Supporting Information

Visible-Light-Induced 4CzIPN/LiBr System: A Tireless Electron Shuttle to Enable Reductive Deoxygenation of N-Heteroaryl Carbonyls

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List of Contents

1. General information ---------------------------------------------------------------------------------------------------------------------S2
2. General procedure for the synthesis of substrates -------------------------------S3
3. General procedure for the reductive deoxygenation of heteroaryl ketones -------------------S6
4. Optimization of reaction conditions -----------------------------------------------S8
5. Mechanistic studies -------------------------------------------------------------------------------------------------------------------S12
   5.1. Radical trapping experiments ---------------------------------------------------------S12
   5.2. Exploratory experiments ----------------------------------------------------------------S12
   5.3. Stern–Volmer quenching ----------------------------------------------------------------S13
   5.4. Cyclic Voltammetry ---------------------------------------------------------------------S15
   5.5. Light on/off experiment ---------------------------------------------------------------S17
6. Characterization data of products -----------------------------------------------------S18
7. References -------------------------------------------------------------------------S35
8. Copies of $^1$H and $^{13}$C NMR spectra of all products ----------------------------------S36
1. General information

The reactions via general procedure was carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using CDCl$_3$ as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their $^1$H NMR, $^{13}$C NMR data and HRMS data with those in literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Cyclic voltammograms were recorded with a CHI604E electrochemical analyzer/workstation at room temperature in anhydrous acetonitrile. n-Bu$_4$NBF$_4$ was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 40 mV·s$^{-1}$. 
2. General procedure for the synthesis of substrates.

![Chemical structures](image)

**Figure S1.** Starting materials.

### 2.1 Synthesis of aryl N-heteroaryl ketones

**Method A:** To the solution of 4-methylquinoline (0.25 mmol) in DCE (1.2 mL) was added benzaldehyde (0.5 mmol), TFA (0.25 mmol), and TBHP (70% solution in water, 0.75 mmol). The resulting solution was heated at 110 °C with vigorous stirring for 12 h. Then the reaction mixture was cooled to room temperature and treated with saturated aqueous NaHCO₃. The mixture was extracted with ethyl acetate (3×25 mL), and the combined organic layer was dried over MgSO₄, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography using petroleum ether/ethyl acetate (60:1 to 10:1).
Method B: A mixture of 4-methylquinoline (2.5 mmol), aryl-keto acid (7.5 mmol), AgNO₃ (0.2 mmol), NH₄S₂O₈ (0.2 mmol), and CF₃COOH (0.2 mmol) in 25 mL of water and 25 mL of CH₂Cl₂ was stirred for 2 h at 40 °C. The aqueous solution was made basic with NaOH, the organic solvent was separated, and the aqueous solution was further extracted with CH₂Cl₂ (3×25 mL). The reaction products were isolated by flash chromatography using petroleum ether/ethyl acetate (5:1).

Method C: A mixture of acetophenone (1.0 mmol), iodine (1.6 mmol) in DMSO (3 mL), the mixture was stirred at 100 °C, till almost completed conversion of the substrates by TLC, then 1,4-dithane-2,5-diol (1.0 mmol), Aniline (1.0 mmol) were added to the reaction vessel. The solution extracted with ethyl acetate (3×25 mL). The extract was washed with 10% Na₂S₂O₃ solution (3×50 mL). The extract was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The reaction products were isolated by flash chromatography using petroleum ether/ethyl acetate (10:1).

2.2 Synthesis of aryl N-heteroaryl methanols

The corresponding aryl N-heteroaryl ketone (0.4 mmol) was dissolved in 2.0 mL MeOH and 0.5 mL DCM, and NaBH₄ (0.8 mmol) was added slowly. The mixture was stirred for 3-6 h. Then 10.0 mL of H₂O was added slowly, and the residue was extracted with ethyl acetate (3×25 mL). The combined organic layer was dried over MgSO₄ and evaporated in vacuo. The product was further purified by silica gel column using petroleum ether/ethyl acetate (2:1).
2.3 Synthesis of benzothiazol-2-aryl methanones\textsuperscript{5,6}

**Method A:** A sealed tube was charged with benzothiazole (0.5 mmol), CuI (2 mol%), acetophenone (1.0 mmol), HBF\textsubscript{4} (0.25 mmol, 40% in aq.) and DMSO (0.75 mL). The resulting solution was purged by N\textsubscript{2} and sealed, then stirred at 130 °C under N\textsubscript{2} for 9 hours. After cooling down to room temperature, ethyl acetate (10 mL) was added, and the organic layer was washed with saturate NaHCO\textsubscript{3} solution and brine. The combined aqueous layers were extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvents were removed via rotary evaporator and the product was purified by silica gel column using petroleum ether/ethyl acetate (30:1).

![Chemical structure of benzothiazol-2-aryl methanones]

**Method B:** Styrene (0.4 mmol), aniline (1.0 mmol), sulfur (1.6 mmol), NH\textsubscript{4}I (0.4 mmol), N-methyl-2-pyrrolidone (1.2 mL) were added to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 160 °C for 48 h. And then 30% hydrogen peroxide aqueous solution (1.0 equiv.), dimethyl sulfoxide (1.0 mL) was added to the reaction vessel. The sealed reaction vessel was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layer was dried over magnesium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1).
3. General procedure for the reductive deoxygenation of heteroaryl ketones.

Reaction set-up for irradiation of mixture with blue LEDs: A commercially available blue LED (35W, HIPAR30) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the reaction light source, and the homemade insulation attached to the apparatus was used to maintain the reaction temperature at 60 °C.

