

Supporting Information for

Lanthanum(III) Isopropoxide-Catalyzed Chemoselective Transesterification of Dimethyl Carbonate and Methyl Carbamates

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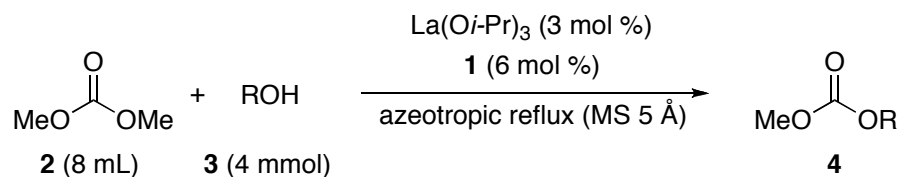
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Table of contents

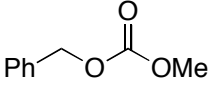
1. General information.....	S2
2. General procedure for the transesterification of dimethyl carbonate (Figure 1).....	S2
3. A gram-scale synthesis of 6 (Scheme 1).....	S5
4. General procedure for the double transesterification (Figure 2).....	S6
5. Representative procedure for the chemoselective deprotection of diesters (Scheme 2).....	S7
6. General procedure for the transesterification of methyl carbamates (Figure 3).....	S9
7. References.....	S12

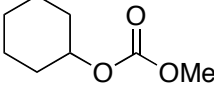
1. General information. ^1H NMR spectra were measured on a JEOL ECS400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.00 ppm). The products were purified by column chromatography on silica gel (E. Merck Art. 9385). Low and high resolution mass spectral analyses (LRMS and HRMS) were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO_4 , and phosphomolybdic acid. Dimethyl carbonate, ethyl acetate, *n*-hexane, and *n*-octane were freshly distilled in prior to use. Other simple chemicals were analytical-grade and obtained commercially.

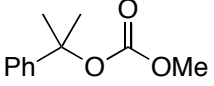
2. General procedure for the transesterification of dimethyl carbonate (Figure 1).

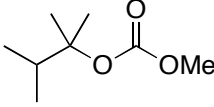


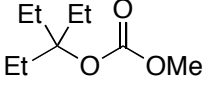
A mixture of La(Oi-Pr)_3 (37.8 mg, 0.12 mmol) and **1** (28.2 μL , 0.24 mmol) in anhydrous dimethyl carbonate (**2**) (8 mL) was stirred at room temperature for 1–2 min. As soon as alcohol (**3**) (4.0 mmol) was added to the solution, the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 2.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating for several hours at 110 °C (bath temp.), the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over MgSO_4 , and the organic phase was concentrated in vacuo by a Kugelrohr distillation oven or a rotary evaporator (75–85% of unreacted **2** was easily recovered.), and the crude product was purified by column chromatography on silica gel with *n*-hexane–ethyl acetate as eluents. Physical properties of ester products (**4**) are as follows:

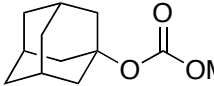
 **Benzyl methyl carbonate (4a):**¹ ¹H NMR (400 MHz, CDCl₃) δ 3.79 (s, 3H), 5.16 (s, 2H), 7.30–7.42 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 54.8, 69.5, 128.2 (2C), 128.4, 128.5 (2C), 135.1, 155.8. IR (neat) 2958, 1750, 1442, 1269, 948 cm⁻¹. HRMS (ESI+) calcd for C₉H₁₀NaO₃ [M+Na]⁺ 189.0528, found 189.0529.

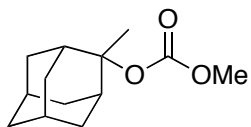
 **Cyclohexyl methyl carbonate (4b):**² ¹H NMR (400 MHz, CDCl₃) δ 1.18–1.60 (m, 6H), 1.75 (m, 2H), 1.91 (m, 2H), 3.76 (s, 3H), 4.61 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 23.5 (2C), 25.1, 31.5 (2C), 54.4, 76.7, 155.2. IR (neat) 2940, 2861, 1746, 1444, 1276, 1258 cm⁻¹. HRMS (FAB+) calcd for C₈H₁₄NaO₃ [M+Na]⁺ 181.0841, found 181.0849.

 **Methyl 2-phenylpropan-2-yl carbonate (4c):**³ ¹H NMR (400 MHz, CDCl₃) δ 1.80 (s, 6H), 3.66 (s, 3H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 28.3 (2C), 54.0, 83.1, 124.3 (2C), 127.2, 128.3 (2C), 144.9, 153.6. IR (neat) 2984, 1751, 1439, 1269, 1138 cm⁻¹. HRMS (FAB+) calcd for C₁₁H₁₄O₃ [M]⁺ 194.0943, found 194.0942.

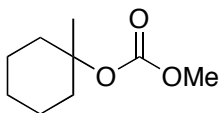
 **2,3-Dimethylbutan-2-yl methyl carbonate (4d):**⁴ ¹H NMR (400 MHz, CDCl₃) δ 0.92 (d, *J* = 6.9 Hz, 6H), 1.42 (s, 6H), 2.23 (septet, *J* = 6.9 Hz, 1H), 3.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 17.2 (2C), 22.3 (2C), 35.9, 53.8, 87.2, 154.0. IR (neat) 2972, 1744, 1441, 1371, 1277, 1141, 1090 cm⁻¹. HRMS (FAB+) calcd for C₈H₁₆NaO₃ [M+Na]⁺ 183.0997, found 183.0989.

 **3-Ethylpentan-3-yl methyl carbonate (4e):**⁵ ¹H NMR (400 MHz, CDCl₃) δ 0.84 (t, *J* = 7.8 Hz, 9H), 1.83 (q, *J* = 7.8 Hz, 6H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 7.5 (3C), 26.5 (3C), 53.8, 89.6, 153.7. IR (neat) 2973, 2884, 1744, 1440, 1260, 1137 cm⁻¹. HRMS (FAB+) calcd for C₉H₁₈NaO₃ [M+Na]⁺ 197.1154, found 197.1156.

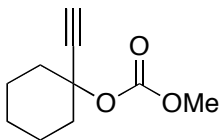
 **1-Adamantyl methyl carbonate (4f):**⁶ ¹H NMR (400 MHz, CDCl₃) δ 1.66 (s, 6H), 2.11 (s, 6H), 2.19 (s, 3H), 3.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 30.8 (3C), 35.9 (3C), 40.9 (3C), 53.7, 81.7, 153.5. IR (KBr) 2911, 1744, 1445, 1311, 1254, 1045 cm⁻¹. HRMS (FAB+) calcd for C₁₂H₁₉O₃ [M+H]⁺ 211.1334, found 211.1335.



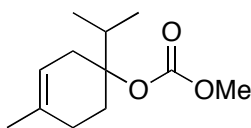
Methyl 2-methyl-2-adamantyl carbonate (4g): ^1H NMR (400 MHz, CDCl_3) δ 1.55–1.62 (m, 2H), 1.62 (s, 3H), 1.68–1.92 (m, 8H), 2.03–2.10 (m, 2H), 2.30 (brs, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 26.5, 27.2, 32.8 (2C), 34.5 (2C), 36.0 (2C), 38.0, 53.8, 88.3, 153.7. IR (KBr) 2911, 1740, 1429, 1257, 1086 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{20}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 247.1310, found: 247.1315.



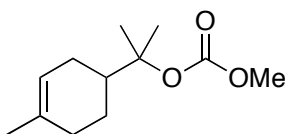
Methyl 1-methylcyclohexyl carbonate (4h): ^1H NMR (400 MHz, CDCl_3) δ 1.28 (m, 1H), 1.40–1.60 (m, 7H), 1.49 (s, 3H), 2.12 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.9 (2C), 24.9, 25.2, 36.2 (2C), 53.8, 83.3, 153.9. IR (neat) 2936, 1743, 1441, 1300, 1270, 1241, 1154 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_9\text{H}_{16}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 195.0997, found 195.1001.



1-Ethynylcyclohexyl methyl carbonate (4i): ^1H NMR (400 MHz, CDCl_3) δ 1.33 (m, 1H), 1.53 (m, 1H), 1.66 (m, 4H), 1.87 (m, 2H), 2.17 (m, 2H), 2.64 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 22.4 (2C), 24.8, 36.7 (2C), 54.2, 74.7, 77.3, 82.9, 153.3. IR (neat) 3287, 2938, 2862, 1754, 1442, 1274, 1246, 1018 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{10}\text{H}_{14}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 205.0841, found 205.0845.

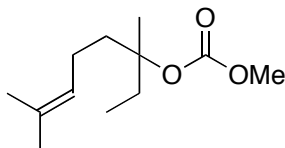


Methyl 4-terpineyl carbonate (4j): ^1H NMR (400 MHz, CDCl_3) δ 0.91 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 1.67 (s, 3H), 1.70 (m, 1H), 1.91 (m, 1H), 2.01 (m, 1H), 2.18 (m, 1H), 2.34 (m, 1H), 2.42 (m, 1H), 2.69 (septet, J = 6.9 Hz, 1H), 3.69 (s, 3H), 5.25 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 16.9, 17.6, 23.1, 27.0, 27.6, 29.6, 32.3, 53.9, 87.2, 117.3, 133.5, 154.0. IR (neat) 2966, 1741, 1440, 1277, 1240, 1201 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{20}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 235.1310, found 235.1306.



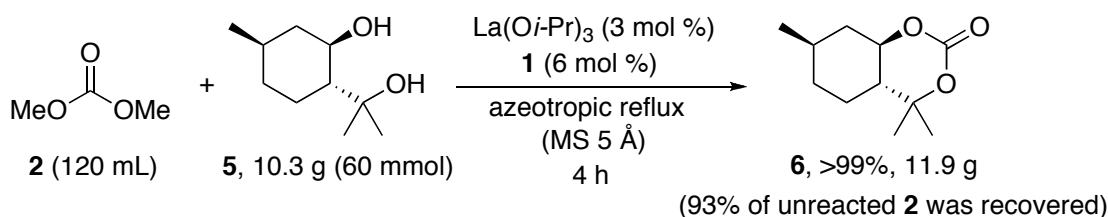
Methyl α -terpineoyl carbonate (4k): ^1H NMR (400 MHz, CDCl_3) δ 1.30 (m, 1H), 1.44 (s, 3H), 1.46 (s, 3H), 1.64 (s, 3H), 1.73–2.15 (m, 6H), 3.72 (s, 3H), 5.36 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 22.5, 22.9, 23.2, 23.8, 26.3, 30.7, 42.3, 53.7, 86.6, 120.0, 133.8, 153.9.

IR (neat) 2928, 1743, 1440, 1275, 1131, 1098 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{20}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 235.1310, found 235.1306.

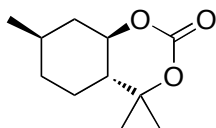


Dihydrolinaloyl methyl carbonate (4l): ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J = 7.8$ Hz, 3H), 1.43 (s, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 1.70–2.04 (m, 6H), 3.70 (s, 3H), 5.09 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 7.8, 17.4, 22.1, 22.8, 25.5, 30.5, 37.3, 53.8, 86.4, 123.7, 131.7, 153.8. IR (neat) 2973, 1744, 1440, 1377, 1263 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{22}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 237.1467, found 237.1465.

3. A gram-scale synthesis of **6** (Scheme 1).



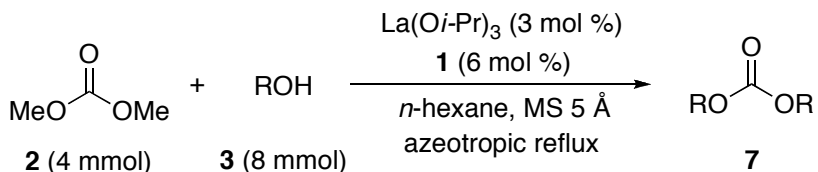
A mixture of La(Oi-Pr)_3 (569 mg, 1.8 mmol), **1** (423 μL , 3.6 mmol) in anhydrous dimethyl carbonate (**2**) (120 mL) was stirred at room temperature for 1–2 min. *trans-p*-Menthane-3,8-diol (10.34 g, 60 mmol) was added to the solution, and the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through 5 \AA molecular sieves (pellets, ca. 50 g) in a Dean-Stark trap. After heating at 110 $^\circ\text{C}$ (bath temp.) for 4 h, the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over MgSO_4 , and the organic phase was concentrated in vacuo by a rotary evaporator, and 93% of unreacted **2** was recovered. The crude product (**6**) was purified by column chromatography on silica gel with *n*-hexane–ethyl acetate as eluents (11.90 g, >99% yield).



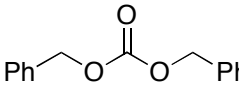
(4aR,7R,8aR)-4,4,7-Trimethylhexahydro-4H-benzo[d][1,3]dioxin-2-one (6):⁸ ^1H NMR (400 MHz, CDCl_3) δ 1.00 (d, $J = 6.9$ Hz, 3H), 1.02–1.23 (m, 3H), 1.35 (s, 3H), 1.43 (s, 3H), 1.45–1.67 (m, 2H), 1.78 (d, $J = 9.9$ Hz, 2H), 2.17 (m, 1H), 4.17 (td, $J = 11.1, 4.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.6, 22.5, 24.8, 27.7, 30.6, 33.4, 39.7, 46.1, 76.8, 84.5, 149.0. IR (KBr) 2923, 1726, 1376, 1303, 1284, 1243, 1150, 1094, 1074 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{11}\text{H}_{18}\text{NaO}_3$

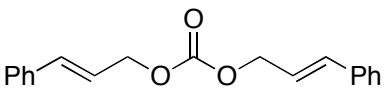
[M+Na]⁺ 221.1154, found 221.1153.

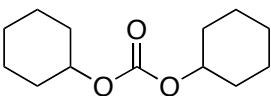
4. General procedure for the double transesterification (Figure 2).



A mixture of La(Oi-Pr)₃ (37.8 mg, 0.12 mmol) and **1** (28.2 μL, 0.24 mmol) in anhydrous *n*-hexane (8 mL) was stirred at room temperature for 1–2 min. As soon as **2** (4.0 mmol) and alcohol (**3**) (8.0 mmol) were added to the solution, the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 6.5 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating for 2–6 hours at reflux temperature (bath temp.; 90 °C), the reaction mixture was allowed to cool to ambient temperature. A drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over MgSO₄, and the organic phase was concentrated in vacuo, and the crude product was purified by column chromatography on silica gel with *n*-hexane–ethyl acetate as eluents. Physical properties of ester products (**7**) are as follows:

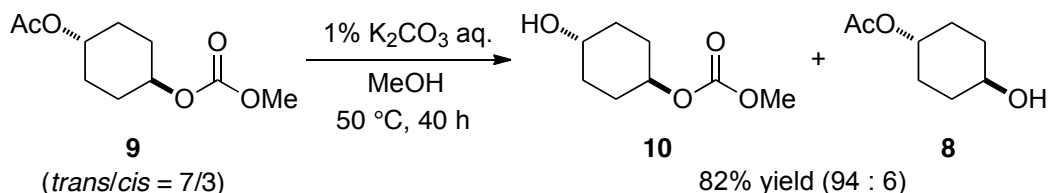
 **Dibenzyl carbonate (7a):**⁹ ¹H NMR (400 MHz, CDCl₃) δ 5.17 (s, 4H), 7.30–7.42 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 69.6 (2C), 128.2 (4C), 128.4 (2C), 128.5 (4C), 135.1 (2C), 155.0. IR (neat) 3034, 1748, 1455, 1392, 1264 cm⁻¹. HRMS (FAB⁺) calcd for C₁₅H₁₄NaO₃ [M+Na]⁺ 265.0841, found 265.0841.

 **Dicinnamyl carbonate (7b):**¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 4.81 (dd, *J* = 6.3, 1.5 Hz, 4H), 6.31 (dt, *J* = 15.9, 6.3 Hz, 2H), 6.70 (d, *J* = 16.0 Hz, 2H), 7.24–7.30 (m, 2H), 7.30–7.37 (m, 4H), 7.37–7.45 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 68.4 (2C), 122.3 (2C), 126.6 (4C), 128.1 (2C), 128.5 (4C), 134.8 (2C), 135.9 (2C), 154.9. IR (KBr) 3045, 1739, 1445, 1260 cm⁻¹. HRMS (FAB⁺) calcd for C₁₉H₁₈NaO₃ [M+Na]⁺ 317.1154, found 317.1166.

 **Dicyclohexyl carbonate (7c):**¹¹ ¹H NMR (400 MHz, CDCl₃) δ 1.16–1.64 (m, 12H), 1.76 (m, 4H), 1.93 (m, 4H), 4.58 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 23.7 (4C), 25.2 (2C), 31.6 (4C), 76.3 (2C), 154.1. IR (KBr) 2935, 2856, 1734, 1452, 1282, 1011 cm⁻¹. HRMS (FAB⁺)

calcd for C₁₃H₂₂NaO₃ [M+Na]⁺ 249.1467, found 249.1474.

5. Representative procedure for the chemoselective deprotection of diesters (Scheme 2).



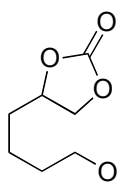
A solution of *trans*-4-(methoxycarbonyloxy)cyclohexyl acetate (**9**) (64.8 mg, 0.30 mmol) in 1% K₂CO₃ aq. (0.75 mL) and MeOH (0.75 mL) was stirred at 50 °C for 40 h. The reaction mixture was allowed to cool to ambient temperature and quenched with saturated NH₄Cl aqueous solution (5 mL). The organic phase was extracted with ether (15 mL × 3), washed with brine (10 mL), and dried over Na₂SO₄. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel chromatography (eluent: *n*-hexane/EtOAc = 2/1), to give the mixture of **10** and **8** (94 : 6) as colorless oil (42.4 mg, 82% yield).

4-Hydroxycyclohexyl methyl carbonate (8) (*trans/cis* = 7/3 mixture):¹² ¹H NMR (400 MHz, CDCl₃) δ 1.37–1.50 (m, 1H), 1.58–1.77 (m, 4H), 1.84–1.91 (m, 1H), 1.93–2.07 (m, 2H), 1.97 (s, 1H), 2.03 (s, 0.9/3H), 2.06 (s, 2.1/3H), 3.67–3.75 (m, 0.3/1H), 3.79 (m, 0.7/1H), 4.72 (m, 0.3/1H), 4.85 (m, 0.7/1H). ¹³C NMR (100 MHz, CDCl₃) δ 21.4, 27.2 (2C), 28.6 (2C), 30.4 (2C), 32.2 (2C), 67.7, 68.9, 69.9, 71.7, 170.6. IR (neat) 3412, 2943, 2865, 1732, 1367, 1246, 1068 cm⁻¹. HRMS (FAB+) calcd for C₈H₁₄NaO₃ [M+Na]⁺ 181.0841, found 181.0846.

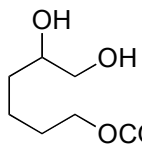
4-((Methoxycarbonyloxy)cyclohexyl acetate (9) (*trans/cis* = 7/3 mixture): ¹H NMR (400 MHz, CDCl₃) δ 1.50–1.93 (m, 6H), 1.95–2.03 (m, 2H), 2.04 (s, 2.1/3H), 2.05 (s, 0.9/3H), 3.778 (s, 2.1/3H), 3.782 (s, 0.9/3H), 4.65–4.75 (m, 1.4/2H), 4.77–4.87 (m, 0.6/2H). ¹³C NMR (100 MHz, CDCl₃) δ 21.3, 27.1, 27.2, 27.3 (2C), 27.6, 27.7, 54.5, 69.7, 70.6, 74.0, 74.8, 155.1, 170.5. IR (neat) 2957, 1746, 1444, 1273, 1042 cm⁻¹. HRMS (FAB+) calcd for C₁₀H₁₆NaO₅ [M+Na]⁺ 239.0895, found 239.0905.

4-Hydroxycyclohexyl methyl carbonate (10) (*trans/cis* = 7/3 mixture): ¹H

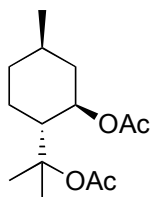
NMR (400 MHz, CDCl₃) δ 1.37–1.78 (m, 5H), 1.91–2.12 (m, 4H), 3.72–3.81 (m, 1H), 3.77 (s, 2.1/3H), 3.78 (s, 0.9/3H), 4.60–4.66 (m, 0.7/1H), 4.72–4.75 (m, 0.3/1H). ¹³C NMR (100 MHz, CDCl₃) δ 27.2 (2C), 28.3 (2C), 30.3 (2C), 31.8 (2C), 54.48, 54.52, 67.5, 68.5, 74.0, 75.6, 155.2. IR (neat) 3394, 2945, 1745, 1445, 1275, 1067 cm⁻¹. HRMS (FAB+) calcd for C₈H₁₄NaO₄ [M+Na]⁺ 197.0790, found 197.0783.



Methyl 4-(2-oxo-1,3-dioxolan-4-yl)butyl carbonate (12): ¹H NMR (400 MHz, CDCl₃) δ 1.44–1.56 (m, 1H), 1.57–1.66 (m, 1H), 1.70–1.80 (m, 3H), 1.81–1.89 (m, 1H), 3.79 (s, 3H), 4.09 (dd, *J* = 8.2, 7.3 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 4.55 (t, *J* = 8.2 Hz, 1H), 4.73 (dq, *J* = 7.3, 5.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 28.1, 33.4, 54.7, 67.3, 69.2, 76.7, 154.8, 155.7. IR (neat) 2958, 1799, 1748, 1443, 1389, 1269, 1173, 1065 cm⁻¹. HRMS (FAB+) calcd for C₉H₁₄NaO₆ [M+Na]⁺ 241.0688, found 241.0688.

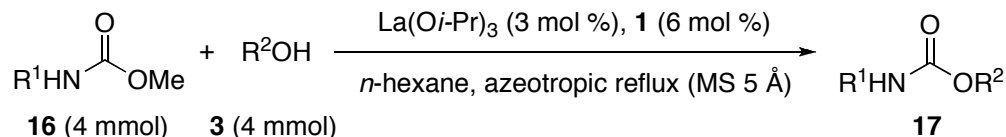


5,6-Dihydroxyhexyl methyl carbonate (13): ¹H NMR (400 MHz, CDCl₃) δ 1.35–1.51 (m, 3H), 1.51–1.61 (m, 1H), 1.62–1.79 (m, 2H), 2.55 (brs, 2H), 3.44 (dd, *J* = 11.0, 7.8 Hz, 1H), 3.59–3.83 (m, 2H), 3.78 (s, 3H), 4.16 (t, *J* = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 28.6, 32.5, 54.7, 66.7, 67.9, 71.9, 155.9. IR (neat) 3389, 2944, 1748, 1445, 1391, 1273, 1064 cm⁻¹. HRMS (FAB+) calcd for C₈H₁₆NaO₅ [M+Na]⁺ 215.0895, found 215.0899.

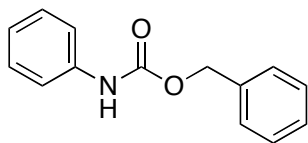


2-((1R,2R,4R)-2-Acetoxy-4-methylcyclohexyl)propan-2-yl acetate (15): ¹H NMR (400 MHz, CDCl₃) δ 0.89 (d, *J* = 6.4 Hz, 3H), 0.91–1.16 (m, 3H), 1.38 (s, 3H), 1.42 (s, 3H), 1.44–1.58 (m, 1H), 1.64–1.71 (m, 1H), 1.78 (dq, *J* = 13.3, 3.2 Hz, 1H), 1.91–1.96 (m, 1H), 1.97 (s, 3H), 2.03 (s, 3H), 2.55 (ddd, *J* = 11.9, 10.6, 3.7 Hz, 1H), 4.83 (dt, *J* = 11.0, 4.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 21.7, 22.6, 24.8, 25.5, 26.3, 31.1, 33.9, 41.0, 46.7, 73.7, 84.3, 170.2, 170.3. IR (neat) 2954, 1731, 1458, 1369, 1245, 1149, 1111, 1022 cm⁻¹. HRMS (FAB+) calcd for C₁₄H₂₄NaO₄ [M+Na]⁺ 279.1572, found 279.1570.

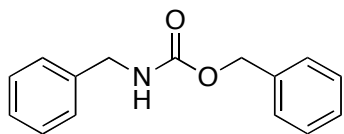
6. General procedure for the transesterification of methyl carbamates (Figure 3).



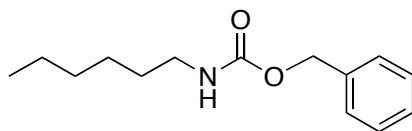
A mixture of La(Oi-Pr)_3 (37.8 mg, 0.12 mmol) and **1** (28.2 μL , 0.24 mmol) in anhydrous *n*-hexane (8 mL) was stirred at room temperature for 1–2 min. As soon as methyl carbamate (**16**) (4 mmol) and alcohol (**3**) (4 mmol) were added to the solution, the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 2.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating for several hours at 90 °C (bath temp.), the reaction mixture was allowed to cool to ambient temperature. A drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over MgSO_4 , and the organic phase was concentrated in vacuo, and the crude product was purified by column chromatography on silica gel with *n*-hexane–ethyl acetate as eluents. Physical properties of ester products (**17**) are as follows:



Benzyl phenylcarbamate (17a):¹³ ^1H NMR (400 MHz, CDCl_3) δ 5.19 (s, 2H), 6.70 (brs, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 7.27–7.43 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 66.9, 118.6, 123.5, 128.0 (2C), 128.3 (2C), 128.6 (2C), 129.0 (2C), 135.9, 137.6, 153.2. IR (KBr) 3272, 1691, 1548, 1445, 1242, 1058 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{13}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 250.0844. Found: 250.0845.

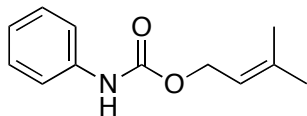


Benzyl benzylcarbamate (17b):¹⁴ ^1H NMR (400 MHz, CDCl_3) δ 4.39 (d, $J = 3.0$ Hz, 2H), 5.05 (br, 1H), 5.14 (s, 2H), 7.26–7.40 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 66.7, 127.4 (3C), 128.0 (3C), 128.4 (2C), 128.6 (2C), 136.4, 138.3, 156.3. IR (KBr) 3324, 1688, 1543, 1260 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 264.1000, found 264.0999.

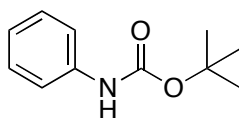


Benzyl hexylcarbamate (17c):¹⁵ ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, $J = 6.9$ Hz, 3H), 1.20–1.36 (m, 6H), 1.48 (m, 2H), 3.18 (q, $J = 6.9$ Hz, 2H), 4.73 (br, 1H), 5.09 (s, 2H), 7.28–7.39 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.4, 26.3, 29.8, 31.3, 41.0, 66.4,

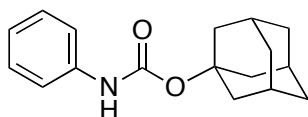
128.0 (2C), 128.4 (3C), 136.6, 156.3. IR (neat) 3335, 2930, 1700, 1535, 1250 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 258.1470, found 258.1478.



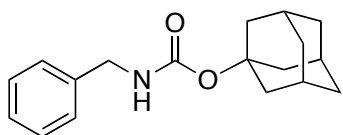
3-Methylbut-2-enyl phenylcarbamate (17d):¹⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.73 (s, 3H), 1.76 (s, 3H), 4.66 (d, $J = 7.2$ Hz, 2H), 5.38 (m, 1H), 6.73 (brs, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 17.9, 25.7, 61.9, 118.6 (2C), 123.2, 128.9 (3C), 137.9, 139.2, 153.6. IR (neat) 3321, 2972, 1703, 1600, 1540, 1444, 1313, 1227, 1056 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{15}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 228.1000, found 228.1005.



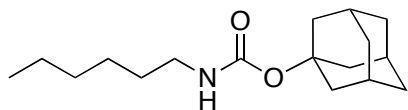
tert-Butyl phenylcarbamate (17e):¹⁷ 1 Equiv of *t*-BuOH was added every 10 hours. Totally, 4 equiv of *t*-BuOH was used. ^1H NMR (400 MHz, CDCl_3) δ 1.51 (s, 9H), 6.51 (br, 1H), 7.02 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.35 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 28.2 (3C), 80.4, 118.4, 122.9 (2C), 128.9 (2C), 138.2, 152.7. IR (KBr) 3313, 1688, 1597, 1530, 1440, 1314, 1245, 1151 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 194.1181, found 194.1181.



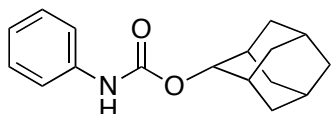
1-Adamantyl phenylcarbamate (17f):¹⁸ ^1H NMR (400 MHz, CDCl_3) δ 1.66 (s, 6H), 2.16 (s, 9H), 6.59 (br, 1H), 7.00 (t, $J = 7.2$ Hz, 1H), 7.26 (t, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 30.7 (3C), 36.0 (3C), 41.5 (3C), 80.3, 118.3, 122.8 (2C), 128.8 (2C), 138.2, 152.2. IR (KBr) 3327, 2911, 1698, 1541, 1444, 1241, 1066 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{21}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 294.1470, found 294.1462.



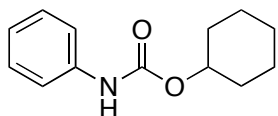
1-Adamantyl benzylcarbamate (17g):¹⁹ ^1H NMR (400 MHz, CDCl_3) δ 1.65 (s, 6H), 2.11 (s, 6H), 2.15 (s, 3H), 4.30 (d, $J = 6.0$ Hz, 2H), 4.87 (br, 1H), 7.22–7.36 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 30.7 (3C), 36.1 (3C), 41.6 (3C), 44.6, 79.3, 127.2, 127.4 (2C), 128.5 (2C), 138.8, 155.4. IR (KBr) 3308, 2909, 1681, 1535, 1455, 1260, 1055 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 308.1626, found 308.1625.



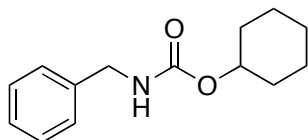
1-Adamantyl hexylcarbamate (17h): ^1H NMR (400 MHz, CDCl_3) δ 0.88 (m, 3H), 1.20–1.40 (m, 6H), 1.46 (m, 2H), 1.64 (s, 6H), 2.09 (s, 6H), 2.14 (s, 3H), 3.10 (m, 2H), 4.59 (br, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.5, 26.4, 29.9, 30.7 (3C), 31.4, 36.1 (3C), 40.4, 41.6 (3C), 78.7, 155.5. IR (KBr) 3359, 2911, 1687, 1528, 1252, 1061 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{29}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 302.2096, found 302.2103.



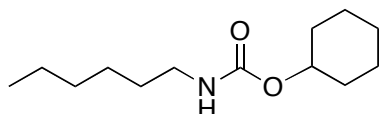
2-Adamantyl phenylcarbamate (17i):¹⁸ ^1H NMR (400 MHz, CDCl_3) δ 1.55–1.63 (m, 2H), 1.72–1.93 (m, 8H), 2.00–2.14 (m, 4H), 4.93 (brs, 1H), 6.62 (br, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.40 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.8, 27.1, 31.7 (2C), 31.9 (2C), 36.2 (2C), 37.2, 77.8, 118.4 (2C), 123.0, 128.8 (2C), 138.1, 153.2. IR (KBr) 3305, 2909, 1697, 1546, 1233, 1059 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{21}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 294.1470, found 294.1471.



Cyclohexyl phenylcarbamate (17j):²⁰ ^1H NMR (400 MHz, CDCl_3) δ 1.18–1.60 (m, 6H), 1.73 (m, 2H), 1.93 (m, 2H), 4.75 (m, 1H), 6.62 (br, 1H), 7.04 (t, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.7 (2C), 25.3, 31.8 (2C), 73.5, 118.4 (2C), 123.1, 128.9 (2C), 138.0, 153.1. IR (KBr) 3356, 2927, 2858, 1705, 1602, 1531, 1444, 1234, 1057 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 242.1157, found 242.1157.

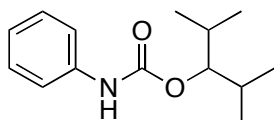


Cyclohexyl benzylcarbamate (17k):²¹ ^1H NMR (400 MHz, CDCl_3) δ 1.15–1.60 (m, 6H), 1.72 (m, 2H), 1.88 (m, 2H), 4.36 (d, $J = 5.4$ Hz, 2H), 4.67 (br, 1H), 4.91 (br, 1H), 7.26–7.40 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.7 (2C), 25.3, 31.8 (2C), 44.8, 73.1, 127.2 (2C), 127.4, 128.5 (2C), 138.6, 156.2. IR (KBr) 3291, 1684, 1541, 1257 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 256.1313, found 256.1320.

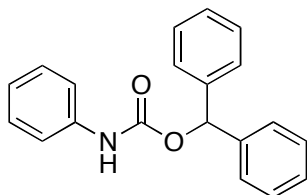


Cyclohexyl hexylcarbamate (17l): ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.10–1.42 (m, 11H), 1.42–1.58 (m, 3H), 1.70 (m, 2H), 1.86 (m, 2H), 3.15 (q,

$J = 6.9$ Hz, 2H), 4.50–4.80 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.5, 23.8 (2C), 25.3, 26.3, 29.9, 31.4, 32.0 (2C), 40.8, 72.7, 156.2. IR (neat) 3334, 2933, 2858, 1694, 1534, 1251 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{25}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 250.1783, found 250.1787.



2,4-Dimethylpentan-3-yl phenylcarbamate (17m):²² ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 6.9$ Hz, 12H), 1.93 (octet, $J = 6.9$ Hz, 2H), 4.53 (t, $J = 6.9$ Hz, 1H), 6.61 (br, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 17.1 (2C), 19.4 (2C), 29.4 (2C), 83.5, 118.3 (2C), 123.0, 128.9 (2C), 138.2, 154.1. IR (KBr) 3342, 1697, 1529, 1444, 1233, 1055 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 258.1470, found 258.1478.

