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# Supporting information

#### Hydrogen-Bonding-Controlled Stereospecific Synthesis of Z-Enamides

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#### 1. General information

All reagents were purchased from commercial suppliers and used without further purification. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm Merck silica gel precoated plates (60F-254). Visualization was accomplished by irradiation with UV light at 254 nm. Flash column chromatography was performed using Merck silica gel 60 (particle size 0.040–0.063 mm).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, on a Bruker Ascend 400 (400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C). Chemical shifts were reported in ppm from tetramethylsilane with solvent resonance as the internal standard (CDCl<sub>3</sub>,  $\delta = 7.26$  ppm). Spectra were reported as follows: chemical shifts ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration and assignment. <sup>13</sup>C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>,  $\delta = 77.0$ ). Mass spectra were recorded on a Waters Vion IMS QTof system equipped with an ESI source.

#### 2. Preparation of starting materials

DCM (3 ml) and sat. NaHCO<sub>3</sub> (6 mL) were stirred vigorously and chilled in an ice bath. Acyl chloride (2.6 mmol, 1.3 equiv.) was added, followed immediately by 2aminoacetophenone hydrochloride (2 mmol). Stirring was continued while warming to room temperature over a period of 2 h. The mixture was extracted with DCM (3\*5 mL), the combined organic layers washed with sat. NaCl (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure produced the crude product that could be purified if necessary by silica gel chromatography or crystallization.



# 3. General Synthetic Procedures

Table S1. Screening the reaction conditions<sup>a</sup>

	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} $	O Base Solvent	→	
Entry	Base	Solvent	Temp. (°C)	Yield (%)
1	Et <sub>3</sub> N	DCM	r.t.	87
2	DBU	DCM	r.t.	25
3	pyridine	DCM	r.t.	N.R.
4	DMAP	DCM	r.t.	8
5	DIPEA	DCM	r.t.	N.R.
6	DBACO	DCM	r.t.	67
7	TEMED	DCM	r.t.	51
8	DIPA	DCM	r.t.	34
9	$K_2CO_3$	DCM	r.t.	N.R.
10	$Cs_2CO_3$	DCM	r.t.	N.R.
11	NaHCO <sub>3</sub>	DCM	r.t.	N.R.
12	NaOH	DCM	r.t.	N.R.
13	Et <sub>3</sub> N	DCE	r.t.	93
14	Et <sub>3</sub> N	CDCl <sub>3</sub>	r.t.	64

15	Et <sub>3</sub> N	MeCN	r.t.	69
16	Et <sub>3</sub> N	DMF	r.t.	53
17	Et <sub>3</sub> N	toluene	r.t.	44
18	Et <sub>3</sub> N	1,4-Dioxane	r.t.	31
19	Et <sub>3</sub> N	THF	r.t.	38
20	Et <sub>3</sub> N	CH <sub>3</sub> COCH <sub>3</sub>	r.t.	45
21	Et <sub>3</sub> N	$H_2O$	r.t.	N.R.
22	Et <sub>3</sub> N	DCE	10	73
23	Et <sub>3</sub> N	DCE	40	65
24	Et <sub>3</sub> N	DCE	55	68
25	Et <sub>3</sub> N	DCE	70	73
26	Et <sub>3</sub> N	DCE	83	57

<sup>a</sup> Reaction conditions: 1a (0.2 mmol), 2a (0.2 mmol), base (0.2eq.), solvent (2 mL) for 16h.

#### **Discussion of Non-reactive Substrates**

To provide additional insights into the substrate scope and limitations of this methodology, we replaced the substrate N-phenacylbenzamide with the three compounds shown in the **Figure S1** under standard reaction conditions. In all cases, the target product was not obtained. Specifically, when using phenylacetone (**Figure S1**, 1) or when a phenyl group was introduced at the  $\beta$ -position (**Figure S1**, 3), no reaction occurred. When a methoxy group was introduced at the  $\beta$ -position (**Figure S1**, 2), the reaction system became too complex to identify the main product. Comprehensive analysis confirms that the highly reactive amino group is critically important for both this reaction and our primary research objective - the synthesis of *Z*-enamides.



