Supporting Information

Visible Light-Promoted Synthesis of Organic Carbamates from Carbon Dioxide under Catalyst- and Additive-Free Conditions

Ruixiang Cheng,[a] Chaorong Qi,*[a, b] Lu Wang,[a] Wenfang Xiong,[a] Hongjian Liu[a] and Huanfeng Jiang*[a]

[a] *Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China*

[b] *State Key Lab of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

E-mail: crqi@scut.edu.cn or jianghf@scut.edu.cn

List of Contents

A. General methods

^{1}H and ^{13}C NMR spectra were recorded by using a 400 or 500 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with an infrared spectrometer. Melting points were determined with a digital melting point measuring instrument. Substrates **1a-1q** were prepared according to the literature procedure,[1] and other reagents were commercially purchased and used without further purification.

B. General procedure for the preparation of carbamates 3

To a 25 ml dried Schlenk tube equipped with a magnetic stirring bar was added 0.1 mmol of *α*-aryldiazoester **1**. The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged further with 0.1 mmol of amine **2** and 1 mL of THF via a syringe. The reaction mixture was stirred at room temperature for 1 h under 10 W blue LEDs irradiation. After the reaction was completed, the mixture was concentrated under reduced pressure using a rotary evaporator, so the unreacted THF could be recovered and then purified by fractional distillation for reuse. The crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate as the eluent to give the desired product **3**.

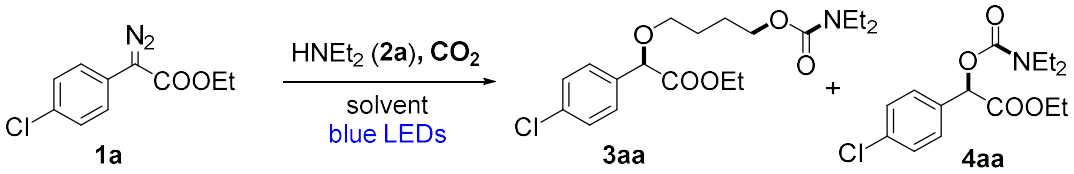
C. General procedure for the preparation of carbamates 4

To a 25 ml dried Schlenk tube equipped with a magnetic stirring bar was added 0.1 mmol of *α*-aryldiazoester **1**. The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged further with 0.1 mmol of amine **2**, 0.5 ml of CH_3CN and 0.5 mL of 1,4-dioxane via a syringe. The reaction mixture was stirred at room temperature for 1 h under 10 W blue LEDs irradiation. After the reaction was completed, the mixture was concentrated under reduced pressure using a rotary evaporator, so the solvent could be recovered and then purified by fractional distillation for reuse. The crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate as the eluent to give the desired products **4**.

D. The influence of different bases on the reaction

Different organic or inorganic bases, including K_2CO_3, Na_2CO_3, Li_2CO_3, K_3PO_4, DABCO, TBD and ^{t}BuOK were investigated for the reaction (Table S1). The results showed that the addition of different bases (even 3 equivalents) had no positive effect on the reaction.

Table S1 The influence of different bases on the reaction [a]



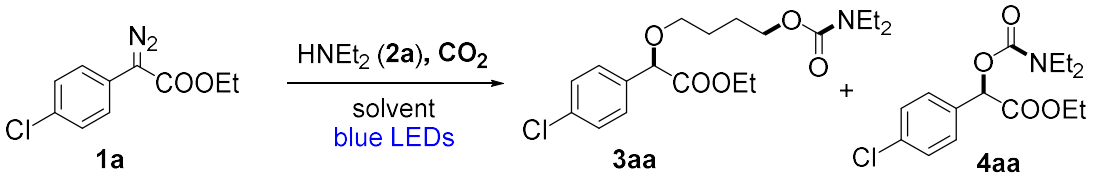
Entry	Solvent (v:v)	Base (equiv.)	Conversion of **1a** (%)[b]	Yield (%)[c]	
				3aa	**4aa**
1	THF	K_2CO_3 (1.0)	100	81	/
2	THF	K_2CO_3 (2.0)	100	81	/
3	THF	K_2CO_3 (3.0)	100	82	/
4	THF	Na_2CO_3 (1.0)	100	81	/
5	THF	Li_2CO_3 (1.0)	100	80	/
6	THF	K_3PO_4 (1.0)	100	82	/
7	THF	DABCO (1.0)	100	34	/
8	THF	DBU (1.0)	100	83	/
9	THF	TBD (1.0)	100	78	/
10	THF	^{t}BuOK (1.0)	100	45	/
11[d]	THF	-	100	83	/
12	1,4-dioxane/MeCN (1:1)	K_2CO_3 (1.0)	100	/	72
13	1,4-dioxane/MeCN (1:1)	K_2CO_3 (2.0)	100	/	71
14	1,4-dioxane/MeCN (1:1)	K_2CO_3 (3.0)	100	/	70
15[d]	1,4-dioxane/MeCN (1:1)	-	100	/	75

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), solvent (1 mL), CO_2 (1 atm), 10 W blue LEDs, room temperature, 24 h. [b] Determined by ^{1}H NMR analysis. [c] Yields were based on ^{1}H NMR analysis of the crude product using CH_2Br_2 or CH_3NO_2 as an internal standard; number in parentheses is the yield of isolated product. [d] Reaction time: 1 h. DABCO (1,4-Diazabicyclo[2.2.2]octane). DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene). TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene).

E. The influence of the amount of diethylamine (2a) on the reaction

The addition amount of diethylamine (**2a**) on the reaction was also examined. As can be seen from Table S2, the addition of 1.0 equivalent of **2a** was enough for the reaction to complete. Increasing the amount of **2a** from 1 equivalent to 3 equivalents did not lead to the improvement of the yields of the desired products.

Table S2 The influence of the amount of diethylamine (**2a**) on the reaction [a]



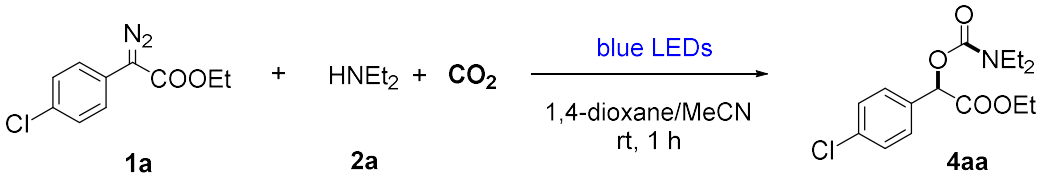
Entry	Solvent (v:v)	**2a** (equiv.)	Yield (%)[b]	
			3aa	**4aa**
1	THF	1.0	83	/
2	THF	2.0	82	/
3	THF	3.0	83	/
4	1,4-dioxane/MeCN (1:1)	1.0	/	75
5	1,4-dioxane/MeCN (1:1)	2.0	/	73
6	1,4-dioxane/MeCN (1:1)	3.0	/	74

[a] Reaction conditions: **1a** (0.1 mmol), solvent (1 mL), CO_2 (1 atm), 10 W blue LEDs, room temperature,1 h. [b] Yield based on ^{1}H NMR analysis of the crude product using CH_2Br_2 or CH_3NO_2 as an internal standard.

F. The influence of the volume ratio of 1,4-dioxane to MeCN on the synthesis of 4aa

The influence of the volume ratio of 1,4-dioxane to MeCN on the three-component reaction of **1a, 2a** and CO_2 was investigated (Table S3). The experiment results showed that the 1:1 mixture of 1,4-dioxane and MeCN was the best solvent for the reaction, giving the desired product **4aa** in 75% yield (entry 1).

Table S3 The influence of the volume ratio of 1,4-dioxane to acetonitrile on the formation of **4aa** [a]



1a **2a** **4aa**

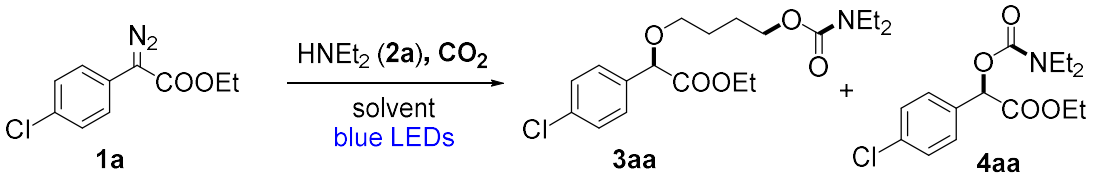
Entry[a]	Solvent (v:v)	Yield of **4aa** (%)[b]
1	1,4-dioxane/MeCN (1:1)	75
2	1,4-dioxane/MeCN (1:2)	63
3	1,4-dioxane/MeCN (1:3)	60
4	1,4-dioxane/MeCN (1:4)	58
5	1,4-dioxane/MeCN (1:5)	56
6	1,4-dioxane/MeCN (1:10)	48
7	1,4-dioxane/MeCN (2:1)	69
8	1,4-dioxane/MeCN (3:1)	66
9	1,4-dioxane/MeCN (4:1)	64
10	1,4-dioxane/MeCN (5:1)	66
11	1,4-dioxane/MeCN (10:1)	58

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), solvent (1 mL), CO_2 (1 atm), 10 W blue LEDs, room temperature, 1 h. [b] Yields were based on ^{1}H NMR analysis of the crude product using CH_3NO_2 as an internal standard.

G. The influence of temperature on the reaction

The influence of temperature on the reaction was also studied. As can be seen from Table S4, under room temperature (25 °C), the desired products **3aa** and **4aa** could be obtained in 83% and 75% yield, respectively (entries 3 and 7). Decreasing the reaction temperature to 10 °C or increasing the temperature to 30 °C had little influence on the reaction.

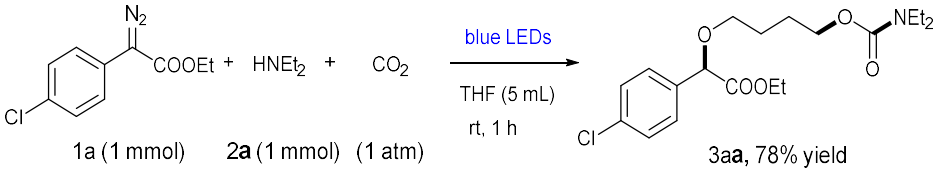
Table S4 Influence of the reaction temperature on the reaction [a]



Entry[a]	Solvent (v:v)	Temperature (°C)	Yield[b] (%)	
			3aa	**4aa**
1	THF	10	81	/
2	THF	20	83	/
3	THF	25 (room temperature)	83	/
4	THF	30	82	/
5	1,4-dioxane/MeCN (1:1)	10	/	75
6	1,4-dioxane/MeCN (1:1)	20	/	74
7	1,4-dioxane/MeCN (1:1)	25 (room temperature)	/	75
8	1,4-dioxane/MeCN (1:1)	30	/	73

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.1 mmol), solvent (1 mL), CO_2 (1 atm), 10 W blue LEDs, 1 h. [b] Yields were based on ^{1}H NMR analysis of the crude product using CH_2Br_2 or CH_3NO_2 as an internal standard.

H. Procedure for the synthesis 3aa in a larger scale

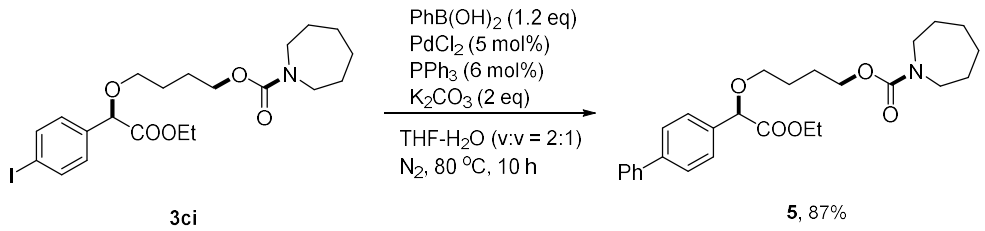


To a 100 ml dried Schlenk tube equipped with a magnetic stirring bar was added 1 mmol of ethyl 2-(4-chlorophenyl)-2-diazoacetate (**1a**). The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged further with 1 mmol of diethylamine (**2a**) and 5 mL of THF via a syringe.

The reaction mixture was stirred at room temperature for 1 h under 10 W blue LEDs irradiation. After the reaction was completed, the mixture was concentrated under reduced pressure using a rotary evaporator, so the solvent could be recovered and then purified by fractional distillation for reuse. The crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (v:v = 5:1) as the eluent to give the desired product **3aa** in 78% yield.

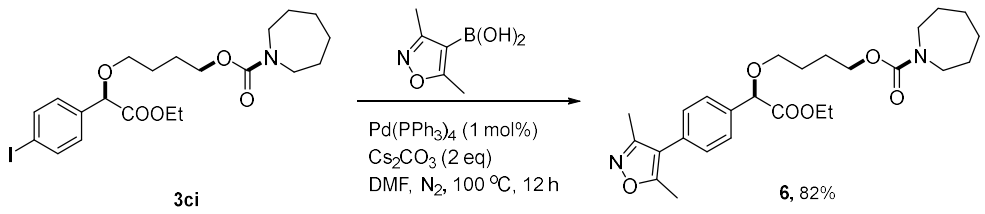
I. Procedure for the synthesis of compound 5-7

Procedure for the synthesis of compound 5:



To a solution of 4-(2-ethoxy-1-(4-iodophenyl)-2-oxoethoxy)butyl azepane-1-carboxylate (**3ci**, 0.2 mmol) in a mixed solvent of THF/H_2O (v:v = 2:1, 3 ml) was added the mixture of phenylboronic acid (0.24 mmol), $PdCl_2$ (0.01 mmol), PPh_3 (0.012 mmol) and K_2CO_3 (0.4 mmol) successively. The resulting mixture was stirred at 80 ºC for 10 h under an atmosphere of N_2. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na_2SO_4, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to give the desired product **5** in 87% yield.

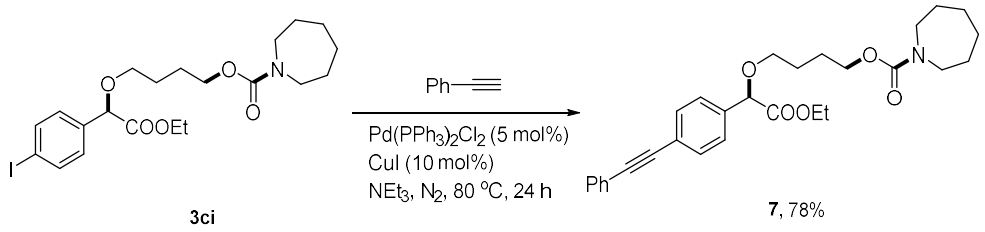
Procedure for the synthesis of compound 6:



To a solution of 4-(2-ethoxy-1-(4-iodophenyl)-2-oxoethoxy)butyl azepane-1-carboxylate (**3ci**, 0.2 mmol) in DMF (3 mL) was added the mixture of (3,5-dimethylisoxazol-4-yl)boronic acid (0.24

mmol), $Pd(PPh_3)_4$ (0.002 mmol) and Cs_2CO_3 (0.4 mmol) successively. The resulting mixture was stirred at 100 °C for 12 h under an atmosphere of N_2. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na_2SO_4, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to give the desired product **6** in 82% yield.

Procedure for the synthesis of compound 7:



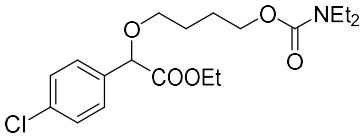
To a solution of 4-(2-ethoxy-1-(4-iodophenyl)-2-oxoethoxy)butyl azepane-1-carboxylate (**3ci**, 0.2 mmol) in Et_3N (3 mL) was added the mixture of phenylacetylene (0.24 mmol), $Ph(Ph_3)_2Cl_2$ (0.01 mmol) and CuI (0.02 mmol) successively. The resulting mixture was stirred at 80 °C for 24 h under an atmosphere of N_2. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na_2SO_4, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (7:1) as the eluent to give the desired product **7** in 78% yield.

J. Procedure for the synthesis of azepan-1-ium azepane-1-carboxylate 8[3]

To a 25 mL dried Schlenk tube equipped with a magnetic stirring bar was added azepan (1 mL). Then CO_2 was charged into the flask using a balloon of CO_2 at room temperature for 12 h. The resultant azepan-1-ium azepane-1-carboxylate was collected as a yellow viscous oil and characterized by NMR technique referred to the literature.[4]

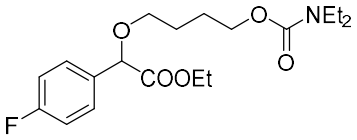
K. Analytical data

Ethyl 2-(4-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3aa)



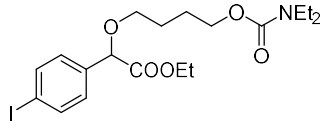
Yellow oil (31.2 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.79 (s, 1H), 4.14 (dd, J = 9.0, 7.5 Hz, 2H), 4.07 (s, 2H), 3.57 – 3.56 (m, 1H), 3.45 – 3.44 (m, 1H), 3.23 (s, 4H), 1.71 (s, 4H), 1.19 (t, J = 6.5 Hz, 3H), 1.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.5, 155.9, 135.2, 134.3, 128.6, 128.3, 80.3, 69.4, 64.5, 61.2, 41.6, 41.1, 26.1, 25.8, 14.0, 13.8, 13.5. IR (KBr): 2980, 2933, 2876, 1745, 1693, 1596, 1544, 1479, 1430, 1387, 1320, 1270, 1171, 1087, 1016, 919, 825, 764, 500, 458 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{28}ClNO_5Na$ $[M+Na]^+$: 408.1548, found 408.1549.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-fluorophenyl)acetate (3ba)



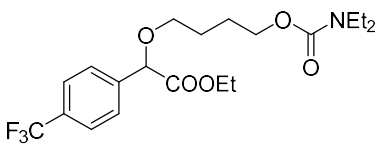
Yellow oil (26.6 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 – 7.41 (m, 2H), 7.07 – 7.01 (m, 2H), 4.82 (s, 1H), 4.21 – 4.12 (m, 2H), 4.10 – 4.08 (m, 2H), 3.61 – 3.56 (m, 1H), 3.49 – 3.44 (m, 1H), 3.26 (s, 4H), 1.75 – 1.73 (m, 4H), 1.24 – 1.19 (m, 3H), 1.12 – 1.08 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 162.7 (d, J = 245.5 Hz), 155.9, 132.5 (d, J = 3.2 Hz), 128.7 (d, J = 8.3 Hz), 115.4 (d, J = 21.5 Hz), 80.3, 69.4, 64.5, 61.1, 41.5, 41.1, 26.2, 25.8, 14.0, 13.8, 13.5. IR (KBr): 3030, 2973, 1745, 1694, 1604, 1507, 1472, 1429, 1376, 1271, 1221, 1171, 1086, 1019, 840, 810, 758, 517 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{29}FNO_5$ $[M+H]^+$: 370.2024, found 370.2020.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-iodophenyl)acetate (3ca)



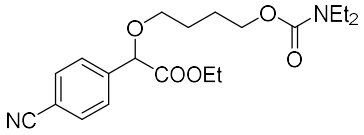
Yellow oil (36.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 4.75 (s, 1H), 4.20 – 4.09 (m, 2H), 4.09 – 4.05 (m, 2H), 3.58 – 3.54 (m, 1H), 3.46 – 3.42 (m, 1H), 3.23 (s, 4H), 1.71 (s, 4H), 1.18 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 155.9, 137.5, 136.4, 128.8, 94.2, 80.5, 69.4, 64.5, 61.2, 41.5, 41.2, 26.1, 25.7, 14.0, 13.7, 13.5. IR (KBr): 2972, 2933, 2876, 1746, 1695, 1477, 1429, 1378, 1322, 1272, 1173, 1094, 1008, 768, 704, 492 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{28}INO_5Na$ $[M+Na]^+$: 500.0904, found 500.0901.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-(trifluoromethyl)phenyl)acetate (3da)



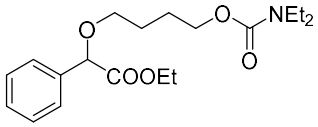
Yellow oil (28.1 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.56 (m, 4H), 4.88 (s, 1H), 4.22 – 4.12 (m, 2H), 4.09 – 4.08 (m, 2H), 3.62 – 3.60 (m, 1H), 3.49 – 3.46 (m, 1H), 3.24 (s, 4H), 1.74 – 1.73 (m, 4H), 1.22 – 1.18 (m, 3H), 1.09 – 1.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 156.0, 140.6, 130.6 (q, J = 31.6 Hz), 127.2, 125.4 (q, J = 3.8 Hz), 123.9 (q, J = 269.8 Hz), 80.5, 69.7, 64.5, 61.4, 41.6, 41.2, 26.2, 25.8, 14.0, 13.8, 13.5. IR (KBr): 2963, 2923, 2859, 1740, 1692, 1596, 1486, 1425, 1235, 1089, 1017, 959, 843, 761, 570, 466 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{28}F_3NO_5Na$ $[M+Na]^+$: 442.1812, found 442.1809.

Ethyl 2-(4-cyanophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ea)



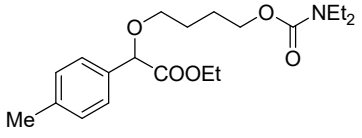
Yellow oil (23.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 4.87 (s, 1H), 4.17 – 4.12 (m, 2H), 4.07 (s, 2H), 3.63 – 3.61 (m, 1H), 3.48 – 3.46 (m, 1H), 3.23 (s, 4H), 1.73 (s, 4H), 1.19 (t, J = 7.0 Hz, 3H), 1.08 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 155.9, 141.8, 132.2, 127.5, 118.4, 112.3, 80.3, 69.8, 64.5, 61.6, 41.6, 41.2, 26.1, 25.7, 14.0, 13.8, 13.5. IR (KBr): 3850, 2970, 2932, 2873, 1742 1691, 1556, 1467, 1430, 1376, 1322, 1266, 1168, 1082, 101, 924, 764, 697, 495 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{28}N_2O_5Na$ $[M+Na]^+$: 399.1890, found 399.1810.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3fa)



Yellow oil (29.9 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 6.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 4.82 (s, 1H), 4.18 – 4.09 (m, 2H), 4.06 (s, 2H), 3.56 – 3.55 (m, 1H), 3.46 – 3.44 (m, 1H), 3.23 (s, 4H), 1.71 (s, 4H), 1.18 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 155.9, 136.6, 128.4, 126.9, 81.0, 69.2, 64.5, 61.0, 41.6, 41.1, 26.1, 25.7, 13.9, 13.7, 13.4. IR (KBr): 2970, 2936, 2875, 1742, 1690, 1425, 1375, 1267, 1167, 1074, 1018, 758, 694, 484 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{29}NO_5Na$ $[M+Na]^+$: 374.1938, found 374.1936.

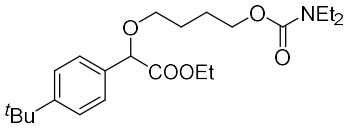
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(*p*-tolyl)acetate (3ga)



Pale yellow oil (31.8 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.81 (s, 1H), 4.21 – 4.12 (m, 2H), 4.08 – 4.07 (m, 2H), 3.58 – 3.55 (m, 1H),

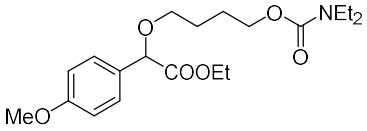
3.48 – 3.45 (m, 1H), 3.25 (s, 4H), 2.33 (s, 3H), 1.73 (s, 4H), 1.21 (t, J = 7.3 Hz, 3H), 1.10 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 156.0, 138.3, 133.7, 129.1, 127.0, 80.9, 69.1, 64.6, 61.0, 41.6, 41.1, 26.2, 25.8, 21.1, 14.0, 13.9, 13.4. IR (KBr): 2973, 2950, 2883, 1745, 1697, 1473, 1429, 1377, 1274, 1174, 1099, 1023, 767, 502 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{31}NO_5Na$ $[M+Na]^+$: 388.2094, found 388.2091.

Ethyl 2-(4-(*tert*-butyl)phenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ha)



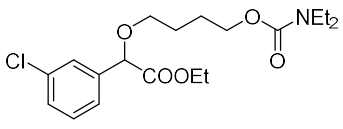
Pale yellow oil (28.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 4H), 4.81 (s, 1H), 4.21 – 4.12 (m, 2H), 4.07 (s, 2H), 3.54 (s, 1H), 3.47 (s, 1H), 3.24 (s, 4H), 1.72 (s, 4H), 1.29 (s, 9H), 1.21 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 156.0, 151.4, 133.5, 126.7, 125.4, 80.9, 69.3, 64.6, 61.0, 41.6, 41.1, 34.5, 31.2, 26.2, 25.8, 14.0, 13.9, 13.5. IR (KBr): 2960, 2873, 1743, 1691, 1469, 1426, 1375, 1267, 1168, 1087, 1014, 929, 833, 767, 698, 554, 474 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{37}NO_5Na$ $[M+Na]^+$: 430.2564, found 430.2562.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-methoxyphenyl)acetate (3ia)



Yellow oil (29.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 4.78 (s, 1H), 4.20 – 4.10 (m, 2H), 4.07 (s, 2H), 3.79 (s, 3H), 3.53 (s, 1H), 3.45 (s, 1H), 3.24 (s, 4H), 1.72 (s, 4H), 1.20 (t, J = 7.0 Hz, 3H), 1.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 159.7, 156.0, 128.8, 128.4, 113.9, 80.6, 69.1, 64.7, 61.0, 55.2, 41.6, 41.1, 26.2, 25.8, 14.1, 14.0, 13.6. IR (KBr): 2965, 2930, 2886, 1741, 1690, 1609, 1509, 1466, 1424, 1374, 1265, 1168, 1088, 1024, 831, 761, 466 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{31}NO_6Na$ $[M+Na]^+$: 404.2044, found 404.1983.

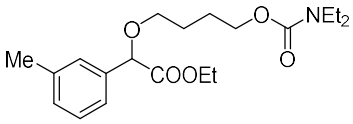
Ethyl 2-(3-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ja)



Pale yellow oil (30.1 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.33 (s, 1H), 7.29 (s, 2H), 4.81 (s, 1H), 4.19 – 4.16 (m, 2H), 4.09 (s, 2H), 3.60 – 3.58 (m, 1H), 3.49 – 3.47 (m, 1H), 3.26 (s, 4H), 1.74 (s, 4H), 1.22 (t, J = 7.0 Hz, 3H), 1.10 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 155.9, 138.6, 134.4, 129.7, 128.6, 127.0, 125.1, 80.3, 69.5, 64.5, 61.3, 41.5, 41.1, 26.1, 25.7, 14.0, 13.8, 13.4. IR (KBr): 2972, 2933, 2880, 1744, 1692, 1584, 1473, 1430, 1377, 1269,

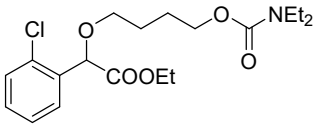
1173, 1080, 1017, 876, 773, 691, 618, 552 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{28}ClNO_5Na$ $[M+Na]^+$: 408.1548, found 408.1541.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(*m*-tolyl)acetate (3ka)



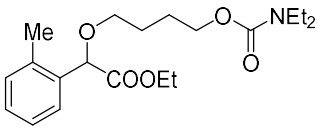
Yellow oil (31.8 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 7.21 – 7.20 (m, 2H), 7.11 – 7.10 (m, 1H), 4.78 (s, 1H), 4.22 – 4.11 (m, 2H), 4.06 (s, 2H), 3.55 – 3.54 (m, 1H), 3.47 – 3.44 (m, 1H), 3.23 (s, 4H), 2.32 (s, 3H), 1.72 (s, 4H), 1.19 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 155.9, 138.1, 136.4, 129.2, 128.3, 127.5, 124.1, 81.0, 69.2, 64.5, 61.0, 41.5, 41.1, 26.1, 25.7, 21.2, 13.9, 13.8, 13.4. IR (KBr): 2969, 2873, 1742, 1691, 1608, 1473, 1377, 1321, 1267, 1168, 1079, 1015, 767, 697, 618, 550 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{32}NO_5$ $[M+H]^+$: 366.2275, found 366.2273.

Ethyl 2-(2-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3la)



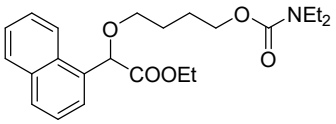
Yellow oil (28.1 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 – 7.53 (m, 1H), 7.41 – 7.38 (m, 1H), 7.32 – 7.27 (m, 2H), 5.35 (s, 1H), 4.25 – 4.16 (m, 2H), 4.10 – 4.08 (m, 2H), 3.67 – 3.65 (m, 1H), 3.53 – 3.51 (m, 1H), 3.27 (s, 4H), 1.75 (s, 4H), 1.25 (q, *J* = 7.4 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 156.0, 134.8, 133.6, 129.6, 129.4, 128.6, 127.1, 77.3, 69.8, 64.6, 61.2, 41.5, 41.1, 26.2, 25.7, 14.0, 13.9, 13.5. IR (KBr): 2972, 2873, 1746, 1696, 1743, 1433, 1377, 1322, 1272, 1177, 1100, 1025, 755, 617, 452 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{29}ClNO_5$ $[M+H]^+$: 386.1729, found 386.1725.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(*o*-tolyl)acetate (3ma)



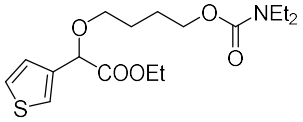
Colorless oil (30.3 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 6.4 Hz, 1H), 7.20 – 7.19 (m, 2H), 7.16 (s, 1H), 5.05 (s, 1H), 4.21 – 4.11 (m, 2H), 4.07 (s, 2H), 3.58 – 3.56 (m, 1H), 3.46 – 3.44 (m, 1H), 3.24 (s, 4H), 2.41 (s, 3H), 1.72 (s, 4H), 1.20 (t, *J* = 7.2 Hz, 4H), 1.09 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 156.0, 136.3, 135.1, 130.5, 128.3, 127.3, 126.2, 78.2, 69.3, 64.6, 61.0, 41.6, 41.1, 26.3, 25.8, 19.3, 14.0, 13.8, 13.5. IR (KBr): 2968, 2933, 2860, 1742, 1690, 1470, 1425, 1373, 1267, 1167, 1078, 1012, 746,671, 448 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{31}NO_5Na$ $[M+Na]^+$: 388.2094, found 388.2091.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(naphthalen-1-yl)acetate (3na)



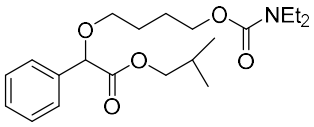
Pale yellow oil (30.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.0 Hz, 1H), 7.84 (t, J = 8.6 Hz, 2H), 7.61 (d, J = 7.2 Hz, 1H), 7.55 – 7.44 (m, 3H), 5.47 (s, 1H), 4.23 – 4.09 (m, 2H), 4.07 – 4.05 (m, 2H), 3.66 – 3.63 (m, 1H), 3.52 – 3.49 (m, 1H), 3.23 (s, 4H), 1.73 (s, 4H), 1.14 (t, J = 7.0 Hz, 3H), 1.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 156.0, 133.9, 132.6, 131.0, 129.2, 128.6, 126.4, 126.3, 125.8, 125.2, 124.1, 79.6, 69.4, 64.6, 61.2, 41.6, 41.1, 26.3, 25.8, 14.0, 13.7, 13.5. IR (KBr): 2970, 2936, 2870, 1745, 1695, 1599, 1476, 1428, 1376, 1273, 1173, 1106, 1022, 778, 547 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{31}NO_5Na[M+Na]^+$: 424.2094, found 424.2083.

Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(thiophen-3-yl)acetate (3oa)



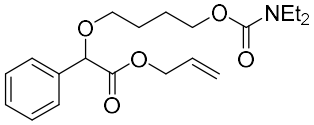
Yellow oil (22.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 7.29 (s, 1H), 7.14 (s, 1H), 4.96 (s, 1H), 4.22 – 4.18 (m, 2H), 4.09 (s, 2H), 3.60 – 3.59 (m, 1H), 3.50 – 3.49 (m, 1H), 3.26 (s, 4H), 1.74 (s, 4H), 1.26 – 1.22 (m, 3H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 155.9, 137.2, 126.1, 126.0, 123.2, 77.3, 69.4, 64.5, 61.1, 41.5, 41.0, 26.1, 25.7, 14.0, 13.9, 13.4. IR (KBr): 2967, 2946, 2878, 1748, 1695, 1477, 1429, 1376, 1321, 1273, 1172, 1108, 1083, 993, 929, 772, 734, 699, 552, 491 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{17}H_{27}NO_5SNa$ [M+Na]$^+$: 380.1502, found 380.1463

Isobutyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3pa)



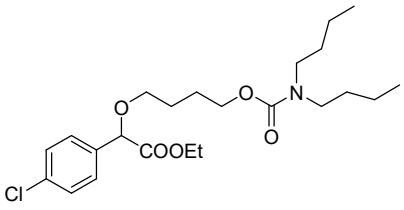
White solid (30.7 mg, 81%); mp: 80 – 81 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.2 Hz, 2H), 7.35 – 7.27 (m, 3H), 4.84 (s, 1H), 4.07 (s, 2H), 3.91 – 3.83 (m, 2H), 3.58 – 3.56 (m, 1H), 3.47 – 3.46 (m, 1H), 3.23 (s, 4H), 1.90 – 1.80 (m, 1H), 1.73 (s, 4H), 1.08 (t, J = 6.8 Hz, 6H), 0.80 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 155.9, 136.8, 128.4, 128.4, 127.0, 81.0, 70.9, 69.3, 64.6, 41.6, 41.1, 27.6, 26.2, 25.8, 18.8, 14.0, 13.4. IR (KBr): 3590, 3503, 3448, 2958, 2866, 1640, 1586, 1493, 1415, 1364, 1281, 1220, 1145, 1091, 1020, 950, 843, 755, 649, 551, 487 cm. HRMS-ESI (*m/z*): calcd for $C_{21}H_{33}NO_5Na$ [M+Na]$^+$: 402.2251, found 402.1676.

Allyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3qa)



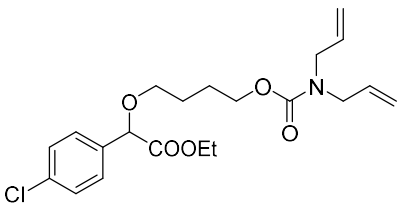
Yellow oil (28.0 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 2H), 7.36 – 7.30 (m, 3H), 5.88 – 5.80 (m, 1H), 5.21 – 5.16 (m, 2H), 4.90 (s, 1H), 4.61 (s, 2H), 4.09 (s, 2H), 3.59 (s, 1H), 3.50 (s, 1H), 3.26 (s, 4H), 1.75 (s, 4H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 155.8, 136.4, 131.4, 128.4, 128.4, 126.9, 118.2, 80.9, 69.2, 65.3, 64.5, 41.5, 41.1, 26.1, 25.7, 13.8, 13.4. IR (KBr): 2980, 2930, 2876, 1744, 1693, 1474, 1429, 1376, 1270, 1174, 1089, 1019, 848, 770, 590 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{28}ClNO_5Na$ $[M+Na]^+$: 420.1548, found 420.1480.

Ethyl 2-(4-chlorophenyl)-2-(4-((dibutylcarbamoyl)oxy)butoxy)acetate (3ab)



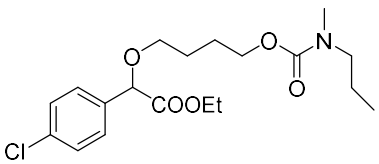
Pale yellow oil (35.7 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.79 (s, 1H), 4.16 – 4.11 (m, 2H), 4.06 (s, 2H), 3.57 – 3.55 (m, 1H), 3.45 (s, 1H), 3.16 (s, 4H), 1.71 (s, 4H), 1.47 (s, 4H), 1.26 (s, 4H), 1.19 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.3, 135.2, 134.3, 128.6, 128.3, 80.3, 69.4, 64.5, 61.2, 47.1, 46.5, 30.7, 30.2, 26.1, 25.8, 19.9, 14.0, 13.8. IR (KBr): 2956, 2870, 1745, 1694, 1593, 1476, 1427, 1376, 1259, 1222, 1169, 1094, 1020, 937, 826, 765 500 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{37}ClNO_5$ $[M+H]^+$: 442.2355, found 442.2354.

Ethyl 2-(4-chlorophenyl)-2-(4-((diallylcarbamoyl)oxy)butoxy)acetate (3ac)



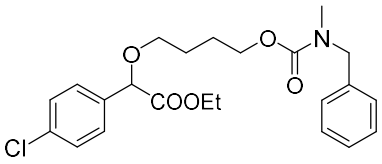
Yellow oil (29.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.73 (s, 1H), 5.12 – 5.10 (m, 4H), 4.79 (s, 1H), 4.21 – 4.08 (m, 4H), 3.83 – 3.80 (m, 4H), 3.58 – 3.53 (m, 1H), 3.46 – 3.41 (m, 1H), 1.72 – 1.70 (m, 4H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.1, 135.2, 134.3, 133.5, 128.6, 128.3, 116.9, 116.4, 80.3, 69.4, 65.0, 61.2, 48.9, 48.4, 26.1, 25.7, 14.0. IR (KBr): 2951, 2873, 1747, 1699, 1463, 1415, 1244, 1178, 1095, 1019, 926, 829, 769, 698, 555, 501 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{28}ClNO_5Na$ $[M+Na]^+$: 432.1548, found 432.1546.

Ethyl 2-(4-chlorophenyl)-2-(4-((methyl(propyl)carbamoyl)oxy)butoxy)acetate (3ad)



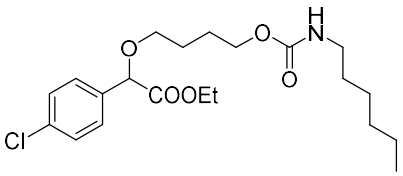
Pale yellow oil (30.1 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.81 (s, 1H), 4.18 – 4.11 (m, 2H), 4.08 (s, 2H), 3.59 – 3.57 (m, 1H), 3.47 (s, 1H), 3.19 (s, 2H), 2.87 (s, 3H), 1.73 (s, 4H), 1.53 – 1.51 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.4, 135.2, 134.3, 128.6, 128.3, 80.3, 69.4, 64.7, 61.2, 50.5, 50.1, 34.3, 33.7, 26.1, 25.7, 21.0, 20.6, 13.9, 11.0. IR (KBr): 2964, 2931, 2873, 1752, 1711, 1485, 1403, 1268, 1215, 1168, 1092, 1022, 910, 841, 762, 603, 507, 436 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{29}ClNO_5$ $[M+H]^+$: 386.1729, found 386.1723.

Ethyl 2-(4-((benzyl(methyl)carbamoyl)oxy)butoxy)-2-(4-chlorophenyl)acetate (3ae)



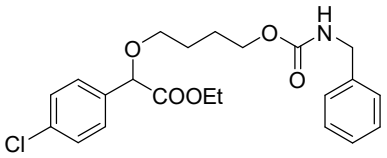
Yellow oil (36.8 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 2H), 7.31 (d, J = 7.2 Hz, 4H), 7.27 – 7.20 (m, 3H), 4.81 – 4.79 (m, 1H), 4.46 – 4.45 (m, 2H), 4.21 – 4.12 (m, 4H), 3.57 (s, 1H), 3.45 (s, 1H), 2.88 – 2.81 (m, 3H), 1.76 (s, 4H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.8, 137.5, 135.2, 134.3, 128.6, 128.5, 128.3, 127.7, 127.2, 127.1, 80.3, 69.4, 65.1, 61.2, 52.4, 52.2, 34.3, 33.4, 26.1, 25.7, 14.0. IR (KBr): 2933, 2870, 1742, 1692, 1479, 1402, 1273, 1270, 1133, 1088, 1017, 953, 818, 752, 698, 585, 489 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{28}ClNO_5Na$ $[M+Na]^+$: 456.1548, found 456.1548.

Ethyl 2-(4-chlorophenyl)-2-(4-((hexylcarbamoyl)oxy)butoxy)acetate (3af)



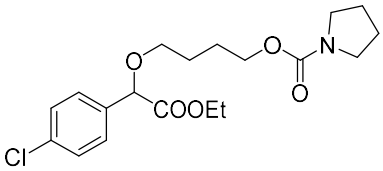
Yellow oil (31.8 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 4.79 (s, 1H), 4.71 (s, 1H), 4.17 – 4.10 (m, 2H), 4.04 (s, 2H), 3.56 – 3.54 (m, 1H), 3.44 (s, 1H), 3.13 – 3.11 (m, 2H), 1.69 (s, 4H), 1.45 – 1.43 (m, 2H), 1.26 (s, 6H), 1.19 (t, J = 7.0 Hz, 3H), 0.86 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5, 156.6, 135.2, 134.3, 128.6, 128.3, 80.3, 69.4, 64.3, 61.2, 40.9, 31.4, 29.9, 26.3, 26.0, 25.7, 22.5, 14.0, 13.9. IR (KBr): 3552, 2930, 2864, 1713, 1528, 1486, 1251, 1175, 1096, 1021, 827, 769, 498 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{33}ClNO_5$ $[M+H]^+$: 414.2042, found 414.2036.

Ethyl 2-(4-((benzylcarbamoyl)oxy)butoxy)-2-(4-chlorophenyl)acetate (3ag)



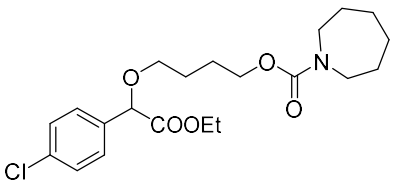
Pale yellow oil (32.3 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.4 Hz, 2H), 7.34 – 7.31 (m, 4H), 7.28 – 7.24 (m, 3H), 5.04 (s, 1H), 4.80 (s, 1H), 4.36 – 4.34 (m, 2H), 4.20 – 4.11 (m, 4H), 3.58 – 3.56 (s, 1H), 3.46 – 3.45 (s, 1H), 1.72 (s, 4H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.6, 138.5, 135.1, 134.3, 128.7, 128.6, 128.3, 127.4, 127.4, 80.3, 69.3, 64.6, 61.3, 44.9, 26.0, 25.7, 14.0. IR (KBr): 3346, 2937, 1713, 1519, 1241, 1102, 1023, 740, 610, 456 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{26}ClNO_5Na$ $[M+Na]^+$: 442.1392, found 442.1393.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl pyrrolidine-1-carboxylate (3ah)



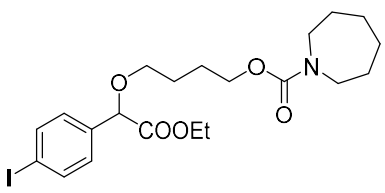
Yellow oil (29.2 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.80 (s, 1H), 4.20 – 4.11 (m, 2H), 4.08 (s, 2H), 3.57 – 3.56 (m, 1H), 3.46 – 3.44 (m, 1H), 3.35 – 3.29 (m, 4H), 1.83 (s, 4H), 1.72 (s, 4H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 155.1, 135.2, 134.4, 128.7, 128.3, 80.4, 69.5, 64.5, 61.3, 46.0, 45.6, 26.1, 25.8, 25.7, 24.9, 14.0. IR (KBr): 2956, 2877, 1746, 1697, 1595, 1486, 1425, 1368, 1264, 1177, 1098, 1021, 829, 758, 501 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{26}ClNO_5Na$ $[M+Na]^+$: 406.1392, found 406.1393.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (3ai)



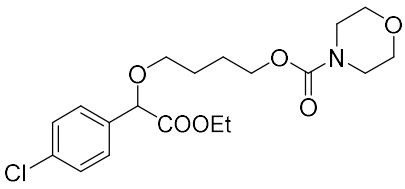
Yellow oil (33.3 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.79 (s, 1H), 4.18 – 4.11 (m, 2H), 4.10 – 4.07 (m, 2H), 3.58 – 3.54 (m, 2H), 3.46 – 3.42 (m, 1H), 3.39 (t, J = 6.2 Hz, 2H), 3.32 (t, J = 5.8 Hz, 2H), 1.71 (s, 4H), 1.66 – 1.61 (m, 4H), 1.51 – 1.50 (m, 4H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.3, 135.2, 134.3, 128.6, 128.3, 80.3, 69.4, 64.6, 61.2, 46.8, 46.4, 28.4, 28.2, 27.3, 26.8, 26.1, 25.7, 14.0. IR (KBr): 2930, 2863, 1747, 1694, 1596, 1542, 1482, 1425, 1373, 1265, 1204, 1091, 1019, 903, 828, 769, 501 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{30}ClNO_5Na$ $[M+Na]^+$: 434.1705, found 434.1696.

