

## Supporting Information

| <b>Table of contents</b>                              | <b>Page</b> |
|---|-------------|
| 1. General information                                | S1          |
| 2. Experimental Section                               | S1          |
| 3. Spectroscopic data for the products                | S6          |
| 4. X-ray Single Crystal Diffraction Data of <b>5d</b> | S19         |
| 5. H-NMR determination of reaction processes          | S20         |
| 6. General applicability                              | S22         |
| 7. Mechanism Exploration                              | S27         |
| 8. Proposed mechanism conclusions                     | S36         |
| 9. NMR spectra  | S37         |
| 10. References  | S79         |

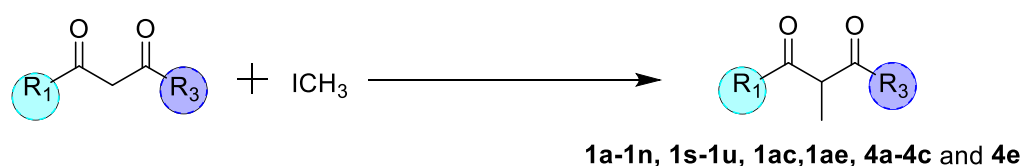
## 1. General information

Unless otherwise noted, all reactions were carried out in quartz tubes.  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE III 400 and AVANCE III 500 spectrometer at room temperature. Chemical shifts (ppm) were referenced to tetramethylsilane (TMS,  $\delta = 0$  ppm) in  $\text{CDCl}_3$  as an internal standard.  $^{13}\text{C}$  NMR spectra and  $^{19}\text{F}$  NMR spectra were obtained by the same NMR spectrometer and were calibrated with  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm). Data for  $^1\text{H}$  NMR were reported as follows: chemical shifts ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved), coupling constant (Hz) and integration. Data for  $^{13}\text{C}$  NMR were reported in terms of chemical shift and multiplicity where appropriate. High-Resolution Mass Spectrometry (HRMS) were performed on a Thermo Fisher LTQ Orbit rap XL. Melting points were measured on SGW X-4 melting point apparatus and uncorrected. Anhydrous solvents were from J&K Scientific Ltd or Adamas and dried by standard procedures. The water comes from the Wahaha Company. All other commercially available reagents were from Innochem Chemicals or Bidepharm and used as received. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. The crude product was purified by reverse phase flash with the following conditions (lineal gradient of 0-100% MeCN in  $\text{H}_2\text{O}$  in 30 min. flux of 40 mL/min, in a symmetry column C18 (30g), detection at 254 nm and 220 nm) to afford Products. The starting Materials **1** were obtained by previous reports.<sup>1-7</sup>

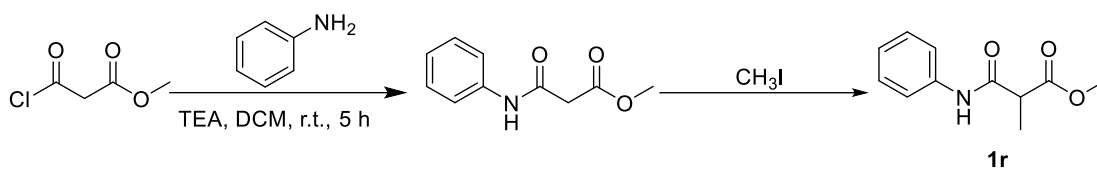
## 2. Experimental Section

### 1) Materials preparation

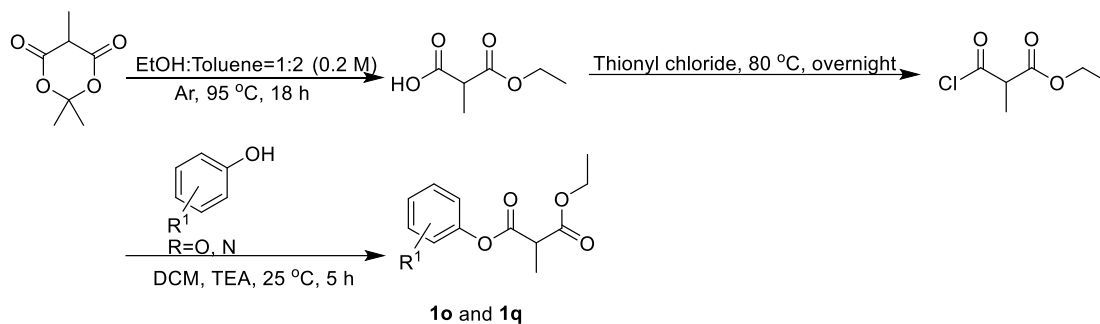
**Method A:** Substrate **1a-1n**, **1s-1u**, **1ac**, **1ae**, **4a-4c** and **4e** were prepared according to literatures.<sup>1-3</sup>



**Method B:** Substrate **1r** were prepared according to literatures.<sup>1-3</sup>



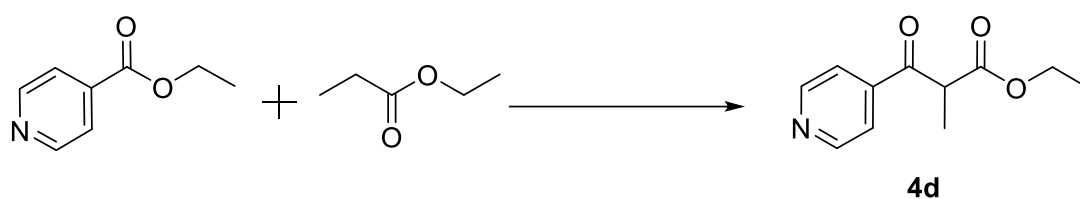
**Method C:** Substrate **1o** and **1q** were prepared according to literatures.<sup>4</sup>



**Method D:** Substrate **1x-1z** and **1aa** were prepared according to literatures.<sup>4-6</sup>

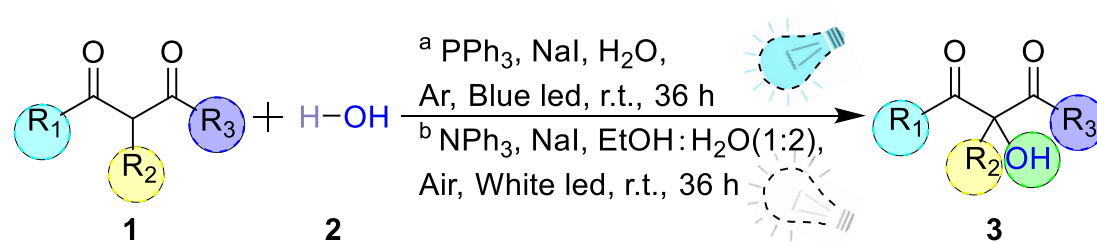


**Method E:** Substrate **4d** were prepared according to literatures.<sup>7</sup>



All other substrates can be purchased.

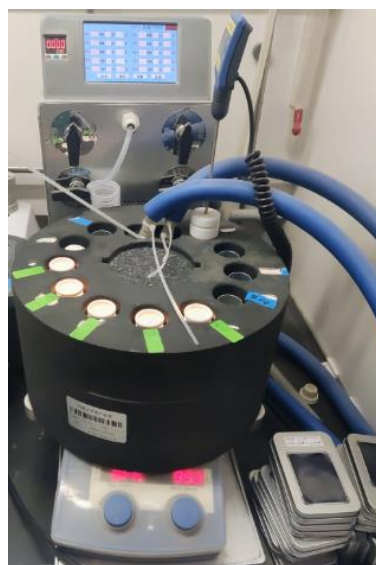
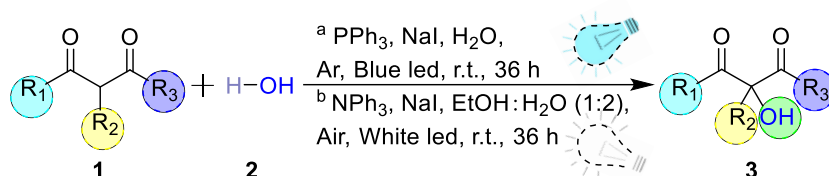
## 2) Optimization of reaction conditions.



| Entry                 | Variation from standard conditions  | Yield <sup>c</sup> (%)                            |
|-----------------------|---|---|
| <b>1<sup>a</sup></b>  | <b>None</b>   | <b>94</b>   |
| 2 <sup>a</sup>        | LiI, KI, CsI, NaBr instead of NaI   | 76/87/83/trace                                    |
| 3 <sup>a</sup>        | Aryl-substituted phosphorus ( <i>p</i> -OCH <sub>3</sub> , <i>p</i> -F, <i>p</i> -Me), TBP instead of PPh <sub>3</sub>                        | 88/64/81/trace                                    |
| 4 <sup>a</sup>        | NaI (1.0 equiv., 1.2 equiv., 1.3 equiv.) instead of NaI 1.1 equiv.  | 80/86/77  |
| 5 <sup>a</sup>        | PPh <sub>3</sub> (5%, 10%, 30%) instead of PPh <sub>3</sub> 20%   | 49/75/93  |
| 6 <sup>a</sup>        | Toluene, THF, DMF, Acetone, MeCN, MeOH, MeCN:MeOH:H <sub>2</sub> O = 1:1:1 instead of H <sub>2</sub> O  | trace/trace/trace/trace/<br>81/89/94              |
| 7 <sup>a</sup>        | Dark, White LED (6000-6500 K) instead of Blue LED (455 nm)  | trace/75  |
| 8 <sup>a</sup>        | 30% of (PPh <sub>3</sub> , NaI); 50% of (PPh <sub>3</sub> , NaI) instead of NaI 1.1 equiv, PPh <sub>3</sub> 20%                               | 56 <sup>d</sup> /67 <sup>e</sup> /85 <sup>f</sup> |
| 9 <sup>a</sup>        | Air   | 59  |
| <b>10<sup>b</sup></b> | <b>None</b>   | <b>94</b>   |
| 11 <sup>b</sup>       | LiI, KI, CsI, NaBr instead of NaI   | 89/94/81/trace                                    |
| 12 <sup>b</sup>       | TMPA, TEA instead of NPh <sub>3</sub>   | 91/trace  |
| 13 <sup>b</sup>       | NaI (20%, 1.0 equiv., 1.1 equiv.) instead of NaI 30%  | 85/91/88  |
| 14 <sup>b</sup>       | NPh <sub>3</sub> (10%, 30%, 40%) instead of NPh <sub>3</sub> 20%  | 79/94/93  |
| 15 <sup>b</sup>       | Acetone, MeCN, MeOH, H <sub>2</sub> O, MeCN:MeOH:H <sub>2</sub> O = 1:1:1, EtOH:H <sub>2</sub> O = 3:1 instead of EtOH:H <sub>2</sub> O = 1:2 | 47/75/82/65/91/94                                 |
| 16 <sup>b</sup>       | Dark, LED (455 nm, 510 nm, 565 nm) instead of White LED (6000-6500K)  | Trace/83/78/73                                    |
| 17 <sup>b</sup>       | (30, 40) hours instead of 36 hours  | 88/94   |

Reaction conditions: <sup>a</sup> **1a** (0.1 mmol, 1.0 equiv.), PPh<sub>3</sub> (20 mmol %), NaI (0.11 mmol, 1.1 equiv.) in H<sub>2</sub>O (2 mL) were stirred under argon for 36 hours at room temperature under the irradiation of a 10 W blue LED (455 nm); <sup>b</sup> **1a** (0.1 mmol, 1.0 equiv.), NPh<sub>3</sub> (20 mmol %), NaI (30 mmol %) in EtOH:H<sub>2</sub>O = 1:2 (2 mL) were stirred under air for 36 hours at room temperature under the irradiation of a 10 W white LED (6000-6500 K); <sup>c</sup> Isolated yields; <sup>d</sup> NPh<sub>3</sub> (30 mmol %), NaI (30 mmol %), 36 h; <sup>e</sup> NPh<sub>3</sub> (30 mmol %), NaI (30 mmol %), 60 h; <sup>f</sup> NPh<sub>3</sub> (50 mmol %), NaI (50 mmol %), 36 h; TBP: Tributyl phosphate, PPh<sub>3</sub>: Triphenylphosphine, THF: Tetrahydrofuran, DMF: *N,N*-dimethylformamide, MeCN: Acetonitrile, MeOH: Methanol, TMPA: tris(4-methoxyphenyl)amine, TEA: Triethylamine, NPh<sub>3</sub>: Triphenylamine, EtOH: Ethanol.

### 3) General procedure for synthesis of compound 3 or 5:

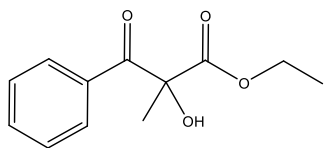


<sup>a</sup> To a 25 mL quartz tube was charged with  $\beta$ -dicarbonyl **1** (0.2 mmol, 1.0 equiv.), PPh<sub>3</sub> (20 mmol %), NaI (0.22 mmol, 1.1 equiv.) and H<sub>2</sub>O (2 mL). The mixture was evacuated and backfilled with argon three times. Then the mixture was stirred for 36 h under 10 W blue LED irradiation at room temperature. After completion, the mixture was quenched with water (5 mL), and extracted with ethyl acetate (10 mL  $\times$  4). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **3** or **5**. The crude product was purified by reverse phase flash with the following conditions (lineal gradient of 0-100% MeCN in H<sub>2</sub>O in 30 min. flux of 40 mL/min, in a symmetry column C18 (30g), detection at 254nm and 220 nm) to afford Products.

<sup>b</sup> To a 25 mL quartz tube was charged with  $\beta$ -dicarbonyl **1** (0.2 mmol, 1.0 equiv.), NPh<sub>3</sub> (20 mmol %), NaI (30 mmol %) and EtOH:H<sub>2</sub>O = 1:2 (2 mL). Then the mixture was stirred for 36 h under 10 W white LED irradiation at room temperature. After completion, the mixture was quenched with water (5 mL), and extracted with ethyl acetate (10 mL  $\times$  4). The combined organic layers

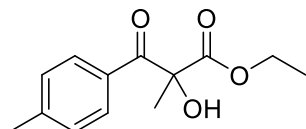
were dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **3** or **5**. The crude product was purified by reverse phase flash with the following conditions (lineal gradient of 0-100% MeCN in  $\text{H}_2\text{O}$  in 30 min. flux of 40 mL/min, in a symmetry column C18 (30g), detection at 254nm and 220 nm) to afford Products.

### 3. Spectroscopic data



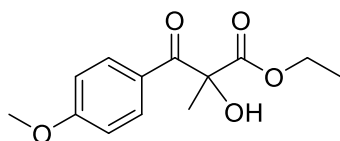
#### ethyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (3a)

Colorless oil;  $R_f = 0.45$  (petroleum ether : EtOAc = 10 : 1); 94% (41.7 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.01 – 7.99 (m, 2H), 7.62 – 7.58 (m, 1H), 7.47 (t,  $J = 7.8$  Hz, 2H), 4.51 (s, 1H), 4.24 (q,  $J = 7.2$  Hz, 2H), 1.76 (s, 3H), 1.17 (t,  $J = 7.2$  Hz, 3H).;  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  195.86, 172.22, 133.66, 133.01, 129.40, 128.57, 79.37, 62.45, 23.46, 13.76. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 223.0965, found: 223.0964.



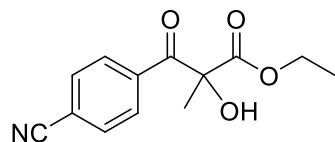
#### ethyl 2-hydroxy-2-methyl-3-oxo-3-(p-tolyl)propanoate (3b)

Colorless oil;  $R_f = 0.55$  (petroleum ether : EtOAc = 10 : 1); 79% (37.4 mg), 78% (36.9 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.00 (d,  $J = 7.2$  Hz, 2H), 6.93 (d,  $J = 7.2$  Hz, 2H), 4.64 (s, 1H), 4.21 (q,  $J = 7.2$  Hz, 2H), 3.88 (s, 3H), 1.74 (s, 3H), 1.16 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  194.32, 172.32, 163.96, 131.99, 125.49, 113.84, 79.10, 62.29, 55.48, 23.72; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 237.1121, found: 237.1118.



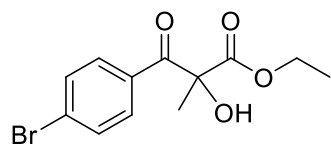
#### ethyl 2-hydroxy-3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (3c)

Colorless oil;  $R_f = 0.50$  (petroleum ether : EtOAc = 10 : 1); 83% (42.1 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.88 (d,  $J = 8.5$  Hz, 2H), 7.25 (d,  $J = 8.5$  Hz, 2H), 4.53 (s, 1H), 4.21 (q,  $J = 7.0$  Hz, 2H), 2.41 (s, 3H), 1.73 (s, 3H), 1.16 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  195.60, 172.24, 144.79, 130.39, 129.63, 129.32, 79.33, 62.36, 23.58, 21.67, 13.81. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_5$  [ $\text{M} + \text{H}^+$ ]: 253.1070, found: 253.1067.



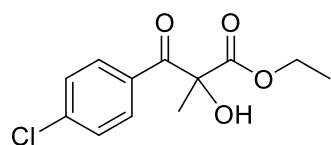
**ethyl 3-(4-cyanophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3d)**

Colorless oil;  $R_f = 0.50$  (petroleum ether : EtOAc = 5 : 1); 87% (43.1 mg), 86% (42.7 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.10 – 8.07 (m, 2H), 7.75 – 7.73 (m, 2H), 4.25 (q,  $J = 7.0$  Hz, 2H), 4.09 (s, 1H), 1.72 (s, 3H), 1.18 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.34, 172.51, 137.14, 132.25, 129.85, 117.72, 116.61, 79.94, 63.07, 23.38, 13.85; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_4$  [ $\text{M} + \text{H}^+$ ]: 247.0845, found: 247.0846.



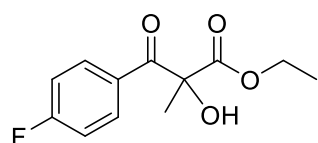
**ethyl 3-(4-bromophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3e)**

Colorless oil;  $R_f = 0.43$  (petroleum ether : EtOAc = 10 : 1); 85% (51.1 mg), 84% (50.6 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.87 (d,  $J = 8.5$  Hz, 2H), 7.59 (d,  $J = 8.5$  Hz, 2H), 4.24 (m, 3H), 1.72 (s, 3H), 1.18 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.80, 172.43, 132.13, 131.92, 130.99, 128.93, 79.64, 62.72, 23.48, 13.84; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{26}\text{F}_2\text{INO}_4\text{S}$  [ $\text{M} + \text{H}^+$ ]: 301.0069, found: 301.0062.



**ethyl 3-(4-chlorophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3f)**

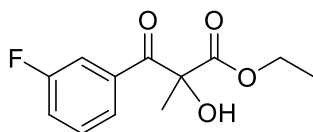
Colorless oil;  $R_f = 0.43$  (petroleum ether : EtOAc = 10 : 1); 88% (45.4 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J = 8.5$  Hz, 2H), 7.42 (d,  $J = 8.5$  Hz, 2H), 4.30 (s, 1H), 4.23 (q,  $J = 7.0$  Hz, 2H), 1.72 (s, 3H), 1.17 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.57, 172.44, 140.14, 131.69, 130.93, 128.90, 79.63, 62.68, 23.48, 13.82; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{ClO}_4$  [ $\text{M} + \text{H}^+$ ]: 257.0575, found: 257.0572.



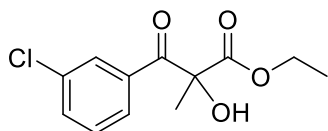


**ethyl 3-(4-fluorophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3g)**

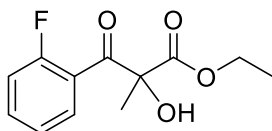
Colorless oil;  $R_f = 0.45$  (petroleum ether : EtOAc = 10 : 1); 89% (43.1 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.07 – 8.03 (m, 2H), 7.15-7.11 (m, 2H), 4.34 (s, 1H), 4.23 (q,  $J = 7.2$  Hz, 2H), 1.73 (s, 3H), 1.17 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  194.18, 172.46, 167.18, 164.63, 132.34 (d,  $J = 9.5$  Hz), 129.54 (d,  $J = 3.1$  Hz), 115.82 (d,  $J = 22.0$  Hz), 79.52, 62.67, 23.57, 13.84;  $^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -103.49. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{FO}_4$  [ $\text{M} + \text{H}^+$ ]: 241.0871, found: 241.0863.

**ethyl 3-(3-fluorophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3h)**

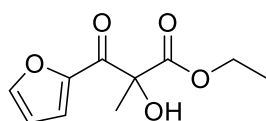
Colorless oil;  $R_f = 0.43$  (petroleum ether : EtOAc = 10 : 1); 92% (44.0 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.77 (d,  $J = 8.0$  Hz, 1H), 7.73 – 7.70 (m, 1H), 7.46-7.40 (m, 1H), 7.30 – 7.26 (m, 1H), 4.29 (s, 1H), 4.24 (q,  $J = 7.2$  Hz, 2H), 1.73 (s, 3H), 1.18 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  194.56, 194.54, 172.36, 163.76, 161.29, 135.34 (d,  $J = 6.6$  Hz), 130.22 (d,  $J = 7.7$  Hz), 125.16 (d,  $J = 3.0$  Hz), 120.63 (d,  $J = 21.4$  Hz), 116.30 (d,  $J = 23.0$  Hz), 79.66, 62.76, 23.43, 13.81;  $^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -111.22. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{FO}_4$  [ $\text{M} + \text{H}^+$ ]: 241.0871, found: 241.0868.

**ethyl 3-(3-chlorophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3i)**

Colorless oil;  $R_f = 0.44$  (petroleum ether : EtOAc = 10 : 1); 90% (46.2 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.99 (s, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.55–7.53 (m, 1H), 7.38 (t,  $J = 8.0$  Hz, 1H), 4.27-4.23 (m, 3H), 1.72 (s, 3H), 1.19 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.60, 172.37, 135.09, 134.91, 133.43, 129.81, 129.50, 127.46, 79.75, 62.79, 23.43, 13.82. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{ClO}_4$  [ $\text{M} + \text{H}^+$ ]: 257.0575, found: 257.0579.

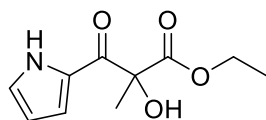
**ethyl 3-(2-fluorophenyl)-2-hydroxy-2-methyl-3-oxopropanoate (3j)**

Colorless oil;  $R_f = 0.45$  (petroleum ether : EtOAc = 10 : 1); 84% (40.8 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.80 (t,  $J = 7.4$  Hz, 1H), 7.55 (q,  $J = 7.2$  Hz, 1H), 7.28 – 7.24 (m, 1H), 7.14-7.09 (m, 1H), 4.32 (s, 1H), 4.27 (q,  $J = 7.2$  Hz, 2H), 1.68 (s, 3H), 1.25 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  196.36 (d,  $J = 3.0$  Hz), 170.97 (d,  $J = 1.3$  Hz), 161.62, 159.11, 134.70 (d,  $J = 9.1$  Hz), 131.24 (d,  $J = 2.9$  Hz), 124.65 (d,  $J = 3.3$  Hz), 123.20 (d,  $J = 14.3$  Hz), 116.23 (d,  $J = 23.3$  Hz), 80.62, 62.55, 22.70 (d,  $J = 1.9$  Hz), 13.89;  $^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -107.76. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{FO}_4$  [ $\text{M} + \text{H}^+$ ]: 241.0871, found: 241.0866.



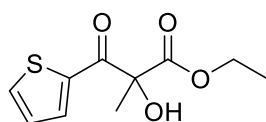
**ethyl 3-(furan-2-yl)-2-hydroxy-2-methyl-3-oxopropanoate (3k)**

Colorless oil;  $R_f = 0.65$  (petroleum ether : EtOAc = 5 : 1); 85% (36.6 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.634 – 7.631 (m, 1H), 7.41 (d,  $J = 3.5$  Hz, 1H), 6.582-6.572 (m, 1H), 4.38 (s, 1H), 4.24 – 4.19 (m, 2H), 1.72 (s, 3H), 1.18 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  184.58, 171.30, 149.43, 147.26, 120.51, 112.52, 78.75, 62.33, 22.45, 13.83; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_5$  [ $\text{M} + \text{H}^+$ ]: 213.0757, found: 213.0752.



**ethyl 2-hydroxy-2-methyl-3-oxo-3-(1H-pyrrol-2-yl)propanoate (3l)**

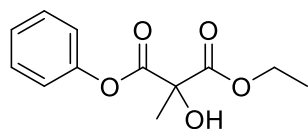
Colorless oil;  $R_f = 0.6$  (petroleum ether : EtOAc = 5 : 1); 85% (35.8 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  9.54 (s, 1H), 7.14 – 7.10 (m, 2H), 6.34-6.32 (m, 1H), 4.58 (s, 1H), 4.23 (q,  $J = 7.0$  Hz, 2H), 1.79 (s, 3H), 1.23 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  185.75, 172.28, 127.27, 125.61, 118.99, 111.58, 79.02, 62.42, 24.29, 13.89; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_{13}\text{NO}_4$  [ $\text{M} + \text{H}^+$ ]: 212.0917, found: 212.0915.



**ethyl 2-hydroxy-2-methyl-3-oxo-3-(thiophen-2-yl)propanoate (3m)**

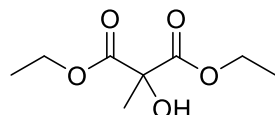
Colorless oil;  $R_f = 0.6$  (petroleum ether : EtOAc = 5 : 1); 84% (38.4 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J = 3.5$  Hz, 1H), 7.71 (d,  $J = 5.0$  Hz, 1H), 7.13 (t,

$J = 4.5$  Hz, 1H), 4.44 (s, 1H), 4.23 (q,  $J = 7.0$  Hz, 2H), 1.77 (s, 3H), 1.20 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  189.03, 172.18, 138.85, 135.05, 134.52, 128.19, 80.02, 62.66, 23.67, 13.82.; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$  [ $\text{M} + \text{H}^+$ ]: 229.0529, found: 229.0524.



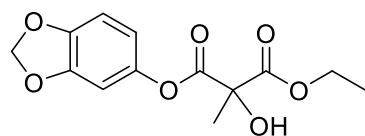
### 1-ethyl 3-phenyl 2-hydroxy-2-methylmalonate (3o)

Colorless oil;  $R_f = 0.73$  (petroleum ether : EtOAc = 10: 1); 83% (39.2 mg);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.414 – 7.373 (m, 2H), 7.278 – 7.244 (m, 1H), 7.100 – 7.075 (m, 2H), 4.397 – 4.302 (m, 2H), 4.224 (s, 1H), 1.774 (s, 3H), 1.349 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  170.82, 169.41, 150.43, 129.58, 126.39, 120.95, 76.32, 62.83, 21.63, 14.09; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_5$  [ $\text{M} + \text{H}^+$ ]: 239.0914, found: 239.0910.



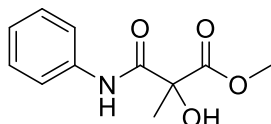
### diethyl 2-hydroxy-2-methylmalonate (3p)

Colorless oil;  $R_f = 0.71$  (petroleum ether : EtOAc = 10: 1); 70% (26.7 mg);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  4.26 (q,  $J = 7.0$  Hz, 4H), 3.74 (s, 1H), 1.63 (s, 3H), 1.29 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  170.95, 76.05, 62.44, 21.55, 13.98; HRMS (ESI):  $m/z$  calcd for  $\text{C}_8\text{H}_{14}\text{O}_5$  [ $\text{M} + \text{H}^+$ ]: 191.0914, found: 239.0915.



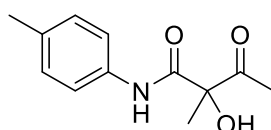
### 1-(benzo[d][1,3]dioxol-5-yl) 3-ethyl 2-hydroxy-2-methylmalonate (3q)

Colorless oil;  $R_f = 0.48$  (petroleum ether : EtOAc = 10 : 1); 80% (45.2 mg);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  6.77 (d,  $J = 8.0$  Hz, 1H), 6.59 (d,  $J = 2.0$  Hz, 1H), 6.53 (dd,  $J = 8.5, 2.5$  Hz, 1H), 5.99 (s, 2H), 4.37-4.31 (m, 2H), 3.86 (s, 1H), 1.75 (s, 3H), 1.34 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  170.77, 169.65, 148.12, 145.78, 144.63, 113.39, 107.99, 103.08, 101.84, 76.25, 62.83, 21.60, 14.08; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_7$  [ $\text{M} + \text{H}^+$ ]: 283.0812, found: 283.0808.



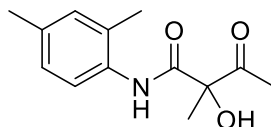
**ethyl 2-hydroxy-2-methyl-3-oxo-3-(phenylamino)propanoate (3r)**

Colorless oil;  $R_f = 0.30$  (petroleum ether : EtOAc = 5 : 1); 87% (39 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.74 (s, 1H), 7.57 – 7.55 (m, 2H), 7.35 – 7.31 (m, 2H), 7.15 – 7.12 (m, 1H), 4.32 (s, 1H), 3.89 (s, 3H), 1.76 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  173.33, 167.46, 136.98, 129.06, 124.80, 119.67, 76.97, 54.11, 24.41; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_{13}\text{NO}_4$  [ $\text{M} + \text{H}^+$ ]: 224.0917, found: 224.0912.



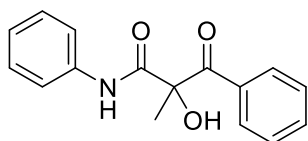
**2-hydroxy-2-methyl-3-oxo-N-(p-tolyl)butanamide (3s)**

Colorless oil;  $R_f = 0.38$  (petroleum ether : EtOAc = 5 : 1); 75% (33.2 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.75 (s, 1H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.12 (d,  $J = 8.0$  Hz, 2H), 5.01 (s, 1H), 2.52 (s, 3H), 2.31 (s, 3H), 1.71 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  207.61, 167.74, 134.45, 134.29, 129.68, 129.31, 119.82, 119.53, 82.06, 24.41, 20.93, 20.72. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_3$  [ $\text{M} + \text{H}^+$ ]: 222.1120, found: 222.1125.



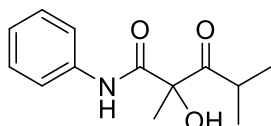
**N-(2,4-dimethylphenyl)-2-hydroxy-2-methyl-3-oxobutanamide (3t)**

Colorless oil;  $R_f = 0.45$  (petroleum ether : EtOAc = 5 : 1); 79% (37.3 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.70 (s, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.03-7.00 (m, 2H), 5.01 (s, 1H), 2.53 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 1.73 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  208.08, 167.86, 135.01, 132.27, 131.19, 128.63, 127.29, 121.79, 82.27, 24.66, 24.54, 20.85, 17.42. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}_3$  [ $\text{M} + \text{H}^+$ ]: 236.1281, found: 236.1279.



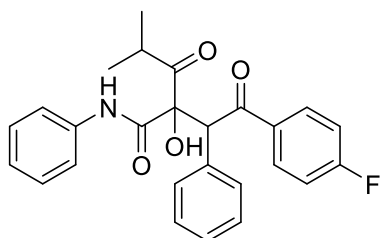
**2-hydroxy-2-methyl-3-oxo-N,3-diphenylpropanamide (3u)**

white solid; m. p.: 132–135 °C; 30% (16.1 mg), 81% (43.6 mg); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.38 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 1.91 (s, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 198.62, 169.28, 137.11, 133.63, 133.30, 132.03, 131.95, 130.80, 128.94, 128.53, 128.44, 128.30, 124.64, 119.82, 81.58, 25.69; HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub> [*M* + H<sup>+</sup>]: 270.1125, found: 270.1122.



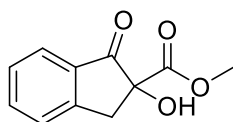
### 2-hydroxy-2,4-dimethyl-3-oxo-N-phenylpentanamide (3v)

Colorless oil; R<sub>f</sub> = 0.5 (petroleum ether : EtOAc = 5 : 1); 71% (32.9 mg); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.54 – 7.51 (m, 2H), 7.35 – 7.32 (m, 2H), 7.15–7.12 (m, 1H), 5.02 (s, 1H), 3.74–3.66 (m, 1H), 1.71 (s, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 214.83, 168.08, 136.96, 129.09, 124.82, 119.76, 81.65, 34.42, 24.39, 19.61, 19.46. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub> [*M* + H<sup>+</sup>]: 236.1281, found: 236.1278.



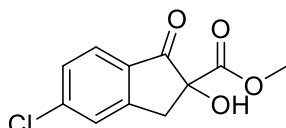
### 2-(2-(4-fluorophenyl)-2-oxo-1-phenylethyl)-2-hydroxy-4-methyl-3-oxo-N-phenylpentanamide (3w)

Yellow solid; m. p.: 109–112 °C; 20% (17.2 mg), 15% (13.4 mg), 69% (59.2 mg), 71% (61.0 mg); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.99–7.96 (m, 2H), 7.29 – 7.20 (m, 10H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.16 (s, 1H), 5.69 (s, 1H), 3.36–3.27 (m, 1H), 1.17 (d, *J* = 6.5 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 211.10, 200.99, 167.13, 165.45, 165.09, 136.40, 132.20, 131.96 (d, *J* = 9.7 Hz), 129.61, 128.92 (d, *J* = 3.7 Hz), 128.27, 124.93, 120.13, 115.88 (d, *J* = 22.1 Hz), 87.59, 55.0, 35.85, 19.65 (d, *J* = 24.4 Hz); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -103.29. HRMS (ESI): *m/z* calcd for C<sub>26</sub>H<sub>24</sub>FNO<sub>4</sub> [*M* + H<sup>+</sup>]: 434.1762, found: 434.1757.



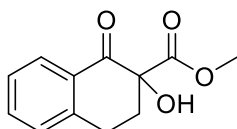
**methyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3x)**

Colorless oil;  $R_f = 0.62$  (petroleum ether : EtOAc = 10 : 1); 79% (32.4 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.80 (d,  $J = 8.0$  Hz, 1H), 7.69-7.66 (m, 1H), 7.49 (d,  $J = 7.5$  Hz, 1H), 7.43 (t,  $J = 7.5$  Hz, 1H), 4.00 (s, 1H), 3.75-3.72 (m, 4H), 3.26 (d,  $J = 17.0$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  200.75, 171.89, 152.17, 136.15, 133.54, 128.14, 126.46, 125.31, 80.37, 53.42, 39.25. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_{10}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 207.0652, found: 207.0651.



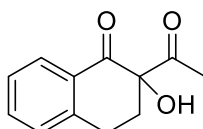
**methyl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3y)**

Colorless oil;  $R_f = 0.61$  (petroleum ether : EtOAc = 10 : 1); 79% (38.1 mg), 77% (37.3 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.73 (d,  $J = 8.5$  Hz, 1H), 7.49 (s, 1H), 7.41 (d,  $J = 8.5$  Hz, 1H), 3.99 (s, 1H), 3.75 (s, 3H), 3.70 (d,  $J = 17.5$  Hz, 1H), 3.23 (d,  $J = 17.5$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  199.33, 171.50, 153.50, 142.85, 131.97, 129.06, 126.74, 126.37, 80.41, 53.59, 38.92. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_9\text{ClO}_4$  [ $\text{M} + \text{H}^+$ ]: 241.0262, found: 241.0264.



**methyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3z)**

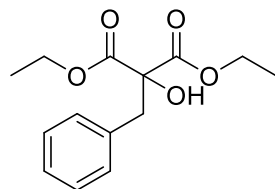
Colorless oil;  $R_f = 0.49$  (petroleum ether : EtOAc = 10 : 1); 84% (36.8 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.05 (d,  $J = 8.0$  Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 1H), 7.35 (t,  $J = 7.5$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 4.34 (s, 1H), 3.75 (s, 3H), 3.16-3.10 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.48, 171.01, 143.99, 134.38, 130.14, 128.90, 128.20, 126.95, 77.69, 52.92, 32.69, 25.53. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 221.0808, found: 221.0806.



**2-acetyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (3aa)**

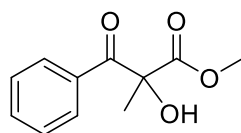
Colorless oil;  $R_f = 0.43$  (petroleum ether : EtOAc = 10 : 1); 81% (33.3 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 1H), 7.34 (t,  $J = 7.5$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 1H), 4.60 (s, 1H), 3.13-3.09 (m, 2H), 2.62-2.57

(m, 1H), 2.27 (s, 3H), 2.22-2.16 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  206.82, 196.61, 144.22, 134.51, 130.45, 128.97, 127.83, 126.93, 81.80, 32.35, 25.53, 25.01. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_3$  [ $\text{M} + \text{H}^+$ ]: 205.0859, found: 205.0857.



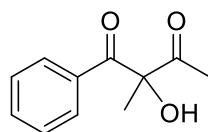
**diethyl 2-benzyl-2-hydroxymalonate (3ab)**

Colorless oil;  $R_f = 0.56$  (petroleum ether : EtOAc = 10 : 1); 83% (44.1 mg);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.20-7.16 (m, 5H), 4.18 (q,  $J = 7.2$  Hz, 4H), 3.67 (s, 1H), 3.28 (s, 2H), 1.21 (t,  $J = 7.2$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  169.91, 134.58, 130.34, 128.10, 127.13, 79.18, 62.57, 40.44, 14.00. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_5$  [ $\text{M} + \text{H}^+$ ]: 267.1227, found: 267.1222.



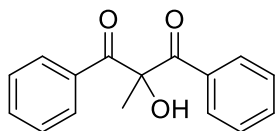
**methyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (3ac)**

Colorless oil;  $R_f = 0.45$  (petroleum ether : EtOAc = 10 : 1); 92% (38.5 mg);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.98 (d,  $J = 7.5$  Hz, 2H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.46 (t,  $J = 8.0$  Hz, 2H), 4.50 (s, 1H), 3.76 (s, 3H), 1.75 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  195.97, 172.65, 133.76, 132.98, 129.47, 128.67, 79.50, 53.26, 23.58. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 209.0808, found: 221.0804.



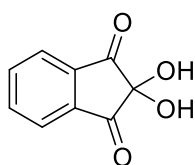
**methyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (3ad)**

Colorless oil;  $R_f = 0.41$  (petroleum ether : EtOAc = 10 : 1); 78% (30 mg);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J = 8.0$  Hz, 2H), 7.57 (t,  $J = 7.5$  Hz, 1H), 7.44 (t,  $J = 7.5$  Hz, 2H), 4.95 (s, 1H), 2.21 (s, 3H), 1.69 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  206.53, 197.97, 133.85, 133.68, 129.82, 128.66, 85.85, 24.73, 23.46. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_3$  [ $\text{M} + \text{H}^+$ ]: 193.0859, found: 193.0857.



### 2-hydroxy-2-methyl-1,3-diphenylpropane-1,3-dione (3ae)

White solid; m. p.: 103–106 °C; 29% (15.0 mg), 26% (13.4 mg), 74% (37.4 mg); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.2 Hz, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 4H), 5.25 (s, 1H), 1.83 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 197.75, 133.86, 133.81, 133.59, 129.65, 128.74, 128.42, 84.17, 25.52. HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> [M + H<sup>+</sup>]: 255.1016, found: 255.1013.



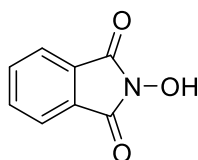
### 2,2-dihydroxy-1H-indene-1,3(2H)-dione (3af)

Red solid; m. p.: 241–247 °C (capillary tube measurement, easy sublimation of slides); 86% (30.7 mg); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.07-8.02 (m, 4H), 7.52 (s, 2H).

**3af** <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 197.02, 138.49, 137.22, 123.87, 87.61.

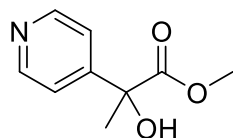
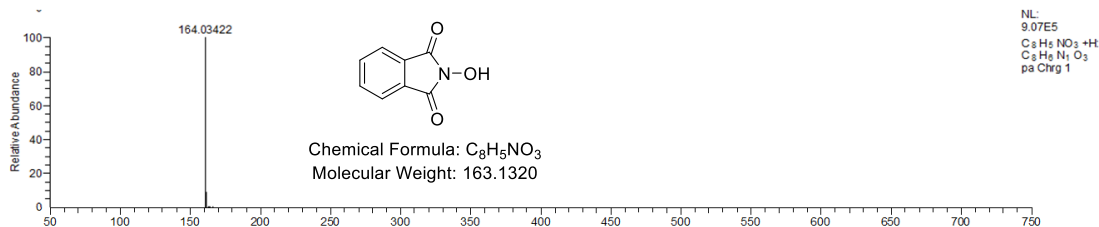
**3ag** <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 1186.81, 183.47, 140.01, 136.53, 123.75.

HRMS (ESI): *m/z* calcd for C<sub>9</sub>H<sub>6</sub>O<sub>4</sub> [M + H<sup>+</sup>]: 179.0336, found: 179.0339.



### 2-hydroxyisoindoline-1,3-dione (3ah <5% (by HRMS))

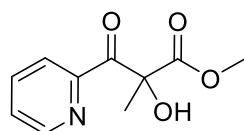
HRMS (ESI): *m/z* calcd for C<sub>8</sub>H<sub>5</sub>NO<sub>3</sub> [M + H<sup>+</sup>]: 164.03420, found: 164.03422.



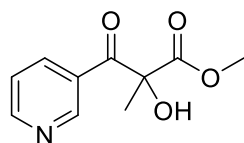


**methyl 2-hydroxy-2-(pyridin-4-yl)propanoate (5a)**

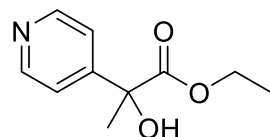
Colorless oil;  $R_f = 0.47$  (petroleum ether : EtOAc = 5 : 1); 80% (29.0 mg), 76% (27.4 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.61 – 8.60 (m, 2H), 7.52 – 7.50 (m, 2H), 4.09 (s, 1H), 3.82 (s, 3H), 1.79 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  174.91, 151.49, 149.85, 120.34, 75.14, 53.58, 26.78. HRMS (ESI):  $m/z$  calcd for  $\text{C}_9\text{H}_{11}\text{NO}_3$  [ $\text{M} + \text{H}^+$ ]: 182.0812, found: 182.0809.