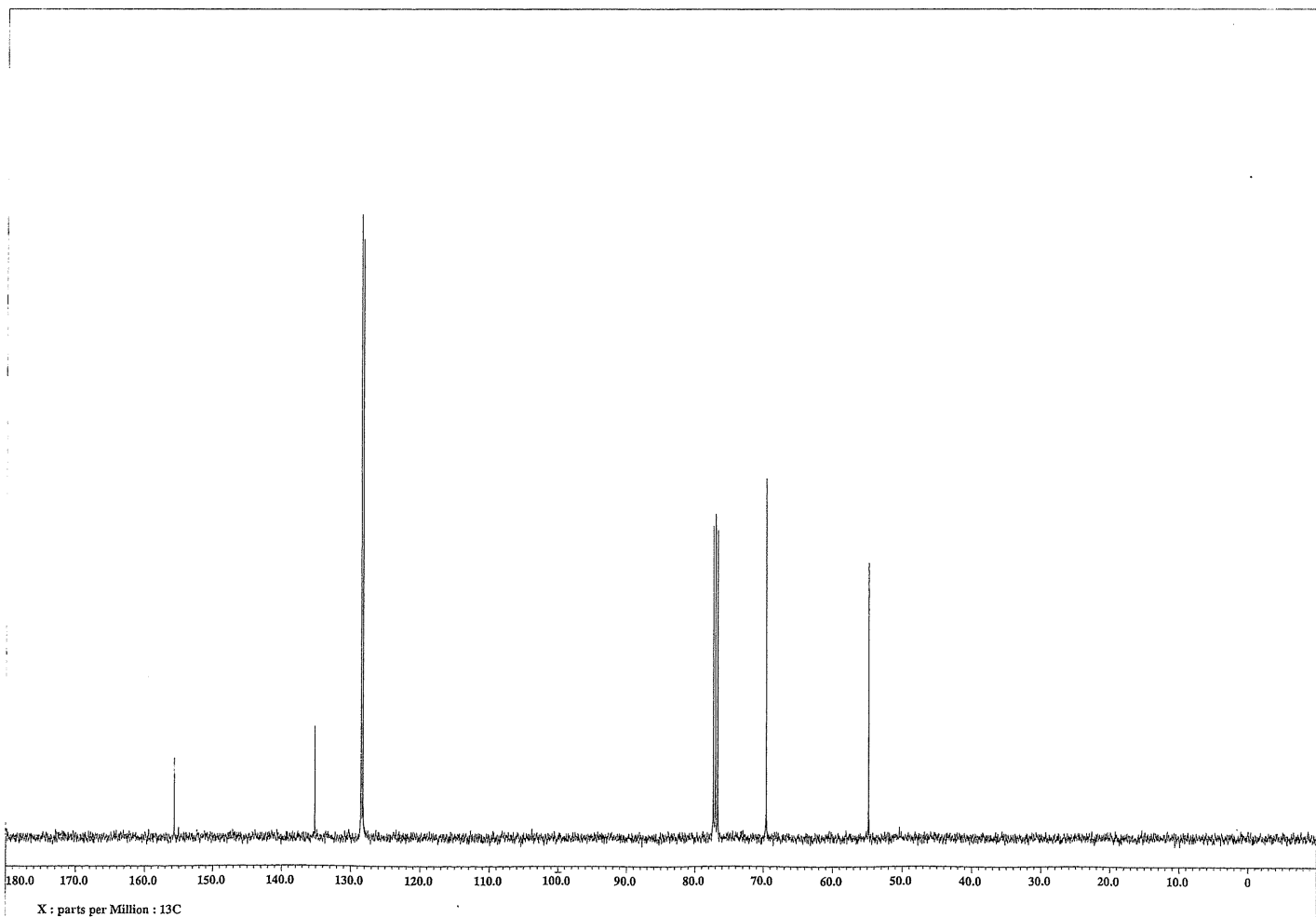
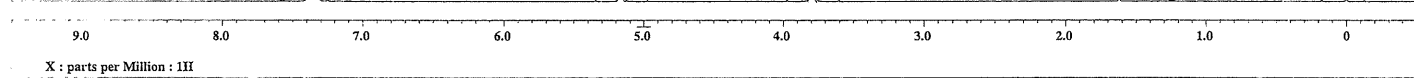
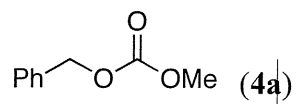


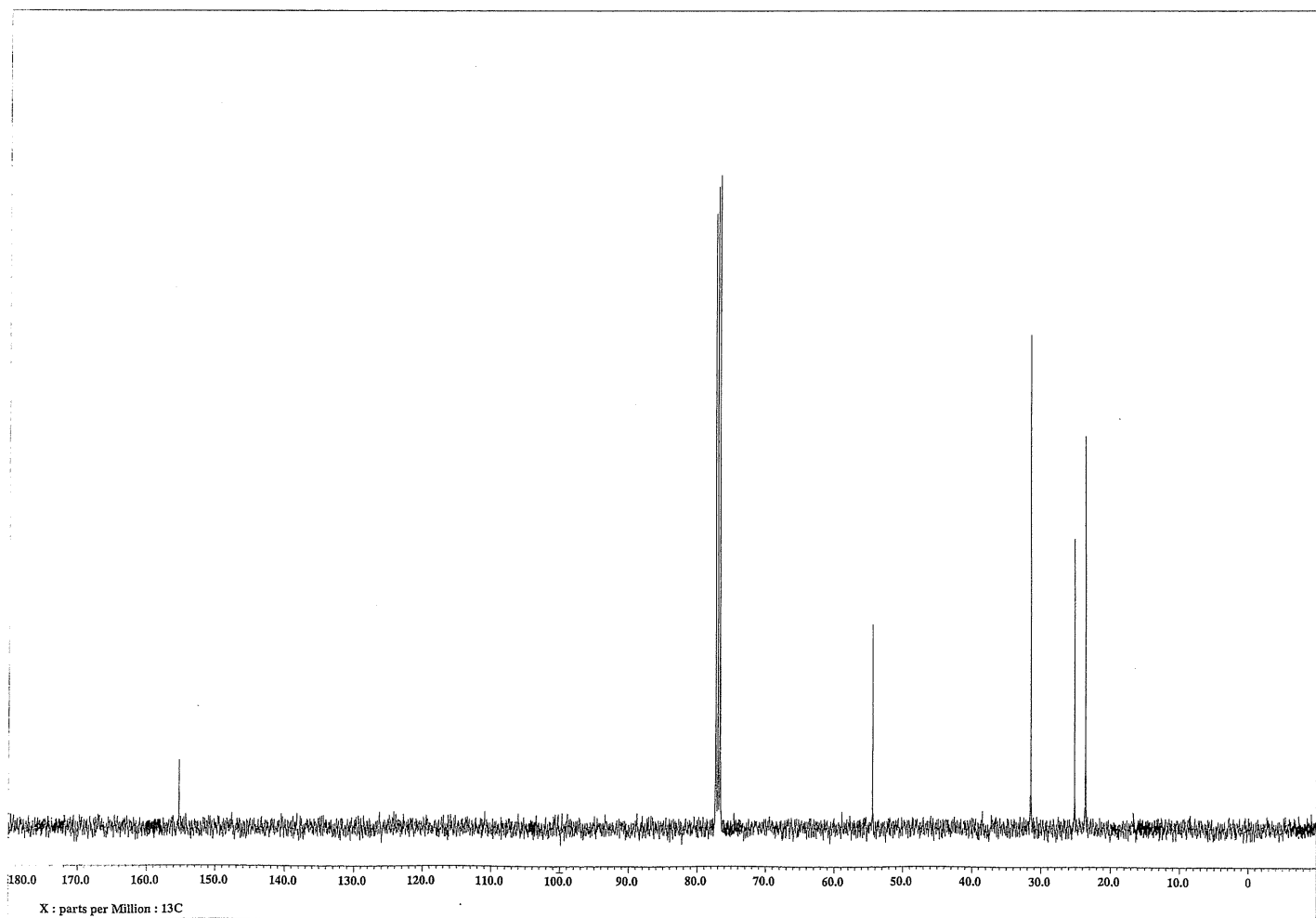
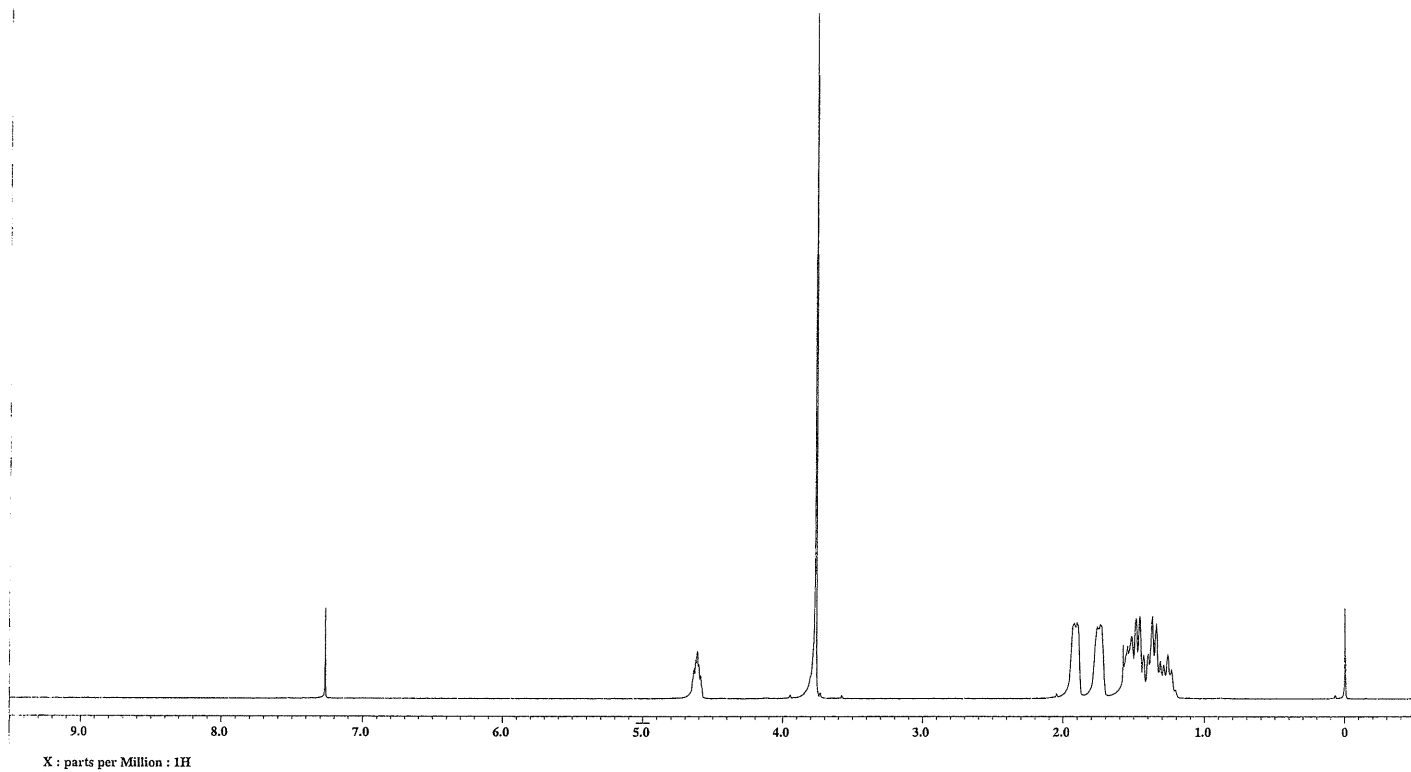
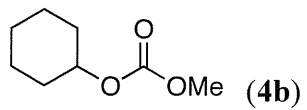
Benzhydryl phenylcarbamate (17n):²³ ^1H NMR (400 MHz, CDCl_3) δ 6.83 (br, 1H), 6.89 (s, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 7.20–7.40 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 77.7, 118.5 (2C), 123.4, 127.9 (4C), 127.9 (2C), 128.5 (4C), 129.0 (2C), 137.6, 140.0 (2C), 152.5. IR (KBr) 3331, 1702, 1536, 1444, 1234, 1058 cm^{-1} . HRMS (FAB+) calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 326.1157, found 326.1161.

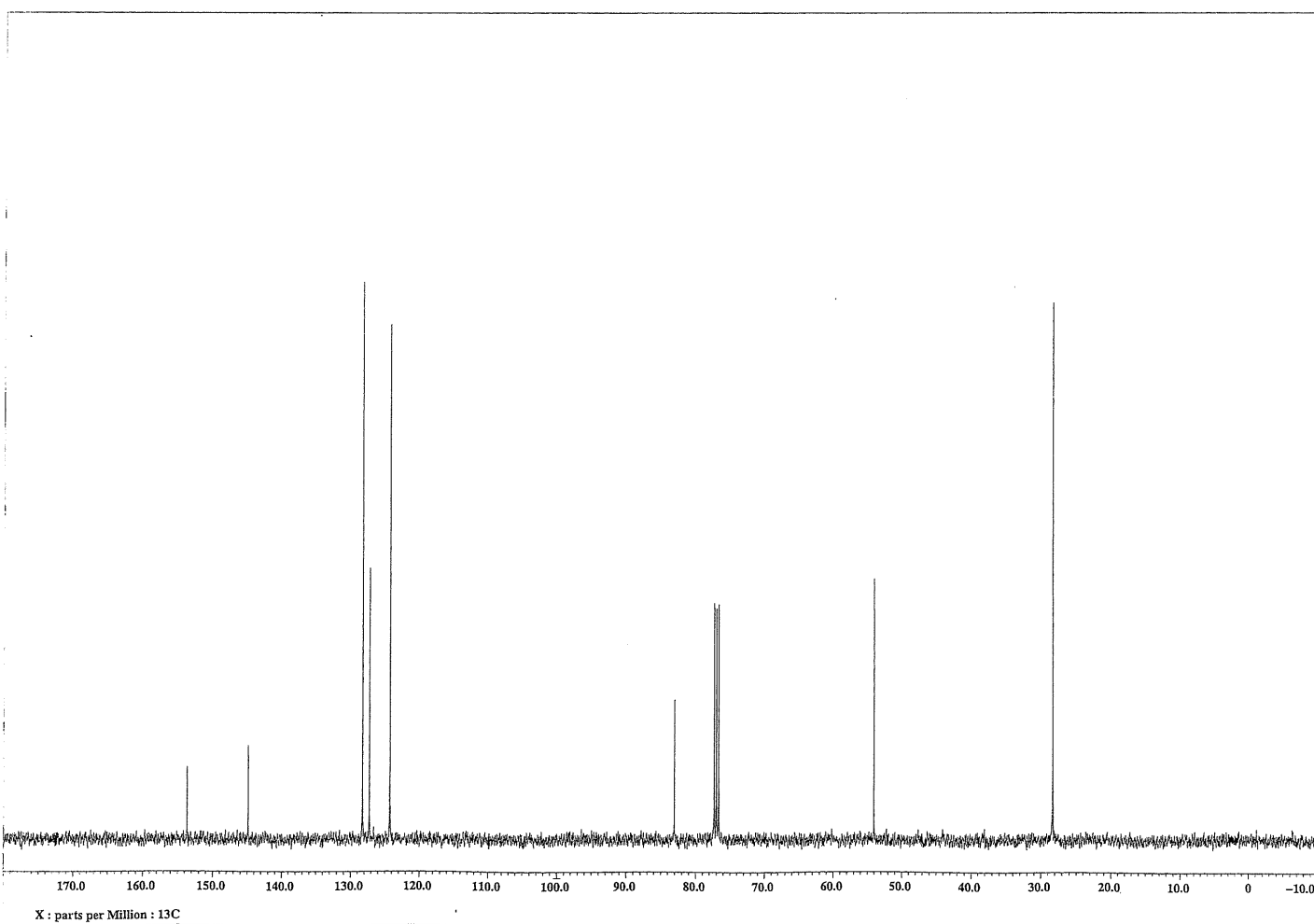
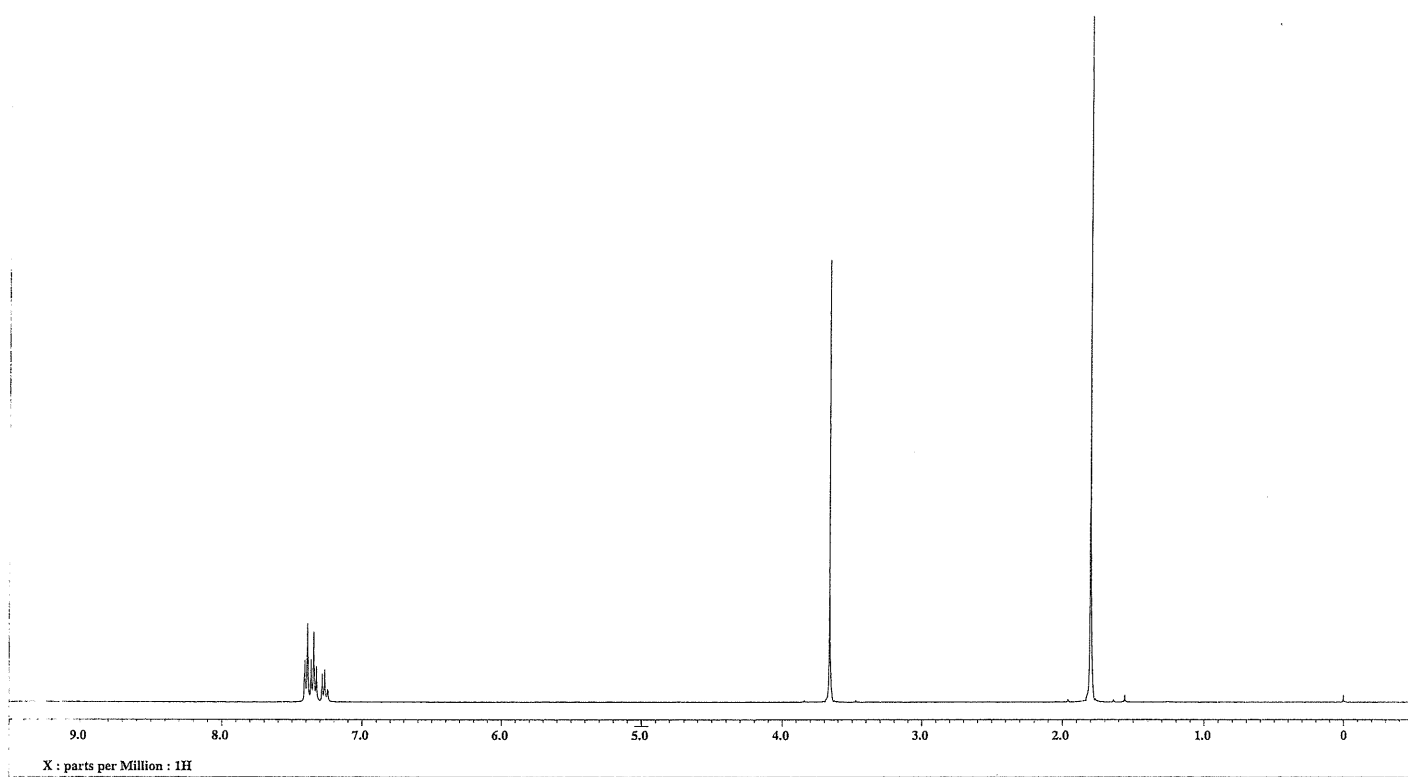
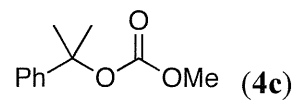
7. References.

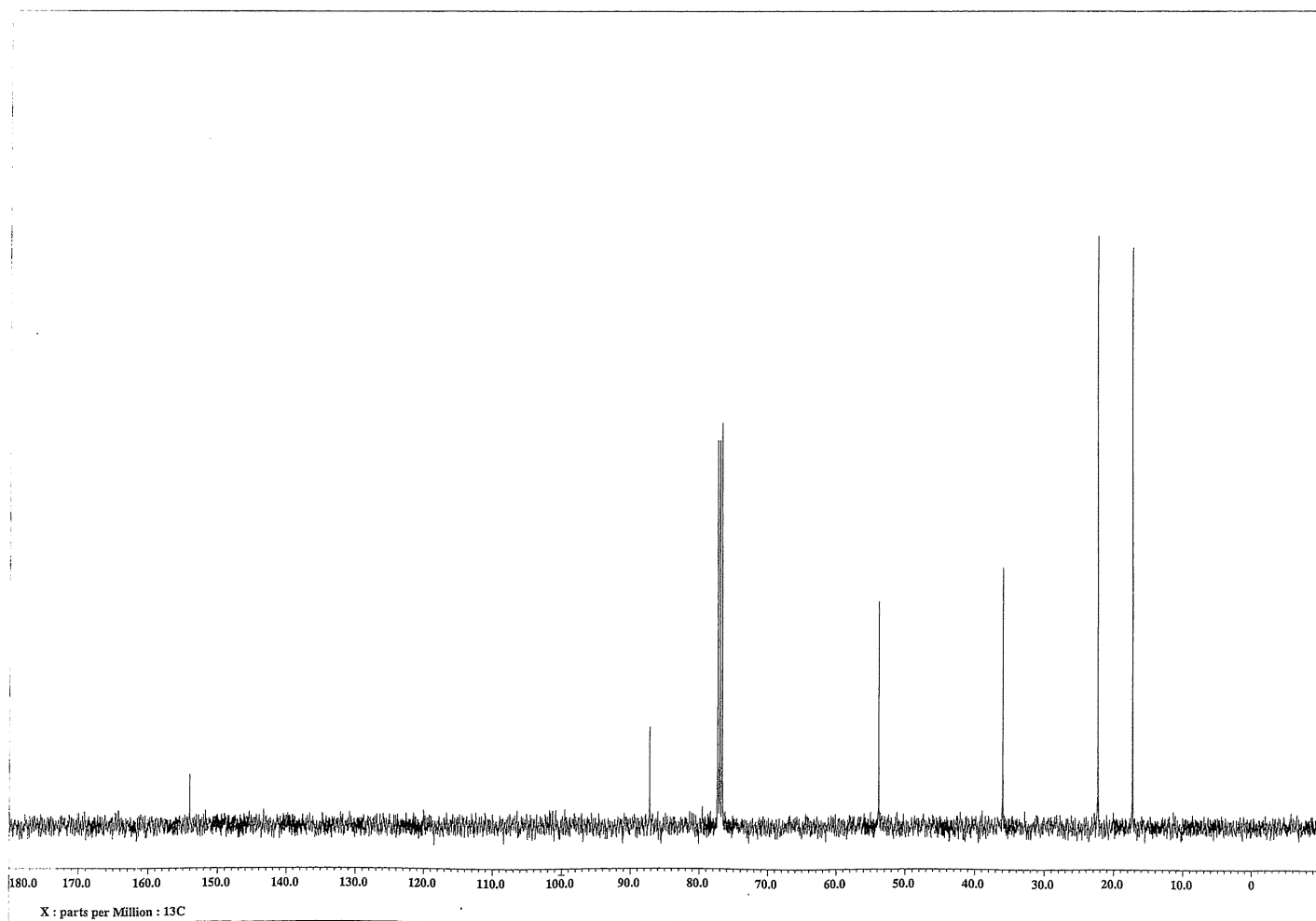
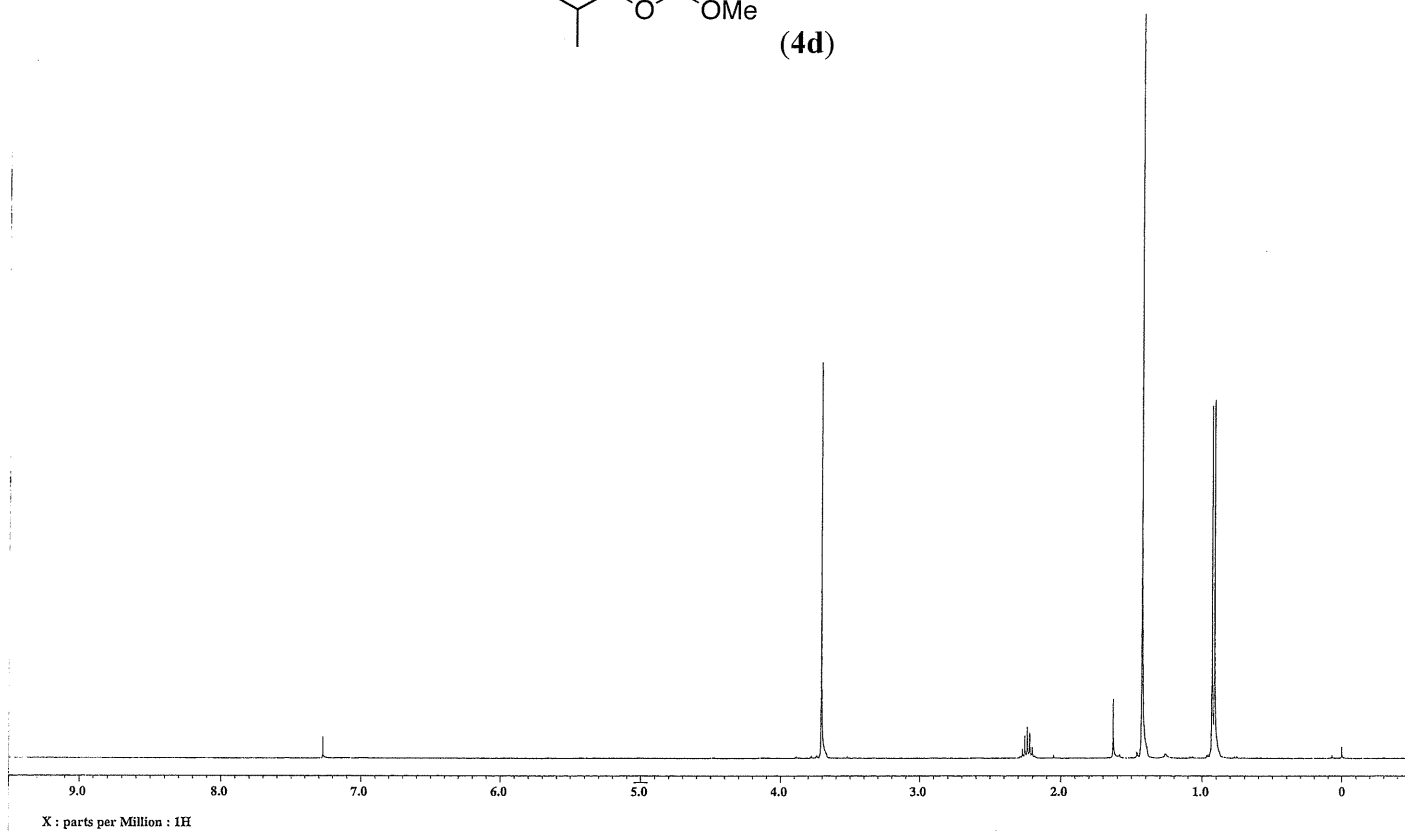
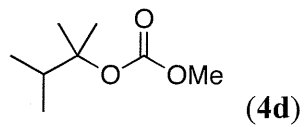
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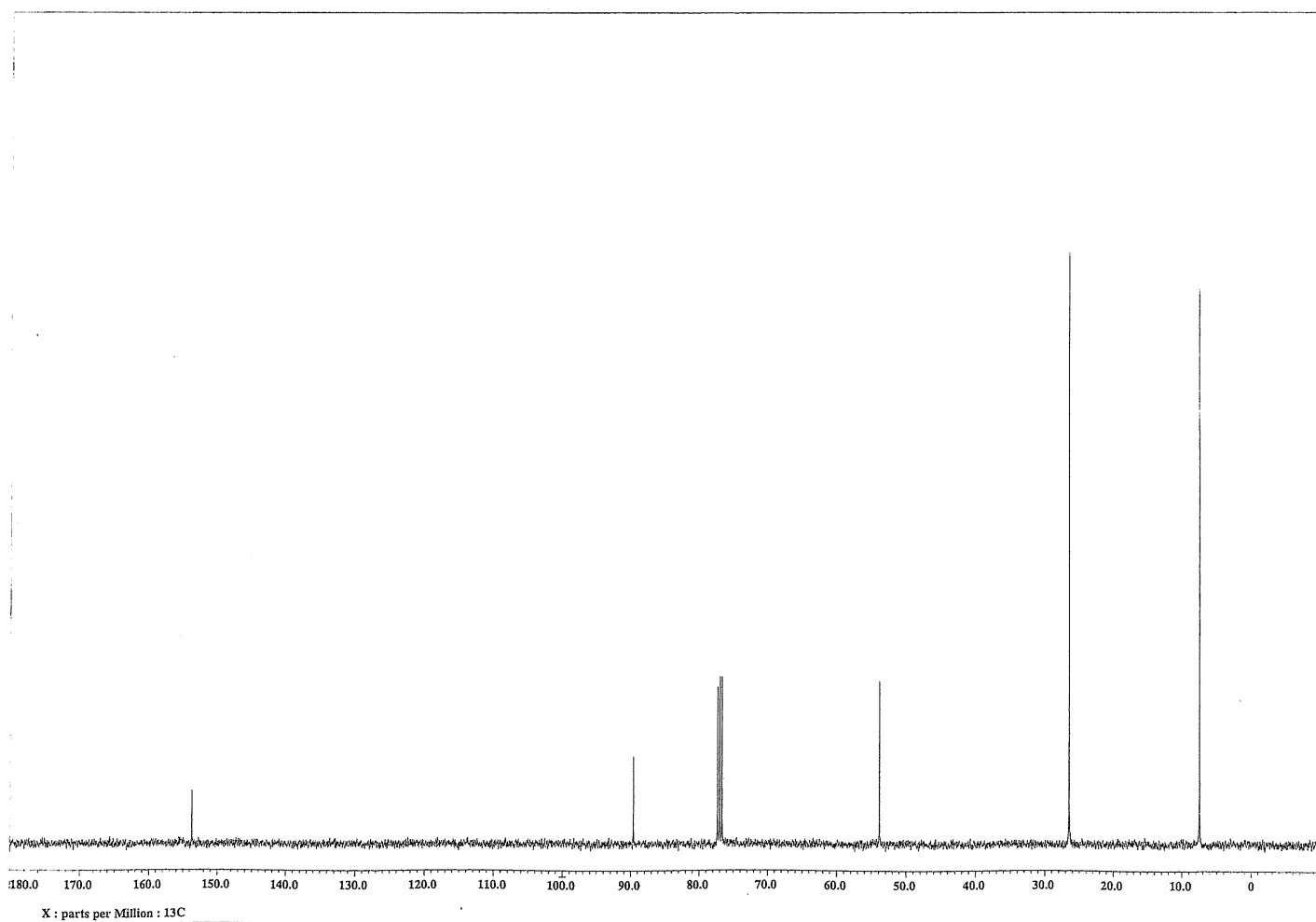
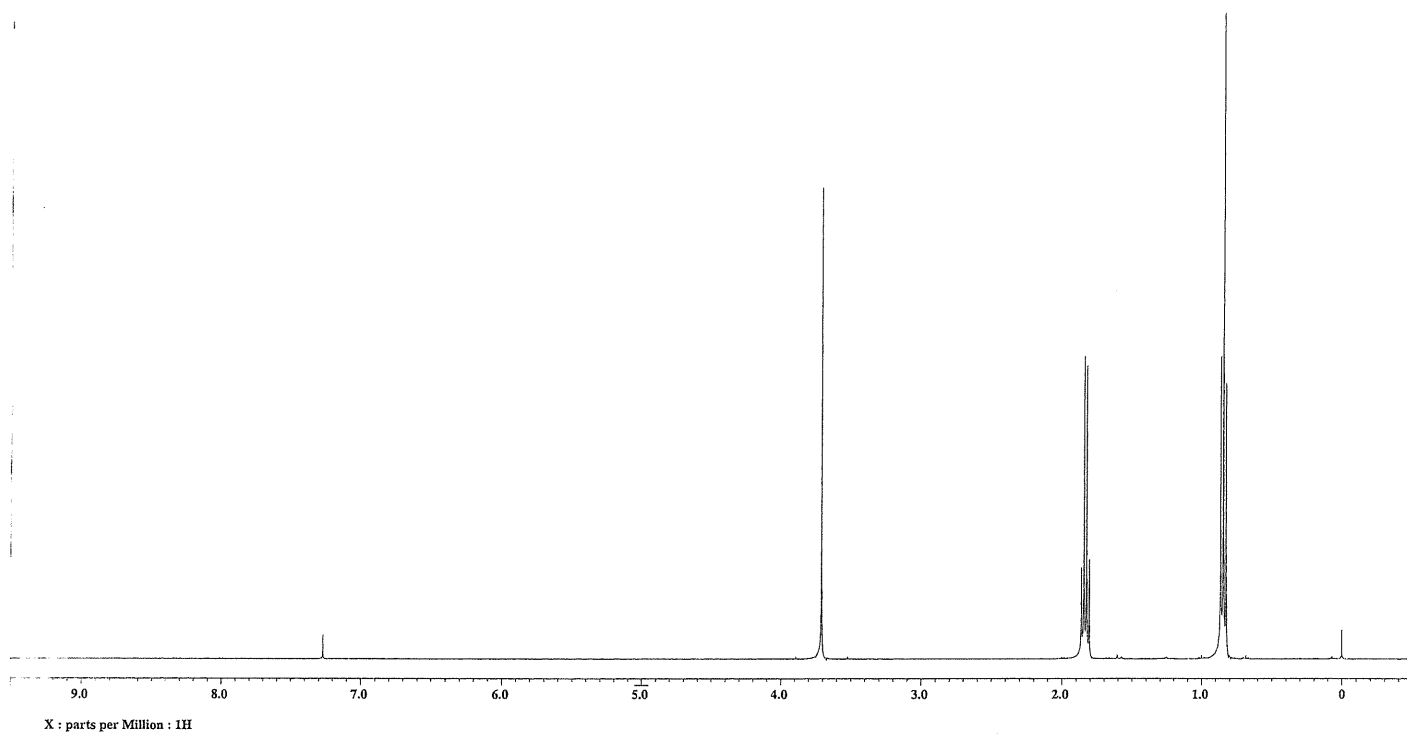
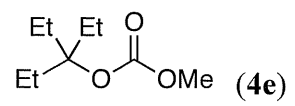
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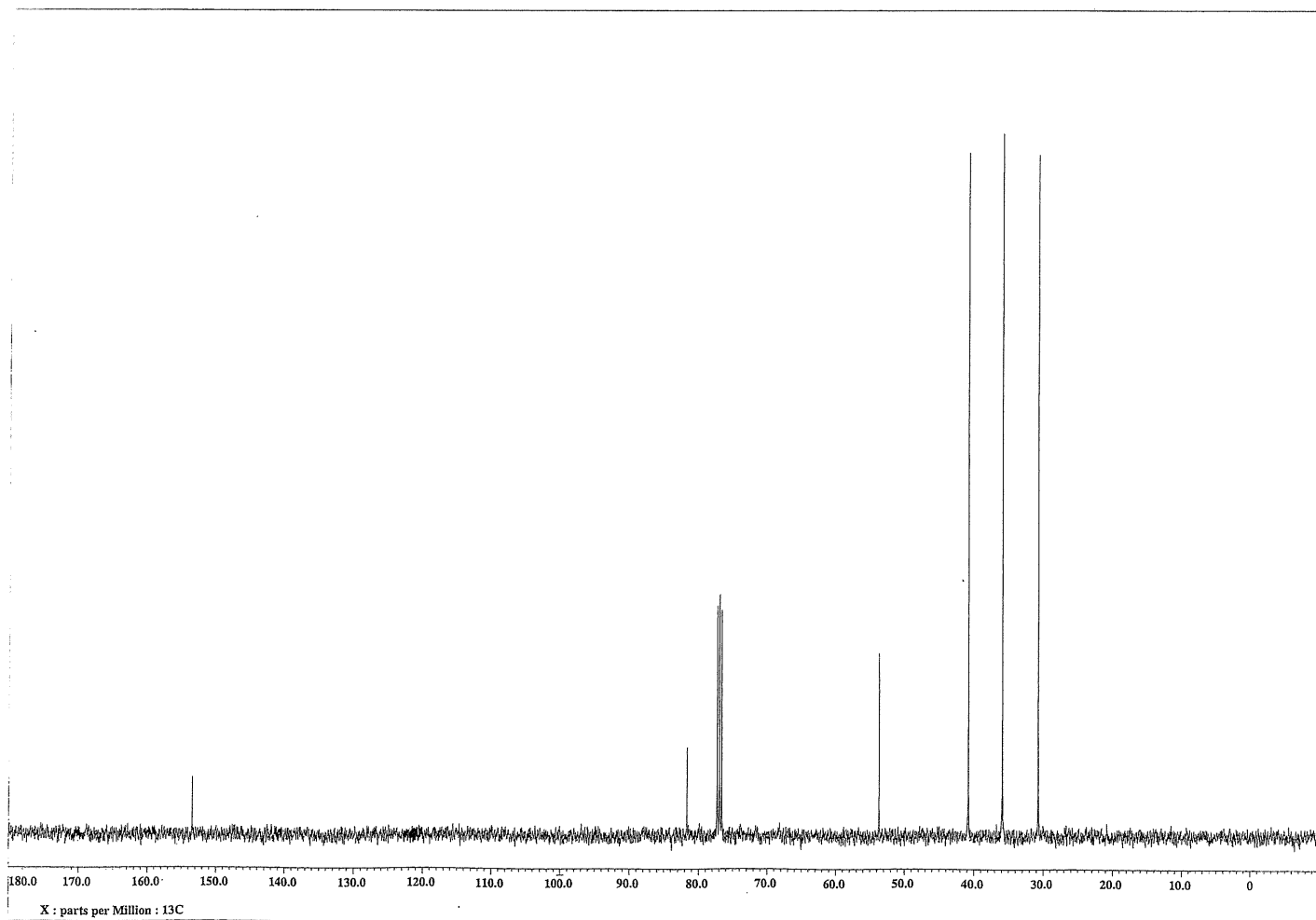
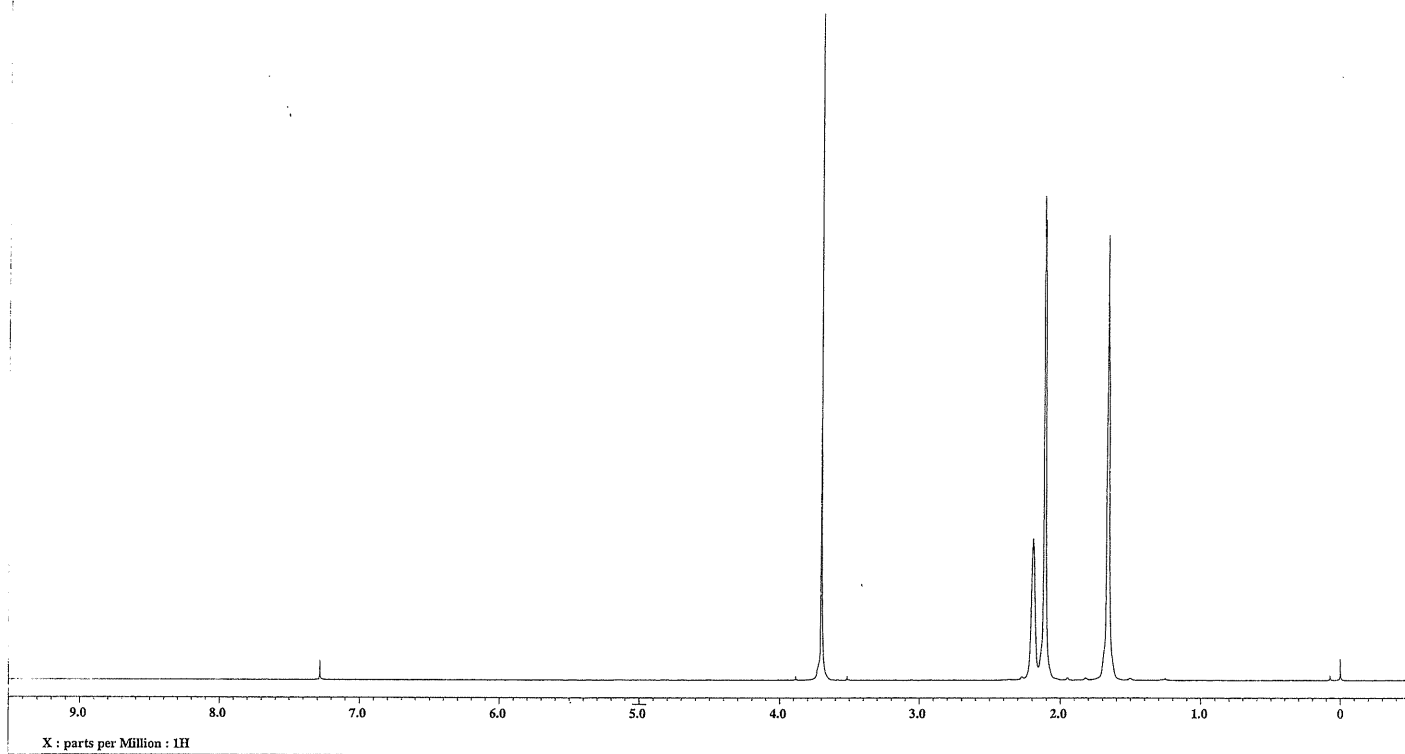
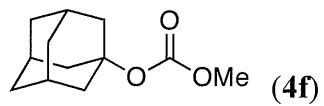


