Supporting Information

Visible Light Mediated Desilylative C(sp²)-C(sp²) Cross-Coupling Reactions of Arylsilanes with Aryldiazonium Salts under Au(I)/Au(III) Catalysis

Indradweep Chakrabarty, Manjur O. Akram, Suprakash Biswas and Nitin T. Patil

SI 33 examples up to 88% yields

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1. General information

1.1 Practical considerations:

All reactions were performed in oven dried vessels with magnet bar under inert atmosphere. Oven-dried or hypodermic syringes were cooled down to room temperature in desiccator for the use of dried solvents and liquid chemicals. Unless specified, all the desilylative cross-coupling reactions were performed under inert atmosphere using Schlenk techniques. In each catalytic run, the reaction mixture was degassed through three freeze-thaw-pump cycles under dark environment (reaction vessel was wrapped by aluminium foil). Then the reaction mixture was placed ca 10 cm away from a 23 W CFL Bulb. All performed reactions were checked by analytical thin layer chromatography (TLC) and after elution; plate was visualized by UV illumination at 254 nm for UV active materials. In some cases KMnO₄ staining has been used for further visualization. Solvents were removed using rotary evaporator at 35 °C. For column chromatography silica gel finer than 200 mesh has been used.

1.2 Instrumentation:

All ¹H NMR and ¹³C NMR spectra were recorded on Bruker AV, 400/500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards. The chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), br. s (broad signal), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet)… etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. UV-Vis absorption spectra measured with Shimadzu UV-1800 spectrophotometer by using 1 cm path length quartz cuvettes and fluorescence spectra measurement was performed by HORIBA JobinYvon fluorolog fluorimeter.

1.3 Materials:

Unless notified, all chemicals obtained from the commercial suppliers, were used without further purification. THF was distilled from Na/benzophenone under inert atmosphere. DCE, toluene, CH₃CN, MeOH, 1,4-dioxane, THF, DCM and benzene were dried using standard procedure and kept under inert atmosphere. Gold, copper salts and photocatalysts were purchased from Sigma-Aldrich and stored under inert atmosphere.
2. **Optimization of the reactions conditions:**

2.1 **Screening of gold complexes (in absence of copper catalyst):**

\[
\text{entry} \quad \text{[Au] cat.} \quad \text{yield} \\
1 \quad \text{Ph}_3\text{PAuCl} \quad \text{NR} \\
2 \quad \text{IPrAuCl} \quad \text{NR} \\
3 \quad \text{JohnPhosAuCl} \quad \text{NR} \\
4 \quad \text{CyJohnPhosAuCl} \quad \text{NR} \\
5 \quad (\text{C}_6\text{F}_5)_3\text{PAuCl} \quad \text{NR} \\
6 \quad (p\text{-OMe-C}_6\text{H}_4)_3\text{PAuCl} \quad \text{NR} \\
7 \quad \text{Ph}_3\text{PAuOTf} \quad \text{NR} \\
8 \quad \text{Ph}_3\text{PAuNTf}_2 \quad \text{NR}
\]

Reaction conditions: 0.1 mmol 1a, 0.2 mmol 2a, 10 mol% [Au] cat., 2.5 mol% [Ru(bpy)_3](PF_6)_2, 2 equiv K_2CO_3, CH_3CN (0.1 M), rt, 24 h. “Generated in situ” by mixing equimolar amount of Ph_3PAuCl and AgX (X = OTf, NTf_2). NR = no reaction.

2.2 **Screening of copper catalysts:**

\[
\text{entry} \quad \text{[Cu] cat.} \quad \text{yield’} \\
1 \quad \text{CuI} \quad 30 \\
2 \quad \text{CuBr} \quad 45 \\
3 \quad \text{CuCl} \quad 40 \\
4 \quad \text{Cu(OOTf)}_2 \quad 39 \\
5 \quad \text{Cu(OAc)}_2 \quad 50 \\
6 \quad \text{CuBr.DMS} \quad 55 \\
7 \quad \text{CuBr}_2 \quad 53 \\
8 \quad \text{CuO} \quad \text{NR} \\
9 \quad \text{Cu(acac)}_2 \quad 48 \\
10 \quad \text{CuTc} \quad 57 \\
11 \quad \text{Cu(MeCN)}_4\text{BF}_4 \quad 65 \\
12 \quad \text{Cu(MeCN)}_4\text{PF}_6 \quad 61
Reaction conditions: 0.1 mmol 1a, 0.2 mmol 2a, 10 mol% Ph₃PAuCl, 2.5 mol% [Ru(bpy)₃(PF₆)₂], 20 mol% [Cu] cat., 2 equiv K₂CO₃, CH₃CN (0.1 M), rt, 24 h. *Isolated yields. NR = no reaction.

2.3 Screening of gold complexes in presence of [Cu(MeCN)₄]BF₄:

![Reaction conditions](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>[Au(I)] cat.</th>
<th>yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph₃PAuCl</td>
<td>65</td>
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<tr>
<td>2</td>
<td>IPrAuCl</td>
<td>NR</td>
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<tr>
<td>3</td>
<td>JohnphosAuCl</td>
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<tr>
<td>4</td>
<td>CyJohnPhosAuCl</td>
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</tr>
<tr>
<td>5</td>
<td>(C₆F₅)₃PAuCl</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>(p-OMe-C₆H₄)₃PAuCl</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>Ph₃PAuOTf*</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>Ph₃PAuNTf₂*</td>
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</tr>
</tbody>
</table>

Reaction conditions: 0.1 mmol 1a, 0.2 mmol 2a, 10 mol% [Au] cat., 2.5 mol% [Ru(bpy)₃(PF₆)₂], 20 mol% [Cu(MeCN)₄]BF₄, 2 equiv K₂CO₃, CH₃CN (0.1 M), rt, 24 h. *Isolated yields. *Generated in situ. NR = no reaction.

