

Supporting Information

Kinetic Resolution of Racemic Carboxylic Acids through Asymmetric Protolactonization Promoted by Chiral Phosphonous Acid Diester

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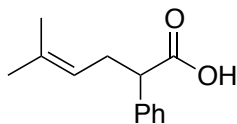
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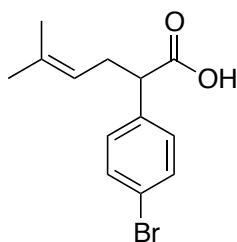
General Methods. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ¹H NMR spectra were measured on a JEOL ECS-400 spectrometer (400 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. ¹³C NMR spectra were measured on a JEOL ECS-400 spectrometer (100 MHz). Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.00 ppm). High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-20 AD coupled diode array-detector SPD-M20A and chiral column of Daicel CHIRALCEL OD-H (4.6 mm \times 25 cm), Daicel CHIRALCEL OJ-H (4.6 mm \times 25 cm), Daicel CHIRALPAK AS-H (4.6 mm \times 25 cm), Daicel CHIRALPAK AS-3 (4.6 mm \times 25 cm), Daicel CHIRALPAK AD-3 (4.6 mm \times 25 cm), Daicel CHIRALPAK IA (4.6 mm \times 250 mm), Daicel CHIRALPAK IA-3 (4.6 mm \times 250 mm), Daicel CHIRALPAK IB-3 (4.6 mm \times 250 mm), Daicel CHIRALPAK IC-3 (4.6 mm \times 250 mm) or Daicel CHIRALPAK ID-3 (4.6 mm \times 250 mm). Gas-liquid-phase chromatography (GC) was performed with Shimadzu GC-2010 Plus with a flame-ionization detector and a capillary column of CP-Cyclodextrin- β -2,3,6-M-19 (i.d. 0.25 mm \times 25 m; CHROMPACK; GL Science Inc.) or CHIRALDEX β -TA, γ -TA (i.d. 0.25 mm \times 20 m; Tokyo Kasei Kogyo Co., Ltd). Optical rotations were measured on a RUDOLPH AUTOPOL IV digital polarimeter. The reactions were carried out under an atmosphere of dry nitrogen. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plate (silica gel 60 F₂₅₄ 0.25 mm) was used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385) or preparative thin-layer chromatography (Merck precoated PLC plate, silica gel 60 F₂₅₄ 0.5 mm). High resolution mass spectral analysis (HRMS) was performed at Chemical Instrumentation Facility, Nagoya University (JEOL JMS-700, JEOL JMS-T100GCV, Bruker Daltonics micrOTOF-QII). Dry tetrahydrofuran was purchased from Kanto as the “anhydrous” and stored under nitrogen. Chloroform were freshly distilled from diphosphorus pentoxide, and stored over MS 4Å under nitrogen in the dark. Other simple chemicals were analytical-grade and obtained commercially. Chiral phosphorus(III) compound **1** was reported previously.¹

Preparation of (\pm)- α -Substituted Carboxylic Acids **2** and **6**.



(\pm)-5-Methyl-2-phenyl-4-hexenoic acid (2a**):**² To a solution of *i*-Pr₂NH

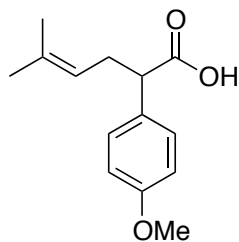
(1.7 mL, 12 mmol) in THF (40 mL) was added *n*-BuLi (1.6 M in hexane, 6.9 mL, 11 mmol) dropwise at -78 °C, and the reaction mixture was stirred for 30 minutes. To this reaction mixture, a solution of ethyl 2-phenylacetate (1.6 mL, 10 mmol) in THF (5 mL) was added dropwise at -78 °C. After stirring at the same temperature for 1 h, 1-bromo-3-methyl-2-butene (1.4 mL, 12 mmol) was added at -78 °C. It was then warmed to room temperature and stirred for 5 h. The reaction was quenched with saturated aqueous NH₄Cl, and the mixture was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous MgSO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 10:1) to give ethyl ester of **2a** (1.97 g, 85% yield) as colorless oil. To a solution of ethyl ester of **2a** in EtOH (30 mL) was added a solution of 2 M aqueous NaOH (6.8 mL) and was heated to reflux for 1 day. The reaction mixture was cooled, and then concentrated under reduced pressure to remove the solvent. The residue was taken with water and acidized with 1 M aqueous HCl. The reaction mixture was extracted with EtOAc, dried over anhydrous MgSO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 2:1) to give of **2a** (1.72 g, 99% yield) as colorless oil. IR (neat) 3250–2750, 1706, 1495, 1415, 1288 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.64 (s, 3H), 2.45 (ddd, $J = 7.3, 7.8, 14.2$ Hz, 1H), 2.77 (ddd, $J = 7.3, 7.8, 14.2$ Hz, 1H), 3.56 (t, $J = 7.8$ Hz, 1H), 5.05 (t, $J = 7.3$ Hz, 1H), 7.26–7.34 (m, 5H), 9.68–11.17 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 31.8, 51.7, 120.5, 127.4, 128.0 (2C), 128.6 (2C), 134.3, 138.3, 179.5; HRMS (FAB⁺) calcd for C₁₃H₁₇O₂ [M+H]⁺ 205.1229, found 205.1228.



(\pm)-2-(4-Bromophenyl)-5-methyl-4-hexenoic acid (2b**):** Compound **2b**

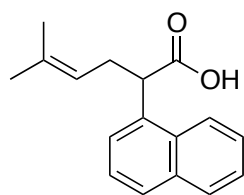
was prepared from ethyl 4-bromophenylacetate and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1706, 1485, 1073, 1011 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.55 (s, 3H), 1.64 (s, 3H), 2.43 (ddd, $J = 7.3, 7.8, 14.6$ Hz, 1H), 2.74 (ddd, $J = 7.3, 7.8, 14.6$ Hz, 1H), 3.52 (t, $J = 7.8$ Hz, 1H), 5.00 (t, $J = 7.3$ Hz, 1H), 7.20 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 10.24–11.18 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 31.6, 51.2, 120.0,

121.4, 129.8 (2C), 131.7 (2C), 134.7, 137.1, 180.1; HRMS (FAB+) calcd for C₁₃H₁₆BrO₂ [M+H]⁺ 283.0334, found 283.0323.



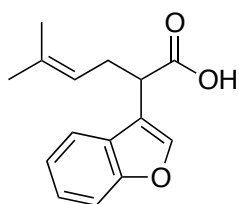
(±)-2-(4-Methoxyphenyl)-5-methyl-4-hexenoic acid (2c): Compound **2c**

was prepared from ethyl 4-methoxyphenylacetate and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1704, 1512, 1251, 1179, 1036 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.64 (s, 3H), 2.42 (ddd, *J* = 7.3, 7.8, 14.6 Hz, 1H), 2.74 (ddd, *J* = 7.3, 7.8, 14.6 Hz, 1H), 3.51 (t, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 5.03 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 9.92–11.08 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 31.7, 50.9, 55.2, 113.9 (2C), 120.6, 129.0 (2C), 130.3, 134.2, 158.8, 180.5; HRMS (FAB+) calcd for C₁₄H₁₉O₃ [M+H]⁺ 235.1334, found 235.1345.



(±)-5-Methyl-2-(1-naphthalenyl)-4-hexenoic acid (2d): Compound **2d**

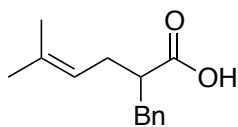
was prepared from methyl 1-naphthylacetate and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1704, 1511, 1414, 1255 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.58 (s, 3H), 1.63 (s, 3H), 2.60 (ddd, *J* = 6.4, 6.9, 14.5 Hz, 1H), 2.95 (ddd, *J* = 6.9, 8.7, 14.5 Hz, 1H), 4.41 (dd, *J* = 6.4, 8.7 Hz, 1H), 5.14 (t, *J* = 6.9 Hz, 1H), 7.43–7.57 (m, 4H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 10.01–10.76 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 31.4, 46.9, 120.9, 123.1, 125.0, 125.5, 125.6, 126.4, 128.0, 128.9, 131.6, 133.9, 134.3, 134.5, 180.5; HRMS (FAB+) calcd for C₁₇H₁₈O₂ [M]⁺ 254.1307, found 254.1330.



(±)-2-(3-Benzofuranyl)-5-methyl-4-hexenoic acid (2e): Compound **2e**

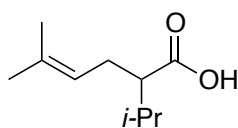
was prepared from ethyl 3-benzofuranylacetate³ and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1710, 1453, 1282, 1104 cm⁻¹; ¹H NMR (400 MHz,

CDCl₃) δ 1.58 (s, 3H), 1.65 (s, 3H), 2.63 (ddd, *J* = 7.3, 7.6, 14.6 Hz, 1H), 2.84 (ddd, *J* = 7.3, 7.6, 14.6 Hz, 1H), 3.81 (t, *J* = 7.6 Hz, 1H), 5.12 (t, *J* = 7.3 Hz, 1H), 7.22–7.33 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.65 (dd, *J* = 0.9, 6.9 Hz, 1H), 10.08–10.94 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 30.4, 42.2, 111.6, 117.4, 120.2 (2C), 122.6, 124.5, 126.8, 134.9, 142.5, 155.3, 179.7; HRMS (FAB+) calcd for C₁₅H₁₇O₃ [M+H]⁺ 245.1178, found 245.1176.



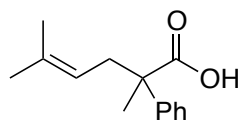
(±)-2-Benzyl-5-methyl-4-hexenoic acid (2f): Compound **2f** was prepared

from ethyl 3-phenylpropionate and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1705, 1455, 1242 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.70 (s, 3H), 2.24 (td, *J* = 7.3, 14.6 Hz, 1H), 2.34 (td, *J* = 7.3, 14.6 Hz, 1H), 2.66–2.75 (m, 1H), 2.78 (dd, *J* = 6.6, 13.5 Hz, 1H), 2.96 (dd, *J* = 8.0, 13.5 Hz, 1H), 5.12 (t, *J* = 7.3 Hz, 1H), 7.16–7.23 (m, 3H), 7.26–7.30 (m, 2H), 9.86–11.22 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.8, 30.2, 37.3, 47.6, 120.4, 126.4, 128.4 (2C), 128.9 (2C), 134.4, 139.1, 181.7; HRMS (FAB+) calcd for C₁₄H₁₉O₂ [M+H]⁺ 219.1385, found 219.1397.



(±)-2-Isopropyl-5-methyl-4-hexenoic acid (2g):⁴ Compound **2g** was

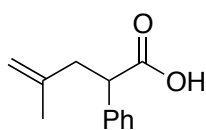
prepared from methyl isovalerate and 1-bromo-3-methyl-2-butene according to the same manner as **2a**. IR (neat) 3250–2750, 1706, 1440, 1223 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.98 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 1.61 (s, 3H), 1.68 (s, 3H), 1.91 (dsept, *J* = 6.9, 6.9 Hz, 1H), 2.12–2.35 (m, 3H), 5.09 (t, *J* = 6.9 Hz, 1H), 10.82–11.52 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.6, 20.1, 20.3, 25.8, 28.0, 30.0, 52.9, 121.2, 133.6, 182.4; HRMS (ESI-) calcd for C₁₀H₁₇O₂ [M-H]⁻ 169.1234, found 169.1238.



(±)-2,5-Diethyl-2-phenyl-4-hexenoic acid (2h): To a solution of *i*-Pr₂NH

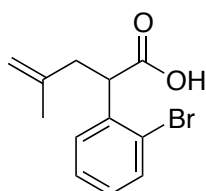
(1.8 mL, 13 mmol) in THF (10 mL) was added *n*-BuLi (1.6 M in hexane, 7.8 mL, 12.5 mmol) dropwise at -78 °C, and the reaction mixture was stirred for 30 minutes. To this reaction mixture, a solution of 2-phenylpropionic acid (0.68 mL, 5 mmol) in THF (2.5 mL) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. The mixture was then cooled to 0 °C, and 1-bromo-3-methyl-2-butene (1.4 mL, 12.5 mmol) was added. It was then warmed to

room temperature and stirred for 20 h. The reaction was quenched with saturated aqueous NH_4Cl , and extracted with 0.5 M aqueous KOH . The aqueous layer was washed with ether and acidized with 1 M aqueous HCl . The product was extracted with ether, dried over anhydrous MgSO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane– EtOAc 2:1) to give of **2h** (0.92 g, 84% yield) as colorless oil. IR (neat) 3250–2750, 1699, 1446, 1278 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.54 (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 2.61 (dd, $J = 7.3, 14.2$ Hz, 1H), 2.79 (dd, $J = 7.3, 14.2$ Hz, 1H), 5.00 (t, $J = 7.3$ Hz, 1H), 7.23–7.29 (m, 1H), 7.31–7.42 (m, 4H), 9.82–10.86 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.0, 22.1, 26.0, 37.4, 50.2, 119.3, 126.3 (2C), 126.9, 128.4 (2C), 135.0, 142.8, 182.4; HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found 219.1399.



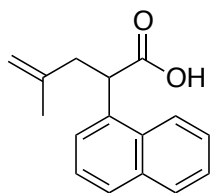
(±)-4-Methyl-2-phenyl-4-pentenoic acid (6a):⁵ Compound **6a** was prepared

from ethyl 2-phenylacetate and 3-bromo-2-methyl-1-propene according to the same manner as **2a**. IR (neat) 3250–2750, 1708, 1452, 1284 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.72 (s, 3H), 2.45 (dd, $J = 6.9, 14.6$ Hz, 1H), 2.83 (dd, $J = 8.7, 14.6$ Hz, 1H), 3.81 (dd, $J = 6.9, 8.7$ Hz, 1H), 4.71 (s, 1H), 4.75 (s, 1H), 7.25–7.35 (m, 5H), 10.27–11.36 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.6, 40.7, 49.9, 112.4, 127.5, 128.0 (2C), 128.6 (2C), 138.0, 142.1, 180.0; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$ 191.1072, found 191.1050.



(±)-2-(2-Bromophenyl)-4-methyl-4-pentenoic acid (6b): Compound **6b** was

prepared from methyl 2-bromophenylacetate and 3-bromo-2-methyl-1-propene according to the same manner as **2a**. IR (neat) 3250–2750, 1709, 1471, 1280, 1022 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.76 (s, 3H), 2.49 (dd, $J = 7.4, 14.6$ Hz, 1H), 2.77 (dd, $J = 8.2, 14.7$ Hz, 1H), 4.46 (dd, $J = 7.4, 8.2$ Hz, 1H), 4.71 (s, 1H), 4.76 (s, 1H), 7.13 (dt, $J = 1.8, 7.8$ Hz, 1H), 7.30 (dt, $J = 1.2, 7.8$ Hz, 1H), 7.41 (dd, $J = 1.8, 7.8$ Hz, 1H), 7.58 (dd, $J = 1.2, 7.8$ Hz, 1H), 10.05–11.30 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.4, 40.4, 48.2, 112.8, 124.9, 127.7, 128.8, 128.9, 133.1, 137.4, 141.8, 179.1; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{14}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ 269.0177, found 269.0181.



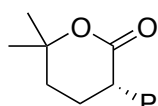
(±)-4-Methyl-2-(1-naphthalene)-4-pentenoic acid (6c):⁶ Compound **5c** was

prepared from methyl 1-naphthylacetate and 3-bromo-2-methyl-1-propene according to the same manner as **2a**. IR (neat) 3250–2750, 1707, 1415, 1290 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.77 (s, 3H), 2.60 (dd, $J = 5.7, 15.1$ Hz, 1H), 3.01 (dd, $J = 9.2, 15.1$ Hz, 1H), 4.68 (dd, $J = 5.7, 9.2$ Hz, 1H), 4.79 (s, 2H), 7.42–7.59 (m, 4H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 8.16 (d, $J = 8.2$ Hz, 1H), 9.49–10.56 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 40.4, 44.7, 112.3, 122.9, 124.9, 125.5, 125.7, 126.5, 128.1, 129.0, 131.4, 133.9, 134.2, 142.4, 179.9; HRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240.1150, found 240.1144.

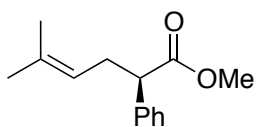
Typical Procedure for the Kinetic Resolution of (±)-**2a**.

To a solution of **1** (18.2 mg, 0.020 mmol) in CHCl₃ (1.8 mL) was added a 0.05 M solution of ClSO₃H in CHCl₃ (0.10 mL, 0.0050 mmol) at -40 °C, and the mixture was stirred for ca. five minutes. To this solution, a solution of **2a** (21.8 mg, 0.10 mmol) in CHCl₃ (0.1 mL) was added dropwise at -40 °C, and the mixture was stirred at -40 °C for 1 day. The reaction was quenched with water (3 mL) and the reaction mixture was extracted with ether. The combined organic layers were dried over anhydrous MgSO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane-CHCl₃-EtOAc 3:3:1) to give **3a** as a pale yellow solid (8.4 mg, 40% yield) and **2a** (10.6 mg, 52% yield). To a stirring solution of the recovered carboxylic acid **2a** in THF (1.0 mL) and MeOH (0.25 mL) was added dropwise (trimethylsilyl)diazomethane (2.0 M in diethyl ether, 0.10 mL) at 0 °C. The yellow solution was stirred at the same temperature for 10 minutes. The reaction was quenched with AcOH (ca. 0.10 mL) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane-EtOAc 10:1) to give **4a** as pale yellow oil (10.5 mg, 93% yield).

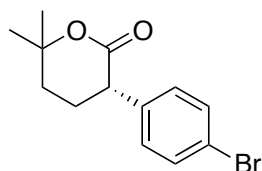
The corresponding physical and spectroscopic data for **3**, **4**, **5** and **6** are as follows.



(S)-6,6-Dimethyl-3-phenyltetrahydro-2H-pyran-2-one (3a):⁷ [α]_D²³ +8.7 (*c* 0.42, CHCl₃) for 95% ee; HPLC (Daicel Chiralpak AS-H, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) *t*_R = 22.2 (minor enantiomer), 38.3 (major enantiomer) min; IR (neat) 1712, 1284, 1258, 1209, 1120 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.50 (s, 3H), 1.52 (s, 3H), 1.83–1.96 (m, 2H), 2.07–2.26 (m, 2H), 3.67 (dd, *J* = 6.9, 9.6 Hz, 1H), 7.19–7.30 (m, 3H), 7.32–7.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.7, 28.3, 29.9, 33.4, 47.2, 82.9, 127.1, 128.1 (2C), 128.8 (2C), 139.8, 172.2; HRMS (FAB⁺) calcd for C₁₃H₁₇O₂ [M+H]⁺ 205.1229, found 205.1241.

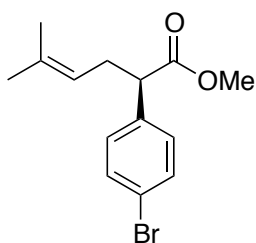


(R)-Methyl 5-methyl-2-phenyl-4-hexenoate (4a): [α]_D²⁵ -76.3 (*c* 0.49, CHCl₃) for 98% ee; HPLC (Daicel Chiralpak IB-3, hexane-*i*-PrOH 200:1, flow rate 0.3 mL/min) *t*_R = 17.8 (major enantiomer), 19.3 (minor enantiomer) min; IR (neat) 1738, 1435, 1154 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.65 (s, 3H), 2.44 (ddd, *J* = 7.1, 7.3, 14.2 Hz, 1H), 2.76 (ddd, *J* = 7.3, 8.5, 14.2 Hz, 1H), 3.55 (d, *J* = 7.1, 8.5 Hz, 1H), 3.65 (s, 3H), 5.03 (t, *J* = 7.3 Hz, 1H), 7.23–7.34 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 32.2, 51.8, 51.9, 120.8, 127.2, 127.9, 128.5, 134.1, 139.0, 174.3; HRMS (FAB⁺) calcd for C₁₄H₁₉O₂ [M+H]⁺ 219.1385, found 219.1413.



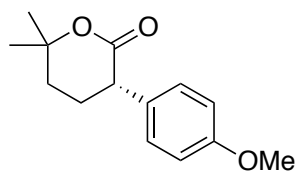
(S)-3-(4-Bromophenyl)-6,6-dimethyltetrahydro-2H-pyran-2-one (3b):

$[\alpha]_D^{22} +8.8$ (c 0.41, CHCl_3) for 84% ee; HPLC (Daicel Chiralpak AS-H, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_R = 19.7$ (minor enantiomer), 33.5 (major enantiomer) min; IR (neat) 1717, 1490, 1204, 1115, 1010 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.50 (s, 6H), 1.84–1.96 (m, 2H), 2.04–2.24 (m, 2H), 3.61 (dd, $J = 6.9, 10.1$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.5, 28.3, 29.9, 33.5, 46.7, 83.1, 121.1, 129.9 (2C), 131.8 (2C), 138.7, 171.6; HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{16}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ 283.0334, found 283.0332.



(R)-Methyl 2-(4-bromophenyl)-5-methyl-4-hexenoate (4b): $[\alpha]_D^{22} -46.5$

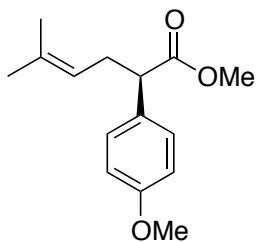
(c 1.26, CHCl_3) for 75% ee; HPLC (Daicel Chiralpak ID-3, hexane-*i*-PrOH 200:1, flow rate 0.5 mL/min) $t_R = 11.6$ (minor enantiomer), 12.0 (major enantiomer) min; IR (neat) 1738, 1488, 1436, 1154, 1073, 1011 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.56 (s, 3H), 1.64 (s, 3H), 2.42 (ddd, $J = 7.3, 7.8, 14.6$ Hz, 1H), 2.73 (ddd, $J = 7.3, 7.8, 14.6$ Hz, 1H), 3.51 (t, $J = 7.8$ Hz, 1H), 3.66 (s, 3H), 4.99 (t, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.44 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.8, 25.7, 32.1, 51.2, 52.1, 120.4, 121.1, 129.7 (2C), 131.6 (2C), 134.4, 137.9, 173.8; HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{18}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ 297.0490, found 297.0482.



(S)-3-(4-Methoxyphenyl)-6,6-dimethyltetrahydro-2H-pyran-2-one (3c):

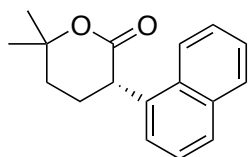
$[\alpha]_D^{21} +18.3$ (c 0.73, CHCl_3) for 90% ee; HPLC (Daicel Chiralpak AS-3, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_R = 28.5$ (minor enantiomer), 47.5 (major enantiomer) min; IR (neat) 1719, 1514, 1248, 1114, 1034 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.49 (s, 3H), 1.50 (s, 3H), 1.82–1.96 (m, 2H), 2.04–2.23 (m, 2H), 3.61 (dd, $J = 6.8, 10.1$ Hz, 1H), 3.80 (s, 3H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.7, 28.3, 29.9, 33.5, 46.4, 55.3, 82.9,

114.1 (2C), 129.1 (2C), 131.8, 158.6, 172.5; HRMS (FAB+) calcd for C₁₄H₁₉O₃ [M+H]⁺ 235.1334, found 235.1341.



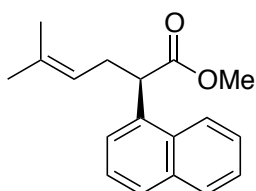
(R)-Methyl 2-(4-methoxyphenyl)-5-methyl-4-hexenoate (4c): $[\alpha]_D^{22}$

−38.5 (*c* 0.70, CHCl₃) for 56% ee; HPLC (Daicel Chiralpak AD-3, hexane-*i*-PrOH 200:1, flow rate 1.0 mL/min) *t*_R = 17.8 (minor enantiomer), 19.3 (major enantiomer) min; IR (neat) 1738, 1512, 1250, 1153, 1038 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.64 (s, 3H), 2.41 (ddd, *J* = 7.1, 7.8, 14.5 Hz, 1H), 2.73 (ddd, *J* = 7.1, 7.8, 14.5 Hz, 1H), 3.50 (t, *J* = 7.8 Hz, 1H), 3.65 (s, 3H), 3.79 (s, 3H), 5.02 (t, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.7, 32.2, 50.9, 51.9, 55.2, 113.9, 120.9, 128.9, 131.0, 133.9, 158.7, 174.5; HRMS (FAB+) calcd for C₁₅H₂₀O₃ [M]⁺ 248.1412, found 248.1413.



(S)-6,6-Dimethyl-3-(1-naphthalenyl)tetrahydro-2H-pyran-2-one (3d):

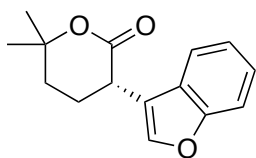
$[\alpha]_D^{22}$ −50.8 (*c* 0.85, CHCl₃) for 91% ee; HPLC (Daicel Chiralpak AS-3, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) *t*_R = 66.4 (major enantiomer), 83.9 (minor enantiomer) min; IR (neat) 1717, 1112 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 1.56 (s, 3H), 1.60 (s, 3H), 1.86–2.01 (m, 2H), 2.18–2.38 (m, 2H), 4.44 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.47–7.56 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.85–7.91 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 25.7, 28.7, 29.6, 33.2, 43.9, 83.1, 122.9, 125.4, 125.7, 125.9, 126.3, 128.0, 129.2, 130.8, 134.1, 136.2, 172.3; HRMS (FAB+) calcd for C₁₇H₁₉O₂ [M+H]⁺ 255.1385, found 255.1404.



(R)-Methyl 5-methyl-2-(1-naphthalenyl)-4-hexenoate (4d): $[\alpha]_D^{22}$

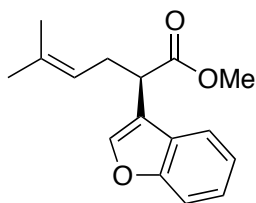
−66.9 (*c* 0.84, CHCl₃) for 66% ee; HPLC (Daicel Chiralcel OJ-H, hexane-*i*-PrOH 200:1, flow rate 1.0 mL/min) *t*_R = 13.5 (major enantiomer), 16.4 (minor enantiomer) min; IR (neat) 1737, 1435, 1203,

1150 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.59 (s, 3H), 1.65 (s, 3H), 2.59 (ddd, $J = 6.4, 7.3, 14.6$ Hz, 1H), 2.95 (ddd, $J = 7.3, 8.3, 14.6$ Hz, 1H), 3.65 (s, 3H), 4.39 (dd, $J = 6.4, 8.3$ Hz, 1H), 5.14 (t, $J = 7.3$ Hz, 1H), 7.43–7.57 (m, 4H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 8.13 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.8, 25.7, 31.9, 47.1, 52.0, 121.2, 123.1, 124.8, 125.5, 125.6, 126.3, 127.7, 128.9, 131.5, 133.9, 134.0, 135.2, 174.5; HRMS (FAB+) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ $[\text{M}]^+$ 269.1463, found 268.1456.



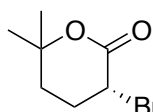
3-(3-Benzofuranyl)-6,6-dimethyltetrahydro-2H-pyran-2-one (3e): $[\alpha]_{\text{D}}^{21}$

–3.7 (c 1.15, CHCl_3) for 75% ee; HPLC (Daicel Chiralpak AS-H, hexane–*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_{\text{R}} = 40.8$ (minor enantiomer), 78.1 (major enantiomer) min; IR (neat) 1720, 1453, 1279, 1200, 1113 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.54 (s, 6H), 1.89–2.02 (m, 2H), 2.24–2.30 (m, 2H), 3.88 (t, $J = 8.2$ Hz, 1H), 7.23–7.34 (m, 2H), 7.47–7.54 (m, 2H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.6, 28.3, 29.8, 33.7, 37.3, 83.1, 111.8, 118.6, 119.8, 122.7, 124.5, 126.5, 142.2, 155.4, 170.7; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$ 245.1178, found 245.1194.



Methyl 2-(benzofuranyl)-5-methyl-4-hexenoate (4e): $[\alpha]_{\text{D}}^{22}$

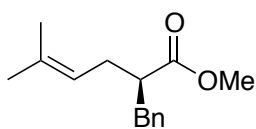
–29.4 (c 0.69, CHCl_3) for 94% ee; HPLC (Daicel Chiralpak AS-3, hexane–*i*-PrOH 200:1, flow rate 0.50 mL/min) $t_{\text{R}} = 24.7$ (major enantiomer), 26.2 (minor enantiomer) min; IR (neat) 1737, 1435, 1203, 1150 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.59 (s, 3H), 1.66 (s, 3H), 2.61 (ddd, $J = 7.1, 7.6, 14.5$ Hz, 1H), 2.82 (ddd, $J = 7.1, 7.6, 14.5$ Hz, 1H), 3.69 (s, 3H), 3.79 (t, $J = 7.6$ Hz, 1H), 5.10 (t, $J = 7.1$ Hz, 1H), 7.22–7.33 (m, 2H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.58 (s, 1H), 7.65 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.8, 25.7, 30.7, 42.1, 52.1, 111.5, 118.1, 120.1, 120.5, 122.5, 124.4, 126.9, 134.5, 142.2, 155.3, 173.6; HRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$ $[\text{M}]^+$ 258.1256, found 258.1247.



(S)-3-Benzyl-6,6-dimethyltetrahydro-2H-pyran-2-one (3f):⁸ $[\alpha]_{\text{D}}^{24}$

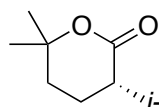
–17.8 (c 0.65, CHCl_3) for 49% ee; HPLC (Daicel Chiralpak AS-H, hexane–*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_{\text{R}} = 15.6$ (minor enantiomer), 19.0 (major enantiomer) min; IR (neat) 1709, 1454, 1369, 1113 cm^{-1} ;

¹H NMR (400 MHz, CDCl₃) δ 1.26 (s, 3H), 1.40 (s, 3H), 1.59–1.78 (m, 4H), 2.58–2.66 (m, 1H), 2.83 (dd, *J* = 9.2, 13.7 Hz, 1H), 3.35 (dd, *J* = 4.1, 13.7 Hz, 1H), 7.18–7.25 (m, 3H), 7.27–7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 27.8, 29.9, 33.7, 37.5, 41.5, 82.2, 126.5, 128.5 (2C), 129.3 (2C), 138.9, 173.4; HRMS (FAB+) calcd for C₁₄H₁₉O₂ [M+H]⁺ 219.1385, found 219.1382. The absolute configuration was assigned to be (*S*) by comparing the sign of measured optical rotation (Lit.⁸ [α]_D²³ +60.1 (*c* 1.06, CHCl₃) for 94% ee of (*R*)-**3f**).



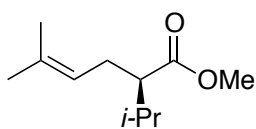
Methyl 2-benzyl-5-methyl-4-hexenoate (4f):⁸ [α]_D²⁷ −8.7 (*c* 0.39, CHCl₃)

for 42% ee; HPLC (Daicel Chiralpak IB-3, hexane–*i*-PrOH 200:1, flow rate 0.5 mL/min) *t*_R = 15.1 (minor enantiomer), 16.4 (major enantiomer) min; IR (neat) 1738, 1436, 1207, 1162 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 1.57 (s, 3H), 1.69 (s, 3H), 2.21 (td, *J* = 7.3, 14.6 Hz, 1H), 2.32 (td, *J* = 7.3, 14.6 Hz, 1H), 2.64–2.72 (m, 1H), 2.77 (dd, *J* = 6.4, 13.3 Hz, 1H), 2.93 (dd, *J* = 8.5, 13.3 Hz, 1H), 3.59 (s, 3H), 5.08 (t, *J* = 7.3 Hz, 1H), 7.13–7.22 (m, 3H), 7.24–7.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 17.8, 25.8, 30.5, 37.7, 47.8, 51.4, 120.7, 126.2, 128.3 (2C), 128.8 (2C), 134.1, 139.5, 175.7; HRMS (FAB+) calcd for C₁₅H₂₁O₂ [M+H]⁺ 233.1542, found 233.1546.



