

# Titanocene Dichloride and Poly(o-aminophenol) as a New Heterogeneous Cooperative Catalysis System for Three-component Mannich Reaction

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## Materials and methods

All the chemicals and reagents used are of analytical grade and were used without further purification. The  $\beta$ -amino ketones were isolated and characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR. FTIR spectra was recorded on a Bruker tensor 27 spectrometer in KBr with absorptions in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were run on Bruker Avance-400 MHz in  $\text{CDCl}_3$  solution with tetramethylsilane ( $^1\text{H}$ ) as internal standard. Chemical shifts are given in ppm and referenced internally to the residual solvent signal.  $J$  values are in Hz.

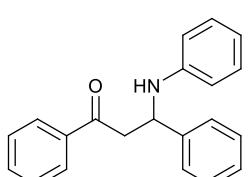
## General procedure for sample preparation

A mixture of aldehyde (1.0 mmol), amine (1.1 mmol), ketone (1.5 mmol or 27.0 mmol), and  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol in the case of 10 mmol%), POAP (10 mg) was stirred at 25 or 50 °C for 6–7 h until the reaction was completed as monitored by TLC. After the reaction, the catalyst was washed by THF and the crude product easily separated via filtration and purified either by crystallization from  $\text{CH}_2\text{Cl}_2$ -hexane or by column chromatography on silica gel using ethyl acetate/hexane as the eluent. The catalyst was retested the activity directly in the next cycle.

## Preparation of the catalyst

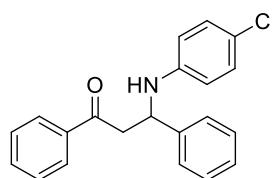
A mixture of POAP (250 mg),  $\text{Cp}_2\text{TiCl}_2$  (25 mmol) and aniline (2.5 mmol) was stirred in  $\text{CH}_2\text{Cl}_2$  (30 mL) at 25 °C for 24 h. After the reaction, the solid was washed by water for three times and filtered. Followed by drying in vacuum drying chamber at 50 °C, the heterogeneous catalyst was obtained.

## Characterization data of products

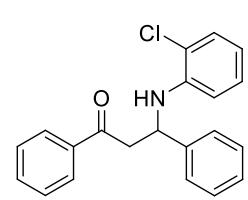


**1,3-diphenyl-3-(phenylamino)-1-propanone.** The reaction of benzaldehyde (1 mmol), aniline (1.1 mmol), acetophenone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 25 °C for 7

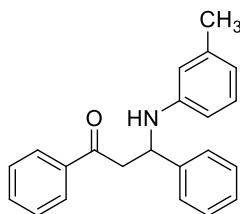
h, afforded 97% yield. White solid; m.p.: 170-172 °C; IR (KBr, v, cm<sup>-1</sup>): 3383, 1669; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89-7.91 (m, 2H), 7.56 (dd, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.3 Hz, 1H), 7.45 (dd, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.5 Hz, 4H), 7.32 (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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 198.3, 146.8, 142.8, 136.8, 133.4, 129.1, 128.8, 128.7, 128.2, 127.4, 126.4, 118.0, 114.0, 55.0, 46.2.



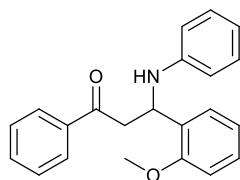
**1,3-diphenyl-3-(4-chlorophenylamino)-1-propanone.** The reaction of benzaldehyde (1 mmol), *p*-chloroaniline (1.1 mmol), acetophenone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 25 °C for 6 h, afforded 95% yield. Yellow solid; m.p.: 167-168 °C; IR (KBr): 3370, 1665; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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.



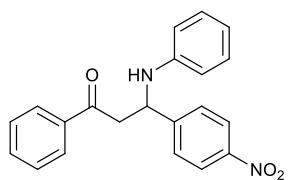
**1,3-diphenyl-3-(2-chlorophenylamino)-1-propanone.** The reaction of benzaldehyde (1 mmol), *o*-chloroaniline (1.1 mmol), acetophenone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 6 h, afforded 86% yield. Yellow solid; m.p.: 117-118 °C; IR (KBr): 3478, 3554, 3413, 1620; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90-7.92 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41-7.44 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21-7.25 (m, 2H), 6.95-6.99 (m, 1H), 6.58 (td, *J*<sub>1</sub> = 7.7 Hz, *J*<sub>2</sub> = 1.3 Hz, 1H), 6.51 (dd, *J*<sub>1</sub> = 8.2 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 5.15 (s, 1H), 5.09 (t, *J* = 6.3 Hz, 1H), 3.52 (d, *J* = 6.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.7, 141.8, 141.4, 135.8, 132.4, 128.0, 127.9, 127.7, 127.2, 126.6, 126.5, 125.3, 118.6, 116.7, 111.7, 53.5, 45.4.



**1,3-diphenyl-3-(3-methylphenylamino)-1-propanone.** The reaction of benzaldehyde (1 mmol), *m*-methylaniline (1.1 mmol), acetophenone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 87% yield. White solid; m.p.: 131-132 °C; IR (KBr): 3388, 1666, 1596; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90-7.92 (m, 2H), 7.54-7.56 (m, 1H), 7.44 (dt, *J*<sub>1</sub> = 7.4 Hz, *J*<sub>2</sub> = 3.8 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23-7.25 (m, 1H), 6.97 (t, *J* = 7.8, 1H), 6.49 (d, *J* = 7.5, 1H), 6.42 (s, 1H), 6.34-6.36 (m, 1H), 5.00 (dd, *J*<sub>1</sub> = 7.4 Hz, *J*<sub>2</sub> = 5.5 Hz, 1H), 4.48 (s, 1H), 3.38-3.53 (m, 2H), 2.20 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.3, 146.0, 142.1, 137.8, 135.7, 132.3, 128.0, 127.8, 127.6, 127.2, 126.3, 125.3, 117.7, 113.7, 109.8, 53.7, 45.2, 20.5.

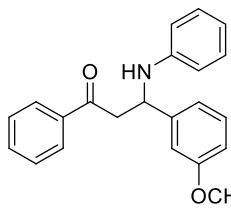


**3-(2-methoxyphenyl)-1-phenyl-3-(phenylamino)-1-propanone.** The reaction of *o*-anisaldehyde (1 mmol), aniline (1.1 mmol), acetophenone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 6 h, afforded 92% yield. White solid; m.p.: 156-157 °C; IR (KBr): 3403, 1682; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.91 (m, 2H), 7.41-7.43 (m, 1H), 7.30-7.34 (m, 3H), 7.12 (dd, *J*<sub>1</sub> = 12.8 Hz, *J*<sub>2</sub> = 4.7 Hz, 1H), 6.96 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 7.4 Hz, 2H), 6.80 (m, 2H), 6.53 (d, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 7.7 Hz, 2H), 5.18 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 4.5 Hz, 1H), 3.85 (s, 3H), 3.55 (dd, *J*<sub>1</sub> = 15.1 Hz, *J*<sub>2</sub> = 4.5 Hz, 1H), 3.13 (dd, *J*<sub>1</sub> = 15.2 Hz, *J*<sub>2</sub> = 8.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.1, 156.6, 147.1, 136.8, 133.3, 130.1, 129.1, 128.6, 128.6, 128.4, 128.3, 127.7, 121.0, 117.5, 113.7, 110.6, 55.4, 50.7, 44.5.



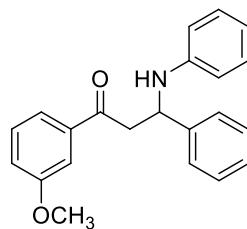
**3-(4-nitrophenyl)-1-phenyl-3-(phenylamino)-1-propanone.** The reaction of *p*-nitrobenzaldehyde (1 mmol), aniline (1.1 mmol), acetophenone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 94% yield. Yellow solid; m.p.: 154-156 °C; IR (KBr, v, cm<sup>-1</sup>): 3398, 1669; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.87-7.78 (m, 2H), 7.58-7.47 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.9 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 2H), 5.03 (s, 1H), 4.61 (s, 1H), 3.43

(d,  $J = 6.2$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 150.8, 147.2, 146.3, 136.4, 133.8, 129.3, 128.9, 128.2, 127.5, 124.1, 118.5, 113.9, 77.4, 77.1, 76.8, 54.2, 45.7.



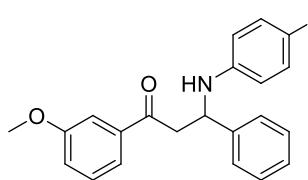
**3-(3-methoxyphenyl)-1-phenyl-3-(phenylamino)-1-propanone.**

The reaction of *m*-anisaldehyde (1 mmol), aniline (1.1 mmol), acetophenone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 83% yield. White solid; m.p.: 106-107 °C; IR (KBr): 3382, 1660;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.81 (m, 2H), 7.43-7.45 (m, 1H), 7.33 (t,  $J = 7.7$  Hz, 2H), 7.14 (t,  $J = 7.9$  Hz, 1H), 6.92-6.99 (m, 4H), 6.67 (dd,  $J_1 = 8.2$  Hz,  $J_2 = 1.9$  Hz, 1H), 6.57 (t,  $J = 7.3$  Hz, 1H), 6.46-6.48 (m, 2H), 4.88 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 5.2$  Hz, 1H), 3.66 (s, 3H), 3.34 (ddd,  $J_1 = 23.8$  Hz,  $J_2 = 16.1$  Hz,  $J_3 = 6.4$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 159.0, 146.0, 143.8, 135.7, 132.3, 128.8, 128.0, 127.6, 127.1, 117.6, 116.7, 112.8, 111.5, 111.2, 54.1, 53.7, 45.2.



**1-(3-methoxyphenyl)-3-phenyl-3-(phenylamino)-1-propanone.**

The reaction of benaldehyde (1 mmol), aniline (1.1 mmol), *m*-methoxyacetophenone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 6 h, afforded 84% yield. White solid; m.p.: 115-116 °C; IR (KBr): 3392, 1680;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.37 (m, 4H), 7.23 (td,  $J_1 = 7.9$  Hz,  $J_2 = 5.9$  Hz, 3H), 7.14 (dd,  $J_1 = 5.4$  Hz,  $J_2 = 1.8$  Hz, 1H), 6.97-6.99 (m, 3H), 6.56 (t,  $J = 7.3$  Hz, 1H), 6.46-6.48 (m, 2H), 4.91 (dd,  $J_1 = 7.5$  Hz,  $J_2 = 5.3$  Hz, 1H), 3.72 (s, 3H), 3.35 (dd,  $J_1 = 16.1$  Hz,  $J_2 = 6.4$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.0, 158.9, 146.0, 142.0, 137.1, 128.6, 128.1, 127.8, 126.3, 125.3, 119.8, 119.0, 116.8, 112.8, 111.3, 54.4, 53.8, 45.4.

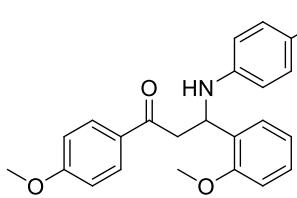


**1-(3-methoxyphenyl)-3-phenyl-3-(4-chlorophenylamino)**

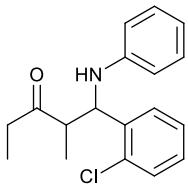
**-1-propanone.** The reaction of benaldehyde (1 mmol),

*p*-chloroaniline (1.1 mmol), *m*-methoxyacetophenone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 94% yield. Yellow solid; m.p.: 135-136 °C; IR (KBr): 3395, 1682;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$

7.38 (d,  $J = 7.7$  Hz, 1H), 7.32 (d,  $J = 8.3$  Hz, 3H), 7.27-7.21 (m, 3H), 7.18-7.14 (m, 1H), 7.01 (dd,  $J_1 = 8.1$  Hz,  $J_2 = 2.6$  Hz, 1H), 6.93 (d,  $J = 8.8$  Hz, 2H), 6.38 (d,  $J = 8.8$  Hz, 2H), 4.86 (s, 1H), 4.52 (s, 1H), 3.73 (s, 3H), 3.34 (dd,  $J_1 = 16.2$  Hz,  $J_2 = 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 158.9, 144.6, 141.5, 137.0, 128.7, 127.9, 127.9, 126.5, 125.3, 121.4, 119.8, 119.0, 113.9, 111.4, 54.4, 53.9, 45.3.

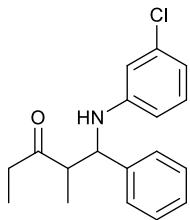


**1-(4-methoxyphenyl)-3-(2-methoxyphenyl)-3-(4-chlorophenyl)propanone.** The reaction of *o*-anisaldehyde (1 mmol), *p*-chloroaniline (1.1 mmol), *p*-methoxyacetophenone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 95% yield. Yellow solid; m.p.: 145-146 °C; IR (KBr): 3399, 1681;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.8$  Hz, 2H), 7.26 (d,  $J = 7.5$  Hz, 1H), 7.13 (t,  $J = 7.1$  Hz, 1H), 6.90 (d,  $J = 8.8$  Hz, 2H), 6.80 (dd,  $J_1 = 16.2$  Hz,  $J_2 = 8.2$  Hz, 4H), 6.34 (d,  $J = 8.8$  Hz, 2H), 5.09 (d,  $J = 3.5$  Hz, 1H), 4.73 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.49 (dd,  $J_1 = 15.1$  Hz,  $J_2 = 4.2$  Hz, 1H), 3.06 (dd,  $J_1 = 15.1$  Hz,  $J_2 = 8.6$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 162.7, 155.5, 144.7, 129.7, 128.7, 128.7, 127.8, 127.3, 126.4, 120.9, 120.0, 113.7, 112.7, 109.5, 54.5, 54.4, 49.8, 43.0.

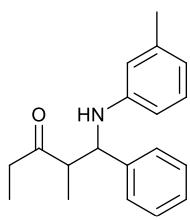


**1-(2-chlorophenyl)-2-methyl-1-(phenylamino)-3-pentanone.** The reaction of *o*-chlorobenzaldehyde (1 mmol), aniline (1.1 mmol), 3-pentanone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 70% yield. Yellow solid; m.p.: 105-106 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3401, 1707;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33-7.28 (m, 1H), 7.19-7.14 (m, 1H), 7.14-7.09 (m, 1H), 7.07 (dd,  $J_1 = 8.1$  Hz,  $J_2 = 3.6$  Hz, 1H), 6.99 (dd,  $J_1 = 13.1$  Hz,  $J_2 = 5.5$  Hz, 2H), 6.61-6.51 (m, 1H), 6.37 (dd,  $J_1 = 24.3$  Hz,  $J_2 = 7.9$  Hz, 2H), 5.23 (s, 0.66H), 5.07 (s, 0.34H), 4.85 (d,  $J = 4.8$  Hz, 0.66H), 4.32 (s, 0.34H), 3.27-3.07 (m, 1H), 2.67-1.77 (m, 2H), 1.19 (d,  $J = 7.1$  Hz, 2H), 0.96 (t,  $J = 7.2$  Hz, 1H), 0.91 (d,  $J = 7.1$  Hz, 1H), 0.77 (t,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  214.6, 211.9, 145.6, 145.5, 137.8, 136.6, 132.0, 131.2, 129.0, 128.8, 128.2, 128.1,

127.6, 126.8, 126.2, 126.0, 117.0, 116.3, 112.5, 111.9, 55.9, 54.4, 47.9, 46.8, 35.8, 33.6, 14.5, 8.3, 6.7, 6.1.

