Supplementary Information

Metal-free electrochemical synthesis of α-ketoamides via decarboxylative coupling of α-keto acids with isocyanides and water

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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. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ on a Bruker Avance III spectrometer with TMS as internal standard (500/400 MHz $^1$H, 125/400 MHz $^{13}$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). The instrument for electrolysis is dual-display potentiostat (DJS-292B) (made in China), the carbon rod (d: 6 mm), Pt (1.5 x 1.5 cm x 2 ) was purchased from Xuzhou Xinke Instrument and Meter Co. LTD.

2. **General procedure for electrochemical synthesis of $\alpha$-ketoamides from $\alpha$-oxocarboxylic acids, isocyanides and water.**

\[
\begin{align*}
\text{R}^1\text{COOH} + \text{NC-R}^2 & \rightarrow \text{CH}_3\text{CN/H}_2\text{O (5:1)} \\
\text{n-Bu}_4\text{NI} (0.5 eq), \text{rt, air} & \rightarrow \text{R}^1\text{O} - \text{N}\text{H}-\text{R}^2
\end{align*}
\]

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, $\alpha$ -oxocarboxylic acids 1 (0.2 mmol), isocyanide 2 (0.4 mmol), n-Bu$_4$NI (0.01 mmol) and CH$_3$CN/H$_2$O (5:1, 12 ml) were combined and added. The flask was equipped with graphite rod (d: 6.0 mm) anode and graphite rod cathode (distance between electrodes (5 - 10 mm)). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 5 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 (10:1) as eluent to give the desired
product 3.

3. Preliminary mechanistic studies

3.1 The reaction of 1a and 2a was carried out in the absence of H₂O.

\[
\begin{align*}
1a & \quad 2a \\
\text{OH} & \quad \text{CN-COOEt} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, α-oxocarboxylic acid 1 (0.2 mmol), isocyanide 2 (0.4 mmol), n-Bu₄NI (0.01 mmol), 4Å Ms and CH₃CN (10 mL) were combined and added. The flask was equipped with graphite rod (d: 6.0 mm) anode and graphite rod cathode (distance between electrodes (5 - 10 mm)). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 5 h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of the desired product 3a was detected.

3.2 The reaction of 1a and 2a was carried out under H₂O¹⁸.

\[
\begin{align*}
1a & \quad 2a \\
\text{O} & \quad \text{CN-COOEt} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, α-oxocarboxylic acid 1a (0.2 mmol), isocyanide 2a (0.4 mmol), n-Bu₄NI (0.01 mmol), CH₃CN/H₂O¹⁸ (5:1, 12 ml) were combined and added. The flask was equipped with graphite rod (d: 6.0 mm) anode and graphite rod cathode (distance between electrodes (5 - 10 mm)). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 5 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 ¹⁸O-3a (33.1mg, 70%).
3.3 The reaction of 1a and 2a in the presence of I₂.

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{COOH} & \quad + \quad \text{CNCOOEt} \\
1a & \quad \quad 2a \\
\text{I}_2 (2 \text{eq}) , \quad \text{CH}_3\text{CN/H}_2\text{O (5:1)} \\
\text{rt}, \text{air} & \quad \quad \rightarrow \\
\text{C}_{6}\text{H}_{5}\text{COO} & \quad \quad \text{CONH} \\
3a \text{ (trace)} & \quad \quad \\
\end{align*}
\]

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, α-oxocarboxylic acid 1a (0.2 mmol), isocyanide 2a (0.4 mmol), I₂ (0.4 mmol), CH₃CN/H₂O (5:1, 2.4 ml) were combined and added. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. Only a trace amount of product 3a was detected.

3.4 The reaction of 1a and 2a in the presence of NIS.

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{COOH} & \quad + \quad \text{CNCOOEt} \\
1a & \quad \quad 2a \\
\text{NIS (2 eq)} , \quad \text{CH}_3\text{CN/H}_2\text{O (5:1)} \\
\text{rt}, \text{air} & \quad \quad \rightarrow \\
\text{C}_{6}\text{H}_{5}\text{COO} & \quad \quad \text{CONH} \\
3a \text{ (51%)} & \quad \quad \\
\end{align*}
\]

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, α-oxocarboxylic acid 1a (0.2 mmol), isocyanide 2a (0.4 mmol), NIS (0.4 mmol), CH₃CN/H₂O (5:1, 2.4 ml) were combined and added. The reaction mixture was stirred at room temperature for 24 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 3a (23.8mg, 51%).

