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# Supporting Information

## **Decarboxylative 1,4-Addition of $\alpha$ -Oxocarboxylic Acids with Michael Acceptors Enabled by Photoredox Catalysis**

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## 1. General

All manipulations were carried out in an oven-dried tube under ambient condition. Commercial reagents were purchased from TCI and Aldrich without further purification. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for  $^1\text{H}$ -NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), 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). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System.

## 2. Preparation of photoredox catalysts and substrates

### 2.1 Synthesis of photocatalysts $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$ (Ir-cat. 1) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (Ir-cat. 2)

The photocatalysts were synthesized according to literature. (Reference: Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.) The spectral data of Ir-cat.2 is consistent with the literature data.

The spectral data of  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$  (Ir-cat. 1):

$^1\text{H}$  NMR (400 MHz,  $d_6$ -Acetone)  $\delta$  9.01 (dd,  $J$  = 8.3, 1.4 Hz, 2H), 8.67 (dd,  $J$  = 5.1, 1.3 Hz, 2H), 8.61 (dd,  $J$  = 8.8, 2.7 Hz, 2H), 8.45 (s, 2H), 8.37 – 8.30 (m, 2H), 8.14 (dd,  $J$  = 8.3, 5.1 Hz, 2H), 7.87 – 7.83 (m, 2H), 6.91 (ddd,  $J$  = 12.7, 9.3, 2.3 Hz, 2H), 6.06 (dd,  $J$  = 8.5, 2.2 Hz, 2H).

### 2.2 Synthesis of Substrates

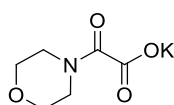
The  $\alpha$ -oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones by  $\text{SeO}_2$  according to the reported procedure. (Reference: Kuldeep, W.; Yang, C.; West, P. R.; Deming, K. C.; Chemburkar, S.; Reddy, R. R. E. *Synth Commun.* **2008**, *38*, 4434.)

Preparation of potassium oxalate monoamide.

To a mixture of 20 wt %  $\text{K}_2\text{CO}_3$  aqueous solution (14 mL) and toluene (15 mL) was added the corresponding amine (12 mmol). The mixture was cooled to 0  $^\circ\text{C}$ , a solution of ethyl

2-chloro-2-oxoacetate (10 mmol) in toluene (6.0 mL) was added dropwise in 20 min. After stirring for 1 h at room temperature, the two layers were separated. The aqueous phase was washed with toluene (2 x 10 mL). The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The product was dissolved in EtOH (20 mL), and H<sub>2</sub>O (10 mmol) was added. The mixture was heated to 60 °C, and a solution of *t*-BuOK (10 mmol) in EtOH (10 mL) was added dropwise in 30 min. After completion of addition, the reaction mixture was stirred at 60 °C for 10 h. The solvent was removed under vacuo and the resulting white solid was purified by recrystallization using mixed solvent of EtOH and Et<sub>2</sub>O.

**Potassium 2-morpholino-2-oxoacetate (I):** This compound was obtained as a white solid.

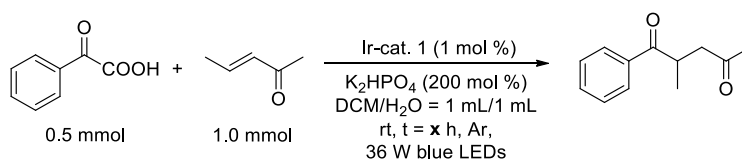


<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 3.82 – 3.71 (m, 4H), 3.62 – 3.54 (m, 2H), 3.52 – 3.45 (m, 2H).

<sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O) δ 169.62, 167.96, 66.43, 66.03, 46.40, 40.96.

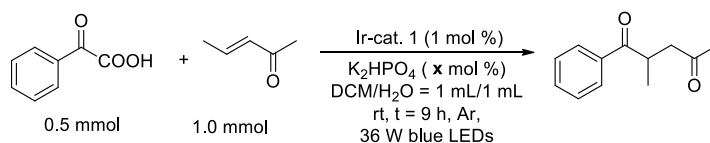
### 3. Investigation of the key reaction parameters

#### 3.1. Study of reaction time



entry	catalyst	base	solvent	time/h	yield
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	1	55%
2	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	3	67%
3	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	6	78%
4	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	9	83%
5	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	12	84%
6	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	K <sub>2</sub> HPO <sub>4</sub>	DCM/H <sub>2</sub> O	15	84%

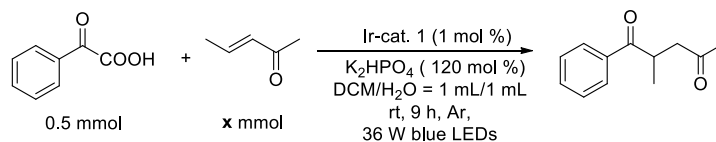
#### 3.2. Study the amount of the base required



entry	catalyst	base (x mol %)	solvent	time/h	yield
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	10	DCM/H <sub>2</sub> O	9	14%
2	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	20	DCM/H <sub>2</sub> O	9	25%

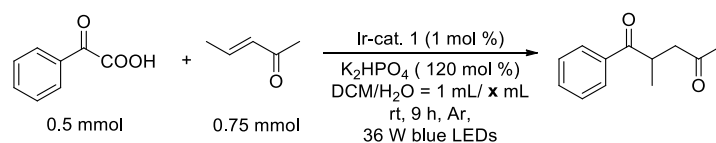
3	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	50	DCM/ $\text{H}_2\text{O}$	9	48%
4	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	100	DCM/ $\text{H}_2\text{O}$	9	76%
5	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	DCM/ $\text{H}_2\text{O}$	9	84%
6	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	150	DCM/ $\text{H}_2\text{O}$	9	88%
7	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	200	DCM/ $\text{H}_2\text{O}$	9	87%

### 3.3. Study the ratio of substrates



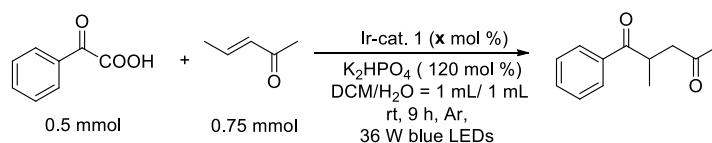
entry	catalyst	base (x mol %)	1a : 2a	time/h	yield
1	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	2:1	9	58%
2	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	1.5:1	9	62%
3	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	1:1	9	66%
4	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	1:1.2	9	83%
5	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	1:1.5	9	90%
6	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	120	1:2	9	89%

### 3.4. The amount of the water solvent



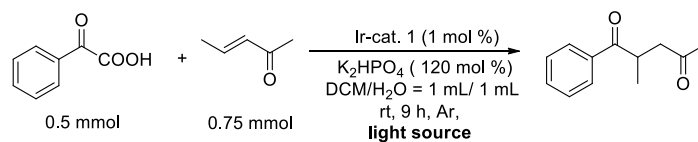
entry	catalyst	$\text{H}_2\text{O}$	time/h	yield
1	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	None	9	18%
2	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	18 $\mu\text{L}$	9	37%
3	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	90 $\mu\text{L}$	9	65%
4	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	0.45 mL	9	81%
5	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	0.9 mL	9	88%
6	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	1.35 mL	9	84%
7	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	1.8 mL	9	81%
9	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	1 mL	9	87%

### 3.5. Study the catalyst loadings



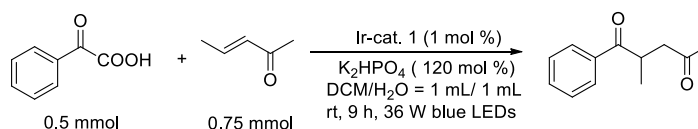
entry	catalyst	x mol %	time/h	yield
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	0	9	0
2	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	0.5 mol %	9	58%
3	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	1 mol %	9	90%
4	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	1.5 mol %	9	89%
5	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	2 mol %	9	87%

### 3.6. Light Sources



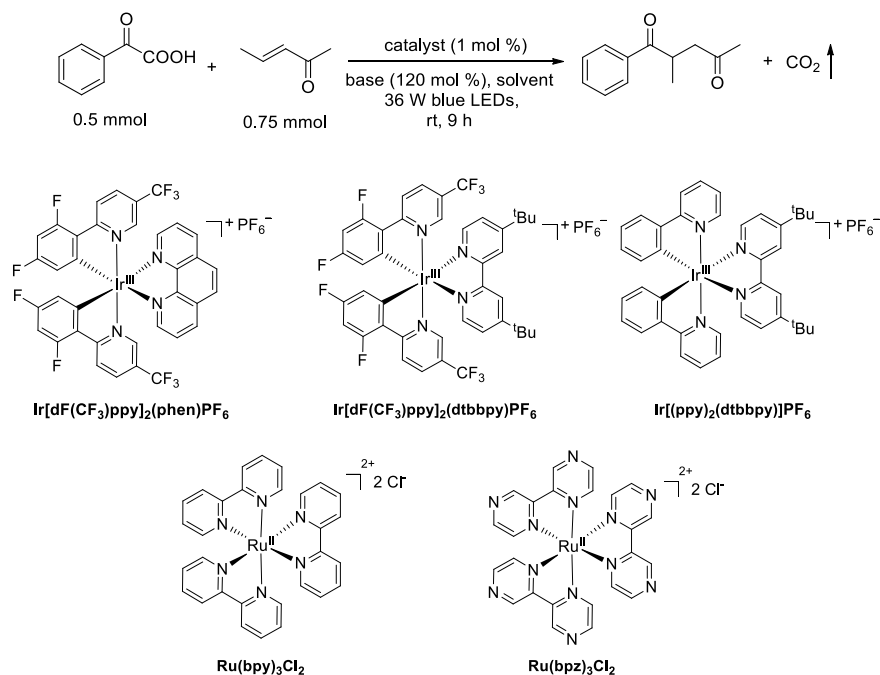
entry	catalyst	irradiation	time/h	yield
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	dark	9	0
2	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	36w blue LEDs	9	92%
3	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	18w blue LEDs	9	80%
3	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	36w CFL	9	55%

### 3.7. Protection atmosphere



entry	catalyst	atmosphere	yield
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	Ar	90%
2	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	air	92%
3	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (phen)PF <sub>6</sub>	O <sub>2</sub>	18%

### 3.8. Condition Optimization



entry	catalyst (1 %)	base	solvent (1 mL/1 mL)	yield <sup>a</sup>
1	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	92%(89% <sup>b</sup> )
2	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	90%
3	$\text{Ir}[(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	N.R.
4	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	N.R.
5	$[\text{Ru}(\text{bpz})_3]\text{Cl}_2$	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	28%
6	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{DMF}/\text{H}_2\text{O}$	45%
7	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	61%
8	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{Dioxane}/\text{H}_2\text{O}$	15%
9	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{HPO}_4$	$\text{Acetone}/\text{H}_2\text{O}$	71%
10	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{CsCO}_3$	$\text{DCM}/\text{H}_2\text{O}$	86%
11	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	$\text{K}_2\text{CO}_3$	$\text{DCM}/\text{H}_2\text{O}$	90%
12	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	KOAc	$\text{DCM}/\text{H}_2\text{O}$	75%
13	/	$\text{K}_2\text{HPO}_4$	$\text{DCM}/\text{H}_2\text{O}$	N.R.
14	$\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{phen})\text{PF}_6$	/	$\text{DCM}/\text{H}_2\text{O}$	N.R.

<sup>a</sup> GC yield using benzophenone as internal standard. <sup>b</sup> Isolated yield.

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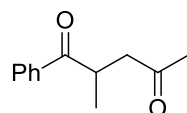
## 4. General Procedure and Spectral Data

### 4.1 General procedure

$\alpha$ -Oxocarboxylic acid (0.5 mmol), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(phen)PF<sub>6</sub> (1 mol %, 5 mg), olefins (0.75 mmol) and K<sub>2</sub>HPO<sub>4</sub> (0.6 mmol, 104 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The solvents DCM (1 mL) and H<sub>2</sub>O (1 mL) were added under air atmosphere. The reaction mixture was stirred under the irradiation of a 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 9 h. After 9 h, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether).

### 4.2 Spectral data

**2-methyl-1-phenylpentane-1,4-dione (2a)** [CAS Number: 83188-09-4]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 89 % yield as a colorless liquid (84 mg). (Reference: Srikrishna, A.; Krishnan, K.; Venkateswarlu, S.; Kumar, P. P. *J. CHEM. SOC. PERKIN TRANS.* **1995**, 16, 2033.)

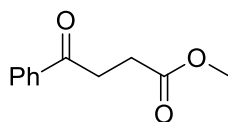


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d,  $J$  = 7.3 Hz, 2H), 7.56 (t,  $J$  = 7.3 Hz, 1H), 7.47 (t,  $J$  = 7.6 Hz, 2H), 4.09 – 3.88 (m, 1H), 3.17 (dd,  $J$  = 18.1, 8.5 Hz, 1H), 2.56 (dd,  $J$  = 18.1, 5.0 Hz, 1H), 2.18 (s, 3H), 1.19 (d,  $J$  = 7.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  207.17, 203.28, 135.95, 132.99, 128.88, 128.46, 46.83, 36.21, 30.11, 17.79.

**Methyl 4-oxo-4-phenylbutanoate (2b)** [CAS Number: 25333-24-8]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 61 % yield as a colorless liquid (58.5 mg). (Reference: Jo, E.-A.; Jun, C.-H. *Eur. J. Org. Chem.* **2006**, 11, 2504.)

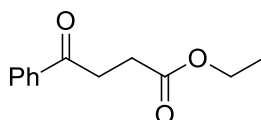




$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.4$  Hz, 2H), 7.58 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 3.71 (s, 3H), 3.33 (t,  $J = 6.6$  Hz, 2H), 2.78 (t,  $J = 6.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.07, 173.40, 136.52, 133.26, 128.63, 128.05, 51.85, 33.41, 28.02.

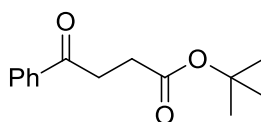
**ethyl 4-oxo-4-phenylbutanoate (2c)** [CAS Number: 6270-17-3]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 65 % yield as a colorless liquid (70 mg). (Reference: Jo, E.-A.; Jun, C.-H. *Eur. J. Org. Chem.* **2006**, 11, 2504.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.4$  Hz, 2H), 7.57 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 4.16 (q,  $J = 7.1$  Hz, 2H), 3.32 (t,  $J = 6.6$  Hz, 2H), 2.76 (t,  $J = 6.6$  Hz, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.16, 172.93, 136.59, 133.21, 128.62, 128.04, 60.67, 33.40, 28.30, 14.20.

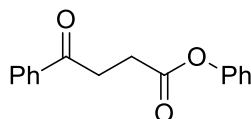
**tert-butyl 4-oxo-4-phenylbutanoate (2d)** [CAS Number: 55666-45-0]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 71 % yield as a colorless liquid (83 mg). (Reference: Jo, E.-A.; Jun, C.-H. *Eur. J. Org. Chem.* **2006**, 11, 2504.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.3$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.26 (t,  $J = 6.7$  Hz, 2H), 2.69 (t,  $J = 6.7$  Hz, 2H), 1.45 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.36, 172.17, 136.73, 133.11, 128.58, 128.03, 80.60, 33.49, 29.45, 28.08.

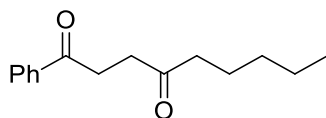
**phenyl 4-oxo-4-phenylbutanoate (2e)** [CAS Number: 86357-75-7]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 75 % yield as a colorless liquid (95 mg).



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.22 (dd, *J* = 14.8, 7.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 3.01 (t, *J* = 6.5 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.86, 171.56, 150.77, 136.48, 133.33, 129.39, 128.66, 128.07, 125.79, 121.57, 33.45, 28.48.

**1-phenylnonane-1,4-dione (2f)** [CAS Number: 117937-13-0]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 73 % yield as a colorless liquid (84 mg). (Reference: K. Tanaka, T. Shoji, M. Hirano, *Eur. J. Org. Chem.* **2007**, 16, 2687.)

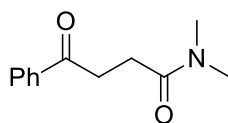


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.38 – 1.23 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 209.82, 198.71, 136.70, 133.13, 128.57, 128.06, 42.99, 36.18, 32.37, 31.42, 23.57, 22.47, 13.94.

**N,N-dimethyl-4-oxo-4-phenylbutanamide (2g)** [CAS Number: 26976-88-5]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 45 % yield as a white solid (46 mg). (Reference: Tanaka,

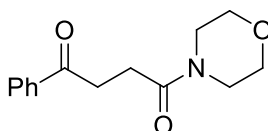
K.; Shibata, Y.; Suda, T.; Hagiwara, Y.; Hirano, M. *Org. Lett.* **2007**, 9, 1215.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 7.1$  Hz, 2H), 7.58 – 7.51 (m, 1H), 7.46 (t,  $J = 7.8$  Hz, 2H), 3.35 (t,  $J = 6.6$  Hz, 2H), 3.09 (s, 3H), 2.96 (s, 3H), 2.78 (t,  $J = 6.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.36, 171.74, 136.85, 133.05, 128.54, 128.12, 37.15, 35.59, 33.69, 27.28.

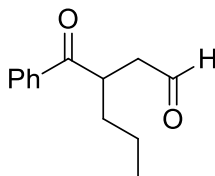
**1-morpholino-4-phenylbutane-1,4-dione (2h)** [CAS Number: 6045-93-8]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 48 % yield as a white solid (59 mg). (Reference: Allen, C. L.; Chhatwal, A. R.; Williams, J. M. *J. Chem. Commun.* **2012**, 48, 666.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.2$  Hz, 2H), 7.49 (t,  $J = 7.9$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 2H), 3.67 – 3.48 (m, 8H), 3.29 (t,  $J = 6.5$  Hz, 2H), 2.70 (t,  $J = 6.5$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.11, 170.45, 136.74, 133.16, 128.59, 128.12, 66.88, 66.60, 45.86, 42.14, 33.52, 26.91.

**3-benzoylhexanal (2i)**: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 78 % yield as a colorless liquid (79.5 mg).

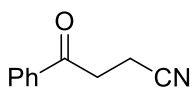


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.79 (s, 1H), 7.99 (d,  $J = 7.3$  Hz, 2H), 7.57 (t,  $J = 8.0$  Hz, 1H), 7.48 (t,  $J = 6.4$  Hz, 2H), 4.06 – 3.88 (m, 1H), 3.16 (dd,  $J = 18.5, 9.0$  Hz, 1H), 2.65 (dd,  $J = 18.5, 4.3$  Hz, 1H), 1.74 – 1.64 (m, 1H), 1.53 – 1.42 (m, 1H), 1.35 – 1.25 (m, 2H), 0.88 (t,  $J = 7.2$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 202.53, 200.68, 136.49, 133.08, 128.68, 128.39, 45.38, 39.93, 34.50, 20.34, 14.01.

HRMS (ESI) calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>H<sup>+</sup>[(M+H)<sup>+</sup>] 204.1150, found 204.1153.

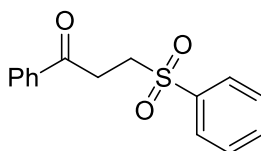
**4-oxo-4-phenylbutanenitrile (2j)** [CAS Number: 5343-98-6]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1), obtained in 63 % yield as a colorless liquid (50 mg). (Reference: Miura, K.; Fujisawa, N.; Saito, H.; Wang, D.; Hosom, A. *Org. Lett.* **2006**, 3, 2591.)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 3.39 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.38, 135.59, 133.91, 128.88, 128.02, 119.27, 34.25, 11.79.

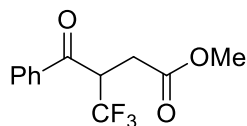
**1-phenyl-3-(phenylsulfonyl)propan-1-one (2k)** [CAS Number: 65885-28-1]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1), obtained in 71 % yield as a white solid (97 mg). (Reference: Bhunia, A.; Yetra, S. R.; Bhojgude, S. S.; Biju, A. T. *Org. Lett.* **2012**, 14, 2830.)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (m, 4H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 2H), 3.62 – 3.47 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.44, 139.06, 135.80, 133.97, 133.82, 129.45, 128.82, 128.08, 128.01, 51.04, 31.38.

**methyl 3-benzoyl-4,4,4-trifluorobutanoate (2l)** Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 61 % yield as a colorless liquid (69 mg).



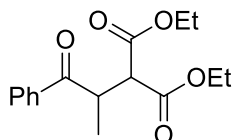
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.4$  Hz, 2H), 7.56 (t,  $J = 6.9$  Hz, 1H), 7.44 (t,  $J = 7.0$  Hz, 2H), 4.75 – 4.53 (m, 1H), 3.58 (s, 3H), 3.30 (dd,  $J = 17.4, 10.7$  Hz, 1H), 2.79 (dd,  $J = 17.4, 3.5$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.04, 170.95, 136.34, 134.10, 128.94, 128.86, 124.28 (d,  $J = 280.8$  Hz), 52.37, 45.62 (q,  $J = 26.3$  Hz), 31.07 (d,  $J = 2.5$  Hz).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.34.

HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_3\text{H}^+[(\text{M}+\text{H})^+]$  260.0660, found 260.0662.

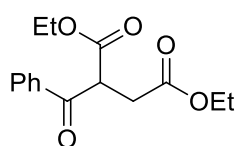
**diethyl 2-(1-oxo-1-phenylpropan-2-yl)malonate (2m)** [CAS Number: 7315-66-4]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 91 % yield as a colorless liquid (133 mg). (Reference: Chudasama, V.; Akhbar, A. R.; Bahou, K. A. R.; Fitzmaurice, J.; Caddick, S. *Org. Biomol. Chem.* **2013**, *11*, 7301.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.2$  Hz, 2H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 2H), 4.31 – 4.06 (m, 5H), 3.99 (d,  $J = 10.8$  Hz, 1H), 1.32 (t,  $J = 7.1$  Hz, 3H), 1.18 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.23, 171.27, 168.74, 135.95, 133.65, 128.89, 128.71, 61.81, 61.07, 49.62, 33.28, 29.72, 14.10, 13.90.

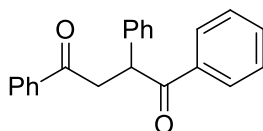
**diethyl 2-benzoylsuccinate (2n)** Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 94 % yield as a colorless liquid (130 mg). (Reference: Mattson, A. E.; Bharadwaj, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006**, *71*, 5715.)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.95 – 4.79 (m, 1H), 4.14 (m, 4H), 3.06 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.63, 168.78, 168.37, 135.61, 133.23, 128.71, 128.54, 61.68, 61.65, 54.95, 40.51, 15.88, 13.89.

