

## Supplementary Information

### Visible-light-mediated metal-free decarboxylative acylations of isocyanides with $\alpha$ -oxocarboxylic acids and water leading to $\alpha$ - ketoamides

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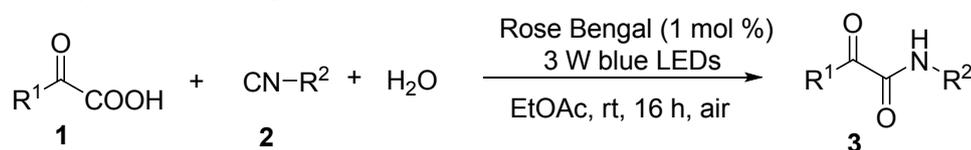
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## 1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Bidepharm and Energy Chemical Company and used as received without further purification unless otherwise stated.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in  $\text{CDCl}_3$  on a Bruker Avance III spectrometer with TMS as internal standard (500 MHz  $^1\text{H}$ , 125 MHz  $^{13}\text{C}$ ) at room temperature, the chemical shifts ( $\delta$ ) were expressed in ppm and  $J$  values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

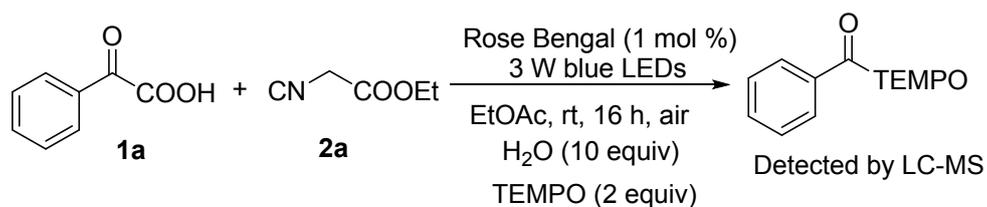
## 2. General procedure for visible-light-induced synthesis of $\alpha$ -ketoamides from $\alpha$ -oxocarboxylic acids, isocyanides and water.



To a solution of  $\alpha$ -oxocarboxylic acids **1** (0.3 mmol), Rose Bengal (0.002 mmol, 1 mol %),  $\text{H}_2\text{O}$  (2 mmol) and EtOAc (2 mL) was added isocyanide **2** (0.2 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3 W blue LEDs at room temperature for 16 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate (5:1) as eluent to give the desired product **3**.

## 3. Preliminary mechanistic studies

### 3.1 The addition of TEMPO in the model reaction system.



To a solution of 2-oxo-2-phenylacetic acid **1a** (0.3 mmol), TEMPO (0.4 mmol), Rose Bengal (0.002 mmol, 1 mol %), H<sub>2</sub>O (2 mmol) and EtOAc (2 mL) was added ethyl 2-isocyanoacetate (**2a**) (0.2 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3 W blue LEDs at room temperature for 16 h. The reaction was completely inhibited, and TEMPO-trapped complex (PhCO-TEMPO) was detected by LC-MS analysis (Figure S1).

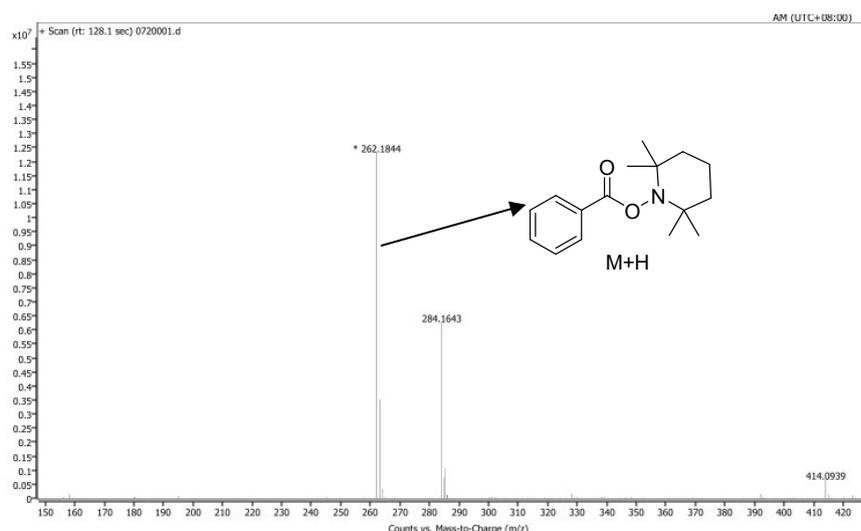
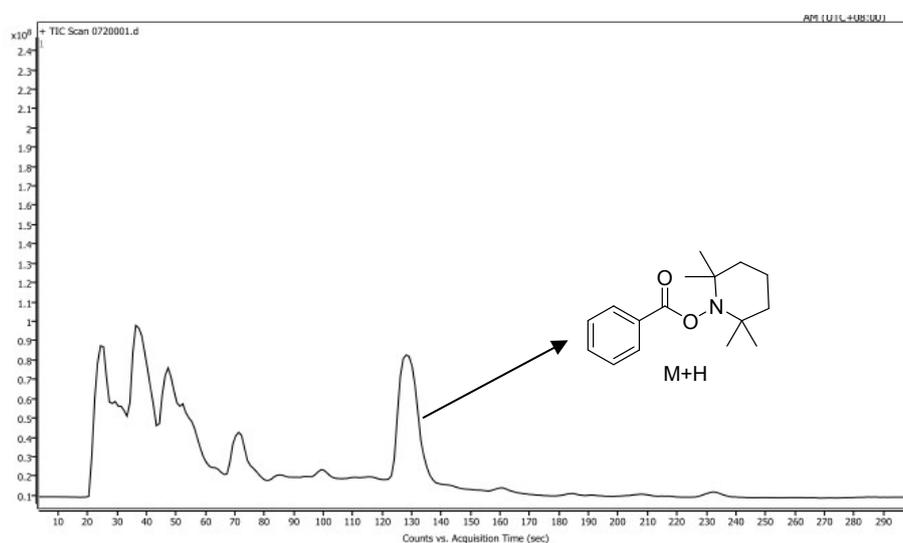
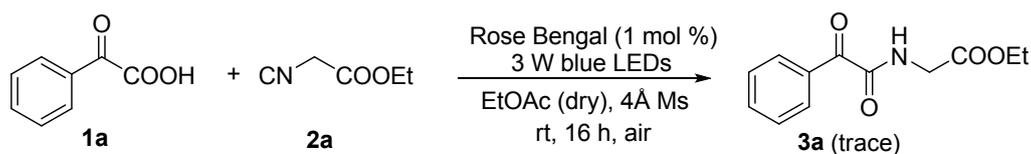


