

## Supporting Information

### Rhodium-Catalyzed Highly Enantioselective Direct Intermolecular Hydroacylation of 1,1-Disubstituted Alkenes with Unfunctionalized Aldehydes

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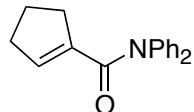
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### I. General

Anhydrous  $\text{CH}_2\text{Cl}_2$  (No. 27,099-7) and  $(\text{CH}_2\text{Cl})_2$  (No. 28,450-5) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. Aldehydes were purified by distillation prior to use for catalysis. Aldehyde **1h**<sup>1</sup>, amides **2a**,<sup>2</sup> **2b**,<sup>2</sup> **2c**,<sup>3</sup> and **2d**<sup>4</sup> were already reported. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

### II. Synthesis of acrylamide

#### Cyclopent-1-enecarboxylic acid diphenylamide (**2e**)



To a stirred solution of 1-cyclopentenecarboxylic acid (1.00 g, 8.92 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added thionyl chloride (1.1 mL, 14 mmol) at room temperature, and the mixture was refluxed (40 °C) for 1 hour, which furnished the corresponding crude acid chloride. The resulting mixture was added to a mixture of diphenylamine (1.51 g, 8.92 mmol), pyridine (5 mL), and  $\text{CH}_2\text{Cl}_2$  (5 mL) at 0 °C, and the mixture was refluxed (40 °C) for 2 hours. After cooling to room temperature, the reaction was quenched with aqueous 1N HCl and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was purified by a silica gel column chromatography (hexane/EtOAc = 10:1) to give (**2e**, 1.52 g, 5.77 mmol, 65% yield) as a pale yellow solid.

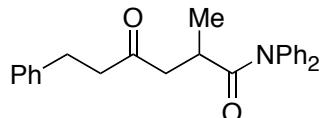
Mp 79.0–80.0 °C; IR (KBr) 1654, 1592, 1491, 1352, 759  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.39–7.07 (m, 10H), 6.08–5.99 (m, 1H), 2.32–2.16 (m, 4H), 1.73 (quint,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  168.1, 143.3, 140.0, 139.9, 128.8, 127.1, 126.3, 33.0, 32.9, 23.2; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{17}\text{NONa}$  [M+Na]<sup>+</sup> 286.1202, found 286.1197.

### III. Rhodium-Catalyzed Enantioselective Intermolecular Hydroacylations

**Representative procedure for Rh-catalyzed enantioselective intermolecular hydroacylation (Table 2, entry 1):** (*R,R*)-QuinoxP\* (8.4 mg, 0.025 mmol) and  $[\text{Rh}(\text{nbd})_2]\text{BF}_4$  (9.3 mg, 0.025 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) and the mixture was stirred at room temperature for 5 min.  $\text{H}_2$  was

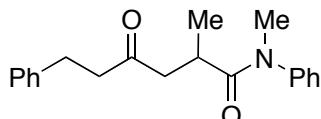
introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting mixture was concentrated to dryness. To the residue was added a solution of **1a** (73.8 mg, 0.550 mmol) and **2a** (118.7 mg, 0.500 mmol) in  $(\text{CH}_2\text{Cl})_2$  (1.0 mL) at room temperature. The mixture was stirred at 80 °C for 16 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/EtOAc = 3:1), which furnished (+)-**3aa** (160.9 mg, 0.433 mmol, 87% yield, 98% ee) as a colorless solid.

**(+)-2-Methyl-4-oxo-6-phenylhexanoic acid diphenylamide [(+)-3aa, Table 2, entry 1]**



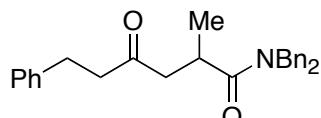
Mp 80.5–82.0 °C;  $[\alpha]^{25}_{\text{D}} +149.0^\circ$  (*c* 8.07,  $\text{CHCl}_3$ , 98% ee); IR (neat) 1703, 1666, 1492, 1393, 1293  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.79–6.91 (m, 15H), 3.23–3.00 (m, 2H), 2.94–2.58 (m, 4H), 2.35–2.18 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  208.7, 176.0, 142.9, 140.9, 128.9, 128.4, 128.2, 126.6, 125.9, 46.9, 44.1, 32.9, 29.5, 17.5; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 394.1778, found 394.1775; CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 11.0 min (minor isomer) and 15.9 min (major isomer).

**(+)-2-Methyl-4-oxo-6-phenylhexanoic acid methylphenylamide [(+)-3ab, Table 2, entry 2]**



Reaction time: 24 h; Colorless oil;  $[\alpha]^{25}_{\text{D}} +97.6^\circ$  (*c* 5.38,  $\text{CHCl}_3$ , 96% ee); IR (neat) 1713, 1654, 1596, 1496, 1393  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.53–7.08 (m, 10H), 3.24 (s, 3H), 3.09 (dd, *J* = 17.6, 10.1 Hz, 1H), 2.96–2.55 (m, 5H), 2.22 (dd, *J* = 17.6, 3.8 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  208.6, 175.5, 143.8, 140.8, 129.4, 128.2, 128.0, 127.5, 125.8, 46.7, 44.0, 37.4, 31.8, 29.4, 17.5; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 332.1621, found 332.1626; CHIRALPAK AS-H, hexane/*i*-PrOH = 95:5, 1.0 mL/min, retention times: 9.9 min (minor isomer) and 11.3 min (major isomer).

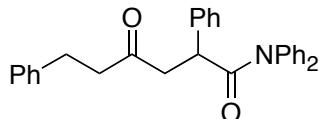
**(+)-2-Methyl-4-oxo-6-phenylhexanoic acid dibenzylamide [(+)-3ac, Table 2, entry 3]**



Reaction time: 16 h; Colorless oil;  $[\alpha]^{25}_{\text{D}} +5.6^\circ$  (*c* 7.80,  $\text{CHCl}_3$ , 97% ee); IR (neat) 1713, 1640, 1454, 752, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.46–7.05 (m, 15H), 4.69 (d, *J* = 15.0 Hz, 1H), 4.59 (d, *J* = 17.0 Hz, 1H), 4.52 (d, *J* = 17.0 Hz, 1H), 4.44 (d, *J* = 15.0 Hz, 1H), 3.37–3.23 (m, 1H), 3.16 (dd, *J* = 17.5, 9.4 Hz, 1H), 2.96–2.62 (m, 4H), 2.38 (dd, *J* = 17.4, 3.8 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  208.6, 176.0, 140.8, 137.2, 136.5, 128.7, 128.4, 128.3, 128.1, 127.7, 127.4, 127.0, 126.8, 125.9, 49.7, 47.8, 46.9, 44.2, 31.3, 29.5, 17.7; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{29}\text{NO}_2\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 422.2091, found 422.2082; CHIRALPAK AD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 8.1 min (minor isomer) and 9.5 min (major isomer).

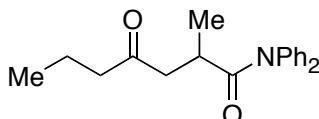
A small amount of starting material **2c** (3 wt%) could not be separated by a preparative TLC. The yield of **3ac** (73%) was calculated by removal of the contaminated **2c**.

**(+)-4-Oxo-2,6-diphenylhexanoic acid diphenylamide [(+)-3ad, Table 2, entry 4]**



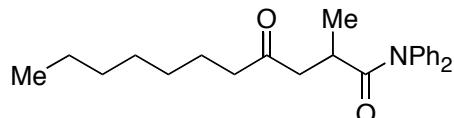
Reaction time: 72 h; Pale yellow oil;  $[\alpha]^{25}_D +172.1^\circ$  (*c* 8.99, CHCl<sub>3</sub>, 99% ee); IR (neat) 1713, 1668, 1595, 1492, 1371 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.42–7.04 (m, 18H), 7.00–6.88 (m, 2H), 4.24 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.54 (dd, *J* = 17.8, 11.1 Hz, 1H), 3.00–2.56 (m, 4H), 2.43 (dd, *J* = 17.8, 3.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  208.3, 172.4, 142.8, 142.0, 140.8, 138.5, 129.4, 129.1, 128.7, 128.5, 128.3, 128.1, 127.7, 127.0, 126.3, 125.9, 48.0, 45.4, 44.0, 29.4; HRMS (ESI) calcd for C<sub>30</sub>H<sub>27</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 456.1934, found 456.1934; CHIRALPAK AD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 12.4 min (major isomer) and 14.0 min (minor isomer).

**(+)-2-Methyl-4-oxoheptanoic acid diphenylamide [(+)-3ba, Table 2, entry 5]**



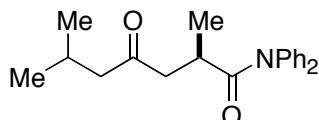
Reaction time: 24 h; Pale yellow oil;  $[\alpha]^{25}_D +158.2^\circ$  (*c* 6.19, CHCl<sub>3</sub>, 98% ee); IR (neat) 1710, 1669, 1492, 1396, 1270 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.84–6.84 (m, 10H), 3.23–2.98 (m, 2H), 2.49–2.19 (m, 3H), 1.60 (quint, *J* = 7.4 Hz, 2H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  209.9, 176.1, 142.9, 129.5, 129.0, 127.7, 126.6, 126.0, 46.8, 44.6, 32.9, 17.5, 17.1, 13.7; HRMS (ESI) calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 332.1621, found 332.1627; CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 5.0 min (minor isomer) and 6.0 min (major isomer).

**(+)-2-Methyl-4-oxoundecanoic acid diphenylamide [(+)-3ca, Table 2, entry 6]**



Reaction time: 24 h; Pale yellow oil;  $[\alpha]^{25}_D +141.3^\circ$  (*c* 7.12, CHCl<sub>3</sub>, 98% ee); IR (neat) 1712, 1668, 1492, 1395, 1267 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.87–6.84 (m, 10H), 3.23–2.98 (m, 2H), 2.50–2.21 (m, 3H), 1.64–1.46 (m, 2H), 1.34–1.17 (m, 8H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  209.9, 176.0, 142.8, 128.9, 127.5, 126.5, 125.8, 121.3, 46.7, 42.6, 32.8, 31.5, 29.0, 28.9, 23.5, 22.4, 17.4, 13.9; HRMS (ESI) calcd for C<sub>24</sub>H<sub>31</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 388.2247, found 388.2245; CHIRALCEL OD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min, retention times: 5.9 min (minor isomer) and 7.1 min (major isomer).

**(R)-(+)2,6-Dimethyl-4-oxoheptanoic acid diphenylamide [(R)-(+)3da, Table 2, entry 7]**

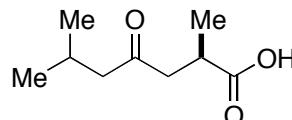


Reaction time: 24 h; Pale yellow oil;  $[\alpha]^{25}_D +150.5^\circ$  (*c* 5.05, CHCl<sub>3</sub>, 98% ee); IR (neat) 1708, 1668,

1490, 1387, 1276 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.83–6.91 (m, 10H), 3.22–2.98 (m, 2H), 2.38–2.03 (m, 4H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.904 (d, *J* = 6.6 Hz, 3H), 0.897 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 209.6, 176.0, 142.9, 129.4, 129.0, 127.6, 127.0, 126.5, 125.9, 51.7, 47.3, 32.8, 24.5, 22.52, 22.47, 17.5; HRMS (ESI) calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 346.1778, found 346.1781; CHIRALPAK AD-H, hexane/i-PrOH = 80:20, 1.0 mL/min, retention times: 5.0 min (major isomer) and 5.7 min (minor isomer).

The absolute configuration of (+)-**3da** was determined as R configuration by converting to (*R*)-(+)2,6-dimethyl-4-oxoheptanoic acid<sup>5</sup> as shown below.

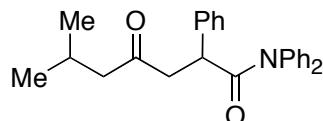
**(R)-(+)-2,6-Dimethyl-4-oxoheptanoic acid<sup>5</sup>**



Aqueous NaOH (1N, 2.0 mL, 2.0 mmol) was added to a solution of (+)-**3da** (64.7 mg, 0.200 mmol) in MeOH (2.0 mL). The mixture was stirred at 80 °C for 20 h. The resulting mixture was washed with ether, acidified with 1N aqueous HCl, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give 2,6-dimethyl-4-oxoheptanoic acid (15.7 mg, 0.0912 mmol, 46%) as a yellow oil.

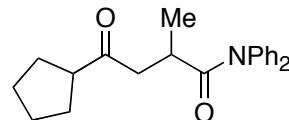
[α]<sup>25</sup><sub>D</sub> +5.7° (c 0.785, CHCl<sub>3</sub>) [lit.<sup>5</sup> [α]<sup>18</sup><sub>D</sub> -10.5° (CHCl<sub>3</sub>) for S enantiomer]; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 3.09–2.89 (m, 1H), 2.86 (dd, *J* = 17.7, 8.1 Hz, 1H), 2.46 (dd, *J* = 17.7, 5.2 Hz, 1H), 2.38–2.03 (m, 3H), 1.22 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 208.7, 181.4, 51.8, 46.0, 34.4, 24.7, 22.5, 16.9.

**(+)-6-Methyl-4-oxo-2-phenylheptanoic acid diphenylamide [(+)-3dd, Table 2, entry 8]**



Reaction time: 72 h; Pale yellow oil; [α]<sup>25</sup><sub>D</sub> +216.8° (c 7.68, CHCl<sub>3</sub>, 97% ee); IR (neat) 1711, 1670, 1492, 1368, 1274 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.49–6.84 (m, 15H), 4.22 (dd, *J* = 11.1, 3.3 Hz, 1H), 3.53 (dd, *J* = 18.0, 11.1 Hz, 1H), 2.52–2.05 (m, 4H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 209.2, 172.4, 142.9, 142.1, 138.7, 129.4, 129.1, 128.7, 128.5, 127.7, 127.0, 126.3, 125.9, 51.6, 48.5, 45.3, 24.4, 22.52, 22.47; HRMS (ESI) calcd for C<sub>26</sub>H<sub>27</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 408.1934, found 408.1939; CHIRALCEL OD-H, hexane/i-PrOH = 90:10, 1.0 mL/min, retention times: 5.1 min (minor isomer) and 6.3 min (major isomer).

