

## Supporting information

### **Polyelectrolyte Brønsted acid catalyzed three-component Mannich reactions accelerated by emulsion**

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Dedication (Xi Chen and Yanlong Luo are the same important to this article)

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## **1. Materials and methods**

### **1.1. Materials and characterization**

All the chemicals and reagents used are of analytical grade and were used without further purification. The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were detected on a Bruker Avance 400 MHz spectrometer in  $\text{CDCl}_3$  with tetramethylsilane as internal standard. The optical micrographs of the emulsions on transparent glass slides were taken using a BM2000 microscope (Nanjing Jiangnan Novel Optics Co., Ltd, China). The stability of the emulsions was measured using Turbiscan Lab Expert (manufactured by Formulaction, France).

### **1.2. General procedure for Mannich reaction catalyzed by PAA**

The PAA (0.075 mmol) was stirred in 1 mL  $\text{H}_2\text{O}$  for 10 minutes at 25 °C, 5 mmol ketone was added into the mixture under vigorous stirring, resulting in an emulsion. Aldehyde (1 mmol) and aniline (1.1 mmol) was added into the emulsion and the reaction mixture was vigorously stirred at 25 °C for 6-12 h. The reaction mixture was then treated with 5 mL chloroform, and the layers were separated. The PAA remained in the aqueous phase, which is used for next cycle. Then the organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated. Purification by silica gel column chromatography gave the pure Mannich product.

### **1.3. The recyclability of catalyst**

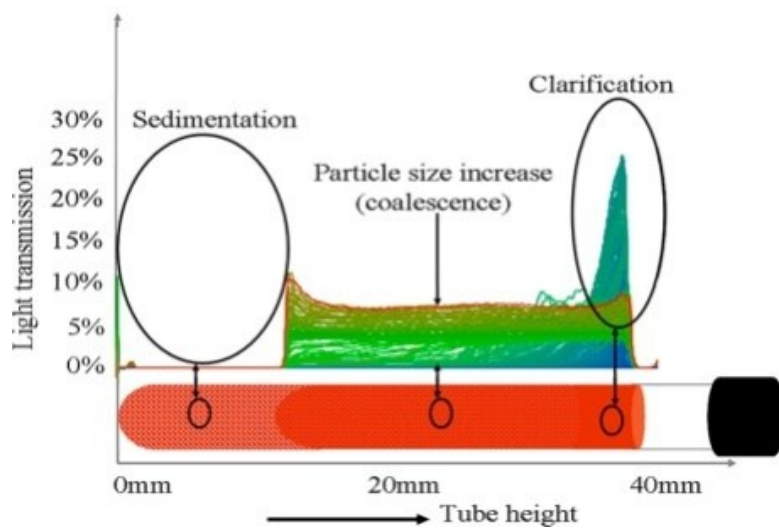
In contrast, the PAA remained in the aqueous phase. Then 5 mmol cyclohexanone was added under vigorous stirring, resulting in an emulsion. Aldehyde (1 mmol) and aniline (1.1 mmol) was added into the emulsion and the reaction mixture was vigorously stirred at 25 °C for 6h. After the completion of the reaction, the reaction mixture was then treated with 5 mL chloroform, and the layers were separated. The aqueous phase was then directly transferred to another flask along with fresh reagents for the next run. This procedure was repeated for every run.

### **1.4. The stability of emulsion**

Aldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5 mmol),  $\text{H}_2\text{O}$  (1 mL) and PAA (0.075 mmol) were mixed with magnetic stirring for 30 min, then the emulsion was used for stability investigation.

The measurement principle for this technique is based on detecting the changes in transmission and backscattering, as a function of particle movements (creaming). When the sample is interrogated using near-infrared light, objects in suspension

(droplets) scatter the light, which are subsequently detected by the Turbiscan instrument. Similarly, it detects the light that is transmitted when there are fewer or no absorbing particles (see Fig S1). The intensity of transmission or backscattering depends on the amount of particles that are suspended. By using Turbiscan Lab Expert, in combination with the Turbiscan EASYSOFT 2005 software packages (manufactured by Formulacion, France), information such as sedimentation kinetics, creaming kinetics, clarification kinetics, migration velocity, phase fraction, Turbiscan stability index (TSI), etc can be acquired based on transmission and backscattering profiles.



**Fig. S1** Example of a Turbiscan transmission profile.

The way of calculating TSI is given in the following formula:

$$TSI = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{BS})^2}{n - 1}}$$

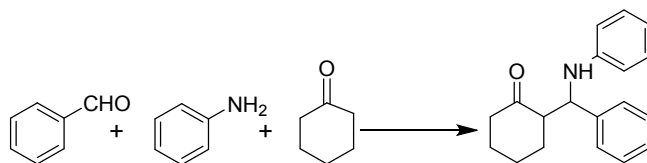
Where:

$x_i$  is the backscattering for each 10 minutes of measurement,  $x_{BS}$  is the average  $x_i$ , and  $n$  is the number of scans.

In this study, the samples were scanned every 10 min for 1.5 h. The measurements were performed at 25°C.

## 2. Reaction conditions of Mannich reaction

**Table S1.** Effects of the amount of catalyst and reaction time on the Mannich reaction<sup>a</sup>

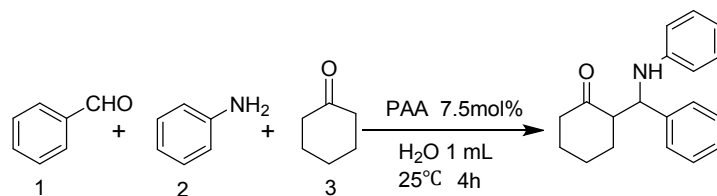


Entry	Amount of catalyst/mmol	Temperature/°C	Yield/% <sup>b</sup>
1	0.005	25	7
2	0.025	25	20
3	0.05	25	26
4	0.075	25	33
5	0.10	25	34
6	0.125	25	35
7	0.075	30	31
8	0.075	35	27
9	0.075	40	21
10	0.075	45	14
11	0.075	50	10
12	0.075	55	7

<sup>a</sup>Reaction conditions: 1.0 mmol benzaldehyde, 1.0 mmol aniline and 1.0 mmol cyclohexanone, 1.0 mL H<sub>2</sub>O, 4h; <sup>b</sup>Isolated yields were obtained after purification by column chromatography.

Table S1 showed the effect of the catalyst amount with increasing of the molar ratio of catalyst PAA. When the loading of catalyst increased from 1 mol% to 7.5 mol%, the yield of product increased sharply from 7% to 33%. At a catalyst loading of 7.5 mol%, the best result could be obtained. Further increasing the amount of catalyst, the yield increased slightly. Therefore 7.5 mol% was selected as the best loading of catalyst amount. Subsequently, we checked the effect of temperature on the progress of the reaction. According to the above figure, we could see that as the temperature increased the yield decreased, because Aldol products increased with temperature increasing, so the optimum temperature was 25°C.

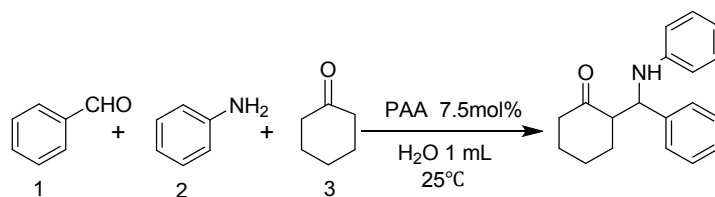
**Table S2.** Effect of substrate concentration on the rate of PAA-catalyzed direct Mannich reaction<sup>a</sup>



Entry	1/2/3	1 (mmol)	2 (mmol)	3 (mmol)	Yield /% <sup>a</sup>
1	1:1:1	1	1	1	33
2	2:1:1	2	1	1	20
3	3:1:1	3	1	1	5
4	4:1:1	4	1	1	13
5	1:1.1:1	1	1.1	1	43
6	1:1.2:1	1	1.2	1	40
7	1:1.3:1	1	1.3	1	37
8	1:1.4:1	1	1.4	1	32
9	1:1.5:2	1	1.5	1	26
10	1:1.1:2	1	1.1	2	54
11	1:1.1:3	1	1.1	3	63
12	1:1.1:4	1	1.1	4	70
13	1:1.1:5	1	1.1	5	77
14	1:1.1:6	1	1.1	6	75
15	1:1.1:7	1	1.1	7	71
16	1:1.1:8	1	1.1	8	64
17	1:1.1:9	1	1.1	9	51
18	1:1.1:10	1	1.1	10	40

<sup>a</sup>Isolated yields were obtained after purification by column chromatography.

The ratio of substrate was shown in Table S2. From this table, we can see the optimal ratio of benzaldehyde, aniline and cyclohexanone were 1:1.1:5.

**Table S3.** Effect of the reaction time on Mannich reaction<sup>a</sup>

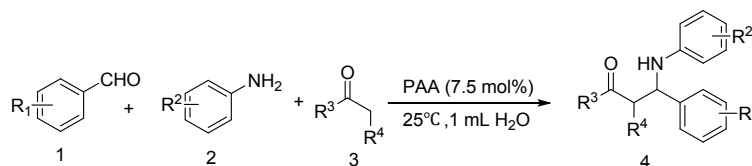
Entry	Time(h)	Yield(%) <sup>b</sup>
1	2	31
2	4	77
3	6	92
4	8	93
5	10	93

<sup>a</sup>Reaction conditions: 1.0 mmol benzaldehyde, 1.1 mmol aniline and 5.0 mmol cyclohexanone, 1.0 mL H<sub>2</sub>O; <sup>b</sup>Isolated yields were obtained after purification by column chromatography.

The effect of reaction time on the yield was also investigated as shown in Table S3. An increase in conversion was observed as the reaction time increased from 2h to 10 h. Further the product yield increased slightly with the reaction time increasing. This finding could be explained by the fact that the Mannich reaction reached equilibrium in approximately 6 h. As such, 6 h was considered the ideal reaction time.

### 3. Polyelectrolyte Brønsted acid catalyzed three-component Mannich reactions with some more ketones

Various ketones were further investigated to demonstrate the pronounced accelerating effect on Mannich reactions. (Table S4) The results are presented in Table 2 and Table S4. When acetophenones were used, the yields of 85% and 79% were afforded, respectively. (Table S4, Entry 1 and 2) The reaction also worked well with cycloalkanones other than cyclohexanone under the same conditions. (Table S4, Entry 13-18) The Mannich condensation of open chain ketones including acetone and 2-pentanone with benzaldehydes and aniline or *p*-methoxyaniline afforded the products in 36%, 27%, 81% and 88% yields. The yield with acetone is obviously slower than 2-pentanone and acetophenone because the emulsion could not form during the reaction. (Table S4, Entry 3-12) This hypothesis was further supported by the polarized microscope images, such as acetophenone (Fig. S2), acetone (Fig. S3), 2-butanone (Fig. S4), 2-pentanone (Fig. S5) and cyclobutanone (Fig. S6).

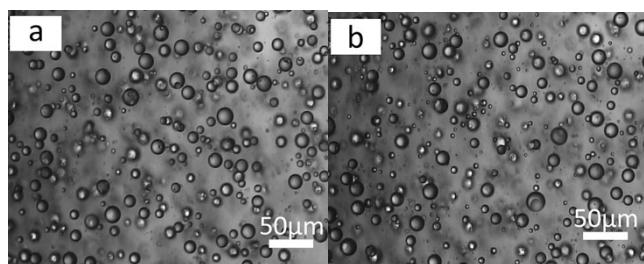
**Table S4** The catalytic activities for three-component Mannich reactions in water<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup> , R <sup>4</sup>	Yield <sup>b</sup> (%)	Solubility [g/100 mL water]
1	H	H	Ph, H	85	0.613
2	H	<i>p</i> -Cl	Ph, H	79	
3	H	H	CH <sub>3</sub> , H	36	100
4	<i>p</i> -CH <sub>3</sub> O	H	CH <sub>3</sub> , H	27	
5	H	H	CH <sub>3</sub> , CH <sub>3</sub>	88	22.3
6	<i>p</i> -CH <sub>3</sub> O	H	CH <sub>3</sub> , CH <sub>3</sub>	86	
7	<i>p</i> -CH <sub>3</sub> O	H	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub>	81	4.3
8	H	H	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub>	77	
9	<i>p</i> -CH <sub>3</sub> O	H	C <sub>2</sub> H <sub>5</sub> , CH <sub>3</sub>	79	4.81
10	H	H	C <sub>2</sub> H <sub>5</sub> , CH <sub>3</sub>	78	
11	<i>p</i> -CH <sub>3</sub> O	H	CH <sub>3</sub> , C <sub>3</sub> H <sub>7</sub>	75	1.75
12	H	H	CH <sub>3</sub> , C <sub>3</sub> H <sub>7</sub>	71	
13	<i>p</i> -CH <sub>3</sub> O	H	(CH <sub>2</sub> ) <sub>2</sub>	84	10.2
14	H	H	(CH <sub>2</sub> ) <sub>2</sub>	81	
15	<i>p</i> -CH <sub>3</sub> O	H	(CH <sub>2</sub> ) <sub>3</sub>	76	0.918
16	H	H	(CH <sub>2</sub> ) <sub>3</sub>	73	
17	<i>p</i> -CH <sub>3</sub> O	H	(CH <sub>2</sub> ) <sub>5</sub>	68	0.445
18	H	H	(CH <sub>2</sub> ) <sub>5</sub>	65	

<sup>a</sup>Reaction conducted with 1.0 mmol of benzaldehyde, 1.1 mmol of aniline, 5.0 mmol of ketone and 0.075 mmol of PAA in 1.0 mL H<sub>2</sub>O, at 25°C, 8 h. <sup>b</sup>Isolated yields were obtained after purification by column chromatography.

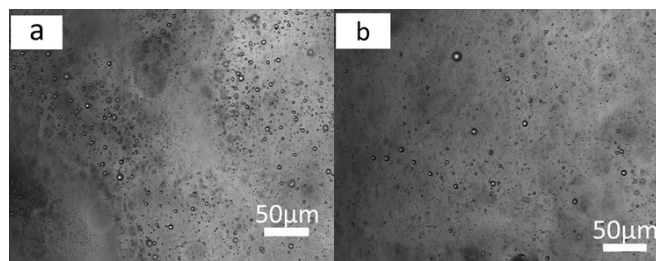
The optical micrographs with various ketones

Acetophenone:

**Fig.S2** The optical micrographs of the reaction at different times; a. Before the

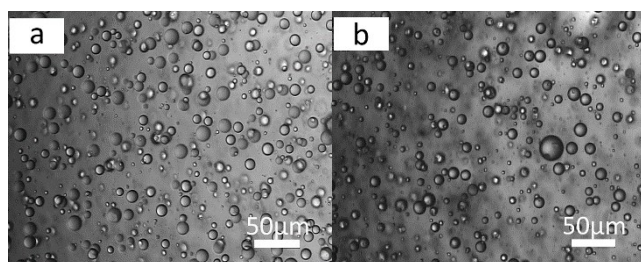
reaction; b. After the reaction

Acetone:



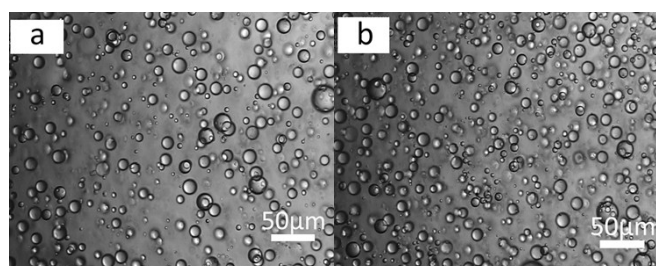
**Fig. S3** The optical micrographs of the reaction at different times; a. Before the reaction; b. After the reaction

2-butanone:



**Fig. S4** The optical micrographs of the reaction at different times; a. Before the reaction; b. After the reaction

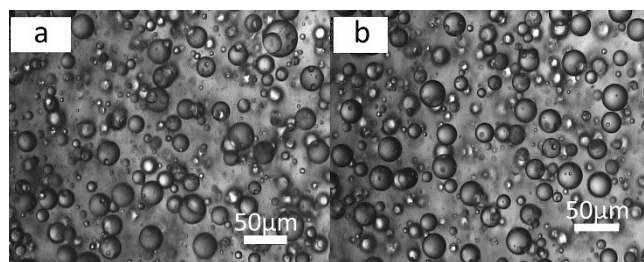
2-pentanone:



**Fig. S5** The optical micrographs of the reaction at different times; a. Before the reaction; b. After the reaction

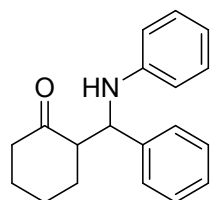


Cyclobutanone:

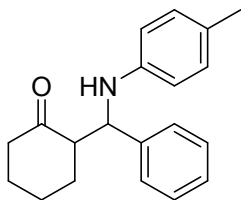


**Fig. S6** The optical micrographs of the reaction at different times; a. Before the reaction; b. After the reaction

#### 4. Characterization data of products

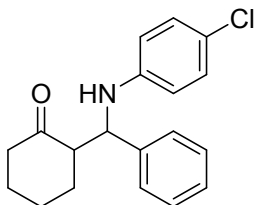


**2-[phenyl(phenylamino)methyl]-cyclohexanone(4a).**The reaction of benzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 92% yield. White solid; m.p.:136-138°C; IR (KBr, v, cm<sup>-1</sup>): 3390, 1704; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (s, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.21 – 7.08 (m, 2H), 6.71 (dd, *J* = 14.5, 7.2 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 2H), 4.90 (d, *J* = 2.9 Hz, 0H), 4.75 (t, *J* = 21.8 Hz, 2H), 2.85 (d, *J* = 16.6 Hz, 1H), 2.54 – 2.31 (m, 2H), 2.07 (d, *J* = 22.9 Hz, 1H), 1.93 (dd, *J* = 13.3, 5.6 Hz, 3H), 1.79 – 1.64 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 212.88, 211.39, 147.64, 147.39, 141.85, 141.73, 129.16, 129.11, 128.56, 128.47, 127.62, 127.38, 127.25, 127.09, 117.72, 117.57, 114.15, 113.70, 58.01, 57.55, 57.28, 56.69, 42.48, 41.85, 31.38, 28.73, 28.00, 27.11, 24.90, 23.74.



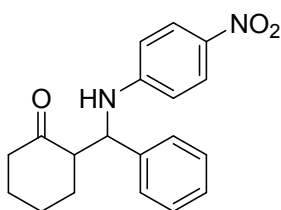
**2-[[4-(4-methylphenyl)amino]phenylmethyl]-cyclohexanone(4b).**The reaction of benzaldehyde (1.0 mmol), 4-methylaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 80% yield. White solid; m.p.:116-117°C; IR (KBr, v,cm<sup>-1</sup>):3380, 1697; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 2H), 4.87 (d, *J* = 3.3 Hz, 0H), 4.79–4.41 (m, 2H), 2.84 (dd, *J* = 21.1, 5.9 Hz, 1H), 2.50 (dd, *J* = 12.1, 6.3 Hz, 1H), 2.37 (dd, *J* = 9.3, 3.7 Hz, 1H), 2.26 (d, *J* = 4.0 Hz, 3H), 1.94 (dd, *J* = 14.9, 9.1 Hz, 3H), 1.74 (dd, *J* = 21.3,

11.9 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.91, 211.44, 145.37, 145.07, 141.99, 141.89, 129.66, 129.62, 128.54, 128.44, 127.62, 127.40, 127.20, 127.02, 126.83, 126.67, 114.36, 113.88, 58.25, 57.60, 56.77, 42.49, 41.78, 31.28, 29.83, 28.71, 27.99, 27.16, 24.93, 23.68, 20.49, 20.46.



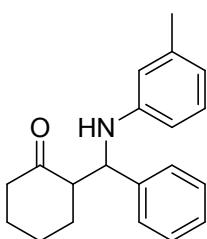
**2-[[4-chlorophenyl]amino]phenylmethyl]-cyclohexanone(4c).**

The reaction of benzaldehyde (1.0 mmol), 4-chloroaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 6 h, afforded 84% yield. Yellow solid; m.p.:  $138\text{-}140^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3401, 1701;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31 (4 H, m), 7.21 (1 H, dd,  $J_1 = 8.1$ ,  $J_2 = 5.8$ ), 6.99 (2 H, m), 6.45 (2 H, m), 4.76 (0.1 H, s), 4.76 (1 H), 4.54 (0.9 H, d,  $J = 6.8$ ), 2.73 (1 H, dt,  $J_1 = 8.1$ ,  $J_2 = 5.8$ ), 2.40 (1 H, dd,  $J_1 = 12.5$ ,  $J_2 = 6.7$ ), 2.32 (1 H, m), 1.86 (4 H, m), 1.67 (2 H, m).  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 212.66, 211.25, 146.10, 145.91, 141.29, 141.03, 128.89, 128.84, 128.55, 128.46, 127.48, 127.32, 127.22, 127.18, 122.34, 122.16, 115.23, 114.80, 58.37, 57.51, 57.39, 56.41, 42.38, 41.97, 31.53, 28.54, 27.91, 26.90, 24.85, 23.87.



**2-[[4-nitrophenyl]amino]phenylmethyl]-**

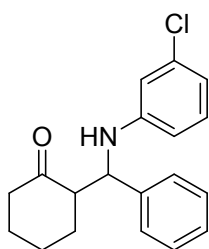
**cyclohexanone(4d).** The reaction of benzaldehyde (1.0 mmol), 4-nitroaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 6 h, afforded 90% yield. Yellow solid; m.p.:  $140\text{-}141^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3374, 1705;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.98 (2 H, d,  $J = 9.27$ ), 7.32 (4 H, d,  $J = 4.3$ ), 7.25 (1 H, d,  $J = 5.4$ ), 6.49 (2 H, d,  $J = 9.2$ ), 5.75 (0.13 H, d,  $J = 7.6$ ), 5.59 (0.85 H, d,  $J = 7.1$ ), 4.86 (0.87 H, dd,  $J_1 = 7.2$ ,  $J_2 = 4.4$ ), 4.65 (0.13 H, m), 2.86 (1 H, dt,  $J_1 = 9.5$ ,  $J_2 = 4.6$ ), 2.37 (2 H, m), 2.05 (2 H, dd,  $J_1 = 15.6$ ,  $J_2 = 9.6$ ), 1.90 (1 H, d,  $J = 6.9$ ), 1.59 (3 H, m).  $\delta_{\text{C}}$  (101 MHz,  $\text{CDCl}_3$ ) 212.50, 211.07, 152.77, 152.66, 140.23, 139.72, 138.24, 138.20, 128.76, 128.69, 127.68, 127.65, 127.45, 126.98, 126.20, 126.14, 112.22, 111.98, 58.12, 57.12, 56.90, 55.61, 42.46, 42.28, 32.32, 28.69, 28.09, 26.59, 24.69, 24.34.



