

**Supplementary Information**

**For**

**Oxidative C-C Bond Cleavage of Aldehydes via  
Visible-Light Photoredox Catalysis**

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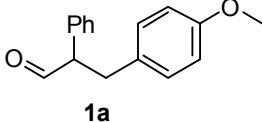
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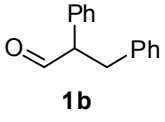
## 1. General Information

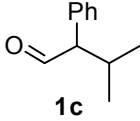
All reagents were purchased from commercial sources unless otherwise noted. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by treatment with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating/or by staining with a solution of 12 g 2,4-dinitrophenylhydrazine in 60 mL conc. H<sub>2</sub>SO<sub>4</sub>, 80 mL H<sub>2</sub>O and 200 mL 95% EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for <sup>1</sup>H NMR spectra were reported in  $\delta$  ppm referenced to an internal SiMe<sub>4</sub> standard. Chemical shifts for <sup>13</sup>C NMR spectra were reported in parts per million relative to the center line signal of the CDCl<sub>3</sub> triplet at 77.0 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on 7890A-5975C/Agilent.

## 2. Preparation and Characterization of Substrates

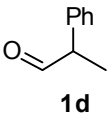
1) **1a**, **1b**, **1c**, **1d**, **1f** and **1g** were prepared from ethyl phenyl acetate and the corresponding bromide according to ref. *Org. Lett.* 2010, **12**, 5128.

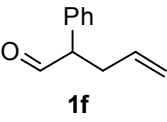
**1a**      **3-(4-methoxyphenyl)-2-phenylpropanal (1a):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.72 (d,  $J$  = 1.2 Hz, 1H), 7.34-7.25 (m, 3H), 7.13-7.11 (m, 2H), 6.96 (d,  $J$  = 8.5 Hz, 2H), 6.74 (d,  $J$  = 8.5 Hz, 2H), 3.78 (t,  $J$  = 7.3 Hz, 1H), 3.73 (s, 3H), 3.39 (dd,  $J$  = 6.8, 14.1 Hz, 1H), 2.91 (dd,  $J$  = 7.8, 14.1 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  200.0, 158.0, 135.8, 130.7, 129.9, 129.0, 128.9, 127.6, 113.7, 61.1, 55.1, 35.3.

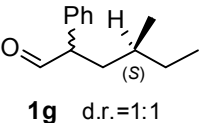
**1b**      **2,3-diphenylpropanal (1b):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.73 (s, 1H), 7.34-7.27 (m, 3H), 7.20-7.11 (m, 5H), 7.05 (d,  $J$  = 7.5 Hz, 2H), 3.82 (t,  $J$  = 7.3 Hz, 1H), 3.46 (dd,  $J$  = 6.8, 14.0 Hz, 1H), 2.96 (dd,  $J$  = 7.9, 14.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  199.8, 138.8, 135.7, 129.0, 128.3, 127.6, 126.3, 60.9, 36.1.

**1c**      **3-methyl-2-phenylbutanal (1c):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.7 (d,  $J$  = 3.3 Hz, 1H), 7.35 (t,  $J$  = 7.3 Hz, 2H), 7.28 (t,  $J$  = 7.3 Hz, 1H), 7.18 (d,  $J$  = 7.0 Hz, 2H), 3.18 (dd,  $J$  = 3.2, 9.5 Hz, 1H), 2.48-2.35 (m, 1H), 1.04 (d,

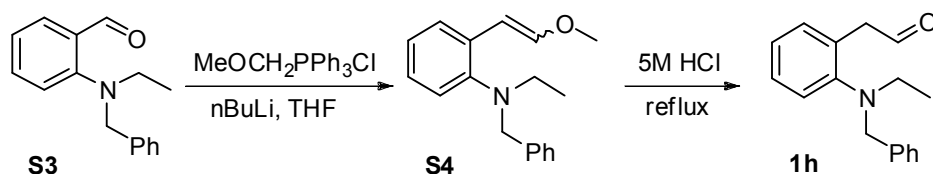
$J = 6.6$  Hz, 3H), 0.76 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.0, 135.5, 129.3, 128.8, 127.4, 66.8, 28.7, 21.1, 20.0.

 **2-phenylpropanal (1d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (d,  $J = 1.3$  Hz, 1H), 7.38 (t,  $J = 7.4$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.21 (d,  $J = 7.1$  Hz, 2H), 3.63 (q,  $J = 7.1$  Hz, 1H), 1.44 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.1, 137.7, 129.1, 128.3, 127.5, 53.0 14.6.

