Electronic Supplementary Information

Metal-Free Transesterification Catalyzed by Tetramethylammonium Methyl Carbonate

Manabu Hatano, Yuji Tabata, Yurika Yoshida, Kohei Toh, Kenji Yamashita, Yoshihiro Ogura, and Kazuaki Ishihara*

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan.

e-mail: ishihara@cc.nagoya-u.ac.jp

Table of Contents:

1. General information.

^{1}H 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 (deuterochloroform at 77.00 ppm). ^{31}P NMR spectra were measured on a JEOL ECS-400 (161 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard (H_3PO_4 at 0 ppm). Optical rotations were measured on Rudolph Autopol IV digital polarimeter. The products were purified by column chromatography on silica gel (E. Merck Art. 9385; Kanto Chemical Co., Inc. 37560; Fuji Silysia Chemical LTD. Chromatorex-NH DM1020). High resolution mass spectral analyses were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700 (FAB), JEOL JMS-T100GCV (EI), Bruker Daltonics micrOTOF-QII (ESI)). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. Melting points were measured on MPA100, Standard Research Systems. High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-M20A and chiral column of Daicel CHIRALCEL, CHIRALPAK; AS-3 and OD-3. 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. *n*-Hexane, ethyl acetate, methyl acetate, dimethyl carbonate and were freshly distilled in prior to use. Anhydrous solvents, such as toluene, 2-propanol, methyl methacrylate (MMA), THF and DMF, were used as received commercially.

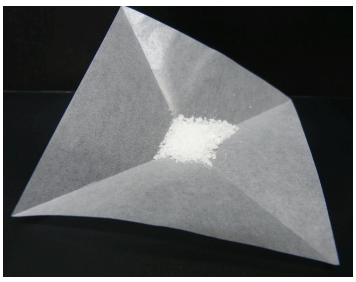
2. Preparation of phosphonium and ammonium salts.

$[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ (2a), $[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (3a): These compounds were known and prepared by the reported procedure.[1,2] Prepared compounds (pale yellow liquids) were stored at room temperature in a sealed vial under an inert gas-atmosphere.

$[Me_2(n\text{-octyl})_2N]^+[OCO_2Me]^-$ (3b): A pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 (t, J = 6.9 Hz, 6H), 1.19-1.34 (m, 20H), 1.58-1.66 (m, 4H), 2.97 (s, 6H), 3.15 (s, 3H), 3.19-3.23 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.8 (2C), 21.7 (2C), 22.1 (2C), 25.8 (2C), 28.5 (2C), 28.6 (2C), 31.2 (2C), 49.6 (2C), 50.7, 62.5 (2C), 155.7. IR (KBr) 3433, 2926, 2856, 1697, 1467, 1308, 1080 cm^{-1}. M.p. 66-74 °C.

$[Me_3(n\text{-octyl})N]^+[OCO_2Me]^-$ (3c): A pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 (t, J = 6.4 Hz, 3H), 1.21-1.34 (m, 10 H), 1.62-1.70 (m, 2H), 3.03 (s, 9H), 3.15 (s, 3H), 3.23-3.27 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9, 22.1 (2C), 25.8, 28.6 (2C), 31.2, 50.9, 51.8 (3C), 65.0, 155.8. IR (KBr) 3411, 2926, 2857, 1654, 1481, 1301, 1080 cm^{-1}. M.p. 174-181 °C.

$[Me_4N]^+[OCO_2Me]^-$ (3d):[3] To a solution of 10 wt. % tetramethylammonium hydroxide in methanol (2.7 mL, 2.5 mmol) was added dimethyl carbonate (2.1 mL, 25 mmol). The mixture was stirred under a nitrogen atmosphere at room temperature for 15 h. The volatiles were removed under reduced pressure to yield $[Me_4N]^+[OCO_2Me]^-$ quantitatively as a white solid. Obtained $[Me_4N]^+[OCO_2Me]^-$ was stored and handled in glovebox filled with argon. White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.11 (s, 12H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 50.9, 54.3 (4C), 155.7. IR (KBr) 3432, 1654, 1488, 1447, 1403, 1312, 1083 cm^{-1}. M.p. 126-144 °C.

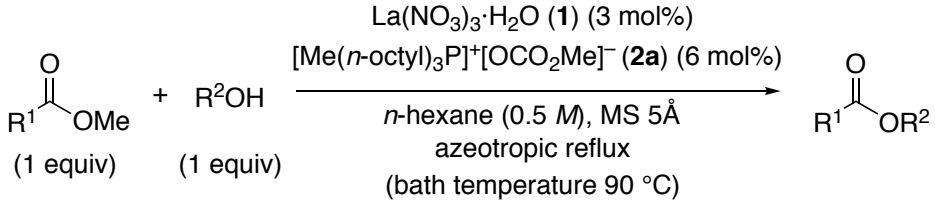


$[Et_4N]^+[OCO_2Me]^-$ (3e):[3] Tetraethylammonium hydroxide in water (35 wt. %, 1.5 mL, 2.5 mmol) was fully concentrated, and then water was replaced by methanol (2 mL). Dimethyl carbonate (2.1 mL, 25 mmol) was added, and the mixture was stirred under a nitrogen atmosphere at room temperature for 15 h. The volatiles were removed under reduced pressure to yield $[Et_4N]^+[OCO_2Me]^-$ as a white solid quantitatively. Obtained $[Et_4N]^+[OCO_2Me]^-$ was stored and handled in glovebox filled with argon. White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.13-1.17 (m, 12H), 3.15 (s, 3H), 3.20 (q, J = 7.3 Hz, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 7.1 (4C), 50.9, 51.4 (4C), 155.7. IR (KBr) 3470, 2991, 1696, 1493, 1439, 1397, 1310, 1173, 1079 cm^{-1}. M.p. 210-215 °C.

$[Me_4N]^+[OCO_2H]^-$ (3f): A white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.10 (s, 12 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 54.4 (t, $J_{C\text{-}N}$ = 4.0 Hz, 4C), 158.3. IR (KBr) 3019, 1655, 1488, 1404, 1008 cm^{-1}. M.p. 194-205 °C.

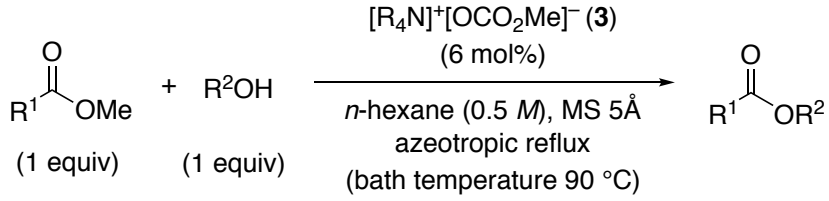
$[Me_4N]^+[OH]^-$ (3g) and $[Me_4N]^+[Cl]^-$ (3h): Commercially available.

3. General procedure for the $La(NO_3)_3{\cdot}H_2O$–$[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ complex $1{\cdot}2a_2$ -catalyzed transesterification in *n*-hexane.



A mixture of $La(NO_3)_3{\cdot}H_2O$ (**1**) (20.6 mg, 0.06 mmol) and methyltrioctylphosphonium methyl carbonate (**2a**) (55.3 mg, 0.12 mmol) in *n*-hexane (4 mL) was stirred at room temperature for 1–2 min. As soon as alcohol (2.0 mmol) was added, methyl ester (2.0 mmol) and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added to the solution. The mixture was heated under azeotropic reflux conditions (bath temperature 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and activated 5Å molecular sieves (pellets, 1 g). After the azeotropic reflux for the indicated reaction time, the reaction mixture was allowed to cool to room temperature. To quench the catalyst, 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 under reduced pressure. The rough yield was determined by ^1H NMR analysis based on 4,4'-di-*tert*-butylbiphenyl as an internal standard, and the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 50:1 to 10:1) to give the desired product. The isolated yield was determined by the purified compound.

4. General procedure for the $[R_4N]^+[OCO_2Me]^-$ (3)-catalyzed transesterification in *n*-hexane.



To a solution of tetraalkylammonium methyl carbonate (**3**) (0.12 mmol) in *n*-hexane (4 mL), alcohol (2.0 mmol), methyl ester (2.0 mmol), and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was heated under azeotropic reflux conditions (bath temperature 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and activated 5Å molecular sieves (pellets, 1 g). See Figure S1 for a typical reaction vessel in this transesterification. After the azeotropic reflux for the indicated reaction time, the reaction mixture was allowed to cool to room temperature. To remove the catalyst, the reaction mixture was filtered through flash silica pad using *n*-hexane–ethyl acetate (1:1) and the filtrate was

concentrated under reduced pressure. The rough yield was determined by ^{1}H NMR analysis based on 4,4'-di-*tert*-butylbiphenyl as an internal standard, and the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 100:1 to 1:1) to give the desired product. The isolated yield was determined by the purified compound.

General reaction conditions (solvent, boiling point, and bath temperature):

n-Hexane (4 mL), b.p. 69 °C, bath temperature 90 °C, azeotropic reflux with pellet MS 5Å.
Ethyl acetate (4 mL), b.p. 77 °C, bath temperature 100 °C, azeotropic reflux with pellet MS 5Å.
Methyl acetate (4 mL), b.p. 57 °C, bath temperature 70 °C powdered MS 5Å in the flask.
Dimethyl carbonate (4 mL), b.p. °C, bath temperature 110 °C, azeotropic reflux with pellet MS 5Å.
Toluene (4 mL), b.p. 110 °C, bath temperature 140 °C, azeotropic reflux with pellet MS 5Å.
2-Propanol (4 mL), b.p. 82 °C, bath temperature 105 °C, azeotropic reflux with pellet MS 5Å.
THF (4 mL), b.p. 66 °C, bath temperature 90 °C, azeotropic reflux with pellet MS 5Å.
Methyl methacrylate (MMA) (4 mL), b.p. 110 °C, bath temperature 70 °C, powdered MS 5Å in the flask.
DMF (4 mL), b.p. 153 °C, bath temperature 90 °C, powdered MS 5Å in the flask.

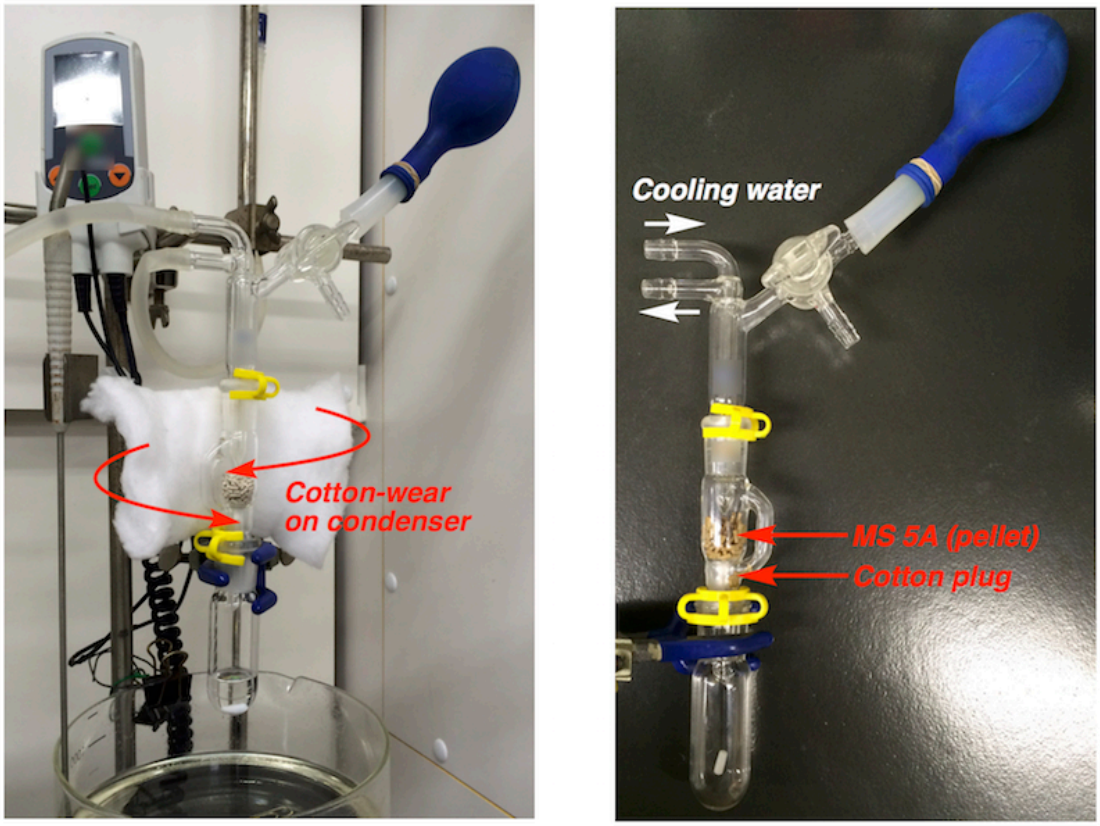
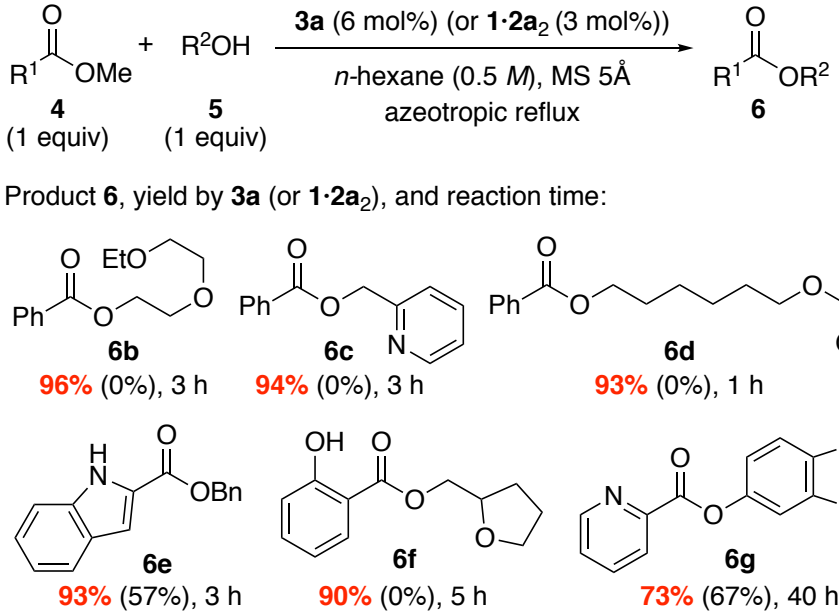


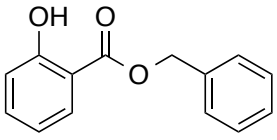
Figure S1. A typical reaction vessel in this transesterification.

5. Products in Table 1 and the related control experiments.

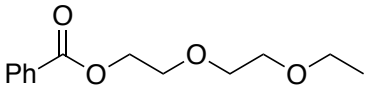
The generality of **3a**-catalysis was briefly examined in comparison with our previous La(III) catalyst **1**·**2a**$_2$ in *n*-hexane (Scheme S1). As a result, chelating alcohols could be used and the corresponding esters **6b–d** were obtained in high yields. Chelating esters also could be used (see **6e–g**). In particular, the combination of chelating ester and chelating alcohol was tolerable, as seen in **6f**. Sesamol, as a relatively nucleophilic phenol, could be used, although a reactive trifluoroethyl ester was used (see **6g**).



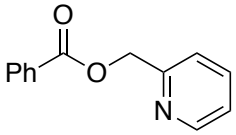
Scheme S1. Transesterification with the use of ammonium salt catalyst **3a**. The reaction was carried out under the standard conditions as seen in Table 1 unless otherwise noted. [a] Trifluoroethyl ester was used.



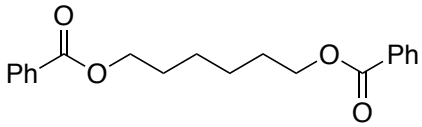
Benzyl 2-hydroxybenzoate (6a):[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 2H), 6.87 (t, J = 8,2 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 7.33-7.50 (m, 6H), 7.89 (d, J = 8.2 Hz, 1H), 10.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.9, 112.3, 117.5, 119.1, 128.2 (2C), 128.5, 128.6 (2C), 129.9, 135.3, 135.7, 161.7, 169.9. IR (neat) 3188, 1674, 1485, 1299, 1250, 1213, 1157 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{13}O_3$ $[M+H]^+$ 229.0859, found 229.0872.



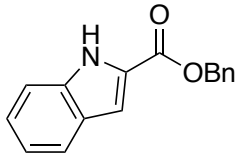
2-(2-Ethoxyethoxy)ethyl benzoate (6b):[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 6.9 Hz, 3H), 3.53 (q, J = 6.9 Hz, 2H), 3.61 (m, 2H), 3.71 (m, 2H), 3.85 (m, 2H), 4.49 (m, 2H), 7.44 (t, J = 8.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 64.2, 66.8, 69.3, 69.9, 70.8, 128.4 (2C), 129.7 (2C), 130.2, 133.0, 166.6. IR (neat) 2870, 1719, 1275, 1110 cm^{-1}. HRMS (ESI+) calcd for $C_{13}H_{18}NaO_4$ $[M+Na]^+$ 261.1097, found 261.1095.



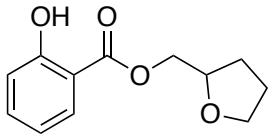
Pyridin-2-ylmthyl benzoate (6c):[6] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 2H), 7.25 (dd, J = 7.8, 4.6 Hz, 1H), 7.42-7.48 (m, 3H), 7.59 (t, J = 7.3 Hz, 1H), 7.72 (td, J = 7.8, 1.8 Hz, 1H), 8.13 (d, J = 7.3 Hz, 2H), 8.62 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.3, 121.7, 122.9, 128.5 (2C), 129.8 (2C), 129.9, 133.3, 136.9, 149.6, 156.1, 166.3. IR (neat) 3064, 1722, 1594, 1451, 1276, 1113 cm^{-1}. HRMS (ESI+) calcd for $C_{13}H_{11}NNaO_2$ $[M+Na]^+$ 236.0682, found 236.0684.



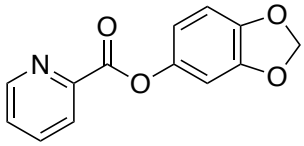
Hexane-1,6-diyl dibenzoate (6d):[7] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49–1.57 (m, 2H), 1.77-1.85 (m, 4H), 4.34 (t, J = 6.9 Hz, 4H), 7.44 (t, J = 7.8 Hz, 4H), 7.56 (t, J = 7.8 Hz, 2H), 8.05 (d, J = 7.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9 (2C), 28.7 (2C), 64.9 (2C), 128.4 (4C), 129.6 (4C), 130.4 (2C), 132.9 (2C), 166.7 (2C). IR (KBr) 3036, 1721, 1594, 1451, 1276, 1113 cm^{-1}. M.p. 53-55 °C. HRMS (ESI+) calcd for $C_{20}H_{22}NaO_4$ $[M+Na]^+$ 349.1410, found 349.1407.



Benzyl 1*H*-indole-2-carboxylate (6e):[8] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 2H), 7.14 (t, J = 6.9 Hz 1H), 7.27-7.43 (m, 6H), 7.46 (d, J = 6.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 9.04 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.8, 109.3, 112.0, 120.9, 122.7, 125.6, 127.1, 127.5, 128.3 (2C), 128.5, 128.7 (2C), 135.8, 137.0, 161.9. IR (KBr) 3341, 1687, 1524, 1391, 1340, 1308, 1246, 1196 cm^{-1}. M.p. 136-137 °C. HRMS (ESI+) calcd for $C_{16}H_{13}NNaO_2$ $[M+Na]^+$ 274.0838, found 274.0835.

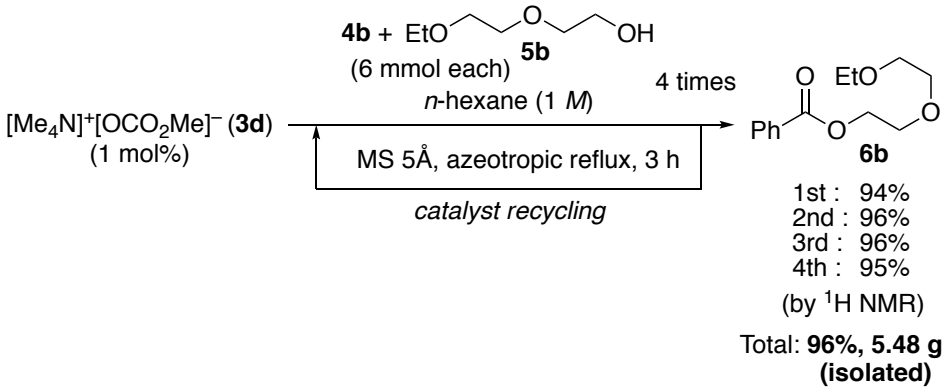


(Tetrahydrofuran-2-yl)methyl 2-hydroxybenzoate (6f):[9] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (m, 1H), 1.89-2.02 (m, 2H), 2.08 (m, 1H), 3.84 (m, 1H), 3.94 (m, 1H), 4.23-4.34 (m, 2H), 4.41 (dd, *J* = 11.0, 3.2 Hz, 1H), 6.88 (t, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.8 Hz, 1H), 10.7 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 28.1, 67.1, 68.6, 76.4, 112.4, 117.6, 119.2, 130.1, 135.8, 161.7, 170.1. IR (neat) 3187, 2976, 2873, 1676, 1614, 1486, 1301, 1251, 1215, 1159, 1083 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{15}O_4$ [M+H]+ 223.0970, found 223.0975.



Benzo[*d*][1,3]dioxol-5-yl picolinate (6g): Instead of methyl ester, trifuluoroethyl ester was used as a starting material. Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 2H), 6.71 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 7.56 (ddd, *J* = 7.8, 4.6, 1.4 Hz, 1H), 7.92 (td, *J* = 7.8, 1.8 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.85 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.8, 103.8, 108.1, 114.1, 125.9, 127.5, 137.2, 145.1, 145.6, 147.4, 148.1, 150.1, 164.2. IR (KBr) 1752, 1504, 1487, 1282, 1236, 1173, 1119, 1068 cm^{-1}. M.p. 72-73 °C. HRMS (FAB+) calcd for $C_{13}H_{10}NO_4$ $[M+H]^+$ 244.0610, found 244.0613.

6. Recovery and reuse of the catalyst in gram scale synthesis of 6b (Scheme 1).



A mixture of tetramethylammonium methyl carbonate (**3**) (9.0 mg, 0.060 mmol) in *n*-hexane (6 mL) was stirred at room temperature. (*) 2-(2-Ethoxyethoxy)ethanol (813 μL, 6.0 mmol), methyl benzoate (750 μL, 6.0 mmol), and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added. The mixture was heated under azeotropic reflux conditions (bath temperature, 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and 5Å molecular sieves (pellets, 2 g). After the azeotropic reflux for 3 h, the reaction mixture was allowed to cool to 0 °C and stirred at that temperature for 5 min. After decantation of the insoluble and viscous catalyst at 0 °C (see Figure S2), clear supernatant involving a product **6b** was separated by using a syringe, and the rough yield was determined by ^{1}H NMR analysis based on the internal standard after partially sampling the solution and removal of volatiles. To the remaining residue involving the active catalyst, *n*-hexane (6 mL) was added for the next reaction. The procedure from (*) was repeated additional three times. The all separated solution was combined and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 50:1 to 5:1) to give the desired product **6b** (5.48 g, 96% yield).

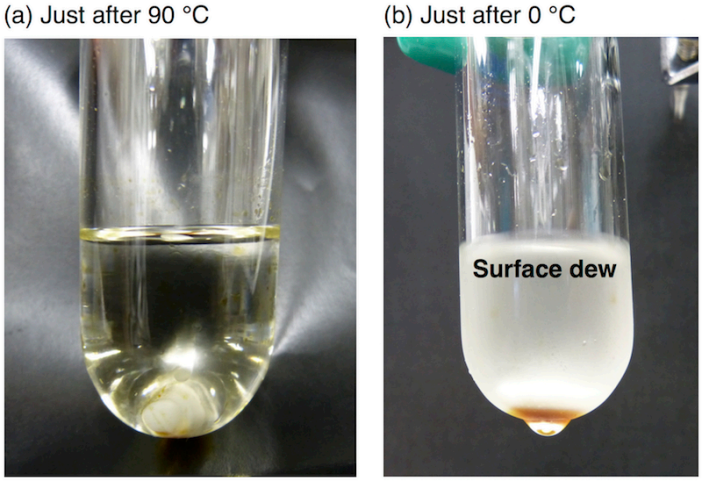
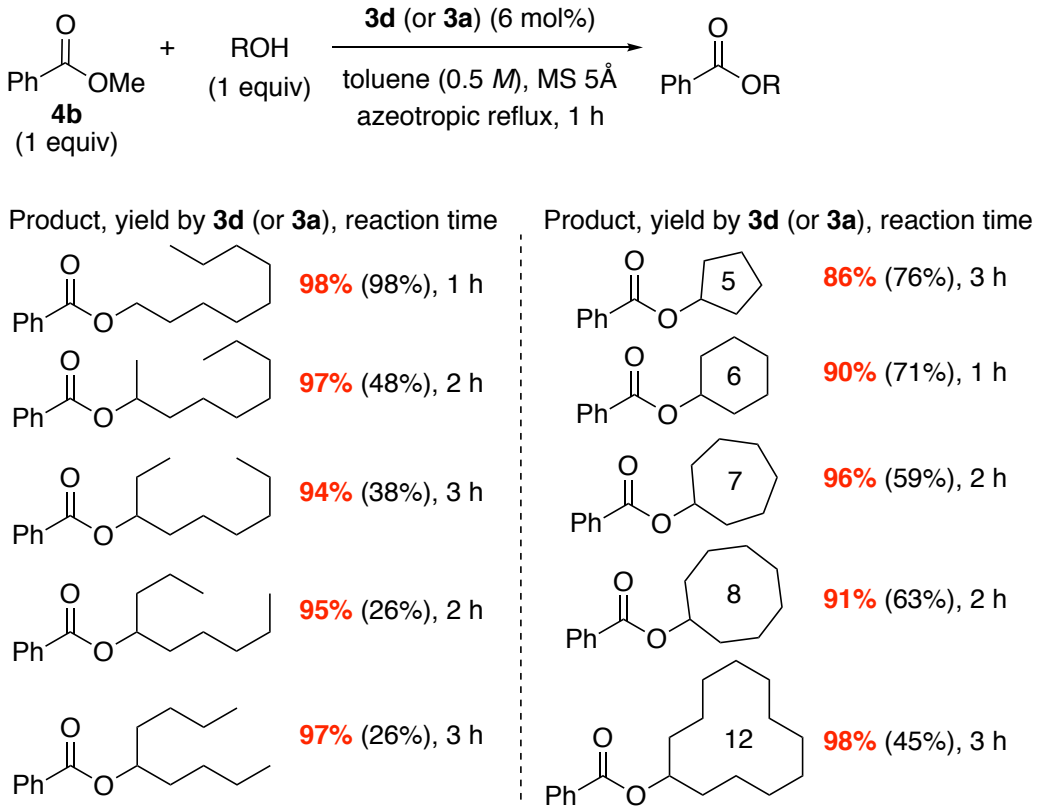


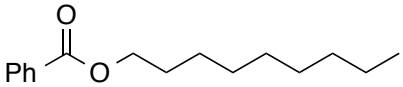
Figure S2. **3d**-Derived viscous deposit in *n*-hexane at 0 °C

7. Products in Table 2 and the related control experiments.

The catalytic performance of **3d** (vs. **3a**) was carefully examined for systematically-selected acyclic and cyclic alcohols in toluene (bp. 110 °C) under azeotropic reaction conditions (Scheme S2). As a result, **3a** was still effective for sterically less-hindered alcohols. However, the yields of the corresponding bulkier products by **3a**-catalysis gradually decreased, whereas **3d**-catalysis continued to show high yields. Since the reactivity of sterically hindered alcohols would be inherently low, **3a**-derived $[Me(n\text{-octyl})_3N]^+[OR]^-$, rather than **3d**-derived $[Me_4N]^+[OR]^-$, might readily decompose before the unlikely nucleophilic attack to ester **4b**.

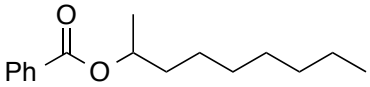


Scheme S2. Transesterification of **4b** with acyclic and cyclic alcohols with the use of **3d** or **3a**.

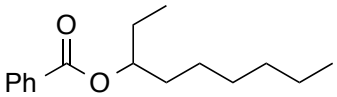


Nonyl benzoate:[10] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.2 Hz, 3H), 1.20-1.50 (m, 12H), 1.76 (quintet, J = 6.9 Hz, 2H), 4.31 (t, J = 6.9 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 8.05 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 26.1, 28.8, 29.3,

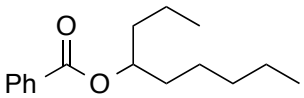
29.4, 29.6, 31.9, 65.2, 128.4 (2C), 129.6 (2C), 130.6, 132.9, 166.8. IR (neat) 2926, 2855, 1721, 1452, 1274, 1112 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{24}O_2$ $[M]^+$ 248.1776, found 248.1776.



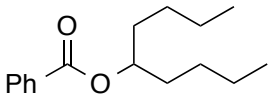
Nonan-2-yl benzoate:[11] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.23-1.43 (m, 10H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.61 (m, 1H), 1.73 (m, 1H), 5.15 (sextet, *J* = 6.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.2, 22.7, 25.5, 29.3, 29.5, 31.9, 36.1, 71.8, 128.3 (2C), 129.6 (2C), 131.0, 132.7, 166.3. IR (neat) 2928, 2857, 1718, 1451, 1275, 1110 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{24}O_2$ $[M]^+$ 248.1776, found 248.1779.



Nonan-3-yl benzoate:[12] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3H), 0.95 (t, *J* = 6.9 Hz, 3H), 1.20-1.45 (m, 8H), 1.63-1.74 (m, 2H), 1.70 (quintet, *J* = 7.3 Hz, 2H), 5.08 (quintet, *J* = 6.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 14.1, 22.7, 25.4, 27.1, 29.3, 31.8, 33.8, 76.3, 128.3 (2C), 129.6 (2C), 130.9, 132.7, 166.5. IR (neat) 2930, 2858, 1718, 1451, 1275, 1109 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{24}O_2$ $[M]^+$ 248.1776, found 248.1777.

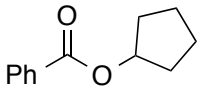


Nonan-4-yl benzoate: Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H), 1.25-1.50 (m, 8H), 1.55-1.75 (m, 4H), 5.15 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 18.7, 22.6, 25.1, 31.8, 34.3, 36.5, 74.9, 128.3 (2C), 129.6 (2C), 130.9, 132.7, 166.4. IR (neat) 2932, 2871, 1718, 1451, 1274, 1110 cm^{-1}. HRMS (FAB+) calcd for $C_{16}H_{25}O_2$ $[M+H]^+$ 249.1855, found 249.1859.

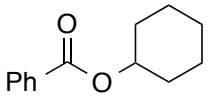


Nonan-5-yl benzoate (8):[13] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (m, 6H), 1.33 (m, 8H), 1.66 (m, 4H), 5.13 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 7.5 Hz,

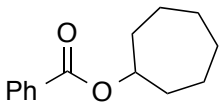
2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C), 22.6 (2C), 27.4 (2C), 33.9 (2C), 75.0, 128.2 (2C), 129.5 (2C), 130.8, 132.6, 166.3. IR (neat) 2957, 2860, 1718, 1452, 1275, 1110 cm^{-1}. HRMS (FAB+) calcd for $C_{16}H_{24}NaO_2$ $[M+Na]^+$ 271.1674, found 271.1682.



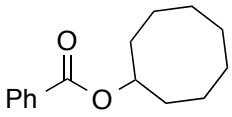
Cyclopentyl benzoate:[14] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61-1.72 (m, 2H), 1.76-1.90 (m, 4H), 1.92-2.01 (m, 2H), 5.41 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9 (2C), 32.8 (2C), 77.7, 128.3 (2C), 129.5 (2C), 130.9, 132.7, 166.4. IR (neat) 2965, 1714, 1584, 1451, 1316, 1277, 1169, 1115, 1070,01026 cm^{-1}. HRMS (ESI+) calcd for $C_{12}H_{14}NaO_2$ $[M+Na]^+$ 213.0886, found 213.0891.



Cyclohexyl benzoate:[13] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-2.10 (m, 10H), 5.03 (m, 1H), 7.40-7.48 (m, 2H), 7.52-7.60 (m, 1H), 8.02-8.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (2C), 25.4, 31.6 (2C), 73.0, 128.2 (2C), 129.4 (2C), 130.9, 132.6, 165.9. IR (neat) 2937, 2858, 1715, 1451, 1277, 1112, 1025 cm^{-1}. HRMS (FAB+) calcd for $C_{13}H_{16}NaO_2$ $[M+Na]^+$ 227.1048, found 227.1051.

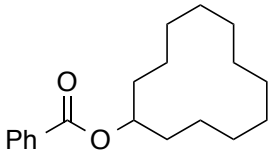


Cycloheptyl benzoate:[15] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49-1.95 (m, 10H), 1.97-2.10 (m, 2H), 5.20 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 8.04 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (2C), 28.4 (2C), 33.9 (2C), 75.6, 128.3 (2C), 129.5 (2C), 131.1, 132.7, 166.0. IR (neat) 2929, 2859, 1714, 1451, 1275, 1114 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{18}NaO_2$ $[M+Na]^+$ 241.1204, found 241.1209.



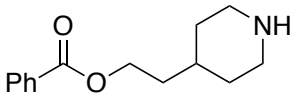
Cyclooctyl benzoate:[16] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54-1.69 (m, 8H), 1.73-1.97 (m, 6H), 5.20 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 8.04 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (2C), 25.4, 27.2 (2C), 31.5 (2C), 75.7, 128.3 (2C), 129.6 (2C), 131.2,

132.7, 166.0. IR (neat) 2925, 2856, 1714, 1450, 1276, 1112 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{20}NaO_2$ $[M+Na]^+$ 255.1361, found 255.1357.

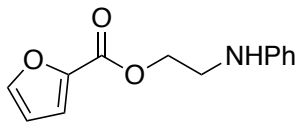


Cyclododecyl benzoate:[17] White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 1.26-1.46 (m, 18H), 1.59-1.74 (m, 2H), 1.79-1.88 (m, 2H), 5.26 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (2C), 23.3 (2C), 23.5 (2C), 24.1, 24.3 (2C), 29.2 (2C), 73.1, 128.4 (2C), 129.6 (2C), 131.1, 132.8, 166.4. IR (KBr) 2930, 2860, 1711, 1469, 1275, 1114 cm^{-1}. M.p. 42 °C. HRMS (FAB+) calcd for $C_{19}H_{28}NaO_2$ $[M+Na]^+$ 311.1987, found 311.1988.

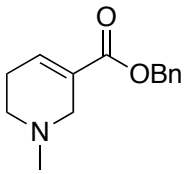
8. Products in Scheme 2.



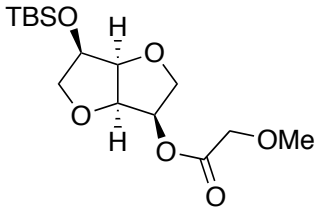
2-(Piperidin-4-yl)ethyl benzoate (10a):[18] Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (qd, *J* = 12.4, 4.1 Hz, 2H), 1.52-1.62 (m, 2H), 1.70-1.77 (m, 4H), 2.61 (td, *J* = 12.4, 2.3 Hz, 2H), 3.08 (d, *J* = 11.9 Hz, 2H), 4.38 (t, *J* = 6.9 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.4, 33.5 (2C), 35.9, 46.7 (2C), 62.8, 128.4 (2C), 129.5 (2C), 130.4, 132.9, 166.6. IR (neat) 3413, 2922, 1715, 1602, 1451, 1315, 1276, 1114 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{20}NO_2$ $[M+H]^+$ 234.1494, found 234.1497.



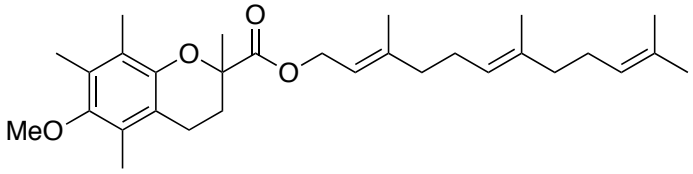
2-(Phenylamino)ethyl furan-2-carboxylate (10b): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (m, 2H), 3.99 (br, 1H), 4.52 (t, *J* = 5.5 Hz, 2H), 6.52 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.67 (dd, *J* = 7.8, 0.9 Hz, 2H), 6.74 (tt, *J* = 7.3, 0.9 Hz, 1H), 7.17-7.22 (m, 3H), 7.59 (dd, *J* = 1.8, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.9, 63.6, 111.9, 112.9 (2C), 117.9, 118.4, 129.3 (2C), 144.3, 146.5, 147.6, 158.7. IR (neat) 3403, 1721, 1604, 1509, 1474, 1297, 1180, 1119 cm^{-1}. HRMS (FAB+) calcd for $C_{13}H_{13}NO_3$ $[M]^+$ 231.0895, found 231.0891.



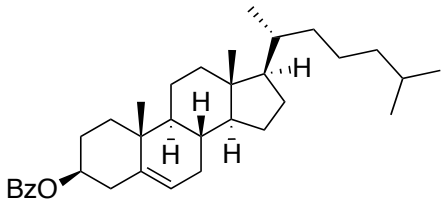
Arecoline benzyl ester (10c):[19] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33-2.43 (m, 2H), 2.40 (s, 3H), 2.49 (t, *J* = 5.5 Hz, 2H), 3.17 (d, *J* = 2.3 Hz, 2H), 5.19 (s, 2H), 7.06 (m, 1H), 7.29-7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 45.8, 50.8, 53.2, 66.1, 128.0 (2C), 128.1, 128.5 (2C), 129.0, 136.1, 138.1, 165.6. IR (neat) 2941, 2786, 1710, 1654, 1456, 1398, 1289, 1264, 1142, 1091, 1027 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1338, found 232.1336.



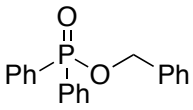
(3*R*,3a*R*,6*R*,6a*S*)-6-((*tert*-Butyldimethylsilyl)oxy)hexahydrofuro[3,2-*b*]furan-3-yl 2-methoxy acetate (10d): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.91 (s, 9H), 3.46 (s, 3H), 3.56 (t, *J* = 8.3 Hz, 1H), 3.85 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.91 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.00 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.10 (s, 2H), 4.28 (m, 1H), 4.33 (t, *J* = 5.0 Hz, 1H), 4.69 (t, *J* = 5.0 Hz, 1H) 5.18 (q, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.9, –4.7, 18.4, 25.9 (3C), 59.4, 69.5, 70.7, 72.4, 73.6, 74.5, 80.3, 81.8, 169.9. IR (neat) 2954, 2857, 1762, 1472, 1387, 1254, 1192, 1133, 1069, 1025 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{28}NaO_6Si$ $[M+Na]^+$ 355.1553, found 355.1550.



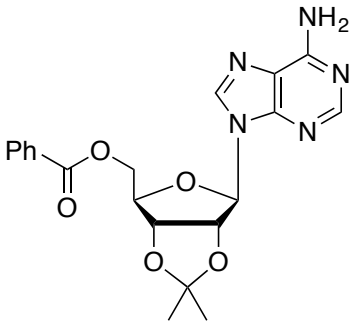
(2*E*,6*E*)-3,7,11-Trimethyldodeca-2,6,10-trien-1-yl 6-methoxy-2,5,7,8-tetramethylchromane-2-carboxylate (10e): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 12H), 1.68 (s, 3H), 1.85 (m, 1H), 1.95-2.08 (m, 8H), 2.08 (s, 3H), 2.15 (s, 3H), 2.18 (s, 3H), 2.39-2.52 (m, 2H), 2.60 (m, 1H), 3.61 (s, 3H), 4.56 (d, *J* = 7.1 Hz, 2H), 5.06-5.09 (m, 2H), 5.26 (t, *J* = 7.1, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 11.8, 12.6, 16.0, 16.3, 17.7, 20.9, 25.4, 25.7, 26.2, 26.7, 30.5, 39.5, 39.7, 60.3, 61.8, 77.1, 117.2, 117.9, 122.9, 123.6, 124.3, 125.6, 127.9, 131.3, 135.4, 143.0, 147.8, 150.0, 173.7. IR (neat) 2928, 1751, 1730, 1456, 1404, 1375, 1286, 1254, 1195, 1168, 1139, 1104, 1015 cm^{-1}. HRMS (FAB+) calcd for $C_{30}H_{44}O_4$ $[M]^+$ 468.3240, found 468.3231.



Cholesterol-derived benzoyl ester (10f):[13] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 (s, 3H), 0.86 (d, J = 6.3 Hz, 6H), 0.92 (d, J = 6.3 Hz, 3H), 0.95-2.10 (m, 29H), 2.46 (d, J = 8.1 Hz, 2H), 4.86 (m, 1H), 5.41 (d, J = 4.5 Hz, 1H), 7.43 (t, J = 6.9 Hz, 2H), 7.54 (t, J = 6.9 Hz, 1H), 8.04 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 18.6, 19.3, 21.0, 22.5, 22.8, 23.8, 24.2, 27.8, 28.0, 28.2, 31.8, 31.9, 35.7, 36.1, 36.6, 37.0, 38.1, 39.4, 39.7, 42.2, 49.9, 56.0, 56.6, 74.5, 122.7, 128.2 (2C), 129.5 (2C), 130.7, 132.6, 139.6, 165.9. IR (KBr) 2943, 2864, 1713, 1273, 1113 cm^{-1}. M.p. 146-147 ºC (decomposition). HRMS (FAB+) calcd for $C_{34}H_{50}NaO_2$ $[M+Na]^+$ 513.3709, found 513.3703.

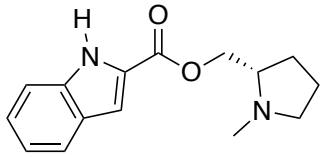


Benzyl diphenylphosphinate (10g):[20] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (d, J_{H-P} = 6.4 Hz, 2H), 7.29-7.38 (m, 5H), 7.42-7.48 (m, 4H), 7.50-7.55 (m, 2H), 7.81-7.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.3 (d, J_{C-P} = 5.7 Hz), 127.9 (2C), 128.3, 128.5 (2C), 128.6 (d, J_{C-P} = 13.3 Hz, 4C), 131.4 (d, J_{C-P} = 136.4 Hz, 2C), 131.8 (d, J_{C-P} = 9.5 Hz, 4C), 132.3 (d, J_{C-P} = 2.9 Hz, 2C), 136.4 (d, J_{C-P} = 7.6 Hz). ^{31}P NMR (161 MHz, $CDCl_3$) δ 32.7. IR (KBr) 2884, 1591, 1497, 1484, 1459, 1440, 1384, 1314, 1209, 1130 cm^{-1}. M.p. 79 °C. HRMS (FAB+) calcd for $C_{19}H_{18}O_2P$ $[M+H]+$ 309.1444, found 309.1057.

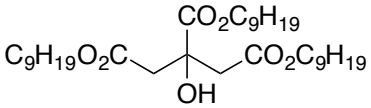


2',3'-*O*-(1-Methylethylidene)-adenosyl 5'-benzoate (10h):[21] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 3H), 1.64 (s, 3H), 4.48 (q, J = 6.4 Hz, 1H), 4.59-4.67 (m, 2H), 5.18 (q, J = 3.2 Hz, 1H), 5.49 (br, 2H), 5.59 (dd, J = 6.2, 1.8 Hz, 1H), 6.11 (d, J = 1.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.89 (s, 1H), 7.91 (d, J = 7.3 Hz, 2H), 8.33 (s, 1H). ^{13}C NMR (100 MHz,

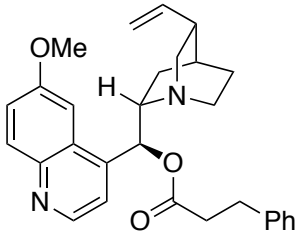
$CDCl_3$) δ 25.5, 27.2, 64.4, 81.7, 84.2, 85.1, 91.4, 114.7, 120.4, 128.4 (2C), 129.4, 129.6 (2C), 133.3, 139.6, 149.3, 153.2, 155.7, 166.1. IR (neat) 3322, 3168, 2988, 1720, 1645, 1599, 1475, 1375, 1273, 1209, 1092 cm^{-1}. HRMS (ESI+) calcd for $C_{20}H_{21}N_5NaO_5$ $[M+Na]^+$ 434.1435, found 434.1424.



(*S*)-(1-Methylpyrrolidin-2-yl)methyl 1*H*-indole-2-carboxylate (10i): Pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 1.71-1.92 (m, 3H), 2.01 (m, 1H), 2.32 (ddd, *J* = 9.6, 8.5, 2.3 Hz, 1H), 2.49 (s, 3H), 2.64 (m, 1H), 3.14 (t, *J* = 7.8 Hz, 1H), 4.32 (dd, *J* = 11.2, 5.0 Hz, 1H), 4.42 (dd, *J* = 11.0, 5.2 Hz, 1H), 7.15 (td, *J* = 7.8, 0.9 Hz, 1H), 7.25 (m, 1H), 7.32 (td, *J* = 8.3, 0.9, 1H), 7.43 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.69 (dd, *J* = 7.8, 0.9 Hz, 1H), 9.53 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 28.2, 41.4, 57.7, 64.2, 66.3, 109.0, 112.1, 120.8, 122.6, 125.4, 127.3, 127.5, 137.1, 162.0. IR (neat) 3329, 2953, 2793, 1710, 1530, 1341, 1308, 1248, 1196, 1147 cm^{-1}. M.p. 83 ºC. HRMS (FAB+) calcd for $C_{15}H_{19}N_2O_2$ $[M+H]^+$ 259.1447, found 259.1443.

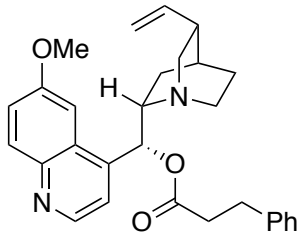


Trinonyl citrate (10j): Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 9H), 1.18-1.37 (brs, 36H), 1.57-1.67 (m, 6H), 2.79 (d, *J* = 15.6 Hz, 2H), 2.89 (d, *J* = 15.6 Hz, 2H), 4.07 (t, *J* = 6.9 Hz, 4H), 4.14 (s, 1H), 4.20 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (3C), 22.7 (3C), 25.8, 25.9 (2C), 28.4, 28.5 (2C), 29.3 (6C), 29.5 (3C), 31.9 (3C), 43.3 (2C), 65.2 (2C), 66.5, 73.2, 169.9 (2C), 173.5. IR (neat) 2925, 2855, 1741, 1467, 1343, 1190 cm^{-1}. HRMS (FAB+) calcd for $C_{33}H_{63}O_7$ $[M+H]^+$ 571.4574, found 571.4568.



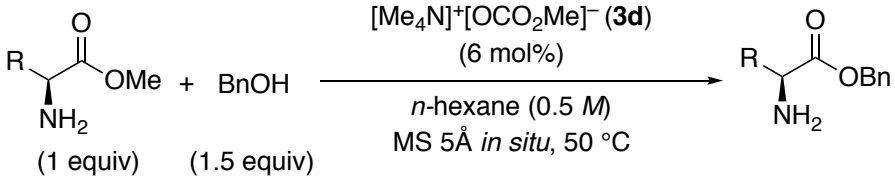
Quinidine-derived phenylpropanoate (10k): Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (m, 1H), 1.59-1.68 (m, 2H), 1.70-1.81 (m, 2H), 2.25 (m, 1H), 2.66-3.01 (m, 8H), 3.25 (q, *J* = 7.3 Hz, 1H), 3.94 (s, 3H), 5.08 (d, *J* = 17.0 Hz, 1H), 5.12 (d, *J* = 9.6 Hz, 1H), 6.00 (ddd, *J* = 17.2, 10.3, 7.3 Hz, 1H), 6.51 (d, *J* = 6.0 Hz, 1H), 7.13-7.26 (m, 6H), 7.36 (d, *J* = 9.6 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H),

8.01 (d, J = 9.6 Hz, 1H), 8.67 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 26.3, 27.8, 30.8, 36.0, 39.7, 49.2, 49.8, 55.6, 58.9, 73.6, 101.3, 114.9, 118.5, 121.9, 126.4, 127.0, 128.2 (2C), 128.6 (2C), 131.8, 140.0, 140.3, 143.6, 144.7, 147.5, 157.9, 171.9. IR (neat) 2937, 2871, 1739, 1621, 1508, 1474, 1454, 1432, 1361, 1227, 1147, 1081, 1030 cm^{-1}. HRMS (FAB+) calcd for $C_{29}H_{33}N_2O_3$ $[M+H]^+$ 457.2491, found 457.2508.



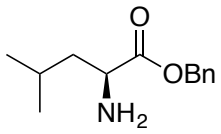
Quinine-derived phenylpropanoate (10l): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (m, 1H), 1.52 (m, 1H), 1.67 (m, 1H), 1.74-1.81 (m, 2H), 2.25 (m, 1H), 2.55-2.65 (m, 2H), 2.72 (td, J = 7.8, 2.3 Hz, 2H), 2.94 (t, J = 7.8 Hz, 2H), 2.98-3.07 (m, 2H), 3.33 (q, J = 8.2 Hz, 1H), 3.93 (s, 3H), 4.99 (dd, J = 10.5, 1.4 Hz, 1H), 5.00 (dd, J = 17.0, 1.4 Hz, 1H), 5.81 (ddd, J = 17.0, 10.5, 7.8 Hz, 1H), 6.47 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 6.4 Hz, 2H), 7.16-7.26 (m, 4H), 7.36 (dd, J = 9.2, 2.8 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 27.5, 27.8, 30.8, 35.9, 39.7, 42.4, 55.6, 56.6, 59.0, 73.8, 101.4, 114.5, 118.9, 121.8, 126.4, 127.0, 128.2 (2C), 128.5 (2C), 131.8, 140.0, 141.8, 143.5, 144.8, 147.5, 157.9, 172.0. IR (neat) 3375, 2941, 1739, 1621, 1508, 1361, 1228, 1079, 1030 cm^{-1}. HRMS (FAB+) calcd for $C_{29}H_{33}N_2O_3$ $[M+H]^+$ 457.2491, found 457.2473.

9. General procedure for the transesterification of α-amino acid esters (Scheme 2).

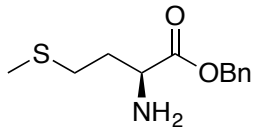


To a suspension of tetramethylammonium methyl carbonate (**3d**) (17.9 mg, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in *n*-hexane (4 mL), benzyl alcohol (310 μL, 3.0 mmol), α-amino acid methyl ester (2.0 mmol), and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at 50 ºC by checking TLC. To remove the catalyst, reaction reaction mixture was filtered through a pad of NH silica gel (Fuji Silysia Chemical LTD. Chromatorex-NH DM1020) using *n*-hexane–ethyl acetate (1:1), and the filtrate was concentrated under reduced pressure. The rough yield was determined by ^{1}H NMR analysis based on

4,4'-di-*tert*-butylbiphenyl as an internal standard, and the resultant residue was purified by NH silica gel column chromatography (eluent: *n*-hexane:EtOAc = 50:1 to 10:1) to give the desired product. The isolated yield and optical purity were determined by the purified compound.

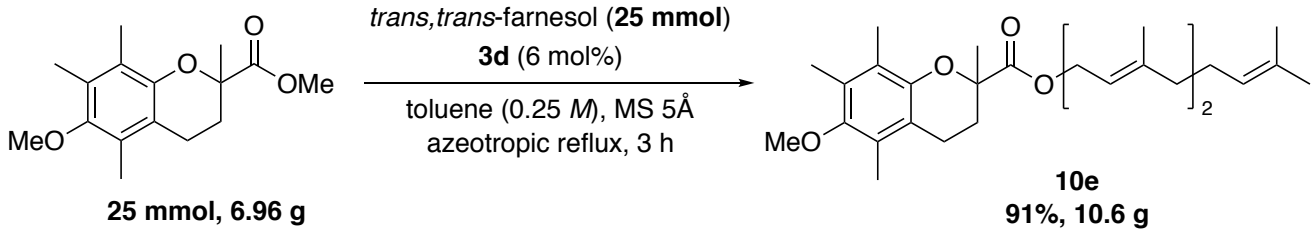


Benzyl *L*-leucinate (10m):[22] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.4 Hz, 3H), 1.40-1.62 (m, 4H), 1.77 (m, 1H), 3.51 (dd, J = 8.7, 5.5 Hz, 1H), 5.13 (d, J = 12.4 Hz, 1H), 5.17 (d, J = 12.4 Hz, 1H), 7.31-7.04 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.9, 24.7, 43.9, 52.9, 66.5, 128.2 (2C), 128.3, 128.5 (2C), 135.7, 176.5. IR (neat) 3380, 2956, 2870, 1735, 1607, 1456, 1367, 1269, 1167 cm^{-1}. $[\alpha]_D^{25}$ = 5.6 (*c* 1.00, $CHCl_3$, >99% ee). Chiral HPLC analysis; AS-3, *n*-hexane/*i*-PrOH = 9/1, 1.0 mL/min, t_R = 6.2 min (*L*) [7.6 min (*D*), not observed.]. HRMS (FAB+) calcd for $C_{13}H_{20}NO_2$ $[M+H]^+$ 222.1494, found 222.1494.



Benzyl *L*-methioninate (10n):[23] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (brs, 2H), 1.82 (ddt, J = 13.7, 8.2, 6.9 Hz, 1H), 2.05 (m, 1H), 2.07 (s, 3H), 2.60 (t, J = 6.9 Hz, 2H), 3.63 (dd, J = 8.2, 5.0 Hz, 1H), 5.15 (d, J = 14.7 Hz, 1H), 5.18 (d, J = 15.1 Hz, 1H), 7.32-7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 30.4, 33.9, 53.4, 66.7, 128.3 (2C), 128.4, 128.6 (2C), 135.6, 175.6. IR (neat) 3378, 2916, 1733, 1605, 1497, 1455 1283, 1170 cm^{-1}. $[\alpha]_D^{25}$ = –8.8 (*c* 1.00, $CHCl_3$, 97% ee). Chiral HPLC analysis; OD-3 × 2, *n*-hexane/*i*-PrOH = 9/1, 1.0 mL/min, t_R = 30.2 min (minor, *D*), 32.7 min (major, *L*). HRMS (FAB+) calcd for $C_{12}H_{18}NO_2S$ $[M+H]^+$ 240.1058, found 240.1059.

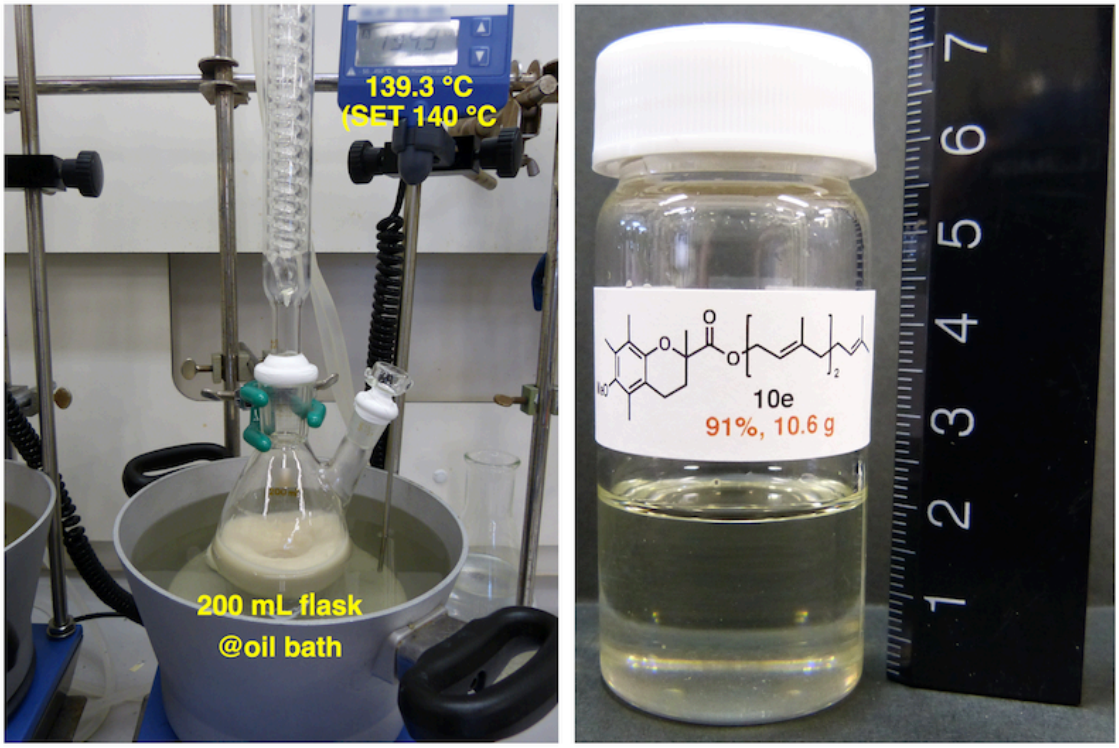
10. Gram scale synthesis of 10e (Scheme 3).



25 mmol, 6.96 g

10e
91%, 10.6 g

To a solution of tetramethylammonium methyl carbonate (**3d**) (223 mg, 1.5 mmol, 6 mol%) in toluene (100 mL), *trans,trans*-farnesol (6.34 mL, 25.0 mmol), methyl ester (6.96 g, 25.0 mmol), and well-dried MS 5Å (25 g) were added at room temperature. The mixture was heated under azeotropic reflux conditions (bath temperature 140 °C). After the azeotropic reflux for 3 h, the reaction mixture was allowed to cool to room temperature. To remove the catalyst and MS 5Å, reaction reaction mixture was filtered through flash silica pad using *n*-hexane–ethyl acetate (1:1) and the filtrate was concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 100:1 to 1:1) to give the desired product (10.61 g, 91% yield). See Figure S3 for this reaction.

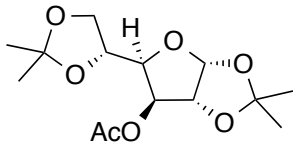


200 mL reactor

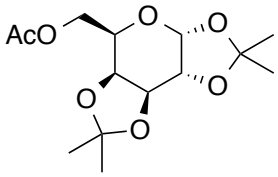
Obtained product **10e** (10.6 g)

Figure S3. Gram scale synthesis of **10e**.

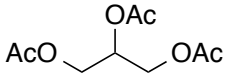
11. Products in Scheme 4.



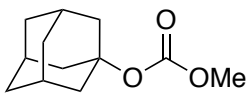
3-*O*-Acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (10o):[24] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.33 (s, 3H), 1.41 (s, 3H), 1.52 (s, 3H), 2.11 (s, 3H), 4.00-4.10 (m, 2H), 4.19-4.25 (m, 2H), 4.50 (d, *J* = 3.7 Hz, 1H), 5.25 (d, *J* = 2.3 Hz, 1H), 5.88 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 25.3, 26.2, 26.8, 26.9, 67.2, 72.5, 76.2, 79.7, 83.4, 105.1, 109.4, 112.3, 169.7. IR (KBr) 2993, 1748, 1374, 1228, 1077, 1025 cm^{-1}. M.p. 57-60 °C. HRMS (FAB+) calcd for $C_{14}H_{22}NaO_7$ $[M+Na]^+$ 325.1258, found 325.1266.



6-*O*-Acetyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (10p):[25] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 3H), 1.34 (s, 3H), 1.45 (s, 3H), 1.52 (s, 3H), 2.09 (s, 3H), 4.03 (ddd, *J* = 7.8, 5.0, 1.8 Hz, 1H), 4.19 (dd, *J* = 11.9, 7.8 Hz, 1H), 4.24 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.29 (dd, *J* = 11.9, 4.6 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.8 Hz, 1H), 4.62 (dd, *J* = 8.2, 2.8 Hz, 1H), 5.55 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 24.5, 25.0, 25.9, 26.0, 63.5, 65.9, 70.4, 70.7, 71.1, 96.3, 108.8, 110.0, 171.0. IR (KBr) 3468, 1762, 1458, 1211 cm^{-1}. M.p. 109-110 °C. HRMS (FAB+) calcd for $C_{14}H_{22}NaO_7$ $[M+Na]^+$ 325.1258, found 325.1275.

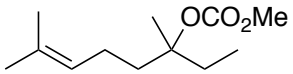


Propane-1,2,3-triyl triacetate (10q):[26] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 6H), 2.10 (s, 3H), 4.16 (dd, *J* = 11.9, 6.0 Hz, 2H), 4.30 (dd, *J* = 11.9, 4.1 Hz, 2H), 5.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (2C), 20.8, 62.2 (2C), 69.0, 170.0, 170.4 (2C). IR (neat) 3468, 1743, 1644, 1372, 1222, 1049 cm^{-1}. HRMS (ESI+) calcd for $C_9H_{14}NaO_6$ $[M+Na]^+$ 241.0683, found 241.0676.

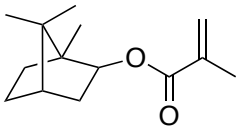


1-Adamantyl methyl carbonate (10r):[27] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.11 (s, 6H), 2.19 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8 (3C), 35.9 (3C), 40.9

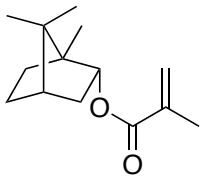
(3C), 53.7, 81.7, 153.5. IR (KBr) 2911, 1744, 1445, 1311, 1254, 1045 cm^{-1}. M.p. 101-103 °C. HRMS (FAB+) calcd for $C_{12}H_{19}O_3$ $[M+H]^+$ 211.1334, found 211.1335.



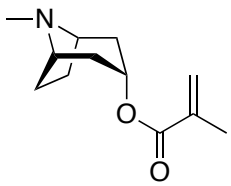
Dihydrolinaloyl methyl carbonate (10s):[27] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.8 Hz, 3H), 1.43 (s, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 1.70–2.04 (m, 6H), 3.70 (s, 3H), 5.09 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.8, 17.4, 22.1, 22.8, 25.5, 30.5, 37.3, 53.8, 86.4, 123.7, 131.7, 153.8. IR (neat) 2973, 1744, 1440, 1377, 1263 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{22}NaO_3$ $[M+Na]^+$ 237.1467, found 237.1465.



Isobornyl methacrylate (10t):[28] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 0.86 (s, 3H), 1.02 (s, 3H), 1.07-1.21 (m, 2H), 1.57 (m, 1H), 1.67-1.88 (m, 4H), 1.93 (s, 3H), 4.71 (m, 1H), 5.52 (d, *J* = 1.4 Hz, 1H), 6.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 18.4, 19.9, 20.1, 27.1, 33.7, 38.9, 45.1, 47.0, 48.9, 81.2, 125.0, 136.9, 166.9. IR (neat) 2955, 2879, 1717, 1638, 1455, 1327, 1298, 1163, 1054 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{22}NaO_2$ $[M+Na]^+$ 245.1517, found 245.1509.

