

## Supporting Information

### Direct Access to $\beta$ -Arylketoesters by NHC/Photoredox Catalyzed

#### Alkoxyacylation-Carbonylation of Styrenes

Yaomei Liu,<sup>‡a</sup> Zuming Wu,<sup>‡a</sup> Wenjing Li,<sup>a</sup> Mengjiao Zhang,<sup>a</sup> Youhui Zhang,<sup>a</sup>  
Shuqin Deng,<sup>a</sup> Shilu Fan,<sup>\*,a</sup> Yanwu Zhu,<sup>\*,a</sup> and Yi-Si Feng,<sup>\*,a</sup>

<sup>a</sup>*School of Chemistry and Chemical Engineering, Hefei University of Technology, 193  
Tunxi Road, Anhui, 230000, China.*

<sup>‡</sup>These authors contributed equally.

\*Corresponding author.

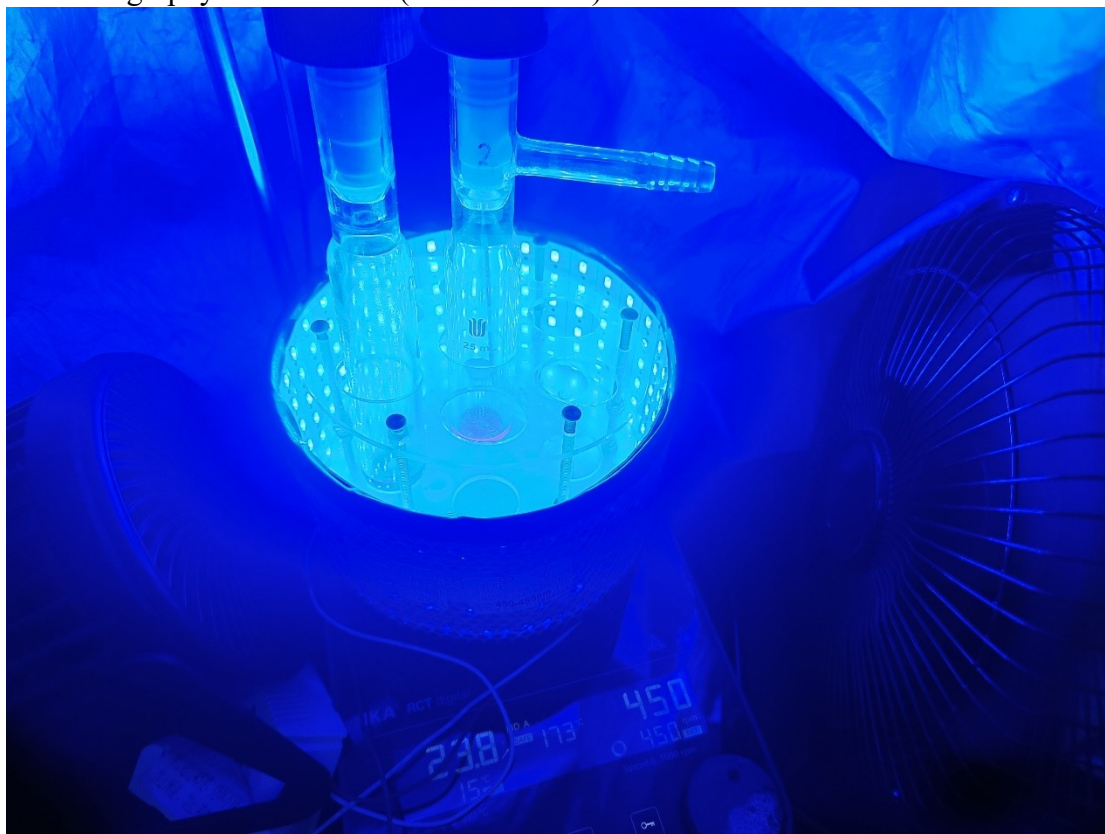
Email: [fanshilu@hotmail.com](mailto:fanshilu@hotmail.com); [shilu.fan@hfut.edu.cn](mailto:shilu.fan@hfut.edu.cn).

## Table of Contents

1. General information .....	S3
2. Preparation of substrates .....	S3
3. Enlarge experiment .....	S4
4. Diverse Control Experiments for Mechanism Elucidation .....	S5
5. General procedure for the synthesis of $\beta$ -arylketoesters .....	S8
6. Characterization data for products .....	S8
7. References .....	S19
8. Copies of $^1\text{H}$ NMR, $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR spectra.....	S20

## 1. General information

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 600 MHz spectrometer in  $\text{CDCl}_3$ . Data for  $^1\text{H}$  NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra were obtained by ESI on a TOF mass analyzer. All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air and refilled with an inert atmosphere of  $\text{N}_2$  at room temperature. Blue LEDs (20 W,  $\lambda_{\text{max}} = 455 \text{ nm}$ ) purchased from Taobao was used for blue light irradiation. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (0.2–0.25 mm thickness). Visualization of TLC was achieved using UV light (254 nm). Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

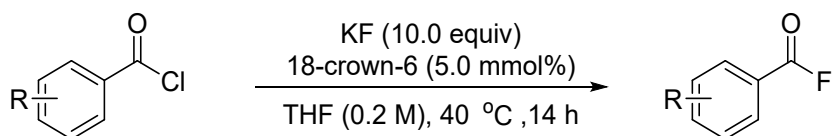


**Fig. 1** Reaction setup for photoinduced

## 1. Preparation of substrates

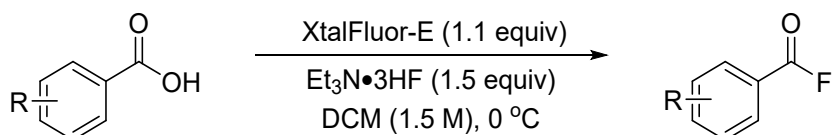
### Synthesis of acyl fluorides

Method A:



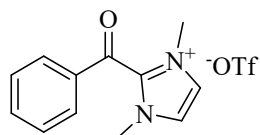
Synthetic procedure<sup>1</sup> for **1r–1y,1aa–1ab** and **1ad**. To a 100 mL Schlenk tube were added 18-crown-6 (132.2 mg, 0.5 mol), KF (5.81 g, 10.0 equiv), and THF (0.2 M). The mixture was evacuated and backfilled with N<sub>2</sub> (3 times). Subsequently, THF (50 mL), corresponding acyl chloride (10 mmol) were added. After the reaction was stirred at 40 °C for 24 h, the insoluble inorganic solid KF/KCl was filtered, and the volatiles were removed using a rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding acyl fluorides. The acyl fluorides can be stored stably for several months in the -20 °C refrigerator.

Method B:



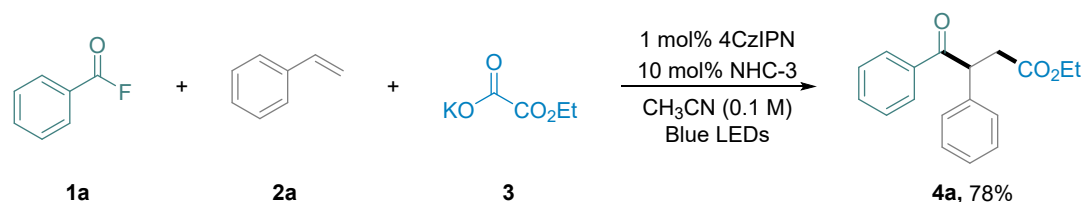
Synthetic procedure<sup>2</sup> for **1z** and **1ac**. To a solution of carboxylic acid (5.0 mmol, 1.0 equiv) in dry DCM (1.5 M), followed by XtalFluor-E (1.26 g, 1.1 equiv) and Et<sub>3</sub>N·3HF (1.5 equiv). After 30 min of stirring at 0 °C, the reaction mixture was purified by filtration over a pad of silica gel to afford pure acyl fluorides. The acyl fluorides can be stored stably for several months in the -20 °C refrigerator.

### Synthesis of acyl imidazole salt **5**



Acyl imidazole salt were prepared according to a previously reported procedure.<sup>3</sup> To a solution of 1-methylimidazole (821 mg, 10.0 mmol) and benzoyl chloride (1.40 g, 15.0 mmol) in anhydrous acetonitrile (30 mL) was added triethylamine (1.52 g, 15.0 mmol) dropwise at 0 °C. The reaction mixture was allowed to slowly warm up to rt and stirred overnight, resulting in a yellow solution and a white precipitate of triethylammonium chloride. The ammonium salt was filtered off, the solvent and other volatiles were removed on a rotary evaporator. Purification by column chromatography on silica gel afforded 2-acyl imidazole. To a solution of 2-acyl imidazole (5.0 mmol) in anhydrous diethyl ether (50 mL) was added methyl triflate (885 mg, 5.5 mmol) at rt and the reaction mixture was stirred overnight. The resulting white precipitate was filtered off and washed with diethyl ether. Drying under vacuum afforded acyl azolium salt **5**.

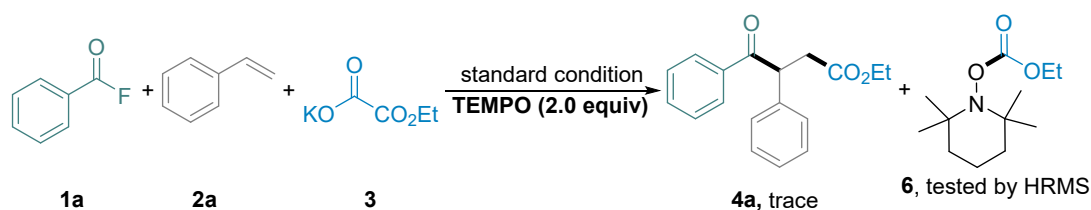
## 2. Enlarge experiment



To a 100 mL of Schlenk tube were added NHC-3 (0.4 mmol, 126.0 mg), 4CzIPN (0.04 mmol, 31.6 mg) and **3** (4 mmol, 628.8 mg). The mixture was evacuated and backfilled with N<sub>2</sub> (3 times). Subsequently, CH<sub>3</sub>CN (40 mL), benzoyl fluoride **1a** (8 mmol, 992.8 mg) and styrene **2a** (12 mmol, 1.2498 g) were added successively. The mixture was stirred at room temperature for 12 h while irradiated by Blue LEDs. After that, the residue was purified by silica gel chromatography using the mixture of petroleum ether and ethyl acetate as an eluent to afford the product. The product (880 mg, 78%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).

## 3. Diverse Control Experiments for Mechanism Elucidation

### 3.1 Radical trapping experiments



To a 25 mL of Schlenk tube were added NHC-3 (0.02 mmol, 6.3 mg), 4CzIPN (0.002 mmol, 1.6 mg), **3** (0.2 mmol, 31.4 mg) and TEMPO (0.2 mmol, 31.3 mg). The mixture was evacuated and backfilled with N<sub>2</sub> (3 times). Subsequently, CH<sub>3</sub>CN (2 mL), benzoyl fluoride **1a** (0.4 mmol, 49.6 mg) and styrene **2a** (0.6 mmol, 62.5 mg) were added successively. The mixture was stirred at room temperature for 12 h while irradiated by Blue LEDs. By TLC monitoring, only a small amount of the target product **4a** was found. Subsequently, the mixture was tested HRMS (ESI) to afford **6**. HRMS ESI (m/z): [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>24</sub>NO<sub>3</sub>: 230.1751, found 230.1744.

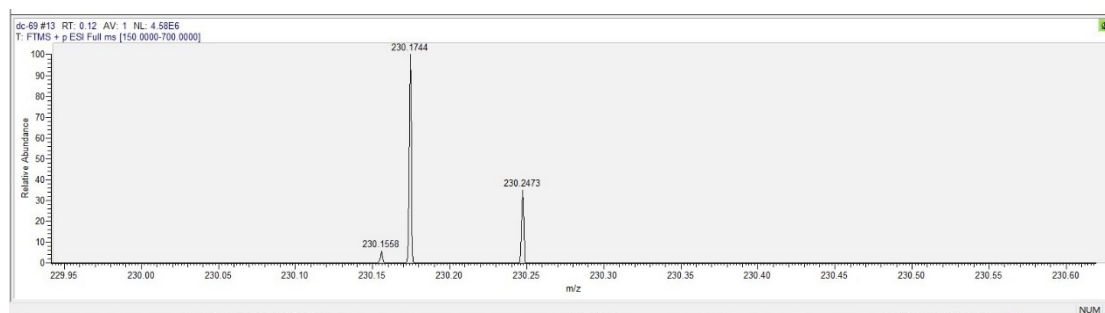
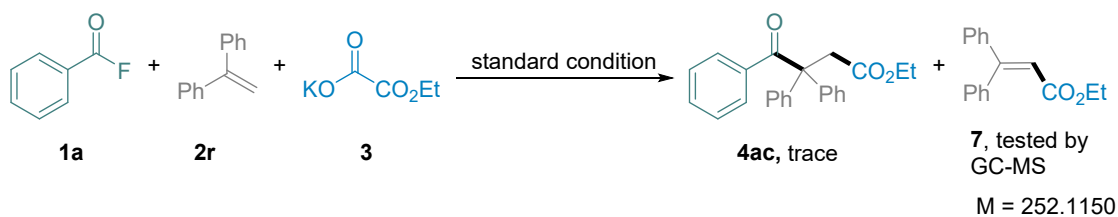
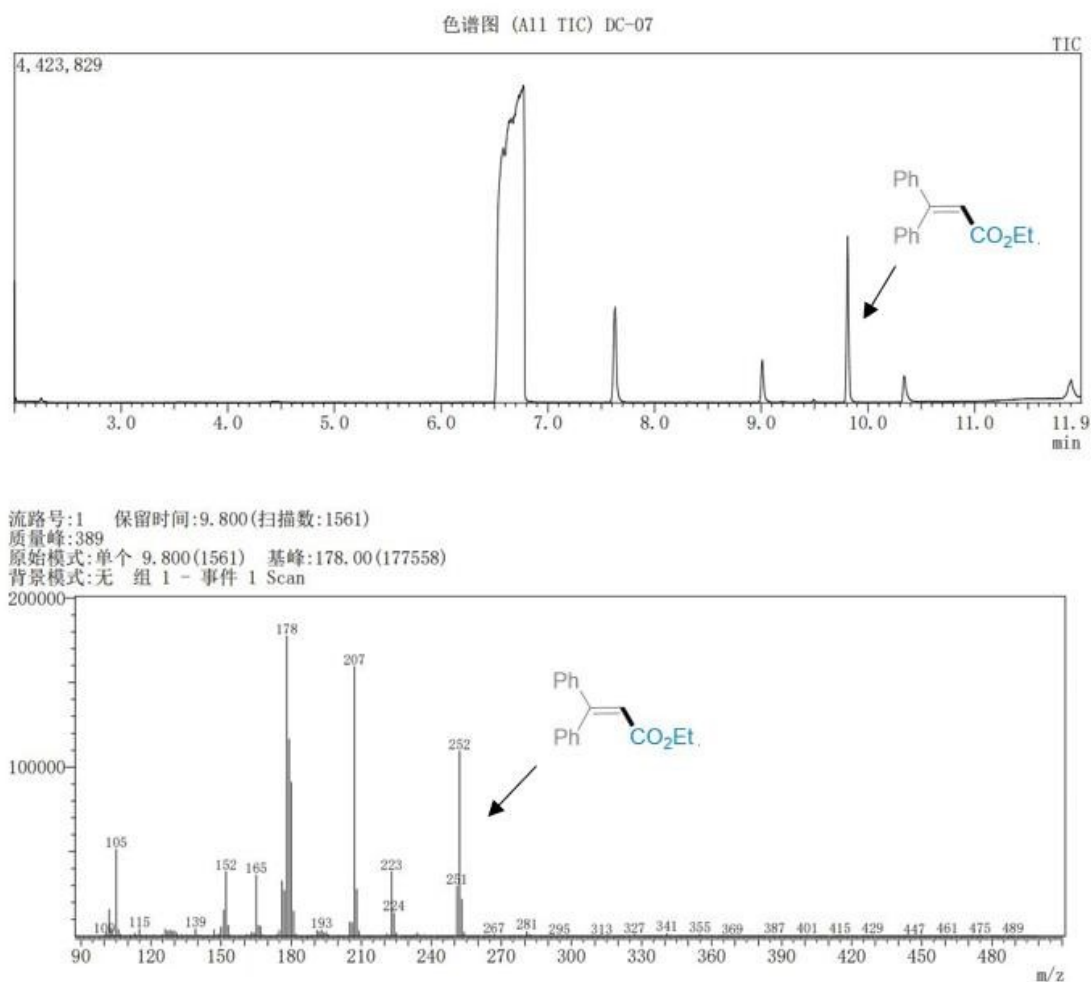


Fig. 2 HRMS Spectra of compound **6**



To a 25 mL of Schlenk tube were added NHC-3 (0.02 mmol, 6.3 mg), 4CzIPN (0.002 mmol, 1.6 mg) and **3** (0.2 mmol, 31.4 mg). The mixture was evacuated and backfilled with N<sub>2</sub> (3 times). Subsequently, CH<sub>3</sub>CN (2 mL), benzoyl fluoride **1a** (0.4 mmol, 49.6 mg) and 1,1-diphenylethylene **2r** (0.6 mmol, 108.1 mg) were added successively. The mixture was stirred at room temperature for 12 h while irradiated by Blue LEDs. By TLC monitoring, only a small amount of the target product **4a** was found. Subsequently, the mixture was tested GC-MS to afford **7**.

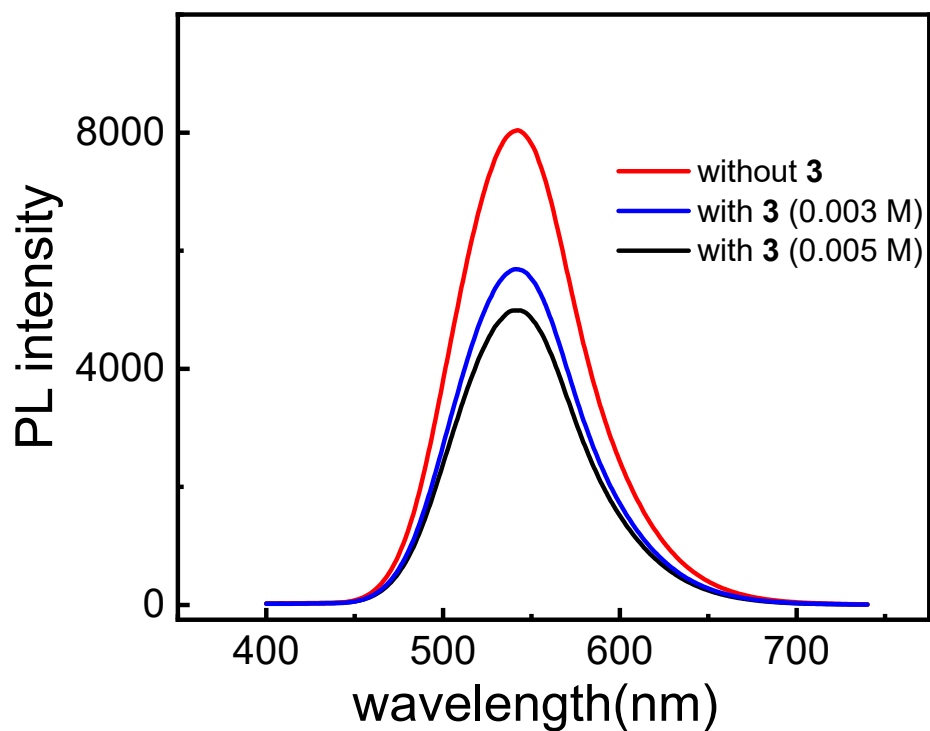


**Fig. 3** The capture experiments by GC-MS

### 3.2 Steady-state Stern–Volmer experiment of 4CzIPN and **3**

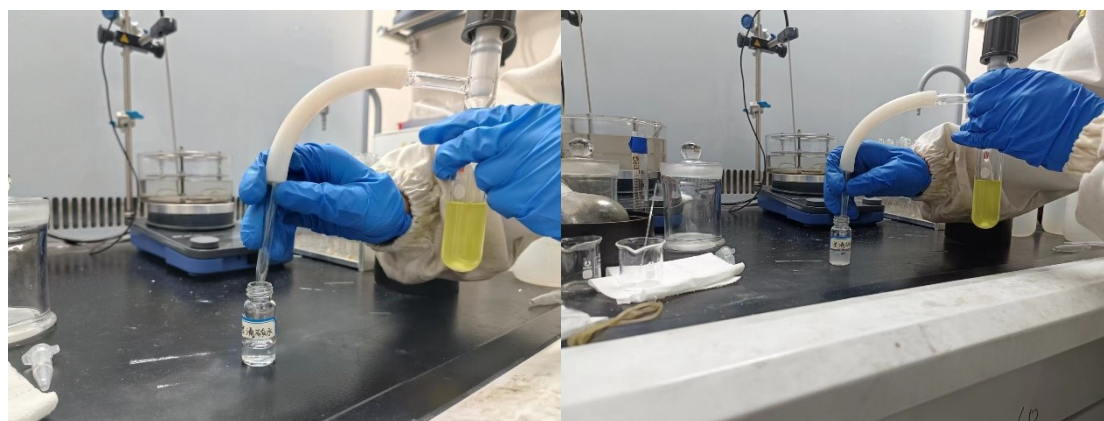
Stern-Volmer emission quenching Fluorescence quenching experiments were measured on a RF-5301PC Spectrofluorophotometer with a 2 mL quartz cuvette.

Anhydrous CH<sub>3</sub>CN was degassed by N<sub>2</sub> bubbling for 30 minutes before using. 4CzIPN was irradiated at 440 nm and the emission intensity at about 536 nm was observed. In a typical experiment, the emission spectrum of a 5\*10<sup>-5</sup> M solution of 4CzIPN in CH<sub>3</sub>CN was collected. **3**: A stock solution of **3** (0.01 M) was prepared. Then, different amounts of this stock solution were added to 1 mL of 4CzIPN in CH<sub>3</sub>CN (5\*10<sup>-5</sup> M). Stern–Volmer experiment of 4CzIPN and **3**, the luminescence of 4CzIPN was readily quenched by **3**.



**Fig. 4** Stern–Volmer fluorescence quenching experiments

### 3.3 CO<sub>2</sub> detection experiments



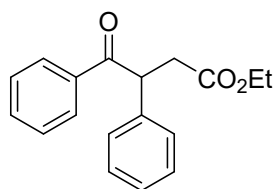
**Fig. 4** CO<sub>2</sub> detection experiments

On the basis of the enlarge experiment, we carefully collected the gas and passed it into a clear aqueous  $\text{Ca}(\text{OH})_2$  solution. A large amount of gas appearance was observed, and the clear  $\text{Ca}(\text{OH})_2$  aqueous solution quickly turned turbid. It briefly explains that  $\text{CO}_2$  is generated in this reaction.

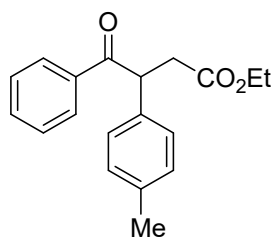
#### 4. General procedure for the synthesis of $\beta$ -arylketoesters

To a 25 mL of Schlenk tube were added NHC-3 (0.02 mmol, 6.3 mg), 4CzIPN (0.002 mmol, 1.6 mg) and **3** (0.2 mmol, 31.4 mg). The mixture was evacuated and backfilled with  $\text{N}_2$  (3 times). Subsequently,  $\text{CH}_3\text{CN}$  (2 mL), acyl fluoride **1** (0.4 mmol, 49.6 mg) and alkene **2** (0.6 mmol, 62.5 mg) were added successively. The mixture was stirred at room temperature for 12 h while irradiated by Blue LEDs. After that, the residue was purified by silica gel chromatography using the mixture of petroleum ether and ethyl acetate as an eluent to afford the product.

#### 5. Characterization data for products



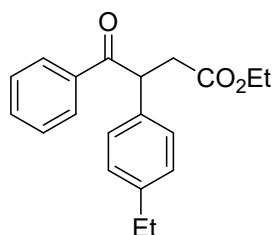
**Ethyl 4-oxo-3,4-diphenylbutanoate (4a)** The product (50 mg, 88%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.97 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.37 (t,  $J = 7.8$  Hz, 2H), 7.30 – 7.27 (m, 4H), 7.22 – 7.19 (m, 1H), 5.09 (dd,  $J = 9.8, 5.0$  Hz, 1H), 4.10 (q,  $J = 7.1$  Hz, 2H), 3.37 (dd,  $J = 16.9, 9.8$  Hz, 1H), 2.72 (dd,  $J = 16.9, 5.0$  Hz, 1H), 1.19 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.6, 172.0, 138.0, 136.2, 133.0, 129.1, 128.9, 128.5, 128.1, 127.4, 60.7, 49.5, 38.7, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{19}\text{O}_3$ : 283.1329, found: 283.1325.



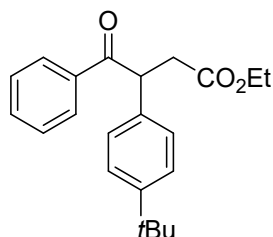
**Ethyl 4-oxo-4-phenyl-3-(p-tolyl)butanoate (4b)** The product (48 mg, 81%) as colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.01 – 7.95 (m, 2H), 7.45 (d,  $J = 7.5$  Hz, 1H), 7.37 (t,  $J = 7.8$  Hz, 2H), 7.20 – 7.16 (m, 2H), 7.09 (d,  $J = 7.9$  Hz, 2H), 5.07 (dd,  $J = 9.8, 4.9$  Hz, 1H), 4.10 (q,  $J = 7.1$  Hz, 2H), 3.36 (dd,  $J = 16.9, 9.8$  Hz, 1H), 2.70 (dd,  $J = 16.9, 5.0$  Hz, 1H), 2.27 (s, 3H), 1.19 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,



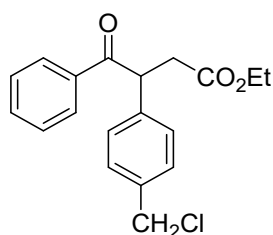
Chloroform-*d*)  $\delta$  198.8, 172.1, 137.1, 136.2, 135.0, 132.9, 129.9, 128.9, 128.5, 128.0, 60.7, 49.1, 38.7, 21.0, 14.1. HRMS ESI(*m/z*):  $[M+H]^+$  calcd. for  $C_{19}H_{21}O_3$ : 297.1485, found: 297.1488.



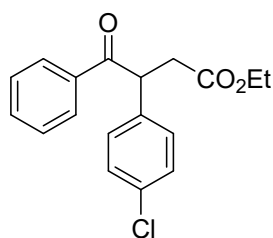
**Ethyl 3-(4-ethylphenyl)-4-oxo-4-phenylbutanoate (4c)** The product (43 mg, 69%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.98 (d,  $J = 7.3$  Hz, 2H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 2H), 7.20 (d,  $J = 8.1$  Hz, 2H), 7.11 (d,  $J = 7.9$  Hz, 2H), 5.07 (dd,  $J = 9.9, 4.9$  Hz, 1H), 4.09 (q,  $J = 7.1$  Hz, 2H), 3.36 (dd,  $J = 17.0, 9.9$  Hz, 1H), 2.70 (dd,  $J = 17.0, 4.9$  Hz, 1H), 2.57 (q,  $J = 7.6$  Hz, 2H), 1.20 – 1.16 (m, 6H).  $^{13}C$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.8, 172.1, 143.4, 136.2, 135.1, 132.9, 128.9, 128.6, 128.5, 128.0, 60.7, 49.1, 38.7, 28.4, 15.3, 14.1. HRMS ESI(*m/z*):  $[M+H]^+$  calcd. for  $C_{20}H_{23}O_3$ : 311.1642, found: 311.1645.



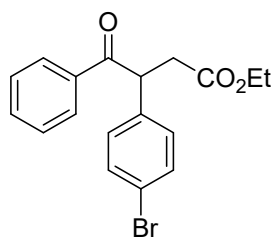
**Ethyl 3-(4-(tert-butyl)phenyl)-4-oxo-4-phenylbutanoate (4d)** The product (48 mg, 71%) as colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.00 (d,  $J = 7.7$  Hz, 2H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 2H), 7.30 (s, 2H), 7.22 (d,  $J = 8.3$  Hz, 2H), 5.08 (dd,  $J = 10.0, 4.8$  Hz, 1H), 4.09 (q,  $J = 7.1$  Hz, 2H), 3.38 (dd,  $J = 17.0, 10.0$  Hz, 1H), 2.71 (dd,  $J = 17.0, 4.8$  Hz, 1H), 1.25 (s, 9H), 1.18 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.8, 172.2, 150.2, 136.3, 134.8, 132.9, 128.9, 128.5, 127.7, 126.1, 60.6, 48.9, 38.7, 34.4, 31.3, 14.1. HRMS ESI(*m/z*):  $[M+H]^+$  calcd. for  $C_{22}H_{27}O_3$ : 339.1955, found: 339.1950.



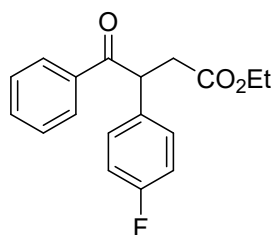
**Ethyl 3-(4-(chloromethyl)phenyl)-4-oxo-4-phenylbutanoate (4e)** The product (46 mg, 70%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.24 (m, 4H), 5.11 (dd, *J* = 9.7, 5.0 Hz, 1H), 4.50 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 17.0, 9.7 Hz, 1H), 2.70 (dd, *J* = 17.0, 5.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.4, 171.9, 138.3, 136.7, 136.0, 133.1, 129.4, 128.8, 128.6, 128.5, 60.7, 49.0, 45.7, 38.5, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>20</sub>ClO<sub>3</sub>: 331.1095, found: 331.1096.



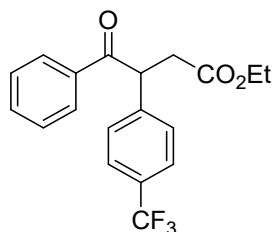
**Ethyl 3-(4-chlorophenyl)-4-oxo-4-phenylbutanoate (4f)** The product (52 mg, 83%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.20 (m, 4H), 5.07 (dd, *J* = 9.4, 5.3 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.33 (dd, *J* = 16.9, 9.5 Hz, 1H), 2.70 (dd, *J* = 16.9, 5.3 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.3, 171.8, 136.5, 135.9, 133.4, 133.2, 129.5, 129.3, 128.8, 128.6, 60.8, 48.7, 38.5, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>ClO<sub>3</sub>: 317.0939, found: 317.0938.