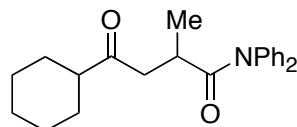
**(+)-4-Cyclopentyl-2-methyl-4-oxo-N,N-diphenylbutyramide [(+)-3ea, Table 2, entry 9]**



Reaction time: 48 h; Pale yellow oil; [α]<sup>25</sup><sub>D</sub> +157.3° (c 7.13, CHCl<sub>3</sub>, 98% ee); IR (neat) 1705, 1668, 1491, 1395, 1266 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.81–6.90 (m, 10H), 3.20 (dd, *J* = 17.4, 10.4 Hz, 1H), 3.18–3.00 (m, 1H), 2.84 (quint, *J* = 8.0 Hz, 1H), 2.34 (dd, *J* = 17.3, 3.2 Hz, 1H), 1.93–1.44 (m, 8H), 1.08 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 211.8, 176.0, 142.9, 129.4, 128.9, 128.7, 127.5, 126.5, 125.8, 51.0, 45.8, 32.8, 28.7, 28.5, 25.9, 25.8, 17.5; HRMS (ESI) calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>2</sub>Na

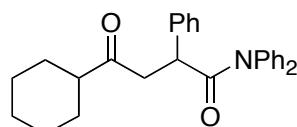
$[M+Na]^+$  358.1778, found 358.1777; CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 4.7 min (minor isomer) and 5.9 min (major isomer).

**(+)-4-Cyclohexyl-2-methyl-4-oxo-*N,N*-diphenylbutyramide [(+)-3fa, Table 2, entry 10]**



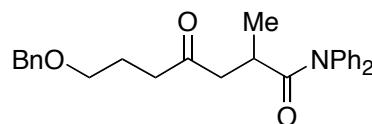
Reaction time: 48 h; Pale yellow oil;  $[\alpha]^{25}_D +161.7^\circ$  (*c* 3.01, CHCl<sub>3</sub>, 98% ee); IR (neat) 1704, 1670, 1492, 756, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.76–6.95 (m, 10H), 3.20 (dd, *J* = 17.4, 10.4 Hz, 1H), 3.14–2.99 (m, 1H), 2.39–2.23 (m, 1H), 2.32 (dd, *J* = 17.4, 3.1 Hz, 1H), 1.98–1.52 (m, 5H), 1.45–1.09 (m, 5H), 1.08 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  212.9, 176.1, 143.0, 129.4, 129.0, 128.8, 128.6, 127.7, 126.6, 125.9, 50.5, 44.8, 32.9, 28.42, 28.36, 25.8, 25.6, 25.5, 17.6; HRMS (ESI) calcd for C<sub>23</sub>H<sub>27</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 372.1934, found 372.1931; CHIRALPAK AD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min, retention times: 7.6 min (major isomer) and 11.2 min (minor isomer).

**(+)-4-Cyclohexyl-4-oxo-2,*N,N*-triphenylbutyramide [(+)-3fd, Table 2, entry 11]**



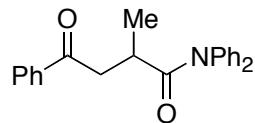
Reaction time: 72 h; Pale yellow oil;  $[\alpha]^{25}_D +211.3^\circ$  (*c* 7.47, CHCl<sub>3</sub>, 97% ee); IR (neat) 1704, 1669, 1492, 1371, 1276 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.39–7.03 (m, 13H), 7.01–6.89 (m, 2H), 4.23 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.59 (dd, *J* = 18.0, 11.1 Hz, 1H), 2.46 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.41–2.25 (m, 1H), 2.04–1.51 (m, 5H), 1.46–1.02 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  212.4, 172.3, 142.9, 142.2, 138.8, 129.4, 129.1, 128.6, 128.4, 127.7, 127.6, 126.9, 126.3, 125.8, 50.4, 46.1, 45.3, 28.3, 25.7, 25.5, 25.4; HRMS (ESI) calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 434.2091, found 434.2080; CHIRALCEL OD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min, retention times: 5.0 min (minor isomer) and 6.5 min (major isomer).

**(+)-7-Benzylxyloxy-2-methyl-4-oxoheptanoic acid diphenylamide [(+)-3ha, Table 2, entry 13]**



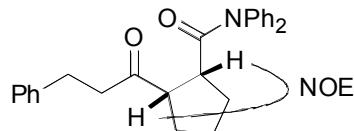
Reaction time: 48 h; Pale yellow oil;  $[\alpha]^{25}_D +123.8^\circ$  (*c* 7.79, CHCl<sub>3</sub>, 98% ee); IR (neat) 1712, 1666, 1492, 756, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.68–6.91 (m, 15H), 4.45 (s, 2H), 3.45 (t, *J* = 6.1 Hz, 2H), 3.21–2.96 (m, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.34–2.19 (m, 1H), 1.88 (tt, *J* = 7.2, 6.1 Hz, 2H), 1.05 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  209.3, 175.9, 142.8, 138.3, 129.4, 128.9, 128.1, 127.4, 127.3, 126.5, 125.9, 72.6, 69.1, 46.7, 39.1, 32.8, 23.6, 17.4; HRMS (ESI) calcd for C<sub>27</sub>H<sub>29</sub>NO<sub>3</sub>Na [M+Na]<sup>+</sup> 438.2040, found 438.2040; CHIRALPAK AD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 8.7 min (minor isomer) and 11.2 min (major isomer).

**(+)-2-Methyl-4-oxo-4,*N,N*-triphenylbutyramide [(+)-3ia]**



Reaction time: 72 h; Pale yellow oil;  $[\alpha]^{25}_{\text{D}} +117.2^\circ$  ( $c$  1.39,  $\text{CHCl}_3$ , 64% ee); IR (neat) 1668, 1596, 1492, 1268, 1218  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.02–7.89 (m, 2H), 7.77–6.85 (m, 13H), 3.74 (dd,  $J = 17.9, 10.1$  Hz, 1H), 3.31–3.15 (m, 1H), 2.85 (dd,  $J = 17.9, 3.8$  Hz, 1H), 1.20 (d,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  198.9, 176.1, 143.0, 136.7, 132.9, 129.6, 129.2, 128.7, 128.4, 128.0, 126.6, 43.2, 33.2, 17.8; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  366.1465, found 366.1466; CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 6.3 min (minor isomer) and 8.7 min (major isomer).

### 2-(3-Phenylpropionyl)cyclopentanecarboxylic acid diphenylamide (3ae)

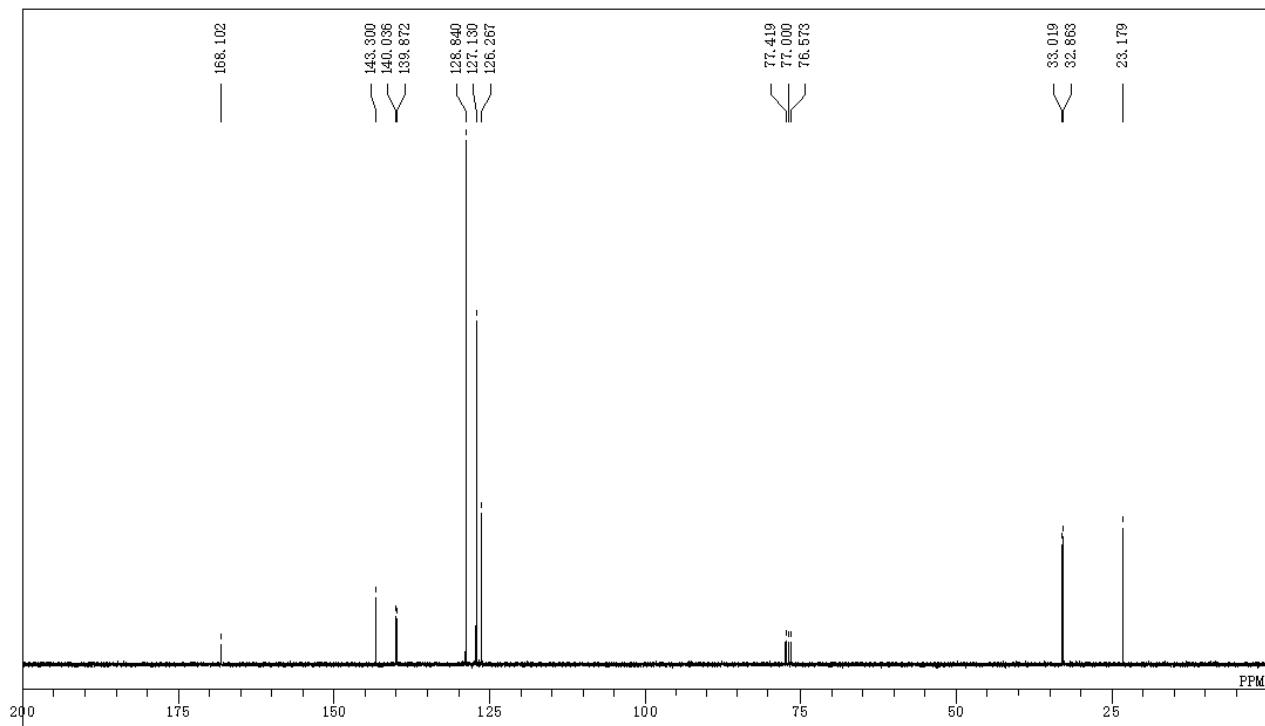
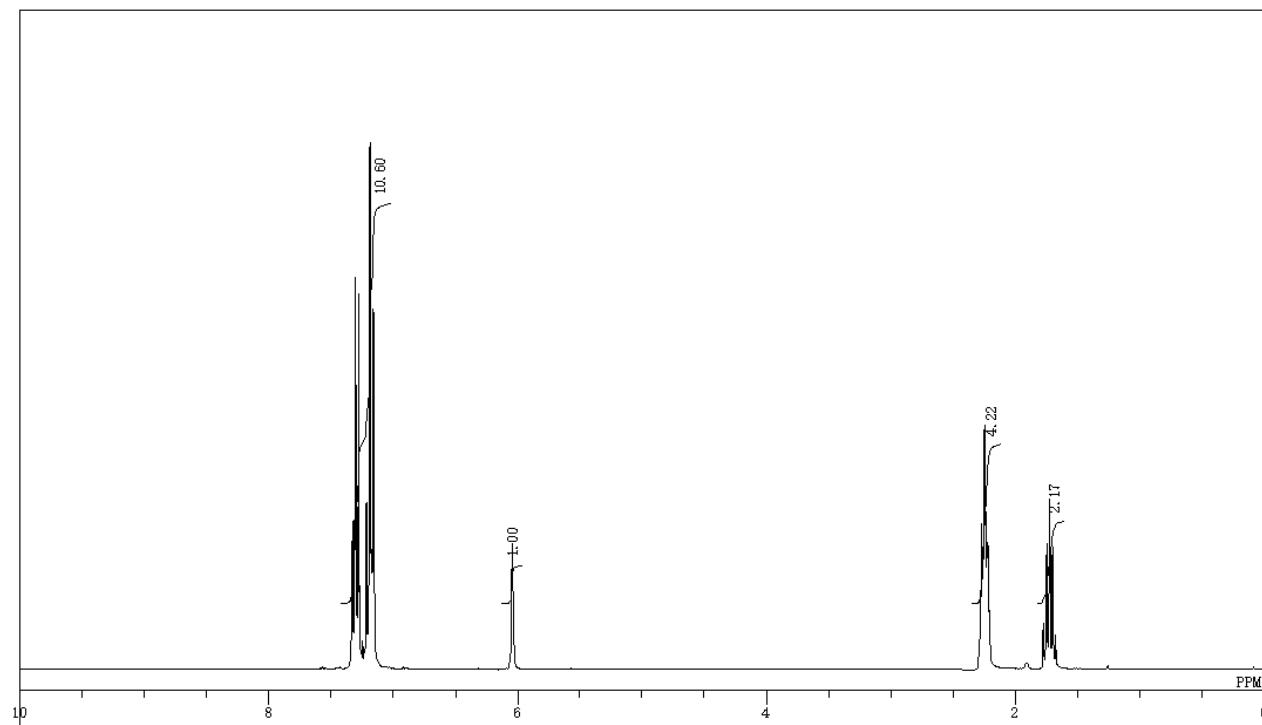
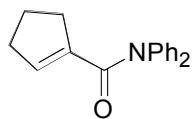


The relative stereochemistry of this compound was determined by NOE experiment. Reaction time: 72 h; Pale yellow solid; Mp 81.0–81.5 °C; IR (KBr) 1705, 1657, 1492, 1402, 1364  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.63–6.94 (m, 15H), 3.53 (q,  $J = 8.9$  Hz, 1H), 3.24–3.09 (m, 1H), 2.93–2.71 (m, 4H), 2.13–1.94 (m, 1H), 1.86–1.65 (m, 3H), 1.62–1.37 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  210.6, 175.0, 142.7, 141.1, 128.9, 128.4, 128.2, 127.2, 126.4, 126.0, 55.7, 44.9, 43.6, 31.1, 29.5, 25.1; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{27}\text{NO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  420.1934, found 420.1931; CHIRALPAK AD-H, hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 15.4 min (major isomer) and 17.3 min (minor isomer).