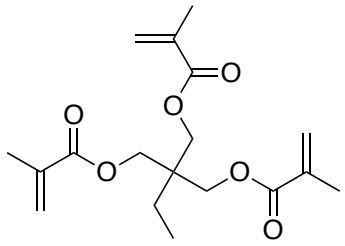


Bornyl methacrylate (10u):[29] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (s, 3H), 0.89 (s, 3H), 0.93 (s, 3H), 1.01 (dd, *J* = 13.7, 3.2 Hz, 1H), 1.21-1.38 (m, 2H), 1.70 (t, *J* = 4.6 Hz 1H), 1.76 (m, 1H), 1.96 (s, 3H), 1.98 (m, 1H), 2.40 (m, 1H), 4.92 (ddd, *J* = 10.1, 3.2, 2.3 Hz, 1H), 5.55 (t, *J* = 1.4 Hz, 1H), 6.12 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 18.4, 18.9, 19.8, 27.3, 28.1, 36.9, 45.0, 47.8, 49.0, 80.2, 125.0, 136.9, 167.8. IR (neat) 2955, 2880, 1718, 1454, 1326, 1303, 1173 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{20}NaO_2$ $[M+Na]^+$ 245.1517, found 245.1523.

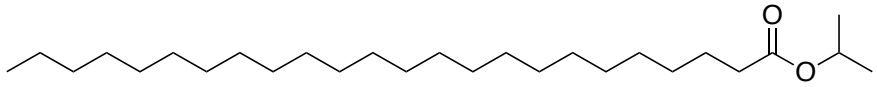


(1*R*,3*r*,5*S*)-8-Methyl-8-azabicyclo[3.2.1]octan-3-yl methacrylate (10v): Colorless oil. ^1H NMR

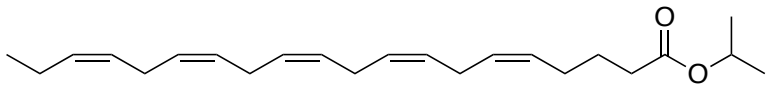
(400 MHz, $CDCl_3$) δ 1.73 (d, *J* = 15.0 Hz, 2H), 1.91-2.10 (m, 4H), 1.96 (s, 3H), 2.15 (dt, *J* = 15.0, 4.1 Hz, 2H), 2.29 (s, 3H), 3.11 (brs, 2H), 5.06 (t, *J* = 5.3 Hz, 1H), 5.57 (s, 1H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 25.7 (2C), 36.7 (2C), 40.5 (2C), 59.8, 67.7, 125.2, 136.9, 166.7. IR (neat) 2943, 1715, 1448, 1316, 1296, 1170, 1063, 1036 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{20}NO_2$ [M+H]+ 210.1494, found 210.1485.



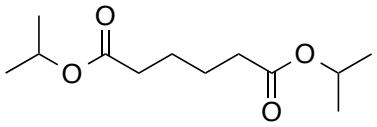
2-Ethyl-2-((methacryloyloxy)methyl)propane-1,3-diyl bis(2-methylacrylate) (10w):[30] Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.8 Hz, 3H), 1.58 (q, *J* = 7.8 Hz, 2H), 1.94 (s, 9H), 4.16 (s, 6H), 5.58 (s, 3H), 6.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.5, 18.3 (3C), 23.5, 41.2, 64.4 (3C), 126.1 (3C), 136.0 (3C), 167.0 (3C). IR (neat) 2967, 1724, 1638, 1455, 1322, 1294, 1154 cm^{-1}. HRMS (FAB+) calcd for $C_{18}H_{26}NaO_6$ $[M+Na]^+$ 361.1627, found 361.1623.



Isopropyl tetracosanoate (10x):[31] White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.17-1.40 (m, 46H), 1.57-1.65 (m, 2H), 2.25 (t, *J* = 7.8 Hz, 2H), 5.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.9 (2C), 22.8, 25.1, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8 (13C), 32.0, 34.8, 67.4, 173.5. IR (KBr) 2915, 2848, 1735, 1473, 1463, 1382, 1175, 1115 cm^{-1}. M.p. 49-51 °C. HRMS (ESI+) calcd for $C_{27}H_{54}NaO_2$ $[M+Na]^+$ 433.4016, found 433.3997.

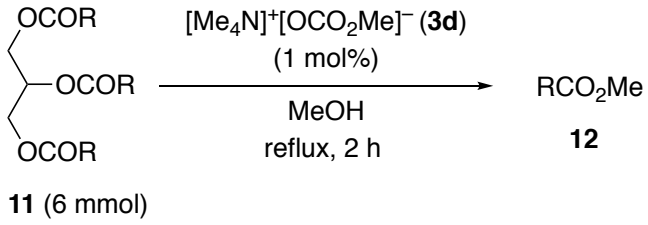


Isopropyl (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-icosa-5,8,11,14,17-pentaenoatee (10y): Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3H), 1.23 (d, *J* = 6.4 Hz, 6H), 1.69 (quintet, *J* = 7.3 Hz, 2H), 2.05-2.14 (m, 4H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.81-2.85 (m, 8H), 5.01 (m, 1H), 5.28-5.43 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.6, 21.9 (2C), 24.9, 25.6, 25.7 (3C), 26.6, 34.1, 67.5, 127.1, 127.9, 128.2 (2C), 128.3, 128.4, 128.6, 128.8, 129.1, 132.1, 173.2. IR (neat) 3012, 2965, 2933, 1732, 1455, 1373, 1178, 1110 cm^{-1}. HRMS (FAB+) calcd for $C_{23}H_{37}O_2$ $[M+H]^+$ 345.2794, found 345.2785.

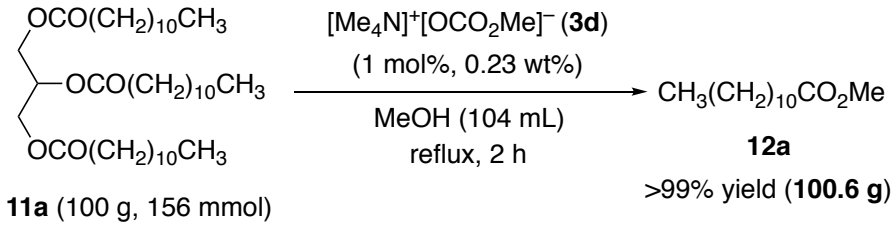


Diisopropyl adipate (10z):[32] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, J = 6.0 Hz, 12H), 1.63-1.67 (m, 4H), 2.26-2.31 (m, 4H), 5.00 (septet, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8 (4C), 24.4 (2C), 34.2 (2C), 67.4 (2C), 172.8 (2C). IR (neat) 2980, 1732, 1375, 1180, 1109 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{22}NaO_4^+$ $[M+Na]^+$ 253.1410, found 253.1419.

12. Transesterification of triglycerides 11 in methanol (Scheme 5).



To a suspension of ammonium salt **3d** (9.0 mg, 0.060 mmol, 1 mol%) in methanol (99 mmol, 4 mL for **11a** (1.5 *M*); 148 mmol, 6 mL for **11b** (1.0 *M*)), tryglyceride **11** (6.0 mmol) was added at room temperature. The mixture was stirred under reflux conditions (bath temperature 90 °C), by checking TLC, for 2 h. After cooling to room temperature, water (30 mL) was added to the concentrated mixture, and the organic layer was extracted with ethyl acetate (30 mL × 3). Catalyst and released glycerol were completely removed through this extraction. The organic layer was washed with brine (30 mL) and combined extracts were dried over Na_2SO_4. The organic phase was concentrated under reduced pressure to give the desired product **12**.



To a suspension of ammonium salt **3d** (233 mg, 1.56 mmol, 1 mol%, 0.23 wt. %) in methanol (2.57 mol, 104 mL, 1.5 *M* based on **11a**), trilaurin **11a** (100 g, 156 mmol) was added at room temperature. The mixture was stirred under reflux conditions (bath temperature 90 °C), by checking TLC, for 2 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. Water (150 mL) was added to the concentrated mixture, and the organic layer was extracted with ethyl

acetate (100 mL × 3). Catalyst and released glycerol were completely removed through this extraction. The organic layer was washed with brine (100 mL) and combined extracts were dried over Na_2SO_4. The organic phase was concentrated under reduced pressure to give the desired product **12a** (>99% yield, 100.6 g).

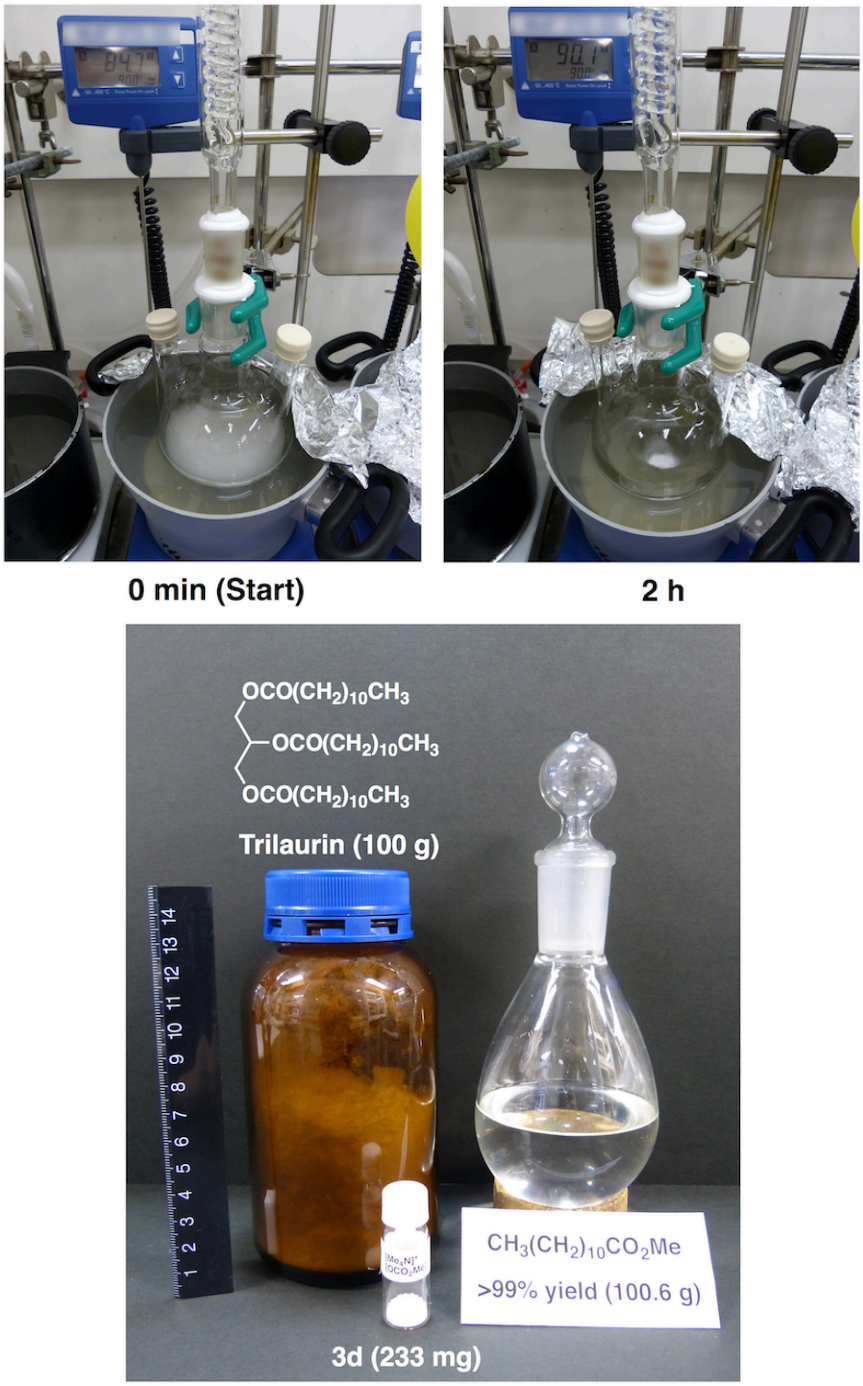
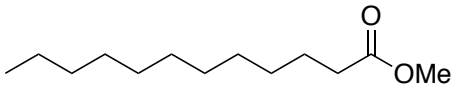
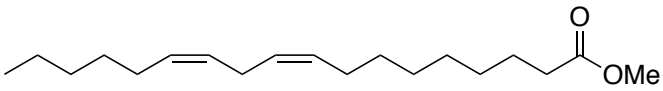


Figure S4. Gram scale synthesis of **12a**.

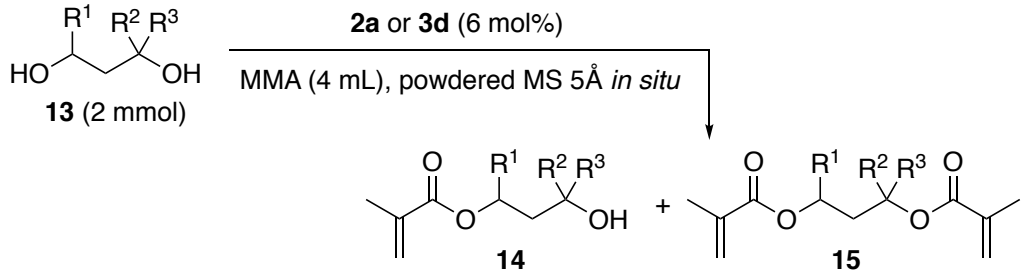


Methyl dodecanoate (12a):[33] With the use of 1 mol% of catalyst **3d** (0.23 wt. %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3H), 1.20-1.36 (m, 16H), 1.62 (quintet, J = 7.3 Hz, 2H), 2.30 (t, J = 7.3 Hz, 2H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 25.0, 29.2, 29.3, 29.4, 29.5, 29.7 (2C), 32.0, 34.2, 51.5, 174.4. IR (neat) 2925, 2854, 1743, 1465, 1436, 1197, 1171 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{26}O_2$ $[M]^+$ 214.1933, found 214.1939.



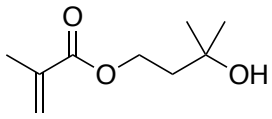
Methyl linoleate (12b):[34] With the use of 1 mol% of catalyst **3d** (0.17 wt. %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 6.4 Hz, 3H), 1.24-1.40 (m, 14H), 1.62 (quintet, J = 7.3 Hz, 2H), 2.05 (q, J = 6.9 Hz, 4H), 2.30 (t, J = 7.3 Hz, 2H), 2.77 (t, J = 6.4 Hz, 2H), 3.67 (s, 3H), 5.29-5.43 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 25.0, 25.7, 27.3 (2C), 29.1 (2C), 29.2, 29.4, 29.7, 31.6, 34.2, 51.5, 128.0, 128.1, 130.1, 130.3, 174.4. IR (neat) 3009, 2927, 2855, 1742, 1464, 1436, 1196, 1171 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{34}O_2$ $[M]^+$ 294.2559, found 294.2551.

13. Transesterification of diols 11 in MMA (Scheme 6).

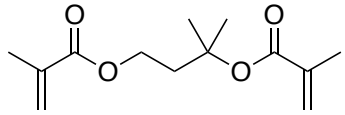


[Selective mono-transesterification by using catalyst 2a] To a suspension of phosphonuium salt **2a** (55.8 μL, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in MMA (38 mmol, 4 mL, unless otherwise noted), diol **13** (2 mmol) and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at that temperature, by checking TLC. After the removal of the most of MMA under reduced pressure, the rough yield was determined by ^{1}H NMR analysis based on 4,4'-di-*tert*-butylbiphenyl as an internal standard. The resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 50:1 to 10:1) to give the desired product **14**.

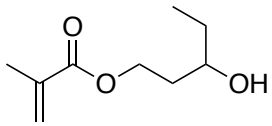
[Selective di-transesterification by using catalyst 3d] To a suspension of ammonium salt **3d** (17.9 mg, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in MMA (38 mmol, 4 mL, unless otherwise noted), diol **13** (2 mmol) and 4,4'-di-*tert*-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at 80 °C, by checking TLC. After the removal of the most of MMA under reduced pressure, the rough yield was determined by ^{1}H NMR analysis based on 4,4'-di-*tert*-butylbiphenyl as an internal standard. The resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 50:1 to 10:1) to give the desired product **15**.



3-Hydroxy-3-methylbutyl methacrylate (14a): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 6H), 1.90 (t, *J* = 6.9 Hz, 2H), 1.95 (dd, *J* = 1.4, 0.9 Hz, 3H), 4.34 (t, *J* = 6.9 Hz, 2H), 5.57 (quintet, *J* = 1.4 Hz, 1H), 6.09 (t, *J* = 1.4 Hz, 1H) [OH was not observed.]. ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 29.7 (2C), 41.6, 61.7, 70.0, 125.6, 136.3, 167.5. IR (neat) 3434, 2972, 1718, 1637, 1455, 1378 1326, 1300, 1168 cm^{-1}. HRMS (FAB+) calcd for $C_9H_{17}O_3$ $[M+H]^+$ 173.1178, found 173.1175.

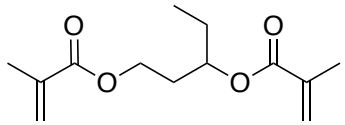


3-Methylbutane-1,3-diyl bis(2-methylacrylate) (15a): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 6H), 1.90 (t, *J* = 1.4 Hz, 3H), 1.93 (t, *J* = 1.4 Hz, 3H), 2.22 (t, *J* = 6.9 Hz, 2H), 4.27 (t, *J* = 6.9 Hz, 2H), 5.50 (quintet, *J* = 1.4 Hz, 1H), 5.55 (quintet, *J* = 1.4 Hz, 1H), 6.02 (t, *J* = 1.4 Hz, 1H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 18.4, 26.4 (2C), 39.3, 61.0, 81.0, 124.9, 125.6, 136.3, 137.6, 166.6, 167.4. IR (neat) 1716, 1637, 1454, 1331, 1298, 1142 cm^{-1}. HRMS (FAB+) calcd for $C_{13}H_{21}O_4$ $[M+H]^+$ 241.1440, found 241.1447.

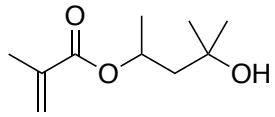


3-Hydroxypentyl methacrylate (14b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.45-1.56 (m, 2H), 1.72 (m, 1H), 1.87 (m, 1H), 1.95 (t, *J* = 1.4 Hz, 3H), 2.00 (d, *J* = 4.6 Hz, 1H), 3.63 (m, 1H), 4.24 (dt, *J* = 11.4, 5.5 Hz, 1H), 4.44 (ddd, *J* = 11.0, 8.7, 5.0 Hz, 1H), 5.58 (quintet, *J* = 1.4 Hz, 1H), 6.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 18.4, 30.3, 35.9, 62.1,

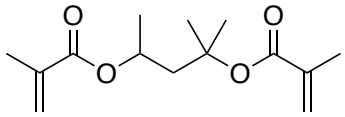
70.1, 125.7, 136.3, 167.8. IR (neat) 3427, 2964, 1717, 1637, 1456, 1323, 1299, 1172 cm^{-1}. HRMS (FAB+) calcd for $C_9H_{17}O_3$ $[M+H]^+$ 173.1178, found 173.1179.



Pentane-1,3-diyl bis(2-methylacrylate) (15b): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.67 (quintet, *J* = 6.9 Hz, 2H), 1.94 (s, 6H), 1.99 (q, *J* = 6.0 Hz, 2H), 4.16 (dt, *J* = 11.0, 6.9 Hz, 1H), 4.24 (dt, *J* = 11.0, 6.0 Hz, 1H), 5.02 (quintet, *J* = 6.0 Hz, 1H), 5.55 (quintet, *J* = 1.4 Hz, 2H), 6.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.4, 18.2, 18.3, 27.1, 32.5, 61.2, 72.6, 125.3, 125.5, 136.2, 136.5, 167.0, 167.3. IR (neat) 2970, 1719, 1637, 1454, 1322, 1296, 1165 cm^{-1}. HRMS (FAB+) calcd for $C_{13}H_{21}O_4$ $[M+H]^+$ 241.1440, found 241.1435.



4-Hydroxy-4-methylpentan-2-yl methacrylate (14c):[35] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 3H), 1.24 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.69 (dd, *J* = 14.7, 3.2 Hz, 1H), 1.94 (d, *J* = 0.9 Hz, 3H), 1.95 (m, 1H), 2.01 (s, 1H), 5.23 (m, 1H), 5.57 (t, *J* = 1.4 Hz, 1H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 21.8, 29.9 (2C), 49.1, 69.2, 70.1, 125.7, 136.7, 167.2. IR (neat) 3450, 2932, 1715, 1636, 1453, 1378, 1321, 1301, 1173, 1127 cm^{-1}. HRMS (FAB+) calcd for $C_{10}H_{19}O_3$ $[M+H]^+$ 187.1334, found 187.1341.



2-Methylpentane-2,4-diyl bis(2-methylacrylate) (15c):[35] 20 mL (189 mmol) of MMA (i.e., 0.1 *M* based on **13c**) was used. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, *J* = 6.0 Hz, 3H), 1.49 (s, 3H), 1.51 (s, 3H), 1.87 (d, *J* = 0.9 Hz, 3H), 1.91 (d, *J* = 0.9 Hz, 3H), 2.07 (dd, *J* = 15.1, 3.2 Hz, 1H), 2.30 (dd, *J* = 15.1, 8.7 Hz, 1H), 5.23 (m, 1H), 5.47 (t, *J* = 1.8 Hz, 1H), 5.53 (t, *J* = 1.8 Hz, 1H), 5.99 (d, *J* = 0.9 Hz, 1H), 6.06 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 18.5, 21.7, 26.4, 27.2, 45.8, 68.1, 81.3, 124.9, 125.4, 136.8, 137.8, 166.8, 166.9. IR (neat) 2980, 1715, 1637, 1453, 1377, 1331, 1302, 1181, 1127 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{23}O_4$ $[M+H]^+$ 255.1596, found 255.1603.

14. ^{1}H NMR experiments with ammonium catalyst and BnOH.

To determine whether or not the estimated active species $[R_4N]^+[OR']^-$ could be rapidly generated *in situ*, ^{1}H NMR (toluene-d_8) experiments were performed. Table S1 shows the results of $[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (**3a**) + BnOH (**5a**). Within 6 min at room temperature, $[Me(n\text{-octyl})_3N]^+[OBn]^-$ (**S1**) was generated in 87% conversion. After an additional 5 min at 50 °C, **S1** was observed in 93% conversion. In contrast, $[Me(n\text{-octyl})_3N]^+[Cl]^-$ (**S2**) + BnOH (**5a**) did not provide **S1** under the same conditions (Table S2). Overall, the active species would be quickly generated *in situ* under our standard reaction conditions.

Table S1. $[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (**3a**) + BnOH (**5a**).

$[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (**3a**) (1 equiv)
+
BnOH (**5a**) (1 equiv)
+
4,4'-di-*tert*-butylbiphenyl
(0.1 equiv as an internal standard)
+
MS 5Å

→ toluene-d_8 (0.5 *M*), ***fast***

$[Me(n\text{-octyl})_3N]^+[OBn]^-$ (**S1**)

^{1}H NMR analysis:
25 °C, 1 min: Figure S5c
+ 25 °C, 5 min: Figure S5d
+ 50 °C for 5 min: Figure S5e

entry	Conditions	**5a** (%)[a]	$[OCO_2Me]^-$ (%)[a]	**S1** (%)[a]
1	25 °C, 1 min	74	46	26
2	25 °C, 1 min + **25 °C, 5 min**	14	9	**87**
3	25 °C, 1 min + 25 °C, 5 min **+ 50 °C, 5 min**	8	1	**93**

[a] Distribution was determined by ^{1}H NMR based on internal standard.

Table S2. $[Me(n\text{-octyl})_3N]^+[Cl]^-$ (**S2**) + BnOH (**5a**).

$[Me(n\text{-octyl})_3N]^+[Cl]^-$ (**S2**) (1 equiv)
+
BnOH (**5a**) (1 equiv)
+
4,4'-di-*tert*-butylbiphenyl
(0.1 equiv as an internal standard)
+
MS 5Å

→ toluene-d_8 (0.5 *M*), ***slow***

$[Me(n\text{-octyl})_3N]^+[OBn]^-$ (**S1**)

^{1}H NMR analysis:
25 °C, 1 min: Figure S6c
+ 25 °C, 5 min: Figure S6d
+ 50 °C for 5 min: Figure S6e

entry	Conditions	**5a** (%)[a]	**S1** (%)[a]
1	25 °C, 1 min	105	**0**
2	25 °C, 1 min + 25 °C, 5 min	104	**0**
3	25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min	104	**0**

[a] Distribution was determined by ^{1}H NMR based on internal standard.

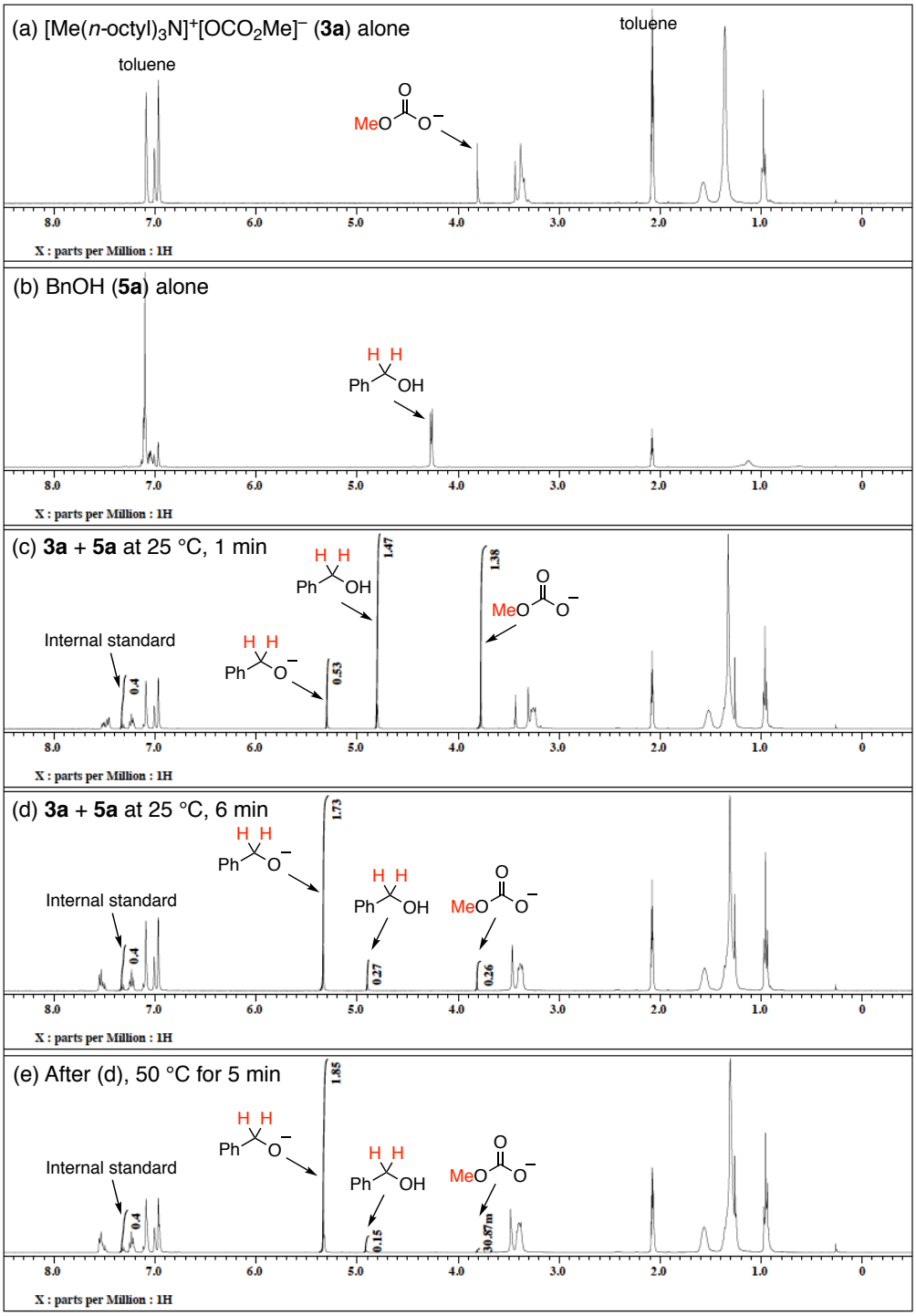


Figure S5. ^{1}H NMR experiment of [Me(*n*-octyl)$_3$N]$^+$[OCO$_2$Me]$^-$ (**3a**) + BnOH (**5a**). (a) **3a** at 25 °C. (b) **5a** at 25 °C. (c) **3a** + **5a** at 25 °C, 1 min. (d) **3a** + **5a** at 25 °C, 1 min + 25 °C, 5 min. (e) **3a** + **5a** at 25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min.

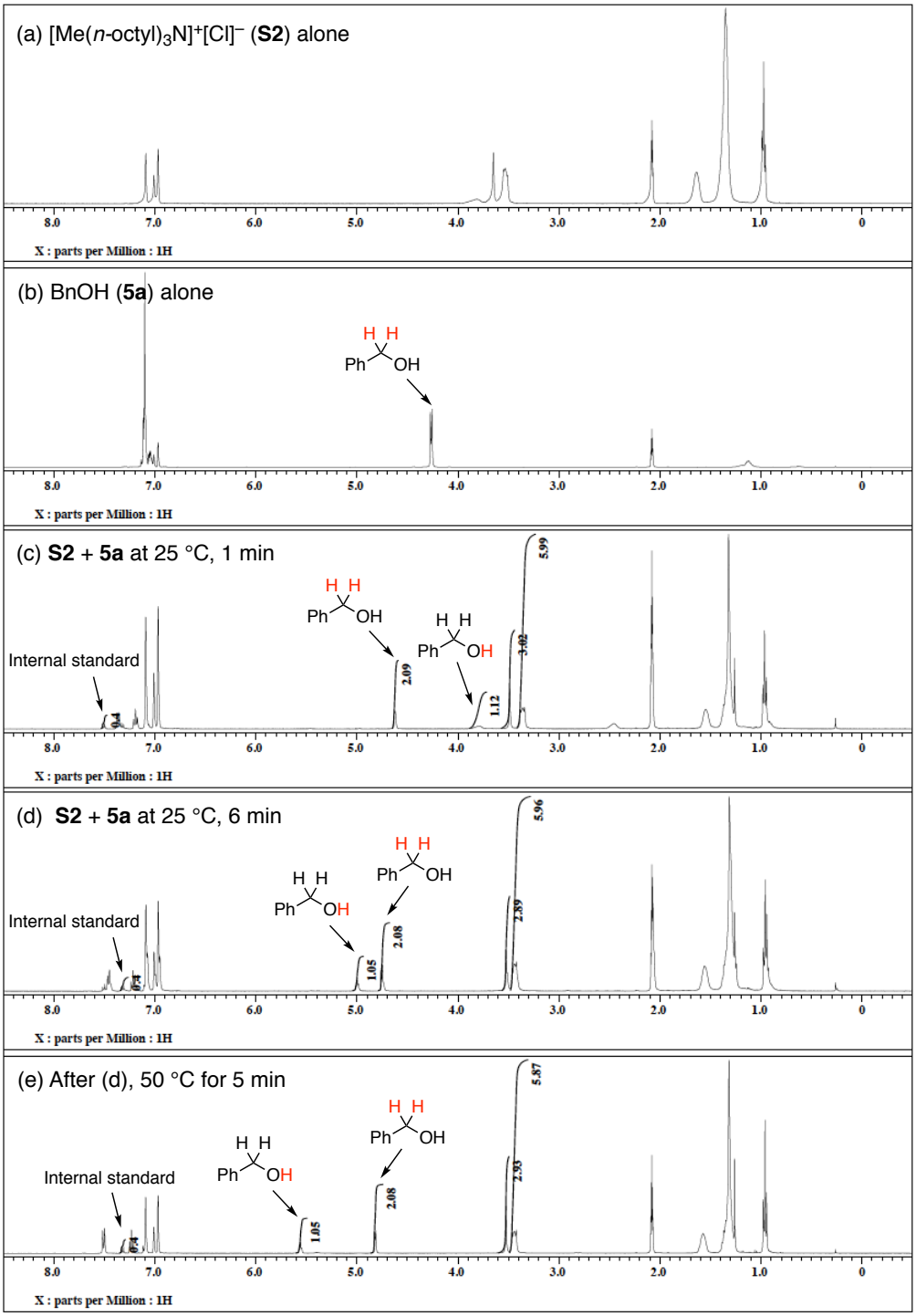


Figure S6. ^{1}H NMR experiment of [Me(*n*-octyl)$_3$N]$^+$[Cl]$^-$ (**S2**) + BnOH (**5a**). (a) **S2** at 25 °C. (b) **5a** at 25 °C. (c) **S2** + **5a** at 25 °C, 1 min. (d) **S2** + **5a** at 25 °C, 1 min + 25 °C, 5 min. (e) **S2** + **5a** at 25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min.

15. Decomposition of catalyst 3a in the reaction of 4b and cyclohexanol.

We monitored the reaction of methyl benzoate **4b** and cyclohexanol in toluene, *n*-hexane, or THF in the presence of catalyst $[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ **3a** under azeotropic reflux conditions. The results are shown in Figure S7. In toluene (bp. 110 °C), **3a** decomposed within 1 h, and the yield of product (68% yield) did not change after 1 h. *n*-Hexane (bp. 69 °C) and THF (bp. 66 °C) showed similar reaction curves, and we did not observe a clear sign of the decomposition of **3a** in either case. The reaction in *n*-hexane showed slightly better conversion than that in THF. Overall, catalyst **3a** would decompose at a relatively high reflux temperature, such as in hexane, whereas **3a** might be used without significant decomposition at a lower reflux temperature, such as in hexane or THF.

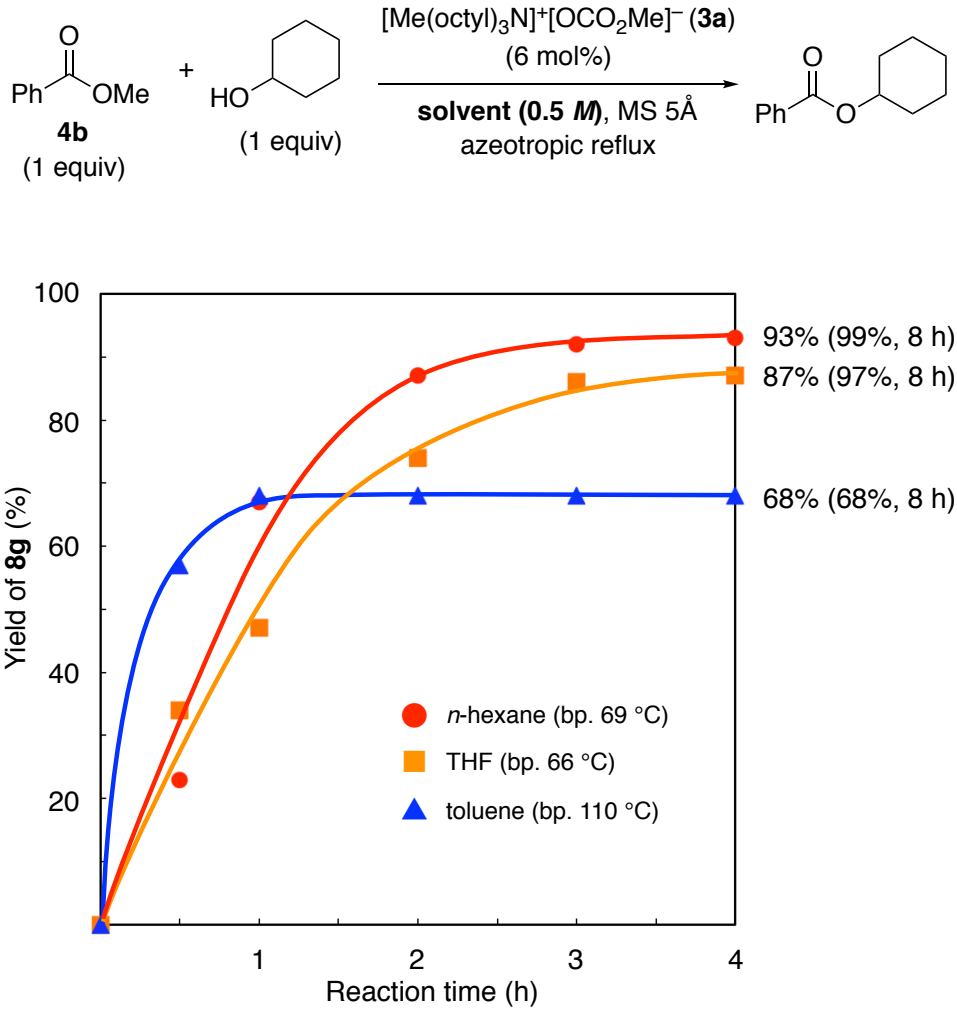
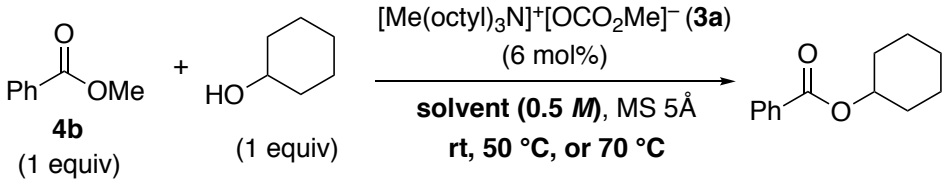


Figure S7. The reaction of **4b** and cyclohexanol with the use of **3a** in toluene, *n*-hexane, or THF.

16. Effect of the reaction temperature.

In the probe reaction of methyl benzoate **4b** and cyclohexanol, we examined the reaction temperature (room temperature, 50 °C, and 70 °C) in the same solvent (Figure S8). Figure S8a shows the results in *n*-hexane (bp. 69 °C), and Figure S8b shows the results in THF (bp. 66 °C). In both cases, at 70 °C (bath temperature), the reaction proceeded smoothly and was almost finished within 6–8 h. At 50 °C (bath temperature), the reaction also proceeded smoothly, but was still ongoing after 20 h. Although *n*-hexane and THF have different chemical properties, the progress of the reaction might strongly depend on the reaction temperature since the reaction curves in *n*-hexane and THF were quite similar. Unfortunately, these reactions did not proceed in *n*-hexane and THF at room temperature. This representative result at room temperature would not deny the possibility of reactions of any other substrates at room temperature, because other reactions, such as shown in Scheme 6 using MMA, could be demonstrated at room temperature. The reaction proceedings strongly depend on alcohols (1° > 2° > 3°) as well as esters (excess (solvent) > 1 equivalent).



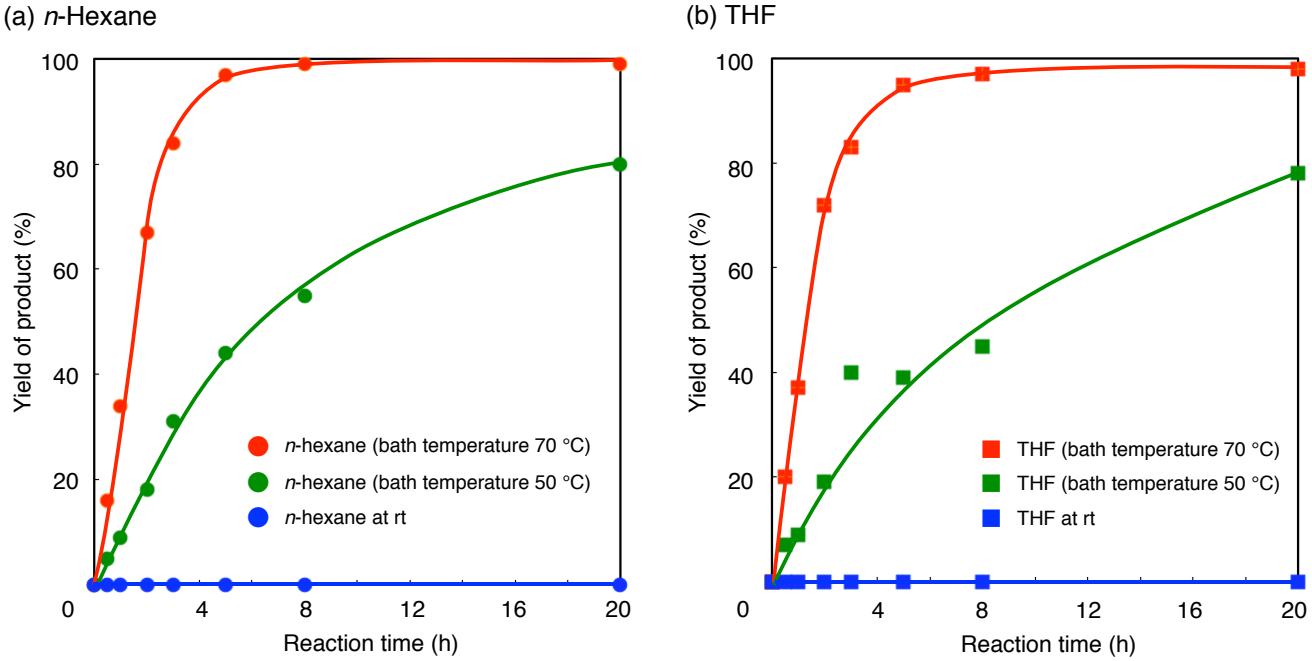
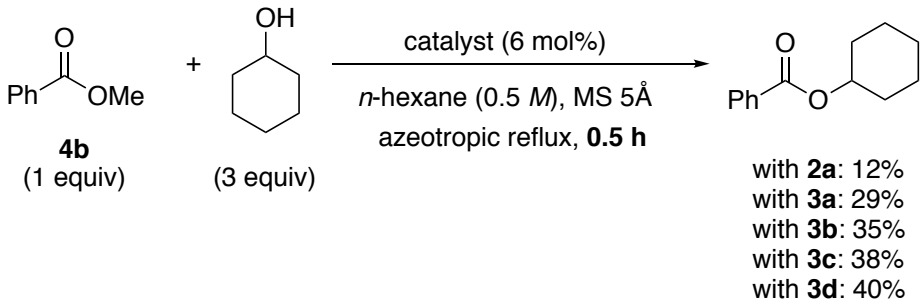


Figure S8. The reaction of **4b** and cyclohexanol with the use of **3a** in different temperatures in the same solvent (*n*-hexane and THF).

17. Screening of catalysts in *n*-hexane under azeotropic reflux conditions.

To exclude the effect of the decomposition of the catalysts and to evaluate only steric effects on the catalysts, we examined the reaction of **4b** (1 equiv) and cyclohexanol (3 equiv) in *n*-hexane (bp. 69 °C) under azeotropic reflux conditions. The reaction was interrupted at 30 min, although the reaction was still proceeding at that time. As a result, phosphonium salt **2a** was less effective than ammonium salts **3a–d**. Among ammonium salts **3a–d**, the yield was in the order **3a** < **3b** < **3c** < **3d**. This order might agree with the size of the ammonium salts. Figure S9 summarized the results. Also see the screening of catalysts in toluene (bp. 111 °C).



Conclusion: The order of catalytic activity and chemical stability are both in the order **3a** < **3b** < **3c** < **3d**.

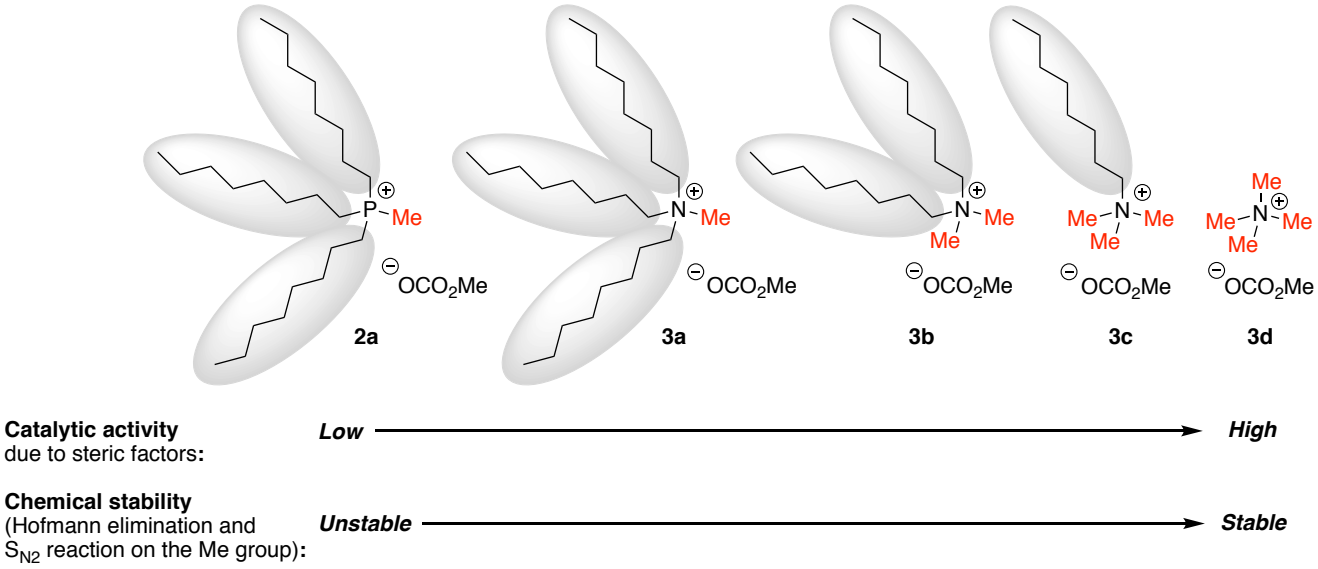
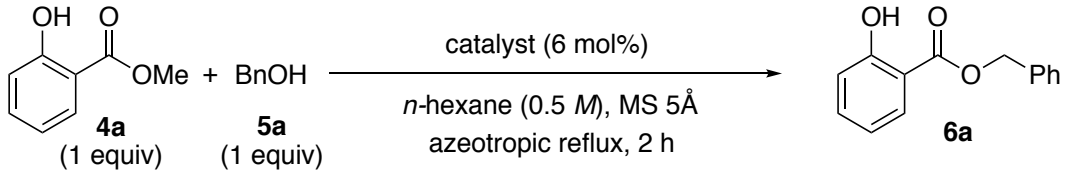


Figure S9. The order of catalytic activity.

18. General catalyst screening.

Catalyst screening was conducted in a probe reaction between methyl salicylate **4a** and benzyl alcohol **5a** (Table S3, also see Table 1 in the paper). The present optimum ammonium salt **3d** was also effective as well as **3a** (entries 4 and 5). Basic metal salt catalysts, such as NaO*t*-Bu, $NaOC_6H_4$(4-*t*-Bu), and KO*t*-Bu, gave **6a** in low to moderate yields (12–54%) (entries 6–9). Brønsted acid catalysts, such as *p*-TsOH and TfOH, were not effective (entries 10 and 11). Acidic metal salt catalysts, such as Sc(III), Ti(IV), Mn(II), Fe(II)/(III), Cu(II), Zn(II), Zr(IV), La(III), and Hf(IV), were not effective (entries 11–25).

Table S3. Screening of catalysts.[a]

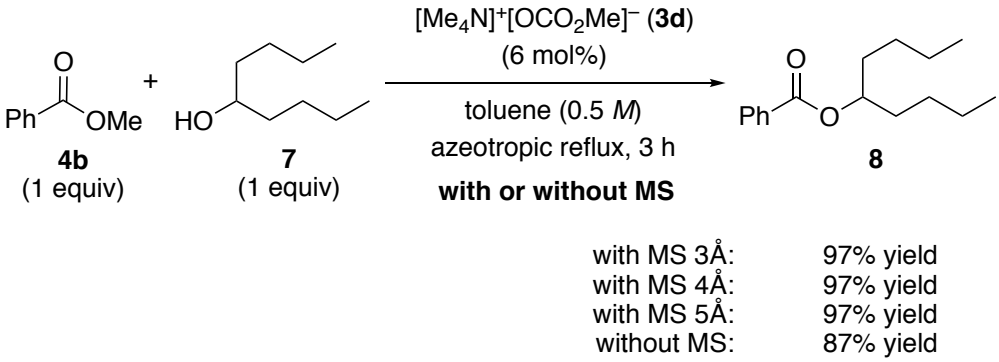


Entry	Catalyst	Yield (%)
1	1/2 La(O*i*-Pr)$_3$ + HO(CH_2CH_2O)$_2$Me	2
2	1/2 La(NO_3)$_3$·H_2O (**1**) + [Me(*n*-octyl)$_3$P]$^+$[OCO_2Me]$^-$ (**2a**)	1
3	[Me(*n*-octyl)$_3$P]$^+$[OCO_2Me]$^-$ (**2a**)	87 (71)[b]
4	**[Me(*n*-octyl)$_3$N]$^+$[OCO_2Me]$^-$ (3a)**	**90 (78)[b]**
5	**[Me_4N]$^+$[OCO_2Me]$^-$ (3d)**	**92 (79)[b] (90)[c]**
6	NaO*t*-Bu	12
7	$NaOC_6H_4$(4-*t*-Bu)	45
8	KO*t*-Bu	54
9	*p*-TsOH	1
10	TfOH	0
11	Sc(OTf)$_3$	0
12	Ti(O*i*-Pr)$_4$	17
13	$TiCl_4$	0
14	Mn(OAc)$_2$	0
15	Fe(OTf)$_2$	0
16	Fe(OTf)$_3$	0
17	Cu(OAc)$_2$	0
18	Zn(OAc)$_2$	0
19	Zn($OCOCF_3$)$_2$	2
20	Zn_4($OCOCF_3$)$_6$O	7
21	$ZnCl_2$	0
22	Zn(OTf)$_2$	0
23	La(OTf)$_3$	0
24	$ZrCl_4$·(thf)$_2$	6
25	$HfCl_4$·(thf)$_2$	9

[a] The reaction was carried out with **4a** (2 mmol), **5a** (2 mmol), and catalyst (6 mol%) in *n*-hexane at 90 °C (bath temperature) for 2 h under azeotropic reflux conditions with MS 5Å. [b] Yield of **6a** for 30 min. [c] Reaction was conducted in the presence of 1 mol% of **3d** for 1 h.

19. Effect of molecular sieves.

We examined whether or not molecular sieves (MS) are necessary in a probe reaction of **4b** and **7** with the use of catalyst **3d** (Scheme S3). As a result, **8** was obtained in 97% yield in the presence of MS 5Å, while **8** was obtained in 87% yield in the absence of MS 5Å. Therefore, MS 5Å is necessary in this equilibrium reaction to remove methanol. We consistently used MS 5Å, although MS 3Å and MS 4Å showed the same performance (97% yield).



Scheme S3. Effect of molecular sieves.

20. References.

1 M. Fabris, V. Lucchini, M. Noé, A. Perosa, M. Selva, *Chem. Eur. J.* **2009**, *15*, 12273.

2 M. Hatano, S. Kamiya, K. Ishihara, *Chem. Commun.* **2012**, *48*, 9465.

3 R. H. G. Brinkhuis, J. A. J. Schutyser, P. J. Dolphijn, A. J. W. Buser, P. J. M. D. Elfrink, M. A. G. Gessner, PCT WO2011/124664A1, **2011**.

4 Z. M. Jászay, I. Petneházy, L. Töke, *Synthesis* **1989**, *1989*, 745.

5 D. Pfaff, G. Nemecek, J. Podlech, *Helv. Chim. Acta* **2012**, *95*, 1851.

6 S. Ko, C. Lee, M.-G. Choi, Y. Na, S. Chang, *J. Org. Chem.* **2003**, *68*, 1607.

7 K. Kishikawa, Y. Haga, T. Inoue, T. Watanabe, M. Takahashi, S. Kohmoto, *Chem. Lett.* **2012**, *41*, 1465.

8 Z. Zhu, J. Yuan, Y. Zhou, Y. Qin, J. Xu, Y. Peng, *Eur. J. Org. Chem.* **2014**, 511.

9 R. T. Wragg, *J. Chem. Soc.* **1965**, 7162.

10 I. Kubo, P. Xiao, K. Nihei, K. Fujita, Y. Yamagiwa, T. Kamikawa, *J. Agric. Food Chem.* **2002**, *50*, 3992.

11 R. J. DeLuca, M. S. Sigman, *Org. Lett.*, **2013**, *15*, 92.

12 R. Roudeau, D. G. Pardo, J. Cossy, *Tetrahedron* **2006**, *62*, 2388.

13 M. Hatano, Y. Furuya, T. Shimmura, K. Moriyama, S. Kamiya, T. Maki, K. Ishihara, *Org. Lett.* **2011**, *13*, 426.

14 J.-d'A. K. Twibanire, T. B. Grindley, *Org. Lett.* **2011**, *13*, 2988.

15 R. J. Kalbasi, A. R. Massah, Z. Barkhordari, *Bull. Korean Chem. Soc.* **2010**, *31*, 2361.

16 O. Chantarasriwong, D. O. Jang, W. Chavasiri, *Synth. Commun.* **2008**, *38*, 2845.

17 N. Wakita, S. Hara, *Tetrahedron* **2010**, *66*, 7939.

18 R. Horikawa, C. Fujimoto, R. Yazaki, T. Ohshima, *Chem. Eur. J.* **2016**, *22*, 12278.

19 E. Mutschler, H. Scherf, O. Wassermann, *Arzneimittelforschung* **1967**, *17*, 833.

20 J. Xu, P. Zhang, X. Li, Y. Gao, J. Wu, G. Tang, Y. Zhao, *Adv. Synth. Catal.* **2014**, *356*, 3331.

21 K. Anzai, J. Uzawa, *J. Org. Chem.* **1984**, *49*, 5076.

22 I. Dilek, M. Madrid, R. Singh, C. P. Urrea, B. A. Armitage, *J. Am. Chem. Soc.* **2005**, *127*, 3339.

23 R. S. Navath, K. B. Pabbisetty, L. Hu, *Tetrahedron Lett.* **2006***, 47*, 389.

24 C.-T. Chen, J.-H. Kuo, V. D. Pawar, Y. S. Munot, S.-S. Weng, C.-H. Ku, C.-Y. Liu, *J. Org. Chem.* **2005**, *70*, 1188.

25 D. Mukherjee, B. A. Shah, P. Gupta, S. C. Taneja, *J. Org. Chem.* **2007**, *72*, 8965.

26 A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi, K. Ishihara, *J. Am. Chem. Soc.* **2007**, *129*, 14775.

27 M. Hatano, S. Kamiya, K. Moriyama, K. Ishihara, *Org. Lett.* **2011**, *13*, 430.

28 E. R. Soulé, J. Borrajo, R. J. J. Williams, *Macromolecules* **2004**, *37*, 1551.

29 J.-H. Liu, H.-T. Liu, F.-R. Tsai, *Polym. Int.* **1997**, *42*, 385.

30 C. Nilsson, E. Malmström, M. Johansson, S. M. Trey, *J. Polym. Sci. Polym. Chem.* **2009**, *47*, 5815.

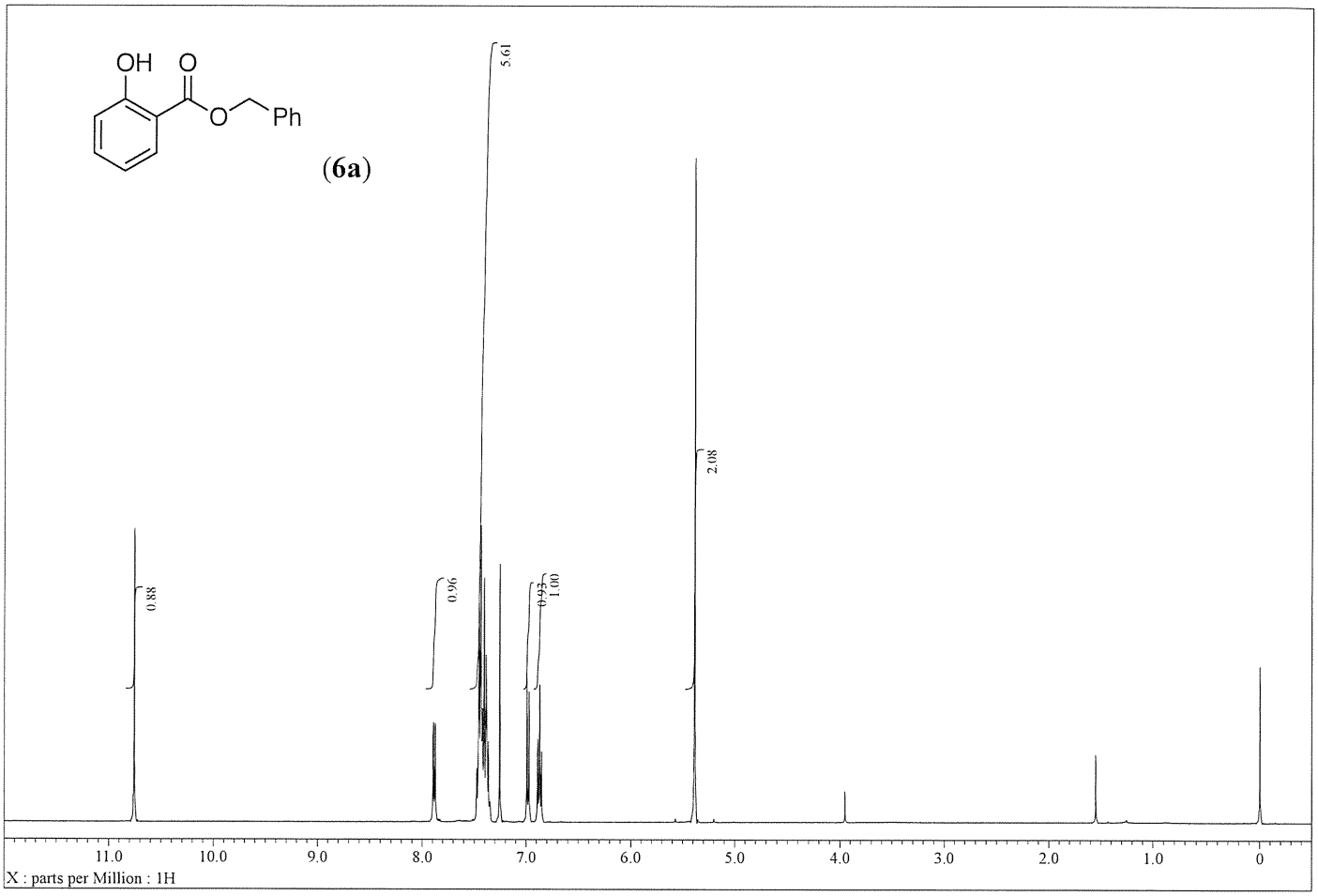
31 W. Schlenk, Jr. *Justus Liebigs Ann. Chem.* **1969**, *727*, 1.

32 Y. Hasegawa, C. Abe, F. Mizukami, Y. Kowata, T. Hanaoka, *J. Membrane Sci.* **2012**, *415–416*, 368.

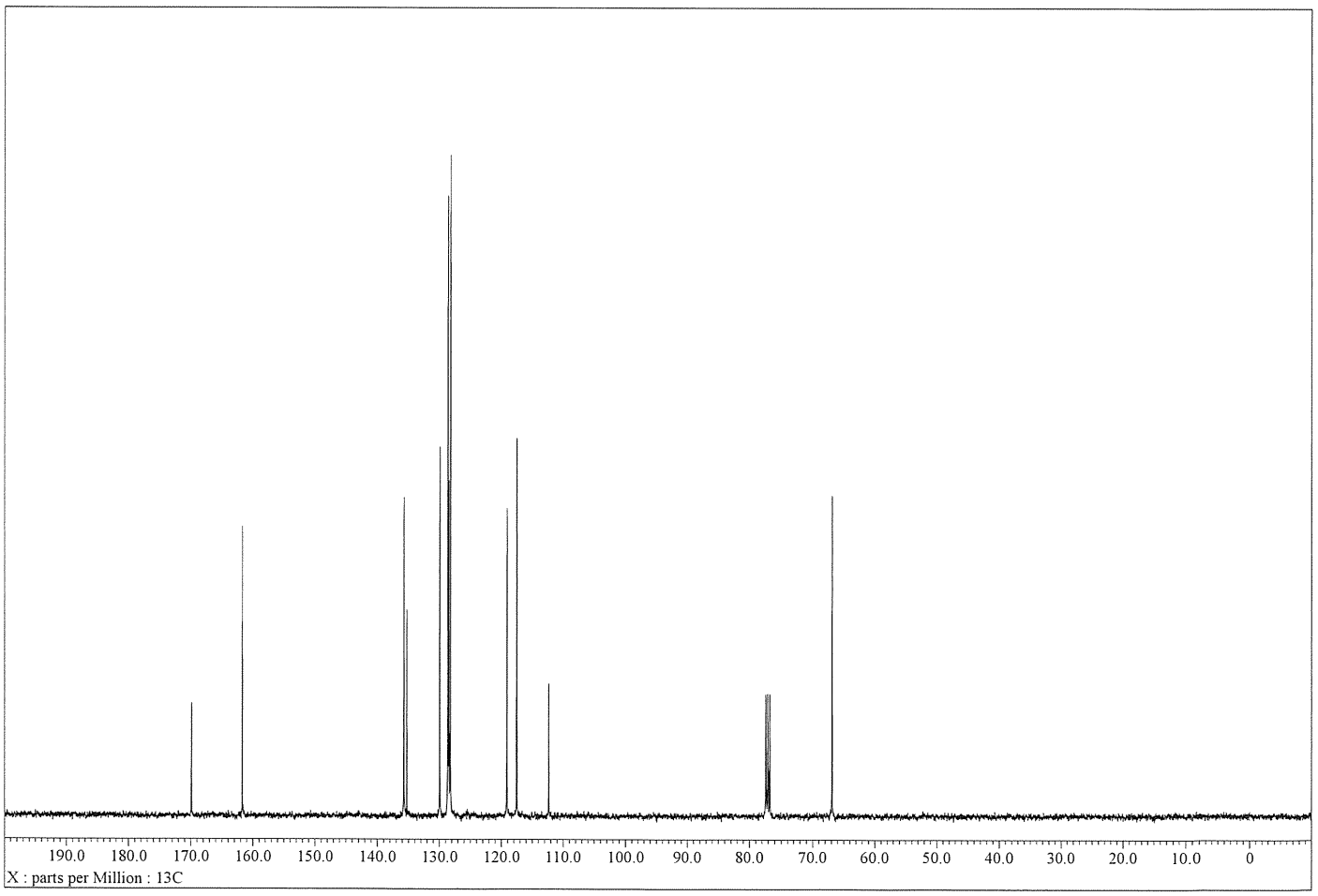
33 S. Bhunia, B. Banerjee, A. Bhaumik, *Chem. Commun.* **2015**, *51*, 5020.