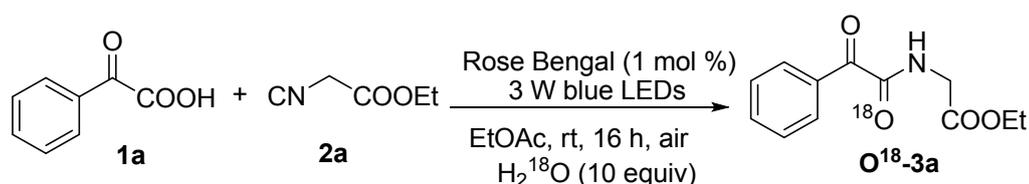
Figure S1

### 3.2 The reaction of **1a** and **2b** was carried out in the absence of H<sub>2</sub>O.

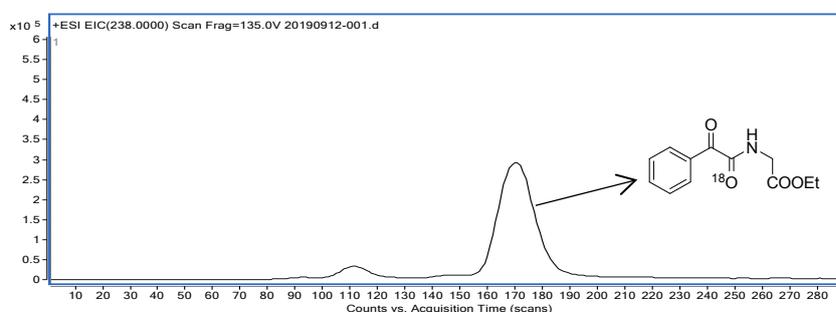


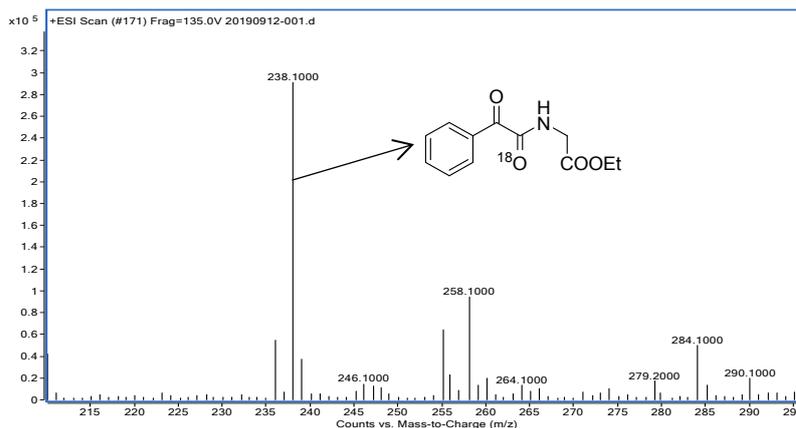
To a solution of 2-oxo-2-phenylacetic acid **1a** (0.3 mmol), Rose Bengal (0.002 mmol, 1 mol %), 4 ÅMs (20mg) in dry EtOAc 2 mL was added ethyl 2-isocyanoacetate (**2a**) (0.2 mmol). The reaction mixture was open to air and stirred under the irradiation of 3 W blue LEDs at room temperature for 16 h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of the desired product **3a** was detected.

### 3.3 The reaction of **1a** and **2b** was carried out under H<sub>2</sub>O<sup>18</sup>.



To a solution of 2-oxo-2-phenylacetic acid **1a** (0.3 mmol), Rose Bengal (0.002 mmol, 1 mol %), H<sub>2</sub><sup>18</sup>O (2 mmol) in EtOAc (2 mL) was added ethyl 2-isocyanoacetate (**2a**) (0.2 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3 W blue LEDs at room temperature for 16 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **<sup>18</sup>O-3a** (39.5 mg, 84 %) (Figure S2).