A 10 mL reaction vessel was charged with LiBr (4.3 mg, 0.05 mmol), 4CzIPN (2.4 mg, 0.003 mmol), 2-benzoyl-4-methylquinoline (1a, 24.7 mg, 0.1 mmol), CH₃SO₃H (20 μL, CH₃SO₃H/H₂O=1/5 aqueous (v/v), 0.1 mmol), (PhO)₂PO₂H (15.0 mg, 0.06 mmol), H₂O (50 equiv) and PhCl (1.5 mL), The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). Then, benzaldehyde (21 μL, 0.2 mmol, 2.0 equiv) was added by syringe. The resulting mixture was stirred for 60 h under irradiation with a 35 W blue LEDs at 60 °C. After cooling to room temperature, the crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) (petroleum ether/ethyl acetate = 10:1) to give product 2a as a yellow solid (20.1 mg, 86%), mp: 63 – 65 °C.
Scale-up experiment:

A 100 mL single neck round bottom flask was charged with LiBr (86.0 mg, 0.05 mmol), 4CzIPN (48.0 mg, 0.003 mmol), 2-benzoyl-4-methylquinoline (494.0 mg, 2.0 mmol), CH$_3$SO$_3$H (aq., 400 μL, 20.0 mmol), (PhO)$_2$PO$_2$H (300.0 mg, 0.06 mmol), H$_2$O (1.56 mL) and PhCl (25.0 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). Then, benzaldehyde (410 μL, 4.0 mmol, 2.0 equiv) was added by syringe. The resulting mixture was stirred for 64 h under irradiation with two 35 W blue LEDs at 60 °C. After cooling to room temperature, the crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3×50 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh, petroleum ether/ethyl acetate = 10:1) to give product 2a as a yellow solid (335.6 mg, 72%).
4. Optimization of reaction conditions

Table S1. Screening of solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>CH₃CN</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>acetone</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>PhCl</td>
<td>89 (86)</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>49</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>N.D.</td>
</tr>
<tr>
<td>7</td>
<td>NMP</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>EtOH</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>t-BuOH</td>
<td>60</td>
</tr>
<tr>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>PhCl</td>
<td>63</td>
</tr>
<tr>
<td>11&lt;sup&gt;d&lt;/sup&gt;</td>
<td>PhCl</td>
<td>60</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF₃SO₃H (aq., 1.0 equiv), (PhO)₂PO₂H (0.6 equiv), H₂O (50 equiv), solvent (1.5 mL), 60 ºC under Ar, 60 h. <sup>b</sup> Yields were determined by crude ¹H NMR with CH₂Br₂ as internal standard and isolated yield was given in parentheses. <sup>c</sup> PhCl (1.0 mL). <sup>d</sup> LiBr (1.0 equiv). N.D.= Not Detected.

Table S2. Screening of acids

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>CF₃SO₃H</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>p-TsOH·H₂O</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>TFA</td>
<td>54</td>
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<tr>
<td>5</td>
<td>p-TsOH·5H₂O</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>AcOH·5H₂O</td>
<td>20</td>
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<td>7</td>
<td>CF₃SO₃H·5H₂O</td>
<td>89 (86)</td>
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<tr>
<td>8</td>
<td>TFA·5H₂O</td>
<td>61</td>
</tr>
<tr>
<td>9</td>
<td>MSA·5H₂O</td>
<td>43</td>
</tr>
<tr>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>CF₃SO₃H·5H₂O</td>
<td>76</td>
</tr>
<tr>
<td>11&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CF₃SO₃H·5H₂O</td>
<td>62</td>
</tr>
</tbody>
</table>
12\textsuperscript{e} CF$_3$SO$_3$H·5H$_2$O 61
13\textsuperscript{f} CF$_3$SO$_3$H·5H$_2$O 61

\textsuperscript{a} Reaction conditions: 1a (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), acid (aq., 1.0 equiv), (PhO)$_2$PO$_2$H (0.6 equiv), H$_2$O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. \textsuperscript{b} Yields were determined by crude $^1$H NMR with CH$_2$Br$_2$ as internal standard and isolated yield was given in parentheses. \textsuperscript{c} (PhO)$_2$PO$_2$H (1.0 equiv). \textsuperscript{d} No (PhO)$_2$PO$_2$H. \textsuperscript{e} CF$_3$SO$_3$H (aq., 0.75 equiv). \textsuperscript{f} CF$_3$SO$_3$H (aq., 0.5 equiv).

Table S3. Screening of photocatalyst\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Yield (%)\textsuperscript{b}</th>
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<tr>
<td>1</td>
<td>-</td>
<td>N.D.</td>
</tr>
<tr>
<td>2</td>
<td>PC-1</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>PC-2</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>PC-3</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>PC-4</td>
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<td>6</td>
<td>PC-5</td>
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<td>7</td>
<td>PC-6</td>
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<tr>
<td>8\textsuperscript{c}</td>
<td>PC-5</td>
<td>59</td>
</tr>
<tr>
<td>9\textsuperscript{d}</td>
<td>PC-5</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 1a (0.1 mmol), PhCHO (2.0 equiv), Photocatalyst (3 mol %), LiBr (0.5 equiv), CF$_3$SO$_3$H (aq., 1.0 equiv), (PhO)$_2$PO$_2$H (0.6 equiv), H$_2$O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. \textsuperscript{b} Yields were determined by crude $^1$H NMR with CH$_2$Br$_2$ as internal standard and isolated yield was given in parentheses. \textsuperscript{c} PC-5 (2.0 mol %). \textsuperscript{d} No light.
Table S4. Screening of additive<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>additive</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>NaBr</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>LiBr</td>
<td>89 (86)</td>
</tr>
<tr>
<td>4</td>
<td>LiCl</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>KI</td>
<td>N.D.</td>
</tr>
<tr>
<td>6</td>
<td>LiBr</td>
<td>69</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), additive (0.5 equiv), CF<sub>3</sub>SO<sub>3</sub>H (aq., 1.0 equiv), (PhO)<sub>2</sub>PO<sub>2</sub>H (0.6 equiv), H<sub>2</sub>O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. <sup>b</sup> Yields were determined by crude <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as internal standard and isolated yield was given in parentheses. <sup>c</sup> LiBr (1.0 equiv).

Table S5. Screening of reductant<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reductant</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCHO</td>
<td>89 (86)</td>
</tr>
<tr>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>PhCHO</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>p-Chlorobenzaldehyde</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>Biphenyl-4-carboxaldehyde</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>p-Methyl benzaldehyde</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>p-Methoxy benzaldehyde</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>52</td>
</tr>
<tr>
<td>8&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>(i-Pr)&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>52</td>
</tr>
<tr>
<td>10</td>
<td>Benzyl alcohol</td>
<td>67</td>
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</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.1 mmol), reductant (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF<sub>3</sub>SO<sub>3</sub>H (aq., 1.0 equiv), (PhO)<sub>2</sub>PO<sub>2</sub>H (0.6 equiv), H<sub>2</sub>O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. <sup>b</sup> Yields were determined by crude <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as internal standard and isolated yield was given in parentheses. <sup>c</sup> Benzaldehyde (1.0 equiv). <sup>d</sup> Et<sub>3</sub>SiH (4.0 equiv).