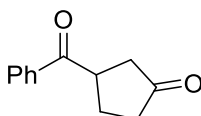
**1,2,4-triphenylbutane-1,4dione (2o)** [CAS Number: 4441-01-4]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 88 % yield as a white solid (138 mg). (Reference: Chen, L.; Du, Y.; Zeng, X.-P.; Shi, T.-Da.; Zhou, F.; Zhou, J. *Org. Lett.* **2015**, *17*, 1557.)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 – 8.00 (m, 2H), 8.00 – 7.95 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.34 (m, 7H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.33 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.21 (dd, *J* = 18.0, 10.1 Hz, 1H), 3.30 (dd, *J* = 18.0, 3.7 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.91, 198.06, 138.63, 136.43, 133.24, 132.88, 129.18, 128.91, 128.55, 128.49, 128.22, 128.15, 127.35, 48.69, 43.87.

**3-benzoylcyclopentanone (2p)** [CAS Number: 92516-43-3]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 81 % yield as a colorless liquid (76 mg).

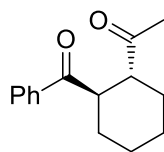


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 4.22 – 4.07 (m, 1H), 2.72 (dd, *J* = 18.4, 7.8 Hz, 1H), 2.51 – 2.13 (m, 5H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 217.02, 200.28, 135.56, 133.57, 128.88, 128.46, 43.01, 40.94, 37.31, 27.00.

**1-((1R,2R)-2-benzoylcyclohexyl)ethanone (2q) (trans)** [CAS Number: 101534-17-2]: Following general procedure, The product was purified by flash column chromatography on silica gel

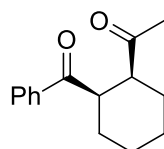
(petroleum ether : ethyl acetate = 10 : 1), obtained in 54 % yield as a colorless liquid (62 mg).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 7.1$  Hz, 2H), 7.52 (t,  $J = 7.4$  Hz, 1H), 7.43 (t,  $J = 7.9$  Hz, 2H), 3.94 (dd,  $J = 9.7, 4.9$  Hz, 1H), 2.65 – 2.55 (m, 1H), 2.33 – 2.18 (m, 4H), 2.17 – 1.98 (m, 2H), 1.85 – 1.70 (m, 2H), 1.54 – 1.28 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.67, 203.01, 136.83, 132.46, 128.51, 128.21, 50.74, 44.40, 28.33, 27.71, 25.59, 24.73, 22.50.

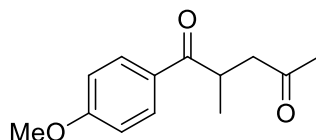
**1-((1S,2R)-2-benzoylcyclohexyl)ethanone (2q) (*cis*)** [CAS Number: 101534-16-1]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 7 % yield as a colorless liquid (8 mg).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.2$  Hz, 2H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.45 (t,  $J = 7.5$  Hz, 2H), 3.65 – 3.53 (m, 1H), 3.13 – 3.00 (m, 1H), 2.21 (s, 3H), 2.16 (d,  $J = 12.8$  Hz, 1H), 2.04 (d,  $J = 13.2$  Hz, 1H), 1.95 – 1.80 (m, 2H), 1.44 – 1.19 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.49, 203.56, 136.26, 132.85, 128.55, 128.39, 52.21, 46.79, 29.92, 28.80, 28.59, 28.87, 28.78.

**1-(4-methoxyphenyl)-2-methylpentane-1,4-dione (3a)** [CAS Number: 376637-33-1]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 82 % yield as a colorless liquid (90 mg).



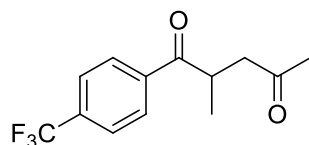
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.9$  Hz, 2H), 6.95 (d,  $J = 8.9$  Hz, 2H), 3.99 – 3.82 (m, 4H), 3.15 (dd,  $J = 18.0, 8.4$  Hz, 1H), 2.53 (dd,  $J = 18.0, 5.1$  Hz, 1H), 2.17 (s, 3H), 1.18 (d,  $J = 7.2$  Hz, 3H).

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$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.35, 201.74, 163.46, 130.76, 128.82, 113.80, 55.47, 46.86, 35.82, 30.18, 18.04.

**2-methyl-1-(4-(trifluoromethyl)phenyl)pentane-1,4-dione (3b)** [CAS Number: 1491568-64-9]:

Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 48 % yield as a colorless liquid (62 mg).

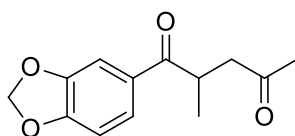


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J$  = 8.8 Hz, 2H), 7.74 (d,  $J$  = 8.3 Hz, 2H), 4.02 – 3.85 (m, 1H), 3.21 (dd,  $J$  = 18.3, 9.1 Hz, 1H), 2.60 (dd,  $J$  = 18.3, 4.5 Hz, 1H), 2.18 (s, 3H), 1.19 (d,  $J$  = 1.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.91, 202.50, 138.93, 134.20 (q,  $J$  = 32.7 Hz), 128.74, 125.68 (q,  $J$  = 3.7 Hz), 123.64 (d,  $J$  = 272.6 Hz), 46.97, 36.46, 29.86, 17.43.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.14.

**1-(furan-2-yl)-2-methylpentane-1,4-dione (3c)** [CAS Number: 1491482-43-9]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 77 % yield as a white solid (117 mg).

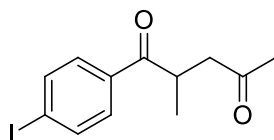


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J$  = 9.6 Hz, 1H), 7.43 (s, 1H), 6.85 (d,  $J$  = 8.2 Hz, 1H), 6.04 (s, 2H), 3.86 (m, 1H), 3.13 (dd,  $J$  = 18.1, 8.6 Hz, 1H), 2.52 (dd,  $J$  = 18.1, 4.9 Hz, 1H), 2.15 (s, 3H), 1.16 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.30, 201.33, 151.73, 148.23, 130.65, 124.65, 108.37, 107.98, 101.82, 46.96, 35.95, 30.13, 18.07.

**1-(4-iodophenyl)-2-methylpentane-1,4-dione (3d)**: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 81 % yield as a colorless liquid (127 mg).



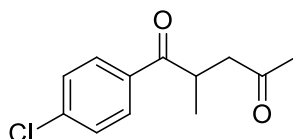


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.2$  Hz, 2H), 7.69 (d,  $J = 8.4$  Hz, 2H), 3.97 – 3.80 (m, 1H), 3.16 (dd,  $J = 18.2, 8.8$  Hz, 1H), 2.56 (dd,  $J = 18.2, 4.7$  Hz, 1H), 2.17 (s, 3H), 1.16 (d,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.02, 202.63, 137.95, 135.27, 129.89, 100.89, 46.87, 36.06, 30.01, 17.66.

HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{13}\text{IO}_2\text{H}^+[(\text{M}+\text{H})^+]$  315.9660, found 315.9662.

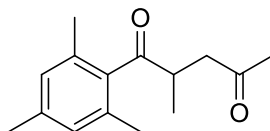
**1-(4-chlorophenyl)-2-methylpentane-1,4-dione (3e)** [CAS Number: 1342230-79-8]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 71 % yield as a colorless liquid (80 mg).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.6$  Hz, 2H), 7.45 (d,  $J = 8.6$  Hz, 2H), 3.99 – 3.82 (m, 1H), 3.17 (dd,  $J = 18.2, 8.8$  Hz, 1H), 2.57 (dd,  $J = 18.2, 4.7$  Hz, 1H), 2.17 (s, 3H), 1.17 (d,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.06, 202.14, 139.40, 134.32, 129.90, 128.95, 46.90, 36.13, 30.02, 17.70.

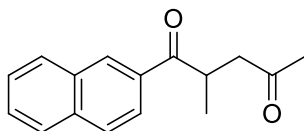
**1-mesityl-2-methylpentane-1,4-dione (3f)** [CAS Number: 1484303-40-3 ]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 94 % yield as a colorless liquid (109 mg).



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.83 (s, 2H), 3.57 – 3.41 (m, 1H), 3.02 (dd,  $J = 17.5, 6.7$  Hz, 1H), 2.43 (dd,  $J = 17.5, 6.3$  Hz, 1H), 2.27 (s, 3H), 2.22 (s, 9H), 1.12 (d,  $J = 7.4$  Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 211.91, 207.04, 138.48, 137.62, 133.57, 128.70, 44.96, 43.39, 30.55, 21.01, 19.65, 16.00.

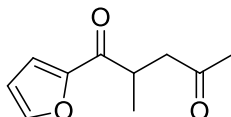
**2-methyl-1-(naphthalen-2-yl)pentane-1,4-dione (3g)** [CAS Number: 1379209-72-9]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 70 % yield as a white solid (84 mg).



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.53 (s, 1H), 8.06 – 7.95 (m, 2H), 7.89 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.63 – 7.50 (m, 2H), 4.22 – 4.04 (m, 1H), 3.22 (dd, *J* = 18.1, 8.4 Hz, 1H), 2.61 (dd, *J* = 18.1, 5.1 Hz, 1H), 2.20 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 207.26, 203.24, 135.59, 133.25, 132.61, 130.03, 129.63, 128.49, 129.39, 127.73, 126.70, 124.32, 46.90, 36.27, 30.16, 18.01.

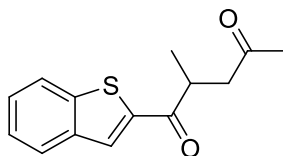
**1-(furan-2-yl)-2-methylpentane-1,4-dione (3h)** [CAS Number: 60930-74-7]: Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1), obtained in 65 % yield as a colorless liquid (58.5 mg).



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 0.7 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 6.56 (m, 1H), 3.80 – 3.67 (m, 1H), 3.13 (dd, *J* = 18.0, 8.7 Hz, 1H), 2.54 (dd, *J* = 18.1, 5.0 Hz, 1H), 2.17 (s, 3H), 1.21 (d, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 206.93, 191.94, 151.90, 146.48, 117.67, 112.25, 46.28, 36.87, 30.05, 17.61.

**1-(benzo[b]thiophen-2-yl)-2-methylpentane-1,4-dione (3i):** Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1), obtained in 58 % yield as a white solid (71 mg).



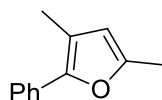
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.88 (dd,  $J$  = 13.6, 8.0 Hz, 2H), 7.43 (m, 2H), 4.02 – 3.84 (m, 1H), 3.18 (dd,  $J$  = 18.2, 8.5 Hz, 1H), 2.61 (dd,  $J$  = 18.2, 5.1 Hz, 1H), 2.18 (s, 3H), 1.29 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.79, 197.59, 142.61, 139.21, 129.27, 127.36, 126.00, 124.95, 122.95, 46.84, 37.62, 30.09, 18.33.

HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{14}\text{SO}_2\text{H}^+[(\text{M}+\text{H})^+]$  246.0715, found 246.0717.

### 3,5-dimethyl-2-phenylfuran (5) [CAS Number: 90904-38-4]:

**2a** (1 mmol), Trifluoromethanesulfonate (3 equiv) were placed in a transparent Schlenk tube equipped with a stirring bar. And then toluene (3 mL) was added under air atmosphere. The reaction mixture was then stirred at 65 °C for 12 h. After 12 h, the mixture was washed with saturated  $\text{NH}_4\text{HCO}_3$  solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 91 % yield as a colorless liquid (156 mg). (Reference: Chen, L.-Q; Fang, Y.-W; Zhao, Q.-W; Shi, Min; Li, C.-Z. *Tetrahedron Lett.* **2010**, 51, 3678.)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 7.2 Hz, 2H), 7.28 (t,  $J$  = 7.8 Hz, 2H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 5.83 (s, 1H), 2.22 (s, 3H), 2.13 (s, 3H).

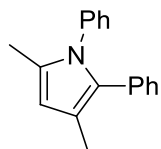
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.40, 146.91, 132.11, 128.44, 126.10, 124.87, 117.22, 111.43, 13.52, 11.91.

### 3,5-dimethyl-1,2-diphenyl-1H-pyrrole (6):

**2a** (1 mmol), Aniline (300 mol %), AcOH/NaOAc = 1 : 1 (100 mol %) were placed in a transparent Schlenk tube equipped with a stirring bar. And then anhydrous toluene (3 mL) was added under air atmosphere. The reaction mixture was then stirred at 65 °C for 12 h. After 12 h, the mixture was washed with saturated  $\text{NH}_4\text{HCO}_3$  solution and extracted with ethyl acetate (3 x 10

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mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 83 % yield as a white solid (205 mg).



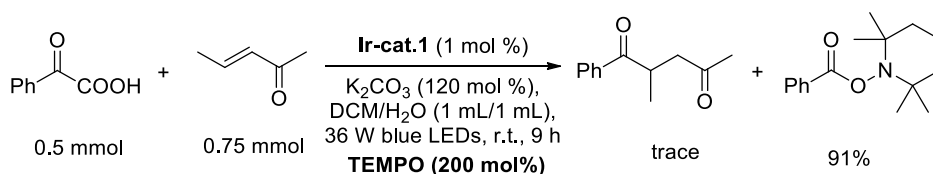
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (m, 3H), 7.16 (t,  $J = 7.3$  Hz, 2H), 7.11 – 7.01 (m, 5H), 6.00 (s, 1H), 2.16 (s, 3H), 2.13 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.44, 133.09, 130.47, 129.99, 129.80, 128.68, 128.43, 127.69, 126.86, 125.69, 116.98, 109.59, 13.13, 12.03.

HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{17}\text{NH}^+[(\text{M}+\text{H})^+]$  247.1361, found 247.1363.

## 5. Radical trapping experiments

To a mixture of  $\alpha$ -Oxocarboxylic acid (0.5 mmol), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(phen)PF<sub>6</sub> (1 mol %, 5 mg), olefins (0.75 mmol), K<sub>2</sub>HPO<sub>4</sub> (0.6 mmol, 104 mg) and TEMPO (200 mol %) placed in a transparent Schlenk tube equipped with a stirring bar, DCM (1 mL) and H<sub>2</sub>O (1 mL) were added. The reaction mixture was then stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 9 h. After 9 h, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1).



When 2.0 equiv of TEMPO was added, only a trace amount of product was obtained and 2,2,6,6-tetramethylpiperidin-1-yl benzoate was obtained in 91 % (based on  $\alpha$ -oxocarboxylic acid) as a red solid.

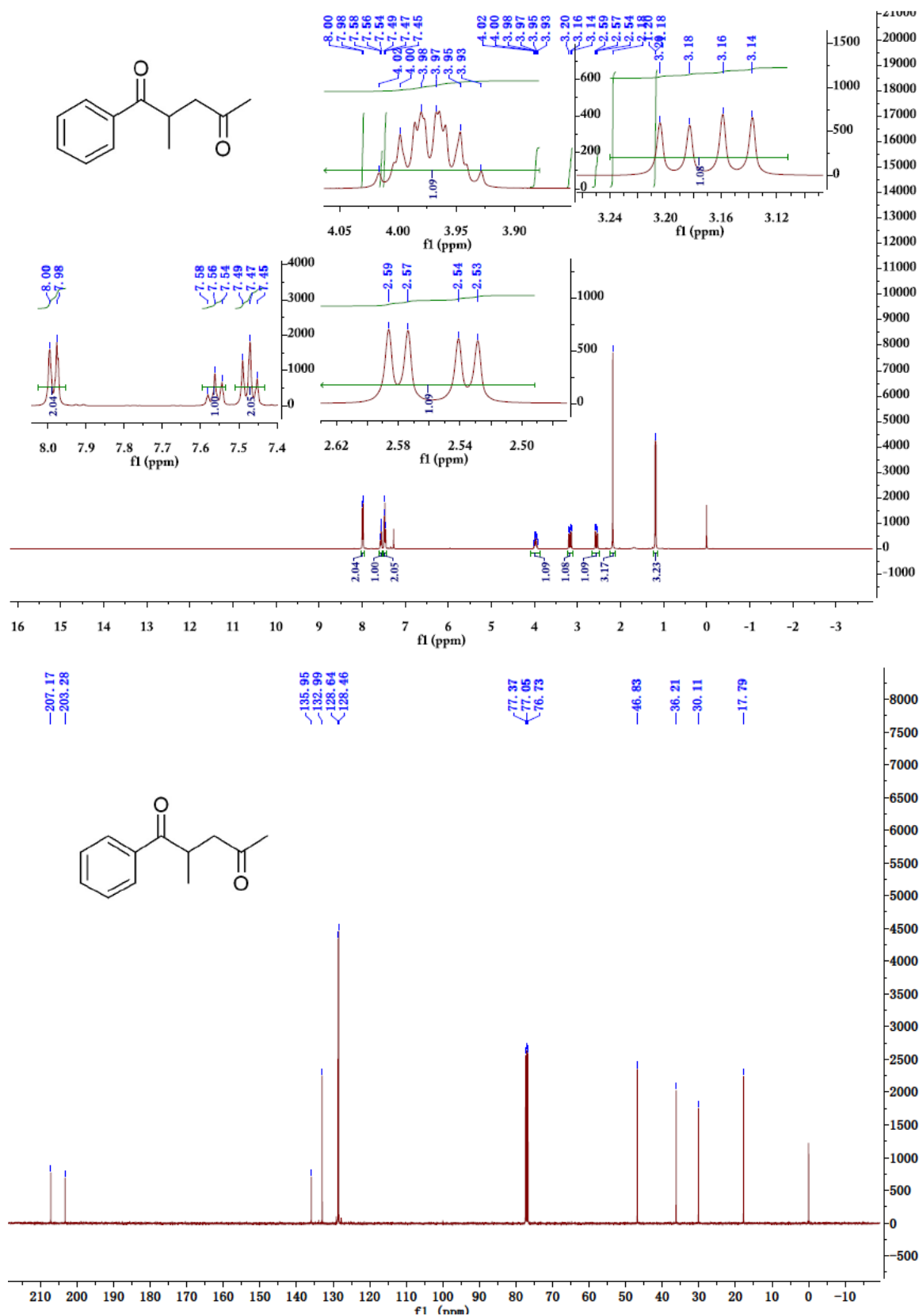
### 2,2,6,6-tetramethylpiperidin-1-yl benzoate (7)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d,  $J$  = 7.3 Hz, 2H), 7.63 – 7.51 (m, 1H), 7.46 (t,  $J$  = 7.0 Hz, 2H), 1.82 – 1.41 (m, 6H), 1.27 (d,  $J$  = 5.3 Hz, 6H), 1.12 (d,  $J$  = 5.2 Hz, 6H).

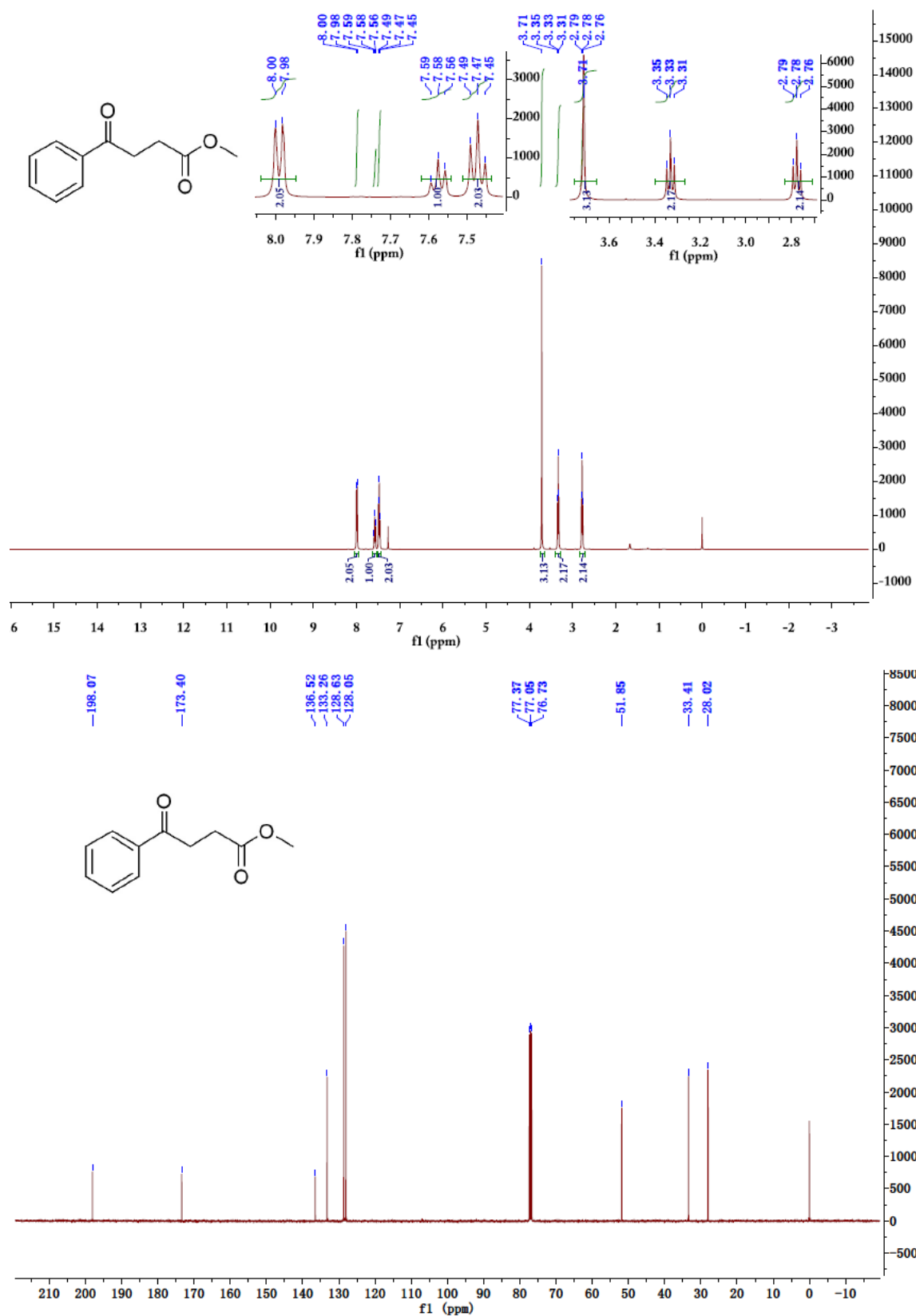
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.55, 130.15, 126.93, 126.79, 125.75, 57.58, 36.29, 29.21, 18.10, 14.26.