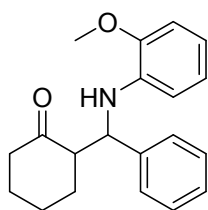
**2-[[3-methylphenyl]amino]phenylmethyl]-cyclohexanone(4e).**

The reaction of benzaldehyde (1.0 mmol), 3-methylaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 7 h, afforded 75% yield. White solid; m.p.:  $122\text{-}123^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3402, 1697;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.27

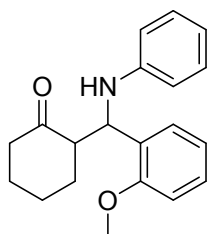
(2 H, m), 7.20 (2 H, d,  $J = 8.8$ ), 7.10 (1 H, d,  $J = 8.8$ ), 6.85 (1 H, d,  $J = 8.1$ ), 6.29 (3 H, d,  $J = 8.3$ ), 4.57 (1 H, br), 4.53 (1 H, d,  $J = 6.2$ ), 2.64 (1 H, dd,  $J_1 = 8.7$ ,  $J_2 = 4.9$ ), 2.32 (1 H, m), 2.21 (1 H, m), 2.09 (3 H, s), 1.78 (4 H, m), 1.60 (2 H, dd,  $J_1 = 11.3$ ,  $J_2 = 7.9$ ).  $^{13}\text{C}$ NMR (101 MHz,  $\text{CDCl}_3$ ) 211.70, 146.25, 140.85, 137.69, 127.90, 127.40, 126.20, 126.06, 117.44, 113.52, 109.48, 56.85, 56.46, 40.68, 30.19, 26.83, 22.58, 20.52.



**2-[(3-chlorophenyl)amino]phenylmethyl]-cyclohexanone(4f).** The reaction of benzaldehyde (1.0 mmol), 3-chloroaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 7 h, afforded 77% yield. Yellow solid; m.p.:  $122\text{--}123^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3340, 1699;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43–7.33 (m, 4H), 7.29 (d,  $J = 7.0$  Hz, 1H), 7.01 (d,  $J = 8.0$ , 3.6 Hz, 1H), 6.70 – 6.56 (m, 2H), 6.47 (d,  $J = 8.1$  Hz, 1H), 4.85 (t,  $J = 41.7$  Hz, 2H), 4.62 (d,  $J = 6.6$  Hz, 1H), 2.95 – 2.76 (m, 1H), 2.51 – 2.33 (m, 1H), 2.13–1.90 (m, 2H), 1.81 – 1.50 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.77, 211.26, 148.70, 148.55, 141.22, 140.92, 134.78, 134.71, 130.09, 130.04, 128.60, 128.52, 127.49, 127.37, 127.25, 127.18, 117.54, 117.38, 113.81, 113.30, 112.18, 111.86, 58.05, 57.36, 57.17, 56.36, 42.39, 42.03, 31.67, 28.62, 28.00, 26.93, 24.84, 23.89.

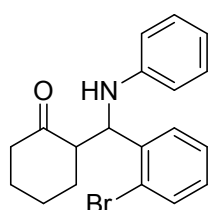


**2-[(2-methoxyphenyl)amino]phenylmethyl]-cyclohexanone(4g).** The reaction of benzaldehyde (1.0 mmol), 2-methoxyaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 7 h, afforded 78% yield. White solid; m.p.:  $113\text{--}114^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3379, 1670;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (dd,  $J = 16.5$ , 8.6 Hz, 2H), 7.30 (t,  $J = 7.2$  Hz, 2H), 7.21 (t,  $J = 6.9$  Hz, 1H), 5.35 – 4.78 (m, 1H), 4.73 (d,  $J = 7.2$  Hz, 1H), 3.87 (s, 3H), 2.86 – 2.77 (m, 1H), 2.46 (dd,  $J = 12.7$ , 6.0 Hz, 1H), 2.33 (dt,  $J = 13.9$ , 8.7 Hz, 1H), 1.95 – 1.59 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.29, 210.80, 147.11, 147.08, 142.04, 141.74, 137.31, 137.11, 130.34, 128.42, 128.35, 127.36, 127.13, 126.92, 121.12, 121.01, 116.68, 116.60, 111.48, 110.95, 109.47, 109.41, 57.56, 57.36, 57.11, 56.39, 55.59, 55.57, 42.34, 41.67, 30.99, 28.49, 27.87, 27.11, 24.84, 23.68.



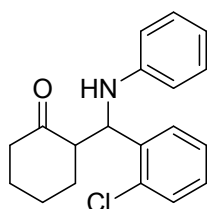
**2-[(2-methoxyphenyl)(phenylamino)methyl]-cyclohexanone(4h).** The reaction of 2-methoxybenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA

(0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 90% yield. White solid; m.p.:118-119 °C; IR (KBr, v, cm<sup>-1</sup>): 3335, 1697;<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, J = 7.5 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.09 (t, J = 7.6 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.60 (dd, J = 12.2, 7.9 Hz, 3H), 5.04 (d, J = 7.1 Hz, 1H), 4.95 (s, 1H), 3.93 (s, 3H), 2.90 (dd, J = 13.2, 7.0 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.36 – 2.28 (m, 1H), 2.08 – 1.85 (m, 5H), 1.77 (dd, J = 12.7, 4.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 213.77, 157.25, 147.42, 129.46, 129.08, 128.24, 128.08, 120.83, 117.24, 113.46, 110.25, 56.03, 55.41, 52.51, 41.89, 31.79, 28.28, 23.70.



**2-[(4-bromophenyl)(phenylamino)methyl]-cyclohexanone(4i).**

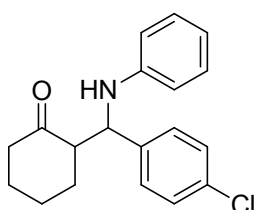
The reaction of 4-bromobenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 94% yield. Yellow solid; m.p.: 134-135°C; IR (KBr, v, cm<sup>-1</sup>): 3386, 1696;<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, J = 7.8, 1.5 Hz, 1H), 7.55 (dd, J = 7.9, 0.9 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.17 – 7.01 (m, 3H), 6.67 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.8 Hz, 2H), 5.44 (s, 1H), 4.86 (d, J = 2.3 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.42 – 2.28 (m, 2H), 2.18 (dd, J = 9.6, 4.2 Hz, 1H), 2.04 (ddd, J = 16.8, 9.2, 6.1 Hz, 3H), 1.78 (dd, J = 10.4, 6.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 213.15, 147.04, 140.79, 132.65, 129.36, 129.25, 128.64, 127.69, 123.97, 117.58, 113.45, 57.91, 55.32, 43.11, 33.06, 28.19, 25.13.



**2-[(2-chlorophenyl)(phenylamino)methyl]-cyclohexanone(4j).**

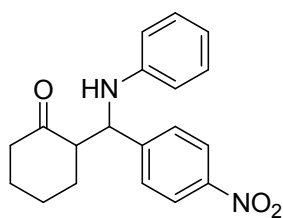
The reaction of 2-chlorobenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 95% yield. Yellow solid; m.p.:136-137°C; IR (KBr, v, cm<sup>-1</sup>): 3394, 1697; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.24 – 7.07 (m, 4H), 6.67 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.8 Hz, 2H), 5.31 (s, 1H), 4.95 (d, J = 4.7 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.46–2.27 (m, 2H), 2.12 (dd, J = 12.6, 5.5 Hz, 1H), 2.03 (dd, J = 16.2, 5.8 Hz, 3H), 1.86–1.72 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 213.16, 147.01, 139.26, 133.38, 129.35, 129.24, 129.05, 128.30, 127.13, 117.61, 113.40, 55.46, 55.41, 42.88, 32.74, 28.18, 24.86.

**2-[(4-chlorophenyl)(phenylamino)methyl]-**



**cyclohexanone(4k).**The reaction of 4-chlorobenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA

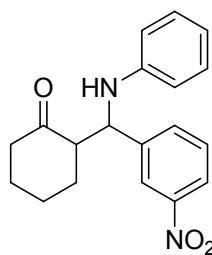
(0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 93% yield. Yellow solid; m.p.: 139–140°C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3386, 1696; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (t,  $J$  = 8.0 Hz, 2H), 7.31 (d,  $J$  = 8.2 Hz, 2H), 7.13 (dd,  $J$  = 10.0, 5.1 Hz, 2H), 6.72 (q,  $J$  = 6.8 Hz, 1H), 6.60 (t,  $J$  = 6.4 Hz, 2H), 4.82 (d,  $J$  = 3.8 Hz, 1H), 4.68 (d,  $J$  = 6.3 Hz, 1H), 2.79 (d,  $J$  = 4.1 Hz, 1H), 2.45 (d,  $J$  = 13.7 Hz, 1H), 2.34 (dt,  $J$  = 13.1, 4.9 Hz, 1H), 2.08–1.89 (m, 3H), 1.81–1.59 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  212.44, 211.22, 147.32, 147.18, 140.54, 140.31, 132.75, 132.67, 129.35, 129.23, 129.16, 128.85, 128.67, 128.58, 117.96, 117.80, 114.13, 113.71, 57.45, 57.33, 56.90, 56.46, 42.50, 42.08, 31.54, 28.93, 27.95, 27.12, 24.92, 24.04.



### 2-[(4-nitrophenyl)(phenylamino)methyl]-cyclohexanone.

The reaction of 4-nitrobenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 6 h, afforded 98% yield.

Yellow solid; m.p.: 155–156°C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3374, 1701; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d,  $J$  = 8.5 Hz, 2H), 7.58 (t,  $J$  = 8.6 Hz, 2H), 7.10 (t,  $J$  = 7.7 Hz, 2H), 6.67 (t,  $J$  = 6.8 Hz, 1H), 6.53 (d,  $J$  = 7.9 Hz, 2H), 4.90 (d,  $J$  = 4.0 Hz, 1H), 4.76 (d,  $J$  = 5.1 Hz, 1H), 2.93–2.84 (m, 1H), 2.45–2.31 (m, 2H), 2.09–1.91 (m, 3H), 1.75 (t,  $J$  = 8.5 Hz, 2H), 1.62 (t,  $J$  = 9.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  211.87, 210.72, 150.05, 149.89, 147.02, 146.99, 146.83, 129.30, 129.21, 128.67, 128.38, 123.66, 123.63, 118.29, 118.04, 115.12, 114.05, 113.54, 57.67, 57.07, 57.00, 56.27, 42.48, 42.42, 32.01, 29.05, 27.87, 27.15, 24.96, 24.50.

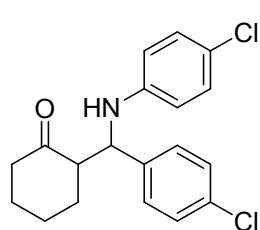


### 2-[(3-nitrophenyl)(phenylamino)methyl]-cyclohexanone (4m).

The reaction of 3-nitrobenzaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8h, afforded 76% yield. Yellow solid; m.p.: 163–

165°C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3373, 1699; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (1 H, d,  $J$  = 7.9), 8.06 (1 H, d,  $J$  = 7.6), 7.77 (1 H, m), 7.45 (1 H, t,  $J$  = 7.9), 7.08 (2 H, t,  $J$  = 7.5), 6.67 (1 H, dd,  $J_1$  = 11.6,  $J_2$  = 7.3), 6.52 (2 H, d,  $J$  = 8.6), 4.85 (0.5 H, d,  $J$  = 3.1), 4.71 (0.5 H, d,  $J$  = 5.3), 4.85 (0.5 H, br), 4.63 (0.5 H, br), 2.86 (1 H, m), 2.37 (2 H, dt,  $J_1$  = 25.6,  $J_2$  = 13.9), 2.06 (2 H, m), 1.93 (1 H, d,  $J$  = 5.6), 1.67 (3 H, m). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  211.86, 210.71, 148.44, 148.41, 146.71, 146.64, 144.52, 144.16, 134.18,

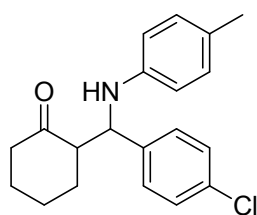
133.60, 129.36, 129.29, 129.27, 129.19, 122.52, 122.29, 122.25, 122.22, 118.31, 118.07, 114.01, 113.51, 57.69, 57.09, 57.08, 56.28, 42.47, 42.41, 32.02, 29.30, 27.81, 27.12, 24.93, 24.46.



**2-[[4-(4-chlorophenyl)amino]methyl]-**

**cyclohexanone(4n).**The reaction of 4-chlorobenzaldehyde (1.0 mmol), 4-chloroaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 9 h, afforded 63% yield. Yellow solid; m.p.:139-140°C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3416,

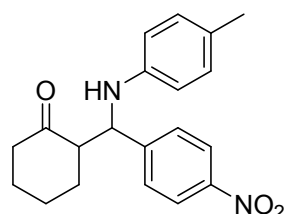
1699; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.27 (4 H, m), 7.01 (2 H, d,  $J = 8.8$ ), 6.42 (2 H, d,  $J = 8.8$ ), 4.79 (1 H, br), 4.52 (1 H, d,  $J = 6.2$ ), 2.72 (1 H, dd,  $J_1 = 8.7$ ,  $J_2 = 4.9$ ), 2.38 (2 H, m), 1.99 (1 H, m), 1.90 (2 H, m), 1.69 (3 H, dd,  $J_1 = 11.3$ ,  $J_2 = 7.9$ ). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 211.29, 144.64, 138.88, 131.92, 127.93, 127.67, 127.60, 121.37, 113.75, 56.81, 56.14, 41.17, 30.68, 26.84, 23.12.



**2-[[4-(4-methylphenyl)amino]methyl]-**

**cyclohexanone(4o).**The reaction of 4-chlorobenzaldehyde (1.0 mmol), 4-methylaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8h, afforded 72% yield. Yellow solid; m.p.: 132-133°C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3395,

1700; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (t,  $J = 7.8$  Hz, 2H), 7.31 – 7.27 (m, 2H), 6.96 – 6.88 (m, 2H), 6.48 (t,  $J = 6.9$  Hz, 2H), 4.75 (d,  $J = 4.3$  Hz, 0H), 4.62 (d,  $J = 6.5$  Hz, 2H), 2.82–2.70 (m, 1H), 2.47 – 2.41 (m, 1H), 2.38–2.31 (m, 1H), 2.21 (d,  $J = 2.8$  Hz, 2H), 2.06–1.88 (m, 2H), 1.87 – 1.76 (m, 1H), 1.73–1.60 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  212.48, 211.28, 144.93, 144.75, 140.58, 140.33, 132.71, 132.61, 129.68, 129.63, 129.09, 128.78, 128.63, 128.54, 127.13, 126.94, 114.31, 113.83, 57.70, 57.37, 57.22, 56.51, 42.50, 42.00, 31.43, 28.90, 27.89, 27.12, 24.94, 23.97, 20.43, 20.41.

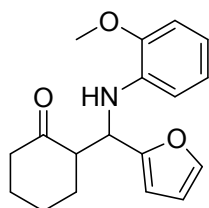


**2-[[4-(4-methylphenyl)amino]methyl]-**

**cyclohexanone(4p).**The reaction of 4-nitrobenzaldehyde (1.0 mmol), 4-methylaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 12 h, afforded 65% yield. Yellow solid; m.p.:136-137°C; IR (KBr,  $\nu$ ,

cm<sup>-1</sup>): 3398, 1707; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 8.15 (2 H, d,  $J = 8.7$ ), 7.56 (2 H, d,  $J = 8.6$ ),

6.89 (2 H, d,  $J = 8.1$ ), 6.42 (2 H, d,  $J = 8.3$ ), 4.81 (0.42 H, d,  $J = 3.1$ ), 4.68 (0.58 H, d,  $J = 5.4$ ), 4.68 (1 H, br), 2.83 (1 H, m), 2.41 (1 H, d,  $J = 12.5$ ), 2.33 (1 H, d,  $J = 11.1$ ), 2.17 (3 H, s), 2.00 (3 H, m), 1.76 (2 H, t,  $J = 18.2$ ), 1.62 (1 H, m).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 211.73, 210.65, 150.10, 149.86, 147.06, 147.03, 144.41, 129.77, 129.69, 128.63, 128.32, 127.63, 127.35, 123.64, 123.59, 114.29, 113.72, 58.04, 57.53, 57.07, 56.29, 42.47, 42.36, 31.90, 29.09, 27.76, 27.11, 24.97, 24.46, 20.34, 20.32.

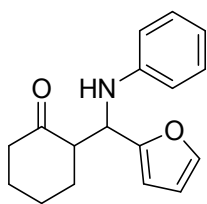


**2-[furan-2-yl(2-methoxyphenylamino)methyl]-**

**cyclohexanone(4q).**The reaction of furanaldehyde (1.0 mmol), 2-methoxyaniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 8 h, afforded 82% yield.

Brownish needles; m.p.:  $105\text{--}107^\circ\text{C}$ . IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3376, 2940,

1676, 1592, 1499;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (dd,  $J = 6.2, 1.0$  Hz, 1H), 6.85 – 6.66 (m, 4H), 6.30 – 6.26 (m, 1H), 6.23 (dd,  $J = 6.5, 3.1$  Hz, 1H), 5.02 (d,  $J = 4.7$  Hz, 1H), 4.97 (d,  $J = 5.6$  Hz, 1H), 3.86 (s, 3H), 3.00 (dt,  $J = 9.3, 5.5$  Hz, 1H), 2.49–2.43 (m, 1H), 2.39 – 2.32 (m, 1H), 2.07 – 1.87 (m, 3H), 1.74–1.62 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.32, 210.62, 155.27, 154.70, 147.27, 147.22, 141.38, 141.25, 137.12, 137.00, 121.23, 121.15, 117.24, 117.13, 111.33, 110.84, 110.34, 110.32, 109.77, 109.75, 106.99, 106.93, 55.57, 55.55, 54.73, 54.36, 51.47, 51.14, 42.23, 41.99, 30.40, 29.39, 27.53, 27.08, 24.74, 24.29.

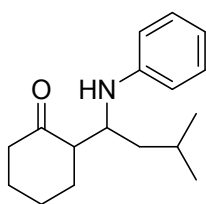


**2-[furan-2-yl(phenylamino)methyl]cyclohexanone(4r).**

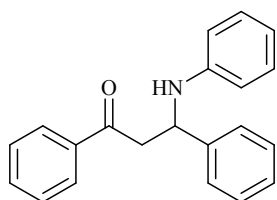
The reaction of furanaldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 8 h, afforded 74% yield. Brownish needles; m.p.:  $102\text{--}103^\circ\text{C}$ . IR (KBr,  $\nu$ ,

$\text{cm}^{-1}$ ): 3376, 2940, 1676, 1592, 1499;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

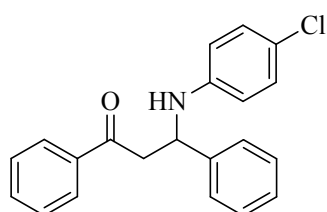
$\delta$  7.31 (d,  $J = 2.6$  Hz, 1H), 7.15 (dd,  $J = 11.4, 4.3$  Hz, 2H), 6.73–6.65 (m, 3H), 6.28 (dd,  $J = 4.9, 3.0$  Hz, 1H), 6.21 (d,  $J = 3.1$  Hz, 1H), 4.91–4.85 (d,  $J = 4.9$  Hz, 1H), 4.54 (s, 1H), 3.02–2.92 (m, 1H), 2.45–2.31 (m, 2H), 2.18 (d,  $J = 6.1$  Hz, 1H), 2.04–1.90 (m, 2H), 1.68 (dd,  $J = 12.4, 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.87, 211.03, 154.94, 154.70, 147.26, 147.23, 141.34, 141.22, 129.24, 129.21, 118.19, 118.04, 114.05, 113.75, 110.40, 110.34, 107.22, 106.94, 54.51, 54.11, 52.22, 51.95, 42.27, 42.14, 30.86, 29.72, 27.67, 26.93, 24.74, 24.33.



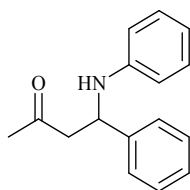
**2-(3-methyl-1-(phenylamino)butyl)cyclohexanone(4s).** The reaction of isovaleraldehyde (1.0 mmol), aniline (1.1 mmol), cyclohexanone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8 h, afforded 72% yield. Brown needles; m.p.: 154-155 °C. IR (KBr, v, cm<sup>-1</sup>): 3409, 2928, 1599, 1501, 1456, 1245, 1220 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18–7.09 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.7 Hz, 2H), 3.94 (s, 1H), 3.83 – 3.78 (m, 1H), 2.61 (dd, J = 11.3, 3.8 Hz, 1H), 2.32 (ddd, J = 19.5, 13.8, 4.2 Hz, 2H), 2.08–2.00 (m, 2H), 1.91 – 1.85 (m, 1H), 1.74 – 1.60 (m, 4H), 1.43 (dddd, J = 47.8, 13.2, 8.7, 4.7 Hz, 3H), 0.92 (dd, J = 6.6, 3.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 213.06, 148.09, 129.37, 116.50, 112.54, 53.39, 51.03, 42.84, 42.67, 29.85, 27.38, 25.31, 25.06, 23.39, 22.21.



**1,3-diphenyl-3-(phenylamino)-1-propanone (4t).** The reaction of benzaldehyde (1.0 mmol), aniline (1.1 mmol), acetophenone (5.0 mmol) and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8 h, afforded 85% yield. White solid; m.p.: 170-172 °C; IR (KBr, v, cm<sup>-1</sup>): 3383, 1669; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 7.89-7.91 (m, 2H), 7.56 (dd, J<sub>1</sub>= 10.5 Hz, J<sub>2</sub>= 4.3 Hz, 1H), 7.45 (dd, J<sub>1</sub>= 10.5 Hz, J<sub>2</sub>= 4.5 Hz, 4H), 7.32 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.06-7.09 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.56-6.59 (m, 2H), 5.02 (dd, J<sub>1</sub>= 7.4 Hz, J<sub>2</sub>= 5.4 Hz, 1H), 3.48 (qd, J<sub>1</sub>= 16.1 Hz, J<sub>2</sub>= 6.4 Hz, 2H). δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 198.26, 146.78, 142.81, 136.76, 133.40, 129.11, 128.82, 128.69, 128.20, 127.39, 126.43, 118.02, 114.04, 55.03, 46.21.



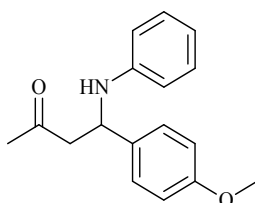
**1,3-diphenyl-3-(4-chlorophenylamino)-1-propanone (4u).** The reaction of benzaldehyde (1 mmol), *p*-chloroaniline (1.1 mmol), acetophenone (5 mmol), and PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8 h, afforded 79% yield. Yellow solid; m.p.: 167-168 °C; IR (KBr, v, cm<sup>-1</sup>): 3370, 1665; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 7.90 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.42-7.44 (m, 4H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (s, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.47 (d, J = 8.7 Hz, 2H), 4.93-4.96 (m, 1H), 4.61 (s, 1H), 3.37-3.47 (m, 2H); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 198.2, 145.6, 142.5, 136.7, 133.5, 128.9, 128.9, 128.7, 128.2, 127.5, 126.3, 122.5, 115.0, 55.0, 46.2.