34 J. Bus, I. Sies, M. S. F. L. K. Jie, *Chem. Phys. Lipids* **1976**, *17*, 501.

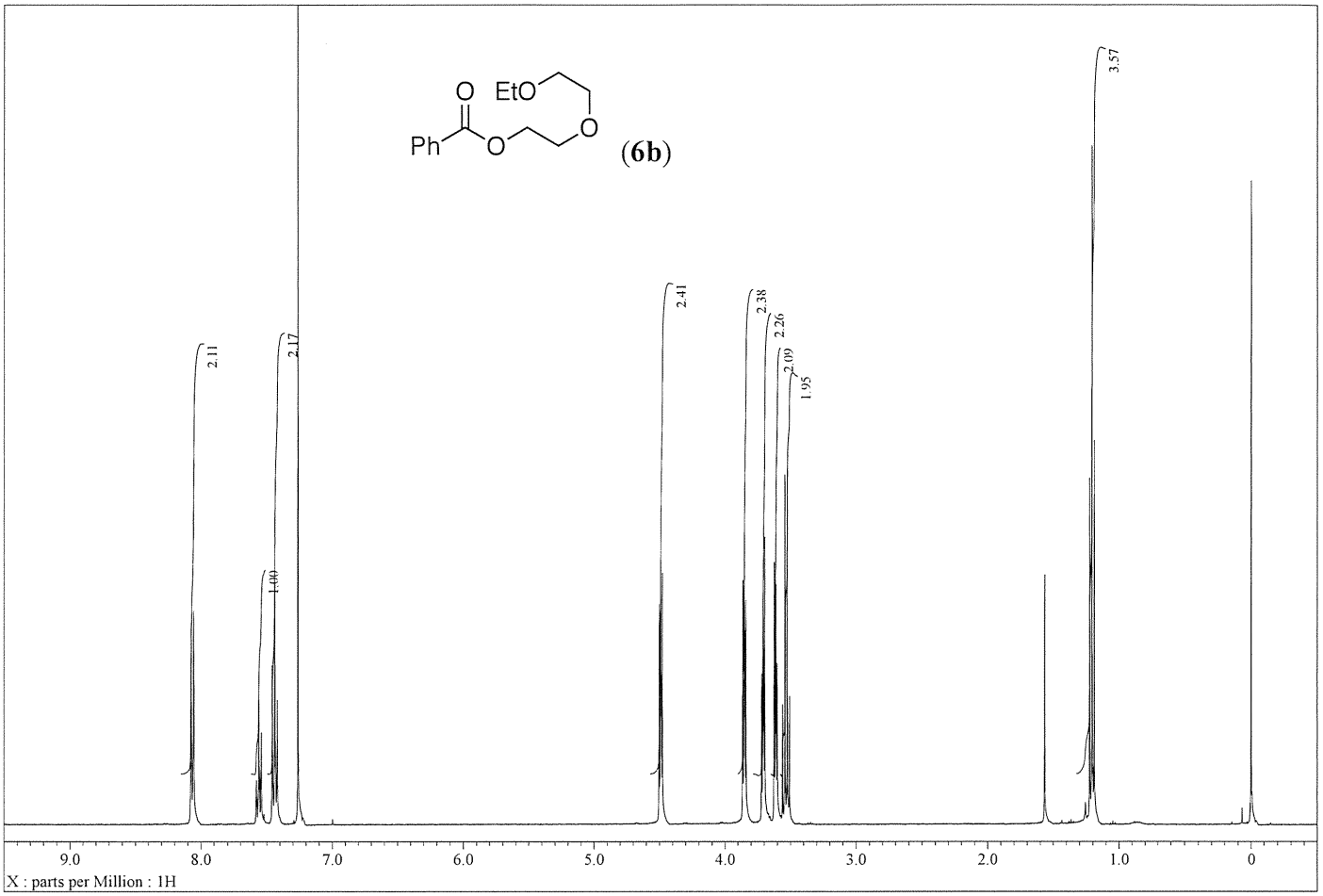
35 D. Kafouris, E. Themistou, C. S. Patrickios, *Chem. Mater.* **2006**, *18*, 85.



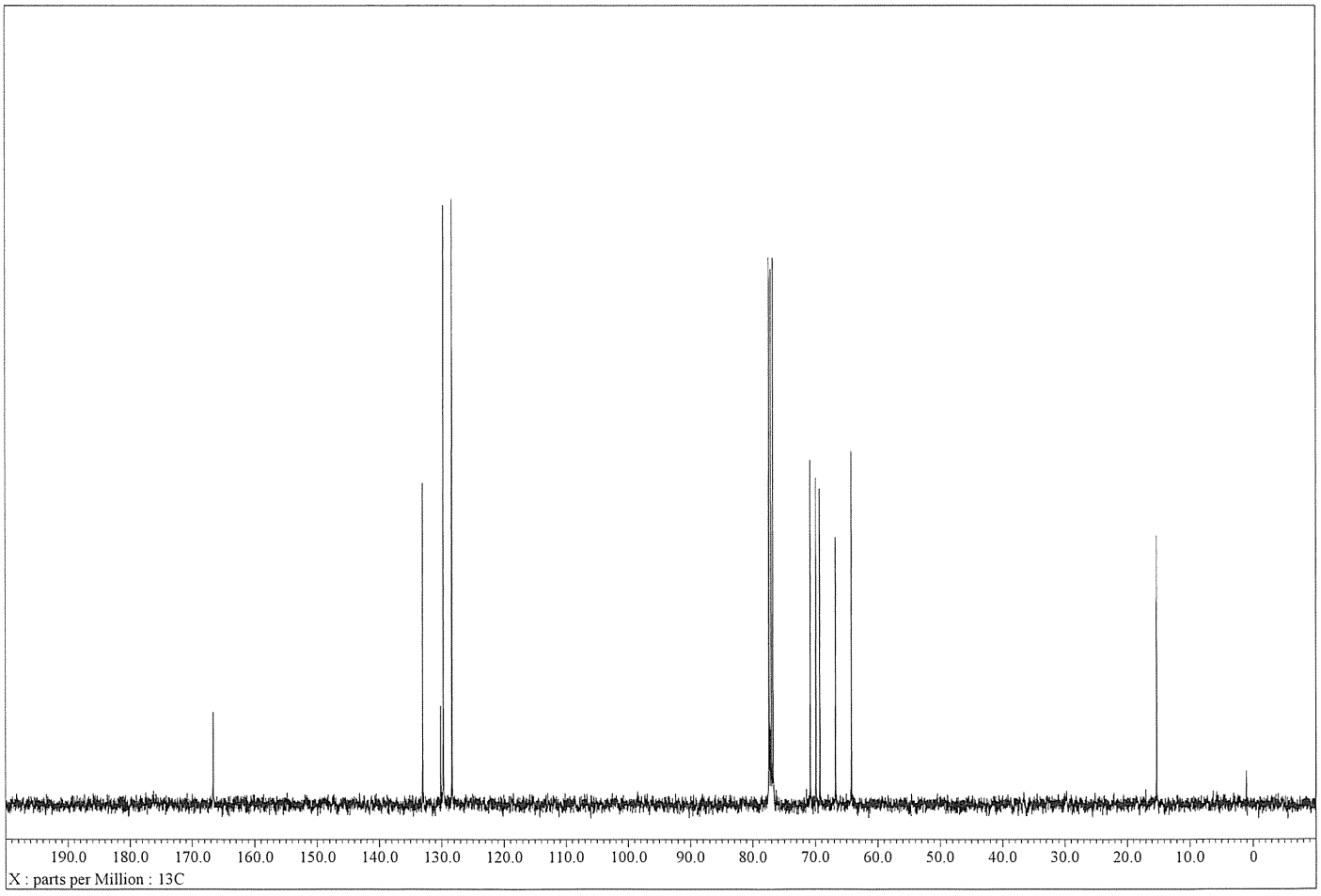
^{1}H NMR, 400 MHz, $CDCl_3$



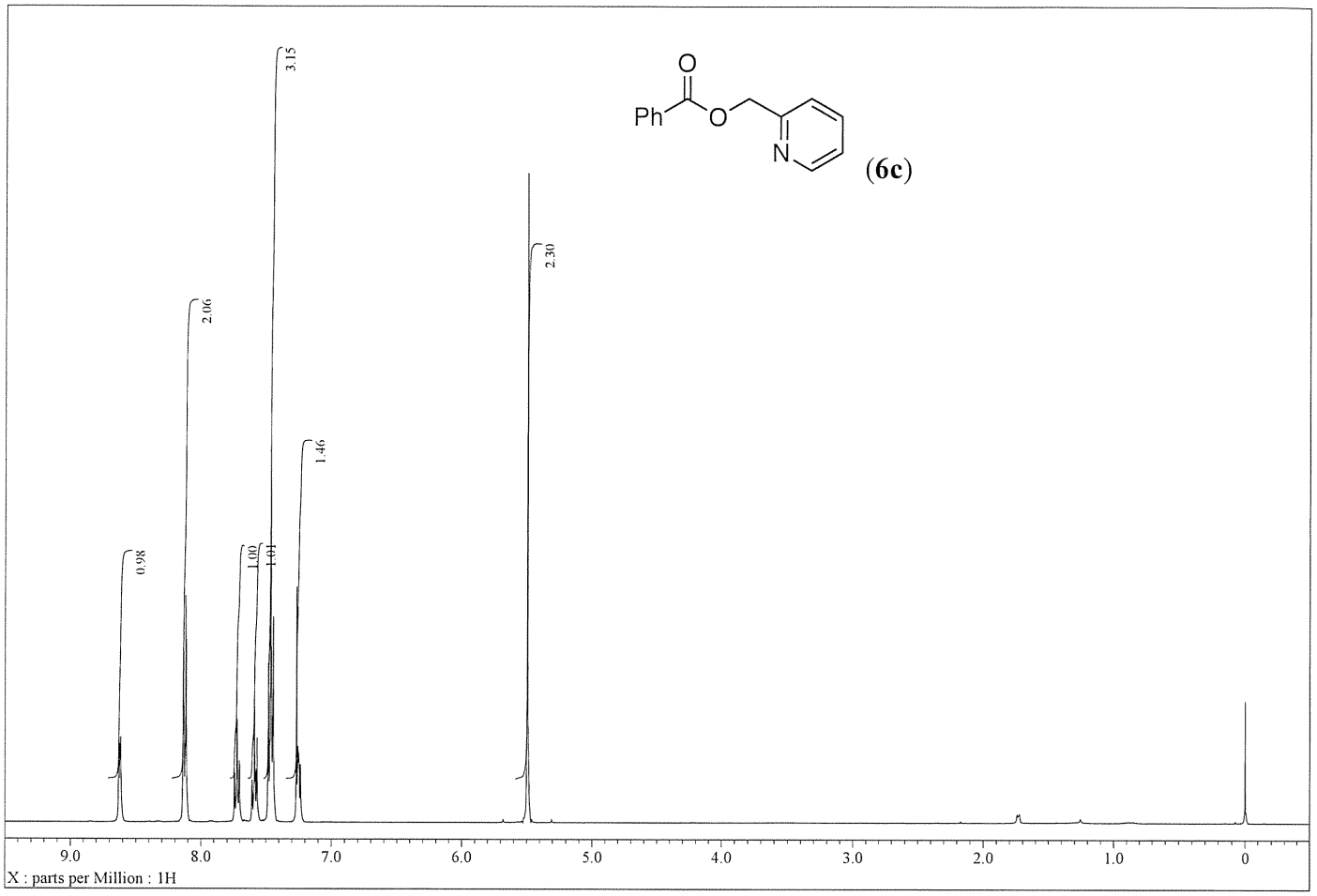
^{13}C NMR, 100 MHz, $CDCl_3$



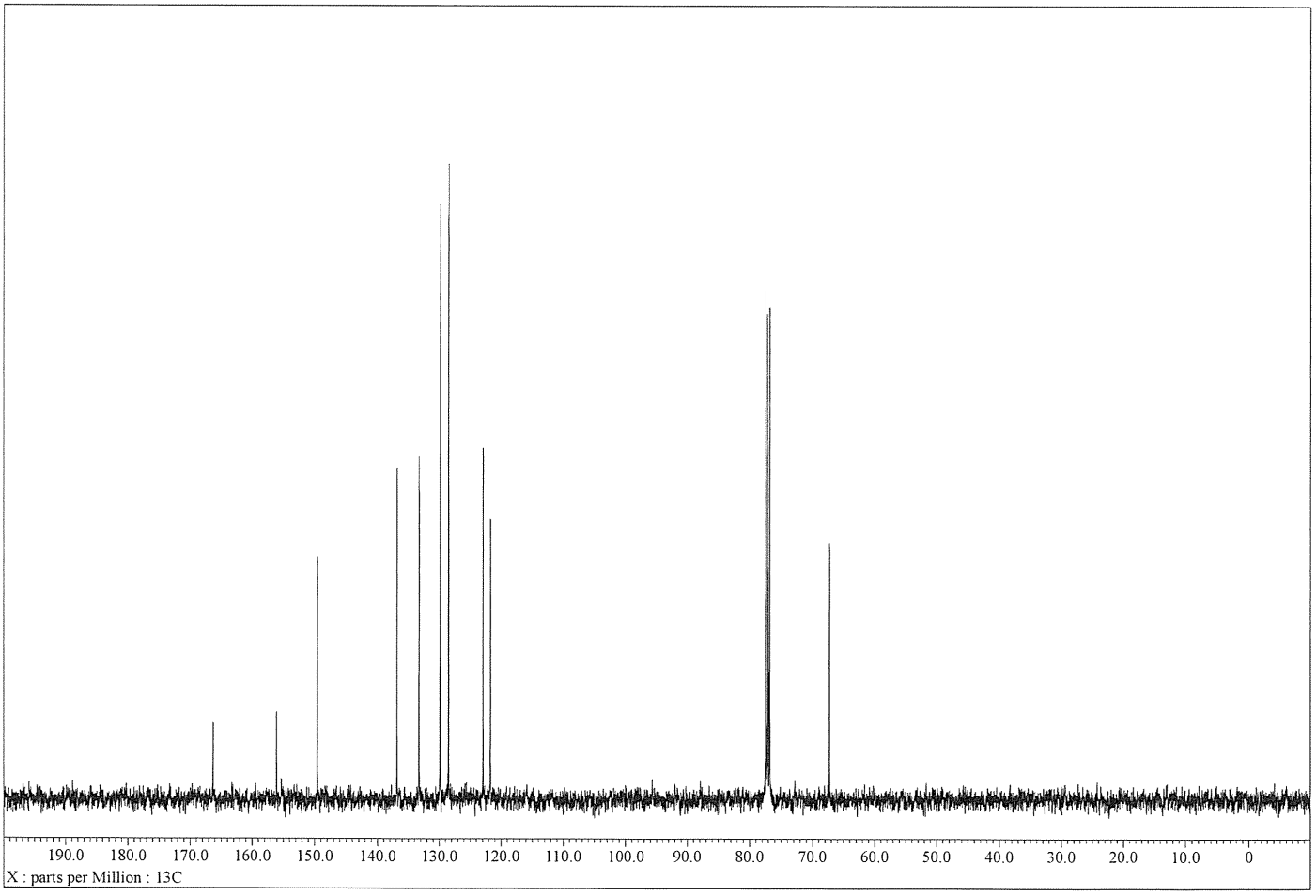
^{1}H NMR, 400 MHz, $CDCl_3$



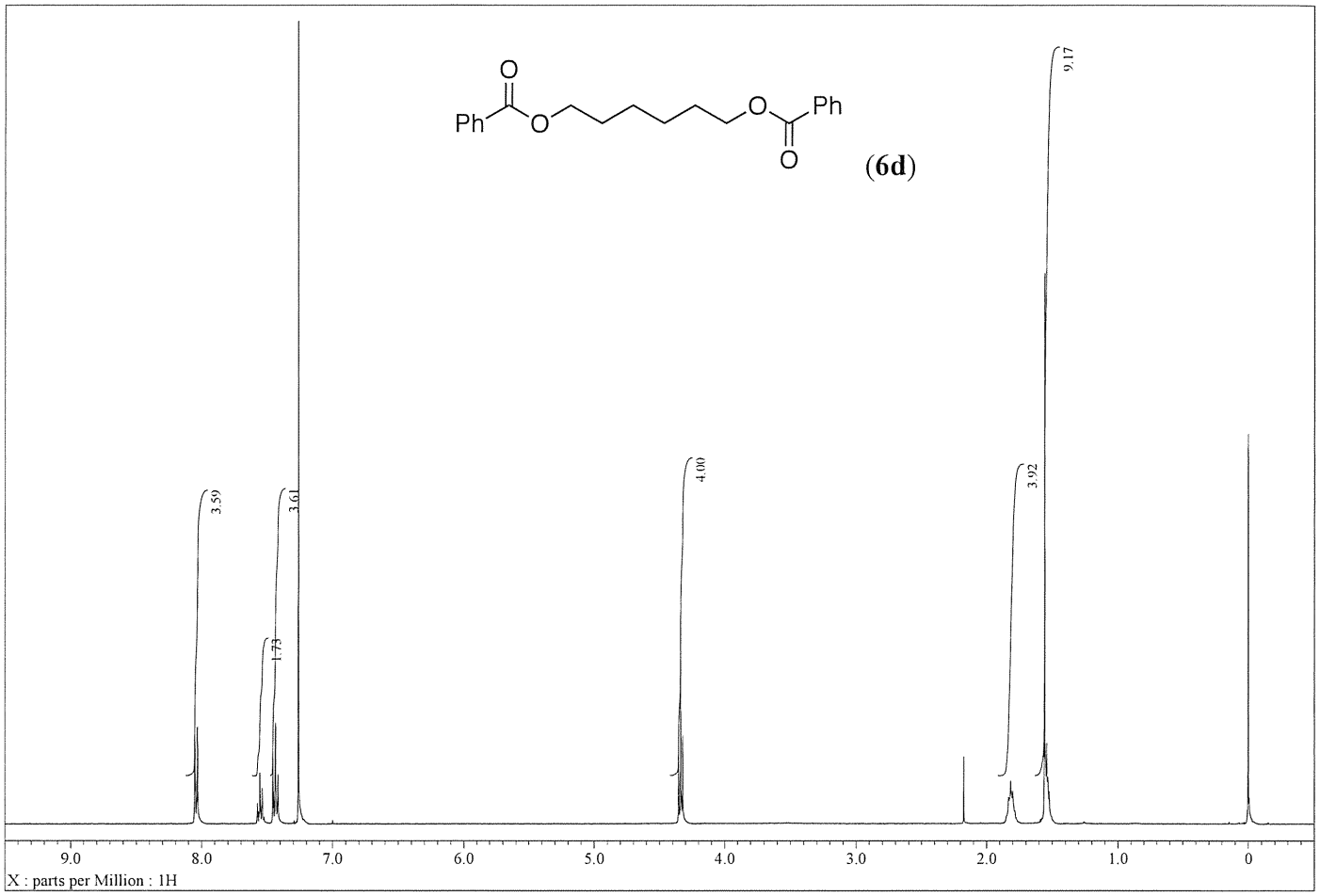
^{13}C NMR, 100 MHz, $CDCl_3$



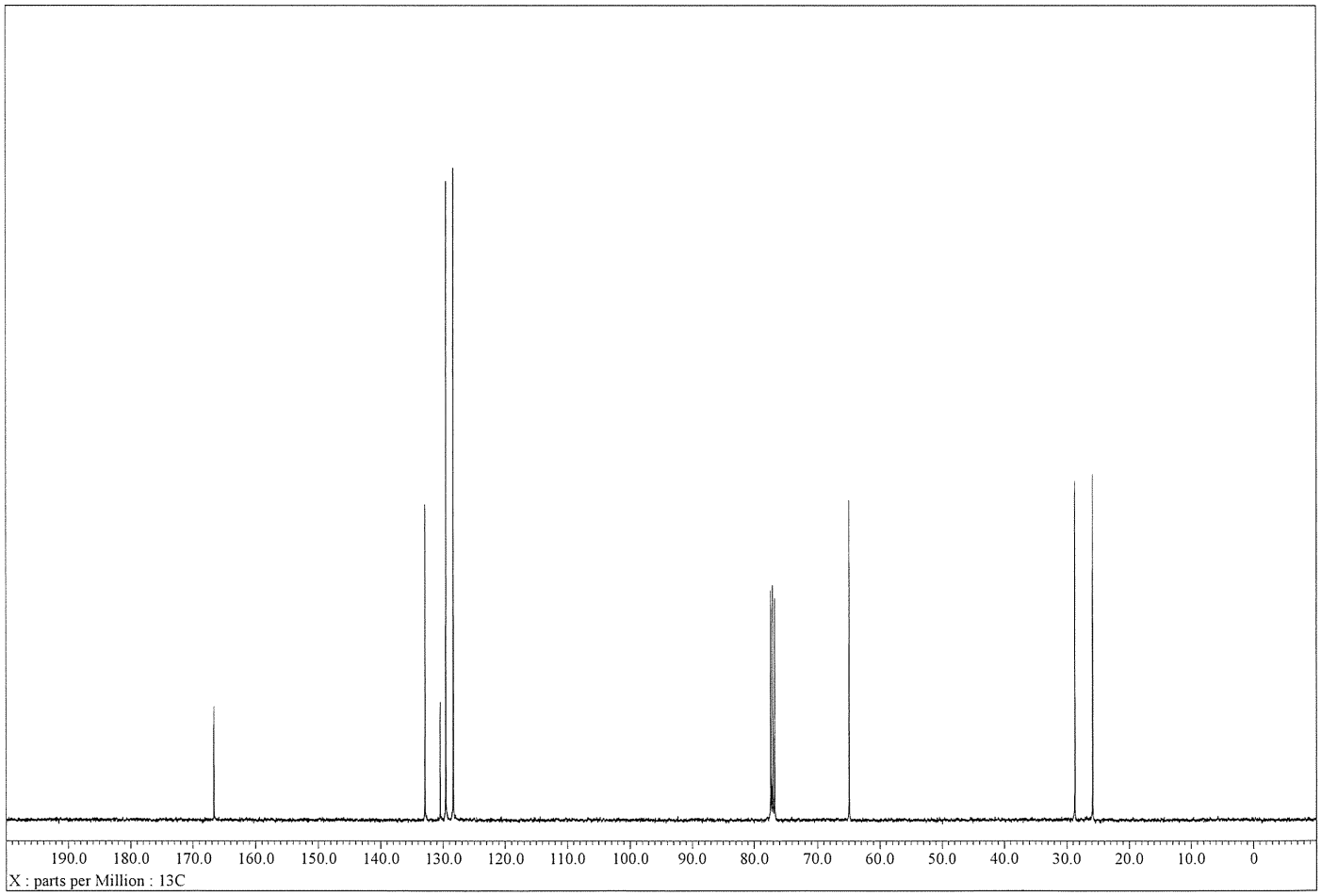
^{1}H NMR, 400 MHz, $CDCl_3$



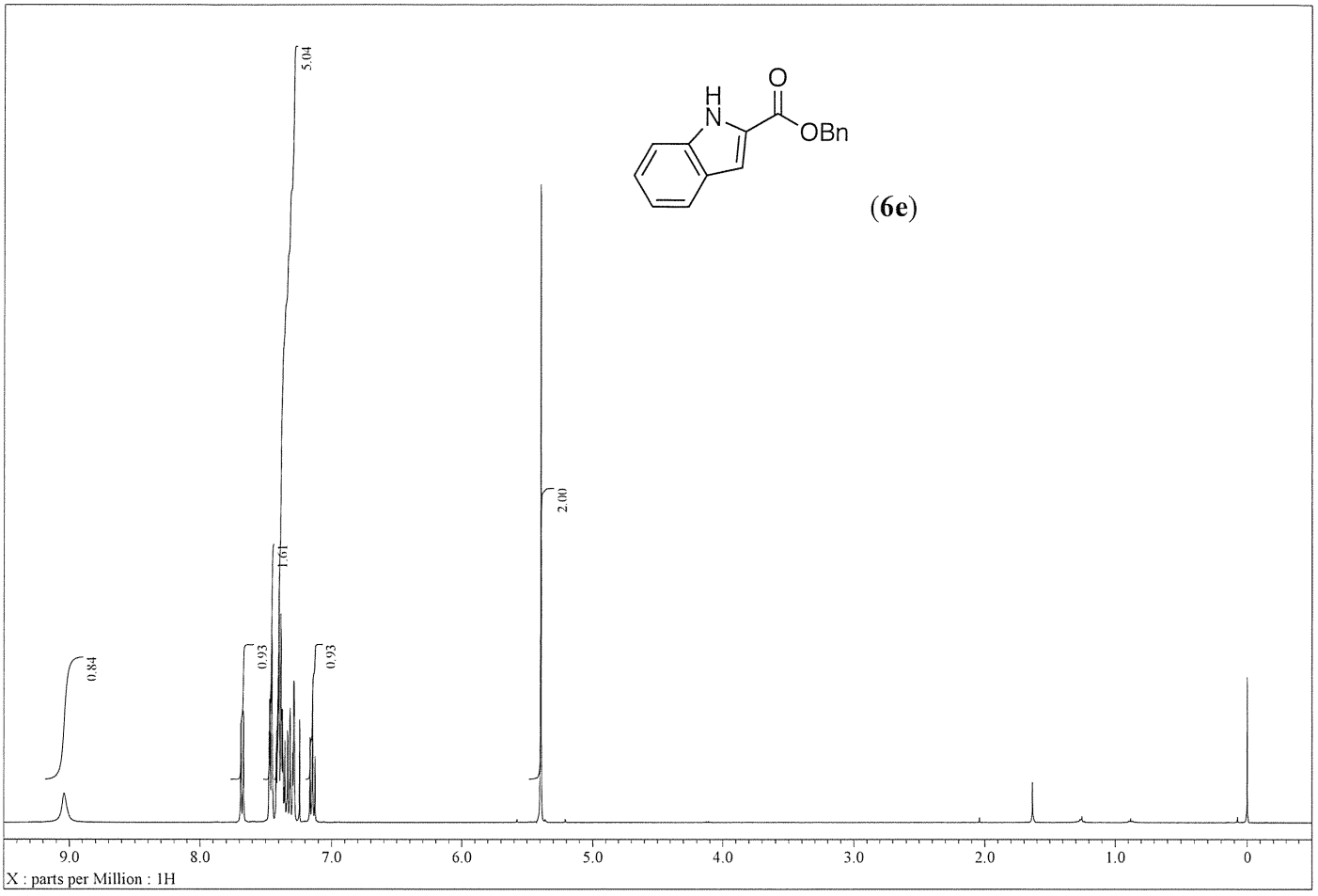
^{13}C NMR, 100 MHz, $CDCl_3$



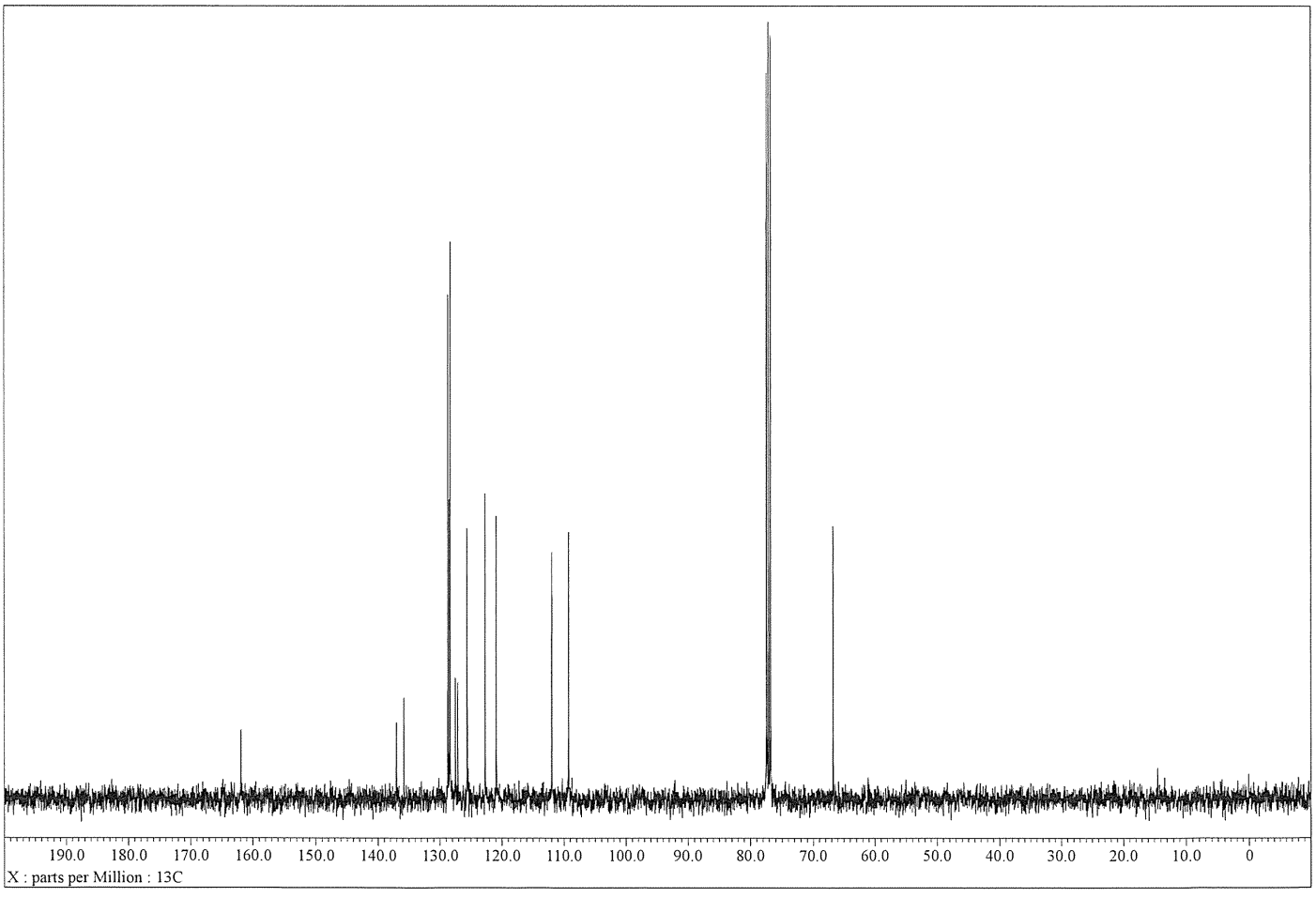
^{1}H NMR, 400 MHz, $CDCl_3$



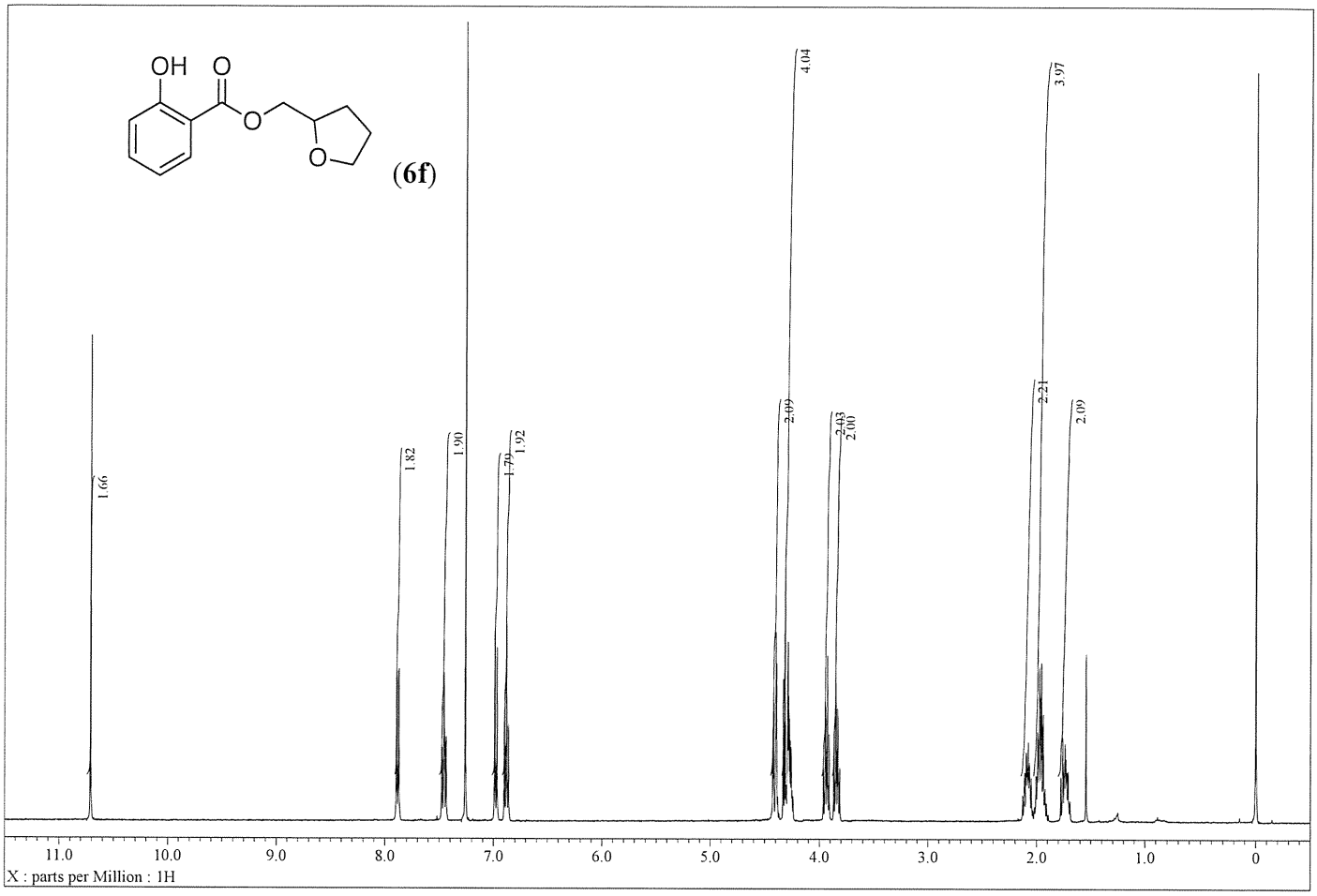
^{13}C NMR, 100 MHz, $CDCl_3$



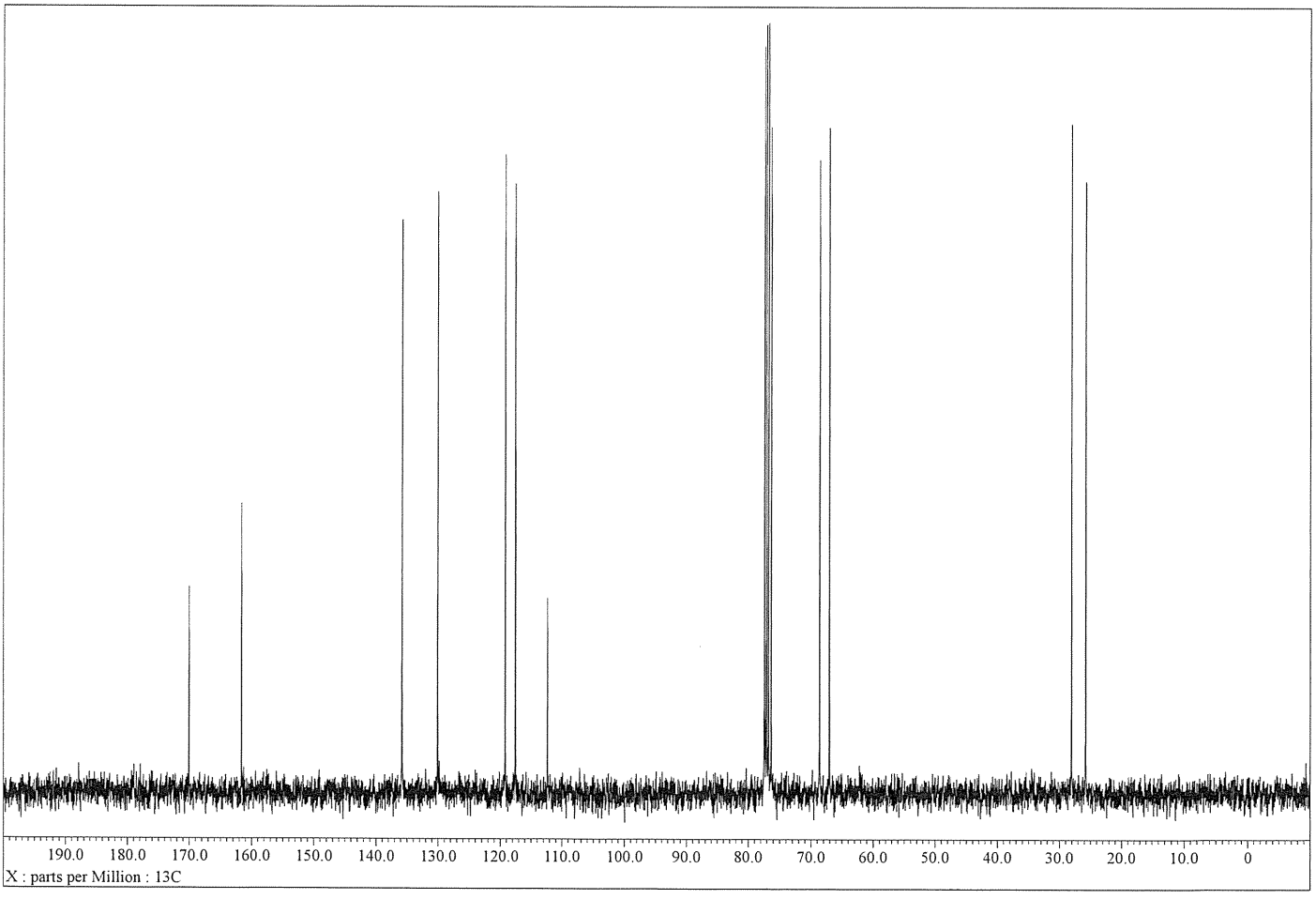
^{1}H NMR, 400 MHz, $CDCl_3$



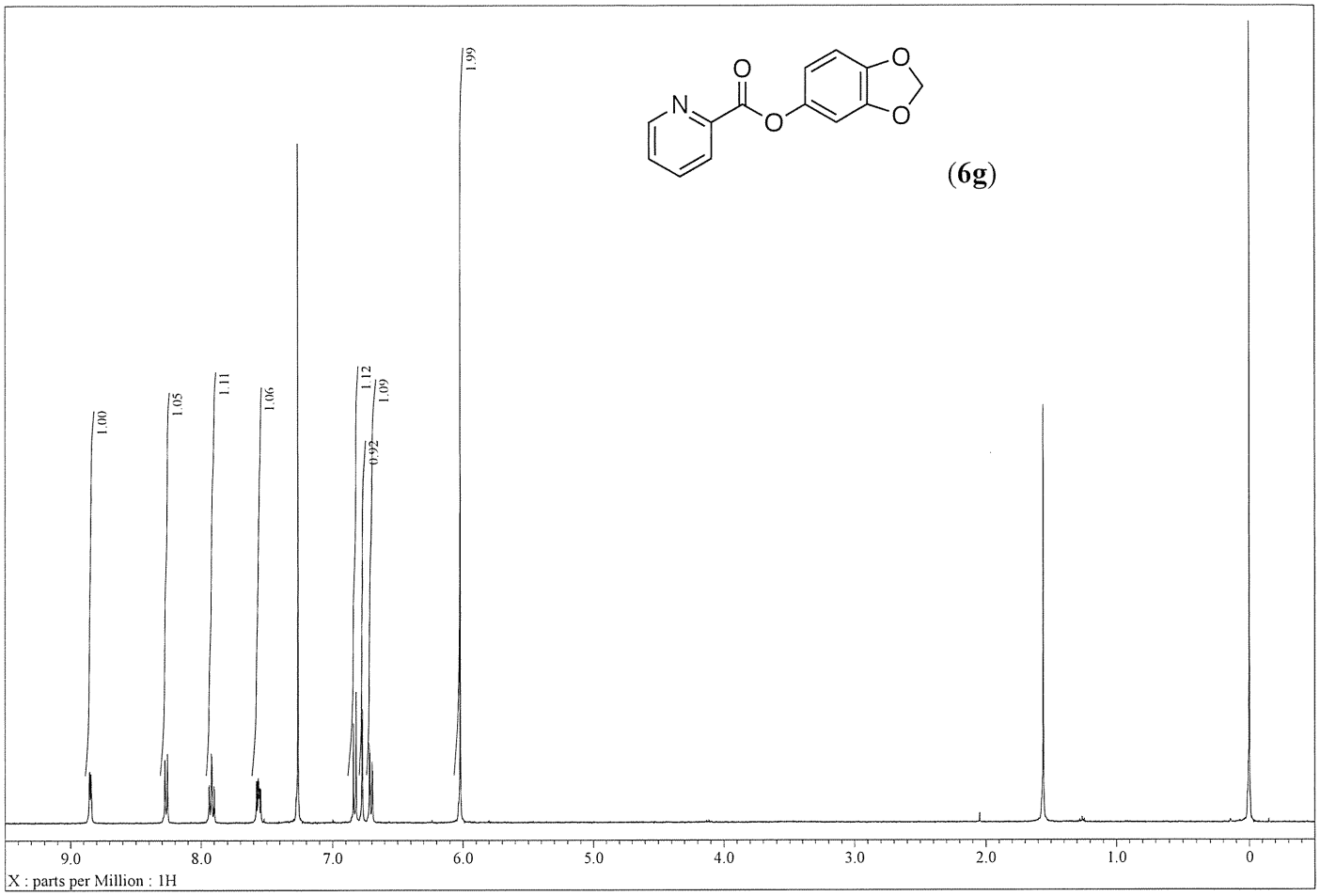
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

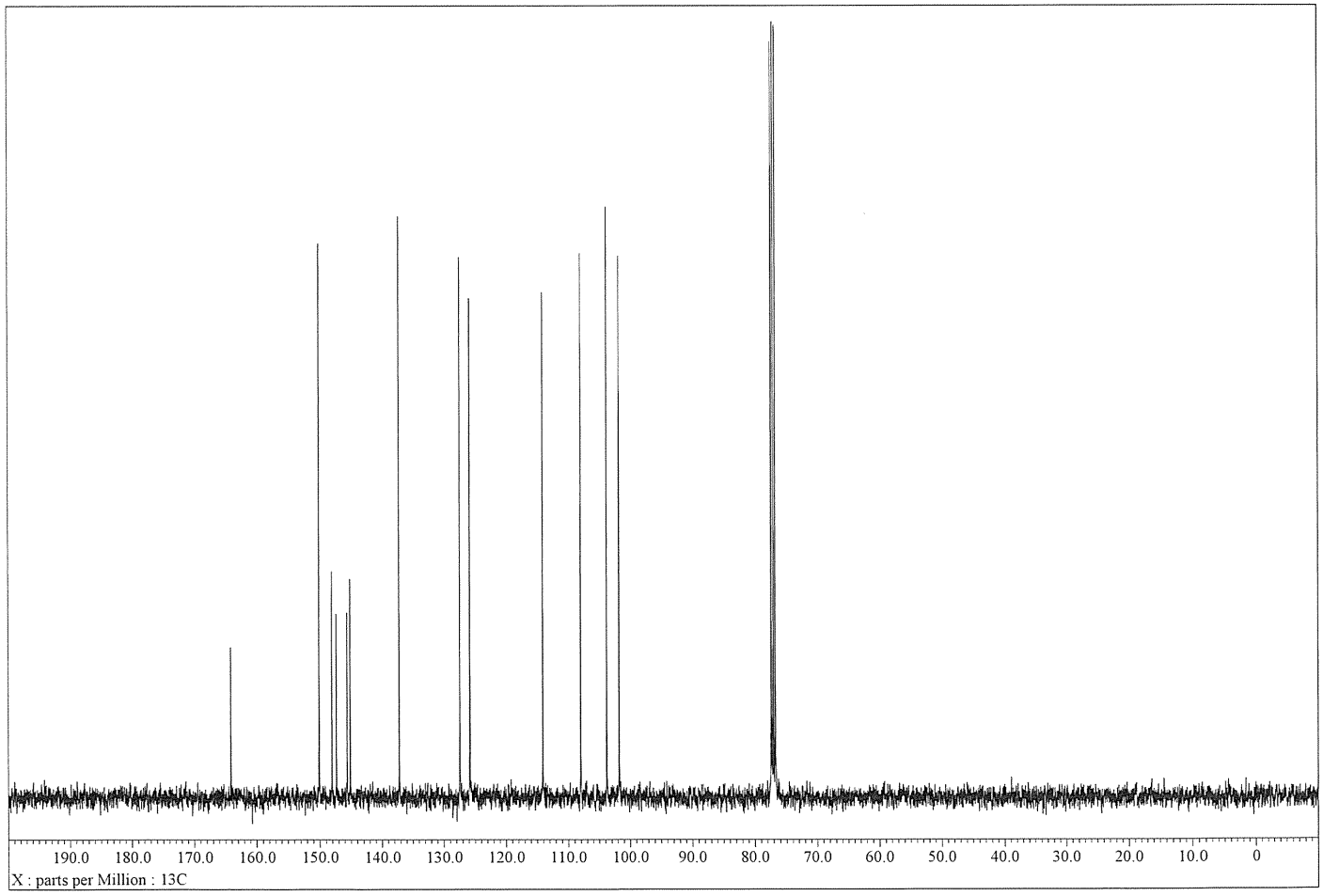


^{13}C NMR, 100 MHz, $CDCl_3$

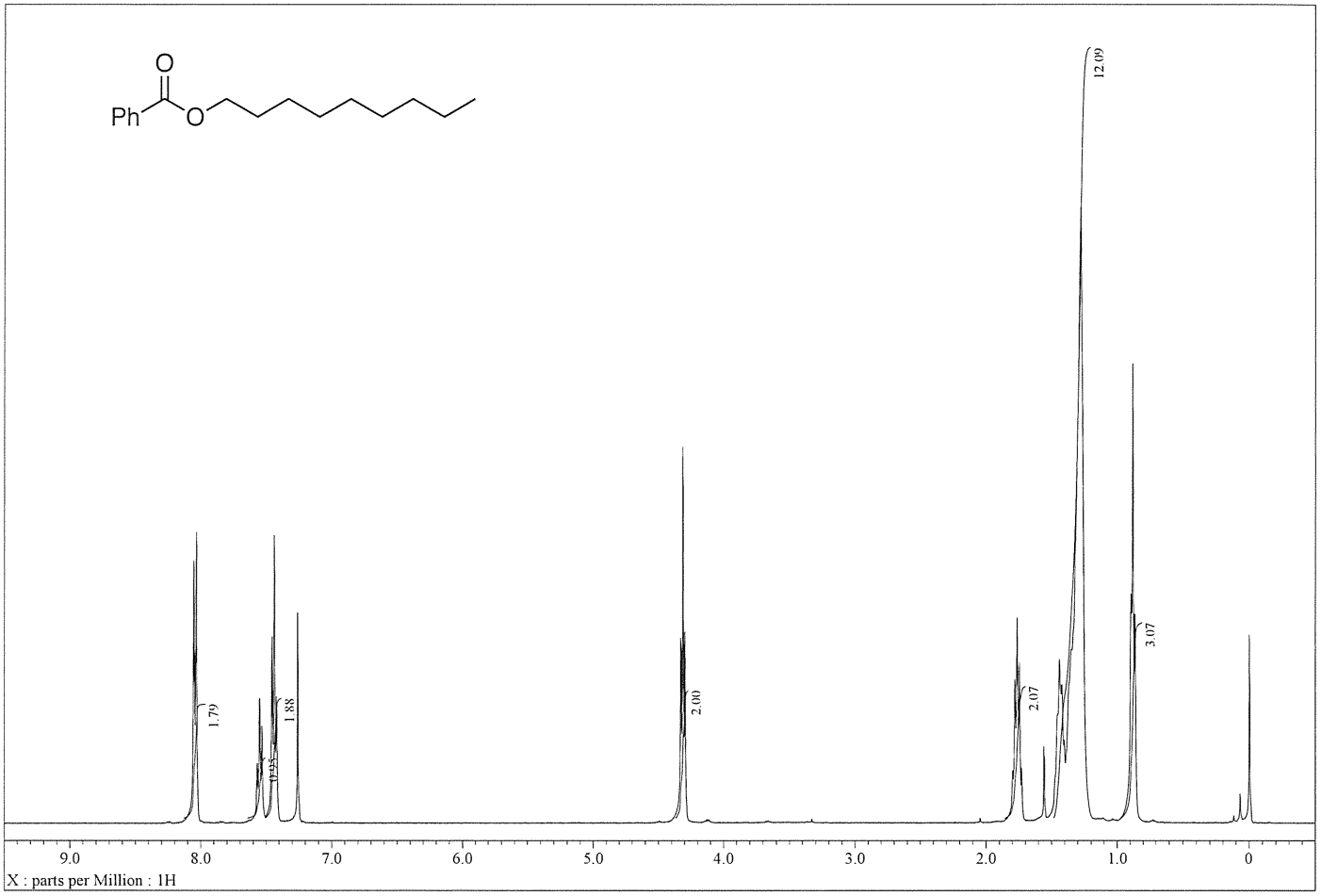


(**6g**)