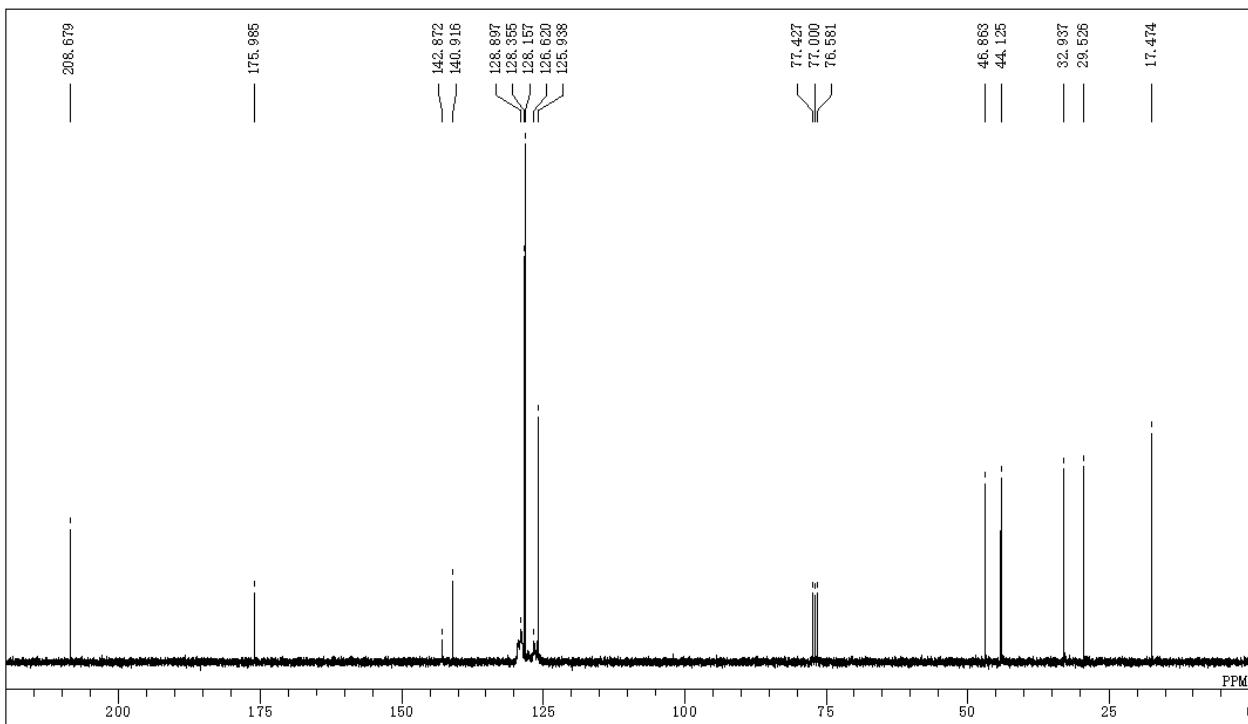
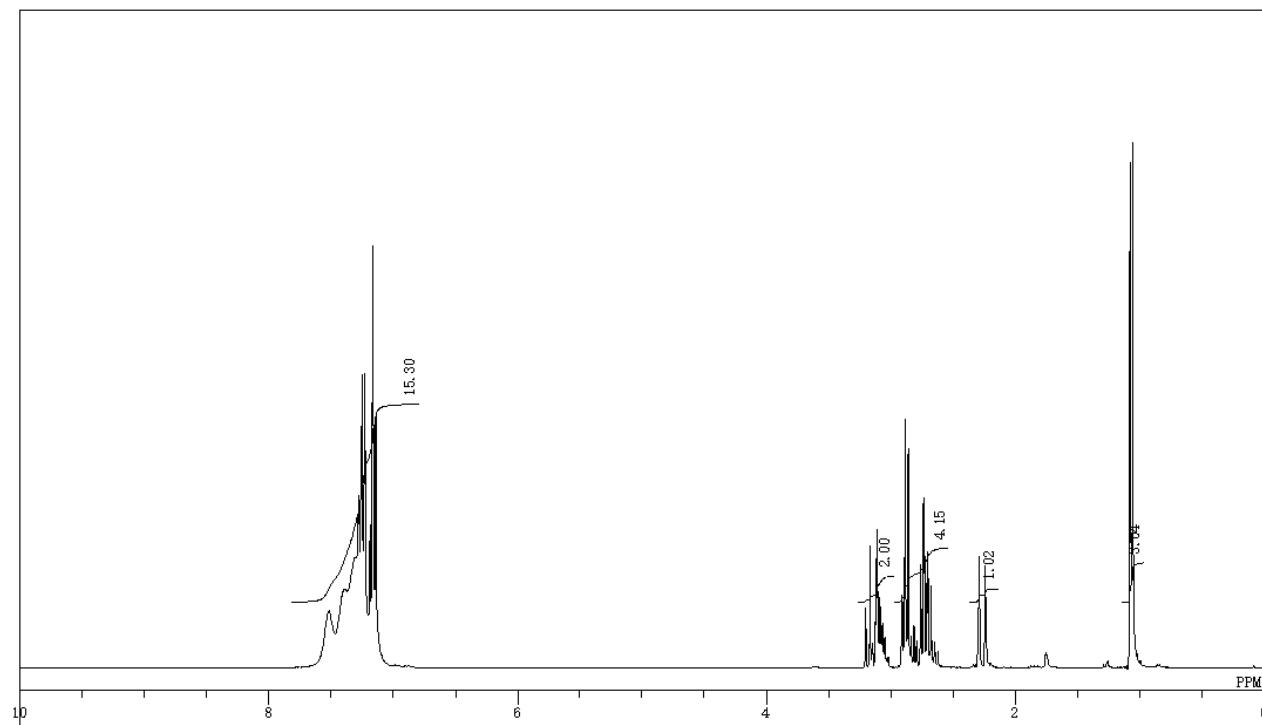
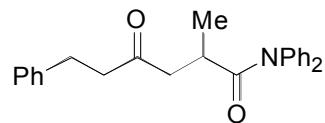
## IV. References

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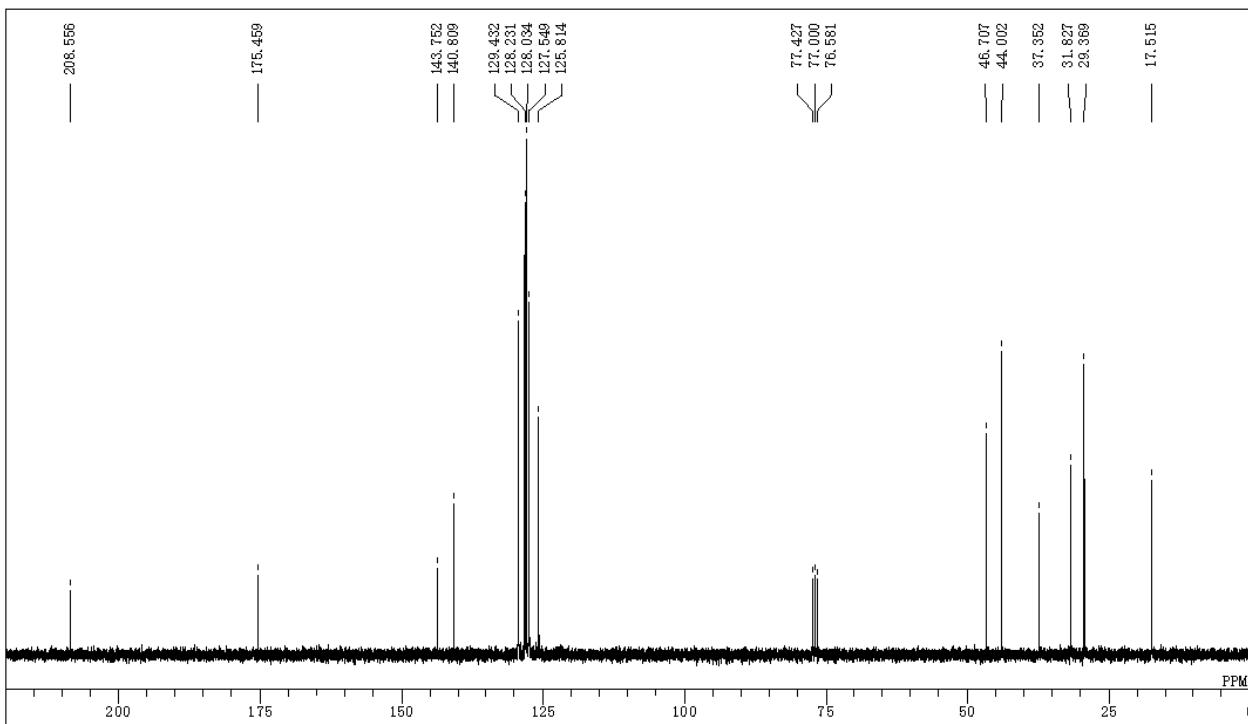
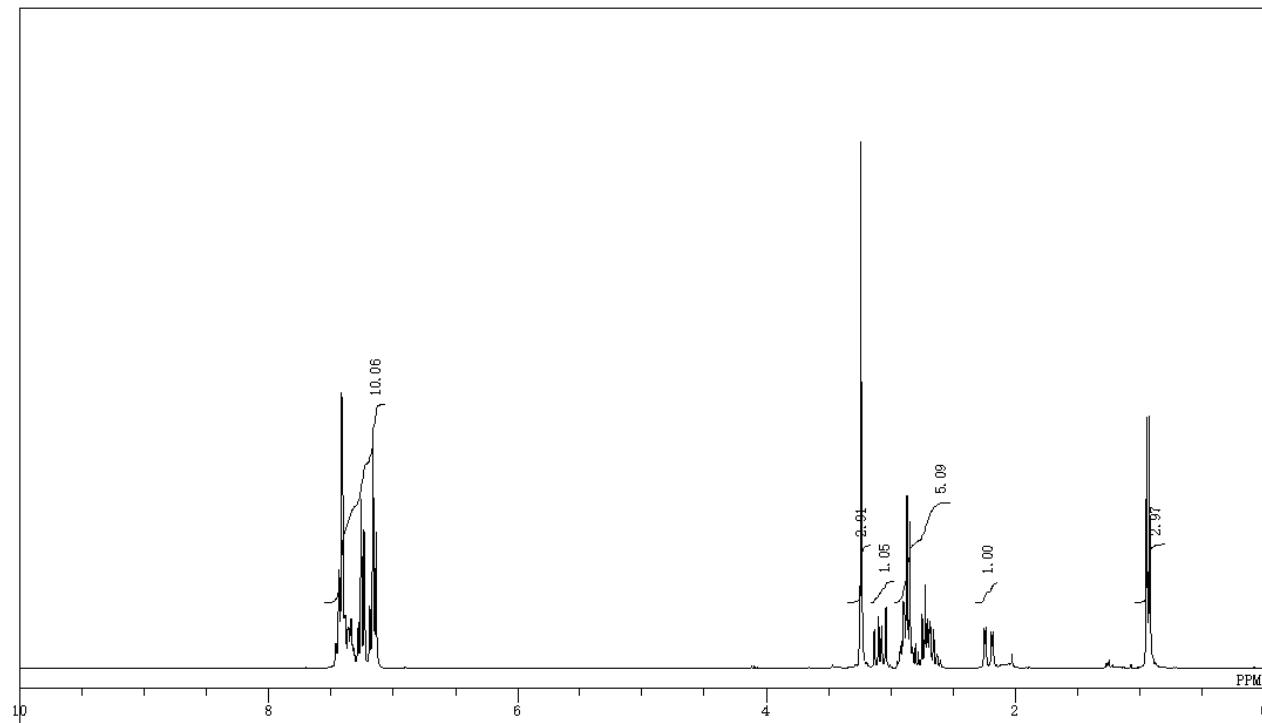
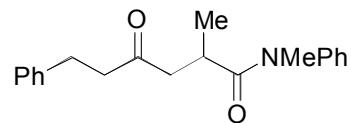
**Cyclopent-1-enecarboxylic acid diphenylamide (2e)**