4-(2-Ethoxy-1-(4-iodophenyl)-2-oxoethoxy)butyl azepane-1-carboxylate (3ci)



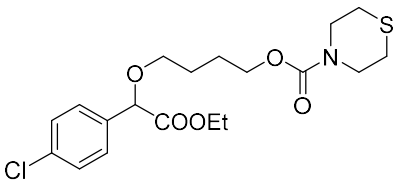
Yellow oil (43.8 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.76 (s, 1H), 4.19 – 4.11 (m, 2H), 4.08 (s, 2H), 3.59 – 3.55 (m, 1H), 3.47 – 3.43 (m, 1H), 3.40 (t, J = 5.8 Hz, 2H), 3.33 (t, J = 5.6 Hz, 2H), 1.71 (s, 4H), 1.67 – 1.62 (m, 2H), 1.54 – 1.52 (m, 4H), 1.20 (t, J = 7.0 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 156.3, 137.6, 136.4, 128.9, 94.3, 80.5, 69.5, 64.6, 61.3, 46.8, 46.4, 28.5, 28.2, 27.3, 26.9, 26.2, 25.8, 14.0. IR (KBr):2929, 1740, 1692, 1469, 1268, 1191, 1099, 1005, 763, 491 cm^{-1}. HRMS-ESI *(m/z)*: calcd for $C_{21}H_{30}INNaO_5$ $[M+Na]^+$, 526.1061, found 526.1057.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl morpholine-4-carboxylate (3aj)



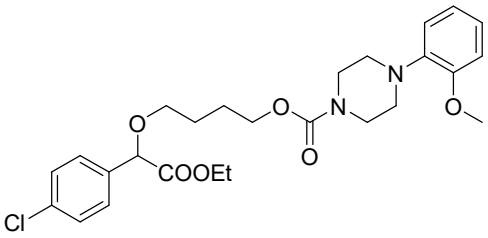
Pale Yellow oil (30.3 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5, 2H), 4.78 (s, 1H), 4.18 – 4.12 (m, 2H), 4.09 (t, J = 5.8 Hz, 2H) 3.61 (s, 4H), 3.56 – 3.53 (m, 1H), 3.45 – 3.41 (m, 5H), 1.74 – 1.68 (m, 4H), 1.18 (t, J = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 155.4, 135.1, 134.3, 128.6, 128.3, 80.4, 69.4, 66.5, 65.1, 61.2, 44.0, 26.1, 25.7, 14.0. IR (KBr): 2959, 2923, 2859, 1740, 1692, 1596, 1486, 1425, 1235, 1089, 1017, 959, 843, 761, 570, 466 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{26}ClNO_6Na$ $[M+Na]^+$: 422.1341, found 422.1339.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl thiomorpholine-4-carboxylate (3ak)



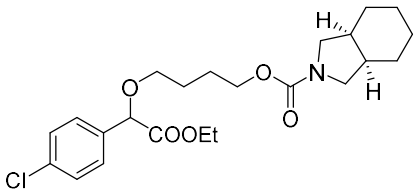
Yellow oil (23.3 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (d, J =8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 4.79 (s, 1H), 4.19 – 4.12 (m, 2H), 4.10 (t, J = 6.0 Hz, 2H), 3.70 (s, 4H), 3.58 – 3.54 (m, 1H), 3.46 – 3.42 (m, 1H), 2.55 (s, 4H), 1.74 – 1.69 (m, 4H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4, 155.1, 135.2, 134.4, 128.7, 128.3, 80.4, 69.4, 65.2, 61.2, 46.3, 27.2, 26.1, 25.7, 14.0. IR (KBr): 2955, 2923, 2876, 1745, 1696, 1467, 1427, 1376, 1291, 1217, 1175, 1080, 1017, 825, 767, 699, 499 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{26}ClNOS_5Na$ $[M+Na]^+$: 438.1112, found 438.1110.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl 4-(2-methoxyphenyl)piperazine-1-carboxylate (3al)



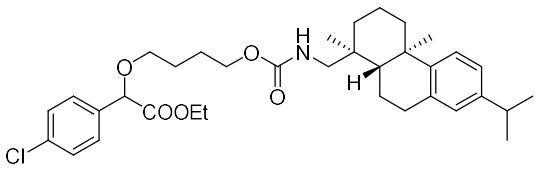
Red oil (30.3 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.04 – 7.00 (m, 1H), 6.91 (d, J = 4.4 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 4.81 (s, 1H), 4.20 – 4.11 (m, 4H), 3.86 (s, 3H), 3.64 (s, 4H), 3.60 – 3.57 (m, 1H), 3.49 – 3.44 (m, 1H), 3.00 (s, 4H), 1.76 – 1.74 (m, 4H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 155.4, 152.2, 140.8, 135.1, 134.3, 128.6, 128.3, 123.3, 120.9, 118.3, 111.2, 80.3, 69.4, 65.0, 61.2, 55.3, 50.5, 43.8, 26.1, 25.7, 14.1, 14.0. IR (KBr): 2948, 2913, 2880, 1746, 1699, 1592, 1496, 1437, 1380, 1240, 1170, 1123, 1092, 1025, 938, 829, 752, 501 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{26}H_{34}ClN_2O_6$ $[M+H]^+$: 505.2100, found 505.2097.

4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl (3a*R*,7a*S*)-octahydro-2*H*-isoindole-2-carboxylate (3am)



Yellow oil (25.7 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.79 (s, 1H), 4.18 – 4.10 (m, 2H), 4.09 – 4.03 (m, 2H), 3.57 – 3.54 (m, 1H), 3.45 – 3.41 (m, 1H), 3.36 – 3.21 (m, 3H), 3.17 – 3.13 (m, 1H), 2.19 – 2.09 (m, 2H), 1.71 (s, 4H), 1.54 – 1.31 (m, 8H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 155.7, 135.3, 134.4, 128.7, 128.4, 80.4, 69.6, 64.5, 61.3, 50.0, 49.7, 37.3, 36.5, 26.2, 25.9, 25.8, 25.8, 22.8, 22.8, 14.1. IR (KBr): 2930, 2868, 1745, 1698, 1594, 1483, 1425, 1366, 1296, 1255, 1179, 1101, 1021, 967, 829, 768, 500 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{32}ClNO_5Na$ $[M+Na]^+$: 460.1861, found 460.1859.

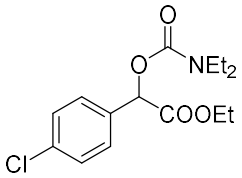
Ethyl 2-(4-chlorophenyl)-2-(4-(((((1*S*,4a*R*,10a*S*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamoyl)oxy)butoxy)acetate (3an)



Yellow oil (31.7 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.90 (s, 1H), 4.81 (s, 1H), 4.71 (s, 1H), 4.20 – 4.13 (m, 2H), 4.06 (s, 2H), 3.58 – 3.56 (m, 1H), 3.45 (s, 1H), 3.19 – 3.15 (m, 1H), 3.00 – 2.80 (m, 4H), 2.30 – 2.28 (m, 1H), 1.87 – 1.86

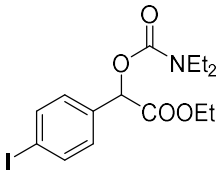
(m, 1H), 1.78 – 1.68 (m, 7H), 1.48 – 1.45 (m, 1H), 1.40 – 1.35 (m, 2H), 1.29 – 1.20 (m, 13H), 0.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.5, 156.9, 147.1, 145.5, 135.2, 134.7, 134.3, 128.6, 128.3, 126.8, 124.1, 123.8, 80.4, 69.4, 64.4, 61.2, 51.5, 44.8, 38.3, 37.3, 35.8, 33.4, 30.1, 26.0, 25.7, 25.2, 23.9, 18.8, 18.6, 18.5, 14.00. IR (KBr): 3354, 2950, 2870, 1719, 1531, 1486, 1457, 1375, 1244, 1095, 1020, 826, 769, 710, 623, 499 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{35}H_{48}ClNO_5Na$ $[M+Na]^+$: 620.3109, found 620.3102.

Ethyl 2-(4-chlorophenyl)-2-((diethylcarbamoyl)oxy)acetate (4aa)



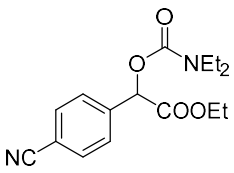
Yellow oil (22.6 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.32 (m, 2H), 5.87 (s, 1H), 4.22 – 4.09 (m, 2H), 3.36 – 3.28 (m, 4H), 1.21 – 1.17 (m, 6H), 1.15 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 154.5, 134.7, 133.3, 128.8, 128.6, 74.1, 61.5, 42.1, 41.6, 13.9, 13.3. IR (KBr): 2971, 2926, 2231, 1698, 1616, 1423, 1265, 1156, 1077, 1020, 957, 844, 753, 605, 544, 458 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{20}ClNO_4Na$ $[M+Na]^+$: 336.0973, found 336.0971.

Ethyl 2-((diethylcarbamoyl)oxy)-2-(4-iodophenyl)acetate (4ca)



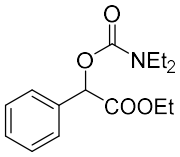
White solid (27.6 mg, 68%); mp: 74 – 75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.83 (s, 1H), 4.22 – 4.10 (m, 2H), 3.34 – 3.26 (m, 4H), 1.20 (t, *J* = 6.6 Hz, 6H), 1.13 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 154.5, 137.7, 134.4, 129.1, 94.7, 74.3, 61.5, 42.1, 41.6, 13.9, 13.3. IR (KBr): 2975, 2930, 1747, 1702, 1472, 1428, 1267, 1214, 1163, 1078, 1019, 962, 890, 768, 701, 682, 579, 498 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{20}INO_4Na$ $[M+Na]^+$: 428.0327, found 428.0326.

Ethyl 2-(4-cyanophenyl)-2-((diethylcarbamoyl)oxy)acetate (4ea)



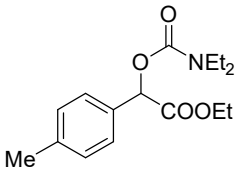
Yellow oil (18.3 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 5.95 (s, 1H), 4.18 – 4.14 (m, 2H), 3.37 – 3.28 (m, 4H), 1.21 – 1.18 (m, 6H), 1.15 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 154.2, 139.7, 132.4, 127.8, 118.3, 112.6, 74.0, 61.8, 42.2, 41.6, 13.9, 13.9, 13.3. IR (KBr): 2972, 2933, 2229, 1698, 1473, 1421, 1265, 1156, 1078, 1021, 843, 753, 605, 543, 445 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}N_2O_4Na$ $[M+Na]^+$:327.1315, found 327.1312.

Ethyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4fa)[2]



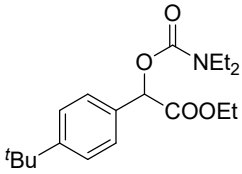
Yellow oil (18.7 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 6.4 Hz, 2H), 7.37 – 7.33 (m, 3H), 5.90 (s, 1H), 4.23 – 4.10 (m, 2H), 3.36 – 3.30 (m, 4H), 1.20 (t, J = 7.0 Hz, 6H), 1.16 – 1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 154.8, 134.7, 128.8, 128.6, 127.3, 74.9, 61.3, 42.1, 41.6, 13.9, 13.4. IR (KBr): 2971, 2928, 2863, 1749, 1701, 1468, 1423, 1374, 1268, 1221, 1161, 1072, 1028, 962, 756, 575, 441 cm^{-1}.

Ethyl 2-((diethylcarbamoyl)oxy)-2-(*p*-tolyl)acetate (4ga)



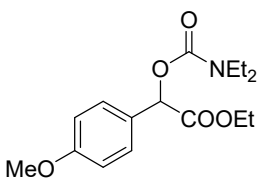
Pale yellow oil (21.7 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 5.87 (s, 1H), 4.21 – 4.12 (m, 2H), 3.36 – 3.32 (m, 4H), 2.35 (s, 3H), 1.20 (t, J = 7.0 Hz, 6H), 1.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 154.9, 138.7, 131.8, 129.3, 127.3, 74.8, 61.3, 42.0, 41.5, 21.1, 13.9, 13.4. IR (KBr): 2974, 2923, 2873, 1748, 1701, 1466, 1424, 1373, 1265, 1214, 1161, 1075, 1026, 962, 761, 613, 500 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{23}NO_4Na$ $[M+Na]^+$: 316.1519, found 316.1520.

Ethyl 2-(4-(*tert*-butyl)phenyl)-2-((diethylcarbamoyl)oxy)acetate (4ha)



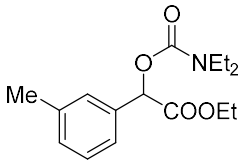
Pale yellow oil (21.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 4H), 5.91 (s, 1H), 4.25 – 4.14 (m, 2H), 3.43 – 3.36 (m, 4H), 1.34 (s, 9H), 1.25 (t, J = 7.0 Hz, 6H), 1.18 – 1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 154.9, 151.7, 131.6, 127.0, 125.5, 74.8, 61.3, 42.0, 41.5, 34.6, 31.2, 14.0, 13.4. IR (KBr): 2967, 2883, 1751, 1707, 1470, 1427, 1373, 1269, 1215, 1167, 1080, 1029, 960, 757, 611, 556 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{29}NO_4Na$ $[M+Na]^+$: 358.1989, found 358.1988.

Ethyl 2-((diethylcarbamoyl)oxy)-2-(4-methoxyphenyl)acetate (4ia)



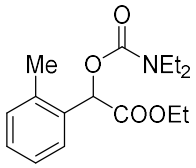
Yellow oil (23.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.83 (s, 1H), 4.20 – 4.12 (m, 2H), 3.80 (s, 3H), 3.35 – 3.32 (m, 4H), 1.20 (t, J = 6.8 Hz, 6H), 1.15 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 159.9, 154.9, 128.8, 126.8, 114.0, 74.5, 61.3, 55.2, 42.0, 41.5, 13.9, 13.4. IR (KBr): 2974, 2940, 2836, 1747, 1699, 1610, 1511, 1466, 1424, 1373, 1250, 1161, 1072, 1025, 962, 831, 758, 613, 529 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{23}NO_5Na$ $[M+Na]^+$: 332.1468, found 332.1464.

Ethyl 2-((diethylcarbamoyl)oxy)-2-(*m*-tolyl)acetate (4ka)



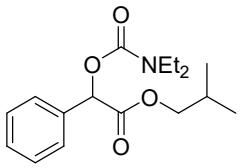
Yellow oil (19.9 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 – 7.29 (m, 3H), 7.18 (d, J = 5.5 Hz, 1H), 5.89 (s, 1H), 4.24 – 4.14 (m, 2H), 3.38 (s, 4H), 2.38 (s, 3H), 1.23 (t, J = 6.8 Hz, 6H), 1.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 154.8, 138.3, 134.6, 129.5, 128.5, 128.1, 124.4, 75.0, 61.3, 42.0, 41.5, 21.3, 13.9, 13.4. IR (KBr): 2976, 2930, 2869, 1748, 1702, 1605, 1470, 1426, 1374, 1267, 1161, 1079, 1027, 965, 772, 694, 566 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{23}NO_4Na$ $[M+Na]^+$: 316.1519, found 316.1518.

Ethyl 2-((diethylcarbamoyl)oxy)-2-(*o*-tolyl)acetate (4ma)



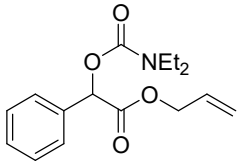
Yellow oil (19.4 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.20 (s, 1H), 4.23 – 4.12 (m, 2H), 3.37 – 3.29 (m, 4H), 2.48 (s, 3H), 1.21 (t, J = 6.6 Hz, 6H), 1.16 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.0, 154.9, 136.8, 133.4, 130.7, 128.7, 127.8, 126.2, 72.1, 61.3, 42.0, 41.5, 19.4, 14.0, 13.4. IR (KBr): 2972, 2928, 2873, 1748, 1702, 1469, 1425, 1375, 1264, 1212, 1163, 1078, 1026, 964, 764, 693, 627, 558, 499 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{23}NO_4Na$ $[M+Na]^+$: 316.1519, found 316.1520.

Isobutyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4pa)



Yellow oil (21.8 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 6.0 Hz, 2H), 7.37 – 7.35 (m, 3H), 5.92 (s, 1H), 3.95 – 3.84 (m, 2H), 3.36 – 3.27 (m, 4H), 1.92 – 1.82 (m, 1H), 1.22 – 1.20 (m, 3H), 1.15 – 1.14 (m, 3H), 0.83 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 154.7, 134.8, 128.8, 128.5, 127.3, 74.9, 71.2, 42.0, 41.5, 27.6, 18.8, 18.7, 13.9, 13.4. IR (KBr): 2966, 2933, 2876, 2357, 1748, 1702, 1468, 1420, 1376, 1265, 1211, 1161, 1078, 1091 764, 692, 632, 557, 502 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{17}H_{25}NO_4Na$ $[M+Na]^+$: 330.1676, found 330.1674.

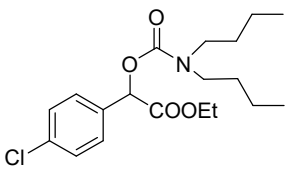
Allyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4qa)



Yellow oil (20.4 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.5 Hz, 2H), 7.39 – 7.34 (m, 2H), 5.95 (s, 1H), 5.86 – 5.78 (m, 1H), 5.21 (s, 0.5H), 5.17 – 5.16 (m, 1H), 5.14 (s, 0.5H), 4.61 (d, J = 5.5 Hz, 2H), 3.37 – 3.31 (m, 4H), 1.22 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.4, 154.7, 134.6, 131.5, 128.9, 128.6, 127.4, 118.1, 74.9, 65.7, 42.1, 41.6, 13.9, 13.4. IR (KBr): 2977, 2933, 2886, 1753,

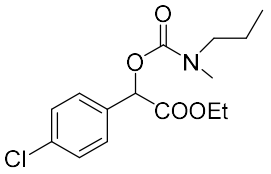
1705, 1471, 1429, 1374, 1268, 1210, 1164, 1081, 1027, 981, 918, 715, 697, 632, 555, 502 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{21}NO_4Na$ $[M+Na]^+$: 314.1363, found 314.1363.

Ethyl 2-(4-chlorophenyl)-2-((dibutylcarbamoyl)oxy)acetate (4ab)



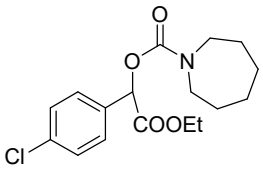
Yellow oil (24.0 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.84 (s, 1H), 4.20 – 4.11 (m, 2H), 3.32 – 3.18 (m, 4H), 1.68 – 1.48 (m, 4H), 1.37 – 1.27 (m, 4H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 154.9, 134.7, 133.3, 128.8, 128.7, 74.3, 61.5, 47.5, 46.9, 30.6, 30.1, 20.0, 19.9, 13.9, 13.8. IR (KBr): 2958, 2870, 1752, 1709, 1471, 1427, 1374, 1264, 1216, 1162, 1092, 1025, 903, 839, 769, 499, 440 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{28}ClNO_4Na$ $[M+Na]^+$: 392.1599, found 392.1596.

Ethyl 2-(4-chlorophenyl)-2-((methyl(propyl)carbamoyl)oxy)acetate (4ad)



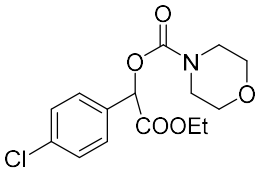
Pale yellow oil (20.7 mg, 66%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.84 (d, *J* = 7.6 Hz, 1H), 4.21 – 4.11 (m, 2H), 3.33 – 3.24 (m, 2H), 2.99 – 2.93 (m, 3H), 1.67 – 1.54 (m, 2H), 1.20 (t, *J* = 6.8 Hz, 3H), 0.90 (dd, *J* = 15.2, 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 155.1, 134.8, 133.2, 128.8, 128.7 (d, *J* = 2.2 Hz), 74.4, 61.6, 50.7 (d, *J* = 19.9 Hz), 34.4 (d, *J* = 74.9 Hz), 20.8 (d, *J* = 49.3 Hz), 13.9, 11.0 (d, *J* = 18.2 Hz). IR (KBr): 2964, 2931, 2873, 1752, 1711, 1485, 1403, 1268, 1215, 1168, 1092, 1022, 910, 841, 762, 603, 507, 436 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{20}ClNO_4Na$ $[M+Na]^+$: 336.0973, found 336.0970.

1-(4-Chlorophenyl)-2-ethoxy-2-oxoethyl azepane-1-carboxylate (4ai)



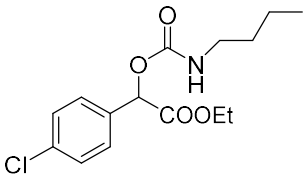
Pale yellow oil (24.4 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 4.22 – 4.09 (m, 2H), 3.58 – 3.49 (m, 2H), 3.44 – 3.33 (m, 2H), 1.85 – 1.82 (m, 1H), 1.69 – 1.55 (m, 7H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 154.9, 134.7, 133.2, 128.8, 128.6, 74.2, 61.5, 47.1, 46.8, 28.2, 28.1, 27.3, 26.7, 13.9. IR (KBr): 2930, 2860, 1751, 1706, 1480, 1425, 1371, 1262, 1205, 1178, 1089, 1019, 964, 894, 838, 767, 599, 500, 438 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{17}H_{23}ClNO_4$ $[M+H]^+$: 340.1310, found 340.1307.

1-(4-Chlorophenyl)-2-ethoxy-2-oxoethyl morpholine-4-carboxylate (4ak)



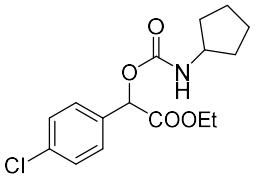
Pale yellow oil (15.4 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.87 (s, 1H), 4.24 – 4.11 (m, 2H), 3.69 (s, 5H), 3.54 – 3.48 (m, 3H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 154.1, 135.1, 132.9, 129.0, 128.8, 74.6, 66.5, 61.7, 44.5, 44.1, 13.9. IR (KBr): 2972, 2922, 2860, 1753, 1712, 1597 1434, 1229, 1110, 1022, 900, 847, 771, 717, 584, 506, 440 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{18}ClNO_5Na$ $[M+Na]^+$: 350.0766, found 350.0761.

Ethyl 2-((butylcarbamoyl)oxy)-2-(4-chlorophenyl)acetate (4ao)



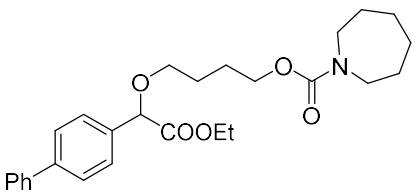
Pale yellow oil (17.2 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 5.87 (s, 1H), 5.02 (s, 1H), 4.23 – 4.13 (m, 2H), 3.20 – 3.19 (m, 2H), 1.49 (t, J = 7.0 Hz, 2H), 1.34 (dd, J = 14.0, 7.0 Hz, 2H), 1.21 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 155.1, 135.0, 133.1, 128.9, 73.9, 61.7, 40.9, 31.9, 19.8, 14.0, 13.7. IR (KBr): 3380, 2953, 2868, 1730, 1527, 1236, 1033, 1016, 928, 827, 774, 593, 507 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{20}ClNO_4Na$ $[M+Na]^+$: 336.0973, found 336.0970.

Ethyl 2-(4-chlorophenyl)-2-((cyclopentylcarbamoyl)oxy)acetate (4ap)



Yellow oil (13.7 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 5.87 (s, 1H), 5.00 (s, 1H), 4.24 – 4.11 (m, 2H), 4.00 – 3.97 (m, 1H), 1.95 (s, 2H), 1.66 (s, 2H), 1.58 (s, 2H), 1.45 – 1.39 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 154.5, 134.9, 133.0, 128.8, 73.7, 61.7, 52.9, 33.1, 23.5, 13.9. IR (KBr): 3357, 2960, 2864, 1725, 1525, 1385, 1222, 1095, 1014, 832, 775, 523 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}ClNO_4Na$ $[M+Na]^+$: 348.0973, found 348.0972.

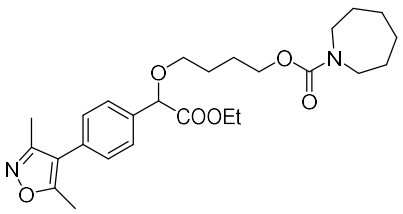
4-(1-([1,1'-Biphenyl]-4-yl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (5)



Yellow oil (78.8 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 – 7.58 (m, 2H), 7.57 – 7.56 (m, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 4.89 (s, 1H), 4.25 – 4.15 (m, 2H), 4.11 (d, J = 5.6 Hz, 2H), 3.63 – 3.60 (m, 1H), 3.53 – 3.50 (m, 1H), 3.42 (t, J = 6.0 Hz, 2H), 3.37 – 3.36 (t, J = 5.6 Hz, 2H),

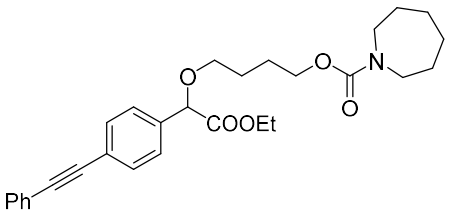
1.78 – 1.76 (m, 4H), 1.68 – 1.65 (m, 4H), 1.54 – 1.52 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 156.3, 141.4, 140.6, 135.7, 128.7, 127.5, 127.4, 127.2, 127.0, 80.9, 69.4, 64.7, 61.1, 46.8, 46.4, 28.5, 28.3, 27.3, 26.9, 26.2, 25.8, 14.1. IR (KBr): 2927, 2859, 1741, 1691, 1463, 1423, 1263, 1199, 1179, 1091, 1000, 892, 842, 761, 550, 479, 436 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{27}H_{35}NO_5Na$ $[M+Na]^+$: 476.2407, found 476.2741.

4-(1-(4-(3,5-Dimethylisoxazol-4-yl)phenyl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (6)



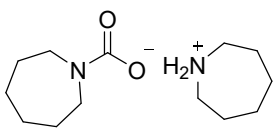
Yellow oil (77.4 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.86 (s, 1H), 4.20 – 4.16 (m, 2H), 4.08 (s, 2H), 3.61 – 3.60 (m, 1H), 3.51 (s, 1H), 3.39 (t, J = 5.2 Hz, 3H), 3.34 (s, 3H), 2.37 (s, 3H), 2.23 (s, 3H), 1.74 (s, 4H), 1.65 – 1.63 (m, 4H), 1.51 (s, 4H), 1.22 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 165.2, 158.5, 156.3, 135.9, 130.6, 129.1, 127.3, 116.1, 80.8, 69.5, 64.6, 61.2, 46.8, 46.4, 28.5, 28.2, 27.3, 26.8, 26.2, 25.8, 14.0, 11.5, 10.7. IR (KBr): 2929, 2862, 1743, 1693, 1470, 1426, 1374, 1266, 1199, 1096, 1017, 843, 758, 697, 557, 499 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{26}H_{36}N_2O_6$ $[M+H]^+$: 473.2640, found 473.2642.

4-(2-Ethoxy-2-oxo-1-(4-(phenylethynyl)phenyl)ethoxy)butyl azepane-1-carboxylate (7)



Yellow oil (74.4 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 4H), 7.42 (d, J = 7.6 Hz, 2H), 7.30 (s, 3H), 4.84 (s, 1H), 4.19 – 4.12 (m, 2H), 4.09 (s, 2H), 3.58 – 3.57 (m, 1H), 3.47 – 3.45 (m, 1H), 3.40 (t, J = 5.6 Hz, 2H), 3.33 (t, J = 5.2 Hz, 2H), 1.73 (s, 4H), 1.66 – 1.62 (m, 4H), 1.51 (s, 4H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 156.2, 136.6, 131.6, 131.4, 128.2, 126.9, 123.4, 122.9, 89.8, 88.8, 80.6, 69.3, 64.6, 61.1, 46.7, 46.3, 28.4, 28.2, 27.2, 26.8, 26.1, 25.7, 13.9. IR (KBr): 3059, 2930, 2864, 1746, 1694, 1603, 1473, 1426, 1371, 1264, 1202, 1094, 1023, 912, 842, 761, 692, 641, 523 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{29}H_{35}NO_5Na$ $[M+Na]^+$: 500.2409, found 500.2405.

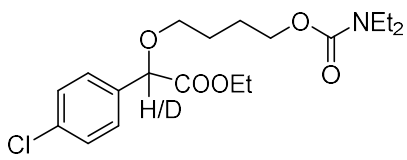
Azepan-1-ium azepane-1-carboxylate (8)



Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (br, 2 H), 3.34 (t, J = 6.0 Hz, 4 H), 3.00 (t, J = 4.2 Hz, 4 H), 1.73 (s, 4 H), 1.59 (s, 8 H), 1.47 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 46.5, 45.8, 29.0,

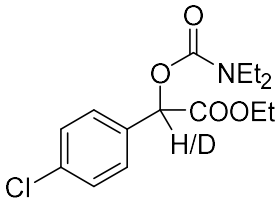
27.5, 26.9, 26.3.

The mixture of 3aa and 3aa-D



Yellow oil (29.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.8 Hz, 2 H), 4.80 (s, 0.22 H), 4.20 – 4.12 (m, 2 H), 4.08 (t, J = 6.0 Hz, 2 H), 3.59 – 3.56 (m, 2 H), 3.48 – 3.44 (m, 2 H), 3.24 (s, 4 H), 1.72 (s, 4 H), 1.20 (t, J = 7.2 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5, 156.0, 135.2, 135.2, 134.4, 128.7, 128.3, 80.4, 69.5, 69.4, 64.6, 61.3, 41.5, 41.4, 26.2, 25.8, 14.0, 13.8, 13.7.

The mixture of 3ad and 3ad-D



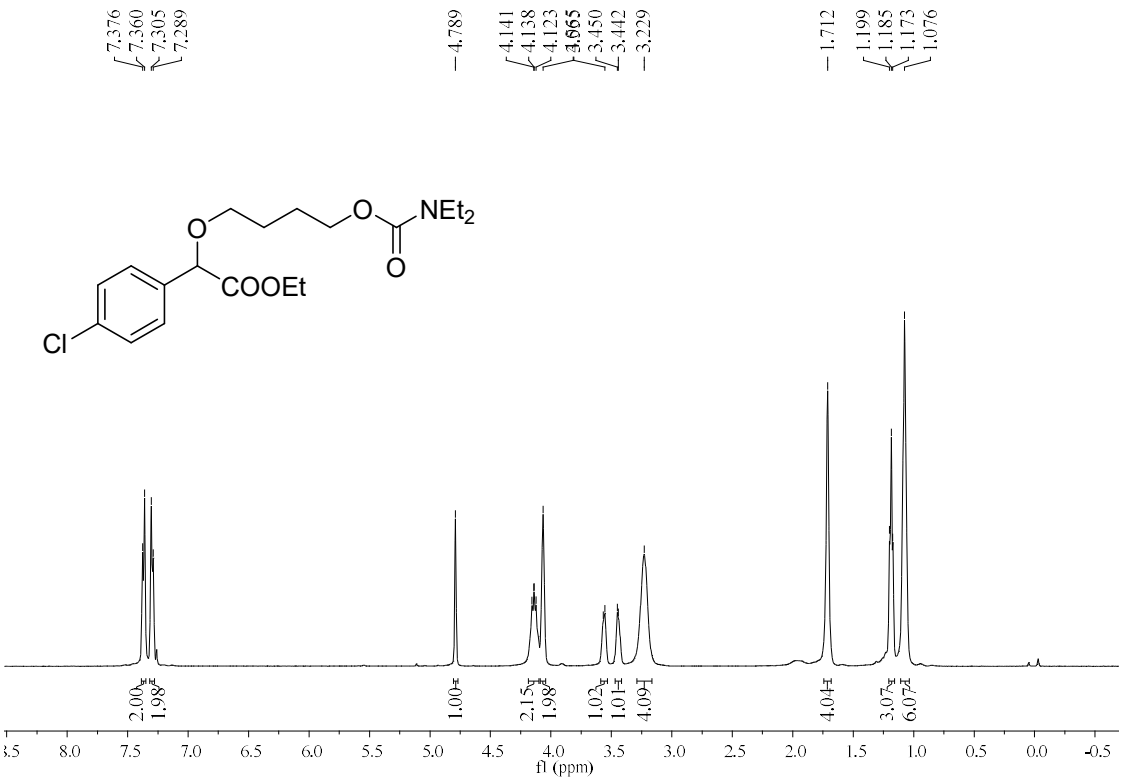
Yellow oil (20.7 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H), 5.90 (s, 0.32 H), 4.24 – 4.15 (m, 2 H), 3.40 – 3.31 (m, 4 H), 1.23 (t, J = 7.0 Hz, 6 H), 1.17 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.3, 154.6, 134.8, 133.3, 133.2, 128.9, 128.7, 74.2, 61.6, 42.2, 41.6, 14.0, 13.4.

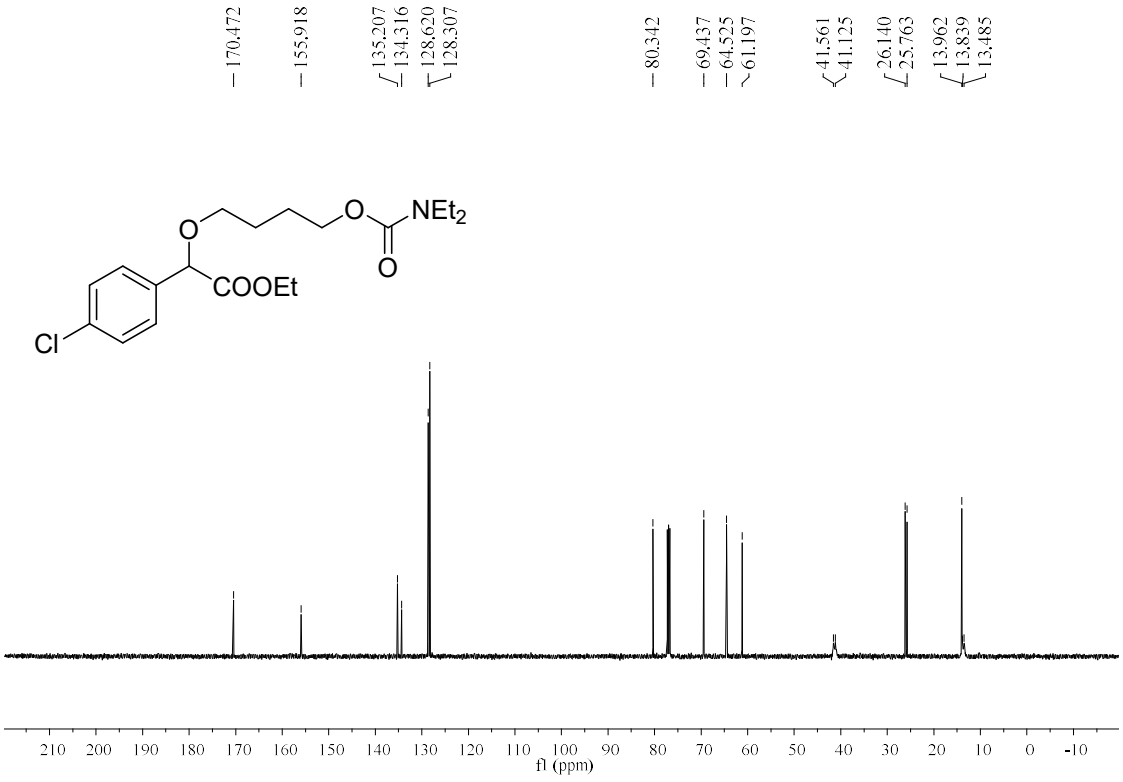
References

1. H. Keipour and T. Ollevier, *Org. Lett.*, 2017, **19**, 5736-5739.
2. C. Qi, D. Yan, W. Xiong and H. Jiang, *Chin. J. Chem.*, 2018, **36**, 399-405.
3. Q. Song, Z.-H. Zhou, H. Yin and L.-N. He, *ChemSusChem*, 2015, **8**, 3967-3972.
4. N. Mase and T. Horibe, *Org. Lett.*, 2013, **15**, 1854-1857.

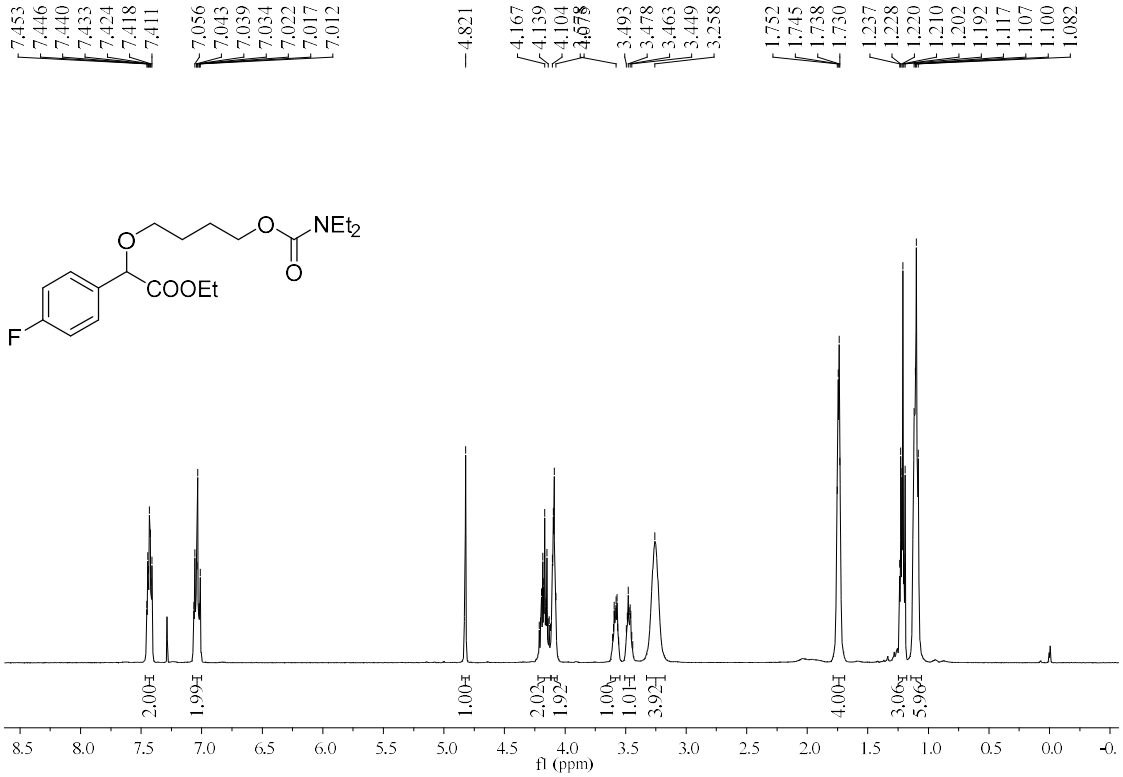
L. NMR Spectra

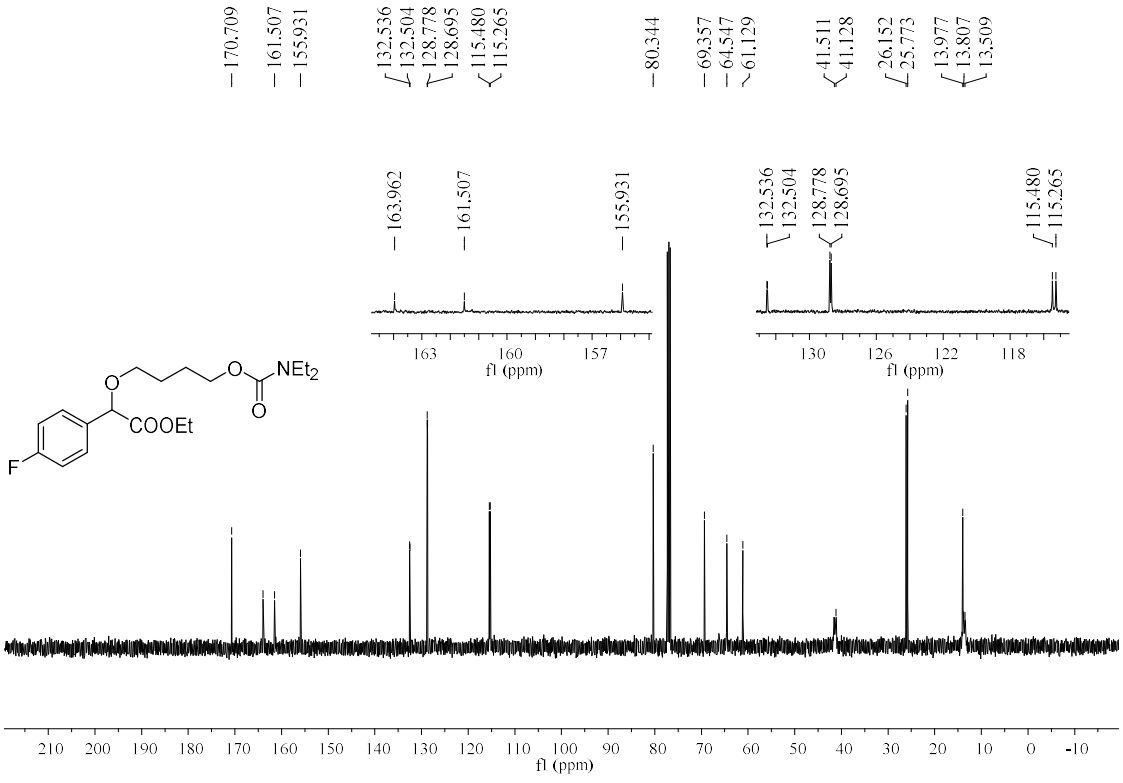
Ethyl 2-(4-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3aa)



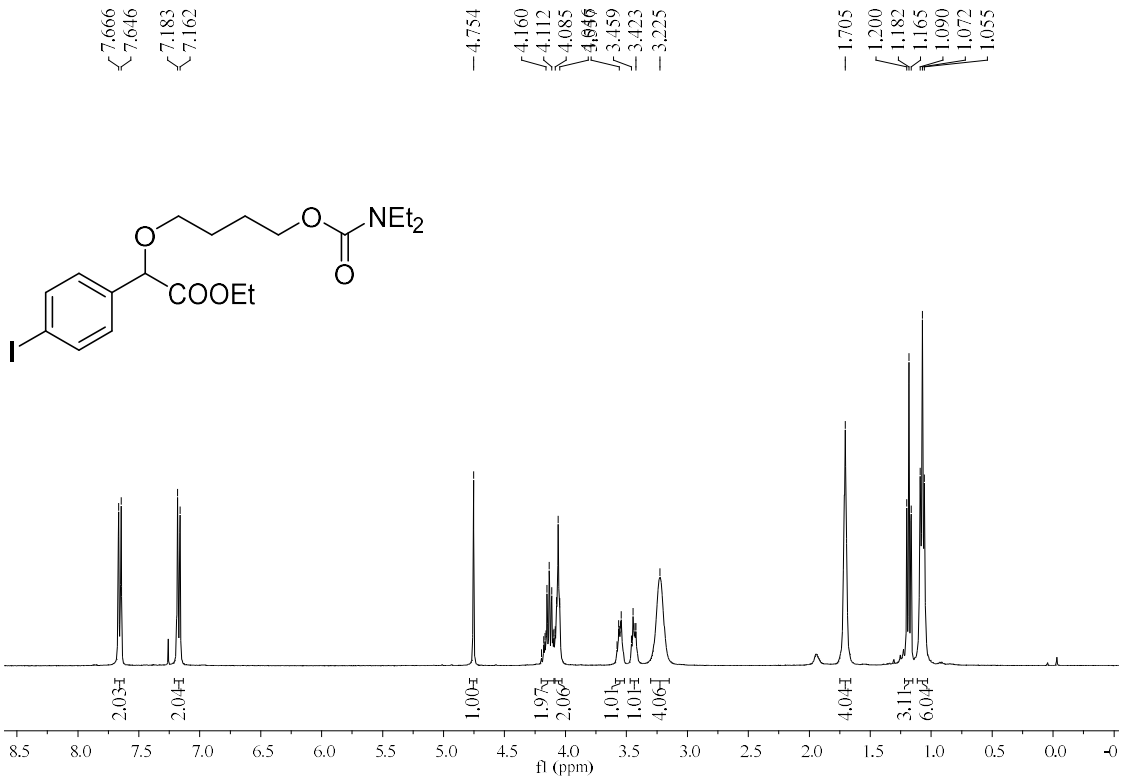


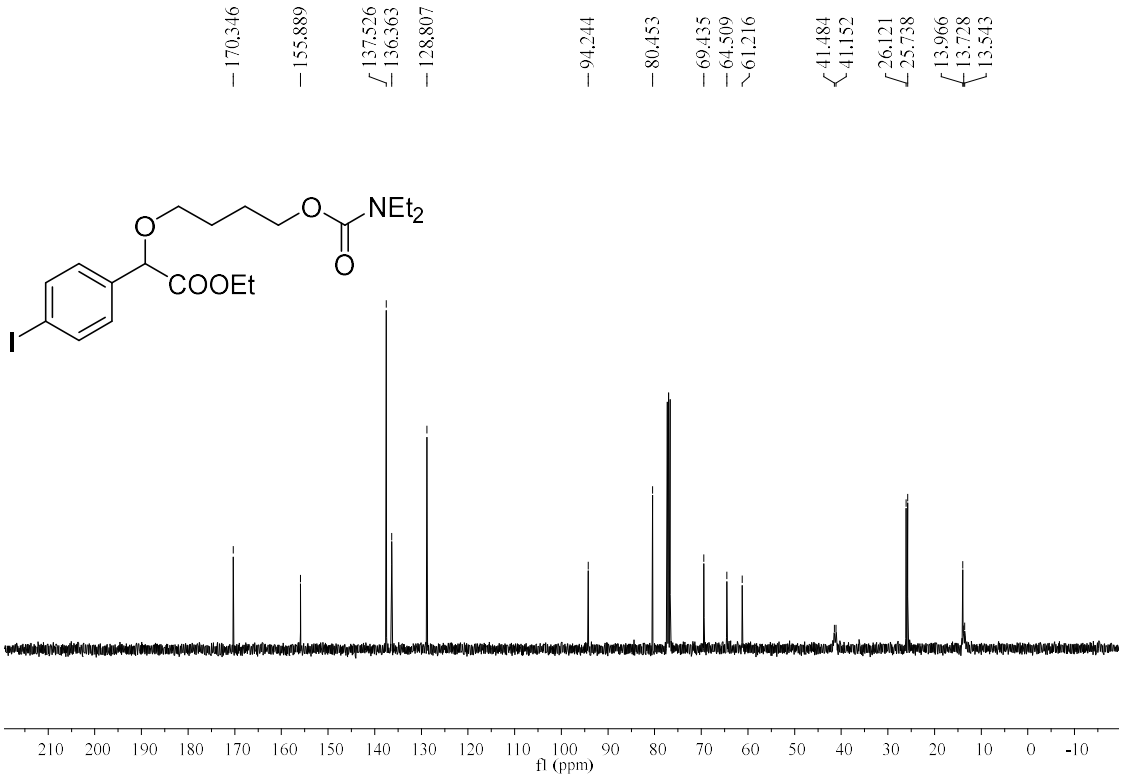
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-fluorophenyl)acetate (3ba)