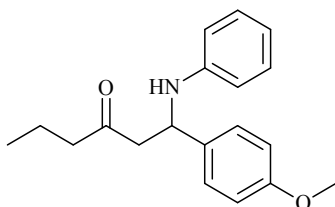
**4-phenyl-4-(phenylamino)-2-butanone (4v).** The reaction of benzaldehyde (1 mmol), aniline (1.1 mmol), acetone (5 mmol), PAA (0.075 mmol) in 1.0 mL H<sub>2</sub>O, at 25°C for 8 h, afforded 36% yield. White solid; m.p.: 90-92 °C; IR (KBr, v, cm<sup>-1</sup>): 3390, 1704; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 7.26 (m, 4H), 7.16 (d, J = 6.0 Hz, 1H), 7.01 (t, J = 7.8 Hz, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.47 (d, J = 8.1 Hz, 2H), 4.77 (t, J = 6.5 Hz, 1H),



4.36 (s, 1H), 2.84 (d,  $J = 6.5$  Hz, 2H), 2.02 (s, 3H).  $\delta_c$  (101 MHz,  $\text{CDCl}_3$ ) 206.10, 145.76, 141.47, 128.11, 127.78, 126.34, 125.24, 116.83, 112.73, 53.34, 50.20, 29.70.

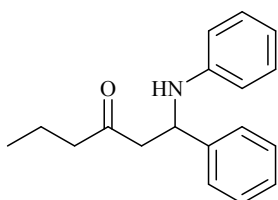


**4-(4-methoxyphenyl)-4-(phenylamino)-2-butanone (4w):** The reaction of *p*-methoxybenzaldehyde (1 mmol), aniline (1.1 mmol), acetone (5 mmol), PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 8 h, afforded 27% yield. Yellow solid; m.p.:  $104\text{--}105^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3363, 1707;  $\delta_H$  (400 MHz,  $\text{CDCl}_3$ ) 7.27 (d,  $J = 7.0$  Hz, 2H), 7.09 (t,  $J = 7.0$  Hz, 2H), 6.85 (d,  $J = 6.9$  Hz, 2H), 6.66 (t,  $J = 7.3$  Hz, 1H), 6.54 (d,  $J = 7.7$  Hz, 2H), 4.80 (t,  $J = 6.3$  Hz, 1H), 4.38 (s, 1H), 3.77 (s, 3H), 2.90 (d,  $J = 6.5$  Hz, 2H), 2.08 (s, 3H).  $\delta_c$  (101 MHz,  $\text{CDCl}_3$ ) 207.30, 158.80, 146.83, 134.44, 129.13, 127.37, 117.79, 114.17, 113.76, 55.23, 53.81, 51.26, 30.79.



**1-(2-methoxyphenyl)-1-(phenylamino)-3-hexanone (4x).** The reaction of *p*-anisaldehyde (1 mmol), aniline (1.1 mmol), 2-pentanone (5 mmol), PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 8 h, afforded 81% yield. White solid; m.p.:  $85\text{--}86^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3370, 1701;  $\delta_H$  (400 MHz,  $\text{CDCl}_3$ ) 7.17 (d,  $J = 8.6$  Hz, 2H), 6.99 (t,  $J = 7.9$  Hz,

2H), 6.74 (d,  $J = 8.7$  Hz, 2H), 6.56 (t,  $J = 7.3$  Hz, 1H), 6.45 (d,  $J = 7.8$  Hz, 2H), 4.70 (t,  $J = 6.4$  Hz, 1H), 4.42 (s, 1H), 3.66 (s, 3H), 2.77 (d,  $J = 6.7$  Hz, 2H), 2.20 (td,  $J_1 = 7.1$  Hz,  $J_2 = 1.7$  Hz, 2H), 1.42 (dd,  $J_1 = 14.7$  Hz,  $J_2 = 7.3$  Hz, 2H), 0.74 (t,  $J = 7.4$  Hz, 3H).  $\delta_c$  (101 MHz,  $\text{CDCl}_3$ ) 208.55, 157.71, 145.90, 133.58, 128.06, 126.35, 116.62, 113.08, 112.71, 54.16, 52.84, 49.22, 44.57, 15.81, 12.56.

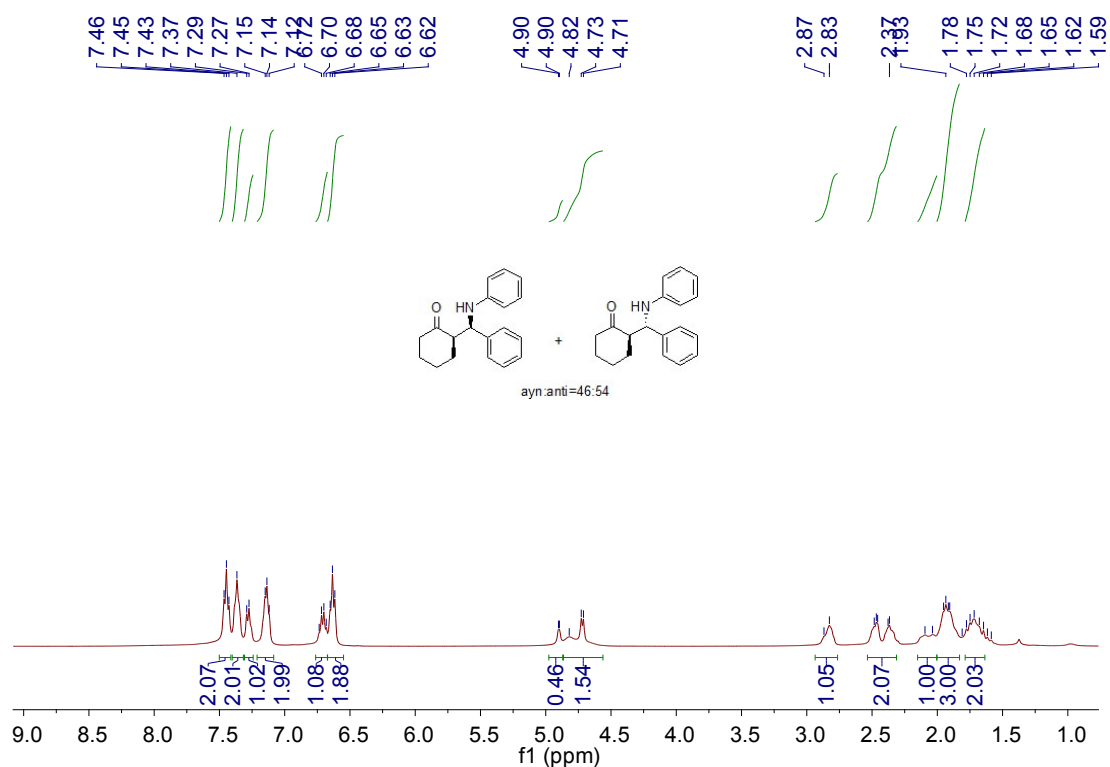


**1-phenyl-1-(phenylamino)-3-hexanone (4y).** The reaction of benzaldehyde (1 mmol), aniline (1.1 mmol), 2-pentanone (5 mmol), PAA (0.075 mmol) in 1.0 mL  $\text{H}_2\text{O}$ , at  $25^\circ\text{C}$  for 8 h, afforded 77% yield. White solid; m.p.:  $87\text{--}88^\circ\text{C}$ ; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3376, 1703;  $\delta_H$  (400 MHz,  $\text{CDCl}_3$ ) 7.29 (d,  $J = 7.9$  Hz, 2H), 7.23 (d,  $J = 7.5$  Hz, 2H), 7.17 (d,  $J = 5.8$  Hz, 1H), 7.02 (t,  $J = 7.6$

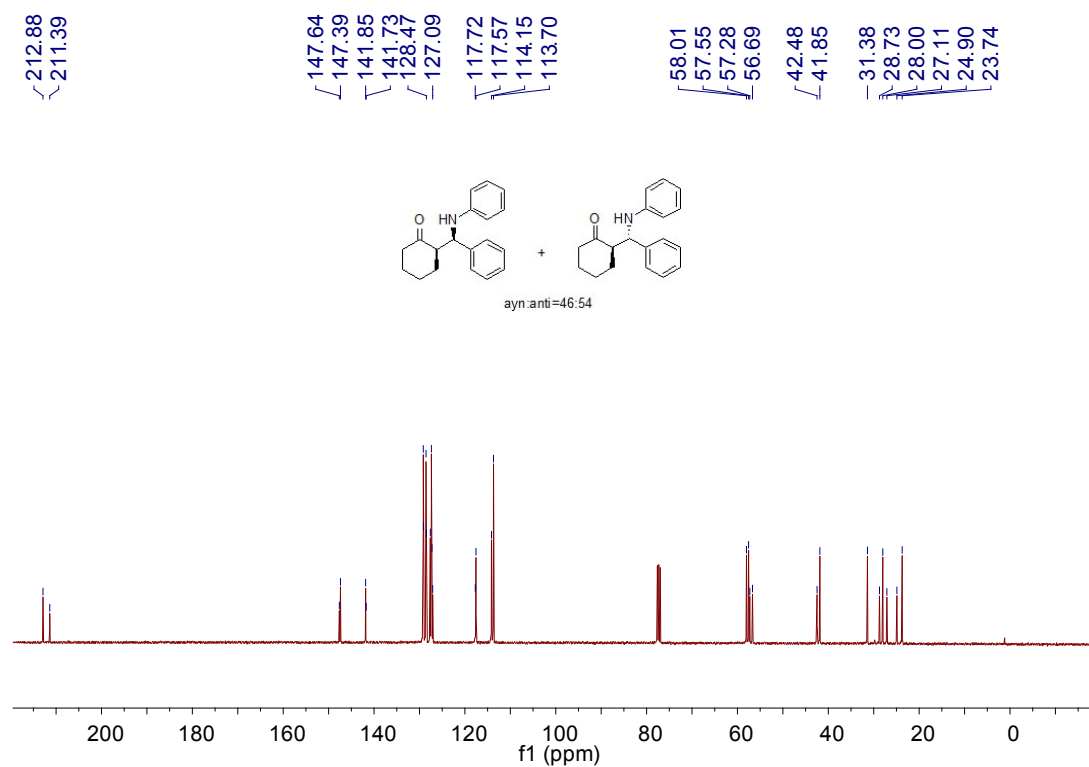
Hz, 2H), 6.59 (t,  $J = 7.3$  Hz, 1H), 6.48 (d,  $J = 7.8$  Hz, 2H), 4.78 (t,  $J = 6.4$  Hz, 1H), 4.48 (s, 1H), 2.82 (d,  $J = 6.4$  Hz, 2H), 2.28-2.17 (m, 2H), 1.51-1.41 (m, 2H), 0.76 (t,  $J = 7.4$  Hz, 3H).  $\delta_c$  (101 MHz,  $\text{CDCl}_3$ ) 208.42, 145.82, 141.59, 128.08, 127.72, 126.26, 125.25, 116.69, 112.69, 53.43, 49.18, 44.55, 15.80, 12.54.

# Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of compounds

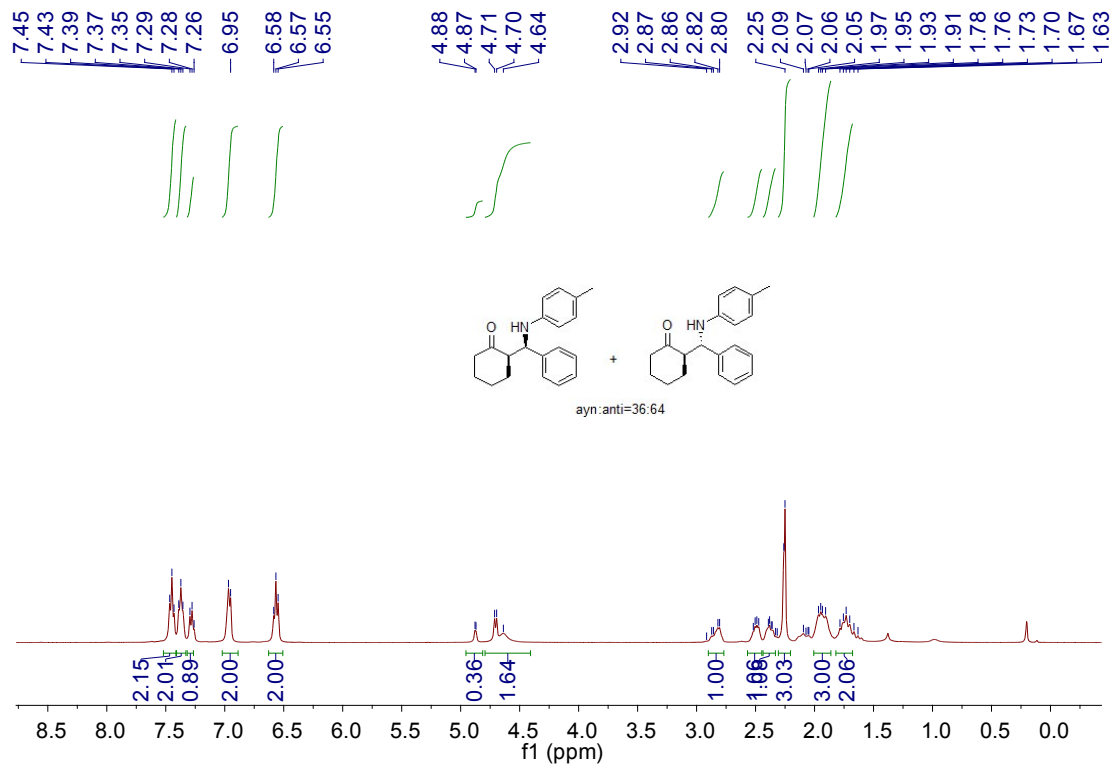
## $^1\text{H}$ NMR



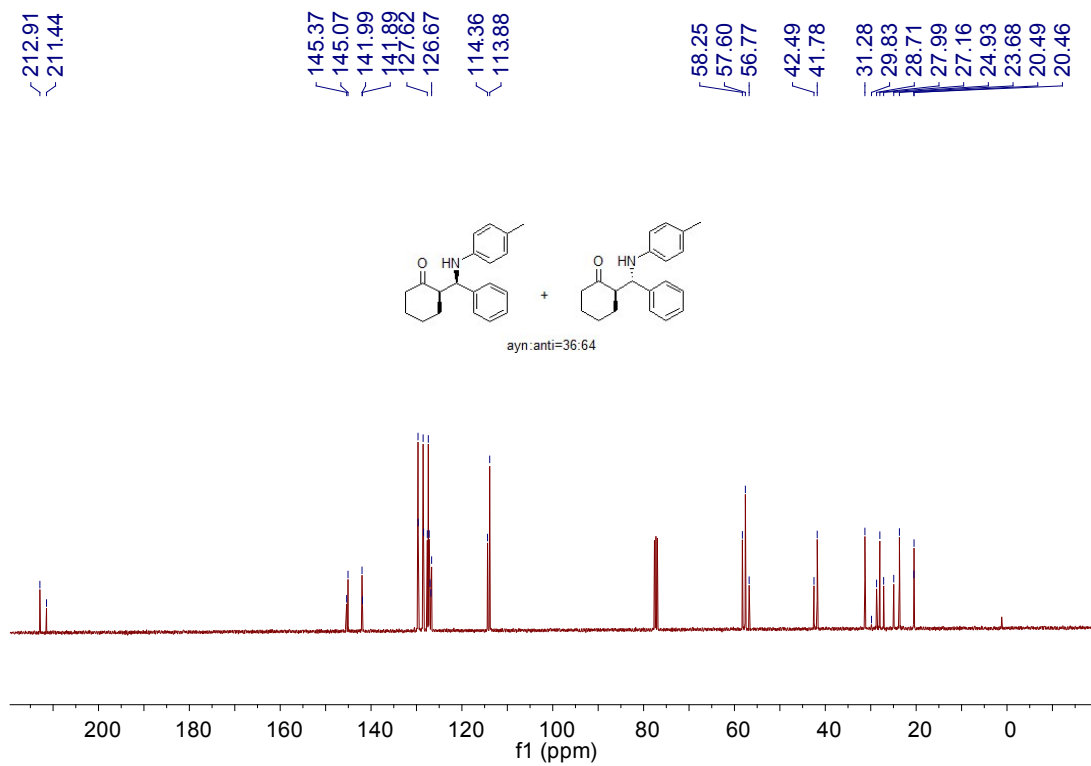
## $^{13}\text{C}$ NMR



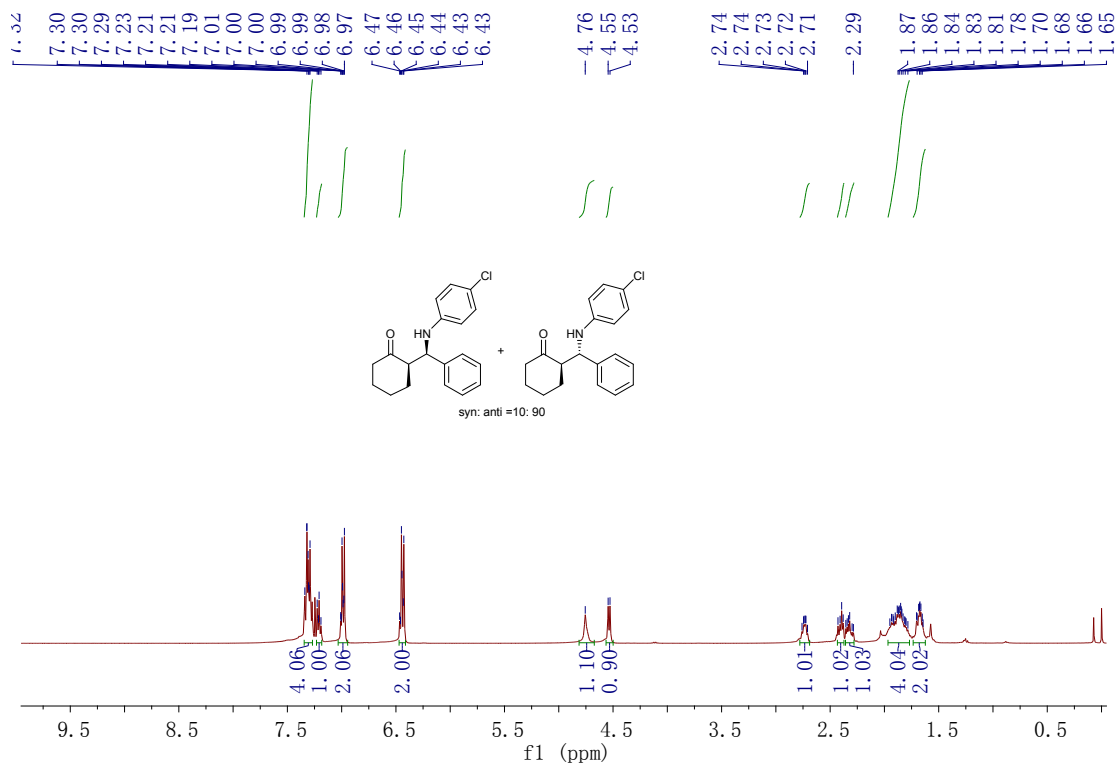
# <sup>1</sup>H NMR



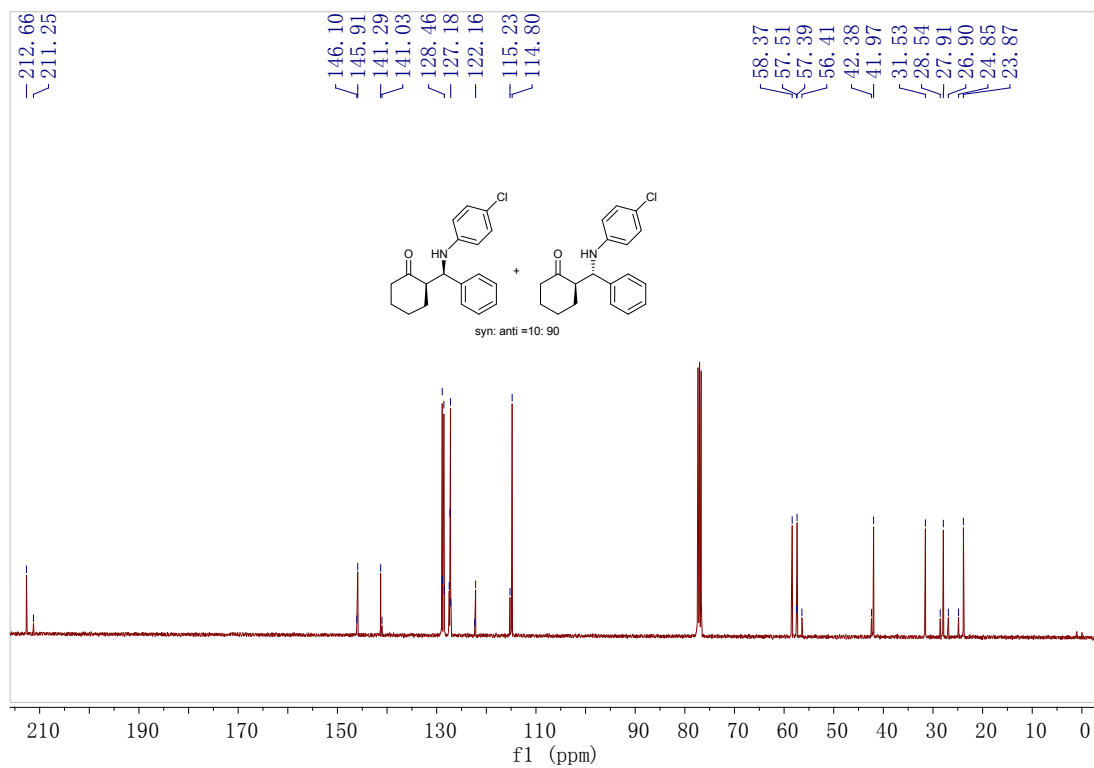
# <sup>13</sup>C NMR



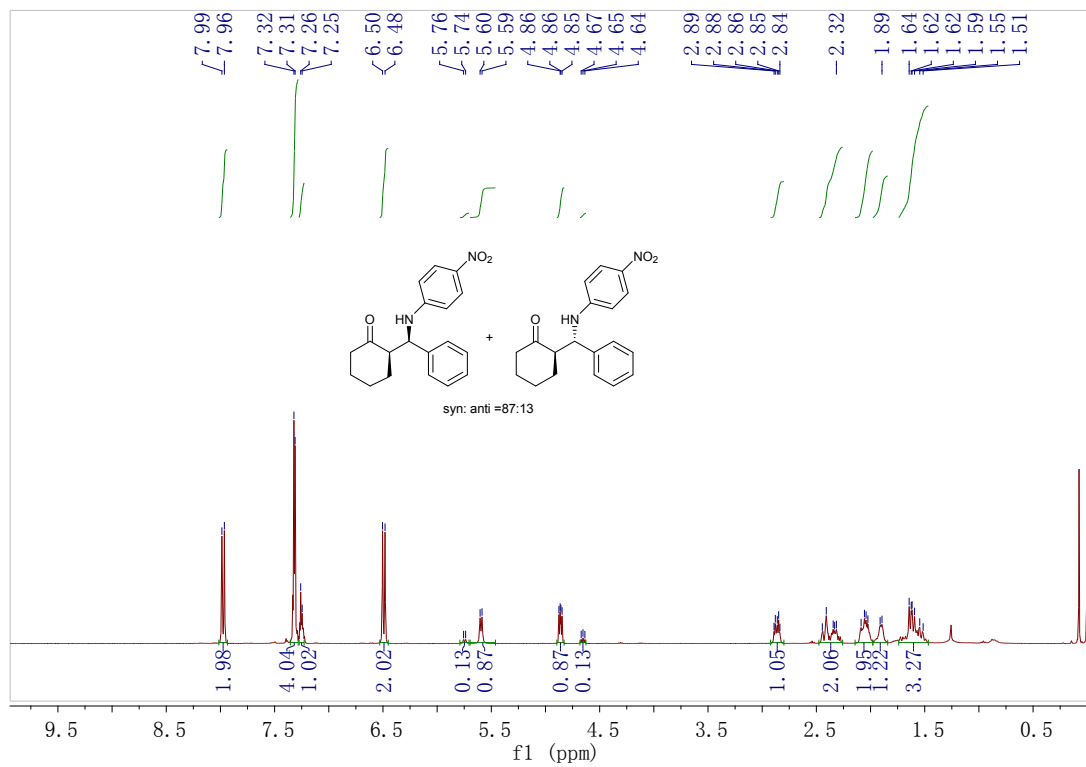
# <sup>1</sup>H NMR



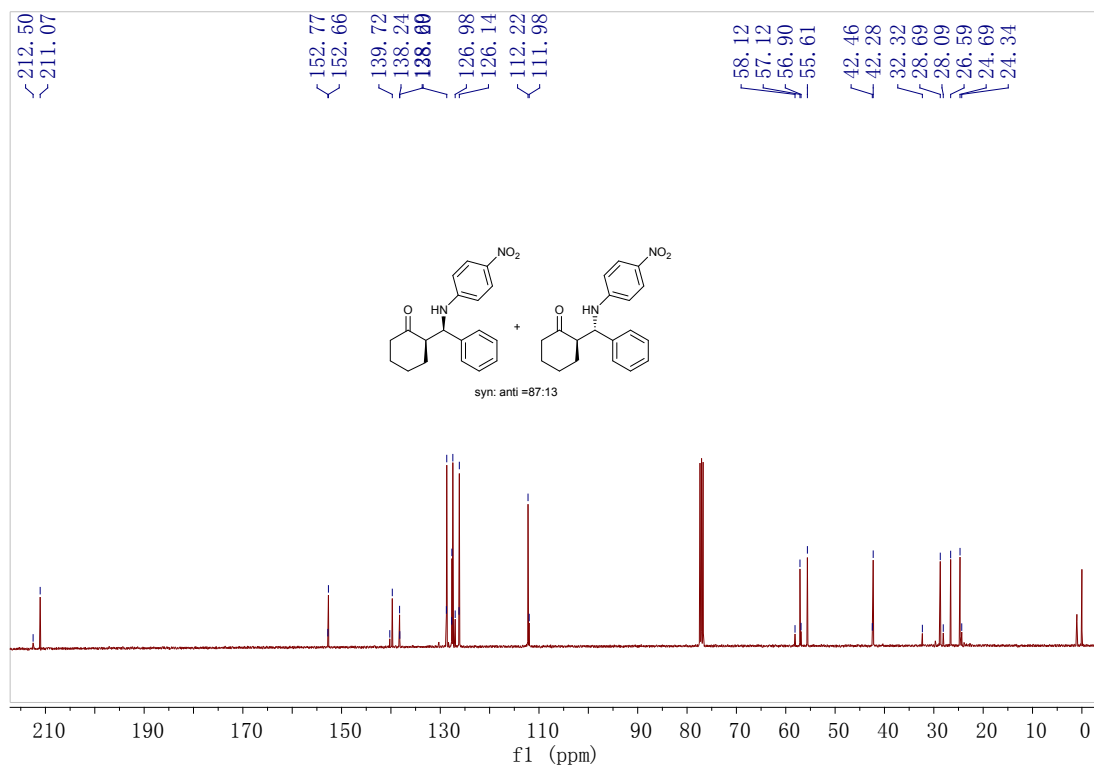
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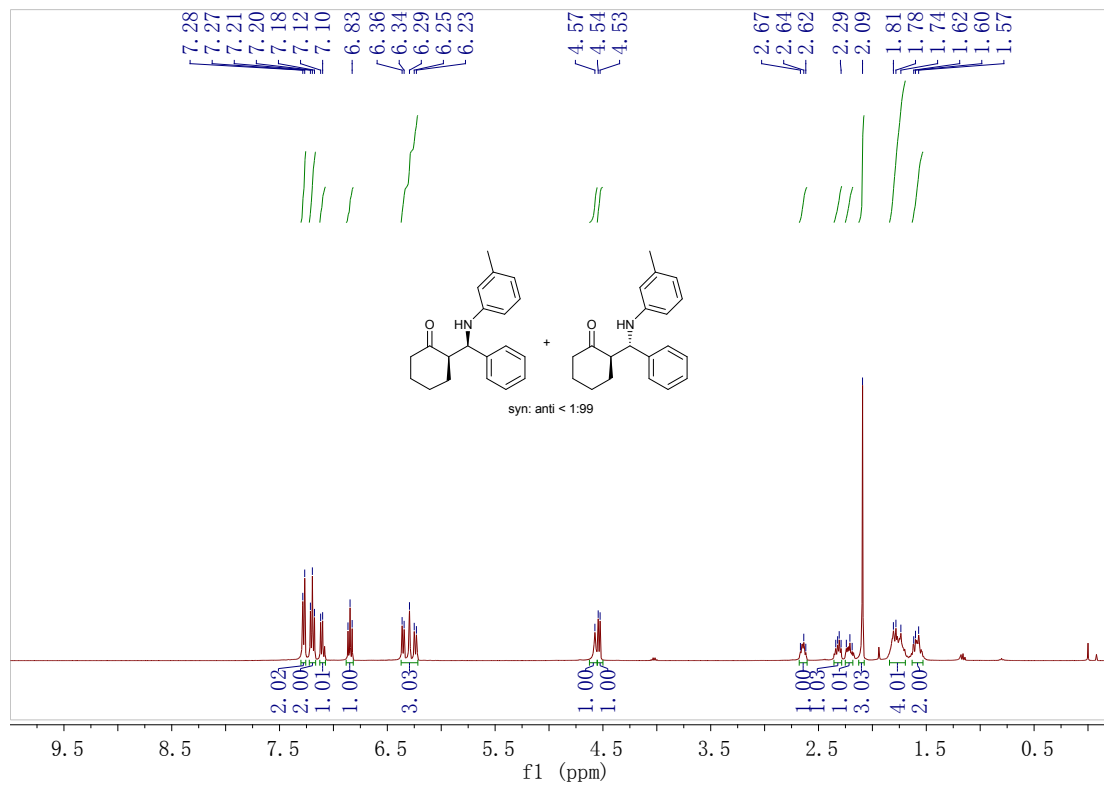
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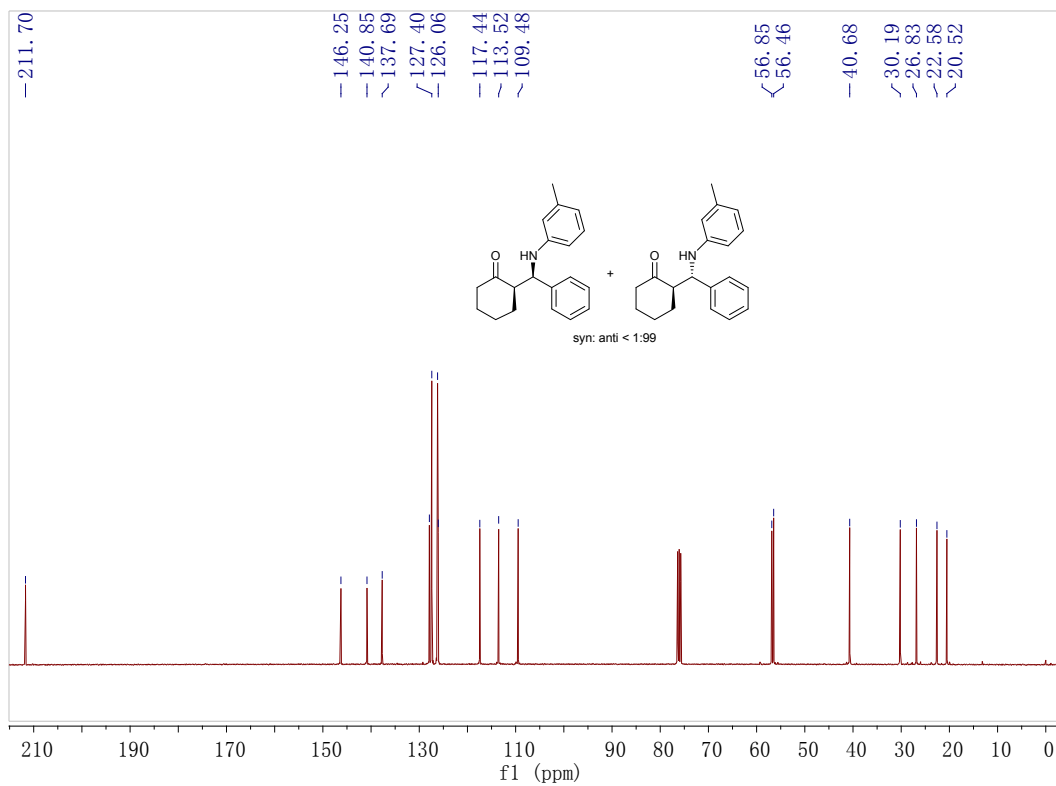
# <sup>13</sup>C NMR



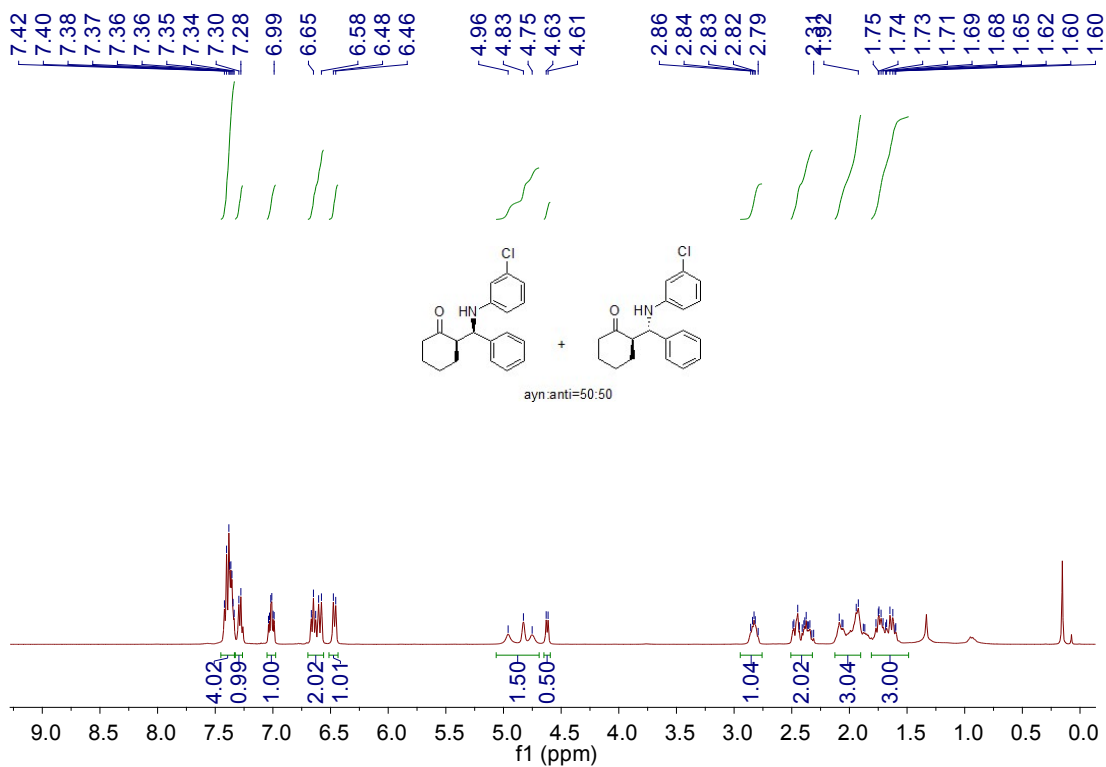
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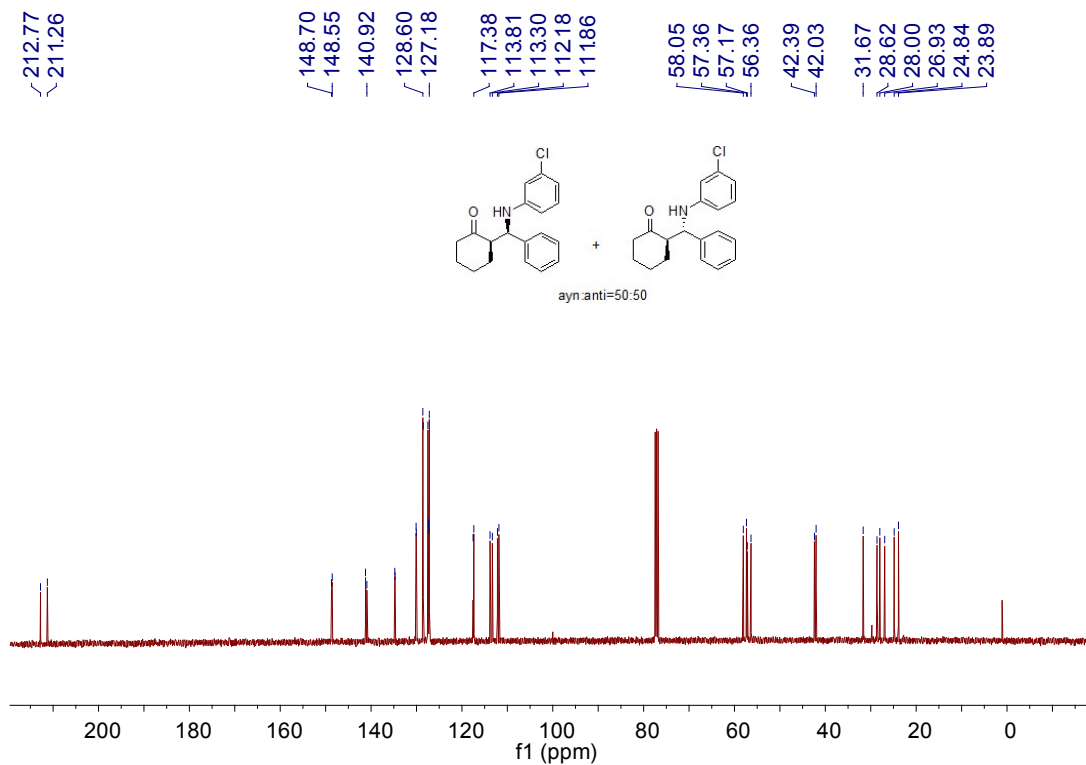
# <sup>13</sup>C NMR



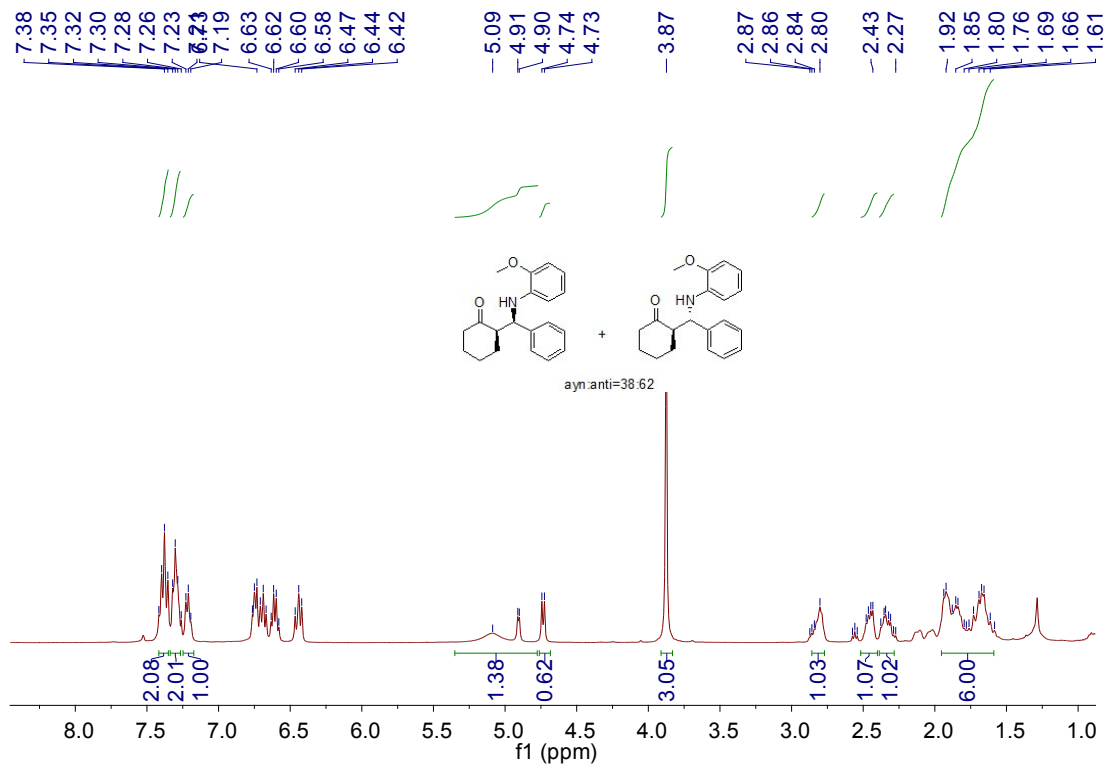
# <sup>1</sup>H NMR



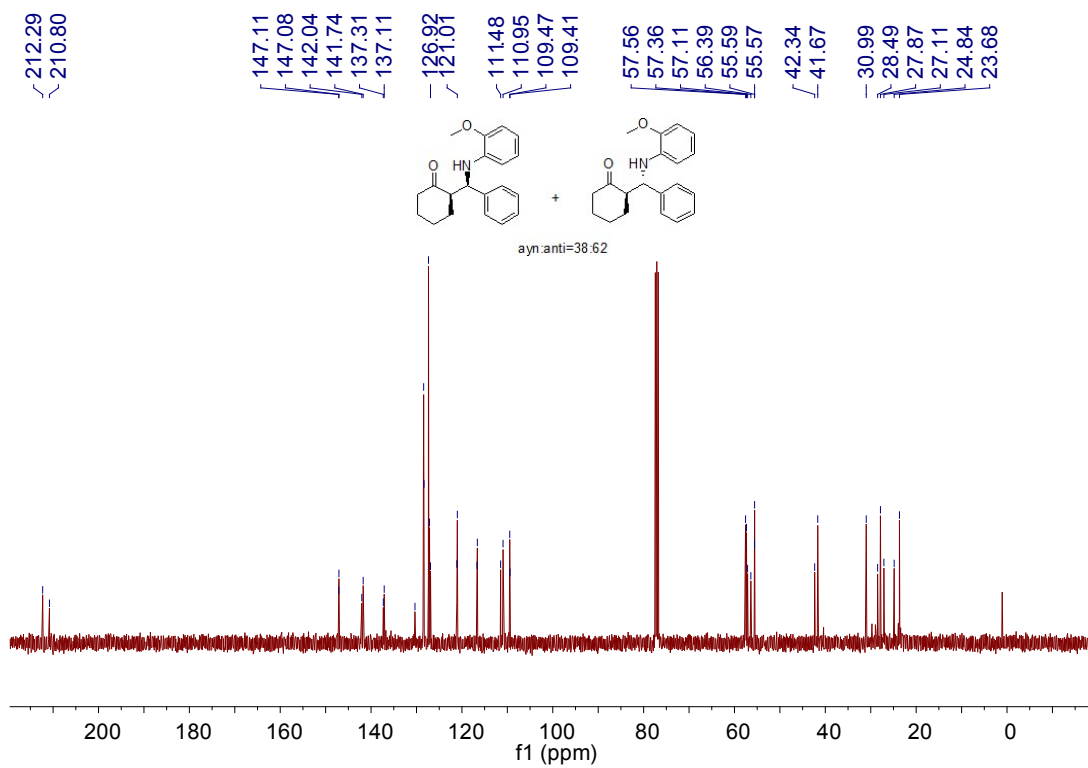
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