 **2-phenylpent-4-enal (1f):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (d,  $J = 1.4$  Hz, 1H), 7.37 (t,  $J = 7.3$  Hz, 2H), 7.29 (t,  $J = 7.3$  Hz, 1H), 7.19 (d,  $J = 7.2$  Hz, 2H), 5.76-5.66 (m, 1H), 5.05 (dd,  $J = 1.3, 17.1$  Hz, 1H), 5.00 (d,  $J = 10.2$  Hz, 1H), 3.61 (t,  $J = 7.4$  Hz, 1H), 2.88-2.80 (m, 1H), 2.53-2.46 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.0, 134.8, 129.0, 128.8, 127.6, 117.1, 58.7, 33.9.

 **(S)-4-methyl-2-phenylhexanal (1g):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (d,  $J = 2.0$  Hz, 1H), 9.65 (d,  $J = 2.3$  Hz, 1H), 7.39-7.35 (m, 4H), 7.31-7.28 (m, 2H), 7.23-7.20 (m, 4H), 3.65-3.60 (m, 2H), 2.14-2.07 (m, 1H), 1.84-1.79 (m, 2H), 1.60-1.53 (m, 1H), 1.46-1.31 (m, 3H), 1.26-1.14 (m, 3H), 0.89-0.81 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201, 200.9, 136.8, 136.4, 12.0, 128.8, 128.7, 127.4, 57.1, 56.9, 36.6, 36.1, 31.7, 31.4, 29.8, 28.8, 19.3, 18.6, 11.1, 10.9.

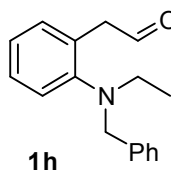
## 2) Synthesis of **1h**



To a suspension of  $\text{MeOCH}_2\text{PPh}_3\text{Cl}$  (650 mg, 1.9 mmol) in dry THF (20 mL) was added  $n\text{BuLi}$  (0.8 mL, 1.9 mmol) at  $-78^\circ\text{C}$ ; the reaction mixture was stirred over 20 min under nitrogen atmosphere. To this solution was added A THF solution (10 mL) of **S3** (400 mg, 1.6 mmol), the mixture was stirred for 12 h at room temperature before it was quenched by saturated  $\text{NH}_4\text{Cl}$ , and extracted with ether. The extracts were washed with saturated  $\text{NaCl}$  solution, dried over anhydrous  $\text{MgSO}_4$ , and concentrated under reduced pressure to give crude **S4**. The crude material was used for next reaction without

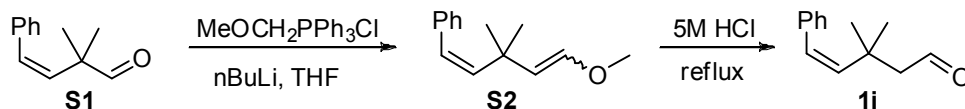
further purification.

A acetone solution of **S4** and HCl (5 N, 1 mL) was refluxed for 1.5 h. The resulting solution was cooled, diluted with ether and washed with water and saturated NaHCO<sub>3</sub>. The solution was dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (5% EtOAc in petroleum ether) to afford aldehyde **1h** (132 mg, 32%).



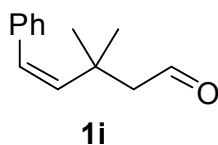
**2-(2-(benzyl(ethyl)amino)phenyl)acetaldehyde (1h):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.54 (t, *J* = 2.3 Hz, 1H), 7.29-7.22 (m, 4H), 7.19-7.17 (m, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 3.97 (s, 2H), 3.68 (d, *J* = 2.3 Hz, 2H), 2.90 (q, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.8, 149.8, 137.6, 131.2, 130.7, 129.0, 128.1, 127.0, 124.7, 123.6, 58.5, 46.7, 46.3, 11.7. HRMS-ESI (*m/z*): [M+H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>19</sub>NO, 254.1539; found: 254.1603.

### 3) Synthesis of **1i**



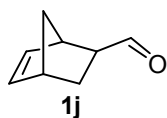
To a suspension of MeOCH<sub>2</sub>PPh<sub>3</sub>Cl (2 g, 6 mmol) in dry THF (20 mL) was added <sup>t</sup>BuOK (672 mg, 6 mmol) at 0 °C; the reaction mixture was stirred over 20 min under nitrogen atmosphere. To this solution was added A THF solution (10 mL) of **S1** (522 mg, 3 mmol), the mixture was stirred for 1 h at room temperature before it was quenched by water, and extracted with ethyl acetate. The extracts were washed with saturated NaCl solution, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure to give crude **S2** (472 mg, 78%). The crude material was used for next reaction without further purification.