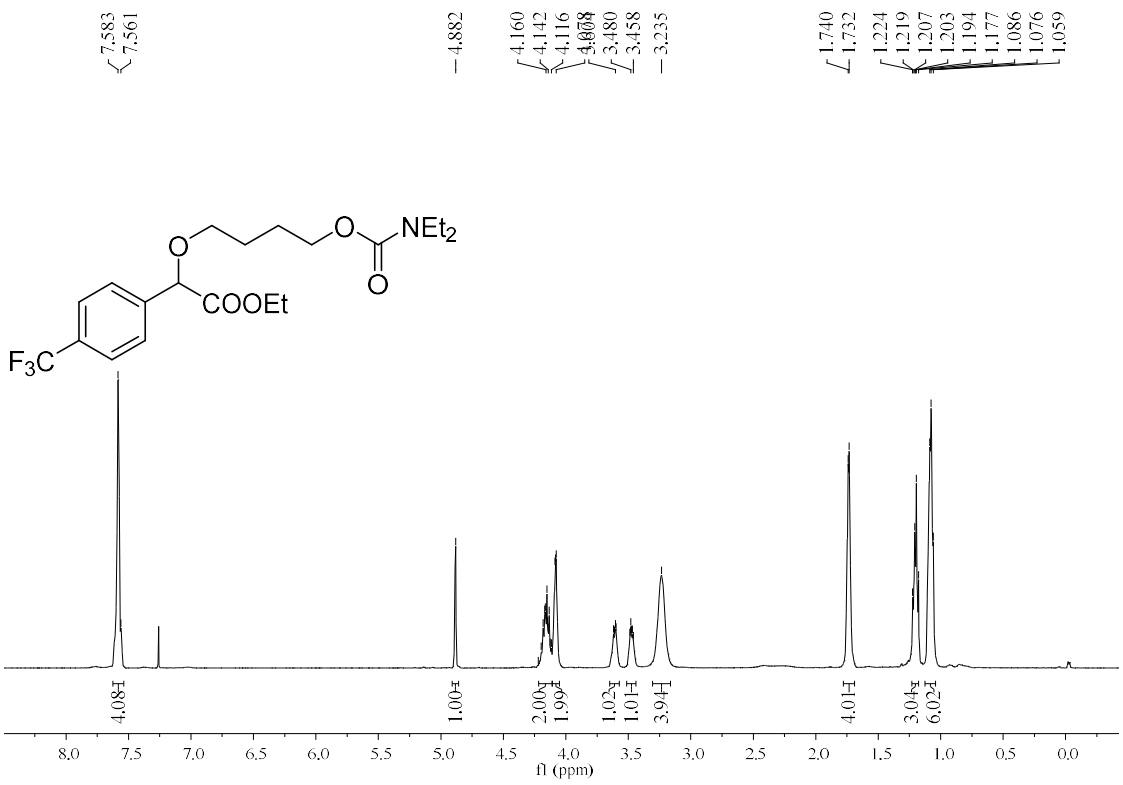


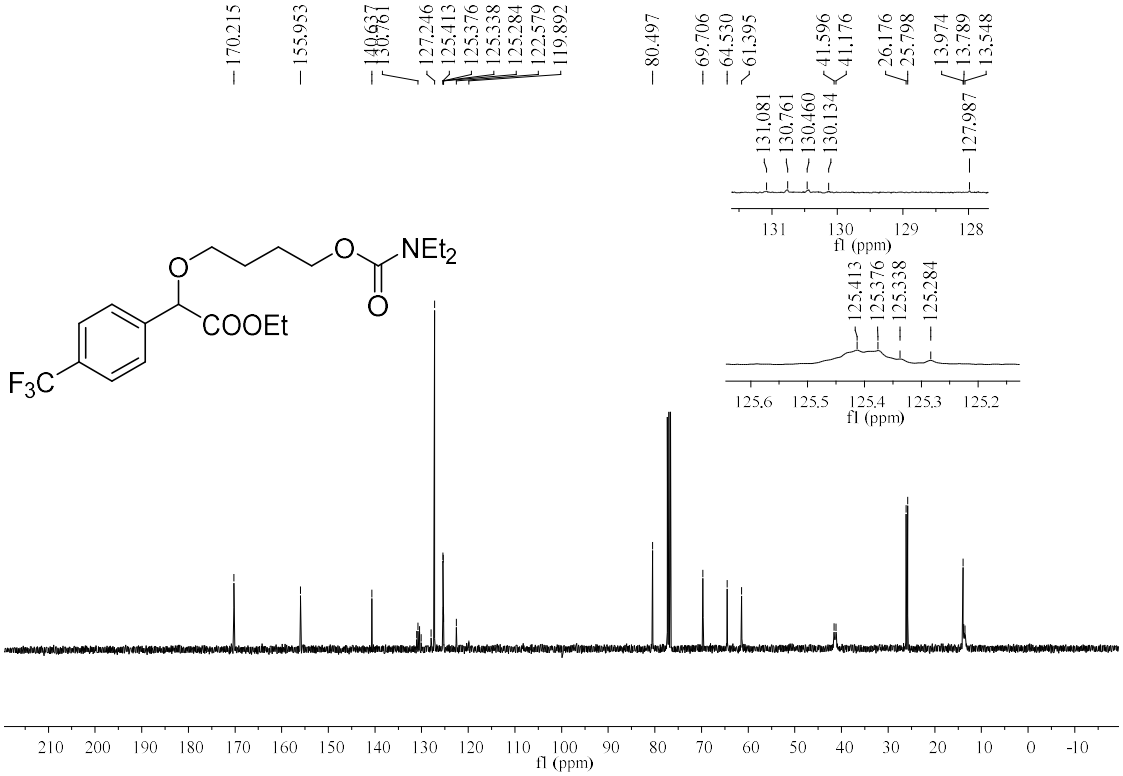
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-iodophenyl)acetate (3ca)



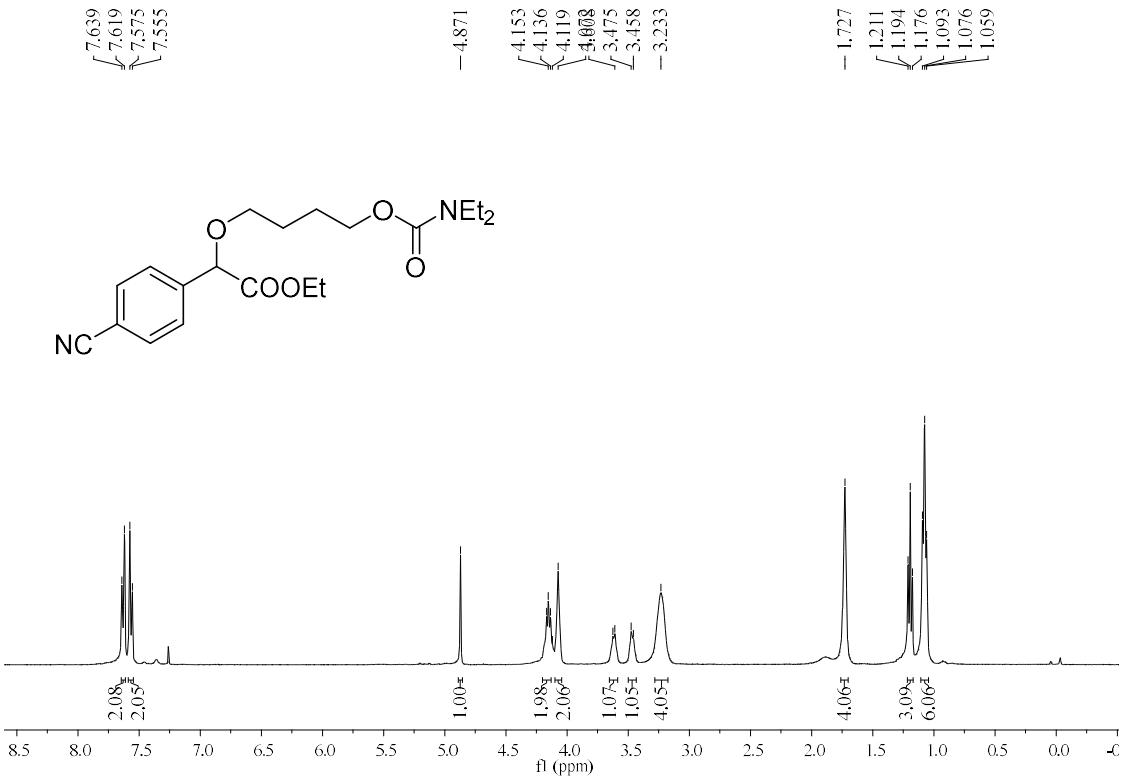


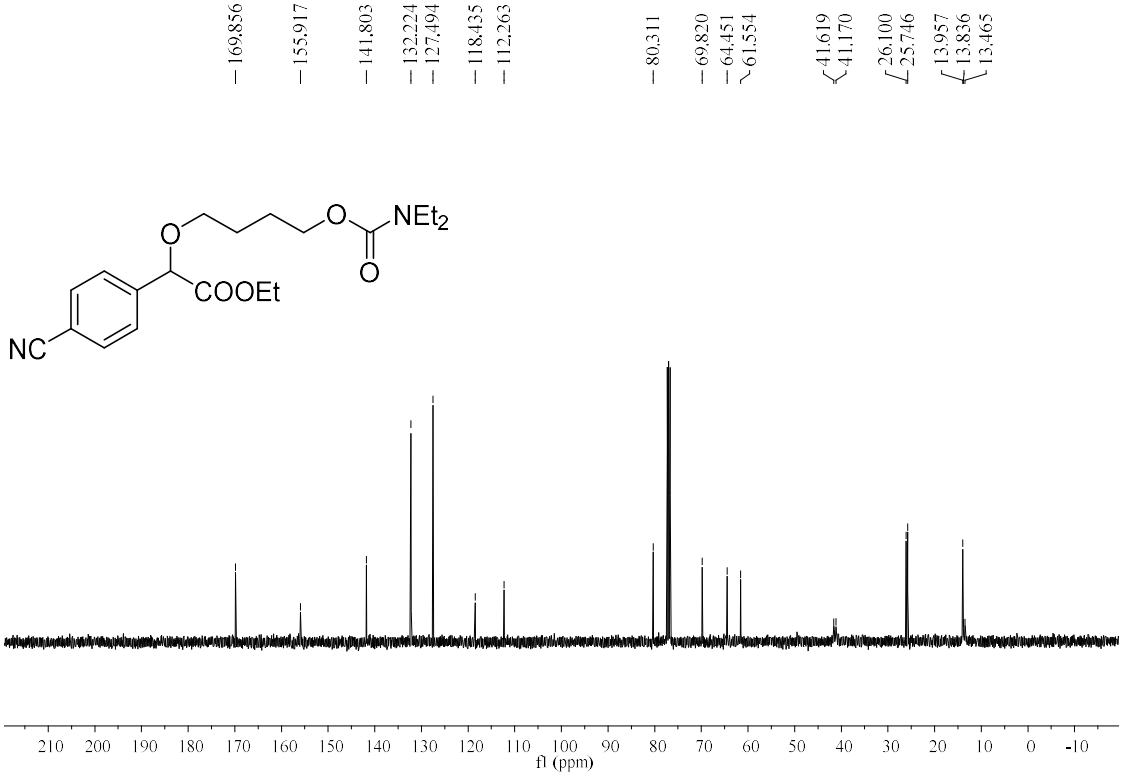
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-(trifluoromethyl)phenyl)acetate (3da)



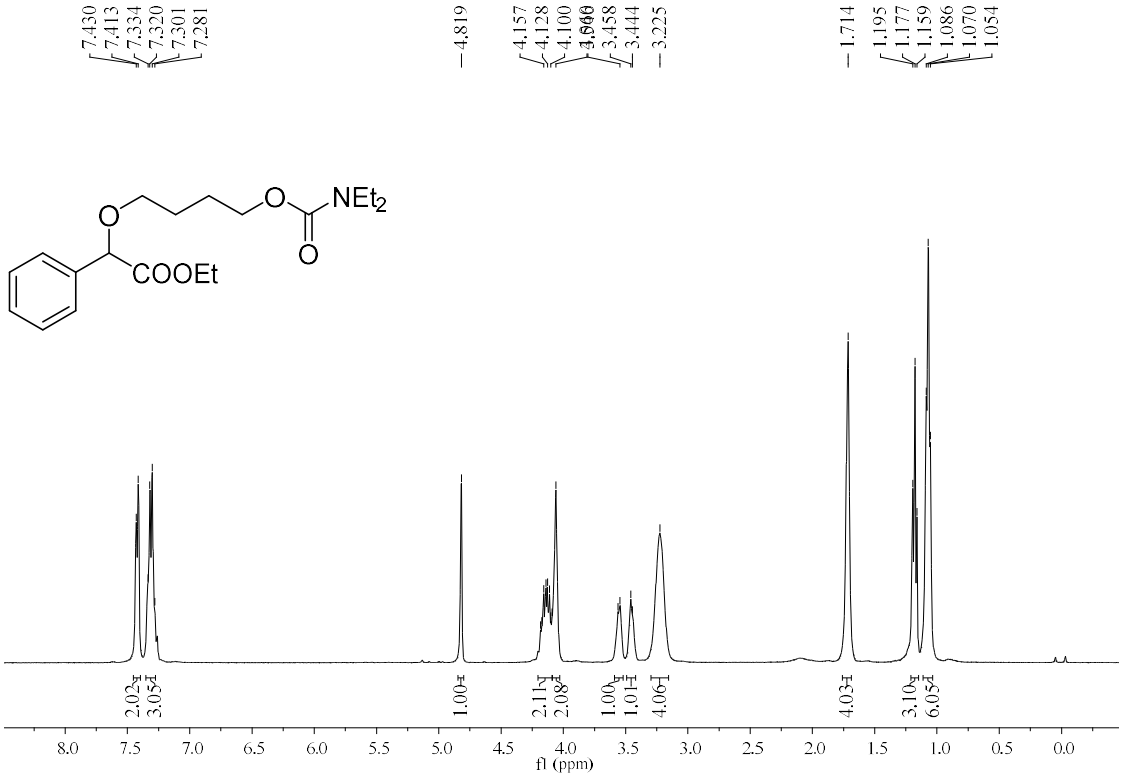


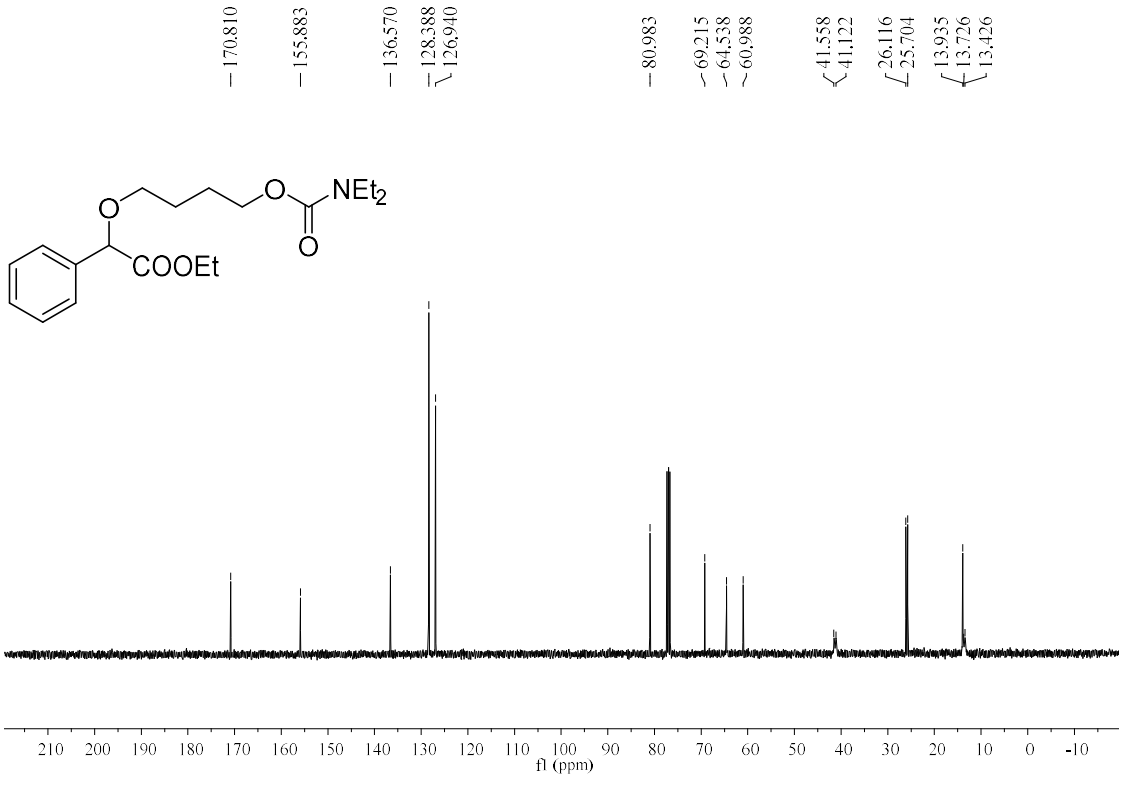
Ethyl 2-(4-cyanophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ea)



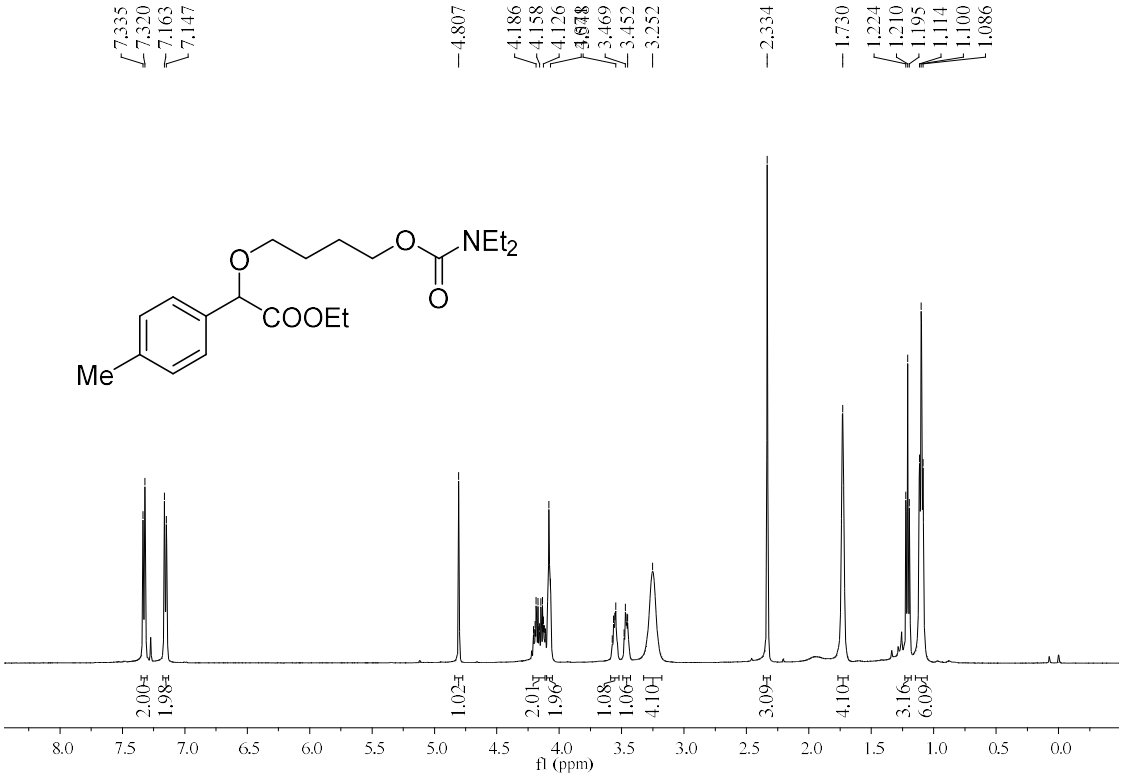


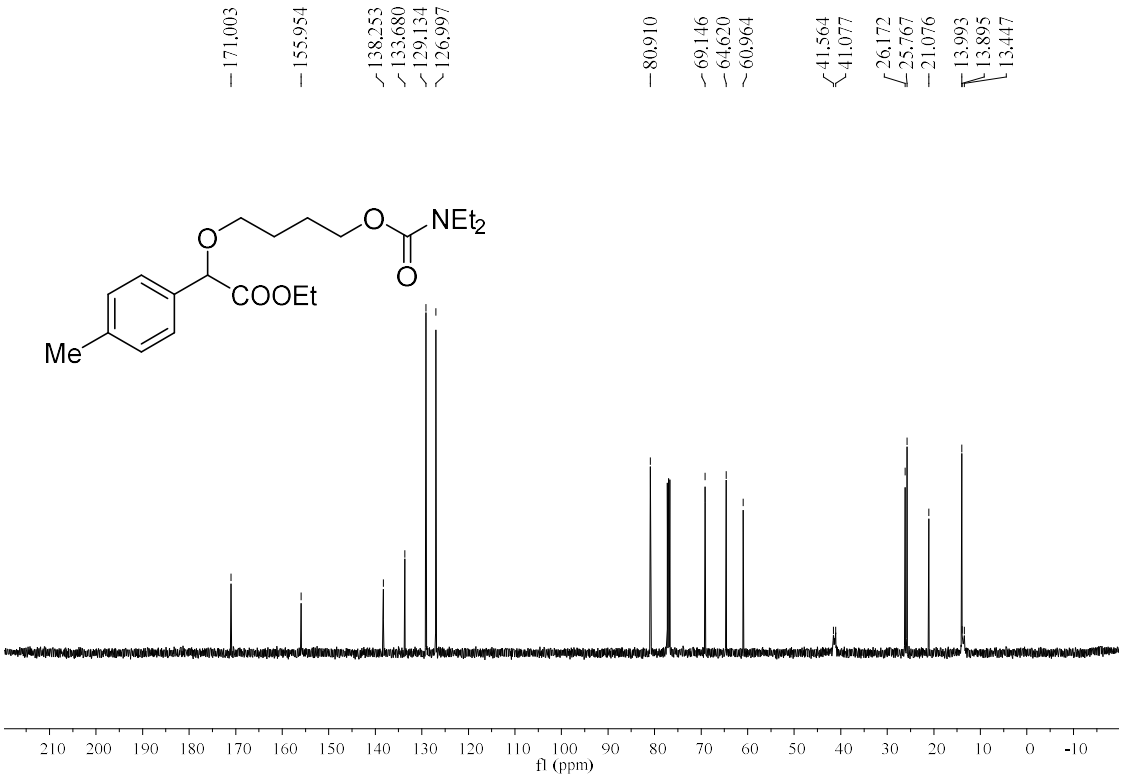
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3fa)



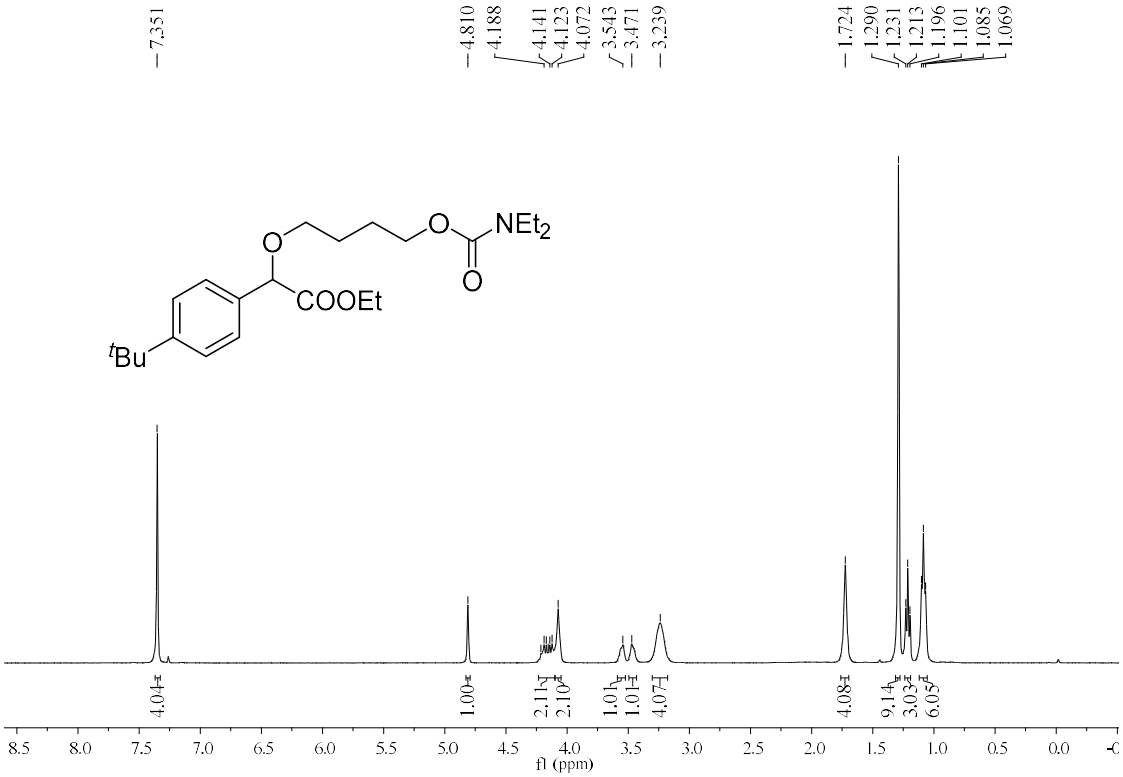


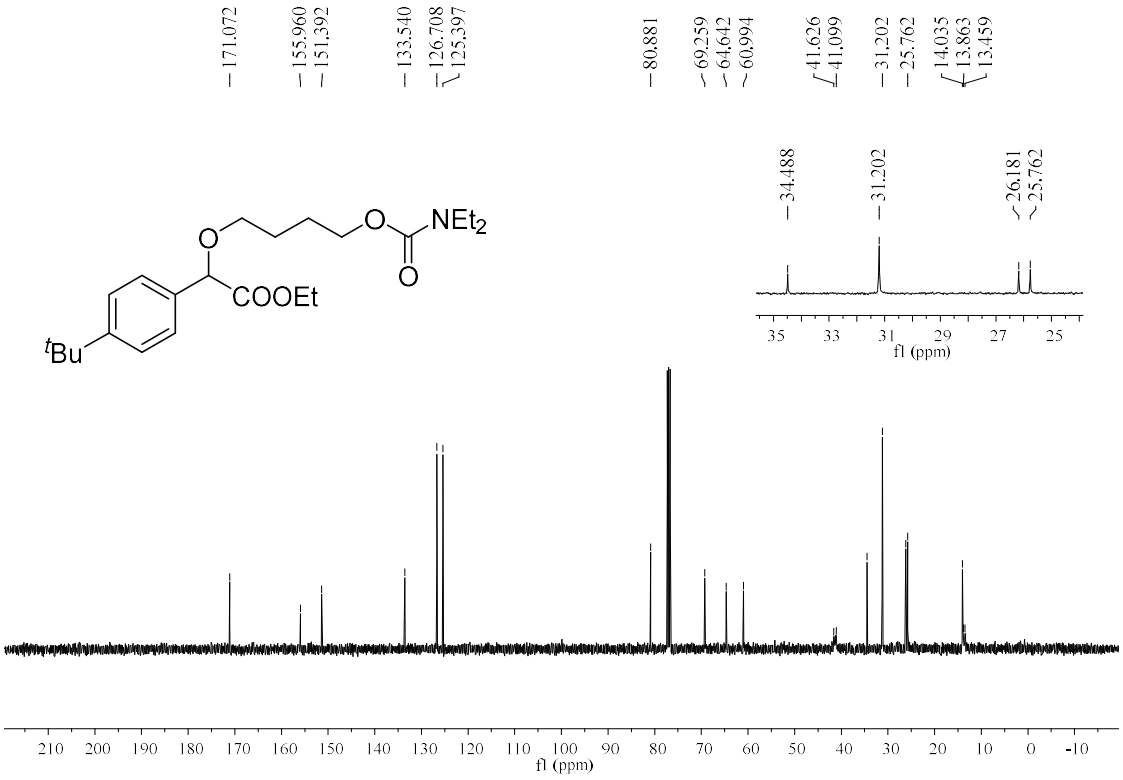
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(*p*-tolyl)acetate (3ga)



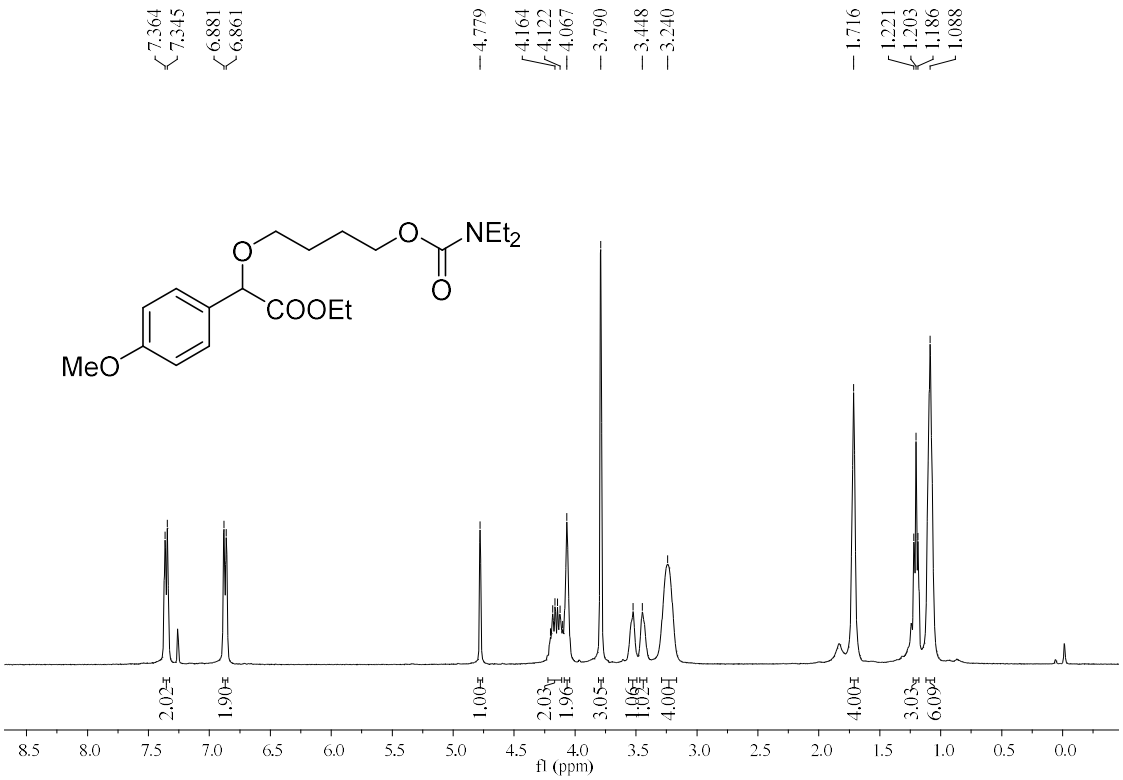


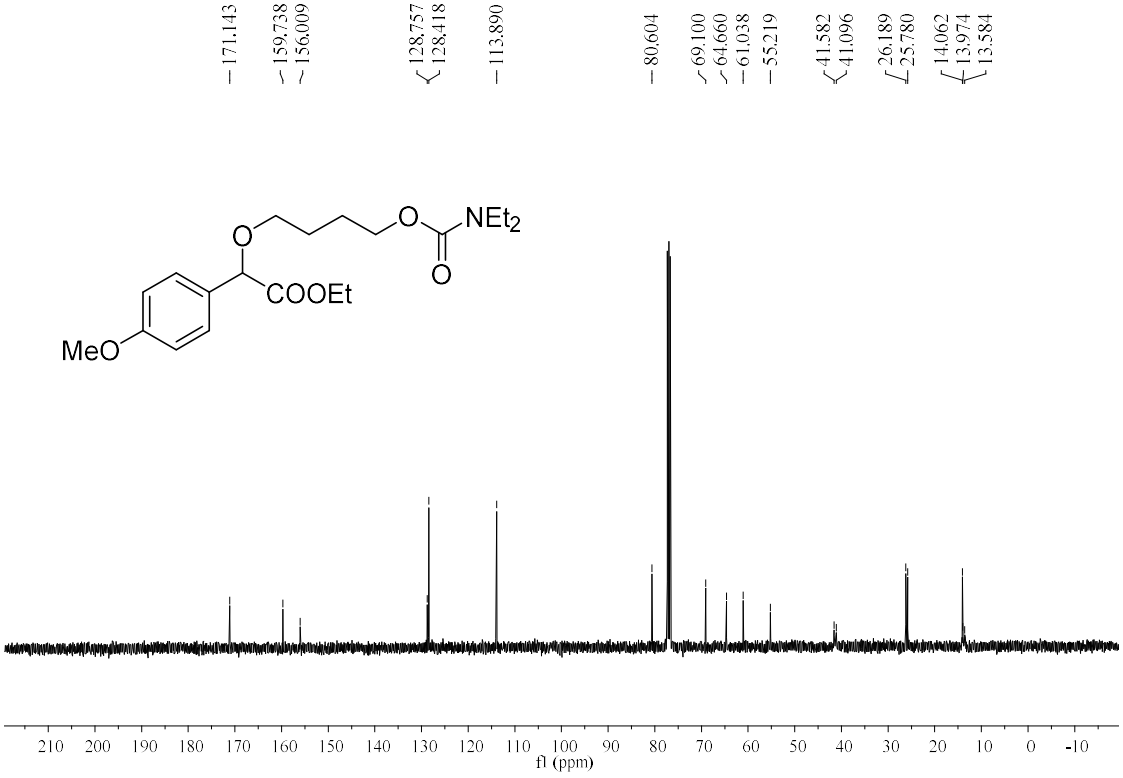
Ethyl 2-(4-(*tert*-butyl)phenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ha)



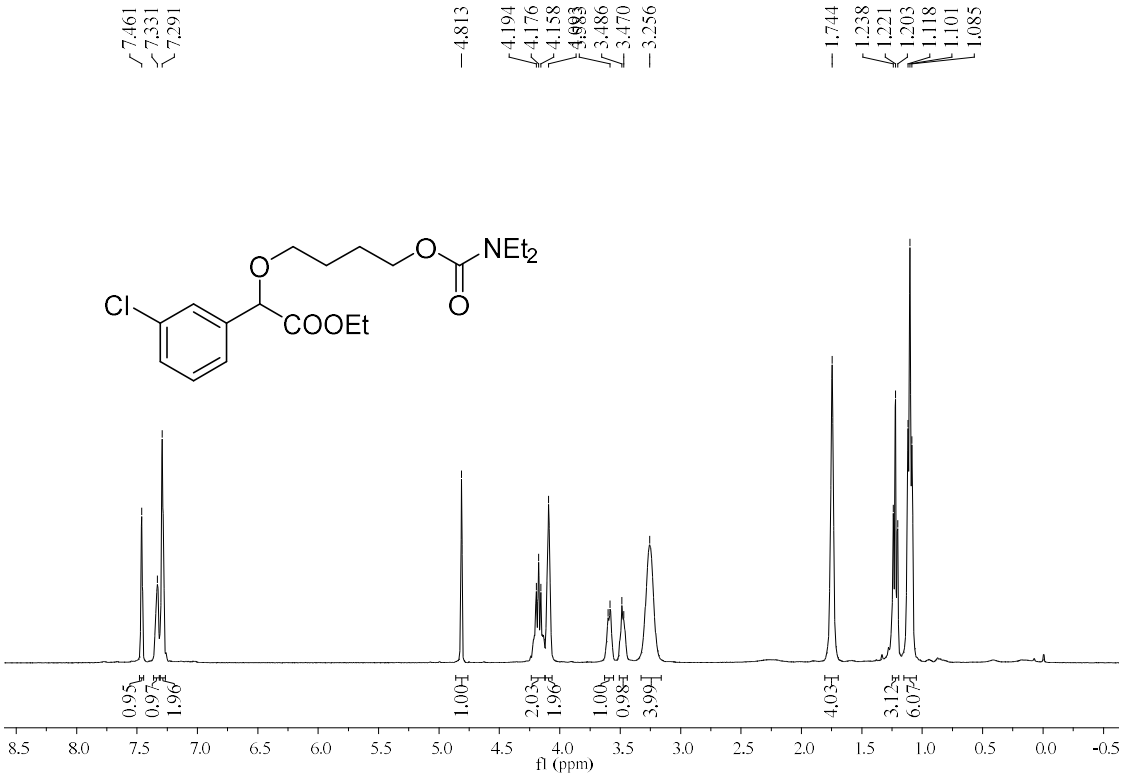


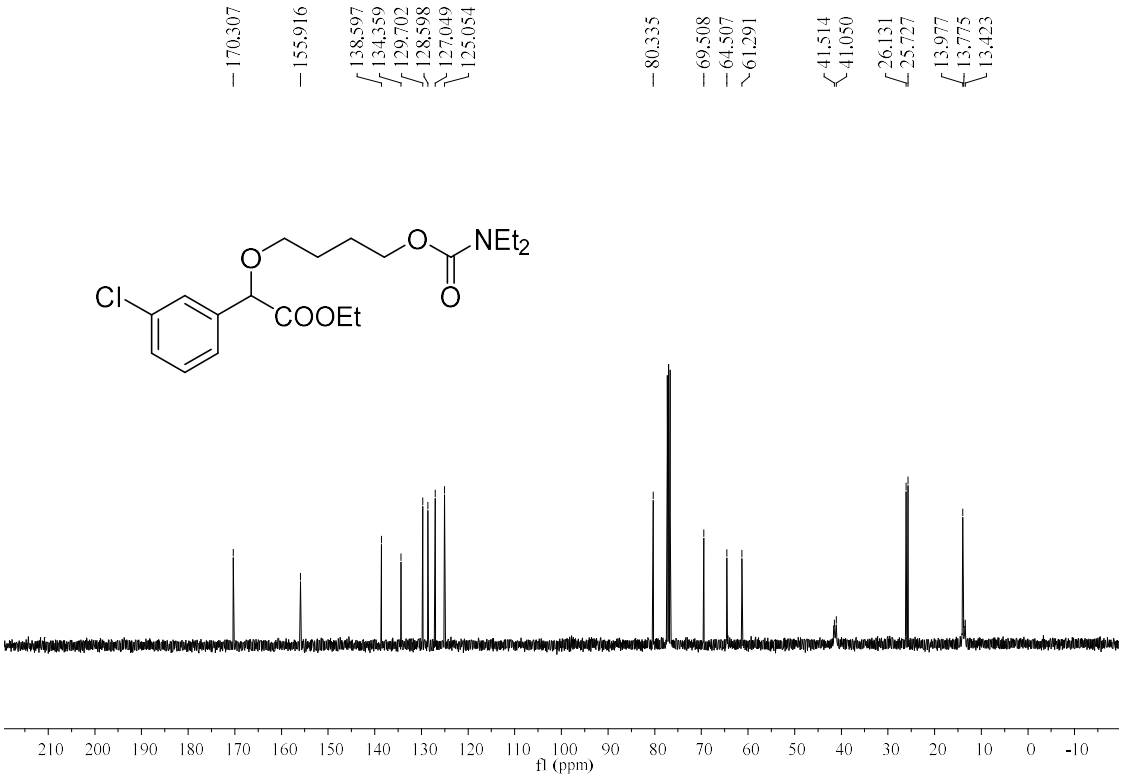
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(4-methoxyphenyl)acetate (3ia)



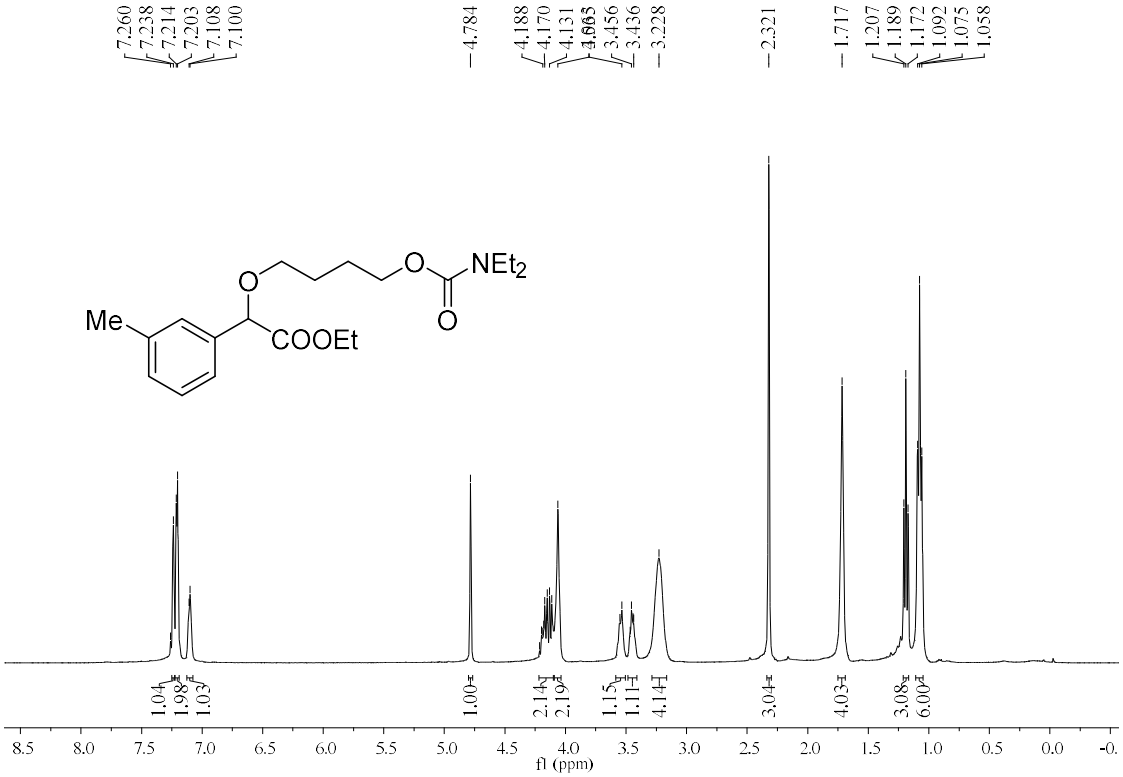


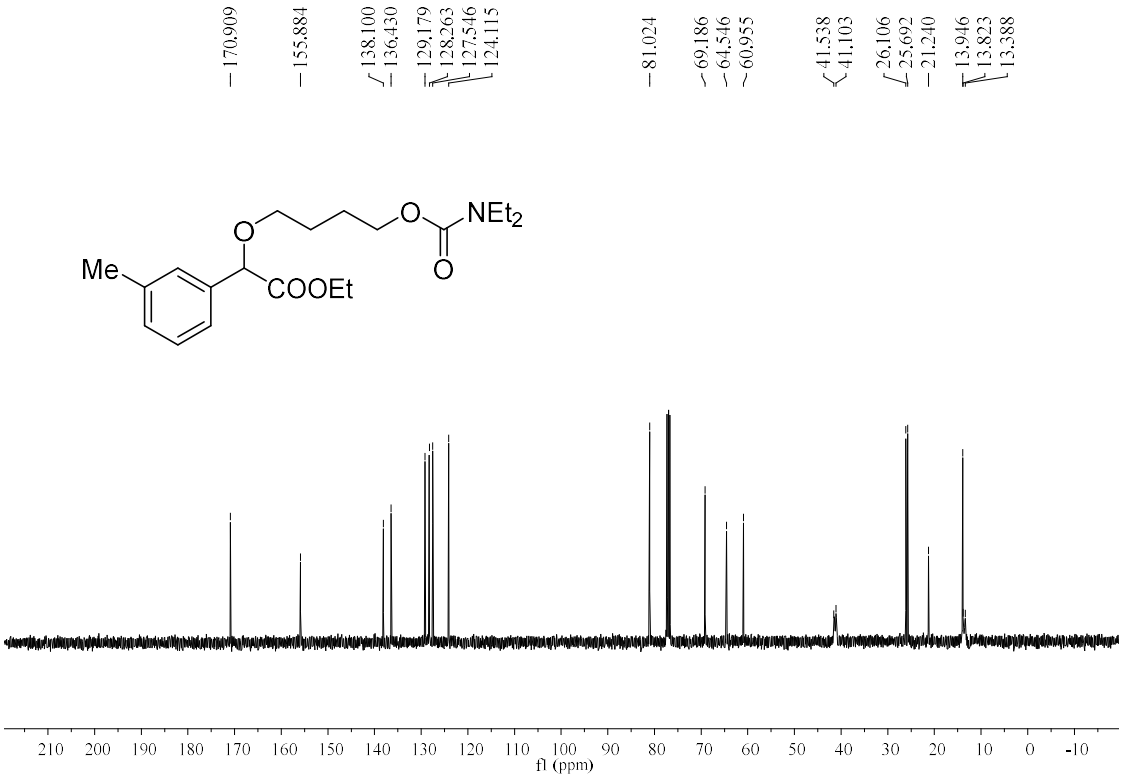
Ethyl 2-(3-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3ja)



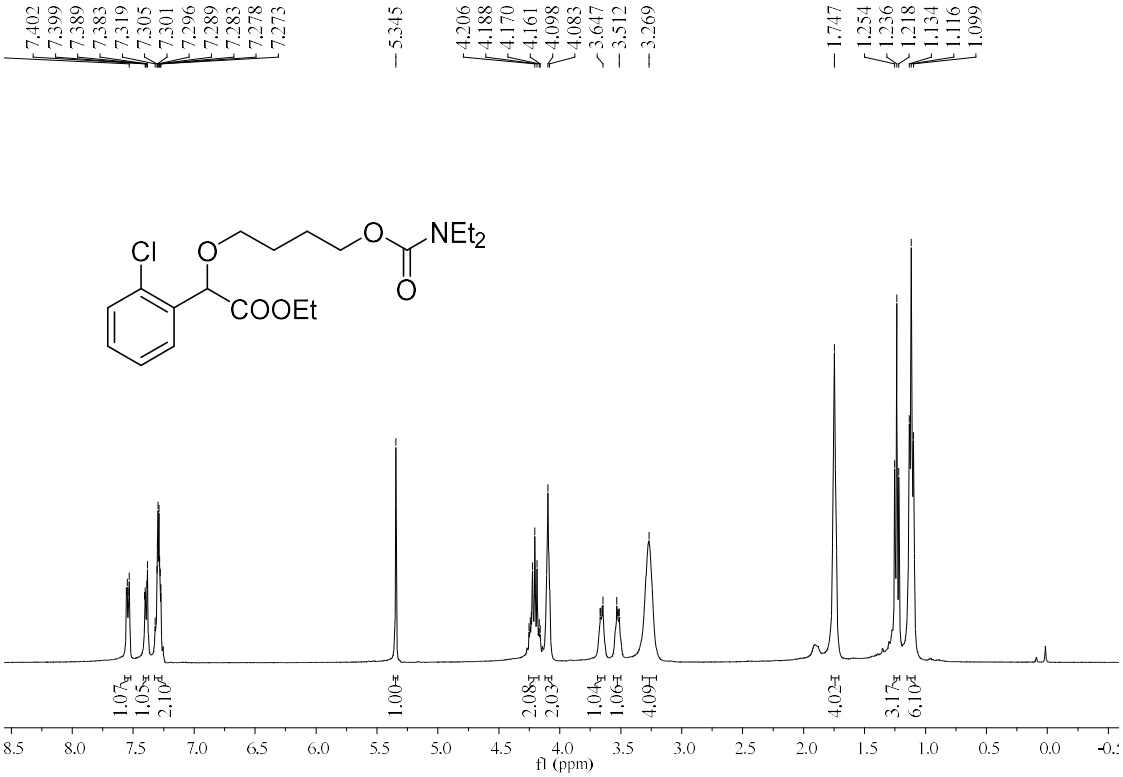


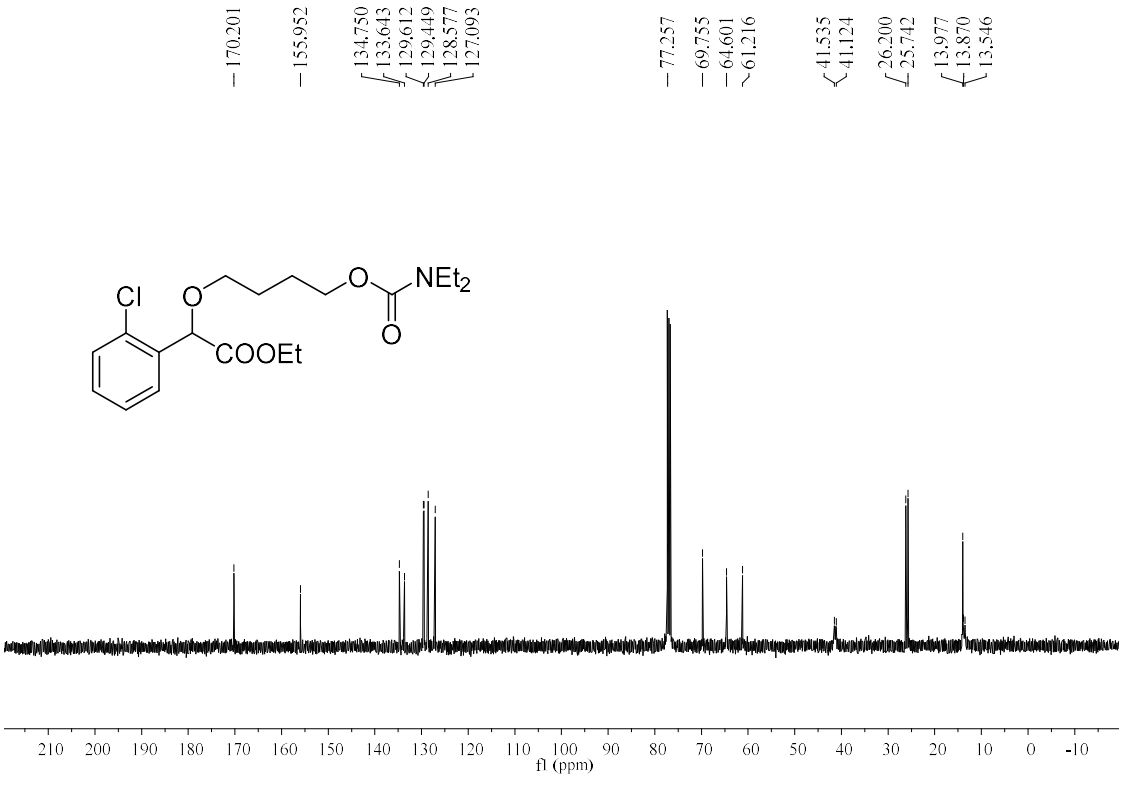
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(m-tolyl)acetate (3ka)



