Supporting information

Photocatalytic C-H Silylation of Heteroarenes by Using Trialkylhydrosilanes

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Table of Contents

1. The optimization of Na₂S₂O₈-mediated photocatalytic C-H silylation…………………………S2
2. The chemical stability study of heteroaryltrialkylsilanes……………………………………S4
3. The study of thiol-mediated photocatalytic C-H silylation……………………………………S5
4. The application of our methodology in organic synthesis……………………………………S7
5. The study of the mechanism of Na₂S₂O₈ mediated photocatalytic C-H silylation……………S11
6. The study of the mechanism of thiol-mediated photocatalytic C-H silylation………………S13
7. Experiment Procedures and Product Characterization……………………………………S15
8. References…………………………………………………………………………………………S43
9. Spectral Data for Products……………………………………………………………………S44
1. The optimization of Na$_2$S$_2$O$_8$-mediated photocatalytic C-H silylation.

Table S1. The optimization of photocatalyst. 

<table>
<thead>
<tr>
<th>entry</th>
<th>photocat.</th>
<th>yield $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1 (100 mol%)</td>
<td>20% $^c$</td>
</tr>
<tr>
<td>2</td>
<td>P1 (100 mol%)</td>
<td>23%</td>
</tr>
<tr>
<td>3</td>
<td>P2 (5 mol%)</td>
<td>25%</td>
</tr>
<tr>
<td>4</td>
<td>P3 (5 mol%)</td>
<td>31%</td>
</tr>
<tr>
<td>5</td>
<td>P4 (5 mol%)</td>
<td>40%</td>
</tr>
<tr>
<td>6</td>
<td>P5 (5 mol%)</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>P6 (1 mol%)</td>
<td>55%</td>
</tr>
<tr>
<td>8</td>
<td>P7 (1 mol%)</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>P8 (1 mol%)</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>P9 (1 mol%)</td>
<td>60%</td>
</tr>
<tr>
<td>11</td>
<td>P9 (0.5 mol%)</td>
<td>53%</td>
</tr>
<tr>
<td>12</td>
<td>P9 (2 mol%)</td>
<td>49%</td>
</tr>
</tbody>
</table>

$^a$ Conditions employed 23 W CFL, 1a (0.5 mmol), 2a (2.5 mmol), photocat. (1 - 100 mol%), Na$_2$S$_2$O$_8$ (1.5 mmol), a solvent mixture (2.5 mL, DMSO : DCE = 1 : 1), air, 30 °C, 24 h, unless otherwise noted; $^b$ Isolated yields were reported; $^c$ The reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with N$_2$.
Table S2. The optimization of the oxidant. \(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>oxidant</th>
<th>yield (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na(_2)S(_2)O(_8) (3 equiv)</td>
<td>60%</td>
</tr>
<tr>
<td>2</td>
<td>(NH(_4))(_2)S(_2)O(_8) (3 equiv)</td>
<td>40%</td>
</tr>
<tr>
<td>3</td>
<td>K(_2)S(_2)O(_8) (3 equiv)</td>
<td>51%</td>
</tr>
<tr>
<td>4</td>
<td>PIDA (3 equiv)</td>
<td>n.d (^c)</td>
</tr>
<tr>
<td>5</td>
<td>BPO (75%) (3 equiv)</td>
<td>46%</td>
</tr>
<tr>
<td>6</td>
<td>O(_2)</td>
<td>n.d (^c)</td>
</tr>
<tr>
<td>7</td>
<td>H(_2)O(_2) (30%) (3 equiv)</td>
<td>6%</td>
</tr>
<tr>
<td>8</td>
<td>TBHP (70%) (3 equiv)</td>
<td>35%</td>
</tr>
<tr>
<td>9</td>
<td>Na(_2)S(_2)O(_8) (2 equiv)</td>
<td>67%</td>
</tr>
<tr>
<td>10</td>
<td>Na(_2)S(_2)O(_8) (1 equiv)</td>
<td>54%</td>
</tr>
</tbody>
</table>

\(^a\) Conditions employed 1\(_a\) (0.5 mmol), 2\(_a\) (2.5 mmol), photocat. (1 mol%), 30 °C, oxidant (1.0 - 1.5 mmol), a solvent mixture (1.5 mL, DMSO:DCE = 1:1), air, 30 °C, 24 h, unless otherwise noted; \(^b\) Isolated yields were reported; \(^c\) not detected.

Table S3. The optimization of the reaction solvent. \(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO/DCE (1:1)</td>
<td>67%</td>
</tr>
<tr>
<td>2</td>
<td>DMSO</td>
<td>32%</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>n.d (^c)</td>
</tr>
<tr>
<td>4</td>
<td>MeCN</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>EtOH</td>
<td>n.d (^c)</td>
</tr>
<tr>
<td>6</td>
<td>DMSO/CH(_3)COOC(_2)H(_5) (1:1)</td>
<td>19%</td>
</tr>
<tr>
<td>7</td>
<td>DMSO/MeCN (1:1)</td>
<td>10%</td>
</tr>
<tr>
<td>8</td>
<td>DMSO/Acetone (1:1)</td>
<td>25%</td>
</tr>
<tr>
<td>9</td>
<td>DMSO/DCE (1:1)</td>
<td>77% (^d)</td>
</tr>
<tr>
<td>10</td>
<td>DMSO/DCE (3:1)</td>
<td>67% (^d)</td>
</tr>
<tr>
<td>11</td>
<td>DMSO/DCE (1:3)</td>
<td>33% (^d)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions employed 1\(_a\) (0.5 mmol), 2\(_a\) (2.5 mmol), photocat. (1 mol%), Na\(_2\)S\(_2\)O\(_8\) (1.0 mmol), solvent (2.5 mL), 30 °C, 24 h, air, unless otherwise noted; \(^b\) Isolated yields were reported; \(^c\) not detected; \(^d\) 5.0 mL of solvent mixture (DMSO:DCE = 1:1) was employed as the reaction solvent.
Table S4. The optimization of the amount of trialkylhydrosilane.

![Chemical structure]

<table>
<thead>
<tr>
<th>entry</th>
<th>tert-butyltrimethylsilane</th>
<th>yield b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 equiv</td>
<td>77%</td>
</tr>
<tr>
<td>2</td>
<td>10 equiv</td>
<td>79%</td>
</tr>
<tr>
<td>3</td>
<td>5 equiv</td>
<td>70% c</td>
</tr>
<tr>
<td>4</td>
<td>5 equiv</td>
<td>66% d</td>
</tr>
</tbody>
</table>

a Conditions employed 23 W CFL, 1a (0.5 mmol), 2a (1.0 - 5.0 mmol), photocat. (1 mol%), Na₂S₂O₈ (1.0 mmol), a solvent mixture (5 mL, DMSO : DCE = 1:1), 30 °C, 24 h, air, unless otherwise noted; b Isolated yields were reported; c The reaction time was extended to 48 h; d The reaction time was shortened to 12 h.

2. The chemical stability study of heteroaryltrialkylsilanes

Table S5. The chemical stability study of heteroaryltrialkylsilanes.

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Si = tert-BuMe₂Si</th>
<th>Si = Et₃Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard reaction conditions (Na₂S₂O₈) b</td>
<td>A (100%)</td>
<td>A (21%), B (74%)</td>
</tr>
<tr>
<td>Standard reaction conditions (iPr₃SiSH) b</td>
<td>A (100%)</td>
<td>A (70%), B (30%)</td>
</tr>
<tr>
<td>HCl (1 mol/L), 25 °C, 24 h</td>
<td>A (100%)</td>
<td>A (80%) + B (20%)</td>
</tr>
<tr>
<td>HCl (1 mol/L), 50 °C, 24 h</td>
<td>A (100%)</td>
<td>A (10%) + B (90%)</td>
</tr>
<tr>
<td>HCl (1 mol/L), 80 °C, 24 h</td>
<td>A (92%) + B (8%)</td>
<td>B (100%)</td>
</tr>
<tr>
<td>NaOH (1 mol/L), 25 °C, 24 h</td>
<td>A (100%)</td>
<td>A (100%)</td>
</tr>
<tr>
<td>NaOH (1 mol/L), 50 °C, 24 h</td>
<td>A (100%)</td>
<td>A (70%) + B (30%)</td>
</tr>
<tr>
<td>NaOH (1 mol/L), 80 °C, 24 h</td>
<td>A (100%)</td>
<td>A (30%) + B (70%)</td>
</tr>
<tr>
<td>TBAF (1 mol/L), 25 °C, 24 h</td>
<td>A (95%) + B (5%)</td>
<td>B (100%)</td>
</tr>
<tr>
<td>TBAF (1 mol/L), 50 °C, 24 h</td>
<td>A (30%) + B (70%)</td>
<td>-</td>
</tr>
<tr>
<td>TBAF (1 mol/L), 80 °C, 24 h</td>
<td>B (100%)</td>
<td>-</td>
</tr>
</tbody>
</table>

a Isolated yields were reported for each reaction; b See general procedure A and B for the experimental details unless otherwise noted.

Notes: Heteroaryltriethylsilane was prepared according to the known procedure, and spectroscopic data is in accordance with literature.¹
3. The study of thiol-mediated photocatalytic Minisci-type C-H silylation of heteroarenes

Table S6. The optimization of the reaction conditions. 

<table>
<thead>
<tr>
<th>entry</th>
<th>thiol</th>
<th>2a</th>
<th>additive</th>
<th>yield $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T1 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>38%</td>
</tr>
<tr>
<td>2</td>
<td>T2 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>33%</td>
</tr>
<tr>
<td>3</td>
<td>T3 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>32%</td>
</tr>
<tr>
<td>4</td>
<td>T4 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>25%</td>
</tr>
<tr>
<td>5</td>
<td>T5 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>31%</td>
</tr>
<tr>
<td>6</td>
<td>T6 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>18%</td>
</tr>
<tr>
<td>7</td>
<td>T7 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>23%</td>
</tr>
<tr>
<td>8</td>
<td>T8 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>43%</td>
</tr>
<tr>
<td>9</td>
<td>T9 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>15%</td>
</tr>
<tr>
<td>10</td>
<td>T10 (0.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>11</td>
<td>T8 (1.0 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>53%</td>
</tr>
<tr>
<td>12</td>
<td>T8 (1.2 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>58%</td>
</tr>
<tr>
<td>13</td>
<td>T8 (1.6 equiv)</td>
<td>5 equiv (1 batch)</td>
<td>-</td>
<td>52%</td>
</tr>
<tr>
<td>14</td>
<td>T8 (1.2 equiv)</td>
<td>5 equiv (3 batches)</td>
<td>-</td>
<td>64%</td>
</tr>
<tr>
<td>15</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>71%</td>
</tr>
<tr>
<td>16</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>71% $^c$</td>
</tr>
<tr>
<td>17</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>72% $^d$</td>
</tr>
<tr>
<td>18</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>CF$_3$SO$_3$H</td>
<td>70%</td>
</tr>
<tr>
<td>19</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>Sc(OTf)$_3$</td>
<td>63%</td>
</tr>
<tr>
<td>20</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>n.d $^e$ $^f$</td>
</tr>
<tr>
<td>21</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>71% $^g$</td>
</tr>
<tr>
<td>22</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>n.d $^e$ $^h$</td>
</tr>
<tr>
<td>23</td>
<td>T8 (1.2 equiv)</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>n.d $^e$ $^i$</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>10 equiv (3 batches)</td>
<td>-</td>
<td>n.d $^f$</td>
</tr>
</tbody>
</table>

$^a$ Conditions employed 23 W CFL, isoquinoline (0.5 mmol), 2a (2.5 - 5.0 mmol), Ir(ppy)$_3$ (0.0025 mmol), thiol (0.1 - 0.6 mmol), 30 °C, 24 h, air, a solvent mixture (2.0 mL, DMA:DCE = 1:1), unless otherwise noted; $^b$ Isolated yields were reported; $^c$ The reaction time was extended to 36h; $^d$ 34 W blue LED was used as light source; $^e$ The reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with N$_2$; $^f$ Not detected; $^g$ Performed under oxygen (1atm); $^h$ Performed in darkness; $^i$ Performed in the absence of Ir(ppy)$_3$.