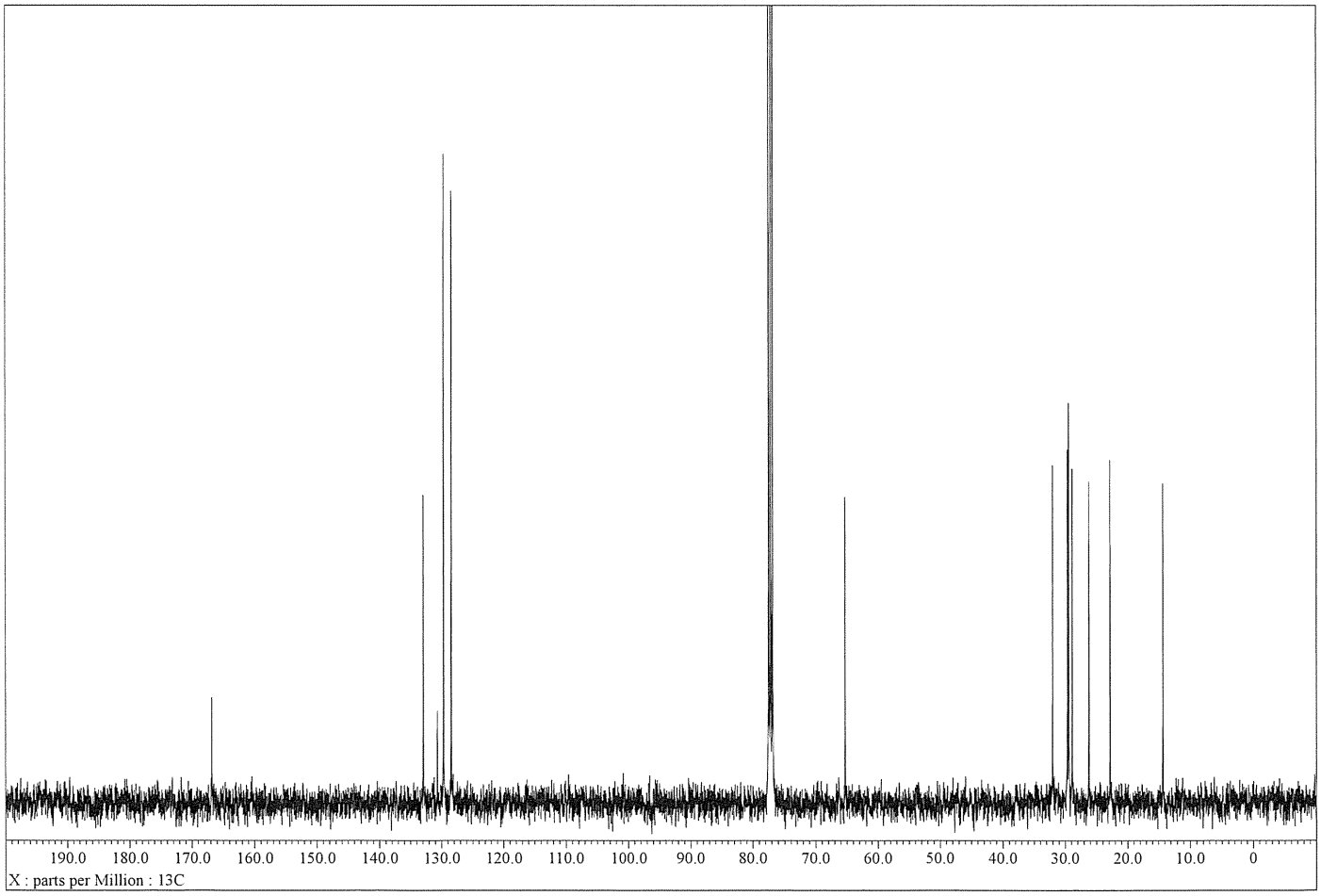
^{1}H NMR, 400 MHz, $CDCl_3$



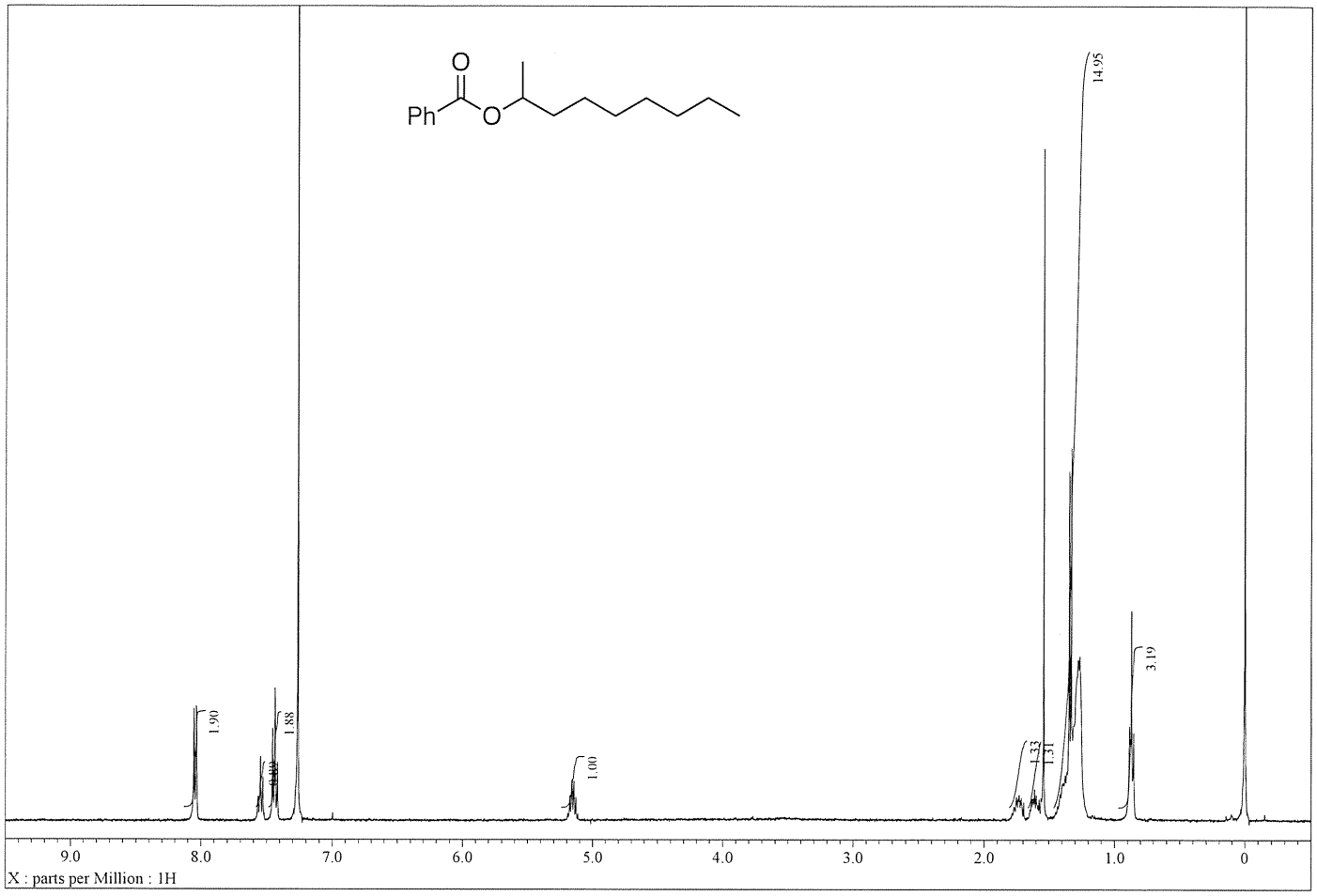
^{13}C NMR, 100 MHz, $CDCl_3$



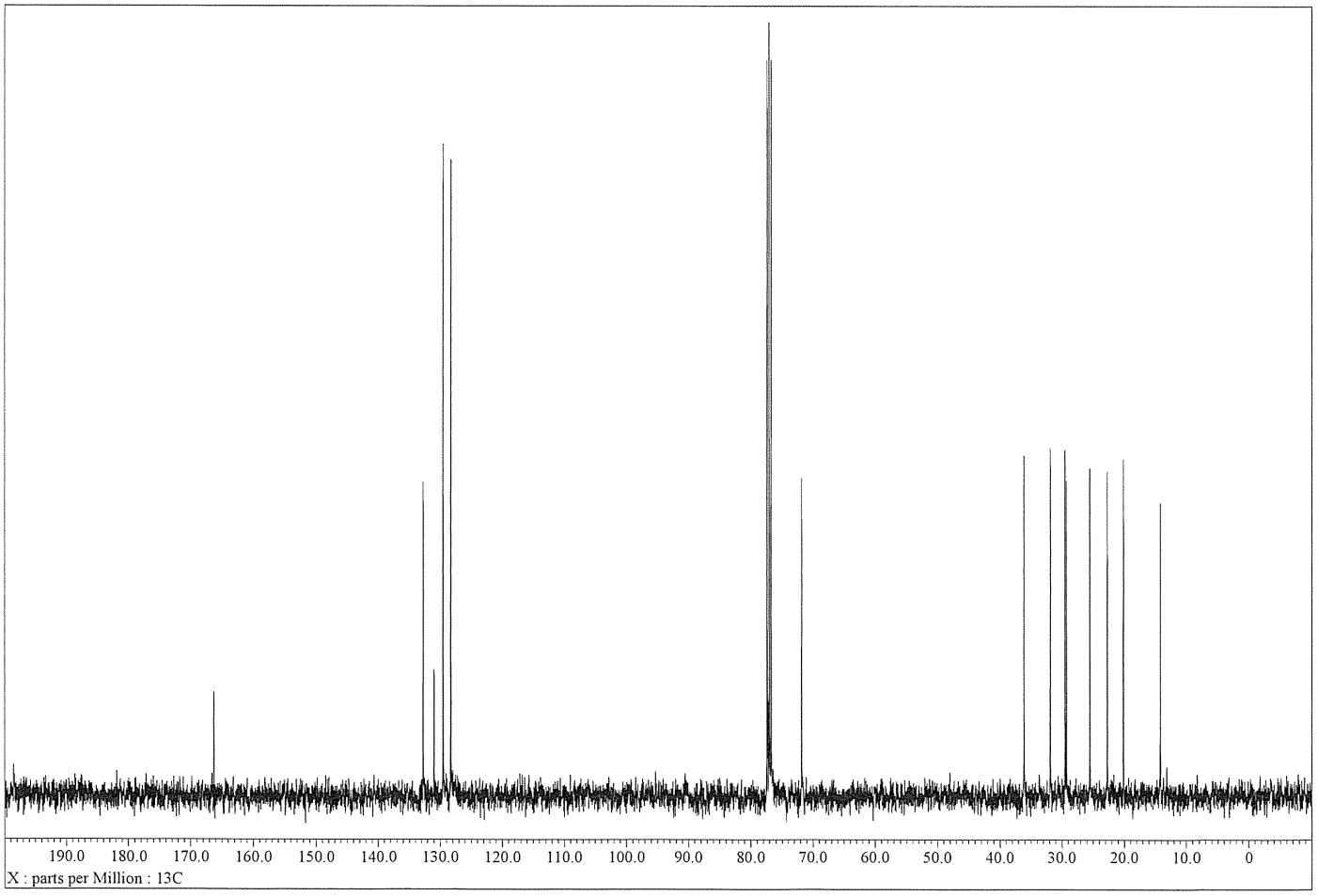
^{1}H NMR, 400 MHz, $CDCl_3$



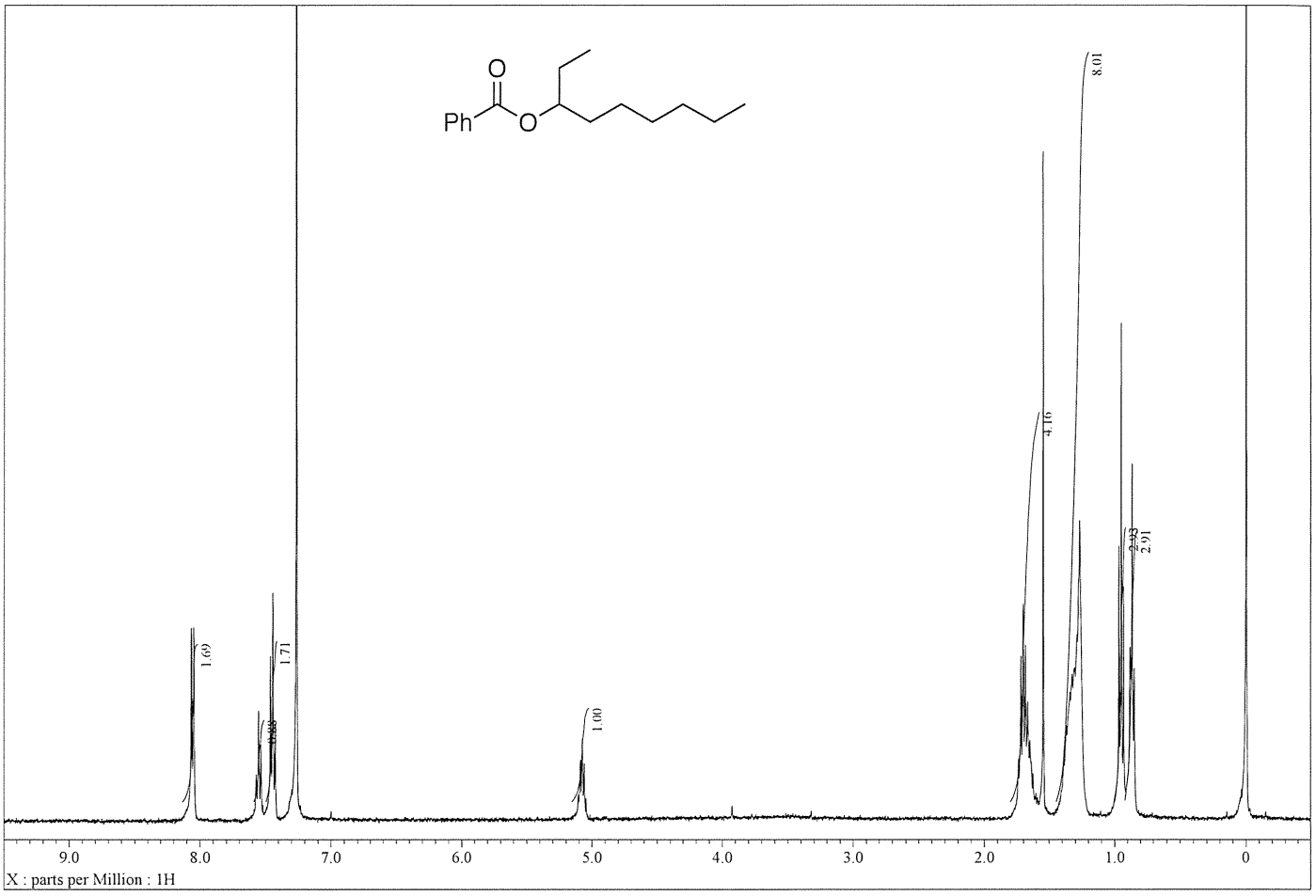
^{13}C NMR, 100 MHz, $CDCl_3$



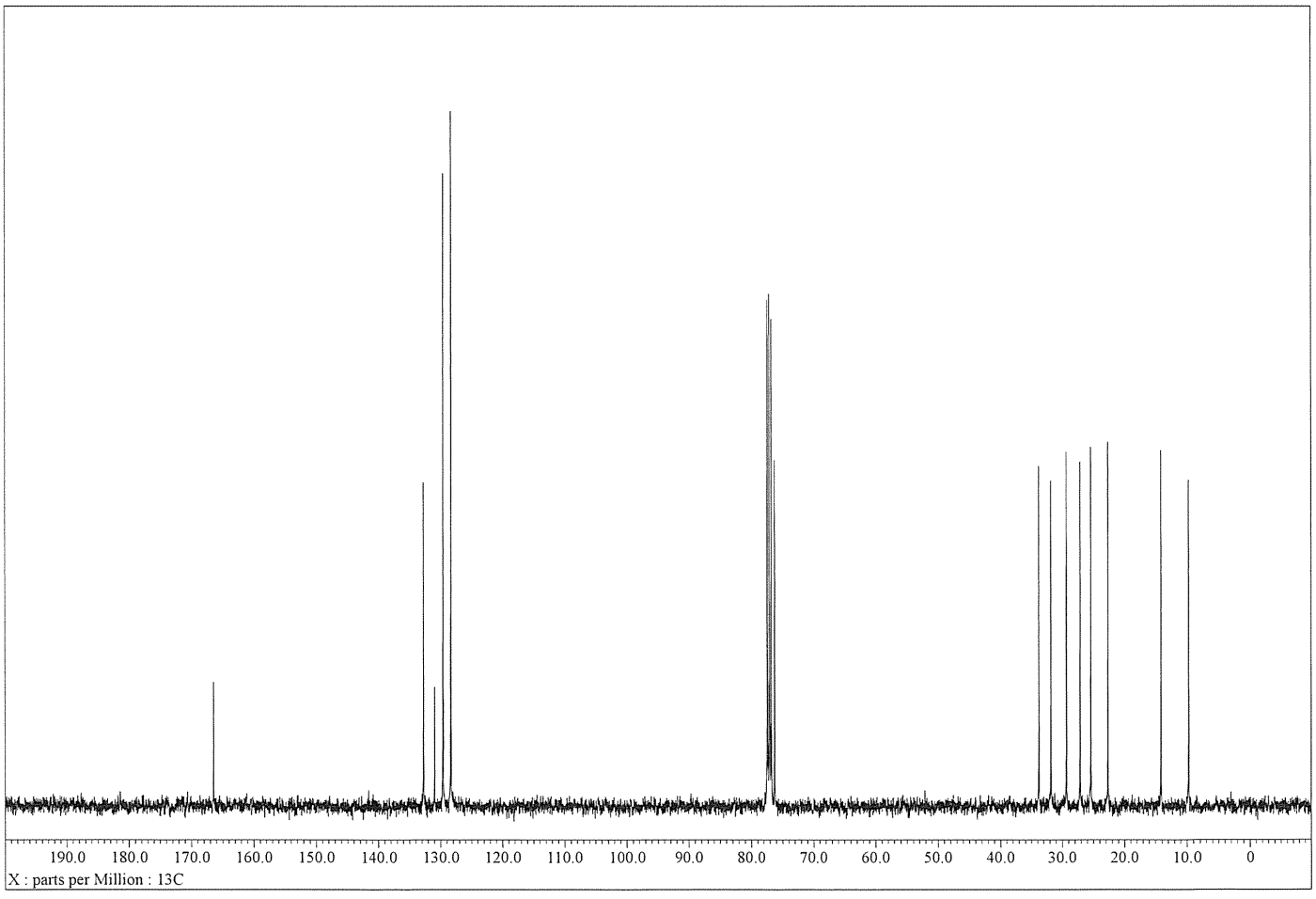
^{1}H NMR, 400 MHz, $CDCl_3$



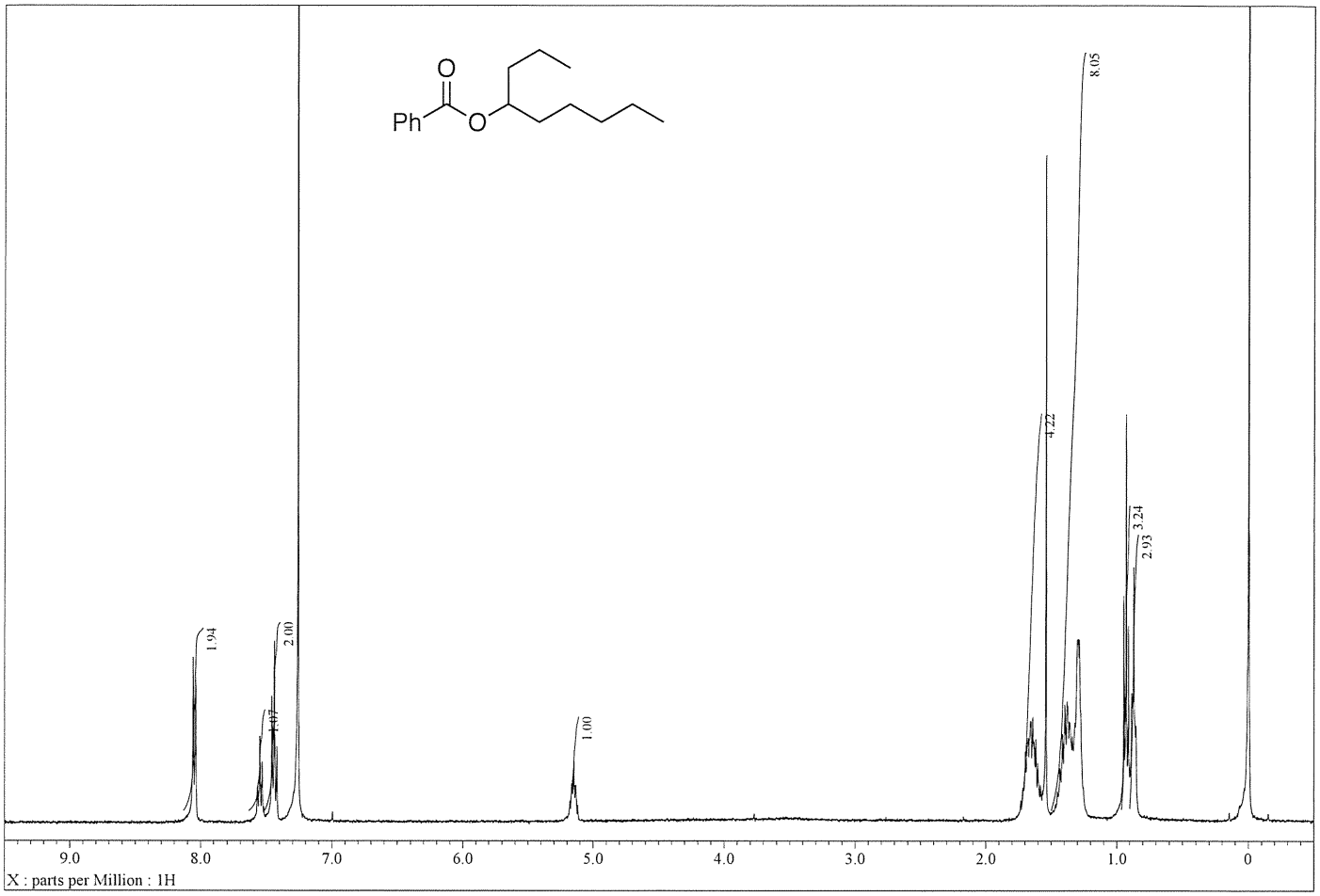
^{13}C NMR, 100 MHz, $CDCl_3$



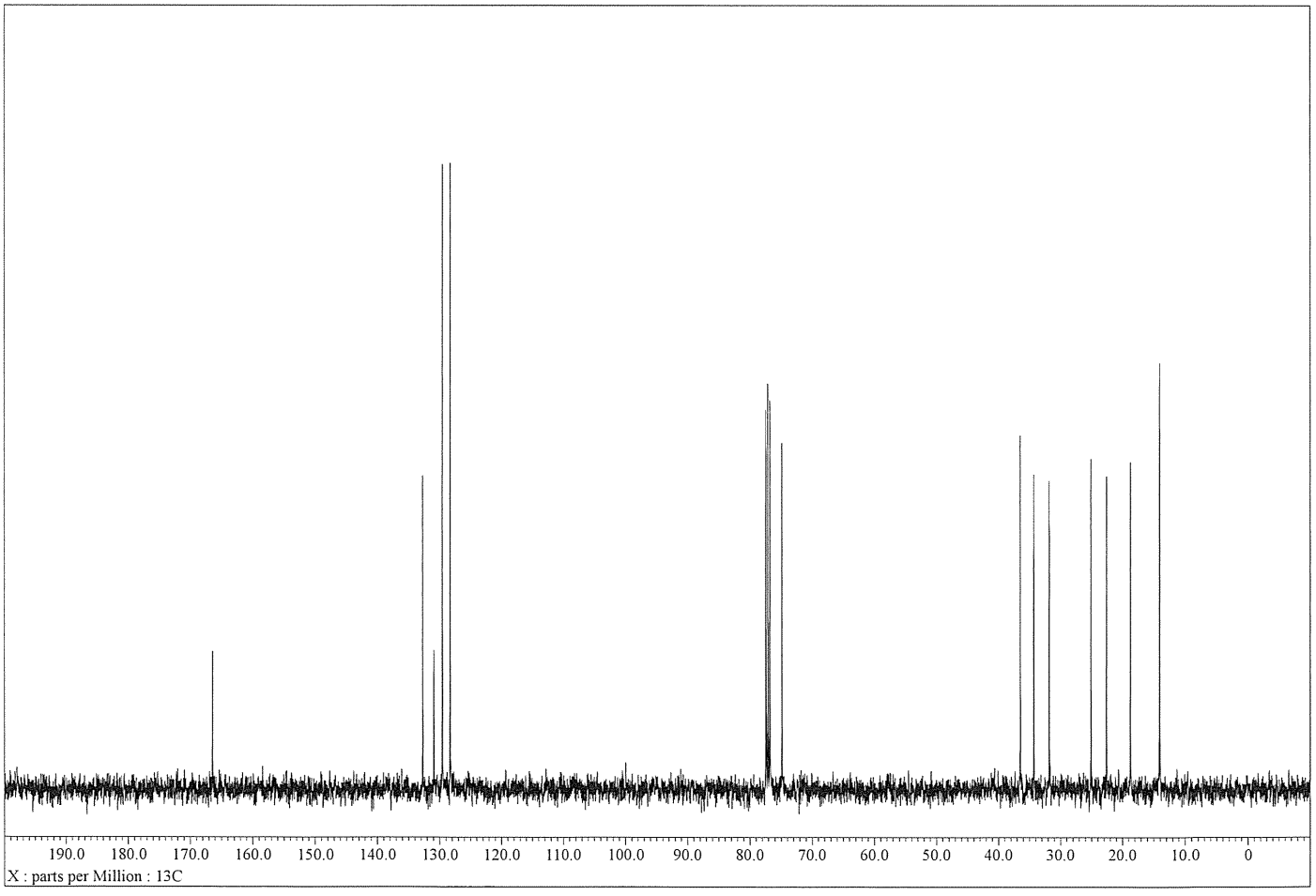
^{1}H NMR, 400 MHz, $CDCl_3$



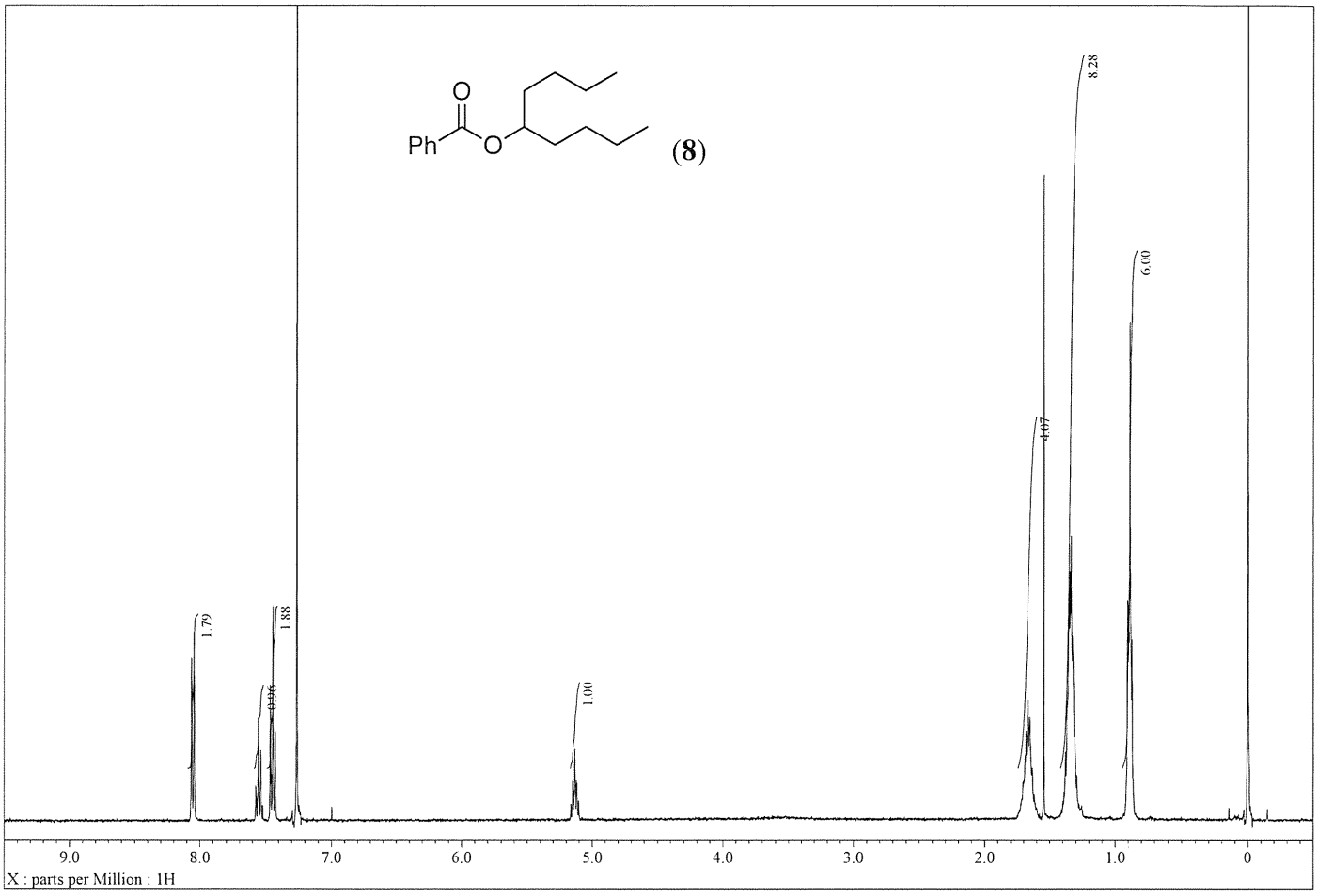
^{13}C NMR, 100 MHz, $CDCl_3$



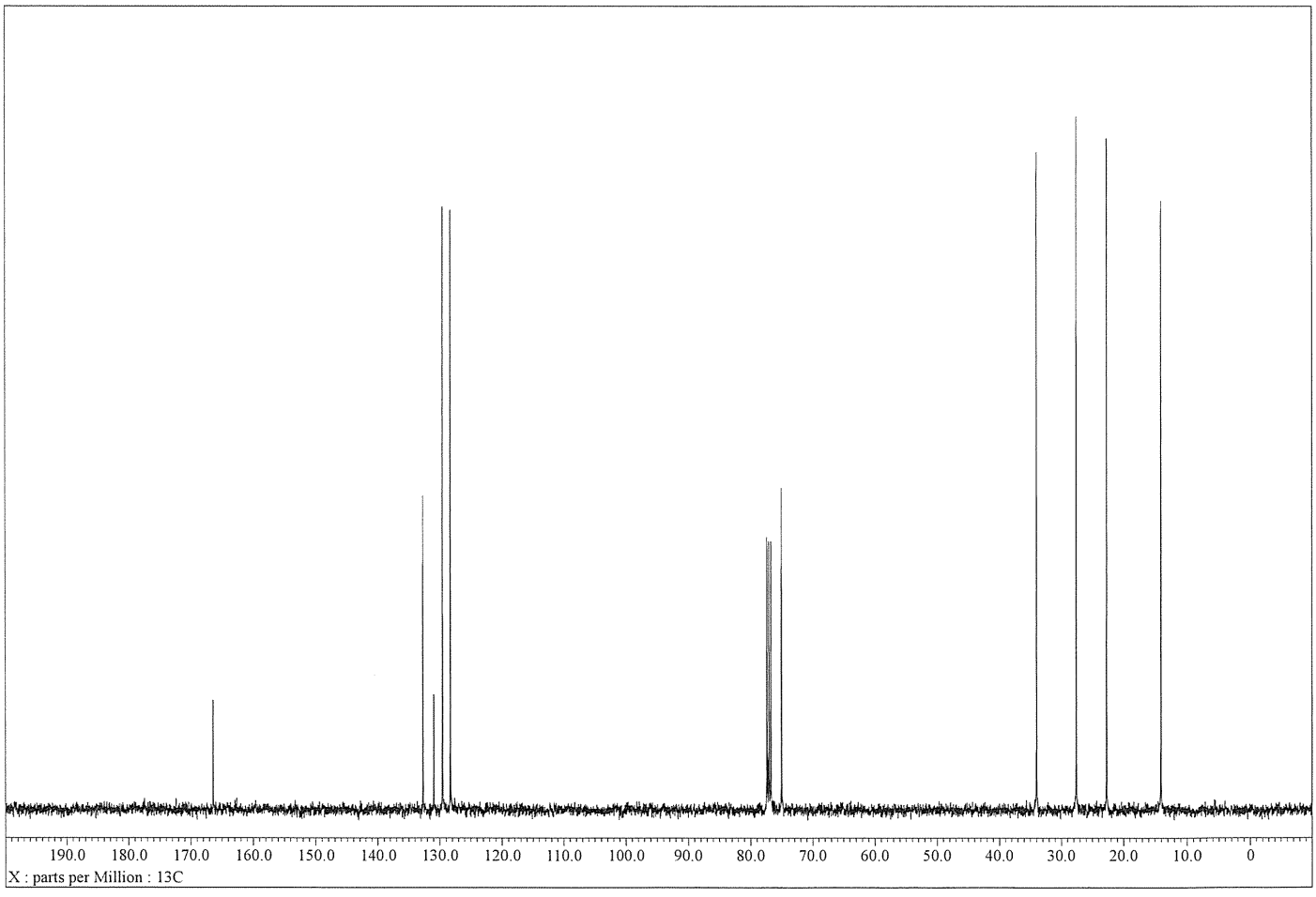
^{1}H NMR, 400 MHz, $CDCl_3$



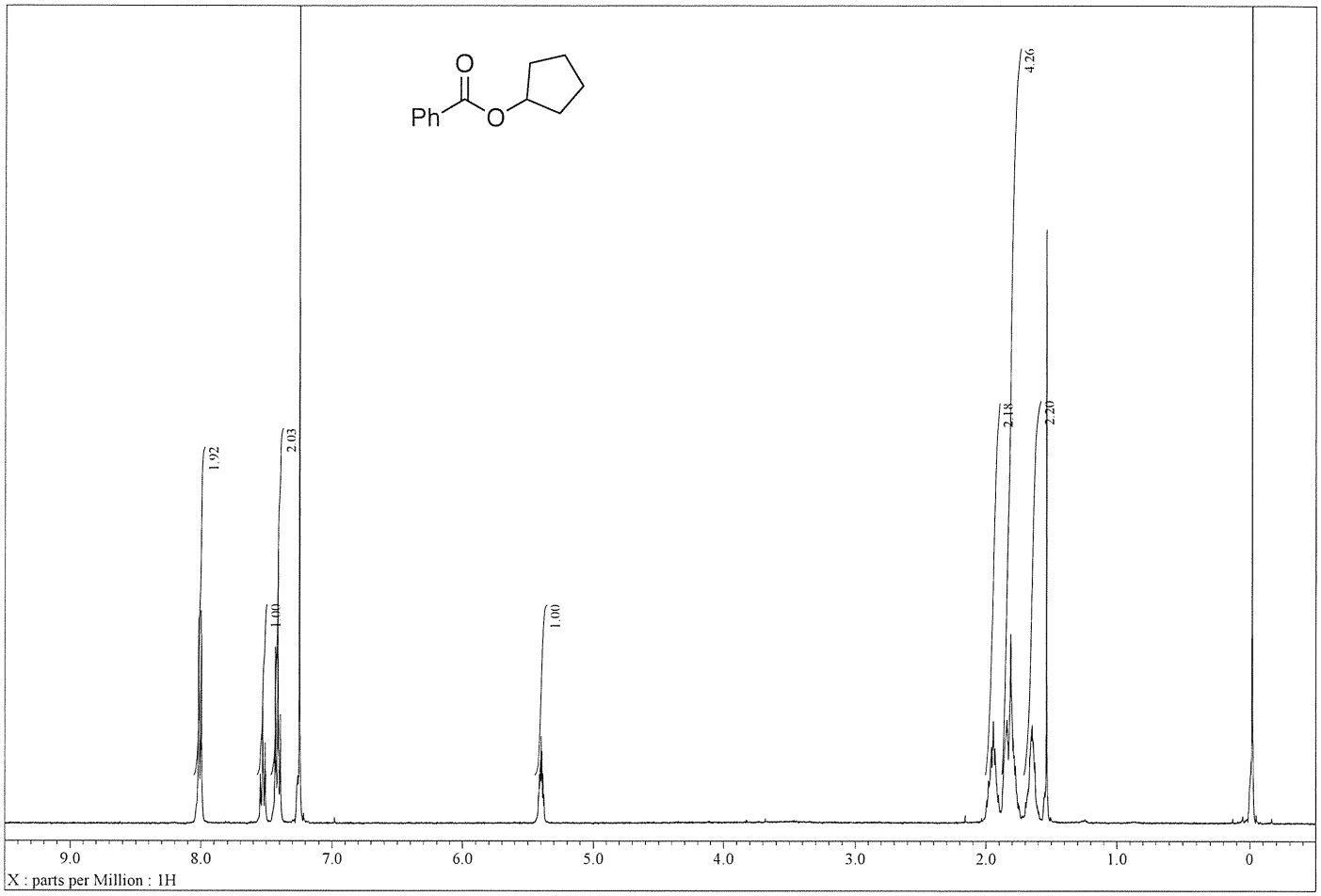
^{13}C NMR, 100 MHz, $CDCl_3$



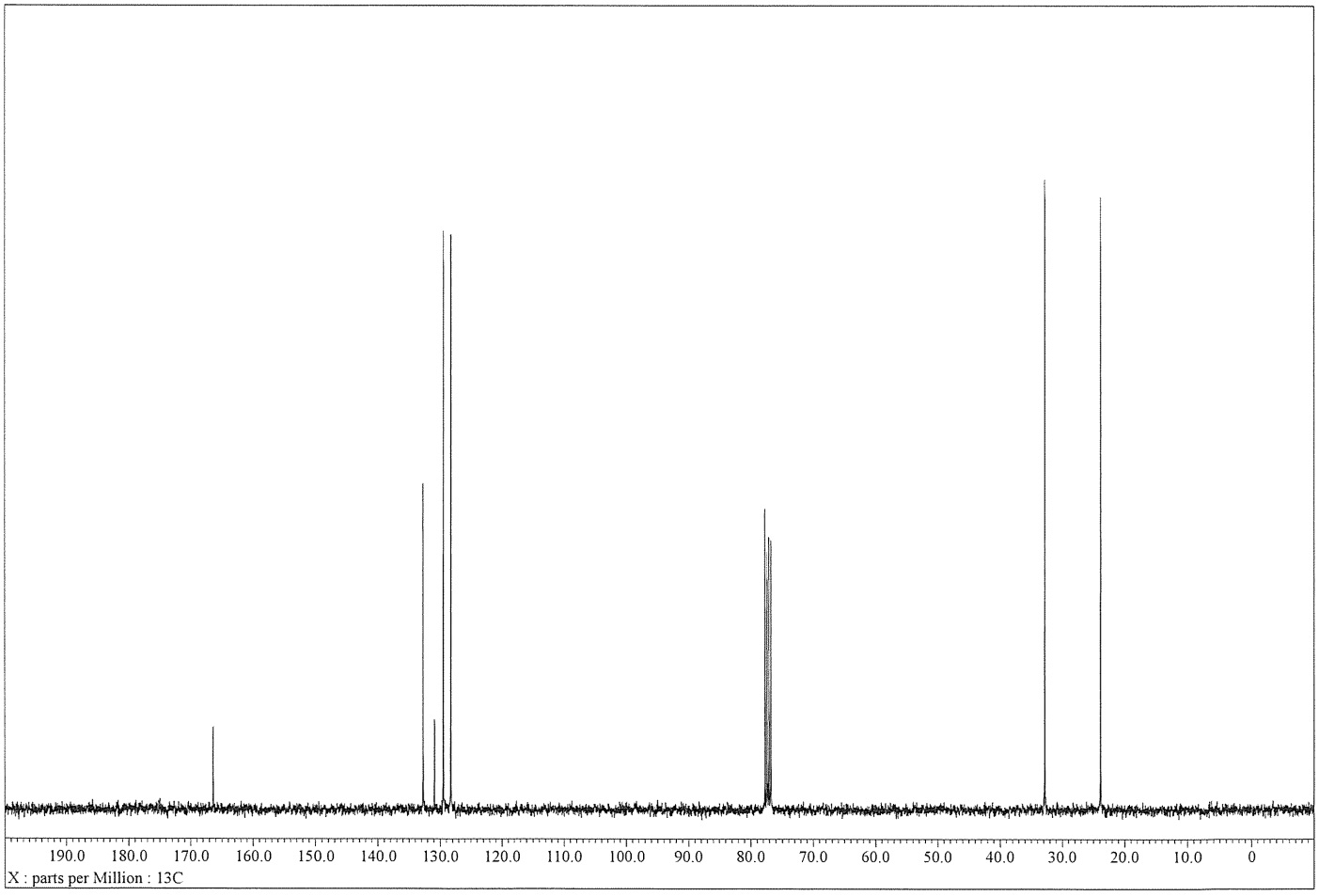
^{1}H NMR, 400 MHz, $CDCl_3$



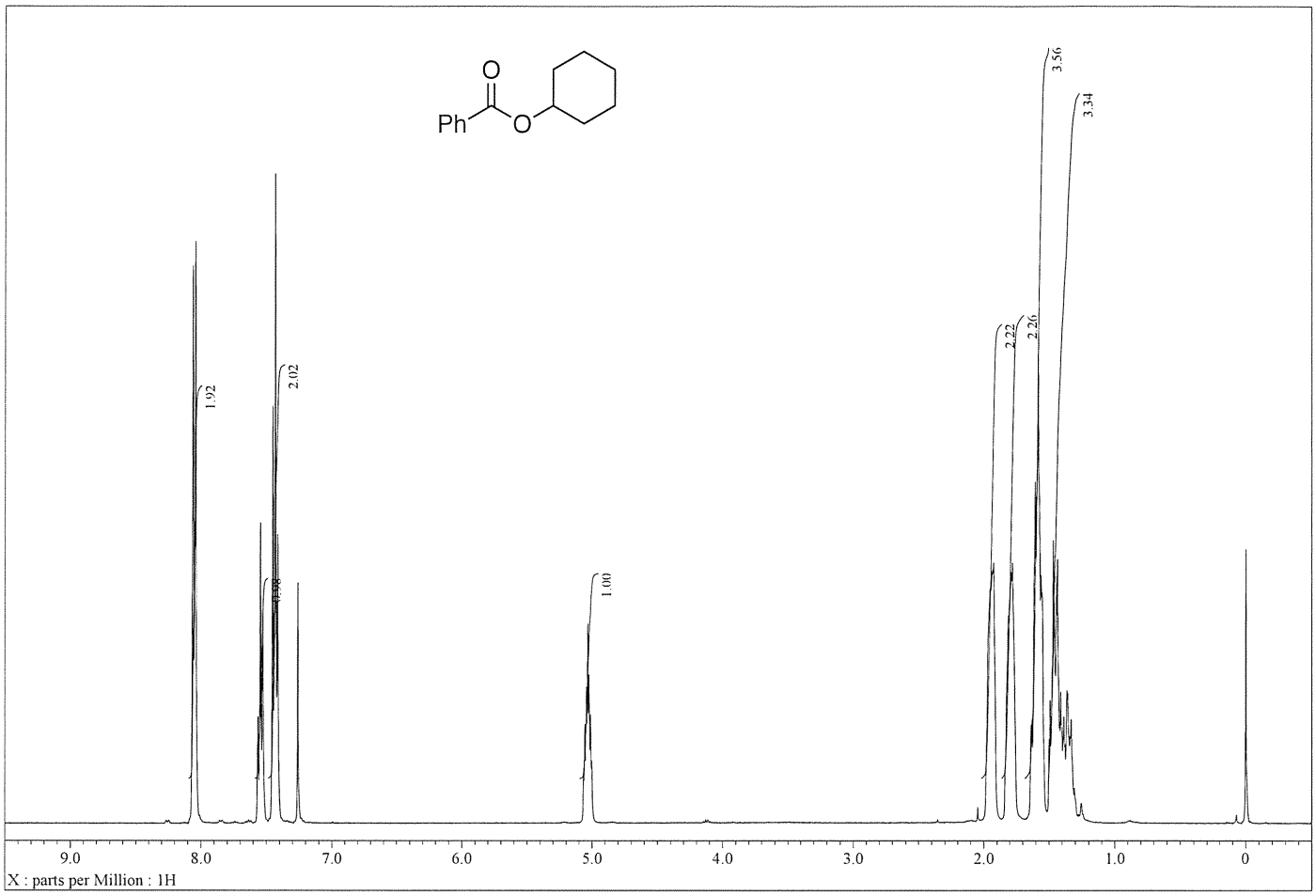
^{13}C NMR, 100 MHz, $CDCl_3$



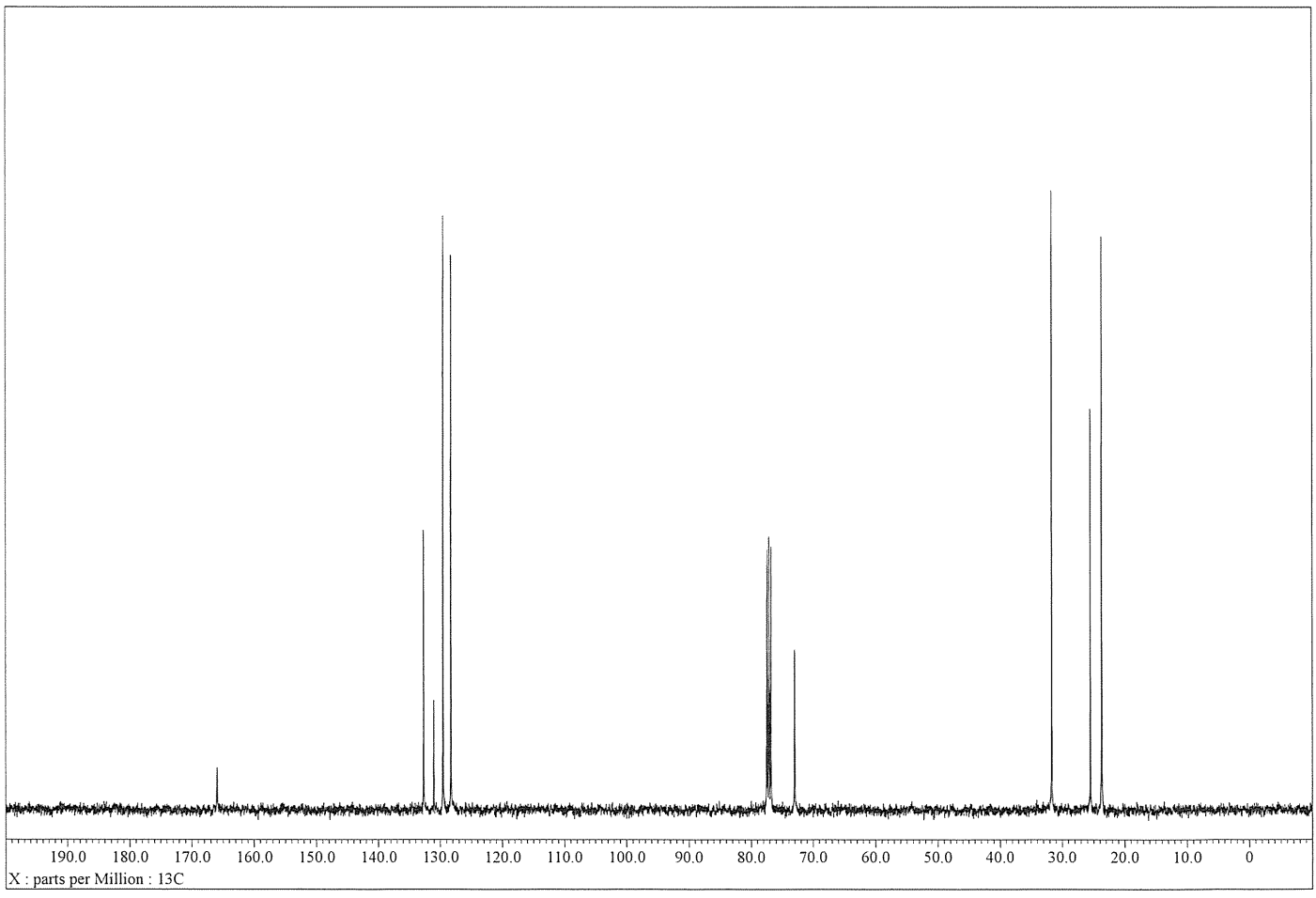
^{1}H NMR, 400 MHz, $CDCl_3$



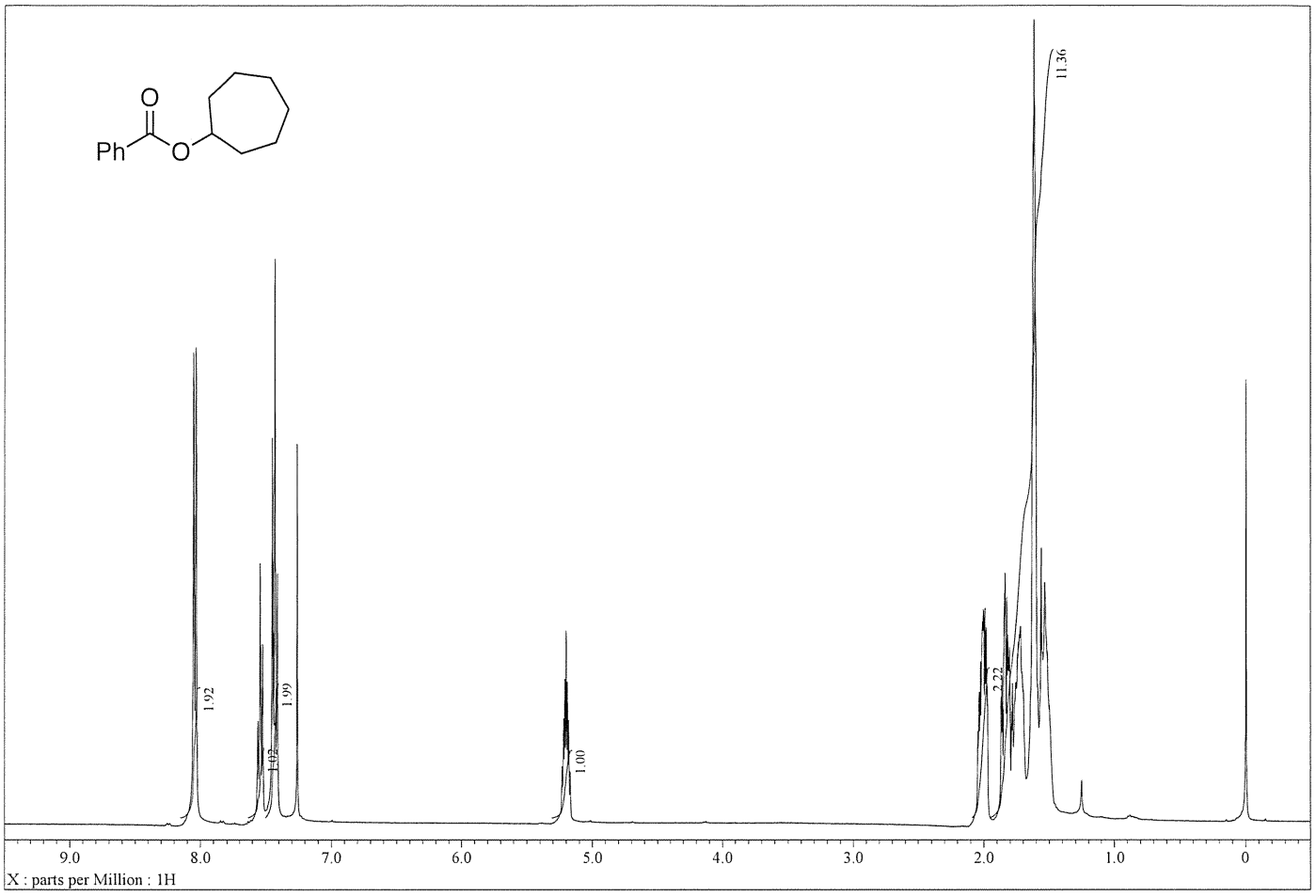
^{13}C NMR, 100 MHz, $CDCl_3$



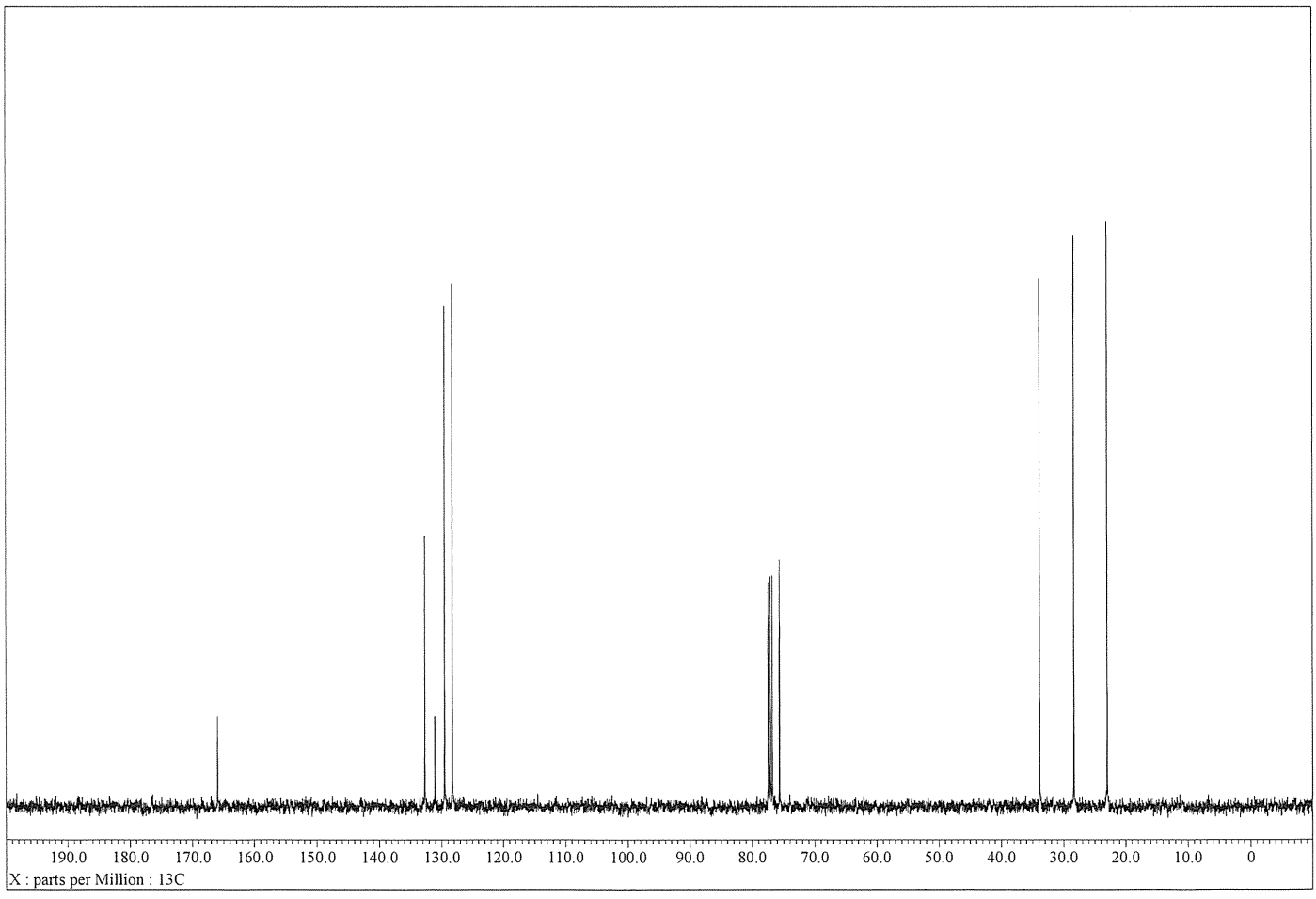
^{1}H NMR, 400 MHz, $CDCl_3$



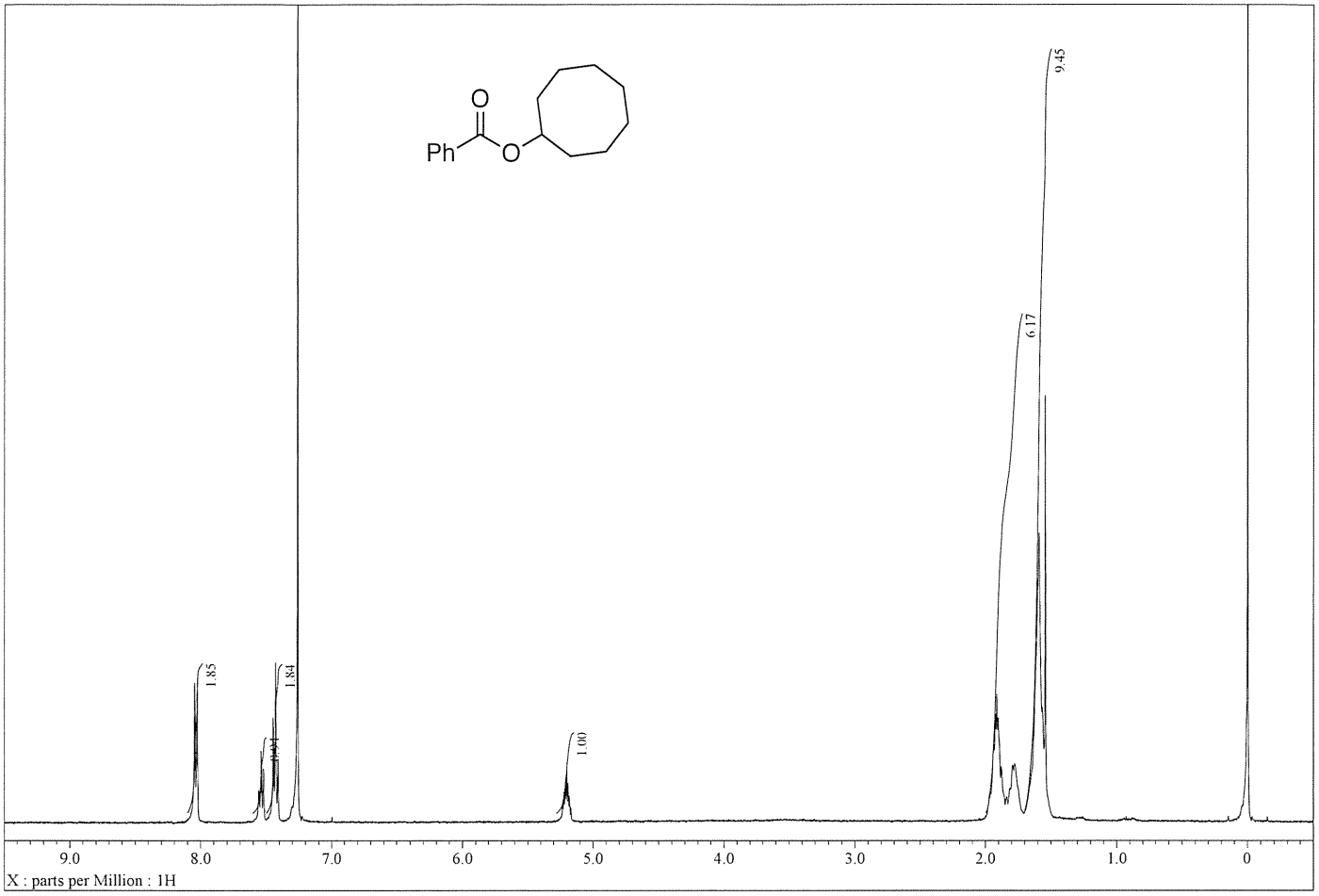
^{13}C NMR, 100 MHz, $CDCl_3$



