Electronic Supplementary Material (ESI) for Chemical Communications

In situ generated "lanthanum(III) nitrate alkoxide" as a highly active and nearly neutral transesterification catalyst

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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). The products were purified by column chromatography on silica gel (E. Merck Art. 9385). Low and high resolution mass spectral analyses (LRMS and HRMS) were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700, JEOL JMS-T100GCV). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. Dimethyl carbonate, hexane, and ethyl acetate were freshly distilled in prior to use. Other simple chemicals were analytical-grade and obtained commercially.

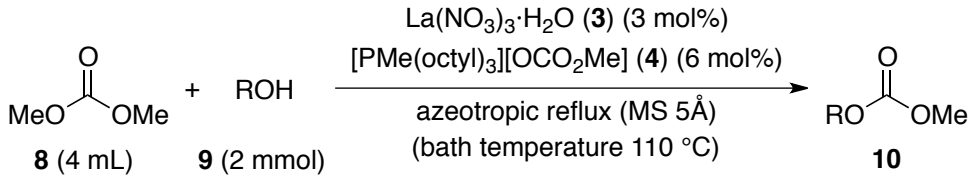
2. Preparation of $La(NO_3)_3 \cdot H_2O$ (3).

According to the reported information,[1] commercially available $La(NO_3)_3 \cdot 6H_2O$ or $La(NO_3)_3 \cdot xH_2O$ was desiccated at 170 °C for 12 h under reduced pressure (<3 Torr). Prepared **3** was stored at room temperature in Schlenk tube under an inert gas-atmosphere.

3. Preparation of $[PMe(octyl)_3](OCO_2Me)$ (4).[2]

$[PMe(octyl)_3](OCO_2Me)$ (**4**) was prepared by the reported procedure quantitatively. Prepared **4** was stored at room temperature in a sealed vial under an inert gas-atmosphere.

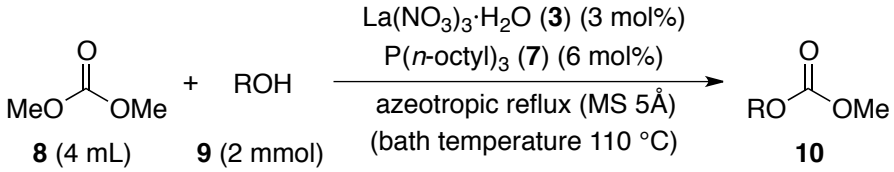
4. General procedure for the $3 \cdot 4_2$-catalyzed transesterification of dimethyl carbonate (Table 1, entry 2; Table 2; *Table S1*).



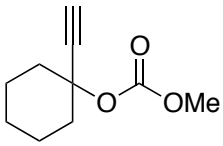
A mixture of $La(NO_3)_3 \cdot H_2O$ (**3**) (20.6 mg, 0.06 mmol) and methyltrioctylphosphonium methyl carbonate (**4**) (55.3 mg, 0.12 mmol) in anhydrous dimethyl carbonate (**8**) (4 mL) was stirred at room temperature for 1–2 min. As soon as alcohol (**9**) (2.0 mmol) was added to the solution, the mixture

was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 1.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating at 110 °C (bath temperature) for 1–12 h, the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over $MgSO_4$, and the organic phase was concentrated in vacuo by a rotary evapolator (ave. 80% of **9** was easily recovered), and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents.

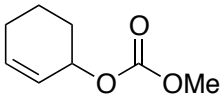
5. General procedure for the $3{\cdot}7_2$-catalyzed transesterification of dimethyl carbonate (Table 1, entry 9; Table 2; *Table S1*).



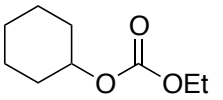
A mixture of $La(NO_3)_3{\cdot}H_2O$ (**3**) (20.6 mg, 0.06 mmol) and trioctylphosphine (**7**) (90% purity, 60 μL, 0.12 mmol) in anhydrous dimethyl carbonate (**8**) (4 mL) was stirred at room temperature for 1–2 min. As soon as alcohol (**9**) (2.0 mmol) was added to the solution, the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 1.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating at 110 °C (bath temperature) for 1–18 h, the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over $MgSO_4$, and the organic phase was concentrated in vacuo by a rotary evapolator (ave. 80% of **8** was easily recovered), and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents. Physical properties of ester products (**10**) are as follows: Compounds **10c** and **10d** have been assigned in the previous report.[3]



1-Ethynylcyclohexyl methyl carbonate (10a):[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (m, 1H), 1.53 (m, 1H), 1.66 (m, 4H), 1.87 (m, 2H), 2.17 (m, 2H), 2.64 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4 (2C), 24.8, 36.7 (2C), 54.2, 74.7, 77.3, 82.9, 153.3. IR (neat) 3287, 2938, 2862, 1754, 1442, 1274, 1246, 1018 cm^{-1}. HRMS (FAB+) calcd for $C_{10}H_{14}NaO_3$ $[M+Na]^+$ 205.0841, found 205.0845.

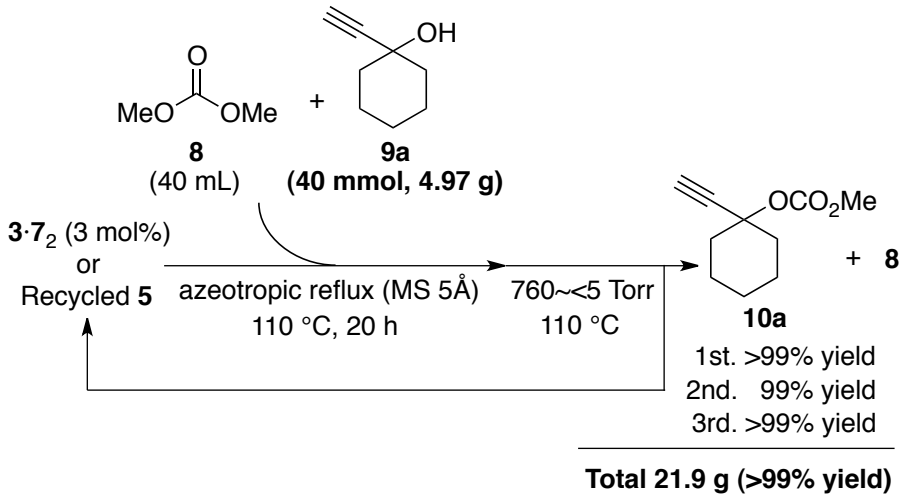


Cyclohex-2-en-1-yl methyl carbonate (10b):[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52–2.16 (m, 6H), 3.77 (s, 3H), 5.12 (m, 1H), 5.77 (m, 1H), 5.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 18.5, 24.7, 28.1, 54.5, 71.8, 124.8, 133.3, 155.4. IR (neat) 2952, 1744, 1267, 1005 cm^{-1}. HRMS (FAB+) calcd for $C_8H_{12}O_3$ $[M]^+$ 156.0786, found 156.0783.



Cyclohexyl ethyl carbonate (10e):[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18–1.60 (m, 6H), 1.30 (t, J = 6.9 Hz, 3H), 1.93 (m, 2H), 1.75 (m, 2H), 4.18 (q, J = 6.9 Hz, 2H), 4.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.6 (2C), 25.1, 31.5 (2C), 63.5, 76.4, 154.6. IR (neat) 2938, 2860, 1741, 1452, 1367, 1255, 1107, 1014 cm^{-1}. HRMS (FAB+) calcd for $C_9H_{16}NaO_3$ $[M+Na]^+$ 195.0997, found 195.1001.

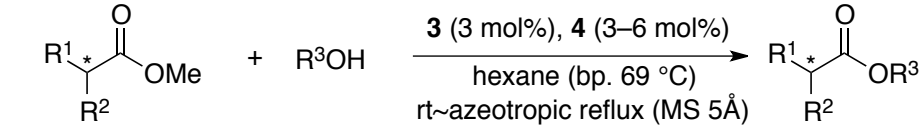
6. Recycle procedure for the 3·7$_2$-catalyzed transesterification of dimethyl carbonate with 9a (eqn (3)).



A mixture of $La(NO_3)_3 \cdot H_2O$ (**3**) (412 mg, 1.2 mmol) and trioctylphosphine (**7**) (90% purity, 1.19 mL, 2.4 mmol) in anhydrous dimethyl carbonate (**8**) (40 mL) was stirred at room temperature for 1–2 min. As soon as 1-ethynyl-1-cyclohexanol (**9a**) (5.14 mL, 40.0 mmol) was added to the solution, the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 20.0 g of 5 Å molecular sieves (pellets). After heating at 110 °C (bath temperature) for 20 h, the reaction mixture was allowed to cool to ambient temperature. (*) The reflux condenser was replaced with the fractional condenser, and the product and volatiles were removed in vacuo (from 760 to <5 Torr) at 110 °C (bath temperature). The fractional condenser was replaced with the reflux condenser. To

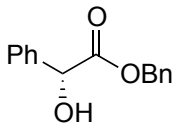
the catalyst residue, anhydrous **8** (40 mL) and **9a** (5.14 mL, 40.0 mmol) was added. Then the mixture was heated again for 20 h under azeotropic reflux conditions with the removal of methanol with new 5 Å molecular sieves (pellets) at condenser. From the distillates, product was obtained after the removal of volatiles and column chromatography on silica gel (1st. 7.29 g, >99% yield. 2nd. 7.28 g, 99% yield.). This recycle procedure (*) was repeated one more time. Finally, to quench the catalysts, a few drops of water was added, and the mixture was stirred for 5 min. The mixture was dried over $MgSO_4$, and the organic phase was concentrated in vacuo by a rotary evapolator, and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents (3rd. 7.29 g, >99% yield.).

7. General procedure for the $3{\cdot}4_2$-catalyzed non-epimerized transesterification of chiral α-substituted carboxylic esters (eqn (4) and Table 3).



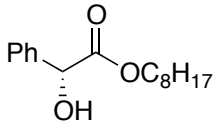
11 (2 mmol, >99% ee) **9** (2 mmol) **12**

A mixture of $La(NO_3)_3{\cdot}H_2O$ (**3**) (20.6 mg, 0.06 mmol) and methyltrioctylphosphonium methyl carbonate (**4**) (27.7–55.3 mg, 0.06–0.12 mmol) in hexane (4 mL) was stirred at room temperature for 5 min. As soon as alcohol (**9**) (2.0 mmol) was added, carboxylic ester (**11**) (2.0 mmol) was added to the solution, and the mixture was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 1.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating at 70–90 °C (bath temperature) for 1–48 h, the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over $MgSO_4$, and the organic phase was concentrated and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents. Physical properties of ester products (**12**) are as follows: Compound **12c** has been assigned in the previous report.[6]

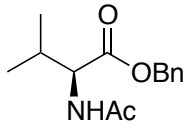


(*R*)-Benzyl mandelate (12a):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (d, J = 6.0 Hz, 1H), 5.12 (d, J = 12.3 Hz, 1H), 5.21 (d, J = 6.0 Hz, 1H), 5.23 (d, J = 12.3 Hz, 1H), 7.16–7.24 (m, 2H), 7.27–7.38 (m, 6H), 7.38–7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.6, 72.9, 126.5 (2C), 127.9 (2C), 128.40, 128.46, 128.51 (2C), 128.55 (2C), 134.9, 138.0, 173.4. M.p. 93 °C. IR (KBr) 3447, 1727, 1445, 1210, 1180, 1096, 1066 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{14}NaO_3$ $[M+Na]^+$ 265.0841,

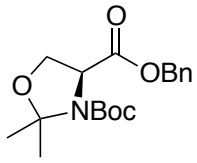
found 265.0841. Chiral HPLC analysis; OD-H, hexane/EtOH = 9/1, 1.0 mL/min, t_R = 11.6 min (major, *R*), 23.2 min (minor, *S*).



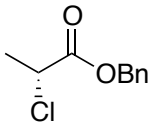
(*R*)-Octyl 2-hydroxy-2-phenylacetate (12b):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.14–1.25 (m, 8H), 1.27 (m, 2H), 1.56 (m, 2H), 3.50 (d, *J* = 5.4 Hz, 1H), 4.15 (m, 2H), 5.16 (d, *J* = 6.0 Hz, 1H), 7.29–7.39 (m, 3H), 7.42 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 25.5, 28.3, 28.9, 29.0, 31.6, 66.2, 72.7, 126.4 (2C), 128.3, 128.4 (2C), 138.4, 173.7. IR (neat) 3441, 2925, 2856, 1739, 1455, 1185, 1098, 1068 cm^{-1}. HRMS (FAB+) calcd for $C_{16}H_{25}O_3$ $[M+H]^+$ 265.1804, found 265.1801. Chiral HPLC analysis; OD-H, hexane/EtOH = 9/1, 1.0 mL/min, t_R = 6.6 min (minor, *S*), 9.0 min (major, *R*).



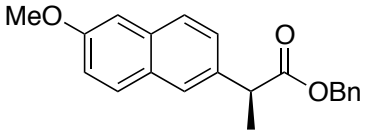
(*S*)-Benzyl 2-acetamido-3-methylbutanoate (12d):[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 2.04 (s, 3H), 2.17 (m, 1H), 4.62 (dd, *J* = 8.7, 5.1 Hz, 1H), 5.14 (d, *J* = 12.3 Hz, 1H), 5.19 (d, *J* = 12.3 Hz, 1H), 6.00 (br, 1H), 7.30–7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 18.8, 23.2, 31.3, 56.9, 67.0, 128.3 (2C), 128.4, 128.5 (2C), 135.2, 169.9, 172.0. IR (neat) 3288, 2965, 1742, 1655, 1543, 1373, 1187, 1149, 1002 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1443, found 250.1449. Chiral HPLC analysis; AD-3, hexane/EtOH = 20/1, 0.5 mL/min, t_R = 59.9 min (minor, *R*), 66.0 min (major, *S*).



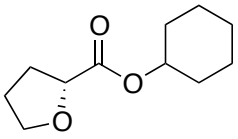
(*S*)-4-Benzyl 3-*tert*-butyl 2,2-dimethyloxazolidine-3,4-dicarboxylate (12e): ^{1}H NMR (400 MHz, $CDCl_3$) 3:2 Ratio of rotamers is observed. major: δ 1.33 (s, 9H), 1.53 (s, 3H), 1.67 (s, 3H), 4.06 (m, 1H), 4.15 (m, 1H), 4.40 (dd, *J* = 6.9, 2.7 Hz, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 5.20 (d, *J* = 12.3 Hz, 1H), 7.30–7.39 (m, 5H). minor: δ 1.48 (s, 9H), 1.49 (s, 3H), 1.61 (s, 3H), 4.06 (m, 1H), 4.15 (m, 1H), 4.53 (dd, *J* = 6.9, 2.7 Hz, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.25 (d, *J* = 12.3 Hz, 1H), 7.30–7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) 3:2 Ratio of rotamers is observed. major: δ 24.2, 24.9, 28.1 (3C), 59.3, 66.2, 67.0, 80.3, 95.0, 128.0, 128.3 (2C), 128.5 (2C), 135.2, 151.1, 171.0. minor: δ 25.0, 25.9, 28.2 (3C), 59.3, 65.9, 67.1, 80.8, 94.3, 128.2, 128.4 (2C), 128.5 (2C), 135.3, 152.0, 170.6. IR (neat) 2978, 1754, 1707, 1378, 1251, 1184, 1093, 1053 cm^{-1}. HRMS (FAB+) calcd for $C_{18}H_{25}NNaO_5$ $[M+Na]^+$ 358.1630, found 358.1624. Chiral HPLC analysis; AD-3, hexane/EtOH = 20/1, 0.5 mL/min, t_R = 11.0 min (minor, *R*), 14.9 min (major, *S*).



(*R*)-Benzyl 2-chloropropanoate (12f):[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, J = 6.9 Hz, 3H), 4.43 (q, J = 6.9 Hz, 1H), 5.20 (s, 2H), 7.32–8.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 52.4, 67.5, 128.1 (2C), 128.5, 128.6 (2C), 135.0, 169.9. IR (neat) 3040, 1746, 1455, 1337, 1268, 1171, 1075 cm^{-1}. HRMS (FAB+) calcd for $C_{10}H_{11}ClNaO_2$ $[M+Na]^+$ 221.0345, found 221.0351. Chiral HPLC analysis; AS-3, hexane/EtOH = 20/1, 0.5 mL/min, t_R = 8.9 min (minor, *S*), 9.3 min (major, *R*).



(*S*)-Benzyl 2-(6-methoxynaphthalen-2-yl)propanoate (12g):[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (d, J = 7.5 Hz, 3H), 3.90 (q, J = 7.5 Hz, 1H), 3.91 (s, 3H), 5.08 (d, J = 12.3 Hz, 1H), 5.15 (d, J = 12.3 Hz, 1H), 7.09–7.16 (m, 2H), 7.20–7.34 (m, 5H), 7.40 (dd, J = 8.7, 1.8 Hz, 1H), 7.63–7.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 45.4, 55.2, 66.4, 105.4, 118.9, 125.9, 126.2, 127.1, 127.9 (2C), 128.0, 128.4 (2C), 128.8, 129.2, 133.6, 135.5, 135.9, 157.5, 174.4. IR (KBr) 2975, 1741, 1604, 1267, 1229, 1165, 1027 cm^{-1}. HRMS (FAB+) calcd for $C_{21}H_{20}NaO_3$ $[M+Na]^+$ 343.1310, found 343.1319. M.p. 75 °C. Chiral HPLC analysis; OD-3, hexane/EtOH = 20/1, 0.5 mL/min, t_R = 14.3 min (minor, *R*), 15.5 min (major, *S*).

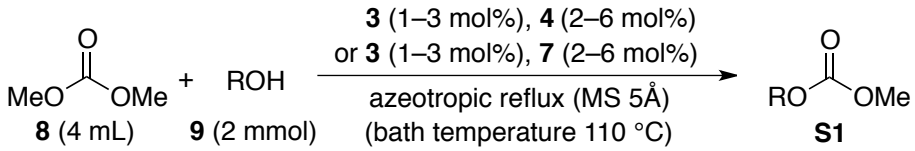


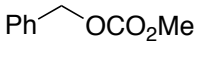
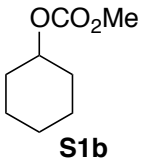
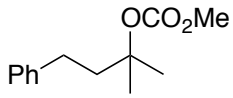
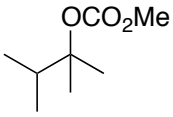
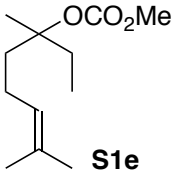
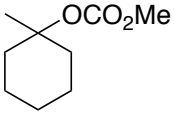
(*R*)-Cyclohexyl tetrahydrofuran-2-carboxylate (12h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (m, 1H), 1.31–1.50 (m, 4H), 1.56 (m, 1H), 1.72 (m, 2H), 1.85 (m, 2H), 1.90–2.03 (m, 3H), 2.24 (m, 1H), 3.92 (m, 1H), 4.02 (m, 1H), 4.43 (dd, J = 8.1, 4.5 Hz, 1H), 4.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (2C), 25.1, 25.2, 30.2, 31.4 (2C), 69.2, 73.0, 76.7, 172.8. IR (neat) 2938, 2860, 1744, 1451, 1278, 1200, 1088 cm^{-1}. HRMS (FAB+) calcd for $C_{11}H_{18}NaO_3$ $[M+Na]^+$ 221.1154, found 221.1152. Chiral HPLC analysis; OD-H, hexane/EtOH = 20/1, 0.5 mL/min, t_R = 9.9 min (minor, *S*), 11.6 min (major *R*).

8. Transesterification of dimethyl carbonate with a variety of 1–3°-alcohols (Table S1).

1°- and 2°-alcohols were highly reactive in the presence of 1 mol% of **3**·$\mathbf{4}_2$ or **3**·$\mathbf{7}_2$, and the corresponding methyl carbonates (**S1a** and **S1b**) were obtained in quantitative yields within 1 h. Other 3°-alcohols were also used regardless of whether they had a cyclic or acyclic structure in the presence of 3 mol% of **3**·$\mathbf{4}_2$ or **3**·$\mathbf{7}_2$, and the desired products (**S1c–f**) were obtained in 74~>99% yields.

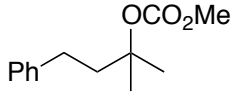
Table S1 *Transesterification of dimethyl carbonate with a variety of 1–3°-alcohols*[a]



Product (**S1**), isolated yield, and reaction time			
			
	S1a	**S1b**	**S1c**
3·$\mathbf{4}_2$:	>99% (1 h)[b]	>99% (1 h)[b]	>99% (1 h)
3·$\mathbf{7}_2$:	>99% (1 h)[b]	>99% (1 h)[b]	94% (5 h)
			
	S1d	**S1e**	**S1f**
3·$\mathbf{4}_2$:	81% (8 h)	98% (12 h)	74% (12 h)
3·$\mathbf{7}_2$:	82% (8 h)	98% (18 h)	83% (14 h)

[a] Unless otherwise noted, 3 mol % of **3**·$\mathbf{4}_2$, **3**·$\mathbf{7}_2$, or **1**·$\mathbf{2}_2$ was used.
[b] 1 mol % of **3**·$\mathbf{4}_2$, **3**·$\mathbf{7}_2$, or **1**·$\mathbf{2}_2$ was used.

Compounds **S1a**, **S1b**, **S1d–f** have been assigned in the previous report.[3]

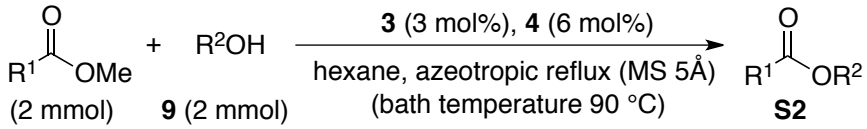


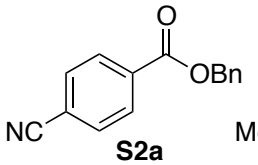
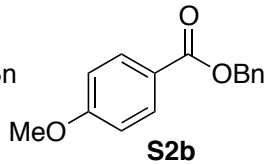
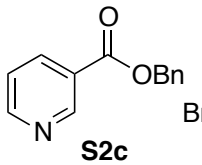
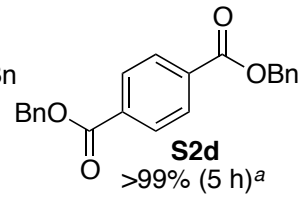
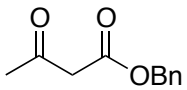
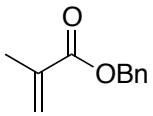
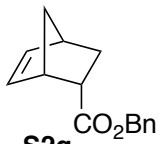
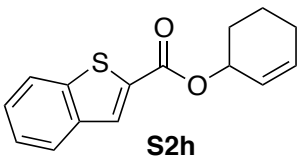
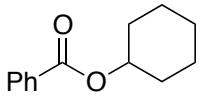
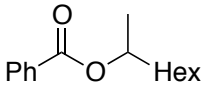
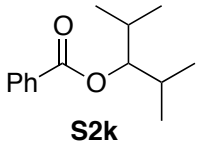
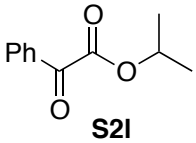
Methyl (2-methyl-4-phenylbutan-2-yl) carbonate (S1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 6H), 2.08 (m, 2H), 2.67 (m, 2H), 3.71 (s, 3H), 7.17 (d, J = 8.1 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7 (2C), 30.2, 42.4, 53.9, 83.6, 125.8, 128.3 (2C), 128.4 (2C), 141.8, 154.0. IR (neat) 2954, 1743, 1440, 1284, 1202, 1099 cm^{-1}. HRMS (FAB+) calcd for $C_{13}H_{18}NaO_3$ $[M+Na]^+$ 245.1154, found 245.1149.

9. Transesterification of methyl carboxylates (Table S2).

In place of chiral **11**, the more common transesterification of achiral carboxylic esters was examined using hexane (bp. 69 °C) as a solvent in the presence of catalyst **3**·$\mathbf{4}_2$ (3 mol%) (*Table S2*). The catalyst in situ was also soluble in less-polar hexane, and the homogeneous reaction conditions were given. Overall, aromatic, heteroaromatic, and aliphatic esters could be used in the reaction with 1°- and 2°-alcohols, and the corresponding colorless products (**S2a–l**) were obtained in good yields. For example, highly coordinatable methyl nicotinate (See **S2c**), chelatable methyl acetoacetate (See **S2e**), and easily polymerizable methyl methacrylate (See **S2f**) could be used without serious problems. In particular, less-reactive 2°-alcohols such as moderately hindered cyclic cyclohexanol and 2-cyclohexen-1-ol, and more bulky acyclic isopropanol, 2-octanol, and 2,4-dimethyl-3-pentanol could be used, although rather prolonged reaction times were required (See **S2h–l**).

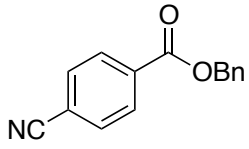
Table S2 *Transesterification of methyl carboxylates*



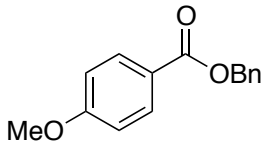
Product (**S2**), isolated yield, and reaction time			
 **S2a** 94% (1 h)	 **S2b** 95% (10 h)	 **S2c** 92% (1 h)	 **S2d** >99% (5 h)[a]
 **S2e** 84% (12 h)	 **S2f** 80% (10 h)	 **S2g** 92% (72 h)	 **S2h** 99% (5 h)
 **S2i** 97% (16 h)	 **S2j** 93% (24 h)	 **S2k** 90% (36 h)	 **S2l** 97% (3 h)[b]

[a] 4 mmol of BnOH was used. [b] 3 mmol of *i*-PrOH was used.

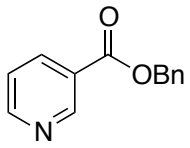
Compound **S2i** has been assigned in the previous report.[6]



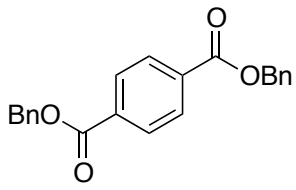
Benzyl 4-cyanobenzoate (S2a):[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 2H), 7.33–7.48 (m, 5H), 7.73 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.4, 116.4, 117.9, 128.3 (2C), 128.5, 128.7 (2C), 130.1 (2C), 132.2 (2C), 133.9, 135.2, 164.7. M.p. 61 °C. IR (KBr) 3034, 2231, 1725, 1272, 1105 cm^{-1}. HRMS (EI+) calcd for $C_{15}H_{11}NO_2$ $[M]^+$ 237.0790, found 237.0800.



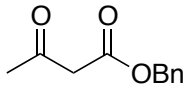
Benzyl 4-methoxybenzoate (S2b):[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.33 (s, 2H), 6.91 (d, J = 8.7 Hz, 2H), 7.30–7.41 (m, 3H), 7.44 (d, J = 7.2 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 66.3, 113.5 (2C), 122.4, 128.0 (2C), 128.1, 128.5 (2C), 131.6 (2C), 136.2, 163.3, 166.1. IR (neat) 2956, 1713, 1606, 1510, 1455, 1257, 1167, 1101, 1029 cm^{-1}. HRMS (EI+) calcd for $C_{15}H_{14}O_3$ $[M]^+$ 242.0943, found 242.0949.



Benzyl nicotinate (S2c):[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 2H), 7.33–7.48 (m, 6H), 8.33 (dt, J = 7.8, 1.8 Hz, 1H), 8.78 (dd, J = 5,1, 1.8 Hz, 1H), 9.26 (dd, J = 2.4, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.0, 123.2, 125.9, 128.2 (2C), 128.4, 128.6 (2C), 135.4, 137.1, 150.9, 153.4, 165.0. IR (neat) 3034, 1724, 1590, 1280, 1110, 1024 cm^{-1}. HRMS (EI+) calcd for $C_{13}H_{11}NO_2$ $[M]^+$ 213.0790, found 213.0798.