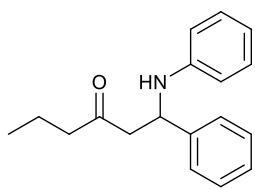


**1-[(3-chlorophenyl)amino]-2-methyl-1-phenyl-3-pentanone.** The reaction of benzaldehyde (1 mmol), *m*-chloroaniline (1.1 mmol), 3-pentanone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 80% yield. Yellow solid; m.p.: 115-116 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3405, 1705; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (d,  $J$  = 7.3 Hz, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.22 (m, 2H), 6.94 (t,  $J$  = 8.1 Hz, 1H), 6.57 (dd,  $J_1$  = 13.2 Hz,  $J_2$  = 7.9 Hz, 1H), 6.47 (t,  $J$  = 2.1 Hz, 1H), 6.36 (t,  $J$  = 9.3 Hz, 1H), 5.17 (br, 0.25H), 4.47 (br, 0.75H), 4.61 (t,  $J$  = 5.6 Hz, 0.75H), 4.46 (d,  $J$  = 5.7 Hz, 0.25H), 3.01 (m, 1H), 2.20 (m, 2H), 1.17 (d,  $J$  = 7.1 Hz, 1H), 1.09 (d,  $J$  = 7.0 Hz, 2H), 0.91 (t,  $J$  = 7.2 Hz, 2H), 0.85 (t,  $J$  = 7.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  214.4, 212.2, 147.2, 147.2, 140.1, 139.5, 133.8, 133.7, 129.1, 129.0, 127.7, 127.7, 126.5, 126.5, 125.8, 125.4, 116.6, 116.1, 112.5, 111.9, 110.8, 110.5, 59.5, 58.1, 51.0, 50.7, 35.6, 34.6, 14.7, 10.7, 6.4, 6.1.

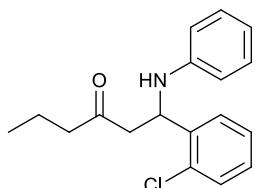


**1-[(3-methylphenyl)amino]-2-methyl-1-phenyl-3-pentanone.** The reaction of benzaldehyde (1 mmol), *m*-methylaniline (1.1 mmol), 3-pentanone (1.5 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 76% yield. White solid; m.p.: 115-117 °C; IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3374, 1721; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (t,  $J$  = 6.0 Hz, 4H), 7.21 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 4.3 Hz, 1H), 6.93 (t,  $J$  = 7.8 Hz, 1H), 6.49-6.40 (m, 1H), 6.35 (s, 1H), 6.27 (t,  $J$  = 9.0 Hz, 1H), 4.86 (s, 0.3H), 4.65 (d,  $J$  = 5.4 Hz, 0.7H), 4.48 (d,  $J$  = 6.2 Hz, 0.3H), 4.27 (s, 0.7H), 2.99 (dq,  $J_1$  = 13.3 Hz,  $J_2$  = 6.8 Hz, 1H), 2.32 (dd,  $J_1$  = 17.9 Hz,  $J_2$  = 7.5 Hz, 1.7H), 2.17 (s, 3H), 1.99 (dd,  $J_1$  = 18.2 Hz,  $J_2$  = 7.1 Hz, 0.3H), 1.11 (dd,  $J_1$  = 25.5 Hz,  $J_2$  = 7.0 Hz, 3H), 0.89 (dt,  $J_1$  = 18.6 Hz,  $J_2$  = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  215.3, 213.3, 147.1, 147.0, 141.9, 141.4, 138.8, 129.0, 129.0, 128.7, 128.6, 127.3, 127.2, 126.9, 126.6, 118.7, 118.3, 114.6, 114.3, 110.6, 110.3, 77.4, 77.1, 76.8, 60.6, 59.2, 52.3, 52.3, 36.2, 35.5, 21.6, 15.6, 11.6, 7.5,

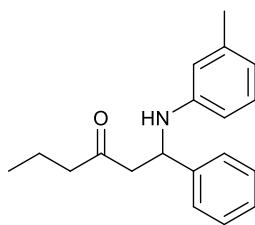
7.3.



**1-phenyl-1-(phenylamino)-3-hexanone.** The reaction of benzaldehyde (1 mmol), aniline (1.1 mmol), 2-pentanone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 77% yield. White solid; m.p.: 87-88 °C; IR (KBr, v,  $\text{cm}^{-1}$ ): 3376, 1703;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.4, 145.8, 141.6, 128.1, 127.7, 126.3, 125.3, 116.7, 112.7, 53.4, 49.2, 44.6, 15.8, 12.5.

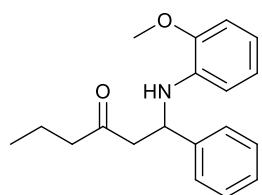


**1-(2-chlorophenyl)-1-(phenylamino)-3-hexanone.** The reaction of *o*-chlorobenzaldehyde (1 mmol), aniline (1.1 mmol), 2-pentanone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 90% yield. Yellow solid; m.p.: 90-91 °C; IR (KBr, v,  $\text{cm}^{-1}$ ): 3401, 1708;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 (dd,  $J_1 = 5.7$  Hz,  $J_2 = 3.7$  Hz, 1H), 7.29 (dd,  $J_1 = 5.7$  Hz,  $J_2 = 3.5$  Hz, 1H), 7.09 (dd,  $J_1 = 5.9$  Hz,  $J_2 = 3.5$  Hz, 2H), 7.00 (t,  $J = 7.9$  Hz, 2H), 6.58 (t,  $J = 7.3$  Hz, 1H), 6.39 (d,  $J = 7.8$  Hz, 2H), 5.14-5.03 (m, 1H), 4.76 (s, 1H), 2.90 (dd,  $J_1 = 15.4$  Hz,  $J_2 = 3.9$  Hz, 1H), 2.69 (dd,  $J_1 = 15.4$  Hz,  $J_2 = 8.5$  Hz, 1H), 2.43-2.19 (m, 2H), 1.47 (dd,  $J_1 = 14.7$  Hz,  $J_2 = 7.3$  Hz, 2H), 0.77 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.7, 145.4, 138.2, 131.3, 128.8, 128.1, 127.5, 126.8, 126.4, 116.9, 112.5, 50.6, 46.7, 44.0, 15.9, 12.6.

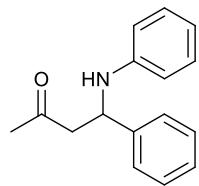


**1-phenyl-1-[(2-methylphenyl)amino]-3-hexanone.** The reaction of benzaldehyde (1 mmol), *m*-methylaniline (1.1 mmol), 2-pentanone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 85% yield. White solid; m.p.: 94-95 °C; IR (KBr, v,  $\text{cm}^{-1}$ ): 3434, 1706;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d, S8

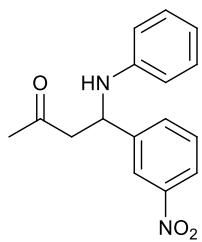
$J = 7.2$  Hz, 2H), 7.22 (d,  $J = 5.0$  Hz, 2H), 7.15 (d,  $J = 8.3$  Hz, 1H), 6.89 (t,  $J = 7.8$  Hz, 1H), 6.41 (d,  $J = 7.5$  Hz, 1H), 6.32 (s, 1H), 6.26 (d,  $J = 8.1$  Hz, 1H), 4.75 (t,  $J = 6.4$  Hz, 1H), 4.38 (s, 1H), 2.80 (d,  $J = 6.5$  Hz, 2H), 2.22 (td,  $J_1 = 7.2$ ,  $J_2 = 3.6$  Hz, 2H), 2.12 (s, 3H), 1.44 (dd,  $J_1 = 14.6$  Hz,  $J_2 = 7.3$  Hz, 2H), 0.75 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.5, 146.9, 142.8, 138.9, 129.0, 128.8, 127.3, 126.3, 118.8, 114.7, 110.7, 54.5, 50.3, 45.6, 21.6, 16.9, 13.6.



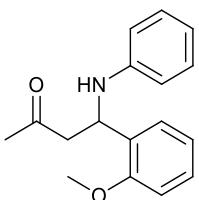
**1-phenyl-1-[(2-methoxyphenyl)amino]-3-hexanone.** The reaction of benzaldehyde (1 mmol), *o*-anisidine (1.1 mmol), 2-pentanone (1.5 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) and POAP (10 mg) at 50 °C for 7 h, afforded 70% yield. White solid; m.p.: 85-86 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400, 1707;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 7.5$  Hz, 1H), 7.12 (t,  $J = 7.8$  Hz, 1H), 7.00 (t,  $J = 7.8$  Hz, 2H), 6.83-6.77 (m, 2H), 6.55 (t,  $J = 7.3$  Hz, 1H), 6.46 (d,  $J = 8.3$  Hz, 2H), 5.05 (dd,  $J_1 = 7.5$  Hz,  $J_2 = 5.1$  Hz, 1H), 4.62 (s, 1H), 3.83 (s, 3H), 2.81 (ddd,  $J_1 = 23.0$  Hz,  $J_2 = 15.2$  Hz,  $J_3 = 6.3$  Hz, 2H), 2.31-2.19 (m, 2H), 1.45 (dd,  $J_1 = 14.7$  Hz,  $J_2 = 7.4$  Hz, 2H), 0.75 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.2, 155.6, 146.0, 128.7, 128.0, 127.2, 126.6, 119.8, 116.5, 112.6, 109.5, 54.3, 49.1, 47.0, 44.1, 15.9, 12.6.



**4-phenyl-4-(phenylamino)-2-butanone.** The reaction of benzaldehyde (1 mmol), aniline (1.1 mmol), acetone (27.0 mmol),  $\text{Cp}_2\text{TiCl}_2$  (0.10 mmol) POAP (10 mg) at 25 °C for 6 h, afforded 86% yield. White solid; m.p.: 90-92 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3369, 1704;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.1, 145.8, 141.5, 128.1, 127.8, 126.3, 125.2, 116.8, 112.7, 53.3, 50.2, 29.7.



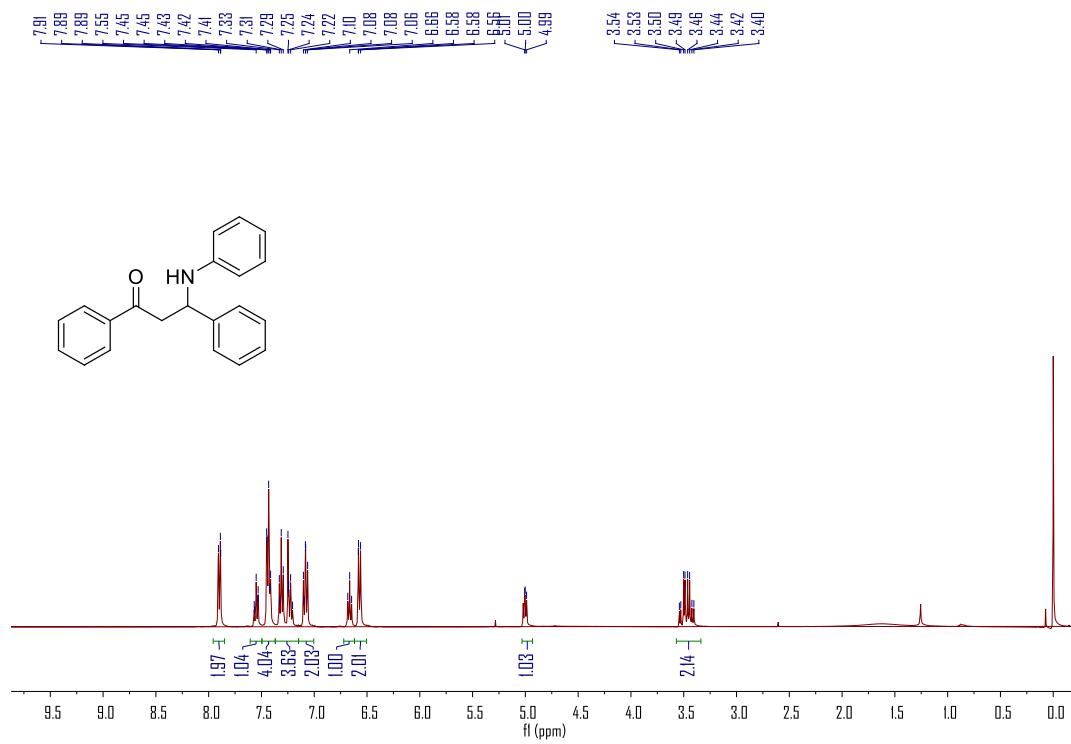
**4-(3-nitrophenyl)-4-(phenylamino)-2-butanone.** The reaction of *m*-nitrobenzaldehyde (1 mmol), aniline (1.1 mmol), acetone (27.0 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 25 °C for 6 h, afforded 72% yield. Yellow solid; m.p.: 125-127 °C; IR (KBr, v, cm<sup>-1</sup>): 3396, 1713; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (s, 1H), 8.09 (dd, *J*<sub>1</sub> = 8.3 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 2H), 4.95 (t, *J* = 6.2 Hz, 1H), 4.56 (s, 1H), 2.99 (d, *J* = 6.3 Hz, 2H), 2.15 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 206.0, 148.7, 146.2, 145.2, 132.9, 129.8, 129.3, 122.5, 121.4, 118.5, 113.8, 53.6, 50.7, 30.6.



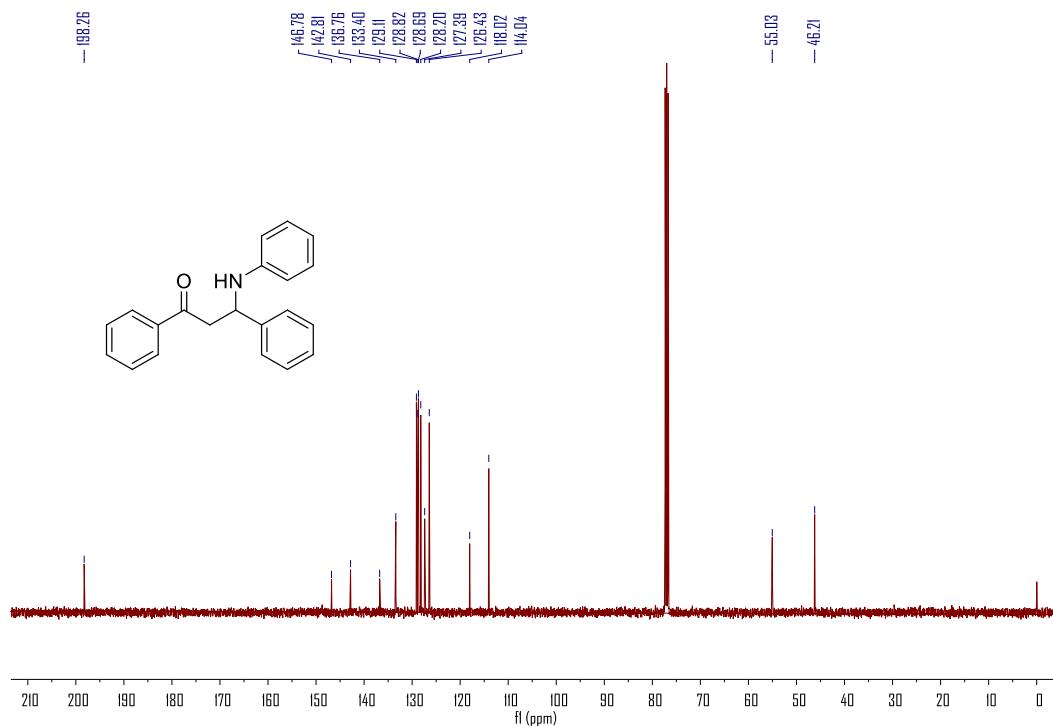
**4-(2-methoxyphenyl)-4-(phenylamino)-2-butanone.** The reaction of *o*-anisaldehyde (1 mmol), aniline (1.1 mmol), acetone (27.0 mmol), Cp<sub>2</sub>TiCl<sub>2</sub> (0.10 mmol) and POAP (10 mg) at 25 °C for 7 h, afforded 67% yield. White solid; m.p.: 104-105 °C; IR (KBr, v, cm<sup>-1</sup>): 3390, 1710; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (dd, *J*<sub>1</sub> = 8.3 Hz, *J*<sub>2</sub> = 3.3 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.97-6.89 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.80 (t, *J* = 6.4 Hz, 1H), 4.41 (s, 1H), 3.76 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.10 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 207.1, 160.0, 146.8, 144.4, 129.8, 129.1, 118.5, 117.9, 113.8, 112.5, 112.1, 55.2, 54.4, 51.2, 30.7.

