

Supporting Information

Copper-catalyzed oxidative coupling reaction of arylboronic acids, amines and carbon dioxide using molecular oxygen as the oxidant

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A. General methods

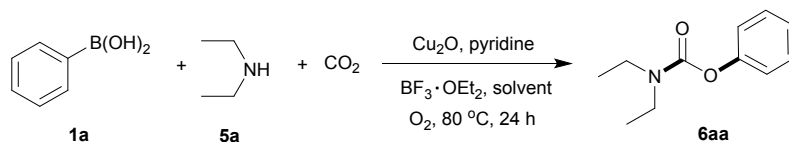
^1H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and CDCl_3 is used as a solvent with TMS as the internal standard. Mass spectra were recorded on a gas chromatograph-mass spectrometer. The data 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. All substrates were commercially purchased and used without further purification.

B. General procedure for the preparation of organic carbamates 6

to a 15 mL autoclave was added the mixture of boronic acid **1** (0.5 mmol), Cu_2O (0.05 mmol), amine **5** (2.5 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.5 mmol) and pyridine (1.5 mmol) in CH_2Cl_2 (3 mL) successively. Then, 0.4 MPa of O_2 and a certain amount of CO_2 were successively charged into the autoclave. The reaction mixture was heated to 80 °C under magnetic stirring and the pressure was adjusted to 4 MPa by introducing compressed CO_2 . After the reaction, the vessel was cooled with an ice bath and slowly depressurized to atmospheric pressure. The residual material 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 to give the desired product.

C. The optimization of reaction conditions

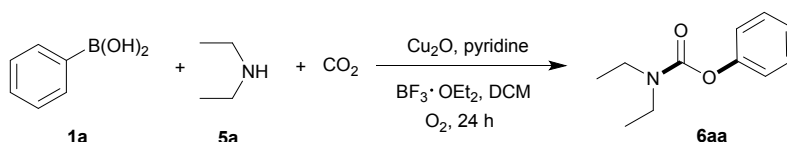
Table S1. The effect of solvent on the coupling of phenylboronic acid (**1a**), diethylamine (**5a**) and CO₂^a



entry	solvent	Yield (%) ^b
1	DCM	91(85)
2	DCE	46
3	DMF	67
4	THF	24
5	MeCN	10
6	1,4-dioxane	13
7	Toluene	68

^a Reaction conditions: **1a** (0.5 mmol), **5a** (2.5 mmol), Cu₂O (10 mol%), pyridine (3 equiv), BF₃·OEt₂ (3 equiv), solvent (3 mL), O₂ (0.4 MPa), total pressure (4.0 MPa), 80 °C, 24 h. ^bGC yield with dodecane as internal standard; number in parentheses is the yield of isolated product.

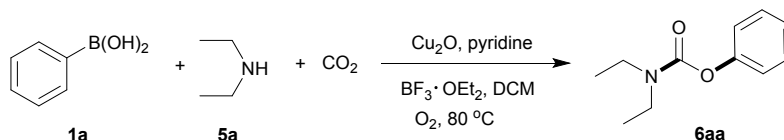
Table S2. The effect of temperature on the coupling of phenylboronic acid (**1a**), diethylamine (**5a**) and CO₂^a



entry	Temperature (°C)	Yield (%) ^b
1	25	trace
2	40	10
3	60	45
4	80	91(85)
5	100	64
6	120	47

^a Reaction conditions: **1a** (0.5 mmol), **5a** (2.5 mmol), Cu₂O (10 mol%), pyridine (3 equiv), BF₃·OEt₂ (3 equiv), solvent (3 mL), O₂ (0.4 MPa), total pressure (4.0 MPa), 24 h. ^bGC yield with dodecane as internal standard; number in parentheses is the yield of isolated product.

Table S3. The effect of reaction time on the coupling of phenylboronic acid (**1a**), diethylamine (**5a**) and CO₂^a



entry	Time (h)	Yield (%) ^b
1	6	37
2	12	78
3	18	72
4	24	91(85)

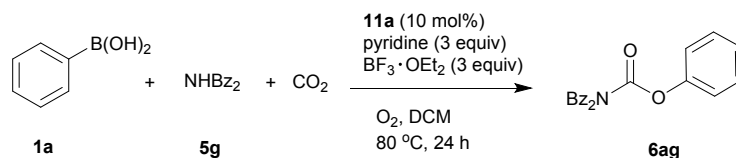
^a Reaction conditions: **1a** (0.5 mmol), **5a** (2.5 mmol), Cu₂O (10 mol%), pyridine (3 equiv), BF₃·OEt₂ (3 equiv), solvent (3 mL), O₂ (0.4 MPa), total pressure (4.0 MPa), 80 °C. ^bGC yield with dodecane as internal standard; number in parentheses is the yield of isolated product.

D. Procedure for the synthesis of complex **11a**

To a 15 mL autoclave was added the mixture of Cu₂O (72.5 mg, 0.5 mmol), dibenzylamine (2.364 g, 12 mmol) in dichloromethane (5 mL). Then, 0.4 MPa of O₂ and a certain amount of CO₂ were successively charged into the autoclave. The reaction mixture was heated to 80 °C under magnetic stirring and the pressure was adjusted to 4 MPa by introducing compressed CO₂. After 24 hours, the reaction was completed, and the vessel was cooled with an ice bath and slowly depressurized to atmospheric pressure. After evaporation of the solvent, a blue-violet solid residue was obtained, which was further purified by washing with heptane (3 × 15 mL) and drying under vacuum to give the desired complex **11a** (0.785 g; 84%). Anal. Calc. for C₅₈H₅₈N₄O₄Cu: C, 74.1; H, 6.2; N, 6.0; Cu, 6.8; CO₂, 9.4. Found: C, 73.6; H, 6.3; N, 5.8; CO₂, 9.5; Cu, 7.4. IR (KBr): 3107, 3028, 2887, 1569, 1457, 1407, 1268, 1208, 1136, 1056, 1009, 963, 892, 799, 746, 695, 593 cm⁻¹. The analytic data match those reported in previous literature. [1]

E. The effect of different conditions on the reactions catalyzed by complex **11a**

Table S4. The effect of different conditions on phenylboronic acid (**1a**), dibenzylamine (**5g**) and CO₂ catalyzed by complex **11a**^a



standard conditons

entry	Variation from standard conditions	Yield (%) ^b
1	None	89
2	Without pyridine	trace
3	Without BF ₃ ·OEt ₂	13
4	Nitrogen instead of O ₂	trace
15	1.5 equiv pyridine and 1.5 equiv BF ₃ ·OEt ₂ were employed	43

^a Standard conditions: **1a** (0.5 mmol), **5g** (2.5 mmol), **11a** (10 mol %), pyridine (3 equiv), BF₃·OEt₂ (3 equiv),

DCM (3 mL), O₂ (0.4 MPa), total pressure (4.0 MPa), 80 °C, 24 h. ^b Isolated product.

F. Crystal structure determination

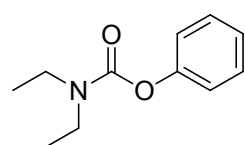
Single-crystal X-ray diffraction data for **6lg** were collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Crystallographic data for compound **6lg** is given in Table S5.

Table S5. Crystal data and structure refinements for **6lg**

Compound	6lg
Empirical formula	C ₂₇ H ₂₃ NO ₂
Formula weight	393.46
Temperature (K)	150(10)
Wavelength (Å)	1.54184
Crystal system	triclinic
Space group	<i>P</i> - 1
	$a = 10.4147(5)$ Å $\alpha = 63.221(7)^\circ$ $b = 10.8221(8)$ Å $\beta = 63.896(5)^\circ$ $c = 11.4326(7)$ Å $\gamma = 74.519(5)^\circ$
Volume (Å ³)	1029.22(11)
Z	2
Density (calcd g cm ⁻³)	1.270
Absorption coeff. (mm ⁻¹)	0.626
<i>F</i> (000)	416
Crystal size (mm)	0.42 × 0.31 × 0.24
Crystal color and shape	Colourless block
θ range for data collection	4.7540 to 70.7650
Limiting indices	-11 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 12, -13 ≤ <i>l</i> ≤ 13
Reflections collected	6952
Unique	3823 [<i>R</i> _{int} = 0.0162]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3823/0/271
Goodness-of-fit on F^2	1.060
Final <i>R</i> indexes [<i>I</i> >= 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0353, <i>wR</i> ₂ = 0.0910
<i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0374, <i>wR</i> ₂ = 0.0927

G. Analytical data

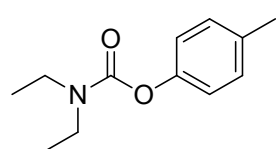
Phenyl diethylcarbamate (6aa).² Pale yellow oil (82.0 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ



= 7.35 (t, J = 7.2 Hz, 2 H), 7.23 – 7.08 (m, 3 H), 3.49 – 3.34 (m, 4 H), 1.23 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.1, 151.4, 129.0, 124.9, 121.6, 42.1, 41.8, 14.1, 13.2. IR (KBr): 2976, 2935, 1722, 1470, 1419,

1380, 1273, 1205, 1158, 1094, 1042, 960, 907, 786, 748, 690 cm⁻¹. MS (EI) m/z : 193[M⁺], 100(100), 77, 72. HRMS-ESI (m/z): calcd for C₁₁H₁₅NO₂Na [M + Na]⁺: 216.0995; found: 216.0999.

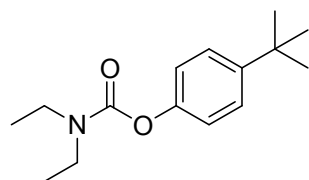
***p*-Tolyl diethylcarbamate (6ba).**² Pale yellow oil (65.2 mg, 63%). ¹H NMR (400 MHz, CDCl₃): δ



= 7.14 (d, J = 7.6 Hz, 2 H), 7.00 (d, J = 7.6 Hz, 2 H), 3.42 (br, 4 H), 2.33 (s, 3 H), 1.26 – 1.17 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 149.3, 134.5, 129.6, 121.4, 42.1, 41.8, 20.8, 14.2, 13.4. IR (KBr):

2974, 2929, 1720, 1512, 1471, 1419, 1380, 1273, 1207, 1156, 1098, 1043, 1019, 961, 747 cm⁻¹. MS (EI) m/z : 207[M⁺], 100(100), 77, 72. HRMS-ESI (m/z): calcd for C₁₂H₁₈NO₂ [M + H]⁺: 208.1332; found: 208.1333.

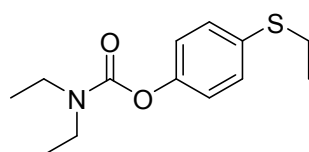
4-(Tert-butyl)phenyl diethylcarbamate (6ca).² Colourless solid (114.5 mg, 92%), mp: 78 – 80



°C. ¹H NMR (400 MHz, CDCl₃): δ = 7.37 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 3.42 (br, 4 H), 1.32 (s, 9 H), 1.23 (br, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 149.1, 147.7, 126.0, 121.0, 42.2, 41.8, 34.3, 31.4, 14.2, 13.3. IR (KBr): 2968, 2872, 2934, 1712,

1513, 1478, 1419, 1378, 1276, 1212, 1176, 1158, 1104, 1042, 1018, 960, 864, 756, 551 cm⁻¹. MS (EI) m/z : 249[M⁺], 135, 100(100), 91, 72. HRMS-ESI (m/z): calcd for C₁₅H₂₃NO₂Na [M + Na]⁺: 272.1621; found: 272.1621.

4-(Ethylthio)phenyl diethylcarbamate (6da). Pale yellow oil (65.6 mg, 52%). ¹H NMR (400

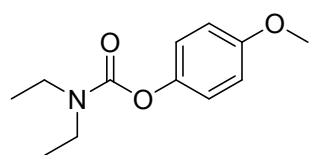


MHz, CDCl₃): δ = 7.33 (d, J = 7.2 Hz, 2 H), 7.05 (d, J = 7.2 Hz, 2 H), 3.49 – 3.30 (m, 4 H), 2.96 – 2.82 (m, 2 H), 1.28 – 1.18 (m, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.0, 150.1, 132.4, 130.9, 122.2,

42.2, 41.9, 29.6, 28.6, 14.2, 14.2, 13.3. IR (KBr): 2973, 2929, 2871, 1722, 1471, 1419, 1379, 1316, 1273, 1208, 1155, 1093, 1042, 1014, 960, 857, 780, 755, 512 cm⁻¹. MS (EI) m/z : 253[M⁺], 153,

125, 100(100), 72. HRMS-ESI (m/z): calcd for $C_{13}H_{20}NO_2S$ [$M + H$] $^+$: 254.1209; found: 254.1209.

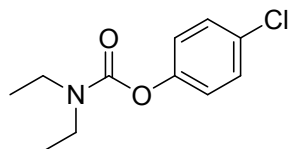
4-Methoxyphenyl diethylcarbamate (6ea).³ Pale yellow oil (43.4 mg, 39%). 1H NMR (400



MHz, $CDCl_3$): δ = 7.03 (d, J = 8.0 Hz, 2 H), 6.86 (d, J = 8.4 Hz, 2 H), 3.79 (s, 3 H), 3.40 (br, 4 H), 1.26 – 1.15 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 154.6, 145.1, 122.5, 114.3, 55.6, 42.2, 41.8,

14.2, 13.4. IR (KBr): 2972, 2931, 2849, 1719, 1510, 1469, 1419, 1379, 1274, 1202, 1154, 1098, 1037, 961, 854, 753, 521 cm^{-1} . MS (EI) m/z : 223[M^+], 109, 100(100), 72. HRMS-ESI (m/z): calcd for $C_{12}H_{18}NO_3$ [$M + H$] $^+$: 224.1281; found: 224.1281.

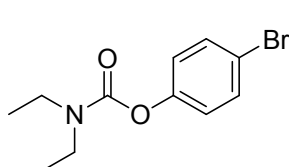
4-Chlorophenyl diethylcarbamate (6fa).² Pale yellow oil (63.2 mg, 56%). 1H NMR (400 MHz,



$CDCl_3$): δ = 7.31 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.4 Hz, 2 H), 3.46 – 3.34 (m, 4 H), 1.27 – 1.17 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 150.0, 130.3, 129.2, 123.1, 42.3, 41.9, 14.2, 13.3. IR

(KBr): 2976, 2932, 1723, 1475, 1419, 1380, 1316, 1274, 1209, 1155, 1088, 1041, 1013, 959, 857, 753, 504 cm^{-1} . MS (EI) m/z : 227[M^+], 128, 100(100), 79, 72. HRMS-ESI (m/z): calcd for $C_{11}H_{14}ClNO_2Na$ [$M + Na$] $^+$: 250.0605; found: 250.0605.

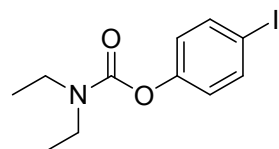
4-Bromophenyl diethylcarbamate (6ga).² Pale yellow oil (92.1 mg, 68%). 1H NMR (400 MHz,



$CDCl_3$): δ = 7.45 (d, J = 8.0 Hz, 2 H), 7.01 (d, J = 8.4 Hz, 2 H), 3.45 – 3.34 (m, 4 H), 1.26 – 1.16 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 150.6, 132.1, 123.5, 117.9, 42.3, 41.9, 14.2, 13.3. IR (KBr):

2975, 2931, 1722, 1473, 1419, 1273, 1208, 1154, 1095, 1069, 1040, 1010, 959, 857, 752 cm^{-1} . MS (EI) m/z : 271[M^+], 273, 171, 100(100), 72. HRMS-ESI (m/z): calcd for $C_{11}H_{15}BrNO_2$ [$M + H$] $^+$: 272.0281; found: 272.0281.

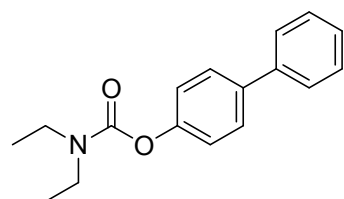
4-Iodophenyl diethylcarbamate (6ha). Pale yellow oil (113.0 mg, 71%). 1H NMR (400 MHz,



$CDCl_3$): δ = 7.64 (d, J = 8.4 Hz, 2 H), 6.89 (d, J = 8.4 Hz, 2 H), 3.44 – 3.33 (m, 4 H), 1.25 – 1.16 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 151.4, 138.1, 123.9, 88.7, 42.2, 41.8, 14.2, 13.3. IR (KBr): 2974,

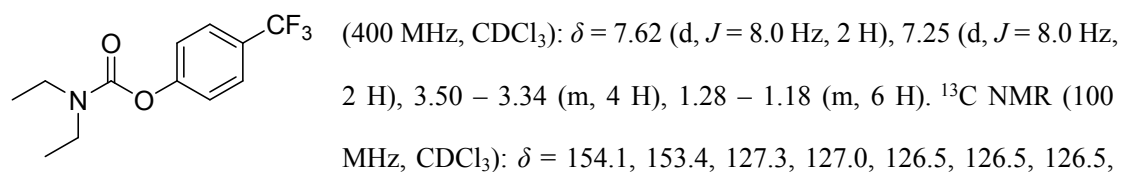
2930, 2879, 1722, 1474, 1419, 1273, 1209, 1154, 1094, 1042, 1008, 959, 856, 647, 498 cm^{-1} . MS (EI) m/z : 319[M^+], 100(100), 191, 72. HRMS-ESI (m/z): calcd for $C_{11}H_{14}INO_2Na$ [$M + Na$] $^+$: 341.9961; found: 341.9961.

[1,1'-Biphenyl]-4-yl diethylcarbamate (6ia).⁴ Pale yellow oil



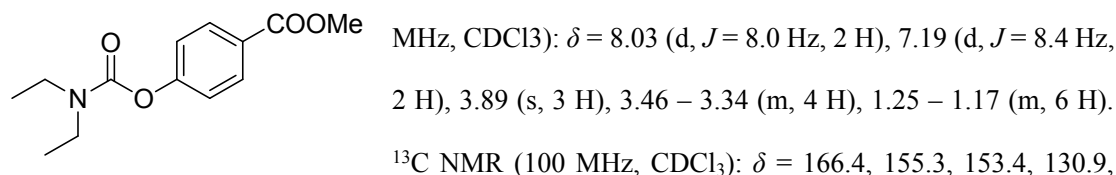
(74.3 mg, 55%). ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (d, *J* = 8.0 Hz, 4 H), 7.41 (t, *J* = 7.2 Hz, 2 H), 7.31 (t, *J* = 6.8 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 2 H), 3.52 – 3.34 (m, 4 H), 1.30 – 1.15 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.1, 151.0, 140.6, 138.1, 128.7, 127.9, 127.1, 127.0, 121.9, 42.2, 41.8, 14.2, 13.3. IR (KBr): 2975, 2931, 1719, 1474, 1418, 1379, 1273, 1210, 1153, 1097, 1042, 1008, 960, 758, 697 cm⁻¹. MS (EI) *m/z*: 269[M⁺], 207, 115, 100(100), 72. HRMS-ESI (*m/z*): calcd for C₁₇H₂₀NO₂ [M + H]⁺: 270.1489; found: 270.1490.

3-(Trifluoromethyl)phenyl diethylcarbamate (6ja). Pale yellow oil (58.5 mg, 45%). ¹H NMR



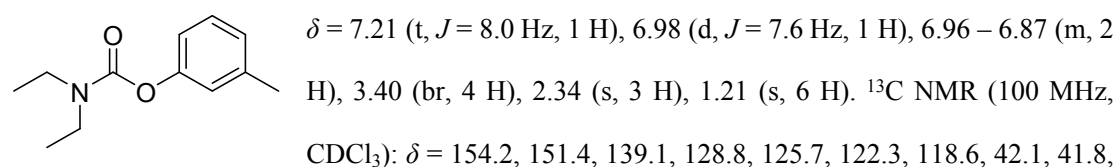
126.4, 125.4, 122.7, 122.0, 42.4, 42.0, 14.2, 13.2. IR (KBr): 2980, 2930, 2852, 1726, 1472, 1420, 1381, 1326, 1274, 1215, 1160, 1126, 1066, 1041, 1016, 959, 865, 752 cm⁻¹. MS (EI) *m/z*: 261[M⁺], 145, 113, 100(100), 72. HRMS-ESI (*m/z*): calcd for C₁₂H₁₄F₃NNaO₂ [M + Na]⁺: 284.0869; found: 284.0869.

Methyl 4-((diethylcarbamoyl)oxy)benzoate (6ka).⁵ Yellow oil (75.1 mg, 60%). ¹H NMR (400



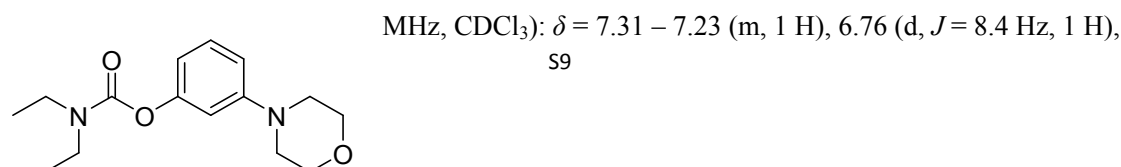
126.7, 121.5, 52.0, 42.3, 41.9, 14.2, 13.2. IR (KBr): 2976, 2953, 2928, 1725, 1505, 1472, 1419, 1381, 1275, 1211, 1159, 1111, 1040, 1016, 960, 873, 759, 695 cm⁻¹. MS (EI) *m/z*: 251[M⁺], 200, 121, 100(100), 72. HRMS-ESI (*m/z*): calcd for C₁₃H₁₈NO₄ [M + H]⁺: 252.1230; found: 252.1230.

***m*-Tolyl diethylcarbamate (6la).**² Pale yellow oil (92.0 mg, 89%). ¹H NMR (400 MHz, CDCl₃):



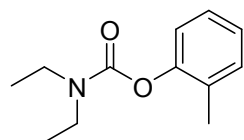
21.1, 14.1, 13.3. IR(KBr): 2976, 2932, 2879, 1722, 1612, 1593, 1472, 1416, 1379, 1315, 1274, 1245, 1160, 1090, 1045, 1000, 965, 909, 765, 688. MS (EI) *m/z*: 207[M⁺], 100(100), 77, 72. HRMS-ESI (*m/z*): calcd for C₁₂H₁₈NO₂ [M + H]⁺: 208.1332; found: 208.1332.

3-Morpholinophenyl diethylcarbamate (6ma). Pale yellow oil (65.1 mg, 47%). ¹H NMR (400



6.72 – 6.64 (m, 2 H), 3.89 – 3.84 (m, 4 H), 3.44 (br, 4 H), 3.21 – 3.17 (m, 4 H), 1.29 – 1.20 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.2, 152.5, 152.3, 129.5, 113.0, 112.3, 109.1, 66.8, 49.1, 42.1, 41.8, 14.2, 13.4. IR (KBr): 2965, 2927, 2854, 1718, 1451, 1416, 1379, 1268, 1174, 1120, 1046, 982, 933, 879, 759, 686 cm⁻¹. MS (EI) *m/z*: 278[M⁺], 121, 100(100), 72. HRMS-ESI (*m/z*): calcd for C₁₅H₂₂N₂O₃Na [M + Na]⁺: 301.1523; found: 301.1523.

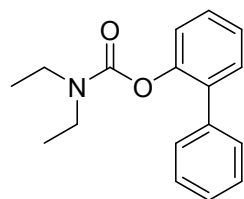
***o*-Tolyl diethylcarbamate (6na).**² Pale yellow oil (51.6 mg, 50%). ¹H NMR (400 MHz, CDCl₃):



δ = 7.25 – 7.16 (m, 2 H), 7.11 (d, *J* = 7.2 Hz, 1 H), 7.07 (d, *J* = 8.4 Hz, 1 H), 3.52 – 3.37 (m, 4 H), 2.23 (s, 3 H), 1.30 – 1.19 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 153.9, 145.0, 130.8, 130.4, 126.7, 125.3, 122.1,

42.2, 41.8, 16.2, 14.2, 13.4. IR (KBr): 2975, 2931, 2879, 1720, 1468, 1417, 1379, 1317, 1274, 1225, 1181, 1156, 1111, 1042, 961, 749 cm⁻¹. MS (EI) *m/z*: 207[M⁺], 107, 100(100), 91, 77, 72. HRMS-ESI (*m/z*): calcd for C₁₂H₁₈NO₂ [M + H]⁺: 208.1332; found: 208.1332.

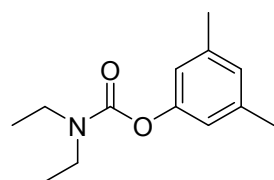
[1,1'-Biphenyl]-2-yl diethylcarbamate (6oa).⁶ Pale yellow oil (70.1 mg, 52%). ¹H NMR (400



MHz, CDCl₃): δ = 7.46 – 7.28 (m, 7 H), 7.27 – 7.18 (m, 2 H), 3.23 (br, 4 H), 1.09 – 0.92 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.0, 148.5, 138.1, 135.1, 130.6, 129.0, 128.2, 128.0, 127.1, 125.4, 123.2, 41.9, 41.5, 13.8, 13.1. IR (KBr): 2975, 2932, 2879, 1719, 1473, 1419, 1380, 1316, 1274, 1199, 1154, 1102, 1046, 1010, 960, 750, 701 cm⁻¹. MS (EI) *m/z*:

269[M⁺], 207, 115, 100(100), 72. HRMS-ESI (*m/z*): calcd for C₁₇H₂₀NO₂ [M + H]⁺: 270.1489; found: 270.1490.

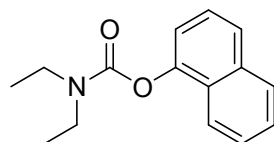
3,5-Dimethylphenyl diethylcarbamate (6pa).⁷ Pale yellow oil (94.0 mg, 85%). ¹H NMR (400



MHz, CDCl₃): δ = 6.82 (s, 1 H), 6.74 (s, 2 H), 3.40 (br, 4 H), 2.30 (s, 6 H), 1.26 – 1.17 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.4, 151.4, 138.9, 126.8, 119.4, 42.1, 41.8, 21.2, 14.2, 13.4. IR(KBr): 2973, 2927, 2863, 1721, 1469, 1417, 1379, 1266, 1161, 1096, 1055, 1016,

967, 916, 855, 783, 756 cm⁻¹. MS (EI) *m/z*: 221[M⁺], 100(100), 77, 72. HRMS-ESI (*m/z*): calcd for C₁₃H₂₀NO₂ [M + H]⁺: 222.1489; found: 222.1489.

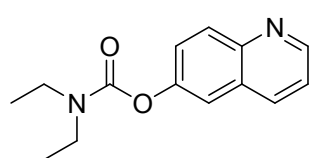
Naphthalen-1-yl diethylcarbamate (6qa).³ Pale yellow oil (99.5 mg, 82%). ¹H NMR (400 MHz,



CDCl₃): δ = 7.89 – 7.79 (m, 3 H), 7.62 (s, 1 H), 7.52 – 7.42 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 3.56 – 3.40 (m, 4 H), 1.34 – 1.22 (m, 6 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.2, 149.1, 133.8, 131.0, 129.0, 127.6, 127.4, 126.2, 125.2, 121.6, 118.3, 42.2, 41.8, 14.2, 13.3$. IR (KBr): 2976, 2932, 2877, 1719, 1511, 1465, 1418, 1378, 1316, 1274, 1244, 1212, 1161, 1090, 1041, 970, 862, 805, 745 cm^{-1} . MS (EI) m/z : 243 $[\text{M}^+]$, 115, 100(100), 72. HRMS-ESI (m/z): calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 266.1151; found: 266.1151.

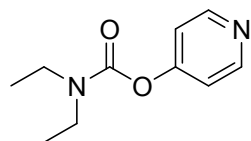
Quinolin-6-yl diethylcarbamate (6ra). Pale yellow oil (54.5 mg, 45%). ^1H NMR (400 MHz,



CDCl_3): $\delta = 8.88 - 8.82$ (m, 1 H), 8.09 (d, $J = 8.8$ Hz, 2 H), 7.58 (s, 1 H), 7.50 (d, $J = 9.2$ Hz, 1 H), 7.40 – 7.34 (m, 1 H), 3.51 – 3.38 (m, 4 H), 1.31 – 1.20 (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.9,$

149.7, 149.4, 145.9, 135.7, 130.5, 128.5, 125.2, 121.3, 118.1, 42.3, 42.0, 14.2, 13.3. IR (KBr): 2974, 2931, 1721, 1501, 1473, 1417, 1378, 1318, 1273, 1211, 1158, 1095, 1039, 970, 881, 843, 815, 790, 757 cm^{-1} . MS (EI) m/z : 244 $[\text{M}^+]$, 145, 116, 100(100), 89, 72. HRMS-ESI (m/z): calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 267.1104; found: 267.1104.

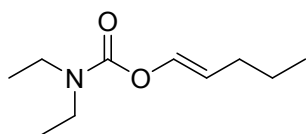
Pyridin-4-yl diethylcarbamate (6sa).⁸ Pale yellow oil (24.0 mg, 25%). ^1H NMR (400 MHz,



CDCl_3): $\delta = 8.58$ (s, 2 H), 7.18 – 7.12 (m, 2 H), 3.45 – 3.37 (m, 4 H), 1.24 – 1.18 (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 158.5, 152.5, 151.1, 116.8, 42.5, 42.1, 14.2, 13.2$. IR (KBr): 2964, 2926, 2855, 1728, 1465,

1418, 1380, 1273, 1243, 1201, 1151, 1096, 1039, 959, 749 cm^{-1} . MS (EI) m/z : 194 $[\text{M}^+]$, 100(100), 77, 72. HRMS-ESI (m/z): calcd for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$: 195.1128; found: 195.1128.

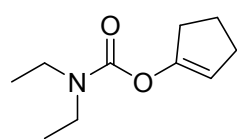
(E)-Pent-1-en-1-yl diethylcarbamate (6ta). Pale yellow oil (32.4 mg, 35%). ^1H NMR [400



MHz, CDCl_3): $\delta = 7.00$ (d, $J = 12.4$, 1 H), 5.35 – 5.24 (m, 1 H), 3.35 – 3.26 (m, 4 H), 2.00 – 1.93 (m, 2 H), 1.45 – 1.35 (m, 2 H), 1.14 (t, $J = 7.2$ Hz, 6 H), 0.91 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (100

MHz, CDCl_3): $\delta = 153.5, 136.8, 112.2, 41.9, 41.4, 29.3, 22.9, 14.1, 13.5, 13.3$. IR (KBr): 2924, 2853, 1721, 1659, 1462, 1376, 1265, 1170, 1094, 1023, 802 cm^{-1} . MS (EI) m/z : 185 $[\text{M}^+]$, 100(100), 72. HRMS-ESI (m/z): calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2\text{Na}$ $(\text{M} + \text{Na})^+$: 208.1308; found: 208.1306.

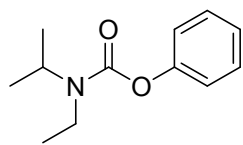
Cyclopent-1-en-1-yl diethylcarbamate (6ua). Pale yellow oil (45.4 mg, 50%). ^1H NMR (400



MHz, CDCl_3): $\delta = 5.35 - 5.30$ (m, 1 H), 3.30 (q, $J = 7.2$ Hz, 4 H), 2.48 – 2.42 (m, 2 H), 2.37 – 2.31 (m, 2 H), 1.98 – 1.89 (m, 2 H), 1.14 (t, $J = 7.2$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 146.5, 144.6, 104.5, 34.9, 34.8,$

24.1, 21.5, 14.2, 7.0, 6.3. IR (KBr): 2961, 2923, 2853, 1723, 1655, 1463, 1262, 1109, 1023, 800 cm^{-1} . MS (EI) m/z : 183[M^+], 100(100), 83, 72. HRMS-ESI (m/z): calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 206.1151; found: 206.1153.

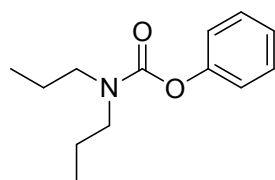
Phenyl ethyl(isopropyl)carbamate (6ab). Pale yellow oil (82.8 mg, 80%). ^1H NMR [400 MHz,



CDCl_3): $\delta = 7.34$ (t, $J = 7.6$ Hz, 2 H), 7.16 (t, $J = 7.6$ Hz, 1 H), 7.12 (d, $J = 8.0$ Hz, 2 H), $4.41 - 4.27$ (m, 1 H), $3.38 - 3.24$ (m, 2 H), 1.23 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.1, 151.5, 129.1, 124.9, 121.7, 48.0, 38.1,$

$37.6, 21.1, 20.5, 16.0$. IR (KBr): 2976, 1717, 1471, 1413, 1285, 1205, 1124, 1018, 744 cm^{-1} . MS (EI) m/z : 207[M^+], 114, 94, 77, 72(100). HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$: 230.1151; found: 230.1153.

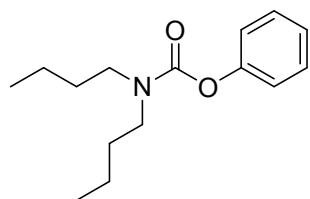
Phenyl dipropylcarbamate (6ac). Pale yellow oil (55.1 mg, 50%). ^1H NMR [400 MHz, CDCl_3]:



$\delta = 7.35$ (t, $J = 7.6$ Hz, 2 H), 7.18 (t, $J = 7.4$ Hz, 1 H), 7.12 (d, $J = 7.6$ Hz, 2 H), $3.38 - 3.26$ (m, 4 H), $1.73 - 1.62$ (m, 4 H), $0.99 - 0.91$ (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.7, 151.6, 129.1, 124.9, 121.7,$

$49.4, 49.1, 22.0, 21.2, 11.2$. IR (KBr): 2965, 2932, 2875, 1722, 1494, $1464, 1416, 1381, 1302, 1239, 1206, 1156, 1103, 1024, 904, 837, 751, 690 \text{ cm}^{-1}$. MS (EI) m/z : 221[M^+], 128(100), 107, 94, 86, 77. HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$: 222.1489; found: 222.1489.