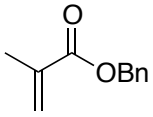


Dibenzyl terephthalate (S2d):[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 4H), 7.32-7.48 (m, 10H), 8.13 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.1 (2C), 128.5 (4C), 128.3 (2C), 128.6 (4C), 129.6 (4C), 133.9 (2C), 135.5 (2C), 165.5 (2C). M.p. 95 °C. IR (KBr) 1715, 1453, 1405, 1274, 1128, 1107, 1020 cm^{-1}. HRMS (FAB+) calcd for $C_{22}H_{18}NaO_4$ $[M+Na]^+$ 369.1103, found 369.1108.

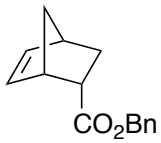


Benzyl 3-oxobutanoate (S2e):[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.49 (s, 2H), 5.18 (s, 2H), 7.30–7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 49.9, 67.1, 128.3 (2C),

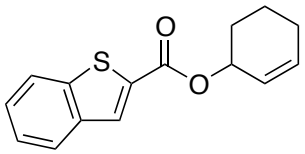
128.4, 128.5 (2C), 135.1, 166.9, 200.3. IR (neat) 3034, 1743, 1409, 1360, 1316, 1149, 1028 cm^{-1}. HRMS (EI+) calcd for $C_{11}H_{12}O_3$ $[M]^+$ 192.0786, found 192.0780.



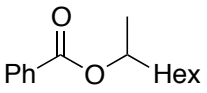
Benzyl methacrylate (S2f):[15] ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 3H), 5.18 (s, 2H), 5.59 (quintet, *J* = 1.5 Hz, 1H), 6.15 (bs, 1H), 7.27–7.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 66.2, 125.7, 127.9 (2C), 128.0, 128.4 (2C), 136.0, 136.1, 167.1. IR (neat) 2957, 1719, 1637, 1454, 1319, 1294, 1159 cm^{-1}. HRMS (FAB+) calcd for $C_{11}H_{12}NaO_2$ $[M+Na]^+$ 199.0735, found 199.0735.



***endo*-Benzyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (S2g):**[16] ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, *J* = 7.8 Hz, 1H), 1.39–1.49 (m, 2H), 1.91 (m, 1H), 2.90 (s, 1H), 3.00 (dt, *J* = 9.6, 3.6 Hz, 1H), 3.23 (s, 1H), 5.05 (d, *J* = 12.9 Hz, 1H), 5.09 (d, *J* = 12.9 Hz, 1H), 5.87 (dd, *J* = 5.4, 2.7 Hz, 1H), 6.19 (dd, *J* = 5.4, 2.7 Hz, 1H), 7.28–7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.1, 42.5, 43.3, 45.7, 49.5, 65.9, 128.0 (3C), 128.4 (2C), 132.2, 136.2, 137.7, 174.5. IR (neat) 2974, 1734, 1455, 1335, 1270, 1170, 1108, 1025 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{17}O_2$ $[M+H]^+$ 229.1229, found 229.1233.

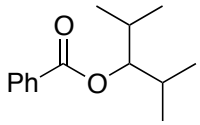


Cyclohex-2-en-1-yl benzo[*b*]thiophene-2-carboxylate (S2h): ^1H NMR (400 MHz, $CDCl_3$) δ 1.60-2.22 (m, 6H), 5.51 (m, 1H), 5.85 (m, 1H), 6.02 (dt, *J* = 10.2, 3.3 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 8.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 24.8, 28.3, 69.3, 122.6, 124.7, 125.2, 125.4, 126.7, 130.2, 133.2, 134.2, 138.7, 142.1, 162.4. IR (neat) 2938, 1704, 1523, 1279, 1244, 1178, 1047 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{14}NaO_2S$ $[M+Na]^+$ 281.0612, found 281.0626.

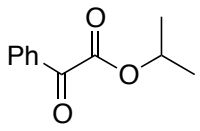


Octan-2-yl benzoate (S2j):[17] H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.3 Hz, 3H), 1.22–1.45 (m, 11H), 1.60 (m, 1H), 1.73 (m, 1H), 5.15 (sextet, *J* = 6.3 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.0, 22.5, 25.3, 29.1, 31.7, 36.0, 71.7, 128.2 (2C), 129.4 (2C), 130.8, 132.6, 166.1. IR (neat) 2930, 2857, 1717, 1451, 1275, 1109 cm^{-1}. HRMS (FAB+) calcd for $C_{15}H_{22}NaO_2$ $[M+Na]^+$ 257.1517, found

257.1519.



2,4-Dimethylpentan-3-yl benzoate (S2k):[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 6.9 Hz, 6H), 2.03 (octet, J = 6.9 Hz, 2H), 4.85 (t, J = 6.0 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 8.07 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3 (2C), 19.6 (2C), 29.6 (2C), 83.2, 128.3 (2C), 129.6 (2C), 130.6, 132.6, 166.5. IR (neat) 2965, 1718, 1451, 1369, 1271, 1176, 1109, 1069 cm^{-1}. HRMS (FAB+) calcd for $C_{14}H_{20}NaO_2$ $[M+Na]^+$ 243.1361, found 243.1373.

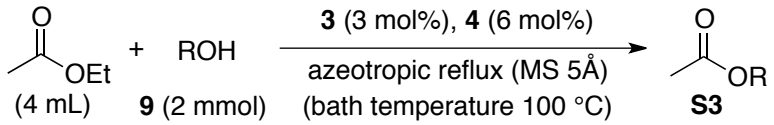


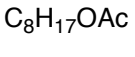
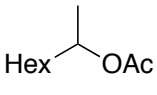
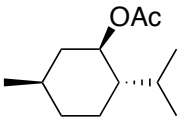
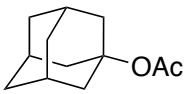
Isopropyl 2-oxo-2-phenylacetate (S2l):[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, J = 6.3 Hz, 6H), 5.33 (septet, J = 6.3 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.66 (t, J = 7.2 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (2C), 70.6, 128.8 (2C), 129.9 (2C), 132.4, 134.7, 163.6, 186.7. IR (neat) 2984, 1732, 1691, 1297, 1206, 1177, 1103, 988 cm^{-1}. HRMS (FAB+) calcd for $C_{11}H_{12}NaO_3$ $[M+Na]^+$ 215.0684, found 215.0681.

10. Transesterification of ethyl acetate (Table S3).

Ethyl esters are generally less reactive than methyl esters. To demonstrate the synthetic utility of this catalysis, the acetylation of alcohols was examined with ethyl acetate (bp. 77 °C) as a low-cost and industrially practical starting material (*Table S3*). Less hindered 1°- and 2°-alcohols could be readily used and the corresponding products were obtained in >99% yield for **S3a**–**c** within 1 h. Basically, 3°-alcohols are much less reactive toward carboxylic esters than toward **3** due to mutual steric hindrance. Nevertheless, due to the small structure of ethyl acetate, bulky 3°-alcohols could also be used in the transesterification of ethyl acetate, and **S3d** was obtained in 71% yield.

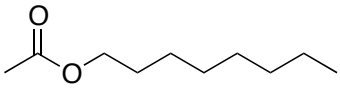
Table S3 *Transesterification of ethyl acetate*



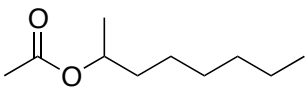
Product (**S3**), isolated yield, and reaction time			
			
S3a	**S3b**	**S3c**	**S3d**
>99% (1 h)	>99% (1 h)	>99% (1 h)	71% (18 h)

General procedure for the 3·4$_2$-catalyzed transesterification of ethyl acetate (Table S3).

A mixture of $La(NO_3)_3 \cdot H_2O$ (**3**) (20.6 mg, 0.06 mmol) and methyltrioctylphosphonium methyl carbonate (**4**) (55.3 mg, 0.12 mmol) in hexane (4 mL) was stirred at room temperature for 5 min. As soon as alcohol (**9**) (2.0 mmol) was added, ethyl acetate (4 mL) was added to the solution, and the mixture was heated under azeotropic reflux conditions with the removal of methanol. Ethanol was removed through a pressure-equalized addition funnel containing a cotton plug and 1.0 g of 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating at 100 °C (bath temperature) for 1–18 h, the reaction mixture was allowed to cool to ambient temperature. To quench the catalysts, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over $MgSO_4$, and the organic phase was concentrated and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents. Physical properties of ester products (**S3**) are as follows: Compound **S3d** has been assigned in the previous report.[6]

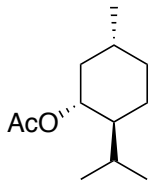


Octyl acetate (S3a):[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3H), 1.20–1.40 (m, 10H), 1.61 (m, 2H), 2.05 (s, 3H), 4.05 (t, J = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.0, 22.6, 25.8, 28.5, 29.1, 29.2, 31.7, 64.6, 171.2. IR (neat) 2928, 2857, 1743, 1467, 1365, 1238, 1040 cm^{-1}. HRMS (FAB+) calcd for $C_{10}H_{20}NaO_2$ $[M+Na]^+$ 195.1361, found 195.1360.



Octan-2-yl acetate (S3b):[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3H), 1.20 (d, J = 6.3 Hz, 3H), 1.23–1.63 (m, 10H), 2.03 (s, 3H), 4.88 (sextet, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.9, 21.3, 22.5, 25.3, 29.0, 31.7, 35.8, 71.0, 170.8. IR (neat) 2931, 2859, 1739, 1460, 1372, 1244, 1124, 1020 cm^{-1}. HRMS (FAB+) calcd for $C_{10}H_{20}NaO_2$

$[M+Na]^+$ 195.1361, found 195.1357.



(–)-Menthyl acetate (S3c):[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (d, J = 7.5 Hz, 3H), 0.88 (m, 1H), 0.89 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.3 Hz, 3H), 0.96 (m, 1H), 1.05 (m, 1H), 1.35 (m, 1H), 1.48 (m, 1H), 1.62–1.73 (m, 2H), 1.86 (m, 1H), 1.99 (m, 1H), 2.03 (s, 3H), 4.67 (td, J = 11.1, 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 20.6, 21.2, 21.9, 23.4, 26.2, 31.3, 34.1, 40.8, 46.9, 74.0, 170.6. IR (neat) 2955, 1735, 1455, 1370, 1244, 1024 cm^{-1}. HRMS (FAB+) calcd for $C_{12}H_{22}NaO_2$ $[M+Na]^+$ 221.1517, found 221.1508.

11. Comparison of the price and toxicity of La(III) and other metal catalysts (Table S4).

We used desiccated $La(NO_3)_3 \cdot H_2O$ (**3**) that was readily prepared from commercially available $La(NO_3)_3 \cdot 6H_2O$ and $La(NO_3)_3 \cdot xH_2O$. Just after $La(NO_3)_3 \cdot H_2O$ (**3**) and trioctylphosphine (**7**) were mixed in situ, the subsequent transesterification reaction would start under azeotropic reflux conditions. In particular, lanthanum(III) nitrate hydrate(s) are highly practical precursors since they are stable under air and moist conditions, but are hygroscopic. Lanthanum(III) nitrate hydrate(s) are 100~300 times less expensive than La(O*i*-Pr)$_3$, 22 times less expensive than $HfCl_4$•2THF, 23 times less expensive than $ZrCl_4$•2THF, and 3~13 times less expensive than $Zn(OCOCF_3)_2 \cdot xH_2O$, which are not available in bulk quantities. Remarkably, $La(NO_3)_3 \cdot 6H_2O$ is much less toxic than Hf(IV) (2 times), Zr(IV) (3 times), Zn(II) (13 times), CF_3CO_2H (23 times), Sn(IV) (100 times), and Sb(III) (<225 times), which are well-known esterification catalysts.

Table S4. *Price list of metal salt catalysts and their toxicity*

Aldrich, 2010

Item	Avail. Max. Size	Price (dollar; $; USD)	Comparison (per gram)
$HfCl_4$•2THF	10 g	89.40	22.4
$ZrCl_4$•2THF	5 g	45.70	22.9
$Zn(OCOCF_3)_2$•xH_2O	5 g	26.00	13.0
La(O*i*-Pr)$_3$ (98% purity)	3 g	232.50	194.3
$La(OTf)_3$•xH_2O	25 g	35.60	3.6
$La(NO_3)_3$•$6H_2O$ (99.99% purity)	500 g	367.00	1.8
$La(NO_3)_3$•xH_2O (99.9% purity)	500 g	199.50	1 (standard)

Alfa Aesar, 2010

Item	Avail. Max. Size	Price (pound; £; GBP)	Comparison (per gram)
$Zn(OCOCF_3)_2 \cdot xH_2O$	250 g	109.00	3.1
$La(O\textit{i}\text{-}Pr)_3$ (98% purity)	10 g	208.00	147.3
$La(OTf)_3 \cdot xH_2O$	25 g	114.90	32.5
$La(NO_3)_3 \cdot 6H_2O$ (99.9% purity)	500 g	70.6	1 (standard)

Spectrum Chemical Manufacturing Corp., 2011

Item	Avail. Max. Size	Price (dollar; $; USD)	Comparison (per gram)
$Zn(OCOCF_3)_2 \cdot xH_2O$	n.a.	–	–
$La(O\textit{i}\text{-}Pr)_3$	n.a.	–	–
$La(OTf)_3 \cdot xH_2O$[1)]	25 g	200	65.5
$La(NO_3)_3 \cdot 6H_2O$ (99+% purity)	10 kg	1,222	1 (standard)

1) From TCI.

Wako Pure Chemical Industries, Ltd., 2010

Item	Avail. Max. Size	Price (yen; ¥; JPY)	Comparison (per gram)
$Zn(OCOCF_3)_2 \cdot xH_2O$[1)]	100 g	48,600	10
$La(O\textit{i}\text{-}Pr)_3$ (98% purity)	1 g	15,000	294
$La(OTf)_3 \cdot xH_2O$	25 g	20,000	15.7
$La(NO_3)_3 \cdot 6H_2O$ (99+% purity)[2)]	1,000 g	51,100	1 (standard)

1) From Alfa Aesar. 2) From Chempur Feinchemikalien und Forschungsbedarf GmbH.

Toxicity

Item	LD_{50} (oral, rat) (mg/kg)	Toxicity
$La(O\textit{i}\text{-}Pr)_3$	>10,000	0.45
$La(NO_3)_3$	4,500	1 (standard)
$HfCl_4$	2,400	2
$ZrCl_4$	1,688	3
$ZnCl_2$	350	13
CF_3CO_2H	200	23
Bu_2SnO	45	100
Sb_2O_3	>20	<225