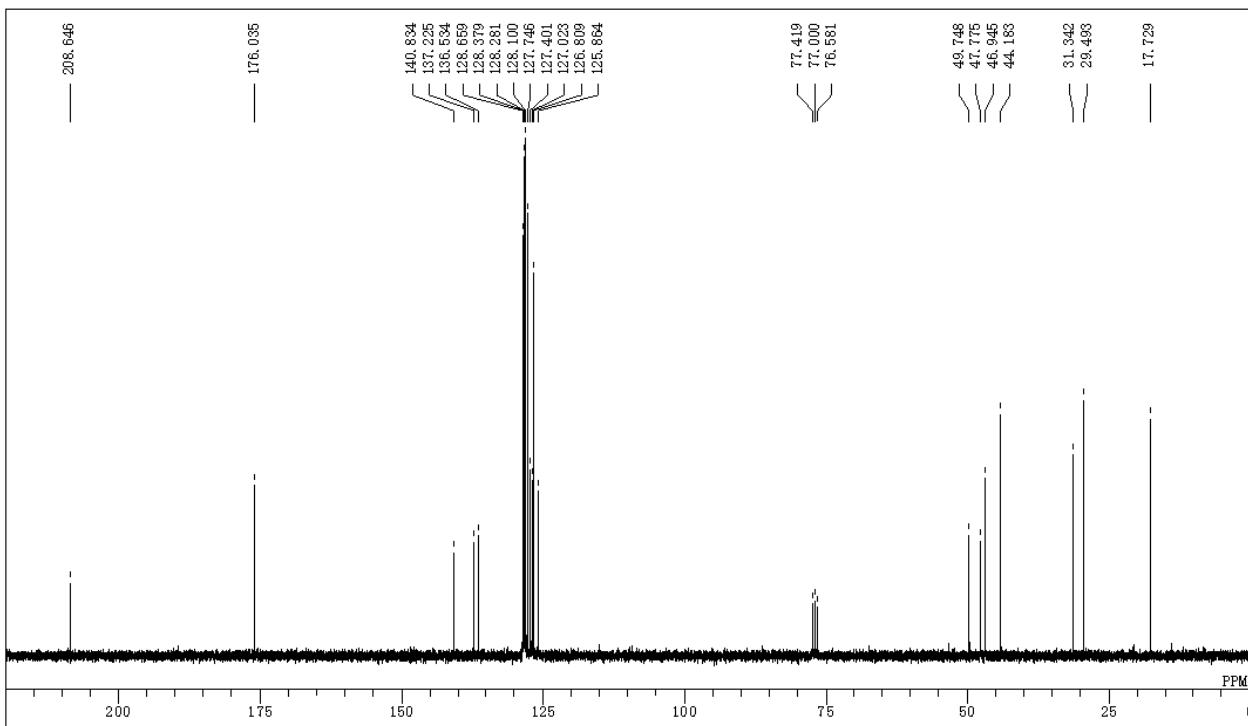
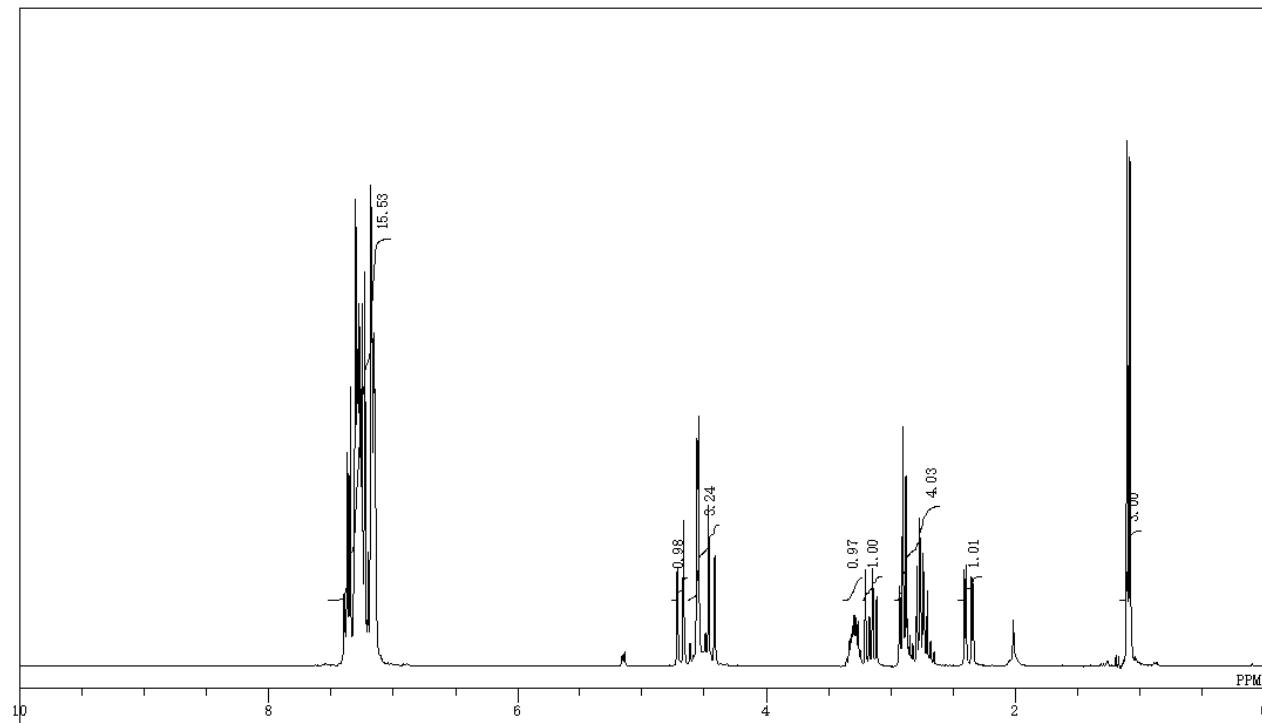
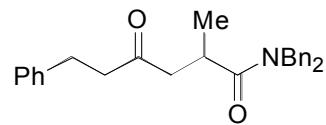
**2-Methyl-4-oxo-6-phenylhexanoic acid diphenylamide (3aa)**



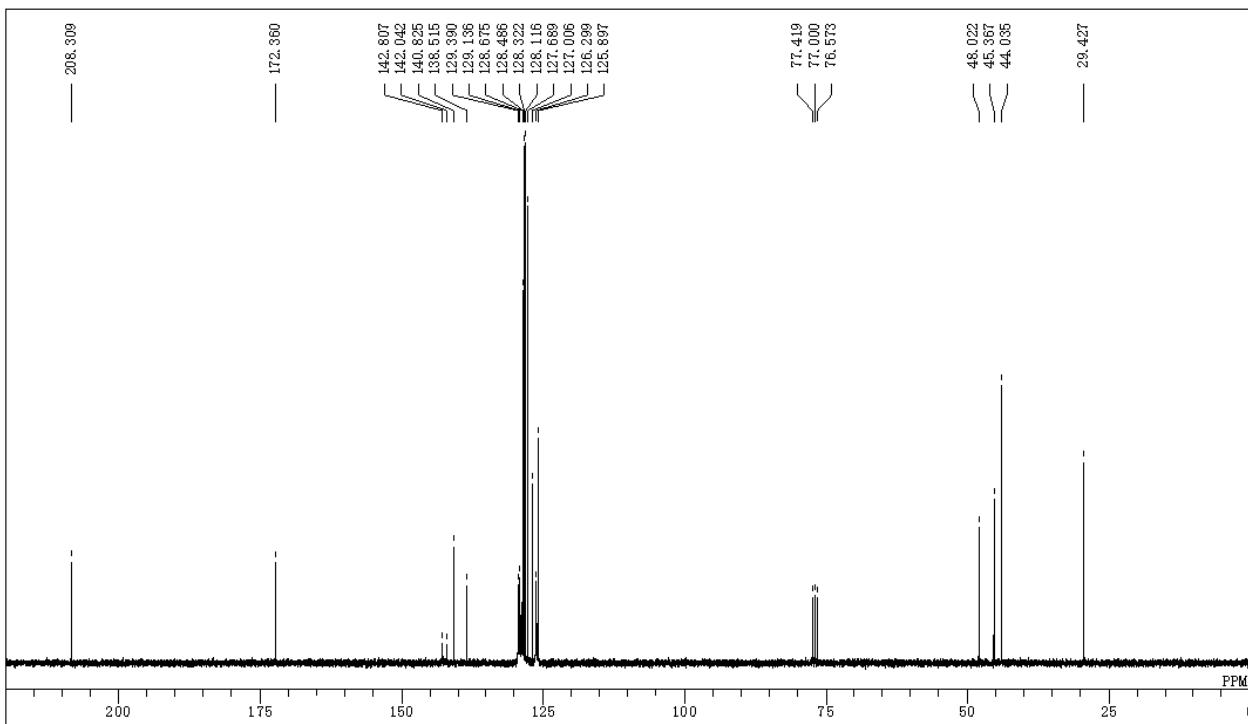
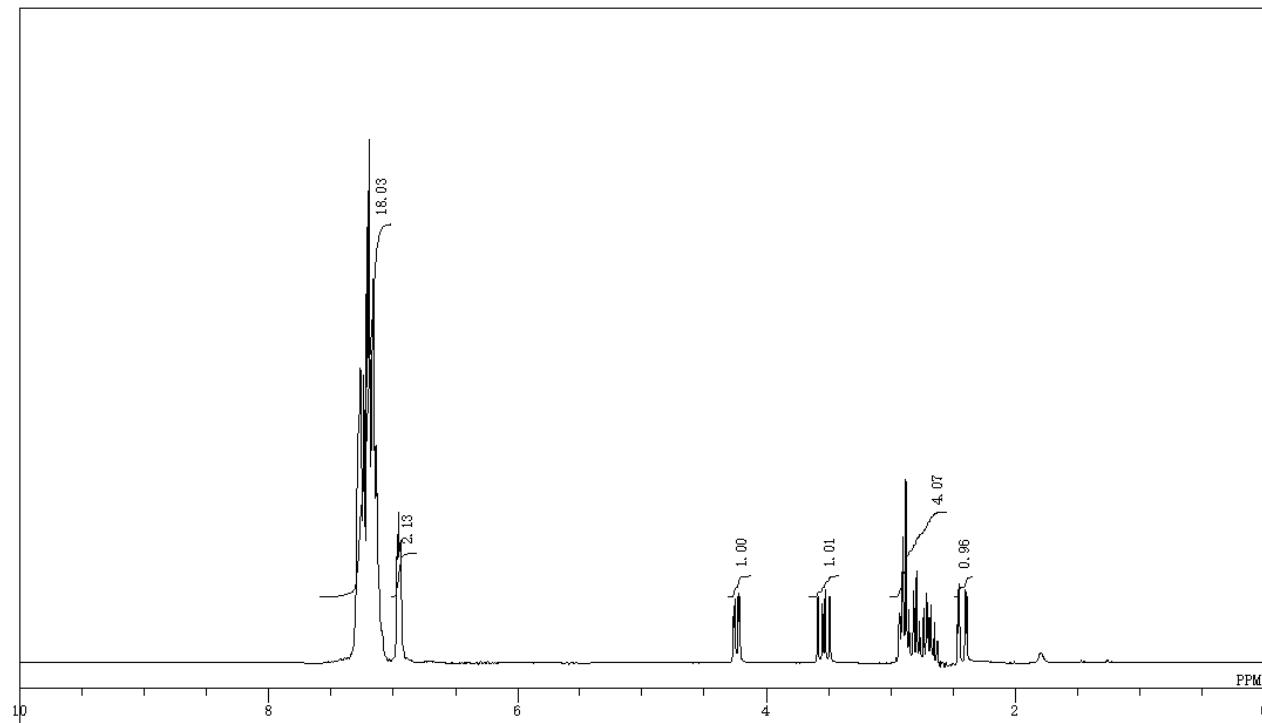
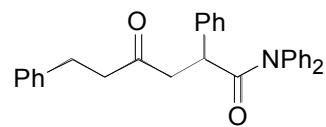
**2-Methyl-4-oxo-6-phenylhexanoic acid methylphenylamide (3ab)**



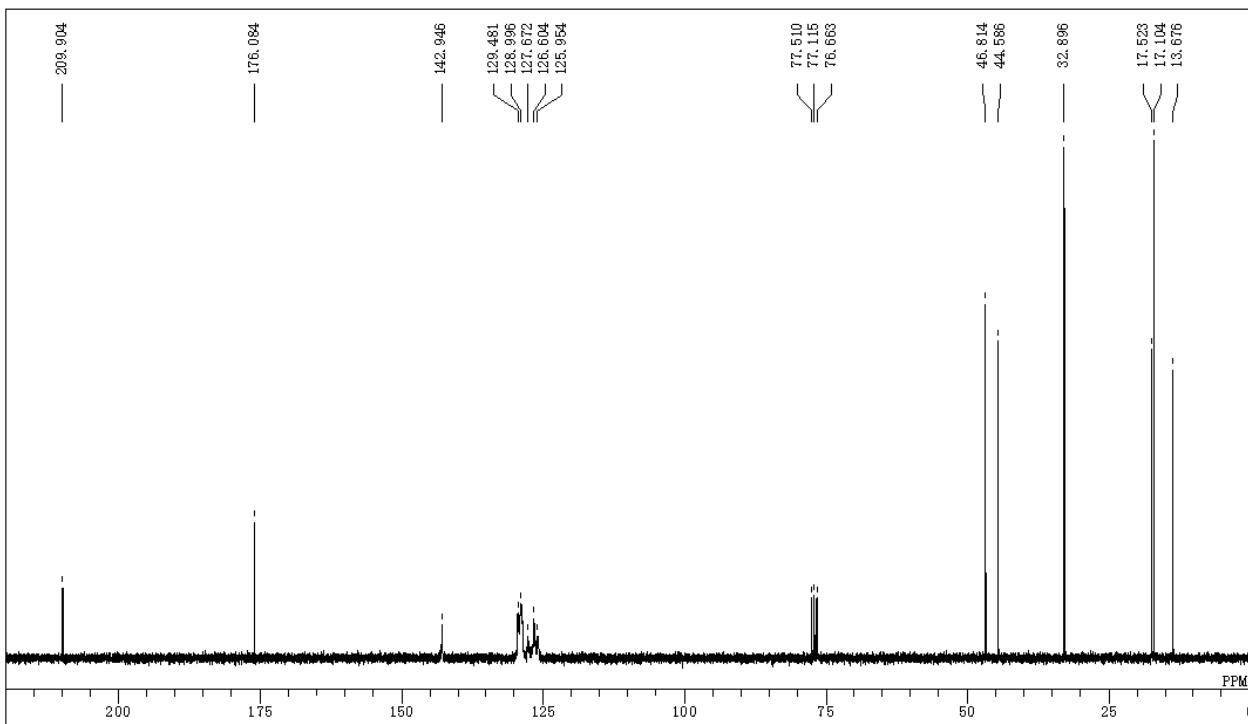
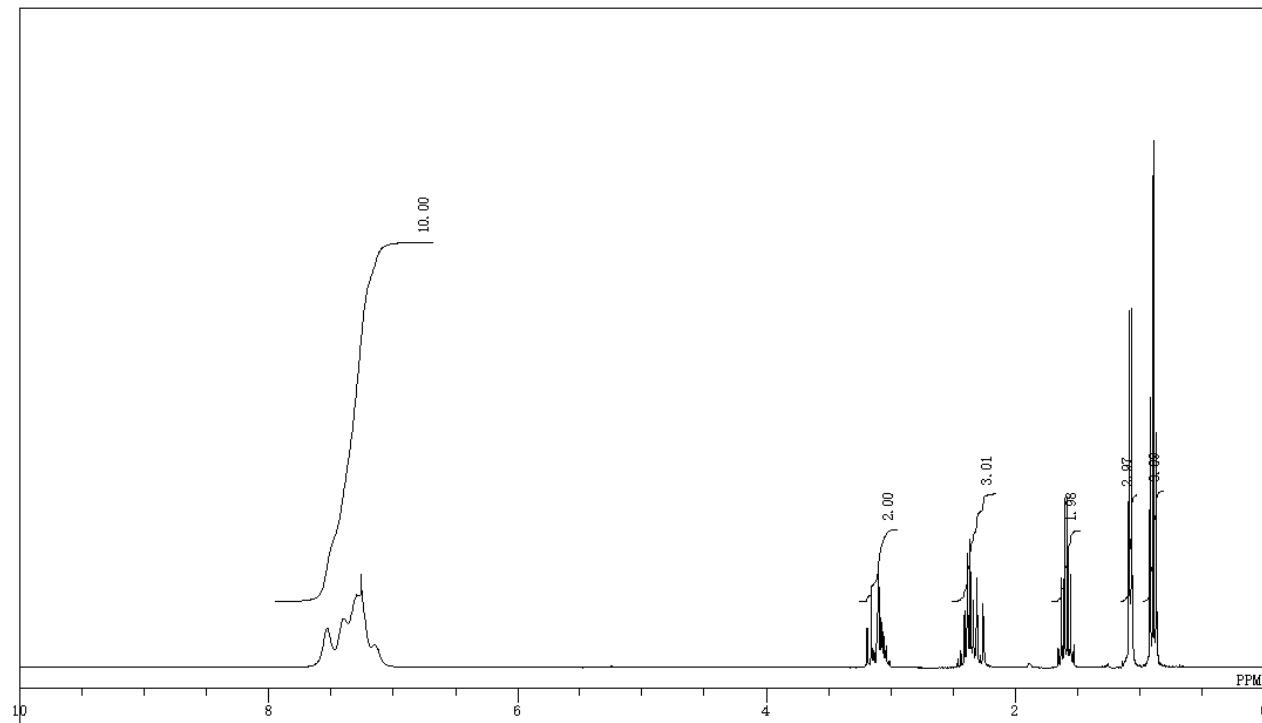
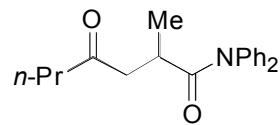
**2-Methyl-4-oxo-6-phenylhexanoic acid dibenzylamide (3ac)**