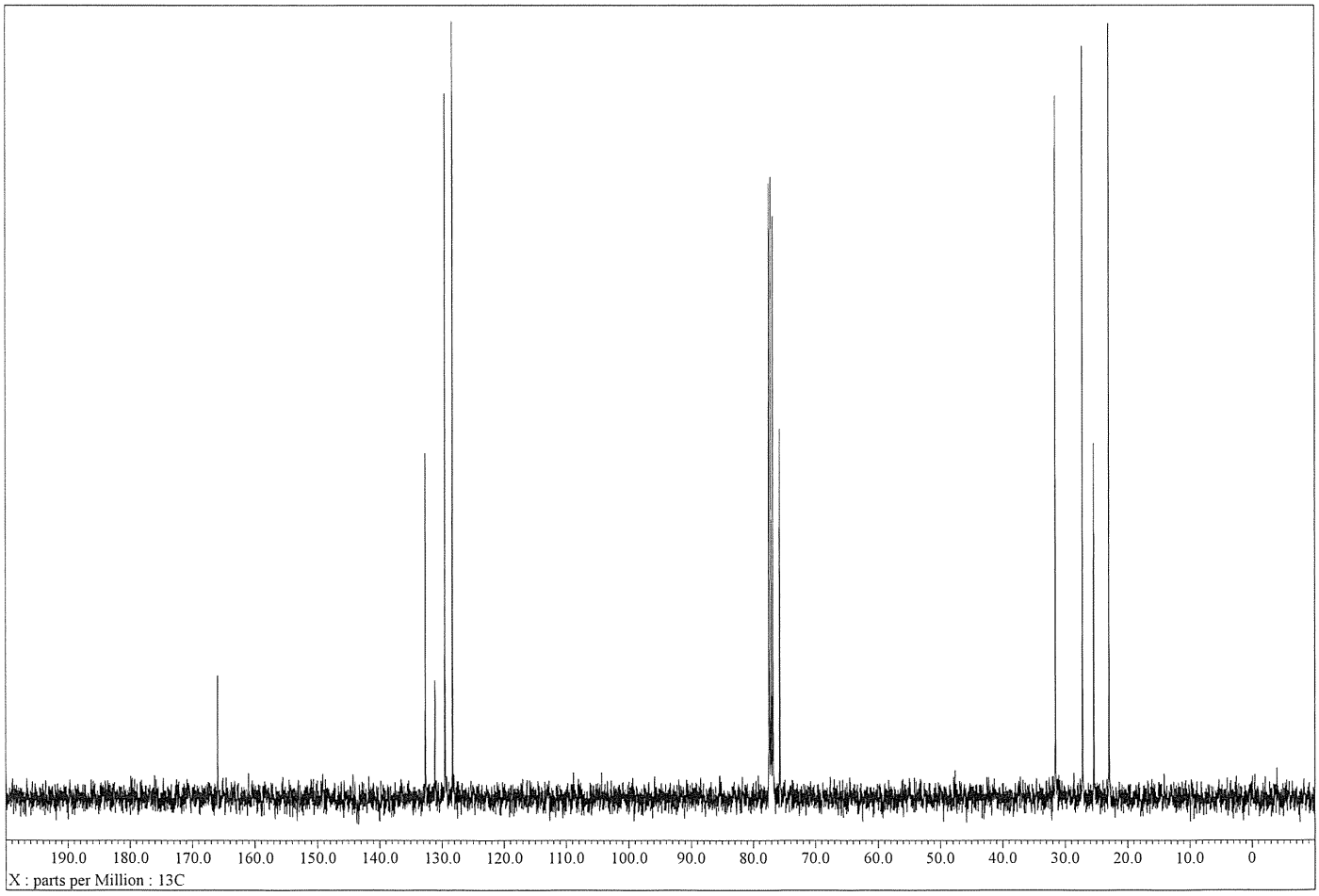
^{1}H NMR, 400 MHz, $CDCl_3$



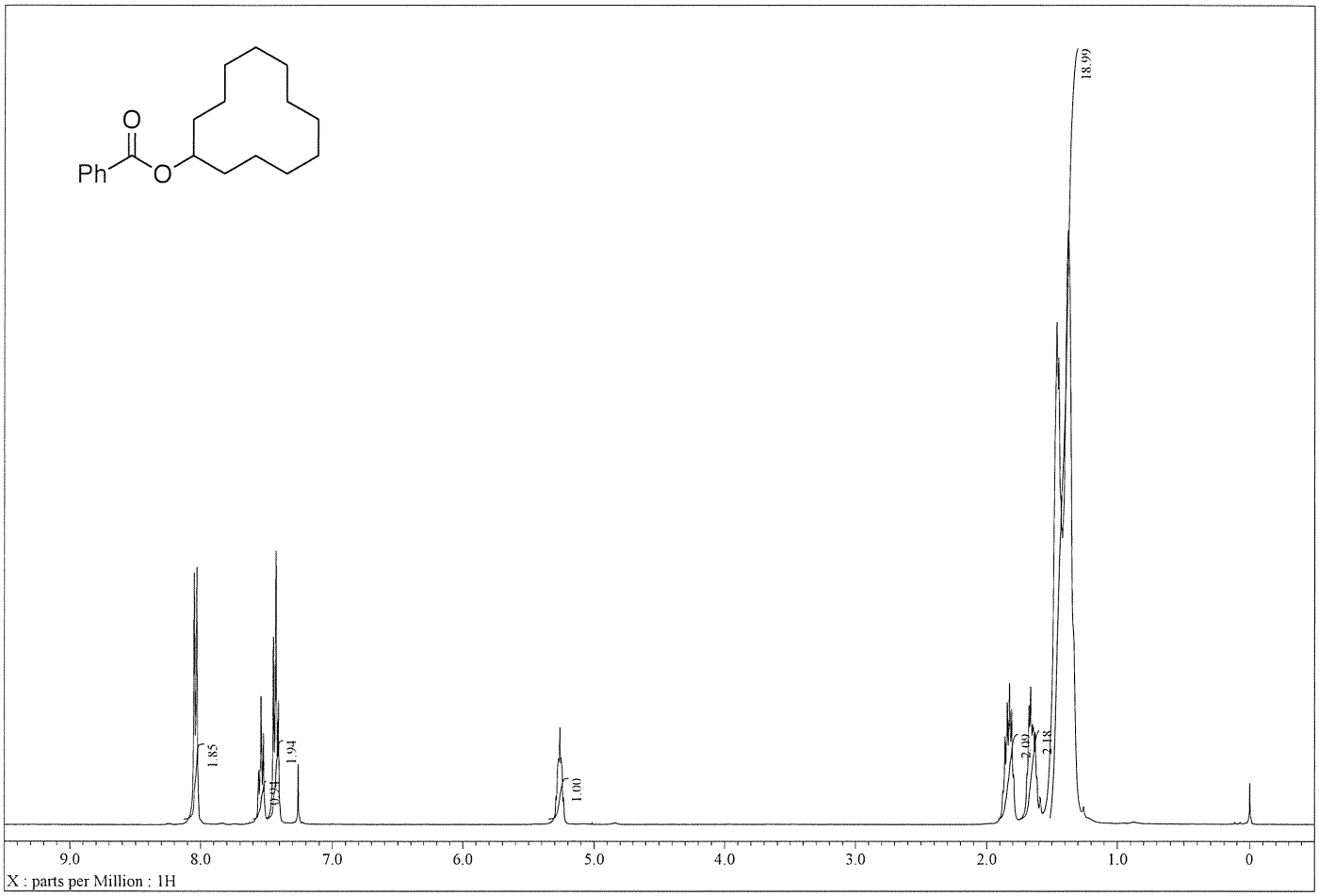
^{13}C NMR, 100 MHz, $CDCl_3$



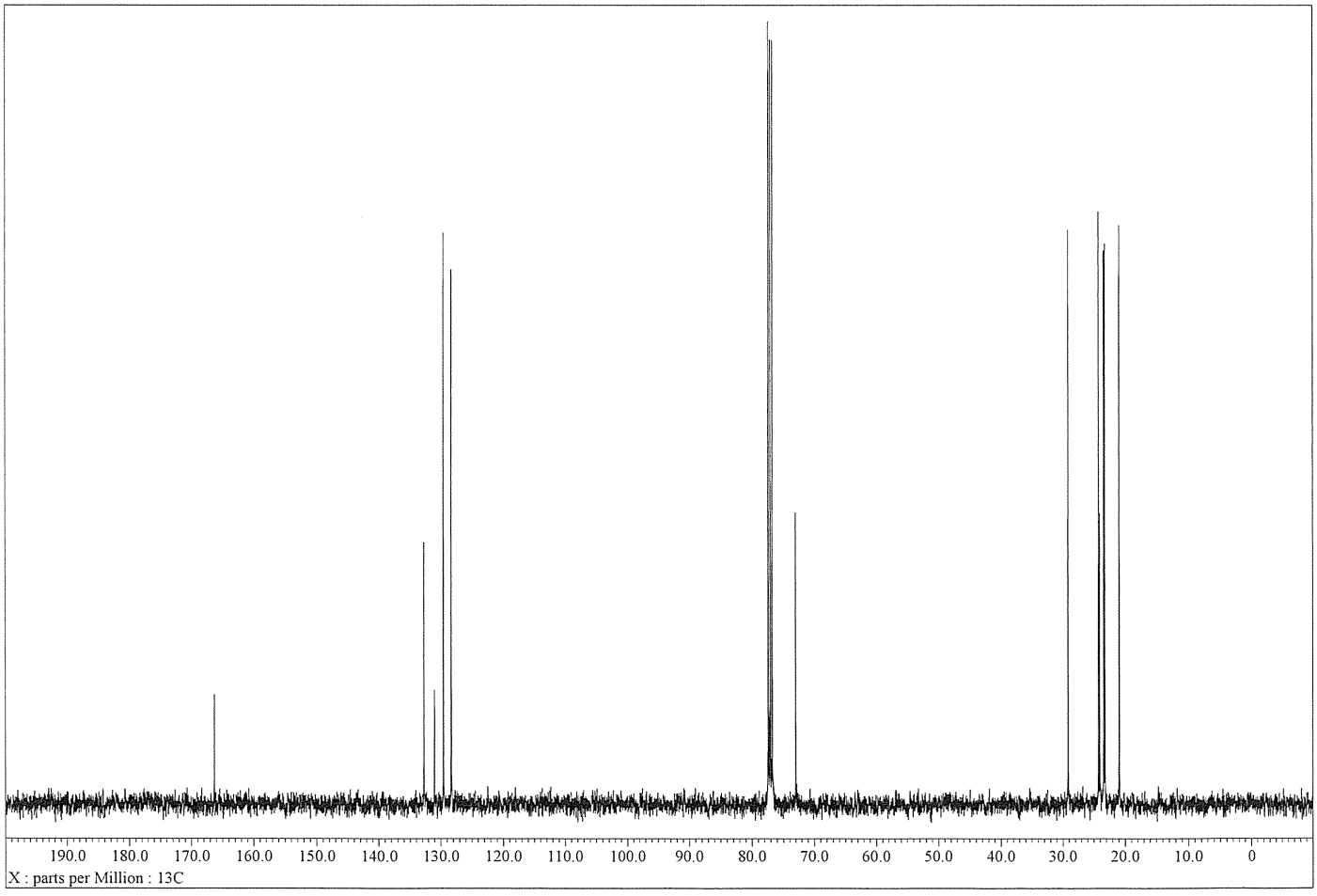
^{1}H NMR, 400 MHz, $CDCl_3$



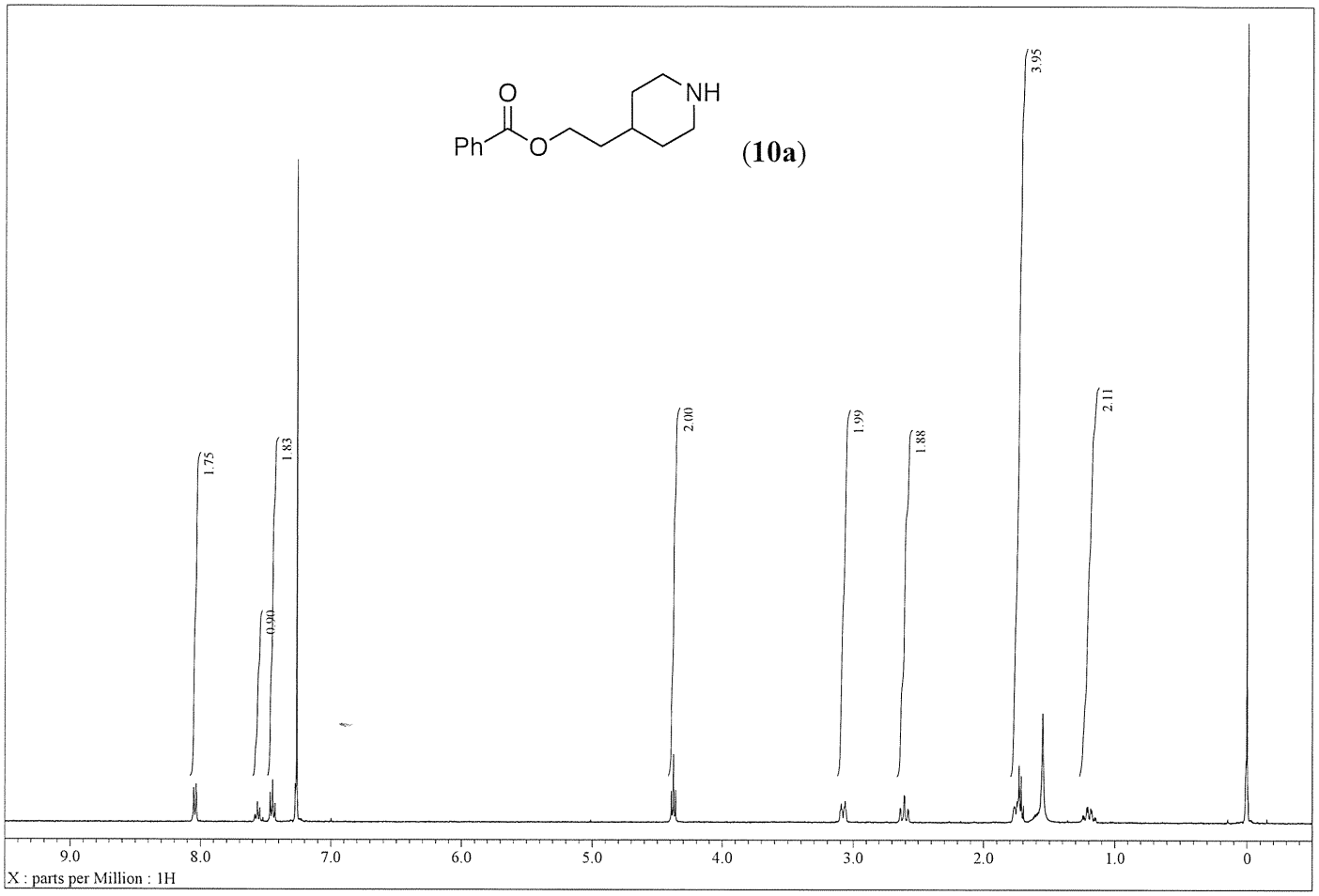
^{13}C NMR, 100 MHz, $CDCl_3$



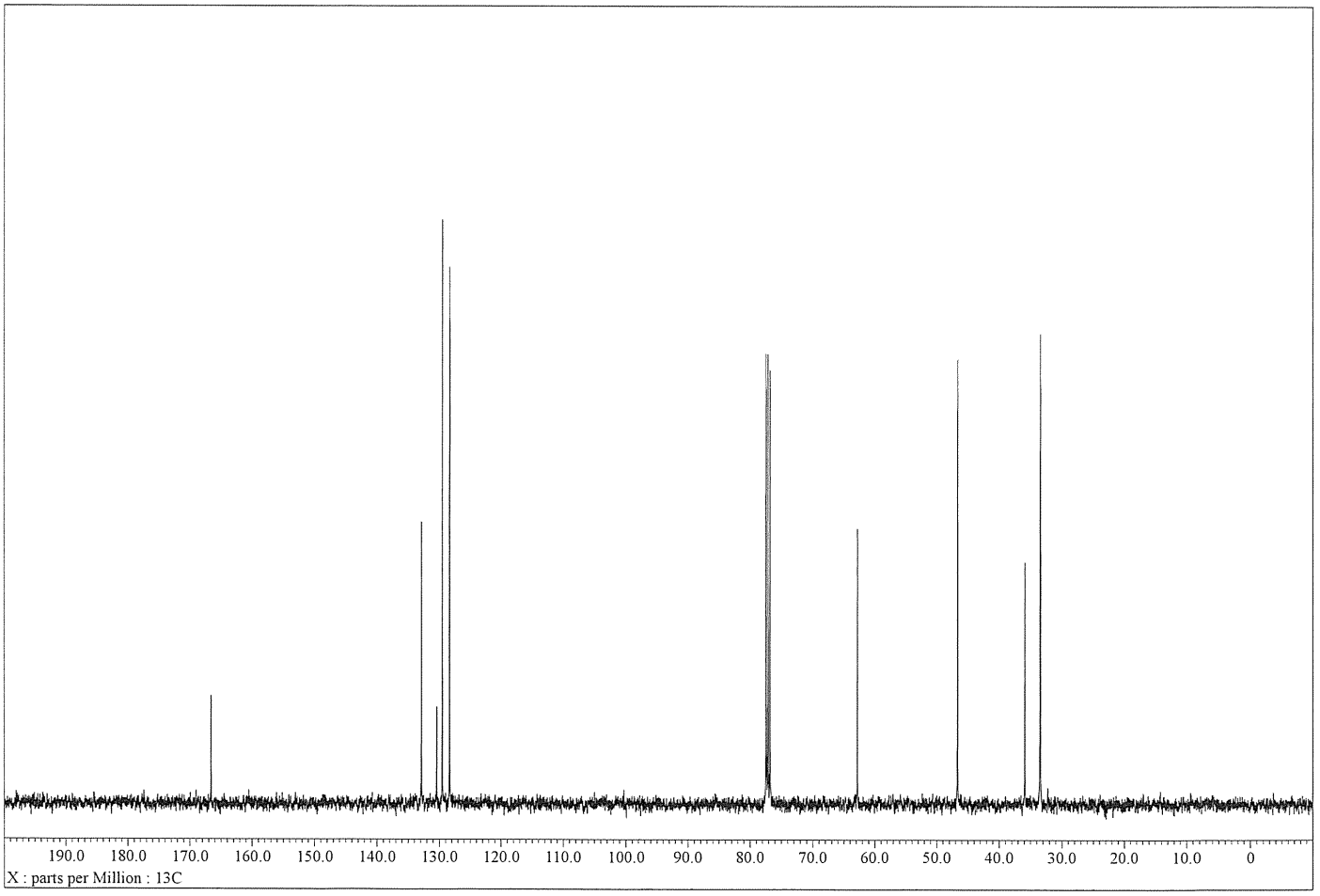
^{1}H NMR, 400 MHz, $CDCl_3$



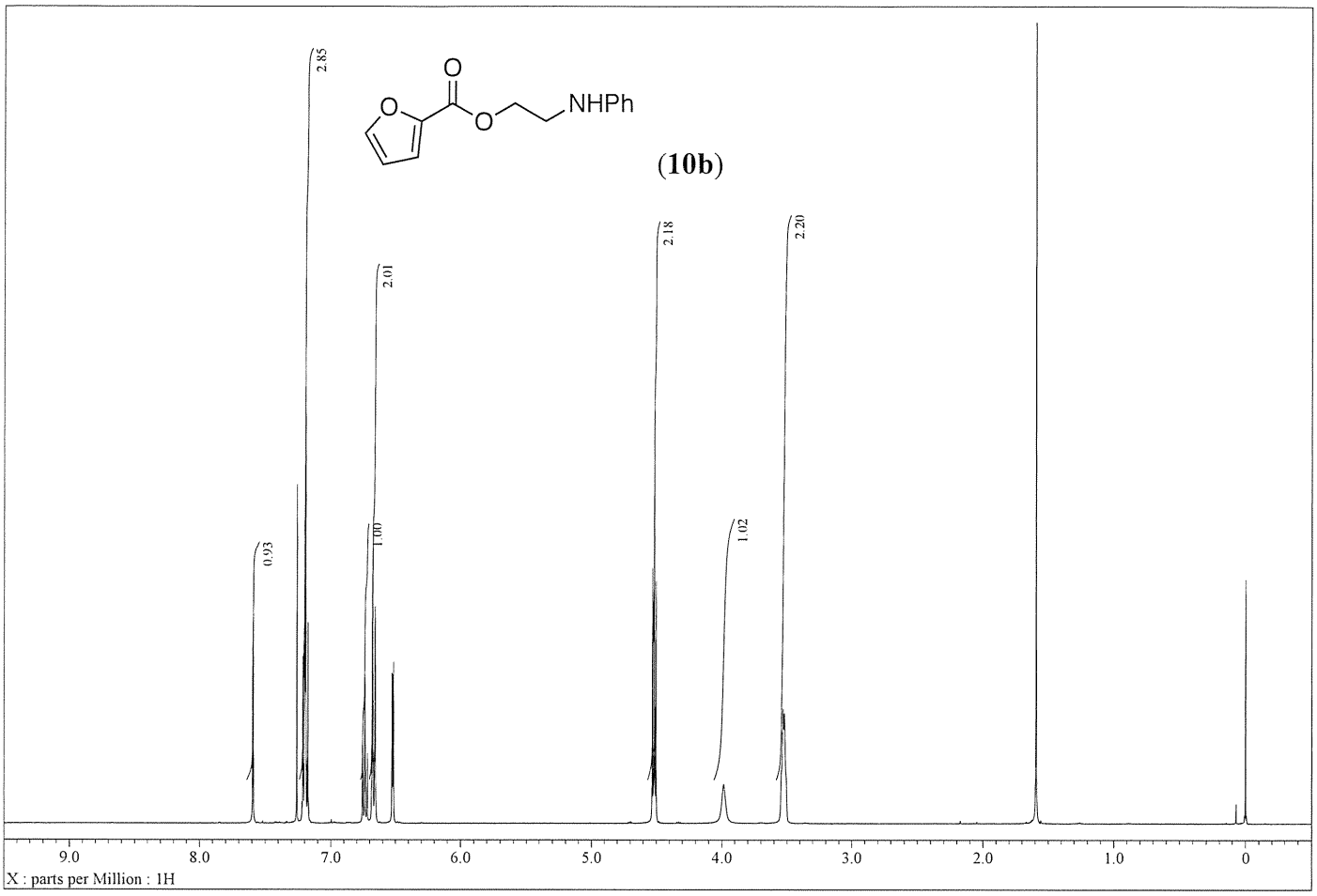
^{13}C NMR, 100 MHz, $CDCl_3$



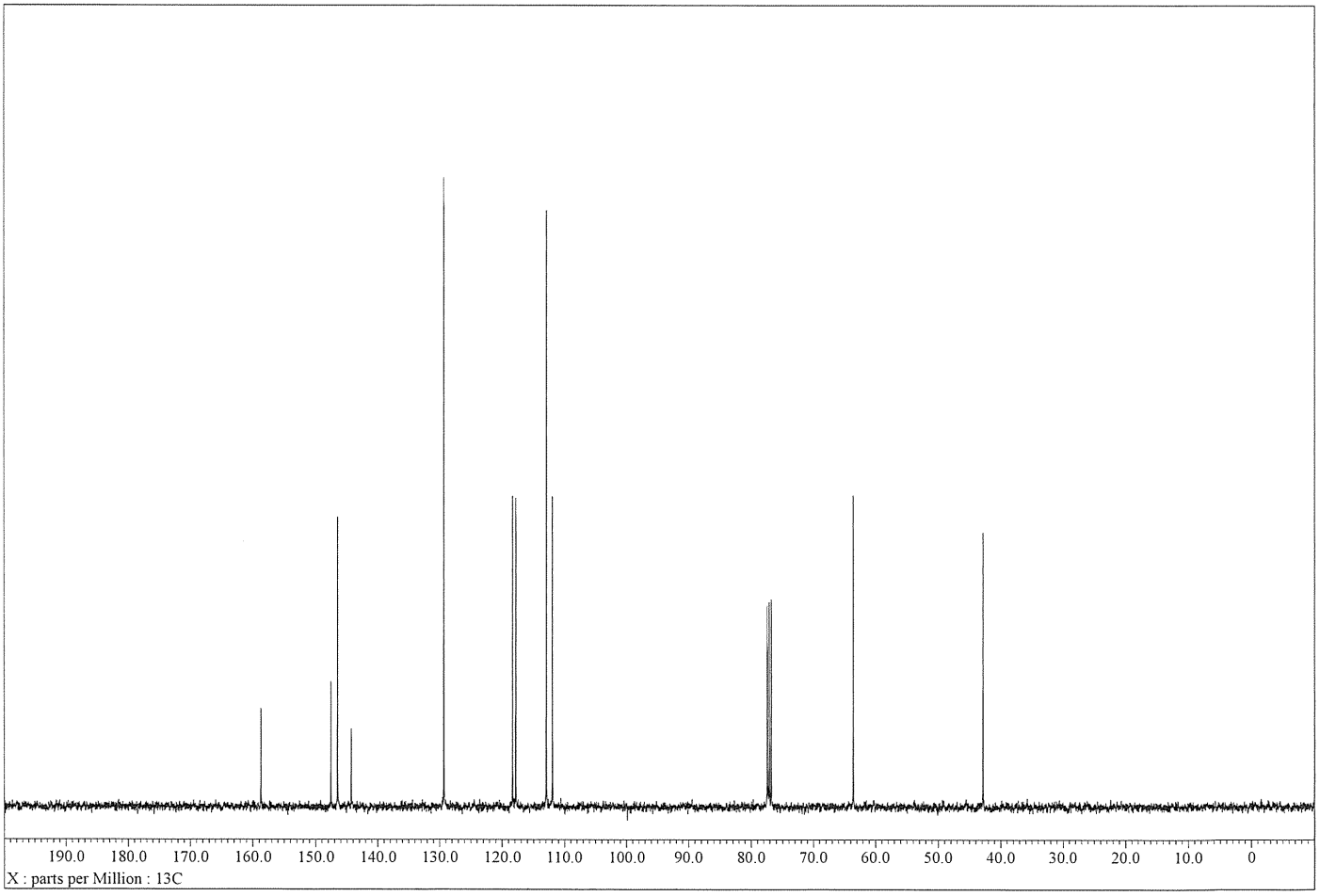
^{1}H NMR, 400 MHz, $CDCl_3$



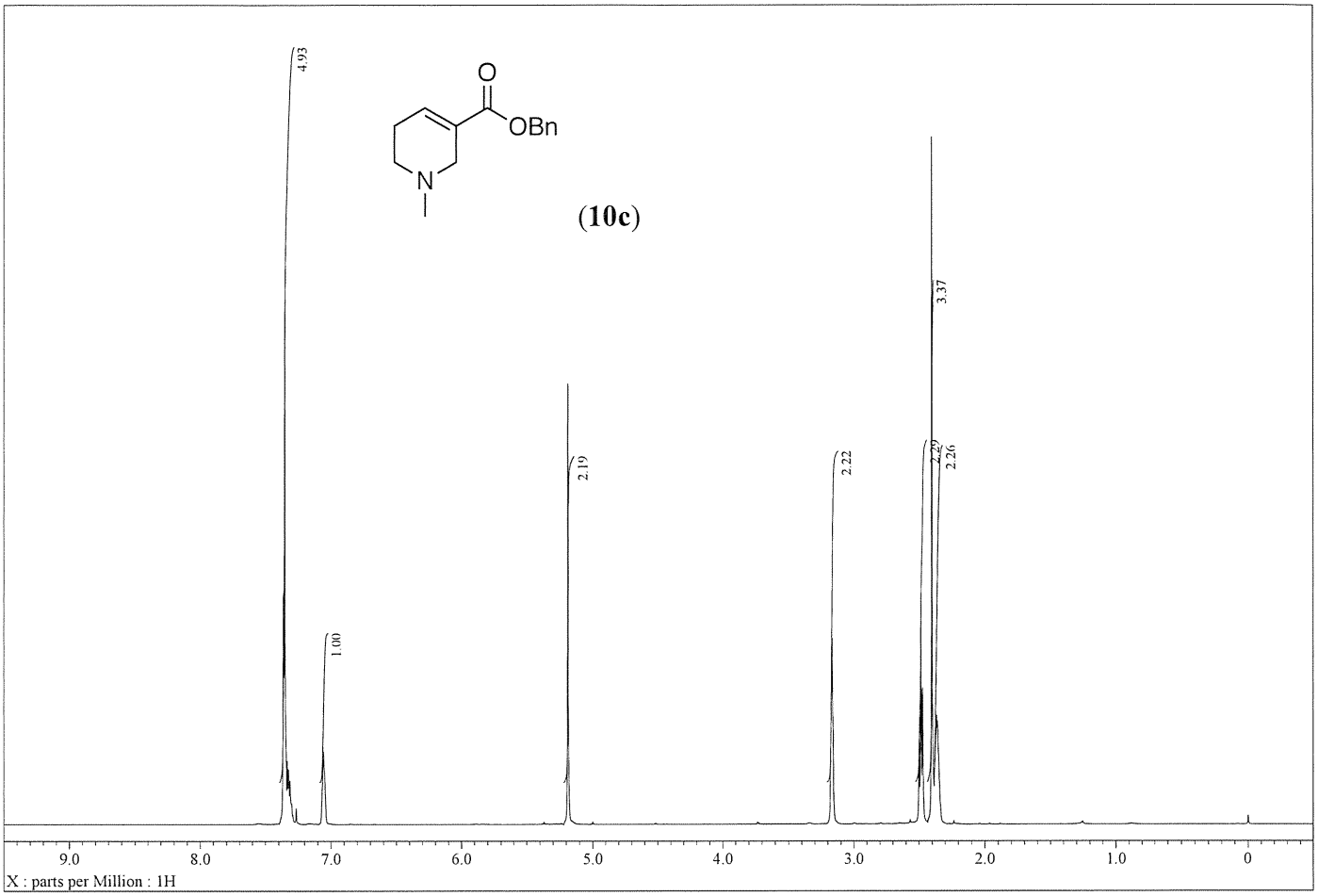
^{13}C NMR, 100 MHz, $CDCl_3$



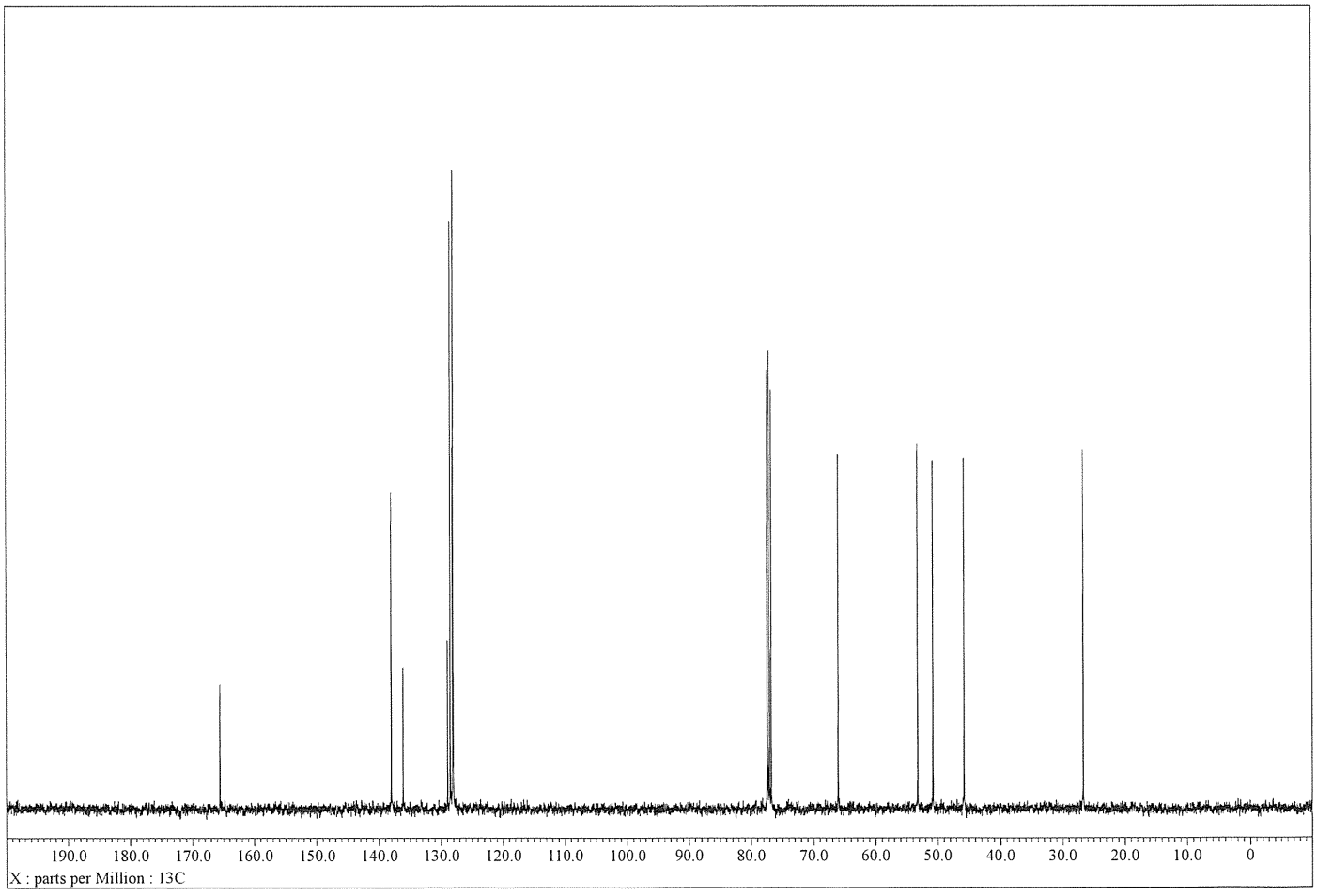
^{1}H NMR, 400 MHz, $CDCl_3$



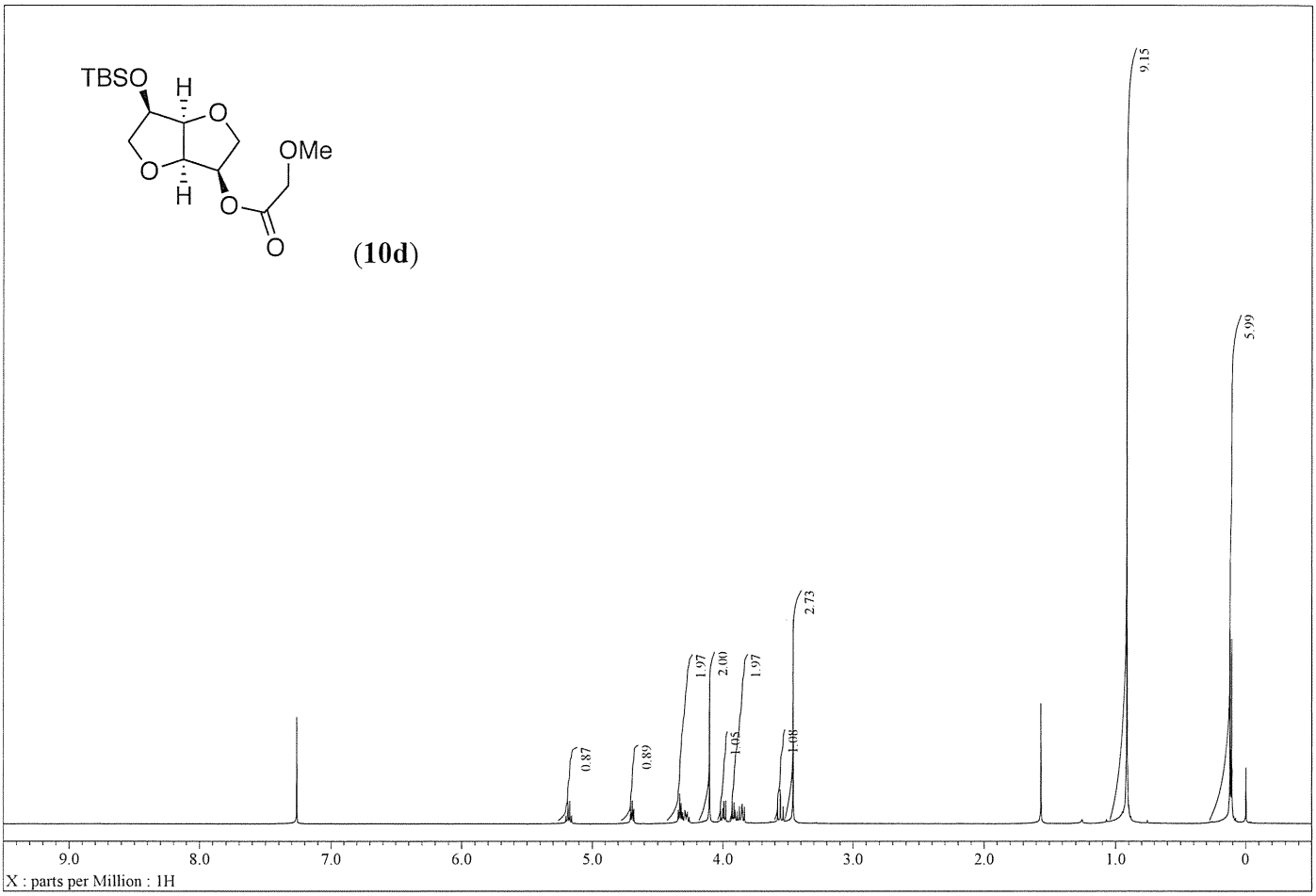
^{13}C NMR, 100 MHz, $CDCl_3$



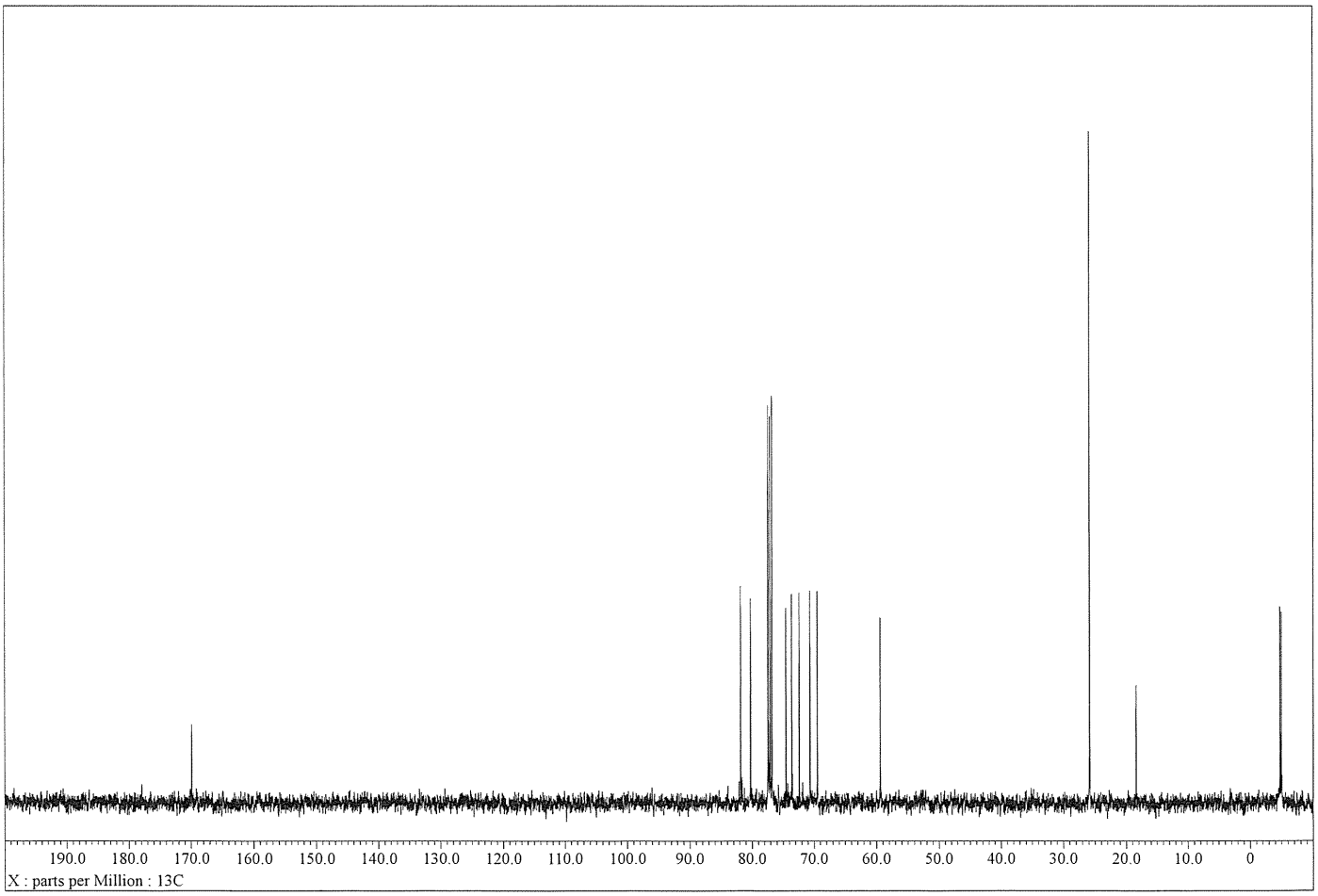
^{1}H NMR, 400 MHz, $CDCl_3$



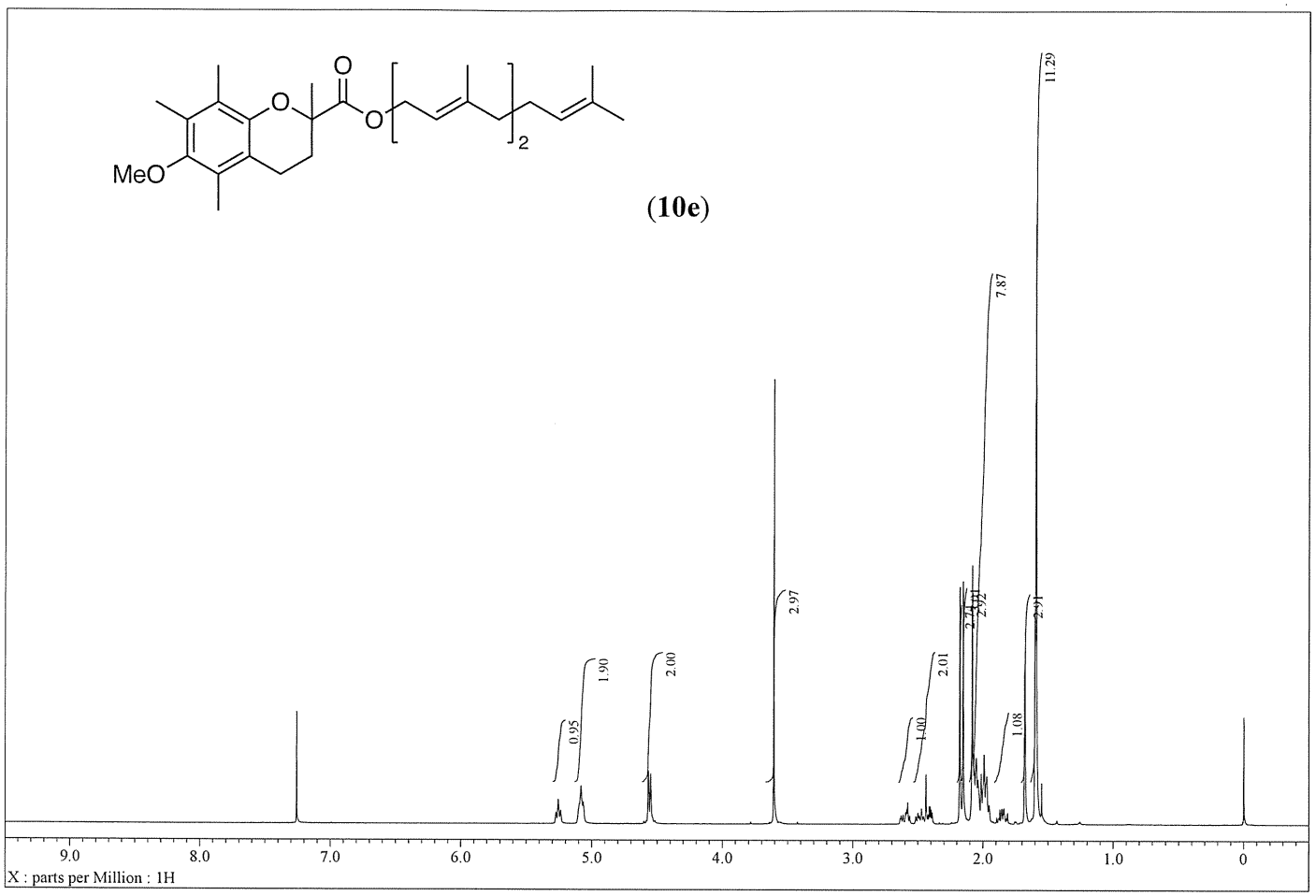
^{13}C NMR, 100 MHz, $CDCl_3$



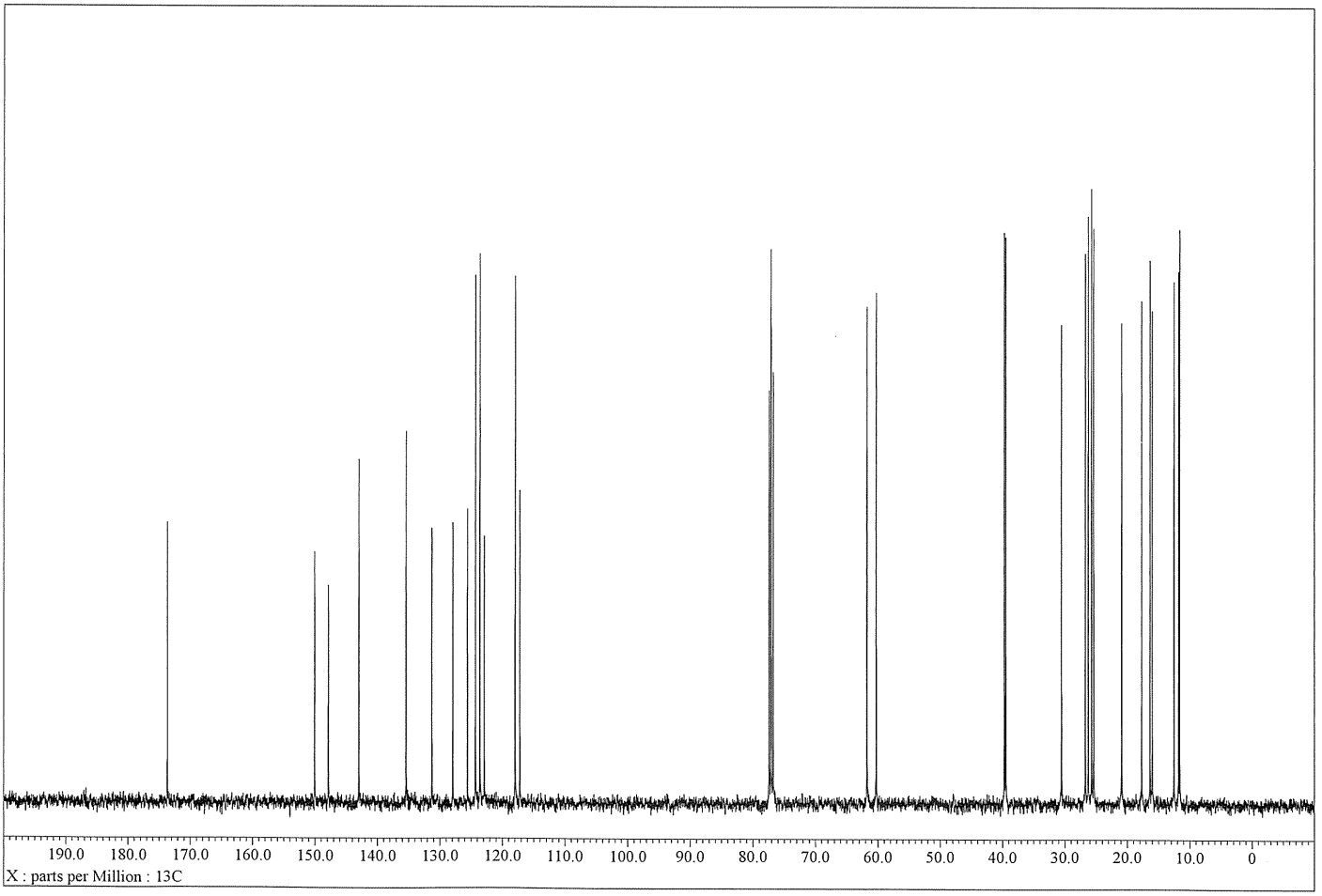
^{1}H NMR, 400 MHz, $CDCl_3$



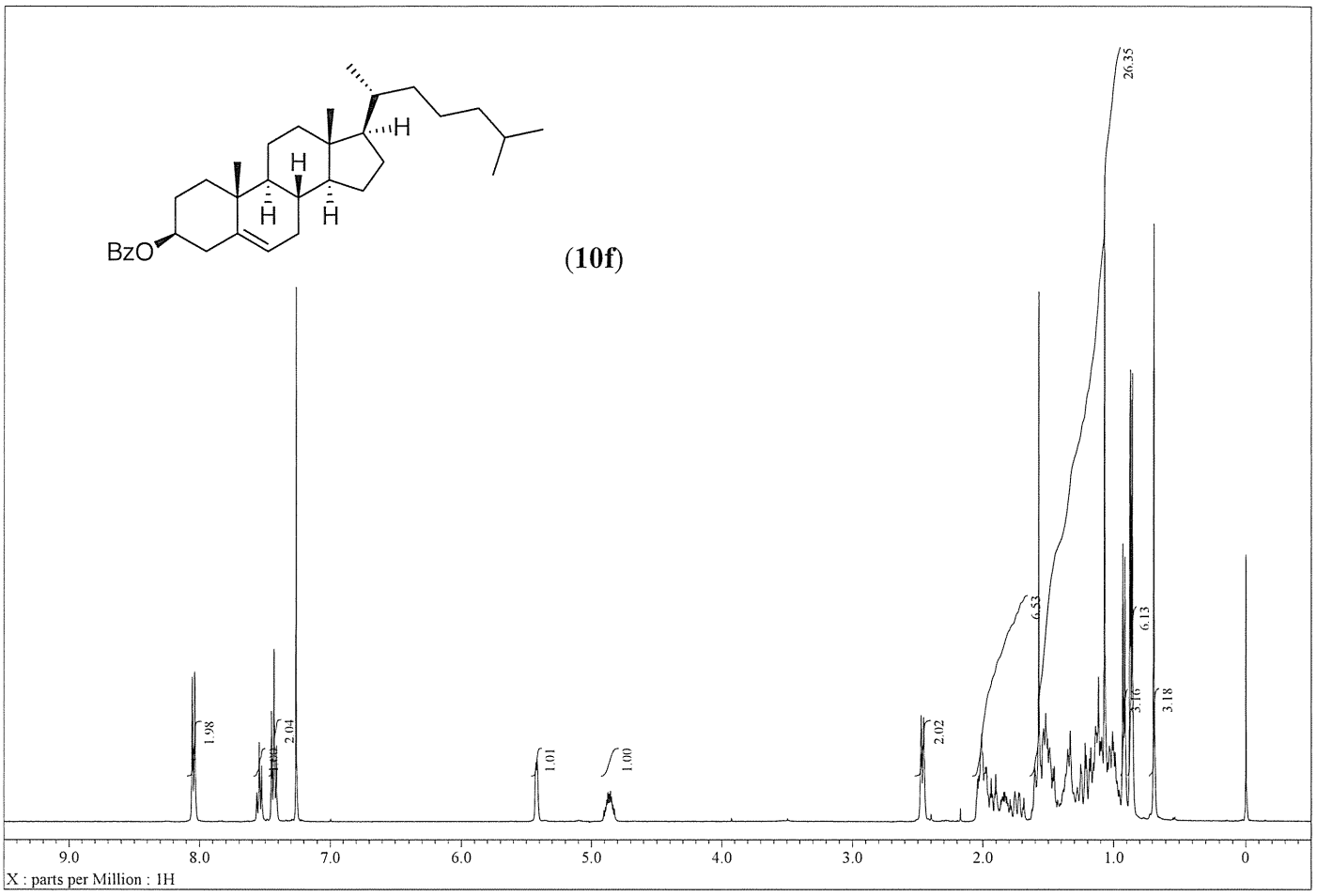
^{13}C NMR, 100 MHz, $CDCl_3$



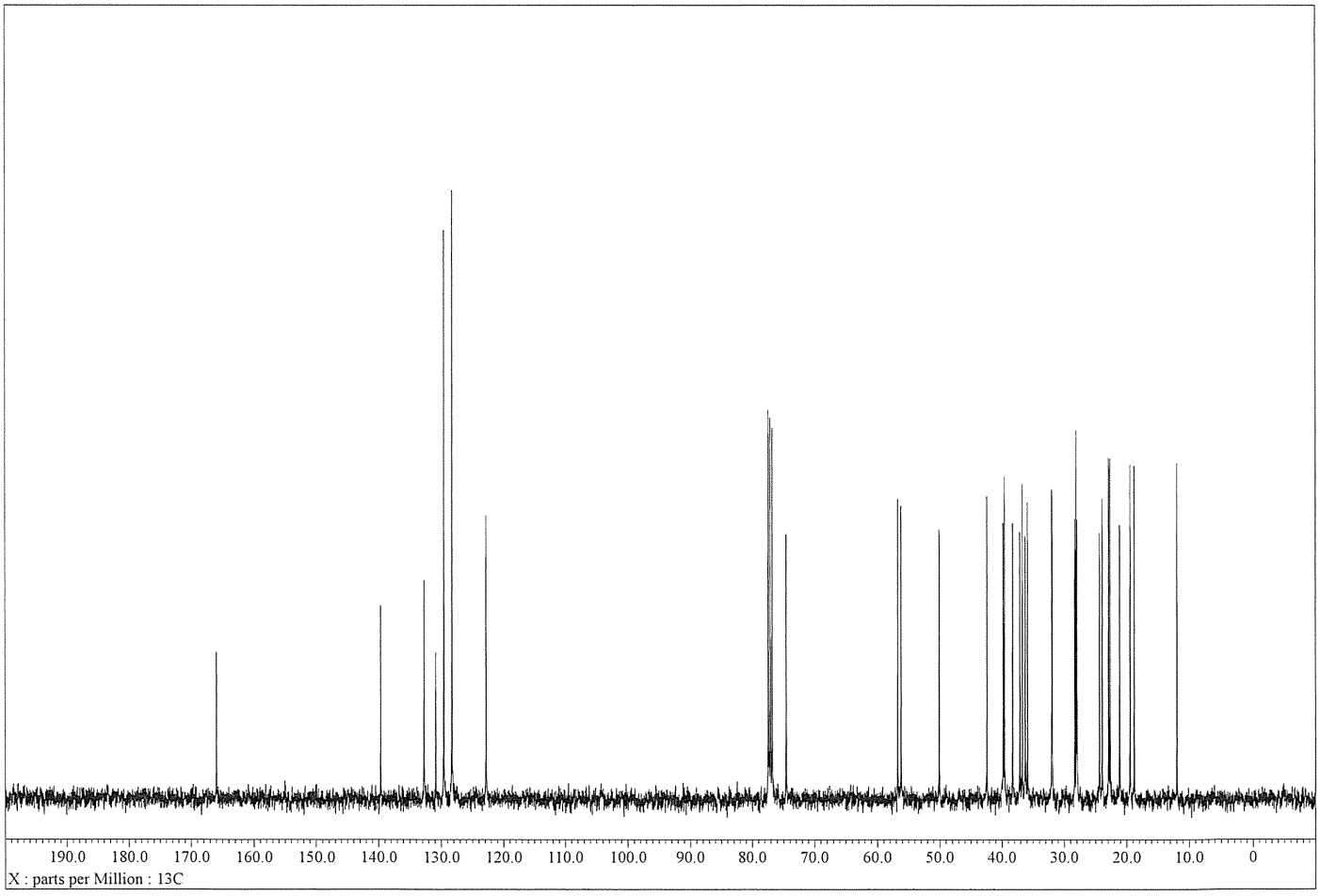
^{1}H NMR, 400 MHz, $CDCl_3$



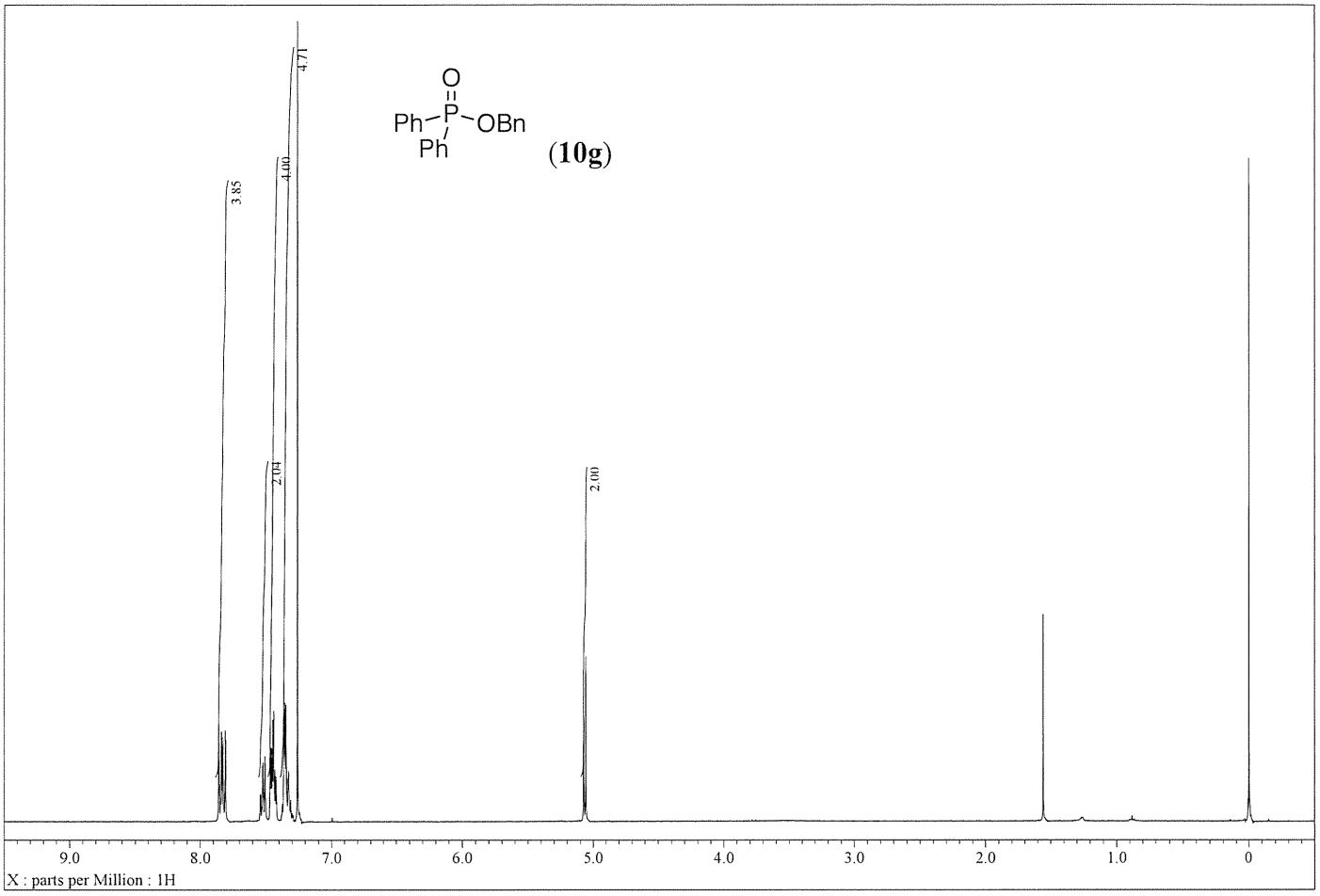
^{13}C NMR, 100 MHz, $CDCl_3$