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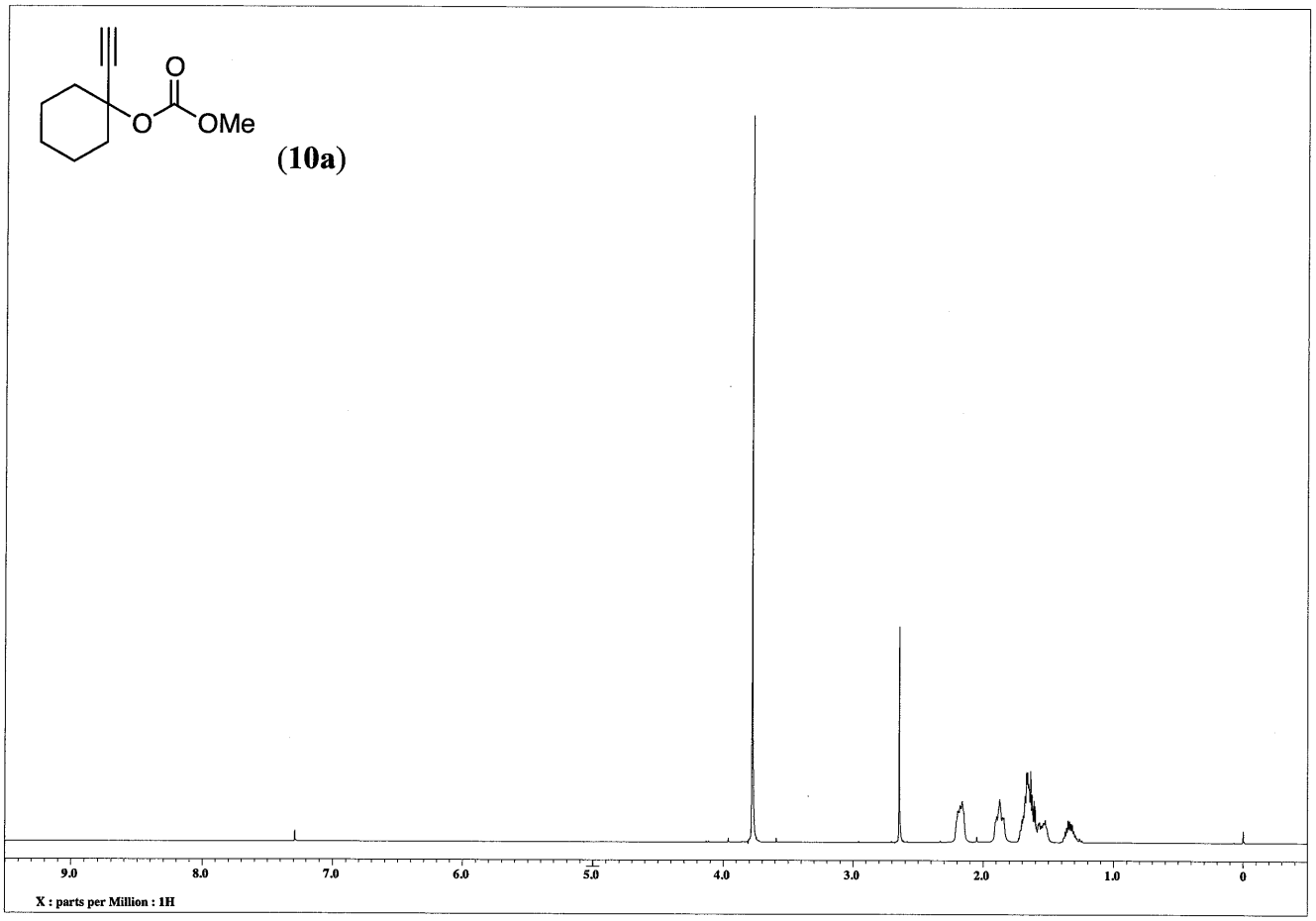
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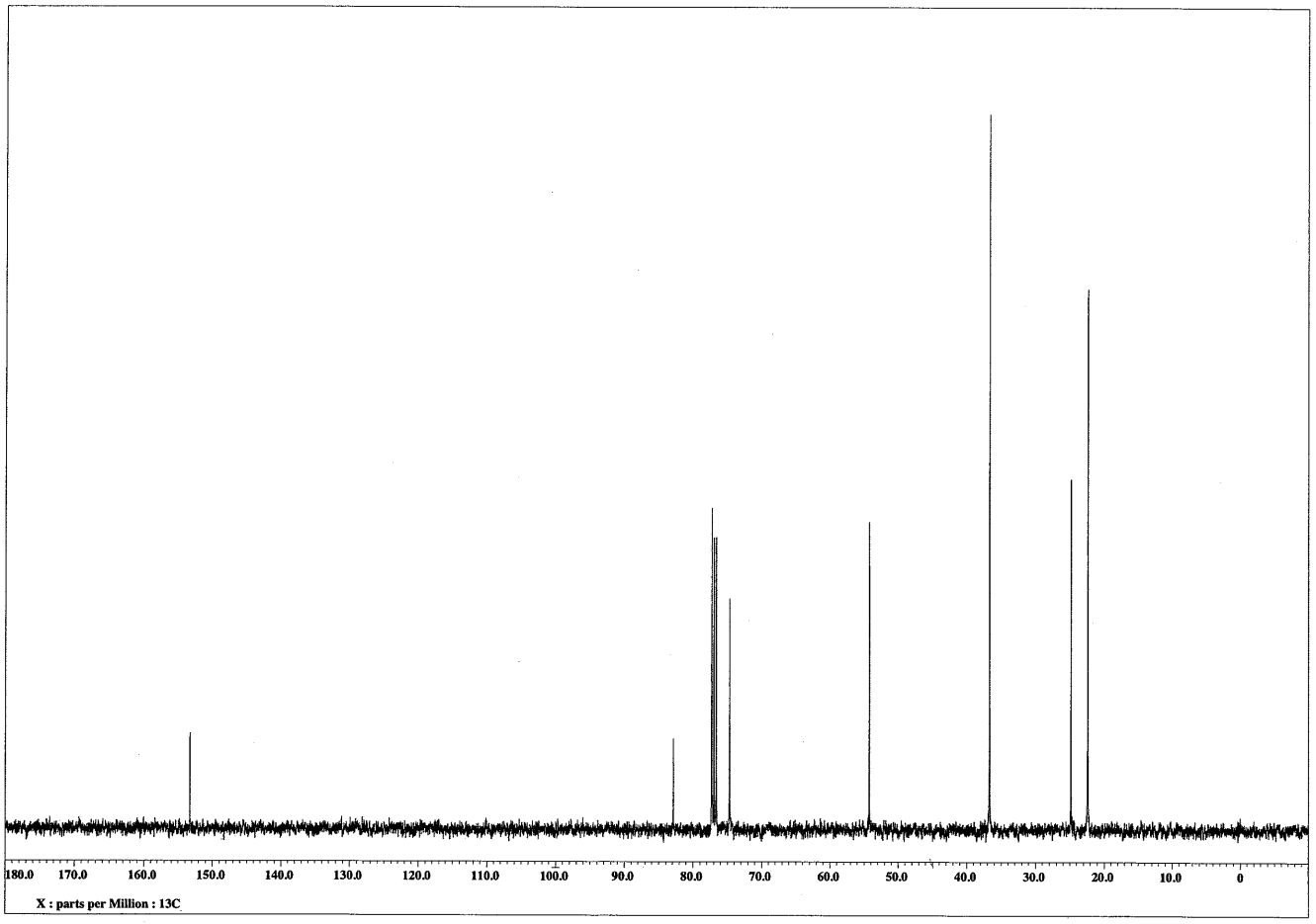
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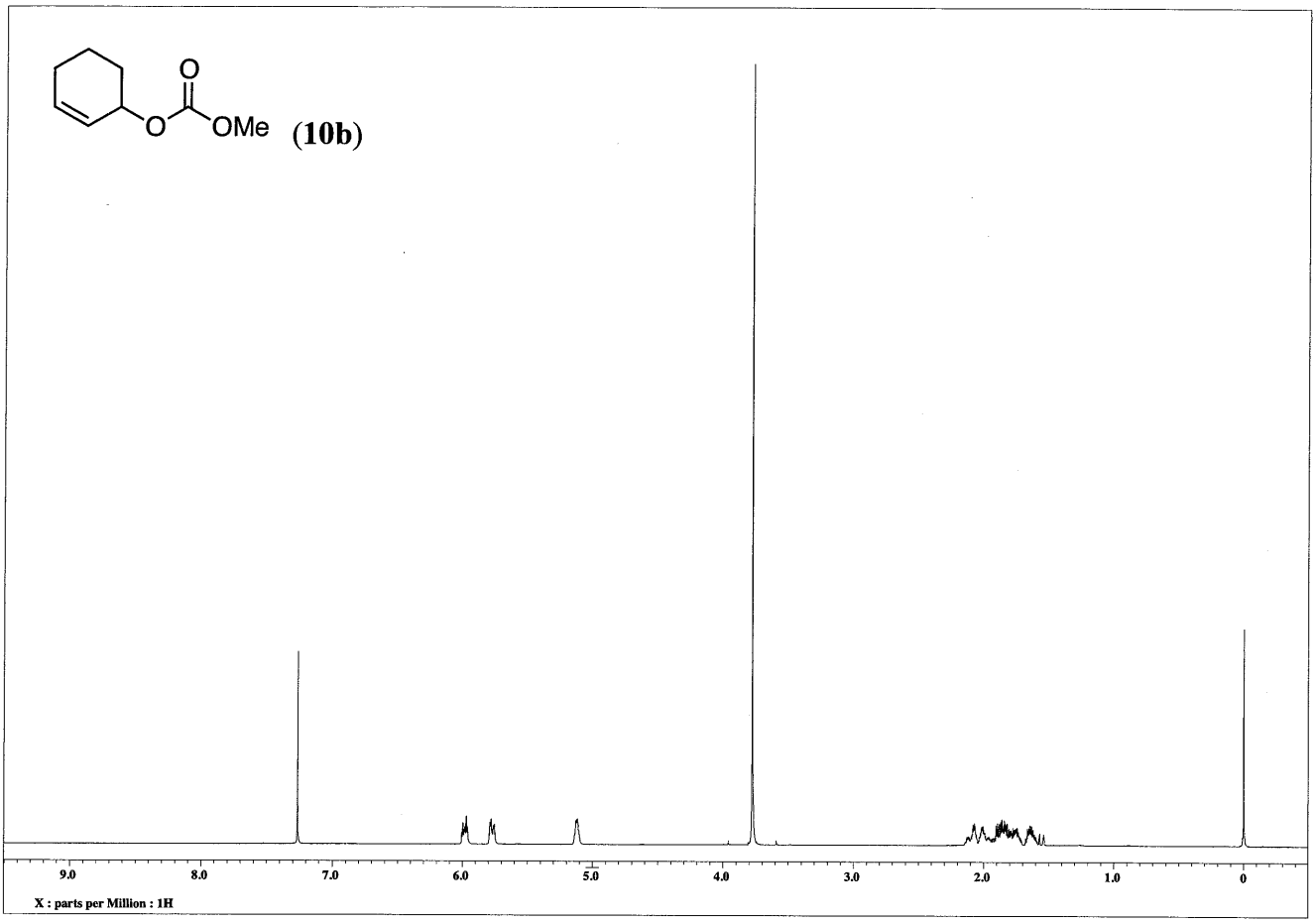
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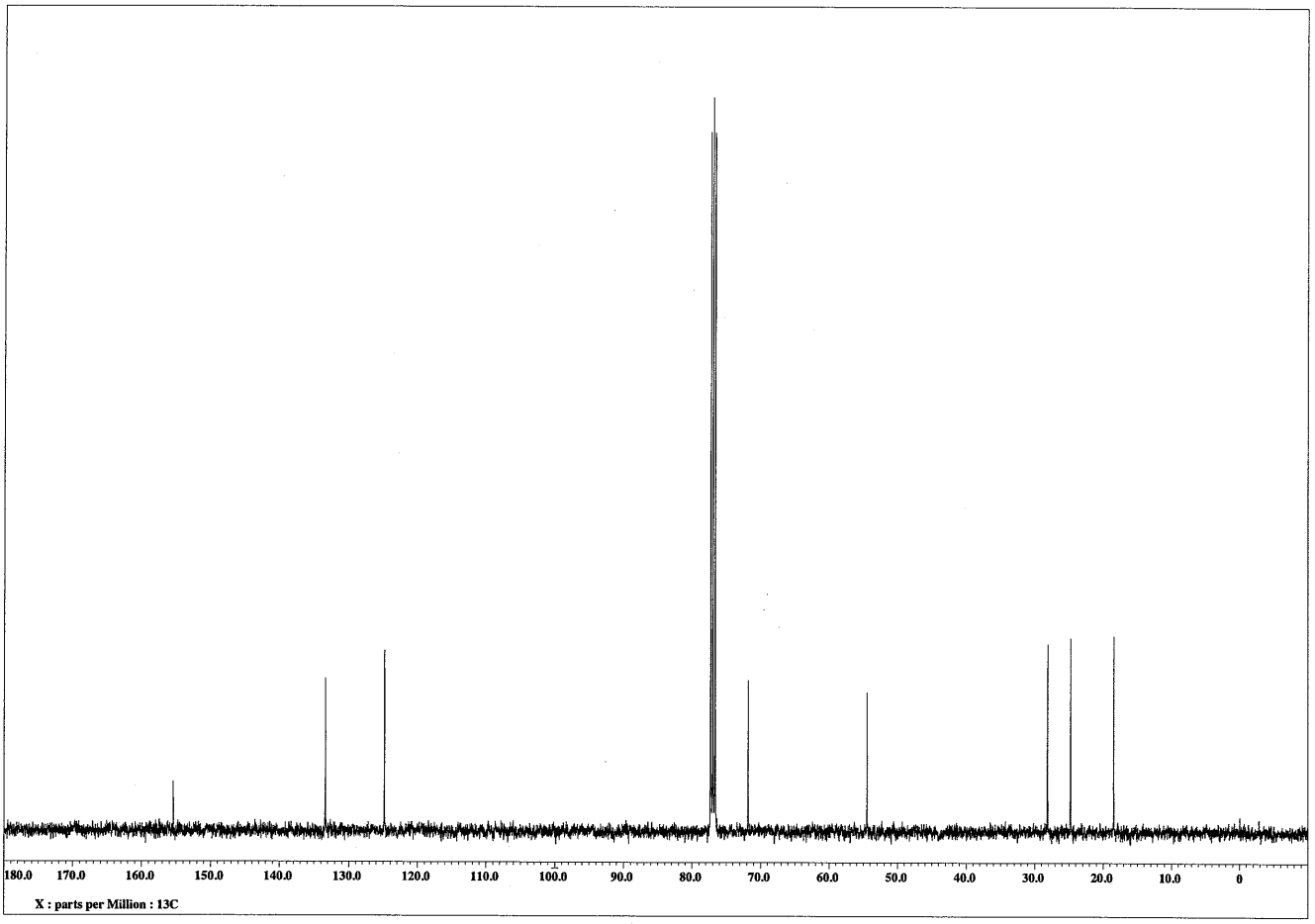
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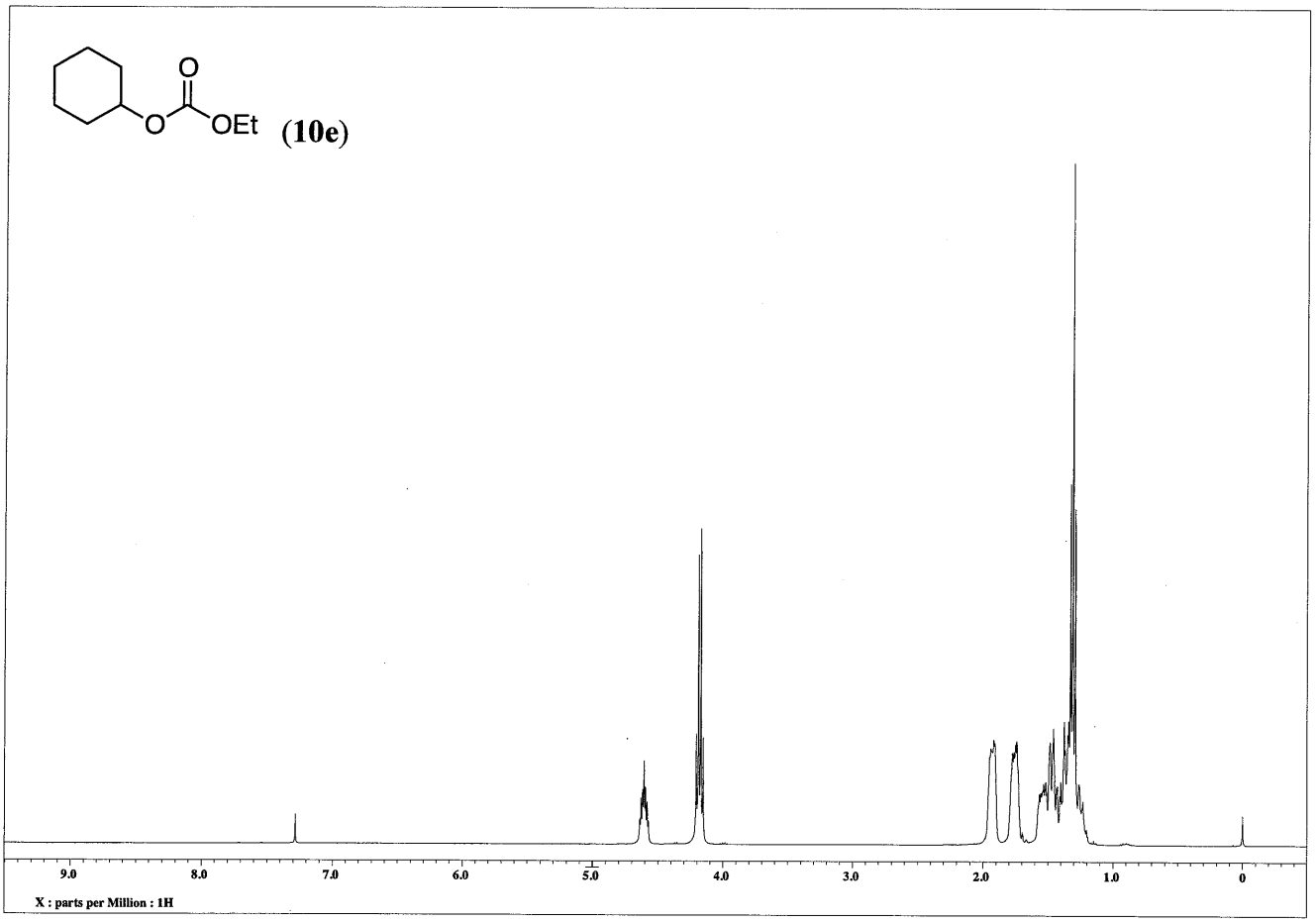
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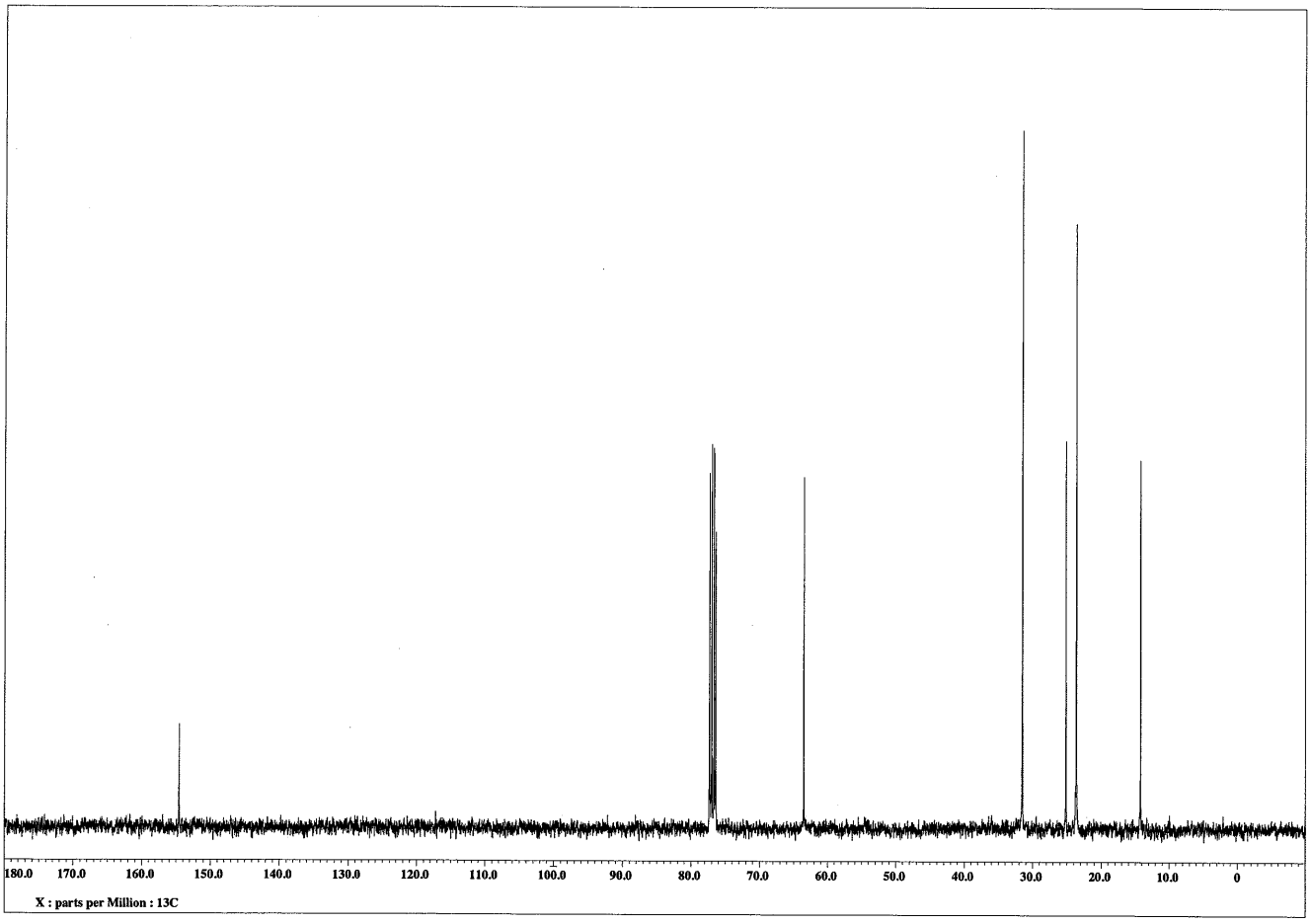
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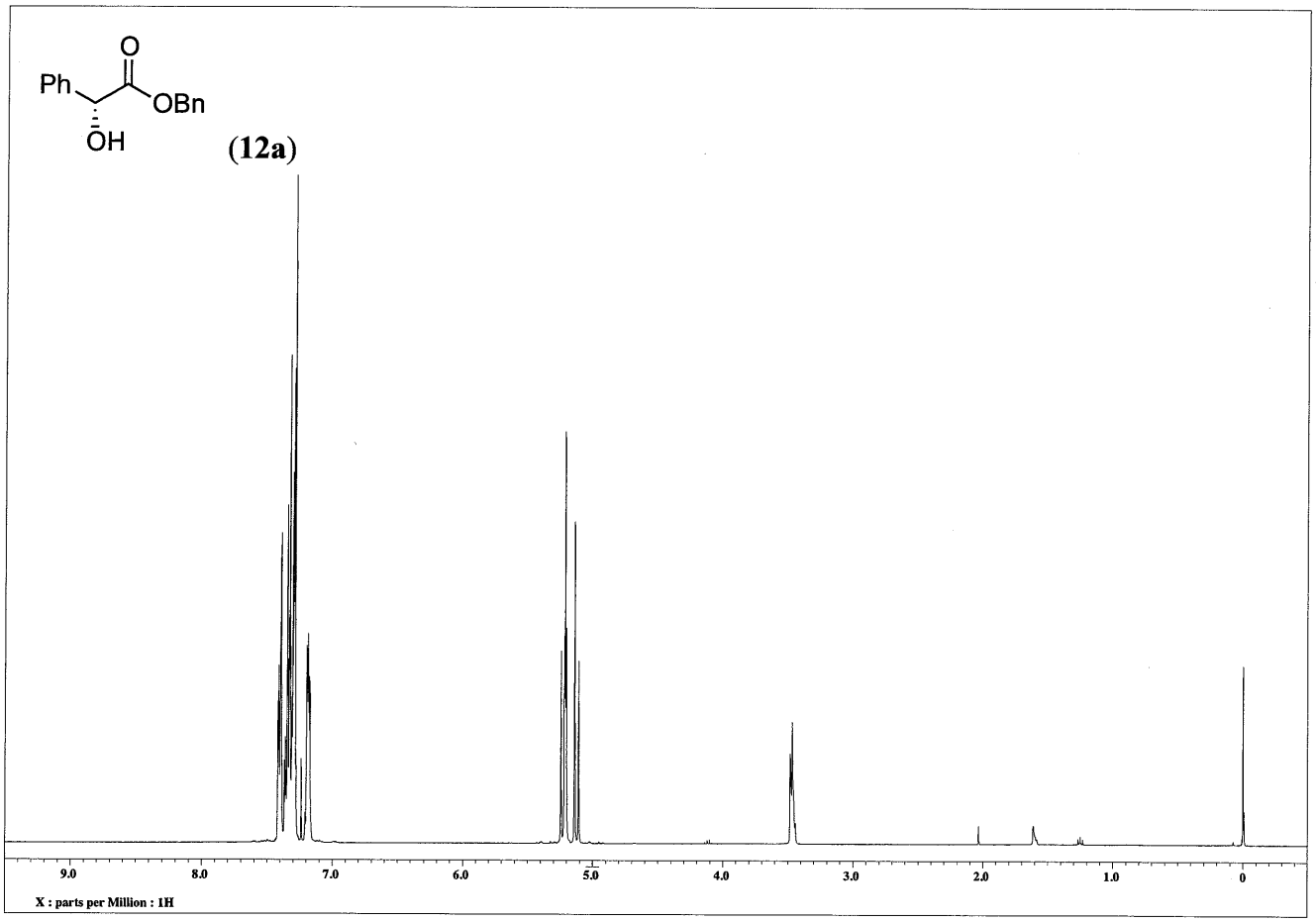
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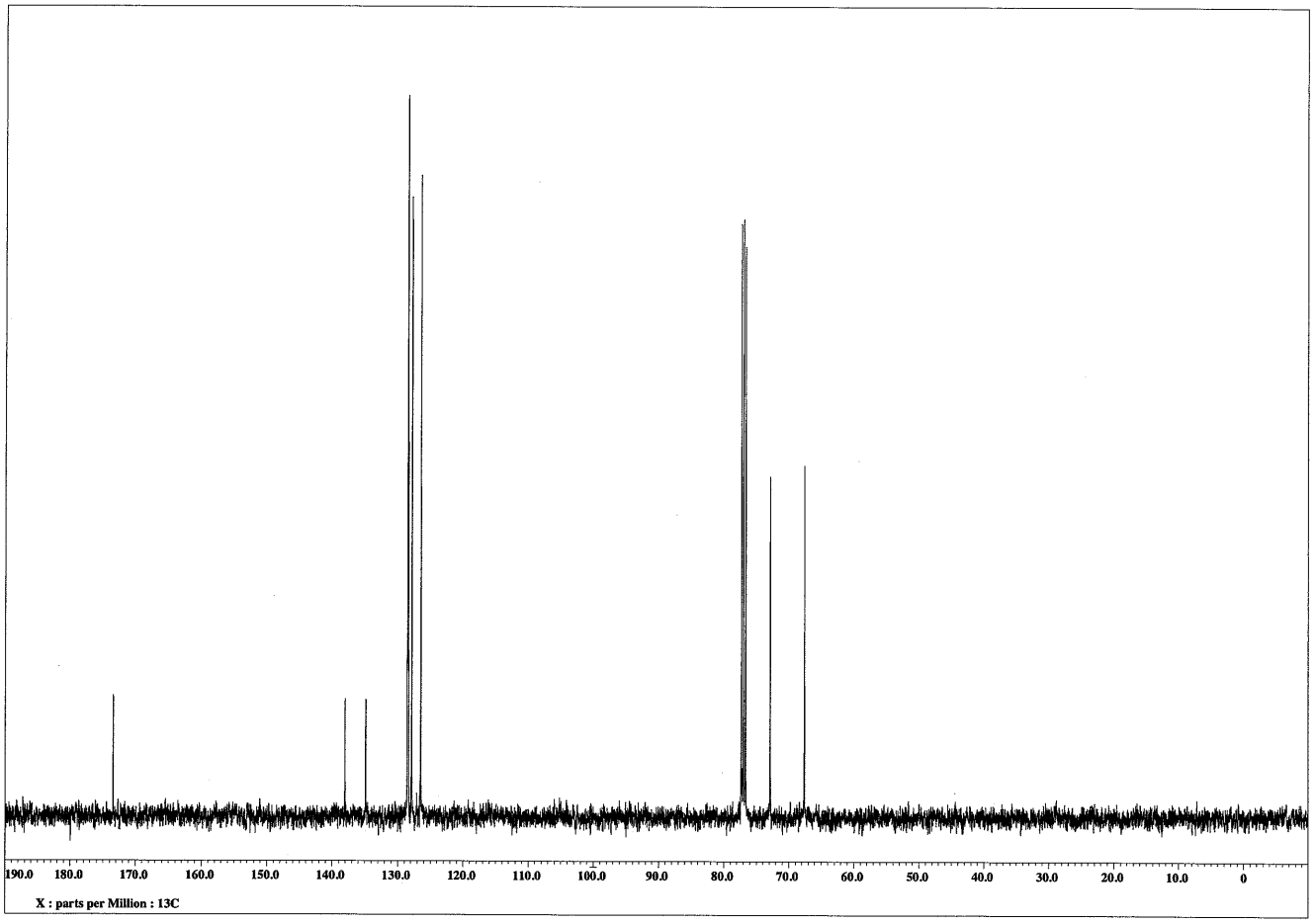
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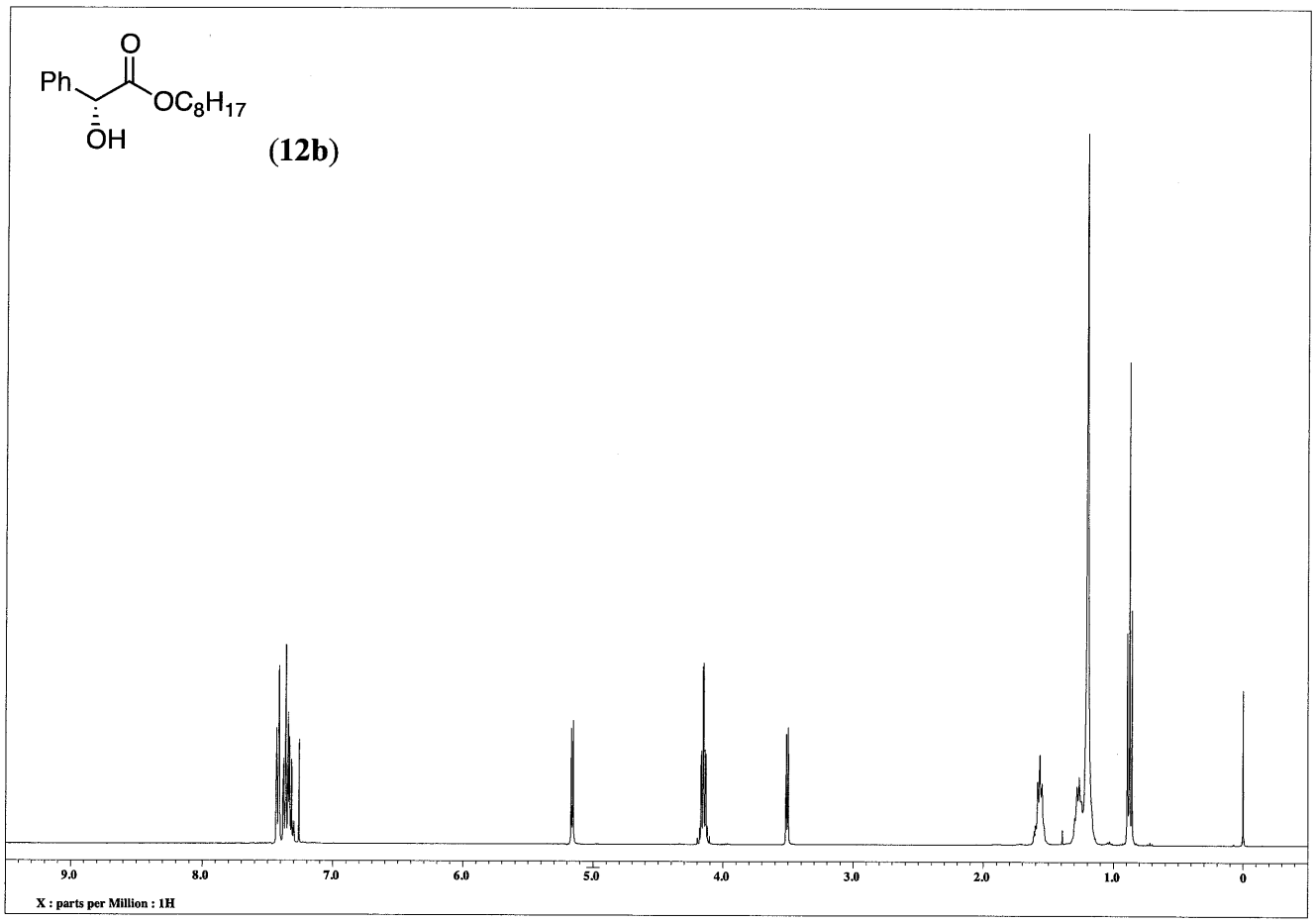
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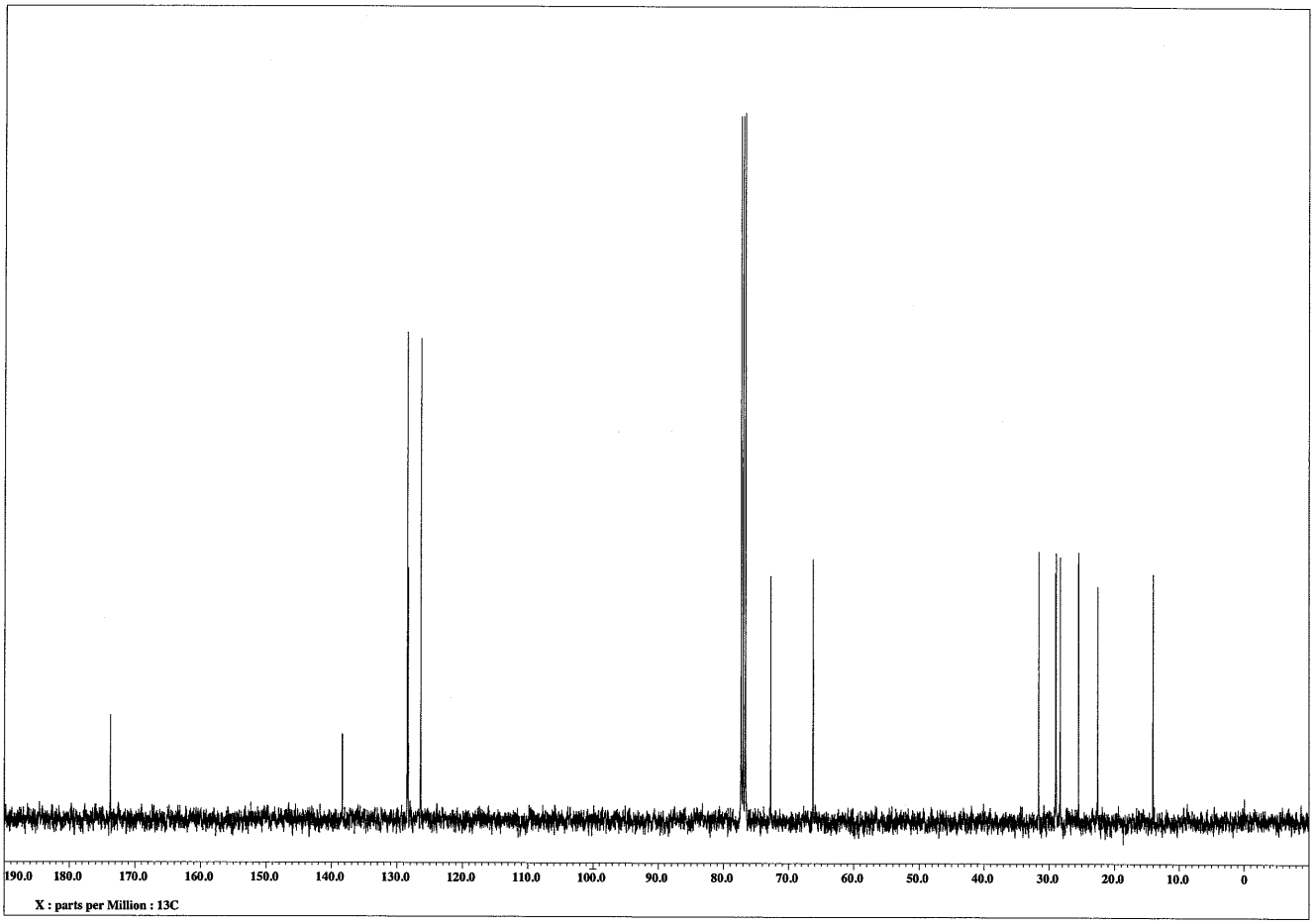
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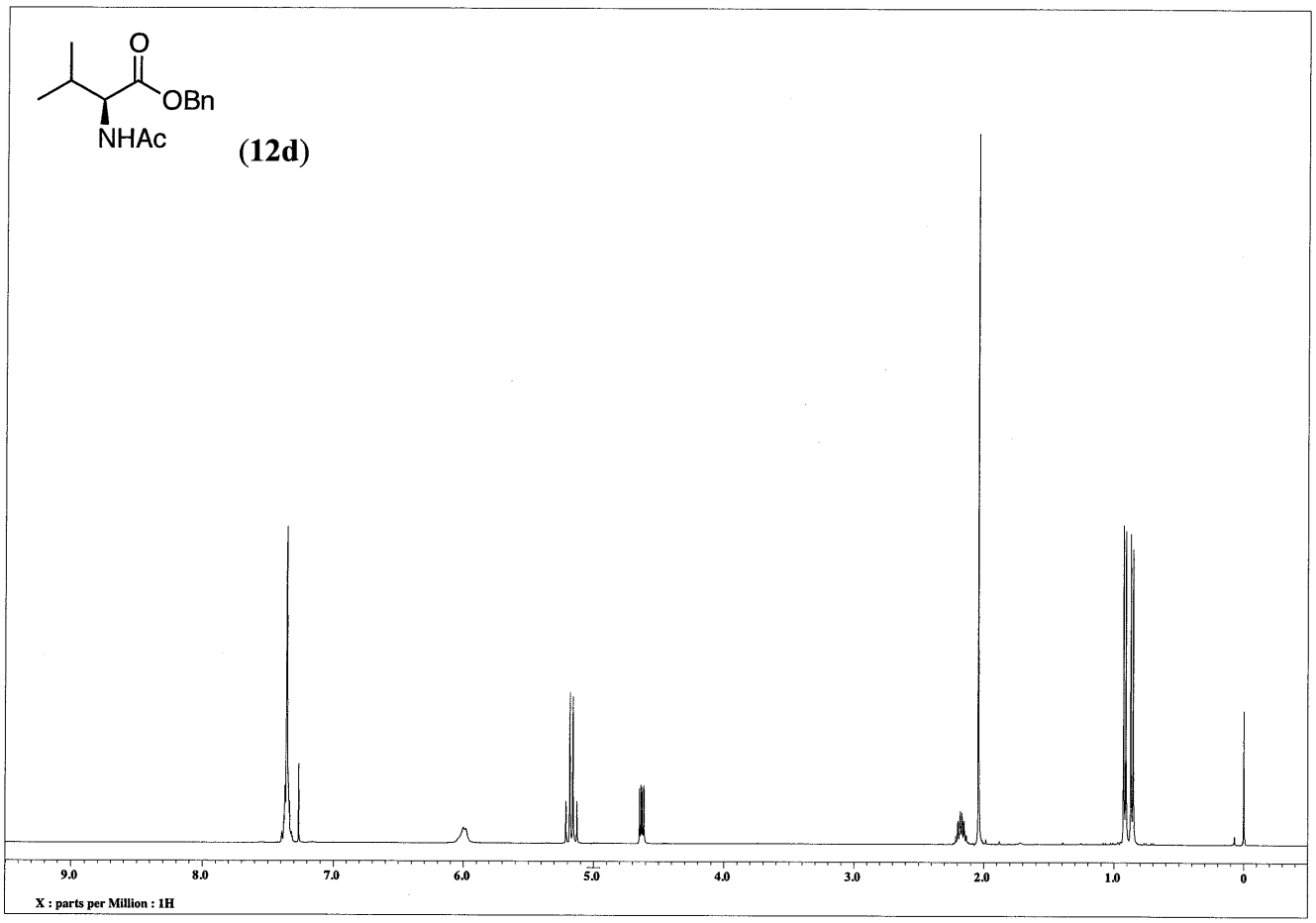