2.4 Screening of bases:

![Reaction conditions](image)

<table>
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<tr>
<th>entry</th>
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<tbody>
<tr>
<td>1</td>
<td>NaOMe</td>
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<tr>
<td>2</td>
<td>NaOH</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>K'OBu</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>Na₂CO₃</td>
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<tr>
<td>5</td>
<td>K₂CO₃</td>
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<tr>
<td>6</td>
<td>Cs₂CO₃</td>
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<tr>
<td>7</td>
<td>NaOAc</td>
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<td>8</td>
<td>KOAc</td>
<td>NR</td>
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</table>

Reaction conditions: 0.1 mmol 1a, 0.2 mmol 2a, 10 mol% Ph₃PAuCl, 2.5 mol% [Ru(bpy)₃(PF₆)₂], 20 mol% [Cu(MeCN)₄]BF₄, 2 equiv base, CH₃CN (0.1 M), rt, 24 h. *Isolated yields. NR = no reaction.
2.5 Screening of solvents:

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield$^\dagger$</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>toluene</td>
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<tr>
<td>3</td>
<td>CH$_3$CN</td>
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<tr>
<td>4</td>
<td>MeOH</td>
<td>NR</td>
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<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
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<td>7</td>
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<td>11</td>
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<tr>
<td>8</td>
<td>benzene</td>
<td>NR</td>
</tr>
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</table>

Reaction conditions: 0.1 mmol 1a, 0.2 mmol 2a, 10 mol% Ph$_3$PAuCl, 2.5 mol% [Ru(bpy)$_3$(PF$_6$)$_2$], 20 mol% [Cu(MeCN)$_4$BF$_4$], 2 equiv K$_2$CO$_3$, solvent (0.1 M), rt, 24 h. $^\dagger$Isolated yields. NR = no reaction.

2.6 Control experiments:

<table>
<thead>
<tr>
<th>entry</th>
<th>[Au] cat.</th>
<th>photo cat.</th>
<th>[Cu] cat.</th>
<th>base</th>
<th>yield</th>
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</thead>
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<tr>
<td>1</td>
<td>Ph$_3$PAuCl</td>
<td>[Ru(bpy)$_3$(PF$_6$)$_2$]</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>--</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>[Ru(bpy)$_3$(PF$_6$)$_2$]</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>Ph$_3$PAuCl</td>
<td>--</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>4$^a$</td>
<td>Ph$_3$PAuCl</td>
<td>[Ru(bpy)$_3$(PF$_6$)$_2$]</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>5$^a$</td>
<td>Ph$_3$PAuCl</td>
<td>[Ru(bpy)$_3$(PF$_6$)$_2$]</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>Ph$_3$PAuCl</td>
<td>--</td>
<td>--</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>7$^a$</td>
<td>Ph$_3$PAuCl</td>
<td>--</td>
<td>--</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>8$^a$</td>
<td>--</td>
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<td>Cu(MeCN)$_4$BF$_4$</td>
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<td>NR</td>
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<td>9$^a$</td>
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<tr>
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<td>Cu(MeCN)$_4$BF$_4$</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>11</td>
<td>--</td>
<td>--</td>
<td>Cu(MeCN)$_4$BF$_4$</td>
<td>--</td>
<td>NR</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 mmol 1a, 0.2 equiv 2a, 10 mol% Ph$_3$PAuCl, 2.5 mol% [Ru(bpy)$_3$(PF$_6$)$_2$], 20 mol% Cu(MeCN)$_4$BF$_4$, 2 equiv K$_2$CO$_3$, CH$_3$CN (0.1 M), rt, 24 h. $^a$Reaction kept in the dark condition. $^b$2 equiv TEMPO has been used. NR = no reaction.
3. General procedure:

3.1 Preparation of starting materials:

3.1.1 Experimental procedure for the synthesis of arylsilanes:

Arylsilanes 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1a′, 1a″ were prepared by literature known procedures while remaining arylsilanes 1c, 1e and 1a″ were prepared by the following procedure.

General procedure: A solution of hetero-aromatic compounds (1 mmol) in anhydrous THF (10 mL) was cooled to −78 ºC. In that cooled solution, nBuLi (1.6 M in hexane, 1.1 mmol) was added slowly and stirred for 1 h at −78 ºC. Then the corresponding chloro(trialkyl)silanes (1.1 mmol) were added to the suspension and the reaction mixture was stirred at rt for 16 h. After the complete conversion of starting material (TLC), the reaction mixture was quenched with saturated aq. solution of NH₄Cl at 0 ºC and the resultant solution was extracted with ethyl acetate. After the removal of solvent under vacuo, the crude reaction mixture was purified by flash column chromatography to afford the corresponding organosilanes.

1c: Colourless liquid; 146 mg, 71% yield; R_f = 0.7 (petroleum ether); ^1H NMR (500 MHz, CDCl₃) δ = 7.93 (dd, J = 1.0, 7.9 Hz, 1 H), 7.87 (dd, J = 1.3, 6.9 Hz, 1 H), 7.54 - 7.51 (m, 1 H), 7.41 - 7.33 (m, 2 H), 0.44 (s, 9 H); ^13C NMR (125 MHz, CDCl₃) δ = 143.5, 142.2, 141.1, 130.8, 124.1, 124.0, 123.4, 122.2.

1a, R = H
1b, R = Me
1c, R = H
1d, R = H
1e, R = Br
1f
1g
1a′
1a″

1e: white solid; 267 mg, 73% yield; mp = 70 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 50/1); 1H NMR (500 MHz, CDCl_3) δ = 7.85 (d, J = 8.8 Hz, 1 H), 7.66 (d, J = 1.5 Hz, 1 H), 7.36 (dd, J = 1.9, 9.2 Hz, 1 H), 6.76 (s, 1 H), 1.72 (s, 10 H), 0.36 (s, 9 H); 13C NMR (125 MHz, CDCl_3) δ = 150.9, 143.9, 136.4, 132.8, 127.0, 123.2, 118.2, 116.8, 115.6, 84.3, 28.2, -0.1; HRMS (ESI) calcd 370.0656 for C_{16}H_{23}BrNO_2Si [M+H]^+, found 370.0109.

1a": colourless liquid; 180 mg, 78% yield; R_f = 0.7 (petroleum ether); 1H NMR (500 MHz, CDCl_3) δ = 7.65 (d, J = 7.7 Hz, 1 H), 7.59 (d, J = 8.3 Hz, 1 H), 7.37 - 7.31 (m, 1 H), 7.30 - 7.24 (m, 1 H), 7.06 (s, 1 H), 1.06 (s, 9 H), 0.40 (s, 6 H); 13C NMR (125 MHz, CDCl_3) δ = 162.1, 158.2, 128.0, 124.2, 122.2, 120.9, 117.3, 111.3, 26.4, 16.8.

3.1.2 Experimental procedure for the synthesis of aryl diazonium salts:

All the aryl diazonium salts (2a-2s, 2t, 2u-2x) were prepared by literature known procedures as given below.

**General procedure:** To a suspension of substituted anilines (10.0 mmol) in water at rt was added HBF_4 (48% in water, 20.0 mmol, 2.0 equiv) and the reaction mixture was stirred for 2 minutes. The mixture was then cooled to 0 °C and a saturated aq. solution of NaNO_2 (10.0 mmol, 1.0 equiv) was added in drop-wise manner. After for 15 min, the resultant solid was filtered, washed with ice-cold water (5 mL) and finally with cold diethyl ether (10 mL) to give the crude product. The crude product was purified by precipitation with diethyl ether from acetone solution to obtain the corresponding aryl diazonium salts as solid.