A THF solution (20 mL) of **S2** (472 mg, 2.3 mmol) and HCl (5 N, 4 mL) was refluxed for 1.5 h; the resulting solution was cooled, diluted with ether and washed with water and saturated NaHCO<sub>3</sub>. The solution was dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (3% EtOAc in petroleum ether) to afford aldehyde **1i** (432 mg, 80%).



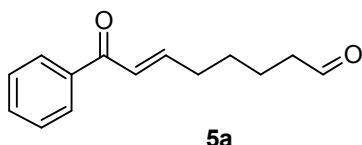
**(Z)-3,3-dimethyl-5-phenylpent-4-enal (1i):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (t,  $J = 2.8$  Hz, 1H), 7.29 (t,  $J = 7.2$  Hz, 2H), 7.22 (t,  $J = 7.3$  Hz, 1H), 7.15 (d,  $J = 7.4$  Hz, 2H), 6.57 (d,  $J = 12.6$  Hz, 1H), 5.67 (d,  $J = 12.6$  Hz, 1H), 2.30 (d,  $J = 2.8$  Hz, 2H), 1.10 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.0, 139.2, 138.5, 129.2, 128.5, 127.9, 126.7, 55.5, 36.0, 29.8.

**4) 1j** was prepared from the corresponding alcohol according ref. *J. Org. Chem.* 1976, **41**, 1229.

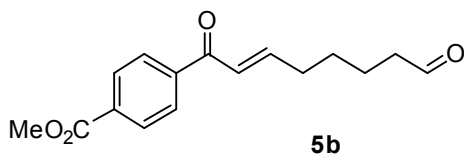


**bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (1j):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.42 (d,  $J = 2.5$  Hz, 1H), 6.22 (dd,  $J = 3.4, 5.3$  Hz, 1H), 6.00 (dd,  $J = 2.4, 5.3$  Hz, 1H), 3.25 (s, 1H), 2.99 (s, 1H), 2.93-2.89 (m, 1H), 1.94-1.88 (m, 1H), 1.47-1.42 (m, 2H), 1.32 (d,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.1, 138.1, 131.8, 52.2, 49.6, 45.0, 42.7, 27.6.

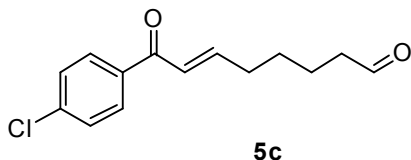
**5) 5a-e** was prepared from 1,6-hexanediol in six steps according to ref. *J. Am. Chem. Soc.* 2005, **127**, 16028.



**8-oxo-8-phenyloct-6-enal (5a):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.78 (t,  $J = 1.3$  Hz, 1H), 7.92 (d,  $J = 7.6$  Hz, 2H), 7.55 (t,  $J = 7.3$  Hz, 1H), 7.46 (t,  $J = 7.5$  Hz, 2H), 7.07-6.98 (m, 1H), 6.89 (d,  $J = 15.4$  Hz, 1H), 2.48 (dt,  $J_d = 1.4$  Hz,  $J_t = 7.1$  Hz, 2H), 2.35 (q,  $J = 7.2$  Hz, 2H), 1.74-1.67 (m, 2H), 1.61-1.54 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.1, 190.6, 148.8, 137.7, 132.6, 128.4, 126.1, 43.4, 32.3, 27.4, 21.4. HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{16}\text{O}_2$ , 217.1223; found: 217.1222.



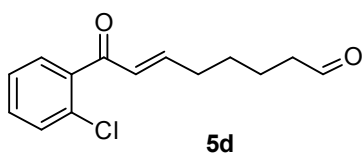
**methyl 4-(8-oxooct-2-enoyl)benzoate (5b):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.78 (s, 1H), 8.12 (d,  $J = 8.2$  Hz, 2H), 7.95 (d,  $J = 8.3$  Hz, 2H), 7.06 (dt,  $J_d = 15.4$  Hz,  $J_t = 6.9$  Hz, 1H), 6.88 (d,  $J = 15.4$  Hz, 1H), 3.95 (s, 3H), 2.49 (t,  $J = 7.3$  Hz, 2H), 2.36 (q,  $J = 7.1$  Hz, 2H), 1.74-1.67 (m, 2H), 1.61-1.54 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.0, 190.2, 166.3, 150.0, 141.3, 133.4, 129.7, 128.4, 126.2, 52.4, 43.6, 32.6, 27.6, 21.6. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_4$ , 215.1278; found, 215.1266.