Figure S1: β-position substrates exploration

Next, We have explore the reactivity of butynes with one ester group constant and the other EWG varied, as well as butynes with both EWGs replaced by groups other than ester. However, despite our efforts, these attempts did not yield the desired products under the current reaction conditions (as shown in **Figure S2**). When one ester group was replaced with another EWG (e.g., trifluoromethyl group, methyl propiolate), the reaction did not proceed as expected, and the target product was not obtained. Similarly, when both ester groups were replaced with other EWGs (e.g., benzoyl group), the reaction failed to generate the anticipated products. We believe that these results may be attributed to the unique electronic and steric properties of the ester group, which play a crucial role in facilitating the reaction.



Figure S2: Butynes having different EWGs

#### General procedure for the preparation of products



In a dried test tube equipped with a magnetic stirrer, N-phenacylbenzamide (0.2 mmol, 1 eq) and 2 mL of 1,2-dichloroethane were added, followed by dimethyl butynedioate (0.3 mmol, 1.5 eq) and triethylamine (0.04 mmol, 0.2 eq). The mixture was stirred at room temperature in air for 16 hours. After completion, the reaction was monitored by TLC, and the reaction mixture was concentrated under vacuum. The desired products 3a-3q were obtained through column chromatography (petroleum ether (PE)/ethyl acetate (EA) = 8:1).



**Dimethyl (Z)-2-(1-benzamido-2-oxo-2-phenylethylidene) succinate (3a)** White powder (70.90 mg, yield: 93%). PE/EA = 8:1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.48 (s, 1H), 8.01 – 7.97 (m, 2H), 7.93 – 7.88 (m, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.43 (m, 4H), 3.85 (s, 3H), 3.54 (s, 3H), 3.16 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.73, 171.10, 169.84, 163.95, 149.26, 135.70, 133.95, 133.23, 131.44, 129.05, 128.98, 128.85, 128.08, 102.72, 52.69, 52.13, 32.64. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>6</sub>Na<sup>+</sup>: 404.1105; found: 404.1113



**Dimethyl (Z)-2-(1-(3-fluorobenzamido)-2-oxo-2-phenylethylidene) succinate (3b)** White powder (65.50 mg, yield: 82%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 – 7.95 (m, 2H), 7.71 – 7.66 (m, 1H), 7.62 – 7.54 (m, 2H), 7.50 – 7.42 (m, 3H), 7.30 – 7.22 (m, 1H), 3.85 (d, J = 1.0 Hz, 3H), 3.55 (d, J = 1.0 Hz, 3H), 3.16 (s, 2H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.54, 170.98, 169.81, 162.75 (d,  $J_{C-F} = 2.3$  Hz), 161.69, 148.91, 135.59, 134.08, 133.80 (d,  $J_{C-F} = 7.1$  Hz), 130.76 (d,  $J_{C-F} = 7.7$  Hz), 128.94 (d,  $J_{C-F} = 16.7$  Hz), 123.40, 120.30 (d,  $J_{C-F} = 21.2$  Hz), 115.50 (d,  $J_{C-F} = 23.3$  Hz), 103.35, 52.79, 52.16, 32.62.

<sup>19</sup>**F NMR** (377 MHz, CDCl<sub>3</sub>) δ -110.67 – -110.80 (m).