**methyl 2-hydroxy-2-methyl-3-oxo-3-(pyridin-2-yl)propanoate (5b)**

Colorless oil;  $R_f = 0.41$  (petroleum ether : EtOAc = 5 : 1); 83% (34.8 mg), 82% (34.3 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.60 (d,  $J = 4.5$  Hz, 1H), 8.12 (d,  $J = 8.0$  Hz, 1H), 7.92 (t,  $J = 7.5$  Hz, 1H), 7.53-7.50 (m, 1H), 5.39 (s, 1H), 3.68 (s, 3H), 1.69 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  193.92, 172.93, 151.00, 148.20, 137.82, 127.58, 123.63, 79.10, 52.58, 21.21. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_{11}\text{NO}_4$  [ $\text{M} + \text{H}^+$ ]: 210.0761, found: 210.0759.

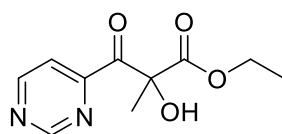
**methyl 2-hydroxy-2-methyl-3-oxo-3-(pyridin-2-yl)propanoate (5c)**

Colorless oil;  $R_f = 0.41$  (petroleum ether : EtOAc = 5 : 1); 82% (34.2 mg), 79% (33.3 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  9.20 (d,  $J = 1.5$  Hz, 1H), 8.76-8.74 (m, 1H), 8.33-8.31 (m, 1H), 7.42-7.39 (m, 1H), 4.96 (s, 1H), 3.79 (s, 3H), 1.75 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  194.83, 172.75, 153.31, 150.57, 136.99, 129.48, 123.43, 80.12, 53.48, 23.40. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{10}\text{H}_{11}\text{NO}_4$  [ $\text{M} + \text{H}^+$ ]: 210.0761, found: 210.0758.

**ethyl 2-hydroxy-2-(pyridin-4-yl)propanoate (5d)**

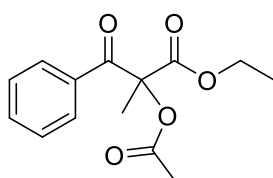
white solid; m. p.: 121–123 °C; 86% (33.5 mg), 81% (31.7 mg);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.58 (d,  $J = 5.6$  Hz, 2H), 7.52 (d,  $J = 6.0$  Hz, 2H), 4.30 – 4.21 (m, 2H), 4.09 (s, 1H), 1.77 (s, 3H), 1.27 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,

Chloroform-*d*)  $\delta$  174.38, 151.75, 149.67, 120.37, 74.97, 62.85, 26.76, 13.95. HRMS (ESI):  $m/z$  calcd for  $C_{10}H_{13}NO_3$  [ $M + H^+$ ]: 196.0968, found: 196.0964.



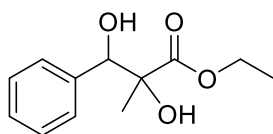
**ethyl 2-hydroxy-2-methyl-3-oxo-3-(pyrimidin-4-yl)propanoate (5e)**

Colorless oil;  $R_f$  = 0.31 (petroleum ether : EtOAc = 5 : 1); 89% (39.8 mg); 86% (37.9 mg);  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  9.29 (s, 1H), 9.06 (d,  $J$  = 5.0 Hz, 1H), 7.98 – 7.97 (m, 1H), 4.66 (s, 1H), 4.21 (q,  $J$  = 7.0 Hz, 2H), 1.69 (s, 3H), 1.14 (t,  $J$  = 7.0 Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*)  $\delta$  193.54, 171.99, 159.88, 157.88, 156.73, 118.97, 78.50, 62.14, 21.05, 13.83. HRMS (ESI):  $m/z$  calcd for  $C_{10}H_{12}N_2O_4$  [ $M + H^+$ ]: 225.0870, found: 225.0868.



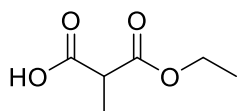
**ethyl 2-acetoxy-2-methyl-3-oxo-3-phenylpropanoate (6)**

Colorless oil;  $R_f$  = 0.36 (petroleum ether : EtOAc = 10 : 1); 89% (117.6 mg);  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.50 – 7.47 (m, 1H), 7.45 – 7.42 (m, 2H), 7.23 – 7.21 (m, 2H), 4.28 (q,  $J$  = 7.0 Hz, 2H), 2.45 (s, 3H), 1.71 (s, 3H), 1.27 (t,  $J$  = 7.0 Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*)  $\delta$  194.35, 168.80, 168.60, 166.90, 130.90, 129.28, 128.86, 127.60, 127.47, 86.74, 63.17, 30.40, 20.31, 13.89. HRMS (ESI):  $m/z$  calcd for  $C_{14}H_{16}O_5$  [ $M + H^+$ ]: 265.1071, found: 265.1063.



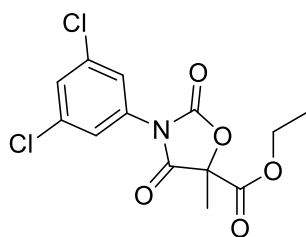
**ethyl 2,3-dihydroxy-2-methyl-3-phenylpropanoate (7)**

Colorless oil;  $R_f$  = 0.36 (petroleum ether : EtOAc = 10 : 1); 85% (95.2 mg);  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.32-7.27 (m, 5H), 4.73 (s, 1H), 4.13 – 3.99 (m, 2H), 3.44 (s, 1H), 3.12 (s, 1H), 1.54 (s, 3H), 1.17 (t,  $J$  = 7.0 Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*)  $\delta$  174.57, 139.19, 128.19, 128.00, 127.02, 78.04, 77.56, 61.96, 22.57, 13.89. HRMS (ESI):  $m/z$  calcd for  $C_{12}H_{16}O_4$  [ $M+H^+$ ]: 225.1121, found: 225.1116.



**ethyl 2,3-dihydroxy-2-methyl-3-phenylpropanoate (9)**

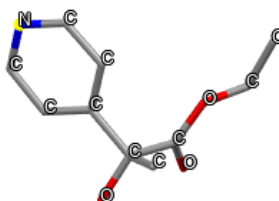
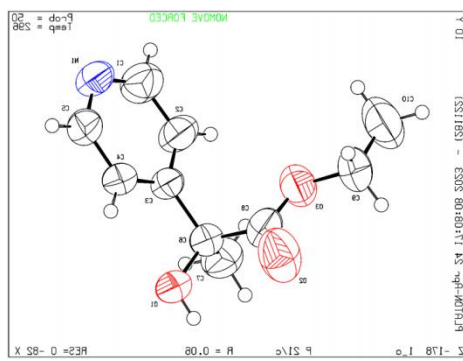
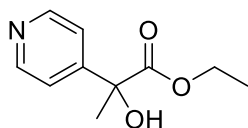
Colorless oil;  $R_f = 0.36$  (petroleum ether : EtOAc = 10 : 1); 93% (1.72 g);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  10.41 (s, 1H), 4.23 (q,  $J = 7.0$  Hz, 2H), 3.48 (q,  $J = 7.5$  Hz, 1H), 1.46 (d,  $J = 7.5$  Hz, 3H), 1.29 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  175.75, 169.89, 61.73, 45.90, 13.96, 13.53. HRMS (ESI):  $m/z$  calcd for  $\text{C}_6\text{H}_{10}\text{O}_4$  [ $\text{M} + \text{H}^+$ ]: 499.0652, found: 147.0648.



**ethyl 3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxazolidine-5-carboxylate (10)**

white solid; m. p.: 127.0–131.0°C; 70% (58.2 mg);  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.46–7.44 (m, 3H), 4.34 (q,  $J = 7.0$  Hz, 2H), 1.90 (s, 3H), 1.34 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz, Chloroform-*d*)  $\delta$  168.39, 164.05, 151.91, 135.72, 132.37, 129.33, 123.71, 83.89, 63.94, 18.80, 13.93. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{NO}_5$  [ $\text{M} + \text{H}^+$ ]: 332.0087, found: 332.0081.

#### 4. X-ray Single Crystal Diffraction Data of 5d (CCDC 2305770)



Bond precision: C-C = 0.0055 Å      Wavelength=0.71073

Cell:                    a=12.712 (3)      b=5.7373 (15)      c=15.256 (4)  
                               alpha=90            beta=112.177 (5)      gamma=90

Temperature:            296 K

|                        | Calculated   | Reported     |
|------------------------|--------------|--------------|
| Volume                 | 1030.4 (5)   | 1030.4 (5)   |
| Space group #          | P 21/c       | P 21/c       |
| Hall group             | -P 2ybc      | -P 2ybc      |
| Moiety formula         | C10 H13 N O3 | ?            |
| Sum formula            | C10 H13 N O3 | C10 H13 N O3 |
| Mr                     | 195.21       | 195.21       |
| Dx, g cm <sup>-3</sup> | 1.258        | 1.258        |
| Z                      | 4            | 4            |
| Mu (mm <sup>-1</sup> ) | 0.093        | 0.093        |
| F000                   | 416.0        | 416.0        |
| F000'                  | 416.22       |              |
| h, k, lmax             | 15, 6, 18    | 15, 6, 18    |
| Nref                   | 1820         | 1812         |
| Tmin, Tmax             | 0.980, 0.983 | 0.864, 0.864 |
| Tmin'                  | 0.980        |              |

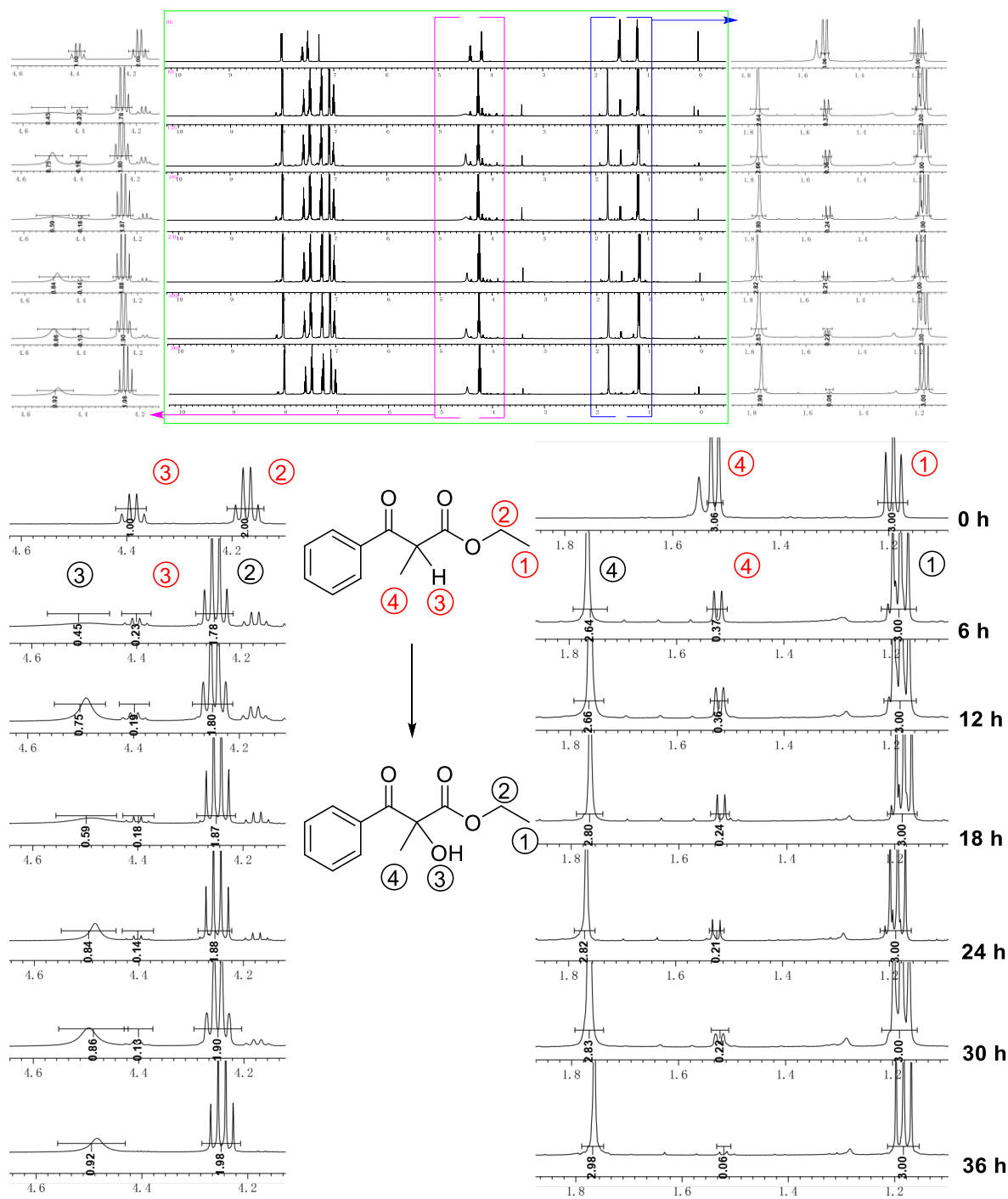
Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864  
 AbsCorr = MULTI-SCAN

Data completeness= 0.996      Theta(max)= 25.000

R(reflections)= 0.0642( 798)      wR2(reflections)=  
 0.2100( 1812)

S = 0.991      Npar= 130

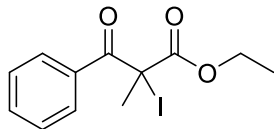
## 5. H-NMR determination of reaction processes



From the H-NMR spectra, it can be seen that when the reaction reaches 6 h, the position of feedstock ④ shows a conversion of 87.9%, the position of product ④ shows a conversion of 88.0%, the position of product ② shows a conversion of 89.0%, the position of feedstock ③ shows a conversion of 77.0%, and the position of product ③ shows a conversion of only 45%, so we speculate that, when the mixture is reacted for 6 h, there is approximately 30% of intermediate **G** was not converted to product **3a**, and this step of conversion was relatively slow. When the

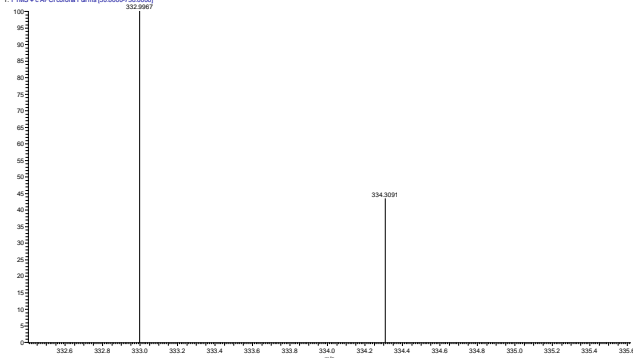
mixture was reacted for 12 hours, only the position of product ③ showed an increase of 30% conversion compared to 6 hours, which corresponds to the amount of NaI we added.

After six hours of reaction, the mixture was concentrated under reduced pressure. The free radical **G** was captured by HRMS detection.



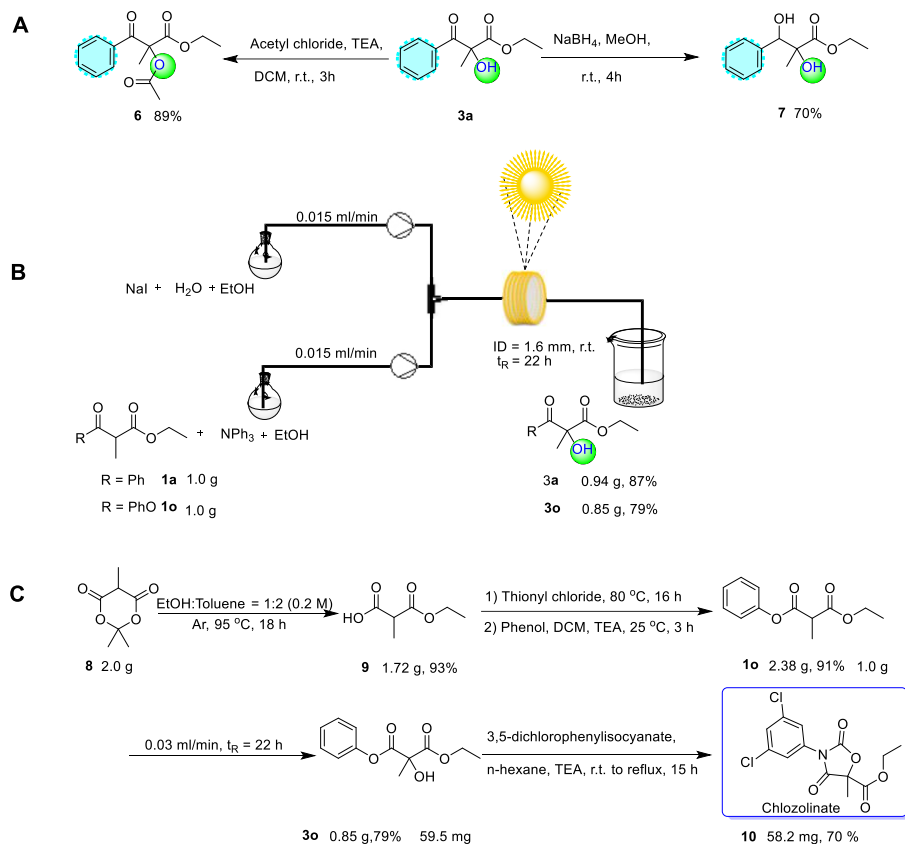
HRMS (ESI):  $m/z$  calcd for  $C_{12}H_{13}IO_3$   $[M + H^+]$ : 332.9982, found: 332.9967.

4\_20231121164317\_#23 RT: 0.23 AV: 1 SB: 5 0.10-0.17 NL: 8.44E5  
T: FTMS + e-APCI cosine Full.ms [50.0000-750.0000]



|  |                                     |             |     |
|--|-------------------------------------|-------------|-----|
| Chemical formula                                 | <input checked="" type="radio"/>    | C12H13IO3   | ▼   |
| Peptide/Protein                                  | <input type="radio"/>               |             | ▼   |
| Plus H2O   | <input checked="" type="checkbox"/> | 332.9982138 | amu |
| <input type="button" value="Change mixture..."/> |                                     |             |     |
| <input checked="" type="checkbox"/> Adduct       |                                     |             |     |
| Identity   | H ▼                                 |             |     |
| Concentration                                    | One ▼                               |             |     |
| Charge distribution                              |                                     |             |     |
| Most abundant :                                  | 1 ▲▼                                |             |     |

## 6. General applicability



### A

To a 50 mL round-bottom flask was charged with ethyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (0.5 mmol, 1.0 equiv.), TEA (1.0 mmol, 2.0 equiv.), DCM (5 mL) add acetyl chloride (0.55 mmol, 1.1 equiv.) in a slow trickle and finish the trickle in 5 min at 0 °C. The resulting mixture was stirred for additional 3 h at 30 °C. The reaction progress was monitored by TLC. After completion, the mixture was quenched with water and sat. Na<sub>2</sub>CO<sub>3</sub> (20 mL), and extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to afford ethyl 2-acetoxy-2-methyl-3-oxo-3-phenylpropanoate (117.6 mg, 89%) as a Colorless oily liquid.

Add NaBH<sub>4</sub> (7.5 mmol) to a solution of ethyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (0.5 mmol) in MeOH (5 mL) in a 25 mL flask under air atmosphere. Stir the reaction mixture at room temperature for 4 hours. Monitor

the reaction by TLC. Upon completion, add HCl (1M, 5 mL) into the reaction mixture, extract the forming alcohol with ethyl acetate (3 × 10 mL) from the reaction mixture. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to afford ethyl 2,3-dihydroxy-2-methyl-3-phenylpropanoate (78.4 mg, 70%) as a Colorless oily liquid.

## B



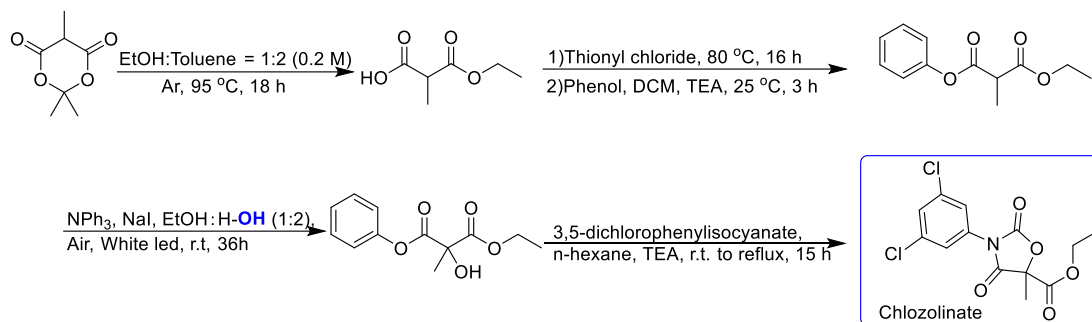
Equipment: Pumps from the brand sanota, tubular reactor from SHENZHEN E-ZHENG TECH CO., LTD, light source for 60W white light (6000-6500 K) from Taobao APP Shenzhen Yu Xiang Technology Development Co.

Solution A consisting ethyl 2-methyl-3-oxo-3-phenylpropanoate **1a** (4.85 mmol, 0.1 M), NPh<sub>3</sub> (20 mmol %) in EtOH (48.5 mL) and solution B consisting NaI (30 mmol %, 0.03 M) in EtOH:H<sub>2</sub>O = 4:1 (48.5 mL) were prepared separately. Each channel, containing a flowing stream, was pumped at 0.015 mL/min (a total of 0.03 mL/min). Both streams were mixed in a Y-mixer and flowing into tubular reactor (*The tubular reactor is made up of coiled FEP tubing (1/8" OD, 1.6mm ID) with a total volume of 40 mL*), which was kept under 60 W white LED irradiation at 25 °C. The reaction retention time is 22 hours. After leaving the flow system, the crude reaction mixture was collected into a 250 mL glass vial. The resulting mixture was concentrated under vacuum. After completion, the mixture was quenched with water (20 mL), and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give ethyl



2-hydroxy-2-methyl-3-oxo-3- phenylpropanoate **3a** (0.94 g, 87%). The same method is used to obtain **3o** (0.85 g, 79%).

**C**



### 3-ethoxy-2-methyl-3-oxopropanoic acid

To a degassed solution of 2,2,5-trimethyl-1,3-dioxane-4,6-dione (12.66 mmol, 1.0 equiv.) in EtOH:Toluene=1:2 (0.1 M) . The resulting mixture was stirred for 18 h at 95 °C under argon atmosphere. After completion of the reaction. Afer completion of was concentrated add H<sub>2</sub>O and sat.NaHCO<sub>3</sub> (20 mL) to the mixture upon completion of the reaction. Extract the mixture with EtOAc (5 mL x 3). Discard the organic layer. Acidify the aqueous layer with conc. HCl (until pH = 2). Extract the mixture with EtOAc (20 mL x 3). Wash the combined organic layer with brine (5 mL x 1). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to obtain the product 3-ethoxy-2-methyl-3-oxopropanoic acid (1.72 g, 93%) as a Colorless oily liquid.

### 1-ethyl 3-phenyl 2-methylmalonate

To a 50 mL round-bottom flask was charged with 3-ethoxy-2-methyl-3-oxopropanoic acid (11.77mmol, 1.0 equiv.), Thionyl chloride (10 mL). The resulting mixture was stirred for 16 h at 80 °C. The resulting mixture was concentrated under vacuum. To the above mixture was added DCM (20 mL), Phenol (12.95 mmol, 1.1 equiv.) and in porions TEA (23.54 mmol, 2.0 equiv.) over 5min at 0 °C. The resulting mixtur was stirred for additional 3 h at 25 °C. The reaction progress was monitored by TLC. After completion, the mixture was quenched with water and sat.Na<sub>2</sub>CO<sub>3</sub> (20 mL), and extracted with dichloromethane (10 mL x 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl

acetate/petroleum ether to afford 1-ethyl 3-phenyl 2-methylmalonate (2.38 g, 91%) as a Colorless oily liquid.

### **1-ethyl 3-phenyl 2-hydroxy-2-methylmalonate**

To a 25 mL quartz tube was charged with 1-ethyl 3-phenyl 2-methylmalonate (0.2 mmol, 1.0 equiv.),  $\text{NPh}_3$  (20 mmol %),  $\text{NaI}$  (30 mmol %) and  $\text{EtOH:H}_2\text{O} = 1:2$  (2 mL). Then the mixture was stirred for 36 h under 10 W white LED irradiation at room temperature. After completion, the mixture was quenched with water (5 mL), and extracted with ethyl acetate (10 mL  $\times$  3). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give 1-ethyl 3-phenyl 2-hydroxy-2-methylmalonate (39.15 mg, 83%).

Solution A consisting 1-ethyl 3-phenyl 2-methylmalonate (4.5 mmol, 0.1 M),  $\text{NPh}_3$  (20% mmol) in  $\text{EtOH}$  (45 mL) and solution B consisting  $\text{NaI}$  (30% mmol, 0.03 M) in  $\text{EtOH:H}_2\text{O} = 4:1$  (45 mL) were prepared separately. Each channel, containing a flowing stream, was pumped at 0.015 mL/min (a total of 0.03 mL/min). Both streams were mixed in a Y-mixer and flowing into tubular reactor (The tubular reactor is made up of coiled FEP tubing (1/8" OD, 1.6mm ID) with a total volume of 40 mL), which was kept under 60 W white LED irradiation at 25 °C. The reaction retention time is 22 hours. After leaving the flow system, the crude reaction mixture was collected into a 250 mL glass vial. The resulting mixture was concentrated under vacuum. After completion, the mixture was quenched with water (20 mL), and extracted with ethyl acetate (20 mL  $\times$  3). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give 1-ethyl 3-phenyl 2-hydroxy-2-methylmalonate (0.85 g, 79%).

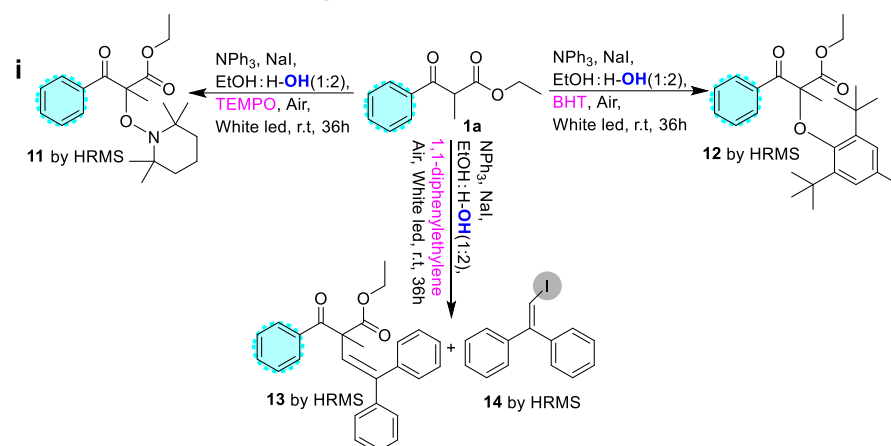
### **ethyl 3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxoxazolidine-5-carboxylate**

A solution of malonic ester 1-ethyl 3-phenyl 2-hydroxy-2-methylmalonate (59.5 mg, 0.25 mmol) in dry n-hexane (10.0 mL) was treated, under  $\text{N}_2$ , with triethylamine (25.3 mg, 0.25 mmol) and 3,5-dichlorophenylisocyanate (70.7

mg, 0.375 mmol). After stirring at rt for 30 min, the reaction mixture was refluxed for overnight (16 h). After cooling, the suspension was filtered and the filtrate evaporated to dryness, the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give ethyl 3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate as a white solid (58.2 mg, 70%).

## 7. Mechanism Exploration

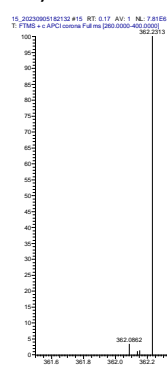
### 1.1 Free radical trapping experiments



Reaction conditions: **1a** (0.1 mmol, 1 equiv.),  $\text{NPh}_3$  (20 mmol %), NaI (30 mmol %), radical trapping agent (0.1 mmol, 1 equiv.) in EtOH:H<sub>2</sub>O = 1:2 (2 mL) were stirred under air for 36 hours at room temperature under the irradiation of a 10 W white LED (6000-6500 K).

In the presence of TEMPO, BHT and 1,1-diphenylethylene, the reaction did not yield the desired product **3a**. However, the generation of **11**, **12**, **13** and **14** was detected from the reaction solution, proving that the reaction was a radical reaction and that iodine radicals and intermediate **E** (Scheme 8), were generated.

**11)**



Chemical formula  C21H31NO4

Peptide/Protein

Plus H2O  362.2325850 amu

Adduct

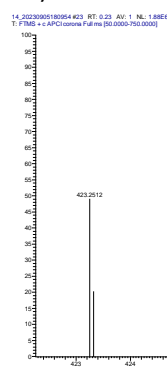
Identity H

Concentration One

Charge distribution

Most abundant : 1

**12)**



Chemical formula  C27H36O4

Peptide/Protein

Plus H2O  425.2686361 amu

Adduct

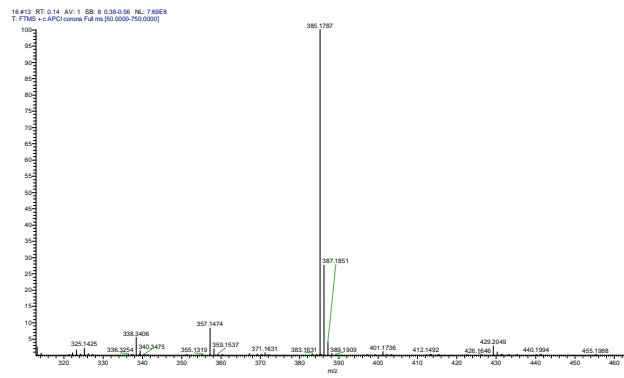
Identity H

Concentration One

Charge distribution

Most abundant : 1

13)



Chemical formula  C26H24O3

Peptide/Protein

Plus H2O  385.1798212 amu

Adduct

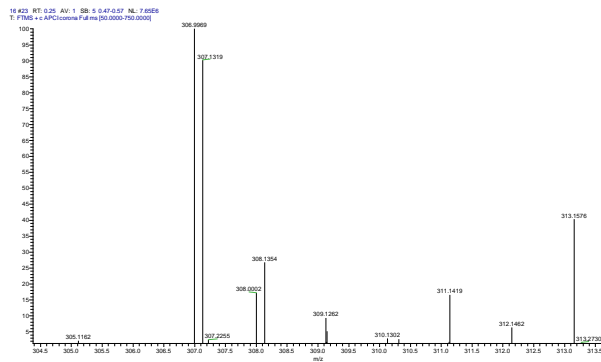
Identity H

Concentration One

Charge distribution

Most abundant : 1

14)



Chemical formula  C14H11I

Peptide/Protein

Plus H2O  306.9978200 amu

Adduct

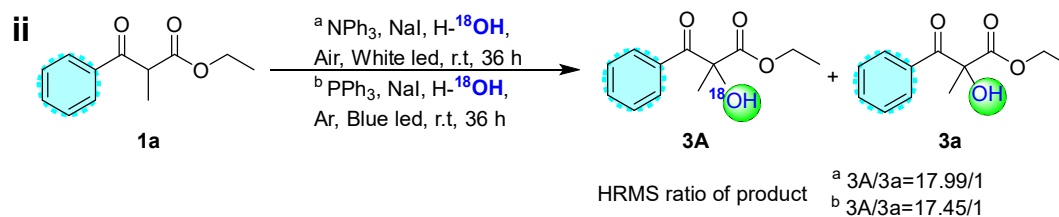
Identity H

Concentration One

Charge distribution

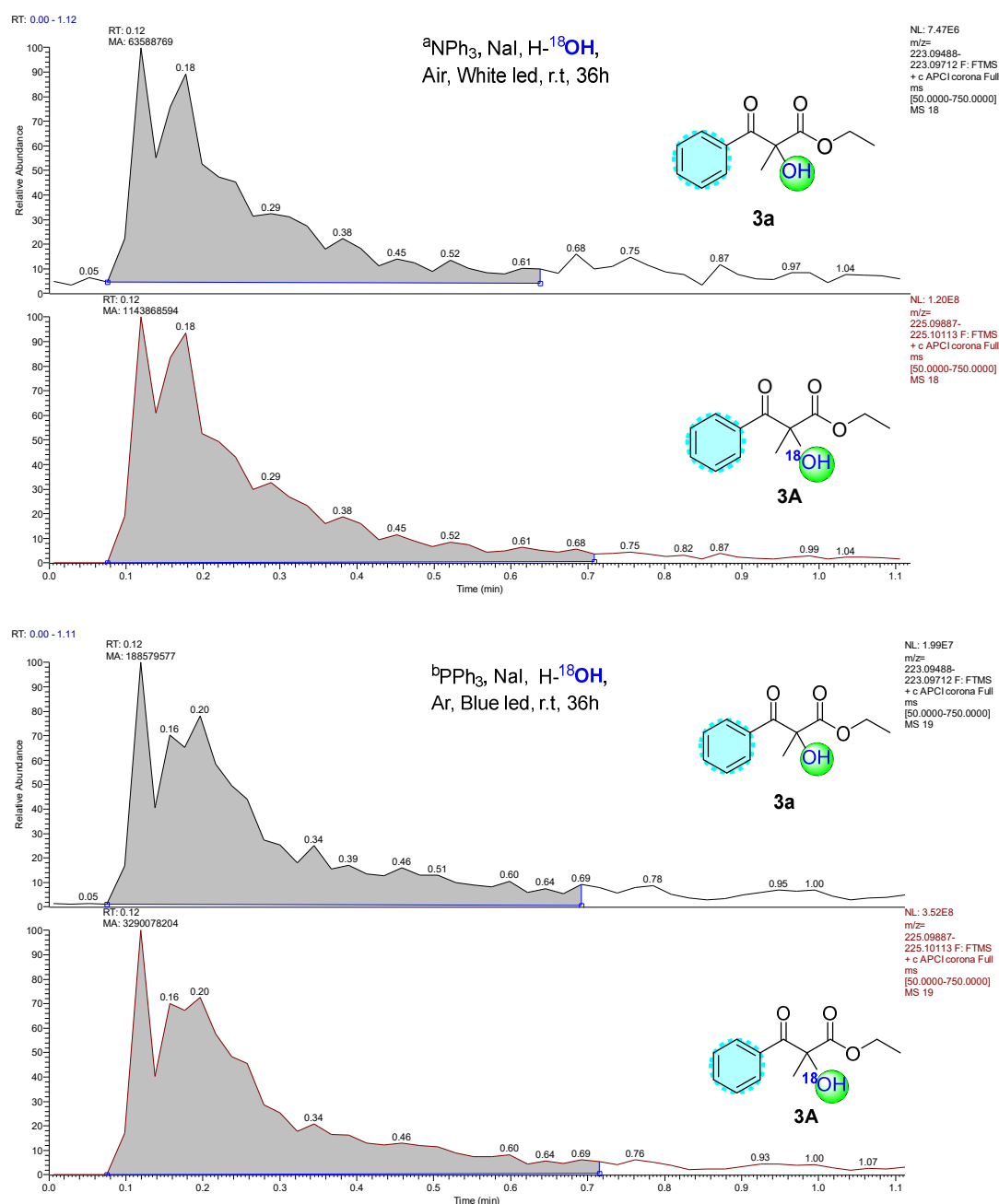
Most abundant : 1

## 1.2 Labeling experiments



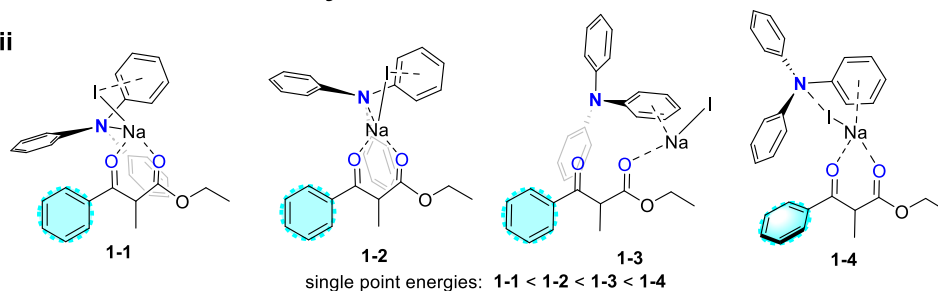
Reaction conditions: <sup>a</sup> **1a** (0.1 mmol), NPh<sub>3</sub> (20 mmol %), NaI (0.11 mmol), H<sub>2</sub><sup>18</sup>O (2 mL), argon, 36 h, r.t., 10 W white LED (6000-6500 k); <sup>b</sup> **1a** (0.1 mmol), PPh<sub>3</sub> (20 mmol %), NaI (30 mmol %), H<sub>2</sub><sup>18</sup>O (2 mL), air, 36 h, r.t., 10 W blue LED (455 nm).

The <sup>18</sup>OH was determined in reaction solution by HRMS. The integral method was used by comparing <sup>18</sup>O and <sup>16</sup>O in HRMS. The data indicate that the hydroxyl group in product **3a** is from water and not air.

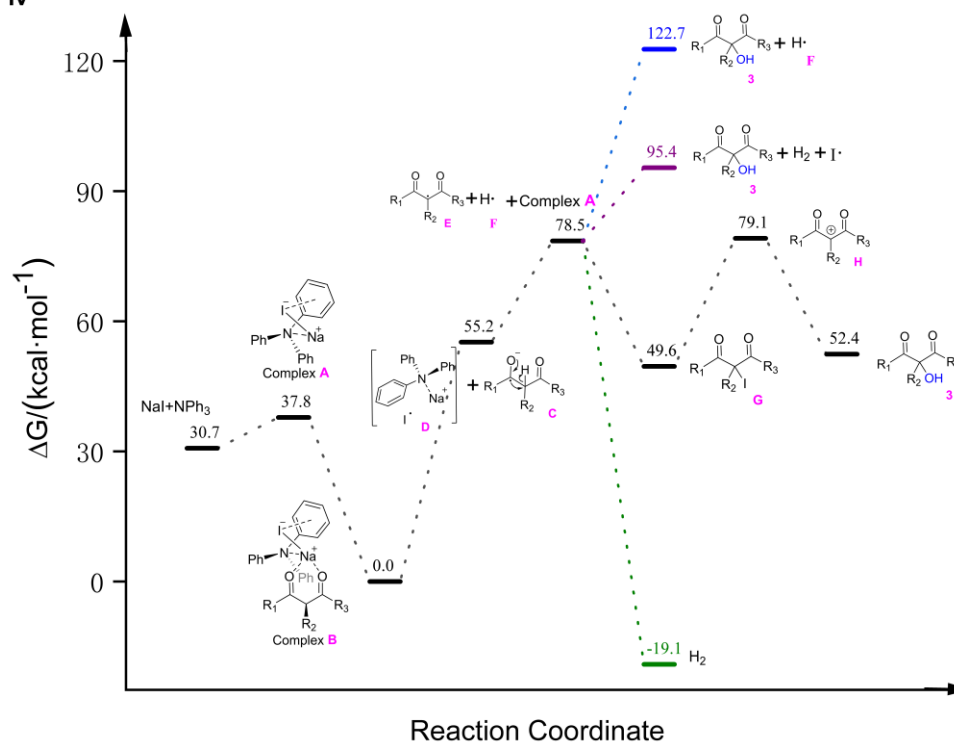


### 1.3 DFT calculations study

iii



iv



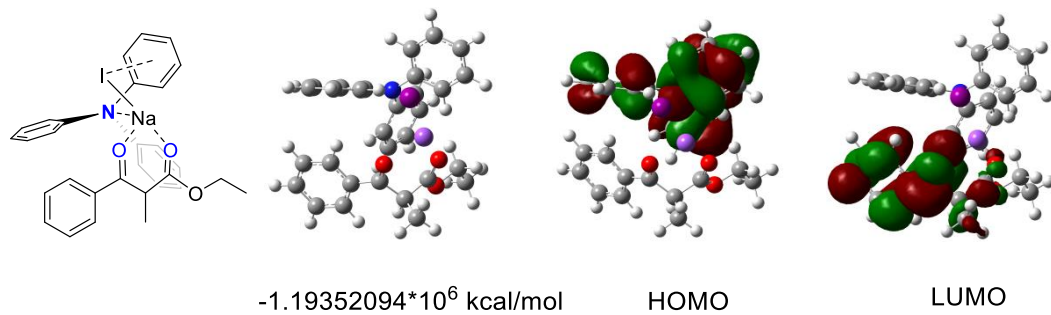
#### 1.3.1 Computational methods

DFT theoretical calculations have been carried out using the Gaussian 16 program package.<sup>8</sup> The B3LYP density functional method with the D3(BJ) dispersion correction was employed in this work to carry out all the computations.<sup>9</sup> Geometry optimizations and harmonic frequency calculations were performed with the SDD<sup>10</sup> basis set for I atom and 6-31g(d)<sup>11</sup> basis set for other elements. All structures have been optimized considering solvent effects using the PCM<sup>12</sup> model for water. The single-point energy calculations were carried out using the def2-TZVP basis set<sup>13</sup> to provide better energy correction. The relative free energies are given in kcal/mol.