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

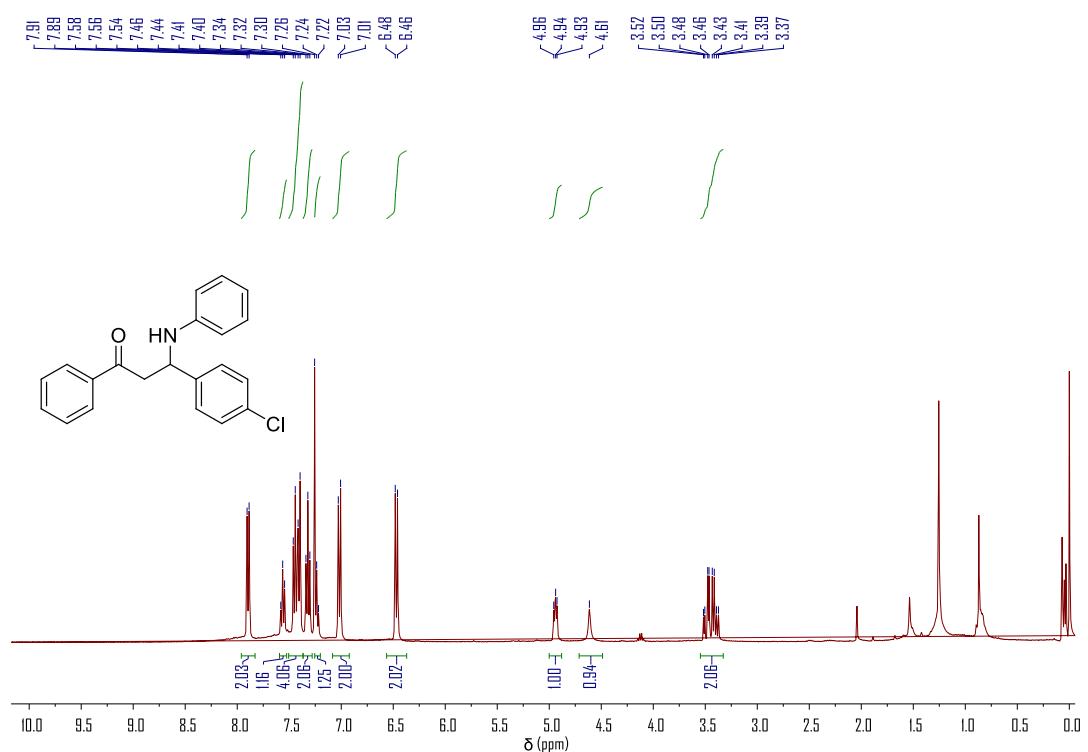
### $^1\text{H}$ NMR



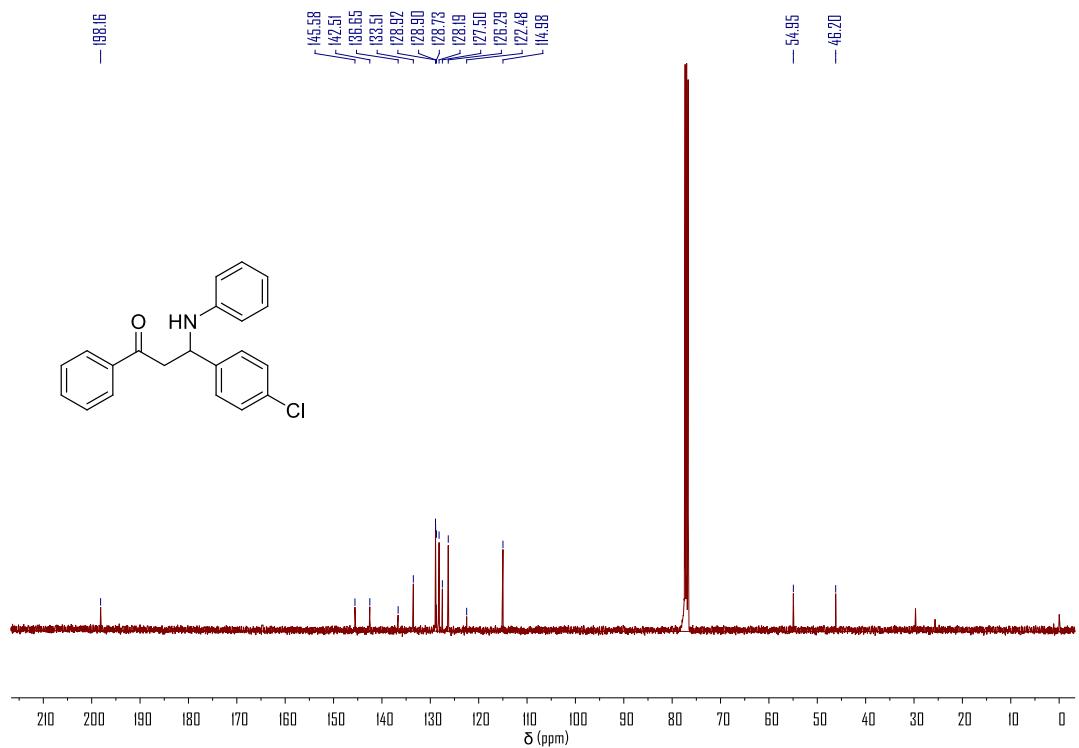
### $^{13}\text{C}$ NMR



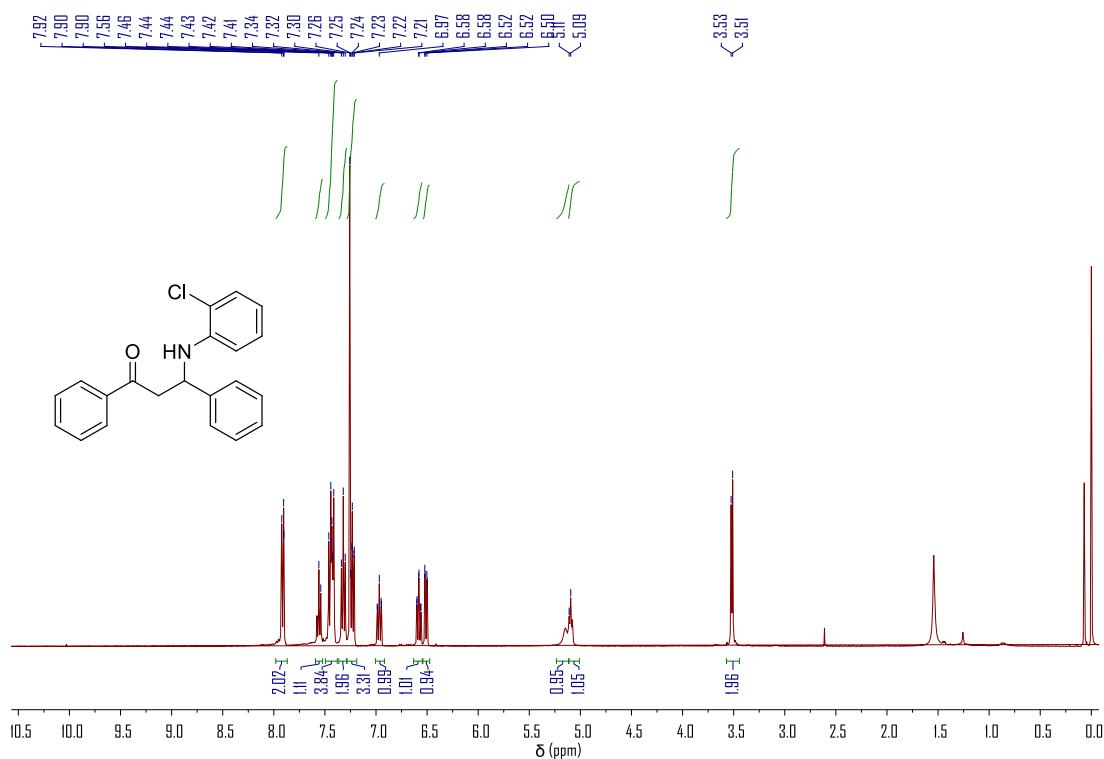
## <sup>1</sup>H NMR



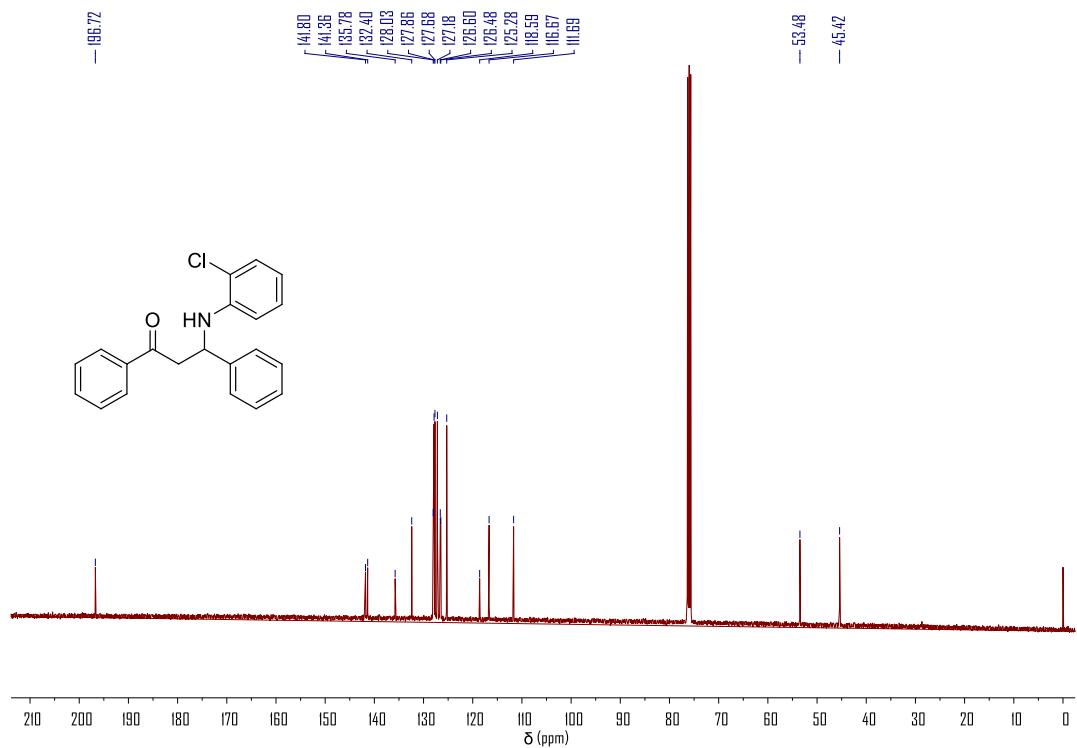
## <sup>13</sup>C NMR



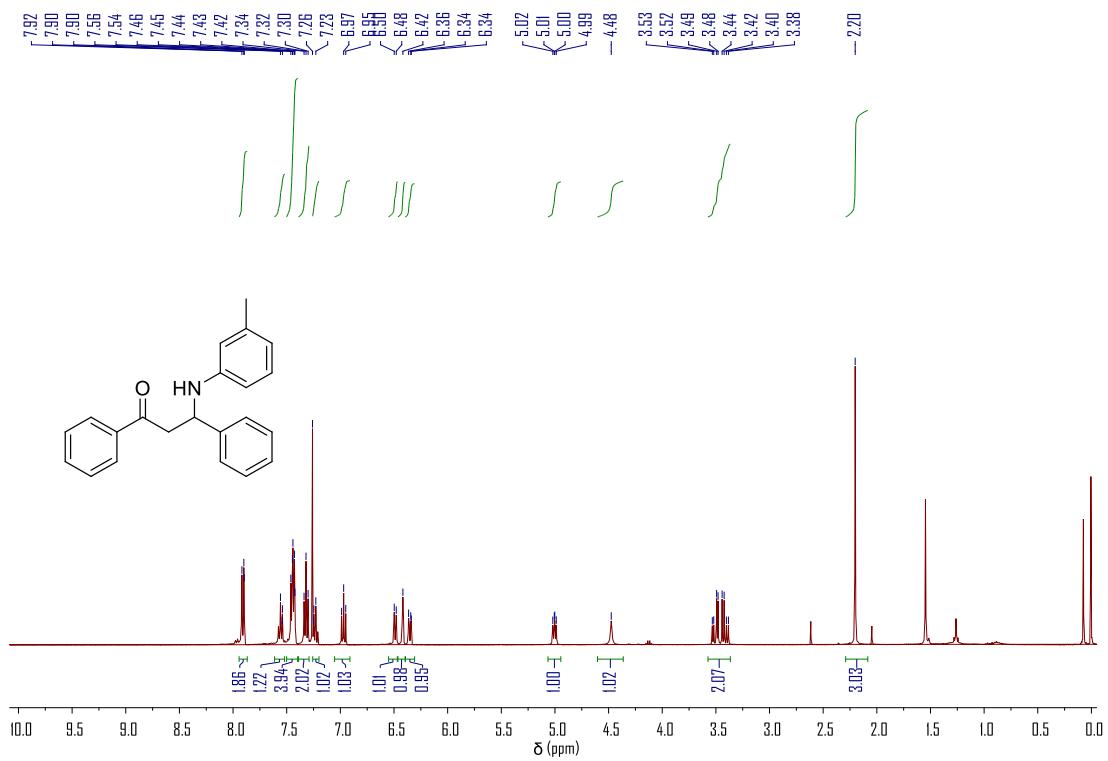
## **<sup>1</sup>H NMR**



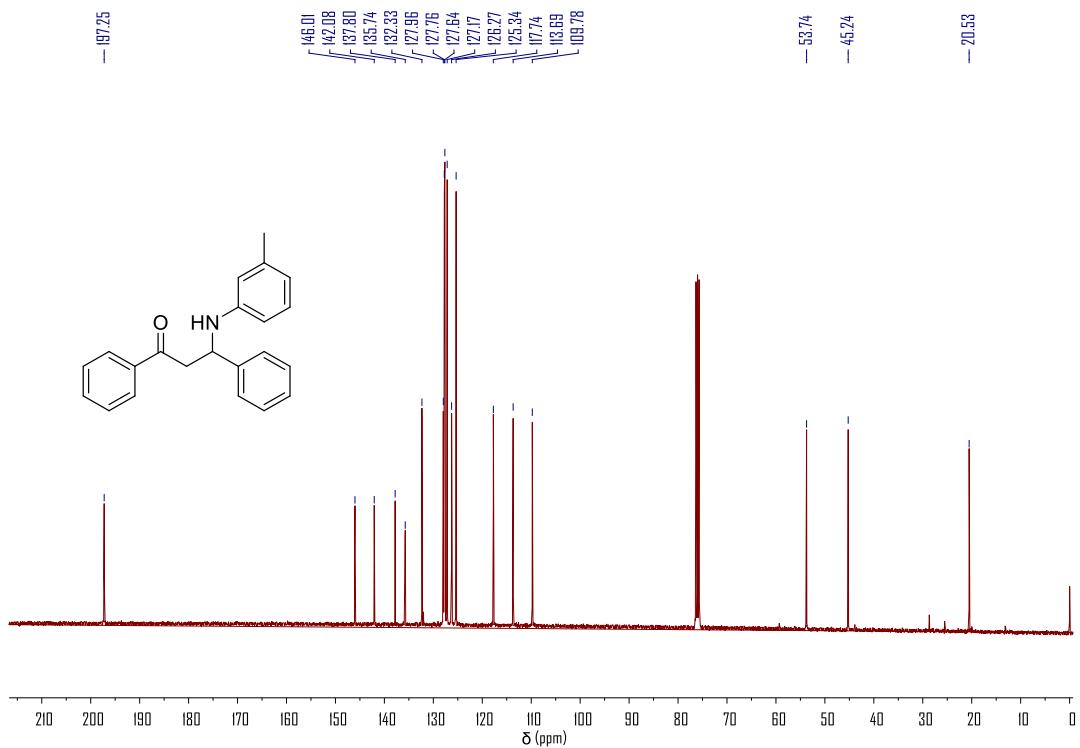
