 7.55 (t, $J$ = 7.0 Hz, 1H), 7.53 (m, 2H), 7.47 (m, 1H), 2.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.0, 148.1, 144.7, 139.8, 130.2, 129.3, 129.1, 128.7 (2C), 127.5 (2C), 127.2, 126.0, 123.6, 119.7, 19.0; HRMS (ESI) m/z calculated for C$_{16}$H$_{14}$N [(M+H)$^+$] 220.1121, found 220.1121. IR (film) 3059, 1596, 1495, 1450, 1347, 1028, 861 cm$^{-1}$. Spectra data are consistent with those reported in the literature: J. Am. Chem. Soc. 136, 11910–11913 (2014).

6-Bromo-2,4-dimethylquinoline (23): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 6-bromo-2-methylquinoline (115.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of
DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (105.0 mg, 89% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.05 (s, 1H), 7.85 (d, $J$ = 8.9 Hz, 1H), 7.71 (dd, $J$ = 8.9, 2.2 Hz, 1H), 7.12 (s, 1H), 2.66 (s, 3H), 2.59 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.2, 146.3, 143.2, 132.4, 130.9, 127.8, 126.0, 123.4, 119.3, 25.2, 18.5; HRMS (ESI) m/z calculated for C$_{11}$H$_{11}$BrN [(M+H)$^+$] 236.0069, found 236.0070. IR (film) 2915, 1600, 1496, 1370, 1216, 1071, 867 cm$^{-1}$.

![Image of 1-Methylphthalazine (24)](image)

**1-Methylphthalazine (24):** According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), phthalazine (66.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (50% ethyl acetate/hexanes) to provide the title compound as a white solid (50.5 mg, 70% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 9.39 (s, 1H), 8.07 (d, $J$ = 7.7 Hz, 1H), 7.87-7.93 (m, 3H), 3.00 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 157.3, 150.5, 132.4, 132.1, 126.7, 126.2, 126.1, 124.2, 19.8; HRMS (ESI) m/z calculated for C$_9$H$_9$N$_2$ [(M+H)$^+$] 145.0760, found 145.0765. IR (film) 3386, 1556, 1495, 1397, 1376, 1235, 952, 895 cm$^{-1}$.
6-Methylphenanthridine (25): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), phenanthridine (91.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (90.0 mg, 93% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.57 (d, $J = 8.1$ Hz, 1H), 8.50 (d, $J = 8.1$ Hz, 1H), 8.17 (d, $J = 8.2$ Hz, 1H), 8.10 (d, $J = 8.1$ Hz, 1H), 7.79 (t, $J = 7.1$ Hz, 1H), 7.70 (t, $J = 7.1$ Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 3.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 158.8, 143.6, 132.4, 129.3, 128.5, 127.2, 126.4, 126.2, 125.8, 123.7, 122.2, 121.9, 23.4; HRMS (ESI) m/z calculated for C$_{14}$H$_{12}$N [(M+H)$^+$] 194.0964, found 194.0964. IR (film) 3066, 1611, 1585, 1485, 1373, 1138, 1035, 860 cm$^{-1}$. Spectra data are consistent with those reported in the literature: Org. Lett. 16, 4642–4645 (2014).

Methyl 4,6-dimethylnicotinate (26): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 6-methylnicotinate (78.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-
mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (67.7 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.96 (s, 1H), 7.03 (s, 1H), 3.90 (s, 3H), 2.57 (s, 3H), 2.54 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 166.7, 161.8, 151.4, 149.6, 125.9, 122.9, 51.9, 24.4, 21.2; HRMS (ESI) m/z calculated for C₉H₁₂NO₂ [(M+H)+] 166.0863, found 166.0868. IR (film) 2953, 1720, 1600, 1439, 1281, 1169, 1089, 780 cm⁻¹. Spectra data are consistent with those reported in the literature: J. Org. Chem. 46, 3040–3048 (1981).

![Methyl 4,6-dimethylpicolinate (27)](image-url)

**Methyl 4,6-dimethylpicolinate (27):** According to the general procedure A, Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 6-methylpicolinate (78.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (66.5 mg, 81% yield). ¹H NMR (500 MHz, CDCl₃): δ 7.78 (s, 1H), 7.15 (s, 1H), 3.97 (s, 3H), 2.59 (s, 3H), 2.37 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 166.2, 158.7, 148.4, 147.3, 127.6,
123.5, 52.9, 24.4, 20.8; HRMS (ESI) m/z calculated for C₉H₁₂NO₂ [(M+H)+] 166.0863, found 166.0864. IR (film) 2953, 1718, 1607, 1438, 1332, 1237, 1196, 1017 cm⁻¹.