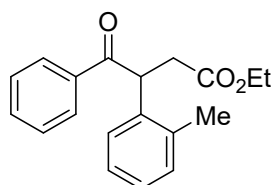
**Ethyl 3-(4-bromophenyl)-4-oxo-4-phenylbutanoate (4g)** The product (52 mg, 72%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.06 (dd, *J* = 9.4, 5.3 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.32 (dd, *J* = 17.0, 9.5 Hz, 1H), 2.69 (dd, *J* = 17.0, 5.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.2, 171.7, 137.0, 135.9, 133.2, 132.3, 129.8, 128.8, 128.6, 121.5, 60.8, 48.8, 38.4, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>BrO<sub>3</sub>: 361.0434, found: 361.0429.



**Ethyl 3-(4-fluorophenyl)-4-oxo-4-phenylbutanoate (4h)** The product (41 mg, 68%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J$  = 7.3 Hz, 2H), 7.49 (t,  $J$  = 7.7 Hz, 1H), 7.39 (t,  $J$  = 7.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 6.97 (t,  $J$  = 8.6 Hz, 2H), 5.08 (dd,  $J$  = 9.5, 5.3 Hz, 1H), 4.09 (q,  $J$  = 7.1 Hz, 2H), 3.33 (dd,  $J$  = 16.9, 9.5 Hz, 1H), 2.70 (dd,  $J$  = 16.9, 5.3 Hz, 1H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.5, 171.8, 162.0 (d,  $J$  = 246.7 Hz), 136.0, 133.7 (d,  $J$  = 3.4 Hz), 133.1, 129.7 (d,  $J$  = 8.2 Hz), 128.8, 128.6, 116.1 (d,  $J$  = 21.5 Hz), 60.8, 48.5, 38.6, 14.1.  $^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)  $\delta$  -117.33. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{FO}_3$ : 301.1234, found: 301.1240.

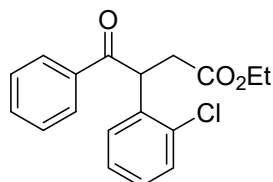


**Ethyl 4-oxo-4-phenyl-3-(4-(trifluoromethyl)phenyl)butanoate (4i)** The product (36 mg, 52%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.96 (d,  $J$  = 7.4 Hz, 2H), 7.56 – 7.48 (m, 3H), 7.41 (dd,  $J$  = 18.3, 8.1 Hz, 4H), 5.17 (dd,  $J$  = 9.5, 5.2 Hz, 1H), 4.10 (q,  $J$  = 7.1 Hz, 2H), 3.37 (dd,  $J$  = 17.0, 9.5 Hz, 1H), 2.73 (dd,  $J$  = 17.0, 5.2 Hz, 1H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.0, 171.6, 142.0, 135.8, 133.3, 129.8 (q,  $J$  = 32.6 Hz), 128.8, 128.7, 128.5, 126.1 (q,  $J$  = 3.7 Hz), 123.9 (q,  $J$  = 272.6 Hz), 60.9, 49.1, 38.4, 14.1.  $^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)  $\delta$  -65.24. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{O}_3$ : 351.1203, found: 351.1211.

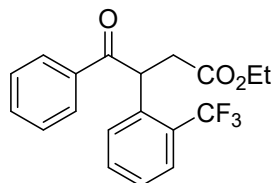


**Ethyl 4-oxo-4-phenyl-3-(o-tolyl)butanoate(4j)** The product (50 mg, 85%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.85 (d,  $J$  = 7.3 Hz, 2H), 7.45 (t,  $J$  = 7.9 Hz, 1H), 7.35 (t,  $J$  = 7.8 Hz, 2H), 7.20 (d,  $J$  = 7.5 Hz, 1H), 7.12 (t,  $J$  = 7.3 Hz, 1H),

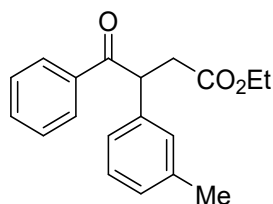
7.09 – 7.01 (m, 2H), 5.21 (dd,  $J = 10.5, 3.9$  Hz, 1H), 4.13 (q,  $J = 7.1$  Hz, 2H), 3.29 (dd,  $J = 17.0, 10.5$  Hz, 1H), 2.57 (dd,  $J = 17.0, 3.9$  Hz, 1H), 2.54 (s, 3H), 1.22 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  199.3, 172.1, 136.6, 136.4, 135.0, 132.8, 131.2, 128.6, 128.5, 127.5, 127.4, 126.8, 60.7, 46.2, 37.6, 19.7, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{21}\text{O}_3$ : 297.1485, found: 297.1487.



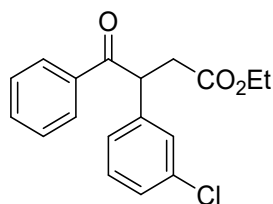
**Ethyl 3-(2-chlorophenyl)-4-oxo-4-phenylbutanoate (4k)** The product (40 mg, 64%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J = 8.0$  Hz, 2H), 7.47 (t,  $J = 7.9$  Hz, 1H), 7.43 – 7.35 (m, 3H), 7.18 – 7.11 (m, 3H), 5.56 (dd,  $J = 10.5, 4.0$  Hz, 1H), 4.12 (q,  $J = 7.1$  Hz, 2H), 3.24 (dd,  $J = 16.9, 10.5$  Hz, 1H), 2.67 (dd,  $J = 16.9, 4.0$  Hz, 1H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.4, 171.6, 135.8, 135.7, 133.2, 133.2, 130.2, 128.9, 128.9, 128.7, 128.6, 127.6, 60.8, 45.7, 37.2, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{ClO}_3$ : 317.0939, found: 317.0945.



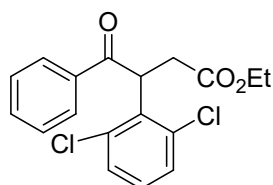
**Ethyl 4-oxo-4-phenyl-3-(2-(trifluoromethyl)phenyl)butanoate (4l)** The product (40 mg, 57%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.94 (d,  $J = 7.7$  Hz, 2H), 7.71 (d,  $J = 7.9$  Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 7.7$  Hz, 1H), 7.38 – 7.31 (m, 3H), 7.27 (d,  $J = 8.0$  Hz, 1H), 5.44 (dd,  $J = 11.2, 3.0$  Hz, 1H), 4.13 (q,  $J = 7.1$  Hz, 2H), 3.29 (dd,  $J = 17.1, 11.2$  Hz, 1H), 2.68 (dd,  $J = 17.2, 3.1$  Hz, 1H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.5, 171.4, 136.4, 136.1, 133.1, 132.6, 130.6, 129.2, 128.8, 128.5, 127.6, 127.0 (q,  $J = 6.0$  Hz), 125.3(m), 60.8, 45.4, 38.9, 14.1.  $^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)  $\delta$  -59.07. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{O}_3$ : 351.1203, found: 351.1206.



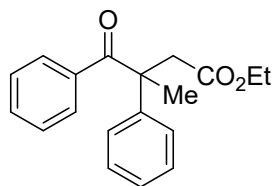
**Ethyl 4-oxo-4-phenyl-3-(m-tolyl)butanoate (4m)** The product (35 mg, 59%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.06 (dd, *J* = 9.9, 4.9 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 16.9, 9.9 Hz, 1H), 2.70 (dd, *J* = 17.0, 4.9 Hz, 1H), 2.28 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.7, 172.1, 138.9, 137.9, 136.2, 132.9, 129.0, 128.9, 128.6, 128.5, 128.2, 125.3, 60.7, 49.4, 38.7, 21.4, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>3</sub>: 297.1485, found: 297.1487.



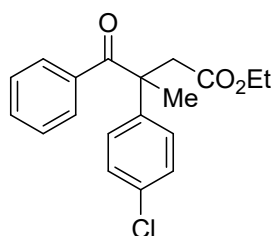
**Ethyl 3-(3-chlorophenyl)-4-oxo-4-phenylbutanoate (4n)** The product (36 mg, 57%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.16 (m, 4H), 5.06 (dd, *J* = 9.6, 5.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.34 (dd, *J* = 17.0, 9.6 Hz, 1H), 2.70 (dd, *J* = 17.0, 5.1 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.1, 171.7, 140.0, 135.9, 134.9, 133.2, 130.4, 128.8, 128.6, 128.2, 127.8, 126.3, 60.8, 48.9, 38.5, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>ClO<sub>3</sub>: 317.0939, found: 317.0937.



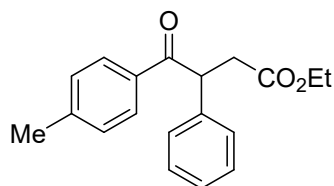
**Ethyl 3-(2,6-dichlorophenyl)-4-oxo-4-phenylbutanoate (4o)** The product (28 mg, 40%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 5.55 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.23 – 4.17 (m, 2H), 3.50 (dd, *J* = 16.2, 9.5 Hz, 1H), 2.46 (dd, *J* = 16.1, 4.1 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 198.0, 171.7, 136.4, 136.1, 135.3, 132.6, 129.2, 128.2, 128.1, 60.9, 48.5, 33.8, 14.2. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>17</sub>Cl<sub>2</sub>O<sub>3</sub>: 351.0549, found: 351.0554.



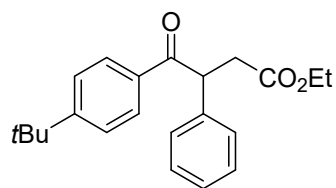
**Ethyl 3-methyl-4-oxo-3,4-diphenylbutanoate (4p)** The product (52 mg, 88%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.41 (d,  $J$  = 7.4 Hz, 2H), 7.39 – 7.33 (m, 5H), 7.31 – 7.28 (m, 1H), 7.21 (t,  $J$  = 7.8 Hz, 2H), 3.98 (q,  $J$  = 7.1 Hz, 2H), 3.15 (d,  $J$  = 15.4 Hz, 1H), 2.93 (d,  $J$  = 15.4 Hz, 1H), 1.83 (s, 3H), 1.10 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  202.3, 171.2, 142.2, 136.6, 131.6, 129.3, 129.1, 128.0, 127.4, 126.2, 60.3, 53.1, 45.2, 23.9, 14.0. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{21}\text{O}_3$ : 297.1485, found: 297.1487.



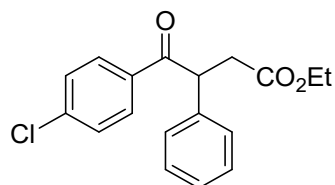
**Ethyl 3-(4-chlorophenyl)-3-methyl-4-oxo-4-phenylbutanoate (4q)** The product (44 mg, 66%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.40 (d,  $J$  = 7.5 Hz, 2H), 7.37 (d,  $J$  = 7.6 Hz, 1H), 7.34 (d,  $J$  = 8.6 Hz, 2H), 7.28 (d,  $J$  = 8.6 Hz, 2H), 7.23 (d,  $J$  = 8.0 Hz, 2H), 3.99 (d,  $J$  = 7.2 Hz, 2H), 3.10 (d,  $J$  = 15.5 Hz, 1H), 2.90 (d,  $J$  = 15.5 Hz, 1H), 1.81 (s, 3H), 1.11 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  201.8, 171.0, 140.8, 136.2, 133.4, 131.8, 129.3, 129.2, 128.1, 127.7, 60.4, 52.7, 45.1, 23.8, 14.0. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{20}\text{ClO}_3$ : 331.1095, found: 331.1096.



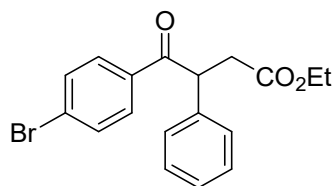
**Ethyl 4-oxo-3-phenyl-4-(p-tolyl)butanoate (4r)** The product (36 mg, 61%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.88 (d,  $J$  = 8.2 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.20 (m, 1H), 7.17 (d,  $J$  = 8.3 Hz, 2H), 5.07 (dd,  $J$  = 9.7, 5.1 Hz, 1H), 4.09 (q,  $J$  = 7.1 Hz, 2H), 3.35 (dd,  $J$  = 16.9, 9.7 Hz, 1H), 2.70 (dd,  $J$  = 16.9, 5.1 Hz, 1H), 2.33 (s, 3H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  198.2, 172.1, 143.8, 138.3, 133.6, 129.2, 129.1, 129.0, 128.1, 127.4, 60.7, 49.3, 38.6, 21.6, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{21}\text{O}_3$ : 297.1485, found: 297.1483.



**Ethyl 4-(4-(tert-butyl)phenyl)-4-oxo-3-phenylbutanoate (4s)** The product (43 mg, 64%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.93 (d,  $J$  = 8.2 Hz, 2H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.32 – 7.26 (m, 4H), 7.22 – 7.19 (m, 1H), 5.09 (dd,  $J$  = 9.8, 5.0 Hz, 1H), 4.09 (q,  $J$  = 7.1 Hz, 2H), 3.36 (dd,  $J$  = 16.9, 9.8 Hz, 1H), 2.71 (dd,  $J$  = 16.9, 5.0 Hz, 1H), 1.28 (s, 9H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  198.1, 172.1, 156.6, 138.3, 133.5, 129.1, 128.8, 128.1, 127.4, 125.5, 60.6, 49.3, 38.7, 35.0, 31.0, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{22}\text{H}_{27}\text{O}_3$ : 339.1955, found: 339.1950.

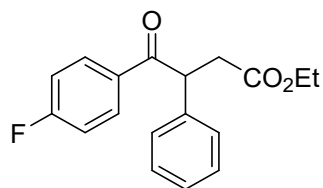


**Ethyl 4-(4-chlorophenyl)-4-oxo-3-phenylbutanoate (4t)** The product (36 mg, 57%) as white solid was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.90 (d,  $J$  = 8.6 Hz, 2H), 7.34 (d,  $J$  = 8.5 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.24 – 7.19 (m, 1H), 5.02 (dd,  $J$  = 9.9, 4.8 Hz, 1H), 4.10 (q,  $J$  = 7.2 Hz, 2H), 3.36 (dd,  $J$  = 17.0, 9.9 Hz, 1H), 2.70 (dd,  $J$  = 17.0, 4.8 Hz, 1H), 1.19 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  197.5, 171.9, 139.4, 137.7, 134.5, 130.2, 129.2, 128.8, 128.0, 127.6, 60.7, 49.6, 38.6, 14.1. HRMS ESI( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{ClO}_3$ : 317.0939, found: 317.0940.

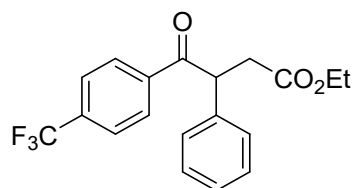


**Ethyl 4-(4-bromophenyl)-4-oxo-3-phenylbutanoate (4u)** The product (45 mg, 62%) as white solid was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.82 (d,  $J$  = 8.5 Hz, 2H), 7.50 (d,  $J$  = 8.4 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.24 – 7.19 (m, 1H), 5.02 (dd,  $J$  = 9.9, 4.8 Hz, 1H), 4.10 (q,  $J$  = 7.1 Hz, 2H), 3.36 (dd,  $J$  = 17.0, 9.9 Hz, 1H), 2.70 (dd,  $J$  = 17.0, 4.8 Hz, 1H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  197.7, 172.0,

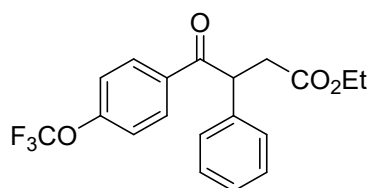
137.7, 134.8, 131.8, 130.4, 129.3, 128.2, 128.1, 127.6, 60.8, 49.5, 38.6, 14.1. HRMS ESI(m/z): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>BrO<sub>3</sub>: 361.0434, found: 361.0429.



**Ethyl 4-(4-fluorophenyl)-4-oxo-3-phenylbutanoate (4v)** The product (40 mg, 68%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 8.00 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.20 (m, 1H), 7.04 (t, *J* = 8.5 Hz, 2H), 5.03 (dd, *J* = 9.9, 4.8 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 17.0, 9.9 Hz, 1H), 2.70 (dd, *J* = 17.0, 4.8 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 197.1, 172.0, 165.5 (d, *J* = 254.9 Hz), 137.9, 132.5 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 9.3 Hz), 129.2, 128.0, 127.6, 115.6 (d, *J* = 21.9 Hz), 60.8, 49.5, 38.6, 14.1. <sup>19</sup>F NMR (564 MHz, Chloroform-d) δ -105.21. HRMS ESI(m/z): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>FO<sub>3</sub>: 301.1234, found: 301.1236.



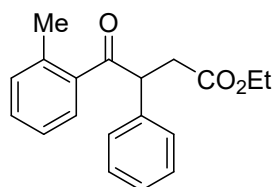
**Ethyl 4-oxo-3-phenyl-4-(4-(trifluoromethyl)phenyl)butanoate (4w)** The product (37 mg, 53%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 5.06 (dd, *J* = 10.1, 4.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.39 (dd, *J* = 17.1, 10.1 Hz, 1H), 2.72 (dd, *J* = 17.1, 4.7 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 197.8, 171.9, 138.9, 137.2, 134.2, 134.0, 129.4, 129.1, 128.1, 127.8, 125.6 (q, *J* = 3.6 Hz), 60.8, 49.9, 38.6, 14.1. <sup>19</sup>F NMR (564 MHz, Chloroform-d) δ -63.21. HRMS ESI(m/z): [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>18</sub>F<sub>3</sub>O<sub>3</sub>: 351.1203, found: 351.1199.



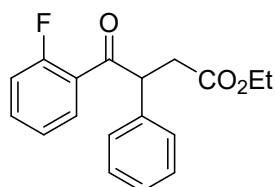
**Ethyl 4-oxo-3-phenyl-4-(4-(trifluoromethoxy)phenyl)butanoate (4x)** The product (45 mg, 61%) as a colorless oil was purified with silica gel chromatography (petroleum



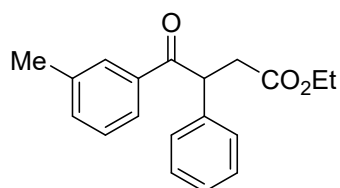
ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.02 (d,  $J$  = 8.7 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 7.19 (d,  $J$  = 8.5 Hz, 2H), 5.05 (dd,  $J$  = 10.0, 4.7 Hz, 1H), 4.10 (q,  $J$  = 7.1 Hz, 2H), 3.38 (dd,  $J$  = 17.1, 10.0 Hz, 1H), 2.71 (dd,  $J$  = 17.1, 4.7 Hz, 1H), 1.19 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  197.1, 172.0, 152.4(m), 137.6, 134.4, 130.9, 129.3, 128.0, 127.7, 120.2, 120.1 (q,  $J$  = 259.1 Hz), 60.8, 49.6, 38.6, 14.1.  $^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)  $\delta$  -57.64. HRMS ESI( $m/z$ ): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{O}_3$ : 367.1152, found: 367.1145.



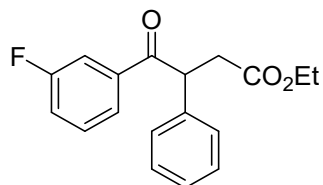
**Ethyl 4-oxo-3-phenyl-4-(o-tolyl)butanoate (4y)** The product (40 mg, 67%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.74 (d,  $J$  = 7.7 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.21 – 7.17 (m, 4H), 7.12 (d,  $J$  = 7.6 Hz, 1H), 4.93 (dd,  $J$  = 10.4, 4.4 Hz, 1H), 4.13 (dd,  $J$  = 7.2, 5.1 Hz, 2H), 3.43 (dd,  $J$  = 17.0, 10.4 Hz, 1H), 2.69 (dd,  $J$  = 17.0, 4.4 Hz, 1H), 2.25 (s, 3H), 1.23 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  202.4, 172.2, 138.1, 138.0, 137.0, 131.4, 130.9, 129.0, 128.3, 128.2, 127.5, 125.4, 60.8, 52.3, 37.8, 20.6, 14.2. HRMS ESI( $m/z$ ): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{19}\text{H}_{21}\text{O}_3$ : 297.1485, found: 297.1492.



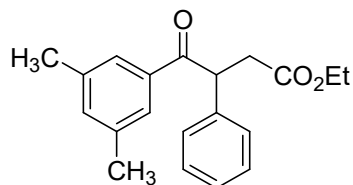
**Ethyl 4-(2-fluorophenyl)-4-oxo-3-phenylbutanoate (4z)** The product (41 mg, 69%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.83 – 7.80 (m, 1H), 7.43 – 7.38 (m, 1H), 7.26 – 7.24 (m, 4H), 7.21 – 7.19 (m, 1H), 7.13 (t,  $J$  = 7.5 Hz, 1H), 7.01 (dd,  $J$  = 11.3, 8.3 Hz, 1H), 5.03 (dd,  $J$  = 9.8, 5.0 Hz, 1H), 4.13 – 4.08 (m, 2H), 3.38 – 3.33 (m, 1H), 2.68 (dd,  $J$  = 16.9, 5.0 Hz, 1H), 1.20 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  197.2, 172.0, 161.1 (d,  $J$  = 255.2 Hz), 137.0, 134.4 (d,  $J$  = 9.2 Hz), 131.1 (d,  $J$  = 2.6 Hz), 128.9, 128.5, 127.5, 125.2 (d,  $J$  = 12.3 Hz), 124.3 (d,  $J$  = 3.4 Hz), 116.6 (d,  $J$  = 23.8 Hz), 60.7, 53.2, 38.5, 14.1.  $^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)  $\delta$  -109.18. HRMS ESI( $m/z$ ): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{FO}_3$ : 301.1234, found: 301.1237.



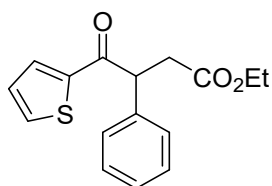
**Ethyl 4-oxo-3-phenyl-4-(m-tolyl)butanoate (4aa)** The product (33 mg, 56%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.80 – 7.75 (m, 2H), 7.30 – 7.24 (m, 6H), 7.22 – 7.19 (m, 1H), 5.08 (dd, *J* = 9.8, 5.0 Hz, 1H), 4.12 – 4.07 (m, 2H), 3.36 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.71 (dd, *J* = 16.9, 5.0 Hz, 1H), 2.34 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 198.9, 172.1, 138.3, 138.1, 136.2, 133.8, 129.3, 129.1, 128.3, 128.1, 127.4, 126.1, 60.7, 49.4, 38.7, 21.4, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>3</sub>: 297.1485, found: 297.1489.



**Ethyl 4-(3-fluorophenyl)-4-oxo-3-phenylbutanoate (4ab)** The product (32 mg, 53%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.35 (m, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.20 (m, 1H), 7.18 – 7.15 (m, 1H), 5.02 (dd, *J* = 10.0, 4.7 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.37 (dd, *J* = 17.0, 10.0 Hz, 1H), 2.71 (dd, *J* = 17.1, 4.7 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 197.5, 171.9, 162.7 (d, *J* = 247.9 Hz), 138.3 (d, *J* = 6.4 Hz), 137.5, 130.1 (d, *J* = 7.5 Hz), 129.3, 128.1, 127.6, 124.6 (d, *J* = 2.9 Hz), 120.0 (d, *J* = 21.4 Hz), 115.6 (d, *J* = 22.5 Hz), 60.8, 49.7, 38.6, 14.1. <sup>19</sup>F NMR (564 MHz, Chloroform-d) δ -111.93. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>18</sub>FO<sub>3</sub>: 301.1234, found: 301.1238.

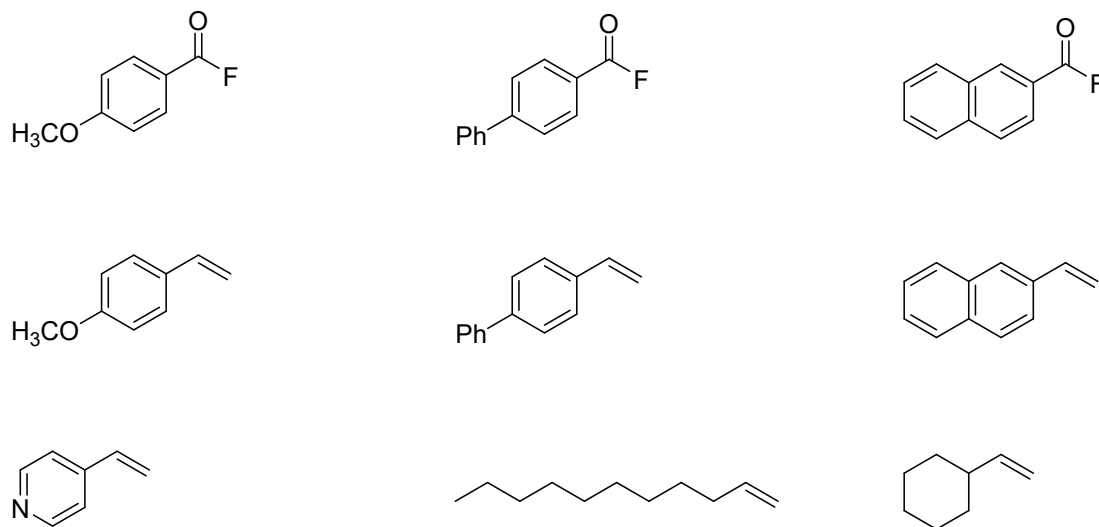


**Ethyl 4-(3,5-dimethylphenyl)-4-oxo-3-phenylbutanoate (4ac)**<sup>4</sup> The product (30 mg, 48%) as white solid was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.59 (s, 2H), 7.31 – 7.25 (m, 4H), 7.21 – 7.19 (m, 1H), 7.11 (s, 1H), 5.08 (dd, *J* = 9.8, 4.9 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 16.9, 9.9 Hz, 1H), 2.70 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.30 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 199.0, 172.1, 138.2, 138.0, 136.3, 134.7, 129.1, 128.1, 127.3, 126.7, 60.7, 49.3, 38.7, 21.2, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>23</sub>O<sub>3</sub>: 311.1642, found: 311.1635.



**Ethyl 4-oxo-3-phenyl-4-(thiophen-2-yl)butanoate (4ad)** The product (29 mg, 50%) as a colorless oil was purified with silica gel chromatography (petroleum ether: ethyl acetate = 50 : 1). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.56 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.21 (m, 1H), 7.04 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.90 (dd, *J* = 9.7, 5.1 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.35 (dd, *J* = 17.0, 9.7 Hz, 1H), 2.71 (dd, *J* = 17.0, 5.1 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 197.1, 172.0, 152.4, 137.6, 134.3, 130.9, 129.3, 128.0, 127.7, 120.2, 60.8, 49.6, 38.6, 14.1. HRMS ESI(*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>S: 289.0893, found: 289.0890.

### Unsuccessful substrates:



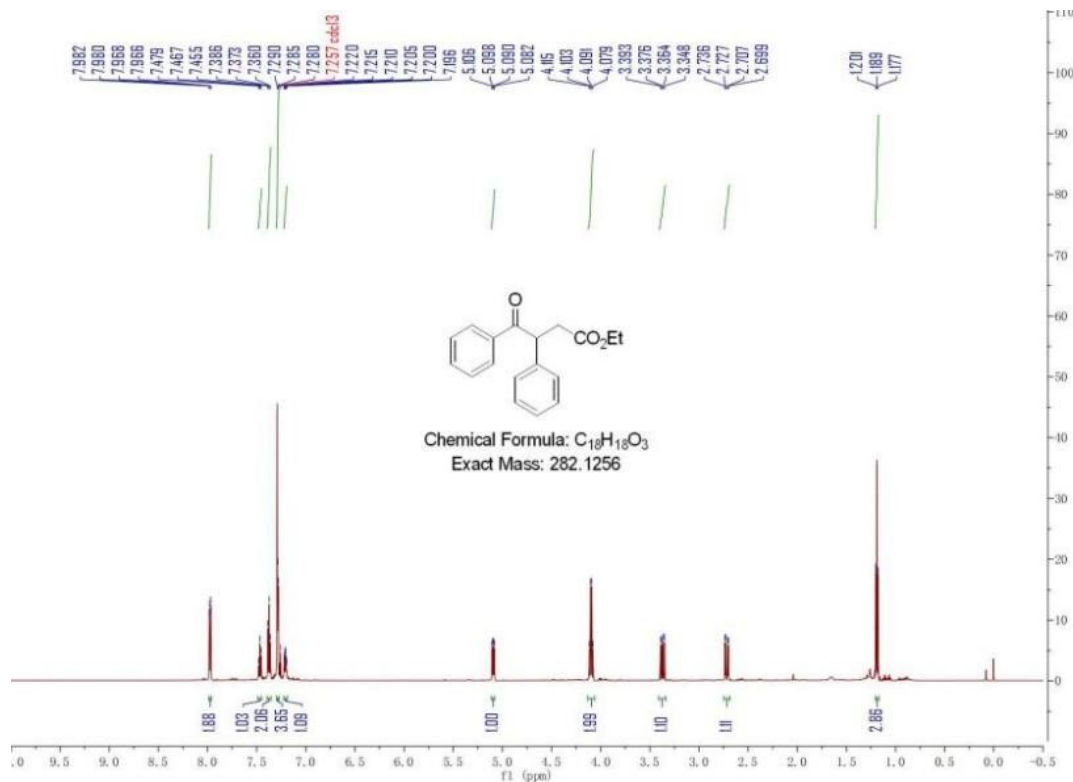
## 6. References

- 1 Z. Wang, X. Wang, and Y. Nishihara, Nickel-catalysed decarbonylative borylation of aroyl fluorides. *Chem. Commun.*, 2018, **54**, 13969-13972.
- 2 A. L'Heureux, F. Beaulieu, C. Bennett, Aminodifluorosulfonium salts: selective fluorination reagents with enhanced thermal stability and ease of handling. *J. Org. Chem.*, 2010, **75**, 3401-3411.
- 3 (a) A. Mavroskoufis, K. Rajes, P. Golz, N-Heterocyclic Carbene Catalyzed Photoenolization/Diels-Alder Reaction of Acid Fluorides. *Angew. Chem. Int. Ed.*, 2020, **59**, 3190-3194; (b) G. Steiner, A. Krajete, H. Kopacka, [1,2]-Rearrangement of Imino-N-heterocyclic Carbenes—Synthesis and Structures of Chelating Iminoimidazole Pd and Ni Complexes. *Eur. J. Inorg. Chem.*, 2004, **2004**, 2827-2836.
- 4 C. Kashima, Y. Shirahata, and Y. Tsukamoto, Preparation of  $\beta$ -Substituted  $\gamma$ -Keto Esters by the Grignard Reaction on N-Acylpyrazoles. *Heterocycles*. 2001, **54**, 309-317.