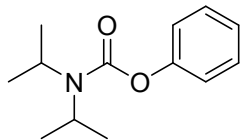
Phenyl dibutylcarbamate (6ad).⁹ Pale yellow oil (64.5 mg, 52%). ^1H NMR (400 MHz, CDCl_3):



$\delta = 7.35$ (t, $J = 7.6$ Hz, 2 H), 7.18 (t, $J = 7.6$ Hz, 1 H), 7.12 (d, $J = 8.0$ Hz, 2 H), $3.42 - 3.28$ (m, 4 H), $1.69 - 1.57$ (m, 4 H), $1.42 - 1.32$ (m, 4 H), $1.01 - 0.92$ (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.6, 151.6, 129.1, 124.9, 121.7, 47.5, 47.2, 30.9, 30.1, 20.0, 13.8$.

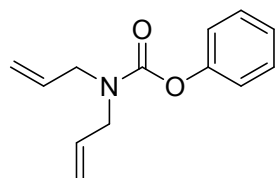
IR (KBr): 2960, 2931, 2870, 1722, 1466, 1417, 1378, 1294, 1207, $1158, 1107, 1040, 753, 690 \text{ cm}^{-1}$. MS (EI) m/z : 249[M^+], 156, 107, 100, 94, 77, 57(100). HRMS-ESI (m/z): calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 250.1802; found: 250.1804.

Phenyl diisopropylcarbamate (6ae).¹⁰ Pale yellow oil (50.8 mg, 46%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.36$ (t, $J = 7.6$ Hz, 2 H), 7.18 (t, $J = 7.2$ Hz, 1 H), 7.12 (d, $J = 7.6$ Hz, 2 H), $4.19 - 3.86$ (m, 2 H), 1.32 (s, 12 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.8, 151.4, 129.1, 124.9, 121.8,$



1153, 1071, 1043, 986, 892, 739, 689, 600, 498 cm^{-1} . MS (EI) m/z : 221[M^+], 164, 128, 94, 86(100), 66. HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 222.1489; found: 222.1489.

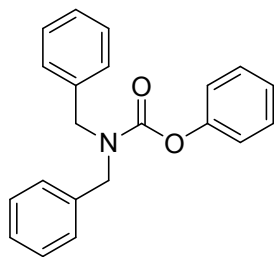
Phenyl diallylcarbamate (6af). Pale yellow oil (40.0 mg, 37%). ^1H NMR (400 MHz, CDCl_3): δ = 7.35 (t, J = 7.6 Hz, 2 H), 7.19 (t, J = 7.2 Hz, 1 H), 7.12 (d, J = 8.0 Hz, 2 H), 5.87 (s, 2 H), 5.26 –



5.20 (m, 4 H), 4.00 (s, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 147.5, 144.4, 126.2, 122.2, 118.2, 114.7, 110.7, 109.9, 42.5, 42.0. IR (KBr): 2926, 2856, 1724, 1494, 1455, 1408, 1238, 1206, 1162, 1064, 993, 923, 848, 754, 691 cm^{-1} . MS (EI) m/z : 217[M^+], 124(100), 96, 81.

HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 240.0995; found: 240.1001.

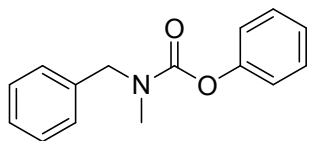
Phenyl dibenzylcarbamate (6af). Pale yellow oil (85.6 mg, 54%). ^1H NMR (400 MHz, CDCl_3):



δ = 7.32 – 7.17 (m, 12 H), 7.14 – 7.09 (m, 1 H), 7.09 – 7.02 (m, 2 H), 4.52 – 4.40 (m, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 155.2, 151.4, 137.0, 129.2, 128.7, 128.3, 127.6, 125.3, 121.7, 49.9, 49.5. IR (KBr): 2958, 2926, 2857, 1719, 1493, 1455, 1413, 1363, 1305, 1202, 1087, 1025, 961, 910, 857, 805, 749, 696, 497 cm^{-1} . MS (EI) m/z : 317[M^+],

224, 105, 91(100), 77. HRMS-ESI (m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 318.1489; found: 318.1488.

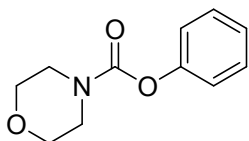
Phenyl benzyl(methyl)carbamate (6ah).¹¹ Pale yellow oil (90.3 mg, 75%). ^1H NMR (400 MHz, CDCl_3): δ = 7.41 – 7.24(m, 7 H), 7.21 – 7.08 (m, 3 H), 4.66 – 4.50



(m, 2 H), 2.99 (d, J = 12.8 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 155.2, 154.7, 151.4, 137.0, 129.2, 128.6, 128.6, 128.0, 127.5,

127.3, 125.2, 121.6, 52.8, 34.6, 34.0. IR(KBr): 3036, 2929, 1721, 1594, 1455, 1398, 1208, 1125, 1022, 748, 696 cm^{-1} . MS (EI) m/z : 241[M^+], 148, 91(100), 77. HRMS-ESI (m/z): calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 264.0995; found: 264.0999.

Phenyl morpholine-4-carboxylate (6ai).¹² Pale yellow oil (63.0 mg, 61%). ^1H NMR (400 MHz, CDCl_3): δ = 7.36 (t, J = 7.6 Hz, 2 H), 7.20 (t, J = 7.6 Hz, 1 H), 7.11 (d, J =

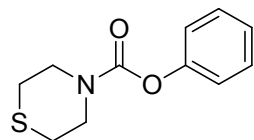


8.0 Hz, 2 H), 3.76 – 3.71 (m, 4 H), 3.69 – 3.53 (m, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 153.6, 151.2, 129.2, 125.3, 121.6, 66.5, 44.8,

44.0. IR (KBr): 2961, 2923, 2857, 1723, 1493, 1455, 1418, 1276, 1238, 1204, 1163, 1117, 1064,

1021, 855, 748, 691, 574 cm^{-1} . MS (EI) m/z : 207 $[\text{M}^+]$, 114(100), 94, 77, 70. HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 208.0968; found: 208.0968.

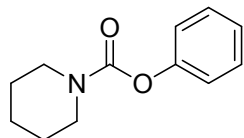
Phenyl thiomorpholine-4-carboxylate (6aj). Pale yellow solid (64.7mg, 58%), mp: 66 – 67 °C.



^1H NMR (400 MHz, CDCl_3): δ = 7.36 (t, J = 7.2 Hz, 2 H), 7.20 (t, J = 7.2 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 2 H), 4.01 – 3.75 (d, 4 H), 2.78 – 2.58 (m, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 153.5, 151.2, 129.2, 125.4,

121.6, 47.1, 46.6, 27.4, 27.1. IR (KBr): 2916, 2866, 1717, 1595, 1419, 1297, 1203, 1069, 958, 748, 690 cm^{-1} . MS (EI) m/z : 223 $[\text{M}^+]$, 130(100), 87, 77. HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 246.0559; found: 246.0556.

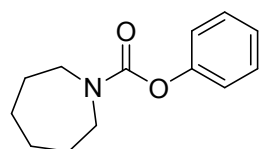
Phenyl piperidine-1-carboxylate (6ak).¹³ Colourless solid (65.0 mg, 63%), mp: 83 – 84 °C. ^1H



NMR (400 MHz, CDCl_3): δ = 7.35 (t, J = 7.2 Hz, 2 H), 7.18 (t, J = 7.2 Hz, 1 H), 7.11 (d, J = 8.0 Hz, 2 H), 3.65 – 3.48 (m, 4 H), 1.68 – 1.59 (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 146.7, 144.6, 122.1, 118.0, 114.7, 38.4,

38.1, 18.9, 18.5, 17.3. IR (KBr): 2935, 2862, 1712, 1592, 1430, 1362, 1247, 1237, 1201, 1139, 1052, 1022, 748, 690 cm^{-1} . MS (EI) m/z : 205 $[\text{M}^+]$, 112(100), 69. HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 228.0995; found: 228.0998.

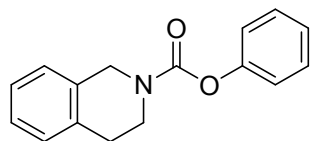
Phenyl azepane-1-carboxylate (6al). Colourless oil (83.1 mg, 76%). ^1H NMR (400 MHz,



CDCl_3): δ = 7.34 (t, J = 7.6 Hz, 2 H), 7.16 (t, J = 7.6 Hz, 1 H), 7.11 (d, J = 7.6 Hz, 2 H), 3.57 (t, J = 6.0 Hz, 2 H), 3.51 (t, J = 6.0 Hz, 2 H), 1.77 (s, 4 H), 1.61 (s, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 154.5, 151.5, 129.1,

124.9, 121.7, 47.3, 47.1, 28.6, 28.0, 27.3, 26.8. IR (KBr): 2928, 2860, 1718, 1468, 1416, 1266, 1199, 1055, 750 cm^{-1} . MS (EI) m/z : 219 $[\text{M}^+]$, 126(100), 77, 56. HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 220.1332; found: 220.1331.

Phenyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (6am).¹⁴

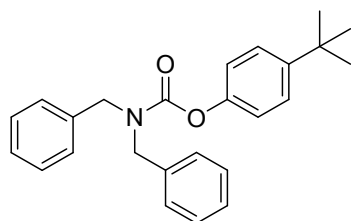


Yellow oil (64.5 mg, 51%). ^1H NMR (400 MHz, CDCl_3): δ = 7.36 (t, J = 7.6 Hz, 2 H), 7.24 – 7.08 (m, 7 H), 4.83 (s, 1 H), 4.71 (s, 1 H), 3.93 – 3.74 (m, 2 H), 2.99 – 2.89 (m, 2 H). ^{13}C NMR (100 MHz,

CDCl_3): δ = 153.9, 151.4, 134.5, 134.3, 133.2, 132.8, 129.2, 128.9, 128.5, 126.7, 126.4, 126.2,

125.3, 121.7, 46.2, 45.9, 42.3, 41.6, 29.1, 28.7. IR (KBr): 2924, 2861, 1719, 1417, 1200, 1069, 927, 746, 691 cm^{-1} . MS (EI) m/z : 253 $[\text{M}^+]$, 176, 160(100), 142, 117, 77. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 276.0995; found:276.0992.

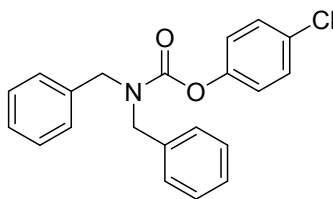
4-(Tert-butyl)phenyl dibenzylcarbamate (6cg). Yellow oil (100.8 mg, 54%). ^1H NMR (400



MHz, CDCl_3): $\delta = 7.42 - 7.26$ (m, 12 H), 7.07 (d, $J = 7.6$ Hz, 2 H), 4.61 – 4.48 (m, 4 H), 1.31 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 155.4, 149.1, 148.1, 137.1, 128.7, 128.4, 127.6, 126.2, 121.0, 49.9, 49.5, 34.4, 31.4$. IR (KBr): 3035, 2958, 1720, 1507, 1456, 1414, 1364, 1213, 1086, 869, 821, 748, 699 cm^{-1} .

MS (EI) m/z : 373 $[\text{M}^+]$, 282, 224, 91(100), 65. HRMS-ESI (m/z): calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 396.1934; found:396.1942.

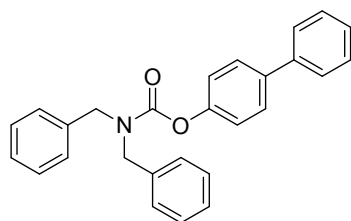
4-Chlorophenyl dibenzylcarbamate (6fg). Yellow oil (107.0 mg, 61%). ^1H NMR (400 MHz,



CDCl_3): $\delta = 7.50 - 7.21$ (m, 12 H), 7.07 (d, $J = 8.0$ Hz, 2 H), 4.53 (s, 4 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.8, 149.9, 136.8, 130.6, 129.2, 128.7, 128.3, 127.7, 127.4, 123.0, 50.0, 49.5$. IR (KBr): 3033, 2929, 1722, 1482, 1452, 1415, 1363, 1289, 1210,

1084, 1014, 958, 868, 813, 748, 701 cm^{-1} . MS (EI) m/z : 351 $[\text{M}^+]$, 224, 132, 91(100), 65. HRMS-ESI (m/z): calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 374.0918; found:374.0925.

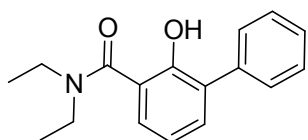
[1,1'-Biphenyl]-4-yl dibenzylcarbamate (6lg). Colourless solid (123.7 mg, 63%), mp: 117 – 118



$^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.46$ (t, $J = 8.0$ Hz, 4 H), 7.33 – 7.18 (m, 13 H), 7.12 (d, $J = 8.0$ Hz, 2 H), 4.51 – 4.41 (m, 4 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 155.2, 150.8, 140.5, 138.5, 136.9, 128.7, 128.3, 128.0, 127.6, 127.5, 127.2, 127.0,$

121.9, 49.9, 49.5. IR (KBr): 3034, 2925, 1717, 1452, 1413, 1207, 1085, 865, 753, 696 cm^{-1} . MS (EI) m/z : 393 $[\text{M}^+]$, 260, 224, 91(100), 65. HRMS-ESI (m/z): calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 416.1621; found:416.1624.

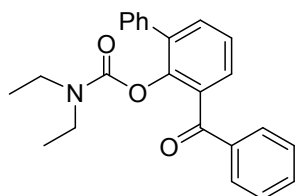
***N,N*-Diethyl-2-hydroxy-[1,1'-biphenyl]-3-carboxamide (7).**⁶ Colourless solid (100.5 mg, 75%).



mp: 93 – 95 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.80$ (s, 1 H), 7.56 (d, $J = 7.6$ Hz, 2 H), 7.43 – 7.29 (m, 4 H), 7.25 – 7.21 (m, 1 H), 6.90 (t, $J = 7.6$ Hz, 1 H), 3.50 (q, $J = 7.2$ Hz, 4 H), 1.25 (t, $J = 7.2$

Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.4, 155.1, 137.5, 132.8, 130.5, 129.2, 128.0, 127.1, 126.5, 118.8, 118.4, 42.0, 13.2$. IR (KBr): 3054, 2977, 2935, 1731, 1605, 1428, 1366, 1251, 1122, 1072, 759, 697 cm^{-1} . MS (EI) m/z : 269 $[\text{M}^+]$, 269(100), 252, 197, 168, 141, 115, 72, 58. HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 292.1308; found: 292.1313.

3-Benzoyl-[1,1'-biphenyl]-2-yl diethylcarbamate (8). Yellow oil (90.7 mg, 81%). ^1H NMR (400

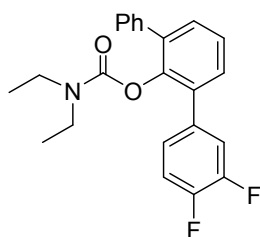


MHz, CDCl_3): $\delta = 7.87$ (d, $J = 7.6$ Hz, 2 H), 7.51 (d, $J = 7.2$ Hz, 2 H), 7.47 – 7.30 (m, 9 H), 3.06 – 2.86 (m, 4 H), 0.79 (d, $J = 5.6$ Hz, 6 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 195.1, 152.7, 146.3, 137.5, 136.4, 133.4, 133.2, 132.8, 130.0, 129.1, 129.0, 128.1, 128.0, 127.4, 125.0,$

41.9, 41.4, 13.5, 12.8. IR (KBr): 3061, 2977, 2933, 2833, 1722, 1670, 1593, 1458, 1413, 1272, 1206, 1154, 1086, 1032, 954, 756, 704 cm^{-1} . MS (EI) m/z : 373 $[\text{M}^+]$, 329, 284, 139, 100(100), 77, 72. HRMS-ESI (m/z): calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 374.1751; found: 374.1754.

3,4-Difluoro-[1,1':3',1''-terphenyl]-2'-yl diethylcarbamate (9). Yellow oil (39.5 mg, 52%). ^1H

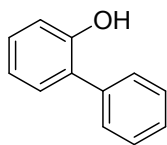


NMR (400 MHz, CDCl_3): $\delta = 7.45 - 7.30$ (m, 9 H), 7.20 – 7.12 (m, 2 H), 3.14 – 2.97 (m, 4 H), 0.85 (t, $J = 6.8$ Hz, 3 H), 0.78 (t, $J = 6.8$ Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.0, 145.7, 138.0, 136.6, 135.2, 134.3, 130.5, 129.6, 129.1, 128.0, 127.3, 125.8, 125.3, 118.3, 118.1, 116.9, 116.8, 100.0, 41.8, 41.4, 13.8, 12.6$. IR (KBr): 3061, 2973,

2928, 2873, 1718, 1603, 1517, 1462, 1412, 1271, 1198, 1154, 1082, 957, 756, 700 cm^{-1} . MS (EI) m/z : 381 $[\text{M}^+]$, 281, 251, 233, 100(100), 72. HRMS-ESI (m/z): calcd for $\text{C}_{23}\text{H}_{21}\text{F}_2\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 404.1433; found: 404.1441.

2-Phenylphenol (10).¹⁵ Yellow solid (72.0 mg, 85%), mp: 56-58 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3):



$\delta = 7.50 - 7.44$ (m, 4 H), 7.40 – 7.36 (m, 1 H), 7.23 (d, $J = 7.6$ Hz, 2 H), 6.97 (t, $J = 8.8$ Hz, 2 H), 5.29 (br, 1 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.4, 137.1,$

130.2, 129.2, 129.1, 129.1, 128.1, 127.8, 120.8, 115.8. IR (KBr): 3542, 3425,

3060, 3031, 2927, 2854, 1695, 1588, 1480, 1433, 1337, 1336, 1276, 1192, 1107, 1046, 1009, 830, 754, 700 cm^{-1} . MS (EI) m/z : 170 $[\text{M}^+]$, 170(100), 141, 115.

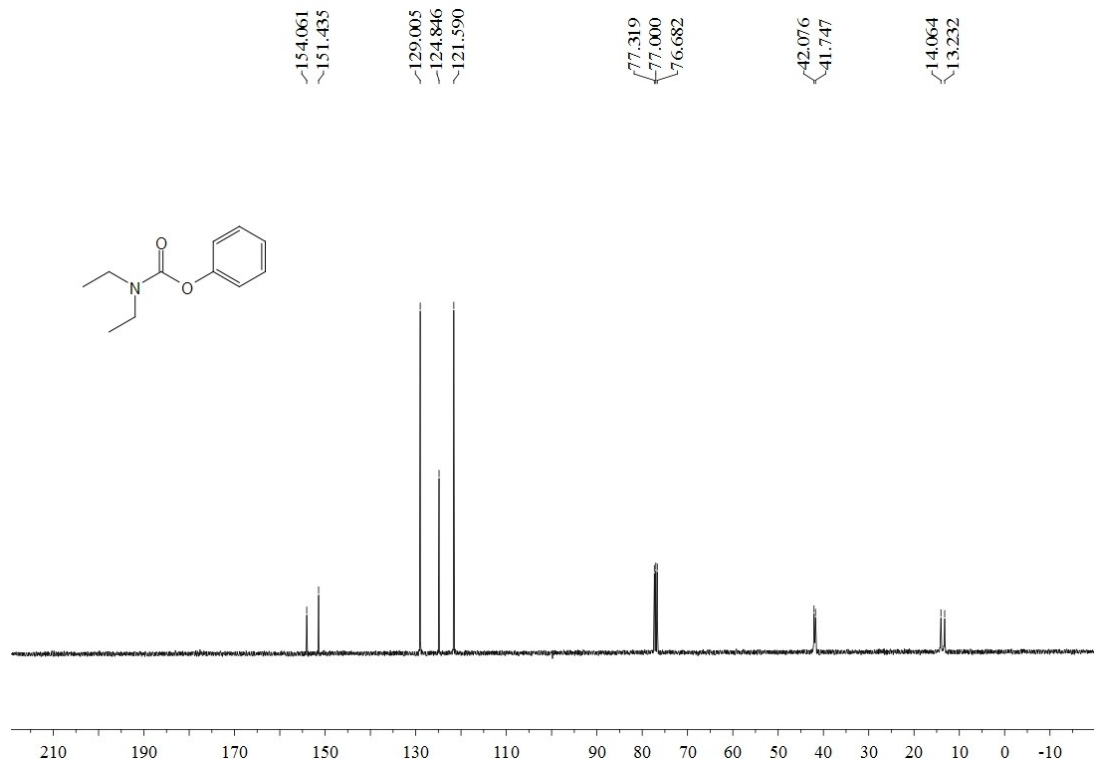
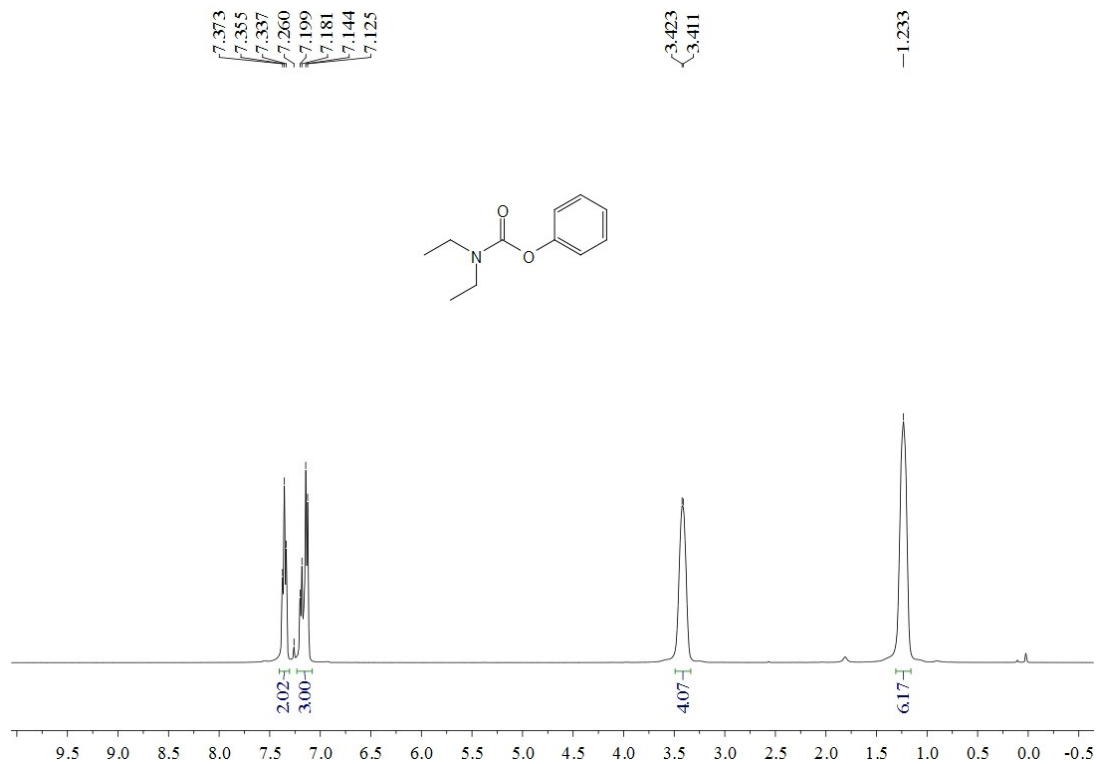
References

1. D. Belli Dell'Amico, F. Calderazzo, S. Farnocchi, L. Labella and F. Marchetti, *Inorg. Chem.*

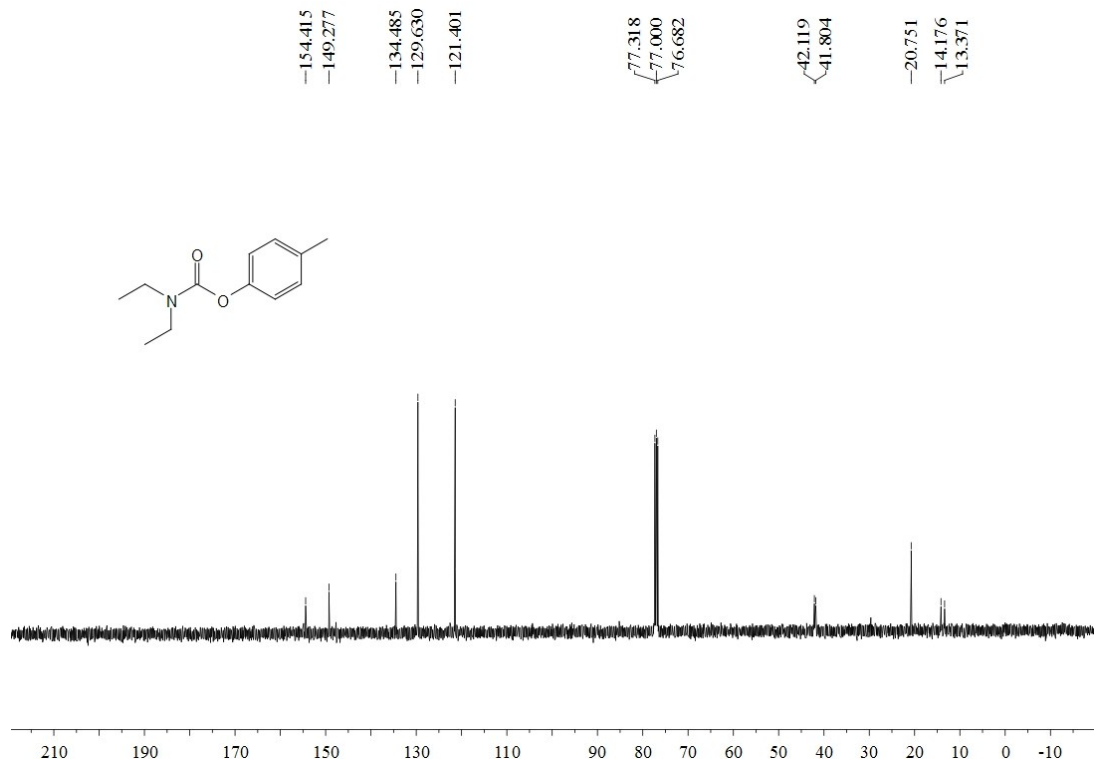
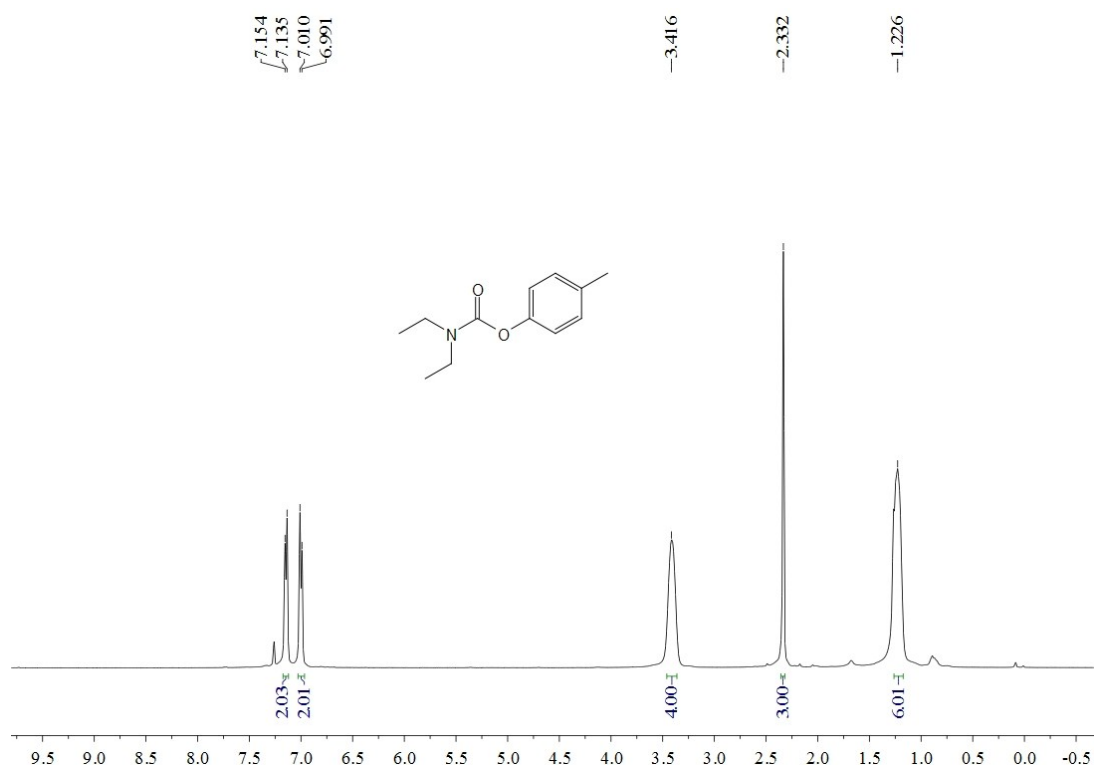
- Commun.*, 2002, **5**, 848.
- W. F. Xiong, C. R. Qi, Y. B. Peng, T. Z. Guo, M. Zhang and H. F. Jiang, *Chem. Eur. J.*, 2015, **21**, 14314.
 - K. W. Quasdorf, M. Riener, K. V. Petrova and N. K. Garg, *J. Am. Chem. Soc.*, 2009, **131**, 17748.
 - Y. G. Zhao and V. Snieckus, *J. Am. Chem. Soc.*, 2014, **136**, 11224.
 - P. Leowanawat, N. Zhang and V. Percec, *J. Org. Chem.*, 2012, **77**, 1018.
 - H. J. Lo, C. Y. Lin, M. C. Tseng and R. J. Chein, *Angew. Chem. Int. Ed.*, 2014, **53**, 9026.
 - J. Morin, Y.G. Zhao and V. Snieckus, *Org. Lett.*, 2013, **15**, 4102.
 - L. Yue, C. Guo, Y. F. Chai, X. C. Yin and Y. J. Pan, *Tetrahedron*, 2014, **70**, 9500.
 - D. L. Kong, L. N. He and J. Q. Wang, *Synth. Commun.*, 2011, **41**, 3298.
 - M. Hutchby, C. E. Houlden, J. G. Ford, S. N. G. Tyler, M. R. Gagn, G. C. Lloyd-Jones and K. I. Booker-Milburn, *Angew. Chem. Int. Ed.*, 2009, **48**, 8721.
 - S. Adachi, M. Onozuka, Y. Yoshida, M. Ide, Y. Saikawa and M. Nakata, *Org. Lett.*, 2014, **16**, 358.
 - L. Sun, J. Wu, M. Luo, X. L. Wang, M. Pan, Z. P. Gou and D. Q. Sun, *Molecules*, 2011, **16**, 9739.
 - R. R. Milburn and V. Snieckus, *Angew. Chem. Int. Ed.*, 2004, **43**, 892.
 - C. C. Yan, Y. X. Liu and Q. M. Wang, *RSC Adv.*, 2014, **4**, 60075.
 - R. K. Rai, K. Gupta, S. Behrens, J. Li, Q. Xu and S. K. Singh, *ChemCatChem*, 2015, **7**, 1806.