Table S6. Screening of the temperature and time<sup>a</sup>
### Table

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp./Time</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60 °C, 48 h</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>65 °C, 48 h</td>
<td>58 (56)</td>
</tr>
<tr>
<td>3</td>
<td>55 °C, 60 h</td>
<td>(68)</td>
</tr>
<tr>
<td>4</td>
<td>60 °C, 60 h</td>
<td>89 (86)</td>
</tr>
<tr>
<td>5</td>
<td>65 °C, 60 h</td>
<td>51 (48)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF$_3$SO$_3$H (aq., 1.0 equiv), (PhO)$_2$PO$_2$H (0.6 equiv), H$_2$O (50 equiv), PhCl (1.5 mL), under Ar.  
<sup>b</sup> Yields were determined by crude $^1$H NMR with CH$_2$Br$_2$ as internal standard and isolated yield was given in parentheses.  
<sup>c</sup> PhCl (1.0 mL).  
<sup>d</sup> LiBr (1.0 equiv).
5. Mechanistic studies

5.1. Radical trapping experiments

5.2. Exploratory experiments

(1) Within 12 h

(2) In dark

(3) No LiBr

(4) Competitive reactivity of C₂ and C₄ carbonyls

(5) Competitive reactivity of heteroaryl ketone and alcohol

(6) Alcohol as solvent
5.3. Stern–Volmer quenching

**Formulation solution:** (4-methylquinolin-2-yl)(phenyl)methanone (1a, 618.3 mg) was dissolved in dichloromethane in a 25 mL volumetric flask to set the concentration to be 0.1 M. CF$_3$SO$_3$H·5H$_2$O (443 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. LiBr (108.6 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.05 M. PhCHO (254 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. (PhO)$_2$P=O H (375.3 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.06 M. Photocatalyst 4CzIPN (2.0 mg) was dissolved in dichloromethane (25 mL) to set the concentration to be 0.1 mM.

**Experimental procedure:** The resulting 0.1 mM solution (200 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding acetone to prepare a 1.0 μM solution. The resulting mixture was sparged with argon for 1 minutes and then irradiated at 375 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of a (4-methylquinolin-2-yl)(phenyl)methanone solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 1 minutes and irradiated at 375 nm. Fluorescence emission spectra of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

(a) 4CzIPN quenched by CF$_3$SO$_3$H in acetone. Linear quenching was not observed.
(b) 4CzIPN quenched by LiBr in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of LiBr.

(c) 4CzIPN quenched by PhCHO in acetone. Linear quenching is not observed.

(d) 4CzIPN quenched by 2-benzoyl-4-methylquinoline in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of 2-benzoyl-4-methylquinoline.

(e) 4CzIPN quenched by (PhO)₂PO₂H in acetone. Linear quenching is not observed.
(f) 4CzIPN quenched by 2-benzoyl-4-methylquinoline + CF₃SO₃H in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of 2-benzoyl-4-methylquinoline + CF₃SO₃H.

5.4. Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI604E electrochemical analyzer/workstation (Shanghai Chen Hua Instrument Co., Ltd) at room temperature in acetonitrile (Adamas-beta, 99.9%, with molecular sieves, water≤50 ppm (by K.F.)). n-Bu₄NBF₄ (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 40 mV·s⁻¹.
5.5. Light on/off experiment
6. Characterization data of products

2-Benzyl-4-methylquinoline (2a)

![Chemical structure of 2a](image)

The reaction was conducted with 2-benzoyl-4-methylquinoline (24.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2a (20.1 mg, 86%) as a light yellow solid, mp: 63 – 65 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.16 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.3$ Hz, 1H), 7.72 – 7.67 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.06 (s, 1H), 4.33 (s, 2H), 2.60 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 160.8, 147.5, 144.6, 139.3, 129.4, 129.2, 129.1, 128.6, 126.8, 126.4, 125.7, 123.6, 122.1, 45.4, 18.7.

2-(2-Chlorobenzyl)-4-methylquinoline (2b)

![Chemical structure of 2b](image)

The reaction was conducted with (2-chlorophenyl)(4-methylquinolin-2-yl)methanone (28.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2b (15.3 mg, 57%) as a light yellow oil.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.08 (d, $J = 8.3$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.71 – 7.67 (m, 1H), 7.54 – 7.50 (m, 1H), 7.43 – 7.39 (m, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 7.04 (s, 1H), 4.44 (s, 2H), 2.62 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 159.6, 147.7, 144.7, 137.0, 134.3, 131.4, 129.5, 129.5, 129.2, 128.0, 126.9, 125.8, 123.6, 121.9, 42.4, 18.7.

4-Methyl-2-(2-methylbenzyl)quinolone (2c)
The reaction was conducted with (4-methylquinolin-2-yl)(o-tolyl)methanone (26.1 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2c (13.8 mg, 56%) as a white solid, mp: 53 – 55 °C.

1H NMR (400 MHz, Chloroform-d) δ 8.08 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 8.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 2.6 Hz, 4H), 6.94 (s, 1H), 4.31 (s, 2H), 2.59 (s, 3H), 2.30 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 160.6, 147.6, 144.6, 137.4, 137.1, 130.4, 130.2, 129.4, 129.1, 126.8, 126.1, 125.7, 123.6, 121.6, 43.2, 19.9, 18.7.

2-(3-Fluorobenzyl)-4-methylquinoline (2d)

The reaction was conducted with (3-fluorophenyl)(4-methylquinolin-2-yl)methanone (26.5 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2d (15.6 mg, 62%) as a yellow oil.

1H NMR (400 MHz, Chloroform-d) δ 8.09 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.54 – 7.50 (m, 1H), 7.28 – 7.23 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 7.03 – 6.99 (m, 1H), 6.93 – 6.89 (m, 1H), 4.28 (s, 2H), 2.62 (s, 3H); 13C NMR (100 MHz, Chloroform-d) δ 162.9 (d, J = 244.2 Hz), 160.0, 147.6, 144.9, 141.7 (d, J = 7.3 Hz), 129.9 (d, J = 8.4 Hz), 129.5, 129.3, 126.9, 125.9, 124.8 (d, J = 2.8 Hz), 123.6, 122.1, 116.0 (d, J = 20.9 Hz), 113.3 (d, J = 21.2 Hz), 45.0 (d, J = 1.8 Hz), 18.7. HRMS (ESI) m/z calcd for C17H15FN+ (M+H)+ 252.1183, found 252.1186.

2-(3-Chlorobenzyl)-4-methylquinoline (2e)
The reaction was conducted with (3-chlorophenyl)(4-methylquinolin-2-yl)methanone (28.2 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2e (14.2 mg, 53%) as a yellow oil.