Notes: The initial screening campaign identified Ir(ppy)$_3$ (0.5 mol%) and the solvent mixture (DMA:DCE = 1:1, 0.25M) as the optimal reaction conditions (data not shown here). Various thiol additives were then screened using 5 equiv of tBuMe$_2$SiH (2a) as coupling partner. The thiol with large
steric hindrance displayed better reaction efficiency (entry 1 and entry 8, 38% - 43% yield). \( ^{3}\)Pr\(_3\)SiSH (1.2 equiv) provided the best reaction outcome (entry 12, 58% yield). The stability of thiol additives under oxidation might help to explain this result. The use of 10 equiv of \(^{1}\)BuMe\(_2\)SiH in three batches showed the best reaction efficiency (entry 15, 71% yield). The extension of reaction time to 36 h, the use of 34 W blue LED as an alternative light source, as well as the addition of acid as additives, have little effect on the reaction efficiency (entries 16 - 19, 63% - 71% yield). The oxygen was proved essential for this transformation, while the running of the reaction under \( O_2 \) cannot further improve the yield (entry 21, 71% yield). Furthermore, control reactions show that visible light, Ir(ppy), and thiol, are also essential for this process (entries 22 - 24, Table 1). Therefore, the reaction conditions screening campaign identified the optimal conditions as: in the presence of 23 W CFL, 0.5 mol% of Ir(ppy), 1.2 equiv of \(^{3}\)Pr\(_3\)SiSH, treating heteroarenes with 10 equiv of \(^{1}\)BuMe\(_2\)SiH (three batches) in solvent mixture (DMA : DCE = 1:1, 0.25 M) for 24 h at 30 °C under air (entry 15).

**Scheme S1.** Direct C-H silylation of substituted isoquinolines via thiol-mediated photocatalytic Minisci-type reaction.\(^a\)

\[ \text{N} - \text{H} + \text{H-SiMe}_2\text{Bu} \rightarrow \text{N-SiMe}_2\text{Bu} \]

\[ 1a, 1b \rightarrow 2a \rightarrow 3a, 3b \]

\[ \text{Me} \]

\[ \text{Cl} \]

\[ \text{Ph} \]

\[ \text{MeO} \]

\[ \text{MeO} \]

\[ \text{NPhth} \]

\[ 3a, 74\% \]

\[ 3b1, 62\% \]

\[ 3b2, 61\% \]

\[ 3b3, 75\% \]

\[ 3b4, 72\% \]

\[ 3b5, 69\% \]

\[ 3b6, 68\% \]

\[ 3b7, 60\% \]

\[ 3b8, 62\% \]

\[ 3b9, 62\% \]

\[ 3b10, 51\% \]

\[ 3b12, 45\% \]

\[ 23 \text{ W CFL} \]

\[ \text{Ir(ppy)}_3 \text{(0.5 mol\%)} \]

\[ \text{Pr}_3\text{SiSH} \text{(1.2 equiv)} \]

\[ \text{DMA/DCE (1:1)} \]

\[ 30^\circ \text{C, 24 h, open to air} \]

\[ 30^\circ \text{C, 24 h, open to air} \]

\[ \text{See general procedure B for the experimental details unless otherwise noted; the isolated yields were reported.} \]

**Notes:** Only C-1 mono-silylation products were detected.
4. The study of the mechanism of Na$_2$S$_2$O$_8$-mediated photocatalytic C-H silylation

**Figure S1.** The GC-MS study of the reaction mixture.

GC-MS data of the coupling reaction of 6-methylisoquinoline 1a with tert-butyldimethylsilane 2a.

GC-MS data of the coupling reaction of 6-methylisoquinoline 1a with triethylsilane 2d
Notes: The reaction solution was directly used for GC-MS analysis. The formation of silanol and siloxane was observed by GC-MS, which indicates that silyl radicals were formed in this process and further validates the radical based mechanism (sila-Minisci-type reaction).³
**Scheme S2.** The proposed mechanisms of the formation of silanol and siloxane.

\[
{\text{tBuMe}_2SiH} + {\text{SO}_4^{2-}} \rightarrow {\text{tBuMe}_2Si} + {\text{HSO}_4^{2-}}
\]

\[
2{\text{tBuMe}_2Si}^* + {\text{O}_2} \rightarrow {\text{tBuMe}_2Si} - {\text{O}} - {\text{O}} - {\text{SiMe}_2Bu}
\]

\[
{\text{tBuMe}_2Si} - {\text{O}} - {\text{O}} - {\text{SiMe}_2Bu} + 2{\text{tBuMe}_2Si}^* \rightarrow 2{\text{tBuMe}_2Si} - {\text{O}} - {\text{SiMe}_2Bu}
\]

\[
{\text{visible light}} \text{photocat.} \ 2{\text{tBuMe}_2Si} - {\text{O}}^*
\]

\[
{\text{tBuMe}_2Si} - {\text{O}}^* + {\text{tBuMe}_2SiH} \rightarrow {\text{BuMe}_2Si} - {\text{OH}} + {\text{BuMe}_2Si}^*
\]

**Scheme S3.** The radical trapping experiment.

**Notes:** TEMPO, \((E)-(2-(phenylsulfonyl)vinyl)benzene, methyl acrylate, and 2-benzylidenemalononitrile were employed to trap the silyl radical. The reaction was shut down by the presence of TEMPO, which is indicative of a radical engaged pathway (Scheme 3A). However, only the radical trapping product was detected using 2-benzylidenemalononitrile as additive (Scheme 3B).
**Scheme S4.** The control reactions employing t-BuMe₂SiOOSiMe₂Bu as the radical initiator.

**Notes:** t-BuMe₂SiOOSiMe₂Bu was prepared according to known procedure, and spectroscopic data is in accordance with literature.³

**Figure S2.** Emission Quenching Experiment

Emission intensities were recorded using a FluoroMax-4 (Horiba Scientific) fluorescence spectrophotometer. All Ir(ppy)₂(dtbbpy)PF₆ solutions were excited at 337 nm and the emission intensity was collected at 603 nm. In a typical experiment, to a 1 × 10⁻⁶ M solution of Ir(ppy)₂(dtbbpy)PF₆ in DMSO was added the appropriate amount of a quencher in a screw-top quartz cuvette.
5. The study of the mechanism of thiol-mediated photocatalytic C-H silylation

Figure S3. GC-MS study of the reaction mixture.

Scheme S5. The radical quenching and trapping experiments.

Notes: The reaction was completely inhibited by the presence of TEMPO, further suggesting the radical based mechanism (Scheme S5A). However, only the use of 2-benzylidenemalononitrile as additive is able to produce the radial trapping product accompanied with the formation of little target product 3a (Scheme S5B).
Scheme S6. The control reactions.

Notes: No product was detected in the absence of air (O₂) (Scheme S6B). Furthermore, the use of THF (20 equiv) as coupling partner in place of 'BuMe₂SiH resulted in the generation of trace desired product (Scheme S6C). These results, as well as the fact that the use of 'BuMe₂SiOOSiMe₂'Bu (2 equiv) as radical initiator led to comparable yield (62% yield, Scheme S6D), indicate that the in-situ generated 'BuMe₂SiOOSiMe₂'Bu might be involved in this process to mediate the sila-Minisci-type reaction.

Figure S4. Emission Quenching Experiment.

Emission intensities were recorded using a FluoMax-4 (Horiba Scientific) fluorescence spectrophotometer. All Ir(ppy)₃ solutions were excited at 350 nm and the emission intensity was collected at 527 nm. In a typical experiment, to a 1 × 10⁻⁶ M solution of Ir(ppy)₃ in DMSO was added the appropriate amount of a quencher in a screw-top quartz cuvette.
6. The synthetic application of our method

Scheme S7. The study of Hiyama-Denmark cross-coupling of heteroaryl(tert-butyldimethyl)silane. $^a$

\[ \text{H}_3\text{C} \quad \text{N} \quad \text{SiMe}_2\text{Bu} \quad \text{X} \quad \text{Pd(Ph}_3\text{P)}_4 \quad \text{Ag}_2\text{O} \quad \text{TBAF} \quad \text{DMF} \quad 90^\circ\text{C} \quad 2\text{h} \quad \text{H}_3\text{C} \quad \text{N} \quad \text{SiMe}_2\text{Bu} \]

$^{10b} - 10g$

$^a$ See General procedure D for the experimental details unless otherwise noted; isolated yields were reported.
Scheme S8. The comparison of two synthetic routes for the synthesis of norcryptostyline.

Reported synthetic route: 2

Our synthetic route:
7. Experiment Procedures and Product Characterization

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM 400 Spectrometer (400 and 100 MHz for $^1$H and $^{13}$C NMR, respectively) and are internally referenced to residual solvent signals (note: CDCl$_3$ referenced at 7.26 and 77.00 ppm in $^1$H and $^{13}$C NMR, respectively; $d_6$-DMSO referenced at 2.50 and 39.52 ppm in $^1$H and $^{13}$C NMR, respectively). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for $^{13}$C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

**General Procedure A:**

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (2.5 mmol, 5.0 equiv.), Na$_2$S$_2$O$_8$ (1.0 mmol, 2.0 equiv.) and Ir(ppy)$_2$(dtbpy)PF$_6$ (0.005 mmol, 0.01 equiv.) The vial was sealed and placed under atmosphere, then DMSO/DCE (1:1) (5 mL, 0.1 M) were added. The reaction was placed in between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. The reaction mixture was diluted with saturated NaHCO$_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous 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:**

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (1.67 mmol, 3.33 equiv.), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.) and Ir(ppy)$_3$ (0.0025 mmol, 0.005 equiv.) The vial was sealed and placed under atmosphere, then DMA/DCE (1:1) (2 mL, 0.25 M) were added. The reaction was placed in between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. In this period, another two batch (1.67 mmol, 3.33 equiv.) added after every 8 hours. The reaction mixture was diluted with saturated NaHCO$_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous 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 C:**

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (2.5 mmol, 5.0 equiv.), BTMSPO (1.0...
mmol, 2.0 equiv.) and Ir(ppy)$_2$(dtbpy)PF$_6$ (0.005 mmol, 0.01 equiv.) The vial was sealed and placed under atmosphere, then DMSO/DCE (1:1) (5 mL, 0.1 M) were added. The reaction was placed between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. The reaction mixture was diluted with H$_2$O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous 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-(tert-butyl(dimethyl)silyl)-6-methylisoquinoline (3a): According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), tert-butyl(dimethyl)silane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (100 mg, 77 %). And according to the general procedure B, the product was obtained (96 mg, 74 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.67 (d, $J = 5.6$ Hz, 1H), 8.15 (d, $J = 5.6$ Hz, 1H), 7.56 (s, 1H), 7.47 (d, $J = 5.6$ Hz, 1H), 7.39 (dd, $J = 8.6$, 1.7 Hz, 1H), 2.53 (s, 3H), 0.97 (s, 9H), 0.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.49, 142.63, 139.24, 134.83, 132.53, 128.59, 128.41, 126.37, 119.41, 27.09, 21.75, 17.96, -3.08; HRMS (ESI) Calcd. for C$_{16}$H$_{24}$NSi [(M+H)$^+$] 258.1678, found 258.1676.