H. NMR Spectra.

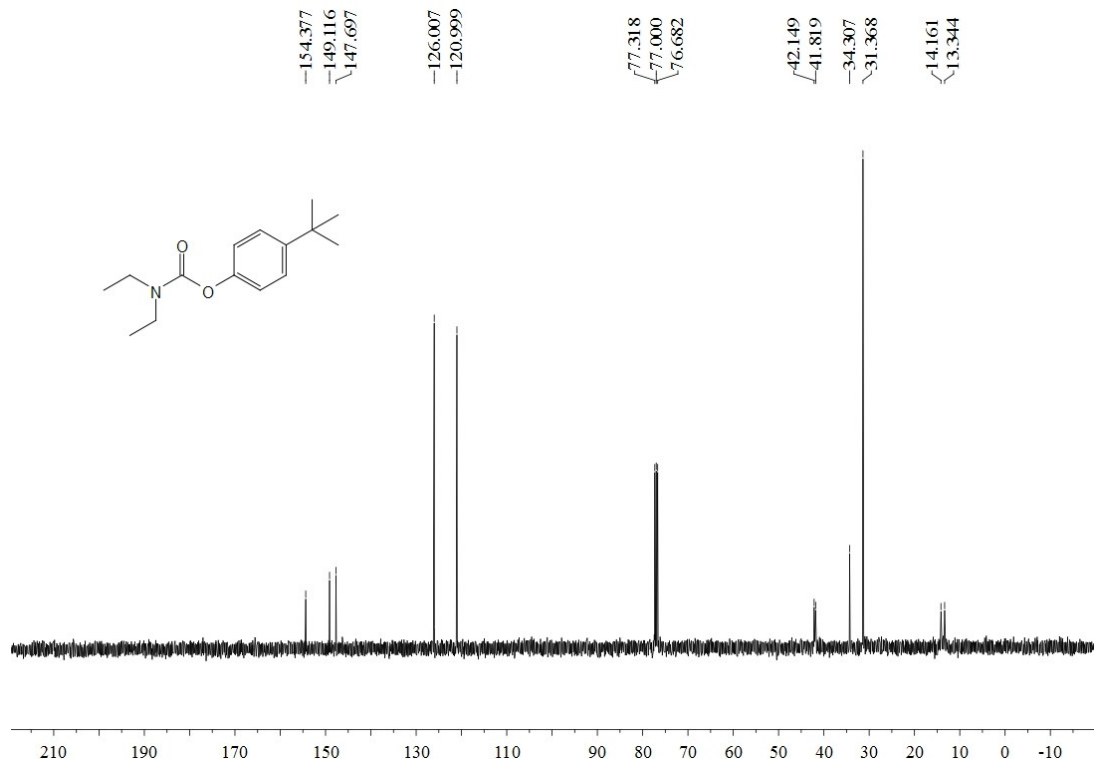
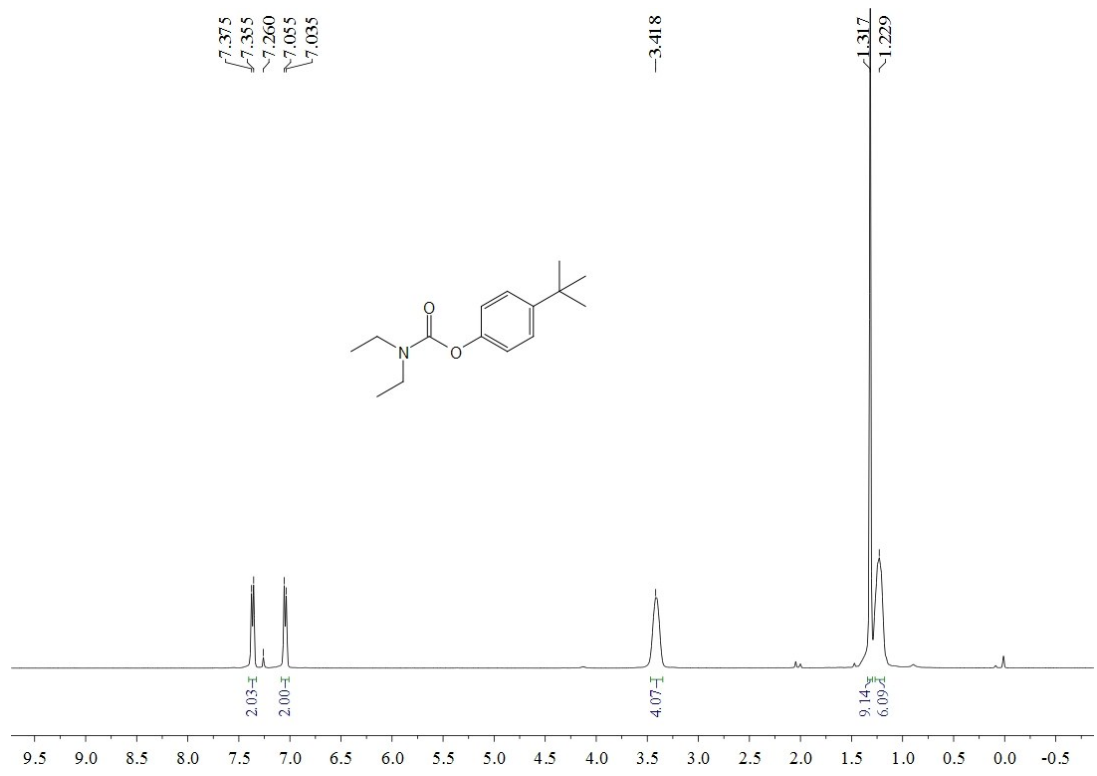
Phenyl diethylcarbamate (6aa)



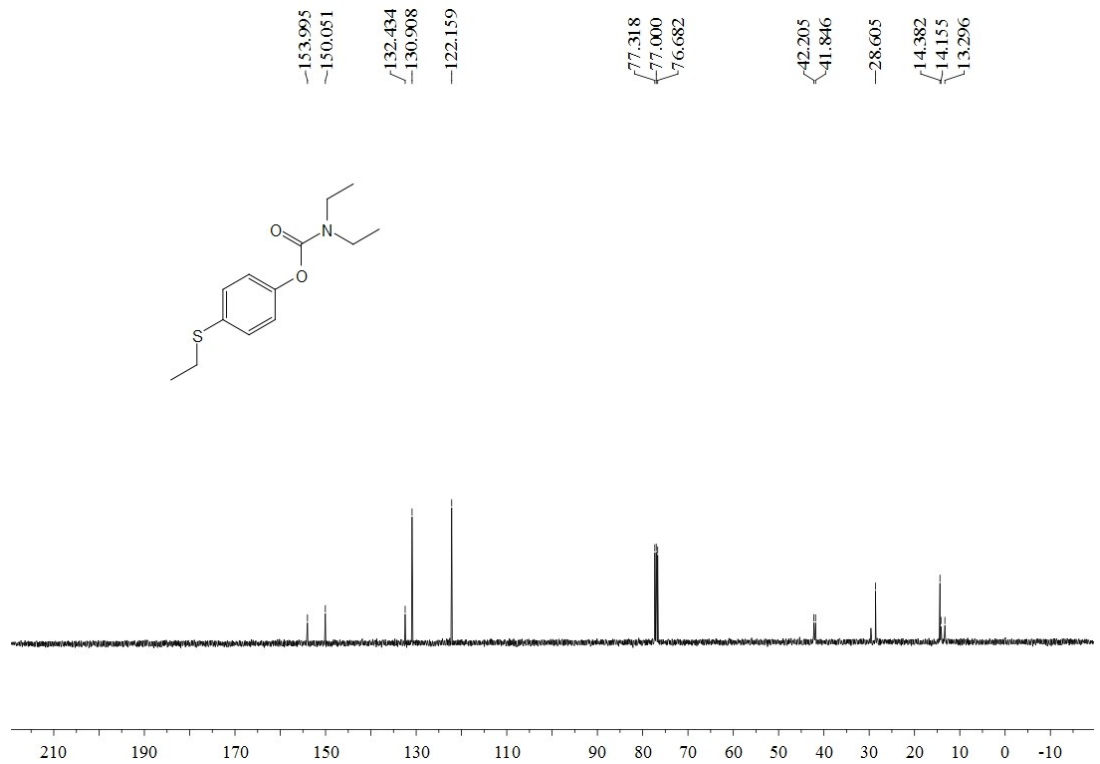
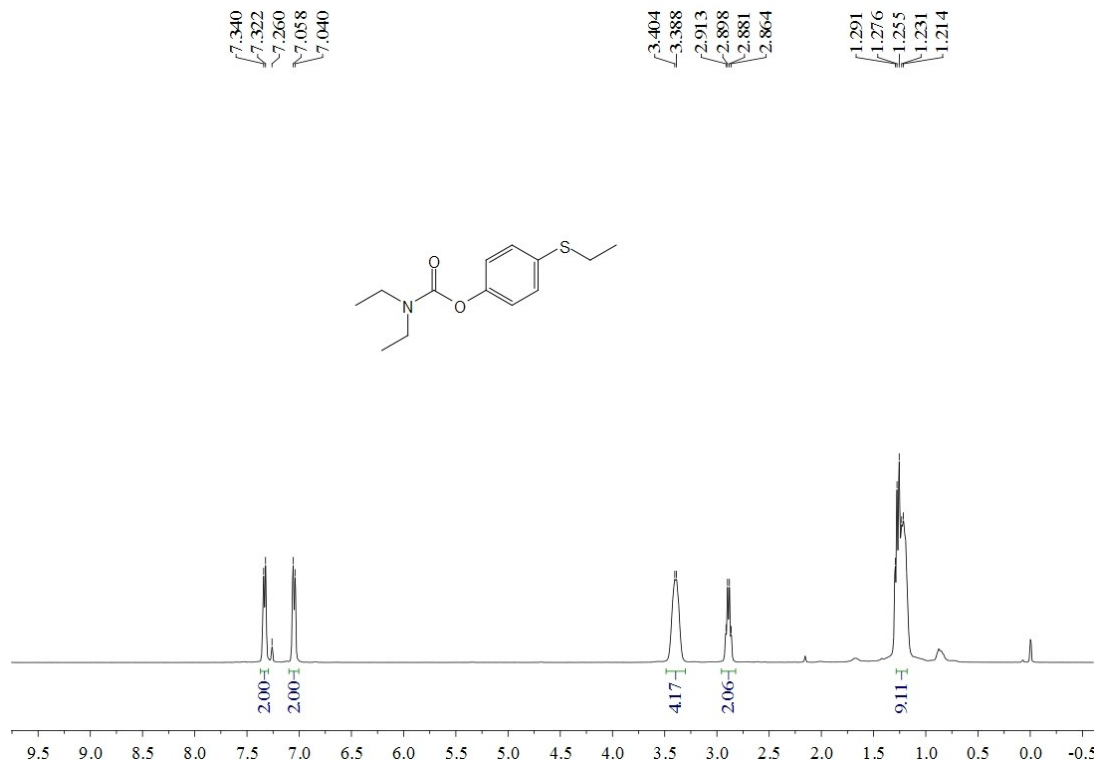
p-Tolyl diethylcarbamate (6ba)



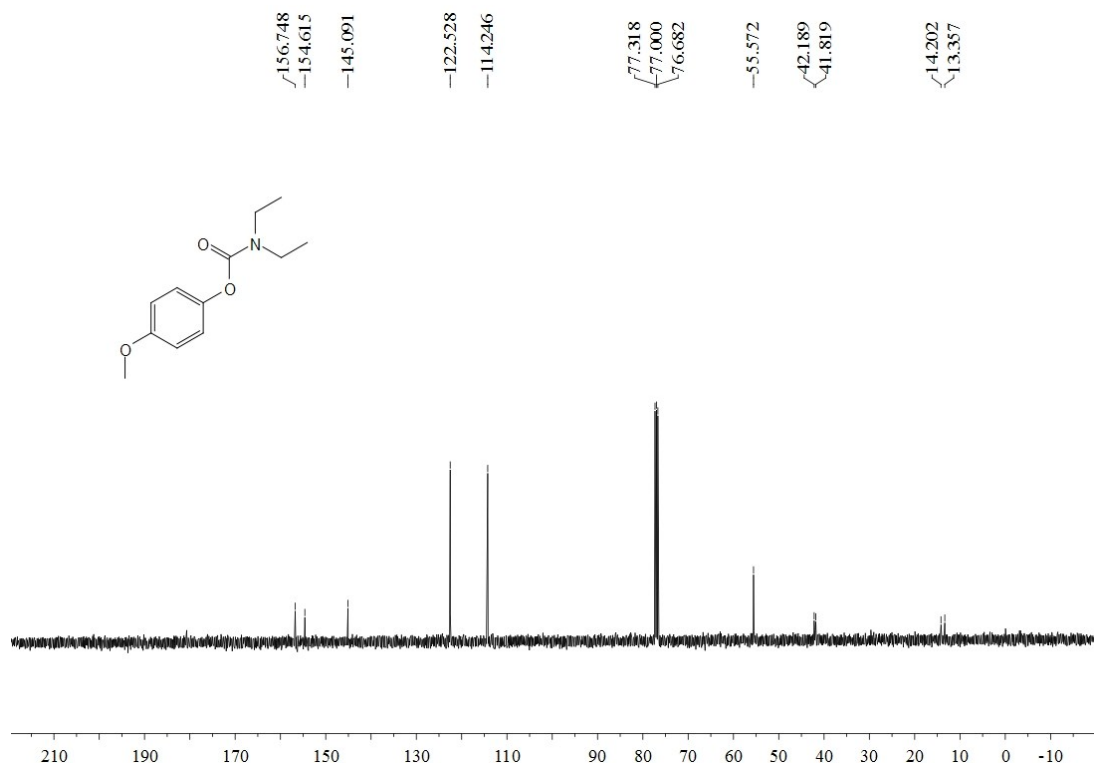
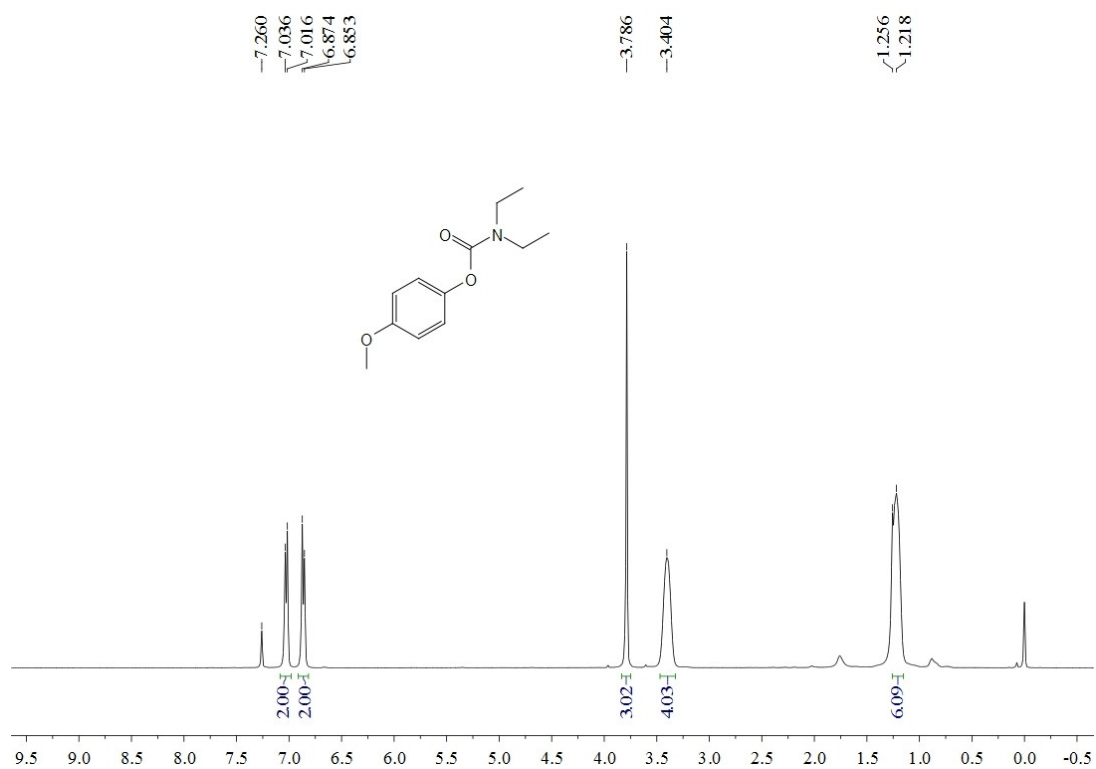
4-(Tert-butyl)phenyl diethylcarbamate (6ca)



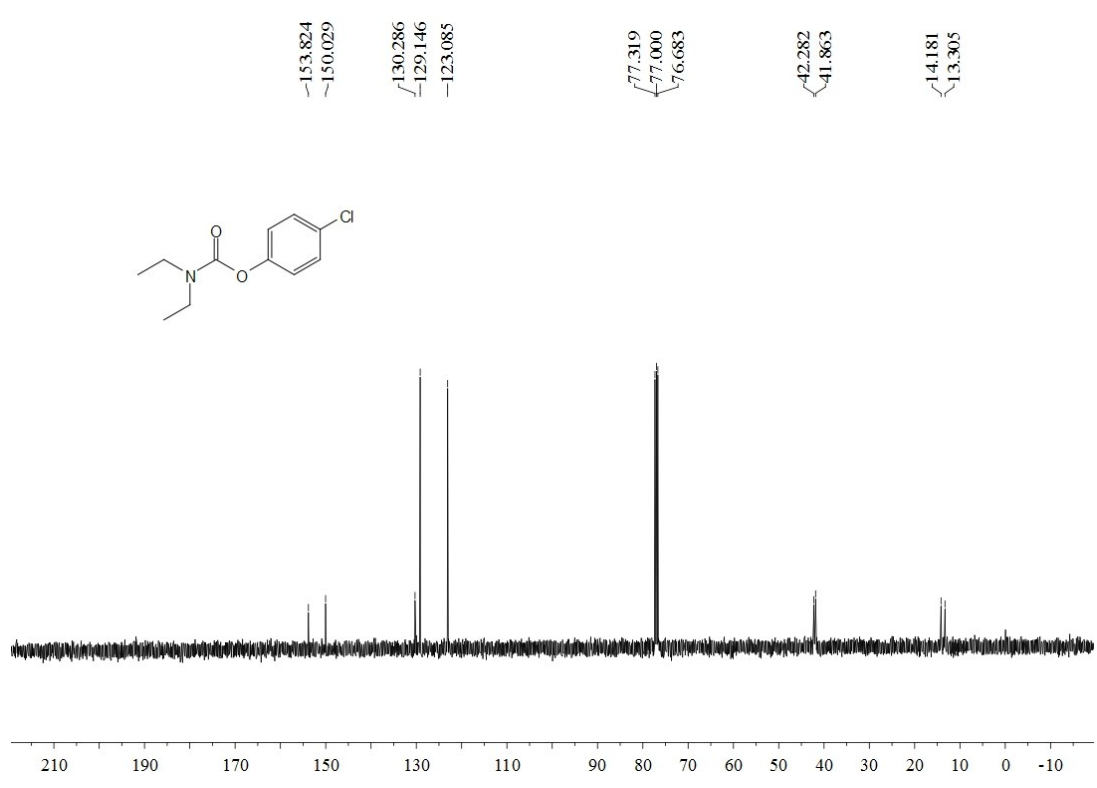
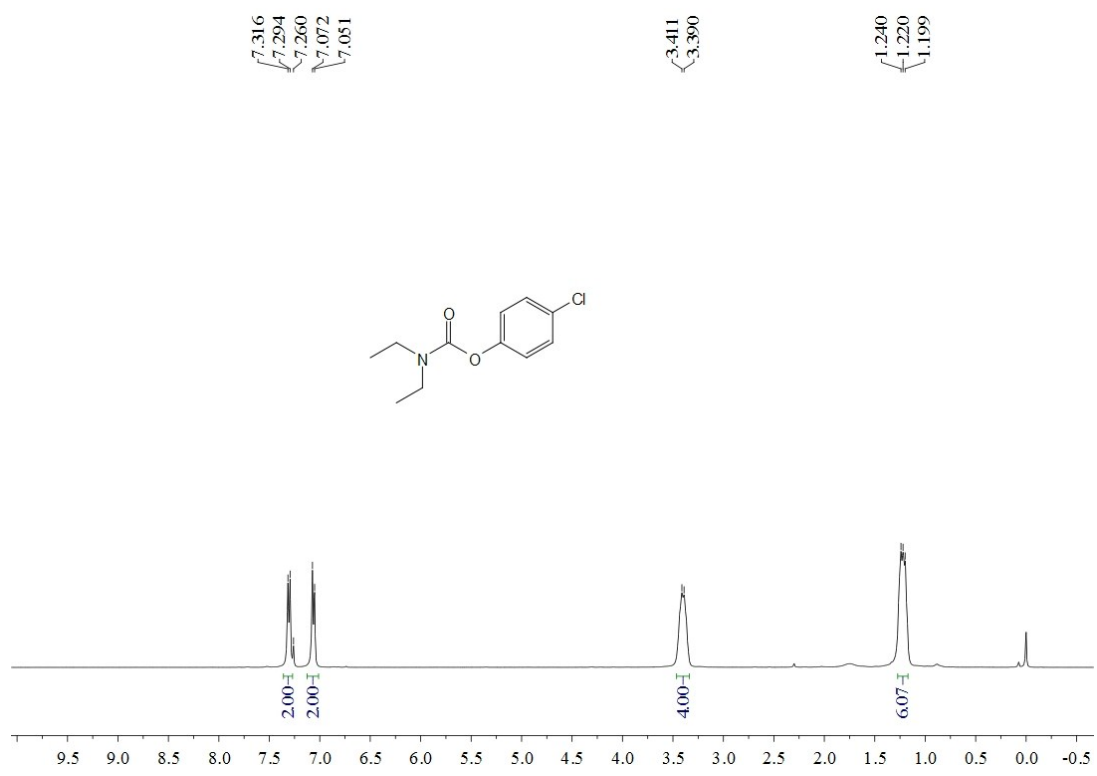
4-(Ethylthio)phenyl diethylcarbamate (6da)



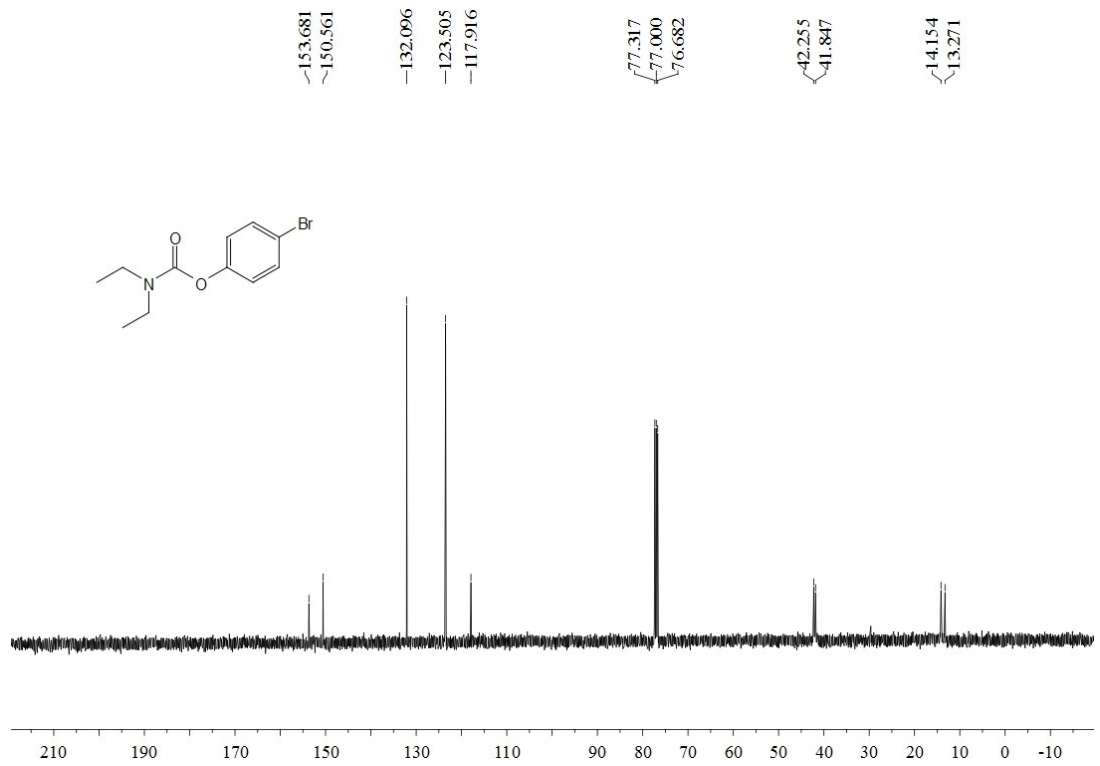
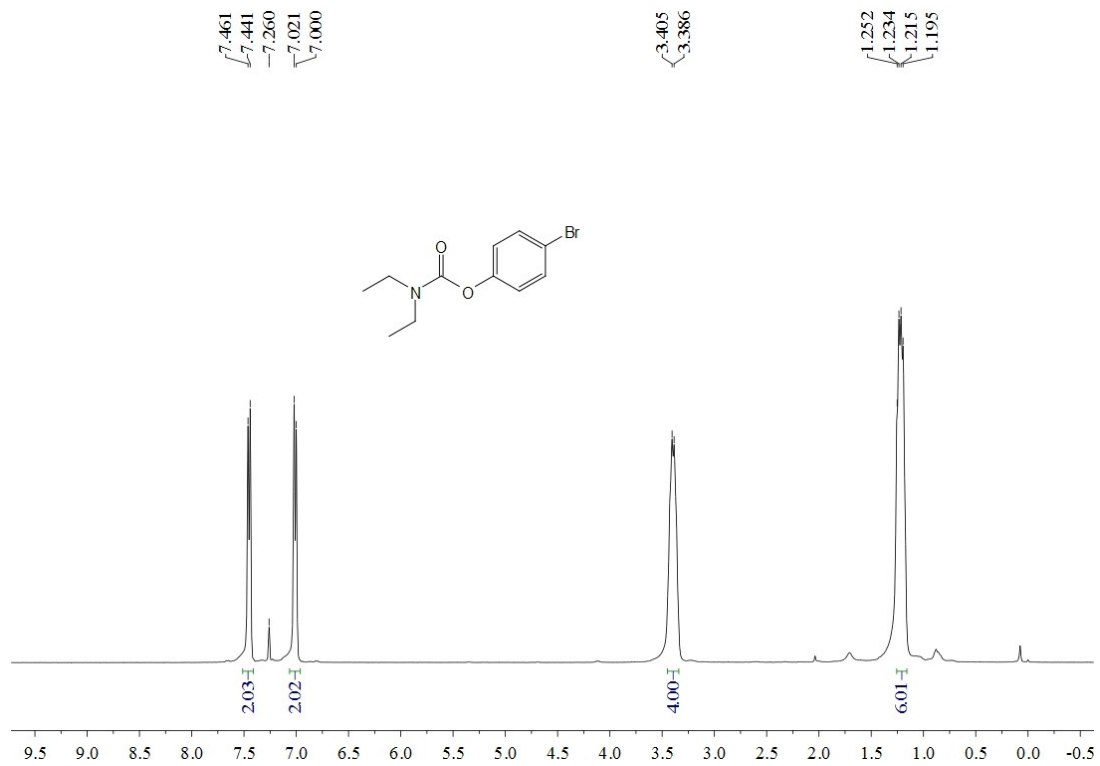
4-Methoxyphenyl diethylcarbamate (6ea)



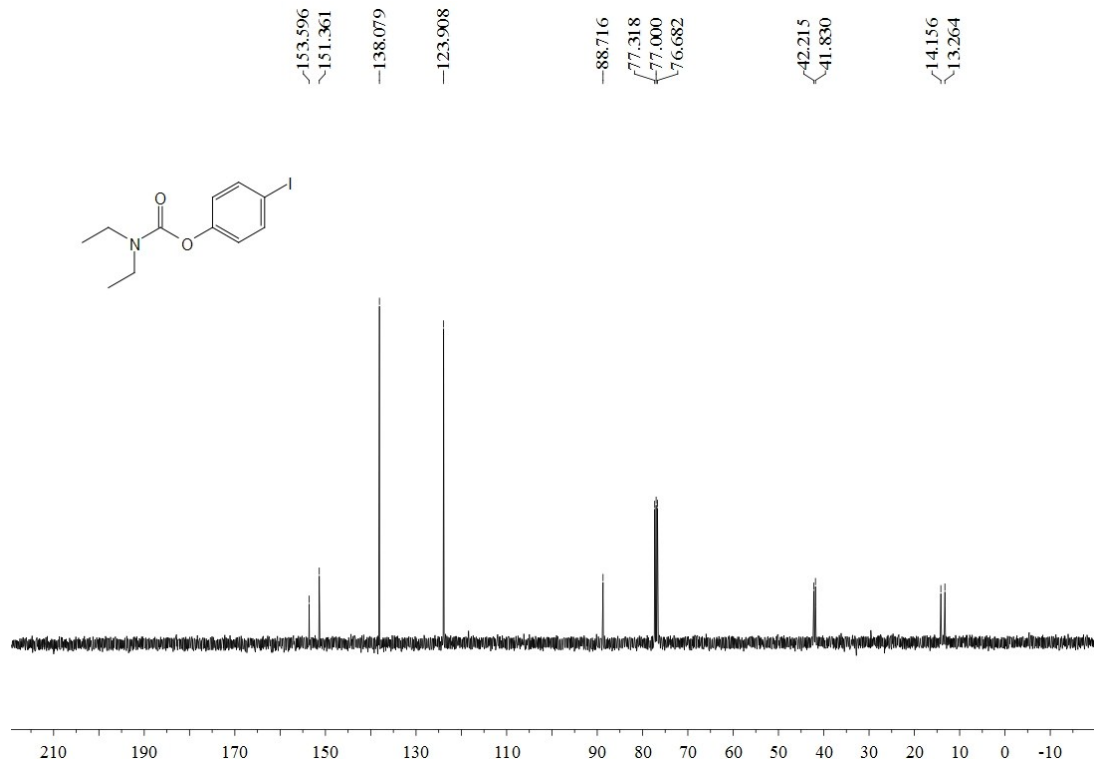
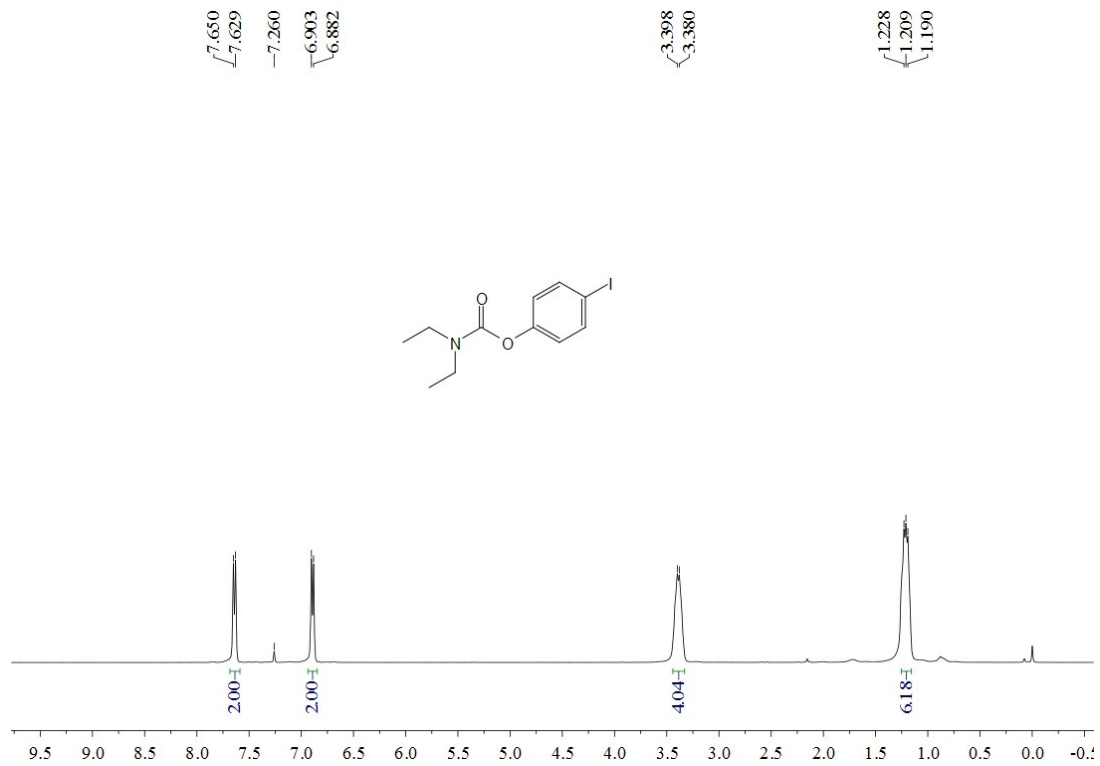
4-Chlorophenyl diethylcarbamate (6fa)



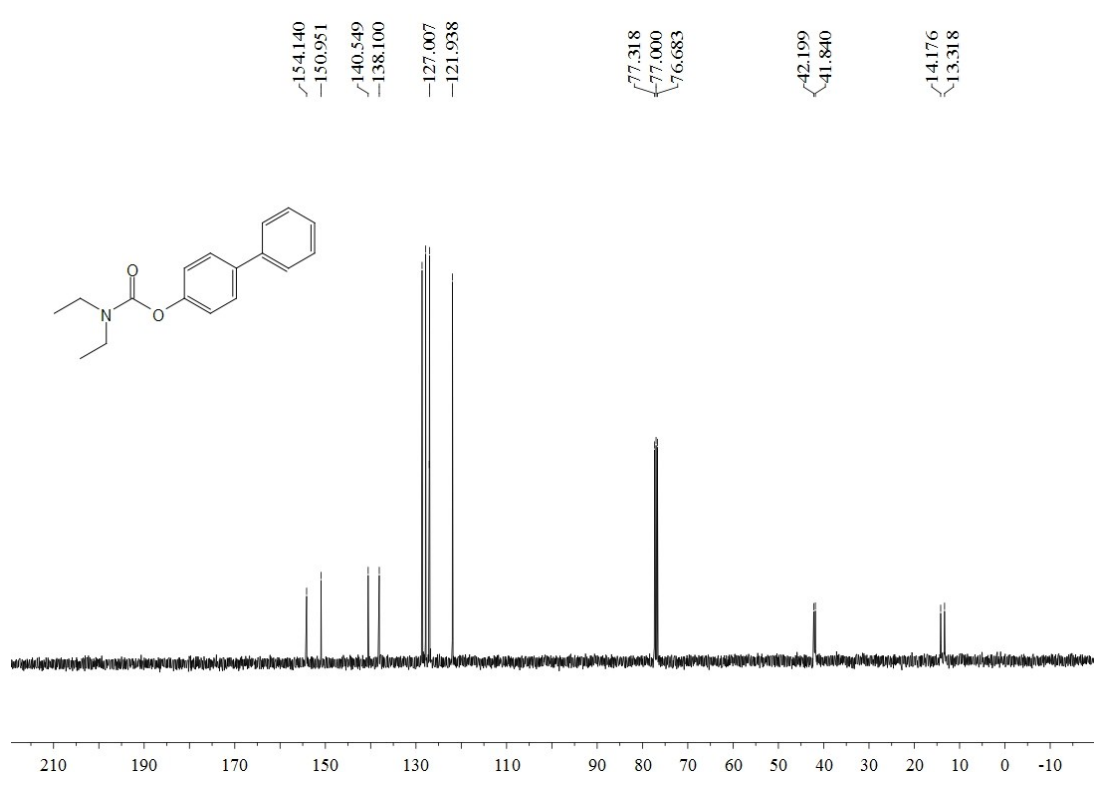
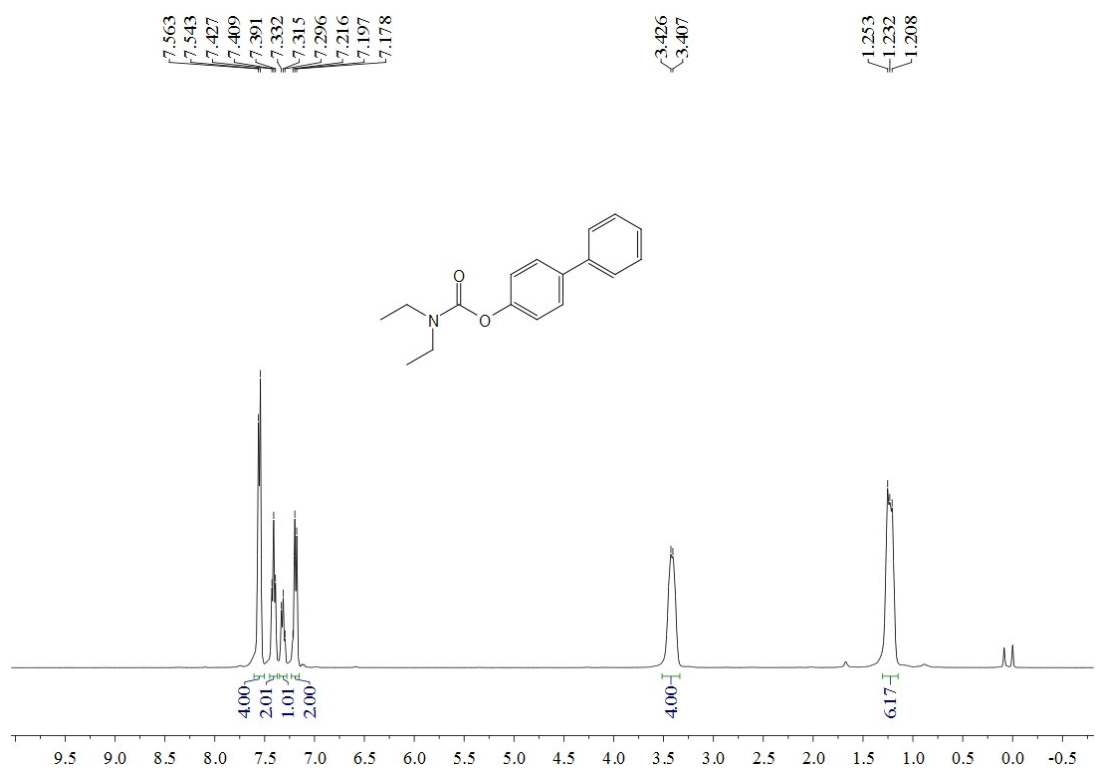
4-Bromophenyl diethylcarbamate (6ga)