## 7. NMR Spectras

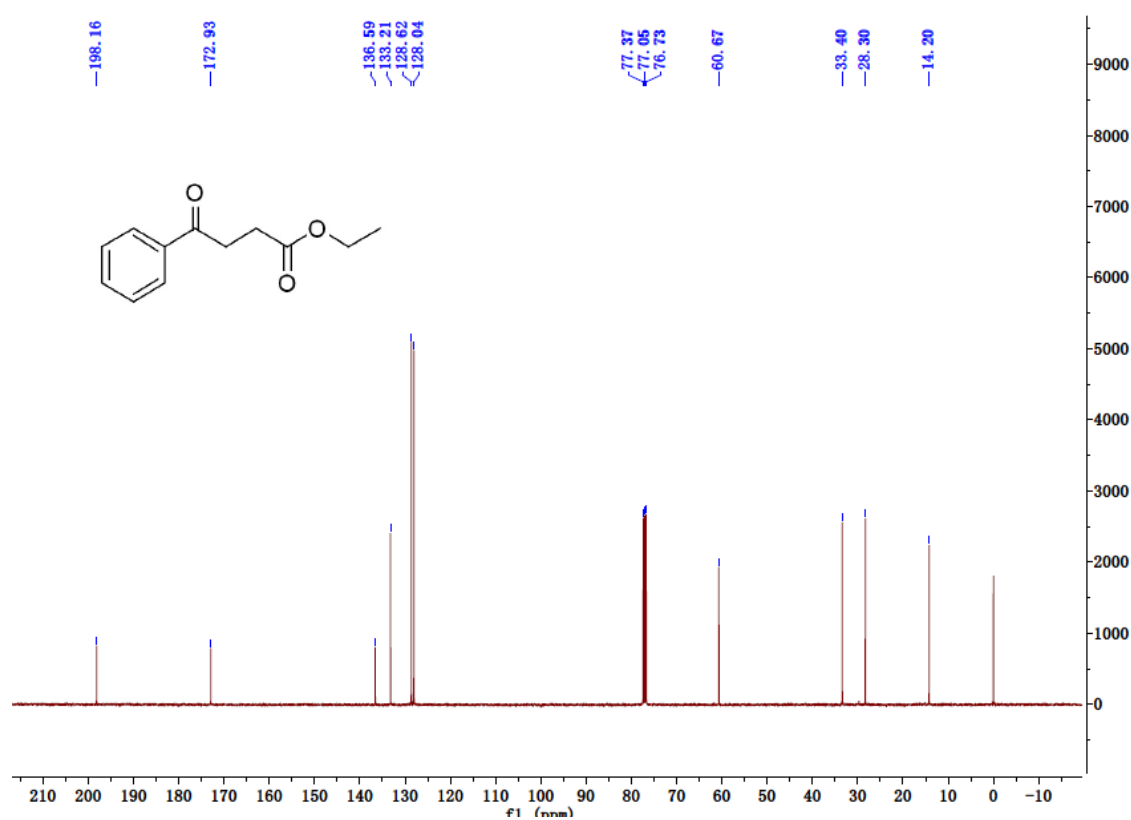
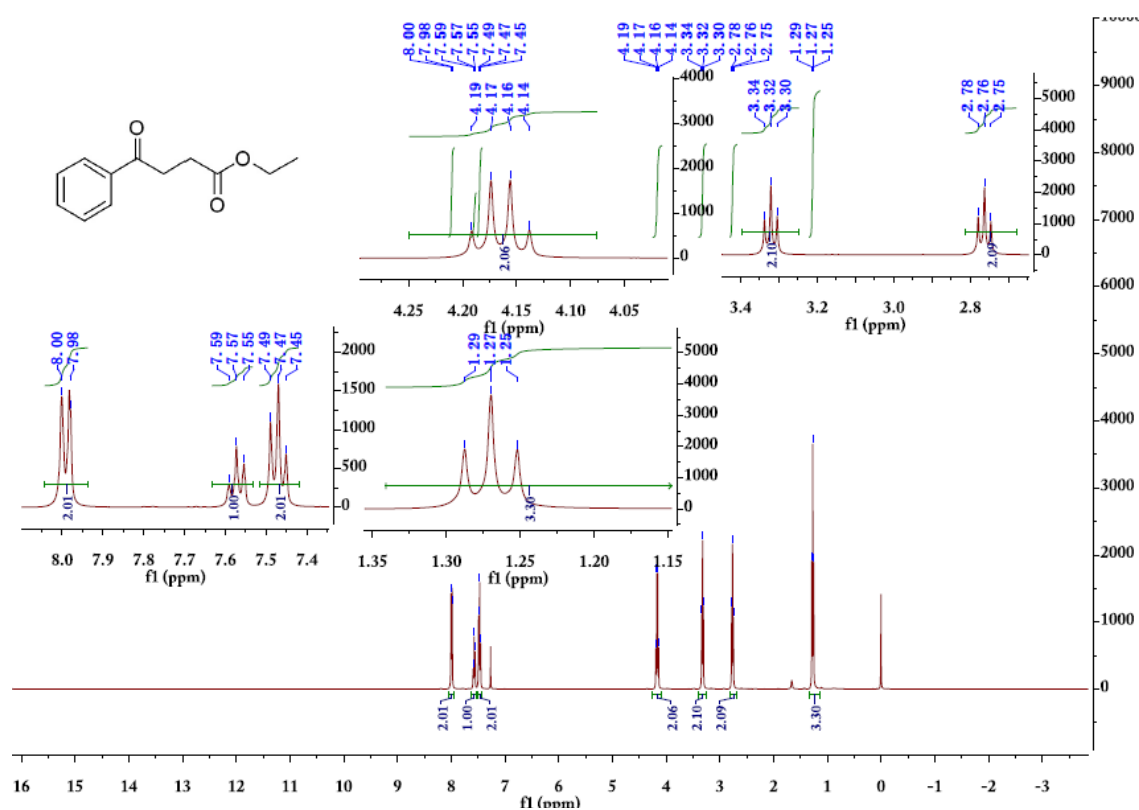
### 2-methyl-1-phenylpentane-1,4-dione (2a)



methyl 4-oxo-4-phenylbutanoate (2b)

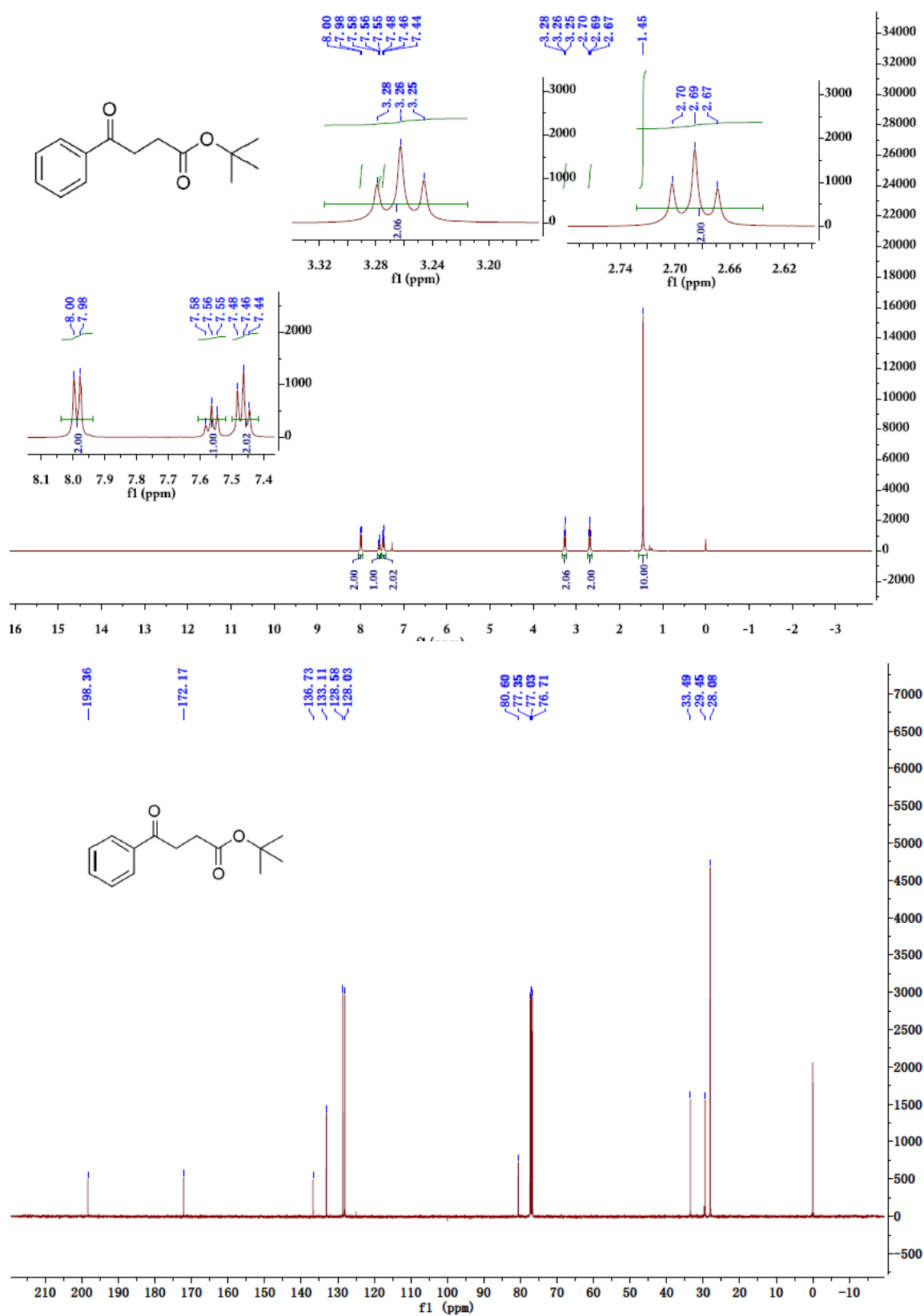


ethyl 4-oxo-4-phenylbutanoate (2c)

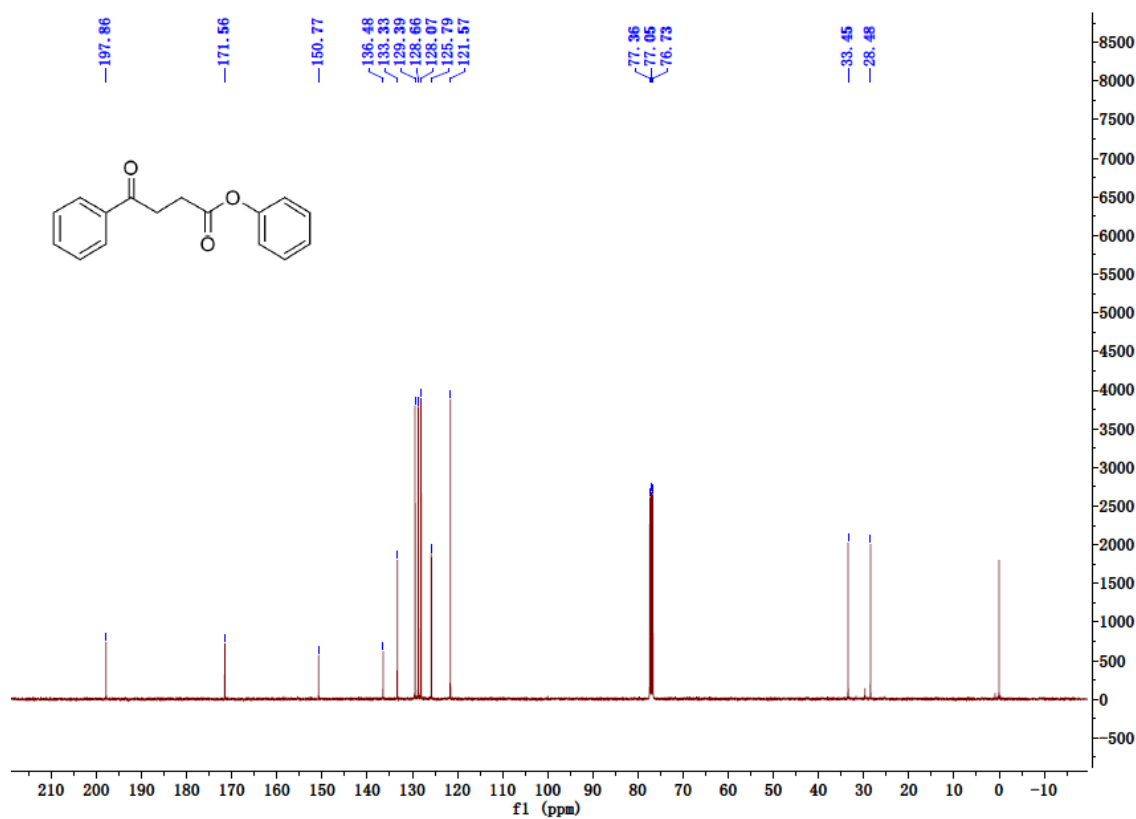
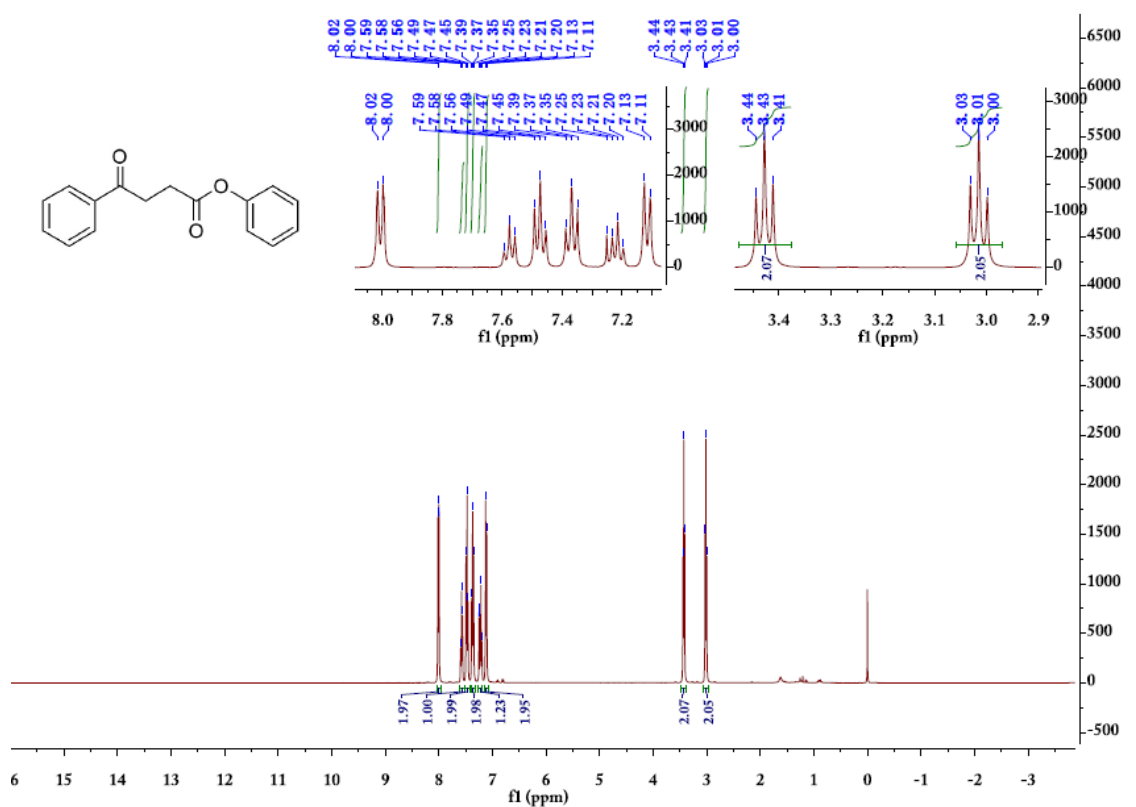




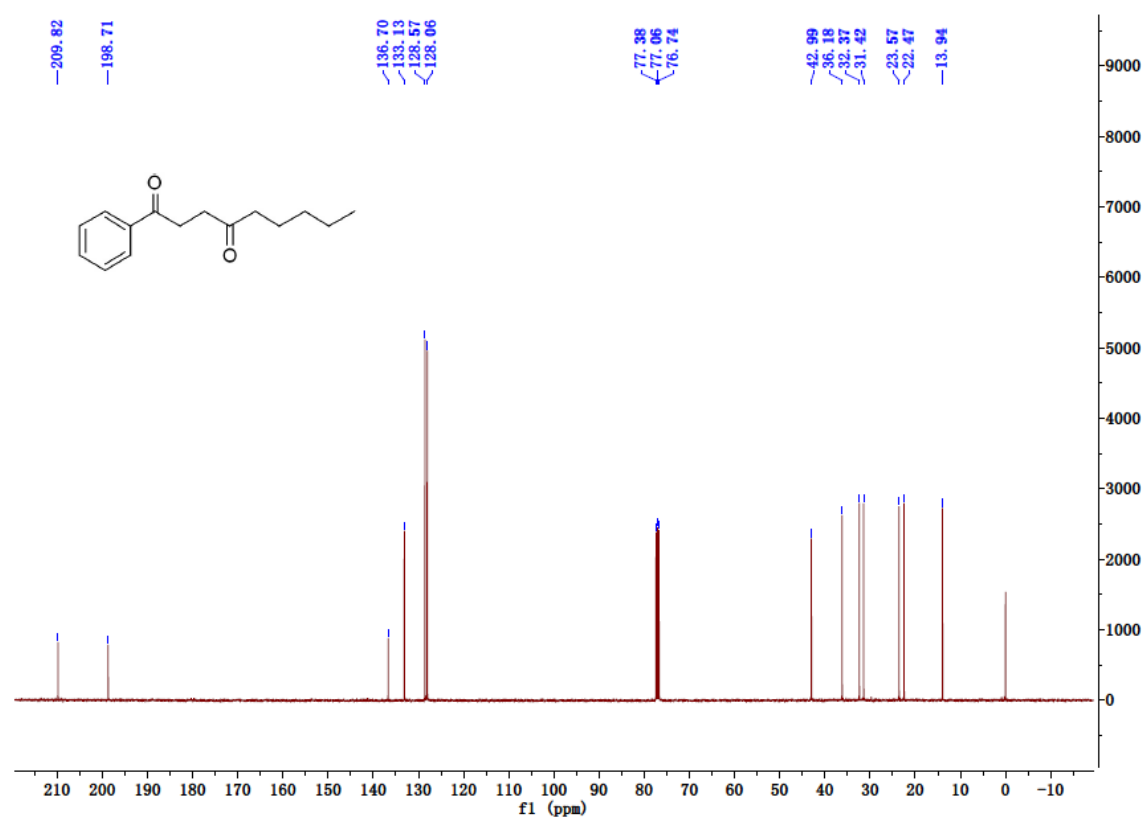
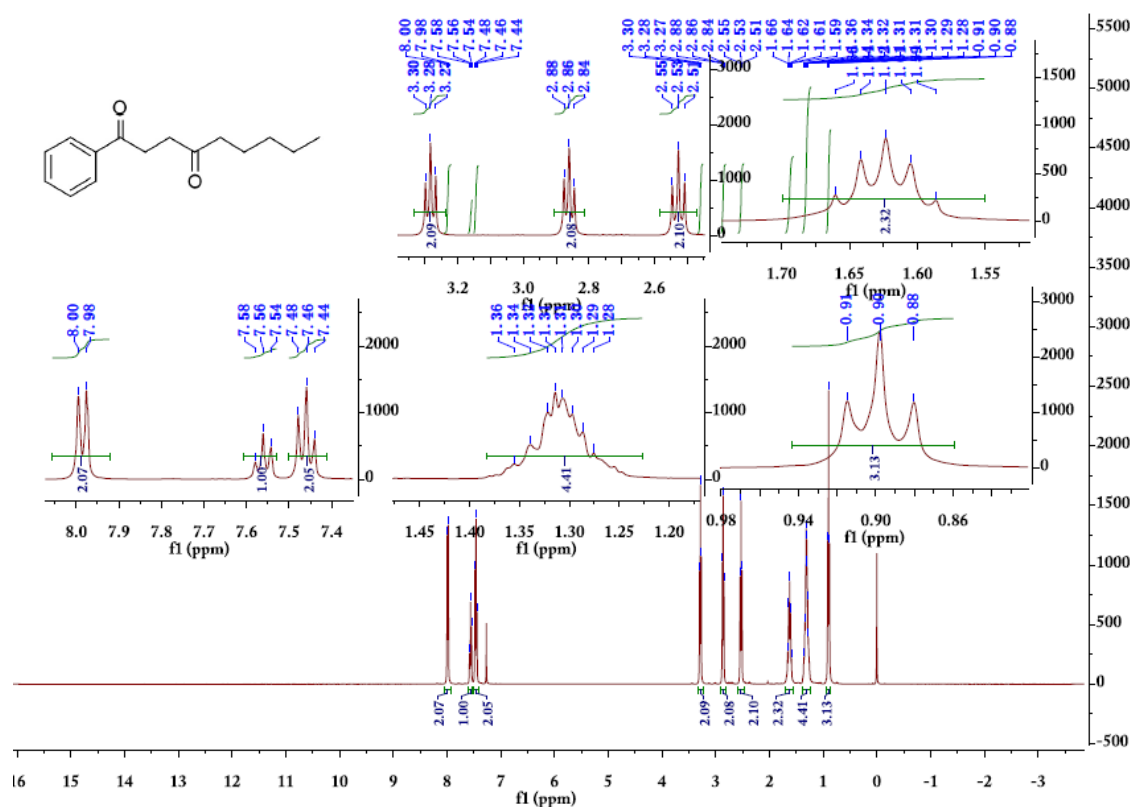
tert-butyl 4-oxo-4-phenylbutanoate (2d)