**8-(4-chlorophenyl)-8-oxooct-6-enal (5c):**  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.76 (s, 1H), 7.49-7.44 (m, 2H), 7.34 (t,  $J = 7.9$  Hz, 1H), 7.09 (dd,  $J = 1.9, 8.2$  Hz, 1H), 7.02 (dt,  $J_d = 15.4$  Hz,  $J_t$

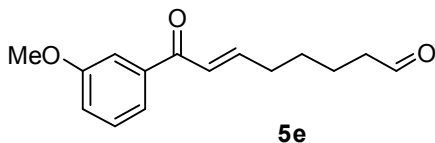
$= 6.8$  Hz, 1H), 6.86 (d,  $J = 15.4$  Hz, 1H), 3.84 (s, 3H), 2.48 (t,  $J = 7.0$  Hz, 2H), 2.34 (q,  $J = 7.2$  Hz, 2H), 1.73-1.65 (m, 2H), 1.60-1.52 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.9, 189.3, 149.3, 139.1, 136.1, 129.9, 128.8, 125.7, 43.5, 32.5, 27.5, 21.5. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{15}\text{ClO}_2$ , 251.0833; found, 251.0828.



**8-(2-chlorophenyl)-8-oxooct-6-enal (5d):**  $^1\text{H}$  NMR

(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.76 (s, 1H), 7.42-7.30 (m, 4H), 6.69 (dt,  $J_d = 15.8$  Hz,  $J_t = 6.8$  Hz, 1H), 6.47 (d,  $J =$

$15.8$  Hz, 1H), 2.46 (dt,  $J_d = 1.2$  Hz,  $J_t = 7.1$  Hz, 2H), 2.30 (q,  $J = 7.1$  Hz, 2H), 1.70-1.63 (m, 2H), 1.56-1.48 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.0, 194.1, 151.3, 138.9, 131.1, 130.7, 130.1, 129.1, 126.7, 43.5, 32.4, 27.3, 21.5. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{15}\text{ClO}_2$ , 251.0833; found, 251.0828.



**8-(3-methoxyphenyl)-8-oxooct-6-enal (5e):**  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.77 (s, 1H), 7.86 (d,  $J = 8.5$  Hz, 2H), 7.43 ( $J = 8.4$  Hz, 2H), 7.03 (dt,

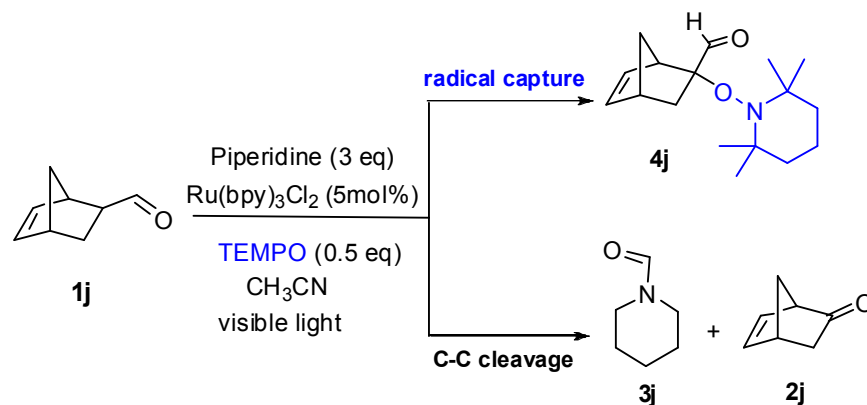
$J_d = 15.4$  Hz,  $J_t = 6.9$  Hz, 1H), 6.85 (d,  $J = 15.4$  Hz, 1H), 2.47 (dt,  $J_d = 1.4$  Hz,  $J_t = 7.1$  Hz, 2H), 2.33 (q,  $J = 6.8$  Hz, 2H), 1.72-1.65 (m, 2H), 1.59-1.52 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.9, 189.3, 149.3, 139.1, 136.1, 129.9, 128.8, 125.7, 43.5, 32.5, 27.5, 21.5. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{15}\text{H}_{18}\text{O}_3$ , 247.1329; found, 247.1331.

### 3. General procedure for photocatalytic oxidative C-C bond cleavage reaction

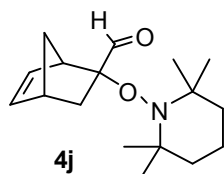
A 10 mL round bottom flask was equipped with magnetic stir bar and was charged with tetrahydroisoquinoline **1a** (24 mg, 0.1 mmol), piperidine (30  $\mu\text{L}$ , 0.3 mmol),  $\text{CH}_3\text{CN}$  (1 mL) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (3.8 mg, 0.005 mmol). The mixture was irradiated with 15 W fluorescent light bulb for 6 h at room temperature and the reaction mixture was exposed to the open air. After the reaction was completed, the solvent was

concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (2% EtOAc in petroleum ether) to afford the desired product **2a** in 80% yield.