HRMS (ESI) m/z: [M+K]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>FNO<sub>6</sub>K<sup>+</sup>: 438.0750; found: 438.0717



**Dimethyl (Z)-2-(1-(4-fluorobenzamido)-2-oxo-2-phenylethylidene) succinate (3c)** White powder (68.70 mg, yield: 86%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.48 (s, 1H), 8.01 – 7.96 (m, 2H), 7.95 – 7.89 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.17 – 7.10 (m, 2H), 3.84 (d, J = 0.7 Hz, 3H), 3.54 (d, J = 0.7 Hz, 3H), 3.15 (s, 2H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.63, 171.02, 169.92, 165.78 (d,  $J_{C-F} = 254.9$  Hz), 162.85, 149.19, 135.63, 134.02, 130.64 (d,  $J_{C-F} = 9.4$  Hz), 128.93 (d,  $J_{C-F} = 16.4$  Hz), 127.72 (d,  $J_{C-F} = 3.0$  Hz), 116.25 (d,  $J_{C-F} = 22.1$  Hz), 102.86, 52.74, 52.14, 32.60.

<sup>19</sup>**F NMR** (377 MHz, CDCl<sub>3</sub>) δ -104.81 – -104.94 (m).

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>FNO<sub>6</sub>Na<sup>+</sup>: 422.1010; found: 422.1020



**Dimethyl (Z)-2-(1-(4-chlorobenzamido)-2-oxo-2-phenylethylidene) succinate (3d)** White powder (55.80 mg, yield: 67%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.49 (s, 1H), 8.01 – 7.94 (m, 2H), 7.86 – 7.81 (m, 2H), 7.57 (s, 1H), 7.51 – 7.40 (m, 4H), 3.85 (d, J = 0.7 Hz, 3H), 3.54 (d, J = 0.7 Hz, 3H), 3.16 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.56, 170.98, 169.87, 162.92, 149.02, 139.66, 135.60, 134.06, 129.89, 129.51, 129.45, 129.36, 129.26, 129.02, 128.84, 128.07, 103.10, 82.82, 53.00, 52.77, 52.15, 50.81, 32.60.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>ClNO<sub>6</sub>Na<sup>+</sup>: 438.0715; found: 438.0724



Dimethyl (Z)-2-(1-(4-bromobenzamido)-2-oxo-2-phenylethylidene) succinate (3e) White powder (66.30 mg, yield: 72%). PE/EA = 6:1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.49 (s, 1H), 8.00 – 7.94 (m, 2H), 7.78 – 7.73 (m, 2H), 7.62 – 7.53 (m, 3H), 7.47 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 3.54 (s, 3H), 3.15 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.57, 170.99, 169.87, 163.08, 149.01, 135.59, 134.07, 132.35, 130.35, 129.57, 129.03, 128.85, 128.32, 103.14, 52.78, 52.16, 32.61, 29.80. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>BrNO<sub>6</sub>Na<sup>+</sup>: 482.0210; found: 482.0219



**Dimethyl (Z)-2-(1-(3-bromobenzamido)-2-oxo-2-phenylethylidene) succinate (3f)** Colorless oil (75.20 mg, yield: 82%). PE/EA = 5:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03 (t, J = 1.9 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.80 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.67 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 7.34 (t, J = 7.9 Hz, 1H), 3.85 (s, 3H), 3.54 (s, 3H), 3.16 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.45, 170.94, 169.76, 162.58, 148.82, 136.11, 135.60, 134.04, 133.45, 131.56, 130.50, 129.01, 128.82, 126.13, 123.31, 103.50, 52.80, 52.14, 32.63. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>BrNO<sub>6</sub>Na<sup>+</sup>: 482.0210; found: 482.0215



**Dimethyl (Z)-2-(1-(4-methylbenzamido)-2-oxo-2-phenylethylidene) succinate (3g)** White powder (63.20 mg, yield: 80%). PE/EA = 4:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.42 (s, 1H), 8.01 – 7.95 (m, 2H), 7.82 – 7.76 (m, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.28 – 7.23 (m, 3H), 3.84 (s, 3H), 3.54 (s, 3H), 3.15 (s, 2H), 2.39 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.75, 171.12, 169.83, 163.89, 149.41, 144.05, 135.75, 133.86, 129.71, 128.94, 128.81, 128.62, 128.12, 102.33, 52.62, 52.08, 32.63, 21.74.
HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>22</sub>H<sub>21</sub>NO<sub>6</sub>Na<sup>+</sup>: 418.1262; found: 418.1267