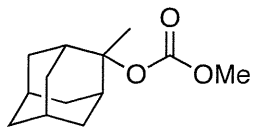




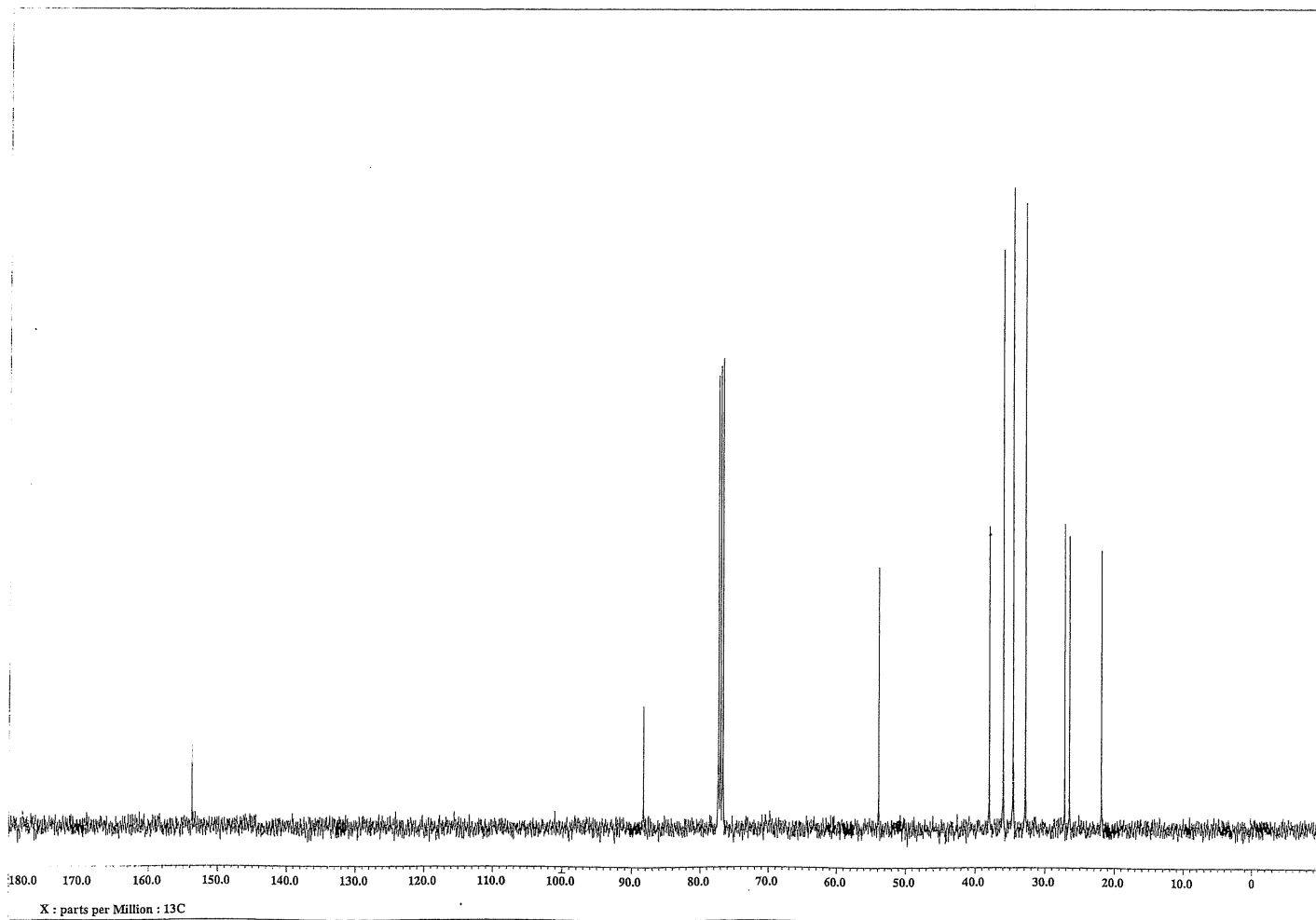
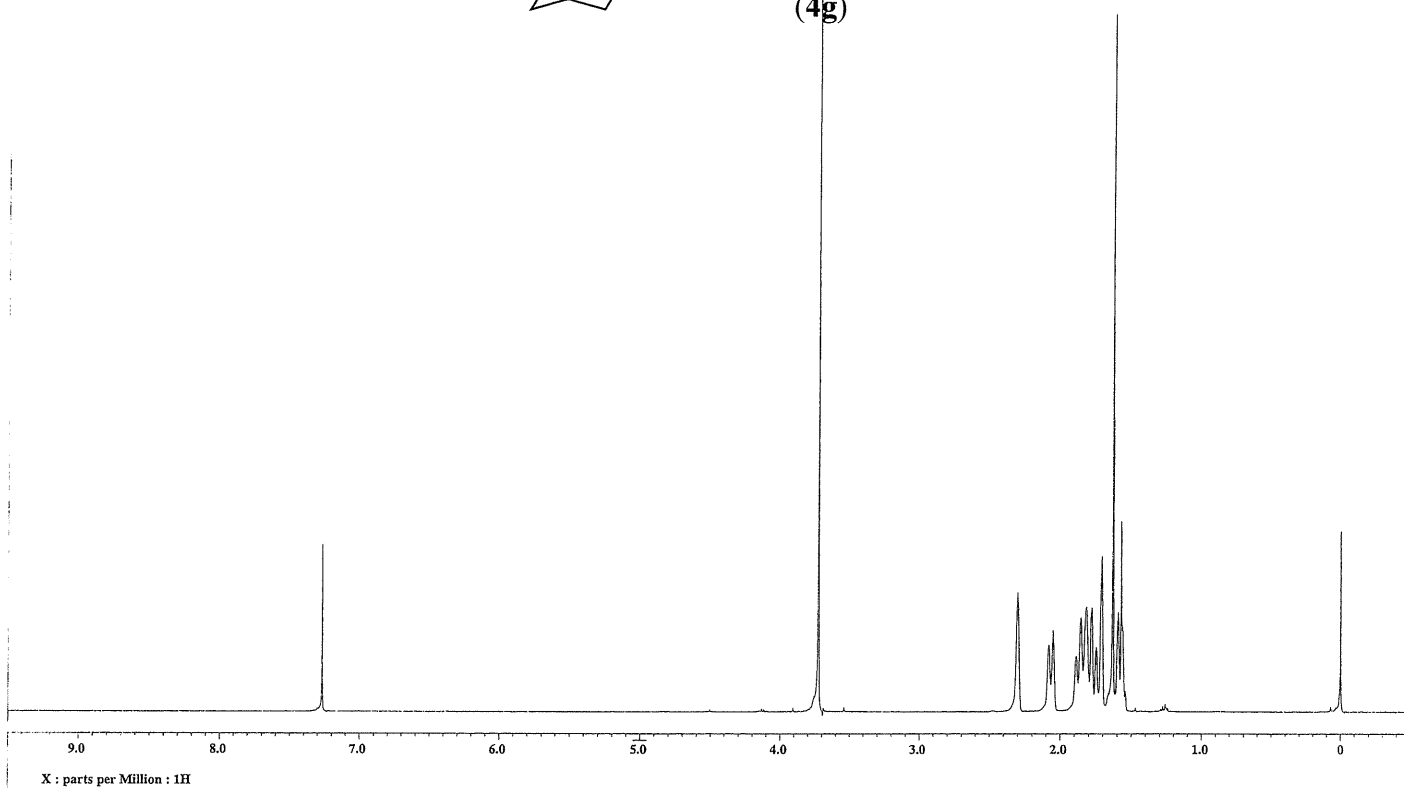


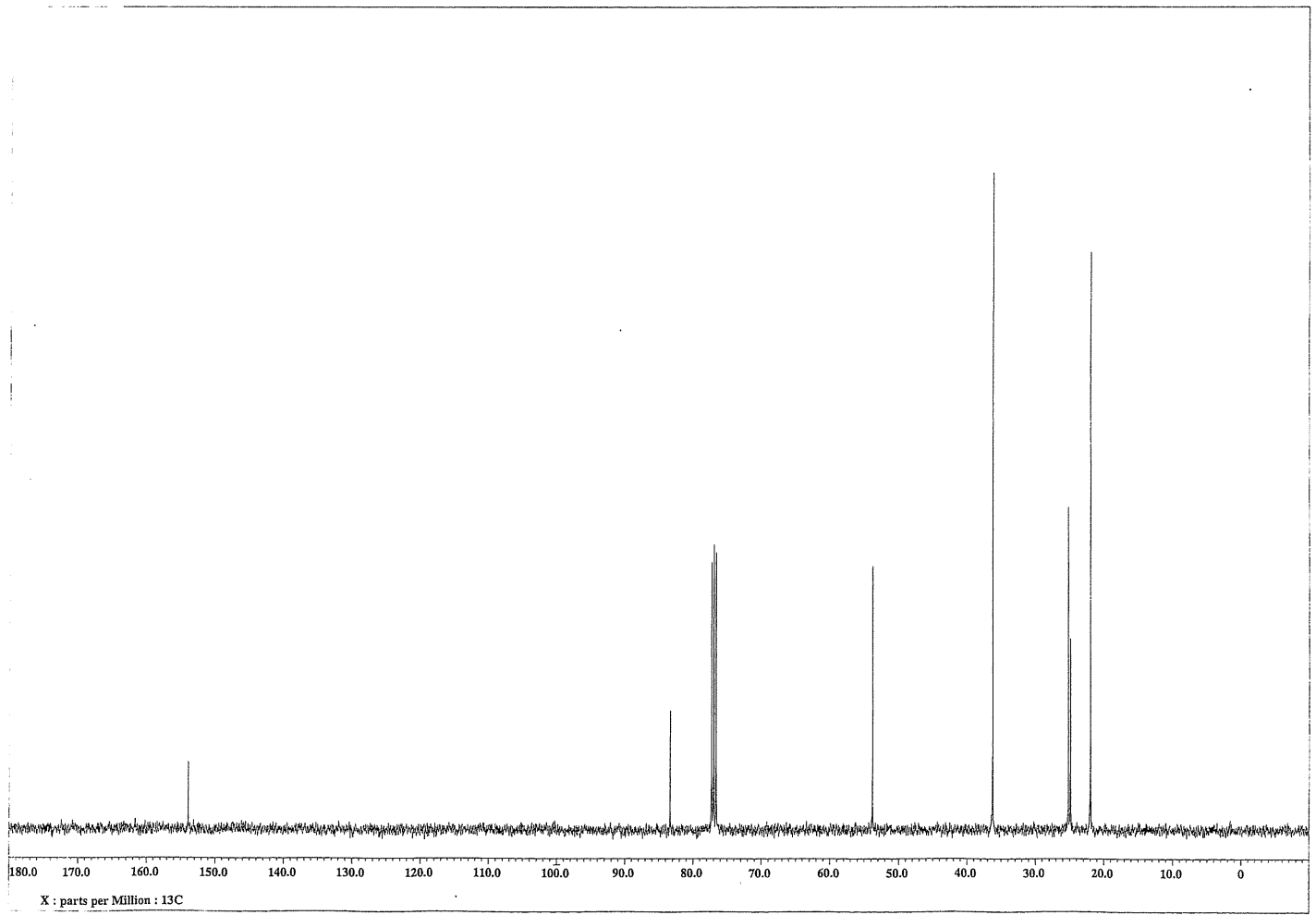
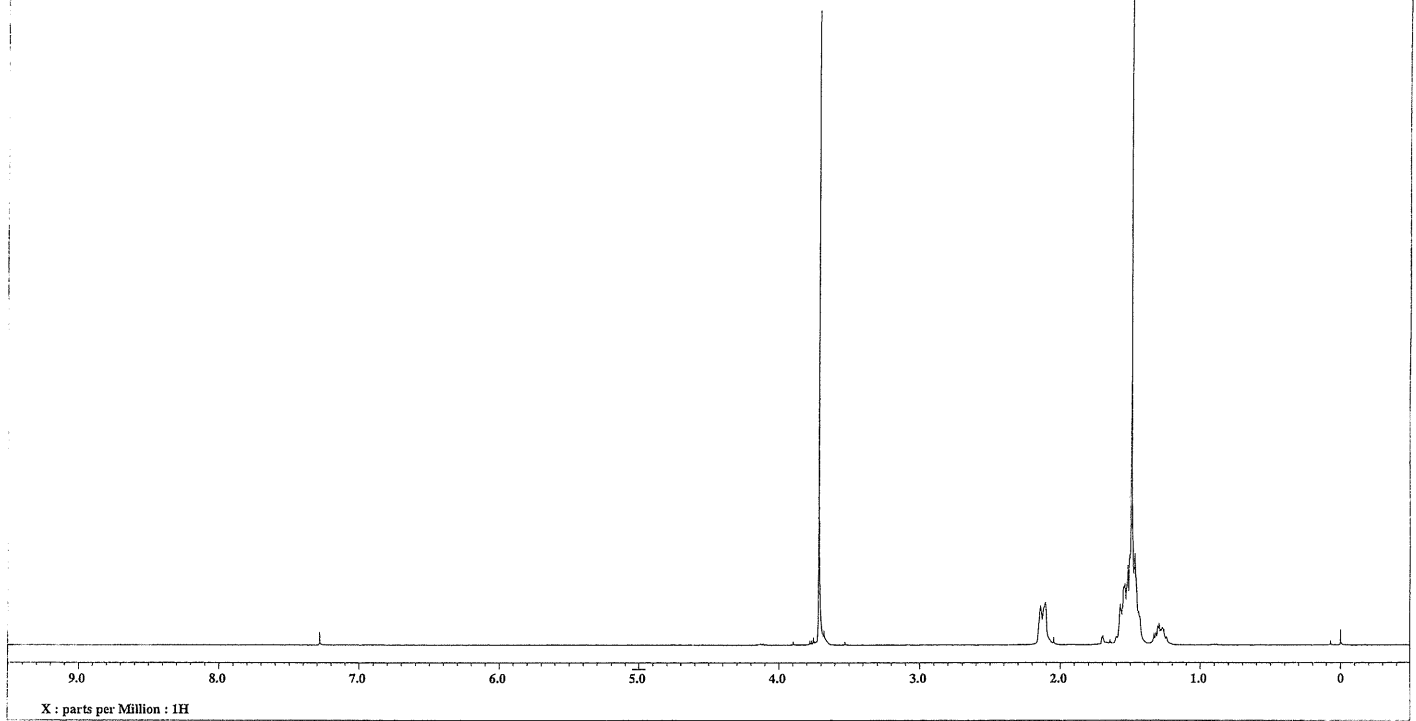
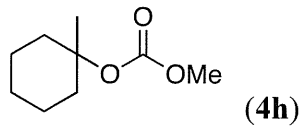


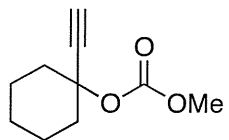




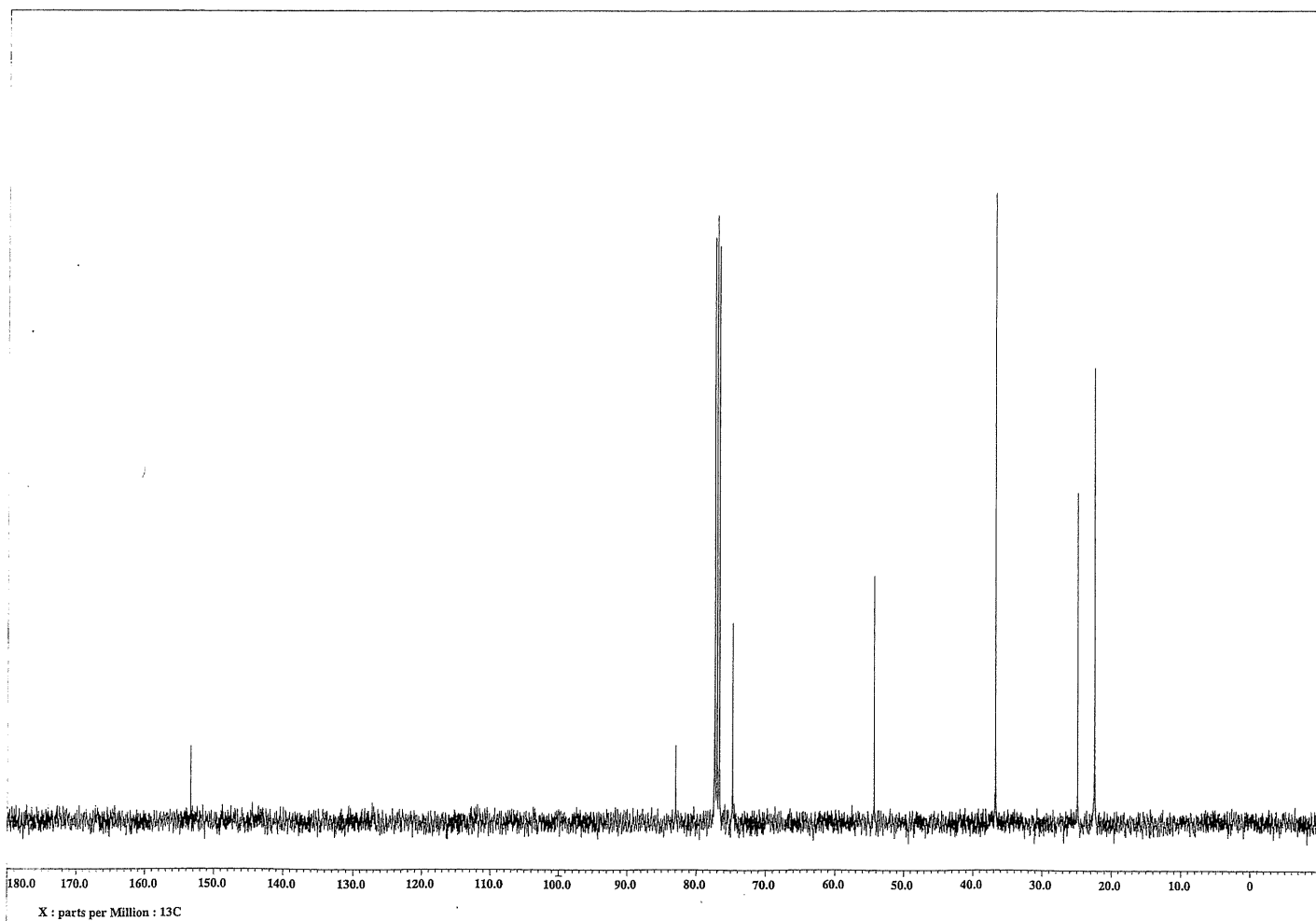
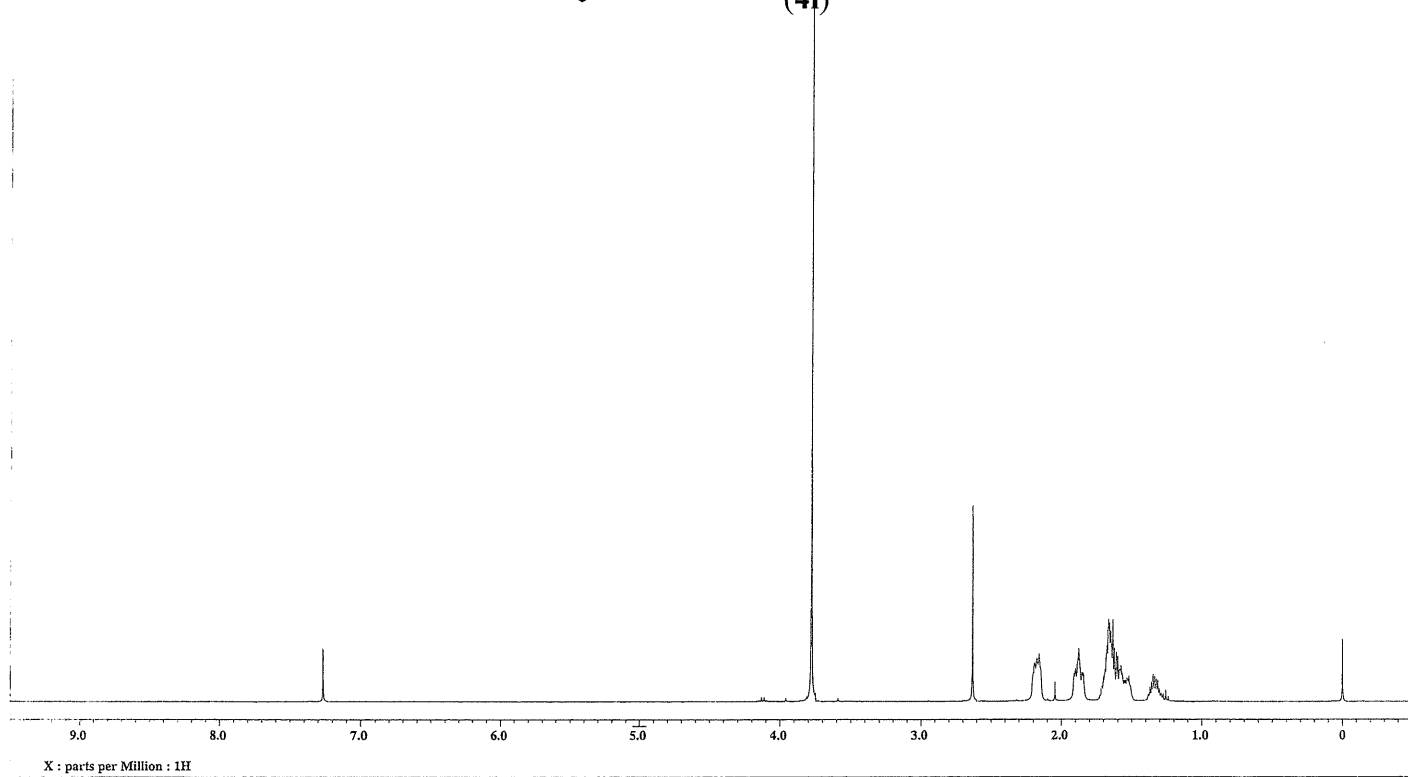
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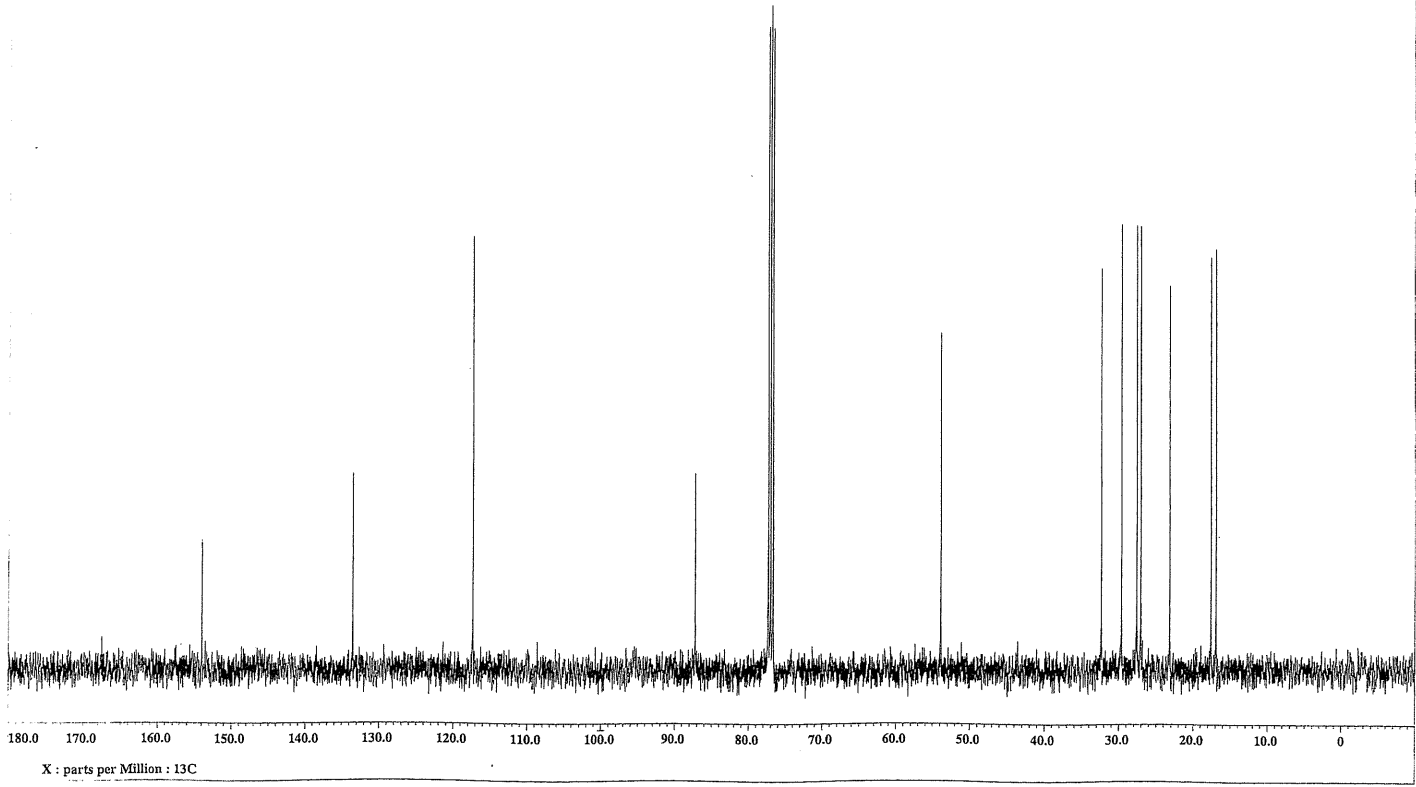
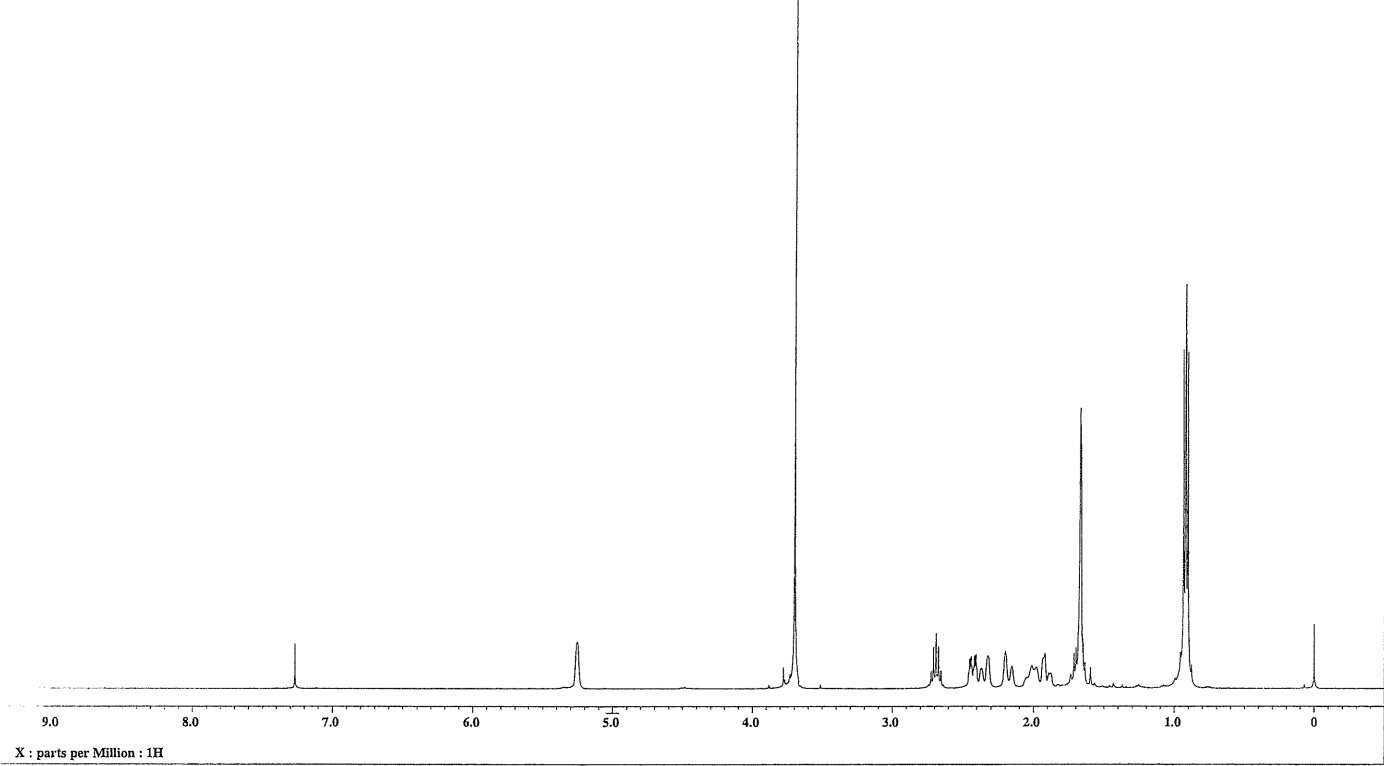
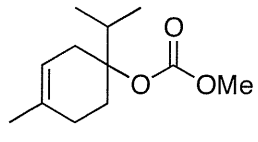