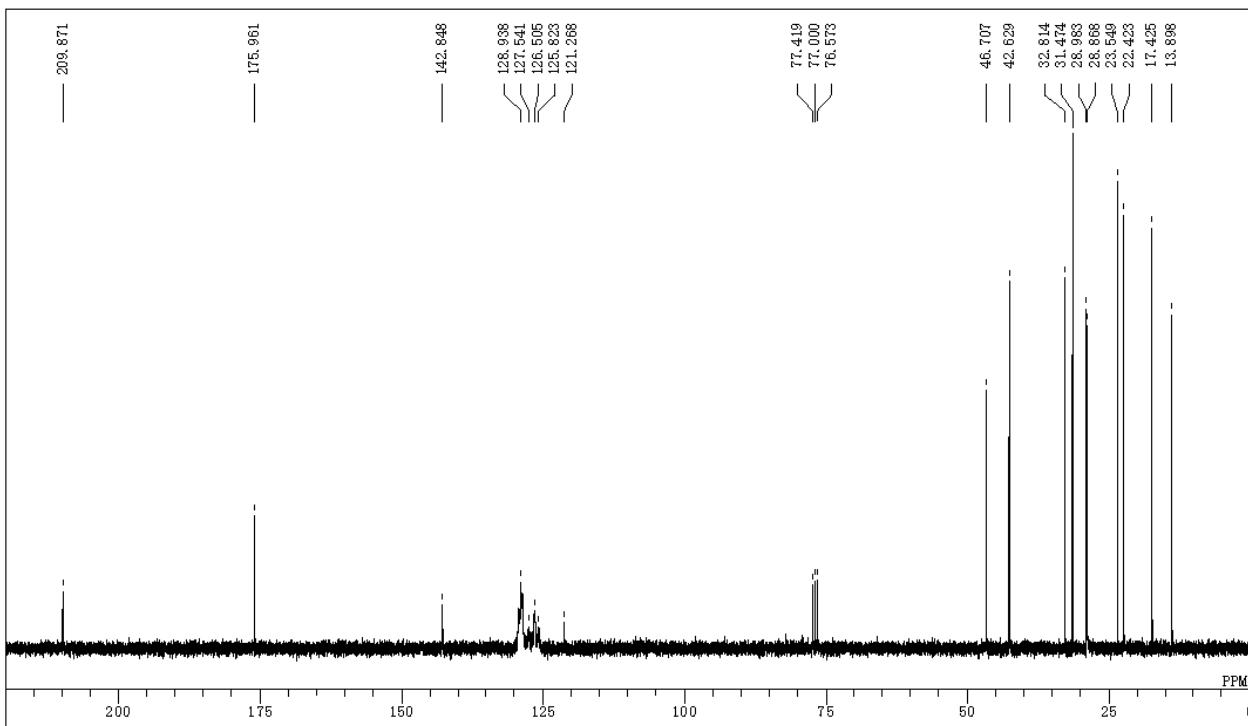
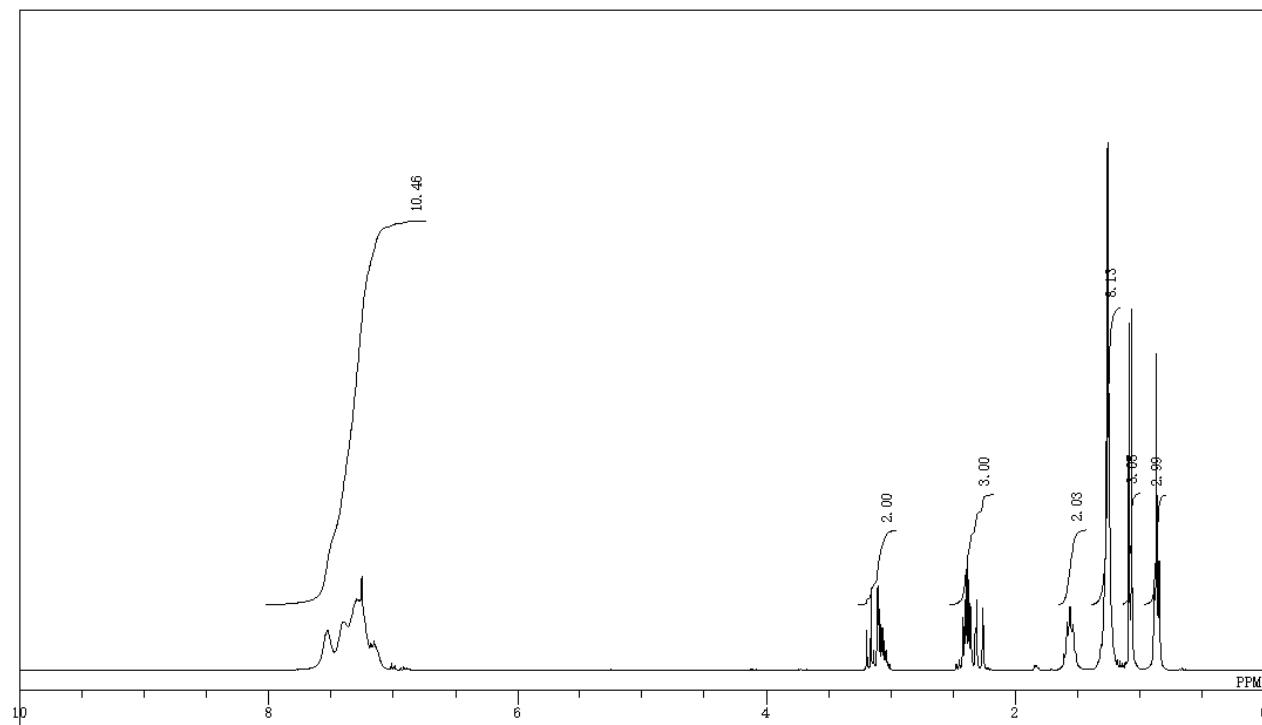
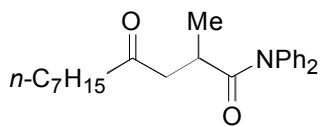
**4-Oxo-2,6-diphenylhexanoic acid diphenylamide (3ad)**



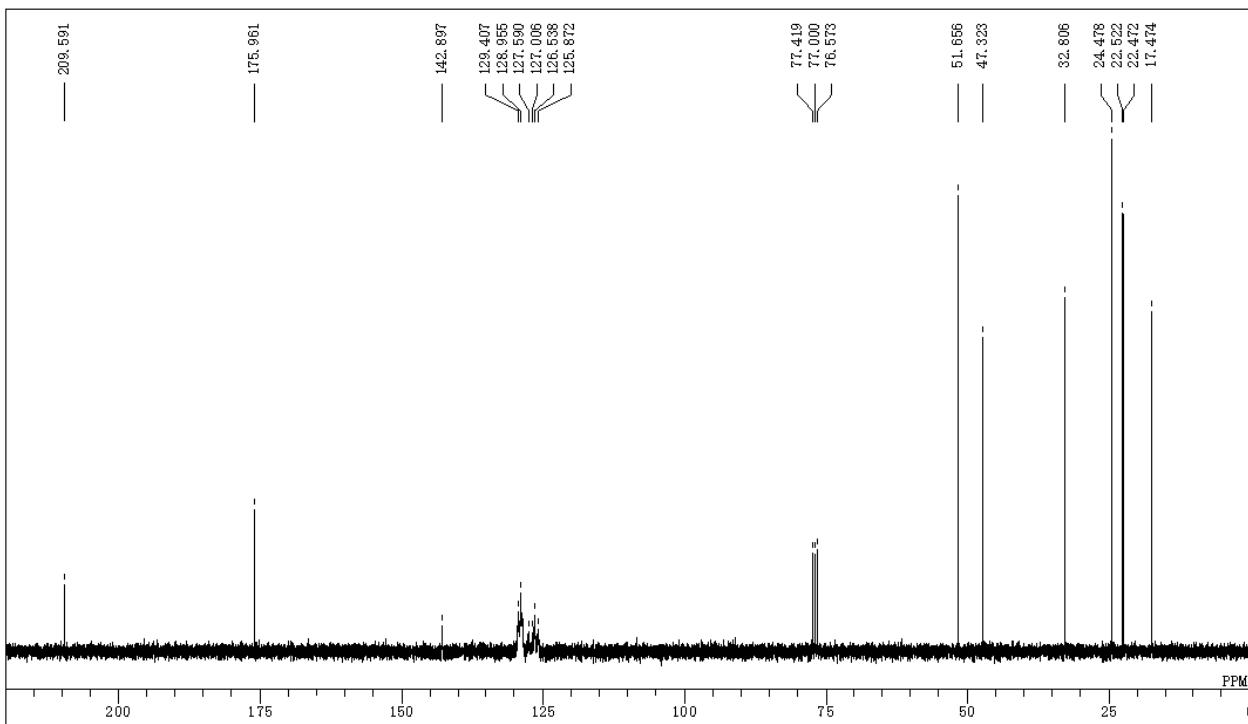
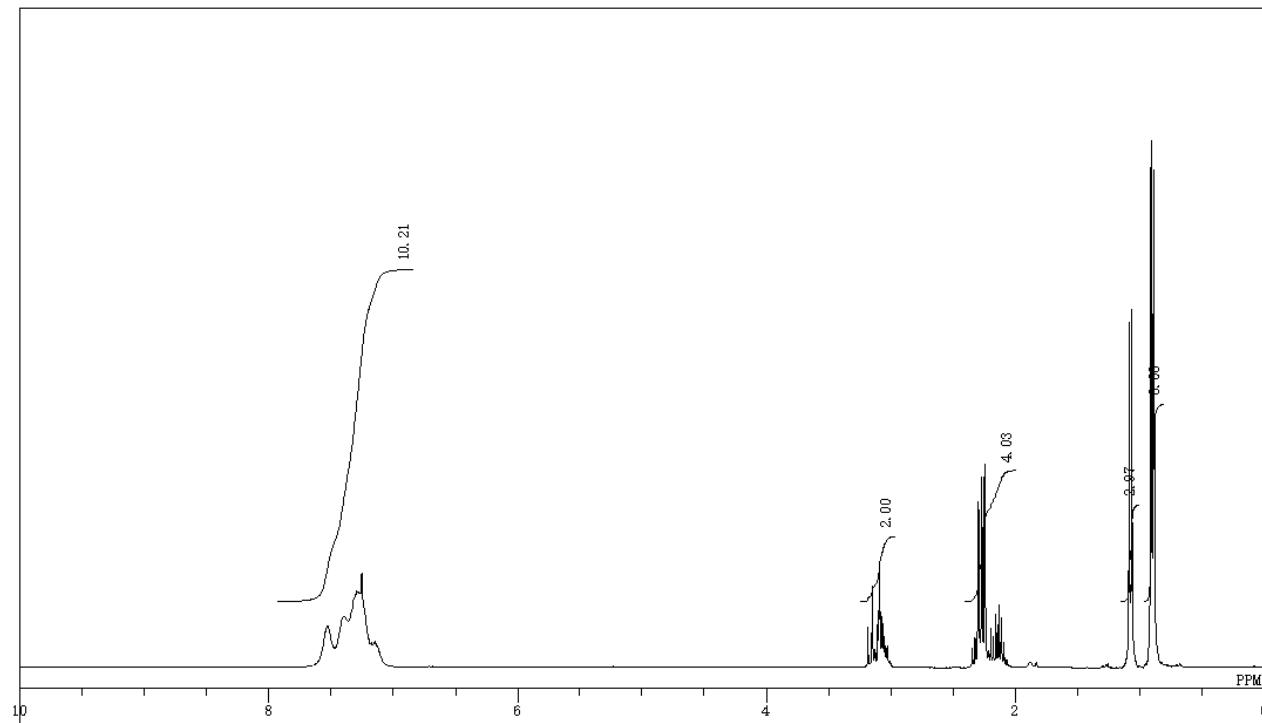
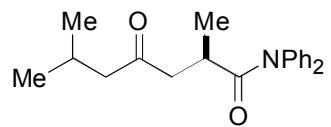
**2-Methyl-4-oxoheptanoic acid diphenylamide (3ba)**