On the other hand compounds 2y and 2a'-2a" were prepared by the literature known procedures.\textsuperscript{11}

\[ 
\begin{align*}
2y & \quad N_2BF_4 \\
2a' & \quad X = PF_6 \\
2a'' & \quad X = O(CF_3) \\
2a''' & \quad X = OTs
\end{align*}
\]

3.2 General procedure for the C(sp\(^2\))-C(sp\(^2\)) cross-coupling reactions:

A Schlenk tube was loaded with the arylsilanes (0.20 mmol), aryldiazonium salts 2 (0.4 mmol, 2 equiv), Ph\(_3\)PAuCl (0.02 mmol, 10 mol%), Cu(MeCN)\(_4\)BF\(_4\) (0.04 mmol, 20 mol%), [Ru(bpy)\(_3\)]PF\(_6\) (0.005 mmol, 2.5 mol%) and K\(_2\)CO\(_3\) (2 equiv). Then the Schlenk tube was wrapped in aluminium foil before CH\(_3\)CN (2 mL, 0.1 M) was added and the reaction mixture was degassed by using 3 freeze-pump-thaw cycles. The foil was removed and the reaction mixture was stirred for 24 h at rt under light irradiation using 23 W CFL bulb. The mixture was then diluted with DCM (5 mL) and the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluents to afford cross-coupled products 3.

**Characterization data:**

3a:\textsuperscript{12} white solid; 29 mg, 65% yield; mp = 143 °C; \(R_f = 0.7\) (petroleum ether); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.86 - 7.78\) (m, \(J = 8.4\) Hz, 2 H), 7.61 (d, \(J = 7.6\) Hz, 1 H), 7.55 (d, \(J = 8.0\) Hz, 1 H), 7.47 - 7.41 (m, \(J = 8.4\) Hz, 2 H), 7.36 - 7.30 (m, 1 H), 7.30 - 7.25 (m, 1 H), 7.03 (s, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 154.9, 154.8, 134.3, 129.0, 129.0, 126.1, 124.5, 123.1, 121.0, 111.2, 101.7\).

3b:\textsuperscript{13} white solid; 33 mg, 69% yield; mp = 43 °C; \(R_f = 0.5\) (petroleum ether/ethyl acetate = 100/1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.77\) (d, \(J = 8.4\) Hz, 2 H), 7.56 (d, \(J = 7.6\) Hz, 1 H), 7.51 - 7.46 (m, 3 H), 7.33 - 7.28 (m, 2 H), 2.49 (s, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 153.8, 149.6, 133.7, 131.0, 129.9, 128.8, 127.8, 124.6, 122.5, 119.3, 111.7, 110.9, 9.5\).

3c: white solid; 32 mg, 65% yield; mp = 190 ºC; Rf = 0.5 (petroleum ether); 1H NMR (500 MHz, CDCl3) δ = 7.86 - 7.82 (m, 1 H), 7.79 (dd, J = 1.1, 7.1 Hz, 1 H), 7.66 - 7.65 (m, 1 H), 7.64 - 7.63 (m, 1 H), 7.53 - 7.53 (m, 1 H), 7.42 - 7.41 (m, 1 H), 7.40 - 7.39 (m, 1 H), 7.38 - 7.32 (m, 2 H); 13C NMR (125 MHz, CDCl3) δ = 142.8, 140.6, 139.5, 134.1, 132.8, 127.6, 124.6, 124.6, 123.6, 122.3, 119.9.

3d: yellow solid; 38 mg, 59% yield; mp = 70 ºC; Rf = 0.4 (petroleum ether/ethyl acetate = 100/1); 1H NMR (500 MHz, CDCl3) δ = 8.22 (d, J = 8.4 Hz, 1 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.42 - 7.35 (m, 5 H), 7.30 - 7.29 (m, 1 H), 6.58 (s, 1 H), 1.39 (s, 9 H); 13C NMR (125 MHz, CDCl3) δ = 150.1, 140.3, 136.1, 133.9, 132.9, 130.7, 130.0, 128.1, 127.3, 123.1, 116.8, 116.3, 109.4, 84.2, 27.6; HRMS (ESI) calcd 407.0105 for C19H17BrClNO2 [M]+, found 407.9627.

3e: white solid; 52 mg, 65% yield; mp = 135 ºC; Rf = 0.3 (petroleum ether/ethyl acetate = 50/1); 1H NMR (500 MHz, CDCl3) δ = 7.56 (d, J = 8.4 Hz, 1 H), 7.41 (d, J = 7.8 Hz, 1 H), 7.29 - 7.27 (m, 1 H), 7.23 - 7.20 (m, 2 H), 7.13 - 7.10 (m, 2 H), 6.98 - 6.96 (m, 1 H), 6.88 (d, J = 8.5 Hz, 2 H), 6.76 (d, J = 8.2 Hz, 2 H), 6.42 (s, 1 H), 2.36 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ = 144.1, 140.4, 138.8, 138.1, 135.5, 135.0, 134.6, 134.0, 132.9, 132.0, 129.9, 129.9, 129.6, 128.1, 127.8, 127.4, 127.3, 124.4, 123.2, 120.1, 115.3, 111.3, 21.3.

3f: white solid; 53 mg, 69% yield; mp = 135 ºC; Rf = 0.3 (petroleum ether/ethyl acetate = 50/1); 1H NMR (500 MHz, CDCl3) δ = 8.04 (d, J = 8.7 Hz, 2 H), 7.66 (d, J = 8.7 Hz, 2 H), 7.57 (d, J = 8.7 Hz, 2 H), 7.45 (d, J = 8.7 Hz, 2 H), 2.65 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ = 197.6, 144.4, 138.2, 136.0, 134.4, 129.1, 129.0, 128.5, 127.0, 26.6.

3h: \(^{18}\) white solid; 27 mg, 66% yield; mp = 119 °C; \(R_f = 0.8\) (petroleum ether); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.88 - 7.85\) (m, 2 H), 7.61 (d, \(J = 7.6\) Hz, 1 H), 7.55 (d, \(J = 8.0\) Hz, 1 H), 7.36 - 7.24 (m, 2 H), 7.17 (t, \(J = 8.8\) Hz, 2 H), 6.98 (s, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 163.9 - 161.9\) (d, \(^{1}J_{C,F} = 248.91\) Hz), 155.0 - 154.8 (d, \(^{2}J_{C,F} = 20.98\) Hz), 129.2, 126.8, 126.7 (d, \(^{3}J_{C,F} = 8.58\) Hz), 124.3, 123.0, 120.9, 115.9, 115.8, 111.1, 101.0.