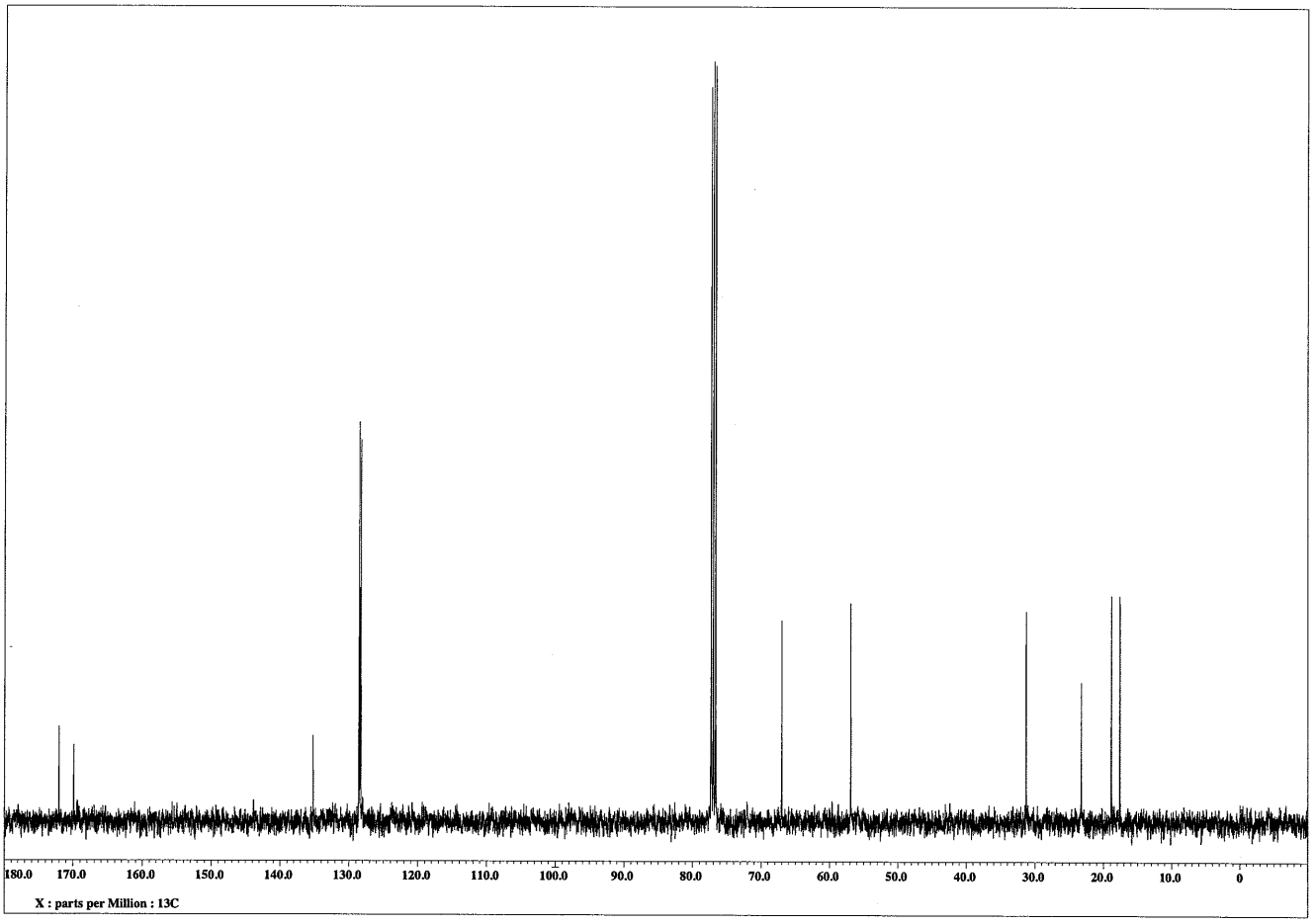

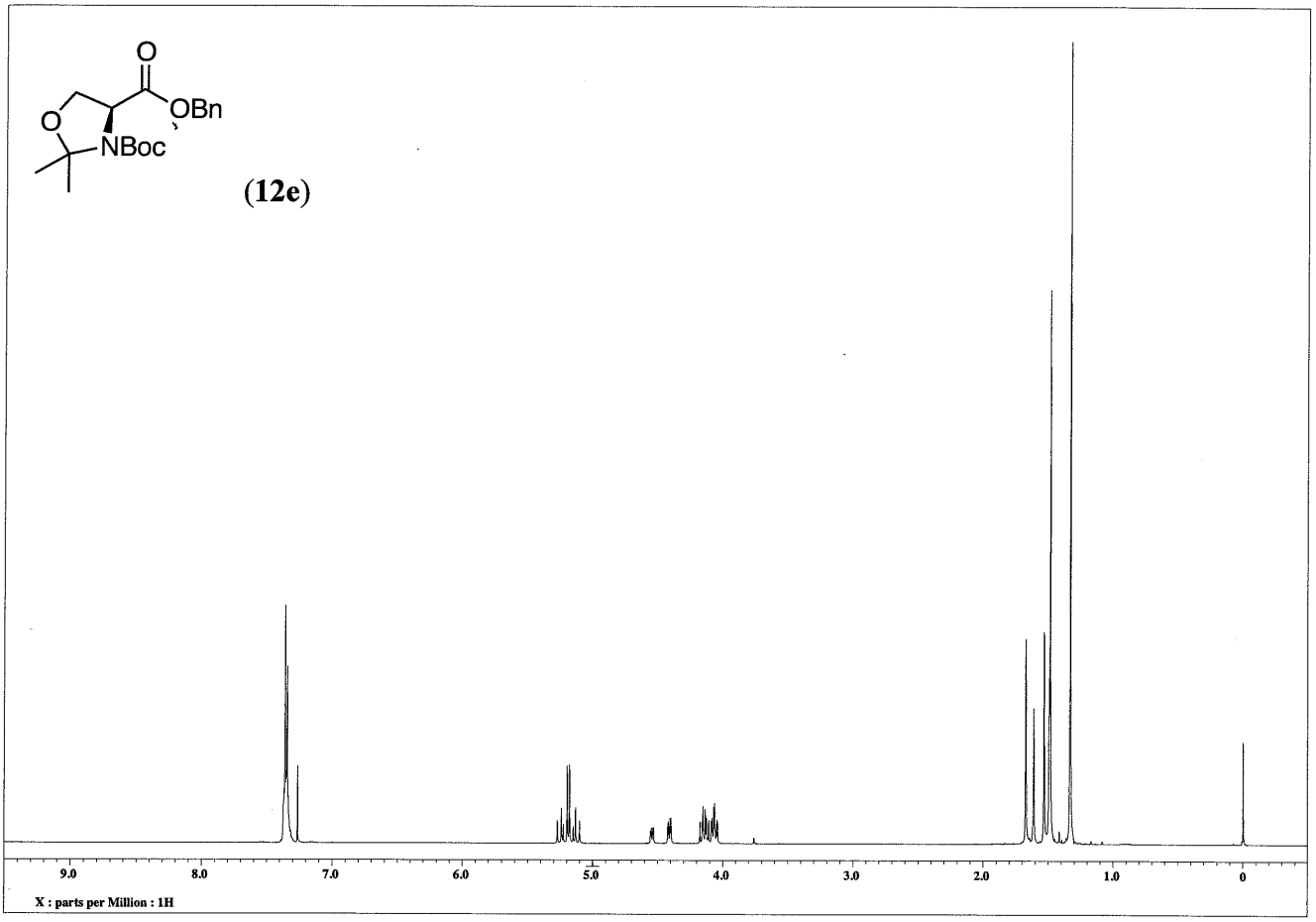
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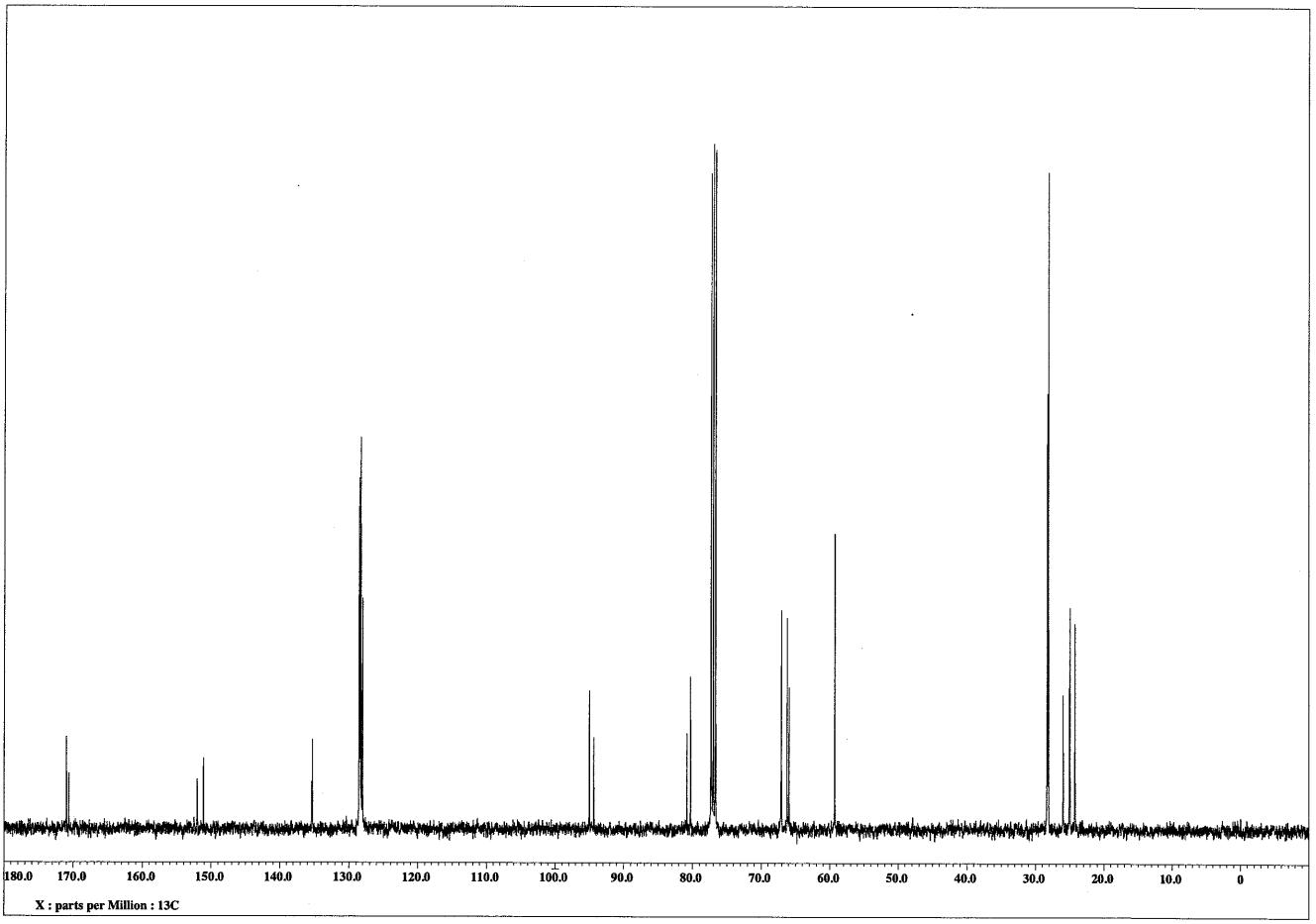
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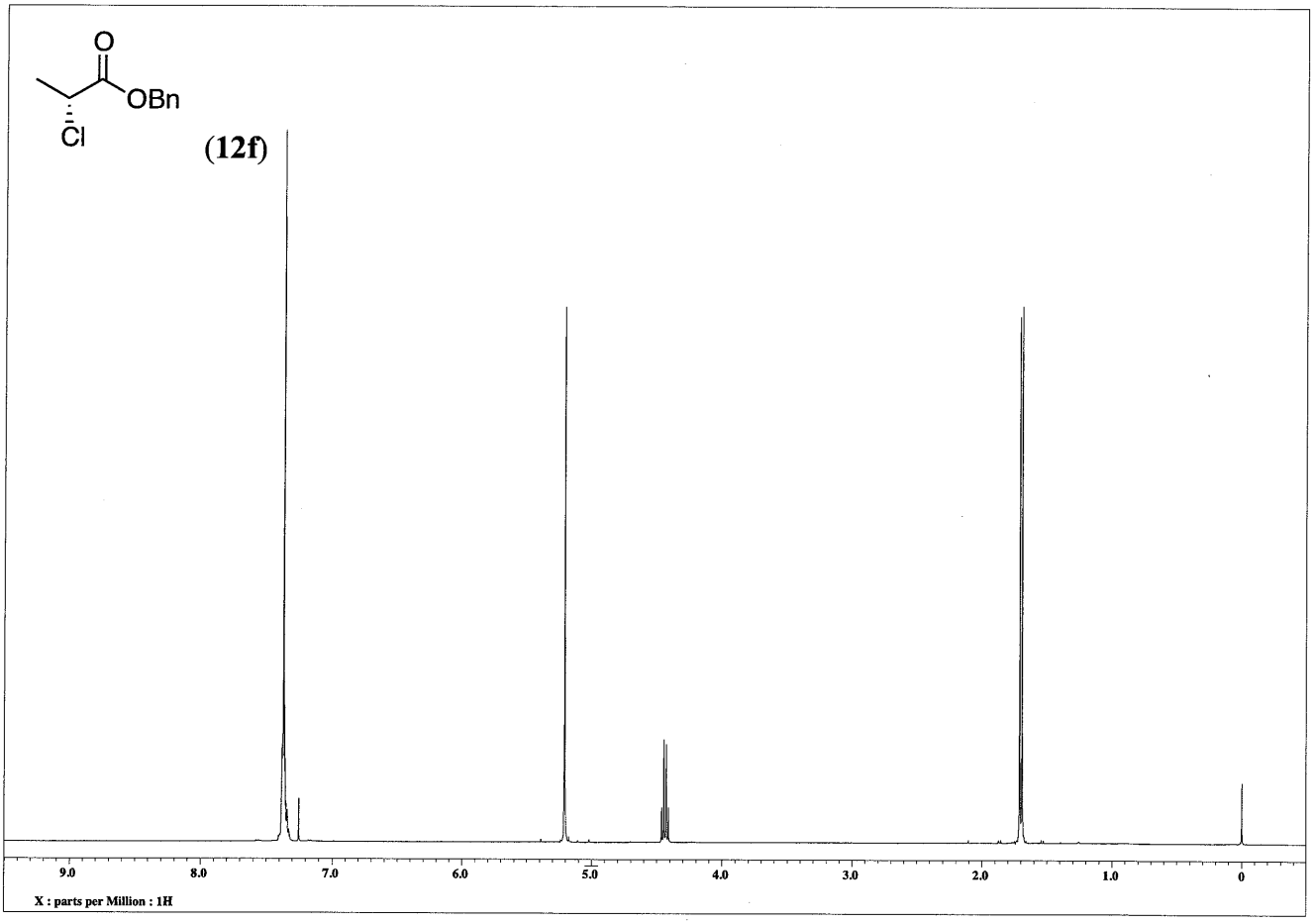
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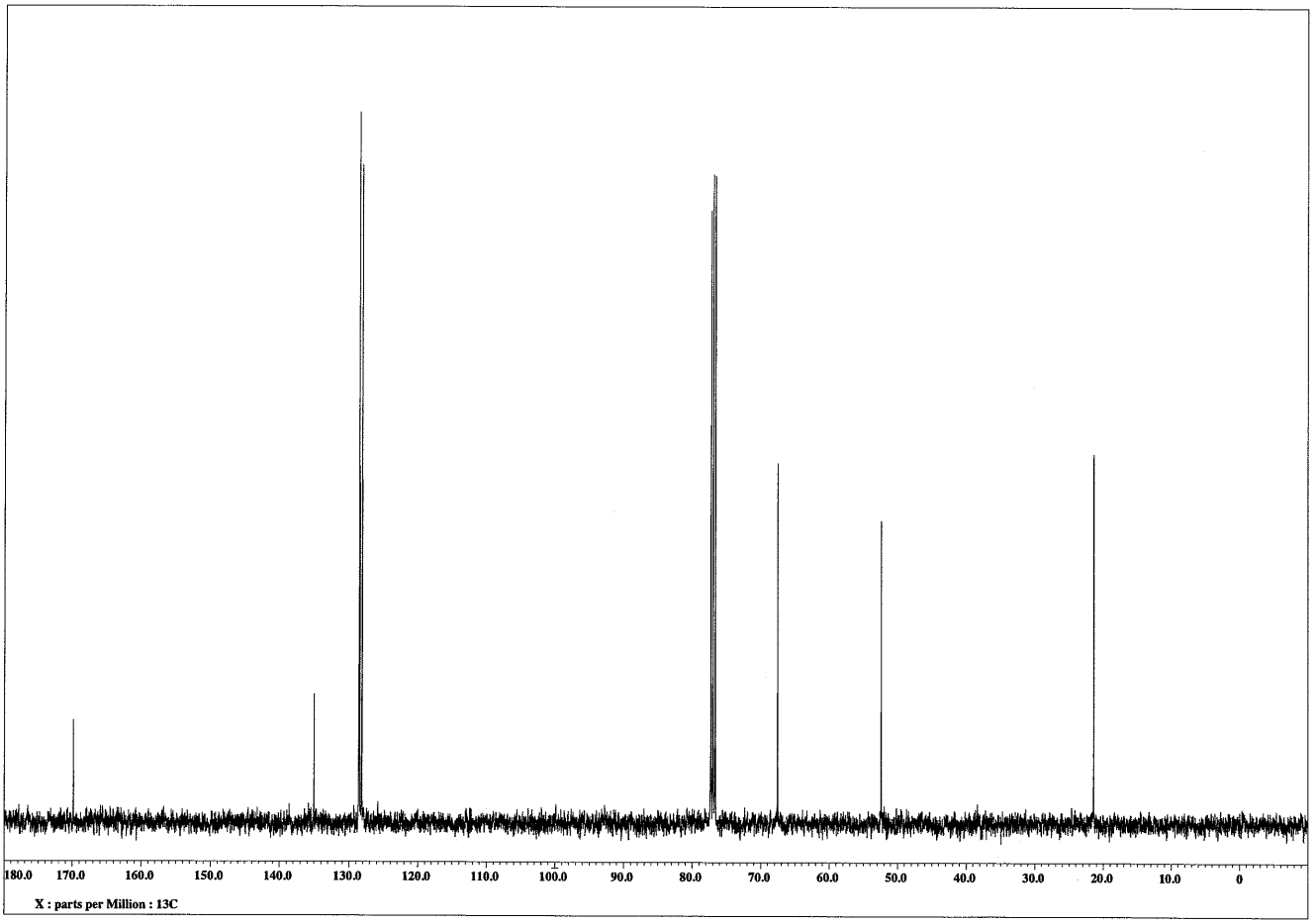
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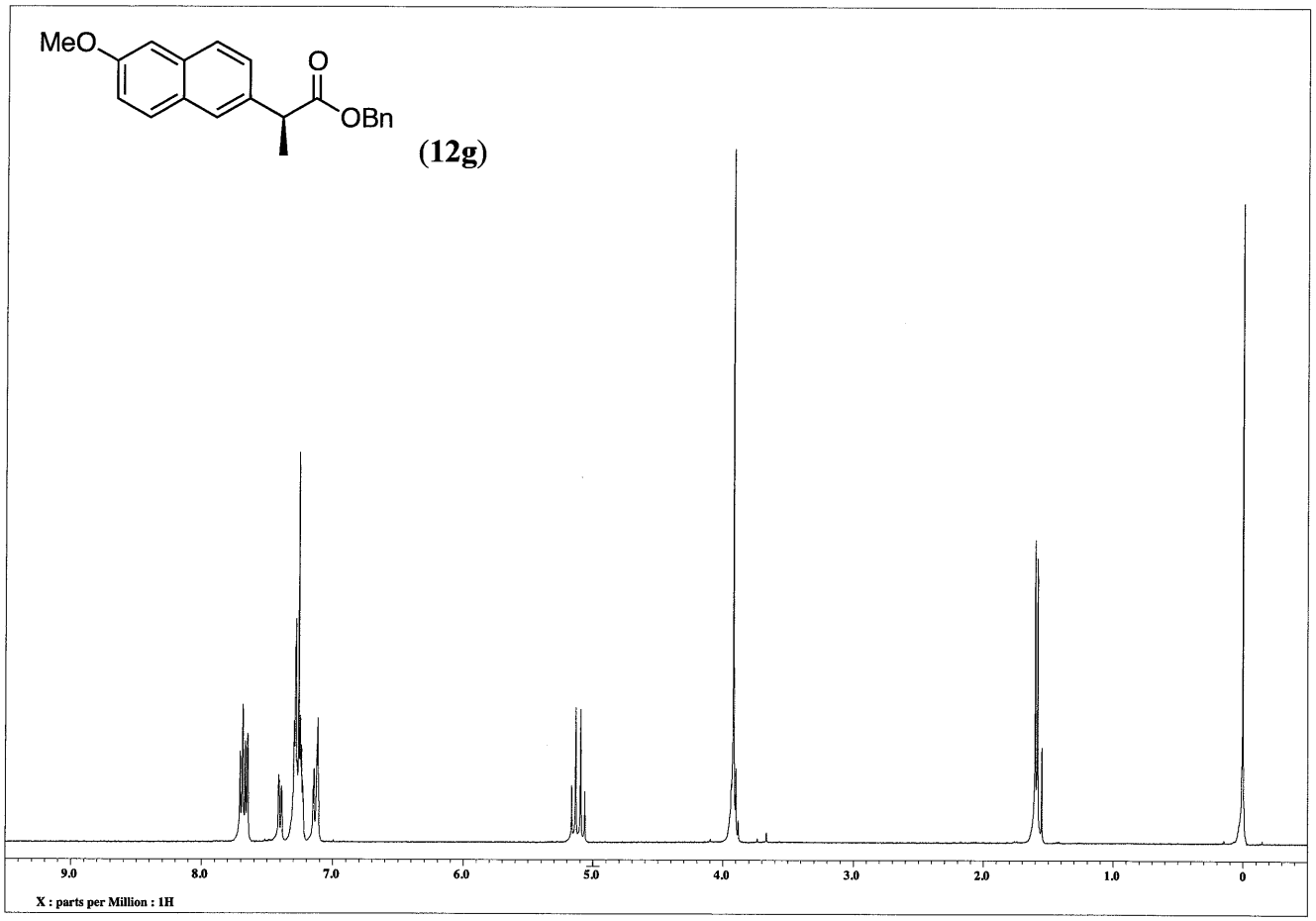