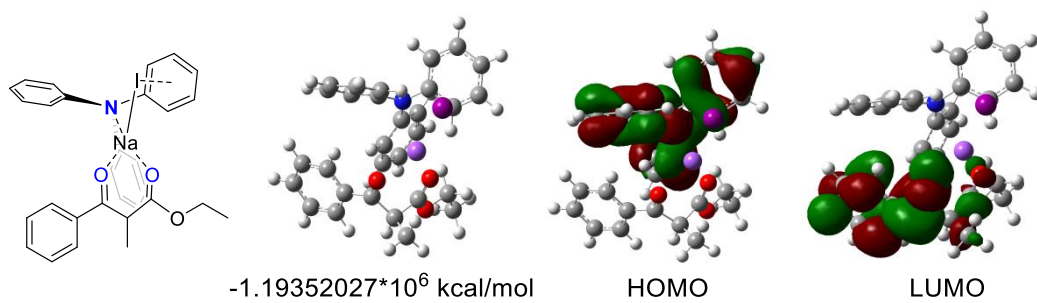
## 1.2 Calculated molecular orbitals and single point energies of EDA complexes in the S0 ground state

### i 1-NPh<sub>3</sub>-NaI EDA complex

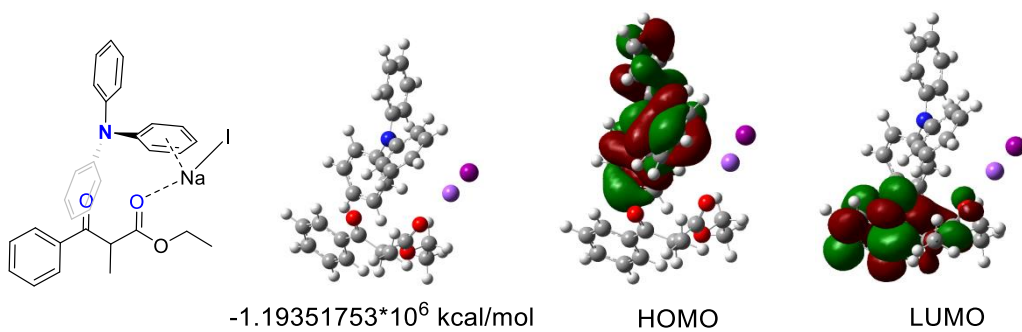
1-1



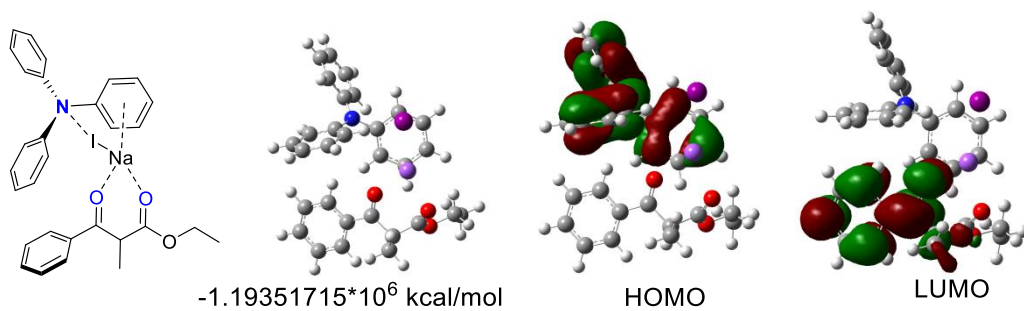
1-2



1-3



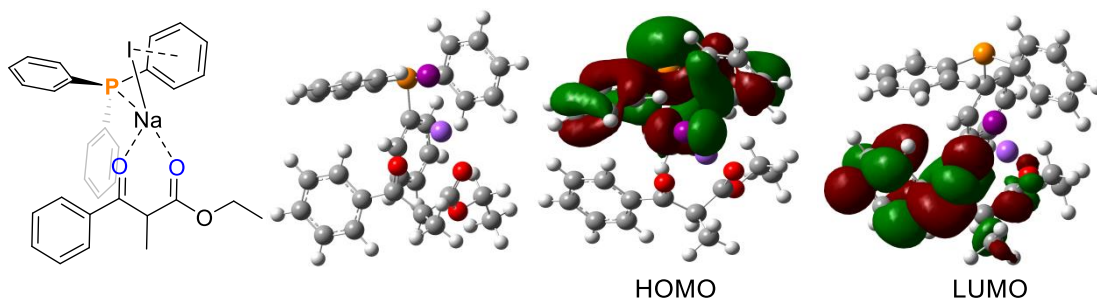
1-4



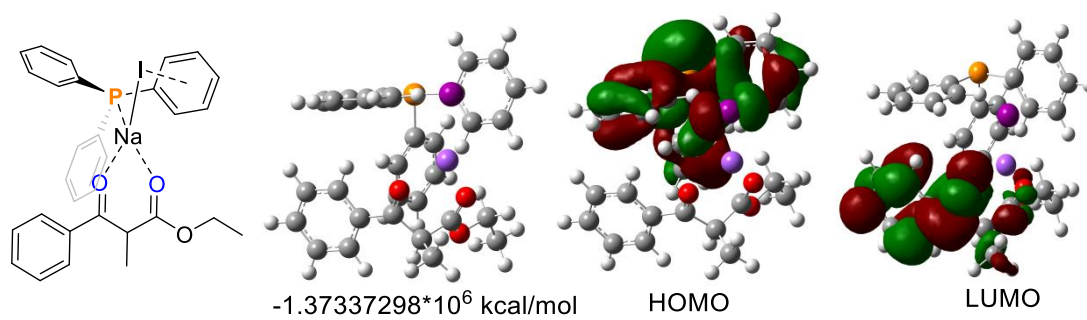


ii 1-PPh<sub>3</sub>-NaI EDA complex

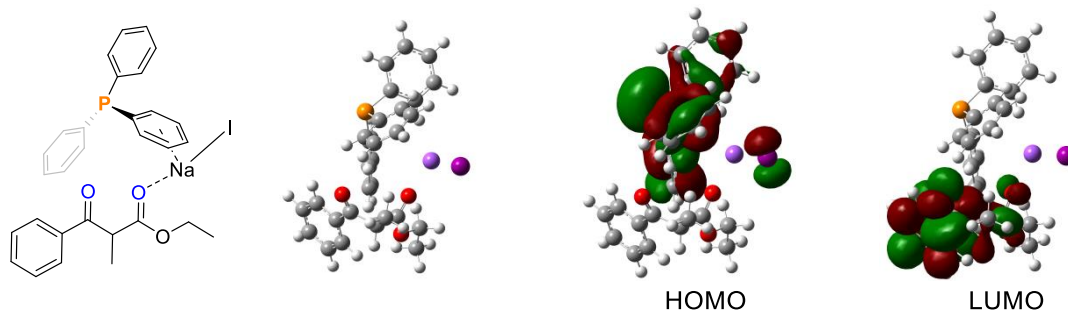
2-1



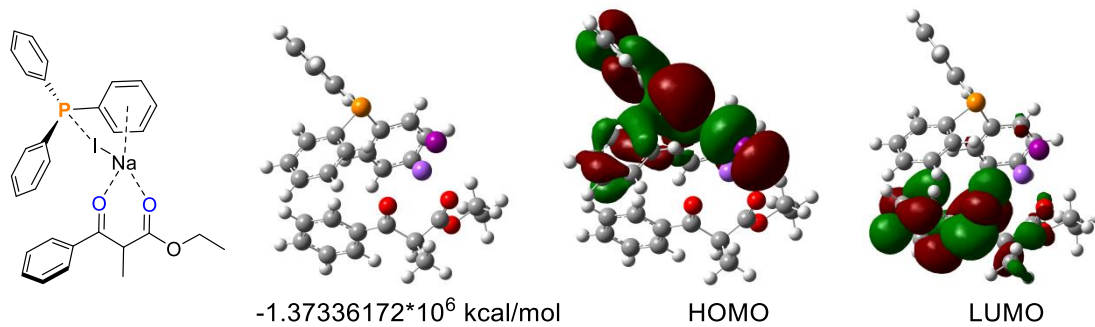
2-2



2-3

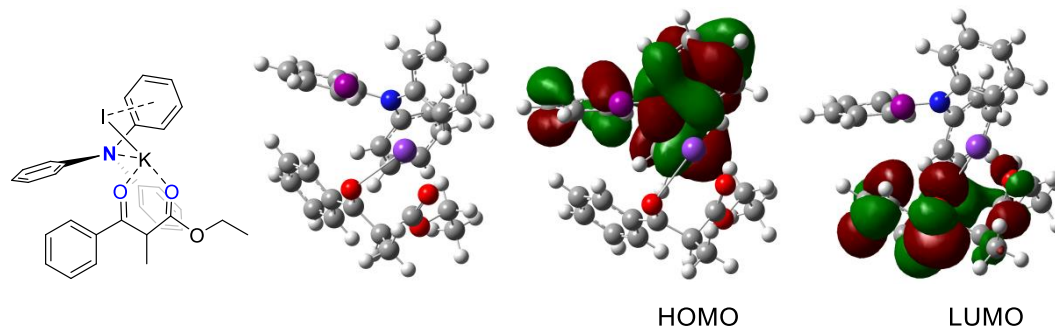


2-4

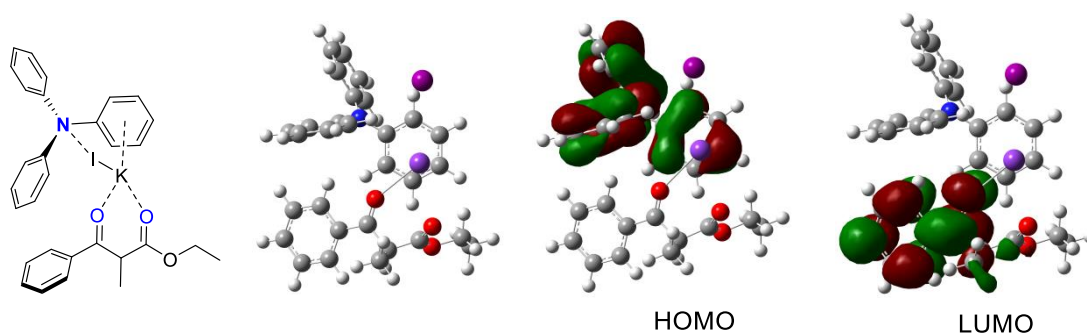


iii 1-NPh<sub>3</sub>-KI EDA complex

3-1



3-4

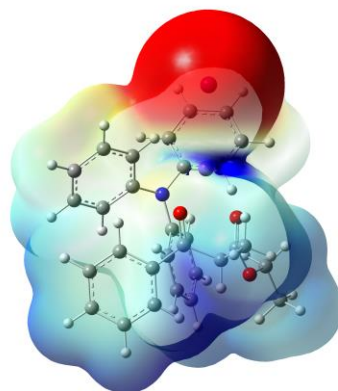


1-NPh<sub>3</sub>-NaI EDA complex (1-1) single point energies = -1901.99661427 Hartree

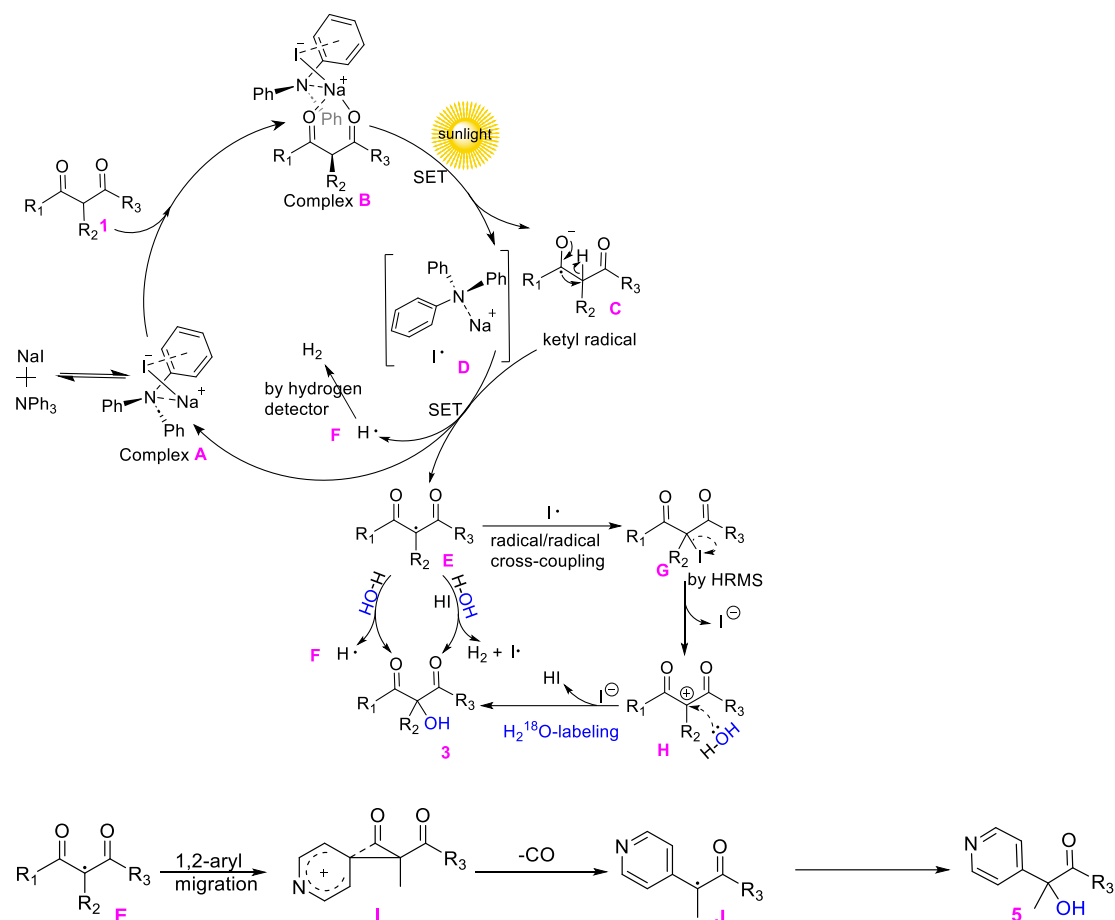
|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -3.64244100 | 4.18050800  | -0.53611400 |
| C | -4.29805700 | 3.46529300  | 0.46984300  |
| C | -3.59707300 | 2.53826300  | 1.24009500  |
| C | -2.22314700 | 2.32874700  | 1.01866300  |
| C | -1.57009900 | 3.06442600  | 0.00895300  |
| C | -2.27725700 | 3.97612900  | -0.76652900 |
| H | -4.19504900 | 4.89256100  | -1.14240100 |
| H | -5.35618100 | 3.62545300  | 0.65256800  |
| H | -4.12613600 | 1.99984100  | 2.01796700  |
| H | -0.51759900 | 2.88506000  | -0.17848900 |
| H | -1.76561800 | 4.51602900  | -1.55667400 |
| C | -1.41543200 | 1.34210200  | 1.77896900  |
| O | -0.18764600 | 1.33447500  | 1.68598300  |
| C | -2.09460500 | 0.30135100  | 2.68145300  |
| H | -3.17753700 | 0.40026400  | 2.65572500  |
| C | -1.59820100 | 0.46535000  | 4.13697500  |
| H | -1.87341400 | 1.45520000  | 4.51280900  |
| H | -2.06105100 | -0.28939600 | 4.77940300  |
| H | -0.51202000 | 0.35983000  | 4.18766700  |
| C | -1.76459500 | -1.10249900 | 2.18210700  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| O  | -0.63134400 | -1.52598800 | 1.99535100  |
| O  | -2.85916100 | -1.83013100 | 2.00815200  |
| C  | -2.67526400 | -3.20050600 | 1.53711800  |
| H  | -2.25461000 | -3.15088600 | 0.52981800  |
| H  | -1.96018500 | -3.69813500 | 2.19771100  |
| C  | -4.03717600 | -3.86145400 | 1.55553600  |
| H  | -4.73297200 | -3.32561500 | 0.90391500  |
| H  | -3.94558400 | -4.89008600 | 1.19183700  |
| H  | -4.44633200 | -3.88609900 | 2.57044900  |
| Na | 1.40337800  | -0.39782700 | 1.77203400  |
| N  | 0.06828700  | -0.77795500 | -1.91080800 |
| C  | -1.26176200 | -1.26945900 | -1.81182200 |
| C  | -1.59841100 | -2.53547800 | -2.31934100 |
| C  | -2.26376000 | -0.49066700 | -1.21128300 |
| C  | -2.90954800 | -3.00335900 | -2.22599500 |
| H  | -0.83193000 | -3.14581100 | -2.78580200 |
| C  | -3.57394900 | -0.95885900 | -1.13313700 |
| H  | -2.01490900 | 0.49081800  | -0.82891900 |
| C  | -3.90774000 | -2.21748000 | -1.64128500 |
| H  | -3.15315200 | -3.98374500 | -2.62603700 |
| H  | -4.32964900 | -0.33774300 | -0.66034400 |
| H  | -4.92838500 | -2.58280700 | -1.58026500 |
| C  | 1.16188200  | -1.65351100 | -1.67381700 |
| C  | 2.32264600  | -1.58039200 | -2.46107500 |
| C  | 1.09650300  | -2.60690000 | -0.64259000 |
| C  | 3.40283100  | -2.42347600 | -2.20144200 |
| H  | 2.37678000  | -0.85611200 | -3.26720400 |
| C  | 2.17743200  | -3.45525600 | -0.39917500 |
| H  | 0.20585800  | -2.66986700 | -0.02701800 |
| C  | 3.33980500  | -3.36656200 | -1.17075800 |
| H  | 4.29353100  | -2.35070800 | -2.81961200 |
| H  | 2.10932900  | -4.18338500 | 0.40490100  |
| H  | 4.18093600  | -4.02538700 | -0.97632500 |
| I  | 4.41779300  | 0.73659600  | 1.26674000  |
| C  | 0.29875900  | 0.58614800  | -2.23743100 |
| C  | -0.53649100 | 1.25010400  | -3.15238700 |
| C  | 1.36275300  | 1.29581500  | -1.65408600 |
| C  | -0.32573000 | 2.59485600  | -3.45379200 |
| H  | -1.35503900 | 0.71154100  | -3.61811700 |
| C  | 1.57580100  | 2.63612400  | -1.97523600 |
| H  | 2.03526000  | 0.80108600  | -0.96233100 |
| C  | 0.73103400  | 3.29953900  | -2.87010900 |
| H  | -0.98773300 | 3.08990200  | -4.15903500 |
| H  | 2.40317200  | 3.16445400  | -1.50867800 |

iv Electrostatic potential (ESP) analysis of **1-1** structure



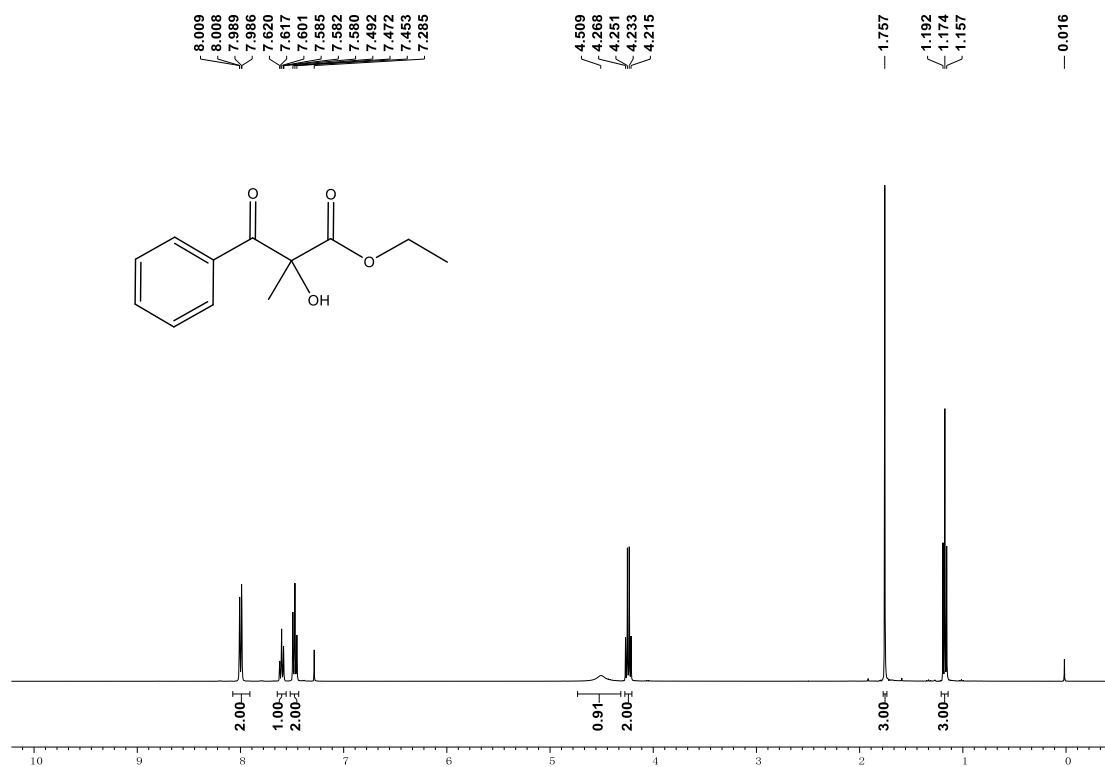
## 8. Proposed mechanism conclusions



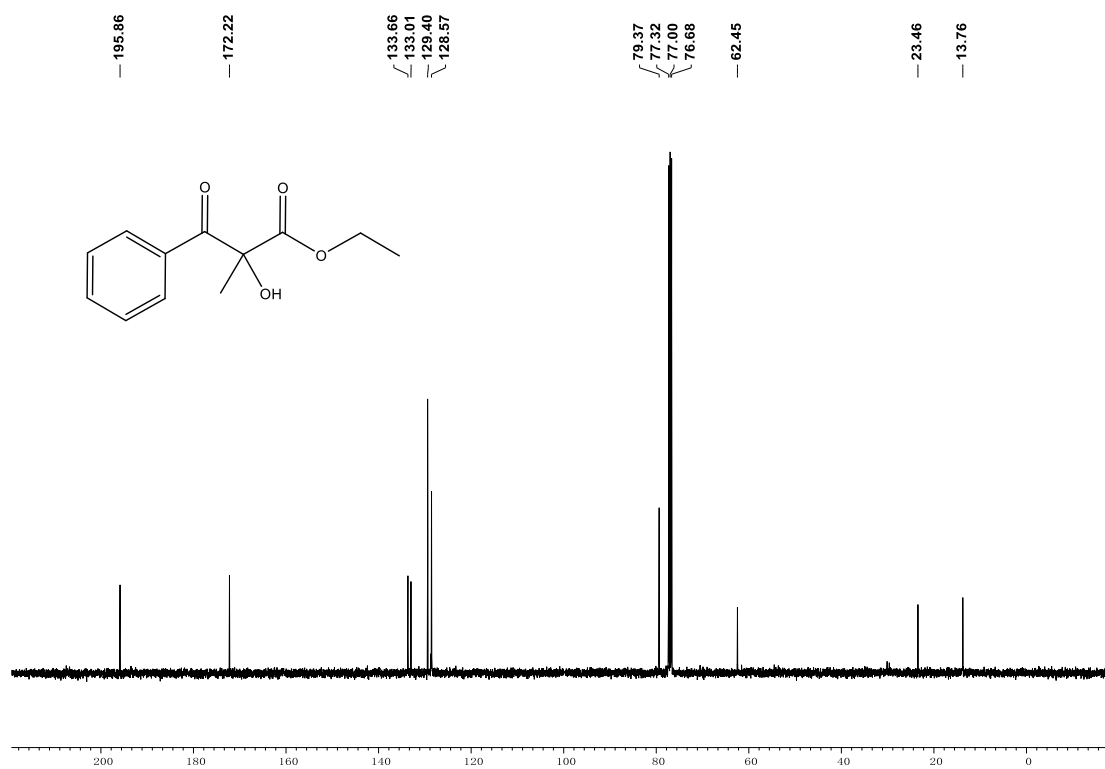
Based on mechanism study experiments and previous literatures, we propose a rational mechanism for this reaction (see Scheme 8 for proposed full catalytic cycles for NaI-NPh<sub>3</sub> EDA complex system). Preliminary density functional theory (DFT) calculations support the viability of this path way (Scheme 7, iv). Initially, NaI and NPh<sub>3</sub> form complex **A**, which in turn generates complex **B** with substrate **1**, which undergoes single electron transfer (SET) by light to produce iodine radical **D** and ketyl radical **C**. The free-energy barrier of 55.2 kcal/mol indicates that the process does not react spontaneously at ambient temperature and pressure, which is in agreement with the experimental photoexcitation. Subsequently, radicals **C** and **D** undergo radical rearrangement and single electron transfer (SET) to form the persistent radical **E**, complex **A**, and hydrogen radical **F**. The free energy barriers are shown to be able to proceed spontaneously. The Hydrogen Detector can detect hydrogen generation by **F**. DFT calculations indicate that radical **E** is more susceptible to **G** formation via **D** radical/radical cross-coupling (by HRMS) than direct hydration hydroxylation of radical **E** to product **3**. Intermediate **G** was then hydrolyzed to product **3** by SN1 reaction. However, when hydrolysis produces HI, it may prompt a shift from **E** to **3**. Unusually, when the R<sup>1</sup> substituent is *p*-pyridine, it generates the persistent radical **J** is formed by 1,2-aryl migration and elimination of one portion of the CO. Similarly, **J** undergoes radical/radical cross-coupling, dehalogenation, and hydration to form  $\alpha$ -hydroxy- $\beta$ -monocarbonyl **5**.

## 9. NMR spectra

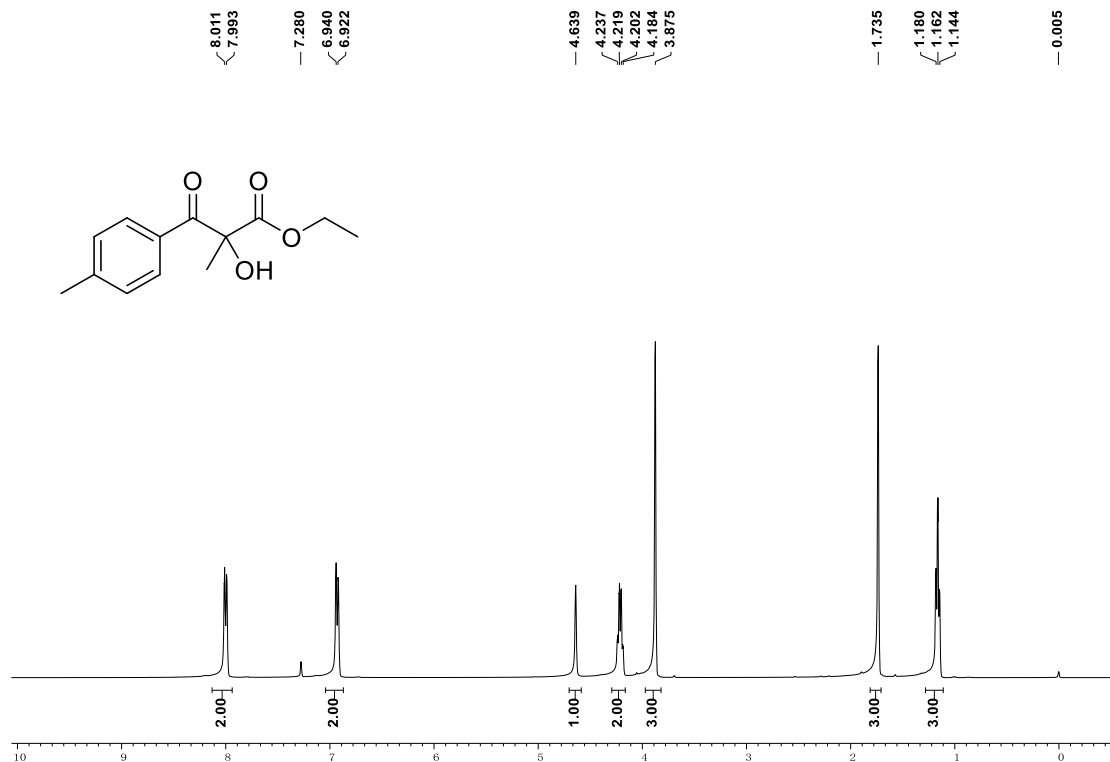
### 3a <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



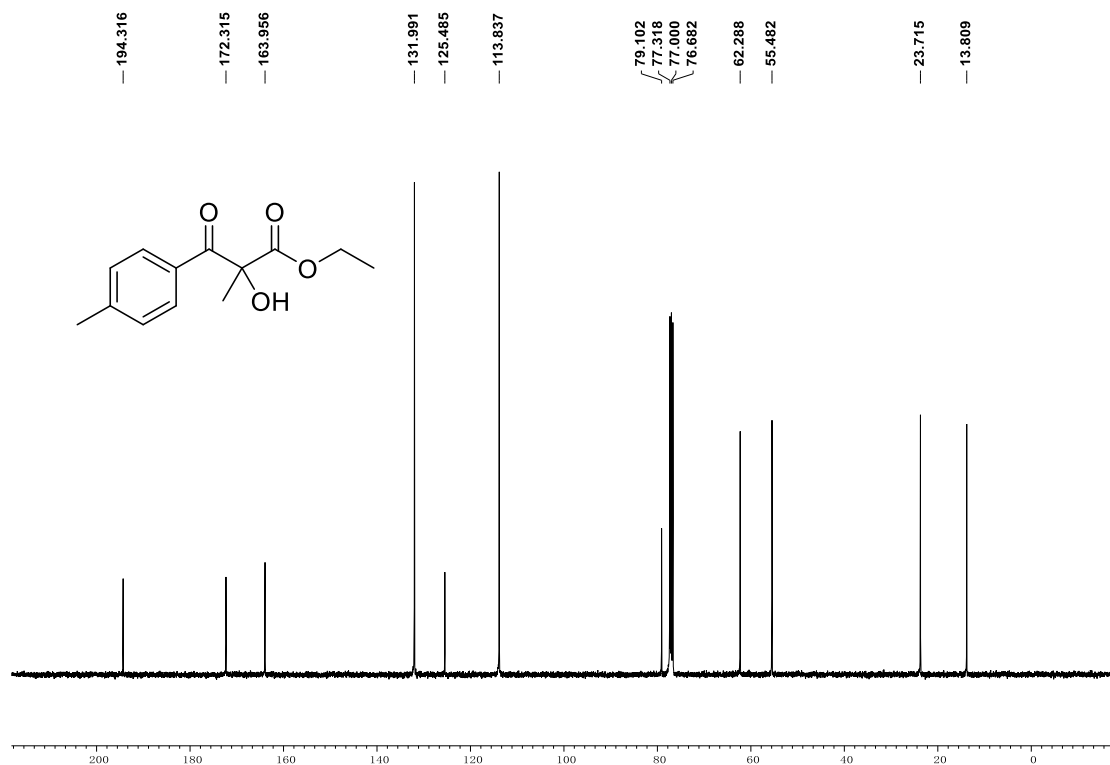
### 3a <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



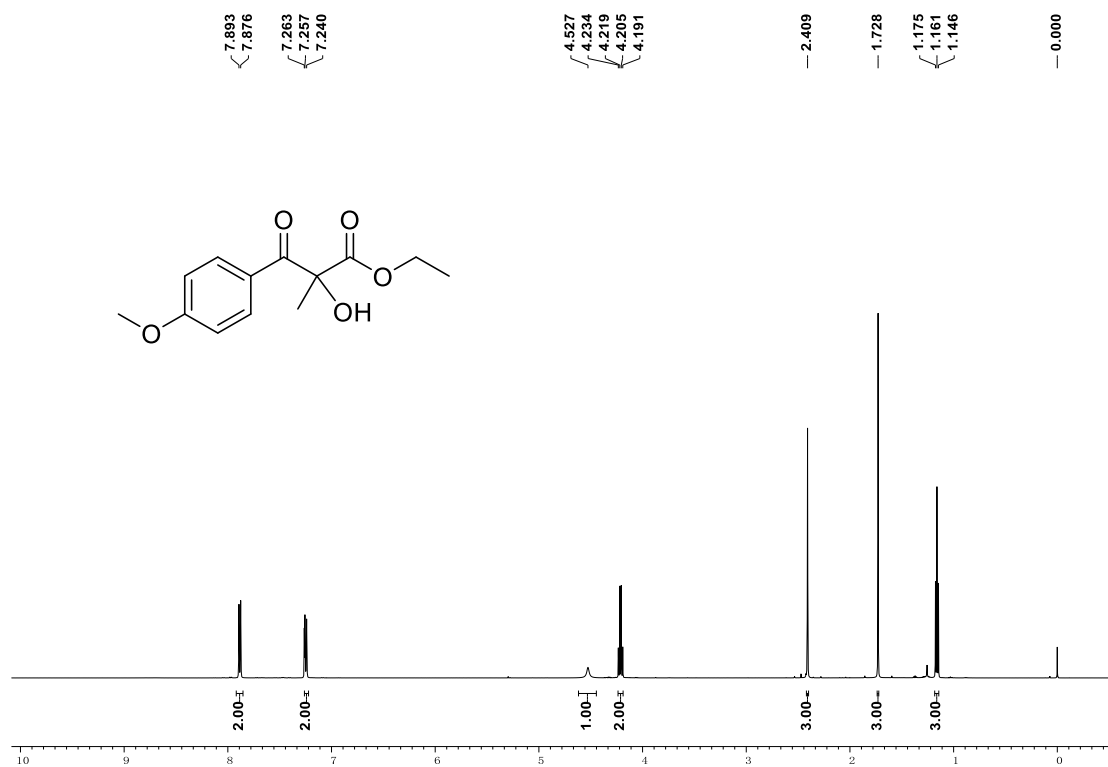
### 3b <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



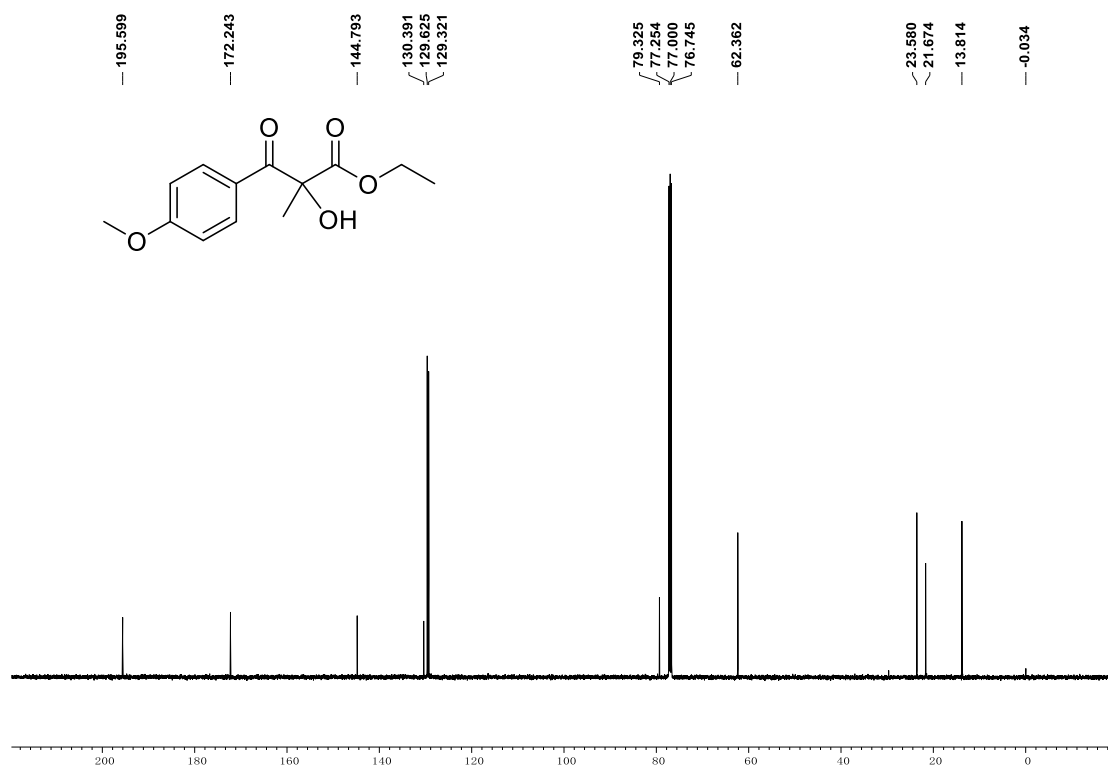
### 3b <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



### 3c <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

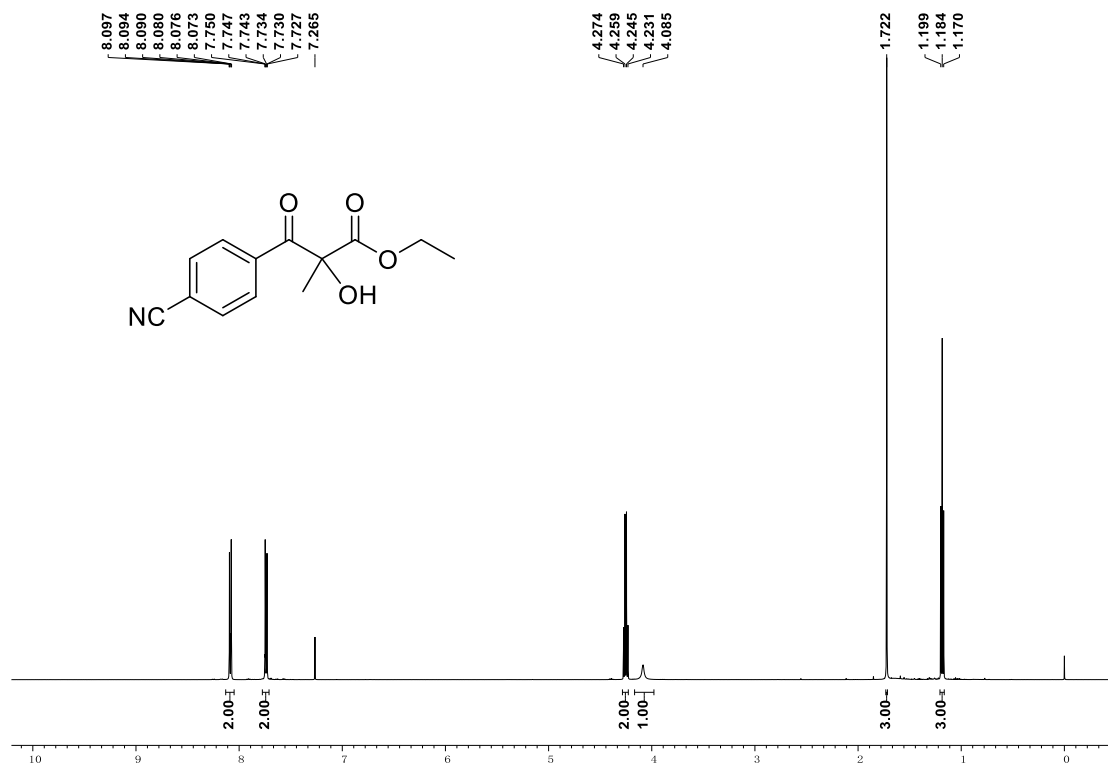


### 3c <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

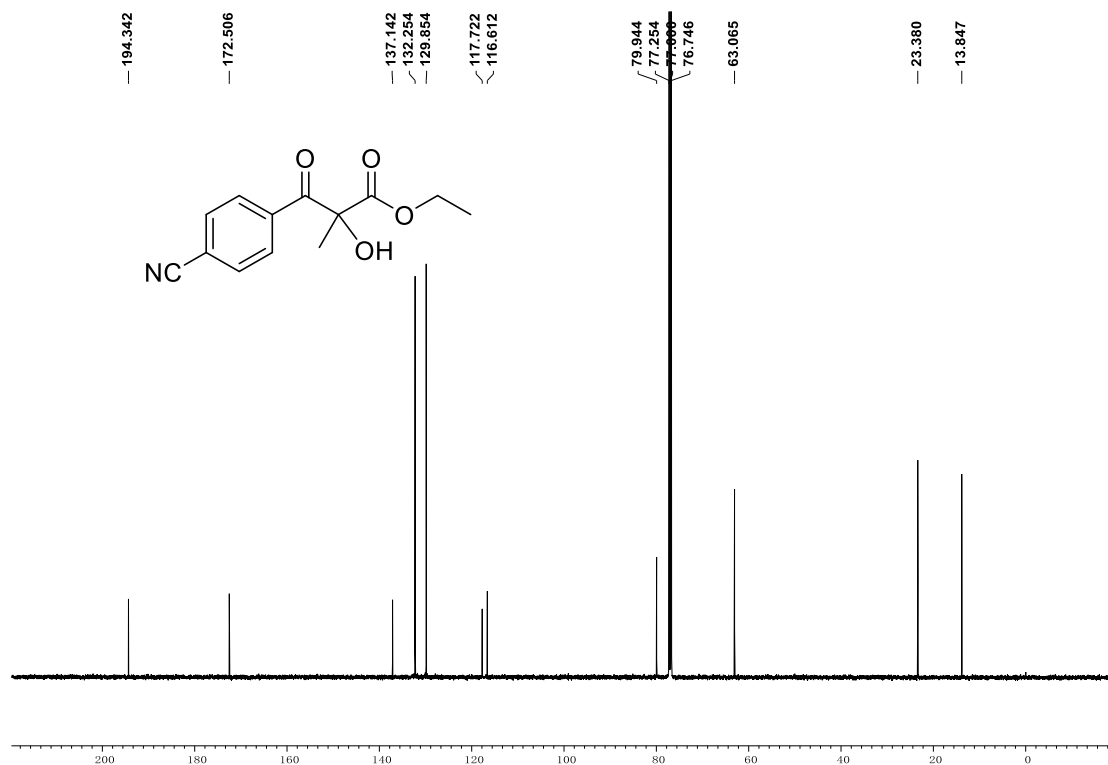




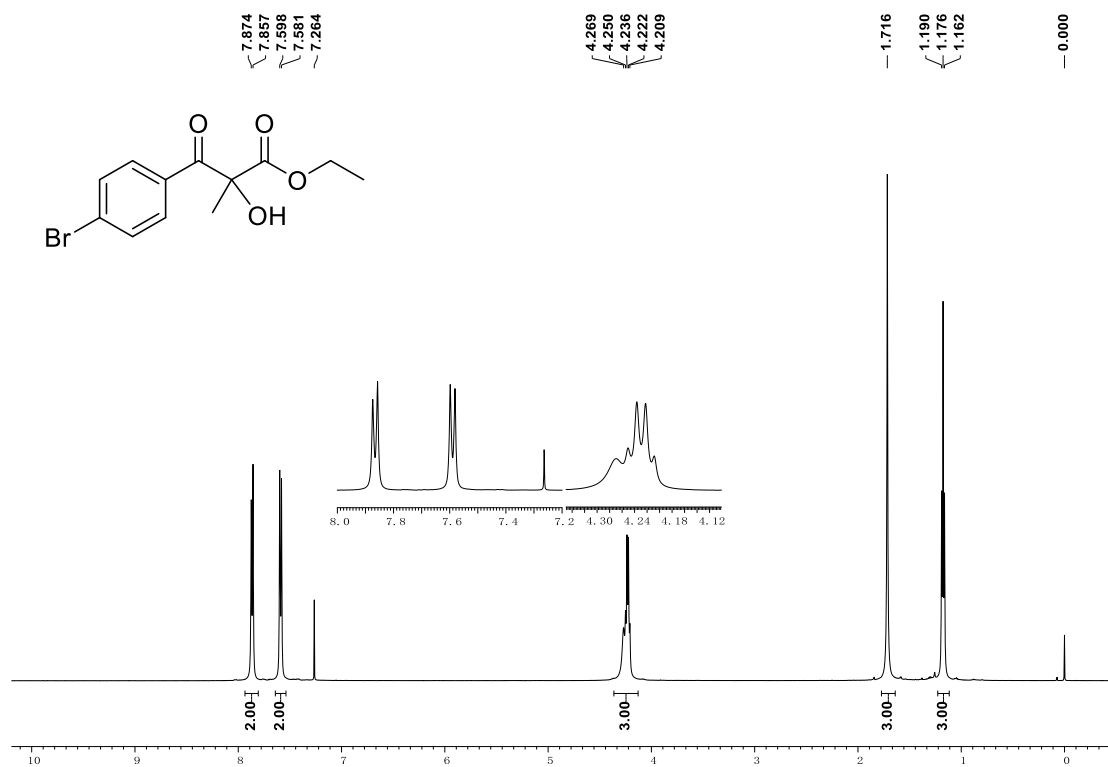
### 3d <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



