

## Supporting Information

### ***n*Bu<sub>4</sub>NI-catalyzed oxidative cross-coupling of carbon dioxide, amines, and aryl ketones: access to *O*-β-oxoalkyl carbamates**

Youbin Peng,<sup>a†</sup> Juan Liu,<sup>b†</sup> Chaorong Qi,<sup>\*a</sup> Gaoqing Yuan,<sup>\*b</sup> Jiawei Li,<sup>b</sup> and Huanfeng Jiang<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, State Key Lab of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

<sup>b</sup> Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

\*Fax: (+86) 20-8711-2906; e-mail: crqi@scut.edu.cn or gqyuan@scut.edu.cn

## List of Contents

|                                                               |     |
|---------------------------------------------------------------|-----|
| A. General methods .....                                      | S1  |
| B. General procedure for the preparation of Carbamate 3 ..... | S1  |
| C. Optimization of the reaction conditions .....              | S2  |
| D. Analytical Data .....                                      | S2  |
| E. NMR Spectra .....                                          | S16 |
| F. Crystal structure determination .....                      | S49 |

## A. General methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DRX-400 spectrometer using  $\text{CDCl}_3$  as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. 2-Hydroxy-1-phenylpropan-1-one<sup>[1]</sup>, 2-iodo-1-phenylpropan-1-one<sup>[2]</sup> and 2-(2,2-diphenylcyclopropyl)-1-phenylethan-1-one (**4**)<sup>[3a]</sup> were prepared according to literature procedures. Other compounds were commercially purchased and used without further purification.

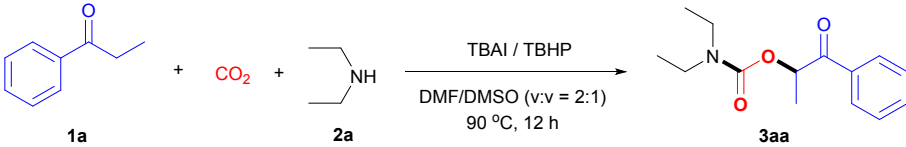
## B. General procedure for the preparation of Carbamate 3

To a dried 15 mL polytetrafluoroethylene (PTFE) reaction vessel, the mixture of TBAI ( $\text{Bu}_4\text{NI}$ , 0.2 mmol), ketone **1** (1 mmol), DMF (2 mL), DMSO (1 mL), TBHP (*t*-butylhydroperoxide, 70% in water, 6 mmol), and amine **2** (7 mmol) was added successively. The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. Then the autoclave was sealed and  $\text{CO}_2$  was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 12 h and the pressure was kept constant during the reaction. After the reaction was completed, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. Then reaction mixture was diluted with  $\text{H}_2\text{O}$  (20 mL) and extracted with EtOAc (15 mL  $\times$  3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then filtered. The volatile compounds were

removed in vacuo and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to give the desired product **3**.

### C. Optimization of the reaction conditions

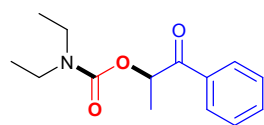
**Table S1.** The effect of the amount of oxidant and **2a** on the reaction<sup>a</sup>

|  |                 |                   |                        |
|------------------------------------------------------------------------------------|-----------------|-------------------|------------------------|
| Entry                                                                              | Oxidant (equiv) | <b>2a</b> (equiv) | yield (%) <sup>b</sup> |
| 1                                                                                  | TBHP (2)        | 7                 | 49                     |
| 2                                                                                  | TBHP (3)        | 7                 | 61                     |
| 3                                                                                  | TBHP (4)        | 7                 | 76                     |
| 4                                                                                  | TBHP (5)        | 7                 | 81                     |
| 5                                                                                  | TBHP (6)        | 7                 | 92                     |
| 6                                                                                  | TBHP (6)        | 6                 | 88                     |
| 7                                                                                  | TBHP (6)        | 5                 | 78                     |
| 8                                                                                  | TBHP (6)        | 4                 | 70                     |
| 9                                                                                  | TBHP (6)        | 3                 | 62                     |
| 10                                                                                 | TBHP (6)        | 2                 | 53                     |

<sup>a</sup> Reaction conditions: **1a** (1 mmol), *n*Bu<sub>4</sub>NI (0.2 mmol), DMF/DMSO (v:v = 2:1, 3 mL), CO<sub>2</sub> (3 MPa), 90 °C, 12 h. <sup>b</sup> Yields were determined by GC-MS analysis with n-dodecane as internal standard.

### D. Analytical Data

#### 1-Oxo-1-phenylpropan-2-yl diethylcarbamate (**3aa**)

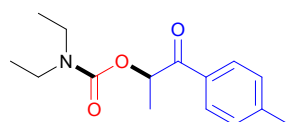


**3aa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 87% yield (216.3 mg, 0.87 mmol). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* = 8.0 Hz, 2 H), 7.53 – 7.49 (m, 1 H), 7.43 – 7.39 (m, 2

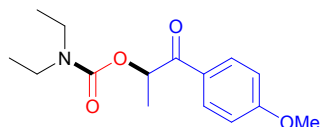
H), 5.92 (q,  $J = 6.8$  Hz, 1 H), 3.28 (br, 4 H), 1.47 (d,  $J = 6.8$  Hz, 3 H), 1.09 (br, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.99, 154.91, 134.75, 133.08, 128.49, 128.31, 71.46, 41.80, 41.32, 17.05, 13.79, 13.25$ . IR (KBr): 3065, 2978, 1697, 1594, 1442, 1277, 1170, 1090, 963, 777, 700  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^{+}$ : 272.1257; found: 272.1254.

### 1-Oxo-1-(*p*-tolyl)propan-2-yl diethylcarbamate (3ba)



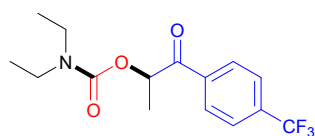
**3ba** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 64% yield (168.3 mg, 0.64 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.83$  (d,  $J = 7.6$  Hz, 2 H), 7.22 (d,  $J = 7.6$  Hz, 2 H), 5.91 (q,  $J = 6.8$  Hz, 1 H), 3.29 (br, 4 H), 2.36 (s, 3 H), 1.47 (d,  $J = 6.8$  Hz, 3 H), 1.10 (br, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.64, 155.08, 144.08, 132.26, 129.31, 128.60, 71.46, 41.94, 41.46, 21.64, 17.31, 13.90, 13.40$ . IR (KBr): 2968, 1694, 1610, 1438, 1273, 1170, 1090, 961, 765  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^{+}$ : 286.1414; found: 286.1420.

### 1-(4-Methoxyphenyl)-1-oxopropan-2-yl diethylcarbamate (3ca)



**3ca** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a brown oil in 54% yield (150.7 mg, 0.54 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.94$  (d,  $J = 8.4$  Hz, 2 H), 6.92 (d,  $J = 8.4$  Hz, 2 H), 5.92 (q,  $J = 6.8$  Hz, 1 H), 3.85 (s, 3 H), 3.31 (br, 4 H), 1.48 (d,  $J = 6.8$  Hz, 3 H), 1.12 (br, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 196.42, 163.63, 155.09, 130.78, 127.65, 113.83, 71.23, 55.42, 41.88, 41.41, 17.37, 13.92, 13.41$ . IR (KBr): 2971, 1692, 1597, 1437, 1256, 1168, 1092, 959, 841, 769  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{NNaO}_4$  [ $\text{M} + \text{Na}$ ] $^{+}$ : 302.1363; found: 302.1368.

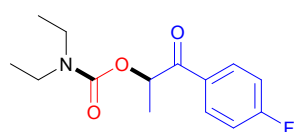
### 1-Oxo-1-(4-(trifluoromethyl)phenyl)propan-2-yl diethylcarbamate (3da)



**3da** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 88% yield (279.0 mg,

0.88 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.03 (d,  $J$  = 8.0 Hz, 2 H), 7.69 (d,  $J$  = 8.0 Hz, 2 H), 5.86 (q,  $J$  = 6.8 Hz, 1 H), 3.27 (br, 4 H), 1.48 (d,  $J$  = 6.8 Hz, 3 H), 1.11 – 1.06 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.49, 154.87, 137.79, 134.33 (q,  $J$  = 32.4 Hz), 128.71, 125.58 (q,  $J$  = 3.6 Hz), 123.47 (q,  $J$  = 270.9 Hz), 71.70, 41.94, 41.42, 16.75, 13.81, 13.23. IR (KBr): 3076, 2977, 1670, 1440, 1314, 1152, 965, 854, 772  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 340.1131; found: 340.1138.

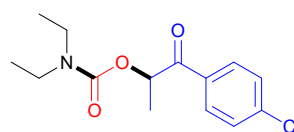
### 1-(4-Fluorophenyl)-1-oxopropan-2-yl diethylcarbamate (**3ea**)



**3ea** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as an orange oil in 78% yield (208.3 mg, 0.78 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.95 – 7.92 (m, 2 H), 7.07 (t,  $J$  = 8.4 Hz, 2 H), 5.84 (q,  $J$  = 6.8 Hz, 1 H), 3.25 (br, 4 H), 1.44 (d,  $J$  = 6.8 Hz, 3 H), 1.14 – 0.99 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.40, 165.59 (d,  $J$  = 253.4 Hz), 154.82, 131.09 (d,  $J$  = 3.0 Hz), 130.98 (d,  $J$  = 9.3 Hz), 115.60 (d,  $J$  = 21.8 Hz), 71.26, 41.79, 41.30, 16.91, 13.75, 13.20. IR (KBr): 3073, 2975, 1696, 1597, 1434, 1273, 1231, 1165, 1090, 961, 844, 767  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{FNNaO}_3$   $[\text{M} + \text{Na}]^+$ : 290.1163; found: 290.1168.

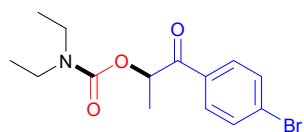
### 1-(4-Chlorophenyl)-1-oxopropan-2-yl diethylcarbamate (**3fa**)



**3fa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 83% yield (234.9 mg, 0.83 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.88 (d,  $J$  = 7.6 Hz, 2 H), 7.41 (d,  $J$  = 7.2 Hz, 2 H), 5.86 (q,  $J$  = 6.8 Hz, 1 H), 3.29 (br, 4 H), 1.47 (d,  $J$  = 6.8 Hz, 3 H), 1.17 – 1.03 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.98, 154.92, 139.61, 133.17, 129.84, 128.92, 71.42, 41.94, 41.42, 17.00, 13.88, 13.33. IR (KBr): 3078, 2978, 1698, 1587, 1435, 1277, 1170, 1090, 964, 840, 770  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_3$   $[\text{M} + \text{Na}]^+$ : 306.0867; found: 306.0867.

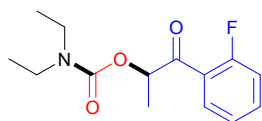
### 1-(4-Bromophenyl)-1-oxopropan-2-yl diethylcarbamate (**3ga**)



**3ga** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 71% yield (232.2 mg, 0.71 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.80 (d,  $J$  = 8.4 Hz, 2 H), 7.58 (d,  $J$  = 8.0 Hz, 2 H), 5.85 (q,  $J$  = 6.8 Hz, 1 H), 3.29 (br, 4 H), 1.47 (d,  $J$  = 7.2 Hz, 3 H), 1.18 – 1.03 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.19, 154.90, 133.58, 131.91, 129.93, 128.33, 71.41, 41.94, 41.44, 16.99, 13.92, 13.35. IR (KBr): 3081, 2978, 1698, 1583, 1433, 1276, 1171, 1085, 962, 837, 772  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{BrNNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 350.0362; found: 350.0369.

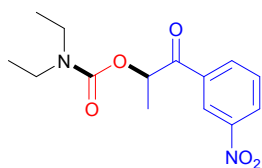
### 1-(2-Fluorophenyl)-1-oxopropan-2-yl diethylcarbamate (**3ha**)



**3ha** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 80% yield (213.6 mg, 0.80 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.86 (td,  $J$  = 7.6, 1.6 Hz, 1 H), 7.54 – 7.46 (m, 1 H), 7.22 (td,  $J$  = 8.0, 0.8 Hz, 1 H), 7.11 (ddd,  $J$  = 8.8, 8.0, 0.4 Hz, 1 H), 5.74 (dq,  $J$  = 7.2, 1.6 Hz, 1 H), 3.28 (br, 4 H), 1.49 (dd,  $J$  = 6.8, 1.2 Hz, 3 H), 1.17 – 1.03 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.79 (d,  $J$  = 4.4 Hz), 161.2 (d,  $J$  = 252.6 Hz), 155.04, 134.58 (d,  $J$  = 8.9 Hz), 131.04 (d,  $J$  = 3.0 Hz), 124.53 (d,  $J$  = 3.3 Hz), 123.74 (d,  $J$  = 14.0 Hz), 116.40 (d,  $J$  = 23.5 Hz), 74.70 (d,  $J$  = 7.7 Hz), 41.86, 41.40, 16.24 (d,  $J$  = 2.0 Hz), 13.83, 13.31. IR (KBr): 3083, 2929, 1692, 1614, 1278, 1460, 1089, 962, 765  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{FNNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 290.1163; found: 290.1169.

### 1-(3-Nitrophenyl)-1-oxopropan-2-yl diethylcarbamate (**3ia**)

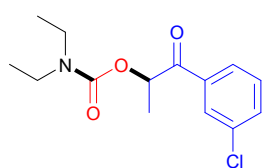


**3ia** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a yellow oil in 86% yield (266.6 mg, 0.86 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.75 (s, 1 H), 8.38 (d,  $J$  = 8.0 Hz, 1 H), 8.25 (d,  $J$  = 7.6 Hz, 1 H), 7.65 (t,  $J$  = 8.0 Hz, 1 H), 5.81 (q,  $J$  = 6.8 Hz, 1 H), 3.30 – 3.23 (m, 4 H), 1.52 (d,  $J$  = 6.8 Hz, 3

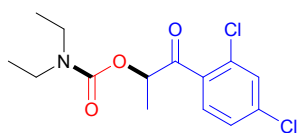
H), 1.12 (t,  $J = 6.4$  Hz, 3 H), 1.04 (t,  $J = 6.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 196.33, 154.77, 148.27, 136.10, 133.99, 129.88, 127.30, 123.19, 71.90, 41.95, 41.43, 16.81, 13.84, 13.21$ . IR (KBr): 3091, 2977, 1699, 1535, 1446, 1357, 1446, 1357, 1277, 1169, 1088, 981, 777, 711  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{NaO}_5$  [ $\text{M} + \text{Na}$ ] $^+$ : 317.1108; found: 317.1113.

### 1-(3-Chlorophenyl)-1-oxopropan-2-yl diethylcarbamate (3ja)



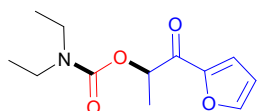
**3ja** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 70% yield (198.1 mg, 0.70 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.87$  (s, 1 H), 7.77 (d,  $J = 8.0$  Hz, 1 H), 7.47 (d,  $J = 8.0$  Hz, 1 H), 7.37 – 7.33 (m, 1 H), 5.79 (q,  $J = 6.8$  Hz, 1 H), 3.27 – 3.23 (m, 4 H), 1.45 (d,  $J = 6.8$  Hz, 3 H), 1.10 – 1.05 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 196.93, 154.76, 136.31, 134.76, 132.94, 129.84, 128.34, 126.36, 71.59, 41.84, 41.33, 16.86, 13.78, 13.20$ . IR (KBr): 3075, 2975, 1698, 1572, 1447, 1278, 1166, 1089, 976, 784  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 306.0867; found: 306.0873.

### 1-(2,4-Dichlorophenyl)-1-oxopropan-2-yl diethylcarbamate (3ka)



**3ka** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 82% yield (259.9 mg, 0.82 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.62$  (d,  $J = 8.0$  Hz, 1 H), 7.44 (s, 1 H), 7.31 (d,  $J = 8.4$  Hz, 1 H), 5.66 (q,  $J = 6.8$  Hz, 1 H), 3.26 (q,  $J = 6.8$  Hz, 4 H), 1.48 (d,  $J = 6.8$  Hz, 3 H), 1.09 (t,  $J = 6.8$  Hz, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 199.94, 154.79, 137.19, 135.57, 132.18, 130.24, 130.08, 126.99, 74.10, 41.91, 41.37, 15.99, 13.76, 13.24$ . IR (KBr): 3085, 2976, 1704, 1580, 1447, 1275, 1168, 1093, 960, 817  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{Cl}_2\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 340.0478; found: 340.0485.

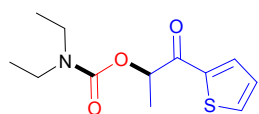
### 1-(Furan-2-yl)-1-oxopropan-2-yl diethylcarbamate (3la)



**3la** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a white

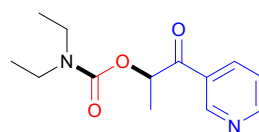
solid in 64% yield (153.0 mg, 0.64 mmol); mp: 99-101 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.55 (s, 1 H), 7.22 (d, *J* = 3.2 Hz, 1 H), 6.52 – 6.43 (m, 1 H), 5.65 (q, *J* = 6.8 Hz, 1 H), 3.30 – 3.22 (m, 4 H), 1.46 (d, *J* = 6.8 Hz, 3 H), 1.12 (br, 3 H), 1.05 (br, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 186.50, 154.80, 150.47, 146.55, 118.10, 112.12, 71.56, 41.76, 41.32, 16.90, 13.75, 13.21. IR (KBr): 3121, 2973, 1685, 1567, 1454, 1274, 1181, 1045, 974, 894, 788 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>12</sub>H<sub>17</sub>NNaO<sub>4</sub> [M + Na]<sup>+</sup>: 262.1050; found: 262.1054.

### 1-Oxo-1-(thiophen-2-yl)propan-2-yl diethylcarbamate (3ma)



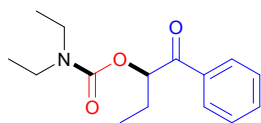
**3ma** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 68% yield (173.4 mg, 0.68 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.79 (d, *J* = 3.2 Hz, 1 H), 7.63 (d, *J* = 4.8 Hz, 1 H), 7.11 (t, *J* = 4.2 Hz, 1 H), 5.70 (q, *J* = 6.8 Hz, 1 H), 3.34 – 3.25 (m, 4 H), 1.52 (d, *J* = 6.8 Hz, 3 H), 1.15 (br, 3 H), 1.08 (br, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 190.71, 154.85, 140.76, 133.92, 132.39, 128.04, 72.43, 41.87, 41.38, 17.63, 13.88, 13.29. IR (KBr): 3094, 2976, 1690, 1431, 1269, 1169, 1081, 925, 850, 734 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>12</sub>H<sub>17</sub>NNaO<sub>3</sub>S [M + Na]<sup>+</sup>: 278.0821; found: 278.0824.

### 1-Oxo-1-(pyridin-3-yl)propan-2-yl diethylcarbamate (3na)



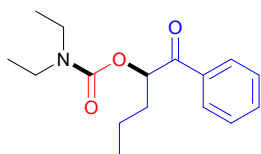
**3na** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 75% yield (187.5 mg, 0.75 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.08 (s, 1 H), 8.69 (d, *J* = 4.8 Hz, 1 H), 8.16 (d, *J* = 8.0 Hz, 1 H), 7.35 (t, *J* = 6.4 Hz, 1 H), 5.75 (q, *J* = 6.8 Hz, 1 H), 3.25 – 3.20 (m, 4 H), 1.46 (d, *J* = 7.2 Hz, 3 H), 1.07 (br, 3 H), 1.01 (br, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 197.23, 154.75, 153.41, 149.56, 135.74, 130.30, 123.53, 71.84, 41.90, 41.37, 16.73, 13.83, 13.21. IR (KBr): 2978, 1699, 1582, 1433, 1273, 1171, 1092, 963, 777, 711 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>3</sub> [M + Na]<sup>+</sup>: 273.1210; found: 273.1215.

### 1-Oxo-1-phenylbutan-2-yl diethylcarbamate (3oa)



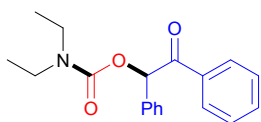
**3oa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 77% yield (202.5 mg, 0.77 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.94 (d,  $J$  = 7.6 Hz, 2 H), 7.55 – 7.51 (m 1 H), 7.43 (t,  $J$  = 7.6 Hz, 2 H), 5.78 (dd,  $J$  = 8.0, 4.4 Hz, 1 H), 3.34 – 3.25 (m, 4 H), 1.96 – 1.75 (m, 2 H), 1.18 (br, 3 H), 1.09 (br, 3 H), 1.01 (t,  $J$  = 7.6 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.76, 155.24, 135.25, 133.08, 128.55, 128.28, 76.40, 41.93, 41.48, 24.80, 13.95, 13.34, 9.84. IR (KBr): 3064, 2975, 2894, 1698, 1593, 1436, 1273, 1171, 1086, 982, 773, 698  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{22}\text{NO}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 264.1594; found: 264.1598.

### 1-Oxo-1-phenylpentan-2-yl diethylcarbamate (3pa)



**3pa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 70% yield (193.9 mg, 0.70 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.94 (d,  $J$  = 8.0 Hz, 2 H), 7.54 (t,  $J$  = 7.2 Hz, 1 H), 7.44 (t,  $J$  = 7.6 Hz, 2 H), 5.84 (t,  $J$  = 6.3 Hz, 1 H), 3.32 – 3.27 (m, 4 H), 1.80 (q,  $J$  = 7.2 Hz, 2 H), 1.52 – 1.43 (m, 2 H), 1.18 (br, 3 H), 1.09 (br, 3 H), 0.94 (t,  $J$  = 7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.96, 155.27, 135.20, 133.10, 128.57, 128.32, 75.21, 41.94, 41.48, 33.50, 18.85, 13.98, 13.72, 13.38. IR (KBr): 3064, 2963, 1698, 1593, 1438, 1273, 1171, 1088, 969, 775, 698  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{23}\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 300.1570; found: 300.1577.

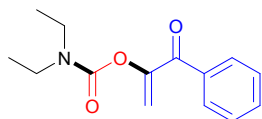
### 2-Oxo-1,2-diphenylethyl diethylcarbamate (3qa)



**3qa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as an orange oil in 42% yield (130.6 mg, 0.42 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.96 (d,  $J$  = 8.0 Hz, 2 H), 7.51 – 7.47 (m, 3 H), 7.41 – 7.31 (m, 5 H), 6.86 (s, 1 H), 3.38 – 3.28 (m, 4 H), 1.22 (br, 3 H), 1.13 (br, 3 H),  $^{13}\text{C}$  NMR (100

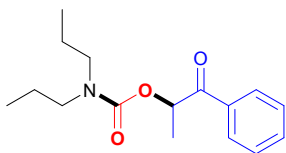
MHz, CDCl<sub>3</sub>):  $\delta$  = 195.26, 155.03, 135.06, 134.36, 133.16, 128.87, 128.75, 128.51, 128.34, 77.61, 42.04, 41.61, 13.92, 13.36. IR (KBr): 3061, 2973, 1696, 1596, 1439, 1266, 1169, 1081, 979, 766, 697 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>21</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup>: 334.1414; found: 334.1423.

### 3-Oxo-3-phenylprop-1-en-2-yl diethylcarbamate (**3ra**) <sup>[4]</sup>



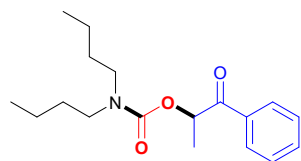
**3ra** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a pale yellow oil in 52% yield (128.4 mg, 0.52 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91 – 7.86 (m, 2 H), 7.56 – 7.50 (m, 1 H), 7.45 – 7.39 (m, 2 H), 5.60 (d, *J* = 2.0 Hz, 1 H), 5.41 (d, *J* = 2.0 Hz, 1 H), 3.40 (q, *J* = 7.2 Hz, 2 H), 3.27 (q, *J* = 7.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.09 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.55, 153.44, 151.50, 136.41, 132.65, 129.60, 128.16, 111.89, 42.12, 42.04, 13.91, 13.10. IR (KBr): 3452, 3066, 2928, 1699, 1443, 1265, 1152, 1071, 970, 903, 703 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>17</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup>: 270.1101; found: 270.1105.

### 1-Oxo-1-phenylpropan-2-yl dipropylcarbamate (**3ab**)



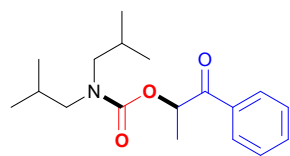
**3ab** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 82% yield (227.1 mg, 0.82 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, *J* = 7.6 Hz, 2 H), 7.55 – 7.52 (m, 1 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 5.92 (q, *J* = 6.8 Hz, 1 H), 3.28 – 3.12 (m, 4 H), 1.67 – 1.50 (m, 4 H), 1.48 (d, *J* = 6.8 Hz, 3 H), 0.85 (dd, *J* = 17.2, 7.6 Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.09, 155.46, 134.85, 133.14, 128.56, 128.41, 71.58, 49.25, 48.76, 21.71, 21.15, 17.07, 11.19, 11.06. IR (KBr): 3066, 2960, 1698, 1594, 1451, 1239, 1165, 1097, 970, 909, 772, 699 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>23</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup>: 300.1570; found: 300.1577.

### 1-Oxo-1-phenylpropan-2-yl dibutylcarbamate (3ac)



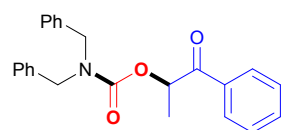
**3ac** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 85% yield (259.2 mg, 0.85 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92 (d,  $J$  = 7.6 Hz, 2 H), 7.53 – 7.50 (m, 1 H), 7.41 (t,  $J$  = 7.6 Hz, 2 H), 5.90 (q,  $J$  = 6.8 Hz, 1 H), 3.24 – 3.12 (m, 4 H), 1.55 – 1.38 (m, 7 H), 1.29 – 1.20 (m, 4 H), 0.87 (t,  $J$  = 7.2 Hz, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.96, 155.28, 134.79, 133.06, 128.48, 128.34, 71.52, 47.22, 46.62, 30.51, 30.02, 19.83, 16.97, 13.69. IR (KBr): 3066, 2947, 2875, 1699, 1594, 1451, 1230, 1058, 1099, 967, 772, 700  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{27}\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 328.1883; found: 328.1891.

### 1-Oxo-1-phenylpropan-2-yl diisobutylcarbamate (3ad)



**3ad** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 60% yield (183.0 mg, 0.60 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d,  $J$  = 7.6 Hz, 2 H), 7.56 – 7.48 (m, 1 H), 7.43 (t,  $J$  = 7.6 Hz, 2 H), 5.91 (q,  $J$  = 6.8 Hz, 1 H), 3.17 – 3.00 (m, 4 H), 2.03 – 1.86 (m, 2 H), 1.48 (d,  $J$  = 7.2 Hz, 3 H), 0.90 – 0.81 (m, 12 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.99, 155.86, 134.89, 133.10, 128.55, 128.41, 71.66, 55.13, 54.71, 27.36, 26.78, 20.10, 20.06, 19.94, 19.83, 16.99. IR (KBr): 3067, 2955, 1699, 1594, 1452, 1246, 1167, 1102, 961, 775, 699  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{27}\text{NNaO}_3$  [ $\text{M} + \text{Na}$ ] $^+$ : 328.1883; found: 328.1892.

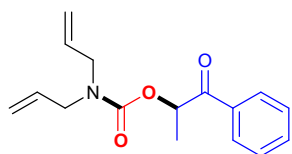
### 1-Oxo-1-phenylpropan-2-yl dibenzylcarbamate (3ae)



**3ae** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 63% yield (235.0 mg, 0.63 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.98 (d,  $J$  = 7.6 Hz, 2 H), 7.56 (t,  $J$  = 7.2 Hz, 1 H), 7.45 (t,  $J$  = 7.2 Hz, 2 H), 7.31 (d,  $J$  = 6.8 Hz, 3 H), 7.28 (br, 5 H), 7.19 (d,  $J$  = 6.8 Hz,

2 H), 6.04 (q,  $J = 6.8$  Hz, 1 H), 4.51 – 4.45 (m, 2 H), 4.42 – 4.31 (m, 2 H), 1.54 (d,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.70, 155.86, 136.99, 136.94, 134.67, 133.24, 128.63, 128.50, 128.42, 127.87, 127.77, 127.34, 72.52, 49.19, 49.04, 17.11$ . IR (KBr): 3047, 2931, 1697, 1595, 1443, 1232, 1119, 968, 902, 752, 700  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 396.1570; found: 396.1579.

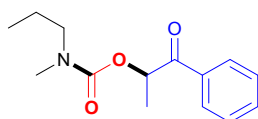
### 1-Oxo-1-phenylpropan-2-yl diallylcarbamate (**3af**)



**3af** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a tawny oil in 38% yield (103.7 mg, 0.38 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.94$  (d,  $J = 7.6$  Hz, 2 H), 7.63 – 7.53 (m, 1 H), 7.45 (t,  $J = 7.5$  Hz, 2 H), 5.95 (q,  $J = 6.8$  Hz, 1 H), 5.77 (s, 2 H), 5.15 (s, 2 H), 5.12 (d,  $J = 4.4$  Hz, 2 H), 3.99 – 3.79 (m, 4 H), 1.51 (d,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 197.79, 155.28, 134.71, 133.33, 133.28, 133.14, 128.63, 128.46, 117.04, 116.89, 72.10, 49.03, 48.74, 17.15$ . IR (KBr): 3077, 2928, 1699, 1595, 1453, 1239, 1143, 1104, 925, 774, 698  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{19}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 296.1257; found: 296.1263.