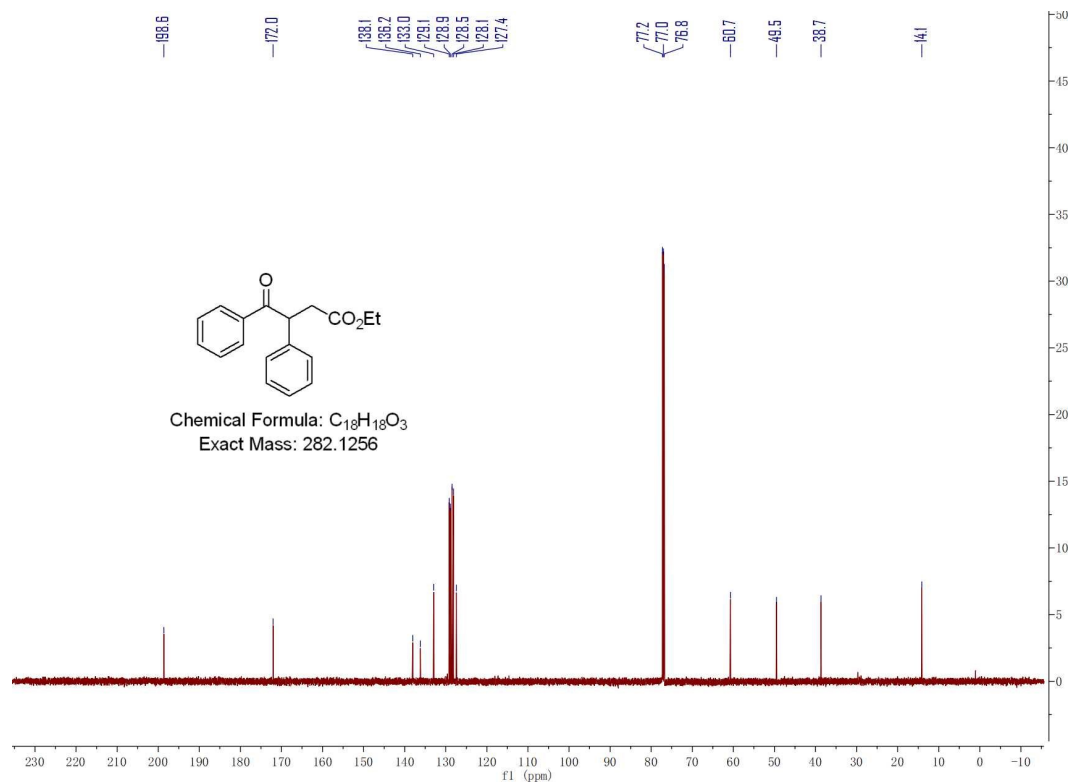
## 7. Copies of $^1\text{H}$ NMR, $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR spectra

### Ethyl 4-oxo-3,4-diphenylbutanoate (4a)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

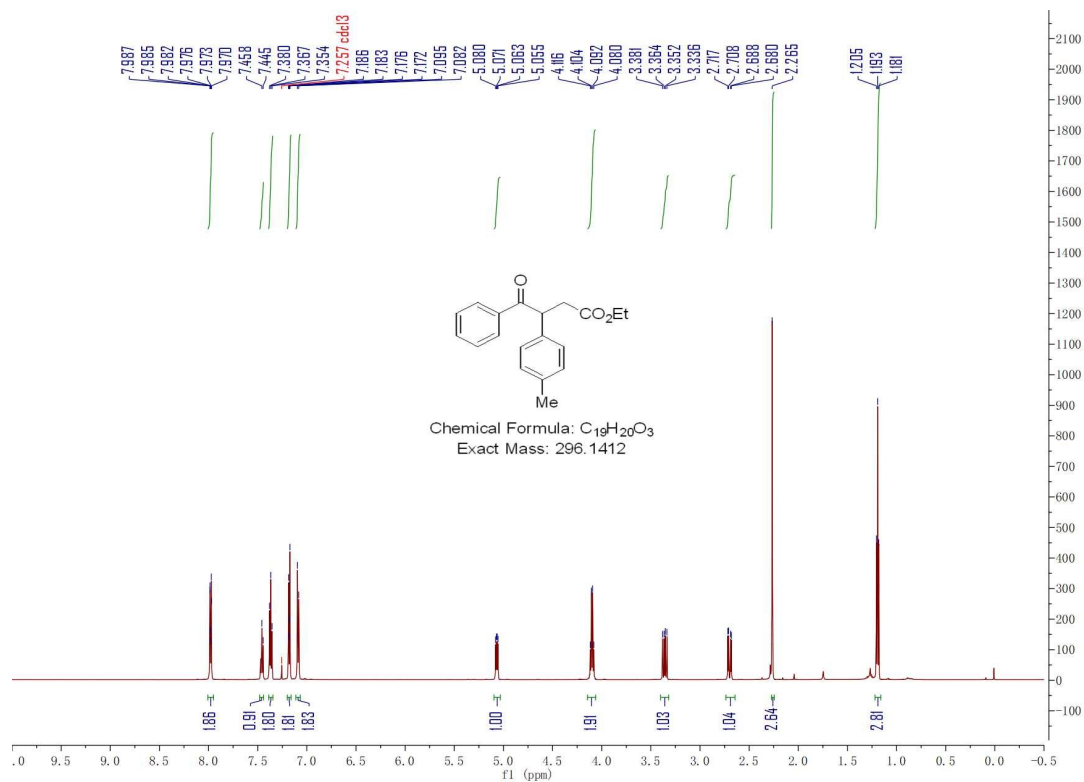


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

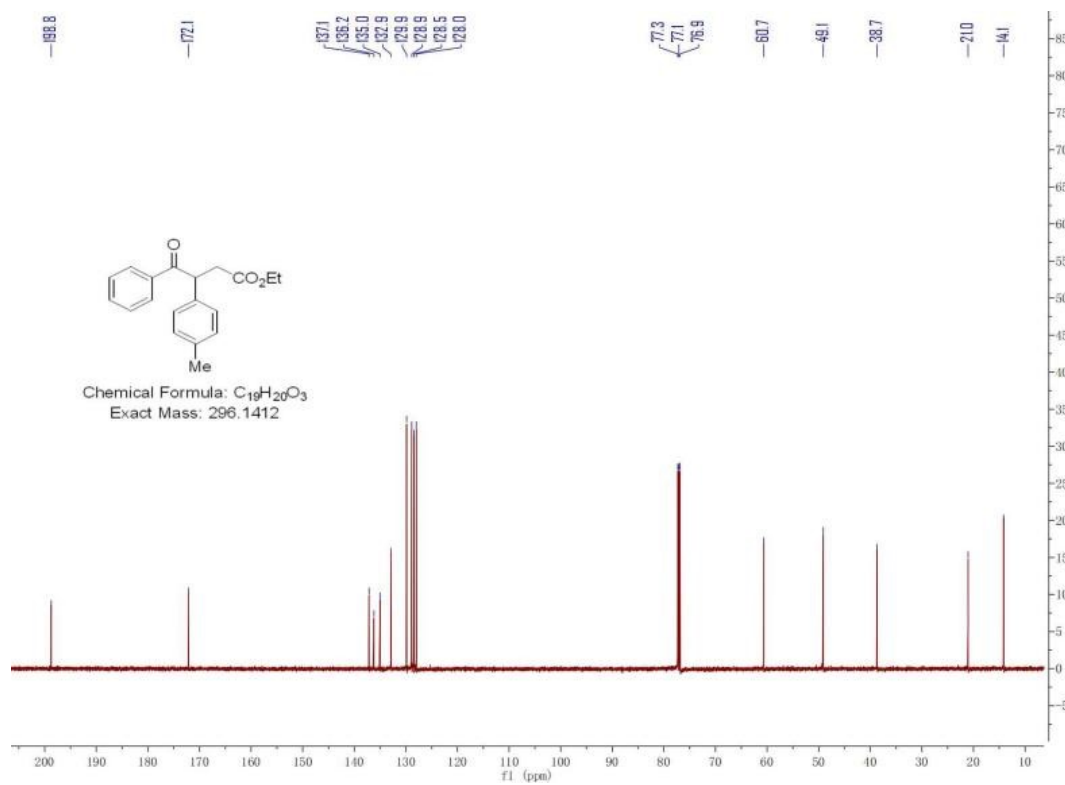


## Ethyl 4-oxo-4-phenyl-3-(p-tolyl)butanoate (4b)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

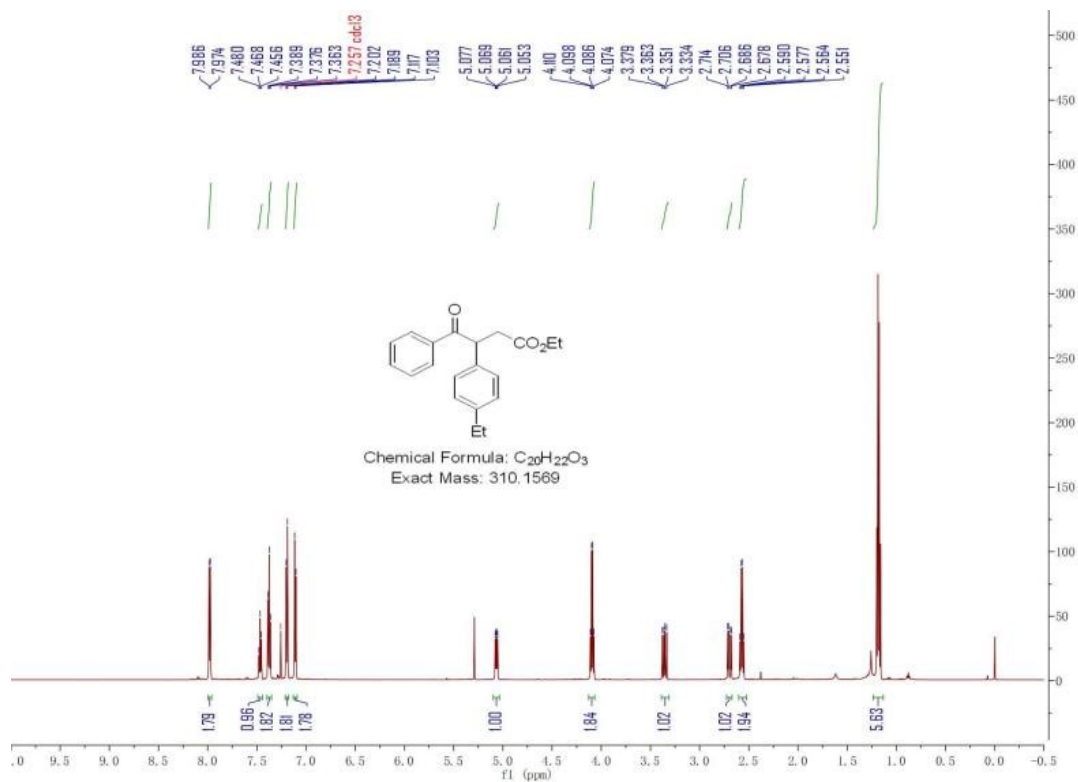


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

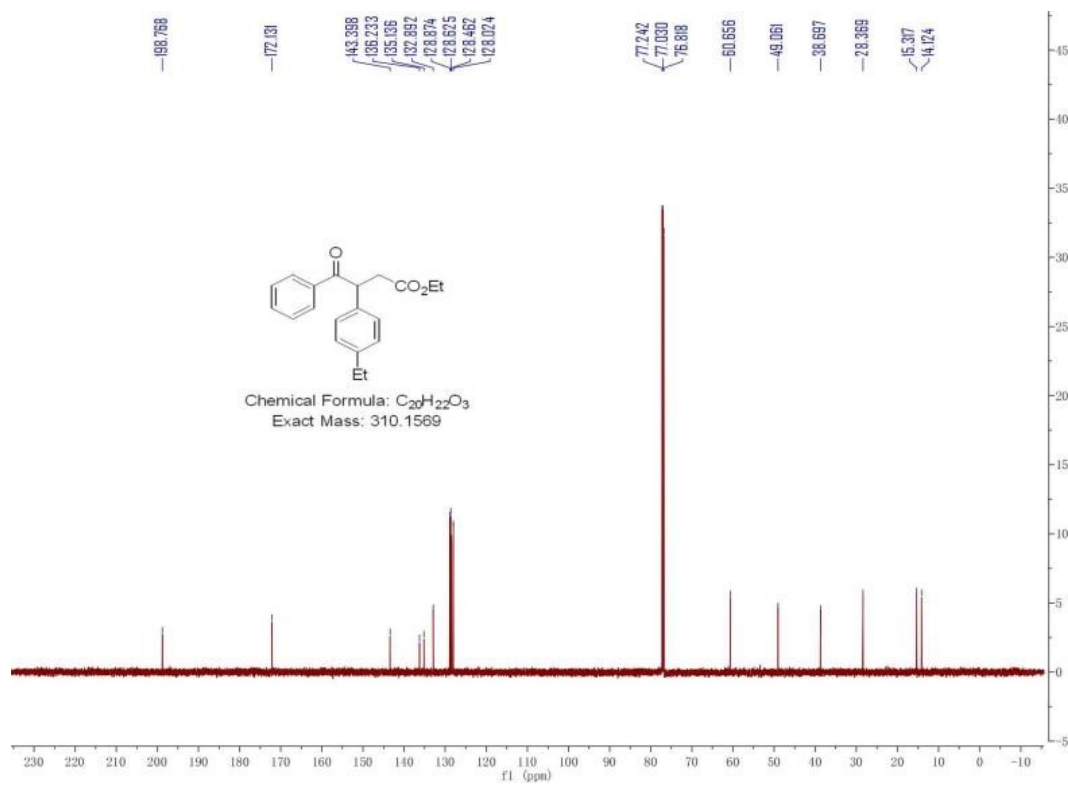


# Ethyl 3-(4-ethylphenyl)-4-oxo-4-phenylbutanoate (4c)

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

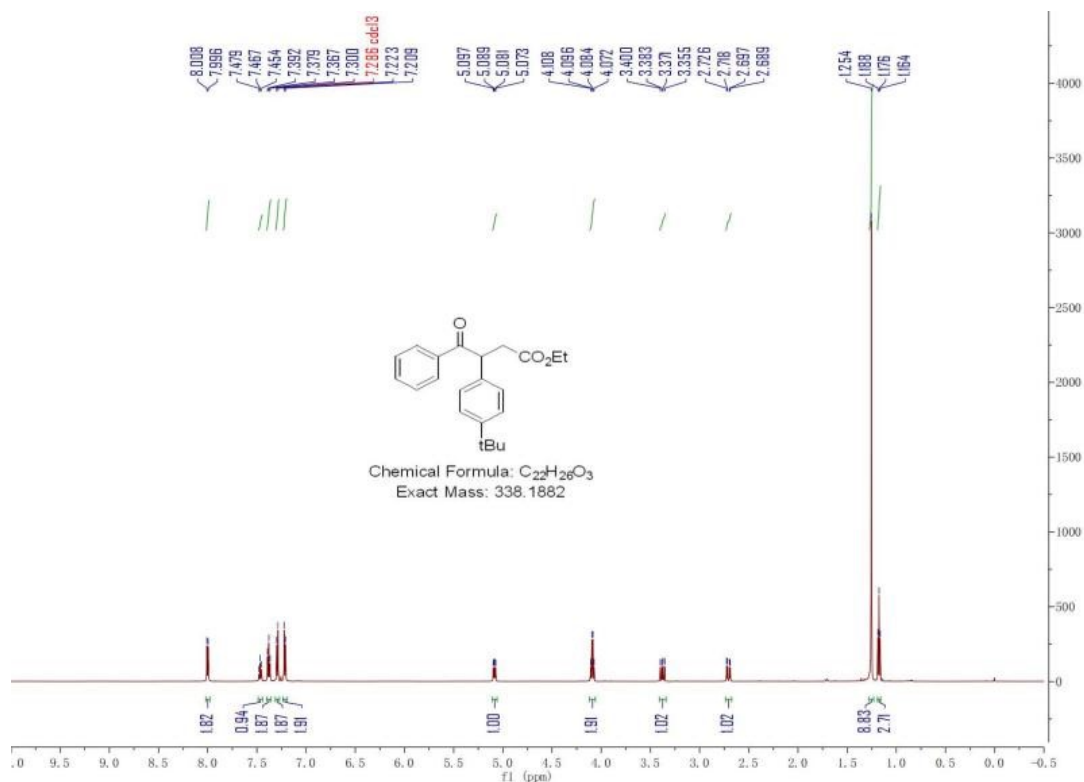


<sup>13</sup>C NMR (151 MHz, Chloroform-*d*)

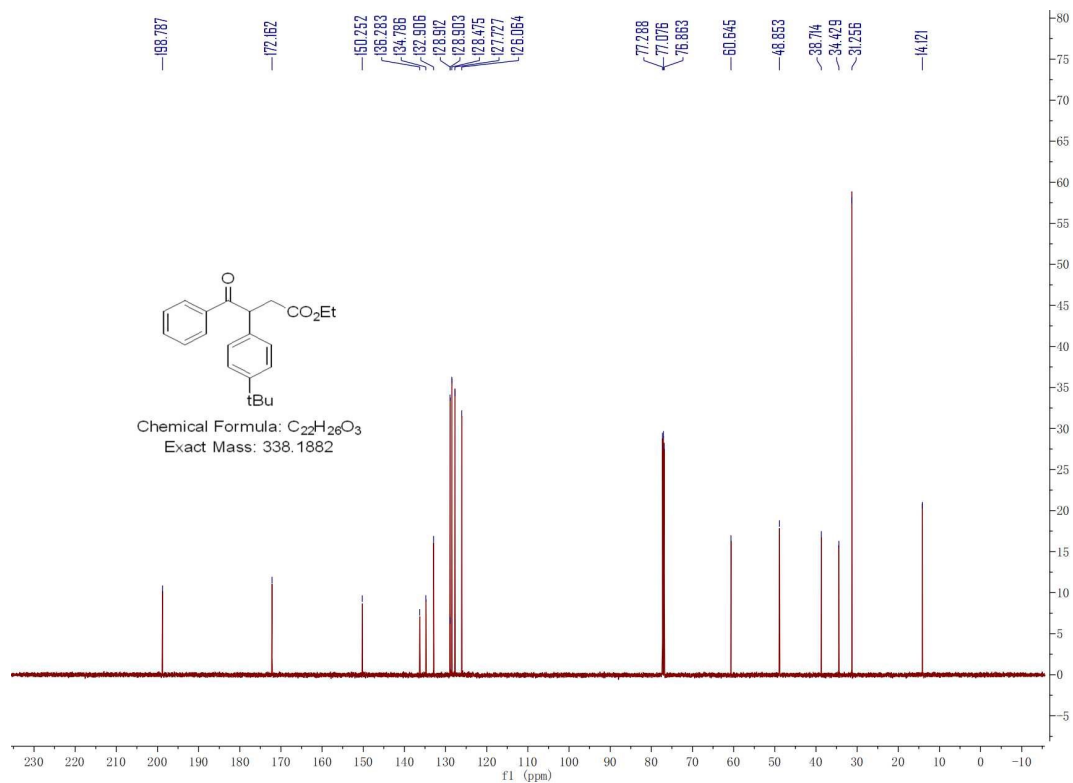


# Ethyl 3-(4-(tert-butyl)phenyl)-4-oxo-4-phenylbutanoate (4d)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

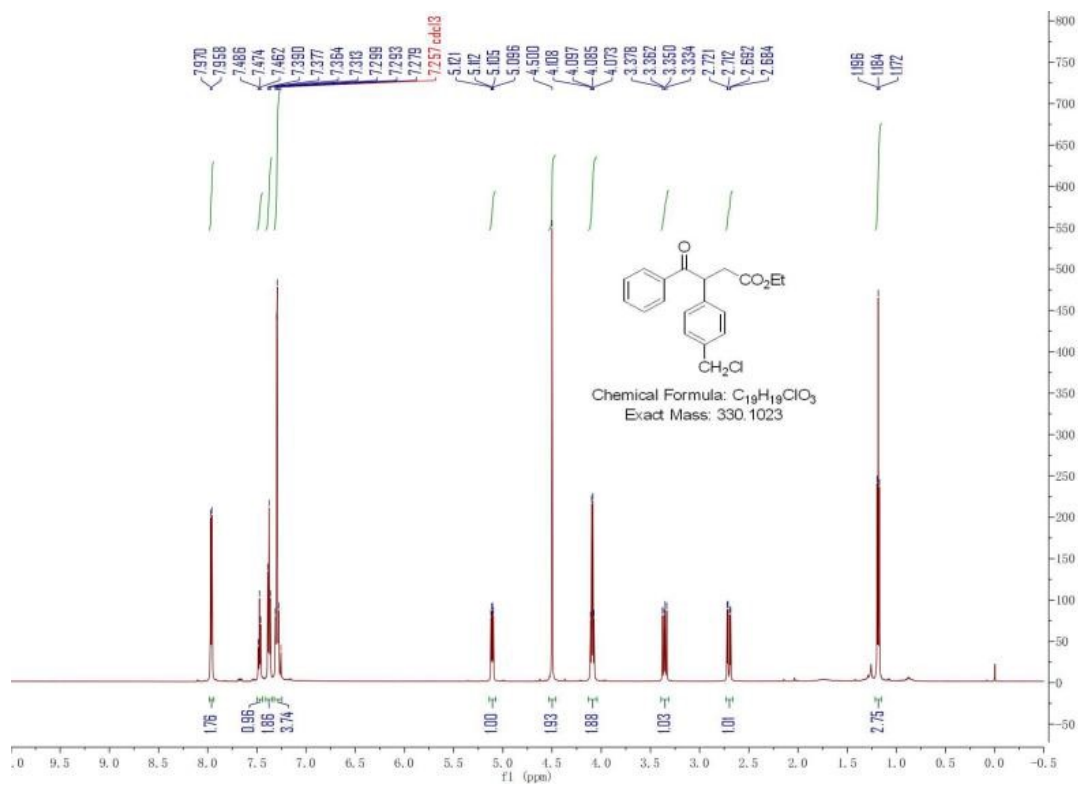


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

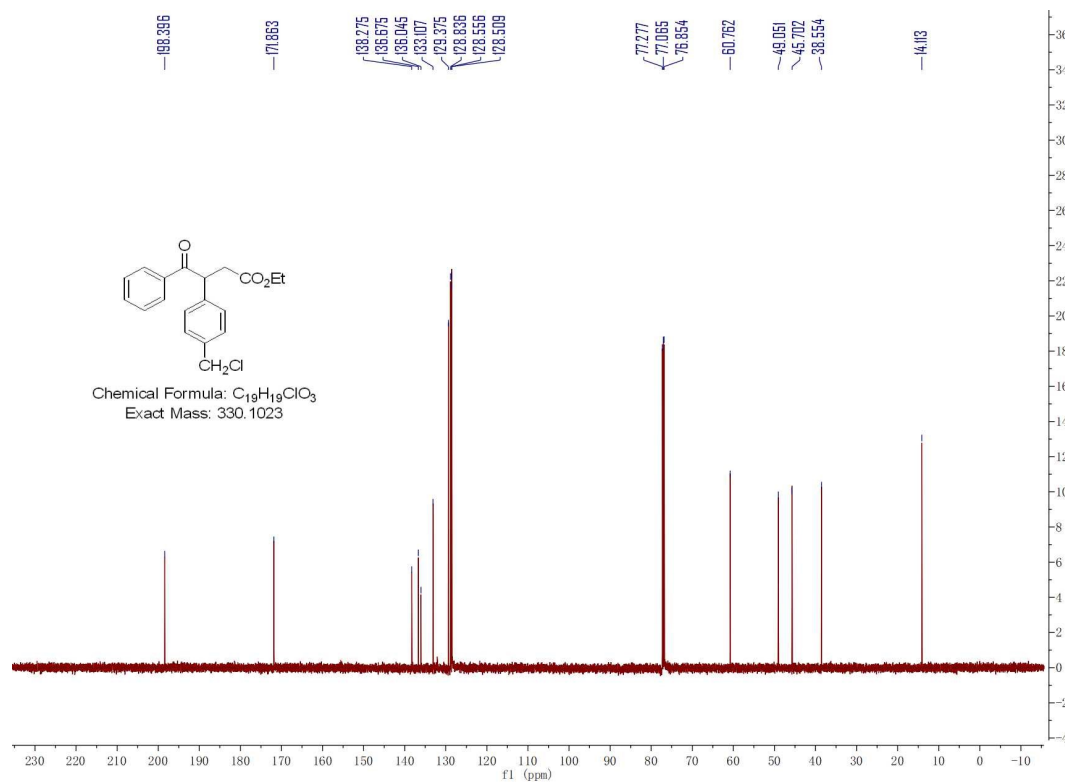


### Ethyl 3-(4-(chloromethyl)phenyl)-4-oxo-4-phenylbutanoate (4e)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)



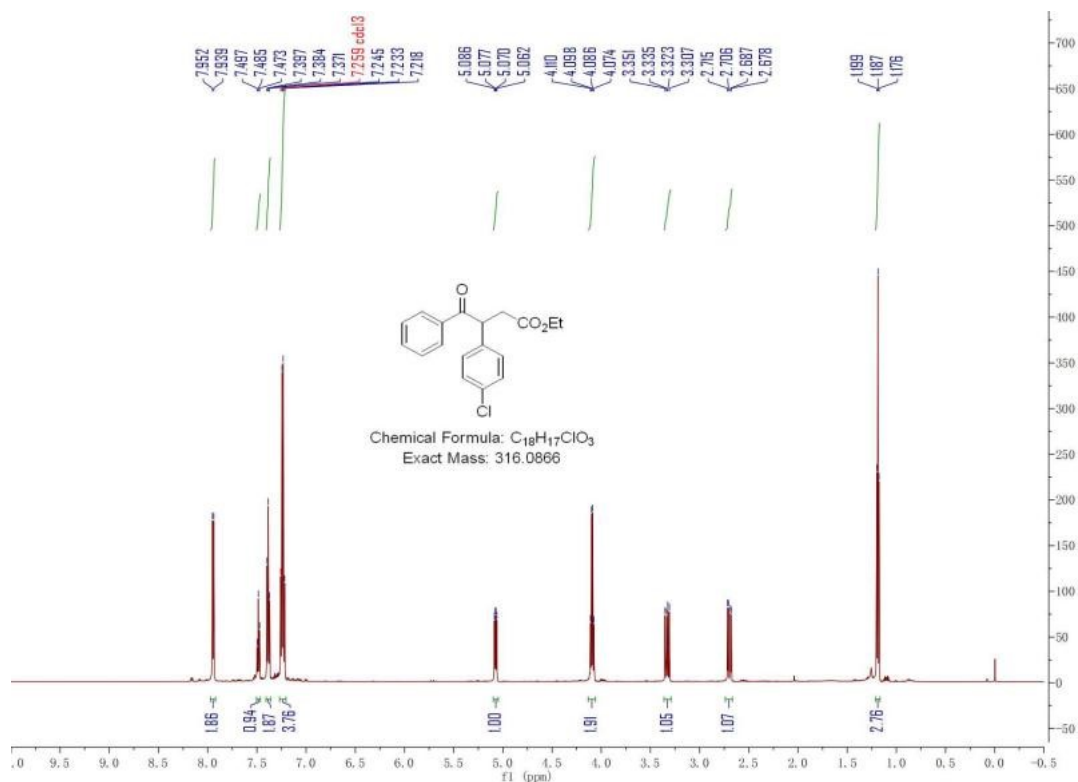
$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)