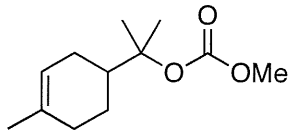




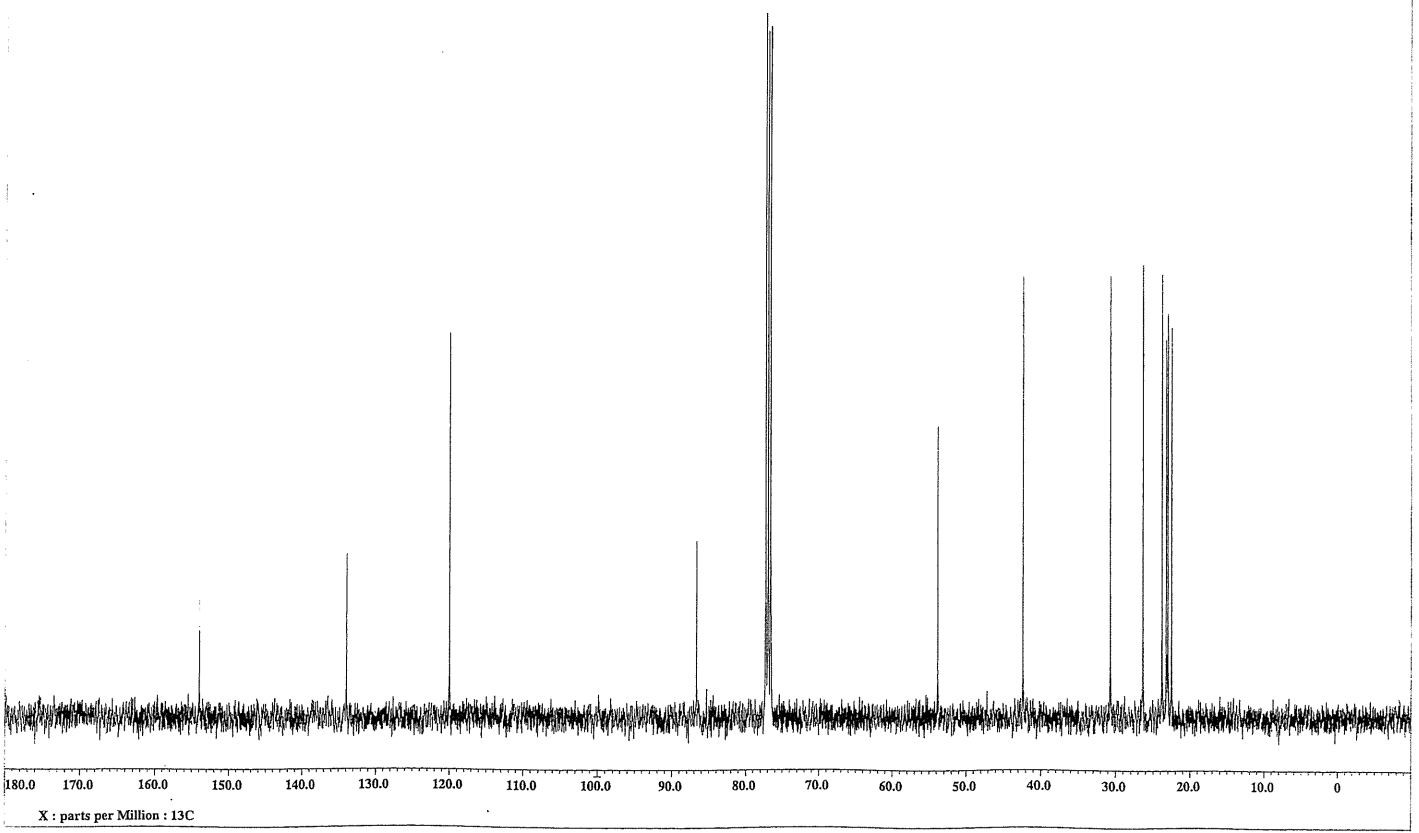
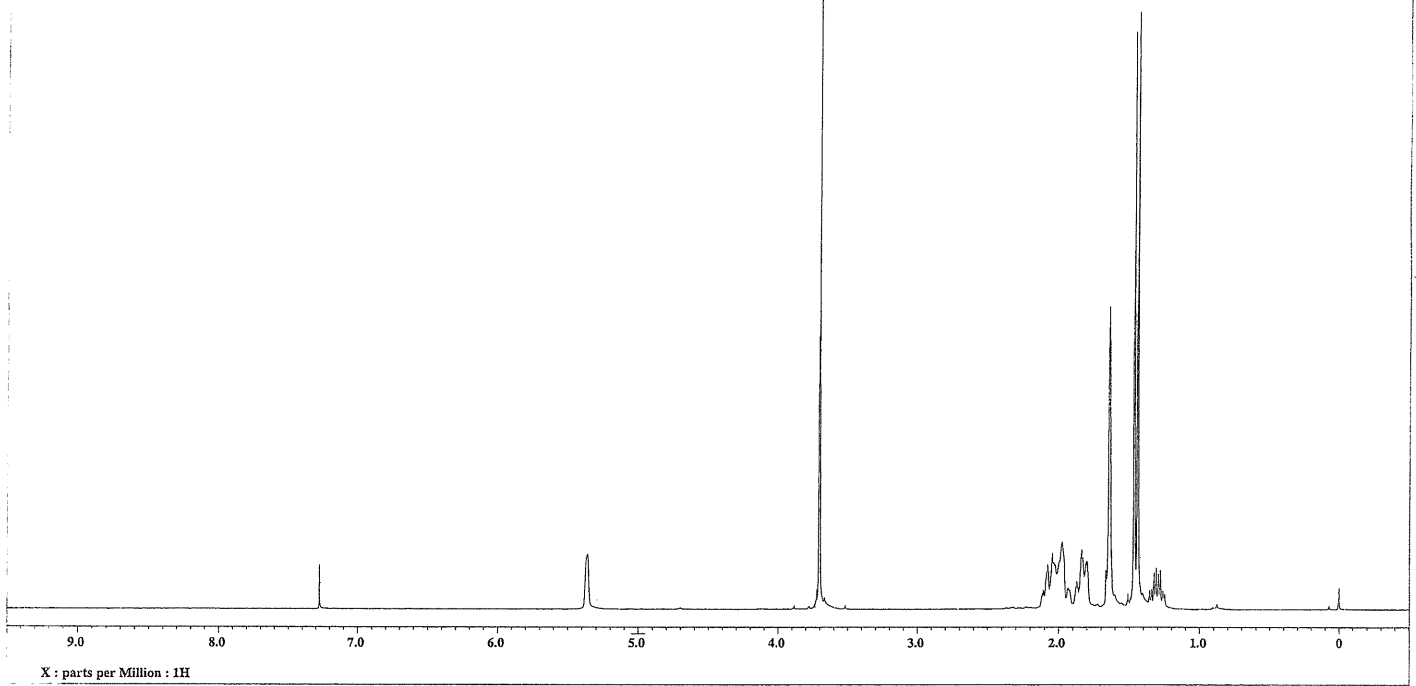
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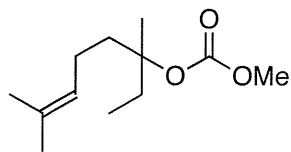




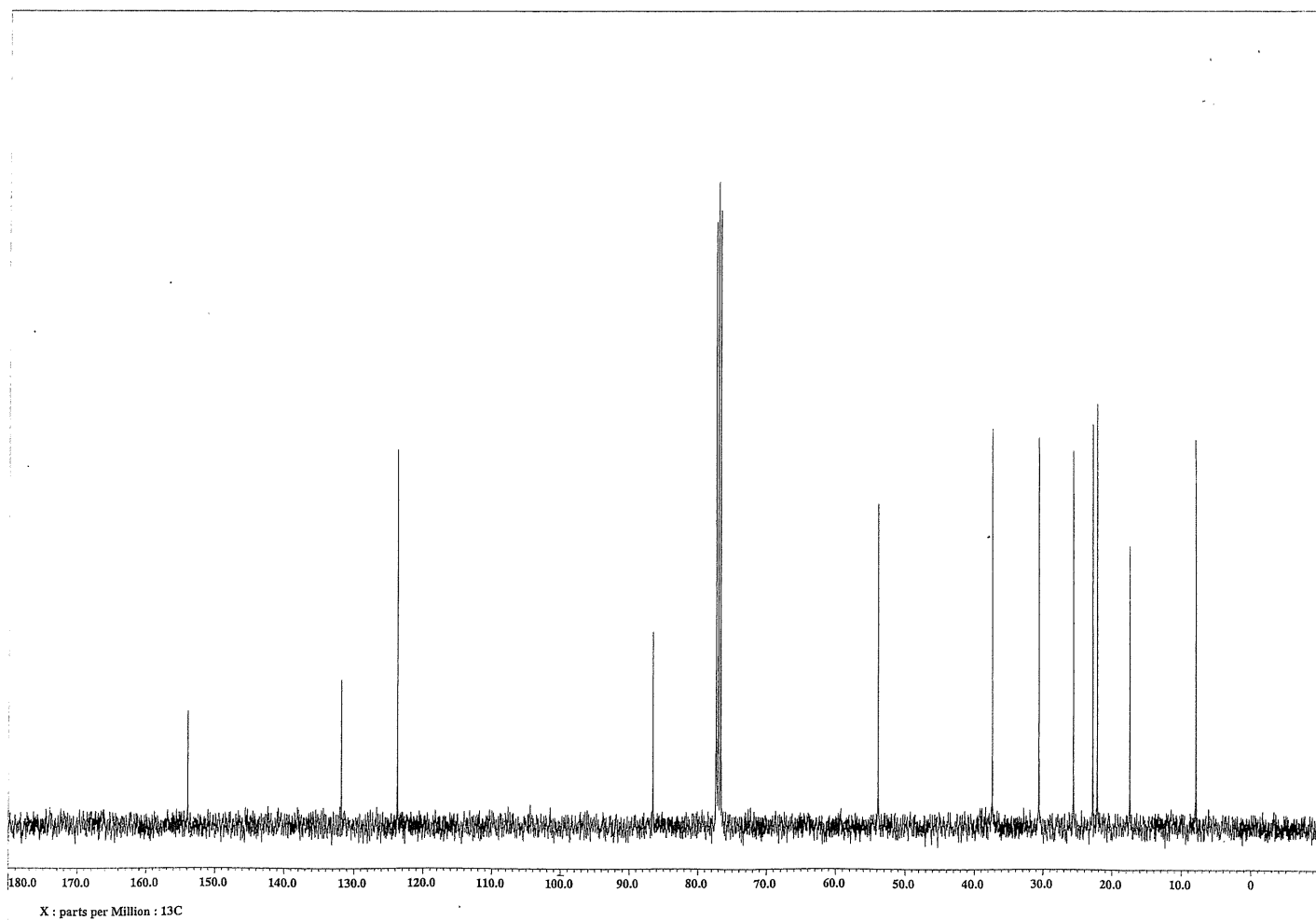
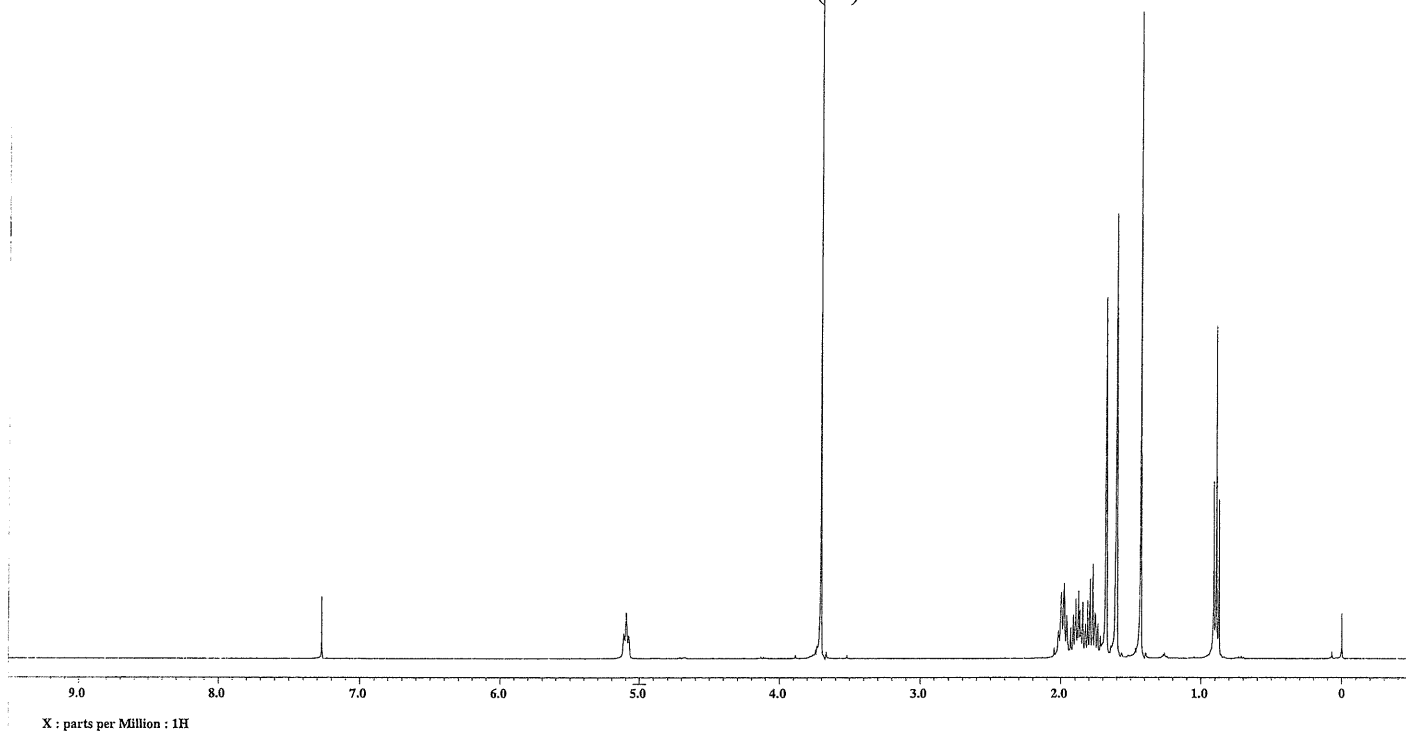


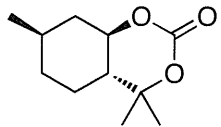
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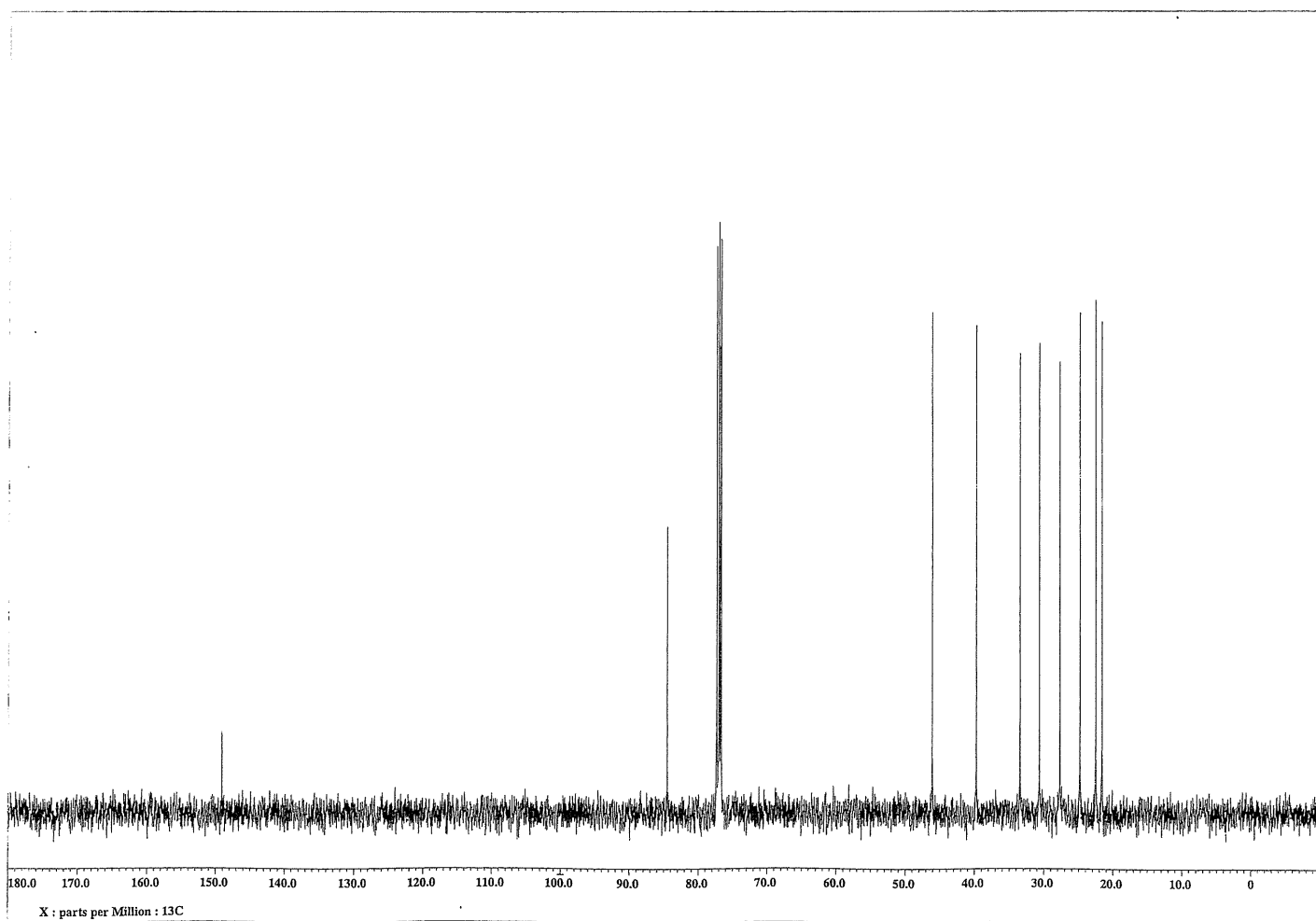
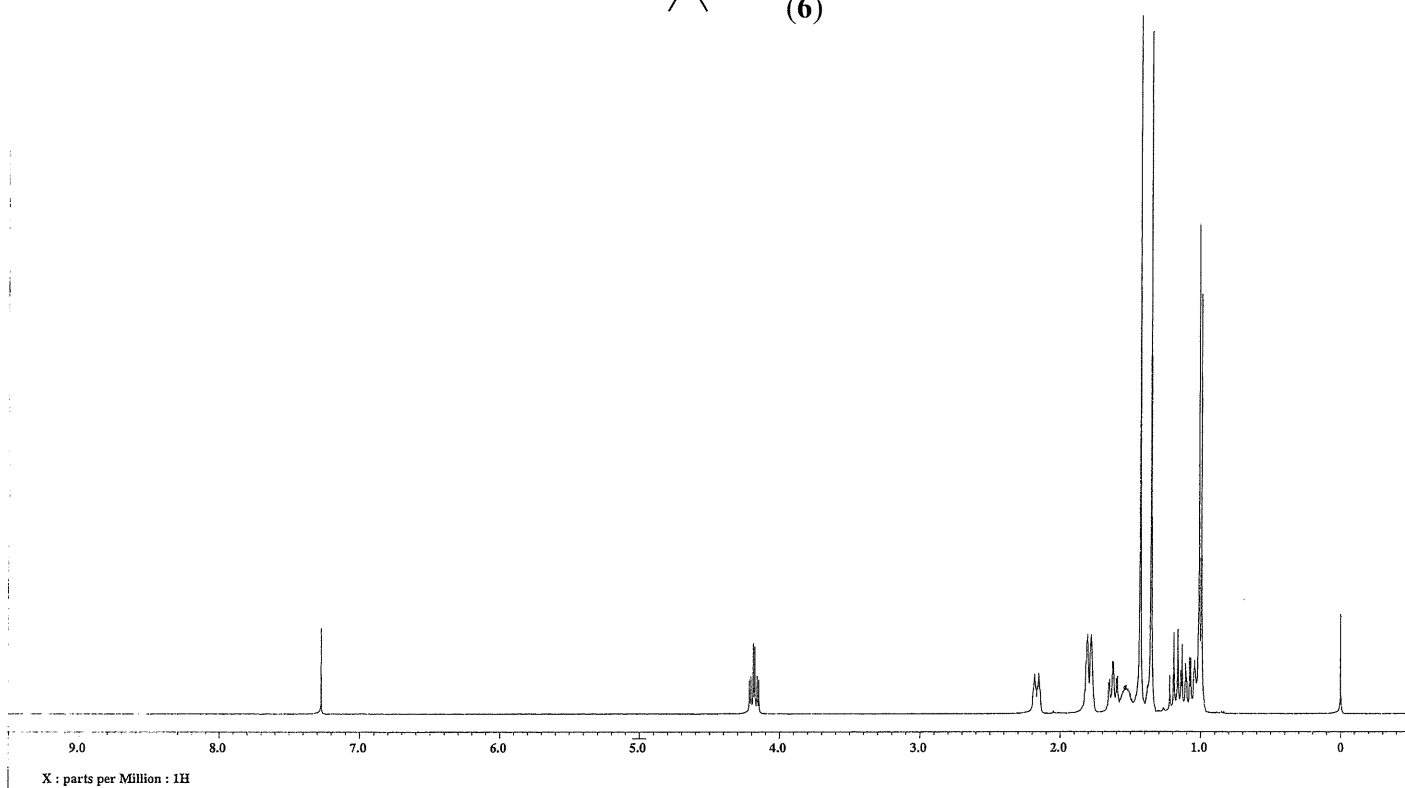


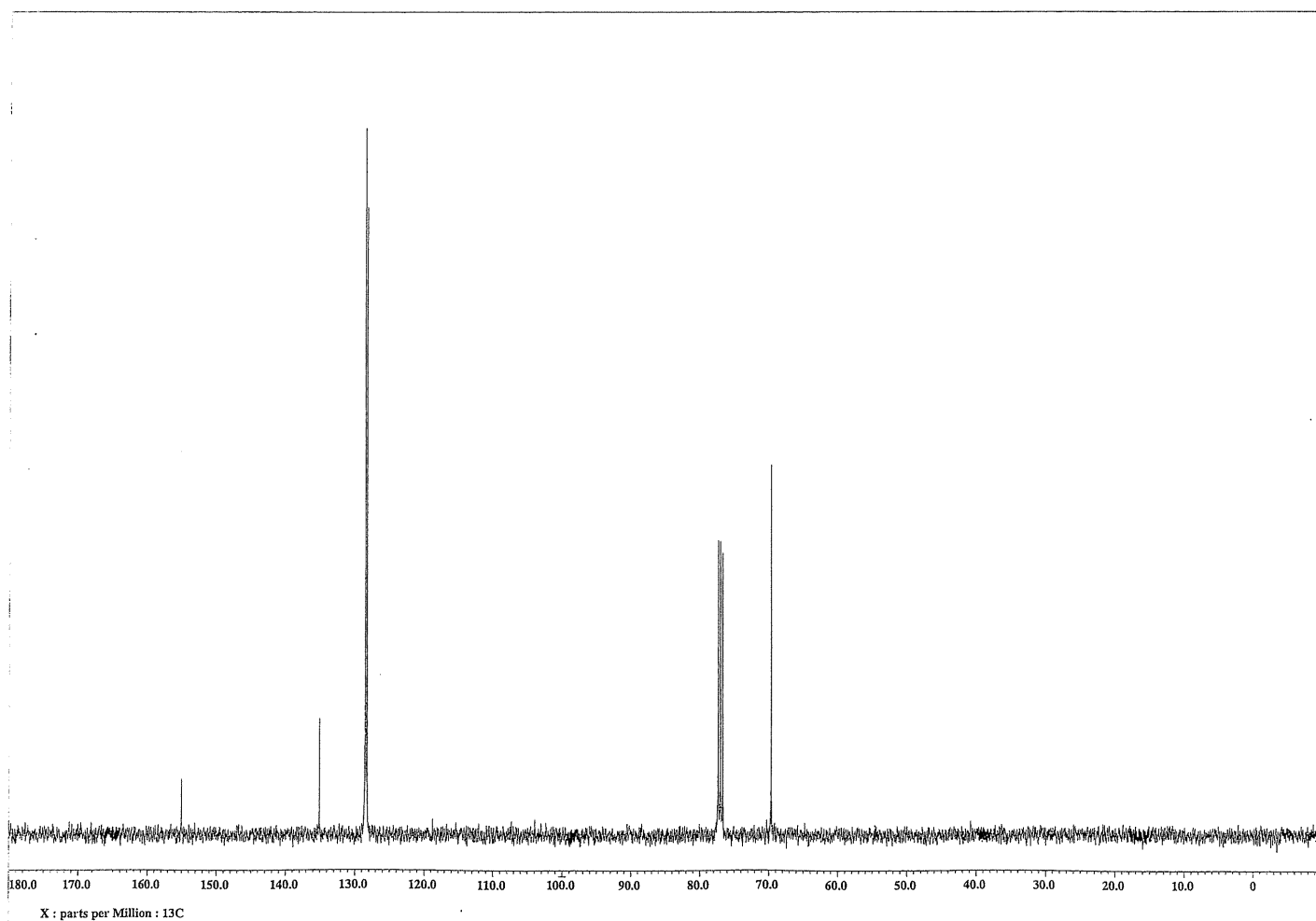
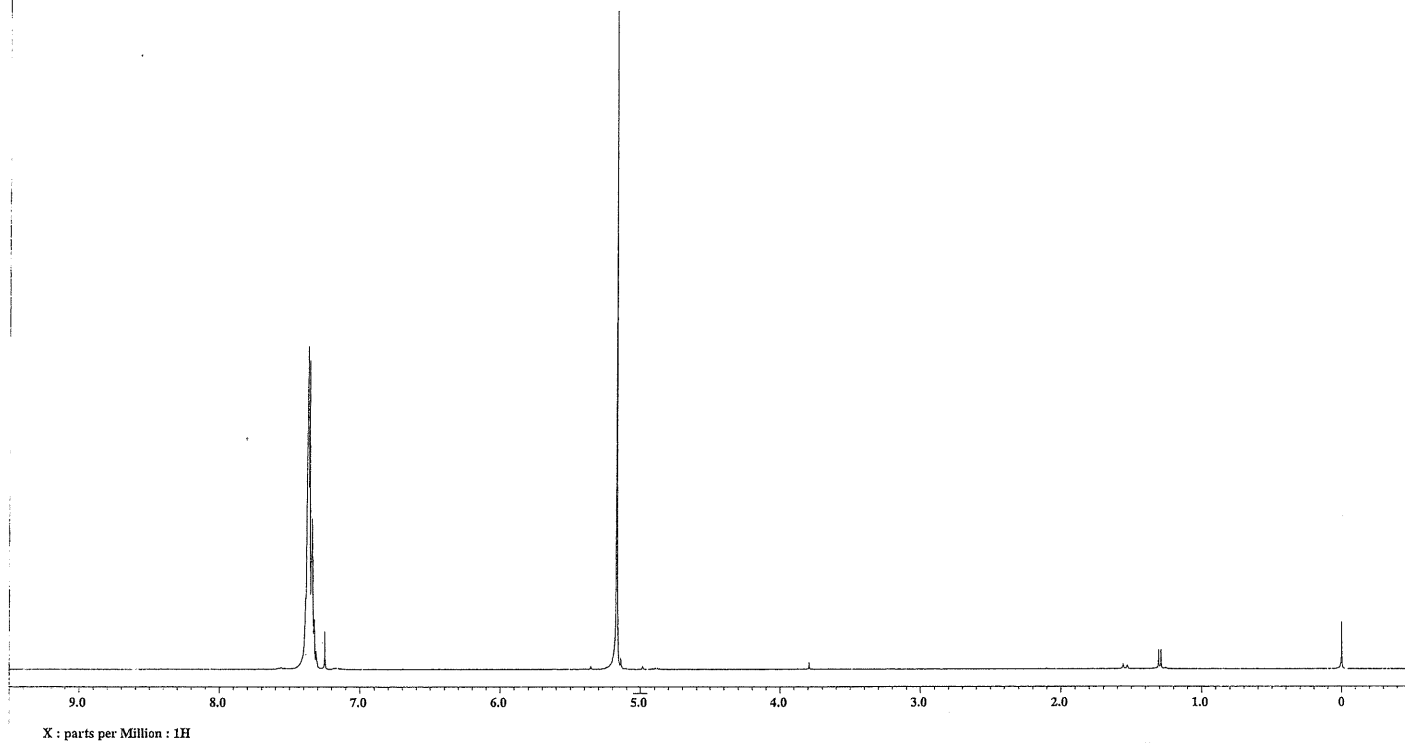
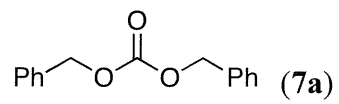
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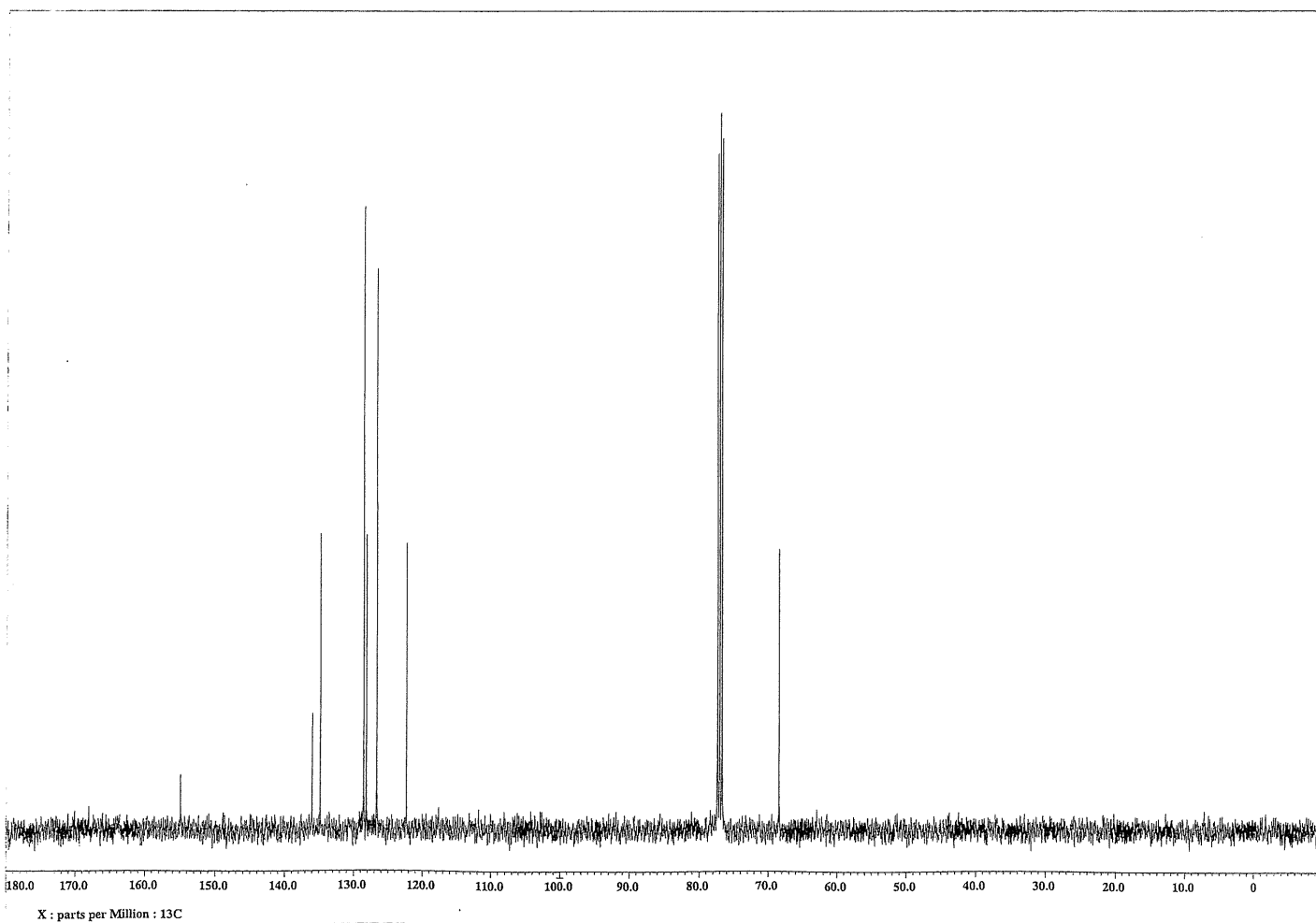
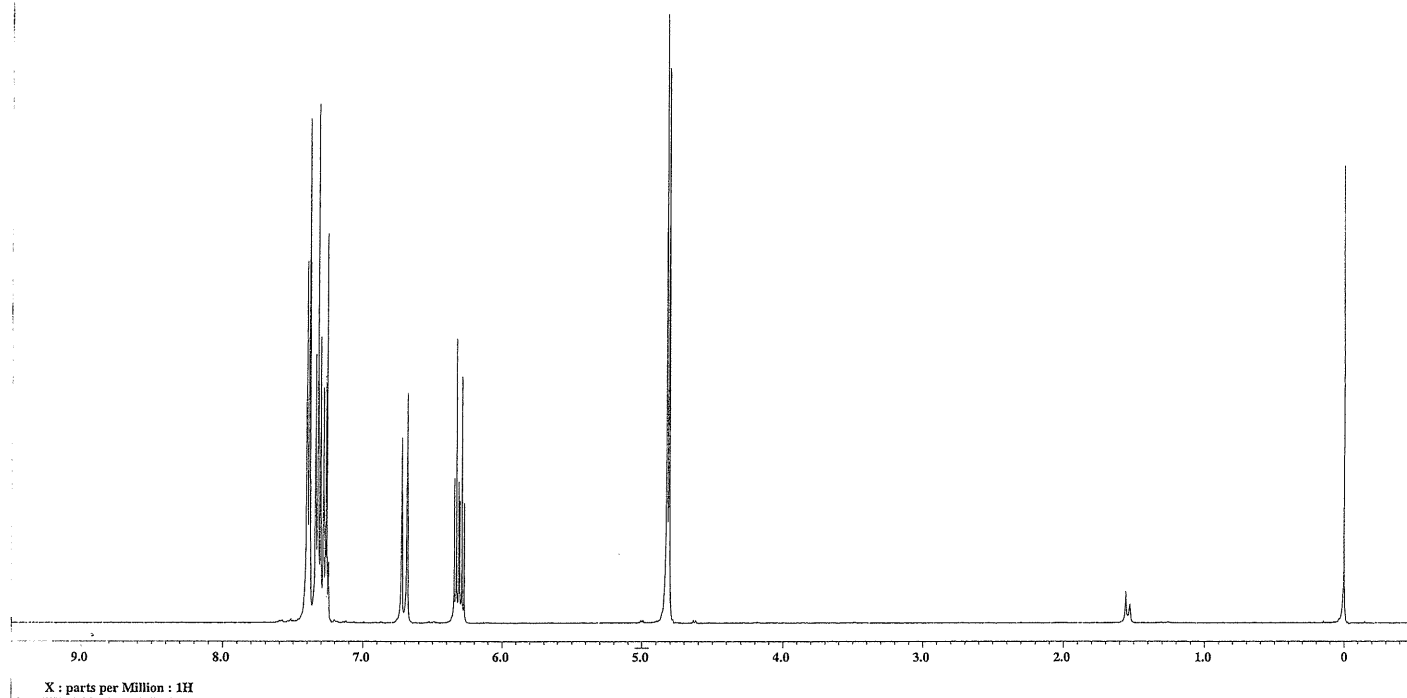
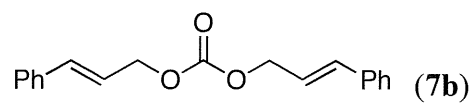