**<sup>13</sup>C NMR**



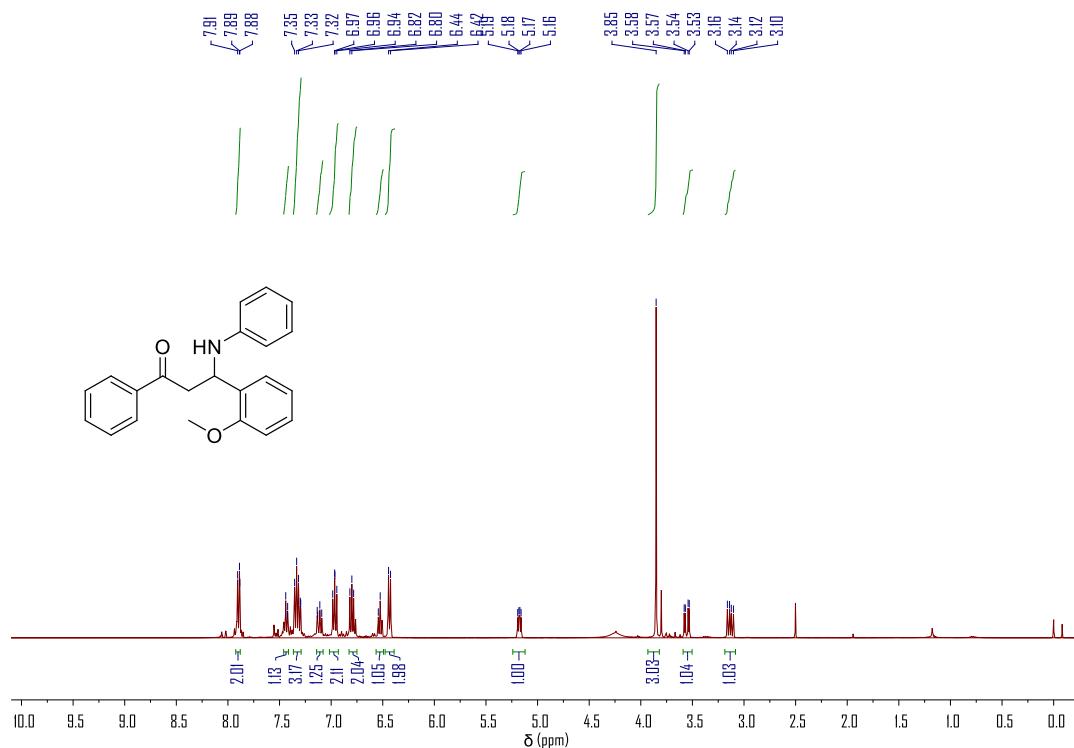
## **<sup>1</sup>H NMR**



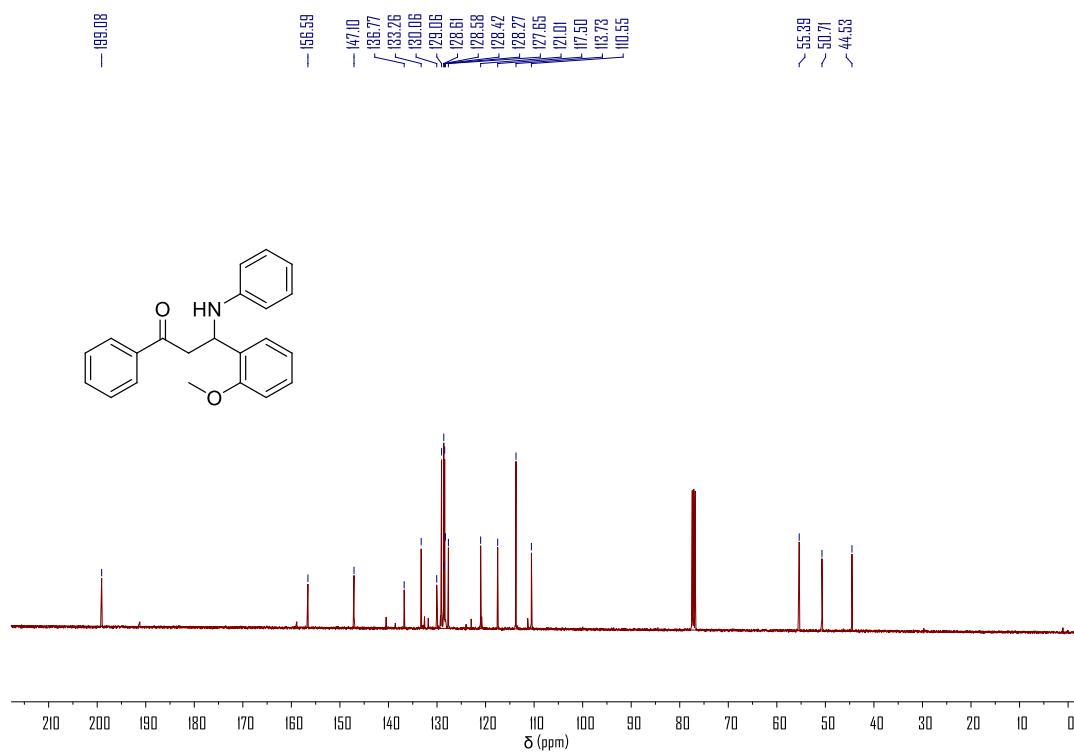
**<sup>13</sup>C NMR**



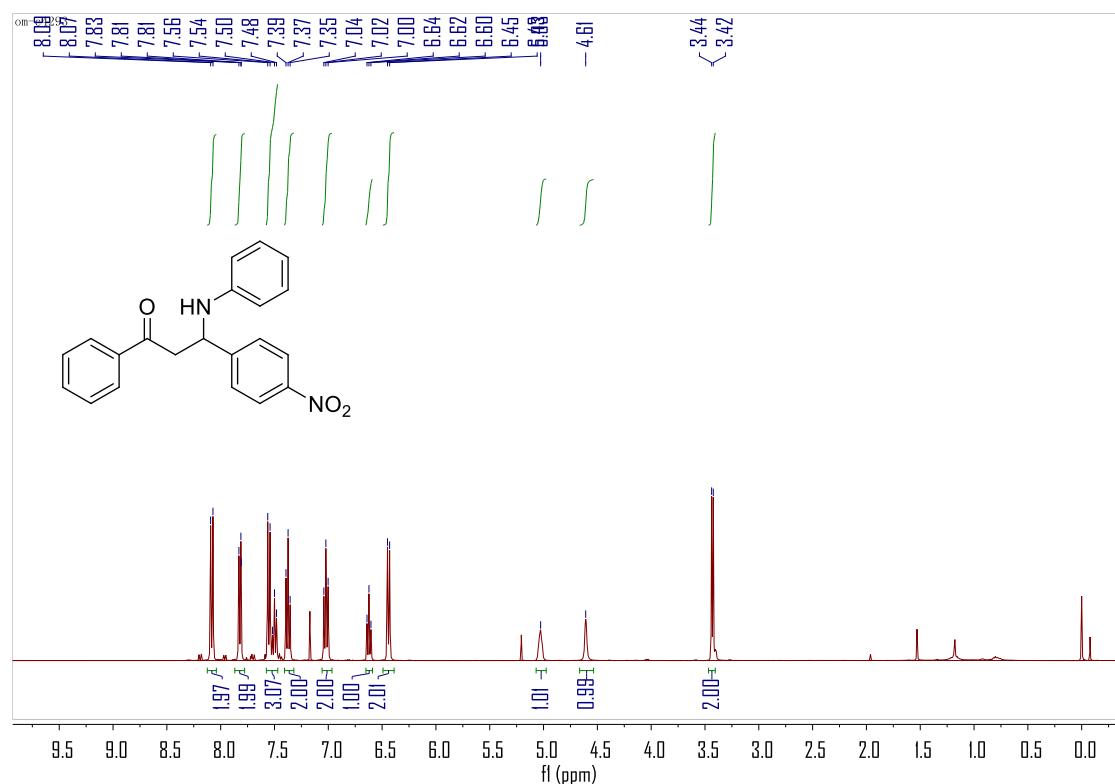
## <sup>1</sup>H NMR



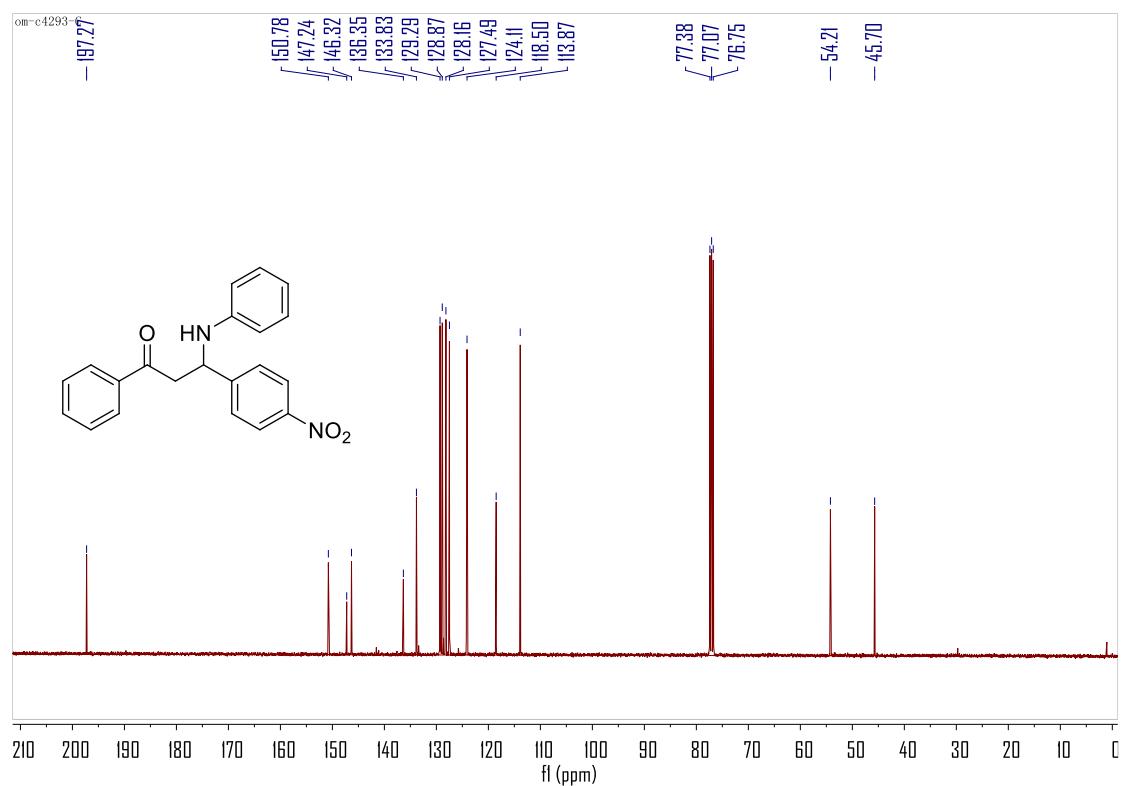
## <sup>13</sup>C NMR



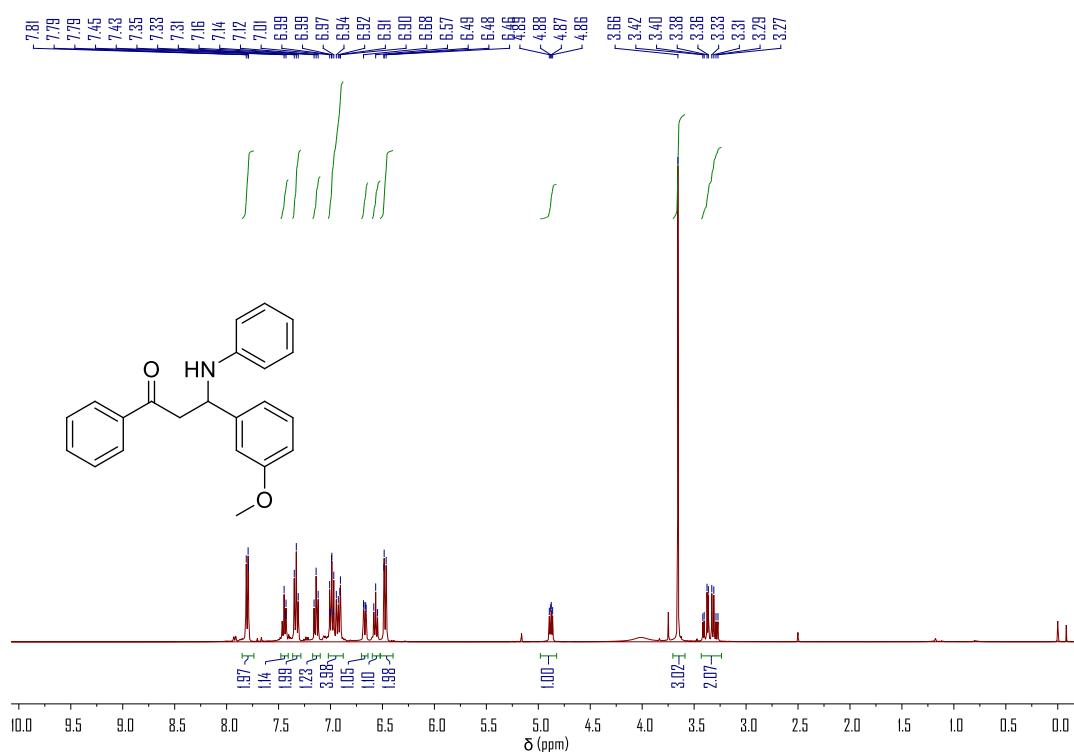
## <sup>1</sup>H NMR



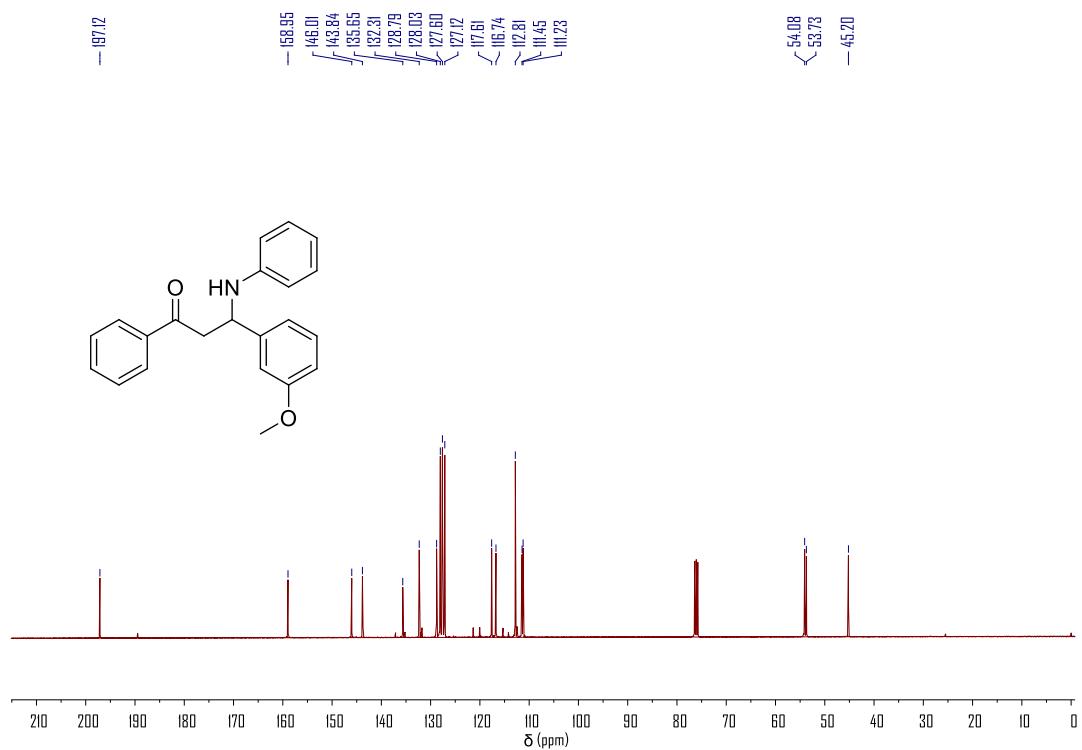