3i: \(^{19}\) white solid; 33 mg, 61% yield; mp = 158 °C; \(R_f = 0.8\) (petroleum ether); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.74\) (d, \(J = 8.5\) Hz, 2 H), 7.62 - 7.56 (m, 4 H), 7.48 (m, 2 H), 7.34 - 7.20 (m, 2 H), 7.04 (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 154.0, 132.4, 132.0, 131.8, 131.5, 131.3, 128.5, 126.4, 125.2, 124.6, 123.3, 123.1, 122.8, 121.0, 119.8, 111.3, 101.9.

3j: \(^{20}\) white solid; 43 mg, 67% yield; mp = 175 °C; \(R_f = 0.7\) (petroleum ether); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.79\) (d, \(J = 8.5\) Hz, 2 H), 7.61 - 7.59 (m, 3 H), 7.53 (d, \(J = 8.1\) Hz, 1 H), 7.33 - 7.30 (m, 1 H), 7.27 - 7.24 (m, 1 H), 7.05 (s, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 154.9, 154.8, 137.9, 129.9, 129.0, 126.5, 124.6, 123.1, 121.0, 111.2, 101.9, 94.1.

3k: \(^{12}\) white solid; 33 mg, 62% yield; mp = 111 °C; \(R_f = 0.3\) (petroleum ether); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.14 - 8.12\) (m, 2 H), 7.94 - 7.92 (m, 2 H), 7.62 (d, \(J = 7.6\) Hz, 1 H), 7.58 - 7.55 (m, 1 H), 7.35 - 7.34 (m, 1 H), 7.28 - 7.25 (m, 1 H), 7.18 (s, 1 H), 4.42 (q, \(J = 7.1\) Hz, 2 H), 1.43 (t, \(J = 7.1\) Hz, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 166.2, 155.1, 154.7, 134.4, 130.1, 130.0, 128.9, 125.0, 124.6, 123.2, 121.2, 111.3, 103.4, 61.1, 14.3.

3l: \(^{12}\) white solid; 33 mg, 70% yield; mp = 183 °C; \(R_f = 0.7\) (petroleum ether/ethyl acetate = 25/1); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.30\) (d, \(J = 8.8\) Hz, 2 H), 8.00 (d, \(J = 8.8\) Hz, 2 H), 7.65 (d, \(J = 7.6\) Hz, 1 H), 7.57 (d, \(J = 8.4\) Hz, 1 H), 7.38 (t, \(J = 7.2\) Hz, 1 H), 7.32 - 7.27 (m, 1 H), 7.24 (s, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 155.4, 153.2, 147.2, 136.2, 128.6, 125.8, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1.

**3m**: 19 white solid; 11 mg, 25% yield; mp = 150 °C; Rₖ = 0.7 (petroleum ether/ethyl acetate = 5/1); ¹H NMR (500 MHz, CDCl₃) δ = 8.08 (dd, J = 1.5, 7.6 Hz, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.38 - 7.30 (m, 2 H), 7.30 - 7.27 (m, 1 H), 7.25 - 7.20 (m, 1 H), 7.10 (t, J = 7.4 Hz, 1 H), 7.03 (d, J = 8.4 Hz, 1 H), 4.02 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ = 129.2, 127.1, 124.1, 122.6, 121.0, 120.8, 111.0, 110.8, 106.3, 55.5.

**3n**: 21 white solid; 29 mg, 69% yield; mp = 78 °C; Rₖ = 0.7 (petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ = 7.67 - 7.54 (m, 4 H), 7.46 - 7.39 (m, 1 H), 7.37 - 7.31 (m, 1 H), 7.30 - 7.24 (m, 1 H), 7.11 - 7.06 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 164.3 - 161.9 (d, 1J_C-F = 245.84 Hz), 154.9 - 154.6 (d, 2J_C-F = 36.22 Hz), 132.6 (d, 3J_C-F = 8.48 Hz), 130.4, 130.3, 128.9, 124.7, 123.1, 121.1, 120.6 (d, 4J_C-F = 3.08 Hz), 115.4, 115.2, 111.9, 111.7, 111.2, 102.3.

**3o**: 20 white solid; 28 mg, 63% yield; mp = 87 °C; Rₖ = 0.8 (petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ = 7.88 (t, J = 1.7 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 1 H), 7.38 (d, J = 7.6 Hz, 1 H), 7.35 - 7.31 (m, 2 H), 7.28 (s, 1 H), 7.05 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ = 154.9, 154.3, 134.9, 132.2, 130.0, 128.9, 124.9, 124.7, 123.1, 122.9, 121.1, 111.2, 102.4.

**3p**: 22 white solid; 35 mg, 65% yield; Rₖ = 0.7 (petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ = 8.03 (t, J = 1.5 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.51 - 7.46 (m, 1 H), 7.35 - 7.27 (m, 3 H), 7.04 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ = 154.9, 154.1, 132.4, 131.3, 130.3, 128.9, 127.7, 124.7, 123.3, 123.1, 122.9, 121.1, 111.2, 102.4.

**3q**: 21 white solid; 34 mg, 78% yield; mp = 111 °C; Rₖ = 0.6 (petroleum ether/ethyl acetate = 25/1); ¹H NMR (500 MHz, CDCl₃) δ = 8.13 (d, J = 8.1 Hz, 1 H), 7.79 (d, J = 7.6 Hz, 1 H), 7.74 - 7.67 (m, 3 H), 7.56 (d, J = 8.1 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.39 - 7.36 (m, 1 H), 7.29 (t, J = 7.8 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ = 154.7, 151.2, 134.4, 133.0, 133.0, 128.7, 128.2, 127.0, 125.7, 123.4, 121.9, 118.9, 111.3, 108.1, 106.8.

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3r: white solid; 26 mg, 54% yield; mp = 136 °C; Rf = 0.5 (petroleum ether/ethyl acetate = 50/1); $^1$H NMR (200 MHz, CDCl$_3$) $\delta =$ 8.71 (s, 1 H), 8.21 - 8.16 (m, 2 H), 7.65 - 7.62 (m, 2 H), 7.57 (d, $J =$ 8.2 Hz, 1 H), 7.38 - 7.35 (m, 1 H), 7.31 - 7.27 (m, 1 H), 7.20 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta =$ 155.1, 153.1, 148.7, 132.1, 130.2, 129.8, 125.3, 123.4, 122.8, 121.4, 119.6, 111.4, 103.5.