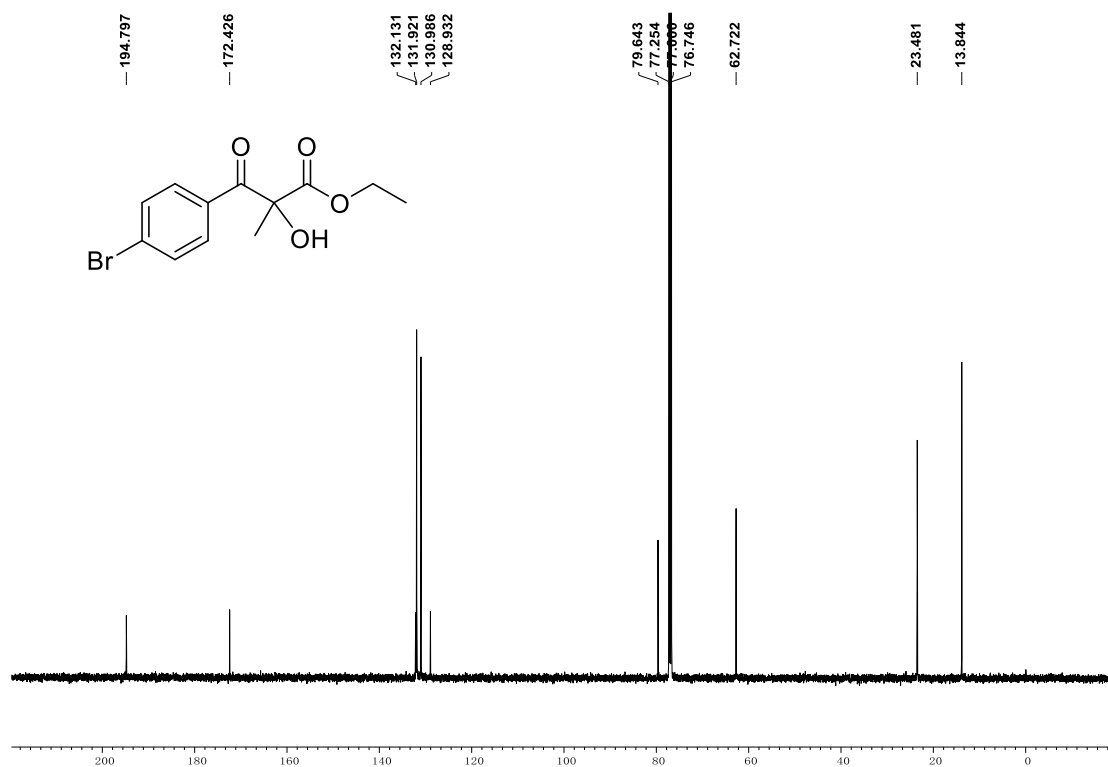
### 3d <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



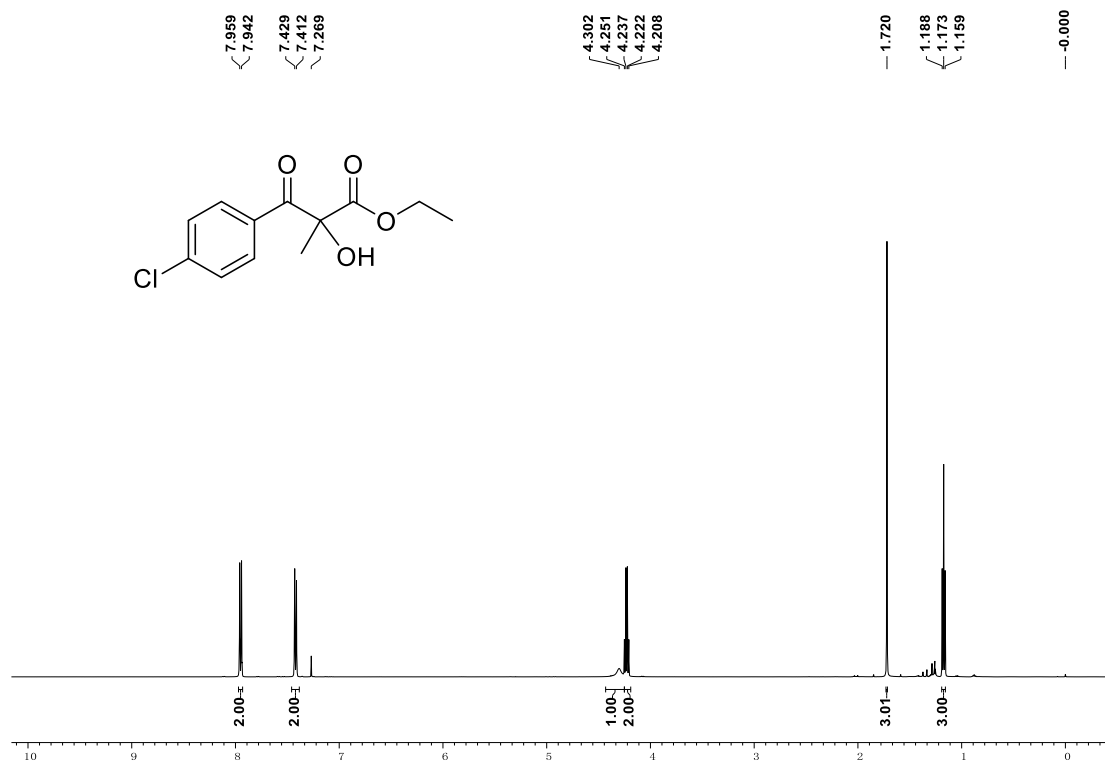
### 3e <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



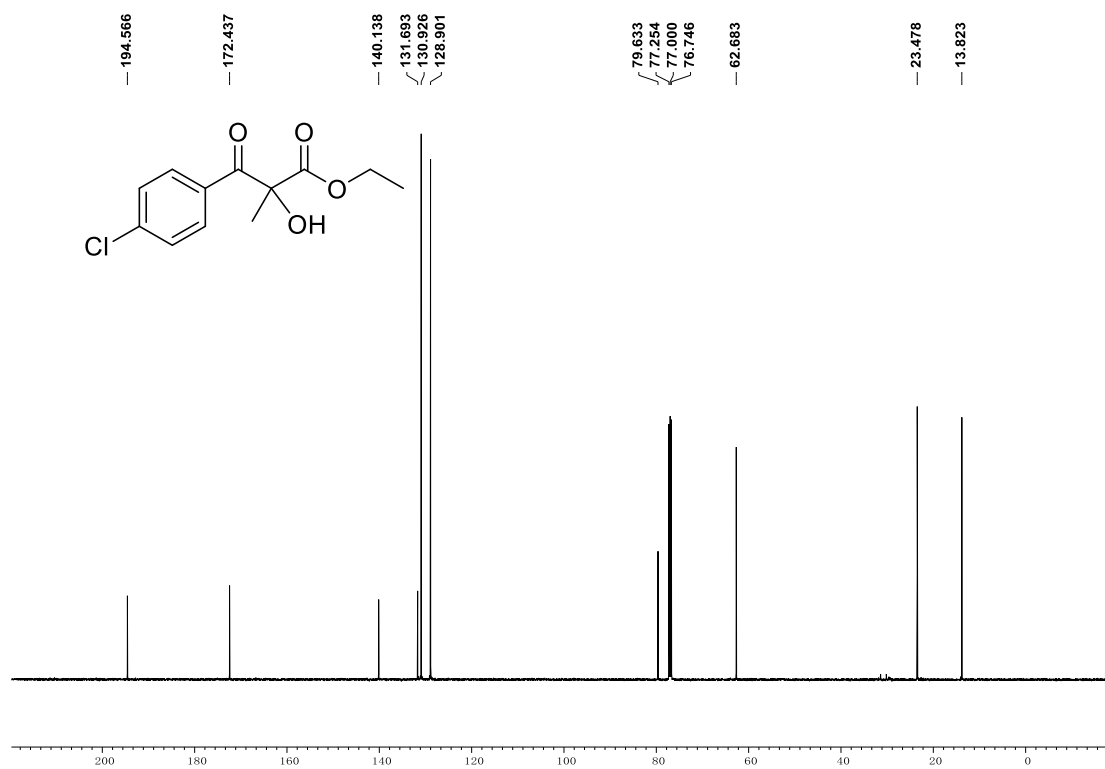
### 3e <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



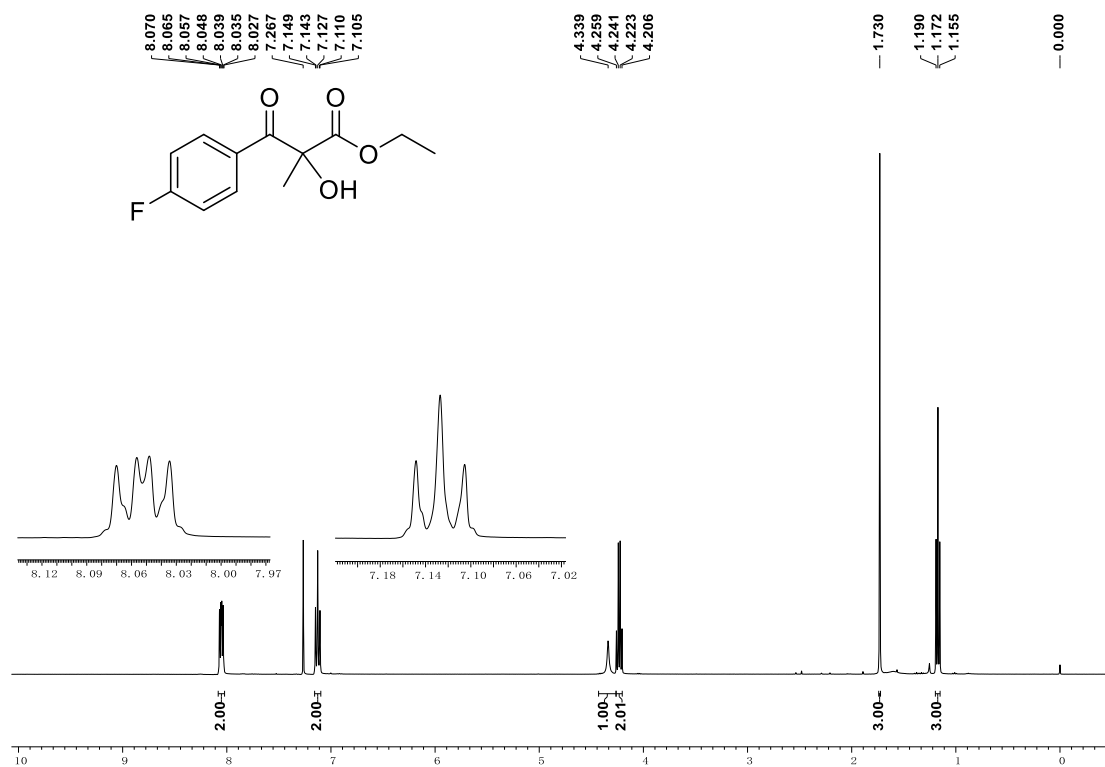
### 3f <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



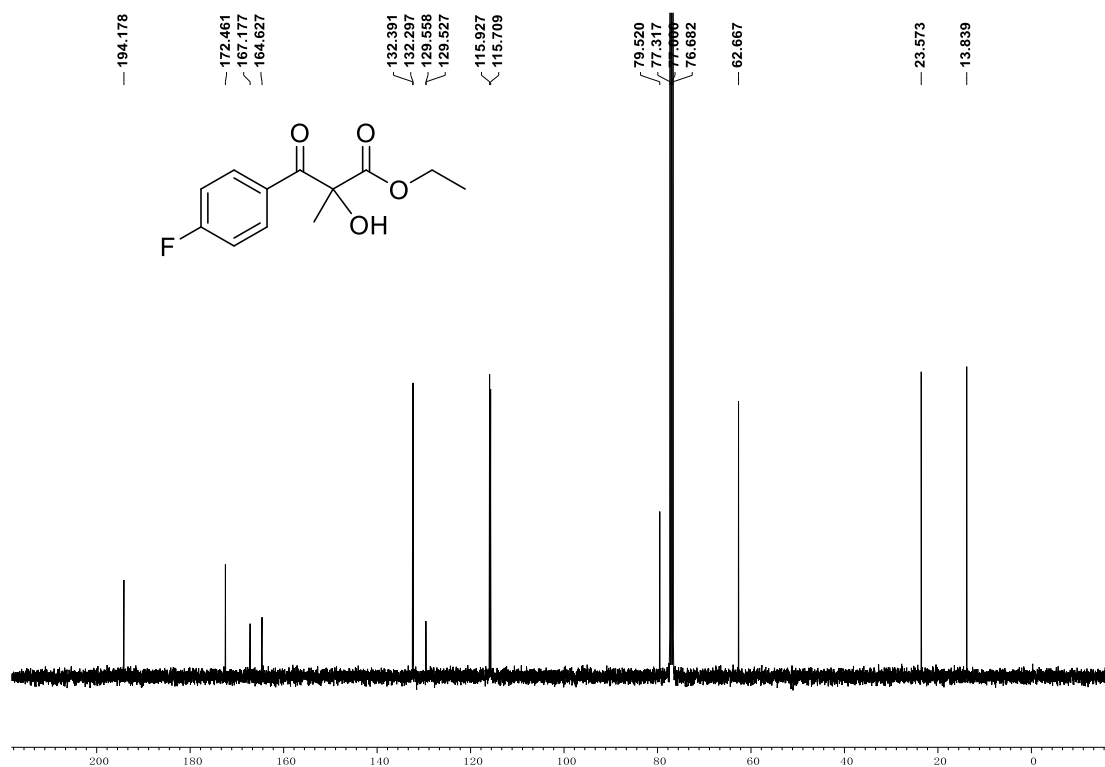
### 3f <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



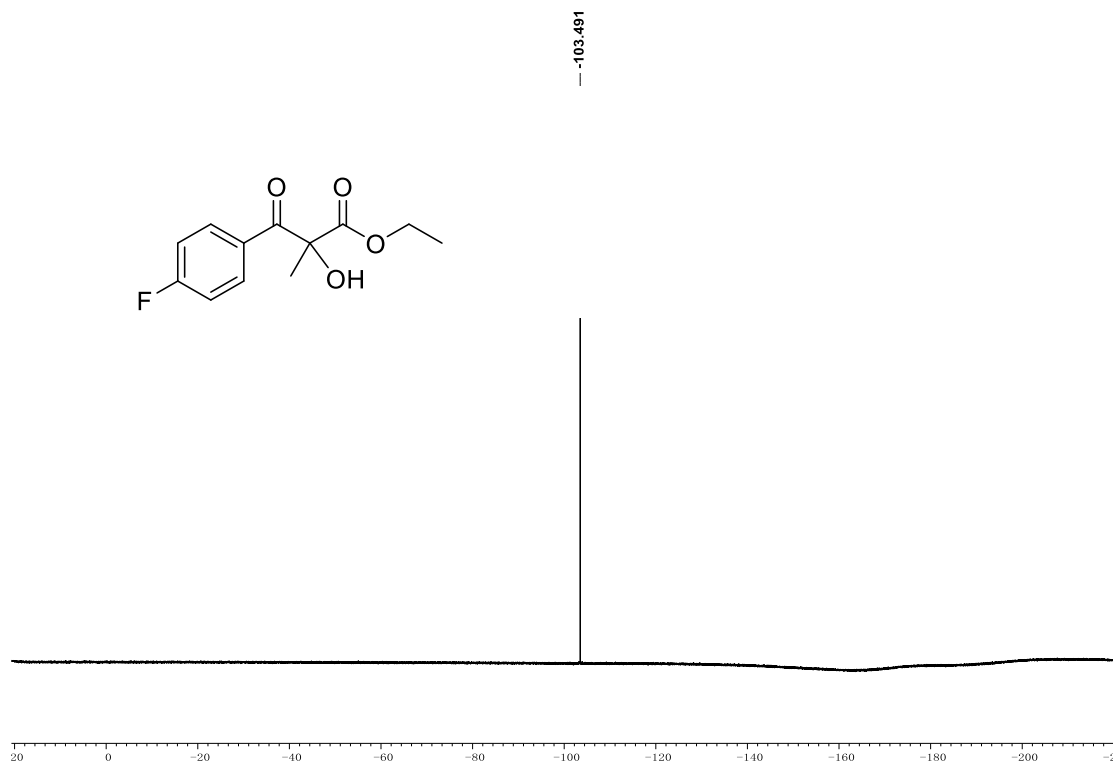
### 3g <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



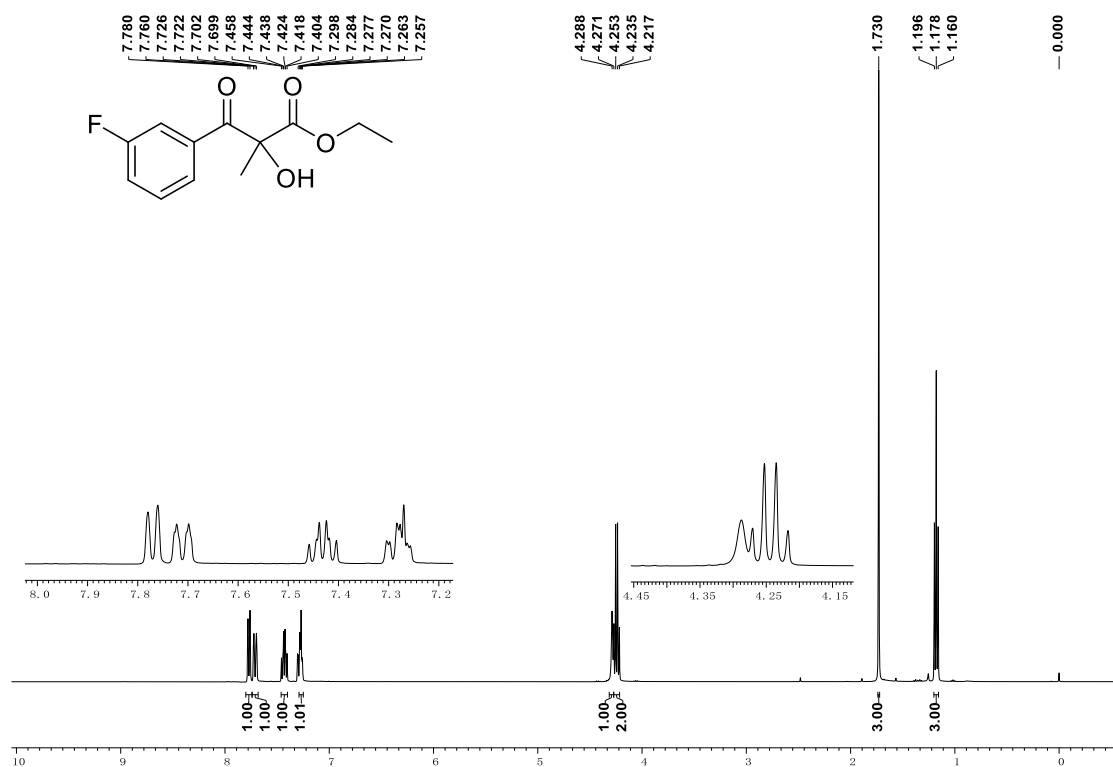
### 3g <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



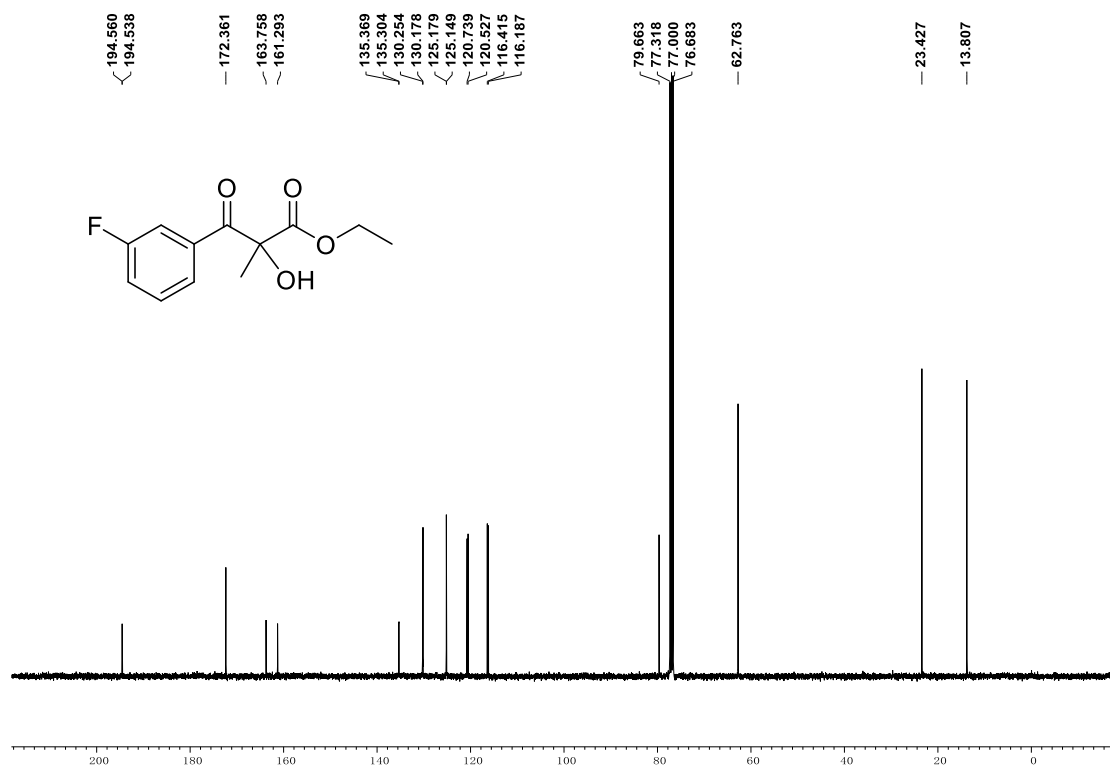
### 3g $^{19}\text{F}$ NMR (376 MHz, $\text{CDCl}_3$ )



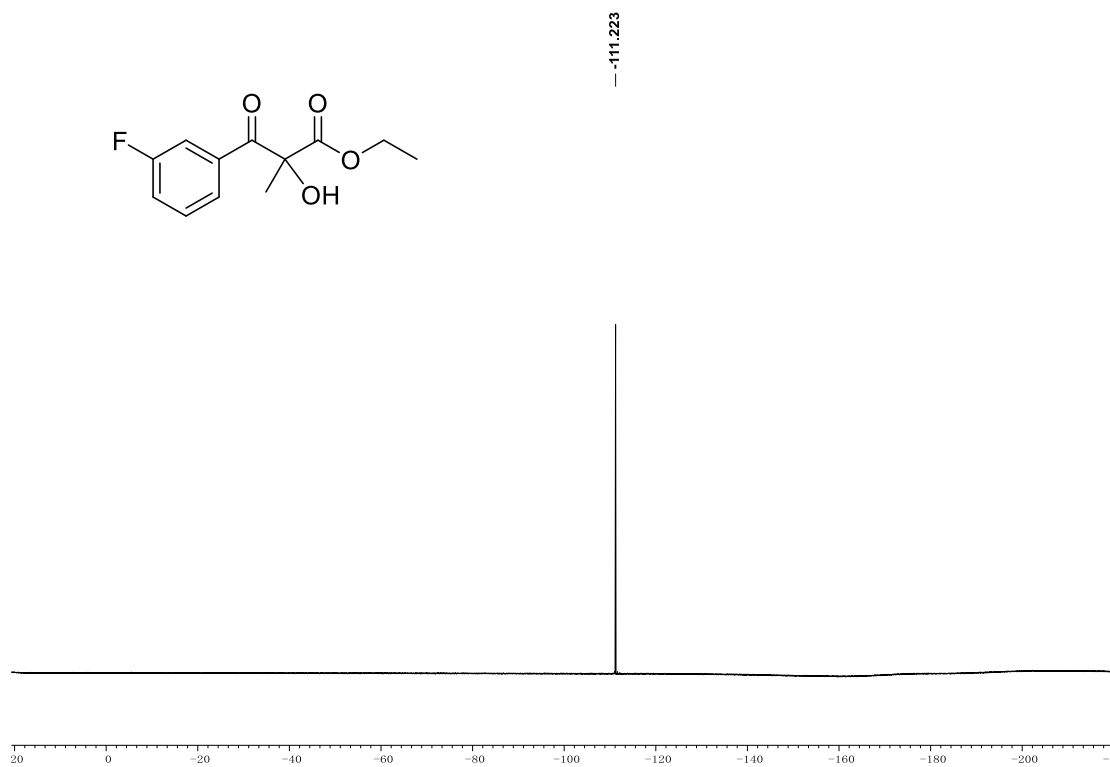
### 3h $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



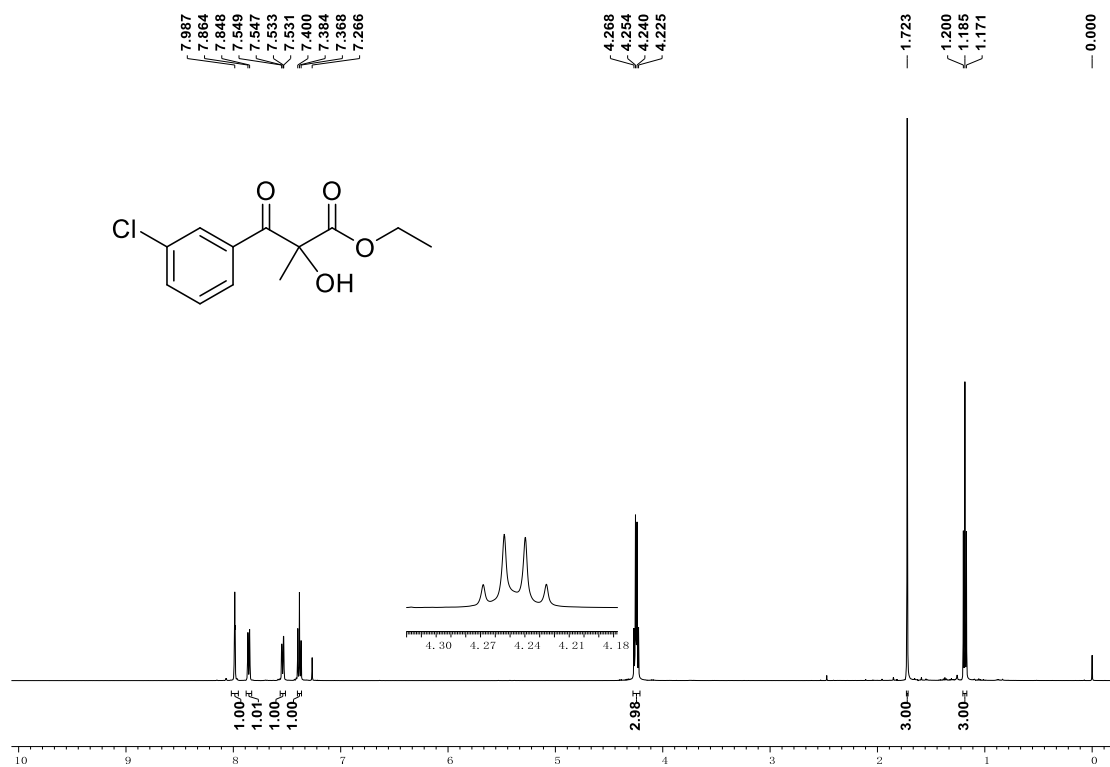
### 3h <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



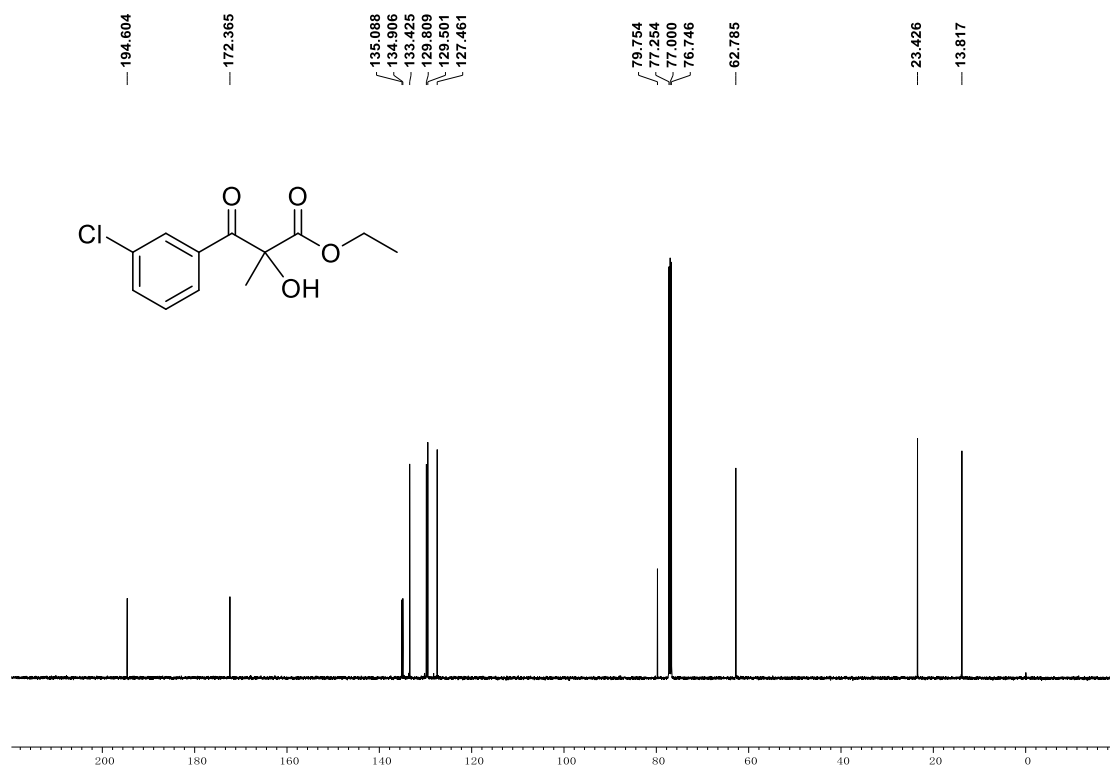
### 3h <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



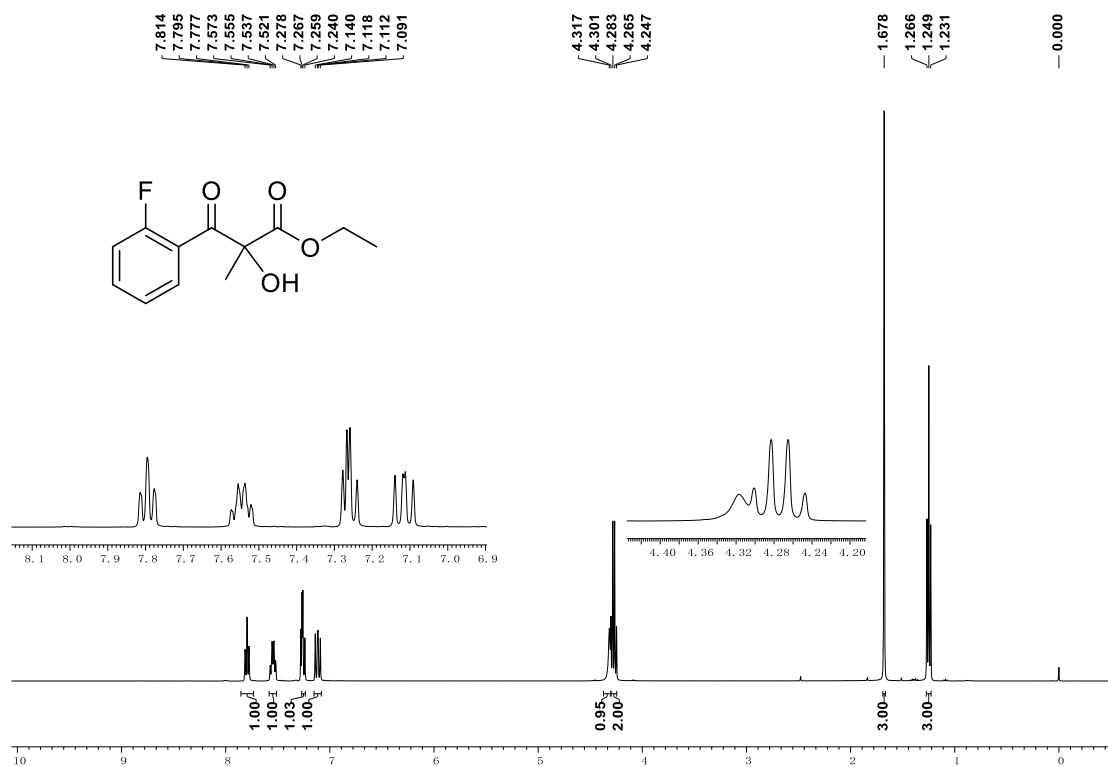
### 3i <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



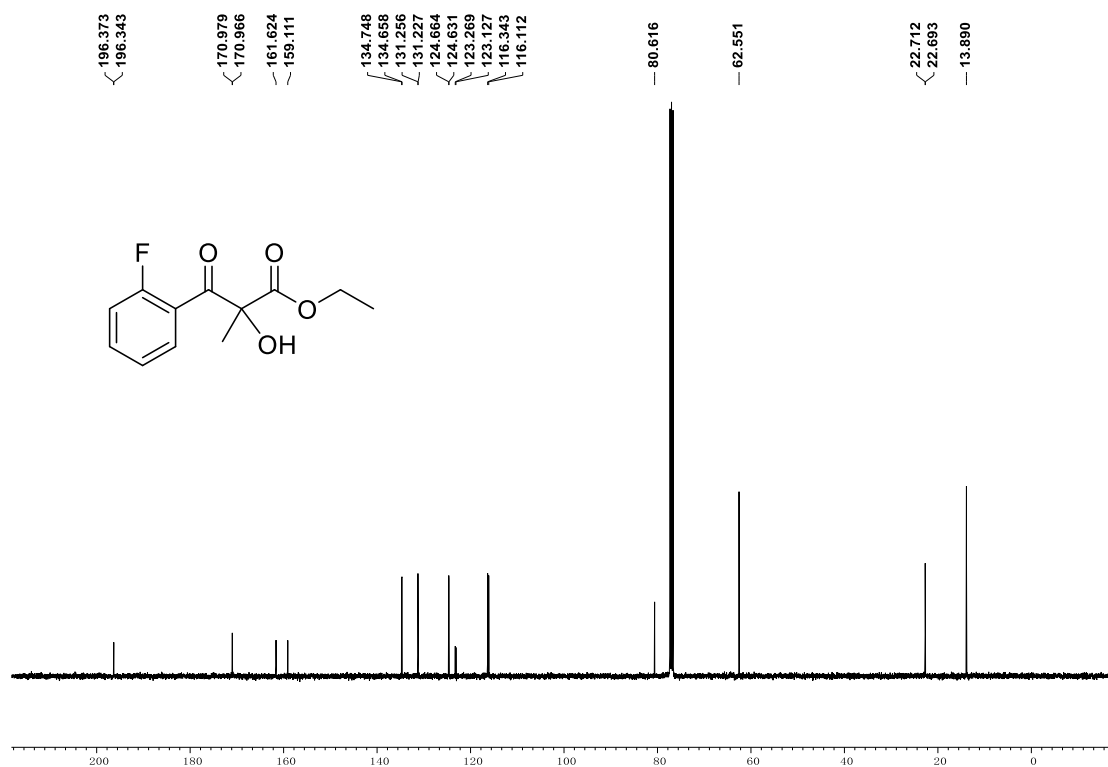
### 3i <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