3.5 Cyclic voltammetry (CV) tests

![Graph](image-url)

**Figure S1.** Conditions: glass carbon as work electrode, Pt plate (1.5 x 1.5 cm²) as counter electrode Ag/AgCl (KCl) as reference electrode in 0.1 M LiClO₄ with different solvent under 1a (0.2 mM), the mixed solvent of CH₃CN/H₂O, scan rate: 100 mV s⁻¹.

![Graph](image-url)

**Figure S2.** Conditions: glass carbon as work electrode, Pt plate (1.5 x 1.5 cm²) as counter electrode and Ag/AgCl (KCl) as reference electrode in 0.1 M LiClO₄ at 100 mV s⁻¹: (I) 0.1 mM of n-Bu₄NI, anhydrous CH₃CN, (II) 0.2 mM of PhCOOH, CH₃CN/H₂O (5 : 1) and (III) 0.2 mM of PhCOOH, anhydrous CH₃CN.
Figure S3. Cyclic voltammograms of 0.2 mM PhCOCOOH in 0.1 M LiClO₄ in (a) CH₃CN/H₂O (5 : 1), and (b) anhydrous CH₃CN using glass carbon as the working electrode, Pt plate (1.5 x 1.5 cm²) and Ag/AgCl (KCl) as the counter and reference electrodes at 100 mV s⁻¹.

4. Characterization data of products 3a – 3u

**ethyl (2-oxo-2-phenylacetyl)glycinate**

Compound 3a was obtained in 78% yield (36.7 mg) according to the general procedure (petroleum ether/EtOAc, 10:1). Yellow oil. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.32 (d, J = 8.3 Hz, 2H), 7.64 - 7.60 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.17 (d, J = 5.6 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 186.9, 169.0, 161.9, 134.5, 133.1, 131.2, 128.5, 61.8, 41.2, 14.1; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₂H₁₄NO₄ 236.0923; found 236.0856.

**ethyl (2-oxo-2-(p-tolyl)acetyl)glycinate**

Compound 3b was obtained in 71% yield (35.4 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). Yellow solid. mp = 80.7 - 81.2 °C; ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.25 (d, J = 8.3 Hz, 2H), 7.56 (s, 1H), 7.28 (d, J = 8.3 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.16 (d, J = 5.6 Hz, 2H), 2.42 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 186.4, 169.0, 162.1, 145.8, 131.4, 130.7, 129.3, 61.8,
ethyl (2-oxo-2-(o-tolyl)acetyl)glycinate

Compound 3c was obtained in 64% yield (31.9 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.93 - 7.91 (m, 1H), 7.54 (s, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.30 - 7.27 (m, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 4.16 (d, $J = 5.6$ Hz, 2H), 2.51 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): δ 190.4, 169.0, 162.3, 140.3, 132.9, 132.5, 132.1, 131.7, 125.4, 61.8, 41.4, 20.9, 14.2; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{16}$NO$_4$ 250.1079; found 250.0975.

ethyl (2-(3,4-dimethylphenyl)-2-oxoacetyl)glycinate

Compound 3d was obtained in 76% yield (39.8 mg) according to the general procedure (petroleum ether/EtOAc, 10:1). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.10 - 8.08 (m, 2H), 7.56 (s, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.16 (d, $J = 5.6$ Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): δ 186.7, 169.0, 162.3, 144.6, 137.0, 132.0, 131.0, 129.1, 129.9, 129.9, 61.8, 41.2, 20.3, 19.7, 14.2; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{16}$NO$_5$ 264.1236; found 264.1185.

ethyl (2-(4-methoxyphenyl)-2-oxoacetyl)glycinate

Compound 3e was obtained in 75% yield (39.7 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). Yellow solid. mp = 99.7 - 100.2 ºC; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 8.39 (d, $J = 8.8$ Hz, 2H), 7.61 (s, 1H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.26
(q, J = 7.1 Hz, 2H), 4.15 (d, J = 5.6 Hz, 2H), 3.88 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 184.9, 169.0, 164.8, 162.5, 133.9, 126.2, 113.9, 61.7, 55.6, 41.2, 14.1; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₂H₁₄NO₄ 266.1028; found 266.0972.