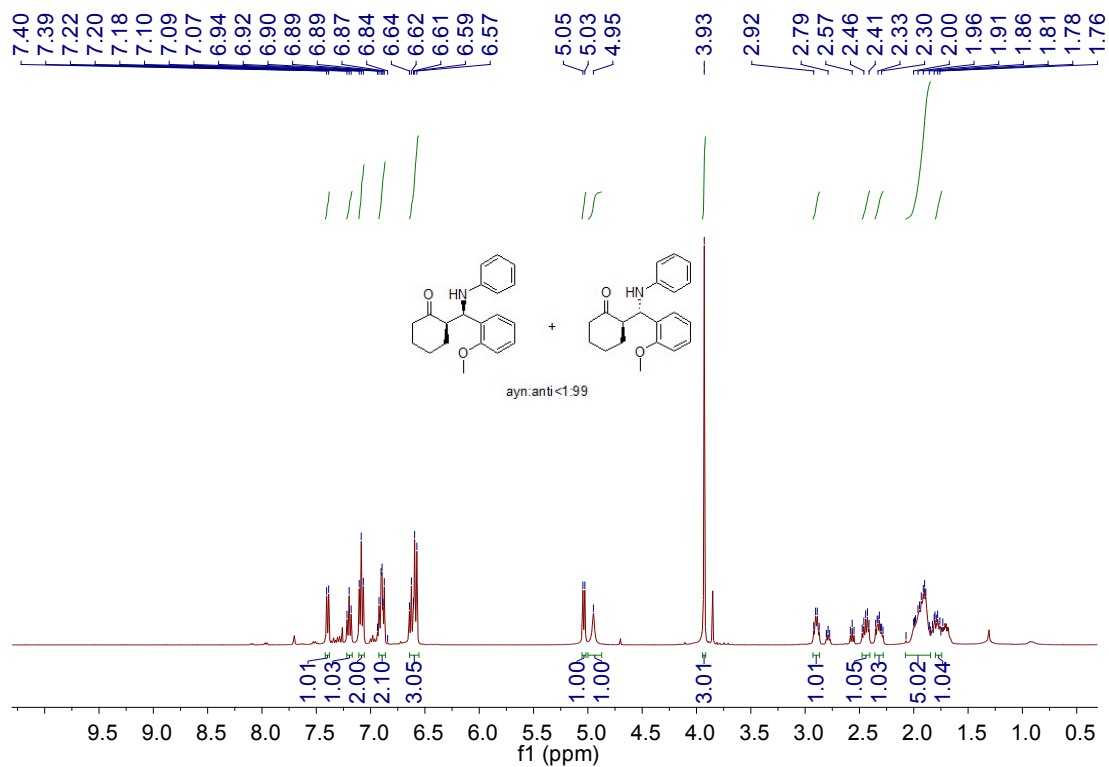


# <sup>13</sup>C NMR

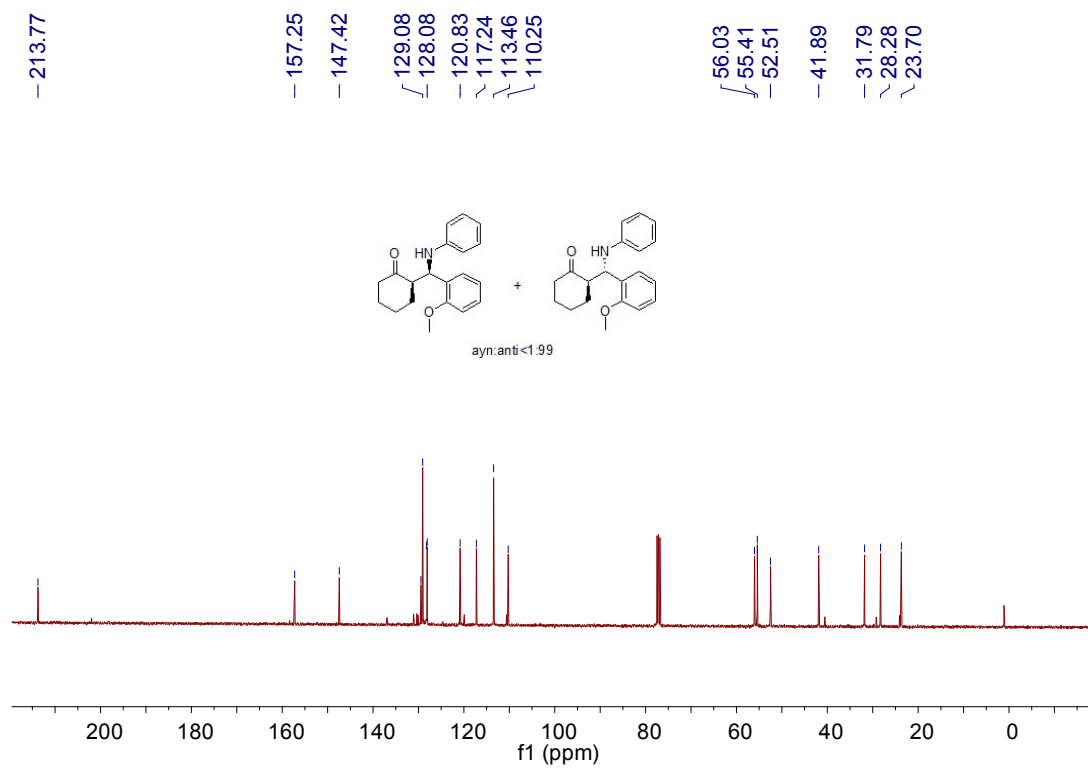




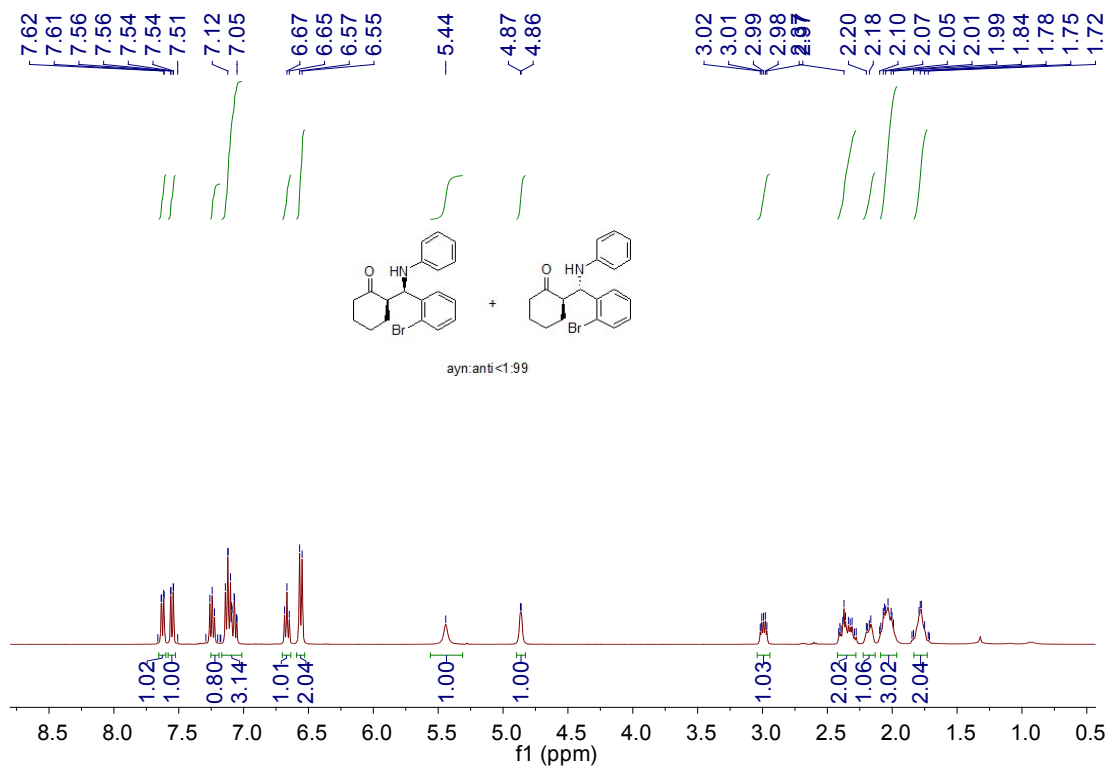
# <sup>1</sup>H NMR



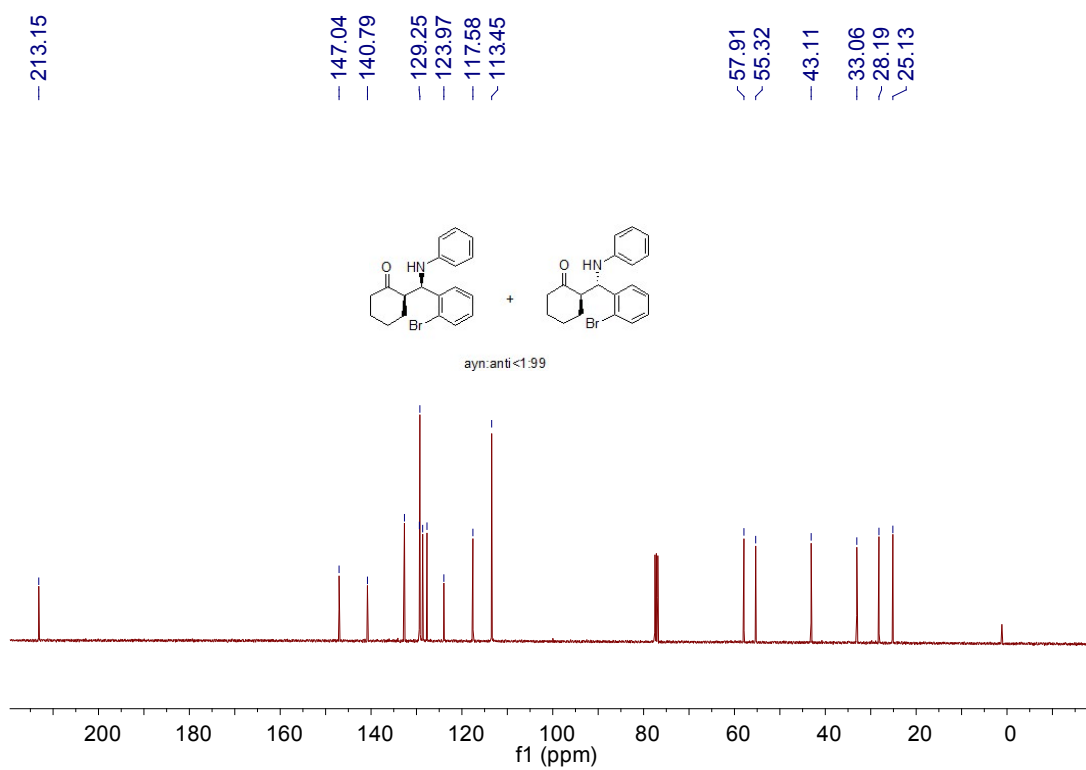
# <sup>13</sup>C NMR



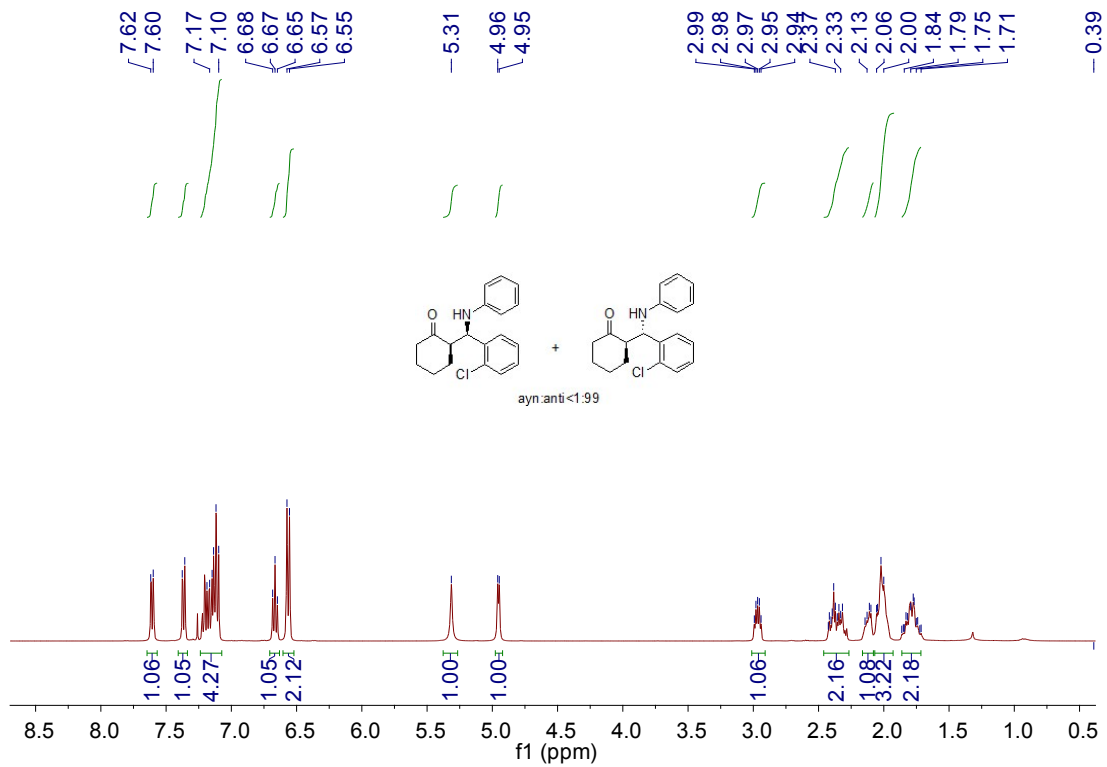
# <sup>1</sup>H NMR



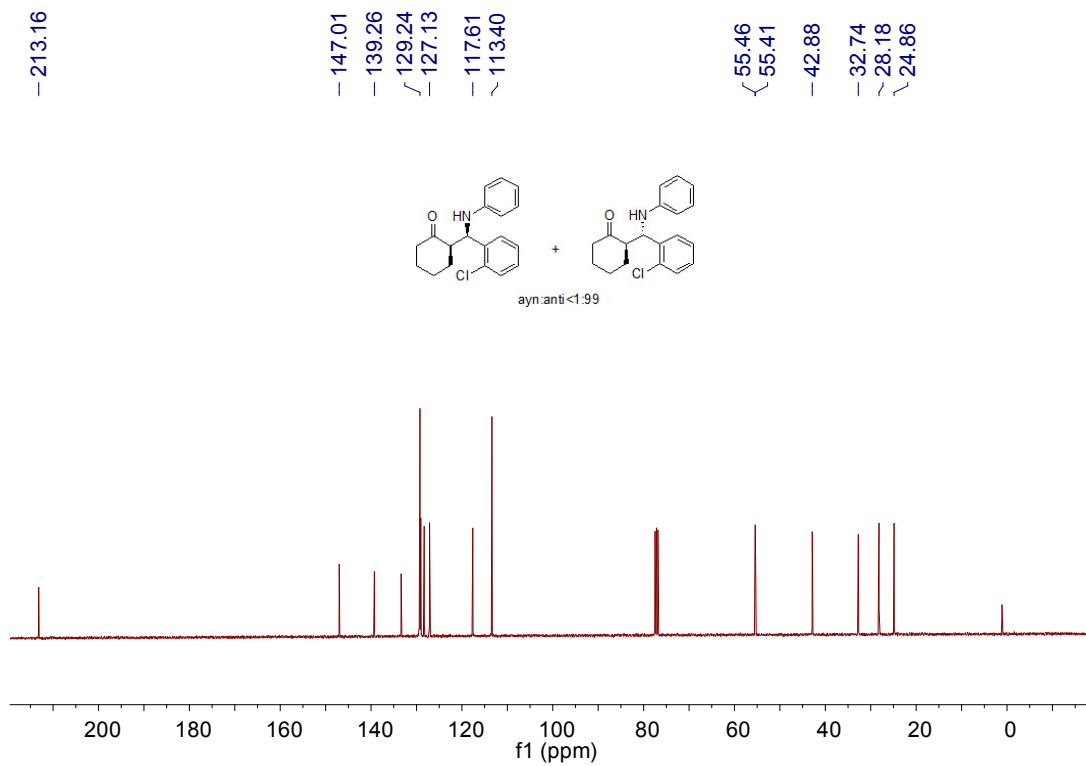
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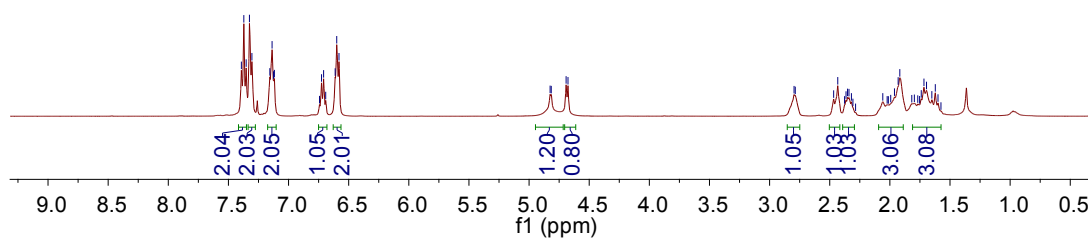
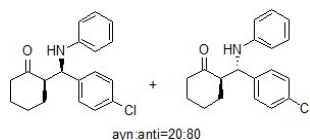
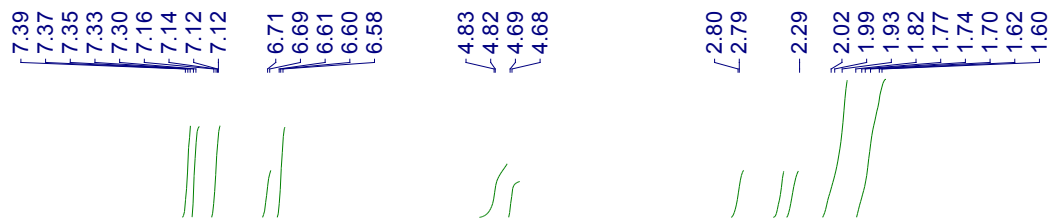
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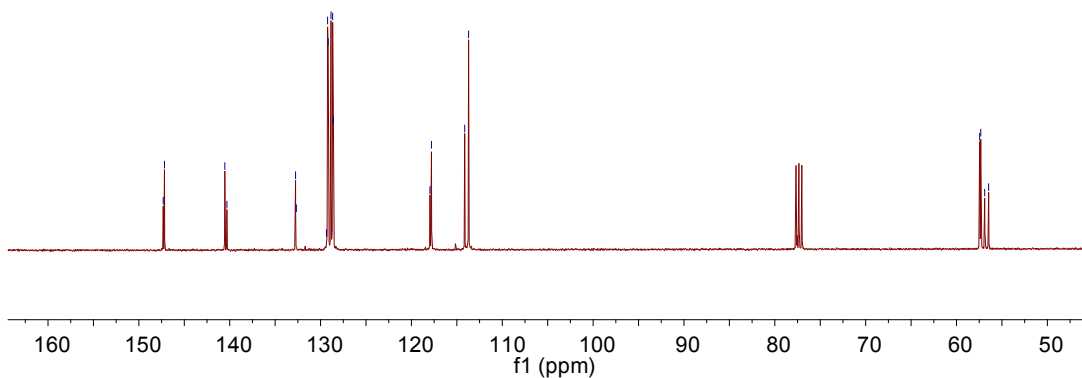
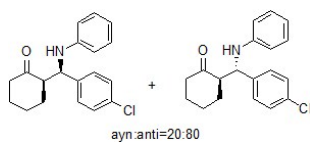
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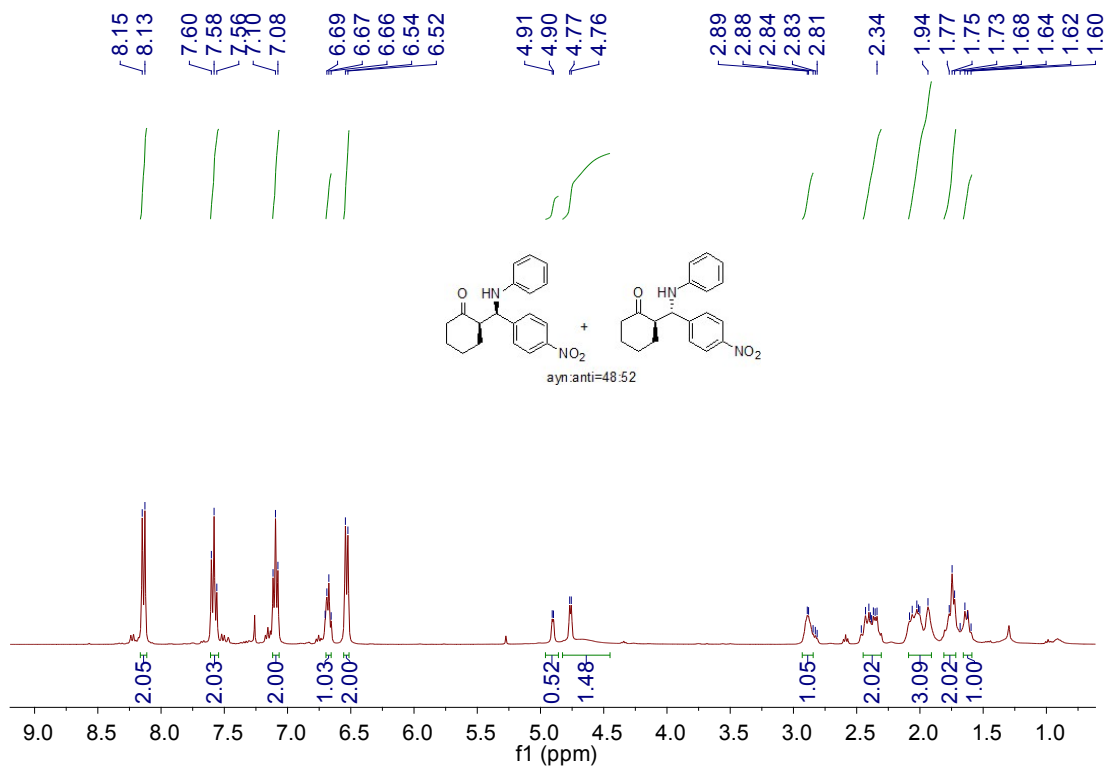
# <sup>1</sup>H NMR



