Supporting Information

Palladium-Catalyzed Four-Component Cascade Reaction for the Synthesis of Highly Functionalized Acyclic *O,O*-Acetals

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A. General methods

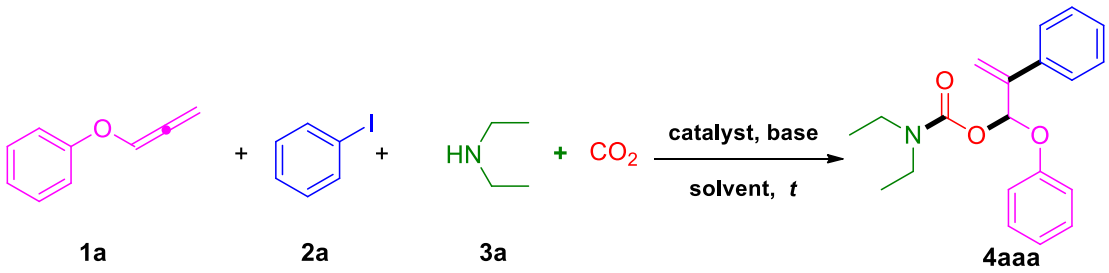
^{1}H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is used as a solvent with TMS as the internal standard. Mass spectra were recorded on a gas chromatograph-mass spectrometer with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with an infrared spectrometer. Substrates **1a-1k** were prepared according to the literature procedure. [1] Other reagents were commercially purchased and used without further purification.

B. General procedure for the preparation of acyclic *O,O*-acetals 4

To a dried 15 mL polytetrafluoroethylene (PTFE) reaction vessel, the mixture of $Pd(PPh_3)_4$ (0.004 mmol), TBD (0.6 mmol), allenes **1** (0.2 mmol), aryl iodide **2** (0.3 mmol) and amine **3** (0.4 mmol) in toluene (2 mL) was added successively. The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 10 h and the pressure was kept constant during the reaction. After the reaction was completed, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The reaction mixture was extracted with ethyl acetate (10 mL) and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on silica gel to give the desired product.

C. Optimization of reaction conditions

Table S1. Reaction Optimization[a]



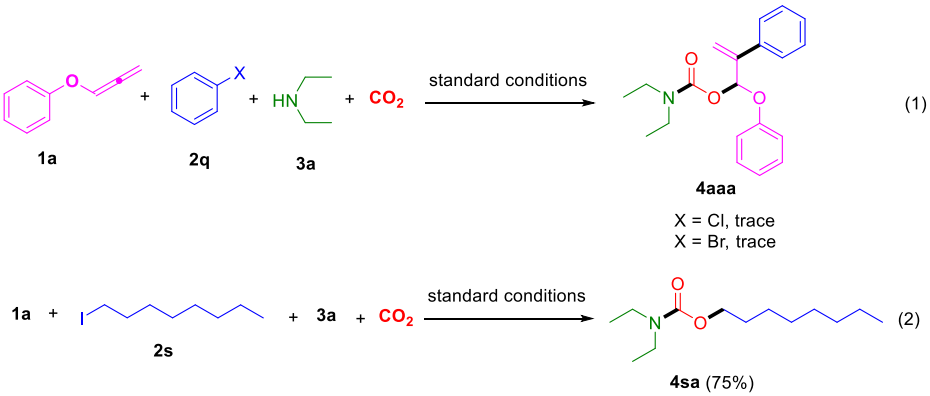
entry	catalyst	base	solvent	*t*(°C)	yield(%)[b]
1	$Pd_2(dba)_3$	TBD	toluene	60	72
2	$Pd(Allyl)_2Cl_2$	TBD	toluene	60	43
3	$Pd(COD)_2Cl_2$	TBD	toluene	60	41
4	$Pd(OAc)_2$	TBD	toluene	60	65
5	$Pd(PPh_3)_4$	TBD	toluene	60	86 (82)
6	$Pd(PPh_3)_4$	guanidine	toluene	60	28
7	$Pd(PPh_3)_4$	DBU	toluene	60	14
8	$Pd(PPh_3)_4$	DABCO	toluene	60	trace
9	$Pd(PPh_3)_4$	K_2CO_3	toluene	60	trace
10	$Pd(PPh_3)_4$	TBD	THF	60	54
11	$Pd(PPh_3)_4$	TBD	DMF	60	18
12	$Pd(PPh_3)_4$	TBD	DCM	60	20
13	$Pd(PPh_3)_4$	TBD	dioxane	60	64
14[c]	$Pd(PPh_3)_4$	TBD	toluene	60	22
15[d]	$Pd(PPh_3)_4$	TBD	toluene	60	73
16	$Pd(PPh_3)_4$	TBD	toluene	40	49
17	$Pd(PPh_3)_4$	TBD	toluene	80	76
18[e]	$Pd(PPh_3)_4$	TBD	toluene	60	61
19	$Pd(PPh_3)_4$	-	toluene	60	25
20	-	TBD	toluene	60	n.d[f]

Table S1. [a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), **3a** (0.4 mmol), solvent (2 mL), catalyst (0.004 mmol), base (0.6 mmol), CO_2 (0.7 MPa), 10 h. [b] GC yield with dodecane as the internal standard. The number in the parentheses is isolated yield. [c] **3a** (0.24 mmol). [d] **3a** (0.6 mmol). [e] CO_2 (1 atm). [f] n.d. = not detected. TBD = triazabicyclo[4.4.0]dec-5-ene.

D. Procedure for the synthesis 4aia in a larger scale

To a dried 15 mL polytetrafluoroethylene (PTFE) reaction vessel, the mixture of $Pd(PPh_3)_4$ (0.02 mmol), TBD (3.0 mmol), allenes **1a** (1.0 mmol), aryl iodide **2i** (1.5 mmol) and amine **3a** (2.0 mmol) in toluene (5 mL) was added successively. The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 10 h and the pressure was kept constant during the reaction. After the reaction was completed, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The reaction mixture was extracted with ethyl acetate (30 mL) and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on silica gel (20:1) to give **4aia** in 61% isolated yield.

E. Reaction of other halohydrocarbons



Scheme S1. Reaction of other halohydrocarbons

F. ^{13}C NMR investigation on the reaction of CO_2 and diethylamine

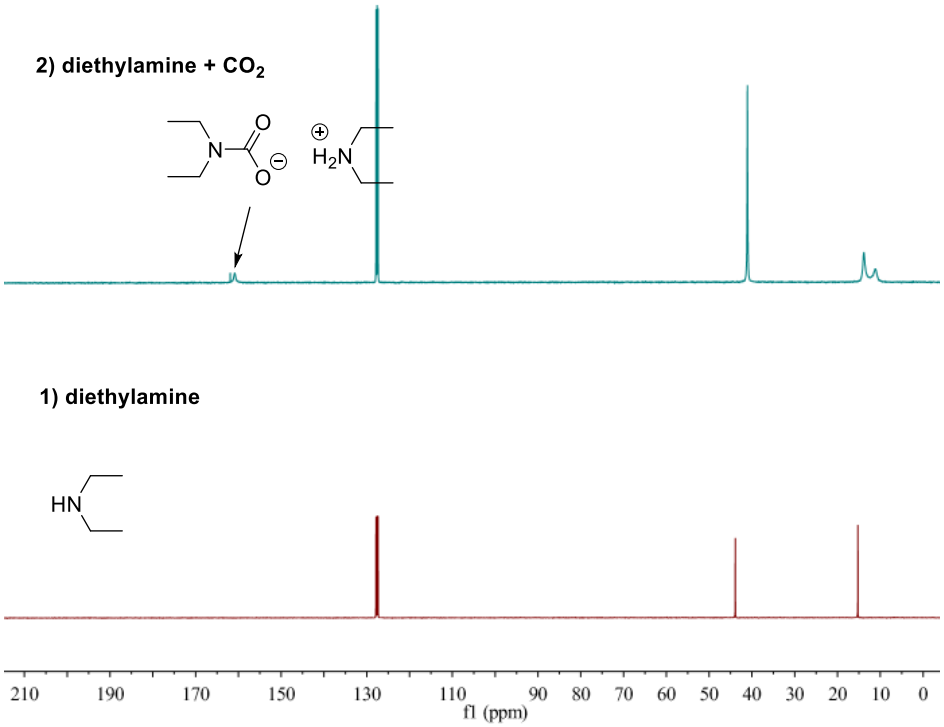
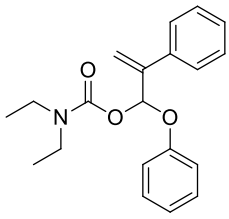


Figure S1. ^{13}C NMR spectra. 1) diethylamine (1 mmol) in 1.5 mL of C_6D_6. 2) reaction mixture of diethylamine and CO_2. Reaction conditions: CO_2 (0.1 MPa) was bubbled to the solution of diethylamine (1 mmol) in 1.5 mL of C_6D_6 at room temperature for 1 h.

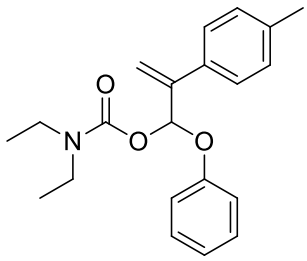
G. Analytical data

1-Phenoxy-2-phenylallyl diethylcarbamate (4aaa)



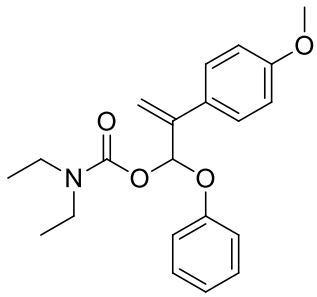
4aaa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 82% yield (53.1 mg, 0.16 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.52 (m, 2 H), 7.37 – 7.25 (m, 5 H), 7.15 (s, 1 H), 7.08 (d, J = 8.0 Hz, 2 H), 7.02 (t, J = 7.6 Hz, 1 H), 5.64 (d, J = 10.4 Hz, 2 H), 3.36 – 3.06 (m, 4 H), 1.09 (t, J = 6.8 Hz, 3 H), 0.92 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 154.0, 144.3, 137.2, 129.5, 128.2, 127.9, 127.1, 122.6, 117.2, 116.8, 96.5, 41.9, 41.4, 13.8, 13.3. IR (KBr): 2975, 2936, 2887, 1705, 1591, 1485, 1425, 1272, 1222, 1160, 1053, 980, 760, 694 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{23}NNaO_3^+$ $[M + Na]^+$: 348.1570; found 348.1572.

1-Phenoxy-2-(*p*-tolyl)allyl diethylcarbamate (4aba)



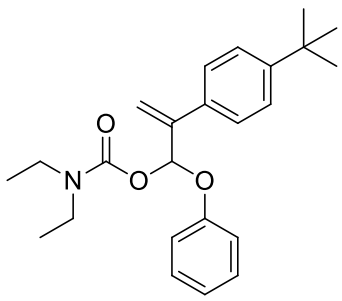
4aba was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 78% yield (52.9 mg, 0.16 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, J = 7.8 Hz, 2 H), 7.27 (t, J = 7.6 Hz, 2 H), 7.14 (d, J = 7.6 Hz, 3 H), 7.07 (d, J = 8.0 Hz, 2 H), 7.01 (t, J = 7.6 Hz, 1 H), 5.62 – 5.58 (m, 2 H), 3.55 – 2.95 (m, 4 H), 2.34 (s, 3 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.94 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.0, 144.0, 137.6, 134.2, 129.4, 128.9, 126.9, 122.6, 117.1, 116.0, 96.5, 41.9, 41.3, 21.1, 13.8, 13.3. IR (KBr): 3043, 2977, 2935, 2882, 1706, 1595, 1486, 1430, 1381, 1275, 1226, 1163, 1055, 981, 829, 761, 693, 508 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{25}NNaO_3^+$ $[M + Na]^+$: 362.1727; found 362.1723.

2-(4-Methoxyphenyl)-1-phenoxyallyl diethylcarbamate (4aca)



4aca was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a pale yellow oil in 69% yield (48.7 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.0 Hz, 2 H), 7.27 (t, J = 7.6 Hz, 2 H), 7.12 (s, 1 H), 7.07 (d, J = 8.0 Hz, 2 H), 7.02 (t, J = 7.6 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 2 H), 5.56 (s, 2 H), 3.80 (s, 3 H), 3.31 – 3.11 (m, 4 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.95 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.4, 156.2, 154.0, 143.5, 129.6, 129.5, 128.2, 122.6, 117.1, 115.3, 113.6, 96.7, 55.2, 41.9, 41.4, 13.8, 13.3. IR (KBr): 3051, 2975, 2840, 1712, 1602, 1508, 1378, 1226, 1165, 964, 922, 841, 755, 696, 515 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{25}NNaO_4^+$ $[M + Na]^+$: 378.1676; found 378.1679.

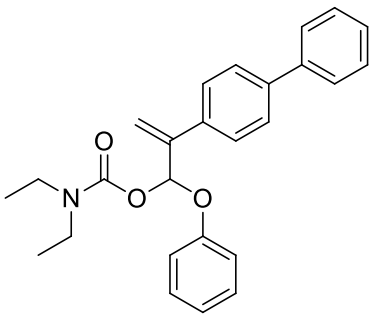
2-(4-(Tert-butyl)phenyl)-1-phenoxyallyl diethylcarbamate (4ada)



4ada was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 46% yield (35 mg, 0.09 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.0 Hz, 2 H), 7.36 (d, J = 7.6 Hz, 2 H), 7.28 (t, J = 7.6 Hz, 2 H), 7.14 (s, 1 H), 7.08 (d, J = 8.0 Hz, 2 H), 7.02 (t, J = 7.6 Hz, 1 H), 5.62 (s, 2 H), 3.31 – 3.15 (m, 4 H), 1.32 (s, 9 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.92 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.0, 150.9, 144.0, 134.2, 129.5, 126.7, 125.1, 122.6, 117.1, 116.0, 96.5, 41.9, 41.4, 34.5, 31.2,

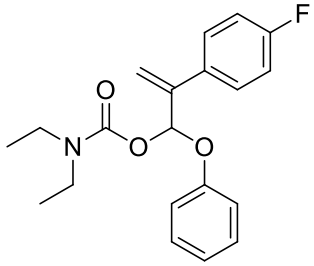
13.8, 13.3. IR (KBr): 2969, 1705, 1594, 1486, 1424, 1273, 1225, 1162, 1056, 982, 757 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{24}H_{31}NNaO_3^+$ $[M + Na]^+$: 404.2196; found 404.2202.

2-([1,1'-Biphenyl]-4-yl)-1-phenoxyallyl diethylcarbamate (4aea)



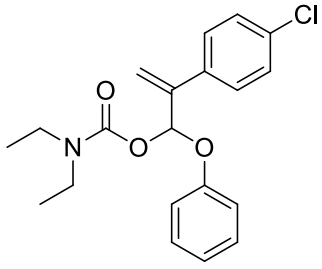
4aea was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 66% yield (53 mg, 0.13 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 7.6 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 4 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.35 – 7.26 (m, 3 H), 7.19 (s, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.02 (t, *J* = 7.2 Hz, 1 H), 5.68 (d, *J* = 4.8 Hz, 2 H), 3.31 – 3.13 (m, 4 H), 1.14 – 1.05 (m, 3 H), 0.98 – 0.90 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 154.0, 143.8, 140.6, 140.6, 136.0, 129.5, 128.7, 127.4, 127.3, 126.9, 126.9, 122.7, 117.1, 116.7, 96.5, 41.9, 41.4, 13.8, 13.3. IR (KBr): 3047, 2976, 1704, 1594, 1483, 1430, 1274, 1226, 1163, 1058, 986, 844, 759, 695 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{26}H_{27}NNaO_3^+$ $[M + Na]^+$: 424.1883; found 424.1886.

2-(4-Fluorophenyl)-1-phenoxyallyl diethylcarbamate (4afa)



4afa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 83% yield (56.7 mg, 0.16 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.49 (m, 2 H), 7.28 (t, *J* = 7.4 Hz, 2 H), 7.11 – 7.00 (m, 6 H), 5.60 (d, *J* = 22.4 Hz, 2 H), 3.30 – 3.11 (m, 4 H), 1.09 (t, *J* = 6.4 Hz, 3 H), 0.92 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8, 161.3, 156.1, 153.9, 143.4, 133.2, 129.5, 128.9, 128.9, 122.7, 117.1, 116.9, 115.2, 115.0, 96.6, 41.9, 41.3, 13.8, 13.3. IR (KBr): 3062, 2978, 2936, 2892, 1708, 1596, 1497, 1429, 1274, 1227, 1162, 1056, 979, 840, 761, 694, 510 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}FNNaO_3^+$ $[M + Na]^+$:366.1476; found 366.1478.

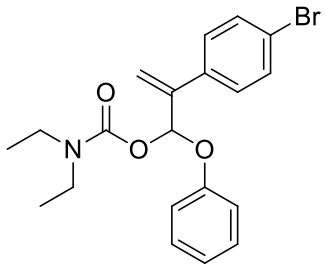
2-(4-Chlorophenyl)-1-phenoxyallyl diethylcarbamate (4aga)



4aga was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 79% yield (56.7 mg, 0.16 mmol). ^1H NMR (400 MHz, $CDCl_3$)

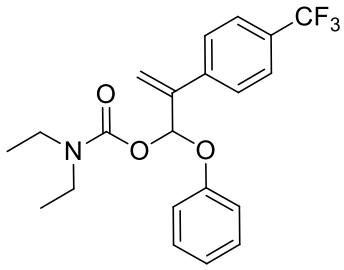
δ = 7.43 (d, J = 7.6 Hz, 2 H), 7.25 – 7.17 (m, 4 H), 7.02 (s, 1 H), 6.99 – 6.92 (m, 3 H), 5.54 (d, J = 18.2 Hz, 2 H), 3.22 – 3.03 (m, 4 H), 1.01 (t, J = 6.8 Hz, 3 H), 0.85 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 153.8, 143.3, 135.6, 133.8, 129.5, 128.5, 128.3, 122.8, 117.4, 117.1, 96.5, 41.9, 41.3, 13.8, 13.3. IR (KBr): 2975, 2946, 1706, 1593, 1487, 1427, 1274, 1223, 1162, 1087, 985, 835, 759 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}ClNO_3Na^+$ [M + Na]$^+$: 382.1180; found 382.1182.

2-(4-Bromophenyl)-1-phenoxyallyl diethylcarbamate (4aha)



4aha was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 54% yield (43.5 mg, 0.11 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 7.40 (m, 4 H), 7.28 (t, J = 7.6 Hz, 2 H), 7.10 (s, 1 H), 7.08 – 6.99 (m, 3 H), 5.63 (d, J = 16.8 Hz, 2 H), 3.33 – 3.10 (m, 4 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.93 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 153.8, 143.4, 136.0, 131.3, 129.5, 128.8, 122.8, 122.1, 117.5, 117.1, 96.4, 42.0, 41.4, 13.8, 13.3. IR (KBr): 3063, 2977, 2936, 2883, 1707, 1593, 1483, 1429, 1380, 1275, 1224, 1163, 1065, 985, 835, 761 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}BrNNaO_3^+$ [M + Na]$^+$: 426.0675; found 426.0678.

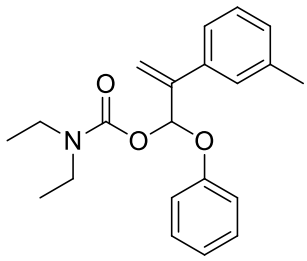
1-Phenoxy-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4aia)



4aia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 84% yield (66.0 mg, 0.17 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.0 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.15 (s, 1 H), 7.09 – 7.01 (m, 3 H), 5.71 (d, J = 23.4 Hz, 2 H), 3.32 – 3.09 (m, 4 H), 1.09 (t, J = 6.6 Hz, 3 H), 0.92 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 153.8, 143.5, 140.8, 129.9(J = 32.4 Hz), 129.6, 127.6, 125.1(J = 3.7 Hz), 124.1 (J = 270.4 Hz), 122.9, 118.7, 117.1, 96.4, 42.0, 41.4, 13.8, 13.2. IR (KBr): 3063, 2979, 1708, 1597, 1483, 1425, 1326, 1276, 1224, 1159, 1066, 984, 847, 761, 693, 612 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{22}F_3NNaO_3^+$ [M + Na]$^+$: 416.1444; found 416.1449.

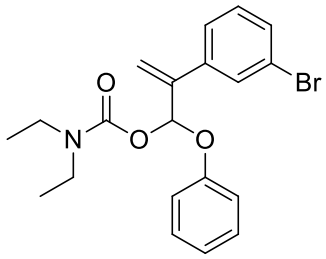
1-Phenoxy-2-(*m*-tolyl)allyl diethylcarbamate (4aja)

4aja was obtained after purification by column chromatography on silica gel (petroleum ether /



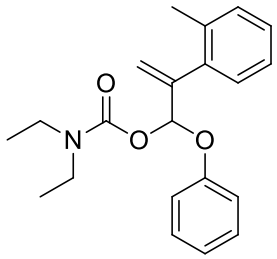
ethyl acetate = 20:1) as a colorless oil in 52% yield (35.0 mg, 0.10 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, J = 9.2 Hz, 2 H), 7.31 – 7.21 (m, 3 H), 7.14 – 7.05 (m, 4 H), 7.02 (t, J = 7.2 Hz, 1 H), 5.62 (d, J = 9.6 Hz, 2 H), 3.32 – 3.12 (m, 4 H), 2.35 (s, 3 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.94 (t, J = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.0, 144.4, 137.7, 137.2, 129.4, 128.6, 128.1, 127.8, 124.2, 122.6, 117.2, 116.6, 96.5, 41.9, 41.4, 21.4, 13.8, 13.3. IR (KBr): 3046, 2972, 1706, 1594, 1480, 1230, 1163, 985, 766, 694 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{25}NNaO_3^+$ [M + Na]$^+$: 362.1727; found 362.1732.

2-(3-Bromophenyl)-1-phenoxyallyl diethylcarbamate (4aka)



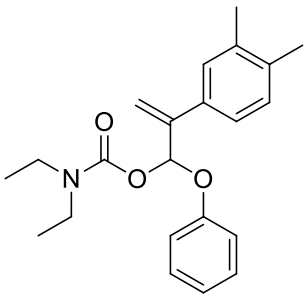
4aka was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 42% yield (33.8 mg, 0.08 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (s, 1 H), 7.49 (d, J = 7.8 Hz, 1 H), 7.44 (d, J = 8.0 Hz, 1 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.21 (t, J = 7.6 Hz, 1 H), 7.09 – 7.01 (m, 4 H), 5.64 (d, J = 17.6 Hz, 2 H), 3.31 – 3.12 (m, 4 H), 1.10 (t, J = 6.6 Hz, 3 H), 0.95 (t, J = 6.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 153.8, 143.2, 139.2, 130.9, 130.4, 129.7, 129.5, 125.8, 122.8, 122.3, 118.2, 117.2, 96.6, 42.0, 41.4, 13.8, 13.3. IR (KBr): 2976, 2934, 2882, 1707, 1592, 1483, 1427, 1274, 1224, 1162, 1058, 985, 762, 690 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}BrNNaO_3^+$ [M + Na]$^+$: 426.0675; found 426.0673.

1-phenoxy-2-(o-tolyl)allyl diethylcarbamate (4ala)



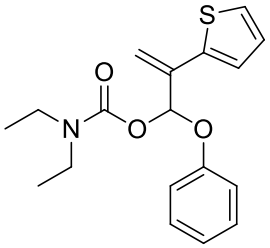
4ala was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a colorless oil in 12% yield (8.4 mg, 0.02 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 – 7.15 (m, 4 H), 7.13 – 7.10 (m, 2 H), 6.93 (d, J = 8.6 Hz, 3 H), 6.89 (s, 1 H), 5.74 (s, 1 H), 5.20 (s, 1 H), 3.20 – 3.08 (m, 4 H), 2.28 (s, 3 H), 1.02 – 0.97 (m, 3 H), 0.88 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.6, 153.9, 144.6, 137.8, 136.2, 123.0, 129.4, 127.5, 125.2, 122.5, 118.4, 116.8, 96.6, 41.8, 41.2, 20.0, 13.9, 13.2. IR (KBr): 3071, 2974, 2931, 1707, 1595, 1488, 1426, 1380, 1275, 1226, 1162, 1053, 986, 760, 692 cm^{-1}. HRMS-ESI (m/z): calcd for $C_{21}H_{25}NNaO_3^+$ [M + Na]$^+$: 362.1727; found 362.1724.

2-(3,4-Dimethylphenyl)-1-phenoxyallyl diethylcarbamate (4ama)



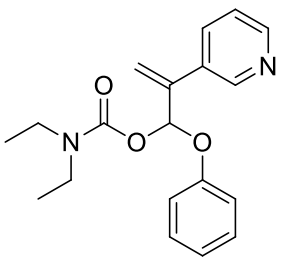
4ama was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 61% yield (43.1 mg, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (s, 1 H), 7.30 – 7.27 (m, 2 H), 7.26 – 7.23 (m, 1 H), 7.12 – 7.05 (m, 4 H), 7.01 (t, *J* = 7.2 Hz, 1 H), 5.58 (s, 2 H), 3.32 – 3.17 (m, 4 H), 2.28 – 2.24 (m, 6 H), 1.10 (t, *J* = 6.4 Hz, 3 H), 0.97 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.0, 144.2, 136.4, 136.2, 134.8, 129.5, 129.4, 128.3, 124.5, 122.6, 117.3, 115.8, 96.6, 41.9, 41.4, 19.8, 19.4, 13.9, 13.3. IR (KBr): 2974, 2930, 1706, 1595, 1485, 1427, 1274, 1225, 1162, 1055, 982, 758 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{27}NNaO_3^+$ $[M + Na]^+$: 376.1883; found 376.1886.

1-Phenoxy-2-(thiophen-2-yl)allyl diethylcarbamate (4ana)



4ana was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) as a pale yellow oil in 68% yield (45.0 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (t, *J* = 7.4 Hz, 3 H), 7.25 – 7.21 (m, 1 H), 7.12 – 7.06 (m, 3 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 7.01 – 6.98 (m, 1 H), 5.61 (d, *J* = 57.1 Hz, 2 H), 3.33 – 3.19 (m, 4 H), 1.11 (t, *J* = 6.8 Hz, 3 H), 0.99 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 153.9, 139.6, 137.9, 129.5, 127.3, 125.5, 125.0, 122.8, 117.2, 115.0, 96.1, 42.0, 41.4, 13.9, 13.3. IR (KBr): 3074, 2976, 2941, 2887, 1706, 1596, 1483, 1429, 1274, 1225, 1162, 983, 842, 761, 702 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{18}H_{21}NNaO_3S^+$ $[M + Na]^+$: 354.1134; found 354.1136.

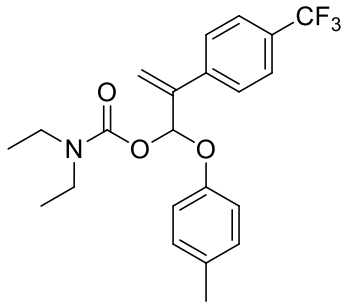
1-Phenoxy-2-(pyridin-3-yl)allyl diethylcarbamate (4aoa)



4aoa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 3:1) as a pale yellow oil in 69% yield (45.0 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83 (s, 1 H), 8.56 (d, *J* = 4.4 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H), 7.32 – 7.26 (m, *J* = 7.2 Hz, 3 H), 7.13 (s, 1 H), 7.09 – 7.01 (m, 3 H), 5.70 (d, *J* = 23.0 Hz, 2 H), 3.33 – 3.08 (m, 4 H), 1.10 (t, *J* = 6.8 Hz, 3 H), 0.92 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 153.7, 149.0, 148.5, 141.6, 134.5, 132.8, 129.5, 122.9, 122.8, 118.7, 117.0, 96.5, 41.9, 41.3, 13.8, 13.2. IR (KBr): 3042, 2977, 1708, 1590, 1482, 1424, 1274,

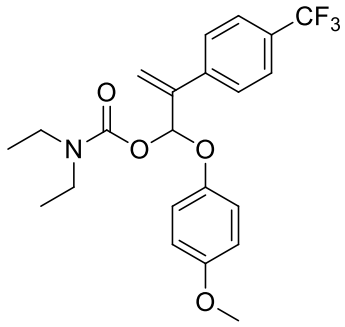
1223, 1162, 981, 817, 762, 701, 624, 507 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{19}H_{22}N_2NaO_3^+$ [M + Na]$^+$: 349.1523; found 349.1525.