3-Isopropyl-6,6-dimethyltetrahydro-2H-pyran-2-one (3g): [α]_D²⁶ −36.3 (*c*

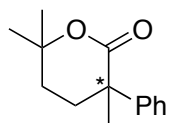
0.54, CHCl₃) for 88% ee; GC (β-TA, 100 kPa, column temperature 70 °C and then warm to 90 °C (+1 °C/min)) *t*_R = 35.9 (minor enantiomer), 37.6 (major enantiomer) min; IR (neat) 1719, 1461, 1375, 1284, 1114 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 1.71–1.87 (m, 4H), 2.29–2.36 (m, 1H), 2.55 (dsept, *J* = 3.4, 6.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 16.9, 17.8, 20.0, 27.6, 28.5, 30.2, 34.1, 45.6, 81.4, 173.4; HRMS (FAB+) calcd for C₁₀H₁₈O₂Na [M+Na]⁺ 193.1204, found 193.1174.



Methyl 2-isopropyl-5-methyl-4-hexenoate (4g):⁹ [α]_D²⁷ −11.8 (*c* 0.20,

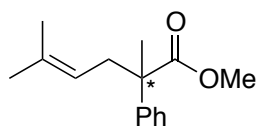
CHCl₃) for 78% ee; GC (β-CP, 50 kPa, column temperature 70 °C and then warm to 75 °C (+0.25 °C/min)) *t*_R = 60.4 (major enantiomer), 61.4 (minor enantiomer) min; IR (neat) 1736, 1461 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.60 (s, 3H),

1.67 (s, 3H), 1.87 (dsept, $J = 6.8, 6.8$ Hz, 1H), 2.10–2.32 (m, 3H), 3.65 (s, 3H), 5.04 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 20.3, 20.4, 25.8, 28.3, 30.3, 51.1, 53.0, 121.5, 133.3, 175.9; HRMS (EI+) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 184.1463, found 184.1456.



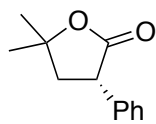
3,6,6-Trimethyltetrahydro-2H-pyran-2-one (3h): $[\alpha]_{\text{D}}^{27} +10.1$ (c 0.53, CHCl_3)

for 62% ee; HPLC (Daicel Chiralpak IC-3, hexane-*i*-PrOH 9:1, flow rate 1.0 mL/min) $t_{\text{R}} = 18.3$ (minor enantiomer), 20.7 (major enantiomer) min; IR (neat) 1716, 1452, 1302, 1275, 1113 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.37 (s, 3H), 1.44 (s, 3H), 1.62 (s, 3H), 1.65 (dd, $J = 5.0, 7.3$ Hz, 2H), 2.09 (td, $J = 7.3, 14.2$ Hz, 1H), 2.21 (td, $J = 5.0, 14.2$ Hz, 1H), 7.23–7.30 (m, 3H), 7.32–7.37 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.6, 28.5, 30.1, 31.4, 32.9, 47.2, 83.4, 125.9 (2C), 126.9, 128.7 (2C), 143.8, 175.2; HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found 219.1384.



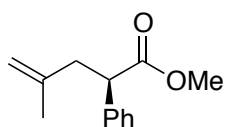
Methyl 2,5-diethyl-2-phenyl-4-hexenoate (4h): $[\alpha]_{\text{D}}^{27} -20.9$ (c 0.61, CHCl_3)

for 33% ee; HPLC (Daicel Chiralpak IC-3, hexane-*i*-PrOH 200:1, flow rate 1.0 mL/min) $t_{\text{R}} = 8.0$ (minor enantiomer), 9.7 (major enantiomer) min; IR (neat) 1732, 1446, 1236, 1100 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.51 (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 2.59 (dd, $J = 7.3, 14.2$ Hz, 1H), 2.79 (dd, $J = 7.3, 14.2$ Hz, 1H), 3.65 (s, 3H), 4.97 (t, $J = 7.3$ Hz, 1H), 7.22–7.27 (m, 1H), 7.30–7.36 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.9, 22.7, 26.0, 37.5, 50.6, 52.1, 119.5, 126.0 (2C), 126.6, 128.3 (2C), 134.7, 143.8, 176.6; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 233.1542, found 233.1534.



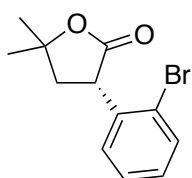
5,5-Dimethyl-3-phenyldihydrofuran-2(3H)-one (7a):¹⁰ $[\alpha]_{\text{D}}^{27} +5.8$ (c 0.62, CHCl_3)

for 83% ee; HPLC (Daicel Chiralcel OD-H, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_{\text{R}} = 8.4$ (major enantiomer), 9.9 (minor enantiomer) min; IR (neat) 1766, 1456, 1376, 1259, 1139, 1113 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.50 (s, 3H), 1.55 (s, 3H), 2.24 (dd, $J = 11.9, 12.8$ Hz, 1H), 2.58 (dd, $J = 9.2, 12.8$ Hz, 1H), 4.04 (dd, $J = 9.2, 11.9$ Hz, 1H), 7.27–7.32 (m, 3H), 7.34–7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.9, 28.9, 44.2, 46.9, 82.1, 127.5, 128.0 (2C), 128.8 (2C), 136.9, 176.5; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$ 191.1072, found 191.1061.



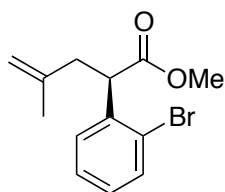
(R)-Methyl 4-methyl-2-phenyl-4-pentenoate (8a):¹⁰ $[\alpha]_{\text{D}}^{27} -40.6$ (*c* 0.78,

CHCl_3) for 43% ee; HPLC (Daicel Chiralpak IB-3, hexane-*i*-PrOH 200:1, flow rate 0.5 mL/min) $t_{\text{R}} = 10.6$ (major enantiomer), 11.3 (minor enantiomer) min; IR (neat) 1739, 1435, 1158 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.72 (s, 3H), 2.43 (dd, $J = 6.4, 14.6$ Hz, 1H), 2.84 (dd, $J = 9.2, 14.6$ Hz, 1H), 3.65 (s, 3H), 3.81 (dd, $J = 6.4, 9.2$ Hz, 1H), 4.69 (s, 1H), 4.75 (s, 1H), 7.24–7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.6, 41.3, 49.9, 52.0, 112.1, 127.3, 127.8 (2C), 128.6 (2C), 138.7, 142.6, 174.1; HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 205.1229, found 205.1208. The absolute configuration was assigned to be (*R*) by comparing the sign of measured optical rotation; optical rotation of **6a** was measured in $[\alpha]_{\text{D}}^{23} -58.6$ (*c* 0.75, CHCl_3) for 74% ee, which is compared with $[\alpha]_{\text{D}}^{20} +72.0$ (*c* 1.0, CHCl_3) for 91% ee of (*S*)-**6a**.⁵



3-(2-Bromophenyl)-5,5-dimethyldihydrofuran-2(3H)-one (7b): $[\alpha]_{\text{D}}^{23} -55.0$

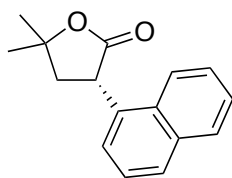
(*c* 0.47, CHCl_3) for 78% ee; HPLC (Daicel Chiralcel OD-H, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_{\text{R}} = 8.3$ (major enantiomer), 9.9 (minor enantiomer) min; IR (neat) 1769, 1474, 1271, 1141 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.52 (s, 3H), 1.55 (s, 3H), 2.11 (dd, $J = 11.9-, 12.8$ Hz, 1H), 2.67 (dd, $J = 9.3, 12.8$ Hz, 1H), 4.46 (dd, $J = 9.3, 11.9$ Hz, 1H), 7.17 (dt, $J = 1.8, 7.8$ Hz, 1H), 7.29 (dd, $J = 1.8, 7.8$ Hz, 1H), 7.34 (dt, $J = 1.4, 7.8$ Hz, 1H), 7.58 (dd, $J = 1.4, 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.1, 28.8, 43.5, 47.7, 82.5, 124.6, 128.1, 129.2, 129.7, 133.1, 137.0, 175.7; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{14}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ 269.0177, found 269.0159.



Methyl 2-(2-bromophenyl)-4-methyl-4-pentenoate (8b): $[\alpha]_{\text{D}}^{23} -18.4$ (*c*

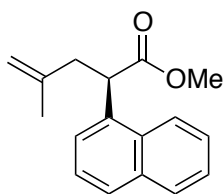
0.76, CHCl_3) for 30% ee; HPLC (Daicel Chiralpak IB-3, hexane-*i*-PrOH 200:1, flow rate 0.5 mL/min) $t_{\text{R}} = 11.0$ (major enantiomer), 12.0 (minor enantiomer) min; IR (neat) 1739, 1435, 1163, 1022 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.77 (s, 3H), 2.45 (dd, $J = 6.4, 14.7$ Hz, 1H), 2.77 (dd, $J = 8.7, 14.7$ Hz, 1H), 3.68 (s, 3H), 4.42 (dd, $J = 6.4, 8.7$ Hz, 1H), 4.70 (s, 1H), 4.75 (s, 1H), 7.12 (dt,

$J = 1.8, 7.8$ Hz, 1H), 7.29 (dt, $J = 1.4, 7.8$ Hz, 1H), 7.41 (dd, $J = 1.8, 7.8$ Hz, 1H), 7.57 (dd, $J = 1.4, 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.4, 40.8, 48.3, 52.1, 112.4, 124.6, 127.7, 128.6 (2C), 133.0, 138.1, 142.2, 173.4; HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{16}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ 283.0334, found 283.0323.



5,5-Dimethyl-3-(1-naphthalenyl)dihydrofuran-2(3H)-one (7c): $[\alpha]_{\text{D}}^{23}$

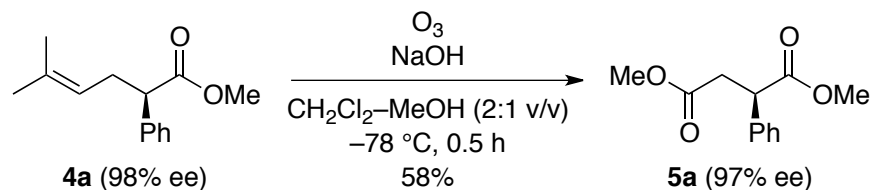
-108.5 (c 0.55, CHCl_3) for 82% ee; HPLC (Daicel Chiralpak IA-3, hexane-*i*-PrOH 4:1, flow rate 1.0 mL/min) $t_{\text{R}} = 11.3$ (major enantiomer), 14.4 (minor enantiomer) min; IR (neat) 1765, 1269, 1138 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.56 (s, 3H), 1.60 (s, 3H), 2.31 (dd, $J = 10.6, 12.8$ Hz, 1H), 2.74 (dd, $J = 9.6, 12.8$ Hz, 1H), 4.72 (dd, $J = 9.6, 10.6$ Hz, 1H), 7.44–7.58 (m, 4H), 7.79–7.592 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.6, 29.0, 44.1, 44.5, 82.6, 122.8, 125.6, 125.8 (2C), 126.4, 128.3, 129.2, 131.2, 133.6, 134.0, 176.8; HRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 241.1229, found 241.1223.



Methyl 4-methyl-2-(1-naphthalenyl)-4-pentenoate (8c): $[\alpha]_{\text{D}}^{23}$

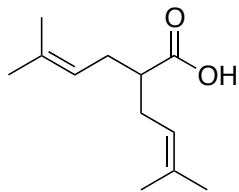
-59.9 (c 0.65, CHCl_3) for 53% ee; HPLC (Daicel Chiralpak IB-3, hexane-*i*-PrOH 200:1, flow rate 0.5 mL/min) $t_{\text{R}} = 17.0$ (minor enantiomer), 18.7 (major enantiomer) min; IR (neat) 1738, 1435, 1155 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.78 (s, 3H), 2.57 (dd, $J = 5.0, 14.7$ Hz, 1H), 3.02 (dd, $J = 9.2, 14.7$ Hz, 1H), 3.65 (s, 3H), 4.67 (dd, $J = 5.0, 9.2$ Hz, 1H), 4.78 (s, 1H), 4.79 (s, 1H), 7.42–7.59 (m, 4H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 1H), 8.16 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 40.9, 45.0, 52.1, 112.0, 122.9, 124.8, 125.5, 125.6, 126.4, 127.8, 129.0, 131.4, 134.0, 134.9, 143.0, 174.3; HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 254.1307, found 254.1328.

Synthesis of 2-Substituted Succinate **5a**.

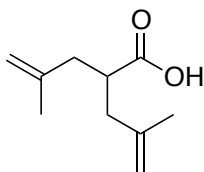


(R)-Dimethyl 2-phenylsuccinate (5a):¹¹ To a solution of **4a** (5.3 mg, 0.024 mmol) in CH₂Cl₂ (1 mL) was added a 2.5 M solution of NaOH in MeOH (0.5 mL). The resulting mixture was cooled to -78 °C and O₃ was bubbled through continuously. After 30 min, the reaction mixture was diluted with H₂O (2 mL) and ether (2 mL) and warmed to room temperature. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous MgSO₄ and concentrated. The residue was purified by preparative TLC (hexane-EtOAc 10:1) to give (*R*)-**5a**¹¹ as a clear oil (3.1 mg, 58% yield). $[\alpha]_D^{21} -78.5$ (*c* 0.21, CHCl₃) for 97% ee; HPLC (Daicel Chiralpak IA, hexane-*i*-PrOH 100:1, flow rate 1.0 mL/min) $t_R = 13.98$ (major enantiomer), 15.4 (minor enantiomer) min; ¹H NMR (400 MHz, CDCl₃) δ 2.67 (dd, *J* = 5.0, 17.0 Hz, 1H), 3.22 (dd, *J* = 10.1, 17.0 Hz, 1H), 3.679 (s, 3H), 3.683 (s, 3H), 4.10 (dd, *J* = 5.0, 10.1 Hz, 1H), 7.25–7.36 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 37.6, 47.0, 51.9, 52.4, 127.7 (3C), 128.9 (2C), 137.6, 172.0, 173.4. The absolute configuration was assigned to be (*R*) by comparing the sign of measured optical rotation (Lit.¹¹ $[\alpha]_D^{20} +47.43$ (*c* 0.58, CHCl₃) for 34% ee of (*R*)-isomer).

Preparation of achiral- α -Substituted Carboxylic Acid **9** and **11**.



5-Methyl-2-(3-methylbut-2-en-1-yl)-4-hexenoic acid (9): To a suspension mixture of NaH (abt. 60% oil suspension, 1.2 g, 30 mmol) in THF (40 mL) was carefully added a solution of diethyl malonate (1.5 mL, 10 mmol) in THF (5 mL) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 2 h. To this suspension, 1-bromo-3-methyl-2-butene (2.9 mL, 25 mmol) was added dropwise, and then the reaction mixture was heated to reflux for 1 day. After cooling to room temperature, the reaction was quenched with saturated aq. NH_4Cl , and the mixture was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous MgSO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 10:1) to give disubstituted malonate as pale yellow oil (2.52 g, 85% yield). The disubstituted malonate was dissolved in DMSO (17 mL), followed by addition of H_2O (460 mL, 25.5 mmol) and LiCl (720 mg, 17 mmol). The reaction mixture was stirred at 180 °C for 1 day. After cooling to room temperature, the mixture was diluted with hexane/ether (1:1) and extracted with hexane/ether (1:1). The residue was purified by column chromatography on silica gel (hexane–EtOAc 10:1) to give ethyl ester of **9** of as pale yellow oil (1.49 g, 78 % yield). To a solution of ethyl ester of **9** in EtOH (30 mL) was added a solution of 2 M aqueous NaOH (5 mL) and was heated to reflux for 1 day. The reaction mixture was cooled, and then concentrated under reduced pressure to remove the solvent. The residue was taken with water and acidized with 1 M aqueous HCl. The reaction mixture was extracted with EtOAc, dried over anhydrous MgSO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 2:1) to give **9** (0.93 g, 72% yield) as colorless oil. IR (neat) 3250–2750, 1706, 1442, 1224 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.61 (s, 6H), 1.69 (s, 6H), 2.21 (td, $J = 7.3, 14.2$ Hz, 2H), 2.32 (td, $J = 7.3, 14.2$ Hz, 2H), 2.34–2.44 (m, 1H), 5.10 (t, $J = 7.3$ Hz, 2H), 9.52–11.12 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7 (2C), 25.8 (2C), 30.0 (2C), 46.1, 120.9 (2C), 134.0 (2C), 182.3; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 197.1542, found 197.1533.

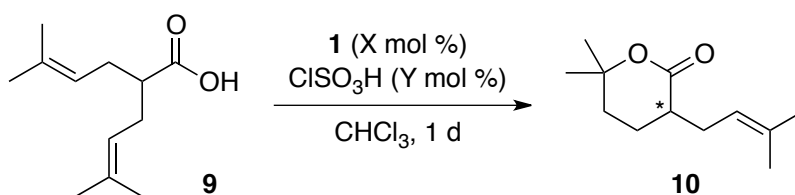


4-Methyl-2-(2-methylallyl)-4-pentenoic acid (11): Compound **11** was prepared from diethyl malonate and 3-bromo-2-methyl-1-propene according to the same manner as **9**. IR (neat) 3250–2750, 1710, 1444, 1291, 1239 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.74 (s, 6H),

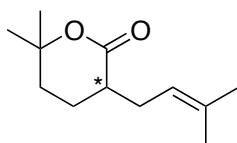
2.18 (dd, $J = 6.0, 14.2$ Hz, 2H), 2.36 (dd, $J = 9.2, 14.2$ Hz, 2H), 2.81 (tt, $J = 6.0, 9.2$ Hz, 1H), 4.75 (s, 2H), 4.79 (s, 2H), 10.03–11.17 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.2 (2C), 40.1 (2C), 42.4, 112.5 (2C), 142.4 (2C), 182.1; HRMS (FAB+) calcd for $\text{C}_{10}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 169.1229, found 169.1259.

Typical Procedure for the Desymmetrization of **9** and **11**.

To a solution of **1** (36.4 mg, 0.040 mmol) in CHCl₃ (1.8 mL) was added a 0.10 M solution of ClSO₃H in CHCl₃ (0.1 mL, 0.010 mmol) at -40 °C, and the mixture was stirred for ca. five minutes. To this solution, a solution of **9** (19.6 mg, 0.10 mmol) in CHCl₃ (0.1 mL) was added dropwise at -40 °C, and the mixture was stirred at -30 °C for 1 day. The reaction was quenched with water (3 mL) and the reaction mixture was extracted with ether. The combined organic layers were dried over anhydrous MgSO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane-CHCl₃-EtOAc 3:3:1) to give **10** (16.0 mg, 82% yield).

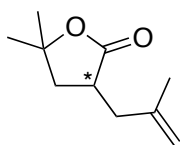


entry	X (mol %)	Y (mol %)	temp (°C)	yield (%) ^a	ee (%) ^b
1	40	10	-30	82	79
2 ^c	100	20	-40	95	81



6,6-Dimethyl-3-(3-methylbut-2-en-1-yl)tetrahydro-2H-pyran-2-one (10):

$[\alpha]_D^{27} -34.1$ (*c* 0.45, CHCl₃) for 79% ee; GC (γ -TA, 100 kPa, column temperature 90 °C and then warm to 110 °C (+1 °C/min)) $t_R = 35.2$ (minor enantiomer), 36.3 (major enantiomer) min; IR (neat) 1722, 1448, 1370, 1280, 1113 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.37 (s, 3H), 1.41 (s, 3H), 1.62–1.85 (m, 3H), 1.64 (s, 3H), 1.72 (s, 3H), 1.85–1.94 (m, 1H), 2.30–2.44 (m, 2H), 2.52–2.60 (m, 1H), 5.12 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.9, 21.9, 25.8, 27.9, 29.8, 30.0, 33.8, 40.0, 82.0, 120.8, 134.4, 173.8; HRMS (FAB⁺) calcd for C₁₂H₂₁O₂ [M+H]⁺ 197.1542, found 197.1545.



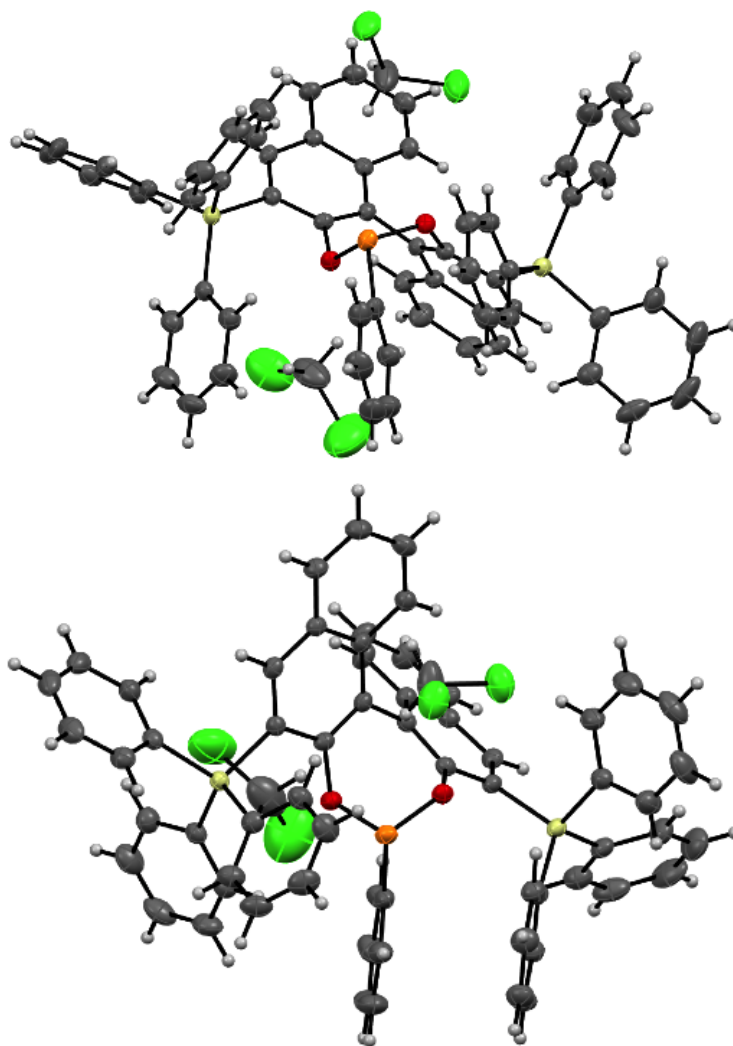
5,5-Dimethyl-3-(2-methylallyl)dihydrofuran-2H(3H)-one (12):

$[\alpha]_D^{22} -44.5$ (*c* 0.62, CHCl₃) for 76% ee; GC (β -TA, 100 kPa, column temperature 70 °C and then warm to 90 °C (+1 °C/min)) $t_R = 32.3$ (major enantiomer), 33.9 (minor enantiomer) min; IR (neat) 1764, 1278, 1133 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.39 (s, 3H), 1.47 (s, 3H), 1.72 (dd, *J* = 11.0, 12.8

Hz, 1H), 1.74 (s, 3H), 2.11 (dd, $J = 10.8, 14.4$ Hz, 1H), 2.22 (dd, $J = 9.2, 12.8$ Hz, 1H), 2.70 (dd, $J = 3.9, 14.4$ Hz, 1H), 2.93 (dddd, $J = 3.9, 9.2, 10.8, 11.0$ Hz, 1H), 4.73 (s, 1H), 4.81 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.0, 27.3, 29.0, 39.1, 39.2, 41.1, 82.4, 112.3, 142.4, 178.4; HRMS (FAB+) calcd for $\text{C}_{10}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 169.1229, found 169.1226.

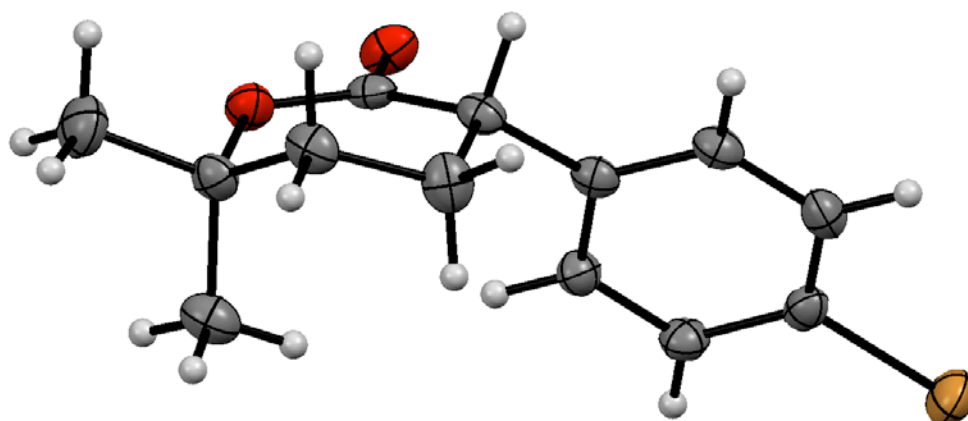
X-Ray Diffraction Analysis of Chiral Phosphorus(III) Compound 1.

Bruker SMART APEX diffractometer with CCD detector (graphite monochromator, MoK α radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. Formula C₆₄H₅₀Cl₄O₂PSi₂, colorless, crystal dimensions 0.30 × 0.20 × 0.20 mm³, monoclinic, space group *P21*(#4), $a = 11.3206(16)$ Å, $b = 15.770(2)$ Å, $c = 15.654(2)$ Å, $\beta = 100.743(2)^\circ$, $V = 2745.7(7)$ Å³, $Z = 2$, and $D_{\text{calc}} = 1.306$ g cm⁻³, $F(000) = 1120$, $\mu = 0.333$ mm⁻¹, $T = 173(2)$ K. 12974 reflections collected, 12271 independent reflections with $I > 2\sigma(I)$ ($2\theta_{\text{max}} = 28.33^\circ$), and 658 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R_1 = 0.0392$ and $wR_2 = 0.1018$, GOF = 1.027. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk]. Supplementary publication no. CCDC-934315.



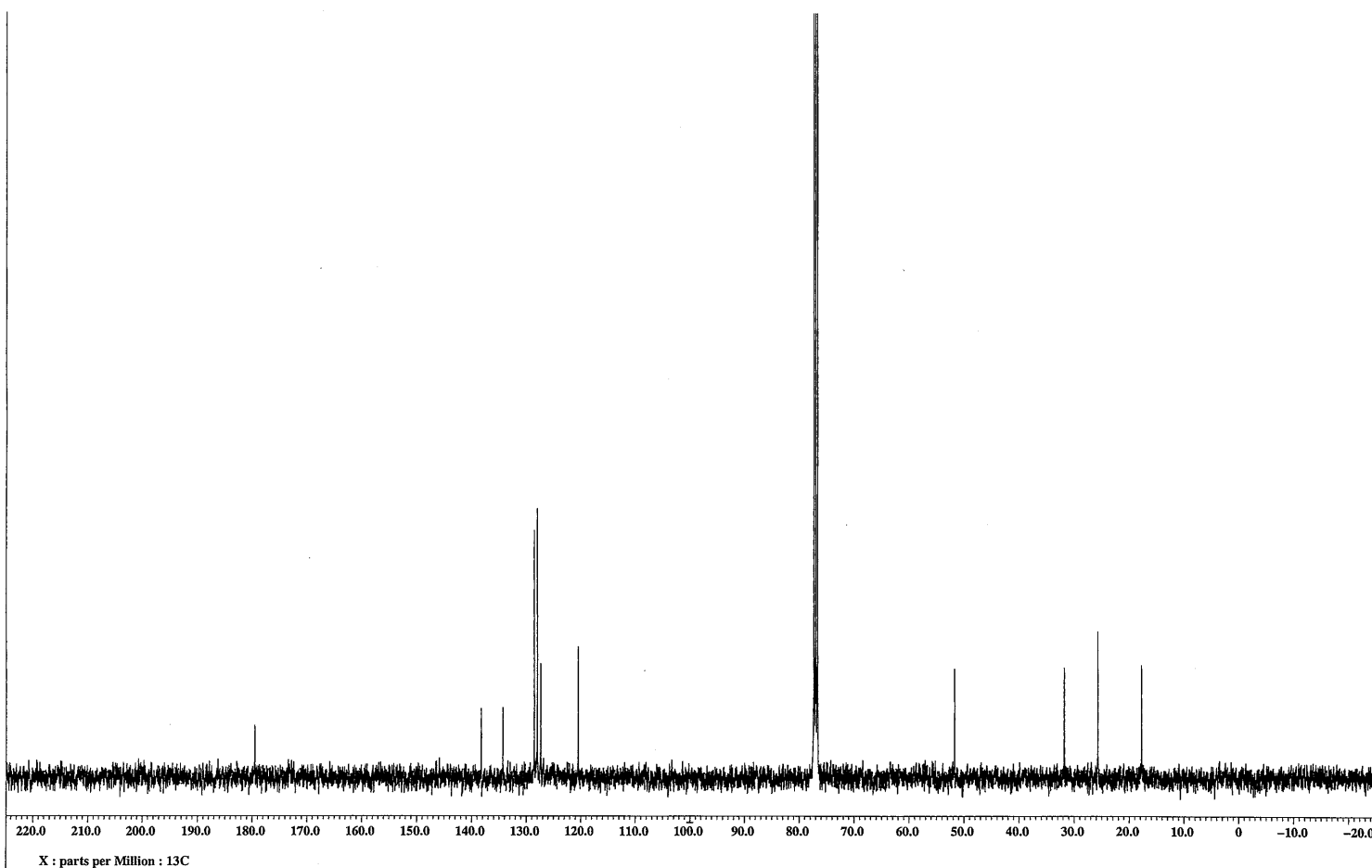
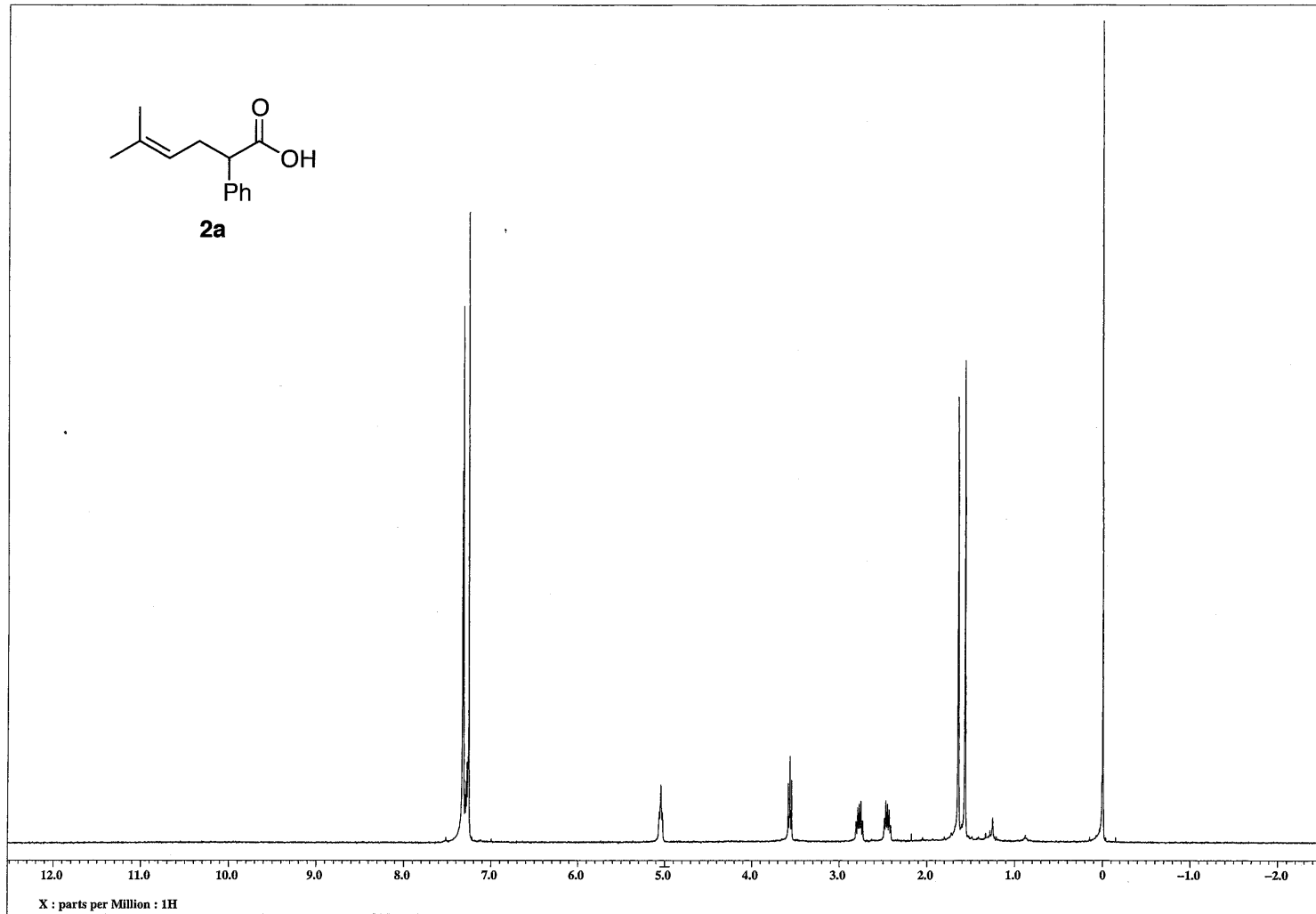
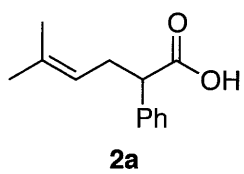
X-Ray Diffraction Analysis of (*S*)-Lactone 3b.