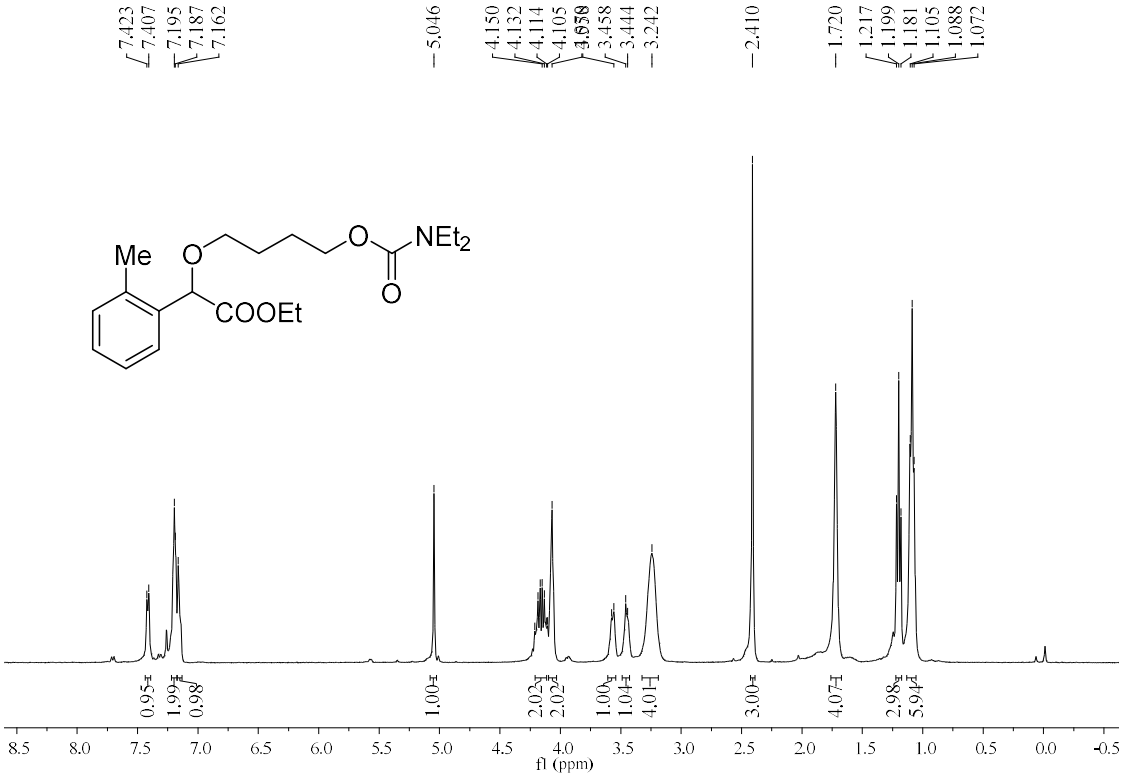


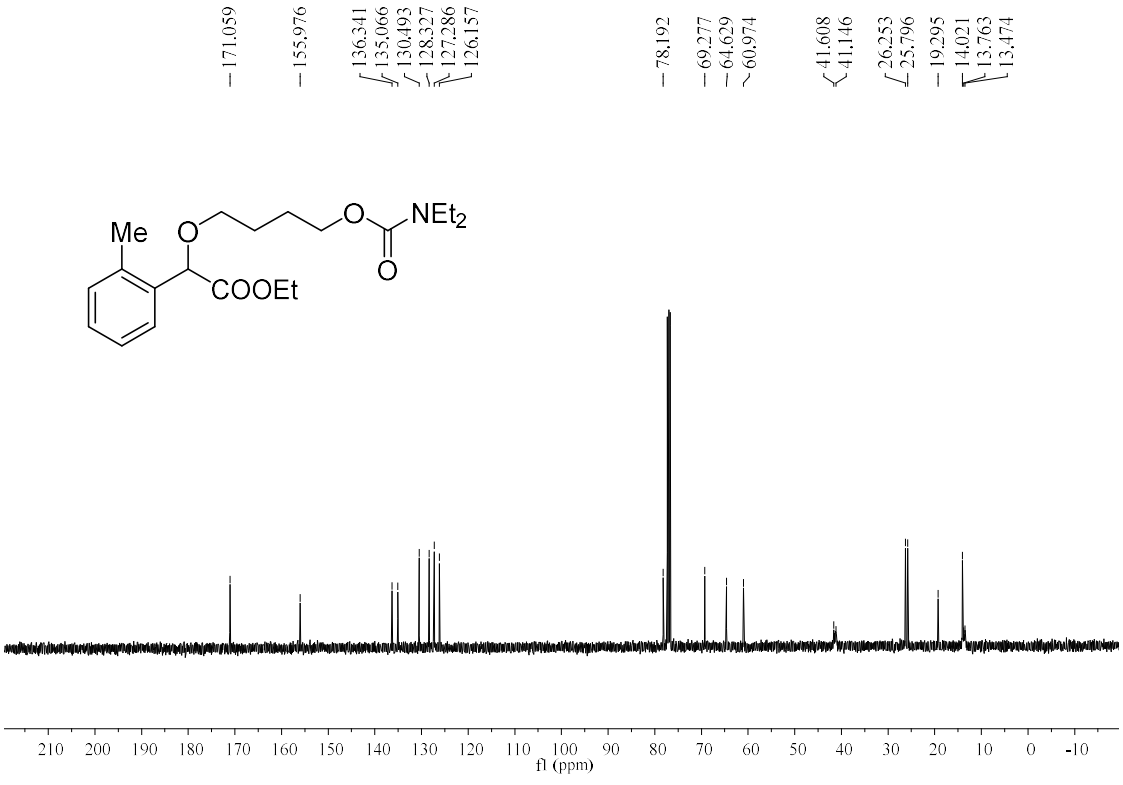
Ethyl 2-(2-chlorophenyl)-2-(4-((diethylcarbamoyl)oxy)butoxy)acetate (3la)



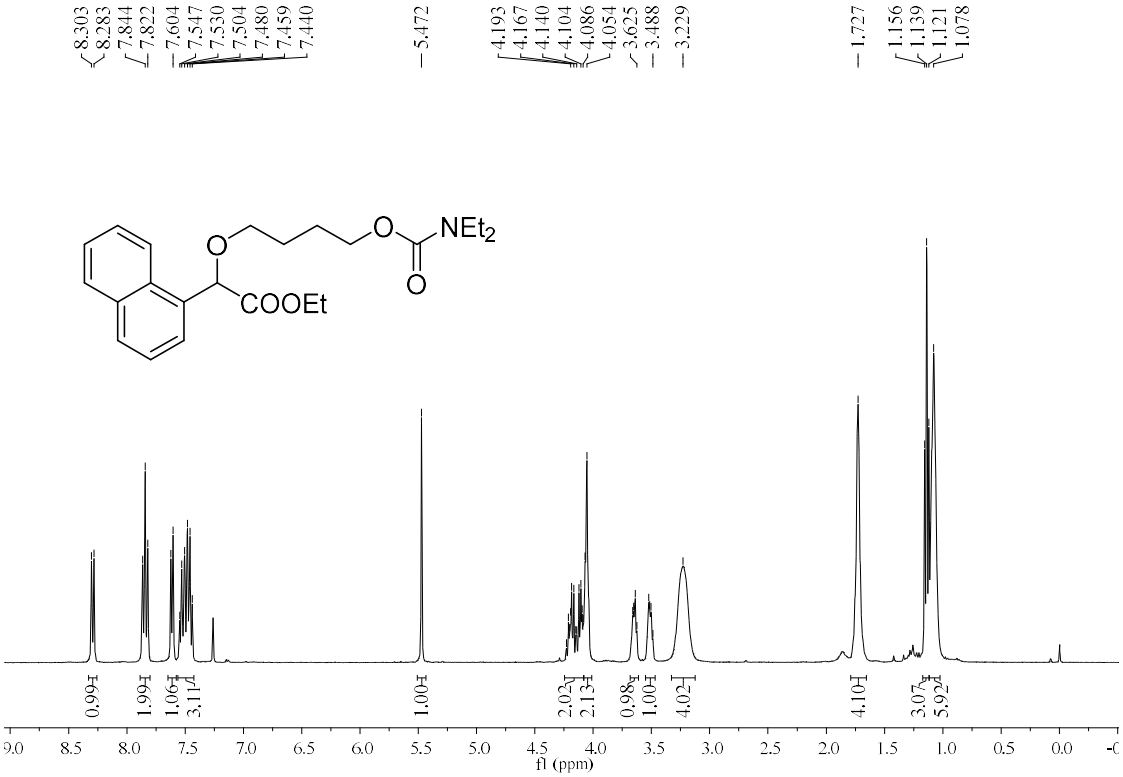


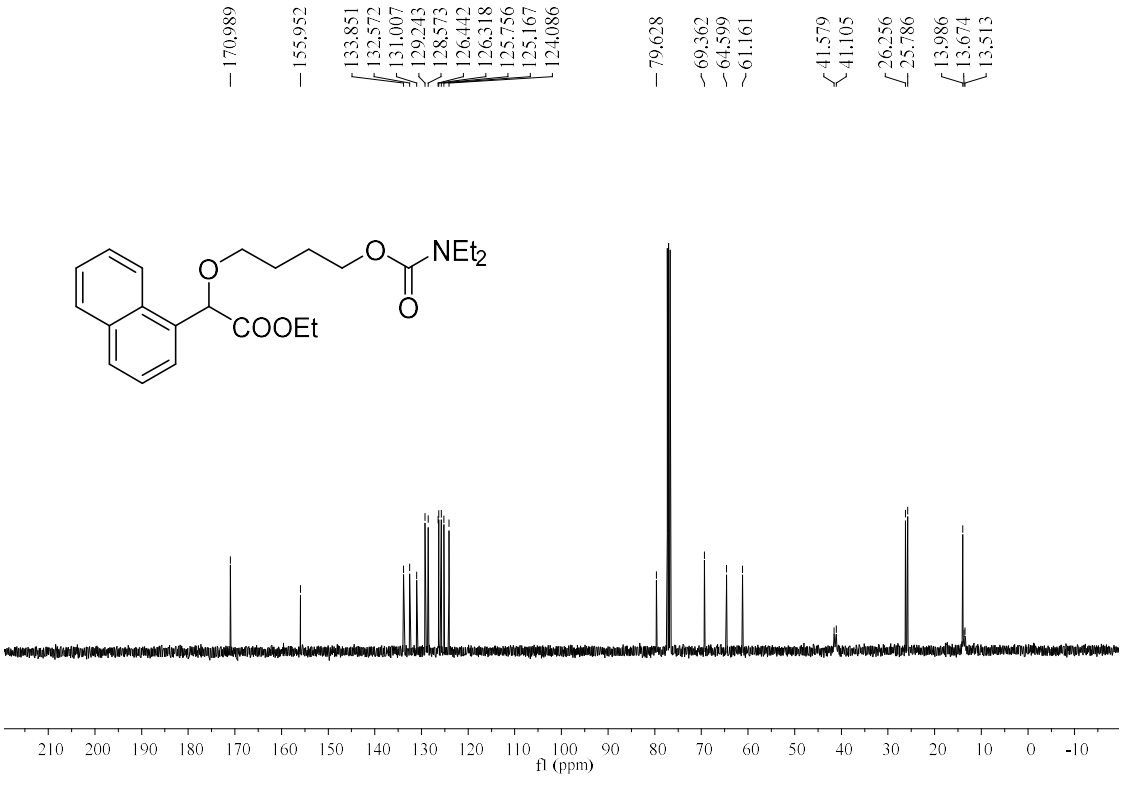
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(*o*-tolyl)acetate (3ma)



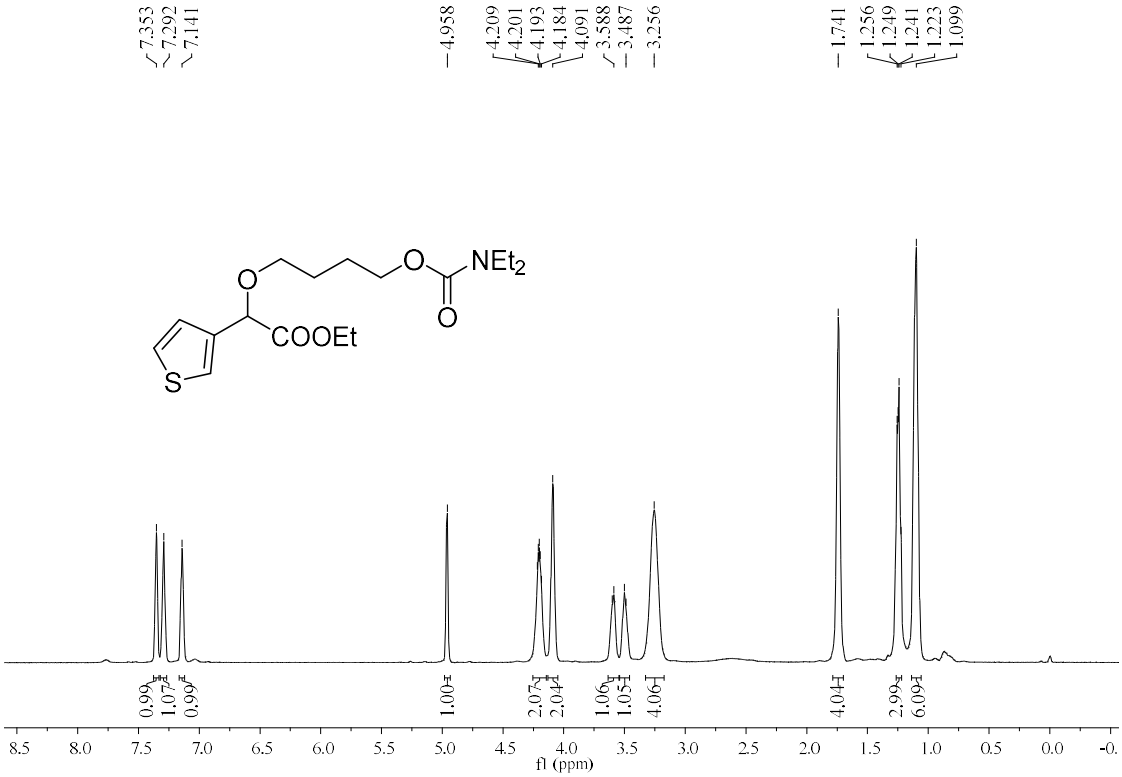


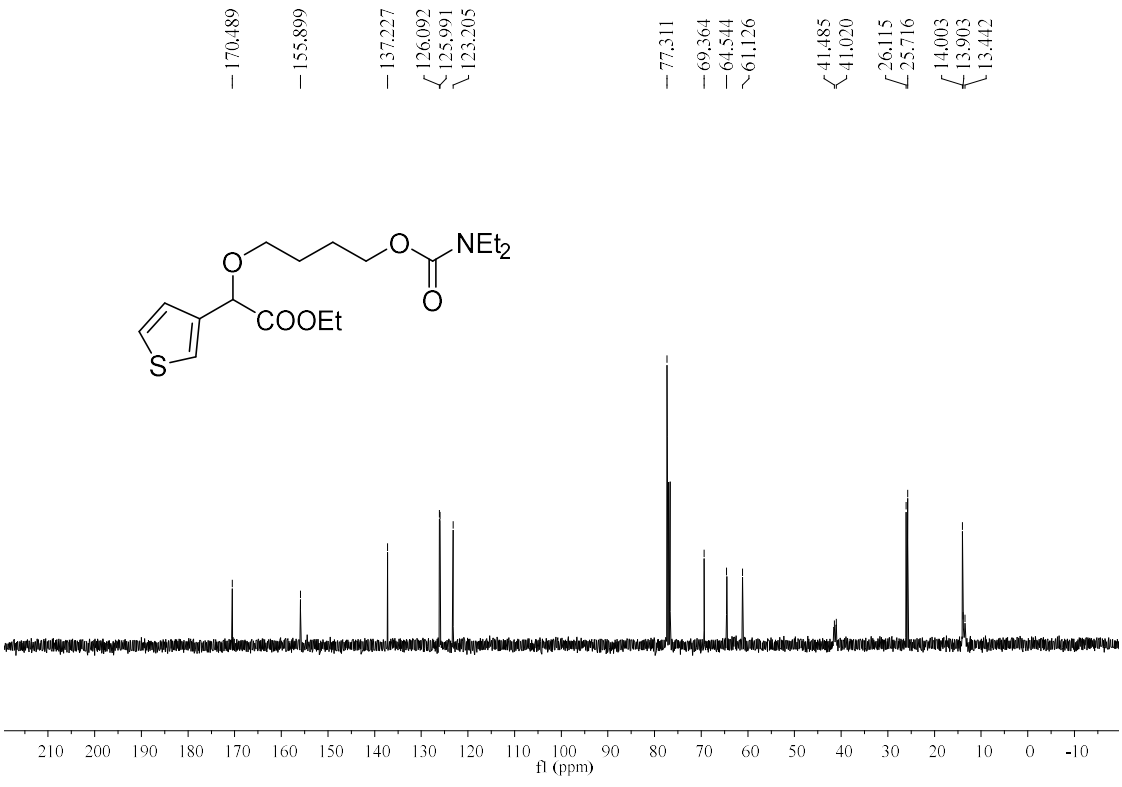
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(naphthalen-1-yl)acetate (3na)



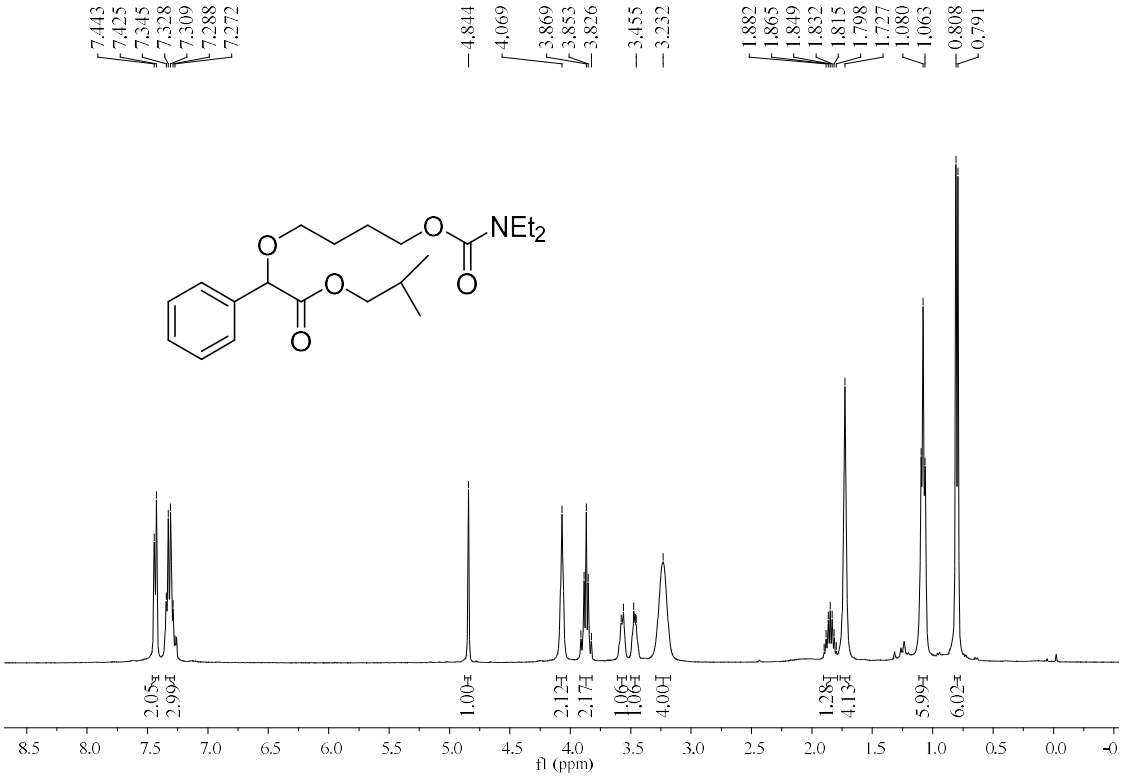


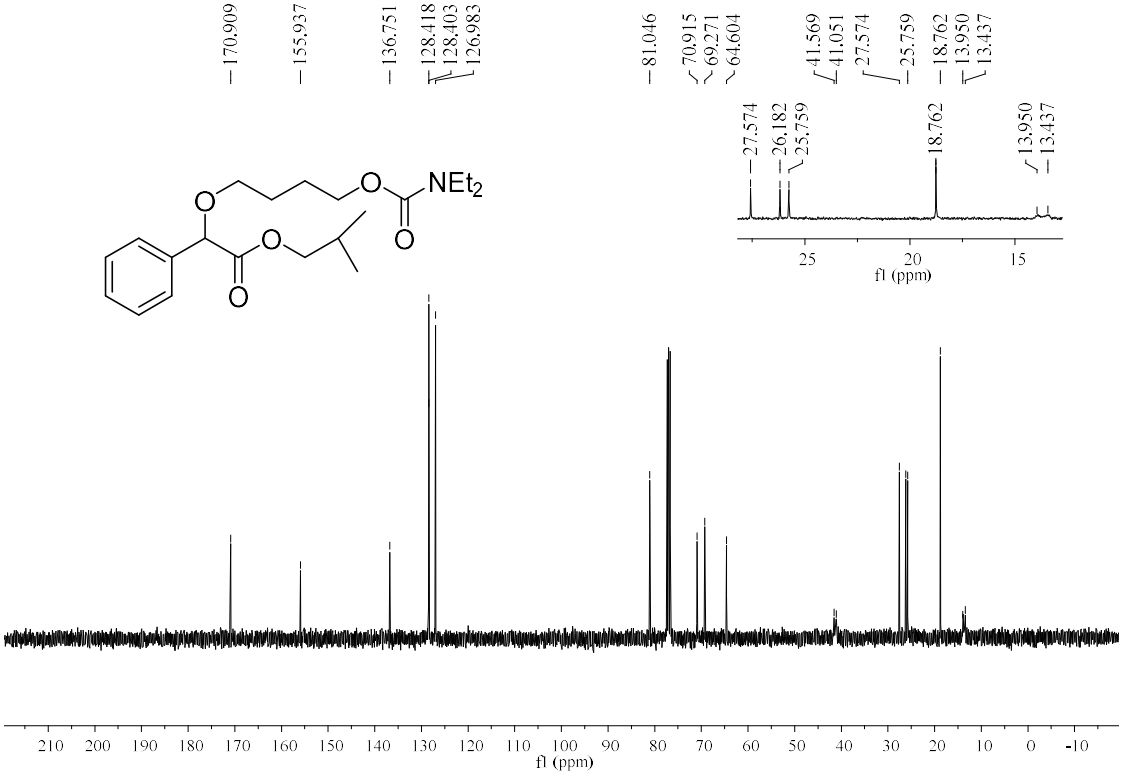
Ethyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-(thiophen-3-yl)acetate (3oa)



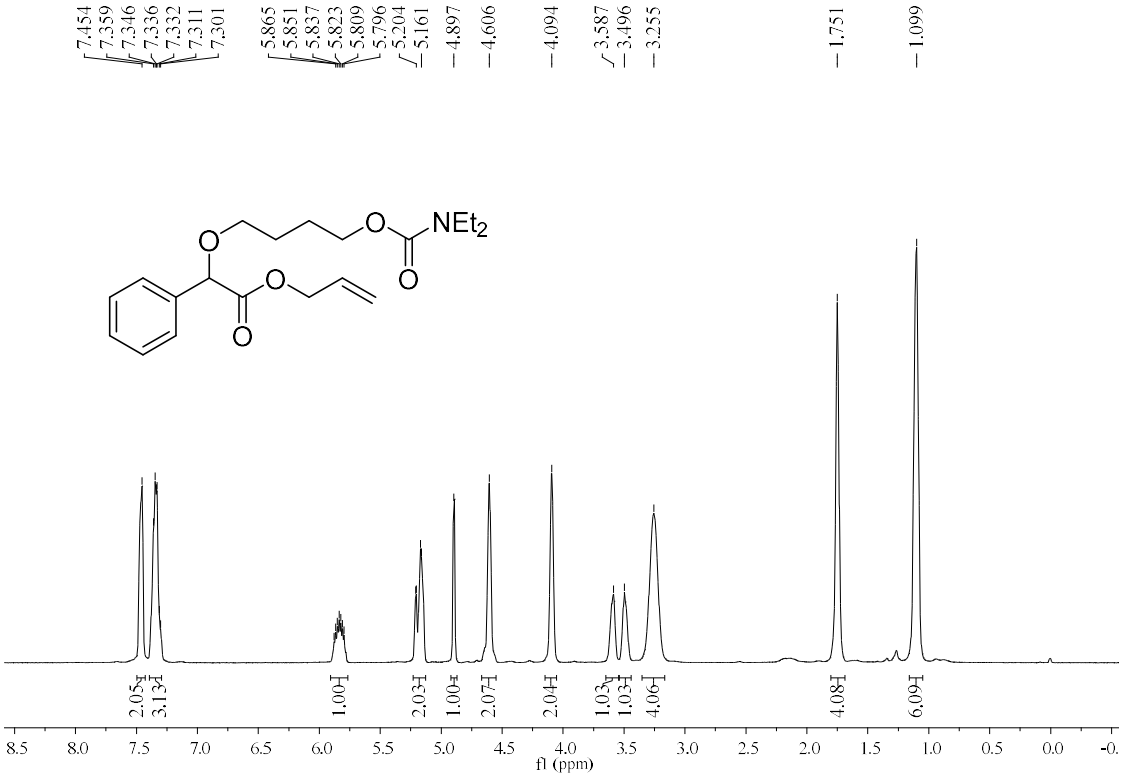


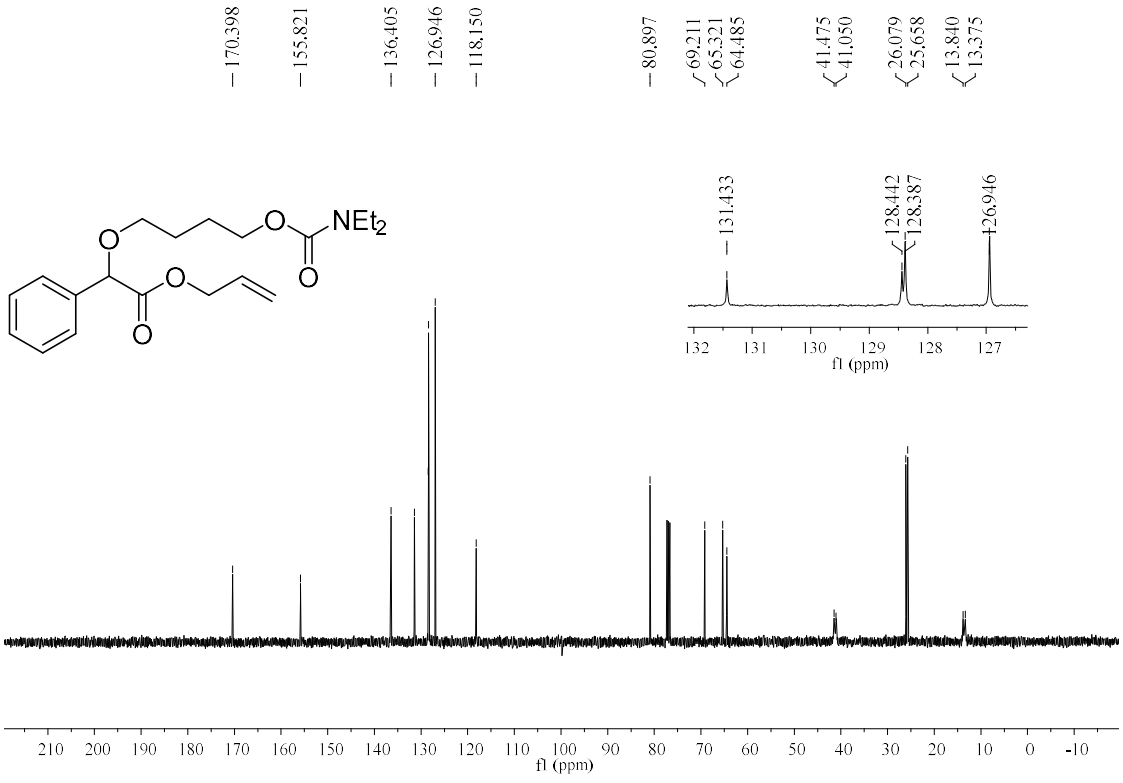
Isobutyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3pa)



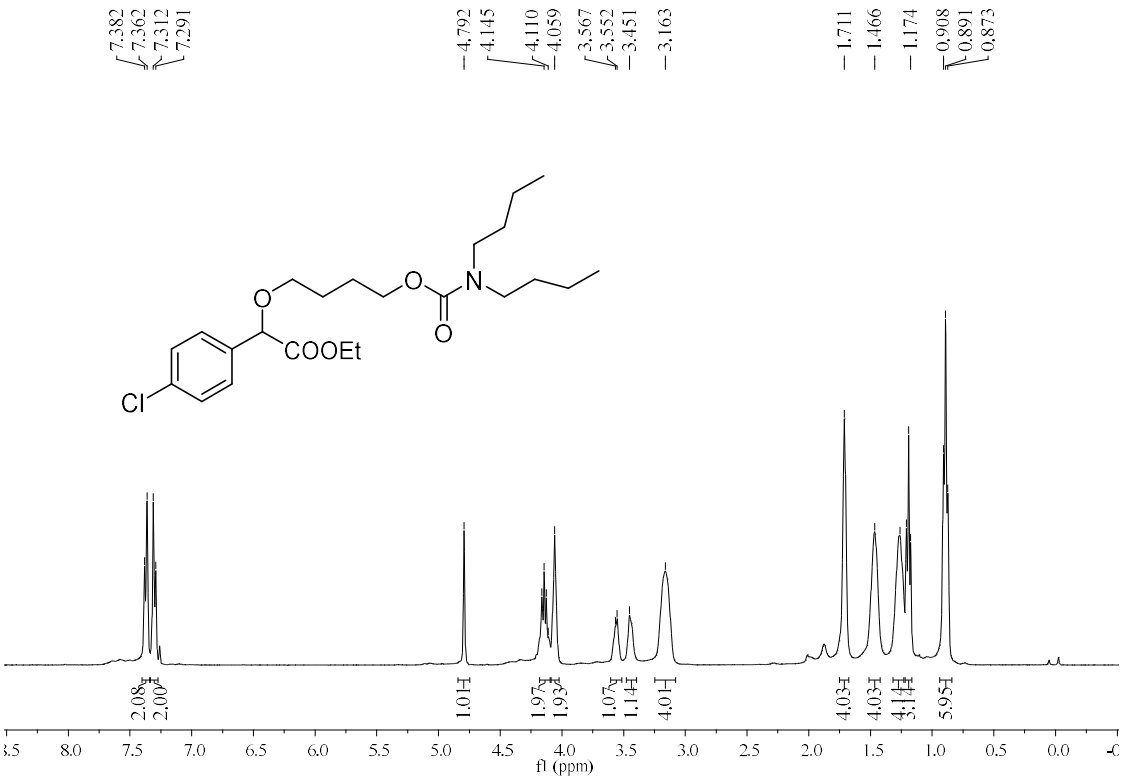


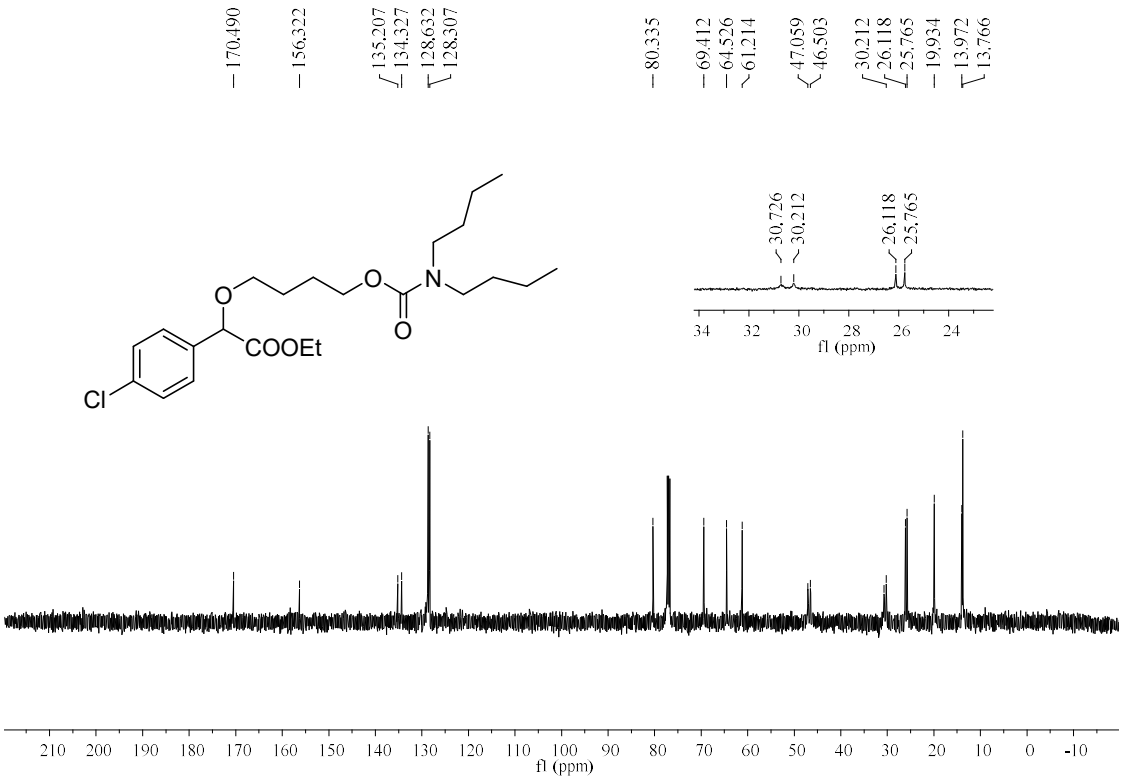
Allyl 2-(4-((diethylcarbamoyl)oxy)butoxy)-2-phenylacetate (3qa)



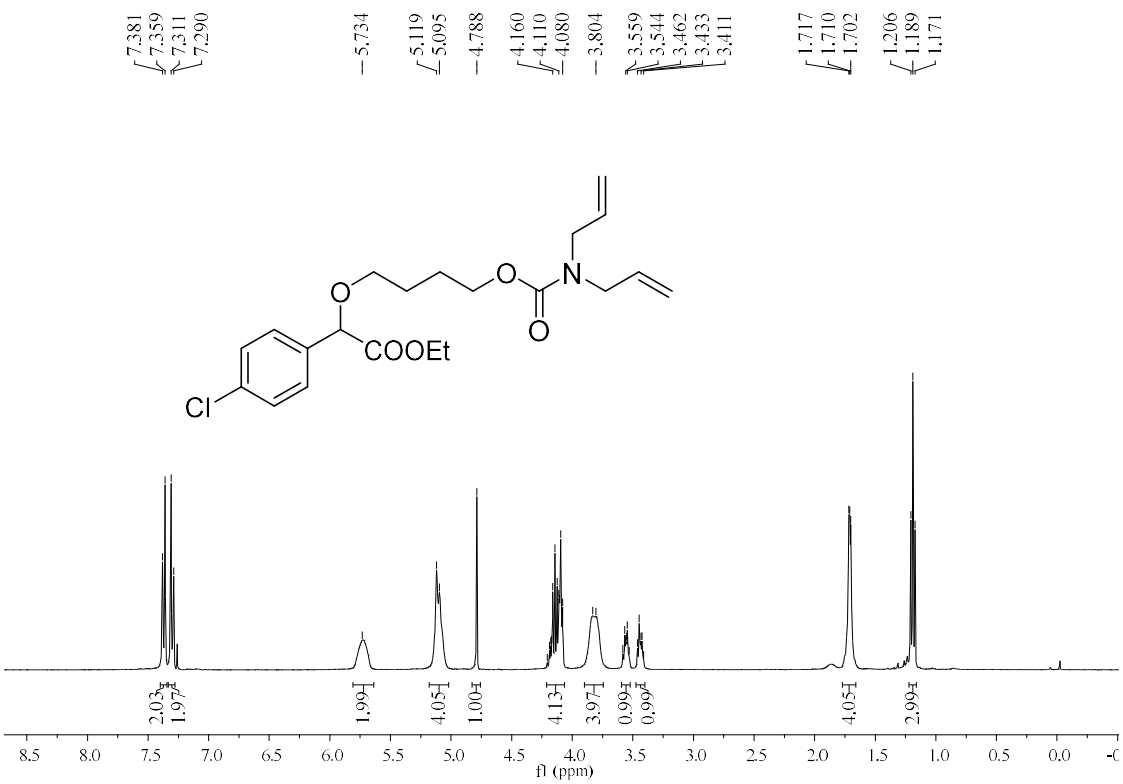


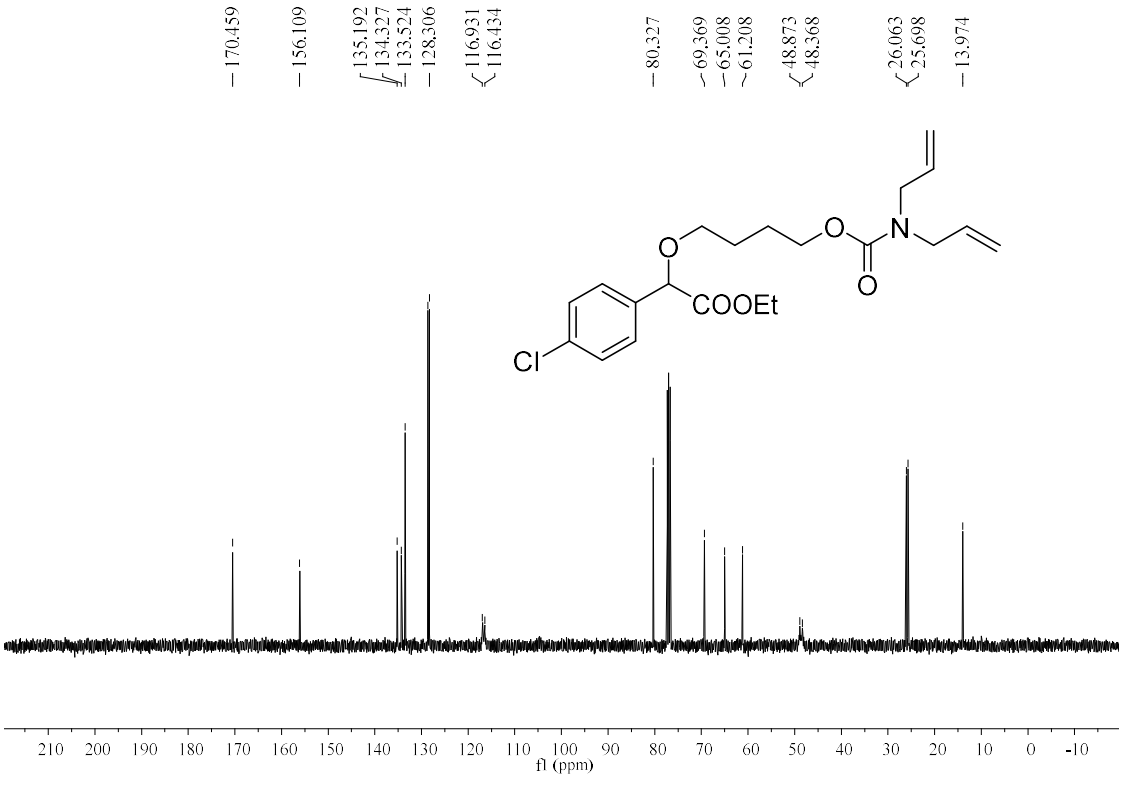
Ethyl 2-(4-chlorophenyl)-2-(4-((dibutylcarbamoyl)oxy)butoxy)acetate (3ab)



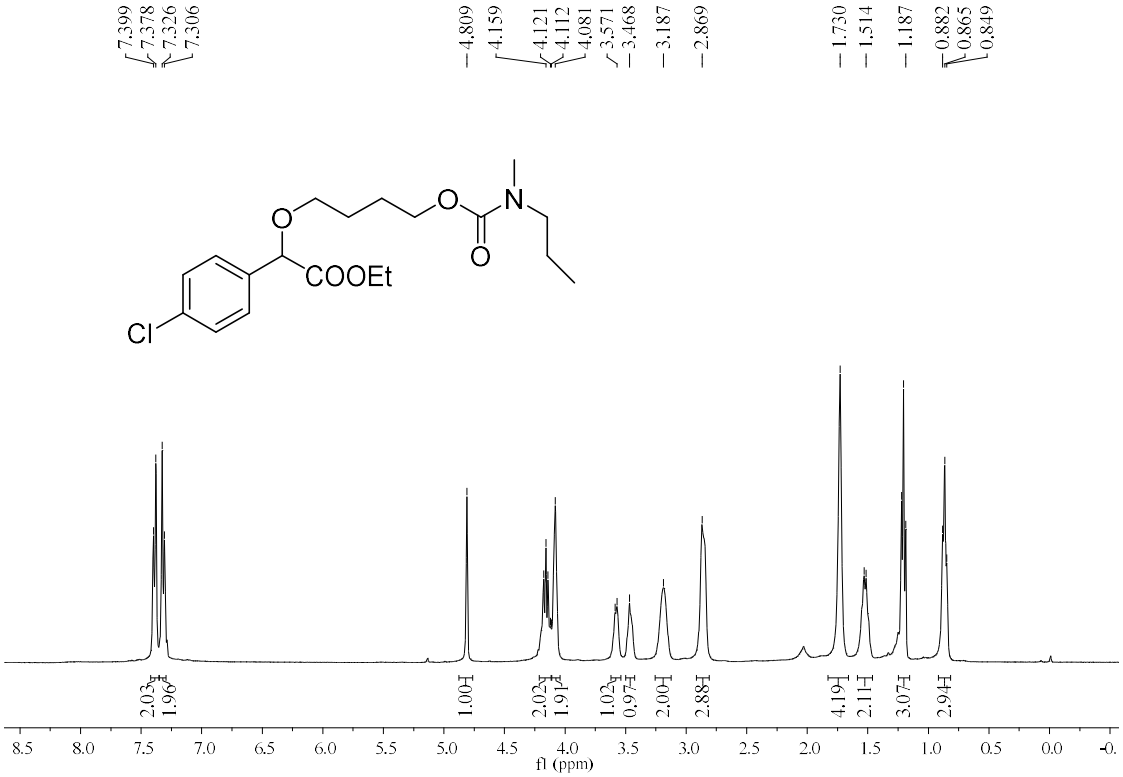


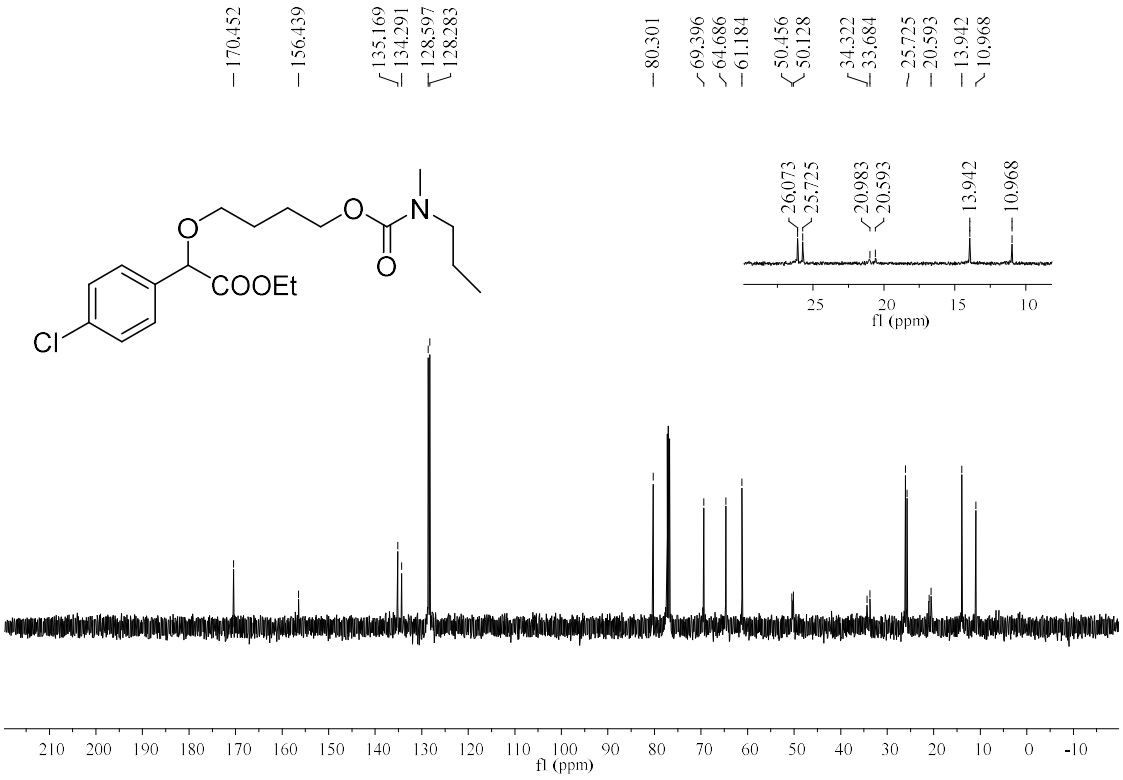
Ethyl 2-(4-chlorophenyl)-2-(4-((diallylcarbamoyl)oxy)butoxy)acetate (3ac)