**ethyl (2-(3,4-dimethoxyphenyl)-2-oxoacetyl)glycinate**

Compound 3f was obtained in 60% yield (35.4 mg) according to the general procedure (petroleum ether/EtOAc, 3:1). Yellow solid. mp = 81.5 - 81.9 °C; ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.24 - 8.21 (m, 1H), 7.85 (d, J = 1.9 Hz, 1H), 7.60 (s, 1H), 6.92 (d, J = 8.6 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.16 (d, J = 5.6 Hz, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 1.31 (t, J = 7.4 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 184.7, 169.0, 162.4, 154.8, 148.9, 127.4, 126.2, 112.5, 110.2, 61.8, 56.2, 56.0, 41.2, 14.2; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₄H₁₈NO₆ 296.1134; found 296.1083.

**ethyl (2-(4-fluorophenyl)-2-oxoacetyl)glycinate**

Compound 3g was obtained in 66% yield (33.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1). Yellow oil. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.44 - 8.41 (m, 2H), 7.64 (s, 1H), 7.17 - 7.14 (m, 2H), 4.29 - 4.24 (m, 2H), 4.16 (d, J = 5.7 Hz, 2H), 1.33 - 1.30 (m, 3H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 185.0, 168.9, 166.7 (d, J = 256.4 Hz), 134.2 (d, J = 9.6 Hz), 129.6 (d, J = 2.9 Hz), 115.8 (d, J = 21.8 Hz), 61.8, 41.2, 14.1; ¹⁹F NMR (CDCl₃, 500 MHz): -101.9; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₁H₁₃FNO₄ 254.0829; found 254.0765.

**ethyl (2-(3-fluorophenyl)-2-oxoacetyl)glycinate**

Compound 3h was obtained in 62% yield (31.3 mg) according to the general procedure
(C/Pt, petroleum ether/EtOAc, 10:1). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$
8.17 (d, $J = 7.8$ Hz, 1H), 8.06 - 8.04 (m, 1H), 7.59 (s, 1H), 7.49 - 7.45 (m, 1H), 7.36 -
7.32 (m, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.17 (d, $J = 5.6$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz,
3H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 185.5, 168.8, 162.4 (d, $J = 246.2$ Hz),
161.3, 134.9 (d, $J = 7.0$ Hz), 130.2 (d, $J = 7.5$ Hz), 127.1 (d, $J = 3.3$ Hz), 121.6 (d, $J =$
21.3 Hz), 117.8 (d, $J = 23.1$ Hz), 61.9, 41.3, 14.1; $^{19}$F NMR (CDCl$_3$, 500 MHz): -111.5;
MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$FNO$_2$ 254.0829; found 254.0766.

**ethyl (2-(4-chlorophenyl)-2-oxoacetyl)glycinate**

Compound 3i was obtained in 70% yield (37.8 mg) according to the general procedure
(petroleum ether/EtOAc, 10:1). Yellow solid. mp = 51.8 - 52.2 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm):
$\delta$ 8.34 - 8.30 (m, 2H), 7.60 (s, 1H), 7.47 - 7.43 (m, 2H), 4.26 (q, $J =$
7.1 Hz, 2H), 4.16 (d, $J = 5.6$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm):
$\delta$ 185.4, 168.8, 161.5, 141.3, 132.7, 131.5, 128.9, 61.9, 41.2, 14.2; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$ClNO$_4$ 270.0533; found 270.0475.

**ethyl (2-(4-bromophenyl)-2-oxoacetyl)glycinate**

Compound 3j was obtained in 62% yield (28.3 mg) according to the general procedure
(petroleum ether/EtOAc, 10:1). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 8.23
(m, $J = 8.6$ Hz, 2H), 7.64 - 7.62 (m, 3H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.15 (d, $J = 5.6$ Hz,
2H), 1.31 (t, $J = 7.2$ Hz, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 185.7, 168.9,
161.4, 132.7, 131.9, 131.9, 130.3, 61.9, 41.2, 14.2; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$BrNO$_4$ 314.0028; found 313.9967.