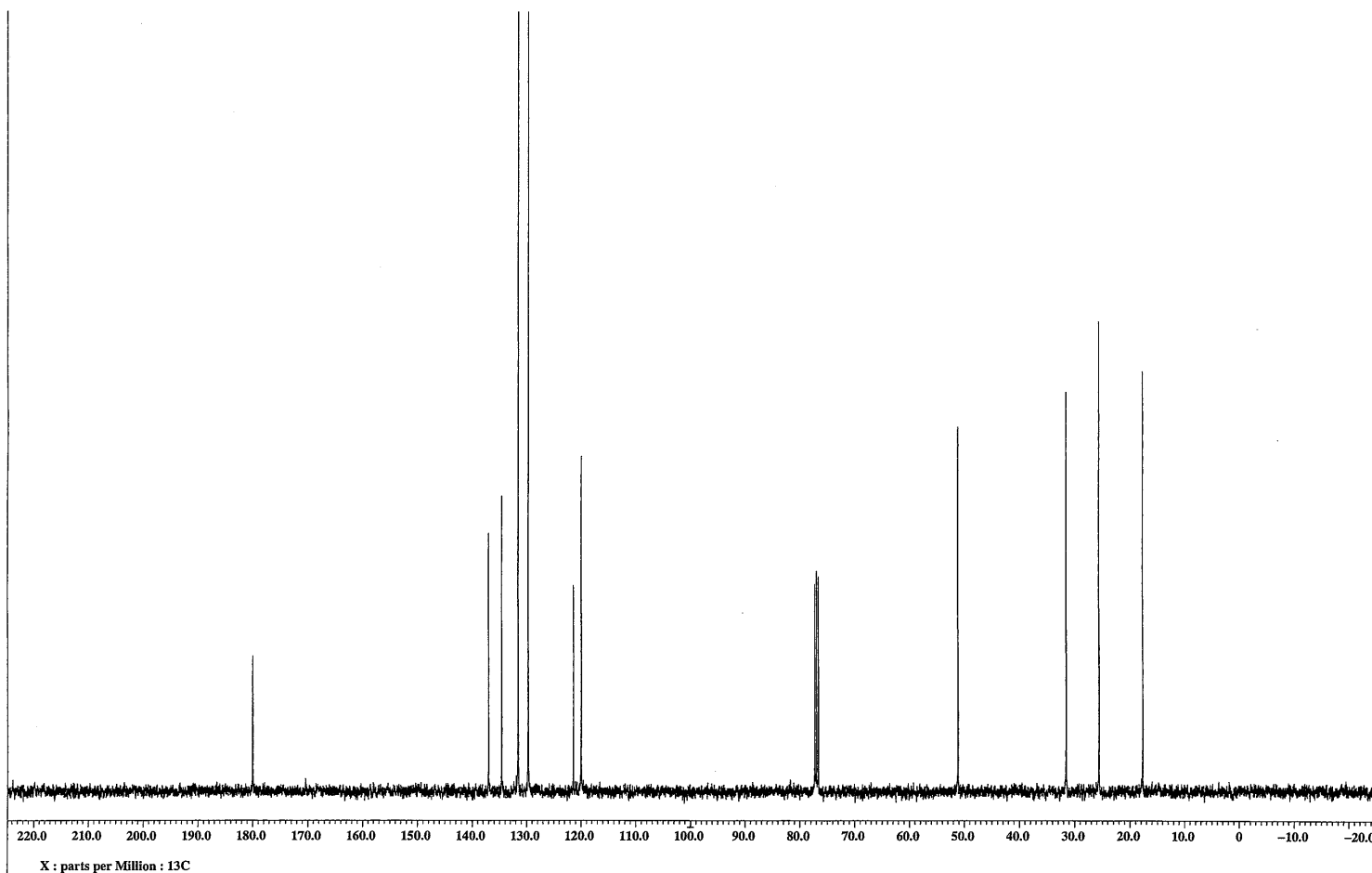
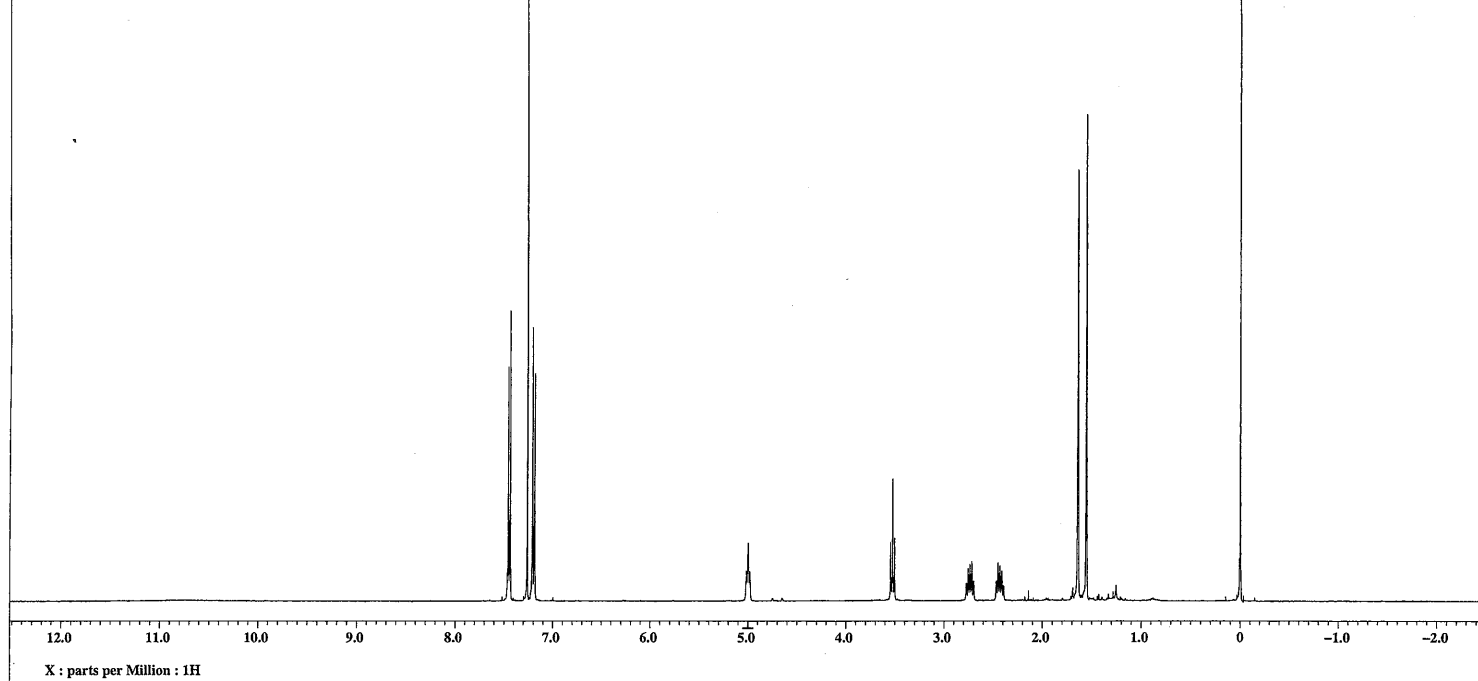
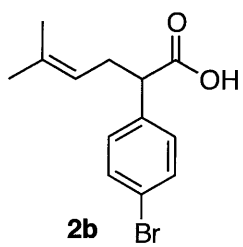
Bruker SMART APEX diffractometer with CCD detector (graphite monochromator, MoK α radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. Formula C₁₃H₁₅BrO₂, colorless, crystal dimensions 0.20 × 0.20 × 0.20 mm³, monoclinic, space group *P21*(#4), $a = 8.3392(16)$ Å, $b = 6.2230(12)$ Å, $c = 23.746(5)$ Å, $\beta = 90.126(3)^\circ$, $V = 1232.3(4)$ Å³, $Z = 4$, and $D_{\text{calc}} = 1.526$ g cm⁻³, $F(000) = 576$, $\mu = 3.319$ mm⁻¹, $T = 123(2)$ K. 4957 reflections collected, 4533 independent reflections with $I > 2\sigma(I)$ ($2\theta_{\text{max}} = 28.33^\circ$), and 293 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R_1 = 0.0258$ and $wR2 = 0.0637$, GOF = 1.051. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk]. Supplementary publication no. CCDC-934314.

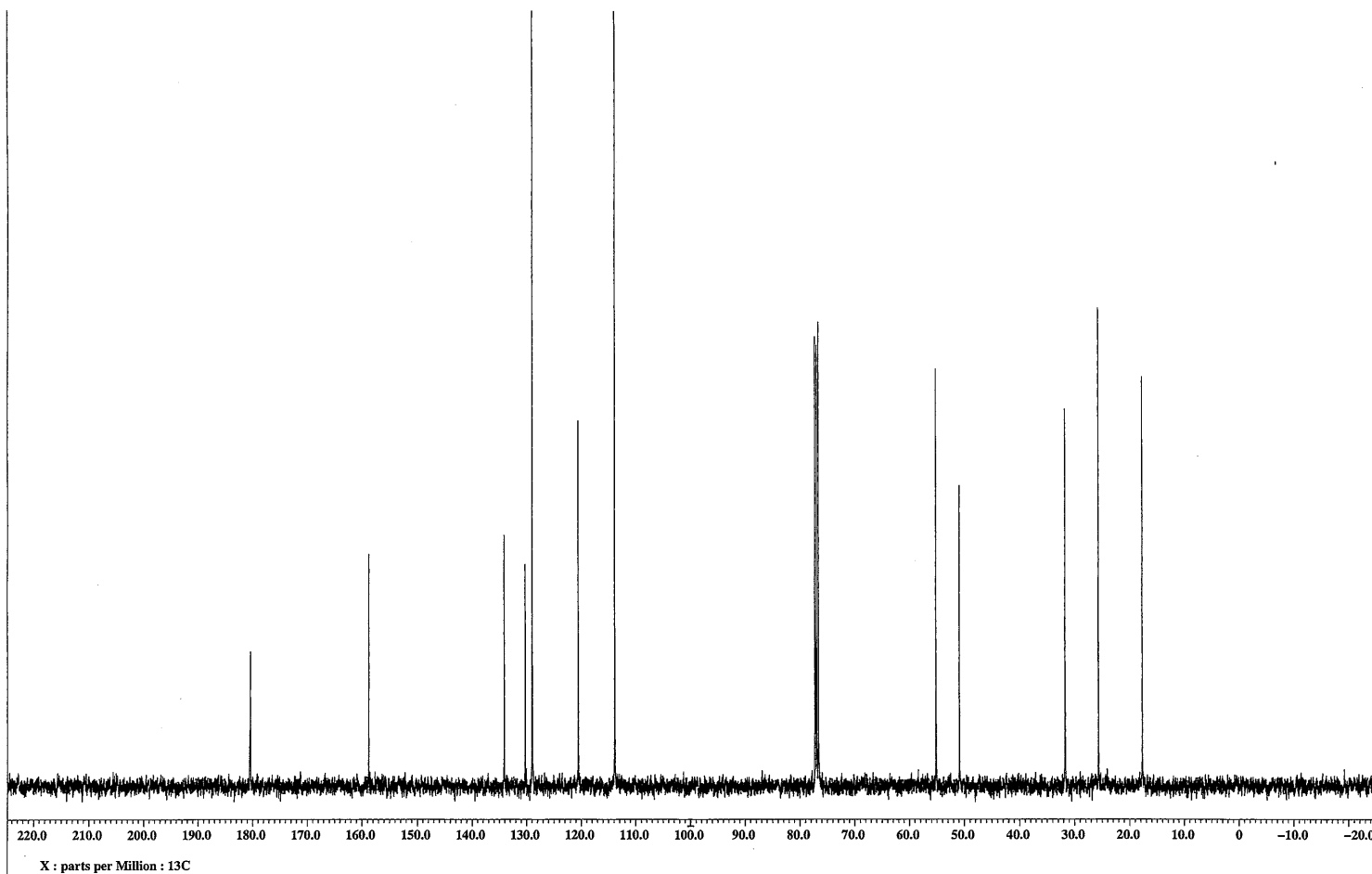
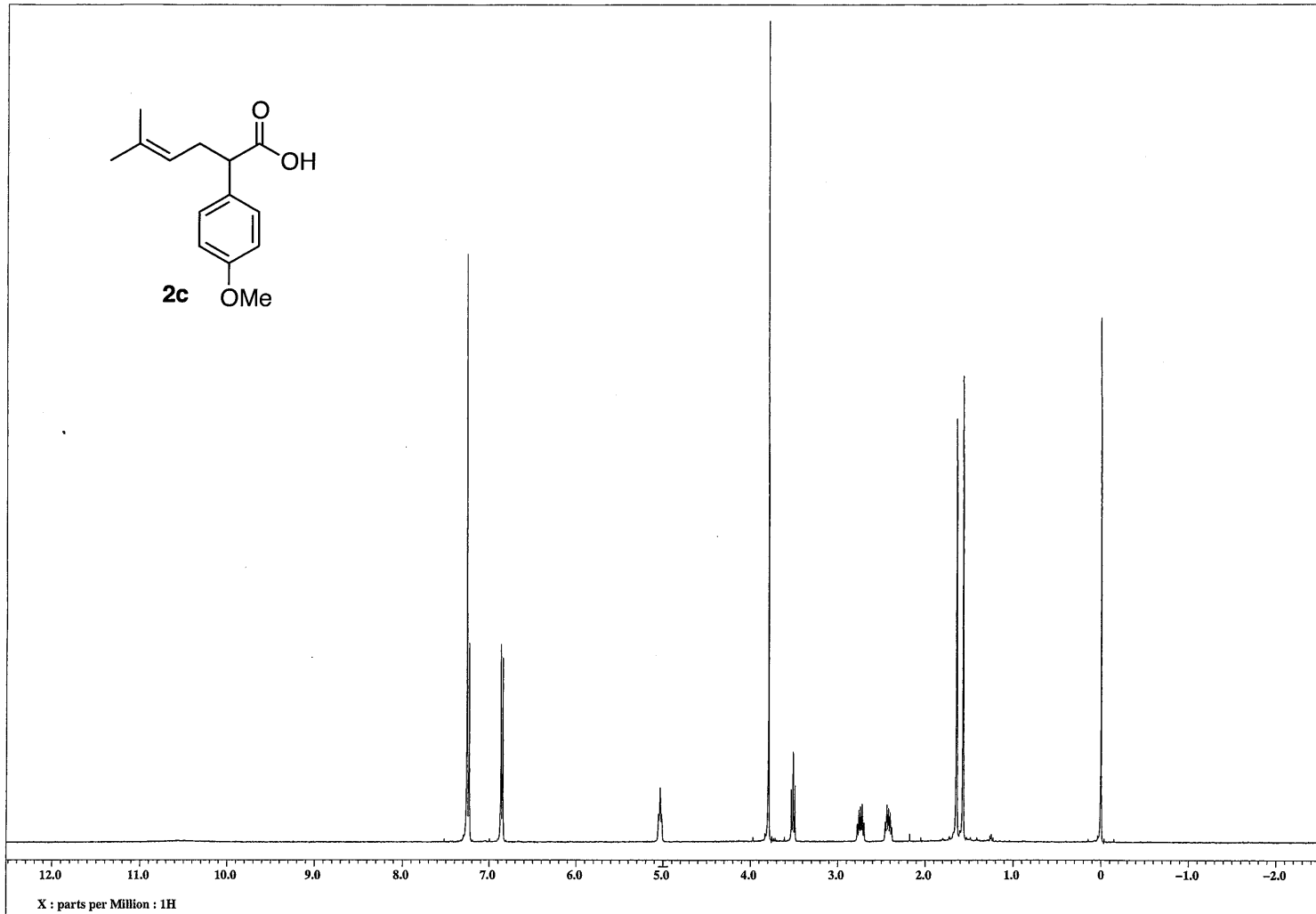
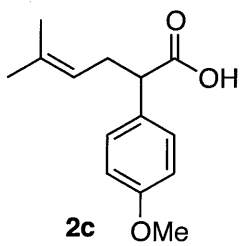


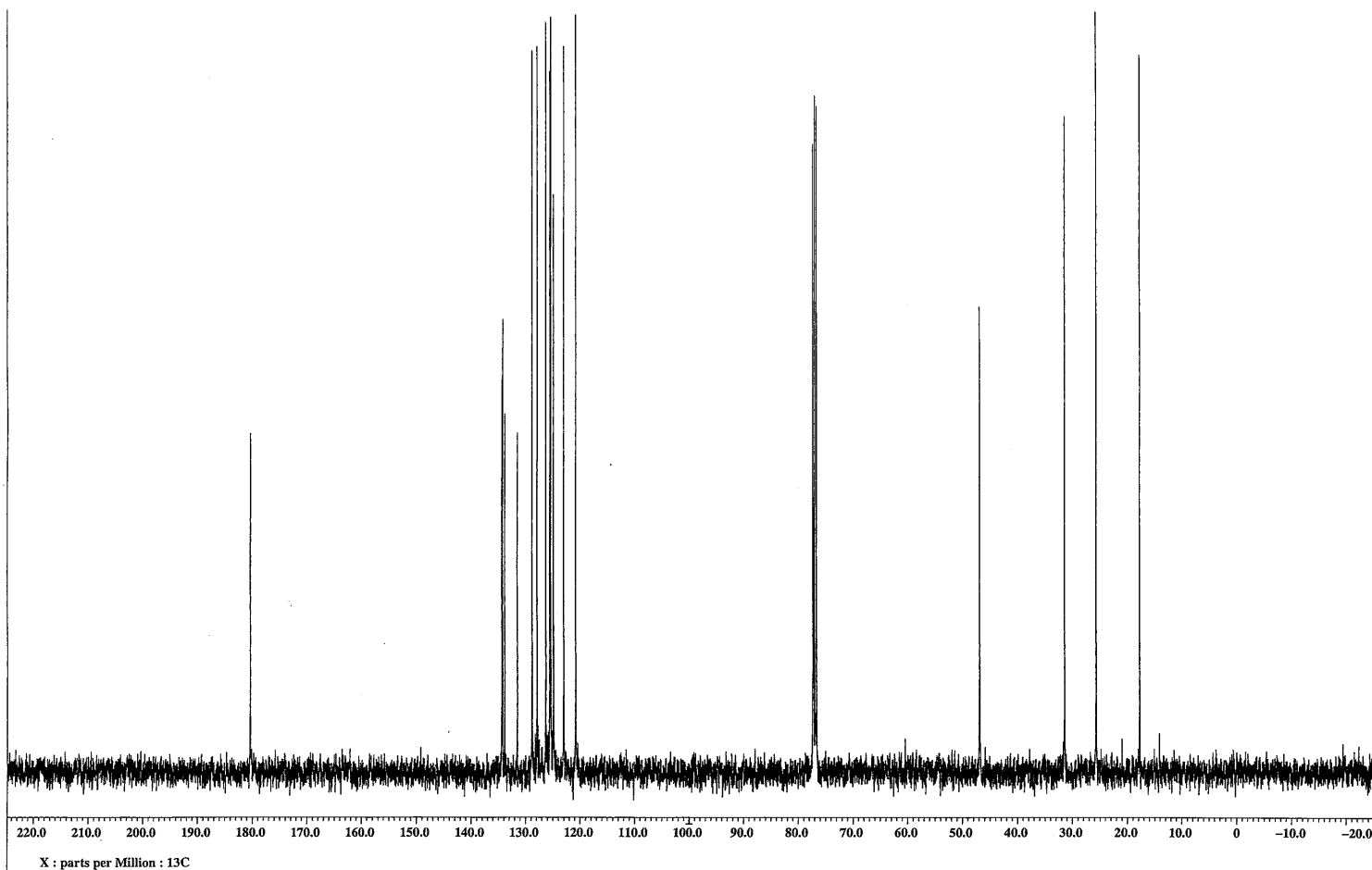
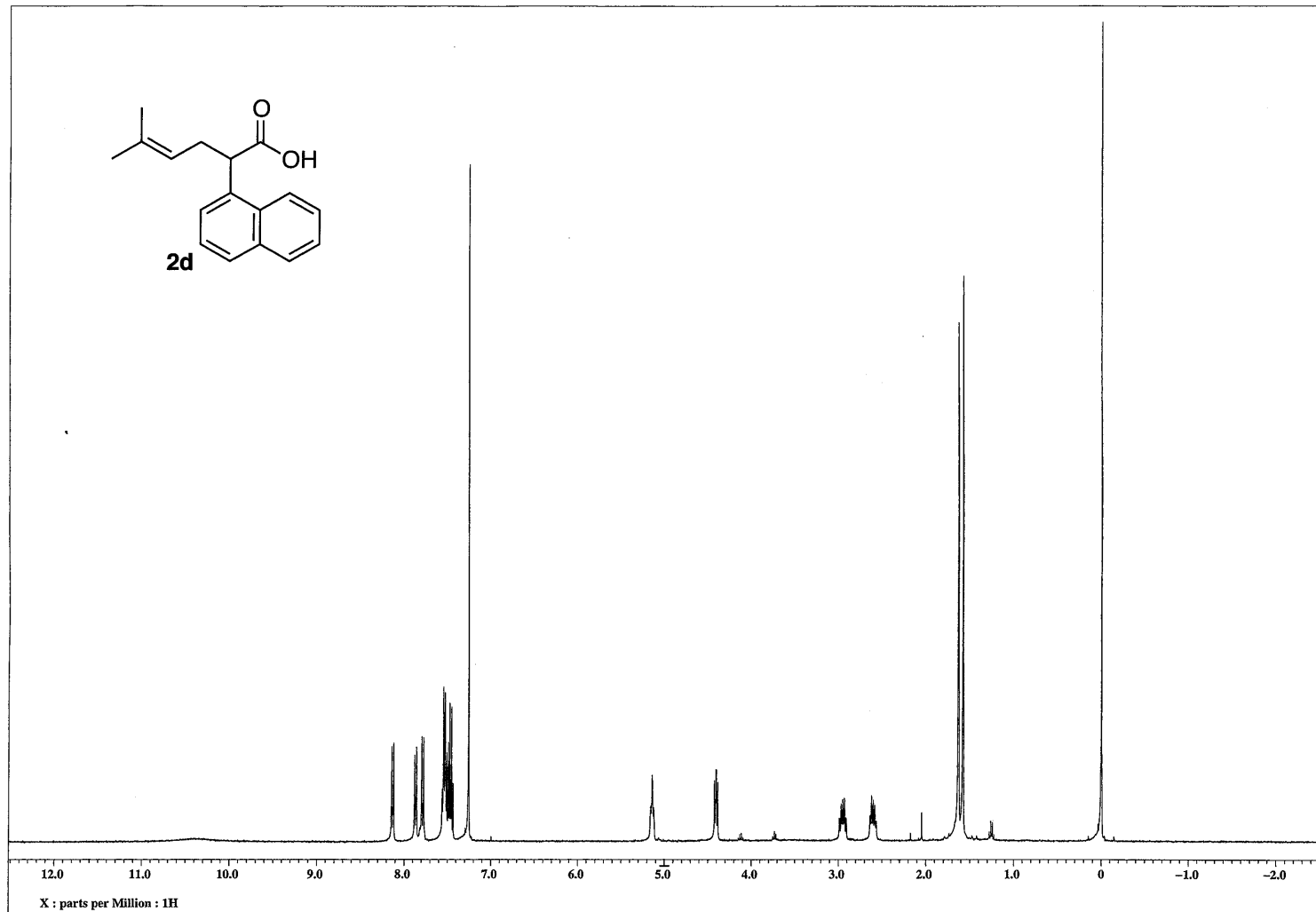
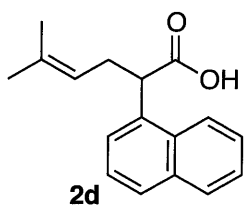
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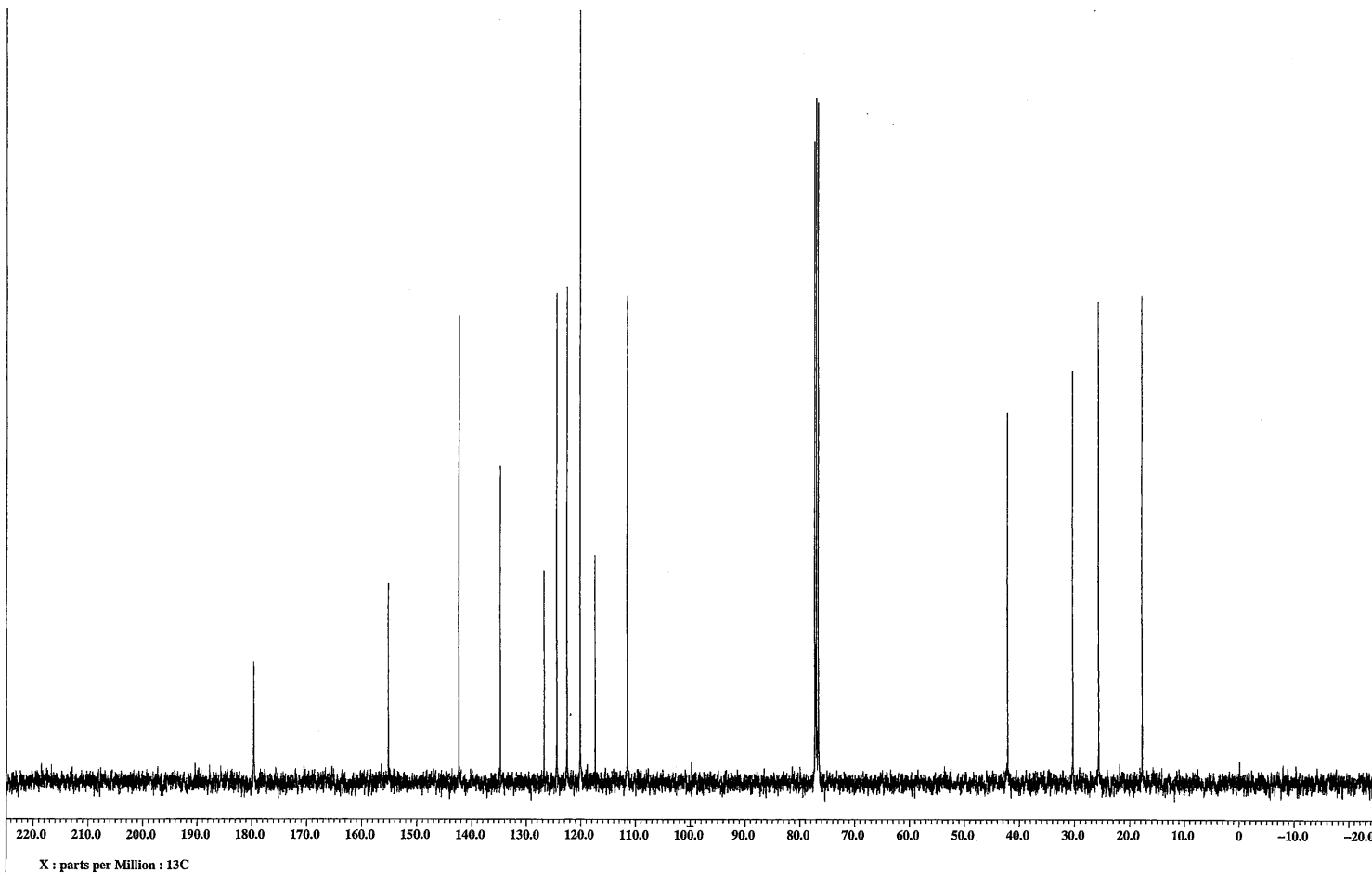
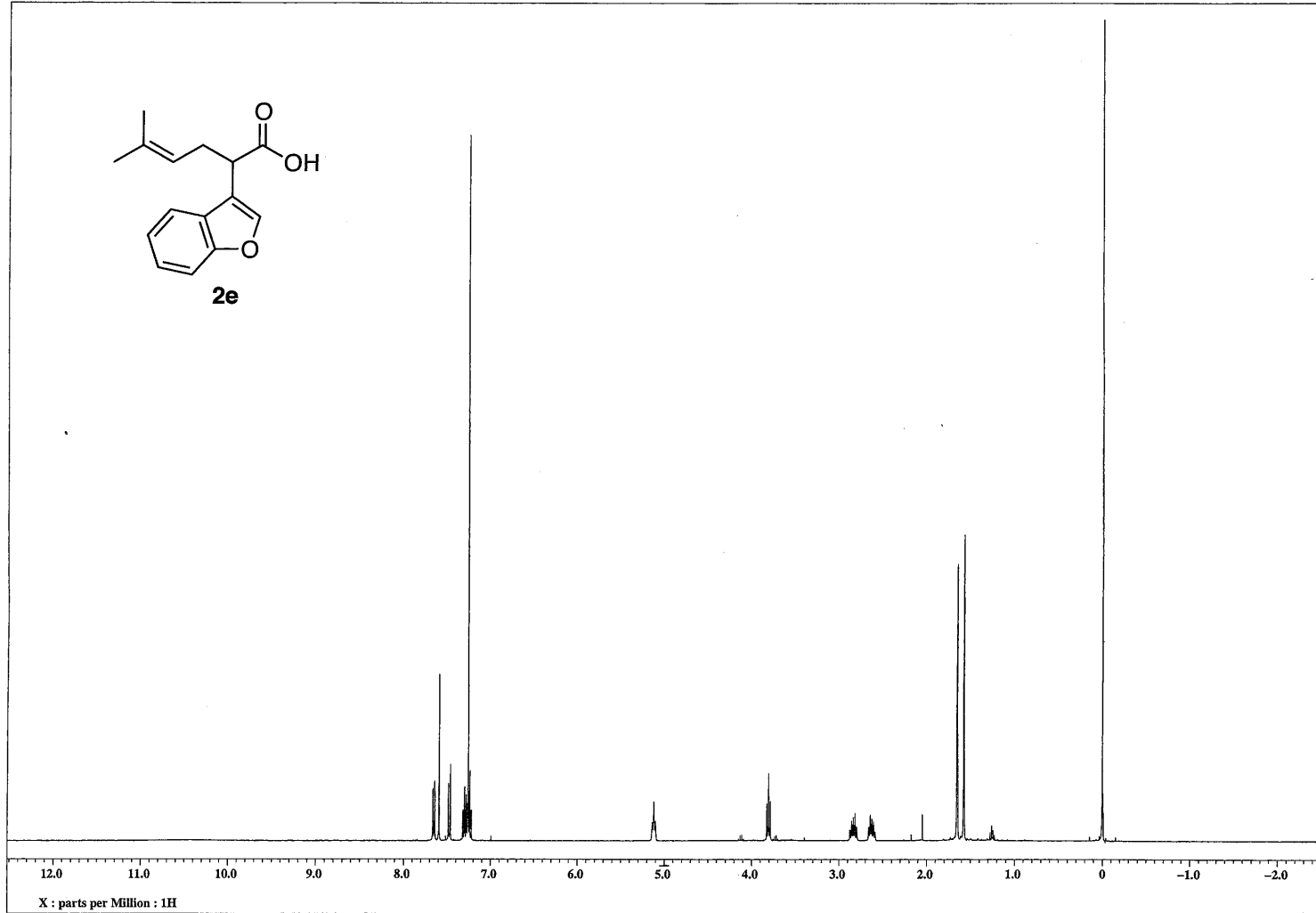
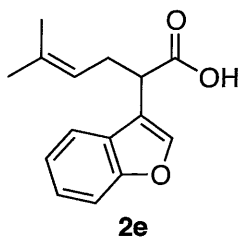
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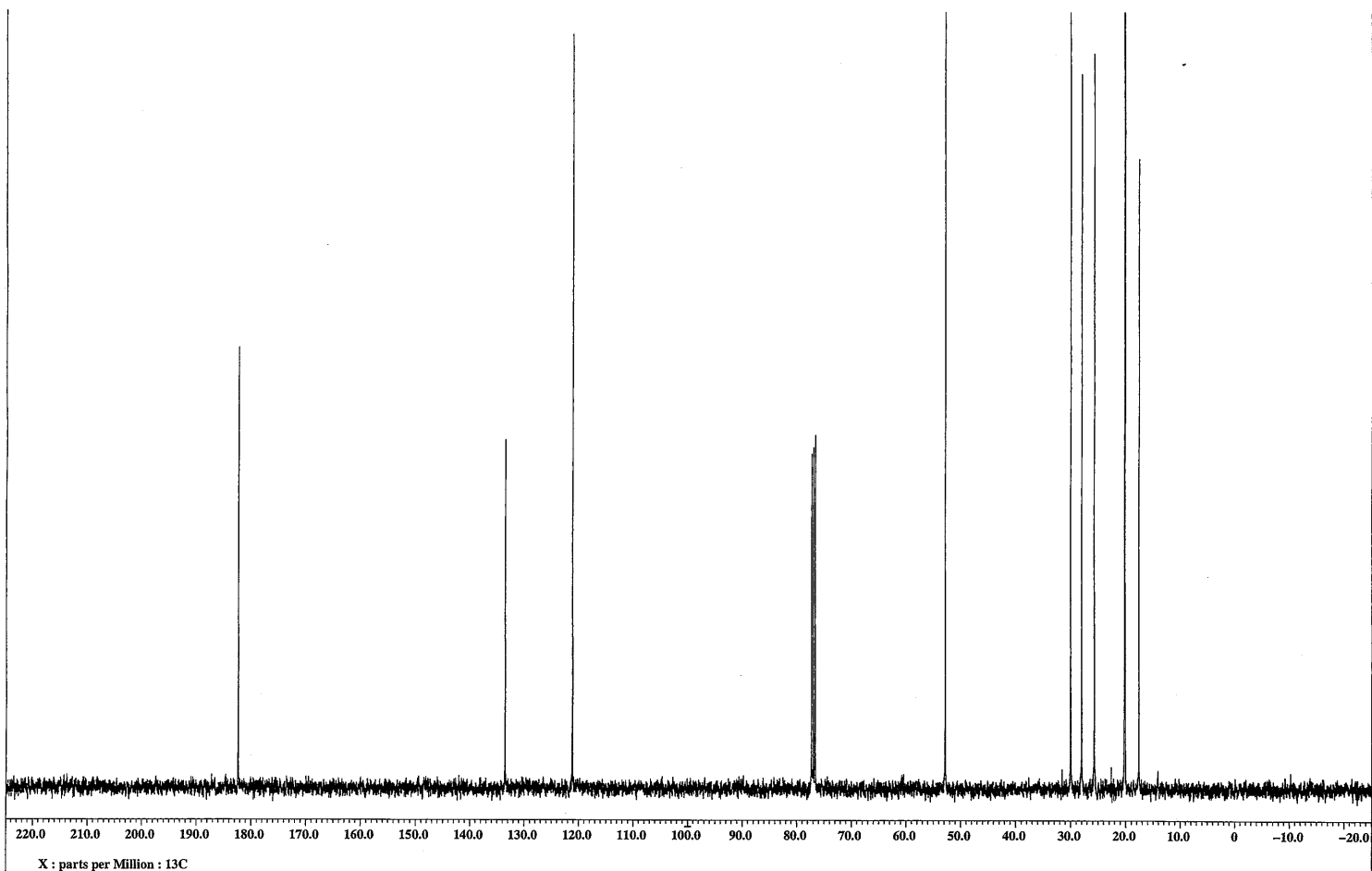
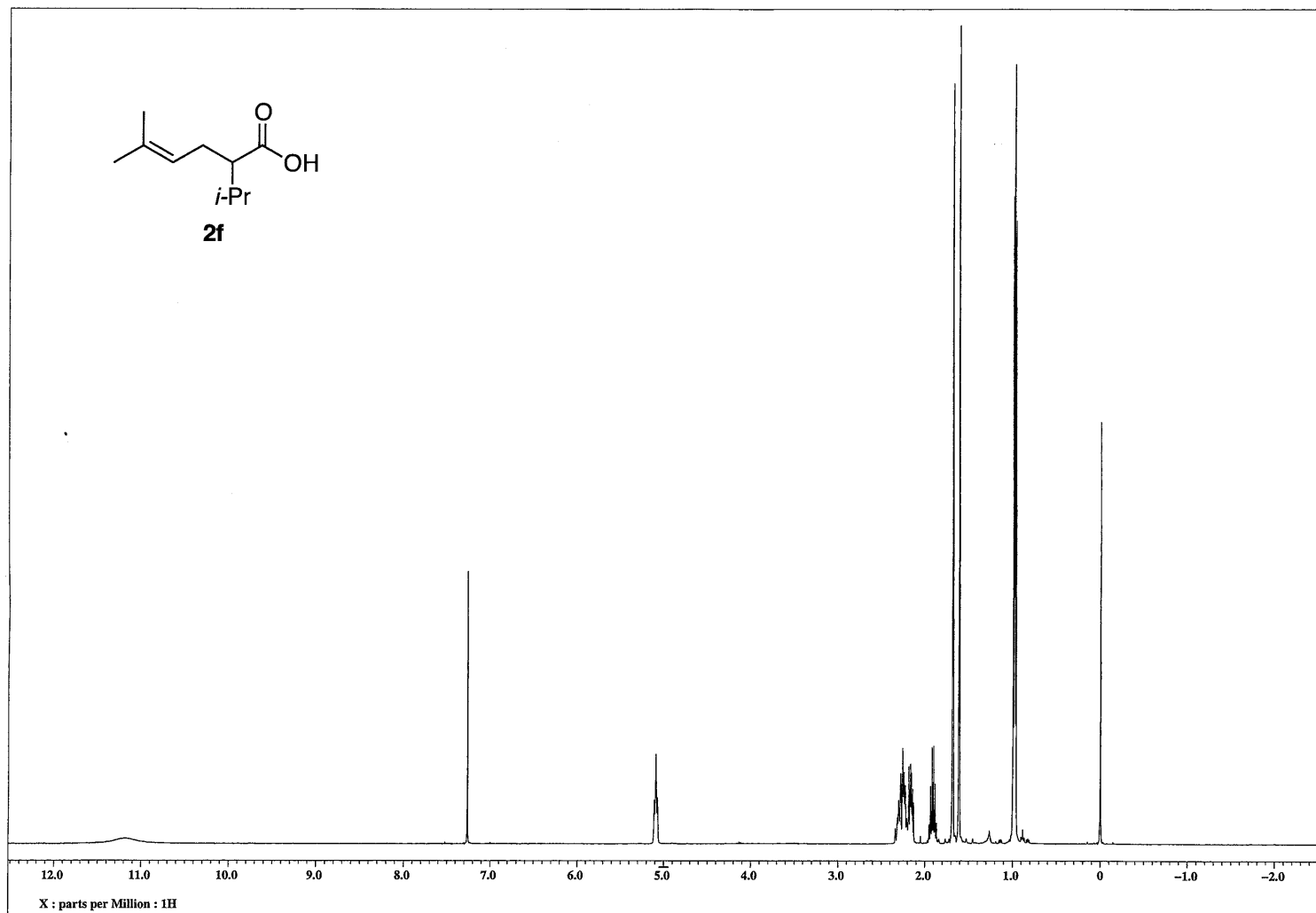
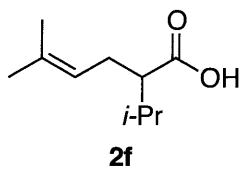