### 3j <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

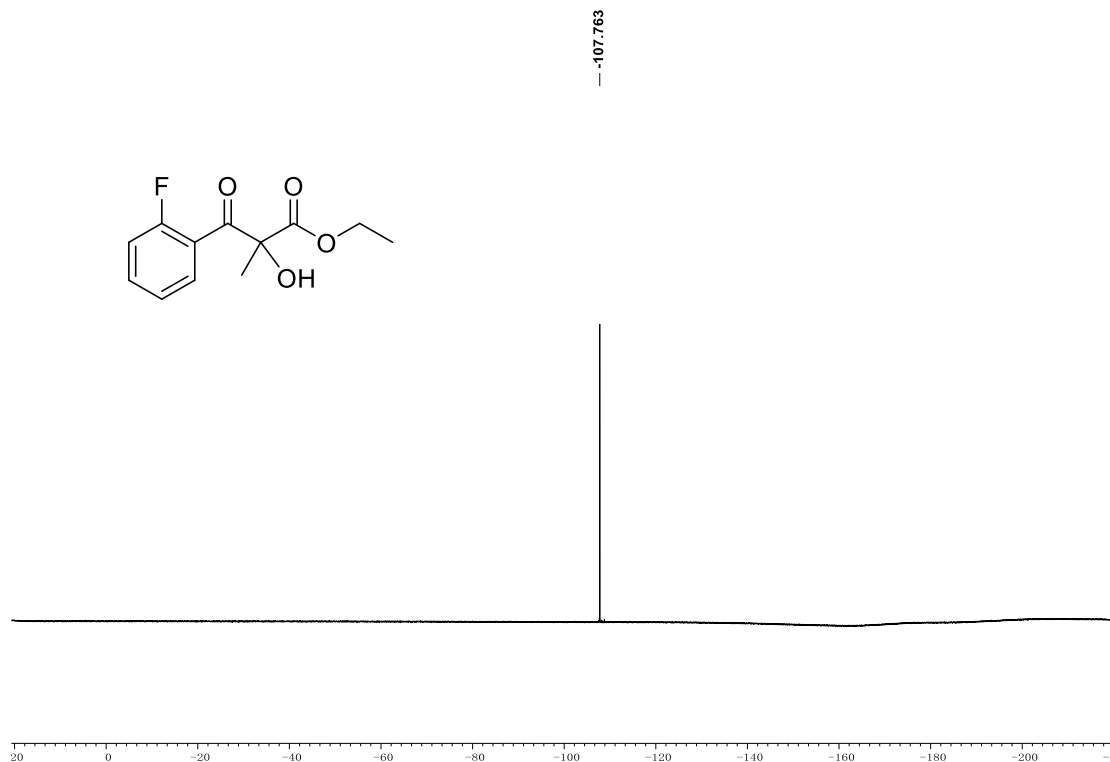


### 3j <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

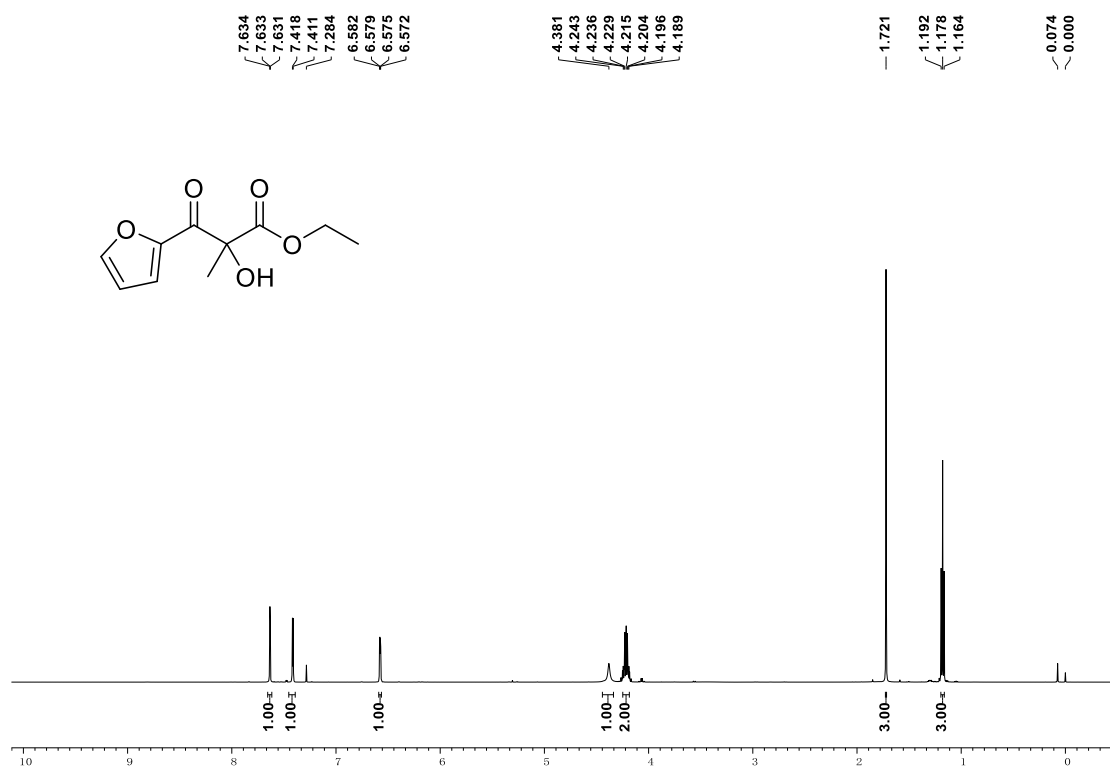




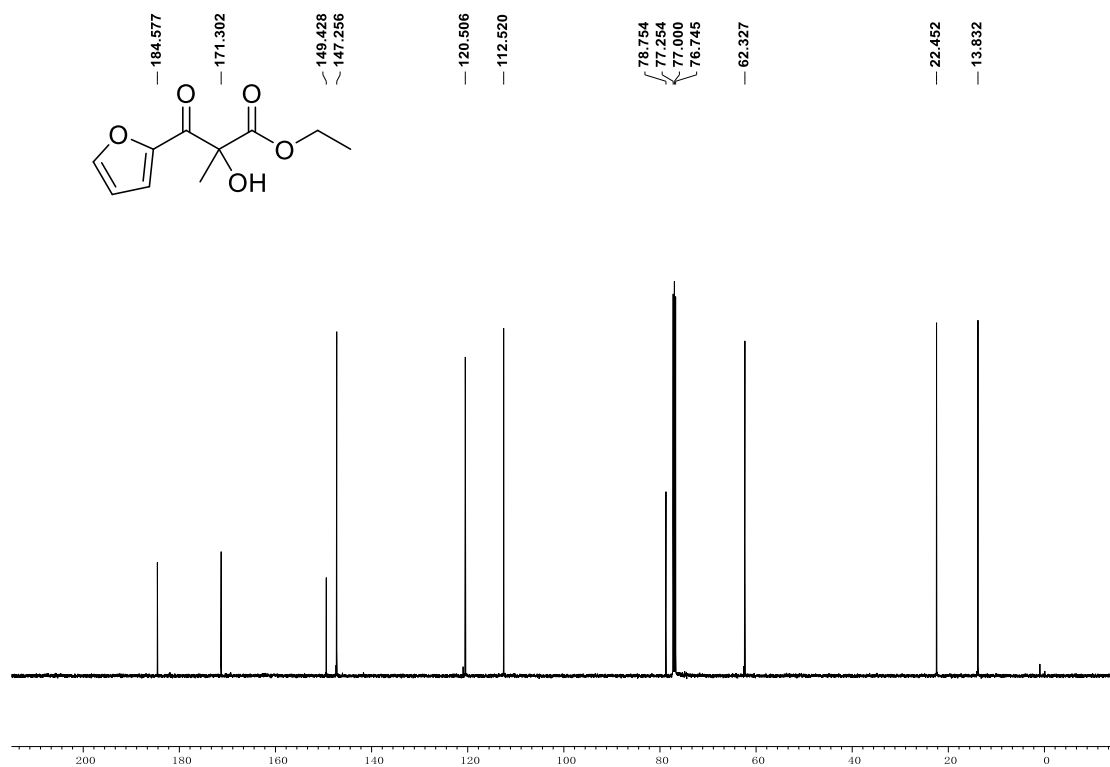
### 3j <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



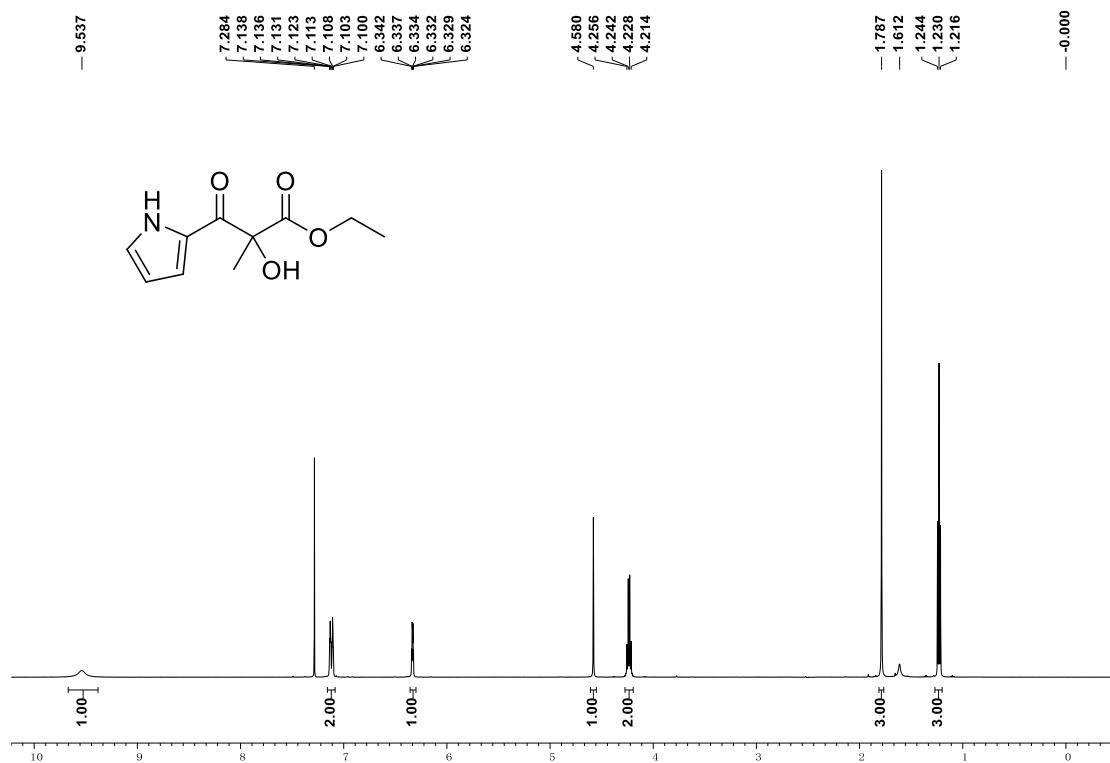
### 3k <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



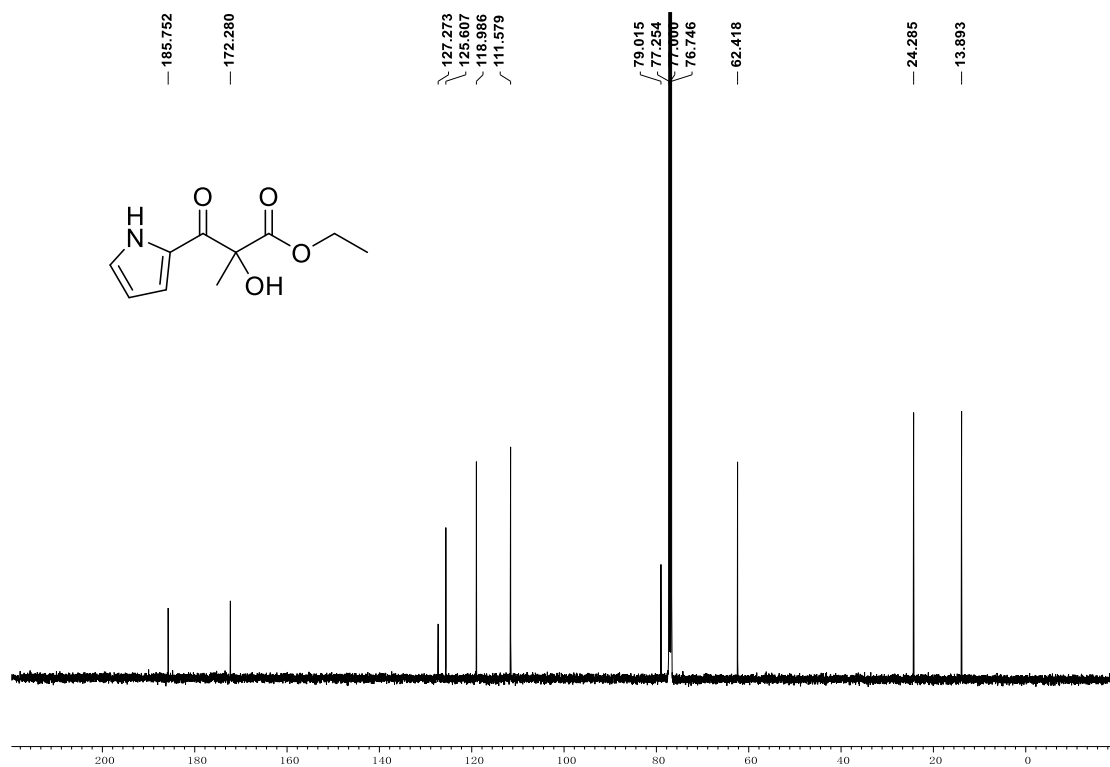
### 3k <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



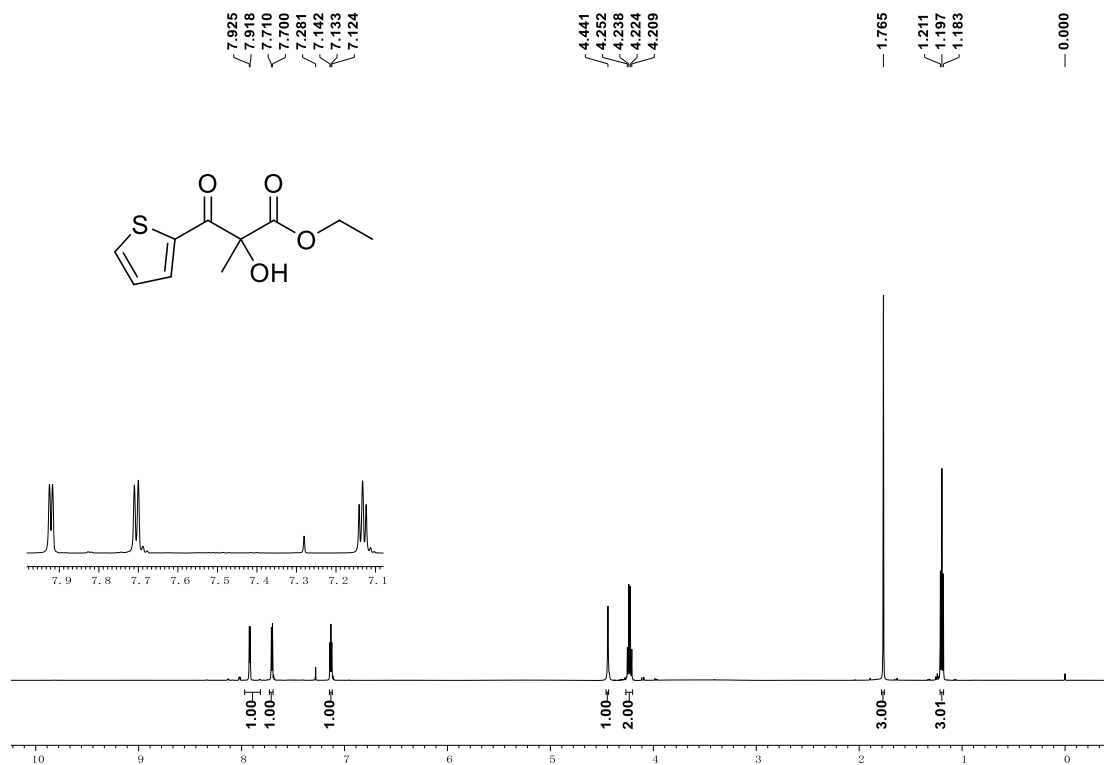
### 3l <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



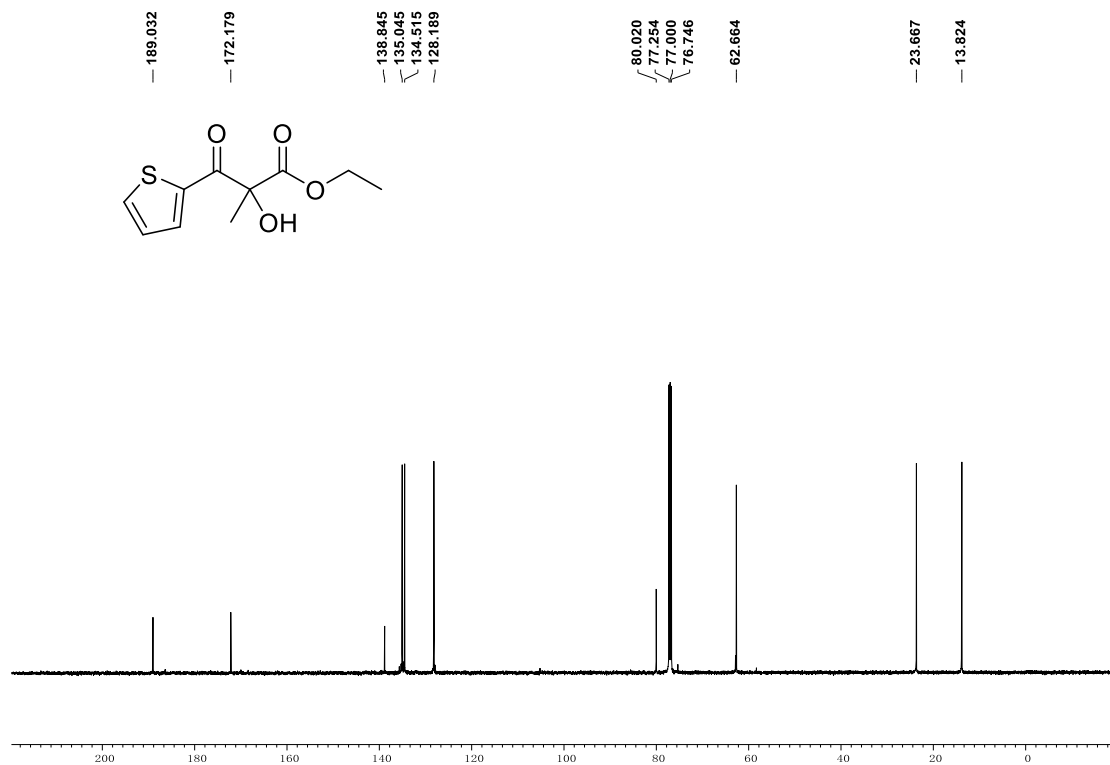
### 3l <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



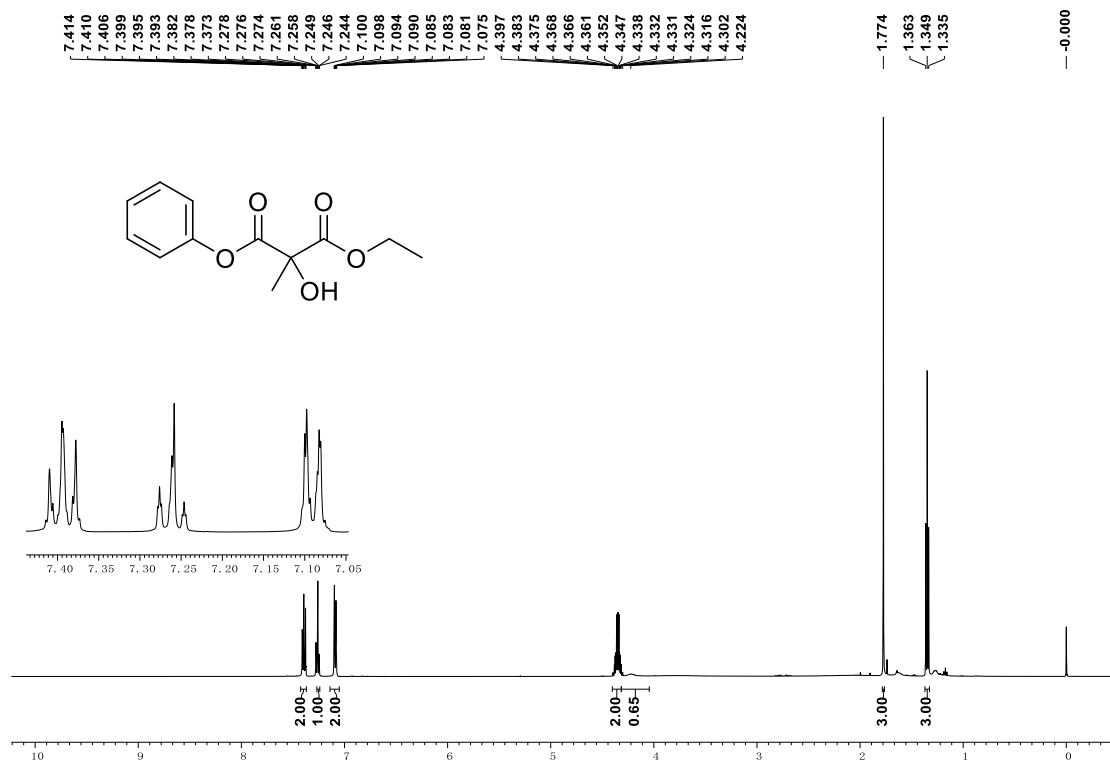
### 3m <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



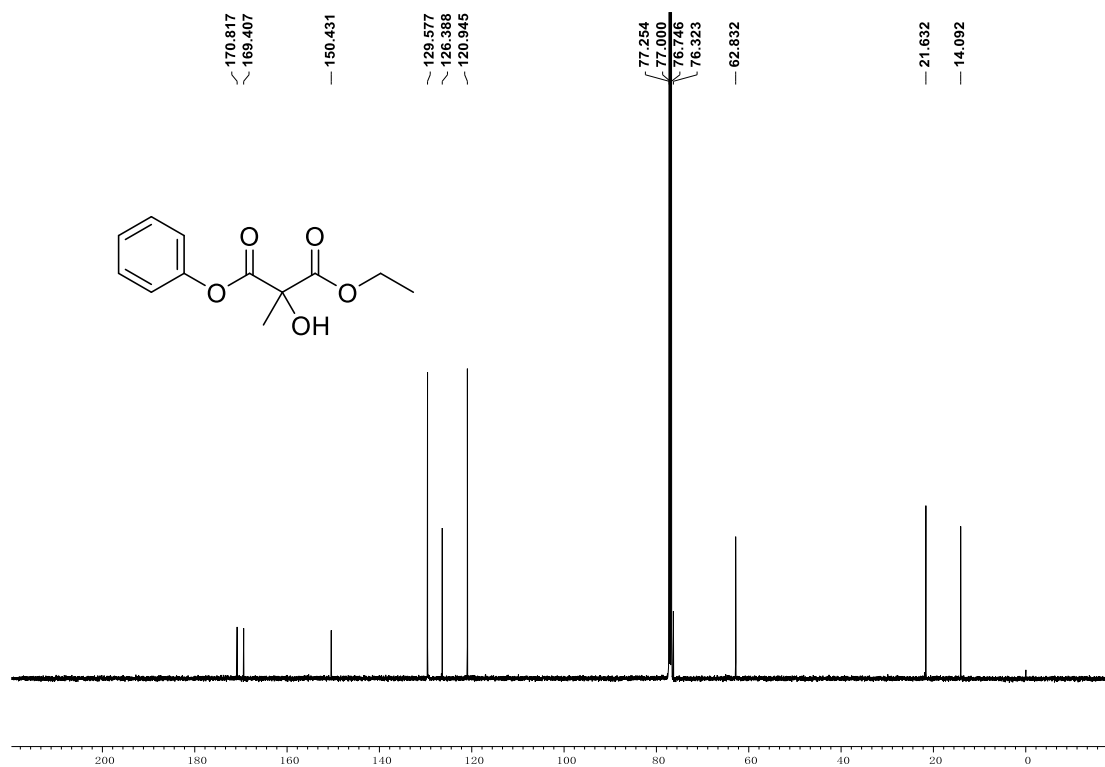
### 3m <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



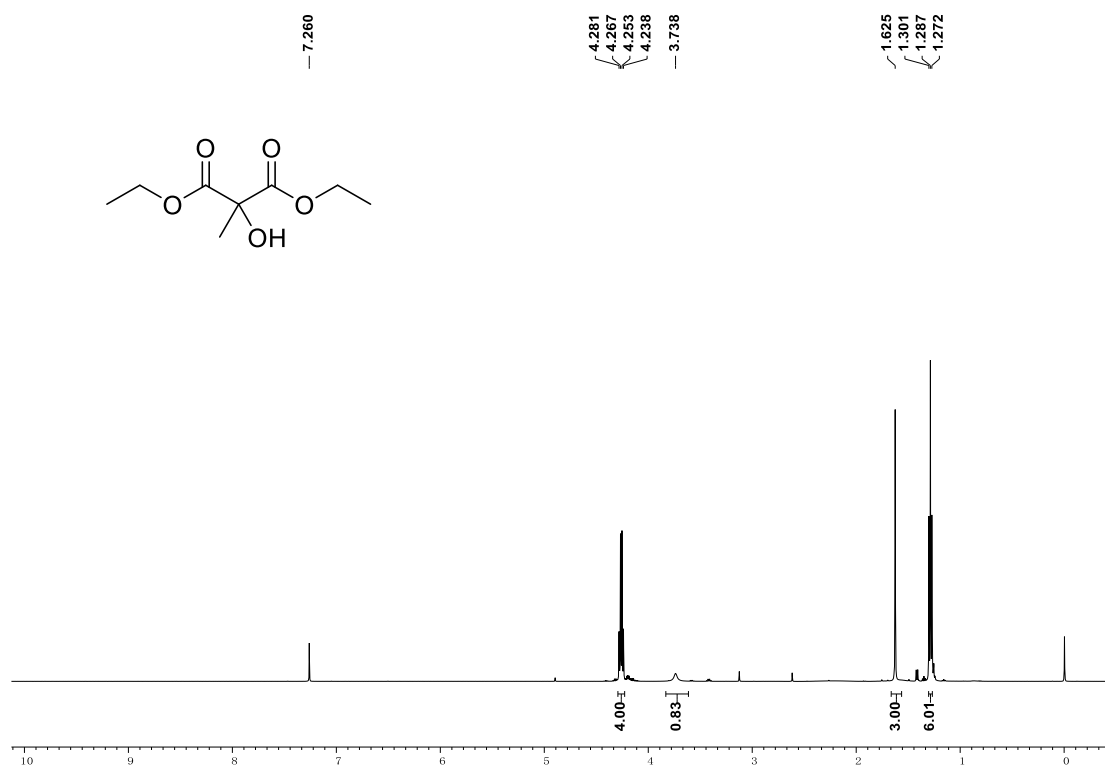
### 3o <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



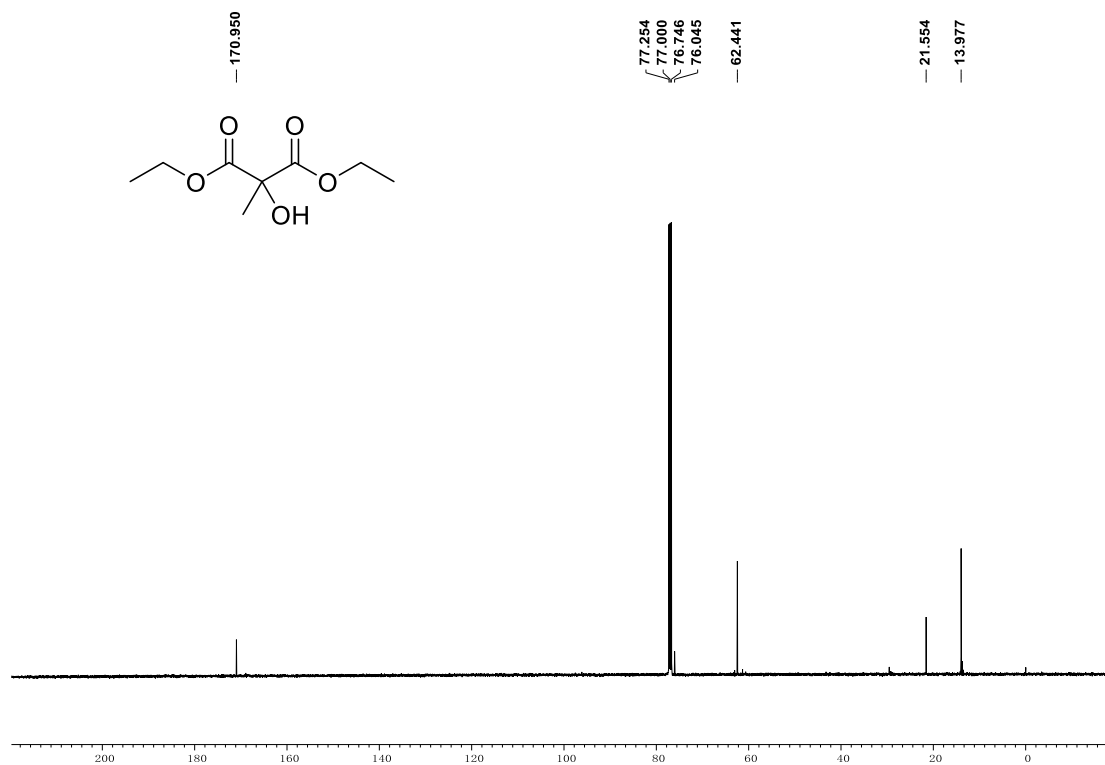
### 3o <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



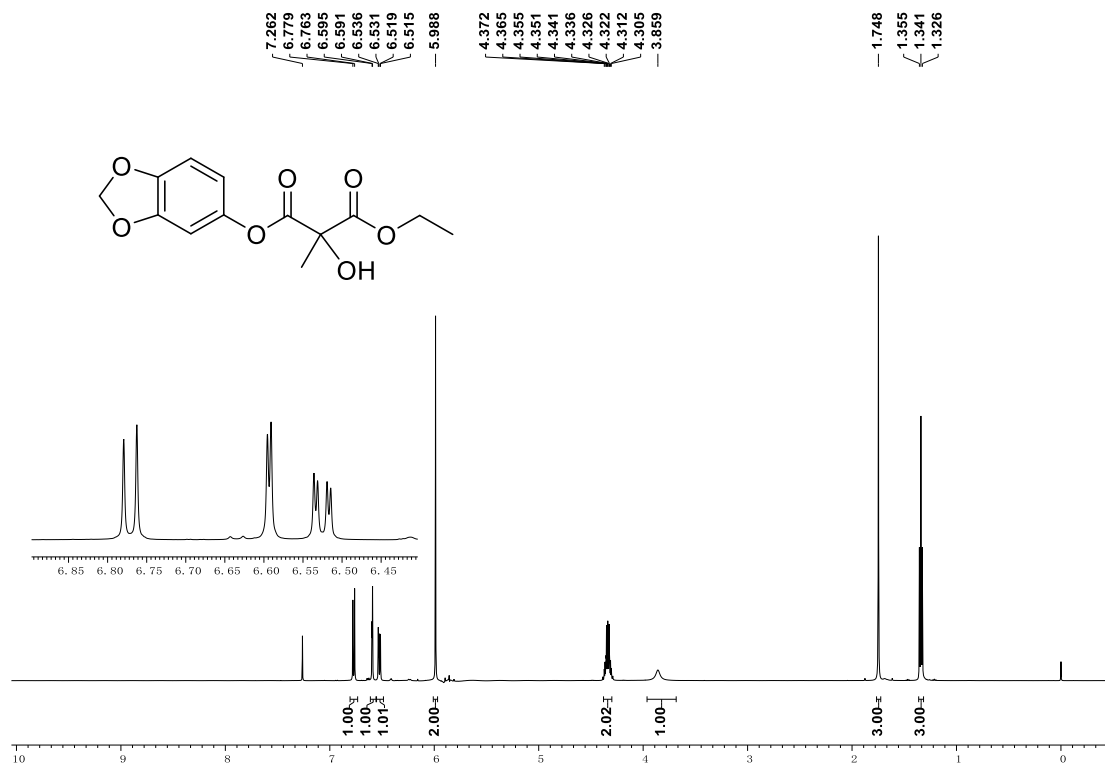
### 3p <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



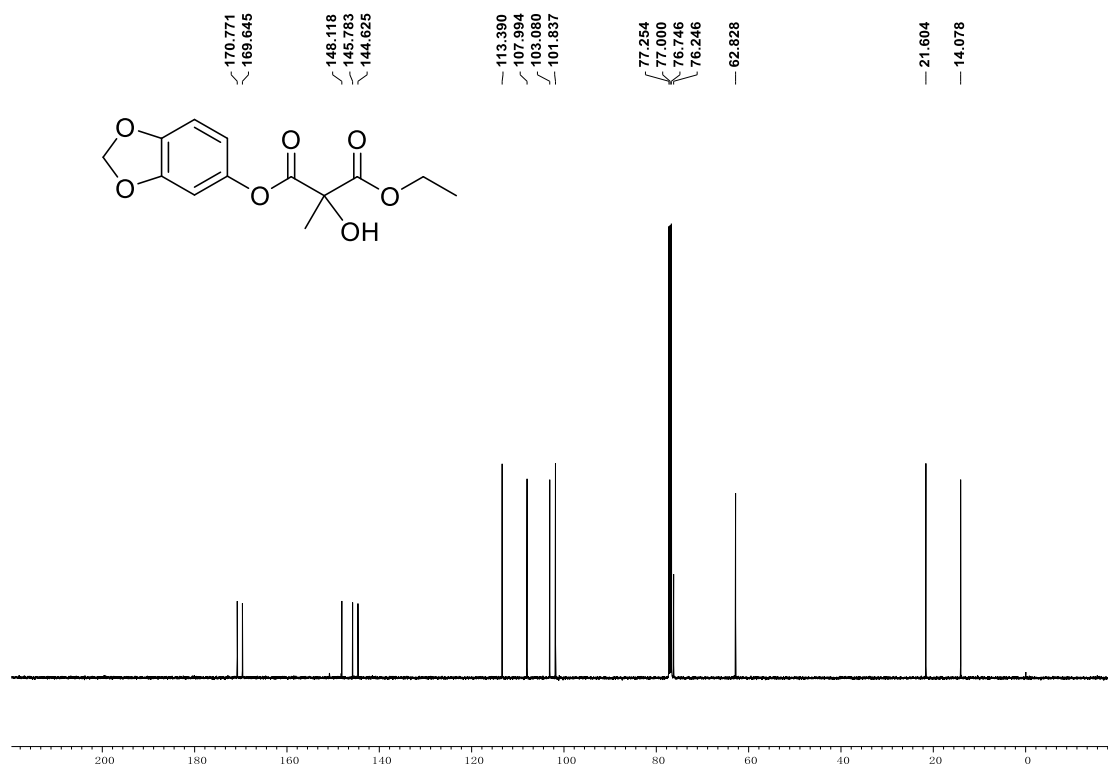
### 3p $^{13}\text{C}$ NMR (126 MHz, $\text{CDCl}_3$ )



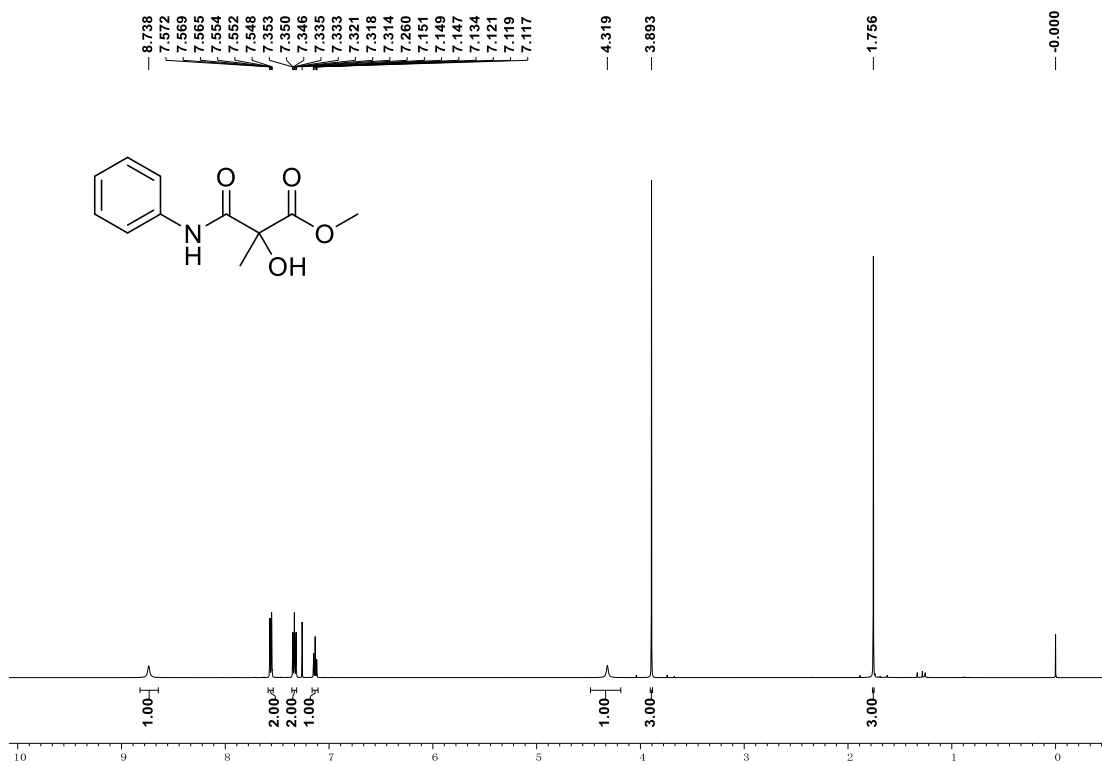
### 3q $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )



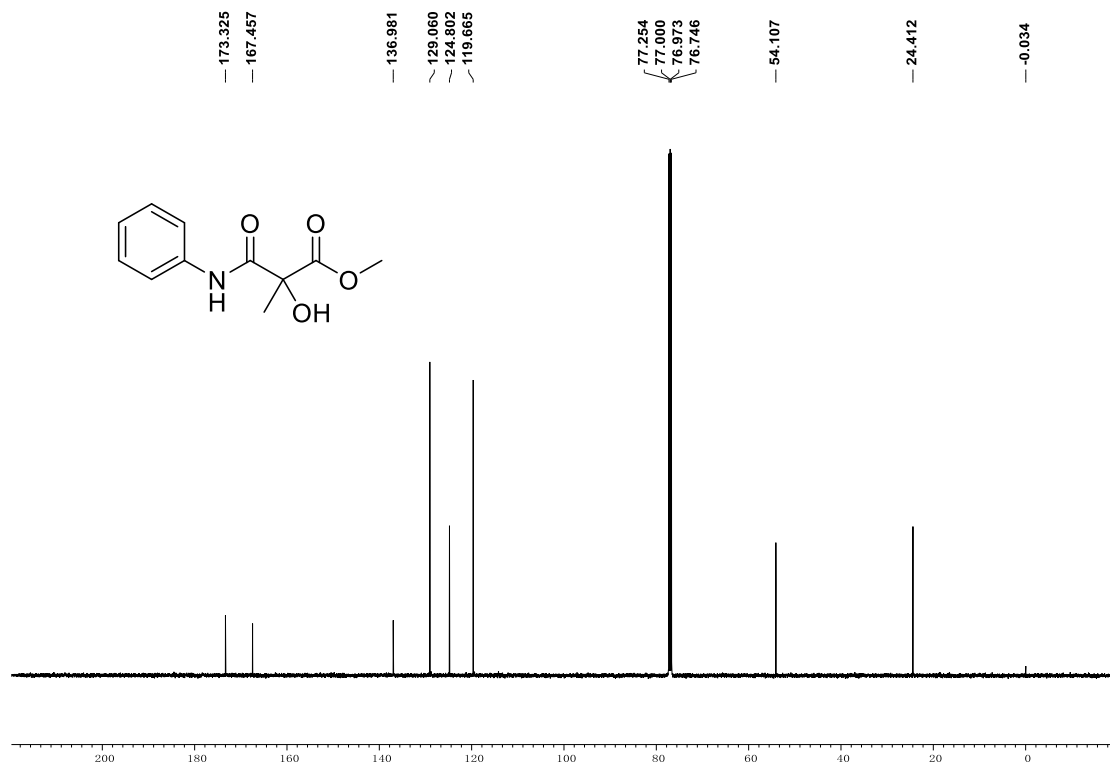
### 3q <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



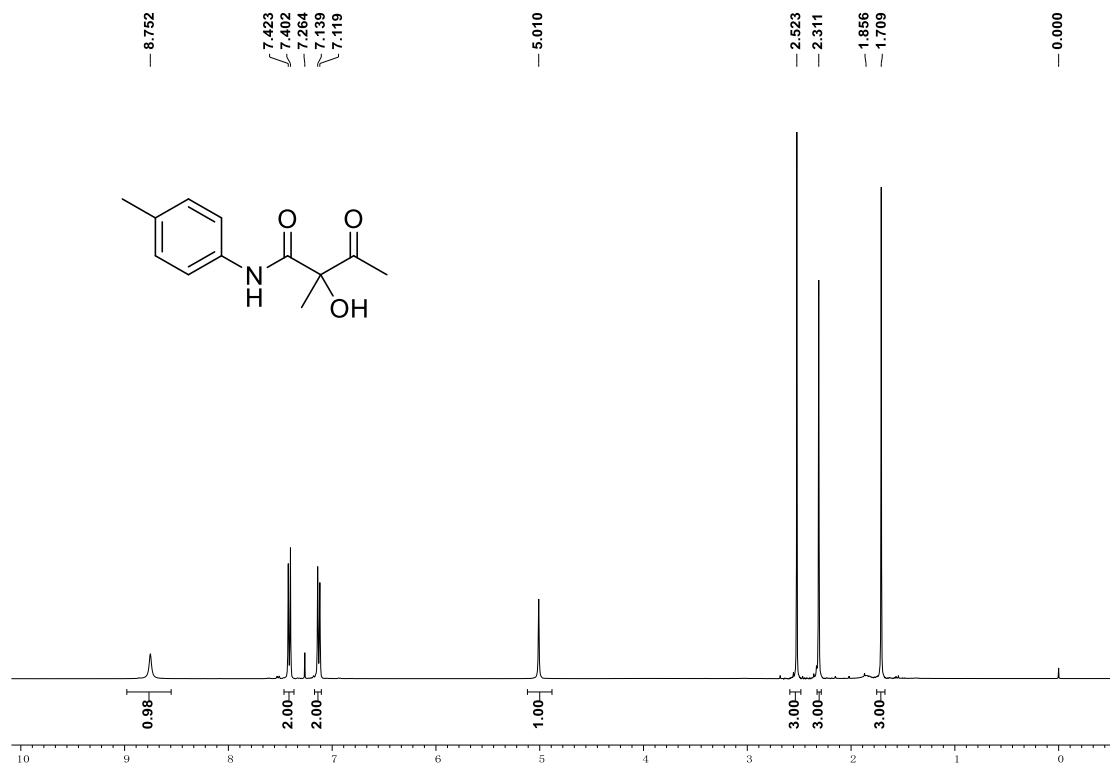
### 3r <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