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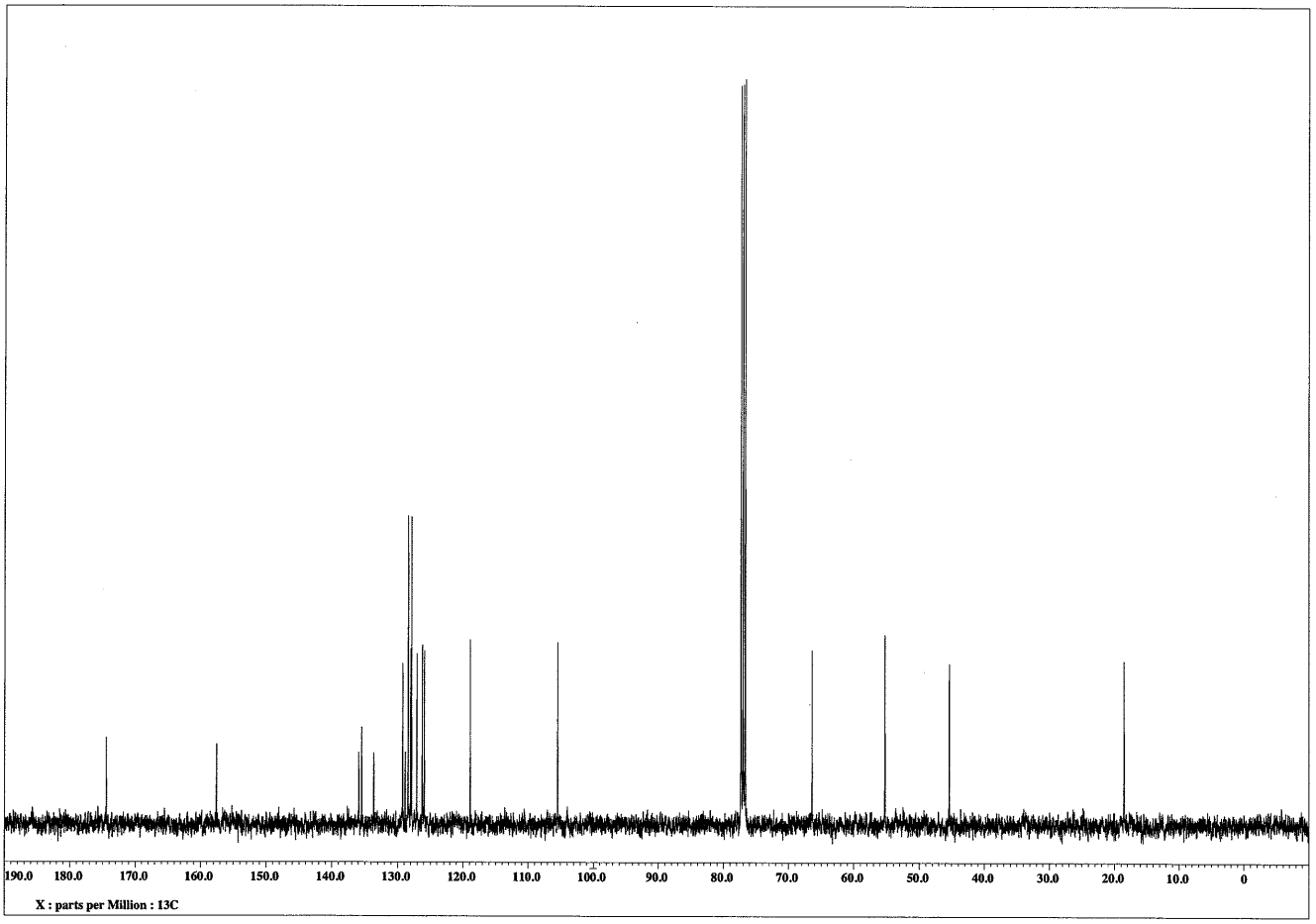
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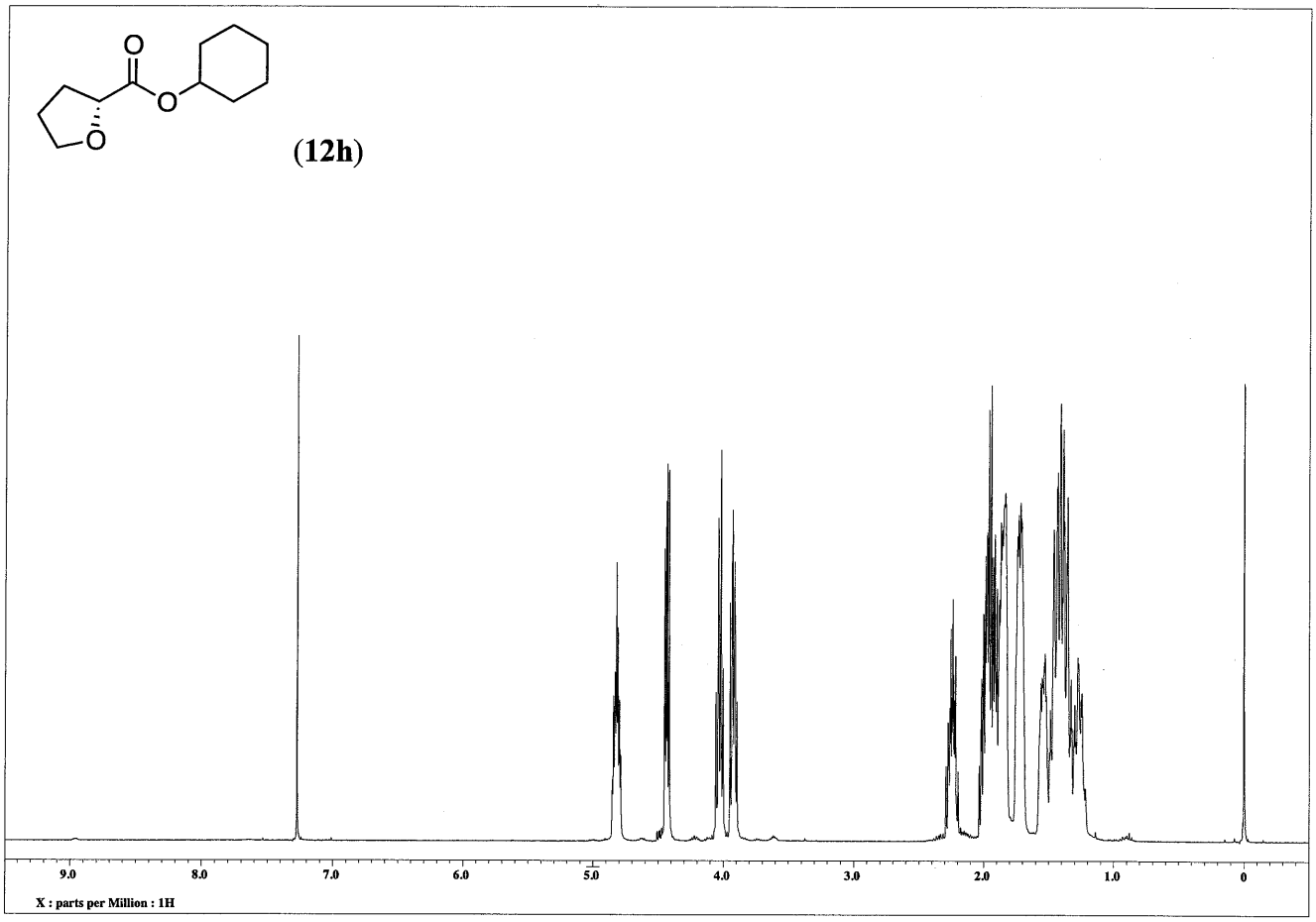
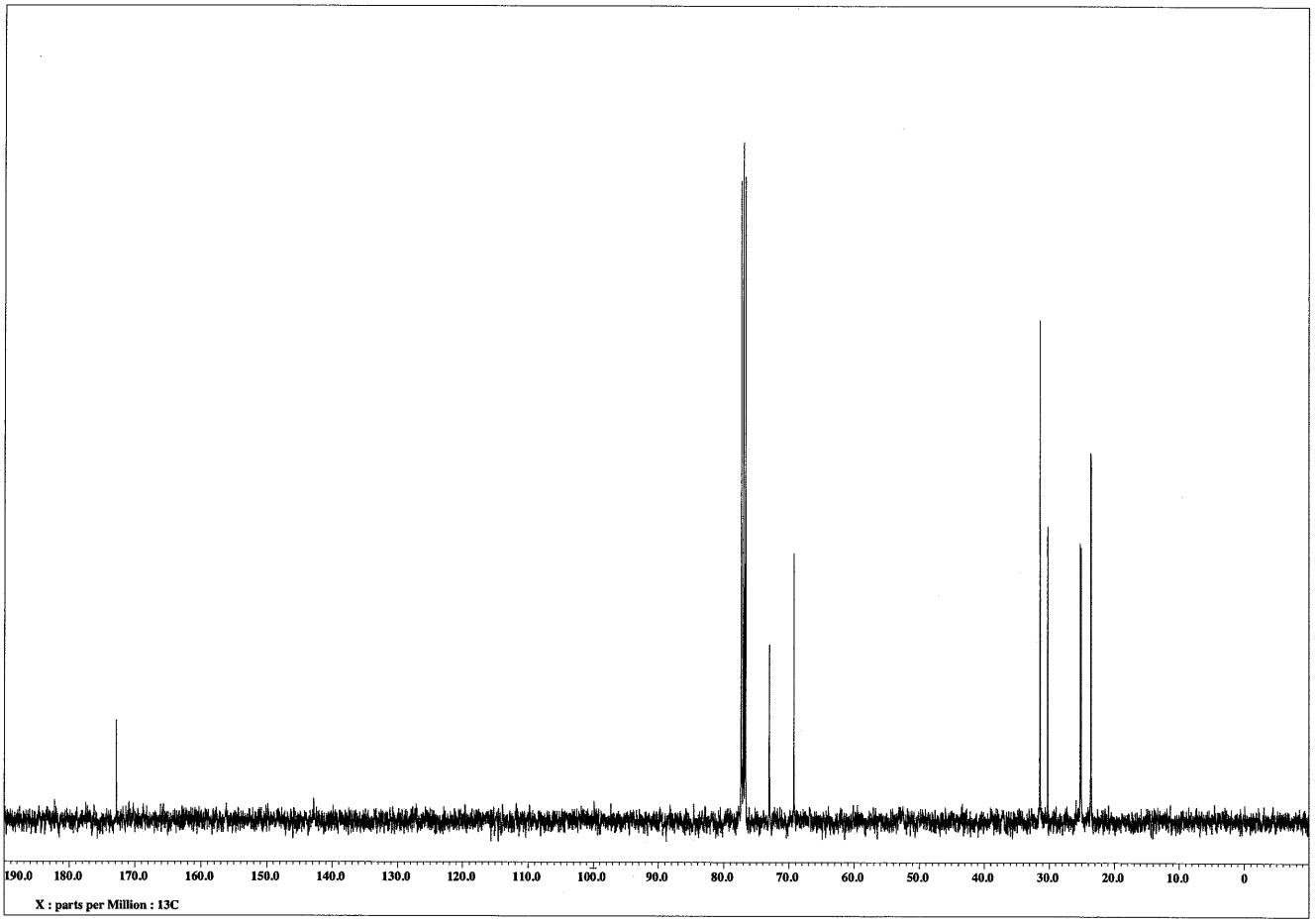
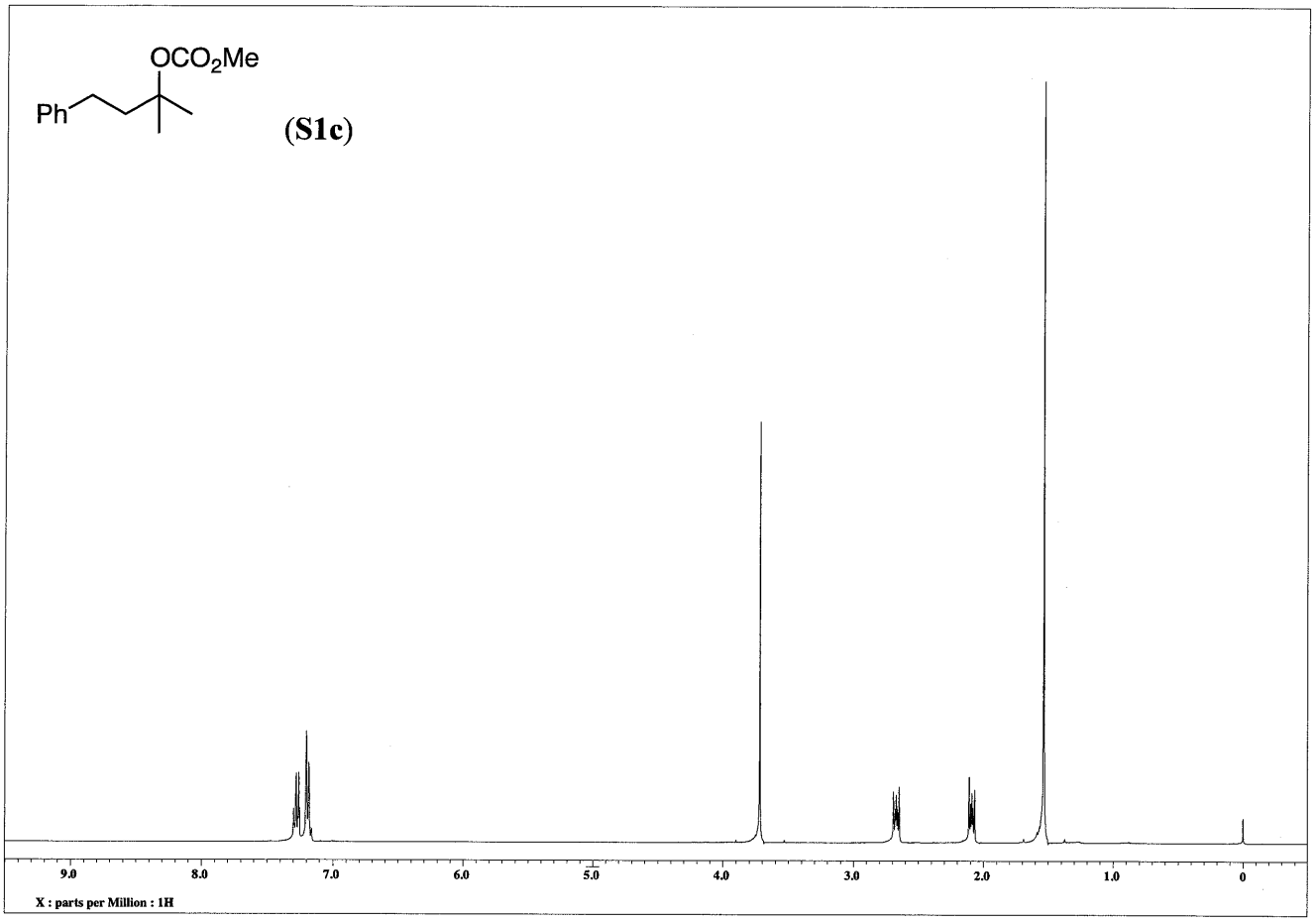
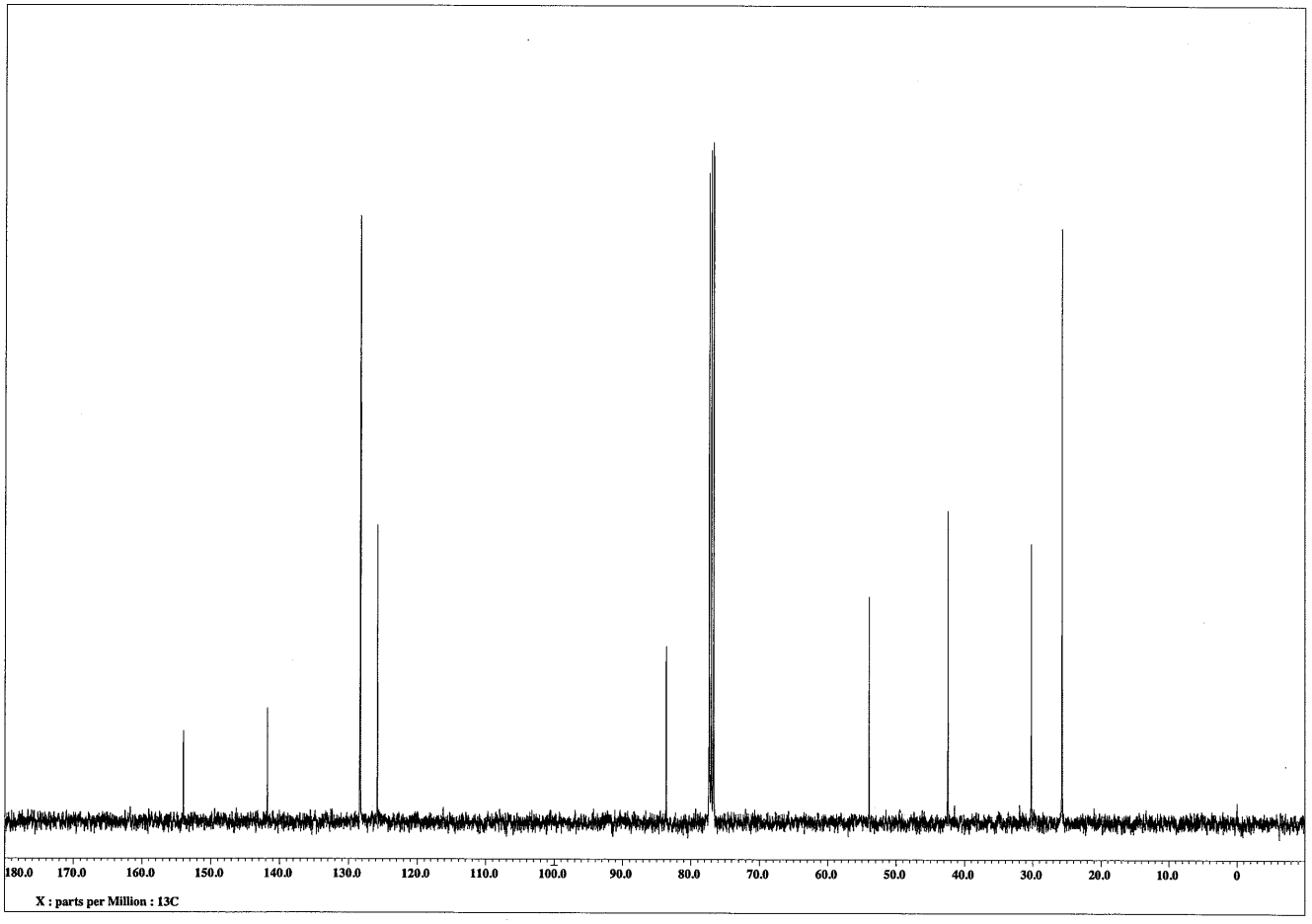
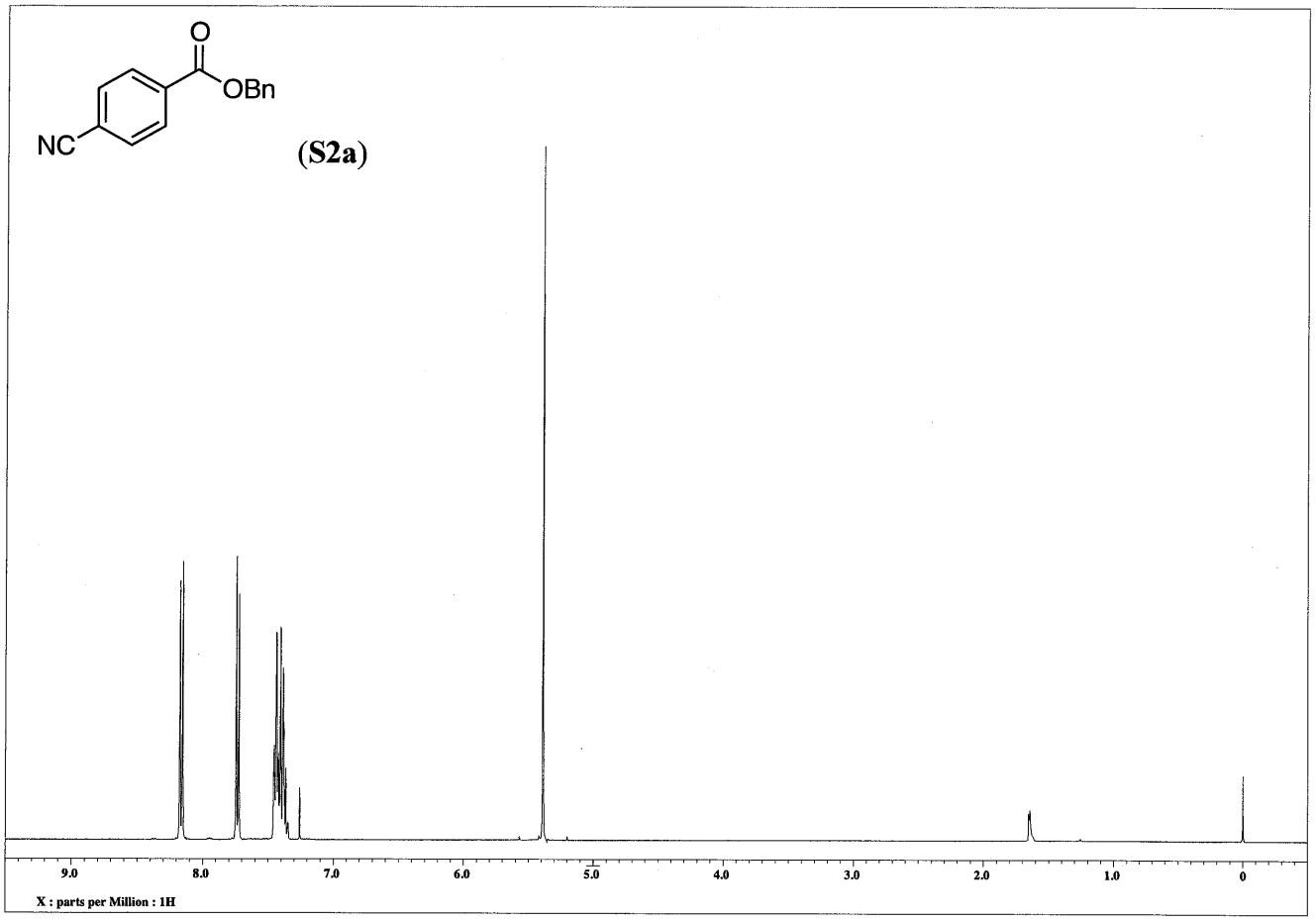
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