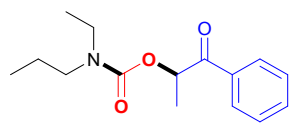
### 1-Oxo-1-phenylpropan-2-yl methyl(propyl)carbamate (**3ag**)



**3ag** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 49% yield (122.0 mg, 0.49 mmol).

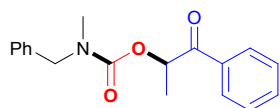
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.92$  (d,  $J = 8.0$  Hz, 2 H), 7.56 – 7.48 (m, 1 H), 7.42 (t,  $J = 7.5$  Hz, 2 H), 5.97 – 5.82 (m, 1 H), 3.37 – 3.11 (m, 2 H), 2.89 (d,  $J = 24.8$  Hz, 3 H), 1.58 – 1.44 (m, 5 H), 0.91 – 0.76 (m, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.03, 197.89, 155.50, 134.69, 133.14, 128.52, 128.35, 71.72, 71.61, 50.58, 50.38, 34.47, 33.83, 20.92, 20.44, 17.07, 10.96, 10.84$ . IR (KBr): 3065, 2955, 2879, 1699, 1594, 1461, 1404, 1235, 1173, 1097, 968, 906, 773, 700  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 272.1257; found: 272.1262.

### 1-Oxo-1-phenylpropan-2-yl ethyl(propyl)carbamate (**3ah**)



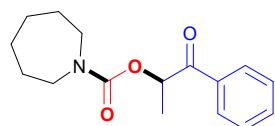
**3ah** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 59% yield (155.2 mg, 0.59 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (d,  $J$  = 7.6 Hz, 2 H), 7.59 – 7.50 (t,  $J$  = 7.3 Hz, 1 H), 7.44 (t,  $J$  = 7.5 Hz, 2 H), 5.93 (q,  $J$  = 6.8 Hz, 1 H), 3.36 – 3.10 (m, 4 H), 1.62 – 1.46 (m, 5 H), 1.18 – 1.05 (m, 3 H), 0.86 (d,  $J$  = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 198.13, 155.32, 134.87, 133.17, 128.59, 128.43, 71.58, 48.87, 48.36, 42.31, 41.87, 21.82, 21.34, 17.13, 13.75, 13.18, 11.18, 11.10. IR (KBr): 3066, 2955, 1697, 1596, 1445, 1378, 1249, 1166, 1092, 962, 776, 699 cm<sup>-1</sup>. HRMS-ESI ( $m/z$ ): calcd for C<sub>15</sub>H<sub>21</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup>: 286.1414; found: 286.1420.

### 1-Oxo-1-phenylpropan-2-yl benzyl(methyl)carbamate (**3ai**)



**3ai** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 61% yield (181.2 mg, 0.61 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (d,  $J$  = 7.6 Hz, 2 H), 7.56 (t,  $J$  = 7.2 Hz, 1 H), 7.45 (t,  $J$  = 7.6 Hz, 2 H), 7.35 – 7.16 (m, 5 H), 6.05 – 5.91 (m, 1 H), 4.61 – 4.42 (m, 2 H), 2.87 (d,  $J$  = 24.0 Hz, 3 H), 1.58 – 1.47 (m, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.88, 197.70, 155.93, 155.40, 137.01, 134.61, 133.20, 128.56, 128.45, 128.36, 127.50, 127.47, 127.27, 127.23, 72.27, 72.03, 52.39, 52.33, 34.02, 33.53, 17.12, 17.07. IR (KBr): 3054, 2934, 1697, 1597, 1467, 1225, 1139, 967, 900, 757, 700 cm<sup>-1</sup>. HRMS-ESI ( $m/z$ ): calcd for C<sub>18</sub>H<sub>19</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup>: 320.1257; found: 320.1263.

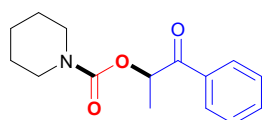
### 1-Oxo-1-phenylpropan-2-yl azepane-1-carboxylate (**3aj**)



**3aj** was obtained after purification by column chromatography on silica gel (petroleum ether / hexane / ethyl acetate = 15:5:1) as a tawny oil in 74% yield (203.5 mg, 0.74 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (d,  $J$  = 7.6 Hz, 2 H), 7.54 (t,  $J$  = 7.3 Hz, 1 H), 7.44 (t,  $J$  = 7.6 Hz, 2 H), 5.94 (q,  $J$  = 6.8 Hz, 1 H), 3.54 – 3.30 (m, 4 H), 1.66 (br, 4 H), 1.53 (br, 4

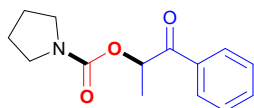
H), 1.49 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.16, 155.36, 134.87, 133.15, 128.57, 128.43, 71.60, 47.05, 46.75, 28.28, 28.12, 27.25, 26.77, 17.11$ . IR (KBr): 3064, 2929, 2867, 1696, 1593, 1369, 1340, 1270, 1204, 1104, 966, 774,  $700\text{ cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{21}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 298.1414; found: 298.1422.

### 1-Oxo-1-phenylpropan-2-yl piperidine-1-carboxylate (3ak)



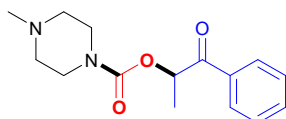
**3ak** was obtained after purification by column chromatography on silica gel (petroleum ether / hexane / ethyl acetate = 15:5:1) as a pale yellow oil in 53% yield (138.3 mg, 0.53 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.94$  (d,  $J = 8.0$  Hz, 2 H), 7.59 – 7.51 (m, 1 H), 7.44 (t,  $J = 7.6$  Hz, 2 H), 5.91 (q,  $J = 6.8$  Hz, 1 H), 3.42 (br, 4 H), 1.60 – 1.46 (m, 9 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.07, 154.54, 134.74, 133.21, 128.58, 128.43, 71.74, 44.96, 25.55, 24.26, 17.15$ . IR (KBr): 3066, 2934, 2859, 1697, 1594, 1440, 1369, 1239, 1149, 1096, 1028, 968, 772,  $701\text{ cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{19}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 284.1257; found: 284.1260.

### 1-Oxo-1-phenylpropan-2-yl pyrrolidine-1-carboxylate (3al)



**3al** was obtained after purification by column chromatography on silica gel (petroleum ether / hexane / ethyl acetate = 15:5:1) as an orange oil in 61% yield (150.7 mg, 0.61 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.95$  (d,  $J = 8.0$  Hz, 2 H), 7.58 – 7.50 (m, 1 H), 7.44 (t,  $J = 7.6$  Hz, 2 H), 5.92 (q,  $J = 6.8$  Hz, 1 H), 3.51 – 3.30 (m, 4 H), 1.84 (br, 4 H), 1.49 (d,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 198.13, 154.10, 134.75, 133.20, 128.56, 128.45, 71.45, 46.13, 45.81, 25.63, 24.84, 17.26$ . IR (KBr): 3068, 2959, 2883, 1698, 1596, 1425, 1222, 1114, 968, 876, 775,  $699\text{ cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{NNaO}_3$   $[\text{M} + \text{Na}]^+$ : 270.1101; found: 270.1102.

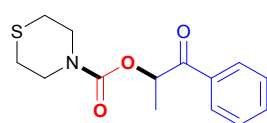
### 1-Oxo-1-phenylpropan-2-yl 4-methylpiperazine-1-carboxylate (3am)



**3am** was obtained after purification by column chromatography on silica gel (petroleum ether /

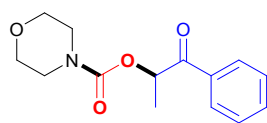
dichloromethane = 1:4) as a brown oil in 48% yield (132.5 mg, 0.48 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d,  $J$  = 8.0 Hz, 2 H), 7.55 (t,  $J$  = 7.2 Hz, 1 H), 7.45 (t,  $J$  = 7.5 Hz, 2 H), 5.92 (q,  $J$  = 6.8 Hz, 1 H), 3.69 – 3.37 (m, 4 H), 2.36 (br, 4 H), 2.28 (s, 3 H), 1.50 (d,  $J$  = 6.8 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.78, 154.45, 134.65, 133.31, 128.64, 128.42, 71.95, 54.61, 46.09, 43.93, 17.18. IR (KBr): 2934, 2865, 2793, 1699, 1595, 1443, 1238, 1145, 997, 773, 700  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 277.1547; found: 277.1553.

### 1-Oxo-1-phenylpropan-2-yl thiomorpholine-4-carboxylate (**3an**)



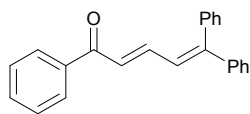
**3an** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a white solid in 54% yield (150.7 mg, 0.54 mmol); mp: 107-109  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.94 (d,  $J$  = 7.6 Hz, 2 H), 7.57 (t,  $J$  = 7.2 Hz, 1 H), 7.47 (t,  $J$  = 7.5 Hz, 2 H), 5.95 (q,  $J$  = 6.8 Hz, 1 H), 4.01 – 3.54 (m, 4 H), 2.58 (br, 4 H), 1.51 (d,  $J$  = 7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.65, 154.34, 134.57, 133.42, 128.70, 128.40, 72.14, 46.45, 27.20, 17.18. IR (KBr): 3064, 2920, 1698, 1595, 1441, 1296, 1220, 1111, 961, 775, 699  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{NNaO}_3\text{S}$  [ $\text{M} + \text{Na}$ ] $^+$ : 302.0821; found: 302.0828.

### 1-Oxo-1-phenylpropan-2-yl morpholine-4-carboxylate (**3ao**)



**3ao** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a yellow oil in 70% yield (184.1 mg, 0.70 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d,  $J$  = 8.0 Hz, 2 H), 7.61 – 7.51 (m, 1 H), 7.45 (t,  $J$  = 7.6 Hz, 2 H), 5.93 (q,  $J$  = 6.8 Hz, 1 H), 3.72 – 3.37 (m, 8 H), 1.50 (d,  $J$  = 6.8 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.57, 154.47, 134.48, 133.36, 128.63, 128.35, 72.04, 66.45, 44.38, 43.93, 17.15. IR (KBr): 3066, 2968, 2865, 1695, 1595, 1440, 1233, 1109, 980, 864, 773, 695  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{NNaO}_4$  [ $\text{M} + \text{Na}$ ] $^+$ : 286.1050; found: 286.1057.

**(E)-1,5,5-Triphenylpenta-2,4-dien-1-one (5)**<sup>[3]</sup>



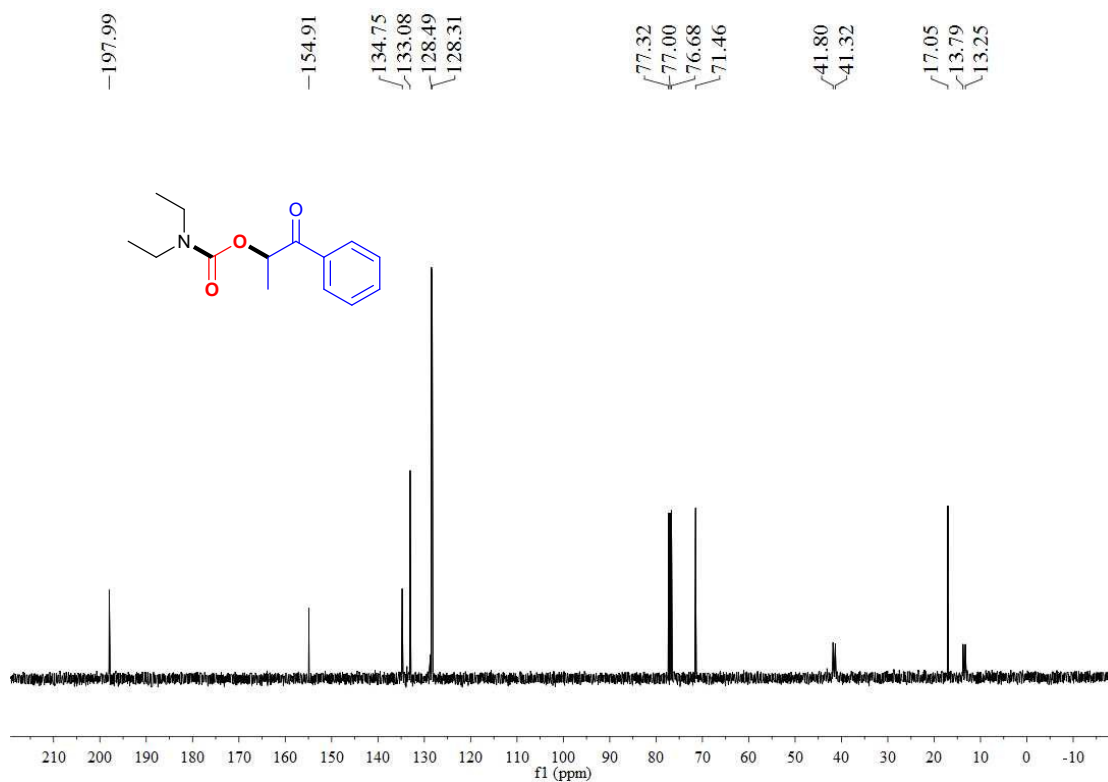
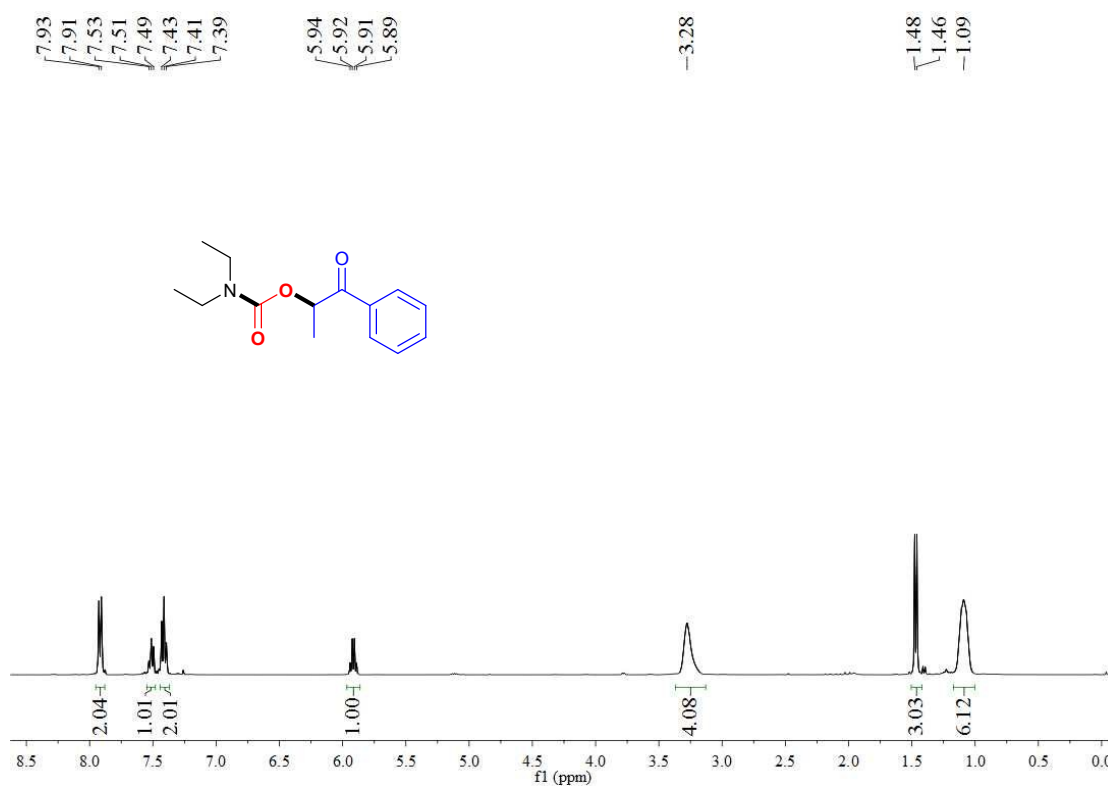
Compound **5** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.95 (d,  $J$  = 7.6 Hz, 2 H), 7.58 – 7.52 (m, 2 H), 7.49 – 7.33 (m, 11 H), 7.24 (s, 1 H), 7.16 (d,  $J$  = 14.8 Hz, 1 H), 6.96 (d,  $J$  = 11.6 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.44, 152.47, 142.58, 141.46, 138.59, 138.29, 132.55, 130.48, 128.81, 128.51, 128.43, 128.37, 128.37, 128.34, 128.22, 126.47, 126.16. IR (KBr): 2923, 2863, 1723, 1623, 1573, 1443, 1364, 1274, 1014, 913, 748, 693 cm<sup>-1</sup>. MS (EI)  $m/z$ : 310 [M<sup>+</sup>], 291, 233, 215, 205, 190, 178, 165, 152, 127, 105, 77.

## References

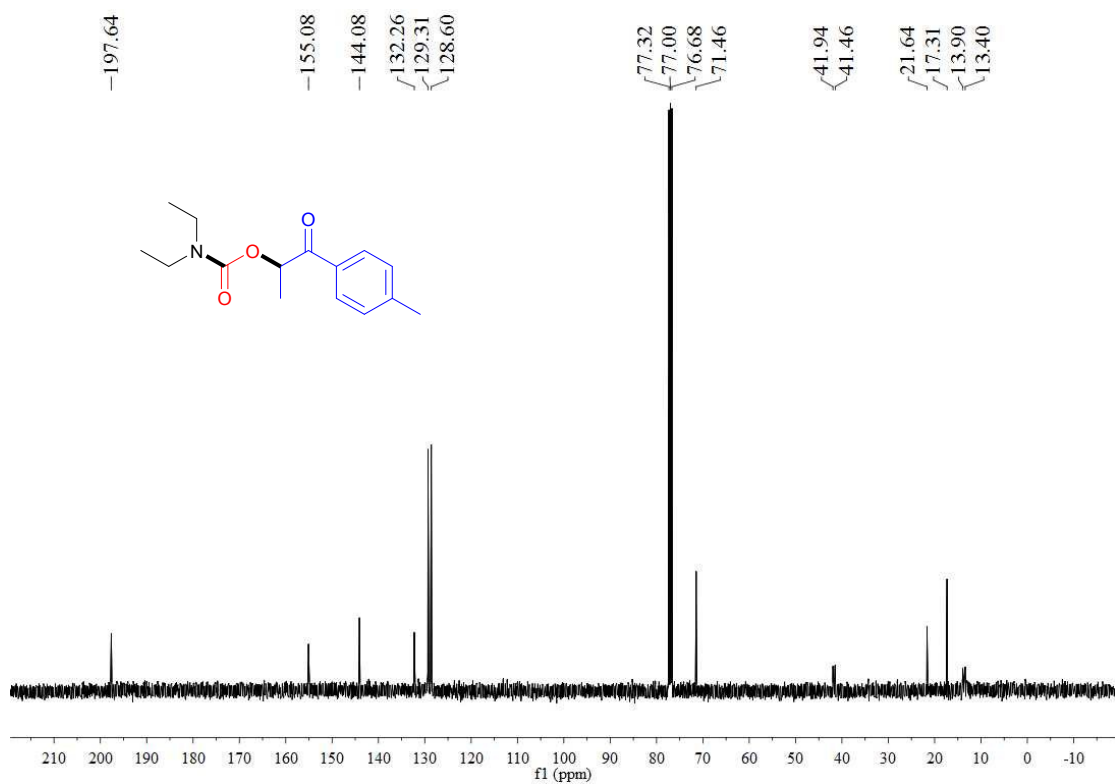
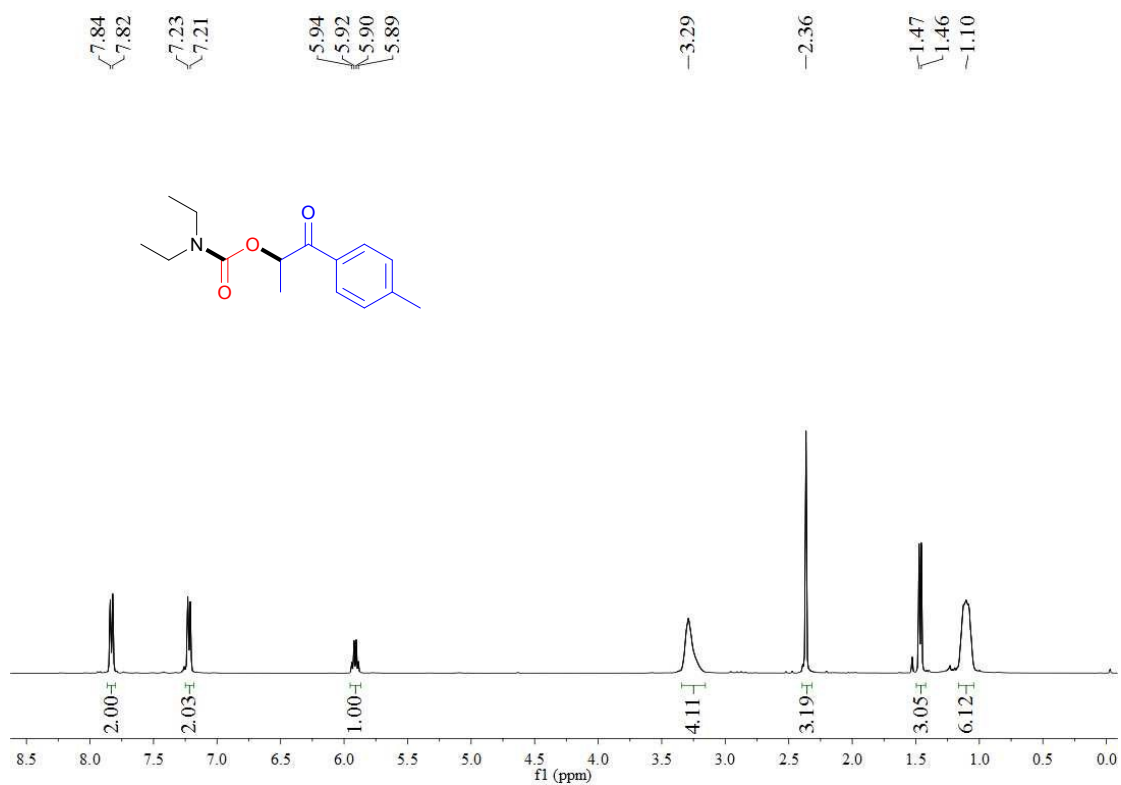
- [1] M. L. N. Rao and D. N. Jadhav, *Tetrahedron Lett.*, 2006, **47**, 6883.
- [2] a) Y-F. Liang, K. Wu, S. Song, X. Li, X. Huang and N. Jiao, *Org. Lett.*, 2015, **17**, 876; b) Y-F. Liang and N. Jiao, *Angew. Chem. Int. Ed.*, 2014, **53**, 548.
- [3] a) M. P. DeMartino, K. Chen and P. S. Baran, *J. Am. Chem. Soc.*, 2008, **130**, 11546; b) M. Uyanik, D. Suzuki, T. Yasui and K. Ishihara, *Angew. Chem. Int. Ed.*, 2011, **50**, 5331.
- [4] S. Sengupta and V. Snieckus, *J. Org. Chem.*, 1990, **55**, 5680.

## E. NMR Spectra

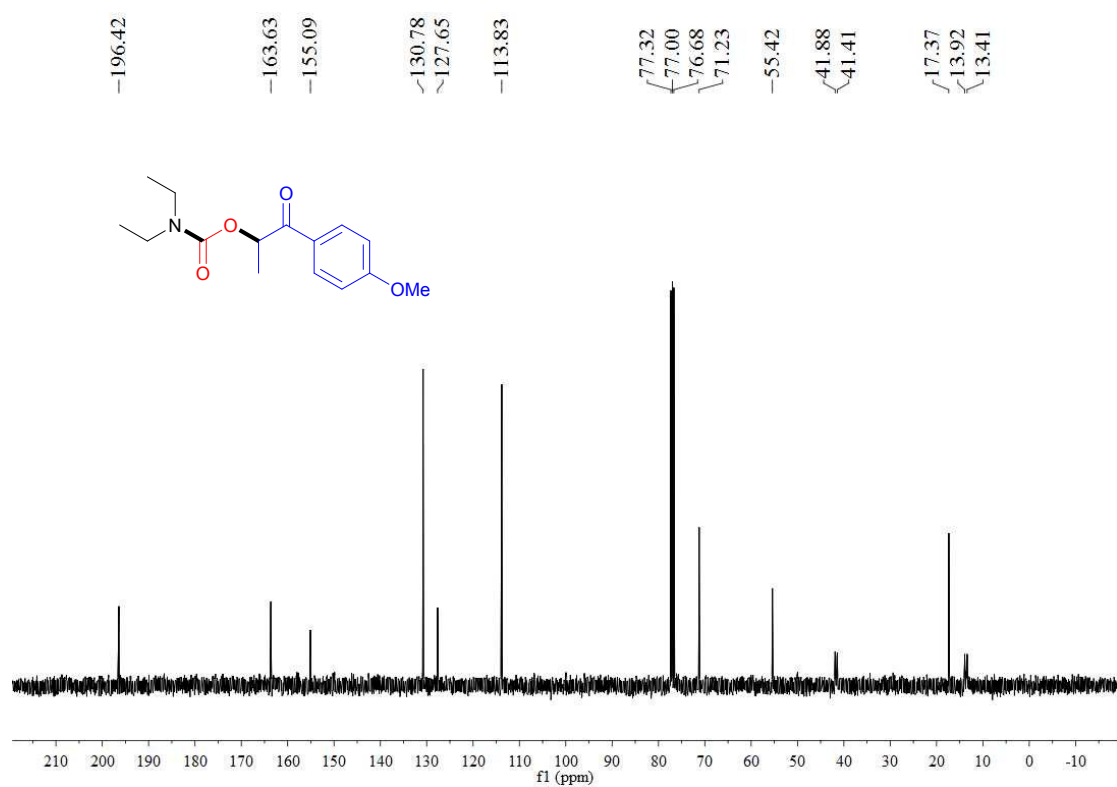
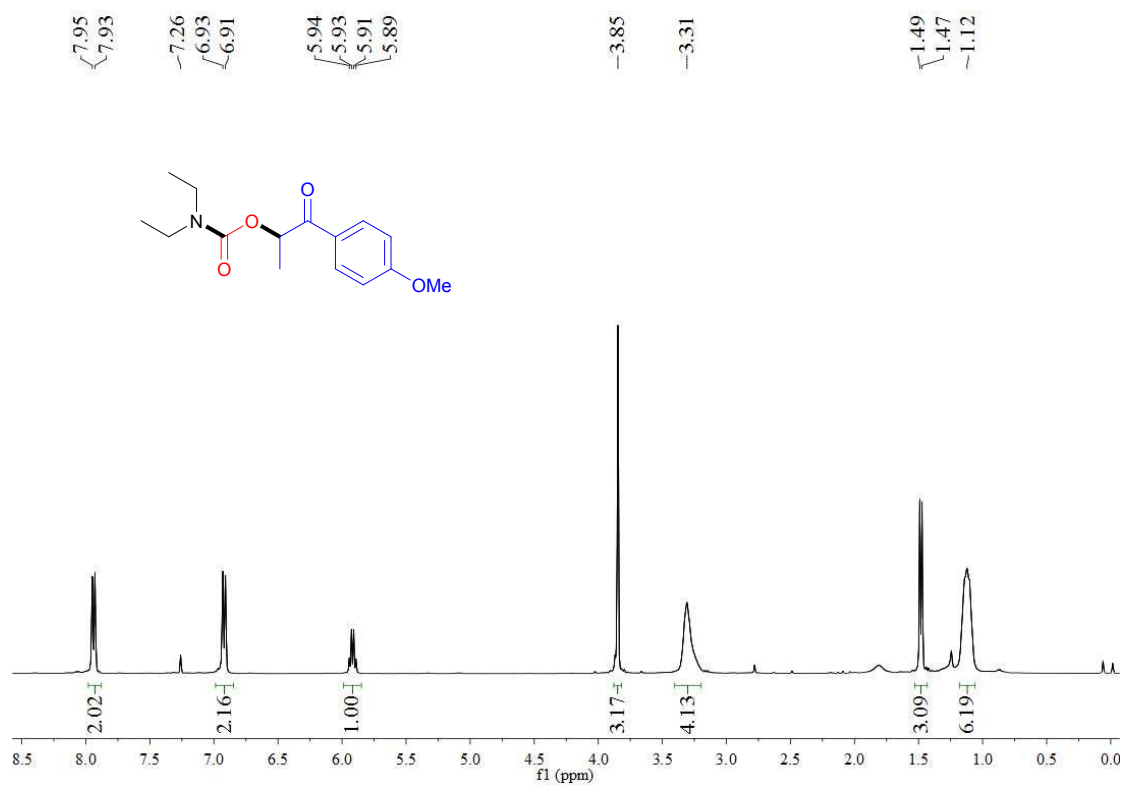
### 1-Oxo-1-phenylpropan-2-yl diethylcarbamate (3aa)