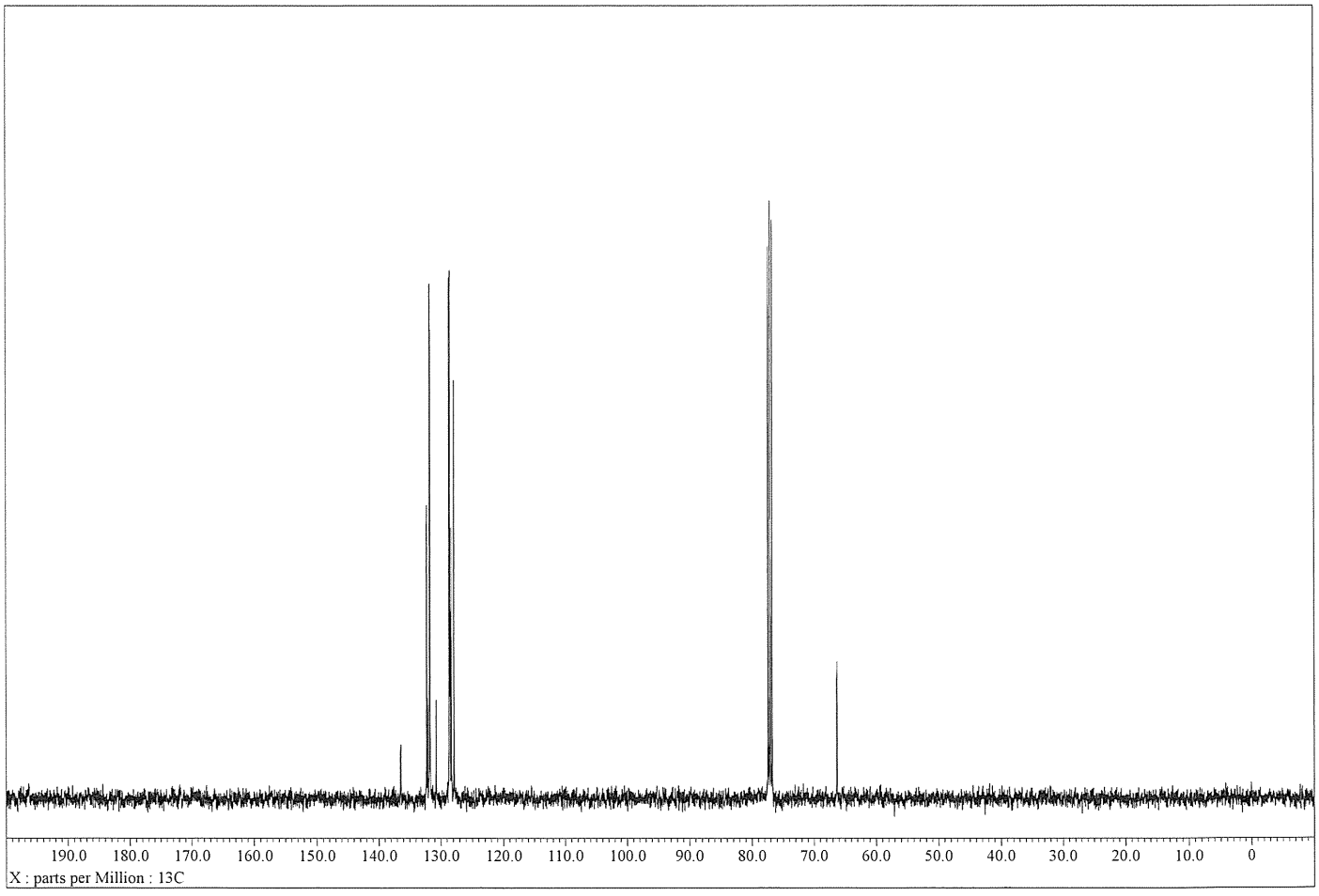
^{1}H NMR, 400 MHz, $CDCl_3$



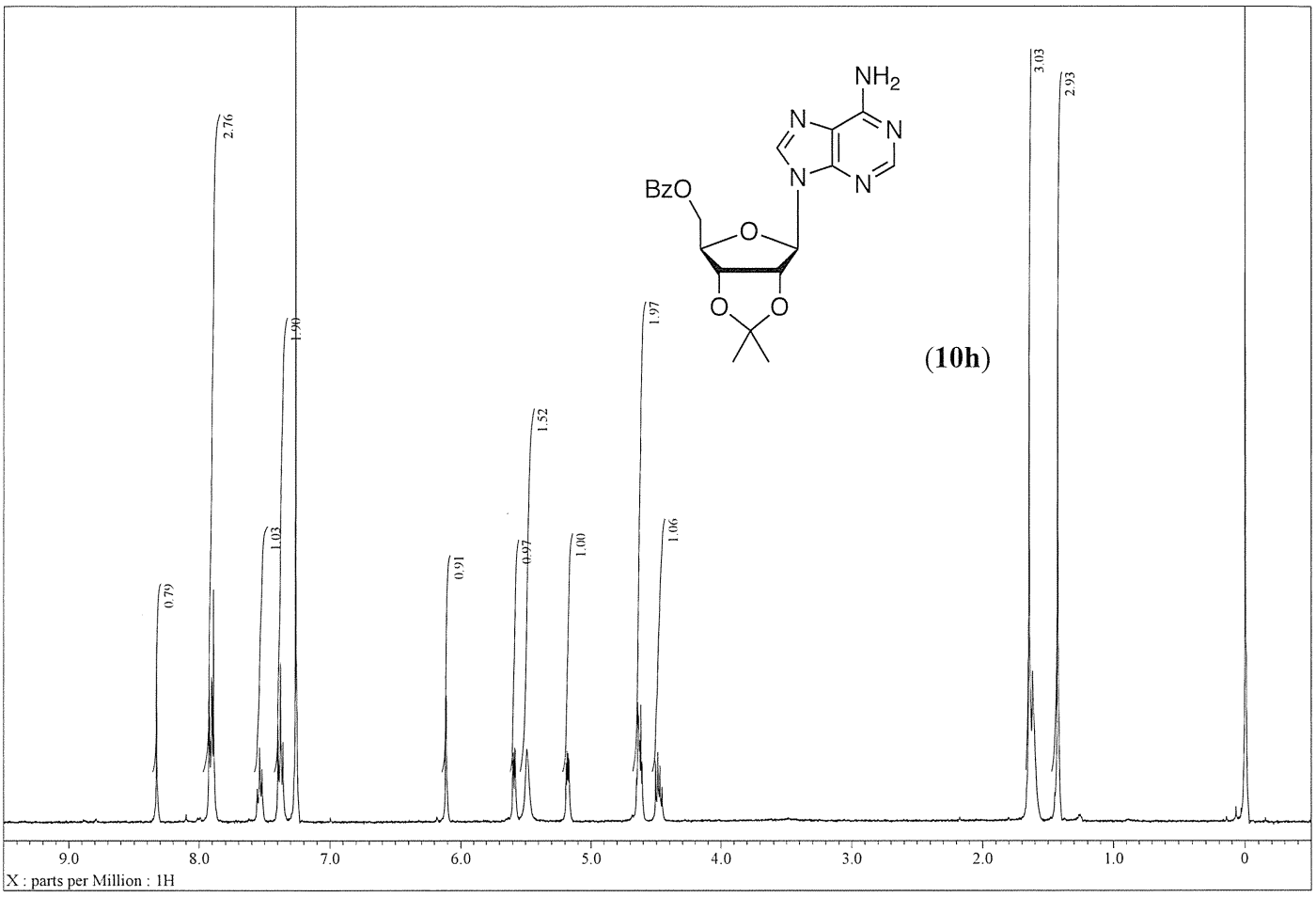
^{13}C NMR, 100 MHz, $CDCl_3$



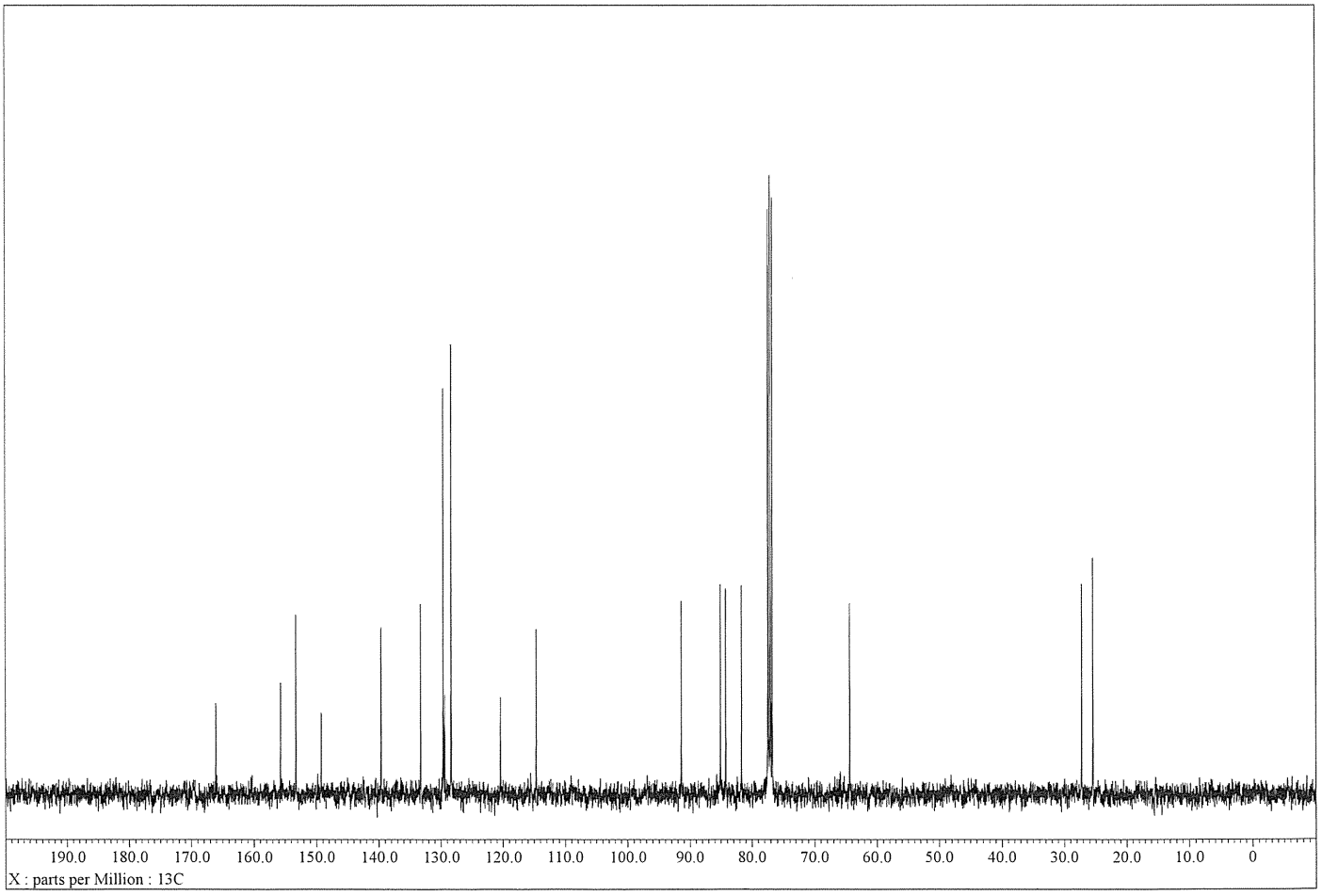
^{1}H NMR, 400 MHz, $CDCl_3$



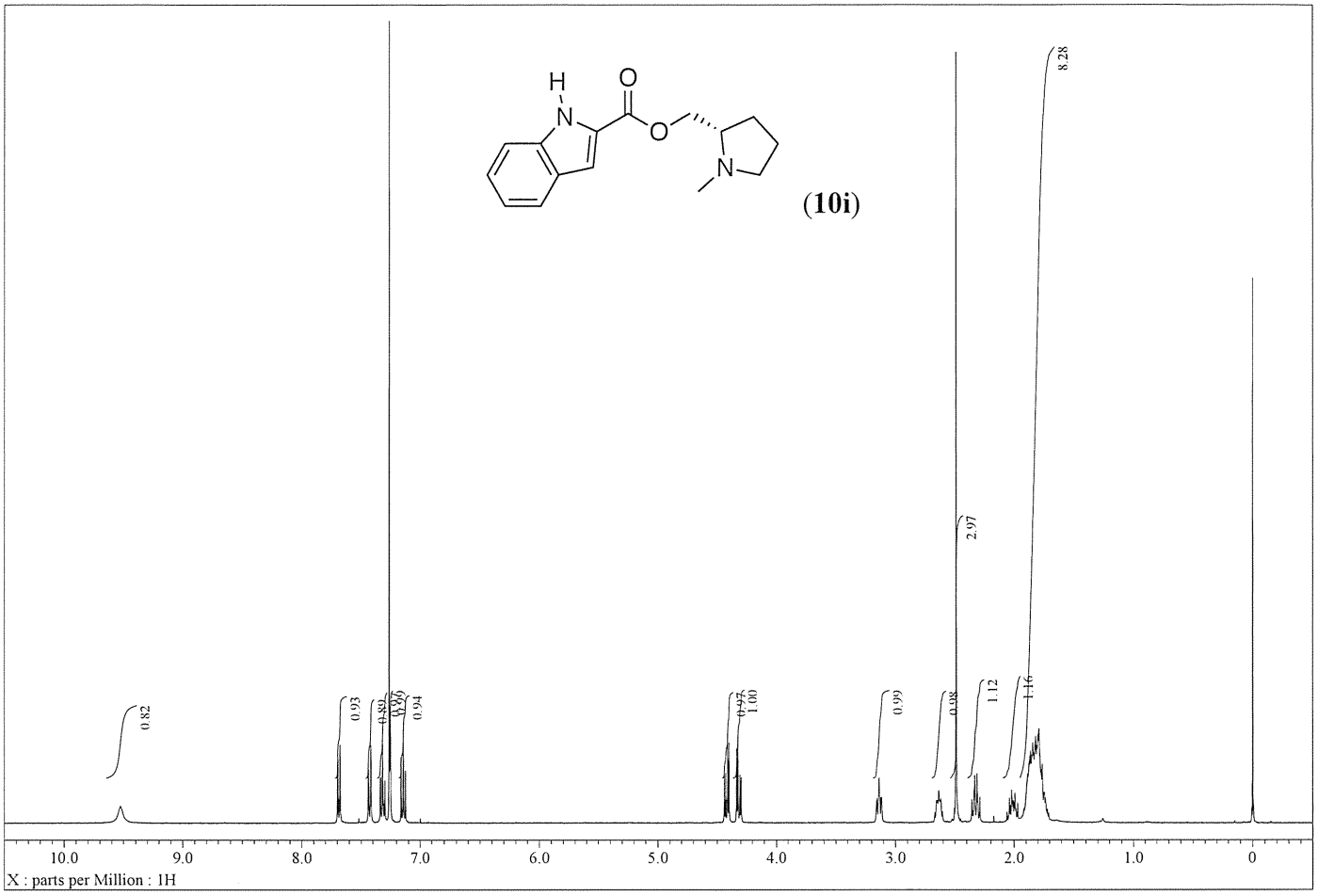
^{13}C NMR, 100 MHz, $CDCl_3$



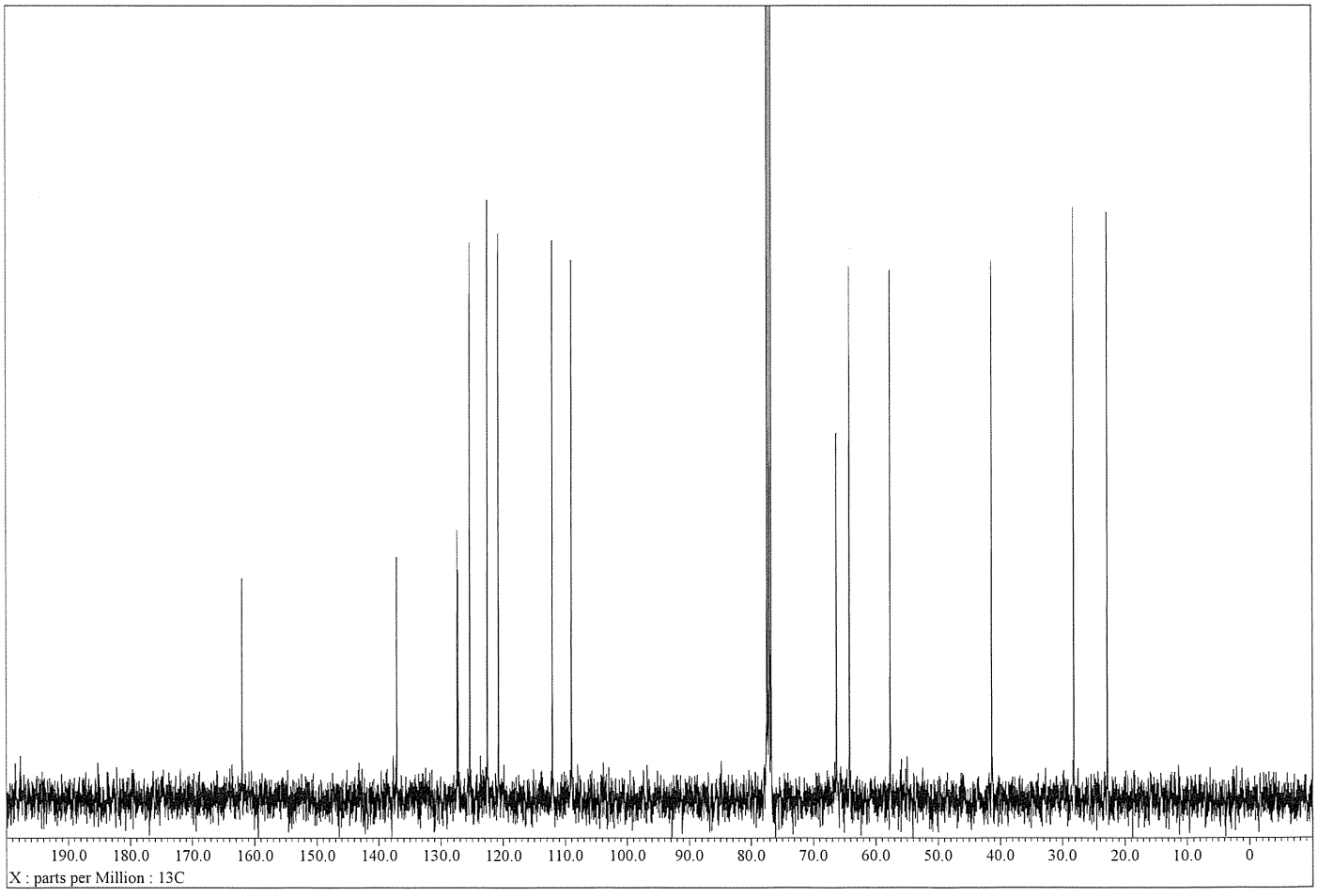
^{1}H NMR, 400 MHz, $CDCl_3$



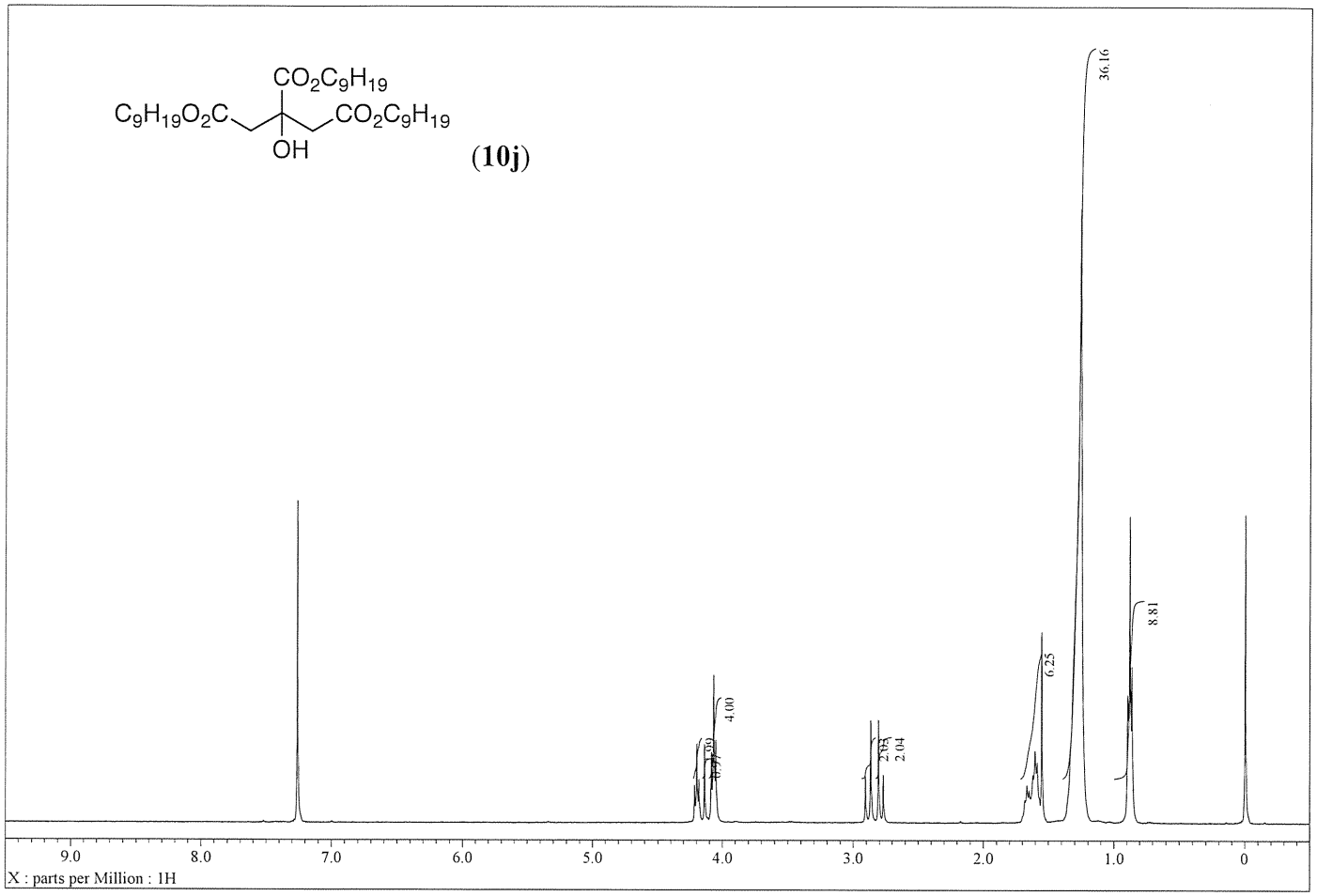
^{13}C NMR, 100 MHz, $CDCl_3$



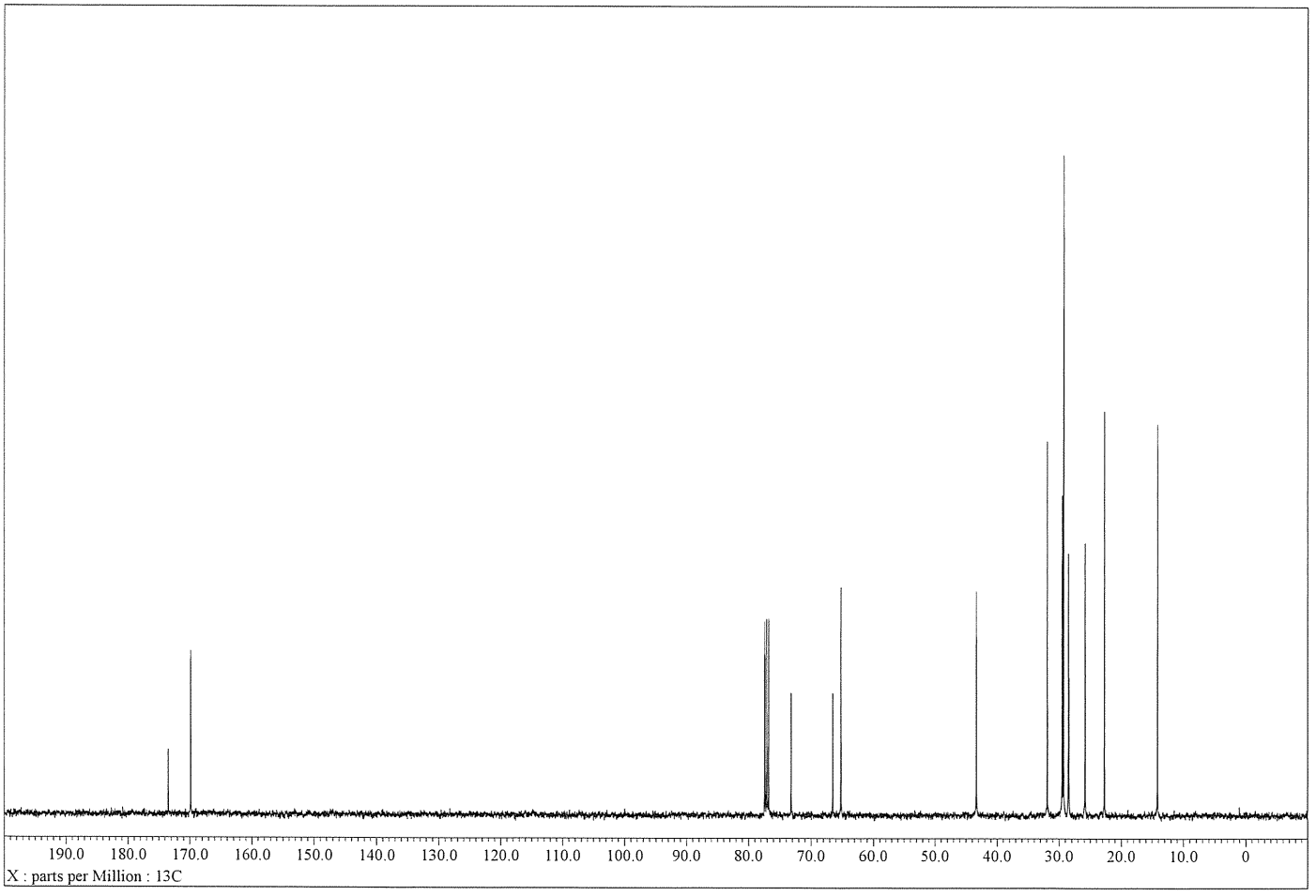
^{1}H NMR, 400 MHz, $CDCl_3$



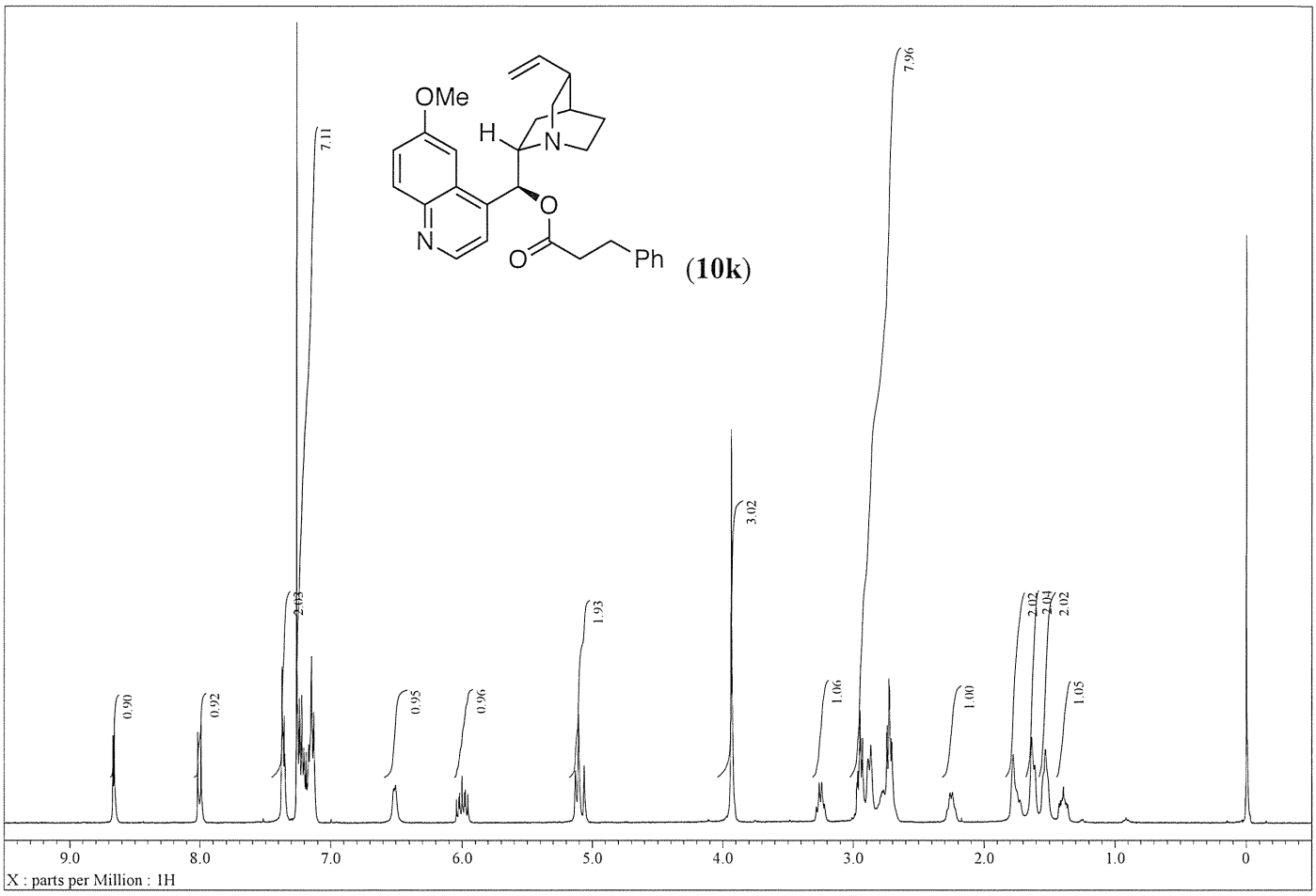
^{13}C NMR, 100 MHz, $CDCl_3$



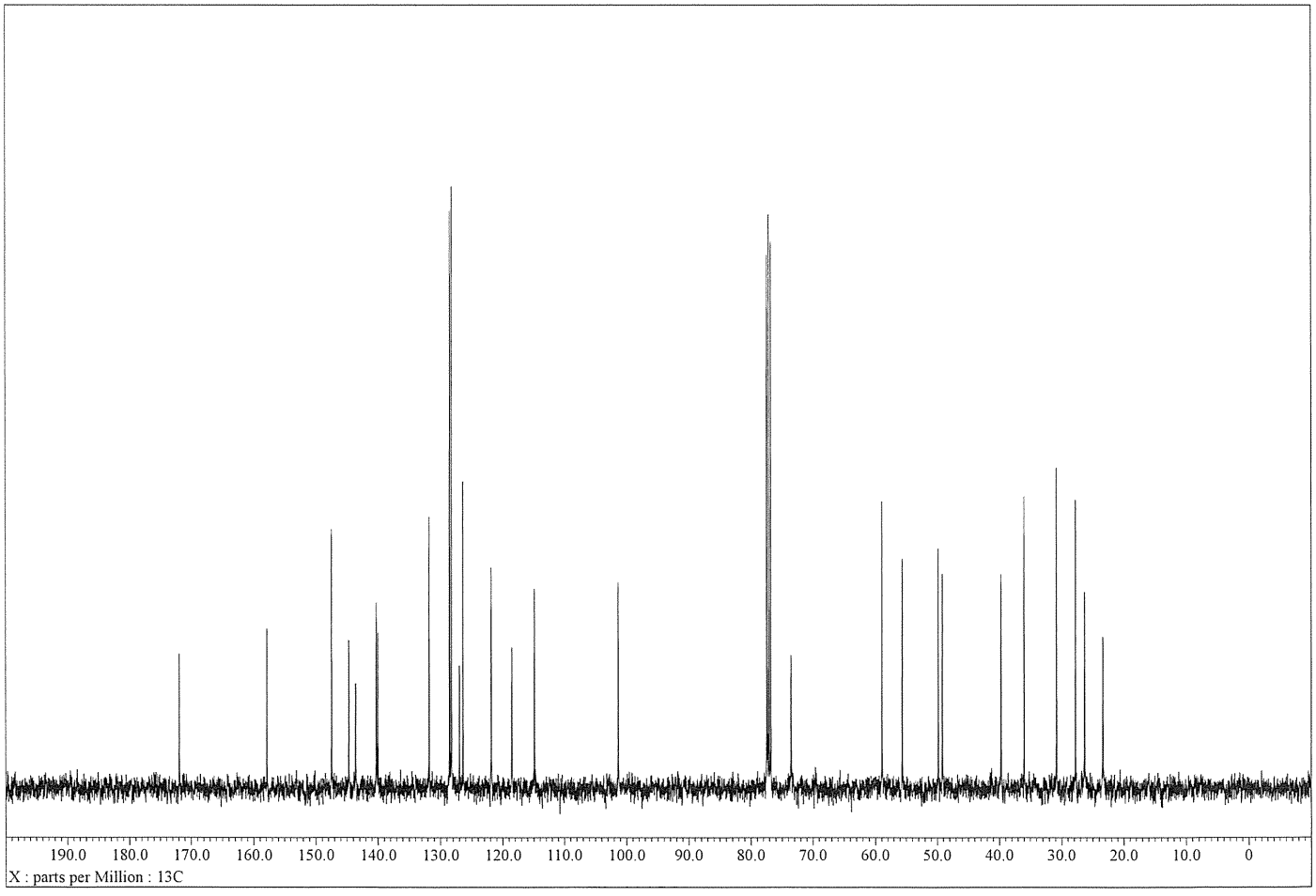
^{1}H NMR, 400 MHz, $CDCl_3$



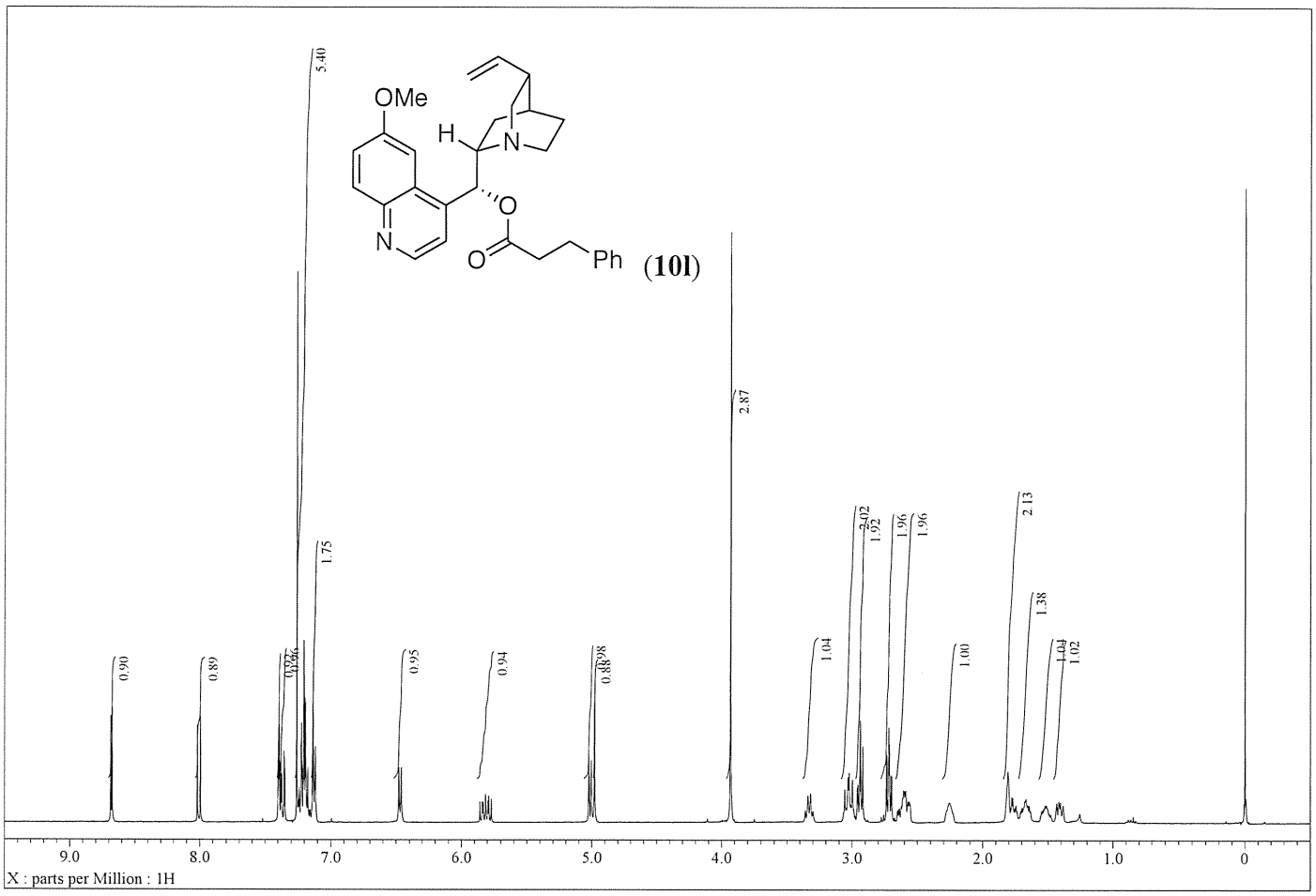
^{13}C NMR, 100 MHz, $CDCl_3$



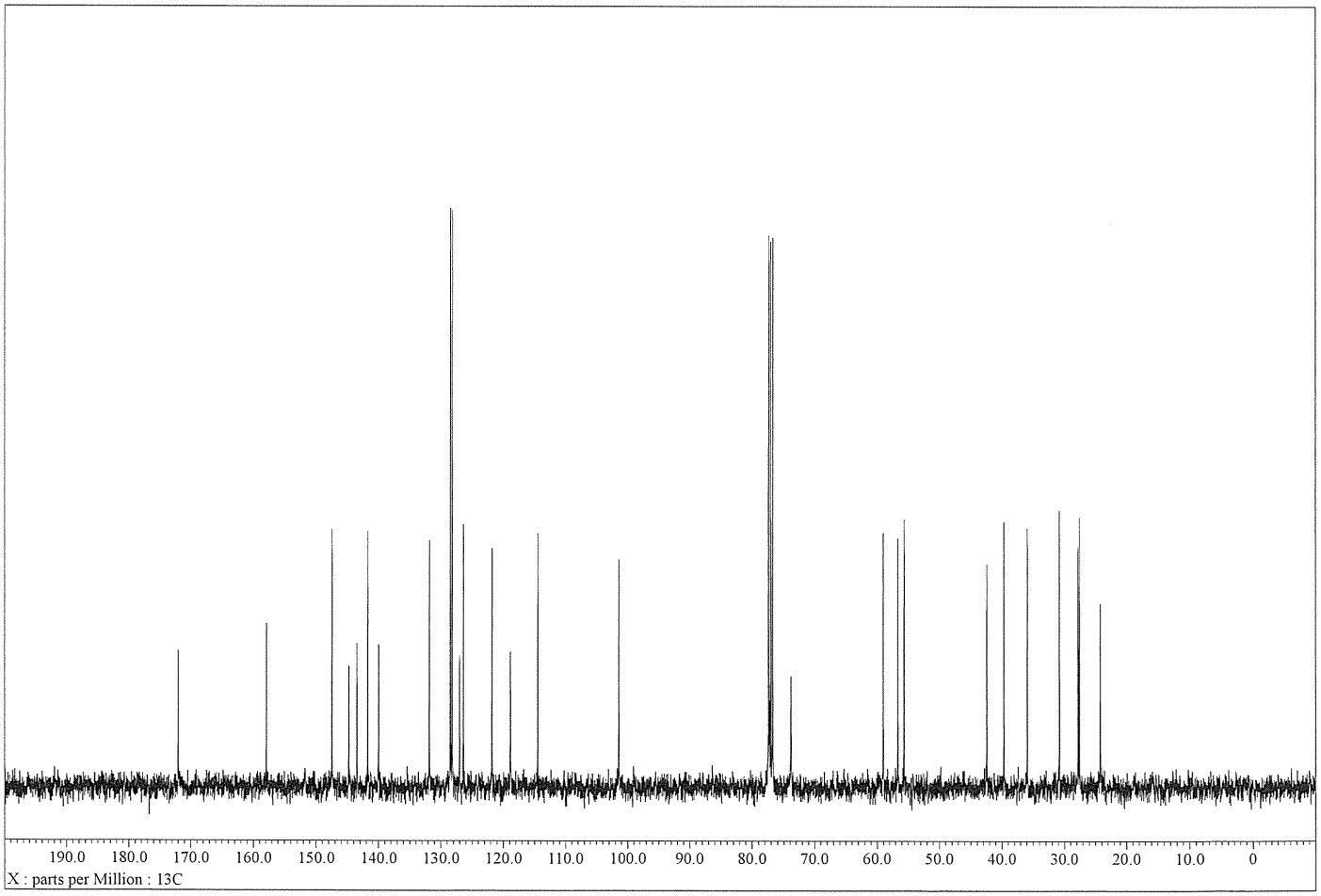
^{1}H NMR, 400 MHz, $CDCl_3$



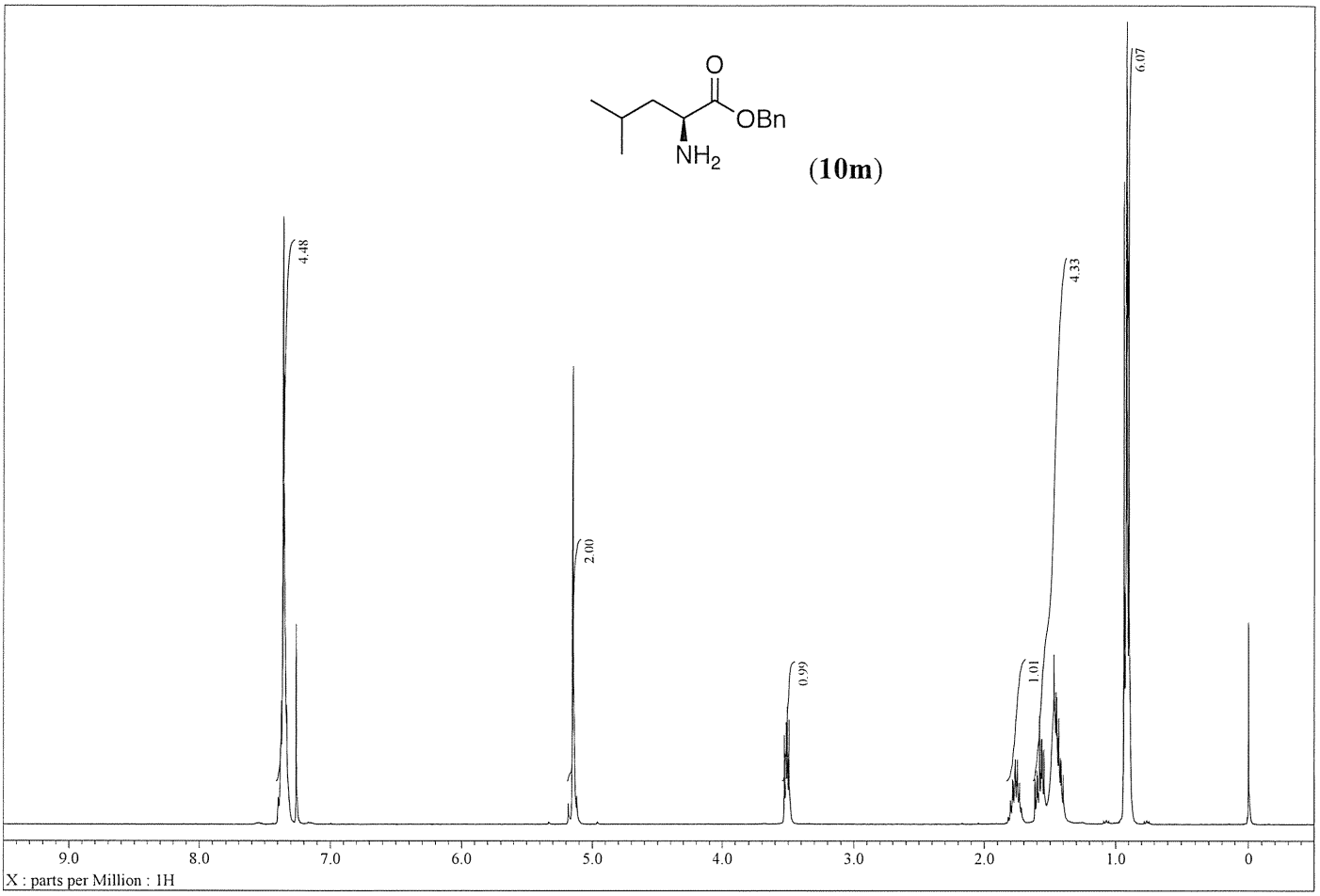
^{13}C NMR, 100 MHz, $CDCl_3$



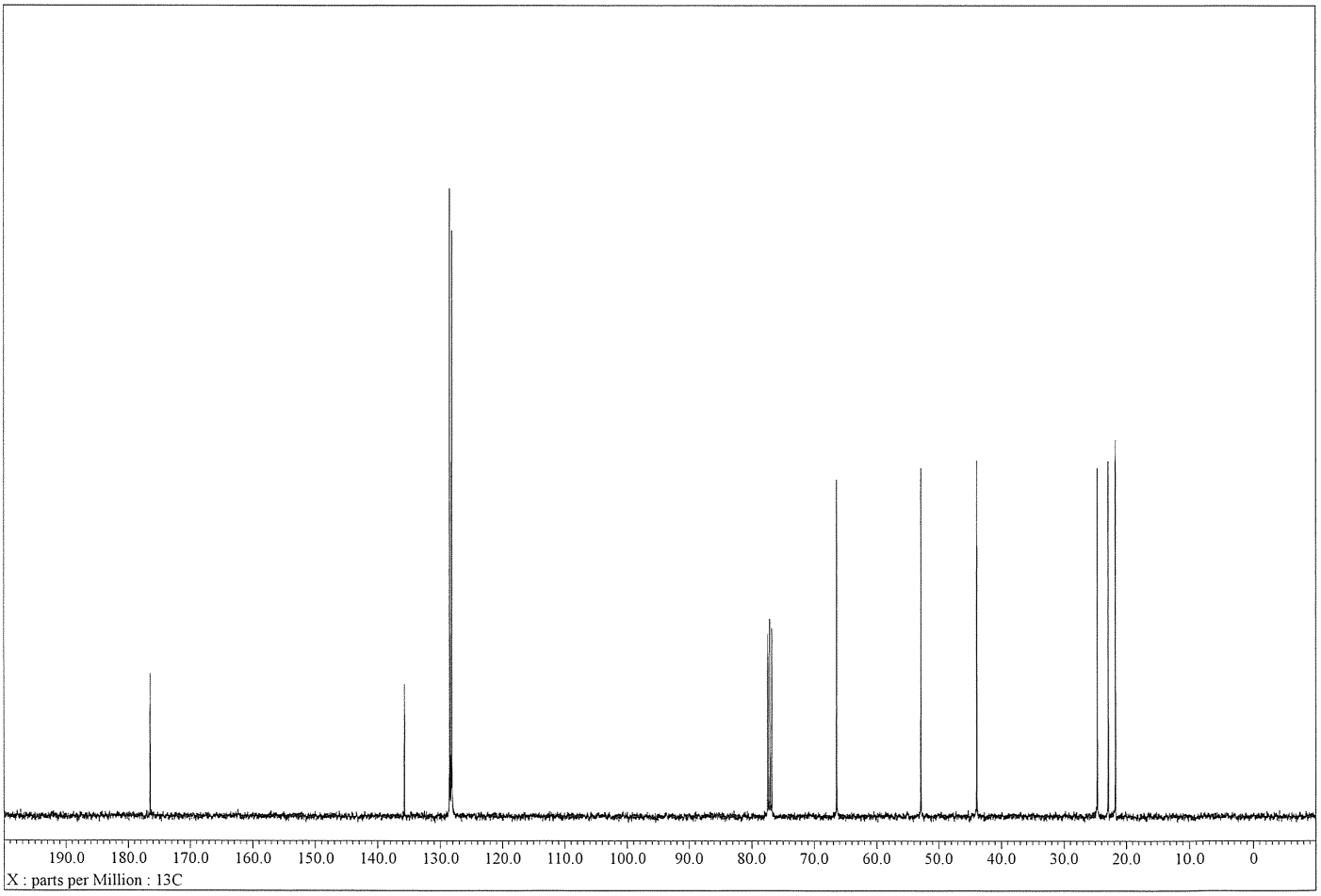
^{1}H NMR, 400 MHz, $CDCl_3$



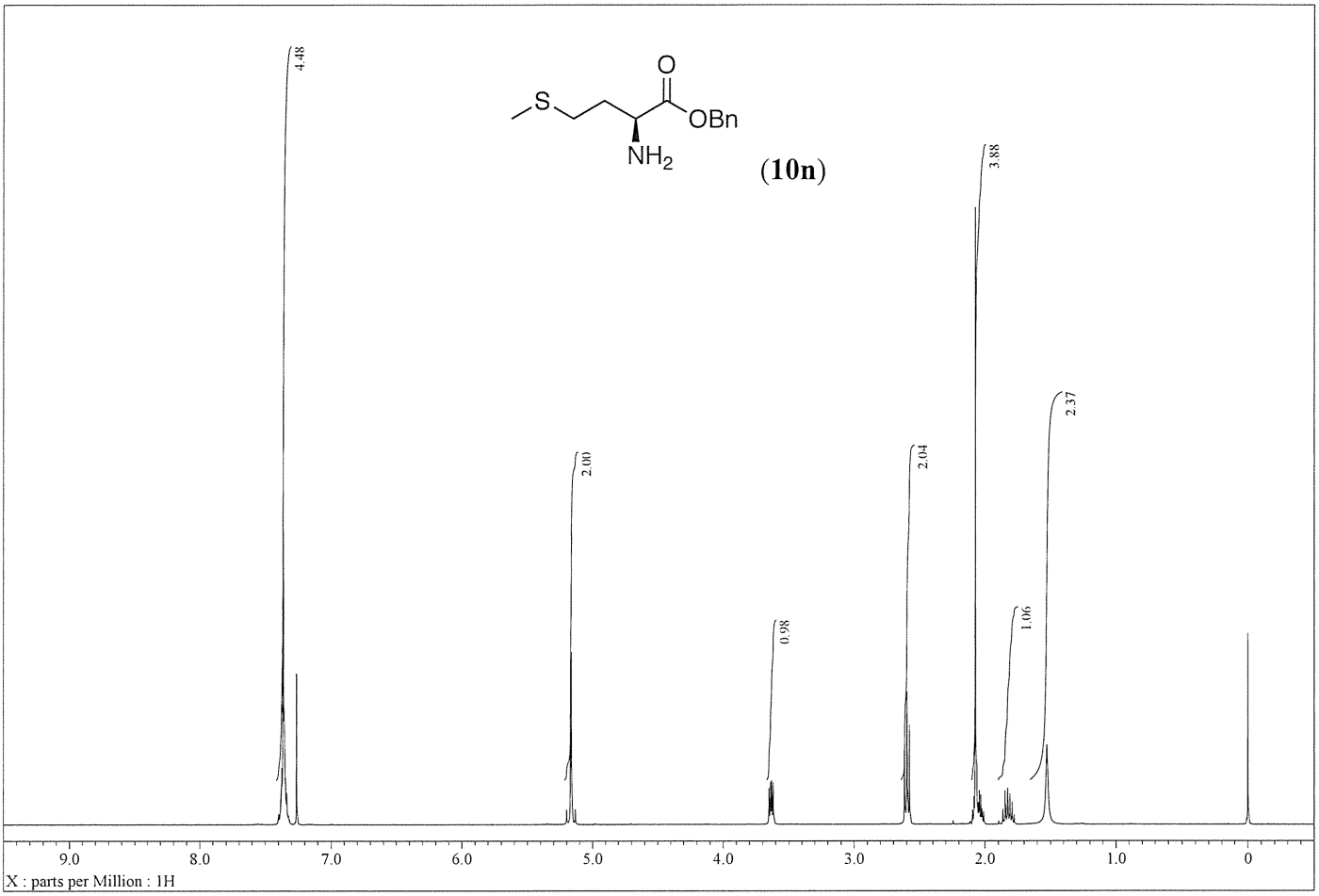
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

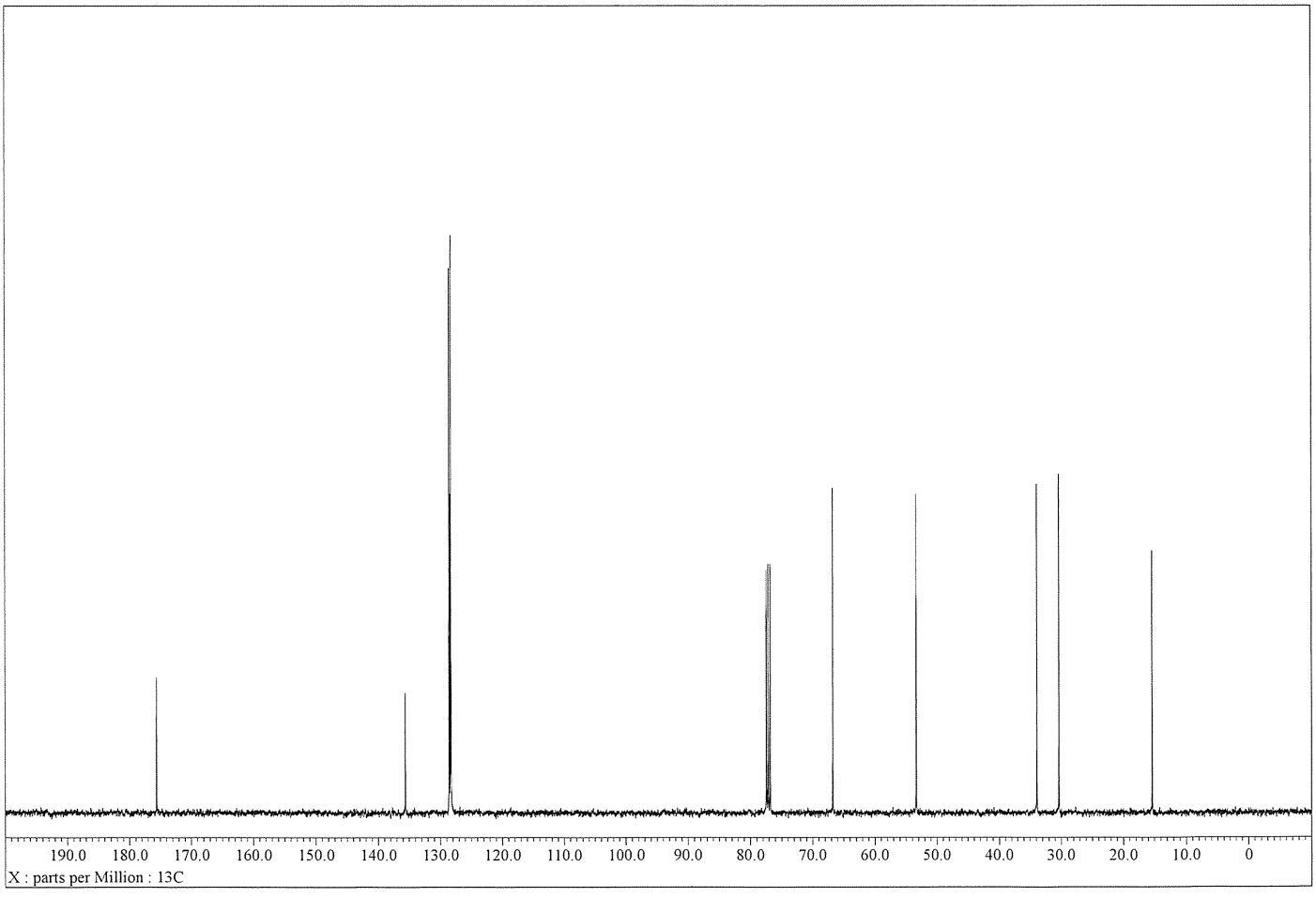


^{13}C NMR, 100 MHz, $CDCl_3$

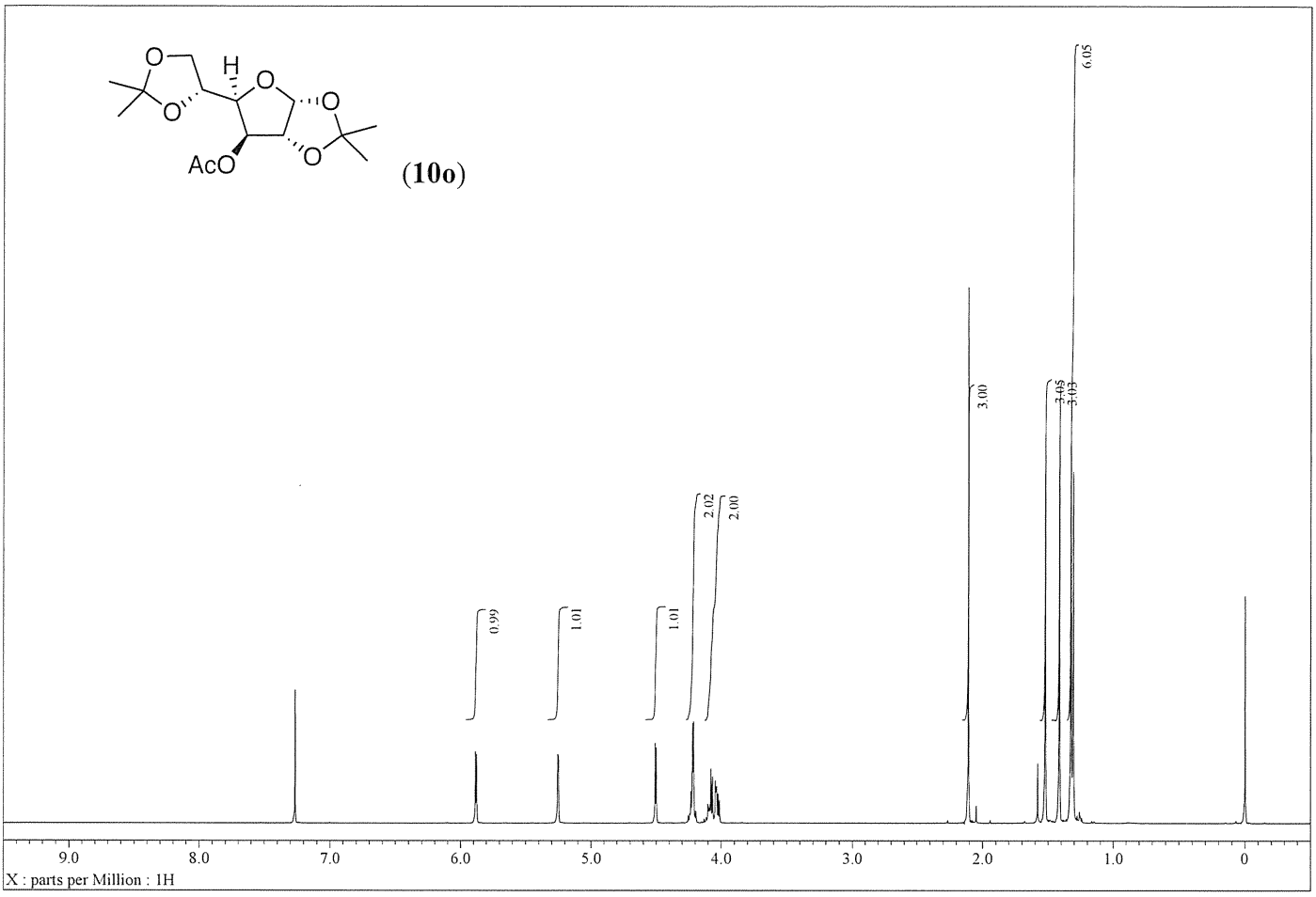


(**10n**)