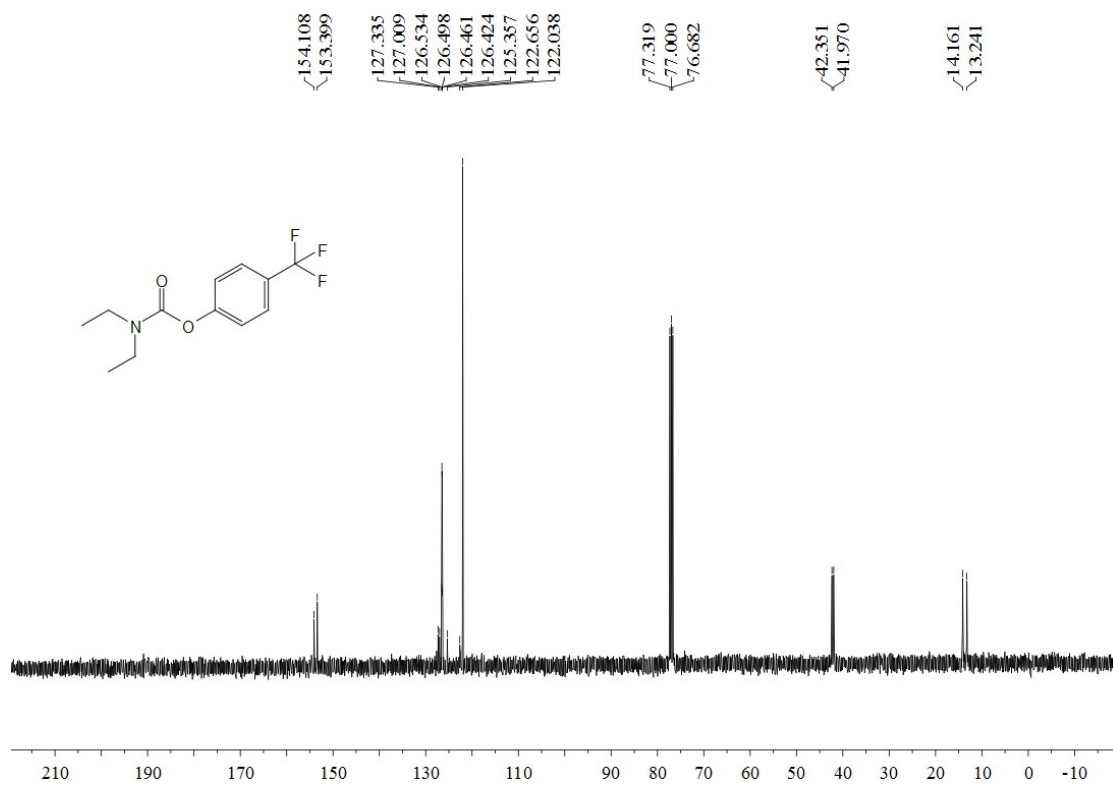
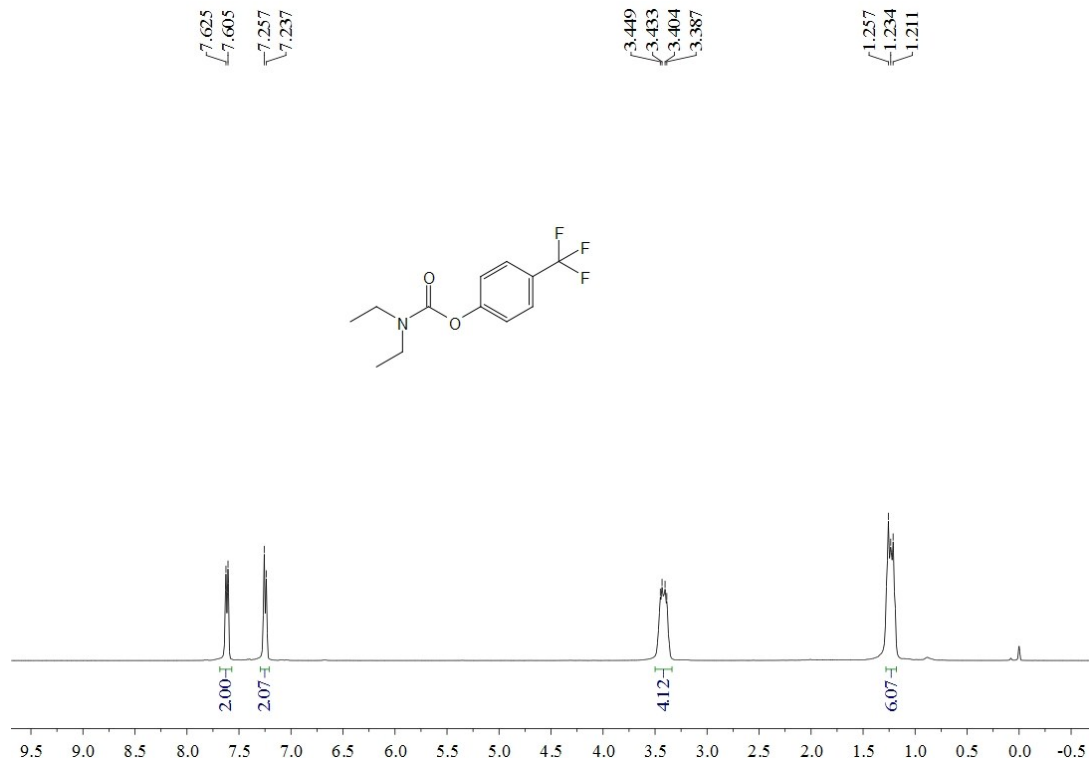
4-Iodophenyl diethylcarbamate (6ha)



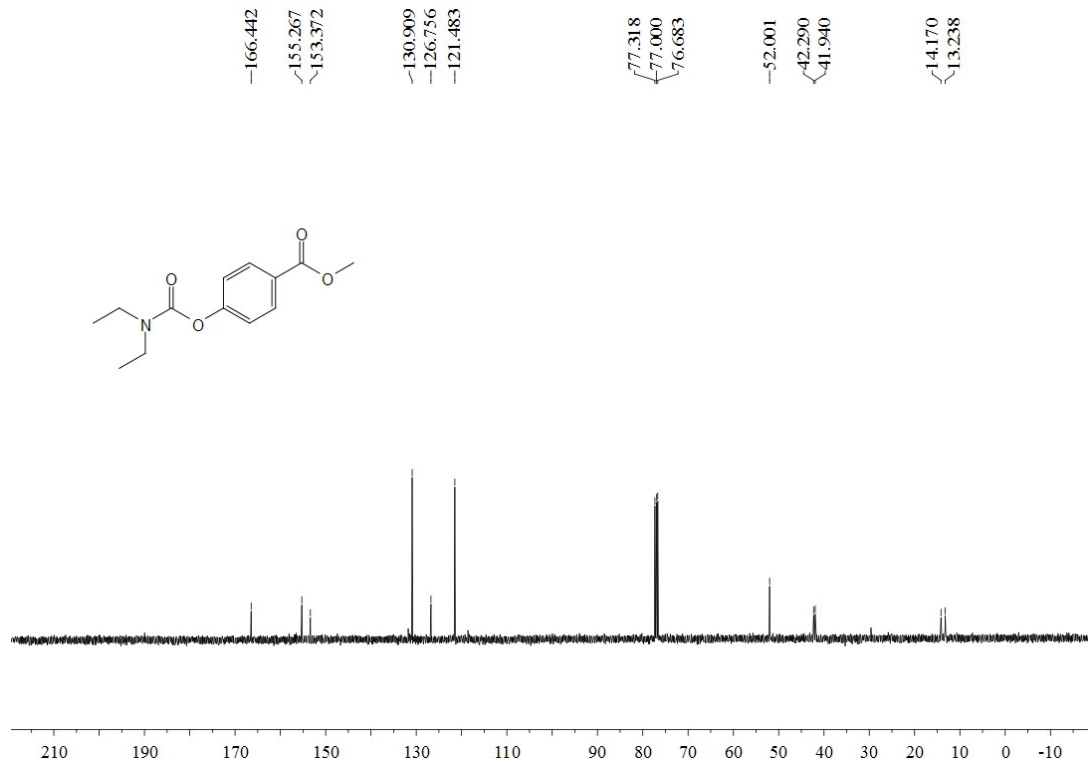
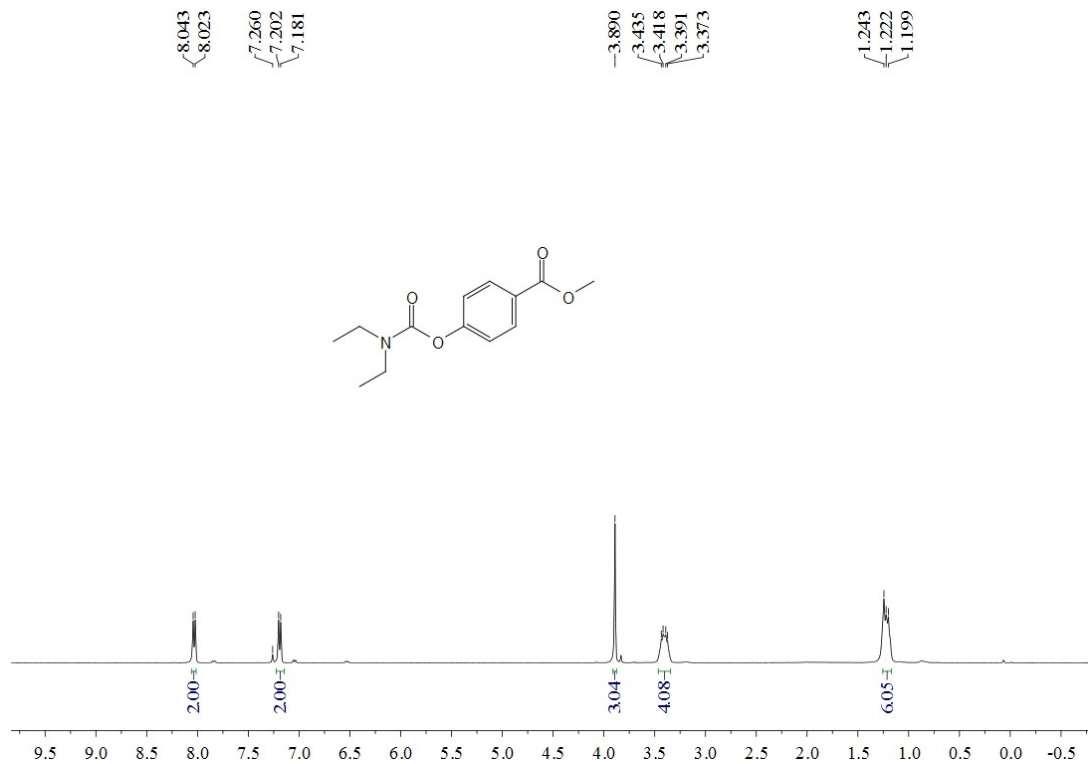
[1,1'-Biphenyl]-4-yl diethylcarbamate (6ia)



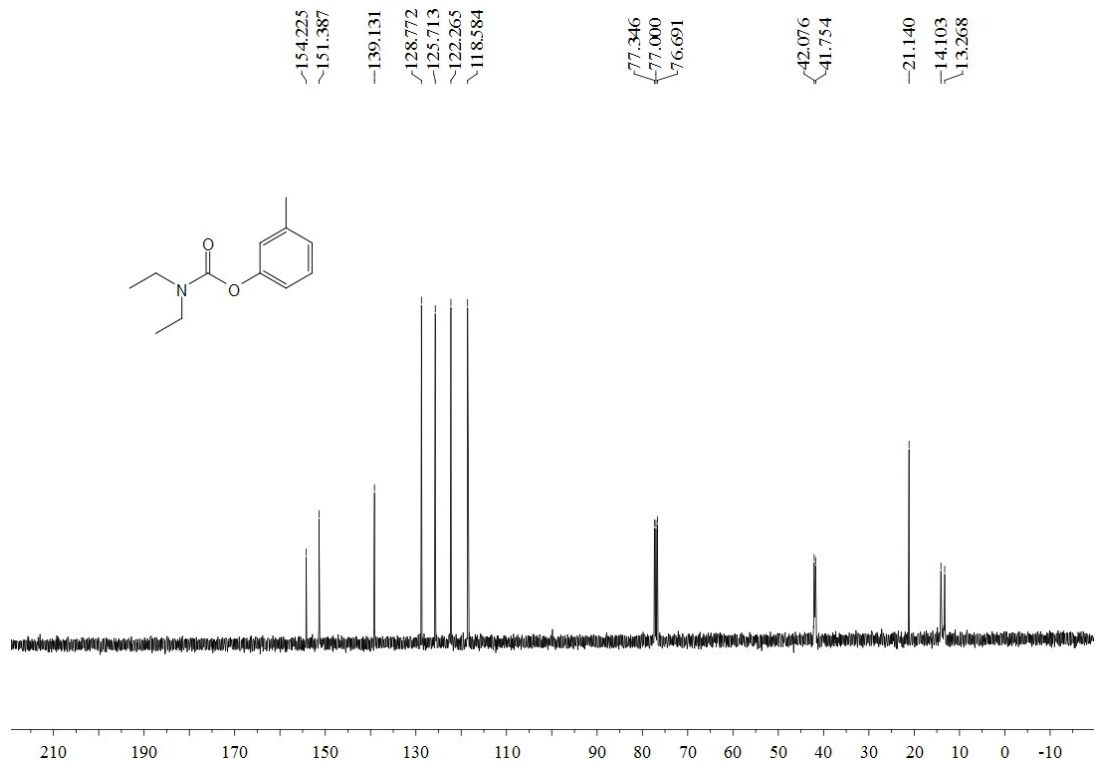
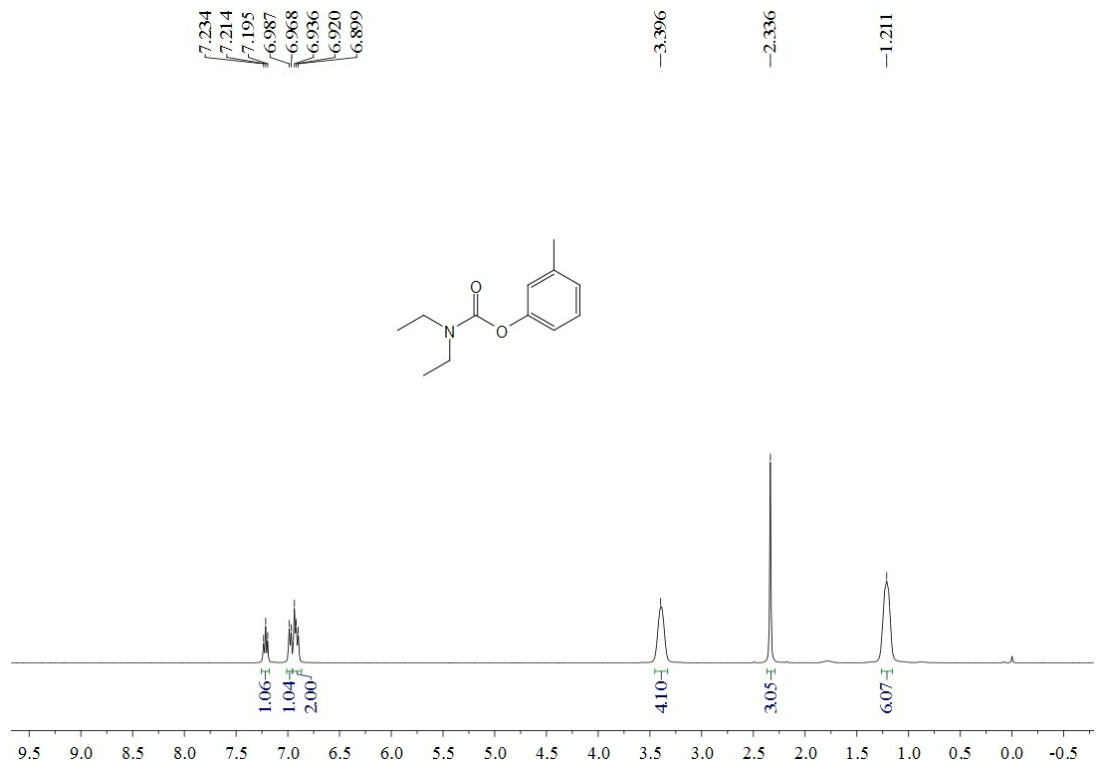
3-(Trifluoromethyl)phenyl diethylcarbamate (6ja)



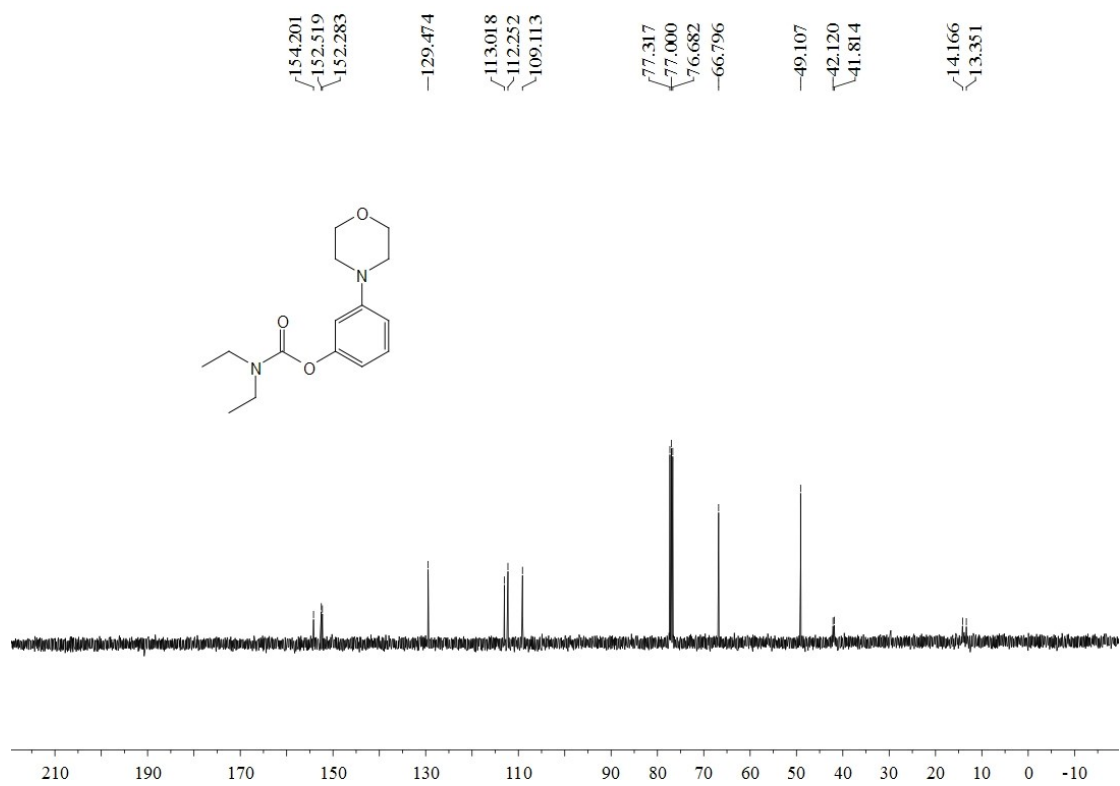
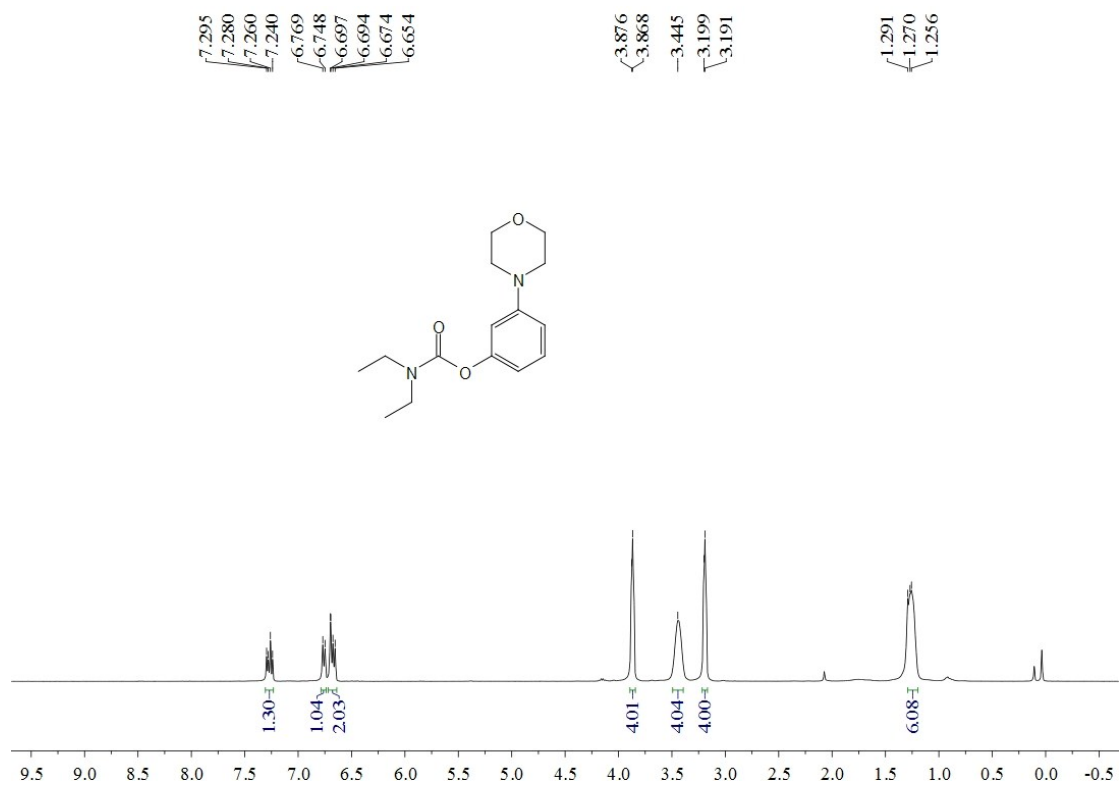
Methyl 4-((diethylcarbamoyl)oxy)benzoate (6ka)



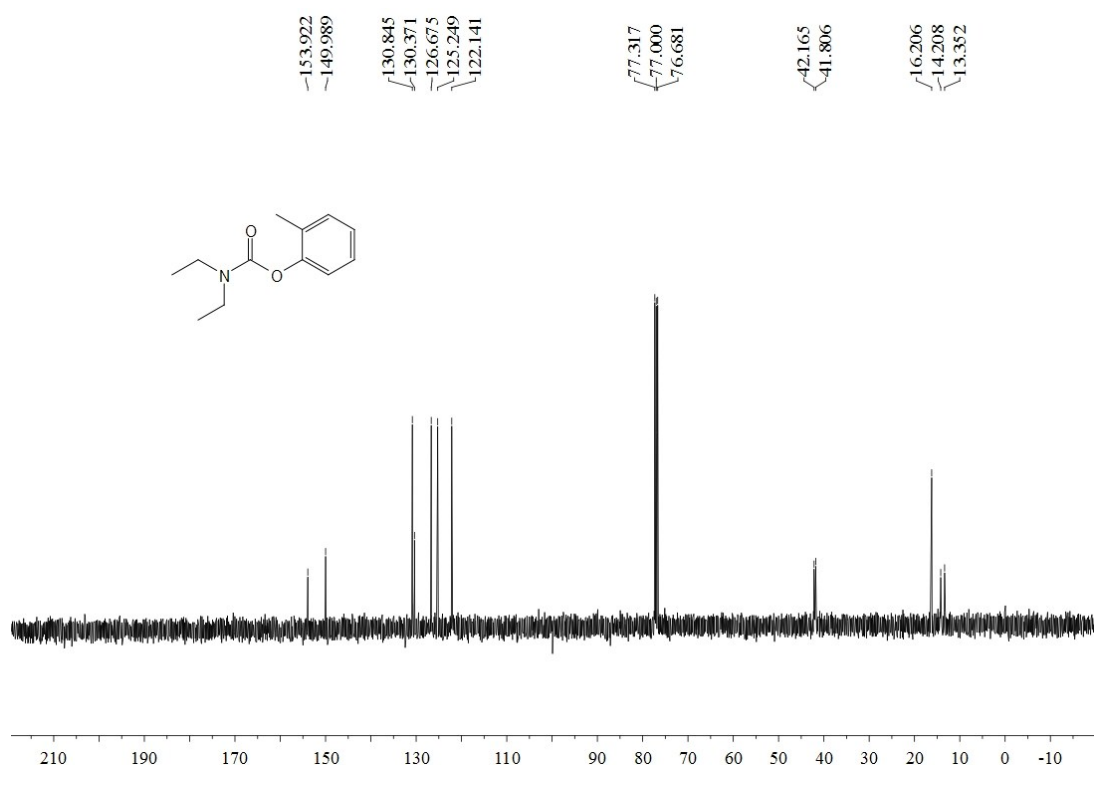
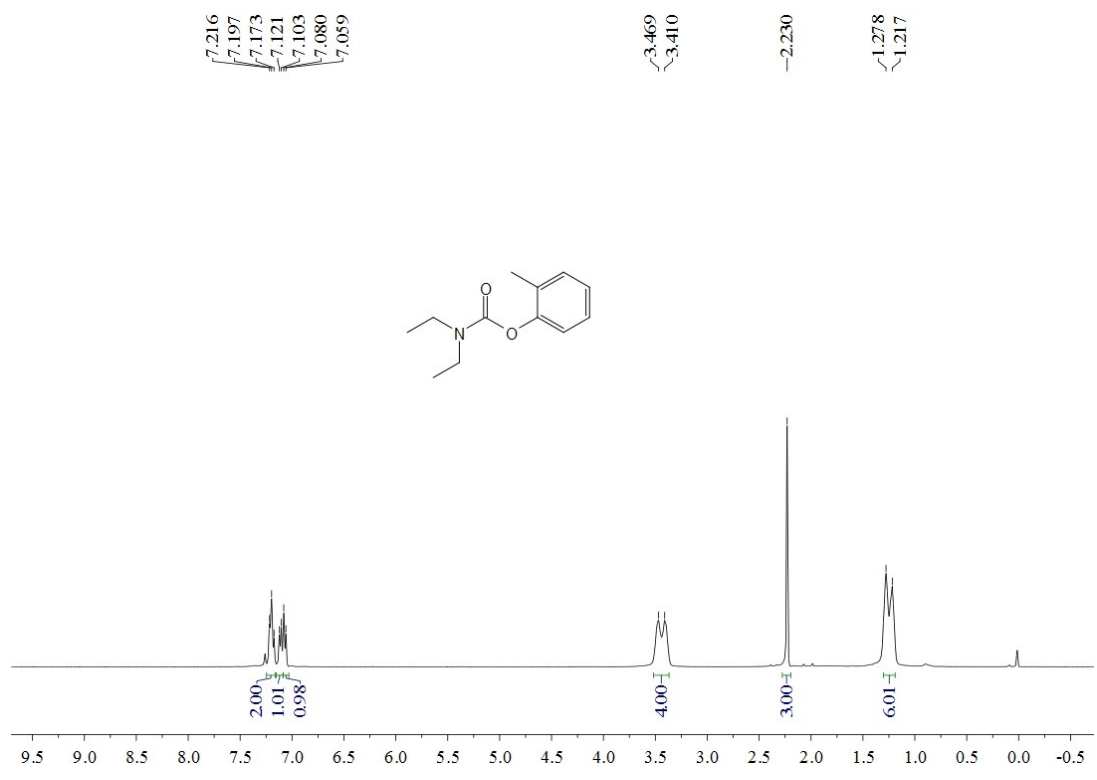
m-Tolyl diethylcarbamate (6la)



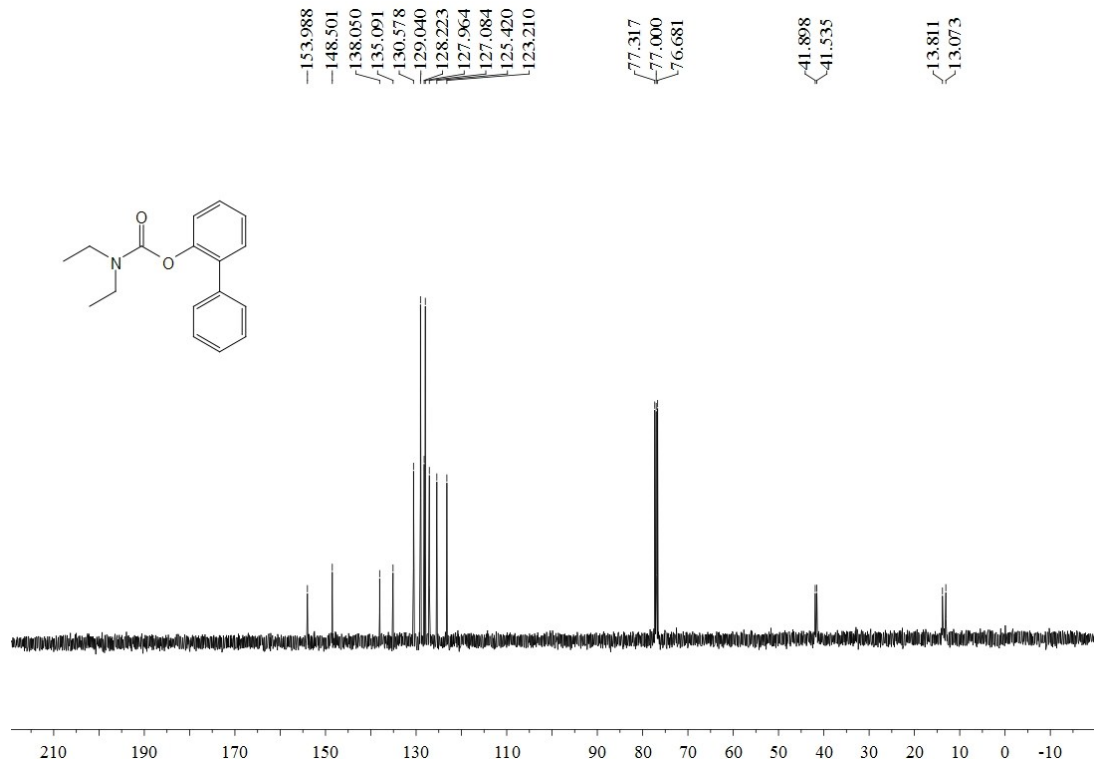
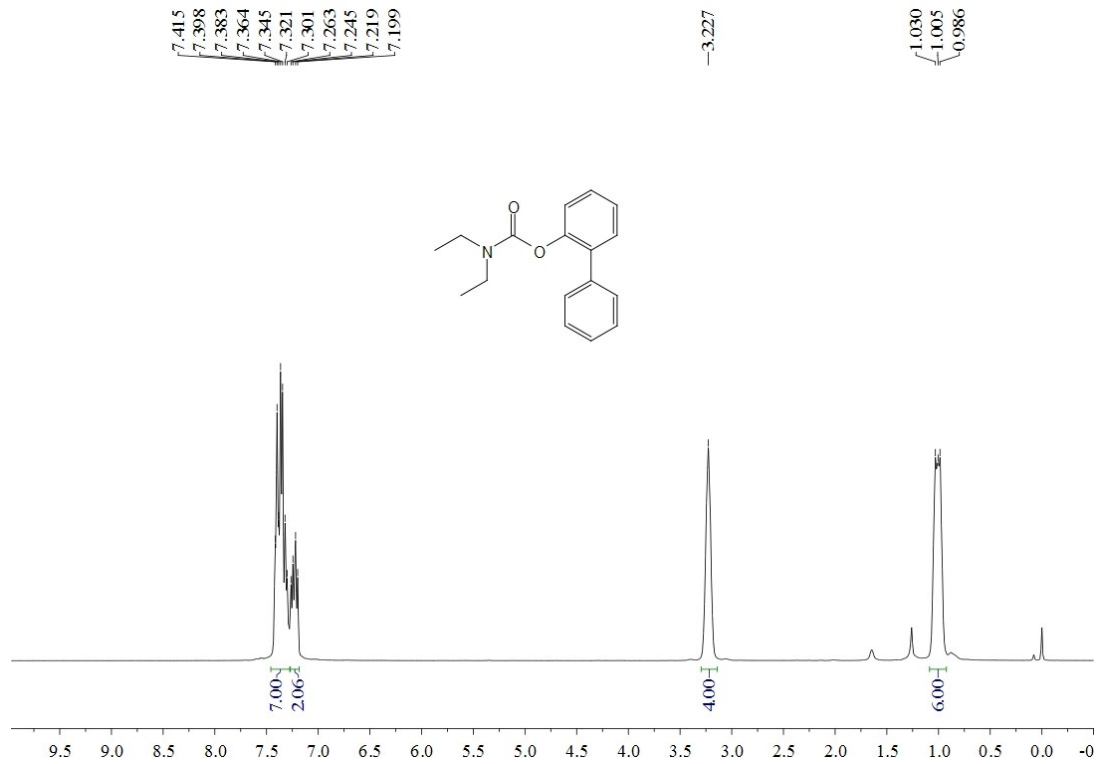
3-Morpholinophenyl diethylcarbamate (6ma)