1-(*p*-Tolyloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4bia)



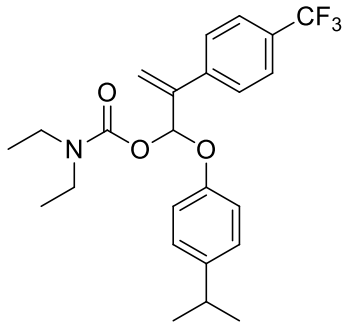
4bia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 70% yield (57.0 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.0 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.13 – 7.04 (m, 3 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 5.70 (d, *J* = 21.6 Hz, 2 H), 3.34 – 3.08 (m, 4 H), 2.29 (s, 3 H), 1.10 (t, *J* = 6.4 Hz, 3 H), 0.94 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 153.9, 143.6, 140.9, 132.4, 130.0, 129.9(*J* = 32.2 Hz), 127.6, 125.1(*J* = 3.8 Hz), 124.2(*J* = 270.2 Hz), 118.6, 117.2, 96.8, 42.0, 41.4, 20.6, 13.8, 13.3. IR (KBr): 2976, 2931, 2876, 1707, 1510, 1474, 1427, 1326, 1274, 1224, 1165, 1125, 1069, 991, 850, 819, 761 $cm^{-1.}$ HRMS-ESI (*m/z*): calcd for $C_{22}H_{24}F_3NNaO_3^+$ [M + Na]$^+$: 430.1600; found 430.1602.

1-(4-Methoxyphenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4cia)



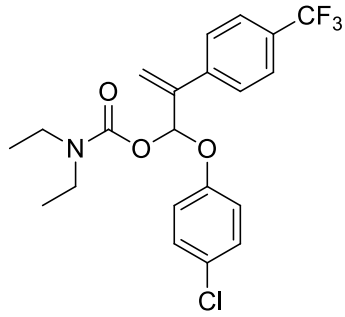
4cia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a yellow oil in 75% yield (63.4 mg, 0.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.1 Hz, 2 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 7.00 (d, *J* = 7.6 Hz, 3 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 5.69 (d, *J* = 17.4 Hz, 2 H), 3.76 (s, 3 H), 3.31 – 3.09 (m, 4 H), 1.09 (t, *J* = 6.5 Hz, 3 H), 0.94 (t, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.5, 153.9, 149.9, 143.6, 140.9, 129.9(*J* = 32.3 Hz), 127.5, 125.1(*J* = 3.8 Hz), 124.1(*J* = 270.3 Hz), 118.9, 118.6, 114.6, 97.55, 55.5, 42.0, 41.4, 13.8, 13.2. IR (KBr): 2978, 2937, 1707, 1508, 1474, 1428, 1326, 1274, 1218, 1165, 1124, 1069, 1042, 992, 832, 759 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{24}F_3NNaO_4^+$ [M + Na]$^+$: 446.1550; found 446.1552.

1-(4-Isopropylphenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4dia)



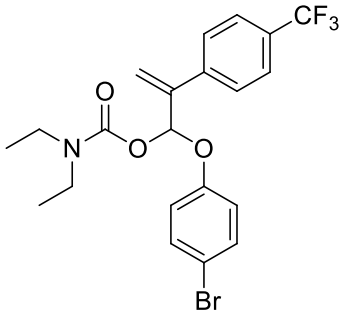
4dia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 72% yield (63.0 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 7.6 Hz, 2 H), 7.10 (s, 1 H), 6.99 (d, J = 7.6 Hz, 2 H), 5.70 (d, J = 24.0 Hz, 2 H), 3.31 – 3.09 (m, 4 H), 2.91 – 2.81 (m, 1 H), 1.21 (d, J = 6.8 Hz, 6 H), 1.09 (t, J = 6.4 Hz, 3 H), 0.92 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.1, 153.9, 143.6, 143.4, 140.9, 129.9(J = 32.3 Hz), 127.6, 127.4, 125.1(J = 3.8 Hz), 124.2(J = 270.3 Hz), 118.6, 117.0, 96.7, 42.0, 41.4, 33.3, 24.1, 24.1, 13.8, 13.3. IR (KBr): 2965, 2933, 2875, 1707, 1510, 1475, 1426, 1326, 1274, 1226, 1165, 1125, 1069, 991, 847, 754 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{24}H_{28}F_3NNaO_3^+$ [M + Na]$^+$: 458.1913; found 458.1916.

1-(4-Chlorophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4eia)



4eia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 60% yield (51.1 mg, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, J = 8.0 Hz, 2 H), 7.61 (d, J = 8.4 Hz, 2 H), 7.24 (d, J = 9.2 Hz, 2 H), 7.09 (s, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 5.70 (d, J = 15.2 Hz, 2 H), 3.32 – 3.10 (m, 4 H), 1.10 (t, J = 6.8 Hz, 3 H), 0.93 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.6, 153.7, 143.2, 140.6, 130.0(J = 32.3 Hz), 129.5, 128.0, 127.5, 125.2(J = 3.7 Hz), 124.1(J = 270.5 Hz), 119.0, 118.6, 96.5, 42.1, 41.4, 13.8, 13.2. IR (KBr): 2978, 2934, 1708, 1489, 1428, 1326, 1274, 1326, 1274, 1228, 1165, 1125, 1069, 991, 930, 829 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{21}ClF_3NNaO_3^+$ [M + Na]$^+$: 450.1054; found 450.1056.

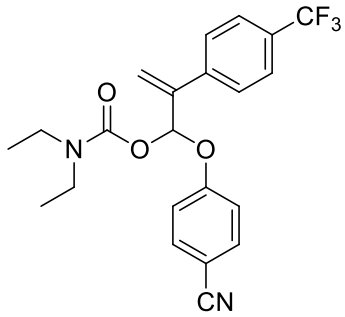
1-(4-Bromophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4fia)



4fia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 72% yield (67.8 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2

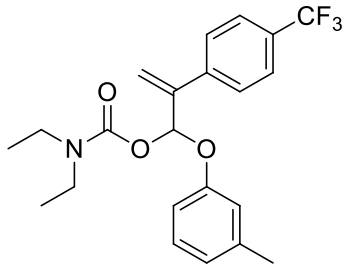
H), 7.44 – 7.39 (m, 2 H), 7.12 (s, 1 H), 7.01 – 6.96 (m, 2 H), 5.73 (d, *J* = 13.6 Hz, 2 H), 3.36 – 3.27 (m, 2 H), 3.24 – 3.09 (m, 2 H), 1.13 (t, *J* = 7.2 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 153.7, 143.1, 140.5, 132.5, 130.0(*J* = 32.4 Hz), 127.5, 125.2(*J* = 3.7 Hz), 124.1(*J* = 270.3 Hz), 119.0, 115.5, 96.4, 42.1, 41.4, 13.8, 13.2. IR (KBr): 2978, 2934, 1708, 1486, 1428, 1326, 1275, 1228, 1165, 1126, 1069, 994, 850 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{21}BrF_3NNaO_3^+$ $[M + Na]^+$: 494.0549; found 494.0550.

1-(4-Cyanophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4gia)



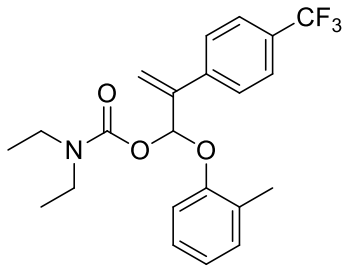
4gia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 51% yield (42.6 mg, 0.10 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.60 (m, 6 H), 7.23 (s, 1 H), 7.19 – 7.15 (m, 2 H), 5.76 (d, *J* = 12.3 Hz, 2 H), 3.32 (q, *J* = 7.1 Hz, 2 H), 3.24 – 3.12 (m, 2 H), 1.14 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.2, 153.5, 142.7, 140.2, 134.1, 130.1(*J* = 32.4 Hz), 127.5, 125.3(*J* = 3.7 Hz),124.0 (*J* = 270.2 Hz), 119.4, 118.7, 117.4, 106.2, 95.6, 95.5, 42.2, 41.5, 13.8, 13.3. IR (KBr): 2978, 2934, 2228, 1709, 1605, 1506, 1427, 1240, 1164, 1124, 1068, 989, 843, 758 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{21}F_3N_2NaO_3^+$ $[M + Na]^+$: 441.1396; found 441.1440.

1-(*m*-Tolyloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4hia)



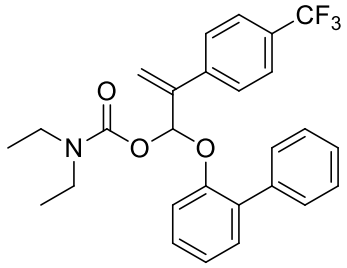
4hia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 68% yield (55.4 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.21 – 7.15 (m, 1 H), 7.12 (s, 1 H), 6.89 – 6.84 (m, 3 H), 5.70 (d, *J* = 21.2 Hz, 2 H), 3.33 – 3.10 (m, 4 H), 2.31 (s, 3 H), 1.10 (t, *J* = 6.8 Hz, 3 H), 0.92 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 153.8, 143.5, 140.8, 139.7, 129.9(*J* = 32.4 Hz), 129.3, 127.6, 125.1(*J* = 3.8 Hz), 124.2(*J* = 270.3 Hz), 123.7, 118.7, 117.9, 113.8, 96.4, 42.0, 41.4, 21.4, 13.8, 13.3. IR (KBr): 2973, 2929, 2874, 1706, 1611, 1588, 1481, 1459, 1426, 1325, 1275, 1252, 1168, 1124, 1068, 1011, 984, 849, 776 cm^{-1}. HRMS-ESI (*m/z*): calcd for$C_{22}H_{24}F_3NO_3Na^+$ $[M + Na]^+$: 430.1600; found 430.1604.

1-(*o*-Tolyloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4iia)



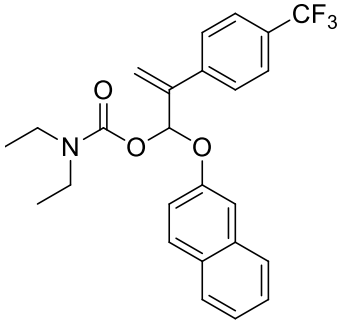
4iia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 63% yield (51.2 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.0 Hz, 2 H), 7.15 – 7.07 (m, 4 H), 6.96 – 6.91 (m, 1 H), 5.71 (d, J = 30.0 Hz, 2 H), 3.30 – 3.09 (m, 4 H), 2.16 (s, 3 H), 1.08 (t, J = 6.5 Hz, 3 H), 0.92 (t, J = 6.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.4, 153.9, 143.8, 140.9, 131.0, 129.9(J = 32.3 Hz), 128.1, 127.6, 126.9, 125.0(J = 3.8 Hz), 124.1(J = 270.1 Hz), 122.7, 118.7, 115.1, 97.0, 42.0, 41.4, 16.3, 13.7, 13.2. IR (KBr): 2978, 2935, 1707, 1590, 1494, 1476, 1427, 1327, 1274, 1233, 1165, 1125, 1069, 988, 850, 755 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{24}F_3NNaO_3^+$ [M + Na]$^+$: 430.1600; found 430.1604.

1-([1,1'-Biphenyl]-2-yloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4jia)



4jia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 58% yield (54.4 mg, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 4 H), 7.38 – 7.34 (m, 2 H), 7.33 – 7.29 (m, 2 H), 7.27 – 7.23 (m, 4 H), 7.14 – 7.09 (m, 1 H), 7.05 (s, 1 H), 5.54 (d, J = 6.8 Hz, 2 H), 3.27 – 3.16 (m, 2 H), 3.10 – 2.95 (m, 2 H), 1.05 (t, J = 6.8 Hz, 3 H), 0.83 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.8, 153.0, 143.6, 140.7, 138.1, 132.9, 131.0, 129.6, 129.6(J = 32.6 Hz), 128.6, 127.8, 127.7, 126.9, 124.9(J = 3.8 Hz), 124.5(J = 270.3 Hz), 123.3, 118.9, 116.8, 97.4, 41.9, 41.3, 13.7, 13.2. IR (KBr): 2977, 2933, 2878, 1706, 1479, 1429, 1326, 1273, 1219, 1164, 1124, 1068, 985, 849, 757, 699 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{27}H_{26}F_3NO_3Na^+$ [M + Na]$^+$: 492.1757; found 492.1758.

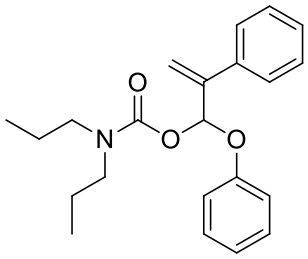
1-(Naphthalen-2-yloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4kia)



4kia was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 63% yield (55.8 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.70 (m, 5 H), 7.61 (d, J = 8.0 Hz, 2 H),

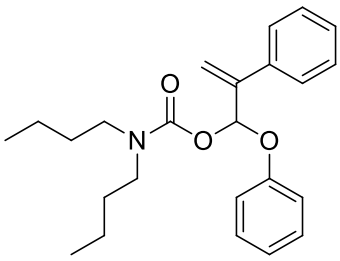
7.46 – 7.41 (m, 2 H), 7.39 – 7.34 (m, 1 H), 7.30 (s, 1 H), 7.26 – 7.22 (m, 1 H), 5.75 (d, *J* = 29.6 Hz, 2 H), 3.33 – 3.10 (m, 4 H), 1.10 (t, *J* = 6.8 Hz, 3 H), 0.91 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 153.7, 143.4, 140.7, 134.3, 130.0, 129.8(*J* = 32.3 Hz), 129.6, 127.6, 127.2, 126.4, 125.1(*J* = 3.8 Hz), 124.5, 124.1(*J* = 270.2 Hz), 119.1, 118.9, 111.4, 96.4, 42.1, 41.5, 13.8, 13.3. IR (KBr): 3060, 2977, 2933, 1707, 1629, 1600, 1471, 1428, 1326, 1275, 1217, 1165, 1124, 1069, 991, 849, 751 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{25}H_{24}F_3NNaO_3^+$ [M + Na]$^+$: 466.1600; found 466.1605.

1-Phenoxy-2-phenylallyl dipropylcarbamate (4aab)



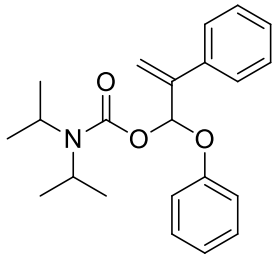
4aab was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 65% yield (45.9 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.6 Hz, 2 H), 7.36 – 7.26 (m, 5 H), 7.14 (s, 1 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 7.02 (t, *J* = 6.8 Hz, 1 H), 5.62 (d, *J* = 5.2 Hz, 2 H), 3.21 – 2.99 (m, 4 H), 1.55 – 1.48 (m, 2 H), 1.40 – 1.27 (m, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H), 0.69 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.4, 144.4, 137.2, 129.5, 128.2, 127.9, 127.1, 122.7, 117.2, 116.9, 96.7, 49.2, 48.7, 21.7, 21.1, 11.0. IR (KBr):2965, 2932, 2874, 1706, 1594, 1491, 1466, 1423, 1223, 1160, 1064, 1024, 963, 757, 694 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{27}NNaO_3^+$ [M + Na]$^+$: 376.1883; found 376.1885.

1-Phenoxy-2-phenylallyl dibutylcarbamate (4aac)



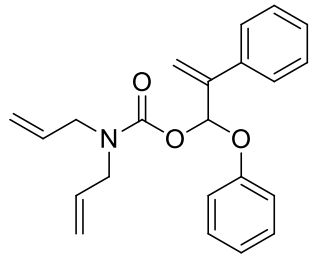
4aac was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 69% yield (52.6 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.2 Hz, 2 H), 7.36 – 7.25 (m, 5 H), 7.15 (s, 1 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 7.02 (t, *J* = 7.6 Hz, 1 H), 5.63 (d, *J* = 5.6 Hz, 2 H), 3.24 – 2.99 (m, 4 H), 1.51 – 1.43 (m, 2 H), 1.30 – 1.22 (m, 4 H), 1.13 – 1.04 (m, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.76 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 154.4, 144.3, 137.2, 129.5, 128.2, 127.9, 127.1, 122.6, 117.2, 116.9, 96.6, 47.3, 46.8, 30.6, 30.0, 19.9, 13.8. IR (KBr): 3057, 2953, 2870, 1707, 1594, 1481, 1429, 1377, 1294, 1225, 1159, 991, 762, 698 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{24}H_{31}NNaO_3^+$ [M + Na]$^+$: 404.2196; found 404.2198.

1-Phenoxy-2-phenylallyl diisopropylcarbamate (4aad)



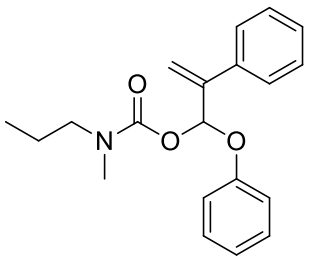
4aad was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow oil in 70% yield (49.4 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.3 Hz, 2 H), 7.36 – 7.25 (m, 5 H), 7.20 (s, 1 H), 7.08 (d, *J* = 7.9 Hz, 2 H), 7.02 (t, *J* = 7.3 Hz, 1 H), 5.65 (d, *J* = 18.3 Hz, 2 H), 4.07 – 3.62 (m , 2 H), 1.22– 0.96 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 153.6, 144.5, 137.5, 129.5, 128.2, 127.9, 127.2, 122.6, 117.4, 116.8, 96.1, 46.5, 45.8, 21.1, 20.4. IR (KBr): 3078, 2983, 1706, 1601, 1493, 1450, 1379, 1307, 1229, 1142, 1027, 767, 703 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{27}NNaO_3^+$ $[M + Na]^+$: 376.1883; found 376.1888.

1-Phenoxy-2-phenylallyl diallylcarbamate (4aae)



4aae was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 66% yield (46.0 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 7.2 Hz, 2 H), 7.36 – 7.26 (m, 5 H), 7.15 (s, 1 H), 7.08 – 7.01 (m, 3 H), 5.79 – 5.67 (m, 1 H), 5.64 (d, *J* = 13.5 Hz, 2 H), 5.60 – 5.48 (m, 1 H), 5.14 – 4.95 (m, 4 H), 3.92 – 3.67 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 154.3, 144.2, 137.2, 133.0, 129.5, 128.3, 128.0, 127.1, 122.8, 117.2, 117.0, 96.8, 49.0, 48.5. IR (KBr): 3071, 2926, 2851, 1705, 1594, 1491, 1459, 1415, 1224, 1074, 992, 923, 756, 695. HRMS-ESI (*m/z*): calcd for $C_{22}H_{23}NNaO_3^+$ $[M + Na]^+$: 372.1570; found 372.1573.

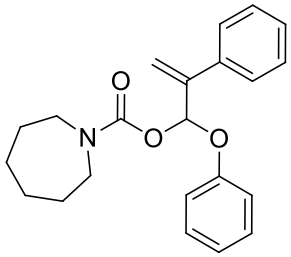
1-Phenoxy-2-phenylallyl methyl(propyl)carbamate (4aaf)



4aaf was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 55% yield (35.6 mg, 0.11 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.1 Hz, 2 H), 7.36 – 7.26 (m, 5 H), 7.13 (s, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 7.02 (t, *J* = 7.1 Hz, 1 H), 5.64 (d, *J* = 11.7 Hz, 2 H), 3.26 – 3.04 (m, 2 H), 2.90 – 2.78 (m, 3 H), 1.54 – 1.30 (m, 2 H), 0.87 – 0.67 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 154.5, 144.3, 129.5, 128.2, 127.9, 127.1, 122.7, 117.2, 117.1, 96.8, 96.6, 50.4, 34.6, 33.8, 20.9, 20.5, 10.8. IR (KBr):3061, 2964, 2931, 2873, 1715, 1594, 1490,

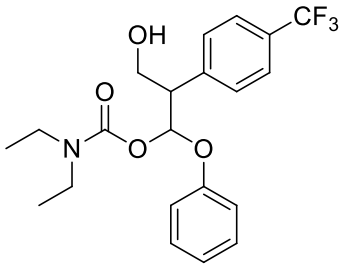
1402, 1300, 1225, 1165, 1021, 960, 831, 758, 694, 588, 508 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{20}H_{23}NNaO_3^+$ $[M + Na]^+$: 348.1570; found 348.1572.

1-Phenoxy-2-phenylallyl azepane-1-carboxylate (4aag)



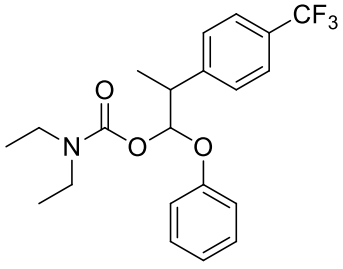
4aag was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 56% yield (39.3 mg, 0.11 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 7.2 Hz, 2 H), 7.29 – 7.19 (m, 5 H), 7.10 (s, 1 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 6.95 (t, *J* = 7.2 Hz, 1 H), 5.57 (d, *J* = 15.2 Hz, 2 H), 3.36 – 3.19 (m, 4 H), 1.62 – 1.56 (m, 2 H), 1.43 – 1.29 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 154.3, 144.4, 137.3, 129.5, 128.2, 127.9, 127.1, 122.6, 117.1, 116.8, 96.3, 47.2, 46.7, 28.2, 28.0, 27.1, 26.6. IR (KBr): 3058, 2929, 2861, 1706, 1593, 1485, 1428, 1264, 1222, 1059, 980, 762, 699, 506 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{25}NNaO_3^+$ $[M + Na]^+$: 374.1727; found 374.1729.

3-Hydroxy-1-phenoxy-2-(4-(trifluoromethyl)phenyl)propyl diethylcarbamate (5)



5 was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1) as a pale yellow oil in 56% yield (45.9 mg, 0.11 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ =7.60 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.28 – 7.24 (m, 2 H), 7.02 (t, *J* = 7.2 Hz, 1 H), 6.96 (d, *J* = 7.6 Hz, 2 H), 6.82 (d, *J* = 4.4 Hz, 1 H), 4.14 – 4.05 (m, 1 H), 3.99 (s, 1 H), 3.59 – 3.47 (m, 1 H), 3.27 – 3.08 (m, 4 H), 1.05 (t, *J* = 7.2 Hz, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.9, 154.5, 141.0, 129.7, 129.6, 125.3, 125.2, 122.9, 116.6, 96.3, 62.6, 52.6, 42.0, 41.4, 13.8, 13.1. IR (KBr): 3448, 2975, 1696, 1595, 1490, 1429, 1326, 1277, 1225, 1165, 1066, 977, 840, 758, 693, 609 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}F_3NO_4Na^+$ $[M + Na]^+$: 434.1550; found 434.1556.

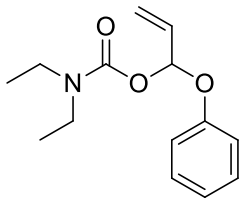
1-Phenoxy-2-(4-(trifluoromethyl)phenyl)propyl diethylcarbamate (6)



6 was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 61% yield (48.0 mg, 0.12 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H),

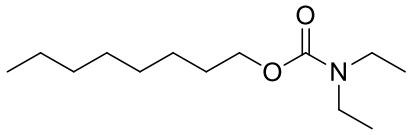
7.27 – 7.21 (m, 2 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 6.52 (d, *J* = 5.2 Hz, 1 H), 3.46 – 3.36 (m, 1 H), 3.32 – 3.21 (m, 2 H), 3.18 – 3.08 (m, 2 H), 1.45 (d, *J* = 6.8 Hz, 3 H), 1.09 (t, *J* = 6.8 Hz, 3 H), 0.94 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.5, 154.2, 145.3, 129.5, 128.9, 125.6, 125.1, 125.0, 122.9, 122.6, 116.8, 98.5, 44.3, 41.9, 41.3, 16.1, 13.9, 13.3. IR (KBr): 2978, 2931, 1704, 1595, 1491, 1427, 1382, 1326, 1276, 1227, 1165, 1124, 1068, 981, 840, 758, 693, 610 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}F_3NO_3Na^+$ [M + Na]$^+$: 418.1600; found 418.1608.

1-Phenoxyallyl diethylcarbamate (7)



7 was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow in 9% yield (4.5 mg, 0.02 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (t, *J* = 7.6 Hz, 2 H), 7.12 – 6.97 (m, 3 H), 6.80 (d, *J* = 4.9 Hz, 1 H), 6.39 – 5.87 (m, 1 H), 5.59 (d, *J* = 17.2 Hz, 1 H), 5.39 (d, *J* = 10.6 Hz, 1 H), 4.08 – 2.66 (m, 4 H), 1.12 (t, *J* = 6.0 Hz, 3 H), 1.04 (t, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 153.9, 133.0, 132.3, 119.4, 118.9, 115.0, 95.3, 41.9, 41.3, 14.0, 13.3. IR (KBr): 2976, 2942, 1705, 1486, 1426, 1274, 1226, 1160, 1055, 971, 759 cm^{-1}. HRMS-ESI (m/z): calcd for $C_{14}H_{19}NNaO_3$ [M + Na]$^+$: 272.1257; found: 272.1261.

Octyl diethylcarbamate (4sa)



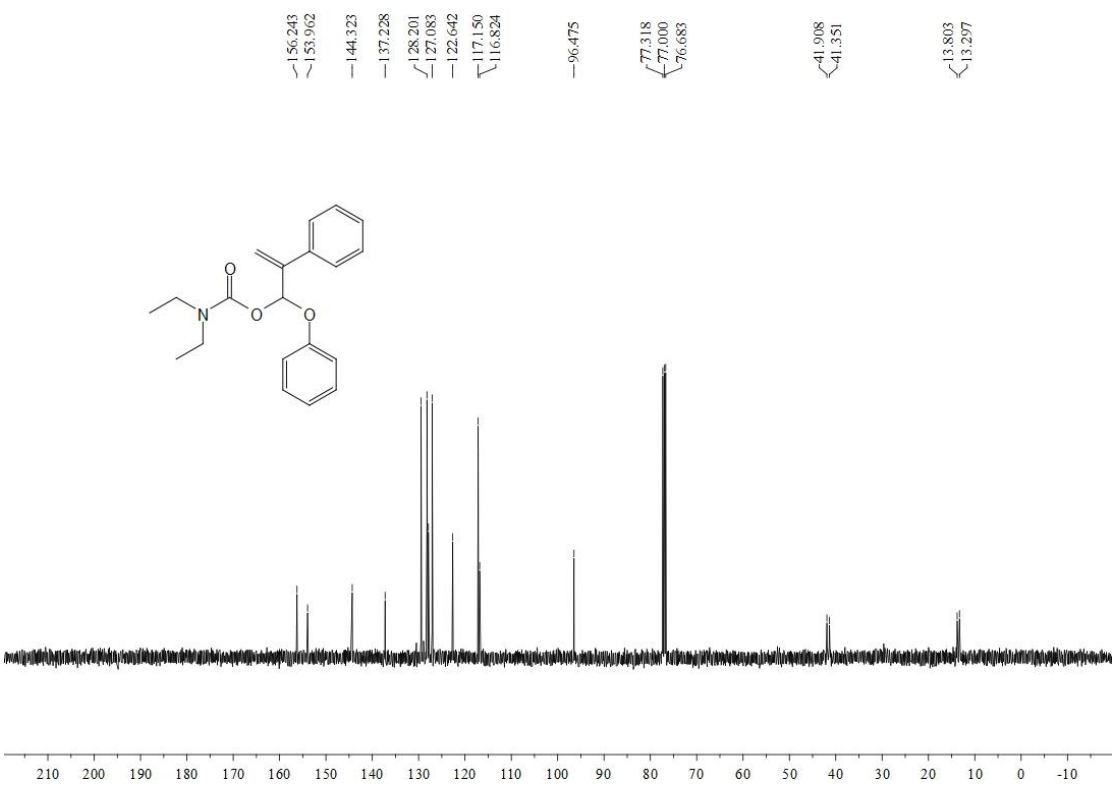
4sa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a pale yellow oil in 75% yield (34.3 mg, 0.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.06 (t, *J* = 6.6 Hz, 2 H), 3.27 (s, 4 H), 1.68 – 1.57 (m, 2 H), 1.38 – 1.24 (m, 10 H), 1.11 (t, *J* = 7.2 Hz, 6 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 65.1, 41.4, 41.182, 31.7, 29.2, 29.2, 29.1, 26.0, 22.6, 14.0. IR (KBr): 2966, 2929, 2859, 1703, 1477, 1427, 1377, 1274, 1173, 1074, 772 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{13}H_{27}NNaO_2^+$ [M + Na]$^+$: 252.1934; found 252.1930.

