# **Supporting Information**

## Photochemical reductive deamination of alpha-amino aryl alkyl

### ketones

Ji-Yuan Liang,<sup>a,b,c</sup> Yi-Wen Su<sup>a,b,c</sup> and You-Quan Zou<sup>\*a,b,c</sup>

<sup>a</sup> Department of Otolaryngology, Zhongnan Hospital of Wuhan University, School of Pharmaceutical Sciences, Wuhan University, Wuhan, Hubei 430071 (China).
<sup>b</sup> Key Laboratory of Combinatorial Biosynthesis and Drug Discovery, Ministry of Education, Wuhan University, Wuhan, Hubei 430071 (China).
<sup>c</sup> TaiKang Center for Life and Medical Sciences, Wuhan University, Wuhan, Hubei 430071 (China).

E-mail: youquanzou@whu.edu.cn;

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### **1. General information**

Unless otherwise noted, all reactions were carried out under air atmosphere. All reagents and solvents were obtained from commercial suppliers and used without further purification. <sup>1</sup>H NMR (400 MHz or 600 MHz) and <sup>13</sup>C NMR (100 MHz or 150 MHz) were recorded on Bruker AV 400 (400 MHz) spectrometer or Bruker AV 600 (600 MHz) spectrometer with CDCl<sub>3</sub> as solvent. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane as an internal reference. The chemical shifts were converted to the TMS scale (CDCl<sub>3</sub>:  $\delta^{1}$ H = 7.26 ppm,  $\delta^{13}$ C = 77.16 ppm). Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants were reported in Hz. HRMS were obtained on Bruker UltiMate3000 & Compact mass spectrometer and Thermo Fisher Orbitrap Elite LTQ XL mass spectrometer. MS were obtained on Thermo Fisher LCQ Fleet mass spectrometer. IR spectra were recorded in Thermo Fisher Nicolet iS50 FTIR. UV absorption was performed using Shimadzu, UV-2600 UV spectrophotometer. All photocatalytic reactions were performed under purple LEDs (24 W, 366 nm). Column chromatography was performed on silica gel 200-300 mesh.

### 2. General procedure for synthesis of *alpha*-amino ketones



Except for compound **1t**, **1u** and **1x**, all other substrates were synthesized through this method. NH<sub>4</sub>I (0.15 equiv) was added to a mixture of sodium percarbonate or TBHP (2 equiv), ketones (1 equiv), and amines (3 equiv) in acetonitrile or DMF at room temperature. The reaction was stirred at 50 °C for the indicated time. The reaction mixture was then allowed to cool to room temperature, after which vacuum filtration to remove solid insoluble matter. Then the crude products were purified by column chromatography on silica gel to afford the pure *alpha*-amino ketones.<sup>1</sup>



The synthesis of compound **1t**, **1u** and **1x** was followed this procedure. A reaction tube equipped with a magnetic stir bar was charged with benzylic secondary alcohols and N-bromosuccinimide (1.3 equiv) under open atmosphere and allowed to stir for few minutes. After the generation of brown color gas (bromine), 1,4-dioxane was added. After 10 minutes, amine (3 equiv) was added dropwise to the reaction mixture and the progress of the reaction was monitored by thin-layer chromatography.

After completion of the reaction, the reaction mixture was washed with saturated NaHCO<sub>3</sub> solution and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give pure *alpha*-amino ketones.<sup>2</sup>

# 3. Characterization for *alpha*-amino ketones

# 3.1 Substrate scope



3a

3b

S4

### 3.2 NMR data of substrates

1-(4-methoxyphenyl)-2-(piperidin-1-yl)propan-1-one (1a)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) δ 8.11 (d, J = 8.9Hz, 2H), 6.88 (d, J = 8.9Hz, 2H), 3.96 (q, J = 6.8 Hz, 1H), 3.83 (s, 3H), 2.48 (m, 4H), 1.56 – 1.44 (m, 4H), 1.37 (m, 2H), 1.21 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 199.68, 163.26, 131.30, 129.52, 113.41, 65.22, 55.41, 50.87, 26.40, 24.49, 11.52. MS: C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup>; calculated: 248.16, found: 248.17. **IR**: 2934, 1676, 1600, 1237, 1170, 843.

1-phenyl-2-(piperidin-1-yl)propan-1-one (1b)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, J = 7.4 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.02 (q, J = 6.8 Hz, 1H), 2.48 (m, 4H), 1.56 – 1.41 (m, 4H), 1.35 (m, 2H), 1.21 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.03, 136.59, 132.77, 128.93, 128.28, 65.16, 50.78, 26.36, 24.45, 11.13. **MS**: C<sub>14</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>; calculated: 218.15, found: 218.25. **IR**: 2934, 1685, 1448, 1231,1205, 696.