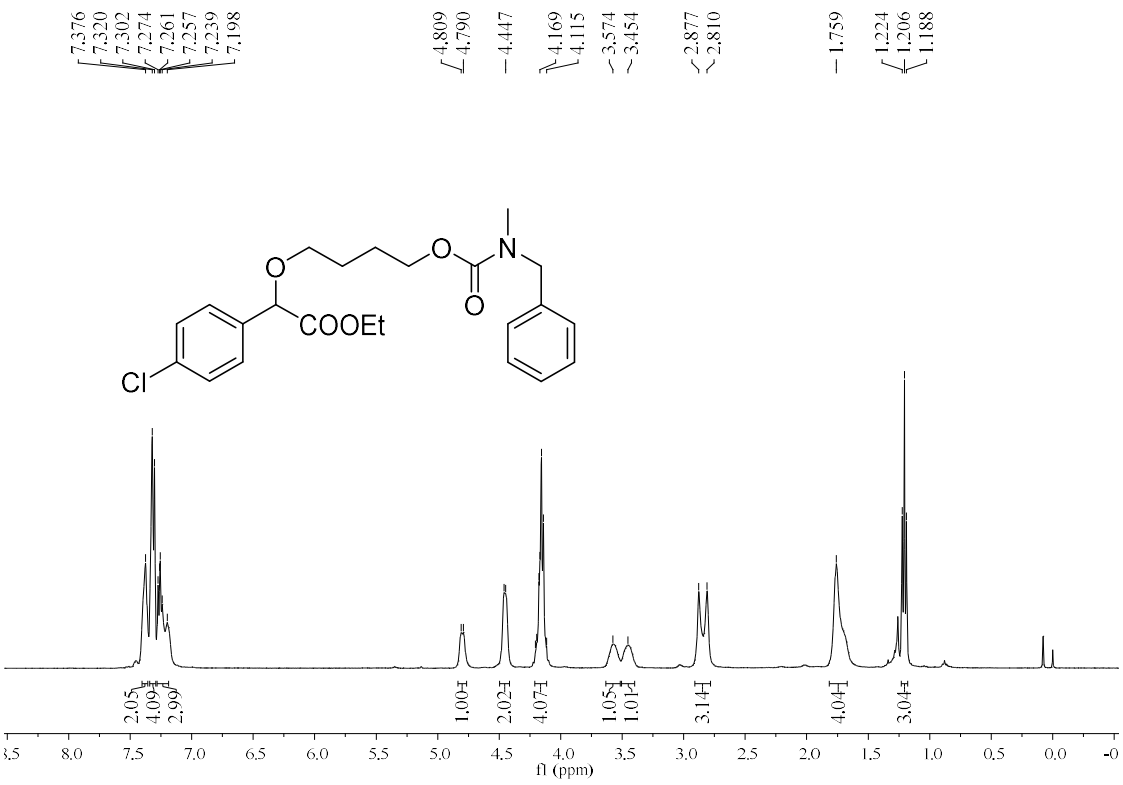


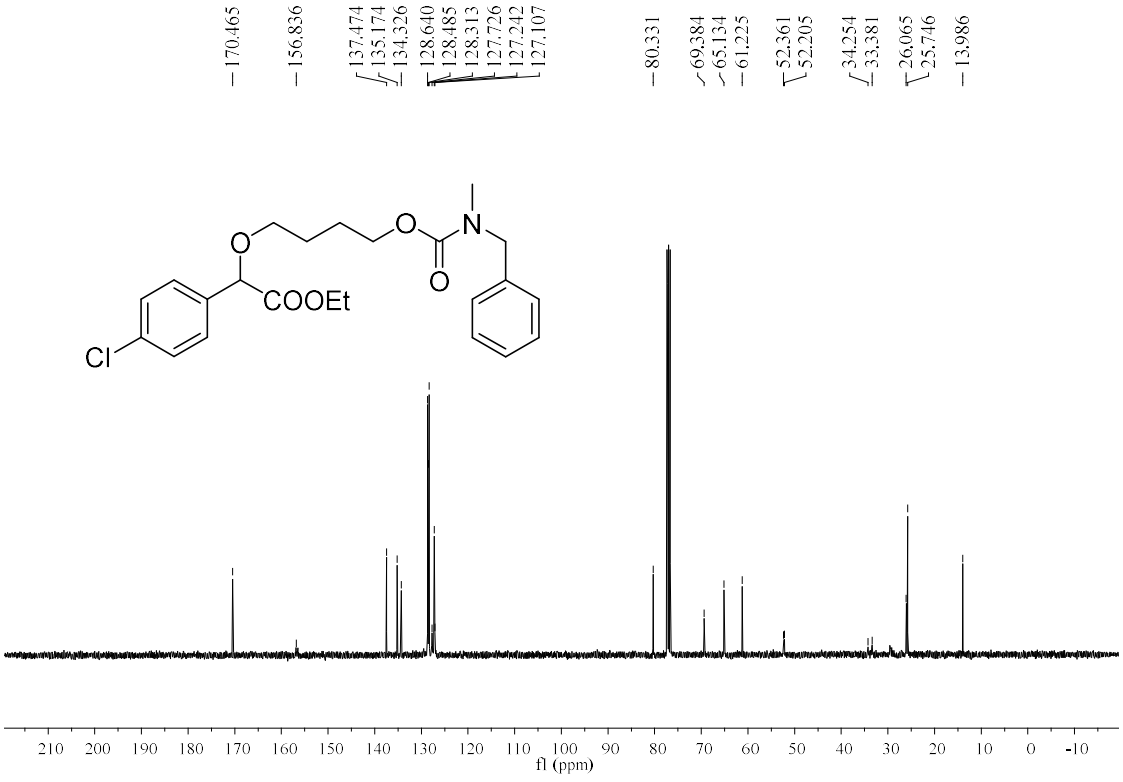
Ethyl 2-(4-chlorophenyl)-2-(4-((methyl(propyl)carbamoyl)oxy)butoxy)acetate (3ad)



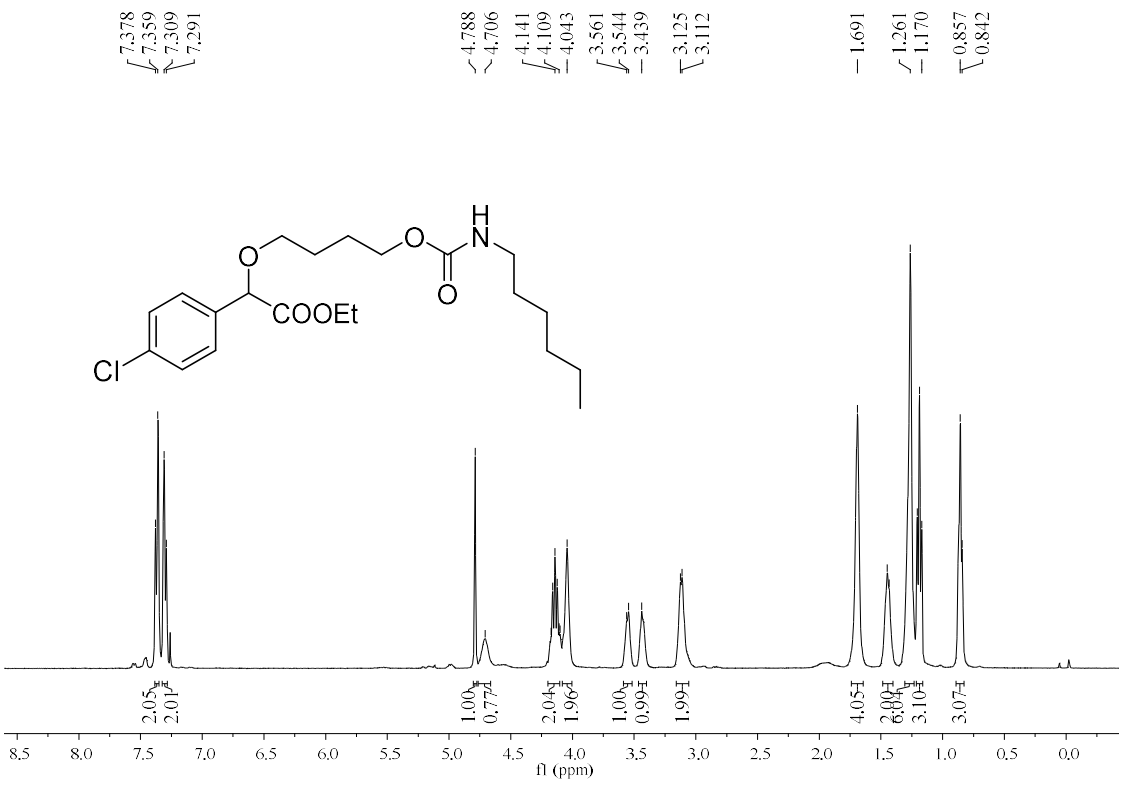


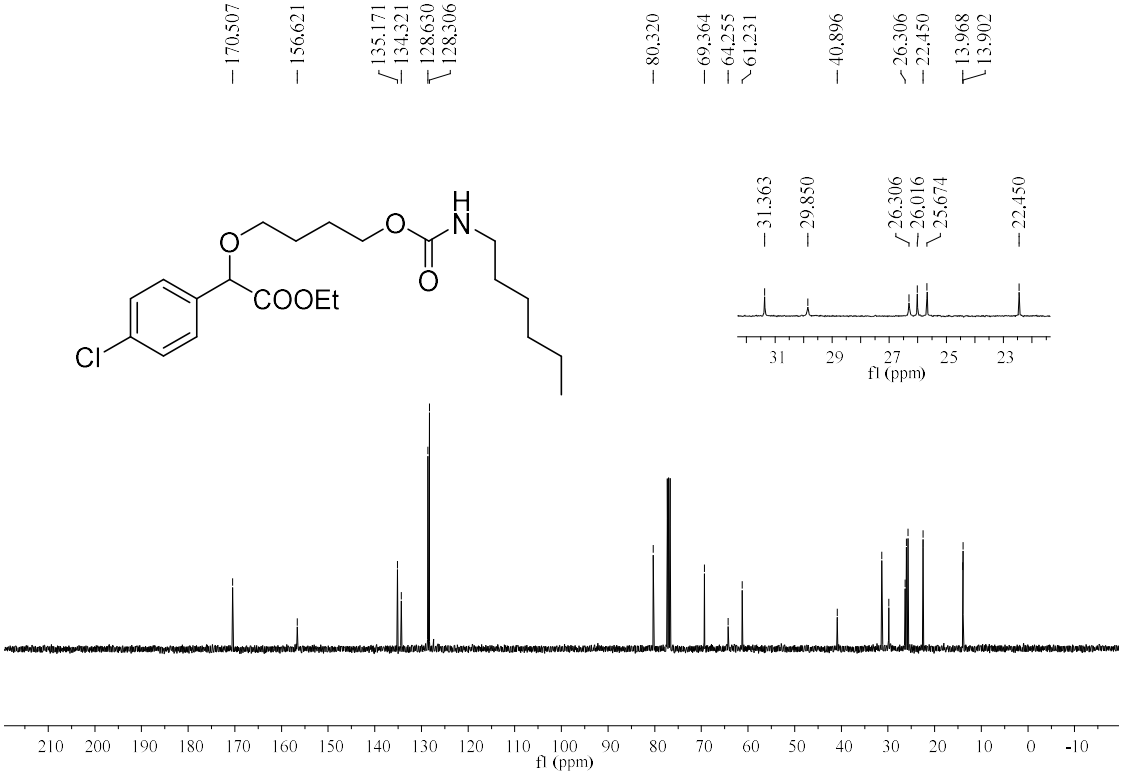
Ethyl 2-(4-((benzyl(methyl)carbamoyl)oxy)butoxy)-2-(4-chlorophenyl)acetate (3ae)



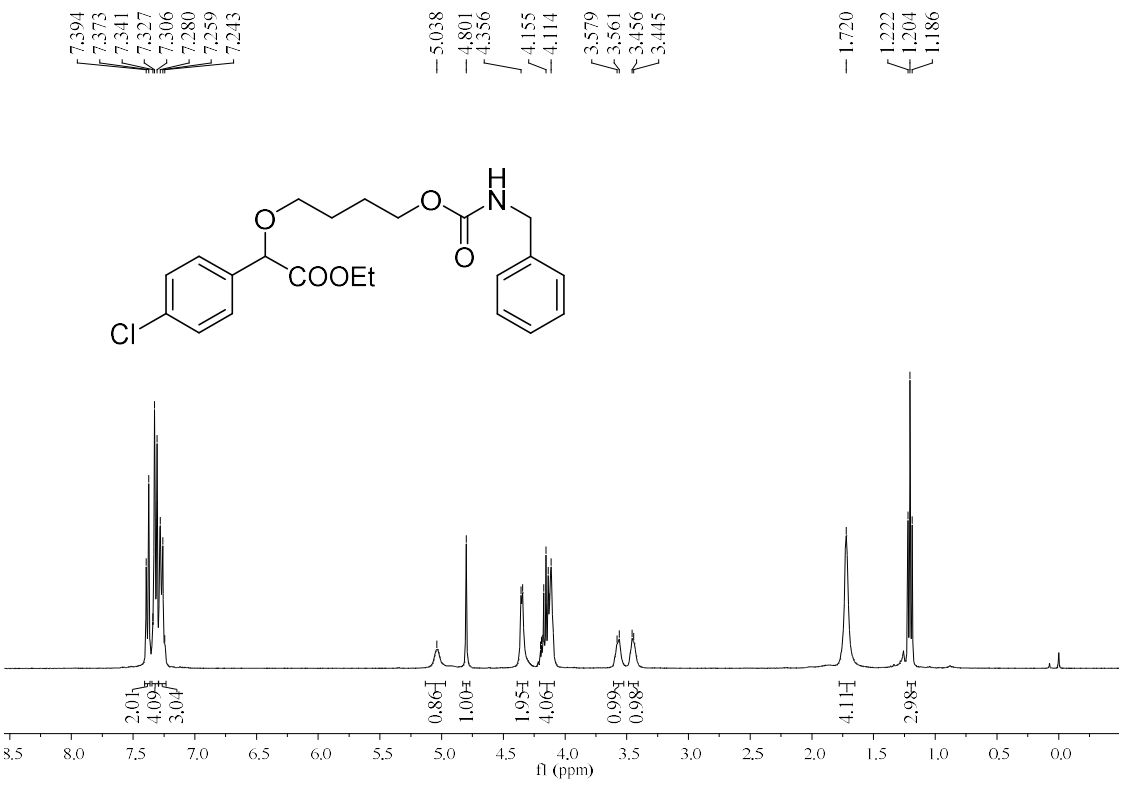


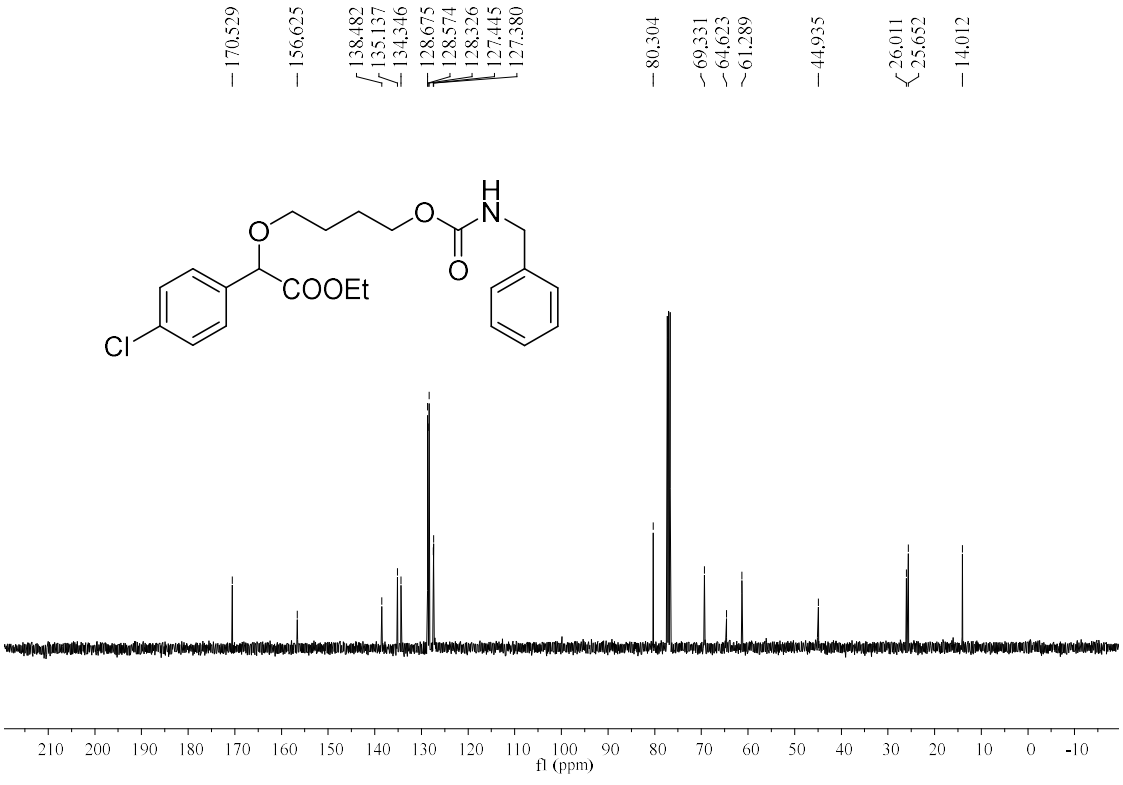
Ethyl 2-(4-chlorophenyl)-2-(4-((hexylcarbamoyl)oxy)butoxy)acetate (3af)



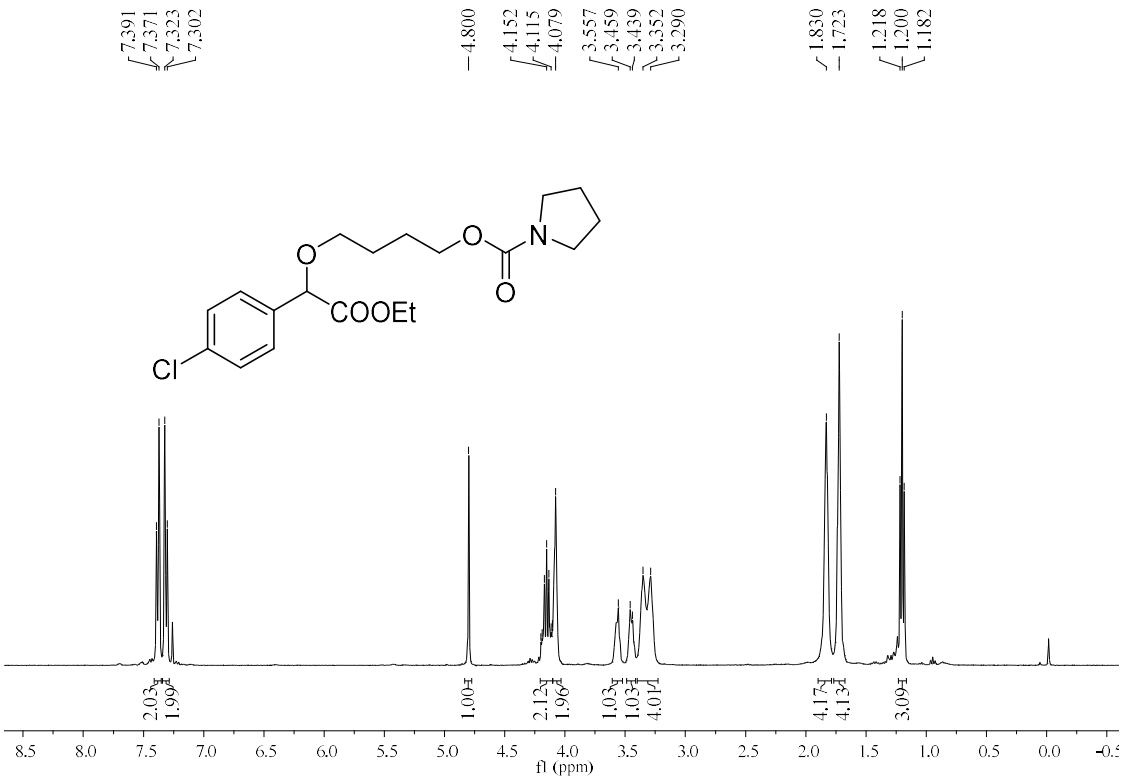


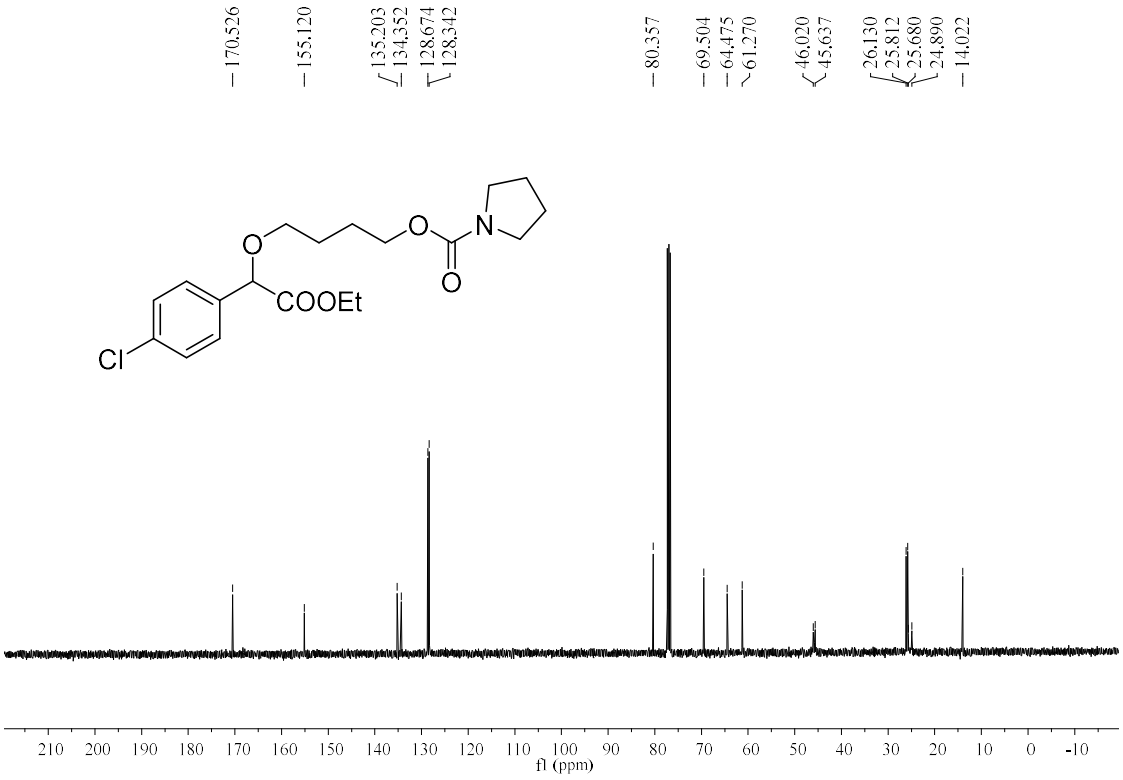
Ethyl 2-(4-((benzylcarbamoyl)oxy)butoxy)-2-(4-chlorophenyl)acetate (3ag)



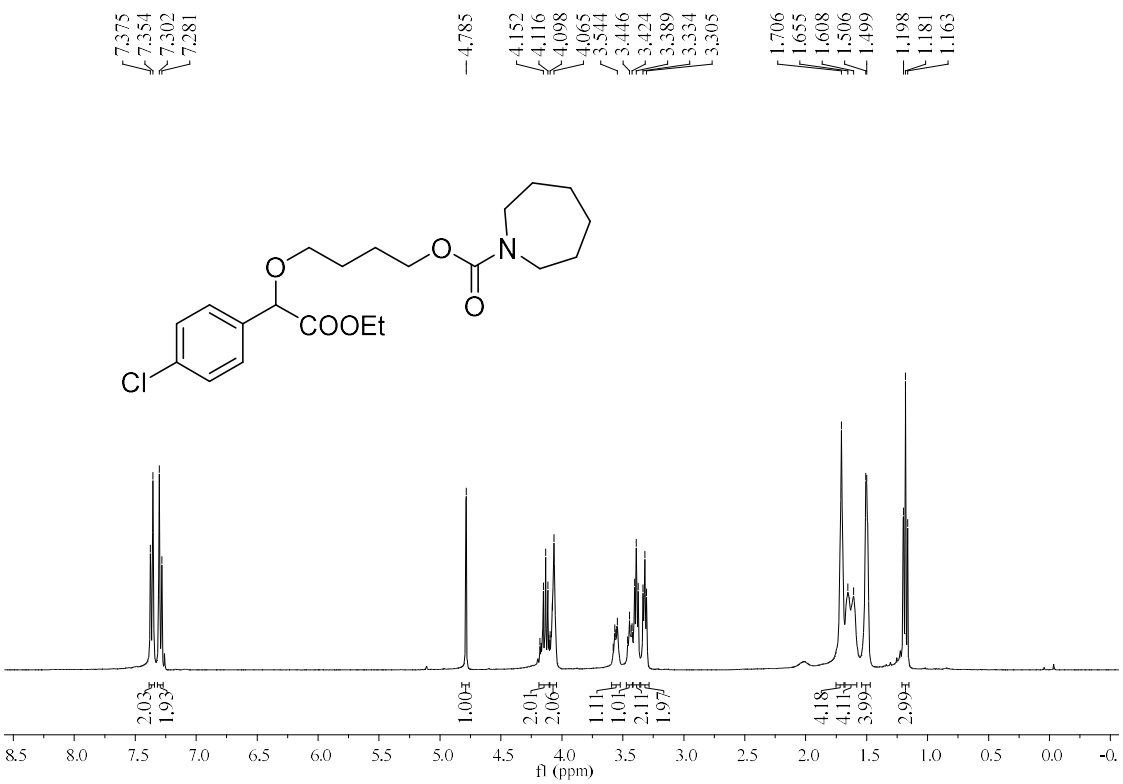


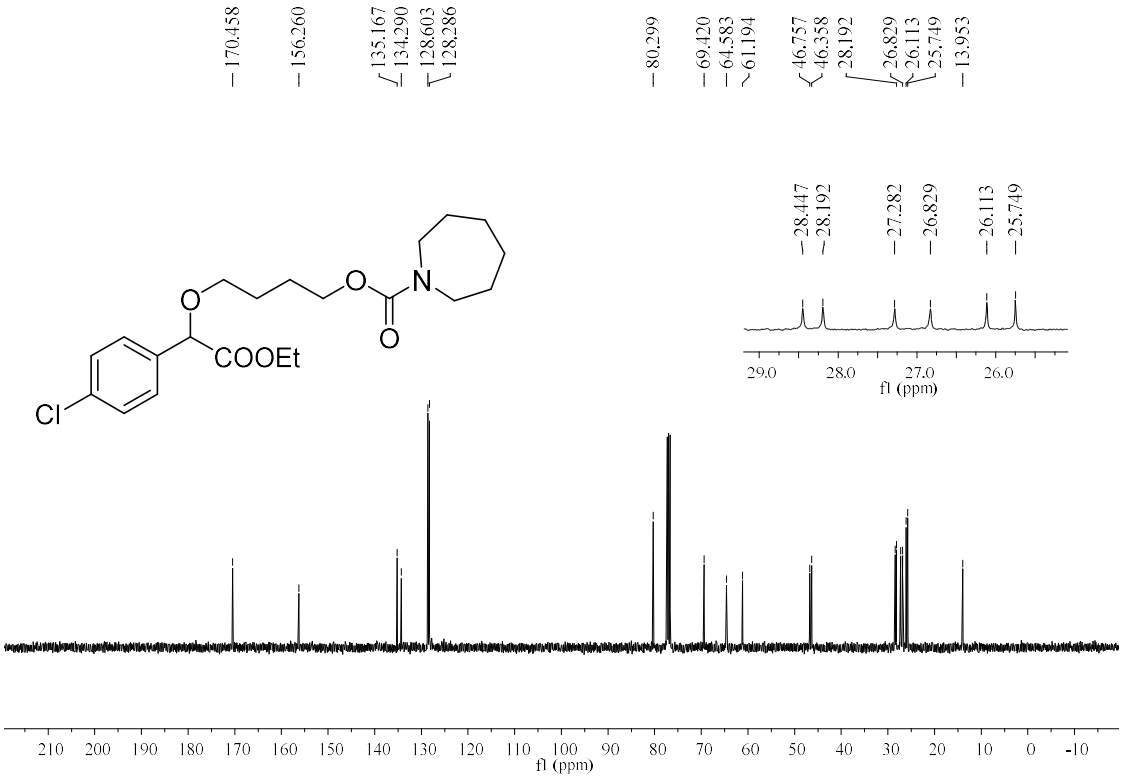
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl pyrrolidine-1-carboxylate (3ah)



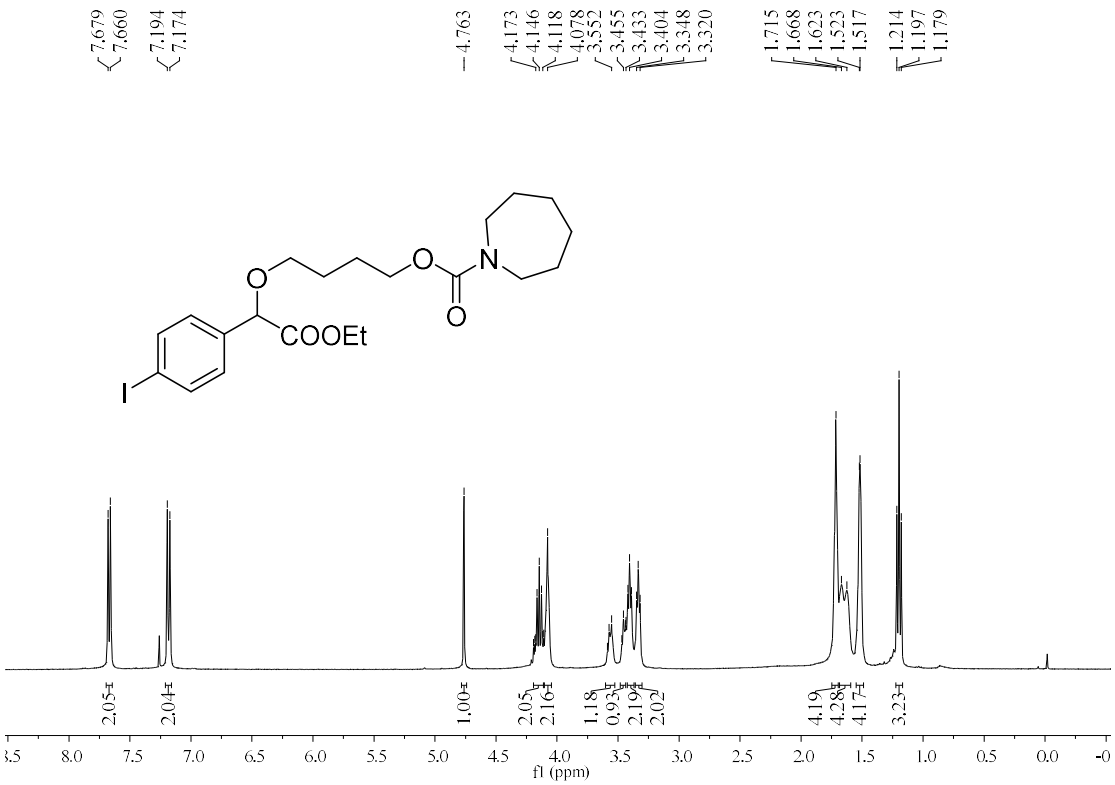


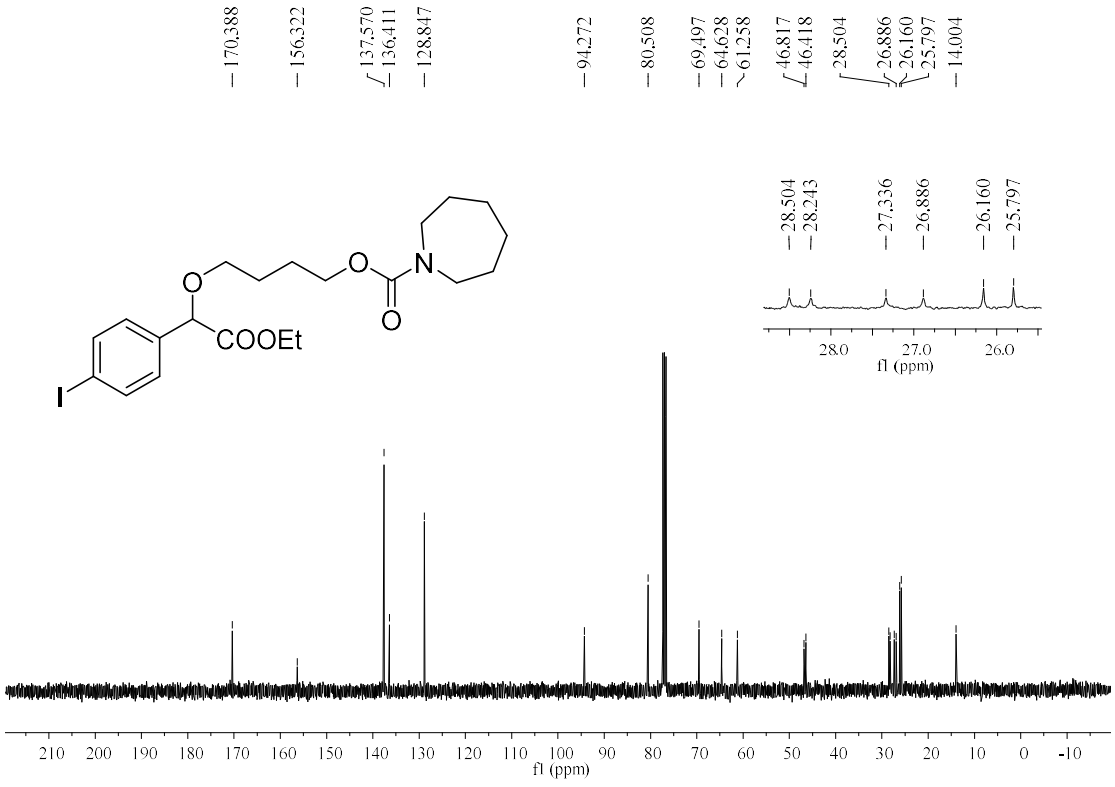
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (3ai)



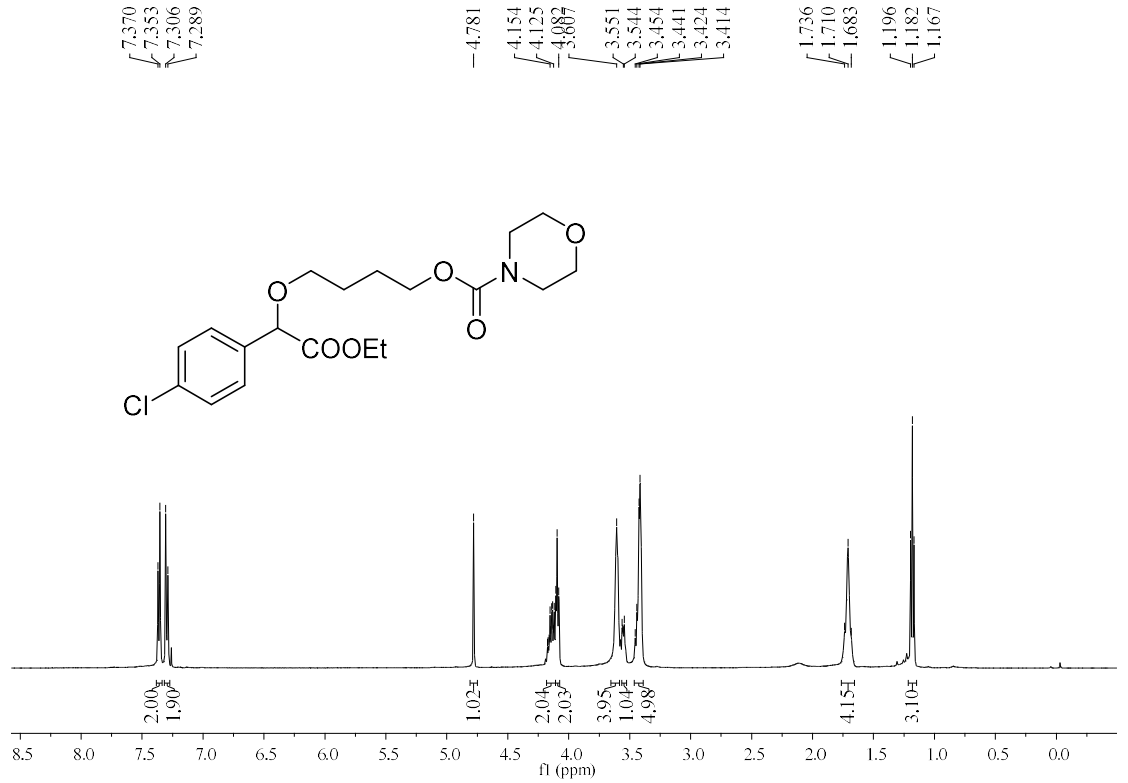


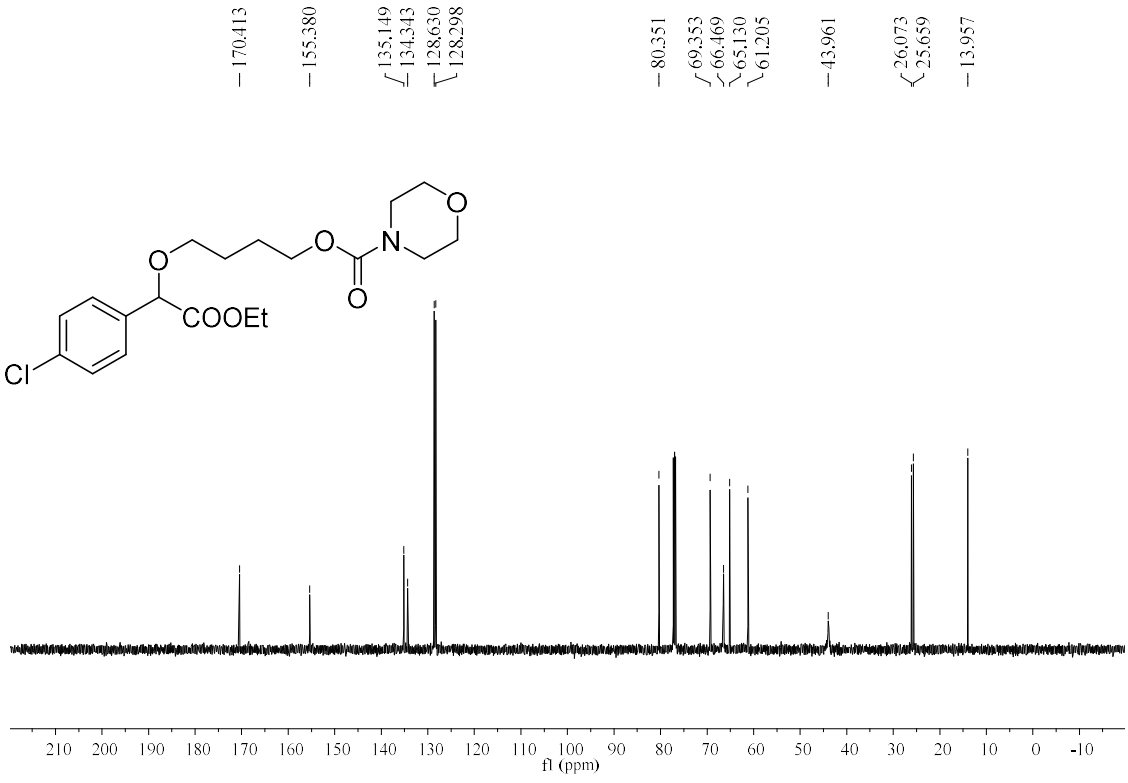
4-(2-Ethoxy-1-(4-iodophenyl)-2-oxoethoxy)butyl azepane-1-carboxylate (3ci)



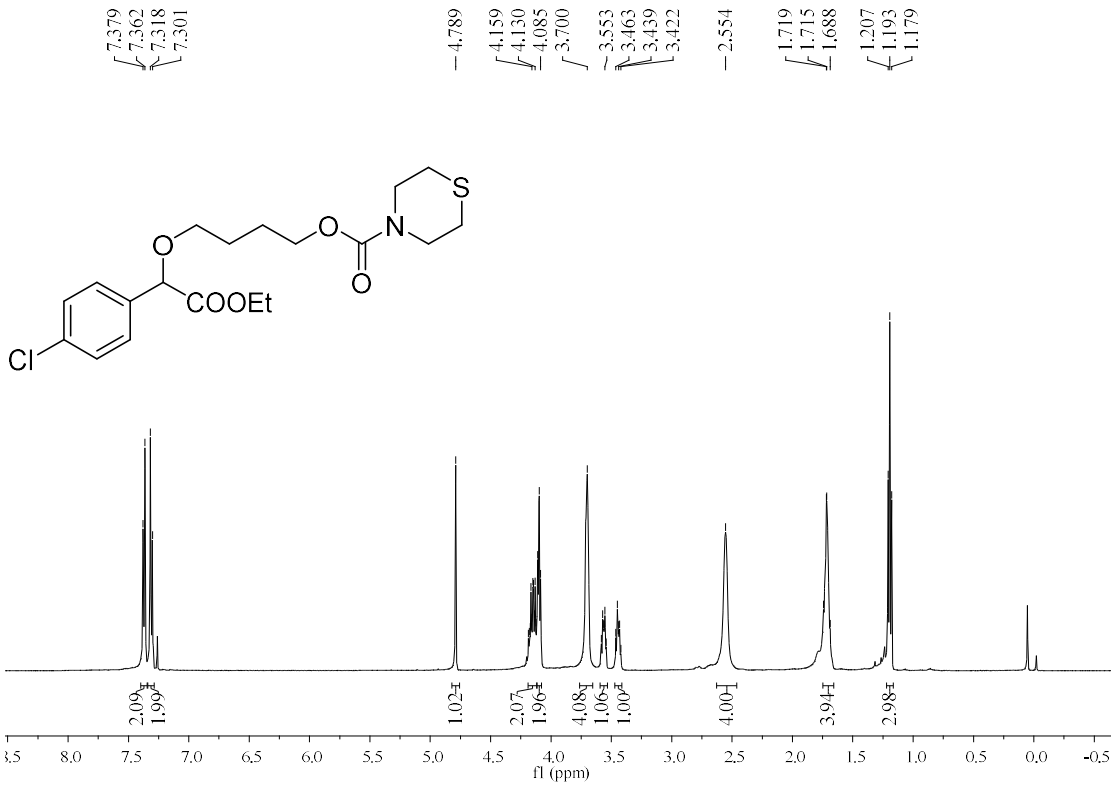


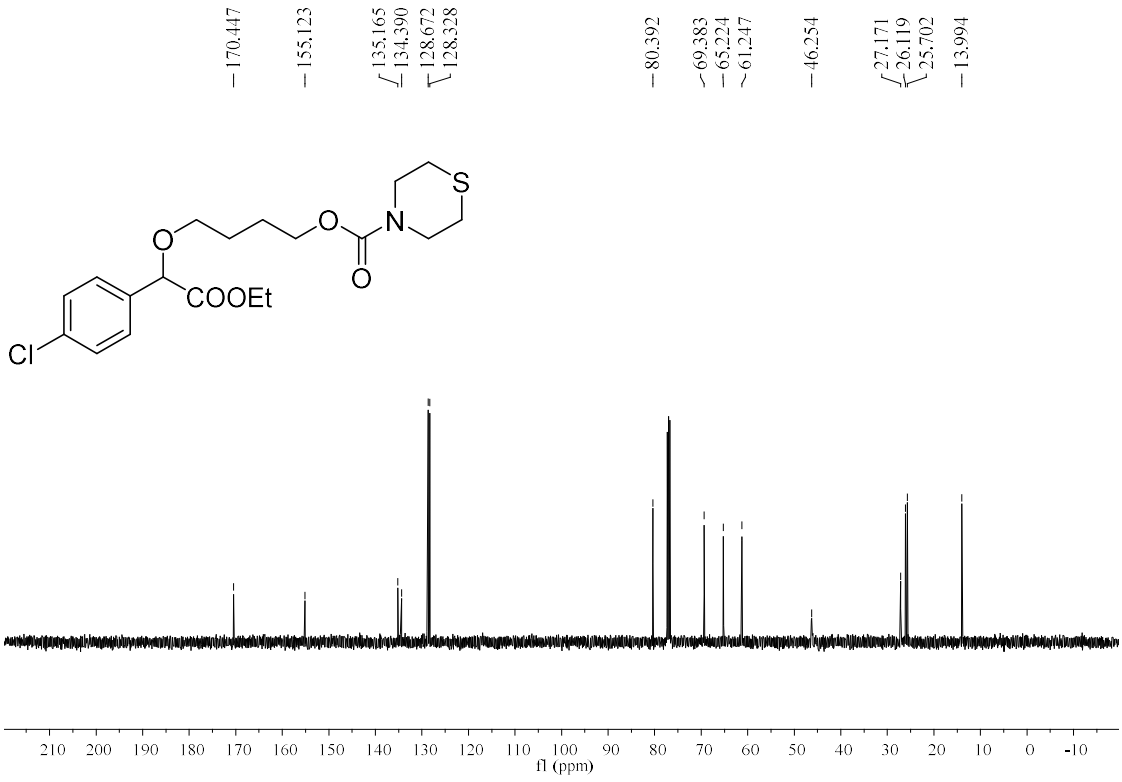
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl morpholine-4-carboxylate (3aj)