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 8.08 (d, J = 8.4 \text{ Hz, } 1\text{H}), 7.94 (d, J = 8.3 \text{ Hz, } 1\text{H}), 7.72 – 7.68 (m, 1\text{H}), 7.54 – 7.50 (m, 1\text{H}), 7.30 (s, 1\text{H}), 7.23 - 7.17 (m, 3\text{H}), 7.05 (s, 1\text{H}), 4.25 (s, 2\text{H}), 2.62 (s, 3\text{H}); ^{13}\text{C NMR (100 MHz, Chloroform-}d\text{)} \delta 159.8, 147.6, 144.9, 141.3, 134.3, 129.8, 129.5, 129.3, 129.2, 127.3, 126.9, 126.6, 125.9, 123.6, 122.1, 45.0, 18.7. \]

2-(3-Bromobenzyl)-4-methylquinoline (2f)\(^7\)

The reaction was conducted with (3-bromophenyl)(4-methylquinolin-2-yl)methanone (32.6 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2f (10.0 mg, 32%) as a white solid, mp: 55 – 57 °C.

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 8.08 (d, J = 8.3 \text{ Hz, } 1\text{H}), 7.94 (d, J = 8.2 \text{ Hz, } 1\text{H}), 7.72 – 7.68 (m, 1\text{H}), 7.55 – 7.51 (m, 1\text{H}), 7.47 (s, 1\text{H}), 7.35 (d, J = 7.9 \text{ Hz, } 1\text{H}), 7.24 (d, J = 7.7 \text{ Hz, } 1\text{H}), 7.16 (t, J = 7.8 \text{ Hz, } 1\text{H}), 7.05 (s, 1\text{H}), 4.25 (s, 2\text{H}), 2.63 (s, 3\text{H}); ^{13}\text{C NMR (100 MHz, Chloroform-}d\text{)} \delta 159.8, 147.6, 144.9, 141.6, 132.1, 130.1, 129.5, 129.5, 129.3, 127.8, 126.9, 125.9, 123.6, 122.6, 122.0, 44.9, 18.7. \]

4-Methyl-2-(3-methylbenzyl)quinolone (2g)

The reaction was conducted with (4-methylquinolin-2-yl)(m-tolyl)methanone (26.1 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2g (14.1 mg, 57%) as a yellow oil.
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.71 – 7.67 (m, 1H), 7.53 – 7.49 (m, 1H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.06 – 7.03 (m, 2H), 4.25 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 160.9, 147.5, 144.5, 139.2, 138.2, 129.9, 129.4, 129.1, 128.4, 127.2, 126.8, 126.2, 125.7, 123.6, 122.2, 45.4, 21.4, 18.7. HRMS (ESI) m/z calcd for C$_{18}$H$_{18}$N$^+$ (M+H)$^+$ 248.1434, found 248.1435.

4-Methyl-2-(4-(trifluoromethoxy)benzyl)quinolone (2h)$^7$

![4-Methyl-2-(4-(trifluoromethoxy)benzyl)quinolone](image)

The reaction was conducted with (4-methylquinolin-2-yl)(4-(trifluoromethoxy)phenyl)methanone (33.1 mg, 0.1mmol) and benzaldehyde (21 $\mu$L, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2h (16.2 mg, 51%) as a yellow oil.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.92 (d, $J = 8.3$ Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.06 (s, 1H), 4.28 (s, 2H), 2.63 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 160.0, 147.8, 147.8 (d, $J = 4.0$ Hz), 147.6, 144.9, 138.0, 130.3, 129.4, 129.3, 126.8, 125.9, 123.6, 122.0, 121.1, 44.6, 18.7.

4-Methyl-2-(4-methylbenzyl)quinolone (2i)

![4-Methyl-2-(4-methylbenzyl)quinolone](image)

The reaction was conducted with (4-methylquinolin-2-yl)(p-tolyl)methanone (26.1 mg, 0.1mmol) and benzaldehyde (21 $\mu$L, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2i (12.3 mg, 54%) as a yellow solid, mp: 63 – 65 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.3$ Hz, 1H), 7.70 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.05 (s, 1H),
4.25 (s, 2H), 2.59 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 161.1, 147.6, 144.5, 136.3, 135.9, 129.5, 129.2, 129.1, 129.0, 126.8, 125.6, 123.6, 122.1, 45.0, 21.0, 18.6. HRMS (ESI) m/z calcd for C$_{18}$H$_{18}$N$^+$ (M+H)$^+$ 248.1434, found 248.1437.

2-(3,4-Dimethylbenzyl)-4-methylquinoline (2j)

The reaction was conducted with (3,4-dimethylphenyl)(4-methylquinolin-2-yl)methanone (27.5 mg, 0.1 mmol) and benzaldehyde (21 $\mu$L, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2j (12.0 mg, 46%) as a white solid, mp: 65 – 67 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.71 – 7.66 (m, 1H), 7.53 – 7.49 (m, 1H), 7.09 – 7.03 (m, 4H), 4.22 (s, 2H), 2.60 (s, 3H), 2.22 (s, 6H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 161.2, 147.5, 144.5, 136.7, 136.7, 134.6, 130.5, 129.8, 129.5, 129.1, 126.9, 126.5, 125.6, 123.6, 122.2, 45.1, 19.7, 19.7, 18.7. HRMS (ESI) m/z calcd for C$_{19}$H$_{20}$N$^+$ (M+H)$^+$ 262.1590, found 262.1591.

4-methyl-2-(thiophen-2-ylmethyl)quinoline (2k)

The reaction was conducted with (4-methylquinolin-2-yl)(thiophen-2-yl)methanone (25.3 mg, 0.1 mmol) and benzaldehyde (21 $\mu$L, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2k (16.7 mg, 70%) as a light yellow solid, mp: 115 – 117 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.3$ Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.19 – 7.17 (m, 2H), 6.97 – 6.93 (m, 2H), 4.47 (s, 2H), 2.64 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 159.7, 147.5, 144.9, 141.5, 129.5, 129.3, 127.0, 126.9,
125.9, 125.9, 124.4, 123.6, 121.7, 39.5, 18.8. HRMS (ESI) m/z calcd for C_{15}H_{14}NS^{+} (M+H)^{+} 240.0841, found 240.0852.

**4-Methyl-2-(2-methylbutyl)quinoline (2l)**

![Chemical structure of 4-Methyl-2-(2-methylbutyl)quinoline](#)

The reaction was conducted with 2-methyl-1-(4-methylquinolin-2-yl)butan-1-one (22.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield 2l (10.3 mg, 48%) as a colorless liquid.