1-(3-methoxyphenyl)-2-(piperidin-1-yl)propan-1-one (1c)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 – 7.66 (m, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.08 (d, J = 9.0 Hz, 1H), 4.05 (q, J = 6.7 Hz, 1H), 3.85 (s, 3H), 2.53 (m, 4H), 1.54 (m, 4H), 1.41 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.96, 159.69, 138.07, 129.37, 121.61, 119.44, 113.32, 65.41, 55.51, 50.93, 26.46, 24.54, 11.60. **MS**: C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup>; calculated: 248.16, found: 248.25. **IR**: 2934, 1686, 1581, 1259, 1043, 771.

#### 1-(2-methoxyphenyl)-2-(piperidin-1-yl)propan-1-one (1d)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 4.19 (q, J = 6.9 Hz, 1H), 3.85 (s, 3H), 2.49 (m, 4H), 1.43 (m, 4H), 1.35 (m, 2H), 1.20 (d, J = 7.0 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  205.68, 157.93, 132.48, 130.08, 129.83, 120.74, 111.13, 67.47, 55.54, 50.73, 26.55, 24.61, 11.32. **HRMS**(ESI): C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup>; calculated: 248.1645, found: 248.1642. **IR**: 2933, 1683, 1598, 1284, 1246, 755.

#### 2-(piperidin-1-yl)-1-(o-tolyl)propan-1-one (1e)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 (m, 1H), 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 3.95 (q, J = 6.9 Hz, 1H), 2.60 – 2.47 (m, 4H), 2.44 (s, 3H), 1.52 (m, 4H), 1.40 (m, 2H), 1.21 (d, J = 6.9 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 205.79, 138.60, 137.95, 131.66, 130.86, 128.41, 125.42, 66.92, 50.99, 26.39, 24.58, 20.92, 11.53. **MS**: C<sub>15</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>; calculated: 232.17, found: 232.25. **IR**: 2933, 1687, 1453, 1229, 920, 743.

2-(piperidin-1-yl)-1-(m-tolyl)propan-1-one (1f)



<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, J = 7.4 Hz, 1H), 7.88 (s, 1H), 7.32 (m, 2H), 4.06 (q, J = 6.8 Hz, 1H), 2.52 (m, 4H), 2.39 (s, 3H), 1.53 (m, 4H), 1.39 (m, 2H), 1.24 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  201.40, 138.09, 136.76, 133.61, 129.39, 128.22, 126.19, 65.08, 50.93, 26.43, 24.55, 21.50, 11.65. **MS**: C<sub>15</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>; calculated: 232.17, found: 232.25. **IR**: 2934, 1684, 1602, 1584, 1251, 701.

2-(piperidin-1-yl)-1-(p-tolyl)propan-1-one (1g)



<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 4.03 (q, J = 6.8 Hz, 1H), 2.57 – 2.45 (m, 4H), 2.39 (s, 3H), 1.57 – 1.47 (m, 4H), 1.39 (m, 2H), 1.24 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.79, 143.55, 134.12, 129.11, 129.04, 65.13, 50.90, 26.42, 24.53, 21.73, 11.54. **MS**: C<sub>15</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>; calculated: 232.17, found: 232.25. **IR**: 2934, 1683, 1607, 1233, 771.

#### 1-(3-fluorophenyl)-2-(piperidin-1-yl)propan-1-one (1h)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 9.9 Hz, 1H), 7.40 (q, J = 6.9 Hz, 1H), 7.23 (t, J = 8.2 Hz, 1H), 3.99 (q, J = 6.5 Hz, 1H), 2.51 (m, 4H), 1.53 (m, 4H), 1.40 (m, 2H), 1.24 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.84, 199.82, 163.96, 161.51, 138.70, 138.64, 129.95, 129.87, 124.84, 124.81, 119.92, 119.70, 116.06, 115.83, 65.84, 50.82, 26.45, 24.47, 10.59. **MS**: C<sub>14</sub>H<sub>19</sub>FNO [M+H]<sup>+</sup>; calculated: 236.14, found: 236.33. **IR**: 2935, 1688, 1587, 1441, 1252, 698.

1-(3-chlorophenyl)-2-(piperidin-1-yl)propan-1-one (1i)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.12 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 3.98 (q, J = 6.7 Hz, 1H), 2.50 (m, 4H), 1.52 (m, 4H), 1.39 (m, 2H), 1.23 (d, J = 6.7 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.78, 138.12, 134.52, 132.72, 129.64, 129.27, 127.22, 65.75, 50.76, 26.43, 24.44, 10.44. **MS**: C<sub>14</sub>H<sub>19</sub>ClNO [M+H]<sup>+</sup>; calculated: 252.12, found: 252.33. **IR**: 2935, 1689, 1569, 1372, 1225, 1202, 734.