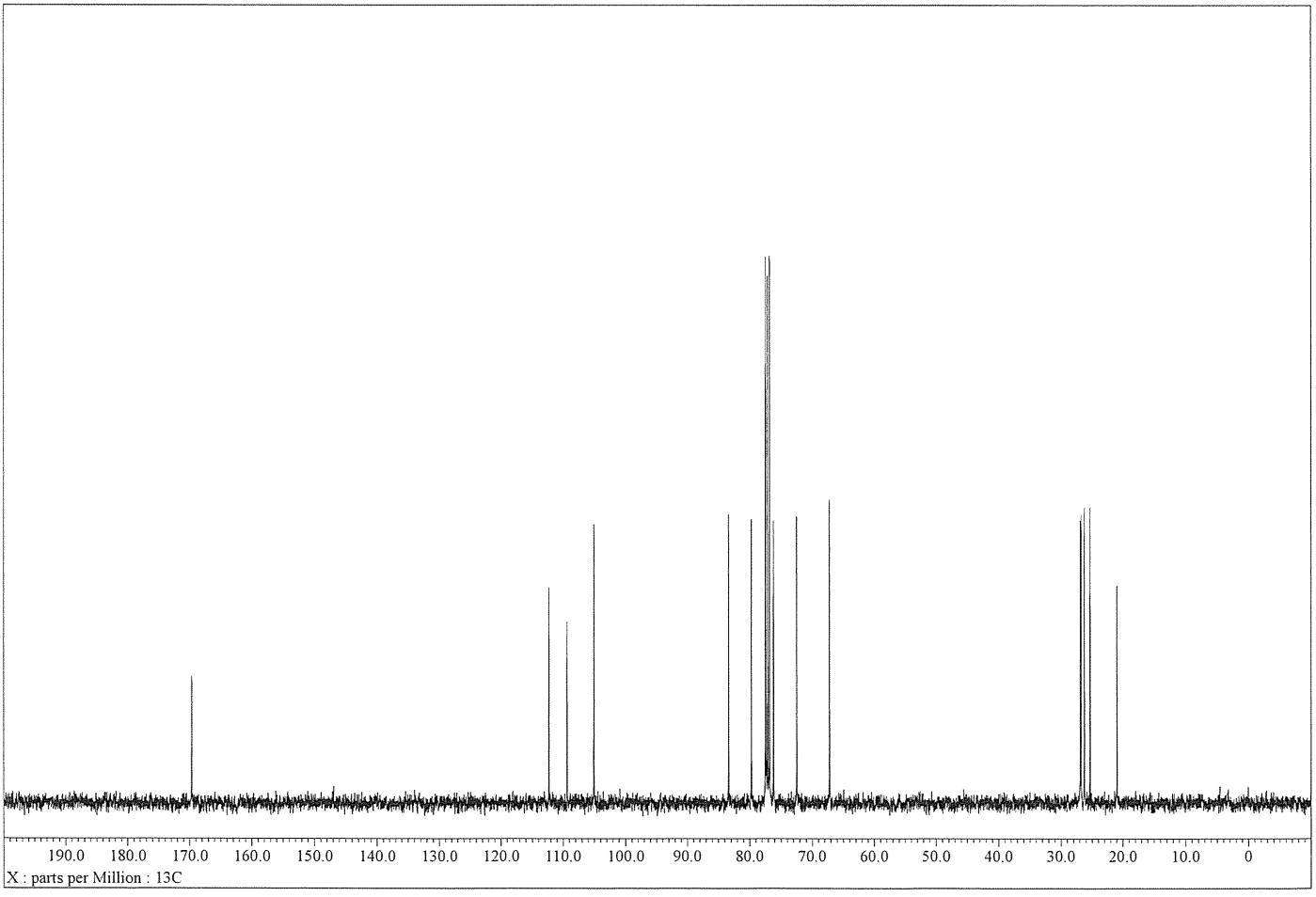
^{1}H NMR, 400 MHz, $CDCl_3$



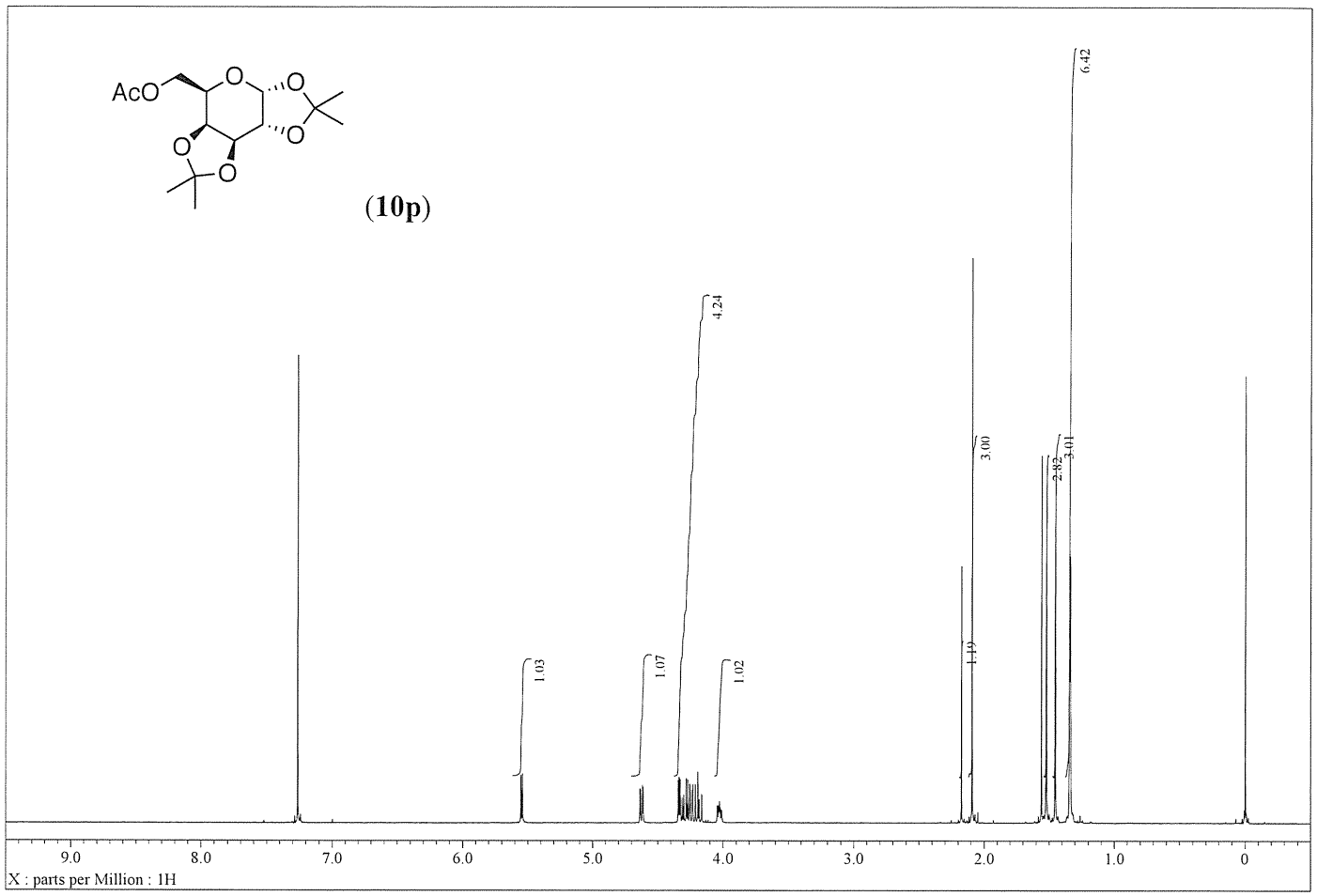
^{13}C NMR, 100 MHz, $CDCl_3$



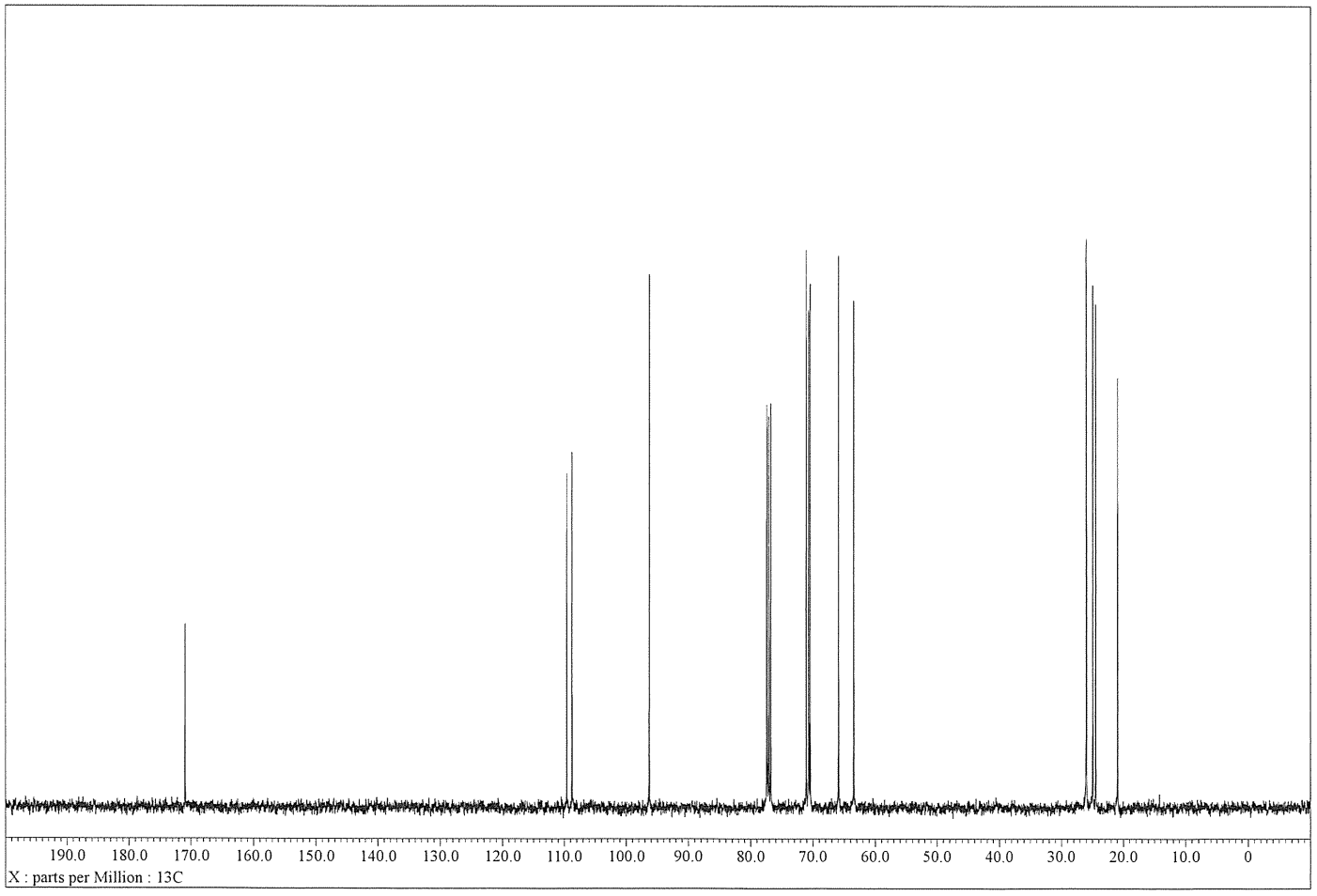
^{1}H NMR, 400 MHz, $CDCl_3$



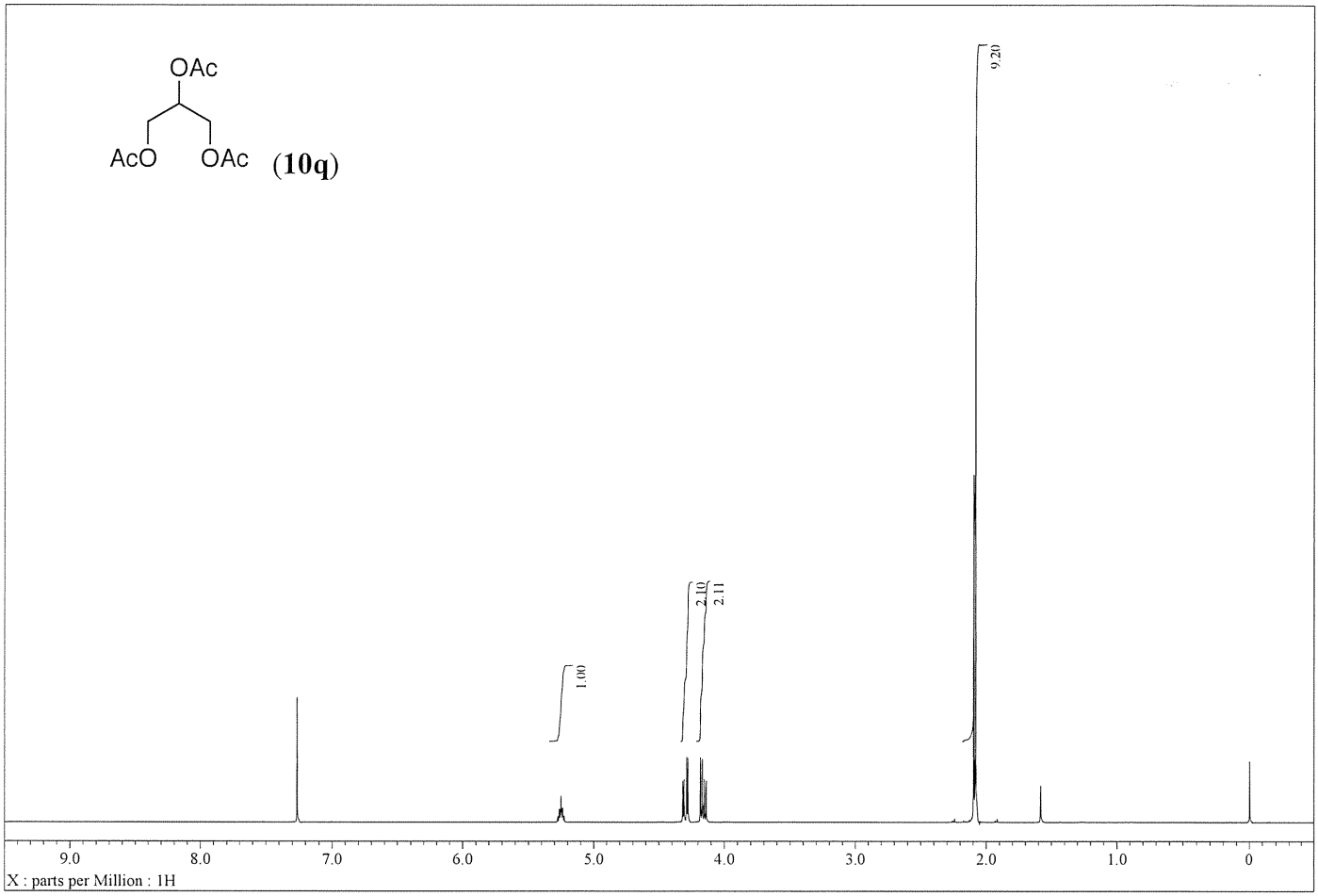
^{13}C NMR, 100 MHz, $CDCl_3$



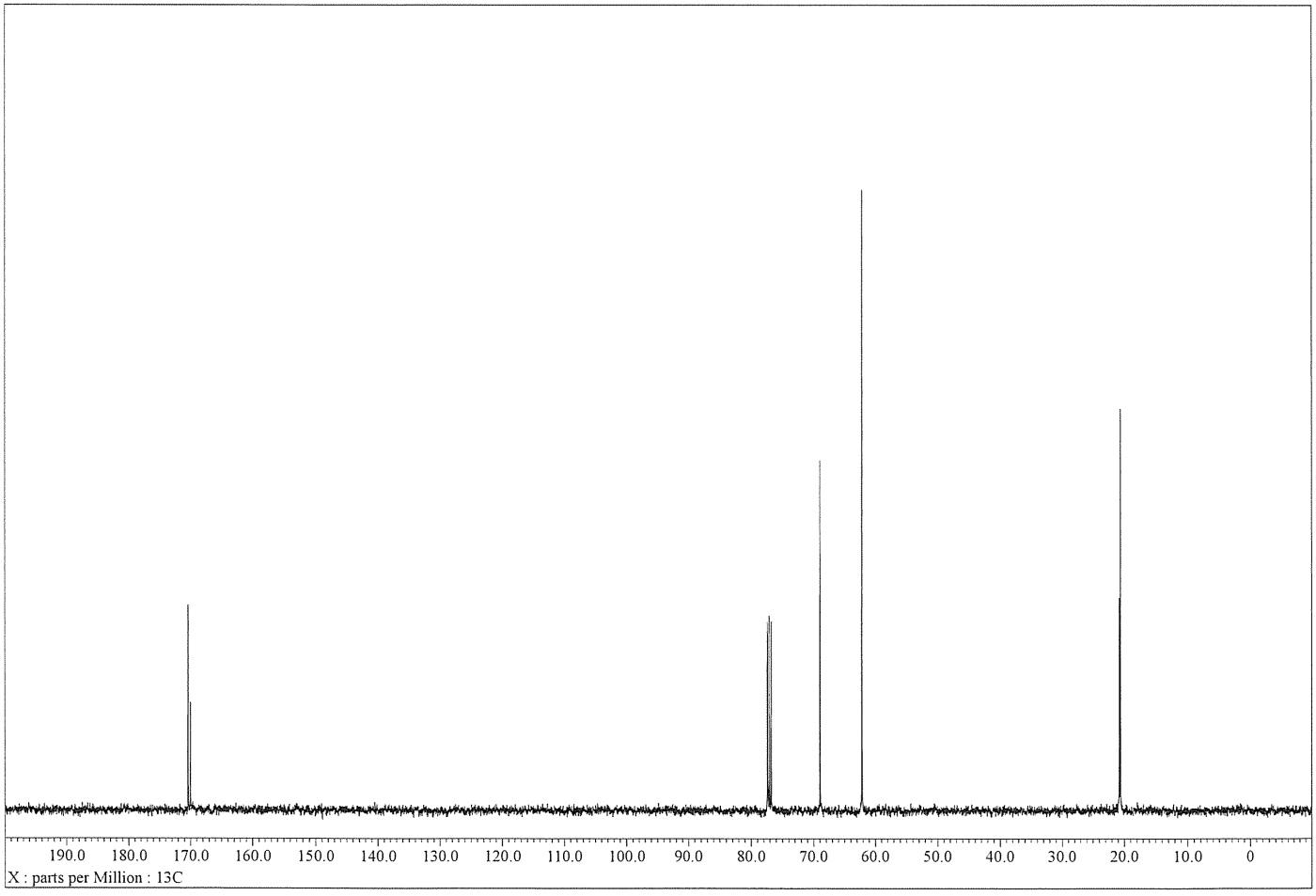
^{1}H NMR, 400 MHz, $CDCl_3$



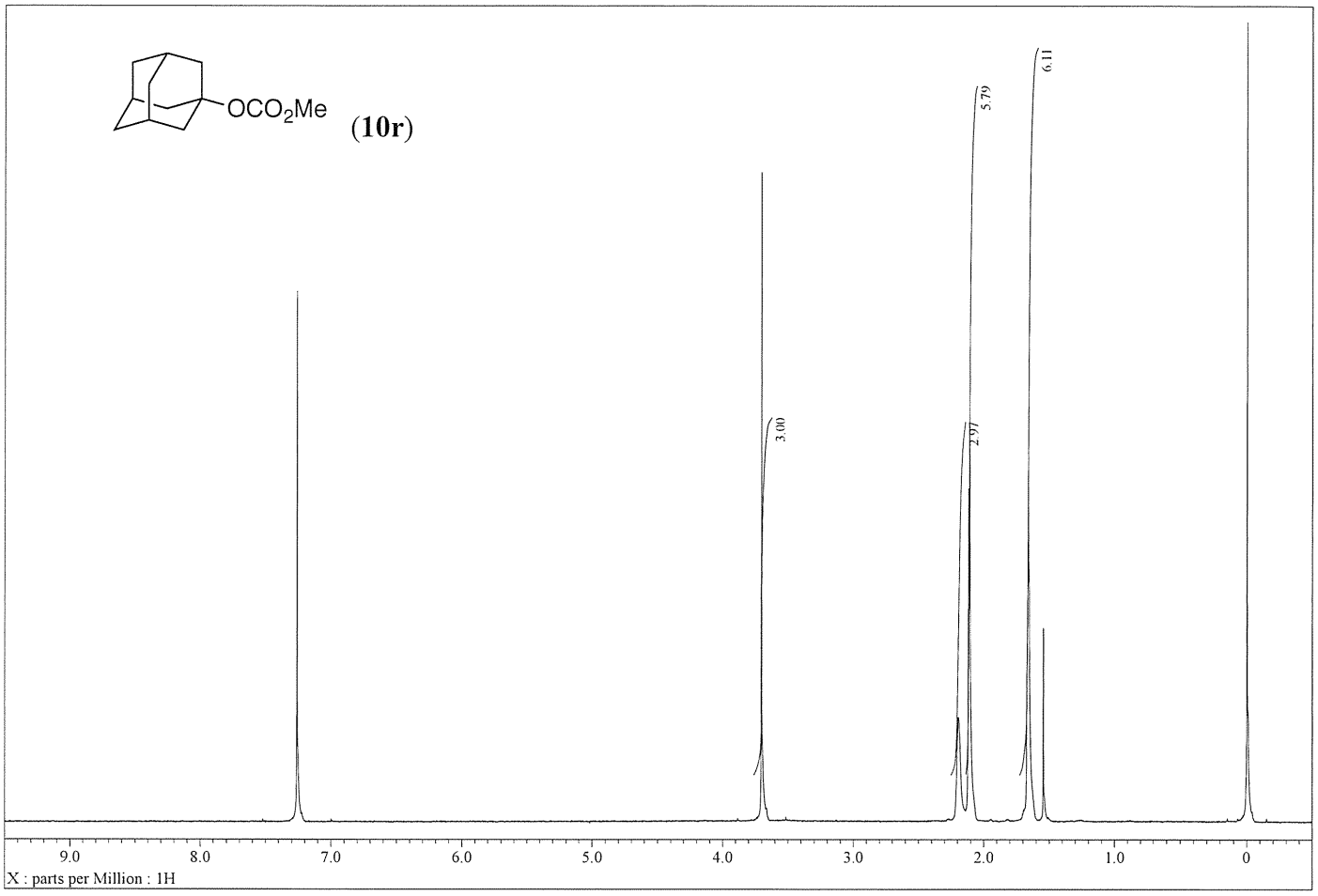
^{13}C NMR, 100 MHz, $CDCl_3$



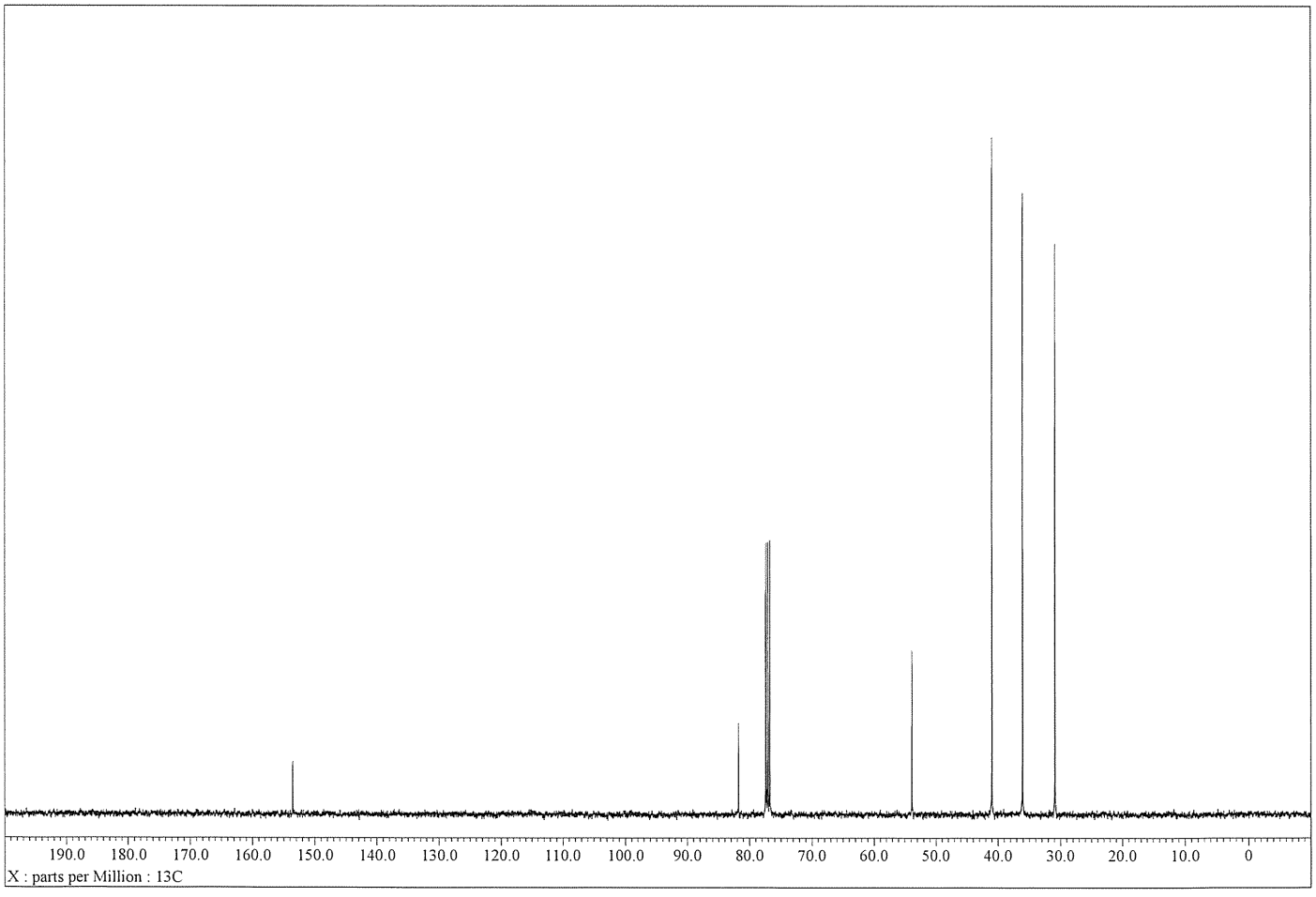
^{1}H NMR, 400 MHz, $CDCl_3$



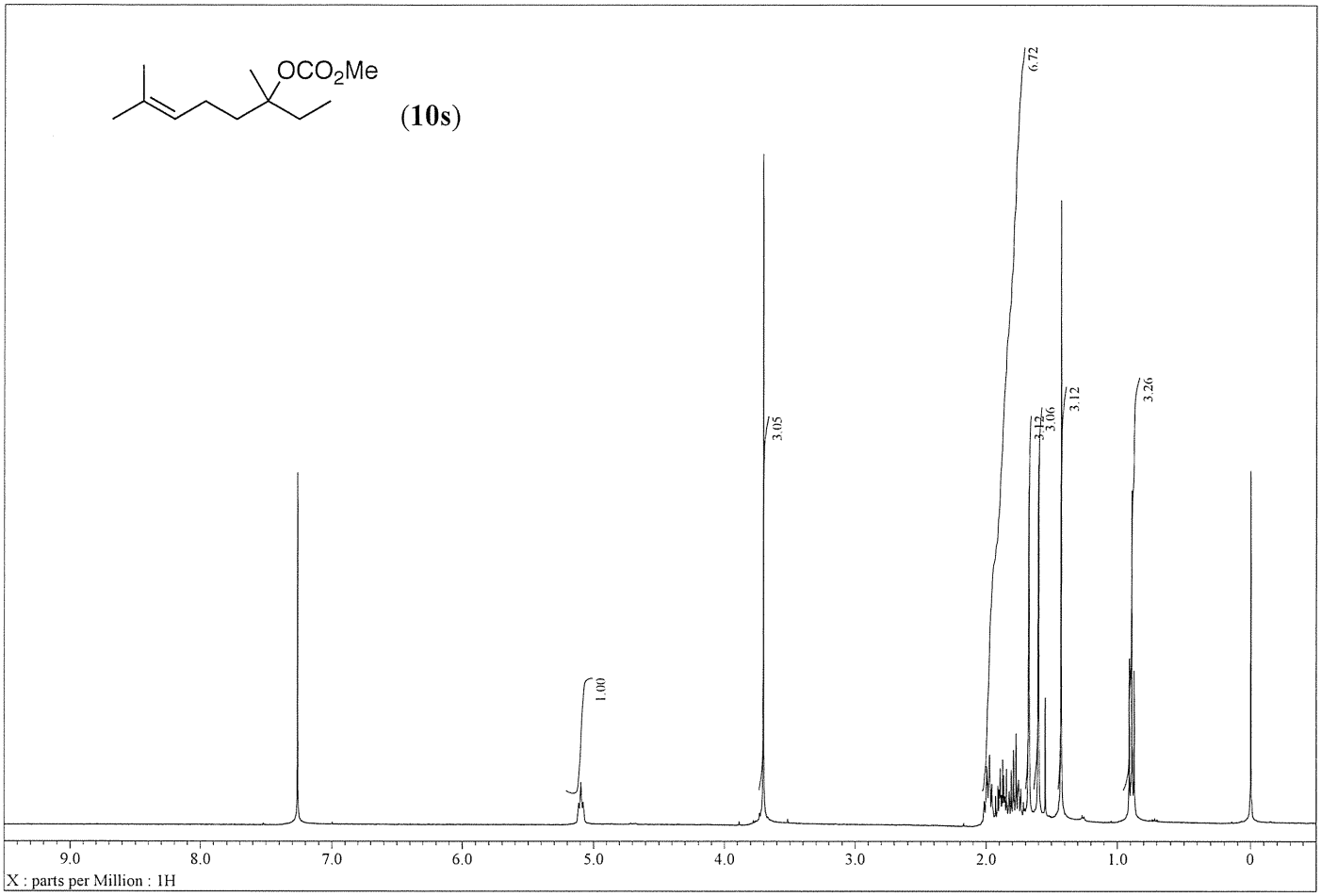
^{13}C NMR, 100 MHz, $CDCl_3$



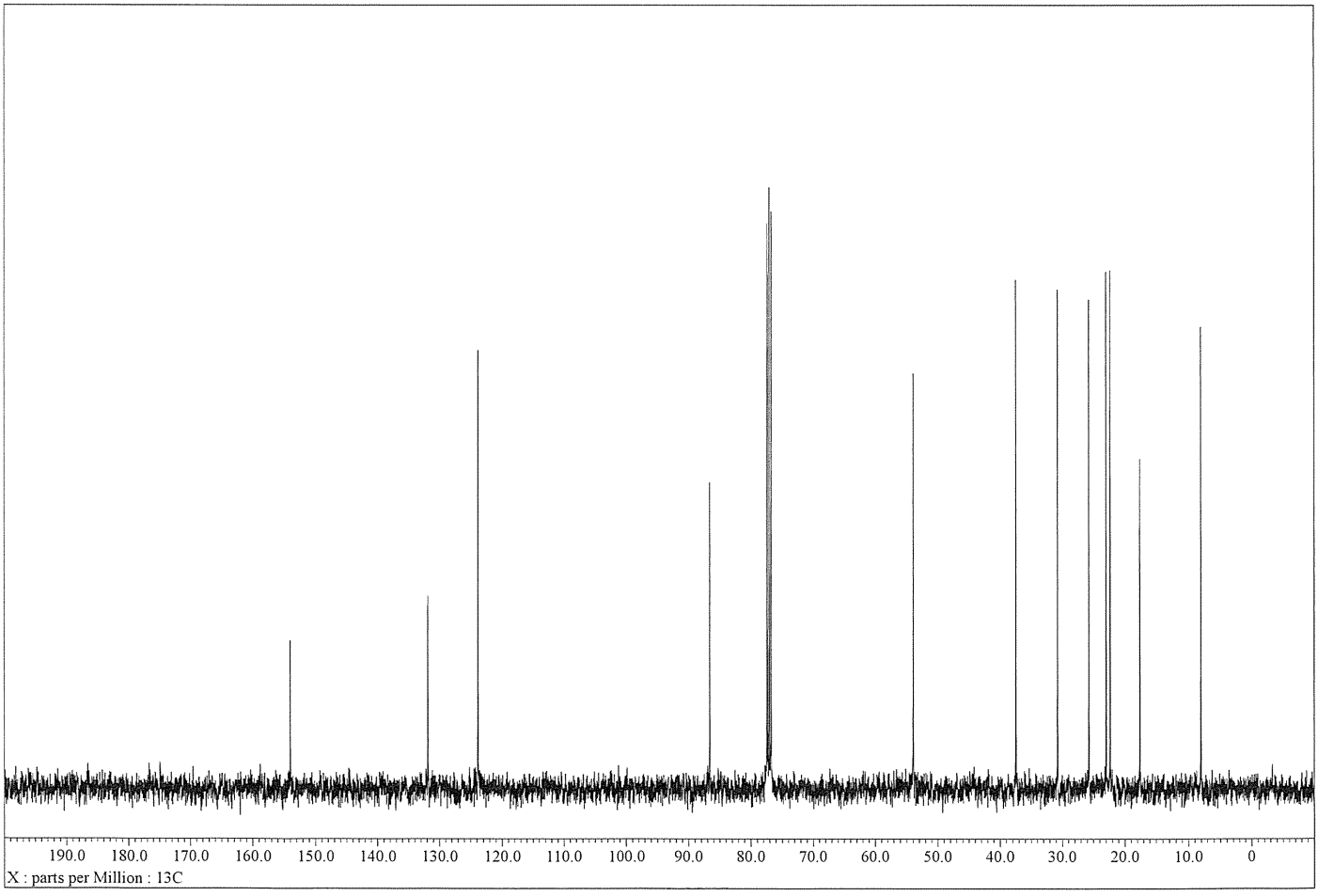
^{1}H NMR, 400 MHz, $CDCl_3$



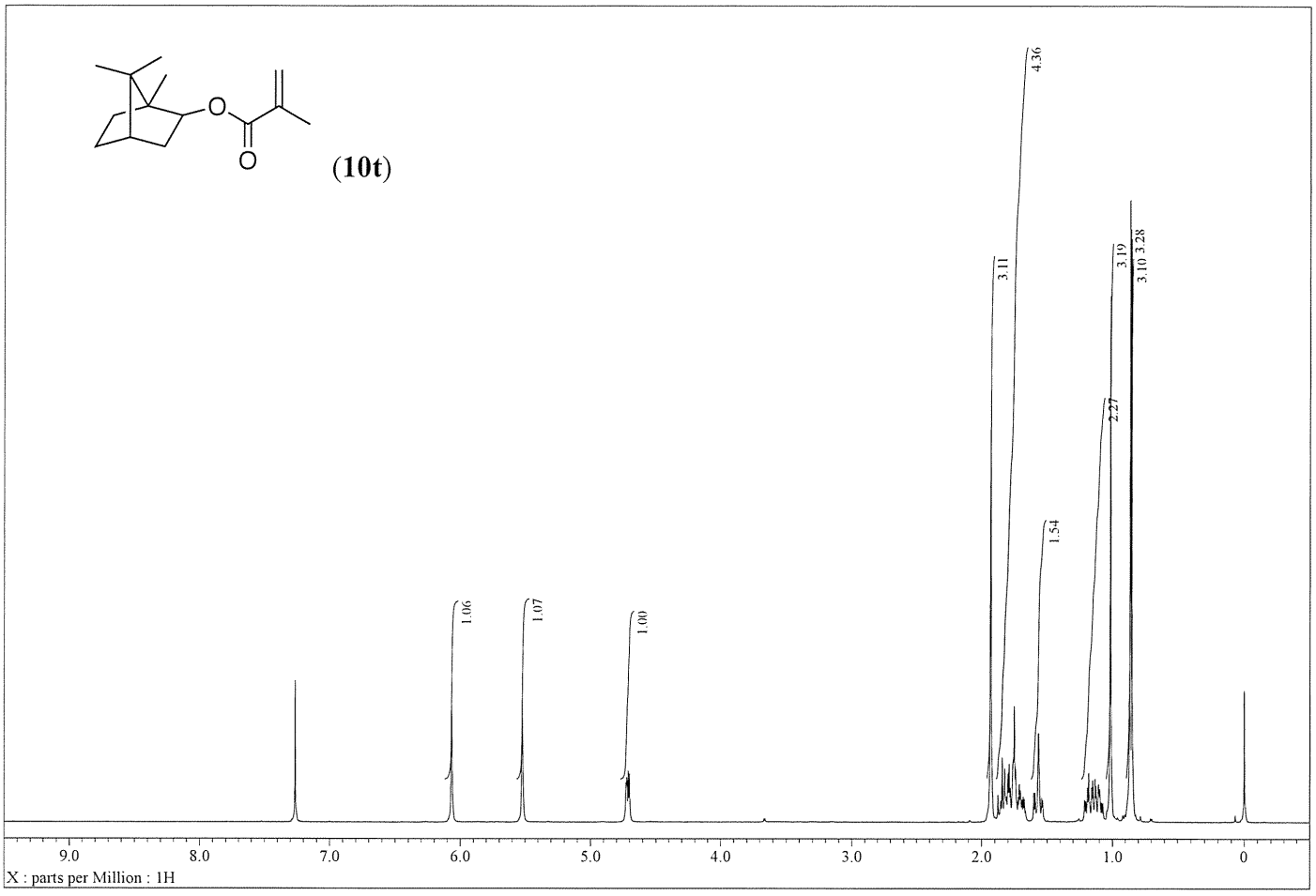
^{13}C NMR, 100 MHz, $CDCl_3$



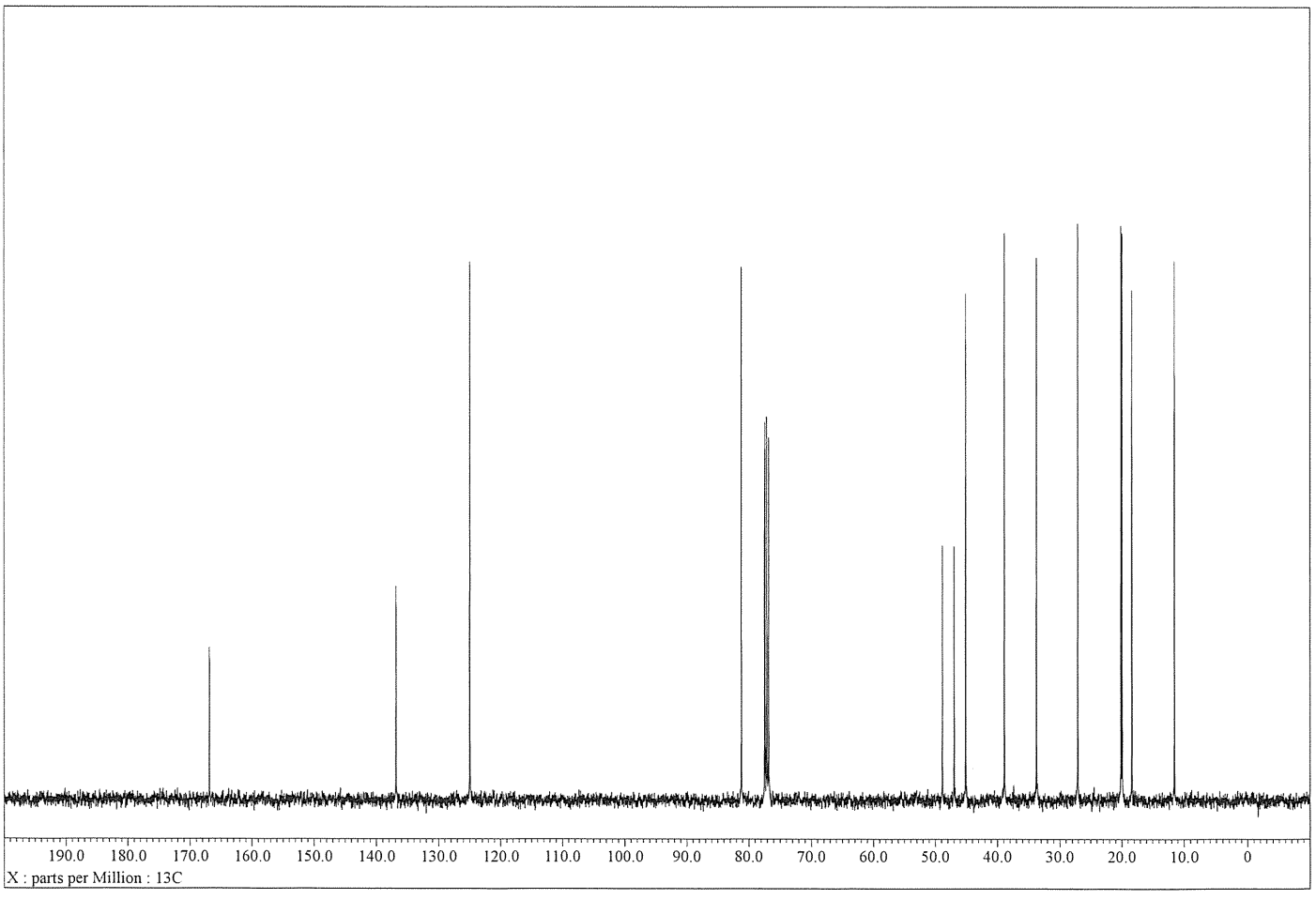
^{1}H NMR, 400 MHz, $CDCl_3$



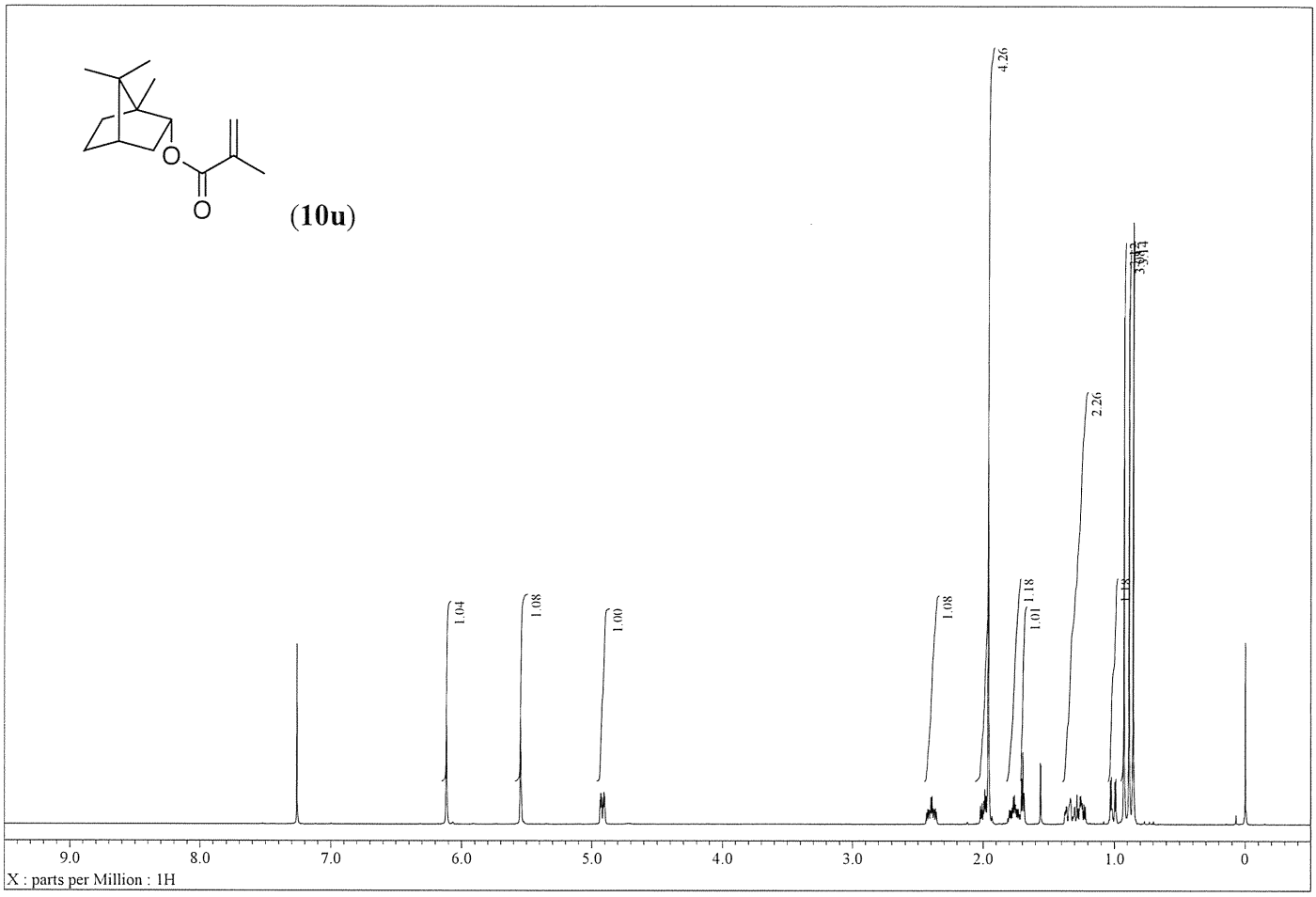
^{13}C NMR, 100 MHz, $CDCl_3$



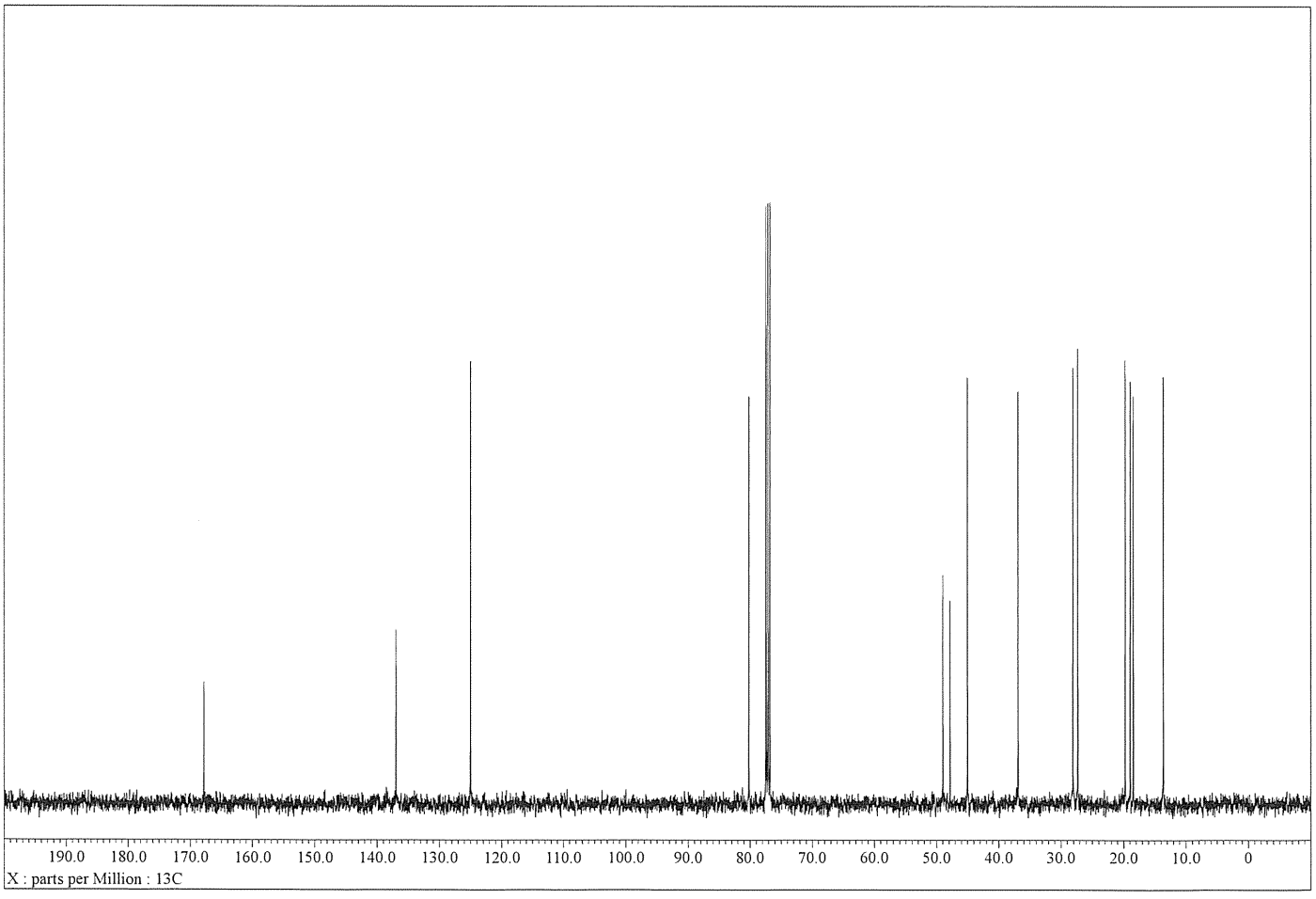
^{1}H NMR, 400 MHz, $CDCl_3$



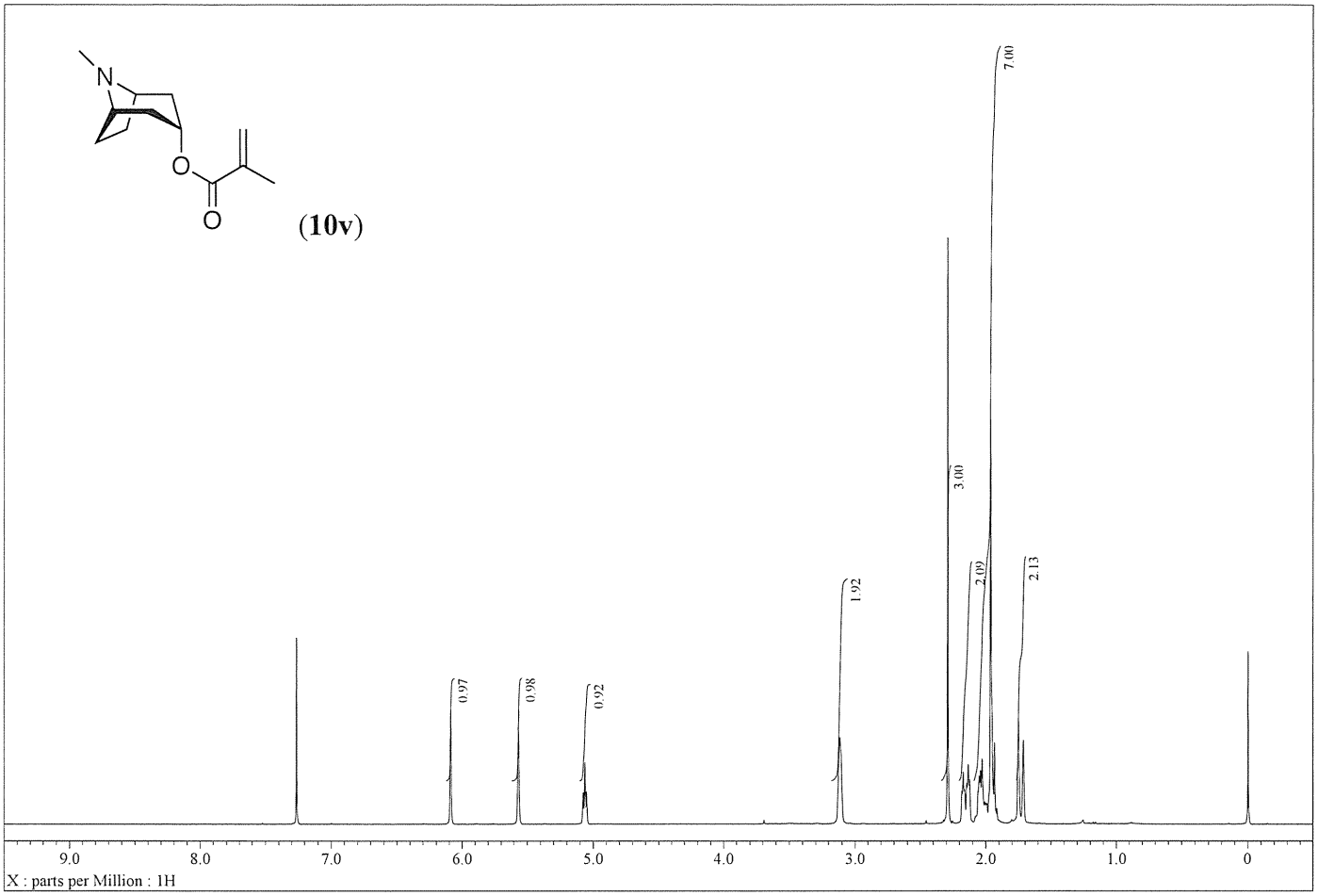
^{13}C NMR, 100 MHz, $CDCl_3$



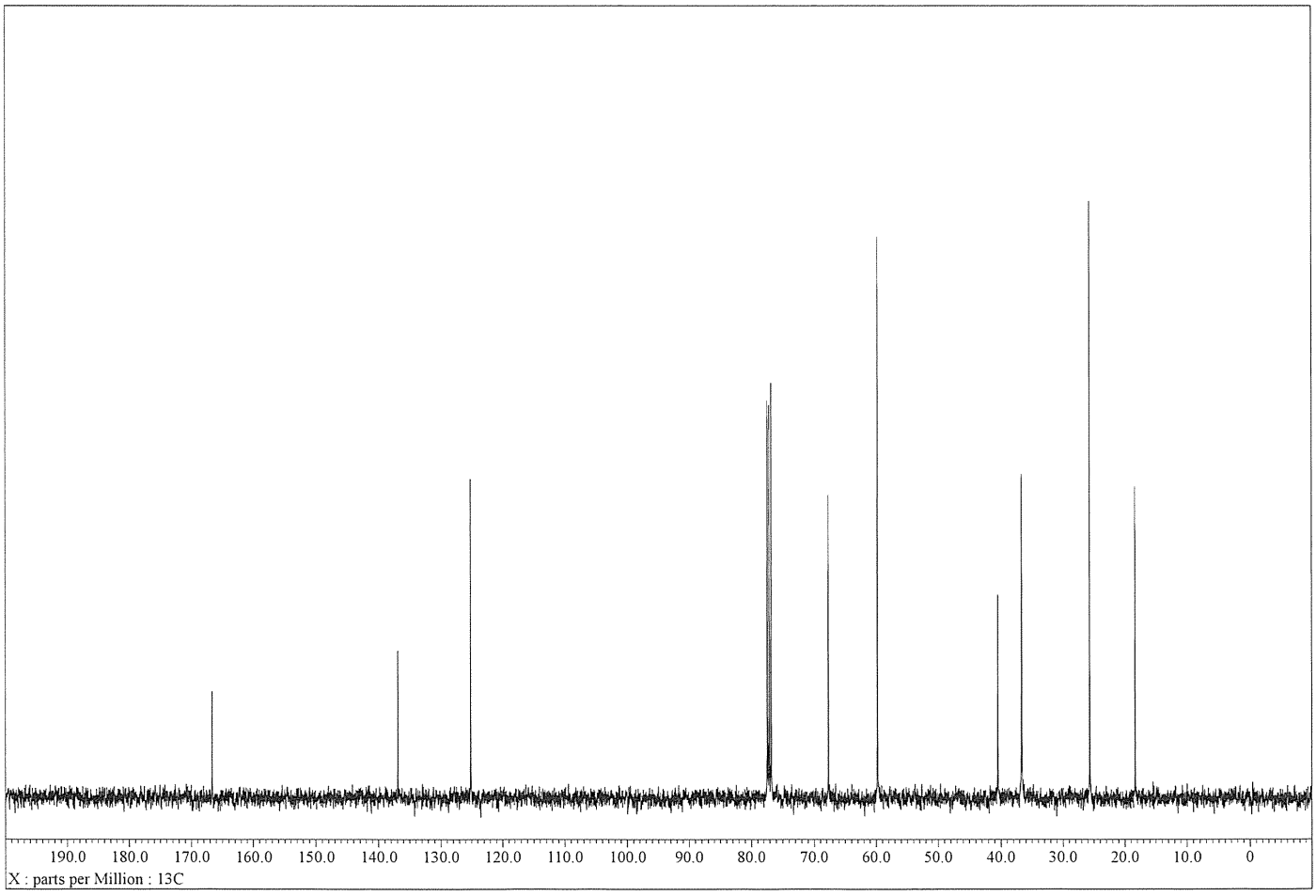
^{1}H NMR, 400 MHz, $CDCl_3$



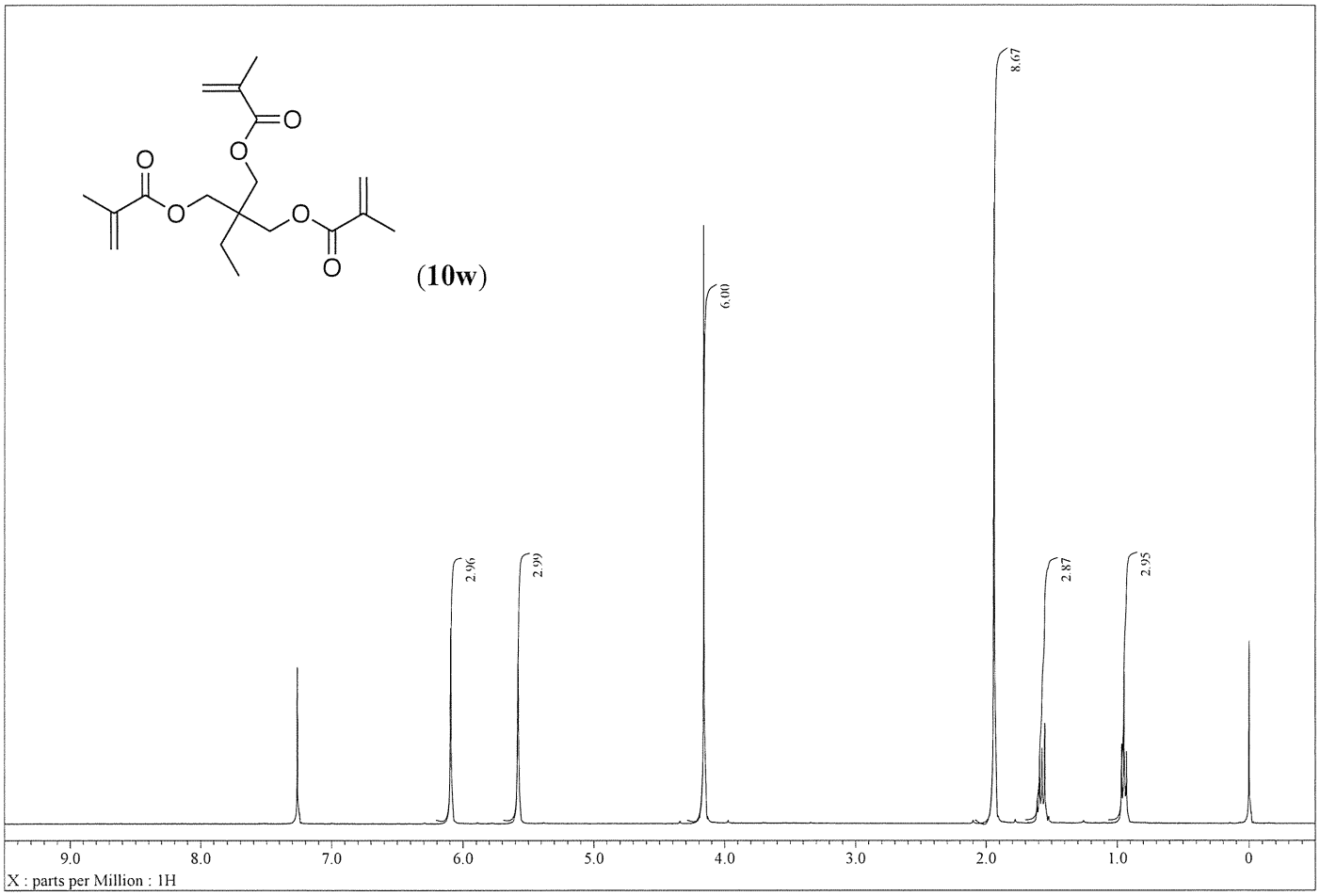
^{13}C NMR, 100 MHz, $CDCl_3$



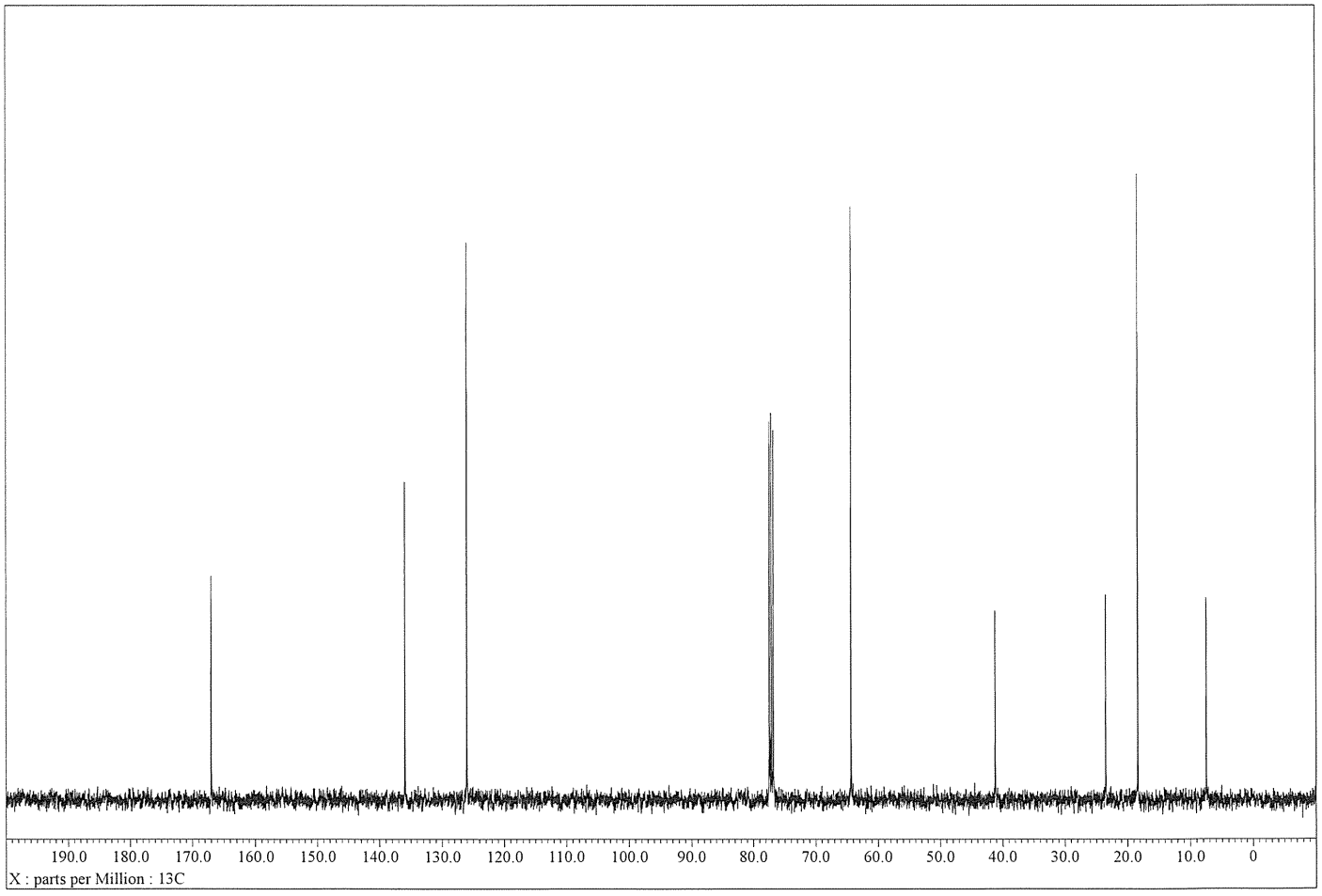
^{1}H NMR, 400 MHz, $CDCl_3$



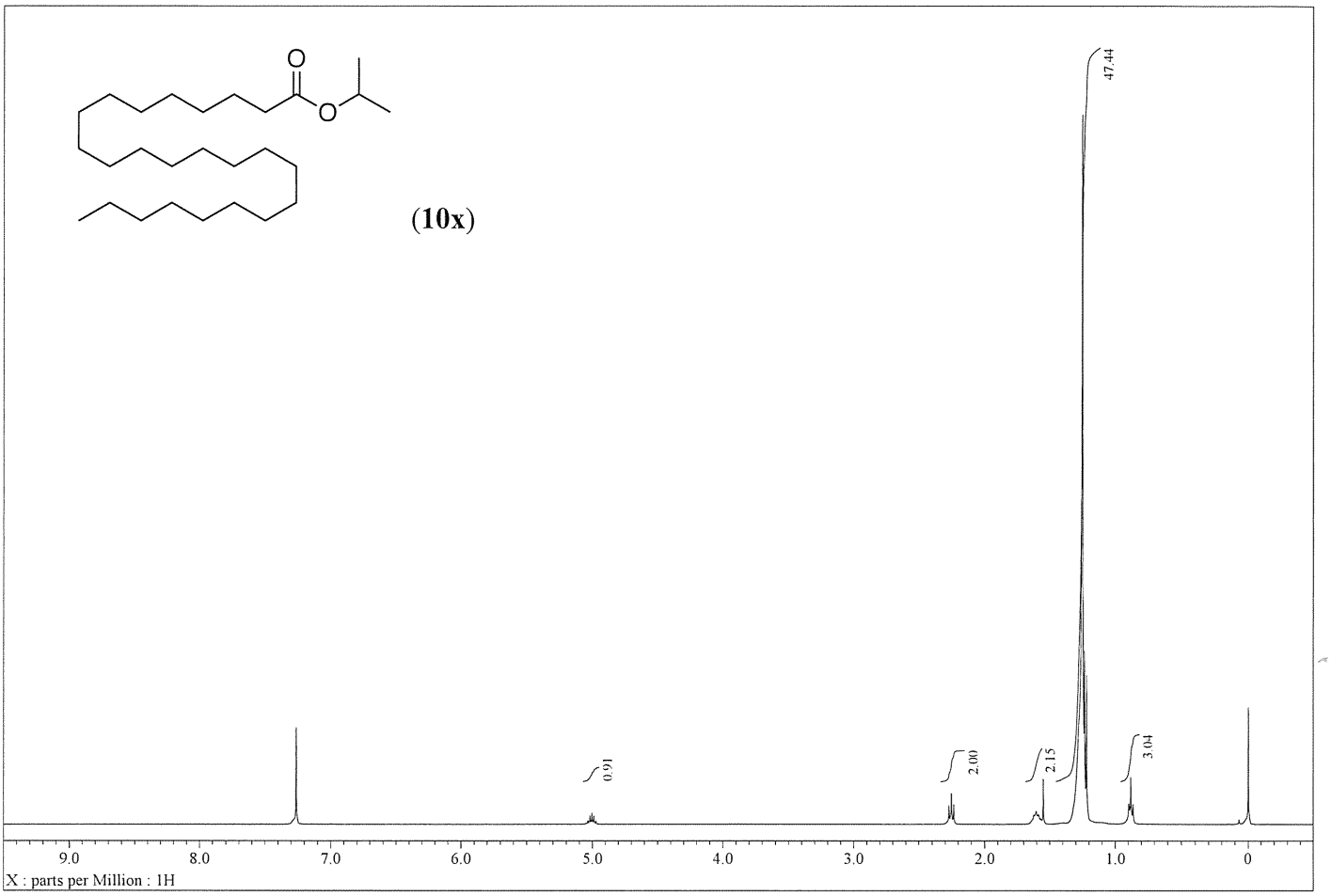
^{13}C NMR, 100 MHz, $CDCl_3$



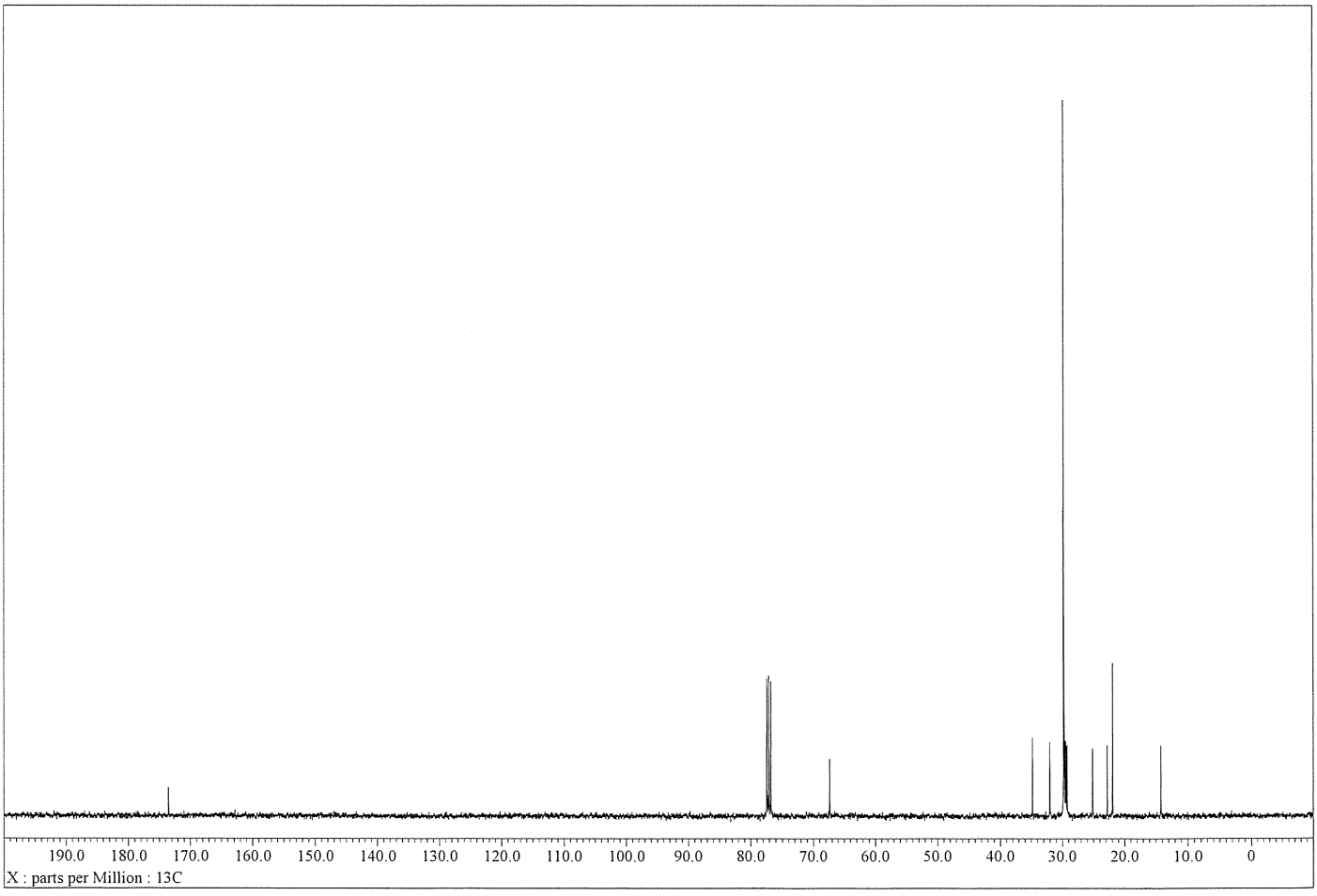
^{1}H NMR, 400 MHz, $CDCl_3$



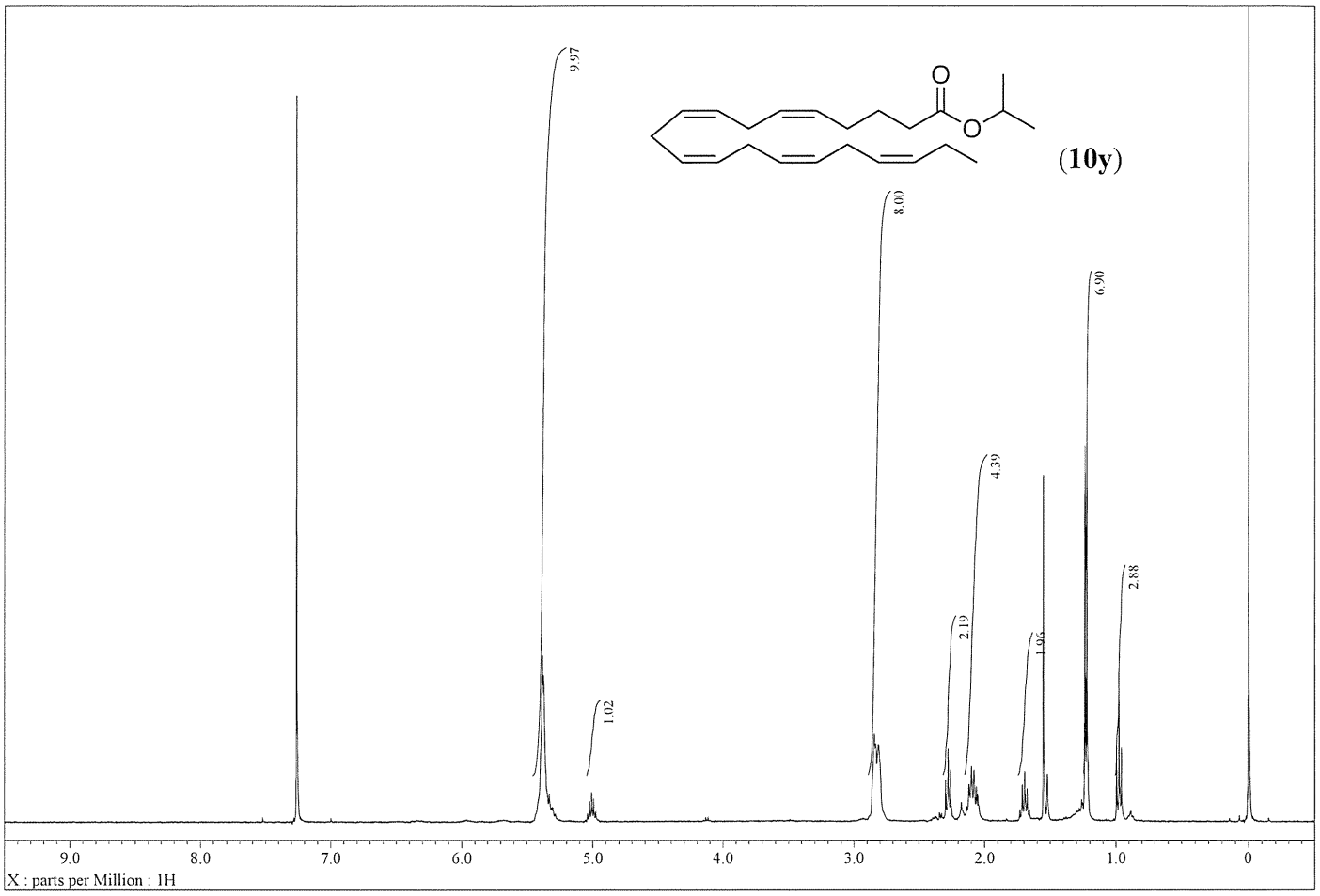