## <sup>13</sup>C NMR



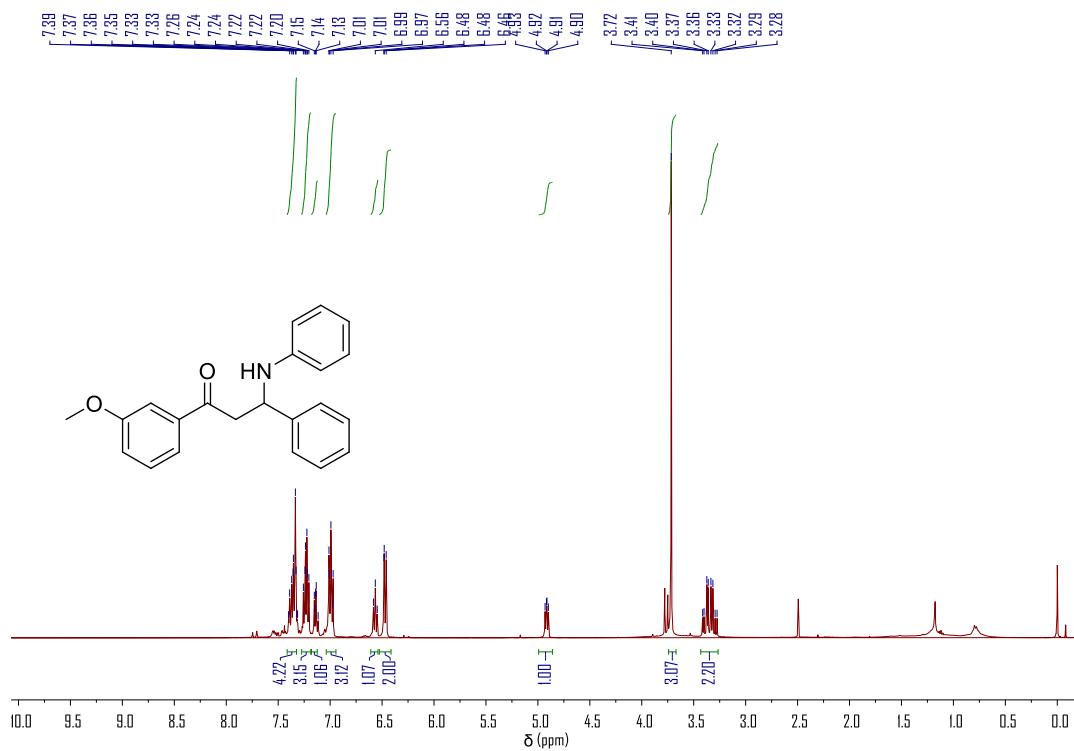
## <sup>1</sup>H NMR



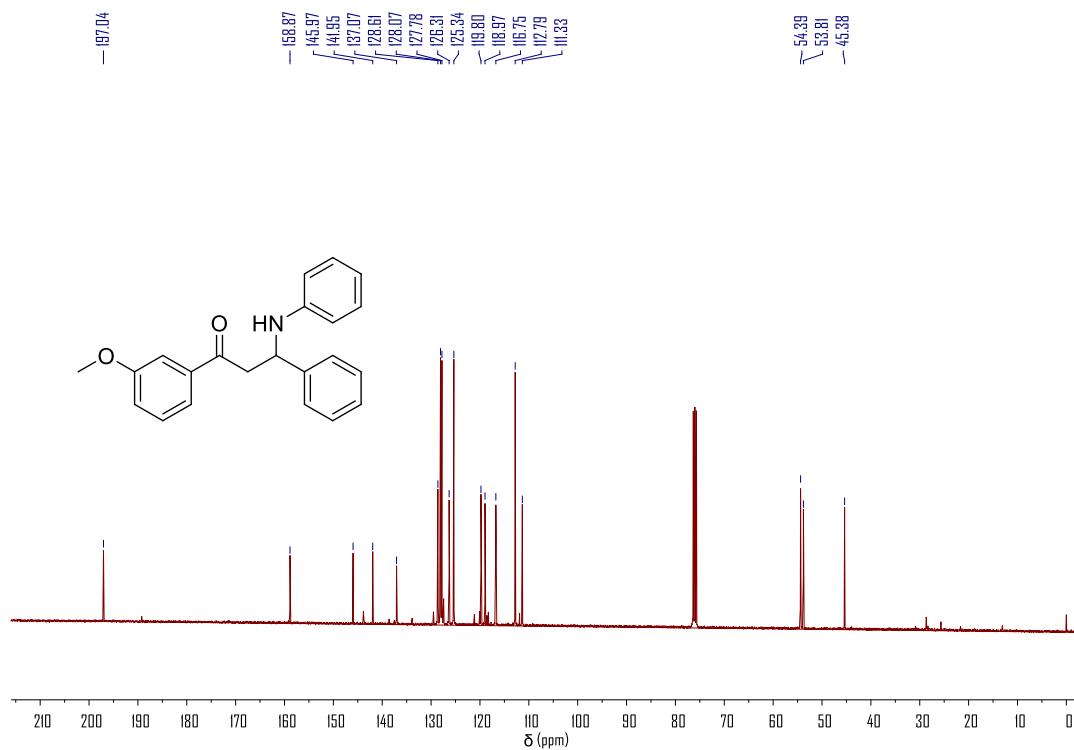
## <sup>13</sup>C NMR



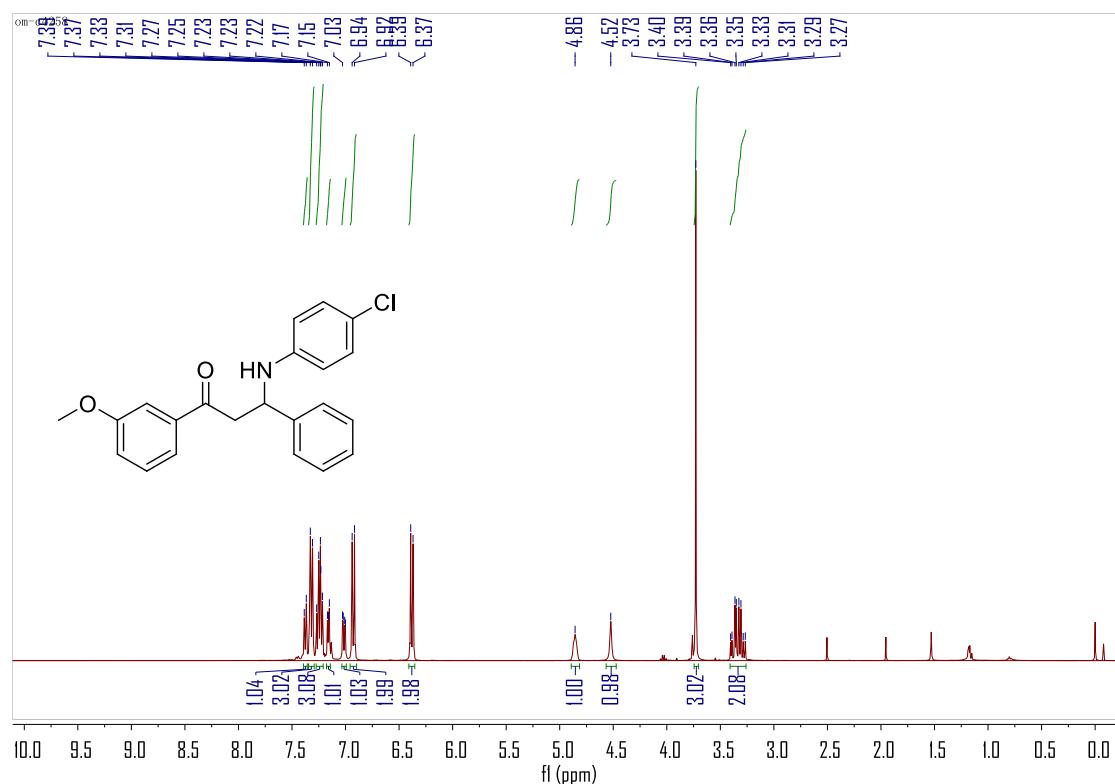
## **<sup>1</sup>H NMR**



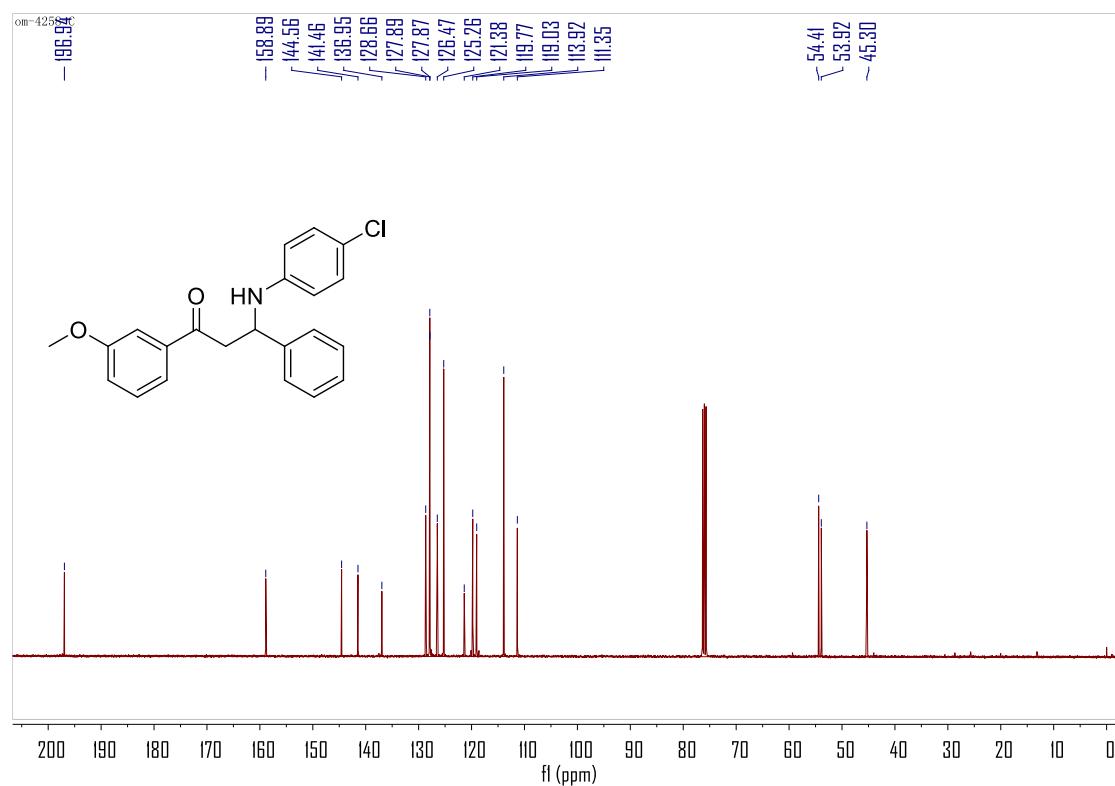
**<sup>13</sup>C NMR**



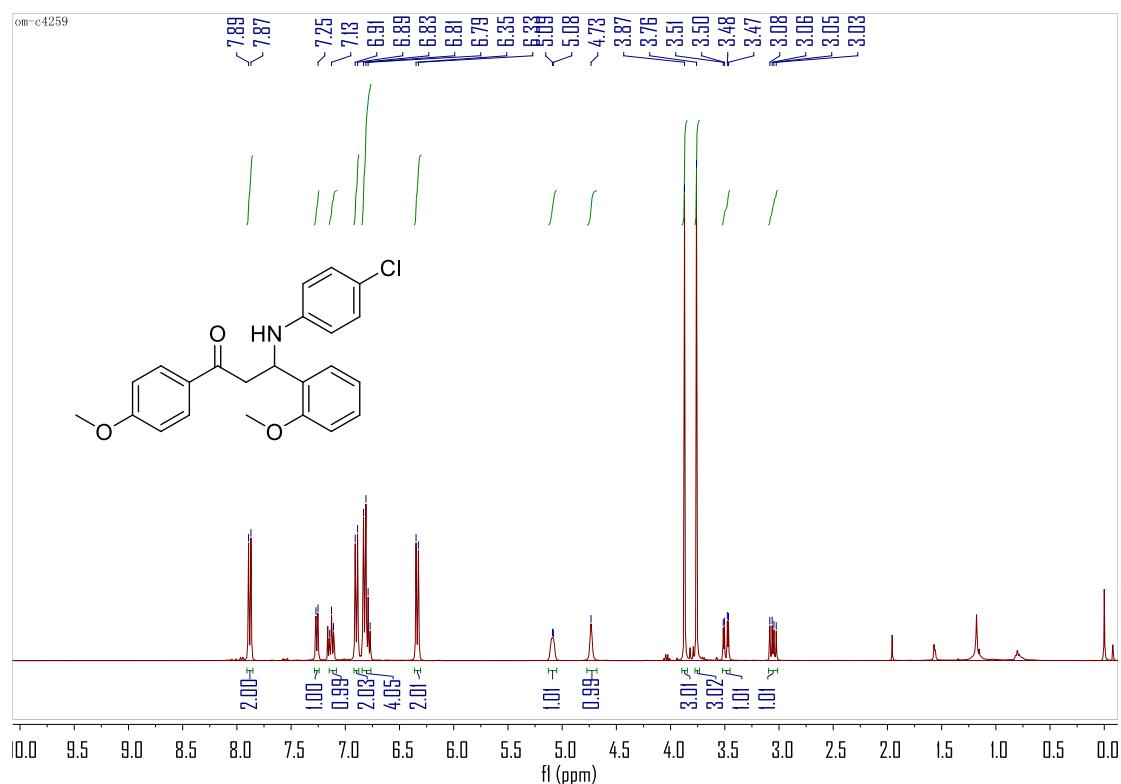
## <sup>1</sup>H NMR



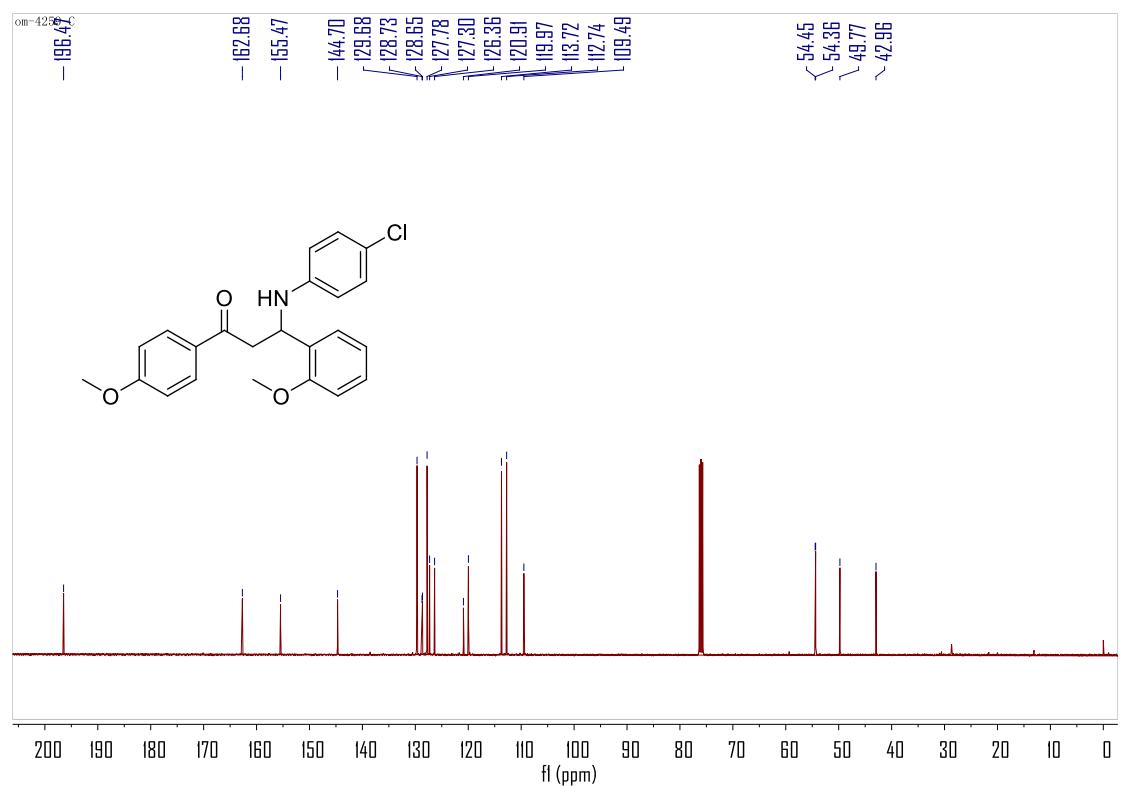
## <sup>13</sup>C NMR



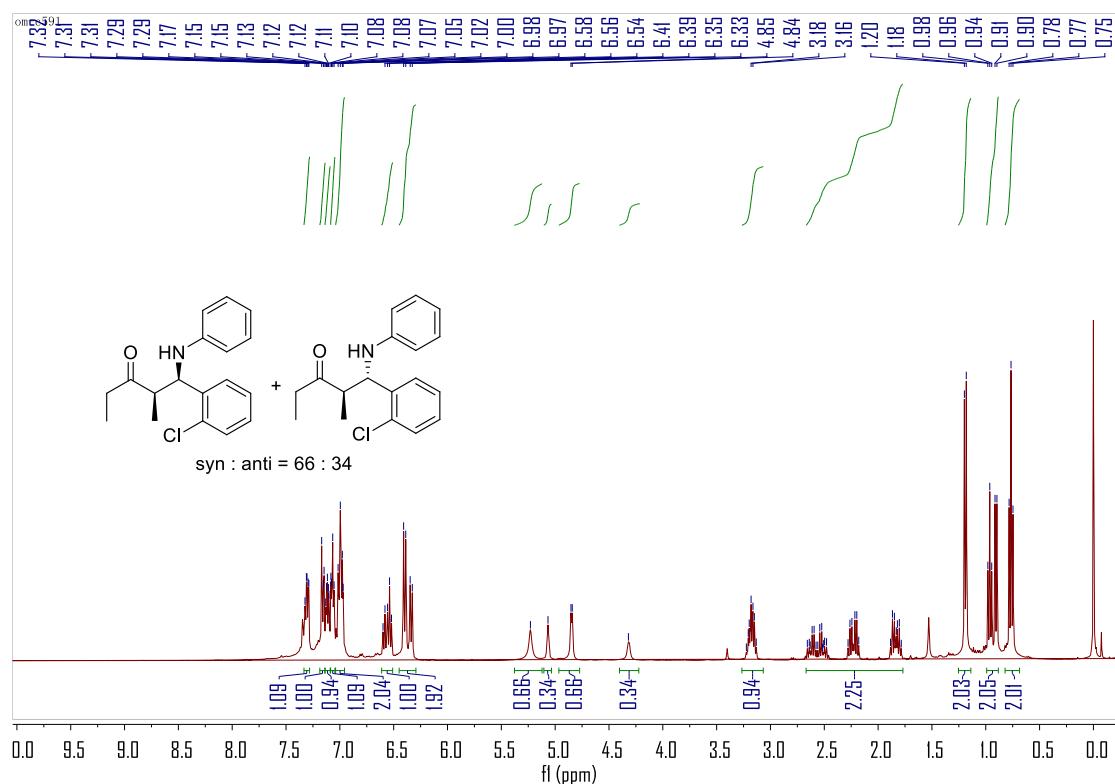