#### 1-(4-chlorophenyl)-2-(piperidin-1-yl)propan-1-one (1j)



<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.07 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 3.95 (q, J = 6.7 Hz, 1H), 2.47 (m, 4H), 1.48 (m, 4H), 1.36 (m, 2H), 1.20 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 199.76, 139.03, 134.73, 130.60, 128.52, 65.72, 50.69, 26.40, 24.39, 10.32. **MS**: C<sub>14</sub>H<sub>19</sub>ClNO [M+H]<sup>+</sup>; calculated: 252.12, found: 252.25. **IR**: 2935, 1687, 1587, 1225, 1204, 1092, 777.

#### 1-(3-bromophenyl)-2-(piperidin-1-yl)propan-1-one (1k)



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 3.98 (q, J = 6.7 Hz, 1H), 2.55 – 2.43 (m, 4H), 1.53 (m, 4H), 1.40 (m, 2H), 1.23 (d, J = 6.7 Hz, 3H). <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.73, 138.34, 135.65, 132.27, 129.93, 127.69, 122.59, 65.81, 50.79, 26.47, 24.47, 10.43. **MS**: C<sub>14</sub>H<sub>19</sub>BrNO [M+H]<sup>+</sup>; calculated: 296.06, found: 296.42. **IR**: 2934, 1688, 1563, 1372, 1223, 1201, 717.

1-(4-bromophenyl)-2-(piperidin-1-yl)propan-1-one (11)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) δ 8.01 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 3.97 (q, J = 6.7 Hz, 1H), 2.49 (m, 4H), 1.57 – 1.44 (m, 4H), 1.39 (m, 2H), 1.22 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 200.09, 135.20, 131.60, 130.79, 127.89, 65.79, 50.77, 26.45, 24.44, 10.42. MS: C<sub>14</sub>H<sub>19</sub>BrNO [M+H]<sup>+</sup>; calculated: 296.06, found: 296.42. **IR**: 2945, 1678, 1582, 1202, 1071, 776.



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.50 (s, 1H), 8.31 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 4.05 (q, J = 6.7 Hz, 1H), 2.54 (m, 4H), 1.59 – 1.47 (m, 4H), 1.41 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.63, 136.87, 132.33, 131.00, 130.68, 129.27, 129.23, 129.20, 129.16, 128.92, 128.53, 126.42, 126.38, 126.34, 126.31, 125.37, 122.66, 77.48, 77.16, 76.84, 66.01, 50.67, 26.37, 24.38, 9.96. **HRMS**(ESI): C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>NO [M+H]<sup>+</sup>; calculated: 286.1413, found: 286.1416. **IR**: 2937, 1694, 1610, 1331, 1199, 1168, 1128, 694.

#### 2-(piperidin-1-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (1n)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) δ 8.24 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 4.02 (q, J = 6.7 Hz, 1H), 2.51 (m, 4H), 1.56 – 1.44 (m, 4H), 1.39 (m, 2H), 1.24 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 200.05, 139.28, 134.32, 134.10, 133.89, 133.67, 129.51, 125.36, 125.34, 125.31, 125.29, 124.78, 122.97, 77.37, 77.16, 76.95, 66.00, 50.72, 26.45, 24.40, 9.92. **HRMS**(ESI): C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>NO [M+H]<sup>+</sup>; calculated: 286.1413, found: 286.1419. **IR**: 2940, 1683, 1331, 1232, 1166, 1125, 782.

#### 1-(furan-2-yl)-2-(piperidin-1-yl)propan-1-one (10)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d, J = 1.7 Hz, 1H), 7.44 (d, J = 3.5 Hz, 1H), 6.50 (m, 1H), 3.81 (q, J = 6.9 Hz, 1H), 2.60 – 2.44 (m, 4H), 1.57 – 1.51 (m, 4H), 1.40 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  190.59, 152.07, 146.53, 118.70, 112.08, 65.57, 51.21, 26.34, 24.49, 12.85. MS: C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>; calculated: 208.13, found: 208.25. IR: 2935, 1669, 1565, 1257, 1163, 765.

#### 2-(piperidin-1-yl)-1-(thiophen-2-yl)propan-1-one (1p)



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, J = 3.8 Hz, 1H), 7.55 (d, J = 4.9 Hz, 1H), 7.08 (t, J = 4.3 Hz, 1H), 3.68 (q, J = 6.8 Hz, 1H), 2.54 (m, 4H), 1.61 (m, 4H), 1.44 (m, 2H), 1.25 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.00, 140.90, 133.84, 133.47, 127.26, 68.18, 51.17, 26.01, 24.43, 11.27. MS: C<sub>12</sub>H<sub>18</sub>NOS [M+H]<sup>+</sup>; calculated: 224.11, found: 224.25. IR: 2934, 1667, 1507, 1357, 1235, 721.