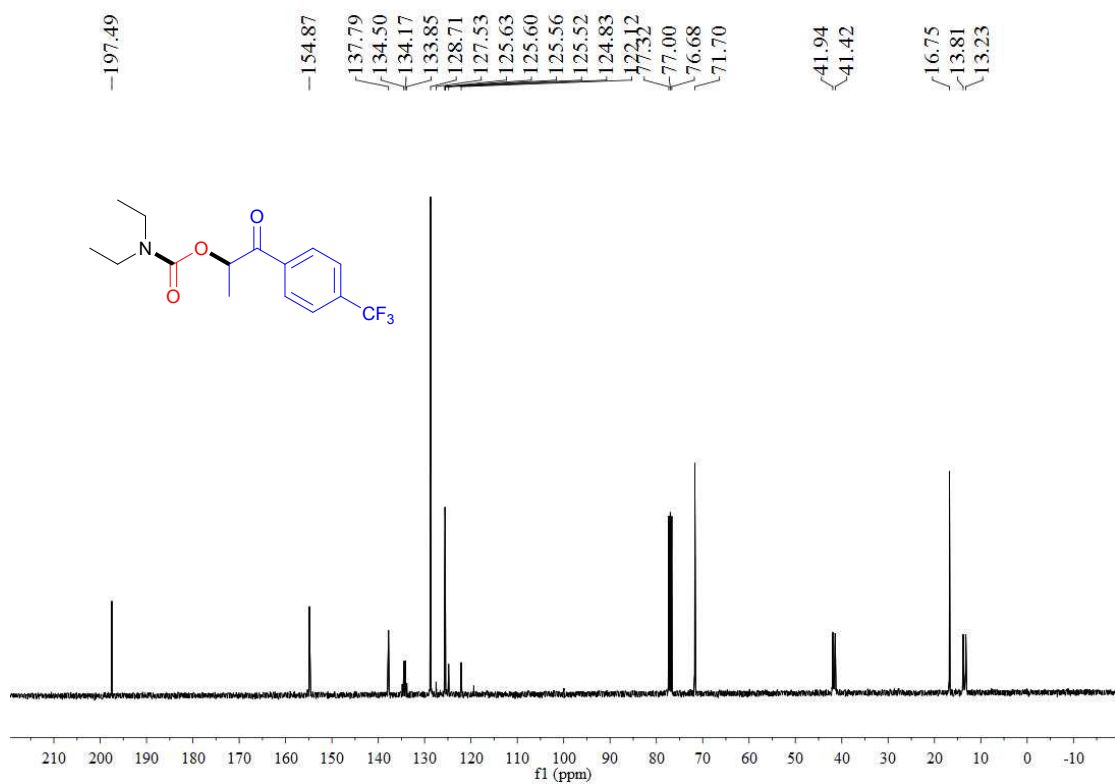
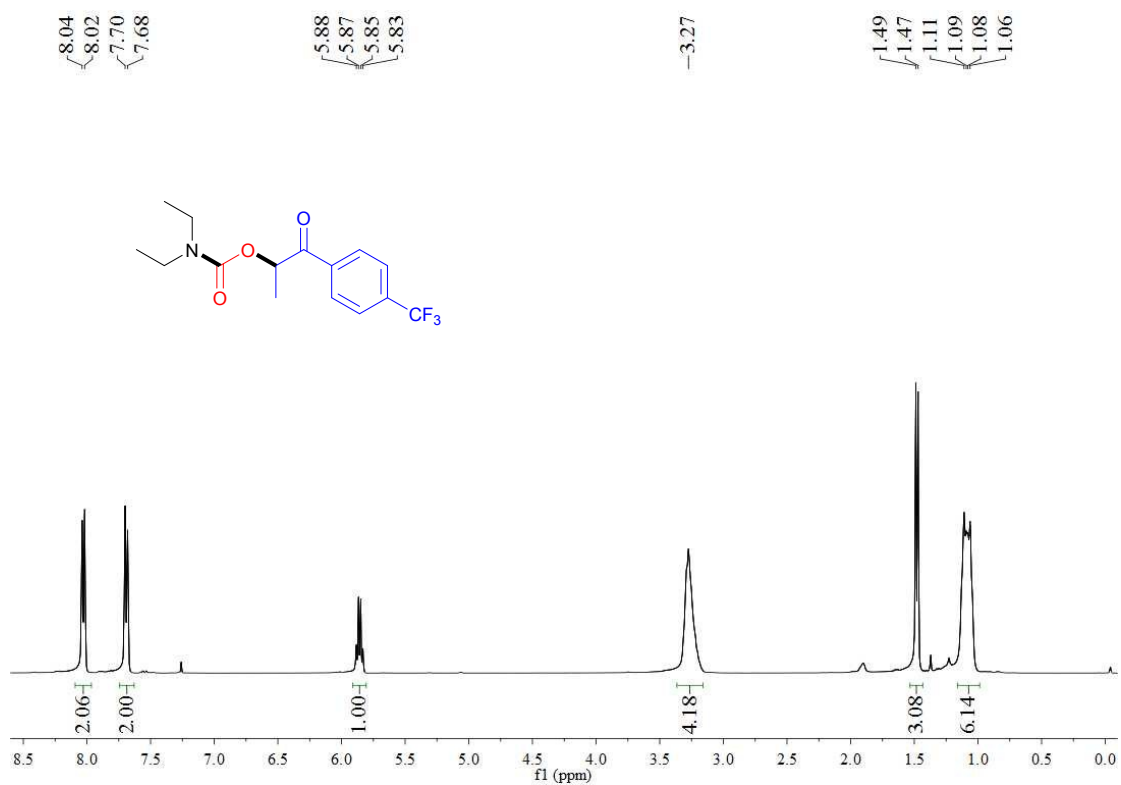
# 1-Oxo-1-(*p*-tolyl)propan-2-yl diethylcarbamate (3ba)



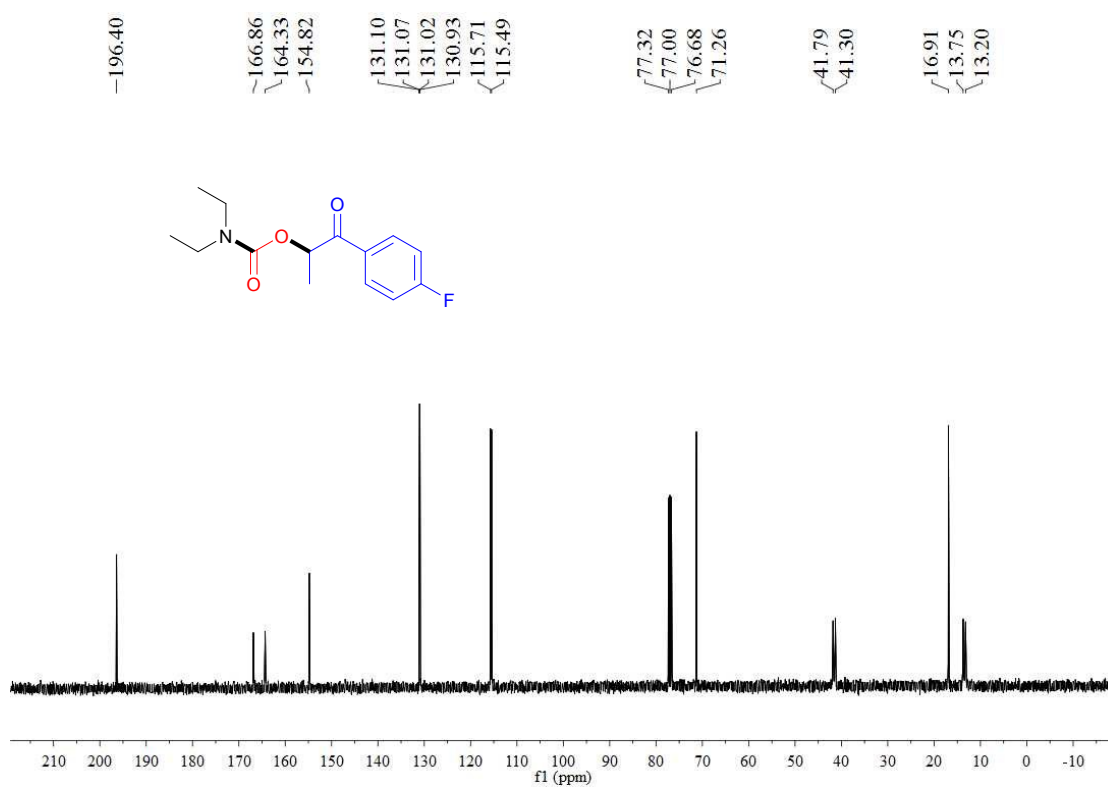
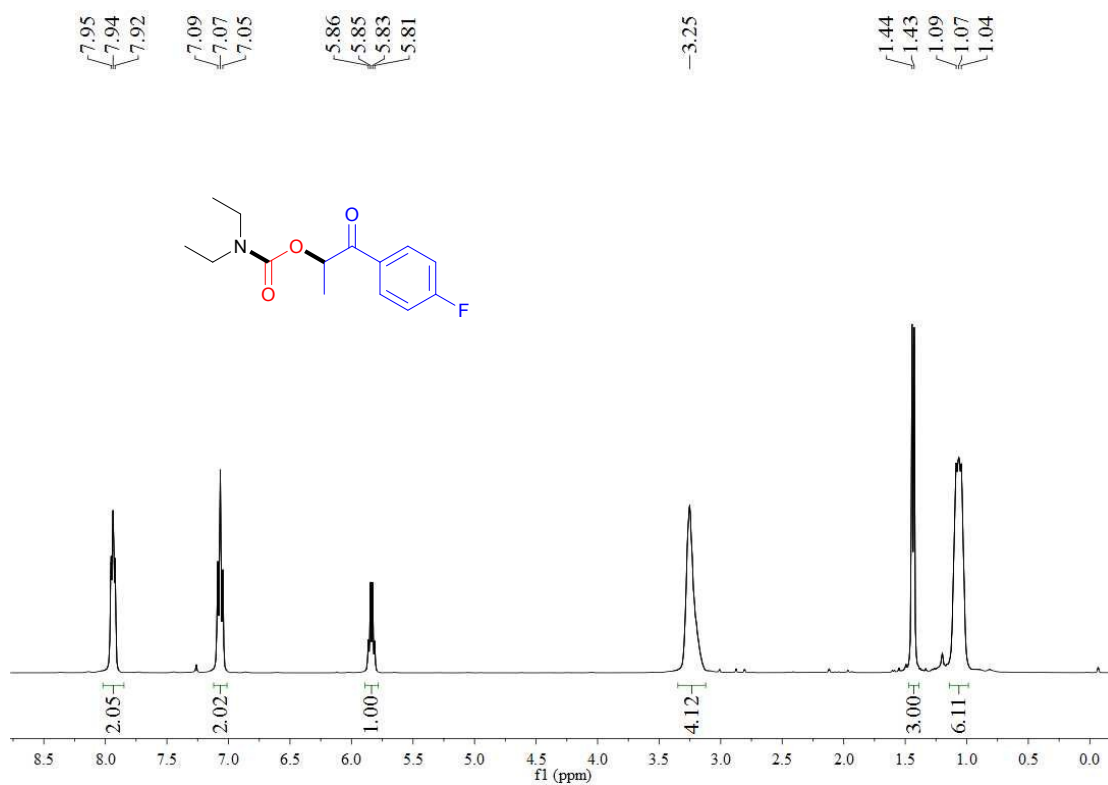
# 1-(4-Methoxyphenyl)-1-oxopropan-2-yl diethylcarbamate (3ca)



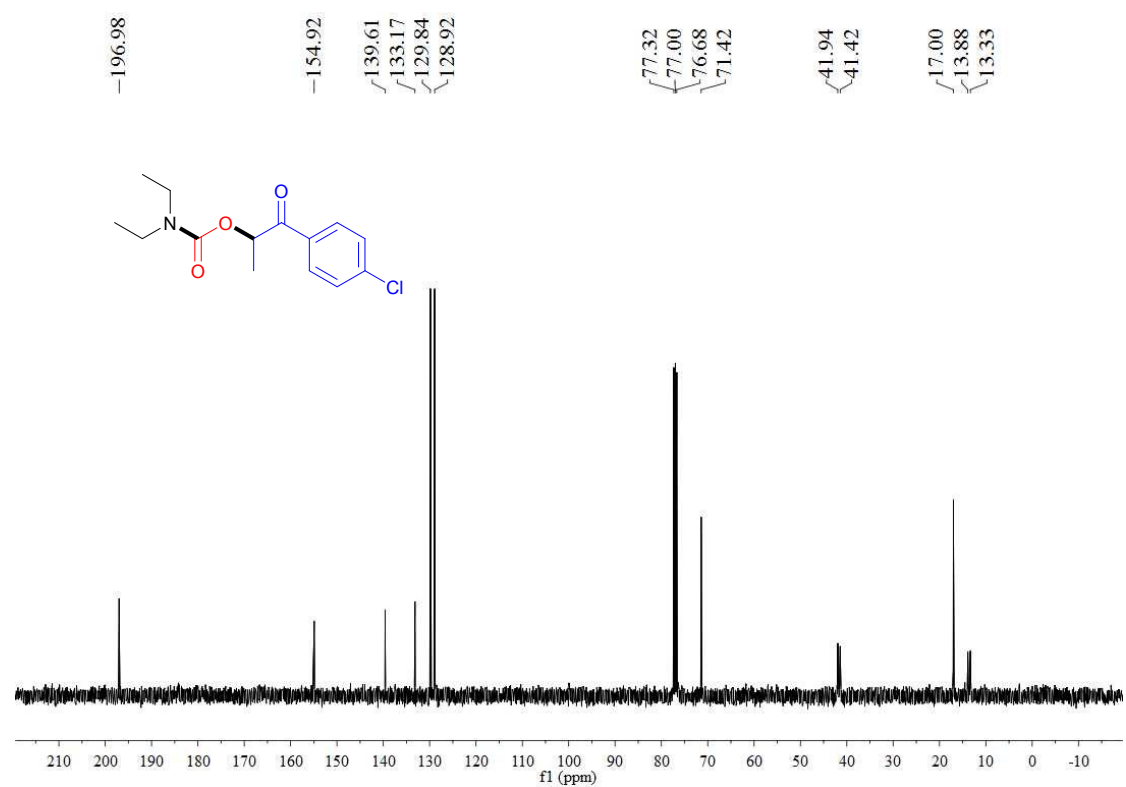
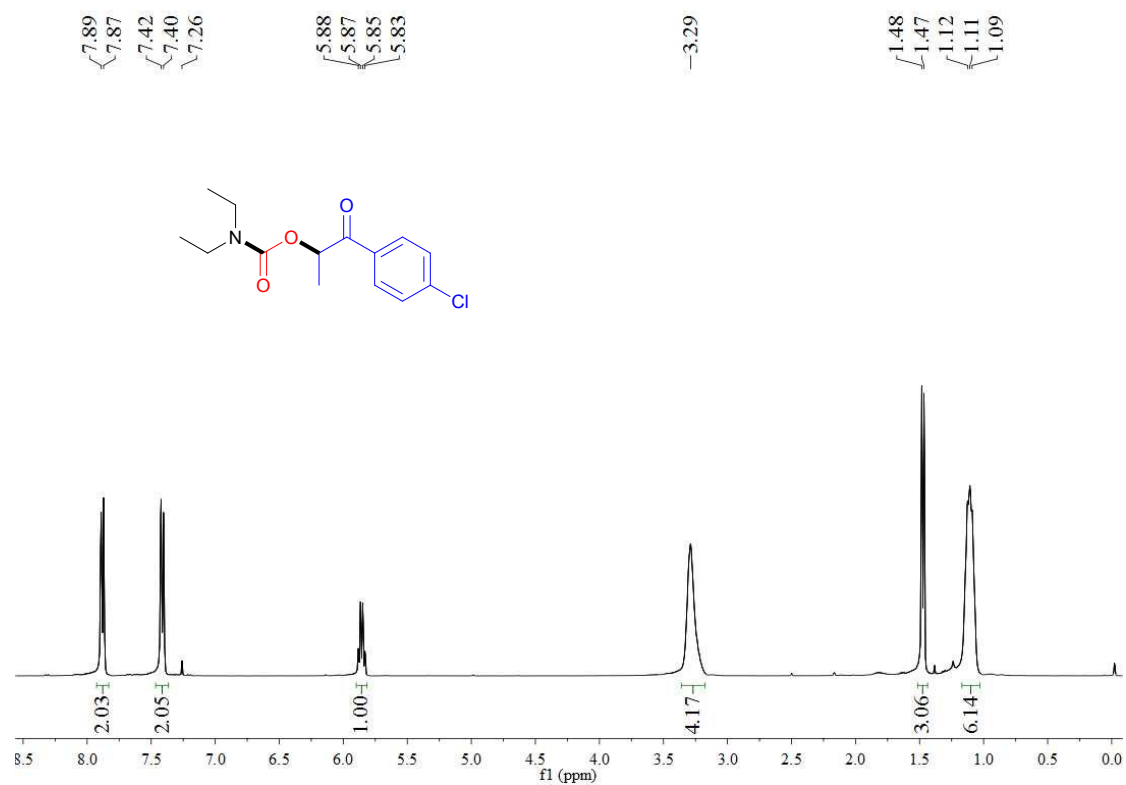
# 1-Oxo-1-(4-(trifluoromethyl)phenyl)propan-2-yl diethylcarbamate (3da)



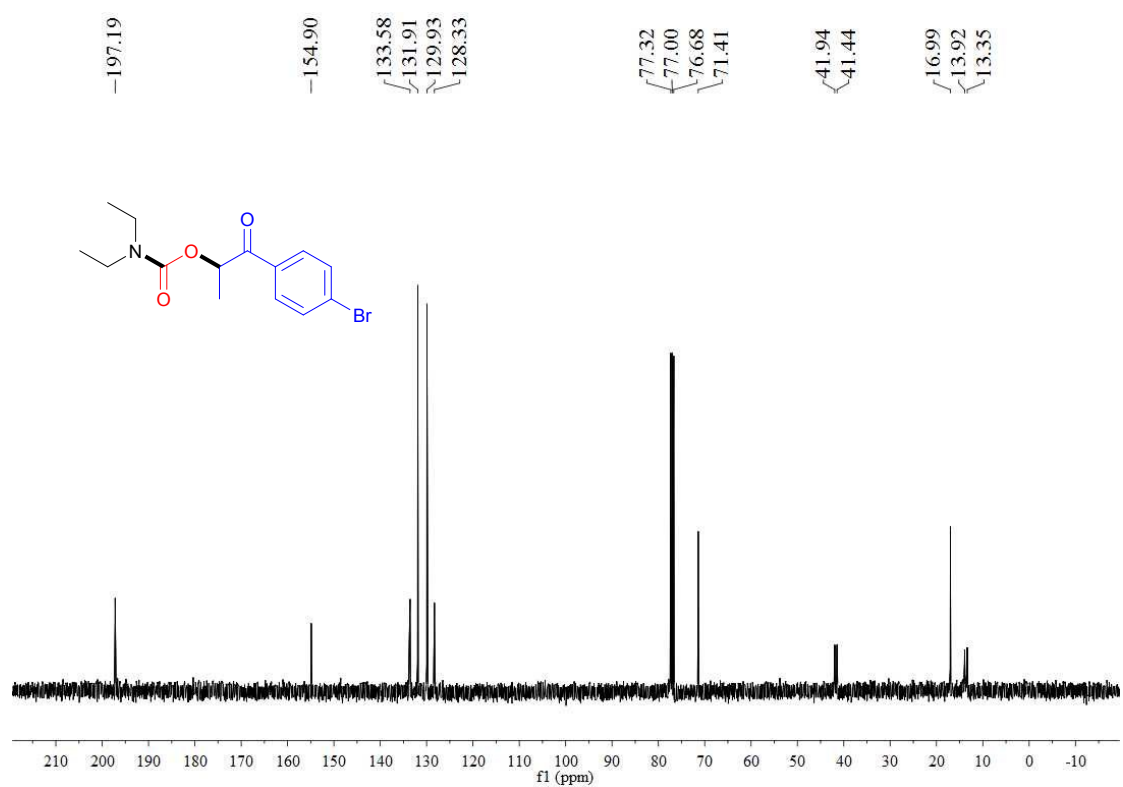
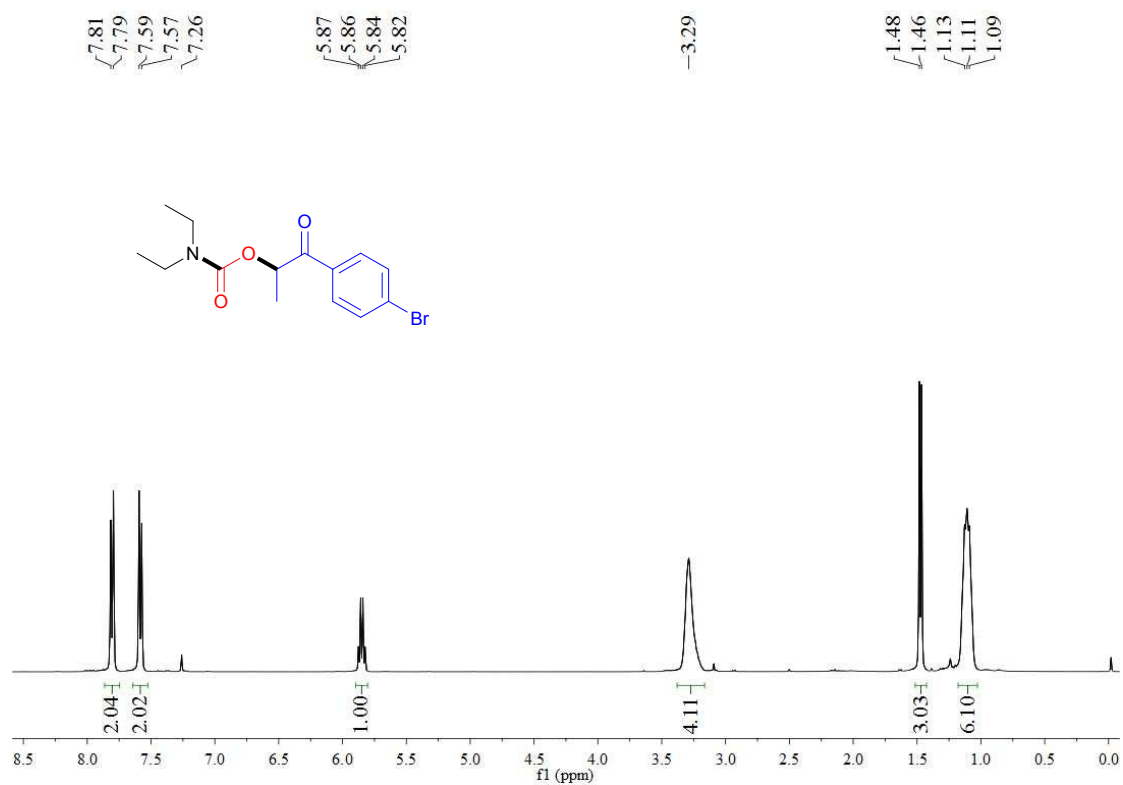
# 1-(4-Fluorophenyl)-1-oxopropan-2-yl diethylcarbamate (3ea)



# 1-(4-Chlorophenyl)-1-oxopropan-2-yl diethylcarbamate (3fa)

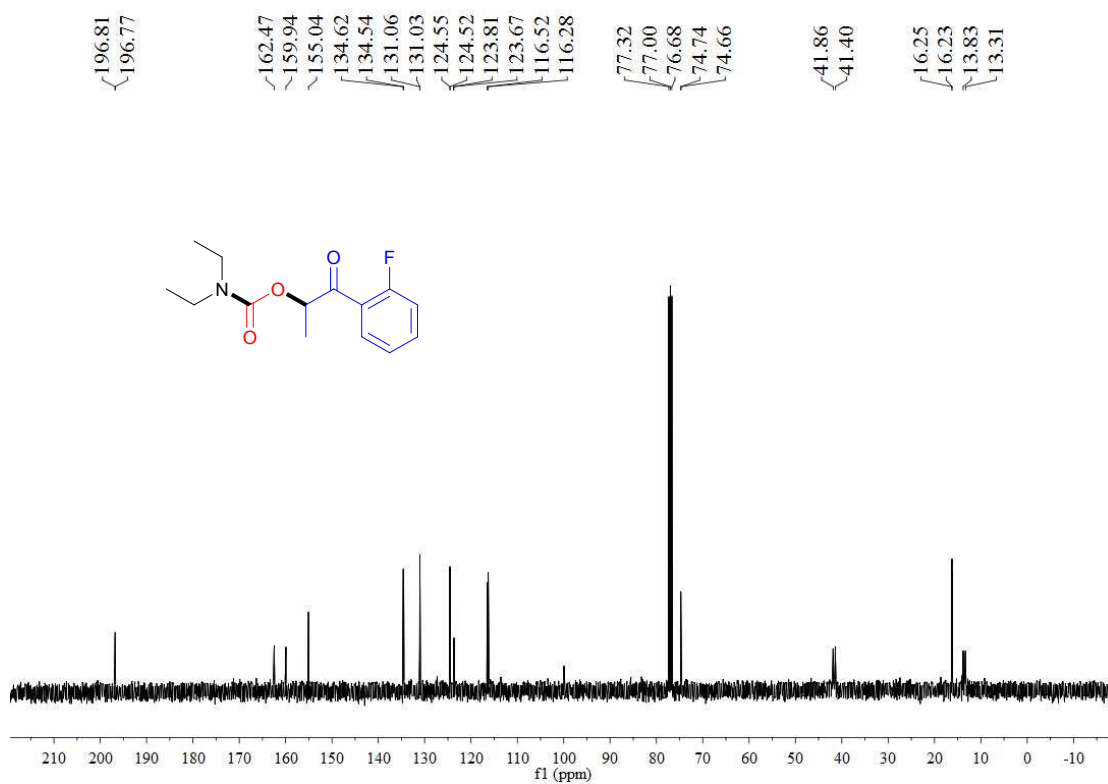
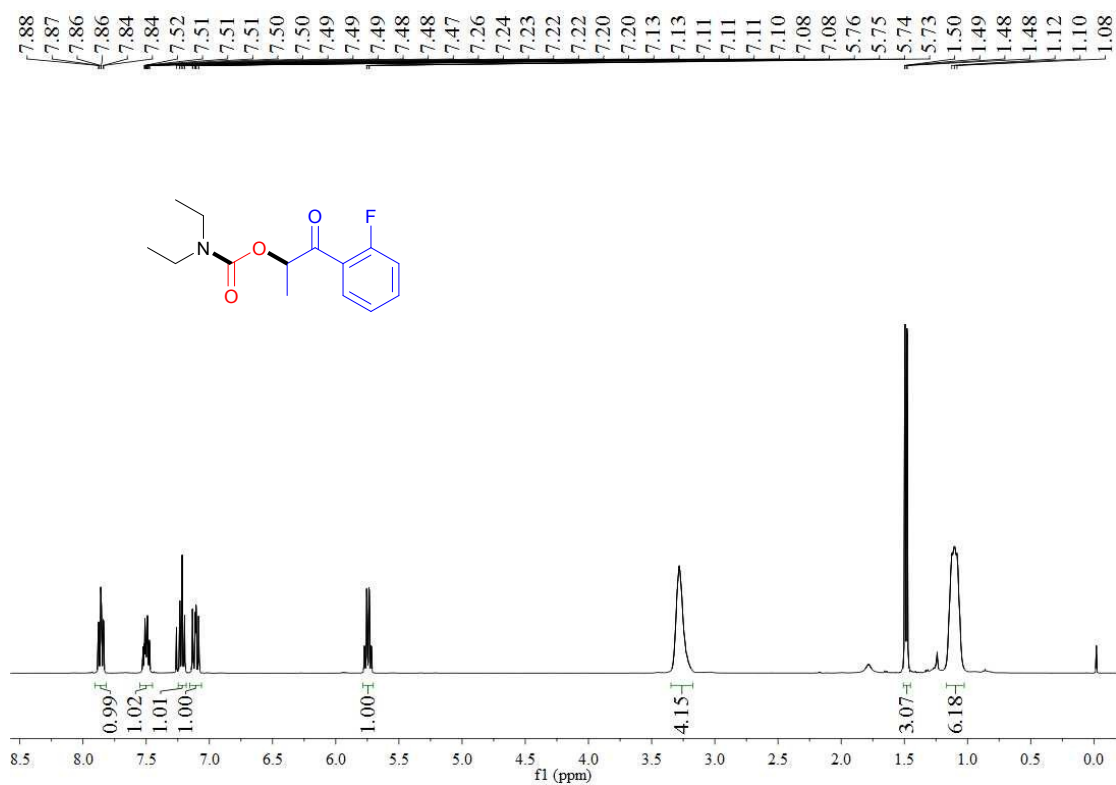