**4,6-Dimethylnicotinamide (28):** According to the general procedure A, Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 6-methylnicotinamide (69.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% methanol/ethyl acetate, containing 0.1% triethylamine) to provide the title compound as a white solid (62.3 mg, 83% yield). ¹H NMR (500 MHz, CD₃OD): δ 8.43 (s, 1H), 7.22 (s, 1H), 4.88 (br s, 2H), 2.51 (s, 3H), 2.46 (s, 3H); ¹³C NMR (125 MHz, CD₃OD): δ 172.4, 160.7, 148.6, 147.7, 131.3, 126.9, 23.6, 19.6; HRMS (ESI) m/z calculated for C₈H₁₁N₂O [(M+H)+] 151.0866, found 151.0867. IR (film) 3290, 3153, 1700, 1638, 1603, 1379, 1125, 860 cm⁻¹.

**2-Methyl-4-phenylpyridine (29a) and 2,6-Dimethyl-4-phenylpyridine (29b):** According to the general procedure A, Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 5.0 µmol, 0.01
equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), (80.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (55.0 mg, 65% yield for 29a; 10.8 mg, 12% yield for 29b). Compound 29a: 1H NMR (500 MHz, CDCl3): δ 8.54 (d, \( J = 5.1 \) Hz, 1H), 7.61 (m, 2H), 7.45 (m, 2H), 7.42 (m, 1H), 7.36 (s, 1H), 7.30 (d, \( J = 4.9 \) Hz, 1H), 2.62 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl3): δ 158.8, 149.5, 148.6, 138.4, 129.0 (2C), 128.8, 126.9 (2C), 121.2, 118.8, 24.5; HRMS (ESI) m/z calculated for C\(_{12}\)H\(_{12}\)N [(M+H)\(^{+}\)] 170.0964, found 170.0967. IR (film) 3027, 1595, 1545, 1473, 1390, 1291, 1002, 838 cm\(^{-1}\). Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **135**, 3756–3759 (2013).

![Structures of 30a, 30b, and 30c](image)

4-Methyl-6-phenylpyridine (30a), 2-Methyl-6-phenylpyridine (30b) and 2,4-Dimethyl-6-phenylpyridine: According to the general procedure A, Ir(ppy)\(_2\)(dtbbpy)PF\(_6\) (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-phenylpyridine (73.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (51.6 mg, 61% yield for 30a; 12.7 mg, 15% yield for
Compound 30a: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.55 (d, $J = 5.0$ Hz, 1H), 7.98 (d, $J = 7.0$ Hz, 2H), 7.55 (s, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 4.6$ Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.3, 149.4, 147.7, 139.5, 128.8, 128.6 (2C), 126.9 (2C), 123.1, 121.5, 21.2; HRMS (ESI) m/z calculated for C$_{12}$H$_{12}$N [(M+H)$^+$] 170.0964, found 170.0962. IR (film) 3053, 1601, 1557, 1445, 1273, 1073, 1030, 866 cm$^{-1}$. Compound 30b: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 7.7$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 2.63 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.3, 157.0, 139.8, 136.8, 128.7 (3C), 127.0 (2C), 121.6, 117.6, 24.8; HRMS (ESI) m/z calculated for C$_{12}$H$_{12}$N [(M+H)$^+$] 170.0964, found 170.0968, found 292.03339. IR (film) 3060, 1590, 1571, 1445, 1234, 1160, 1028, 805 cm$^{-1}$. Spectra data are consistent with those reported in the literature: J. Am. Chem. Soc. 134, 1352–1356 (2012).

2-Methyl-4-(trifluoromethyl)pyridine (31a) and 2,6-Dimethyl-4-(trifluoromethyl)pyridine (31b): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-(trifluoromethyl)pyridine (60.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptpropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was checked by $^1$H NMR using
TsOH as the internal standard (56% yield for 31a; 25% yield for 31b). The products are too volatile to isolated by routine procedure.