1-(tert-butyl(dimethyl)silyl)-6-chloroisooquinoline (3b1): According to the general procedure A, 6-chloroisooquinoline (0.5 mmol, 1 equiv.), tert-butyl(dimethyl)silane (72 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (100 mg, 77 %). And according to the general procedure B, the product was obtained (96 mg, 74 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (d, $J = 5.6$ Hz, 1H), 8.18 (d, $J = 5.6$ Hz, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.78 (d, $J = 1.7$ Hz, 1H), 7.49 (dd, $J = 12.6$, 3.8 Hz, 2H), 0.95 (s, 9H), 0.54 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.43, 143.40, 135.44, 135.23, 132.10, 130.31, 127.41, 126.25, 118.88, 27.00, 17.92, -3.13; HRMS (ESI) Calcd. for C$_{15}$H$_{21}$ClNSi [(M+H)$^+$] 278.1132, found 278.1124.
1-(tert-butyldimethylsilyl)-6-phenylisoquinoline (3b2): According to the general procedure A, 6-phenylisoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbbpy)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (115 mg, 72 %). And according to the general procedure B, the product was obtained (97 mg, 61 %).

$^1$H NMR (400 MHz, CDCl3) $\delta$ 8.74 (d, $J$ = 5.6 Hz, 1H), 8.32 (d, $J$ = 8.8 Hz, 1H), 7.99 (d, $J$ = 8.8, 1H), 7.73 (dd, $J$ = 5.2, 3.3 Hz, 2H), 7.62 (d, $J$ = 5.6 Hz, 1H), 7.51 (dd, $J$ = 10.2, 4.7 Hz, 2H), 7.43 (ddd, $J$ = 7.4, 3.8, 1.2 Hz, 1H), 0.99 (s, 9H), 0.59 (s, 6H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 169.87, 142.82, 141.80, 140.14, 134.96, 133.03, 129.22, 128.98, 128.03, 127.49, 126.19, 125.18, 120.18, 27.10, 18.01, -3.06; HRMS (ESI) Calcd. for C21H26NSi [(M+H)$^+$] 320.1835, found 320.1841.

1-(tert-butyldimethylsilyl)-6-methoxyisoquinoline (3b3): According to the general procedure A, 6-methoxyisoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbbpy)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (94 mg, 69 %). And according to the general procedure B, the product was obtained (102 mg, 75 %).

$^1$H NMR (400 MHz, CDCl3) $\delta$ 8.62 (d, $J$ = 5.7 Hz, 1H), 8.14 (d, $J$ = 9.2 Hz, 1H), 7.46 (d, $J$ = 5.7 Hz, 1H), 7.18 (dd, $J$ = 9.2, 2.6 Hz, 1H), 7.04 (d, $J$ = 2.5 Hz, 1H), 3.94 (s, 3H), 0.95 (s, 9H), 0.54 (s, 6H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 168.99, 159.71, 143.01, 136.59, 130.37, 130.12, 119.29, 119.21, 104.83, 55.37, 27.07, 17.96, -3.06; HRMS (ESI) Calcd. for C16H24NOSi [(M+H)$^+$] 274.1627, found 274.1624.

1-(tert-butyldimethylsilyl)-7-methoxyisoquinoline (3b4): According to the general procedure A, 7-methoxyisoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbbpy)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (95 mg, 71 %). And according to the general procedure B, the product was obtained (96 mg, 72 %).

$^1$H NMR (400 MHz, CDCl3) $\delta$ 8.61 (d, $J$ = 5.5 Hz, 1H), 7.70 (d, $J$ = 8.9 Hz, 1H), 7.55 (d, $J$ = 2.4 Hz, 1H), 7.49 (d, $J$ = 5.5 Hz, 1H), 7.30 (dd, $J$ = 8.9, 2.5 Hz, 1H), 3.94 (s, 3H), 0.98 (s, 9H), 0.57 (s, 6H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 167.78, 157.51, 141.13, 135.10, 130.01, 128.91, 122.21, 119.67, 119.62, 55.27, 27.14, 18.29, -3.20; HRMS (ESI) Calcd. for C16H24NOSi [(M+H)$^+$] 274.1627, found 274.1625.
1-(*tert*-butyldimethylsilyl)-5-methoxyisoquinoline (3b5): According to the general procedure A, 5-methoxyisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (100 mg, 73%). And according to the general procedure B, the product was obtained (95 mg, 69%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J$ = 5.8 Hz, 1H), 7.97 (dd, $J$ = 5.8, 0.6 Hz, 1H), 7.82 (d, $J$ = 8.6 Hz, 1H), 7.49 – 7.42 (m, 1H), 6.94 (d, $J$ = 7.7 Hz, 1H), 3.99 (s, 3H), 0.96 (s, 9H), 0.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.11, 154.84, 142.32, 134.61, 127.15, 126.20, 120.58, 113.92, 106.41, 55.57, 27.10, 18.01, -3.03; HRMS (ESI) Calcd. for C$_{16}$H$_{24}$NOSi [(M+H)$^+$] 274.1627, found 274.1620.

5-(benzyloxy)-1-(*tert*-butyldimethylsilyl)isoquinoline (3b6): According to the general procedure A, 5-(benzyloxy)isoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (123 mg, 70%). And according to the general procedure B, the product was obtained (119 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J$ = 5.8 Hz, 1H), 8.06 (d, $J$ = 5.7 Hz, 1H), 7.83 (d, $J$ = 8.6 Hz, 1H), 7.52 (d, $J$ = 7.3 Hz, 2H), 7.46 - 7.41 (m, 3H), 7.37 (d, $J$ = 7.2 Hz, 1H), 7.03 (d, $J$ = 7.7 Hz, 1H), 5.25 (s, 2H), 0.96 (s, 9H), 0.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.18, 153.91, 142.37, 136.67, 134.70, 128.65, 128.09, 127.35, 126.20, 120.91, 114.10, 107.87, 70.24, 27.12, 18.03, -3.02; HRMS (ESI) Calcd. for C$_{22}$H$_{28}$NOSi [(M+H)$^+$] 350.1940, found 350.1943.

1-(*tert*-butyldimethylsilyl)isoquinolin-5-yl acetate (3b7): According to the general procedure A, isoquinolin-5-yl acetate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2%...
ethyl acetate/hexane) as a colorless oil (95 mg, 63 %). And according to the general procedure B, the product was obtained (90 mg, 60 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 (d, \(J = 5.8\) Hz, 1H), 8.15 (d, \(J = 8.5\) Hz, 1H), 7.56 (dd, \(J = 15.2, 7.2\) Hz, 2H), 7.42 (d, \(J = 7.5\) Hz, 1H), 2.47 (s, 3H), 0.97 (s, 9H), 0.55 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.54, 169.27, 149.27, 142.93, 134.63, 128.32, 126.65, 125.80, 121.23, 112.91, 27.05, 20.95, 17.97, -3.05; HRMS (ESI) Calcd. for C\(_{17}\)H\(_{24}\)NO\(_2\)Si [(M+H)+] 302.1576, found 302.1578.

2-(1-(tert-butyldimethylsilyl)isoquinolin-5-yl)isoindoline-1,3-dione (3b8): According to the general procedure A, 2-(isoquinolin-5-yl)isoindoline-1,3-dione (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na\(_2\)S\(_2\)O\(_8\) (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)\(_2\)(dtbpy)PF\(_6\) (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2 % ethyl acetate/hexane) as a colorless solid (128 mg, 66 %). And according to the general procedure B, the product was obtained (120 mg, 62 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.33 (d, \(J = 8.6\) Hz, 1H), 8.01 (dd, \(J = 5.4, 3.1\) Hz, 2H), 7.87 – 7.77 (m, 4H), 7.59 (d, \(J = 8.5\) Hz, 1H), 7.51 (dd, \(J = 7.3, 0.9\) Hz, 1H), 0.98 (s, 9H), 0.41 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.03, 167.62, 149.12, 135.58, 132.08, 131.82, 128.05, 127.74, 127.50, 127.05, 126.65, 124.48, 123.95, 26.60, 17.16, -6.25; HRMS (ESI) Calcd. for C\(_{23}\)H\(_{25}\)N\(_2\)O\(_2\)Si [(M+H)+] 389.1685, found 389.1891.

5-(tert-butyldimethylsilyl)-[1,3]dioxolo[4,5-g]isoquinoline (3b9): According to the general procedure A, [1,3]dioxolo[4,5-g]isoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na\(_2\)S\(_2\)O\(_8\) (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)\(_2\)(dtbpy)PF\(_6\) (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10 % ethyl acetate/hexane) as a colorless solid (83 mg, 58 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 (d, \(J = 5.5\) Hz, 1H), 7.50 (s, 1H), 7.40 (d, \(J = 5.5\) Hz, 1H), 7.04 (s, 1H), 6.08 (s, 2H), 0.95 (s, 9H), 0.53 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.73, 141.79, 133.01, 119.70, 104.48, 103.10, 101.42, 29.69, 27.07, 18.02, -3.00; HRMS (ESI) Calcd. for C\(_{16}\)H\(_{22}\)NO\(_2\)Si [(M+H)+] 288.1420, found 288.1431.
1-(tert-butyldimethylsilyl)-6,7-dimethoxyisoquinoline (3b10): According to the general procedure A, 6,7-dimethoxyisoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (92 mg, 61%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 (d, $J$ = 5.5 Hz, 1H), 7.54 (s, 1H), 7.42 (d, $J$ = 5.5 Hz, 1H), 7.03 (s, 1H), 4.01 (d, $J$ = 2.6 Hz, 6H), 0.96 (s, 9H), 0.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.25, 151.8, 149.21, 141.76, 131.27, 130.28, 118.79, 107.19, 105.16, 55.91, 55.77, 27.09, 18.28, -3.26; HRMS (ESI) Calcd. for C$_{17}$H$_{26}$NO$_2$Si [(M+H)$^+$] 304.1733, found 304.1740.

1-(tert-butyldimethylsilyl)-3-methylisoquinoline (3b11): According to the general procedure A, 3-methylisoquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (90 mg, 70%). And according to the general procedure B, the product was obtained (66 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, $J$ = 8.4 Hz, 1H), 7.70 (d, $J$ = 8.2 Hz, 1H), 7.56 (t, $J$ = 7.5 Hz, 1H), 7.46 (t, $J$ = 7.5 Hz, 1H), 7.36 (s, 1H), 2.70 (s, 3H), 0.98 (s, 9H), 0.53 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.37, 150.80, 135.32, 132.03, 128.83, 128.30, 127.02, 125.24, 117.54, 27.06, 24.46, 17.91, -3.16; HRMS (ESI) Calcd. for C$_{16}$H$_{24}$NSi [(M+H)$^+$] 258.1678, found 258.1676.