# 1-(4-Bromophenyl)-1-oxopropan-2-yl diethylcarbamate (3ga)

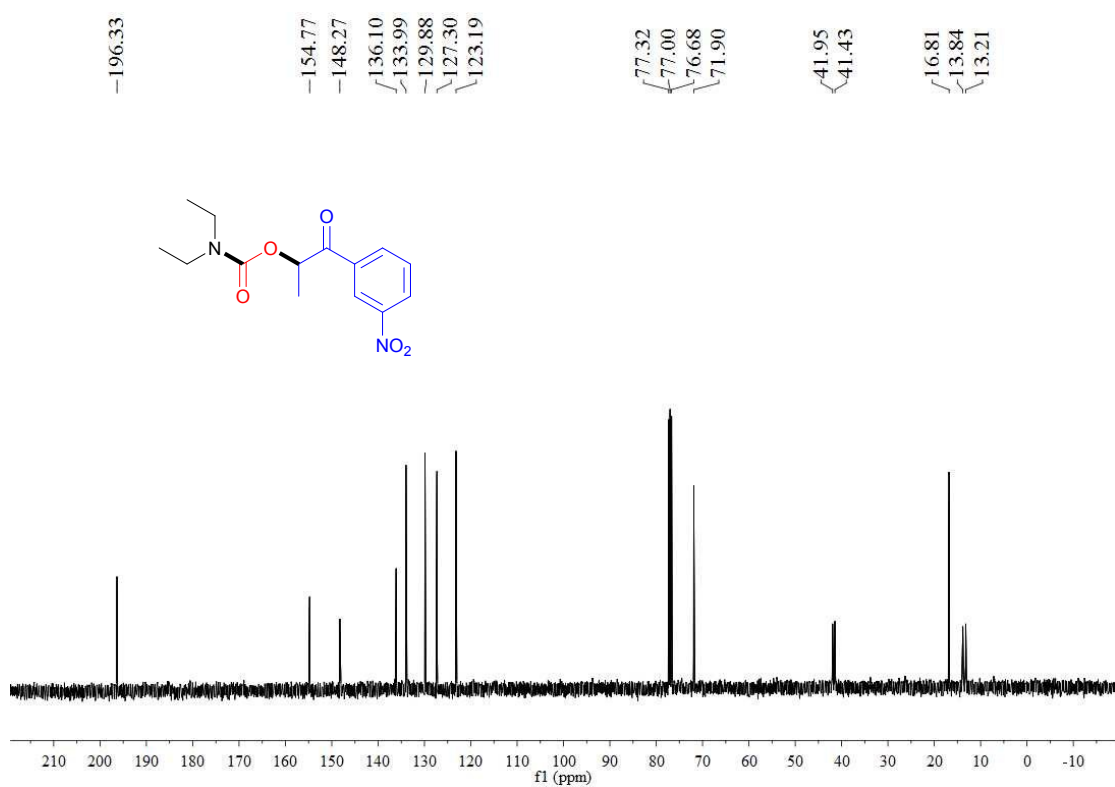
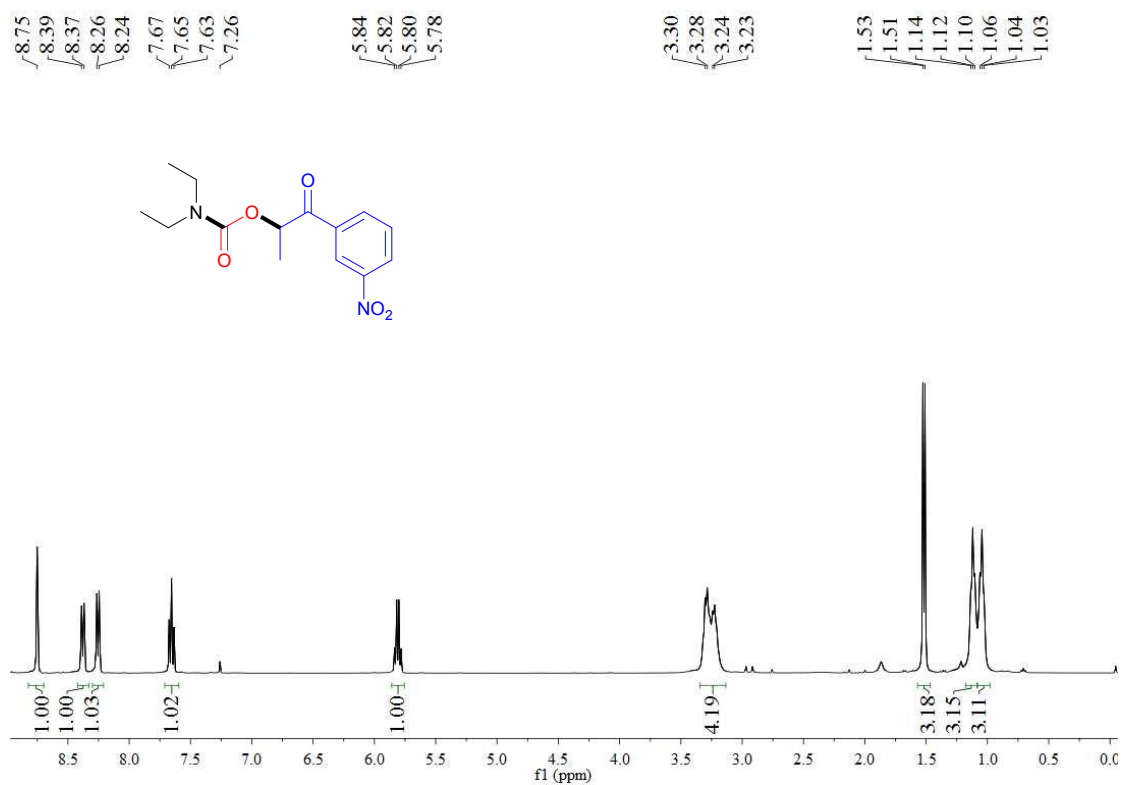




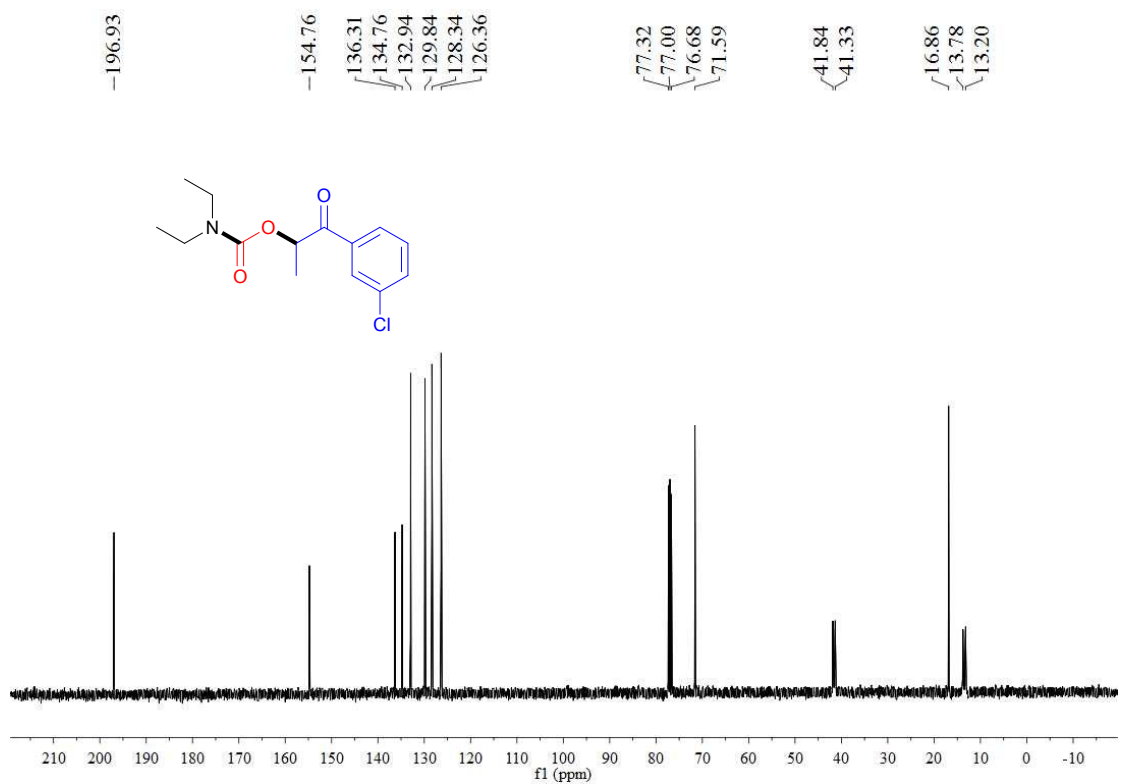
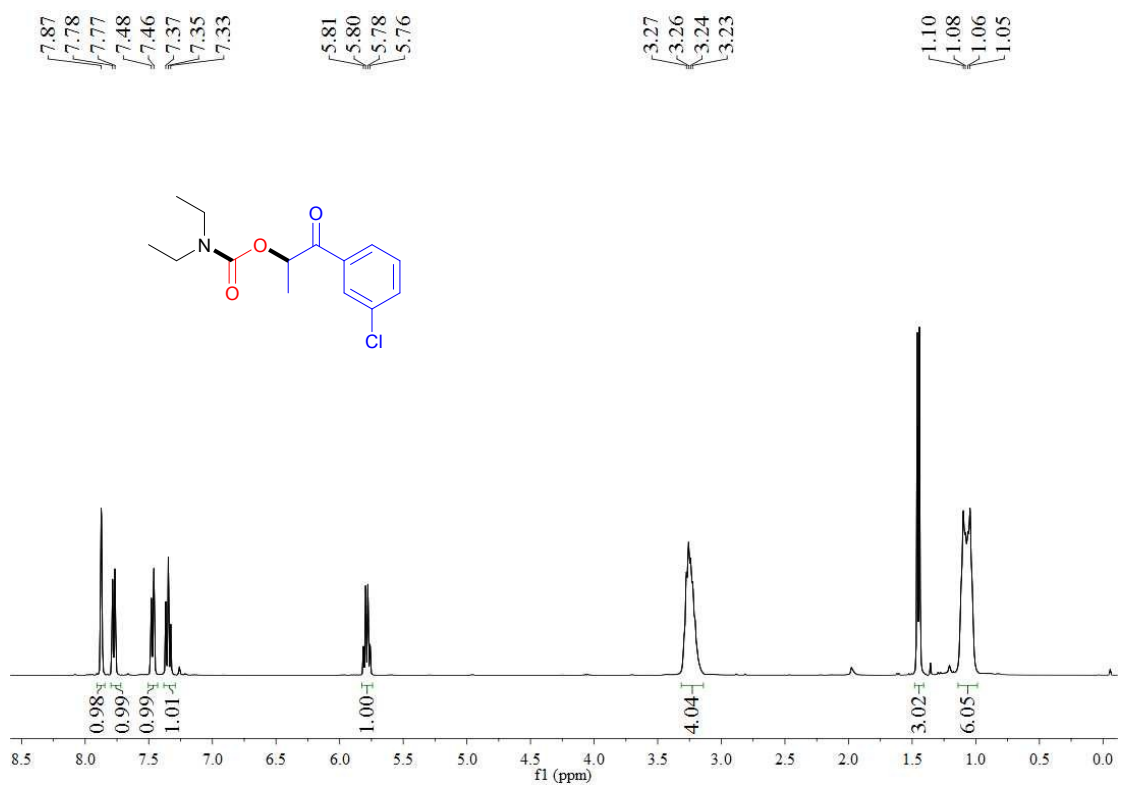
The chemical structure shows an ethyl carbamate group (left) connected via an ester linkage to a 2-oxoethyl chain, which is further connected to a 4-fluorophenyl ring (right). The fluorine atom is highlighted in blue.



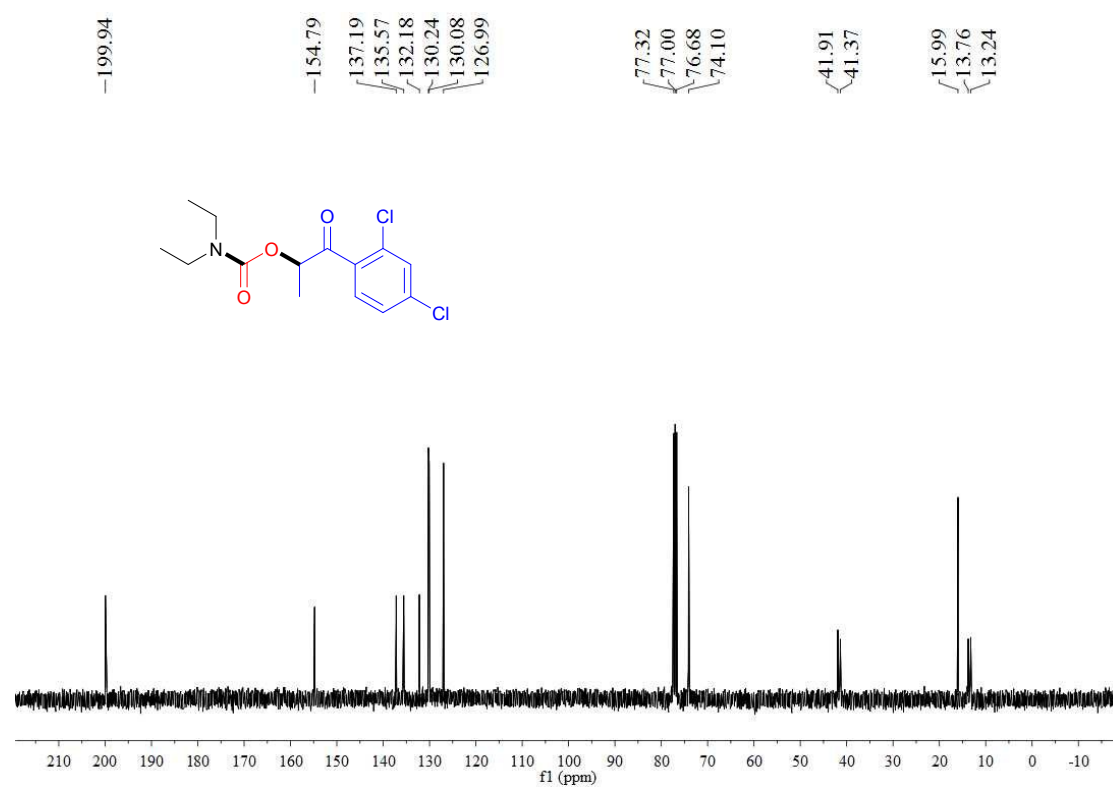
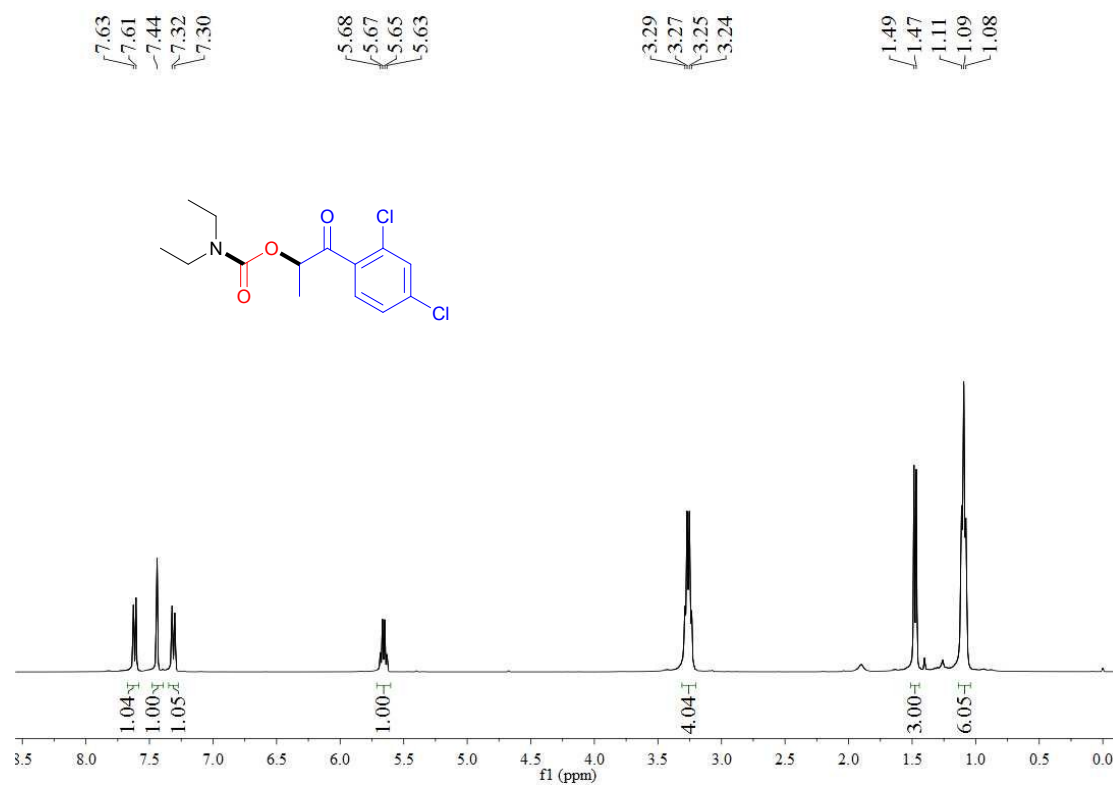
# 1-(3-Nitrophenyl)-1-oxopropan-2-yl diethylcarbamate (3ia)



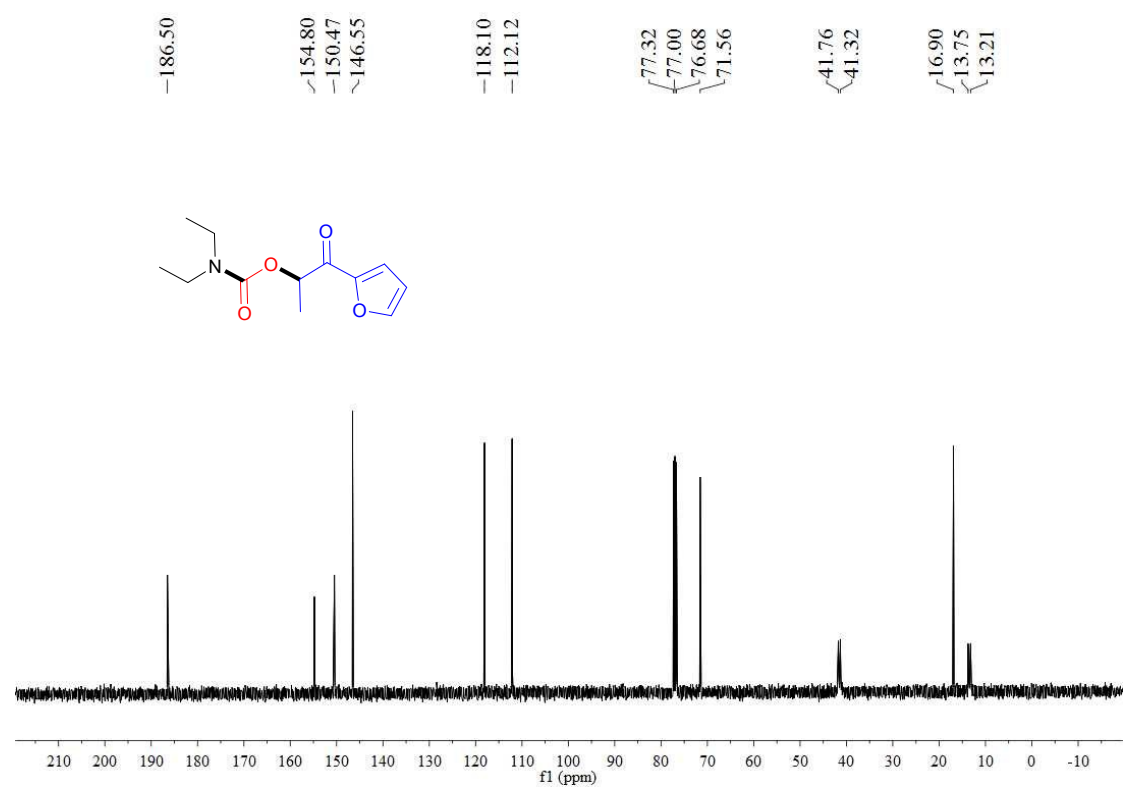
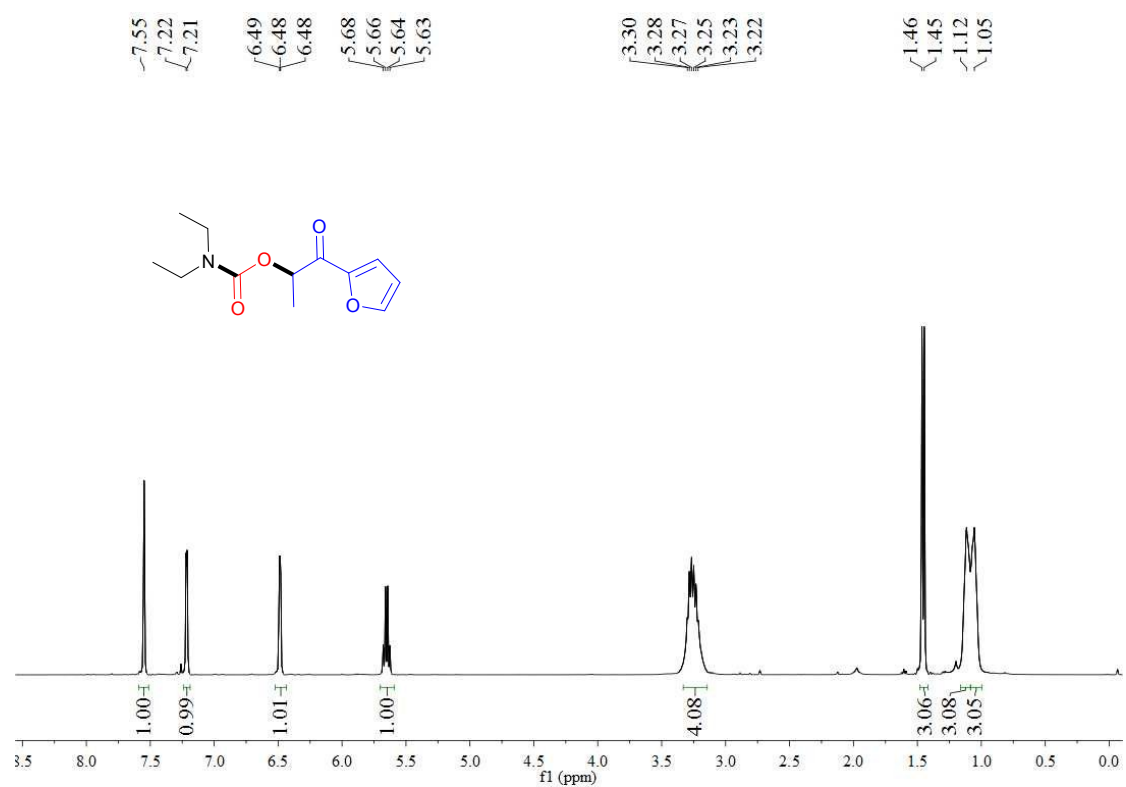
1-(3-Chlorophenyl)-1-oxopropan-2-yl diethylcarbamate (3ja)



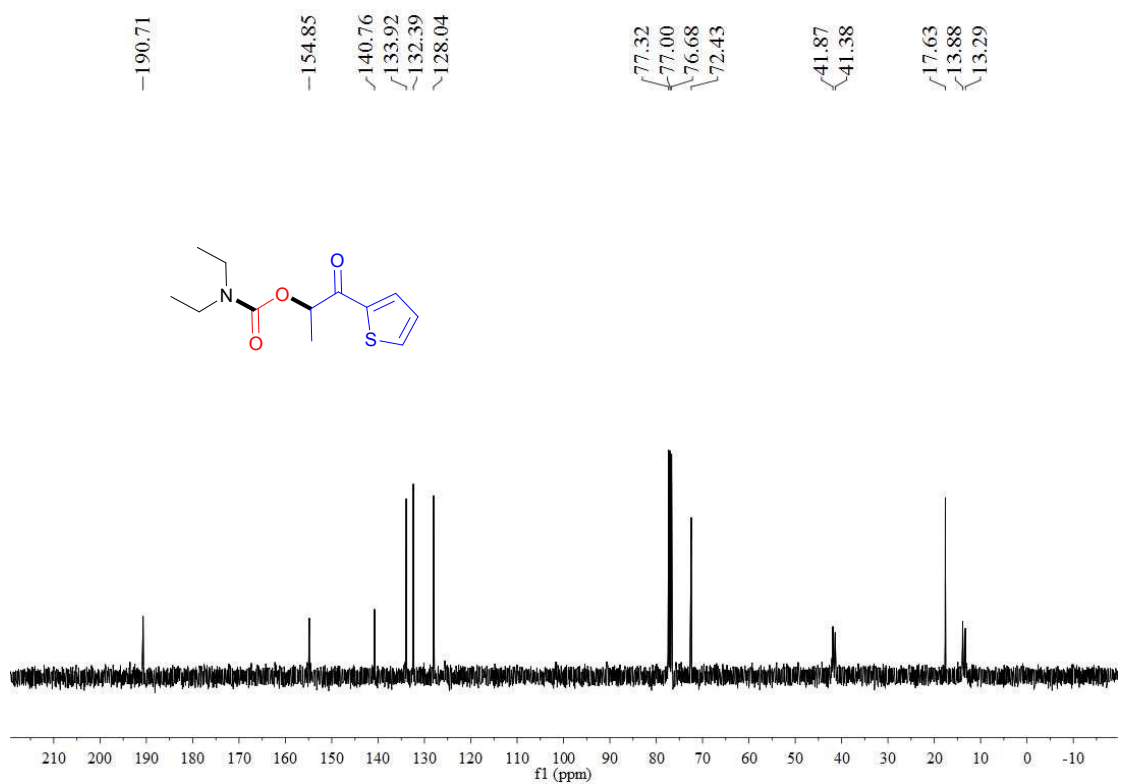
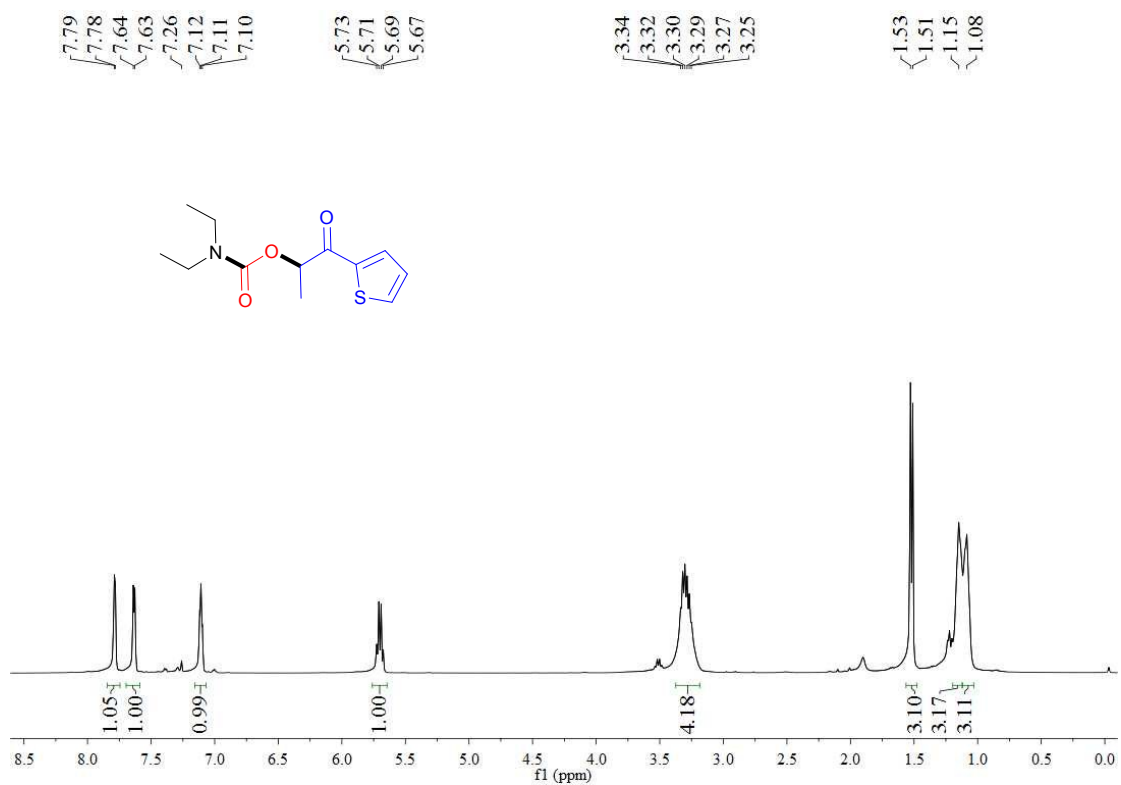
# 1-(2,4-Dichlorophenyl)-1-oxopropan-2-yl diethylcarbamate (3ka)