## <sup>1</sup>H NMR



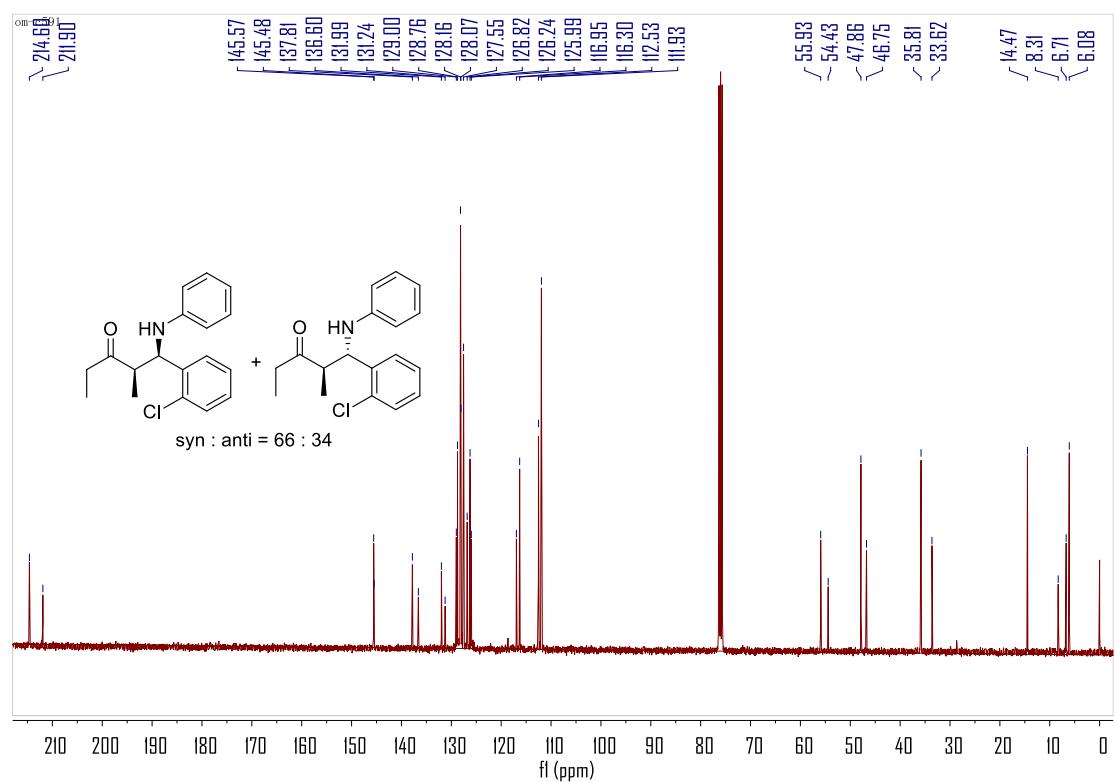
## <sup>13</sup>C NMR



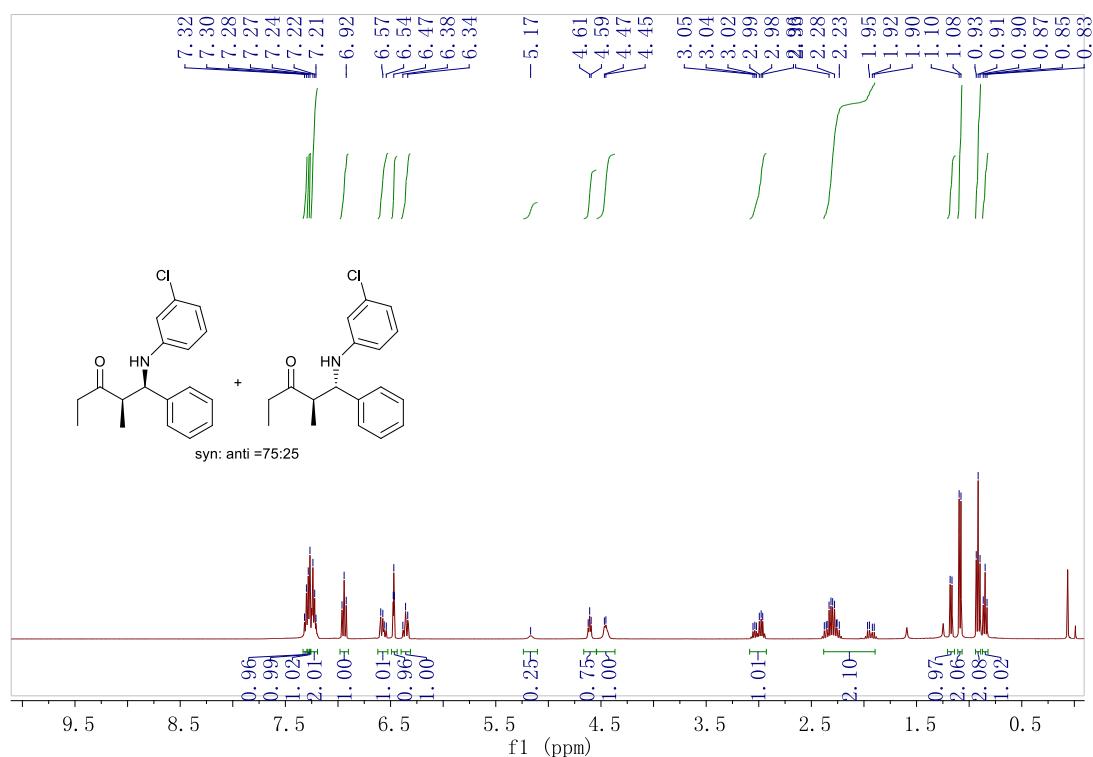
## <sup>1</sup>H NMR



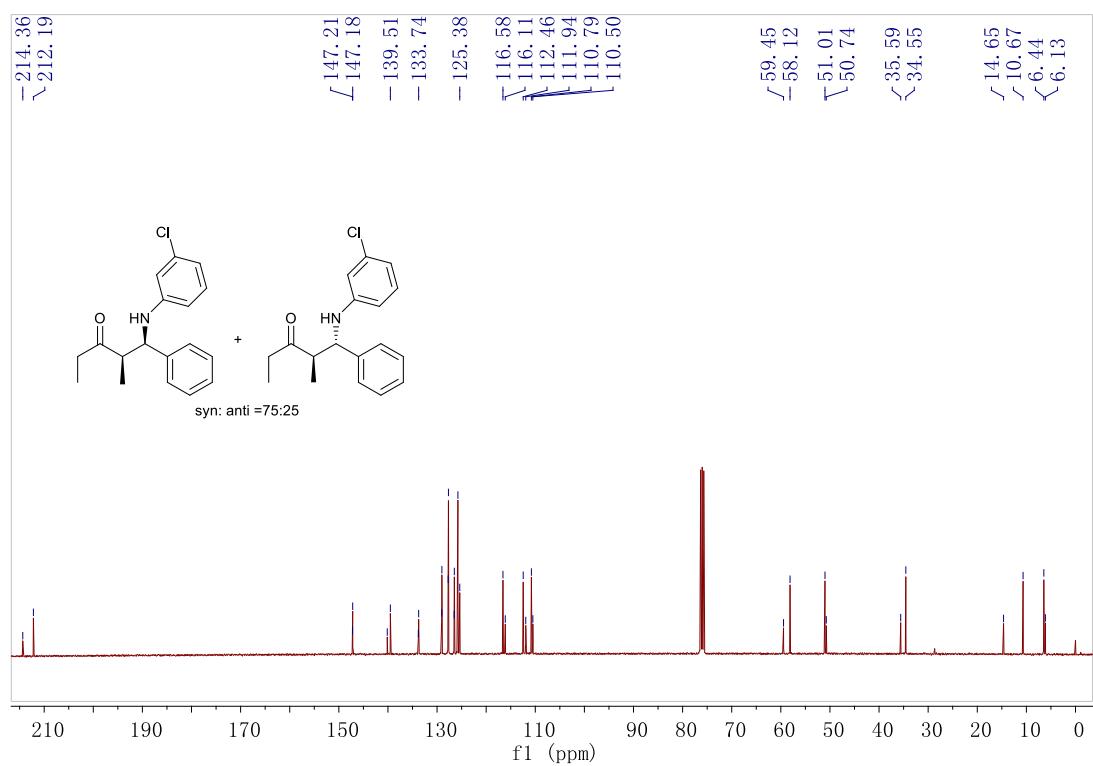
## <sup>13</sup>C NMR



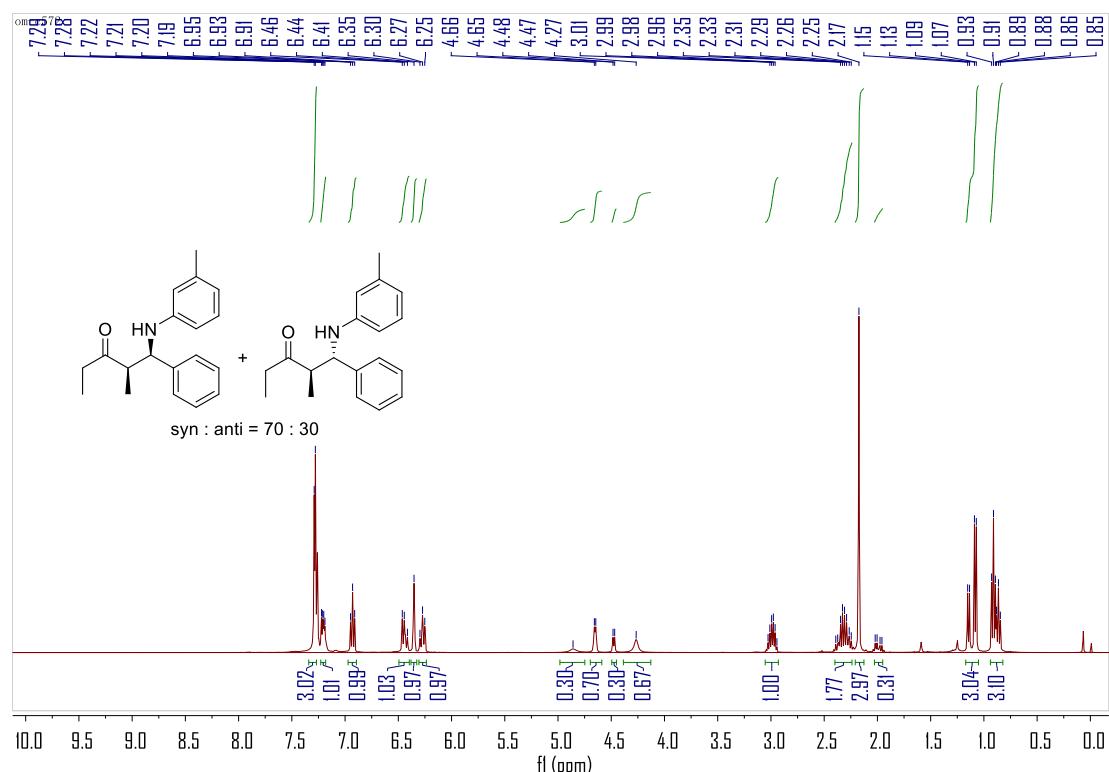
## <sup>1</sup>H NMR



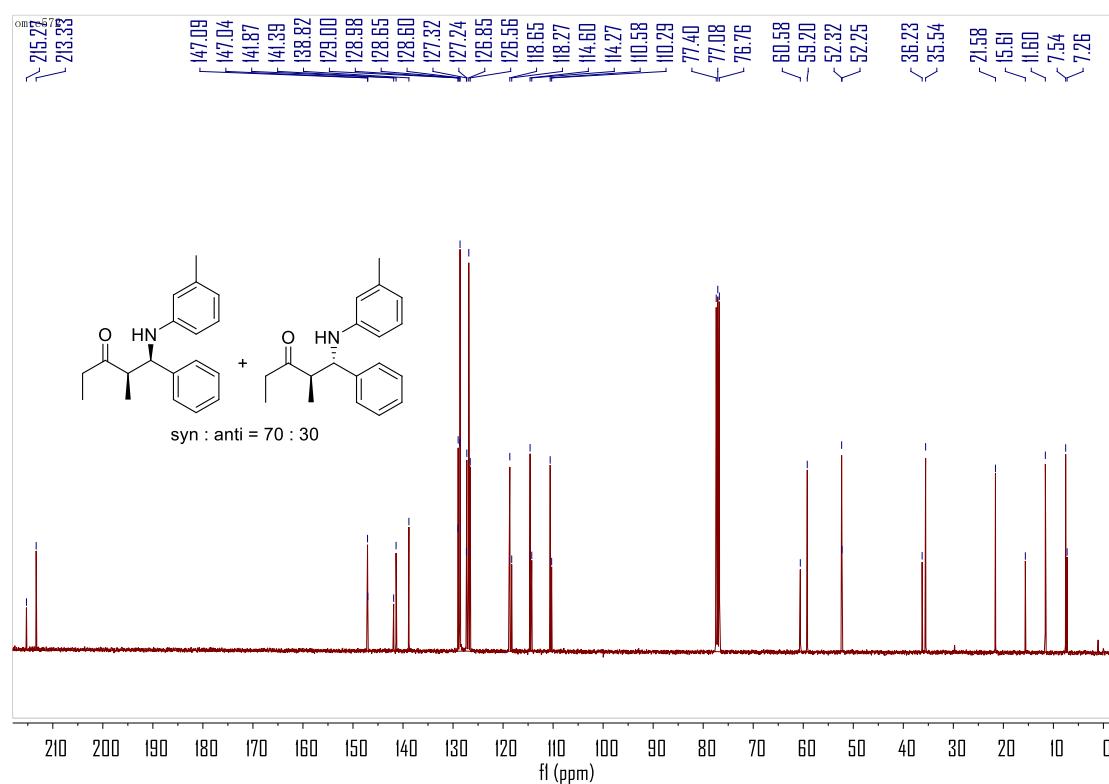
## <sup>13</sup>C NMR



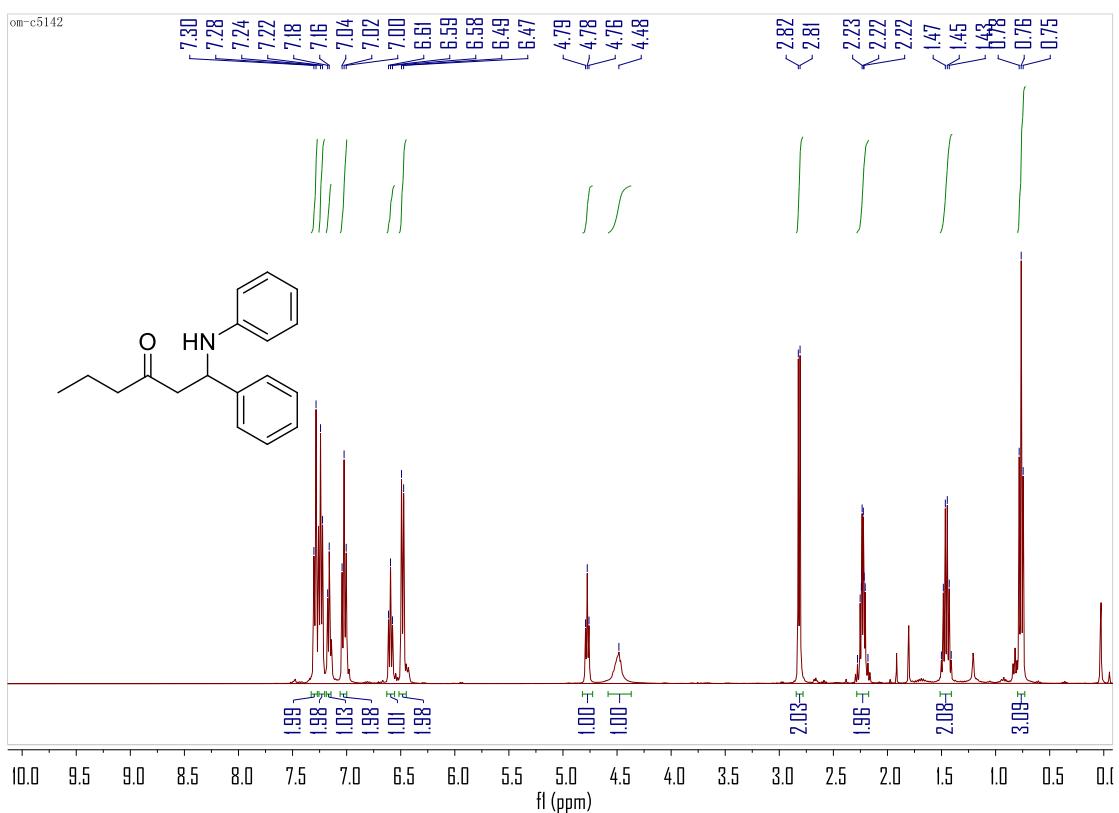