#### 2-(4-methylpiperidin-1-yl)-1-phenylpropan-1-one (1q)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 4.07 (q, J = 6.7 Hz, 1H), 2.89 (d, J = 11.2 Hz, 1H), 2.73 (d, J = 11.0 Hz, 1H), 2.38 (t, J = 11.2 Hz, 1H), 2.12 (t, J = 11.4 Hz, 1H), 1.57 (m, 2H), 1.29 – 1.05 (m, 6H), 0.88 (d, J = 6.2 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 201.28, 136.71, 132.89, 129.03, 128.41, 65.03, 51.90, 48.75, 35.00, 34.62, 30.95, 22.02, 11.55. **MS**: C<sub>15</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>; calculated: 232.17, found: 232.25. **IR**: 2923, 1687, 1448, 1221, 917, 700.

2-morpholino-1-phenylpropan-1-one (1r)



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.07 (q, J = 6.8 Hz, 1H), 3.75 – 3.63 (m, 4H), 2.60 (m, 4H), 1.29 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.37, 136.31, 133.19, 128.92, 128.57, 67.28, 64.90, 50.20, 11.80. MS: C<sub>13</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>; calculated: 220.13, found: 220.25. **IR**: 2853, 1684, 1448, 1223, 1117, 926, 702.

1-phenyl-2-thiomorpholinopropan-1-one (1s)



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 4.13 (q, J = 6.7 Hz, 1H), 2.86 (m, 4H), 2.59 (m, 4H), 1.24 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.12, 136.36, 132.95, 128.96, 128.37, 65.26, 51.67, 28.48, 9.94. MS: C<sub>13</sub>H<sub>18</sub>NOS [M+H]<sup>+</sup>; calculated: 236.11, found: 236.17. **IR**: 2910, 1684, 1448, 1232, 1142, 981, 695.

#### 1-phenyl-2-(pyrrolidin-1-yl)propan-1-one (1t)



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 – 8.06 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 3.98 (q, *J* = 6.9 Hz, 1H), 2.63 (m, 4H), 1.85 – 1.73 (m, 4H), 1.38 (d, *J* = 6.9 Hz, 3H). The <sup>1</sup>H NMR data is consistent with the know literature.<sup>2</sup> **MS**: C<sub>13</sub>H<sub>18</sub>NO [M+H]<sup>+</sup>; calculated: 204.14, found: 204.17. **IR**: 2968, 1687, 1597, 1449, 1377, 1224, 704.

2-(diethylamino)-1-phenylpropan-1-one (1u)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (m, 2H), 7.54 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 4.37 (q, J = 6.7 Hz, 1H), 2.68 – 2.48 (m, 4H), 1.22 (d, J = 6.7 Hz, 3H), 1.00 (t, J = 7.2 Hz, 6H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.16, 136.93, 132.65, 129.03, 128.28, 60.39, 44.39, 13.73, 10.17. **MS**: C<sub>13</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>; calculated: 206.15, found: 206.25. **IR**: 2971, 1684, 1448, 1381, 1226, 692.

2-(allyl(methyl)amino)-1-phenylpropan-1-one (1v)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (m, 2H), 7.55 – 7.50 (m, 1H), 7.43 (m, 2H), 5.89 – 5.79 (m, 1H), 5.14 (m, 2H), 4.29 (q, J = 6.7 Hz, 1H), 3.15 (d, J = 6.4 Hz, 2H), 2.25 (s, 3H), 1.24 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  201.13, 136.63, 136.05, 132.89, 128.93, 128.45, 117.70, 62.00, 57.69, 37.66, 9.97. MS: C<sub>13</sub>H<sub>18</sub>NO [M+H]<sup>+</sup>; calculated: 204.14, found: 204.08. **IR**:2978, 1685, 1449, 1229, 924, 699.

#### 2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-phenylpropan-1-one (1w)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, J = 7.7 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.16 – 6.97 (m, 4H), 4.31 (q, J = 6.7 Hz, 1H), 3.94 – 3.76 (m, 2H), 2.92 – 2.73 (m, 4H), 1.39 (d, J = 6.7 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.69, 136.39, 134.96, 134.60, 133.08, 129.04, 128.82, 128.52, 126.68, 126.12, 125.67, 64.32, 52.17, 47.24, 29.75, 11.42. **MS**: C<sub>18</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>; calculated: 266.15, found: 266.25. **IR**: 2931, 2806, 1683, 1448, 1224, 742.