References

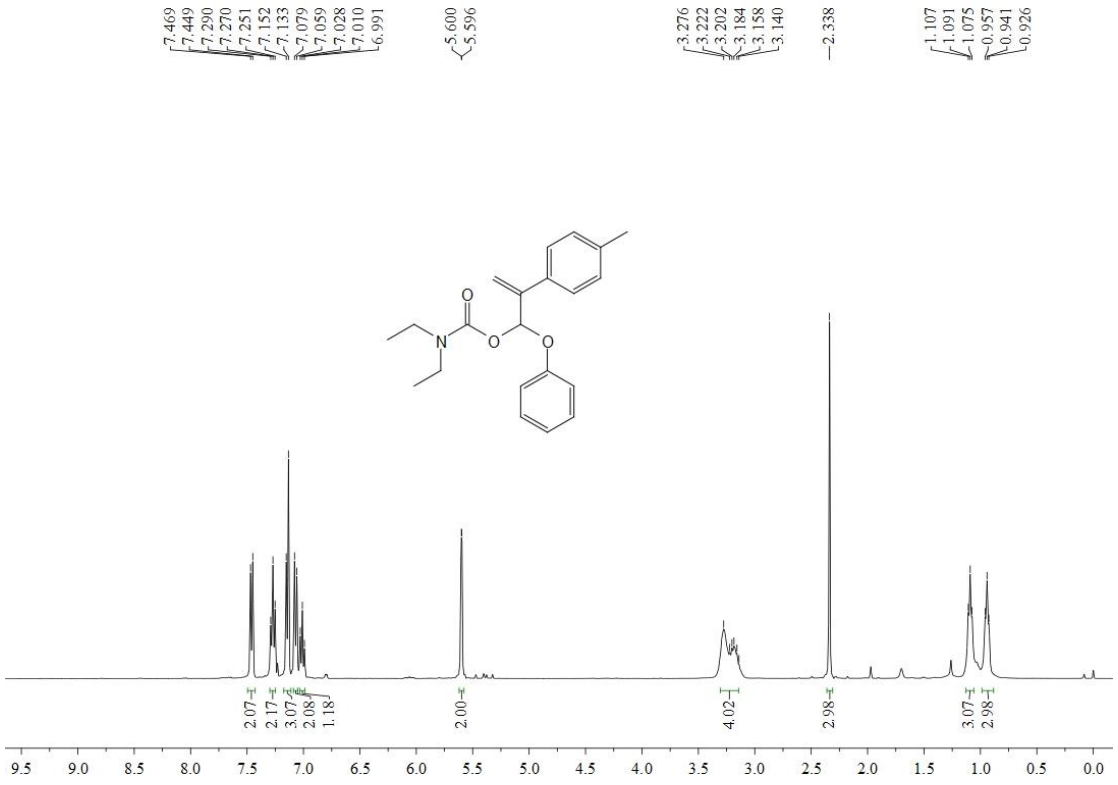
(1) Wang. Y.; Jiang, M.; and Liu, J.-T. *Adv. Synth. Catal.* **2014**, *356*, 2907.

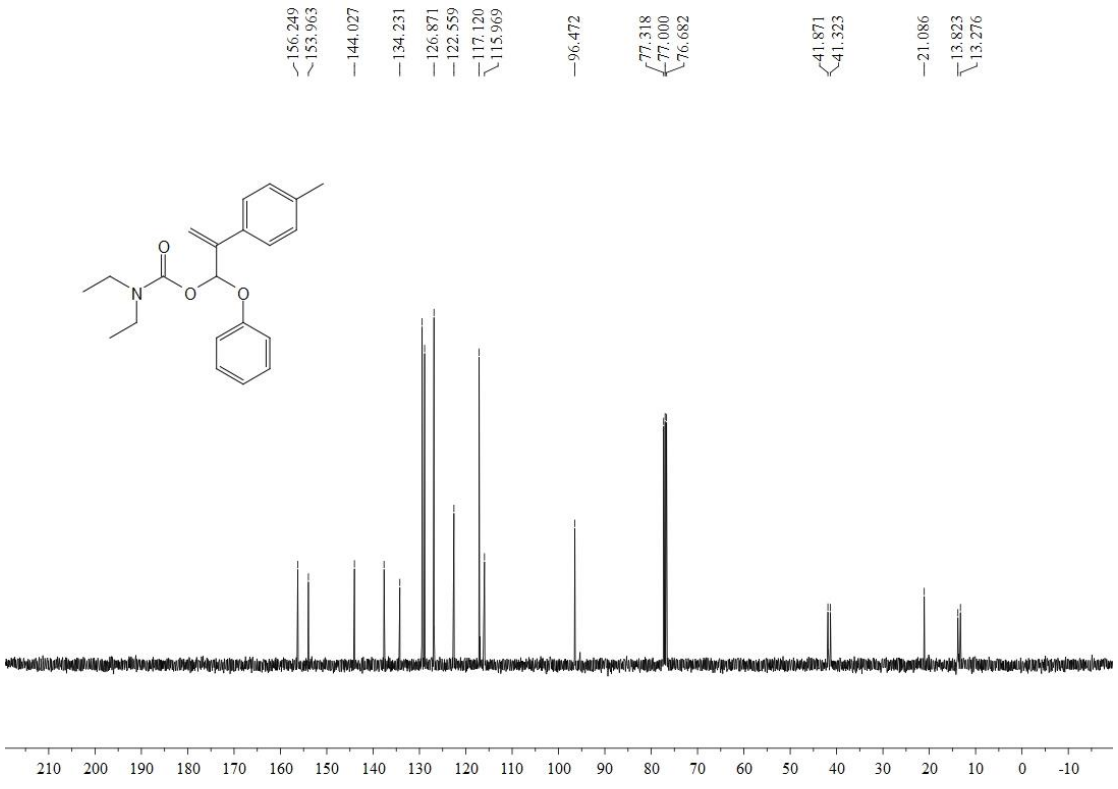
H. NMR Spectra

1- Phenoxy-2-phenylallyl diethylcarbamate (4aaa)

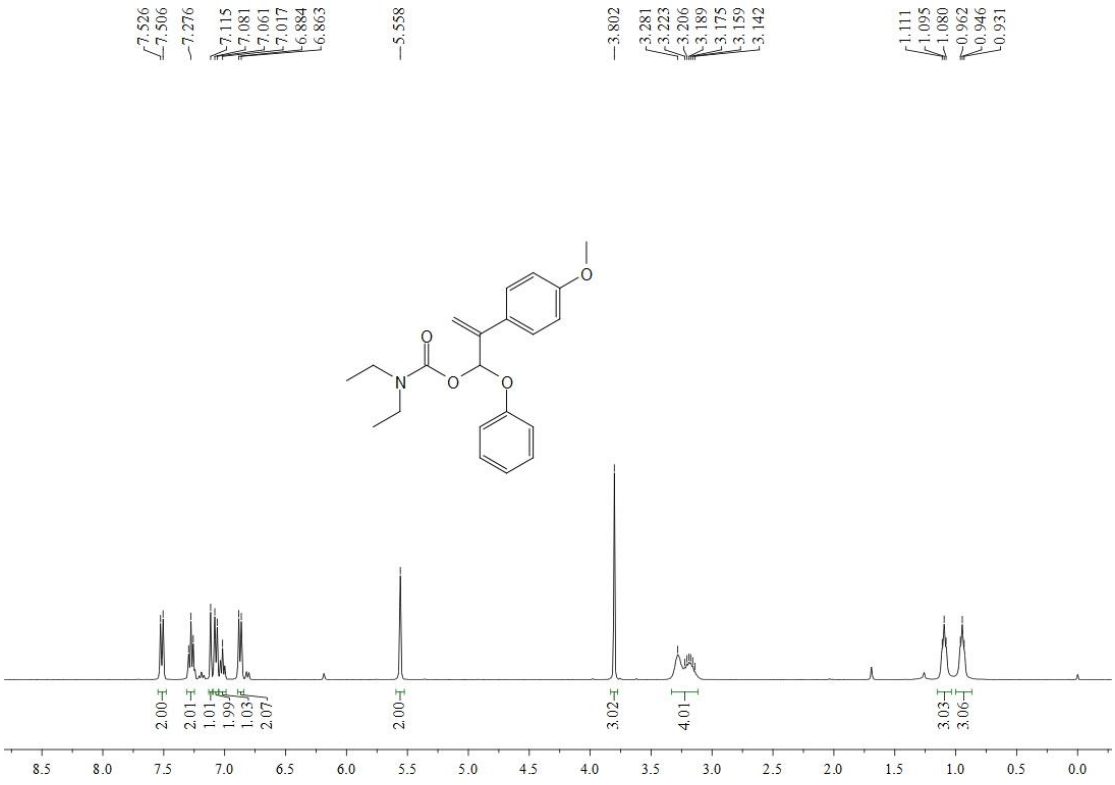


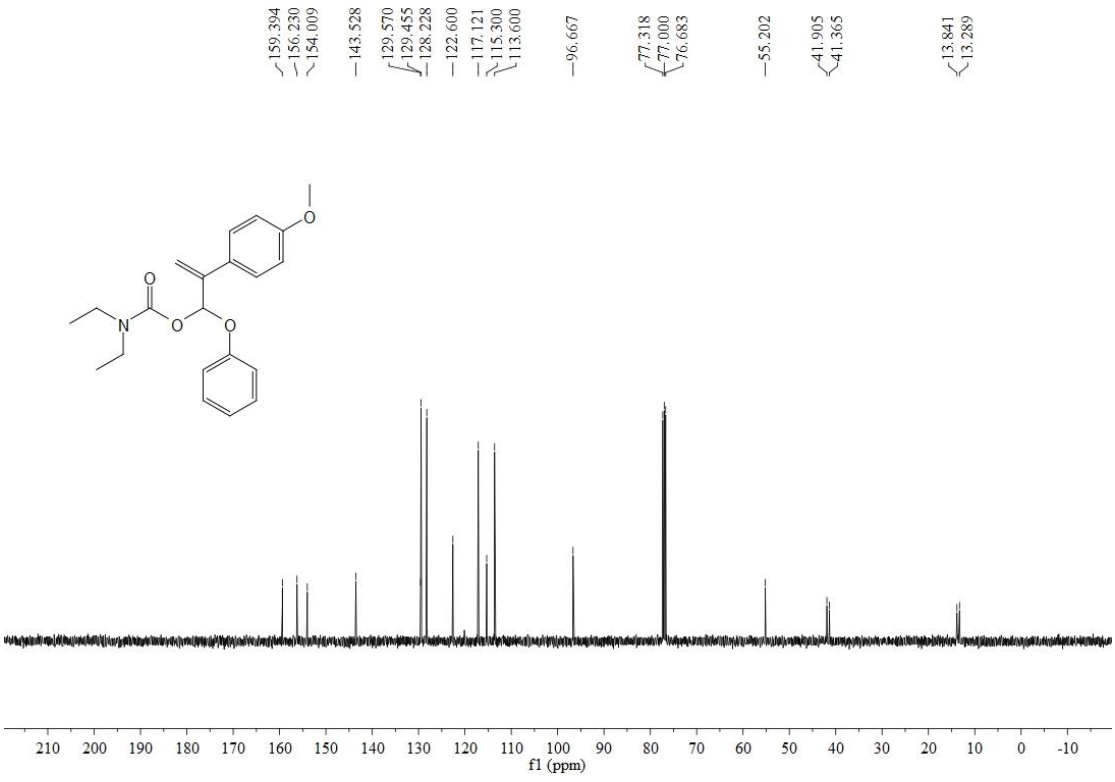
1-Phenoxy-2-(p-tolyl)allyl diethylcarbamate (4aba)



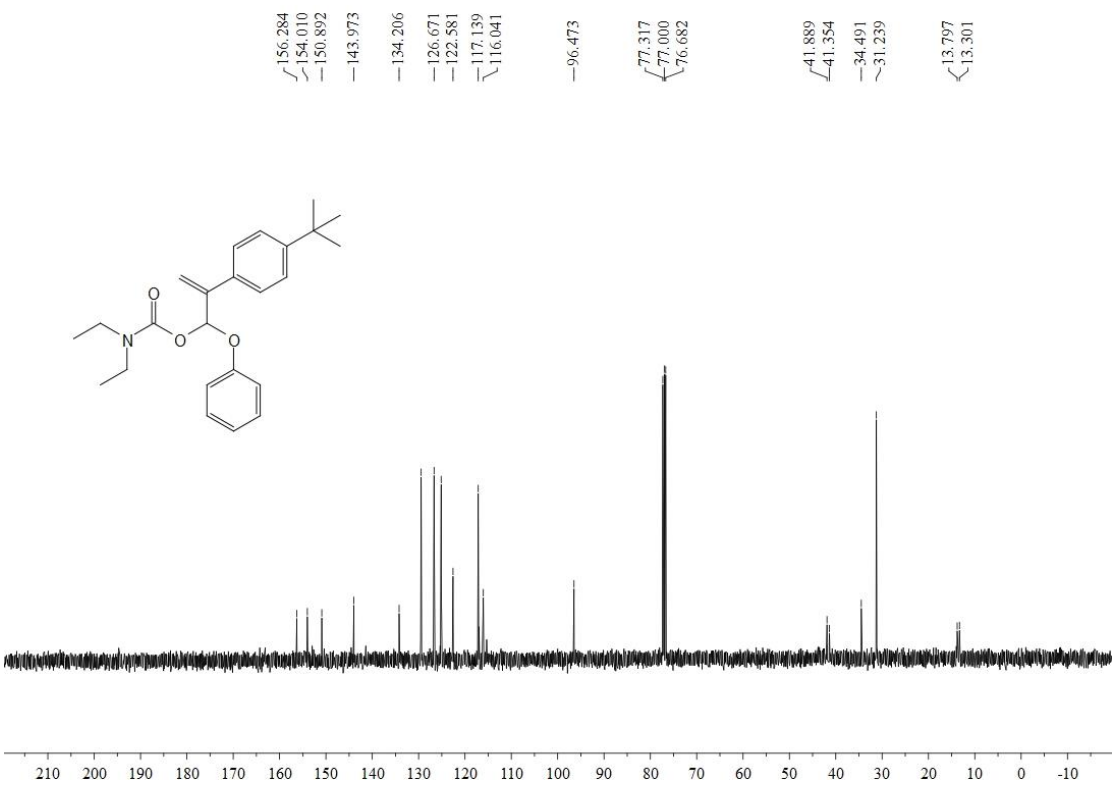


2-(4-Methoxyphenyl)-1-phenoxyallyl diethylcarbamate (4aca)

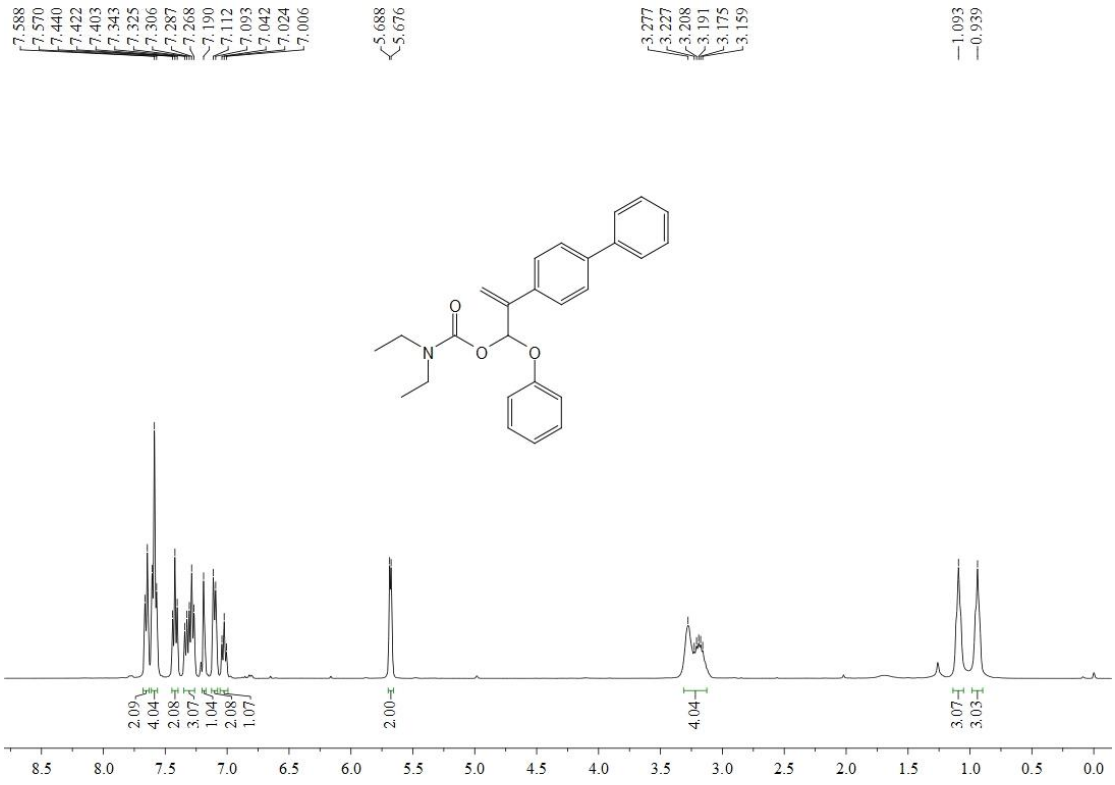


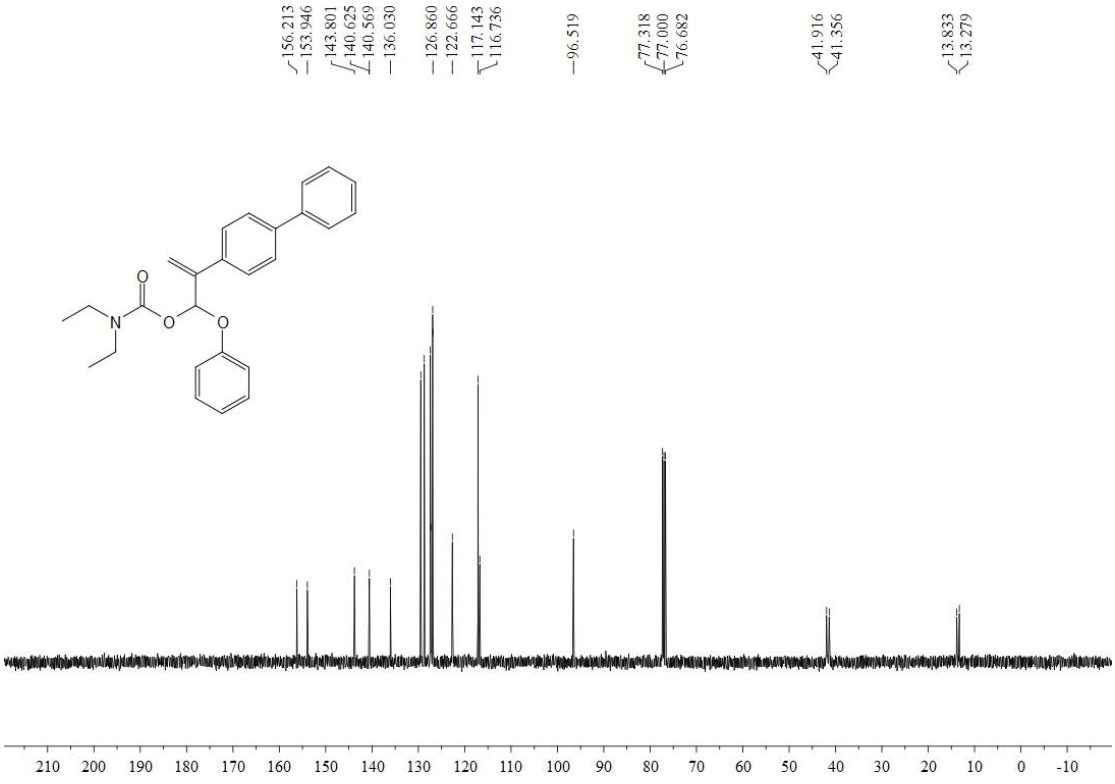


2-(4-(Tert-butyl)phenyl)-1-phenoxyallyl diethylcarbamate (4ada)

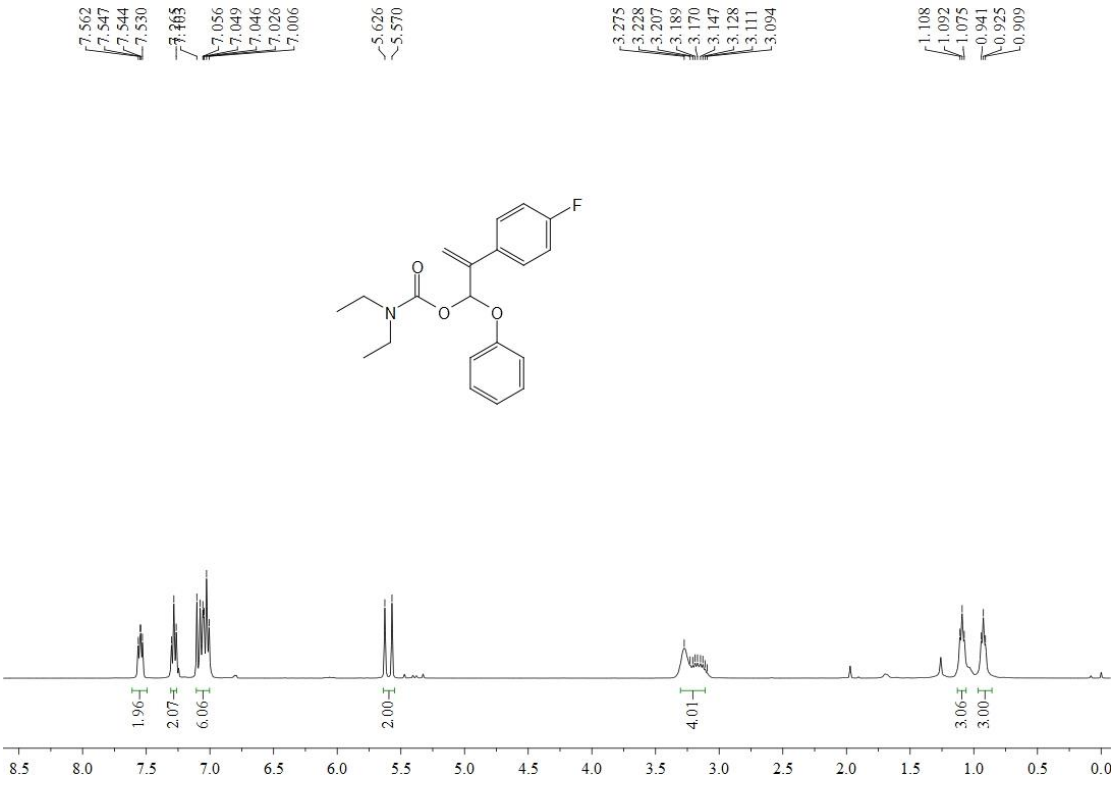


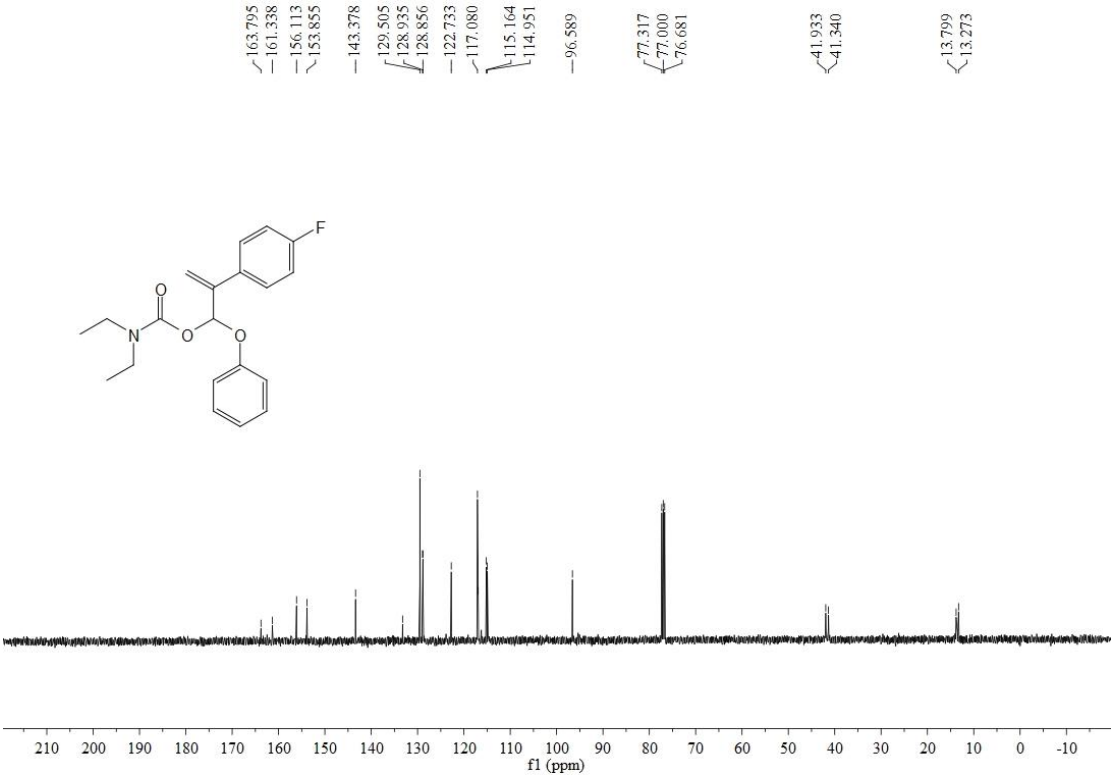
2-([1,1'-Biphenyl]-4-yl)-1-phenoxyallyl diethylcarbamate (4aea)