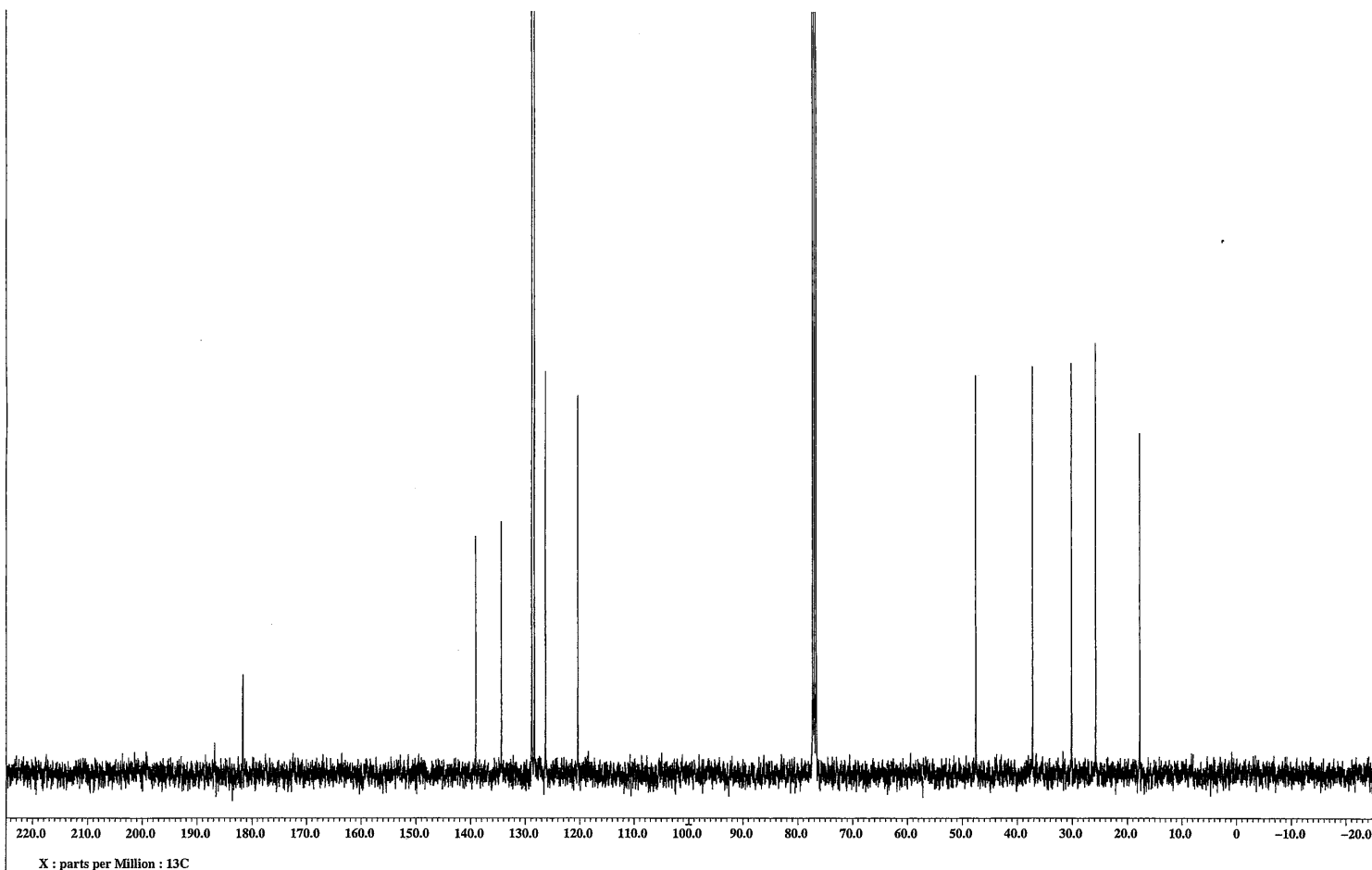
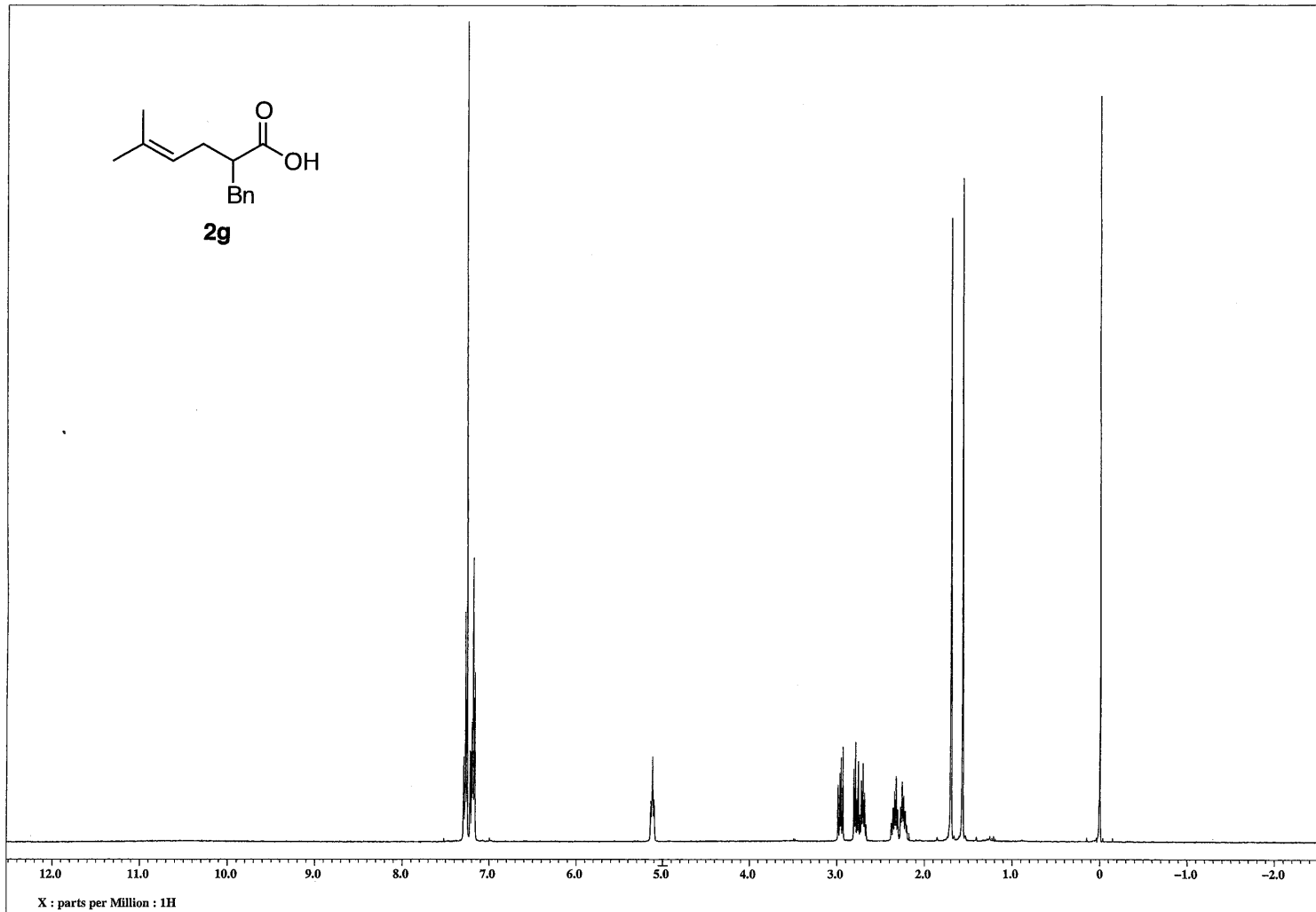
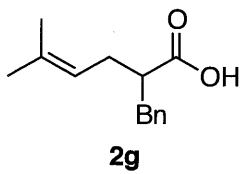


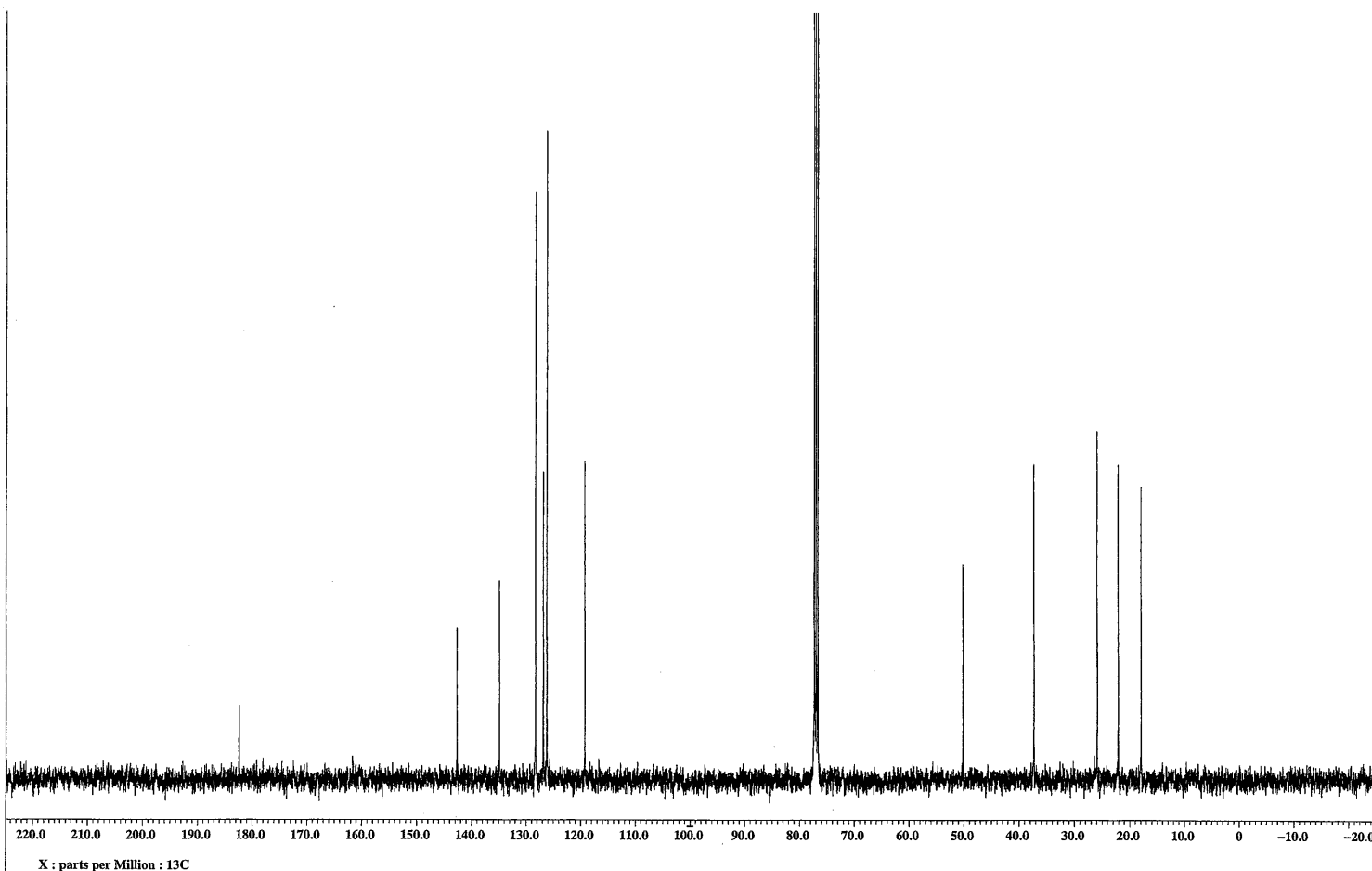
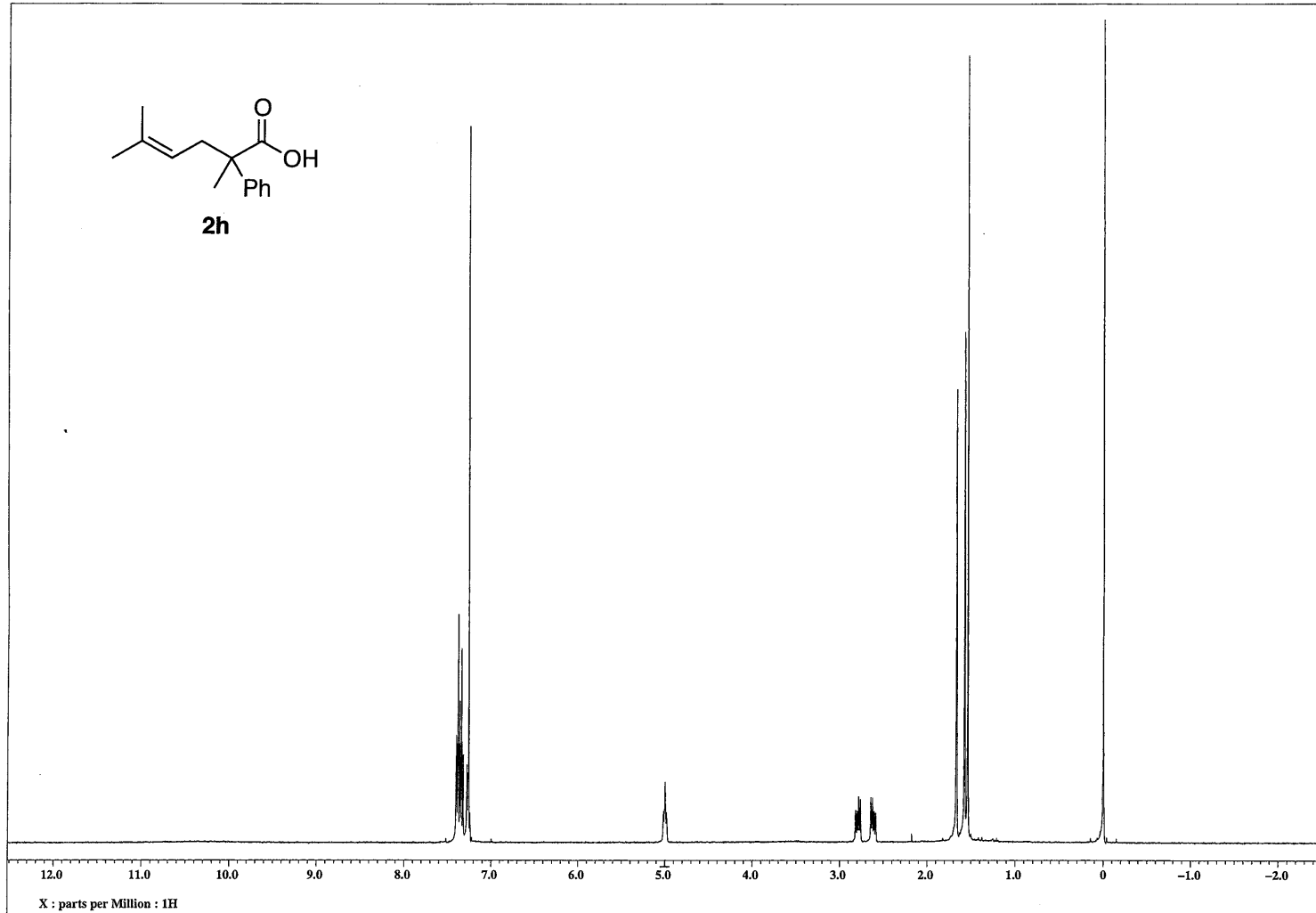
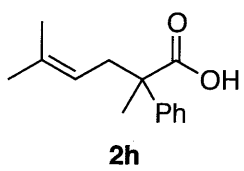


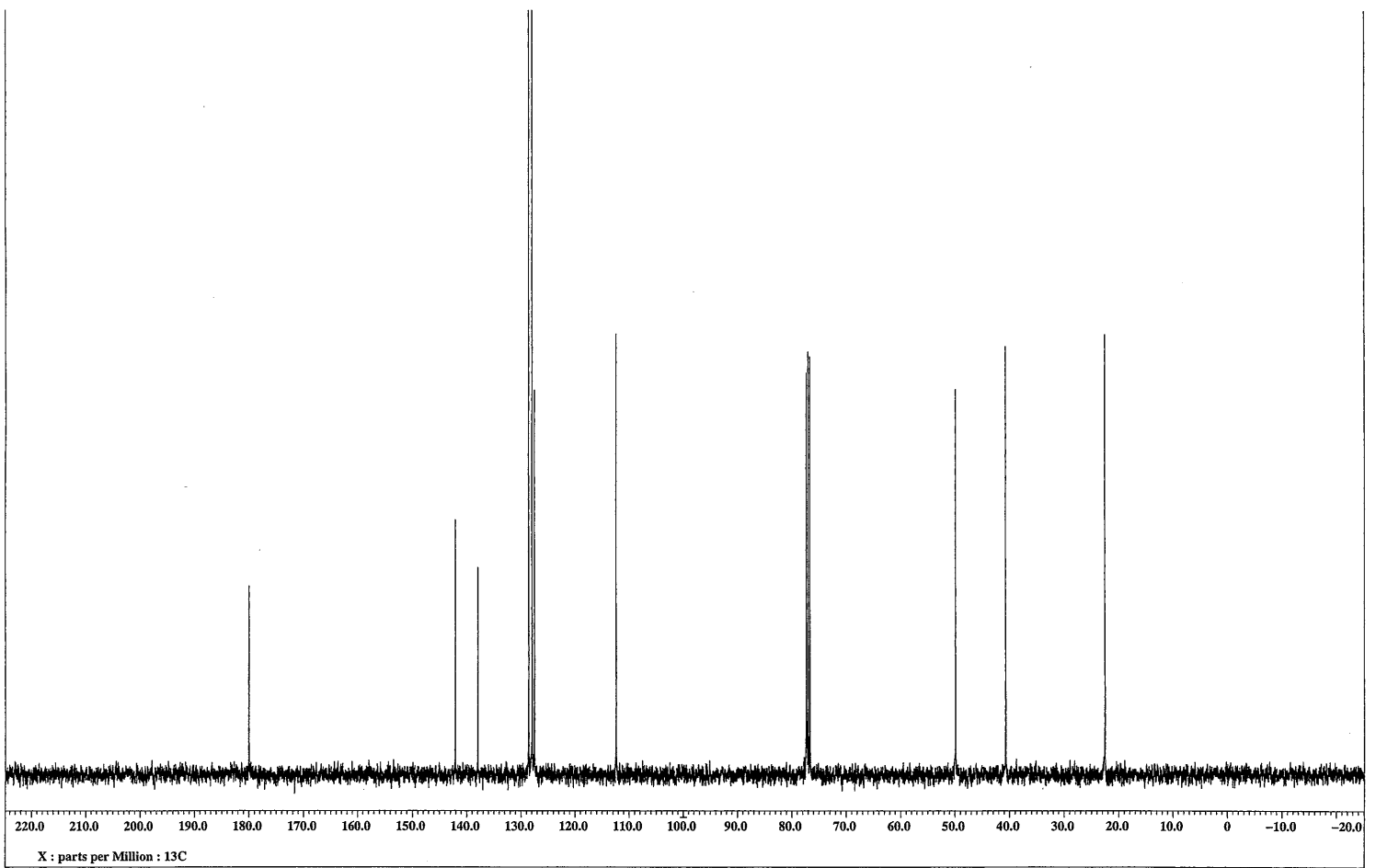
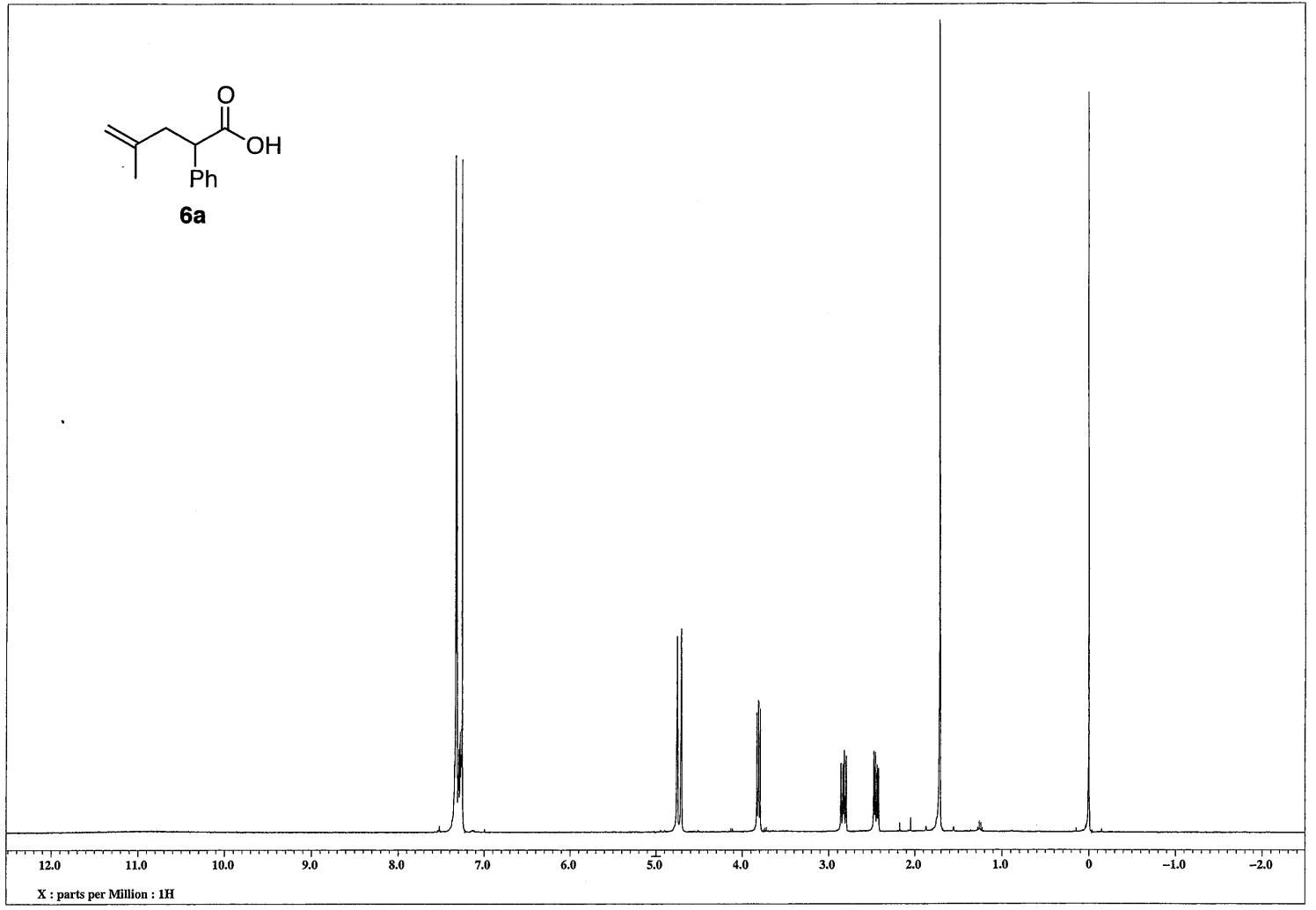
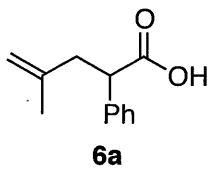