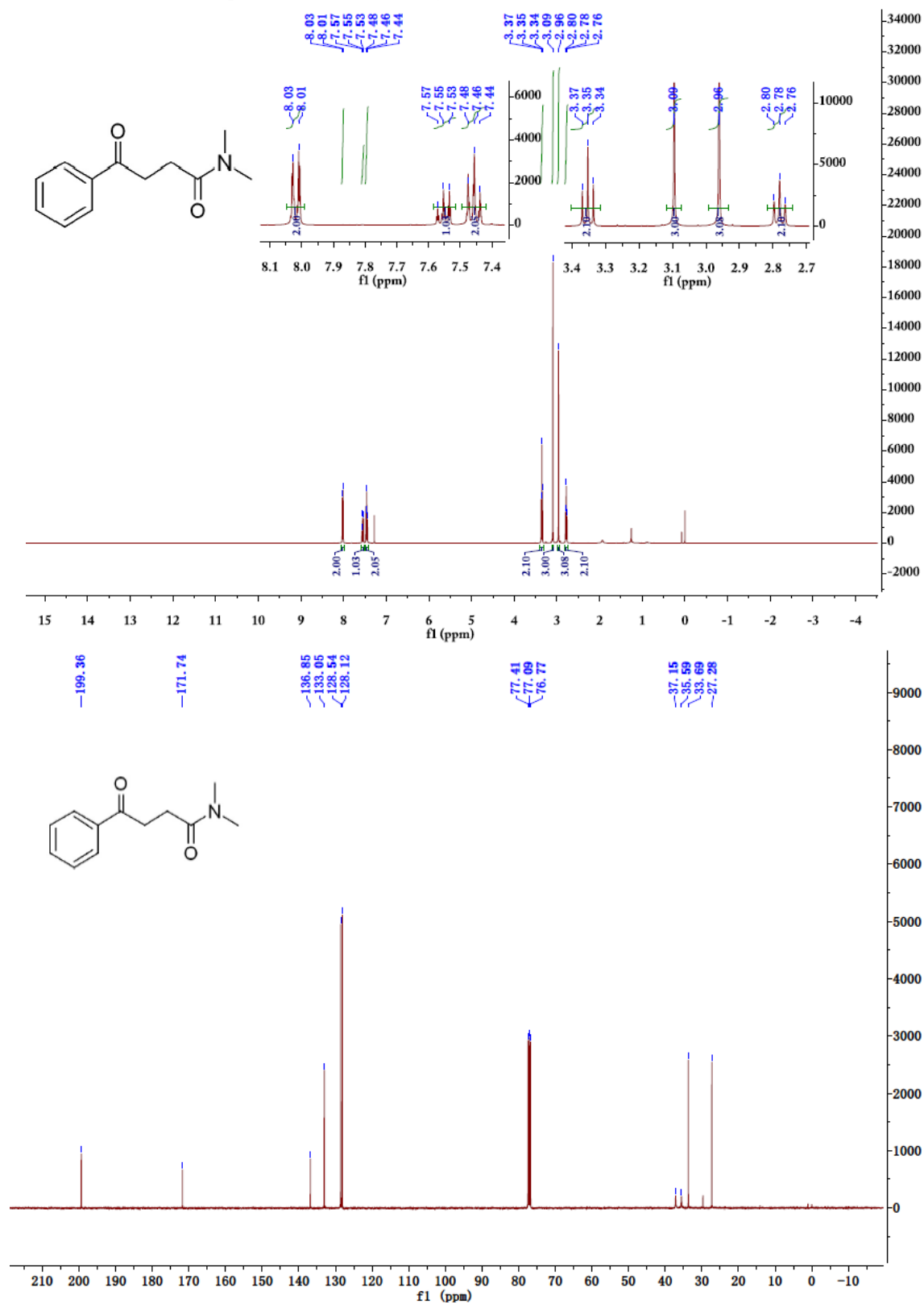
phenyl 4-oxo-4-phenylbutanoate (2e)



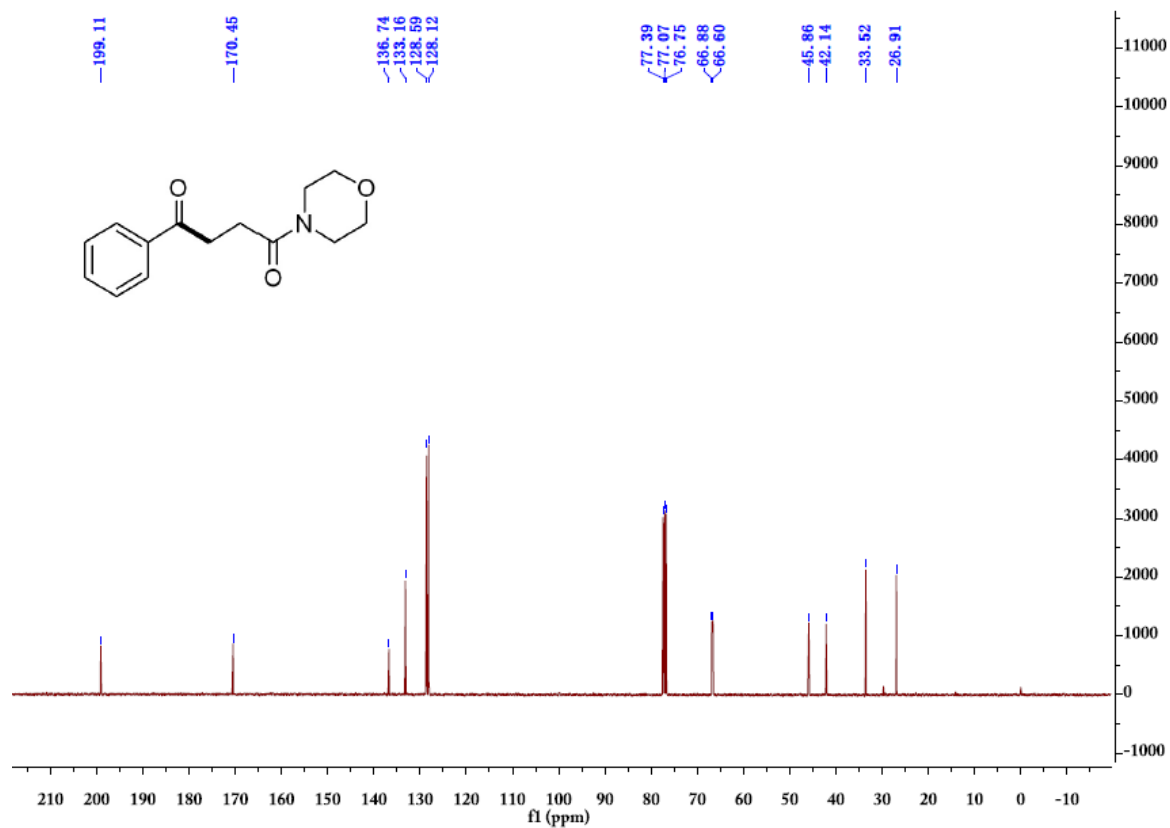
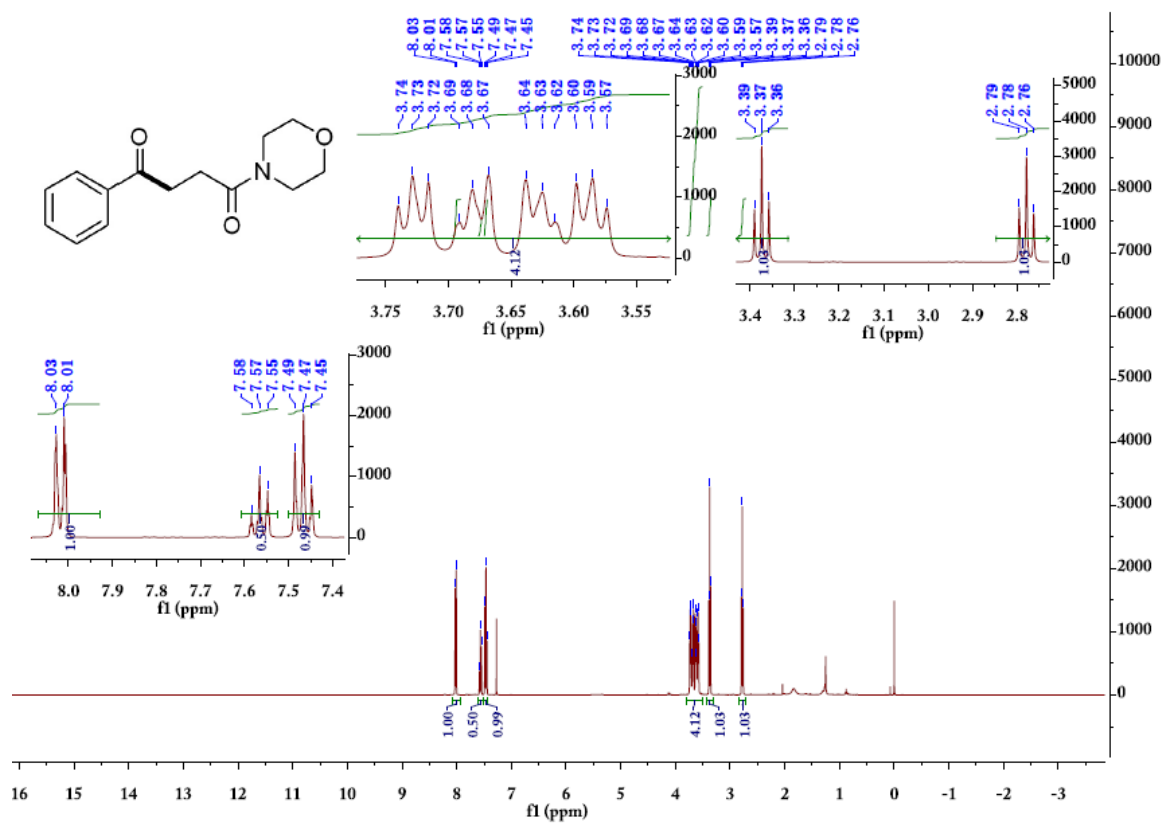
# 1-phenylnonane-1,4-dione (2f)



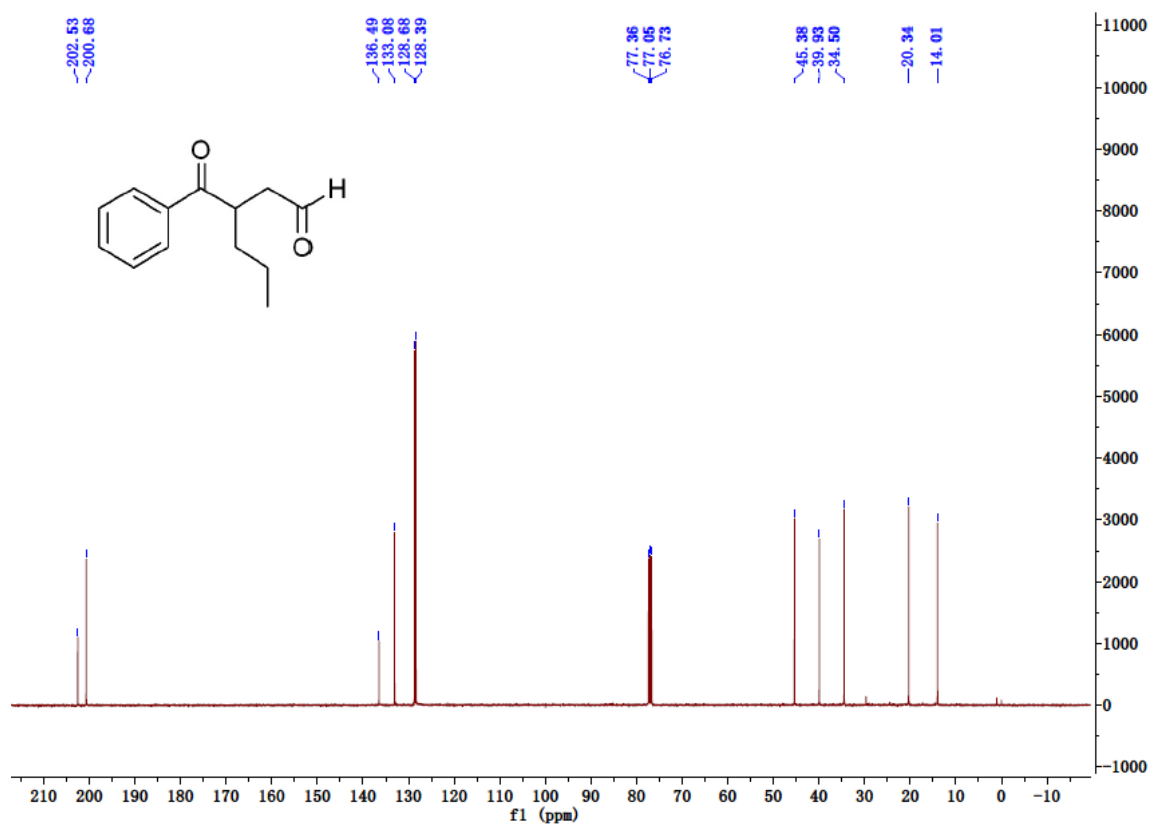
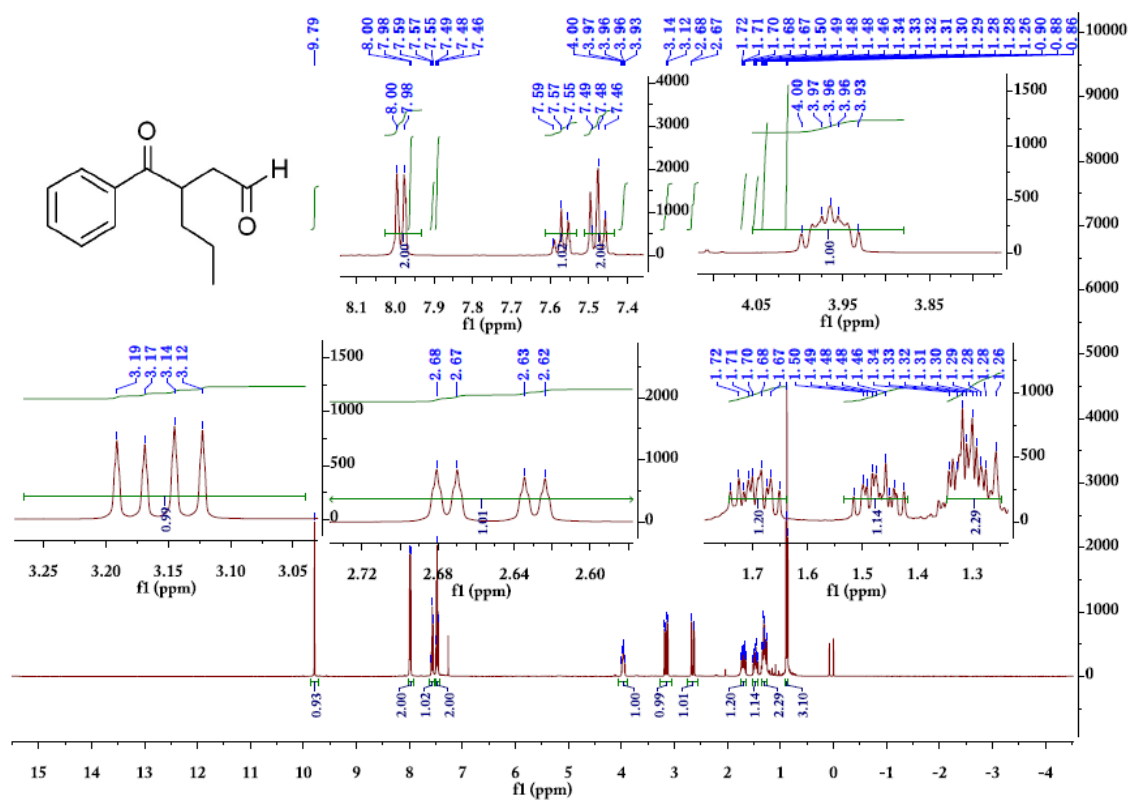
N,N-dimethyl-4-oxo-4-phenylbutanamide (2g)



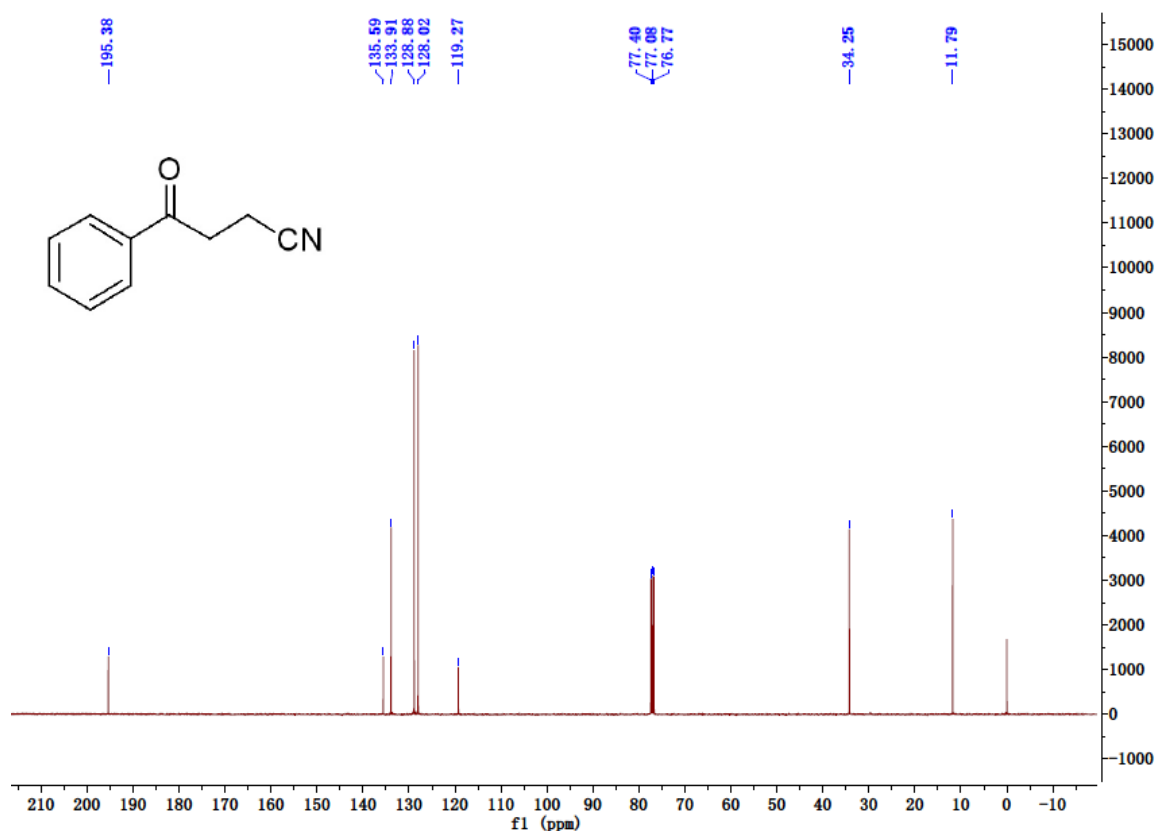
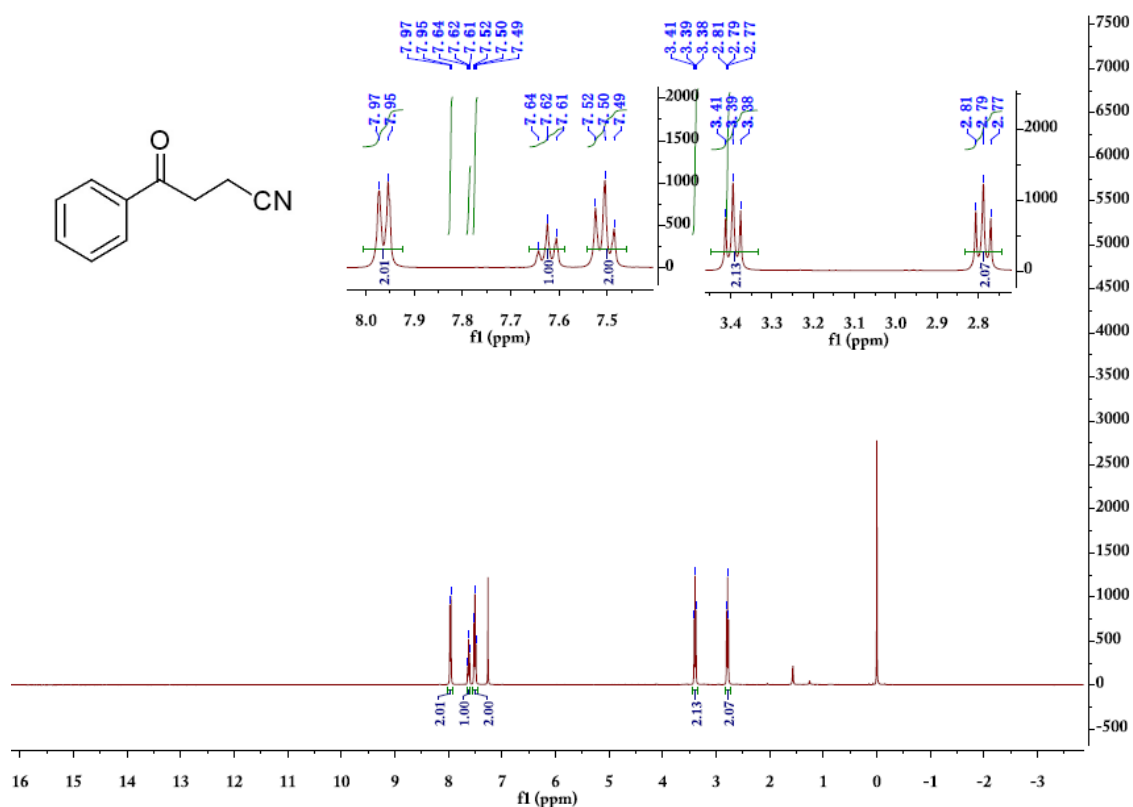
# 1-morpholino-4-phenylbutane-1,4-dione (2h)