2,6-Dimethyl-4-(trifluoromethyl)pyridine (31b): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-(trifluoromethyl)pyridine (60.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptoproopionate (14.0 µL, 0.1 mmol, 0.20 equiv.), 6.0 mL of MeOH and 6.0 mL of DMSO were used. (Caution: volatile product). After 48 hours, the reaction mixture was added with 3 mL of 2 M NaOH aqueous solution and heated at 50 °C for 3 hours (or stirred at room temperature for 24 hours) and then cooled down to room temperature, diluted with CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo with ice water bath carefully. The residue was purified by flash chromatography (dichloromethane) to provide the title compound as a colorless oil (71.0 mg, 81% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.15 (s, 2H), 2.58 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 159.2 (2C), 138.8 (q), 123.0 (q), 115.8 (q, 2C), 24.5 (2C); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.9 (s); HRMS (ESI) m/z calculated for C$_8$H$_9$F$_3$N [(M+H)$^+$] 176.0682, found 176.0681. IR (film) 2929, 1582, 1388, 1350, 1235, 1129, 1107, 863 cm$^{-1}$. 
2,4,6-Trimethylnicotinonitrile (32): According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-methylnicotinonitrile (61.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptpropionate (3.5 µL, 25.0 µmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. (Caution: volatile product). After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% dichloromethane/hexanes) to provide the title compound as a white solid (66.5 mg, 91% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.95 (s, 1H), 2.71 (s, 3H), 2.53 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.3, 161.2, 151.2, 121.7, 116.6, 107.0, 24.7, 23.7, 20.3; HRMS (ESI) m/z calculated for C$_9$H$_{11}$N$_2$ [(M+H)$^+$] 147.0917, found 147.0915. IR (film) 2926, 2219, 1606, 1556, 1449, 1374, 1320, 1028 cm$^{-1}$.

![33](image)

1-Ethylisoquinoline (33): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.05 equiv.), ethanol (0.30 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (74.6 mg, 95% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.43 (d, $J = 5.7$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.64 (dd, $J =
7.8, 6.8 Hz, 1H), 7.56 (dd,  J = 7.7, 6.8 Hz, 1H), 7.48 (d,  J = 5.7 Hz, 1H), 3.32 (q,  J = 7.6 Hz, 2H), 1.44 (t,  J = 7.6 Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 163.0, 141.8, 136.1, 129.7, 127.3, 126.9, 126.6, 125.1, 119.1, 28.4, 13.5\); HRMS (ESI) m/z calculated for C\(_{11}\)H\(_{12}\)N [(M+H\(^{+}\)] 158.0964, found 158.0968. IR (film) 2971, 2934, 1621, 1561, 1501, 1385, 1006, 869 cm\(^{-1}\).

1-Propylisoquinoline (34): According to the general procedure B, Ir(ppy)\(_2\)(dtbbpy)PF\(_6\) (4.6 mg, 5.0 \(\mu\)mol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 \(\mu\)L, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 \(\mu\)L, 25.0 \(\mu\)mol, 0.05 equiv.), 1-propanol (0.38 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (82.2 mg, 96% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.42 (d,  J = 5.7 \text{ Hz}, 1H), 8.14 (d,  J = 8.4 \text{ Hz}, 1H), 7.79 (d,  J = 8.1 \text{ Hz}, 1H), 7.64 (t,  J = 7.5 \text{ Hz}, 1H), 7.57 (dd,  J = 7.7, 6.8 \text{ Hz}, 1H), 7.48 (d,  J = 5.8 \text{ Hz}, 1H), 3.27 (t,  J = 7.8 \text{ Hz}, 2H), 1.90 (m, 2H), 1.06 (t,  J = 7.4 \text{ Hz}, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 162.1, 141.8, 136.2, 129.7, 127.3, 126.9, 126.8, 125.3, 119.1, 37.4, 23.0, 14.3\); HRMS (ESI) m/z calculated for C\(_{12}\)H\(_{14}\)N [(M+H\(^{+}\)] 172.1121, found 172.1126. IR (film) 2959, 2870, 1622, 1561, 1501, 1386, 1009, 863 cm\(^{-1}\).
1-Phenethylisoquinoline (35): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.05 equiv.), 2-phenylethanol (0.60 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a colorless oil (106.2 mg, 91% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.48 (d, $J$ = 5.6 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 8.1 Hz, 1H), 7.68 (t, $J$ = 7.5 Hz, 1H), 7.59 (t, $J$ = 7.7 Hz, 1H), 7.55 (d, $J$ = 5.7 Hz, 1H), 7.32 (m, 4H), 7.23 (m, 1H), 3.62 (t, $J$ = 8.3 Hz, 2H), 3.21 (t, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.0, 141.8, 141.7, 136.2, 129.9, 128.5 (2C), 128.4 (2C), 127.4, 127.1, 126.9, 126.0, 125.0, 119.4, 37.2, 35.5; HRMS (ESI) m/z calculated for C$_{17}$H$_{16}$N [(M+H)$^+$] 234.1277, found 234.1277. IR (film) 3025, 1621, 1561, 1494, 1452, 1387, 1357, 821 cm$^{-1}$.