# Dimethyl (Z)-2-(1-(4-(chloromethyl) benzamido)-2-oxo-2-phenylethylidene) succinate (3h)

White powder (75.60 mg, yield: 88%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.95 (m, 2H), 7.90 – 7.85 (m, 2H), 7.54 (d, J = 7.4 Hz, 1H), 7.49 – 7.43 (m, 4H), 4.57 (s, 2H), 3.84 (s, 3H), 3.53 (s, 3H), 3.16 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.62, 171.03, 169.84, 163.35, 149.10, 142.60, 135.66, 134.00, 131.39, 129.13, 129.00, 128.84, 128.59, 128.51, 103.01, 52.73, 52.13, 45.26, 32.62. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>22</sub>H<sub>20</sub>ClNO<sub>6</sub>Na<sup>+</sup>: 452.0871; found: 452.0881



**Dimethyl (Z)-2-(2-oxo-2-phenyl-1-(thiophene-2-carboxamido) ethylidene) succinate (3i)** White powder (71.30 mg, yield: 92%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.36 (s, 1H), 8.00 – 7.95 (m, 2H), 7.73 (d, J = 1.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.47 (t, J = 7.0 Hz, 2H), 7.14 – 7.10 (m, 1H), 3.84 (s, 3H), 3.54 (s, 3H), 3.14 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.42, 171.04, 169.77, 158.70, 148.94, 136.59, 135.61, 134.01, 133.18, 130.84, 128.98, 128.93, 128.32, 102.36, 52.68, 52.11, 32.59.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>6</sub>SNa<sup>+</sup>: 410.0669; found: 410.0676



**Dimethyl (Z)-2-(1-(furan-2-carboxamido)-2-oxo-2-phenylethylidene) succinate (3j)** White powder (63.80 mg, yield: 86%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.32 (s, 1H), 8.00 – 7.94 (m, 2H), 7.61 – 7.52 (m, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.14 (s, 1H), 6.51 (dd, J = 3.6, 1.7 Hz, 1H), 3.85 (d, J = 0.7 Hz, 3H), 3.54 (d, J = 0.6 Hz, 3H), 3.15 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.48, 171.02, 169.37, 154.92, 148.15, 146.07, 135.64, 133.98, 128.97, 128.87, 117.86, 112.94, 102.97, 52.66, 52.10, 32.66.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>7</sub>Na<sup>+</sup>: 394.0897; found: 394.0902



**Dimethyl (Z)-2-(1-(cyclobutanecarboxamido)-2-oxo-2-phenylethylidene) succinate (3k)** White powder (28.50 mg, yield: 40%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 11.32 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.79 (s, 3H), 3.52 (s, 3H), 3.19 - 3.12 (m, 1H), 3.09 (s, 2H), 2.28 - 2.14 (m, 4H), 1.94 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.68, 172.67, 171.09, 169.37, 148.88, 135.69, 133.75, 128.85, 128.82, 128.71, 101.95, 52.40, 51.98, 39.62, 32.53, 25.07, 18.08.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub>Na<sup>+</sup>: 382.1262; found: 382.1270



**Dimethyl (Z)-2-(1-(cyclohexanecarboxamido)-2-oxo-2-phenylethylidene) succinate (3l)** White powder (34.90 mg, yield: 45%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 11.46 (s, 1H), 7.90 – 7.85 (m, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 6.9 Hz, 2H), 3.78 (s, 3H), 3.51 (s, 3H), 3.09 (s, 2H), 2.23 (s, 1H), 1.94 – 1.81 (m, 2H), 1.78 – 1.70 (m, 2H), 1.66 – 1.58 (m, 1H), 1.35 (dd, J = 12.1, 3.1 Hz, 2H), 1.28 – 1.20 (m, 2H), 1.17 (d, J = 15.3 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.61, 173.61, 171.12, 169.49, 149.03, 135.72, 133.65, 128.79, 128.64, 102.03, 52.41, 51.96, 44.88, 32.50, 29.10, 25.59, 25.50.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>6</sub>Na<sup>+</sup>: 410.1575; found: 410.1578