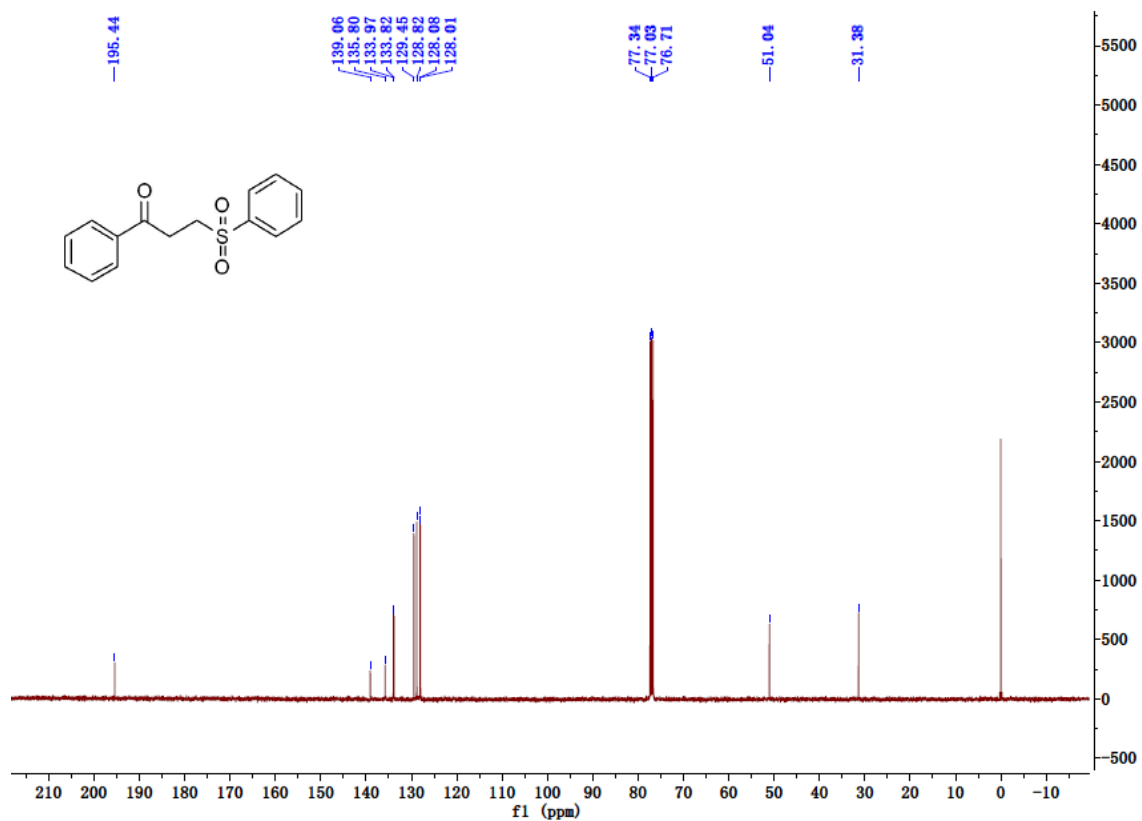
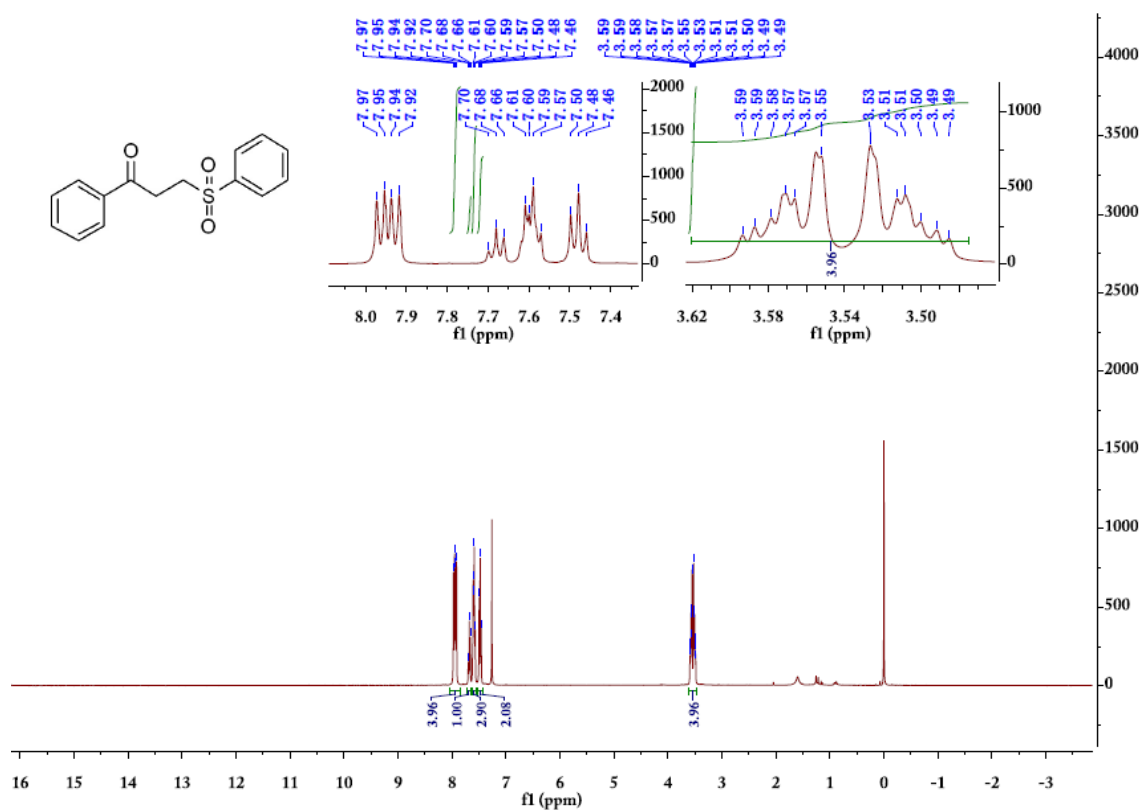
### 3-benzoylhexanal (2i)



# 4-oxo-4-phenylbutanenitrile (2j)

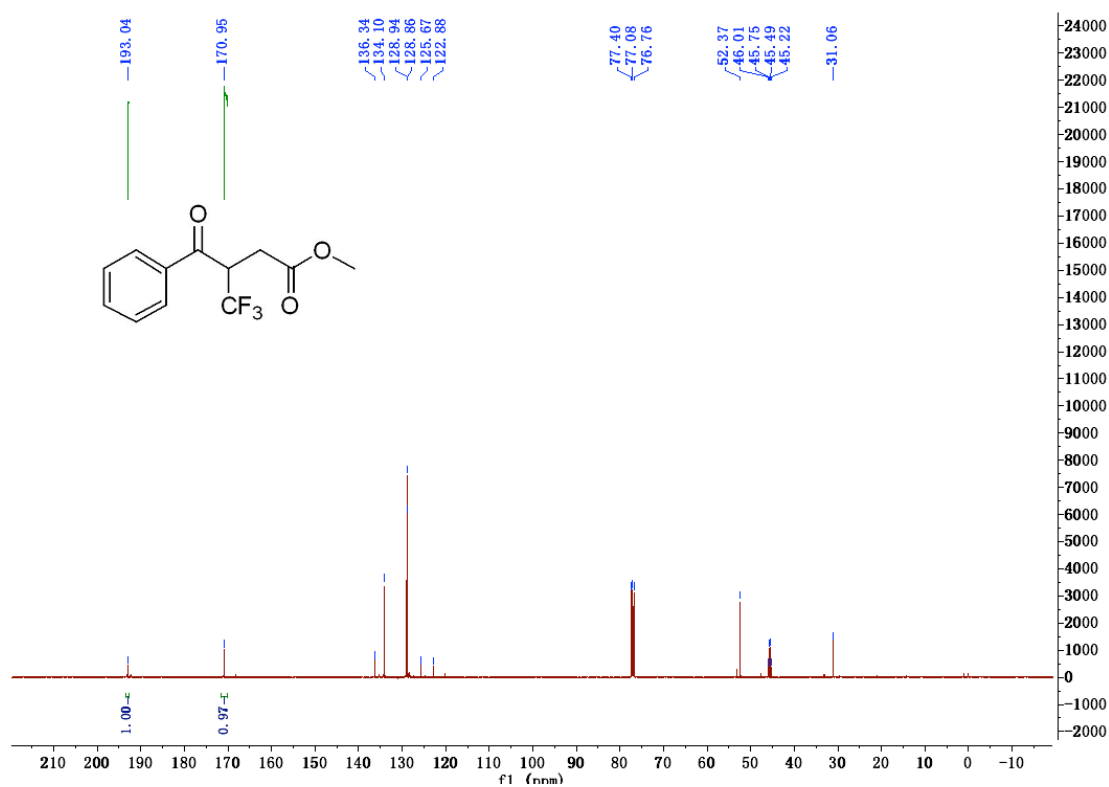
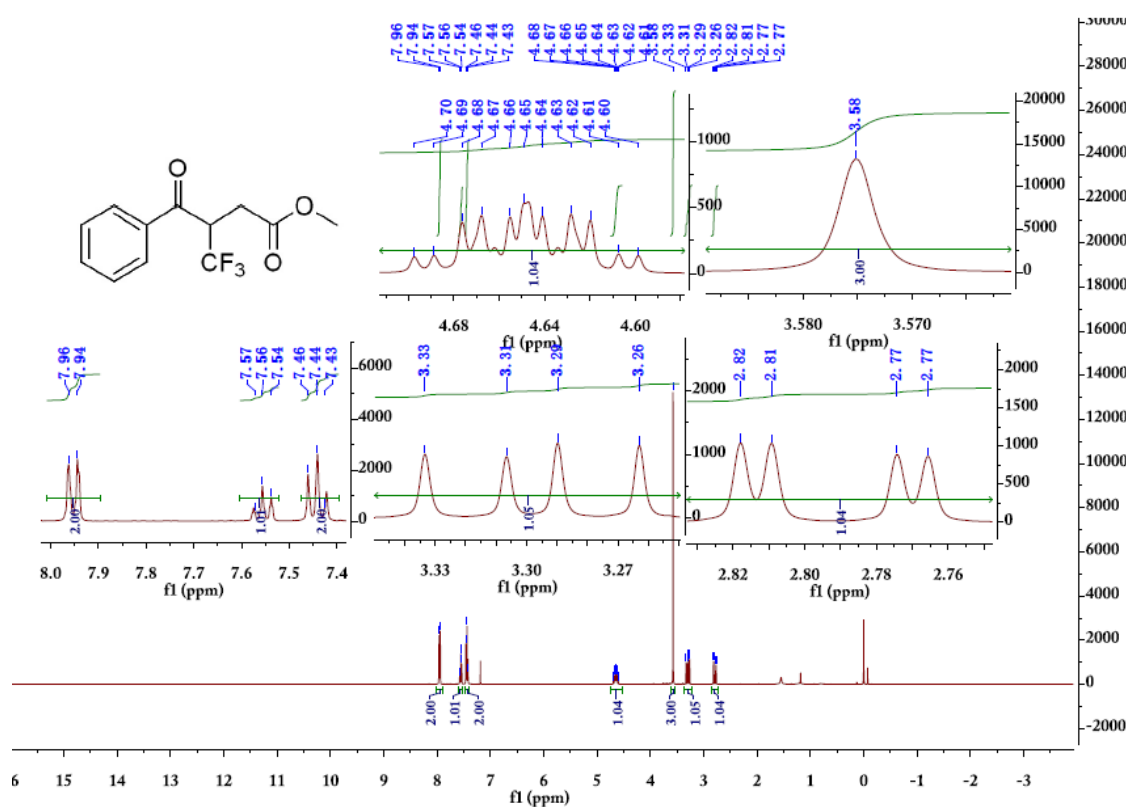


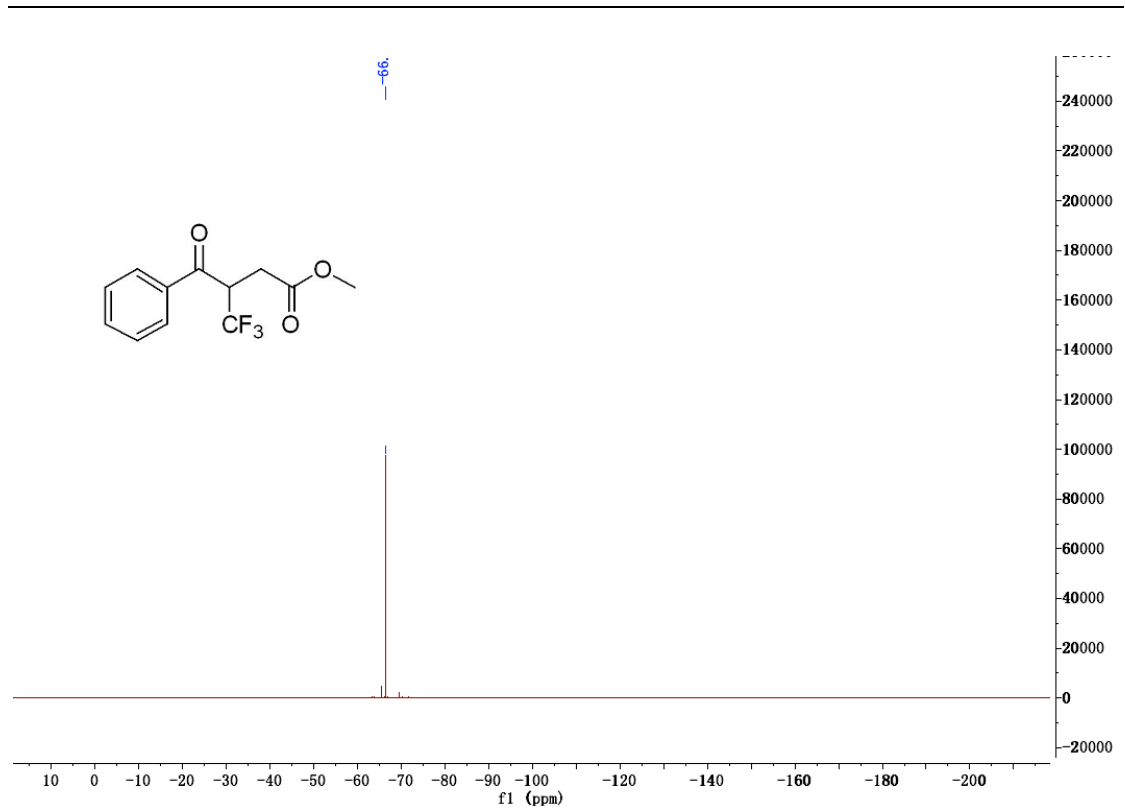
# 1-phenyl-3-(phenylsulfonyl)propan-1-one (2k)



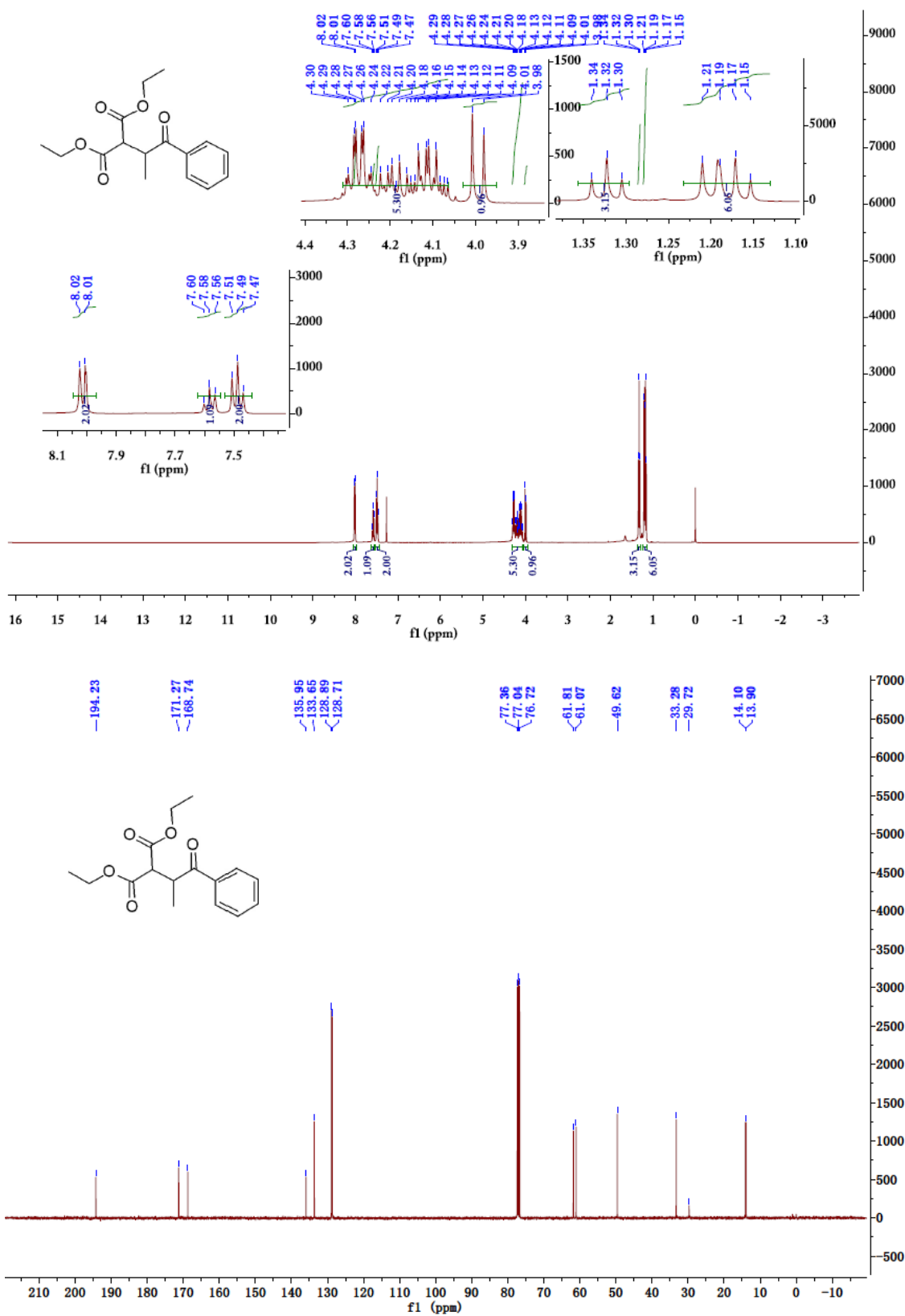


methyl 3-benzoyl-4,4,4-trifluorobutanoate (2l)

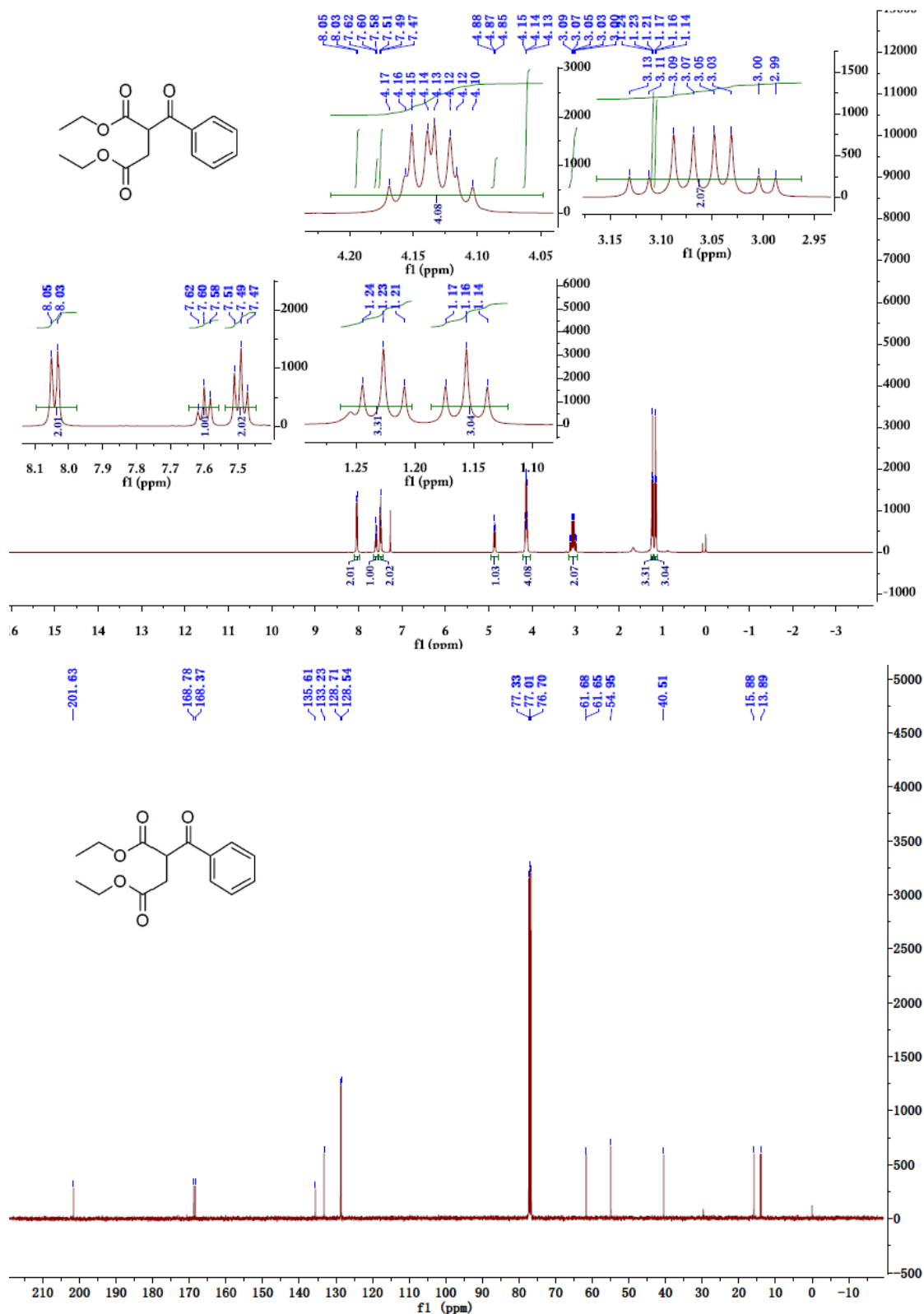




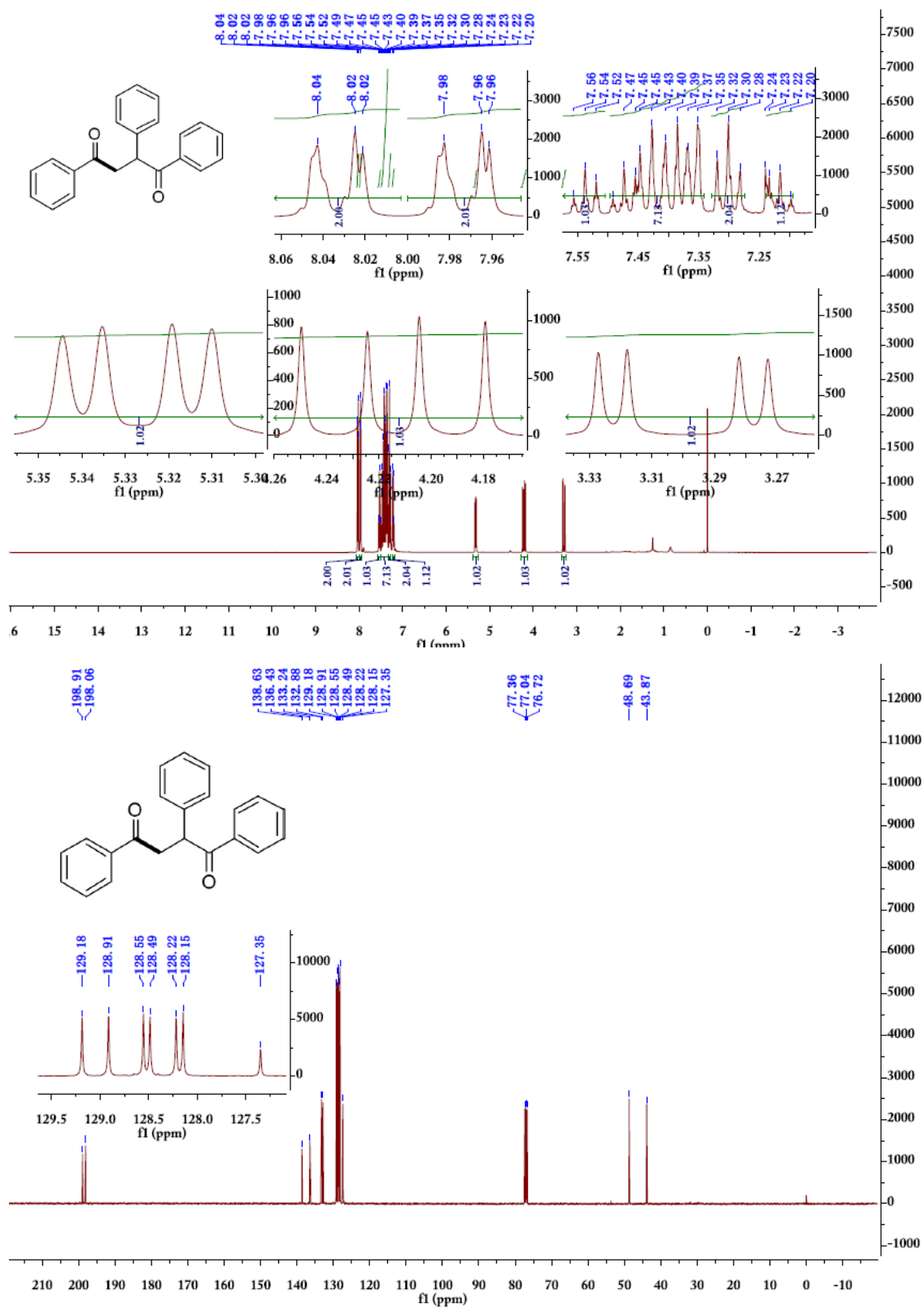
diethyl 2-(1-oxo-1-phenylpropan-2-yl)malonate (2m)