$^{1}$H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.05 (d, \(J = 8.3\) Hz, 1H), 7.95 (d, \(J = 8.2\) Hz, 1H), 7.69 – 7.65 (m, 1H), 7.52 – 7.48 (m, 1H), 7.11 (s, 1H), 2.94 (dd, \(J = 13.1, 6.3\) Hz, 1H), 2.72 – 2.67 (m, 4H), 2.02 – 1.96 (m, 1H), 1.50 – 1.43 (m, 1H), 1.31 – 1.23 (m, 1H), 0.95 – 0.90 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 162.0, 147.7, 143.8, 129.3, 128.9, 126.7, 125.3, 123.5, 122.7, 46.4, 35.6, 29.5, 19.0, 18.7, 11.4.

**2-(5-Chloropentyl)-4-methylquinoline (2m)**

![Chemical structure of 2-(5-Chloropentyl)-4-methylquinoline](#)

The reaction was conducted with 5-chloro-1-(4-methylquinolin-2-yl)pentan-1-one (26.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield 2m (13.1 mg, 53%) as a colorless liquid.

$^{1}$H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.04 (d, \(J = 8.3\) Hz, 1H), 7.94 (d, \(J = 8.3\) Hz, 1H), 7.69 – 7.65 (m, 1H), 7.52 – 7.47 (m, 1H), 7.13 (s, 1H), 3.53 (t, \(J = 6.7\) Hz, 2H), 2.93 (t, \(J = 7.6\) Hz, 2H), 2.67 (s, 3H), 1.87 – 1.80 (m, 4H), 1.59 – 1.51 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 162.1, 147.6, 144.3, 129.2, 129.0, 126.7, 125.4, 123.5, 121.9, 44.9, 38.9, 32.4, 29.1, 26.7, 18.6.

**4-Methyl-2-(undec-10-en-1-yl)quinoline (2n)**

![Chemical structure of 4-Methyl-2-(undec-10-en-1-yl)quinoline](#)
The reaction was conducted with 1-(4-methylquinolin-2-yl)undec-10-en-1-one (30.9 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield 2n (19.6 mg, 66%) as a colorless liquid.

\[ \text{1H NMR (400 MHz, Chloroform-}d\text{) } \delta \]
\[ \begin{align*}
8.04 & (d, J = 8.4 \text{ Hz}, 1H), \\
7.94 & (dd, J = 8.3, 1.4 \text{ Hz}, 1H), \\
7.68 & – 7.64 (m, 1H), \\
7.51 – 7.47 (m, 1H), \\
7.14 & (s, 1H), \\
5.86 & – 5.75 (m, 1H), \\
5.01 & – 4.91 (m, 2H), \\
2.91 & \text{, 2.67 (s, 3H), 2.03 (q, J = 7.1 \text{ Hz}, 2H), 1.83 – 1.75 (m, 2H), 1.44 – 1.27 (m, 12H).} \\
\end{align*} \]
\[ \text{13C NMR (100 MHz, Chloroform-}d\text{) } \delta \]
\[ \begin{align*}
162.7, & 147.6, 144.1, 139.2, 129.3, 129.0, 126.7, 125.3, \\
123.5, 122.0, 114.0, 39.3, 33.8, 30.1, 29.6, 29.5, 29.4, 29.4, 29.1, 28.9, 18.7. \\
\end{align*} \]

4-Methyl-2-octylquinoline (2o)

The reaction was conducted with 1-(4-methylquinolin-2-yl)octan-1-one (26.9 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield 2o (18.9 mg, 74%) as a colorless liquid.

\[ \text{1H NMR (400 MHz, Chloroform-}d\text{) } \delta \]
\[ \begin{align*}
8.04 & (d, J = 8.4 \text{ Hz}, 1H), \\
7.94 & (d, J = 8.3 \text{ Hz}, 1H), \\
7.66 & (t, J = 7.6 \text{ Hz}, 1H), \\
7.49 & (t, J = 7.5 \text{ Hz}, 1H), \\
7.14 & (s, 1H), \\
2.91 & (t, J = 7.8 \text{ Hz}, 2H), \\
2.67 & (s, 3H), \\
1.79 & (p, J = 8.0, 7.5 \text{ Hz}, 2H), \\
1.45 & – 1.26 (m, 10H), \\
0.89 & – 0.86 (m, 3H). \\
\end{align*} \]
\[ \text{13C NMR (100 MHz, Chloroform-}d\text{) } \delta \]
\[ \begin{align*}
162.8, & 147.6, 144.1, 129.2, 128.9, 126.7, 125.3, 123.5, 122.0, 39.3, 31.8, 30.1, \\
29.6, 29.5, 29.2, 22.6, 18.6, 14.1. \\
\end{align*} \]

2-benzyl-6-methylquinoline (2p)

The reaction was conducted with (6-methylquinolin-2-yl)(phenyl)methanone (24.7 mg, 0.1 mmol)
and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2p (18.4 mg, 79%) as a yellow oil.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.98 (d, J = 8.5 \text{ Hz, 1H}), 7.91 (d, J = 8.4 \text{ Hz, 1H}), 7.53 – 7.50 (m, 2H), 7.30 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 7.16 (d, J = 8.4 \text{ Hz, 1H}), 4.32 (s, 2H), 2.50 (s, 3H); ^{13}C \text{ NMR (100 MHz, Chloroform-}d\text{)} \delta 160.2, 146.2, 139.3, 135.8, 135.7, 131.7, 129.1, 128.5, 128.5, 126.7, 126.4, 126.3, 121.4, 45.4, 21.4. \]

2-(3,4-dichlorobenzyl)-6-methylquinoline (2q)

The reaction was conducted with (3,4-dichlorophenyl)(6-methylquinolin-2-yl)methanone (31.6 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2q (14.5 mg, 48%) as a light yellow solid, mp: 89 – 91 °C.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.99 – 7.95 (m, 2H), 7.56 – 7.54 (m, 2H), 7.39 – 7.34 (m, 2H), 7.17 – 7.12 (m, 2H), 4.26 (s, 2H), 2.52 (s, 3H); ^{13}C \text{ NMR (100 MHz, Chloroform-}d\text{)} \delta 158.7, 146.4, 139.5, 136.2, 136.1, 132.4, 132.0, 131.0, 130.5, 130.4, 128.6, 128.5, 126.8, 126.4, 121.3, 44.3, 21.5. \text{ HRMS (ESI) m/z calcd for C}_{17}H_{14}Cl_{2}N^+ (M+H)^+ 302.0498, found 302.0507. \]