Dimethyl (Z)-2-(1-decanamido-2-oxo-2-phenylethylidene) succinate (3m)

Yellow oil (48.40 mg, yield: 56%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.37 (s, 1H), 7.91 – 7.84 (m, 2H), 7.59 – 7.37 (m, 3H), 3.78 (s, 3H), 3.50 (s, 3H), 3.09 (s, 2H), 2.33 – 2.26 (m, 2H), 1.21 (d, J = 4.7 Hz, 14H), 0.84 (t, J = 6.9 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.58, 171.09, 170.87, 169.36, 148.79, 135.75, 133.70, 128.81, 128.70, 101.98, 52.39, 51.97, 36.39, 32.49, 31.89, 29.38, 29.26, 29.23, 29.03, 24.92,

22.70, 14.14. **HRMS** (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>24</sub>H<sub>33</sub>NO<sub>6</sub>Na<sup>+</sup>: 454.2201; found: 454.2210



**Dimethyl (Z)-2-(1-(3-methyl-3-phenylureido)-2-oxo-2-phenylethylidene) succinate (3n)** Yellow oil (36.10 mg, yield: 44%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 10.59 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.58 – 7.41 (m, 6H), 7.31 (d, J = 7.7 Hz, 2H), 3.53 (s, 3H), 3.46 (s, 3H), 3.19 (d, J = 1.0 Hz, 3H), 2.98 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.21, 171.42, 168.83, 152.57, 149.89, 141.67, 136.10, 133.57, 130.42, 128.83, 128.79, 128.61, 127.46, 98.72, 51.92, 51.87, 37.84, 32.68. HRMS (ESI) m/z:  $[M+Na]^+$ : Calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>6</sub>Na<sup>+</sup>: 433.1370; found: 433.1377



**Dimethyl (Z)-2-(1-benzamido-2-(3-nitrophenyl)-2-oxoethylidene) succinate (30)** Yellow oil (59.20 mg, yield: 69%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 12.49 (s, 1H), 8.80 – 8.75 (m, 1H), 8.40 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.33 (ddd, J = 7.8, 1.7, 1.1 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 7.4 Hz, 1H), 7.52 – 7.44 (m, 2H), 3.88 (s, 3H), 3.56 (s, 3H), 3.19 (s, 2H). <sup>13</sup>**C** NMR (101 MHz, CDCl<sub>3</sub>) δ 182.80, 171.12, 169.78, 163.85, 148.46, 142.82, 135.22, 134.21, 133.15, 131.69, 129.03, 128.35, 128.01, 103.12, 52.67, 52.09, 32.73. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>Na<sup>+</sup>: 449.0955; found: 449.0966



**Dimethyl (Z)-2-(1-benzamido-2-(4-nitrophenyl)-2-oxoethylidene) succinate (3p)** White powder (66.30 mg, yield: 78%). PE/EA = 8:1.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, J = 8.6 Hz, 2H), 8.15 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 7.4 Hz, 2H), 7.58 (s, 1H), 7.47 (s, 2H), 3.87 (s, 3H), 3.57 (s, 3H), 3.19 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.77, 170.93, 169.54, 164.31, 150.50, 147.86, 140.39,

133.58, 130.79, 129.59, 129.16, 128.05, 124.17, 103.88, 52.94, 52.30, 32.44. **HRMS** (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>Na<sup>+</sup>: 449.0955; found: 449.0964



**Dimethyl (Z)-2-(1-benzamido-2-(4-cyanophenyl)-2-oxoethylidene) succinate (3q)** Yellow oil (51.80 mg, yield: 64%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 7.4 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 3.86 (d, J = 0.6 Hz, 3H), 3.56 (s, 3H), 3.17 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  189.02, 170.91, 169.55, 164.27, 147.95, 138.96, 133.50, 132.75, 130.93, 129.13, 128.99, 128.04, 117.98, 116.76, 103.77, 52.84, 52.21, 32.43, 29.76. HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup>: 429.1057; found: 429.1065