1-Isobutylisoquinoline (36): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.05 equiv.),
isobutanol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (85.6 mg, 87% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.45 (d, $J$ = 5.7 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.66 (t, $J$ = 7.9 Hz, 1H), 7.58 (t, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 5.7 Hz, 1H), 3.18 (d, $J$ = 7.3 Hz, 2H), 2.29 (m, 1H), 1.00 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.6, 141.6, 136.3, 129.8, 127.4, 127.3, 126.9, 125.6, 119.2, 44.1, 29.6, 22.8 (2C); HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$N [(M+H)$^+$] 186.1277, found 186.1278. IR (film) 2955, 2867, 1623, 1585, 1561, 1463, 1383, 1165 cm$^{-1}$.

![37](image)

1-(2-(tetrahydro-2H-pyran-4-yl)ethyl)isoquinoline (37): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (5.0 µL, 50.0 µmol, 0.10 equiv.), 2-(tetrahydro-2H-pyran-4-yl)ethanol (0.65 g, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (108.6 mg, 90% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.42 (d, $J$ = 5.7 Hz, 1H), 8.13 (d, $J$ = 8.5 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.67 (t, $J$ = 7.5 Hz, 1H), 7.59 (t, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 5.7 Hz, 1H), 3.98 (dd, $J$ = 11.1, 4.0 Hz, 2H), 3.40 (td, $J$ = 11.8, 2.0 Hz,
2H), 3.32 (m, 2H), 1.82 (m, 2H), 1.74 (d, \( J = 13.7 \) Hz, 2H), 1.67 (m, 1H), 1.40 (m, 2H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 162.0, 141.7, 136.3, 129.9, 127.5, 127.1, 126.8, 125.1, 119.3, 68.1(2C), 36.6, 35.2, 33.0(2C), 32.3; HRMS (ESI) m/z calculated for C\(_{16}\)H\(_{20}\)NO \([(M+H)^+\)] 242.1539, found 242.1539. IR (film) 2918, 2840, 1622, 1562, 1443, 1386, 1233, 1135, 1016 cm\(^{-1}\).

![Structure 38](image)

1-(2-(adamantan-1-yl)ethyl)isoquinoline (38): According to the general procedure B, Ir(ppy)_2(dtbbpy)PF\(_6\) (4.6 mg, 5.0 \( \mu \)mol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 \( \mu \)L, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 \( \mu \)L, 25.0 \( \mu \)mol, 0.05 equiv.), 1-adamantaneethanol (460.0 mg, 2.50 mmol, 5.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (134.0 mg, 92% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.42 (d, \( J = 5.7 \) Hz, 1H), 8.13 (d, \( J = 8.4 \) Hz, 1H), 7.81 (d, \( J = 8.1 \) Hz, 1H), 7.66 (t, \( J = 7.5 \) Hz, 1H), 7.59 (, \( J = 7.6 \) Hz, 1H), 7.49 (d, \( J = 5.8 \) Hz, 1H), 3.27 (m, 2H), 2.02 (s, 3H), 1.72 (m, 6H), 1.66 (s, 6H), 1.60 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 163.3, 141.6, 136.3, 129.9, 127.4, 127.0, 126.8, 125.4, 119.2, 44.3, 42.3 (3C), 37.2 (3C), 32.7, 28.9, 28.7 (3C); HRMS (ESI) m/z calculated for C\(_{21}\)H\(_{26}\)NO \([(M+H)^+\)] 292.2060, found 292.2060. IR (film) 2905, 2843, 1621, 1561, 1451, 1387, 1357, 820 cm\(^{-1}\).
1-(3,3,3-trifluoropropyl)isoquinoline (39): According to the general procedure B, Ir(ppy)_2(dtbbpy)PF_6 (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), 2,2,2-trifluoroethanethiol (2.5 µL, 25.0 µmol, 0.05 equiv., volatile, added after the reaction mixture was degassed), 3,3,3-trifluoropropanol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (104.5 mg, 93% yield). ^1H NMR (500 MHz, CDCl_3): δ 8.43 (d, J = 5.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 5.7 Hz, 1H), 3.56 (m, 2H), 2.80 (m, 2H); ^13C NMR (125 MHz, CDCl_3): δ 157.7, 141.6, 136.1, 130.1, 128.4, 127.5, 126.8, 126.3, 124.4, 119.9, 32.1 (q), 26.8 (q); ^19F NMR (376 MHz, CDCl_3): δ -66.5 (t, J = 10.9 Hz); HRMS (ESI) m/z calculated for C_{12}H_{11}F_{3}N [(M+H)^+] 226.0838, found 226.0838. IR (film) 3056, 1566, 1377, 1346, 1245, 1129, 1102, 977 cm^{-1}.