3s: white solid; 14 mg, 32% yield; mp = 51 °C; Rf = 0.6 (petroleum ether/ethyl acetate = 50/1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 7.60 (d, $J =$ 7.6 Hz, 1 H), 7.54 (d, $J =$ 8.0 Hz, 1 H), 7.47 (d, $J =$ 8.0 Hz, 1 H), 7.43 (s, 1 H), 7.37 (t, $J =$ 7.8 Hz, 1 H), 7.30 (t, $J =$ 7.6 Hz, 1 H), 7.24 (t, $J =$ 7.4 Hz, 1 H), 7.04 (s, 1 H), 6.92 (dd, $J =$ 1.9, 8.0 Hz, 1 H), 3.91 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta =$ 129.8, 124.3, 122.9, 120.9, 117.5, 114.5, 111.2, 110.1, 101.6, 55.4.

3t: white solid; 29 mg, 70% yield; mp = 43 °C; Rf = 0.7 (petroleum ether); $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 8.00 (d, $J =$ 7.9 Hz, 1 H), 7.74 - 7.66 (m, 2 H), 7.57 - 7.55 (m, 2 H), 7.44 (t, $J =$ 7.6 Hz, 1 H), 7.38 - 7.34 (m, 1 H), 7.30 - 7.28 (m, 1 H), 7.24 - 7.21 (m, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta =$ 154.2, 153.1, 134.2, 132.5, 131.0, 130.9, 129.8, 129.4, 128.8, 127.5, 127.1, 124.8, 122.9, 121.4, 120.7, 111.1, 107.0.

3u: white solid; 36 mg, 68% yield; Rf = 0.8 (petroleum ether); $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 8.00 (d, $J =$ 7.9 Hz, 1 H), 7.74 - 7.66 (m, 2 H), 7.57 - 7.55 (m, 2 H), 7.44 (t, $J =$ 7.6 Hz, 1 H), 7.38 - 7.34 (m, 1 H), 7.30 - 7.28 (m, 1 H), 7.24 - 7.21 (m, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta =$ 154.2, 153.1, 134.2, 132.5, 131.0, 130.9, 129.8, 129.4, 128.8, 127.5, 127.1, 124.8, 122.9, 121.4, 120.7, 111.1, 107.0.

3v: white solid; 46 mg, 72% yield; mp = 40 °C; Rf = 0.7 (petroleum ether); $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 7.86 - 7.80 (m, 1 H), 7.70 (d, $J =$ 7.5 Hz, 1 H), 7.60 (d, $J =$ 8.2 Hz, 1 H), 7.50 - 7.44 (m, 2 H), 7.41 - 7.36 (m, 1 H), 7.32 (t, $J =$ 7.5 Hz, 1 H), 7.11 - 7.06 (m, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta =$ 155.5, 154.5, 140.9, 138.9, 135.1, 130.2, 129.9, 129.8, 128.5, 128.1, 128.0, 124.7, 123.0, 121.4, 111.2, 106.2, 95.3; HRMS (ESI) calcld 319.9693 for C$_{14}$H$_9$IO $[M]^+$, found 319.9713.

3w: white solid; 35 mg, 80% yield; mp = 72 °C; Rf = 0.4 (petroleum ether/ethyl acetate = 100/1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.12\) (s, 1 H), 8.05 (d, \(J = 8.0 \) Hz, 1 H), 7.62 (t, \(J = 8.0 \) Hz, 2 H), 7.57 - 7.52 (m, 2 H), 7.40 - 7.32 (m, 1 H), 7.31 - 7.25 (m, 1 H), 7.10 (s, 1 H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 155.0, 153.1, 131.6, 131.4, 129.6, 128.6, 128.6, 128.1, 125.2, 123.3, 121.3, 118.4, 113.1, 111.3, 103.1.

3x: thick yellow liquid; 42 mg, 88% yield; Rf = 0.8 (petroleum ether/ethyl acetate = 25/1); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta = 7.83\) (dd, \(J = 1.4, 7.8 \) Hz, 1 H), 7.67 - 7.54 (m, 2 H), 7.52 - 7.41 (m, 2 H), 7.38 - 7.19 (m, 2 H), 7.04 - 6.93 (m, 1 H); \(^1\)C NMR (50 MHz, CDCl\(_3\)) \(\delta = 155.2, 150.4, 148.2, 132.0, 129.9, 129.3, 128.4, 125.3, 124.1, 123.2, 111.4, 106.0.

3y: Compound 3y is literature known. It was detected in \(^1\)H NMR and NMR yield (9%) was calculated in by using dibromomethane as an internal standard.

3z: white solid; 35 mg, 75% yield; Rf = 0.3 (petroleum ether); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.09\) (d, \(J = 8.8 \) Hz, 1 H), 7.68 (d, \(J = 1.9 \) Hz, 1 H), 7.44 - 7.39 (m, 2 H), 7.37 - 7.34 (m, 2 H), 1.36 (s, 9 H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 149.7, 140.3, 136.1, 133.9, 132.9, 130.7, 130.0, 128.1, 127.3, 123.1, 116.8, 116.3, 109.4, 84.2, 27.6.

3aa: white solid; 34 mg, 70% yield; mp = 70 °C; Rf = 0.7 (petroleum ether/ethyl acetate = 50/1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.87\) (d, \(J = 1.7 \) Hz, 1 H), 7.65 (dd, \(J = 1.8, 7.9 \) Hz, 1 H), 7.62 - 7.57 (m, 1 H), 7.53 (dd, \(J = 0.7, 8.2 \) Hz, 1 H), 7.33 - 7.29 (m, 2 H), 7.27 - 7.23 (m, 1 H), 7.02 - 6.98 (m, 1 H), 2.43 (s, 3 H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 154.8, 154.6, 136.3, 134.9, 131.3, 129.7, 129.0, 125.4, 124.5, 123.0, 120.9, 111.2, 101.6, 20.0; HRMS (ESI) calcd 242.0493 for C\(_{15}\)H\(_{11}\)ClO \([M]^+\), found 242.0510.

3ab: white solid; 41 mg, 72% yield; mp = 73 °C; Rf = 0.8 (petroleum ether/ethyl acetate = 50/1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.06\) (d, \(J = 1.8 \) Hz, 1 H), 7.69 (dd, \(J = 1.7, 7.9 \) Hz, 1 H), 7.62 - 7.57 (m, 1 H), 7.53 (dd, \(J = 0.7, 8.2 \) Hz, 1 H), 7.33 - 7.29 (m, 2 H), 7.27 - 7.23 (m, 1 H), 7.02 - 6.98 (m, 1 H), 2.43 (s, 3 H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 154.8, 154.6, 136.3, 134.9, 131.3, 129.7, 129.0, 125.4, 124.5, 123.0, 120.9, 111.2, 101.6, 20.0; HRMS (ESI) calcd 242.0493 for C\(_{15}\)H\(_{11}\)ClO \([M]^+\), found 242.0510.