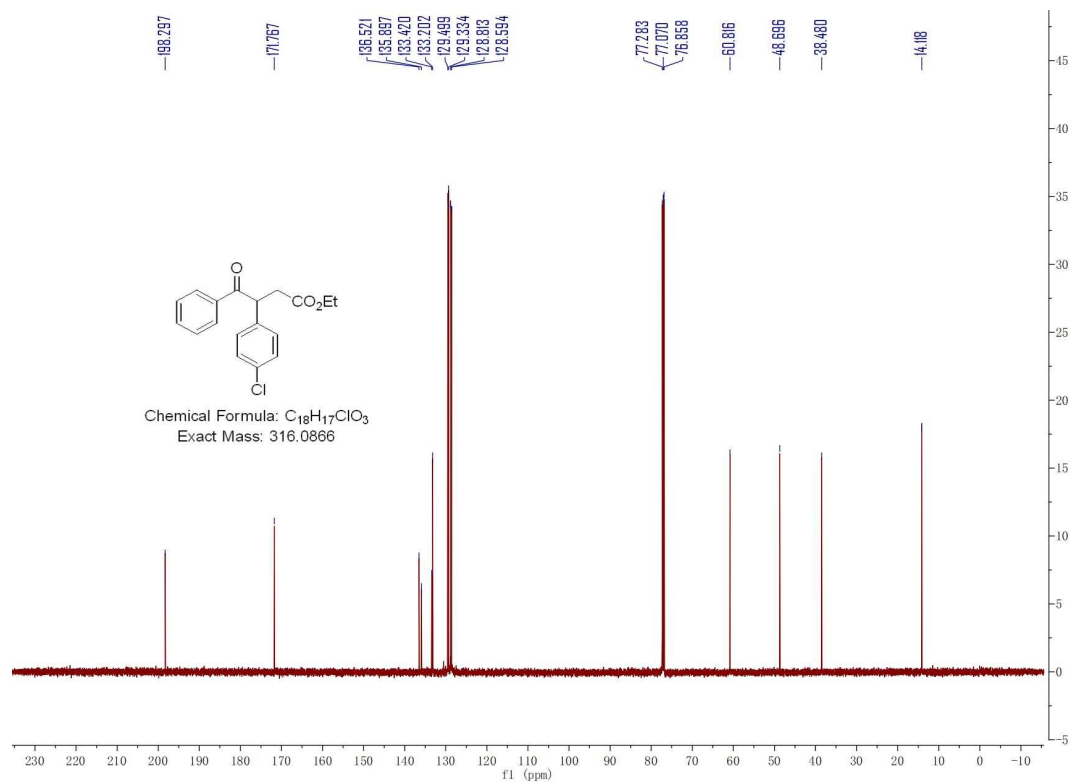


# Ethyl 3-(4-chlorophenyl)-4-oxo-4-phenylbutanoate (4f)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

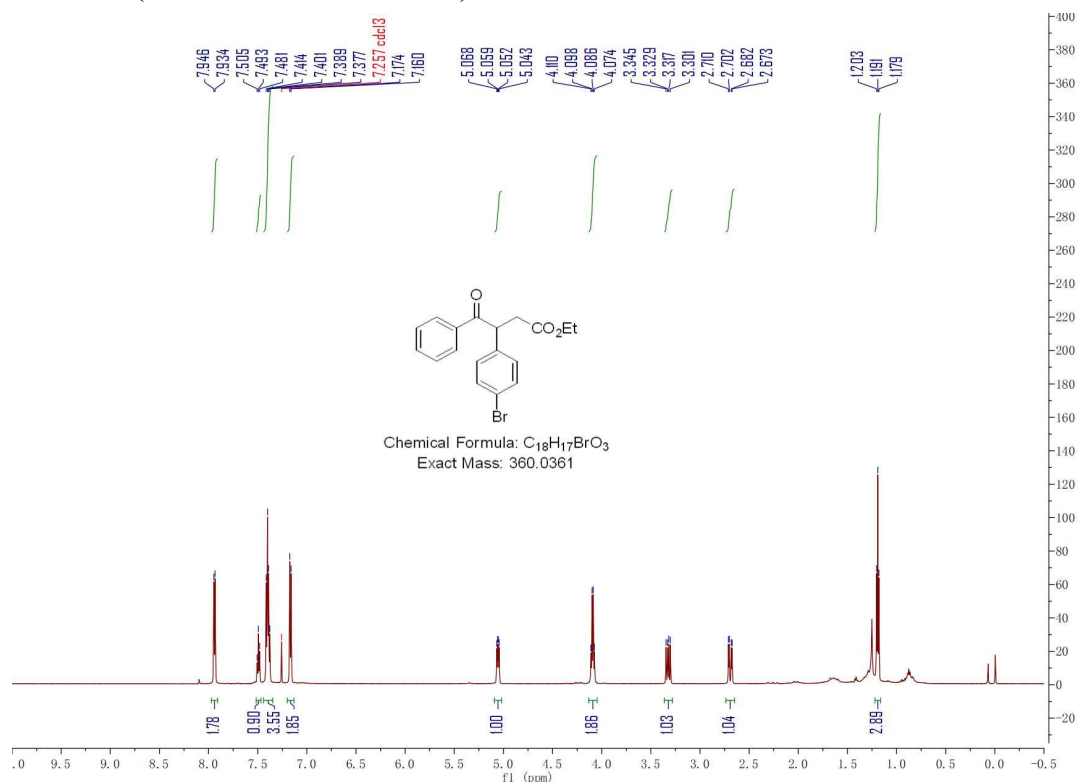


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

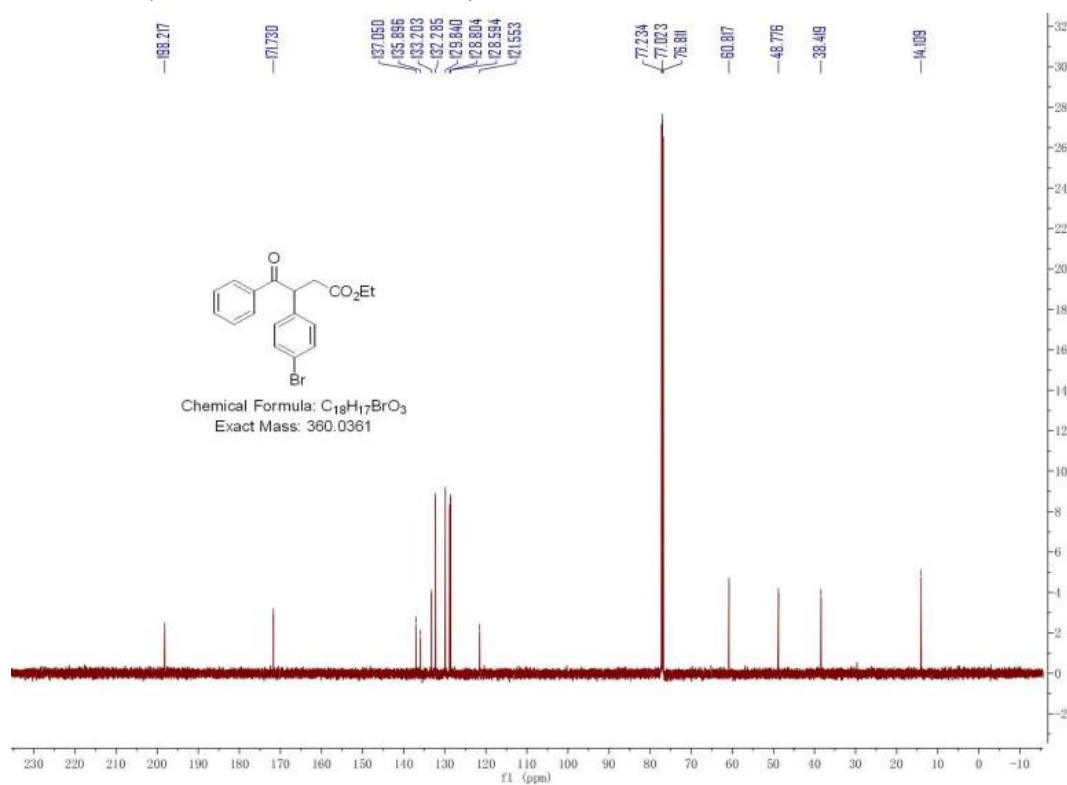


# Ethyl 3-(4-bromophenyl)-4-oxo-4-phenylbutanoate (4g)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

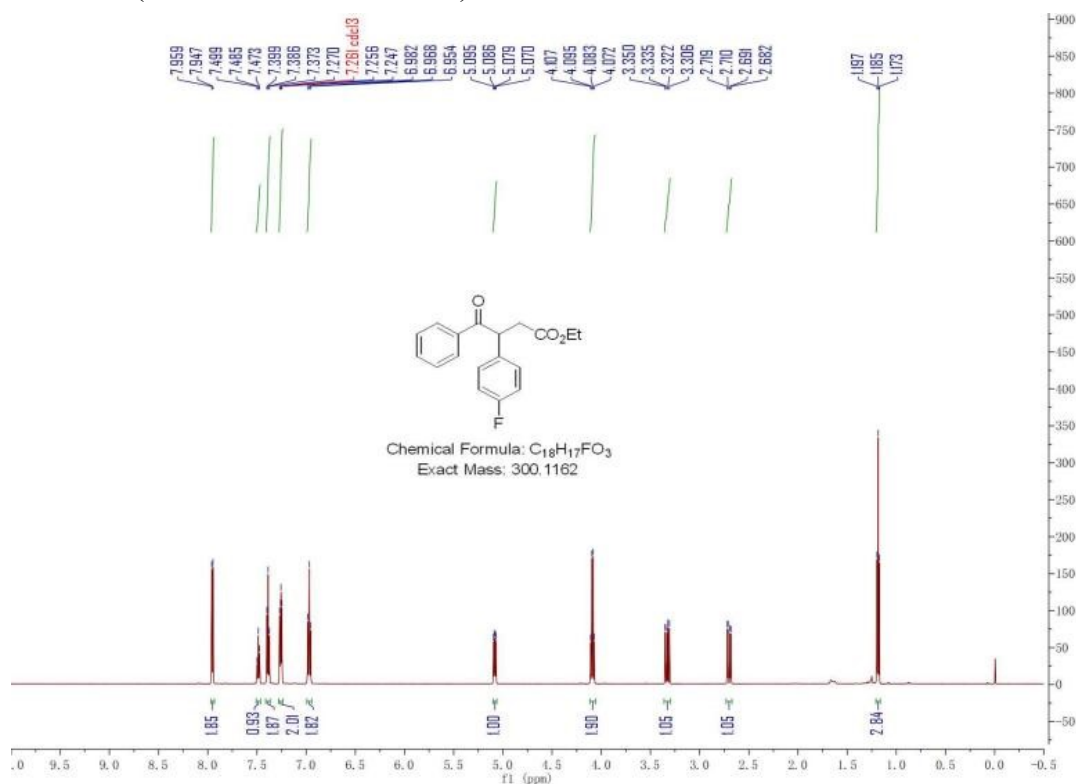


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

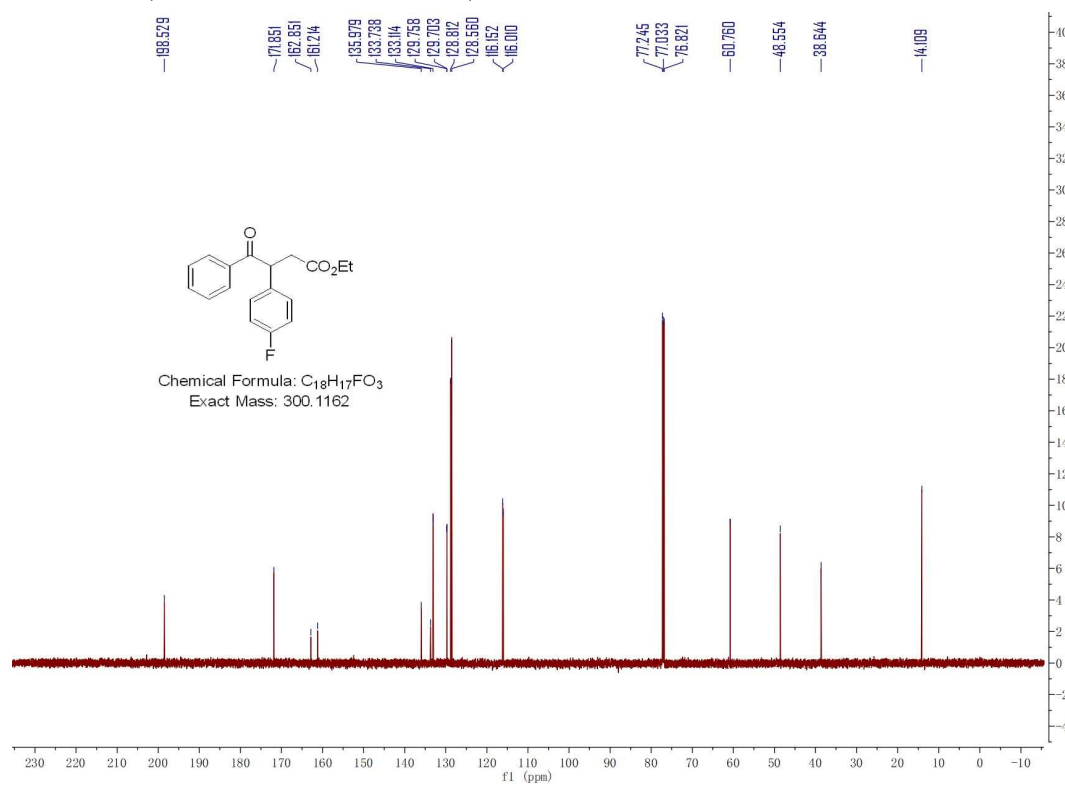


# Ethyl 3-(4-fluorophenyl)-4-oxo-4-phenylbutanoate (4h)

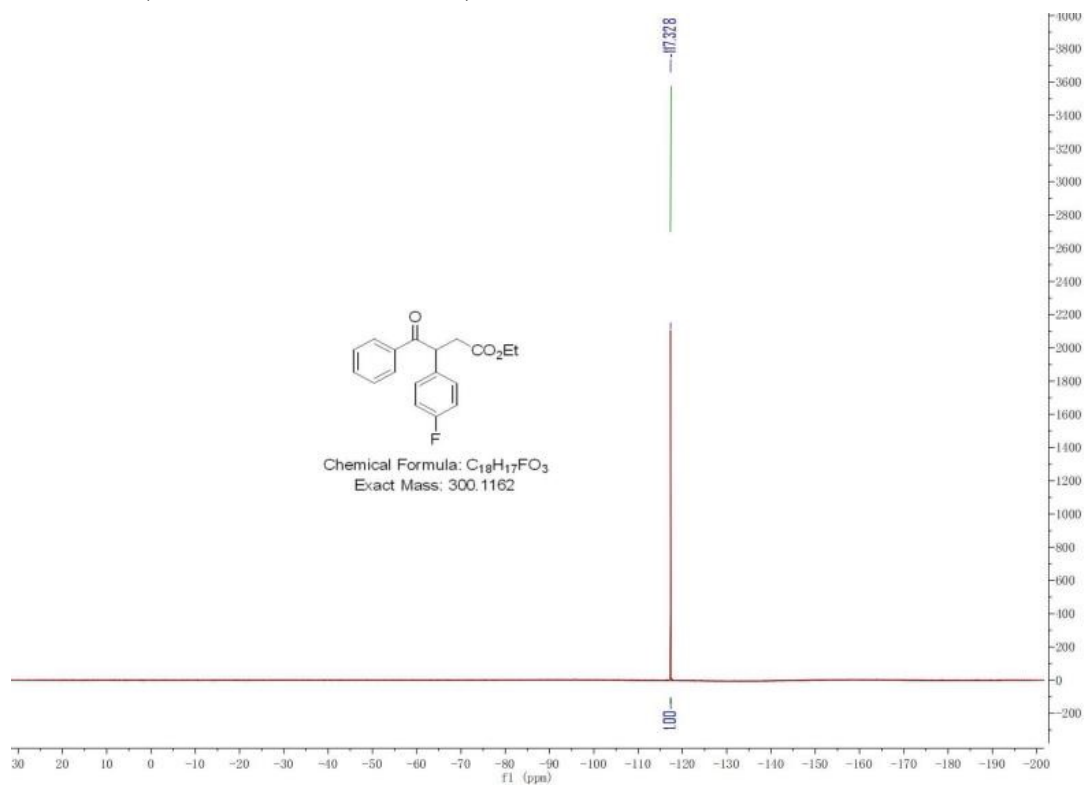
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)



$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

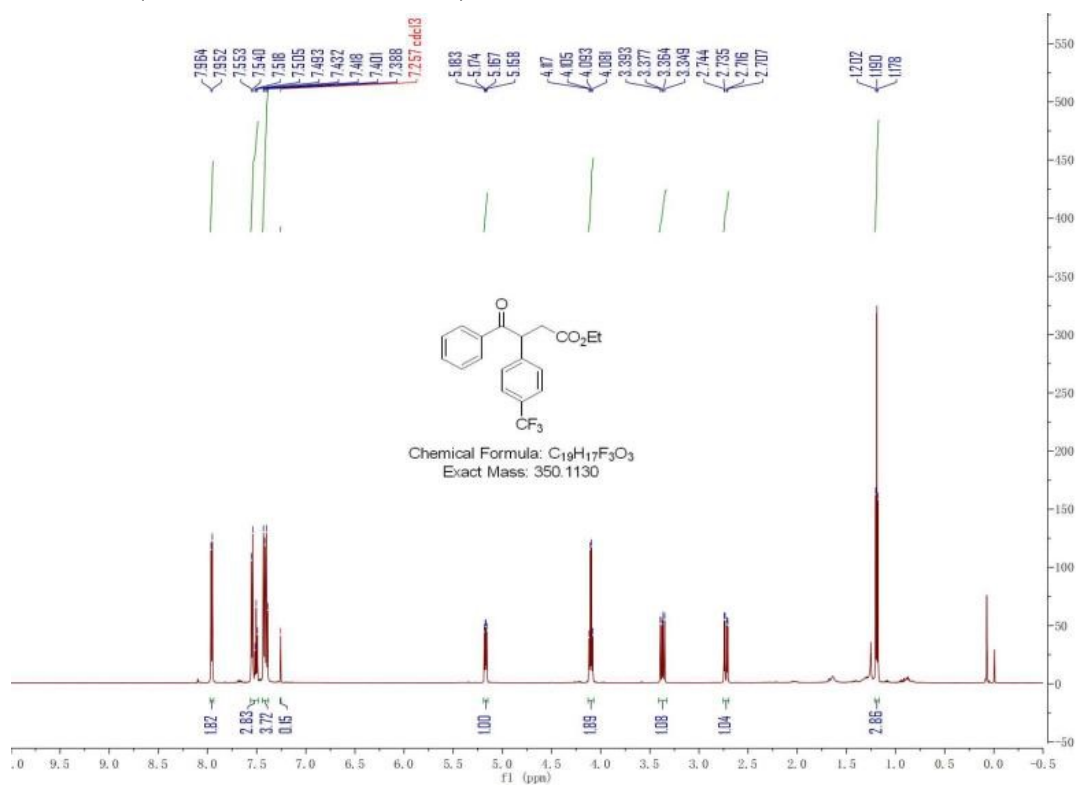


$^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)

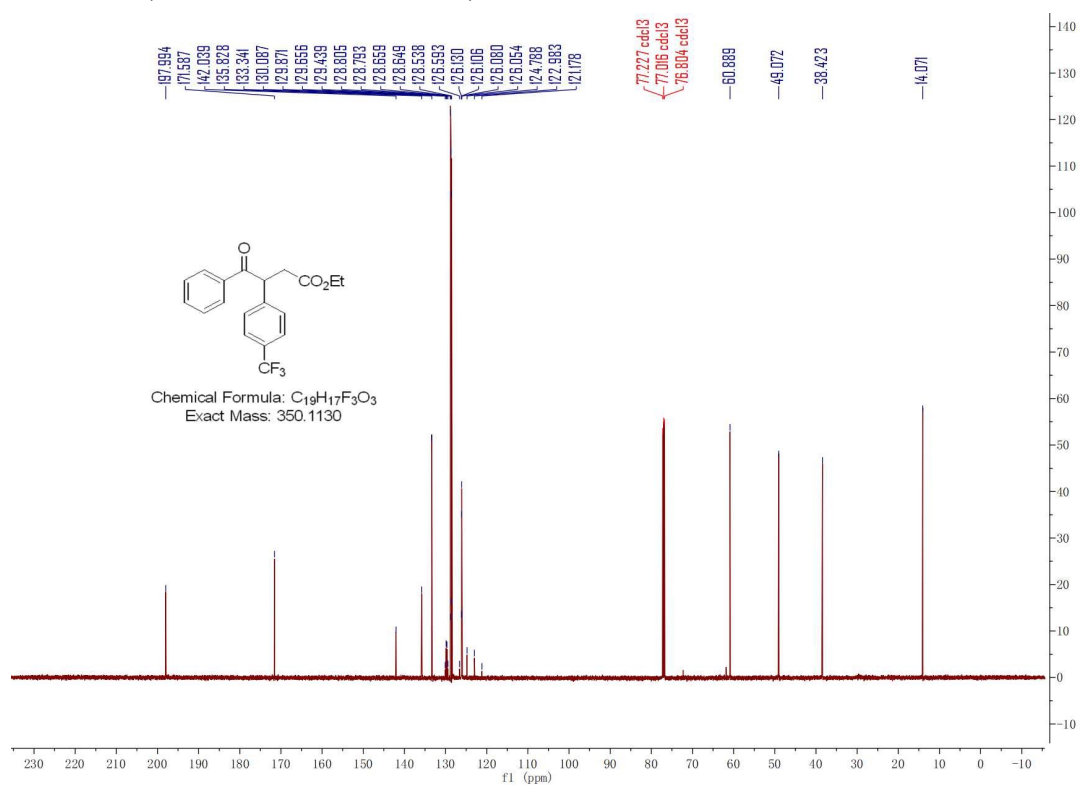


**Ethyl 4-oxo-4-phenyl-3-(4-(trifluoromethyl)phenyl)butanoate (4i)**

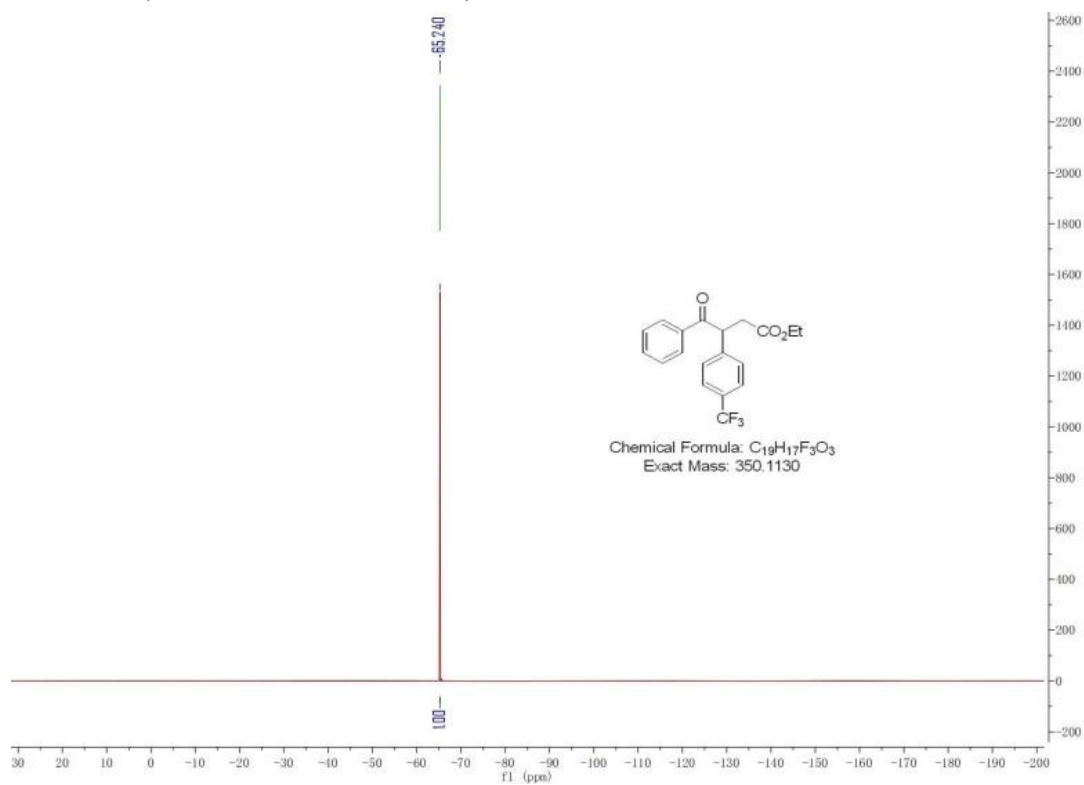
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)



$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

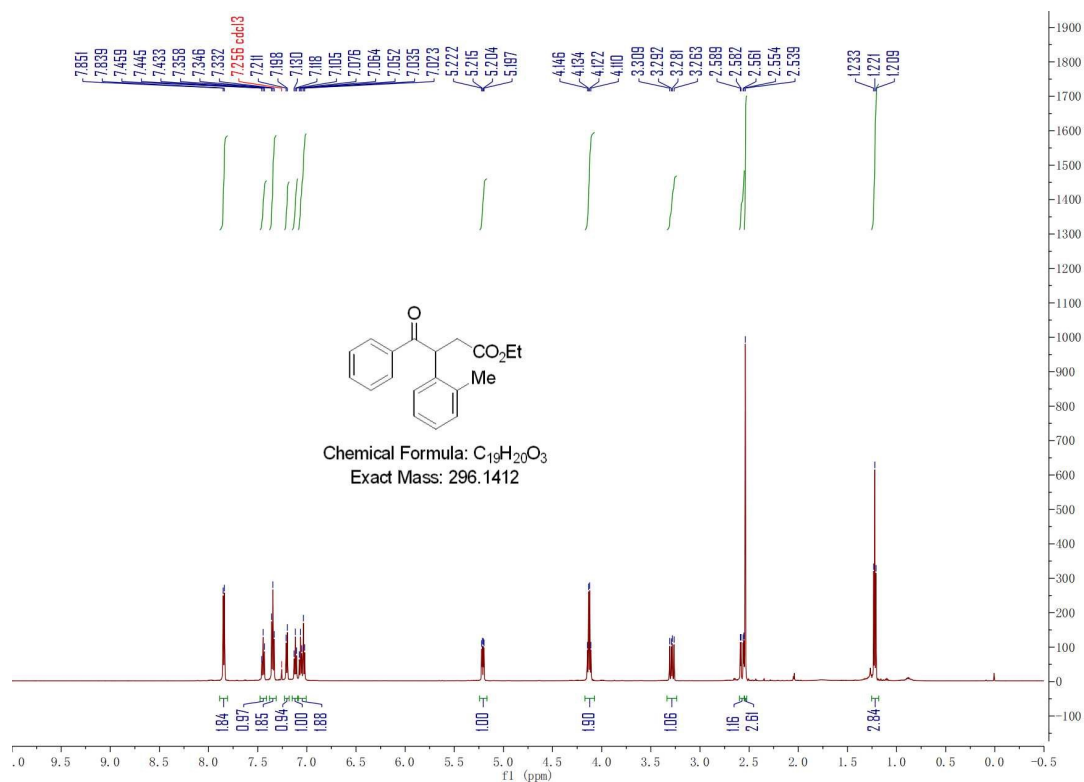


$^{19}\text{F}$  NMR (564 MHz, Chloroform-*d*)

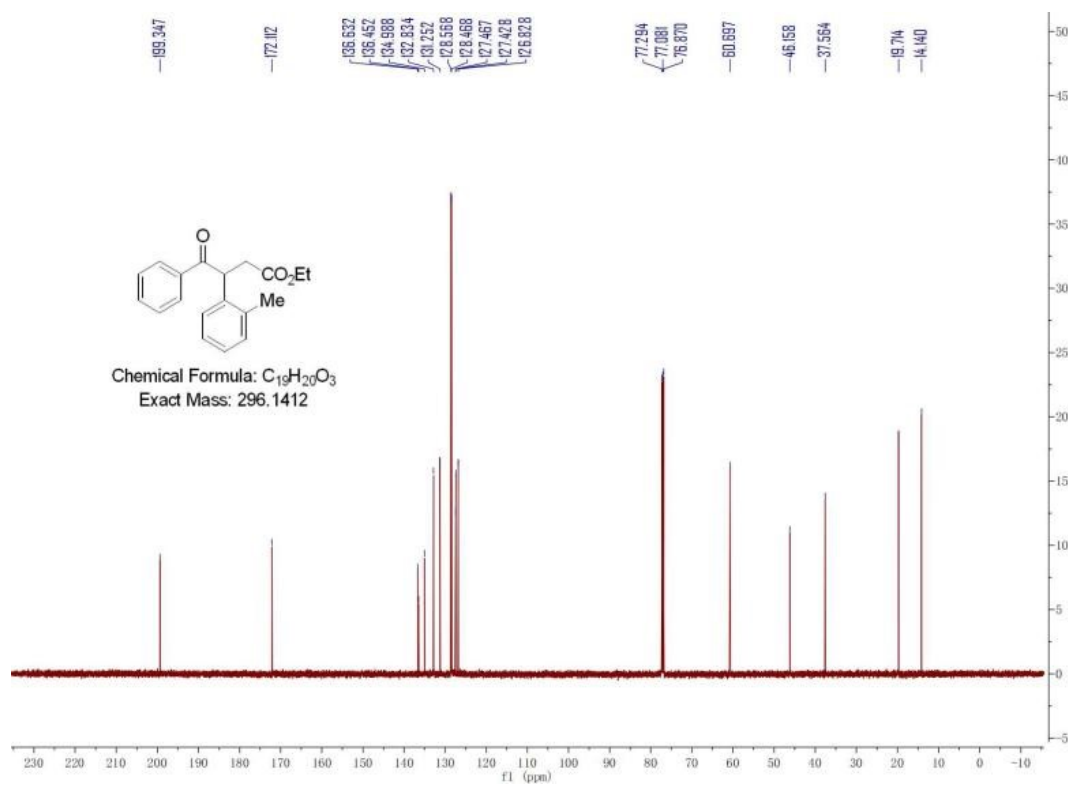


### Ethyl 4-oxo-4-phenyl-3-(o-tolyl)butanoate(4j)

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

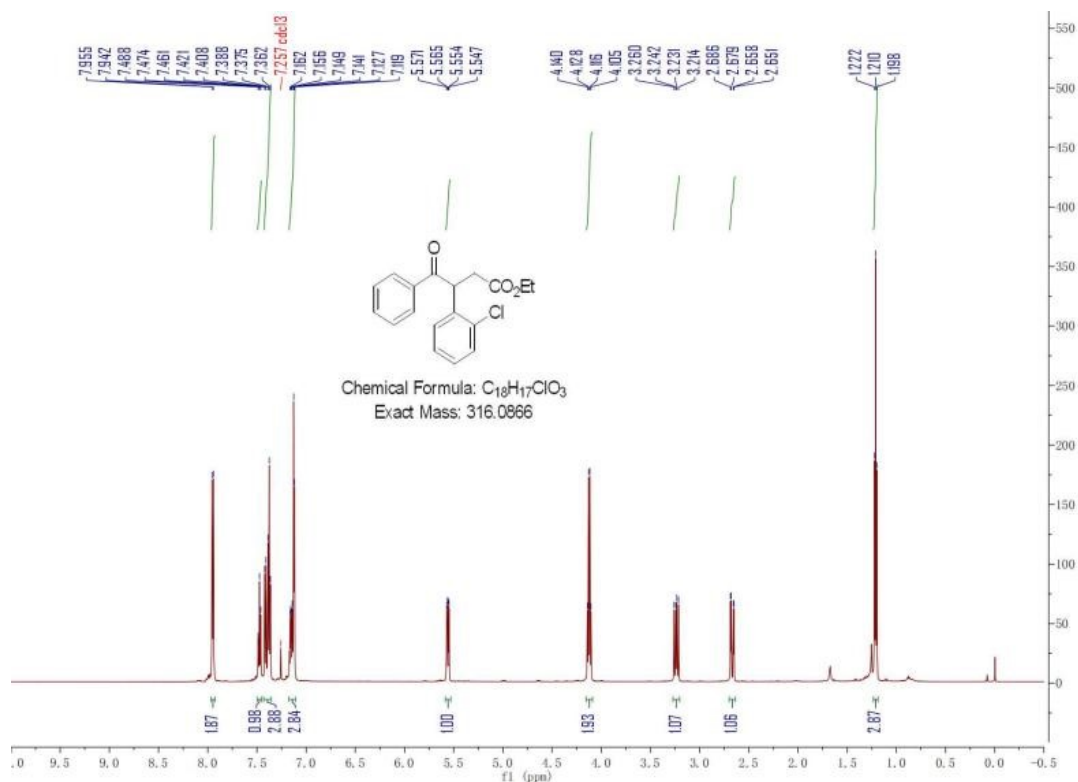


<sup>13</sup>C NMR (151 MHz, Chloroform-*d*)