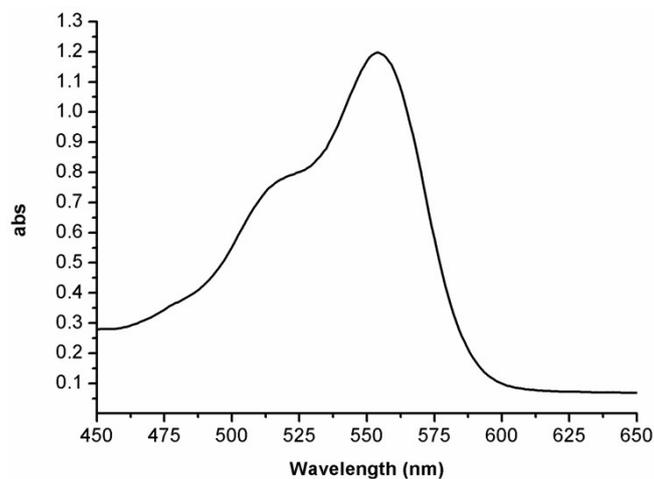


**Figure S2**

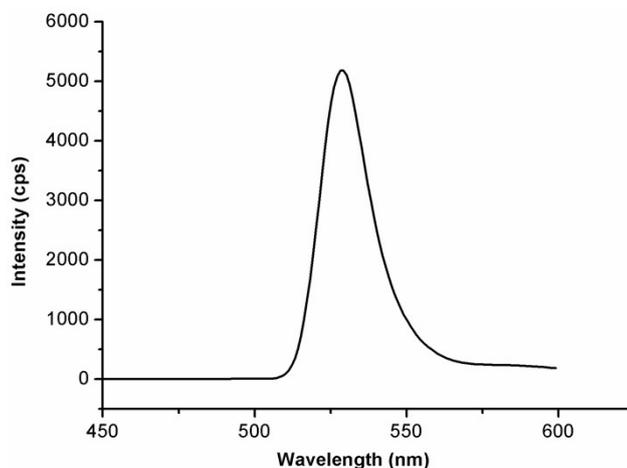
### **3.4 The UV-visible spectroscopy and Fluorescence quenching studies (Stern–Volmer Studies)**

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing Bengal Rose, ethyl isocyanoacetate and 2-oxo-2-phenylacetic with solvent ( $V[\text{EtOAc}] = 2$  mL,  $V[\text{H}_2\text{O}] = 37$  vL), ( $M[\text{Bengal Rose}] = 1.0 \times 10^{-5}$  mol/L,  $M[\text{ethyl 2-isocyanoacetate}] = 1 \times 10^{-3}$  mol/L,  $M[2\text{-oxo-2-phenylacetic}] = 1.5 \times 10^{-3}$  mol/L) in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 550 nm. The absorption was collected and the result was listed in Figure S3.

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4600 spectrofluorimeter. The excitation wavelength was fixed at 521 nm, and the emission wavelength was measured at 578 nm. The sample was prepared by mixing Bengal Rose, ethyl isocyanoacetate, 2-oxo-2-phenylacetic with solvent ( $V[\text{EtOAc}] = 2$  mL,  $V[\text{H}_2\text{O}] = 37$  vL) ( $M[\text{Bengal Rose}] = 1.0 \times 10^{-5}$  mol/L,  $M[\text{ethyl 2-isocyanoacetate}] = 2 \times 10^{-5}$  mol/L,  $M[2\text{-oxo-2-phenylacetic}] = 3.0 \times 10^{-5}$  mol) in a light path quartz fluorescence cuvette. The emission intensity was collected and the result was listed in Figure S4.

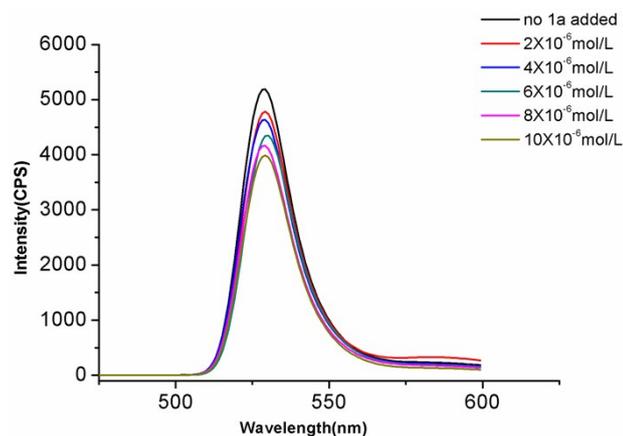


**Figure S3.** UV-vis spectrum of the reaction mixture.



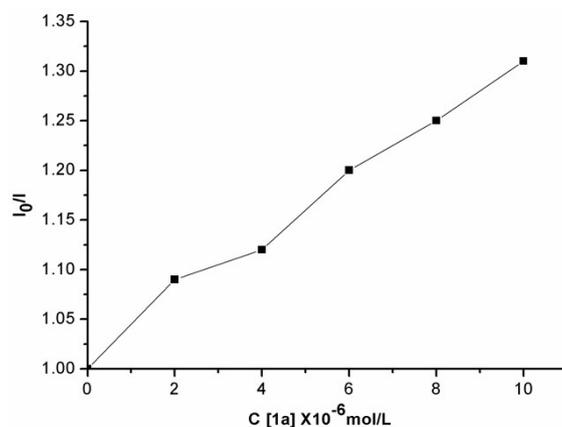
**Figure S4.** Fluorescence spectrum of the reaction mixture.