Methyl 1-(tert-butyldimethylsilyl)isoquinoline-3-carboxylate (3b12): According to the general procedure A, methyl isoquinoline-3-carboxylate (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (93 mg, 62%). And according to the general procedure B, the product was obtained (83 mg, 55%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (s, 1H), 8.33 – 8.22 (m, 1H), 7.93 (dd, $J$ = 6.6, 2.8 Hz, 1H), 7.76 – 7.62 (m, 2H), 4.02 (s, 3H), 1.00 (s, 9H), 0.57 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.98, 167.04, 141.05, 134.86, 134.23, 129.70, 129.07, 128.57, 128.41, 123.07, 52.46, 27.00, 17.94, -3.39; HRMS (ESI) Calcd. for C$_{17}$H$_{24}$NO$_3$Si
According to the general procedure A, isoquinoline (0.5 mmol, 1 equiv.), tert-butylidemethylsilane (72 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (107 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 5.6$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.94 (s, 1H), 7.68 (dd, $J = 8.4$, 1.1 Hz, 1H), 7.55 (d, $J = 5.6$ Hz, 1H), 0.97 (s, 9H), 0.92 (s, 9H), 0.55 (s, 6H), 0.37 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.99, 142.58, 134.61, 133.94, 133.49, 131.48, 126.91, 119.90, 27.11, 26.51, 18.00, 17.05, -3.06, -6.18. HRMS (ESI) Calcd. for C$_{16}$H$_{24}$NOSi [(M+H)$^+$] 358.2381, found 358.2387.

According to the general procedure B, isoquinoline (0.5 mmol, 1 equiv.), tert-butylidemethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (87 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 5.6$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.63 (dd, $J = 7.9$, 7.0 Hz, 1H), 7.60 – 7.51 (m, 2H), 0.97 (s, 9H), 0.57 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.17, 142.50, 134.52, 133.98, 129.16, 128.63, 127.55, 126.35, 119.86, 27.08, 17.98, -3.04; HRMS (ESI) Calcd. for C$_{15}$H$_{22}$NSi [(M+H)$^+$] 244.1522, found 244.1509.

According to the general procedure A, 1-methylisoquinoline (0.5 mmol, 1 equiv.), tert-butylidemethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (45 mg, 35%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.40 (d, $J = 5.8$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.95 (s, 1H), 7.72 (dd, $J = 8.3$, 0.9 Hz, 1H), 7.52 (d, $J = 5.7$ Hz, 1H), 2.96 (s, 3H), 0.91 (s, 9H), 0.37 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.47, 141.40, 134.91, 134.14, 132.27, 123.94, 119.41, 29.69, 26.47, 17.01, -6.21; HRMS (ESI) Calcd. for C$_{16}$H$_{24}$NSi [(M+H)$^+$] 258.1678, found 258.1687.
6-(**tert**-butyldimethylsilyl)-1-phenylisoquinoline (3b15): According to the general procedure A, 1-phenylisoquinoline (0.5 mmol, 1 equiv.), **tert**-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (98 mg, 61%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.62 (d, $J$ = 5.7 Hz, 1H), 8.10 – 7.99 (m, 2H), 7.70 (dd, $J$ = 7.9, 1.4 Hz, 2H), 7.66 (dd, $J$ = 6.6, 3.1 Hz, 2H), 7.57 – 7.47 (m, 3H), 0.92 (s, 9H), 0.38 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.57, 142.13, 141.26, 139.45, 135.83, 133.90, 132.31, 129.89, 128.55, 128.30, 126.67, 125.76, 119.95, 26.48, 17.03, -6.20; HRMS (ESI) Calcd. for C$_{21}$H$_{26}$NSi [(M+H)$^+$] 320.1835, found 320.1837.

6-bromo-1-(**tert**-butyldimethylsilyl)isoquinoline (3b16): According to the general procedure B, 6-bromoisquinoline (0.5 mmol, 1 equiv.), **tert**-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (103 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, $J$ = 5.7 Hz, 1H), 8.11 (d, $J$ = 9.0 Hz, 1H), 7.97 (d, $J$ = 2.0 Hz, 1H), 7.63 (dd, $J$ = 9.0, 2.0 Hz, 1H), 7.47 (d, $J$ = 5.6 Hz, 1H), 0.94 (s, 9H), 0.54 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.57, 143.38, 135.77, 132.26, 130.29, 129.93, 129.64, 123.79, 118.71, 27.00, 17.93, -3.13; HRMS (ESI) Calcd. for C$_{15}$H$_{20}$BrNSi [(M+H)$^+$] 322.0627, found 322.0628.

2-(**tert**-butyldimethylsilyl)-4-methylquinoline (3c): According to the general procedure A, 4-methylquinoline (0.5 mmol, 1 equiv.), **tert**-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (94 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (dd, $J$ = 8.4, 0.5 Hz, 1H), 7.99 (dd, $J$ = 8.4, 0.5 Hz, 1H), 7.70 (dd, $J$ = 8.3, 6.9, 1.3 Hz, 1H), 7.55 (ddd, $J$ = 8.2, 6.9, 1.2 Hz, 1H), 7.44 (d, $J$ = 0.6 Hz, 1H), 2.71 (d, $J$ = 0.8 Hz, 3H), 1.02 (s, 9H), 0.45 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.52, 148.37, 140.21, 130.82, 128.38, 127.26, 126.97, 126.03, 123.59, 26.73, 18.61, 17.21, -6.15; HRMS (ESI) Calcd. for C$_{16}$H$_{26}$NSi [(M+H)$^+$] 258.1678, found 258.1668.
4-(tert-butyldimethylsilyl)-6-fluoro-2-methylquinoline (3d): According to the general procedure A, 6-fluoro-2-methylquinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (97 mg, 70 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (dd, $J$ = 9.2, 5.8 Hz, 1H), 7.62 (dd, $J$ = 10.6, 2.8 Hz, 1H), 7.46 – 7.36 (m, 2H), 2.72 (s, 3H), 0.93 (s, 9H), 0.50 (s, 6H).

13C NMR (100 MHz, CDCl$_3$) δ 160.70, 158.26, 156.42, 156.40, 146.31, 146.25, 144.39 (s), 131.60, 131.51, 131.12, 131.03, 130.92, 118.65, 118.40, 112.28, 112.06, 26.96, 25.07, 17.57, -3.53; HRMS (ESI) Calcd. for C$_{16}$H$_{23}$FNSi [(M+H)$^+$] 276.1584, found 276.1589.

2,4-bis(tert-butyldimethylsilyl)quinolone (3e): According to the general procedure A, quinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (123 mg, 75 %, mixture of 3e$'$ and 3e). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (t, $J$ = 7.6 Hz, 1.3 H), 8.08 – 8.00 (m, 1.3 H), 7.79 (s, 0.3 H), 7.76 (s, 1H), 7.65 – 7.63 (m, 2H), 0.97 (s, 12H), 0.96 (s, 11 H), 0.45 (s, 8 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.54, 148.11, 141.84, 134.27, 132.61, 131.34, 131.21, 130.19, 128.91, 128.77, 128.04, 127.61, 127.15, 126.27, 126.05, 125.71, 26.98, 26.68, 17.70, 17.21, -3.33, -6.17, -6.23. HRMS (ESI) Calcd. for C$_{21}$H$_{36}$NSi [(M+H)$^+$] 358.2381, found 358.2387.

2-(tert-butyldimethylsilyl)quinolone (3e): According to the general procedure B, quinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (81 mg, 66 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, $J$ = 8.4 Hz, 1H), 8.02 (d, $J$ = 8.2 Hz, 1H), 7.77 (d, $J$ = 8.2 Hz, 1H), 7.53 – 7.48 (m, 1H), 0.97 (s, 9H), 0.41 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.05, 148.73, 132.60, 130.20, 128.77, 127.61, 127.16, 126.26, 126.06, 26.67, 17.20, -6.18; HRMS (ESI) Calcd. for C$_{15}$H$_{22}$NSi [(M+H)$^+$] 244.1522, found 244.1526.
6-((tert-butyldimethylsilyl)phenanthridine (3f): According to the general procedure A, phenanthridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)_2(dtbbpy)PF_6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (120 mg, 82%). 1H NMR (400 MHz, CDCl_3) δ 8.66 (d, J = 8.3 Hz, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.84 – 7.76 (m, 1H), 103 (s, 9H), 0.61 (s, 6H). 13C NMR (100 MHz, CDCl_3) δ 171.63, 130.88, 130.69, 129.56, 129.49, 128.16, 126.97, 126.56, 123.06, 122.27, 121.78, 27.19, 18.10, -3.07; HRMS (ESI) Calcd. for C_{19}H_{24}NSi [(M+H)^+] 294.1678, found 294.1676.

Methyl 1-((tert-butyldimethylsilyl)-9H-pyrido[3,4-b]indole-3-carboxylate (3g): According to the general procedure A, Methyl-9H-pyrido[3,4-b]indole-3-carboxylate (this substrate was prepared according to known procedure 4) (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)_2(dtbbpy)PF_6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (111mg, 65 %). 1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 1H), 8.35 (s, 1H), 8.19 (d, J = 7.9 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.34 (ddd, J = 8.0, 6.4, 1.7 Hz, 1H), 4.02 (s, 3H), 1.00 (s, 9H), 0.59 (s, 6H); 13C NMR (100 MHz, CDCl_3) δ 167.23, 148.86, 142.80, 140.06, 128.63, 126.68, 121.89, 121.66, 120.83, 116.86, 111.67, 52.36, 26.64, 17.83, -3.05; HRMS (ESI) Calcd. for C_{19}H_{25}N_{2}O_{2}Si [(M+H)^+] 341.1685, found 341.1683.

8-((tert-butyldimethylsilyl)imidazo[1,2-b]pyridazine (3h): According to the general procedure A, imidazo[1,2-b]pyridazine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)_2(dtbbpy)PF_6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (41 mg, 35 %). 1H NMR (400 MHz, CDCl_3) δ 8.21 (d, J = 4.3 Hz, 1H), 7.92 (d, J = 1.2 Hz, 1H), 7.78 (d, J = 1.1 Hz, 1H), 7.04 (d, J = 4.3 Hz, 1H), 0.95 (s, 9H),
0.48 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.16, 141.80, 138.56, 133.20, 123.30, 115.73, 26.88, 17.33, -5.47; HRMS (ESI) Calcd. for C$_{12}$H$_{20}$N$_3$Si [(M+H)$^+$] 234.1421, found 234.1427.

7-(tert-butyldimethylsilyl)imidazo[1,2-b]pyridazine (3h′): According to the general procedure A, imidazo[1,2-b]pyridazine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % ethyl acetate/hexane) as a colorless solid (20 mg, 17 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.28 (d, J = 1.4 Hz, 1H), 8.05 (d, J = 0.9 Hz, 1H), 7.95 (s, 1H), 7.76 (d, J = 0.7 Hz, 1H), 0.91 (s, 9H), 0.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.56, 138.72, 133.67, 132.19, 126.61, 116.32, 26.24, 16.96, -6.53; HRMS (ESI) Calcd. for C$_{12}$H$_{20}$N$_3$Si [(M+H)$^+$] 234.1421, found 234.1427.