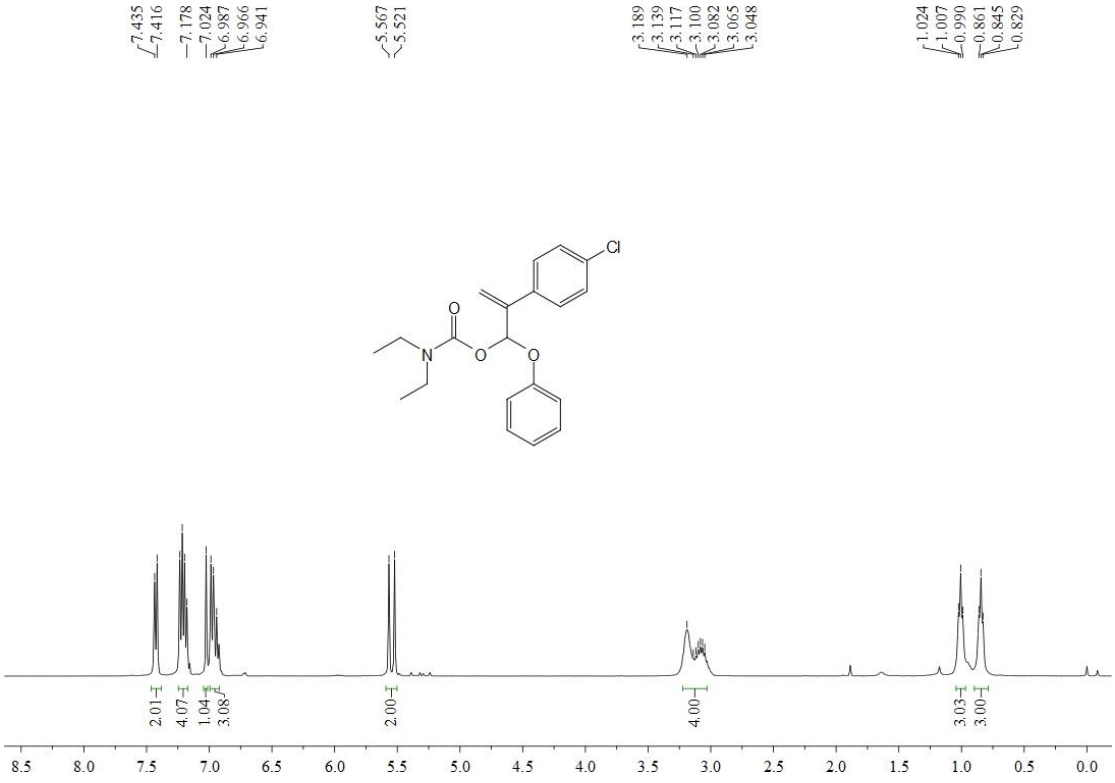


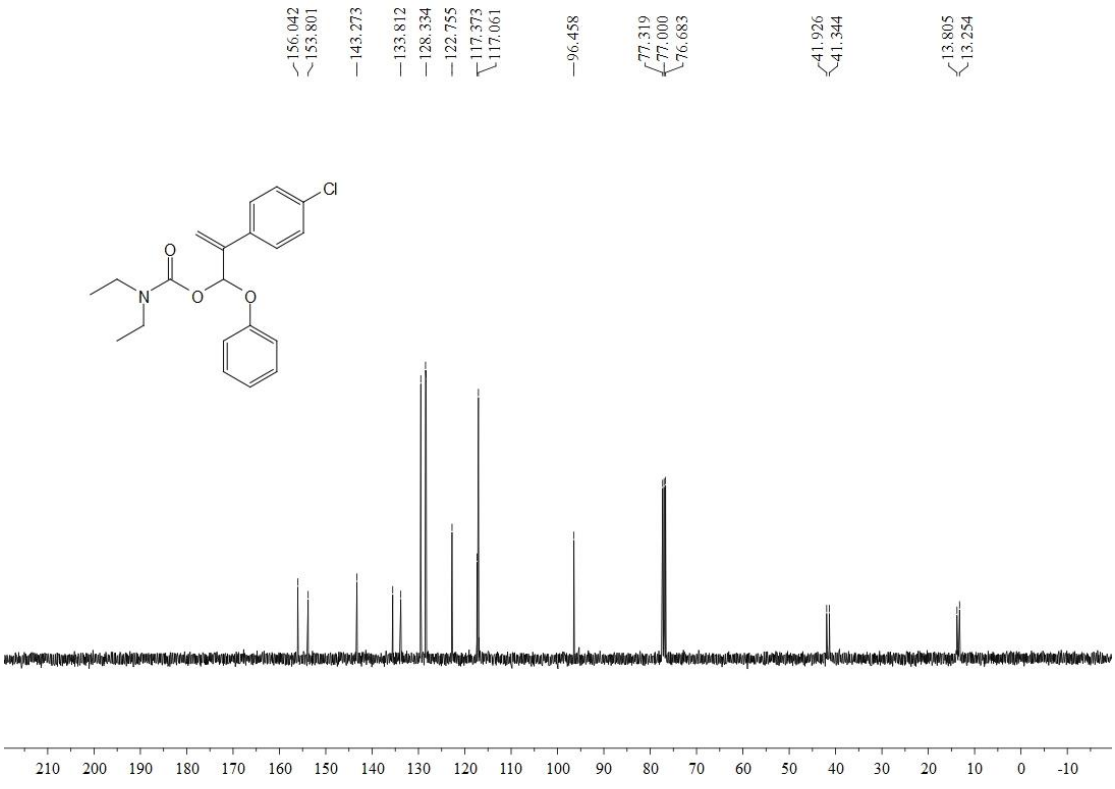
2-(4-Fluorophenyl)-1-phenoxyallyl diethylcarbamate (**4afa**)



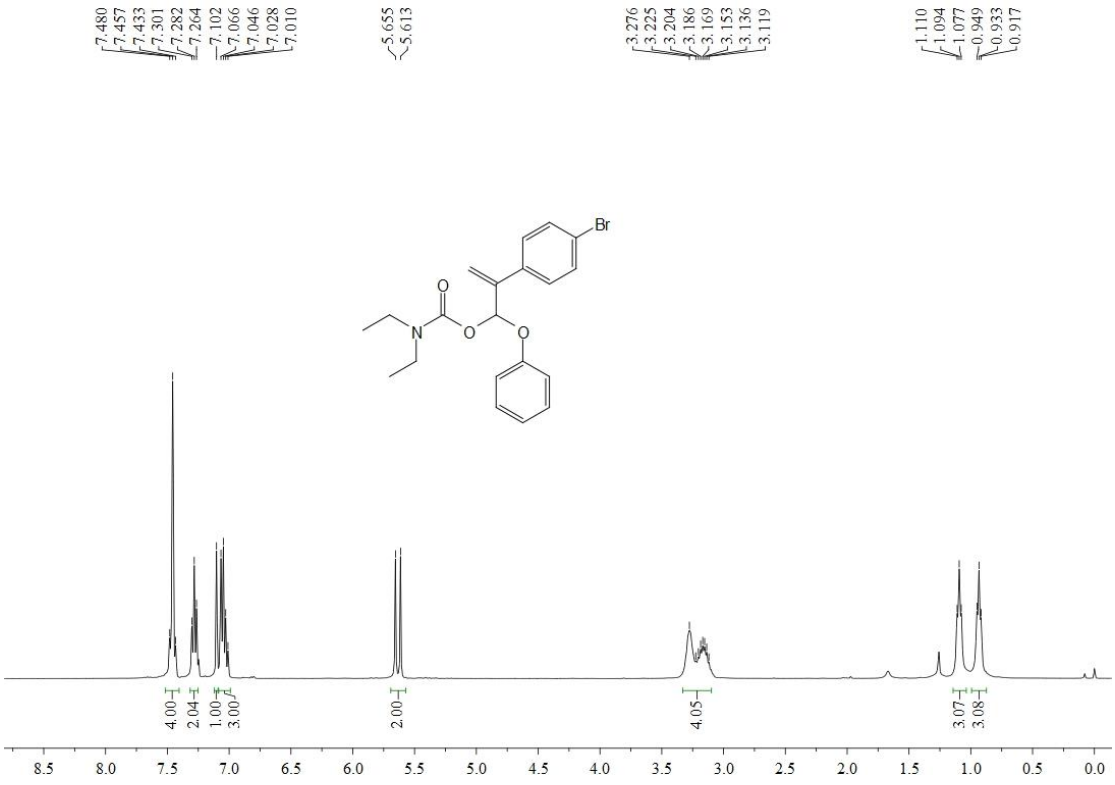


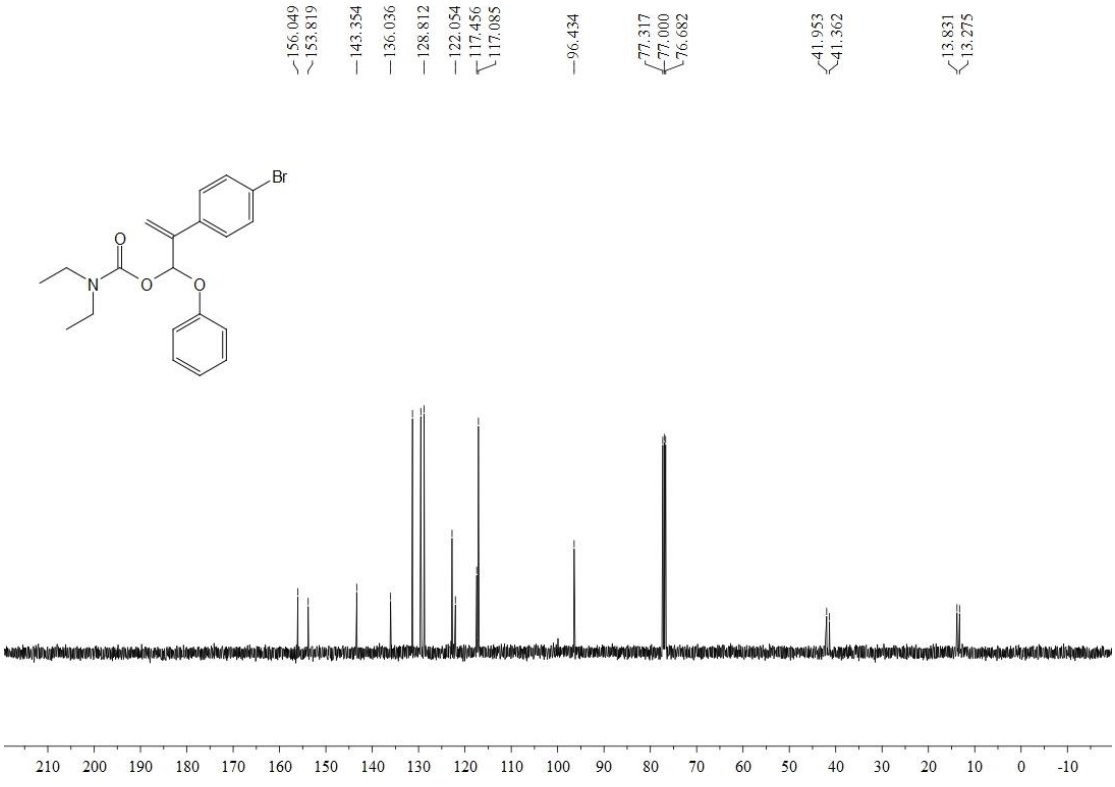
2-(4-Chlorophenyl)-1-phenoxyallyl diethylcarbamate (4aga)



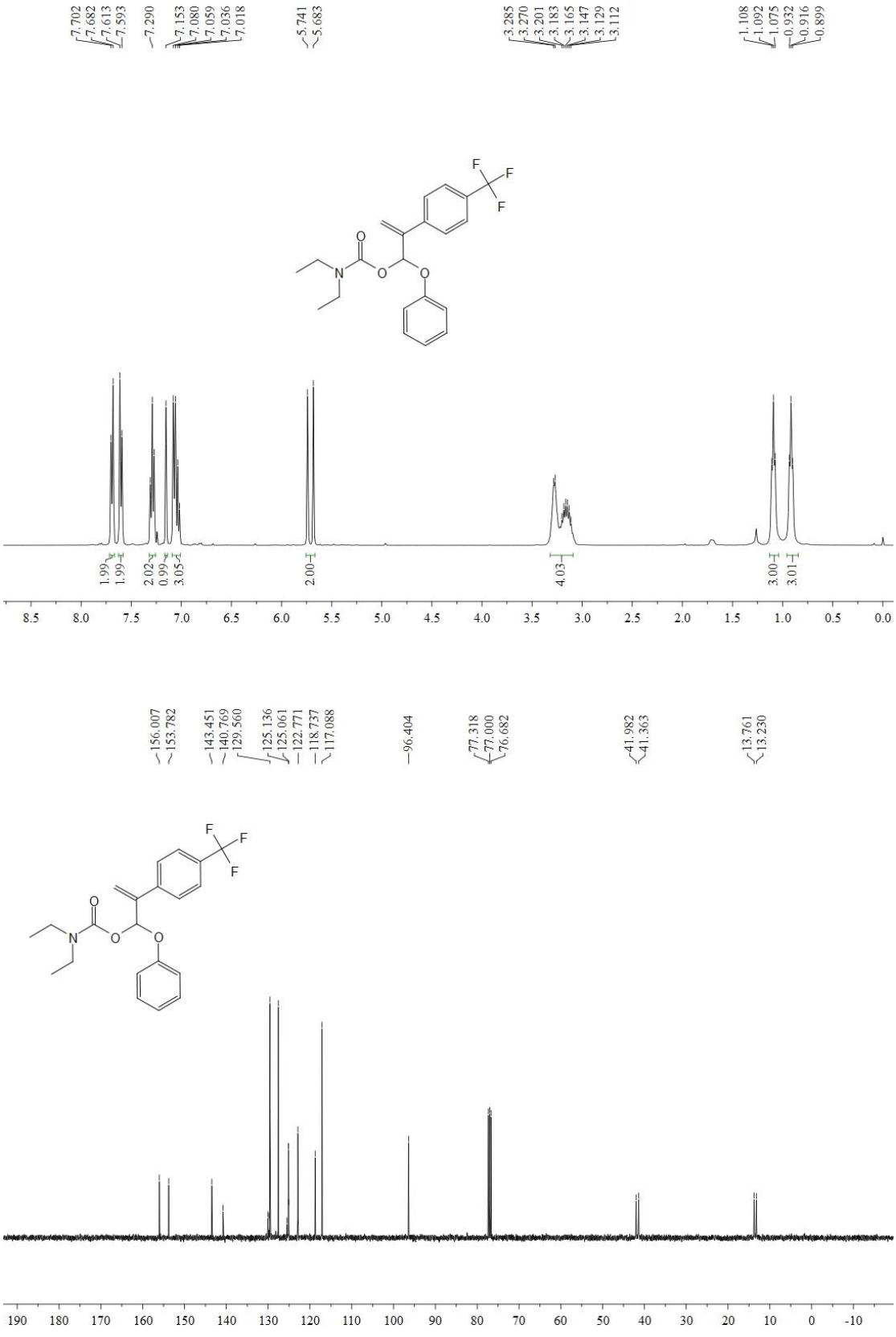


2-(4-Bromophenyl)-1-phenoxyallyl diethylcarbamate (**4aha**)

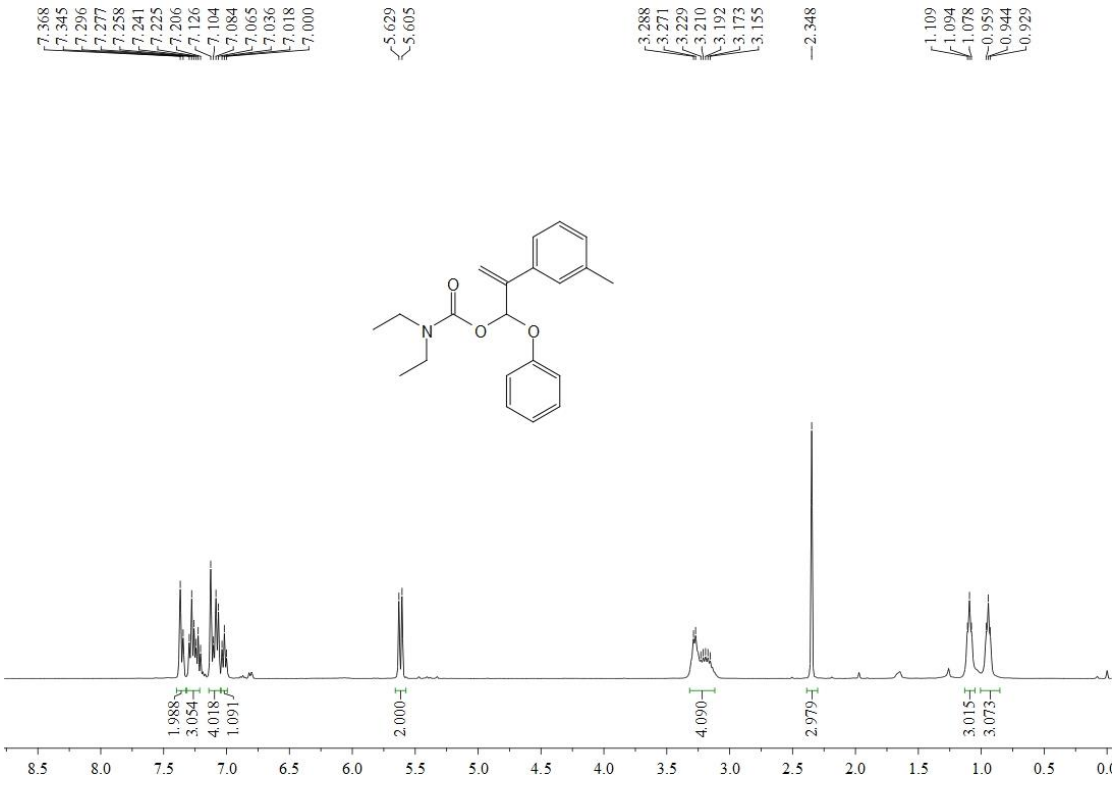


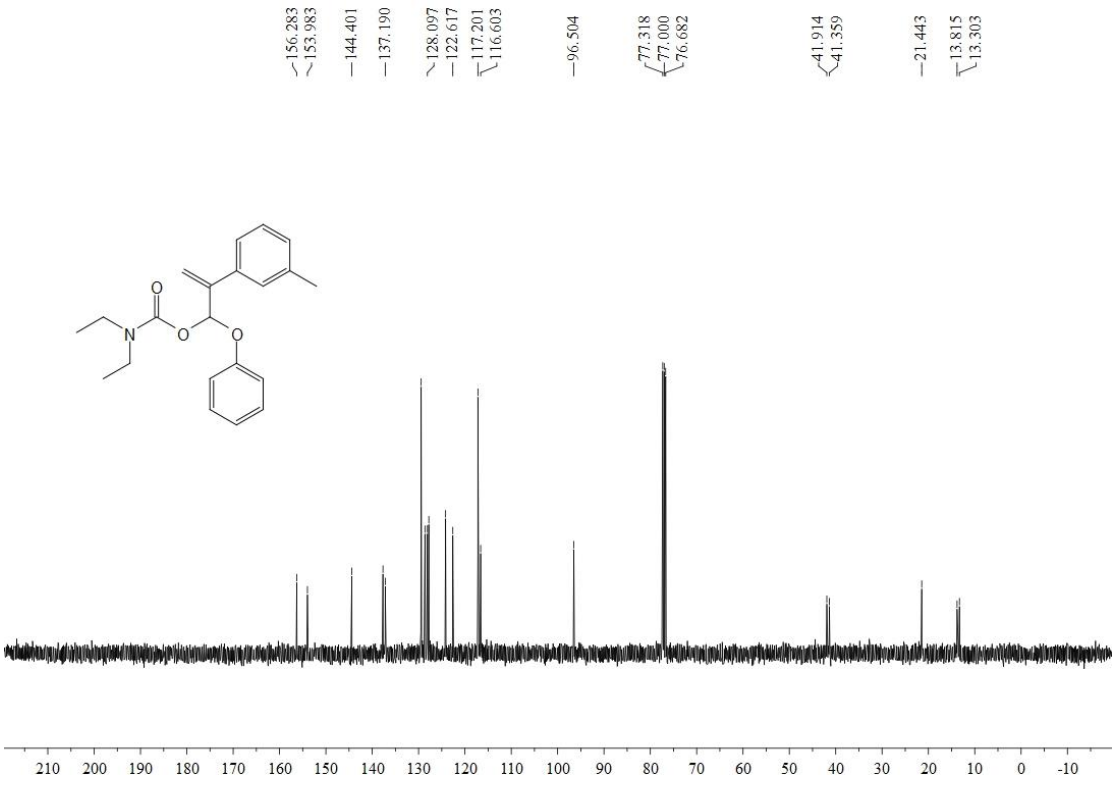


1-Phenoxy-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4aia)

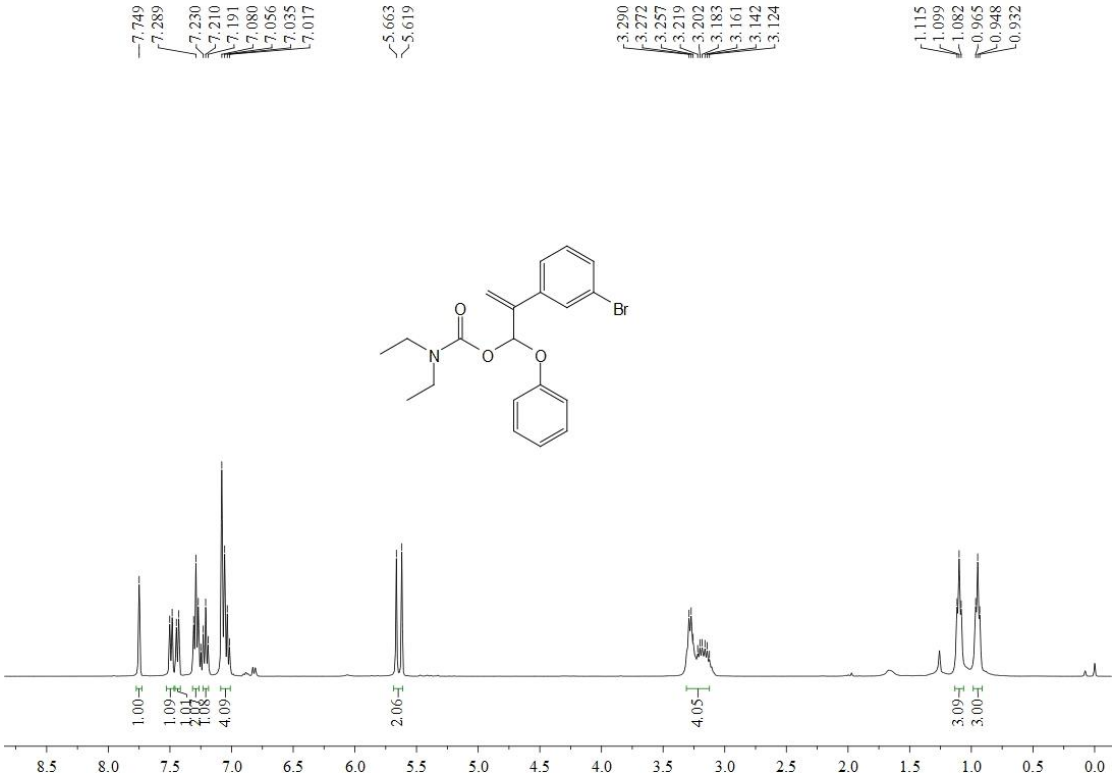


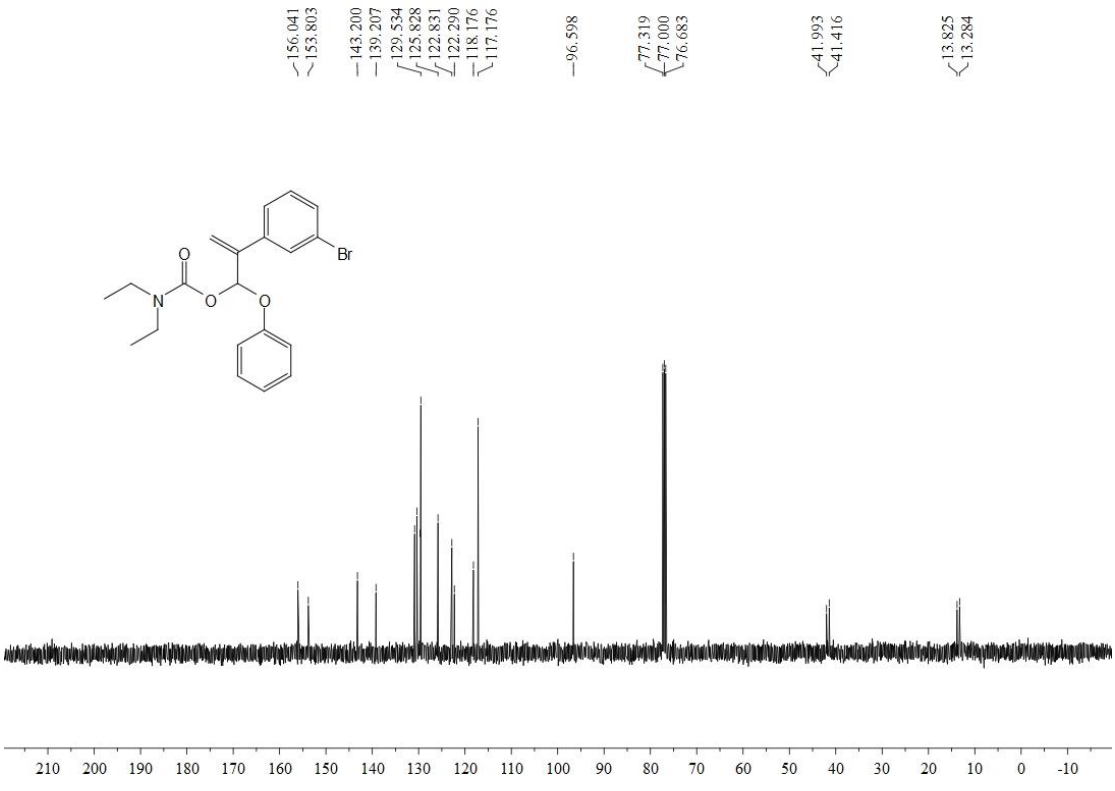
1-Phenoxy-2-(m-tolyl)allyl diethylcarbamate (4aja)