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 521 nm, and the emission wavelength was measured at 578 nm (emission maximum). The samples were prepared by mixing by Rose Bengal ( $1.0 \times 10^{-5}$  mol/L) and different amount of 2-oxo-2-phenylacetic acid **1a** in EtOAc (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of 2-oxo-2-phenylacetic acid stock solution is  $2.0 \times 10^{-6}$  mol/L in EtOAc. For each quenching experiment, 0.1 mL different concentration of 2-oxo-2-phenylacetic acid stock solution was titrated to a mixed solution of 0.1 mL Bengal Rose (in a total volume = 0.2 mL). Then the emission intensity was collected and the results were presented in Figure S5.



**Figure S5.** Quenching of Rose Bengal fluorescence emission in the presence of 2-oxo-2-phenylacetic acid.

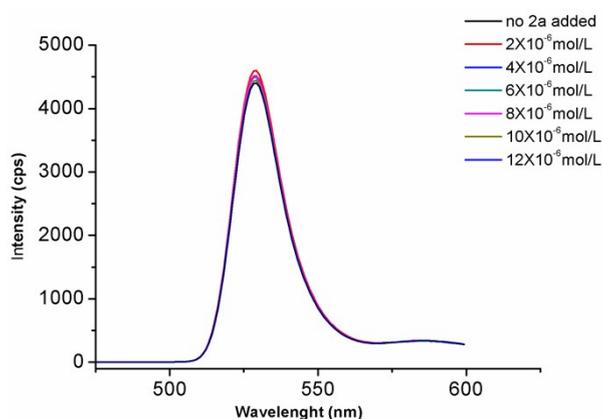
An indeed fluorescence quenching phenomenon of Rose Bengal under various concentrations of 2-oxo-2-phenylacetic acid **1a** was demonstrated in a curve of  $[I_0/I]$  vs  $C[1a]$ , as shown in Figure S6 (Stern-Volmer plots). For example, when  $C[1a]$  is  $2 \times 10^{-6}$  mol/L, the non-linear Stern-Volmer plots indicated energy transfer process occurred between the excited state of  $RB^*$  and 2-oxo-2-phenylacetic acid **1a**.



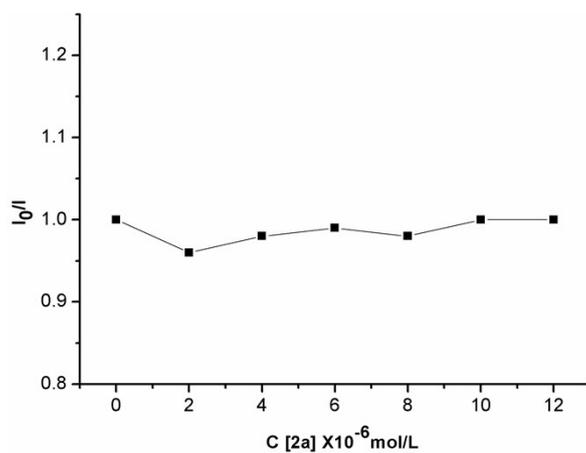
**Figure S6.** Stern-volmer plots.  $I_0$  is the inherent fluorescence intensity of Rose Bengal.  $I$  is the fluorescence intensity of Rose Bengal in the presence of **1a**.

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 521nm, and the emission wavelength was measured at 578 nm (emission maximum). The samples were prepared by mixing by Rose Bengal ( $1.0 \times 10^{-5}$  mol/L) and different amount of ethyl isocyanoacetate **2a** in EtOAc (total volume = 0.2 mL) in a light path quartz

fluorescence cuvette. The concentration of ethyl isocyanoacetate **2a** stock solution is  $2.0 \times 10^{-6}$  mol/L in EtOAc. For each quenching experiment, 0.1 mL of ethyl isocyanoacetate stock solution was titrated to a mixed solution of 0.1 mL Rose Bengal (in a total volume = 0.2 mL). Then the emission intensity was collected and the results were presented in Figure S7. An fluorescence quenching phenomenon of Bengal Rose under various concentrations of ethyl isocyanoacetate was shown in Figure S8 (Stern-Volmer plots).

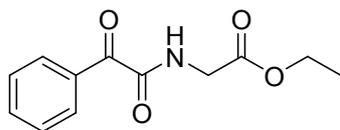


**Figure S7.** Quenching of Rose Bengal fluorescence emission in the presence of Ethyl isocyanoacetate.

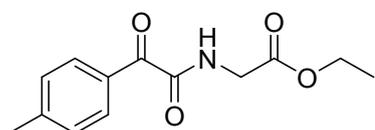


**Figure S8.** Stern-volmer plots.

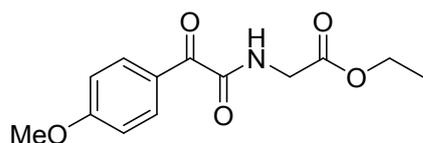
#### 4. Characterization data of products 3a- 3z'



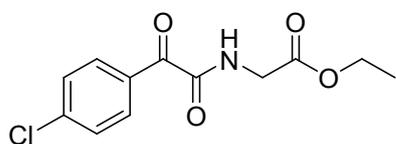
**ethyl 2-(2-oxo-2-phenylacetamido)acetate**<sup>[1]</sup>, Compound **3a** was obtained in 85 % yield (40.0 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm)  $\delta$  8.33 (d,  $J$  = 7.2 Hz, 2H), 7.64 (t,  $J$  = 7.4 Hz, 1H), 7.53 (s, 1H), 7.49 (t,  $J$  = 7.8 Hz, 2H), 4.27 (q,  $J$  = 7.2 Hz, 2H), 4.17 (d,  $J$  = 5.6 Hz, 2H), 1.32 (t,  $J$  = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  187.2, 169.3, 162.4, 133.7, 131.1, 130.2, 128.6, 61.8, 41.2, 14.1; MS (EI); [M+H]<sup>+</sup>: 236.1.