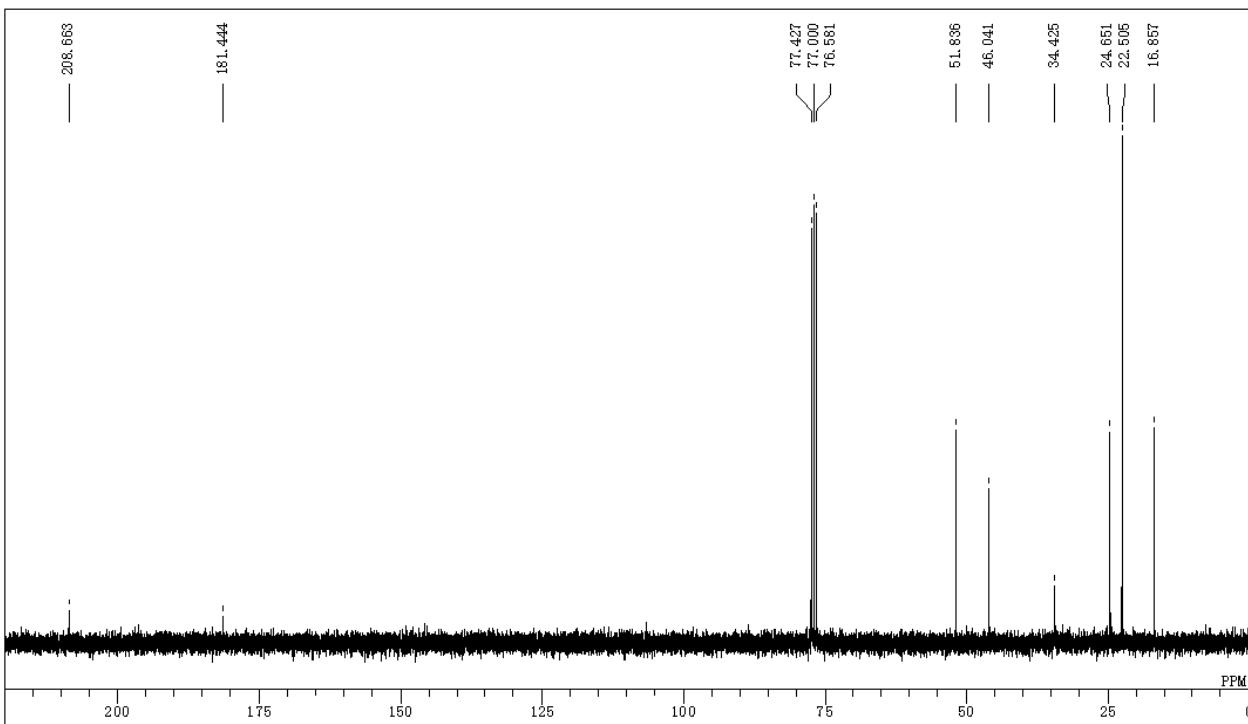
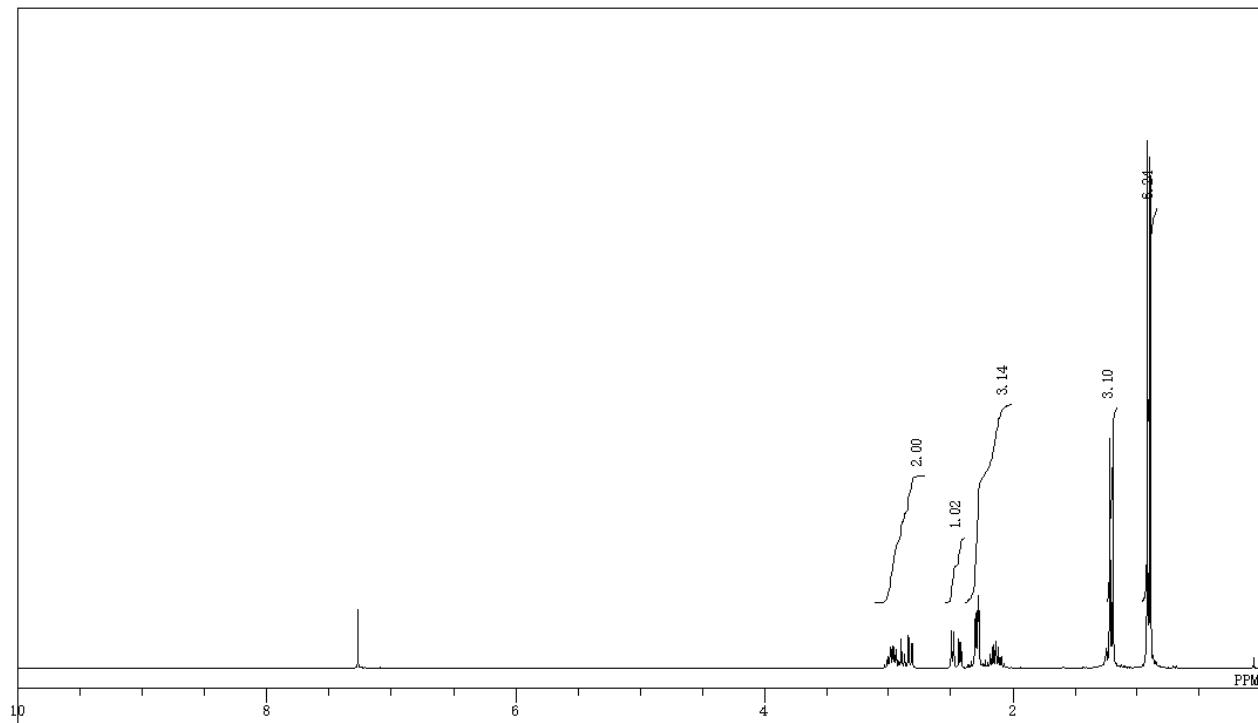
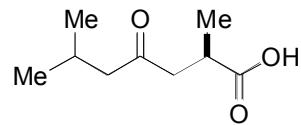
**2-Methyl-4-oxoundecanoic acid diphenylamide (3ca)**



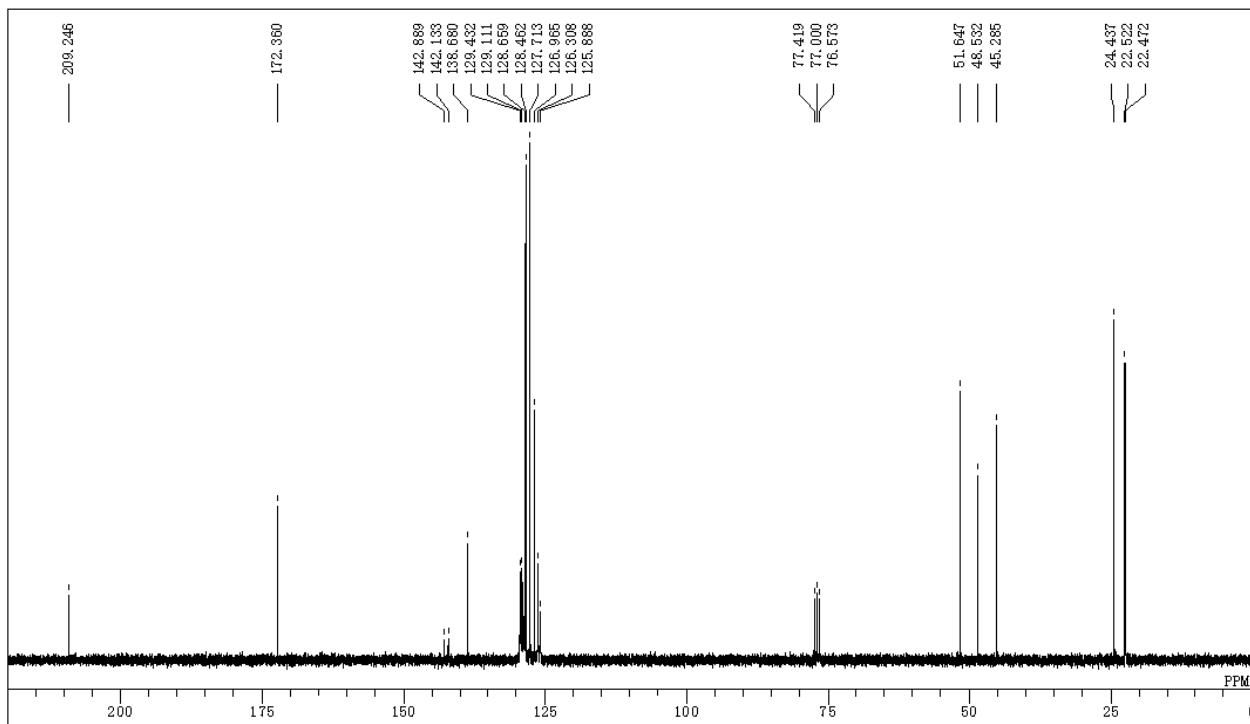
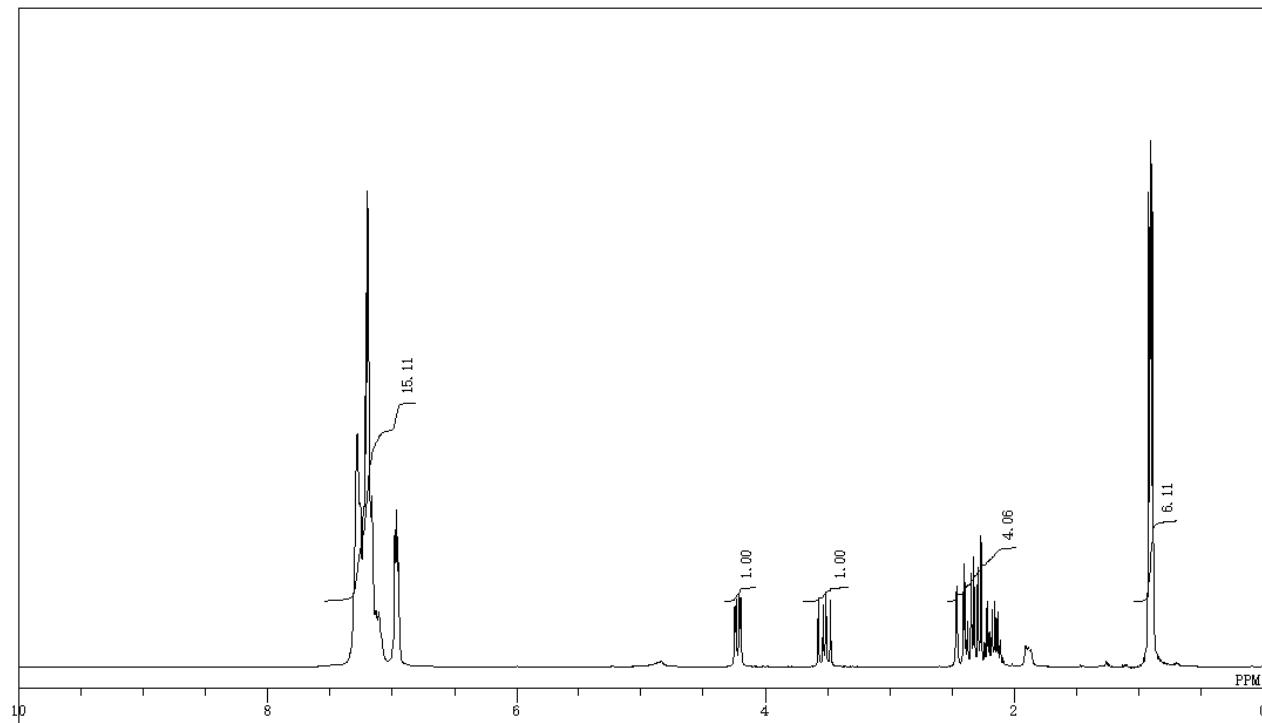
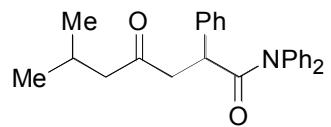
**2,6-Dimethyl-4-oxoheptanoic acid diphenylamide (3da)**