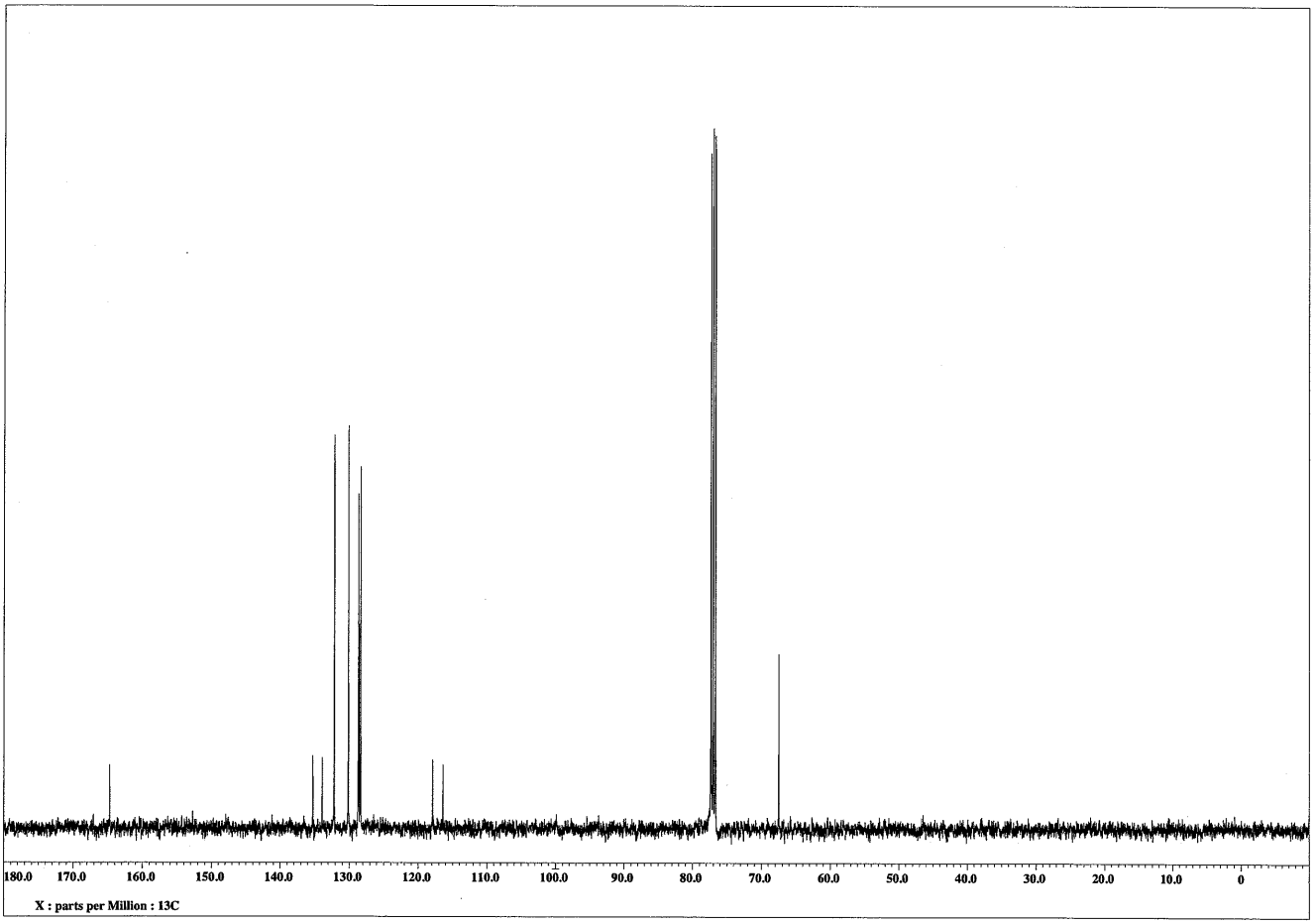

(12h)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

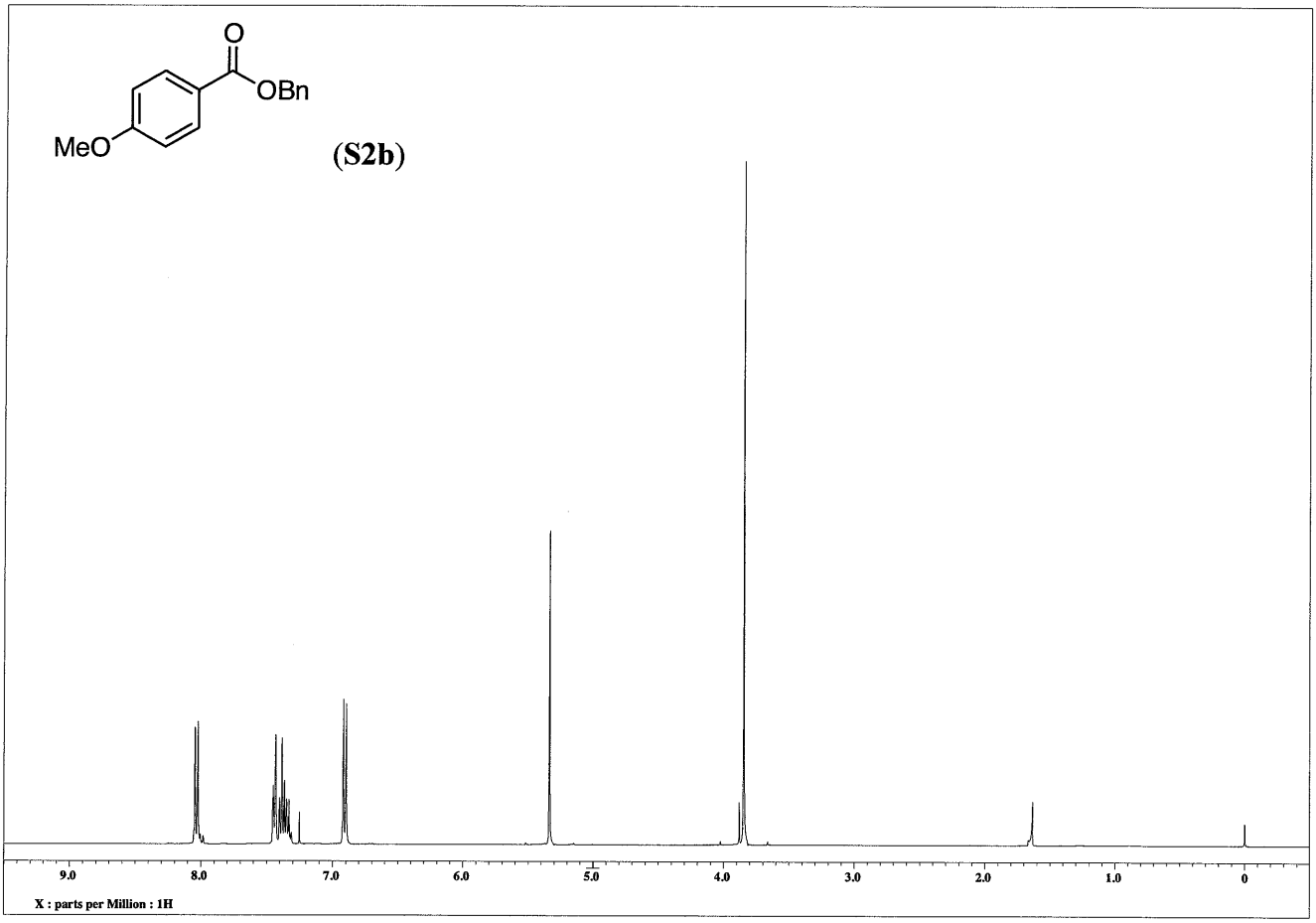

190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C



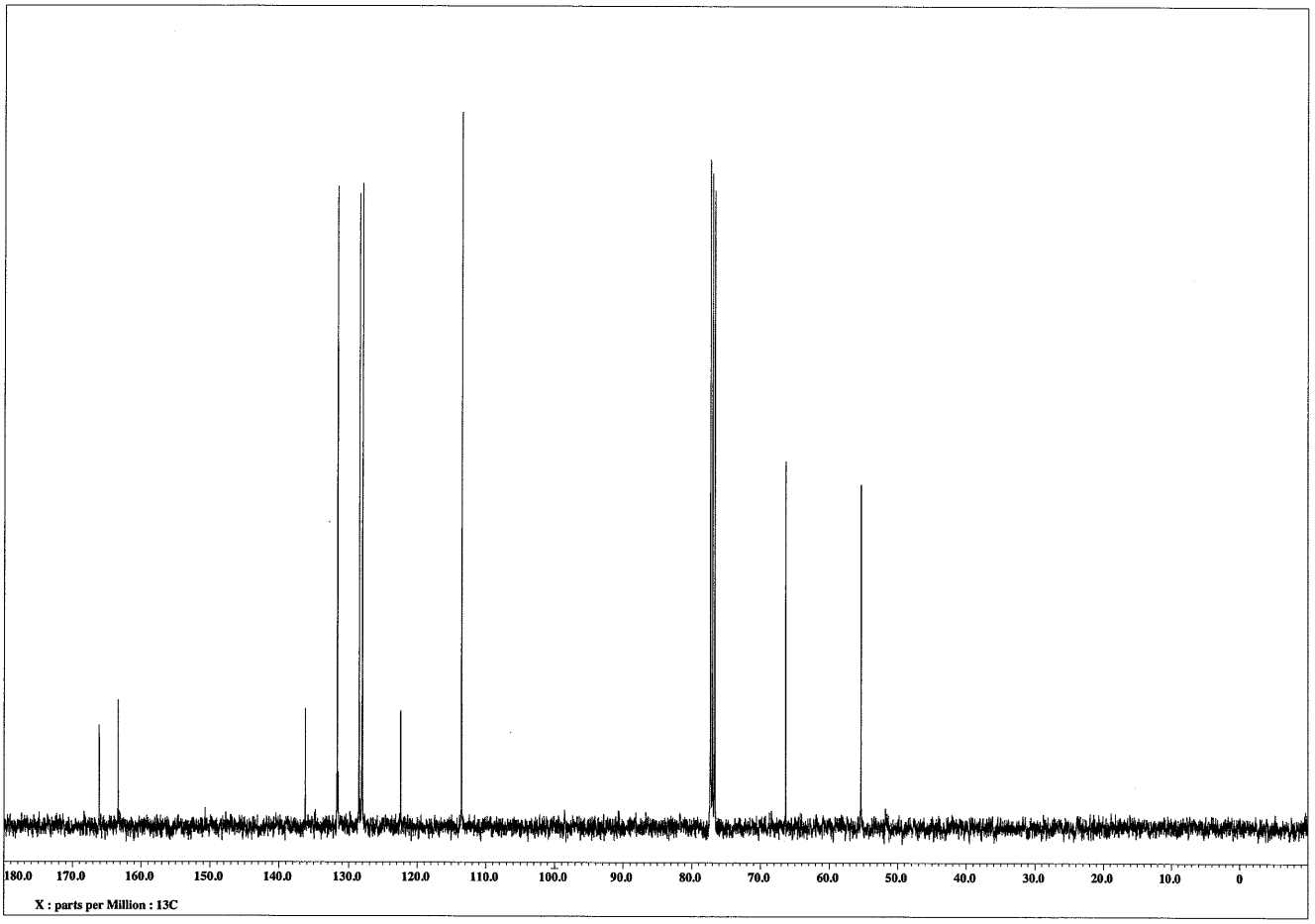


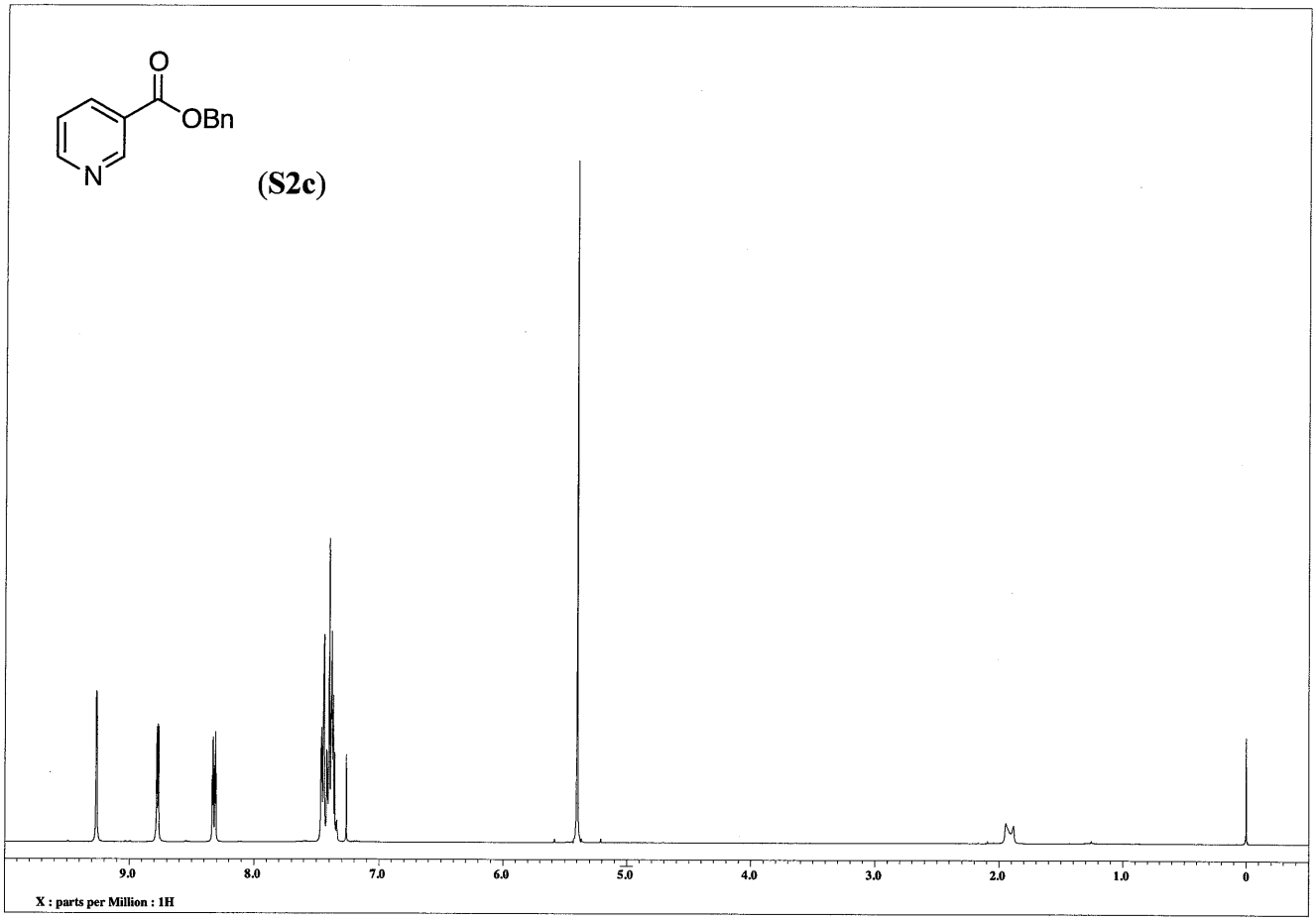

O
OBn
NC
(S2a)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

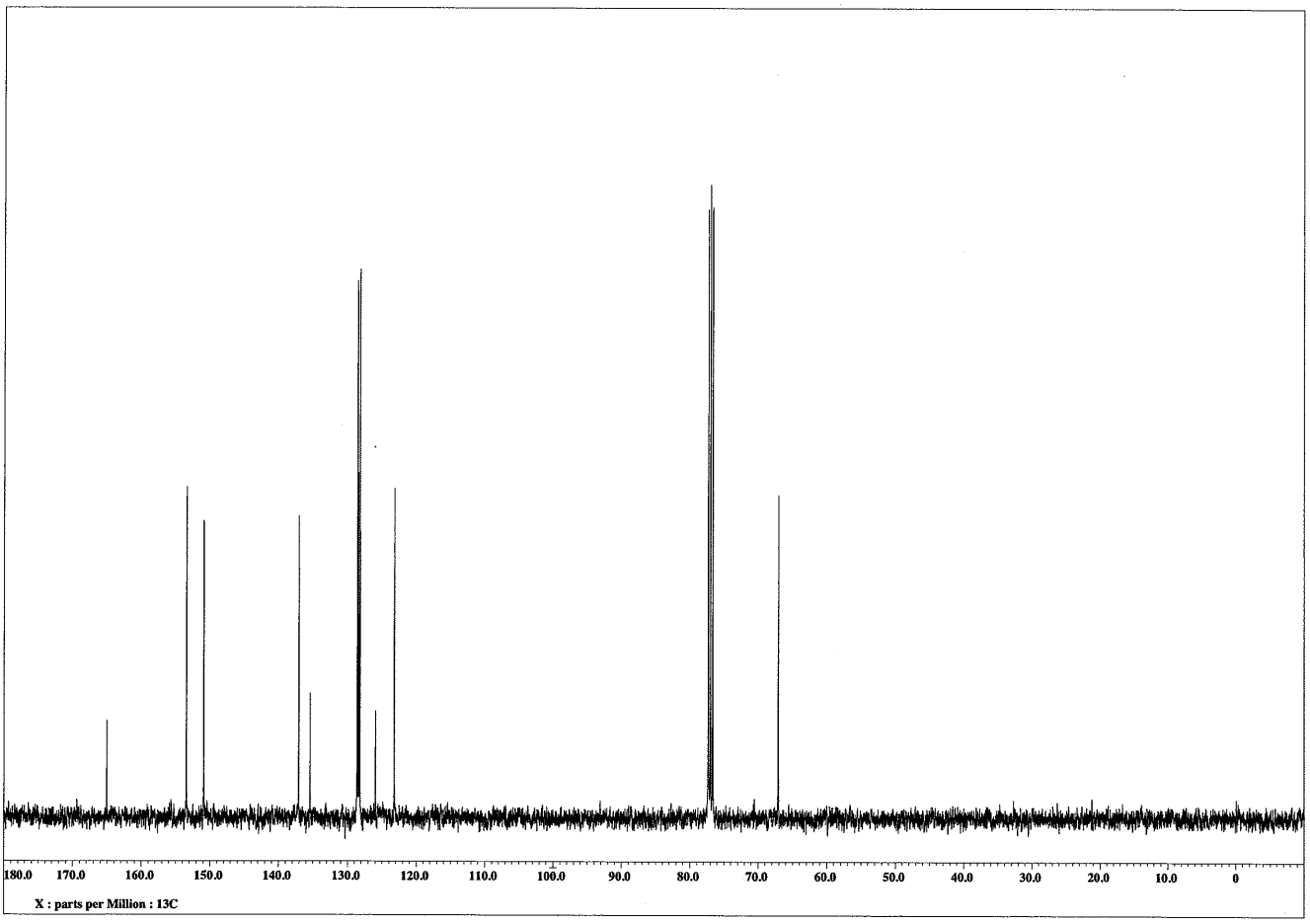

O
OBn
MeO
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

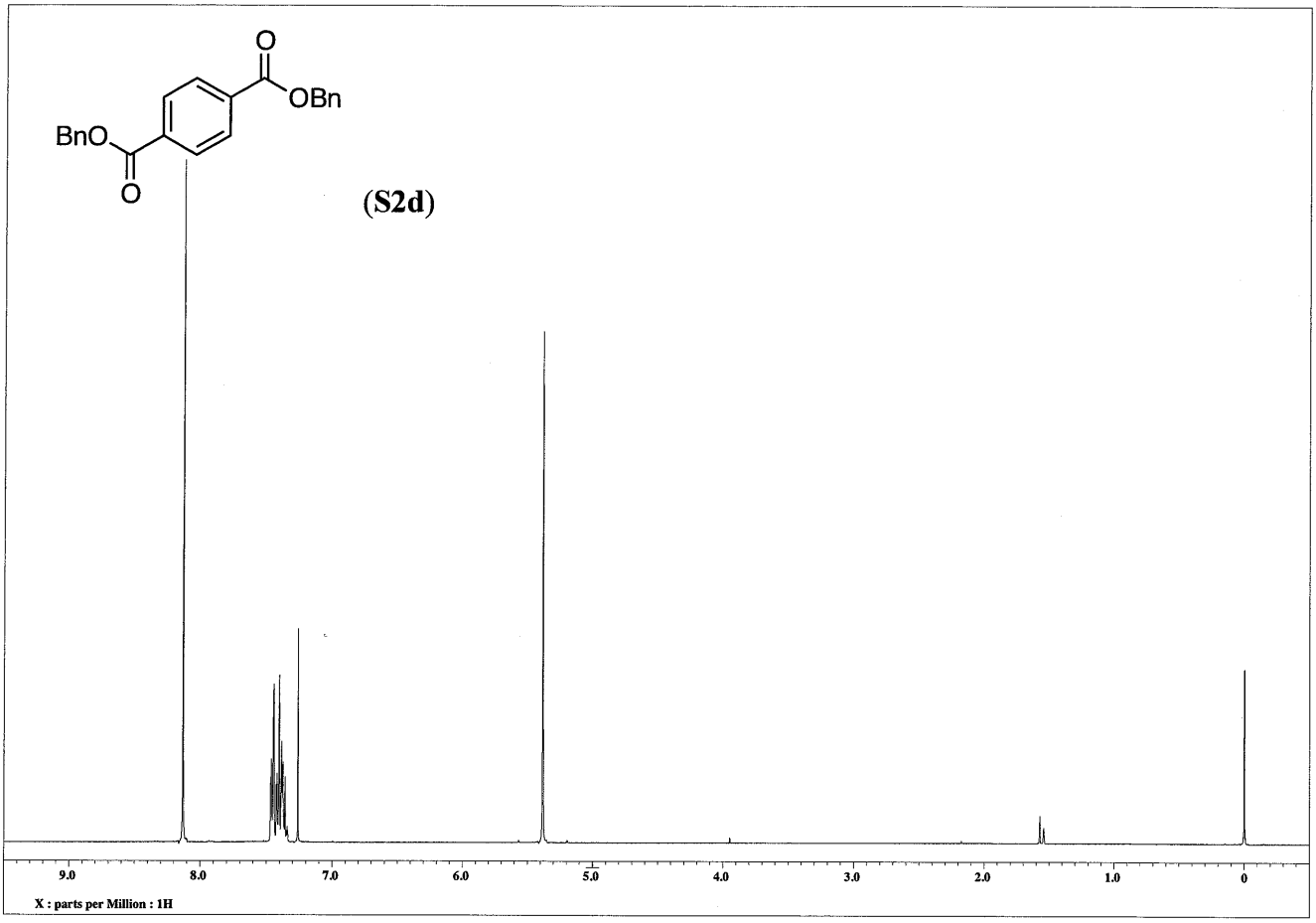
(S2b)

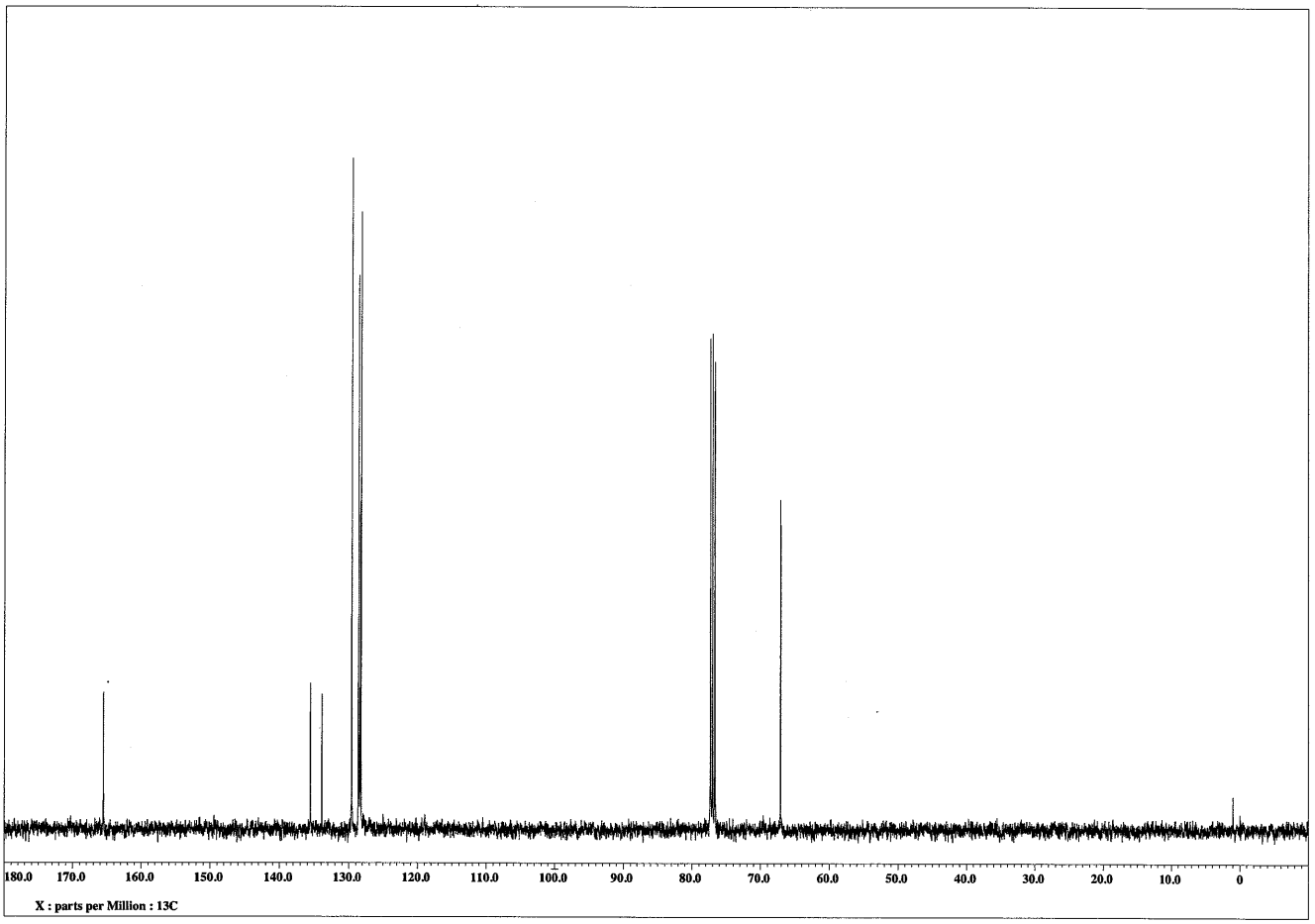

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

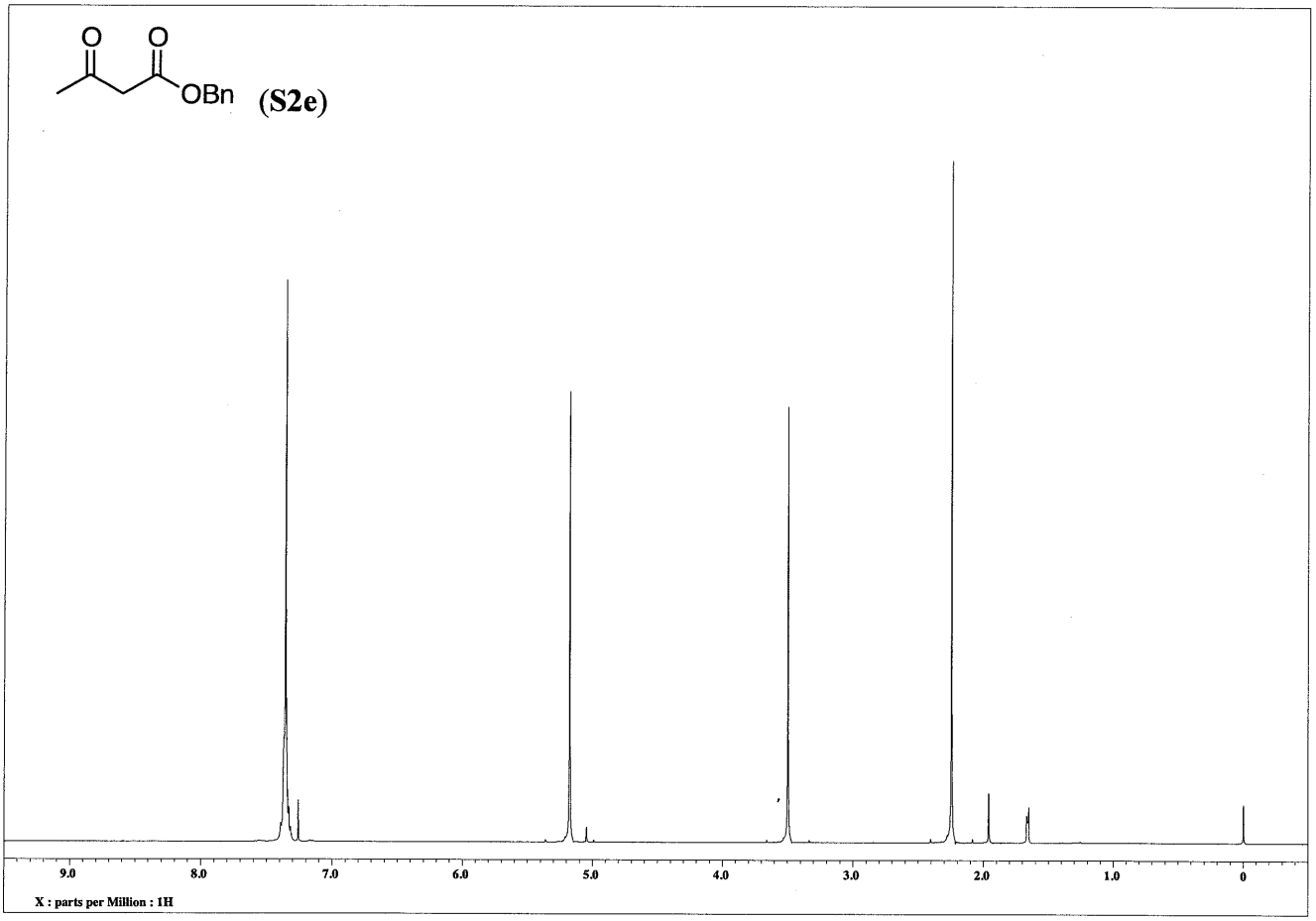

O
OBn
N
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

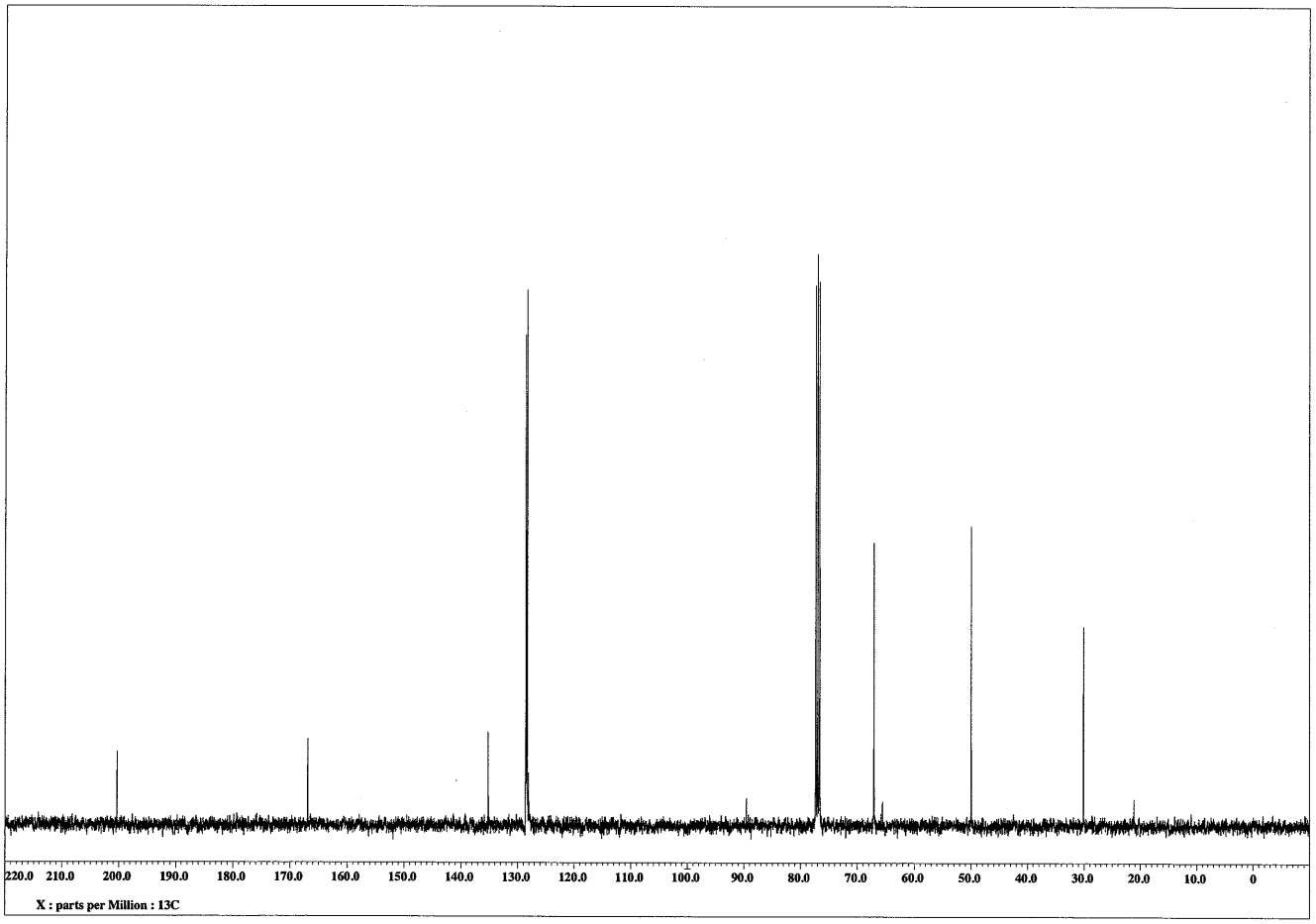
(S2c)