### 3r <sup>13</sup>C NMR (126MHz, CDCl<sub>3</sub>)

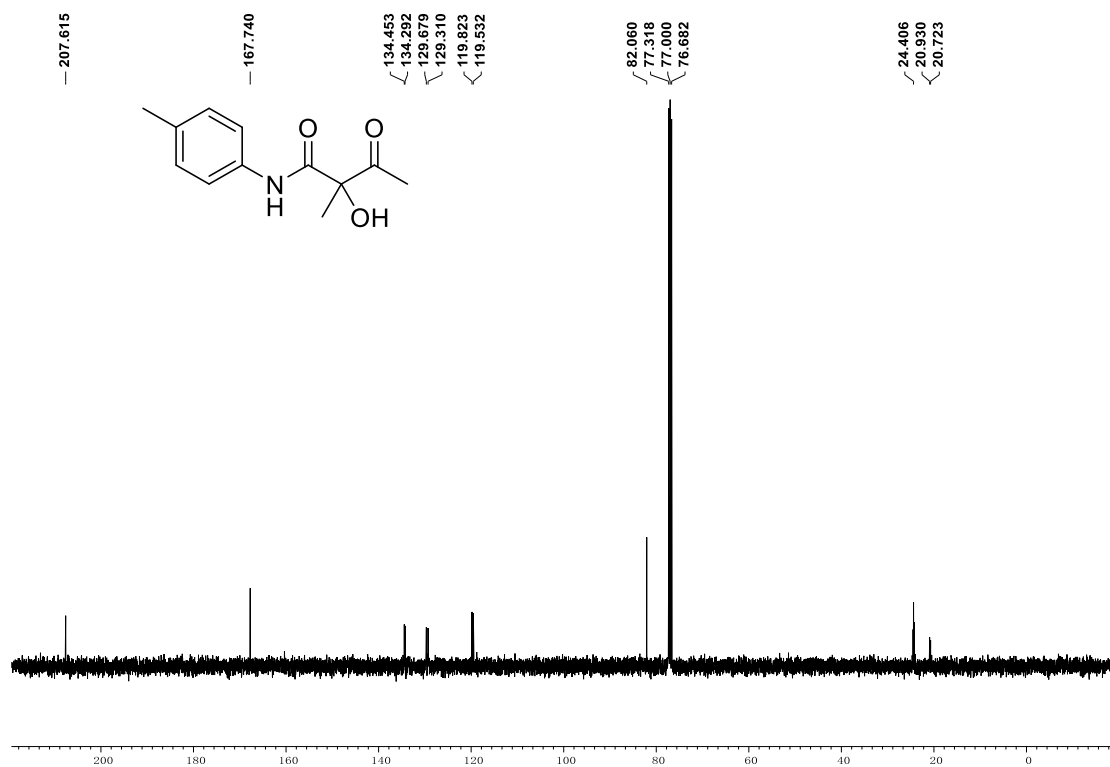


### 3s <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

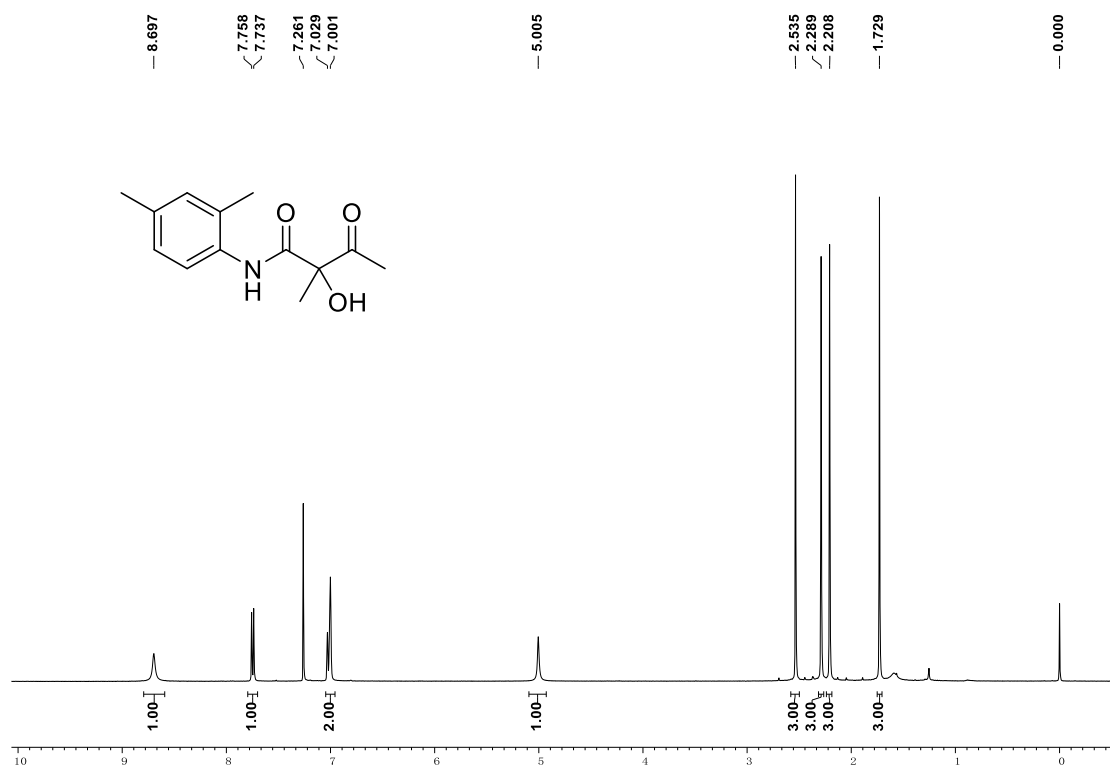




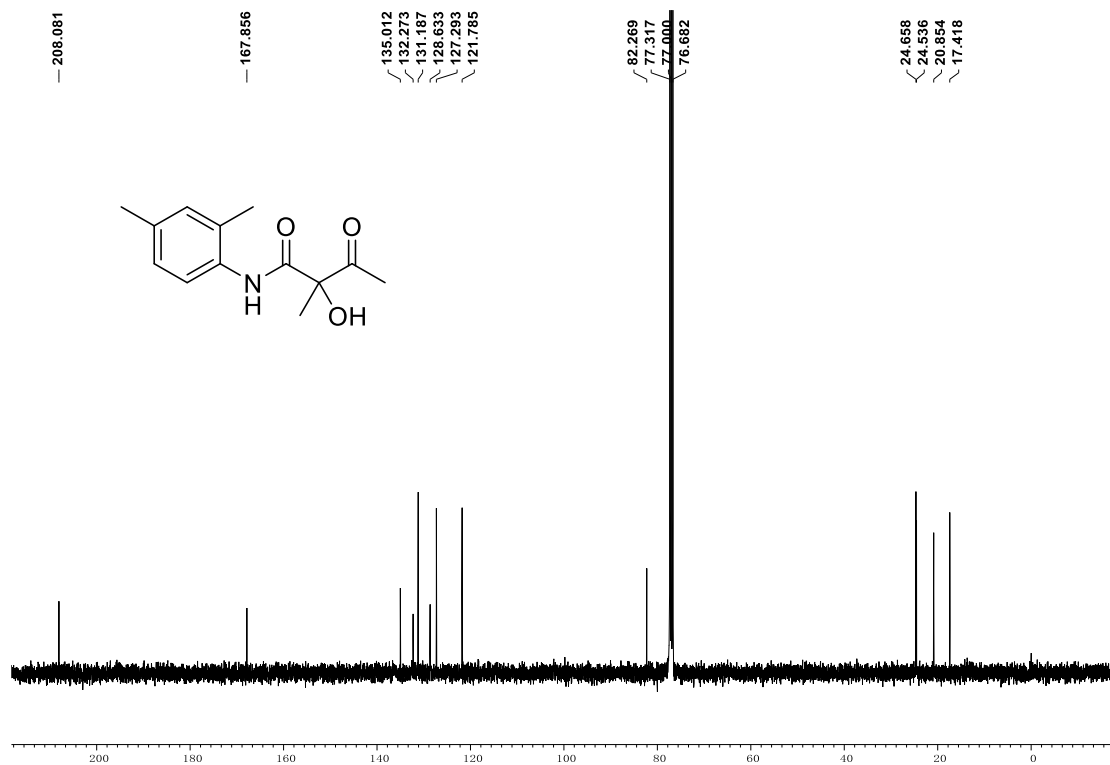
### 3s <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



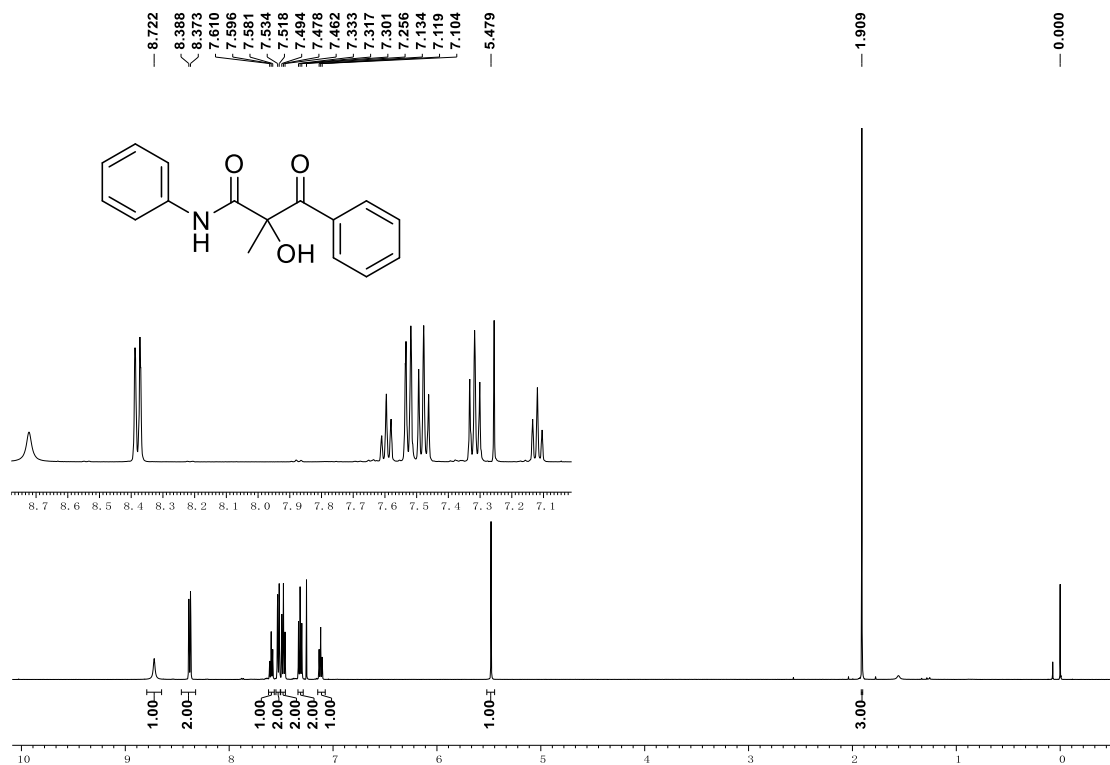
### 3t <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



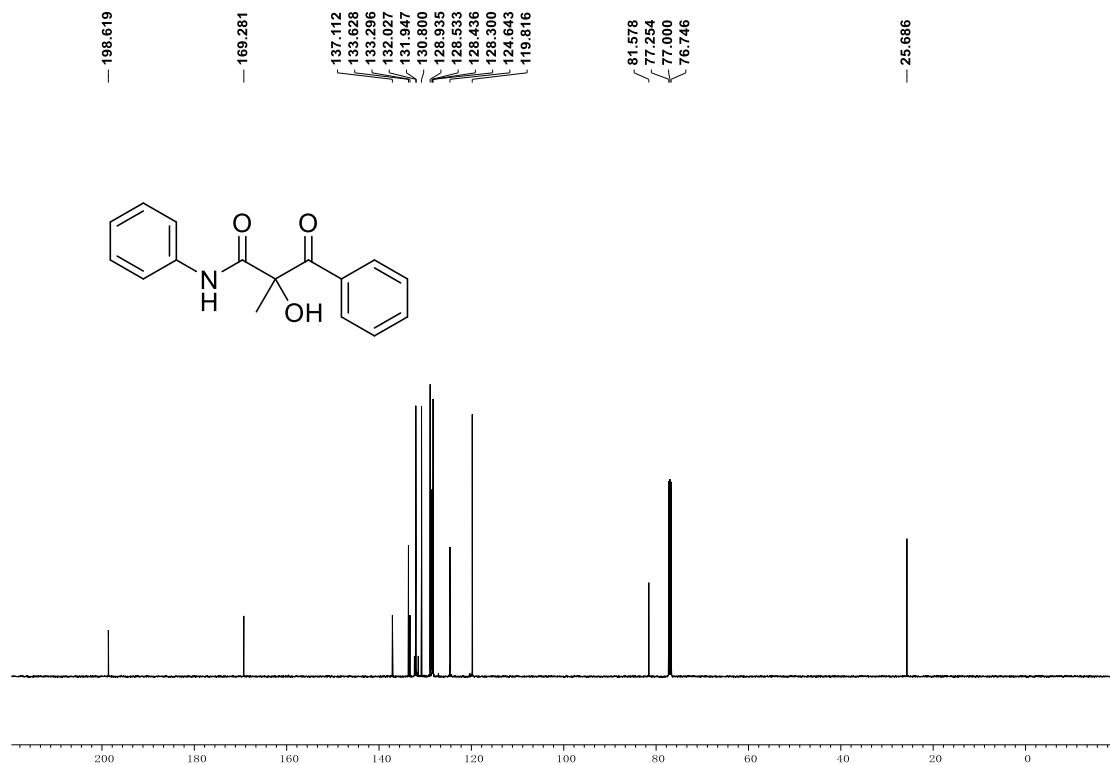
### 3t $^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ )



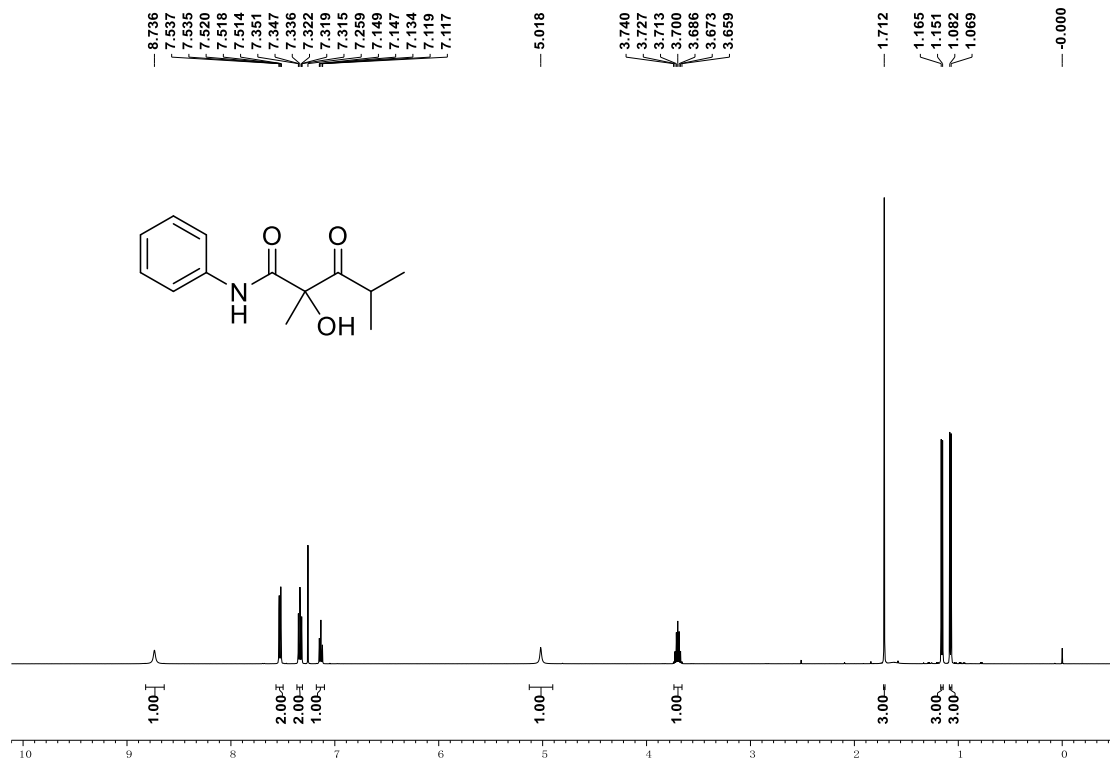
### 3u $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )



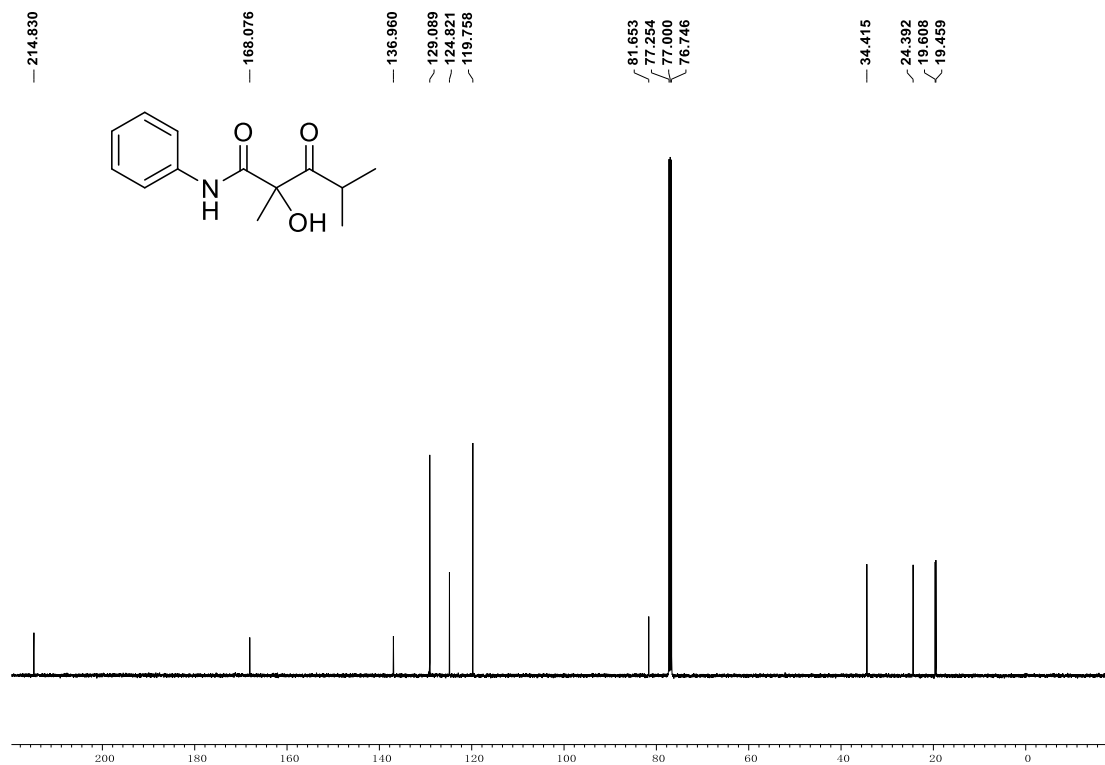
### 3u <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



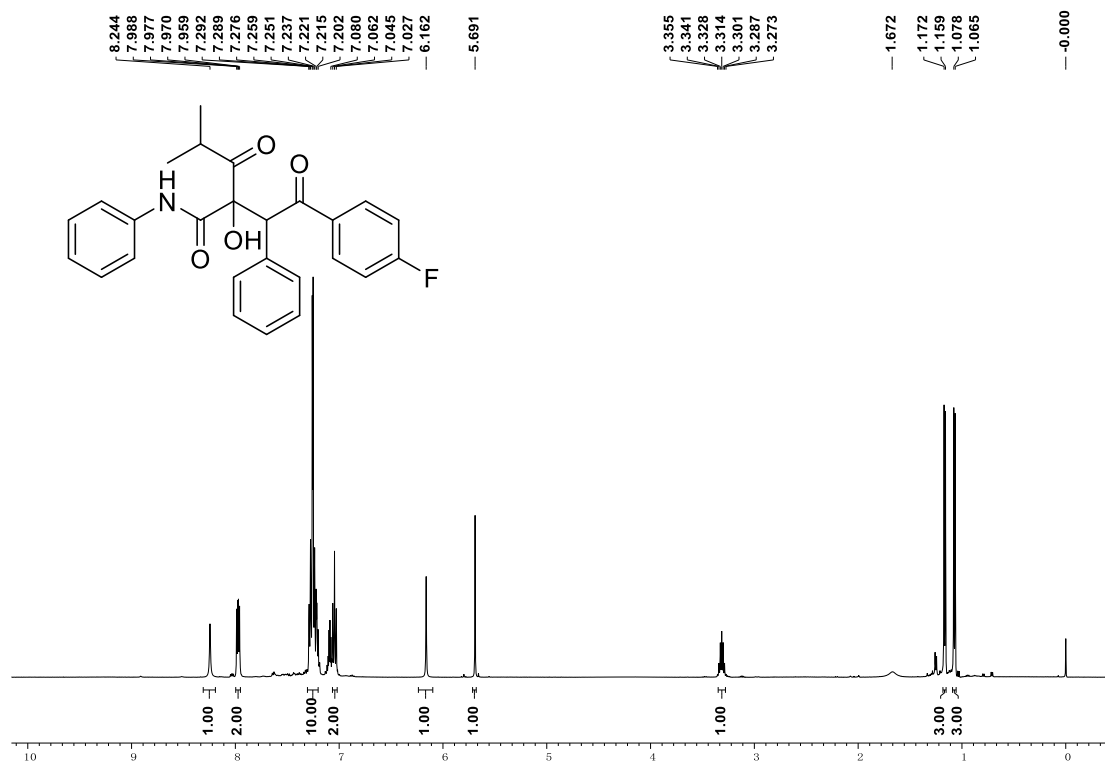
### 3v <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



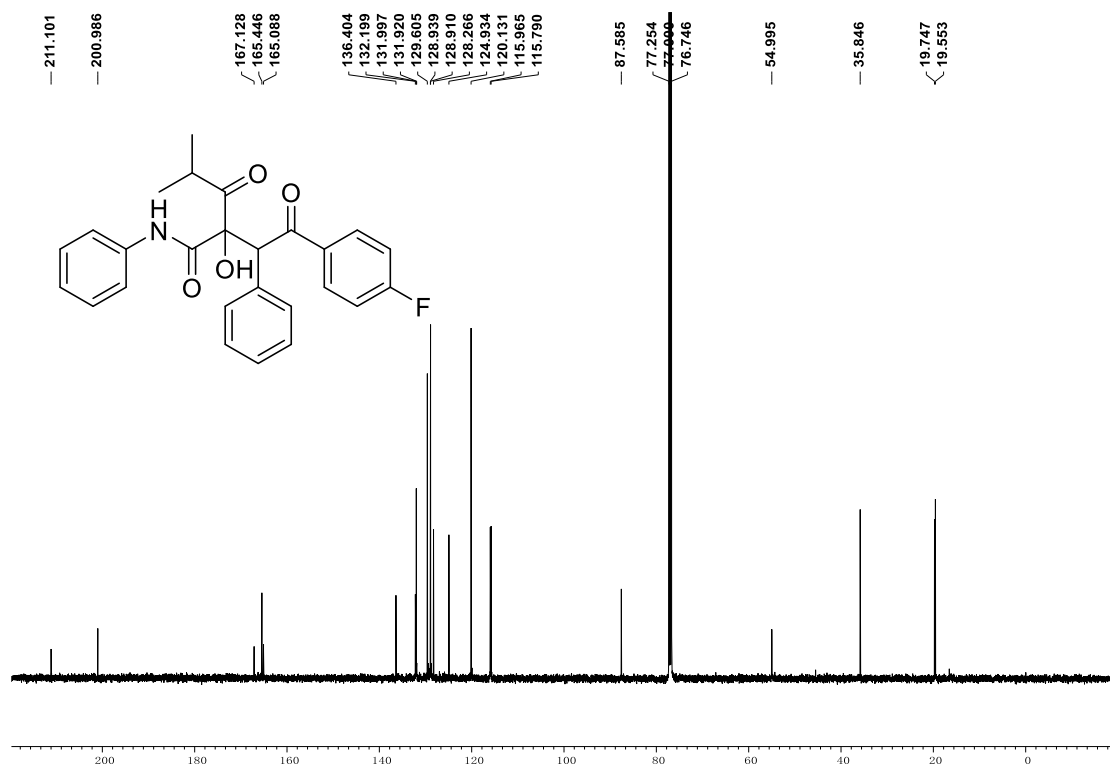
### 3v $^{13}\text{C}$ NMR (126 MHz, $\text{CDCl}_3$ )



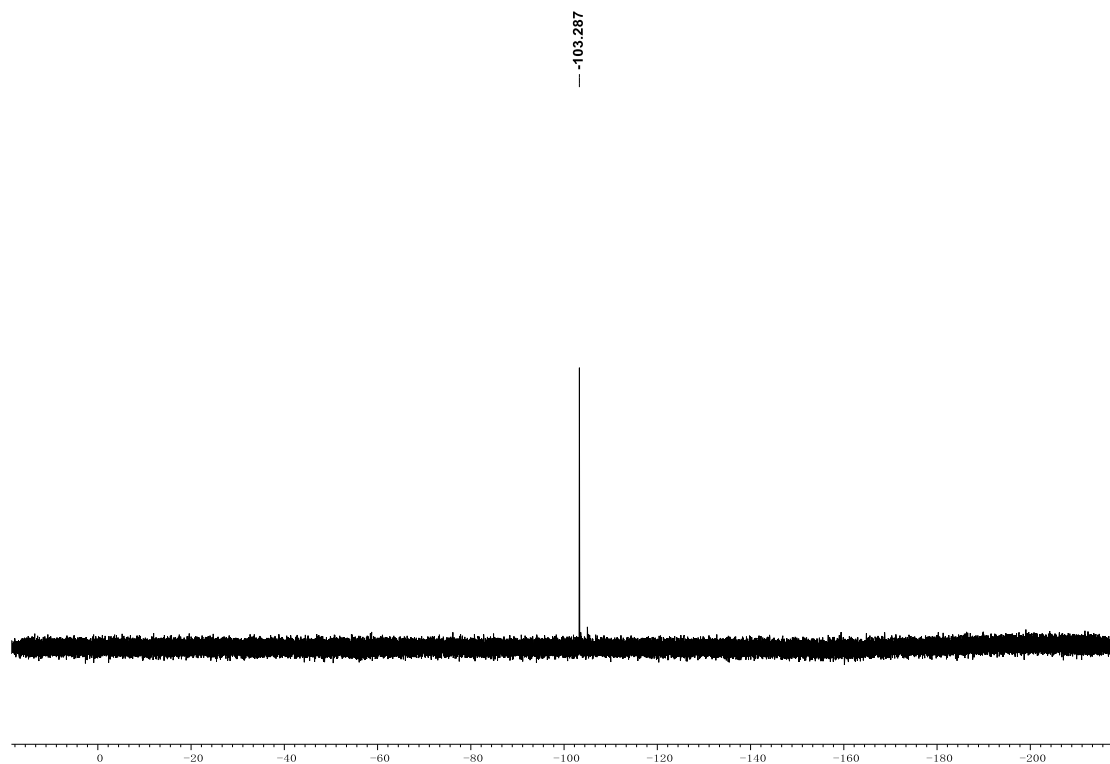
### 3w $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )



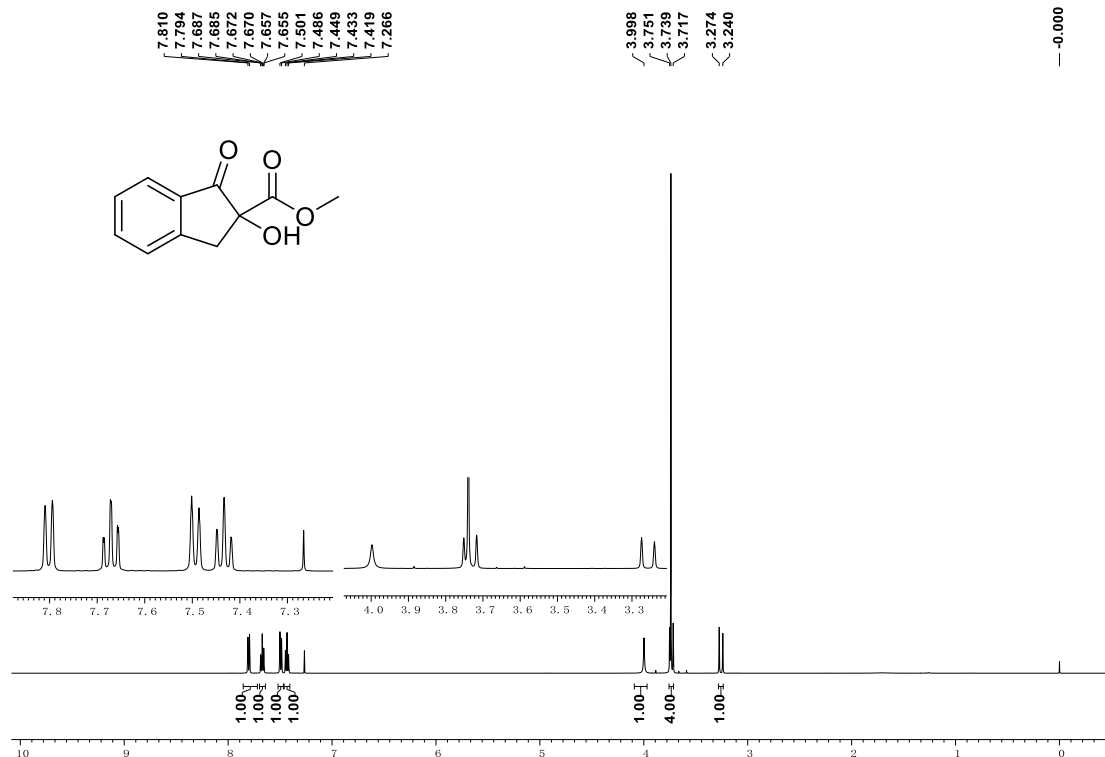
### 3w $^{13}\text{C}$ NMR (126 MHz, $\text{CDCl}_3$ )



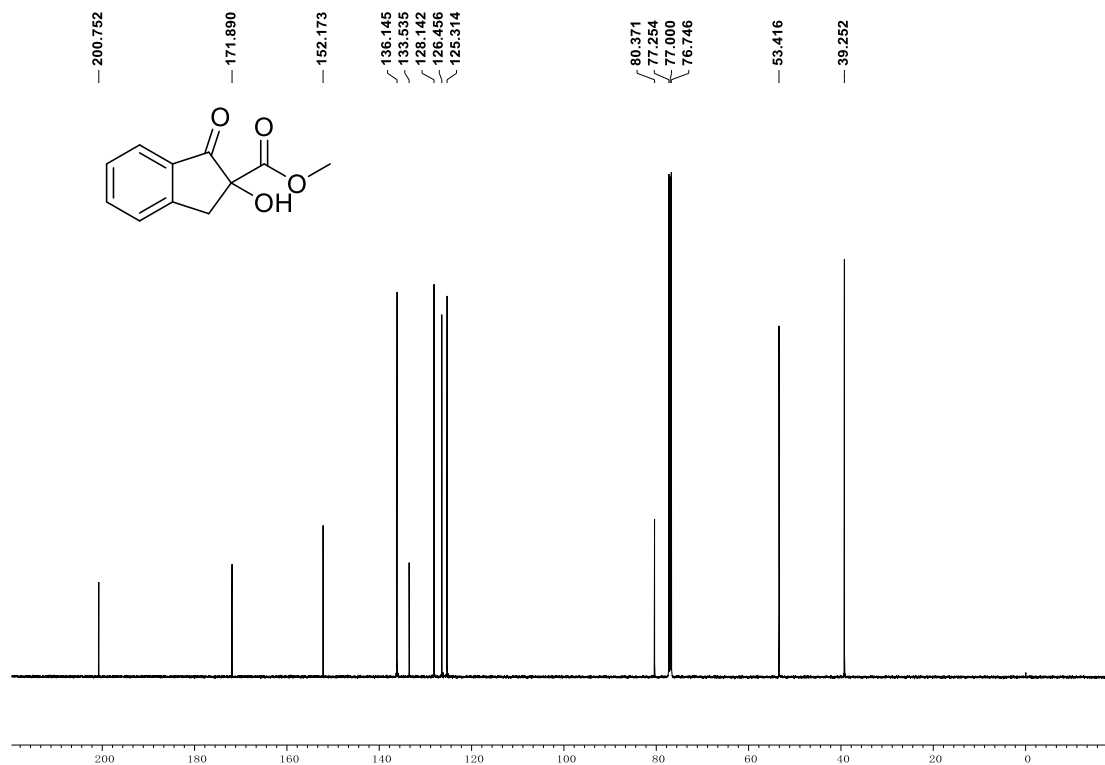
### 3w $^{19}\text{F}$ NMR (376 MHz, $\text{CDCl}_3$ )



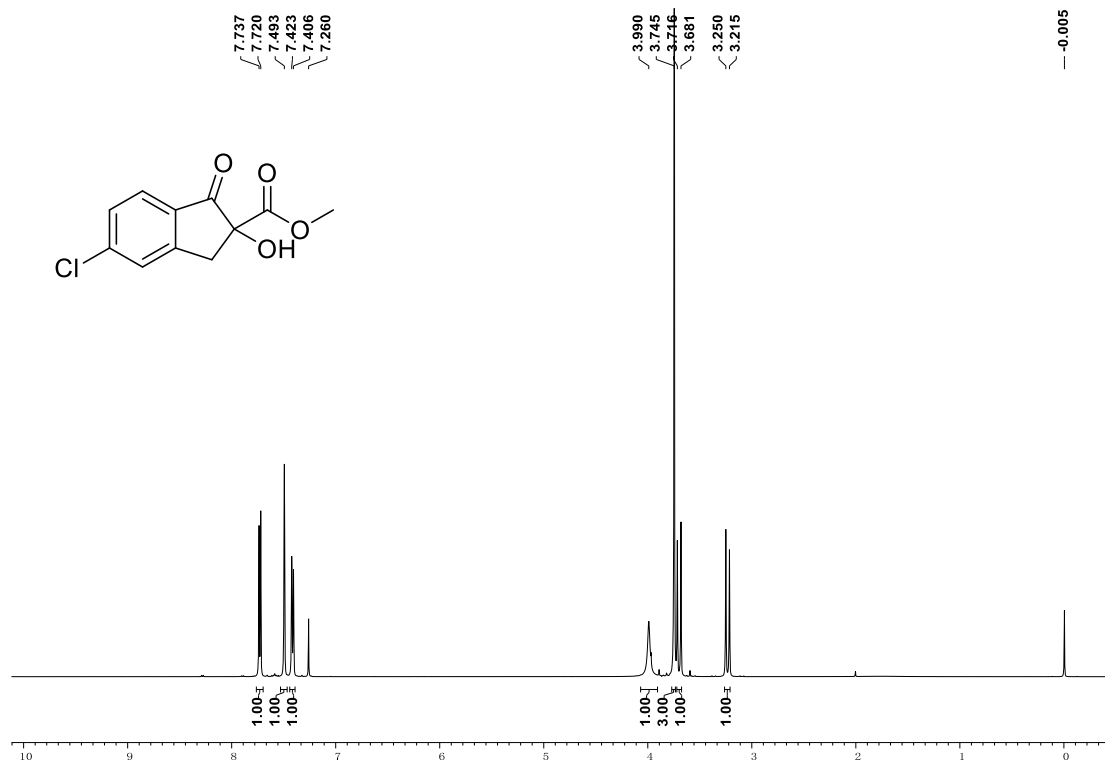
### 3x <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



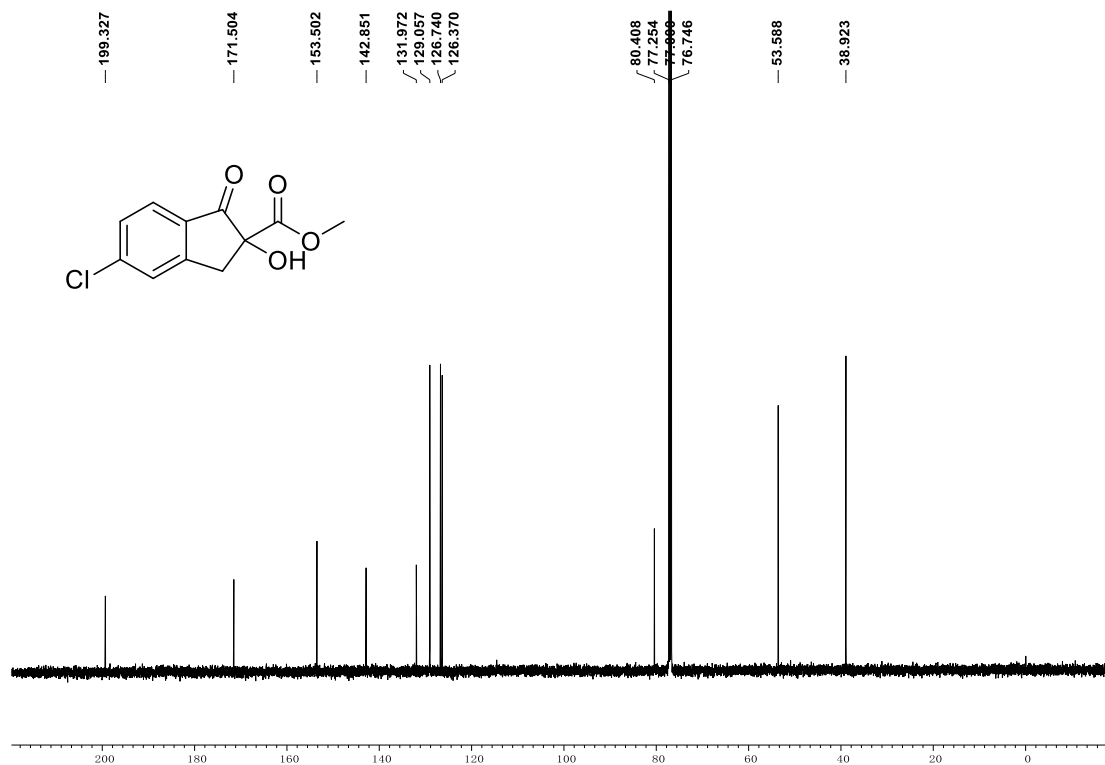
### 3x <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



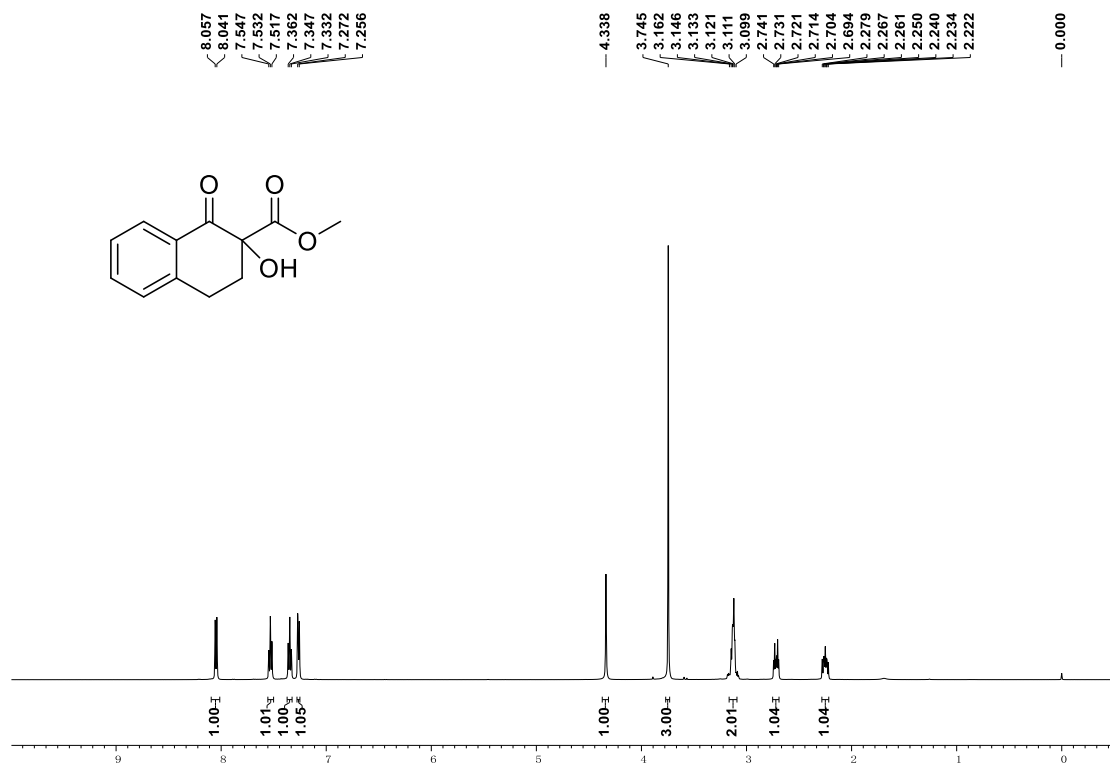
### 3y <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



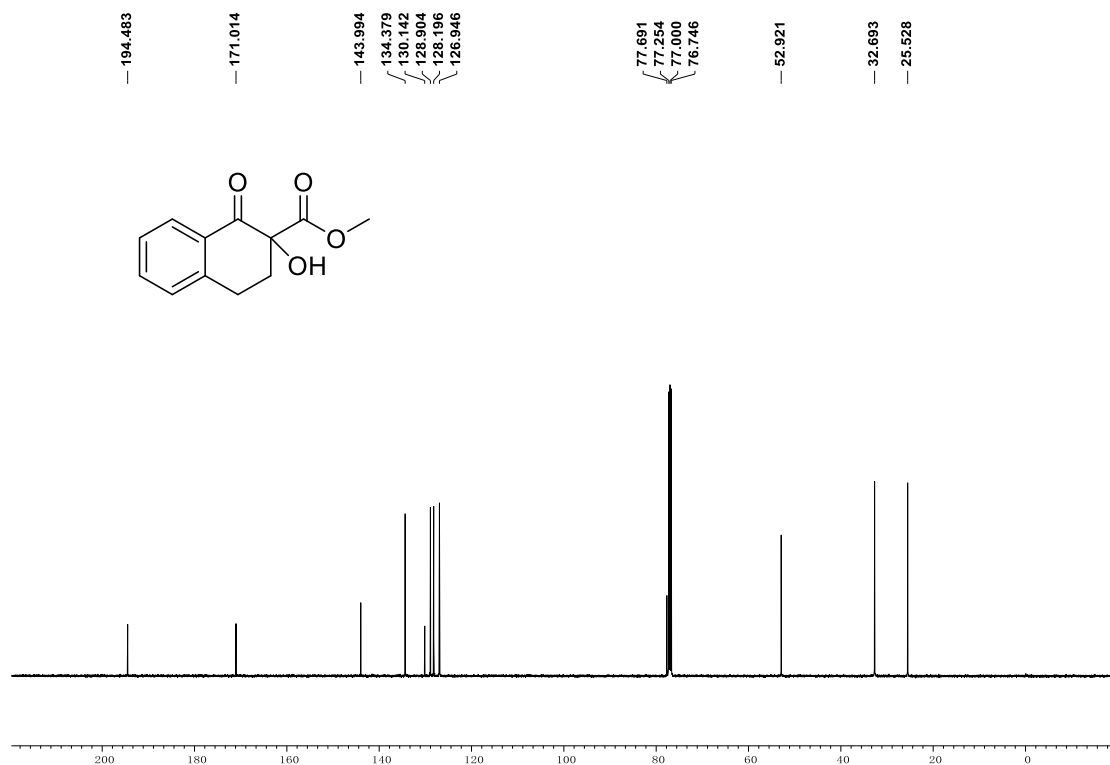
### 3y <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