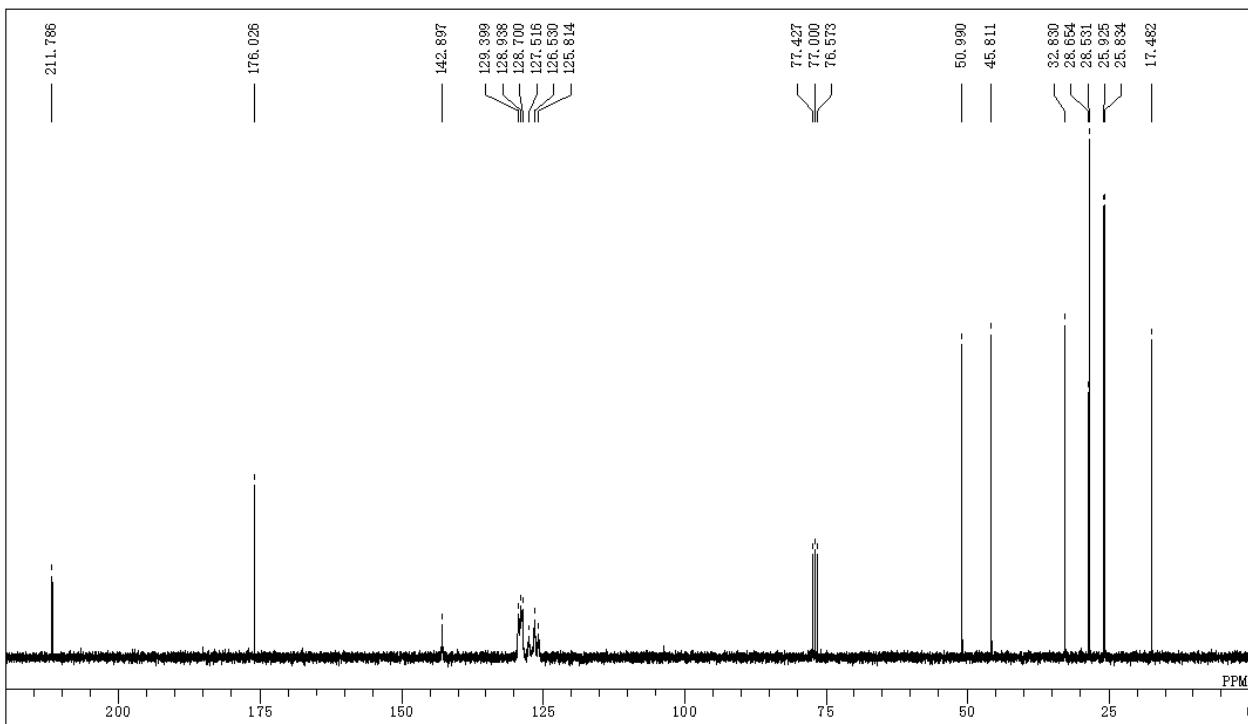
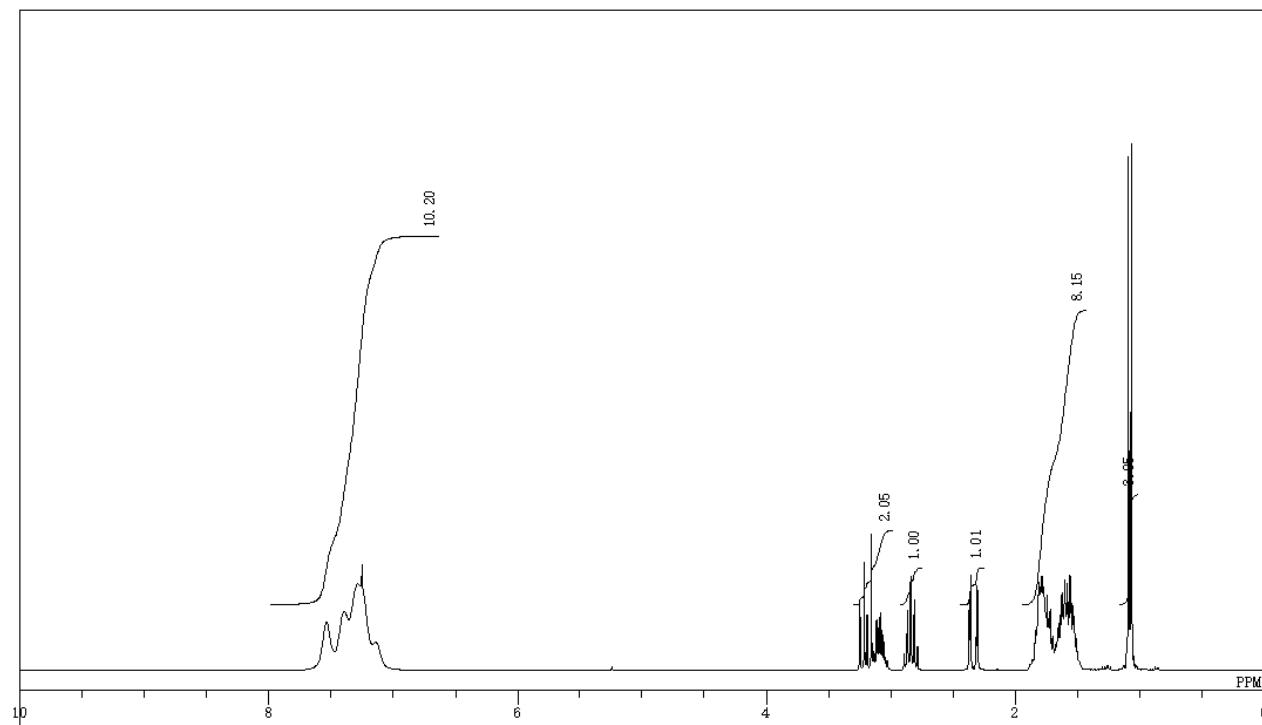
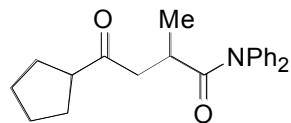
**2,6-Dimethyl-4-oxoheptanoic acid**



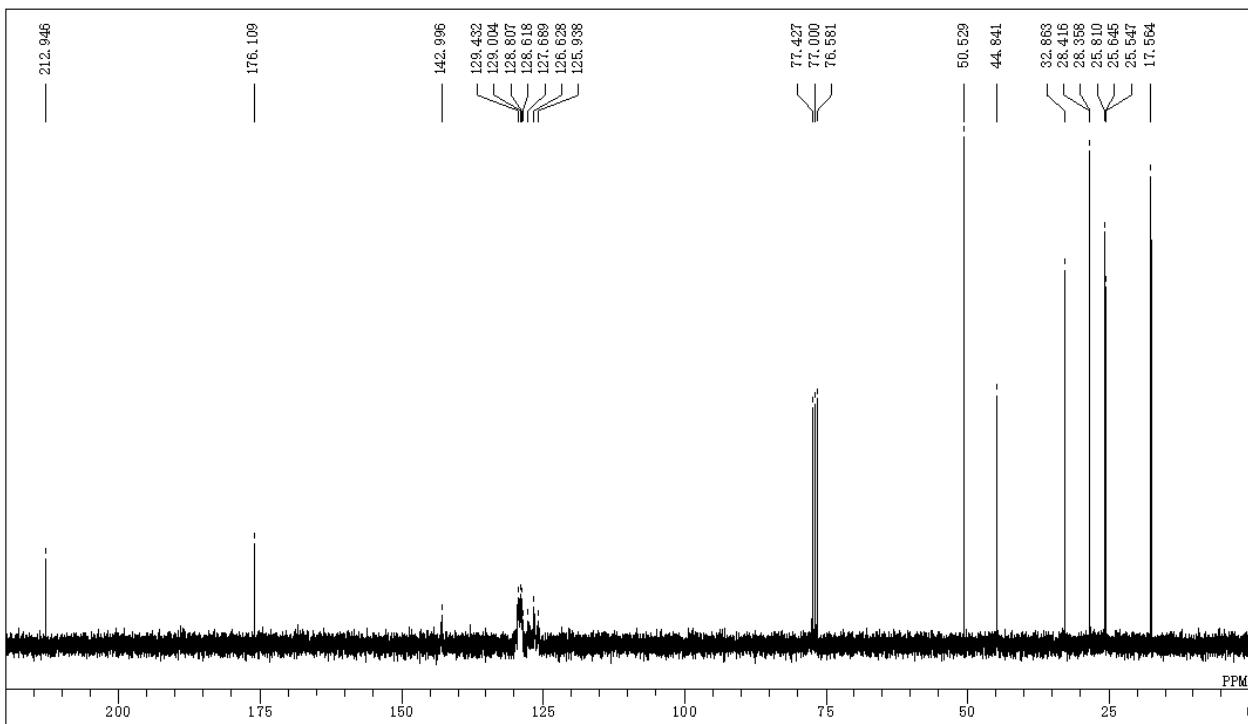
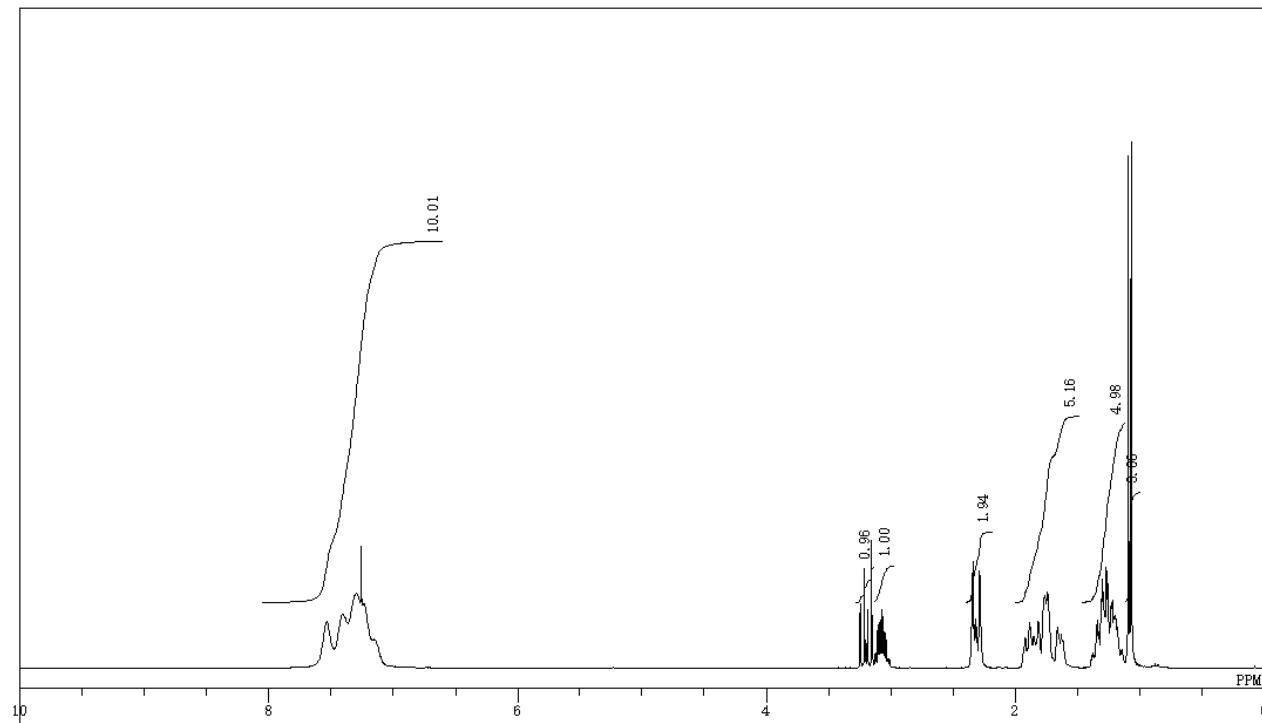
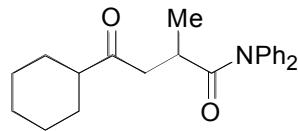
**6-Methyl-4-oxo-2-phenylheptanoic acid diphenylamide (3dd)**



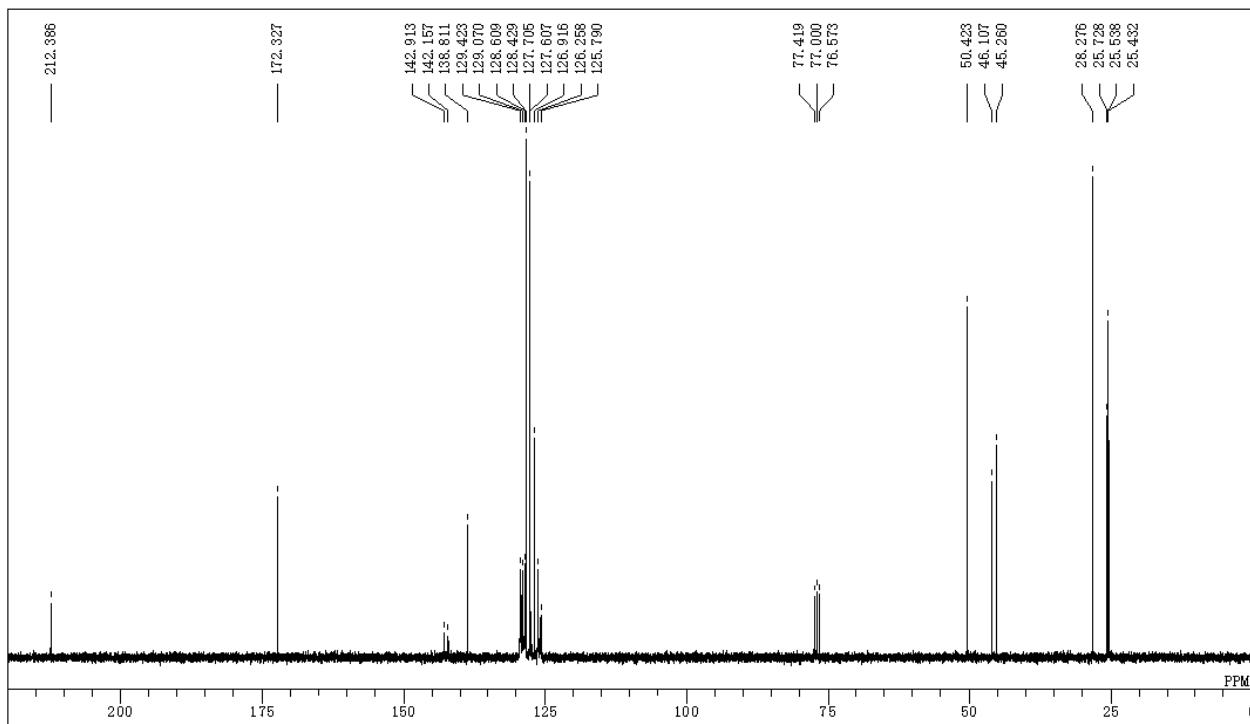
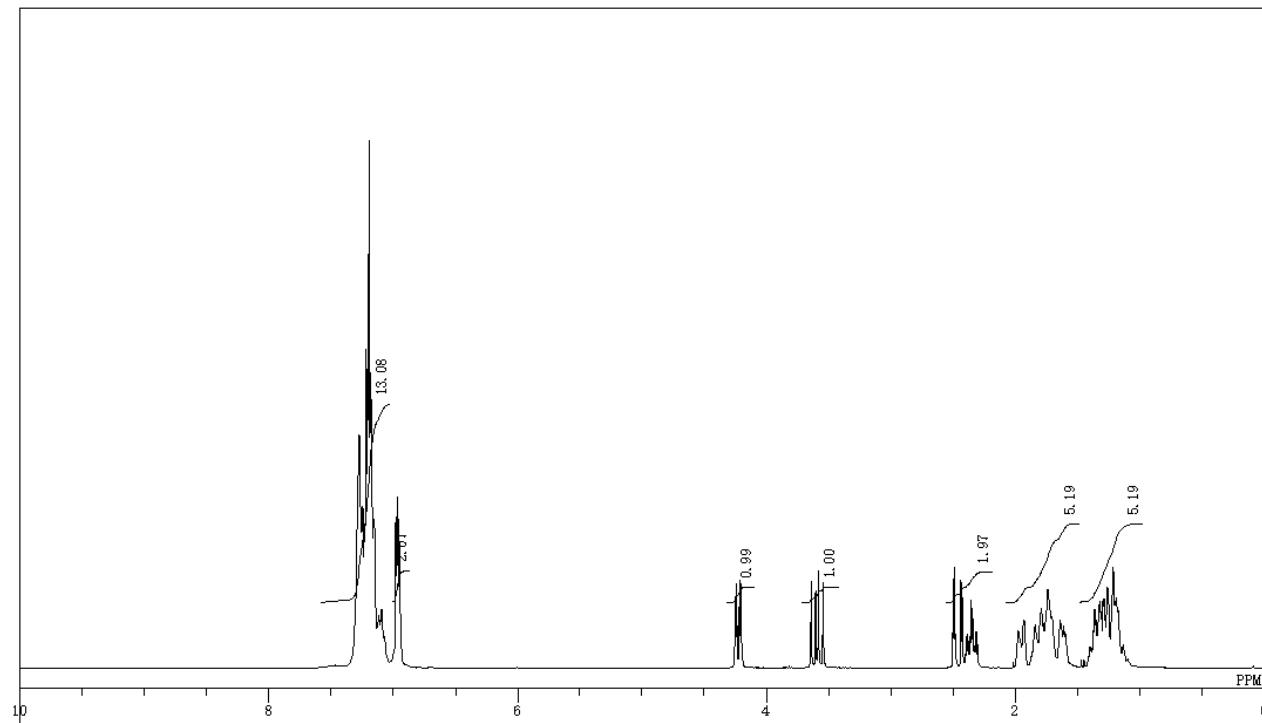
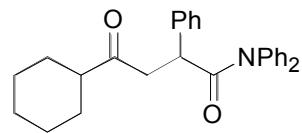
**4-Cyclopentyl-2-methyl-4-oxo-N,N-diphenylbutyramide (3ea)**