3-(Isoquinolin-1-yl)propan-1-ol (40): According to the general procedure B, Ir(ppy)_2(dtbbpy)PF_6 (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.05 equiv.), 1,3-propanediol (0.37 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (96.2 mg, 90% yield). ^1H NMR (500 MHz, CDCl_3): δ 8.43 (d, J = 5.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 5.7 Hz, 1H), 3.56 (m, 2H), 2.80 (m, 2H); ^13C NMR (125 MHz, CDCl_3): δ 157.7, 141.6, 136.1, 130.1, 128.4, 127.5, 126.8, 126.3, 124.4, 119.9, 32.1 (q), 26.8 (q); ^19F NMR (376 MHz, CDCl_3): δ -66.5 (t, J = 10.9 Hz); HRMS (ESI) m/z calculated for C_{12}H_{11}F_{3}N [(M+H)^+] 226.0838, found 226.0838. IR (film) 3056, 1566, 1377, 1346, 1245, 1129, 1102, 977 cm^{-1}.
DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (80% ethyl acetate/hexanes) to provide the title compound as a colorless oil (82.3 mg, 88% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.37 (d, $J = 5.7$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.52 (d, $J = 5.8$ Hz, 1H), 4.48 (br s, 1H), 3.75 (t, $J = 5.7$ Hz, 2H), 3.50 (t, $J = 6.9$ Hz, 2H), 2.16 (p, $J = 6.2$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.4, 140.9, 136.2, 130.2, 127.4, 127.3, 126.9, 125.2, 119.6, 62.2, 31.9, 30.9; HRMS (ESI) m/z calculated for C$_{12}$H$_{14}$NO [(M+H)$^+$] 188.1070, found 188.1068. IR (film) 3250, 2930, 1622, 1561, 1503, 1388, 1056, 1009 cm$^{-1}$.

![Structural diagram](image_url)

4-(Isoquinolin-1-yl)butan-2-ol (41): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (35.0 µL, 0.25 mmol, 0.50 equiv.), 1,3-butanediol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 72 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (81.5 mg, 81% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.38 (d, $J = 5.7$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.7$ Hz, 1H), 7.53 (d, $J = 5.7$ Hz, 1H), 4.22 (br s, 1H), 3.86 (m, 1H), 3.51 (t, $J = 7.0$ Hz, 2H), 2.03 (m,
2H), 1.25 (d, \( J = 6.2 \) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 161.6, 140.9, 136.3, 130.2, 127.4, 127.3, 126.9, 125.2, 119.6, 67.3, 37.2, 31.3, 23.5; HRMS (ESI) m/z calculated for C\(_{13}\)H\(_{16}\)NO \([\text{M+H}]^+\) 202.1226, found 202.1227. IR (film) 3301, 2964, 1623, 1562, 1503, 1388, 1127, 823 cm\(^{-1}\).