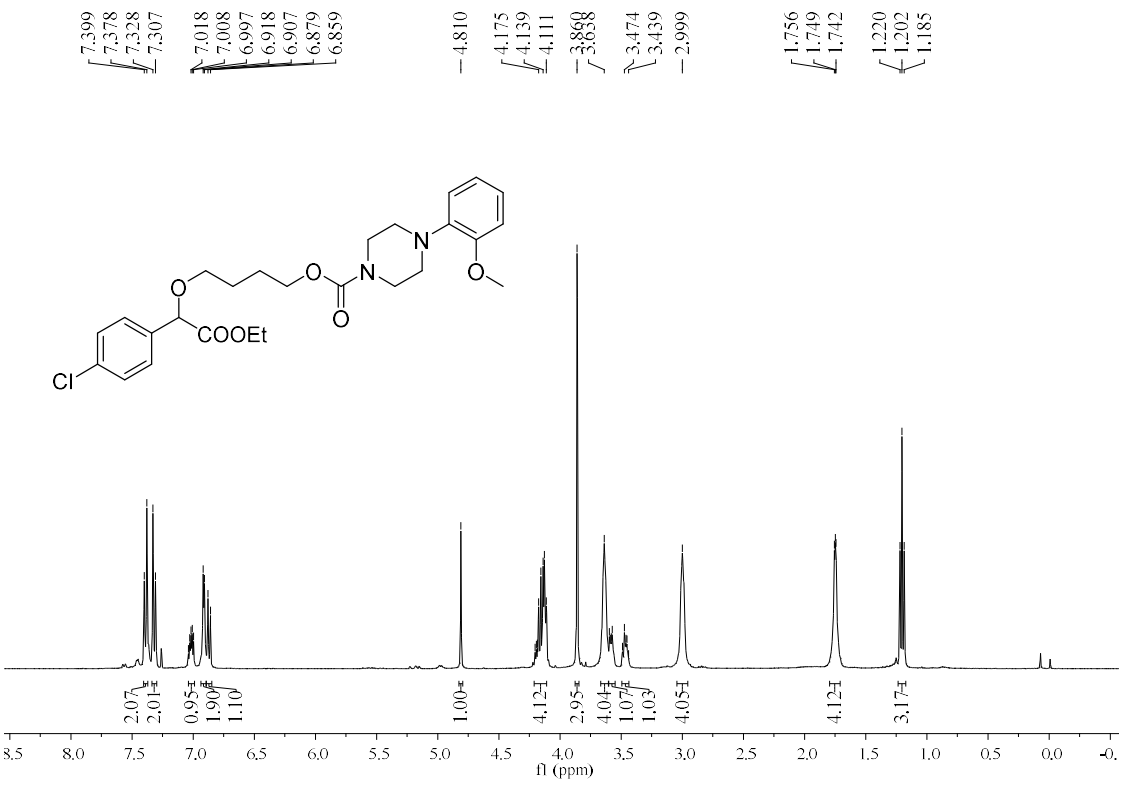


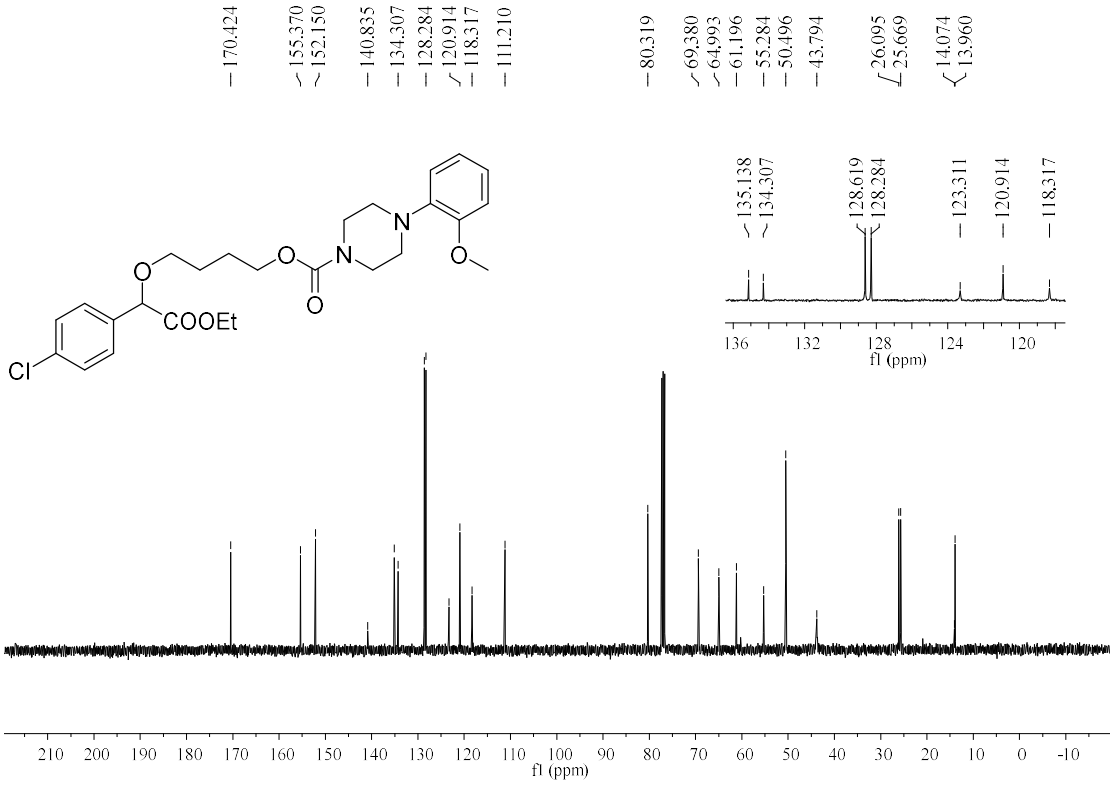
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl thiomorpholine-4-carboxylate (3ak)



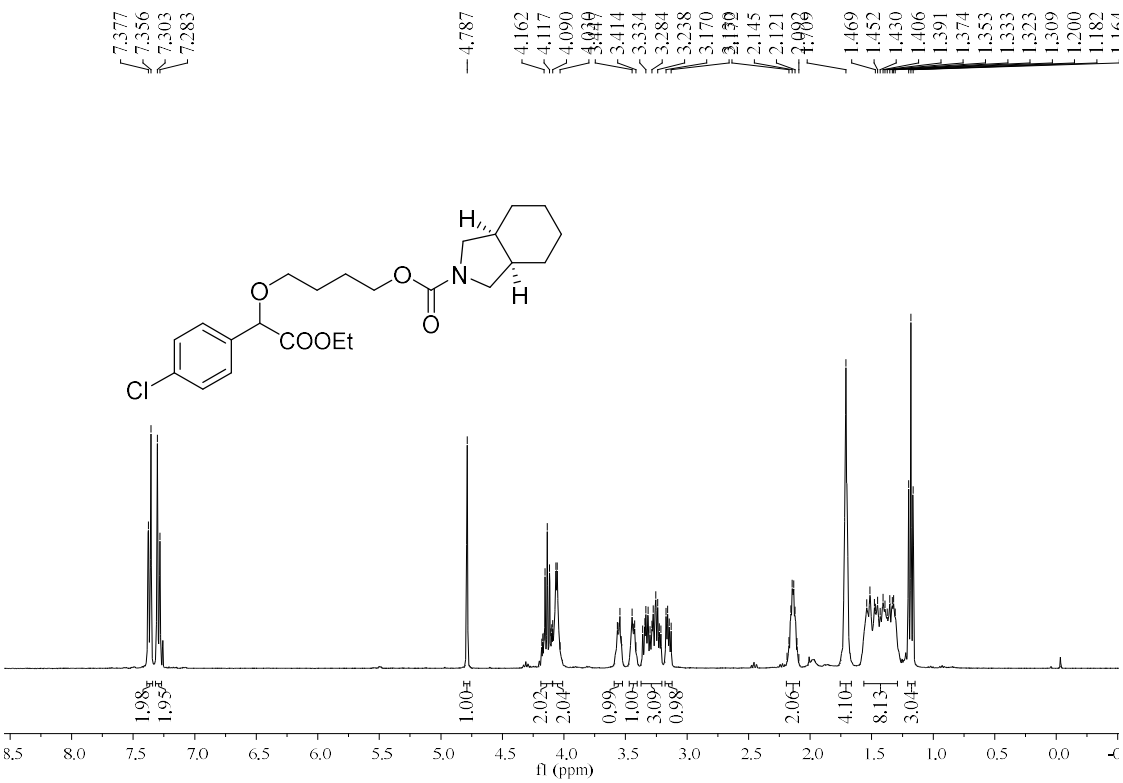


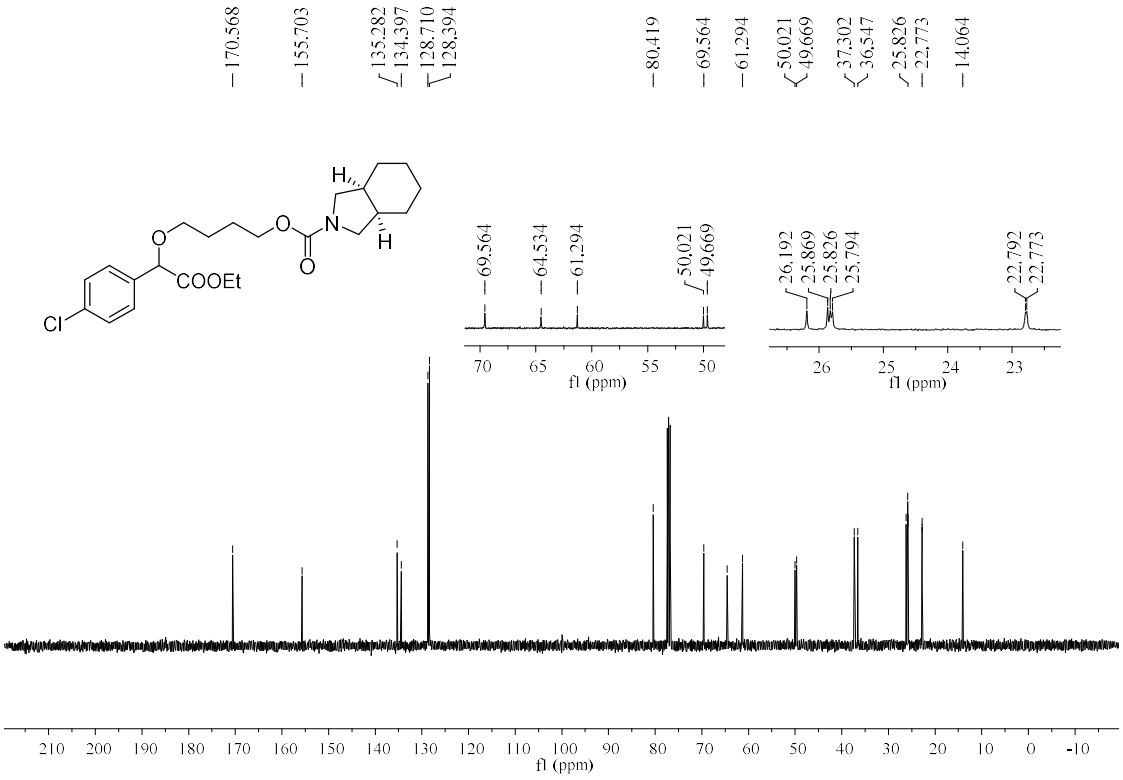
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl 4-(2-methoxyphenyl)piperazine-1-carboxylate (3al)



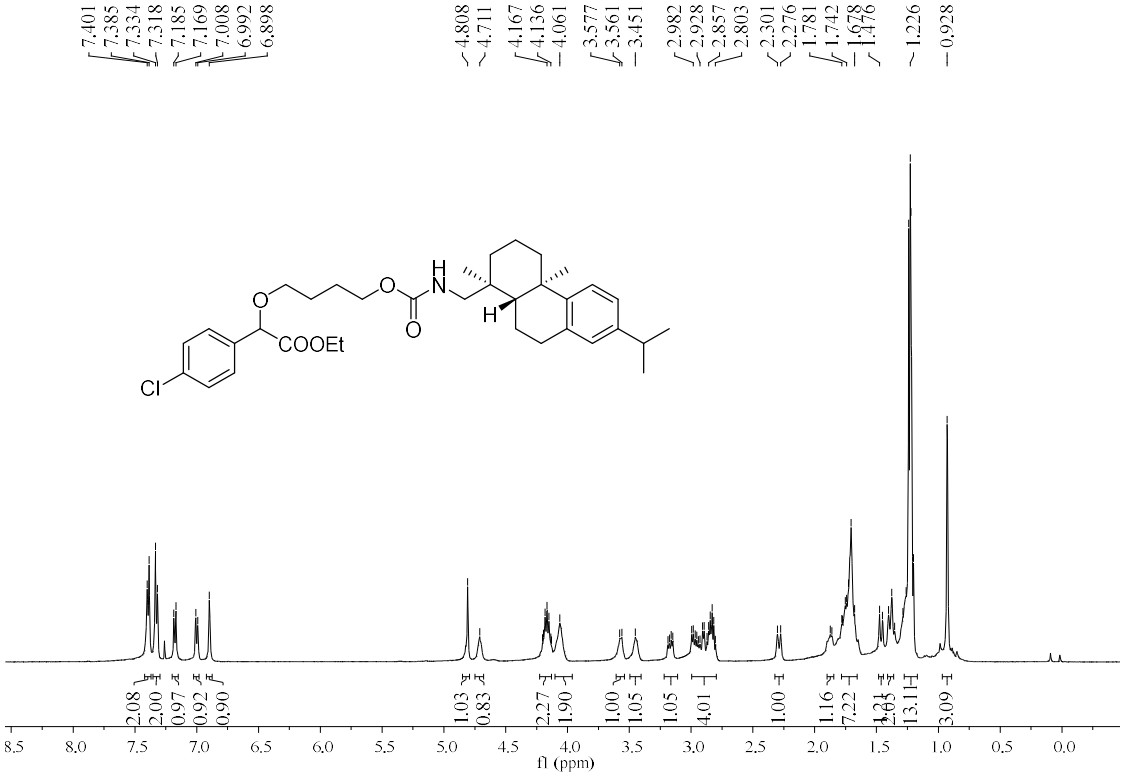


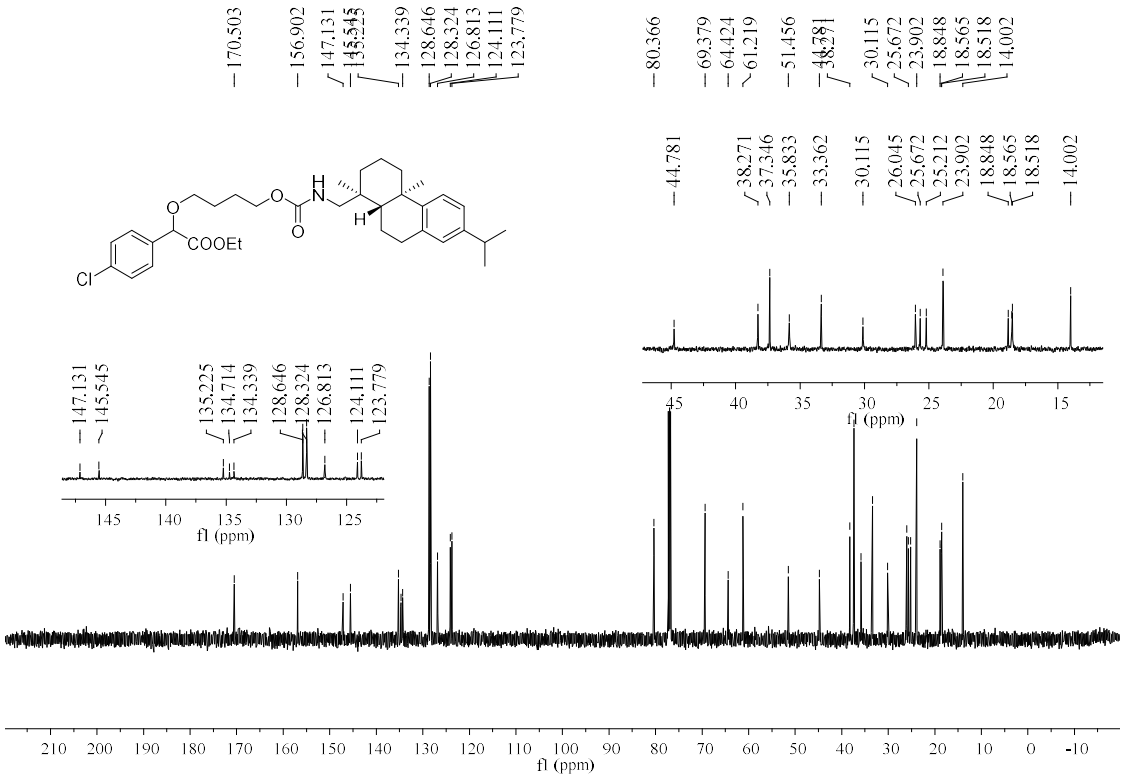
4-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)butyl (4a*R*,8a*R*)-octahydroisoquinoline-2(1*H*)-carboxylate (3am)



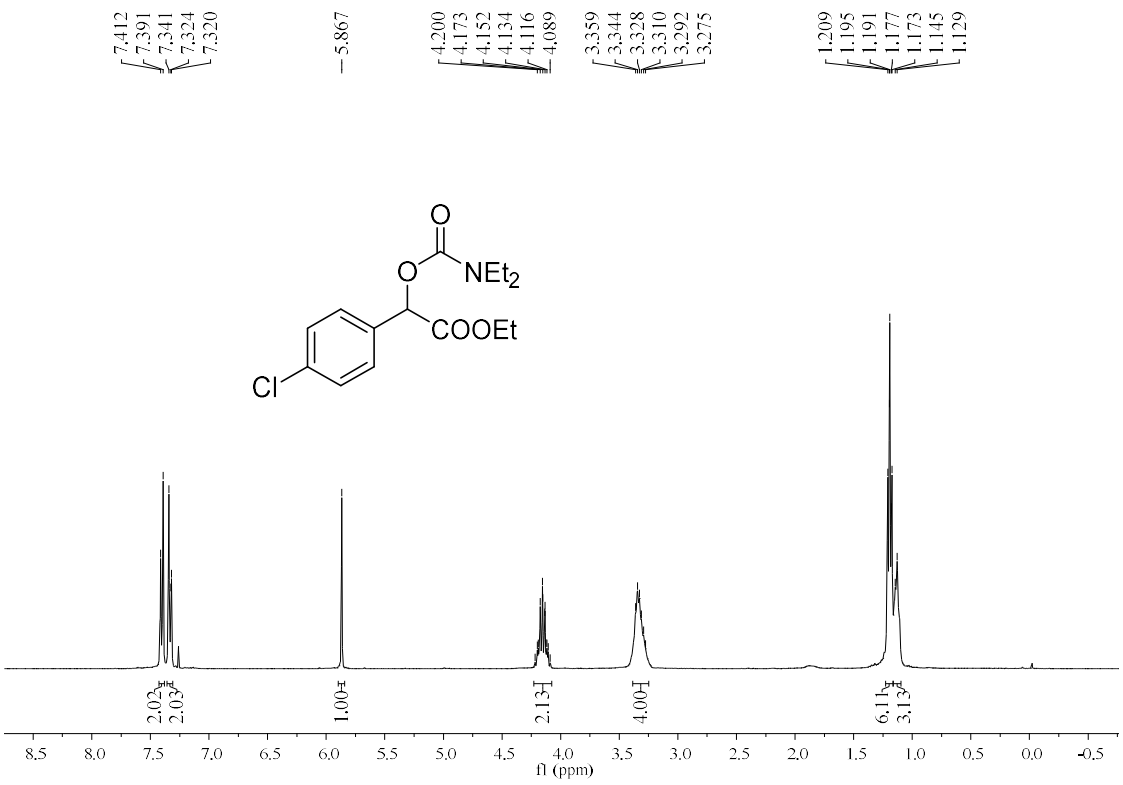


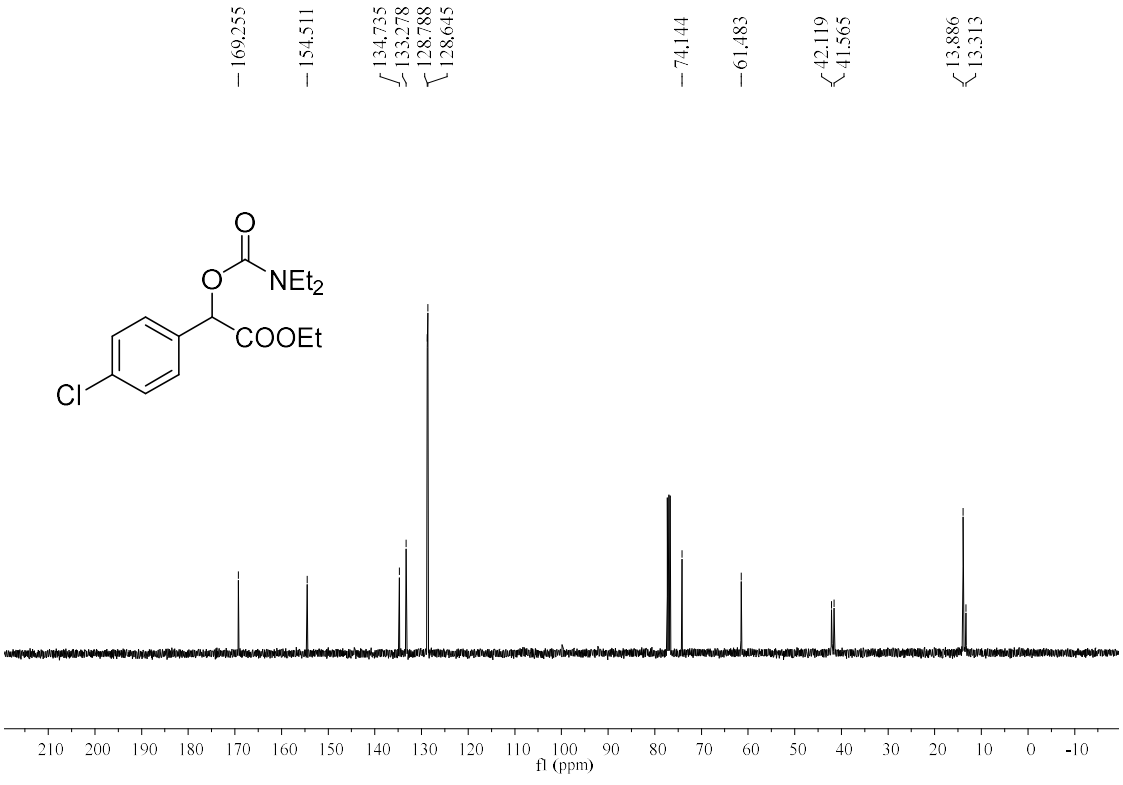
Ethyl 2-(4-chlorophenyl)-2-(4-(((((1*S*,4a*R*,10a*S*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamoyl)oxy)butoxy)acetate (3an)



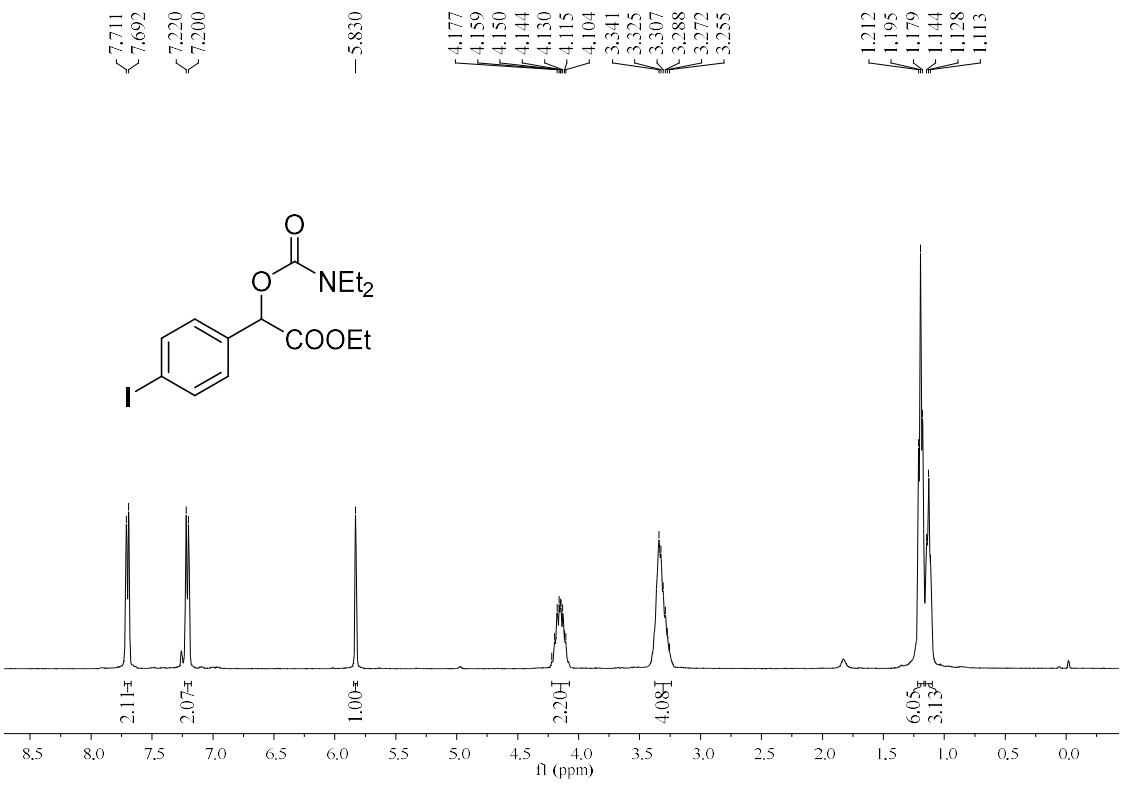


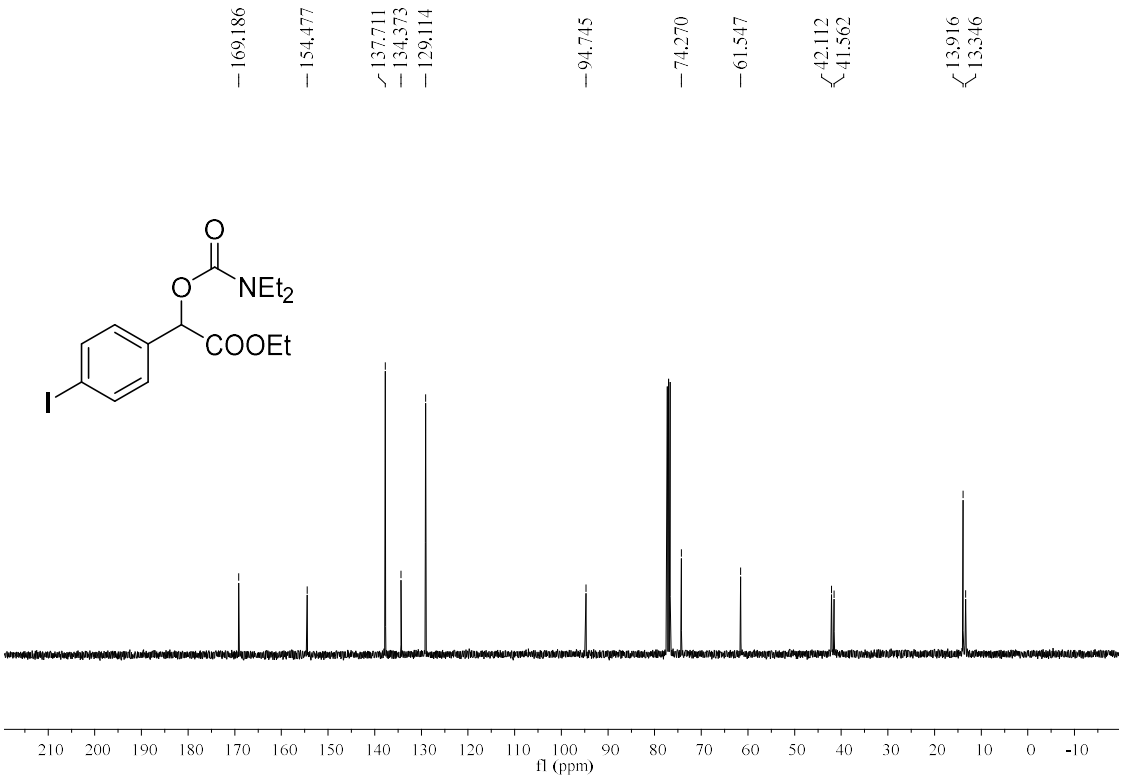
Ethyl 2-(4-chlorophenyl)-2-((diethylcarbamoyl)oxy)acetate (4aa)



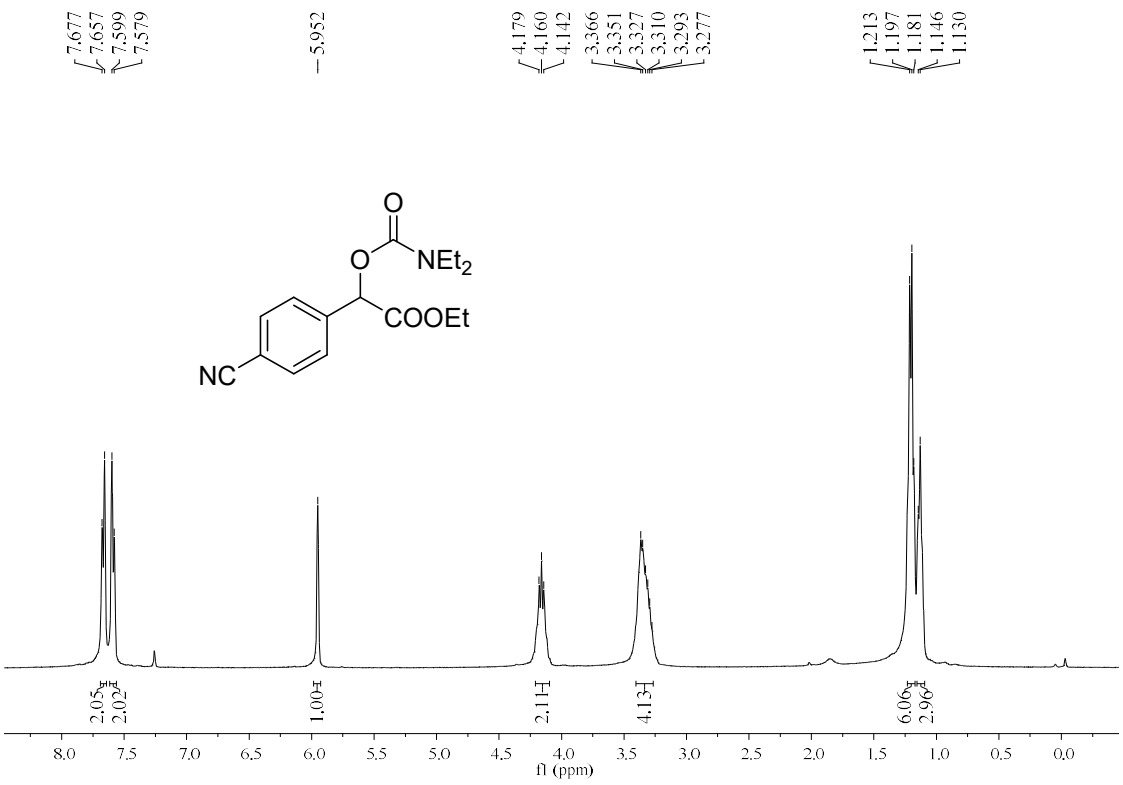


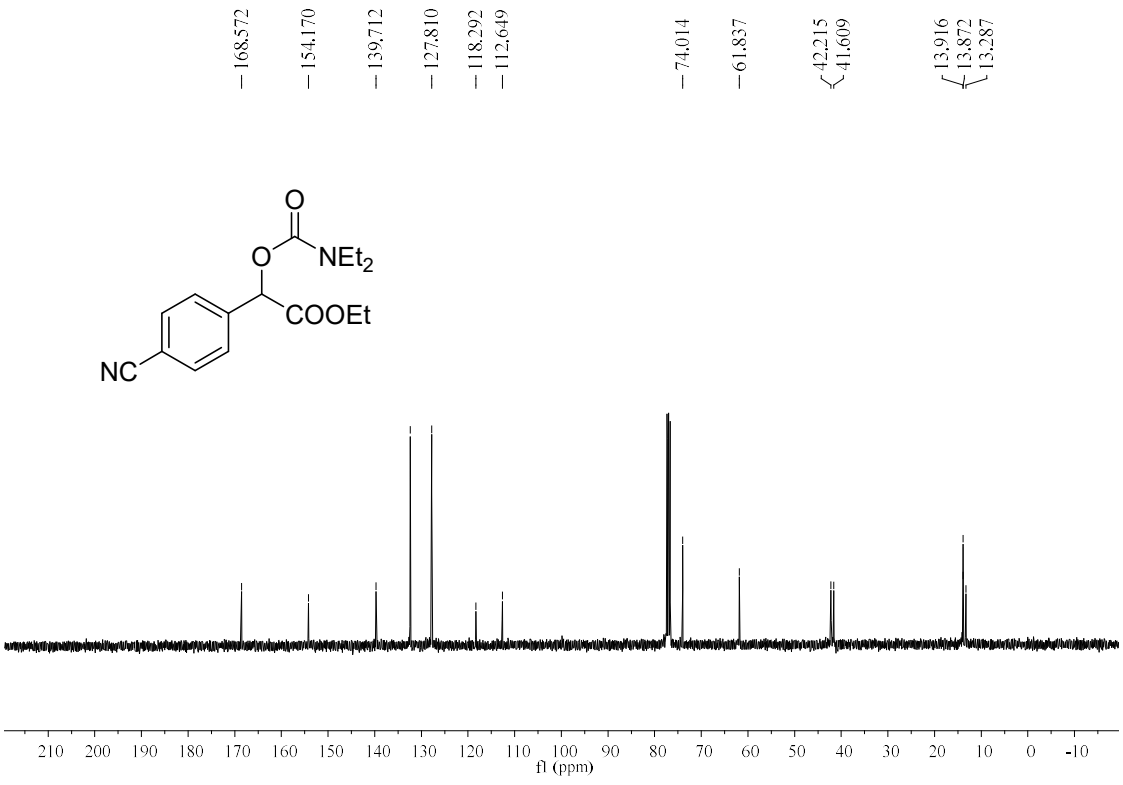
Ethyl 2-((diethylcarbamoyl)oxy)-2-(4-iodophenyl)acetate (4ca)



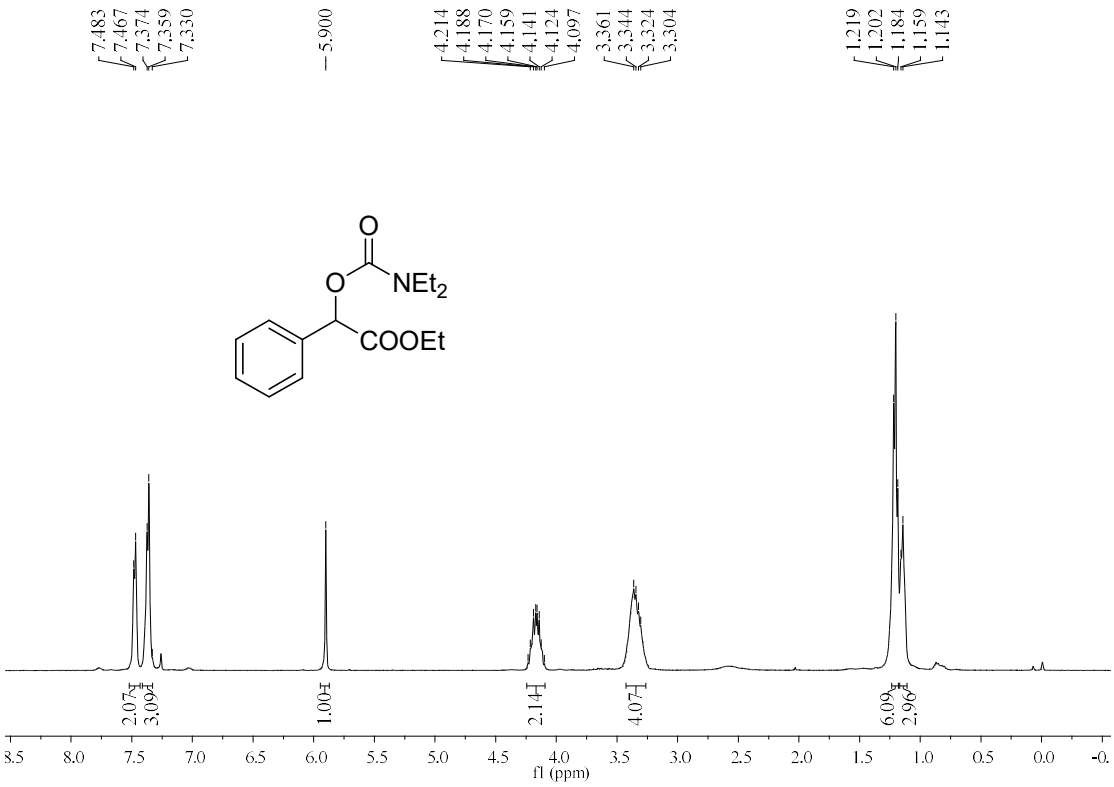


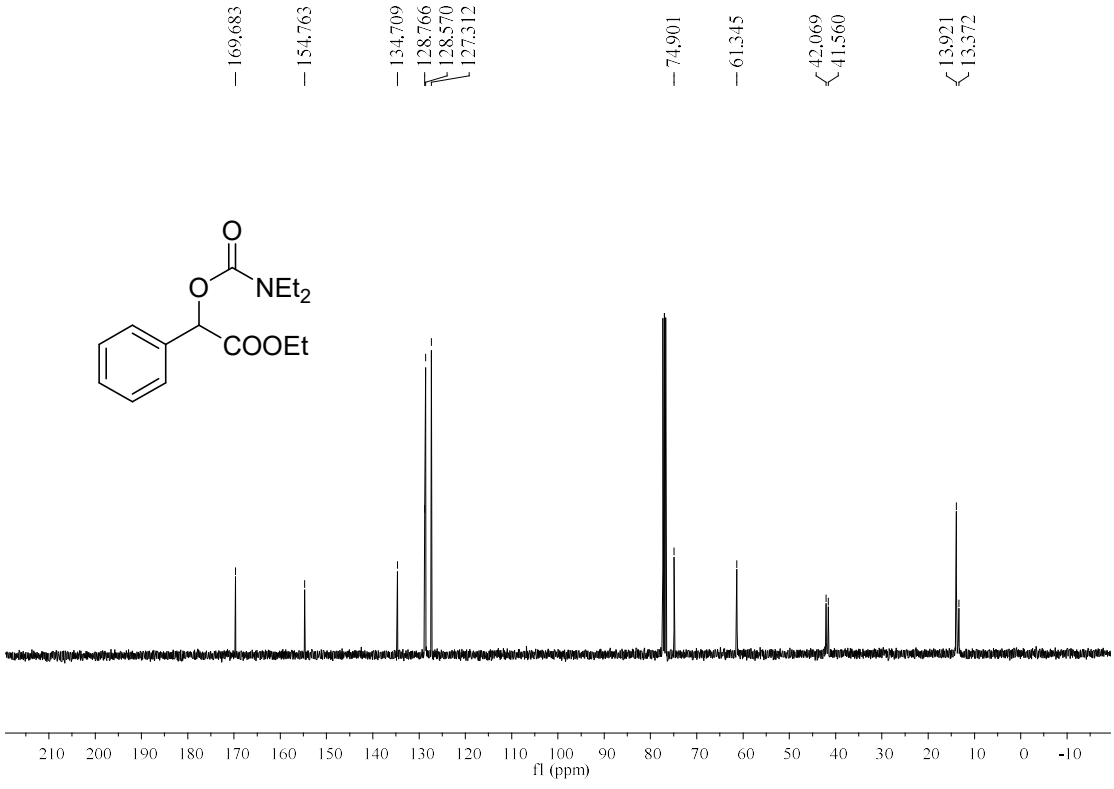
Ethyl 2-(4-cyanophenyl)-2-((diethylcarbamoyl)oxy)acetate (4ea)



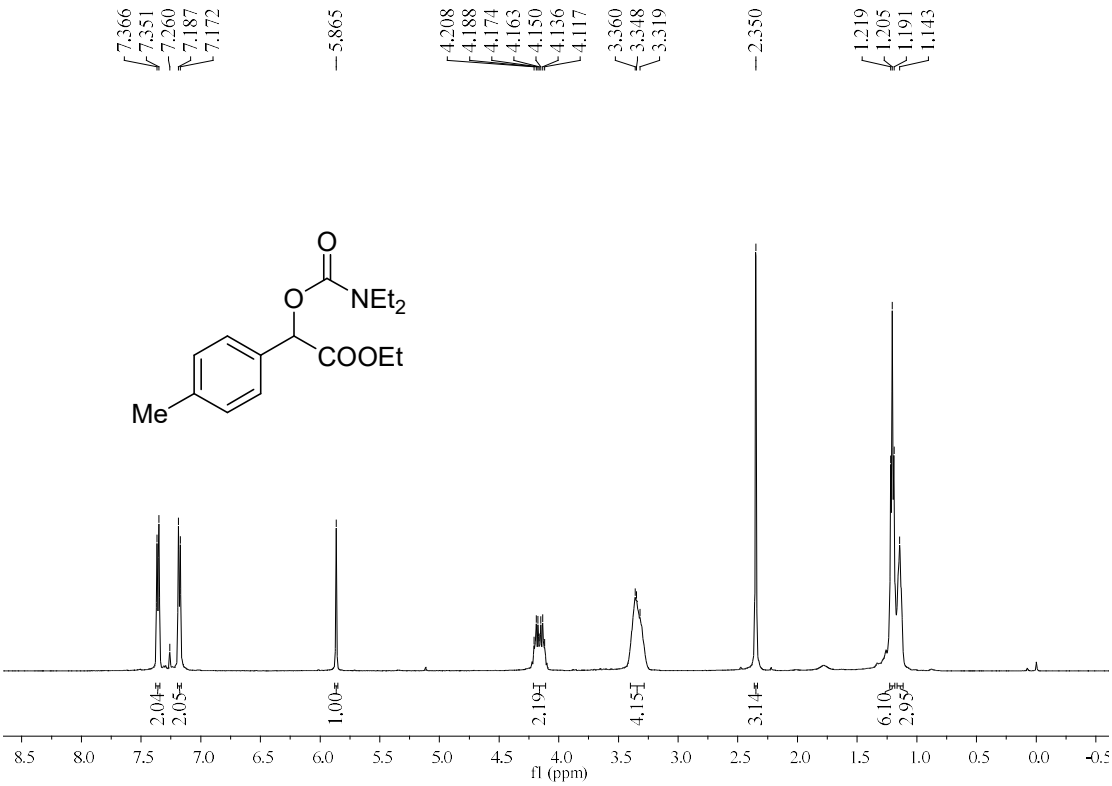


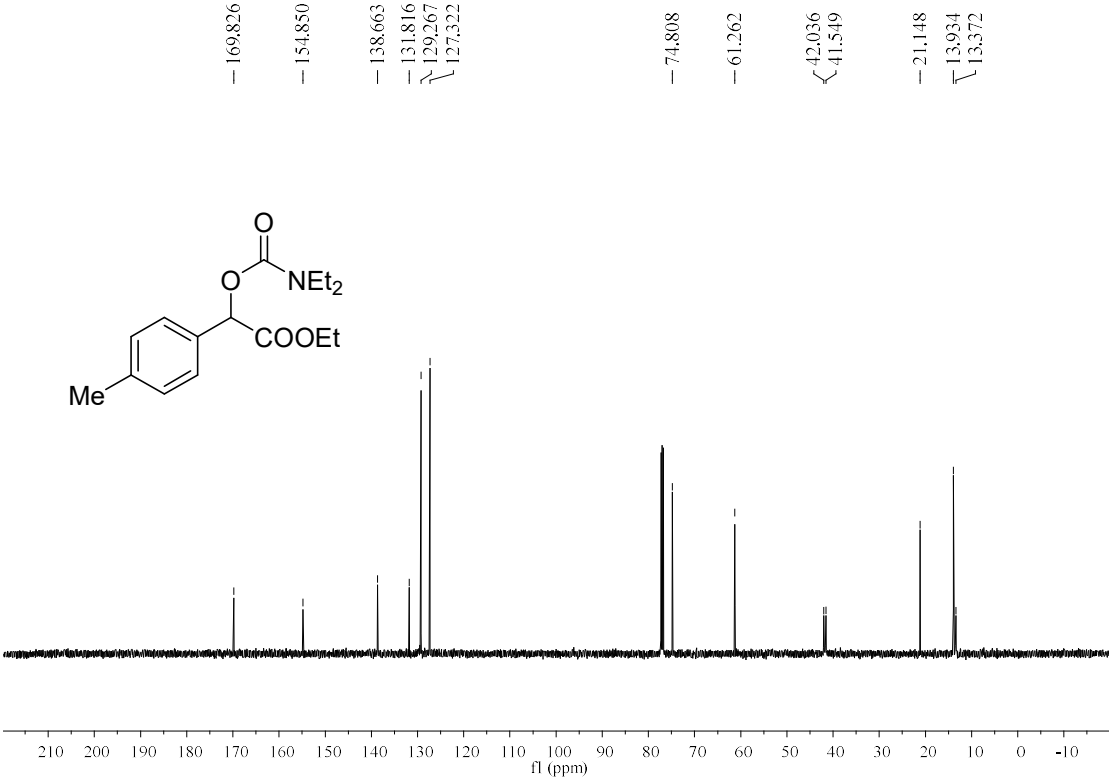
Ethyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4fa)