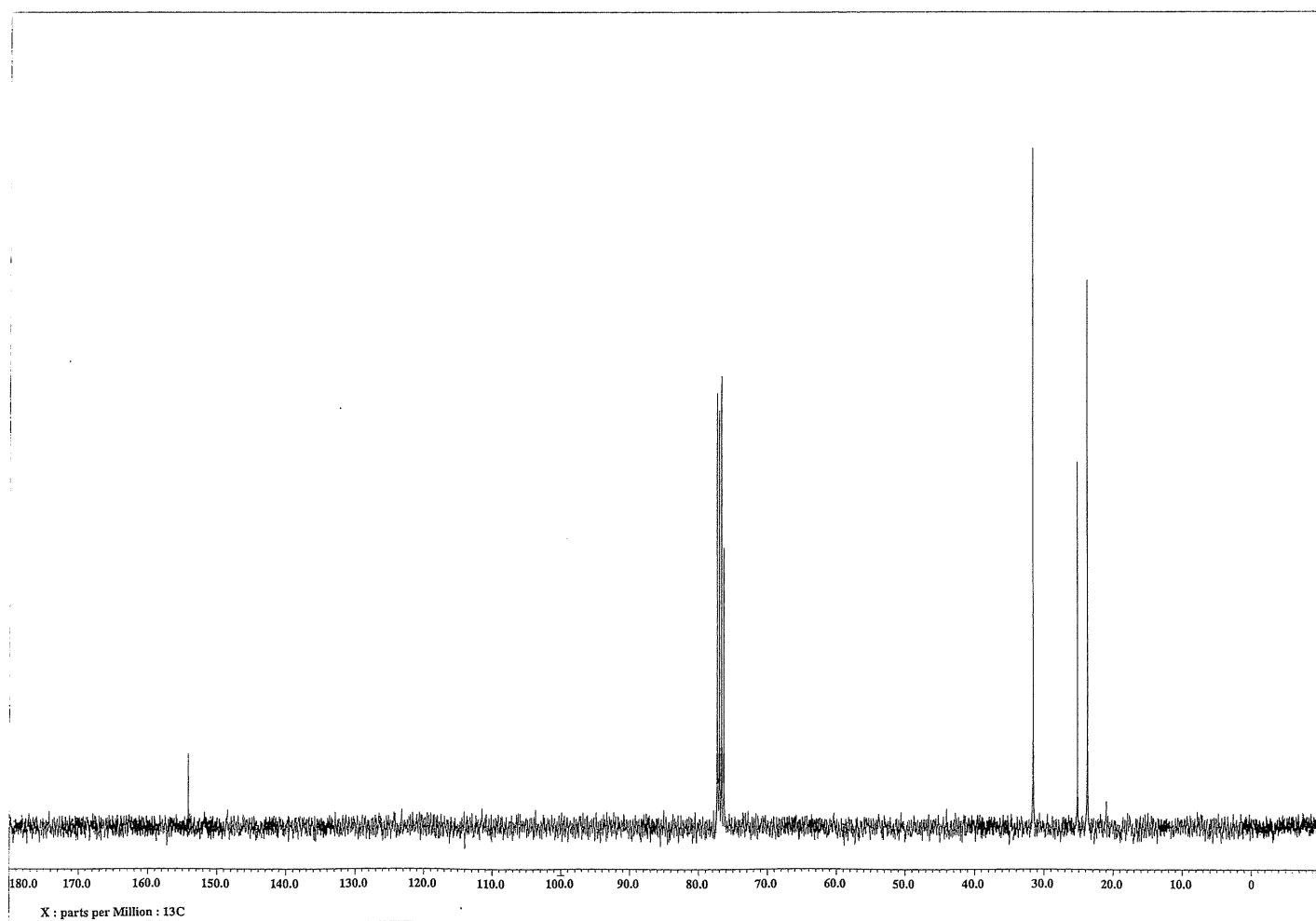
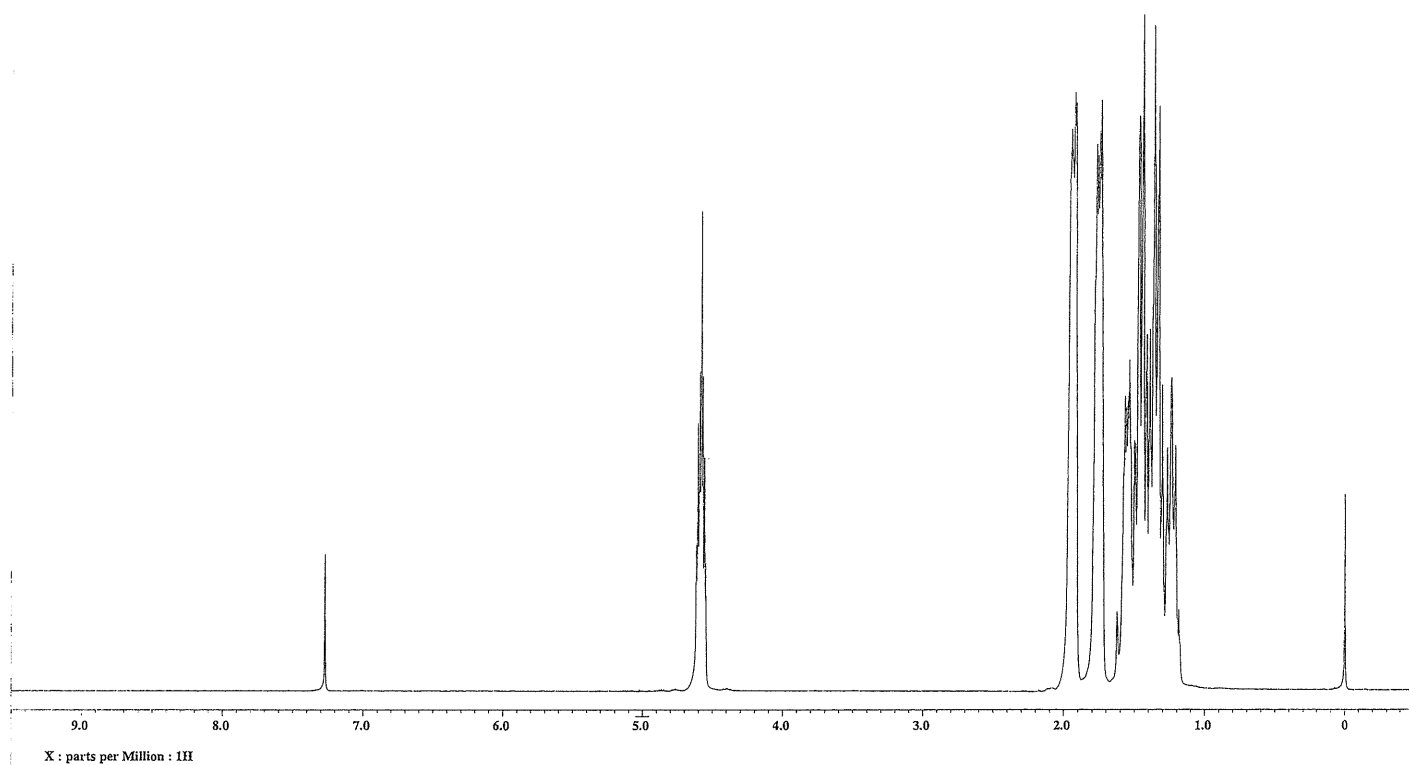
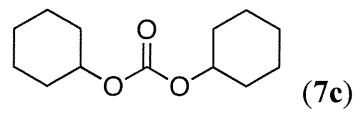


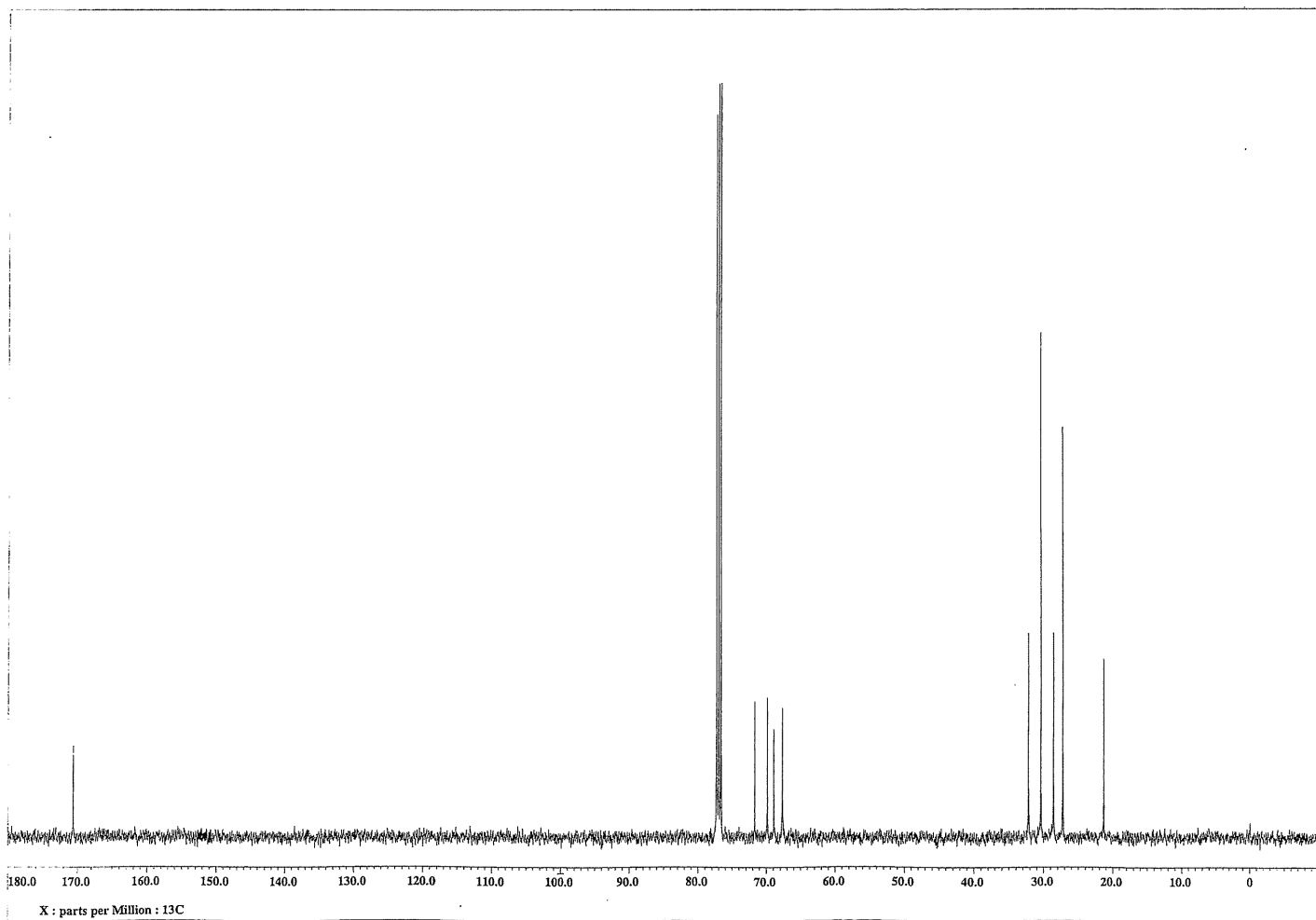
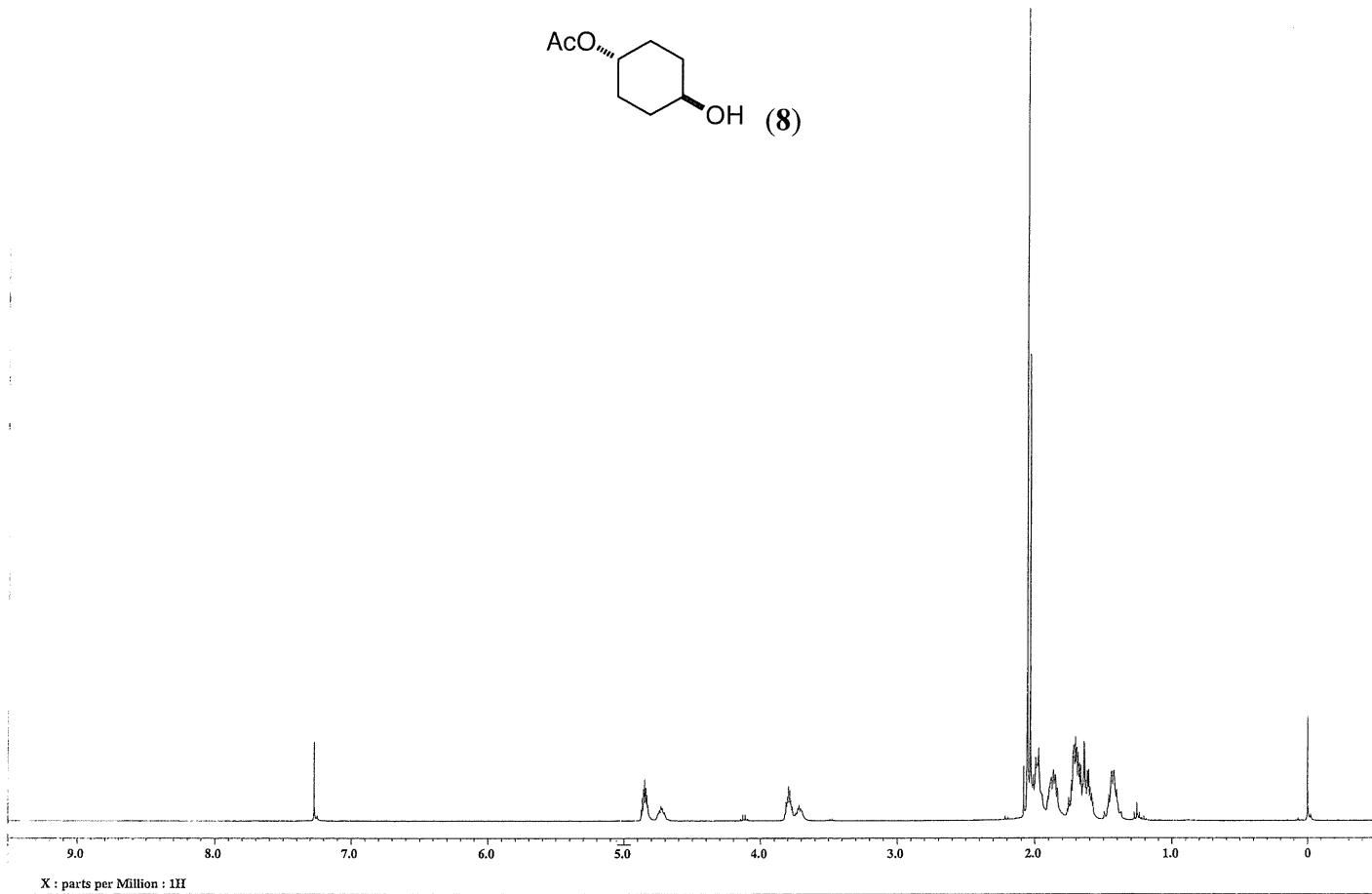
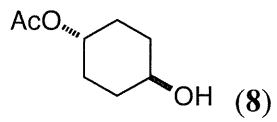
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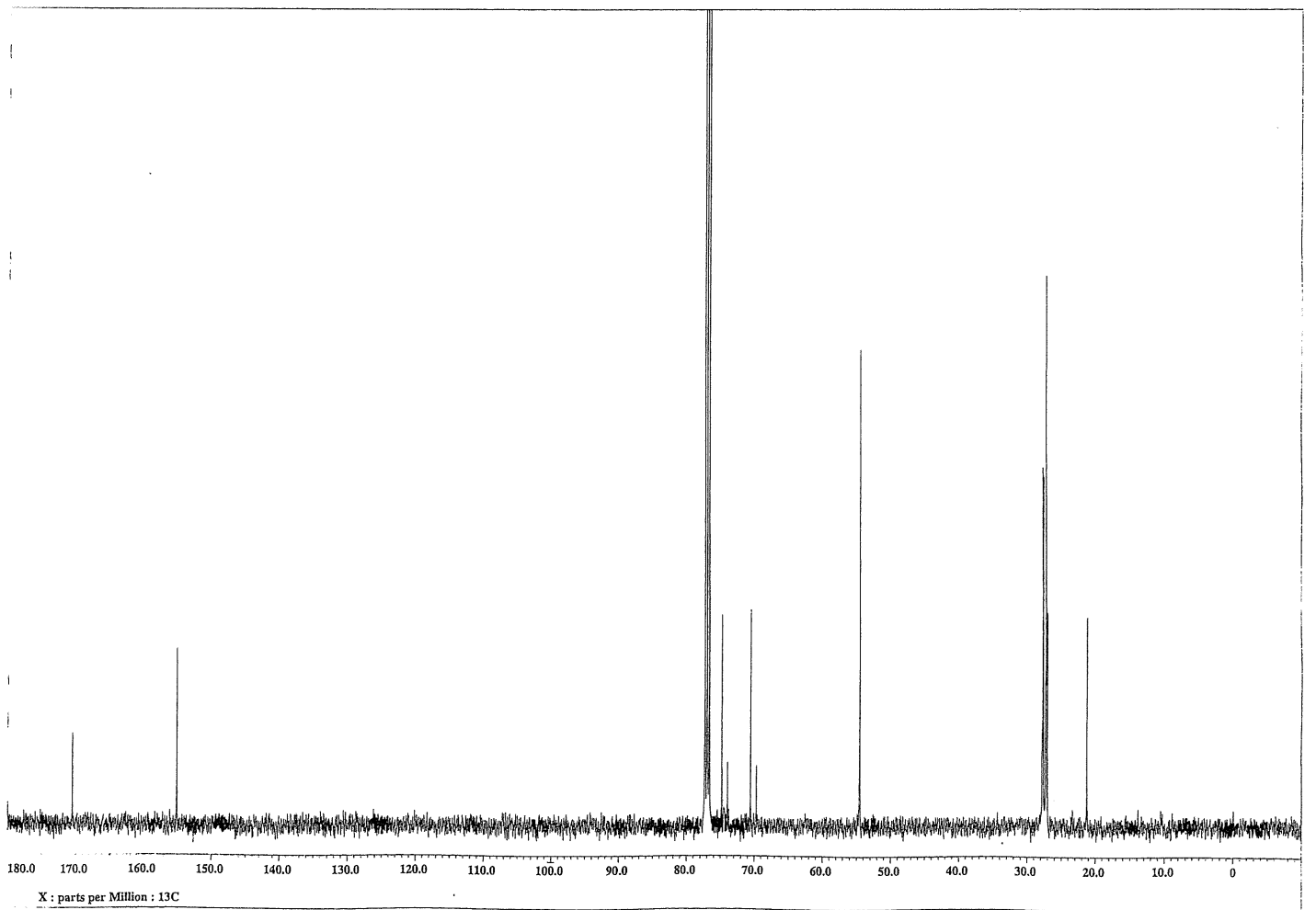
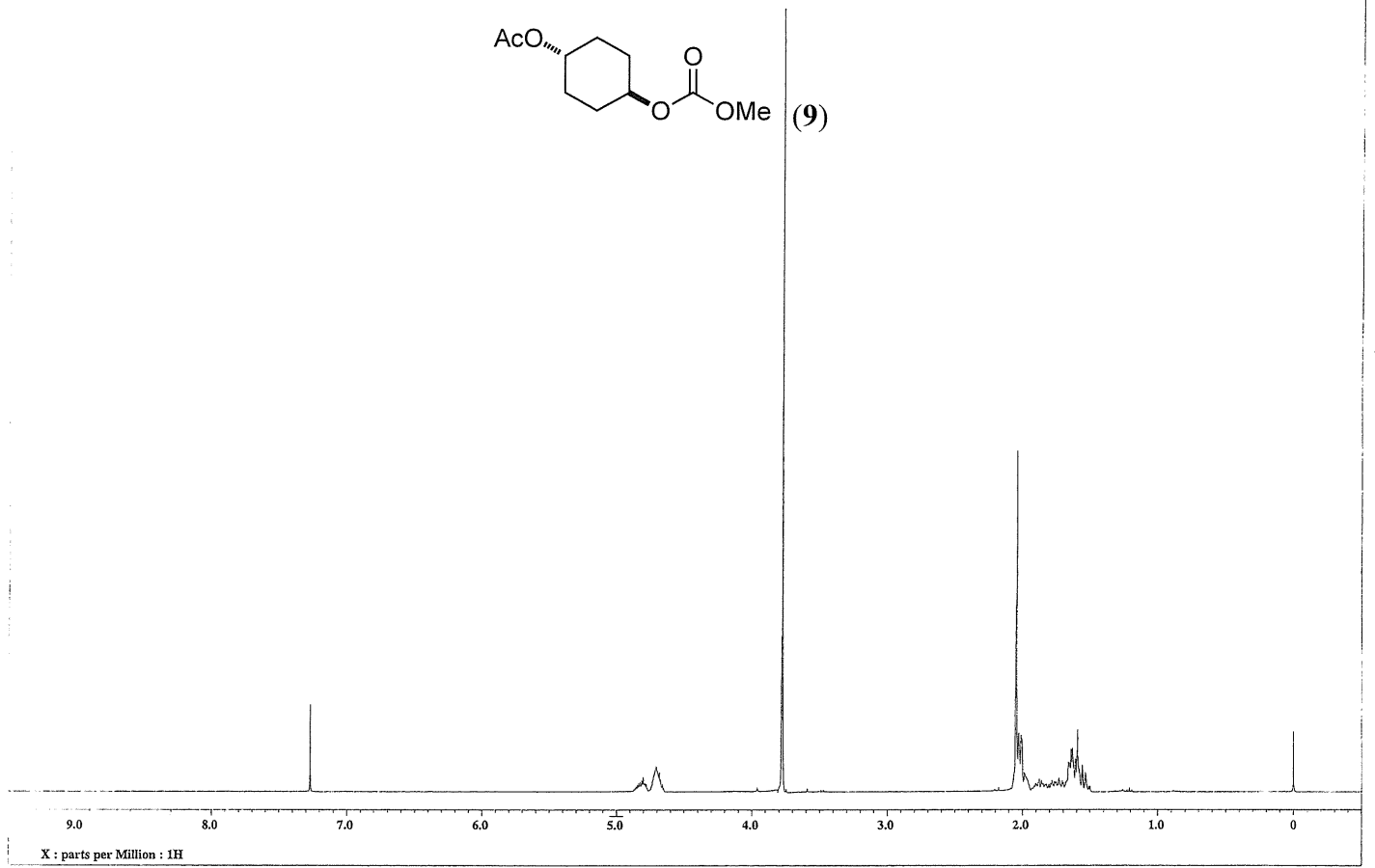
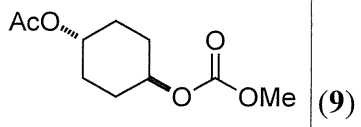


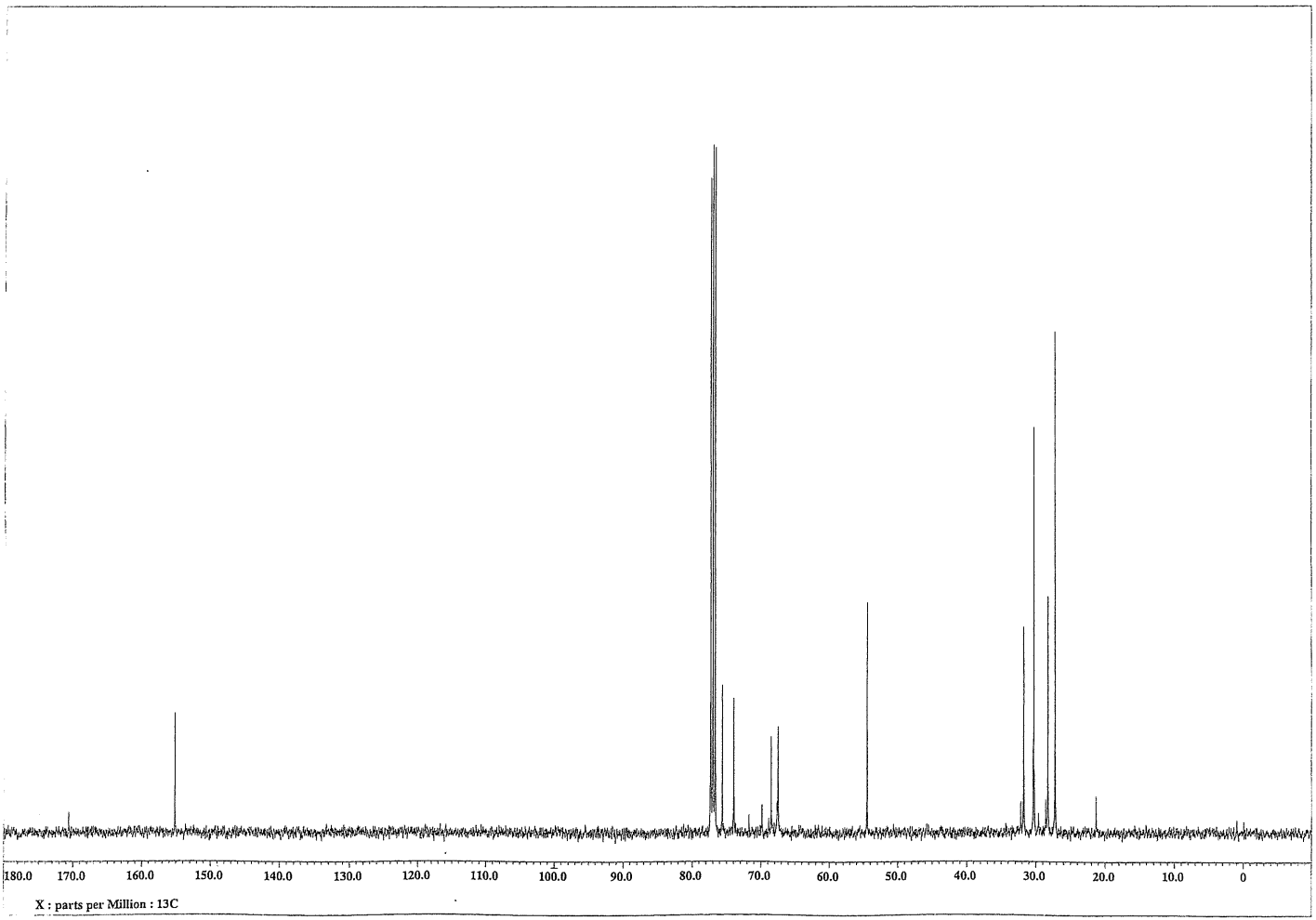
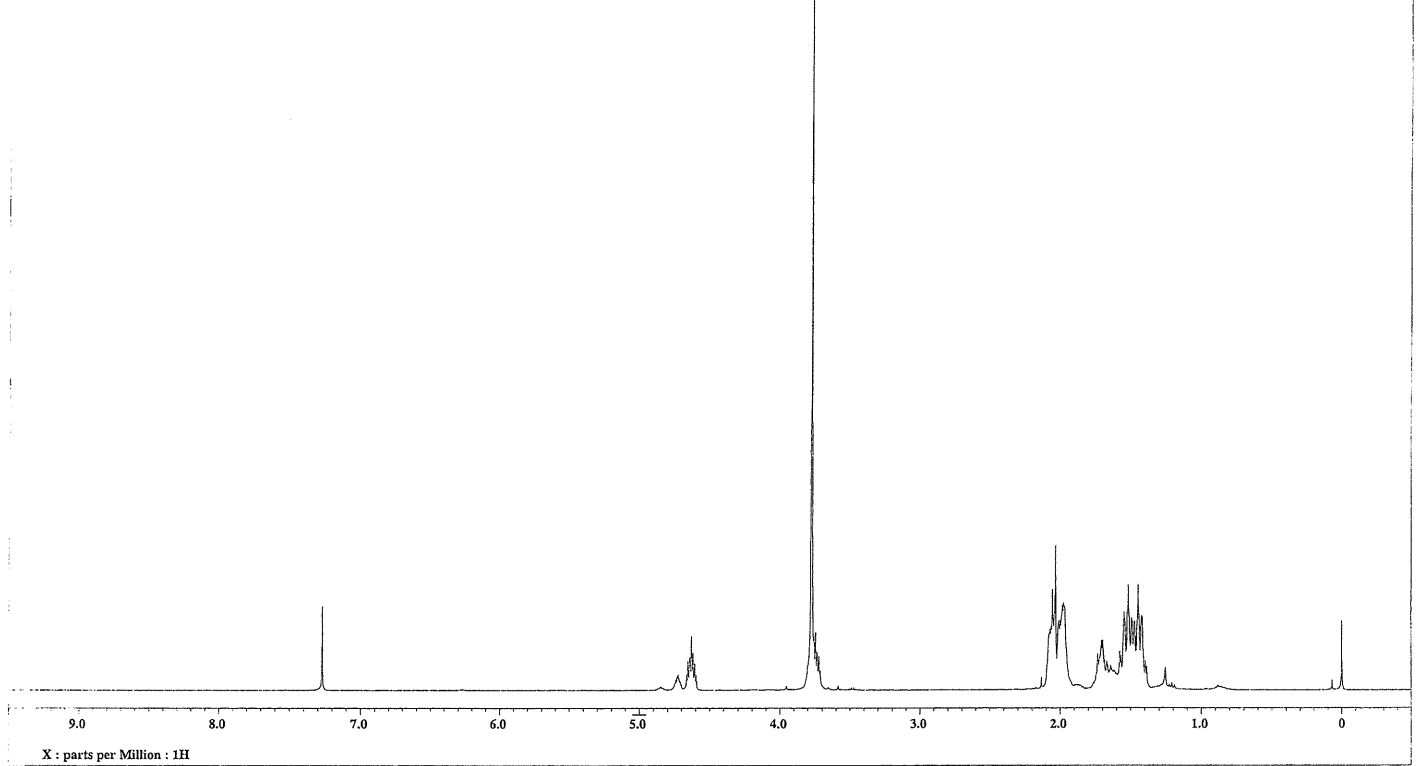
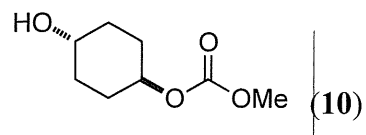


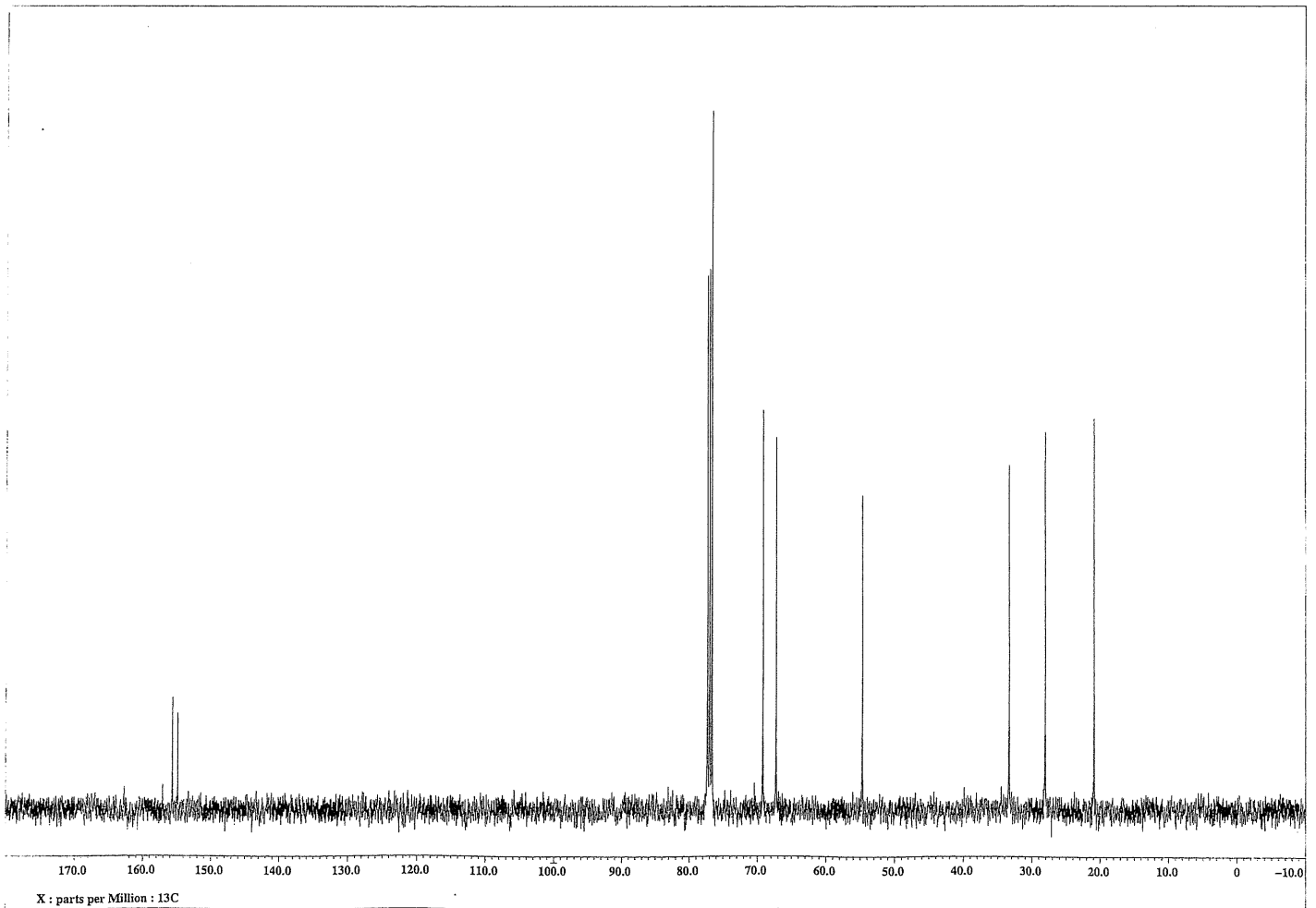
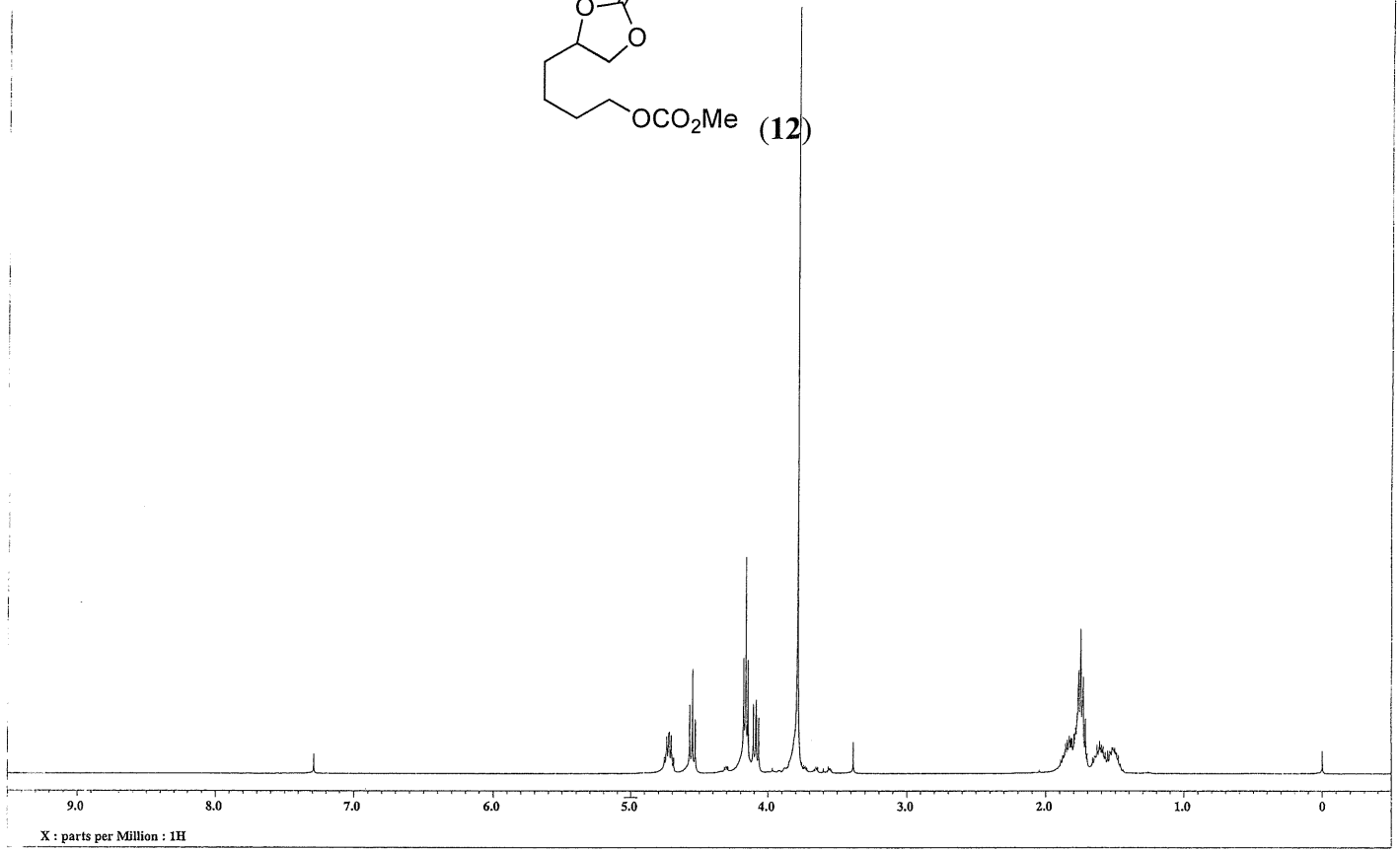
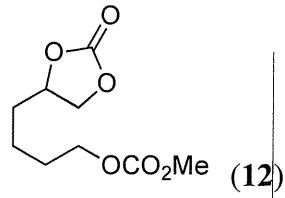