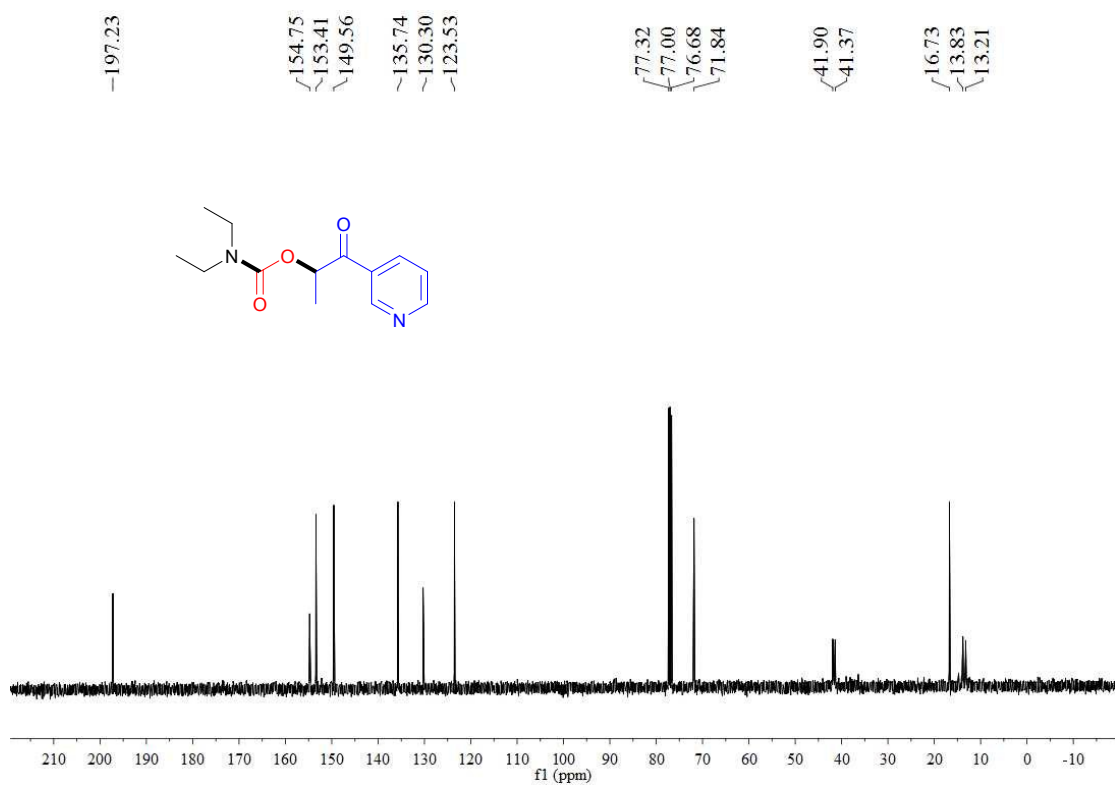
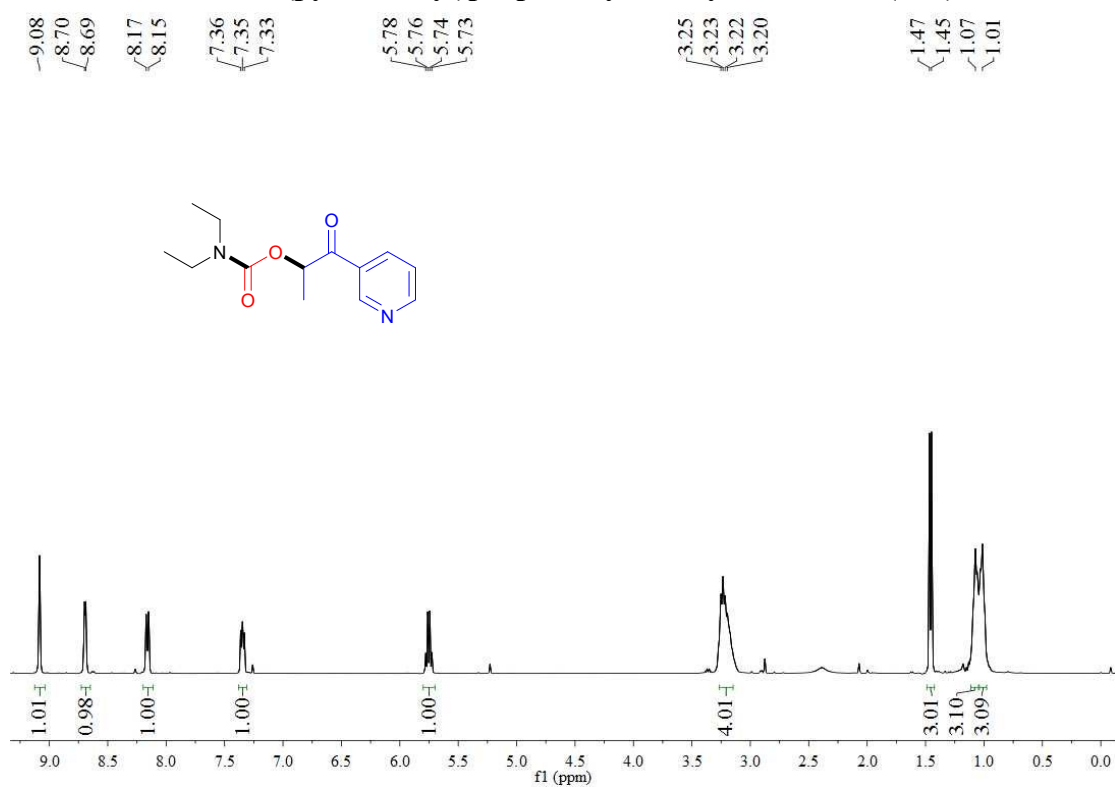
# 1-(Furan-2-yl)-1-oxopropan-2-yl diethylcarbamate (3la)



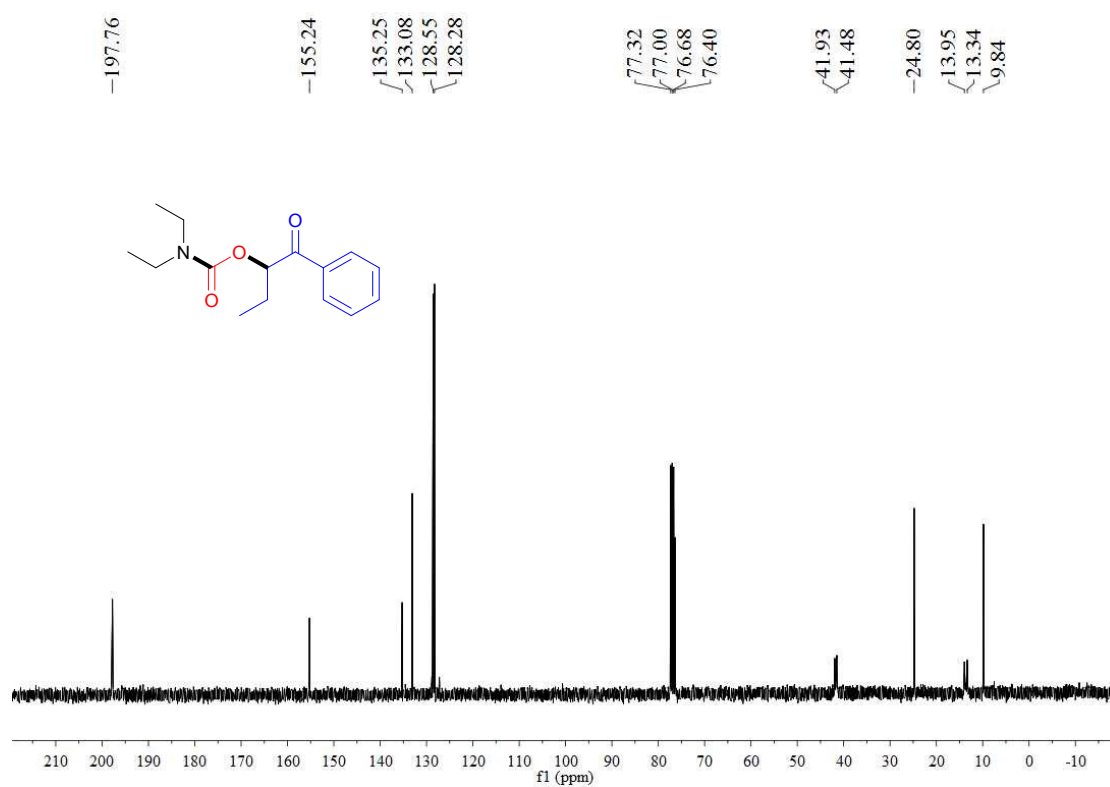
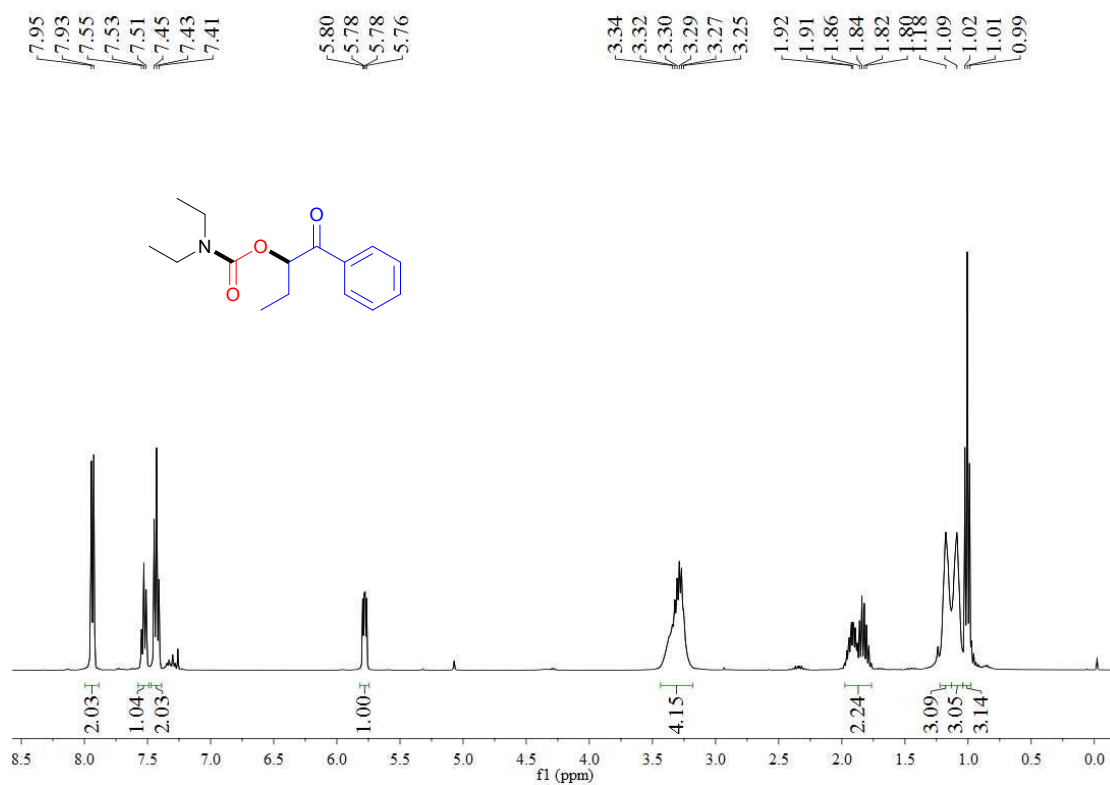
# 1-Oxo-1-(thiophen-2-yl)propan-2-yl diethylcarbamate (3ma)



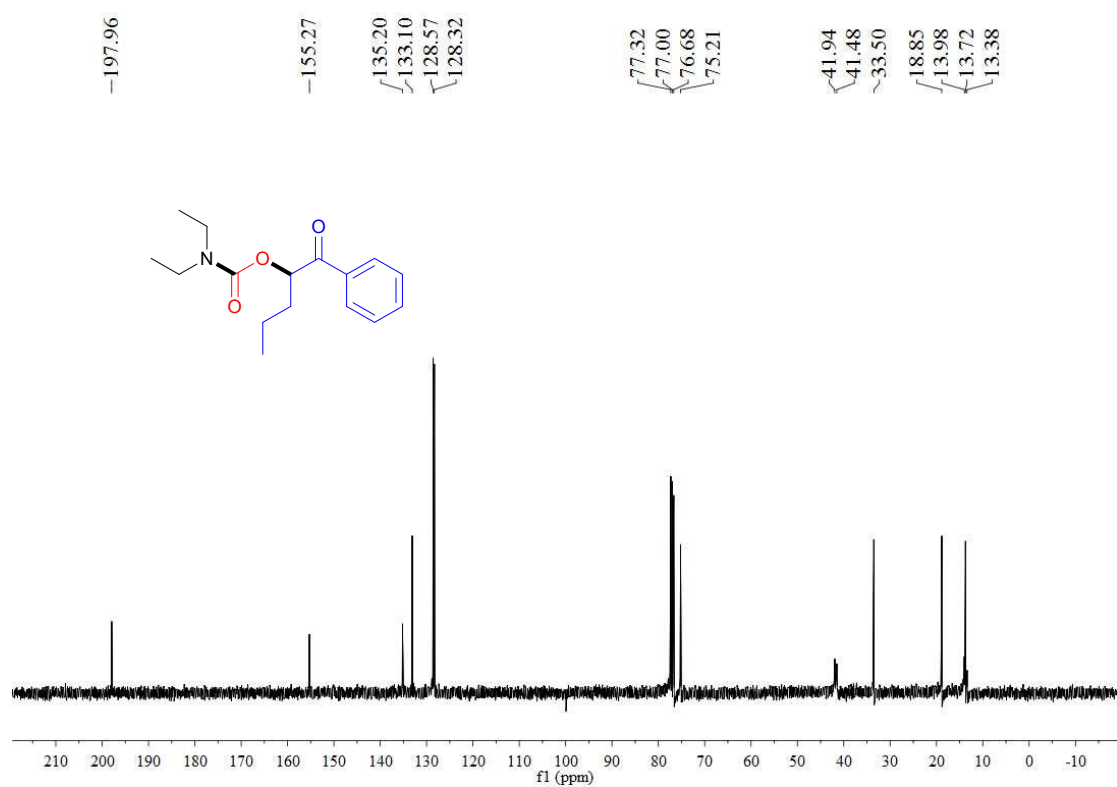
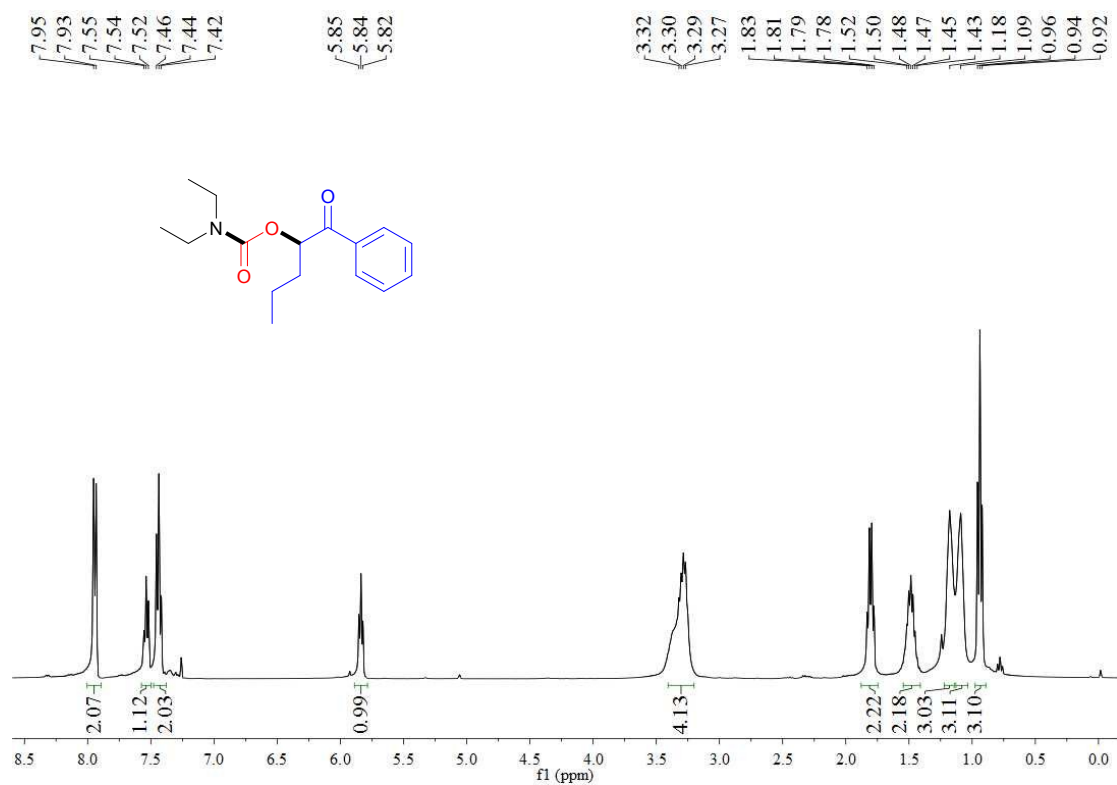
**1-Oxo-1-(pyridin-3-yl)propan-2-yl diethylcarbamate (3na)**



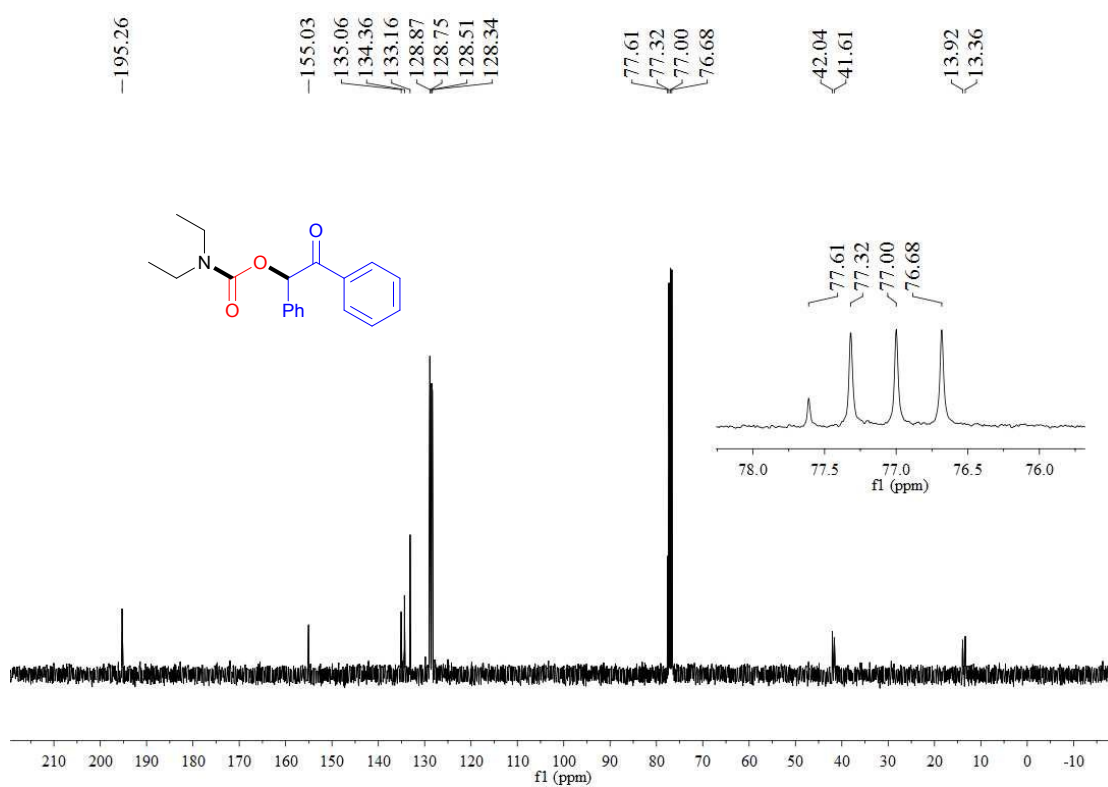
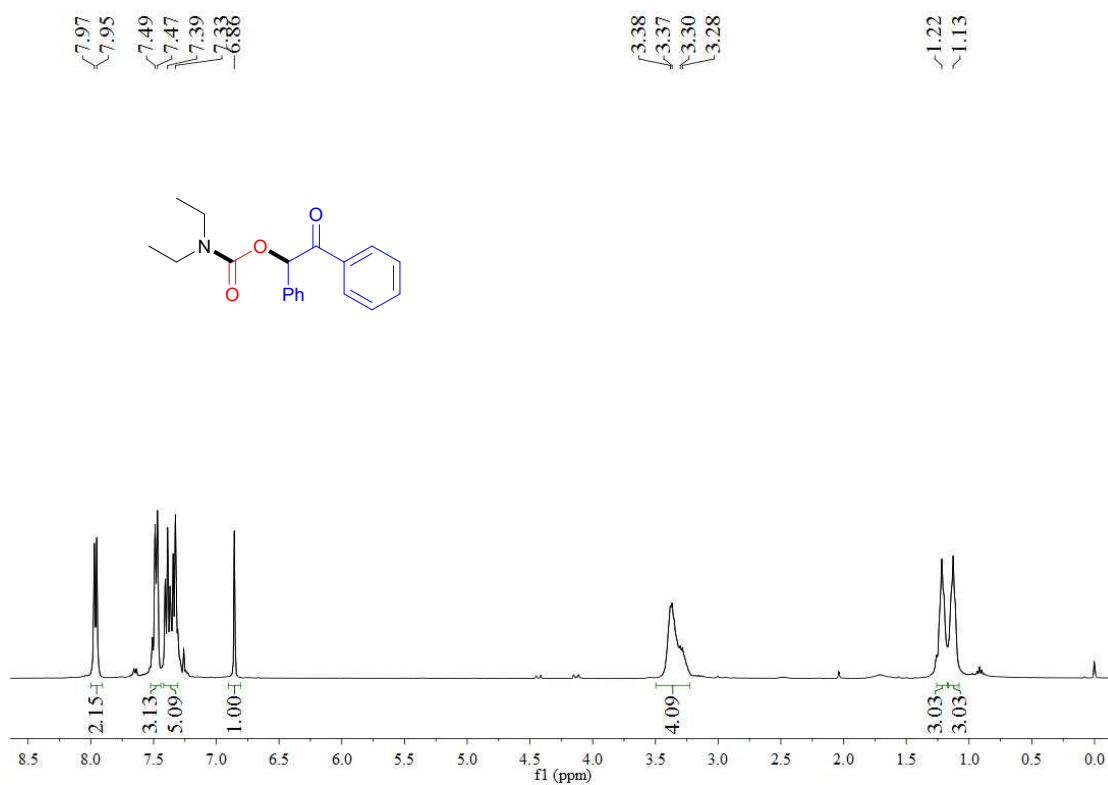
# 1-Oxo-1-phenylbutan-2-yl diethylcarbamate (30a)



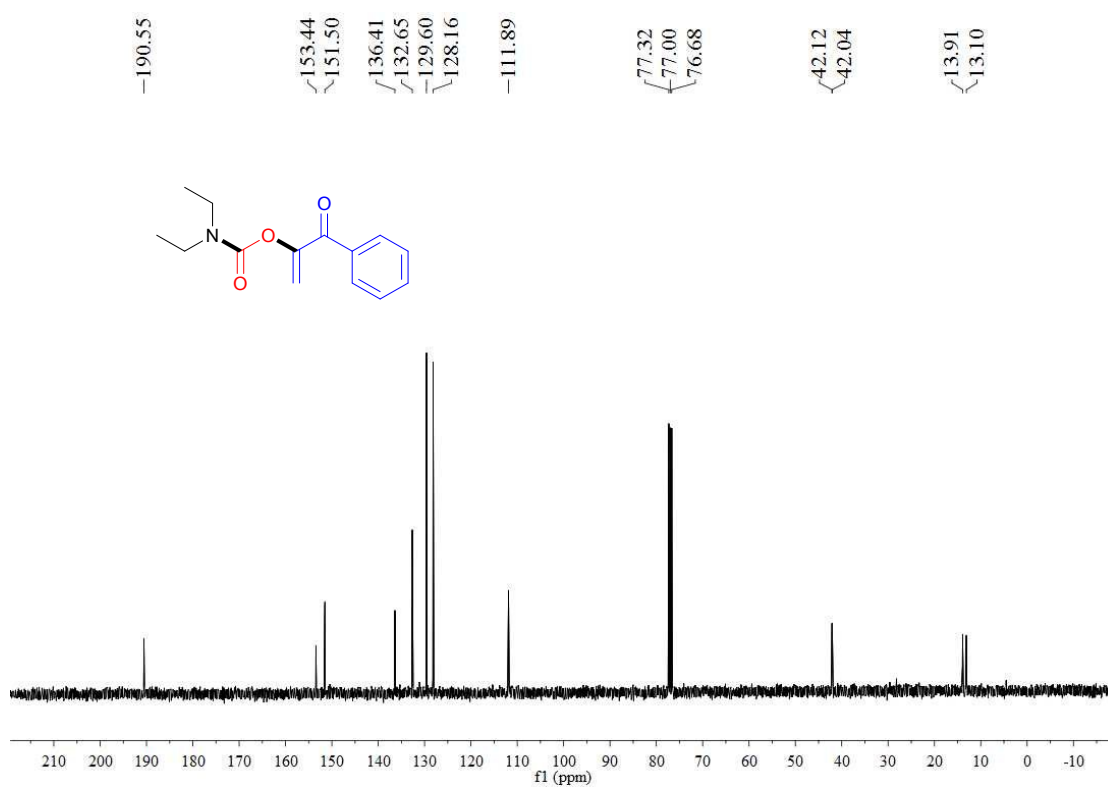
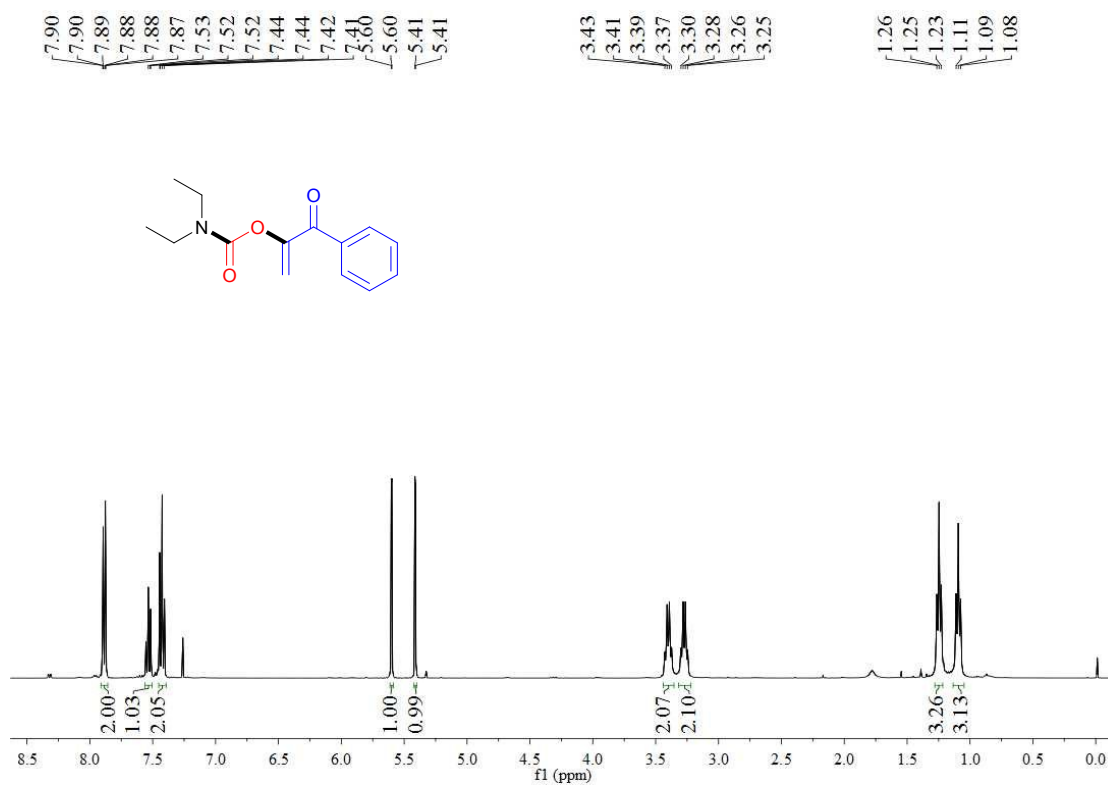
# 1-Oxo-1-phenylpentan-2-yl diethylcarbamate (3pa)