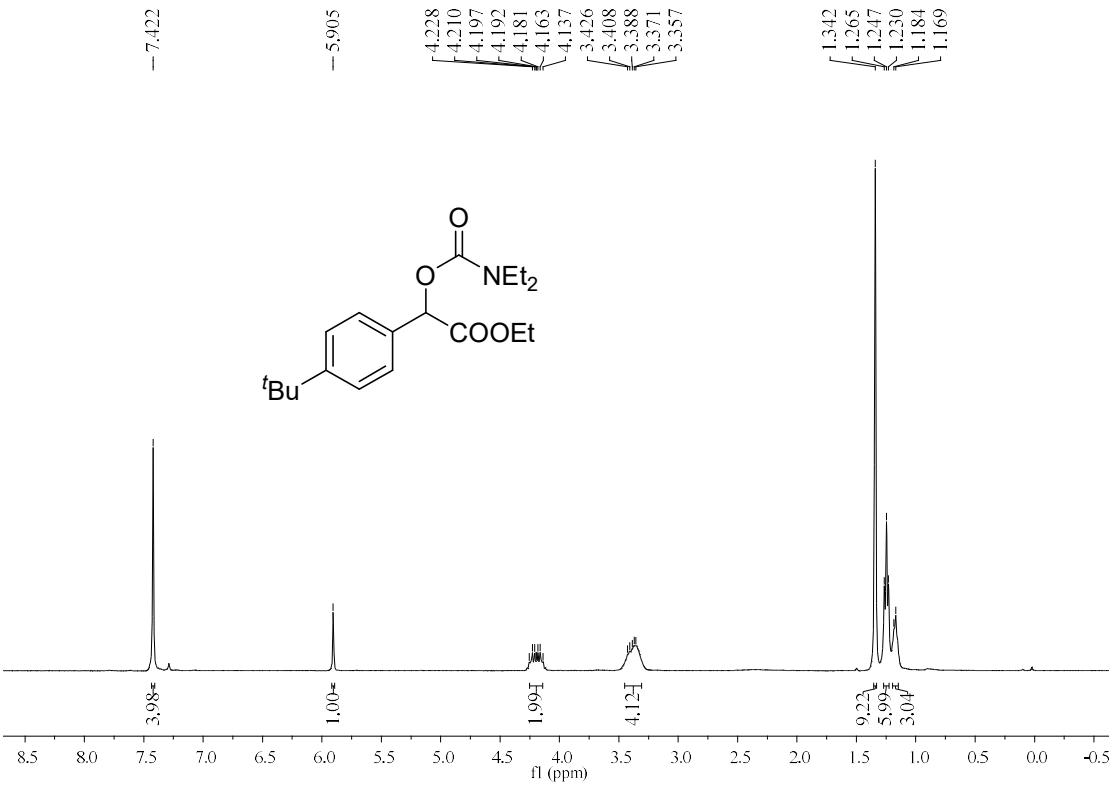


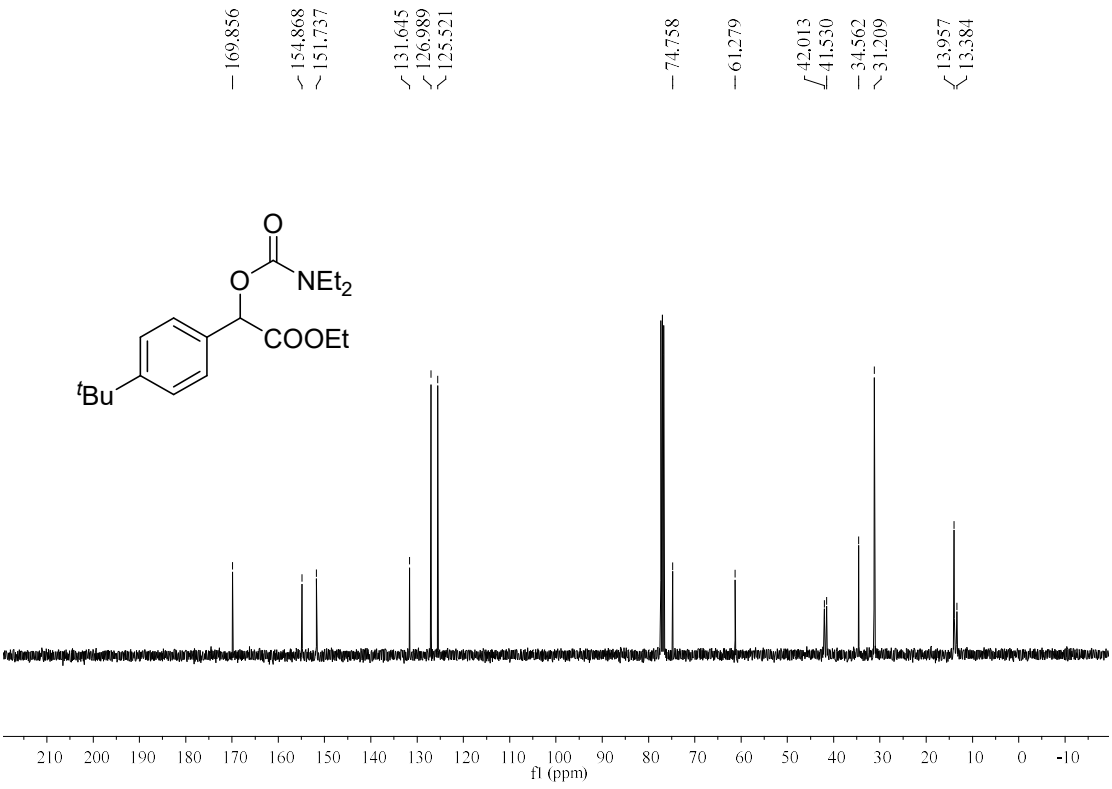
Ethyl 2-((diethylcarbamoyl)oxy)-2-(*p*-tolyl)acetate (4ga)



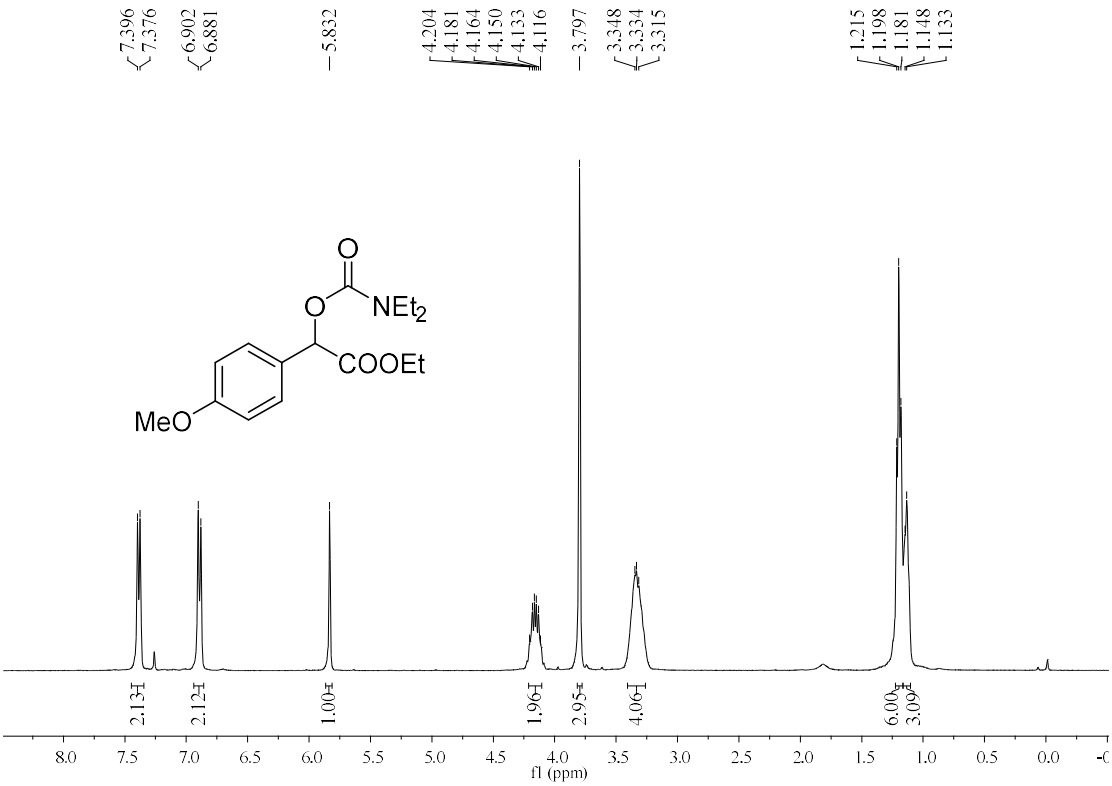


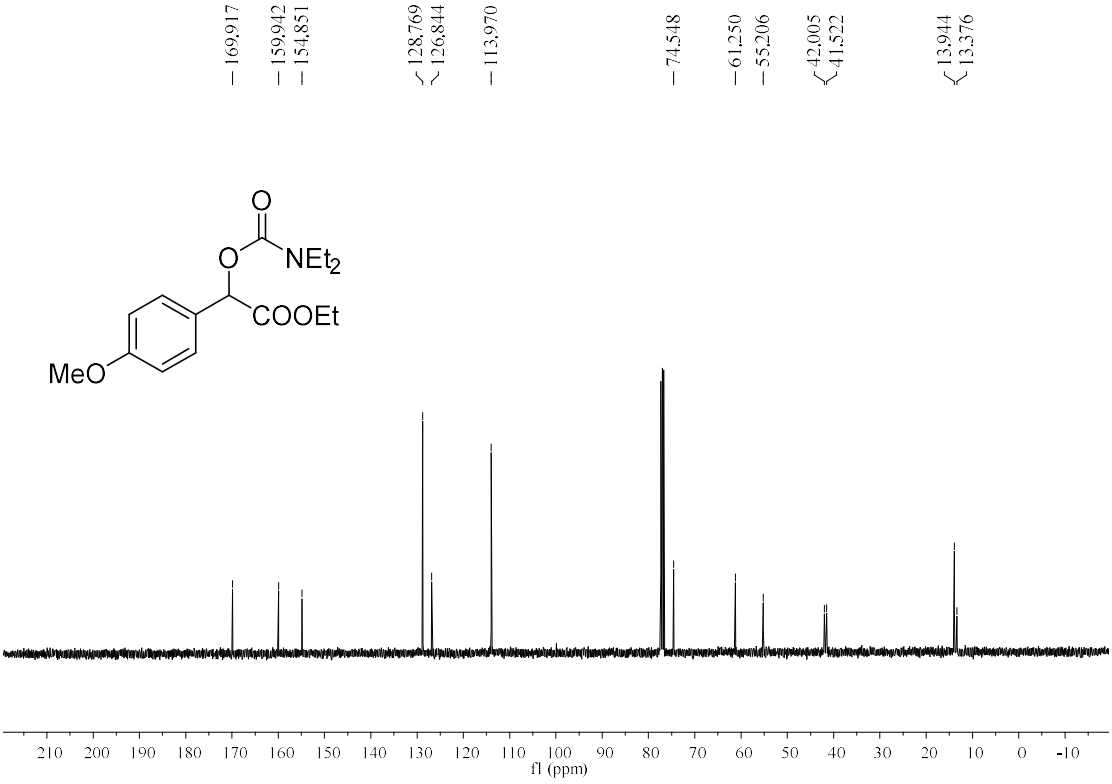
Ethyl 2-(4-(*tert*-butyl)phenyl)-2-((diethylcarbamoyl)oxy)acetate (4ha)



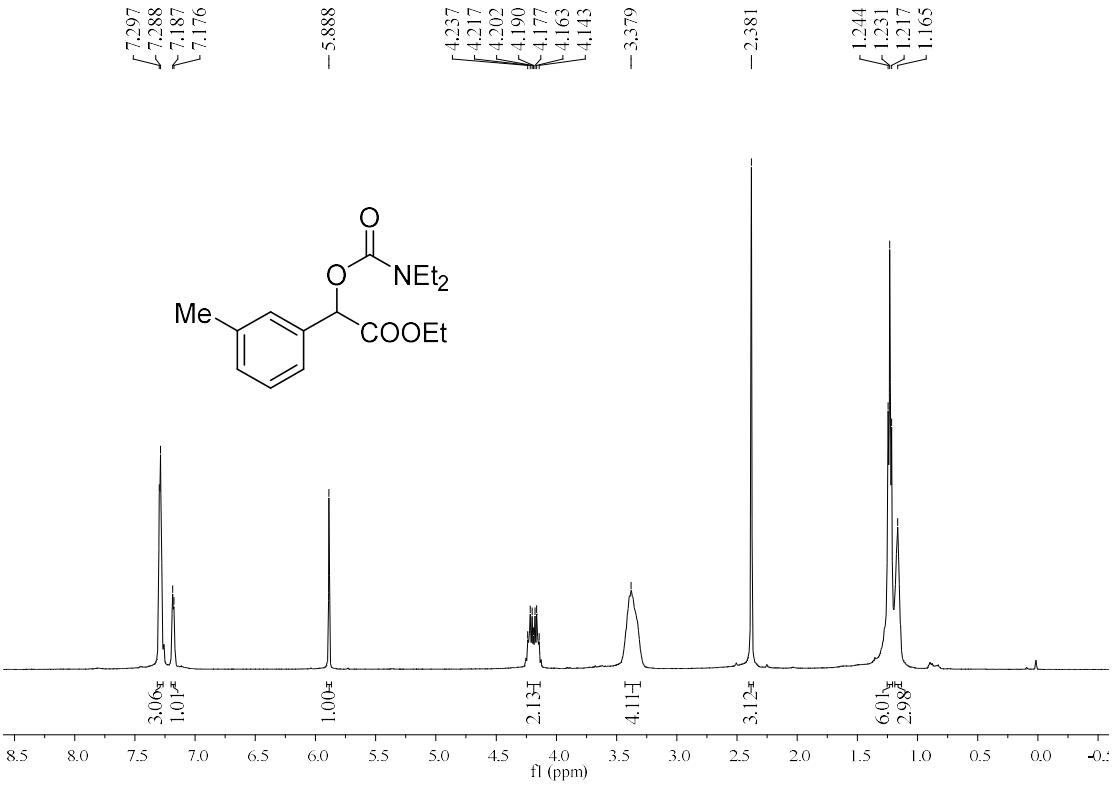


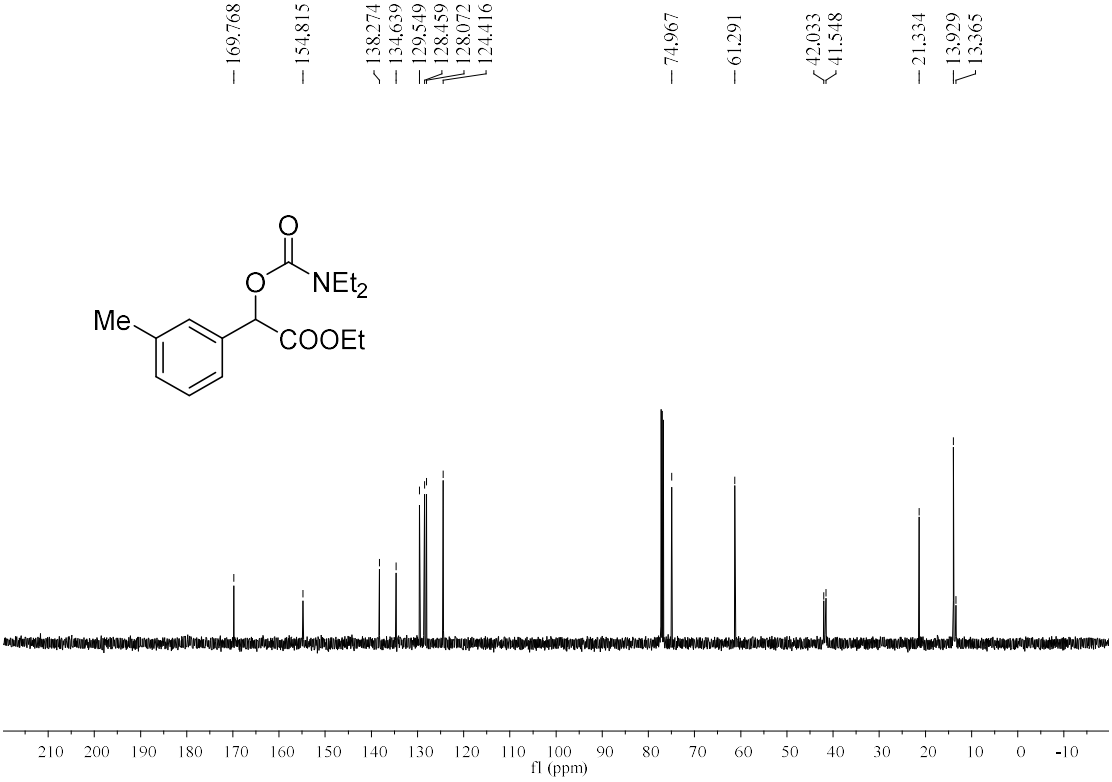
Ethyl 2-((diethylcarbamoyl)oxy)-2-(4-methoxyphenyl)acetate (4ia)



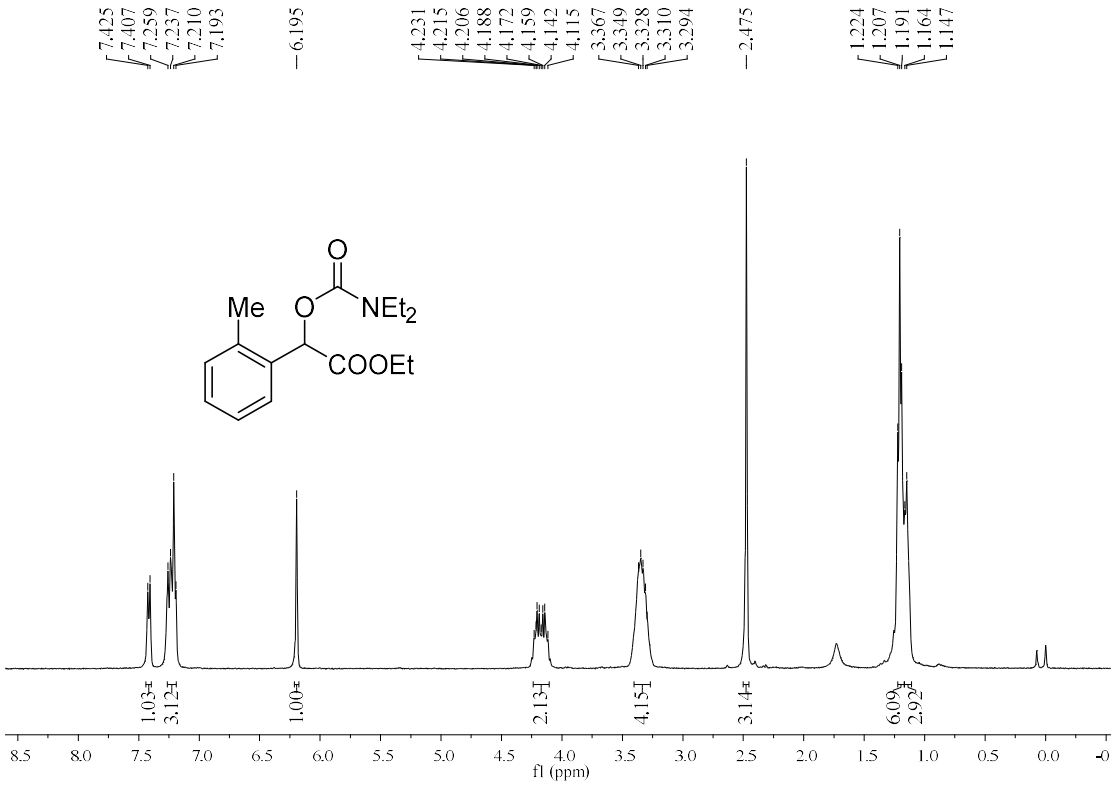


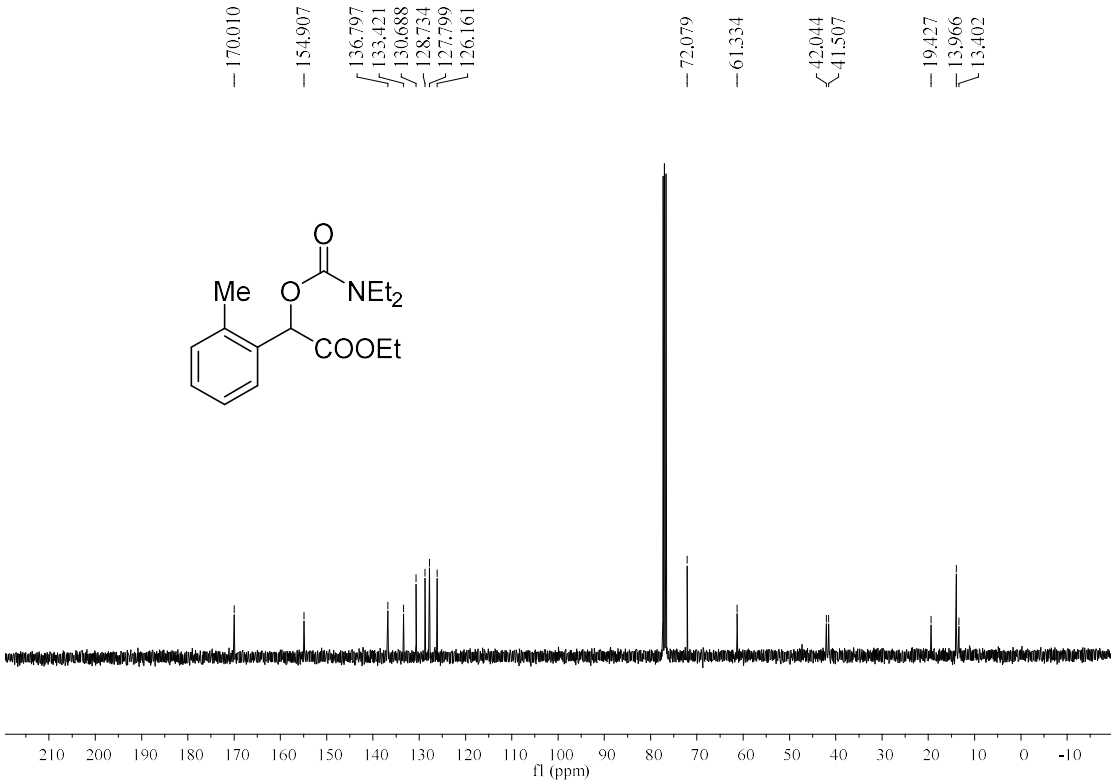
Ethyl 2-((diethylcarbamoyl)oxy)-2-(*m*-tolyl)acetate (4ka)



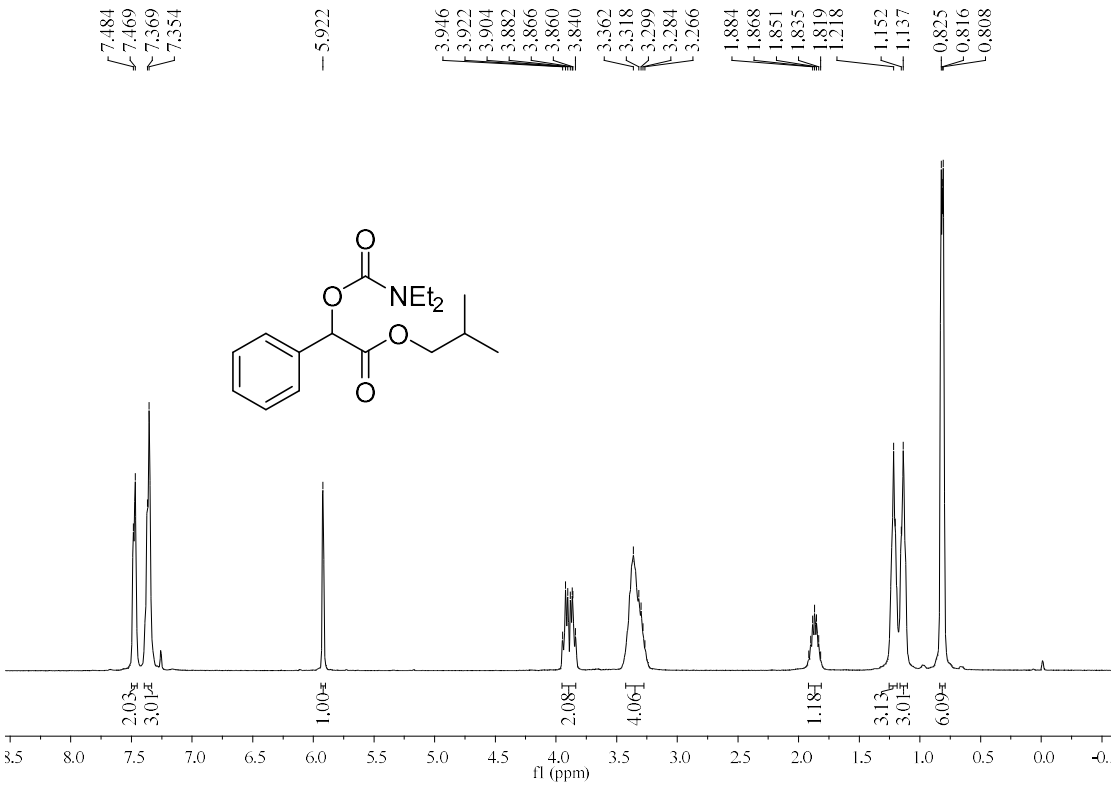


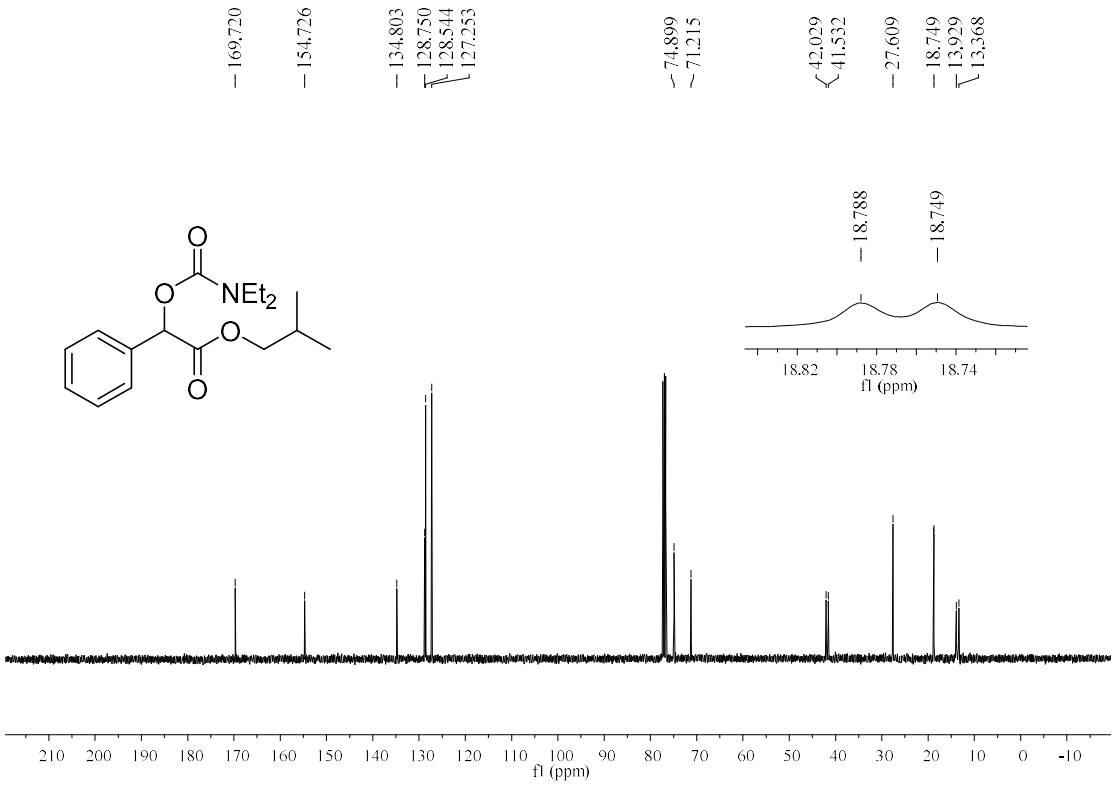
Ethyl 2-((diethylcarbamoyl)oxy)-2-(*o*-tolyl)acetate (4ma)



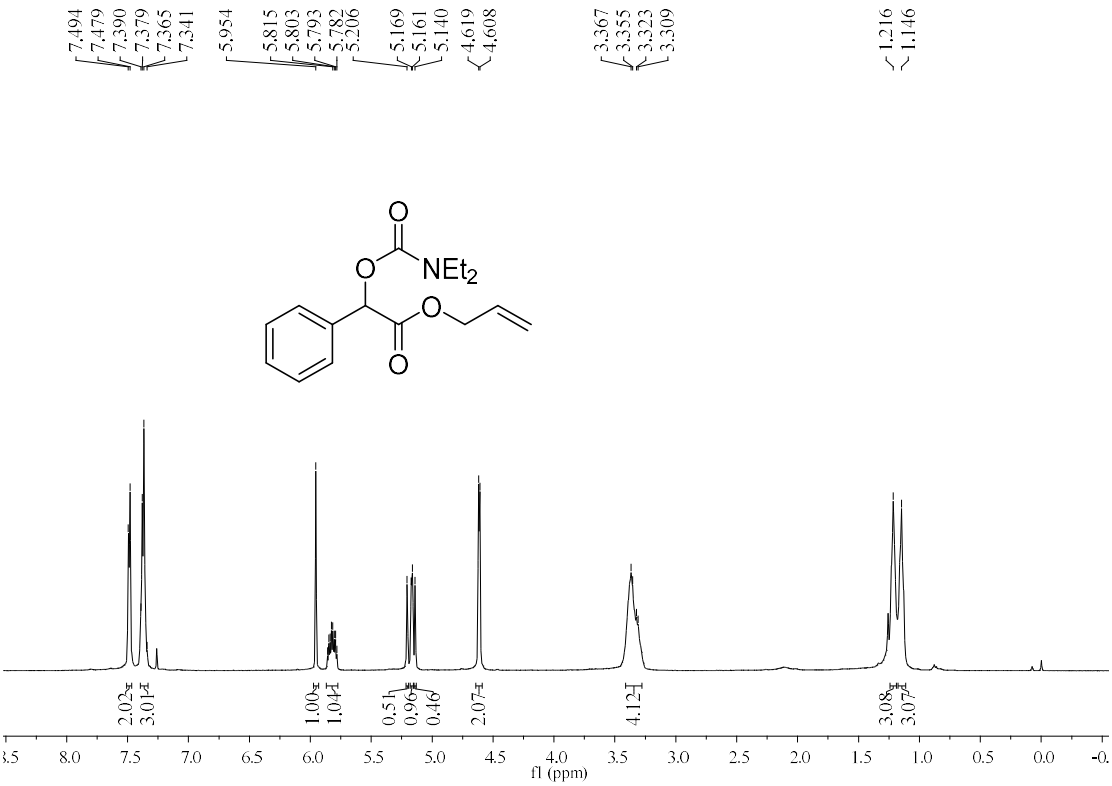


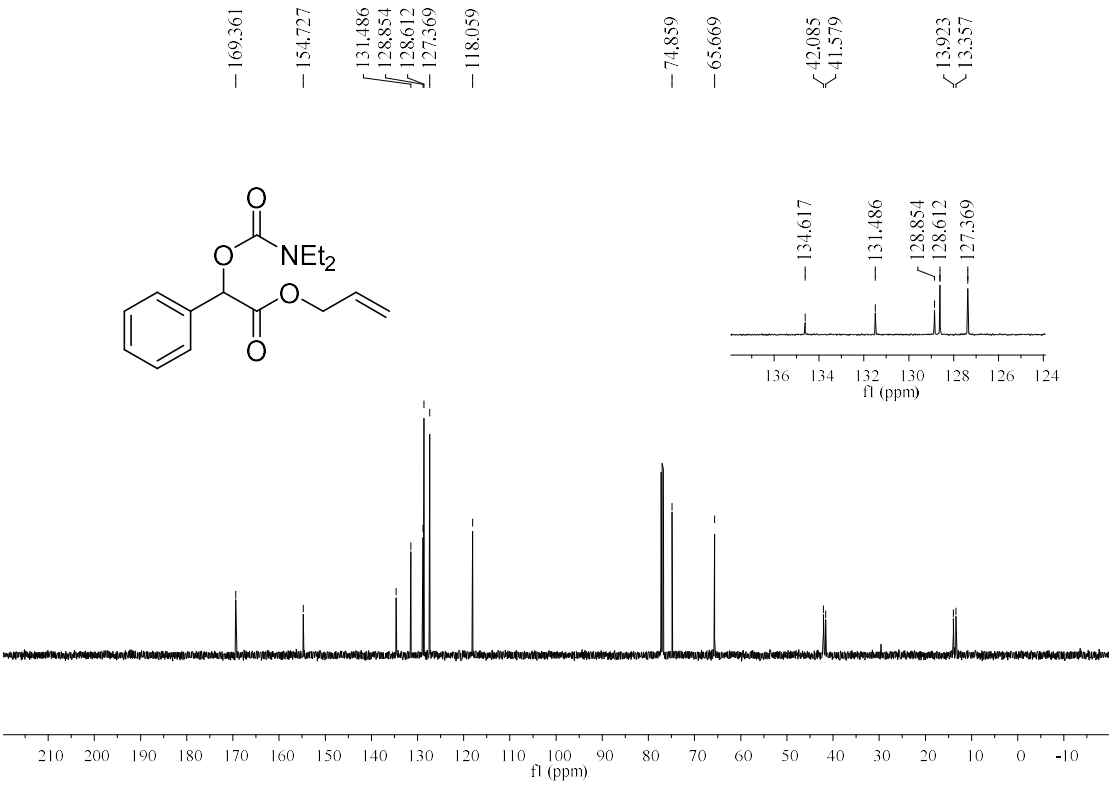
Isobutyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4pa)



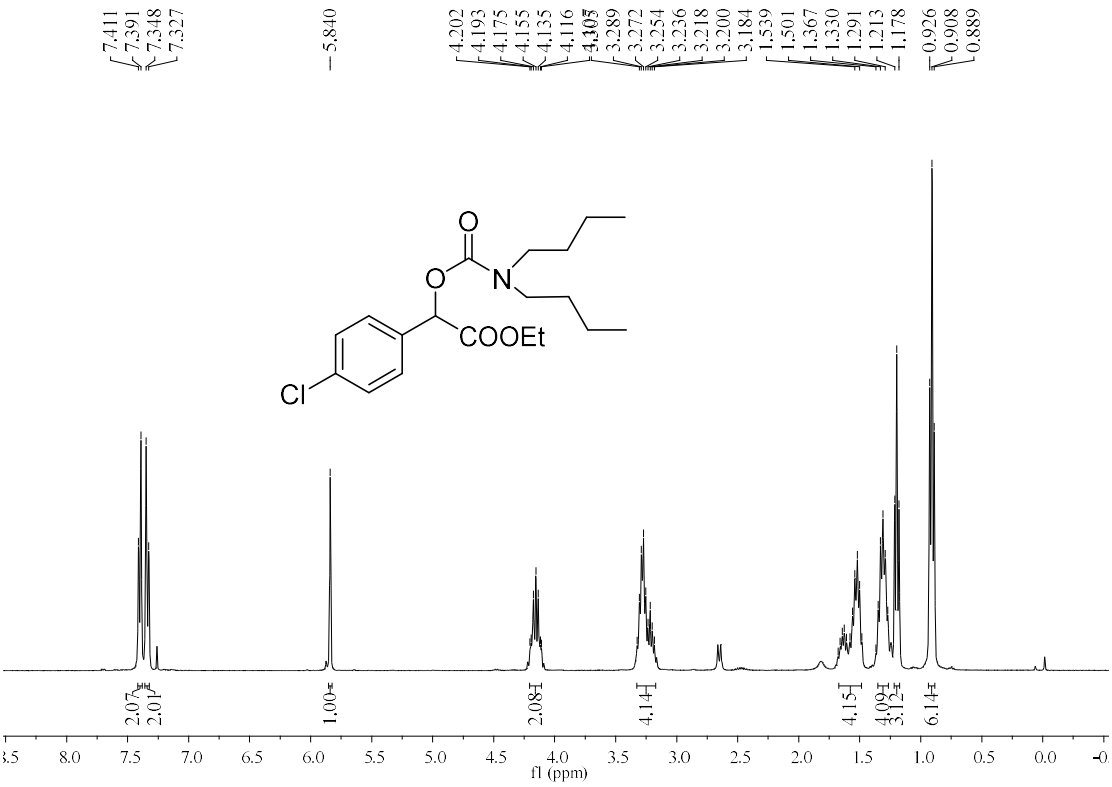


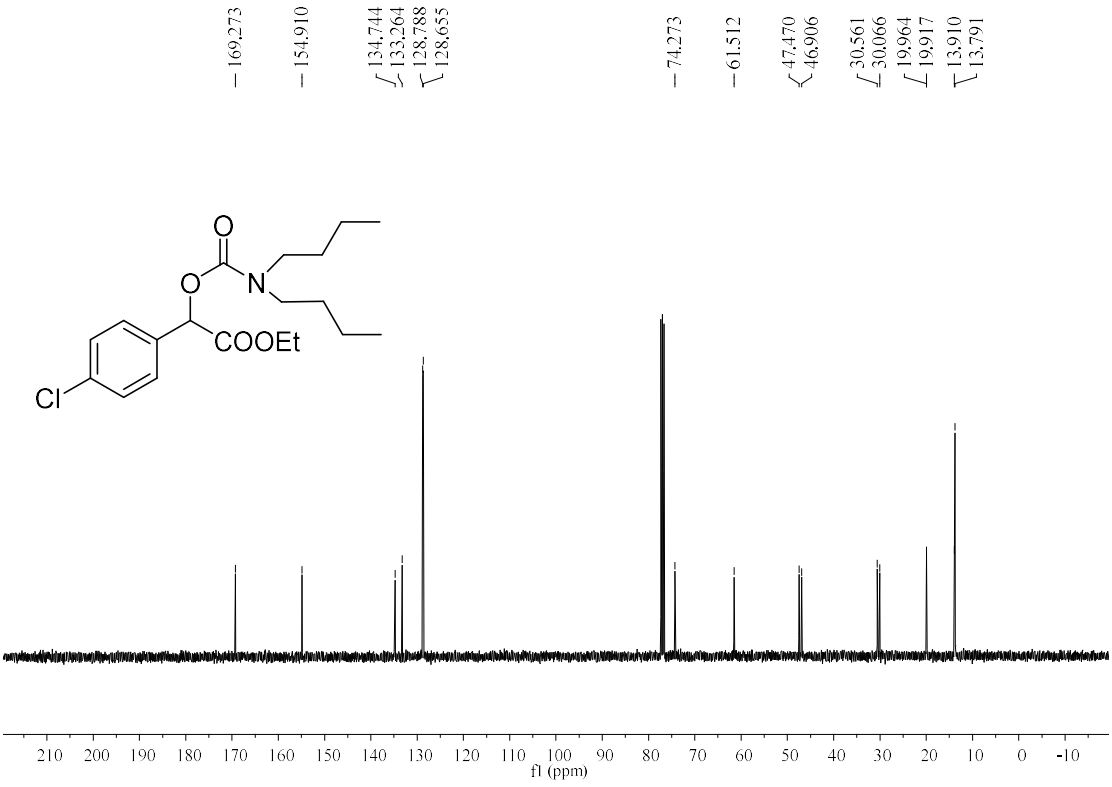
Allyl 2-((diethylcarbamoyl)oxy)-2-phenylacetate (4qa)



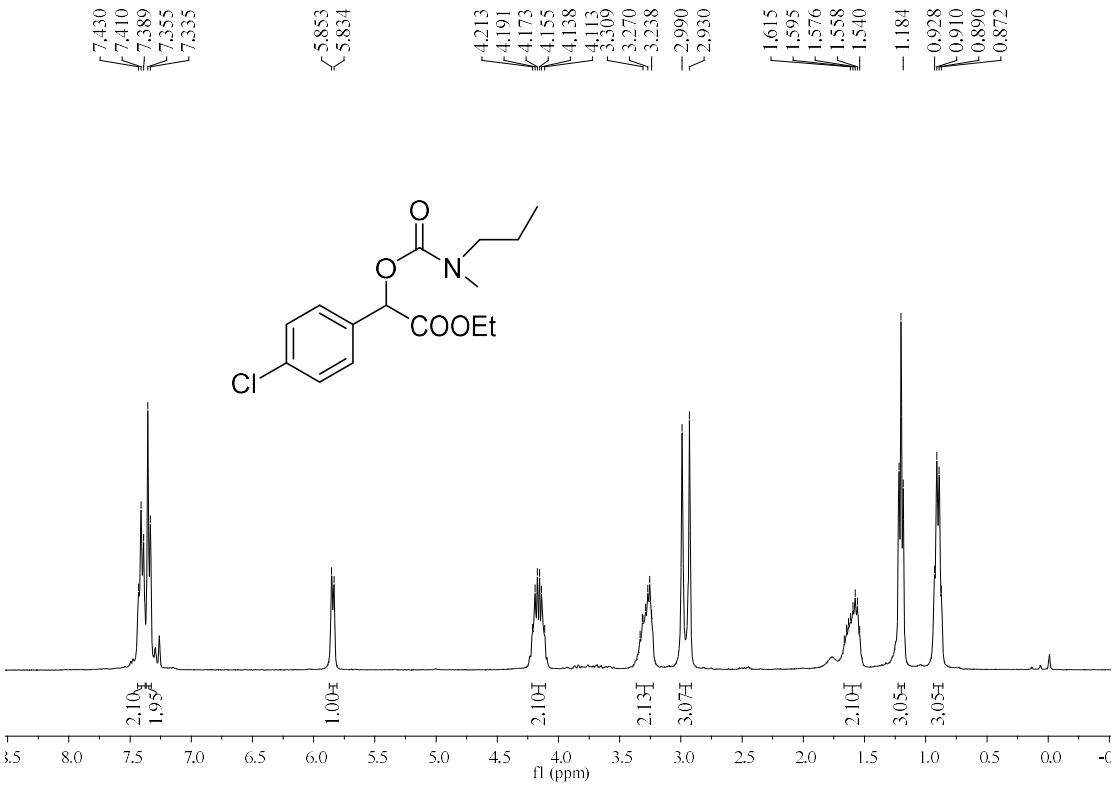


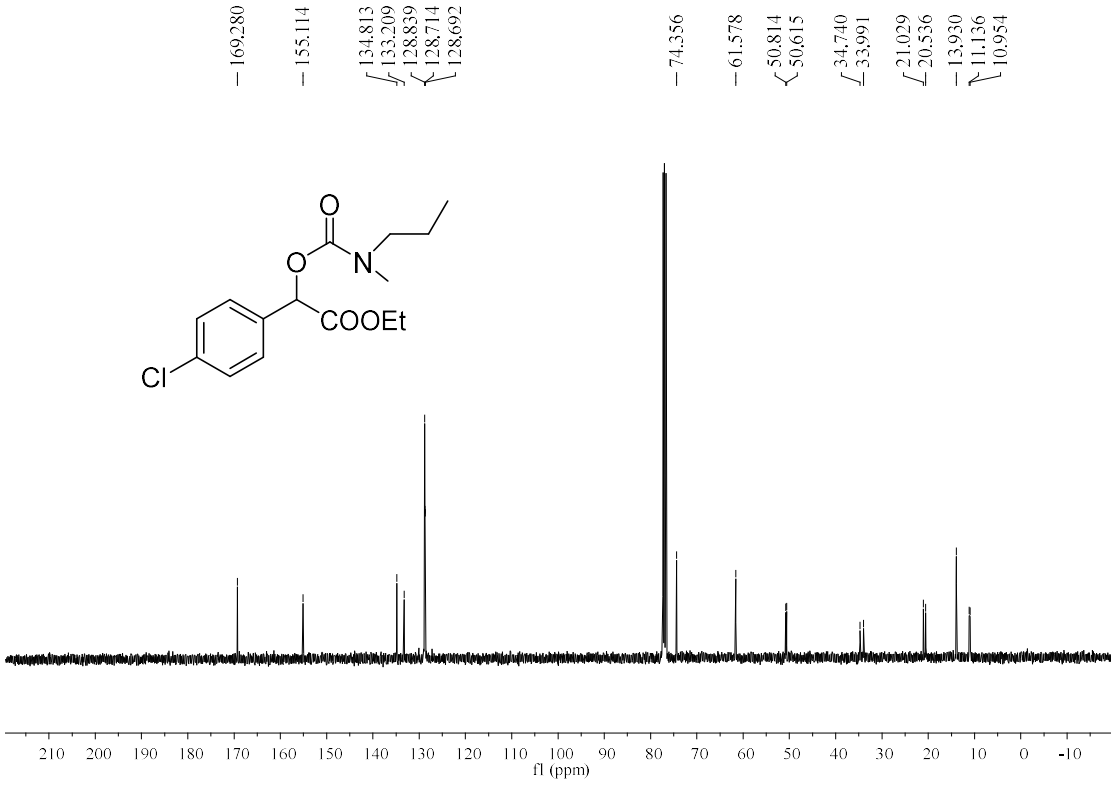
Ethyl 2-(4-chlorophenyl)-2-((dibutylcarbamoyl)oxy)acetate (4ab)



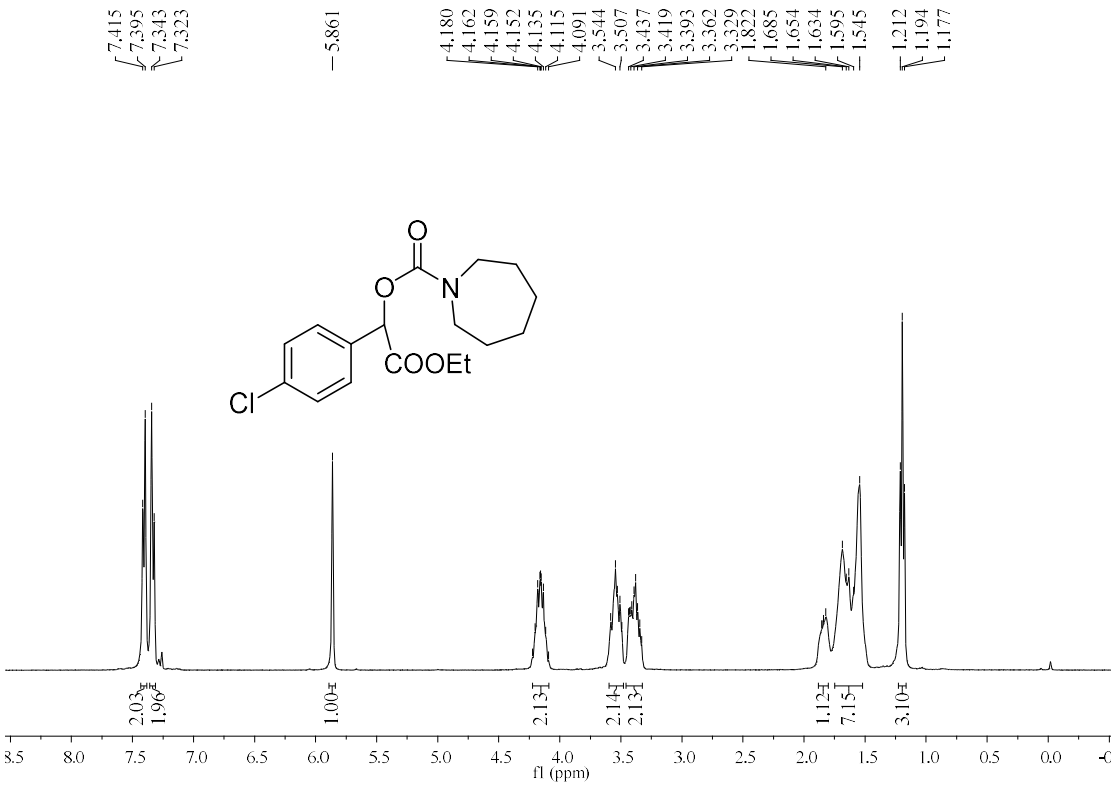


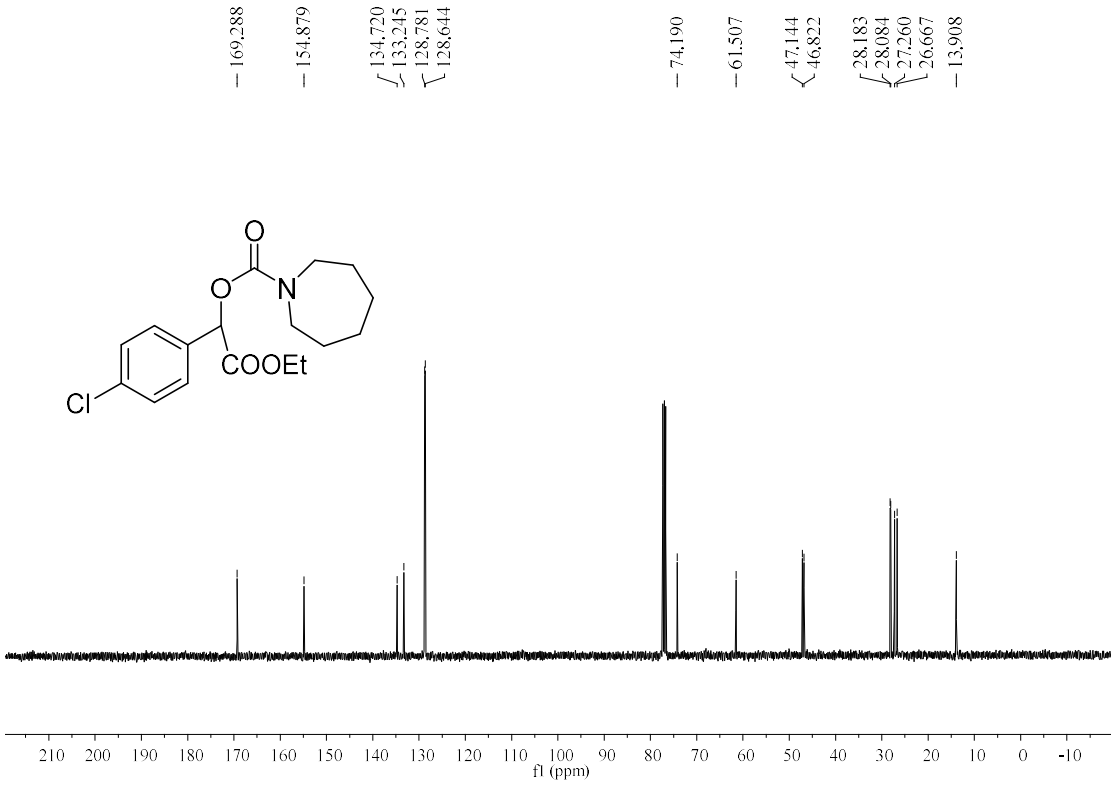
Ethyl 2-(4-chlorophenyl)-2-((methyl(propyl)carbamoyl)oxy)acetate (4ad)