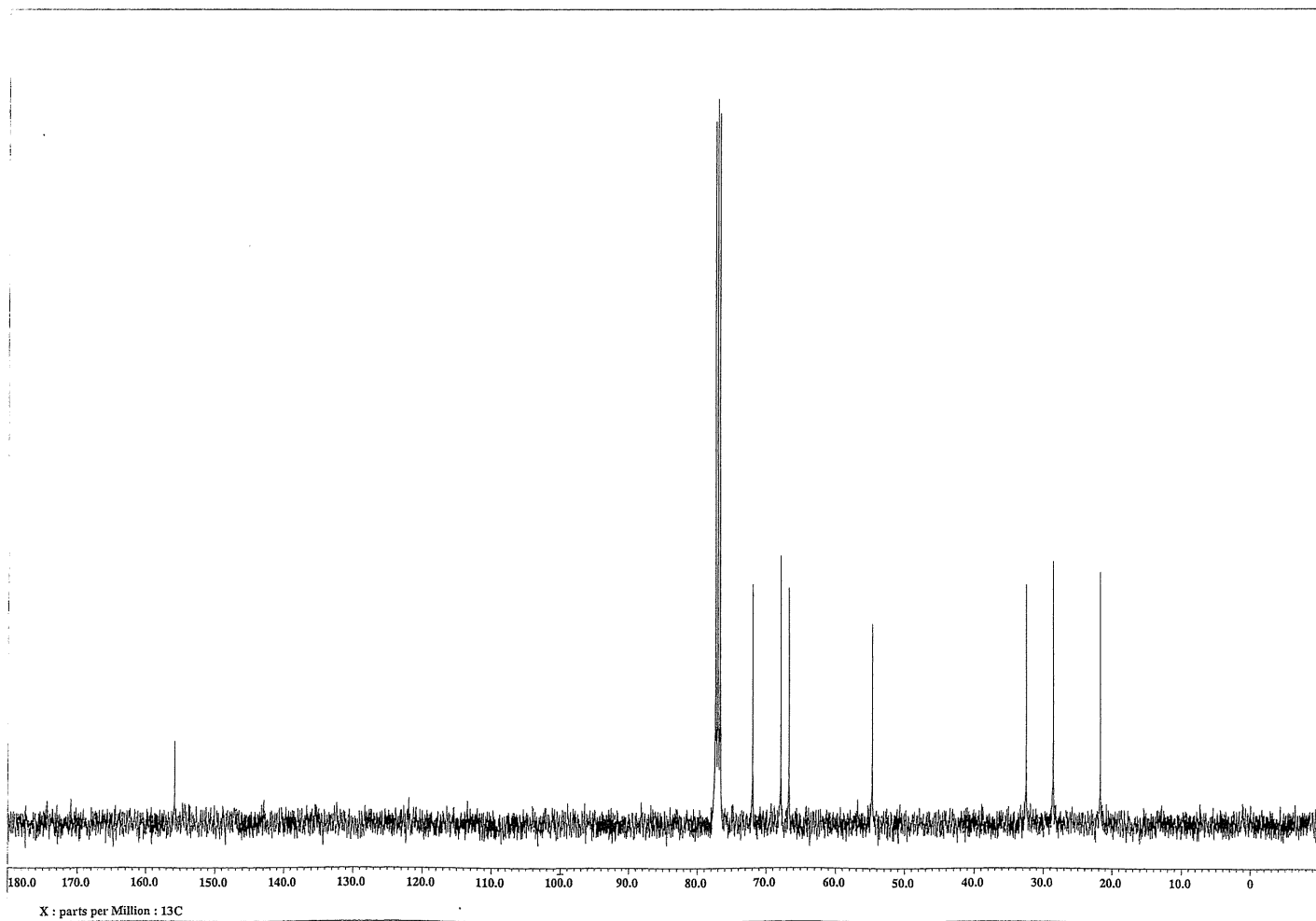
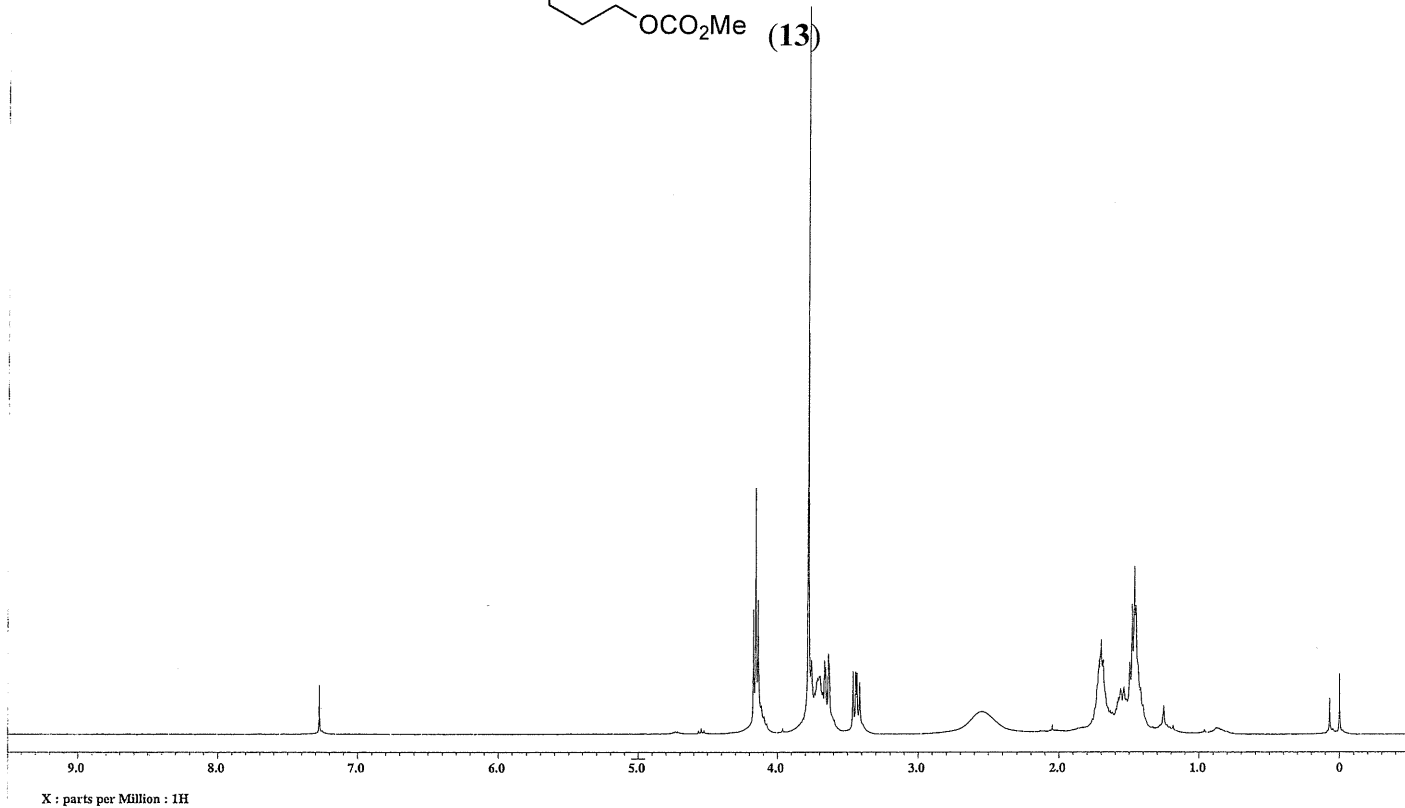
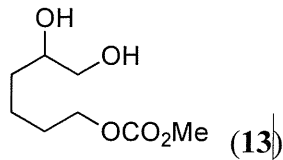


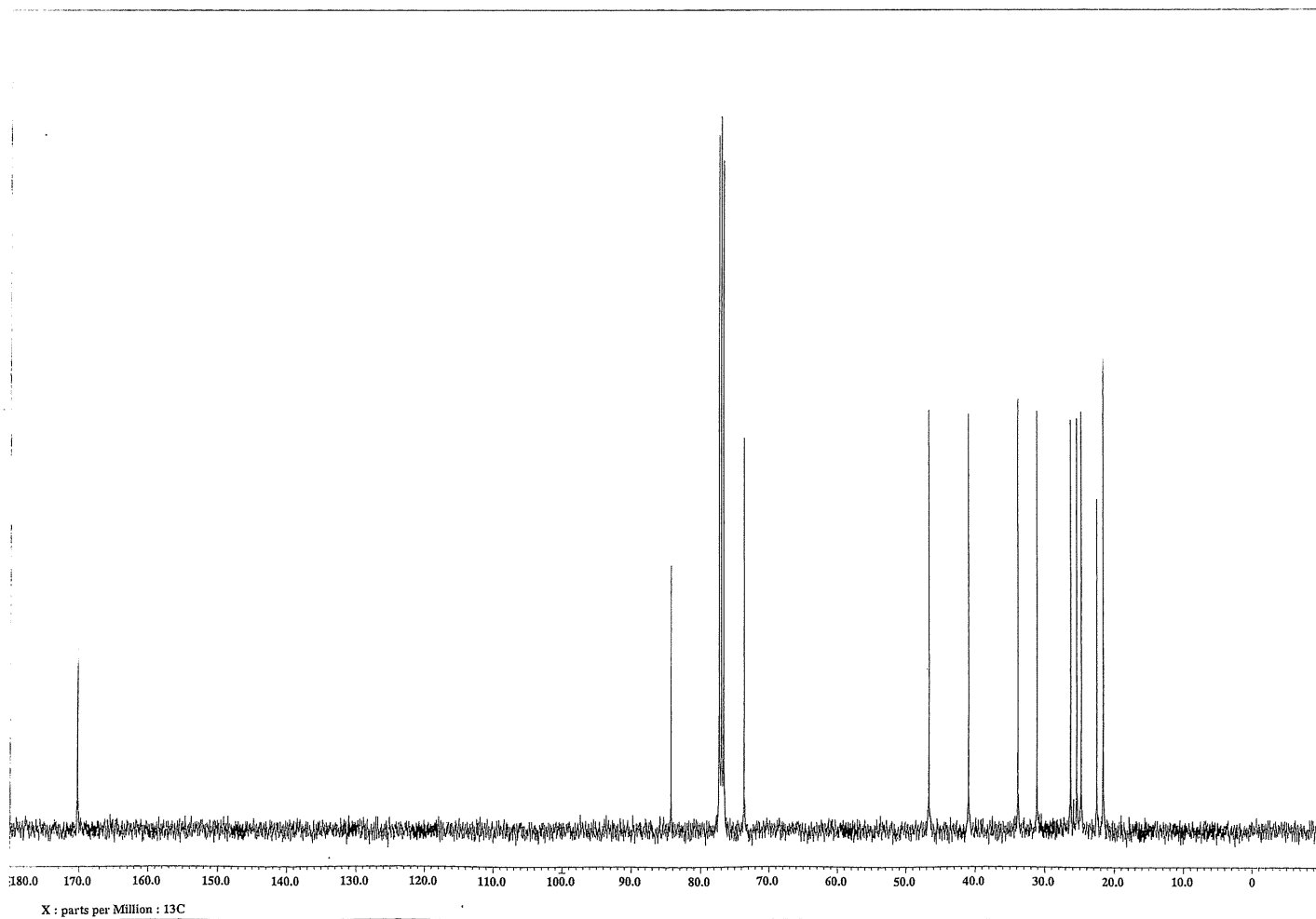
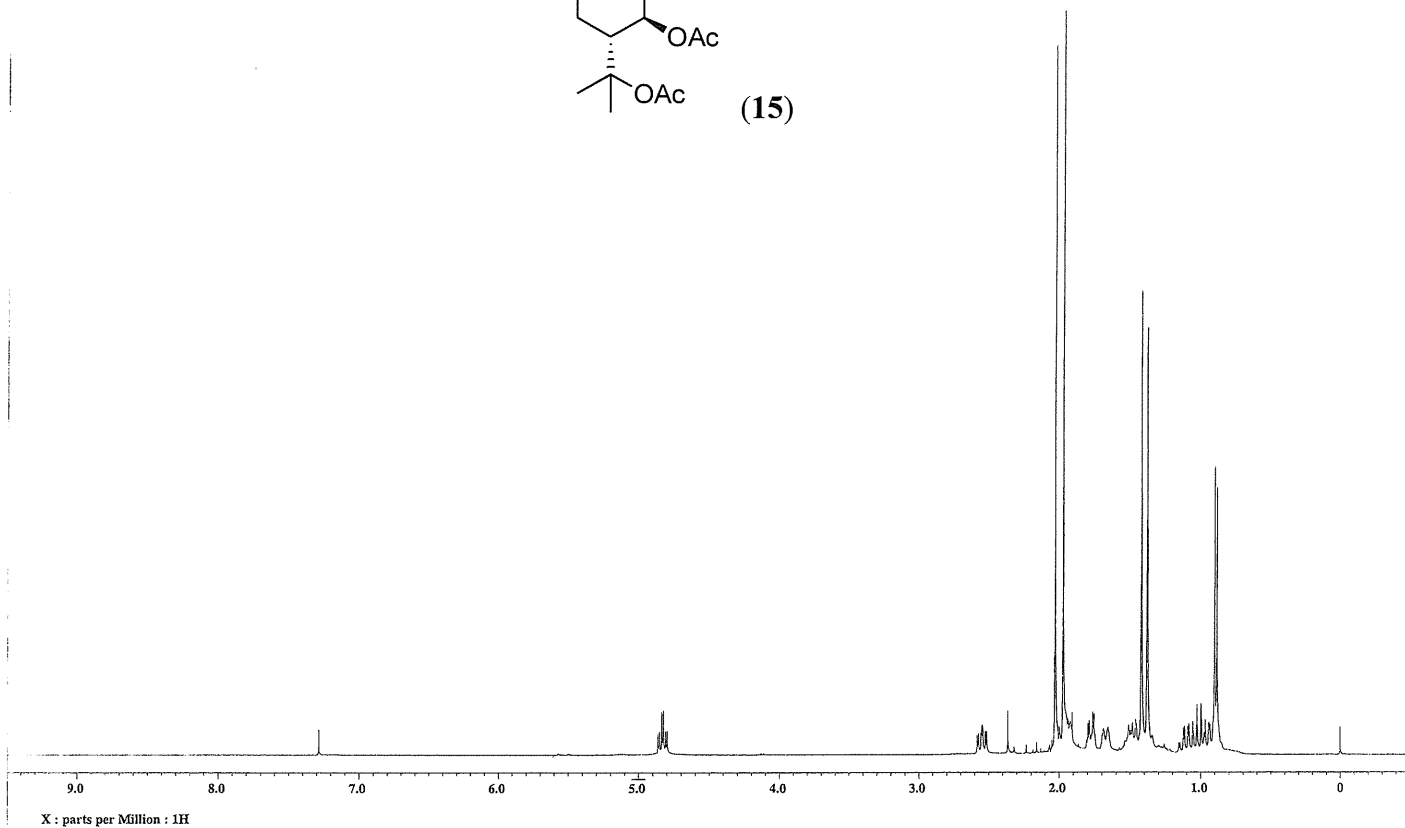
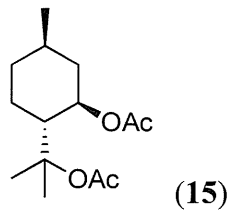


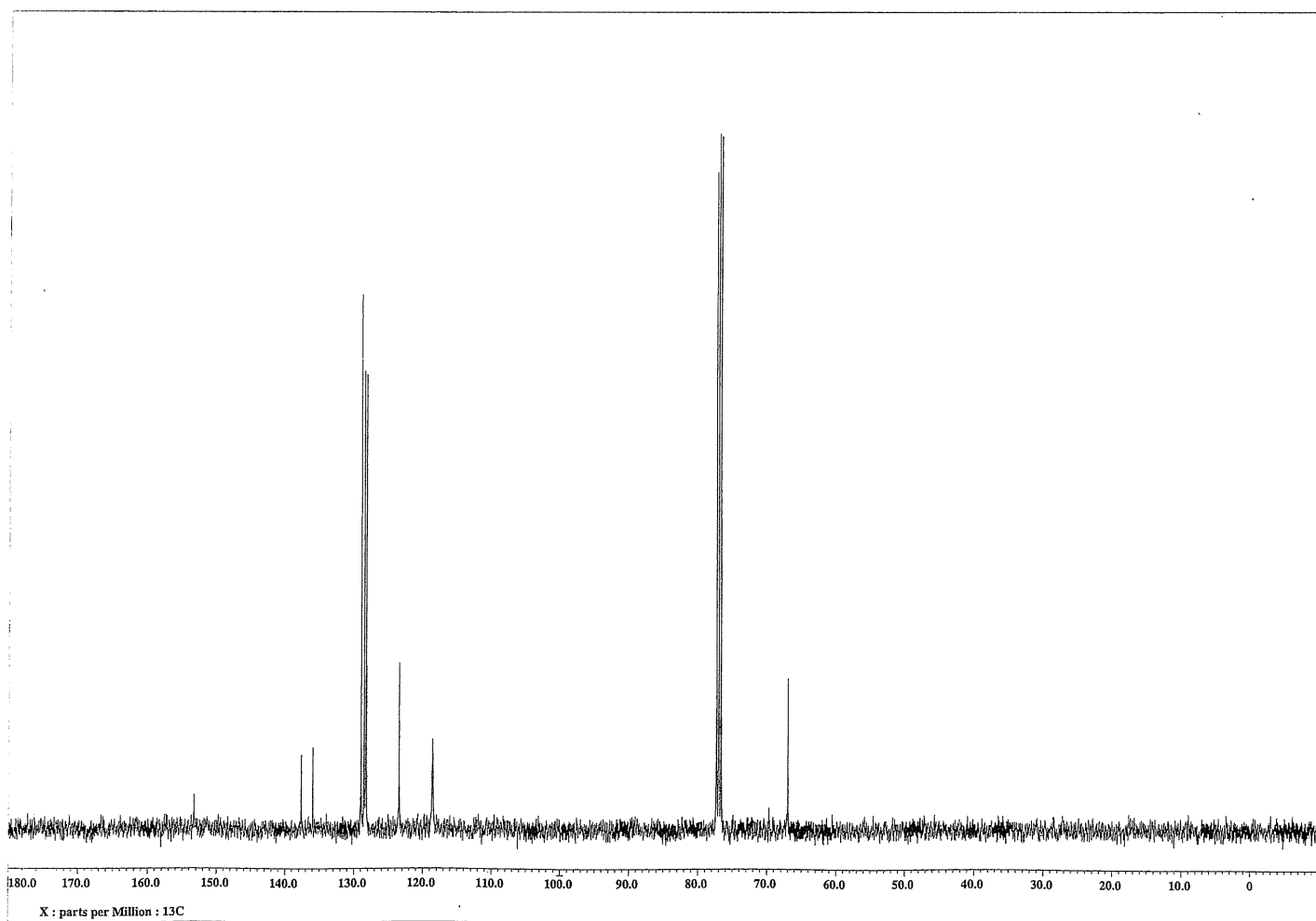
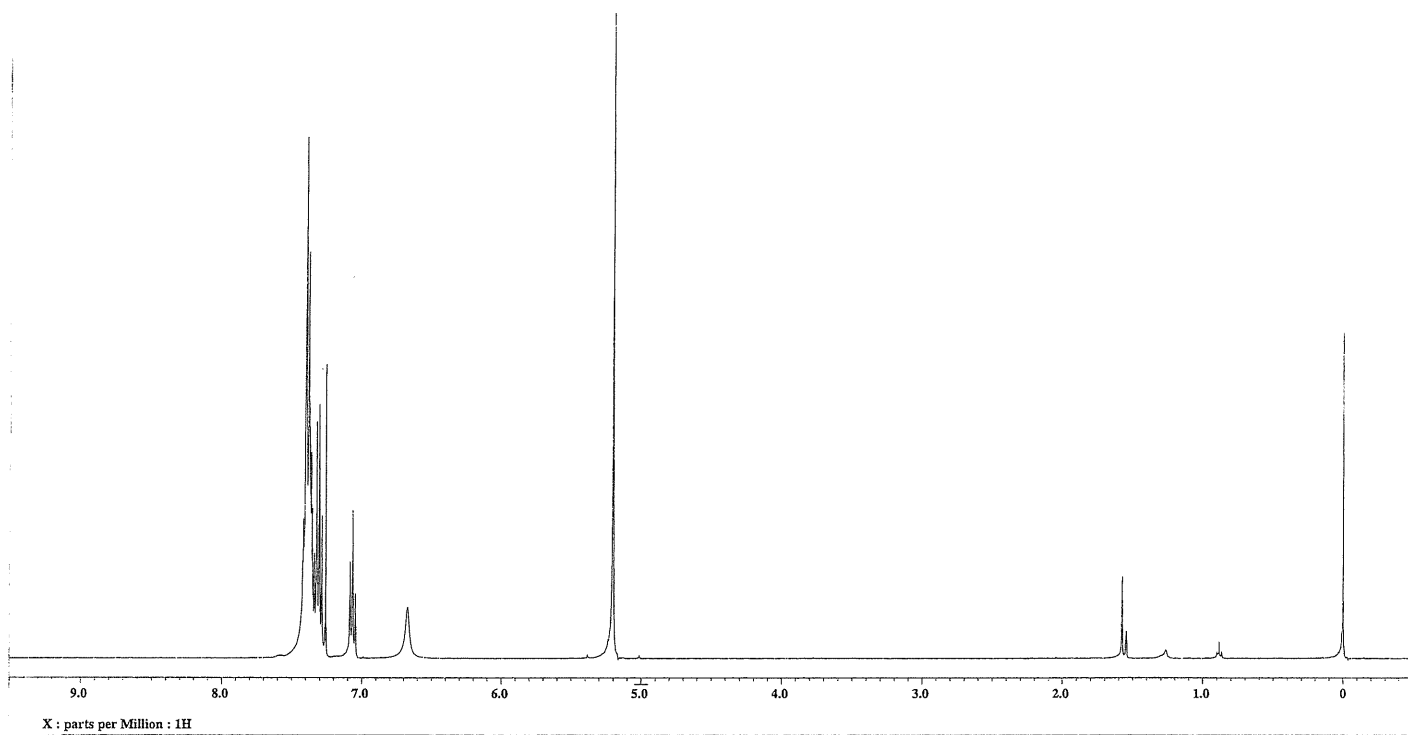
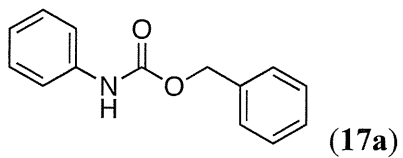


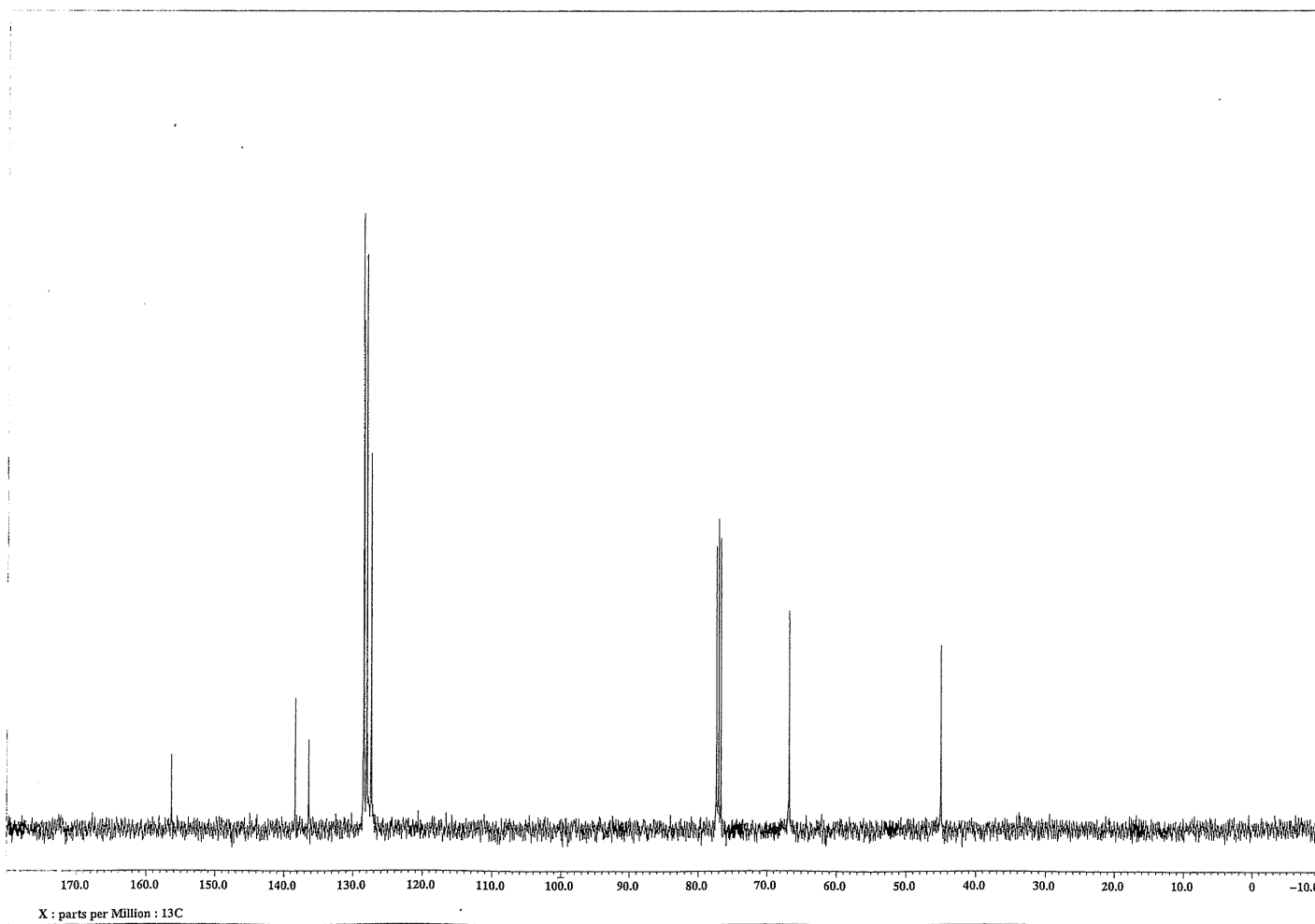
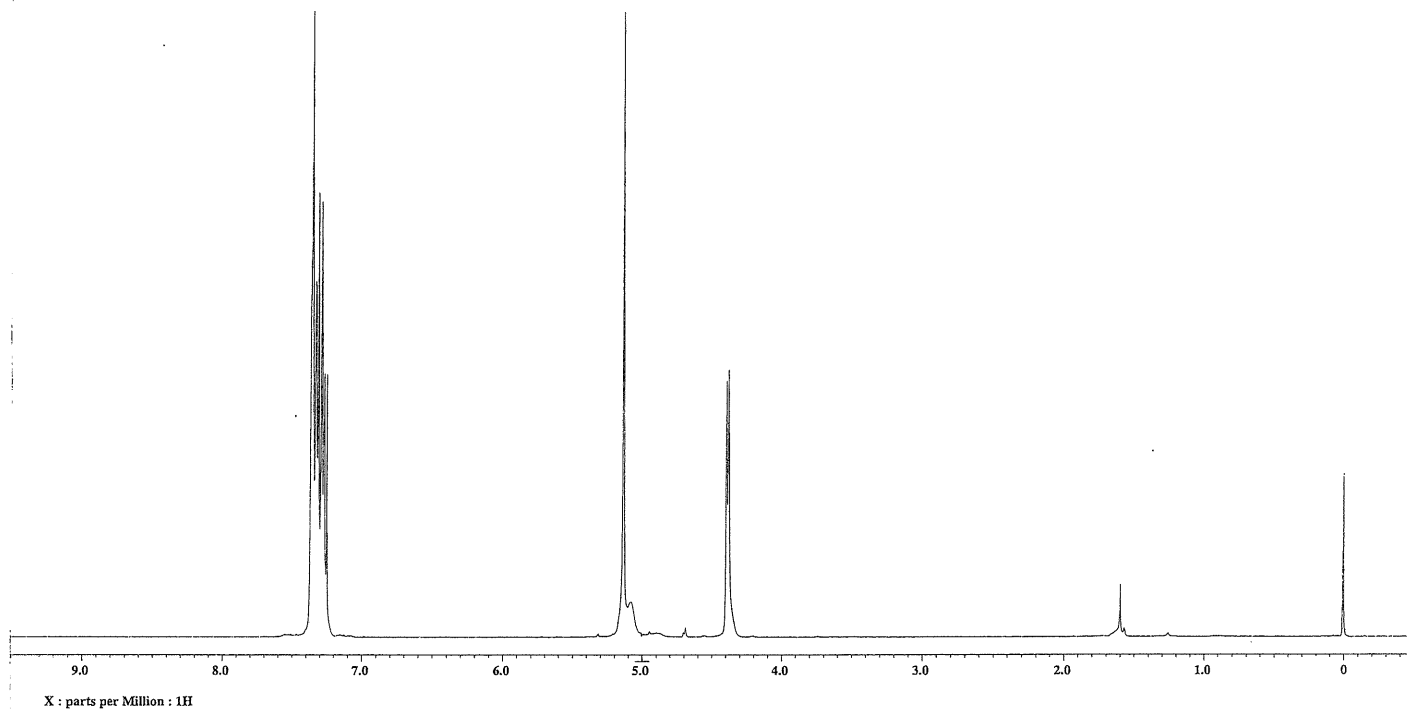
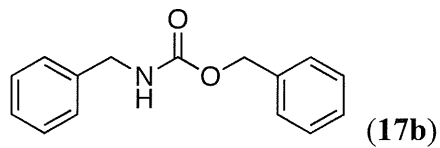