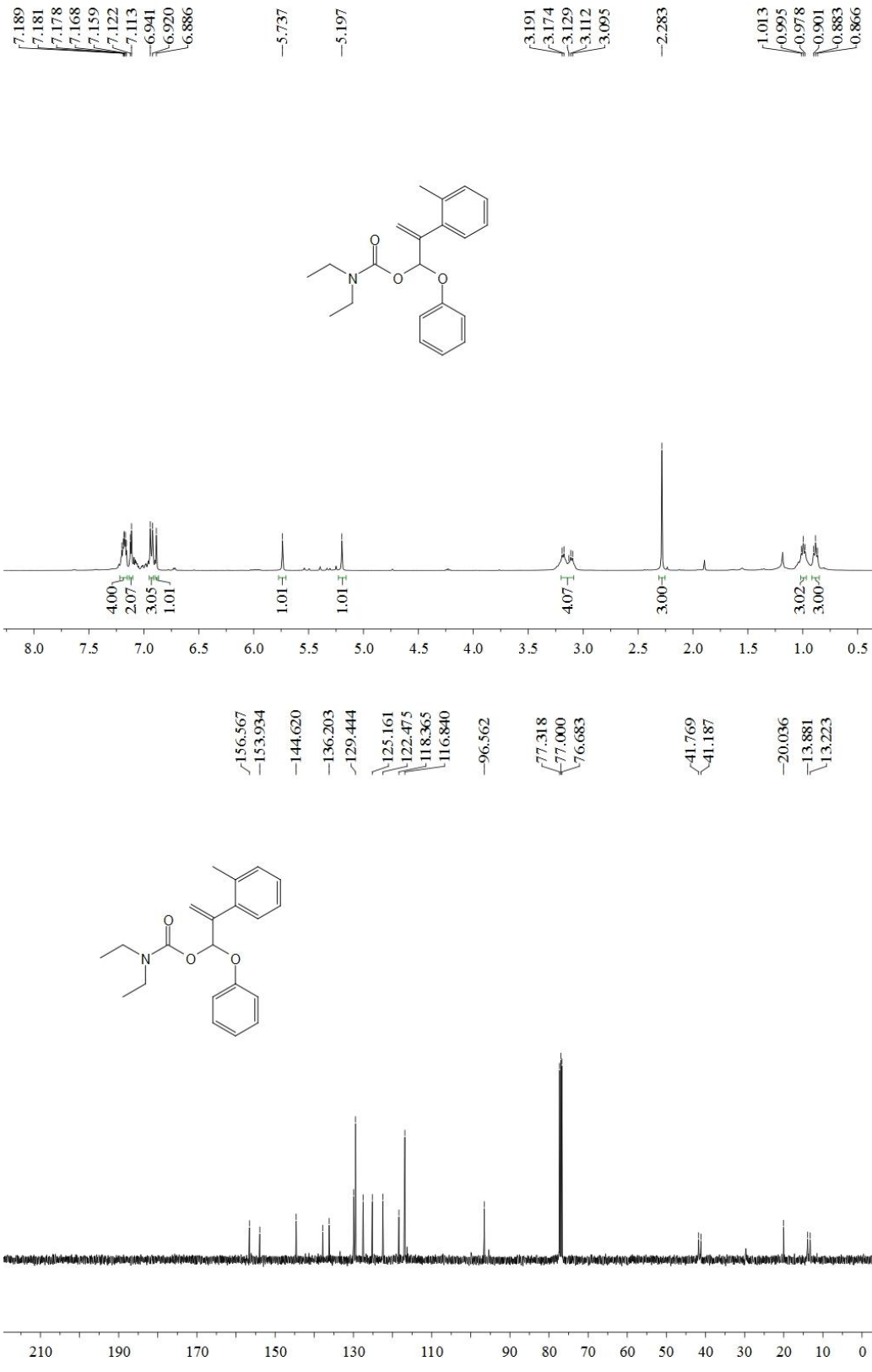


2-(3-Bromophenyl)-1-phenoxyallyl diethylcarbamate (4aka)

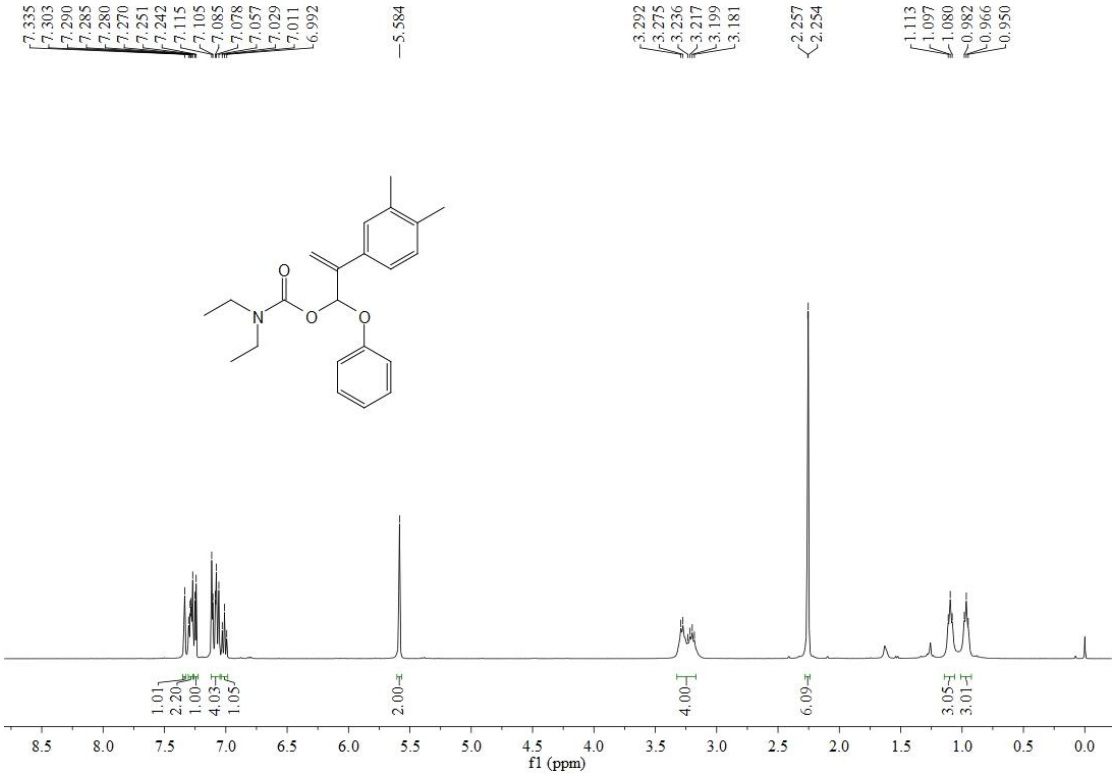


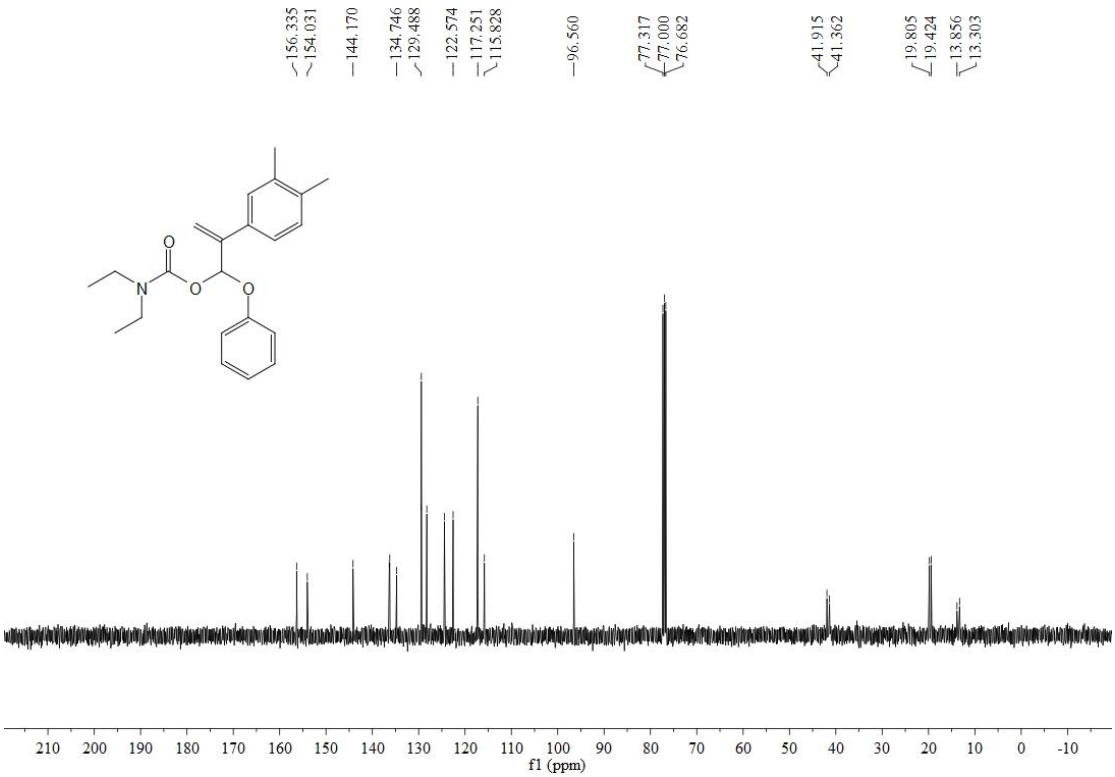


1-phenoxy-2-(o-tolyl)allyl diethylcarbamate (4ala)

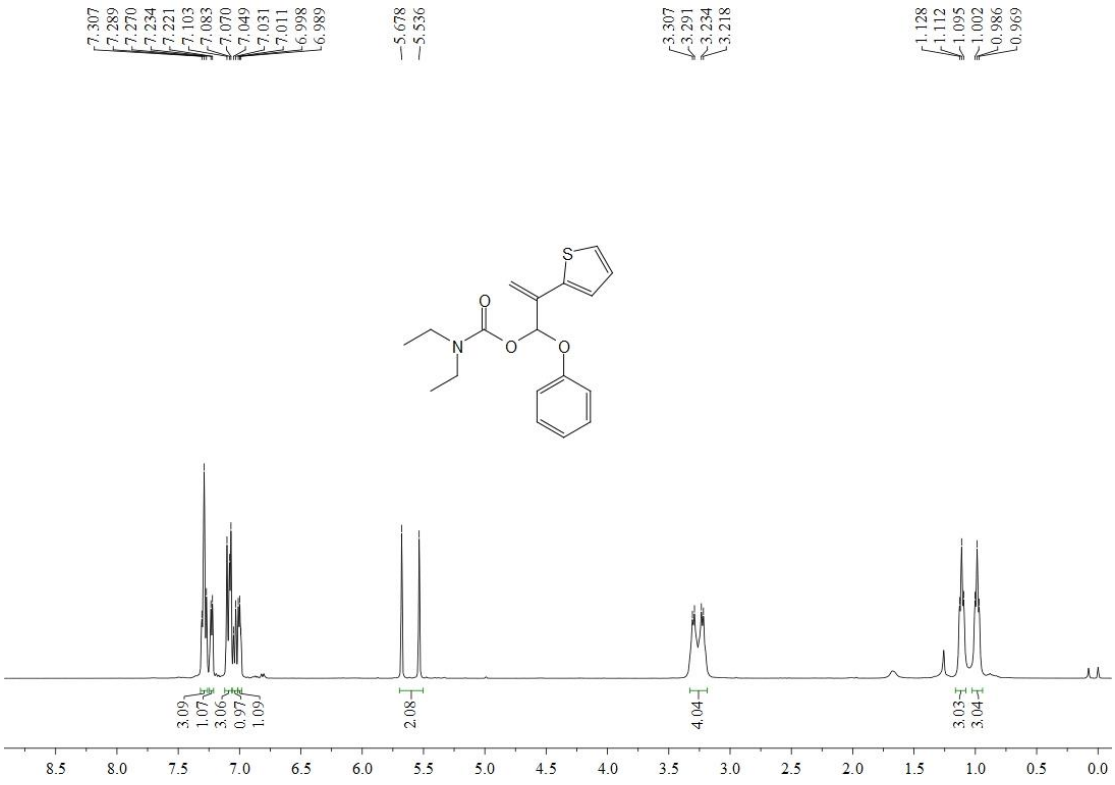


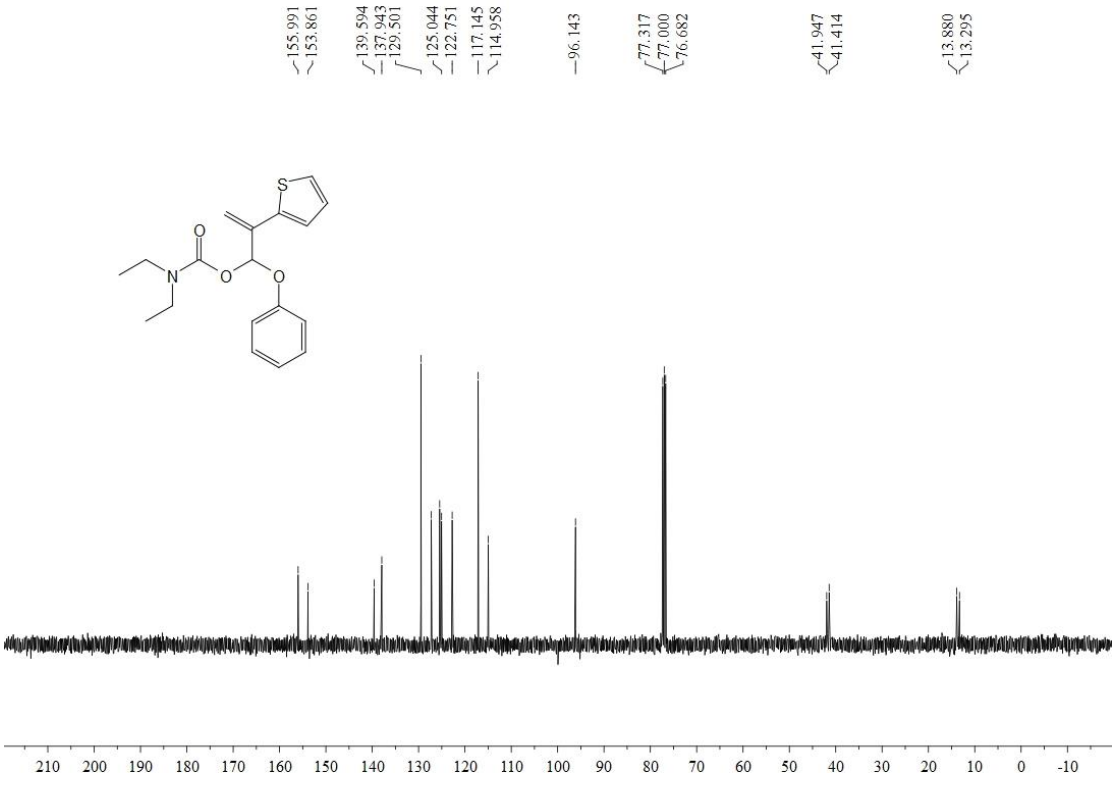
2-(3,4-Dimethylphenyl)-1-phenoxyallyl diethylcarbamate (4ama)



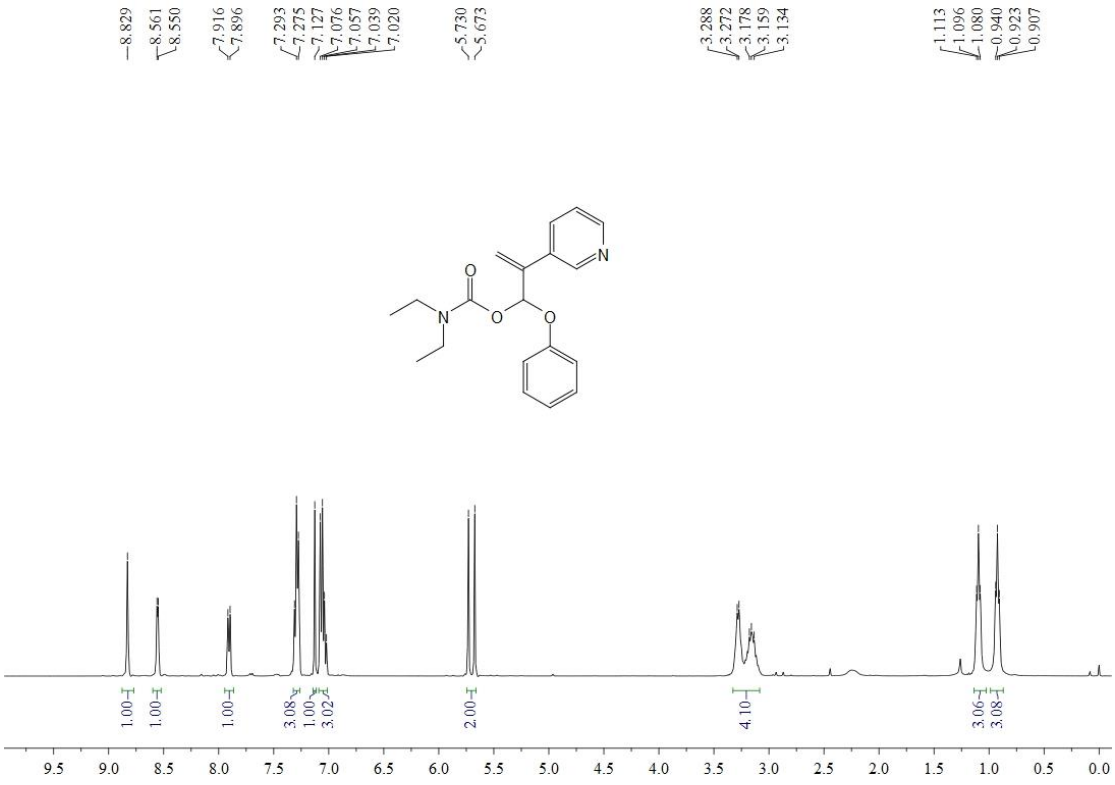


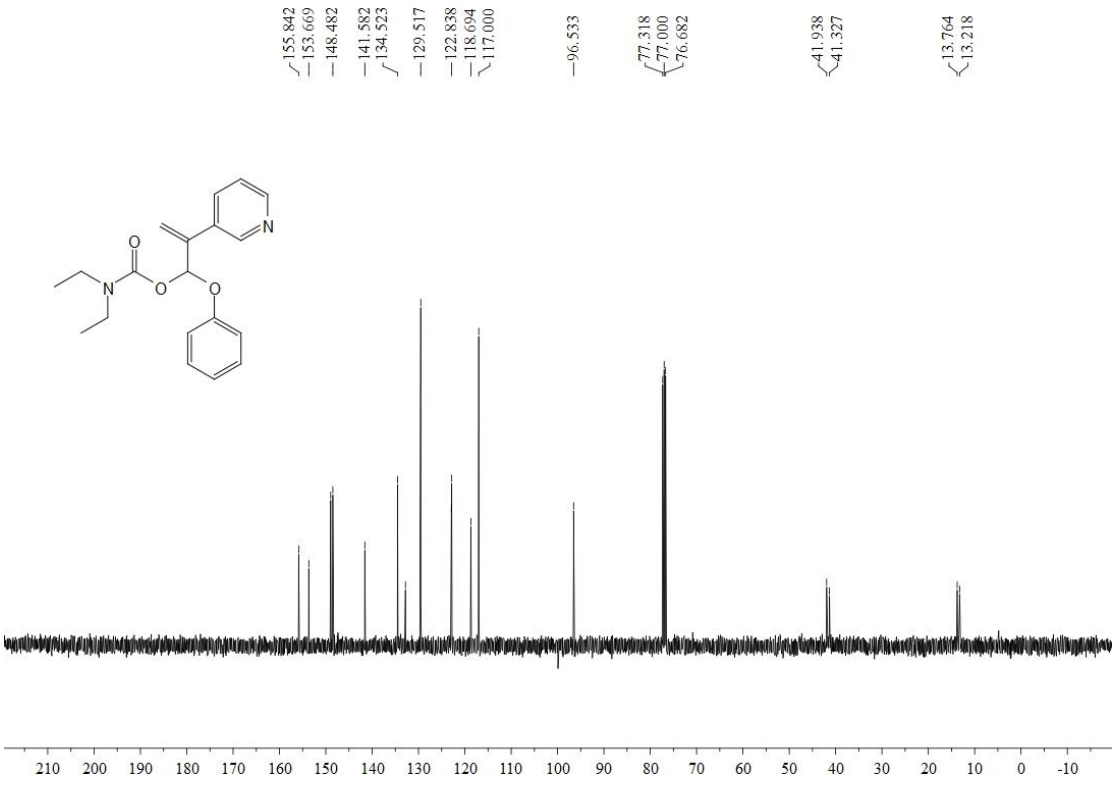
1-Phenoxy-2-(thiophen-2-yl)allyl diethylcarbamate (4ana)



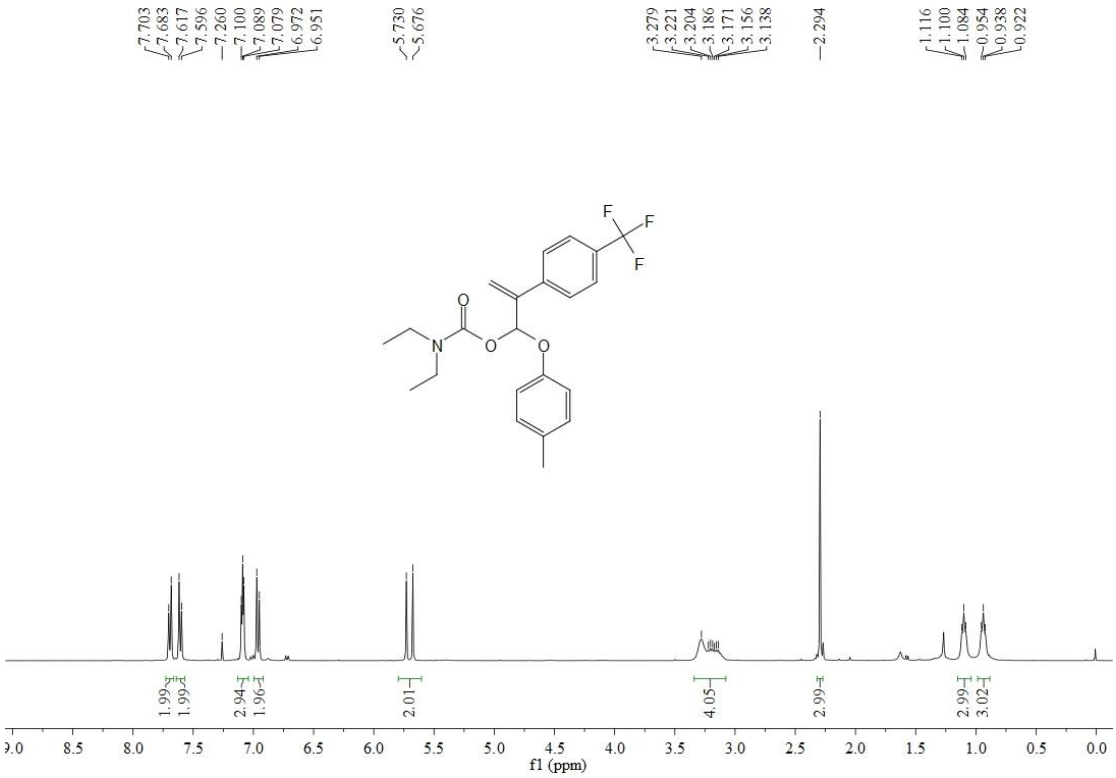


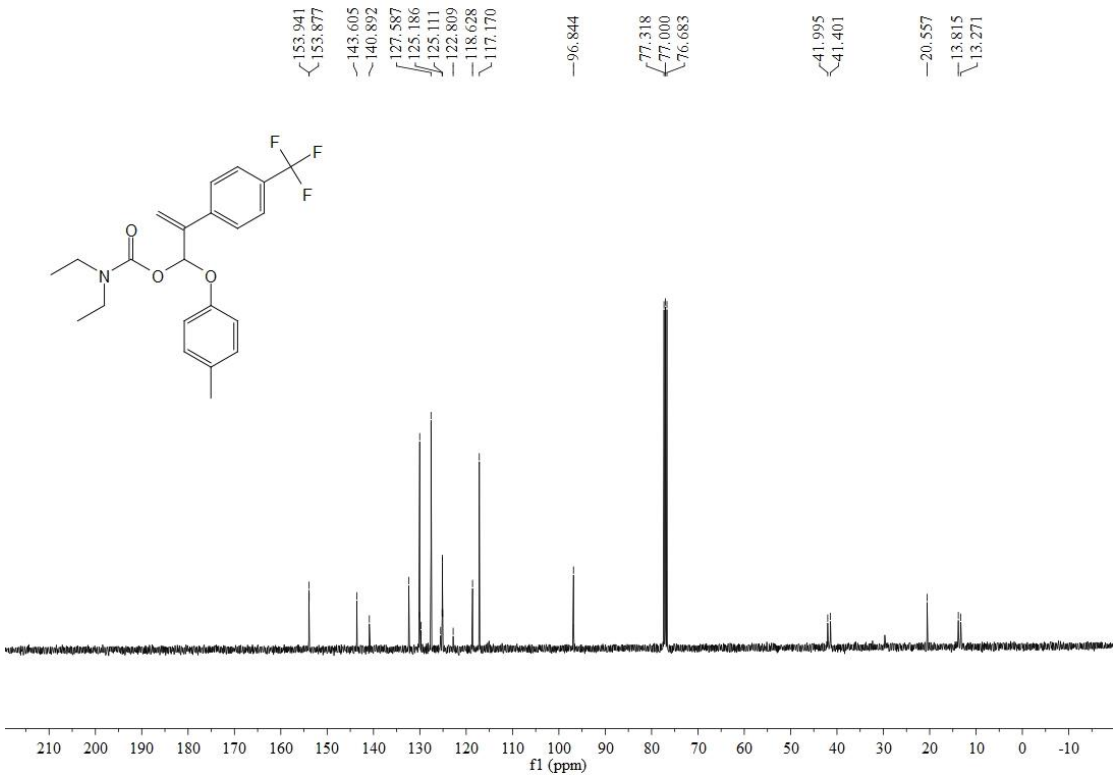
1-Phenoxy-2-(pyridin-3-yl)allyl diethylcarbamate (4aoa)