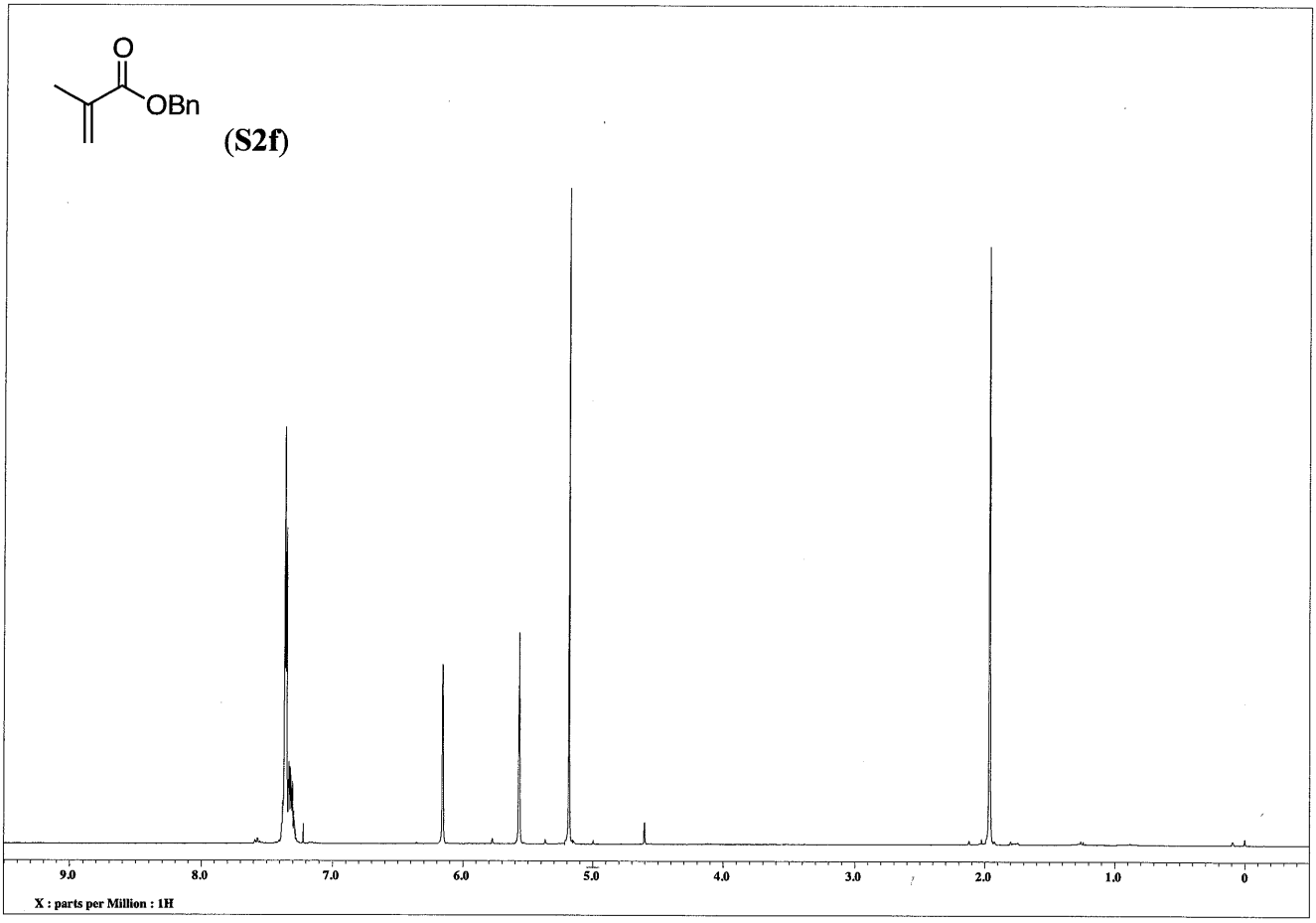

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

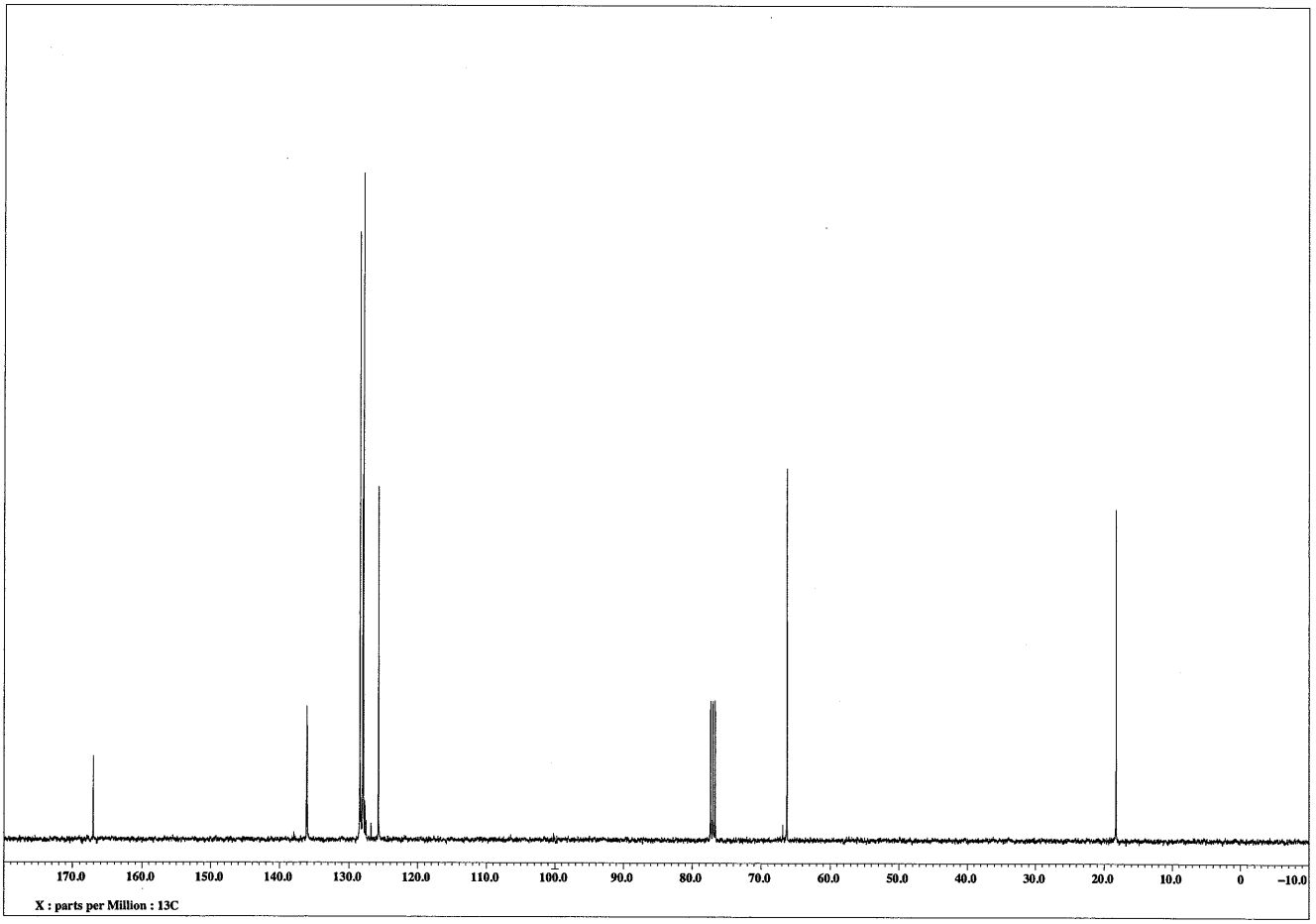

O
OBn
BnO
O
(S2d)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

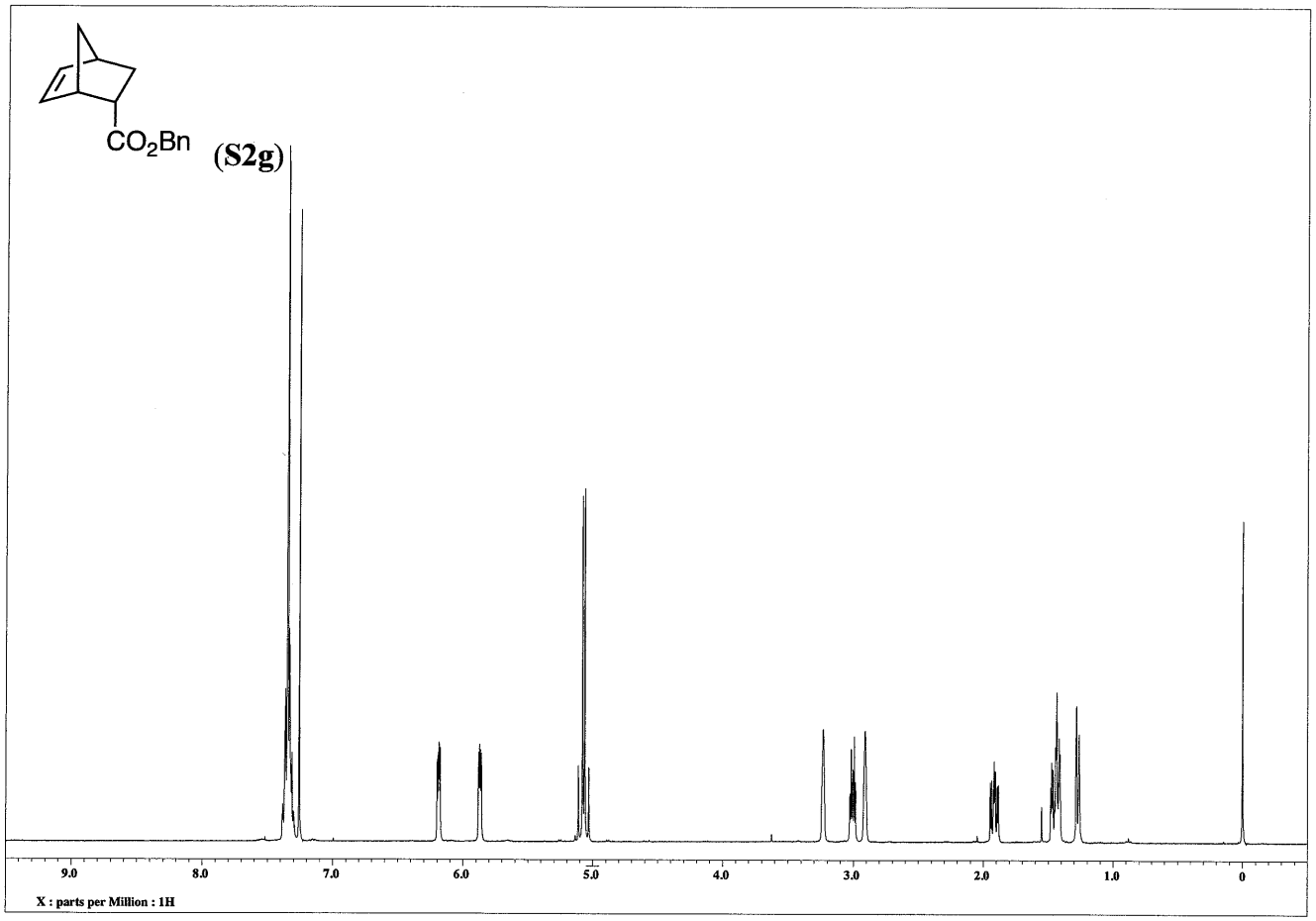

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

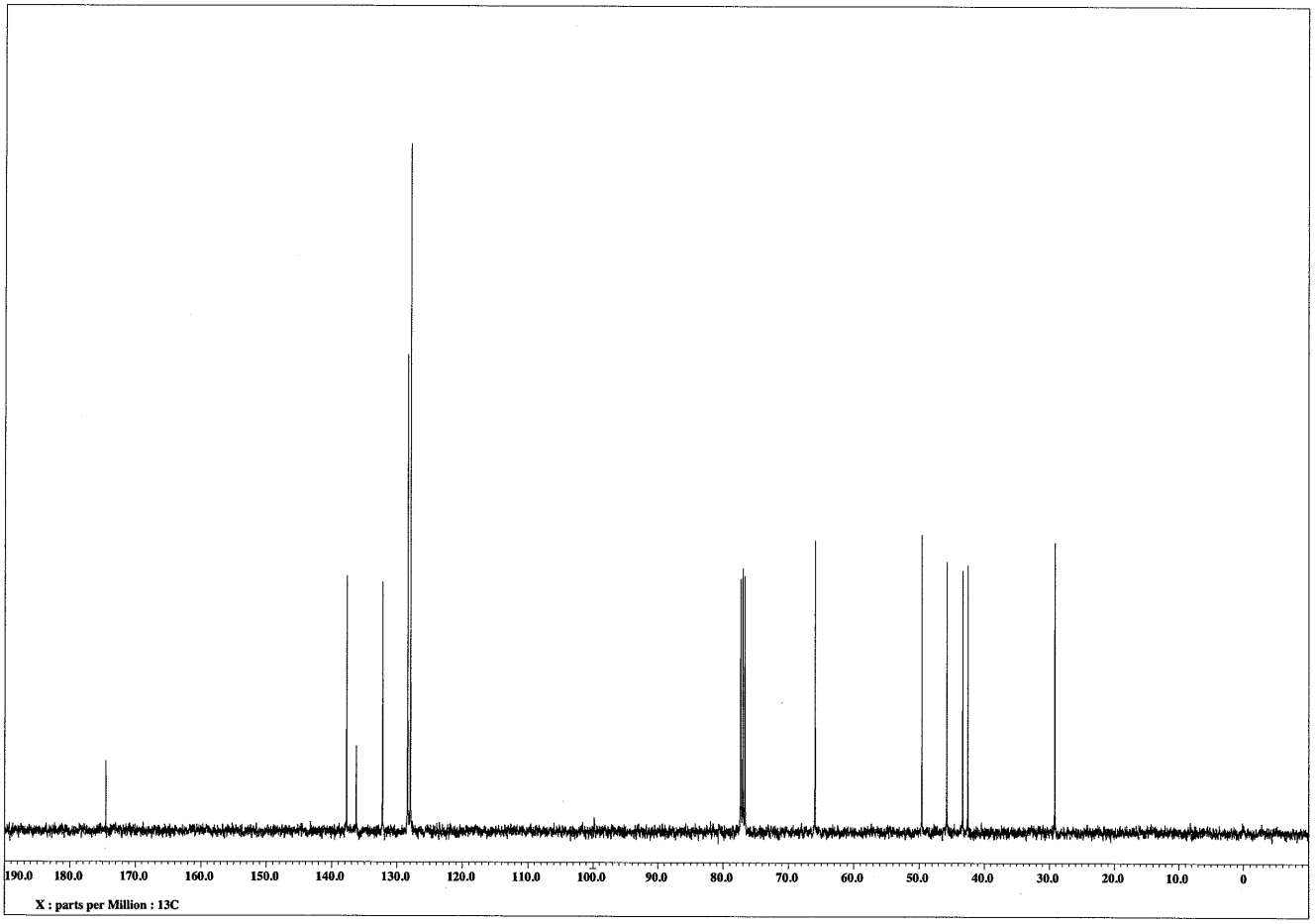

OBn
(S2e)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

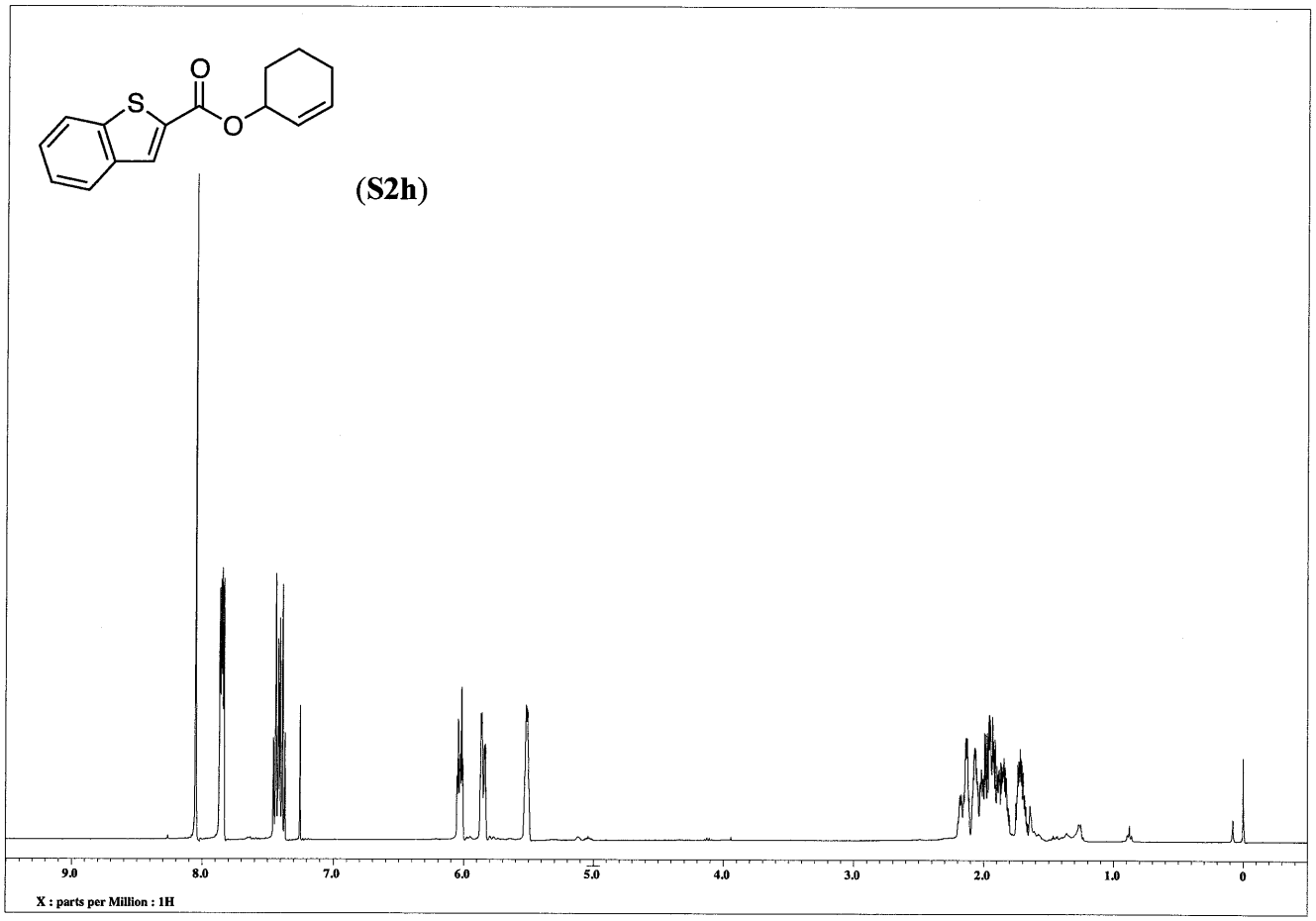

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : 13C

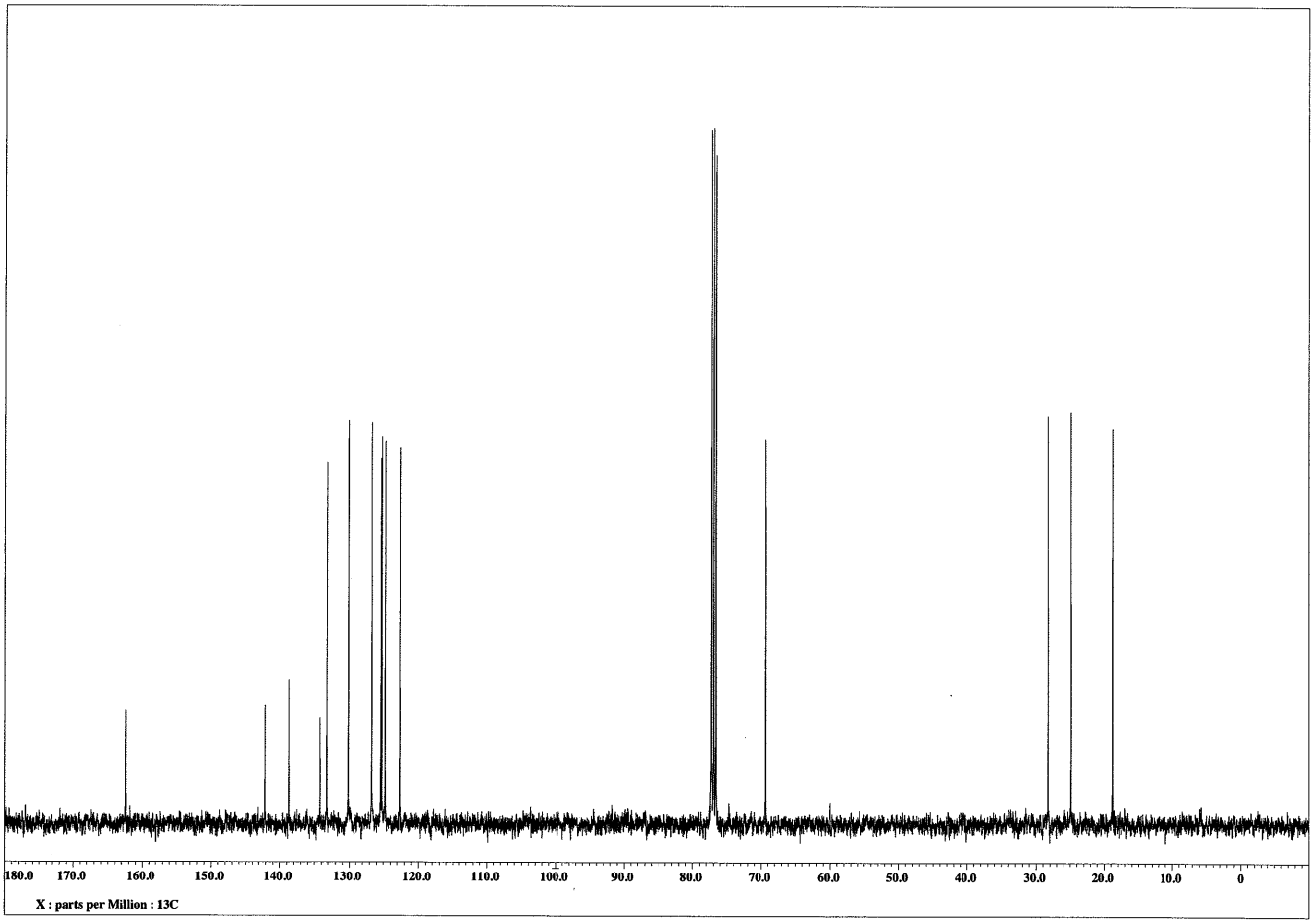

O
OBn
(S2f)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

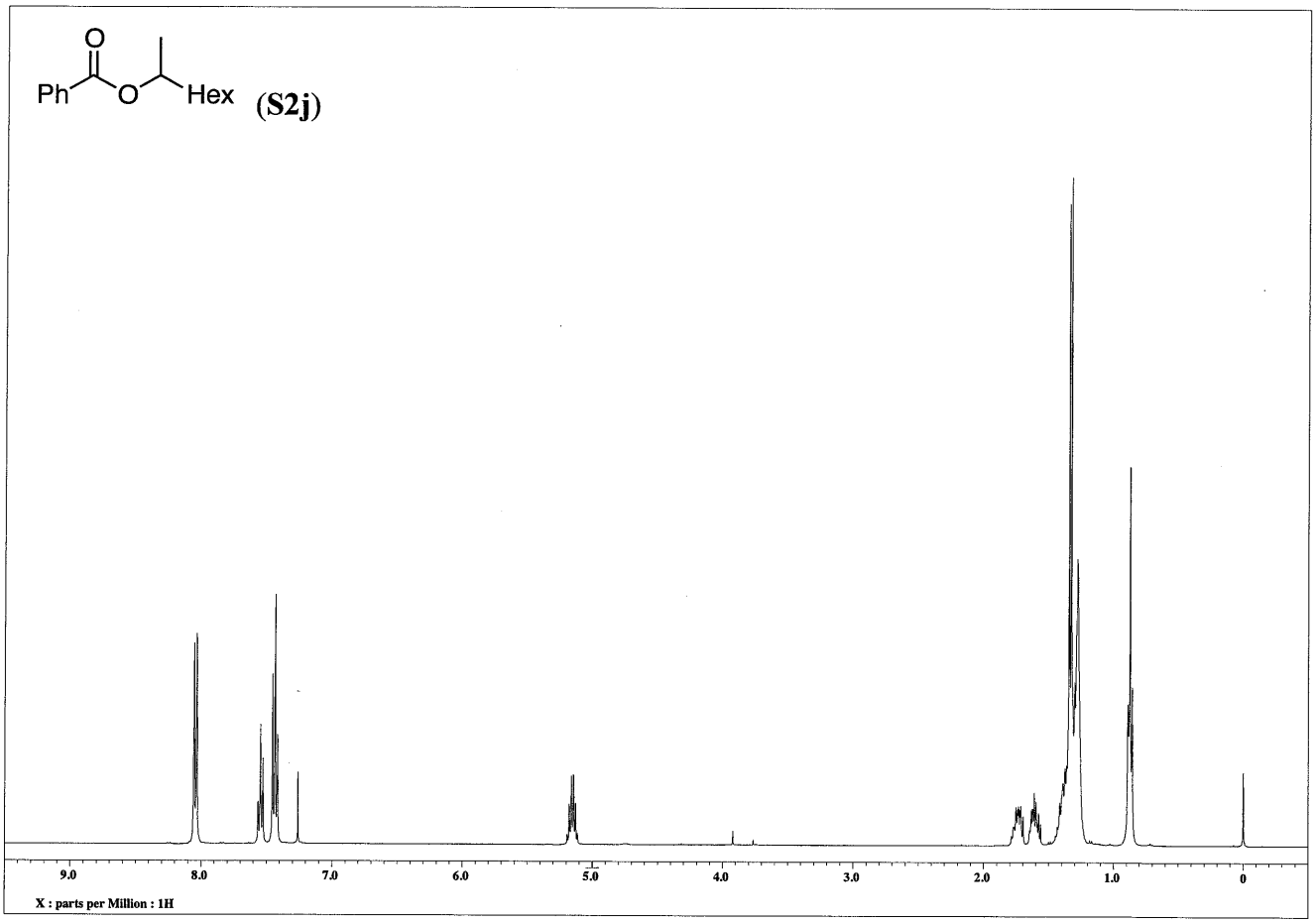

170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
X : parts per Million : 13C