**ethyl (2-oxo-2-(3-(trifluoromethyl)phenyl)acetyl)glycinate**
Compound 3k was obtained in 63% yield (38.1 mg) according to the general procedure (C/Pt, petroleum ether/EtOAc, 10:1). Yellow solid. mp = 50.8 - 51.0 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 8.63 (s, 1H), 8.56 (d, $J$ = 7.7 Hz, 1H), 7.88 (t, $J$ = 7.8 Hz, 1H), 7.65 - 7.62 (m, 2H), 4.27 (q, $J$ = 7.1 Hz, 2H), 4.18 (d, $J$ = 5.6 Hz, 2H), 1.32 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 185.4, 168.8, 161.1, 134.4, 133.7, 131.2 (d, $J$ = 33.0 Hz), 130.8 (q, $J$ = 3.6 Hz), 129.2, 128.1 (q, $J$ = 3.8 Hz), 123.5 (d, $J$ = 270.9 Hz), 61.9, 41.3, 14.1; $^{19}$F NMR (CDCl$_3$, 500 MHz): -62.9; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{13}$F$_3$NO$_4$ 304.0797; found 304.0745.

![ethyl (2-(4-(methylsulfonyl)phenyl)-2-oxoacetyl)glycinate](image)

Compound 3l was obtained in 70% yield (43.7 mg) according to the general procedure (petroleum ether/EtOAc, 1:1). Yellow solid. mp = 112.1 - 112.5 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.98 - 7.97 (m, 4H), 7.11 (s, 1H), 4.29 - 4.23 (m, 4H), 3.08 (s, 3H), 1.32 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 169.8, 165.9, 143.1, 138.7, 128.3, 127.7, 61.8, 44.3, 41.9, 14.2; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{16}$NO$_6$S 314.0698; found 314.0665.

![ethyl (2-(4-nitrophenyl)-2-oxoacetyl)glycinate](image)

Compound 3m was obtained in 41% yield (22.9 mg) according to the general procedure (petroleum ether/EtOAc, 10:1). Yellow solid. mp = 71.2 - 71.5 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 9.19 - 9.18 (m, 1H), 8.71 - 8.69 (m, 1H), 8.49 - 8.47 (m, 1H), 7.72 - 7.69 (m, 2H), 4.28 (q, $J$ = 7.2 Hz, 2H), 4.19 (d, $J$ = 5.7 Hz, 2H), 1.33 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 184.6, 168.7, 160.7, 148.2, 136.8, 134.3, 129.8, 128.5, 126.1, 62.0, 41.3, 14.1; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{13}$N$_2$O$_6$ 281.0774; found 281.0709.
3-methyl-2-oxo-N-(tosylmethyl)pentanamide

Compound 3n was obtained in 47% yield (27.8 mg) according to the general procedure (C/Pt, petroleum ether/EtOAc, 10:1). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.76 (d, $J = 8.2$ Hz, 2H), 7.72 (s, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 4.74 - 4.64 (m, 2H), 3.25 - 3.18 (m, 1H), 2.43 (s, 3H), 1.62 - 1.53 (m, 1H), 1.33 - 1.25 (m, 1H), 0.98 (d, $J = 7.0$ Hz, 3H), 0.81 (t, $J = 7.5$ Hz, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 200.3, 159.0, 145.7, 133.4, 130.0, 129.0, 60.0, 40.6, 25.2, 21.7, 14.8, 11.4; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{20}$NO$_4$S 298.1113; found 298.1052.

2-oxo-2-(p-tolyl)-N-(tosylmethyl)acetamide

Compound 3o was obtained in 71% yield (47.1 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). Yellow solid. mp = 96.9 - 97.0 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.97 - 7.95 (m, 3H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.9$ Hz, 2H), 4.78 (d, $J = 7.0$ Hz, 2H), 2.41 (d, $J = 7.3$ Hz, 6H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 185.6, 161.2, 146.3, 145.6, 133.5, 131.2, 130.1, 130.1, 129.3, 129.1, 60.1, 21.9, 21.7; MS (ESI) m/z: [M + H]$^+$ Calcd for C$_{17}$H$_{18}$NO$_4$S 332.0957; found 332.0903.

2-oxo-2-phenyl-N-(tosylmethyl)acetamide

Compound 3p was obtained in 72% yield (45.5 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). White solid. mp = 99.0 - 99.4 °C; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.99 - 7.97 (m, 2H), 7.81 (s, 1H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.37 - 7.34 (m, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 4.71 (d, $J = 7.0$ Hz, 2H), 2.35 (s, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 186.1, 160.8, 145.7, 134.9, 133.4, 132.5, 131.1, 130.1,
129.1, 128.6, 60.0, 21.7; MS (ESI) m/z: \([M + H]^+\) Calcd for \(C_{16}H_{16}NO_4S\) 318.0800; found 318.0744.