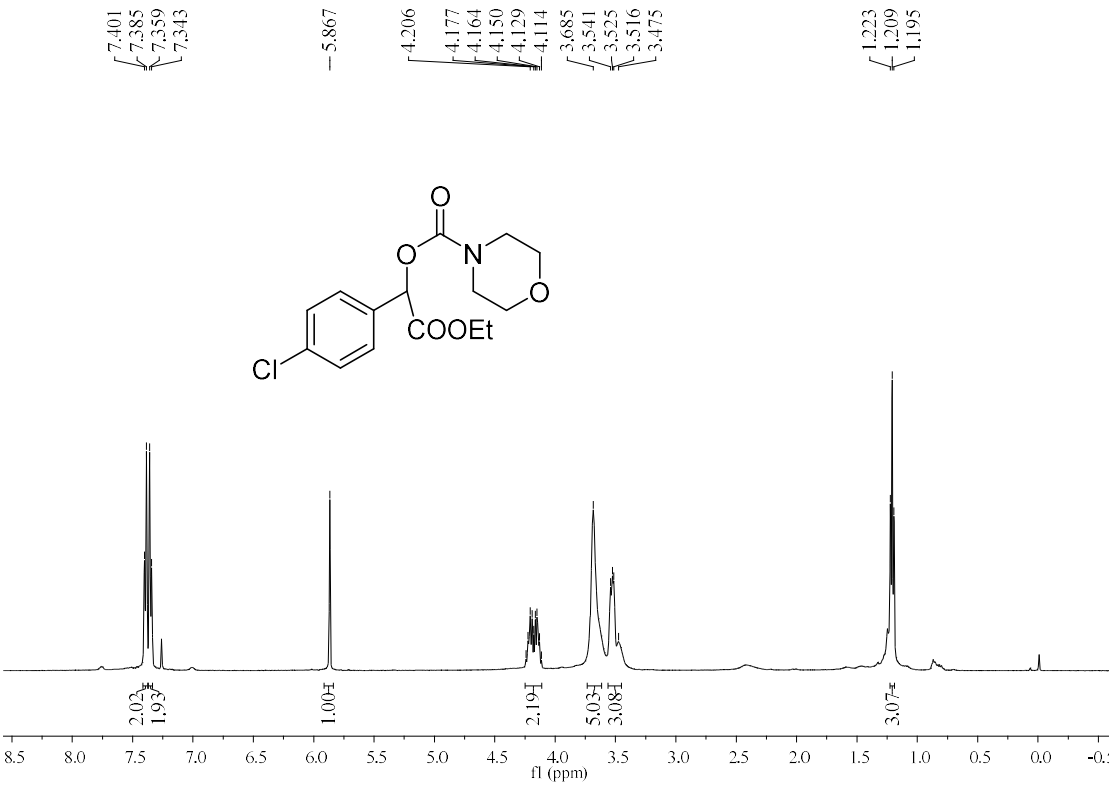


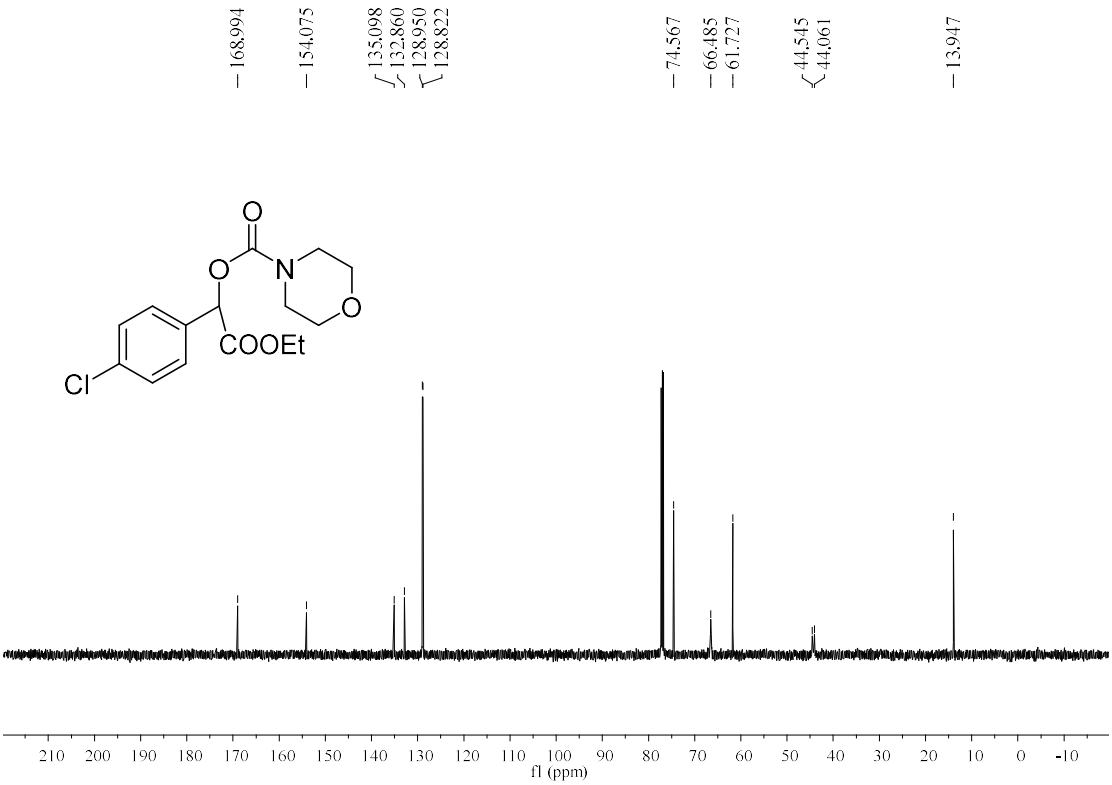
1-(4-Chlorophenyl)-2-ethoxy-2-oxoethyl azepane-1-carboxylate (4ai)



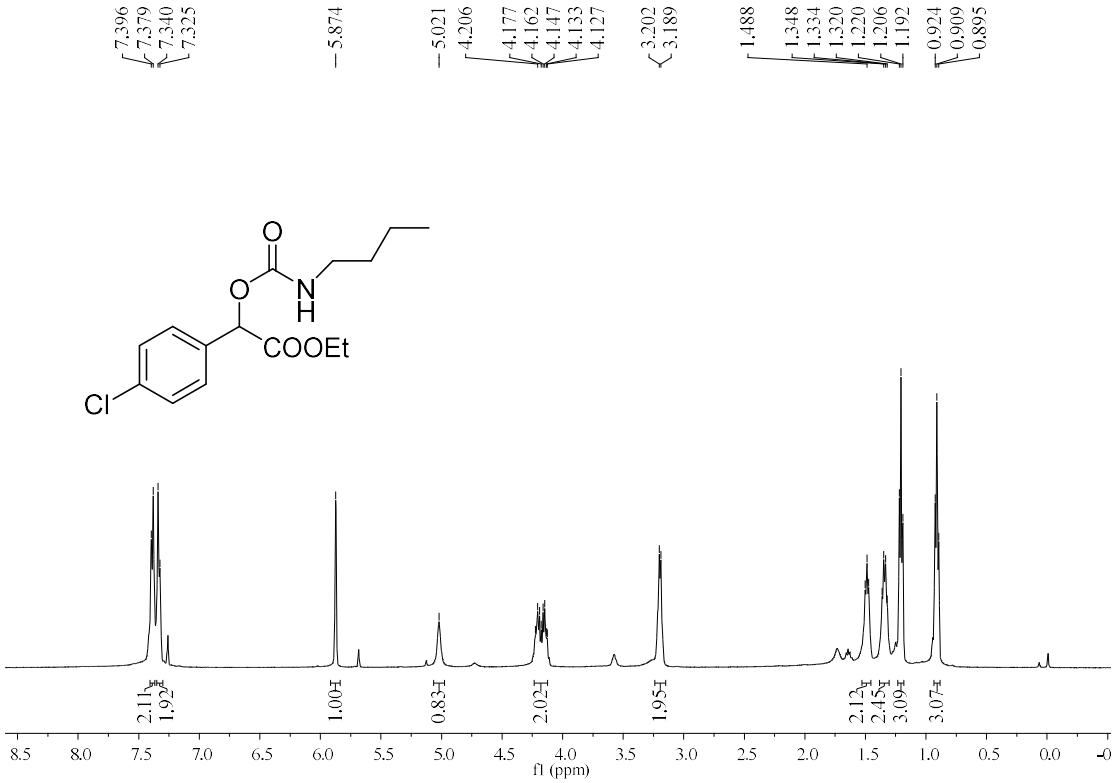


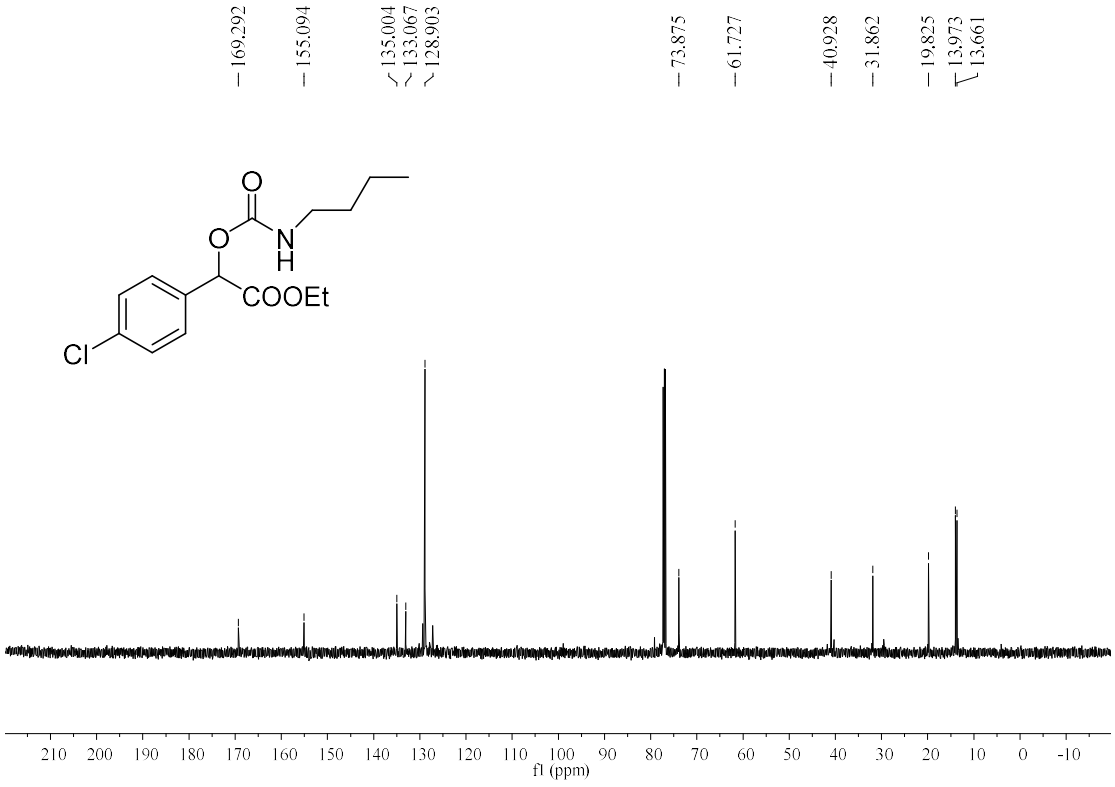
1-(4-Chlorophenyl)-2-ethoxy-2-oxoethyl morpholine-4-carboxylate (4ak)



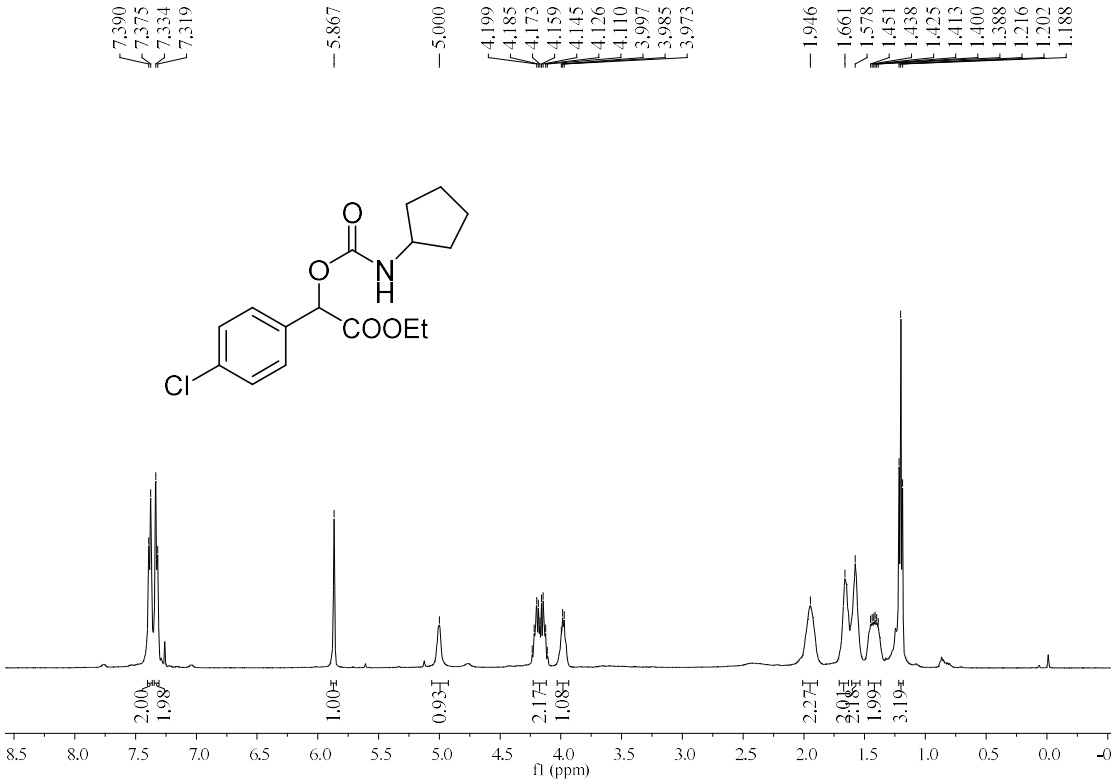


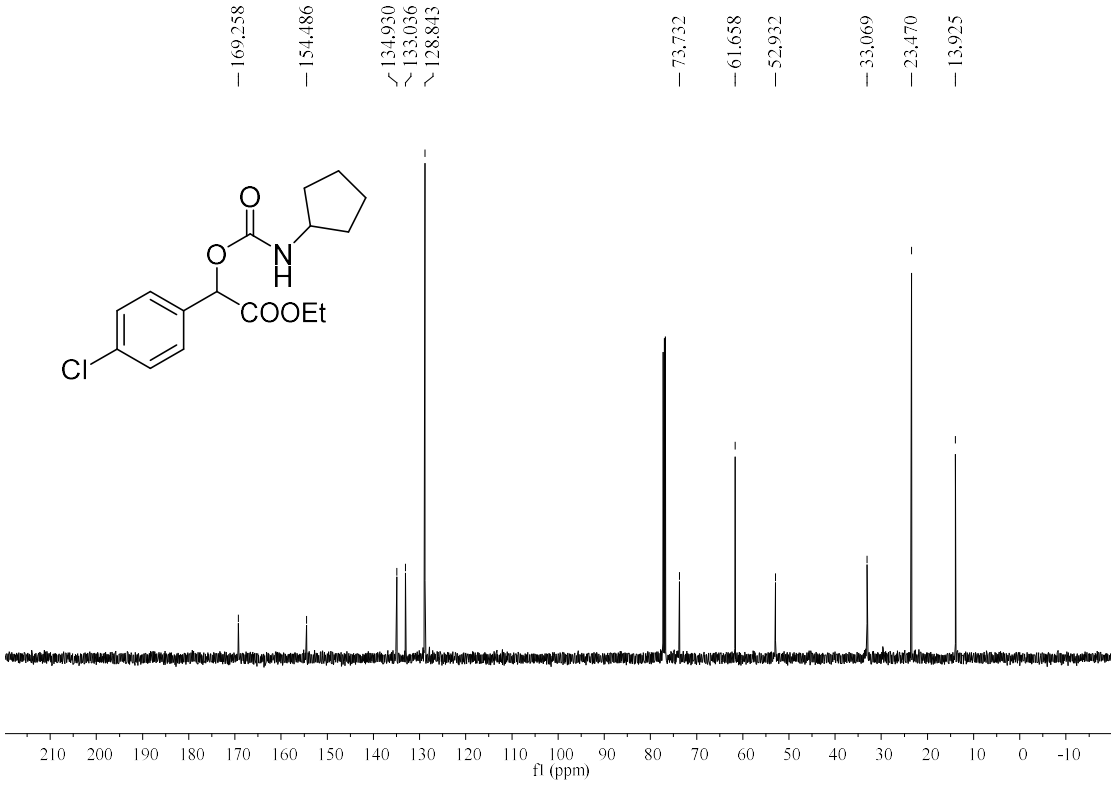
Ethyl 2-((butylcarbamoyl)oxy)-2-(4-chlorophenyl)acetate (4ao)



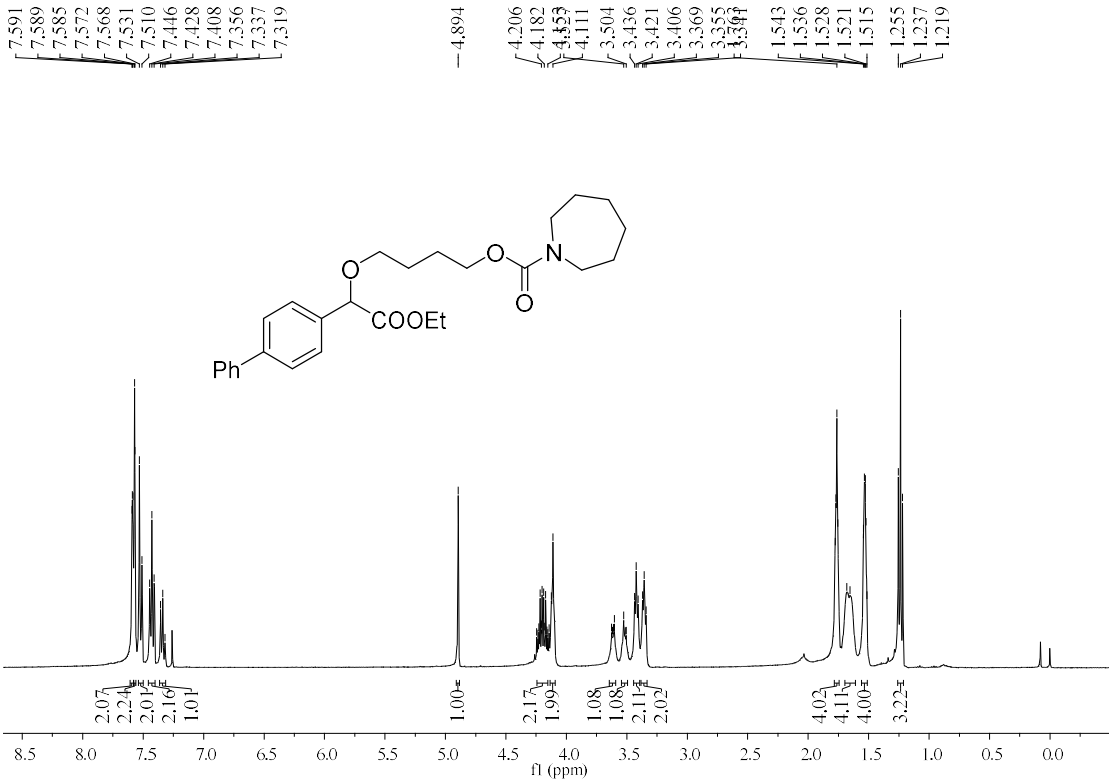


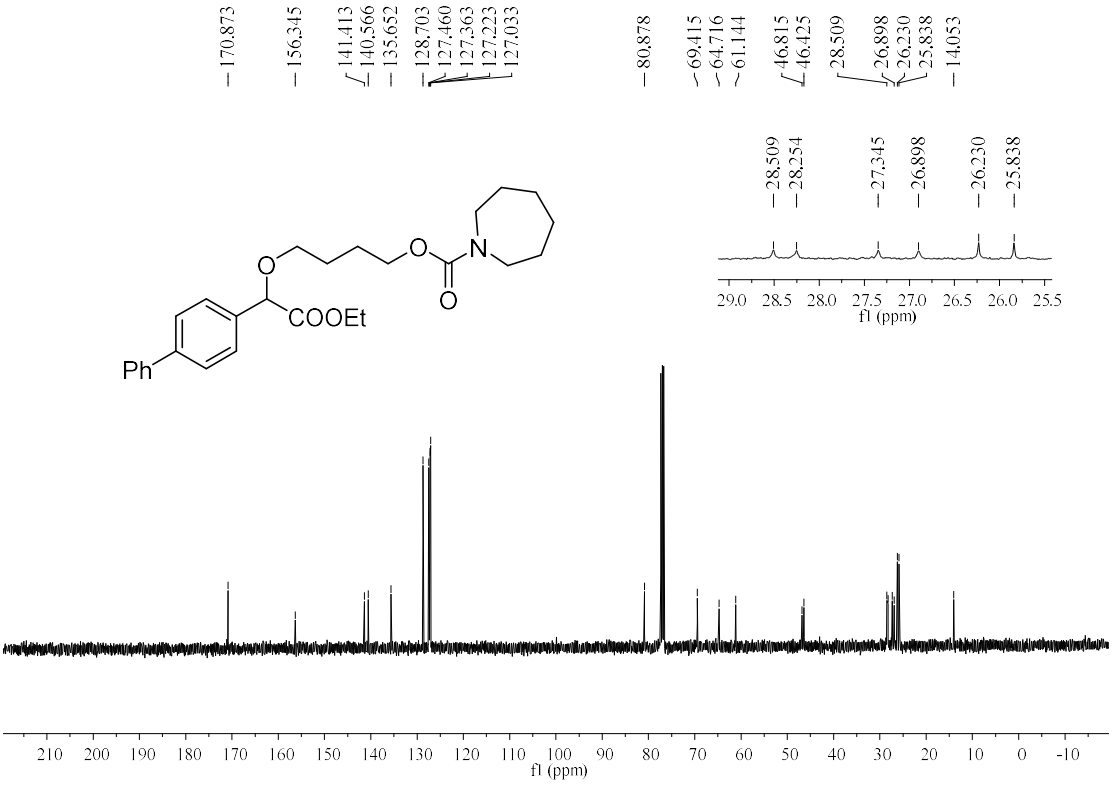
Ethyl 2-(4-chlorophenyl)-2-((cyclopentylcarbamoyl)oxy)acetate (4ap)



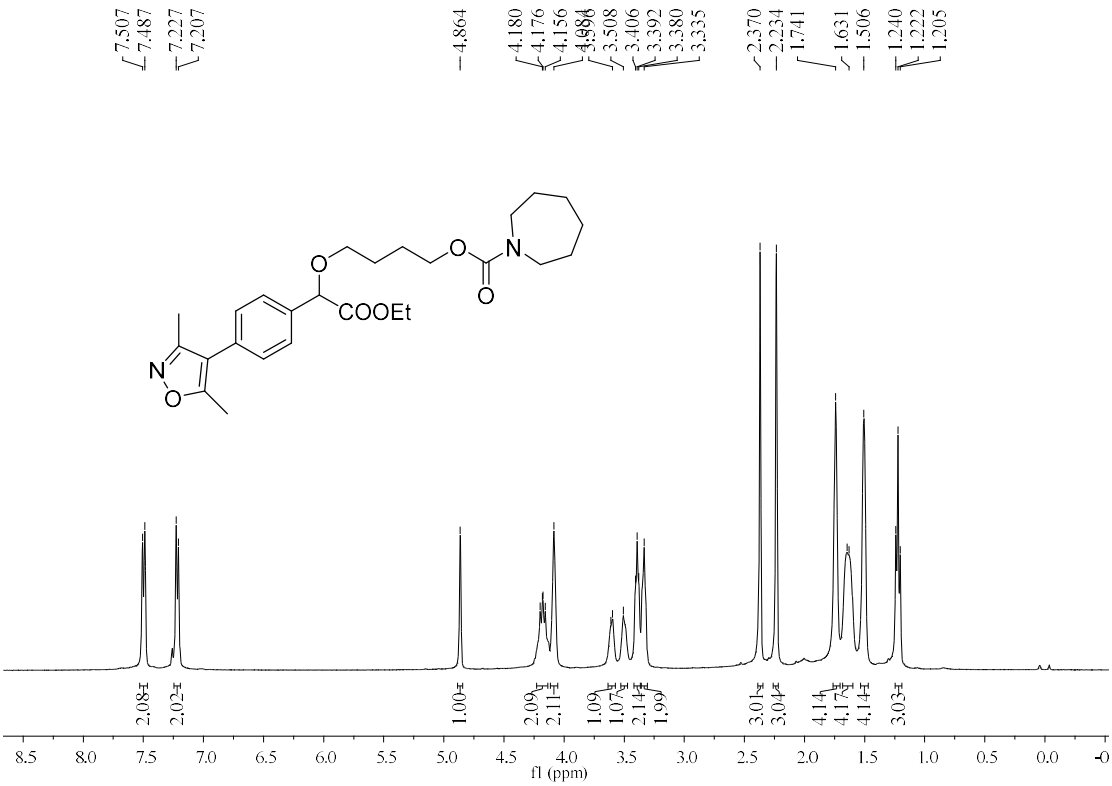


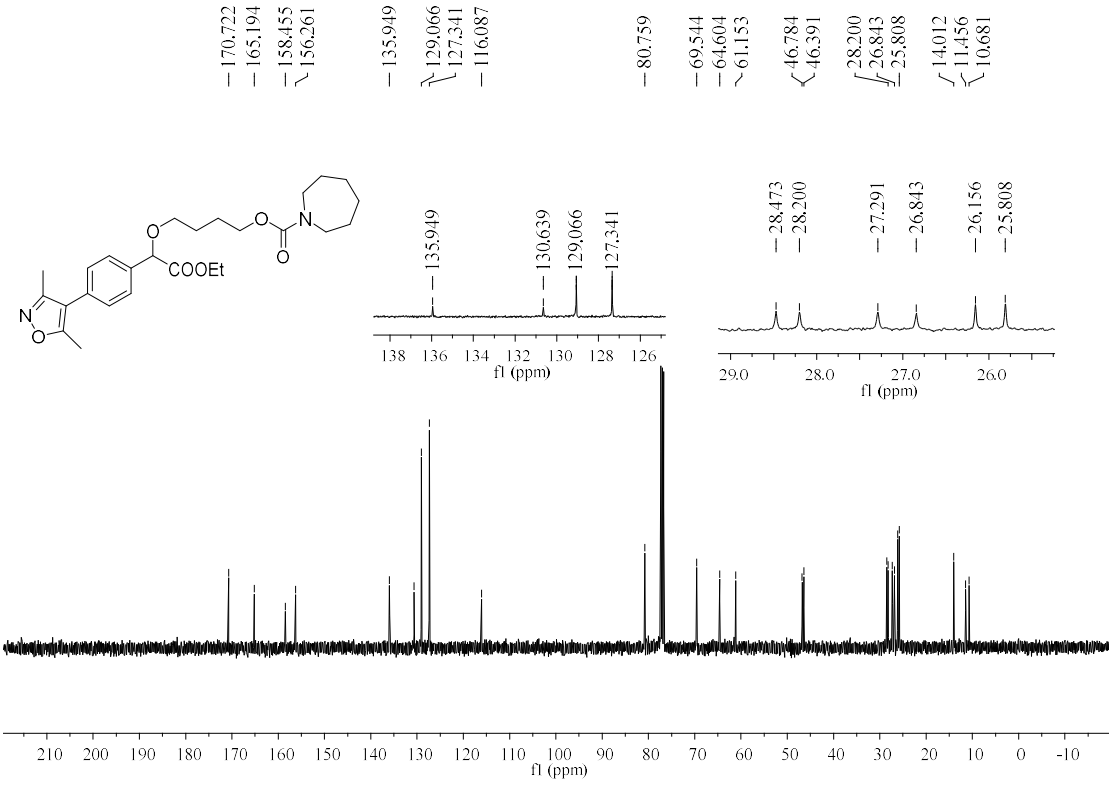
4-(1-([1,1'-Biphenyl]-4-yl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (5)



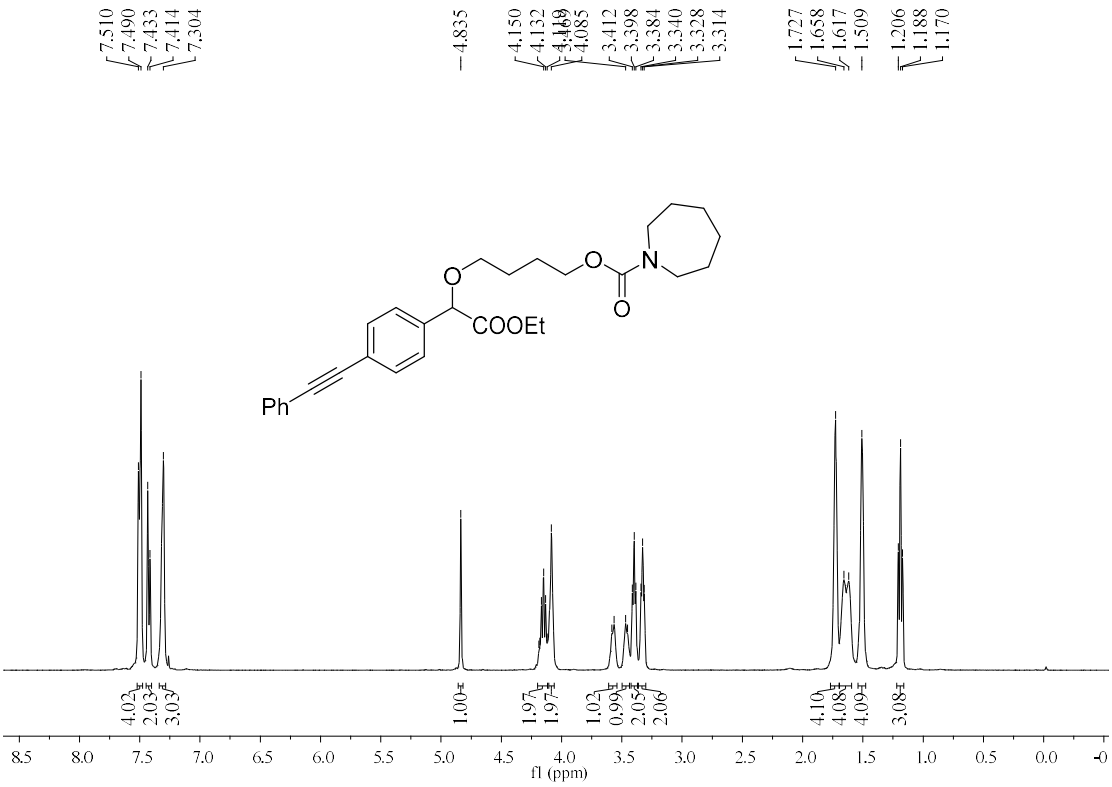


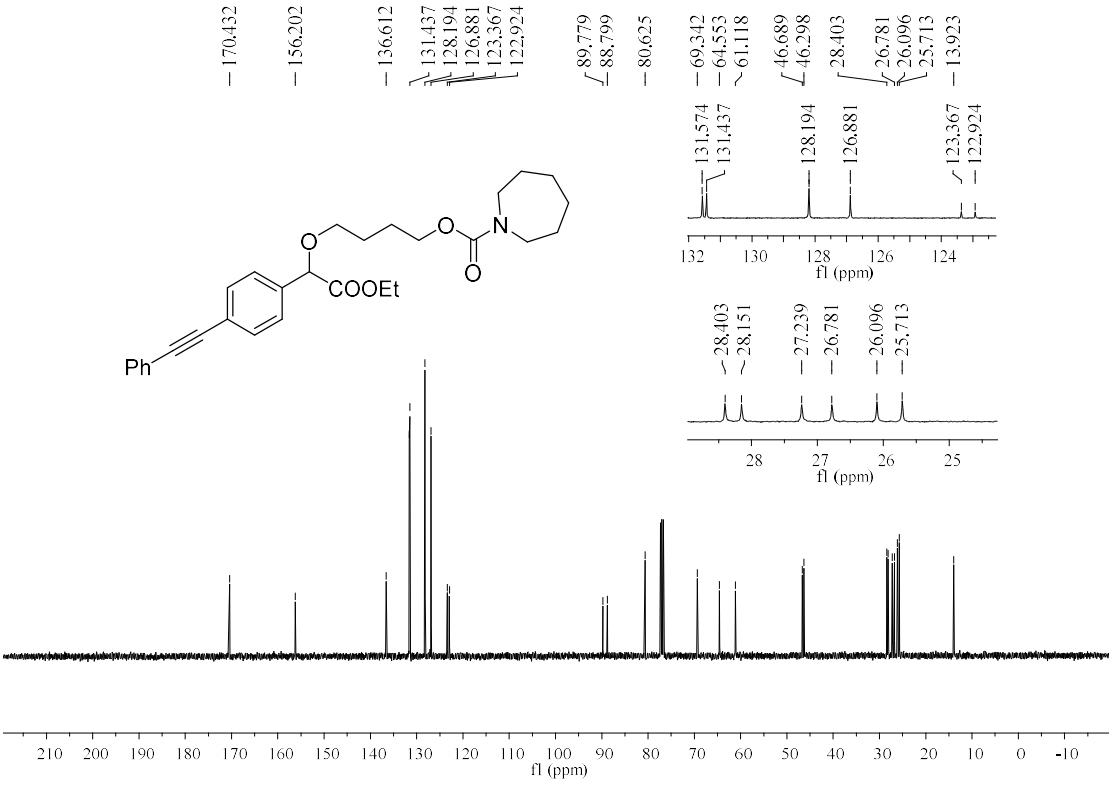
4-(1-(4-(3,5-Dimethylisoxazol-4-yl)phenyl)-2-ethoxy-2-oxoethoxy)butyl azepane-1-carboxylate (6)



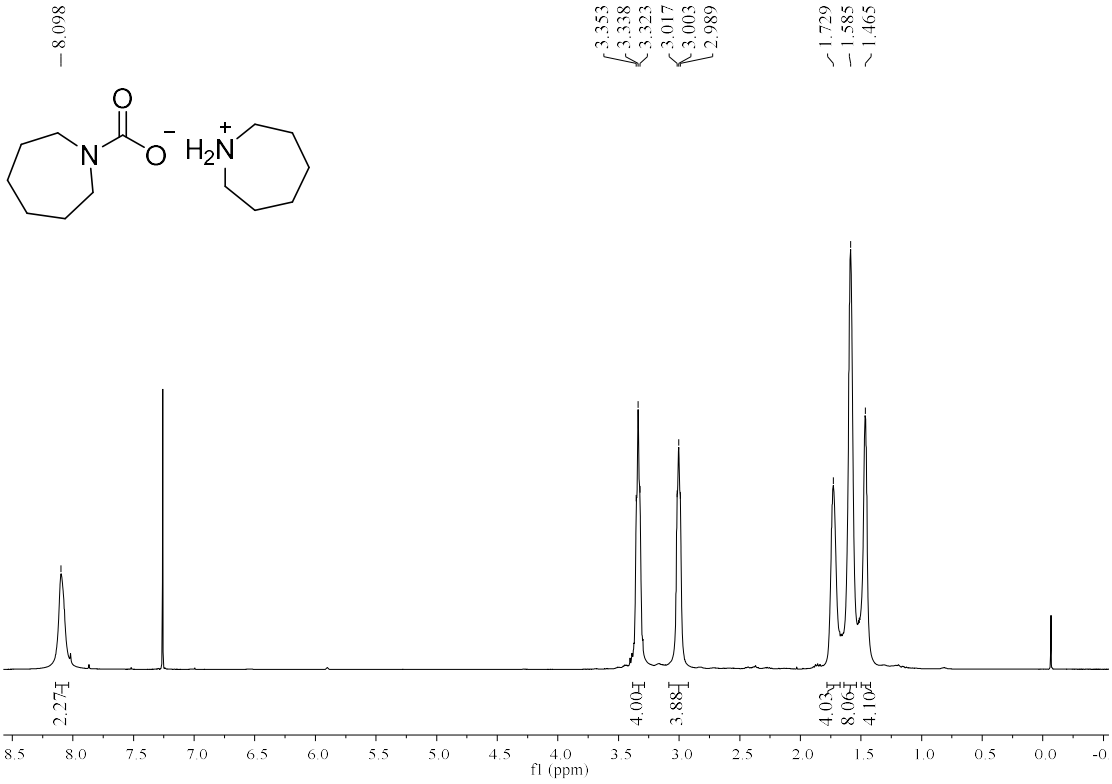


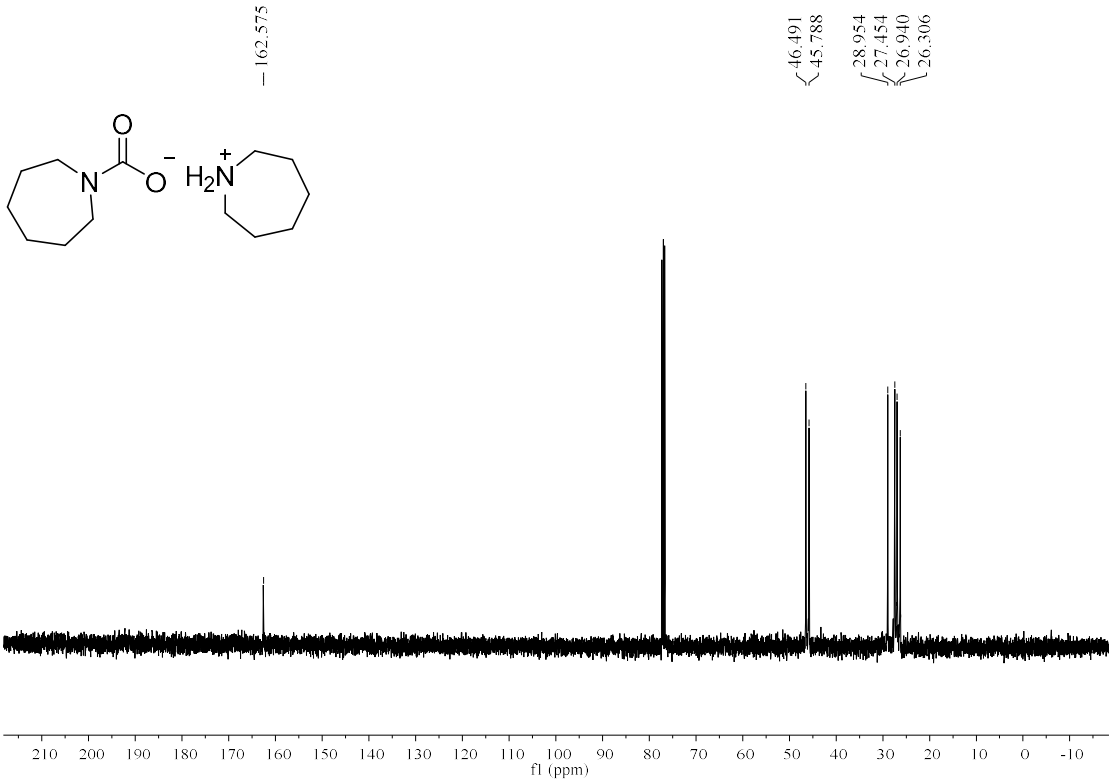
4-(2-Ethoxy-2-oxo-1-(4-(phenylethynyl)phenyl)ethoxy)butyl azepane-1-carboxylate (7)



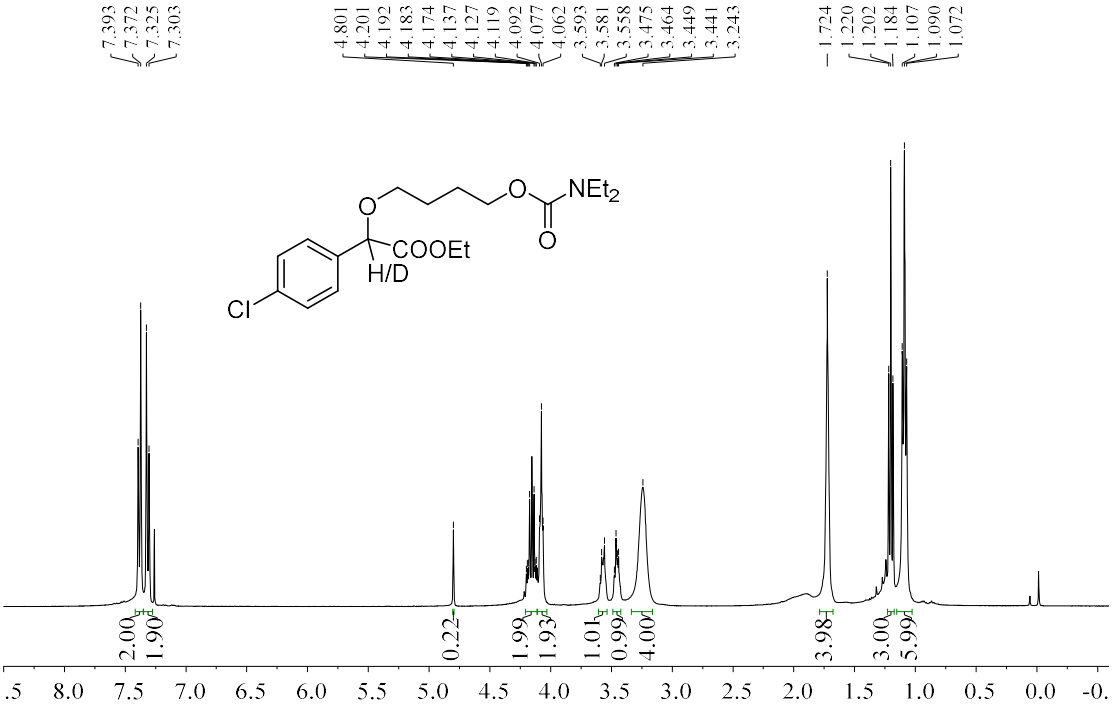


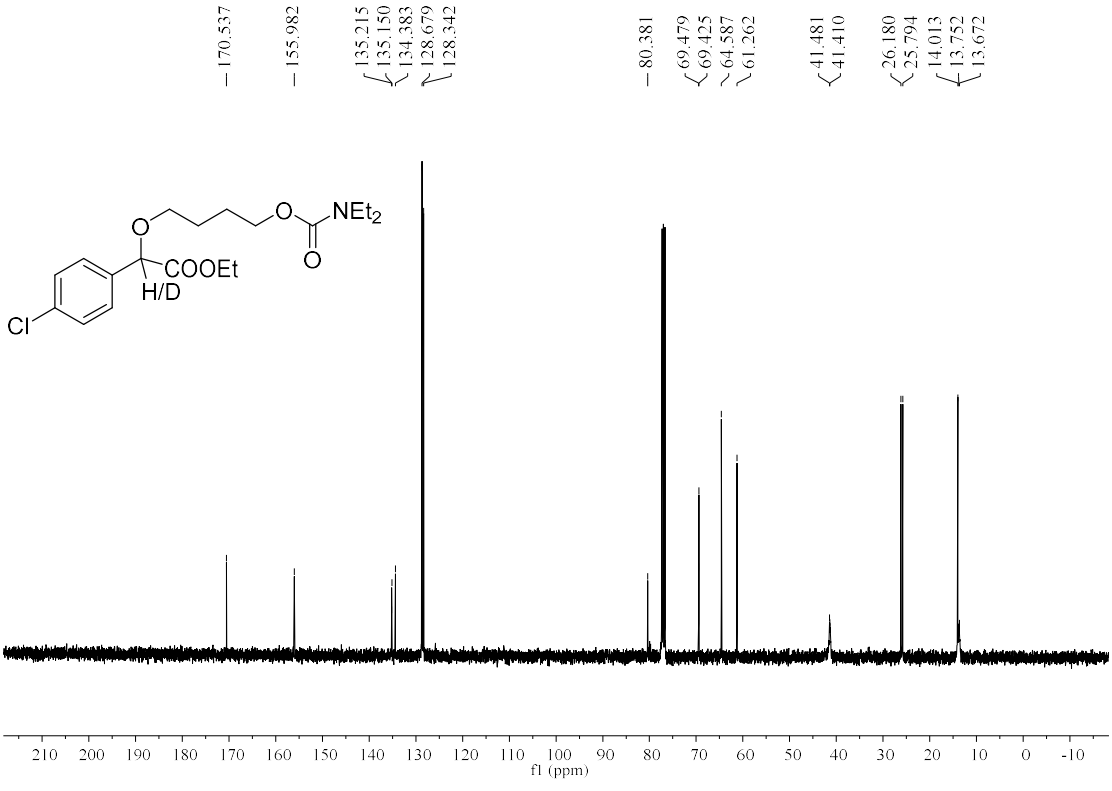
Azepan-1-ium azepane-1-carboxylate (8)





The mixture of 3aa and 3aa-D





The mixture of 4aa and 4aa-D