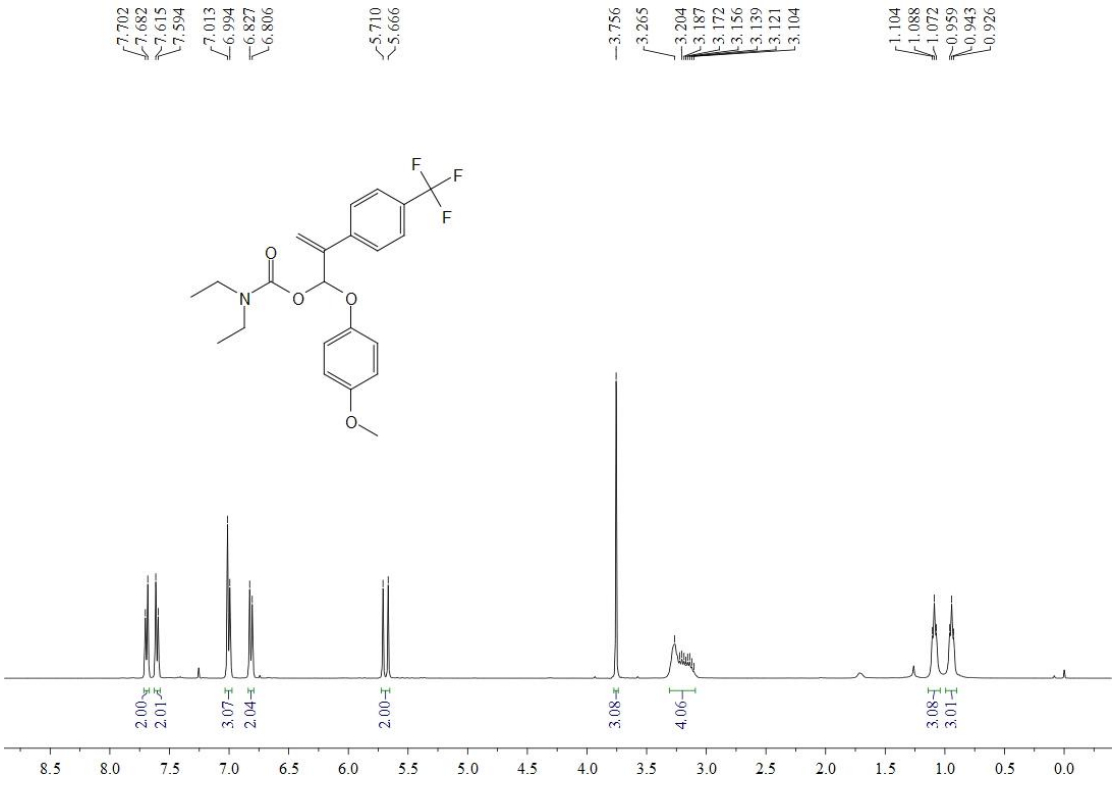


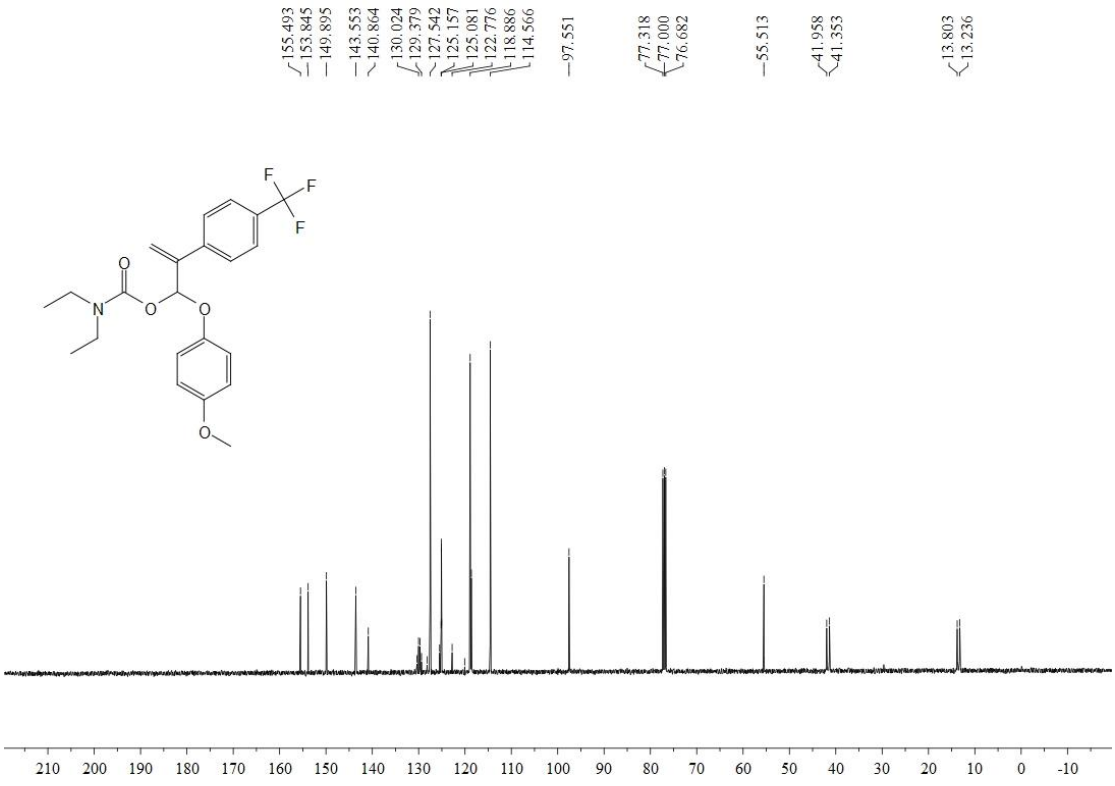
1-(*p*-Tolyloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4bia)



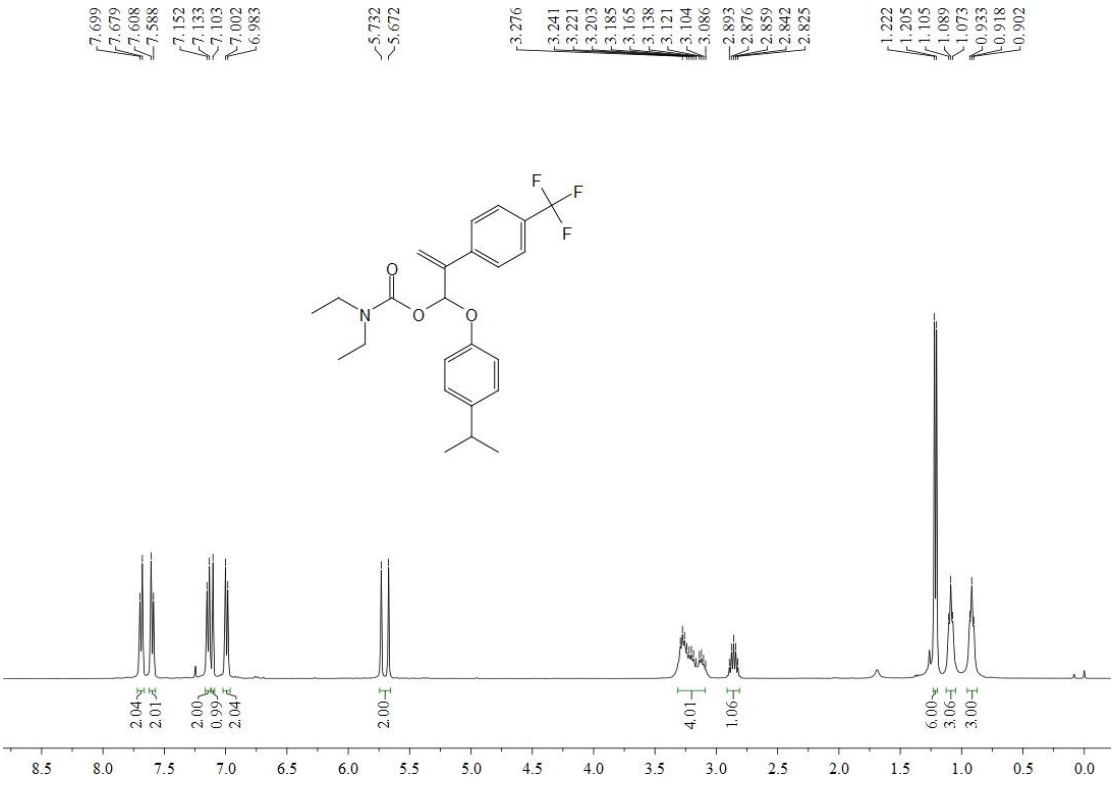


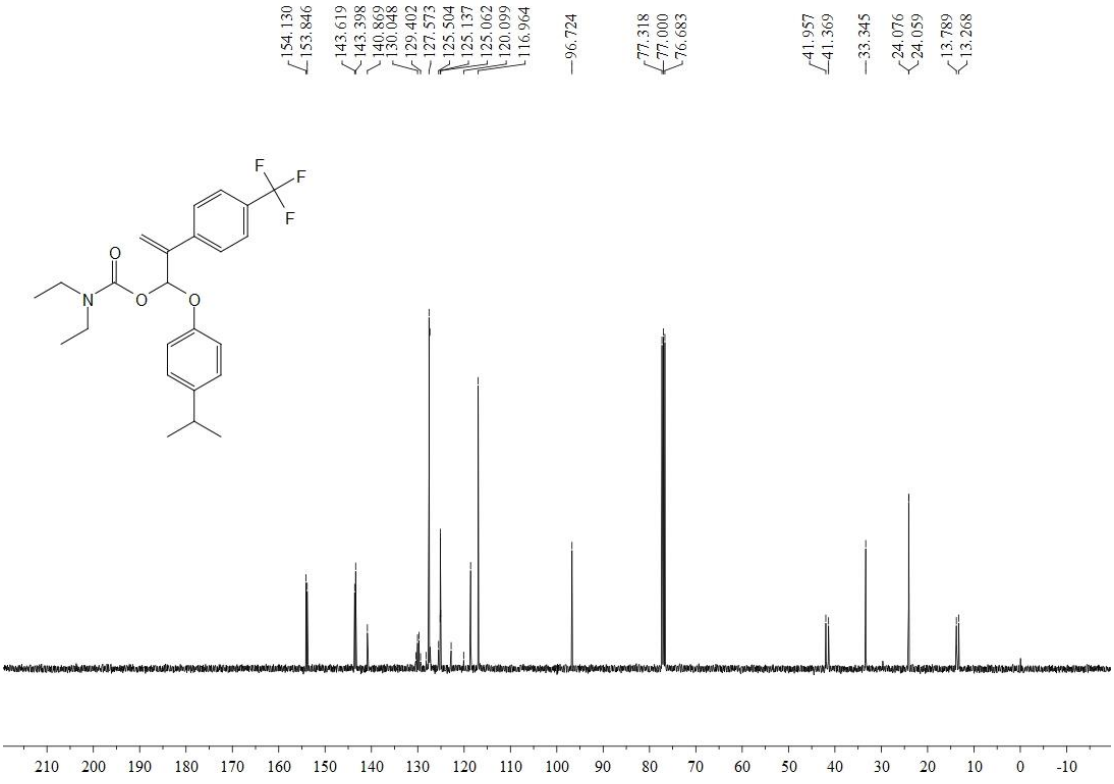
1-(4-Methoxyphenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4cia)



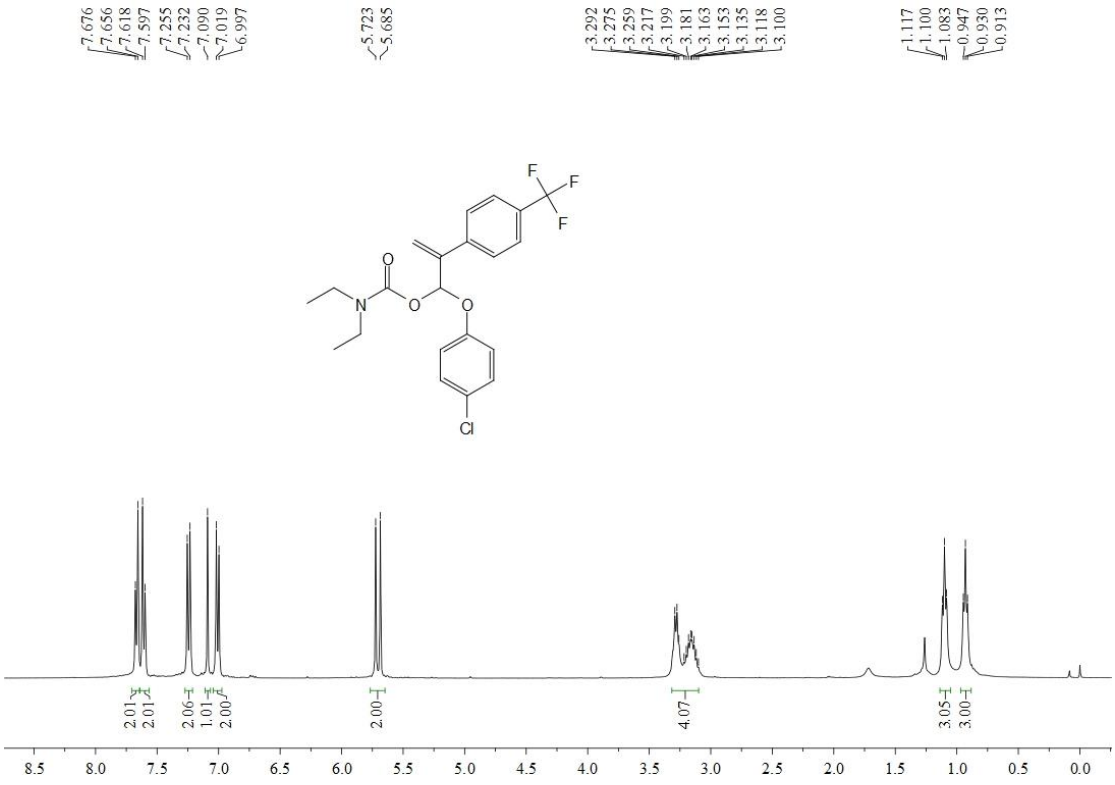


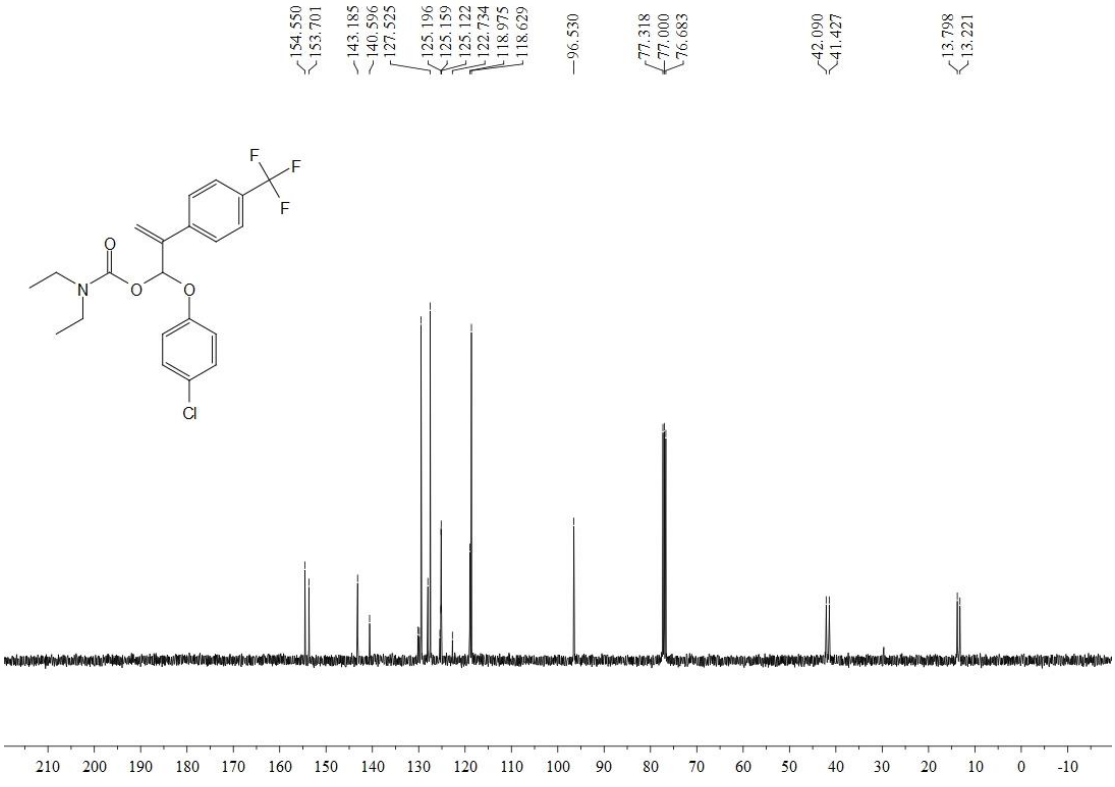
1-(4-Isopropylphenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4dia)



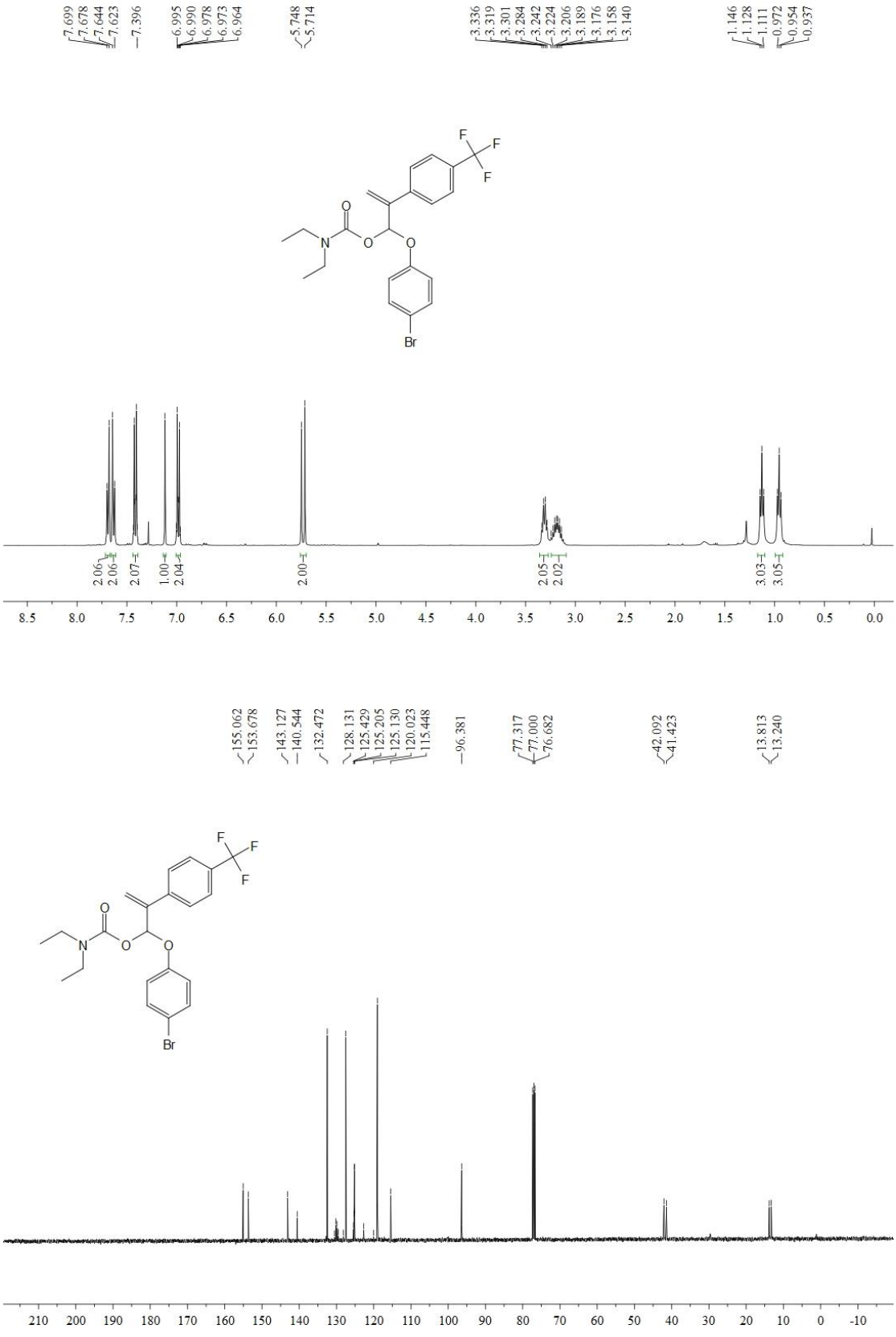


1-(4-Chlorophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4eia)

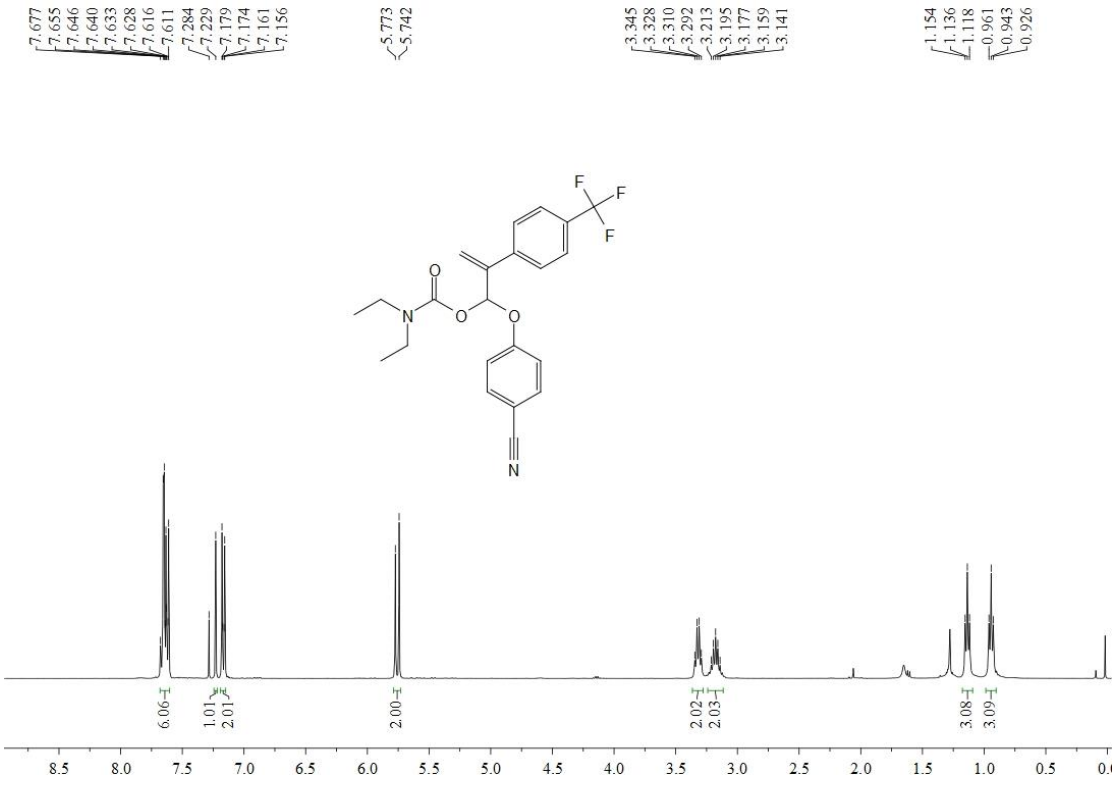


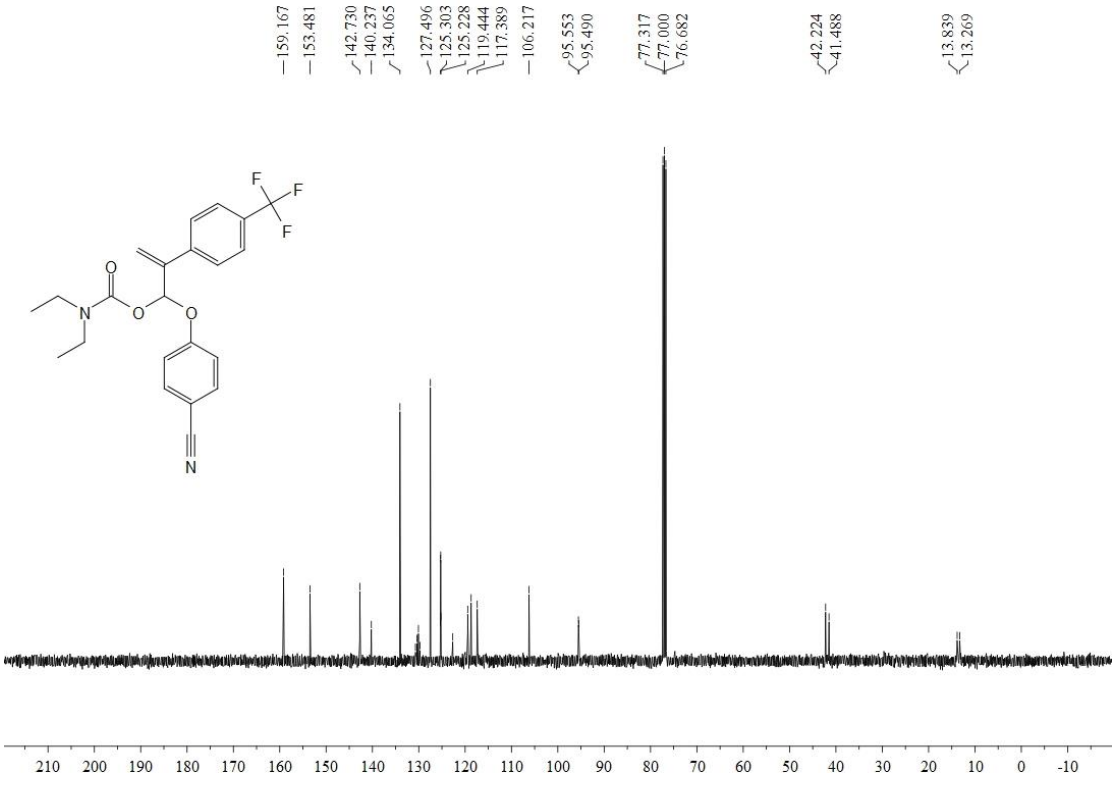


1-(4-Bromophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4fia)

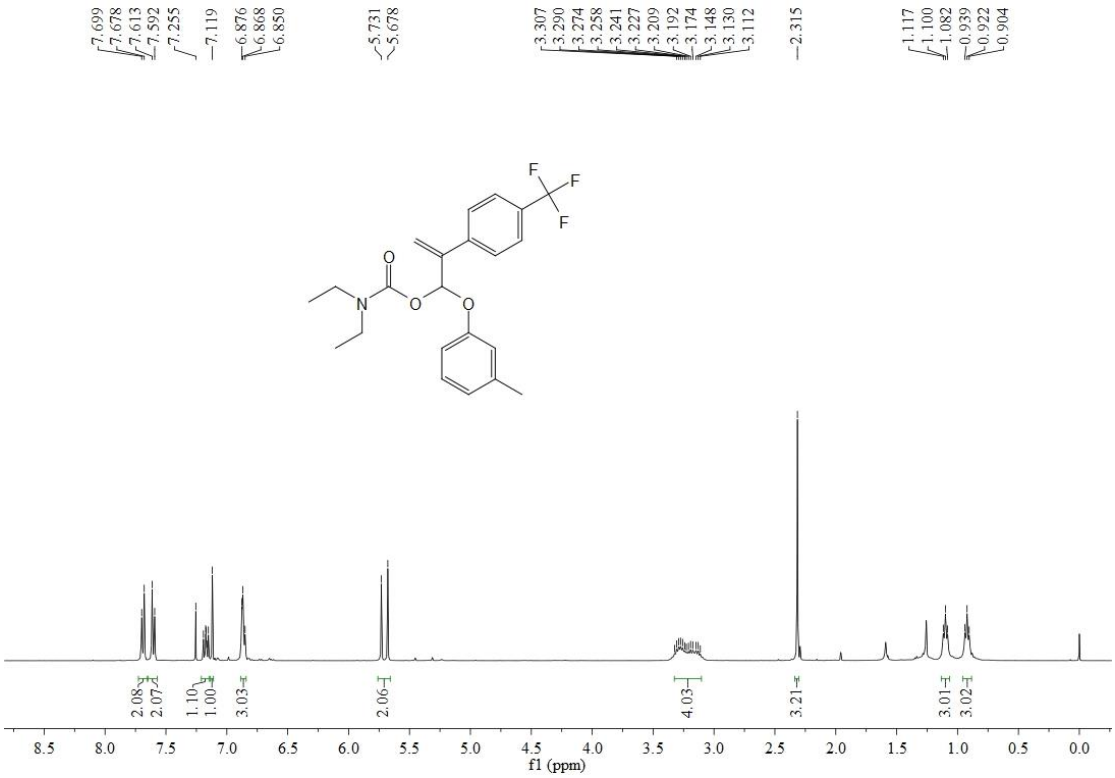


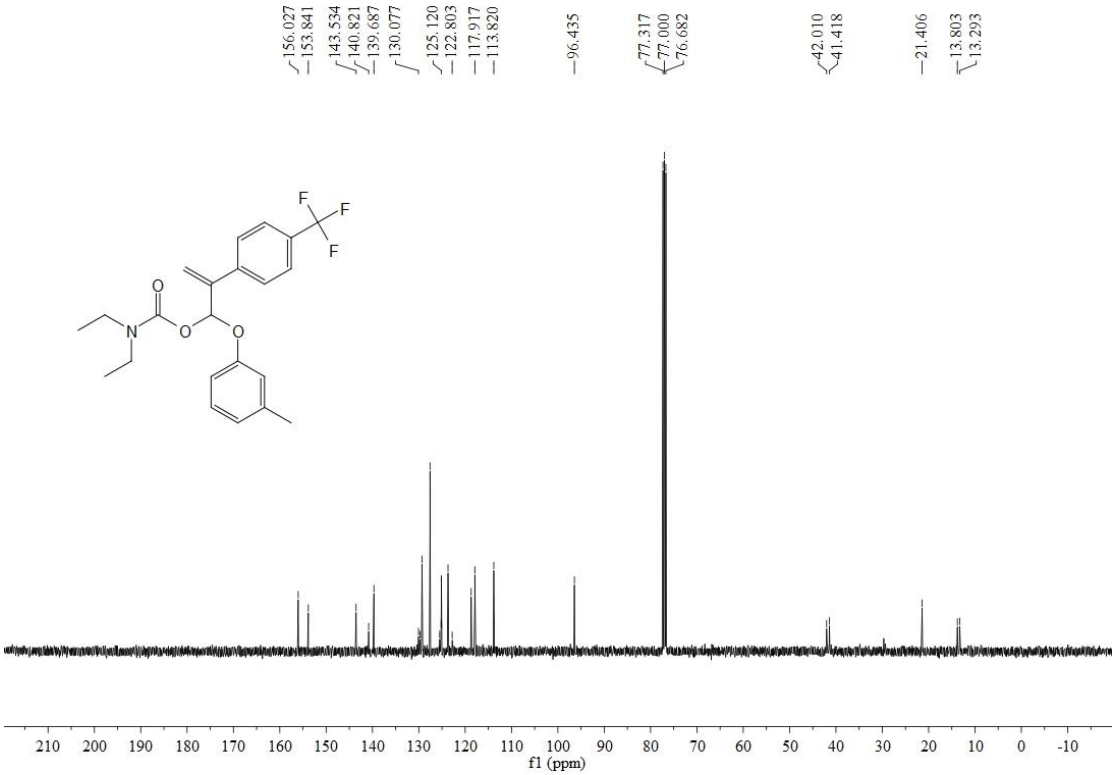
1-(4-Cyanophenoxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4gia)