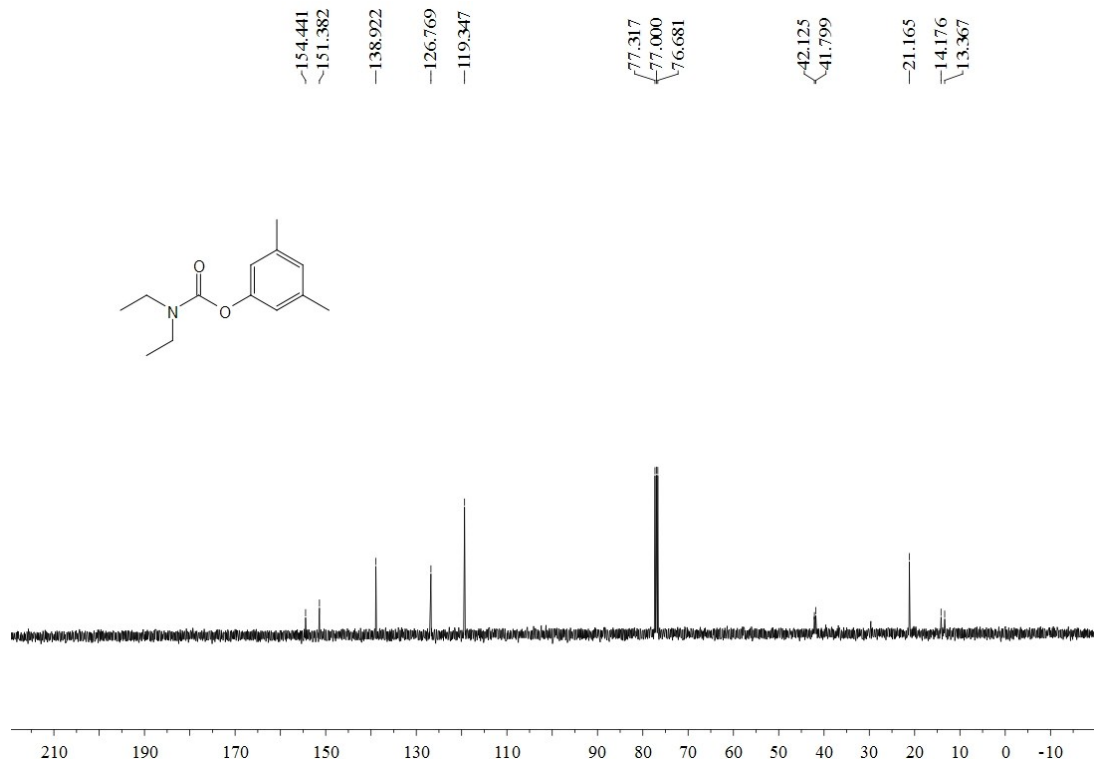
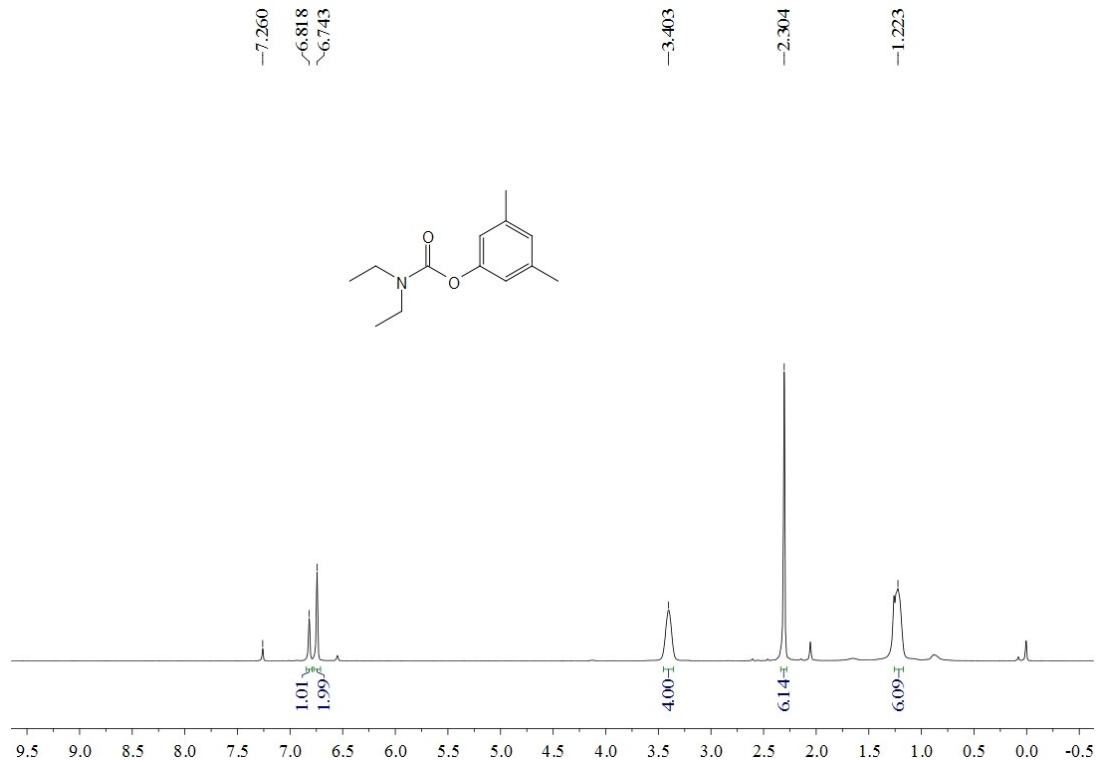
o-Tolyl diethylcarbamate (6na)



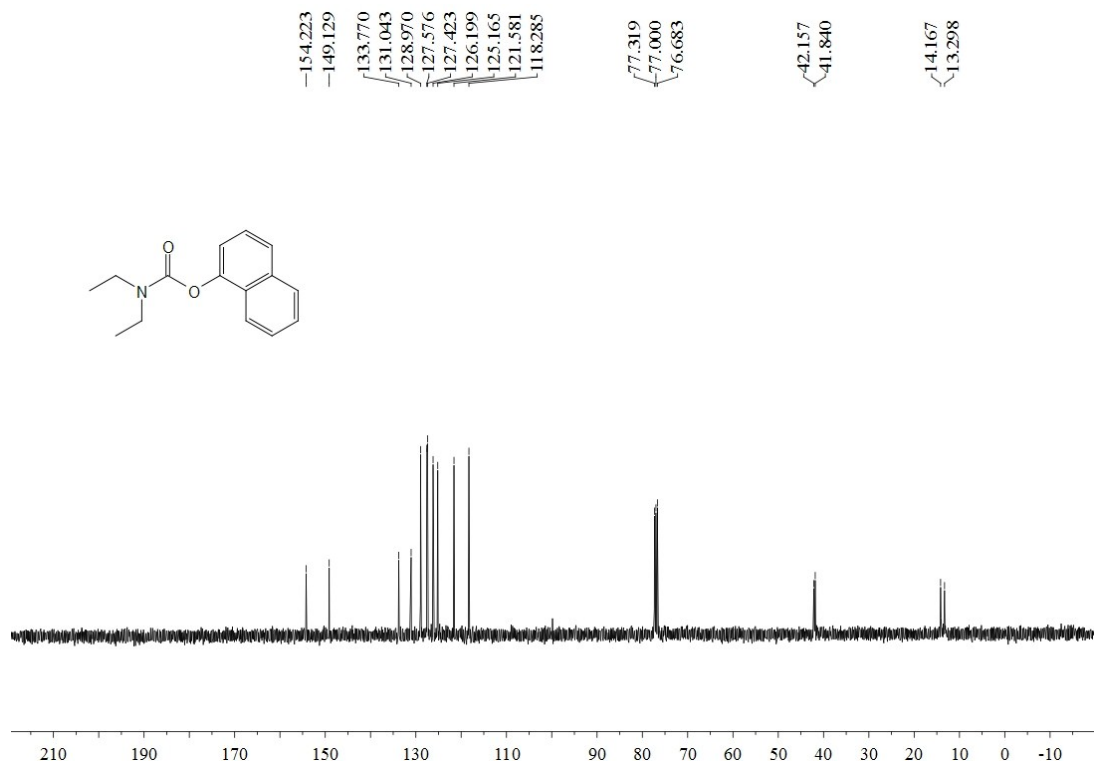
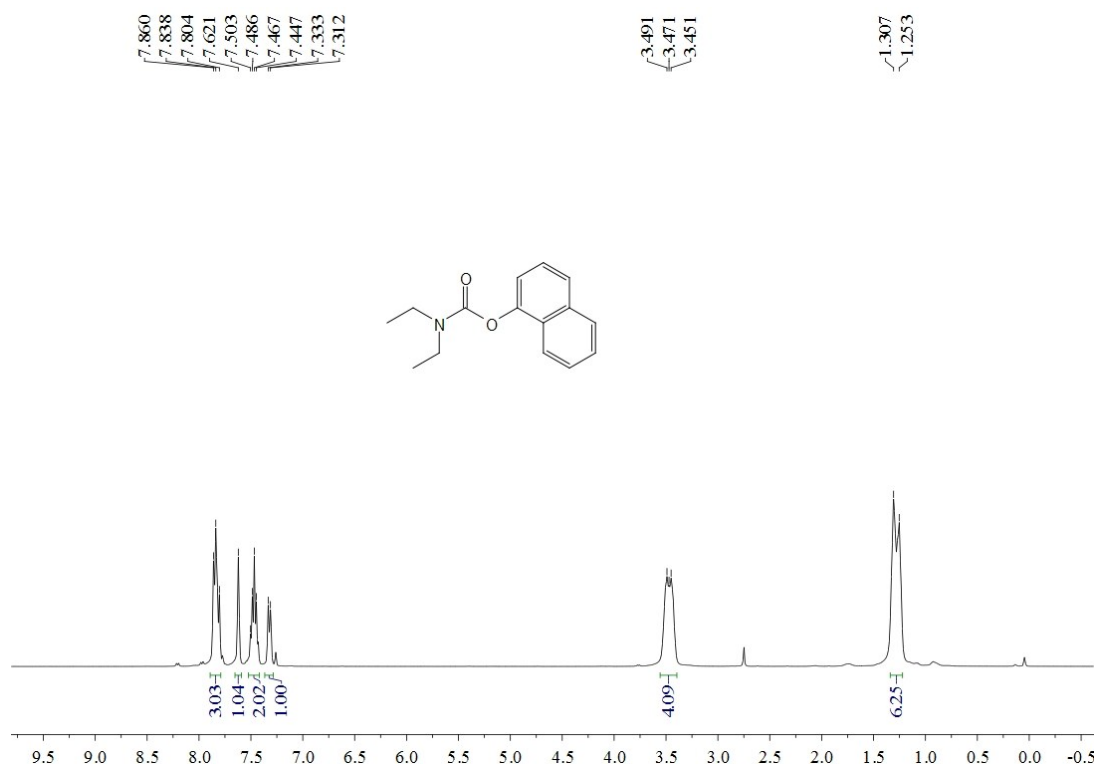
[1,1'-Biphenyl]-2-yl diethylcarbamate (60a)



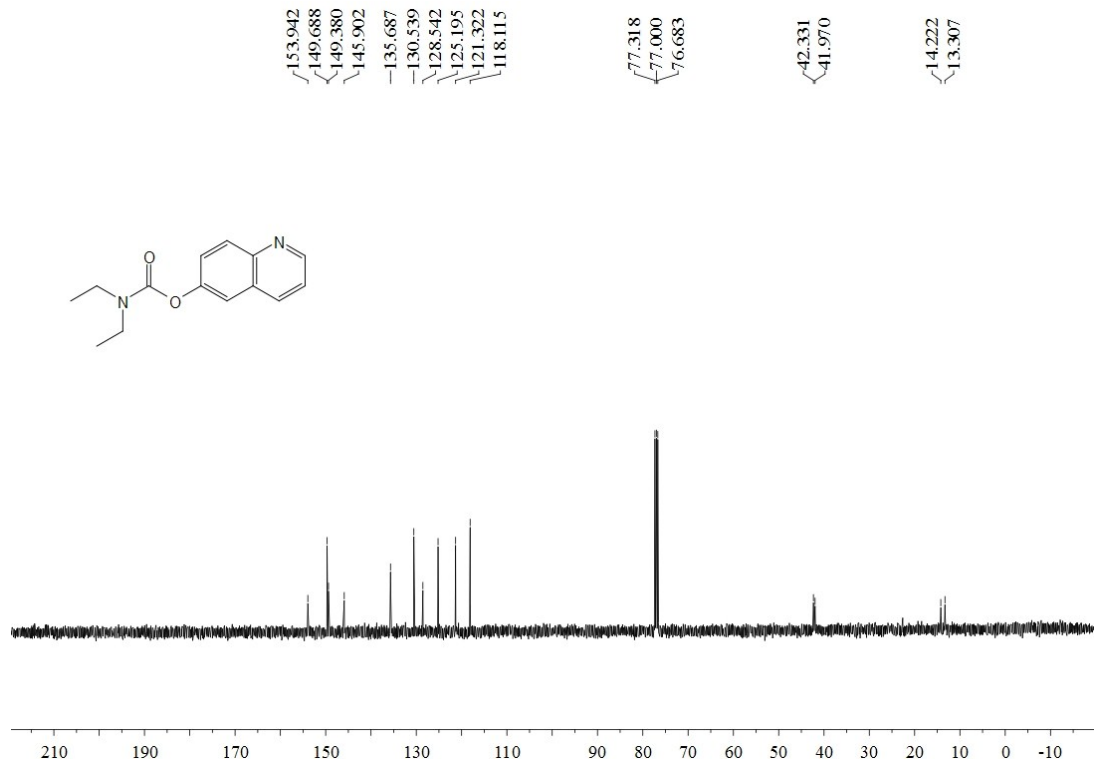
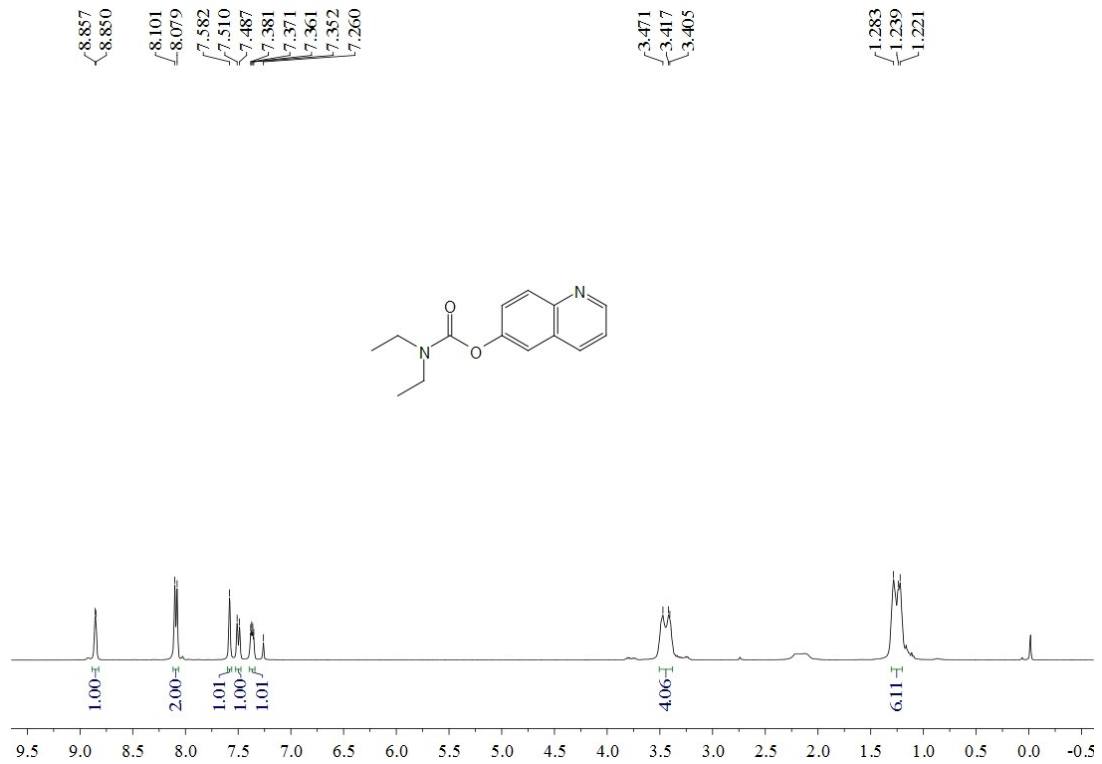
3,5-Dimethylphenyl diethylcarbamate (6pa)



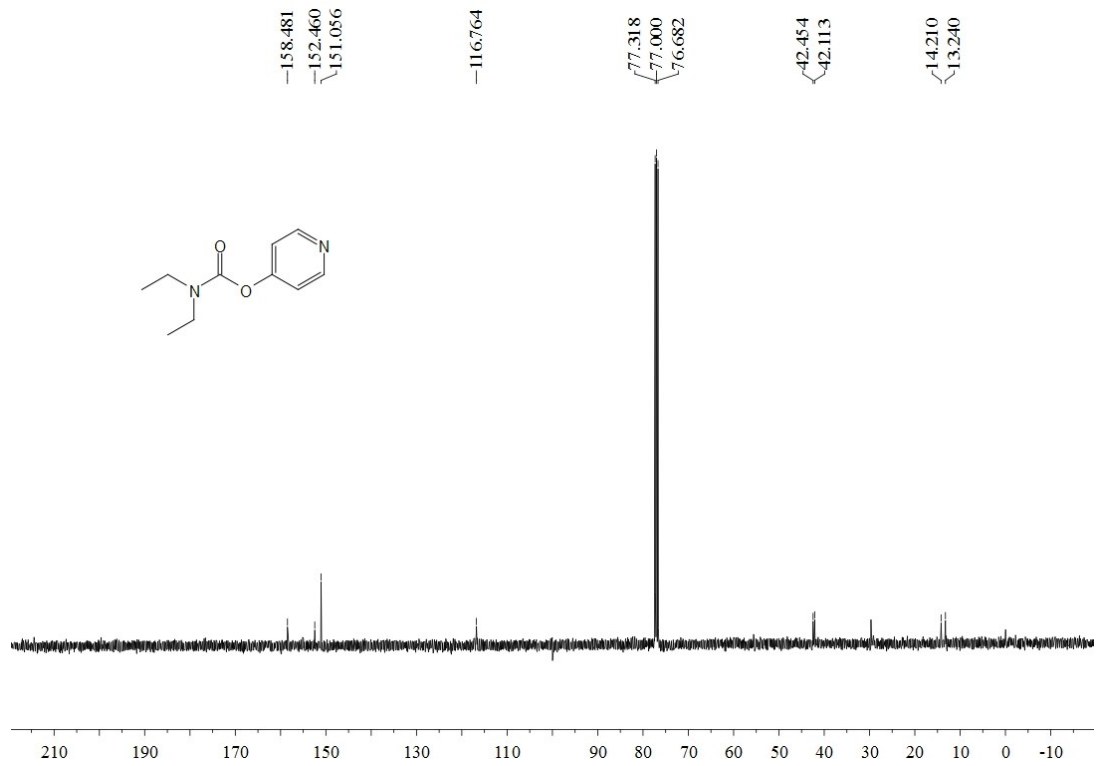
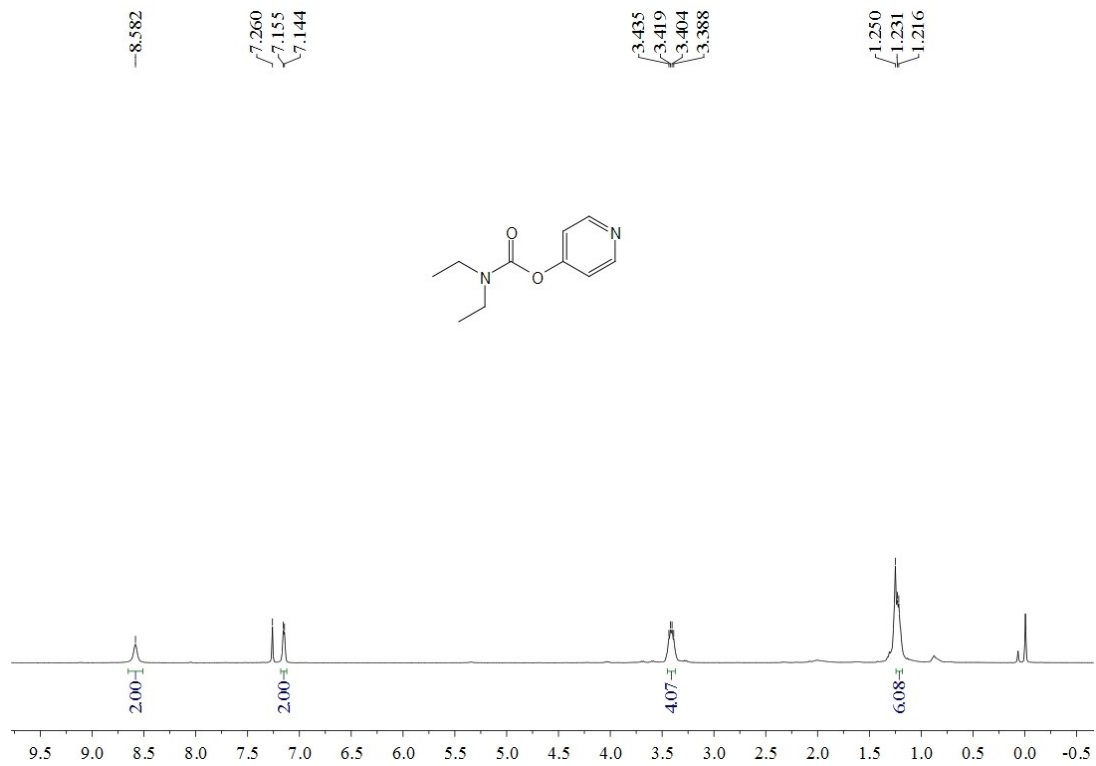
Naphthalen-1-yl diethylcarbamate (6qa)



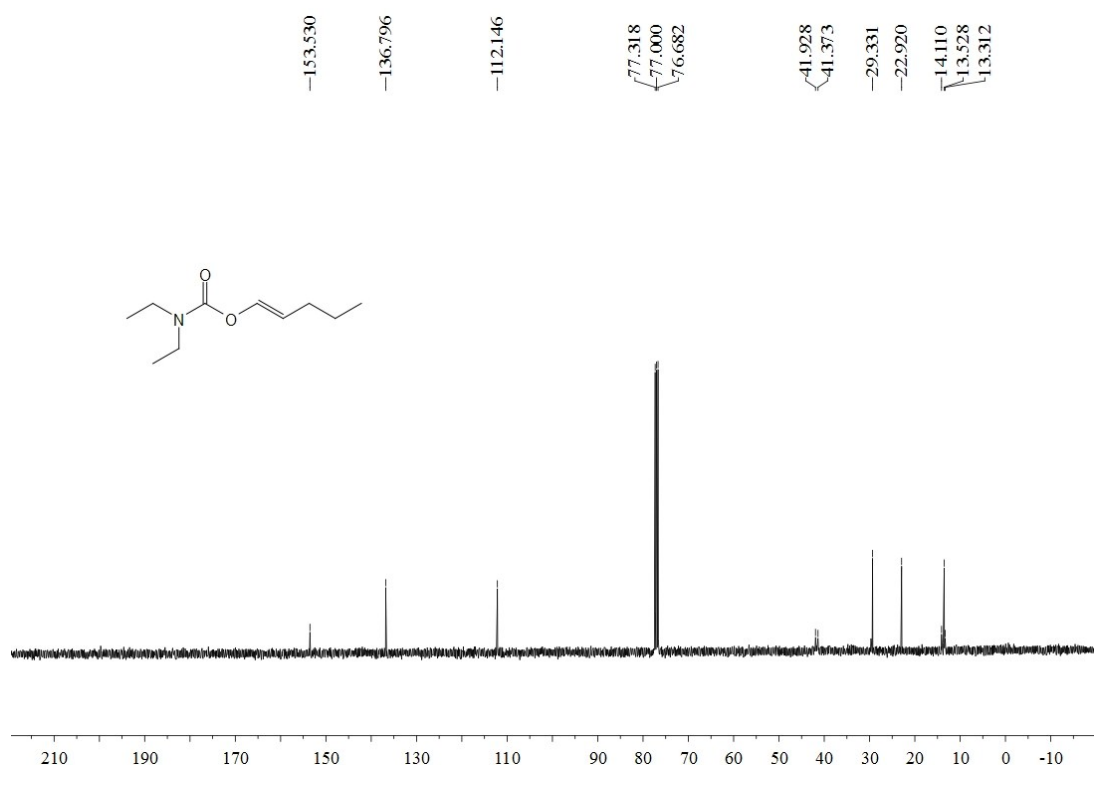
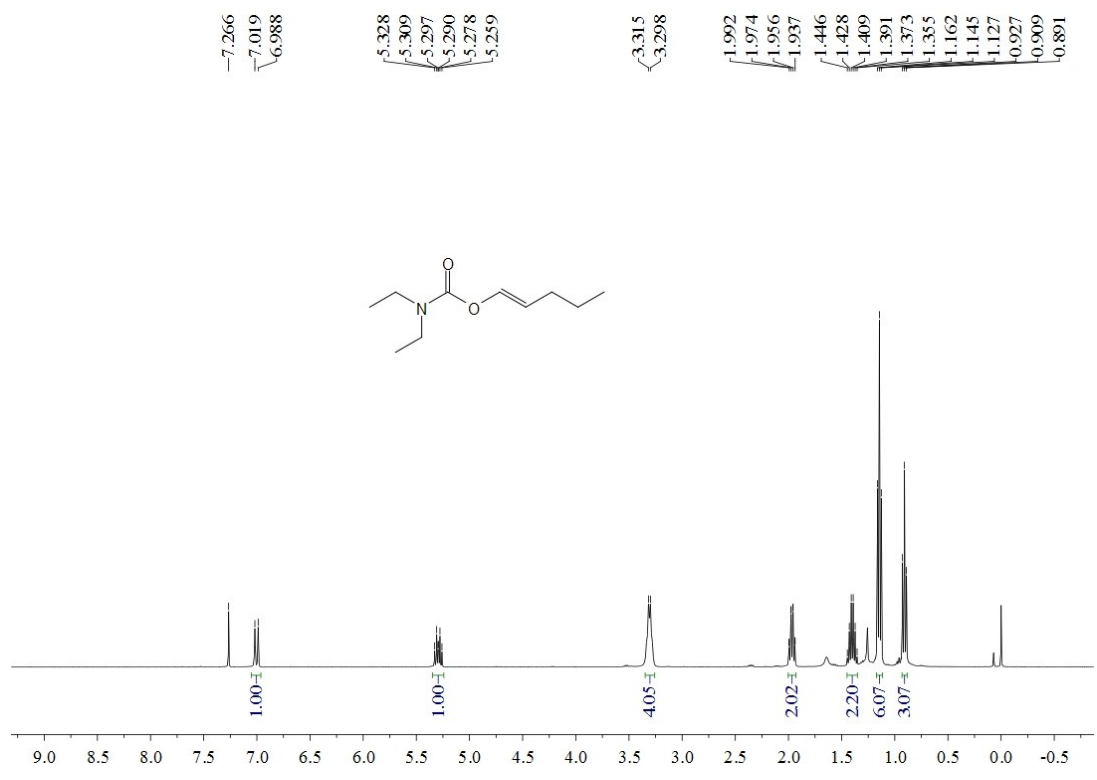
Quinolin-6-yl diethylcarbamate (6ra)



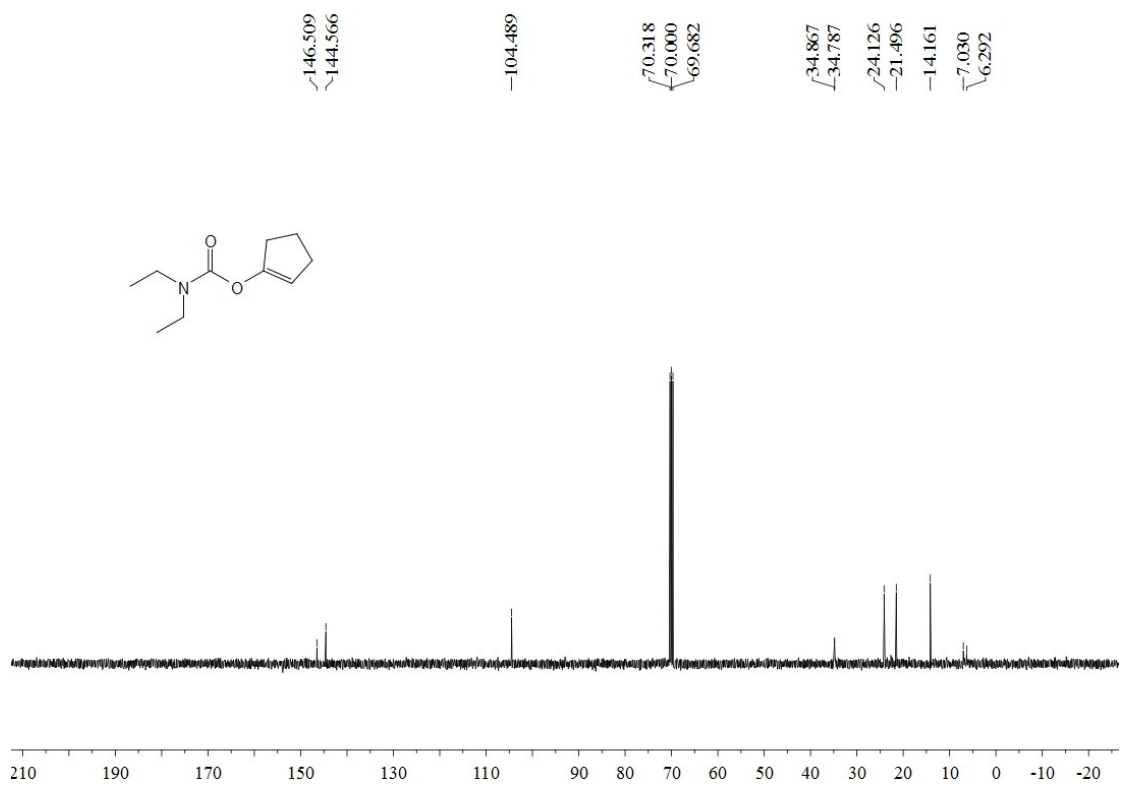
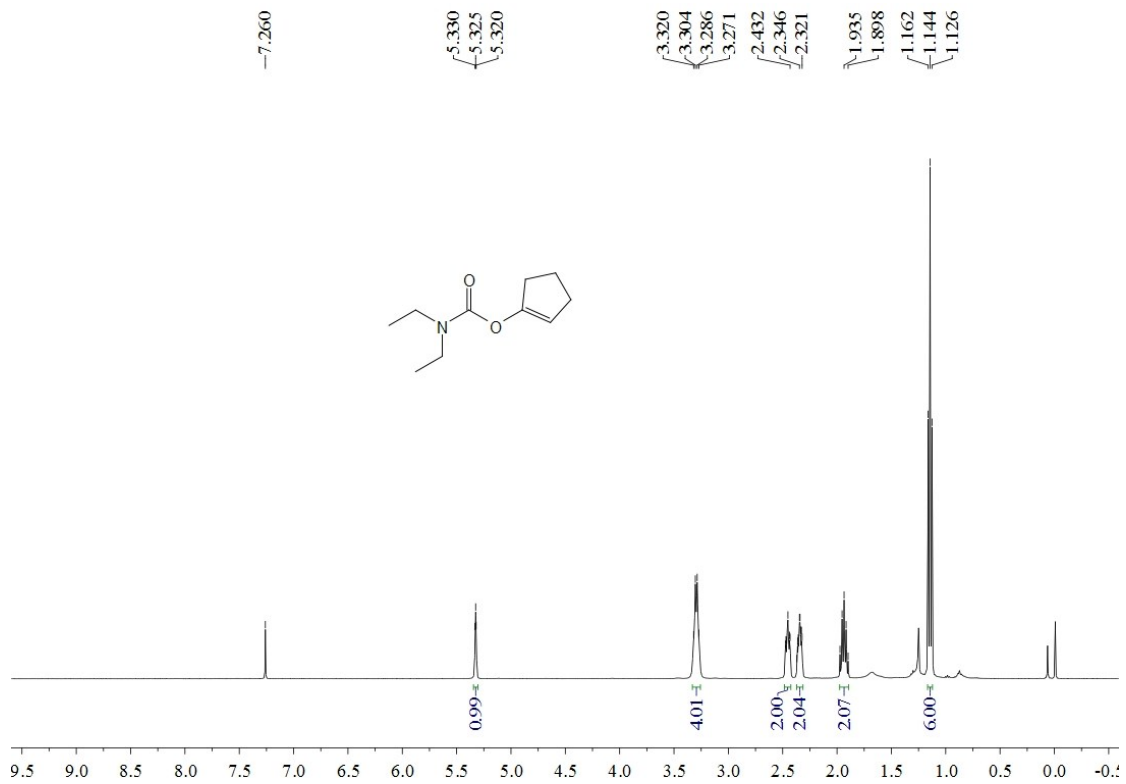
Pyridin-4-yl diethylcarbamate (6sa)