**Dimethyl (Z)-2-(1-benzamido-2-(naphthalen-2-yl)-2-oxoethylidene) succinate (3r)** White powder (71.50 mg, yield: 83%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.31 (d, J = 8.6 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.91 – 7.84 (m, 3H), 7.73 (s, 1H), 7.55 (d, J = 21.7 Hz, 2H), 7.48 – 7.38 (m, 3H), 3.87 (s, 3H), 3.56 (s, 3H), 3.30 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.90, 171.41, 169.99, 164.23, 150.01, 134.81, 134.23, 133.03, 131.95, 131.72, 131.62, 130.90, 129.07, 128.93, 128.49, 128.03, 126.87, 126.59, 124.31, 103.36, 52.62, 52.03, 32.68.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>25</sub>H<sub>21</sub>NO<sub>6</sub>Na<sup>+</sup>: 454.1261; found: 454.1269



**Dimethyl (Z)-2-(1-benzamido-2-(4-methoxyphenyl)-2-oxoethylidene)succinate (3s)** White powder (71.60 mg, yield: 87%). PE/EA = 8:1. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.47 (s, 1H), 7.96 (d, J = 8.8 Hz, 2H), 7.94 – 7.89 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 3.84 (d, J = 1.0 Hz, 6H), 3.56 (s, 3H), 3.17 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.40, 171.21, 169.89, 164.21, 163.79, 149.60, 133.11, 131.64, 131.29, 129.00, 128.84, 128.06, 127.34, 114.28, 102.34, 55.64, 52.61, 52.11, 32.68.
HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>22</sub>H<sub>21</sub>NO<sub>7</sub>Na<sup>+</sup>: 434.1210; found: 434.1220



**Dimethyl (Z)-2-(1-benzamido-2-oxo-2-(thiophen-2-yl) ethylidene) succinate (3t)** White powder (43.30 mg, yield: 56%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.39 (s, 1H), 7.94 – 7.87 (m, 2H), 7.71 – 7.65 (m, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.07 (dd, J = 4.9, 3.9 Hz, 1H), 3.83 (s, 3H), 3.56 (s, 3H), 3.24 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 182.80, 171.12, 169.78, 163.85, 148.46, 142.82, 135.22, 134.21, 133.15, 131.69, 129.03, 128.35, 128.01, 103.12, 52.67, 52.09, 32.73.

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>6</sub>SNa<sup>+</sup>: 410.0669; found: 410.0678



Diethyl (Z)-2-(1-benzamido-2-oxo-2-phenylethylidene) succinate (3u)

White powder (71.20 mg, yield: 87%). PE/EA = 6:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03 – 7.97 (m, 2H), 7.92 – 7.86 (m, 2H), 7.58 – 7.50 (m, 2H), 7.48 – 7.41 (m, 4H), 4.30 (d, J = 7.1 Hz, 2H), 3.99 (d, J = 7.1 Hz, 2H), 3.14 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.86, 170.67, 169.37, 163.91, 148.87, 135.78, 133.91, 133.17, 131.49, 129.02, 128.96, 128.88, 128.05, 103.30, 61.65, 60.94, 33.05, 14.21, 14.19.
HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub>Na<sup>+</sup>: 432.1418; found: 432.1429



**Dimethyl (E)-2-(1-(2-fluorobenzamido)-2-oxo-2-phenylethylidene) succinate (3E)** White powder (63.10 mg, yield: 79%). PE/EA = 8:1.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.40 (s, 1H), 7.98 (s, 2H), 7.46 (s, 5H), 7.20 (d, J = 7.7 Hz, 2H), 3.84 (s, 3H), 3.53 (s, 3H), 3.16 (s, 2H).