1-(*m*-Tolyloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4hia)





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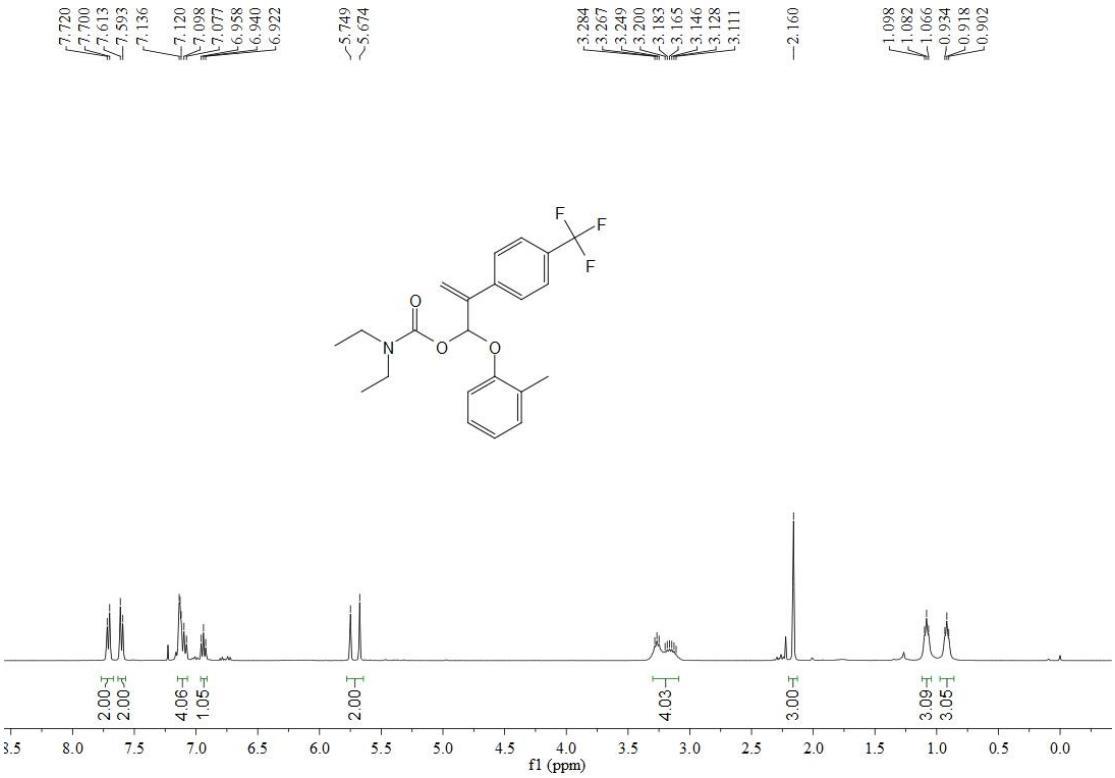
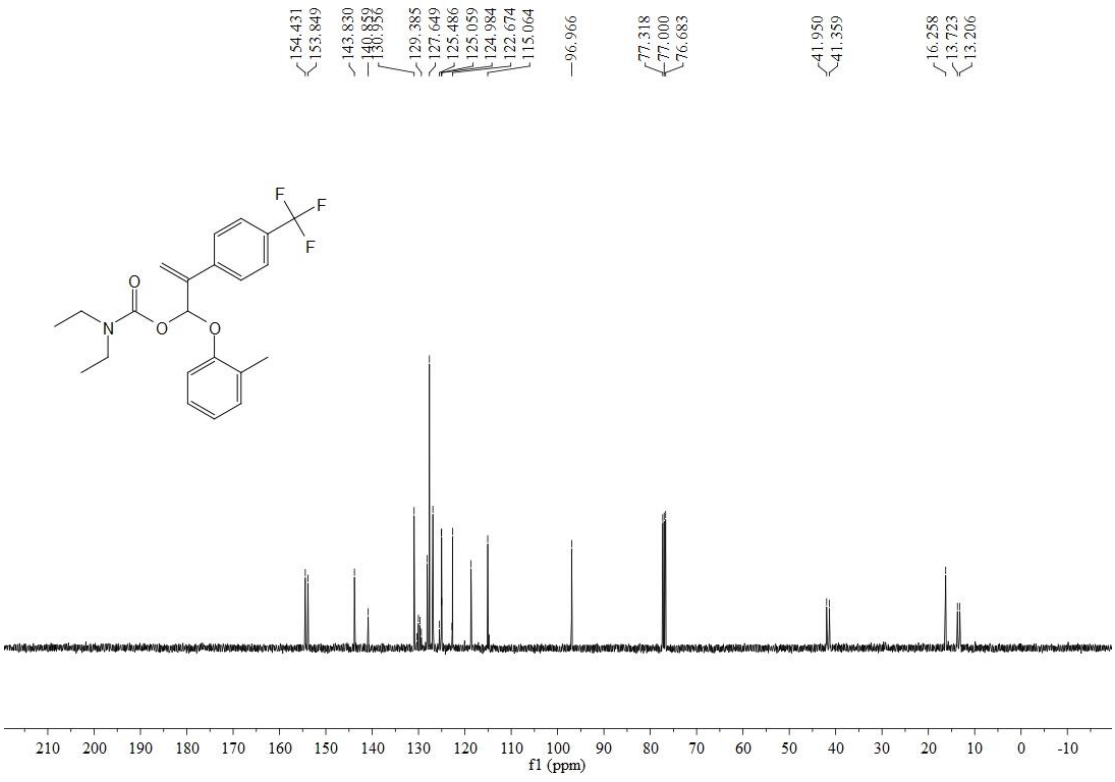
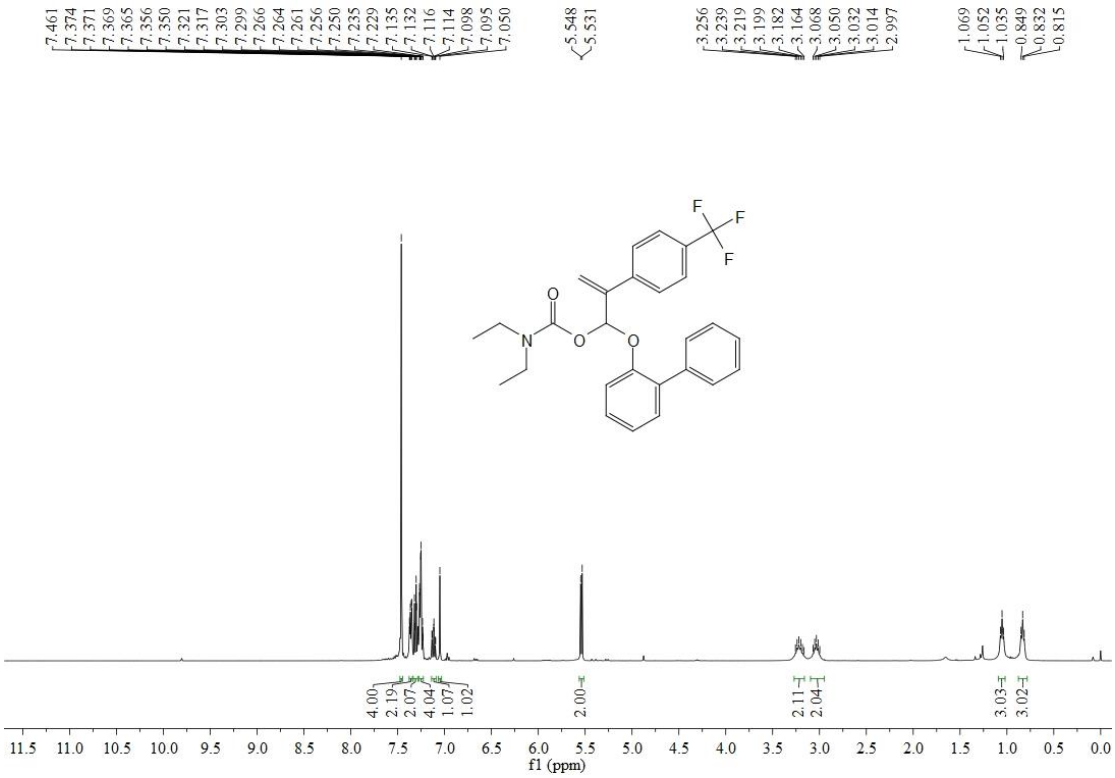
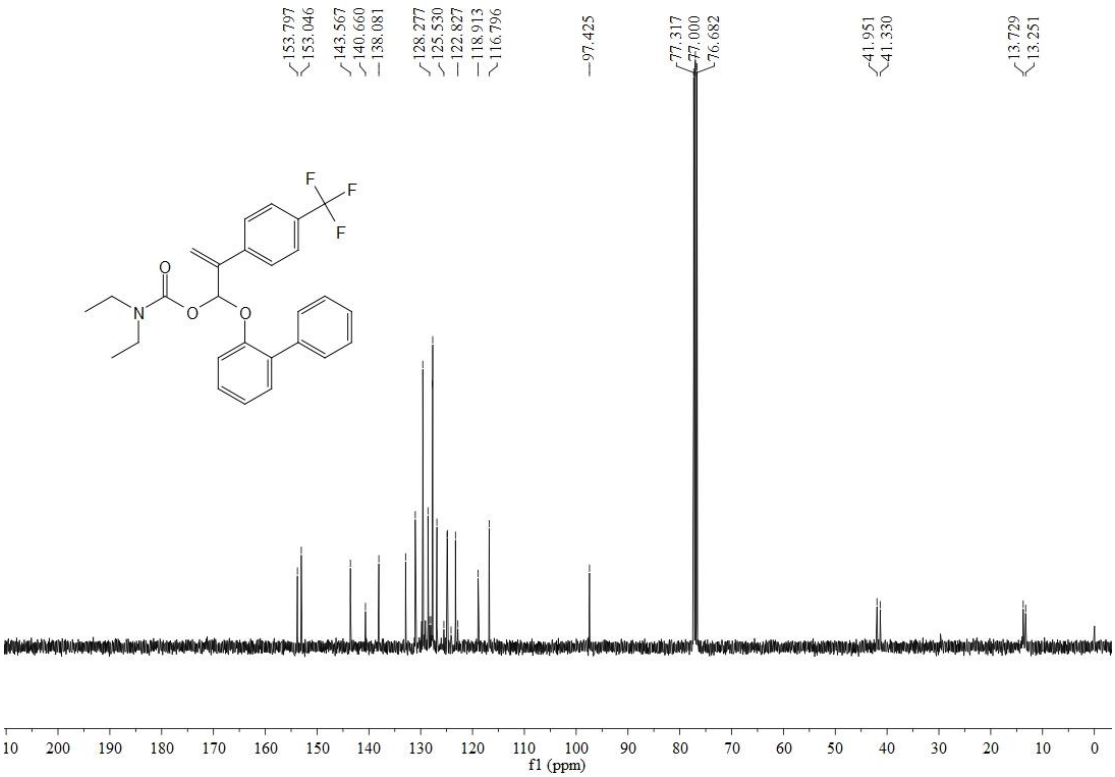


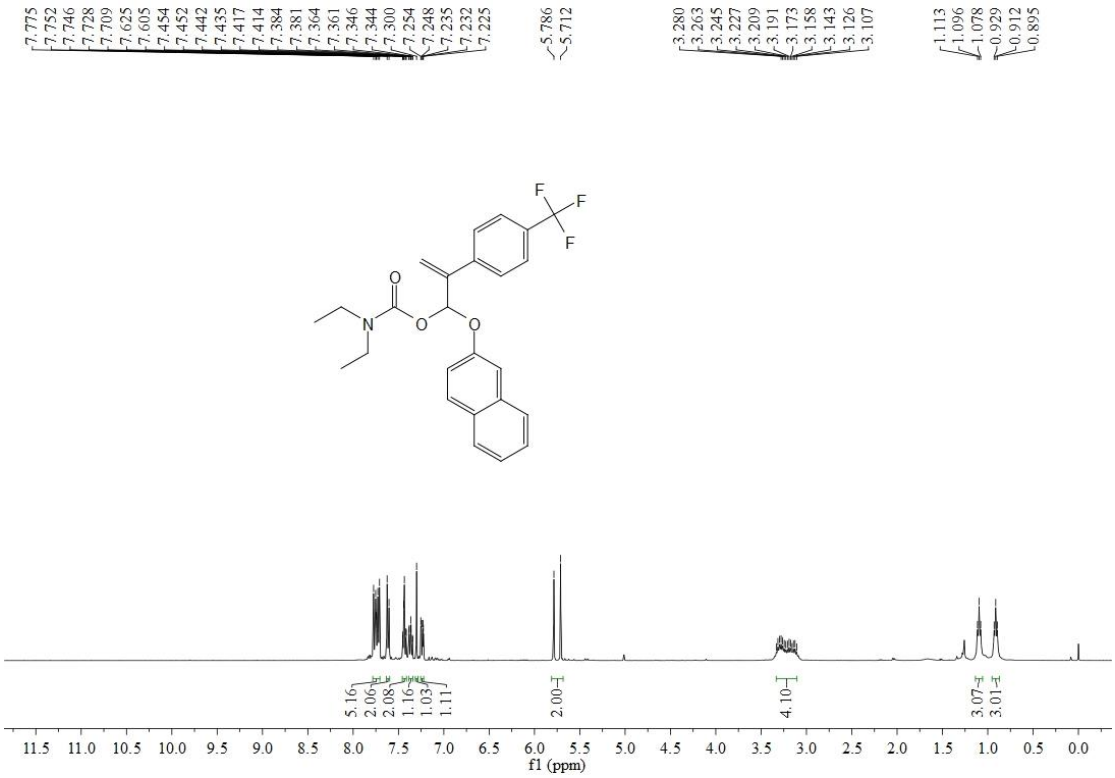


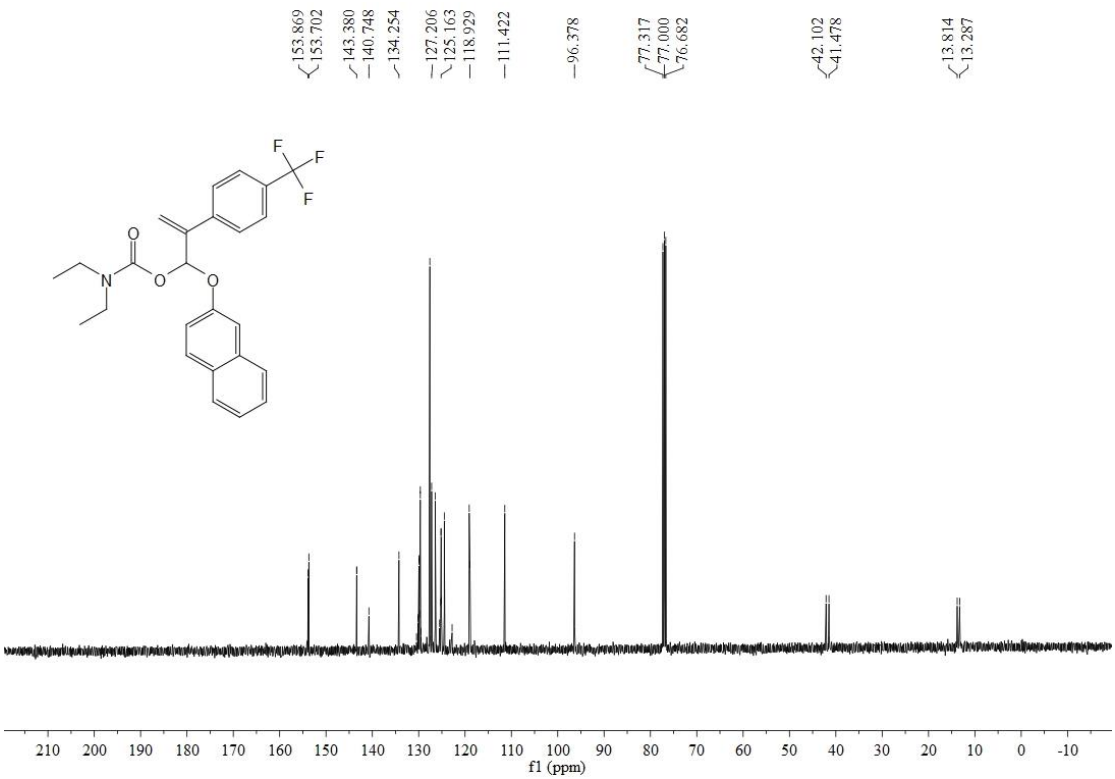
1-([1,1'-Biphenyl]-2-yloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4jia)



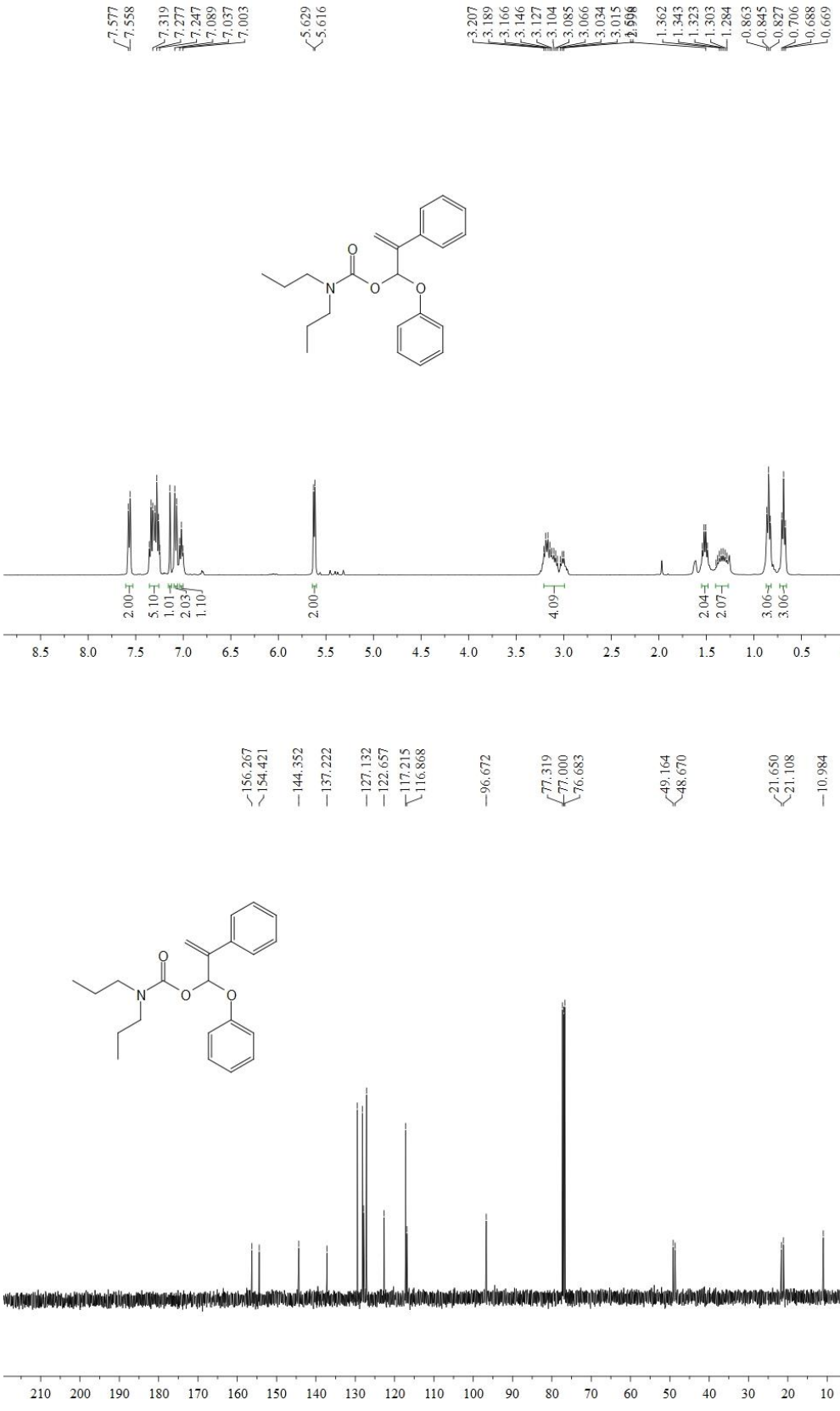


1-(Naphthalen-2-yloxy)-2-(4-(trifluoromethyl)phenyl)allyl diethylcarbamate (4kia)

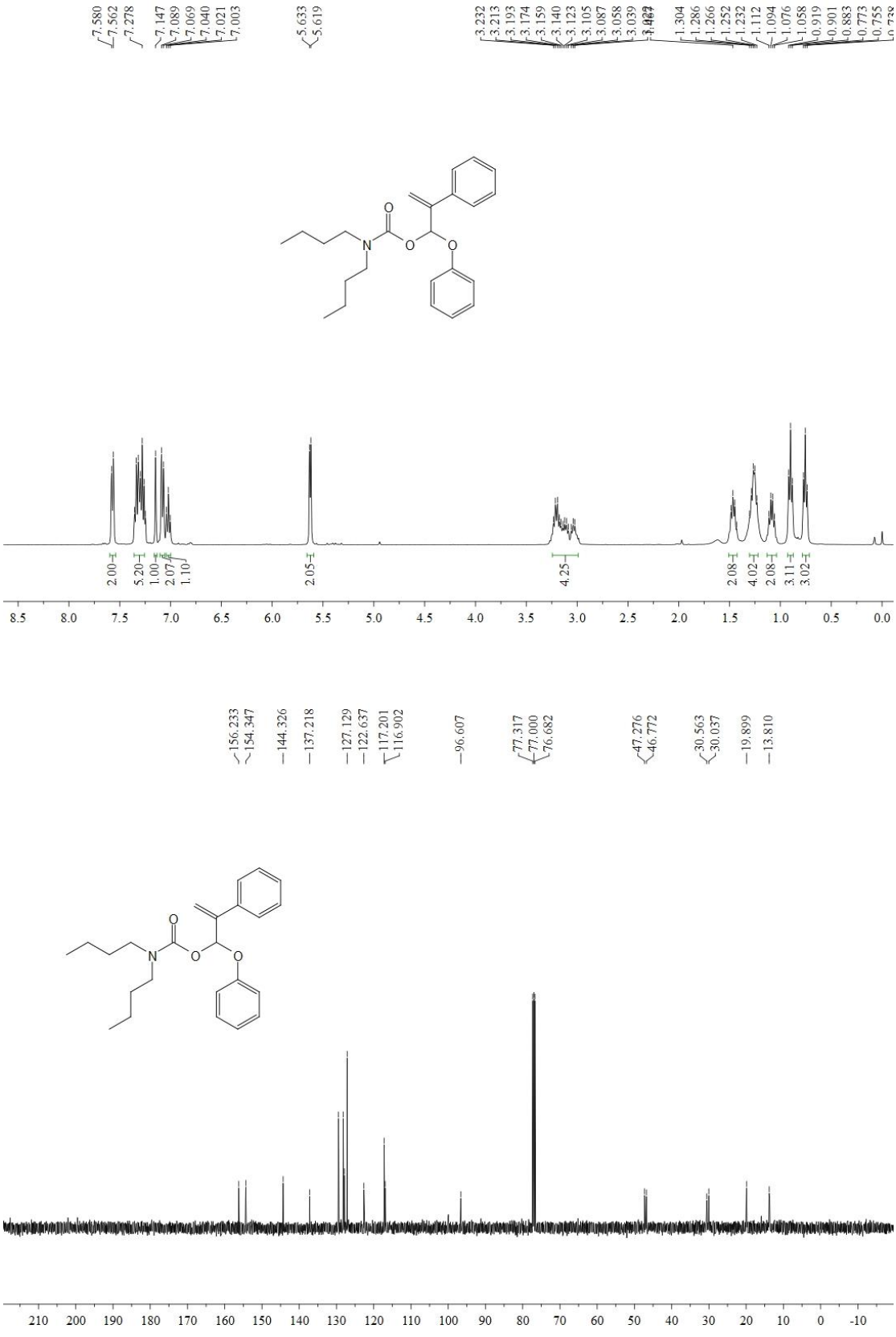




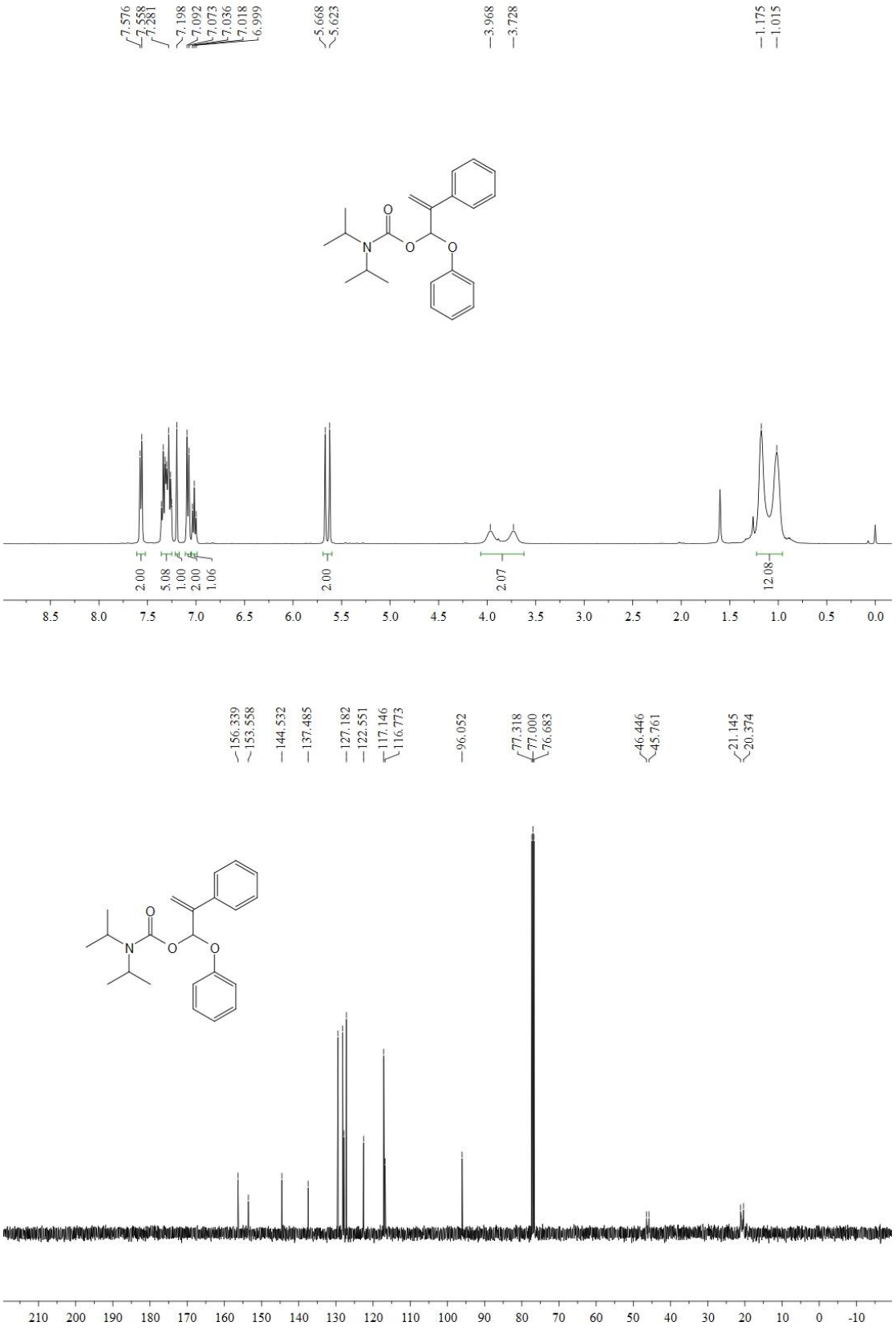
1-Phenoxy-2-phenylallyl dipropylcarbamate (4aab)