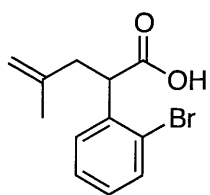




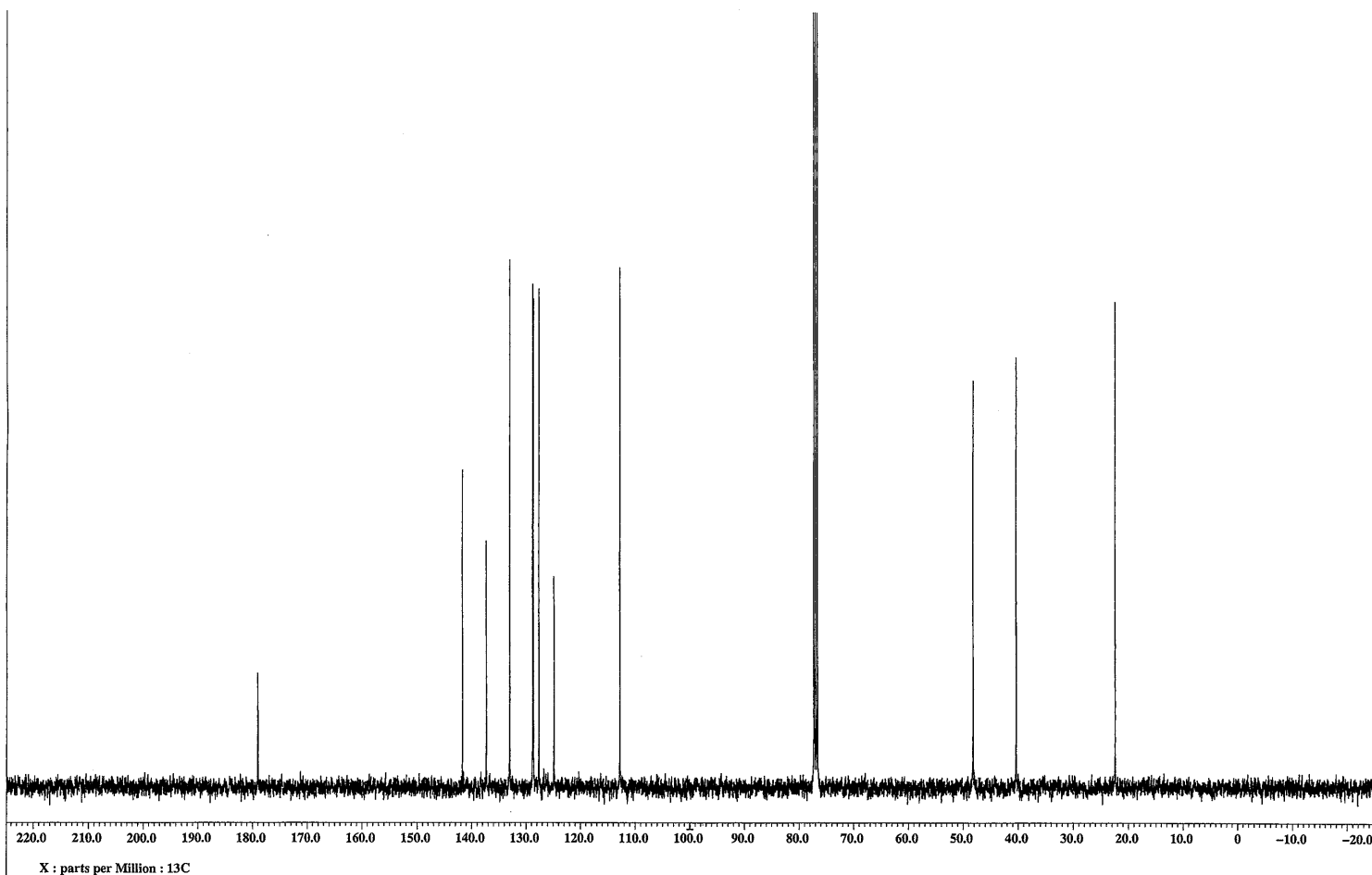
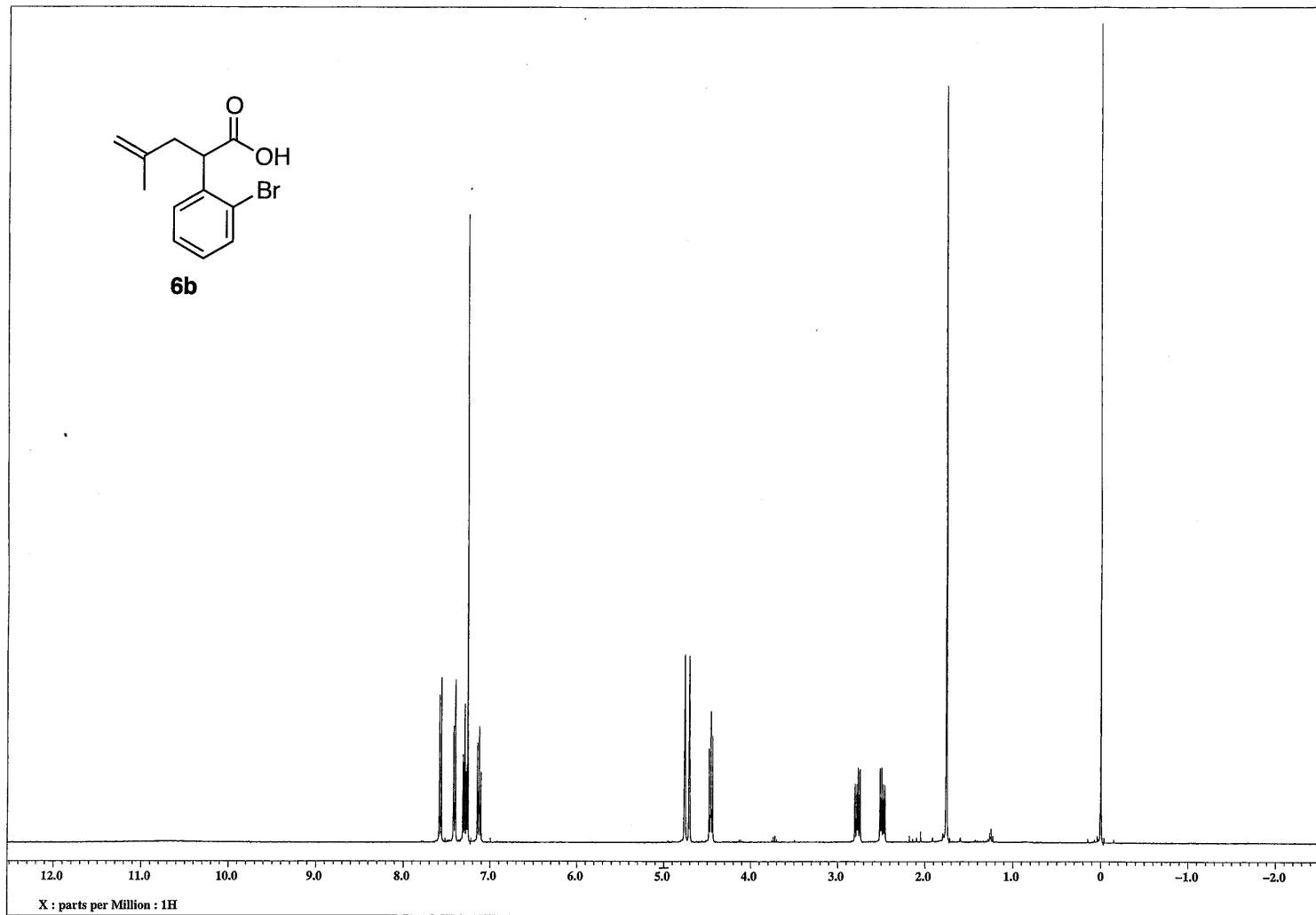


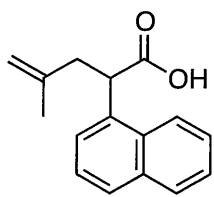




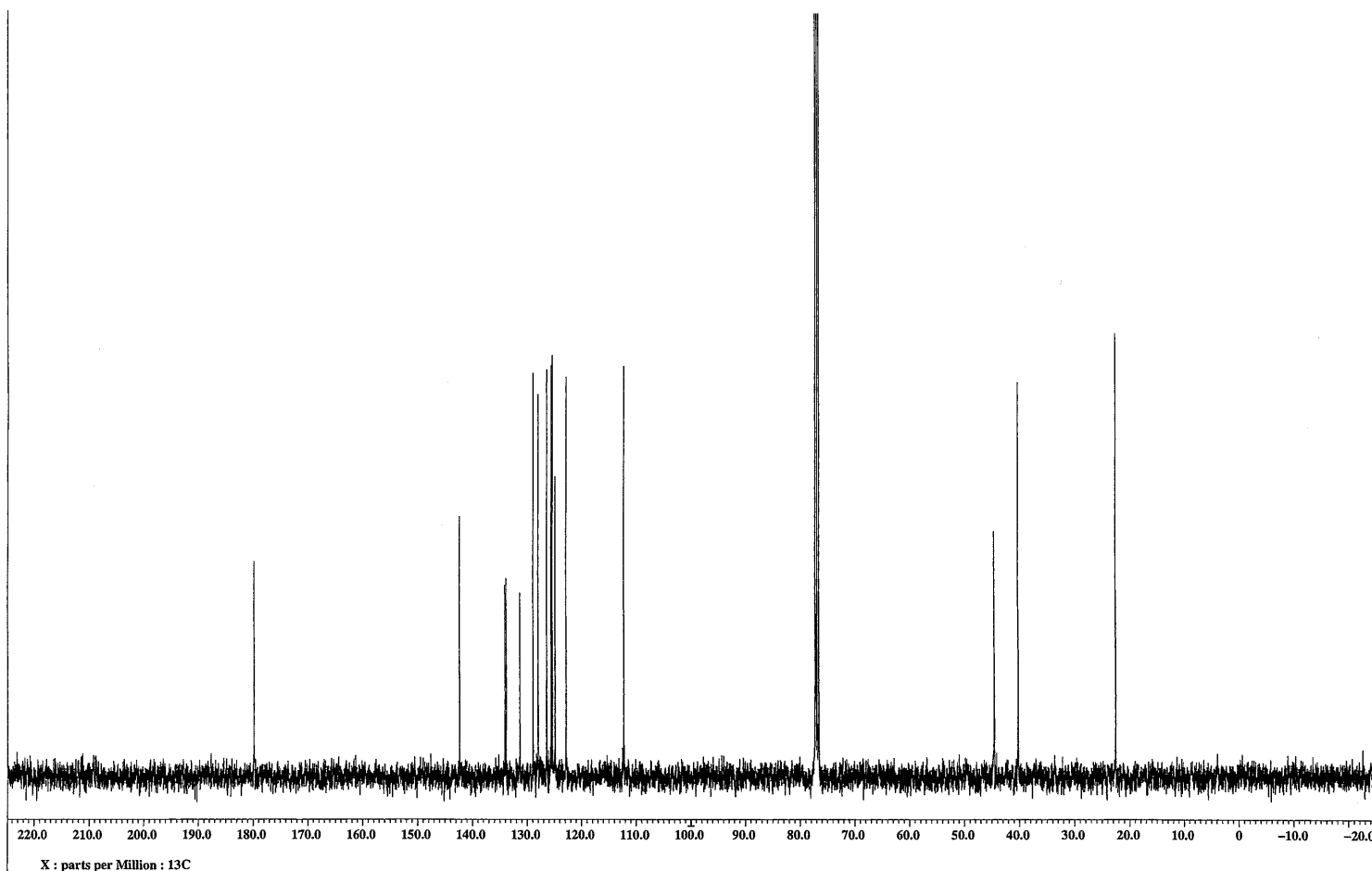
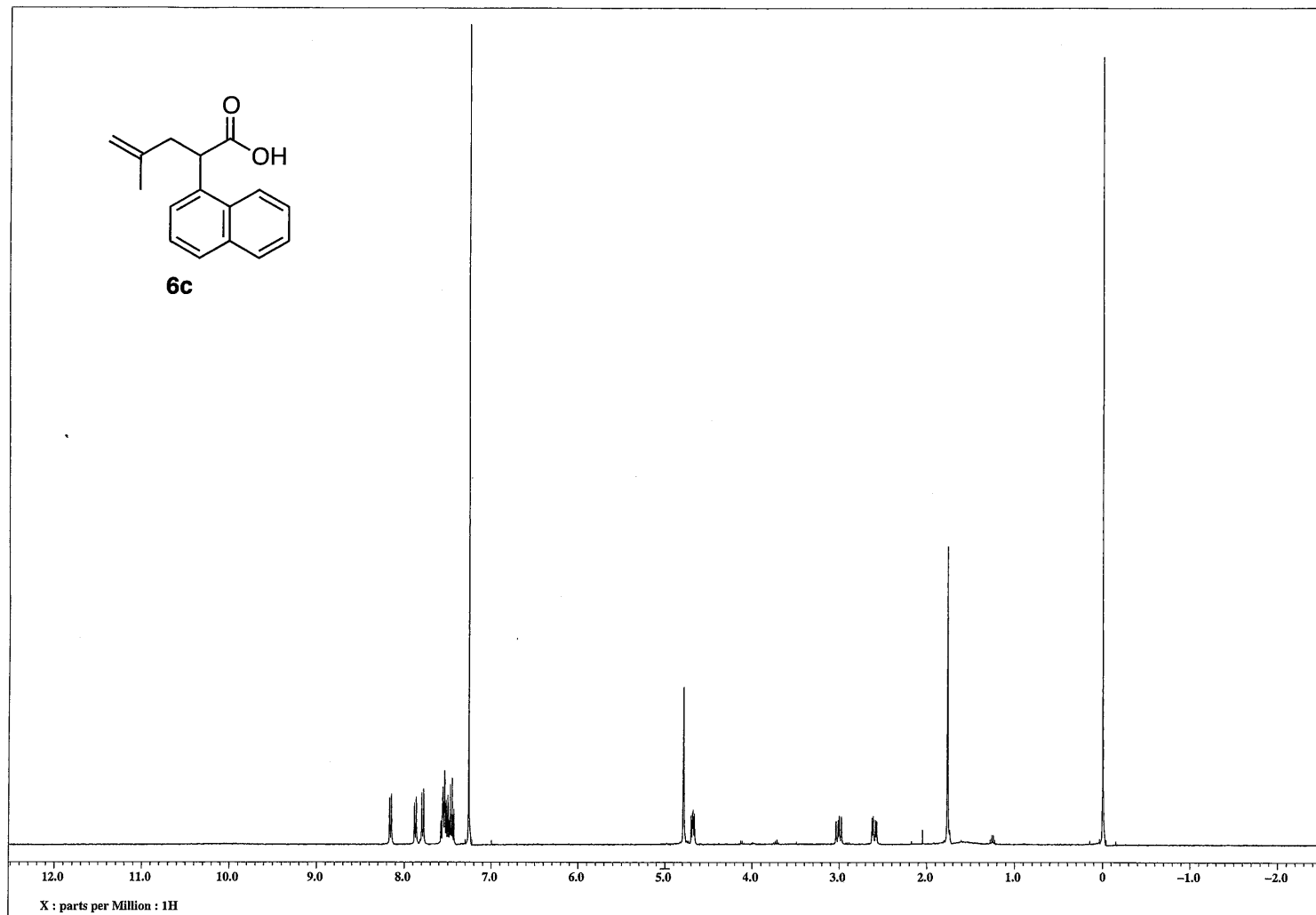


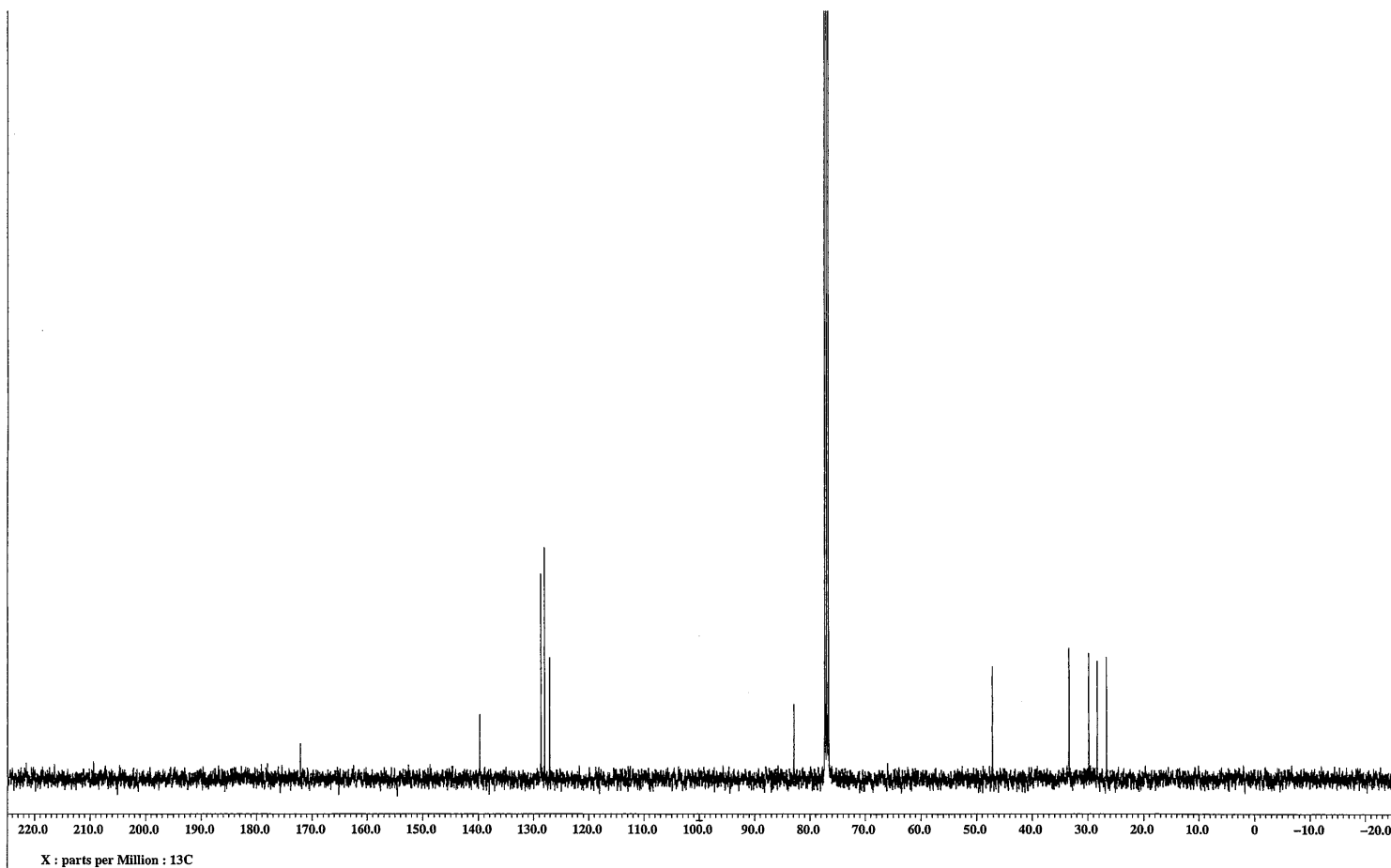
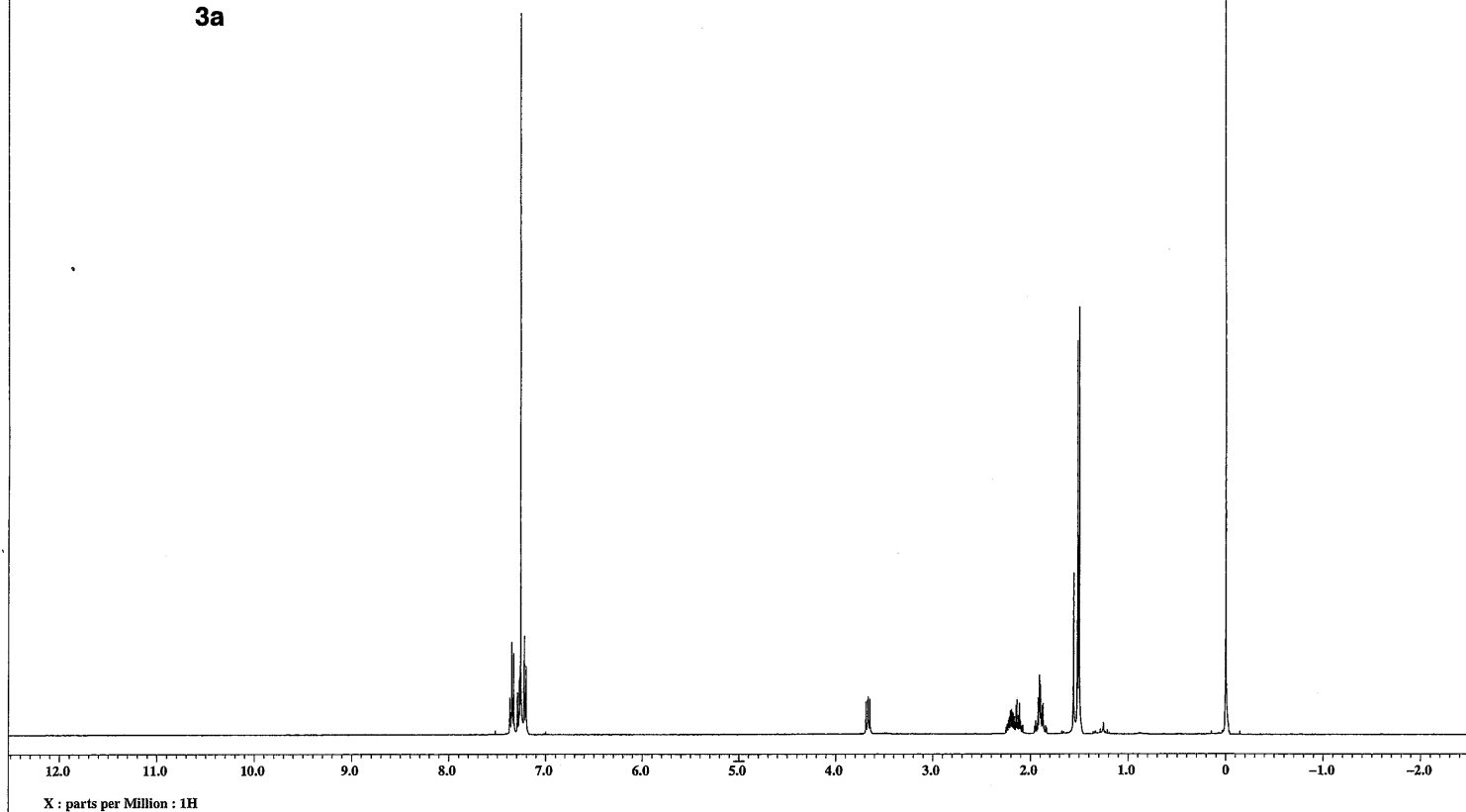
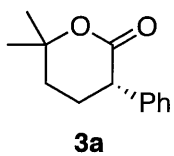
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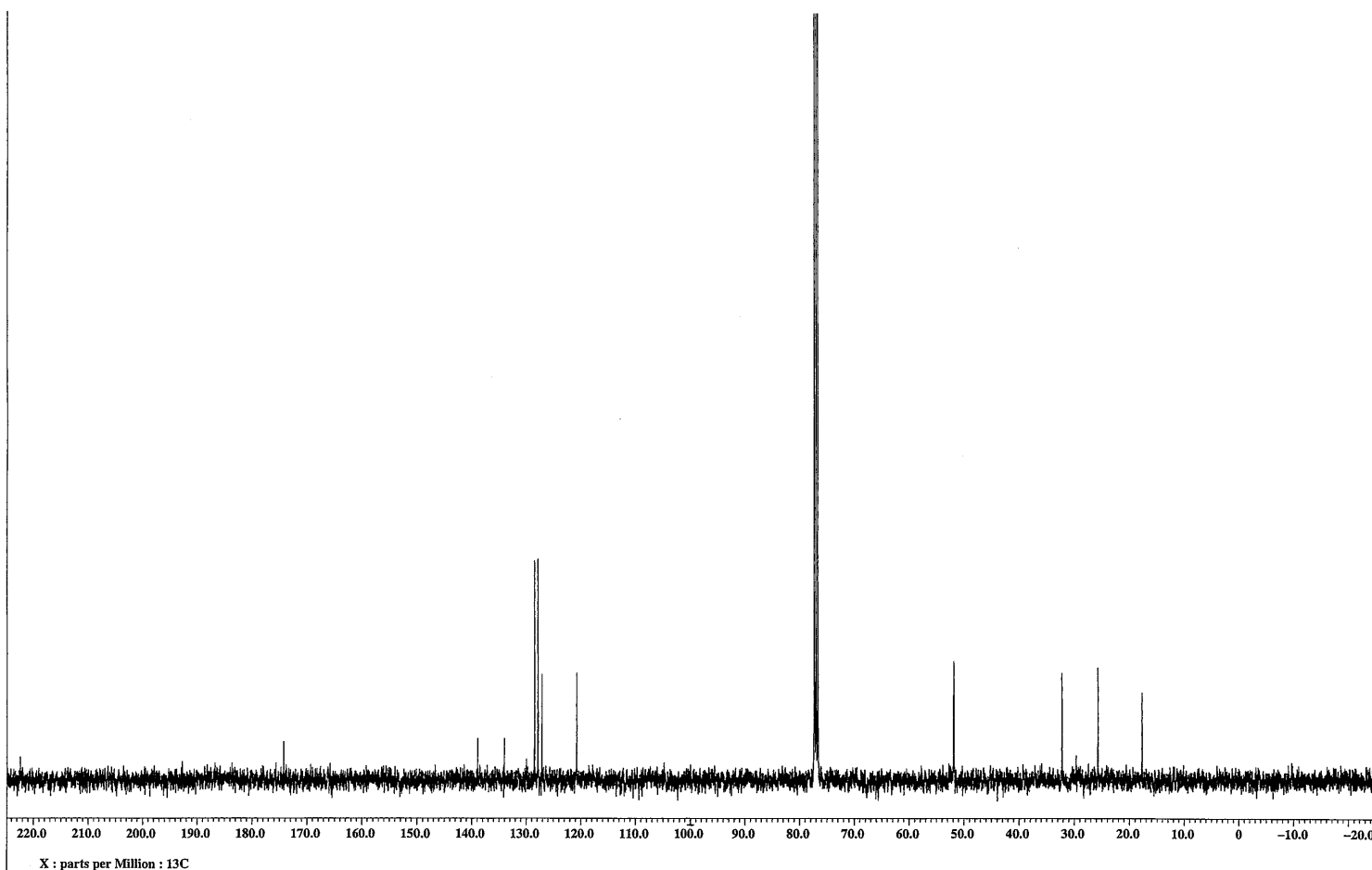
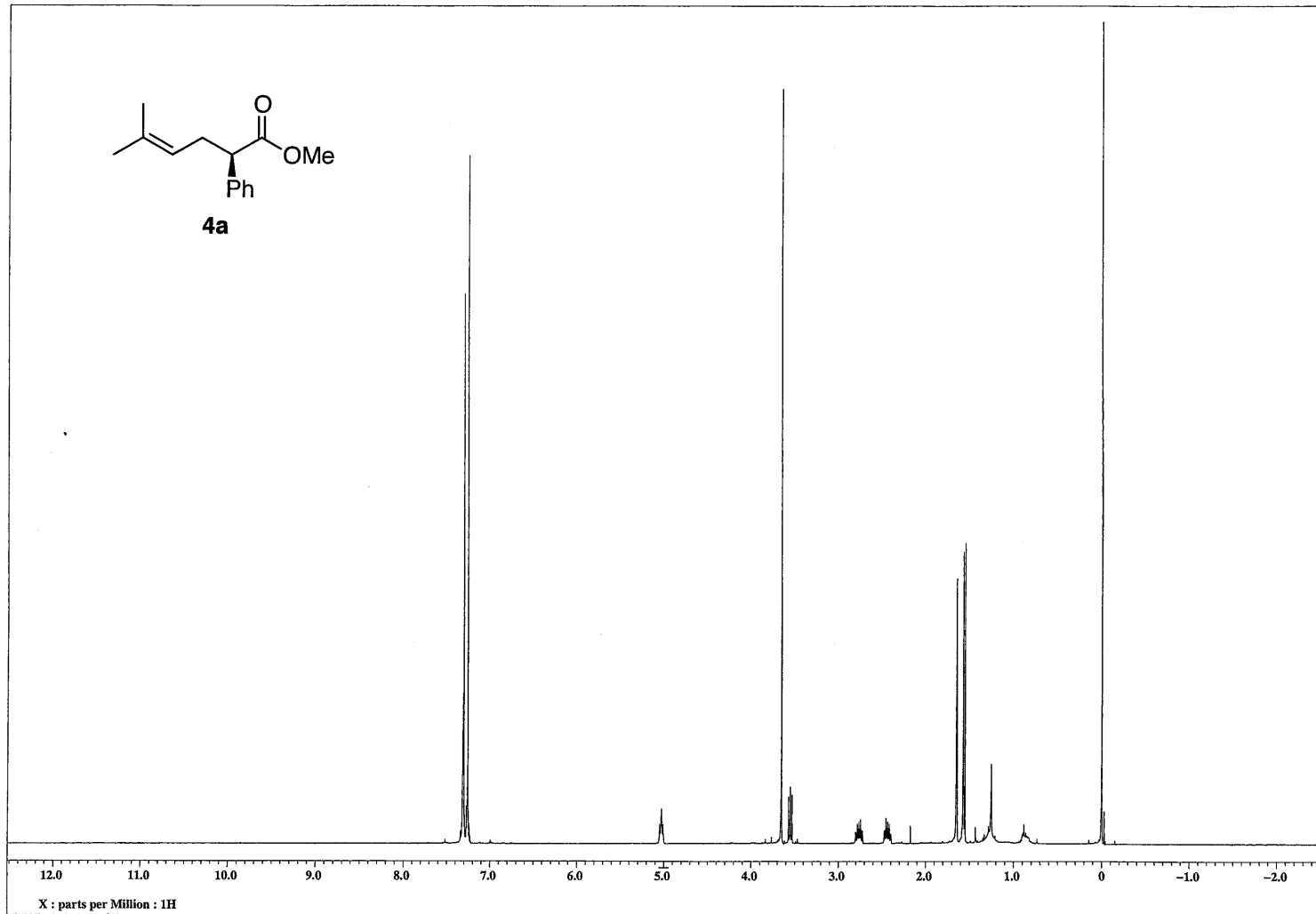
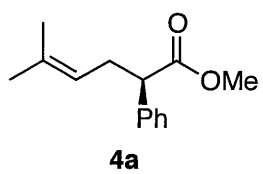