#### 4. Control experiment with TEMPO



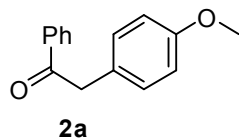
The mixture of **1j** (0.2 mmol), piperidine (0.6 mmol), TEMPO (0.1 mmol), and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (0.001 mmol) was irradiated with 15 W fluorescent light bulb in  $\text{CH}_3\text{CN}$  for 12 hours. Formamide **3j** and oxidative C-C bond cleavage product **2j** were detected by GC-MS, and column chromatography (PE/AcOEt = 10/1) gave the  $\alpha$ -oxyaminated aldehyde product **4j**.



#### 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (**4j**):

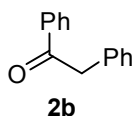
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.97 (s, 1H), 6.20 (dd,  $J = 2.9, 5.5$  Hz, 1H), 5.79 (dd,  $J = 3.1, 5.0$  Hz, 1H), 3.29 (s, 1H), 2.86 (s, 1H), 2.27 (dd,  $J = 2.7, 12.1$  Hz, 1H), 1.88 (d,  $J = 8.3$  Hz, 1H), 1.71 (dd,  $J = 2.7, 13.0$  Hz, 2H), 1.49-1.37 (m, 7H), 1.15 (s, 3H), 1.09 (m, 3H), 1.03 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.2, 141.6, 131.6, 94.6, 60.7, 60.5, 50.9, 48.4, 41.4, 40.4, 40.2, 38.6, 33.7, 20.3, 20.2, 16.8. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{27}\text{NO}_2$ , 278.2115; found, 278.2118.

#### 5. Characterization of products



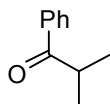
#### 2-(4-methoxyphenyl)-1-phenylethanone (**2a**):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 7.4$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.4$  Hz, 2H), 7.17 (d,  $J = 8.6$  Hz, 2H), 6.86 (d,  $J = 8.6$  Hz, 2H), 4.22 (s, 2H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.9, 158.5, 136.6, 133.0, 130.4, 128.6, 128.5, 126.5, 114.1, 55.2, 44.6.



#### 1,2-diphenylethanone (**2b**):

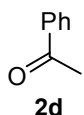
7.7 Hz, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.36 (t,  $J = 7.3$  Hz, 2H), 7.31-7.29 (m, 3H), 4.32 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.6, 136.6, 134.5, 133.1, 129.4, 128.7, 128.6, 126.9, 45.5.



**2c**

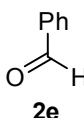
**2-methyl-1-phenylpropan-1-one (2c):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 7.5$  Hz, 2H), 7.55 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 3.62-3.51 (m, 1H), 1.22 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

204.5, 136.2, 132.8, 128.6, 128.3, 35.3, 19.1.



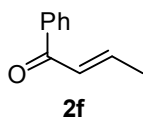
**2d**

**acetophenone (2d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 7.5$  Hz, 2H), 7.57 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 2.62 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.1, 137.1, 133.0, 128.5, 128.2, 26.6.



**2e**

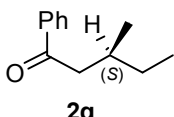
**benzaldehyde (2e):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 7.96 (d,  $J = 7.5$  Hz, 2H), 7.63 (t,  $J = 7.3$  Hz, 1H), 7.53 (t,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.3, 136.3, 134.4, 129.7, 128.9.



**2f**

**1-phenylbut-2-en-1-one (2f):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (d,  $J = 7.8$  Hz, 2H), 7.55 (t,  $J = 7.3$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.12-7.03 (m, 1H), 6.91 (d,  $J = 15.3$  Hz, 1H), 2.00 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR

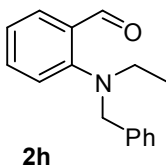
(100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 145.0, 137.9, 132.5, 128.5, 127.5, 18.6.



**2g**

**(S)-3-methyl-1-phenylpentan-1-one (2g):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d,  $J = 7.6$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 2.95 (dd,  $J = 5.7, 15.7$  Hz, 1H), 2.74 (dd,  $J = 8.0, 15.7$  Hz,

1H), 2.15-2.05 (m, 1H), 1.49-1.38 (m, 1H), 1.33-1.23 (m, 1H), 0.96-0.91 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 137.5, 132.8, 128.5, 128.1, 45.6, 31.4, 29.7, 19.5, 11.4.