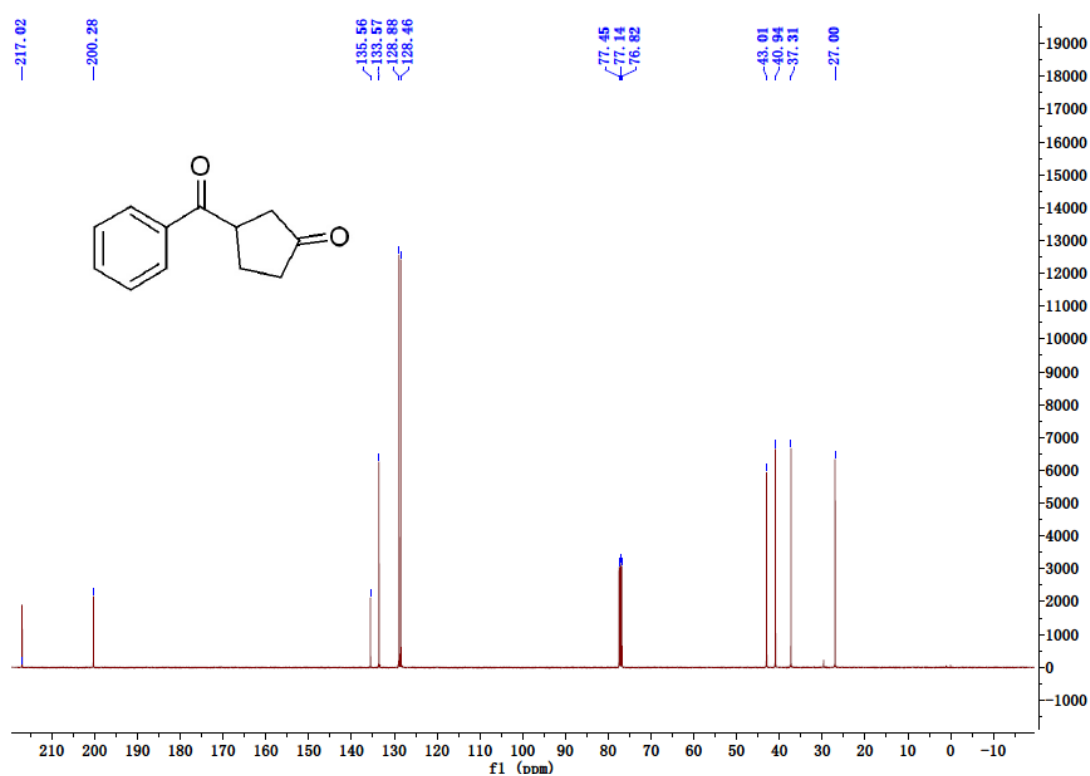
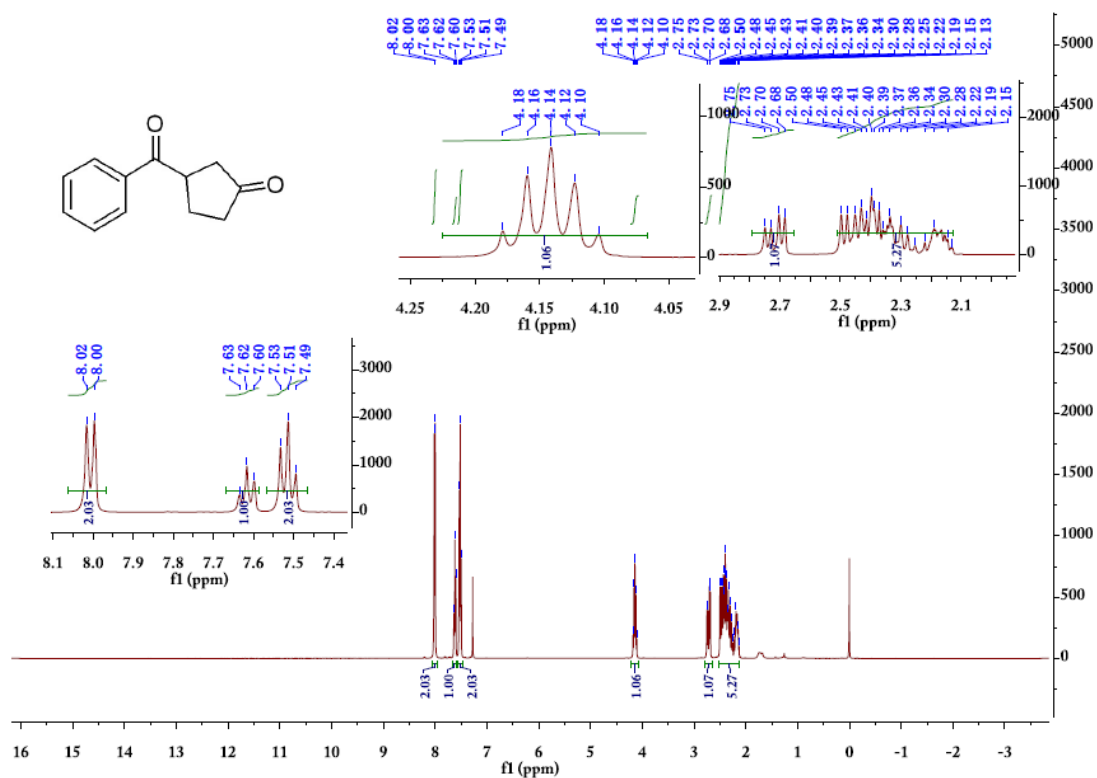
diethyl 2-benzoylsuccinate (2n)



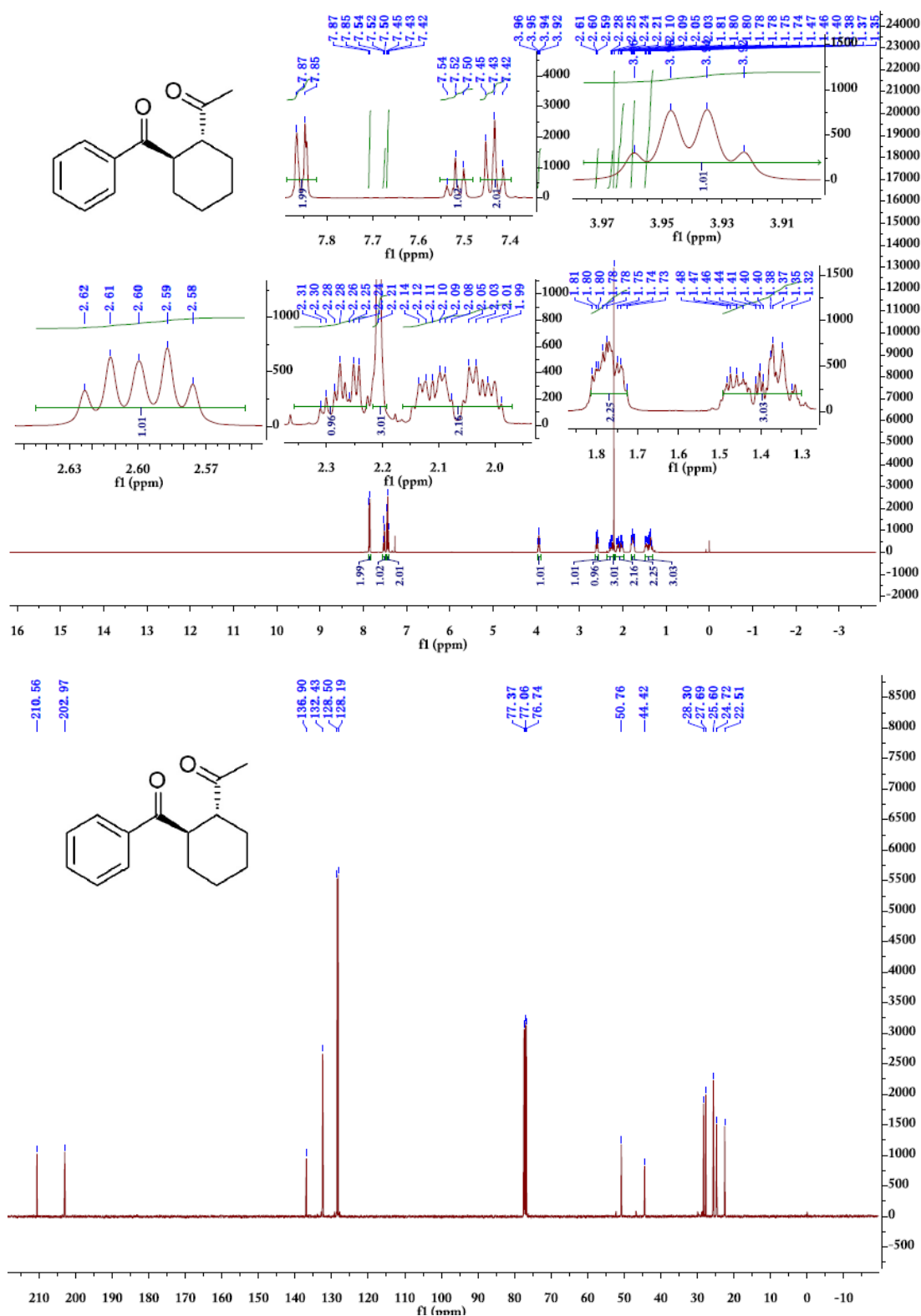
# 1,2,4-triphenylbutane-1,4dione (2o)

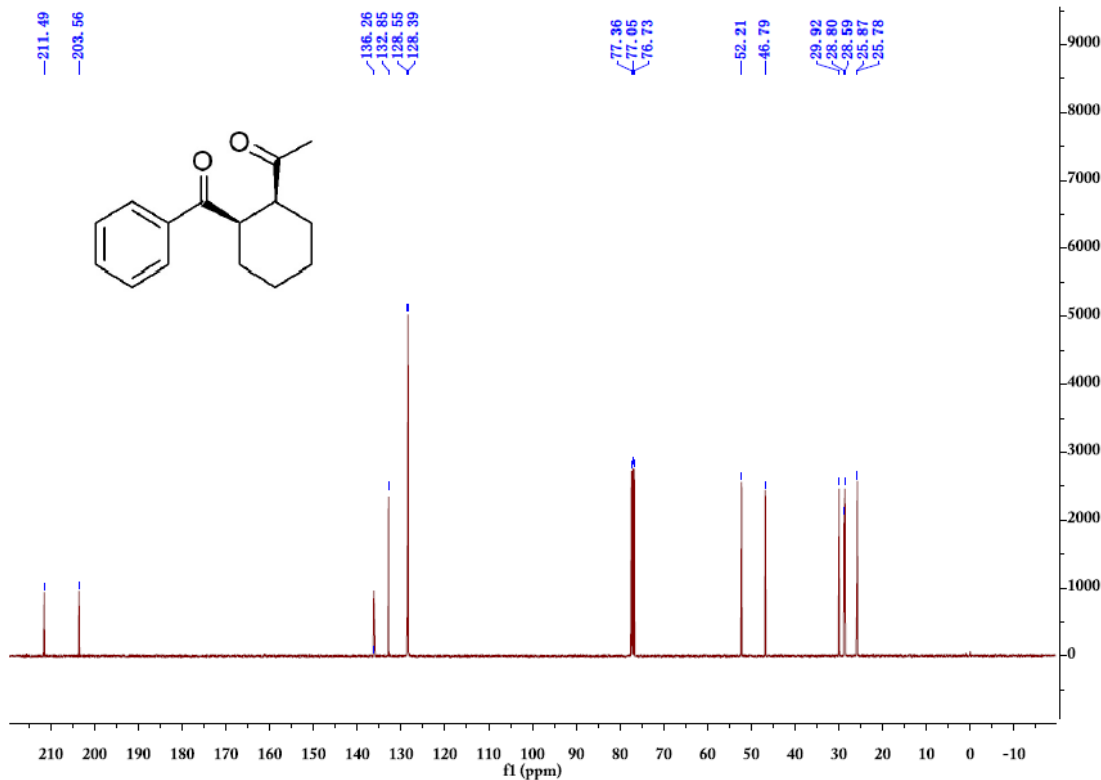


### 3-benzoylcyclopentanone (2p)



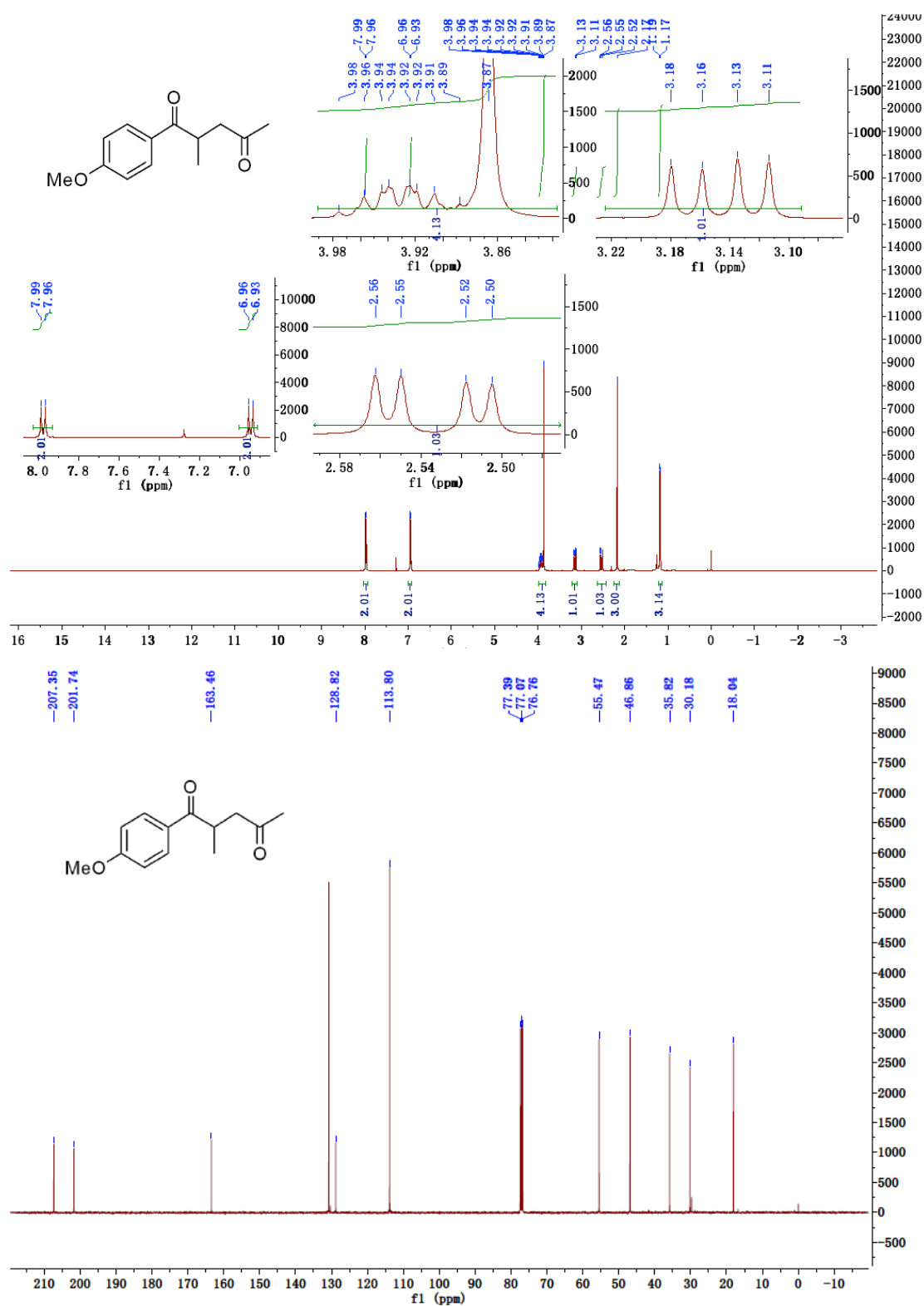
1-((1*R*,2*R*)-2-benzoylcyclohexyl)ethanone (2q, *trans*)