2-Benzyl-4-Chloroquinoline (2r)

The reaction was conducted with (4-chloroquinolin-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2r (11.4 mg, 45%) as a white solid, mp: 57 – 59 °C.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 8.14 – 8.08 (m, 2H), 7.74 – 7.70 (m, 1H), 7.57 – 7.53 (m, 1H), 7.31 – 7.29 (m, 5H), 7.25 – 7.21 (m, 1H), 4.29 (s, 2H); ^{13}C \text{ NMR (100 MHz, Chloroform-}d\text{)} \delta 161.1, 148.5, 142.8, 138.4, 130.3, 129.2, 129.1, 128.7, 126.9, 126.7, 124.9, 123.9, 121.4, 45.2. \]
HRMS (ESI) m/z calcd for C_{16}H_{13}ClN^+ (M+H)^+ 254.0731, found 254.0739.

4-Benzyl-2-phenylquinoline (2s)

![Structure of 4-Benzyl-2-phenylquinoline (2s)]

The reaction was conducted with phenyl(2-phenylquinolin-4-yl)methanone (30.9 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield 2s (19.2 mg, 65%) as a yellow oil.  

H NMR (400 MHz, Chloroform-d) δ 8.20 (d, J = 8.4 Hz, 1H), 8.11 – 8.09 (m, 2H), 8.01 (d, J = 8.3 Hz, 1H), 7.71 - 7.67 (m, 1H), 7.64 (s, 1H), 7.52 – 7.42 (m, 4H), 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 4.49 (s, 2H); 13C NMR (100 MHz, Chloroform-d) δ 157.1, 148.5, 147.0, 139.7, 138.7, 130.4, 129.3, 129.2, 128.8, 128.7, 127.5, 126.6, 126.2, 123.7, 119.9, 38.5.

4-Benzyl-2-methylquinoline (2t)

![Structure of 4-Benzyl-2-methylquinoline (2t)]

The reaction was conducted with (2-methylquinolin-4-yl)(phenyl)methanone (24.7 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield 2t (12.1 mg, 52%) as a white solid, mp: 52 – 54 °C.  

H NMR (400 MHz, Chloroform-d) δ 8.04 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.29 – 7.15 (m, 5H), 6.98 (s, 1H), 4.33 (s, 2H), 2.66 (s, 3H); 13C NMR (100 MHz, Chloroform-d) δ 158.6, 147.9, 146.3, 138.5, 129.1, 129.0, 128.7, 128.5, 126.4, 125.7, 125.5, 123.5, 122.5, 37.9, 25.1.

4-Benzyl-7-chloro-2-methylquinoline (2u)
The reaction was conducted with (7-chloro-2-methylquinolin-4-yl)(phenyl)methanone (28.1 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2u (15.2 mg, 57%) as a yellow solid, mp: 91 – 93 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.03 (d, $J = 2.2$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.40 (dd, $J = 8.9, 2.2$ Hz, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 7.18 – 7.16 (m, 2H), 7.04 (s, 1H), 4.37 (s, 2H), 2.68 (s, 3H); $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 160.1, 148.6, 146.4, 138.3, 134.9, 128.7, 128.7, 128.2, 126.7, 126.5, 125.1, 124.3, 122.9, 38.1, 25.3.

6-Benzylphenanthridine (2v)

The reaction was conducted with phenanthridin-6-yl(phenyl)methanone (28.3 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield 2v (17.5 mg, 65%) as a white solid, mp: 104 – 106 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.63 (d, $J = 8.3$ Hz, 1H), 8.57 (d, $J = 8.2$ Hz, 1H), 8.20 (d, $J = 8.2$ Hz, 2H), 7.81 – 7.73 (m, 2H), 7.68 – 7.64 (m, 1H), 7.61 – 7.56 (m, 1H), 7.32 (d, $J = 7.2$ Hz, 2H), 7.24 – 7.22 (m, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 4.76 (s, 2H); $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 160.1, 143.7, 139.1, 133.2, 130.3, 129.8, 128.7, 128.5, 127.3, 127.1, 126.7, 126.3, 125.4, 123.9, 122.4, 121.9, 43.1. HRMS (ESI) m/z calcd for C$_{20}$H$_{16}$N$_2$ (M+H)$^+$ 270.1277, found 270.1288.

1-Benzylisoquinoline (2w)
The reaction was conducted with isoquinolin-1-yl(phenyl)methanone (23.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2w (5.3 mg, 24%) as a yellow oil.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.50 (d, $J = 5.7$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.64 – 7.69 (m, 1H), 7.56 – 7.49 (m, 2H), 7.29 - 7.22 (m, 4H), 7.18 – 7.16 (m, 1H), 4.67 (s, 2H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 160.1, 142.0, 139.4, 136.5, 129.8, 128.5, 128.5, 127.3, 127.2, 127.1, 126.2, 125.8, 119.8, 42.0.

$^{1}$-(4-Chlorobenzyl)isoquinoline (2x)$^{10}$

The reaction was conducted with (4-chlorophenyl)(isoquinolin-1-yl)methanone (26.8 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield 2x (15.2 mg, 60%) as a yellow oil.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.51 (d, $J = 5.7$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.22 - 7.20 (m, 4H), 4.63 (s, 2H); $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 159.5, 141.9, 137.7, 136.5, 132.0, 129.9, 129.9, 128.5, 127.4, 127.3, 126.9, 125.4, 120.0, 41.1.

$^{1}$-(4-Bromobenzyl)isoquinoline (2y)$^{10}$
The reaction was conducted with (4-bromophenyl)(isoquinolin-1-yl)methanone (31.2 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield 2y (18.2 mg, 61%) as a white solid, mp: 67–69 °C.

\[^1\]H NMR (400 MHz, Chloroform-d) \( \delta \) 8.51 (d, \( J = 5.7 \) Hz, 1H), 8.07 (d, \( J = 8.5 \) Hz, 1H), 7.80 (d, \( J = 8.2 \) Hz, 1H), 7.63 (t, \( J = 7.7 \) Hz, 1H), 7.57 – 7.50 (m, 2H), 7.35 (d, \( J = 8.3 \) Hz, 2H), 7.13 (d, \( J = 8.1 \) Hz, 2H), 4.61 (s, 2H); \[^1\]C NMR (101 MHz, Chloroform-d) \( \delta \) 159.4, 141.9, 138.2, 136.4, 131.4, 130.2, 129.9, 127.3, 127.3, 126.9, 125.4, 120.1, 120.0, 41.2.