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Hz, 1 H), 7.34 - 7.28 (m, 2 H), 7.28 - 7.23 (m, 1 H), 6.99 (d, J = 0.8 Hz, 1 H), 2.45 (s, 3 H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 154.8, 154.4, 138.1, 131.0, 129.9, 129.0, 128.6, 125.3, 124.5, 123.7, 123.0, 120.9, 111.2, 101.6, 22.8; HRMS (ESI) calcd 287.0066 for C$_{15}$H$_{12}$BrO [M+H]$^+$, found 287.0032.

3ac: white solid; 46 mg, 63% yield; mp = 132 °C; R$_f$ = 0.5 (petroleum ether/ethyl acetate = 50/1); ^1^H NMR (500 MHz, CDCl$_3$) δ = 8.33 (d, J = 2.1 Hz, 1 H), 8.10 (d, J = 8.4 Hz, 1 H), 7.72 (dd, J = 2.1, 8.3 Hz, 1 H), 7.64 (d, J = 7.3 Hz, 1 H), 7.55 (dd, J = 0.7, 8.3 Hz, 1 H), 7.40 - 7.34 (m, 1 H), 7.32 - 7.28 (m, 1 H), 7.19 (d, J = 0.8 Hz, 1 H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 155.2, 152.2, 142.3, 131.9, 128.8, 125.7, 123.6, 121.5, 121.3, 111.5, 104.1, 85.0; HRMS (ESI) calcd 364.9543 for C$_{14}$H$_8$INO$_3$ [M]$^+$, found 364.9553.

3ad: thick brown liquid; 36 mg, 68% yield; R$_f$ = 0.5 (petroleum ether/ethyl acetate = 50/1); ^1^H NMR (500 MHz, CDCl$_3$) δ = 7.64 (d, J = 7.3 Hz, 3 H), 7.53 (d, J = 7.9 Hz, 1 H), 7.38 - 7.32 (m, 1 H), 7.30 (d, J = 6.1 Hz, 1 H), 6.99 (s, 1 H), 2.42 (d, J = 7.3 Hz, 6 H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 155.1, 151.0, 146.1, 141.8, 138.7, 131.0, 128.6, 125.2, 125.0, 121.9, 121.3, 111.3, 105.4, 19.8, 19.5; HRMS (ESI) calcd 268.0968 for C$_{16}$H$_{14}$NO$_3$ [M+H]$^+$, found 268.0982.

3ae: thick brown liquid; 52 mg, 65% yield; R$_f$ = 0.6 (petroleum ether/ethyl acetate = 50/1); ^1^H NMR (500 MHz, CDCl$_3$) δ = 8.17 (d, J = 8.4 Hz, 1 H), 7.67 (d, J = 8.4 Hz, 3 H), 7.41 (d, J = 7.6 Hz, 1 H), 7.31 - 7.16 (m, 7 H), 6.35 (s, 1 H), 2.61 (s, 3 H), 2.35 (s, 3 H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 144.6, 137.3, 137.0, 136.4, 129.9, 129.8, 129.7, 126.3, 123.7, 123.4, 119.9, 114.5, 109.5, 21.5, 15.7; HRMS (ESI) calcd 402.1158 for C$_{24}$H$_{20}$NO$_3$S [M+H]$^+$, found 402.1145.

3af: white solid; 22 mg, 52% yield; mp = 121 °C; R$_f$ = 0.7 (petroleum ether); ^1^H NMR (500 MHz, CDCl$_3$) δ = 8.07 (d, J = 8.4 Hz, 2 H), 7.90 (s, 1 H), 7.85 (d, J = 8.0 Hz, 1 H), 7.70 - 7.65 (m, 3 H), 7.62 - 7.57 (m, 1 H), 2.66 (s, 3 H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 197.4, 143.2, 141.1, 136.7, 134.0, 131.5, 131.5, 130.8, 129.8, 129.2, 129.1, 127.2, 118.5, 113.2, 29.6, 26.7.

3ag.\textsuperscript{30} white solid; 31 mg, 57% yield; \( R_f = 0.7 \) (petroleum ether); \( ^1{\text{H NMR (500 MHz, CDCl}}_3) \) \( \delta = 8.03 - 7.96 \text{ (m, 2 H), 7.68 - 7.63 \text{ (m, 1 H), 7.50 - 7.46 \text{ (m, 2 H), 7.37 - 7.32 \text{ (m, 1 H), 7.30 - 7.26 \text{ (m, 1 H), 7.20 \text{ (dt, J = 1.8, 7.8 Hz, 1 H), 2.61 \text{ (s, 3 H); 13C NMR (125 MHz, CDCl}}_3) \) \delta = 197.6, 145.6, 141.3, 136.0, 133.2, 130.9, 129.6, 129.3, 128.0, 127.5, 122.1, 26.6.}

4. Mechanistic Investigations:

4.1 $^{31}$P NMR studies of the standard reaction:

A Schlenk tube was loaded with Ph$_3$PAuCl (50 mg, 0.1 mmol, 1 equiv), 2a (25 mg, 0.11 mmol, 1.1 equiv) and [Ru(bpy)$_3$](PF$_6$)$_2$] (4.3 mg, 0.005 mmol, 5 mol%). The reaction vessel was wrapped with aluminium foil before CH$_3$CN (1 mL) was added at 0 °C and this was followed by degassing with 3 freeze-pump-thaw cycles. The foil was removed and the reaction mixture was stirred for 12 h at rt under light irradiation using 23 W CFL bulb. The mixture was then diluted with diethyl ether (25 mL) and the precipitate was filtered out. The solid precipitate was recrystallized with DCM/diethyl ether to afford the corresponding phosphonium salt [Ph$_3$P(p-$\text{Cl}$-C$_6$H$_4$)]BF$_4$ (A) as brown solid. The spectroscopic data was found to be in good agreements with previously reported compound (A).$^{11}$

**Compound A**: brown solid; 27 mg, 59% yield; $^1$H NMR (500 MHz, CD$_3$CN) $\delta =$ 7.97 - 7.87 (m, 3 H), 7.78 - 7.72 (m, 8 H), 7.72 - 7.61 (m, 8 H); $^{31}$P NMR (202 MHz, CD$_3$CN) $\delta =$ 22.8.
5. Quantum yield calculation:

Following a modified procedure for quantum yield calculation,\(^{31}\) we first synthesized potassium ferrioxalate trihydrate \(K_3[Fe(C_2O_4)_3].3H_2O\) salt.\(^{32}\) Next, an aqueous solution of ferrioxalate actinometer was prepared and kept in dark. In presence of light, the actinometer solution photo-decomposes from ferric oxalate anions to ferrous oxalate anions. Subsequently, these ferrous oxalate anions can react with 1,10-phenanthroline to form the \([Fe(Phen)_3]^{2+}\) complex. Furthermore, the concentration of this \([Fe(Phen)_3]^{2+}\) complex in solution was determined by UV-Vis absorbance at 510 nm in Milli-Q water of resistance 18.2 mΩ. The number of photons absorbed by the ferrioxalate actinometer solution is equivalent to the no. of moles of \([Fe(Phen)_3]^{2+}\) complex formed. This process determines the photon flux which is directly related to our photo-induced reaction and hence the quantum yield of the reaction. Detailed procedure of the quantum yield determination is as follows. All the reactions were carried out at room temperature.

- **Preparation of** \(K_3[Fe(C_2O_4)_3].3H_2O\)** salt:

Oxalic acid dihydrate (3.78 g) was taken in a beaker (properly wrapped with aluminium foil) and 10 mL of distilled water was poured into the beaker to make a solution of oxalic acid. Then, 3.36 g of KOH was added to it portion-wise slowly with vigorous stirring. After that, 1.62 g of FeCl\(_3\) was added to the clear solution with constant stirring. After the complete addition of FeCl\(_3\), the solution was kept in dark for 1 h. Bright green crystals fell out from the solution which were then filtered, washed with distilled water, dried and stored in dark.

5.1 **Preparation of the stock solutions:**

1. Potassium ferrioxalate solution (60 mM): 1.475 g of potassium ferrioxalate trihydrate \(K_3[Fe(C_2O_4)_3]\) and 140 \(\mu\)L of 95-98\% H\(_2\)SO\(_4\) were added to a 50 mL volumetric flask and filled up to the mark with distilled water.

2. Buffer solution (600 mM): 4.94 g of sodium acetate and 1.0 mL of 95-98\% H\(_2\)SO\(_4\) were added to a 100 mL volumetric flask and filled up to the mark with distilled water.

3. 1,10-Phenanthroline solution (13.87 mM): 25 mg of 1,10-phenanthroline was taken in a 10 mL volumetric flask and filled up to the mark with sodium acetate buffer solution.

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5.2. Quantum yield calculation (reaction of 1a with 2v):

1a (100 mg, 0.52 mmol, 1 equiv), 2v (299 mg, 1.05 mmol, 2 equiv), Ph3PAuCl (25.99 mg, 0.052 mmol, 10 mol%, 0.1 equiv), Cu(MeCN)4BF4 (33.05 mg, 0.105 mmol, 20 mol%, 0.2 equiv), [Ru(bpy)3](PF6)2 (11.29 mg, 0.013 mmol, 0.25 mol%, 0.025 equiv), K2CO3 (145.24 mg, 1.05 mmol, 2 equiv) were added in Schlenk tube containing a magnetic bar and dry CH3CN (5 mL) was added under N2 atmosphere in the absence of light.

5.3 Determination of amount of photon absorbed by potassium ferrioxalate solution:

a) The actinometer solution (5 mL) was taken in a glass Schlenk tube while another Schlenk tube contained the reaction mixture. Both the Schlenk tubes (having same diameter) were placed in such a way that they are individually 5 cm apart from the 12 W blue LED of λmax = 457 nm (Figure 1) associated with a bandpass filter (450 nm) (provided by HORIBA). Further, the actinometer solution irradiated for 50, 100 and 150 second intervals, respectively. The reaction mixture was also irradiated for 15, 30, 45 and 60 min intervals and the no. of moles of product formed in each case were measured by 1H-NMR spectroscopy using dibromomethane as an internal standard.

![Emission spectra of blue LED bulb.](image)

Figure 1: Emission spectra of blue LED bulb.

b) After each interval 1 mL of the irradiated actinometer solution was transferred into a 10 mL volumetric flask containing 2 mL of 1,10-phenanthroline solution. Then the volumetric flask filled up to the mark with distilled water, shaken and kept in dark for 1
h for complete complexation. After that, 1 mL of the complex was taken in 1 mL of quartz cuvette and the absorption spectra of the solution were measured. The absorption at $\lambda = 510$ nm corresponds to the amount of amount of Fe$^{2+}$ formed in the photo-decomposition process (Figure 2).

![Figure 2: UV-Vis absorption spectra of [Fe(Phen)$_3$]$^{2+}$ complex at different time interval and the ferrioxalate stock solution.](image)

c) A blank solution was also prepared with 2 mL of 1,10-phenanthroline solution, 1 mL of actinometer (which was not irradiated) and the volume was adjusted with distilled water in a 10 mL of volumetric flask. The absorbance spectrum of the blank solution was also measured (Figure 2).

d) According to Beer’s law, the number of moles of Fe$^{2+}$ formed was determined by

$$Fe^{2+} = \frac{V_1V_2\Delta A (510 \text{ nm})}{10^3V_2\Delta \varepsilon (510 \text{ nm})}$$

Where:

$V_1$ = Irradiated volume of actinometer solution (1 mL).

$V_2$ = The aliquot taken from the irradiated actinometer solution for the estimation of Fe$^{2+}$ ions (1 mL).

$V_3$ = The volume of the solution after complexation with 1,10-phenanthroline (10 mL).

$\varepsilon$ = Molar extinction coefficient of [Fe(Phen)$_3$]$^{2+}$ complex (11100 Lmol$^{-1}$cm$^{-1}$) at 510 nm.

$l$ = Optical path-length of the quartz cuvette (1 cm).
ΔA (510 nm) = Difference of absorbance between the irradiated actinometer solution and the bank actinometer solution stored in dark.

e) No. of moles of Fe$^{2+}$ formed was plotted against time (t) and fitted linearly. The slope (dx/dt) of the line is equal to the number of moles of Fe$^{2+}$ formed per unit time (Figure 3).

f) The no. of incident photons per unit time (F) can be measured by the following equation:

$$\Phi(\lambda) = \frac{dx}{dt} \frac{F}{1 - 10^{-A(\lambda)}}$$

Where,

$dx/dt$ = The no. of moles of Fe$^{2+}$ formed per unit time is $1.57 \times 10^{-8}$ moles/sec.