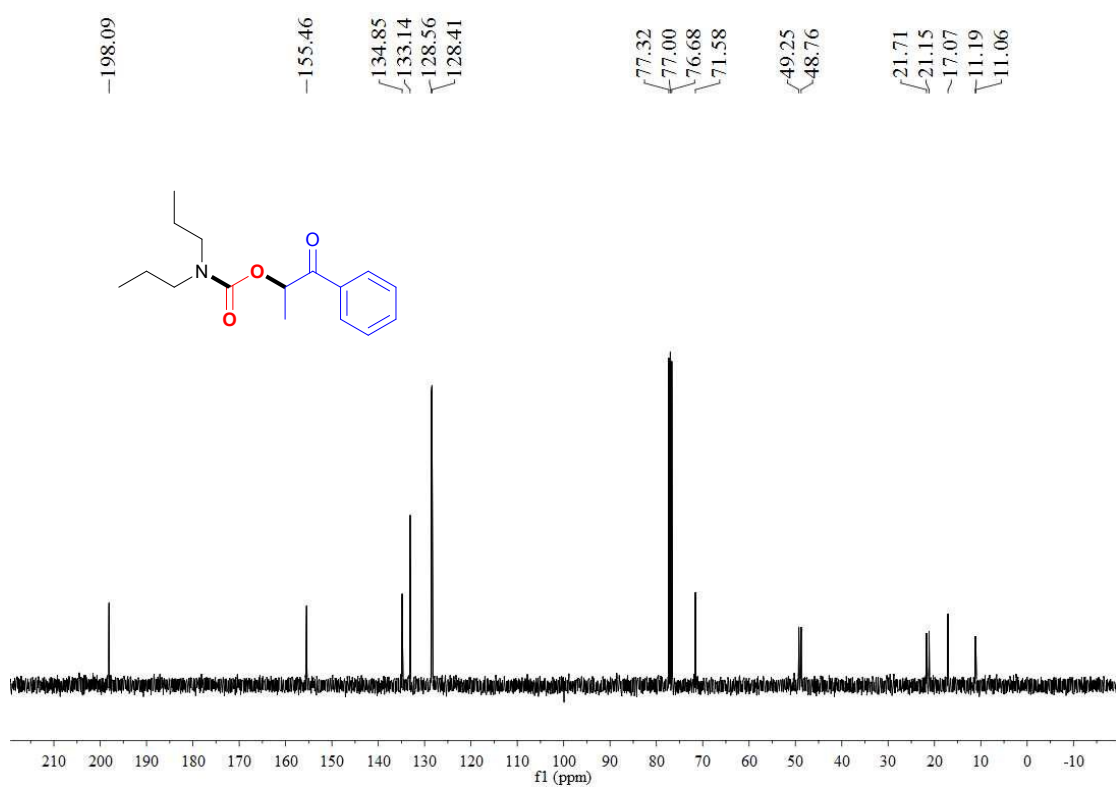
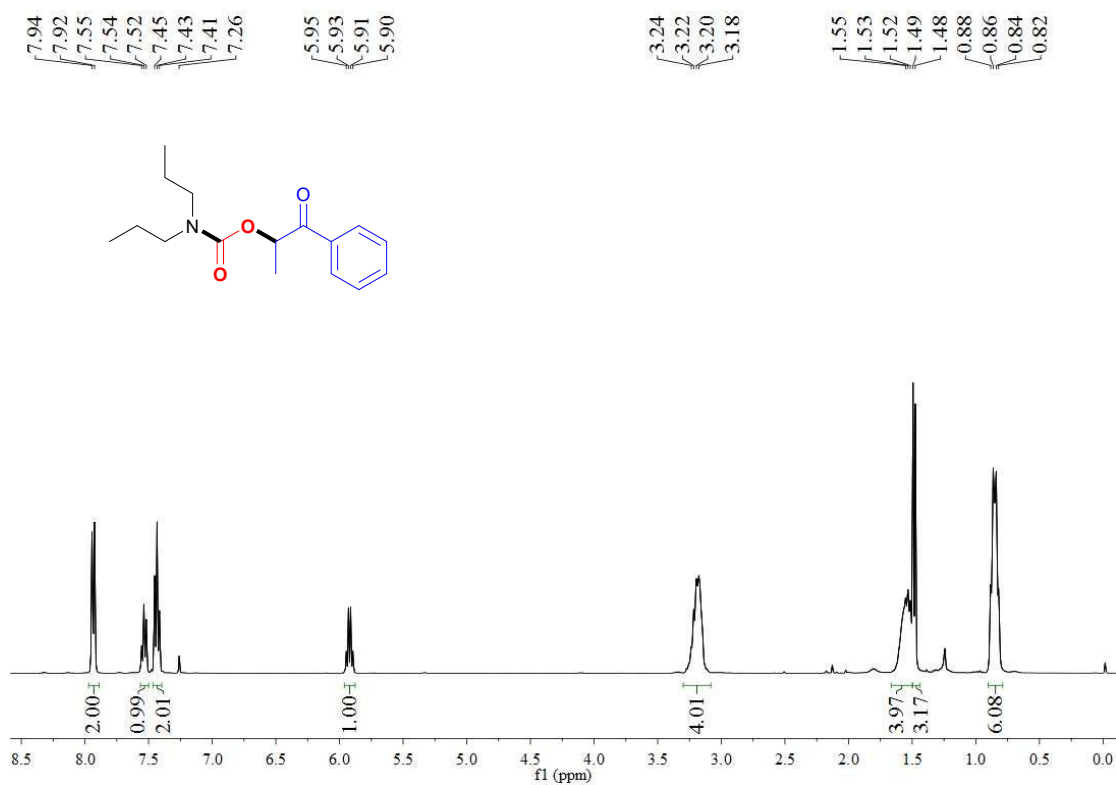
# 2-Oxo-1,2-diphenylethyl diethylcarbamate (3qa)



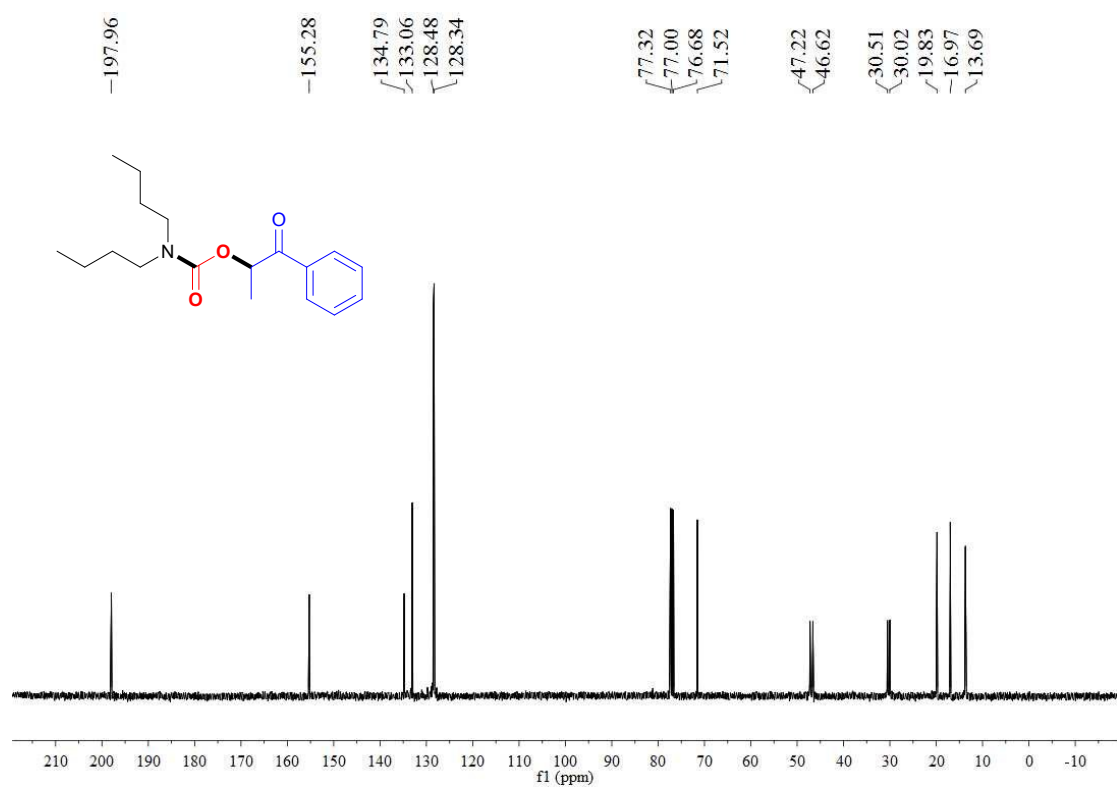
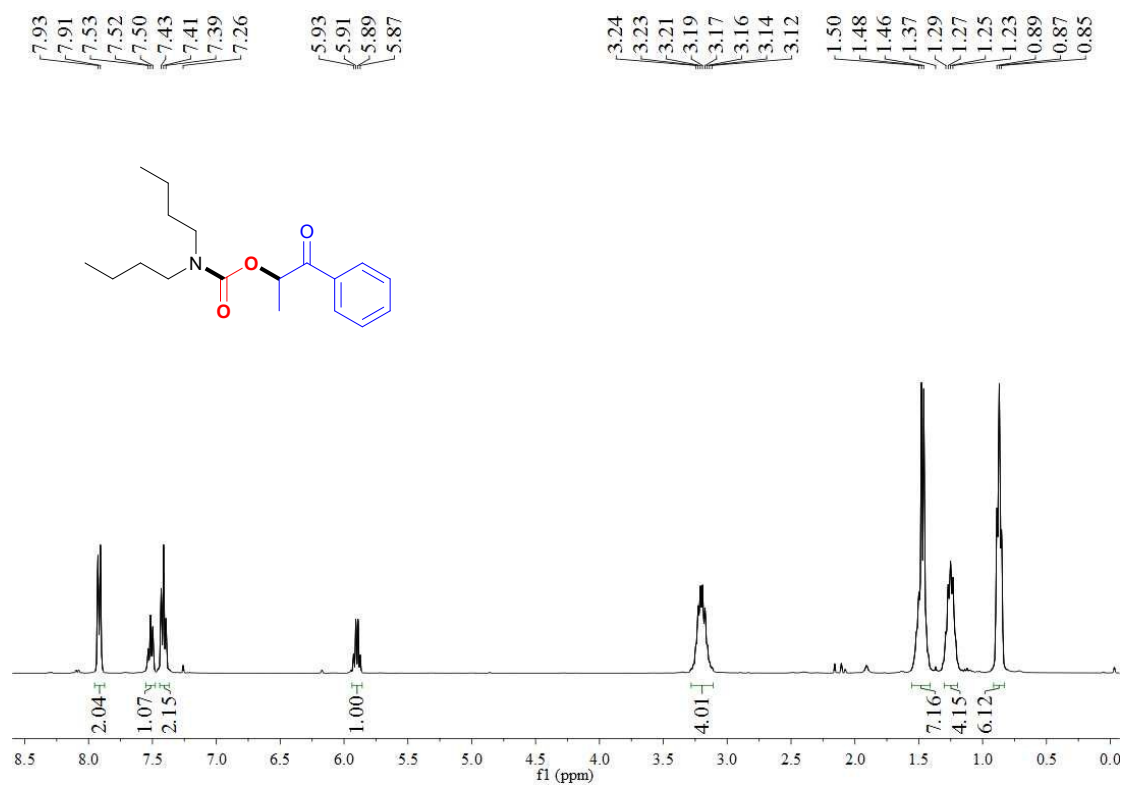
### 3-Oxo-3-phenylprop-1-en-2-yl diethylcarbamate (3ra)



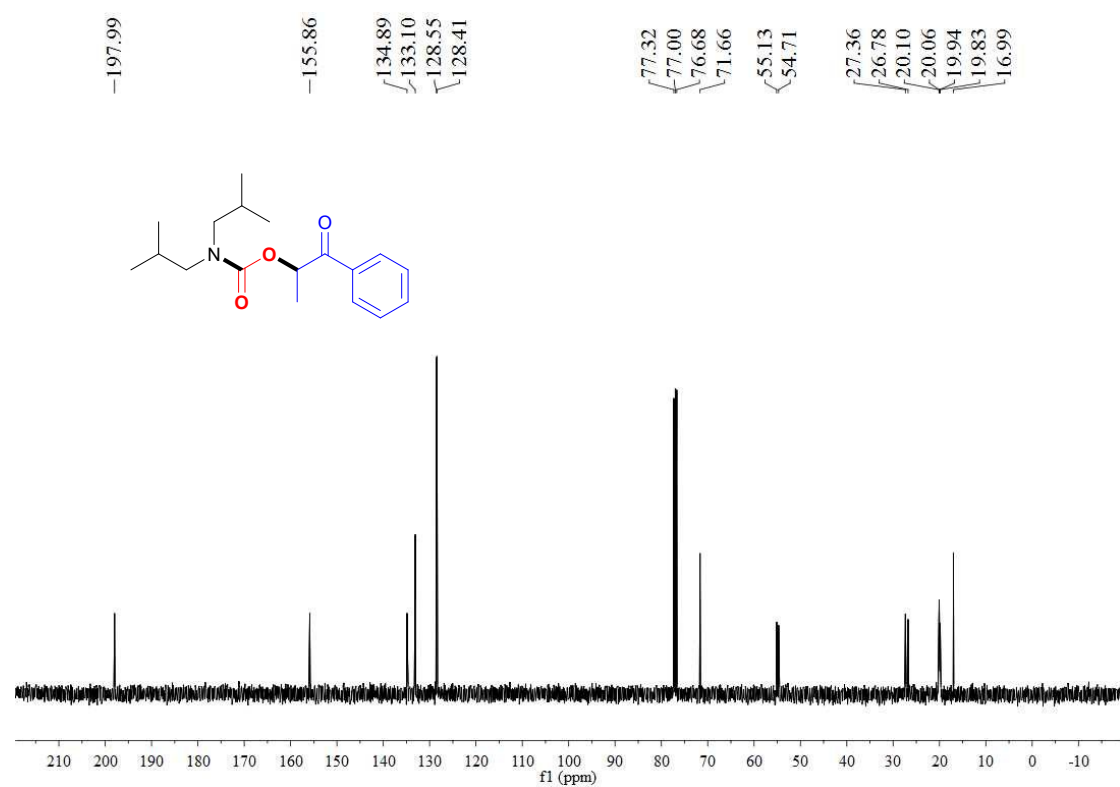
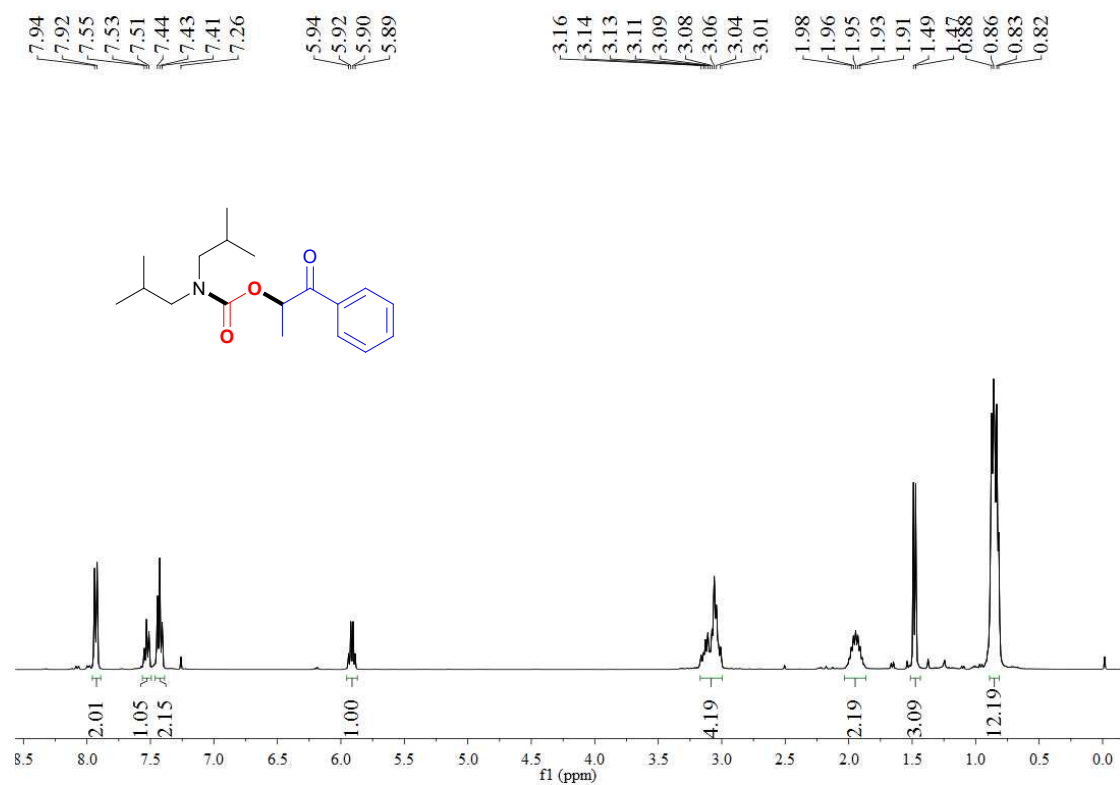
# 1-Oxo-1-phenylpropan-2-yl dipropylcarbamate (3ab)



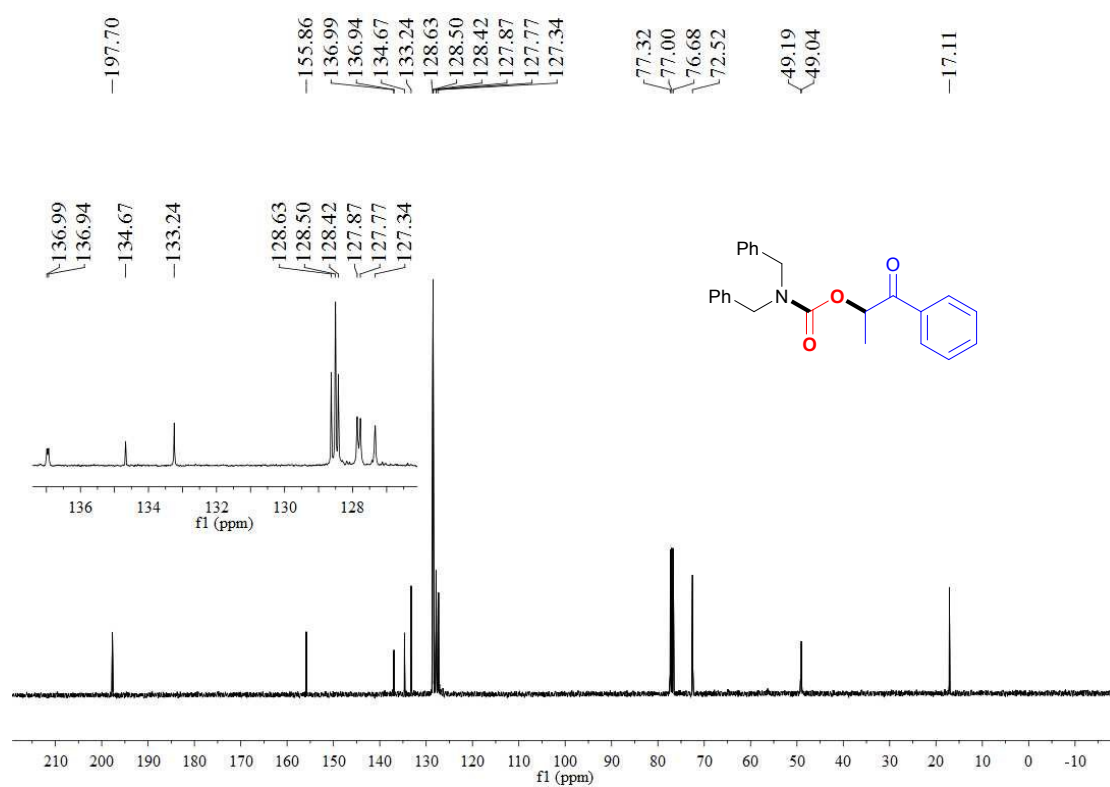
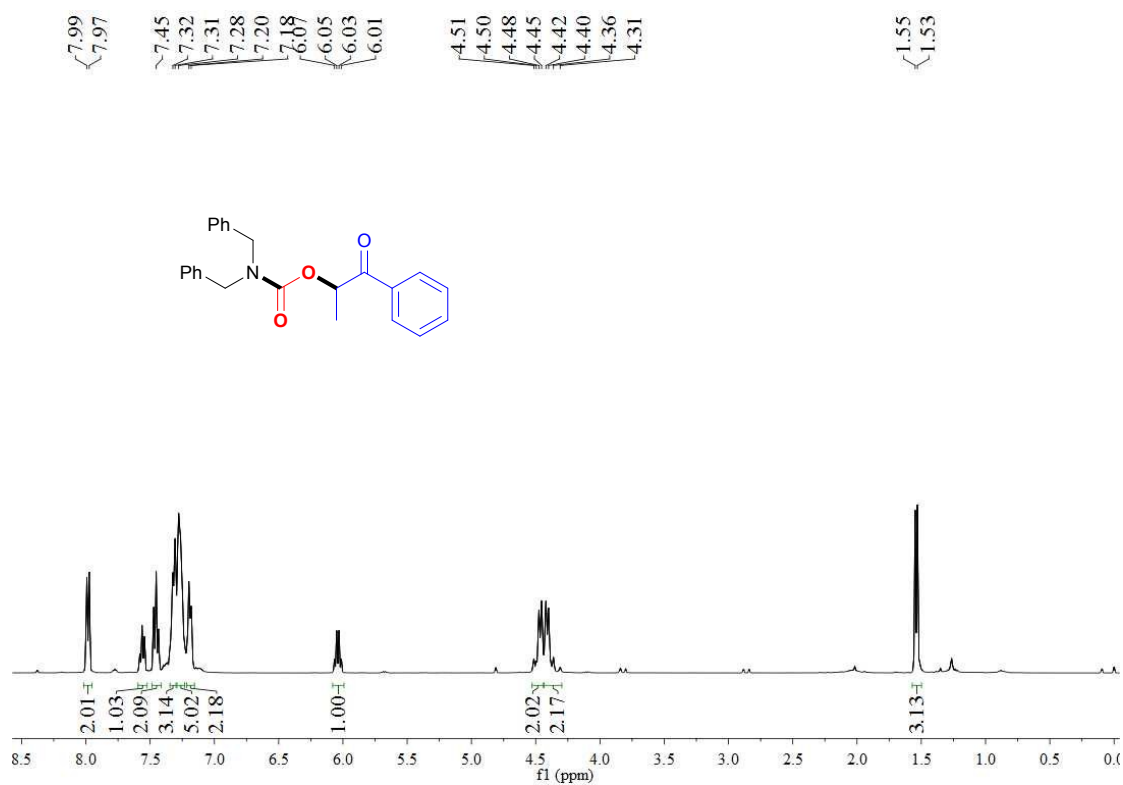
# 1-Oxo-1-phenylpropan-2-yl dibutylcarbamate (3ac)



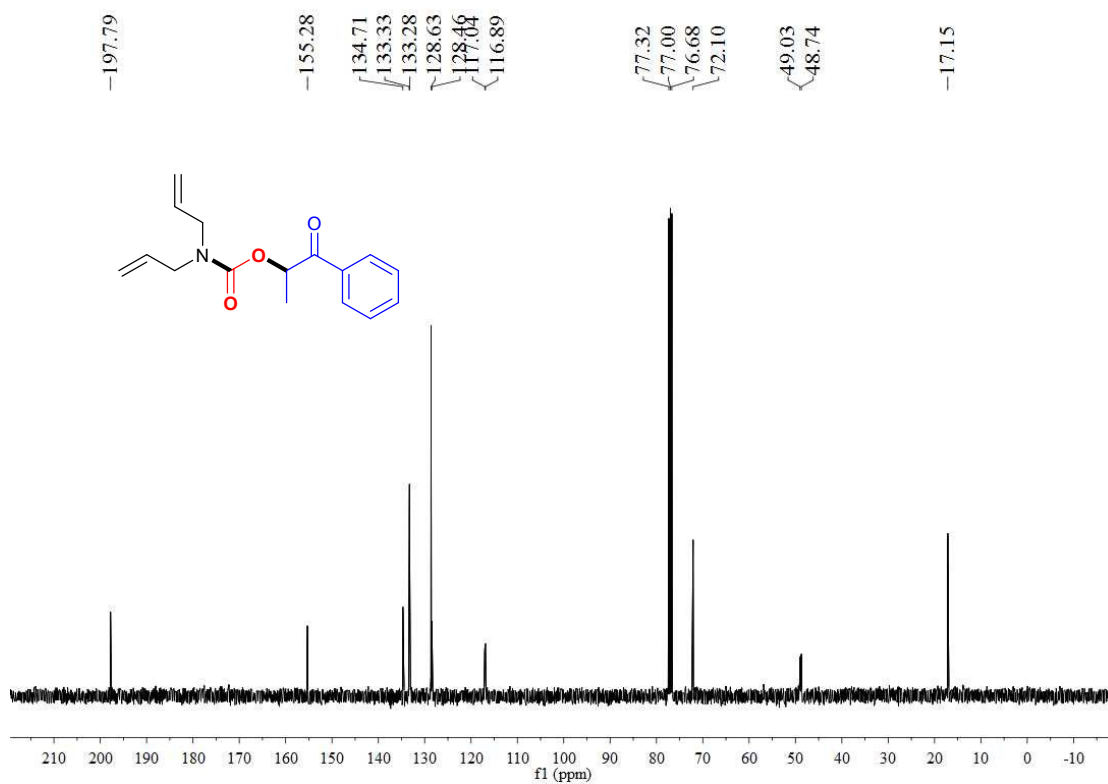
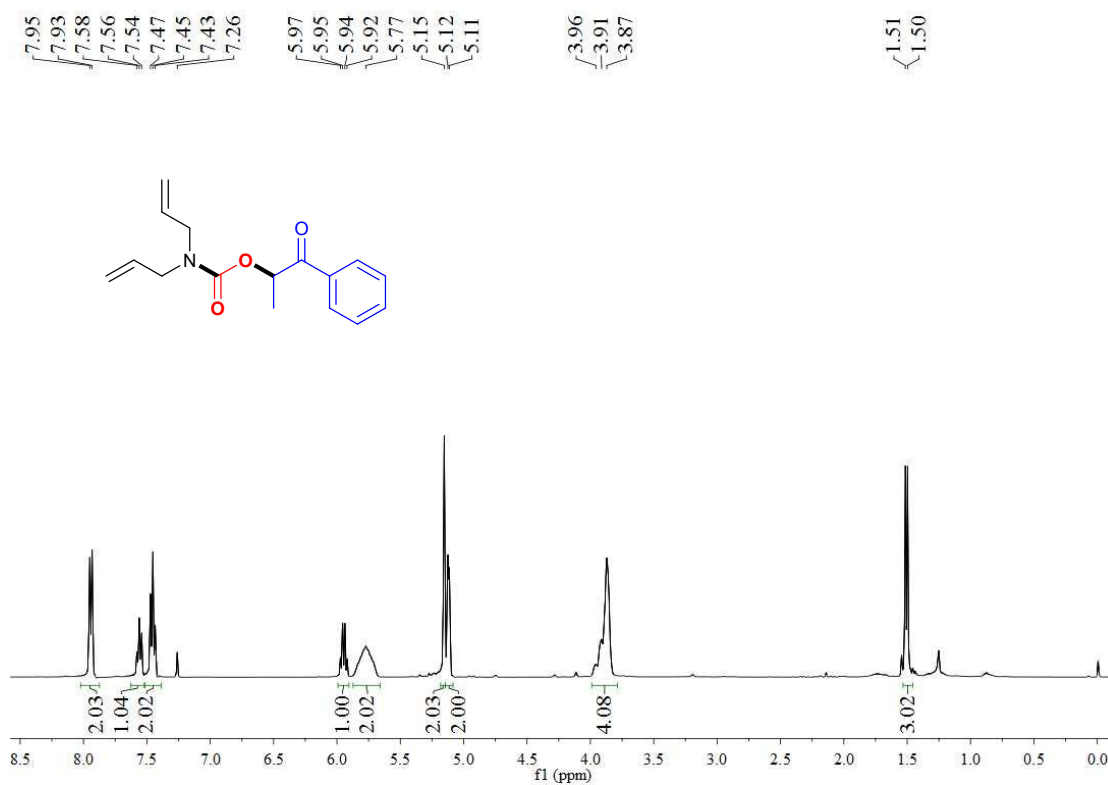
# 1-Oxo-1-phenylpropan-2-yl diisobutylcarbamate (3ad)