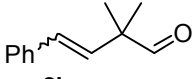


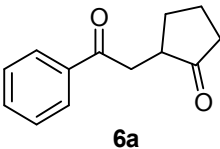
**2h**

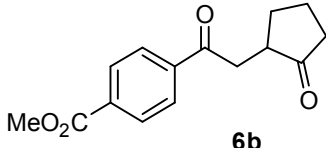
**2-(benzyl(ethyl)amino)benzaldehyde (2h):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.47 (s, 1H), 7.81 (dd,  $J = 1.4, 7.7$  Hz, 1H), 7.41 (td,  $J = 1.6, 7.7$  Hz, 1H), 7.31-7.24 (m, 5H), 7.15 (d,  $J = 8.2$  Hz, 1H), 7.10 (t,  $J = 7.5$  Hz, 1H), 4.32 (s, 2H), 3.19 (q,  $J = 7.1$  Hz, 2H), 1.07 (t,  $J = 7.1$  Hz, 3H).

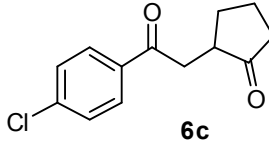
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.6, 154.4, 137.8, 134.4, 130.4, 129.1, 128.4, 128.3, 127.3, 122.7, 122.0, 58.4, 49.5, 11.8. HRMS (ESI):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{16}\text{H}_{17}\text{NO}$ : 240.1383, found: 240.1446.

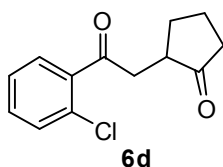



**2,2-dimethyl-4-phenylbut-3-enal (2i):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.45 (s, 3H), 9.24 (s, 1H), 7.38-7.23 (m, 18H), 7.11 (d,  $J$  = 7.1 Hz, 2H), 6.66 (d,  $J$  = 12.1 Hz, 1H), 6.45 (d,  $J$  = 16.3 Hz, 3H), 6.15 (d,  $J$  = 16.3 Hz, 3H), 5.61 (d,  $J$  = 12.1 Hz, 1H), 1.30 (s, 18H), 1.20 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.4, 202.1, 137.0, 136.7, 134.9, 131.3, 131.1, 131.0, 128.7, 128.6, 128.1, 127.8, 127.4, 126.3, 48.8, 48.5, 23.8, 21.6. HRMS (ESI):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{14}\text{O}$ : 175.1117, found: 175.1111.


**2-(2-oxo-2-phenylethyl)cyclopentanone (6a):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J$  = 7.2 Hz, 2H), 7.57 (t,  $J$  = 7.3 Hz, 1H), 7.46 (t,  $J$  = 7.4 Hz, 2H), 3.53 (dd,  $J$  = 3.3, 18.1 Hz, 1H), 3.05 (dd,  $J$  = 8.0, 18.1 Hz, 1H), 2.69-2.61 (m, 1H), 2.44-2.34 (m, 2H), 2.33-2.23 (m, 1H), 2.12-2.05 (m, 1H), 1.92-1.80 (m, 1H), 1.66-1.55 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  220.3, 198.0, 136.6, 133.2, 128.6, 128.0, 45.1, 38.6, 37.5, 29.7, 20.8. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{13}\text{H}_{14}\text{O}_2$ , 203.1067; found, 203.1072.


**methyl 4-(2-(2-oxocyclopentyl)acetyl)benzoate (6b):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (d,  $J$  = 8.5 Hz, 2H), 8.00 (d,  $J$  = 8.5 Hz, 2H), 3.95 (s, 3H), 3.54 (dd,  $J$  = 3.4, 18.2 Hz, 1H), 3.06 (dd,  $J$  = 7.9, 18.2 Hz, 1H), 2.70-2.62 (m, 1H), 2.44-2.35 (m, 2H), 2.32-2.22 (m, 1H), 2.14-2.04 (m, 1H), 1.93-1.81 (m, 1H), 1.64-1.58 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.5, 199.1, 136.7, 133.1, 128.6, 128.0, 57.7, 43.5, 36.6, 32.9, 26.7, 24.7. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_4$ , 261.1121; found, 261.1126.


**2-(2-(4-chlorophenyl)-2-oxoethyl)cyclopentanone (6c):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $J$  = 8.5 Hz, 2H), 7.44 (d,  $J$  = 8.5 Hz, 2H), 3.49 (dd,  $J$  = 3.3, 18.1 Hz, 1H), 3.00 (dd,  $J$  = 8.0, 18.1 Hz, 1H), 2.67-2.61 (m, 1H), 2.44-2.34 (m, 2H), 2.32-2.22 (m, 1H), 2.13-2.04 (m, 1H), 1.90-1.83 (m, 1H), 1.65-1.55 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  220.1, 196.8, 139.7, 134.9, 129.5, 128.9, 45.0, 38.6, 37.5, 29.7, 20.8. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{13}\text{H}_{13}\text{ClO}_2$ , 237.0677; found, 237.0671.