$\Phi(\lambda)$ = The quantum yield for the conversion of Fe$^{3+}$ to Fe$^{2+}$ at 450 nm is 0.9.\textsuperscript{33}

$A(\lambda)$ = Absorbance of the ferrioxalate actinometer stock solution at a wavelength of 450 nm. The obtained value of the absorbance is 0.657.

g) Thus, the calculated value for the incident photons per unit time (F) is $2.247 \times 10^{-8}$ einsteins/sec.

5.4 Determination of quantum yield ($\Phi$) of the standard reaction:

The no. of moles of product formed at 15, 30, 45 and 60 min are $5.69 \times 10^{-6}$, $7.59 \times 10^{-6}$, $18.03 \times 10^{-6}$ and $24.2 \times 10^{-6}$ respectively (determined by $^1$H-NMR spectroscopy using dibromomethane as an internal standard, Figure 6). Now, the no. of moles of product is plotted against the no. of incident photons coming from the light source at the 15, 30, 45 and 60 min respectively (Figure 4) and fitted linearly. The slope of the plot is equal to the quantum yield ($\Phi$) of our reaction, which is 0.3.

Figure 4: Plot of no. of moles of product formed against photon flux.
6. Measurement of the absorbance of reaction mixture:

The UV-Vis absorption spectrum of the optimized reaction in 0.0157 mM scale is given below (Figure 5).

![UV-Vis absorption spectrum](image)

**Figure 5:** UV-Vis absorption spectrum of the optimized reaction.

![Time dependent 1H-NMR measurement](image)

**Figure 6:** Time dependent ¹H-NMR measurement of the reaction mixture (peak at δ = 8.049 ppm indicates the formation of the product).
7. Transmittance spectra of bandpass filter (450 nm) and the glass Schlenk tube:

![Graph showing transmittance spectra of bandpass filter and glass Schlenk tube.]

**Figure 7:** Transmittance spectra of bandpass filter and glass Schlenk tube.

8. Emission spectra of CFL bulb:

![Graph showing emission spectra of CFL bulb.]

**Figure 8:** Emission spectra of CFL bulb.

9. GCMS data of the reaction:
After the completion of the standard reaction (reaction between 1a and 2a), GCMS analysis was performed. Two major peaks were observed which can be assigned to 3a and B (resulted via dimerization of 2a).
3a, Exact Mass: 228.0342
10. NMR Spectra:

**1H NMR, CDCl₃, 500 MHz**

**13C NMR, CDCl₃, 125 MHz**
$^1$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
$^1$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
CHLOROFORM-d

8.23
8.22
7.59
7.57
7.42
7.40
7.39
7.39
7.37
7.37
7.29
6.58
1.39

$^1$H NMR, CDCl$_3$, 500 MHz
$\text{CHLOROFORM-d}$

$\text{13C NMR, CDCl}_3$, 125 MHz

$\text{3e}$

$\text{1H NMR, CDCl}_3$, 500 MHz

$\text{3f}$
$^1$H NMR, CDCl$_3$, 500 MHz

Chemical Shift (ppm)

2.00 1.02 1.00 2.15 2.09 1.06
\textbf{CHLOROFORM-d}

$\begin{align*}
154.02 & \quad 132.38 & \quad 131.98 & \quad 131.80 & \quad 131.29 & \quad 128.46 & \quad 126.38 & \quad 125.20 & \quad 124.61 & \quad 123.27 & \quad 123.11 & \quad 119.85 & \quad 111.26 & \quad 101.85 & \quad 77.26 & \quad 77.00 & \quad 76.75
\end{align*}$

\textbf{CHLOROFORM-d}

$\begin{align*}
7.98 & \quad 7.61 & \quad 7.52 & \quad 7.05 & \quad 7.80 & \quad 7.78 & \quad 7.61 & \quad 7.05 & \quad 7.80 & \quad 7.78 & \quad 7.61 & \quad 7.05 & \quad 7.80 & \quad 7.78 & \quad 7.61 & \quad 7.05
\end{align*}$

$\text{CHLOROFORM-d}$

$\begin{align*}
2.00 & \quad 3.03 & \quad 1.01 & \quad 1.61 & \quad 1.00 & \quad 2.00 & \quad 3.03 & \quad 1.01 & \quad 1.61 & \quad 1.00
\end{align*}$
CHLOROFORM-d

$\text{CHLOROFORM-d}$

$\text{13C NMR, CDC\textsubscript{3}, 125 MHz}$

$\text{1H NMR, CDC\textsubscript{3}, 500 MHz}$

SI42
\[ ^{13}C \text{ NMR, CDCl}_3, 125 \text{ MHz} \]

CHLOROFORM-d
155.42
153.22
147.22
136.24
128.63
125.80
125.18
124.28
123.52
121.61
111.47
105.08
77.26
77.00
76.75
$^1$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
$^{1}$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 100 MHz
CHLOROFORM-d

$^{1}$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz

SI46
{\text{CHLOROFORM-d}}

\text{\textsuperscript{1}H NMR, CDCl\textsubscript{3}, 500 MHz}

\text{\textsuperscript{13}C NMR, CDCl\textsubscript{3}, 125 MHz}
The page contains a 1H NMR and a 13C NMR spectrum of a compound labeled as 3t. The spectra are labeled with chemical shifts in parts per million (ppm) for both CHLOROFORM-d. The 1H NMR spectrum is labeled as 1H NMR, CDCl₃, 500 MHz, and the 13C NMR spectrum is labeled as 13C NMR, CDCl₃, 125 MHz. The chemical structures of the compound are also shown with highlighted peaks corresponding to the chemical shifts.
1H NMR, CDCl₃, 500 MHz

13C NMR, CDCl₃, 125 MHz
| Compound | 
|----------|----------------|
| 3ad      | 6.10, 1.00, 1.11, 1.11, 1.13, 3.13 |
| CHLOROFORM-d | 7.65, 7.63, 7.54, 7.52, 7.37, 7.35, 7.34, 7.30, 7.29, 6.99 |

**1H NMR, CDCl₃, 500 MHz**

| Compound | 
|----------|----------------|
| 3ad      | 155.06, 151.03, 146.05, 141.82, 138.72, 131.00, 128.58, 125.17, 124.96, 123.09, 121.87, 121.30, 111.31, 105.43, 77.31, 77.00, 76.69, 19.75, 19.54 |
| CHLOROFORM-d | 155.06, 151.03, 146.05, 141.82, 138.72, 131.00, 128.58, 125.17, 124.96, 123.09, 121.87, 121.30, 111.31, 105.43, 77.31, 77.00, 76.69, 19.75, 19.54 |

**13C NMR, CDCl₃, 125 MHz**