### 3z <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

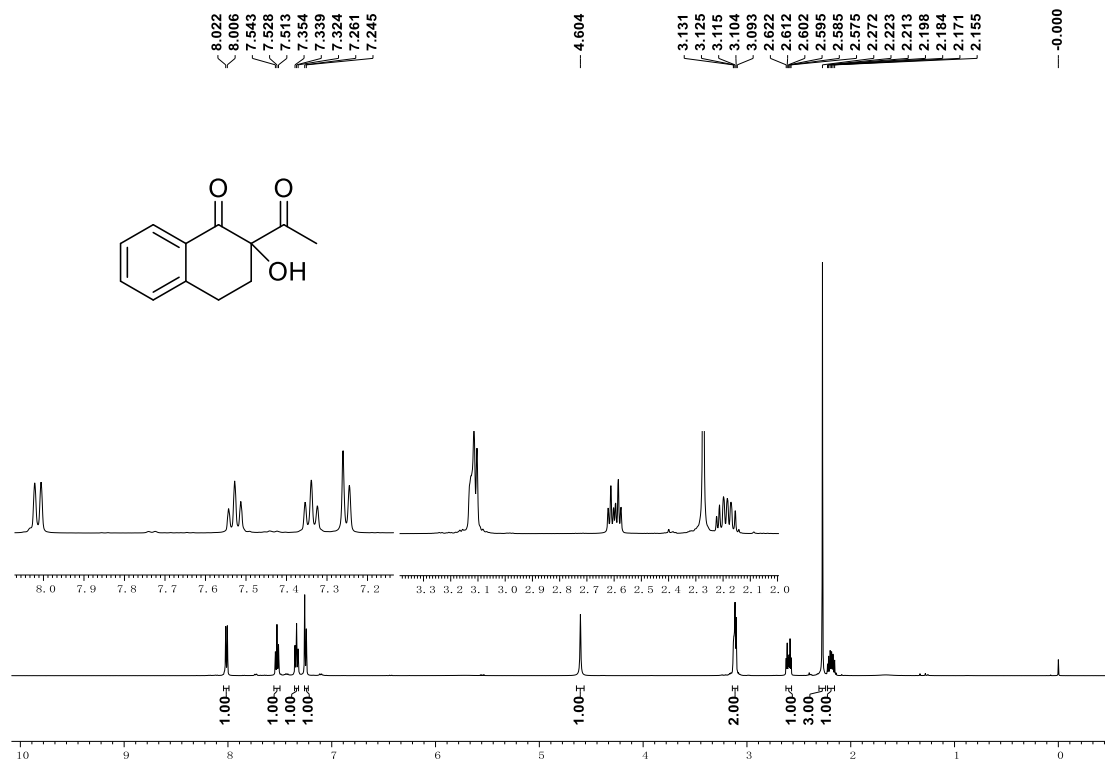


### 3z <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

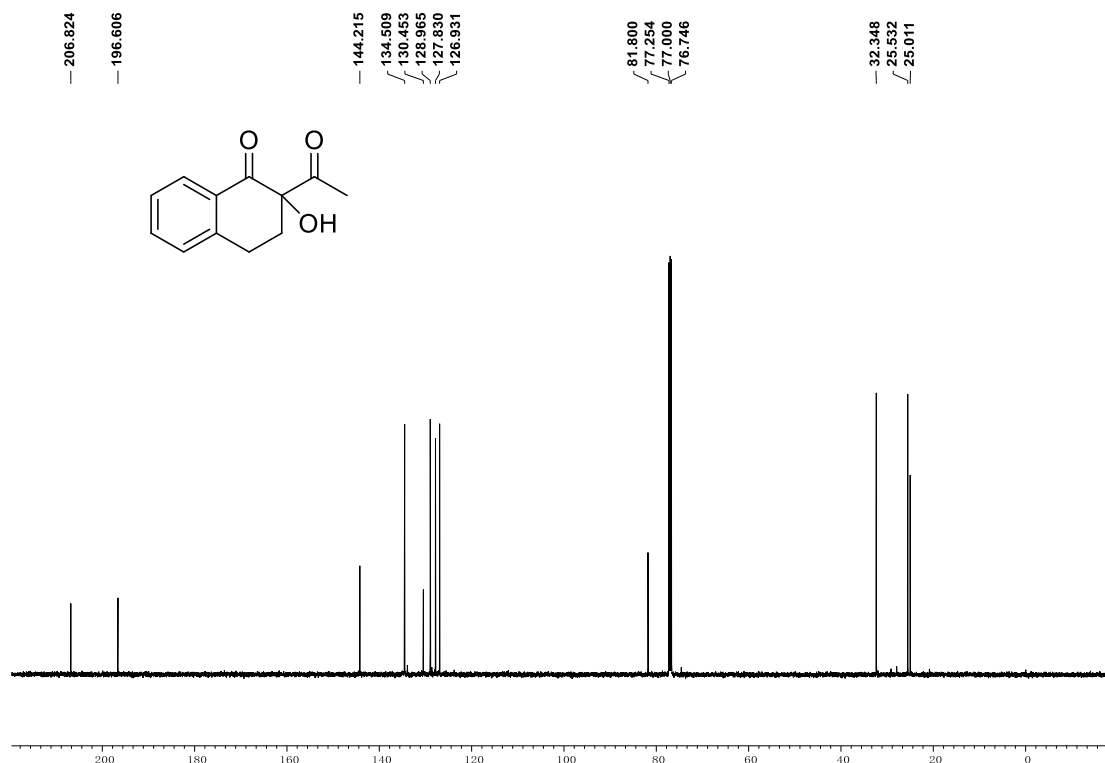




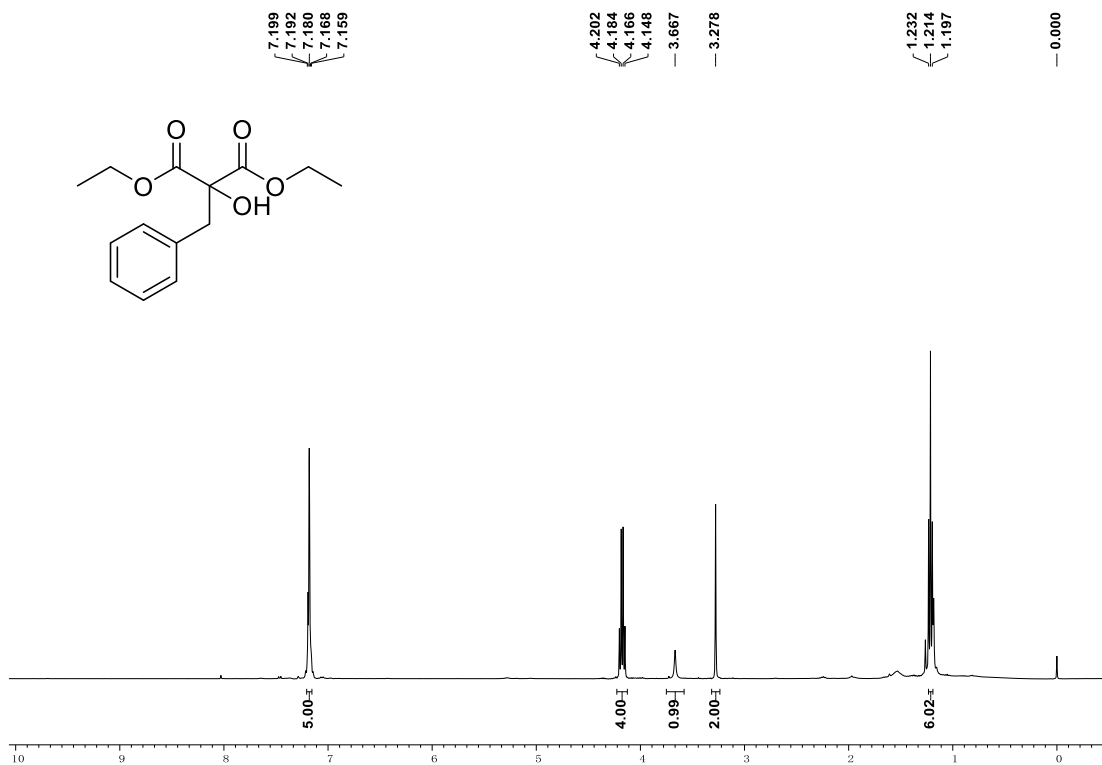
### 3aa <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



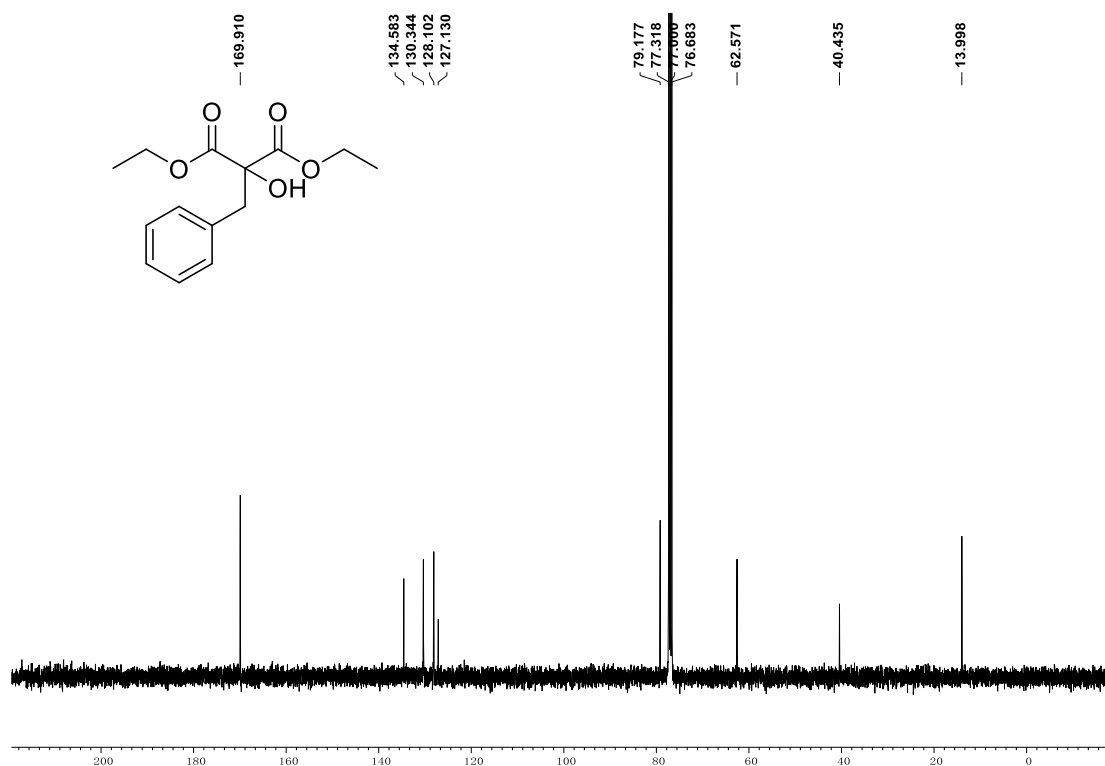
### 3aa <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



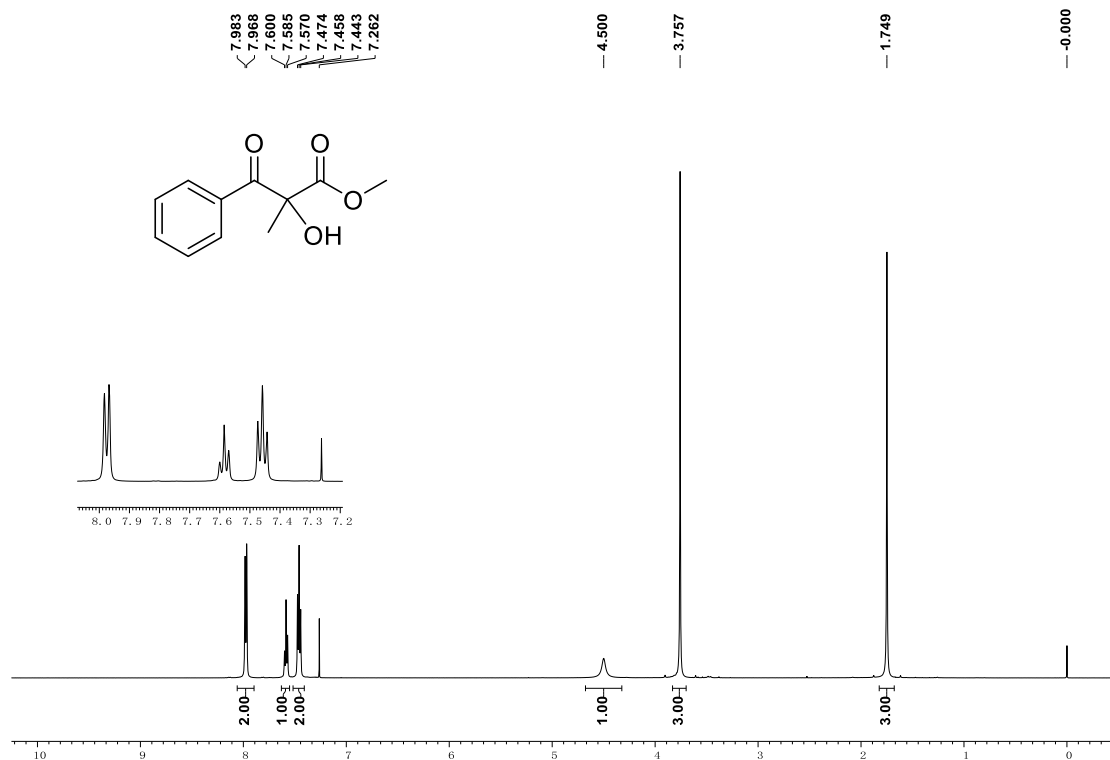
### 3ab <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



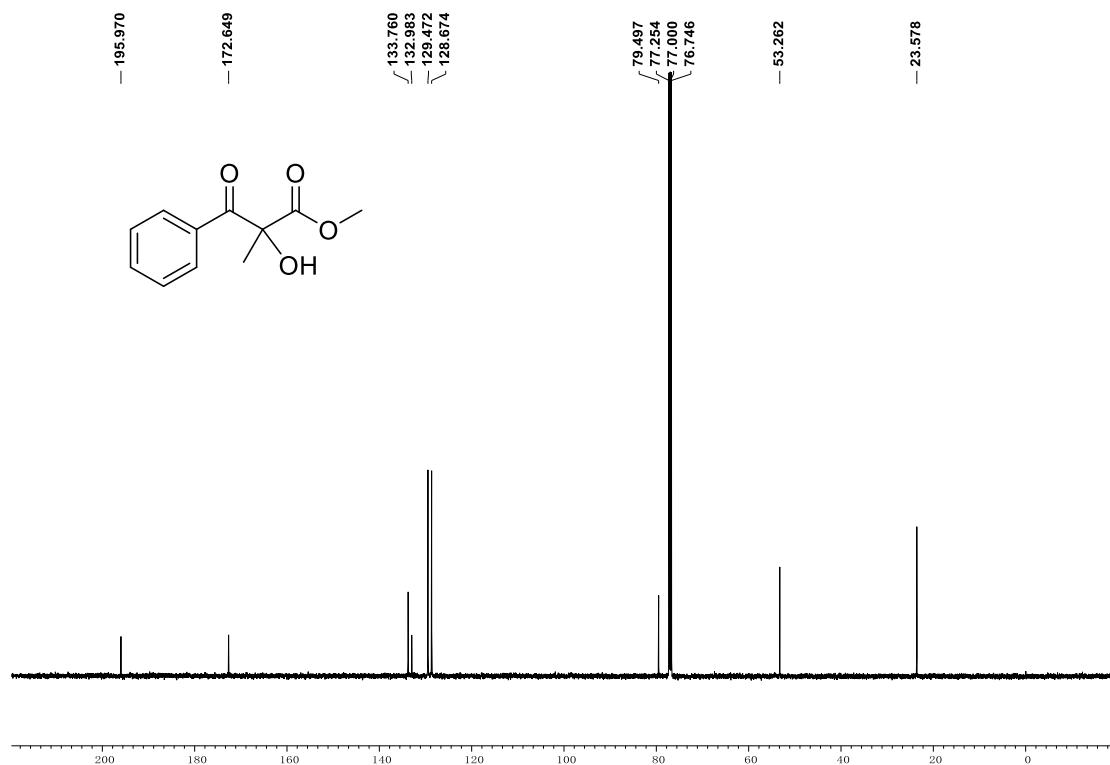
### 3ab <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



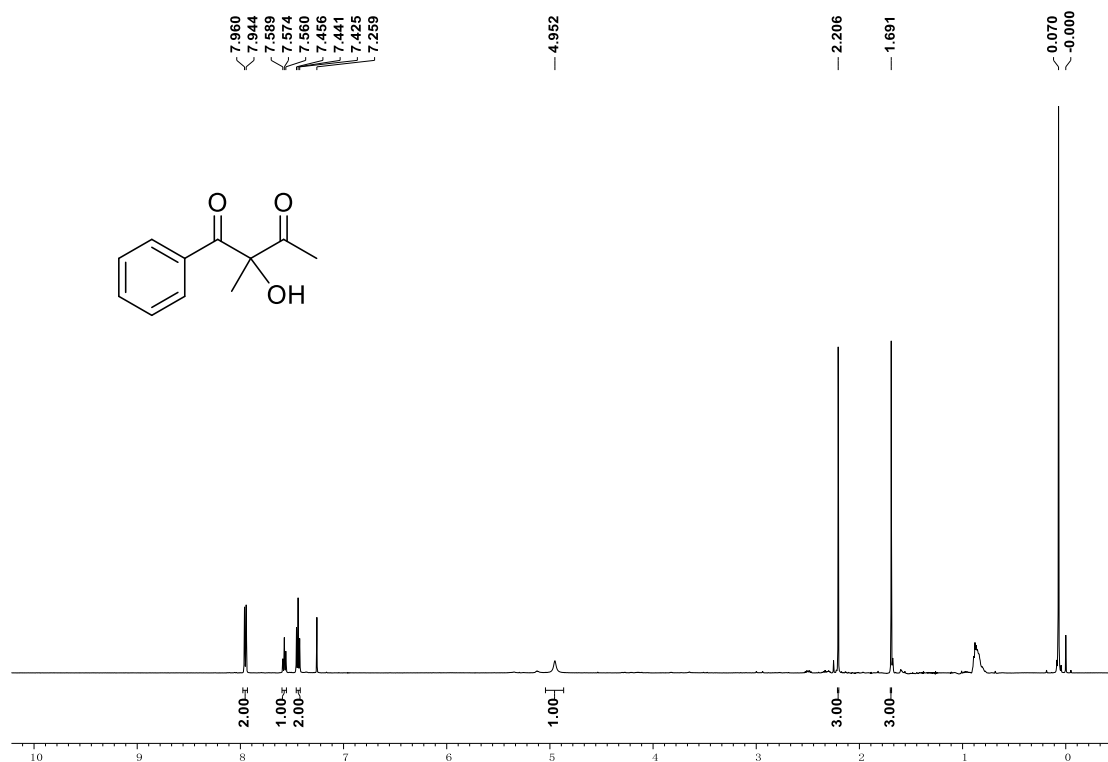
### 3ac <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



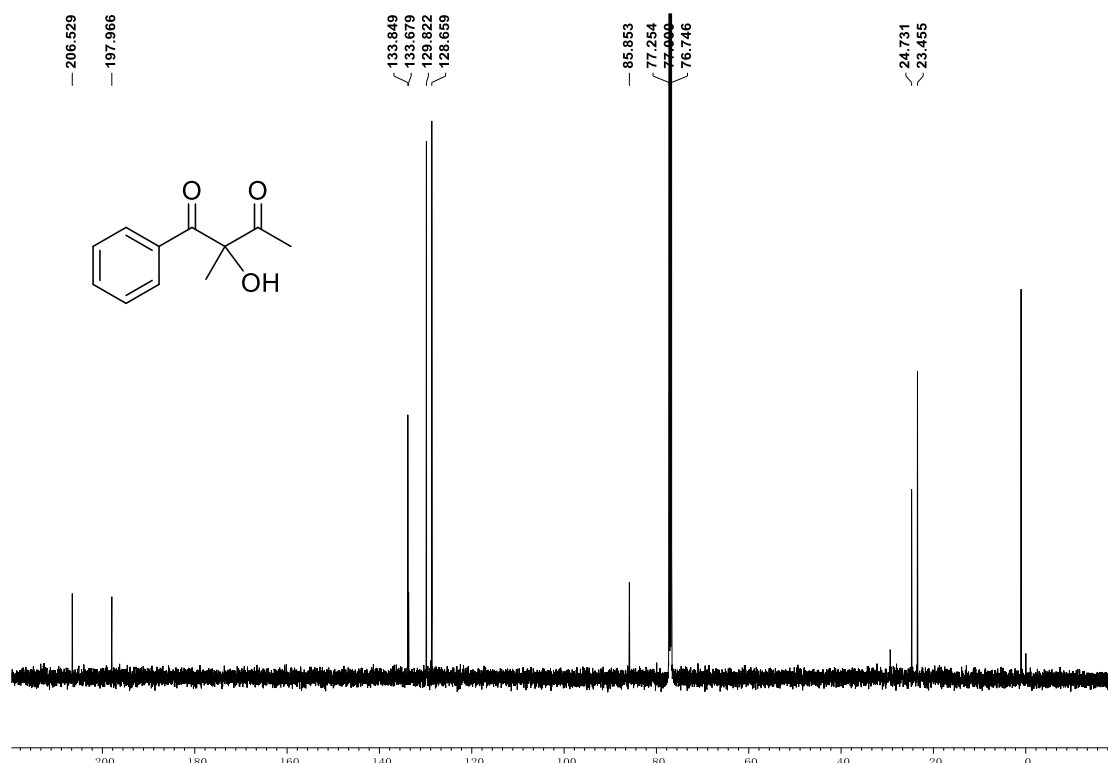
### 3ac <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



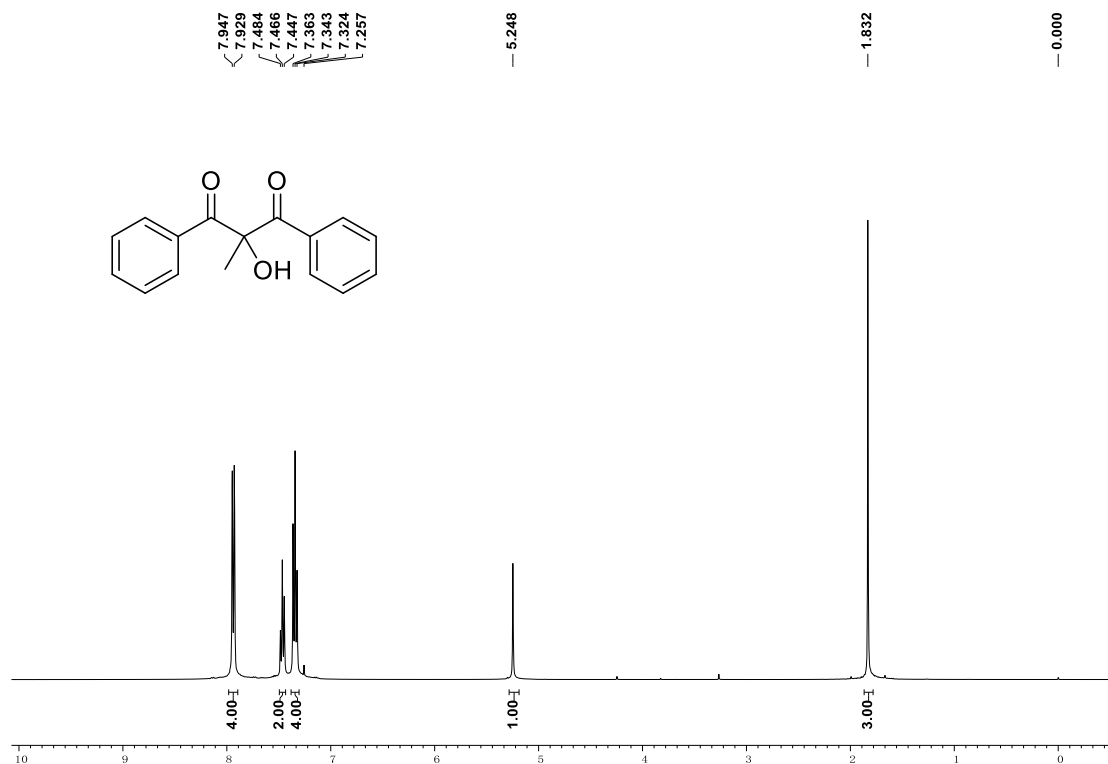
### 3ad <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



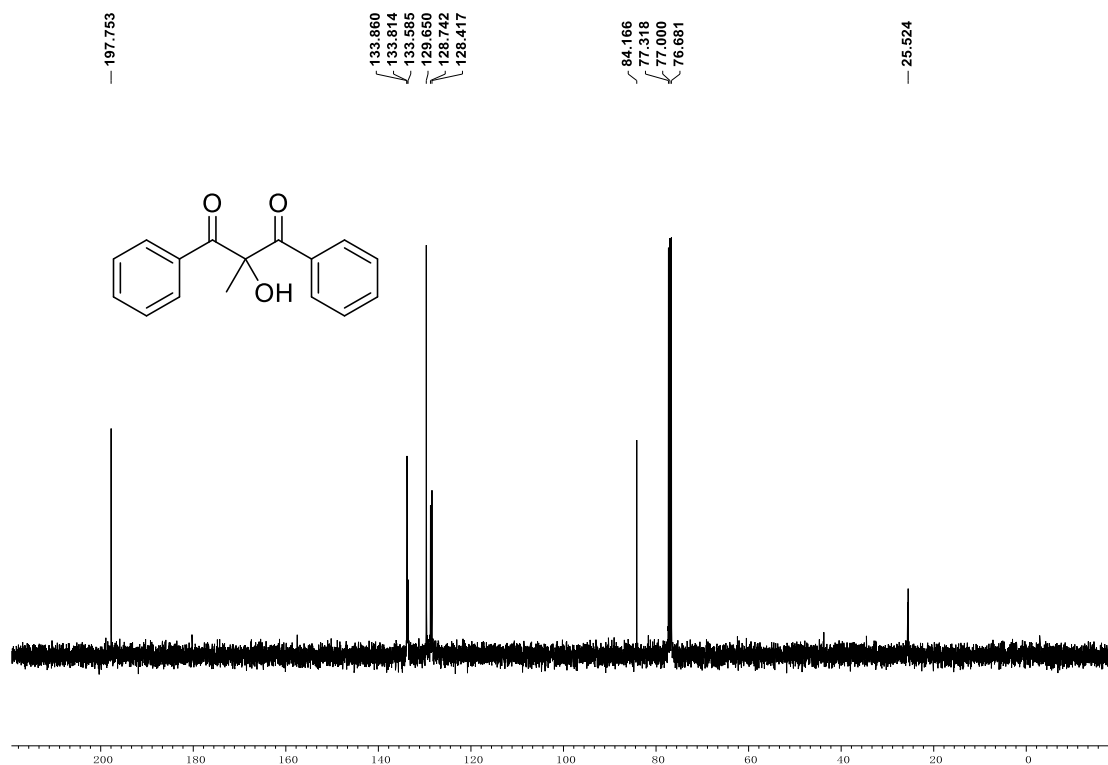
### 3ad <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



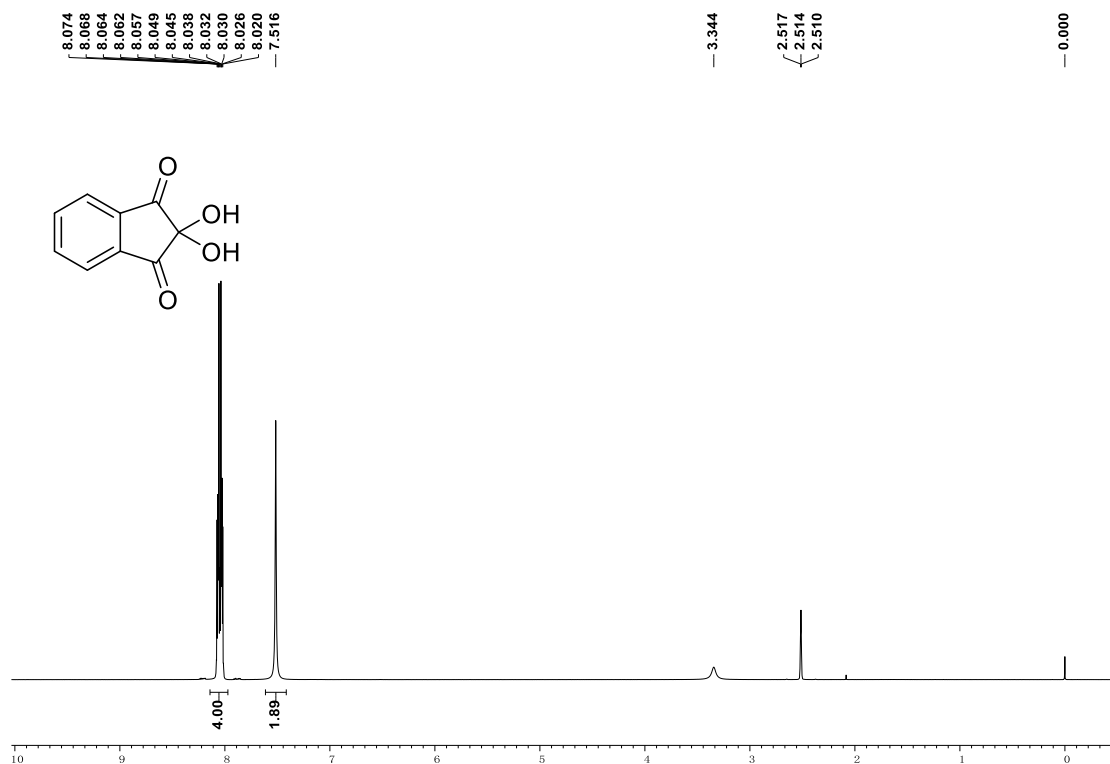
### 3ae <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



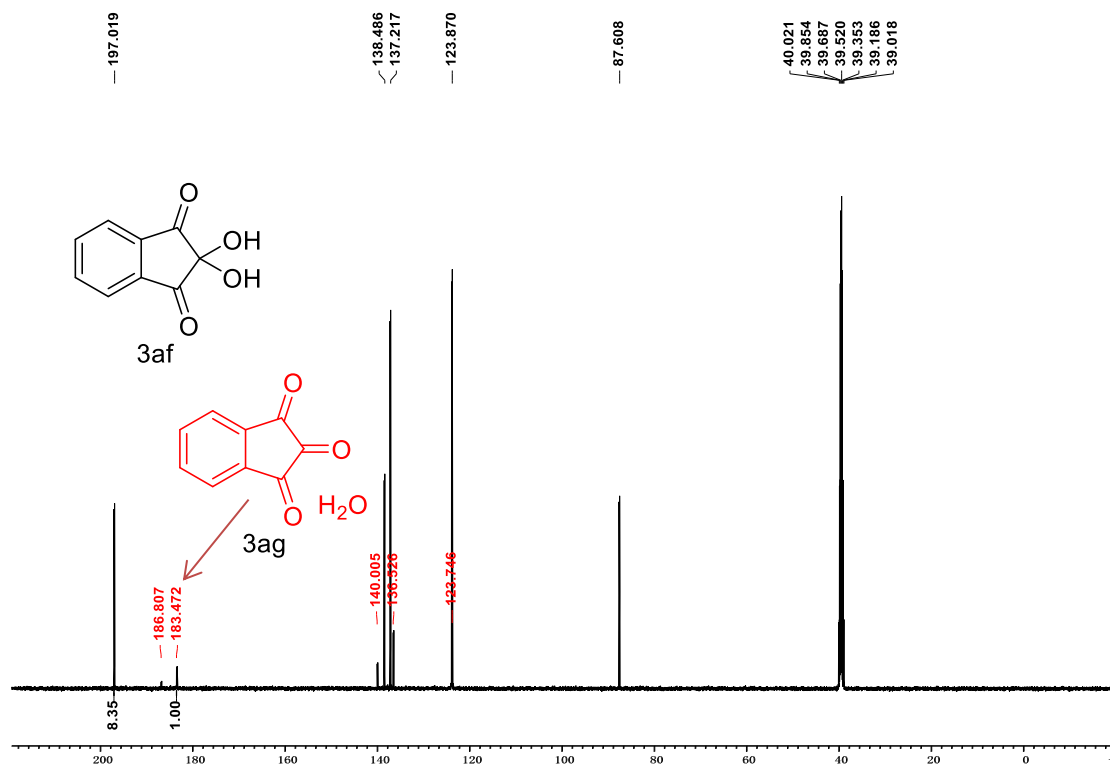
### 3ae <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



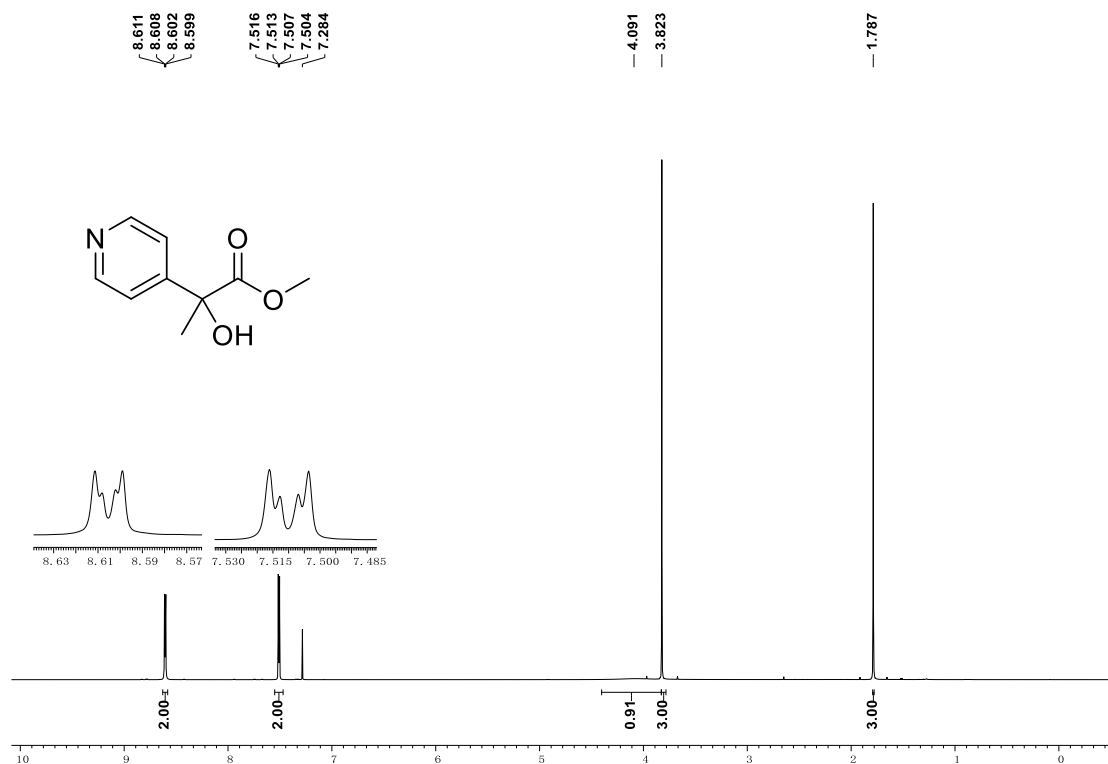
### 3af <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



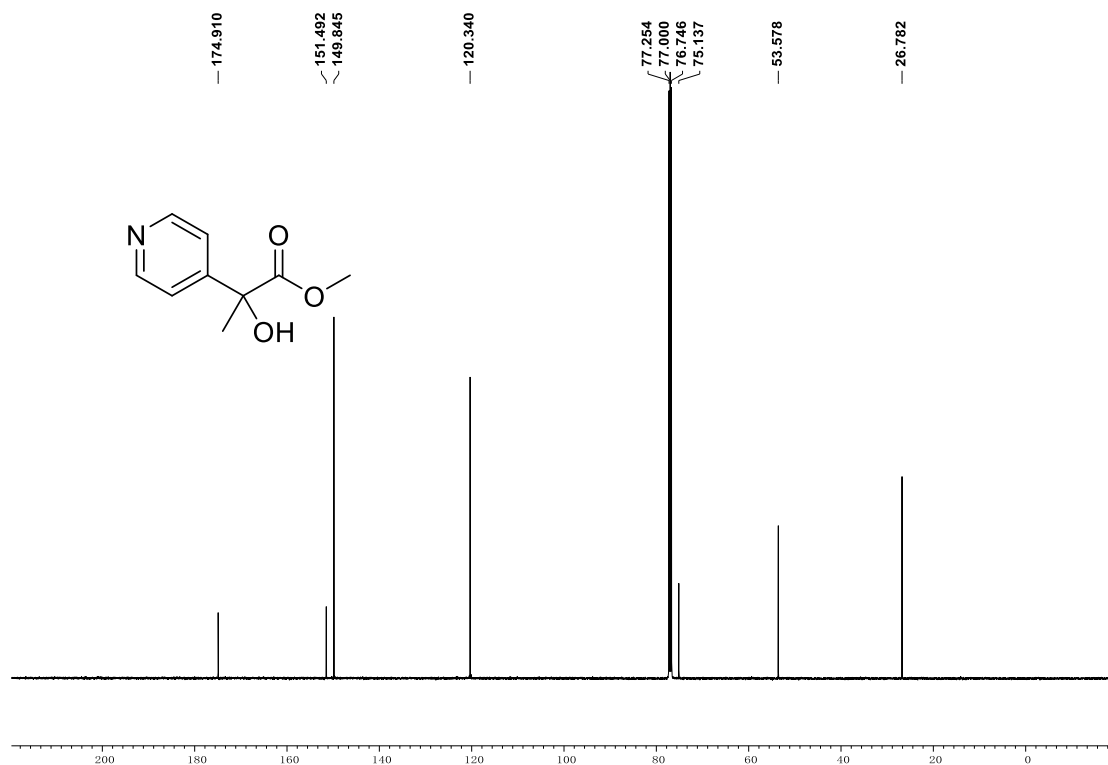
### 3af <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



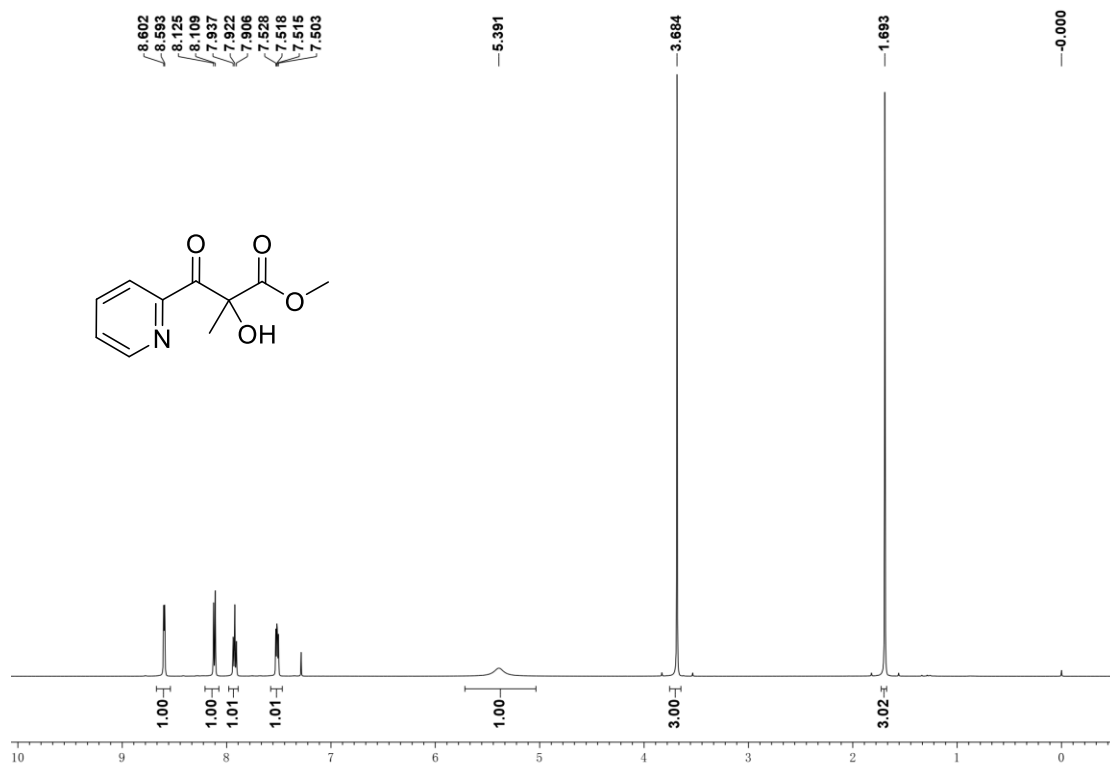
### 5a <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