2-Benzylquinoxaline (2z)

The reaction was conducted with phenyl(quinoxalin-2-yl)methanone (23.4 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2z (13.2 mg, 60%) as a light yellow solid, mp: 81 – 83 °C.

\[^1\]H NMR (400 MHz, Chloroform-d) \( \delta \) 8.71 (s, 1H), 8.08 – 8.04 (m, 2H), 7.74 – 7.66 (m, 2H), 7.33 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 4.36 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-d) \( \delta \) 155.7, 145.8, 141.9, 141.0, 137.7, 129.9, 129.1, 129.0, 128.9, 128.7, 126.8, 42.8.

2-Benzylpyridine (2aa)

The reaction was conducted with phenyl(pyridin-2-yl)methanone (18.3 mg, 0.1 mmol) and
benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield 2aa (14.0 mg, 83%) as a colorless liquid.

\(^{1}\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.55 – 8.53 (m, 1H), 7.57 – 7.52 (m, 1H), 7.32 – 7.25 (m, 4H), 7.23 – 7.19 (m, 1H), 7.08 (dd, \(J = 7.6, 4.5\) Hz, 2H), 4.15 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 160.9, 149.2, 139.4, 136.4, 129.0, 128.5, 126.3, 123.0, 121.1, 44.6.

2-(4-Chlorobenzyl)pyridine (2ab)

The reaction was conducted with (4-chlorophenyl)(pyridin-2-yl)methanone (21.7 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2ab (16.2 mg, 80%) as a colorless liquid.

\(^{1}\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.53 (d, \(J = 5.0\) Hz, 1H), 7.55 (td, \(J = 7.7, 1.9\) Hz, 1H), 7.25 – 7.22 (m, 2H), 7.18 – 7.16 (m, 2H), 7.10 – 7.06 (m, 2H), 4.10 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 160.2, 149.3, 137.8, 136.5, 132.0, 130.2, 128.5, 122.9, 121.2, 43.8.

2-(3-Phenylpropyl)pyridine (2ac)

The reaction was conducted with 3-phenyl-1-(pyridin-2-yl)propan-1-one (21.1 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield 2ac (6.3 mg, 32%) as a colorless liquid.

\(^{1}\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.53 – 8.51 (m, 1H), 7.55 (td, \(J = 7.7, 1.9\) Hz, 1H), 7.26 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 7.12 – 7.05 (m, 2H), 2.84 – 2.80 (m, 2H), 2.69 – 2.66 (m, 2H), 2.10 – 2.03 (m, 1H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 161.8, 149.1, 142.0, 136.1, 128.3, 128.2, 125.6, 122.6, 120.9, 37.8, 35.4, 31.4.

2-Benzyl-4-cyanopyridine (2ad)
The reaction was conducted with 2-benzoylisonicotinonitrile (20.8 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield 2ad (3.0 mg, 15%) as a light yellow liquid.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.69 – 8.67 (m, 1H), 7.34 – 7.29 (m, 4H), 7.26 – 7.23 (m, 3H), 4.19 (s, 2H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 162.5, 150.1, 137.7, 128.9, 128.7, 126.7, 124.4, 122.5, 120.6, 116.4, 44.2.

3-methyl-2-(naphthalen-1-ylmethyl)pyridine (2ae)

The reaction was conducted with (3-methylpyridin-2-yl)(naphthalen-1-yl)methanol (25.0 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield 2ae (9.9 mg, 42%) as a colorless liquid.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.46 (d, \(J = 4.3\) Hz, 1H), 8.19 (d, \(J = 8.1\) Hz, 1H), 7.88 – 7.86 (m, 1H), 7.73 (d, \(J = 8.2\) Hz, 1H), 7.55 – 7.47 (m, 3H), 7.34 (t, \(J = 7.6\) Hz, 1H), 7.13 (dd, \(J = 7.6, 4.8\) Hz, 1H), 6.94 (d, \(J = 7.0\) Hz, 1H), 4.65 (s, 2H), 2.24 (s, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 158.4, 146.9, 138.0, 135.0, 133.7, 132.3, 132.2, 128.6, 126.9, 125.9, 125.7, 125.5, 125.4, 123.8, 121.8, 39.3, 19.0. HRMS (ESI) m/z calced for C\(_{17}\)H\(_{16}\)N\(^+\) (M+H\(^+\)) 234.1277, found 234.1306.

2-Benzylbenzo[d]thiazole (4a)

The reaction was conducted with (benzo[d]thiazol-2-yl)(phenyl)methanone (23.9 mg, 0.1 mmol)
and benzaldehyde (21 µL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield 4a (16.9 mg, 75%) as a yellow oil.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.00 (d, \(J = 8.1\) Hz, 1H), 7.78 (d, \(J = 7.9\) Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 – 7.26 (m, 6H), 4.44 (s, 2H); \(^13\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.2, 153.2, 137.1, 135.6, 129.1, 128.8, 127.3, 125.9, 124.8, 122.7, 121.5, 40.6.

2-Benzyl-6-Methylbenzo[d]thiazole (4b)

\[\text{The reaction was conducted with (6-methylbenzo[d]thiazol-2-yl)(phenyl)methanone (25.3 mg, 0.1mmol) and benzaldehyde (21 µL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield 4b (16.0 mg, 67%) as a white solid, mp: 26 – 28 °C.}\]

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.86 (d, \(J = 8.3\) Hz, 1H), 7.56 (s, 1H), 7.37 – 7.24 (m, 6H), 4.41 (s, 2H), 2.44 (s, 3H); \(^13\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.0, 151.3, 137.3, 135.8, 134.9, 129.1, 128.8, 127.5, 127.3, 122.2, 121.2, 40.5, 21.4.

2-Benzyl-4,6-dimethylbenzo[d]thiazole (4c)

\[\text{The reaction was conducted with (4,6-dimethylbenzo[d]thiazol-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 µL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield 4c (15.9 mg, 63%) as a light yellow solid, mp: 39 – 41 °C.}\]

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.39 – 7.28 (m, 6H), 7.06 (s, 1H), 4.43 (s, 2H), 2.72 (s, 3H), 2.40 (s, 3H); \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 168.9, 150.6, 137.5, 135.7, 134.6, 132.0,
2-Benzyl-6-Ethylbenzo[d]thiazole (4d)

The reaction was conducted with (6-ethylbenzo[d]thiazol-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield 4d (16.5 mg, 65%) as a light yellow oil.