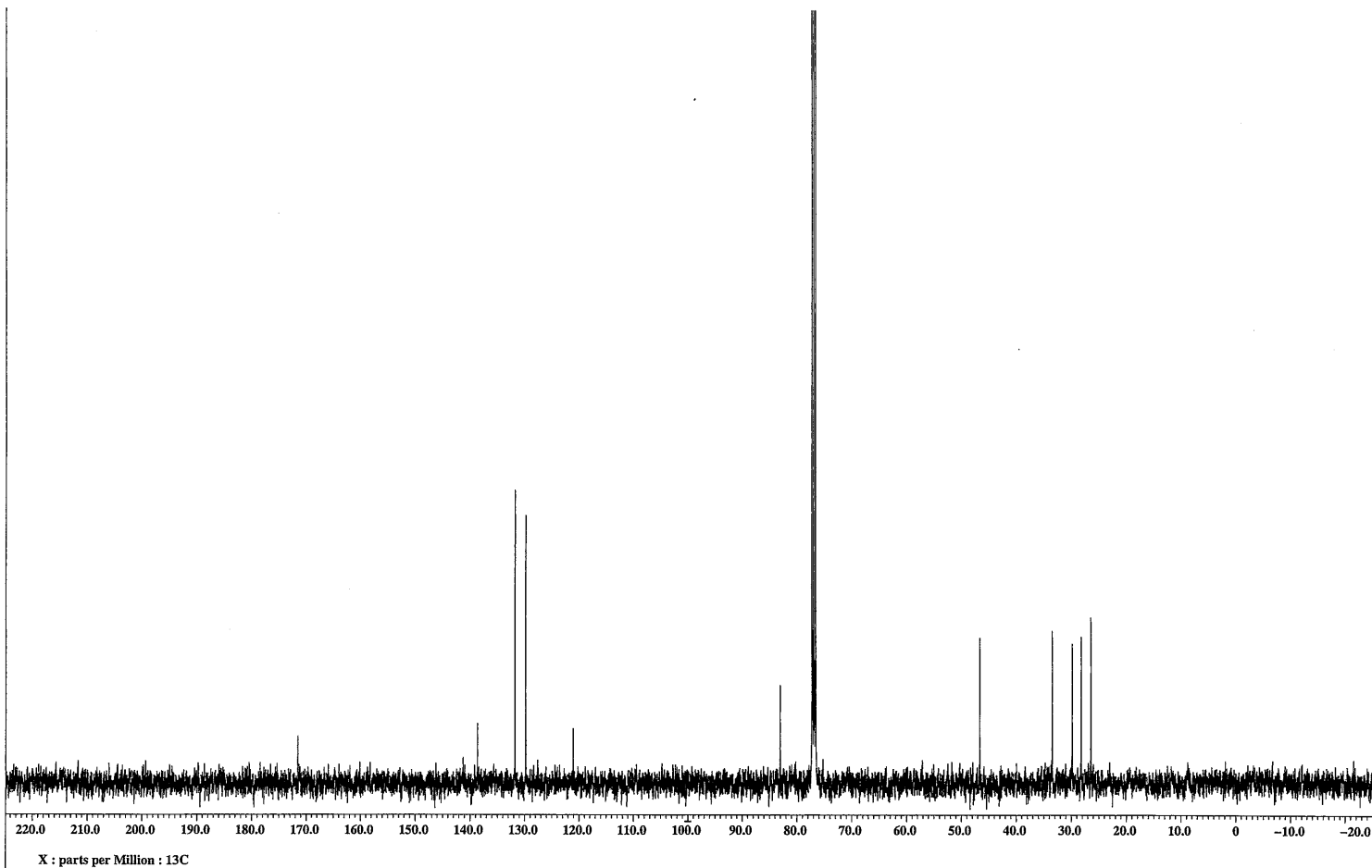
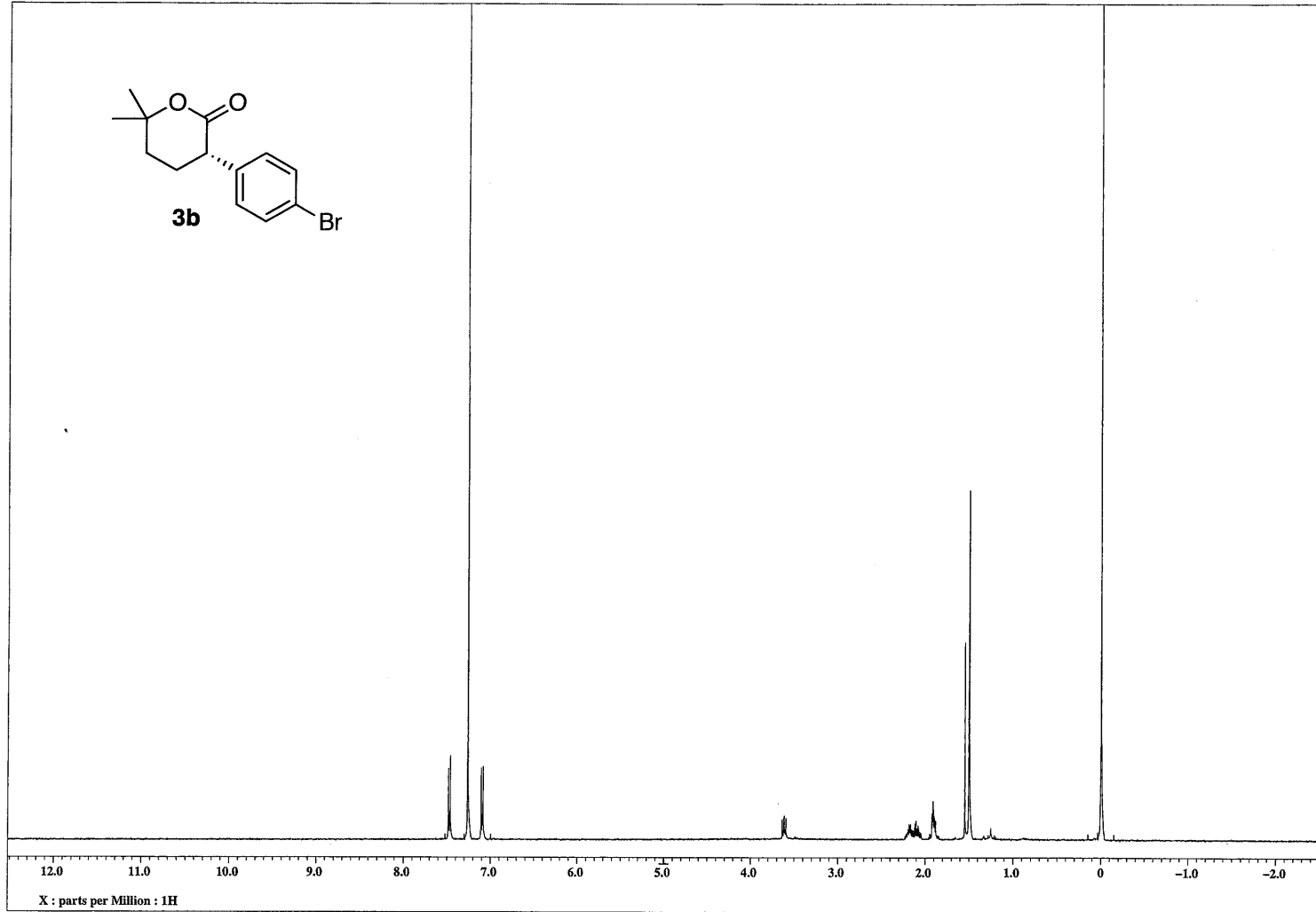
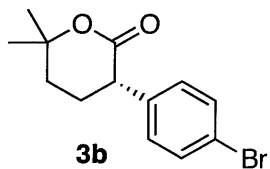


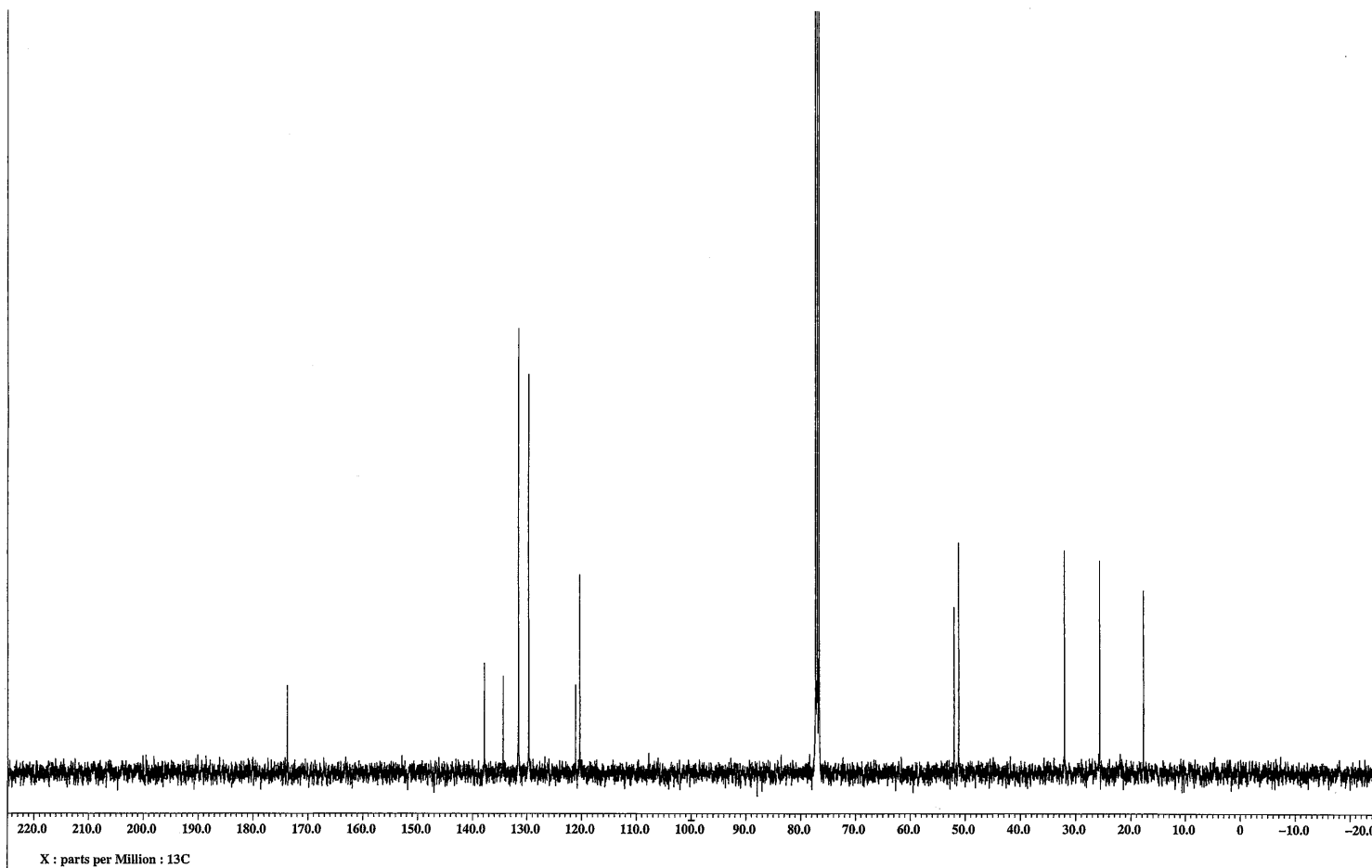
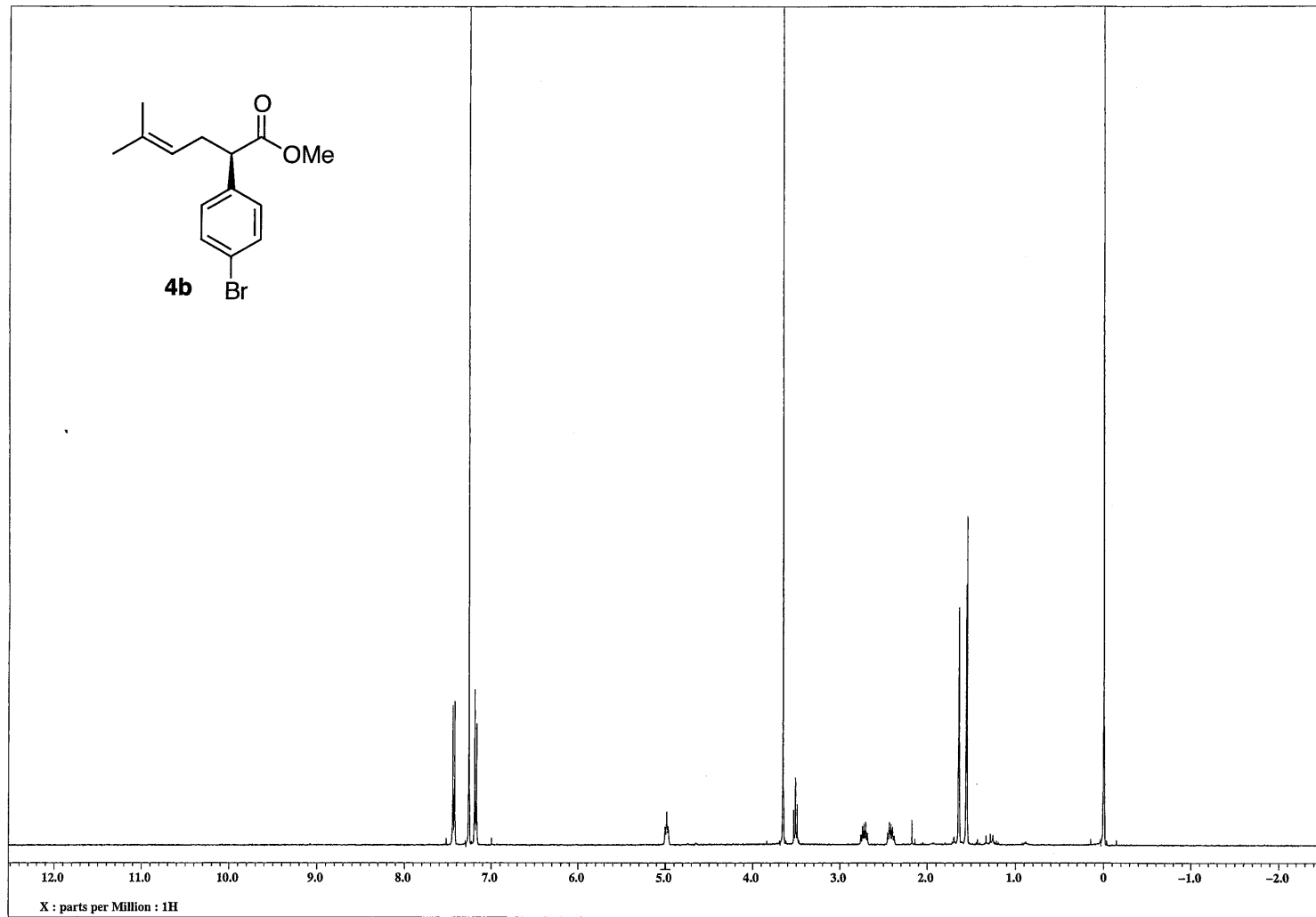
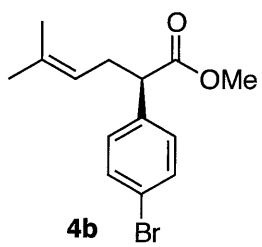
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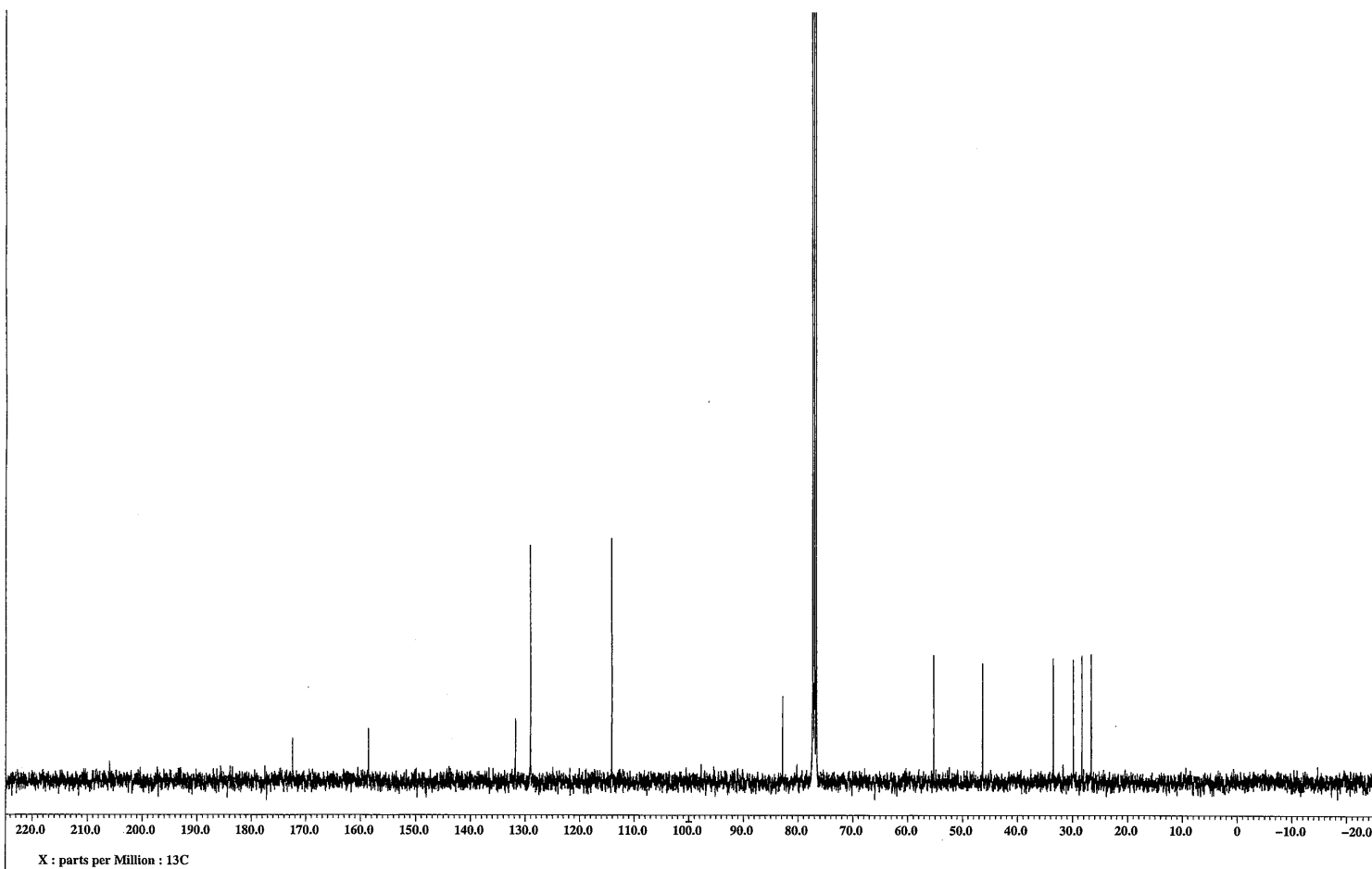
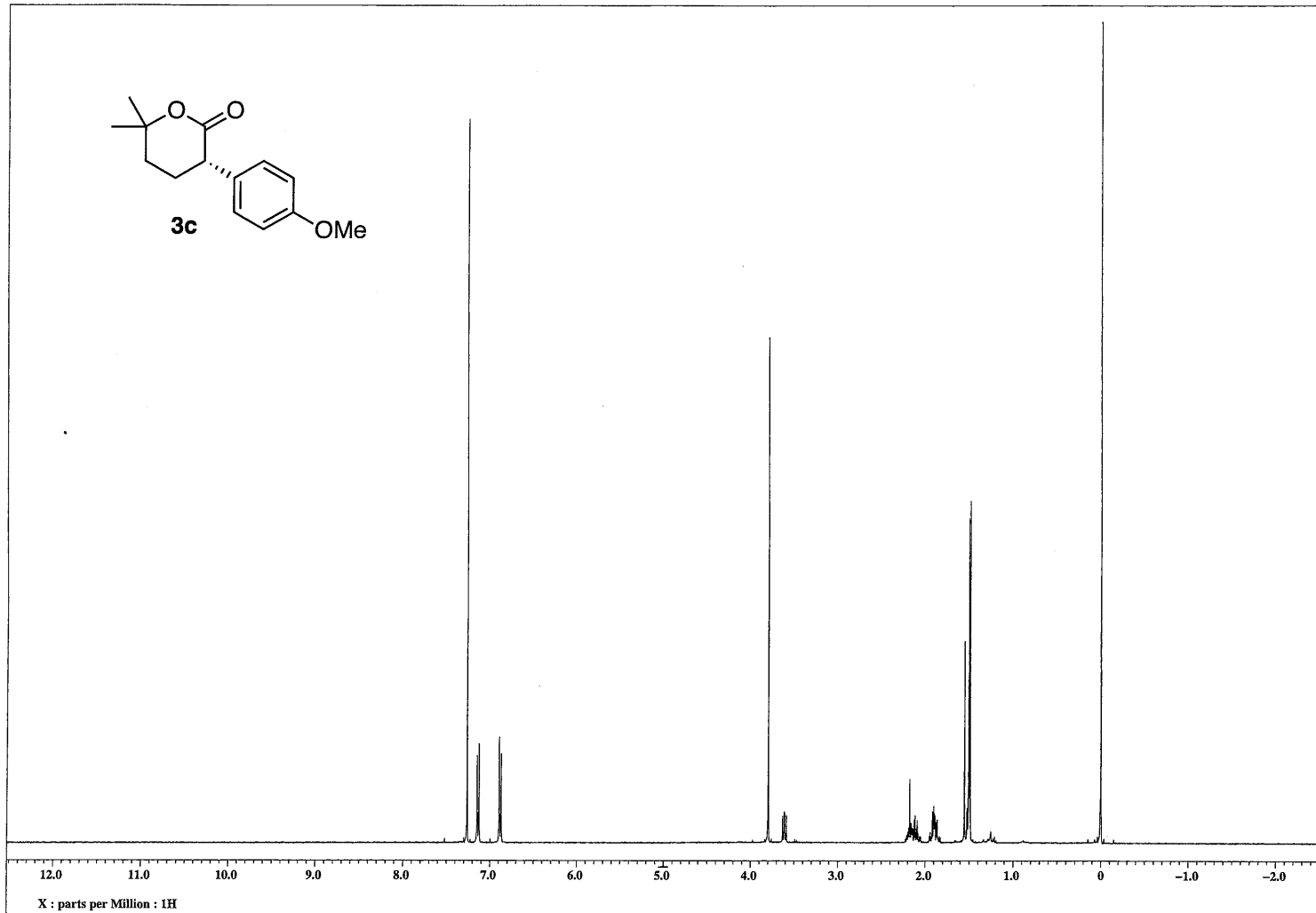
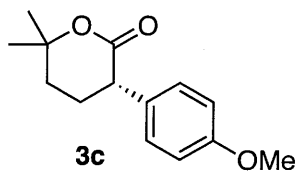


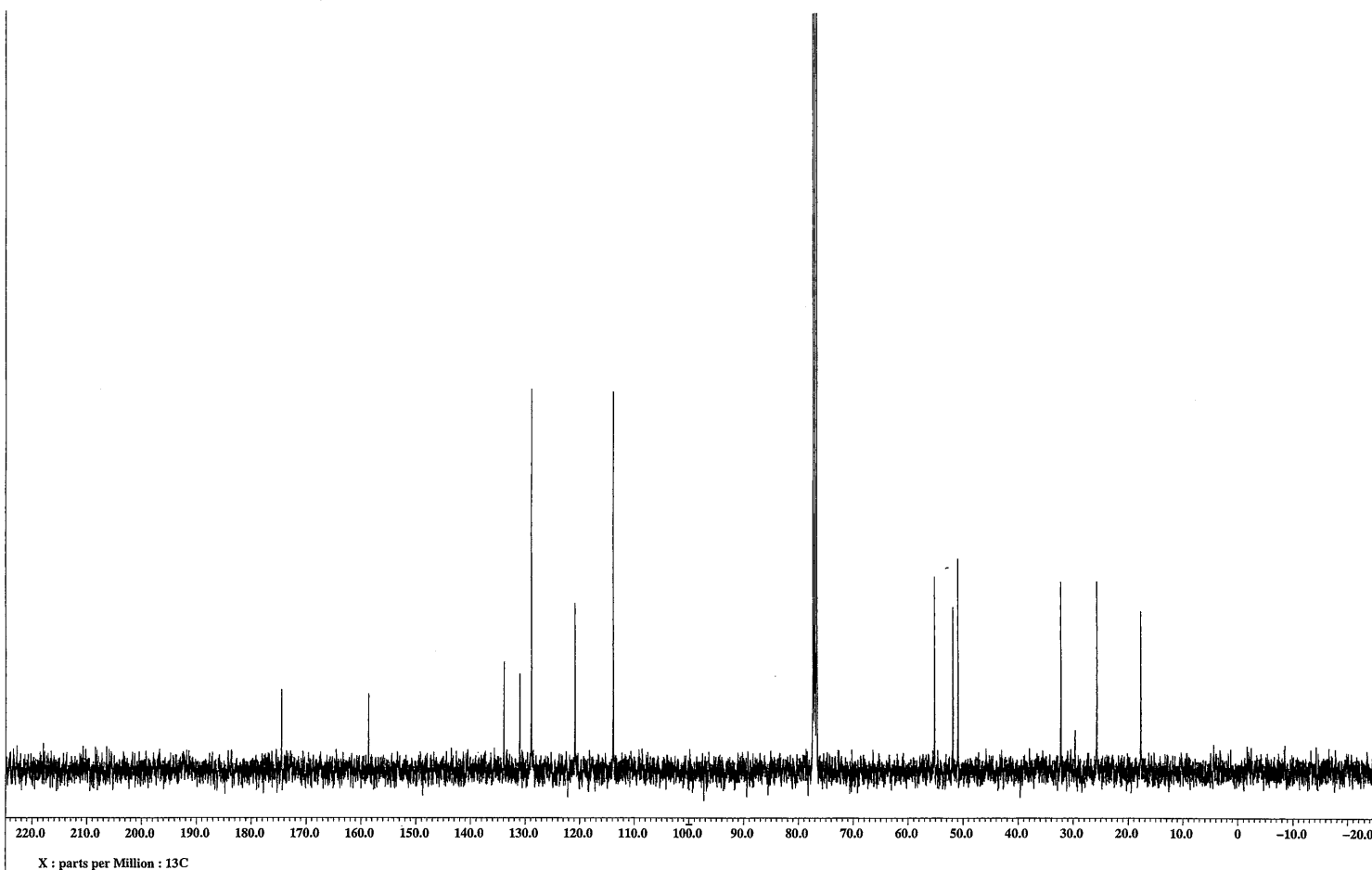
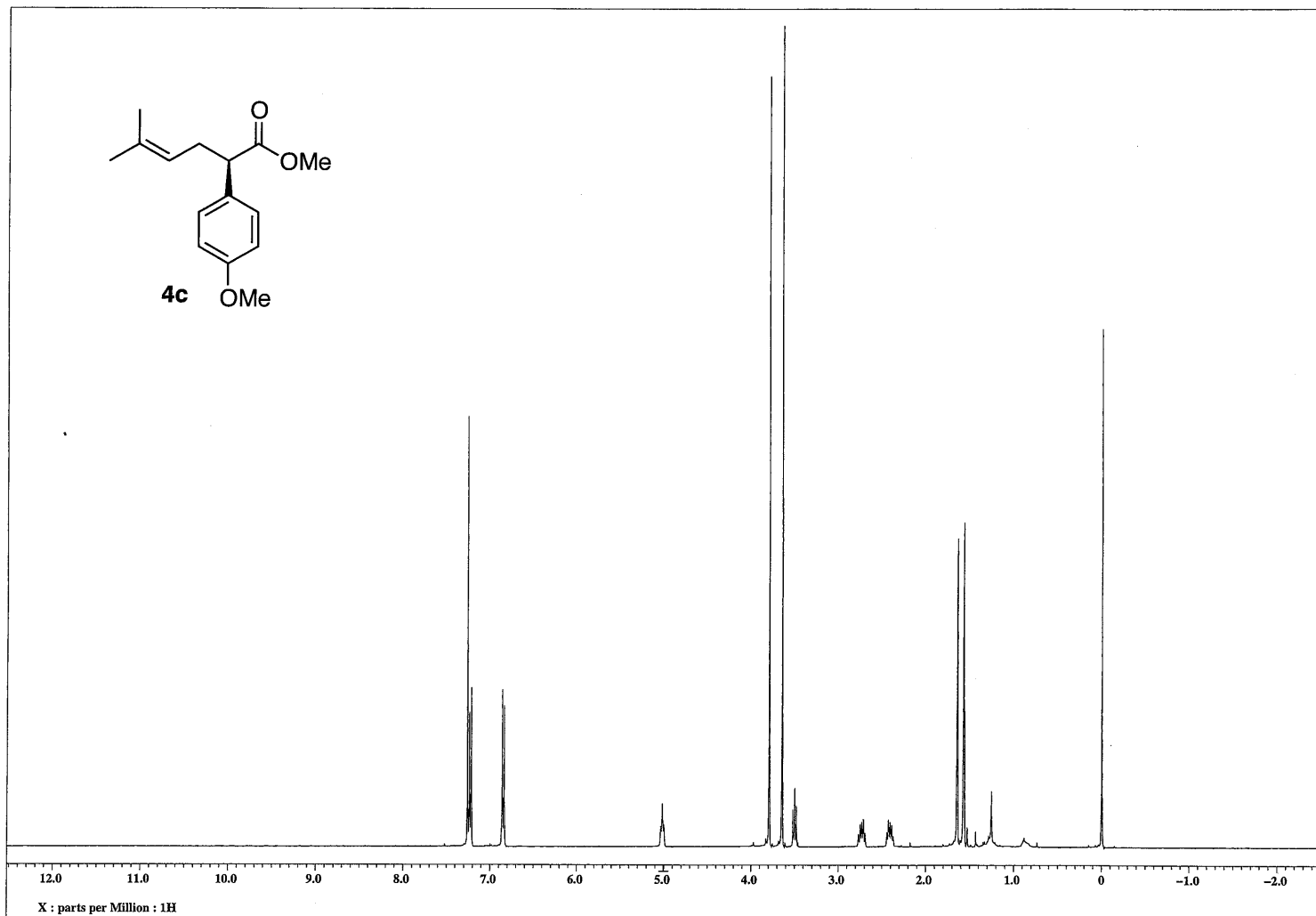
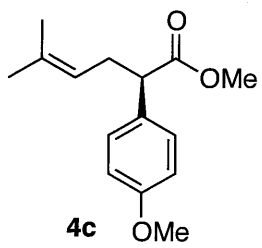