4-(Isoquinolin-1-yl)butan-1-ol (42): According to the general procedure B, Ir(ppy)\(_2\)(dtbbpy)PF\(_6\) (4.6 mg, 5.0 \( \mu \)mol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 \( \mu \)L, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 \( \mu \)L, 25.0 \( \mu \)mol, 0.05 equiv.), tetrahydrofuran (0.40 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (80% ethyl acetate/hexanes) to provide the title compound as a colorless oil (90.5 mg, 90% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.37 (d, \( J = 5.7 \) Hz, 1H), 8.15 (d, \( J = 8.3 \) Hz, 1H), 7.79 (d, \( J = 8.1 \) Hz, 1H), 7.65 (t, \( J = 7.5 \) Hz, 1H), 7.57 (t, \( J = 7.7 \) Hz, 1H), 7.49 (d, \( J = 5.6 \) Hz, 1H), 3.71 (t, \( J = 6.3 \) Hz, 2H), 3.58 (br s, 1H), 3.34 (t, \( J = 7.6 \) Hz, 2H), 1.98 (p, \( J = 7.4 \) Hz, 2H), 1.73 (p, \( J = 6.6 \) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 161.8, 141.2, 136.2, 130.0, 127.3, 127.1, 126.9, 125.2, 119.4, 62.0, 34.2, 32.3, 25.3; HRMS (ESI) m/z calculated for C\(_{13}\)H\(_{16}\)NO \([\text{M+H}]^+\) 202.1225, found 202.1225. IR (film) 3265, 2931, 1622, 1561, 1503, 1388, 1059, 1013 cm\(^{-1}\).
4-(Isoquinolin-1-yl)butane-1,2-diol (43): According to the general procedure B, Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptobutyrate (7.0 µL, 0.05 mmol, 0.10 equiv.), 3-hydroxytetrahydrofuran (0.42 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3×20 mL). The combined organic phase was then dried over Na$_2$SO$_4$, and concentrated in vacuo. and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a white solid (78.3 mg, 72% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.34 (d, $J$ = 5.7 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.79 (d, $J$ = 8.1 Hz, 1H), 7.67 (t, $J$ = 7.5 Hz, 1H), 7.58 (t, $J$ = 7.7 Hz, 1H), 7.50 (d, $J$ = 5.7 Hz, 1H), 5.51 (br s, 1H), 3.90-3.40 (br s, 1H), 3.81 (m, 1H), 3.66 (dd, $J$ = 11.2, 3.6 Hz, 1H), 3.57 (dd, $J$ = 11.1, 6.7 Hz, 1H), 3.51 (t, $J$ = 6.9 Hz, 2H), 2.06 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 161.3, 140.7, 136.2, 130.3, 127.4, 127.3, 126.9, 125.2, 119.7, 71.7, 66.6, 31.4, 30.9; HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$NO$_2$ [(M+H)$^+$] 218.1176, found 218.1175. IR (film) 3325, 3091, 2849, 1559, 1388, 1100, 1038, 1015 cm$^{-1}$. 

4-(Isoquinolin-1-yl)butane-1,2-diol
**5-(Isoquinolin-1-yl)pentane-1,2-diol (44):** According to the general procedure B,  
Ir(ppy)$_2$(dtbbpy)PF$_6$ (4.6 mg, 5.0 µmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 µL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptobutionate (7.0 µL, 0.05 mmol, 0.10 equiv.), tetrahydrofurfuryl alcohol (0.50 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3×20 mL). The combined organic phase was then dried over Na$_2$SO$_4$, and concentrated in vacuo. and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a colorless oil (89.0 mg, 77% yield).  
$^1$H NMR (500 MHz, CDCl$_3$): δ 8.36 (d, $J = 5.7$ Hz, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 5.8$ Hz, 1H), 3.90-3.40 (br s, 2H), 3.80 (m, 1H), 3.65 (dd, $J = 11.2$, 3.3 Hz, 1H), 3.51 (dd, $J = 11.1$, 7.2 Hz, 1H), 3.37 (m, 2H), 2.04 (m, 2H), 1.60 (m, 2H);  
$^{13}$C NMR (125 MHz, CDCl$_3$): δ 161.5, 140.9, 136.3, 130.2, 127.4, 127.3, 127.0, 125.2, 119.6, 71.5, 66.8, 33.9, 32.6, 24.6; HRMS (ESI) m/z calculated for C$_{14}$H$_{18}$NO$_2$ [(M+H)$^+$] 232.1332, found 232.1333. IR (film) 3309, 2924, 1562, 1388, 1264, 1103, 1053, 822 cm$^{-1}$

![Structure of 45](image)