8-(tert-butyldimethylsilyl)-6-chloro-[1,2,4]triazolo[4,3-b]pyridazine (3i): According to the general procedure A, 6-chloro-[1,2,4]triazolo[4,3-b]pyridazine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % ethyl acetate/hexane) as a colorless solid (72 mg, 61 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.00 (s, 1H), 7.07 (s, 1H), 0.98 (s, 9H), 0.51 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.12, 145.49, 142.08, 137.92, 132.19, 126.61, 116.32, 26.24, 16.96, -6.53; HRMS (ESI) Calcd. for C$_{11}$H$_{18}$ClN$_4$Si [(M+H)$^+$] 269.0984, found 269.0988.

7-(tert-butyldimethylsilyl)-1H-pyrrolo[2,3-c]pyridine (3j): According to the general procedure B, 1H-pyrrolo[2,3-c]pyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (68 mg, 58%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, J = 5.4 Hz, 1H), 8.39 (s, 1H), 7.50 (d, J = 5.4 Hz, 1H), 7.35 (d, J = 3.1 Hz, 1H), 6.55 (d, J = 3.1 Hz, 1H), 0.95 (s, 9H), 0.52 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.88, 139.66, 139.32, 130.46, 127.24, 114.64, 101.69, 26.59, 17.84, -5.01; HRMS (ESI) Calcd. for C$_{13}$H$_{21}$N$_2$Si [(M+H)$^+$] 233.1474, found 233.1477.
4,4'-di-tert-butyl-6-(tert-butyldimethylsilyl)-2,2'-bipyridine (3k): According to the general procedure A, 4,4'-di-tert-butyl-2,2'-bipyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (103 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J = 1.6$ Hz, 1H), 8.58 (d, $J = 5.2$ Hz, 1H), 8.33 (d, $J = 1.9$ Hz, 1H), 7.49 (d, $J = 1.9$ Hz, 1H), 7.28 (dd, $J = 5.3$, 2.0 Hz, 1H), 1.38 (d, $J = 5.0$ Hz, 18H), 1.01 (s, 9H), 0.37 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.24, 160.51, 158.06, 157.13, 155.46, 148.76, 126.39, 120.41, 118.64, 116.59, 34.84, 34.80, 30.70, 30.51, 26.65, 16.95, -6.10; HRMS (ESI) Calcd. for C$_{24}$H$_{39}$N$_2$Si [(M+H)$^+$] 383.2883, found 383.2887.

2,9-bis(tert-butyldimethylsilyl)-4,7-dimethyl-1,10-phenanthroline (3l'): According to the general procedure A, 4,7-dimethyl-1,10-phenanthroline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (135 mg, 62%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (s, 2H), 7.60 (s, 2H), 2.75 (s, 6H), 1.05 (s, 18H), 0.46 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.93, 146.32, 140.09, 128.95, 126.71, 122.12, 26.84, 19.03, 17.17, -6.02; HRMS (ESI) Calcd. for C$_{26}$H$_{41}$N$_2$Si$_2$ [(M+H)$^+$] 437.2808, found 437.2811.

methyl 2-(tert-butyldimethylsilyl)-6-methylisonicotinate (3m): According to the general procedure A, methyl 6-methylisonicotinate (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (80 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 0.7$ Hz, 1H), 7.57 (d, $J = 1.3$ Hz, 1H), 3.93 (s, 3H), 2.63 (s, 3H), 0.91 (s, 9H), 0.32 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.65, 166.83, 159.01, 134.83, 125.20, 120.89, 52.44, 26.58, 24.83, 16.89, -6.27; HRMS (ESI) Calcd. for C$_{14}$H$_{24}$NO$_2$Si [(M+H)$^+$] 266.1576, found 266.1578.
4-(tert-butyldimethylsilyl)-2,6-diphenylpyridine (3n): According to the general procedure A, 2,6-
diphenylpyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbp)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (76 mg, 44 %). 1H NMR (400 MHz, CDCl3) δ 8.19 – 8.06 (m, 4H), 7.77 (s, 2H), 7.51 (t, J = 7.4 Hz, 4H), 7.43 (t, J = 7.3 Hz, 2H), 0.95 (s, 9H), 0.38 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 155.50, 149.22, 139.94, 128.78, 128.64, 127.14, 124.32, 26.43, 16.79, -6.46; HRMS (ESI) Calcd. for C23H28NSi [(M+H)+] 346.1986, found 346.1995.

4-(tert-butyl)-2-(tert-butyldimethylsilyl)pyridine (3o): According to the general procedure A, 4-
(tert-butyl)pyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbp)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (90 mg, 72 %). 1H NMR (400 MHz, CDCl3) δ 8.66 (dd, J = 5.3, 0.6 Hz, 1H), 7.47 (dd, J = 2.1, 0.7 Hz, 1H), 7.15 (dd, J = 5.3, 2.1 Hz, 1H), 1.28 (s, 9H), 0.89 (s, 9H), 0.31 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 165.76, 156.84, 149.68, 126.81, 119.48, 34.36, 30.47, 26.50, 16.82, -6.33. HRMS (ESI) Calcd. for C15H28NSi [(M+H)+] 250.1986, found 250.1993.

Methyl 2-(tert-butyldimethylsilyl)isonicotinate (3p): According to the general procedure A, 4-(tert-butyldimethylsilyl)isonicotinate (3p): According to the general procedure A, 4-(tert-butyl)pyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbp)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (50 mg, 40 %). 1H NMR (400 MHz, CDCl3) δ 8.93 (dd, J = 5.0, 0.9 Hz, 1H), 8.00 (dd, J = 1.7, 1.0 Hz, 1H), 7.71 (dd, J = 5.0, 1.8 Hz, 1H), 3.94 (s, 3H), 0.90 (s, 9H), 0.34 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 168.41, 166.39, 150.52, 134.68, 128.20, 121.39, 52.59, 26.48, 16.90, -6.36. HRMS (ESI) Calcd. for C13H22NO2Si [(M+H)+] 252.1414, found 252.1417.
Methyl 2,5-bis(tert-butyldimethylsilyl)isonicotinate (3p’): According to the general procedure A, 4-(tert-butyl)pyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (46 mg, 25 %). ¹H NMR (400 MHz, CDCl₃) δ 9.01 (d, J = 0.9 Hz, 1H), 7.65 (d, J = 0.9 Hz, 1H), 3.89 (s, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.33 (s, 6H), 0.29 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.22, 167.48, 156.52, 143.00, 129.09, 127.79, 52.43, 27.21, 26.54, 17.95, 16.98, -3.89, -6.44. HRMS (ESI) Calcd. for C₁₉H₃₆NO₂Si₂ [(M+H)⁺] 366.2279, found 366.2283.

2,6-bis(tert-butyldimethylsilyl)-4-phenylpyridine (3q’): According to the general procedure A, 4-phenylpyridine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (125 mg, 65 %). ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.58 (m, 2H), 7.55 (s, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 0.94 (s, 18H), 0.33 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 128.97, 128.37, 127.24, 126.22, 26.71, 16.96, -6.17; HRMS (ESI) Calcd. for C₂₃H₃₈NSi₂ [(M+H)⁺] 384.2543, found 384.2541.

4-(tert-butyldimethylsilyl)-2,6-dichloro-5-methylpyrimidine (3r): According to the general procedure A, 2,4-dichloro-5-methylpyrimidine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (59 mg, 43 %). ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H), 0.95 (s, 9H), 0.39 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 180.59, 162.17, 156.50, 134.59, 26.61, 17.99, 17.19, -4.16; HRMS (ESI) Calcd. for C₁₁H₁₅Cl₂N₂Si [(M+H)⁺] 277.0689, found 277.0693.

2-(tert-butyldimethylsilyl)-3,5-dichloropyrazine (3s): According to the general procedure A, 2,6-dichloropyrazine (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (1 % ethyl
acetate/hexane) as a colorless solid (51 mg, 39%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (s, 1H), 0.95 (s, 9H), 0.42 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.02, 153.38, 146.69, 142.32, 26.68, 18.10, -4.80; HRMS (ESI) Calcd. for C$_{10}$H$_{17}$Cl$_2$N$_2$Si [(M+H)$^+$] 263.0533, found 263.0535.

1-(di-tert-butyldimethylsilyl)-6-methylisoquinoline (3t): According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), di-tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (73 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J$ = 5.6 Hz, 1H), 8.44 (d, $J$ = 8.4 Hz, 1H), 7.55 (s, 1H), 7.47 (d, $J$ = 5.6 Hz, 1H), 7.40 (dd, $J$ = 8.6, 1.3 Hz, 1H), 4.63 (s, 1H), 2.53 (s, 3H), 1.09 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.66, 142.57, 139.43, 134.42, 128.83, 128.56, 126.14, 119.21, 28.92, 21.83, 19.53. HRMS (ESI) Calcd. for C$_{18}$H$_{28}$NSi [(M+H)$^+$] 286.1986, found 286.1989.

6-methyl-1-(triisopropylsilyl)isoquinoline (3u): According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), triisopropylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (115 mg, 77%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J$ = 5.6 Hz, 1H), 8.07 (d, $J$ = 8.6 Hz, 1H), 7.56 (s, 1H), 7.46 (d, $J$ = 5.6 Hz, 1H), 7.40 (dd, $J$ = 8.6, 1.6 Hz, 1H), 2.53 (s, 3H), 1.80 - 1.69 (m, 3H), 1.15 (d, $J$ = 7.6 Hz, 18 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.54, 142.70, 139.10, 134.83, 132.83, 128.56, 128.17, 126.48, 119.19, 21.75, 19.03, 13.04. HRMS (ESI) Calcd. for C$_{19}$H$_{30}$NSi [(M+H)$^+$] 300.2142, found 300.2144.

2-(tert-butyldimethylsilyl)terephthalonitrile (5a): According to the general procedure A, terephthalonitrile (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (86 mg, 71%). And according to the general procedure B, the product was obtained (79 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J$ = 1.3 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.73 (dd, $J$ = 7.6 Hz, 18 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.54, 142.70, 139.10, 134.83, 132.83, 128.56, 128.17, 126.48, 119.19, 21.75, 19.03, 13.04. HRMS (ESI) Calcd. for C$_{19}$H$_{30}$NSi [(M+H)$^+$] 300.2142, found 300.2144.
δ 144.45, 139.23, 134.11, 132.18, 121.87, 118.96, 117.53, 115.25, 26.40, 17.85, -5.25; HRMS (ESI) Calcd. for C_{14}H_{19}N_{2}Si [(M+H)^+] 243.1318, found 243.1322.

4-(tert-butyldimethylsilyl)phthalonitrile (5d): According to the general procedure A, phthalonitrile (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na_{2}S_{2}O_{8} (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (59 mg, 50%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (s, 1H), 7.84 (dd, $J$ = 7.7, 1.1 Hz, 1H), 7.76 (d, $J$ = 7.7 Hz, 1H), 0.87 (s, 9H), 0.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.75, 138.85, 138.54, 131.83, 115.80, 115.52, 114.69, 26.15, 16.79, -6.55; HRMS (ESI) Calcd. for C_{14}H_{19}N_{2}Si [(M+H)^+] 243.1318, found 243.1321.