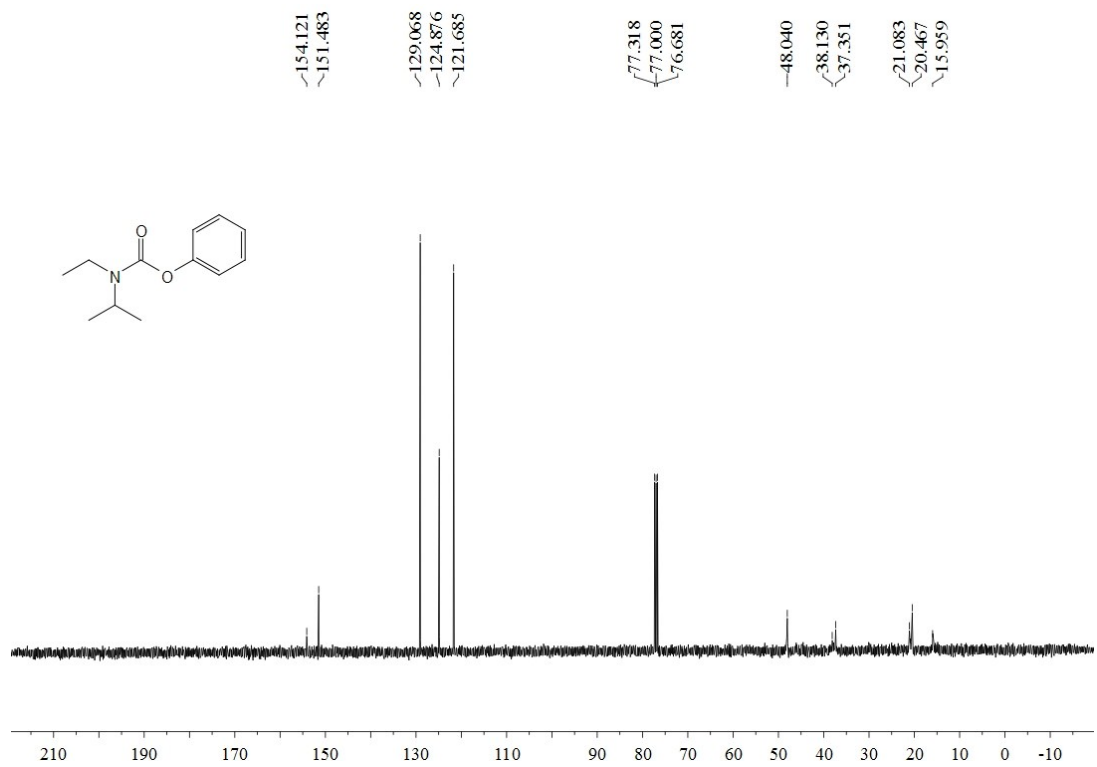
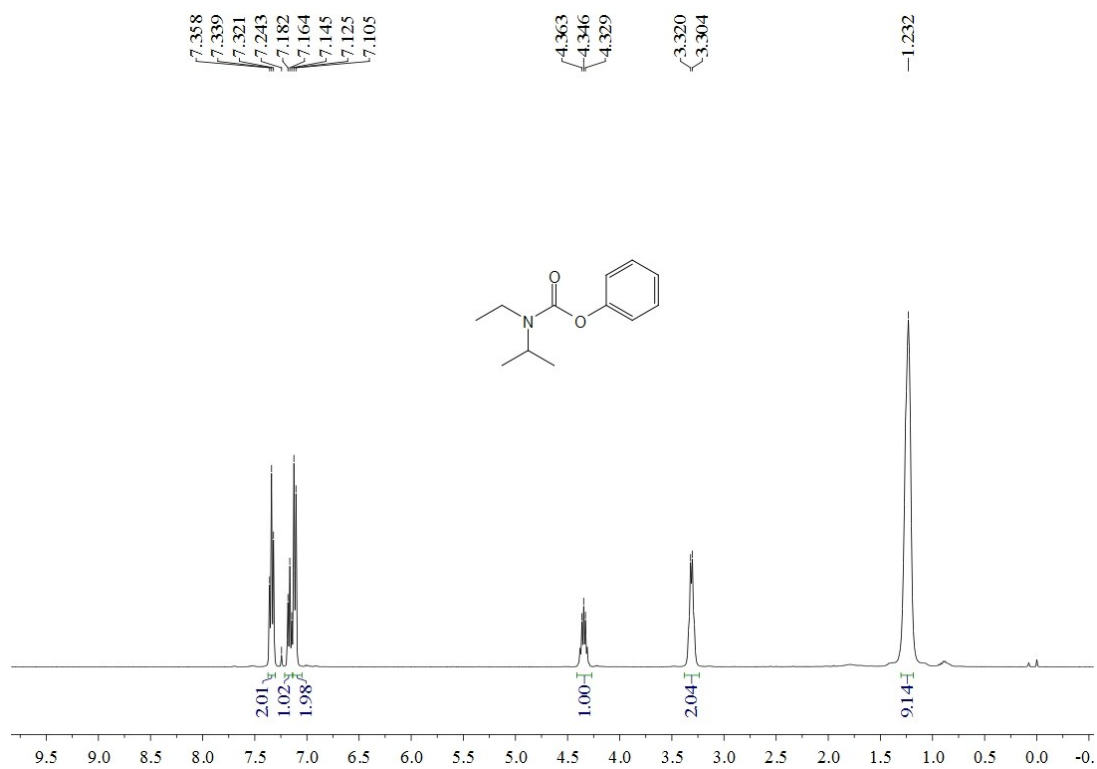
(E)-Pent-1-en-1-yl diethylcarbama (6ta)



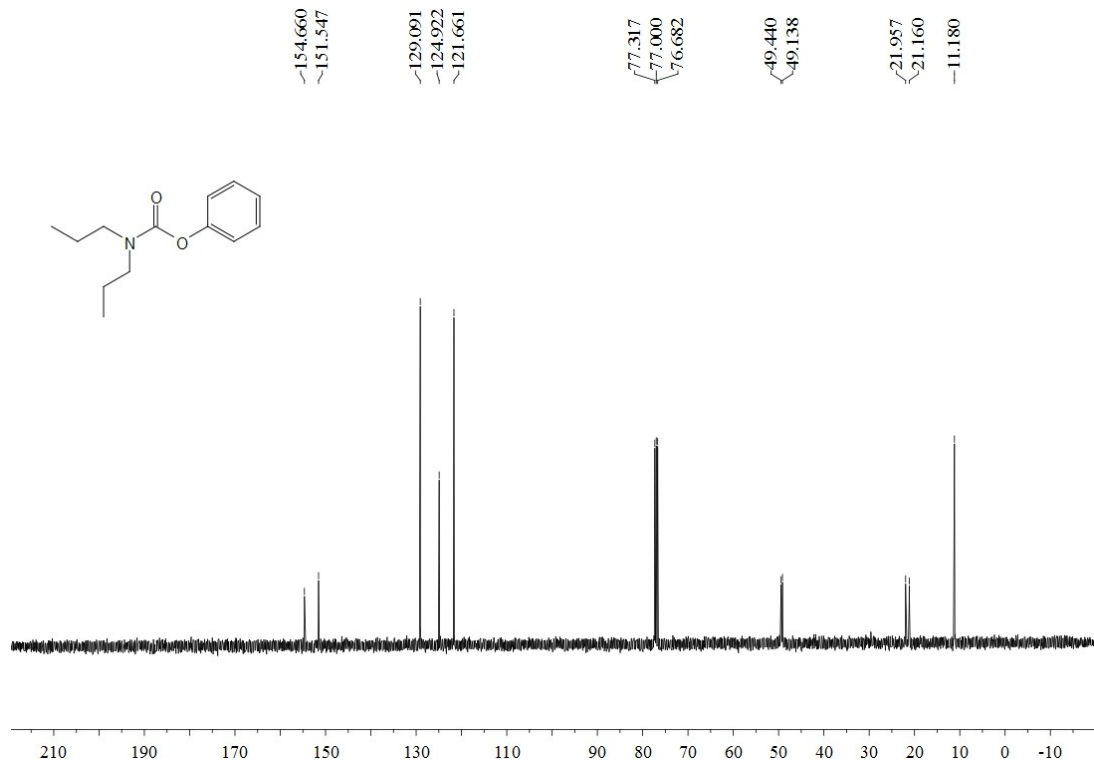
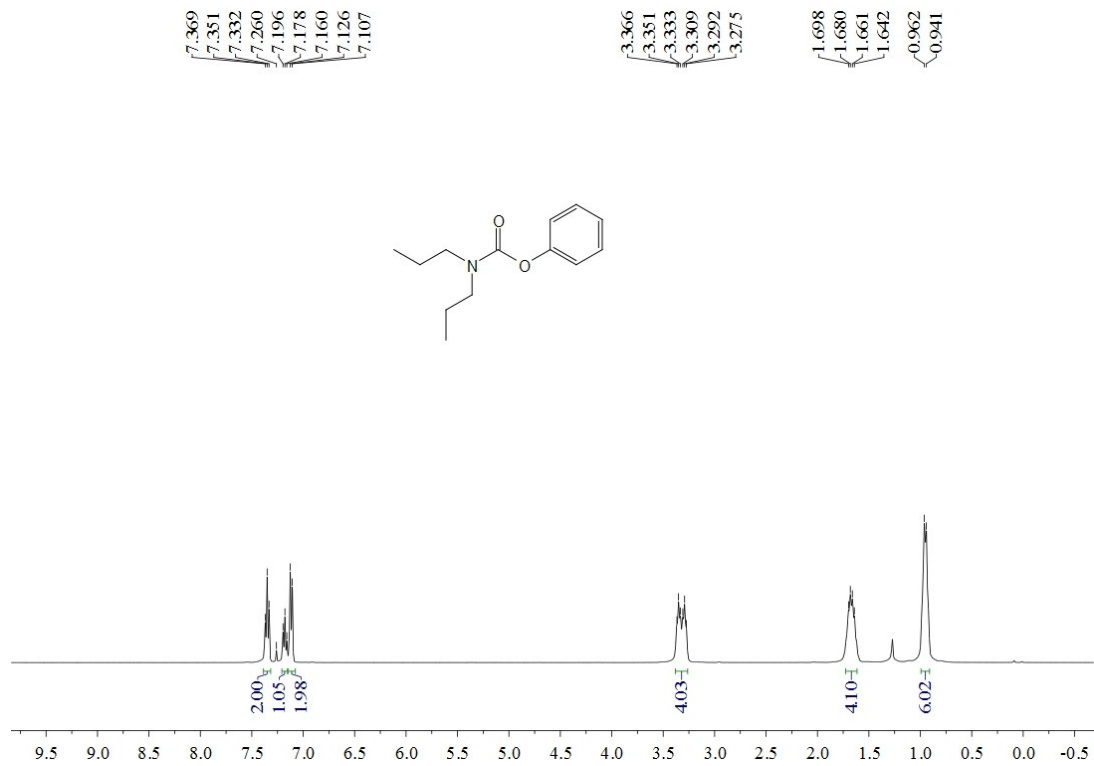
Cyclopent-1-en-1-yl diethylcarbamate (6ua)



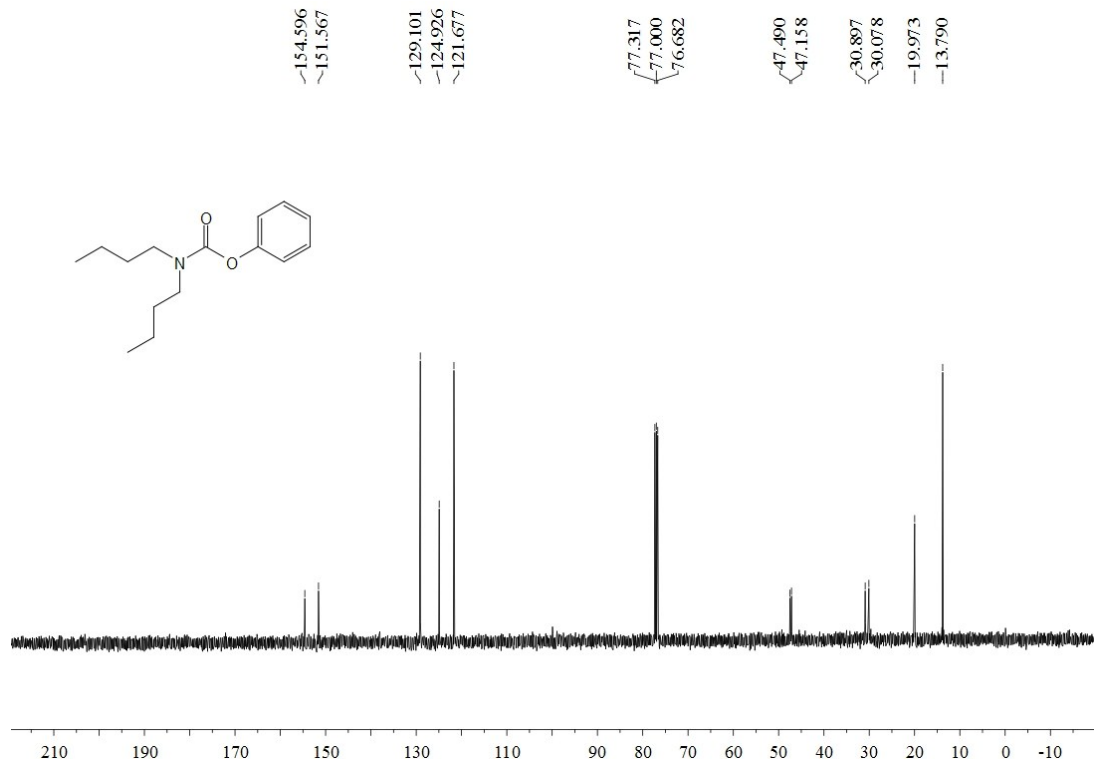
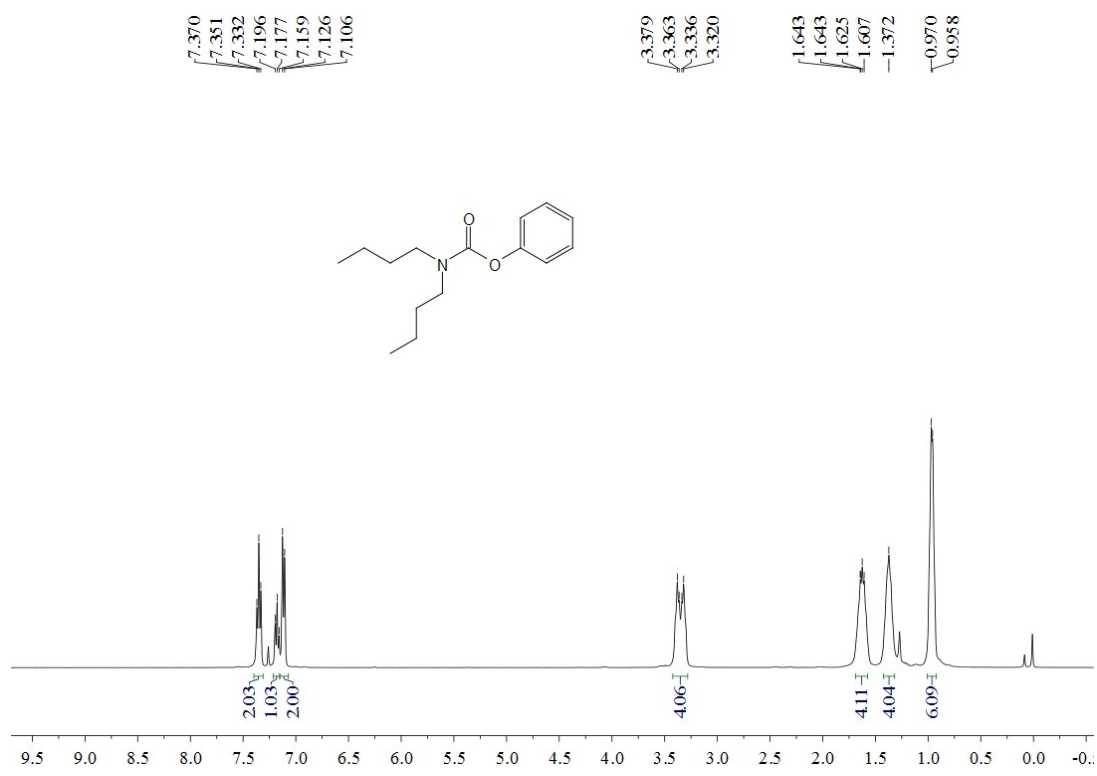
Phenyl ethyl(isopropyl)carbamate (6ab)



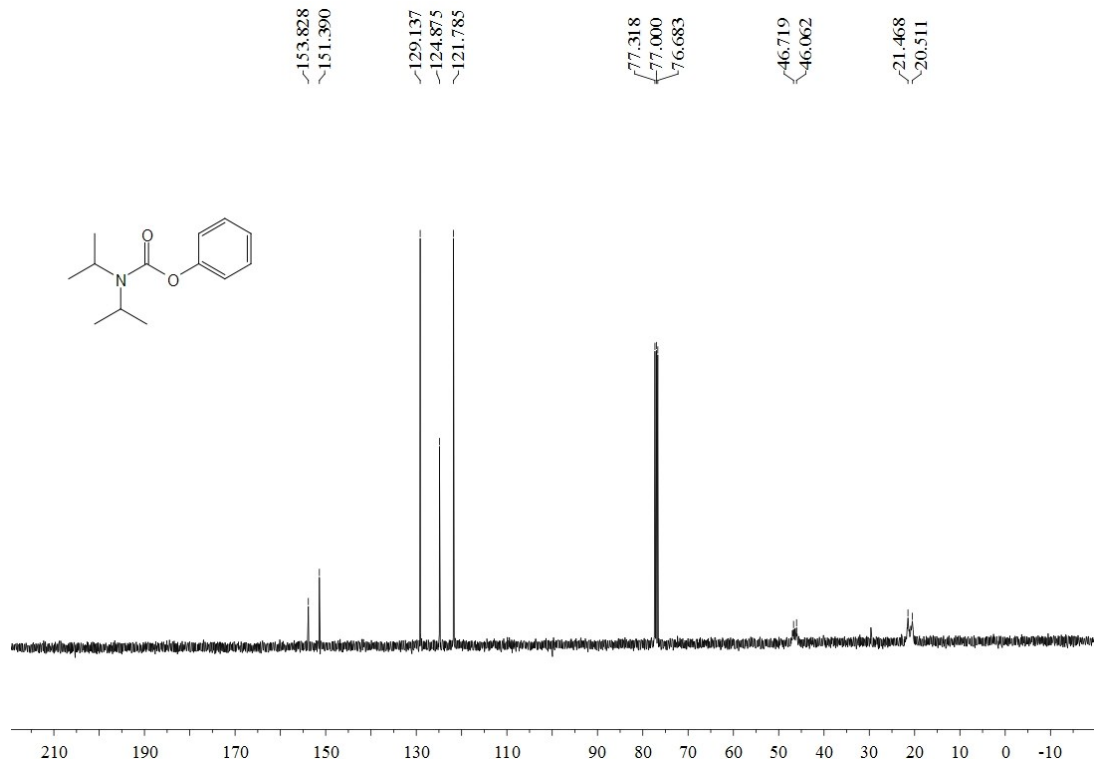
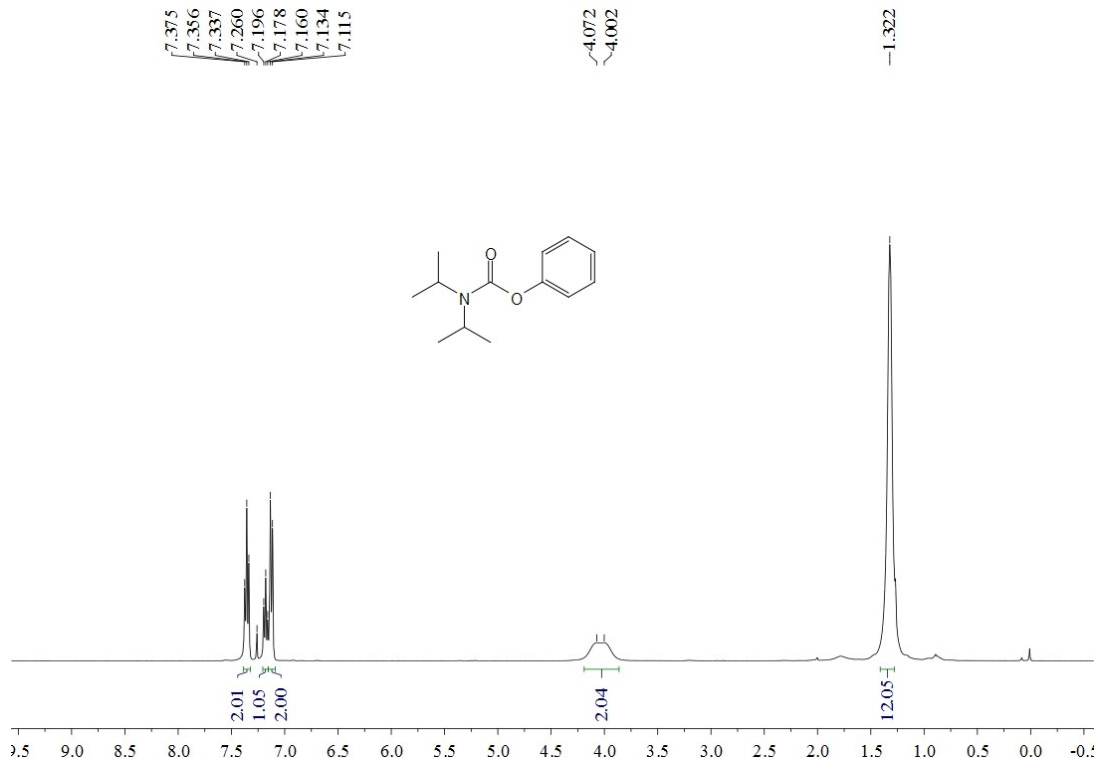
Phenyl dipropylcarbamate (6ac)



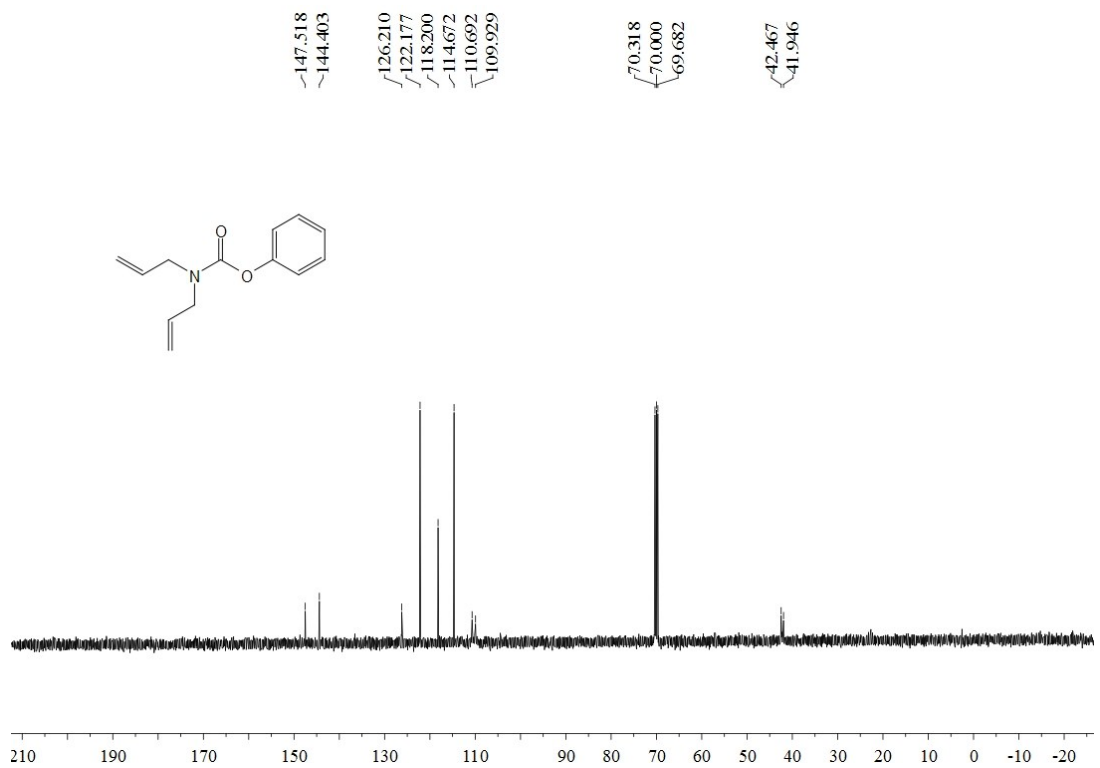
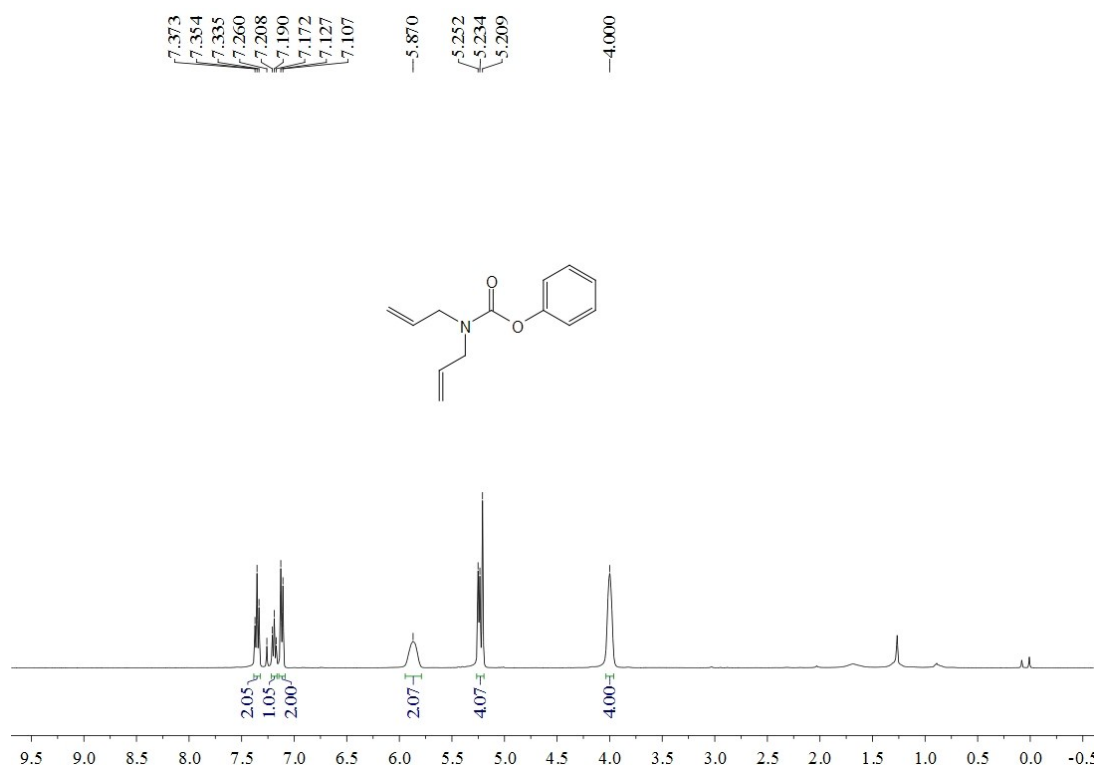
Phenyl dibutylcarbamate (6ad)



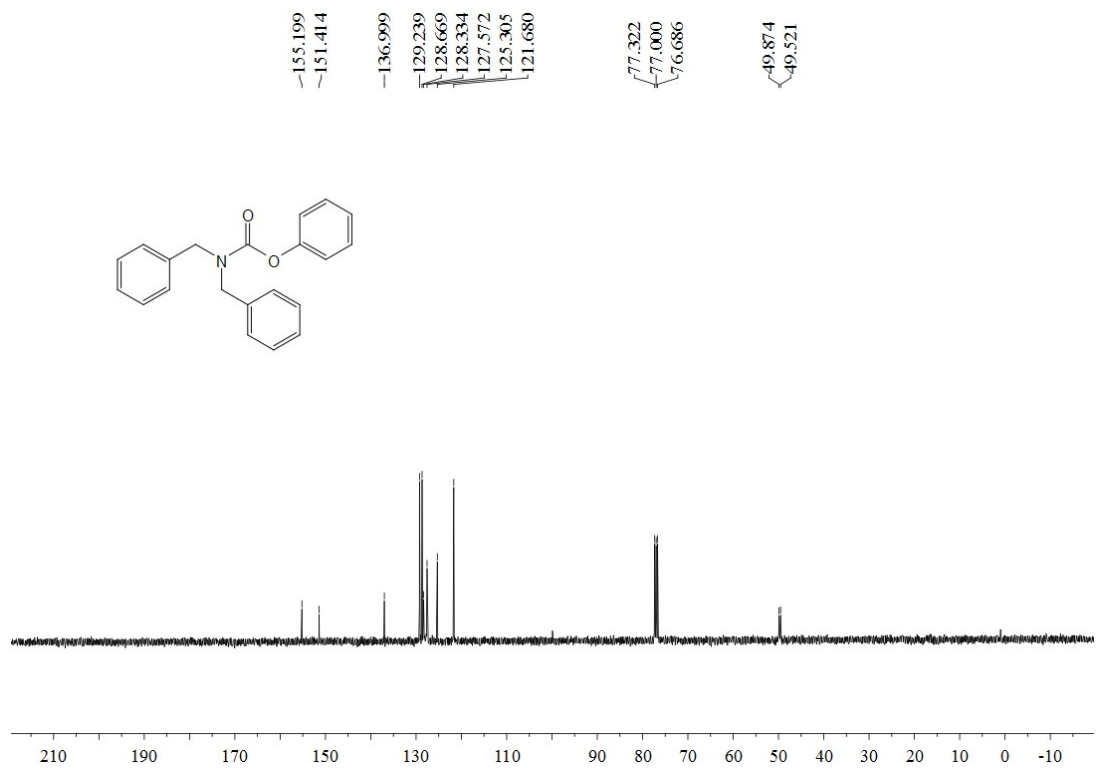
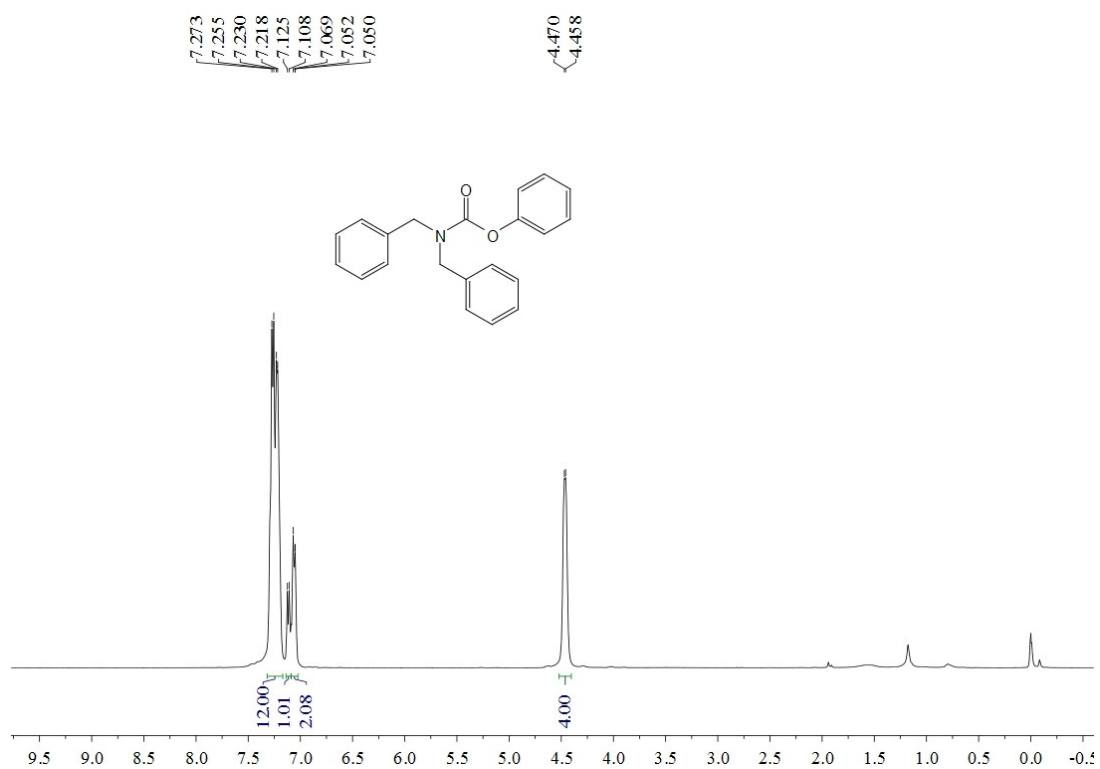
Phenyl diisopropylcarbamate (6ae)