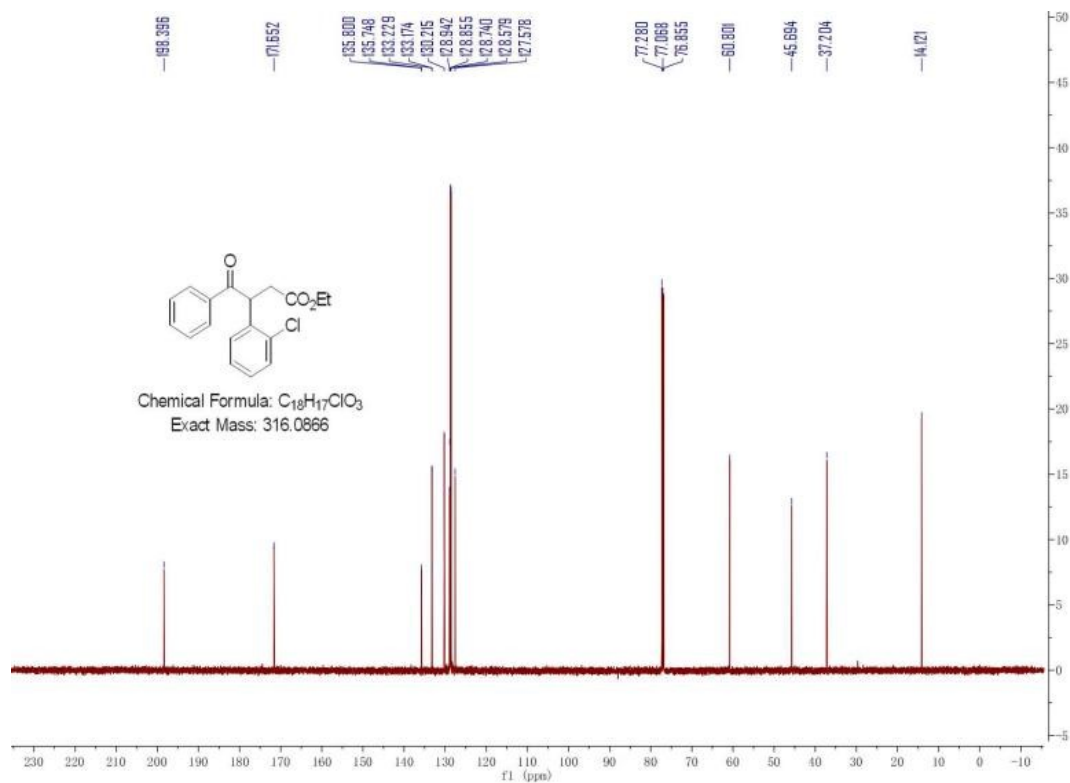


# Ethyl 3-(2-chlorophenyl)-4-oxo-4-phenylbutanoate (4k)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

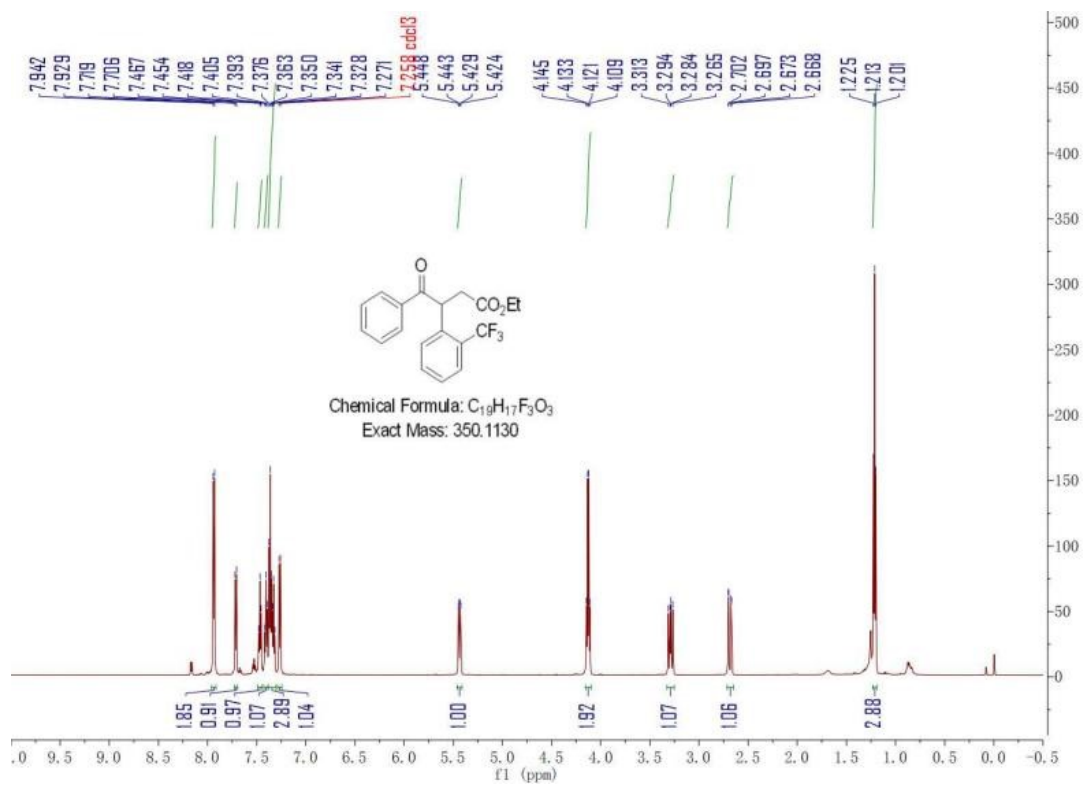


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

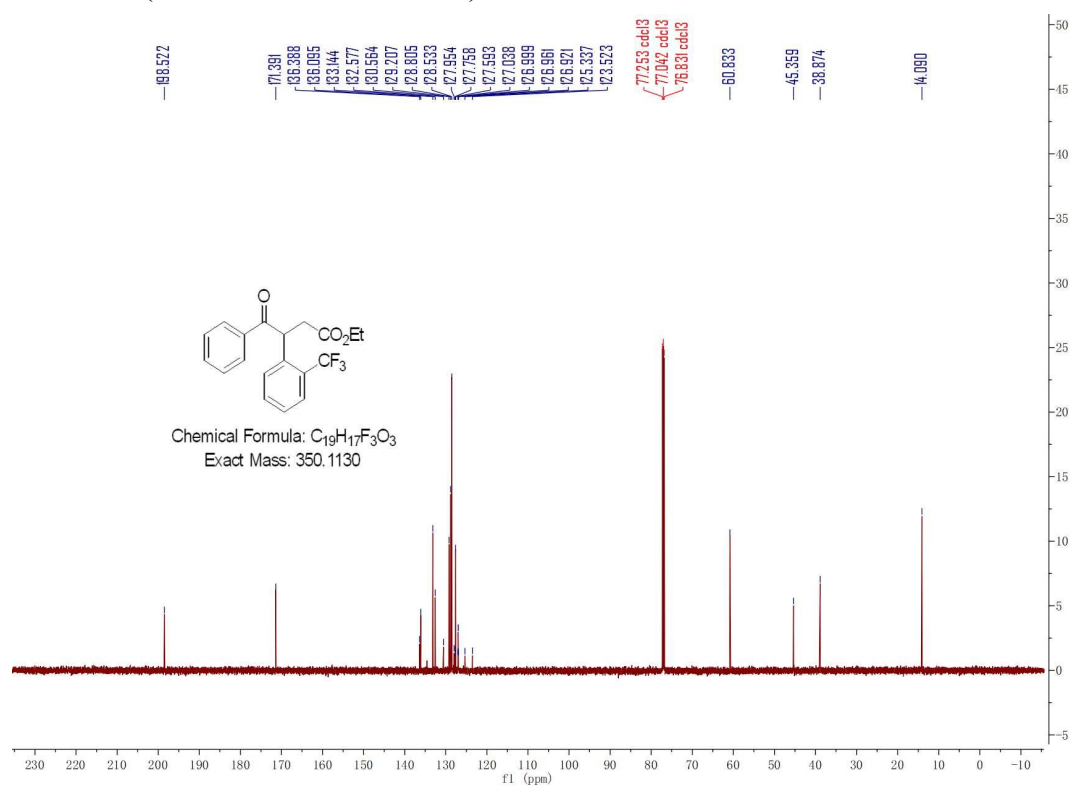


### Ethyl 4-oxo-4-phenyl-3-(2-(trifluoromethyl)phenyl)butanoate (4l)

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

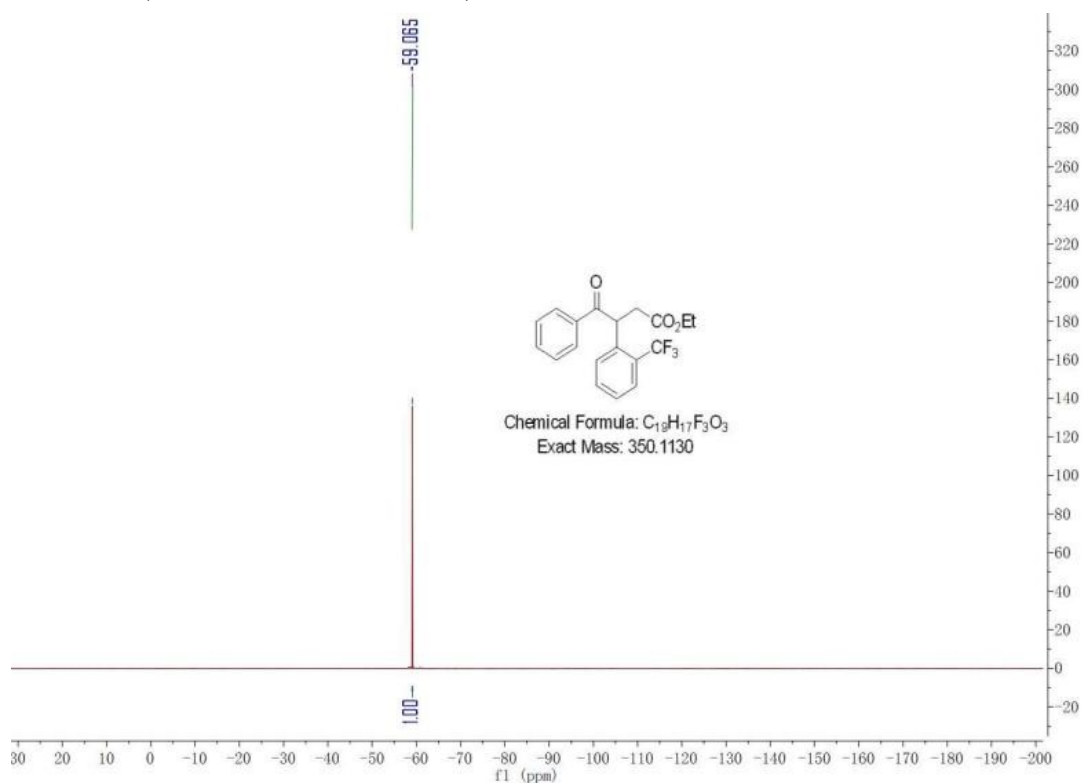


<sup>13</sup>C NMR (151 MHz, Chloroform-d)



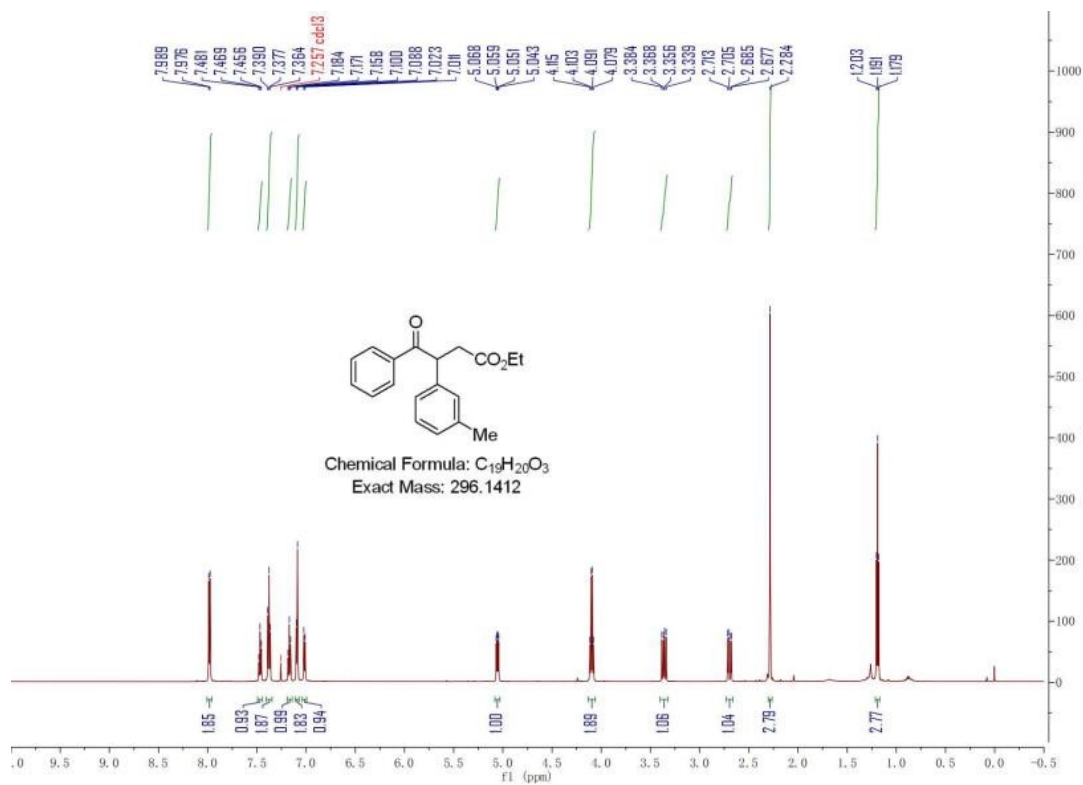


<sup>19</sup>F NMR (564 MHz, Chloroform-d)

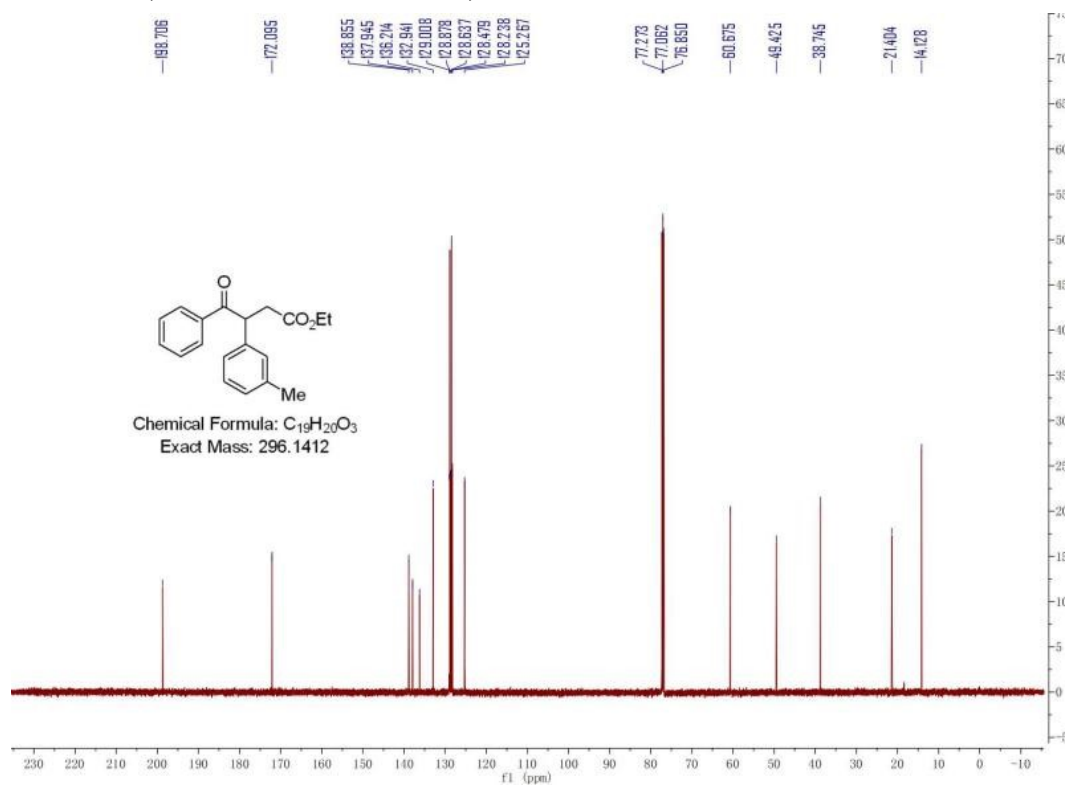


**Ethyl 4-oxo-4-phenyl-3-(m-tolyl)butanoate (4m)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

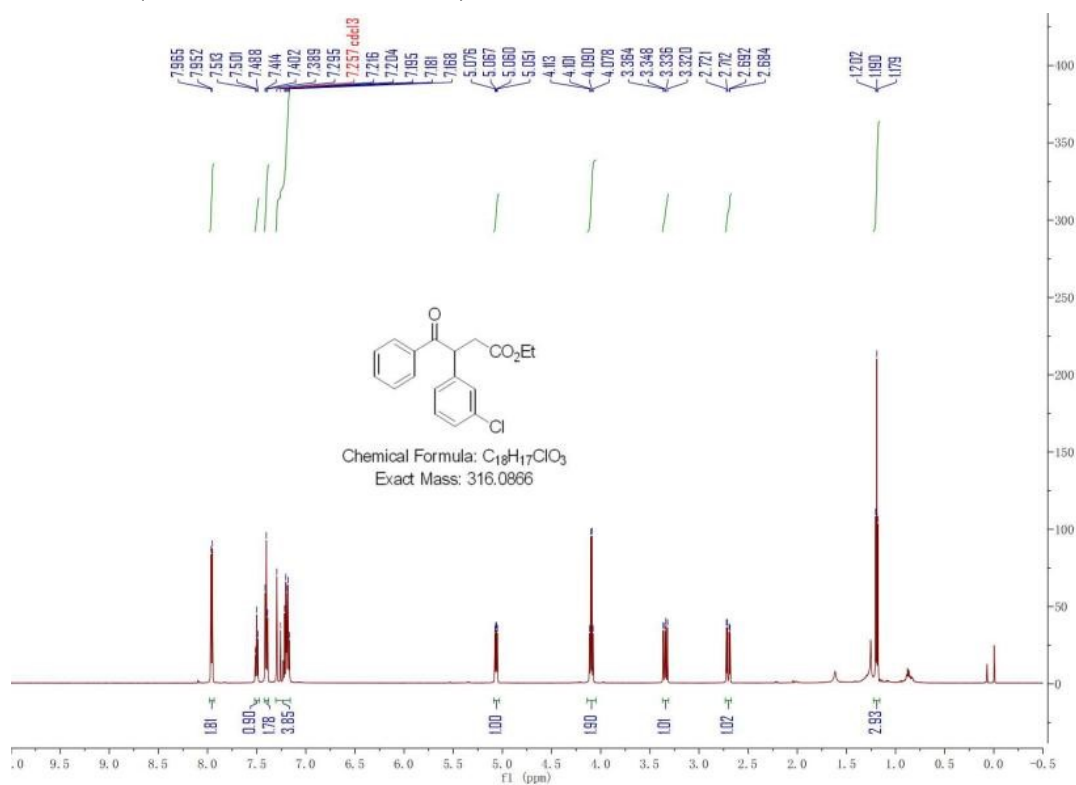


<sup>13</sup>C NMR (151 MHz, Chloroform-*d*)

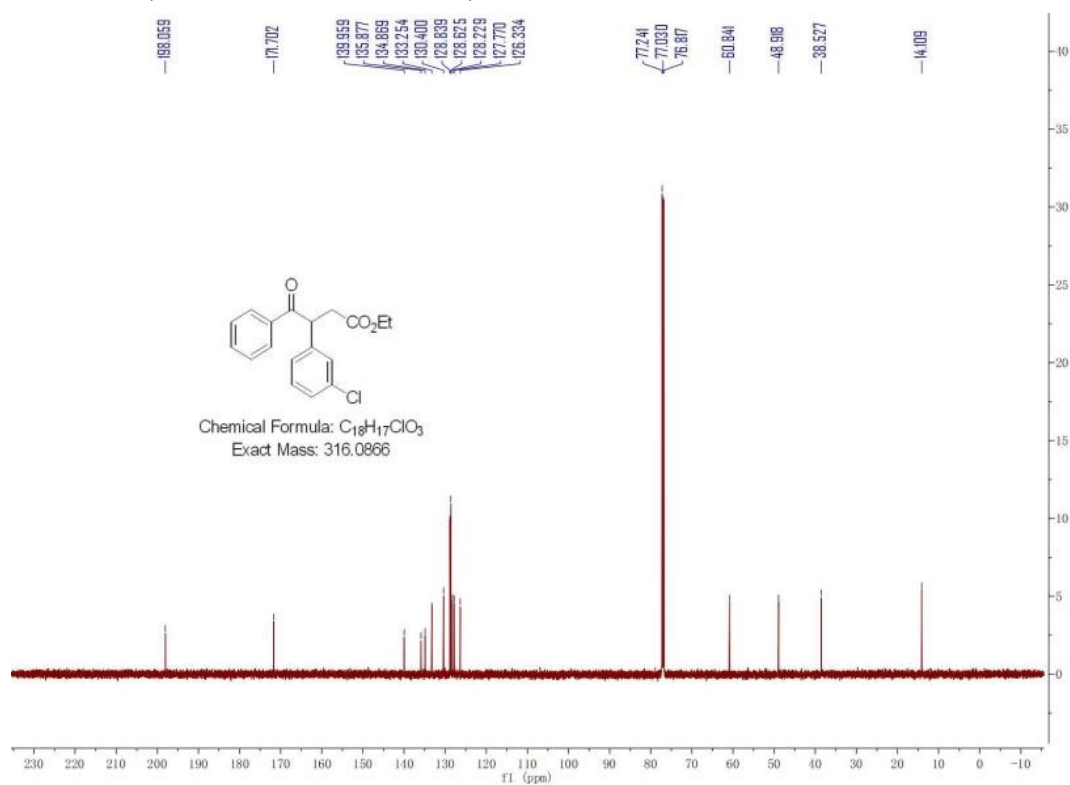


**Ethyl 3-(3-chlorophenyl)-4-oxo-4-phenylbutanoate (4n)**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

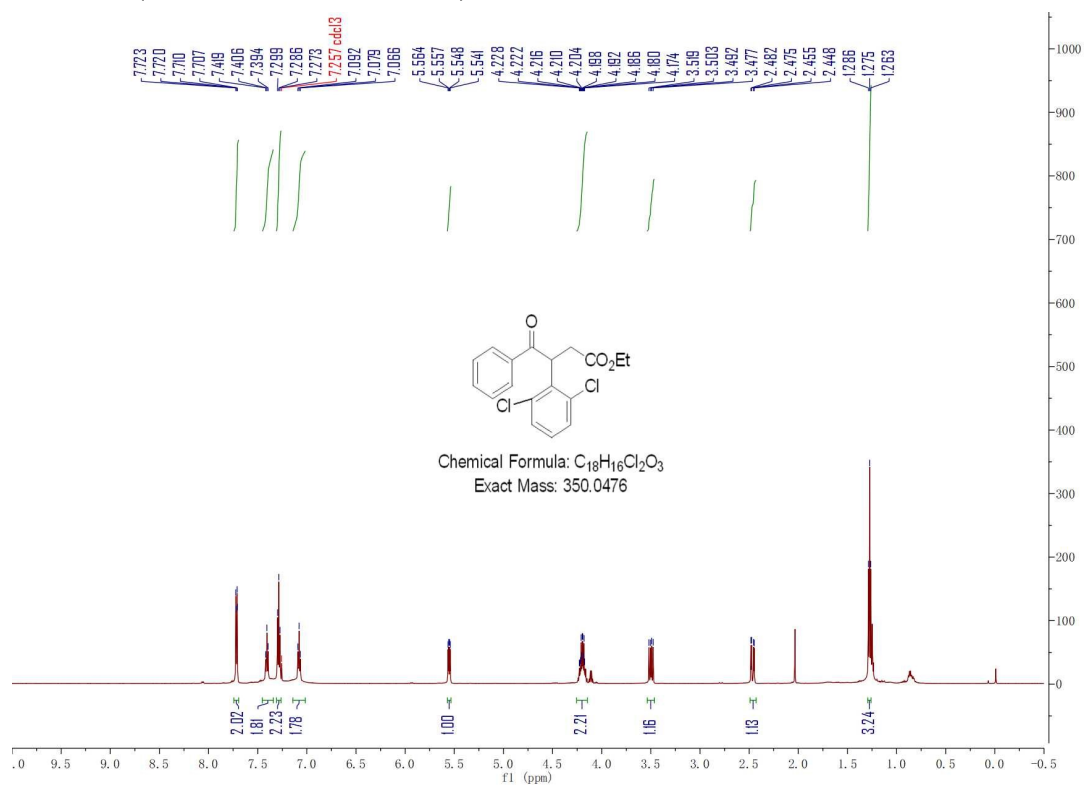


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

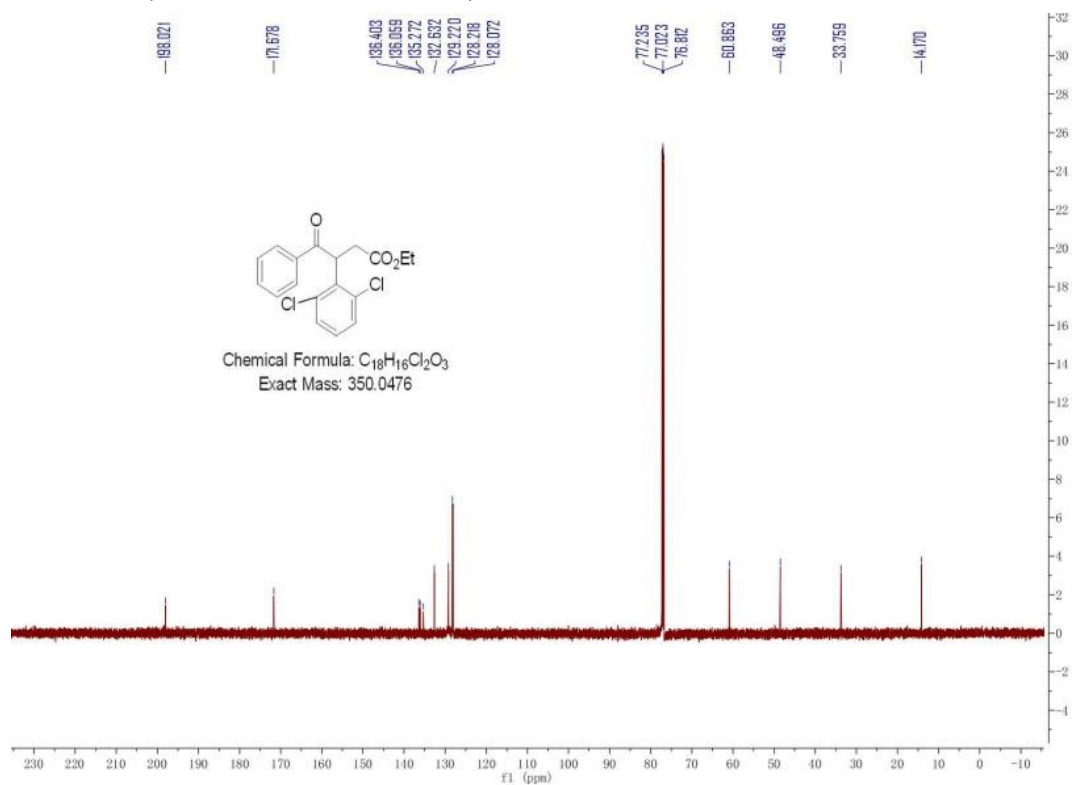


**Ethyl 3-(2,6-dichlorophenyl)-4-oxo-4-phenylbutanoate (4o)**

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

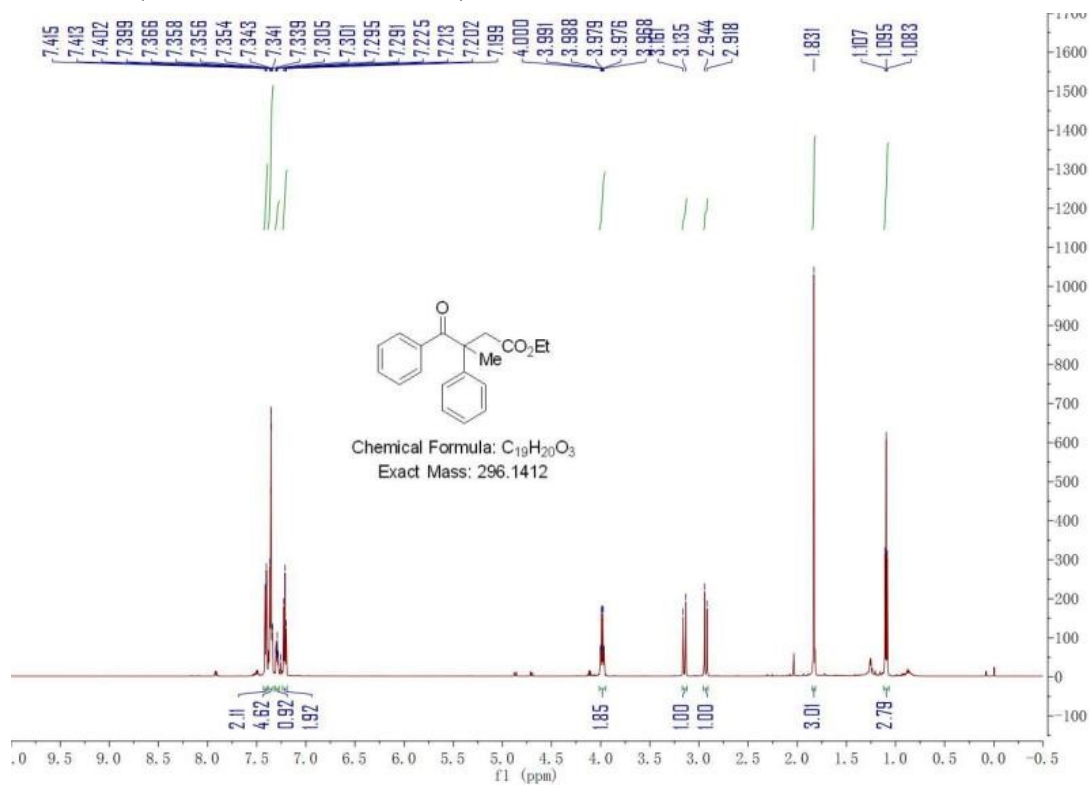


<sup>13</sup>C NMR (151 MHz, Chloroform-*d*)