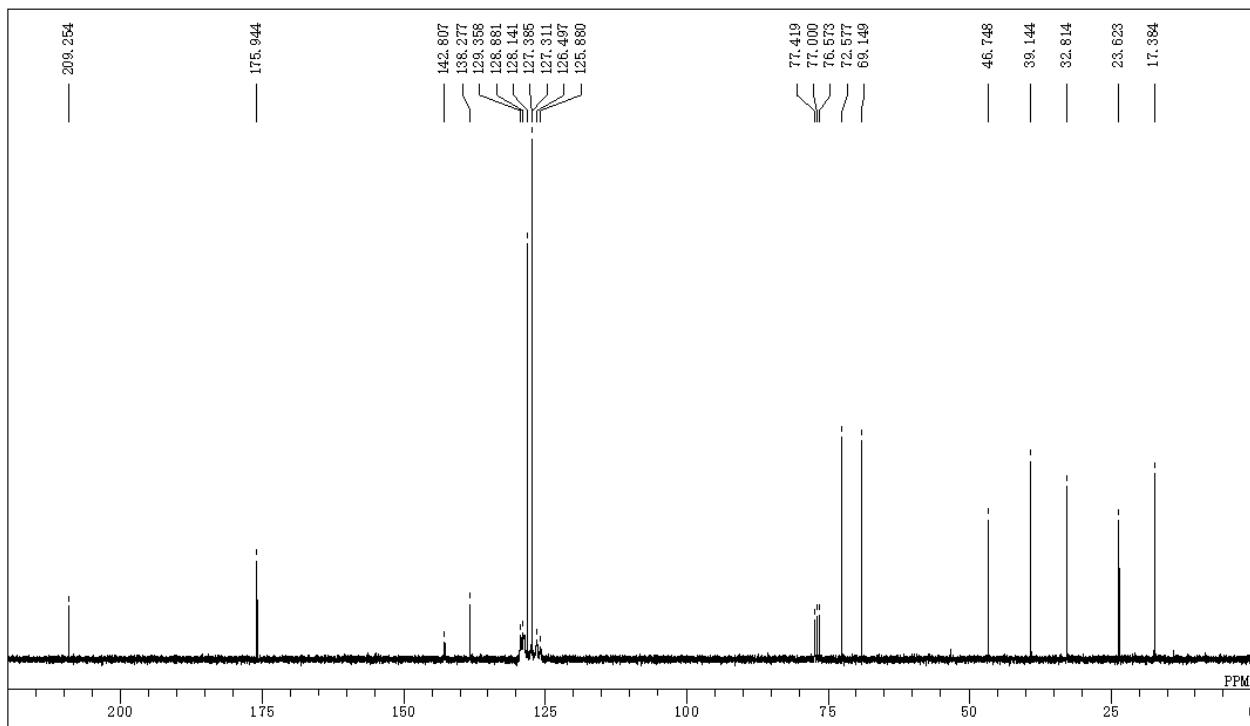
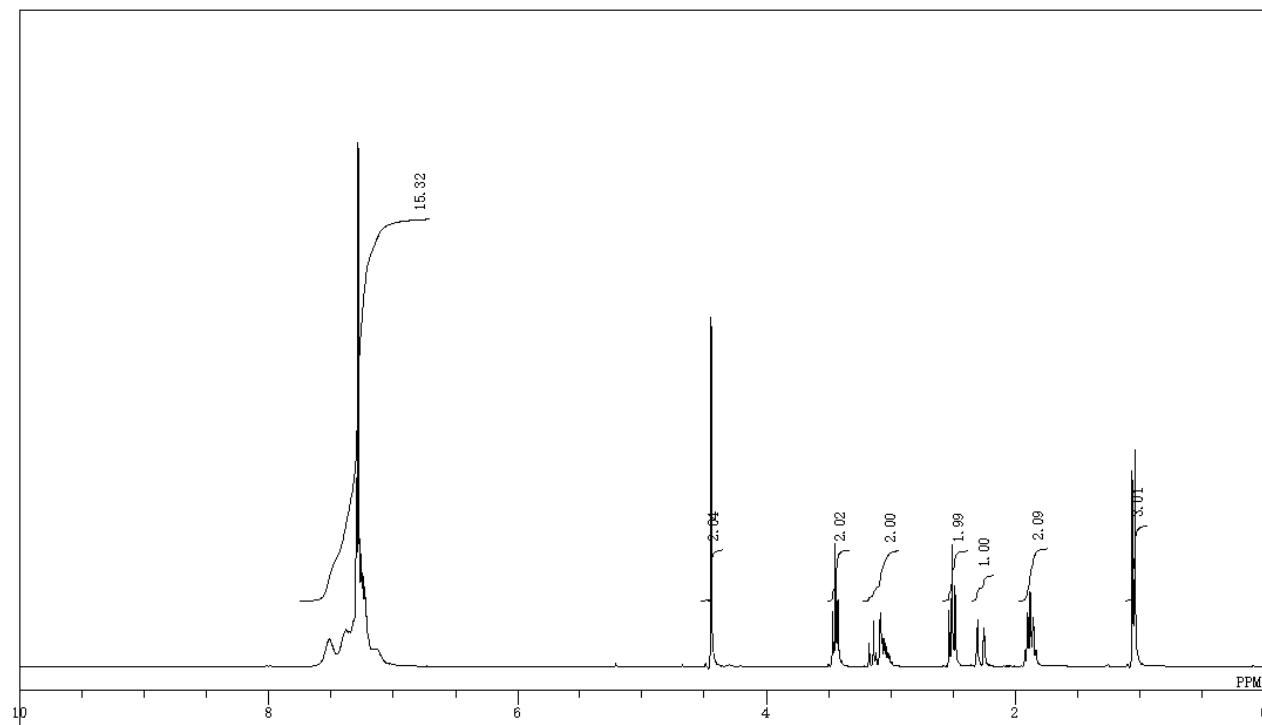
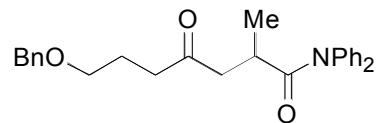
**4-Cyclohexyl-2-methyl-4-oxo-N,N-diphenylbutyramide (3fa)**



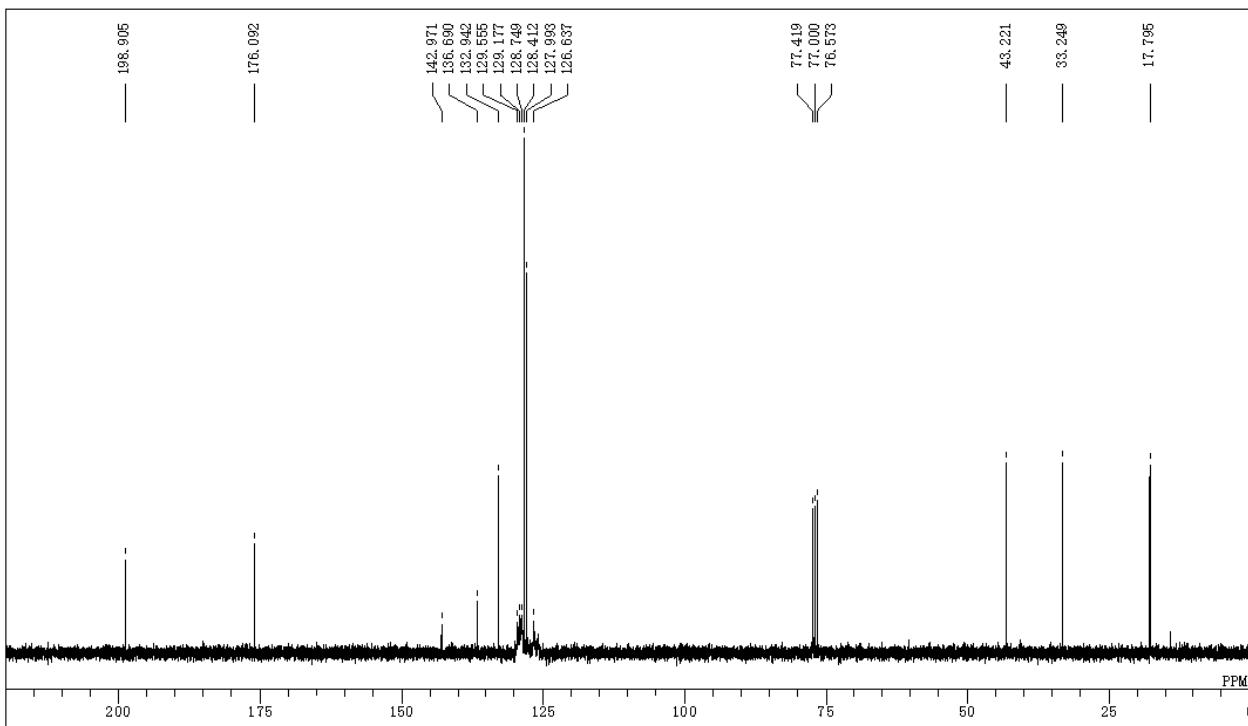
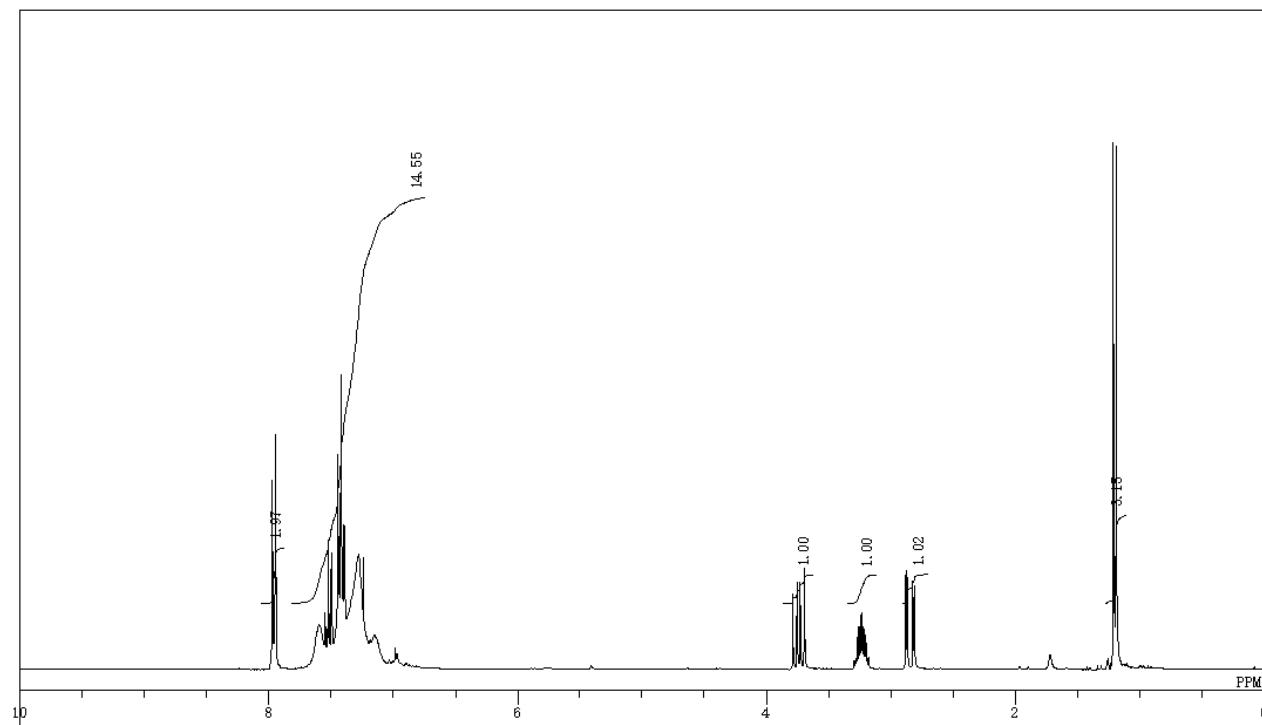
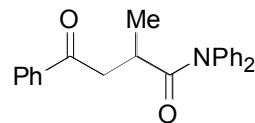
**4-Cyclohexyl-4-oxo-2,N,N-triphenylbutyramide (3fd)**



### **7-Benzyl-2-methyl-4-oxoheptanoic acid diphenylamide (3ha)**



**2-Methyl-4-oxo-4,N,N-triphenylbutyramide (3ia)**



**2-(3-Phenylpropionyl)cyclopentanecarboxylic acid diphenylamide (3ae)**