**2-(2-(2-chlorophenyl)-2-oxoethyl)cyclopentanone (6d):**  $^1\text{H}$

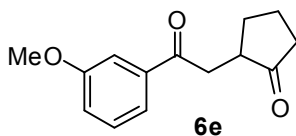
NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (dd,  $J = 1.6, 7.3$  Hz, 1H), 7.43-7.33 (m, 3H), 3.44 (dd,  $J = 4.0, 18.2$  Hz, 1H), 3.06 (dd,  $J =$

7.8, 18.2 Hz, 1H), 2.72-2.65 (m, 1H), 2.44-2.38 (m, 2H), 2.33-2.20

(m, 1H), 2.15-2.07 (m, 1H), 1.93-1.82 (m, 1H), 1.73-1.62 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,

$\text{CDCl}_3$ ):  $\delta$  219.8, 201.4, 139.0, 131.8, 130.5, 129.0, 127.0, 45.4, 42.8, 37.4, 29.4, 20.8.

HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{13}\text{H}_{13}\text{ClO}_2$ , 237.0677; found, 237.0671.



**2-(2-(3-methoxyphenyl)-2-oxoethyl)cyclopentanone (6e):**  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (d,  $J = 7.7$  Hz, 1H), 7.48

(t,  $J = 1.9$  Hz, 1H), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.11 (dd,  $J = 2.5,$

8.2 Hz, 1H), 3.85 (s 3H), 3.52 (dd,  $J = 3.3, 18.1$  Hz, 1H), 3.04 (dd,  $J = 8.0, 18.1$  Hz, 1H),

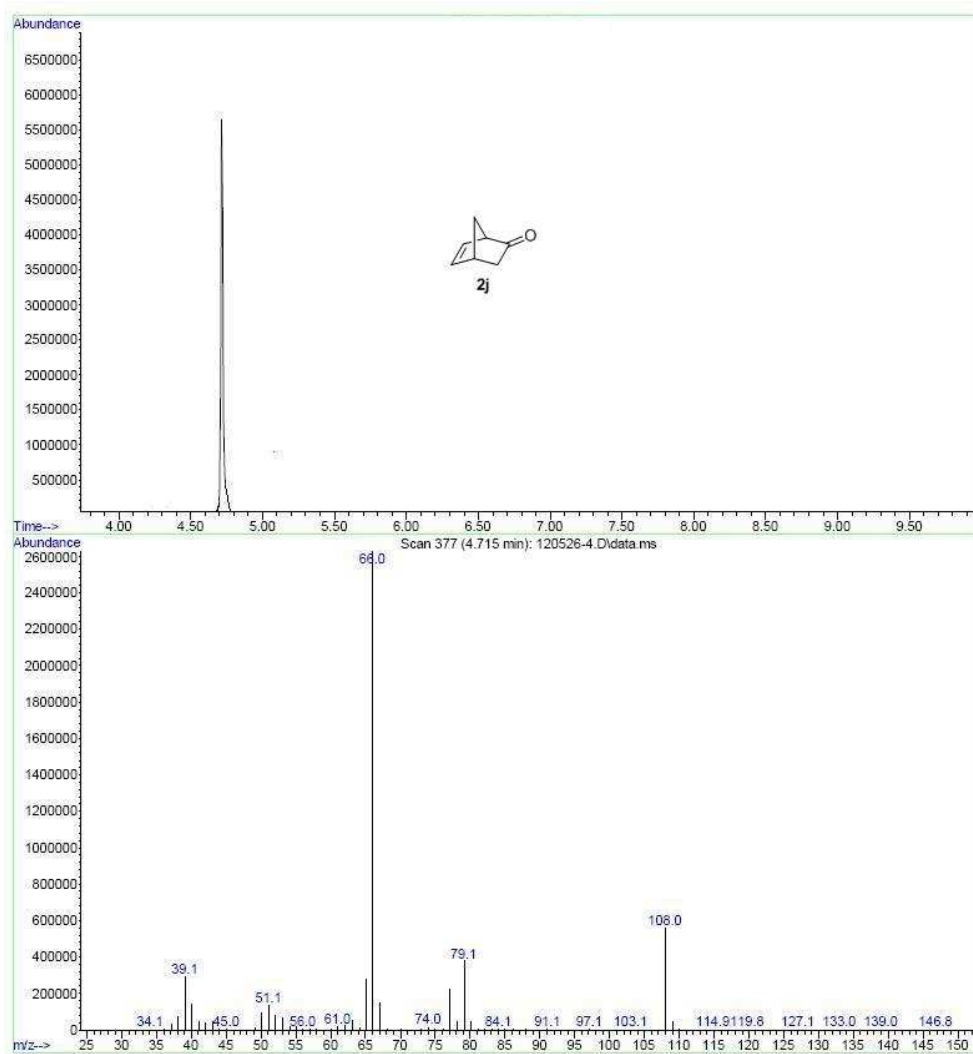
2.68-2.60 (m, 1H), 2.43-2.23 (m, 3H), 2.15-2.05 (m, 1H), 1.92-1.80 (m, 1H), 1.66-1.57