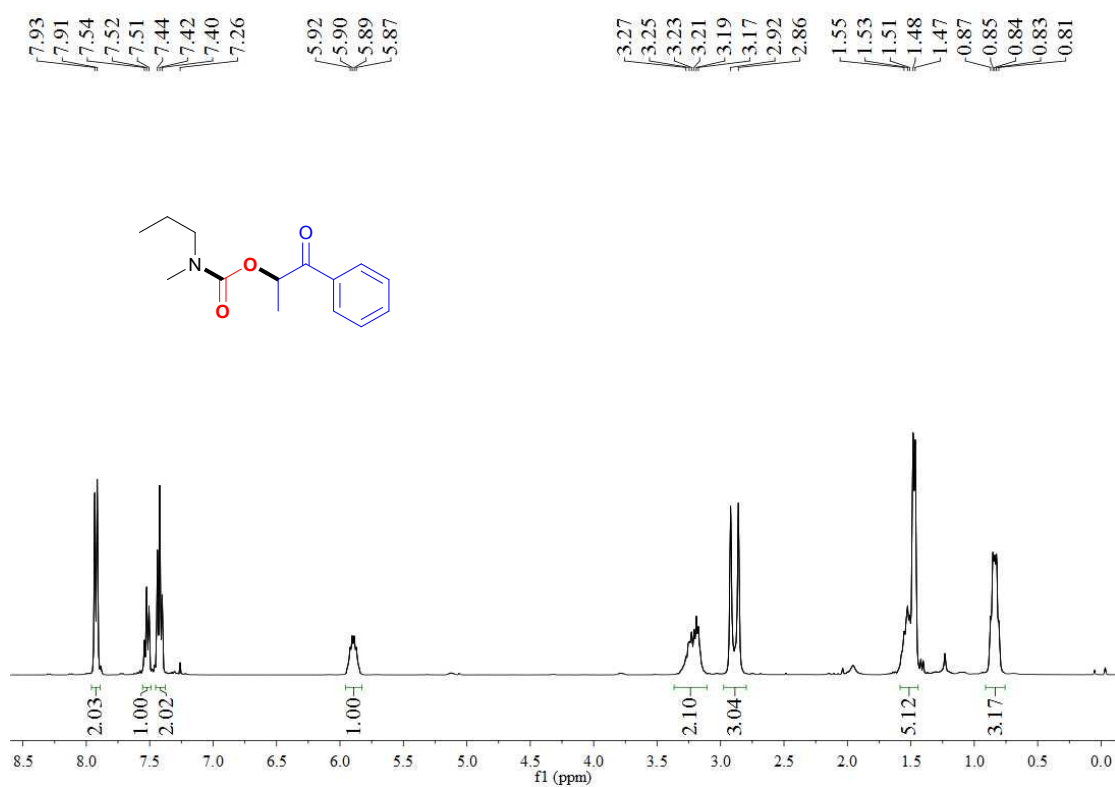
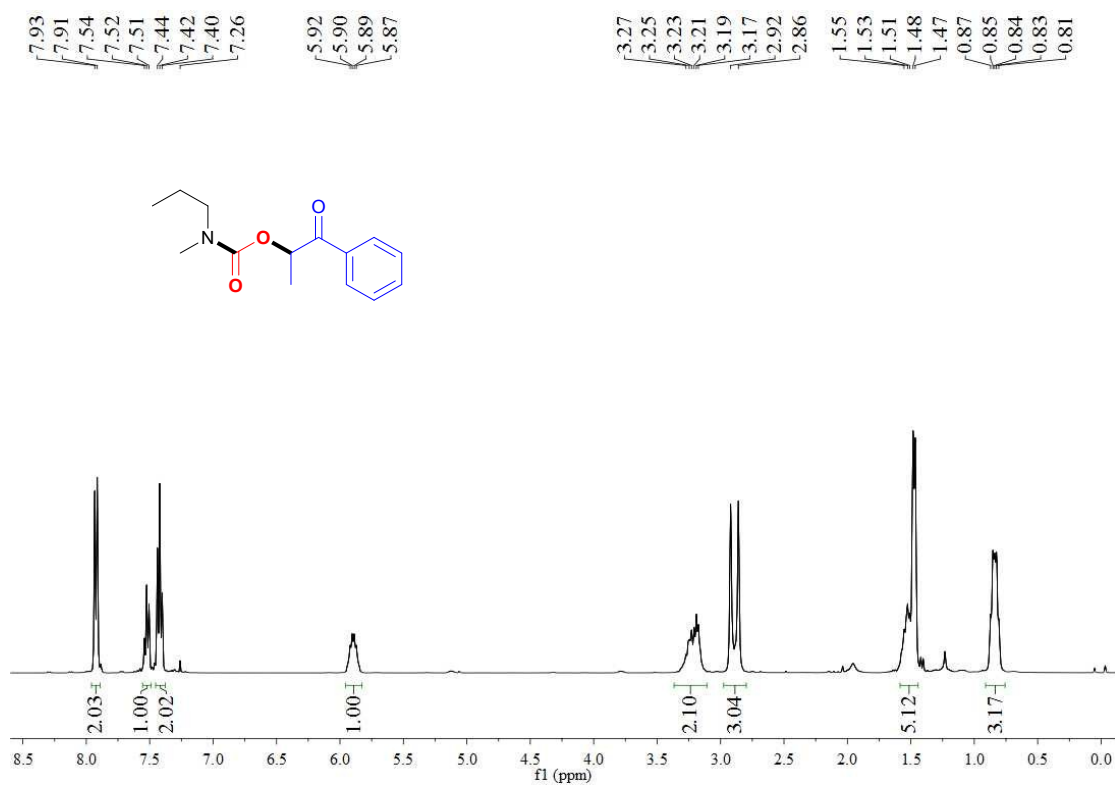
# 1-Oxo-1-phenylpropan-2-yl dibenzylcarbamate (3ae)



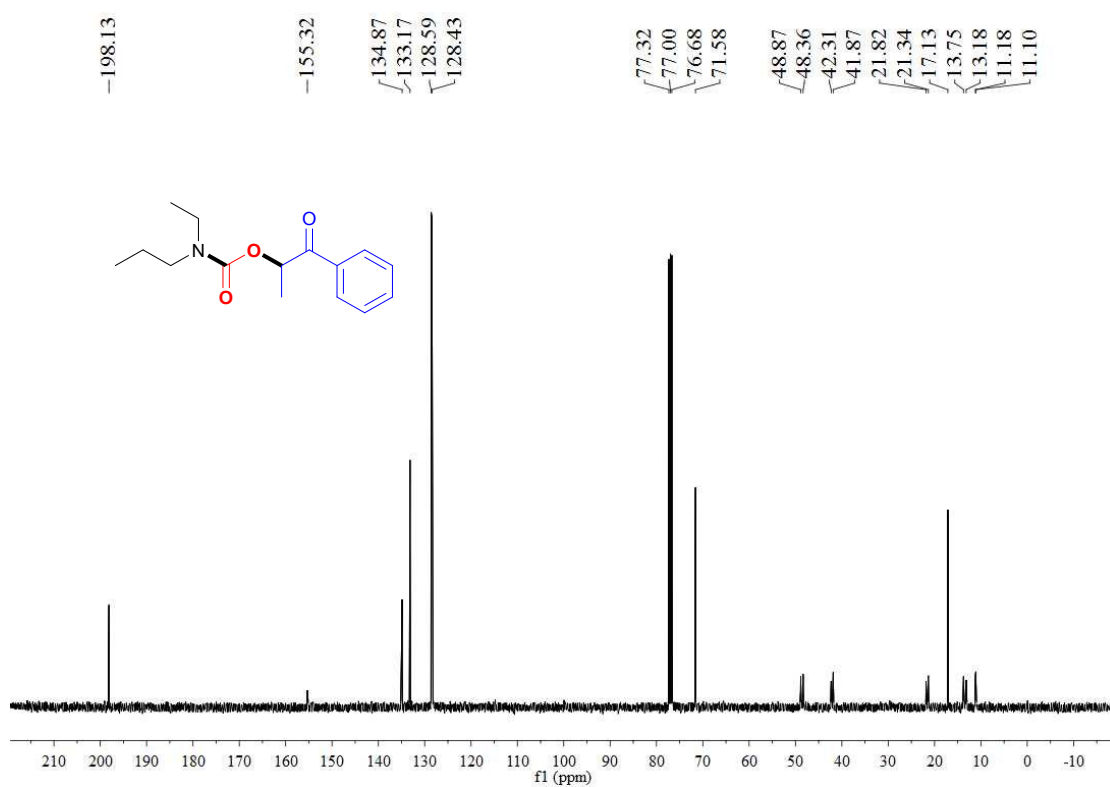
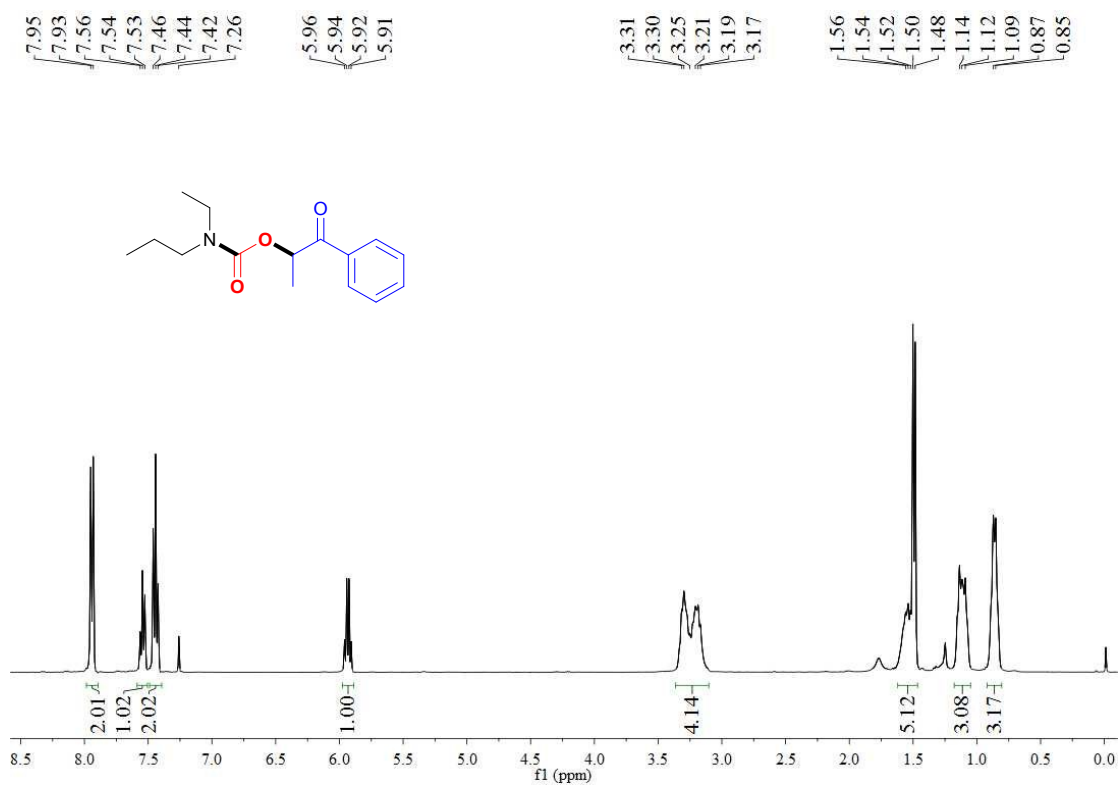
# 1-Oxo-1-phenylpropan-2-yl diallylcarbamate (3af)



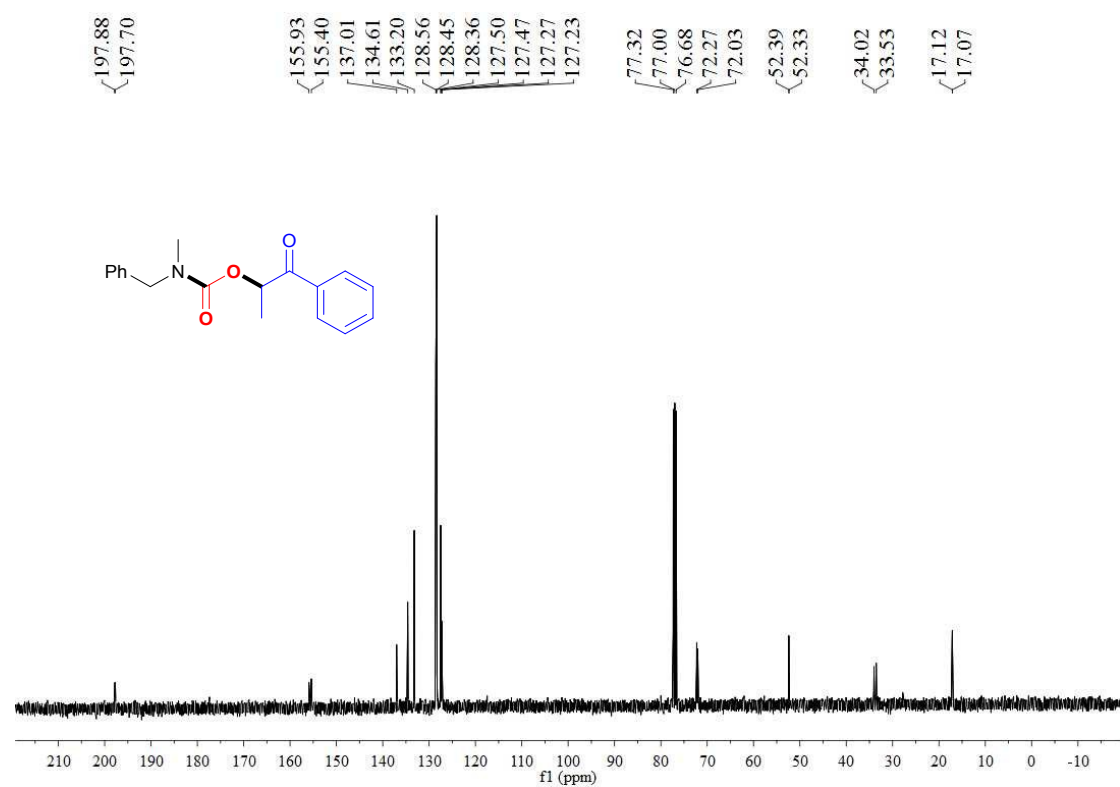
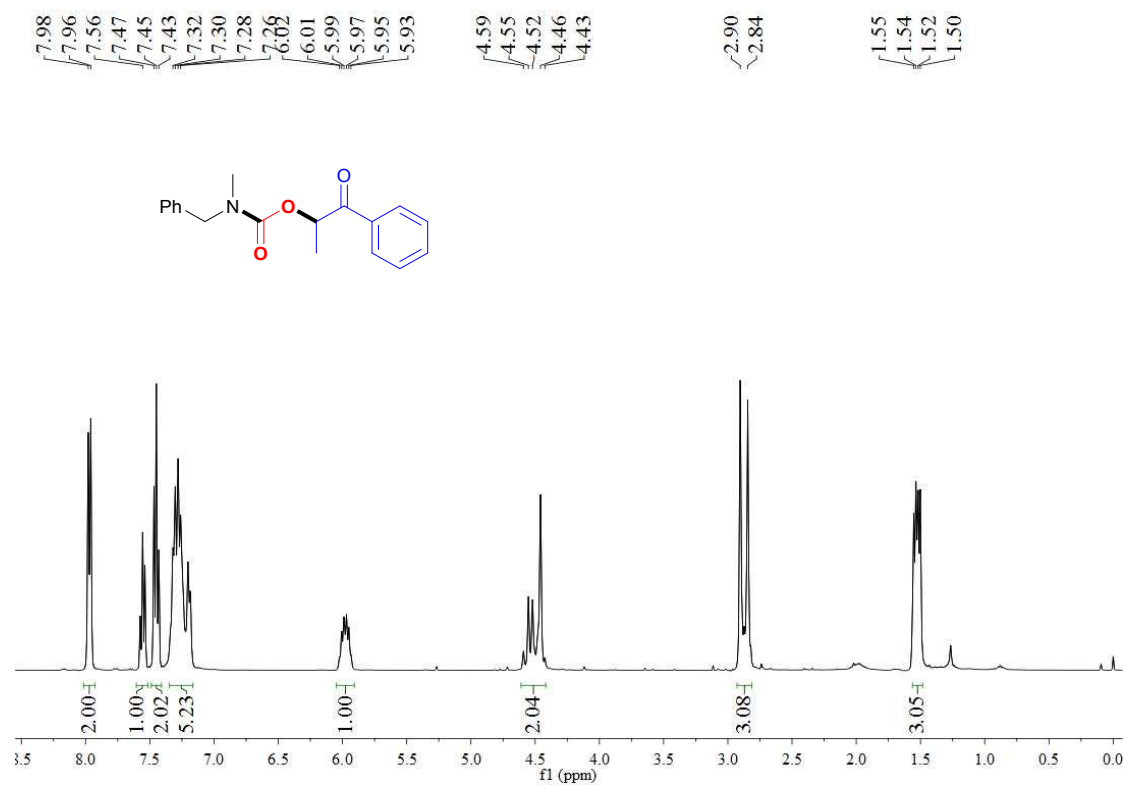
# 1-Oxo-1-phenylpropan-2-yl methyl(propyl)carbamate (3ag)



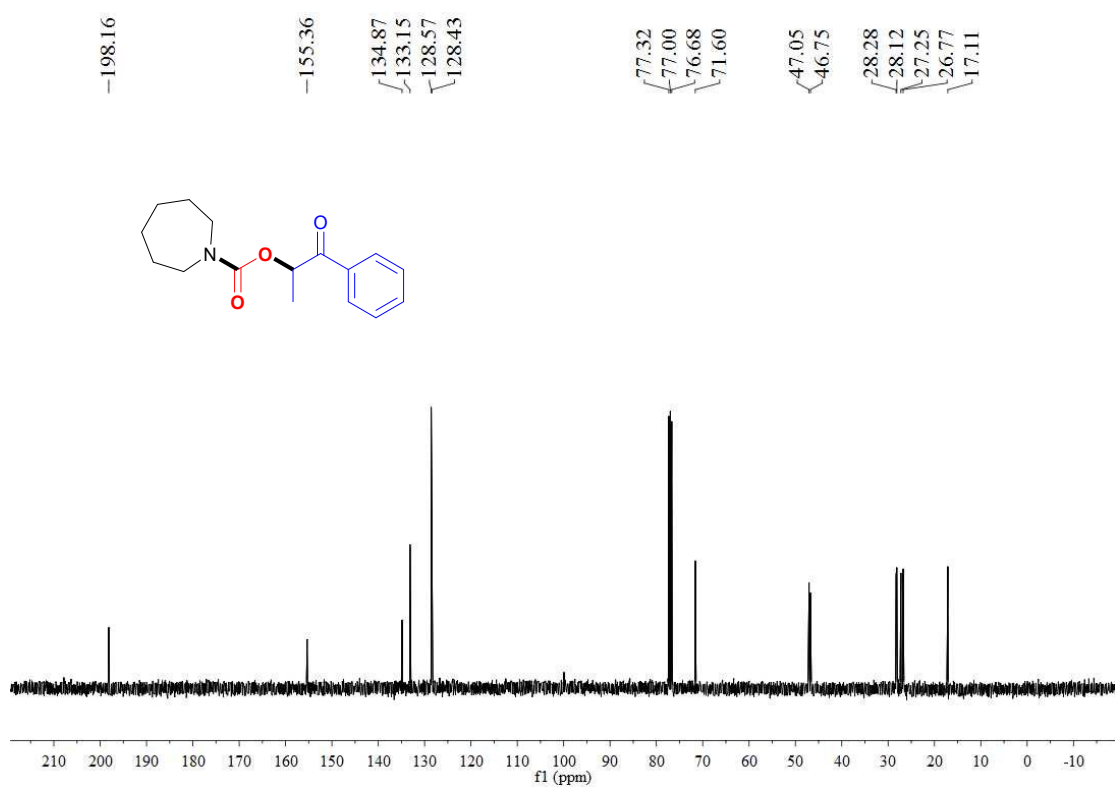
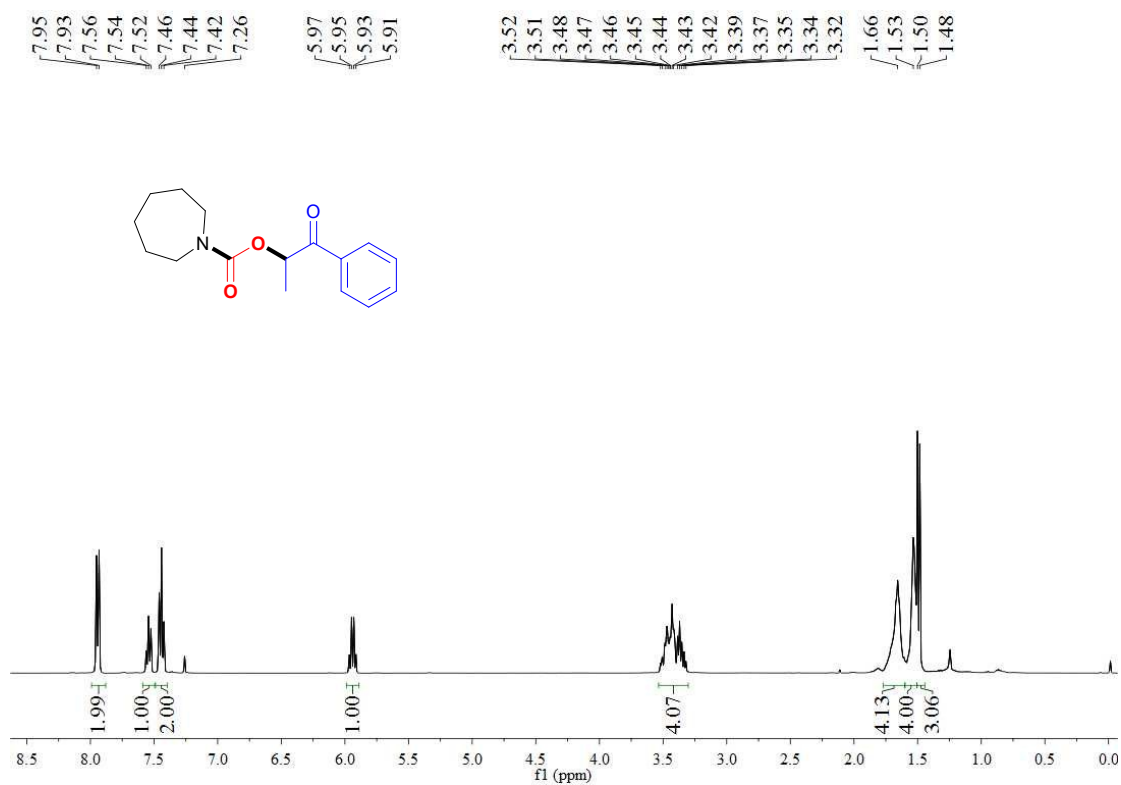
# 1-Oxo-1-phenylpropan-2-yl ethyl(propyl)carbamate (3ah)



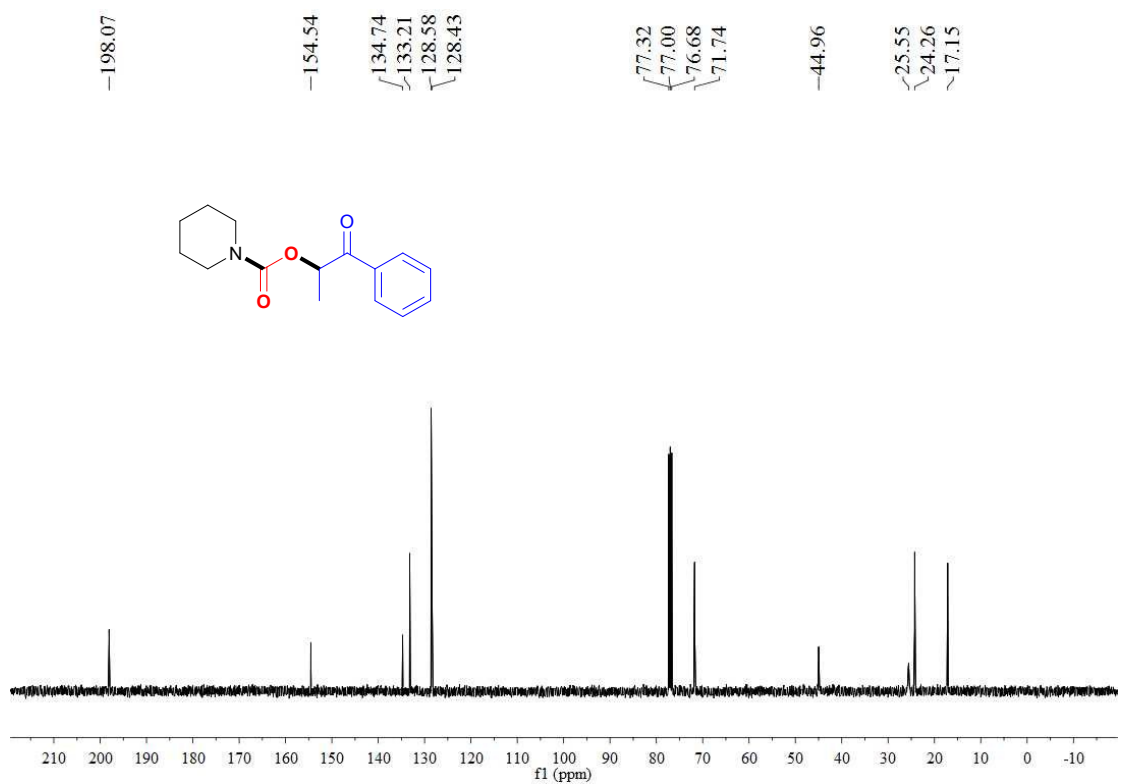
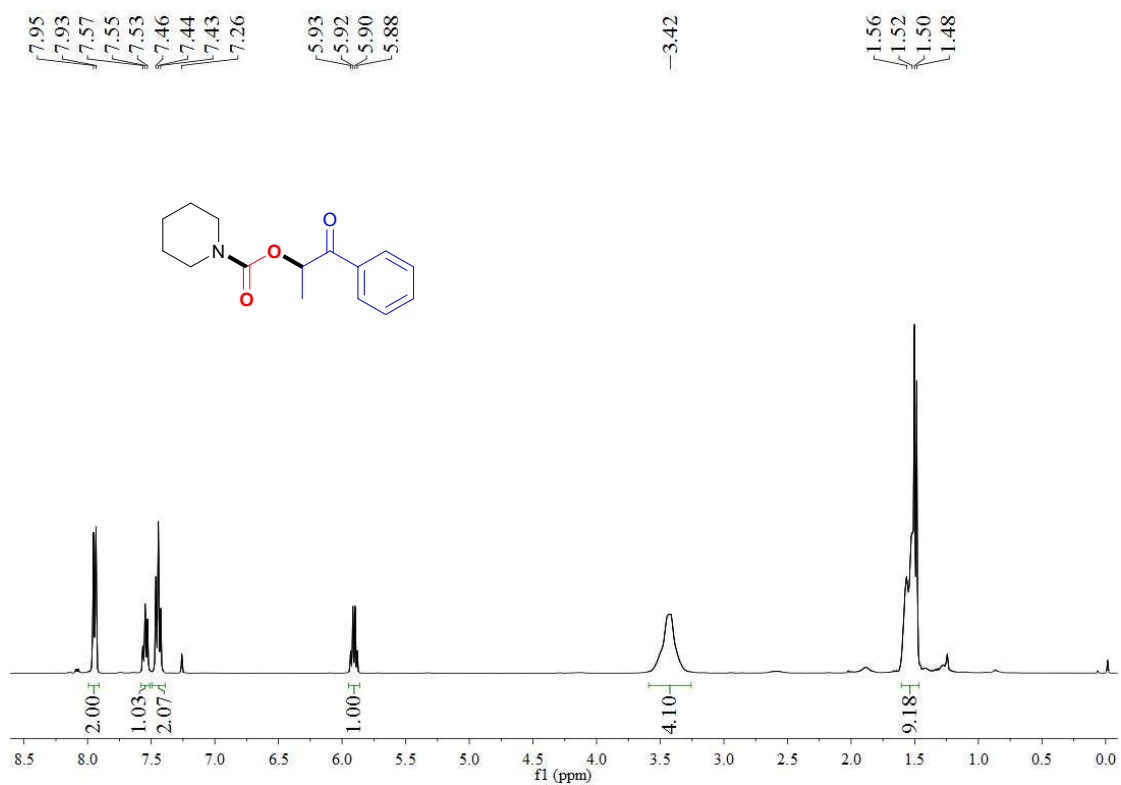
# 1-Oxo-1-phenylpropan-2-yl benzyl(methyl)carbamate (3ai)