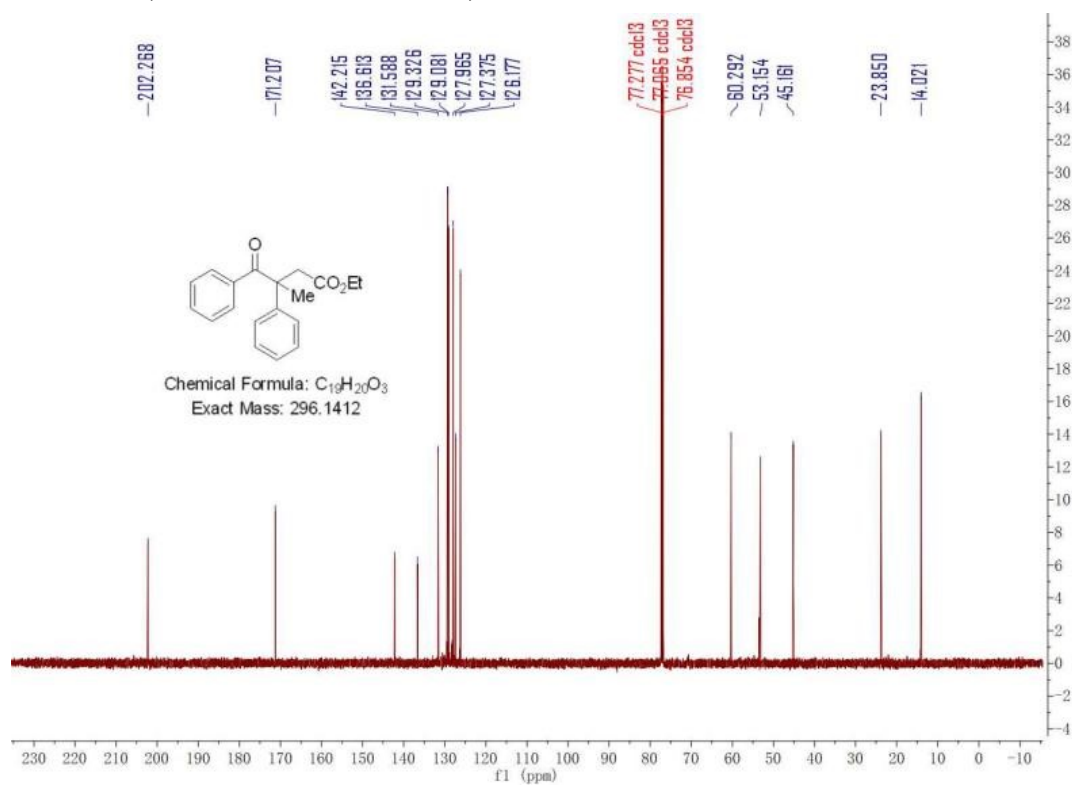


**Ethyl 3-methyl-4-oxo-3,4-diphenylbutanoate (4p)**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)

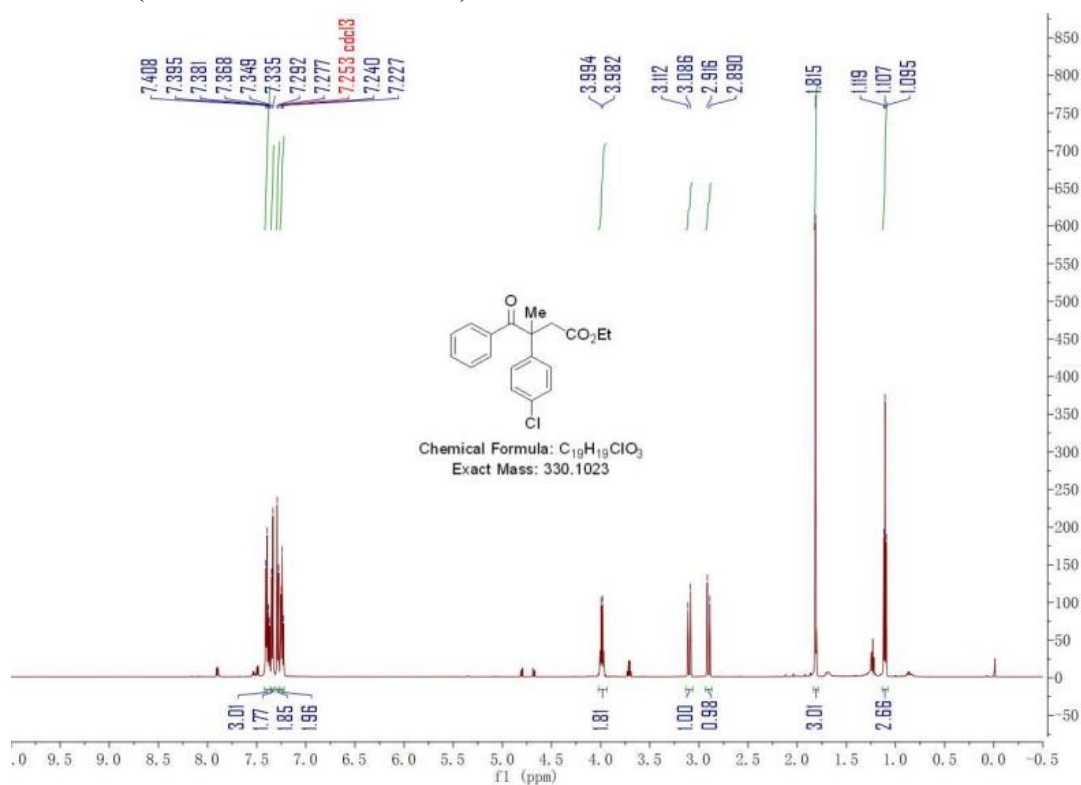


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

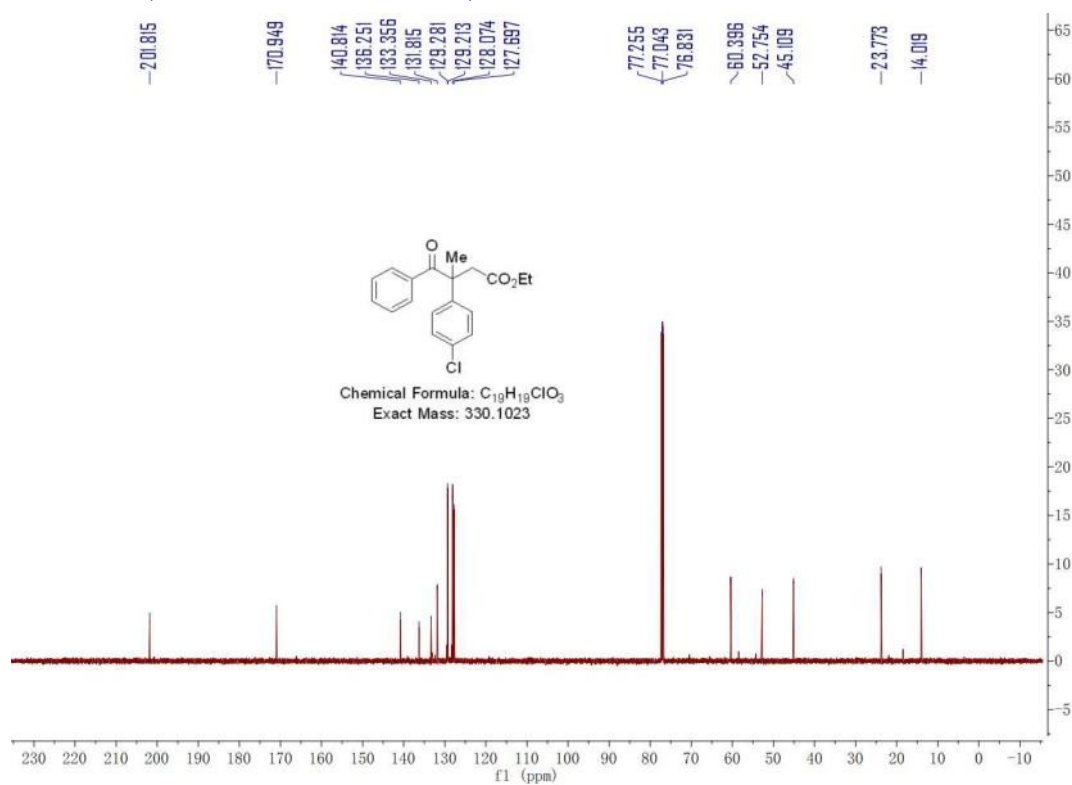


**Ethyl 3-(4-chlorophenyl)-3-methyl-4-oxo-4-phenylbutanoate (4q)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

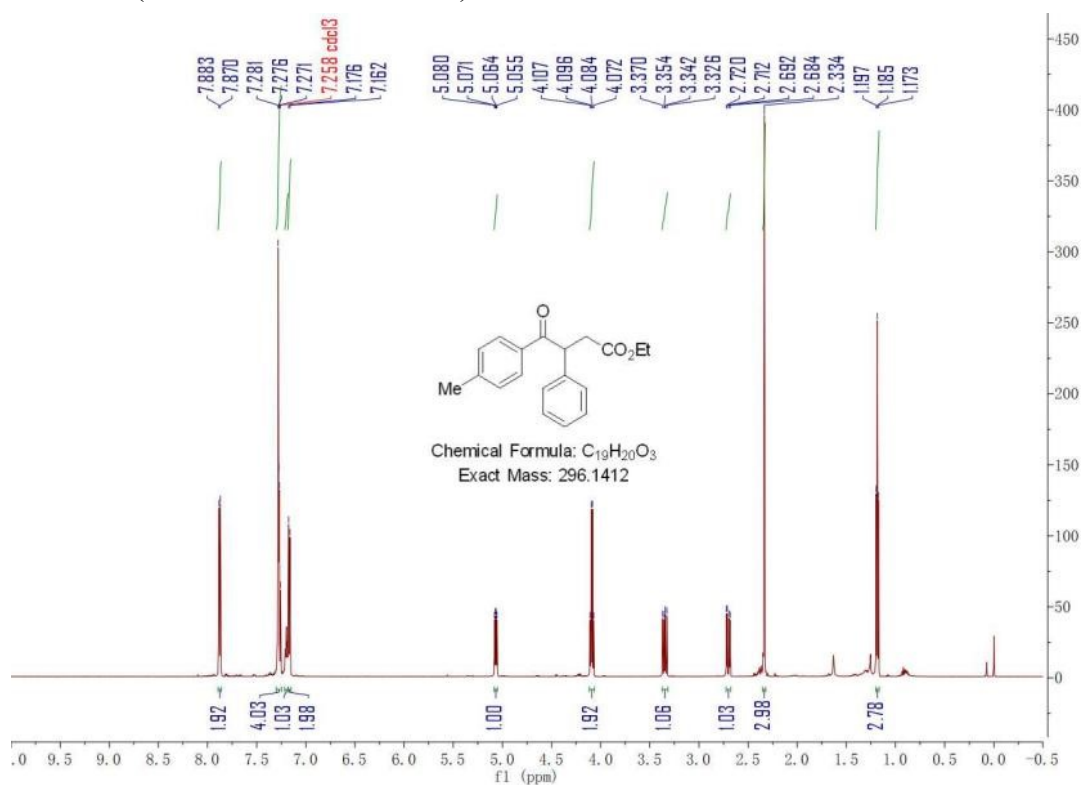


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

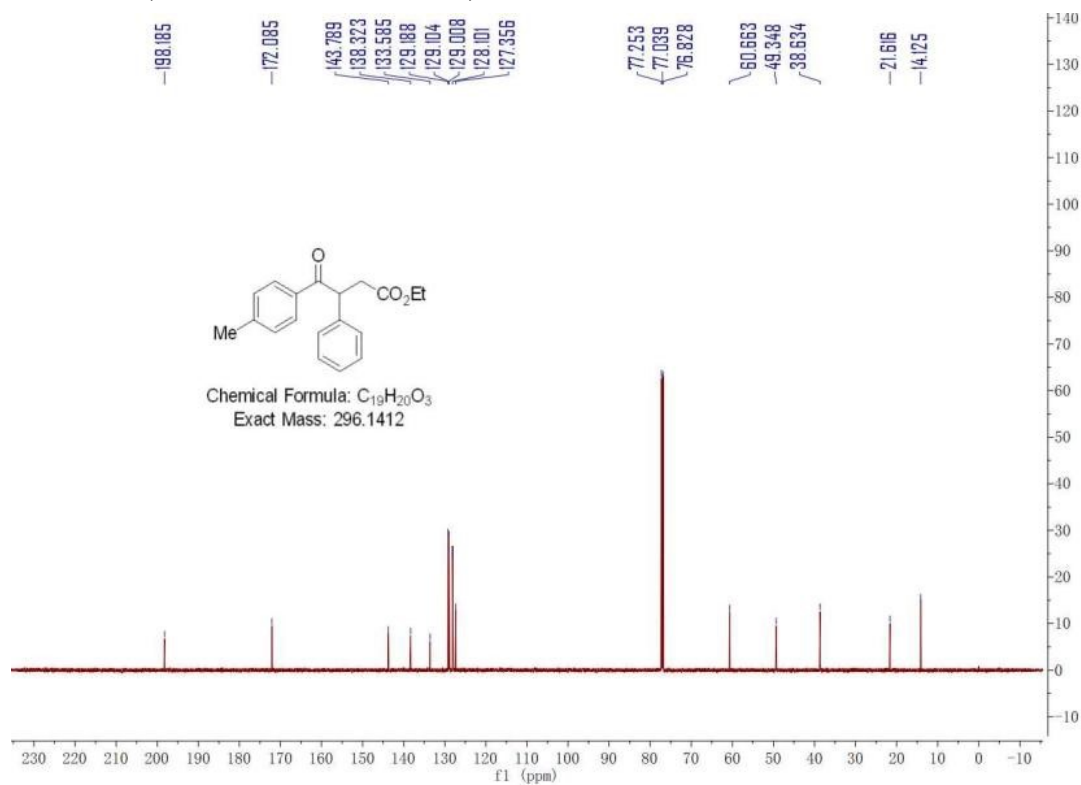


**Ethyl (S)-4-oxo-3-phenyl-4-(p-tolyl)butanoate (4r)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

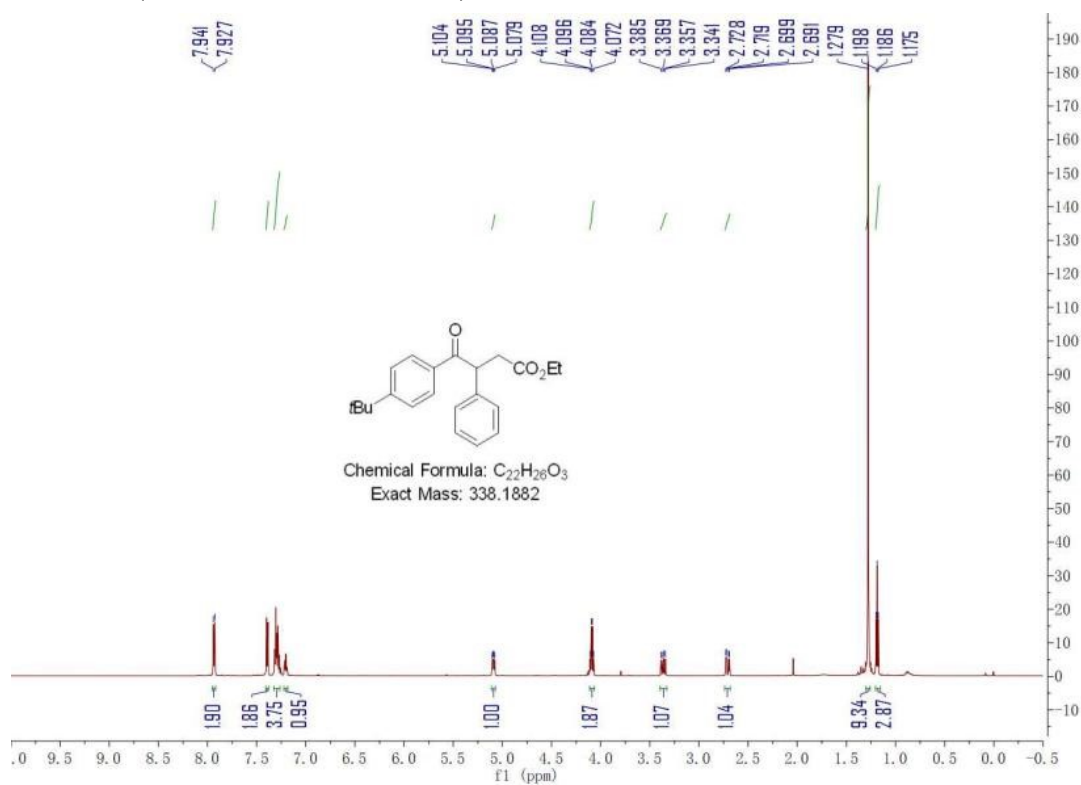


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

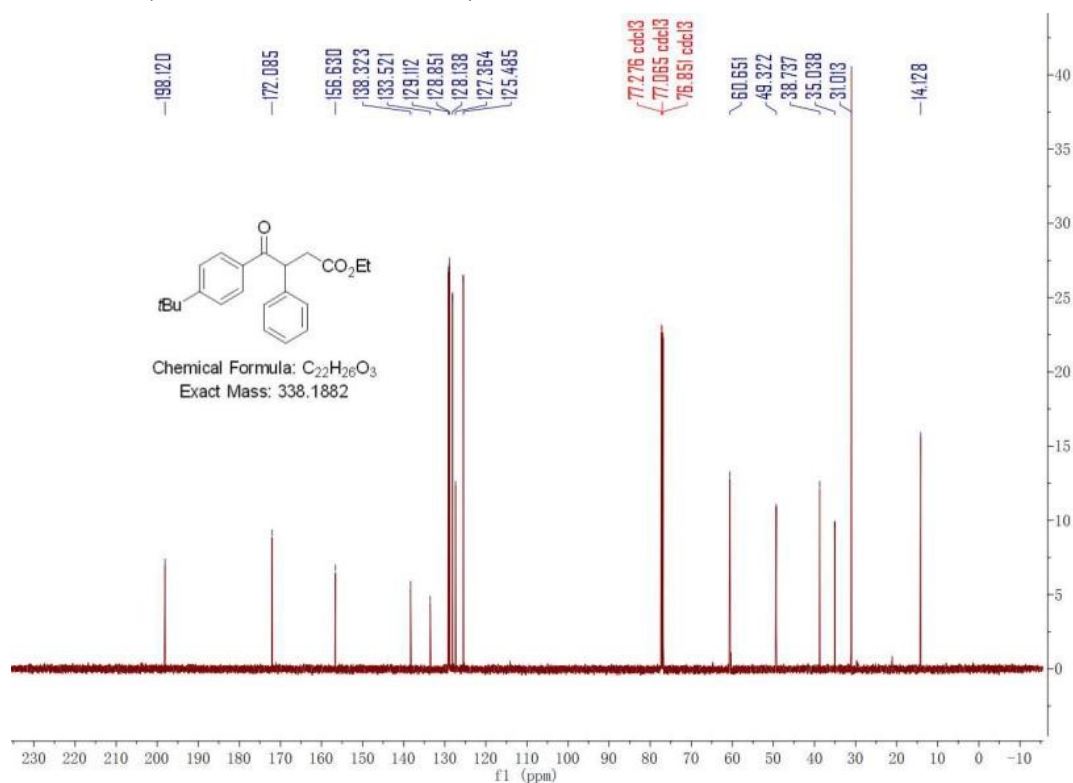


**Ethyl (S)-4-(4-(tert-butyl)phenyl)-4-oxo-3-phenylbutanoate (4s)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

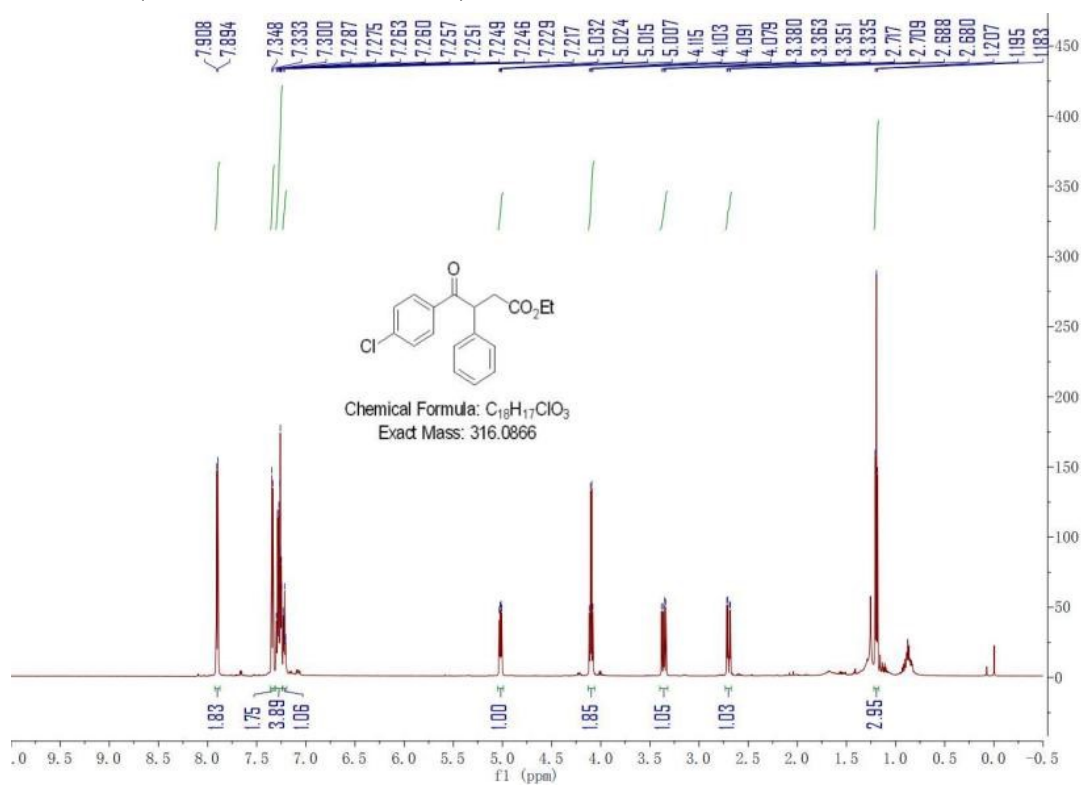


$^{13}\text{C}$  NMR (151 MHz, Chloroform-d)



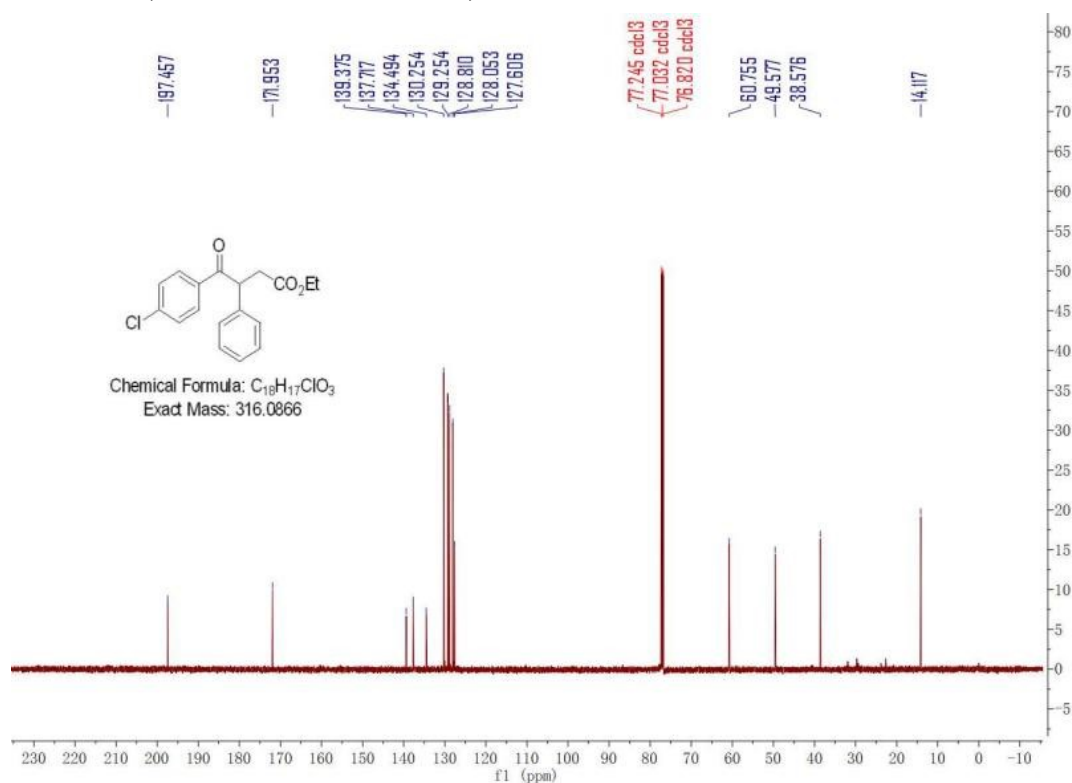
**Ethyl (S)-4-(4-chlorophenyl)-4-oxo-3-phenylbutanoate (4t)**

$^1\text{H}$  NMR (600 MHz, Chloroform-d)