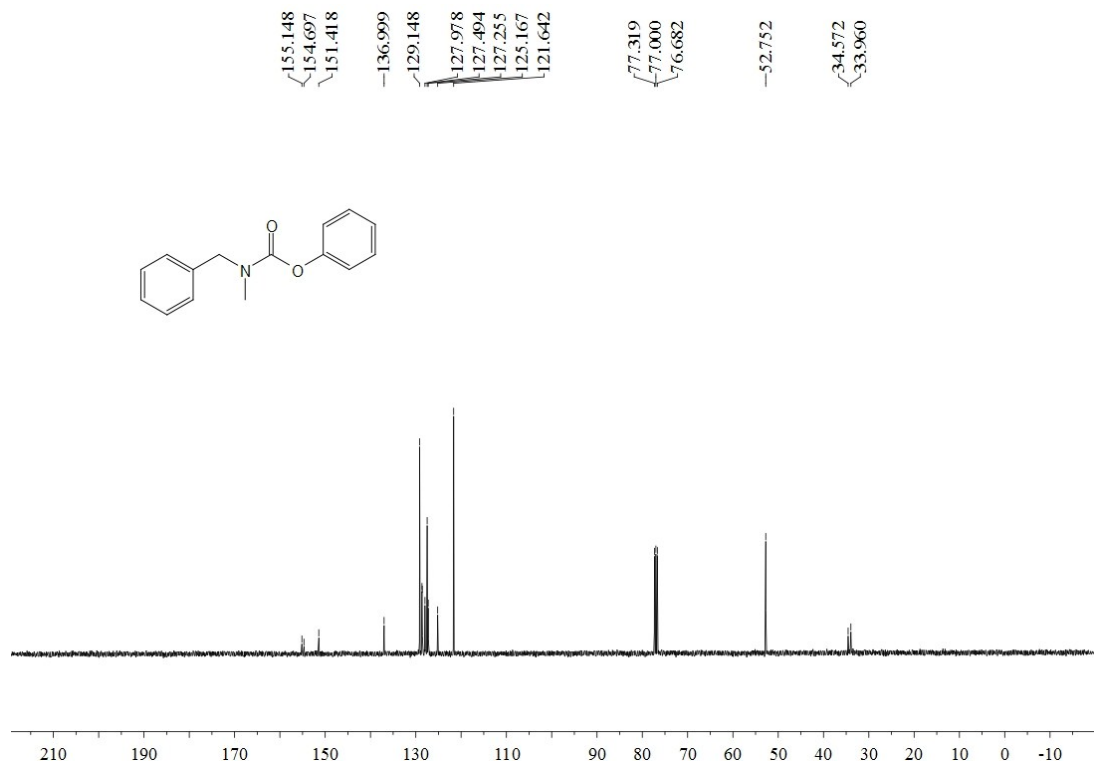
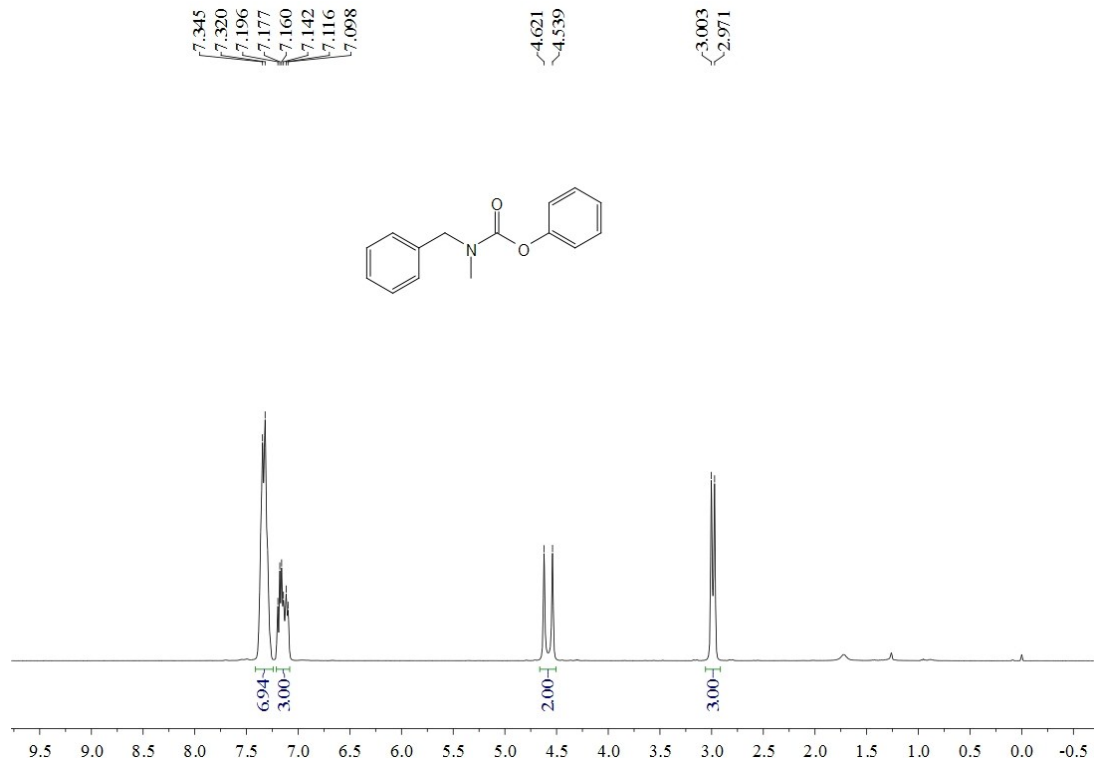
Phenyl diallylcarbamate (6af)



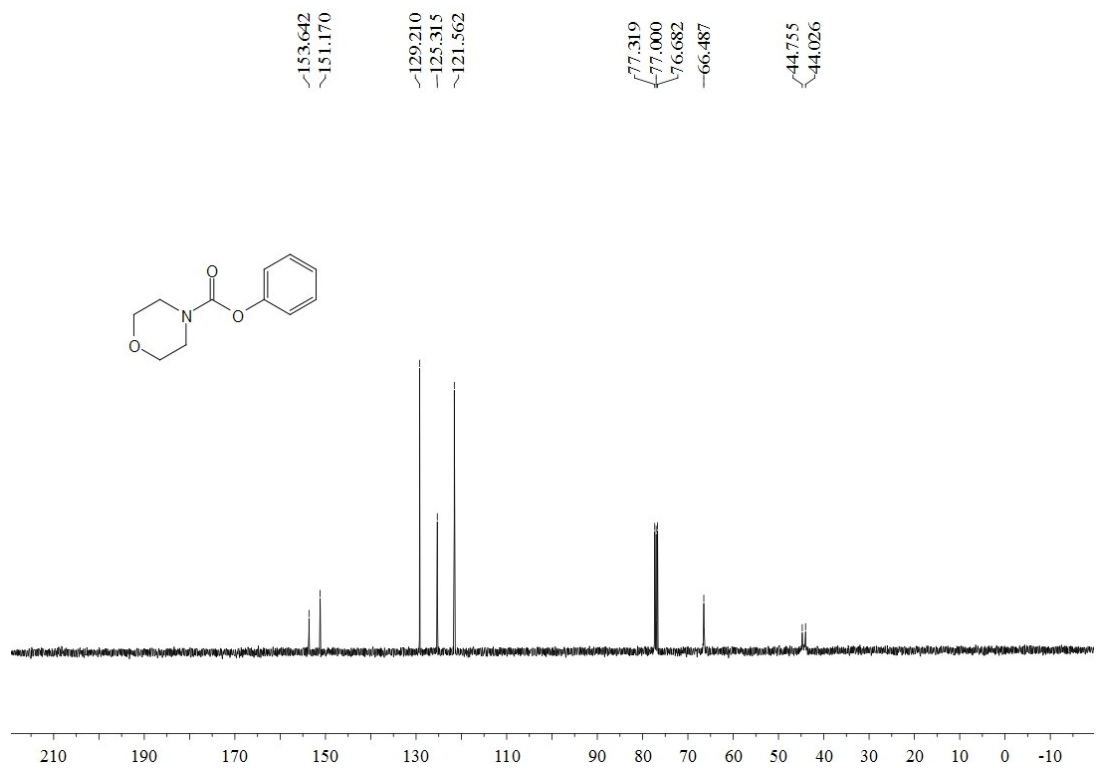
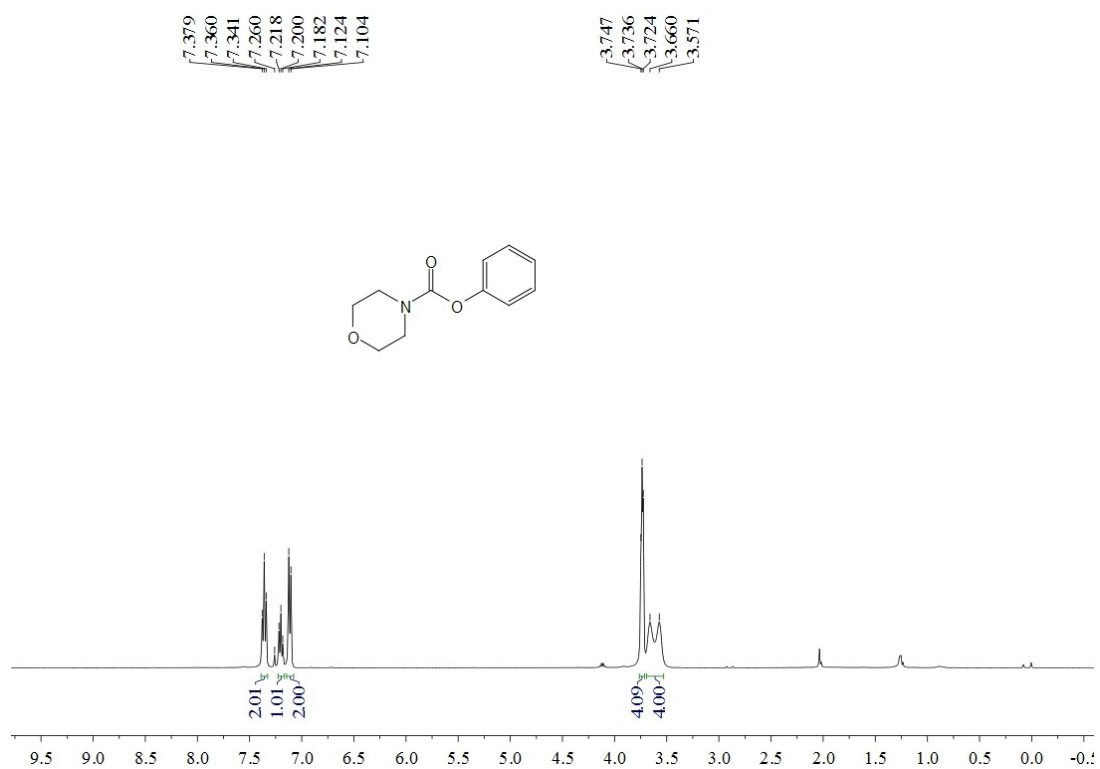
Phenyl dibenzylcarbamate (6ag)



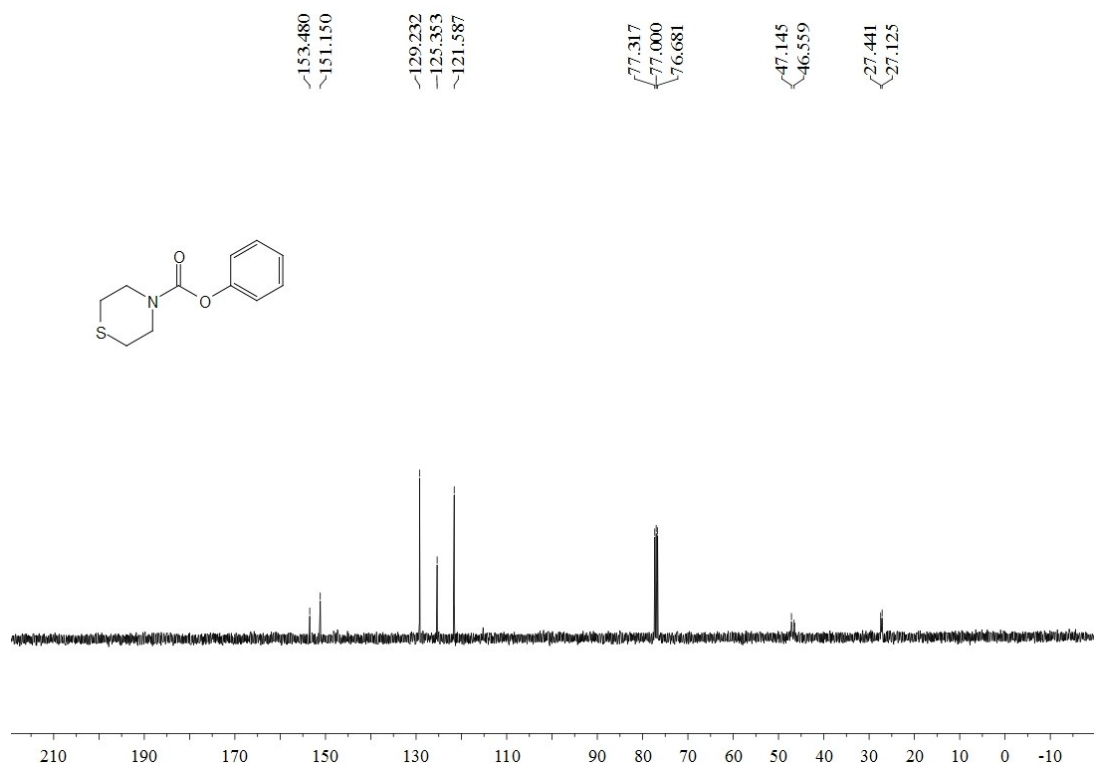
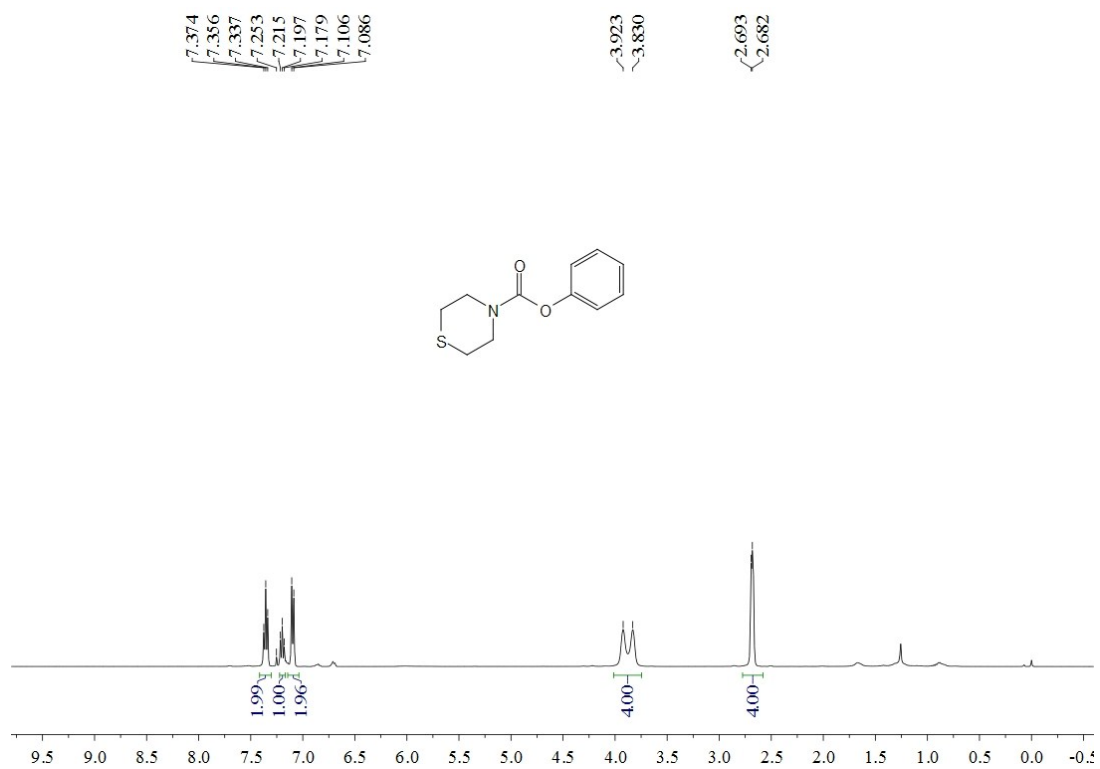
Phenyl benzyl(methyl)carbamate (6ah)



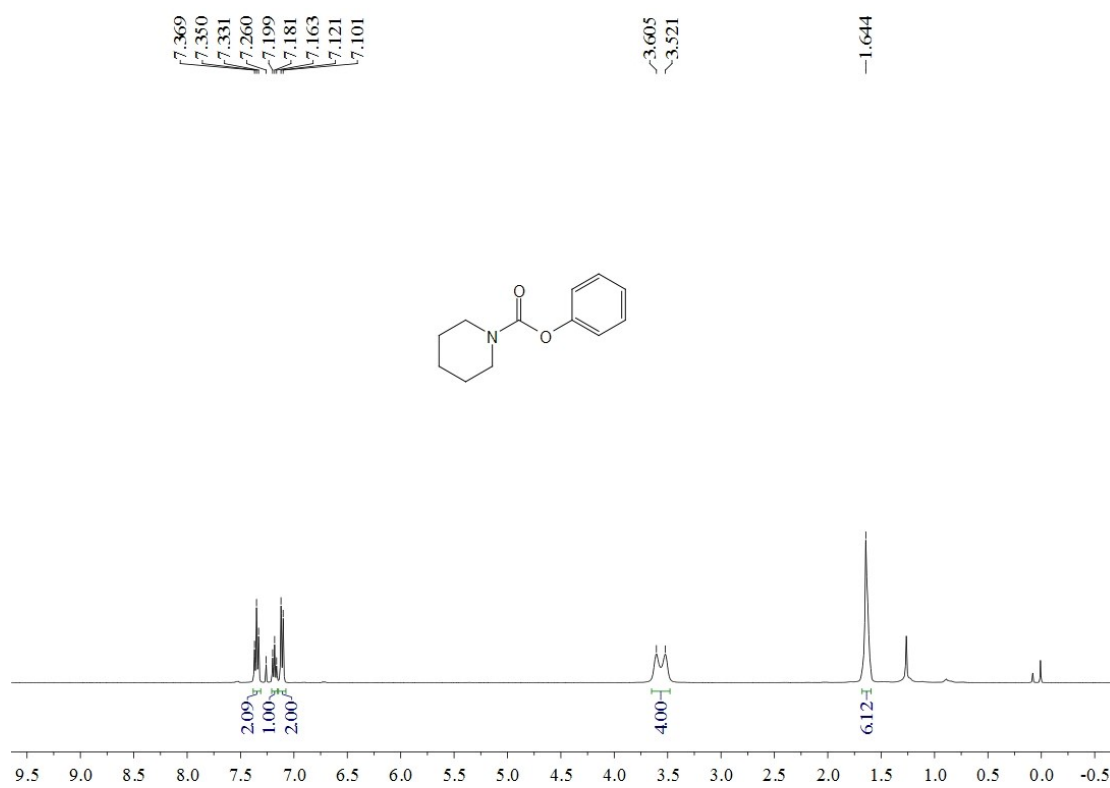
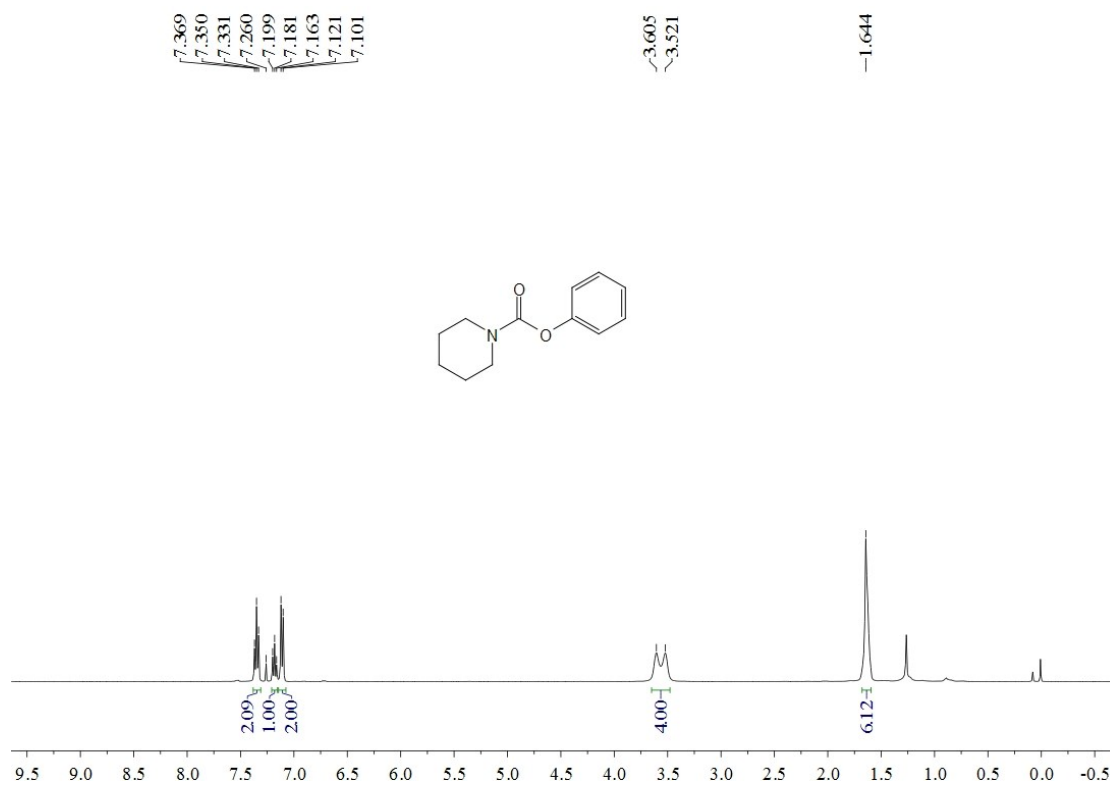
Phenyl morpholine-4-carboxylate (6ai)



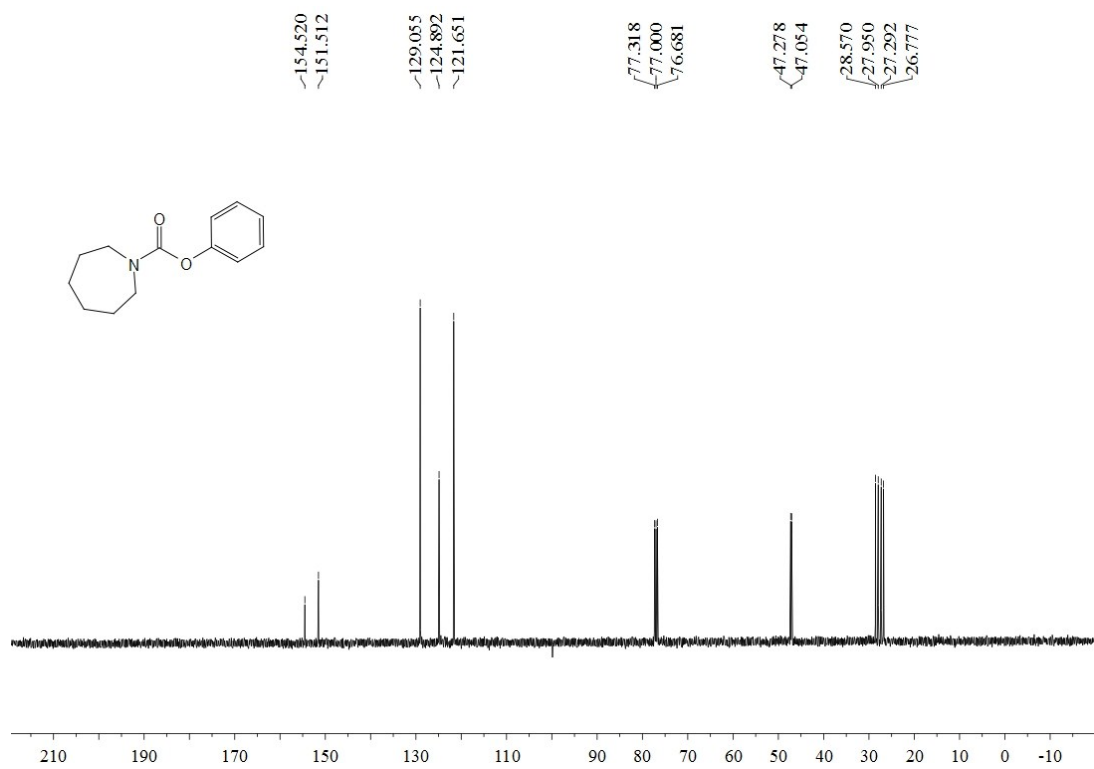
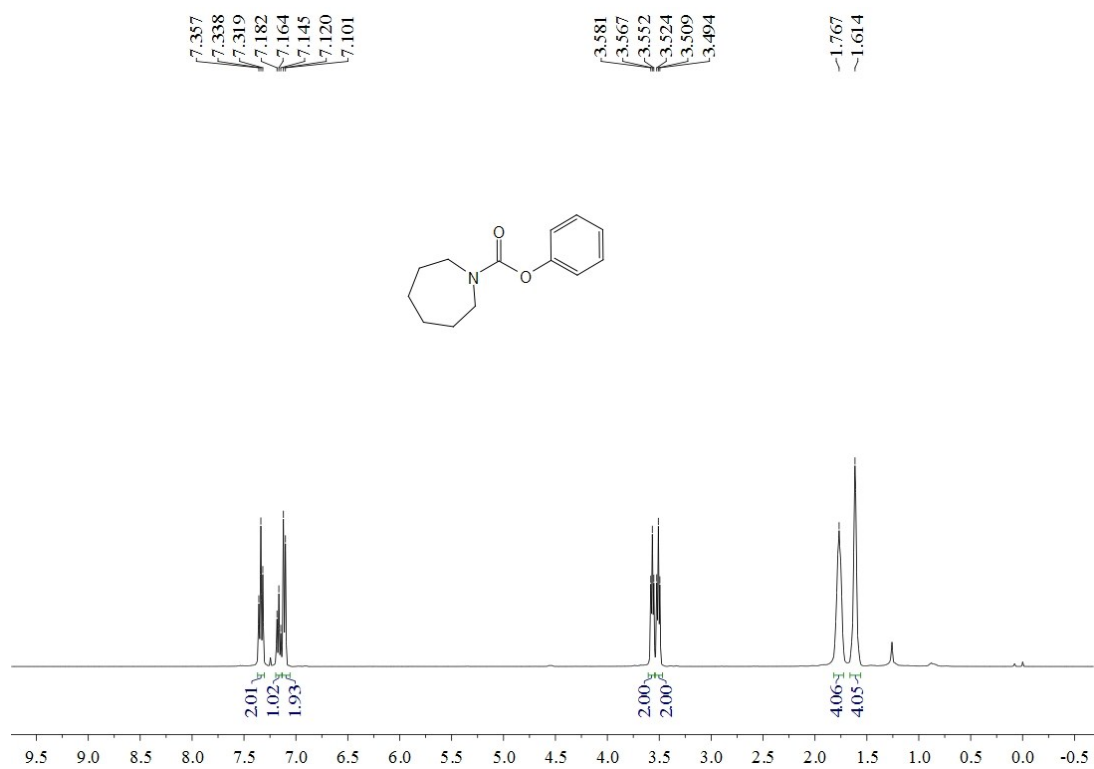
Phenyl thiomorpholine-4-carboxylate (6aj)



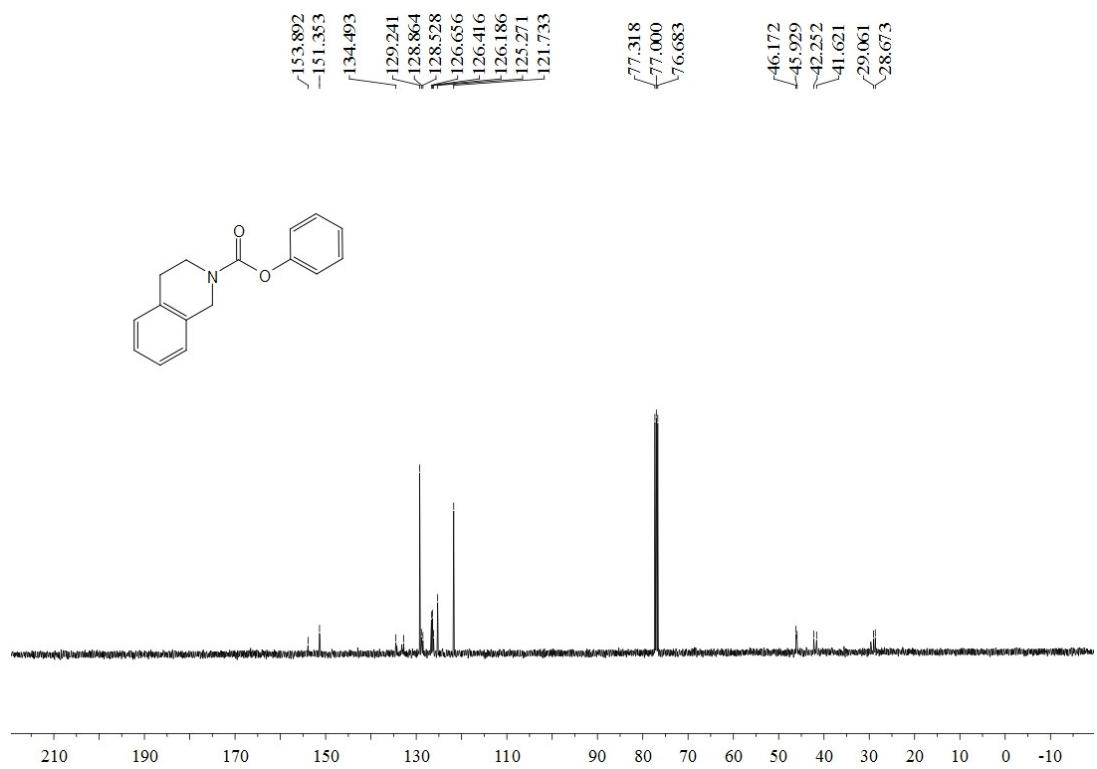
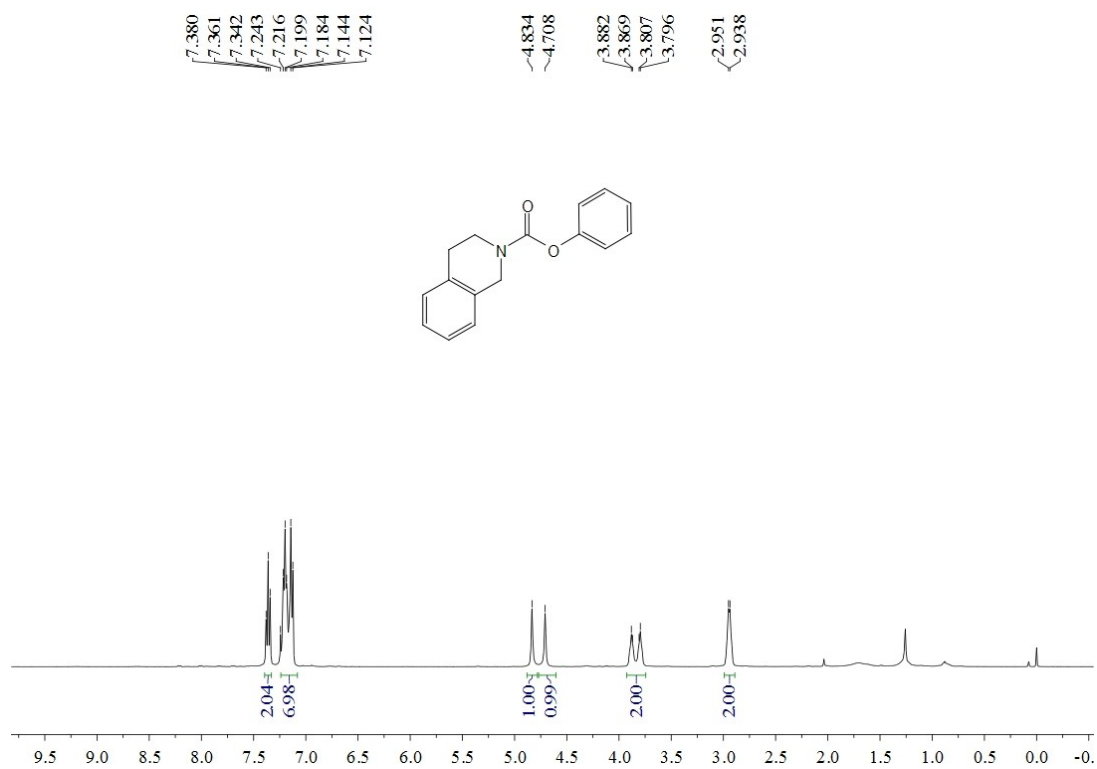
Phenyl piperidine-1-carboxylate (6ak)