3-(tert-butyldimethylsilyl)benzene-1,2,4,5-tetracarbonitrile (5e): According to the general procedure A, 1,2,4,5-tetracarbonitrile (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (72 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (105 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (s, 1H), 1.06 (s, 9H), 0.75 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.12, 136.64, 126.30, 121.89, 115.18, 113.29, 26.61, 19.81, -2.11; HRMS (ESI) Calcd. for C_{16}H_{17}N_{4}Si [(M+H)^+] 293.1222, found 293.1231.

3-(tert-butyldimethylsilyl)-2,5-dichloroterephthalonitrile (5f): According to the general procedure A, 2,5-dichloroterephthalonitrile (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na$_2$S$_2$O$_8$ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (115 mg, 74%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 1.04 (s, 9H), 0.66 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.43, 141.98, 137.79, 134.62, 124.42, 119.12, 115.60, 114.27, 27.05, 19.84, -0.13; HRMS (ESI) Calcd. for C_{14}H_{17}Cl$_2$N$_2$Si [(M+H)^+] 311.0538, found 311.0540.
**2-(tert-butyldimethylsilyl)benzo[d]thiazole (7a):** According to the general procedure C, benzo[d]thiazole (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTHMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (50 mg, 41 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J = 8.2$ Hz, 1H), 7.97 (d, $J = 7.9$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 1.02 (s, 9H), 0.47 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.79, 156.17, 136.14, 125.62, 125.00, 123.44, 121.48, 26.34, 16.98, -5.45; HRMS (ESI) Calcd. for C$_{13}$H$_{20}$NSSi [(M+H)$^+$] 250.1080, found 250.1085.

**ethyl 2-(tert-butyldimethylsilyl)-4-methylthiazole-5-carboxylate (7b):** According to the general procedure C, ethyl 4-methylthiazole-5-carboxylate (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTHMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (3 % ethyl acetate/hexane) as a colorless solid (95 mg, 67 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.32 (q, $J = 7.1$ Hz, 2H), 2.79 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 0.96 (s, 9H), 0.36 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.30, 162.45, 162.33, 124.42, 61.12, 26.20, 17.38, 16.82, 14.31, -5.59; HRMS (ESI) Calcd. for C$_{13}$H$_{24}$NO$_2$SSi [(M+H)$^+$] 286.1292, found 286.1296.

**tert-butyldimethyl(3-methylbenzo[b]thiophen-2-yl)silane (7c):** According to the general procedure C, 3-methylbenzo[b]thiophene (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTHMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (85 mg, 65 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 7.7$ Hz, 1H), 7.76 (d, $J = 7.3$ Hz, 1H), 7.43 - 7.34 (m, 2H), 2.55 (s, 3H), 1.00 (s, 9H), 0.46 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.95, 141.77, 139.40, 132.65, 124.08, 123.55, 121.99, 121.71, 26.70, 18.23, 15.26, -3.83; HRMS (EI) Calcd. for C$_{15}$H$_{22}$SSi [M$^+$] 262.1211, found 262.1214.

**tert-butyldimethyl(3-methylbenzofuran-2-yl)silane (7d):** According to the general procedure C, 3-methylbenzo[b]thiophene (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTHMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography
(hexane) as a colorless solid (78 mg, 63 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.49 (m, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.30 - 7.20 (m, 2H), 2.33 (s, 3H), 0.97 (s, 9H), 0.38 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.49, 156.29, 129.84, 126.15, 124.14, 121.64, 119.15, 111.09, 26.40, 17.78, 9.22, -5.66; HRMS (EI) Calcd. for C$_{15}$H$_{22}$OSi [M$^+$] 246.1440, found 246.1442.

**3-(tert-butyldimethylsilyl)-1-phenyl-1H-pyrrole (7e):** According to the general procedure C, 3-methylbenzo[b]thiophene (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOTMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (66 mg, 51 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.39 (m, 4H), 7.26 (s, 1H), 7.17 (dd, $J = 2.6$, 2.1 Hz, 1H), 7.09 (t, $J = 1.8$ Hz, 1H), 6.40 (dd, $J = 2.7$, 1.6 Hz, 1H), 0.93 (s, 9H), 0.22 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.46, 129.46, 125.55, 125.45, 120.53, 120.30, 117.22, 116.20, 26.48, 16.75, -5.32; HRMS (EI) Calcd. for C$_{16}$H$_{23}$NSi [M$^+$] 257.1600, found 257.1602.

**8-(tert-butyldimethylsilyl)-3,7-dimethyl-1-(5-oxohexyl)-1H-purine-2,6(3H,7H)-dione (7f):** According to the general procedure C, 3,7-dimethyl-1-(5-oxohexyl)-3,4,5,7-tetrahydro-1H-purine-2,6-dione (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOTMS (138 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)$_2$(dtbpy)PF$_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % acetone/hexane) as a colorless solid (88 mg, 45 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.03 (s, 3H), 3.99 (t, $J = 7.0$ Hz, 2H), 3.56 (s, 3H), 2.49 (t, $J = 7.0$ Hz, 2H), 2.13 (s, 3H), 1.63 (dd, $J = 6.5$, 3.2 Hz, 4H), 0.97 (s, 9H), 0.40 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.90, 157.09, 155.33, 148.93, 109.45, 43.19, 40.62, 34.18, 29.93, 29.55, 27.42, 26.36, 26.36, 20.94, 17.69, -4.98; HRMS (ESI) Calcd. for C$_{19}$H$_{33}$N$_4$O$_3$Si [(M+H)$^+$] 393.2316, found 393.2318.
heptan-2-yl 2-((2-(tert-butyldimethylsilyl)-5-chloroquinolin-8-yl)oxy)acetate (8a): According to the general procedure A, heptan-2-yl 2-((5-chloroquinolin-8-yl)oxy)acetate (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (5% ethyl acetate/hexane) as a colorless oil (115 mg, 51%).

1H NMR (400 MHz, CDCl₃) δ 8.39 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.3 Hz, 1H), 5.11 (s, 2H), 5.03 (dd, J = 7.1, 5.8 Hz, 1H), 1.24 (d, J = 6.3 Hz, 8H), 0.96 (s, 10H), 0.88 – 0.82 (m, 4H), 0.42 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 169.09, 168.70, 153.26, 141.81, 129.74, 127.05, 126.22, 126.09, 124.69, 115.33, 35.77, 31.54, 26.62, 24.94, 22.47, 19.90, 17.05, 13.94, -6.23. HRMS (ESI) Calcd. for C₂₄H₃₇ClNO₃Si [(M+H)⁺] 450.2226, found 450.2228.

4-(tert-butyldimethylsilyl)-1-isobutyl-1H-imidazo[4,5-c]quinolone (8b): According to the general procedure A, 1-isobutyl-1H-imidazo[4,5-c]quinoline (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (136 mg, 80%).

1H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 8.1 Hz, 1H), 8.07 (dd, J = 8.2, 1.0 Hz, 1H), 7.88 (s, 1H), 7.65 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.58 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 4.30 (d, J = 7.4 Hz, 2H), 2.47 – 2.25 (m, 1H), 1.05 (s, 9H), 1.03 (s, 3H), 1.01 (s, 3H), 0.62 (s, 6H). 13C NMR (100 MHz, CDCl₃) δ 164.69, 144.89, 143.60, 142.99, 131.70, 130.00, 126.35, 126.10, 119.80, 117.36, 54.98, 28.71, 27.04, 19.82, 17.67, -4.94. HRMS (ESI) Calcd. for C₂₀H₃₀N₃Si [(M+H)⁺] 340.2204, found 340.2208.

3-(((2-(tert-butyldimethylsilyl)pyridin-4-yl)methyl)(ethyl)amino)-3-oxo-2-phenylpropyl acetate (8c): According to the general procedure A, 3-(ethyl(pyridin-4-ylmethyl)amino)-3-oxo-2-phenylpropyl acetate (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (580 mg, 5 mmol, 10 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (5% ethyl acetate/hexane) as a colorless oil (70 mg, 32%).

1H NMR (400 MHz, CDCl₃) δ 8.64(8.69) (d, J = 5.1 Hz, 1H), 7.37 – 7.19 (m, 6H), 6.92(6.89) (d, J = 5.0 Hz, 1H), 4.87(4.49) (d, J = 15.8 Hz, 1H), 4.69 – 4.62 (m, 1H), 4.38 – 4.13(3.92 – 3.88) (m, 3H), 3.43 - 3.36(3.68 – 3.63)(m, 1H), 3.13 – 3.10(3.24- 3.19) (m, 1H), 2.04(2.00) (s, 3H), 1.09 – 1.03 (m, 3H), 0.92 – 0.82 (m, 9H), 0.33 – 0.20 (m, 6H); 13C NMR (100 MHz, CDCl₃) δ 170.87, 170.67, 166.61, 150.06, 149.75, 144.15, 143.44, 135.53, 135.26, 129.17, 128.57, 128.10, 128.01, 127.97, 127.47, 121.20, 119.97, 66.65, 66.45, 49.48, 48.27.
(S)-11-(tert-butyldimethylsilyl)-4-ethyl-4-hydroxy-1H-pyrano[3',4':6,7]indolizin[1,2-b]quinoline-3,14(4H,12H)-dione (8d): According to the general procedure A, Camptothecin (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (580 mg, 5 mmol, 10 equiv.), Na₂S₂O₈ (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (4:1) (0.1 M) were used. Then irradiated at 467 nm Blue Led (Kessil Photoredox LED Lights PR160 Series) (25% intensity) for 24 hours. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a yellow solid (51 mg, 22%).

1H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 3.5 Hz, 1H), 8.22 (d, J = 3.1 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.68 (s, 1H), 7.65 – 7.60 (m, 1H), 5.76 (d, J = 16.3 Hz, 1H), 5.31 (t, J = 8.1 Hz, 3H), 3.72 (s, 1H), 1.90 (dt, J = 14.3, 6.8 Hz, 2H), 1.07 – 1.04 (m, 3H), 0.99 (s, 9H), 0.70 (s, 6H).

Spectroscopic data in accordance with literature.

6-methylisoquinolin-1-ol (9): 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a (52 mg, 0.2 mmol) and 30% H₂O₂ (0.5 mL) were placed into a flask in tetrahydrofuran (1 mL). The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated NaHSO₃ aqueous solution (10 mL) and extracted with ethyl acetate (3 × 10 mL). Organic layers were combined, dried over anhydrous Na₂SO₄ and concentrated to obtain the compound as brown oil, which was purified by column chromatography (20% ethyl acetate/hexane) to yield the title compound (31 mg, 99%) as a white solid. 1H NMR (400 MHz, CDCl₃) δ 11.64 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.17 (d, J = 7.1 Hz, 1H), 6.51 (d, J = 7.1 Hz, 1H), 2.49 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 164.46, 143.25, 138.31, 128.43, 127.71, 127.15, 125.93, 123.73, 106.60, 21.83. HRMS (ESI) Calcd. for C₁₀H₁₀NO [(M+H)^+] 160.0757, found 160.0762.