## <sup>1</sup>H NMR



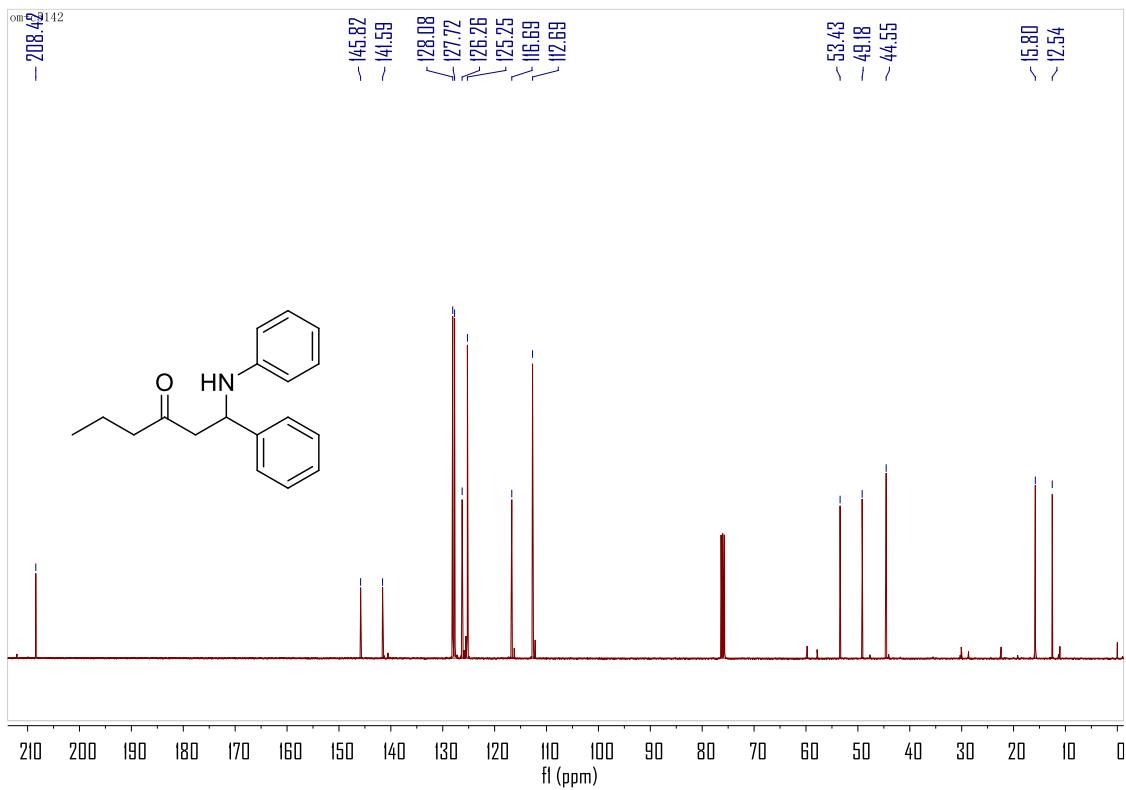
## <sup>13</sup>C NMR



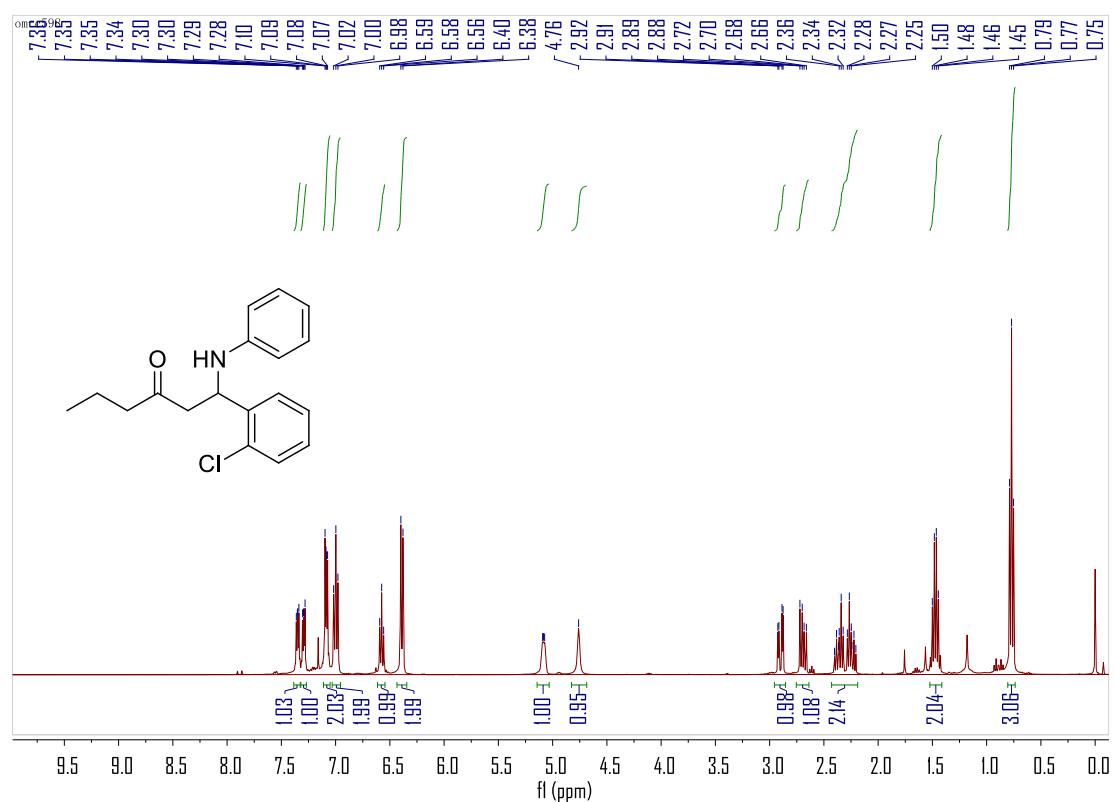
## <sup>1</sup>H NMR



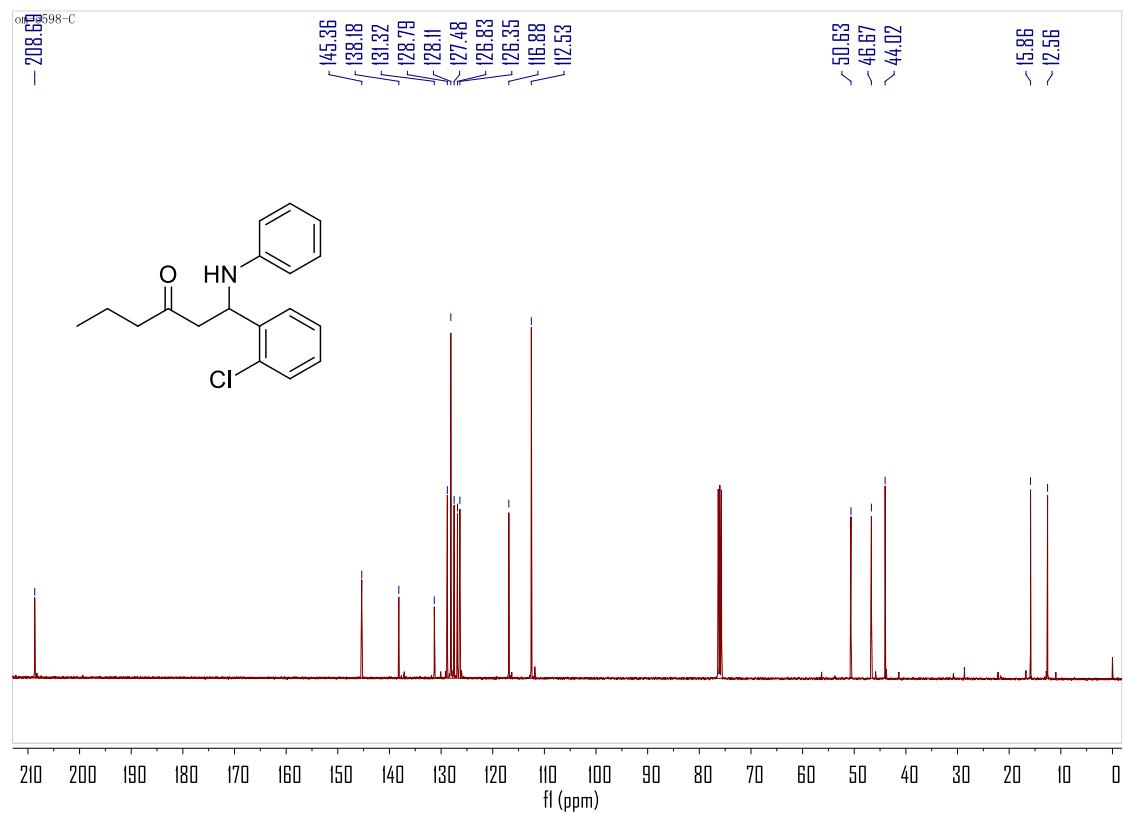
## <sup>13</sup>C NMR



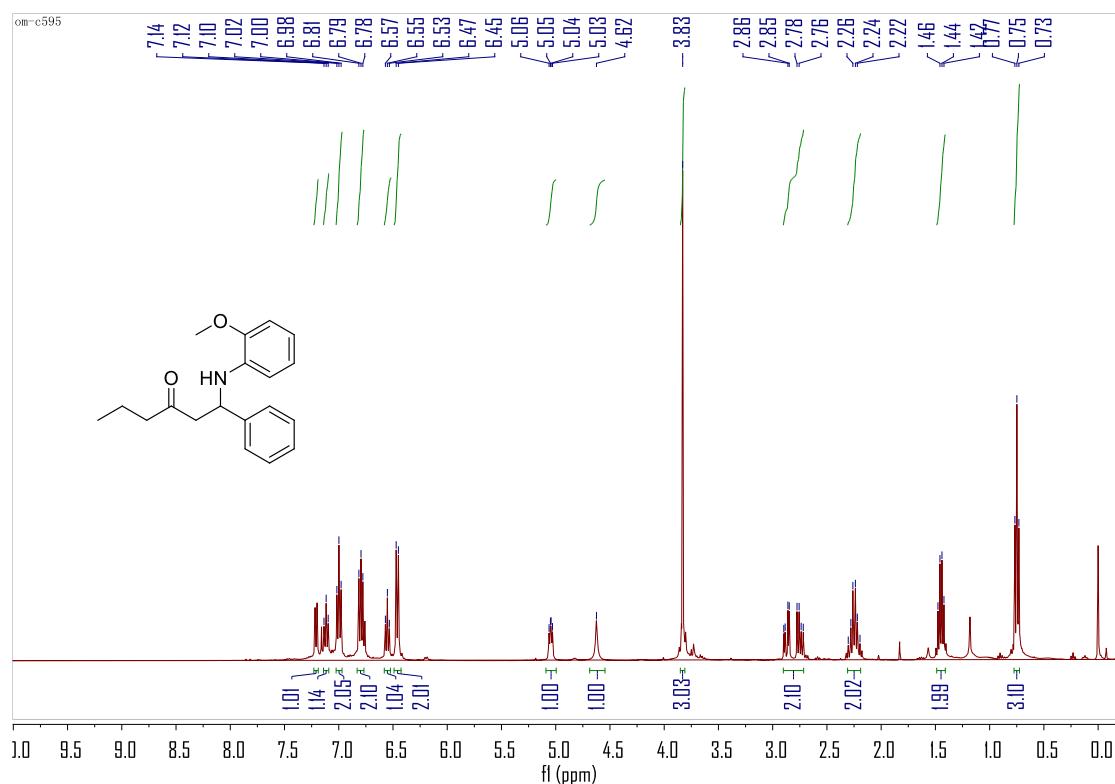
## <sup>1</sup>H NMR



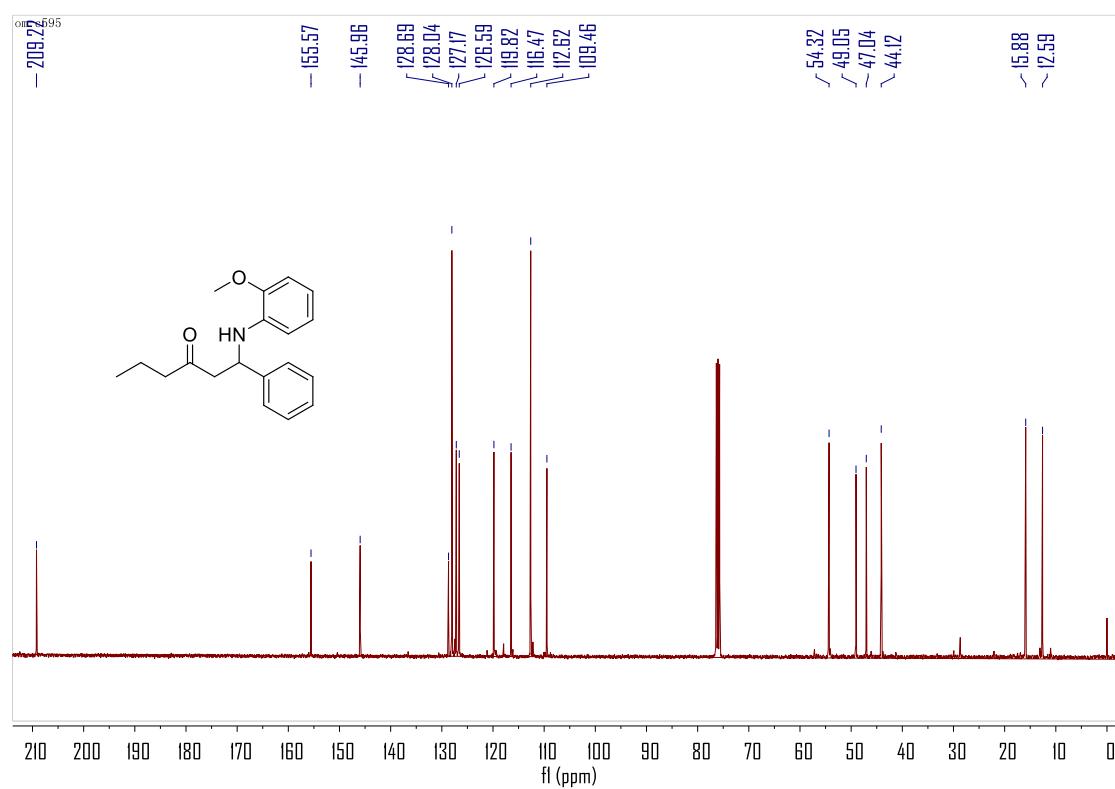
## <sup>13</sup>C NMR



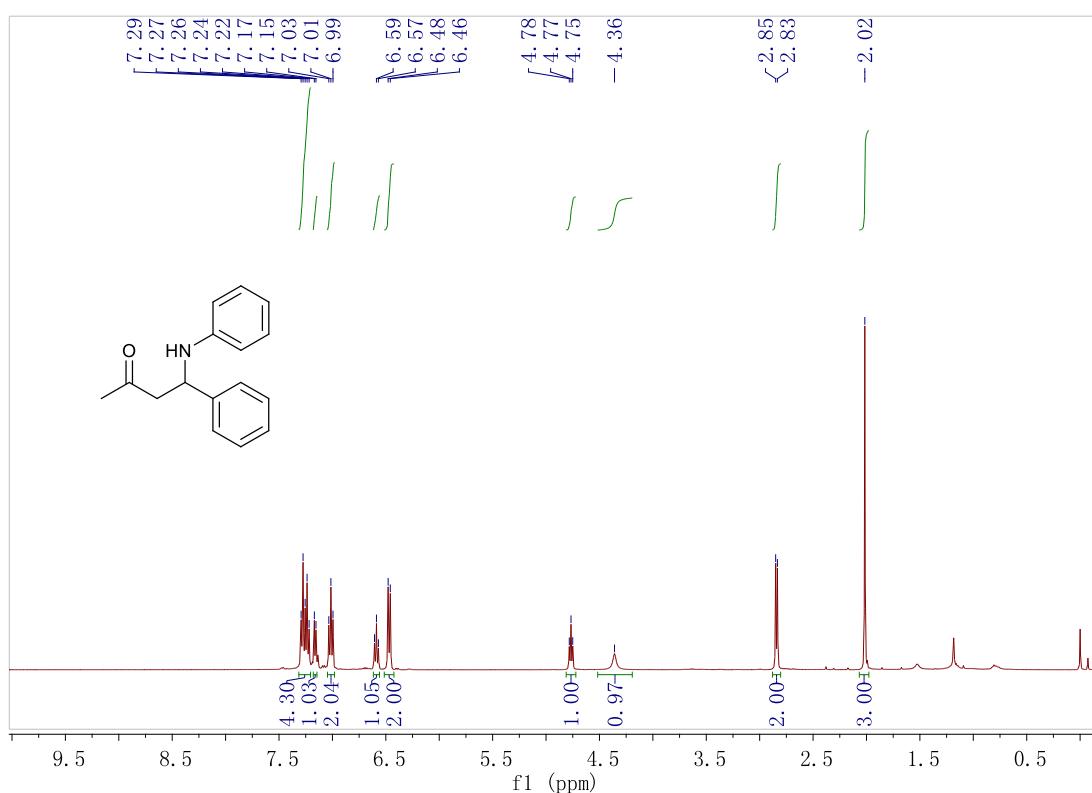
## <sup>1</sup>H NMR



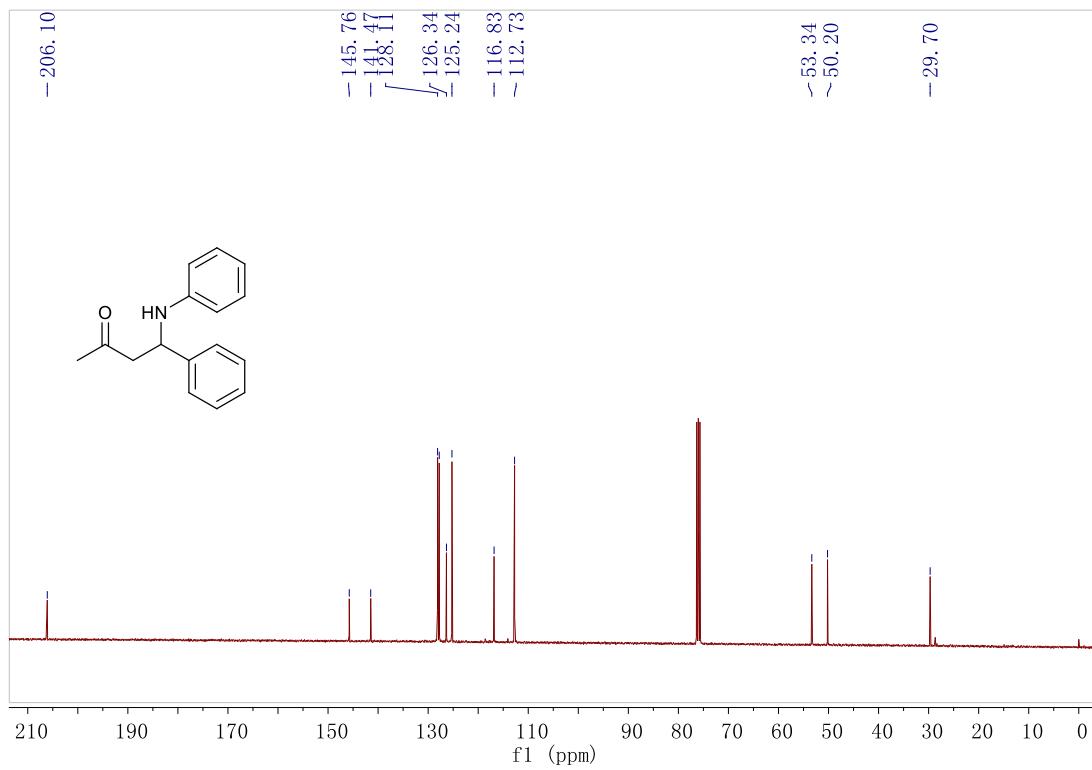