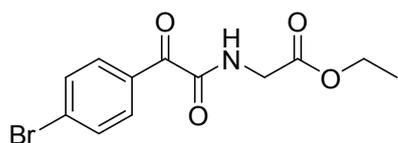
**ethyl 2-(2-oxo-2-p-tolylacetamido)acetate**, Compound **3b** was obtained in 80 % yield (39.8 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d,  $J$  = 8.0 Hz, 2H), 7.52 (s, 1H), 7.28 (d,  $J$  = 8.0 Hz, 2H), 4.27 (q,  $J$  = 7.1 Hz, 2H), 4.16 (d,  $J$  = 5.5 Hz, 2H), 2.43 (s, 3H), 1.32 (t,  $J$  = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm):  $\delta$  185.3, 167.9, 161.1, 144.8, 130.3, 129.6, 128.3, 60.8, 40.2, 20.9, 13.1; MS (EI); [M+H]<sup>+</sup>: 250.2.



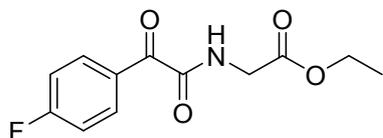
**ethyl 2-(2-(4-methoxyphenyl)-2-oxoacetamido)acetate**, Compound **3c** was obtained in 77 % yield (40.8 mg) according to the general procedure (0.2 mmol). White solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm):  $\delta$  8.32 (d,  $J$  = 9.0 Hz, 2H), 7.52 (s, 1H), 6.87 (d,  $J$  = 9.0 Hz, 2H), 4.18 (q,  $J$  = 7.1 Hz, 2H), 4.08 (d,  $J$  = 5.6 Hz, 2H), 3.82 (s, 3H), 1.24 (t,  $J$  = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm):  $\delta$  183.8, 168.0, 163.8, 161.4, 132.9, 125.2, 112.9, 60.7, 54.6, 40.2, 13.1; MS (EI); [M+H]<sup>+</sup>: 266.2.



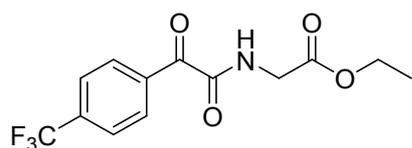
**ethyl 2-(2-(4-chlorophenyl)-2-oxoacetamido)acetate**, Compound **3d** was obtained in 70 % yield (37.7 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.33 (d,  $J = 8.4$  Hz, 2H), 7.57 (s, 1H), 7.46 (d,  $J = 8.5$  Hz, 2H), 4.27 (q,  $J = 7.1$  Hz, 2H), 4.16 (d,  $J = 5.5$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  185.4, 168.8, 161.4, 141.4, 132.7, 131.5, 129.0, 61.9, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 270.1.



**ethyl 2-(2-(4-bromophenyl)-2-oxoacetamido)acetate**, Compound **3e** was obtained in 77 % yield (48.4 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.24 (d,  $J = 8.4$  Hz, 2H), 7.63 (d,  $J = 8.4$  Hz, 2H), 7.58 (s, 1H), 4.27 (q,  $J = 7.1$  Hz, 2H), 4.16 (d,  $J = 5.5$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  185.7, 168.8, 161.4, 132.7, 132.0, 131.9, 130.3, 61.9, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 314.1.

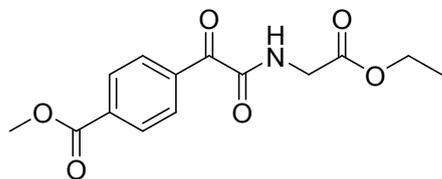


**ethyl 2-(2-(4-fluorophenyl)-2-oxoacetamido)acetate**, Compound **3f** was obtained in 72 % yield (36.4 mg) according to the general procedure (0.2 mmol). Yellow oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.48 – 8.39 (m, 2H), 7.61 (s, 1H), 7.17 – 7.14 (m, 2H), 4.27 (q,  $J = 7.1$  Hz, 2H), 4.16 (d,  $J = 5.6$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  184.97, 168.87, 168.31 (d,  $J = 256.25$  Hz), 161.66, 134.26 (d,  $J = 10.00$  Hz), 129.62 (d,  $J = 3.75$  Hz), 115.85 (d,  $J = 21.25$  Hz), 61.85, 41.25, 14.14; MS (EI);  $[\text{M}+\text{H}]^+$ : 254.1.