General procedure D for Hiyama-Denmark cross-coupling of heteroarylsilane products:
To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding aryl silane (0.5 mmol, 1 equiv.), the corresponding aryl iodides or bromide (1.0 mmol, 2 equiv.), Pd(Ph₃P)₄ (0.025 mmol, 0.05 equiv.) and Ag₂O (0.5 mmol, 1 equiv.). The vial was sealed and placed under an atmosphere of nitrogen, then anhydrous DMF (5 mL, 0.1 M) and TBAF (0.25 mL, 0.5 equiv., 1 mmol/L in THF) were added. The reaction was heated at 90 °C for 4 hours. The reaction mixture was diluted with H₂O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification of
the crude product by flash chromatography on silica gel using the indicated solvent system afforded
the desired product.

6-methyl-1-phenylisoquinoline (10a): According to the general procedure D for Hiyama-Denmark
cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 4-iodobenzene. The
crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the
title compound as a white solid (70 mg, 64%). ^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, J = 5.7 Hz, 1H),
7.99 (d, J = 8.7 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.65 (s, 1H), 7.59 – 7.45 (m, 4H), 7.36 (dd, J = 8.7, 1.6
Hz, 1H), 2.55 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 160.32, 142.21, 140.31, 139.61, 137.14, 129.84,
129.39, 128.47, 128.27, 127.36, 125.85, 125.05, 119.43, 21.83. HRMS (ESI) Calcd. for C_{16}H_{14}N
[(M+H)^+ ] 220.1121, found 220.1119.

1-(4-fluorophenyl)-6-methylisoquinoline (10b): According to the general procedure D for Hiyama-
Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 1-fluoro-4-
iodobenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (83 mg, 70%). ^1H NMR (400 MHz, CDCl_3)
δ 8.59 (d, J = 5.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.60 (d, J = 5.7 Hz, 1H), 7.42
(dd, J = 8.7, 1.6 Hz, 1H), 7.30 – 7.24 (m, 2H), 2.60 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 164.24,
161.78, 159.18, 142.13), 140.47, 137.18, 135.65, 135.61, 131.68, 131.60, 129.57, 127.05, 125.95,
125.00, 119.58, 115.39, 115.18, 21.83. HRMS (ESI) Calcd. for C_{16}H_{13}FN [(M+H)^+ ] 238.1027, found
238.1029.

1-(4-methoxyphenyl)-6-methylisoquinoline (10c): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 1-iodo-4-methoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (95 mg, 76%). ^1H NMR (400 MHz, CDCl_3)
δ 8.53 (d, J = 5.7 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.71 – 7.59 (m, 3H), 7.52 (d, J = 5.7 Hz, 1H), 7.35
(dd, J = 8.7, 1.5 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 2.54 (s, 3H); ^13C NMR (100 MHz,
CDCl$_3$ $\delta$ 159.91, 142.17, 140.19, 137.21, 132.13, 131.20, 129.27, 127.43, 125.84, 125.06, 119.06, 113.70, 55.34, 21.80. HRMS (ESI) Calcd. for C$_{17}$H$_{16}$NO [(M+H)$^+$] 250.1226, found 250.1233.

1-(2-methoxyphenyl)-6-methylisoquinoline (10d): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 1-iodo-2-methoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J$ = 5.7 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.47 (ddd, $J$ = 8.3, 7.6, 1.8 Hz, 1H), 7.38 (dd, $J$ = 7.4, 1.7 Hz, 1H), 7.30 (dd, $J$ = 8.6, 1.6 Hz, 1H), 7.11 (t, $J$ = 7.4Hz, 1H), 7.05 (d, $J$ = 8.3 Hz, 1H), 3.69 (s, 3H), 2.53 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.57, 157.09, 142.20, 140.22, 136.48, 131.17, 129.92, 129.11, 128.64, 127.71, 126.12, 125.58, 120.68, 119.65, 111.05, 55.51, 21.88. HRMS (ESI) Calcd. for C$_{17}$H$_{16}$NO [(M+H)$^+$] 250.1226, found 250.1231.

6-methyl-1-(6-methylpyridin-2-yl)isoquinoline (10e): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 2-bromo-6-methylpyridine. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (83 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J$ = 5.7 Hz, 1H), 8.37 (d, $J$ = 8.7 Hz, 1H), 7.77 (t, $J$ = 7.7 Hz, 1H), 7.69 (d, $J$ = 7.6 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.40 (dd, $J$ = 8.7, 1.6 Hz, 1H), 7.26 (t, $J$ = 3.8 Hz, 2H), 2.69 (s, 3H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.63, 141.97, 140.30, 137.44, 136.96, 129.76, 127.48, 125.69, 125.07, 122.68, 122.06, 120.53, 24.62, 21.86. HRMS (ESI) Calcd. for C$_{16}$H$_{15}$N$_2$ [(M+H)$^+$] 235.1230, found 235.1227.

2-(6-methylisoquinolin-1-yl)quinolone (10f): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a and 2-bromoquinoline. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 67%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.69 (d, $J$ = 8.7 Hz, 1H), 8.64 (d, $J$ = 5.6 Hz, 1H), 8.36 (d, $J$ = 8.5 Hz, 1H), 8.25 (d, $J$ = 8.5 Hz, 1H), 8.13 (d, $J$ = 8.5 Hz, 1H), 7.92 (d, $J$ = 8.1 Hz, 1H), 7.79 (ddd, $J$ = 8.4, 7.0, 1.4 Hz, 1H), 7.70 – 7.58 (m, 3H), 7.45 (dd, $J$ = 8.8, 1.5 Hz, 1H), 2.56 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.13, 157.15,
147.30, 142.00, 140.47, 137.61, 136.78, 130.12, 129.83, 129.68, 127.69, 127.62, 127.55, 127.01 (s), 125.77, 125.31, 120.94, 21.91.

HRMS (ESI) Calcd. for \( \text{C}_{19}\text{H}_{15}\text{N}_{2}\text{[(M+H)]}^+ \) 271.1230, found 271.1234.

7-methyl-1,1'-biisoquinoline (10g): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(\( \text{tert-} \)butyldimethylsilyl)-6-methylisoquinoline 3a and 1-bromoisooquinoline. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (95 mg, 70%).

\[1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.70 (d, J = 5.7 \text{ Hz}, 1\text{H}), 8.66 (d, J = 5.7 \text{ Hz}, 1\text{H}), 7.93 (d, J = 8.3 \text{ Hz}, 1\text{H}), 7.80 (d, J = 5.6 \text{ Hz}, 1\text{H}), 7.75 – 7.61 (m, 4\text{H}), 7.62 (d, J = 8.6 \text{ Hz}, 1\text{H}), 7.46 (dd, J = 8.2, 6.9, 1.1 \text{ Hz}, 1\text{H}), 7.29 (dd, J = 8.6, 1.5 \text{ Hz}, 1\text{H}), 2.54 (s, 3\text{H}); 13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 158.19, 157.67, 141.98, 141.70, 136.39, 132.61, 131.16, 130.42, 127.06, 126.10, 120.86, 21.72. \]

HRMS (ESI) Calcd. for \( \text{C}_{19}\text{H}_{15}\text{N}_{2}\text{[(M+H)]}^+ \) 271.1230, found 271.1231.

1-iodo-6-methylisoquinoline (11): 1-(\( \text{tert-} \)butyldimethylsilyl)-6-methylisoquinoline 3a (52 mg, 0.2 mmol) and NIS (180 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (39 mg, 72%).

\[1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.19 (d, J = 5.6 \text{ Hz}, 1\text{H}), 7.97 (d, J = 9.1 \text{ Hz}, 1\text{H}), 7.55 – 7.43 (m, 3\text{H}), 2.55 (s, 3\text{H}); 13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 143.04, 141.70, 136.39, 132.61, 131.16, 130.42, 127.06, 126.10, 120.86, 21.72. \]

HRMS (ESI) Calcd. for \( \text{C}_{10}\text{H}_9\text{I[N]} \text{[(M+H)]}^+ \) 269.9774, found 269.9781.

6-methyl-1-((trifluoromethyl)thio)isoquinoline (12): 1-(\( \text{tert-} \)butyldimethylsilyl)-6-methyl isoquinoline 3a (52 mg, 0.2 mmol) and 1-((trifluoromethyl)thio)pyrrolidine-2,5-dione (159 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (30 mg, 62%).

\[1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.51 (d, J = 5.6 \text{ Hz}, 1\text{H}), 8.23 (d, J = 8.7 \text{ Hz}, 1\text{H}), 7.67 – 7.59 (m, 2\text{H}), 7.52 (dd, J = 8.7, 1.5 \text{ Hz}, 1\text{H}), 2.57 (s, 3\text{H}); 13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 142.79, 141.71, 137.13, 130.81, 126.21, 125.77, 121.55, 21.89. \]

HRMS (ESI) Calcd. for \( \text{C}_{11}\text{H}_9\text{F}_3\text{NS} \text{[(M+H)]}^+ \) 244.0402, found 244.0406.
6-methylisoquinoline- 1- d (13): 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a (52 mg, 0.2 mmol) and D$_2$O (16 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (29 mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.18 (s, 0.02H), 8.47 (d, $J$ = 5.7 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.43 (dd, $J$ = 8.4, 1.3 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.52 (t, $J$ = 107.6 Hz), 142.75, 140.79, 136.09, 129.53, 127.36, 126.98, 125.32, 120.02, 22.04. HRMS (ESI) Calcd. for C$_{10}$H$_8$DN [(M+H)$^+$] 145.0871, found 145.0880.

6-methyl-1-(phenylselanyl)isoquinoline (14): 1-(tert-butyldimethylsilyl)-6-methylisoquinoline 3a (52 mg, 0.2 mmol) and phenyl hypochloroselenoite (153 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (28 mg, 47%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, $J$ = 5.6 Hz, 1H), 8.16 (d, $J$ = 8.6 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.55 (s, 1H), 7.43 (dd, $J$ = 8.6, 1.6 Hz, 1H), 7.38 (d, $J$ = 5.6 Hz, 1H), 7.34 (dd, $J$ = 4.2, 2.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.64, 142.87, 140.85, 136.24, 135.09, 129.73, 129.18, 128.52, 128.01, 127.77, 126.65, 126.17, 118.95, 21.82. HRMS (ESI) Calcd. for C$_{16}$H$_{14}$NSe [(M+H)$^+$] 300.0286, found 300.0289.