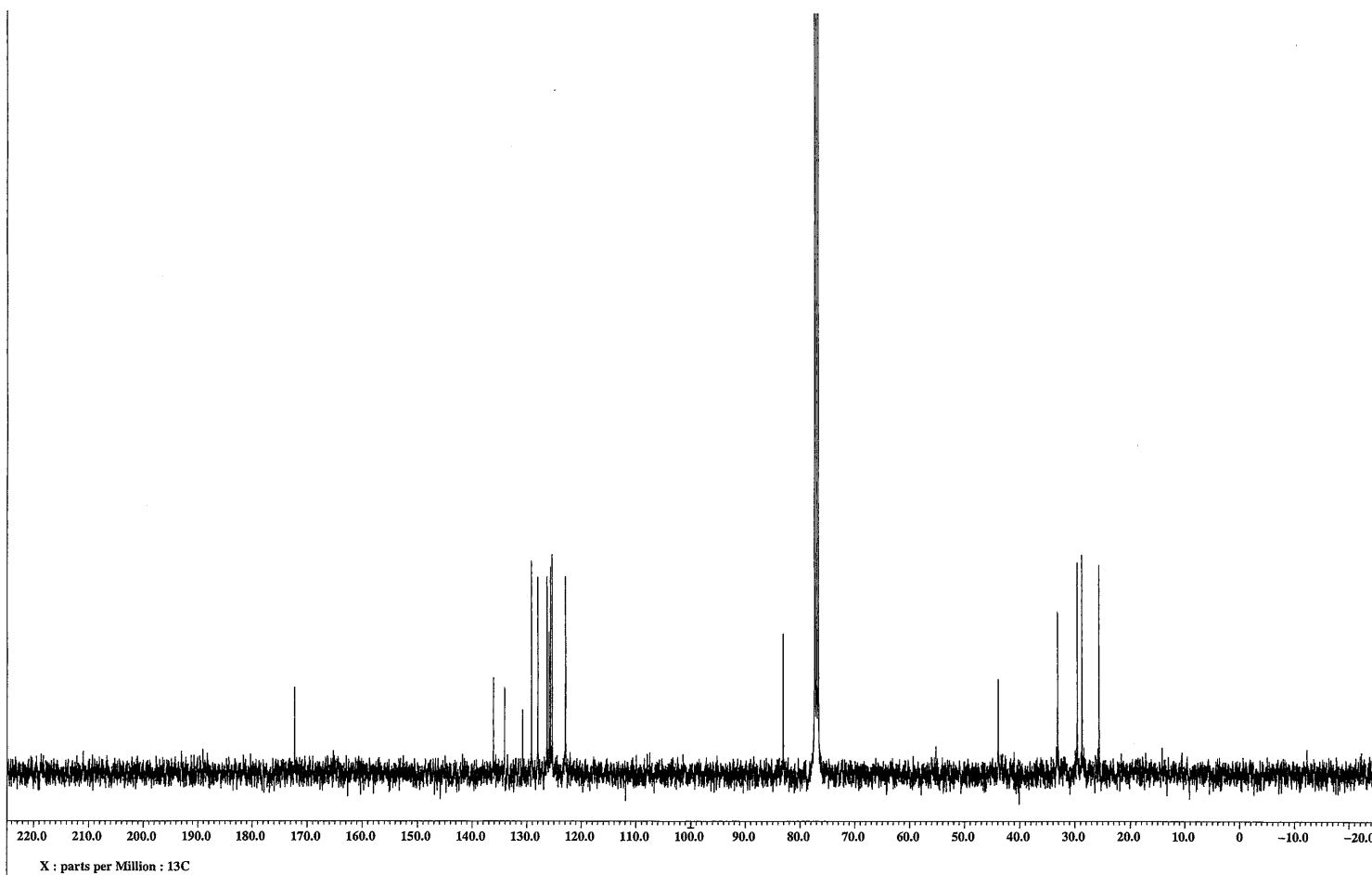
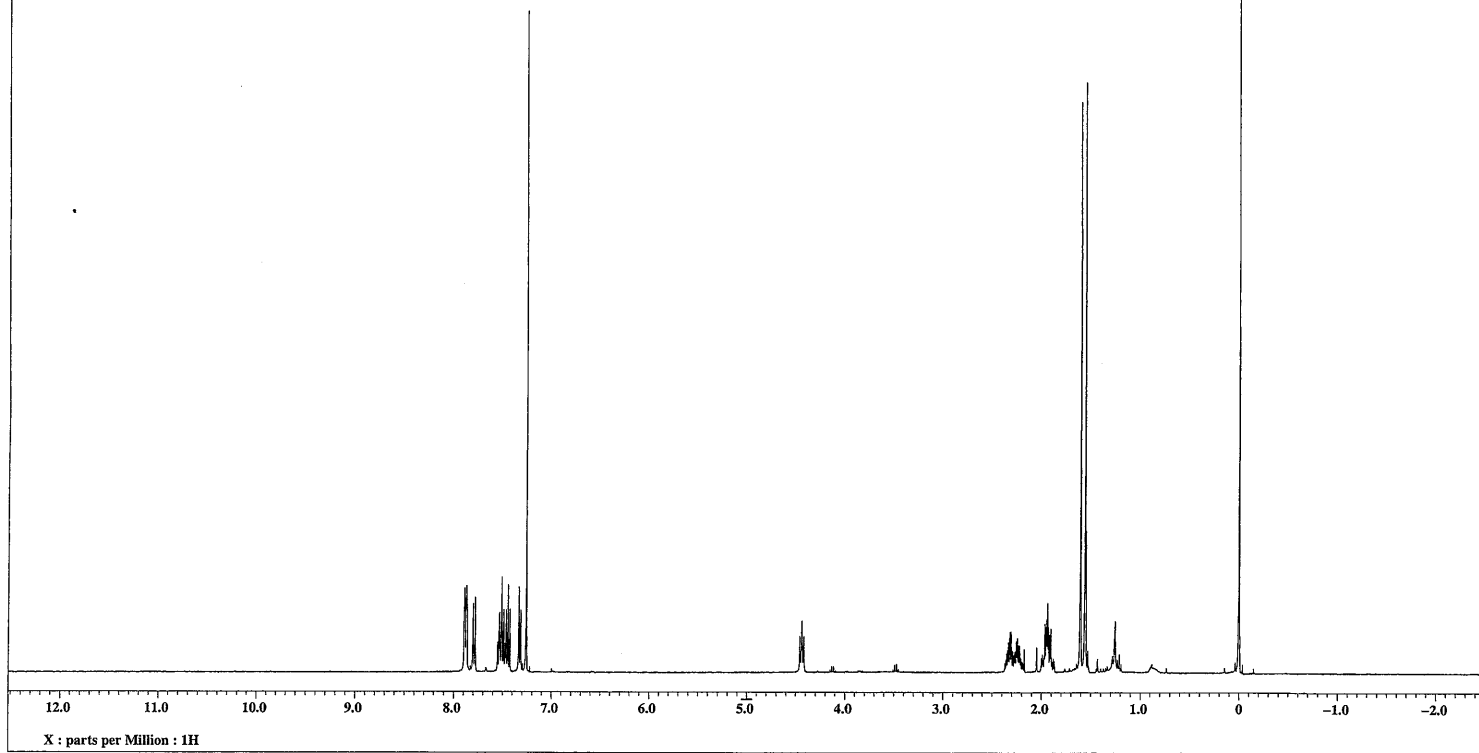
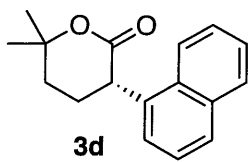


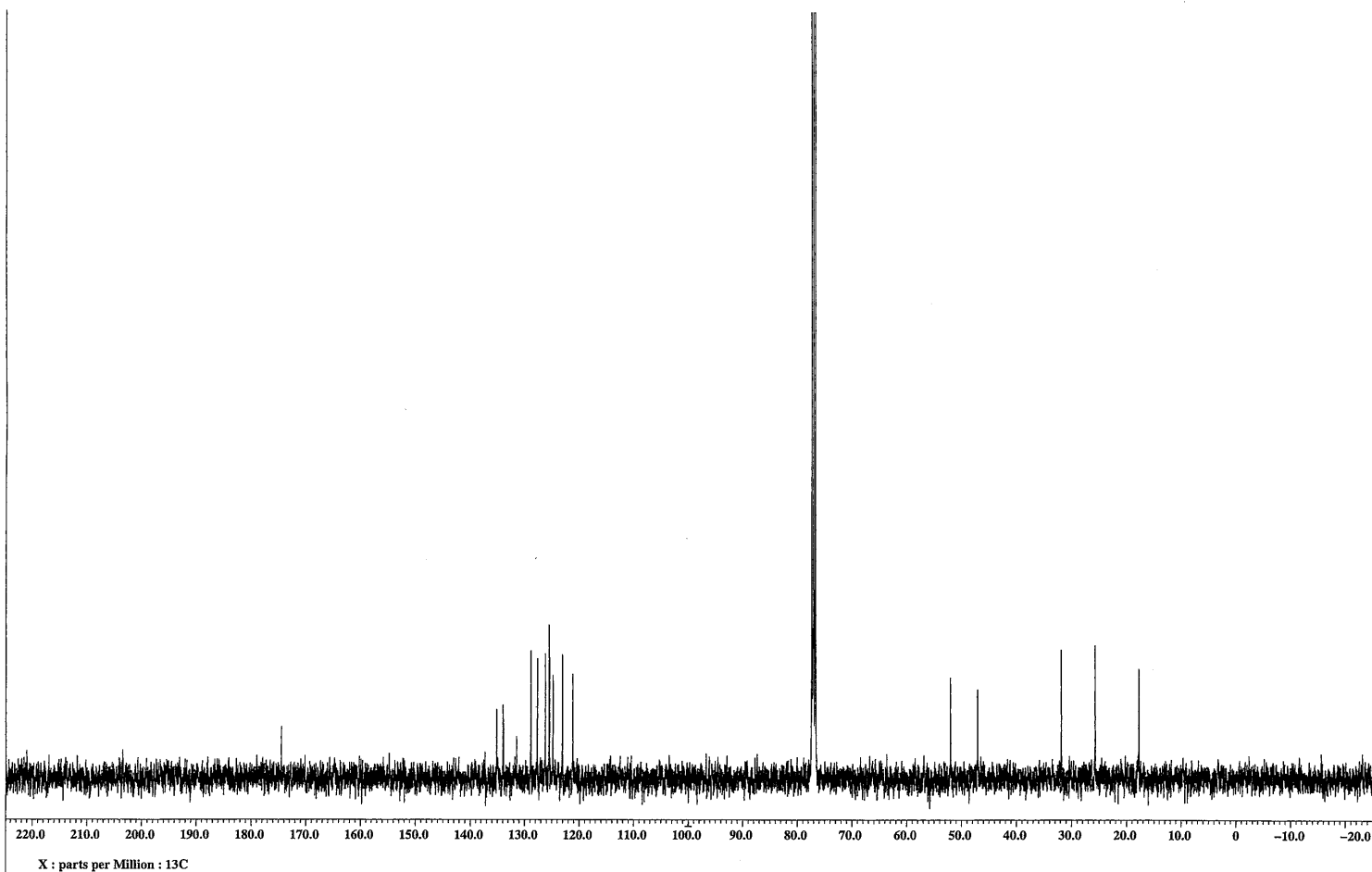
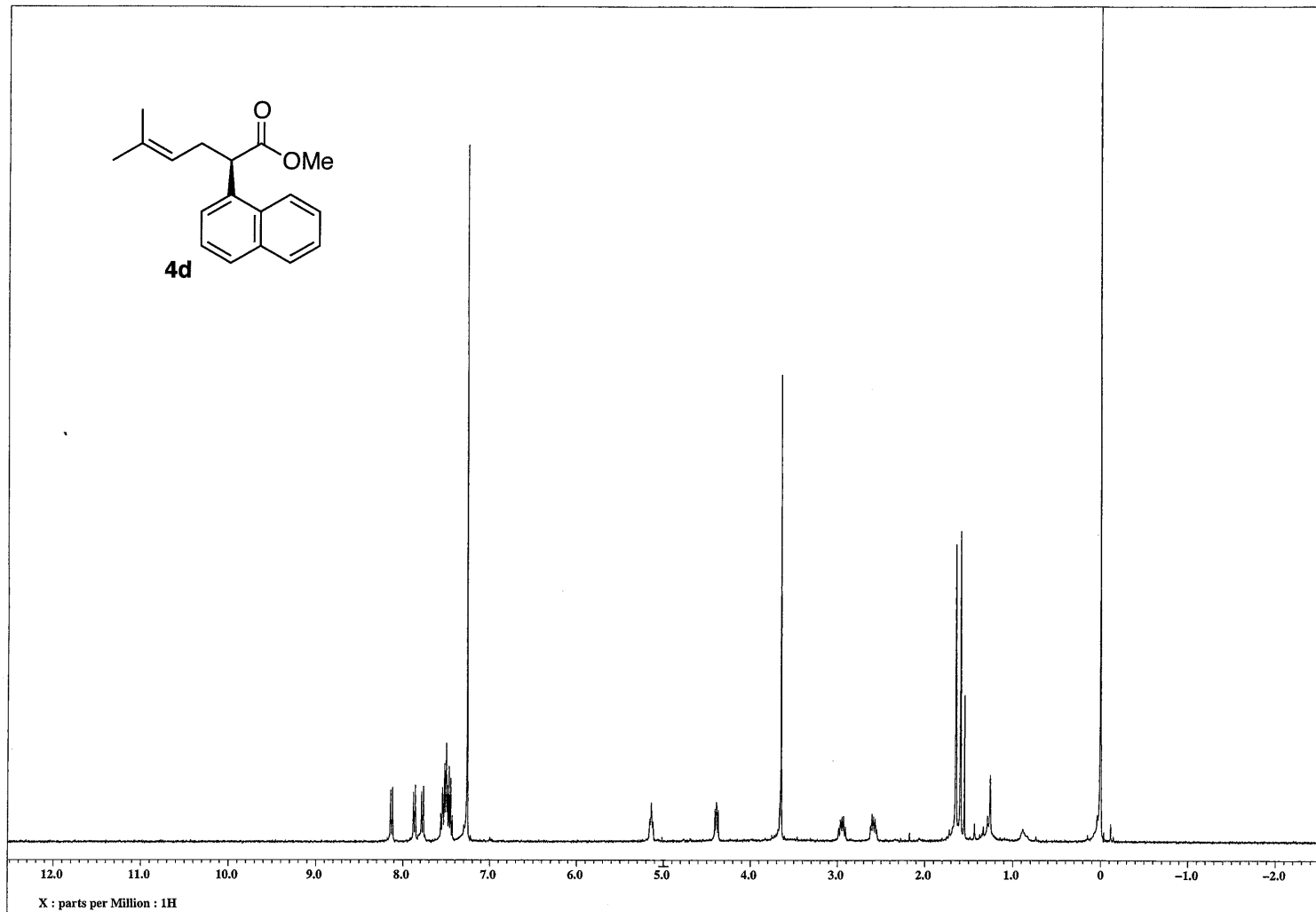
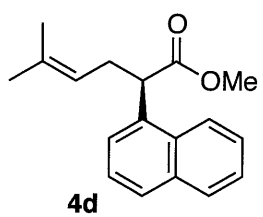


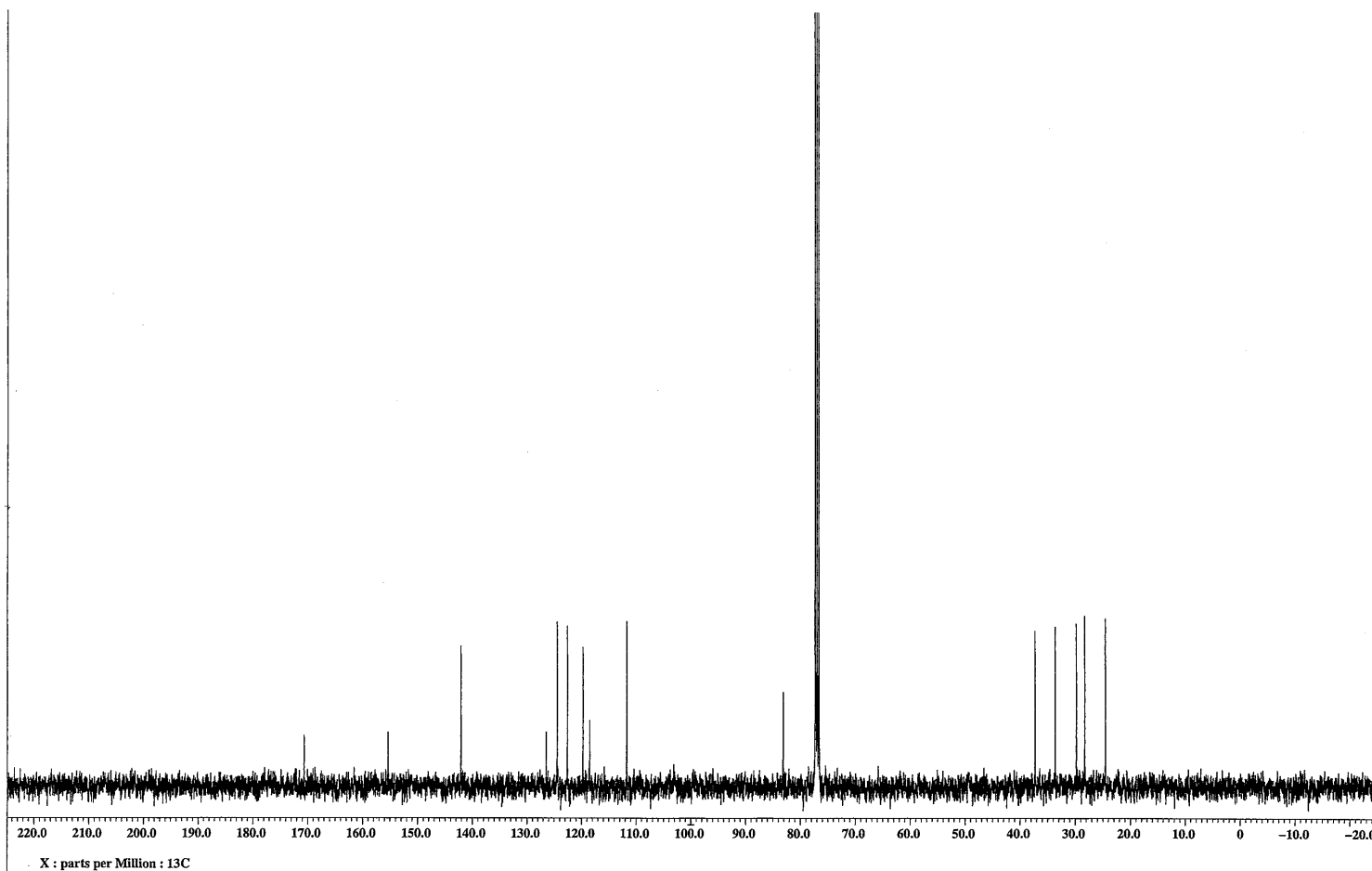
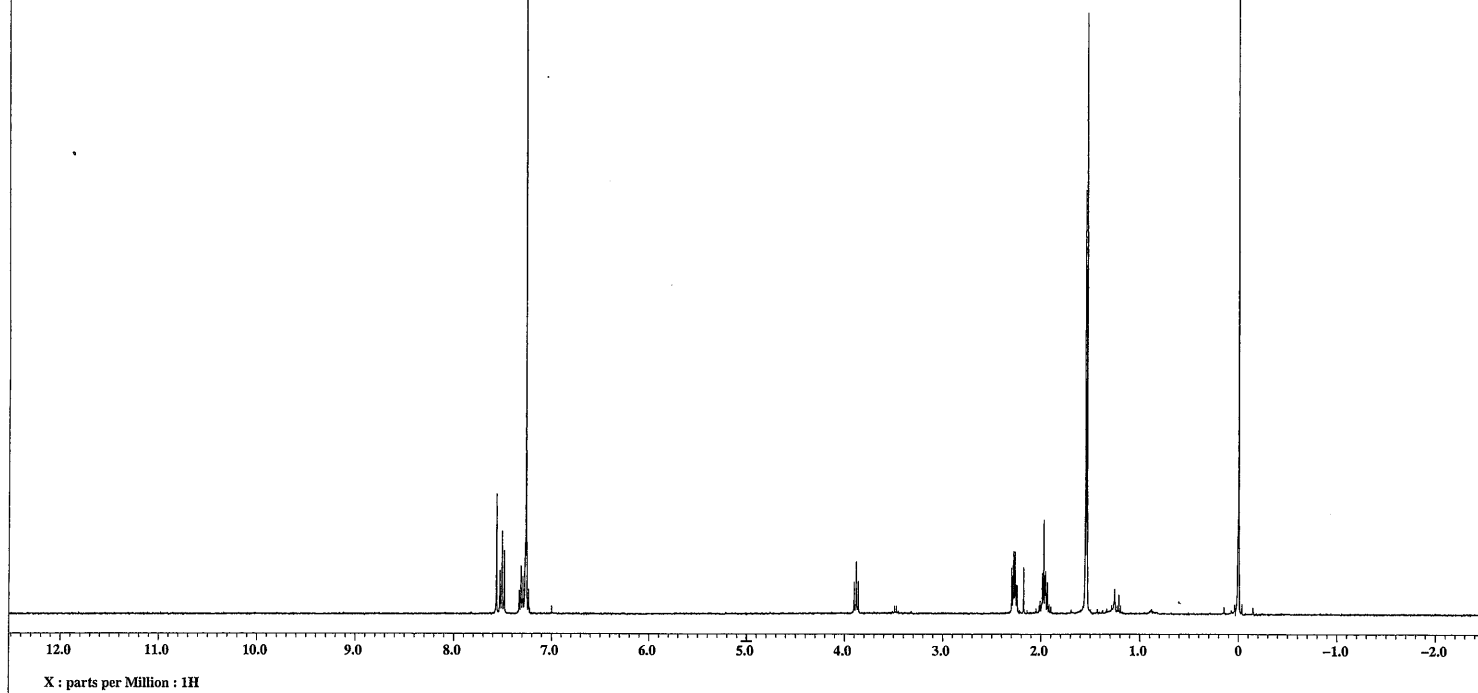
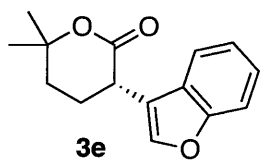


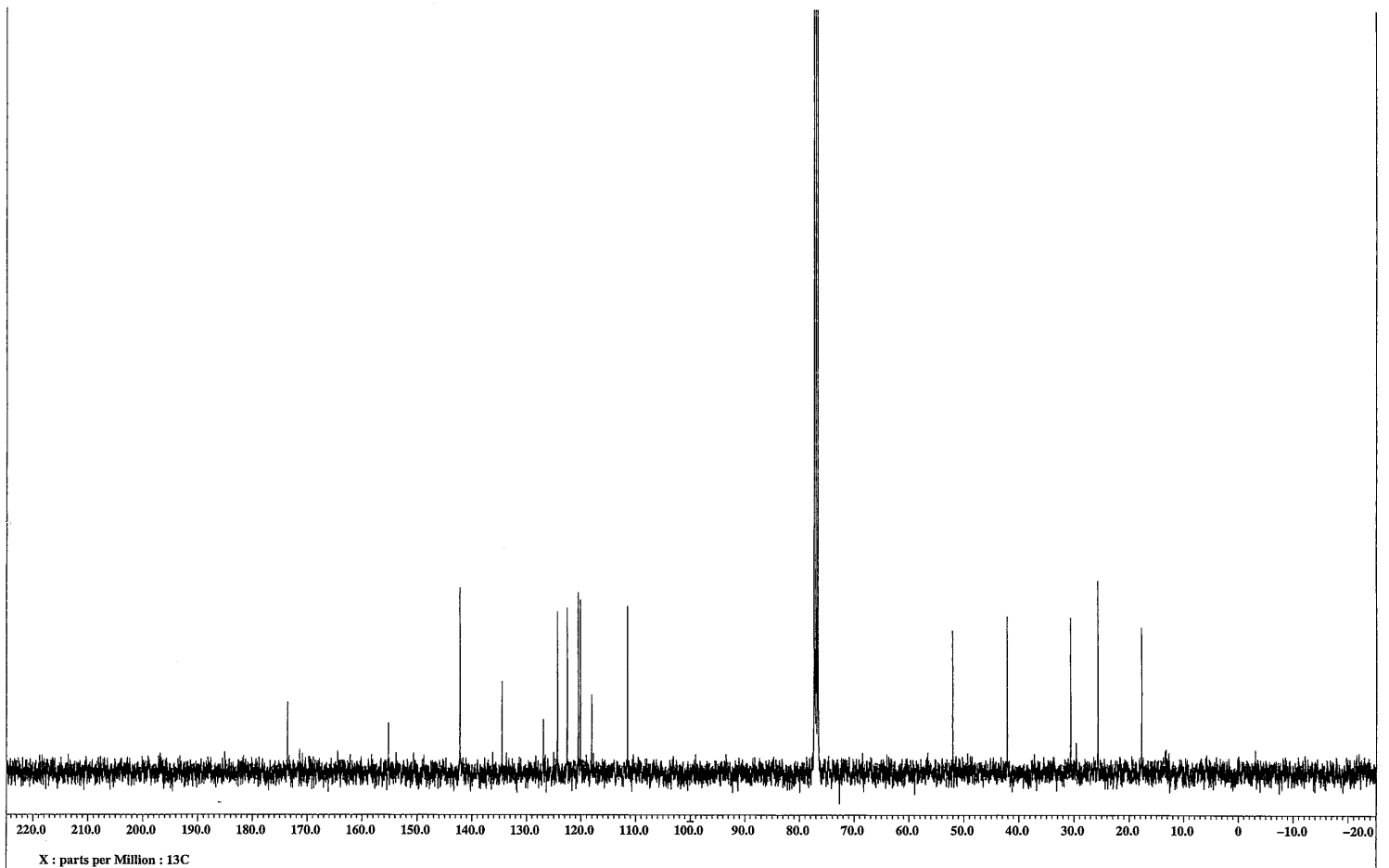
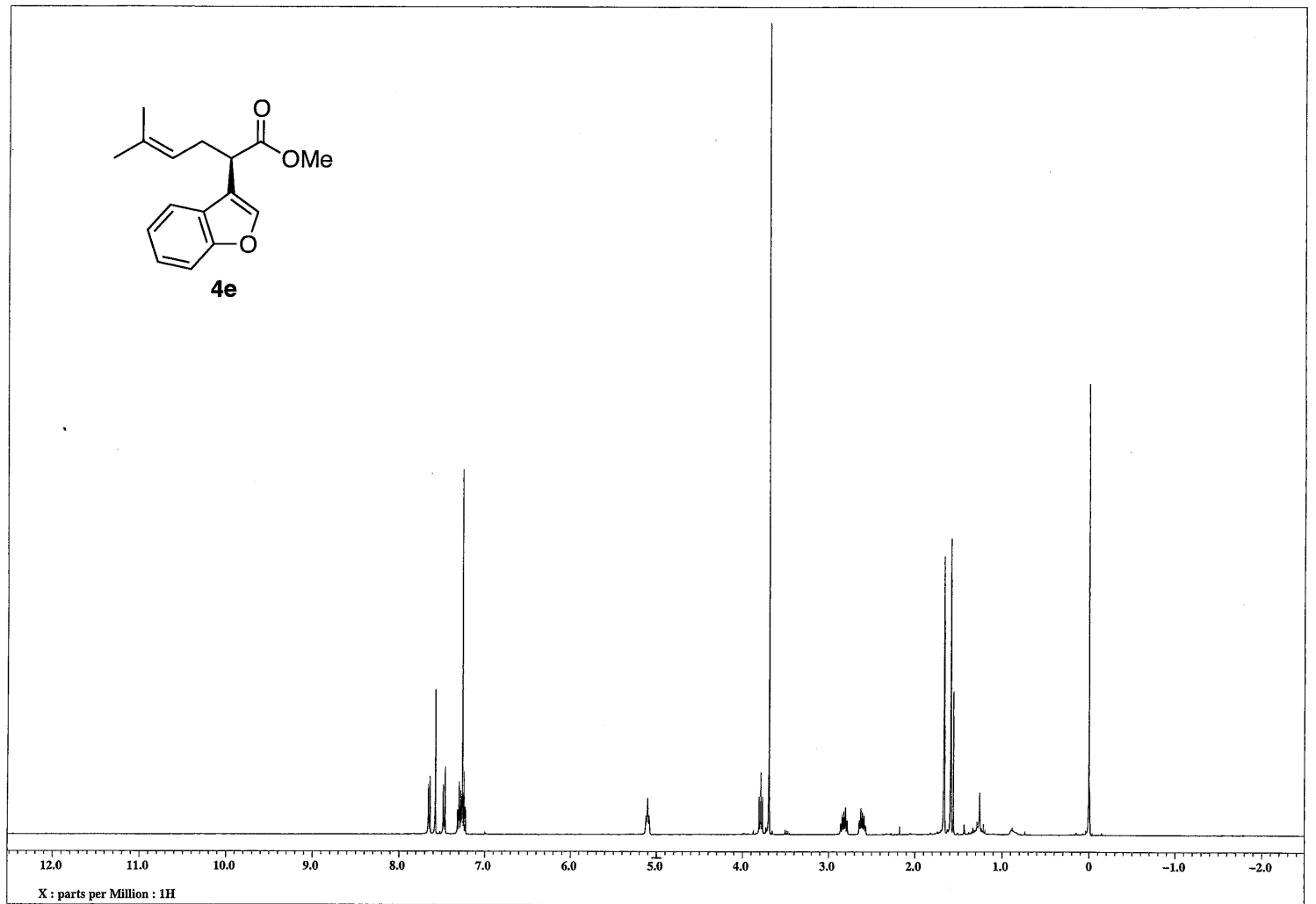
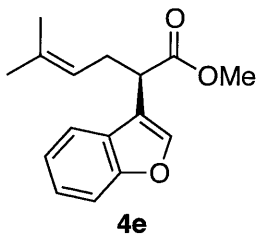