**1-Methylfasudil (45):** According to the general procedure A, Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), fasudil
dihydrochloride (93.0 mg, 0.25 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.10 equiv.), 4.0 mL of MeOH and 1.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a colorless oil (62.5 mg, 82% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.51 (d, J = 6.2 \text{ Hz}, 1\text{H}), 8.35 (d, J = 8.4 \text{ Hz}, 1\text{H}), 8.30 (d, J = 7.8 \text{ Hz}, 1\text{H}), 8.29 (d, J = 7.0 \text{ Hz}, 1\text{H}), 7.64 (t, J = 7.9 \text{ Hz}, 1\text{H}), 3.47 (t, J = 6.2 \text{ Hz}, 2\text{H}), 3.42 (t, J = 5.4 \text{ Hz}, 2\text{H}), 3.00 (s, 3\text{H}), 2.95 (t, J = 5.4 \text{ Hz}, 2\text{H}), 2.92 (t, J = 6.2 \text{ Hz}, 2\text{H}), 2.12 (br s, 1\text{H}), 1.81 (p, J = 6.1 \text{ Hz}, 2\text{H}); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 159.4, 143.7, 135.0, 132.5, 131.8, 131.1, 128.1, 125.4, 116.0, 51.1, 50.2, 47.6, 47.3, 31.1, 23.1\); HRMS (ESI) m/z calculated for C\(_{15}\)H\(_{20}\)N\(_3\)O\(_2\)S [(M+H)\(^+\)] 306.1271, found 306.1270. IR (film) 2932, 1611, 1561, 1317, 1144, 1023, 978, 903 cm\(^{-1}\).

![Chemical structure](46)

**2-(3-Phenylpropyl)milrinone (46):** According to the general procedure B, Ir(ppy)_2(dtbbpy)PF\(_6\) (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), milrinone (53.9 mg, 0.25 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.10 equiv.), 3-phenyl-1-propanol (0.35 mL, 2.5 mmol, 10.0 equiv) and 1.0 mL of DMSO were used. After 72 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5%
methanol/ethyl acetate) to provide the title compound as a white solid (35.3 mg, 43% yield). $^1$H NMR (500 MHz, CD$_3$OD): $\delta$ 8.49 (d, $J = 5.1$ Hz, 1H), 8.05 (s, 1H), 7.29 (s, 1H), 7.25 (d, $J = 5.1$ Hz, 1H), 7.24 (m, 2H), 7.19 (m, 2H), 7.13 (m, 1H), 2.86 (t, $J = 7.8$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 2.36 (s, 3H), 2.06 (m, 2H); $^{13}$C NMR (125 MHz, CD$_3$OD): $\delta$ 163.7, 162.6, 152.5, 151.0, 146.9, 143.2, 129.5(2C), 129.4(2C), 126.9, 125.0, 123.2, 118.8, 116.5, 102.7, 38.4, 36.6, 32.9, 18.6; HRMS (ESI) m/z calculated for C$_{21}$H$_{20}$N$_3$O [(M+H)$^+$] 330.1601, found 330.1601. IR (film) 2925, 2225, 1656, 1599, 1567, 1483, 1173, 1030, 910 cm$^{-1}$.

Reduction of 1-(Hydroxymethyl)isoquinoline via Photoredox Catalysis: To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), Bu$_3$N (120 µL, 0.50 mmol, 2.0 equiv.), HCO$_2$H (21 µL, 0.50 mmol, 2.0 equiv.) and 1.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH$_2$Cl$_2$ (20 mL), washed with brine (3×10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide 1-methylisoquinoline as a colorless oil (21.5 mg, 60% yield).
7-Phenyl-8,9-dihydro-7H-benzo[de]quinoline (50): To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged Ir(ppy)₂(dtbbpy)PF₆ (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), styrene (30 µL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH₂Cl₂ (20 mL), washed with brine (3×10 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (39.8 mg, 65% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.43 (d, J = 5.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.58-7.53 (m, 2H), 7.32 (m, 2H), 7.27 (m, 1H), 7.11 (m, 2H), 7.09 (d, J = 7.2 Hz, 1H), 4.44 (dd, J = 8.3, 4.5 Hz, 1H), 3.30 (t, J = 6.3 Hz, 2H), 2.49 (m, 1H), 2.39 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 159.7, 144.3, 141.5, 140.9, 136.1, 130.3, 128.6(2C), 128.5(2C), 126.6, 126.4, 125.3, 125.0, 119.1, 46.0, 32.0, 31.5; HRMS (ESI) m/z calculated for C₁₈H₁₆N [(M+H)⁺] 246.1277, found 246.1277. IR (film) 3052, 2927, 1613, 1571, 1492, 1345, 1265, 1026, 838 cm⁻¹.
7-((Trimethylsilyl)methyl)-8,9-dihydro-7H-benzo[de]quinoline (51): Following the procedure for compound 50, Ir(ppy)2(dtbbpy)PF6 (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), allyltrimethylsilane (41 µL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO were used. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH2Cl2 (20 mL), washed with brine (3 × 10 mL), dried over Na2SO4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (26.2 mg, 41% yield). 1H NMR (500 MHz, CDCl3): δ 8.38 (d, J = 5.8 Hz, 1H), 7.63-7.56 (m, 2H), 7.47 (d, J = 5.7 Hz, 1H), 7.37 (d, J = 6.6 Hz, 1H), 3.40 (m, 1H), 3.30 (m, 1H), 3.19 (m, 1H), 2.25 (m, 1H), 2.05 (m, 1H), 1.03 (d, J = 7.5 Hz, 2H), 0.10 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 159.5, 145.1, 141.7, 136.2, 130.1, 124.3, 124.2, 124.0, 118.9, 35.3, 30.3, 29.6, 23.7, -0.6(3C); HRMS (ESI) m/z calculated for C16H22NSi [(M+H)+] 256.1516, found 256.1517. IR (film) 3049, 2949, 1616, 1572, 1387, 1344, 1246, 1028, 856 cm−1.