2,2'-(piperazine-1,4-diyl)bis(1-phenylpropan-1-one) (1x)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 7.9 Hz, 4H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 4.06 (q, *J* = 6.8 Hz, 2H), 2.68 – 2.50 (m, 8H), 1.25 (d, *J* = 6.7 Hz, 6H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.66, 200.62, 136.42, 133.09, 128.98, 128.52, 64.63, 64.58, 49.98, 11.96, 11.78. **MS**: C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>; calculated: 351.21, found: 351.33. **IR**: 2823, 1677, 1448, 1221, 928, 709, 683.

2-(1-oxo-1-phenylpropan-2-yl)isoindoline-1,3-dione (1y)



<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (m, 4H), 7.69 (m, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 5.65 (q, J = 7.1 Hz, 1H), 1.72 (d, J = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  196.23, 167.56, 135.34, 134.28, 133.14, 131.87, 128.81, 128.12, 123.61, 51.03, 15.01. **MS**: C<sub>17</sub>H<sub>14</sub>NO<sub>3</sub> [M+H]<sup>+</sup>; calculated: 280.10, found: 280.33. **IR**: 2920, 1708, 1448, 1386, 1233,714.

#### 1-phenyl-2-(piperidin-1-yl)butan-1-one (3a)



<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 – 8.04 (m, 2H), 7.55 – 7.50 (m, 1H), 7.44 (m, 2H), 3.90 (m, 1H), 2.58 (m, 2H), 2.51 (m, 2H), 1.89 (m, 1H), 1.76 – 1.67 (m, 1H), 1.50 (m, 4H), 1.41 – 1.34 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.50, 137.93, 132.81, 128.68, 128.48, 70.75, 51.11, 26.63, 24.66, 19.50, 11.37. **MS**: C<sub>15</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>; calculated: 232.17, found: 232.25. **IR**: 2933, 1683, 1447, 1223, 895, 696.

1-phenyl-2-(piperidin-1-yl)pentan-1-one (3b)



<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 8.03 (m, 2H), 7.51 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 3.98 (m, 1H), 2.57 (m, 2H), 2.50 (m, 2H), 1.85 (m, 1H), 1.63 (m, 1H), 1.48 (m, 4H), 1.39 – 1.33 (m, 2H), 1.24 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.47, 137.84, 132.74, 128.62, 128.43, 68.80, 51.02, 28.55, 26.63, 24.63, 20.18, 14.35. MS: C<sub>16</sub>H<sub>24</sub>NO [M+H]<sup>+</sup>; calculated: 246.19, found: 246.25. **IR**: 2933, 1684, 1448, 1200, 956, 697.

### 4. Photochemical reductive deamination of *alpha*-amino ketones

4.1 General procedure for reductive deamination of *alpha*-amino ketones

$$R^{1} \xrightarrow{\mathsf{MeCN}} R^{2} \xrightarrow{\mathsf{MeCN}} R^{1} \xrightarrow{\mathsf{MeCN}} R^{1} \xrightarrow{\mathsf{MeCN}} R^{2}$$

To a dried 10 mL schlenk tube equipped with a magnetic stir bar was added *alpha*-amino ketones (0.3 mmol) which were dissolved in dry MeCN (3.0 mL). Then, the schlenk tube was placed into a photoreactor and irradiated with purple LEDs (24 W, 366 nm) at room temperature (a continuously rotating fan was used outside of the reactor to maintain room temperature). Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure. Then the crude product was purified by column chromatography on silica gel (petroleum ether / ether = 150/1) to give pure products.

### 4.2 Characterization data for the products

1-(4-methoxyphenyl)propan-1-one (2a)

83% yield; yellow liquid

MeC

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 2.94 (q, J = 7.3 Hz, 2H), 1.20 (t, J = 7.3 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  199.60, 163.40, 130.31, 130.12, 113.76, 55.53, 31.51, 8.54. MS: C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup>; calculated: 165.09, found: 165.08. **IR**: 2976, 1680, 1601, 1509, 1258, 1228, 1171, 800.

propiophenone (2b)

The yields of different amino substituted substrates can be found in the main text; yellow liquid <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 – 7.94 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 3.01 (q, *J* = 7.3 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.98, 137.04, 133.00, 128.67, 128.09, 31.90, 8.36. **MS**: C<sub>9</sub>H<sub>11</sub>O [M+H]<sup>+</sup>; calculated: 135.08, found: 135.08. **IR**: 2937, 1689, 1449, 1220, 952, 745, 691.

1-(3-methoxyphenyl)propan-1-one (2c)

MeO

80% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 – 7.47 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.09 (m, 1H), 3.85 (s, 3H), 2.99 (q, *J* = 7.3 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.78, 159.93, 138.42, 129.65, 120.73, 119.39, 112.41, 55.53, 32.03, 8.41. MS: C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup>; calculated: 165.09, found: 165.08. **IR**: 2939, 1689, 1598, 1583, 1259, 1199, 686.