^{13}C NMR, 100 MHz, $CDCl_3$



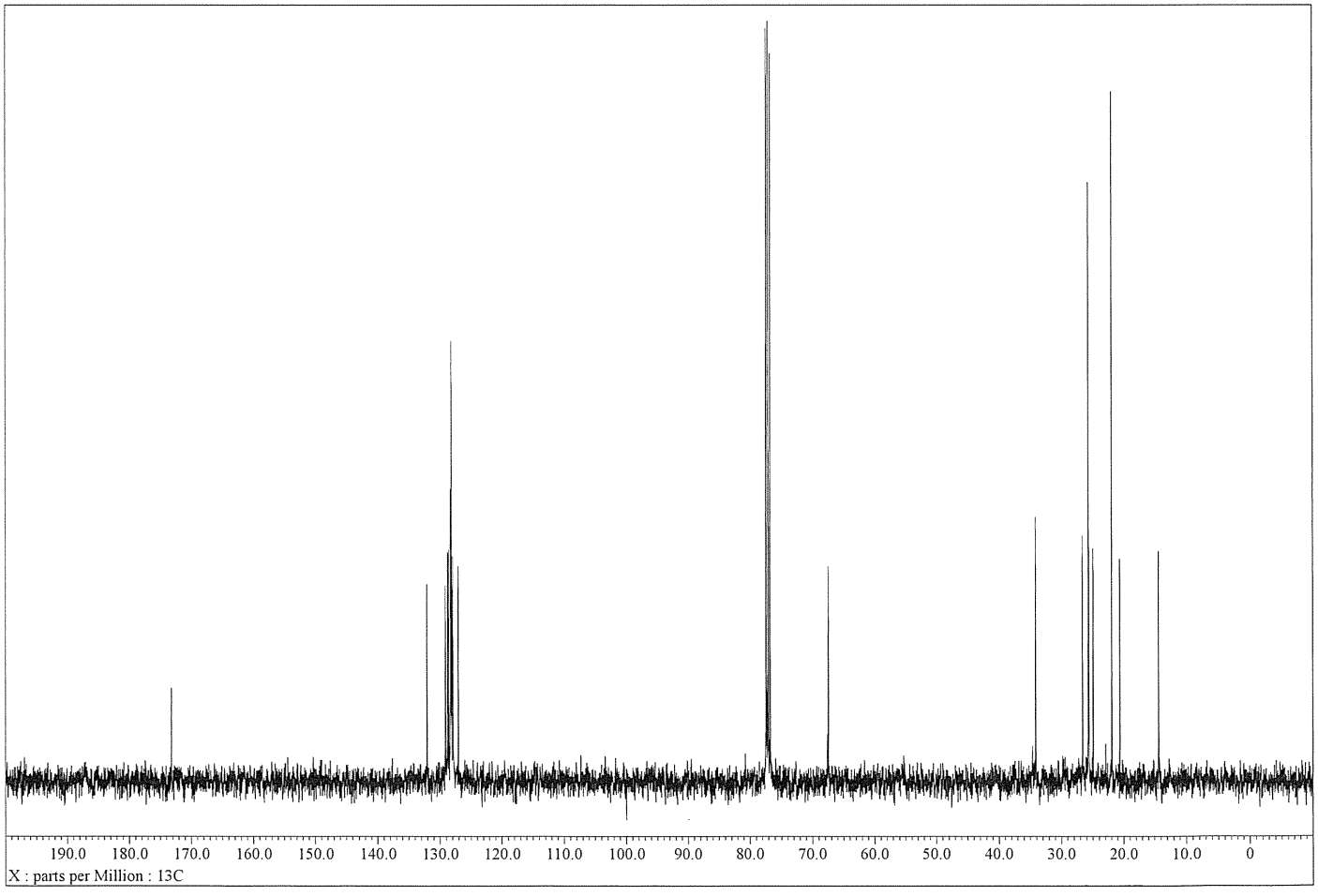
^{1}H NMR, 400 MHz, $CDCl_3$



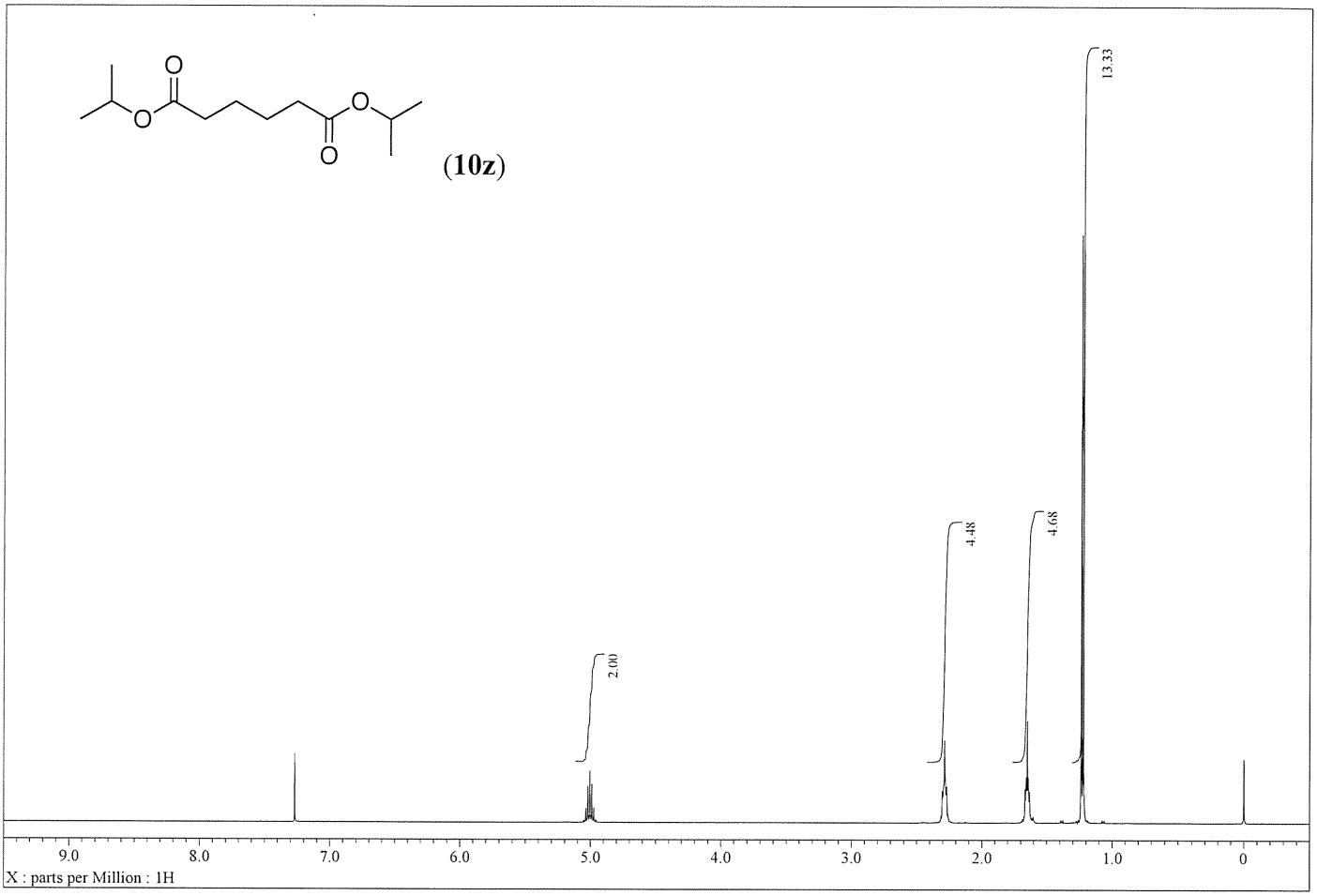
^{13}C NMR, 100 MHz, $CDCl_3$



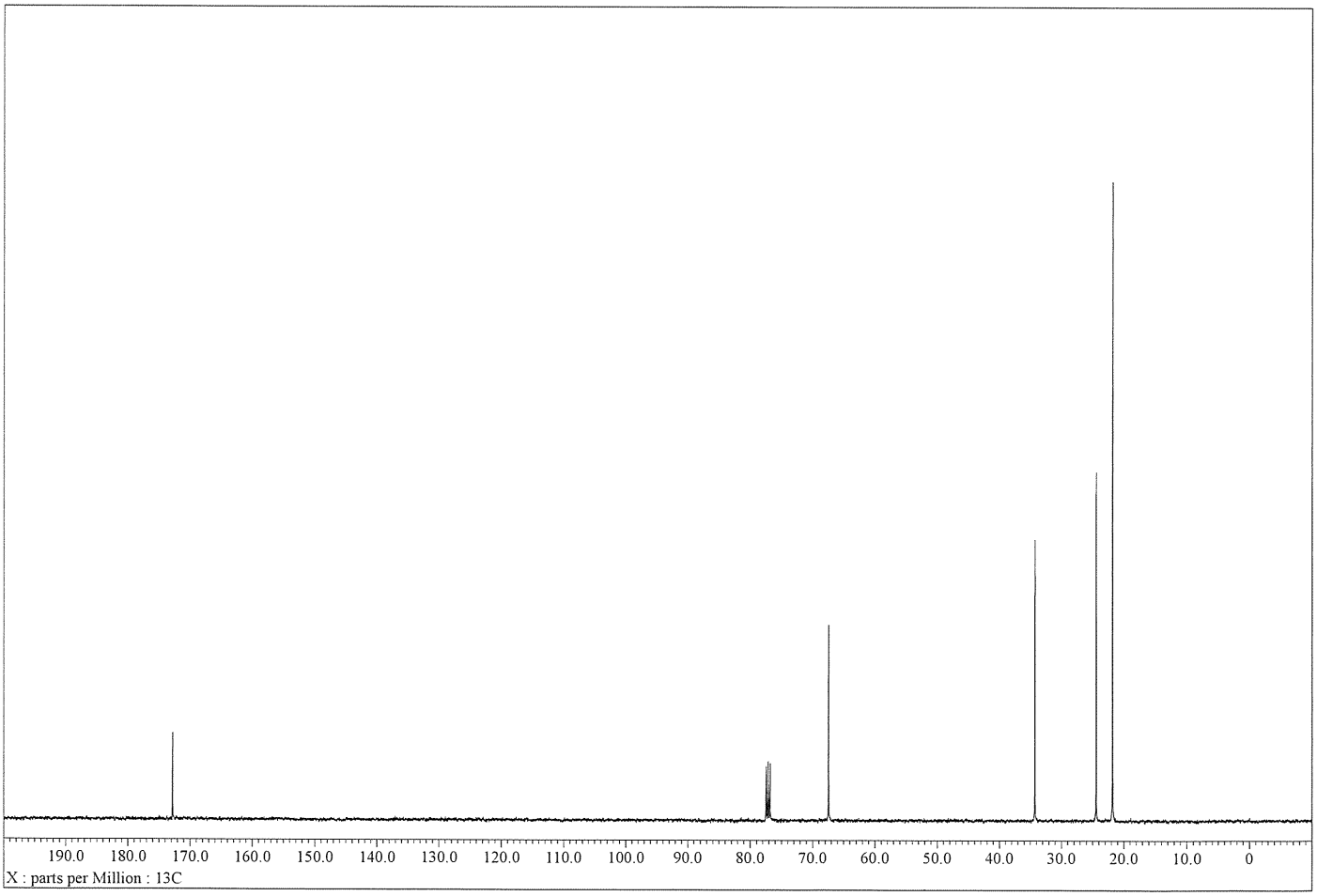
^{1}H NMR, 400 MHz, $CDCl_3$



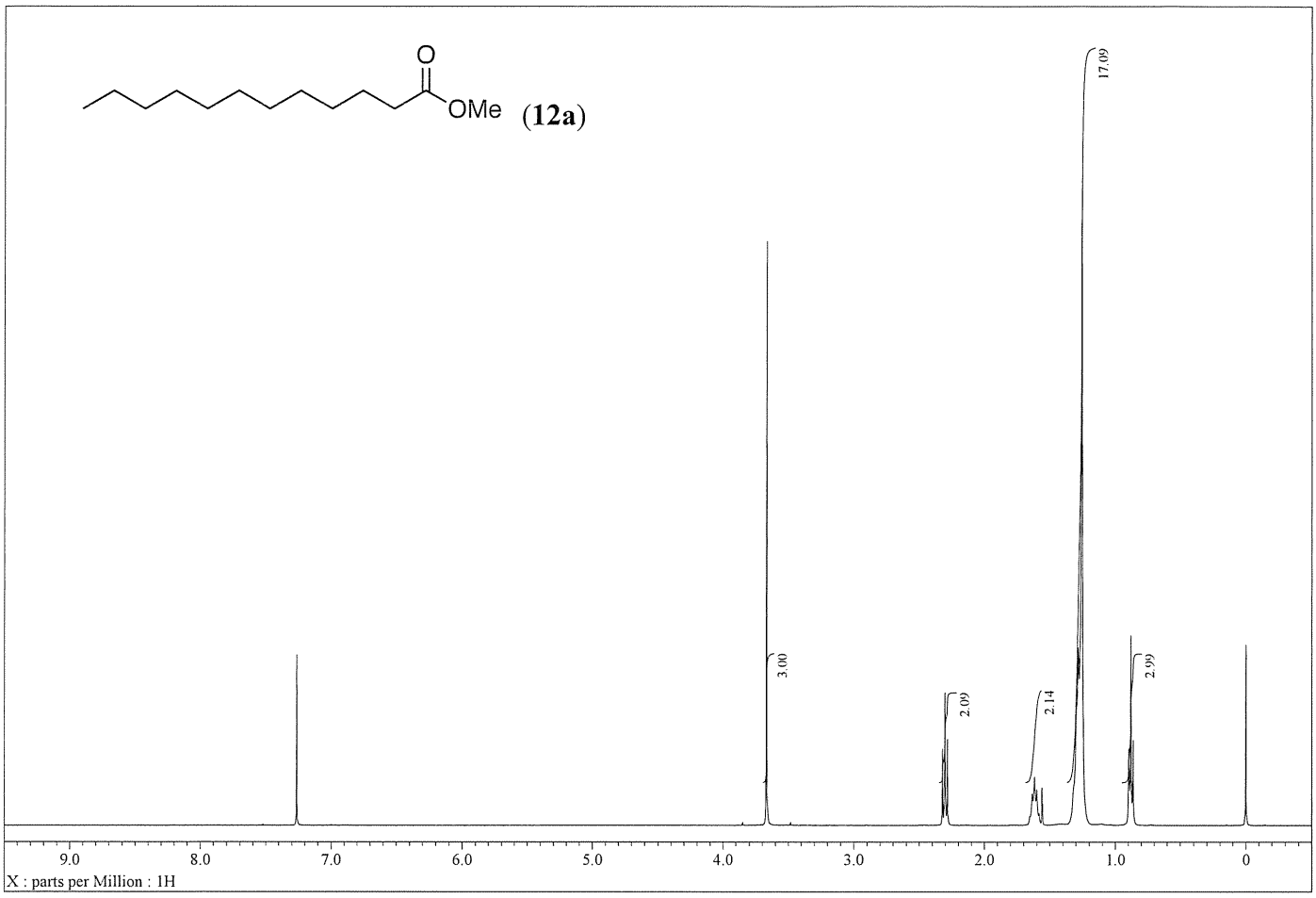
^{13}C NMR, 100 MHz, $CDCl_3$



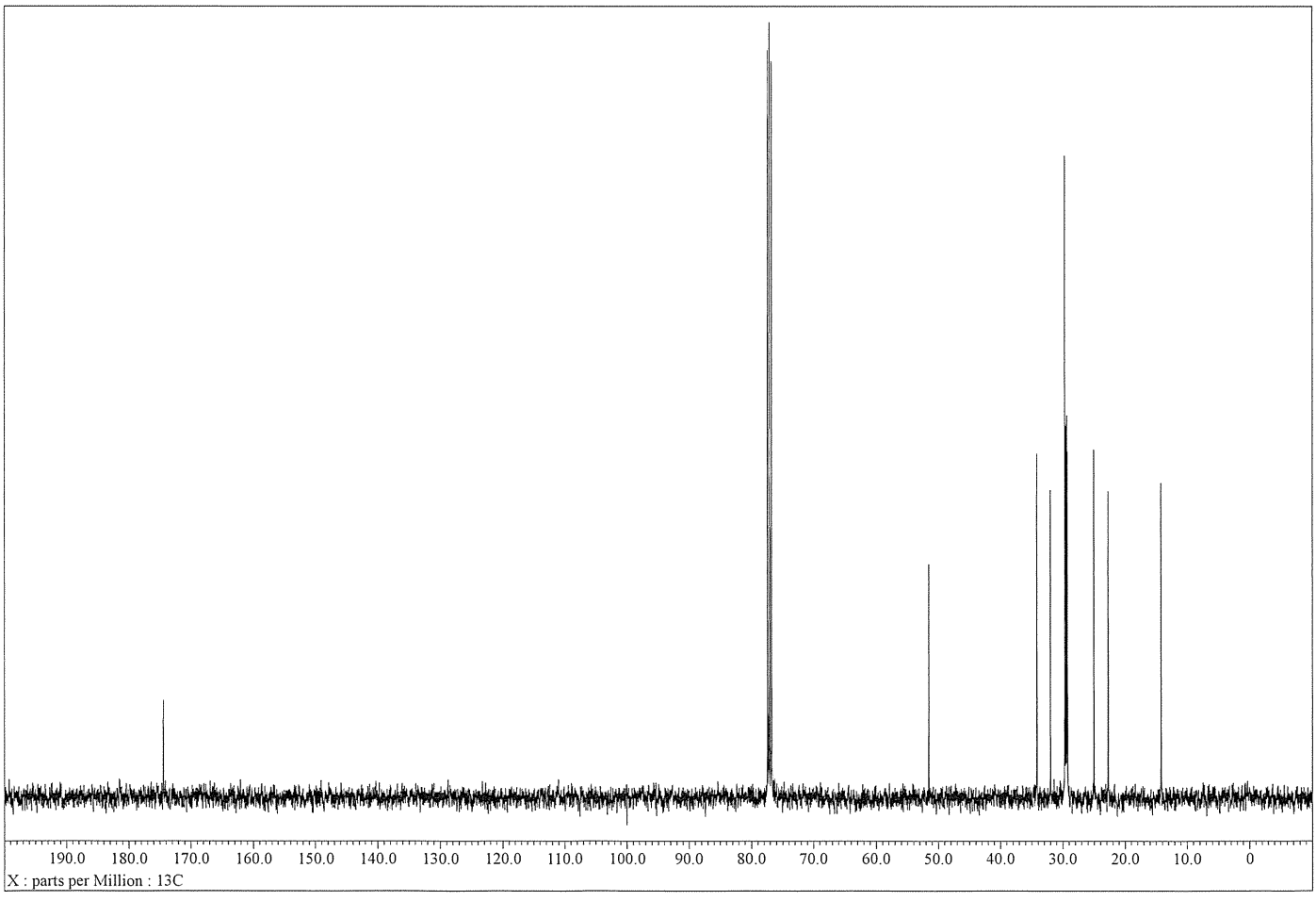
^{1}H NMR, 400 MHz, $CDCl_3$



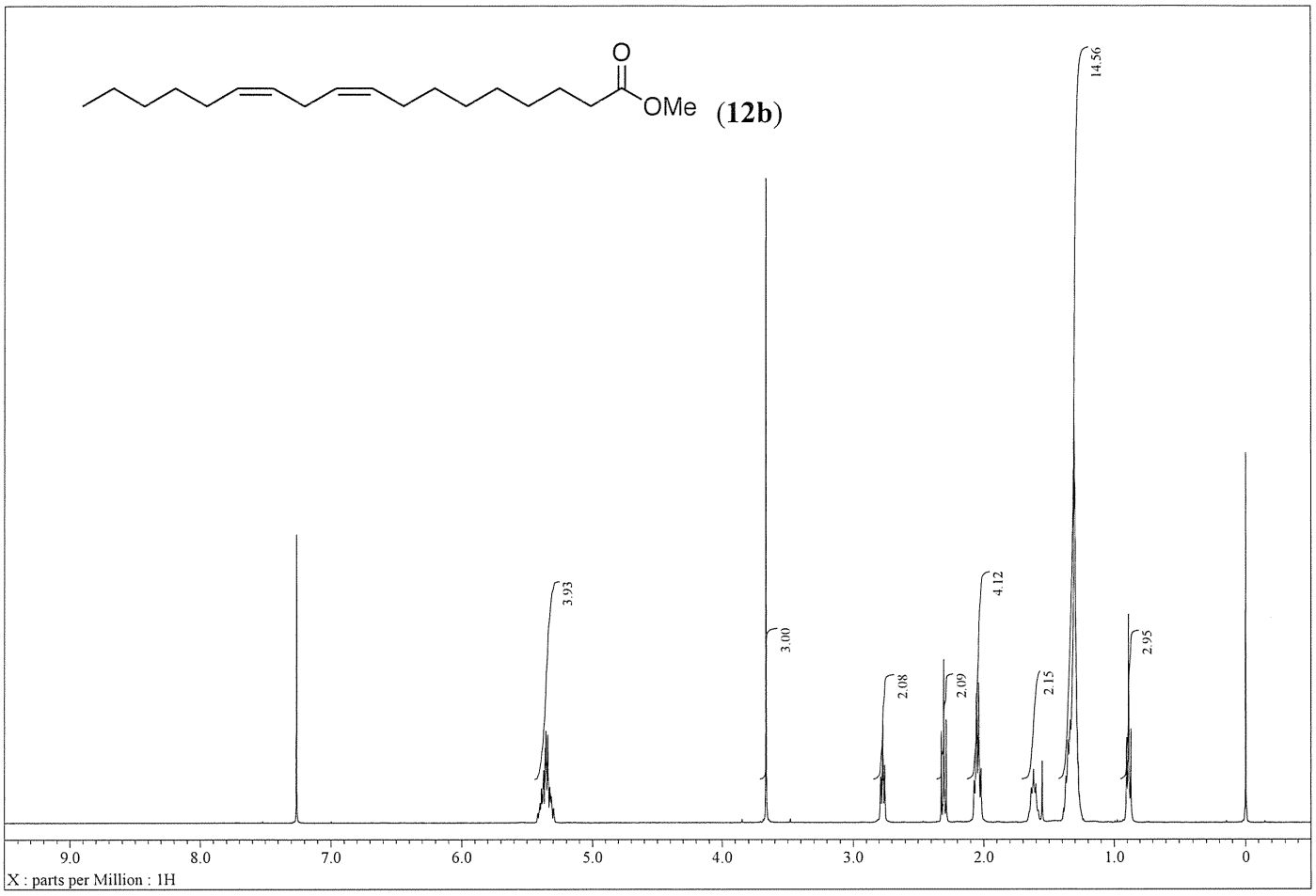
^{13}C NMR, 100 MHz, $CDCl_3$



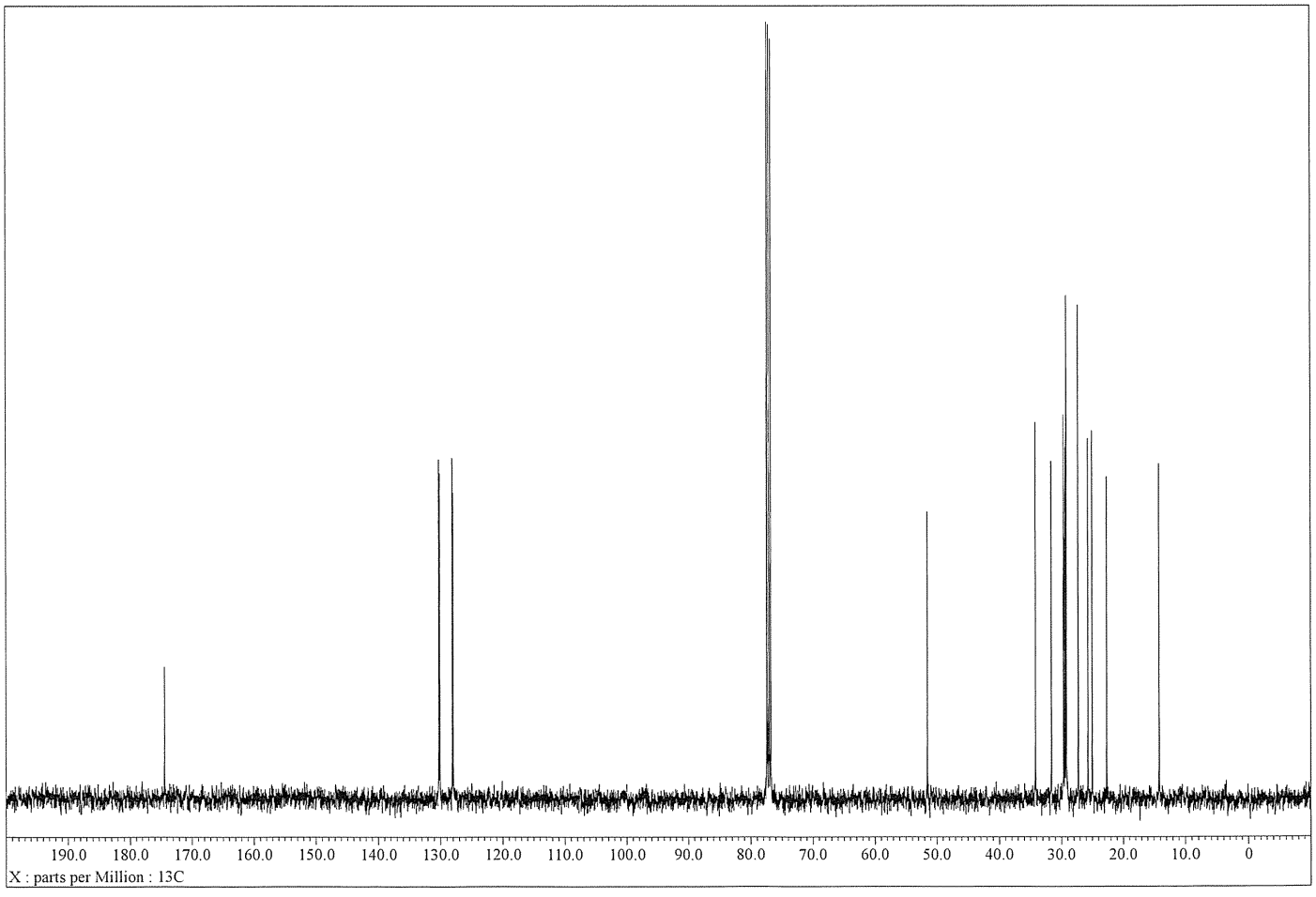
^{1}H NMR, 400 MHz, $CDCl_3$



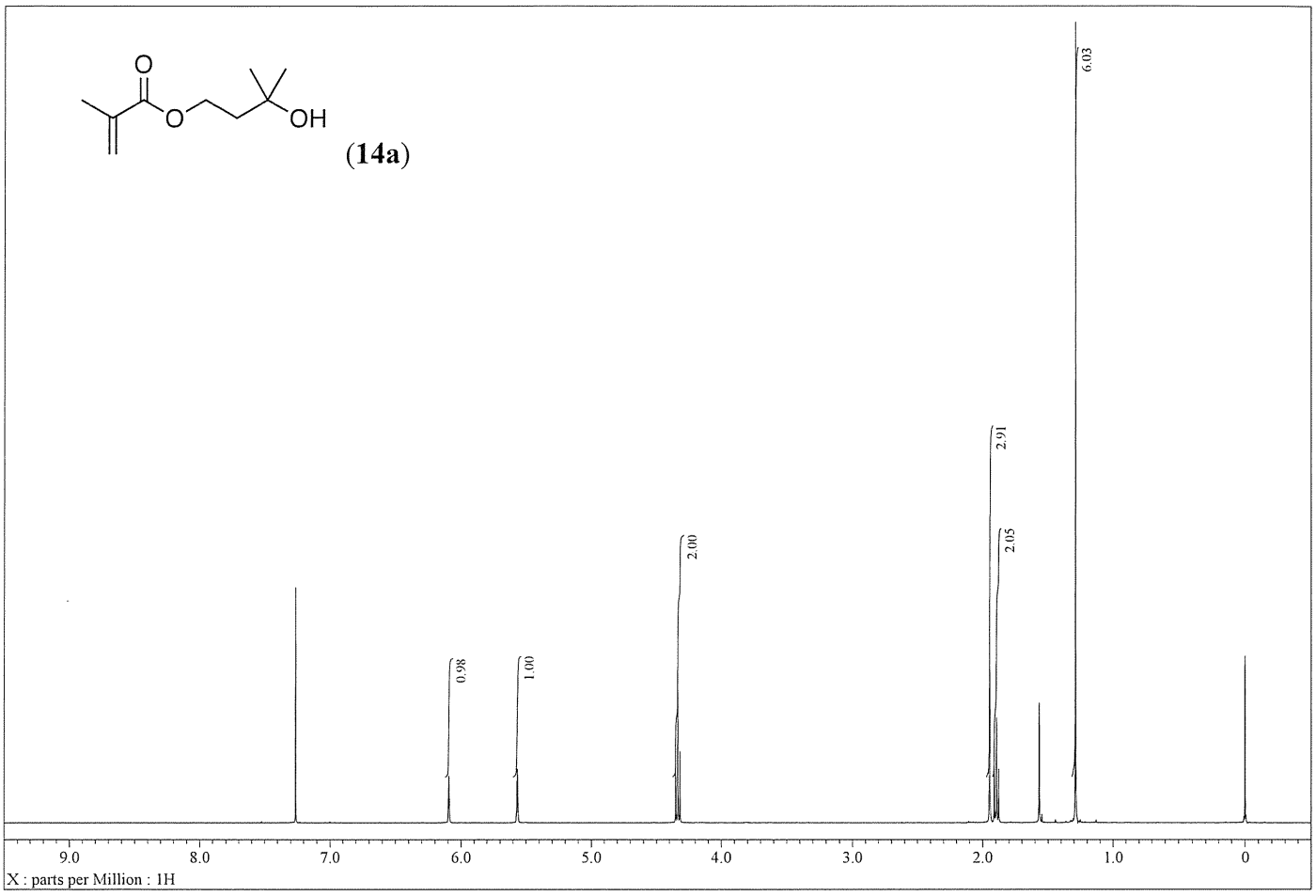
^{13}C NMR, 100 MHz, $CDCl_3$



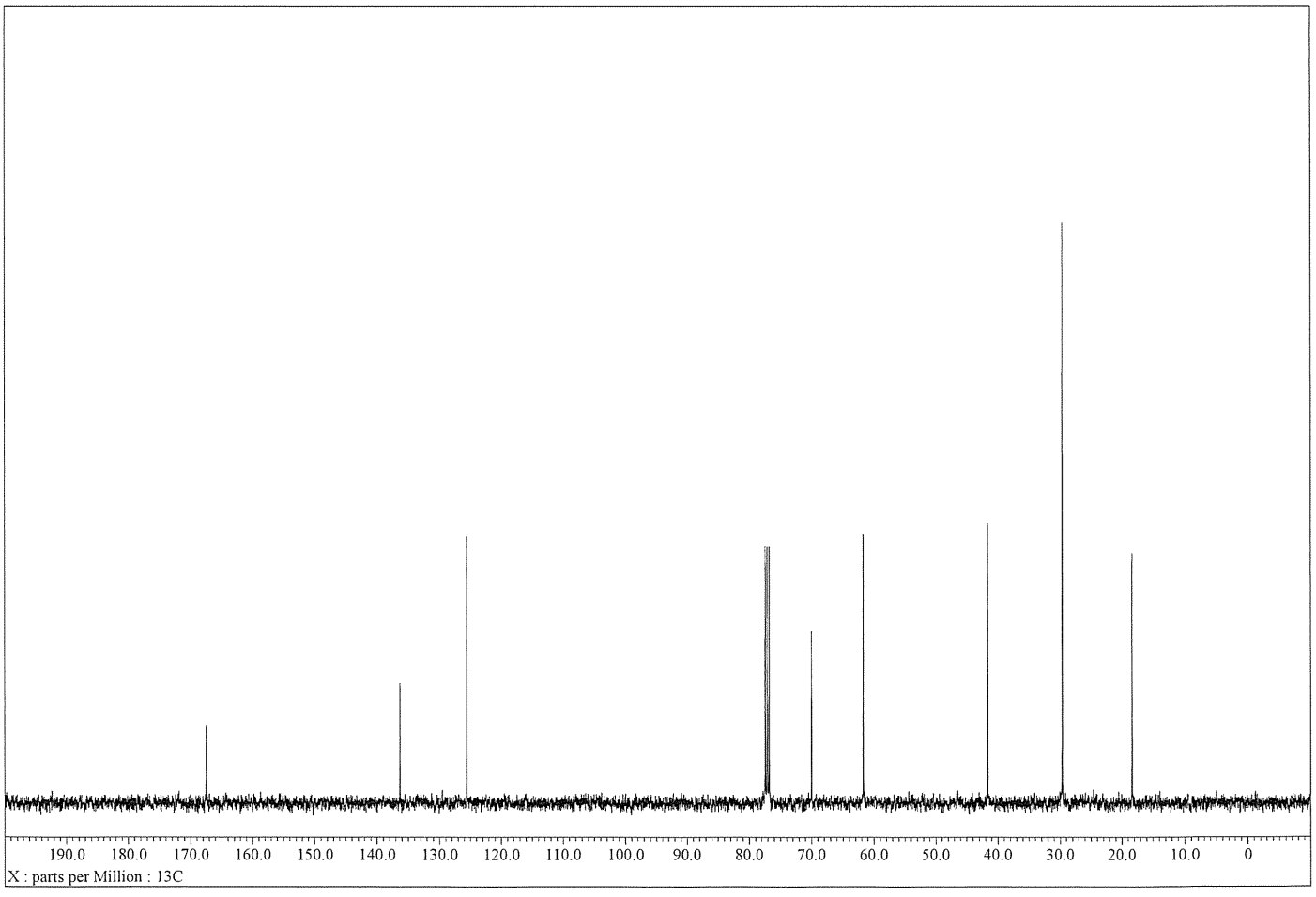
^{1}H NMR, 400 MHz, $CDCl_3$



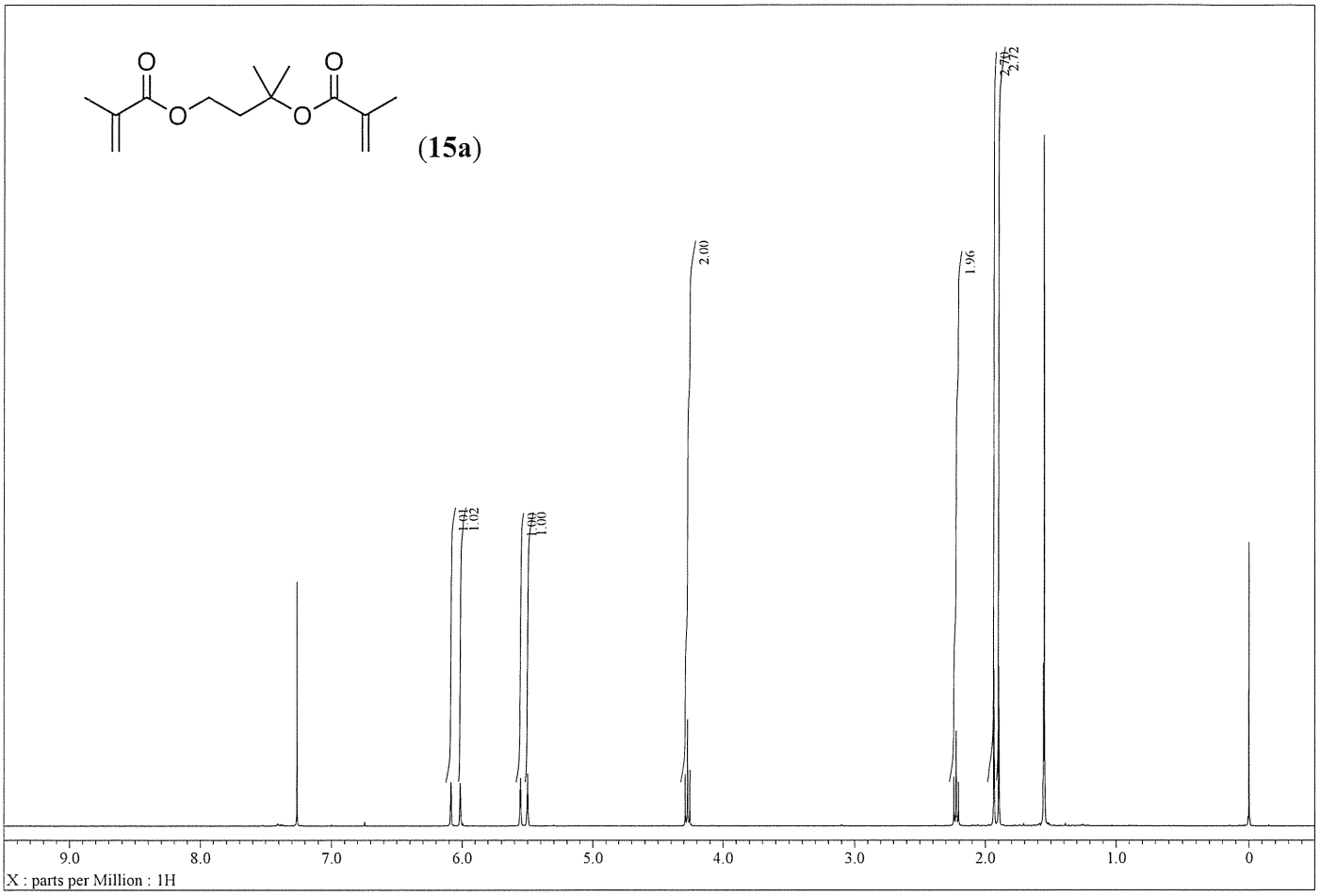
^{13}C NMR, 100 MHz, $CDCl_3$



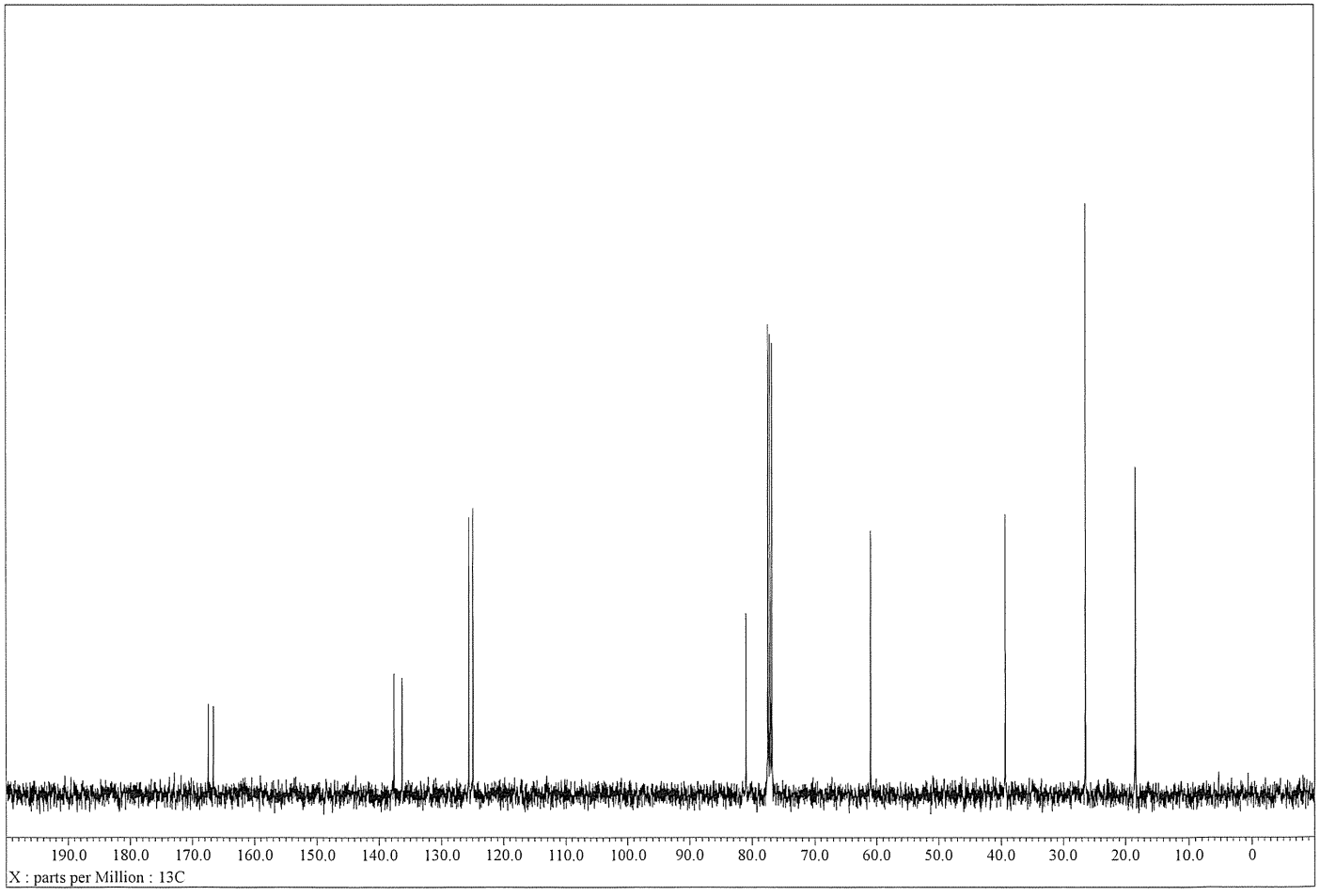
^{1}H NMR, 400 MHz, $CDCl_3$



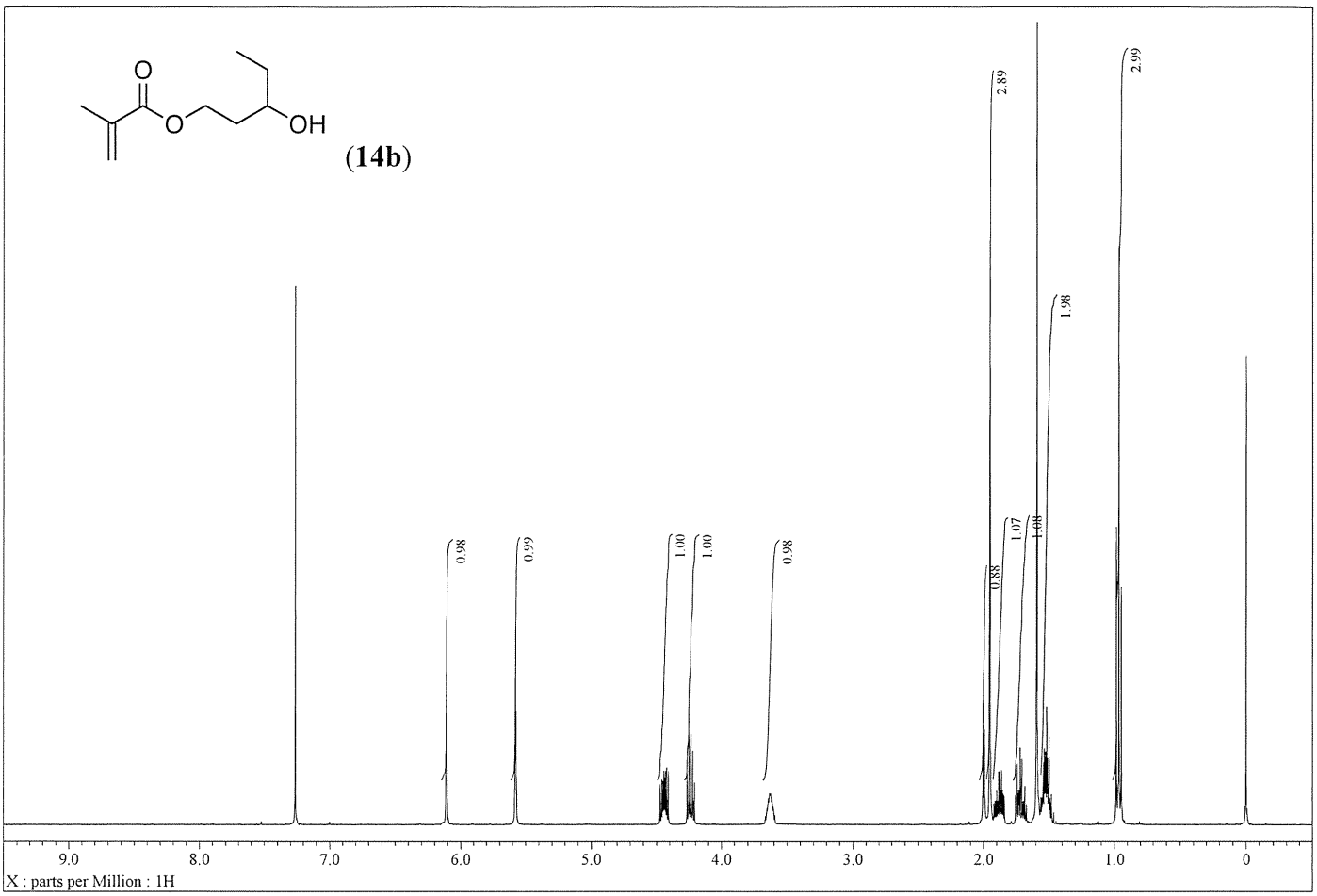
^{13}C NMR, 100 MHz, $CDCl_3$



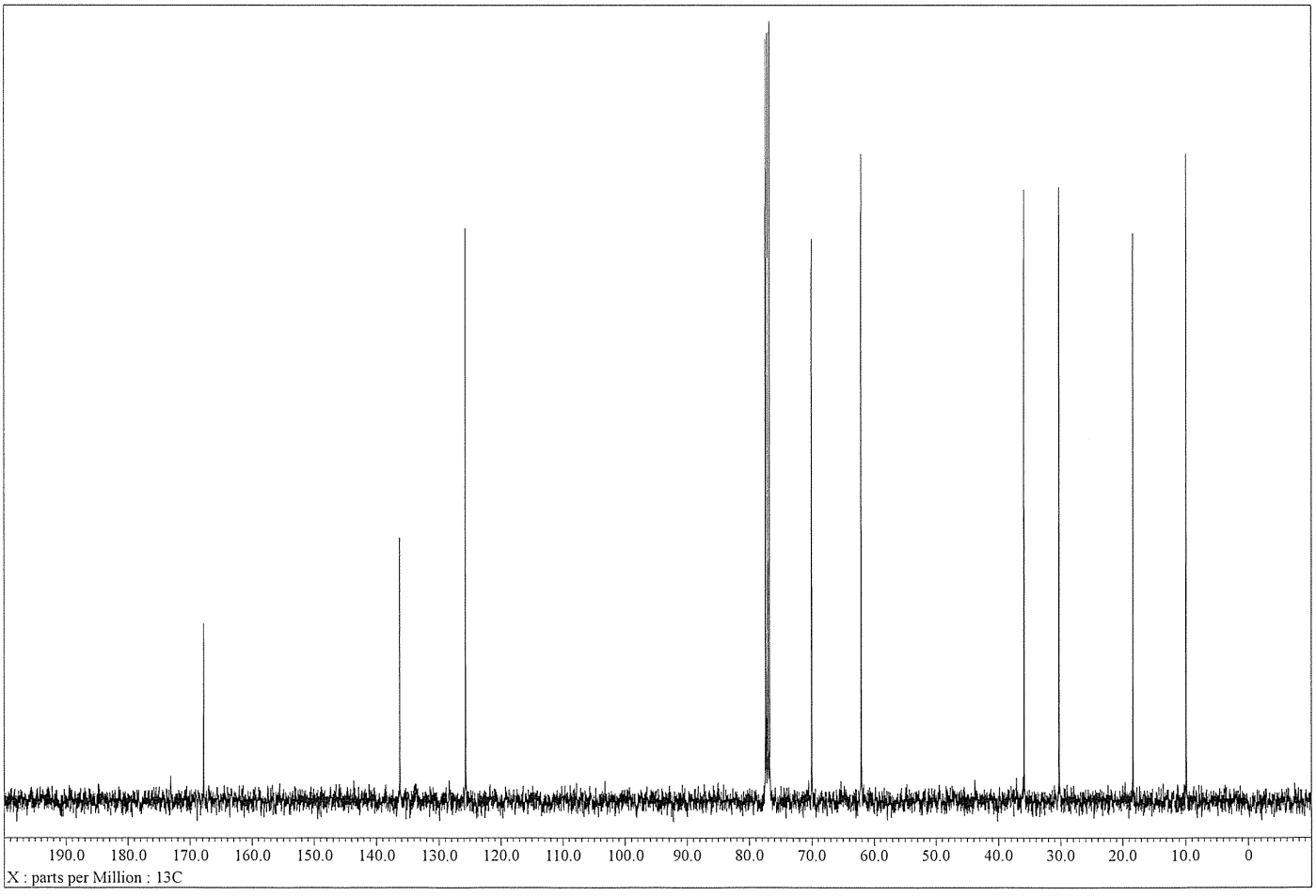
^{1}H NMR, 400 MHz, $CDCl_3$



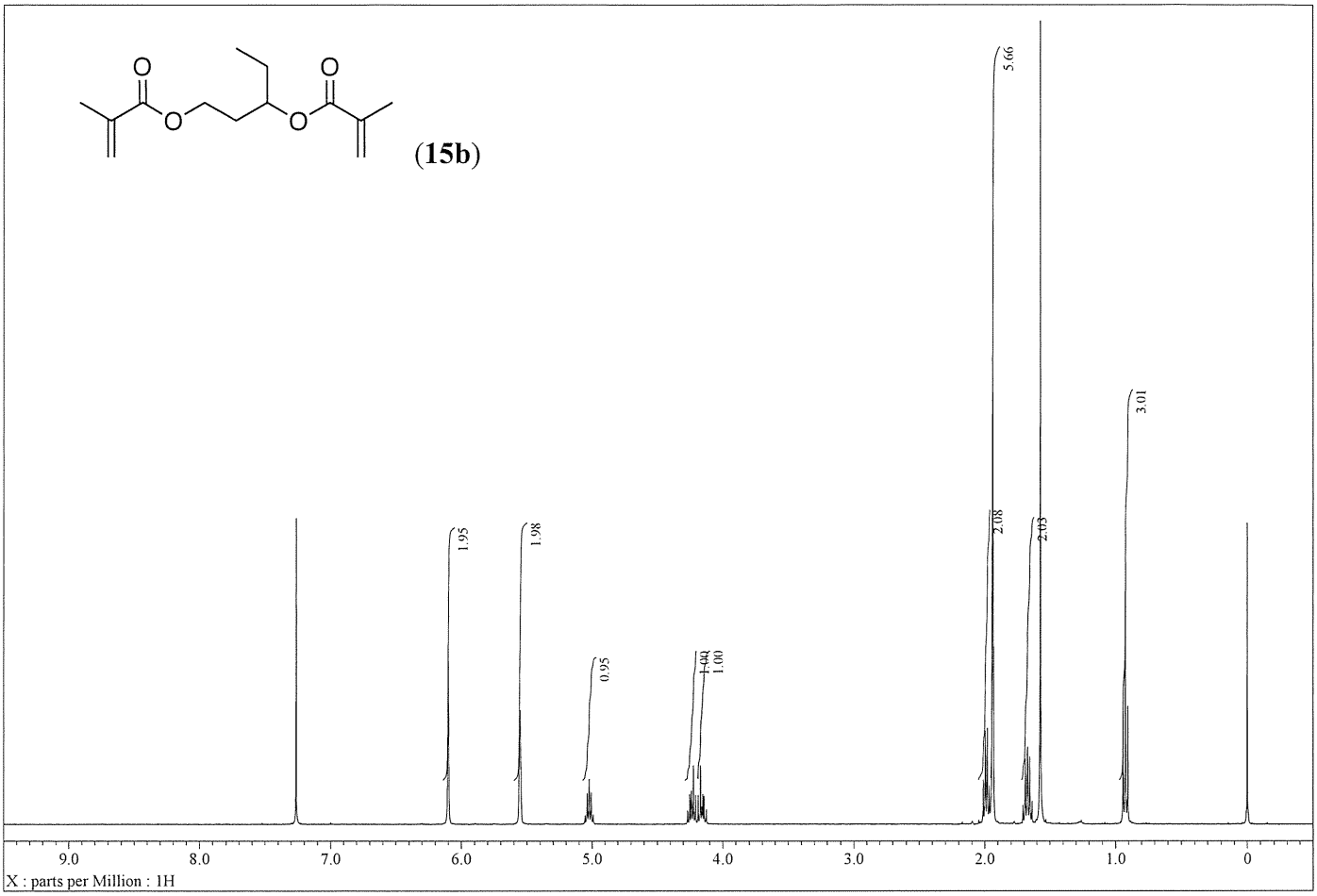
^{13}C NMR, 100 MHz, $CDCl_3$



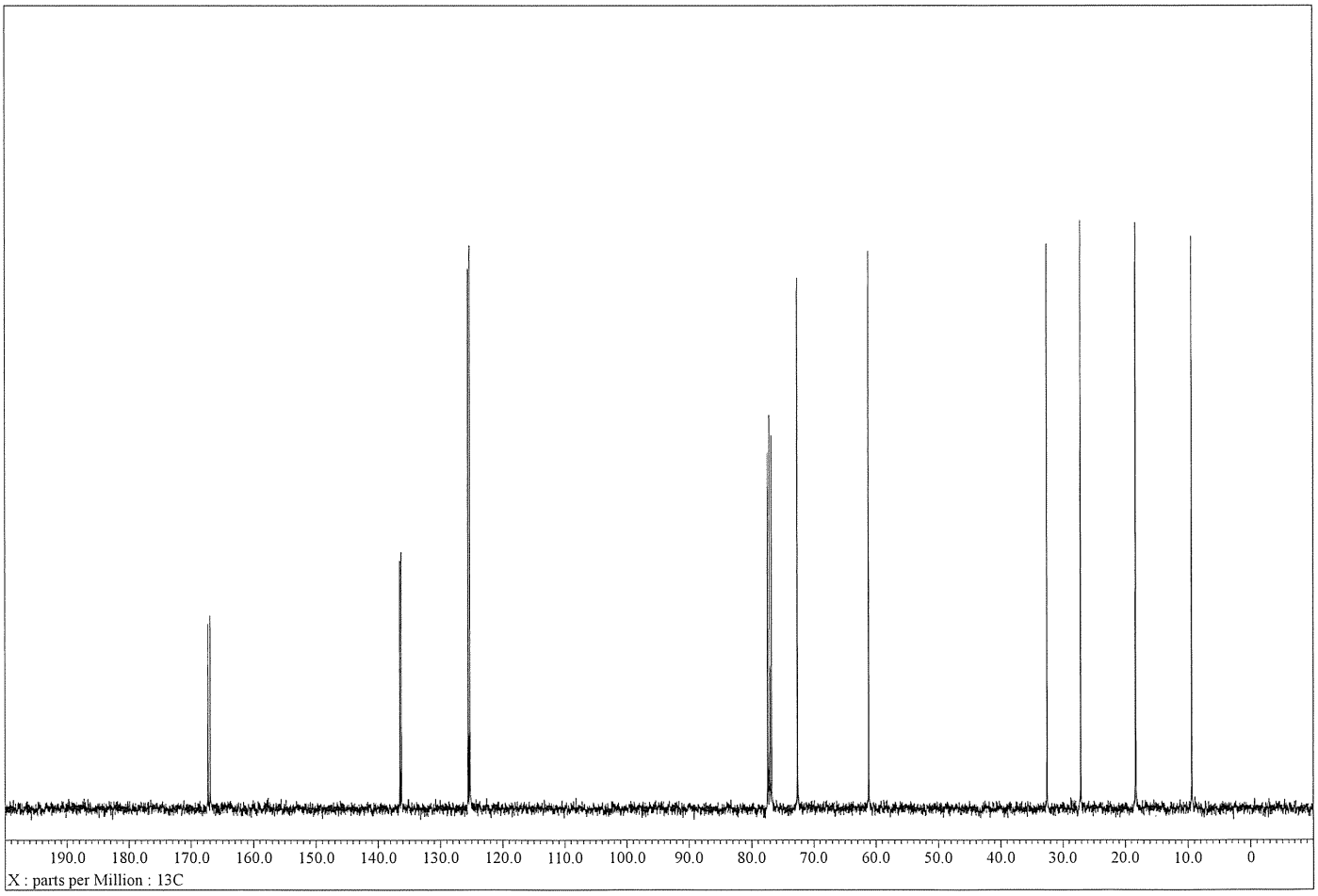
^{1}H NMR, 400 MHz, $CDCl_3$



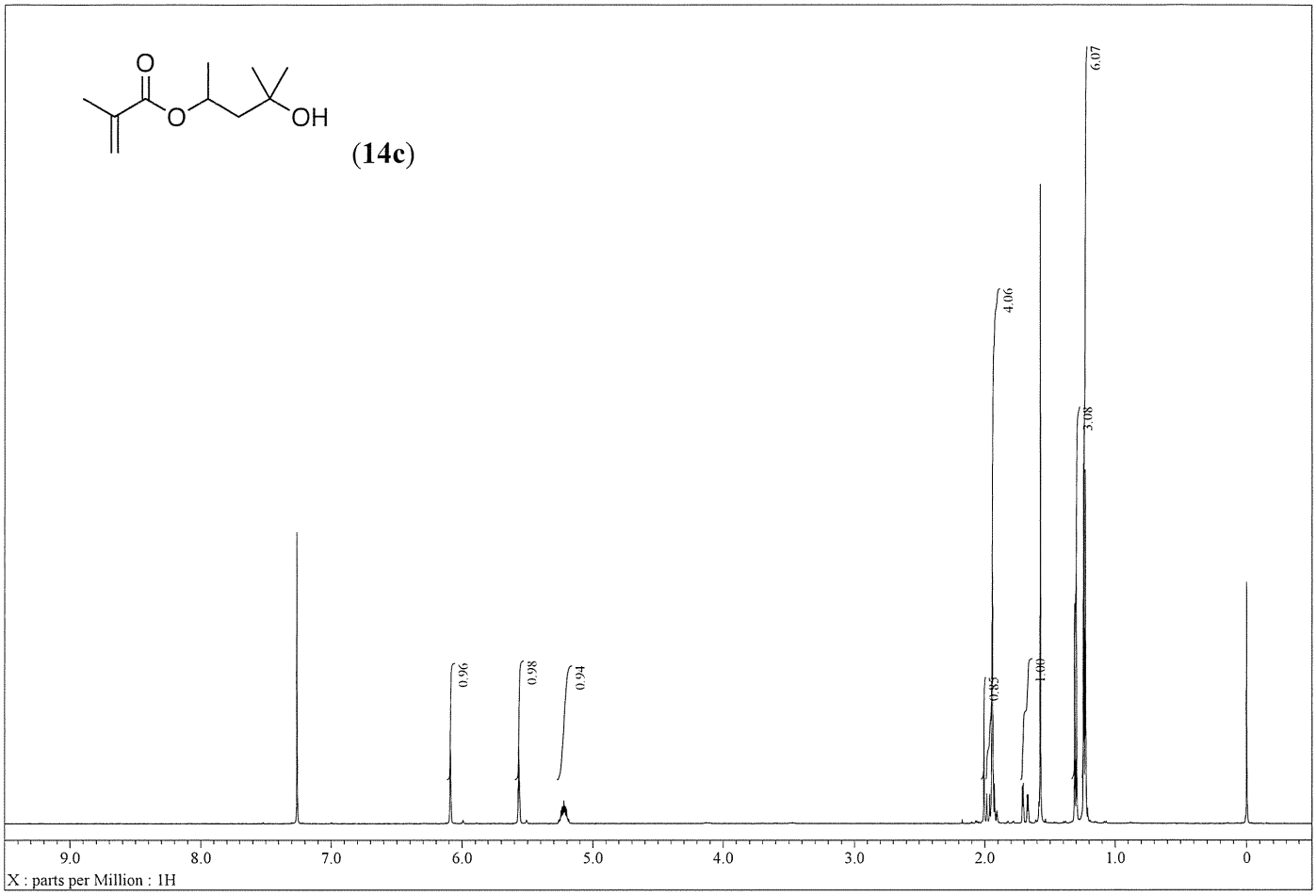
^{13}C NMR, 100 MHz, $CDCl_3$



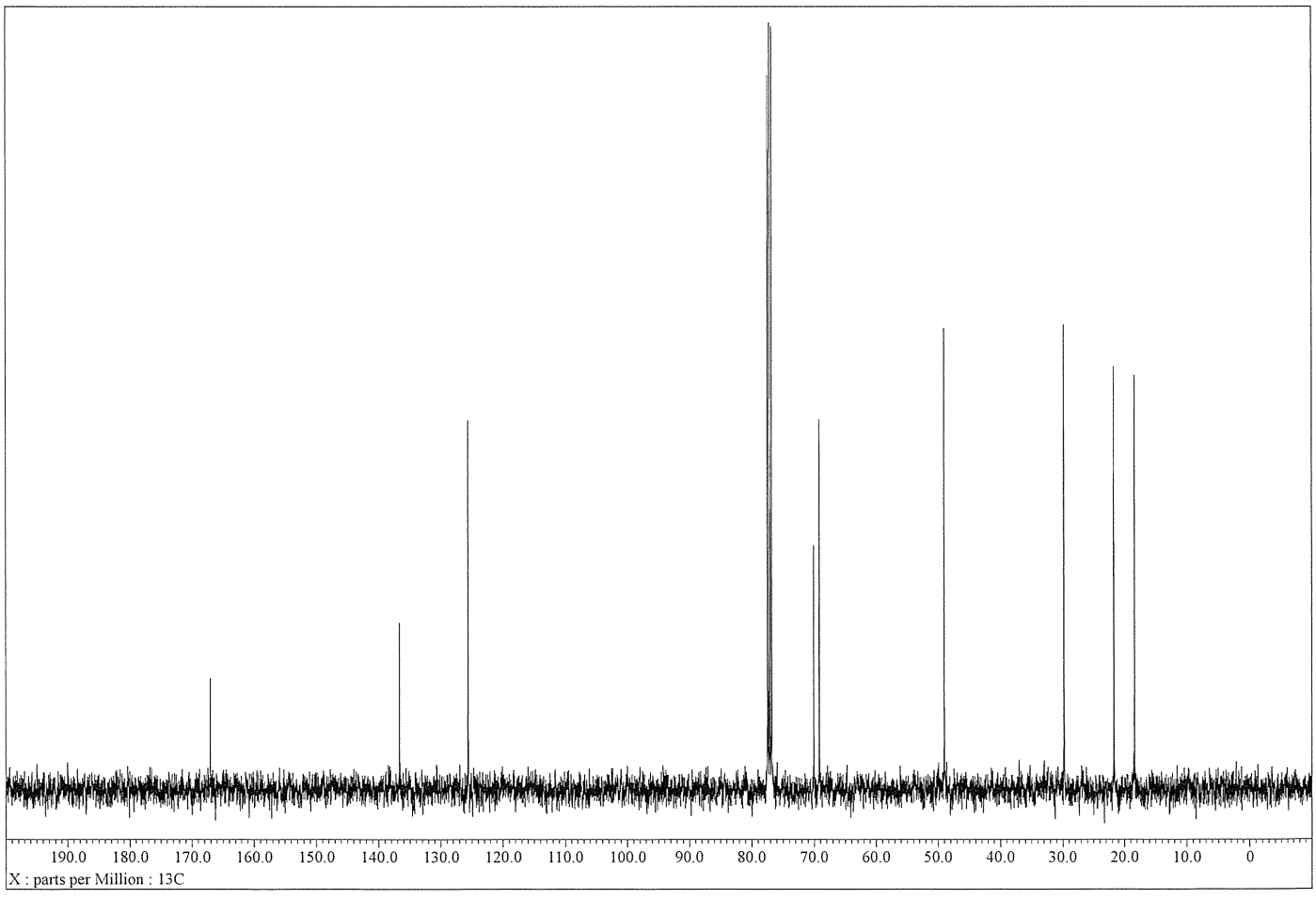
^{1}H NMR, 400 MHz, $CDCl_3$



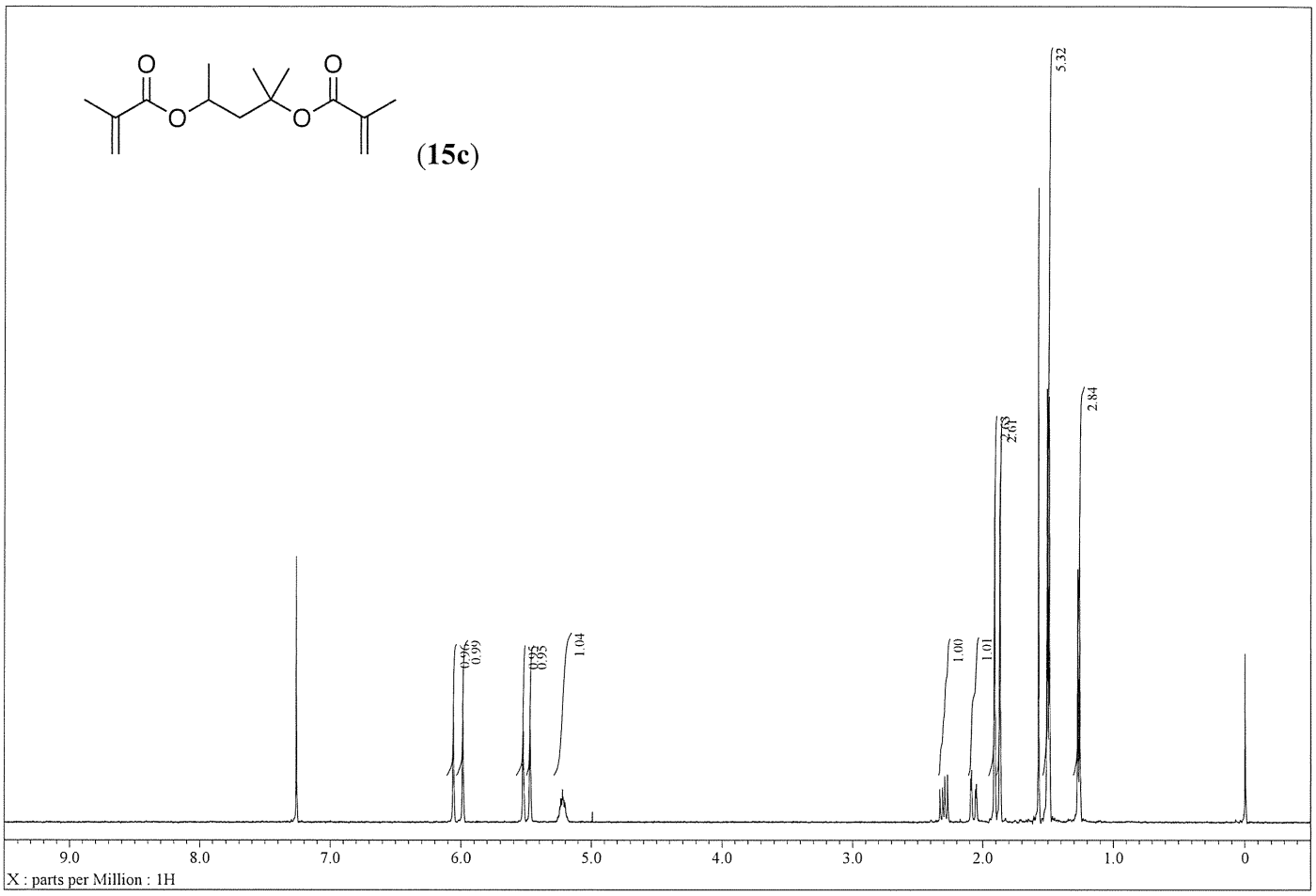
^{13}C NMR, 100 MHz, $CDCl_3$



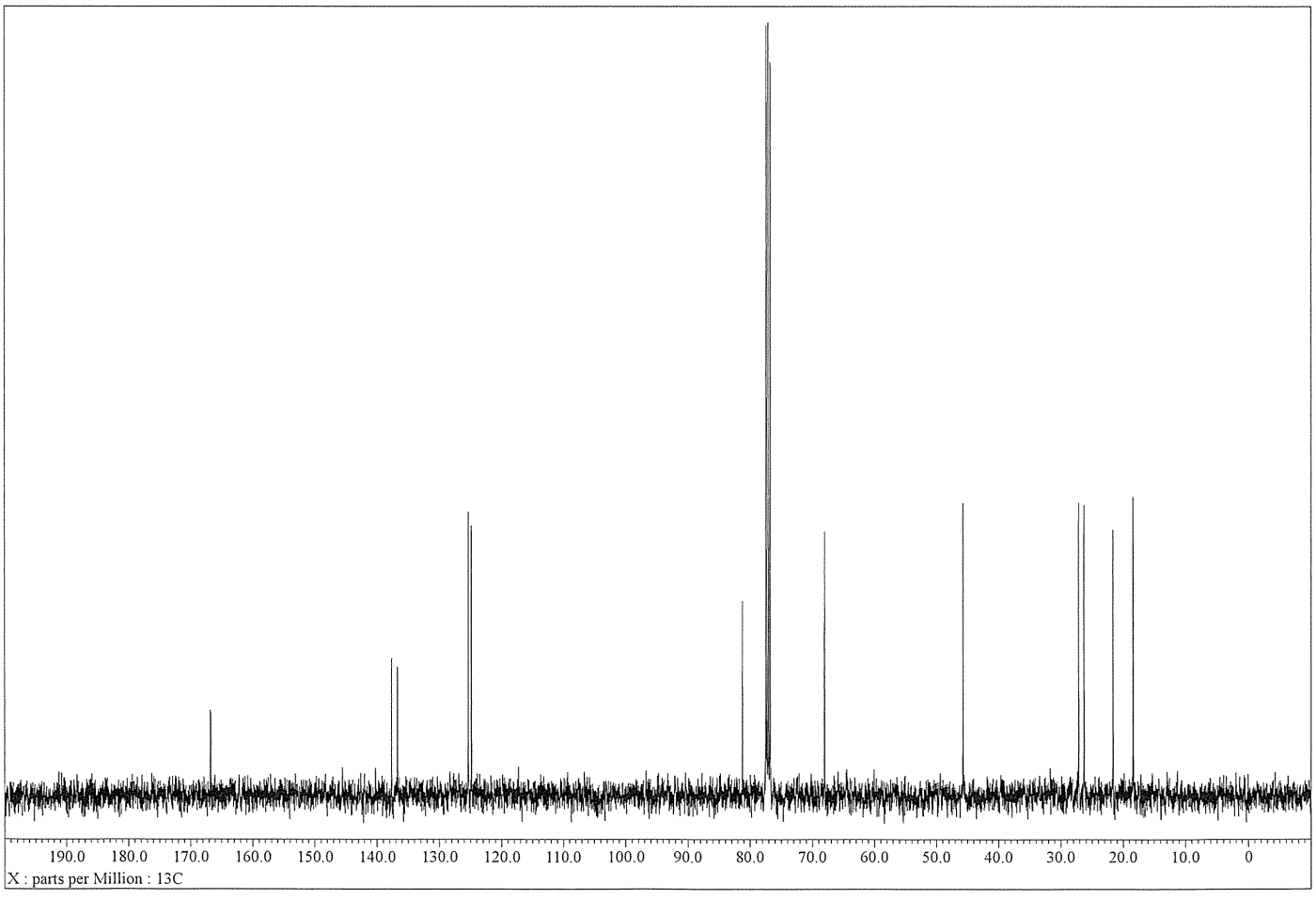
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$