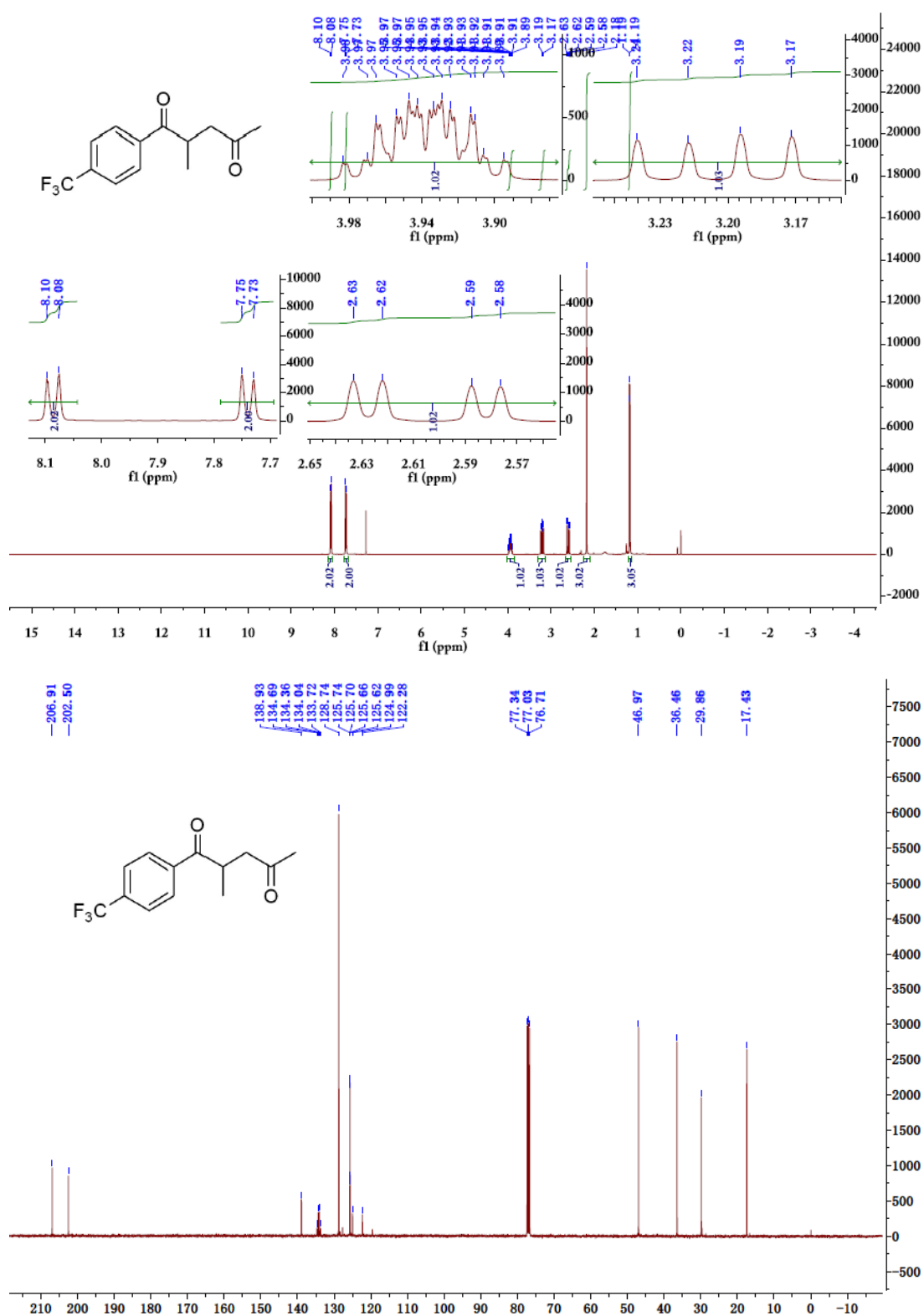


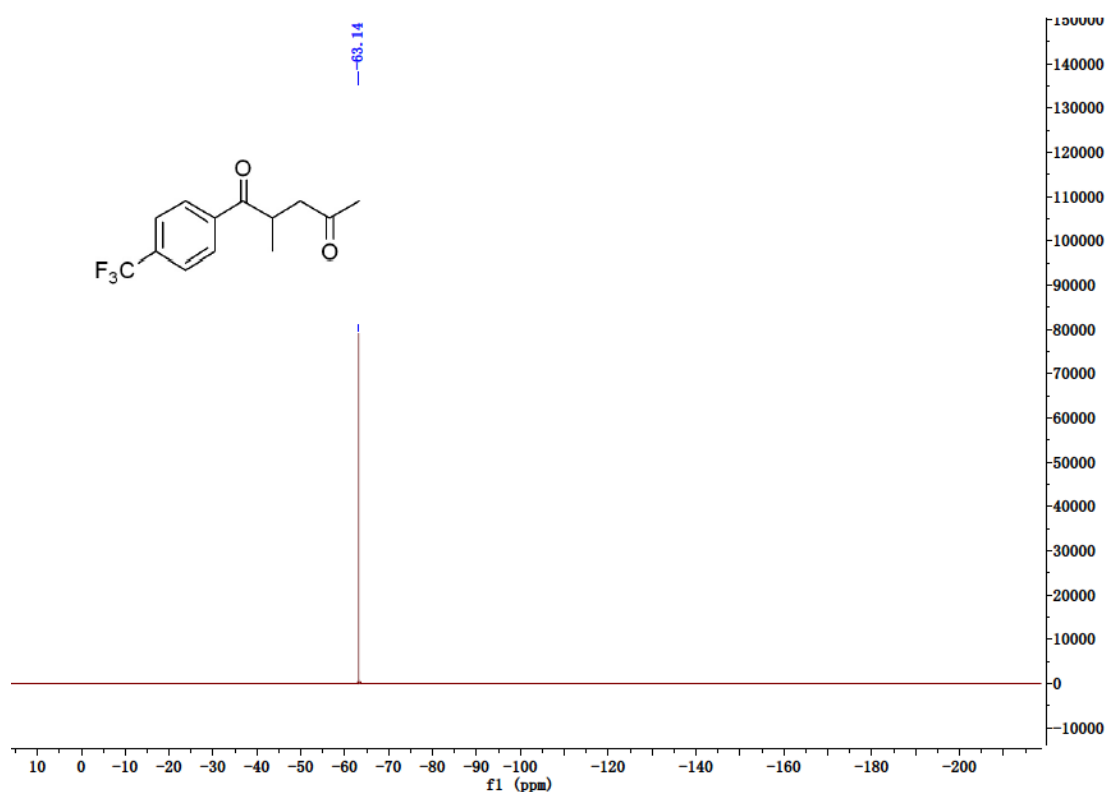


# 1-(4-methoxyphenyl)-2-methylpentane-1,4-dione (3a)

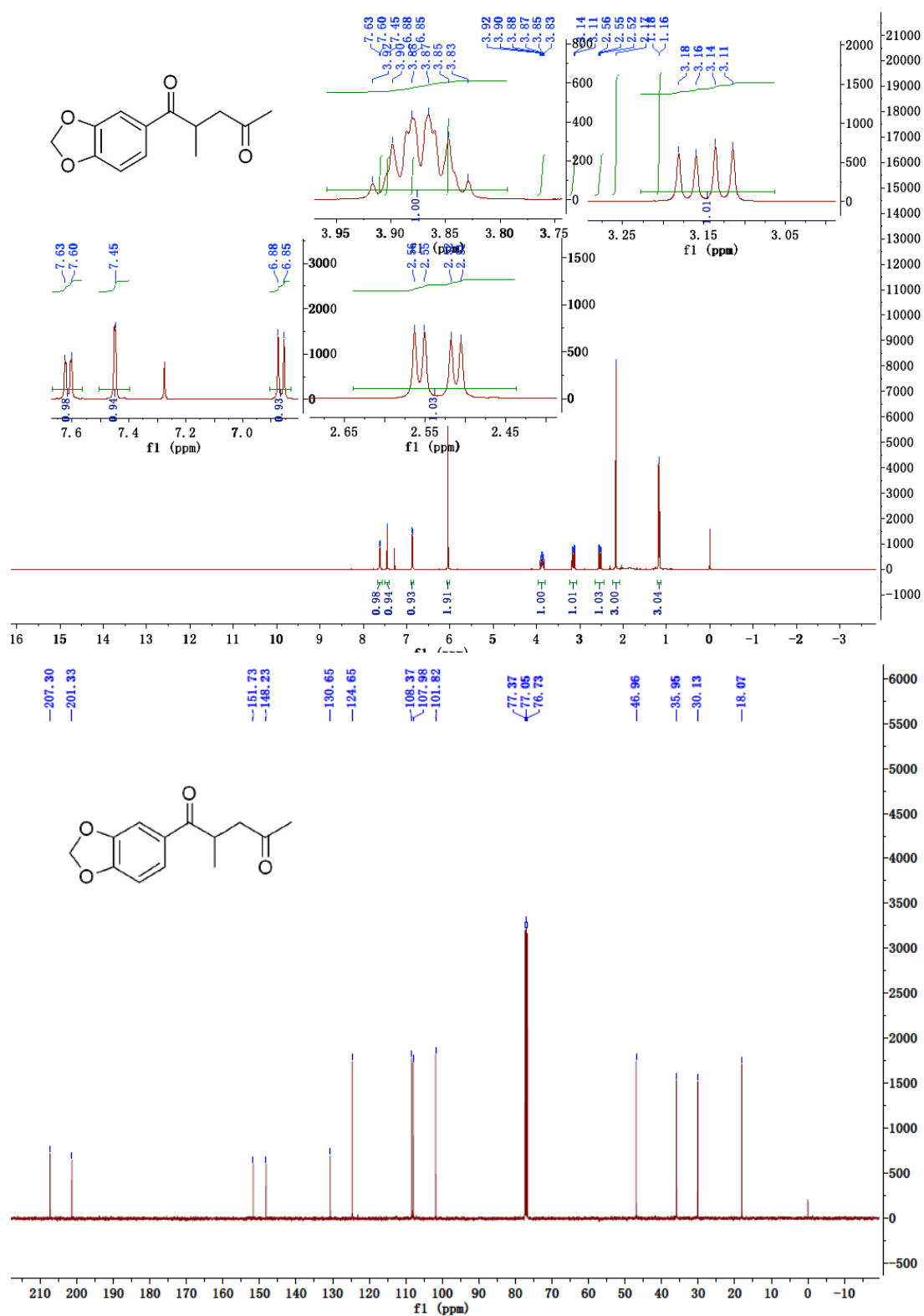


2-methyl-1-(4-(trifluoromethyl)phenyl)pentane-1,4-dione (3b)

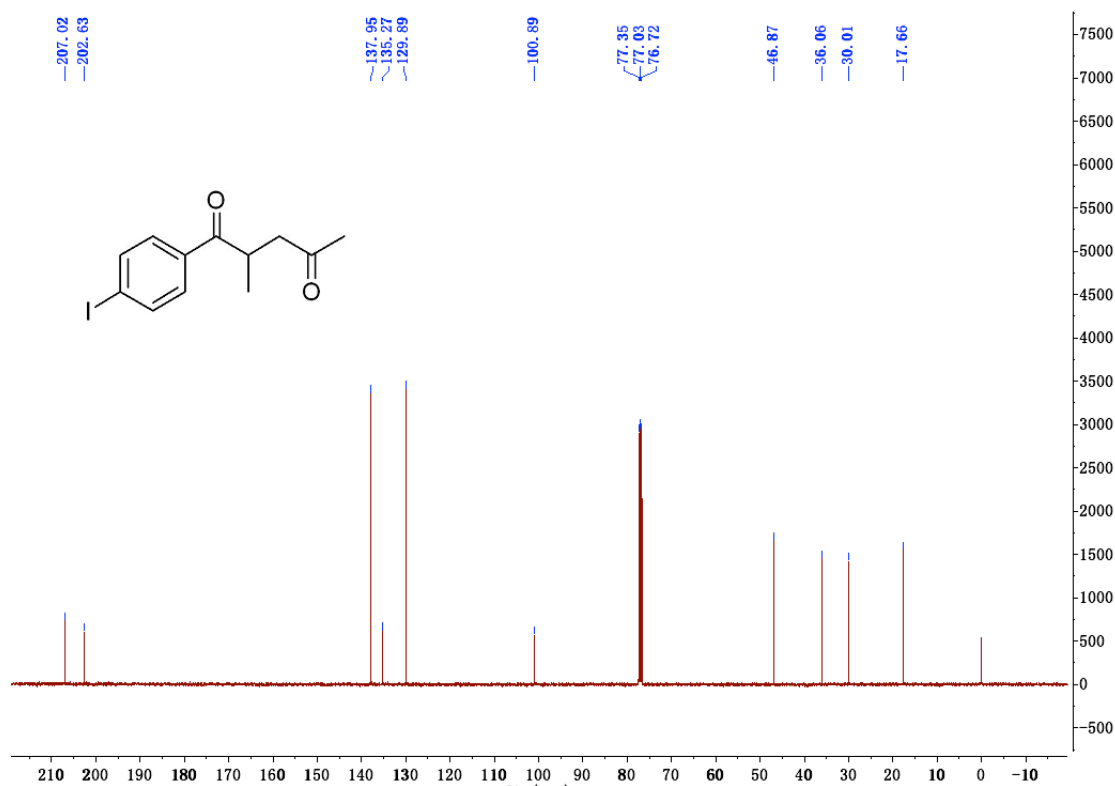
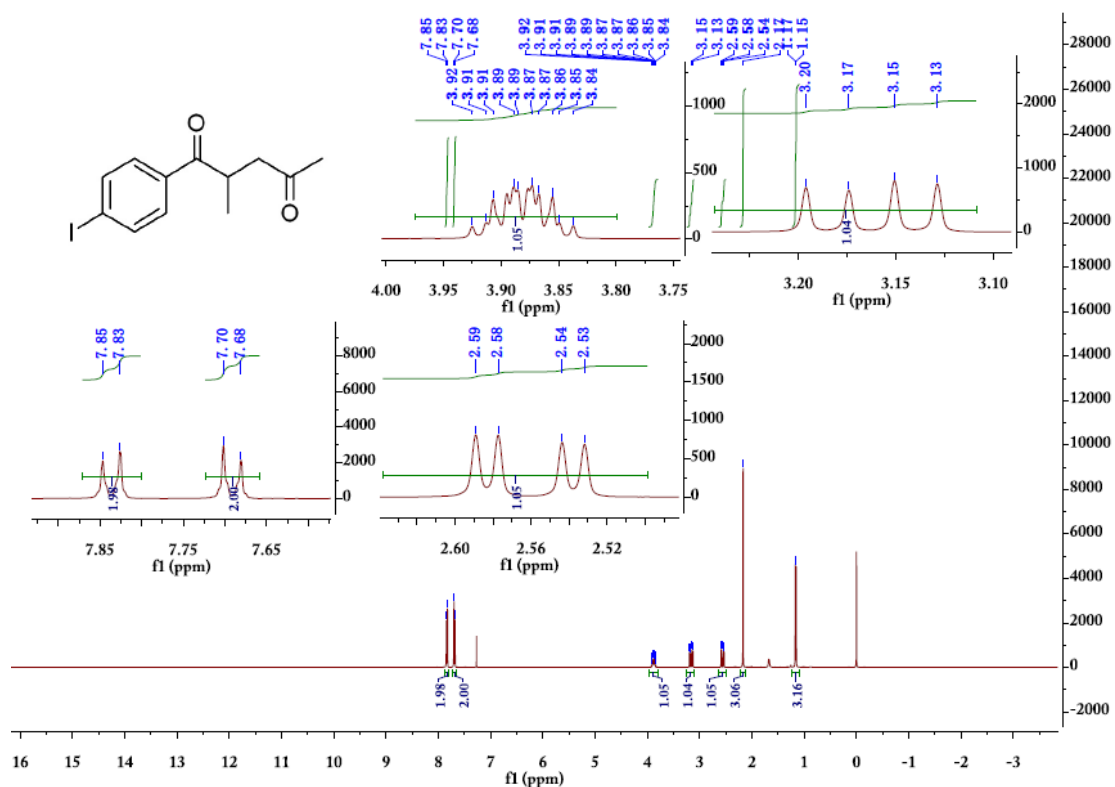




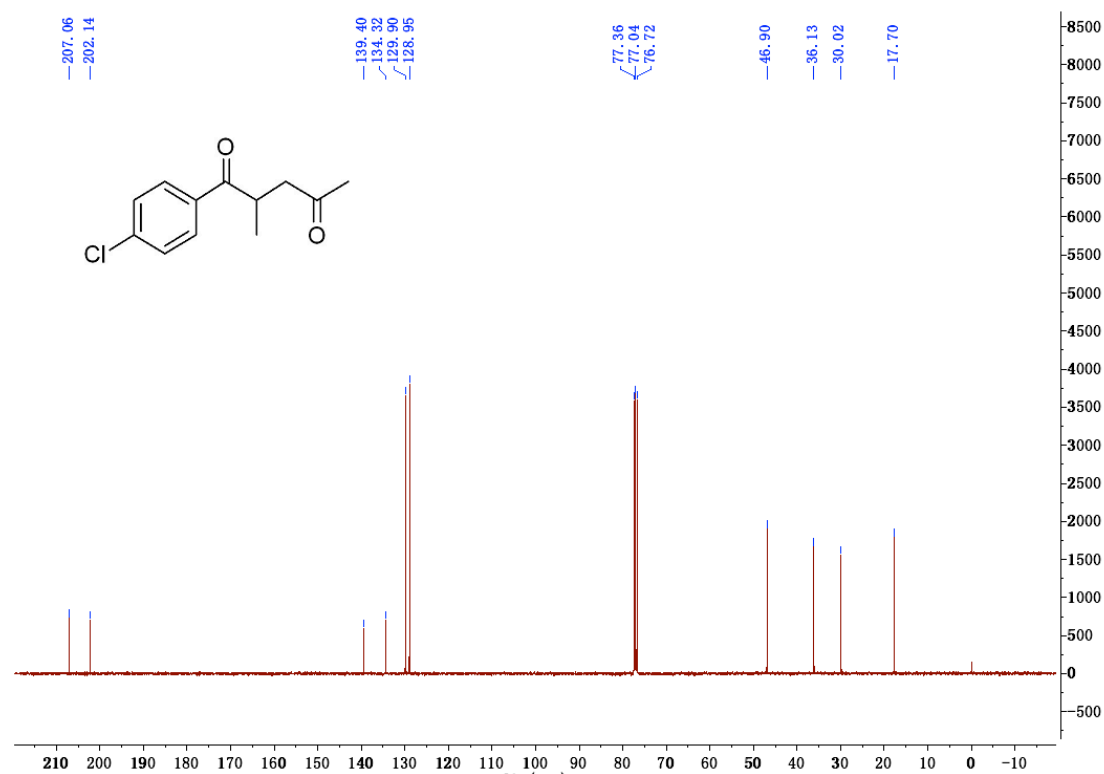
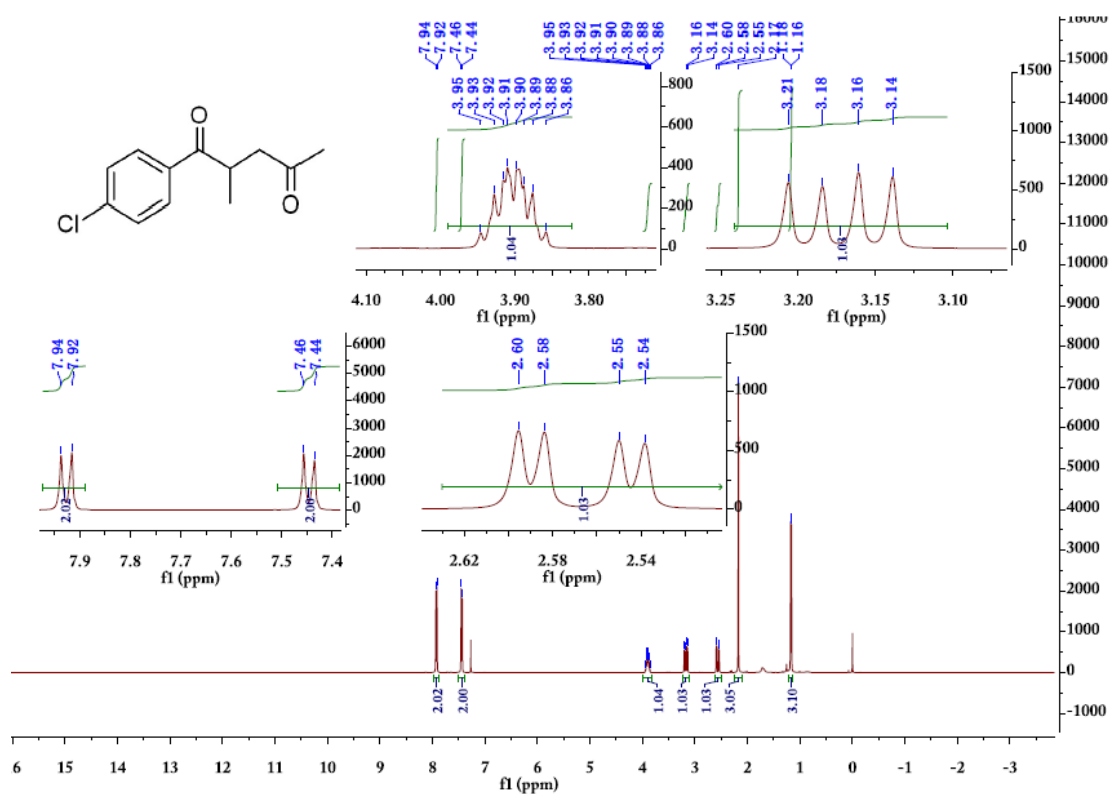
1-(furan-2-yl)-2-methylpentane-1,4-dione (3c)



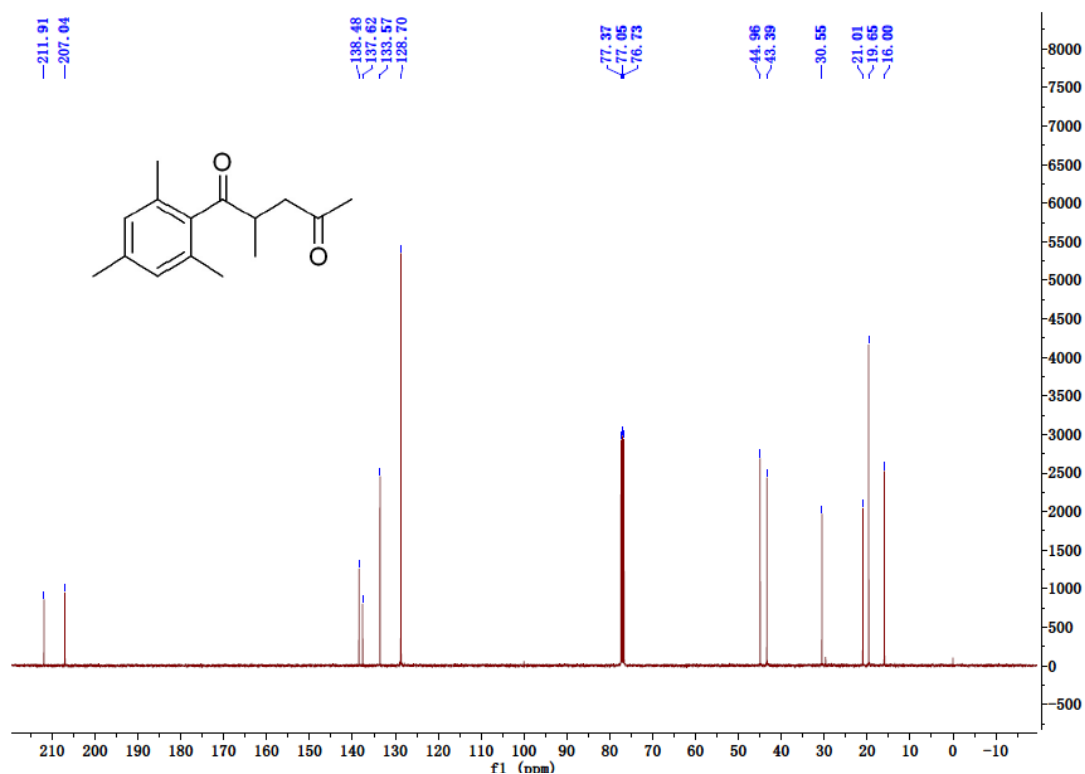
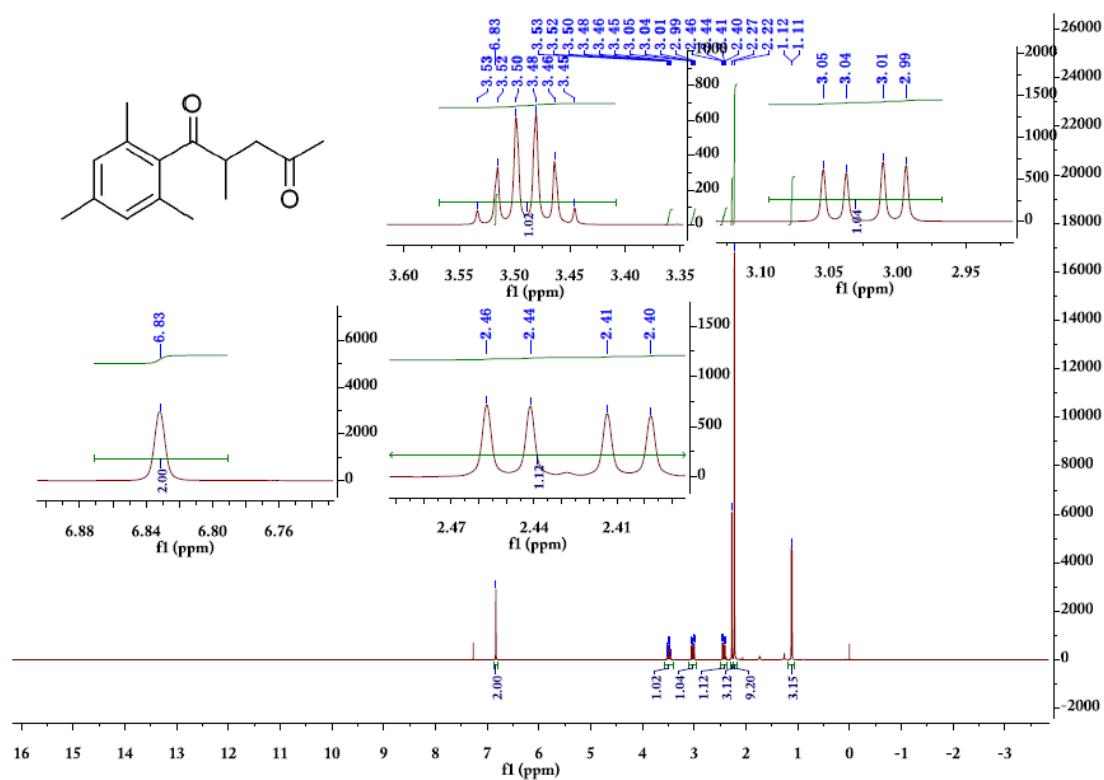
# 1-(4-iodophenyl)-2-methylpentane-1,4-dione (3d)