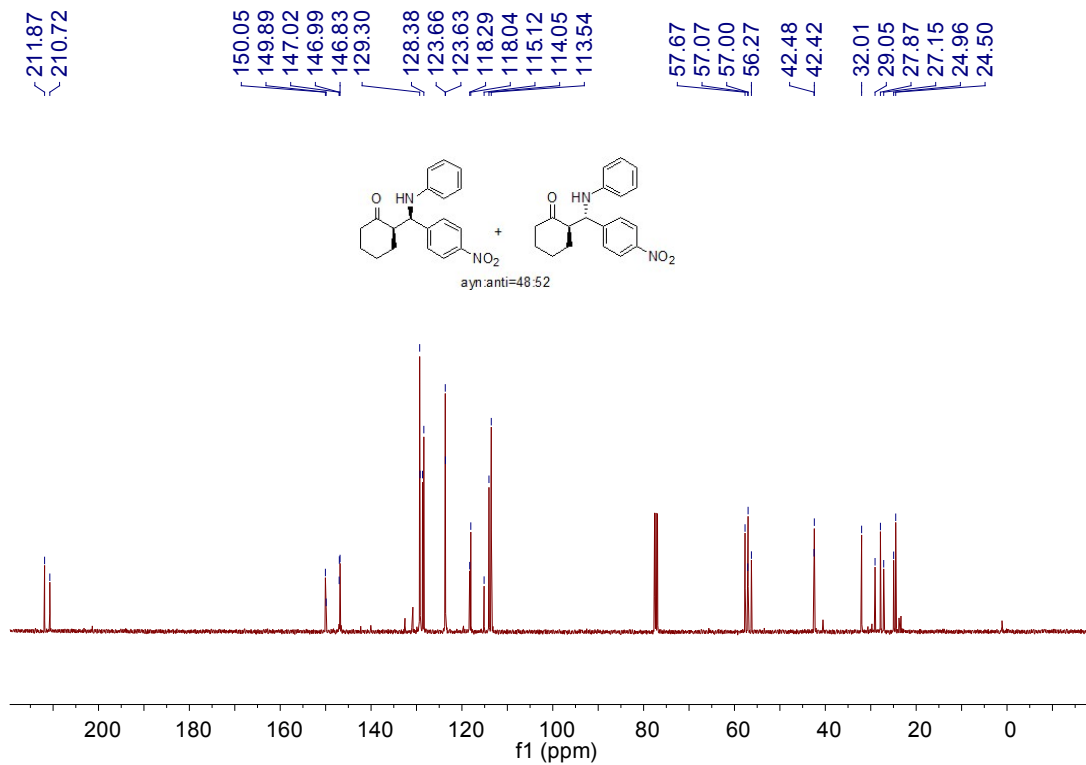
# <sup>13</sup>C NMR



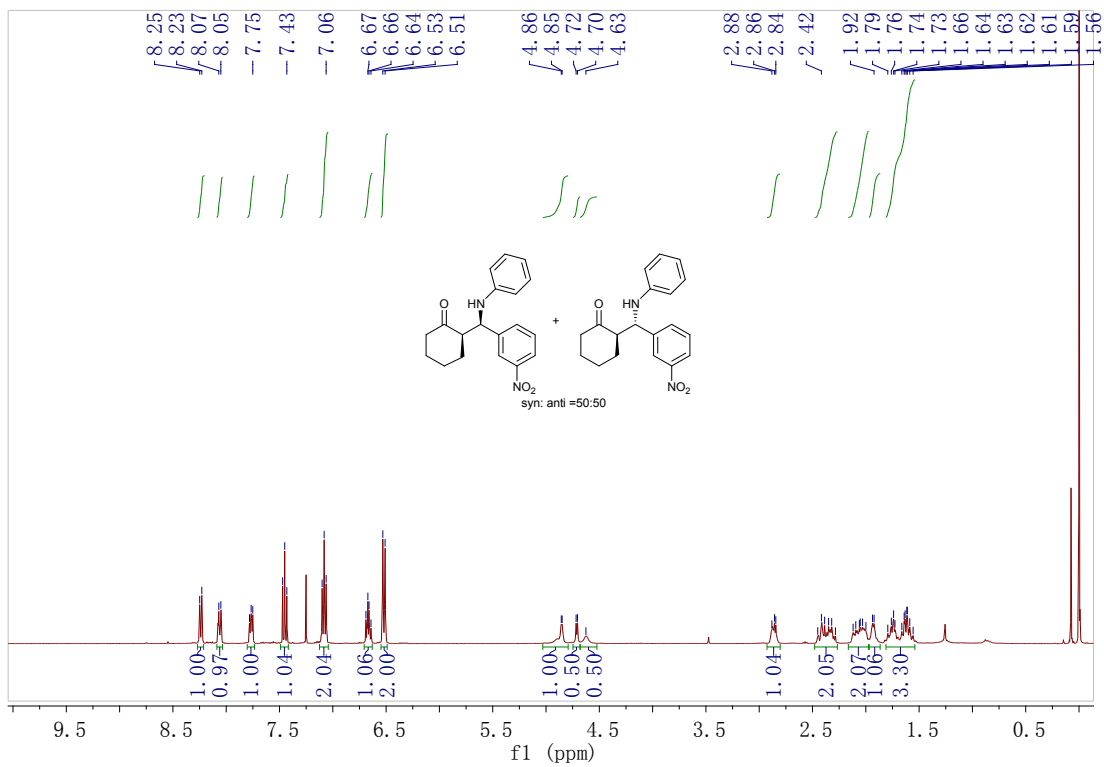
# <sup>1</sup>H NMR



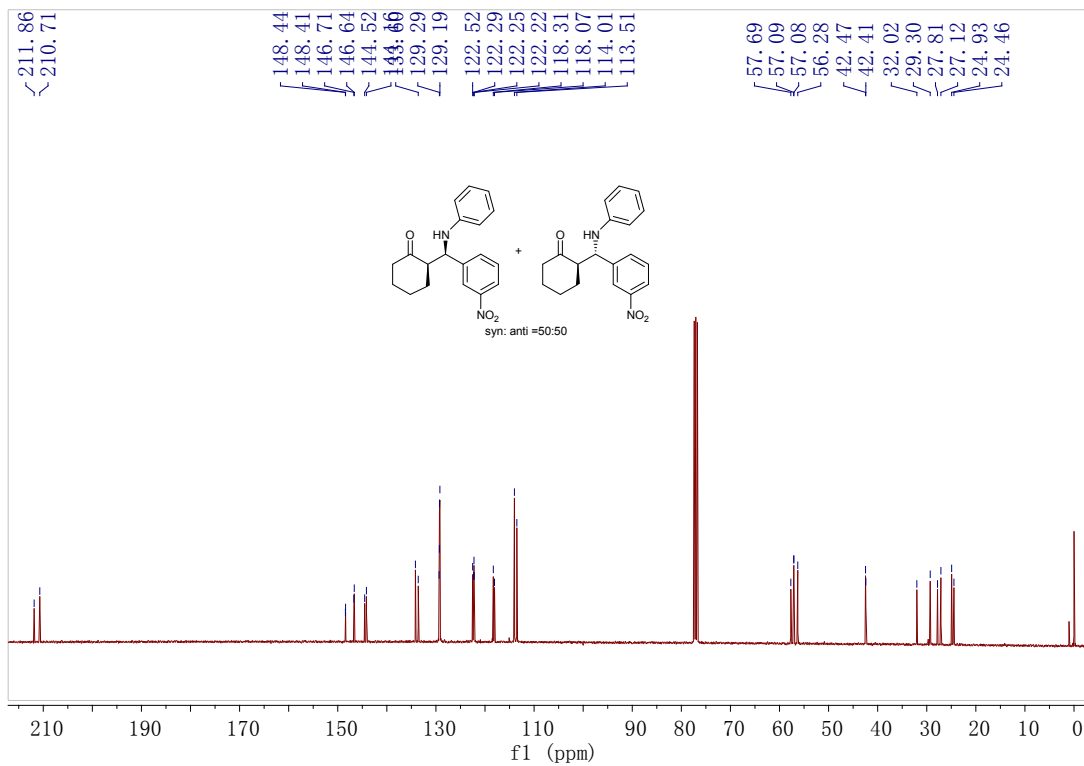
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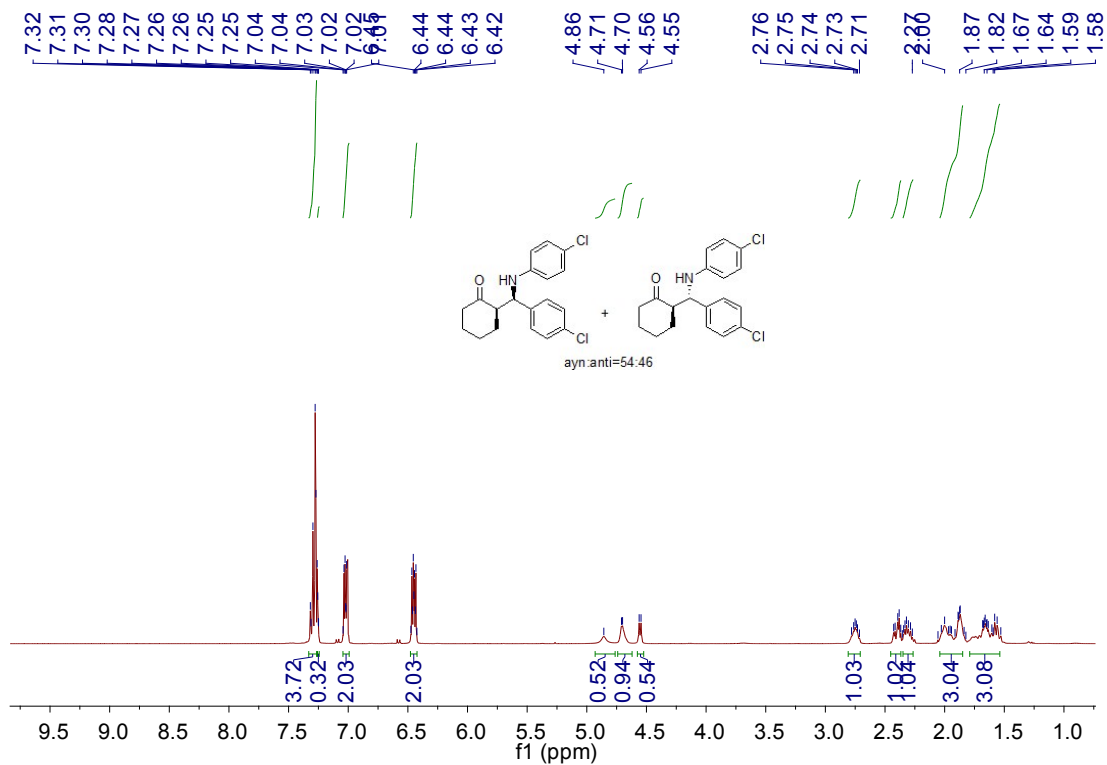
# <sup>1</sup>H NMR



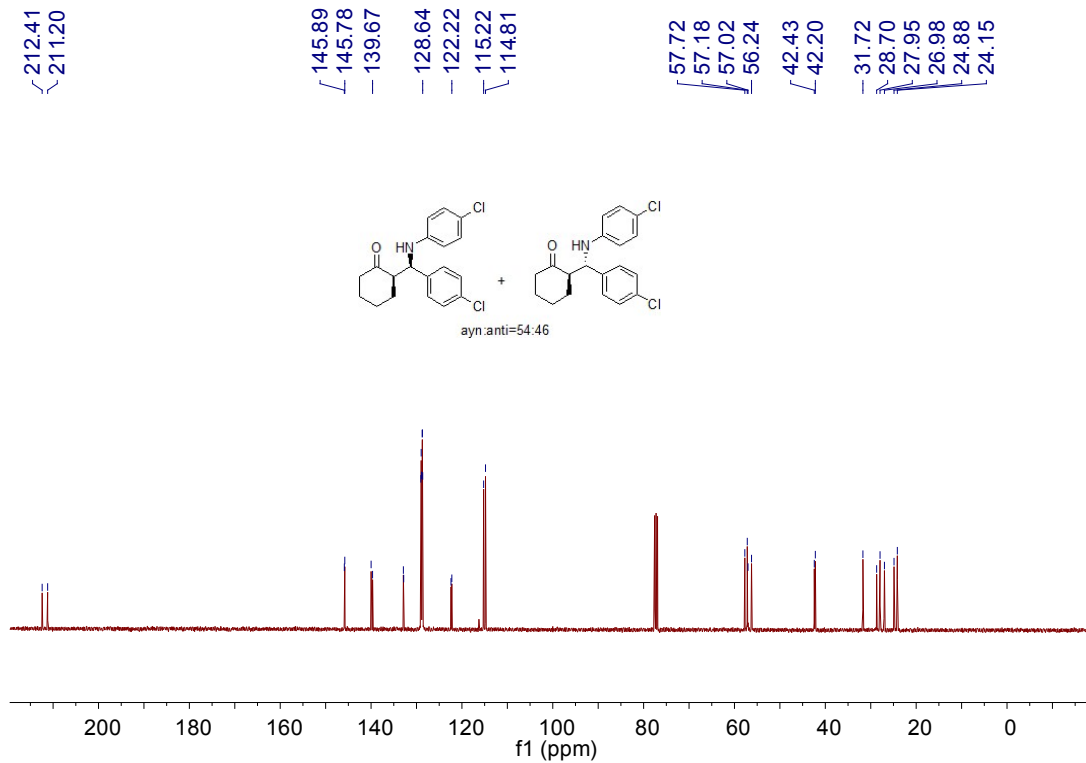
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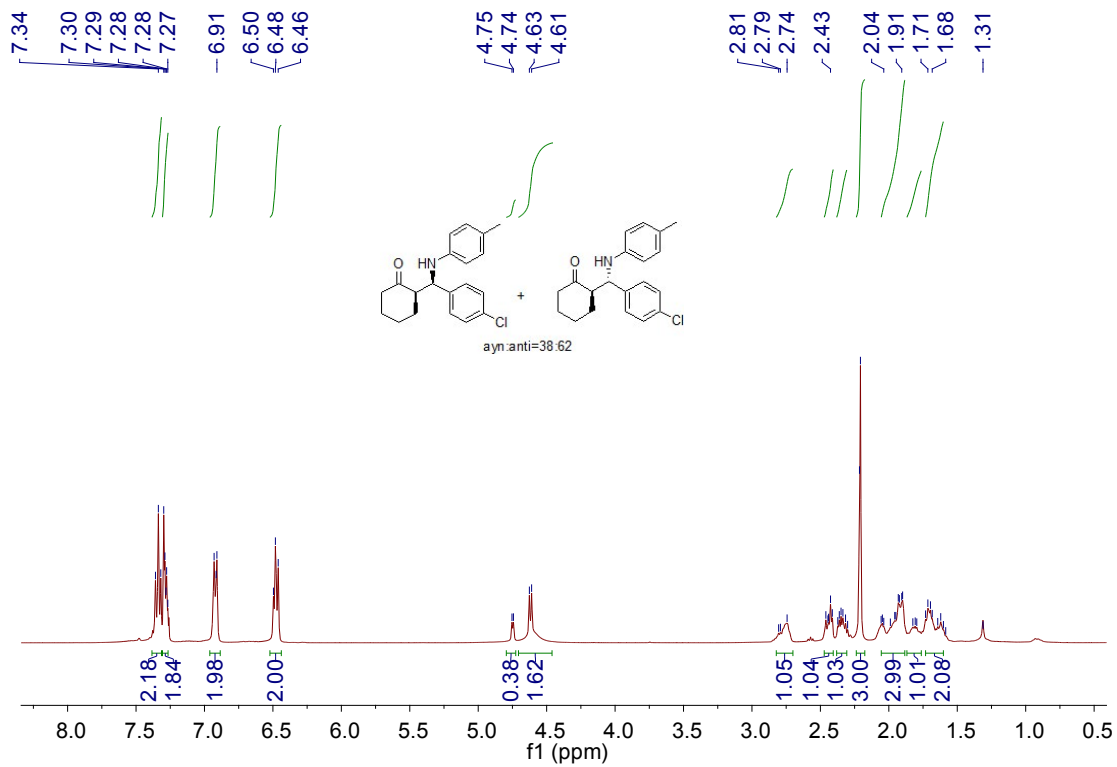
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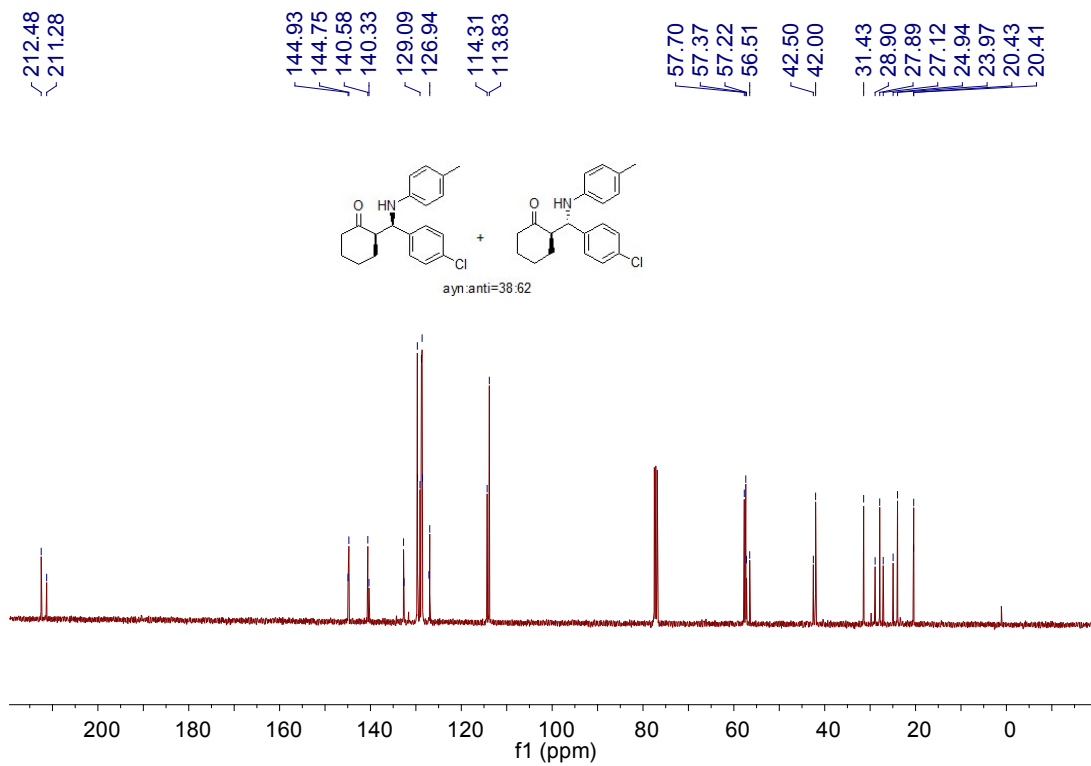
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# <sup>1</sup>H NMR