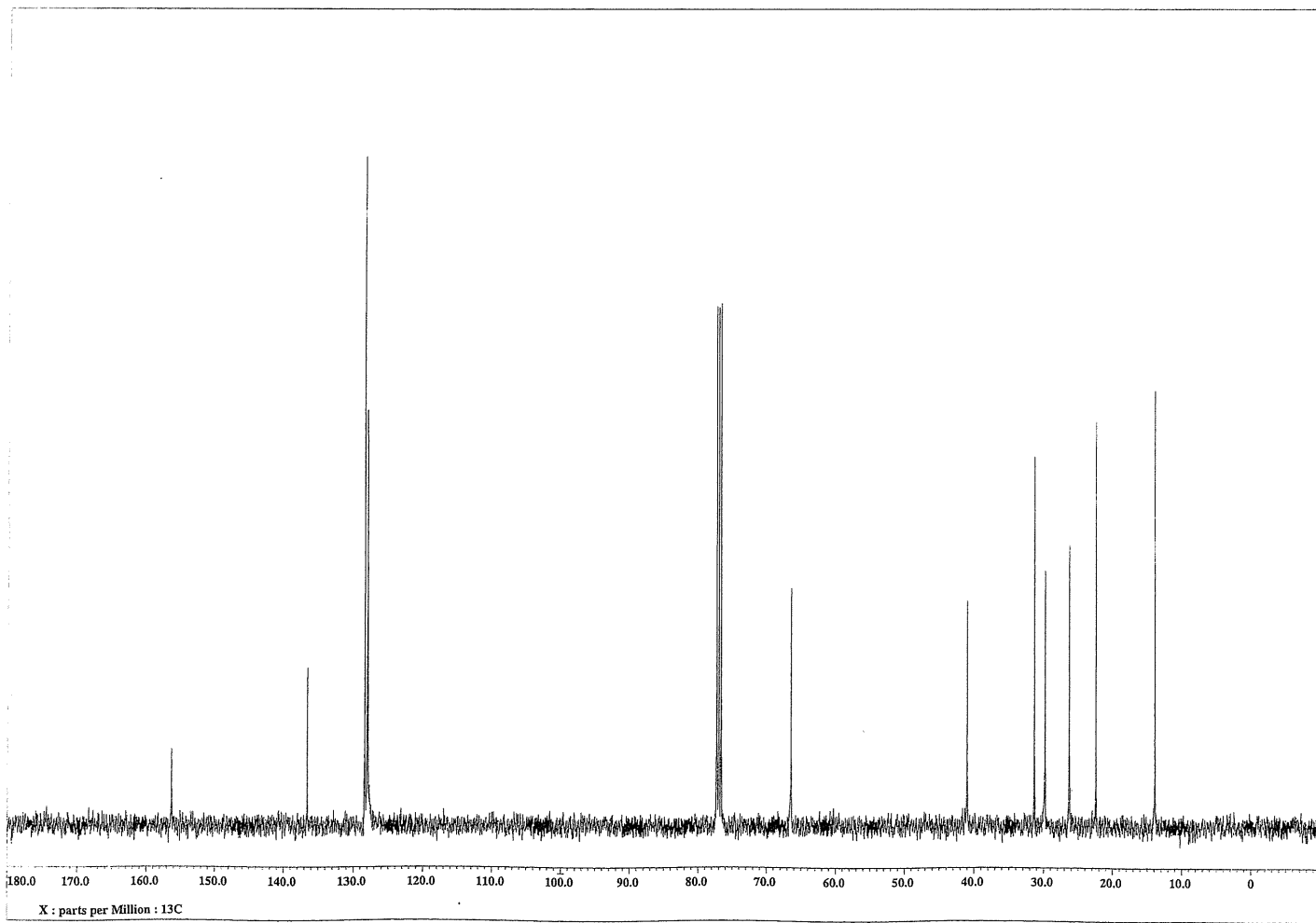
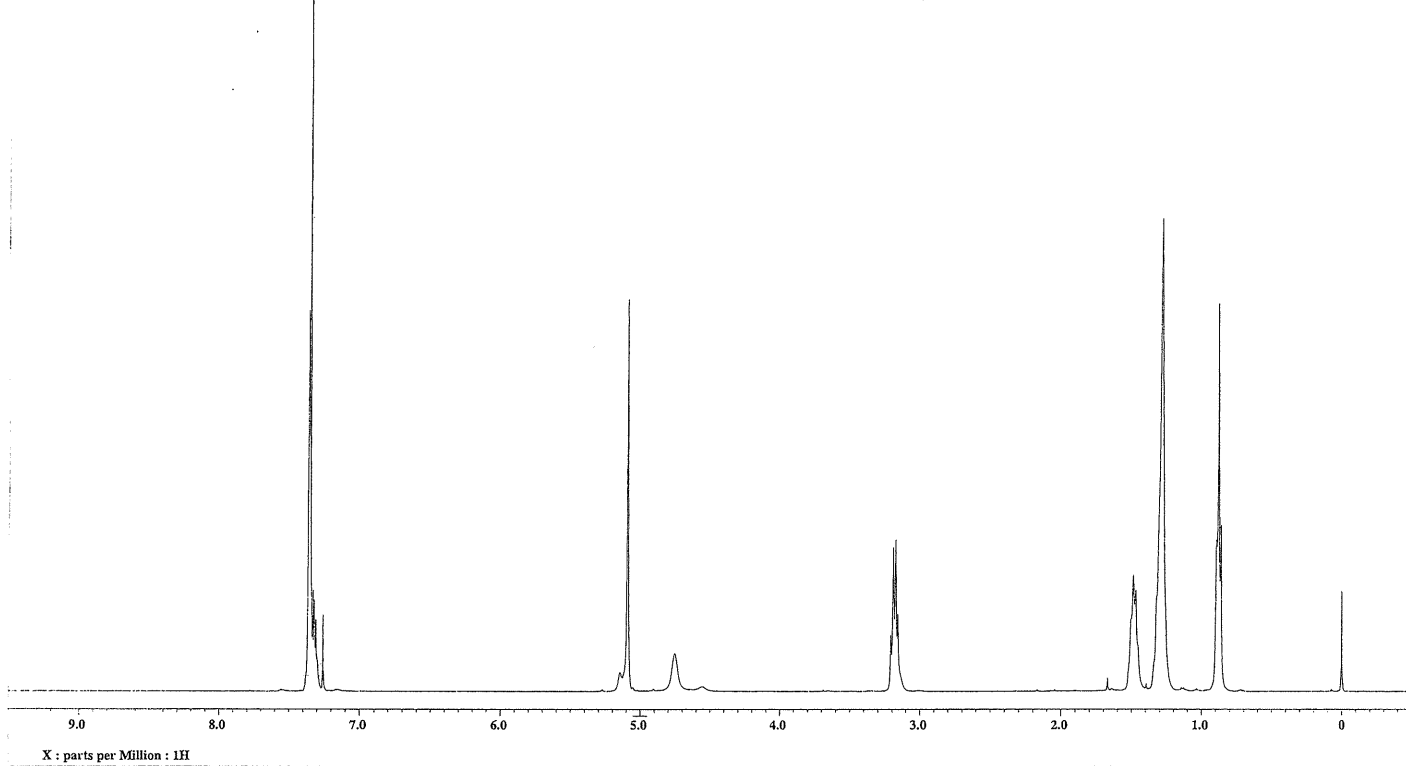
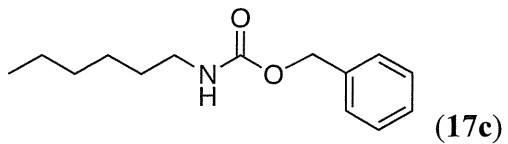


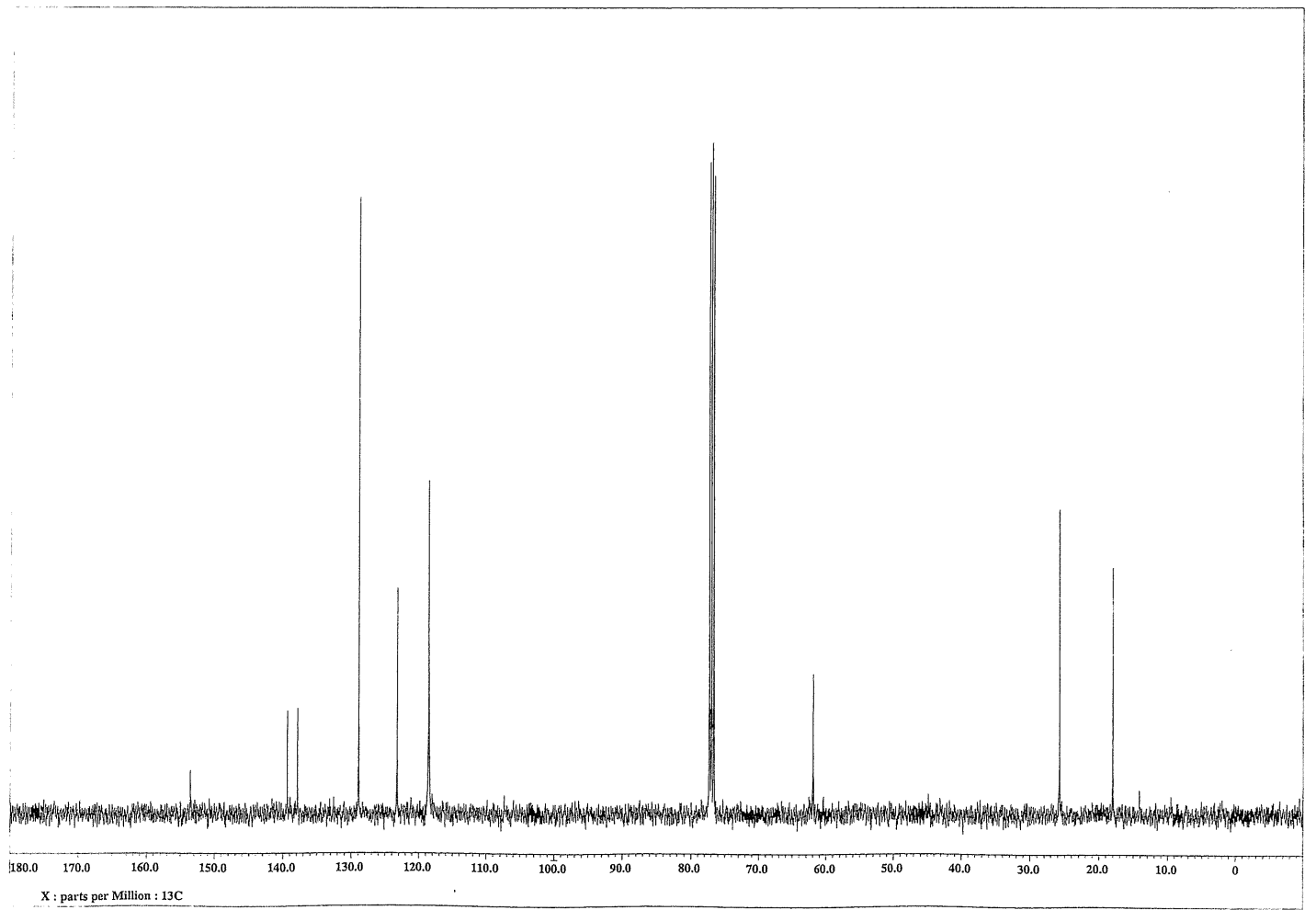
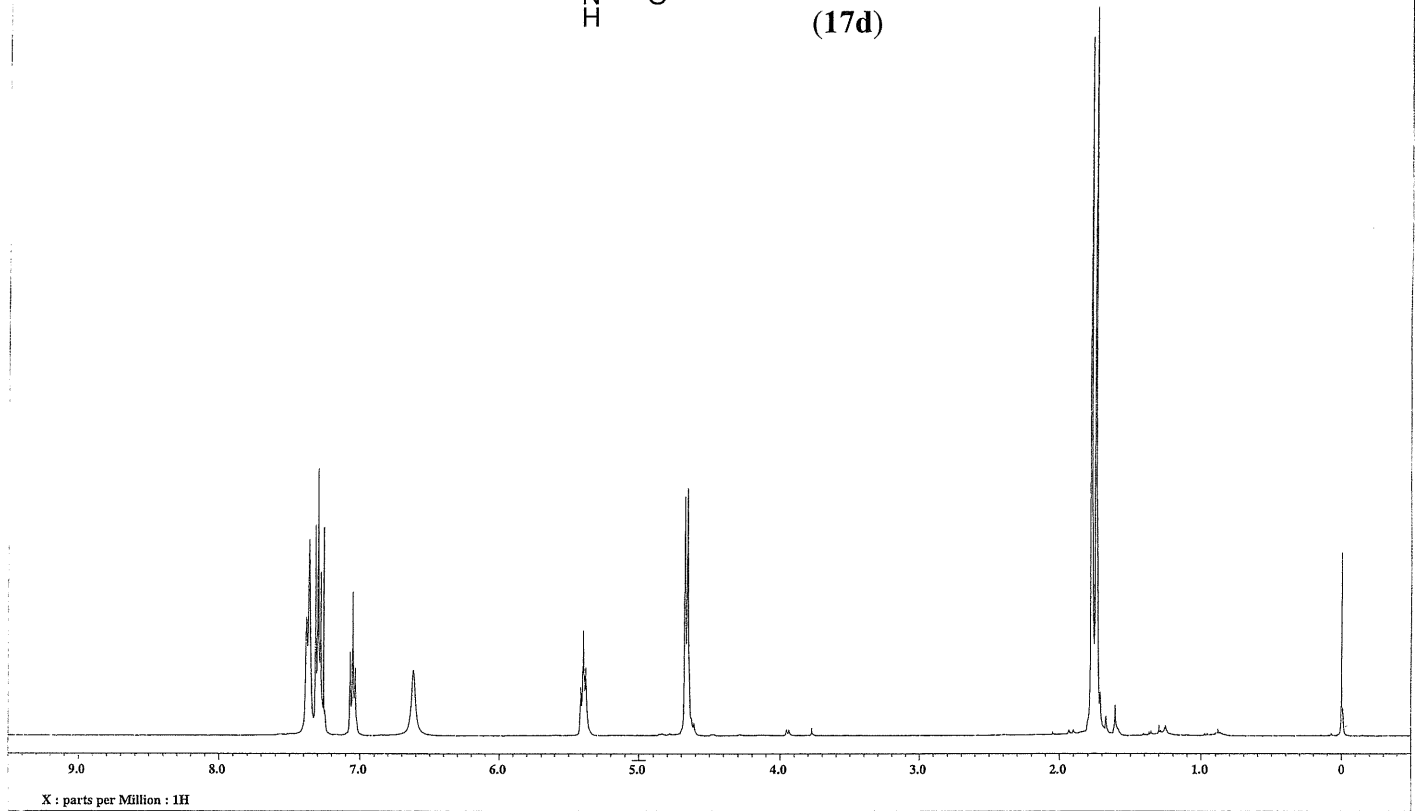
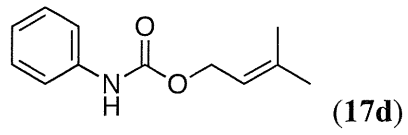


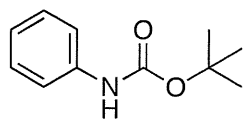




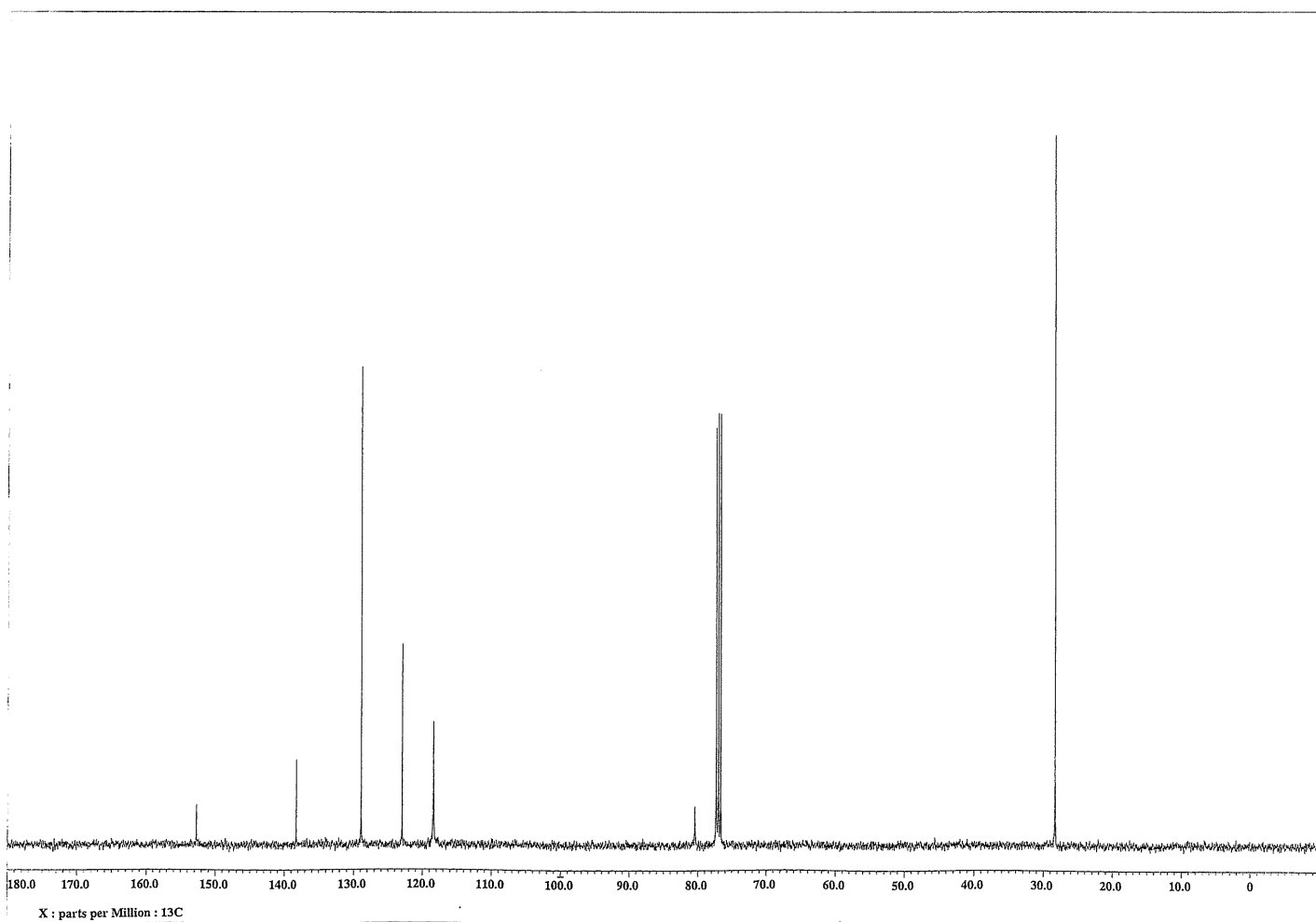
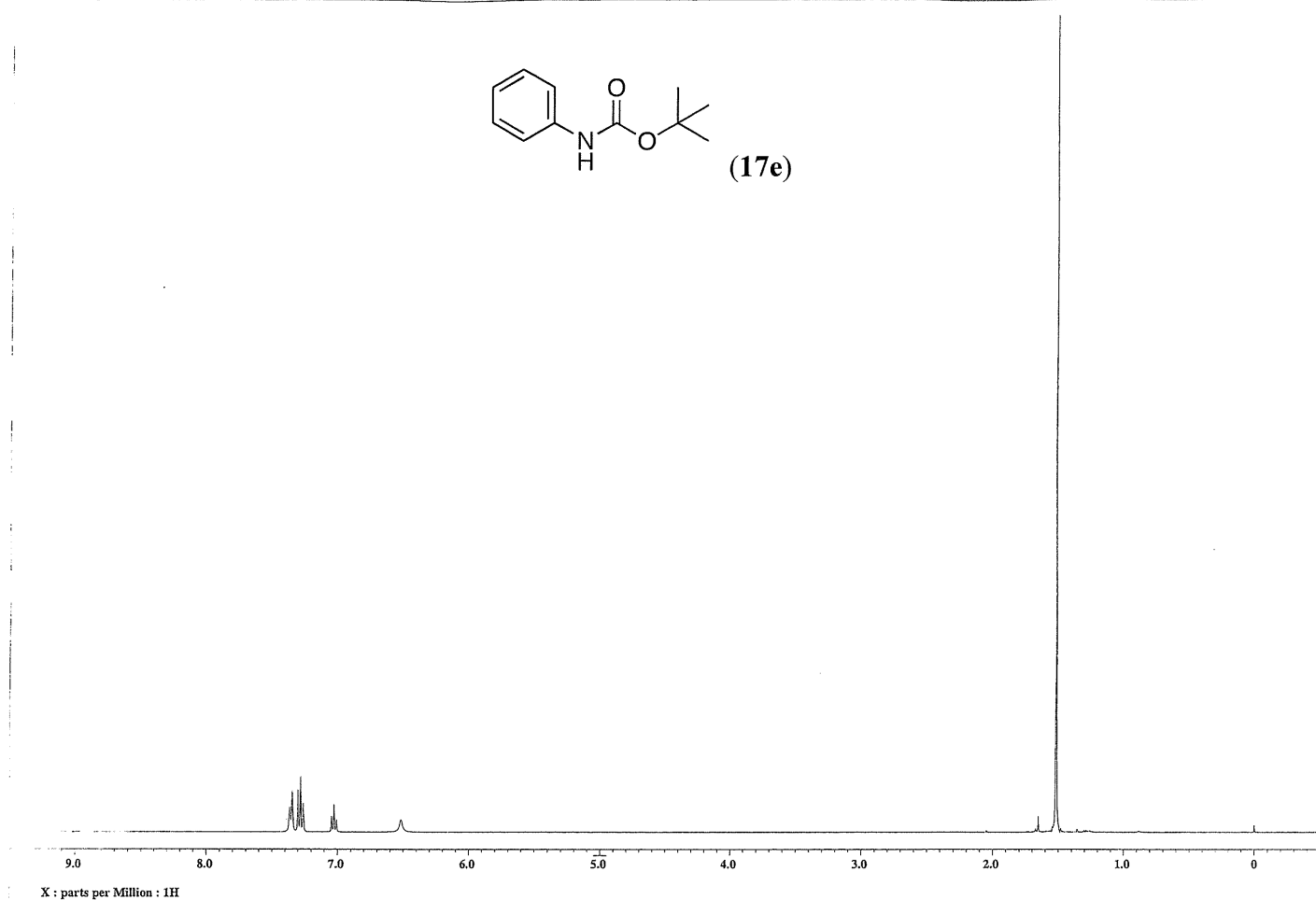


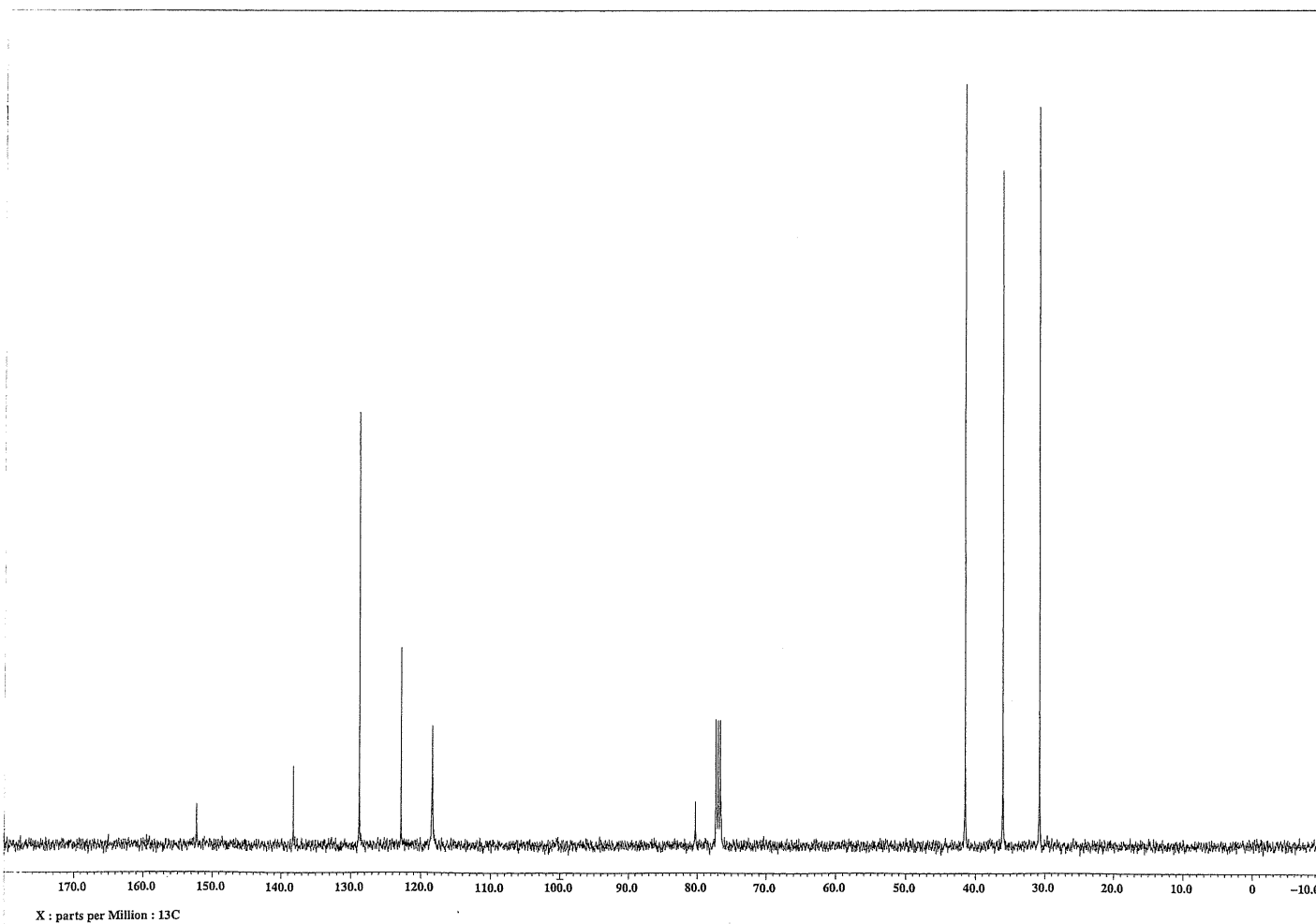
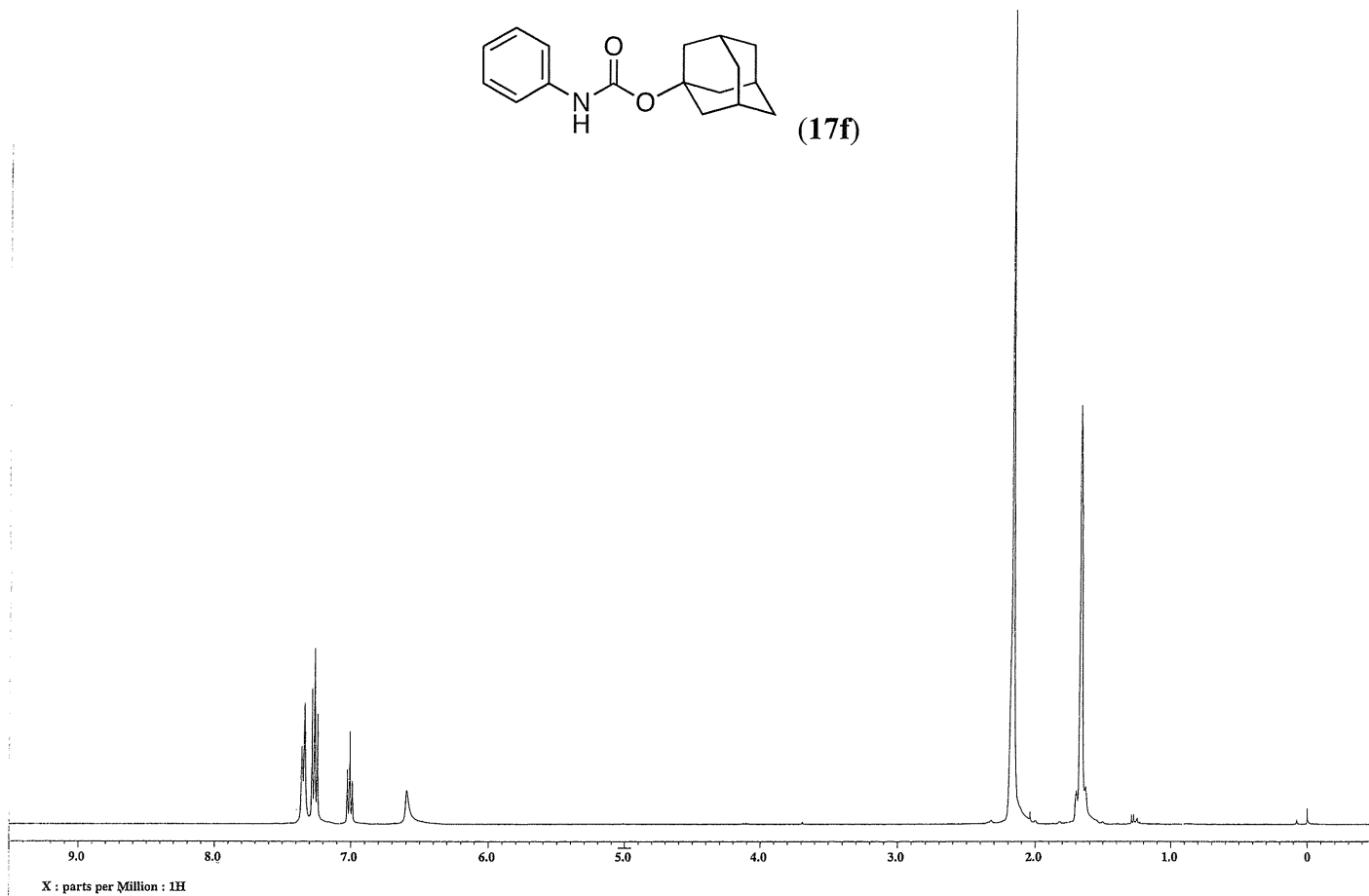
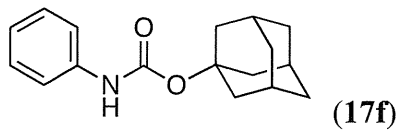


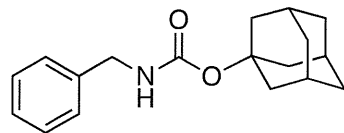




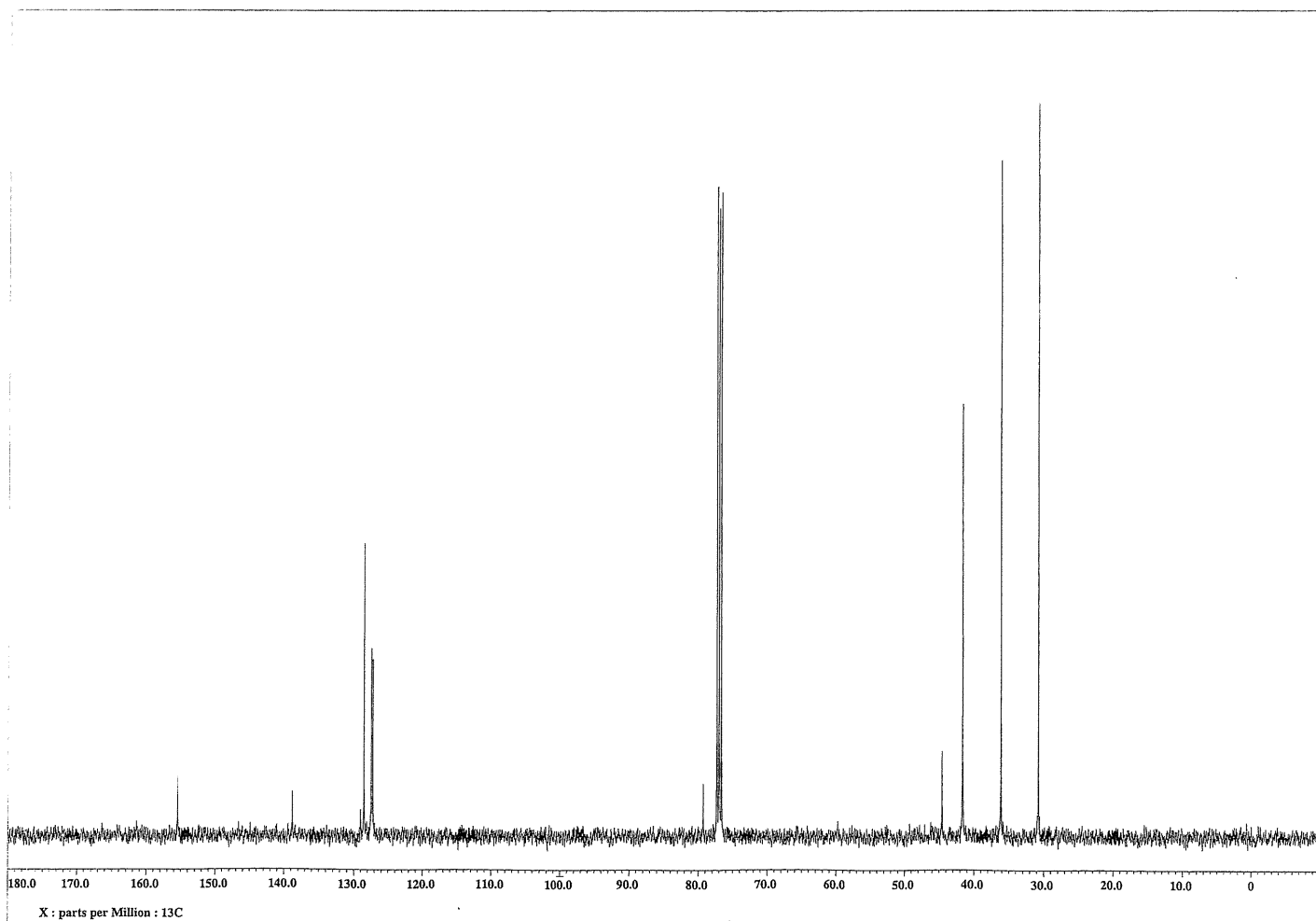
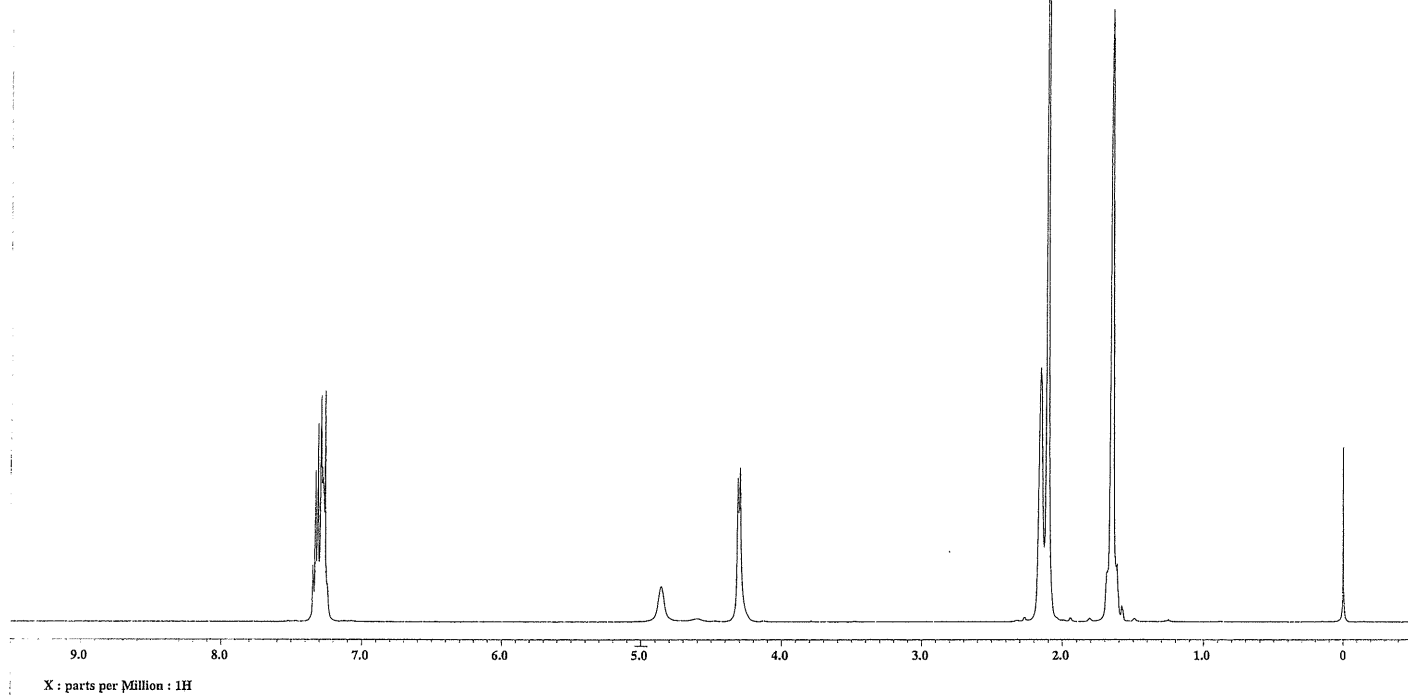
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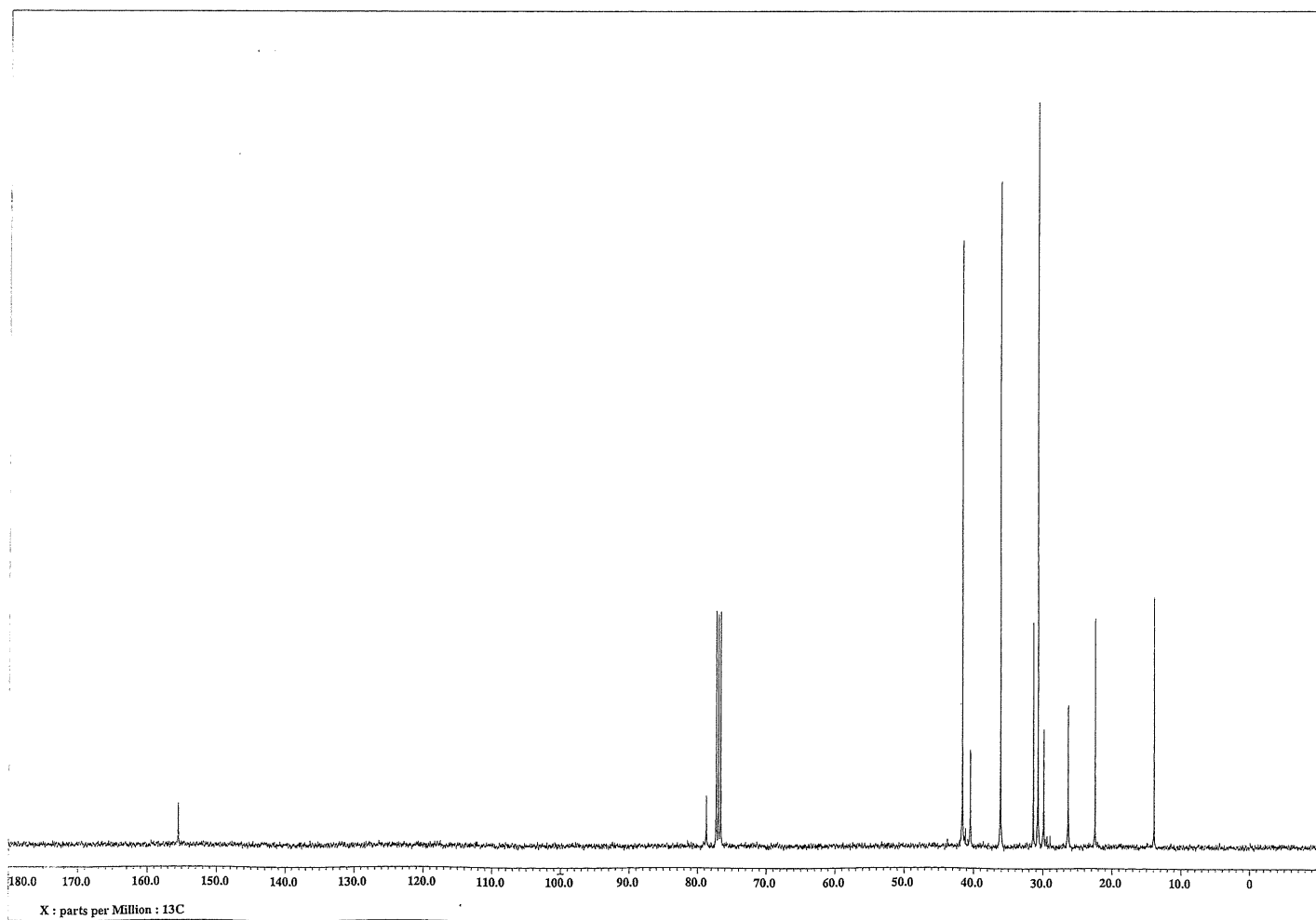
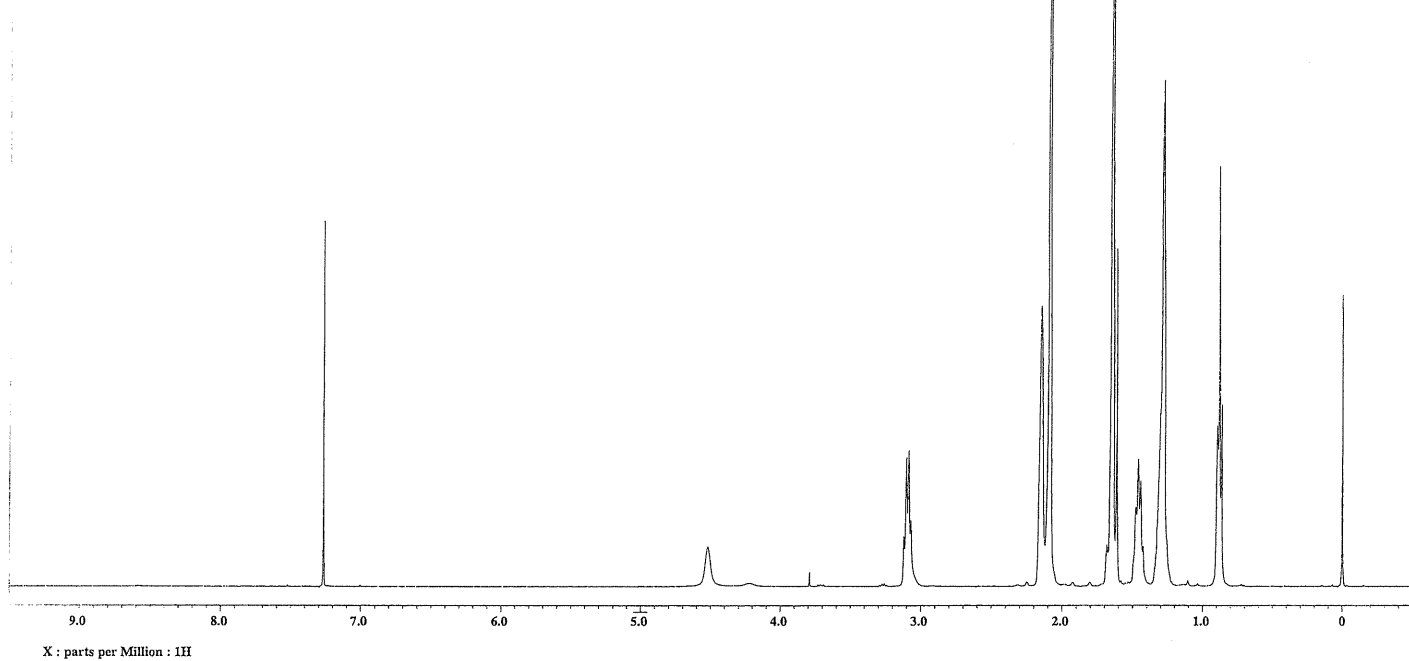
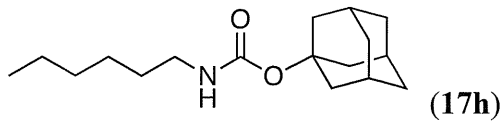