$^{1}$H NMR (400 MHz, Chloroform-d) $\delta$ 7.89 (d, $J = 8.3$ Hz, 1H), 7.58 (d, $J = 1.7$ Hz, 1H), 7.37 – 7.24 (m, 6H), 4.41 (s, 2H), 2.73 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 170.1, 151.4, 141.3, 137.3, 135.8, 129.1, 128.8, 127.2, 126.4, 122.3, 120.0, 40.5, 28.8, 15.9.

2-((1,1'-biphenyl)-4-ylmethyl)benzo[d]thiazole (4e)

The reaction was conducted with [1,1'-biphenyl]-4-yl(benzo[d]thiazol-2-yl)methanone (31.5 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 50/1) to yield 4e (19.9 mg, 66%) as a white solid, mp: 103 – 105 °C.

$^{1}$H NMR (400 MHz, Chloroform-d) $\delta$ 8.01 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 4H), 7.48 – 7.42 (m, 5H), 7.34 (t, $J = 7.5$ Hz, 2H), 4.48 (s, 2H); $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 171.0, 153.2, 140.6, 140.2, 136.1, 135.6, 129.5, 128.7, 127.5, 127.3, 127.0, 126.0, 124.8, 122.8, 121.5, 40.2. HRMS (ESI) m/z calcd for C$_{20}$H$_{16}$NS$^+$ (M+H)$^+$ 302.0998, found 302.1011.
2-(4-Chlorobenzyl)benzo[d]thiazole (4f)\textsuperscript{15}

![Chemical structure of 2-(4-Chlorobenzyl)benzo[d]thiazole (4f)](image)

The reaction was conducted with benzo[d]thiazol-2-yl(4-chlorophenyl)methanone (27.3 mg, 0.1 mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield 4f (21.8 mg, 84%) as a light yellow oil.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.99 (d, \(J = 8.2\) Hz, 1H), 7.79 (d, \(J = 8.1\) Hz, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.28 (m, 5H), 4.39 (s, 2H); \(^13\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 170.3, 153.2, 135.6, 135.5, 133.2, 130.4, 129.0, 126.1, 124.9, 122.8, 121.5, 39.8.

(2-benzylquinolin-4-yl)(phenyl)methanone (7c)

![Chemical structure of (2-benzylquinolin-4-yl)(phenyl)methanone (7c)](image)

7c (16.2 mg, 50%) as a light yellow oil. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.18 (d, \(J = 7.5\) Hz, 1H), 7.80 – 7.72 (m, 4H), 7.61 (t, \(J = 7.4\) Hz, 1H), 7.50 – 7.41 (m, 3H), 7.30 – 7.19 (m, 6H), 4.39 (s, 2H); \(^13\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 196.1, 160.5, 148.2, 144.8, 138.6, 136.5, 134.1, 130.3, 130.1, 129.5, 129.1, 128.7, 127.0, 126.7, 125.2, 123.5, 120.1, 45.5. HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{18}\)NO\(^+\) (M+H)\(^+\) 324.1383, found 324.1402.
7. Reference

8. Copies of $^1$H and $^{13}$C NMR spectra of all products

$^1$H and $^{13}$C NMR spectra of 2a
$^1$H and $^{13}$C NMR spectra of 2b
$^1$H and $^{13}$C NMR spectra of 2c
$^1$H and $^{13}$C NMR spectra of 2d
$^1$H and $^{13}$C NMR spectra of 2e
$^1$H and $^{13}$C NMR spectra of 2f

![NMR Spectra Image]
\(^1\)H and \(^{13}\)C NMR spectra of 2g
$^1$H and $^{13}$C NMR spectra of 2h
$^1$H and $^{13}$C NMR spectra of 2i
$^1$H and $^{13}$C NMR spectra of 2j
$^1$H and $^{13}$C NMR spectra of 2k
$^{1}$H and $^{13}$C NMR spectra of 2l
$^1$H and $^{13}$C NMR spectra of 2m
$^1$H and $^{13}$C NMR spectra of 2n
$^1$H and $^{13}$C NMR spectra of 2o
$^1$H and $^{13}$C NMR spectra of 2p
$^1$H and $^{13}$C NMR spectra of 2q
$^1$H and $^{13}$C NMR spectra of 2r

\[ \text{Diagram of 1H and 13C NMR spectra} \]
$^1$H and $^{13}$C NMR spectra of 2s
$^1$H and $^{13}$C NMR spectra of 2t
$^1$H and $^{13}$C NMR spectra of 2u
$^1$H and $^{13}$C NMR spectra of 2v
$^1$H and $^{13}$C NMR spectra of 2w
$^1$H and $^{13}$C NMR spectra of 2x

![NMR spectra](image)

**$^1$H NMR**
- δ (ppm): 8.51, 8.09, 7.82, 7.60, 7.64, 7.57, 7.55, 7.51, 7.26, 7.21, 7.20, 7.18

**$^{13}$C NMR**
- δ (ppm): 159.30, 141.98, 137.22, 136.48, 131.99, 131.03, 129.67, 128.54, 127.75, 127.32, 125.82, 119.07, 77.32, 77.00, 76.68, 41.15
$^1$H and $^{13}$C NMR spectra of 2y

![NMR spectra image](image-url)
\(^1\)H and \(^{13}\)C NMR spectra of 2z

[Image of NMR spectra with chemical shifts and peaks labeled with corresponding values]
$^1$H and $^{13}$C NMR spectra of 2aa

[Chemical structures and spectra]

S62
$^1$H and $^{13}$C NMR spectra of 2ab

S63
$^1$H and $^{13}$C NMR spectra of 2ac

\begin{center}
\includegraphics[width=\textwidth]{figure.png}
\end{center}
$^1$H and $^{13}$C NMR spectra of 2ad
$^1$H and $^{13}$C NMR spectra of 2ae

[Diagram showing NMR spectra with chemical shift values]
$^1$H and $^{13}$C NMR spectra of 4a
$^1$H and $^{13}$C NMR spectra of 4b

![NMR spectra](image)
$^1$H and $^{13}$C NMR spectra of 4c
$^1$H and $^{13}$C NMR spectra of 4d
\(^1\)H and \(^{13}\)C NMR spectra of 4e
$^1$H and $^{13}$C NMR spectra of 4f
$^{1}$H and $^{13}$C NMR spectra of 7c