## <sup>13</sup>C NMR



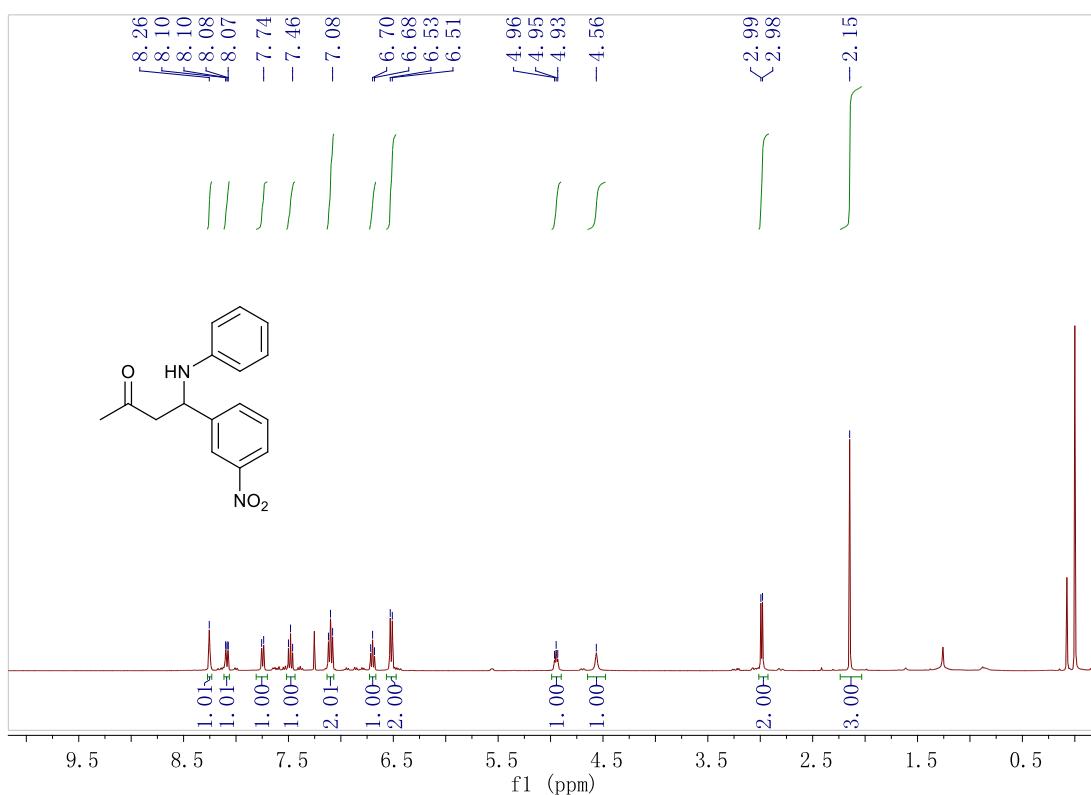
## <sup>1</sup>H NMR



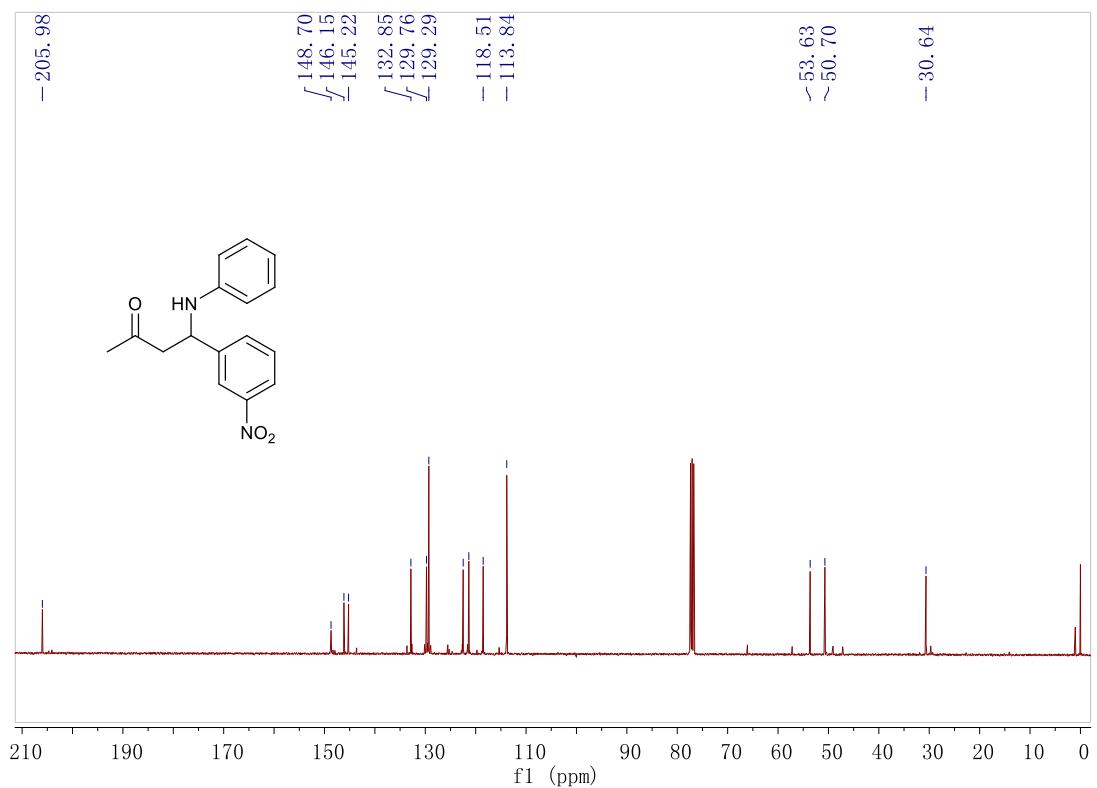
## <sup>13</sup>C NMR



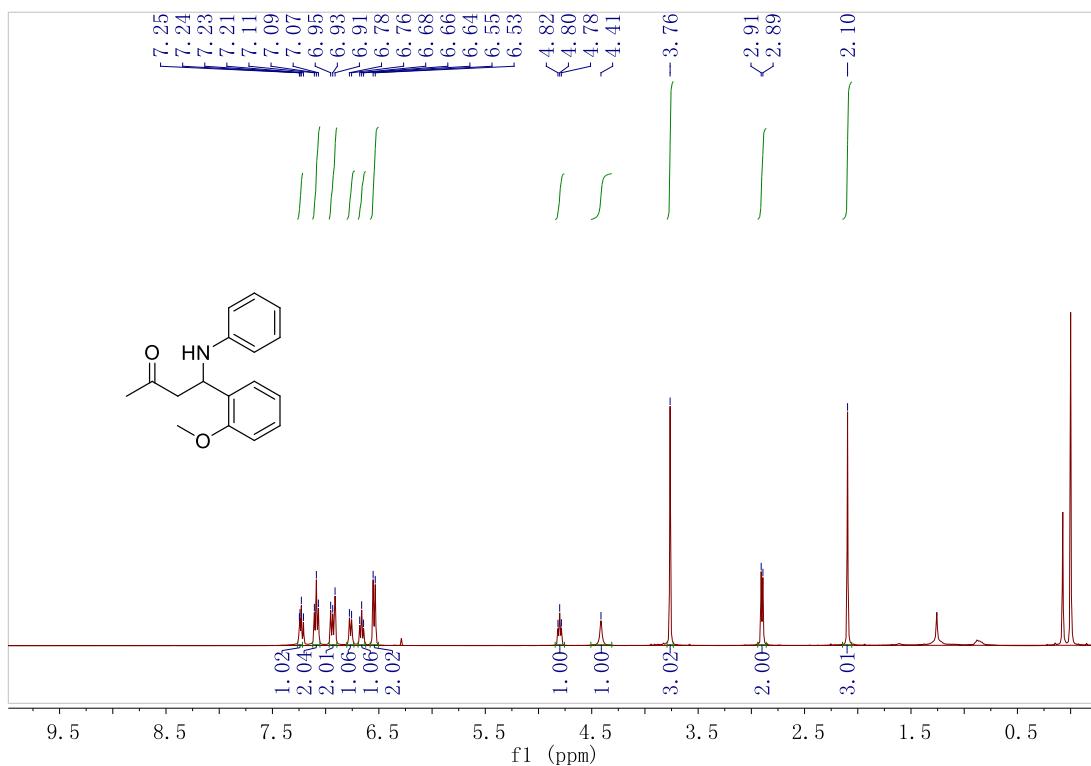
## <sup>1</sup>H NMR



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



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



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