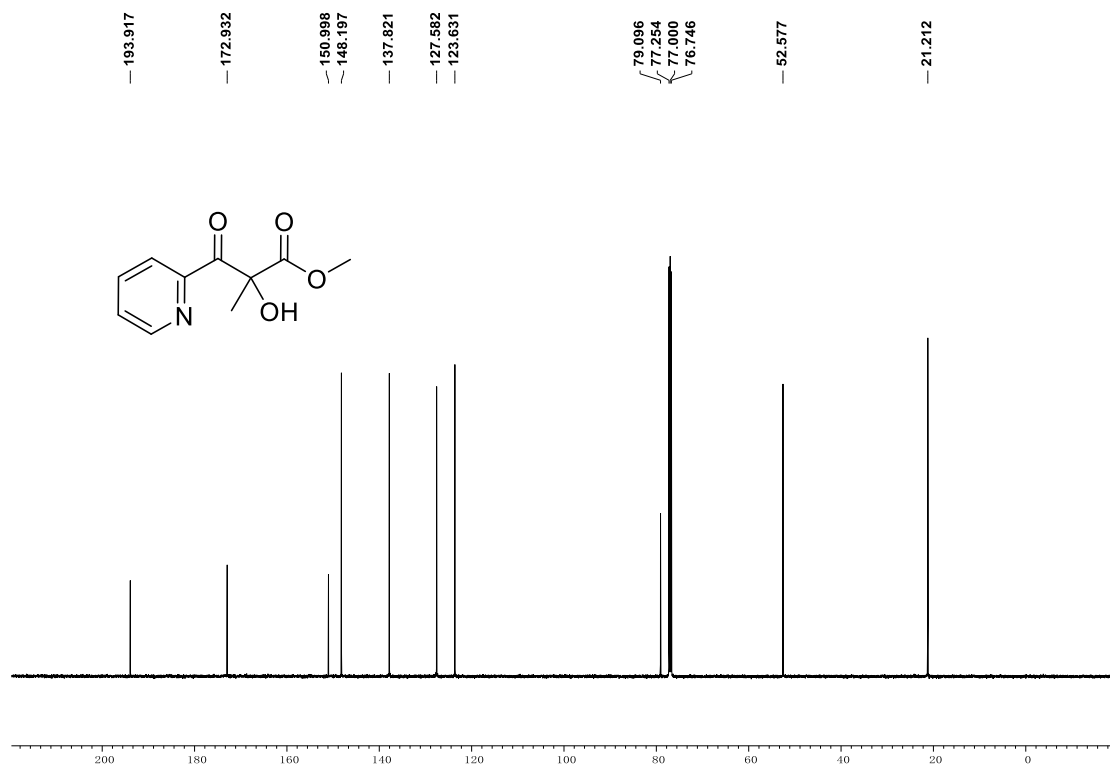
### 5a <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



## 5b <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

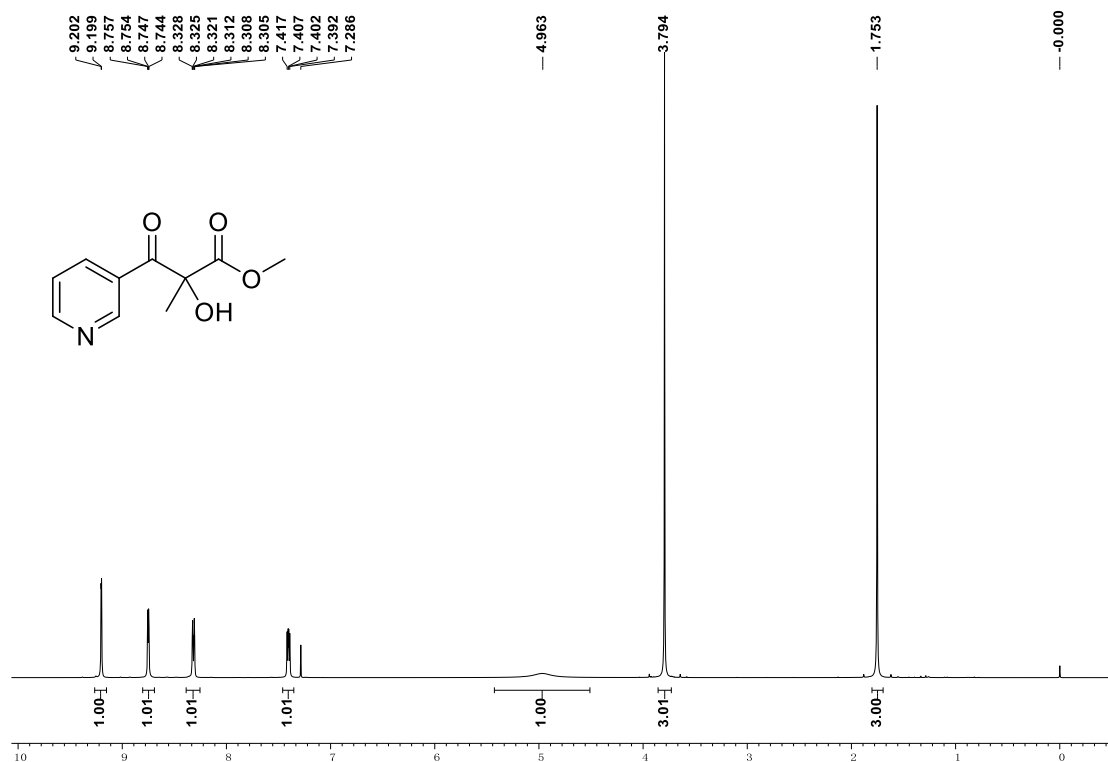


## 5b <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

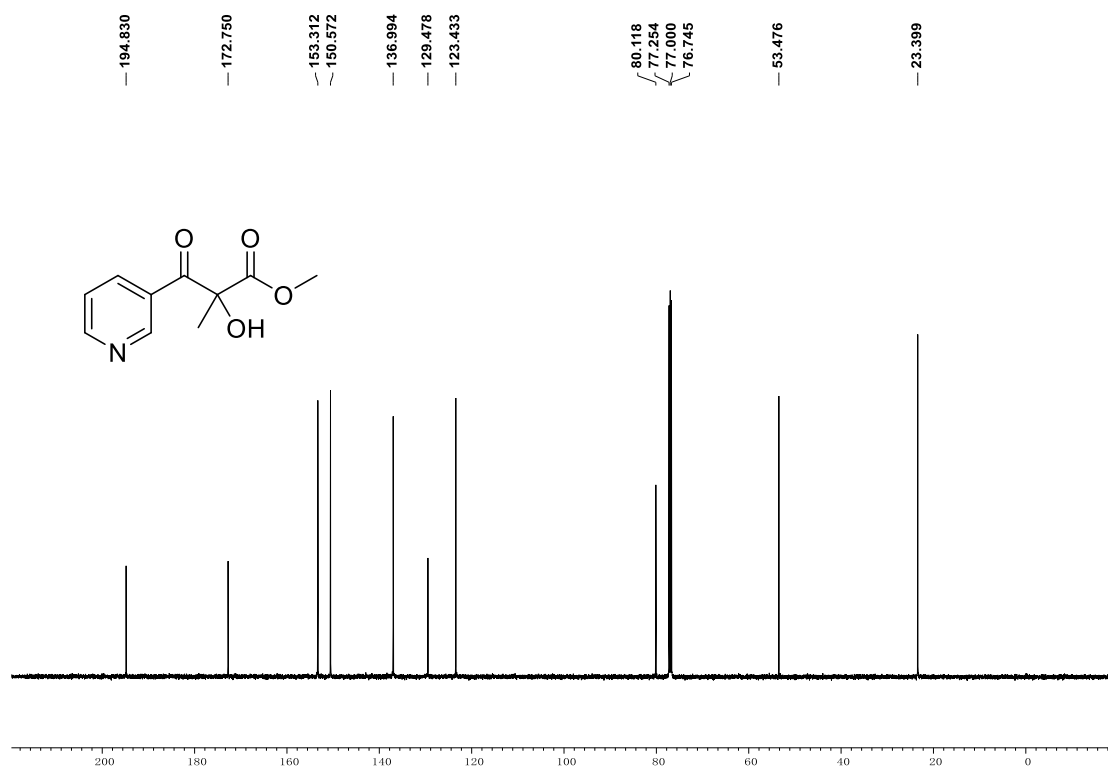




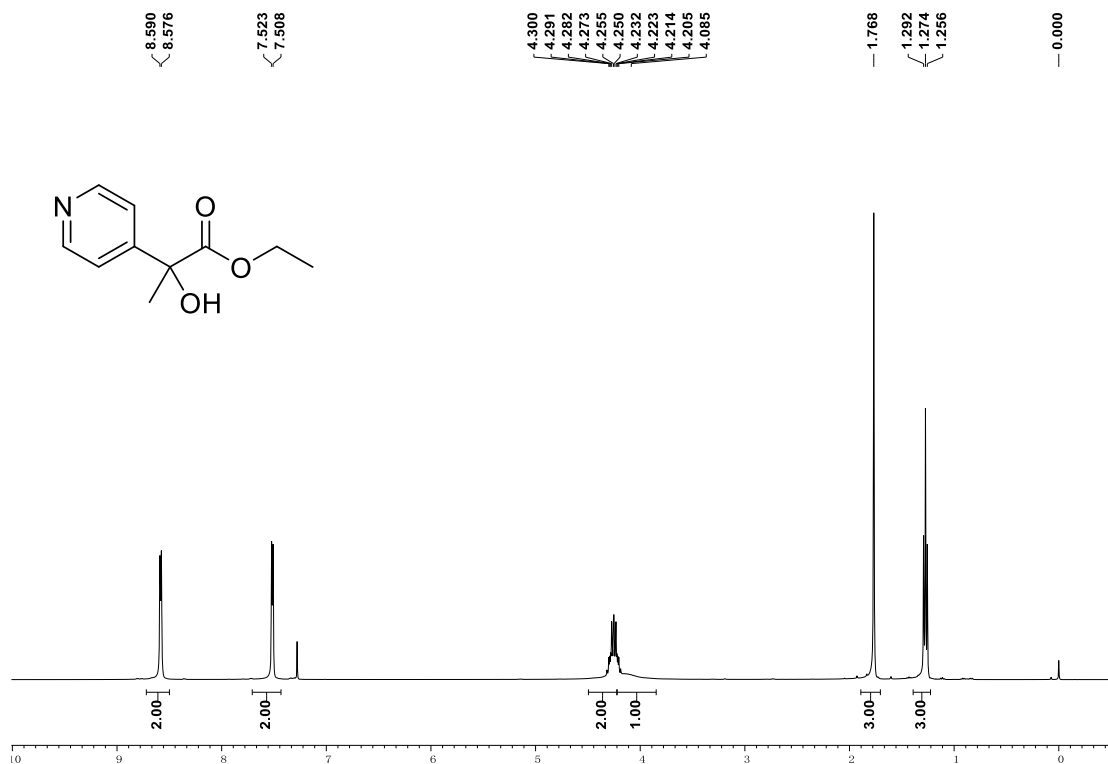
### 5c <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



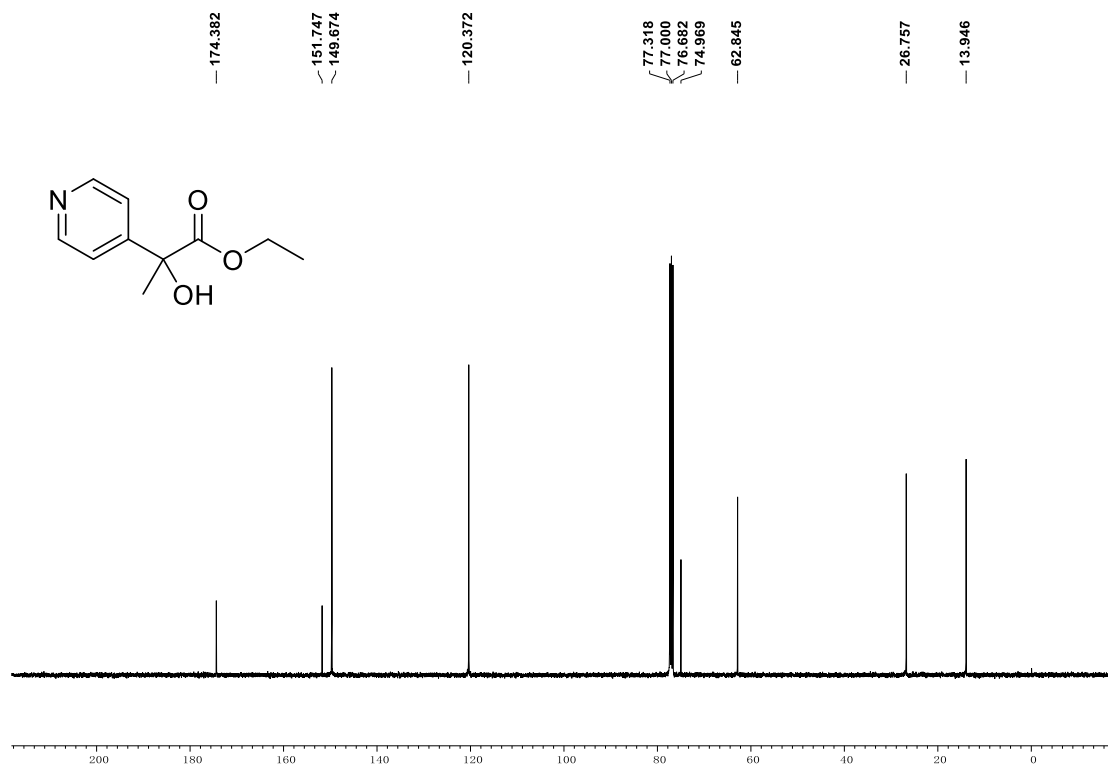
### 5c <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



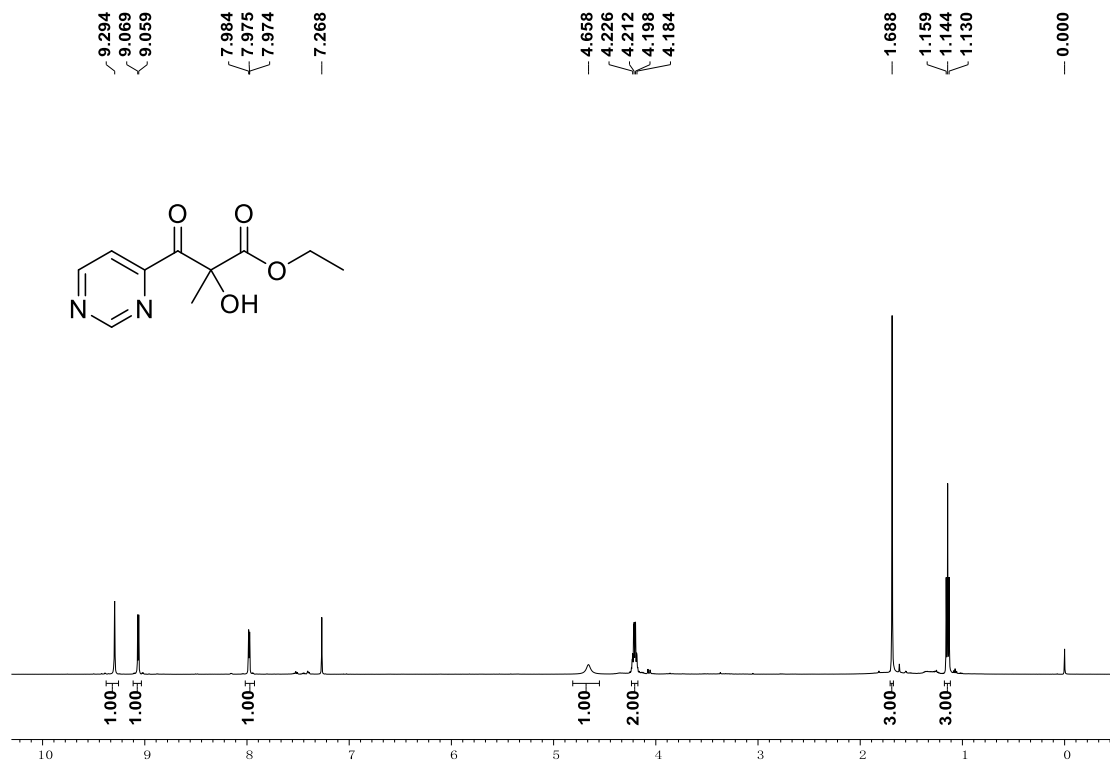
## 5d <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



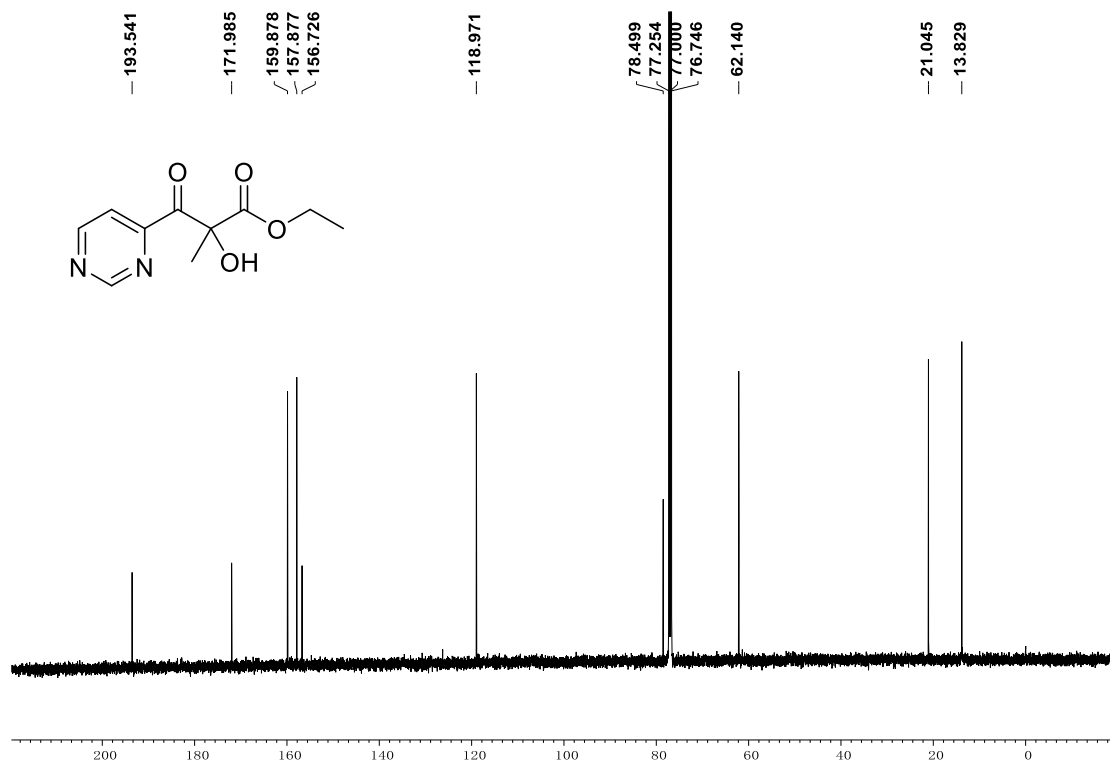
## 5d <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



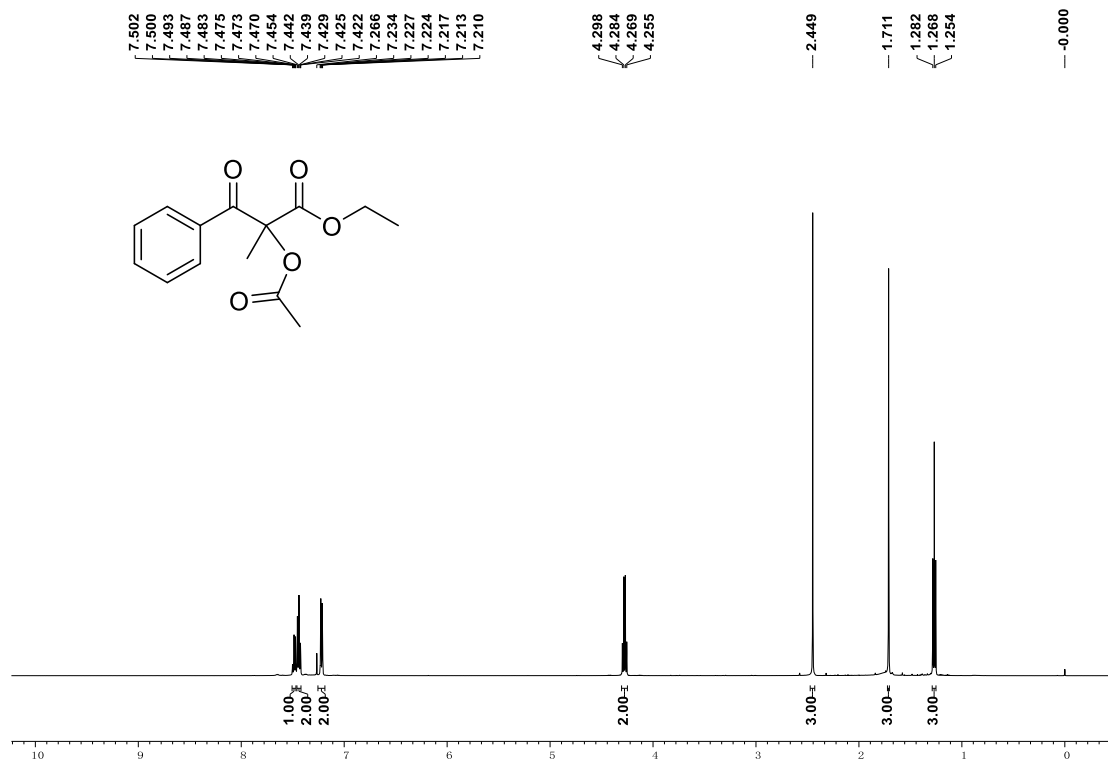
### 5e <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



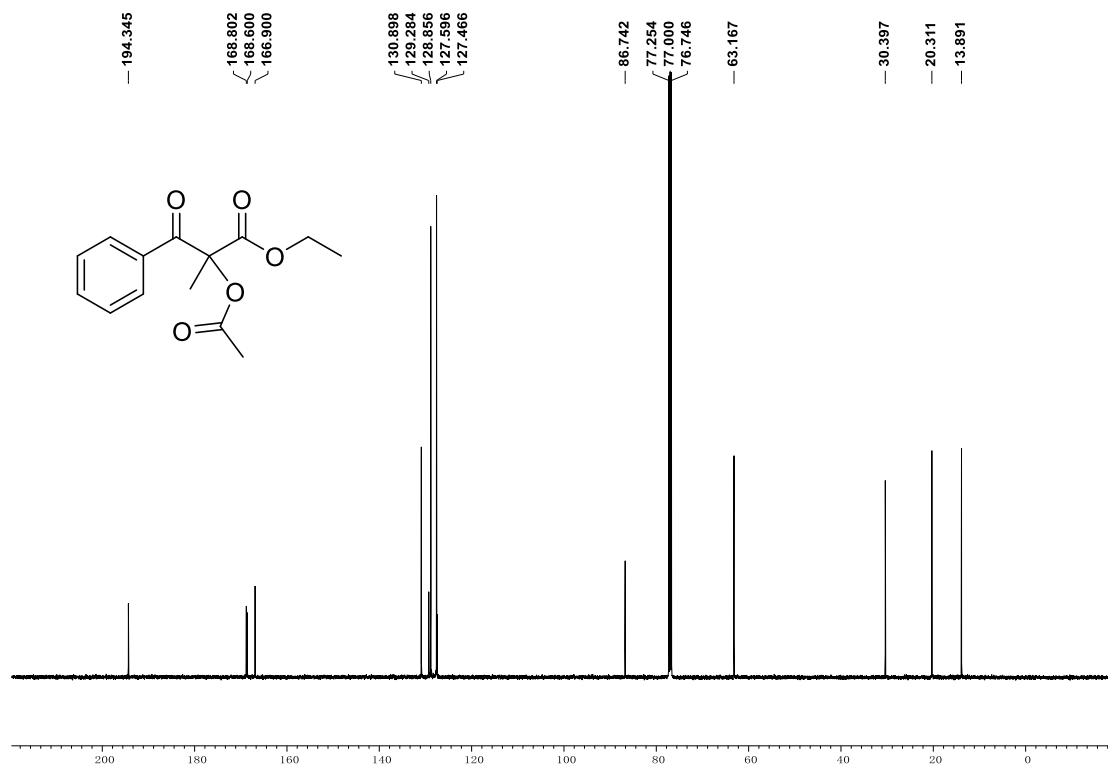
### 5e <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



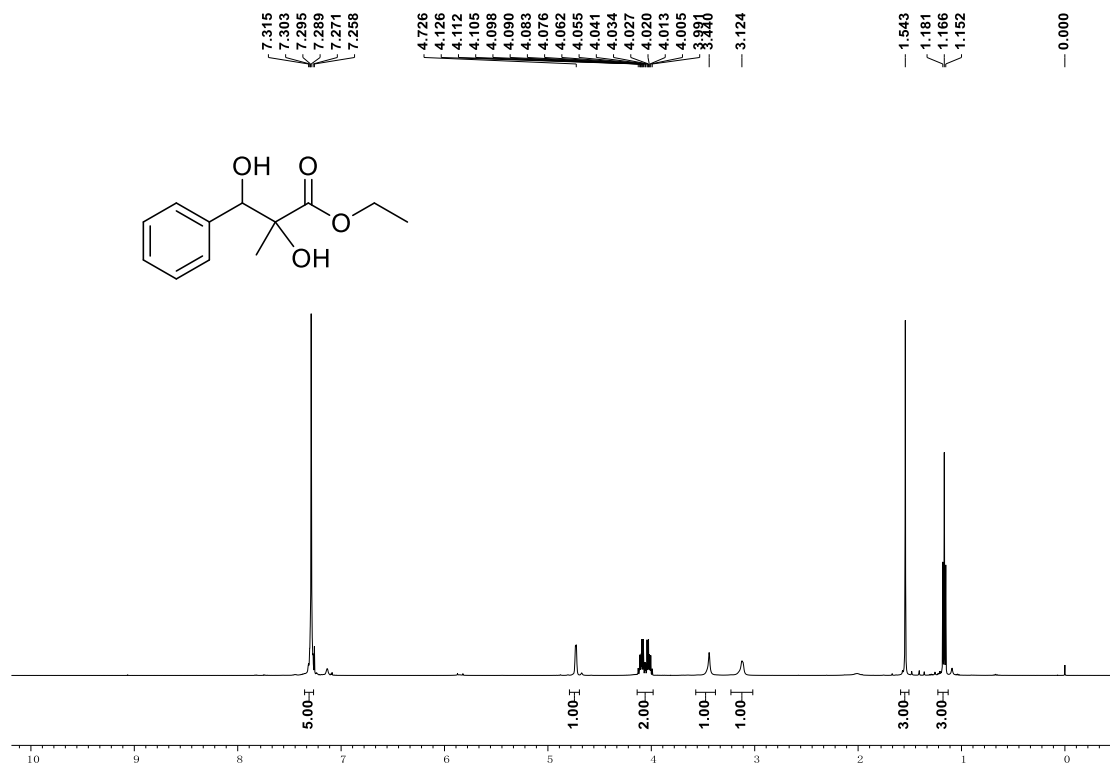
## 6 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



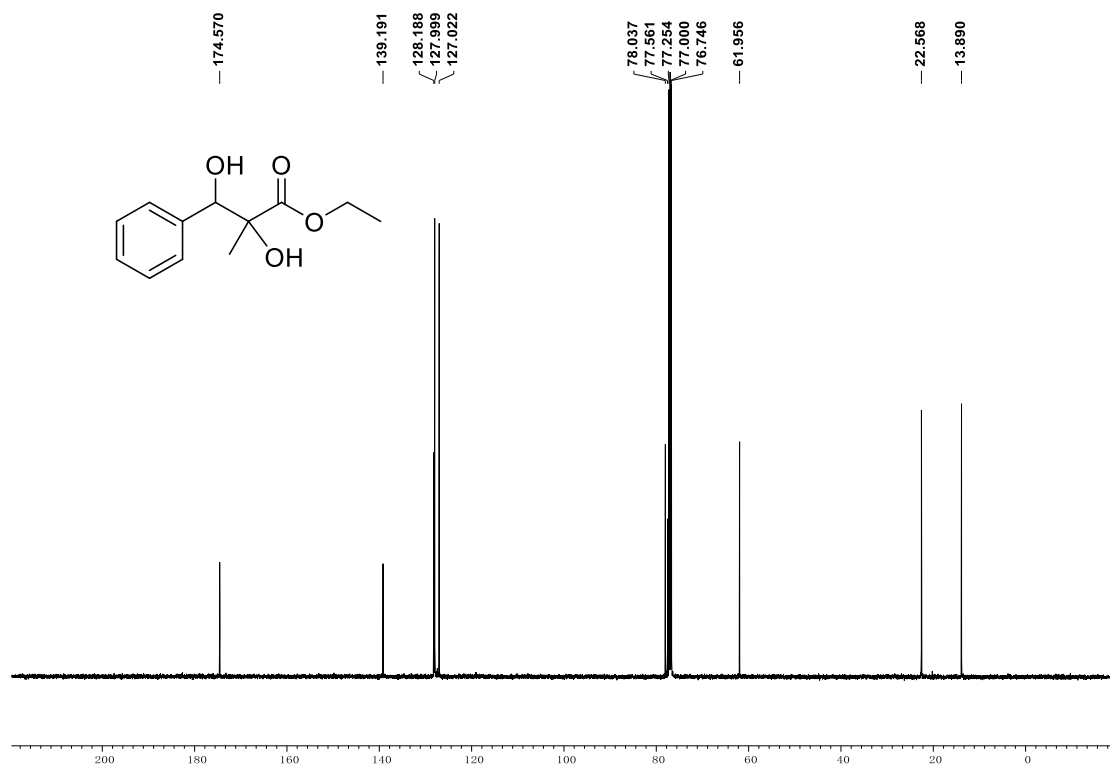
## 6 <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



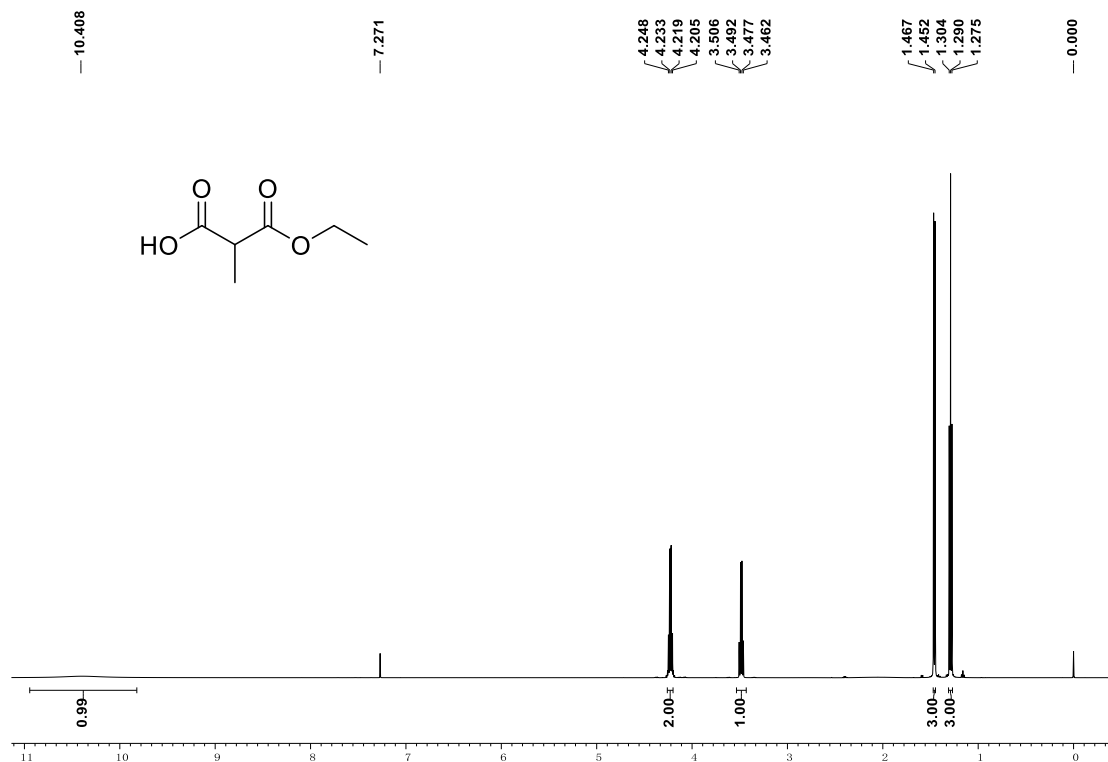
# 7 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



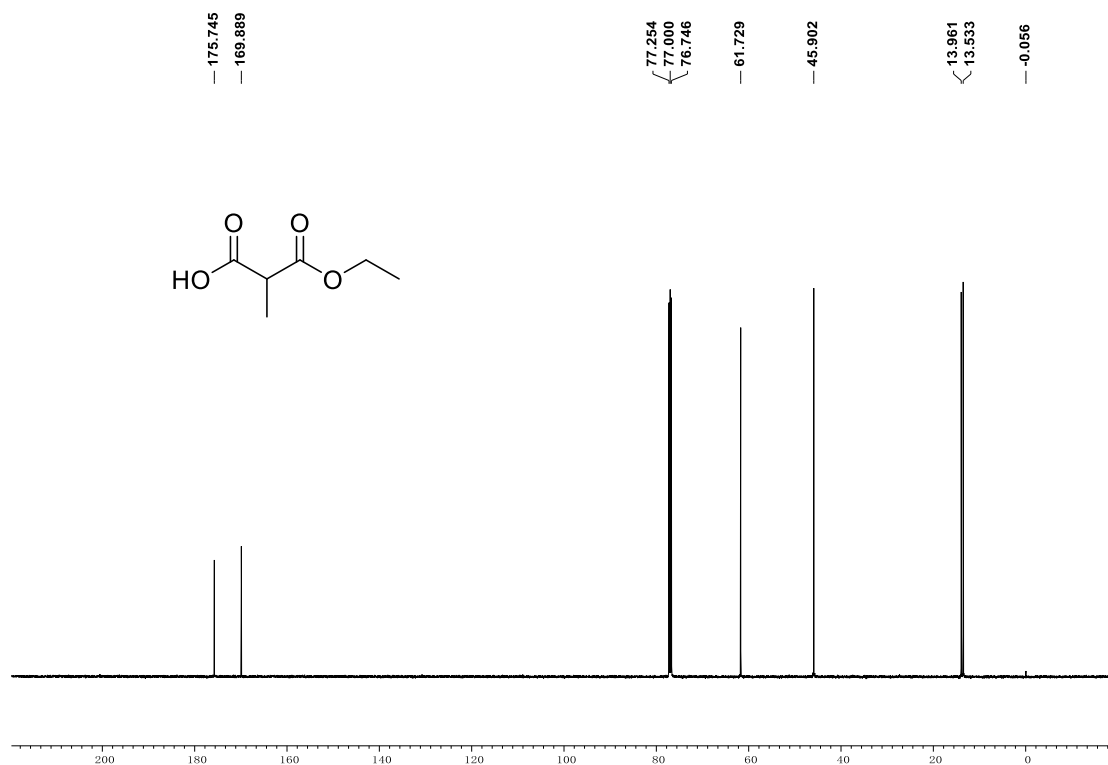
# 7 <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



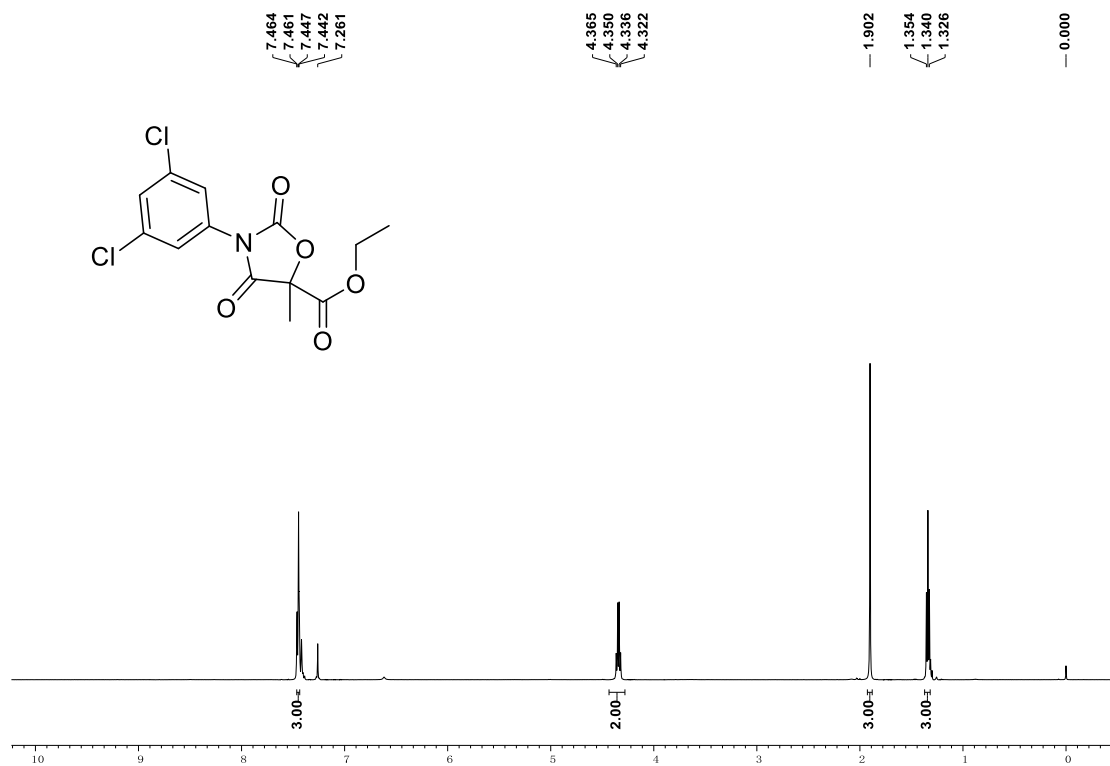
# 9 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



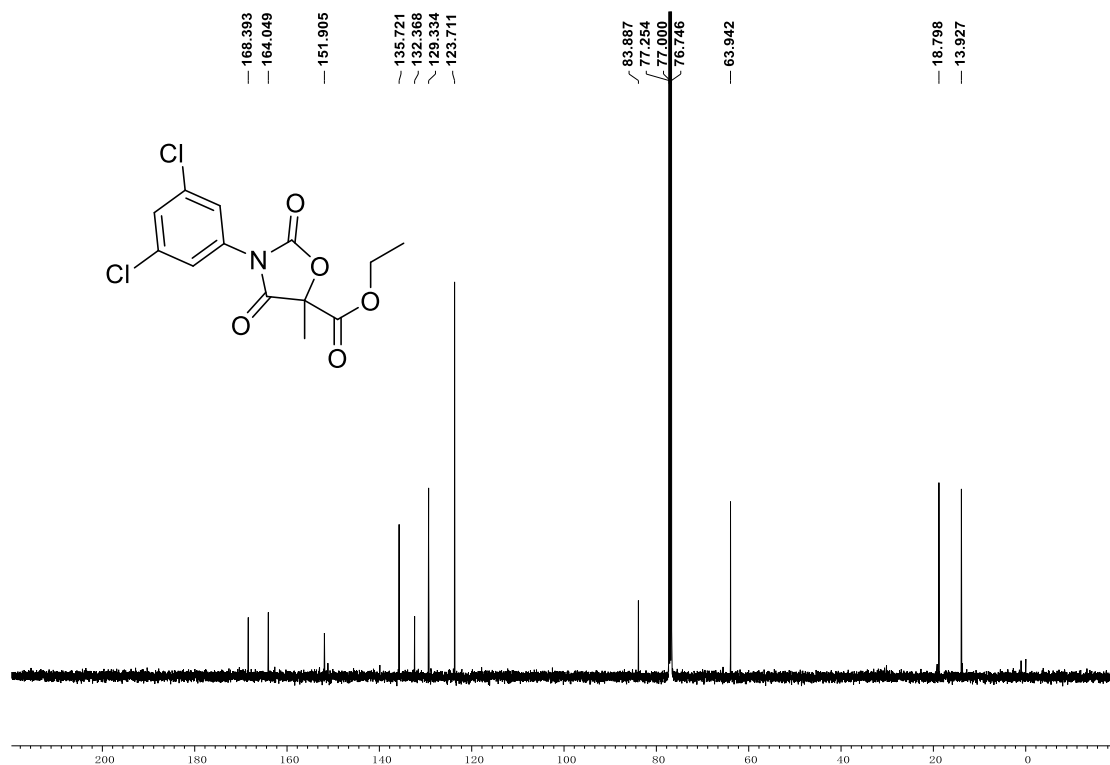
# 9 <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



# 10 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



# 10 <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



## 10. References

- (1) L. Li, F. Han, X. Nie, Y. Hong, S. Ivlev and E. Meggers, *Angew. Chem. Int. Ed.*, 2020, **59**, 12392.
- (2) S. Kobori, S. Huh, S. D. Appavoo and A. K. Yudin, *J. Am. Chem. Soc.*, 2021, **143**, 5166.
- (3) A. L. Gabbey, N. W. Michel, J. M. Hughes, L. C. Campeau and S. A. Rousseaux, *Org. Lett.*, 2022, **24**, 3173.
- (4) Z. Xing, B. Fang, S. Luo, X. Xie, and Wang, X. Generation of Fused Seven-Membered Polycyclic Systems via Ring Expansion and Application to the Total Synthesis of Sesquiterpenoids. *Org. Lett.*, 2022, **24**, 4034.
- (5) F. Wu, H. Li, R. Hong and L. Deng, *Angew. Chem. Int. Ed.*, 2006, **45**, 947.
- (6) K. Wang, B. Wang, X. Liu, H. Fan, Y. Liu and C. Li, *Chin. J. Catal.* 2021, **42**, 1227.
- (7) P. Drouhin and R. J. Taylor, *Eur. J. Org. Chem.*, 2015, **11**, 2333.
- (8) (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. P. G. A. Barone, G. A. Petersson, H. J. R. A. Nakatsuji and X. Li, Gaussian 16 Revision C. 01. Gaussian Inc. Wallingford CT, 2016, **1**, 572. (b) R. D. I. I. Dennington, T. A. Keith and J. M. Millam, GaussView, version 6.0. 16. *Semichem Inc Shawnee Mission KS* (2016.).
- (9) (a) A. D. Becke, *Phys. Rev. A.*, 1988, **38**, 3098. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785. (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372. (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623. (e) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104. (f) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
- (10) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta.*, 1990, **77**, 123.
- (11) (a) M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265. (b) R. H. W. J. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724. (c) P. C. Hariharan and J. A. Pople, *Theor. Chim.*, 1973, **28**, 213.
- (12) R. J. Hall, M. M. Davidson, N. A. Burton and I. H. Hillier, *J. Phys. Chem.*, 1995, **99**, 921.
- (13) (a) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571. (b) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.