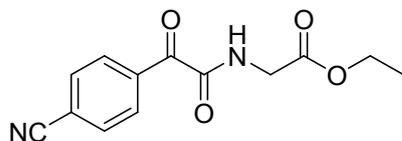


**ethyl 2-(2-oxo-2-(4-(trifluoromethyl)phenyl)acetamido)acetate**, Compound **3g** was obtained in 61 % yield (37.0 mg) according to the general procedure (0.2 mmol). Yellow oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.45 (d,  $J = 8.1$  Hz, 2H), 7.75 (d,  $J =$

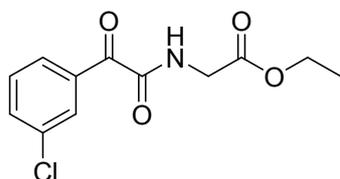
8.3 Hz, 2H), 7.61 (s, 1H), 4.28 (q,  $J = 7.1$  Hz, 2H), 4.18 (d,  $J = 5.6$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  185.84, 168.78, 161.00, 135.84, 135.44 (d,  $J = 32.5$  Hz), 131.54, 125.49 (q,  $J = 3.75$  Hz), 123.47 (q,  $J = 271.25$  Hz), 61.94, 41.28, 14.14; MS (EI);  $[\text{M}+\text{H}]^+$ : 304.1.



**methyl 4-(2-(2-ethoxy-2-oxoethylamino)-2-oxoacetyl)benzoate**, Compound **3h** was obtained in 65 % yield (38.1 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.39 (d,  $J = 8.3$  Hz, 2H), 8.13 (d,  $J = 8.3$  Hz, 2H), 7.56 (s, 1H), 4.28 (q,  $J = 7.1$  Hz, 2H), 4.17 (d,  $J = 5.5$  Hz, 2H), 3.96 (s, 3H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  186.3, 168.8, 166.1, 161.2, 136.4, 134.9, 131.1, 129.6, 61.9, 52.6, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 294.3.

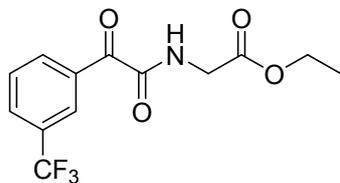


**ethyl 2-(2-(4-cyanophenyl)-2-oxoacetamido)acetate**, Compound **3i** was obtained in 70 % yield (36.4 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.45 (d,  $J = 8.1$  Hz, 2H), 7.79 (d,  $J = 8.1$  Hz, 2H), 7.58 (s, 1H), 4.28 (q,  $J = 7.1$  Hz, 2H), 4.17 (d,  $J = 5.5$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  185.4, 168.7, 160.7, 136.2, 132.2, 131.6, 117.8, 117.5, 62.0, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 261.2.

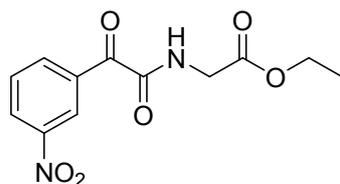


**ethyl 2-(2-(3-chlorophenyl)-2-oxoacetamido)acetate**, Compound **3j** was obtained in 60 % yield (32.3 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  7.71 (d,  $J = 8.2$  Hz, 1H), 7.56 – 7.43 (m, 3H), 7.39 (t,  $J = 7.2$  Hz, 1H), 4.29 (q,  $J = 7.1$  Hz, 2H), 4.19 (d,  $J = 5.5$  Hz, 2H), 1.34 (t,  $J = 7.1$

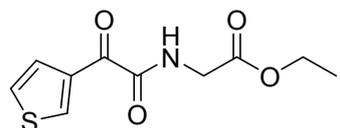
Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  189.1, 168.8, 160.8, 133.7, 133.2, 131.4, 130.5, 126.6, 122.8 61.9, 41.4, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 270.1.



**ethyl 2-(2-oxo-2-(3-(trifluoromethyl)phenyl)acetamido)acetate**, Compound **3k** was obtained in 60 % yield (36.4 mg) according to the general procedure (0.2 mmol). Yellow oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.64 (s, 1H), 8.57 (d,  $J = 7.9$  Hz, 1H), 7.89 (d,  $J = 7.8$  Hz, 1H), 7.64 (t,  $J = 7.9$  Hz, 1H), 7.60 (s, 1H), 4.28 (q,  $J = 7.1$  Hz, 2H), 4.18 (d,  $J = 5.6$  Hz, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  185.34, 168.75, 160.99, 134.44, 133.67, 131.24 (d,  $J = 32.5$  Hz), 130.79 (q,  $J = 2.5$  Hz), 129.20, 128.12 (q,  $J = 6.25$  Hz) 128.0 (d,  $J = 3.75$ Hz), 61.95, 41.27, 14.15; MS (EI);  $[\text{M}+\text{H}]^+$ : 304.2.

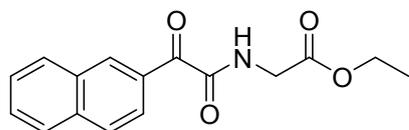


**ethyl 2-(2-(3-nitrophenyl)-2-oxoacetamido)acetate**, Compound **3l** was obtained in 50 % yield (28 mg) according to the general procedure (0.2 mmol). Yellow oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  9.14 (s, 1H), 8.65 (d,  $J = 7.8$  Hz, 1H), 8.41 (d,  $J = 8.1$  Hz, 1H), 7.64 (t,  $J = 7.9$  Hz, 1H), 7.55 (s, 1H), 4.21 (q,  $J = 7.1$  Hz, 2H), 4.12 (d,  $J = 5.5$  Hz, 2H), 1.26 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  184.5, 168.7, 160.6, 148.3, 136.8, 134.4, 129.8, 128.5, 126.2, 62.0, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 281.2.