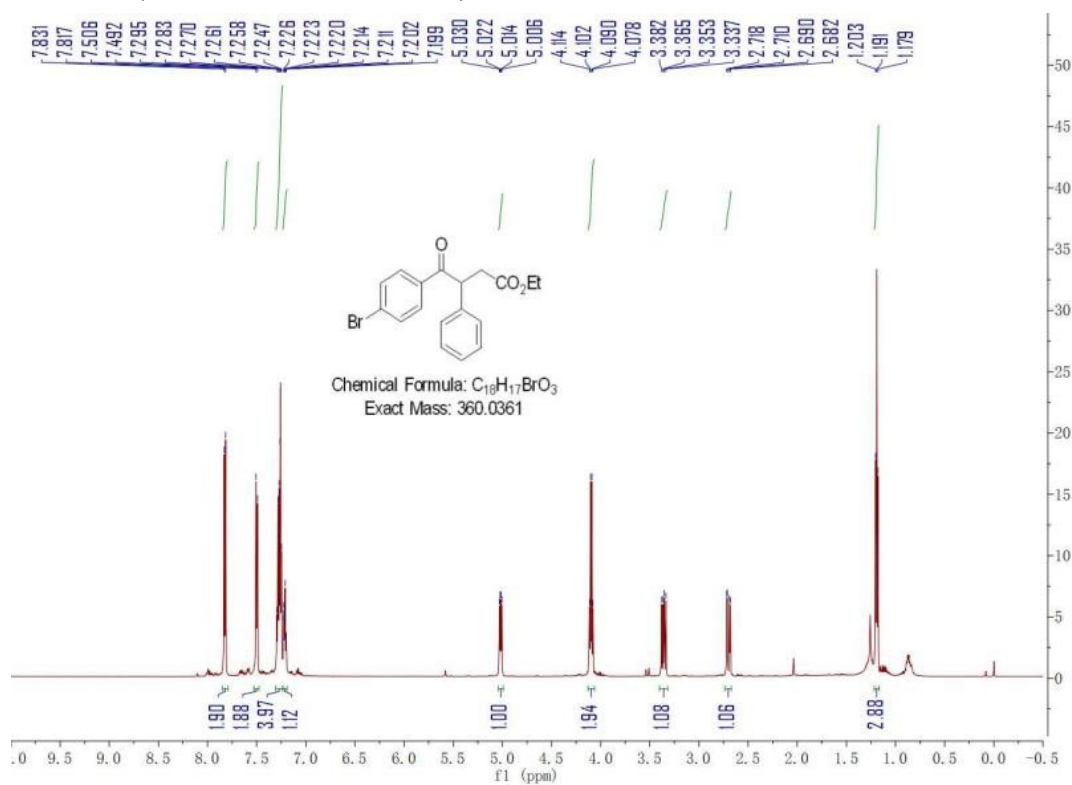


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

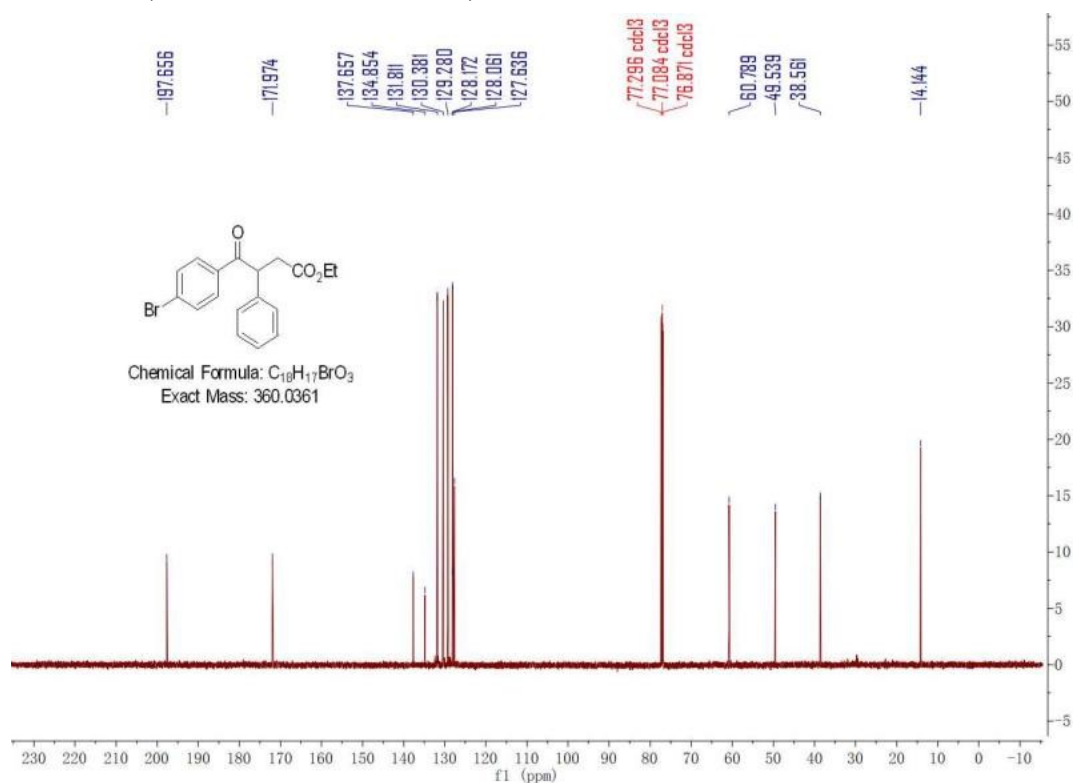


**Ethyl (S)-4-(4-bromophenyl)-4-oxo-3-phenylbutanoate (4u)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

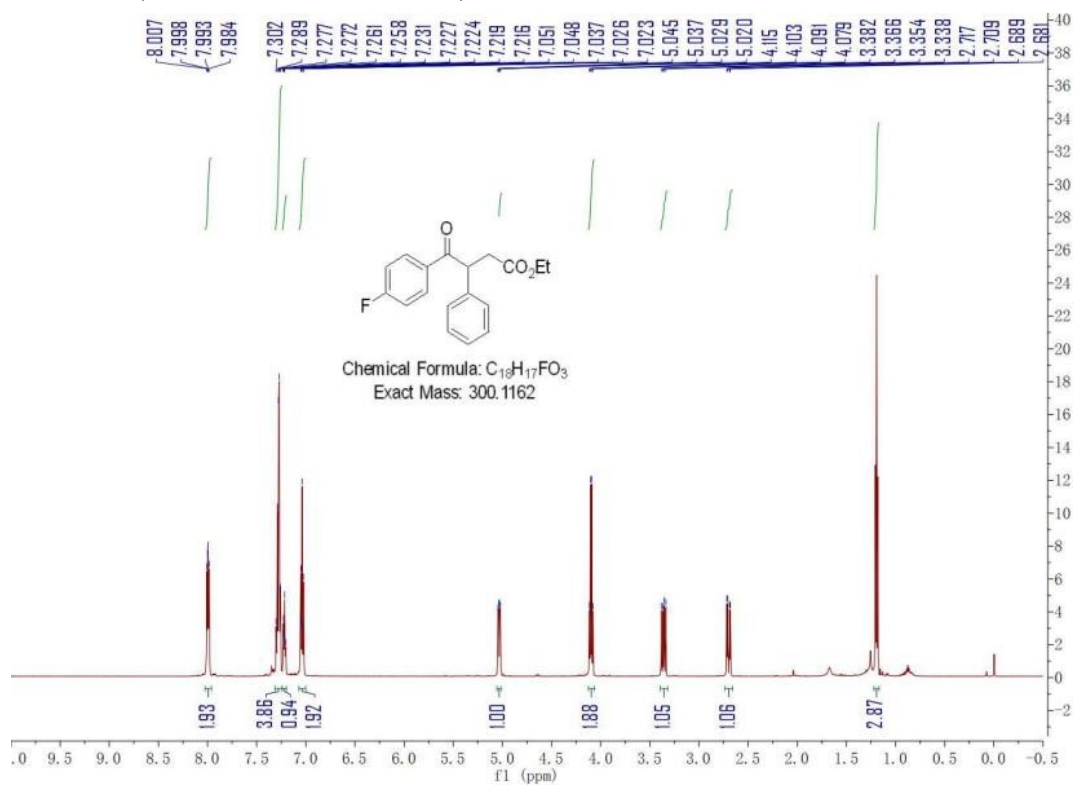


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

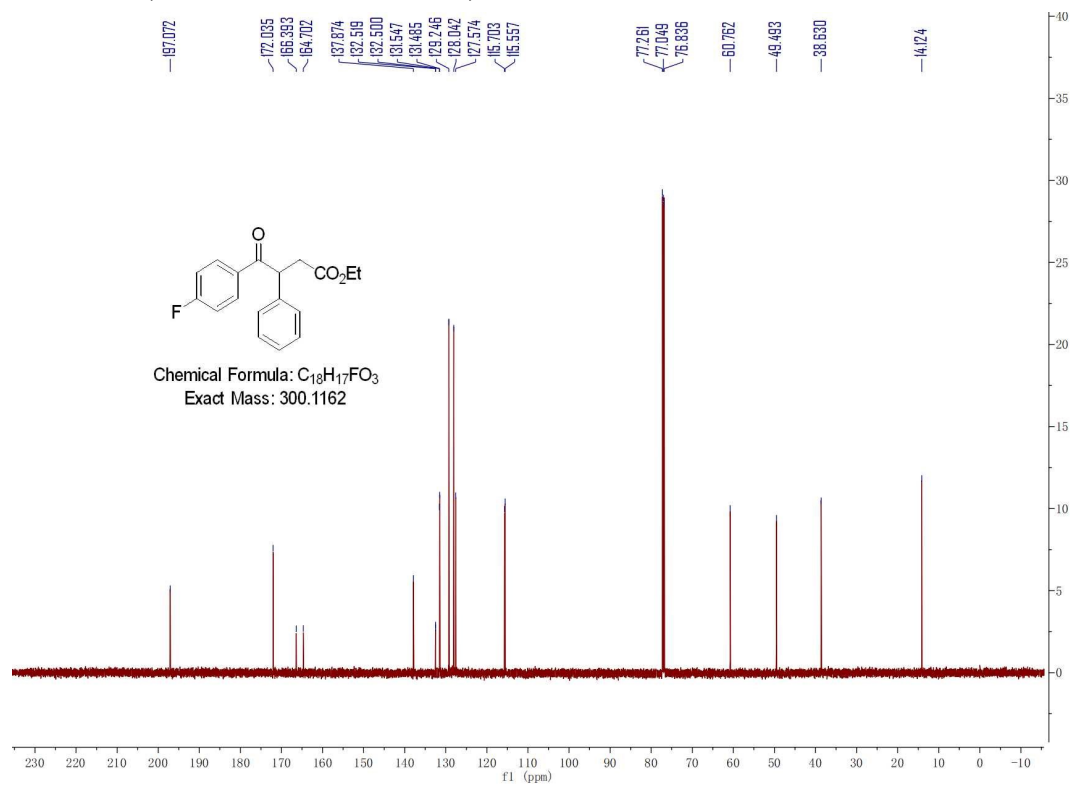


**Ethyl (S)-4-(4-fluorophenyl)-4-oxo-3-phenylbutanoate (4v)**

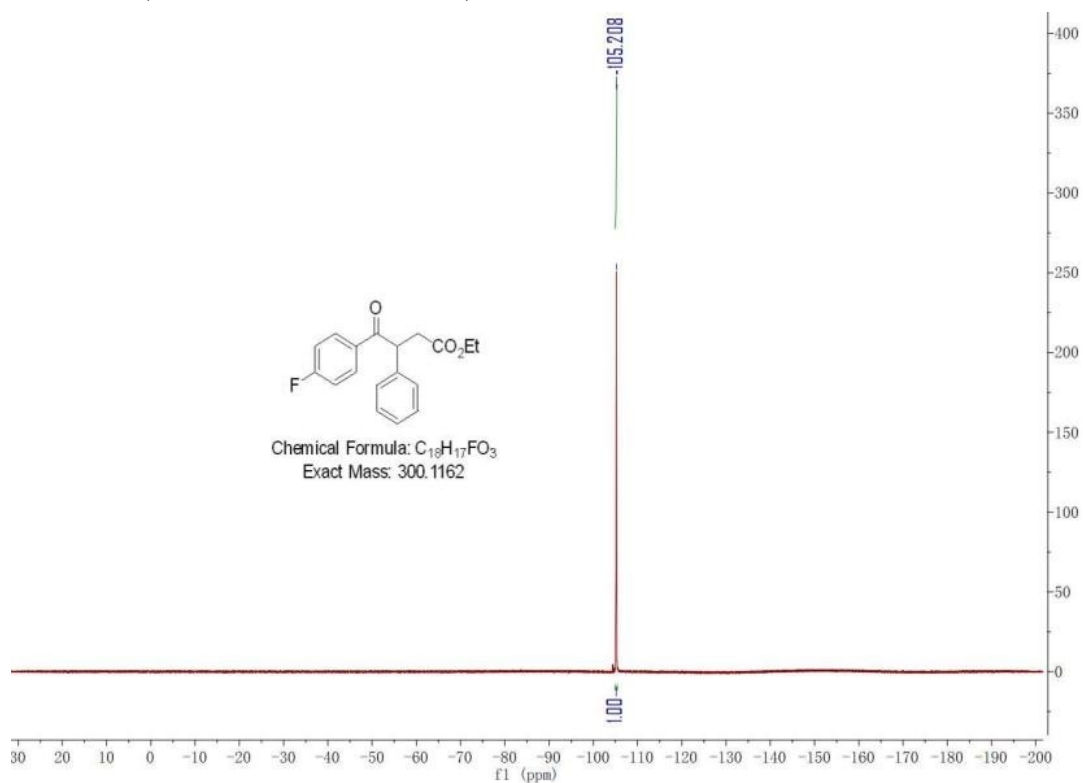
<sup>1</sup>H NMR (600 MHz, Chloroform-d)



### <sup>13</sup>C NMR (151 MHz, Chloroform-d)

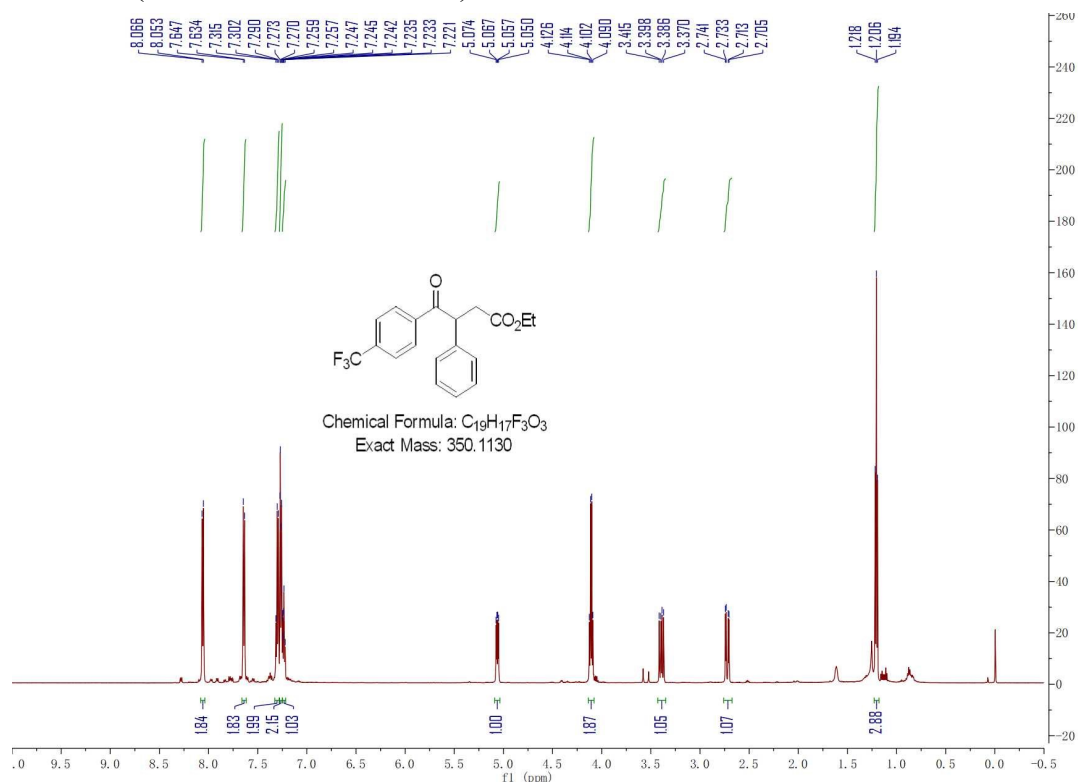


### <sup>19</sup>F NMR (564 MHz, Chloroform-d)

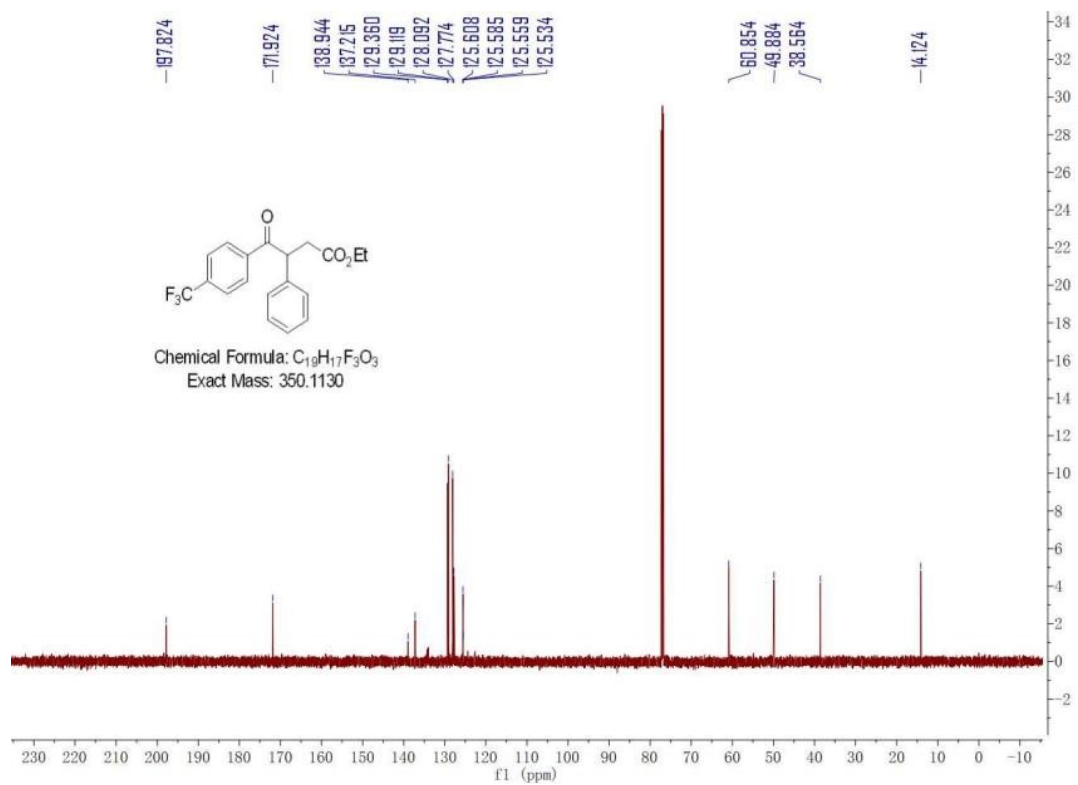


# Ethyl (S)-4-oxo-3-phenyl-4-(4-(trifluoromethyl)phenyl)butanoate (4w)

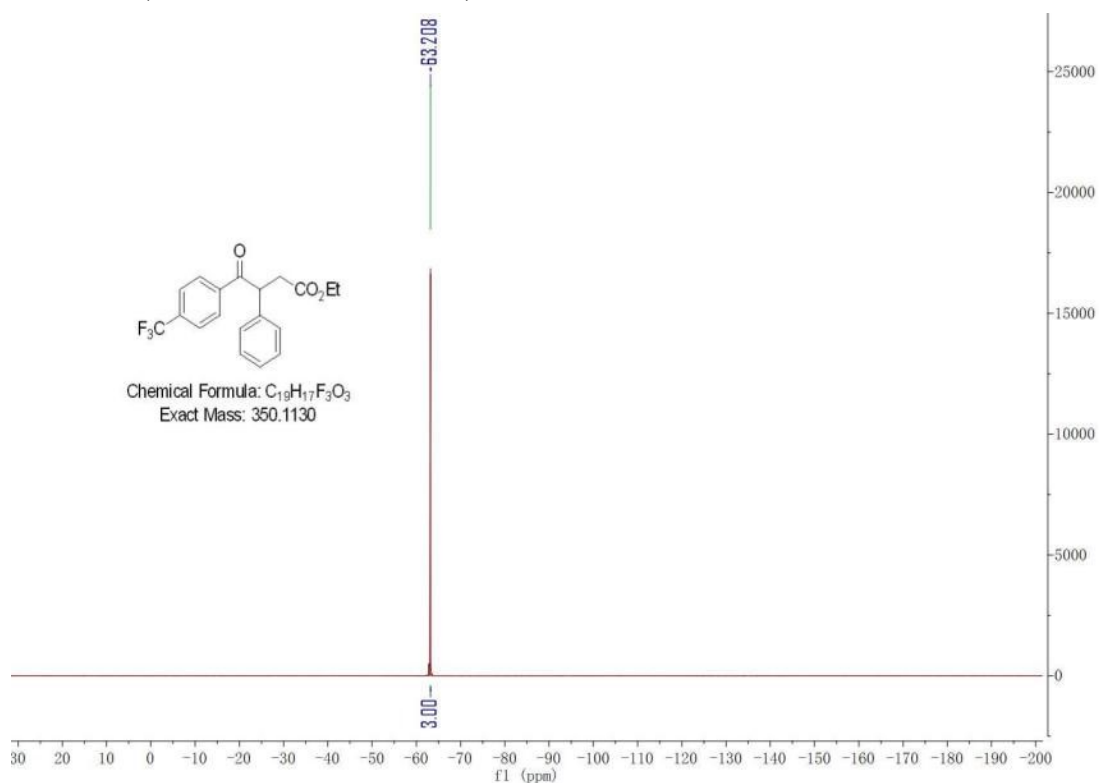
$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )



$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )

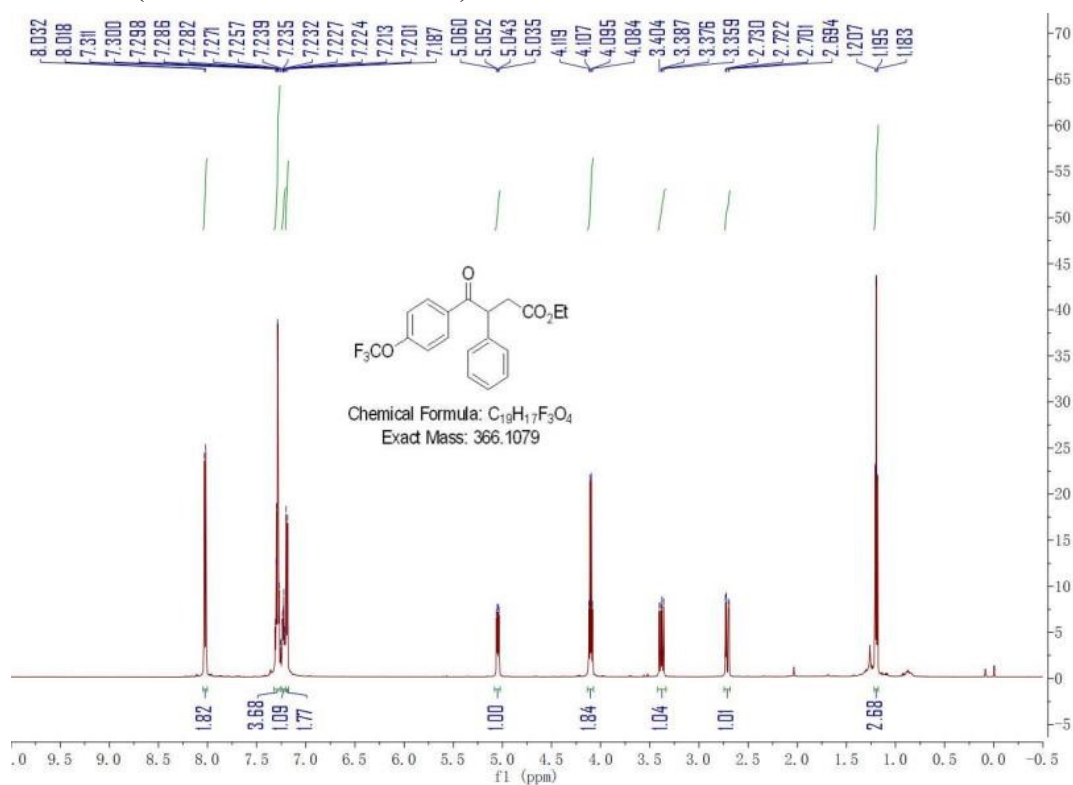


<sup>19</sup>F NMR (564 MHz, Chloroform-d)

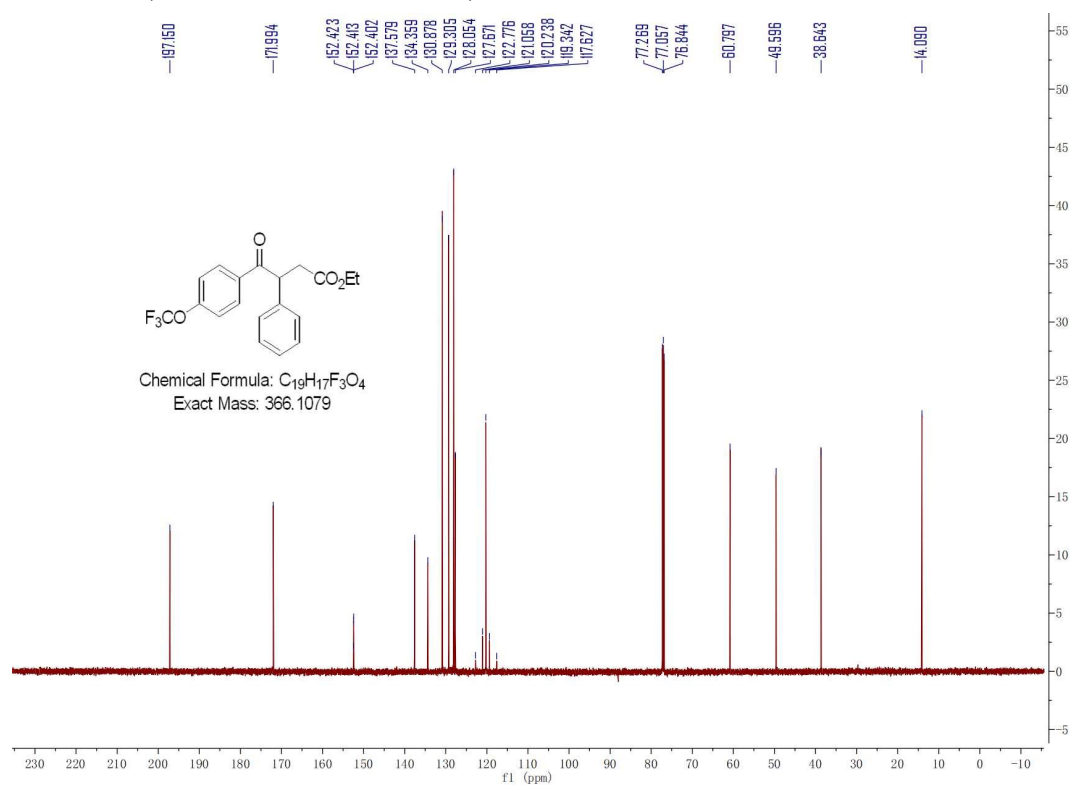


**Ethyl (S)-4-oxo-3-phenyl-4-(4-(trifluoromethoxy)phenyl)butanoate (4x)**

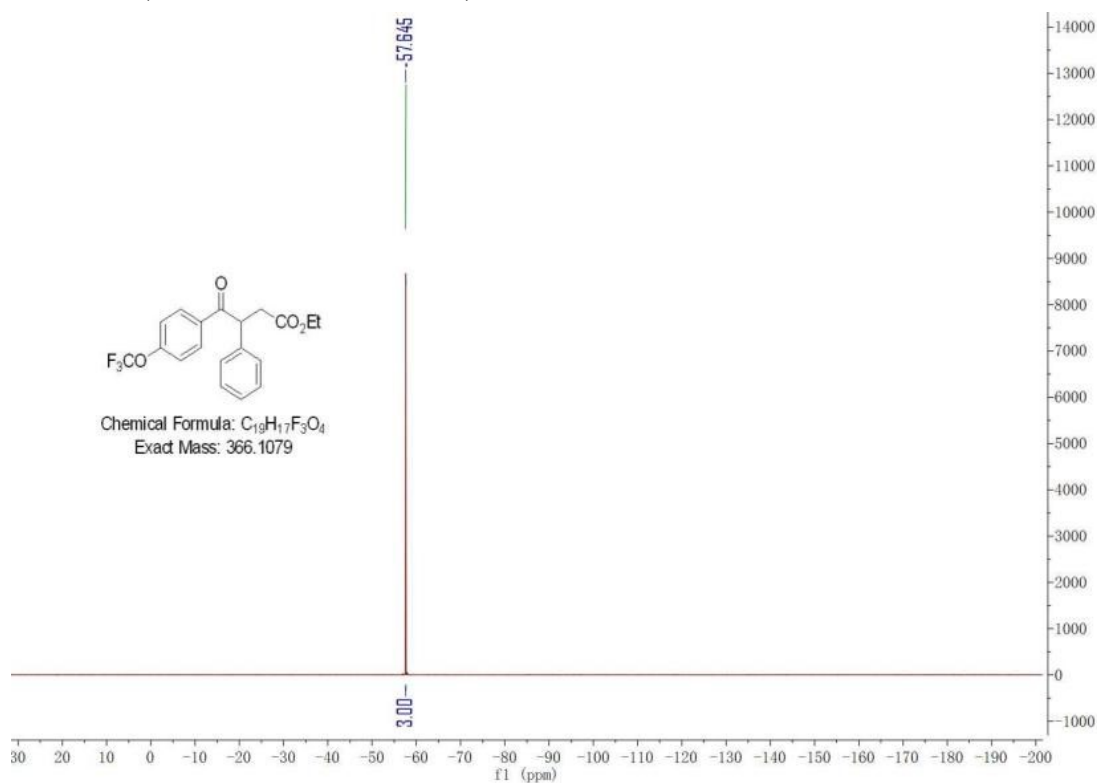
<sup>1</sup>H NMR (600 MHz, Chloroform-d)



### <sup>13</sup>C NMR (151 MHz, Chloroform-d)

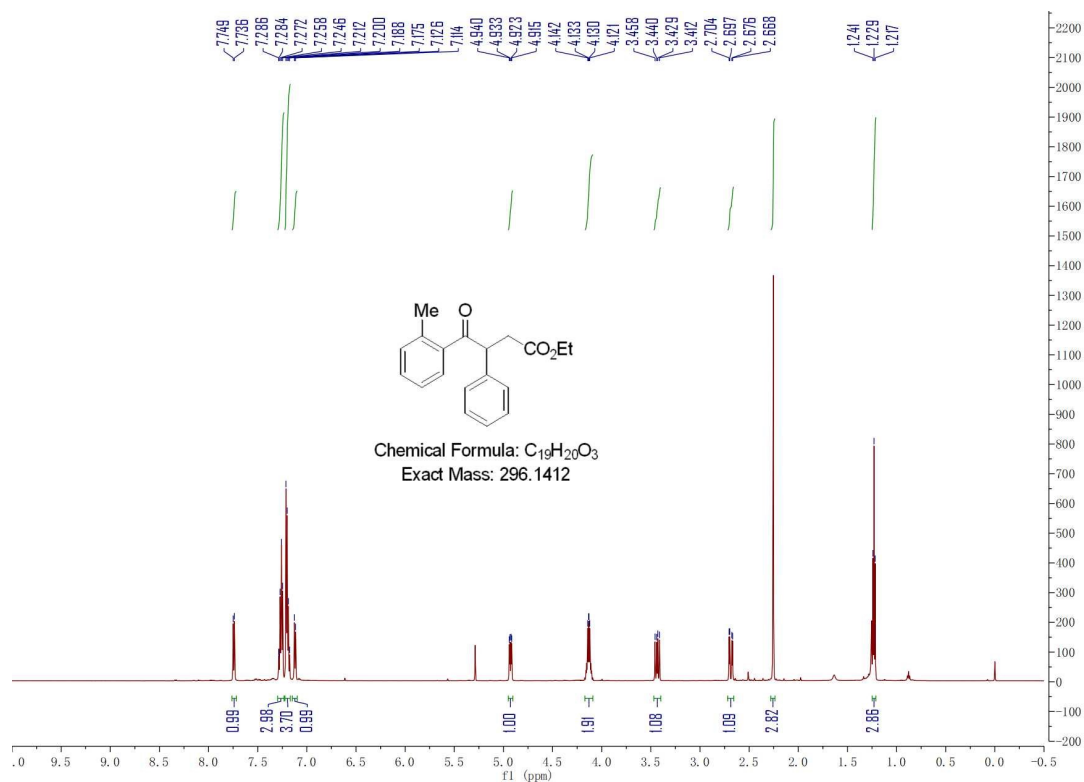


### <sup>19</sup>F NMR (564 MHz, Chloroform-d)

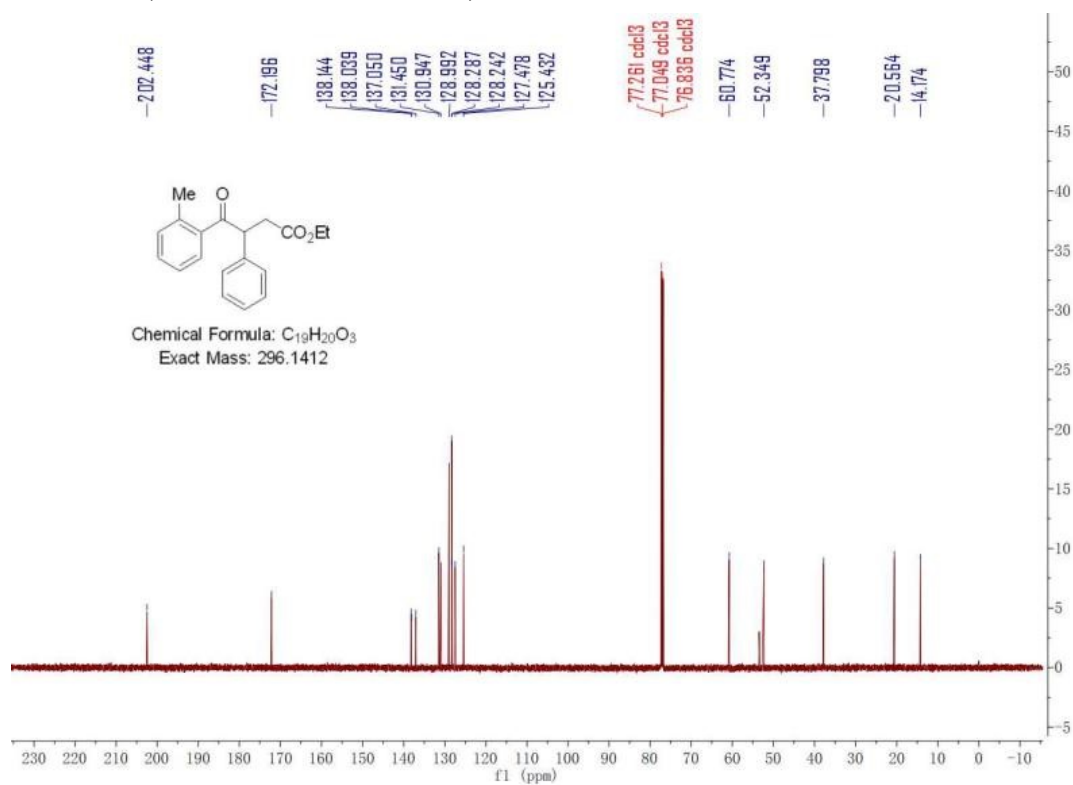


# Ethyl (S)-4-oxo-3-phenyl-4-(o-tolyl)butanoate (4y)

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)