(m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  220.4, 197.8, 159.8, 138.0, 129.6, 120.7,

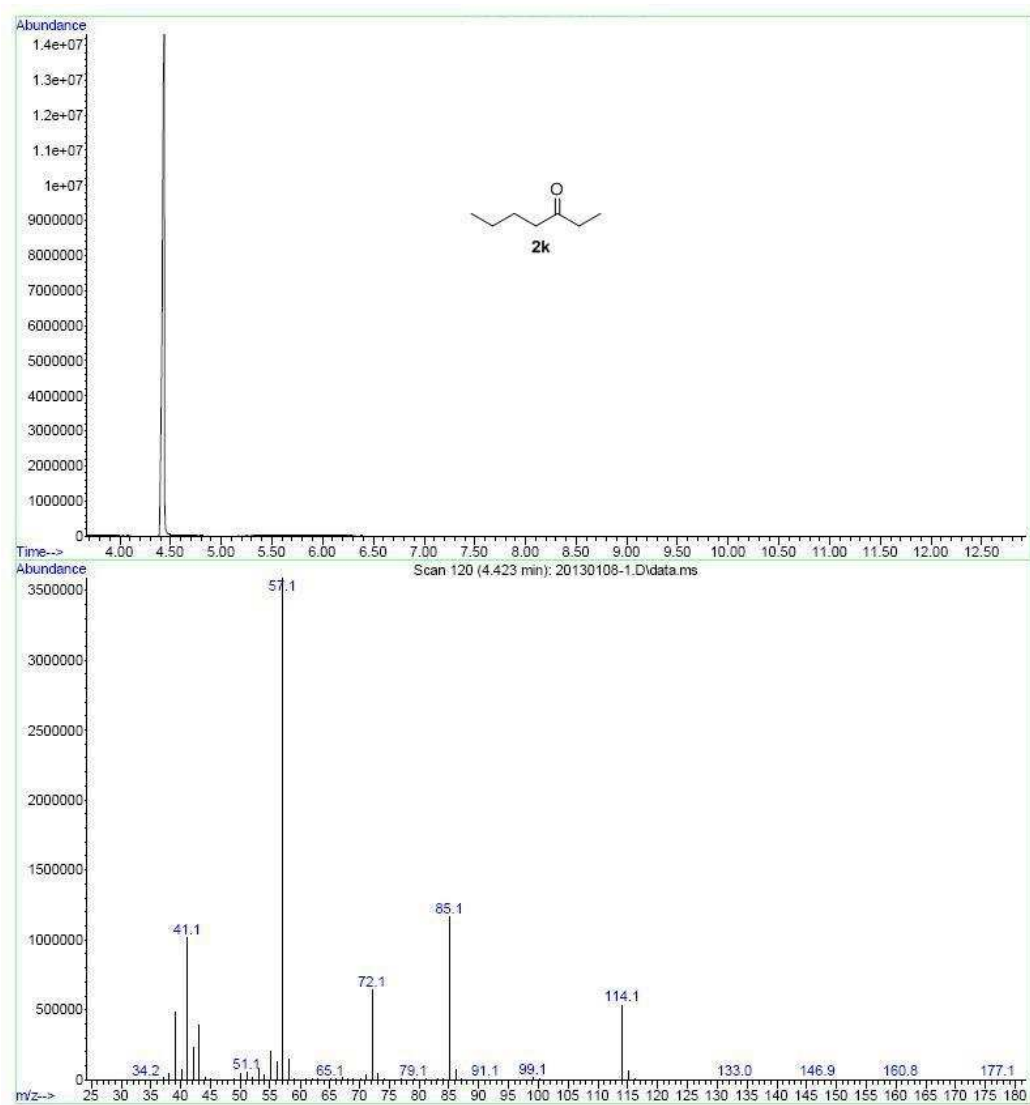
119.8, 112.2, 55.4, 45.1, 38.8, 37.6, 29.7, 20.8. HRMS-ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calculated

for  $\text{C}_{14}\text{H}_{16}\text{O}_3$ , 233.1172; found, 233.1174.

## GC-MS of 2j



## GC-MS of 2k



## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for substrates and products