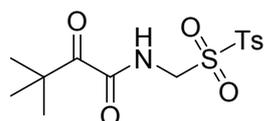


**ethyl 2-(2-oxo-2-(thiophen-3-yl)acetamido)acetate**, Compound **3m** was obtained in 68 % yield (32.8 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  9.09 (d,  $J = 1.9$  Hz, 1H), 7.79 (d,  $J = 4.8$  Hz, 1H), 7.70 (s, 1H), 7.32 (q,  $J = 2.9$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 4.15 (d,  $J = 5.6$  Hz,

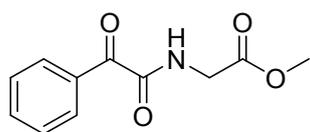
2H), 1.31 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  179.2, 168.9, 161.3, 139.6, 136.9, 128.6, 125.9, 61.8, 41.2, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 242.1



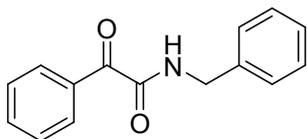
**ethyl 2-(2-(naphthalen-2-yl)-2-oxoacetamido)acetate**<sup>[1]</sup>, Compound **3n** was obtained in 78 % yield (44.5 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  9.16 (s, 1H), 8.19 (d,  $J = 8.7$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 1H), 7.88 (q,  $J = 8.5$  Hz, 2H), 7.72 – 7.60 (m, 2H), 7.56 (t,  $J = 7.5$  Hz, 1H), 4.28 (q,  $J = 7.1$  Hz, 2H), 4.21 (d,  $J = 5.5$  Hz, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  186.5, 169.0, 162.1, 136.2, 135.0, 132.4, 130.4, 129.4, 128.5, 127.8, 126.9, 125.2, 61.9, 41.3, 14.2; MS (EI);  $[\text{M}+\text{H}]^+$ : 286.3.



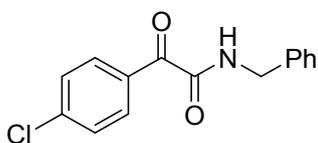
**3,3-dimethyl-2-oxo-N-(tosylsulfonylmethyl)butanamide**, Compound **3o** was obtained in 65 % yield (46.9 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  7.76 (d,  $J = 8.1$  Hz, 2H), 7.68 (s, 1H), 7.33 (d,  $J = 7.9$  Hz, 2H), 4.66 (d,  $J = 7.1$  Hz, 2H), 2.42 (s, 3H), 1.16 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  201.4, 158.3, 145.6, 133.3, 130.0, 129.1, 59.8, 42.9, 25.9, 21.7; MS (EI);  $[\text{M}+\text{H}]^+$ : 362.1



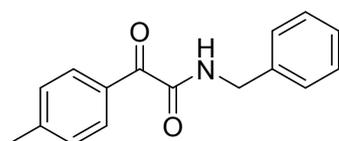
**methyl 2-(2-oxo-2-phenylacetamido)acetate**<sup>[3]</sup>, Compound **3p** was obtained in 81 % yield (35.8 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.33 (d,  $J = 8.3$ , 1H), 8.12 (d,  $J = 8.2$ , 1H), 7.66 – 7.57 (m, 2H), 7.48 (t,  $J = 6.6$  Hz, 2H), 4.19 (d,  $J = 5.6$  Hz, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  186.8, 169.4, 161.8, 134.6, 131.2, 130.2, 128.6, 52.6, 41.1; MS (EI);  $[\text{M}+\text{H}]^+$ : 222.2



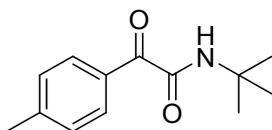
**N-benzyl-2-oxo-2-phenylacetamide**<sup>[1]</sup>, Compound **3q** was obtained in 73 % yield (34.9 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.36 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.29 (m, 6H), 4.57 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 187.58, 161.60, 137.13, 134.48, 133.33, 131.26, 128.87, 128.53, 127.91, 127.86, 43.51; MS (EI); [M+H]<sup>+</sup>: 240.1



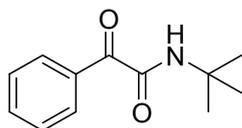
**N-benzyl-2-(4-chlorophenyl)-2-oxoacetamide**<sup>[1]</sup>, Compound **3r** was obtained in 68 % yield (37.1 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.36 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 3H), 7.40 – 7.28 (m, 5H), 4.56 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 186.1, 161.2, 141.3, 137.0, 132.8, 131.7, 128.9, 128.9, 127.9, 43.6, 29.5; MS (EI); [M+H]<sup>+</sup>: 274.1.



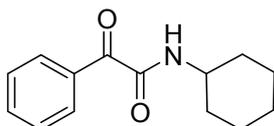
**N-benzyl-2-oxo-2-p-tolylacetamide**<sup>[1]</sup>, Compound **3s** was obtained in 80 % yield (40.5 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.28 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 13.3 Hz, 1H), 7.36 – 7.27 (m, 7H), 4.56 (d, *J* = 6.0 Hz, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 187.0, 161.8, 145.7, 137.2, 131.5, 130.9, 129.3, 128.9, 127.9, 127.8, 43.5, 21.9; MS (EI); [M+H]<sup>+</sup>: 254.4.