#### 1-(2-methoxyphenyl)propan-1-one (2d)



52% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (m, 1H), 7.44 (m, 1H), 7.02 – 6.93 (m, 2H), 3.89 (s, 3H), 2.99 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  203.63, 158.56, 133.24, 130.28, 128.63, 120.71, 111.62, 55.58, 37.10, 8.54. MS: C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup>; calculated: 165.09, found: 165.00. **IR**: 2975, 1675, 1597, 1486, 1284, 1245, 757.

1-(o-tolyl)propan-1-one (2e)

40% yield; yellow liquid

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 2H), 2.92 (q, J = 7.3 Hz, 2H), 2.50 (s, 3H), 1.20 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  205.26, 138.25, 137.95, 132.00, 131.15, 128.36, 125.75, 34.85, 21.37, 8.50. MS: C<sub>10</sub>H<sub>13</sub>O [M+H]<sup>+</sup>; calculated: 149.10, found: 149.01. **IR**: 2977, 1688, 1457, 1218, 753.

1-(*m*-tolyl)propan-1-one (2f)

84% yield; yellow liquid

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 – 7.73 (m, 2H), 7.39 – 7.31 (m, 2H), 2.99 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.18, 138.42, 137.09, 133.72, 128.61, 128.52, 125.31, 31.93, 21.47, 8.41. **MS**: C<sub>10</sub>H<sub>13</sub>O [M+H]<sup>+</sup>; calculated: 149.10, found: 149.08. **IR**: 2978, 1688, 1586, 1250, 690.

#### 1-(p-tolyl)propan-1-one (2g)

90% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 2.99 (q, J = 7.3 Hz, 2H), 2.41 (s, 3H), 1.22 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  200.68, 143.70, 134.57, 129.34, 128.22, 31.77, 21.72, 8.45. **MS**: C<sub>10</sub>H<sub>13</sub>O [M+H]<sup>+</sup>; calculated: 149.10, found: 149.08. **IR**: 2977, 1684, 1608, 1226, 789.

#### 1-(3-fluorophenyl)propan-1-one (2h)

74% yield; yellow liquid

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (m, 1H), 7.63 (m, 1H), 7.43 (m, 1H), 7.24 (m, 1H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  199.58, 199.57, 163.81, 162.17, 139.15, 139.11, 130.36, 130.31, 123.83, 123.81, 120.06, 119.91, 114.90, 114.75, 32.09, 8.21. **MS**: C<sub>9</sub>H<sub>10</sub>FO [M+H]<sup>+</sup>; calculated: 153.07, found: 153.12. **IR**: 2981, 1691, 1589, 1442, 1249, 681.

1-(3-chlorophenyl)propan-1-one (2i)

79% yield; yellow liquid

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.51 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 2.97 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  199.54, 138.56, 135.00, 132.91, 130.02, 128.23, 126.16, 32.05, 8.19. **MS**: C<sub>9</sub>H<sub>10</sub>ClO [M+H]<sup>+</sup>; calculated: 169.04, found: 169.18. **IR**: 2939, 1684, 1574, 1425, 1216, 699.

#### 1-(4-chlorophenyl)propan-1-one (2j)

77% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 2.97 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.63, 139.39, 135.34, 129.51, 128.97, 31.90, 8.25. MS: C<sub>9</sub>H<sub>10</sub>ClO [M+H]<sup>+</sup>; calculated: 169.04, found: 169.14. IR: 2977, 1672, 1592, 1402, 1222, 790.

#### 1-(3-bromophenyl)propan-1-one (2k)

Br

74% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 2.96 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.44, 138.76, 135.83, 131.18, 130.28, 126.60, 123.06, 32.03, 8.20. MS: C<sub>9</sub>H<sub>10</sub>BrO [M+H]<sup>+</sup>; calculated: 212.99, found: 213.00. **IR**: 2938, 1683, 1568, 1423, 1212, 775, 680.

1-(4-bromophenyl)propan-1-one (2l)

78% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 2.99 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.81, 135.73, 131.96, 129.63, 128.09, 31.88, 8.24. MS: C<sub>9</sub>H<sub>10</sub>BrO [M+H]<sup>+</sup>; calculated: 212.99, found: 212.99. **IR**: 2933, 1684, 1588, 1396, 1217, 789.