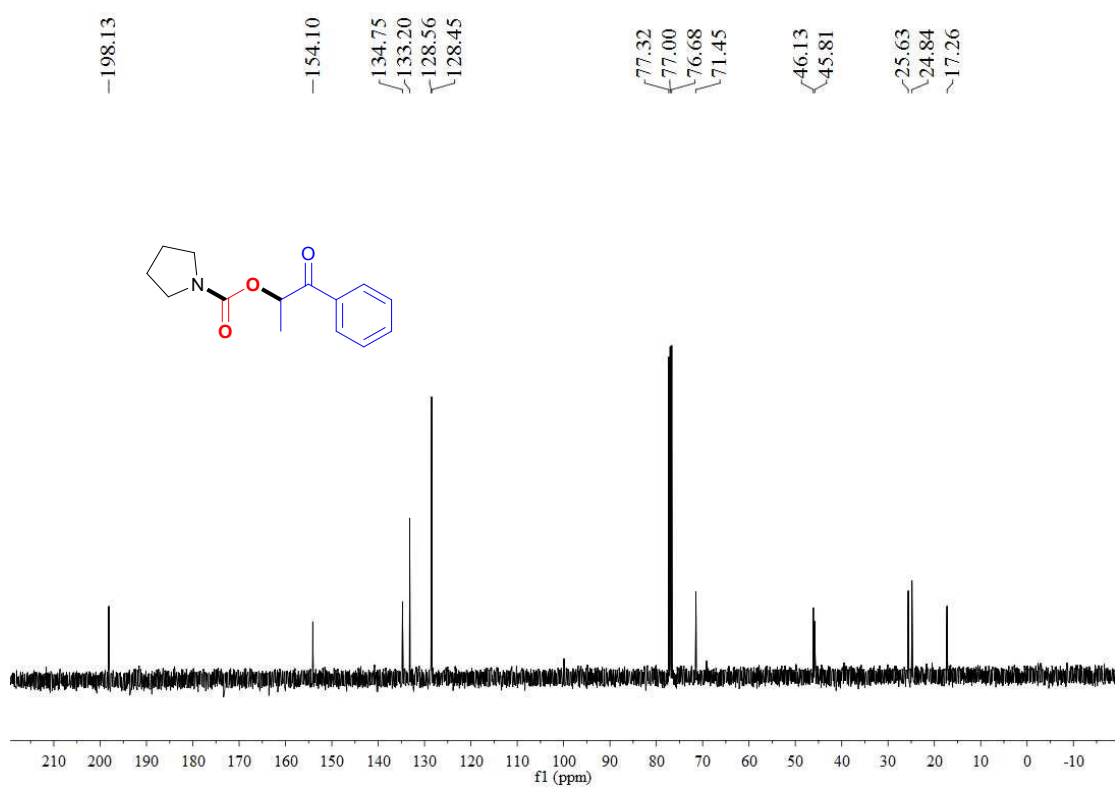
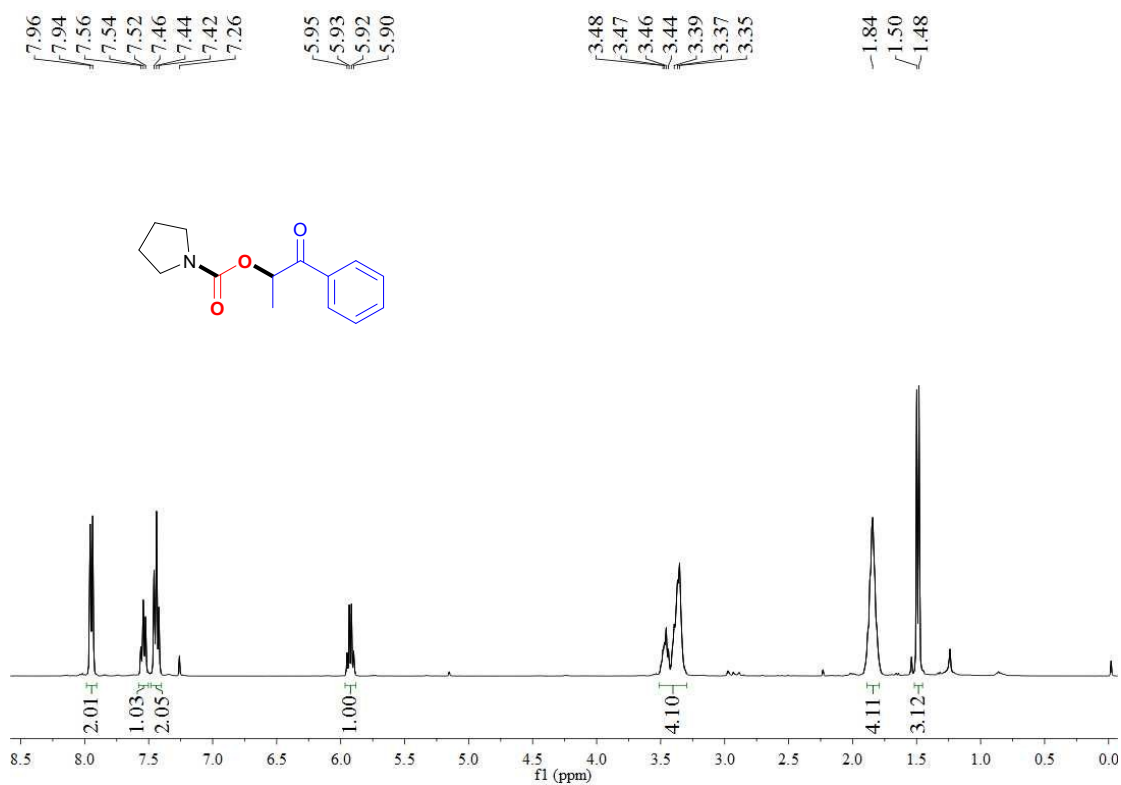
# 1-Oxo-1-phenylpropan-2-yl azepane-1-carboxylate (3aj)



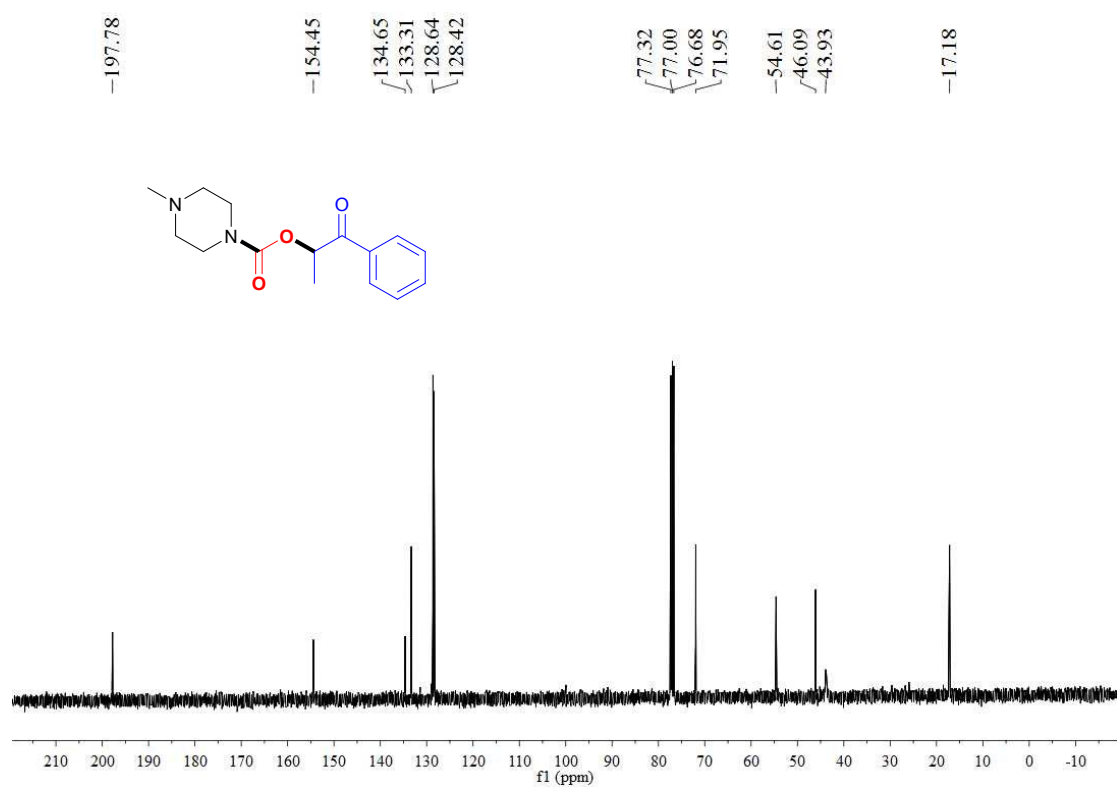
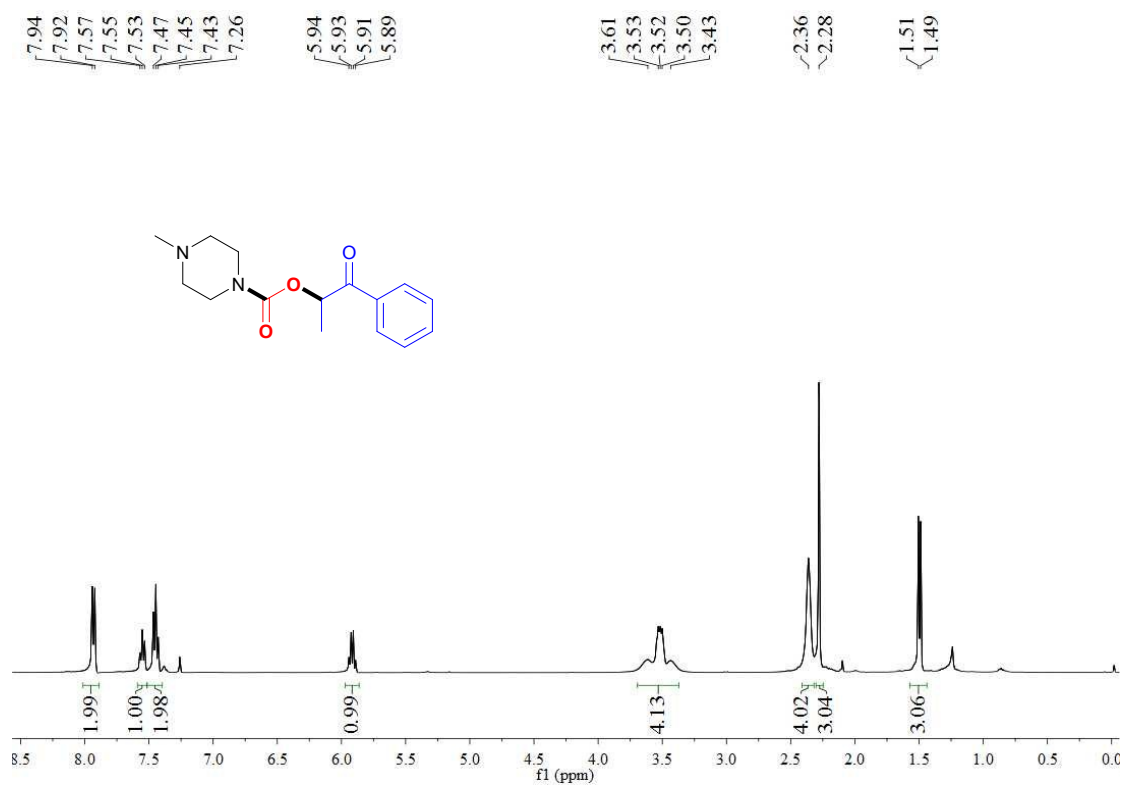
# 1-Oxo-1-phenylpropan-2-yl piperidine-1-carboxylate (3ak)



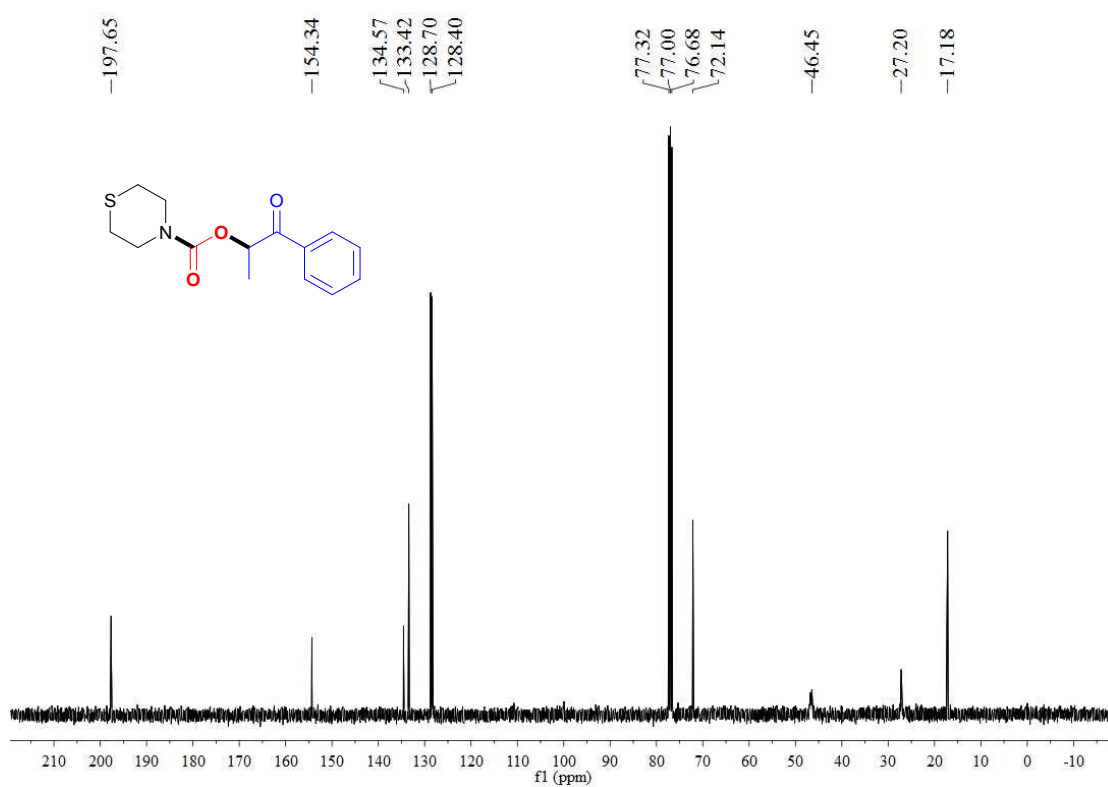
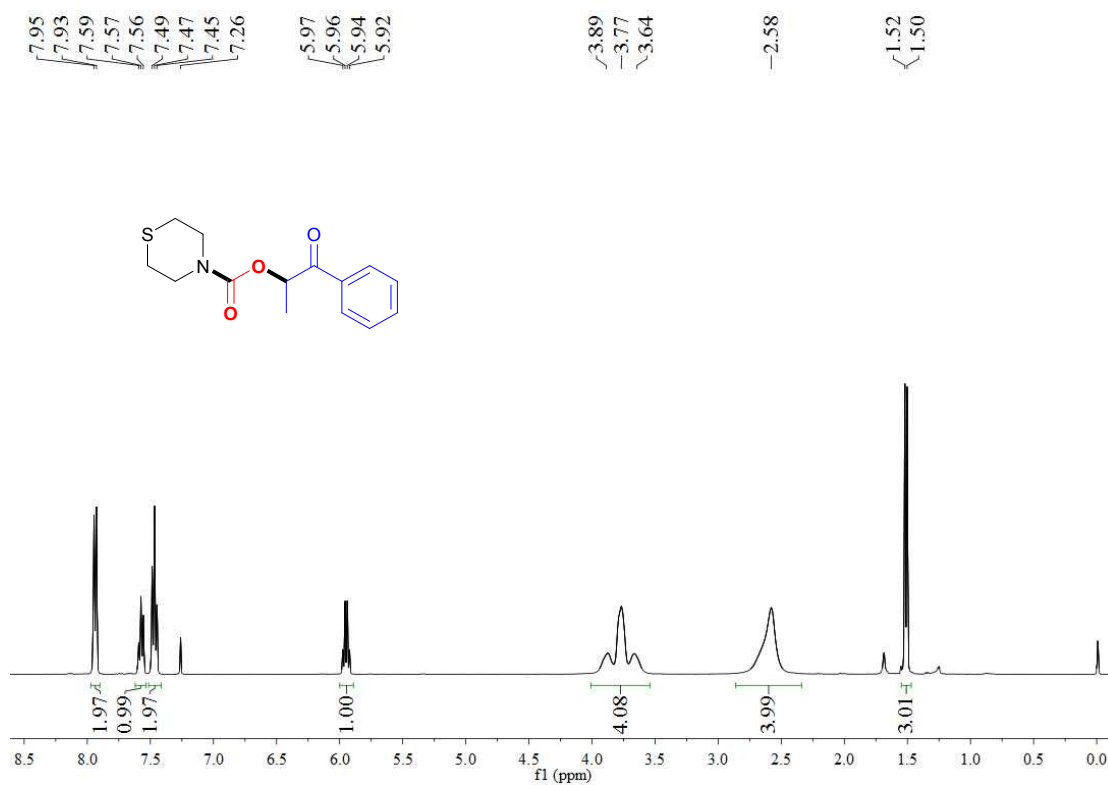
# 1-Oxo-1-phenylpropan-2-yl pyrrolidine-1-carboxylate (3al)



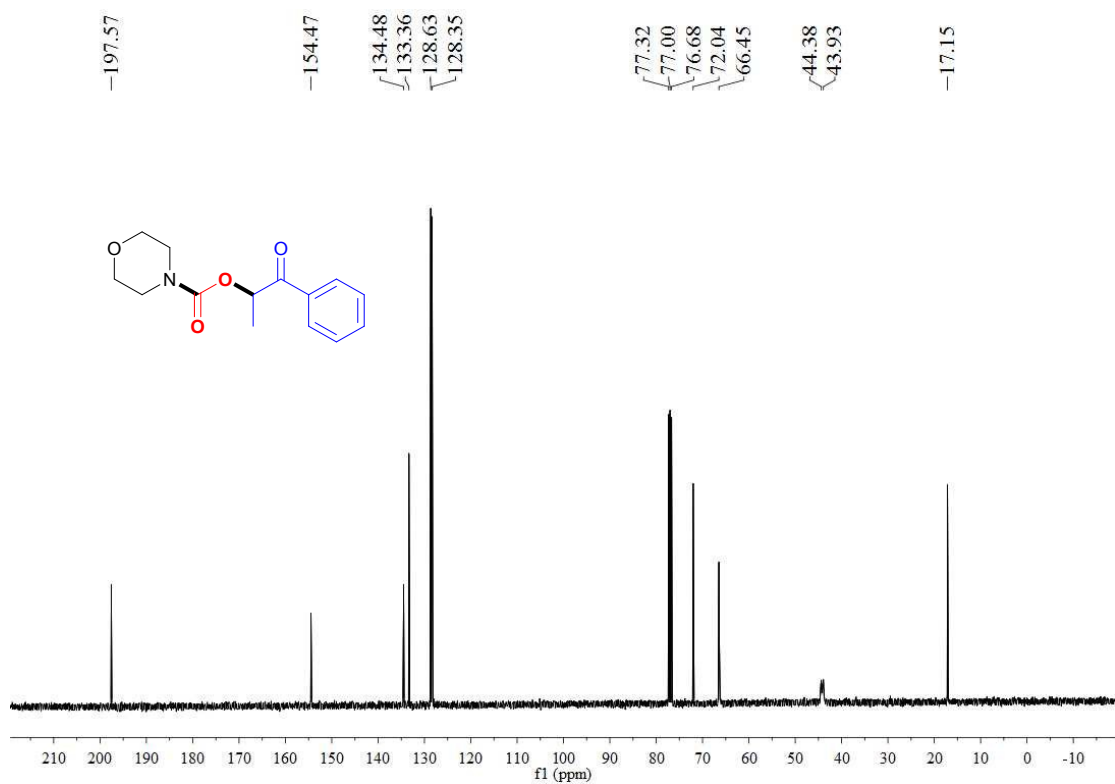
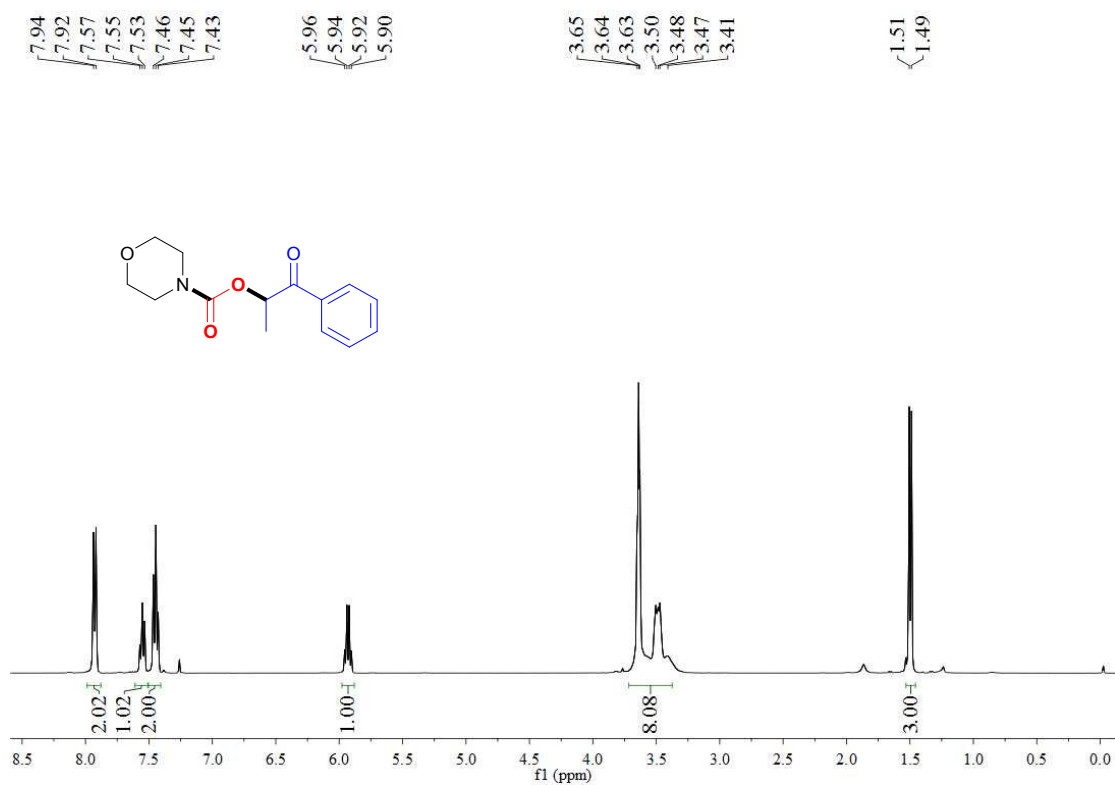
# 1-Oxo-1-phenylpropan-2-yl 4-methylpiperazine-1-carboxylate (3am)



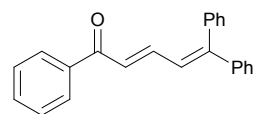
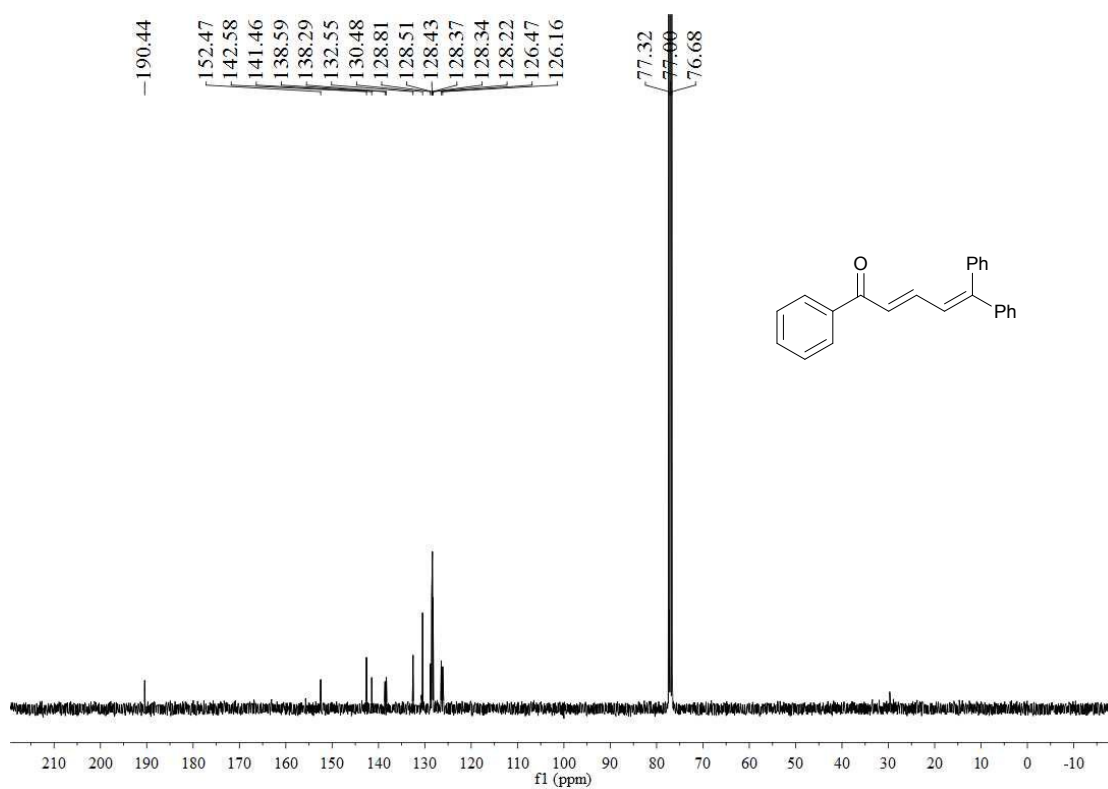
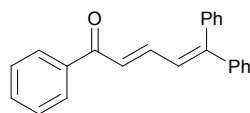
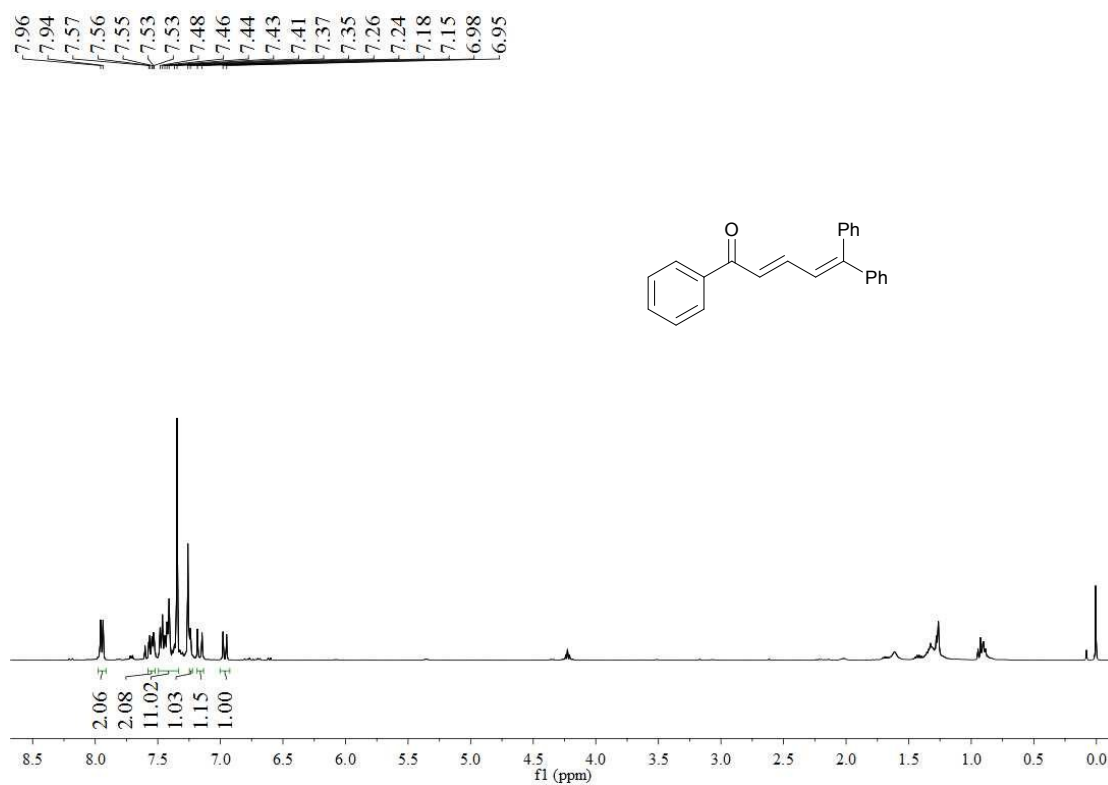
# 1-Oxo-1-phenylpropan-2-yl thiomorpholine-4-carboxylate (3an)



# 1-Oxo-1-phenylpropan-2-yl morpholine-4-carboxylate (3ao)



**(E)-1,5,5-Triphenylpenta-2,4-dien-1-one (5)**



## F. Crystal structure determination

Single-crystal X-ray diffraction data for **3an** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using CuK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on  $F^2$  by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Crystallographic data for compound **3an** is given in Table S2.

**Table S2.** Crystal data and structure refinements for **3an**

| Compound                               | <b>3an</b>                                                                                                                                               |
|----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Empirical formula                      | C <sub>14</sub> H <sub>17</sub> NO <sub>3</sub> S                                                                                                        |
| Formula weight                         | 279.35                                                                                                                                                   |
| Temperature (K)                        | 150.00 (10)                                                                                                                                              |
| Wavelength (Å)                         | 1.54184                                                                                                                                                  |
| Crystal system                         | monoclinic                                                                                                                                               |
| Space group                            | $P2_1/n$<br>$a = 10.04588(15)$ Å $\alpha = 90.00^\circ$<br>$b = 9.57981(12)$ Å $\beta = 109.0008(16)^\circ$<br>$c = 15.0463(2)$ Å $\gamma = 90.00^\circ$ |
| Volume (Å <sup>3</sup> )               | 1369.13(3)                                                                                                                                               |
| Z                                      | 4                                                                                                                                                        |
| Density (calcd g cm <sup>-3</sup> )    | 1.355                                                                                                                                                    |
| Absorption coeff. (mm <sup>-1</sup> )  | 2.140                                                                                                                                                    |
| $F(000)$                               | 592                                                                                                                                                      |
| Crystal size (mm)                      | $0.35 \times 0.32 \times 0.21$                                                                                                                           |
| Crystal color and shape                | Colorless block                                                                                                                                          |
| $\theta$ range for data collection     | 4.6700 to 73.8600                                                                                                                                        |
| Limiting indices                       | $-12 \leq h \leq 11$ , $-11 \leq k \leq 10$ , $-17 \leq l \leq 18$                                                                                       |
| Reflections collected                  | 5057                                                                                                                                                     |
| Unique                                 | 2703 [ $R_{\text{int}} = 0.0136$ ]                                                                                                                       |
| Refinement method                      | Full-matrix least-squares on $F^2$                                                                                                                       |
| Data/restraints/parameters             | 2703/0/173                                                                                                                                               |
| Goodness-of-fit on $F^2$               | 1.071                                                                                                                                                    |
| Final $R$ indexes [ $I > 2\sigma(I)$ ] | $R_1 = 0.0312$ , $wR_2 = 0.0809$                                                                                                                         |
| $R$ indexes (all data)                 | $R_1 = 0.0331$ , $wR_2 = 0.0824$                                                                                                                         |