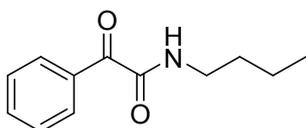
**N-tert-butyl-2-oxo-2-p-tolylacetamide**<sup>[5]</sup>, Compound **3t** was obtained in 77 % yield (33.7 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.23 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 1.8 Hz, 2H), 6.93 (s, 1H), 2.42 (s, 3H), 1.45 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 188.1, 161.4, 145.4, 131.4, 130.9, 129.2, 51.6, 28.4, 21.9; MS (EI); [M+H]<sup>+</sup>: 220.3.



**N-tert-butyl-2-oxo-2-phenylacetamide**<sup>[2]</sup>, Compound **3u** was obtained in 67 % yield (27.5 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.30 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.93 (s, 1H), 1.46 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 188.6, 161.1, 134.2, 133.4, 131.2, 128.4, 51.7, 28.4; MS (EI); [M+H]<sup>+</sup>: 206.2.

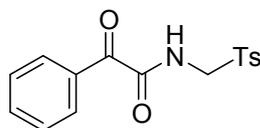


**N-cyclohexyl-2-oxo-2-phenylacetamide**<sup>[2]</sup>, Compound **3v** was obtained in 63 % yield (29.1 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.34 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 6.95 (s, 1H), 3.91 – 3.82 (m, 1H), 2.00 – 1.97 (m, 2H), 1.81 – 1.74 (m, 2H), 1.69 – 1.60 (m, 2H), 1.46 – 1.38 (m, 2H), 1.30 – 1.23 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 188.1, 182.4, 160.8, 134.3, 133.5, 131.2, 128.5, 48.5, 32.7, 25.4, 24.8; MS (EI); [M+H]<sup>+</sup>: 232.2

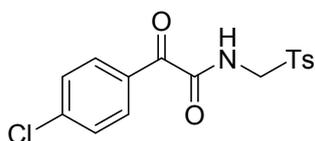


**N-butyl-2-oxo-2-phenylacetamide**<sup>[2]</sup>, Compound **3w** was obtained in 70 % yield (28.7 mg) according to the general procedure (0.2 mmol). Yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 8.39 – 8.31 (m, 2H), 7.65 – 7.60 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 13.4 Hz, 1H), 3.43 – 3.37 (m, 2H), 1.63 – 1.57 (m, 2H), 1.44 –

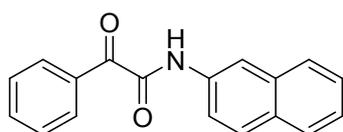
1.38 (m, 2H), 0.96 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  187.9, 161.7, 134.4, 133.4, 131.2, 128.5, 39.2, 31.4, 20.1, 13.7; MS (EI);  $[\text{M}+\text{H}]^+$ : 206.2



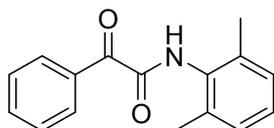
**2-oxo-2-phenyl-N-(tosylmethyl)acetamide**<sup>[4]</sup>, Compound **3x** was obtained in 65 % yield (41.2 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.07 (d,  $J = 7.7$  Hz, 2H), 7.81 (d,  $J = 8.1$  Hz, 3H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.8$  Hz, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H), 4.78 (d,  $J = 7.0$  Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  186.0, 160.8, 145.7, 134.9, 133.4, 132.5, 131.1, 130.1, 129.1, 128.6, 60.0, 21.7; MS (EI);  $[\text{M}+\text{H}]^+$ : 318.3.



**2-(4-chlorophenyl)-2-oxo-N-(tosylmethyl)acetamide**, Compound **3y** was obtained in 60 % yield (42.1 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  8.01 (d,  $J = 7.4$  Hz, 2H), 7.73 (d,  $J = 7.3$  Hz, 2H), 7.34 (d,  $J = 7.4$  Hz, 2H), 7.27 (d,  $J = 7.7$  Hz, 2H), 4.69 (d,  $J = 6.8$  Hz, 2H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  184.6, 160.4, 145.8, 141.9, 133.4, 132.6, 130.8, 130.1, 129.0, 129.0, 60.0, 21.8; MS (EI);  $[\text{M}+\text{H}]^+$ : 352.1.



**N-(naphthalen-2-yl)-2-oxo-2-phenylacetamide**<sup>[6]</sup>, Compound **3z** was obtained in 56 % yield (30.8 mg) according to the general procedure (0.2 mmol). Yellow solid,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta$  9.06 (s, 1H), 8.39 – 8.36 (m, 3H), 7.80 – 7.72 (m, 3H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.54 – 7.52 (m, 1H), 7.47 – 7.40 (m, 3H), 7.39 – 7.36 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm):  $\delta$  186.3, 158.0, 133.7, 133.0, 132.7, 132.1, 130.5, 130.1, 128.1, 127.6, 126.9, 126.6, 125.8, 124.5, 118.5, 116.1; MS (EI);  $[\text{M}+\text{H}]^+$ : 276.2.



**N-(2,6-dimethylphenyl)-2-oxo-2-phenylacetamide**<sup>[6]</sup>, Compound **3z'** was obtained in 76 % yield (38.5 mg) according to the general procedure (0.2 mmol). Yellow solid, <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm): δ 10.38 (s, 1H), 8.20 – 7.98 (m, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 1.7 Hz, 3H), 2.25 (s, 6H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz, ppm): δ 191.0, 164.3, 135.7, 135.3, 133.8, 133.2, 130.2, 129.7, 128.4, 127.7, 18.5; MS (EI); [M+H]<sup>+</sup>: 254.3.

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## 5. Copies of NMR Spectra for 3a-3z'