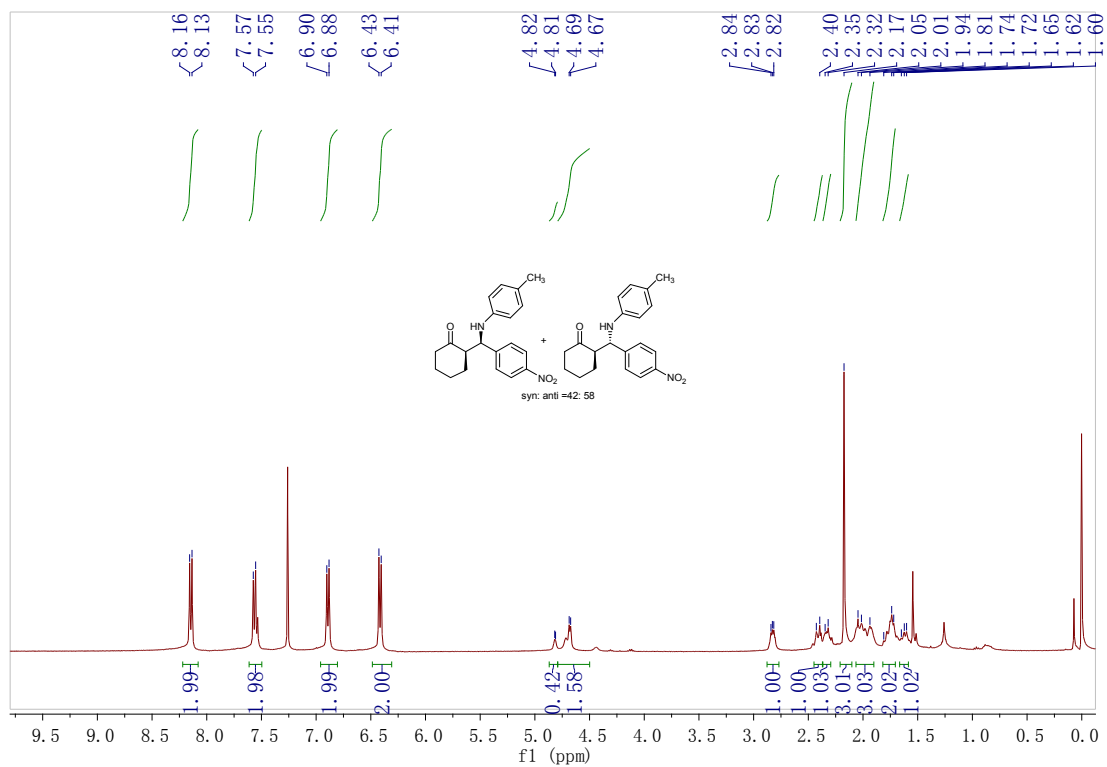


# <sup>13</sup>C NMR

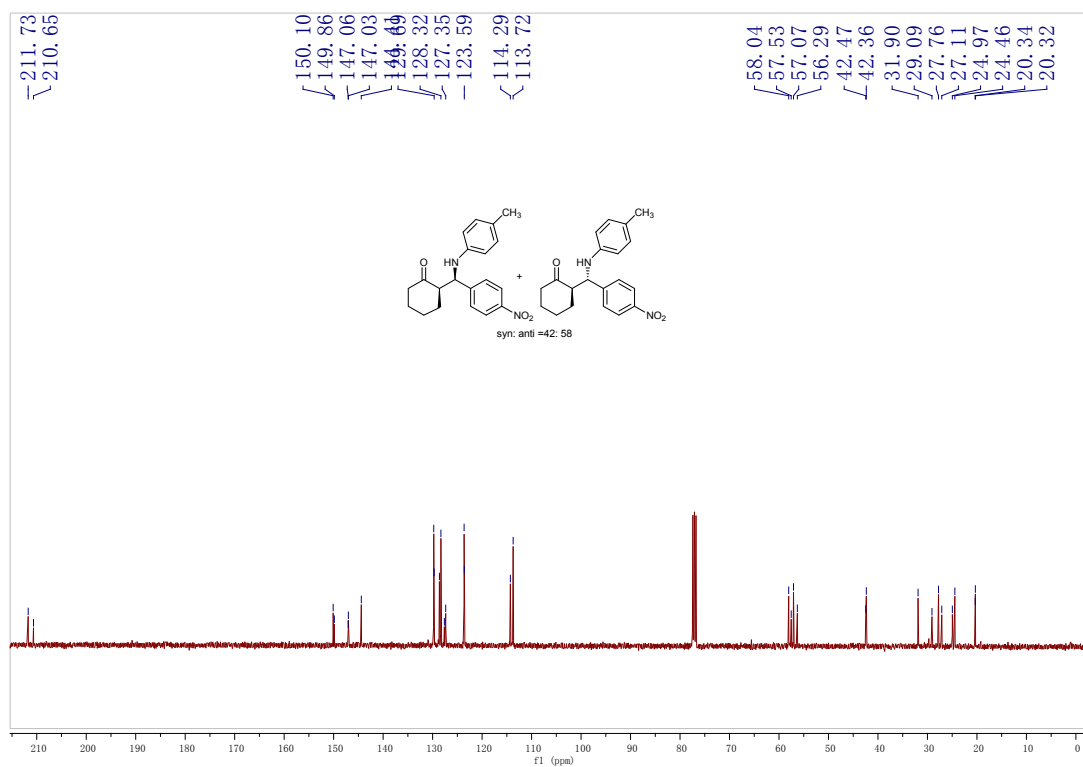




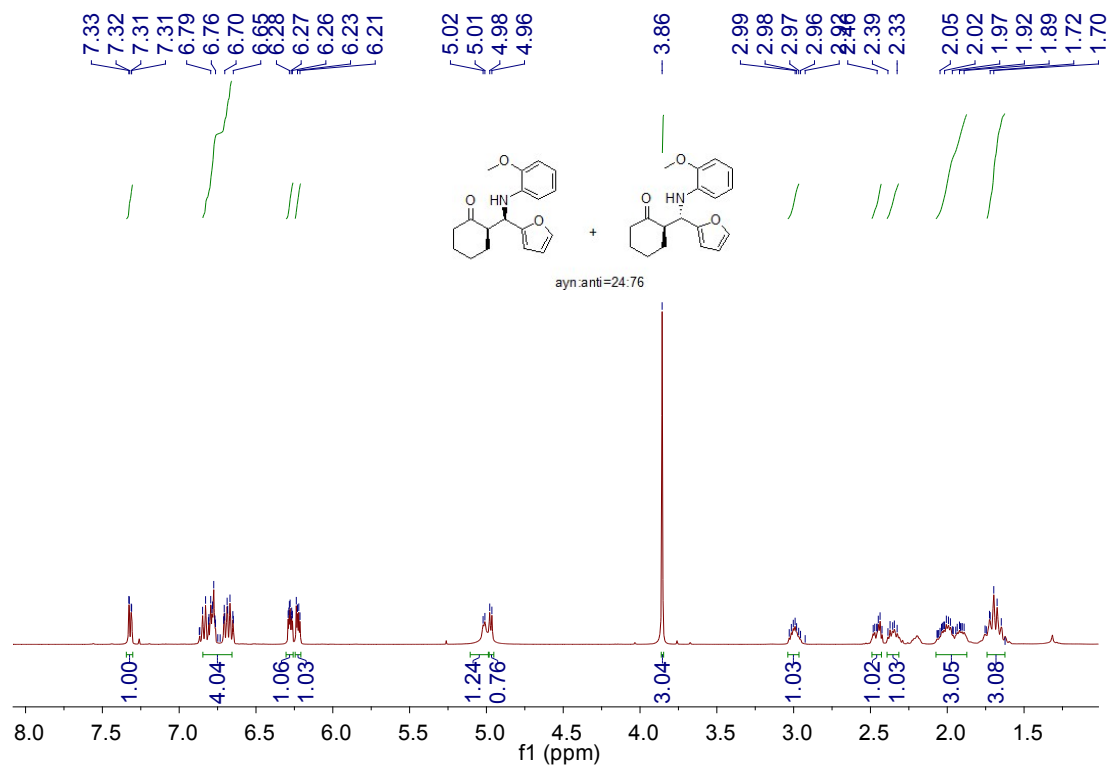
# <sup>1</sup>H NMR



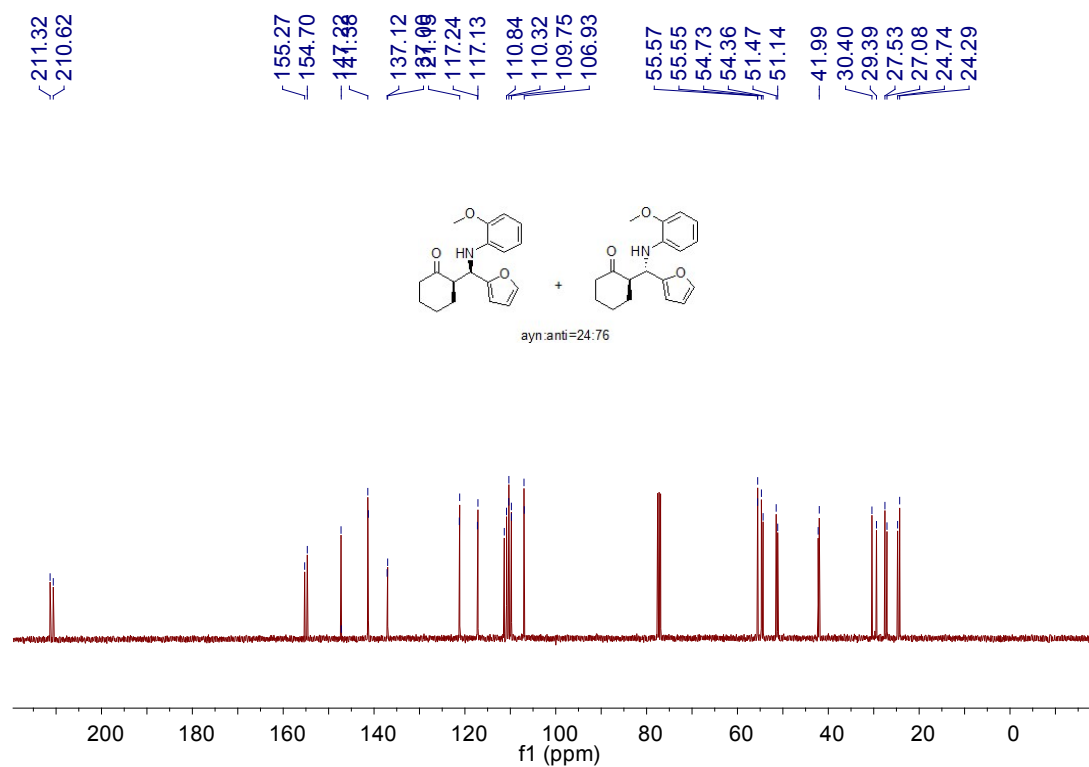
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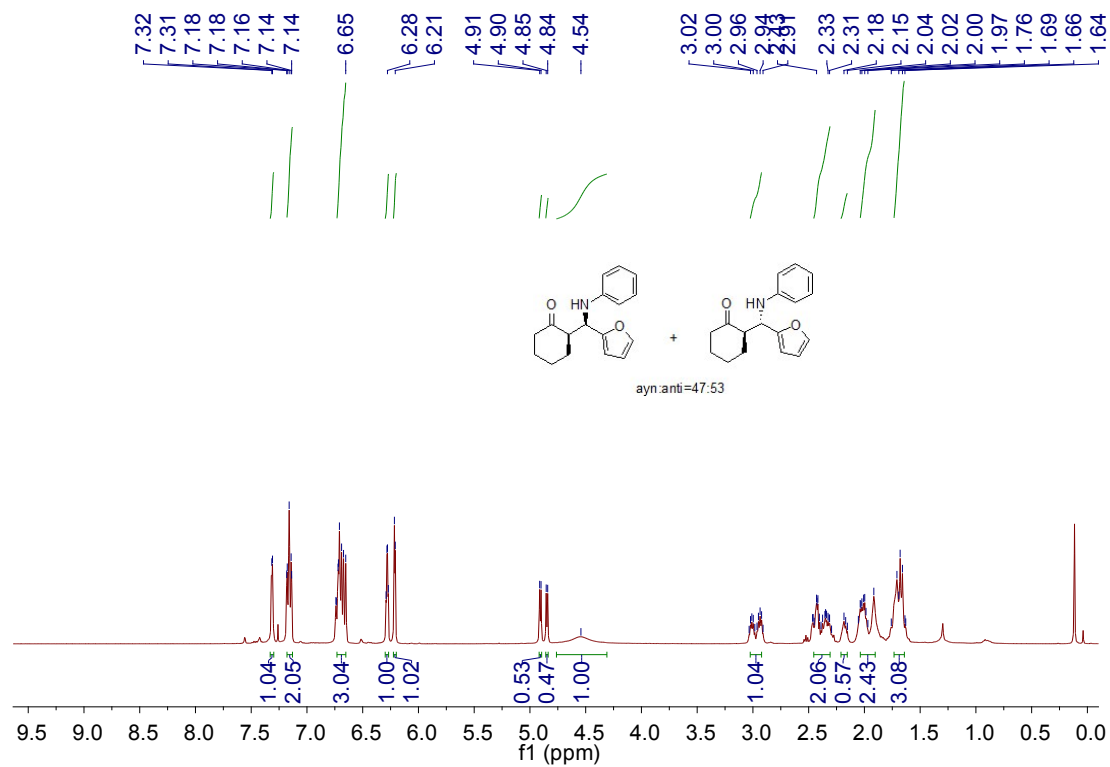
# <sup>1</sup>H NMR