Tert-butyl 2-(isoquinolin-1-ylmethyl)-1H-pyrrole-1-carboxylate (52): Following the procedure for compound 50, Ir(ppy)2(dtbbpy)PF6 (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH
(95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 
1.0 equiv.), N-Boc-pyrrole (43 µL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO were 
used. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution 
(1 mL) and CH₂Cl₂ (20 mL), washed with brine (3×10 mL), dried over Na₂SO₄, and 
concentrated in vacuo. Purification of the crude product by flash chromatography on 
silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil 
(24.0 mg, 31% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.45 (d, J = 5.8 Hz, 1H), 8.13 (d, J 
= 8.5 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 
7.56 (d, J = 6.2 Hz, 1H), 7.31 (m, 1H), 6.04 (t, J = 3.4 Hz, 1H), 5.54 (m, 1H), 4.90 (s, 
2H), 1.46 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 159.0, 149.7, 141.9, 136.2, 131.9, 
130.0, 127.23, 127.20, 127.17, 125.5, 121.2, 119.7, 113.1, 110.1, 83.4, 35.5, 27.9(3C); 
HRMS (ESI) m/z calculated for C₁₉H₂₁N₂O₂ [(M+H)+] 309.1598, found 309.1598. IR 
(film) 3053, 2979, 1734, 1625, 1563, 1410, 1317, 1253, 1156, 1062 cm⁻¹.

**Methyl 2-(isoquinolin-1-ylmethyl)-1H-pyrrole-1-carboxylate (53):** Following the 
procedure for compound 50, Ir(ppy)₂(dtbbpy)PF₆ (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH 
(95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 
1.0 equiv.), methyl 1-pyrrolecarboxylate (28 µL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of 
DMSO were used. After 20 hours, the reaction mixture was diluted with 1 M NaOH 
aqueous solution (1 mL) and CH₂Cl₂ (20 mL), washed with brine (3×10 mL), dried over
Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (16.7 mg, 25% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.45 (d, $J$ = 5.7 Hz, 1H), 8.13 (d, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 8.1 Hz, 1H), 7.67 (m, 1H), 7.56 (m, 1H), 7.55 (d, $J$ = 6.4 Hz, 1H), 7.30 (dd, $J$ = 3.4, 1.7 Hz, 1H), 6.08 (t, $J$ = 3.3 Hz, 1H), 5.61 (m, 1H), 4.92 (s, 2H), 3.85 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.9, 151.5, 142.1, 136.3, 132.8, 130.0, 127.32, 127.26, 127.25, 125.5, 121.0, 119.7, 113.6, 110.1, 53.7, 35.1; HRMS (ESI) m/z calculated for C$_{16}$H$_{15}$N$_2$O$_2$ [(M+H)$^+$] 267.1128, found 267.1127. IR (film) 3053, 2955, 1741, 1624, 1562, 1440, 1317, 1228, 1121, 1065 cm$^{-1}$. 


VI. NMR Spectra