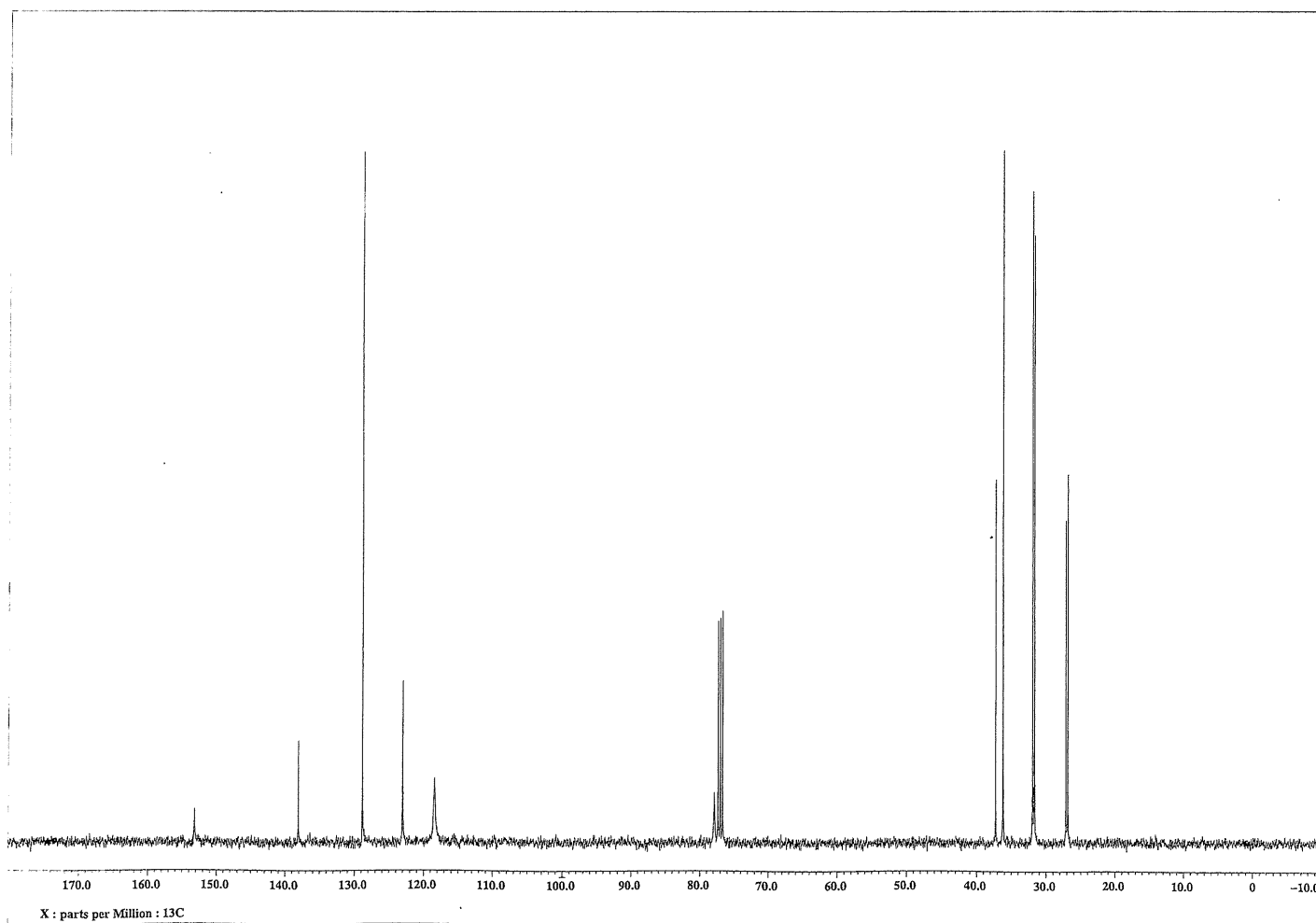
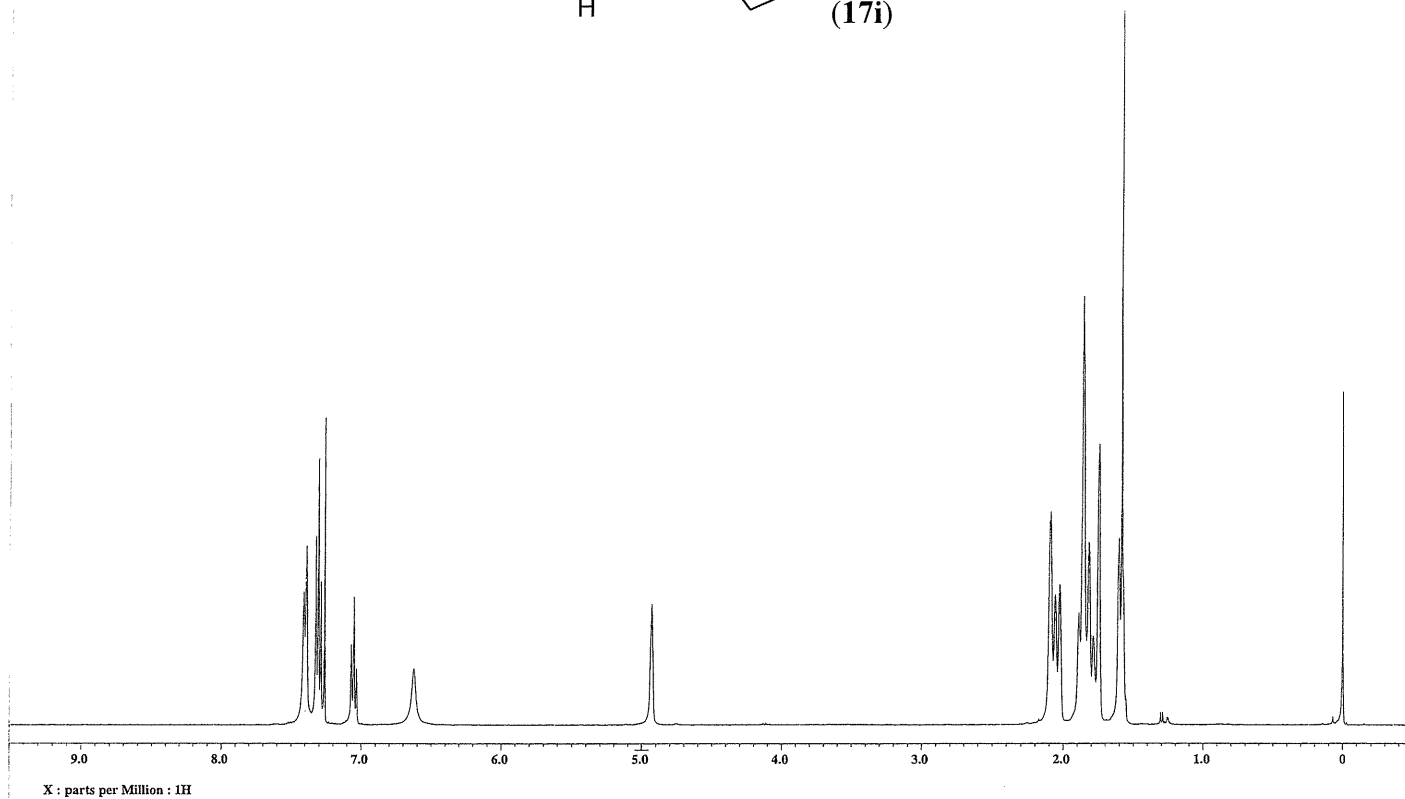
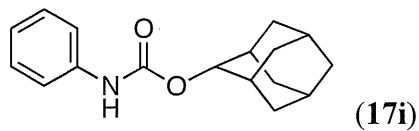


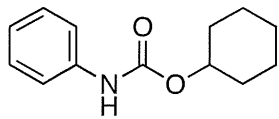


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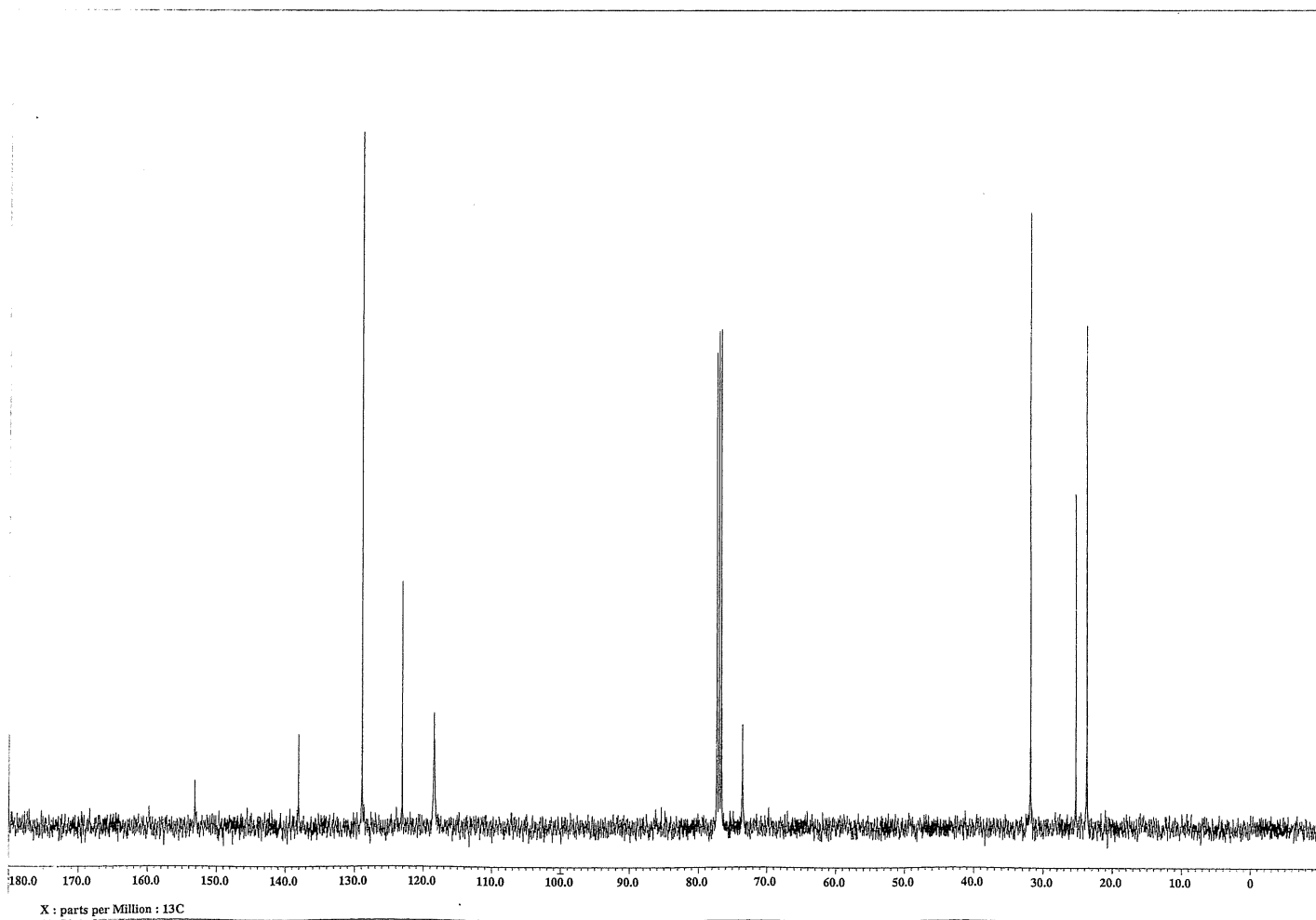
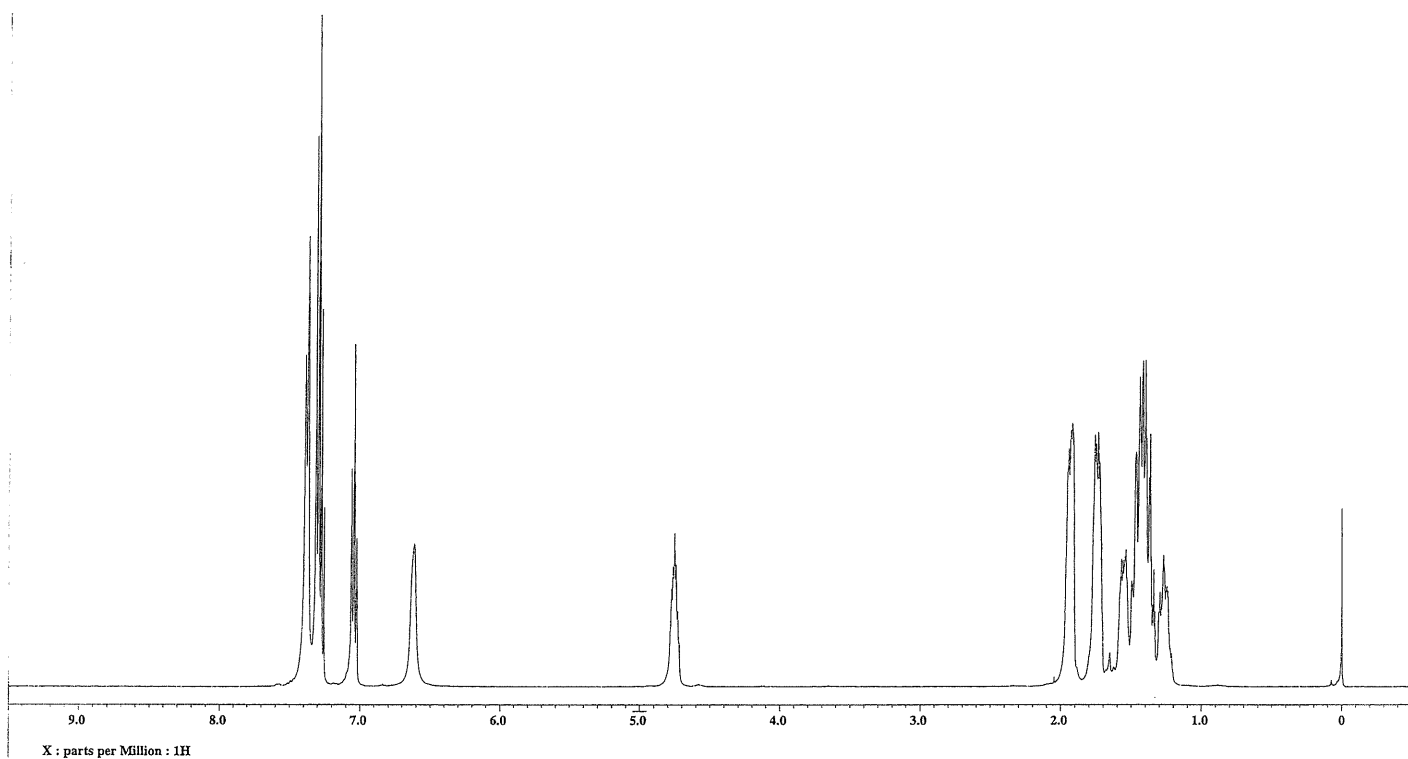


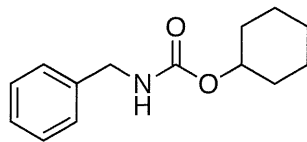




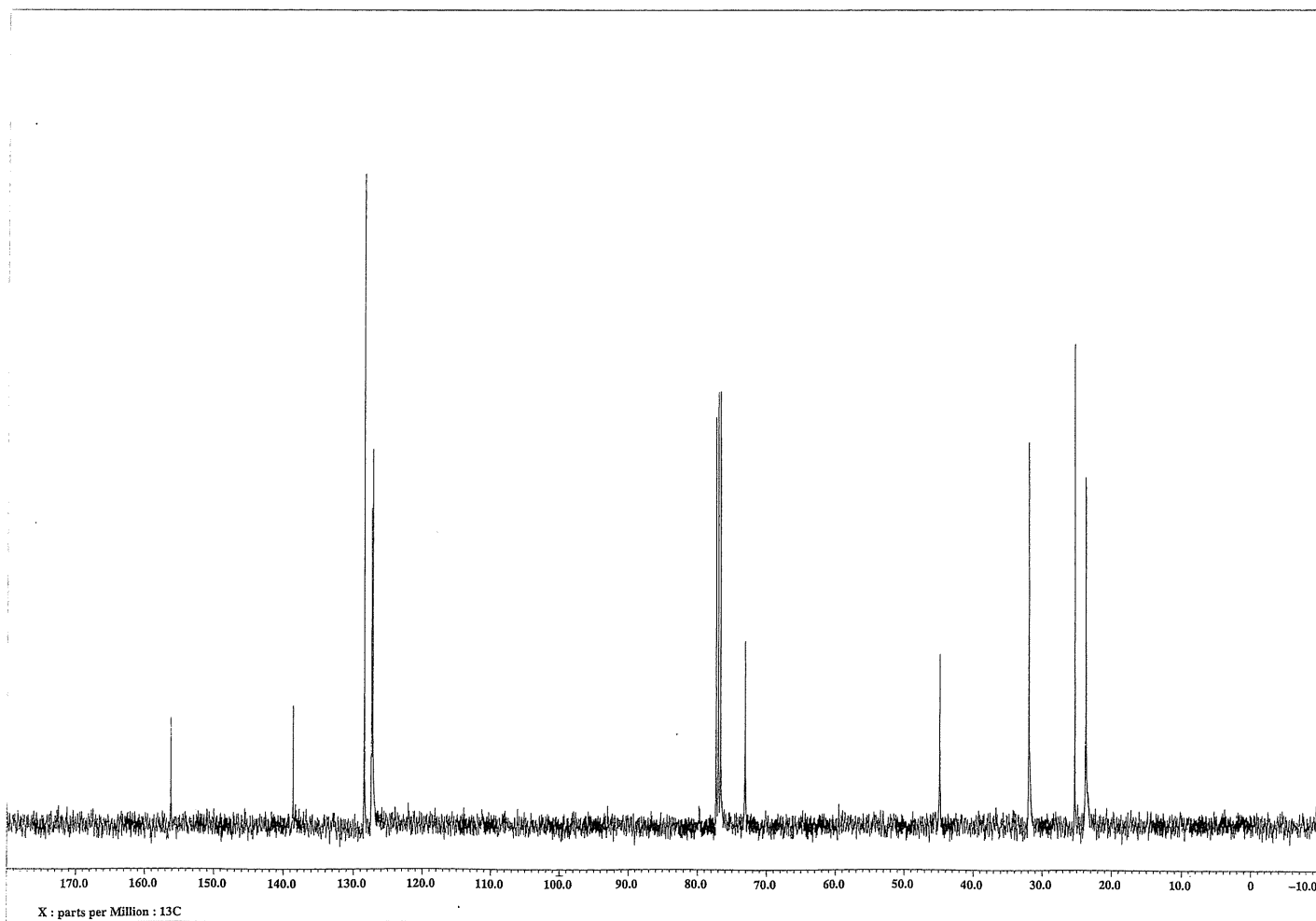
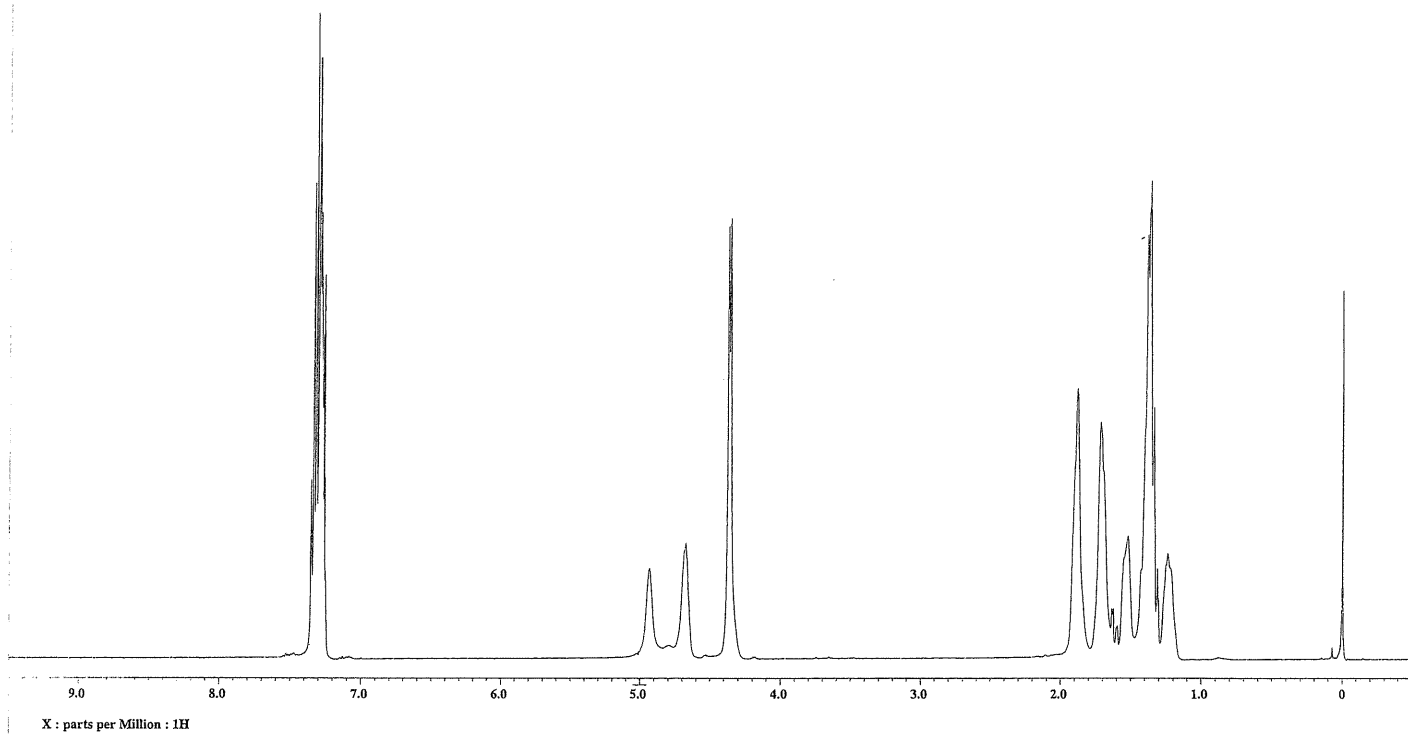


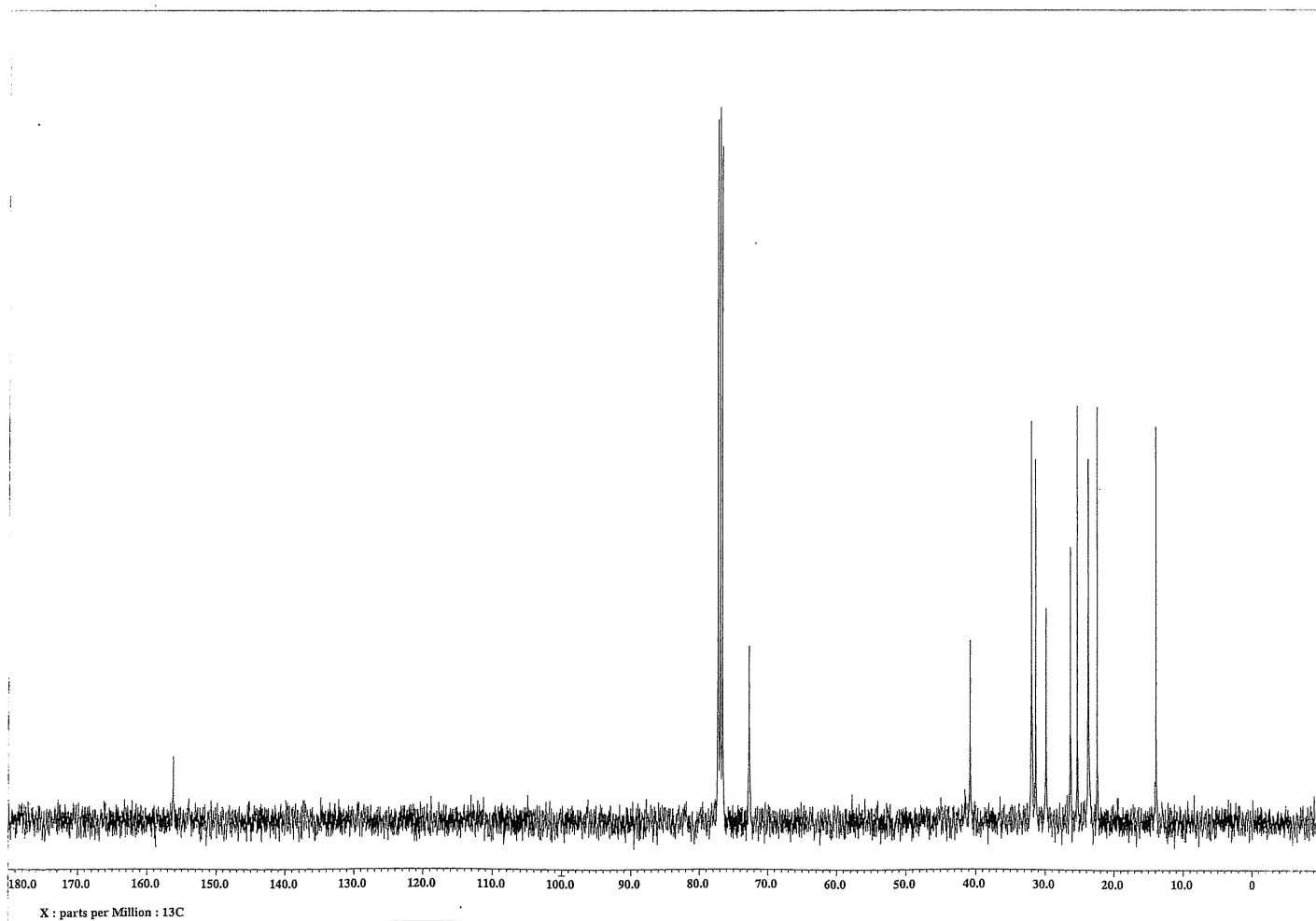
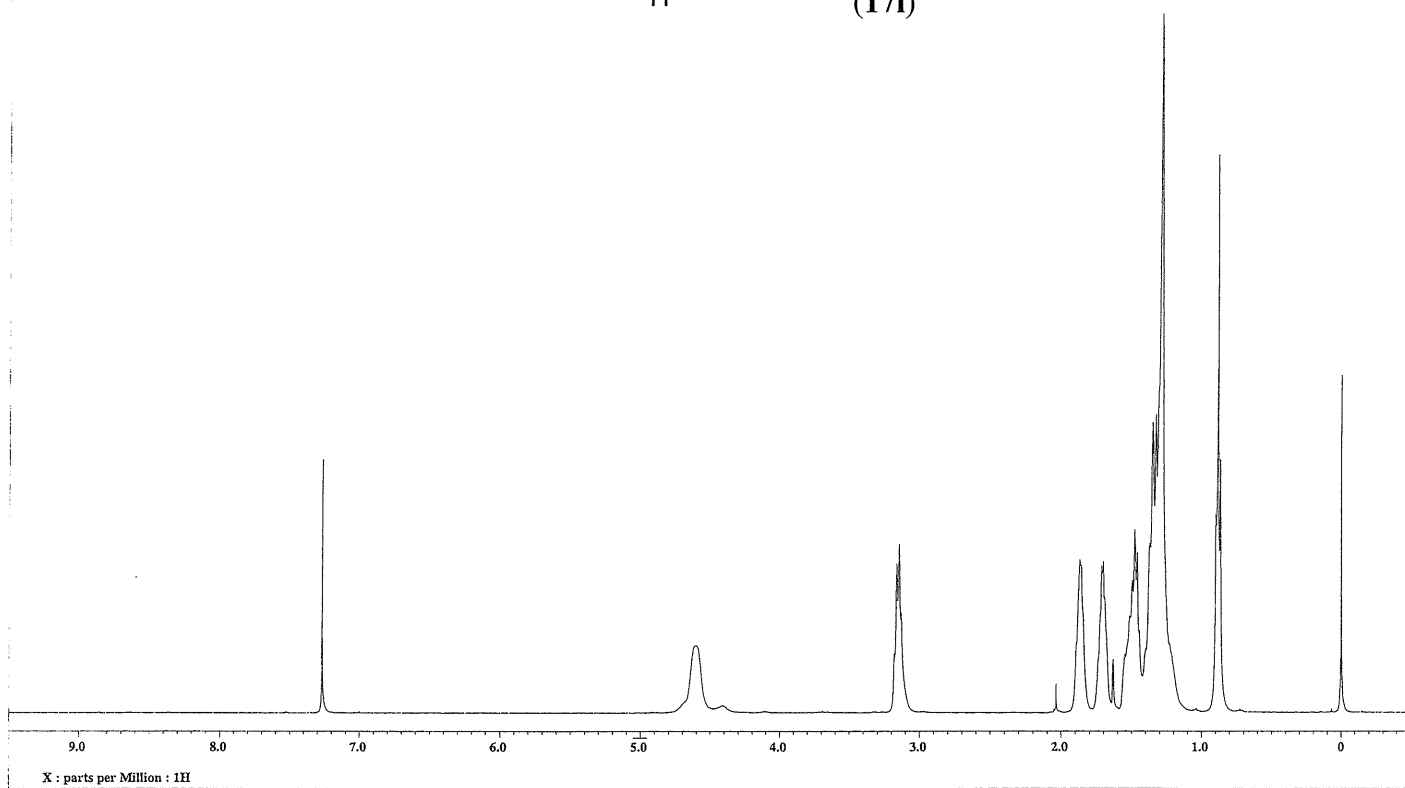
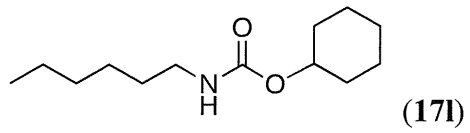
(17j)

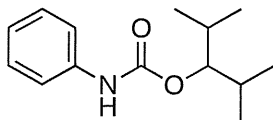




(17k)







(17m)