1-(3-(trifluoromethyl)phenyl)propan-1-one (2m)



63% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (s, 1H), 8.14 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 3.03 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). The <sup>1</sup>H NMR data is consistent with the known literature.<sup>4</sup> **MS**: C<sub>10</sub>H<sub>10</sub>F<sub>3</sub>O [M+H]<sup>+</sup>; calculated: 203.07, found: 203.05. **IR**: 2984, 1696, 1613, 1329, 1207, 1128, 695.

#### 1-(4-(trifluoromethyl)phenyl)propan-1-one (2n)

49% yield; yellow liquid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 3.03 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). The <sup>1</sup>H NMR data is consistent with the known literature.<sup>5</sup> MS: C<sub>10</sub>H<sub>10</sub>F<sub>3</sub>O [M+H]<sup>+</sup>; calculated: 203.07, found: 203.25. **IR**: 2985, 1687, 1512, 1325, 1117, 800.

1-(thiophen-2-yl)propan-1-one (2p)

73% yield; yellow liquid

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 3.7 Hz, 1H), 7.60 (d, J = 4.9 Hz, 1H), 7.11 (m, 1H), 2.93 (q, J = 7.3 Hz, 2H), 1.23 (t, J = 7.4 Hz, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  193.97, 144.27, 133.30, 131.66, 128.13, 32.68, 8.63. MS: C<sub>7</sub>H<sub>9</sub>OS [M+H]<sup>+</sup>; calculated: 141.04, found: 141.00. **IR**: 3090, 2978, 1663, 1417, 1228, 853, 724.

### 5. Mechanistic studies and control experiments



### 5.1 UV-vis absorption spectra

Fig. S1. UV-vis absorption spectra of *alpha*-amino ketone 1a in CH3CN

The UV/Vis spectrum revealed that *alpha*-amino ketone **1a** has some absorption at 366 nm in acetonitrile (Figure S1). It is consistent with the result that alpha-aminoketone **1** can absorb the light ( $\lambda = 366$  nm) and be excited to the excitation state directly.

### **5.2 Control experiments**



To a dried 10 mL schlenk tube equipped with a magnetic stir bar was added **1a** (0.3 mmol) which was dissolved in dry MeCN (3 mL). Then, the reaction solution was vacuum degassed with three freeze-pump-thaw cycles. After that, the schlenk tube was put into a photoreactor and irradiated with purple LEDs (24 W, 366 nm) at room temperature under  $N_2$  atmosphere (a continuously rotating fan was used outside of the reactor to maintain room temperature). Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure. Then the crude product was purified by column chromatography on silica gel (petroleum ether– ether = 150:1) to give pure desired product. The fact that no loss of yield was observed indicated that molecular oxygen may not involve in this reaction.

### **5.3 Deuterium-labelling experiments**

### 5.3.1 Reaction was performed in CD<sub>3</sub>CN



Under standard conditions, ultra-dry acetonitrile was replaced with acetonitrile- $d_3$ . The result that deuterium atom was not incorporated into the terminal product **2a** indicated that *alpha*-hydrogen atom of ketone product **2a** was not originated from acetonitrile.

### 5.3.2 Reaction was performed using d<sub>4</sub>-1u

Procedure for synthesis of *d*<sub>4</sub>-1u

LiAlD<sub>4</sub> (2.0 eq., 10.0 mmol, 420 mg ) was covered with 1,2dimethoxyethane (10.0 mL) under nitrogen. Diacetamide (1.0 eq., 5.0 mmol, 506 mg) was dissolved in 7.0 mL 1,2-dimethoxyethane and added dropwise to the vigorously stirred tetradeuterioaluminate slurry while cooling in an ice bath. The resulting slurry was heated to 70 °C for 6.0 h and then hydrolyzed by successive addition of 0.5 mL of H<sub>2</sub>O, 0.5 mL of 15% NaOH, and 1.5mL of H<sub>2</sub>O followed by stirring overnight. The reaction mixture was transferred into the micro distillation device to obtain the desired product. The distillate was used directly for the next step.<sup>3</sup>



A reaction tube equipped with a magnetic stir bar was charged with benzylic secondary alcohol (1.0 eq., 1.0 mmol, 136 mg) and Nbromosuccinimide (1.3 eq., 1.3 mmol, 231 mg) under open atmosphere and allowed to stir for few minutes. After the generation of brown color gas (bromine), 1,2-dimethoxyethane (2 mL) was added. After 10 minutes,  $d^4$ diethylamine dissolved in 1,2-dimethoxyethane (the distillate) was added dropwise to the reaction mixture and the progress of the reaction was

monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give pure  $d_4$ -1u.<sup>2</sup>



**Fig. S2.** <sup>1</sup>H NMR spectrum of  $d_4$ -1u, CDCl<sub>3</sub>, 400 MHz

### Photochemical reductive deamination of *d*<sub>4</sub>-1u



Under standard conditions, 0.1 mmol of  $d_4$ -1u was added into reaction system, and <sup>1</sup>H NMR spectrum showed that deuterium atom was not incorporated into the terminal product 2b. This result indicated that the *alpha*-hydrogen atom of ketone product **2b** was not originated from the *alpha*-hydrogen of nitrogen atom in substrate **1u**.