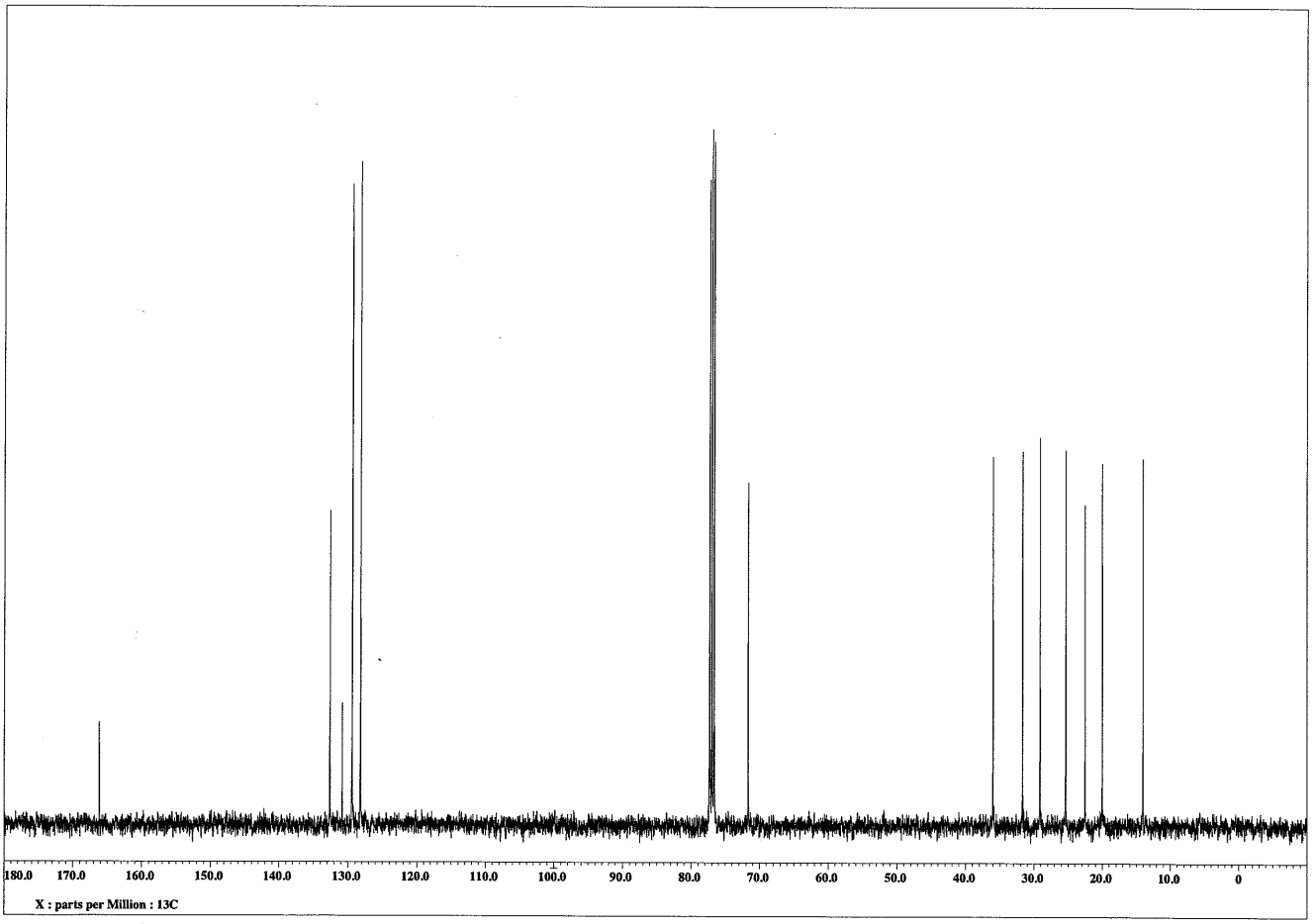

CO2Bn
(S2g)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

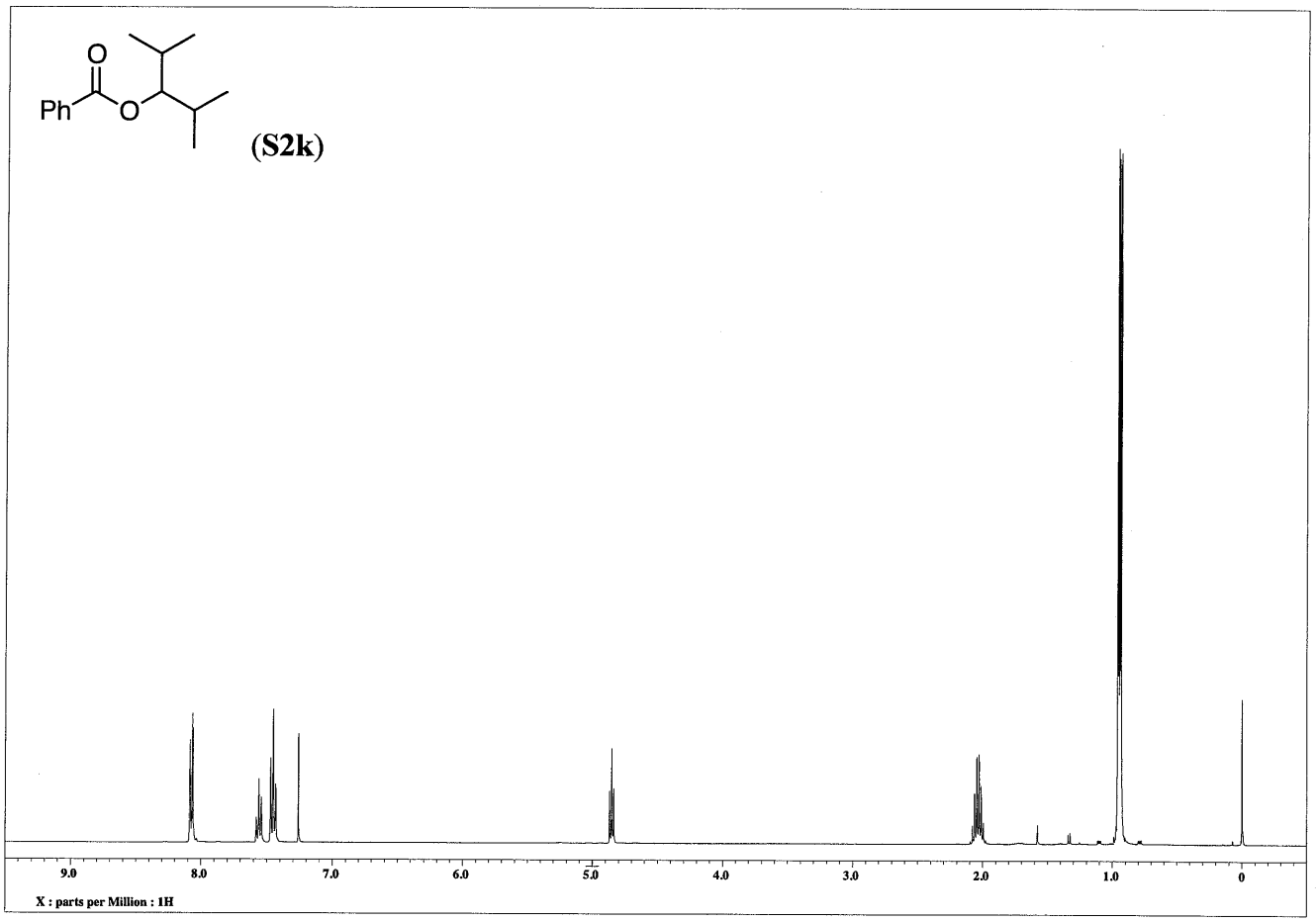

190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

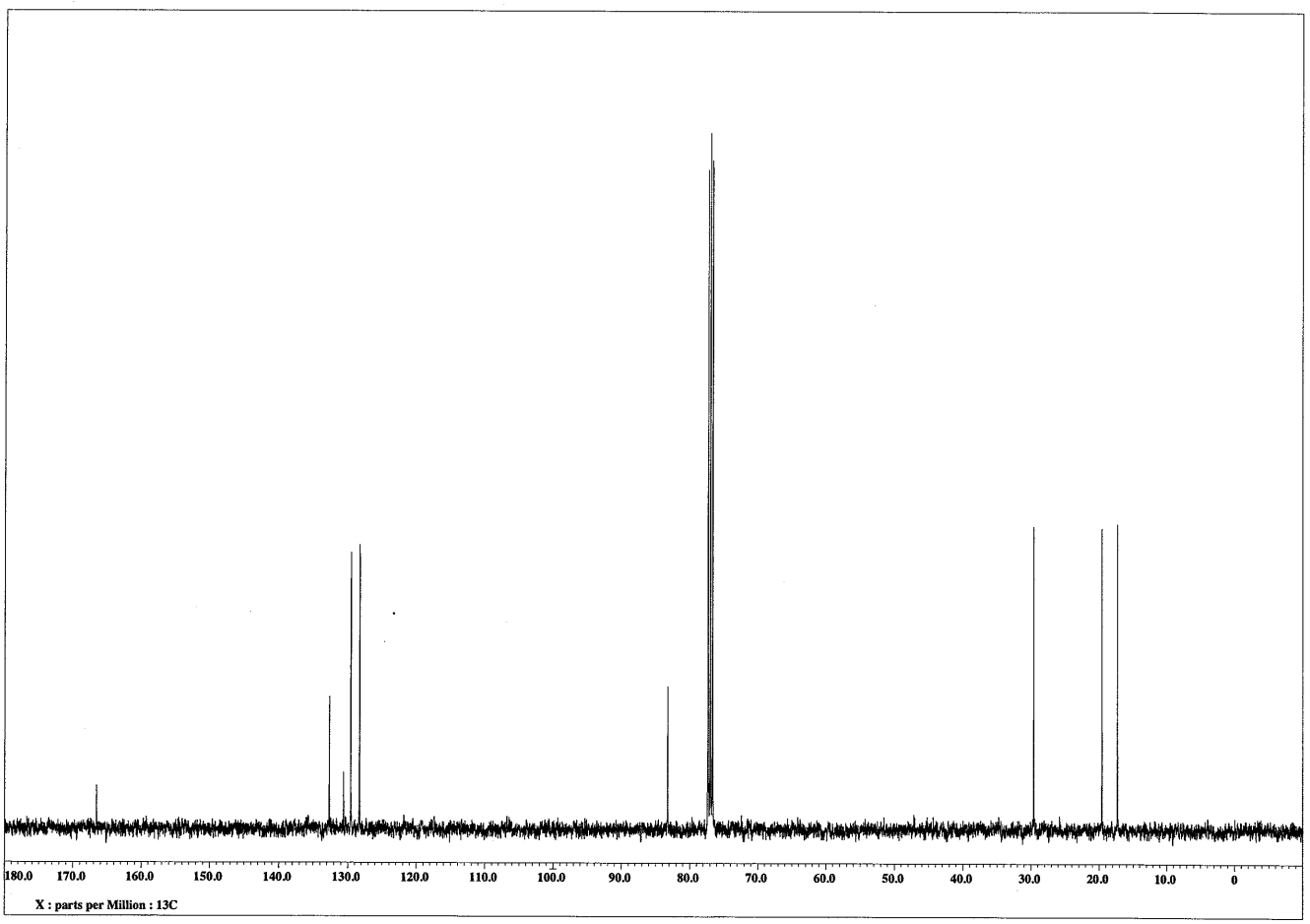

O
S
O
(S2h)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

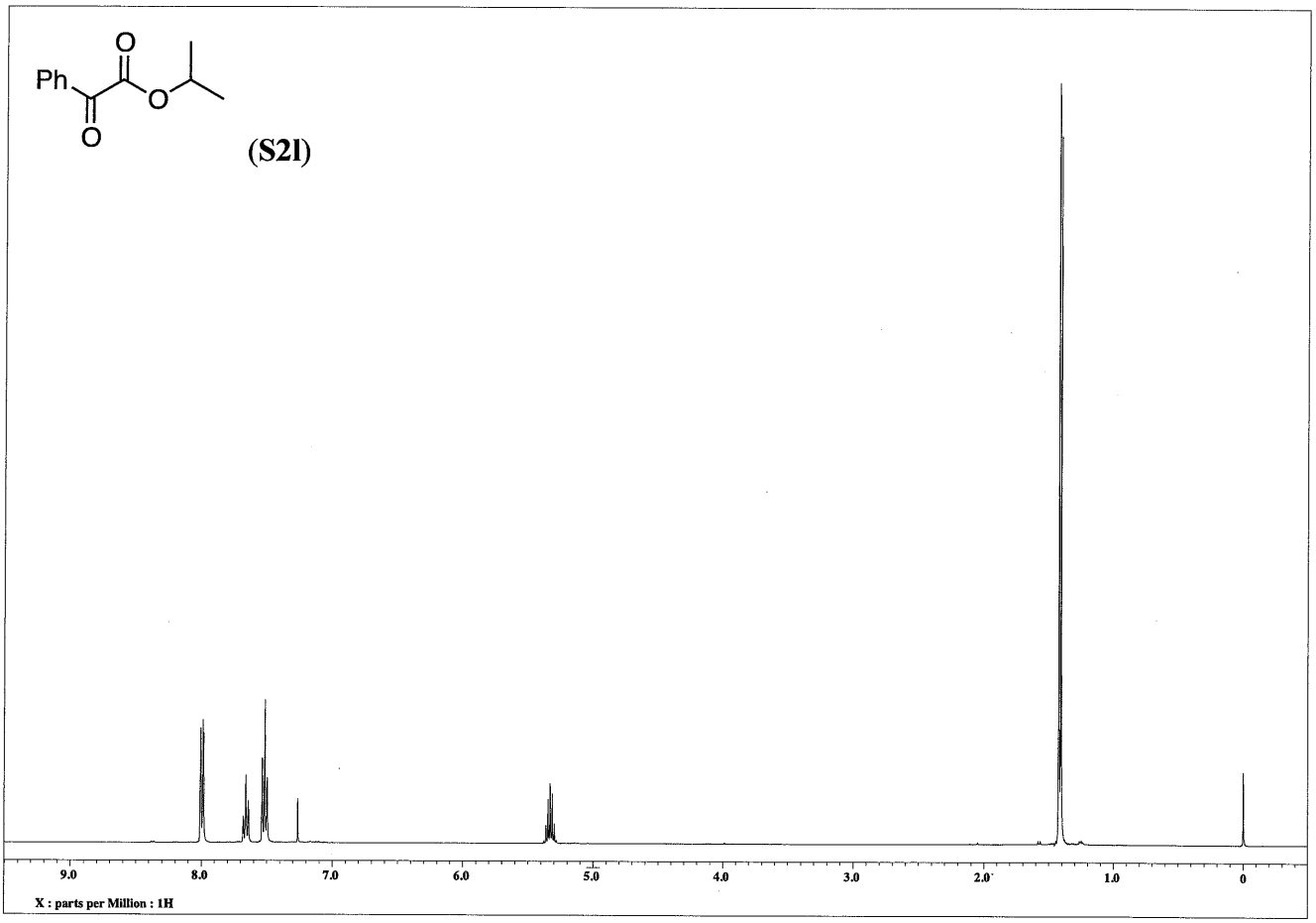

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C


Ph
O
O
Hex
(S2j)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

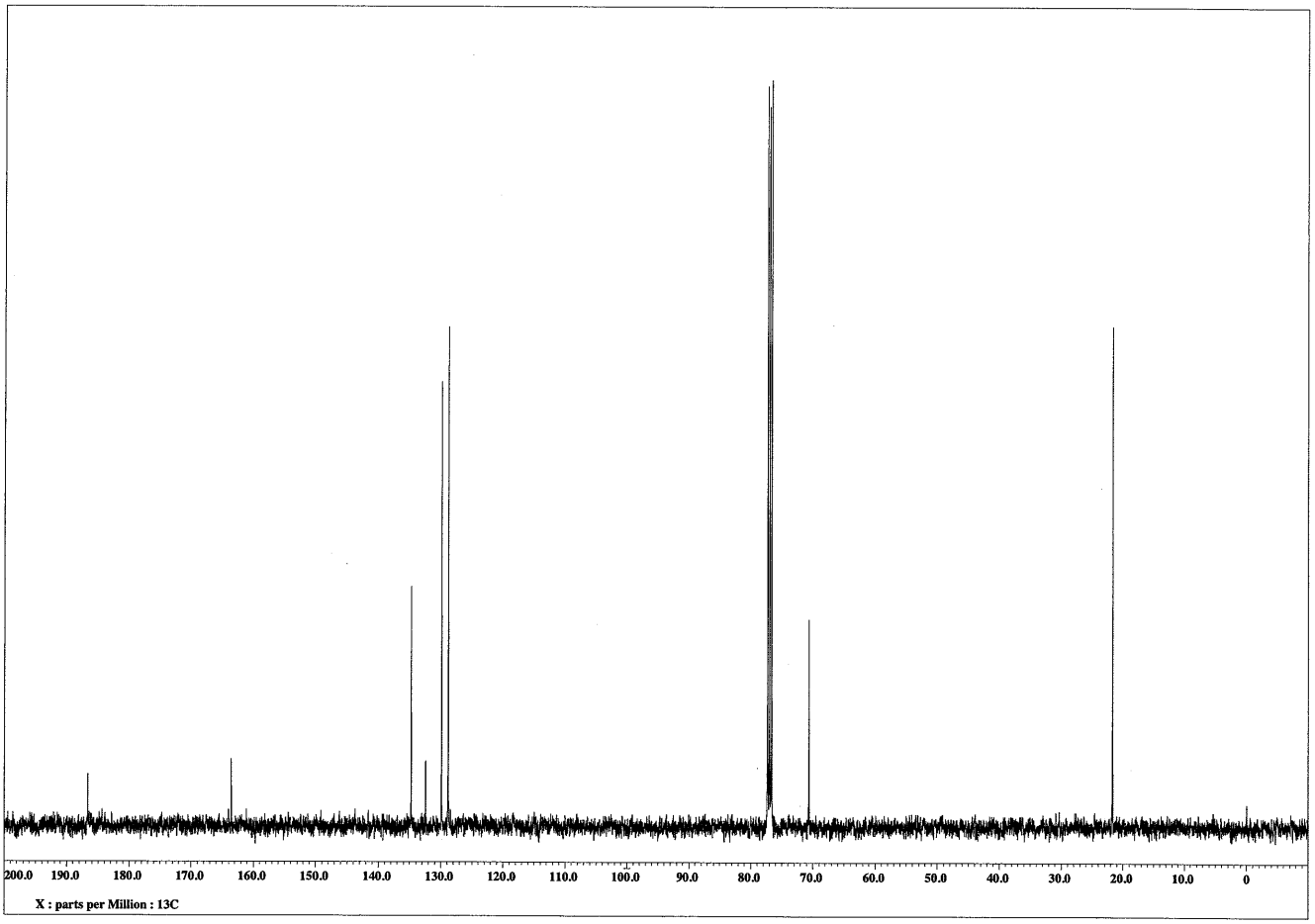

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

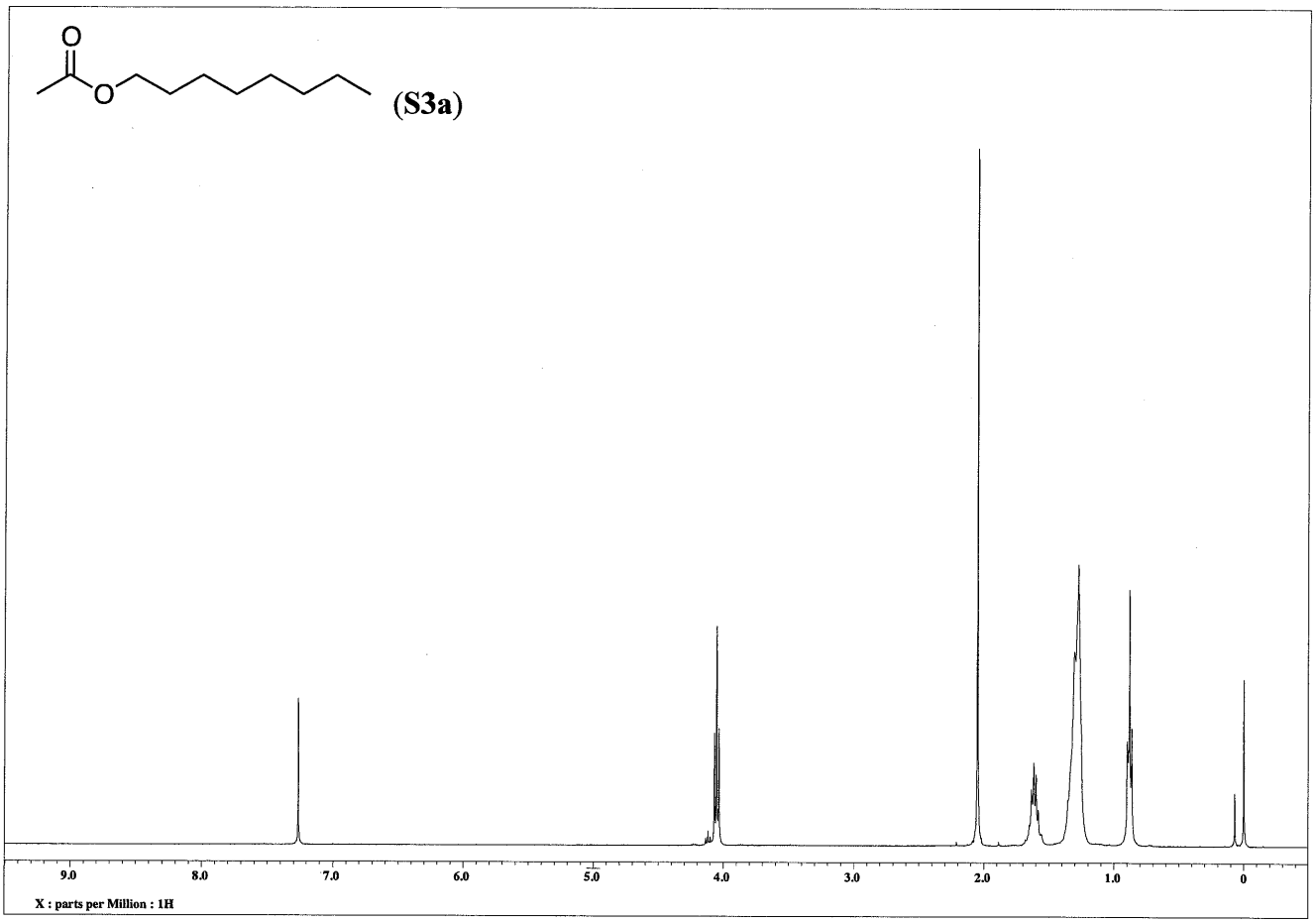

O
Ph
O
(S2k)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

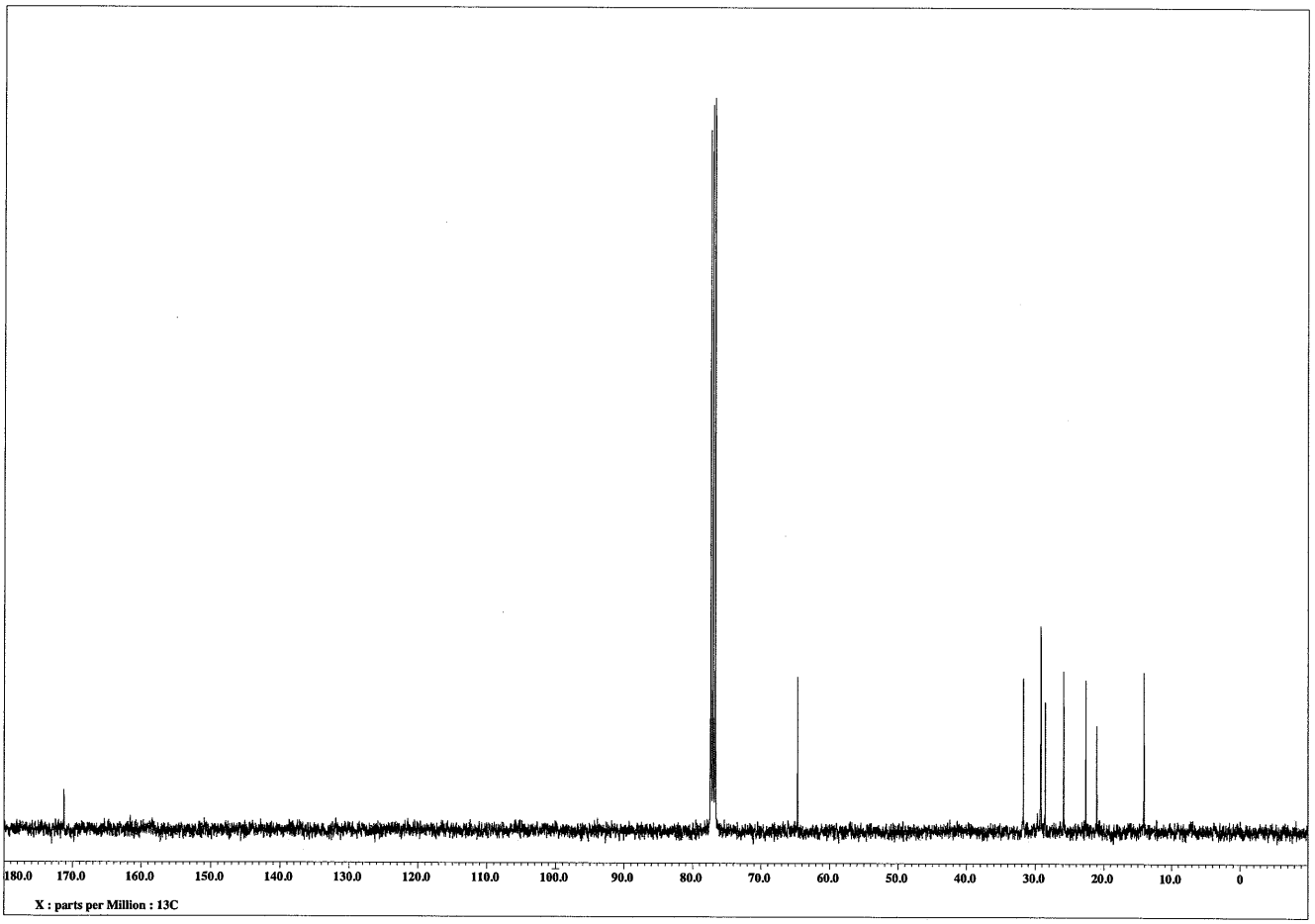

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C

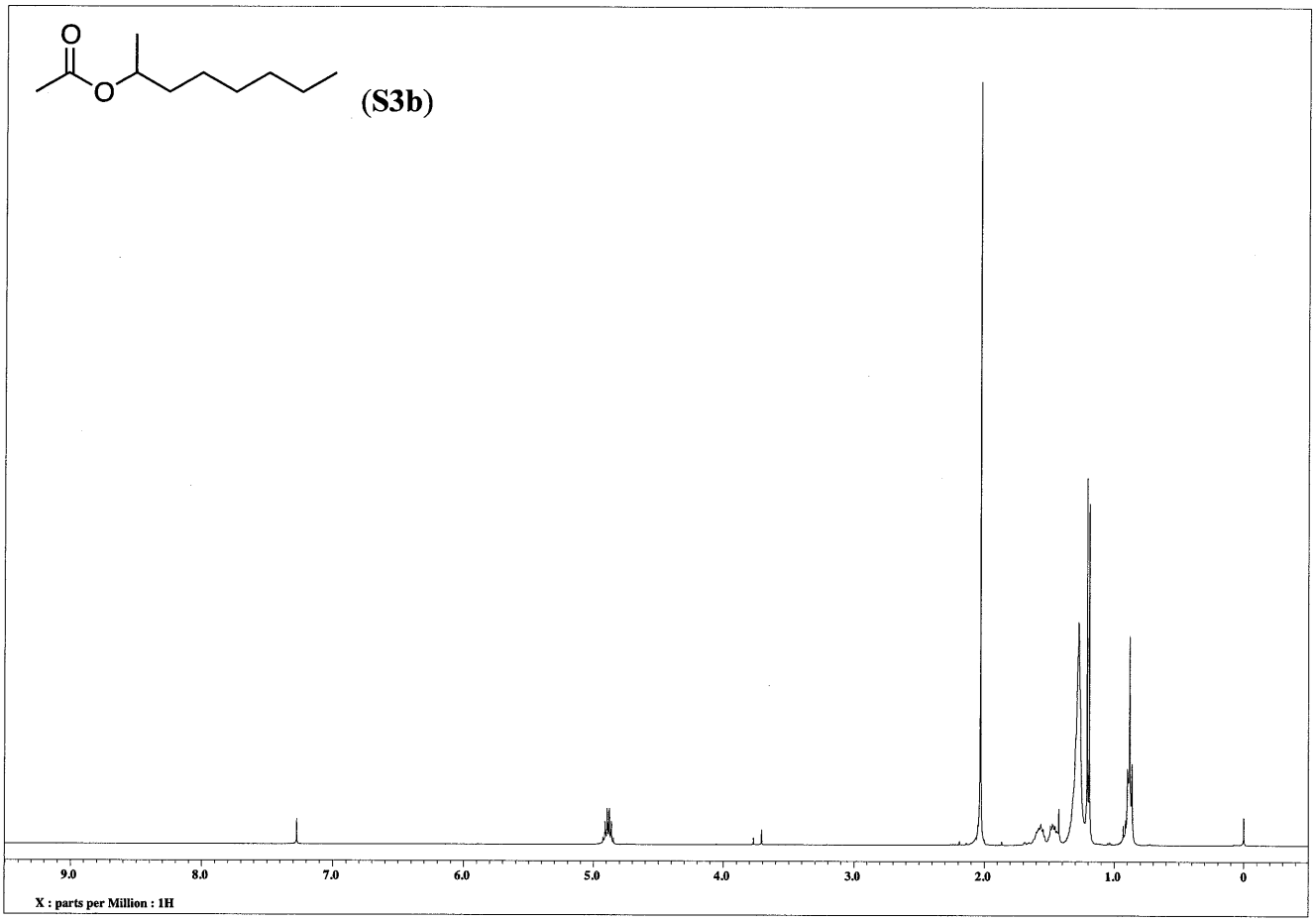

Ph
O
O
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

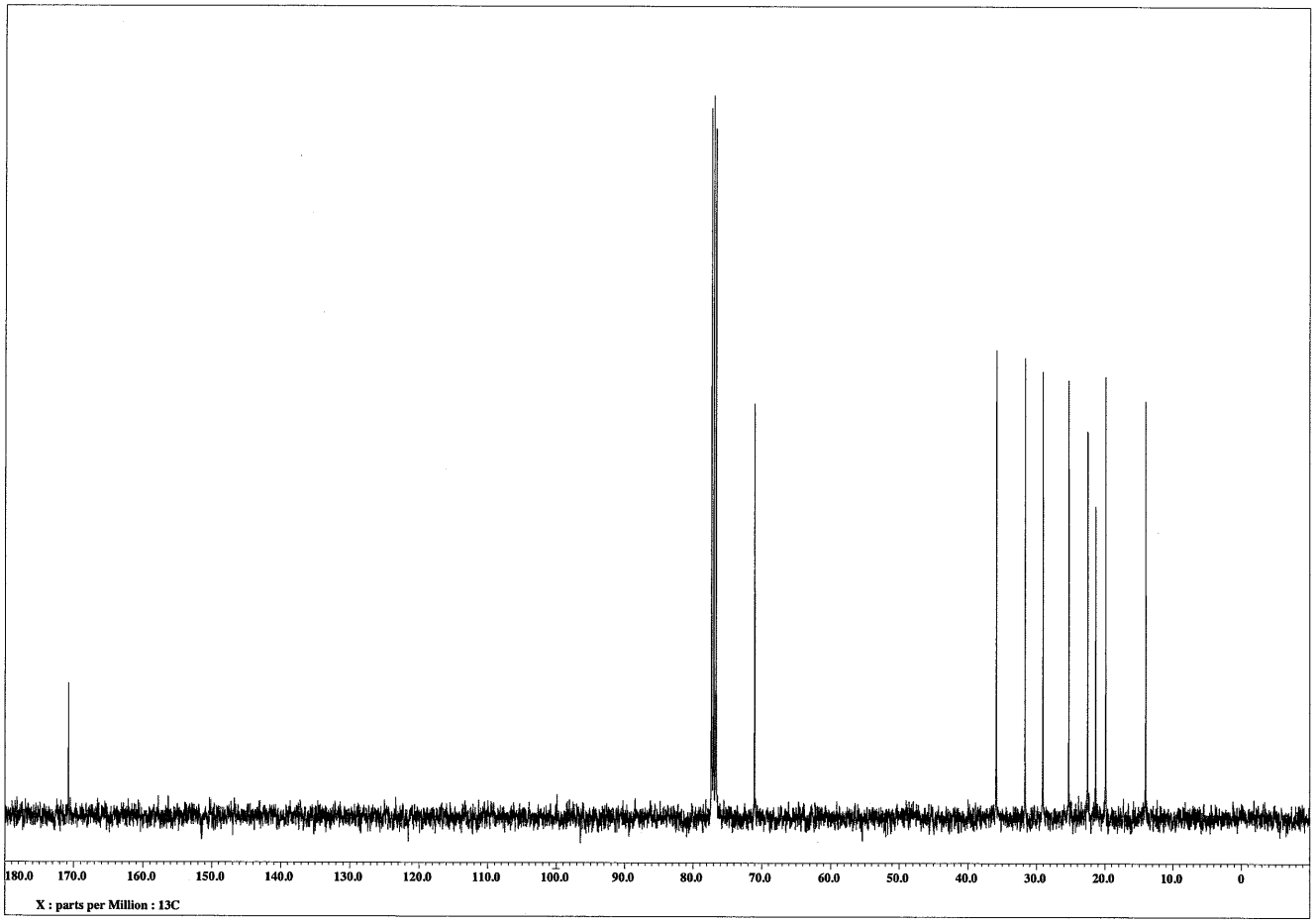
(S2l)


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C


(S3a)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C


(S3b)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C