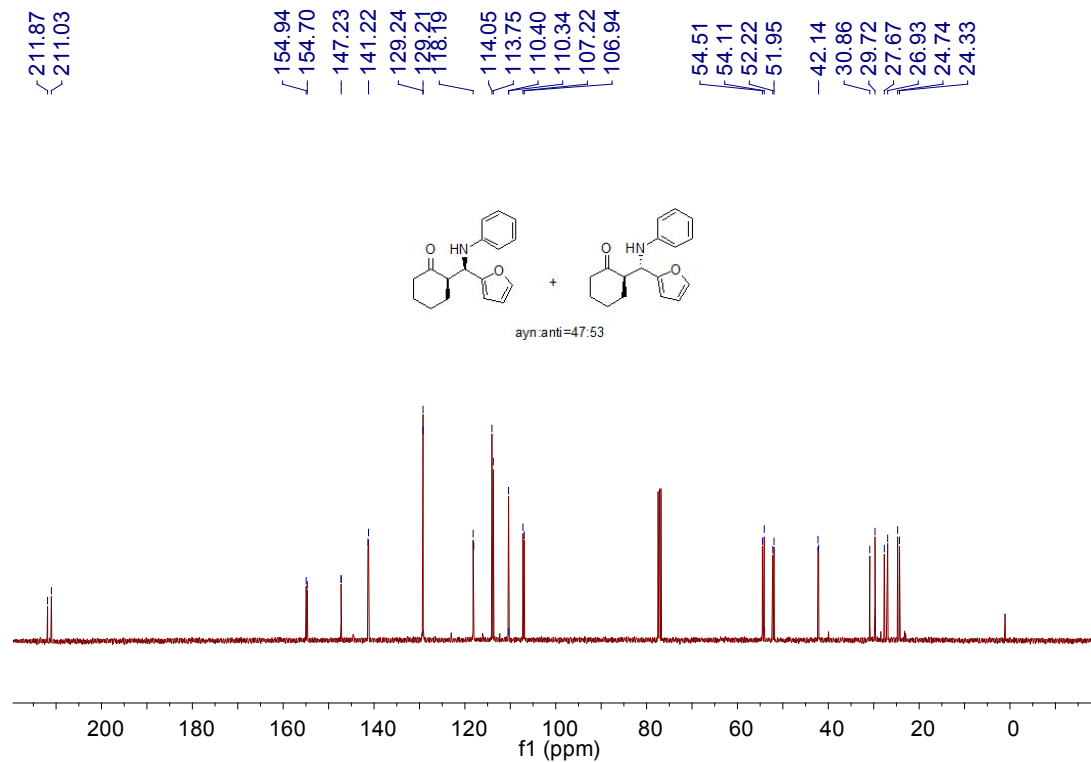
# <sup>13</sup>C NMR



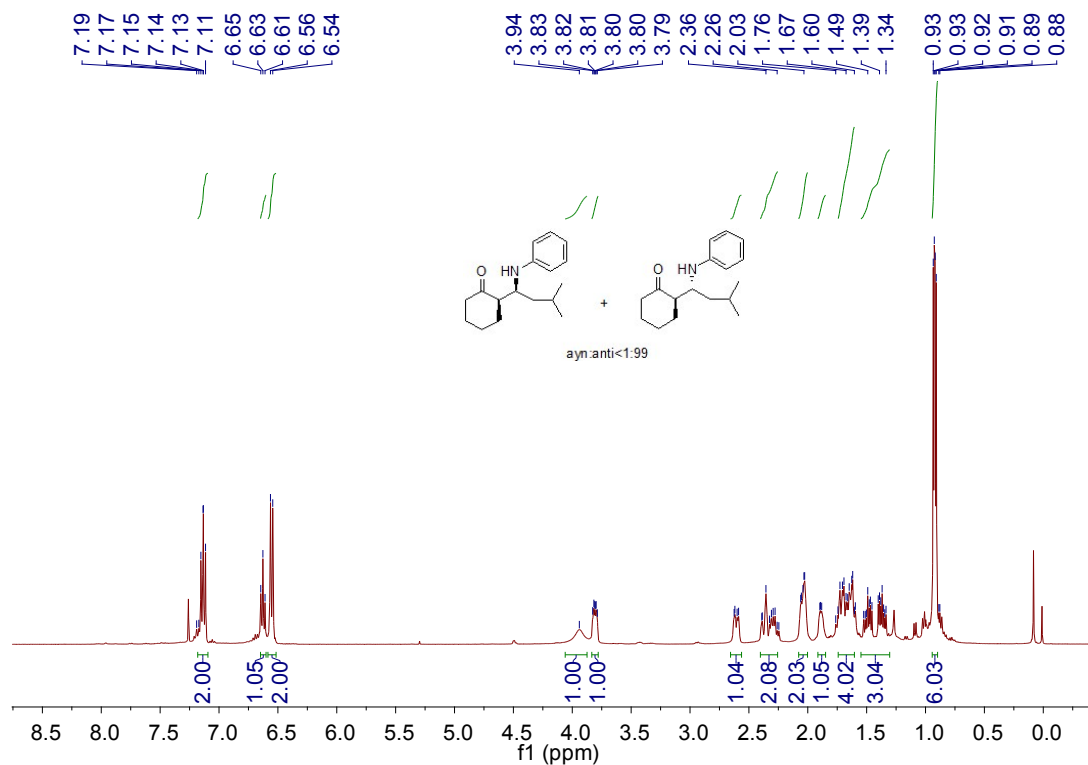
# <sup>1</sup>H NMR



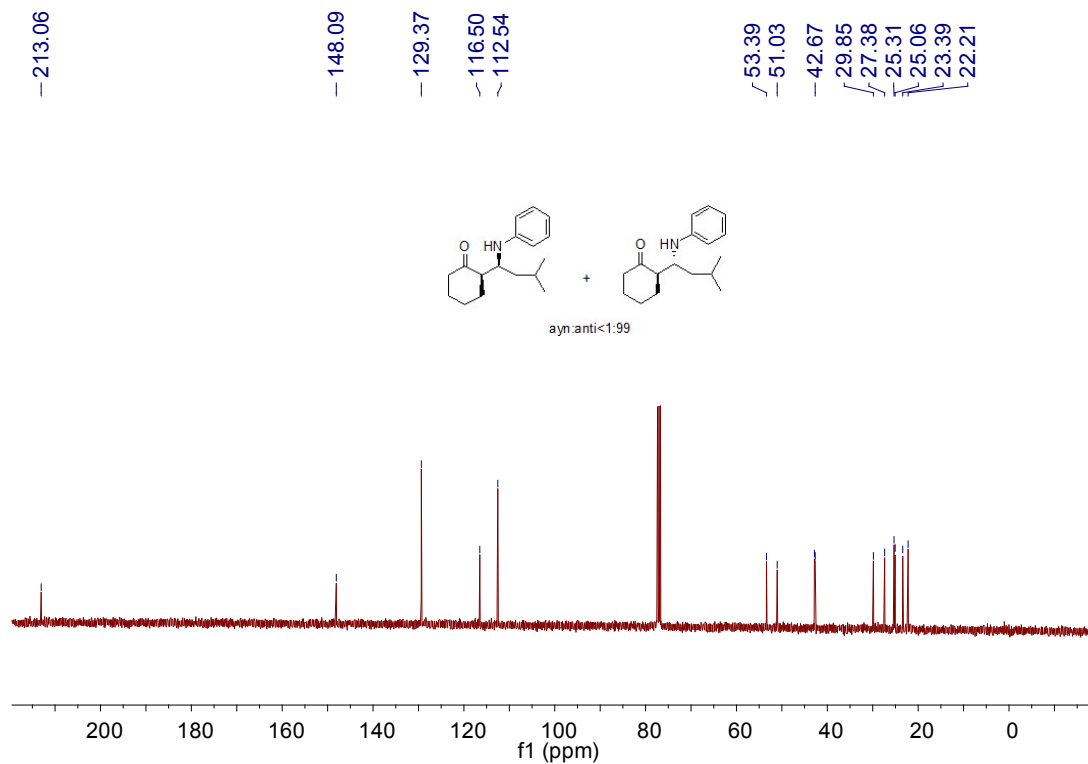
# <sup>13</sup>C NMR



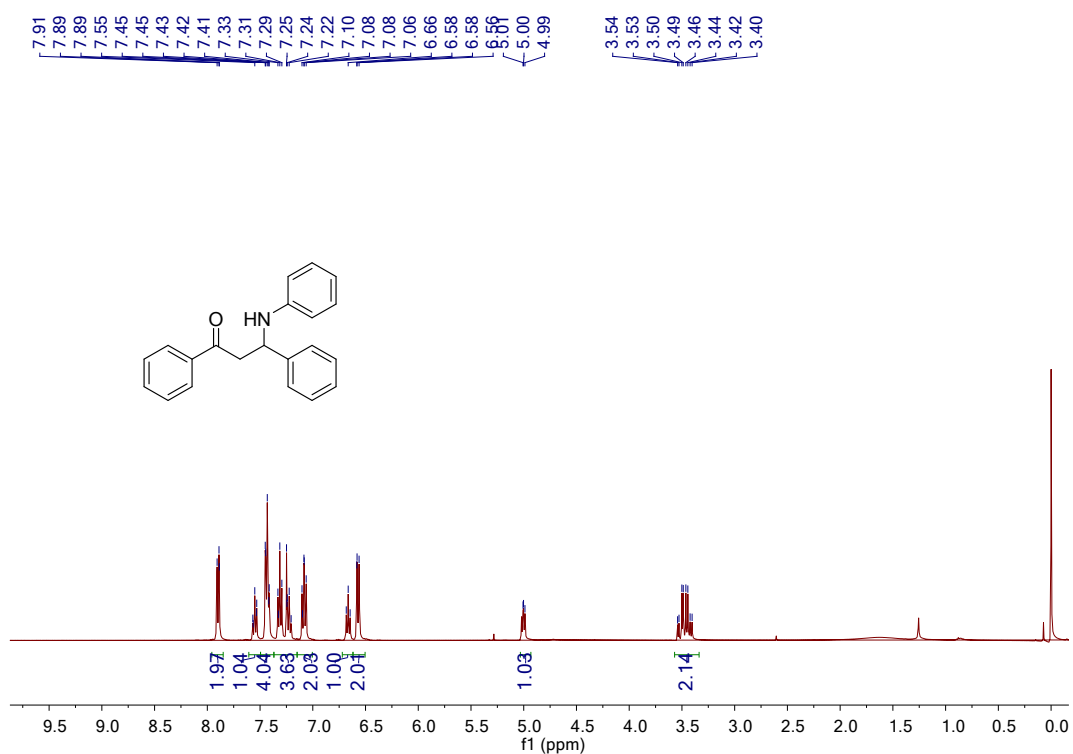
# <sup>1</sup>H NMR



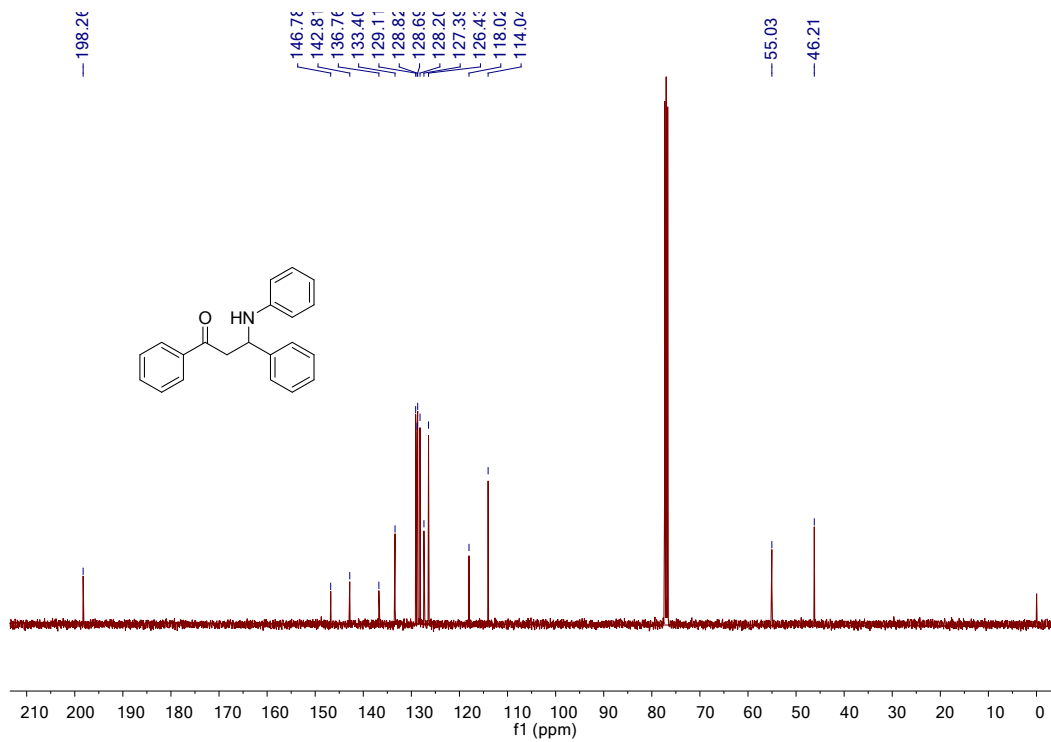
# <sup>13</sup>C NMR



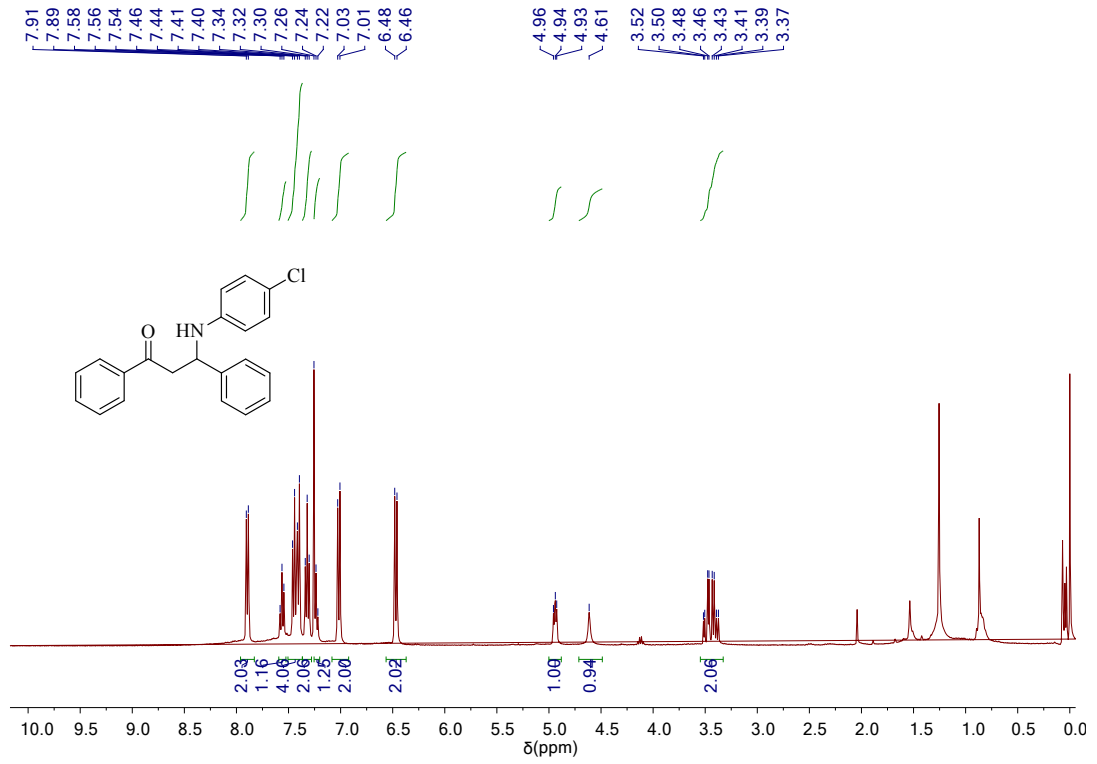
# <sup>1</sup>H NMR



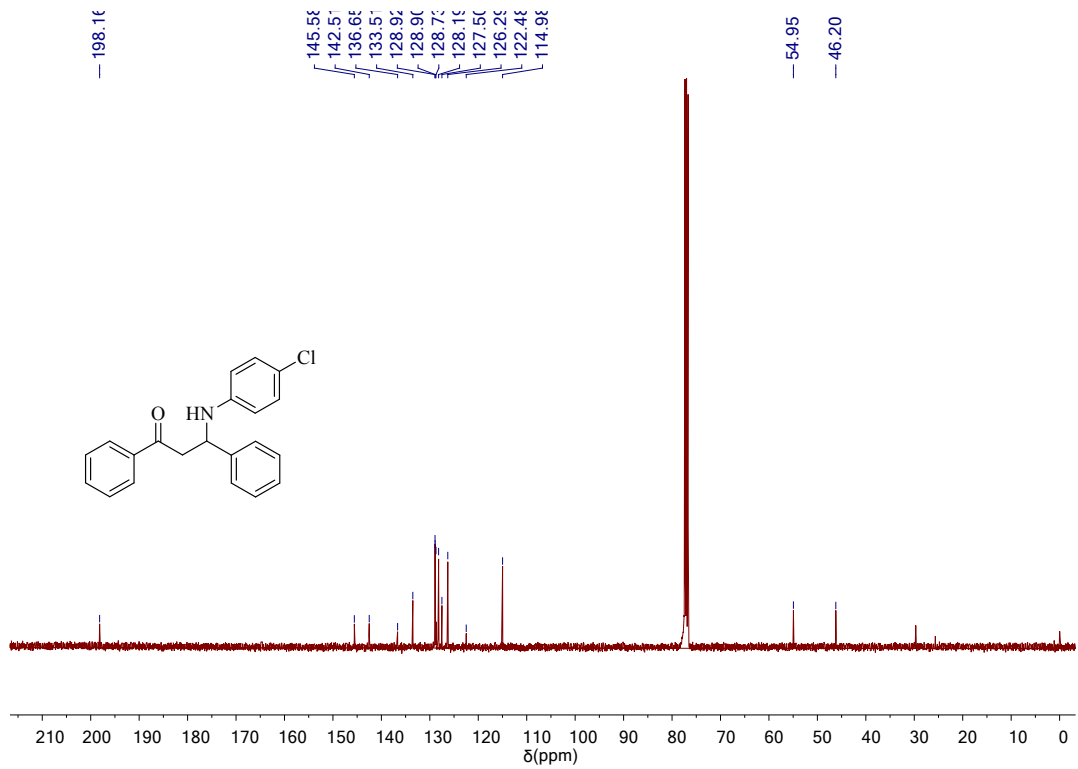
# <sup>13</sup>C NMR



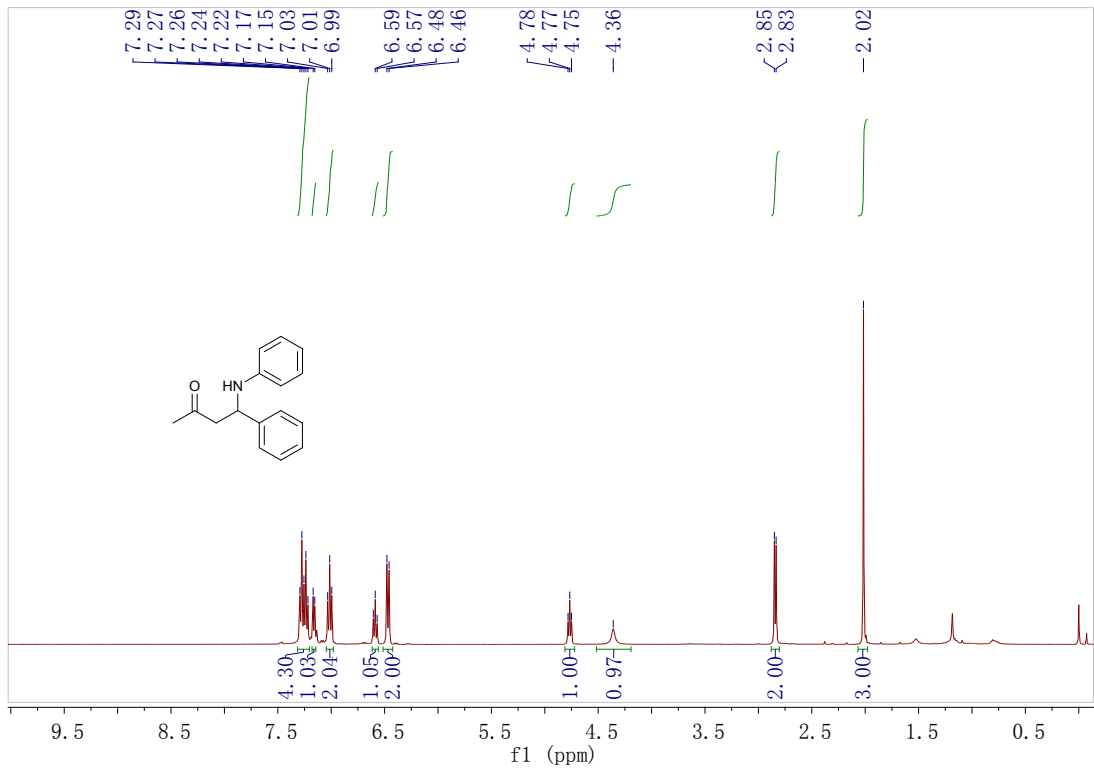
# <sup>1</sup>H NMR



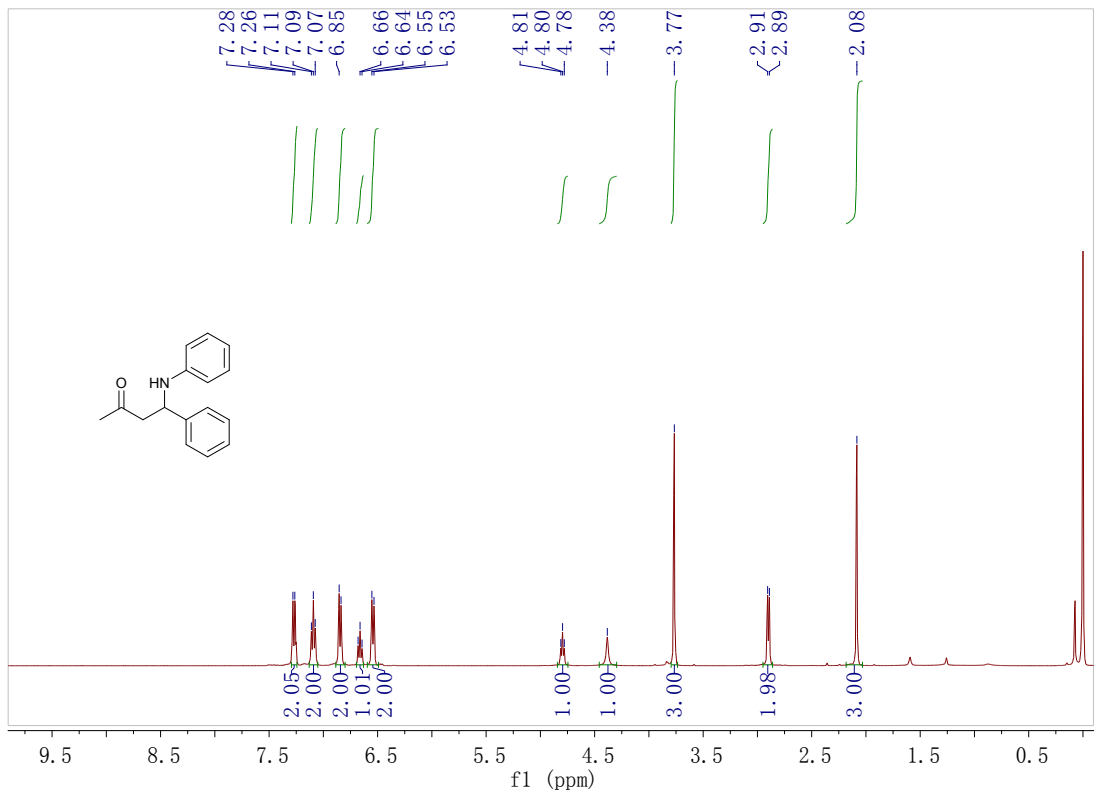
# <sup>13</sup>C NMR



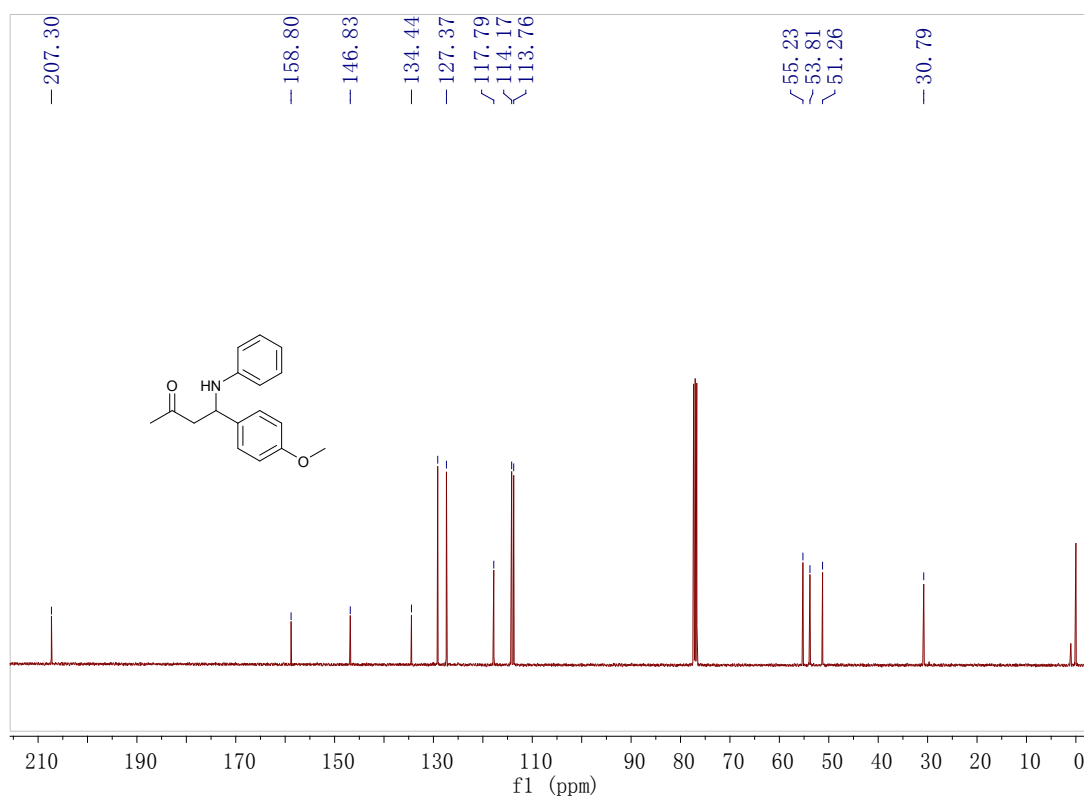
# <sup>1</sup>H NMR



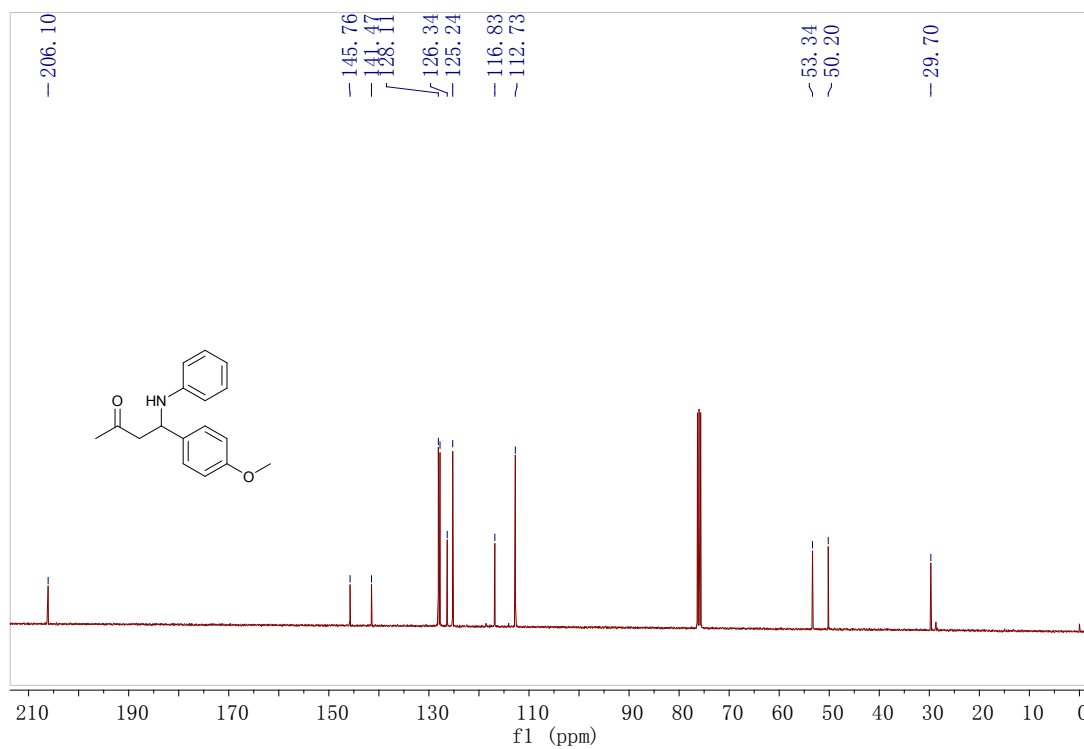
# <sup>13</sup>C NMR



### <sup>1</sup>H NMR

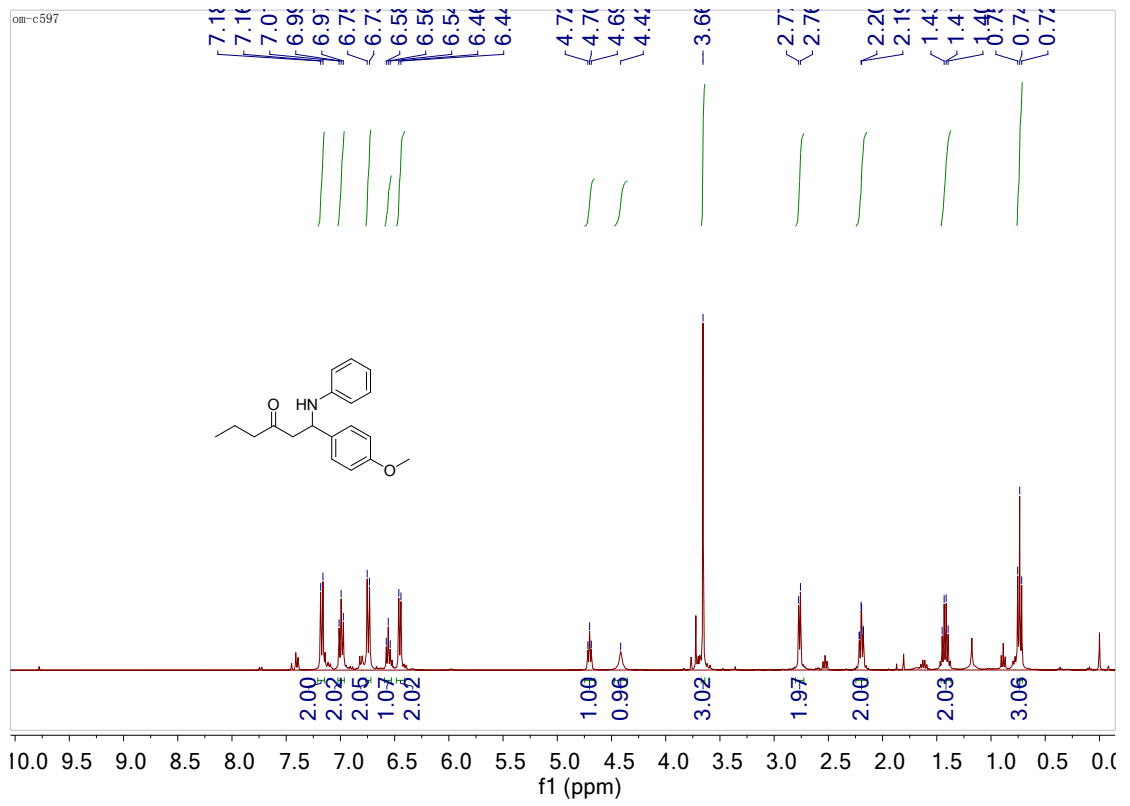


### <sup>13</sup>C NMR

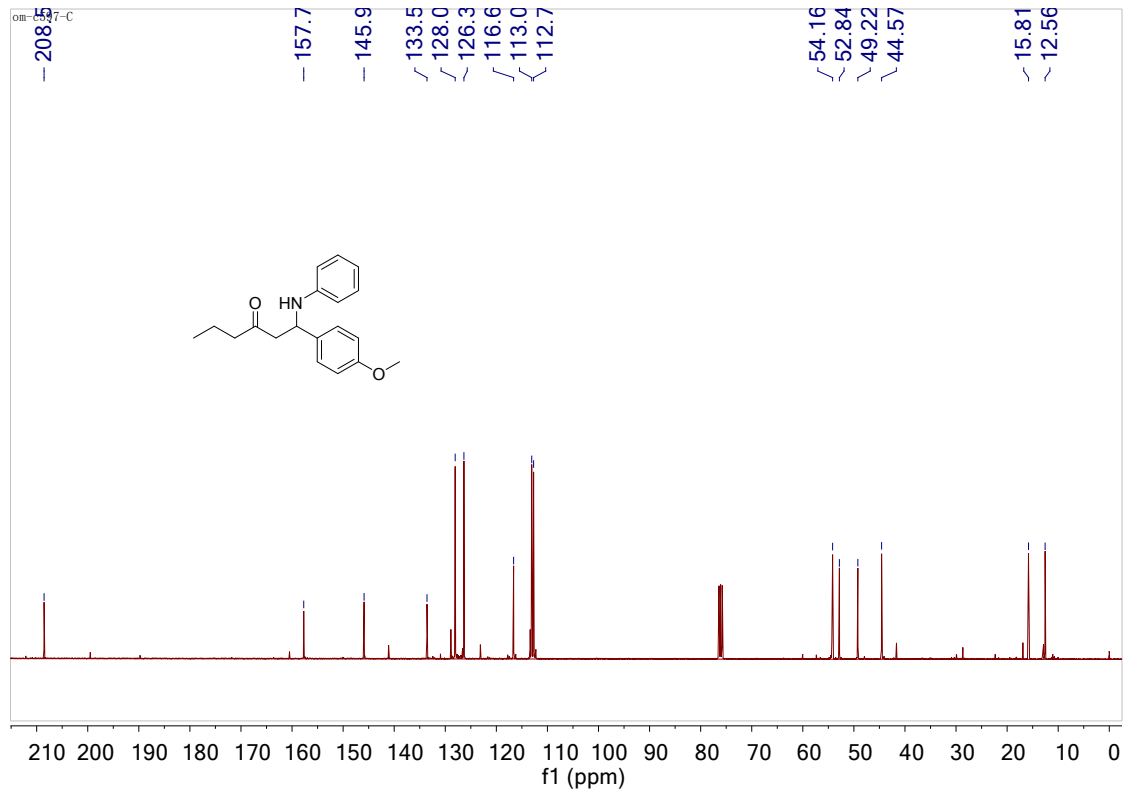




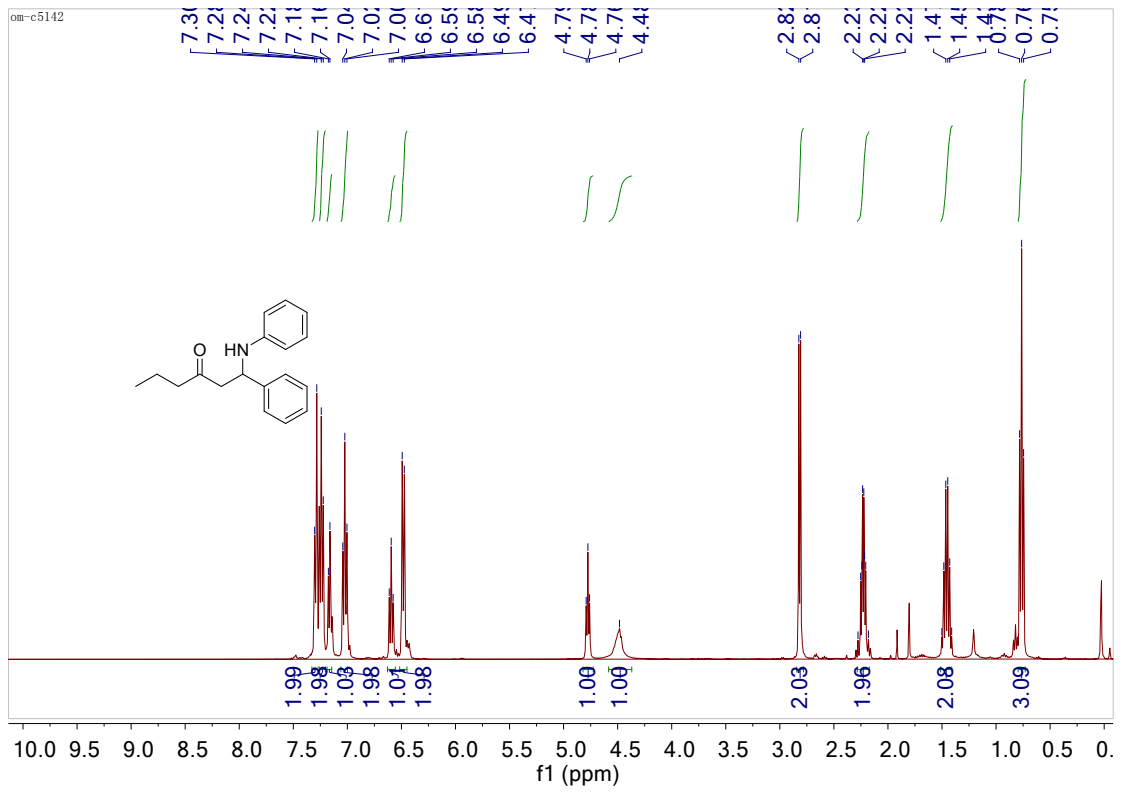
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR



# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