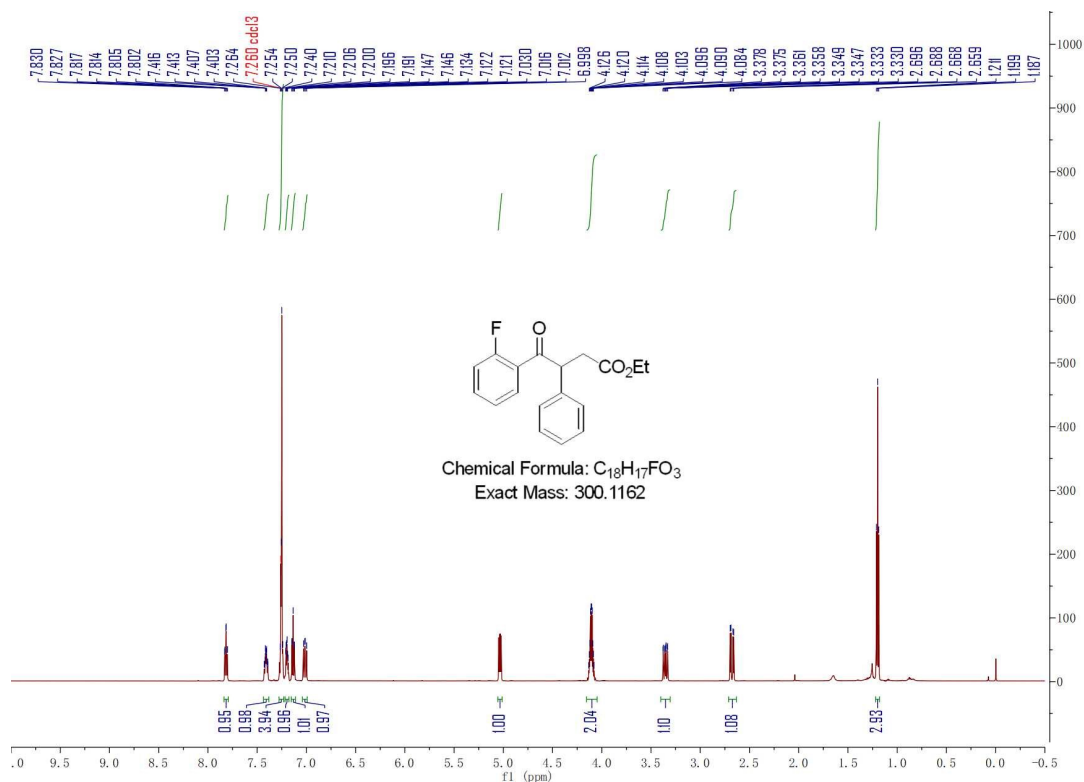


$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)

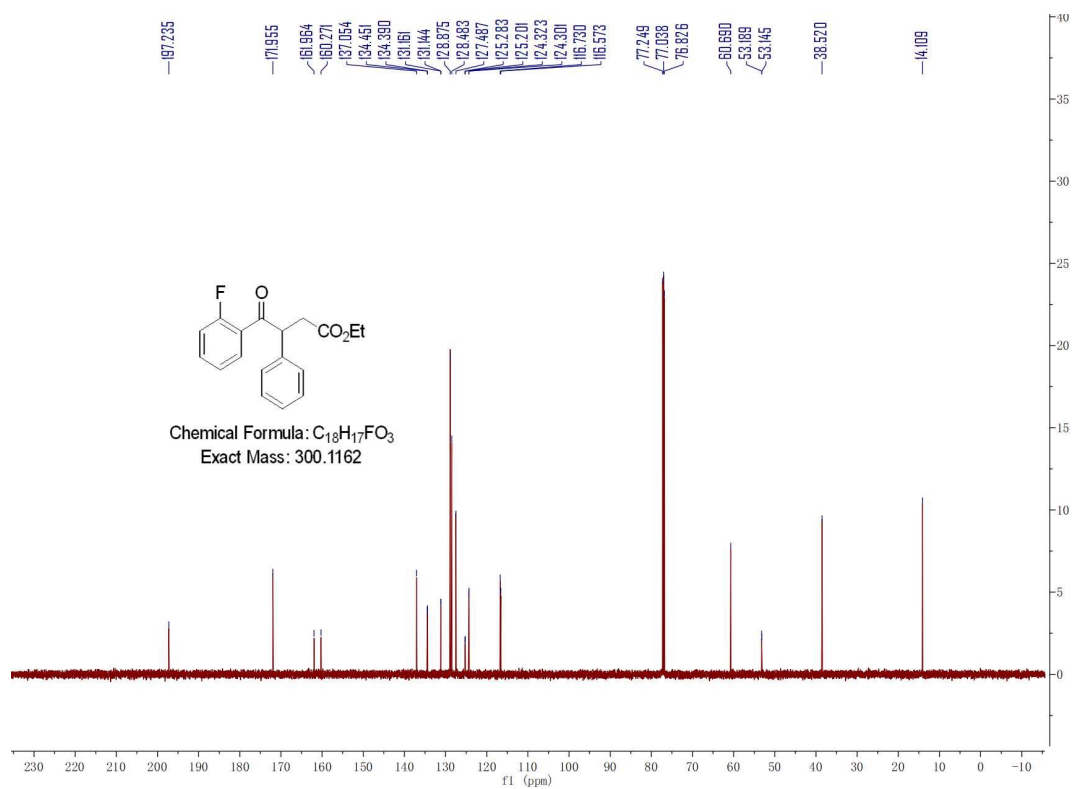


# Ethyl (S)-4-(2-fluorophenyl)-4-oxo-3-phenylbutanoate (4z)

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

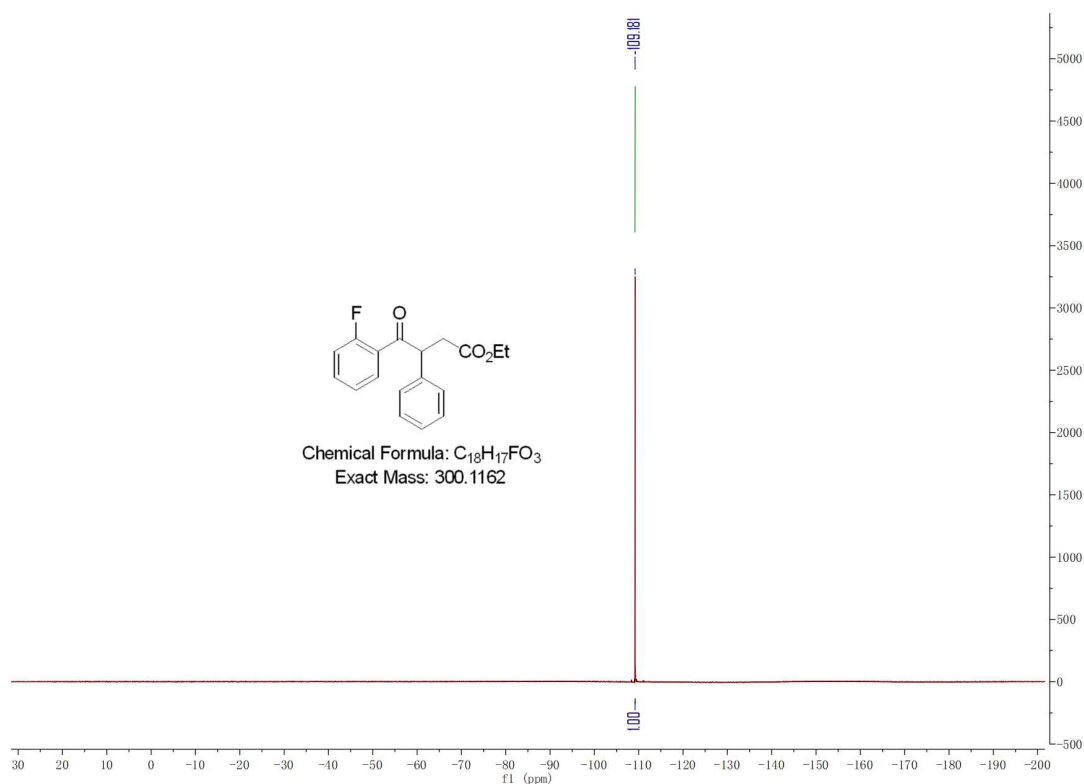


<sup>13</sup>C NMR (151 MHz, Chloroform-d)



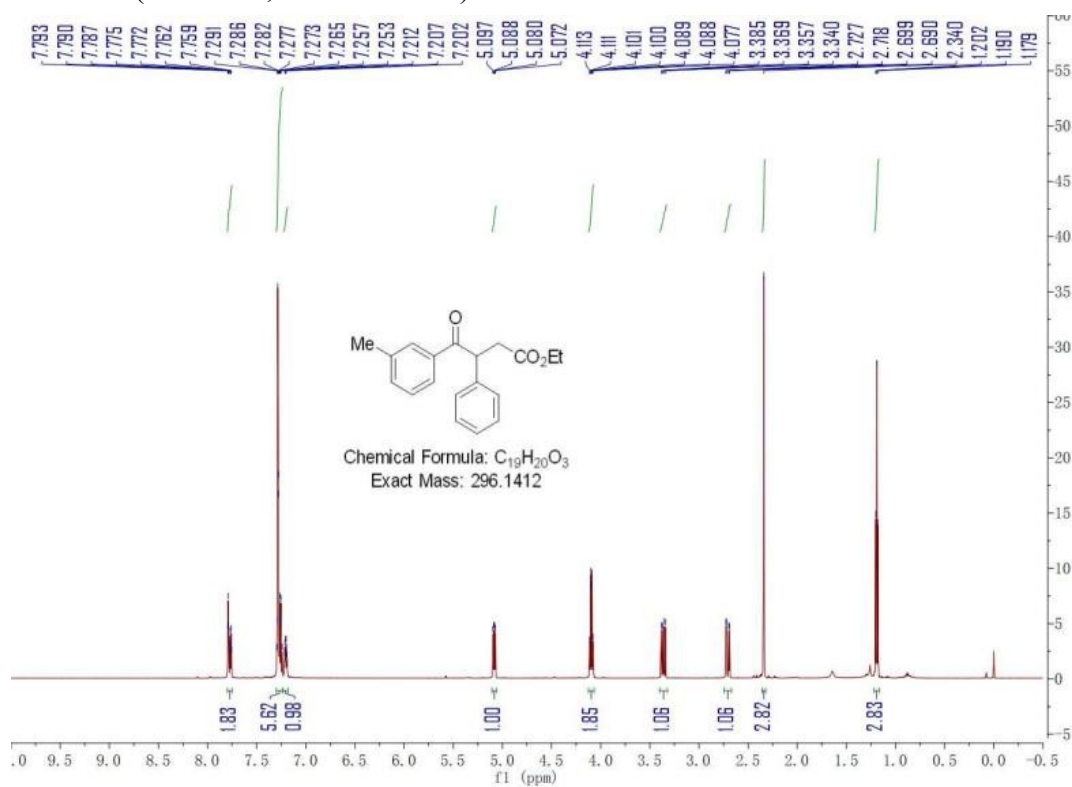


<sup>19</sup>F NMR (564 MHz, Chloroform-d)

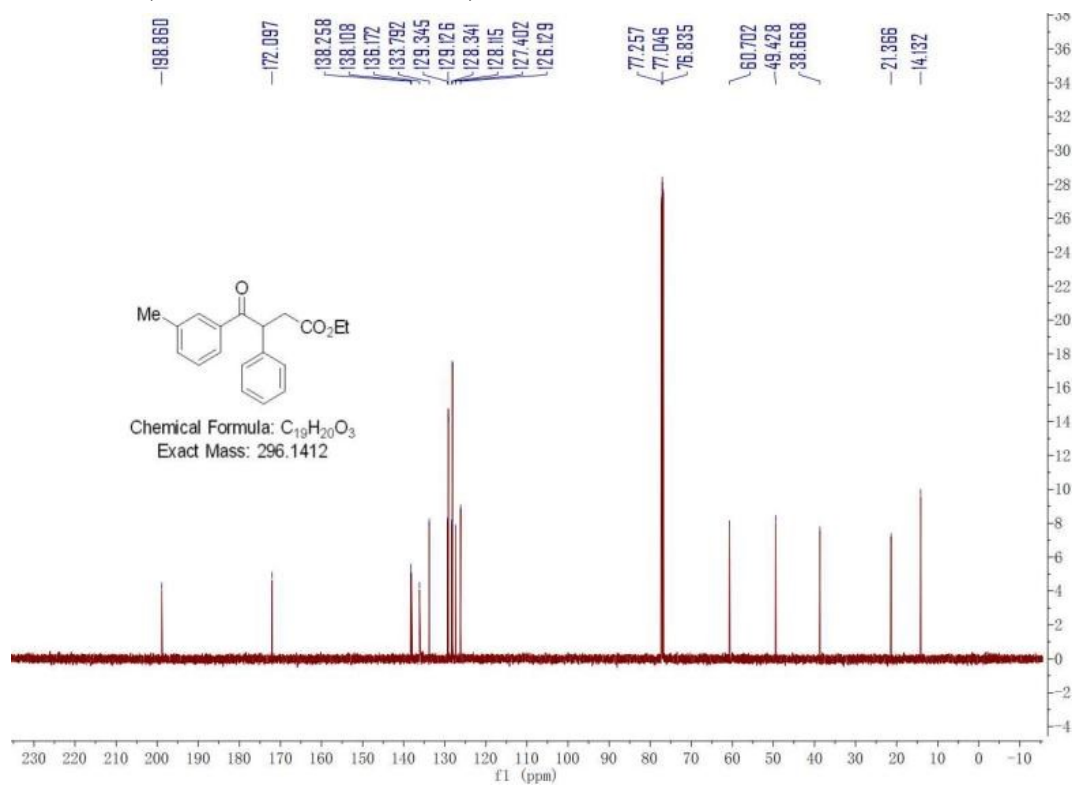


**Ethyl (S)-4-oxo-3-phenyl-4-(m-tolyl)butanoate (4aa)**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)

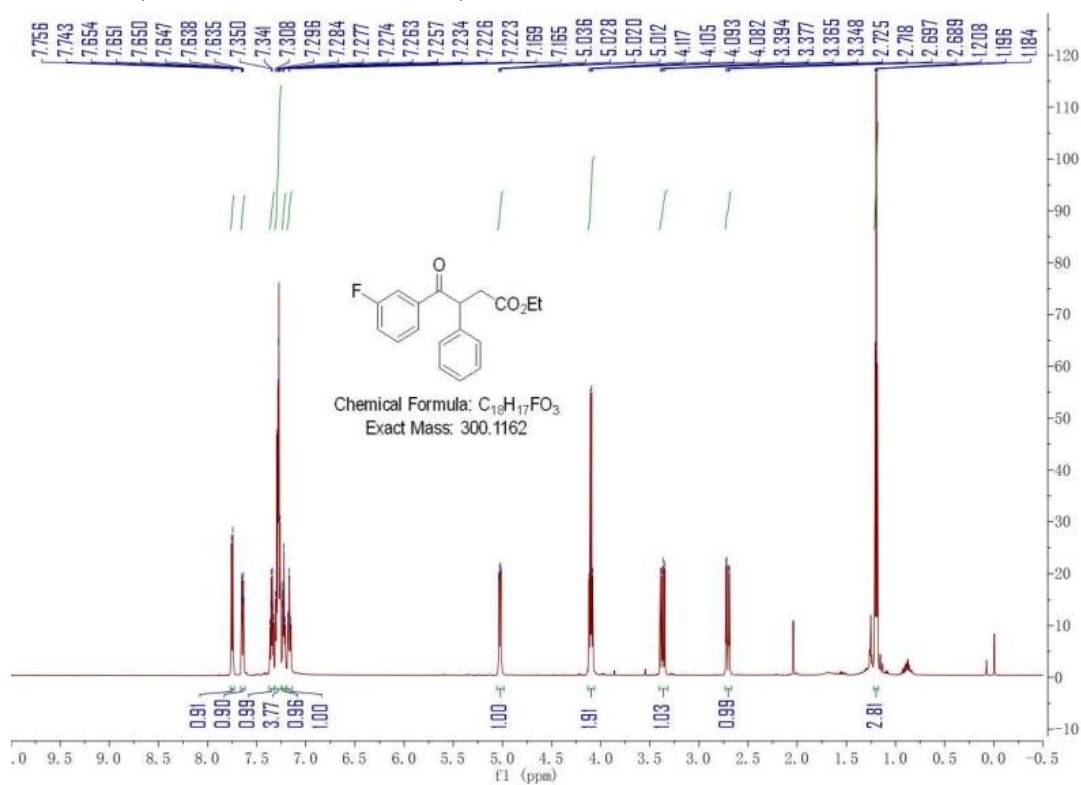


<sup>13</sup>C NMR (151 MHz, Chloroform-d)

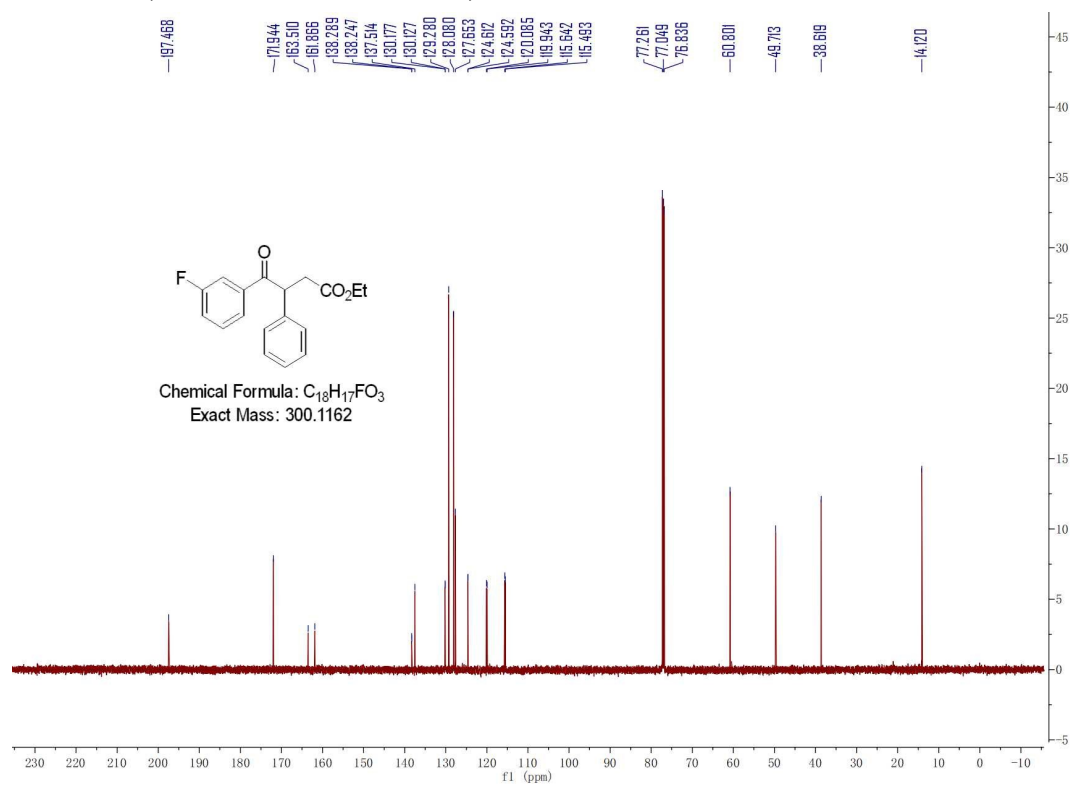


**Ethyl (S)-4-(3-fluorophenyl)-4-oxo-3-phenylbutanoate (4b)**

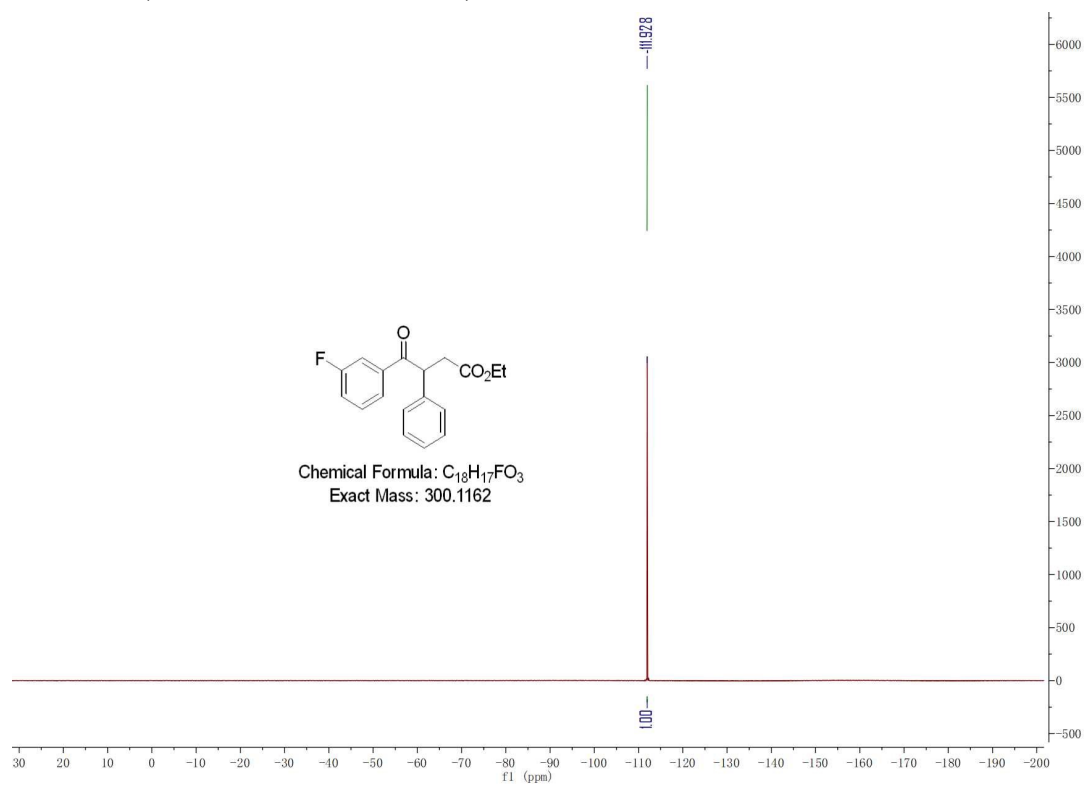
<sup>1</sup>H NMR (600 MHz, Chloroform-d)



### <sup>13</sup>C NMR (151 MHz, Chloroform-d)

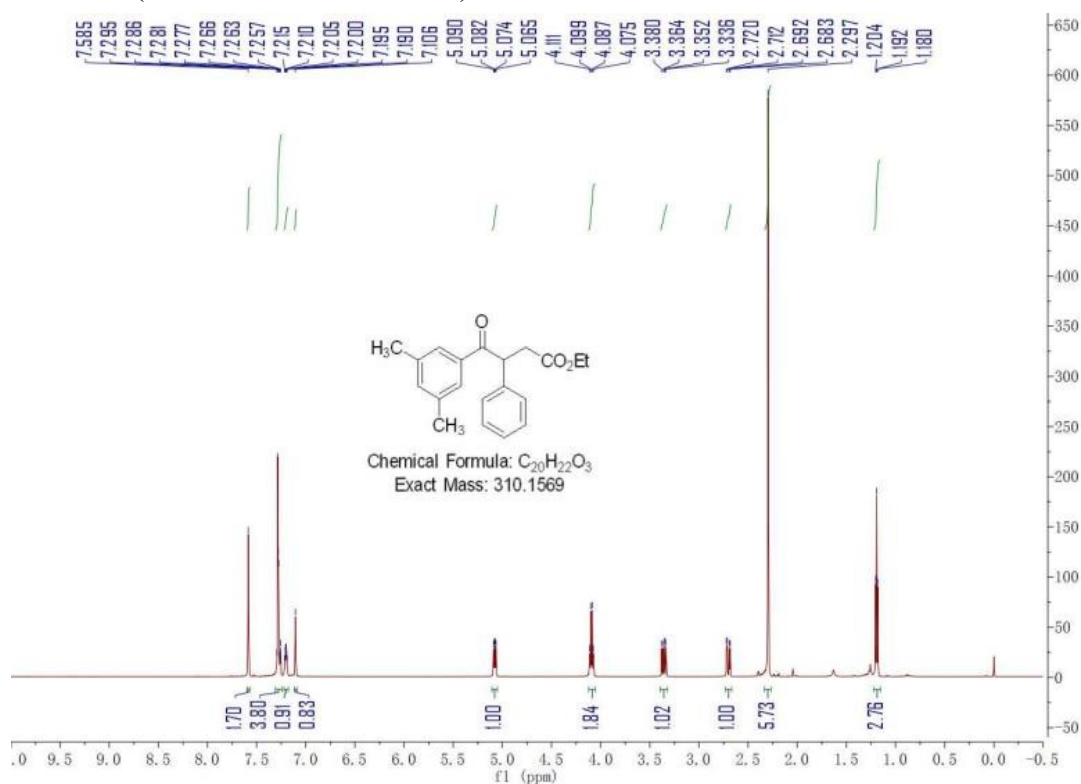


### <sup>19</sup>F NMR (564 MHz, Chloroform-d)

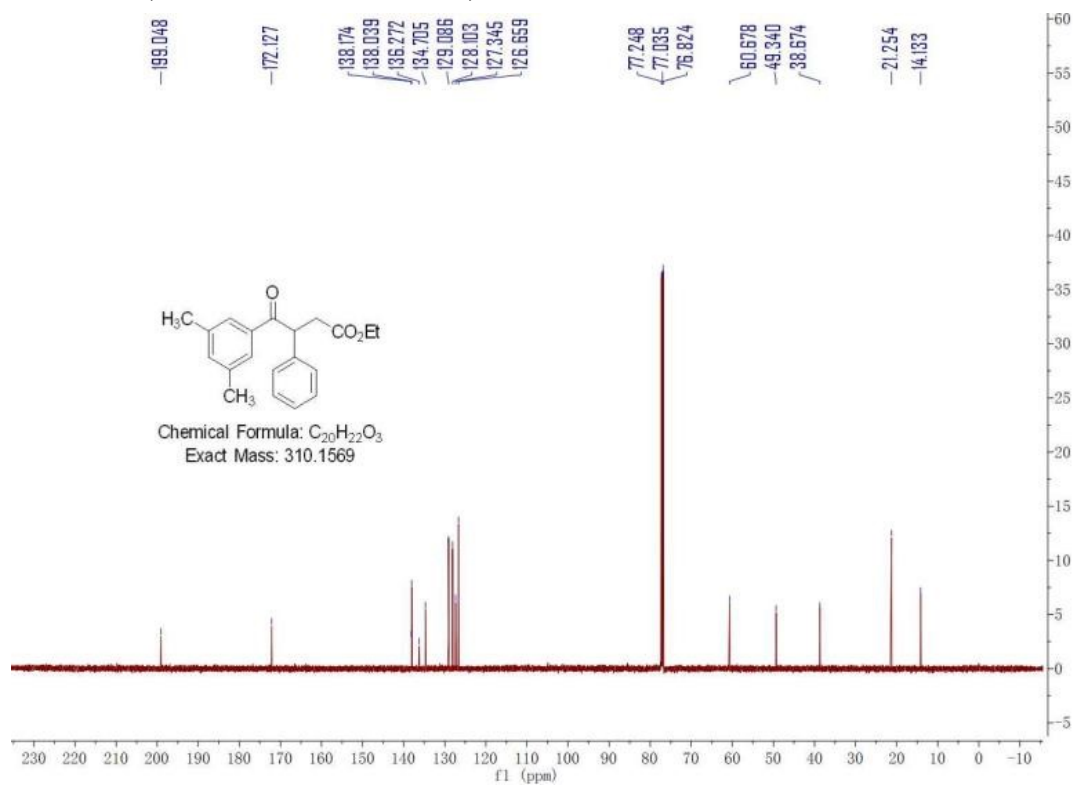


### Ethyl (S)-4-(3,5-dimethylphenyl)-4-oxo-3-phenylbutanoate (4ac)

$^1\text{H}$  NMR (600 MHz, Chloroform-d)

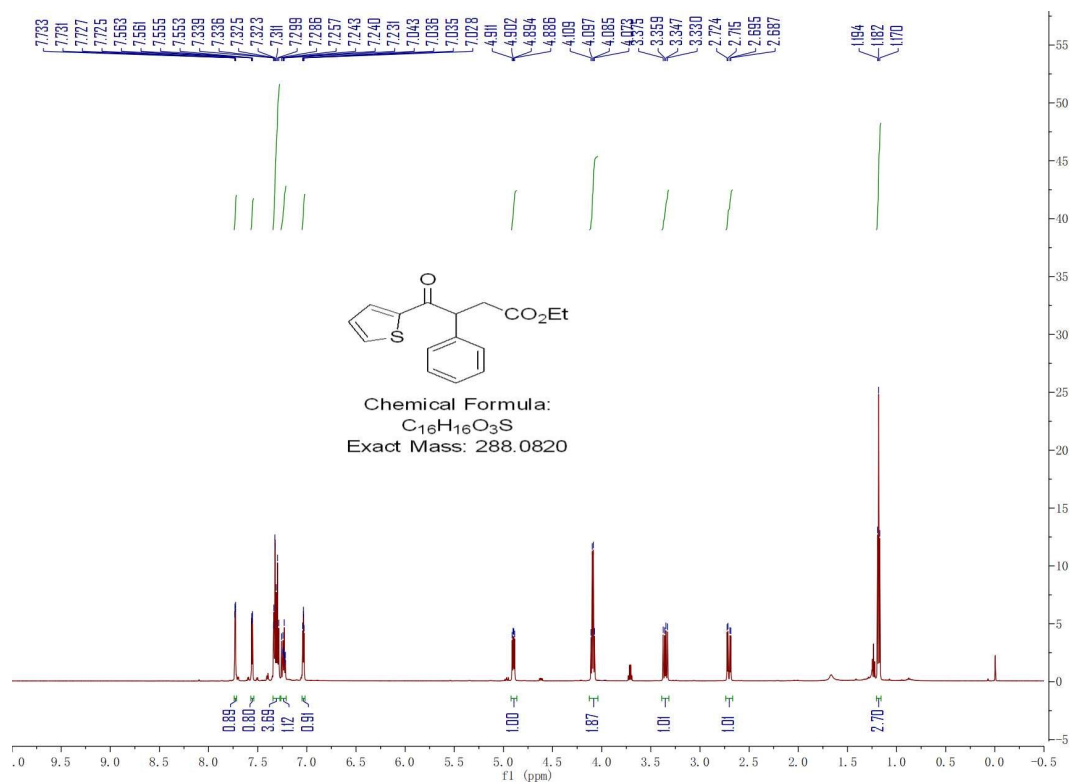


$^{13}\text{C}$  NMR (151 MHz, Chloroform-d)



# Ethyl (S)-4-oxo-3-phenyl-4-(thiophen-2-yl)butanoate (4ad)

<sup>1</sup>H NMR (600 MHz, Chloroform-d)



<sup>13</sup>C NMR (151 MHz, Chloroform-d)