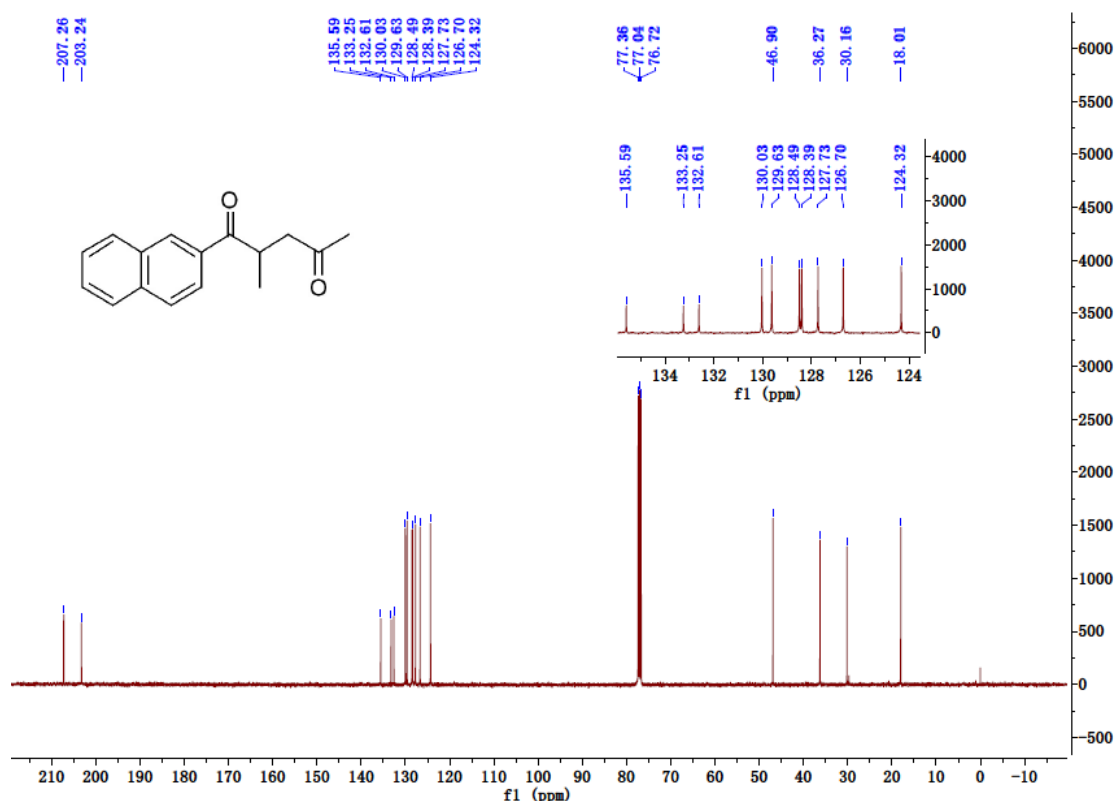
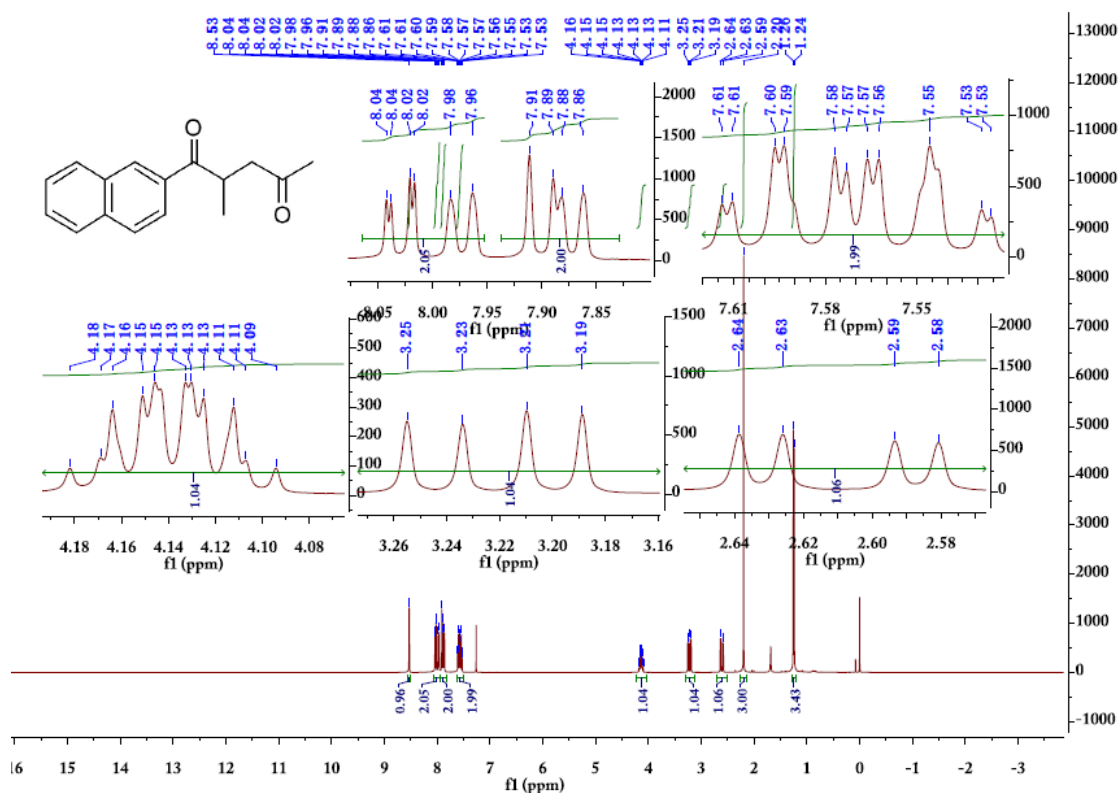
**1-(4-chlorophenyl)-2-methylpentane-1,4-dione (3e)**



# 1-mesityl-2-methylpentane-1,4-dione (3f)

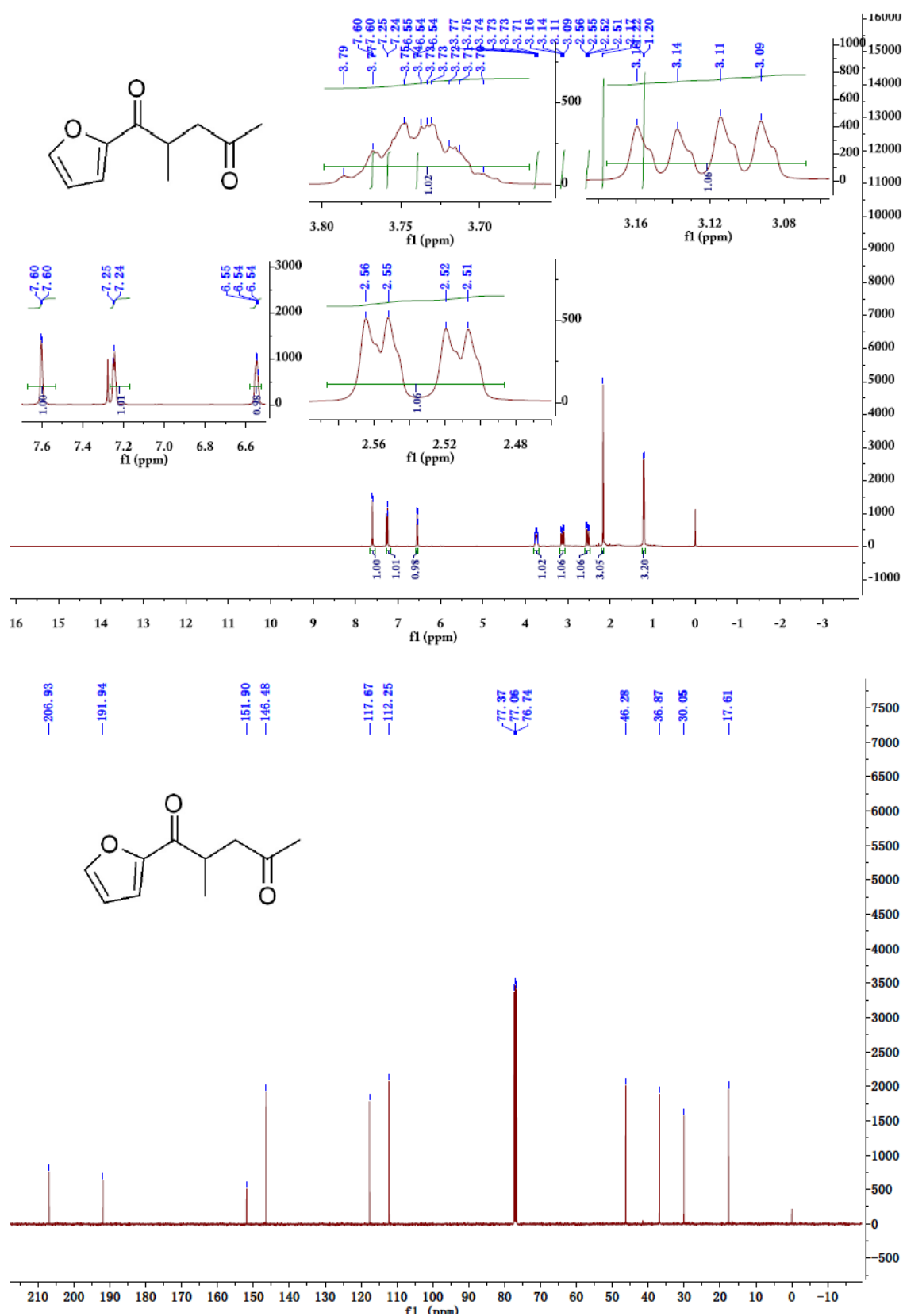


2-methyl-1-(naphthalen-2-yl)pentane-1,4-dione (3g)

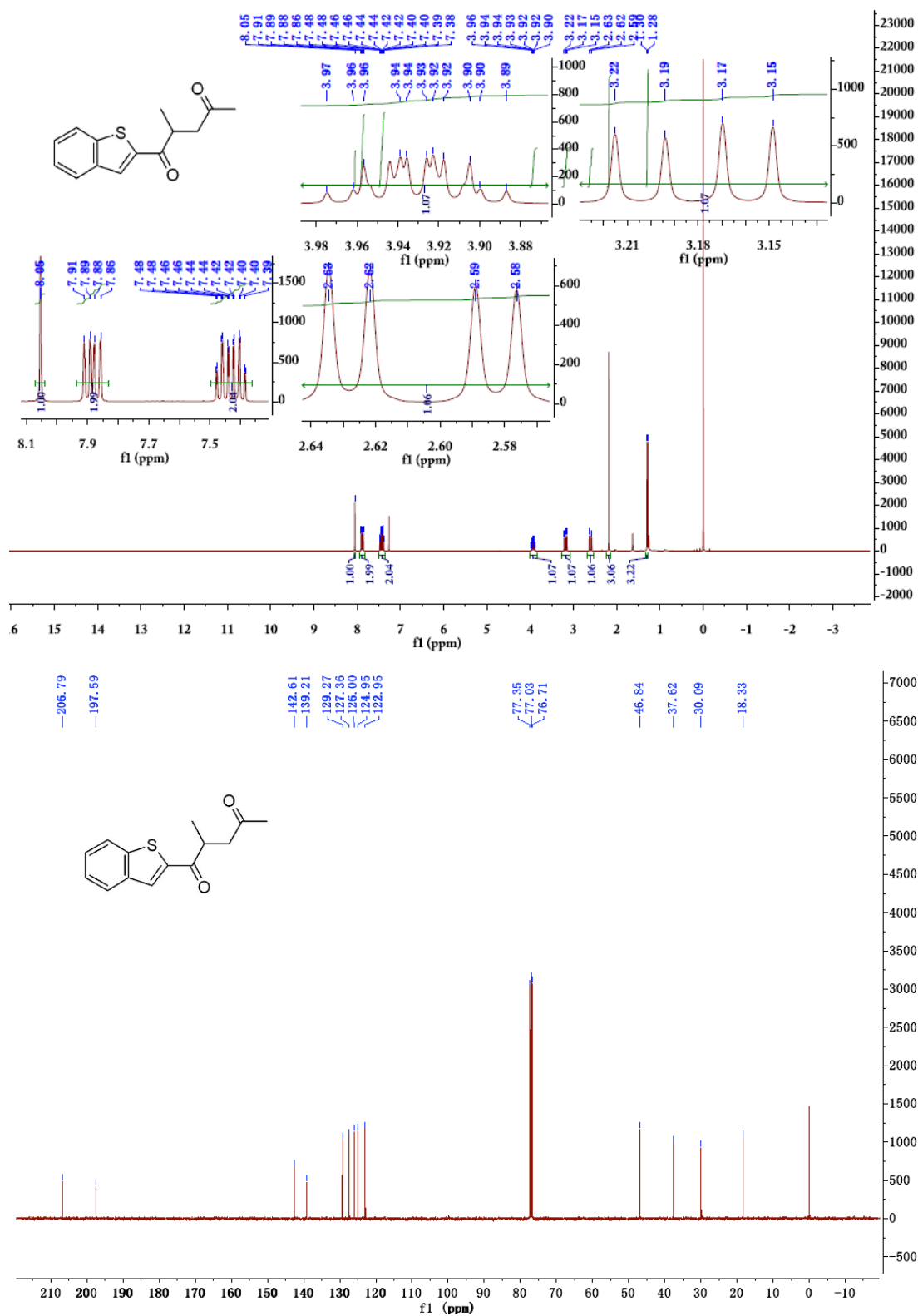




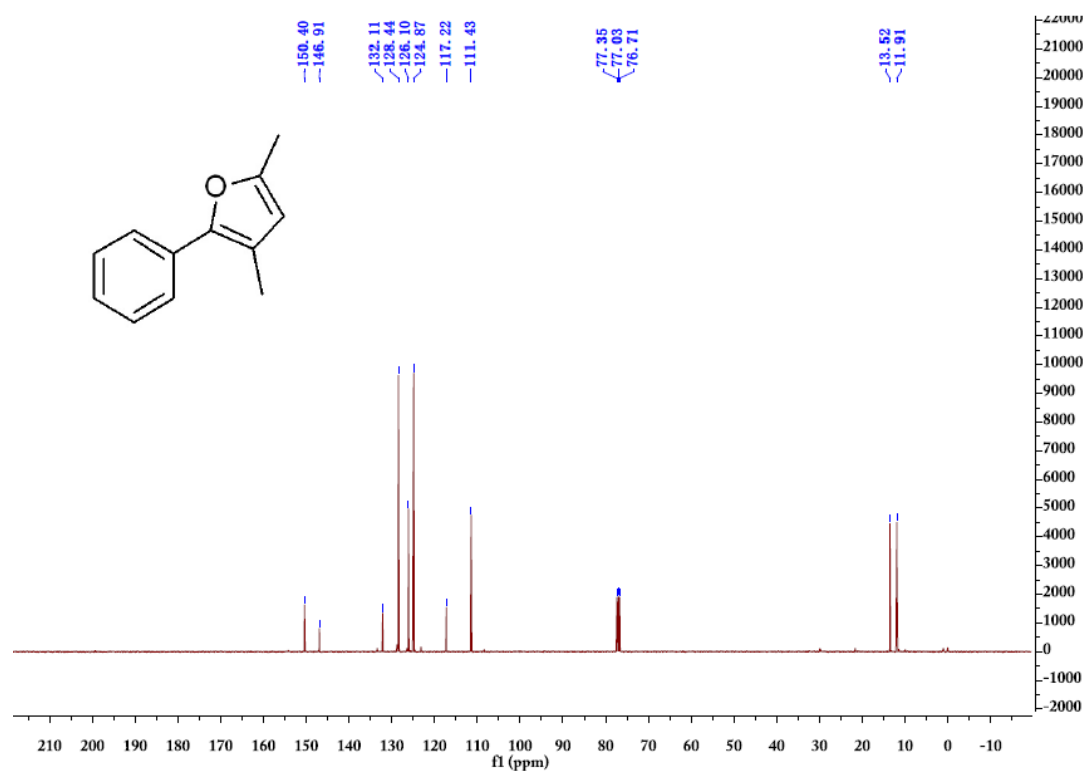
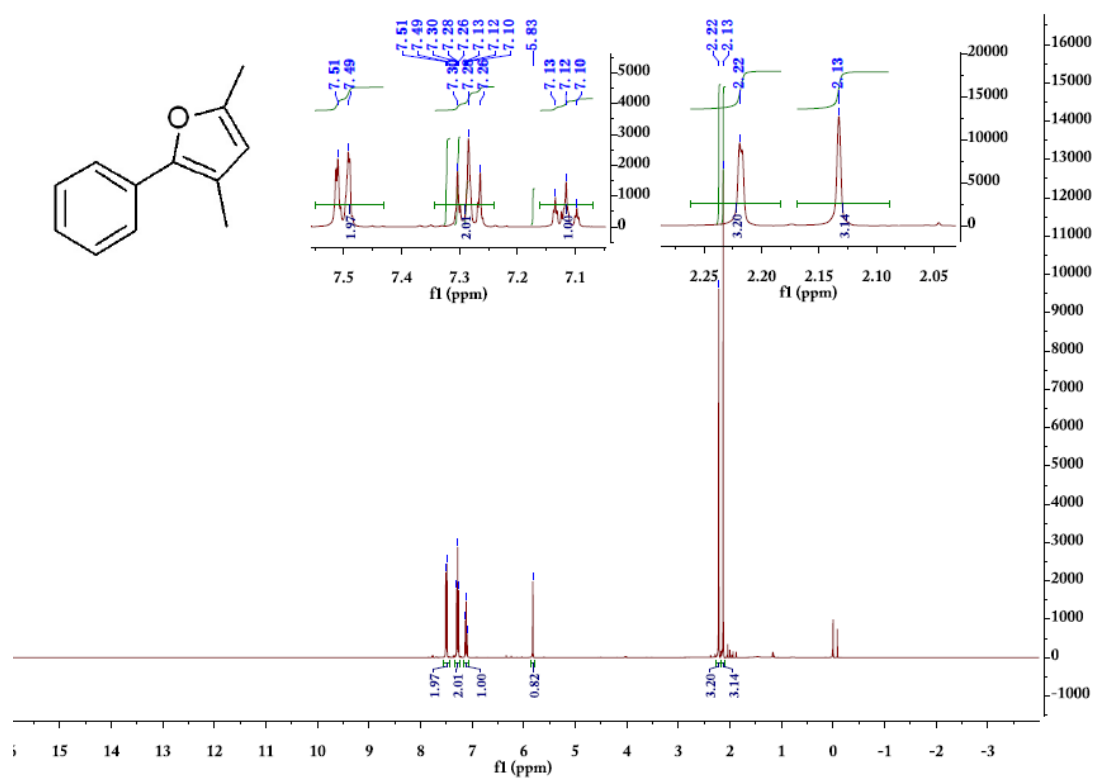
1-(furan-2-yl)-2-methylpentane-1,4-dione (3h)



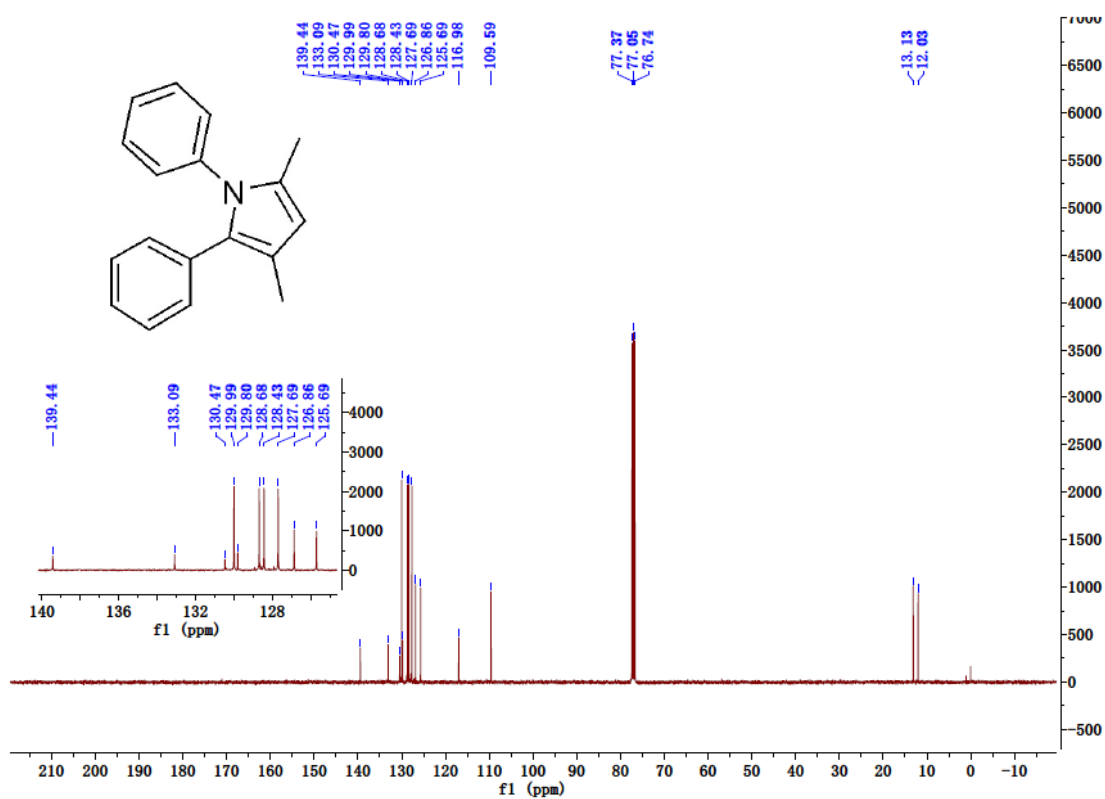
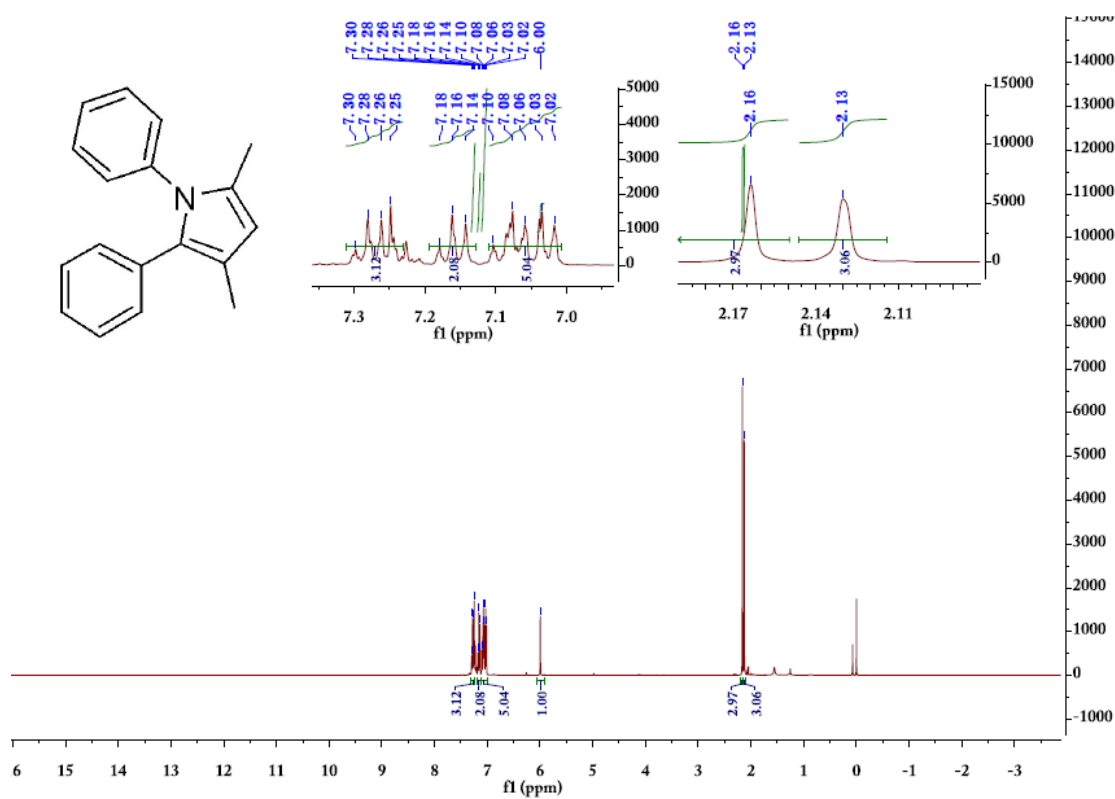
1-(benzo[b]thiophen-2-yl)-2-methylpentane-1,4-dione (3i)



### 3,5-dimethyl-2-phenylfuran (5)



### 3,5-dimethyl-1,2-diphenyl-1H-pyrrole (6)



2,2,6,6-tetramethylpiperidin-1-yl benzoate (7)