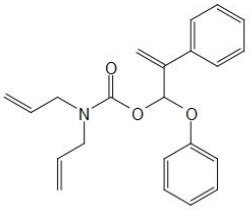
1-Phenoxy-2-phenylallyl dibutylcarbamate (4aac)

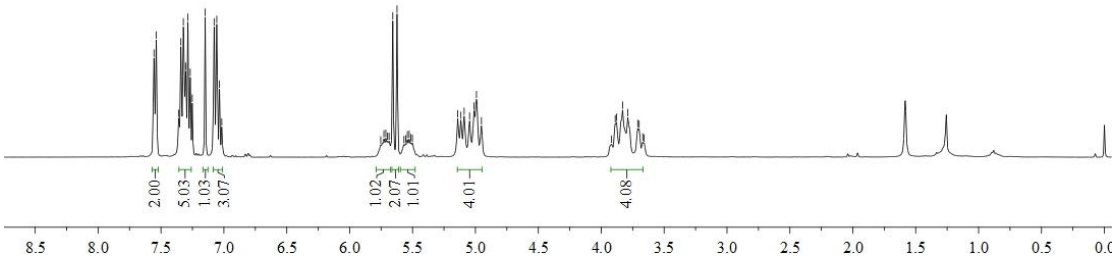


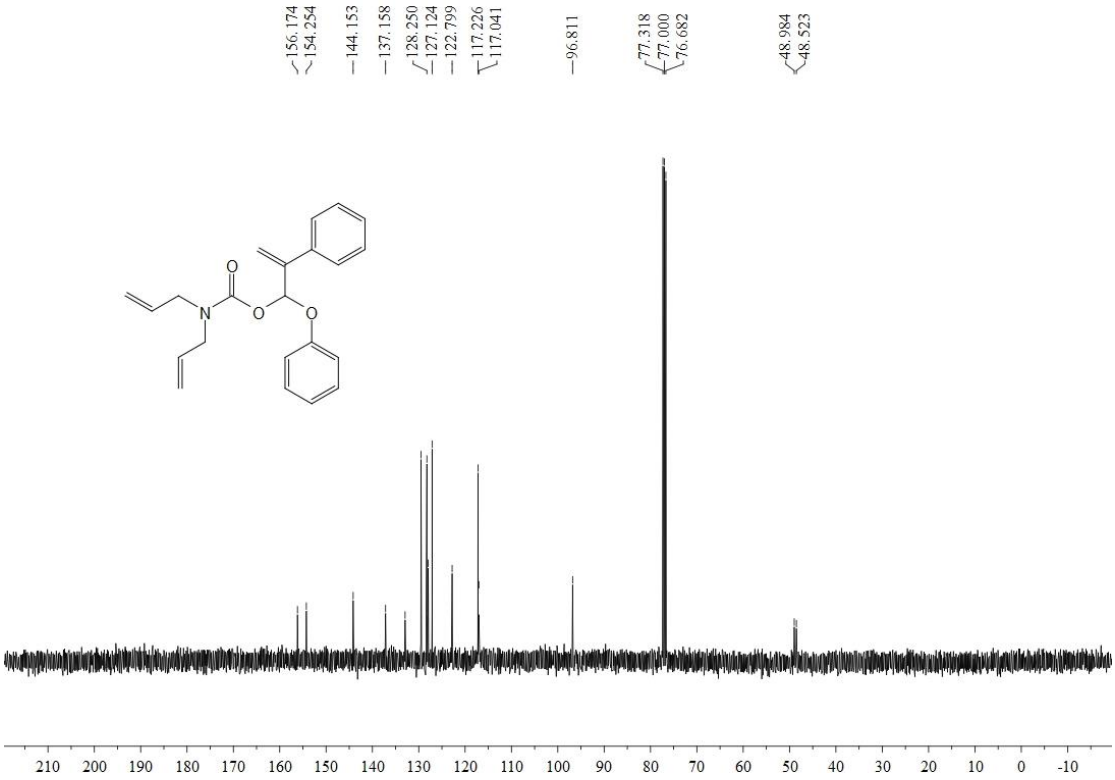
1-Phenoxy-2-phenylallyl diisopropylcarbamate (4aad)



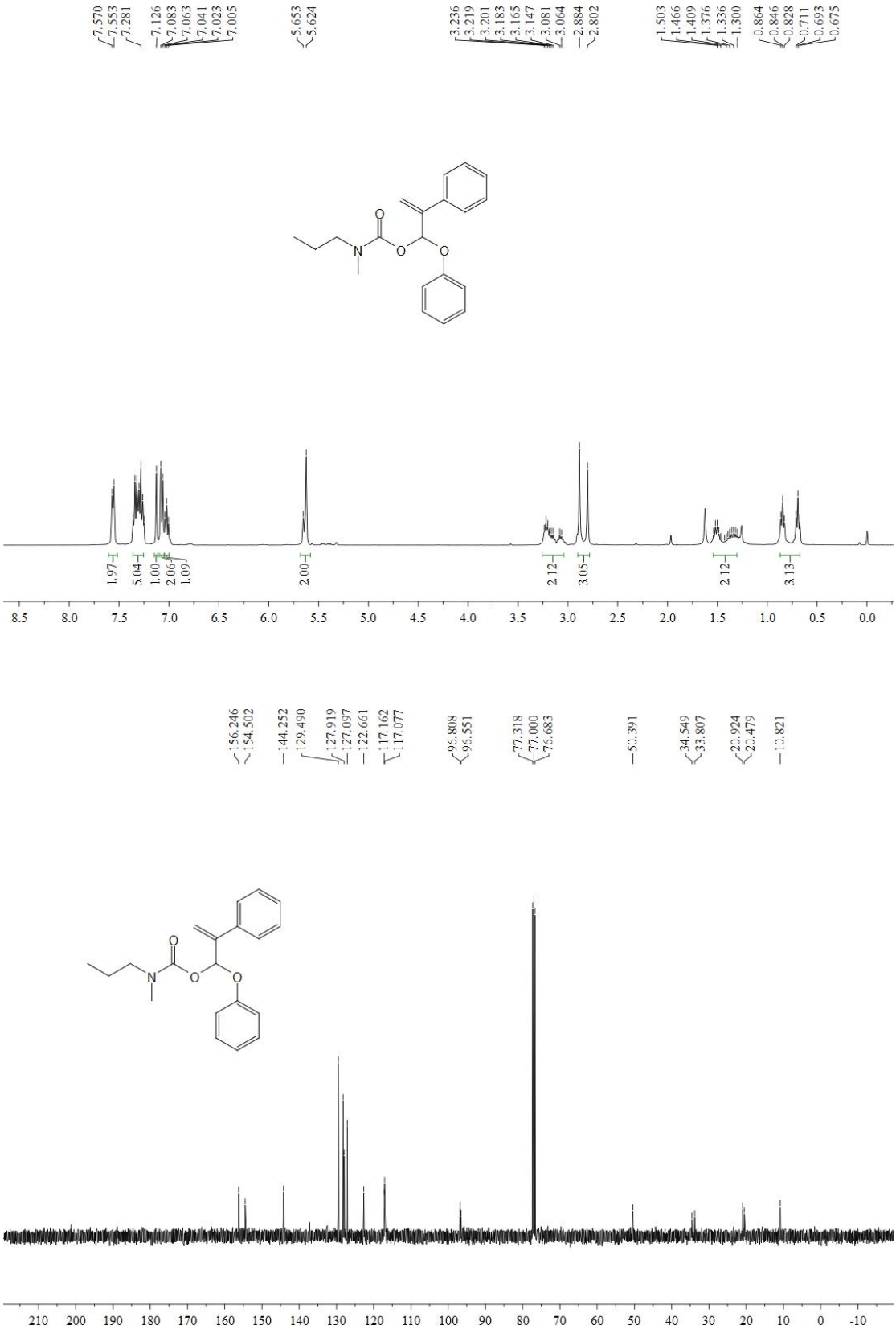
1-Phenoxy-2-phenylallyl diallylcarbamate (4aae)



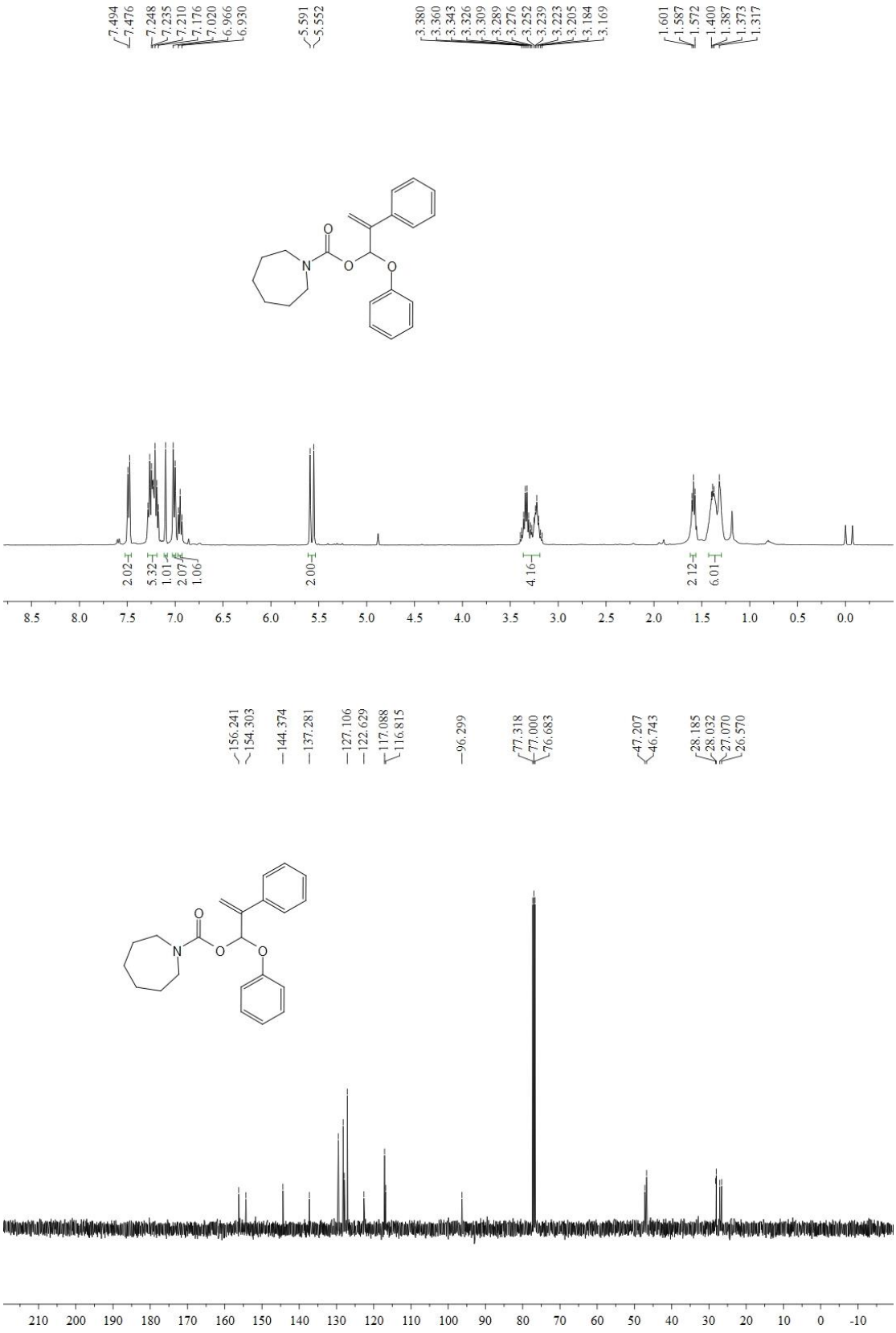




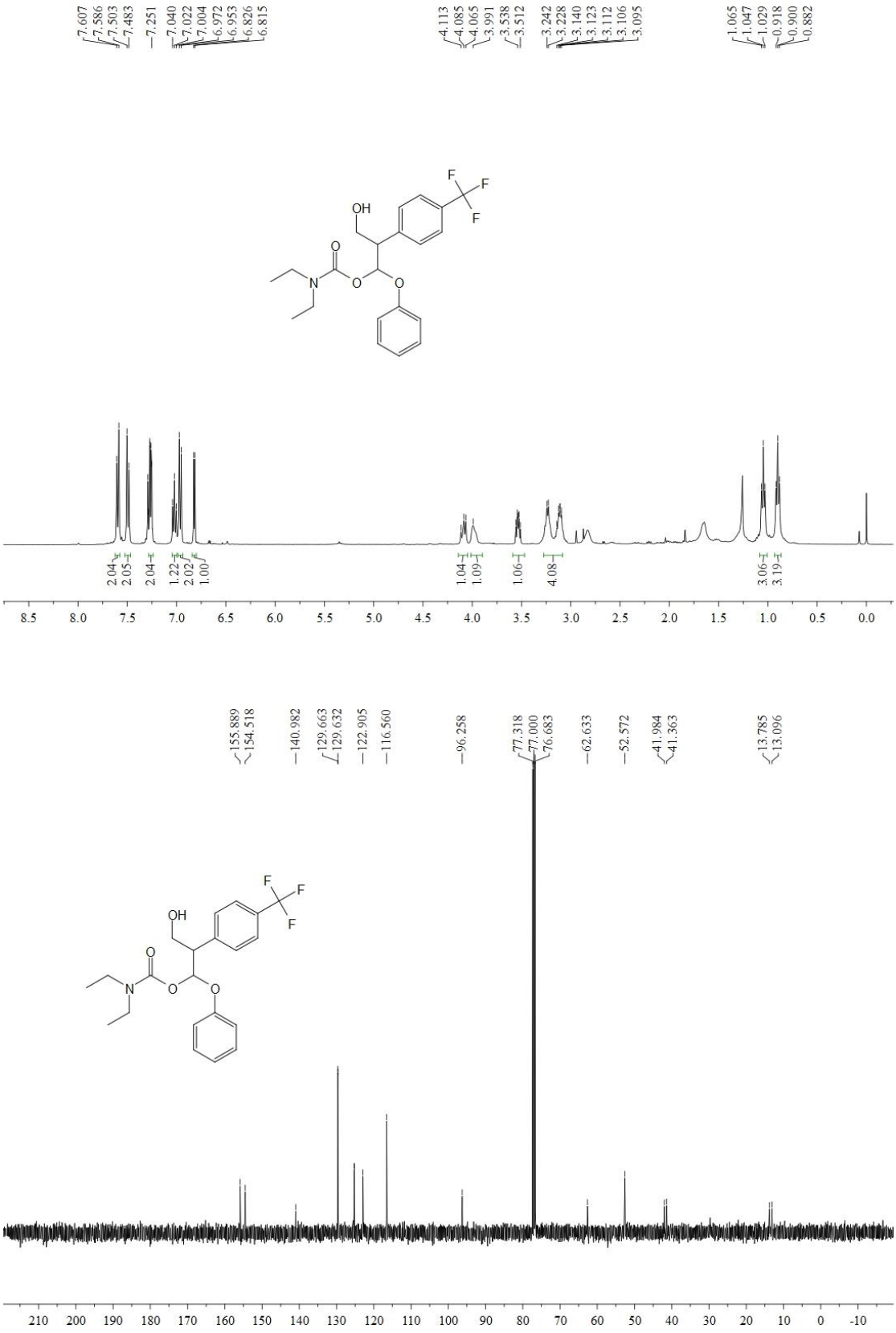
1-Phenoxy-2-phenylallyl methyl(propyl)carbamate (4aaf)



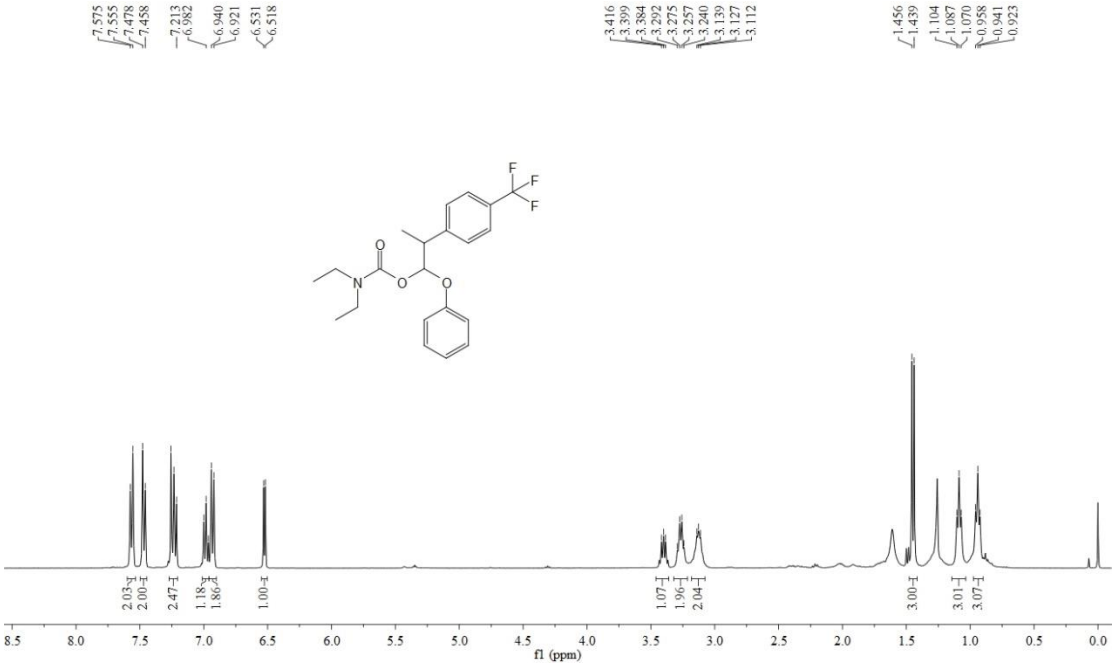
1-Phenoxy-2-phenylallyl azepane-1-carboxylate (4aag)

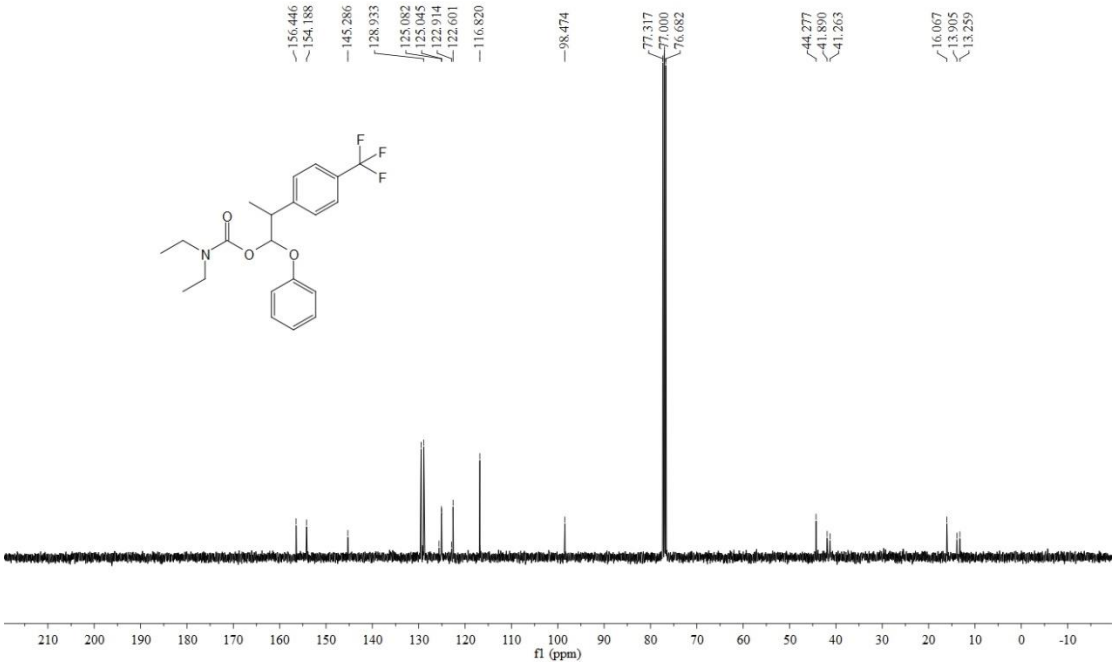


3-Hydroxy-1-phenoxy-2-(4-(trifluoromethyl)phenyl)propyl diethylcarbamate (5)

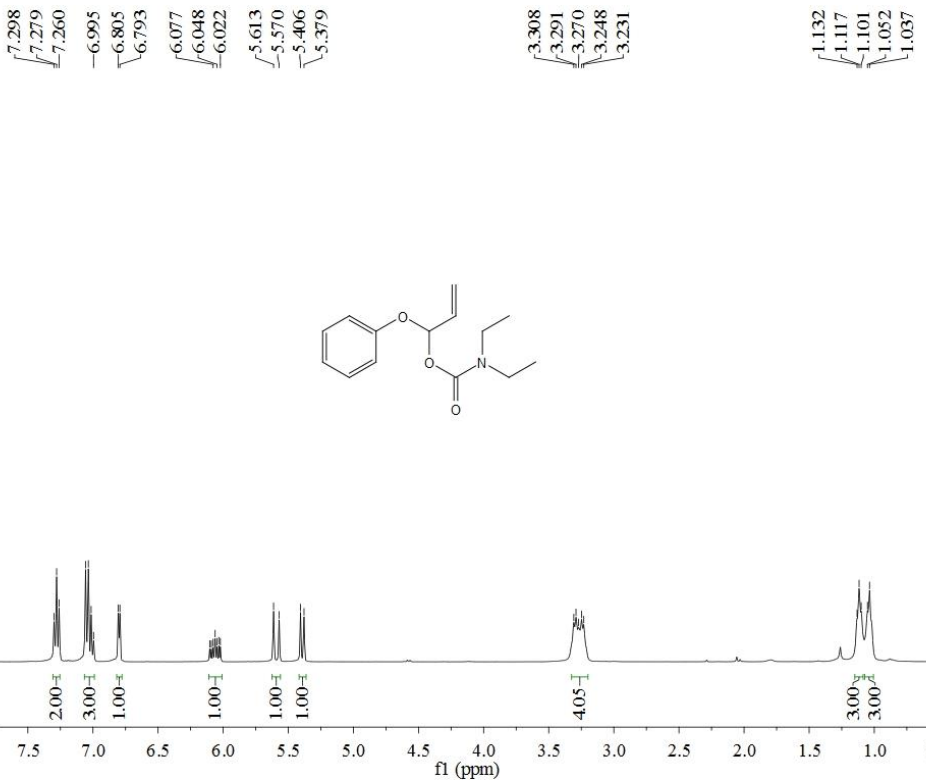


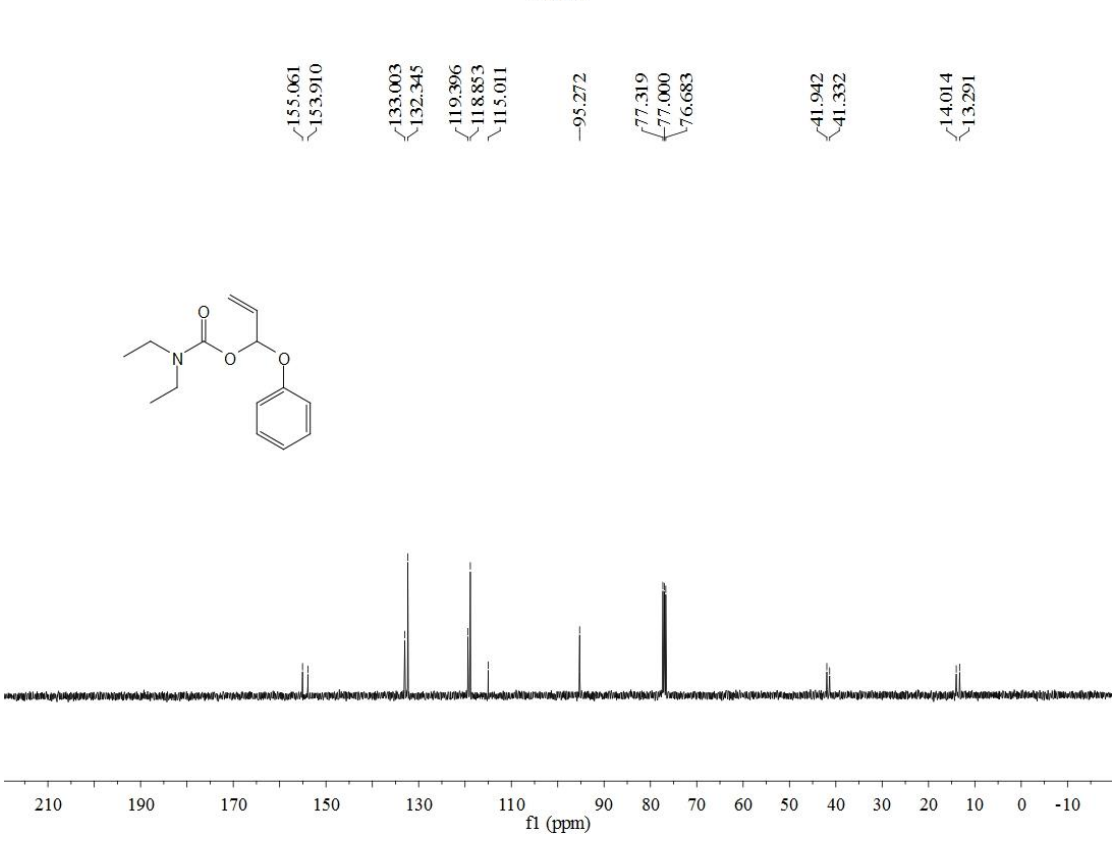
1-Phenoxy-2-(4-(trifluoromethyl)phenyl)propyl diethylcarbamate (6)





1-Phenoxyallyl diethylcarbamate (7)





Octyl diethylcarbamate (4sa)