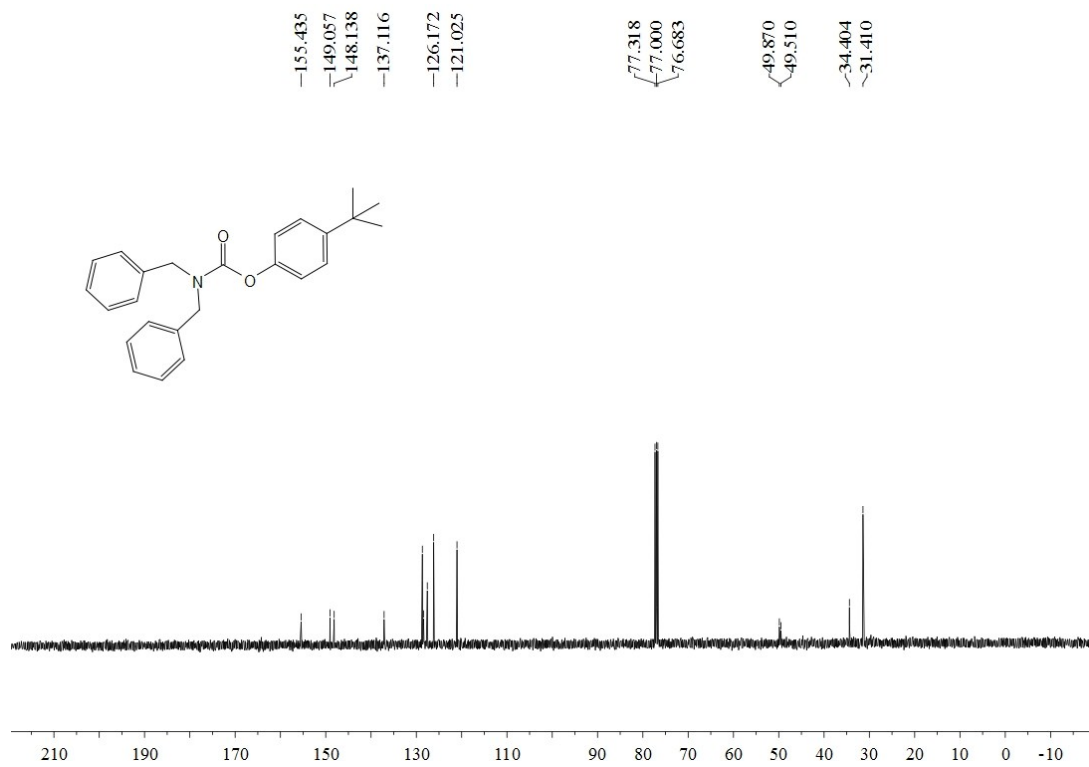
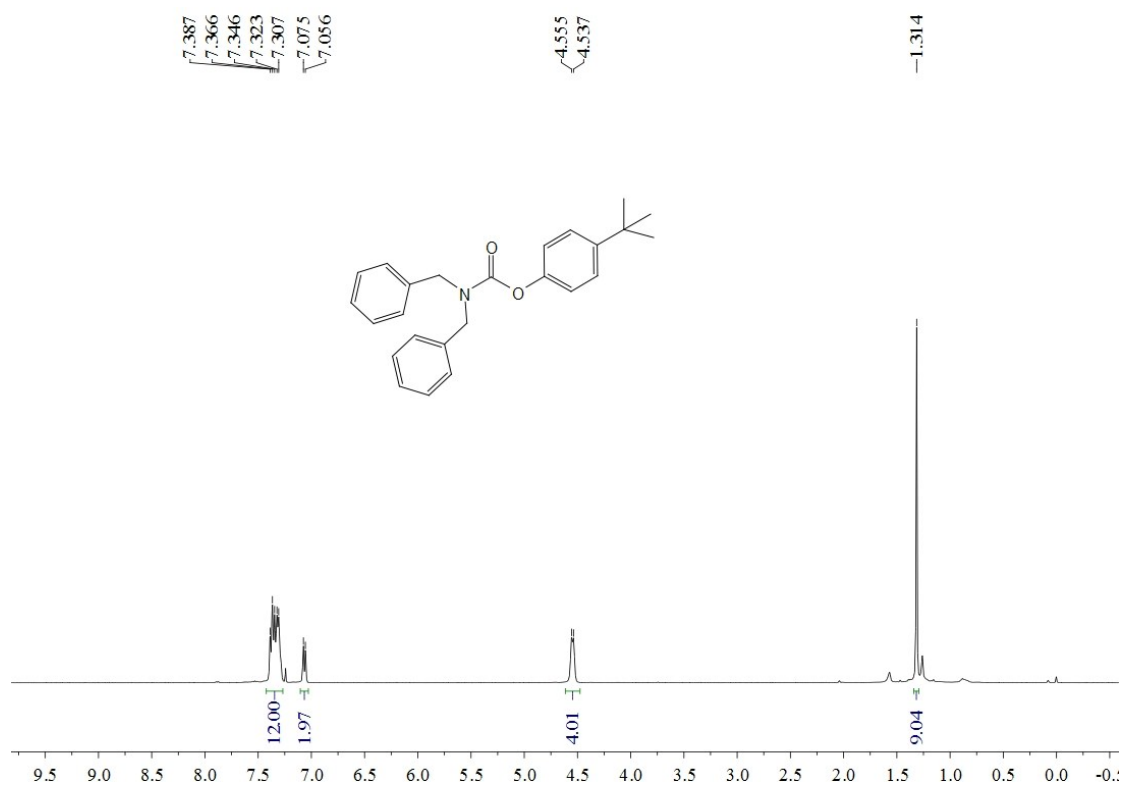
Phenyl azepane-1-carboxylate (6a)



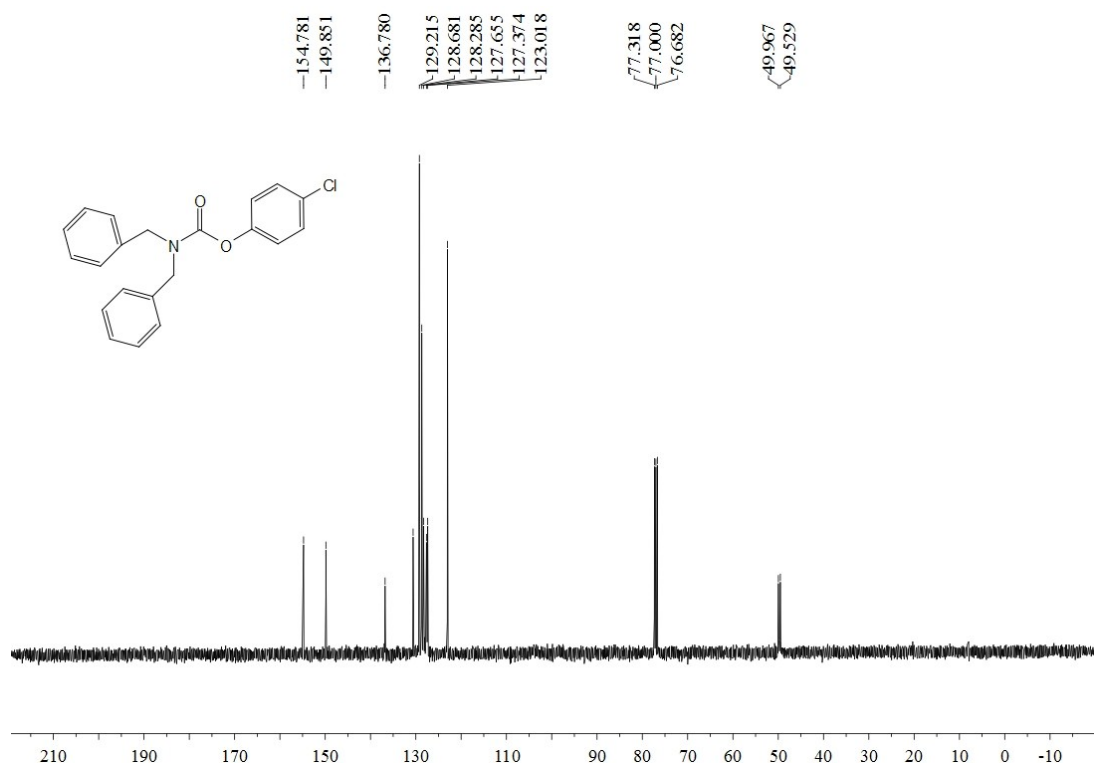
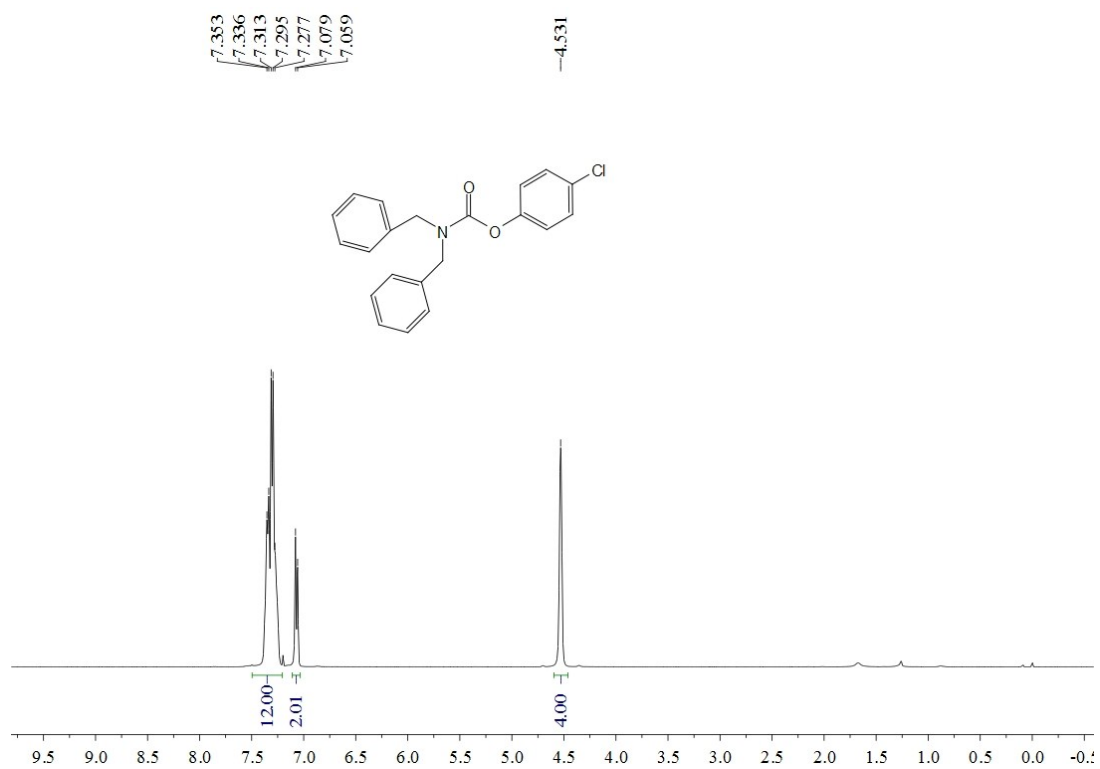
Phenyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (6am)



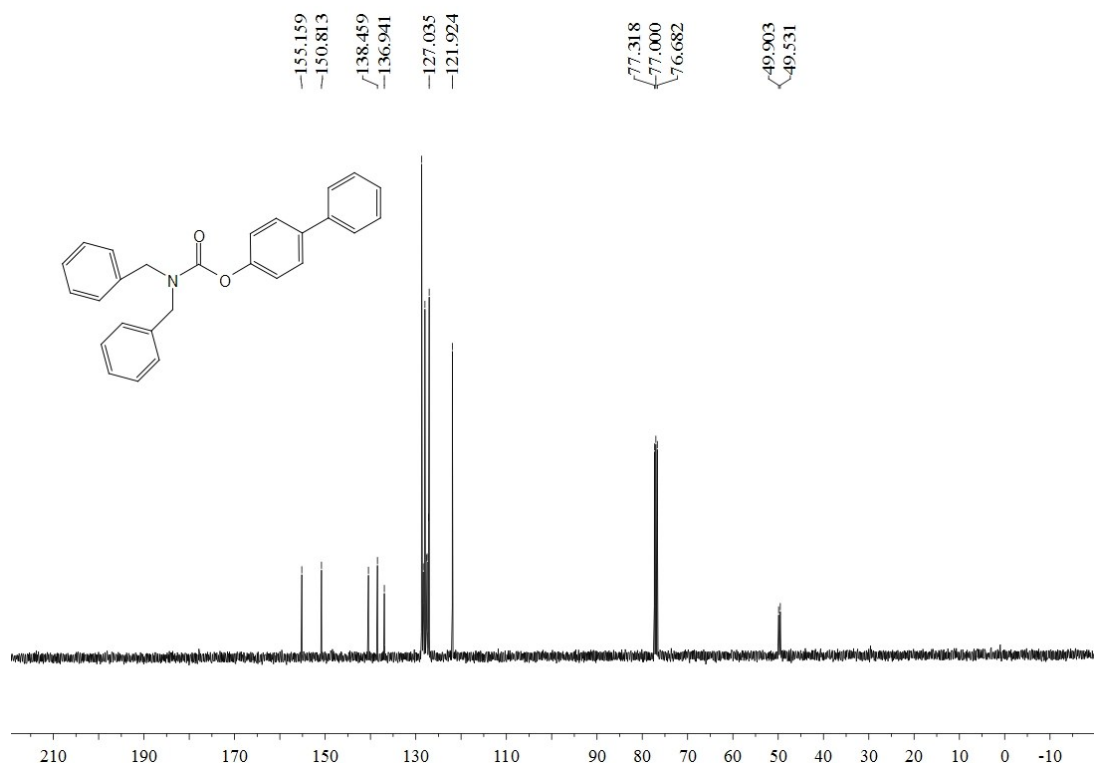
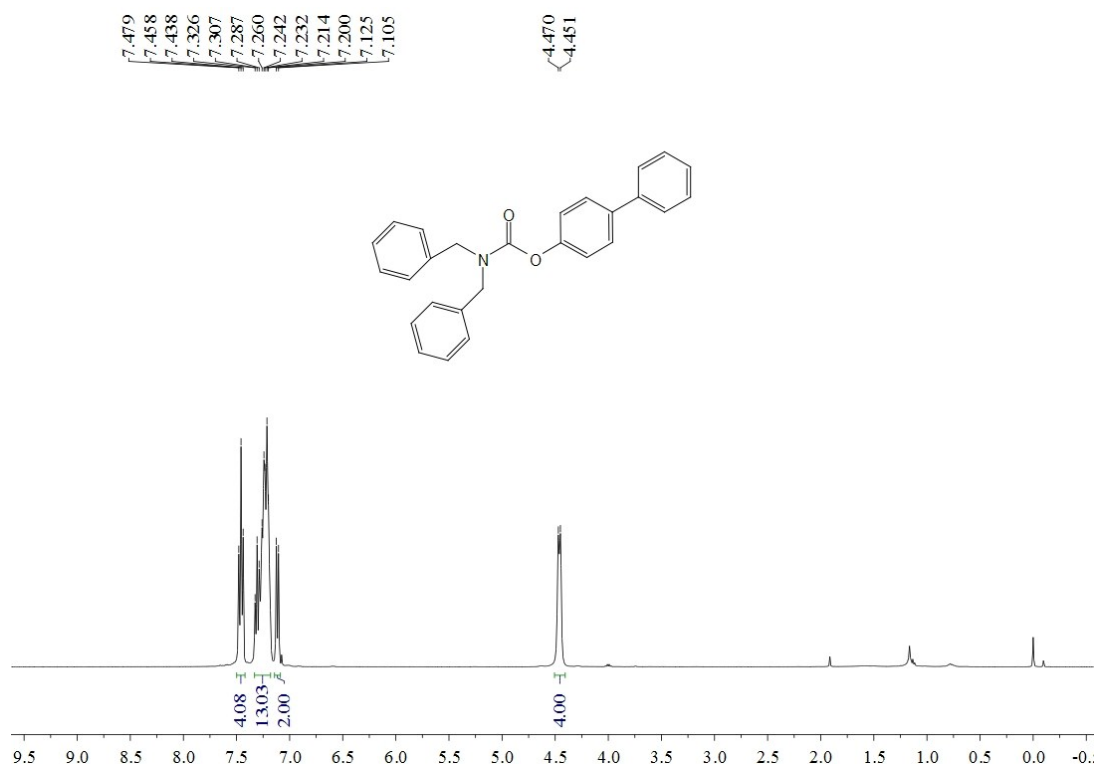
4-(Tert-butyl)phenyl dibenzylcarbamate (6cg)



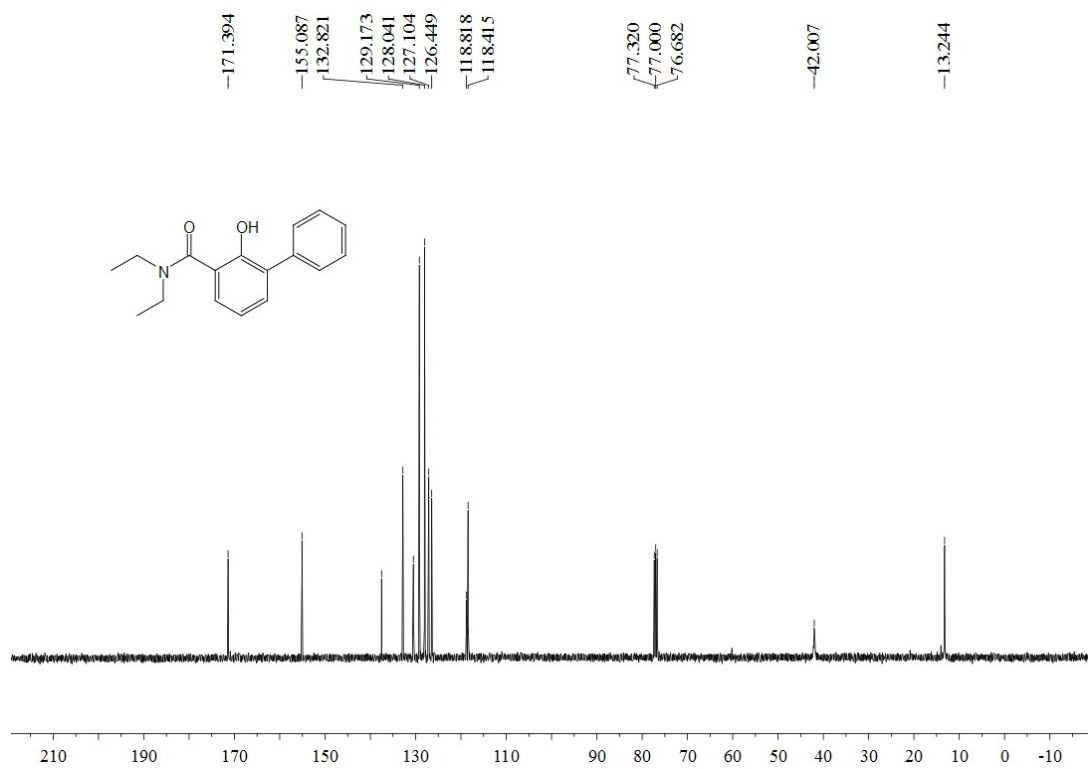
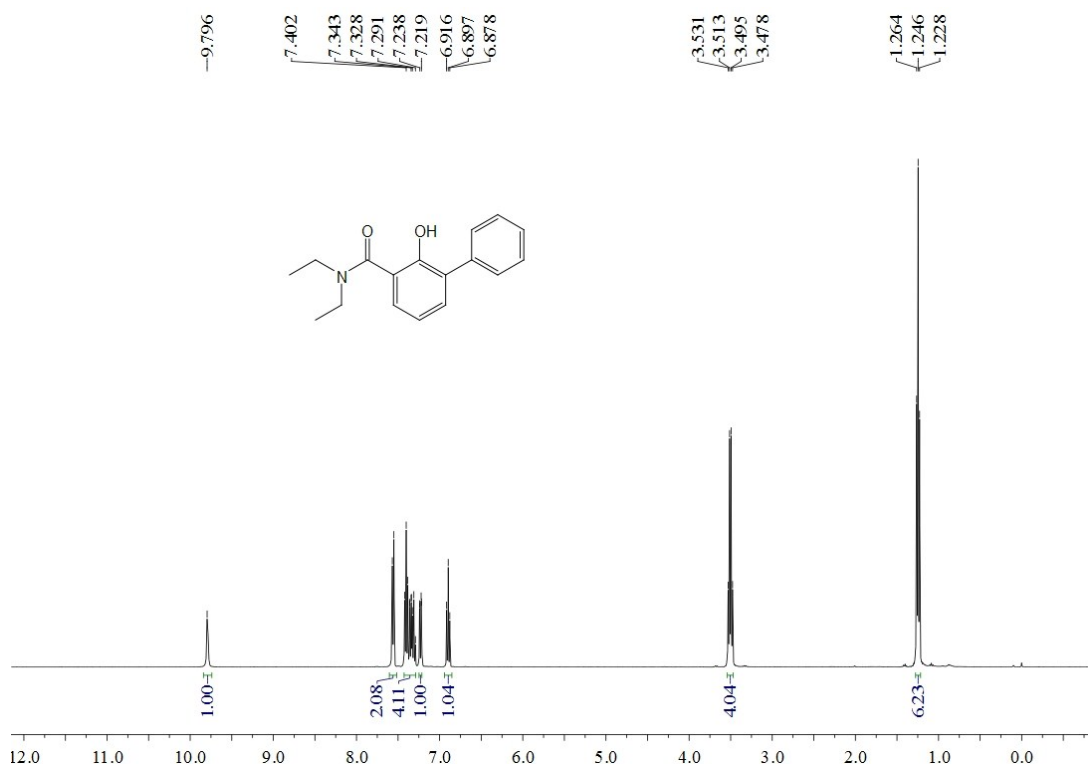
4-Chlorophenyl dibenzylcarbamate (6fg)



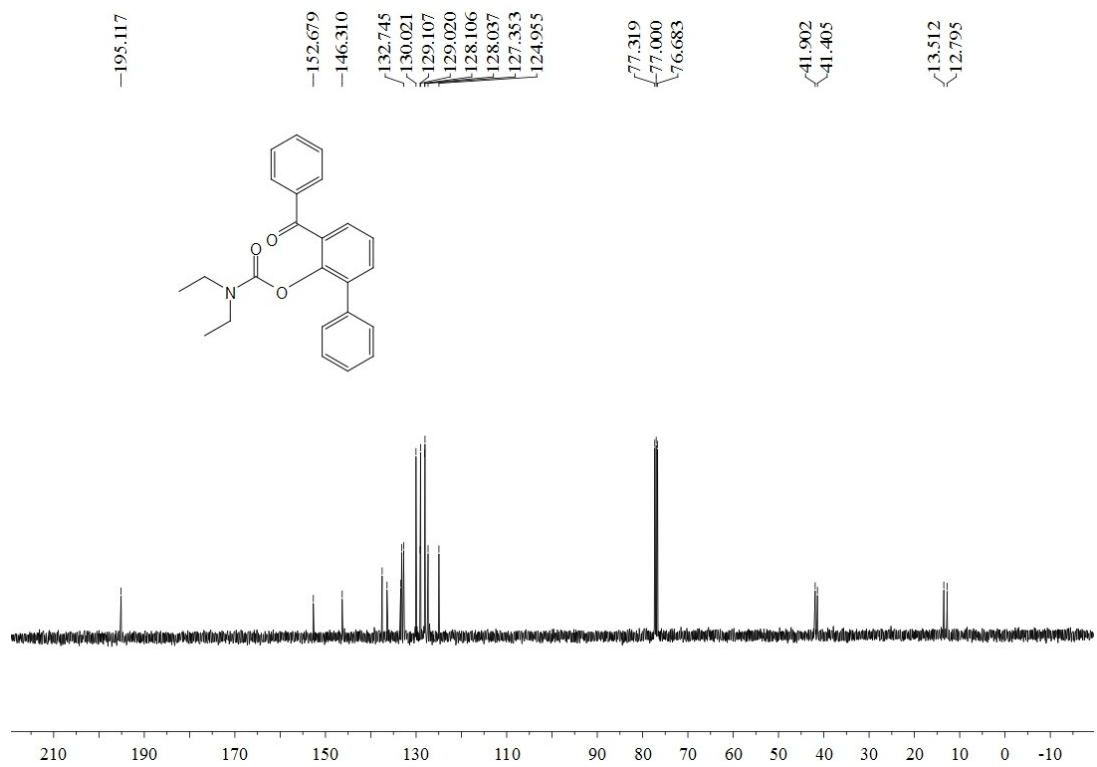
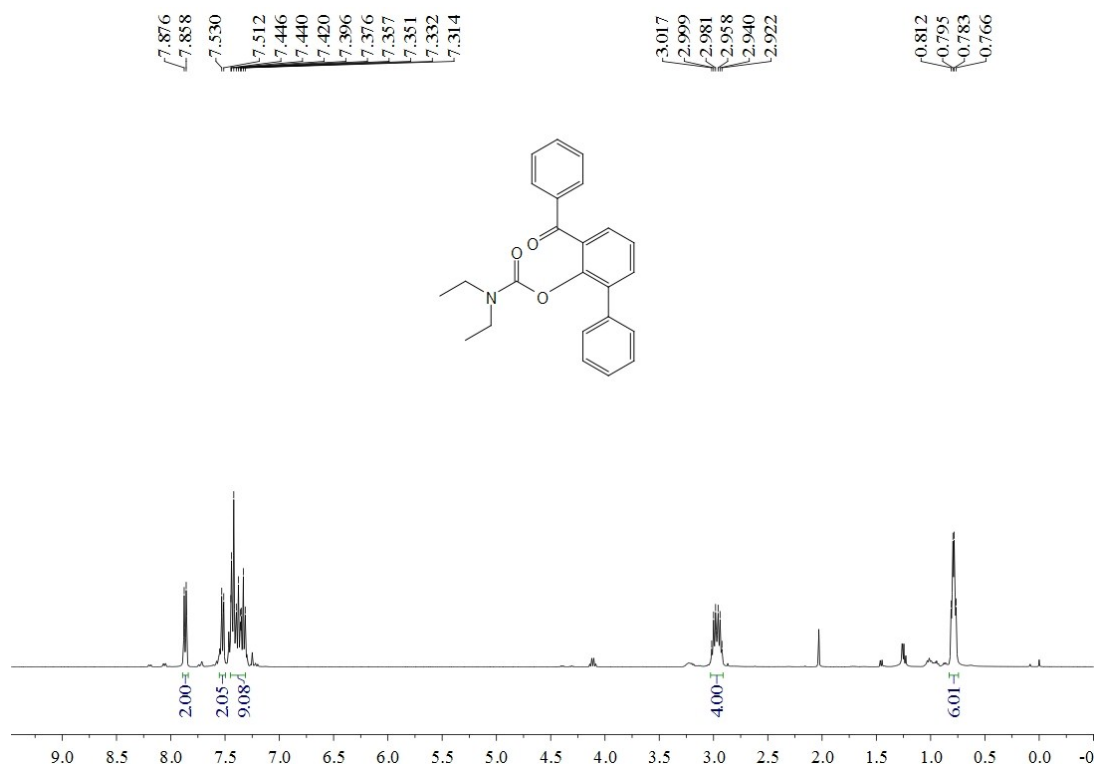
[1,1'-Biphenyl]-4-yl dibenzylcarbamate (6lg)



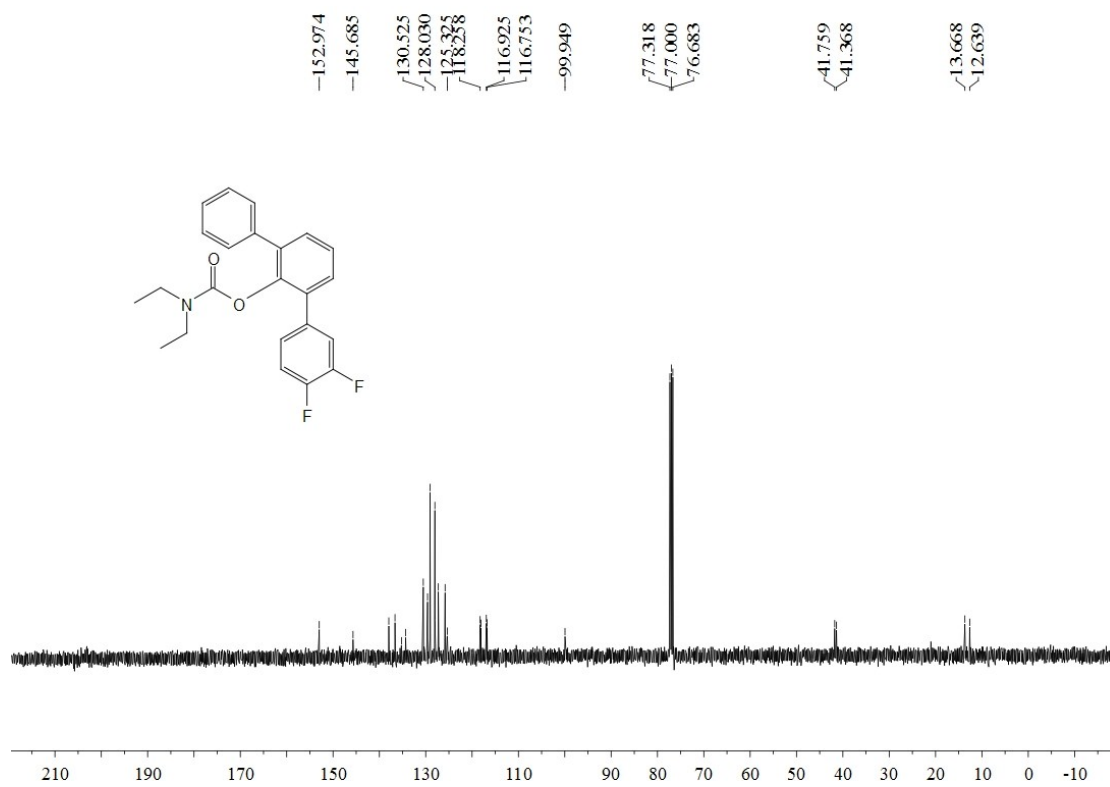
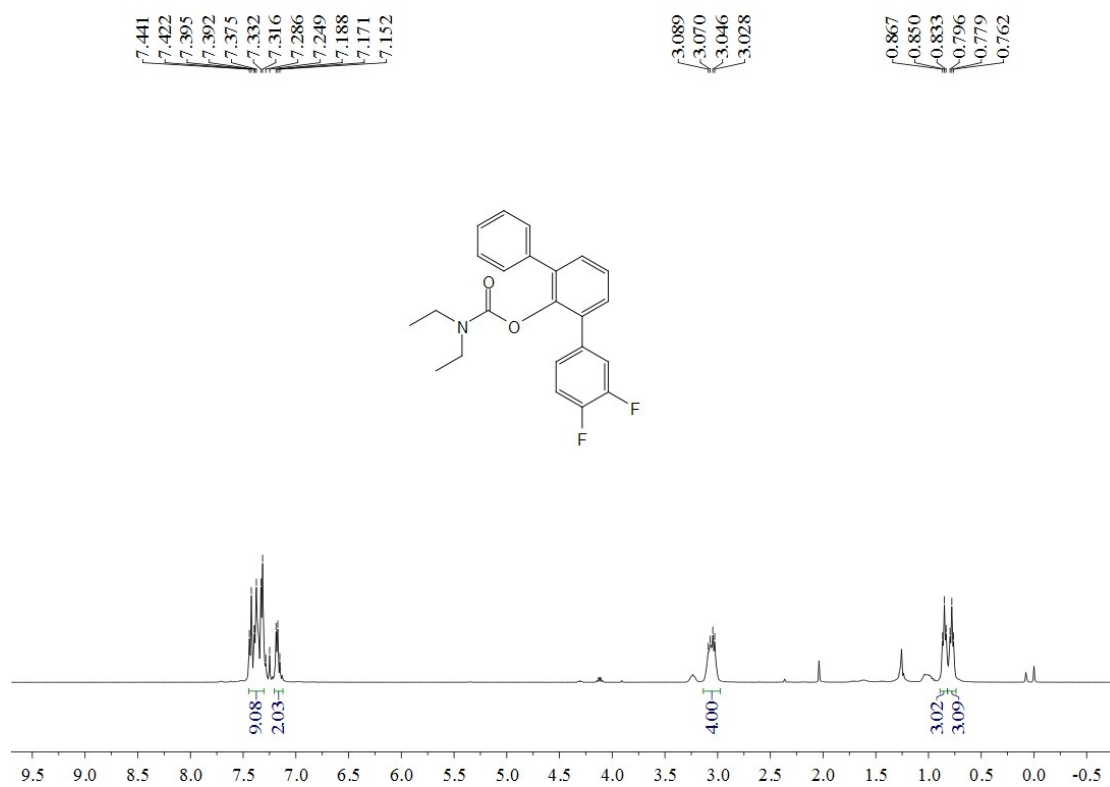
N,N-Diethyl-2-hydroxy-[1,1'-biphenyl]-3-carboxamide (7)



3-Benzoyl-[1,1'-biphenyl]-2-yl diethylcarbamate (8)



3,4-Difluoro-[1,1':3',1''-terphenyl]-2'-yl diethylcarbamate (9)



2-Phenylphenol (10)