4,4'-di-tert-butyl-2,2'-bipyridine (15): According to the general procedure D for Hiyama-Denmark cross-coupling with 4-(tert-butyl)-2-(tert-butyldimethylsilyl)pyridine 3o and 2-bromo-4-(tert-butyl)pyridine. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (74 mg, 55%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 (dd, $J$ = 5.3, 0.4 Hz, 2H), 8.40 (d, $J$ = 1.4 Hz, 2H), 7.28 (dd, $J$ = 5.2, 2.0 Hz, 2H), 1.36 (s, 19H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.87, 156.44, 148.96, 120.64, 118.20, 34.90, 30.55. HRMS (ESI) Calcd. for C$_{18}$H$_{25}$N$_2$ [(M+H)$^+$] 269.2012, found 269.2015.
Methyl 1-(4-fluorophenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (16): According to the general procedure D for Hiyama-Denmark cross-coupling methyl 1-(tert-butyldimethylsilyl)-9H-pyrido[3,4-b]indole-3-carboxylate 3g and 1-fluoro-4-iodobenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 56%). \[^1^H\] NMR (400 MHz, \(d_6\)-DMSO) \(\delta 11.96\) (s, 1H), 8.93 (s, 1H), 8.43 (d, \(J = 7.9\) Hz, 1H), 8.07 (dd, \(J = 8.8, 5.5\) Hz, 2H), 7.69 (d, \(J = 8.2\) Hz, 1H), 7.66 – 7.58 (m, 1H), 7.47 (t, \(J = 8.9\) Hz, 2H), 7.37 – 7.29 (m, 1H), 3.93 (s, 3H); \[^1^H\]NMR (400 MHz, \(d_6\)-DMSO) \(\delta 165.97, 163.79, 161.34, 141.46, 141.05, 136.61, 134.47, 133.93, 130.85, 130.76, 129.23, 128.71, 122.03, 121.10, 120.43, 116.71, 115.76, 115.54, 112.71, 52.03. HRMS (ESI) Calcd. for C\(_{19}\)H\(_{14}\)FN\(_2\)O\(_2\) [(M+H)\(^+\)] 321.1034, found 321.1037.

Quinolin-4-yl(m-tolyl)methanone (18): The 3-methylbenzoyl group was introduced according to the known procedure.\(^6\) To a solution of 2-(tert-butyldimethylsilyl) quinoline 3e (0.2 mmol), 3-methylbenzaldehyde (0.8 mmol) and TMSN\(_3\) (0.4 mmol) in benzene (1.5 mL) phenyliodinebis(trifluoroacetate) (PIFA) (0.4 mmol) was added portionwise in a 5-10 minutes period at room temperature. After stirring the reaction mixture for 2 h at room temperature, Et\(_3\)N (0.5 mL) was added and then stirred for 10 min. The solvents were removed under reduced pressure. The crude mixture was added to 1 mL H\(_2\)O, then TBAF (1.0 mL, 1 mmol/L in THF) were added, the reaction was heated at 80 °C for 4 hours. The reaction mixture was diluted with H\(_2\)O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na\(_2\)SO\(_4\) and concentrated in vacuo. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a colorless oil (22 mg, 44%). \[^1^H\] NMR (400 MHz, CDCl\(_3\)) \(\delta 9.01\) (d, \(J = 4.3\) Hz, 1H), 8.19 (d, \(J = 8.5\) Hz, 1H), 7.82 (d, \(J = 9.0\) Hz, 3H), 7.76 (ddd, \(J = 8.4, 6.9, 1.4\) Hz, 1H), 7.52 (ddd, \(J = 8.2, 6.9, 1.2\) Hz, 1H), 7.39 (d, \(J = 4.3\) Hz, 1H), 7.26 (s, 1H), 6.94 (d, \(J = 9.0\) Hz, 2H), 3.88 (s, 3H); \[^1^H\] NMR (400 MHz, CDCl\(_3\)) \(\delta 194.51, 164.49, 149.52, 148.49, 145.12, 132.73, 129.98, 129.87, 129.55, 127.49, 125.47, 125.04, 119.21, 114.04, 55.60. HRMS (ESI) Calcd. for C\(_{17}\)H\(_{14}\)NO [(M+H)\(^+\)] 248.1070, found 248.1075.

6-(tert-butyldimethylsilyl)-1-(4-fluorophenyl)isoquinoline (20): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)isoquinoline 3b\(_{13}\) (1.0 mmol) and 1-fluoro-4-iodobenzene(2.0 mmol, 2 equiv.). The crude mixture was purified by flash column
chromatography (50% ethyl acetate/hexane) to give the compound 1-(4-fluorophenyl)isoquinoline 19 as a white solid (159 mg, 71%). Then according to the general procedure A, 1-(4-fluorophenyl)isoquinoline 19 (0.5 mmol, 1 equiv.), tert-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), Na2S2O8 (238 mg, 1.0 mmol, 2.0 equiv.), Ir(ppy)2(dtbpy)PF6 (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (101 mg, 60%). 

1H NMR (400 MHz, CDCl3) δ 8.61 (d, J = 5.7 Hz, 1H), 8.08 – 7.95 (m, 2H), 7.75 – 7.60 (m, 4H), 7.23 (dd, J = 12.1, 5.3 Hz, 2H), 0.92 (s, 9H), 0.38 (s, 6H).

13C NMR (100 MHz, CDCl3) δ 164.35, 159.46, 142.08, 141.52, 135.91, 135.49, 134.02, 132.53, 131.79, 131.71, 126.65, 125.51, 120.16, 115.47, 115.26, 26.51, 17.07, -6.17; HRMS (ESI) Calcd. for C21H25FNSi [(M+H)+] 338.1740, found 338.1751.

1-(4-fluorophenyl)-6-phenylisoquinoline (21): To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added 6-(tert-butyldimethylsilyl)-1-(4-fluorophenyl)isoquinoline 20 (0.5 mmol, 1.0 equiv.), 1-fluoro-4-iodobenzene (1.0 mmol, 2 equiv.), PdCl2 (0.025 mmol, 0.05 equiv.). The vial was sealed and placed under an atmosphere of nitrogen, then anhydrous DMF (5 mL, 0.1 M) and TBAF (1.0 mL, 2.0 equiv., 1 mmol/L in THF) were added. The reaction was heated at 90°C for 4 hours. The reaction mixture was diluted with H2O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na2SO4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (10% ethyl acetate/hexane) to give the title compound as a white solid (106 mg, 71%).

1H NMR (400 MHz, CDCl3) δ 8.63 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 1.5 Hz, 1H), 7.82 (dd, J = 8.8, 1.8 Hz, 1H), 7.78 – 7.67 (m, 5H), 7.53 (dd, J = 10.2, 4.7 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.31 – 7.21 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 164.32, 161.86, 159.37, 142.71, 142.43, 139.82, 137.25, 135.38, 131.73, 131.64, 129.02, 128.23, 127.85, 127.48, 127.04, 125.64, 124.63, 120.27, 115.48, 115.27. HRMS (ESI) Calcd. for C21H15FN [(M+H)+] 300.1183, found 300.1185.

1-(3,4-dimethoxyphenyl)-6,7-dimethoxyisoquinoline (22): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6,7-dimethoxyisoquinoline 3b10 and 4-iodo-1,2-dimethoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (114 mg, 70%).

1H NMR (400 MHz, CDCl3) δ 8.45 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 1.5 Hz, 1H), 7.82 (dd, J = 8.8, 1.8 Hz, 1H), 7.78 – 7.67 (m, 5H), 7.53 (dd, J = 10.2, 4.7 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.31 – 7.21 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 164.32, 161.86, 159.37, 142.71, 142.43, 139.82, 137.25, 135.38, 131.73, 131.64, 129.02, 128.23, 127.85, 127.48, 127.04, 125.64, 124.63, 120.27, 115.48, 115.27. HRMS (ESI) Calcd. for C21H15FN [(M+H)+] 300.1183, found 300.1185.
NMR (100 MHz, CDCl$_3$) δ 157.70, 152.66, 149.27, 148.89, 140.76, 133.86, 132.24, 122.43, 122.18, 118.55, 112.75, 110.74, 105.64, 104.93, 55.89. HRMS (ESI) Calcd. for C$_{19}$H$_{20}$NO$_4$ [(M+H)$^+$] 326.1387, found 326.1391.

1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxyisoquinoline (22'): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(tert-butyldimethylsilyl)-6,7-dimethoxyisoquinoline 3b10 and 5-iodobeno[d][1,3]dioxole. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (108 mg, 70%). 1H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J$ = 5.6 Hz, 1H), 7.46 (d, $J$ = 5.6 Hz, 1H), 7.39 (s, 1H), 7.17 (dd, $J$ = 10.4, 2.4 Hz, 2H), 7.10 (s, 1H), 6.95 (d, $J$ = 7.9 Hz, 1H), 6.04 (s, 2H), 4.03 (s, 3H), 3.88 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 157.58, 152.63, 149.94, 147.81, 147.76, 141.01, 133.80, 123.46, 122.43, 118.62, 110.11, 108.19, 105.49, 104.94, 101.20, 56.02, 55.89. HRMS (ESI) Calcd. for C$_{18}$H$_{16}$NO$_4$ [(M+H)$^+$] 310.1074, found 310.1077.

1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (23): To a stirred solution of 1-(3,4-dimethoxyphenyl)-6,7-dimethoxyisoquinoline (65 mg, 0.2 mmol) in THF (2 mL) at room temperature under nitrogen was added methyl iodide (284 mg, 2 mmol). The resulting solution was stirred in the dark at room temperature for 12 h during which time a yellow precipitate formed. The solvent was removed to dryness to afford the iodide salt as an yellow power. Sodium borohydride (15 mg, 0.4 mmol) was added in portions to the solution of this yellow power in methanol (2 mL) at 0 °C with constant stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were combined, dried over anhydrous Na$_2$SO$_4$ and concentrated to obtain the compound as brown oil. 1H NMR (400 MHz, CDCl$_3$) δ 6.86 (s, 1H), 6.81 (s, 2H), 6.60 (s, 1H), 6.13 (s, 1H), 4.44 (s, 1H), 3.93 – 3.77 (m, 9H), 3.58 (s, 3H), 3.28 (d, $J$ = 7.4 Hz, 2H), 2.91 – 2.70 (m, 2H), 2.38 (s, 3H). 13C NMR (100 MHz, CDCl$_3$) δ 149.20, 148.85, 147.92, 147.76, 147.30, 135.53, 125.35, 122.53, 112.11, 111.11, 110.58, 110.30, 70.25, 55.95, 55.76, 51.39, 43.06, 29.61. HRMS (ESI) Calcd. for C$_{20}$H$_{26}$NO$_4$ [(M+H)$^+$] 344.1856, found 344.1859.
1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (24): To a stirred solution of 1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxyisoquinoline (62 mg, 0.2 mmol) in THF (2 mL) at room temperature under nitrogen was added methyl iodide (284 mg, 2 mmol). The resulting solution was stirred in the dark at room temperature for 12 hr during which time a yellow precipitate formed. The solvent was removed to dryness to afford the iodide salt as an yellow powder. Sodium borohydride (15 mg, 0.4 mmol) was added in portions to the solution of this yellow power in methanol (2 mL) at 0 °C with constant stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were combined, dried over anhydrous Na$_2$SO$_4$ and concentrated to obtain the compound as brown oil, which was purified by column chromatography (10% methanol/dichloromethane) to yield the title compound (49 mg, 75%) as brown oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.73 (d, $J$ = 21.6 Hz, 3H), 6.59 (s, 1H), 6.16 (s, 1H), 5.94 (s, 2H), 4.30 (s, 1H), 3.85 (s, 3H), 3.62 (s, 3H), 3.14 (dd, $J$ = 9.5, 6.5 Hz, 2H), 2.86 – 2.61 (m, 2H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.85, 147.71, 147.22, 147.13, 125.93, 123.32, 111.21, 110.62, 109.58, 107.59, 101.02, 69.98, 55.82, 55.77, 51.22, 43.48, 29.65. HRMS (ESI) Calcd. for C$_{19}$H$_{22}$NO$_4$ [(M+H)$^+$] 328.1543, found 328.1545.
8. References

9. Spectral Data for Products
\[ \text{Diagram of chemical structure} \]