## 5.3.3 Reaction was performed with D<sub>2</sub>O

Under standard conditions, the reaction system was irradiated for 2.5 hours with 10 equivalents of D<sub>2</sub>O as additive. D-2a was generated. While treating 2a with D<sub>2</sub>O under the optimal conditions, no reaction took place and D-2a was not observed. This clearly shows the *alpha*-hydrogen atom of ketone product 2 was originated from water.



Fig. S4. <sup>13</sup>C NMR spectrum of D-2a, CDCl<sub>3</sub>, 150 MHz

### The Institute for Advanced Studies, Wuhan University Mass spectrometry center High Resolution MS Data Report

Sample name: LJY-5 Data: 20230927 Instrument: Thermo Orbitrap Elite Ion source: ESI Mode: FTMS positive Parameter: Spray Voltage (kV):3.8 Source Heater Temp (°C):350 Sheath Gas Flow Rate:40 Aux Gas Flow Rate:10 Sweep Gas Flow Rate:0









Fig. S5. HRMS of D-2a

### 5.4 Determination of quantum yield



A cuvette was charged with **1a** (74.2 mg, 0.3 mmol) and anhydrous MeCN (3 mL). The sample was irradiated ( $\lambda = 366$  nm, radius = 3.0 mm with intensity of 21.2 mW/cm<sup>2</sup>) for 3603 s. The yield was determined by <sup>1</sup>H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene (added after irradiation) as an internal standard. Thus, the yield was calculated to be 5%.

# $\phi$ = Mole number for product/Mole number for absorption of photons = 0.23

$$\phi = \frac{n_{2a}N_A/t}{fP\lambda/hc}$$

n<sub>2a</sub>: the mole number of the product **2a**; t: reaction time (3603 s); N<sub>A</sub>: 6.02  $\times 10^{23}$  /mol; f: 1-10<sup>-A</sup> (366 nm, A = 15.84); P: P = E\*S (E: illumination intensity, E = 21.2 mW/cm<sup>2</sup>; S: the area that irradiated, S = 0.09 $\pi$  cm<sup>2</sup>);  $\lambda$ : wavelength ( $\lambda$  = 3.66  $\times 10^{-7}$  m); h: planck constant (h = 6.626  $\times 10^{-34}$  J\*s); c: velocity of light (c = 3  $\times 10^8$  m/s).

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## 7. Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of substrates and products



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2 f1 (ppm)

<sup>13</sup>C NMR spectrum of **1a**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **1b**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1c**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1d**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1e**, CDCl<sub>3</sub>, 100 MHz





<sup>13</sup>C NMR spectrum of **1f**, CDCl<sub>3</sub>, 150 MHz



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2 f1 (ppm)




<sup>13</sup>C NMR spectrum of **1h**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1i**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1***j*, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **1k**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **11**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **1m**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1n**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **10**, CDCl<sub>3</sub>, 150 MHz







<sup>13</sup>C NMR spectrum of **1q**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **1r**, CDCl<sub>3</sub>, 150 MHz







<sup>1</sup>H NMR spectrum of **1t**, CDCl<sub>3</sub>, 400 MHz







<sup>13</sup>C NMR spectrum of **1v**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **1w**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **1x**, CDCl<sub>3</sub>, 100 MHz







## <sup>1</sup>H NMR spectrum of **1y**, CDCl<sub>3</sub>, 600 MHz



<sup>13</sup>C NMR spectrum of **1y**, CDCl<sub>3</sub>, 150 MHz





<sup>13</sup>C NMR spectrum of **3a**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **3b**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2a**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2b**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2c**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of 2d, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2e**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2f**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **2g**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2h**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2i**, CDCl<sub>3</sub>, 150 MHz



<sup>13</sup>C NMR spectrum of **2j**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **2k**, CDCl<sub>3</sub>, 100 MHz



<sup>13</sup>C NMR spectrum of **2l**, CDCl<sub>3</sub>, 100 MHz







<sup>13</sup>C NMR spectrum of **2p**, CDCl<sub>3</sub>, 150 MHz



<sup>1</sup>H NMR spectrum of **20**'s reaction mixture, CDCl<sub>3</sub>, 400 MHz



<sup>1</sup>H NMR spectrum of **3a**'s reaction mixture, CDCl<sub>3</sub>, 400 MHz



 $^1\text{H}$  NMR spectrum of 3b 's reaction mixture, CDCl\_3, 400 MHz