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.43, 170.99, 168.76, 162.27, 160.83 (d, J<sub>C-F</sub> = 3.2 Hz), 159.78, 148.14, 135.74, 135.18 (d, J<sub>C-F</sub> = 9.4 Hz), 133.84, 132.70, 128.89 (d, J<sub>C-F</sub> = 13.5 Hz), 125.07 (d, J<sub>C-F</sub> = 3.2 Hz), 118.98 (d, J<sub>C-F</sub> = 11.0 Hz), 116.56 (d, J<sub>C-F</sub> = 24.1 Hz), 104.06, 52.65, 52.09, 32.89.

<sup>19</sup>**F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  -110.88 (q, J = 8.8 Hz).

HRMS (ESI) m/z: [M+Na]<sup>+</sup>: Calcd for C<sub>22</sub>H<sub>18</sub>FNO<sub>6</sub>Na<sup>+</sup>: 422.1010; found: 422.1019

## 4. X-Ray Crystallographic Data

**Crystal structure details for 3a** (CCDC 2402097). Thermal ellipsoids are shown at 50 % probability level (two molecules in each unit). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of  $CH_2Cl_2$  solution of **3a**.



Table 1 Crystal data and structure refinement for 3a.

Empirical formula	C <sub>21</sub> H <sub>19</sub> NO <sub>6</sub>
Formula weight	381.37
Temperature/K	213.0
Crystal system	triclinic
Space group	P-1
a/Å	5.6083(15)
b/Å	12.004(4)
c/Å	14.983(5)
$\alpha/^{\circ}$	78.692(11)
β/°	84.933(10)
$\gamma/^{\circ}$	79.177(10)
Volume/Å <sup>3</sup>	970.1(5)
Z	2
$ ho_{calc}g/cm^3$	1.306
$\mu/mm^{-1}$	0.096
F(000)	400.0
Crystal size/mm <sup>3</sup>	$0.31 \times 0.07 \times 0.03$
Radiation	MoKa ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/°	4.862 to 49.986
Index ranges	$-5 \le h \le 6, -14 \le k \le 14, -17 \le l \le 17$
Reflections collected	11298
Independent reflections	3413 [ $R_{int} = 0.1003$ , $R_{sigma} = 0.0940$ ]
Data/restraints/parameters	3413/24/276
Goodness-of-fit on F2	1.014
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0637, wR_2 = 0.1497$
Final R indexes [all data]	$R_1 = 0.1213, wR_2 = 0.1904$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.17

Crystal structure details for 3E (CCDC 2402098). Thermal ellipsoids are shown at 50 % probability level (two molecules in each unit). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of  $CH_2Cl_2$  solution of 3E.



Table 2 Crystal data and structure refinement for 3E.

Empirical formula	$C_{21}H_{18}FNO_6$
Formula weight	399.36
Temperature/K	303.0
Crystal system	triclinic
Space group	P-1
a/Å	9.242(3)
b/Å	10.902(4)
c/Å	11.076(4)
$\alpha$ / $_{\circ}$	98.407(9)
β/°	109.822(8)
$\gamma/^{\circ}$	107.406(9)
Volume/Å <sup>3</sup>	963.0(5)
Z	2
$ ho_{calc}g/cm^3$	1.377
µ/mm <sup>-1</sup>	0.108
F(000)	416.0
Crystal size/mm <sup>3</sup>	$0.23\times0.18\times0.11$
Radiation	MoKα ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/°	4.066 to 55.08
Index ranges	-11≤h≤11, -14≤k≤14, -14≤l≤14
Reflections collected	18300
Independent reflections	$4317 \left[R_{int} = 0.0784, R_{sigma} = 0.0725\right]$
Data/restraints/parameters	4317/0/264
Goodness-of-fit on F2	1.028
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0699, wR_2 = 0.1831$
Final R indexes [all data]	$R_1 = 0.1299, wR_2 = 0.2267$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.37/-0.25

#### 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra













































## 6. <sup>19</sup>F NMR spectra