![methyl (2-oxo-2-phenylacetyl)glycinate](image)

**methyl (2-oxo-2-phenylacetyl)glycinate**

Compound 3q was obtained in 68% yield (30.1 mg) according to the general procedure (petroleum ether/EtOAc, 5:1). Yellow oil. \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 8.34 - 8.33 (m, 2H), 7.64 (t, \(J = 7.5\) Hz, 1H), 7.55 (s, 1H), 7.47 (t, \(J = 7.8\) Hz, 2H), 4.19 (d, \(J = 5.6\) Hz, 2H), 3.81 (s, 3H); \(^{13}\)C\(_{\{^1\}H}\) NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 186.8, 169.4, 161.8, 134.6, 133.1, 131.2, 128.6, 52.6, 41.1; MS (ESI) m/z: \([M + H]^+\) Calcd for \(C_{16}H_{16}NO_4S\) 318.0744; found 318.0744.

![N-cyclohexyl-2-oxo-2-phenylacetamide](image)

**N-cyclohexyl-2-oxo-2-phenylacetamide**

Compound 3r was obtained in 55% yield (25.4 mg) according to the general procedure (C/Pt, petroleum ether/EtOAc, 10:1). Yellow solid. mp = 104.8 - 105.1 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 8.33 (d, \(J = 8.2\) Hz, 2H), 7.61 (t, \(J = 7.4\) Hz, 1H), 7.47 (t, \(J = 7.7\) Hz, 2H), 6.97 (s, 1H), 3.88 - 3.83 (m, 1H), 1.99 (d, \(J = 11.9\) Hz, 2H), 1.78 - 1.75 (m, 2H), 1.67 - 1.64 (m, 1H), 1.45 - 1.38 (m, 2H), 1.31 - 1.19 (m, 3H); \(^{13}\)C\(_{\{^1\}H}\) NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 188.1, 160.9, 134.3, 133.5, 131.2, 128.5, 48.5, 32.7, 25.4, 24.8; MS (ESI) m/z: \([M + H]^+\) Calcd for \(C_{14}H_{18}NO_2\) 232.1338; found 232.1286.

![N-benzyl-2-oxo-2-phenylacetamide](image)

**N-benzyl-2-oxo-2-phenylacetamide**

Compound 3s was obtained in 86% yield (41.2 mg) according to the general procedure (petroleum ether/EtOAc, 15:1). Yellow solid. mp = 95.2 - 95.6 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 8.36 - 8.34 (m, 2H), 7.64 - 7.60 (m, 1H), 7.49 - 7.46 (m, 2H), 7.43(s, 1H), 7.37 - 7.28 (m, 5H), 4.57 (d, \(J = 6.1\) Hz, 2H); \(^{13}\)C\(_{\{^1\}H}\) NMR (CDCl\(_3\), 125 MHz,
ppm): δ 187.6, 161.6, 137.2, 134.5, 133.3, 131.3, 128.9, 128.5, 127.9, 127.9, 43.5; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₅H₁₄NO₂ 240.1025; found 240.0951.

N-butyl-2-oxo-2-phenylacetamide

Compound 3u was obtained in 71% yield (29.1 mg) according to the general procedure (petroleum ether/EtOAc, 15:1). Yellow oil. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.34 - 8.32 (m, 2H), 7.64 - 7.60 (m, 1H), 7.49 - 7.45 (m, 2H), 7.14 - 7.11 (m, 1H), 3.40 (q, J = 6.9 Hz, 2H), 1.63 - 1.56 (m, 2H), 1.46 - 1.36 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H); ¹³C {¹H} NMR (CDCl₃, 125 MHz, ppm): δ 187.9, 161.8, 134.3, 133.4, 131.2, 128.5, 39.2, 31.3, 20.1, 13.7; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₂H₁₆NO₂ 206.1181; found 206.1112.

N-(2,6-dimethylphenyl)-2-oxo-2-phenylacetamide

Compound 3t was obtained in 70% yield (35.4 mg) according to the general procedure (petroleum ether/EtOAc, 15:1). Yellow solid. mp = 111.0 - 111.3 °C; ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.41 - 8.40 (m, 3H), 7.65 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.18 - 7.11 (m, 3H), 2.29 (s, 6H); ¹³C {¹H} NMR (CDCl₃, 125 MHz, ppm): δ 187.7, 159.9, 135.2, 134.7, 133.2, 132.5, 131.4, 128.7, 128.4, 127.8, 18.5; MS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₆NO₂ 254.1181; found 254.1123.

5. Copies of NMR Spectra for 3a–3u