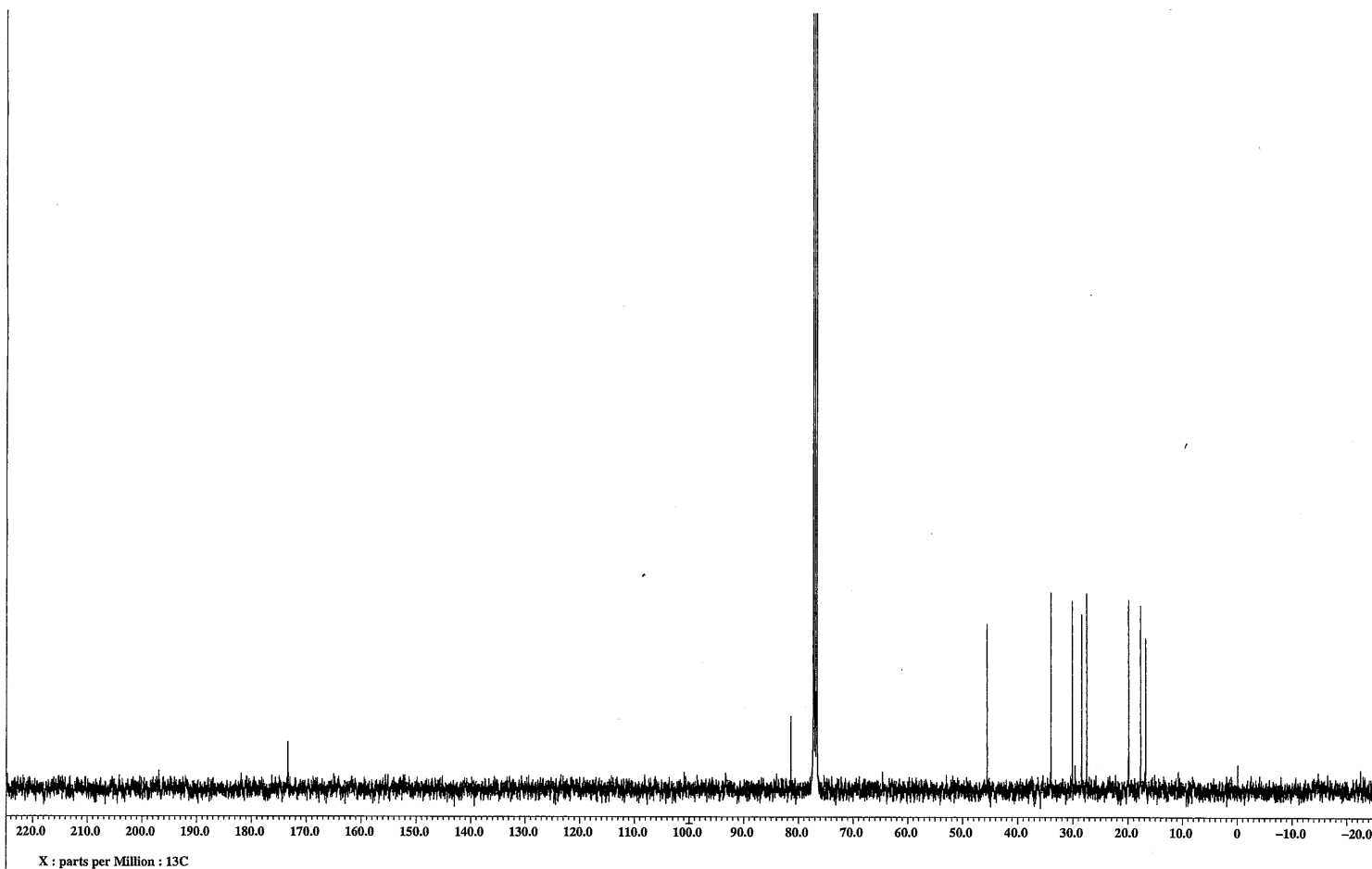
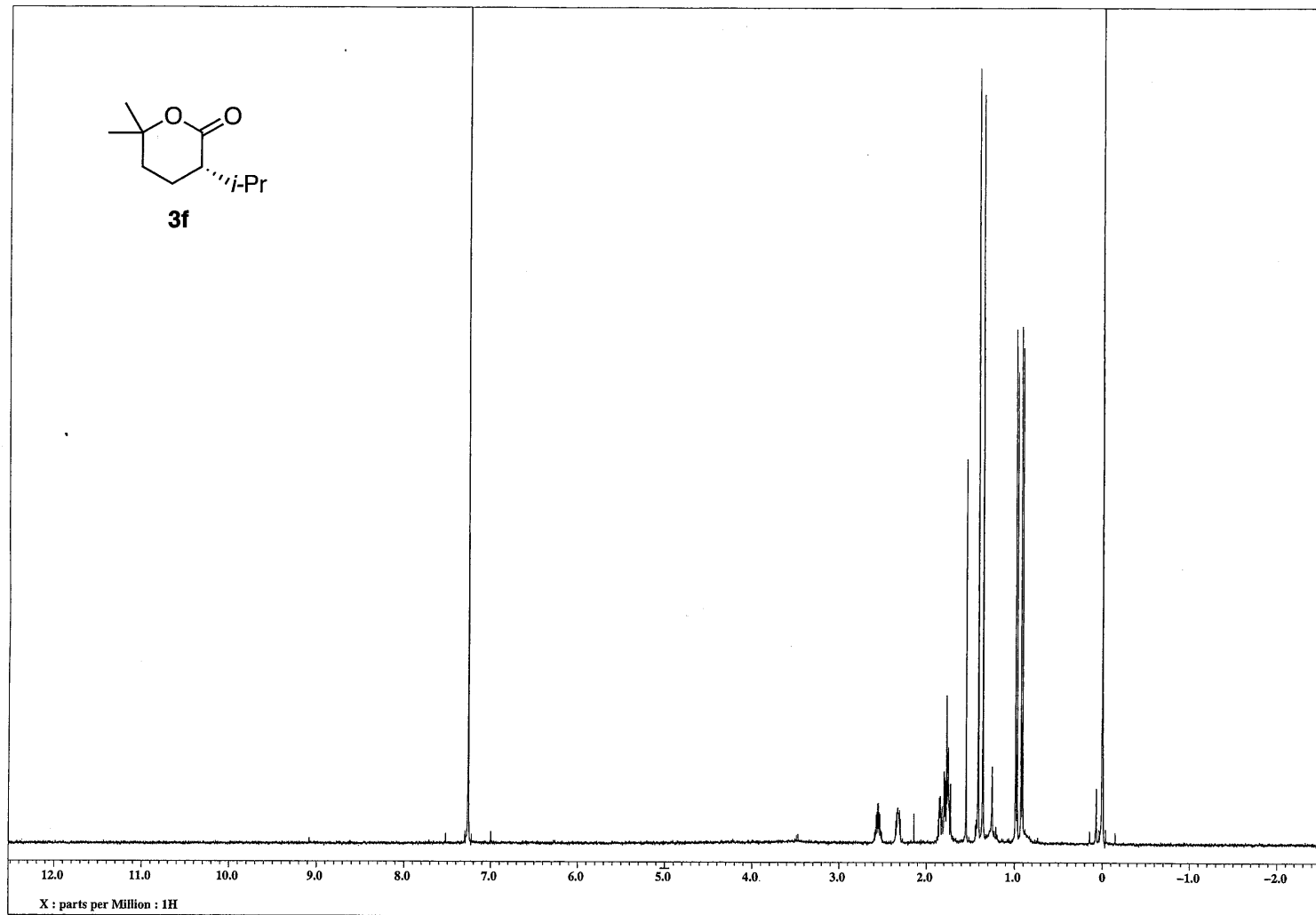
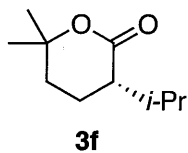


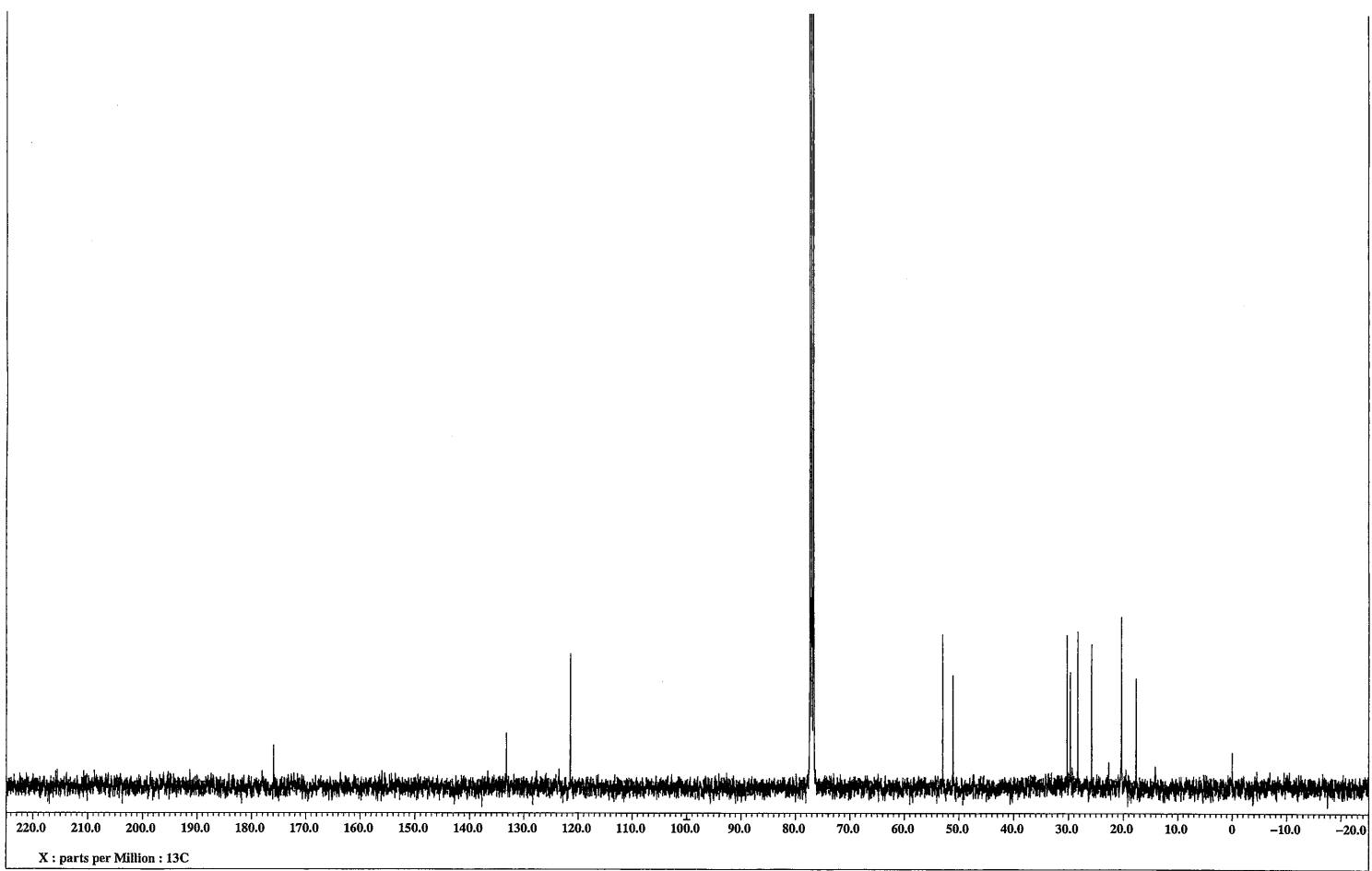
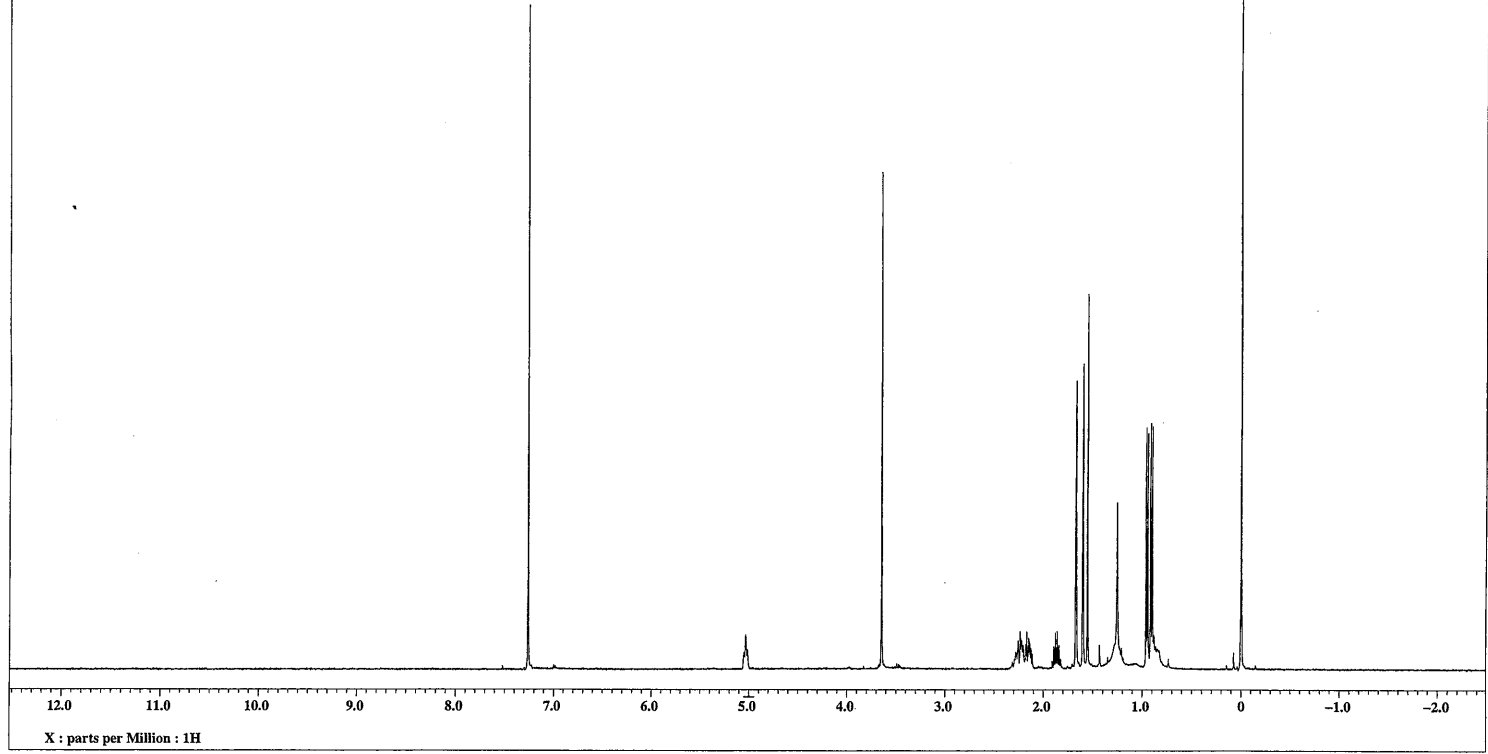
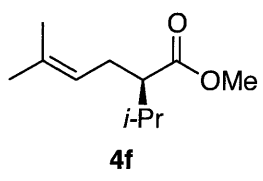


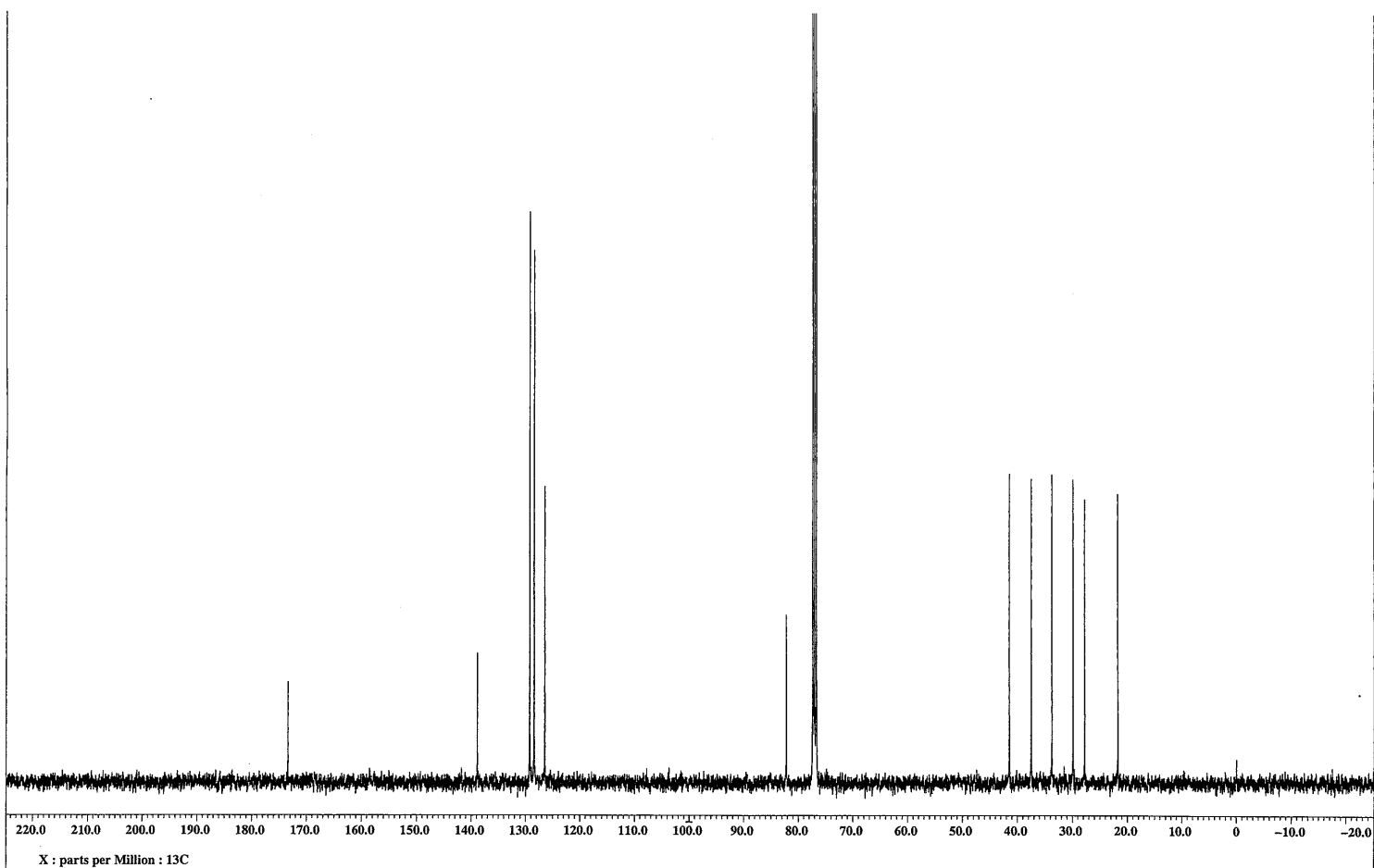
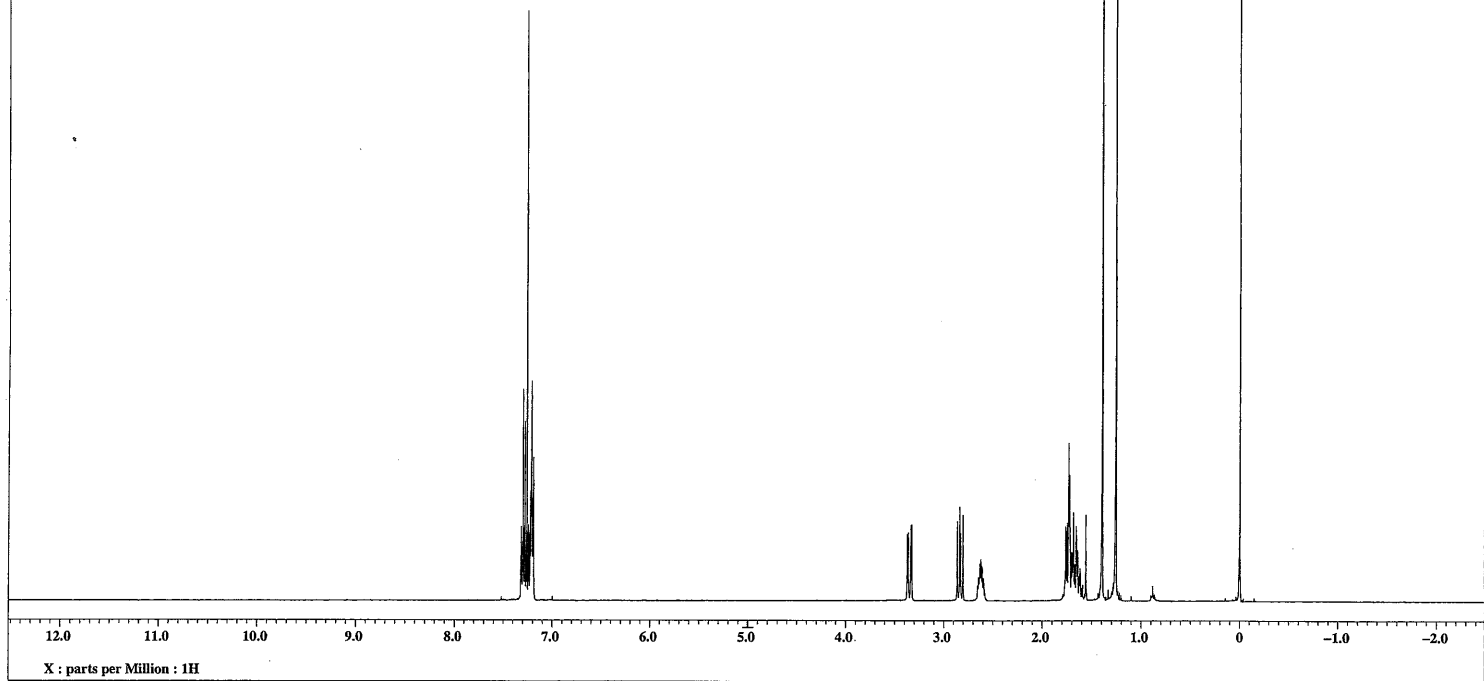
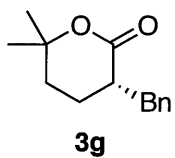


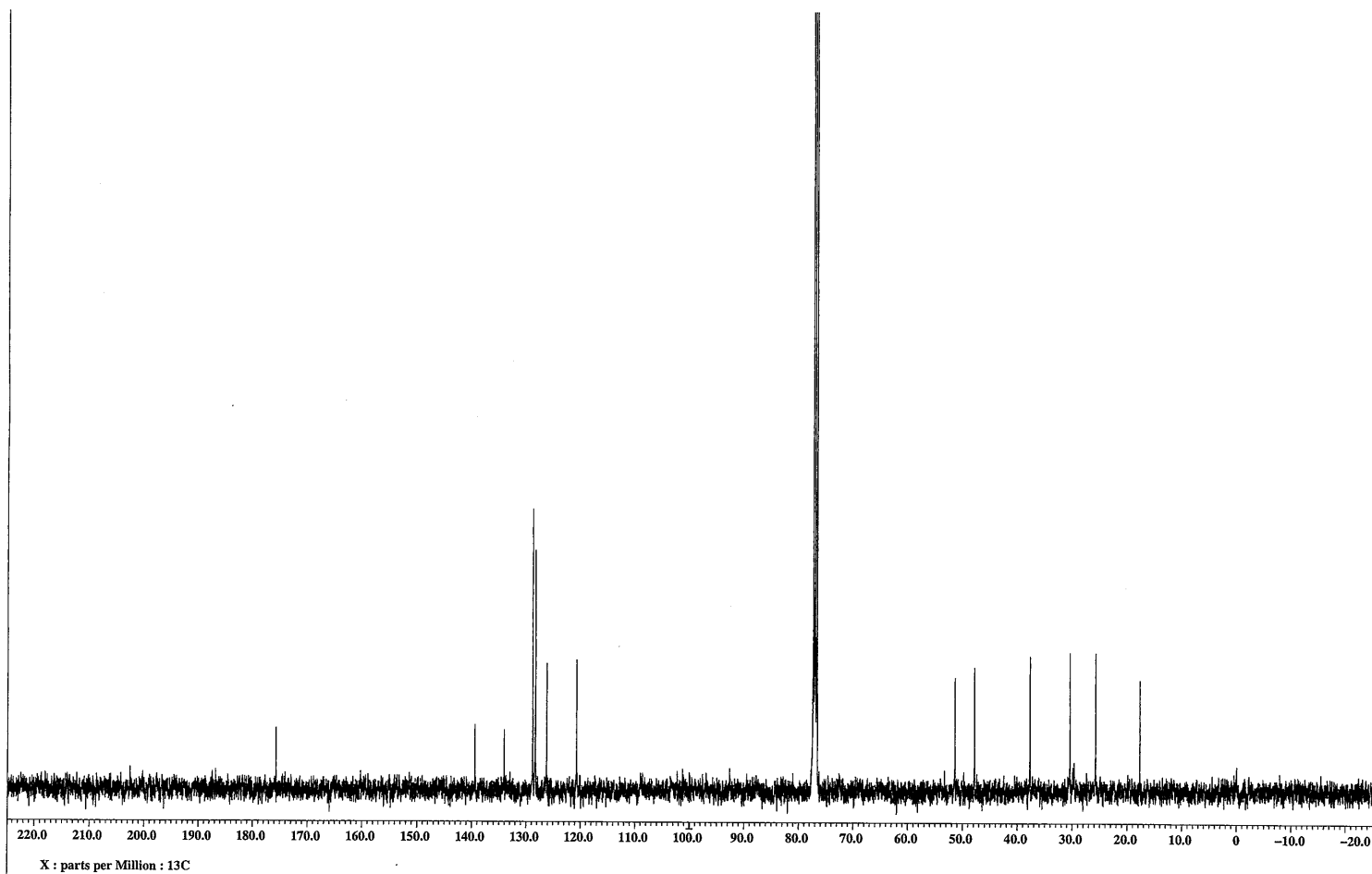
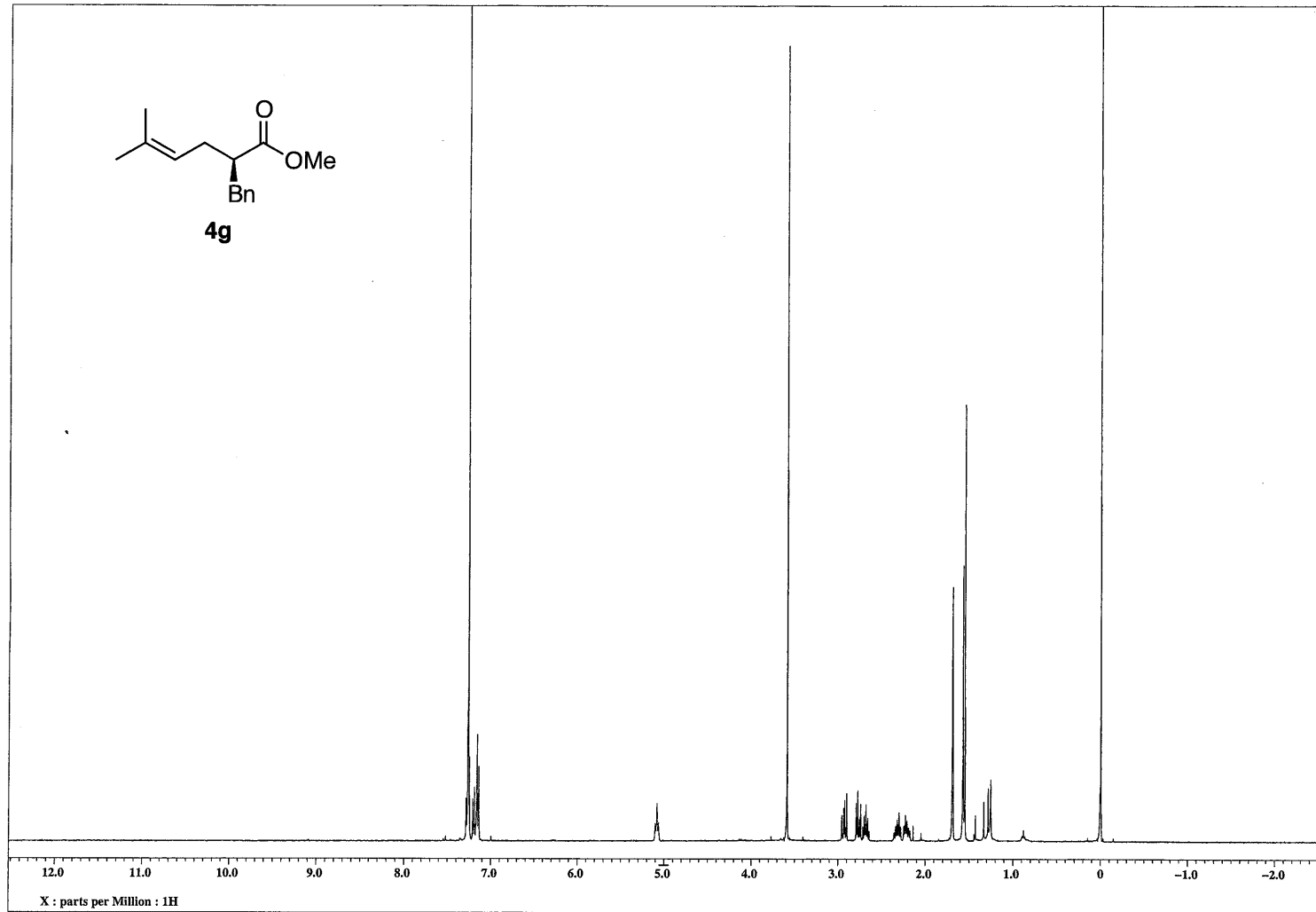
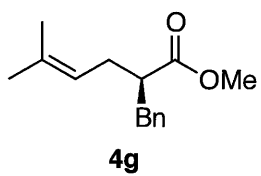


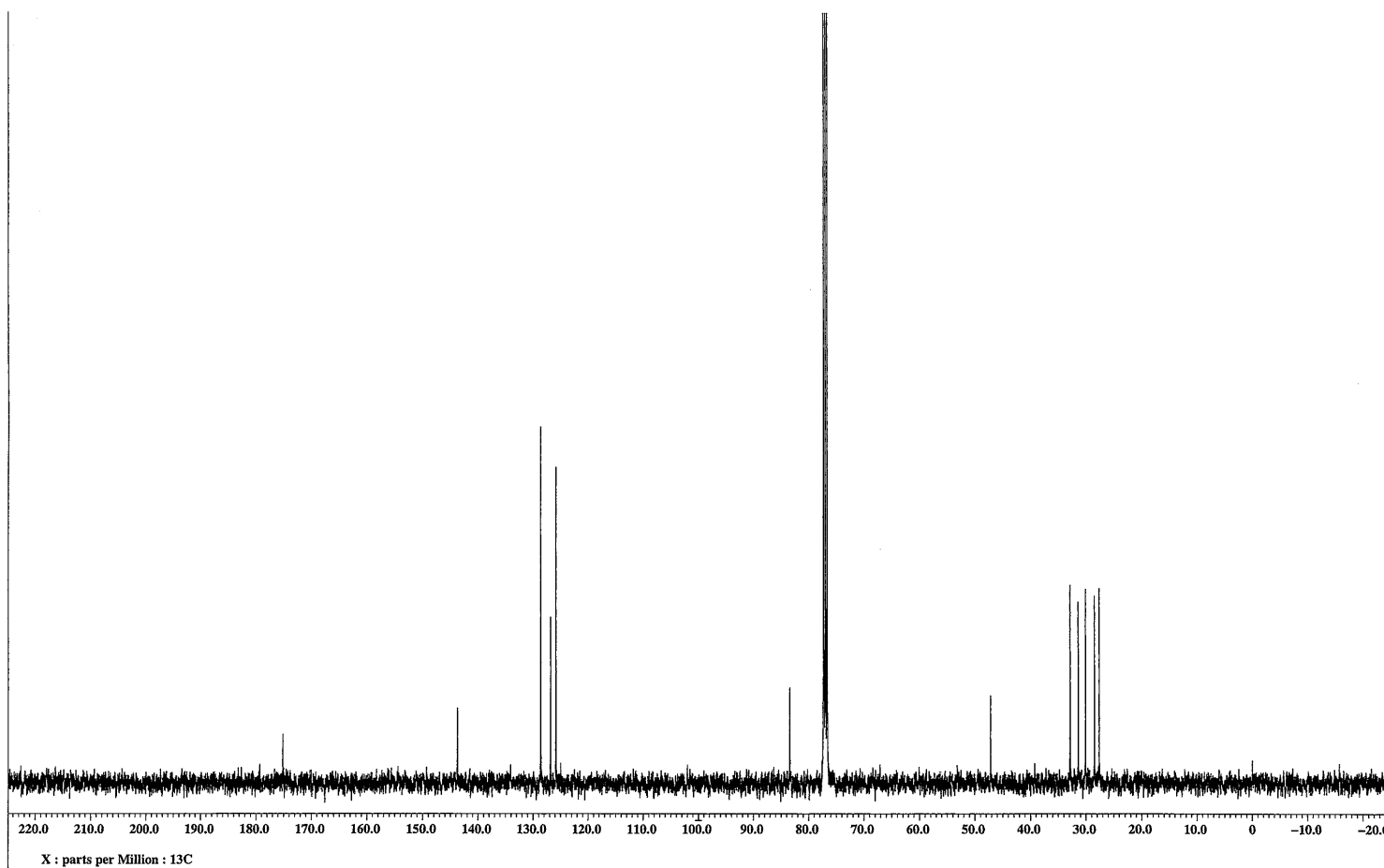
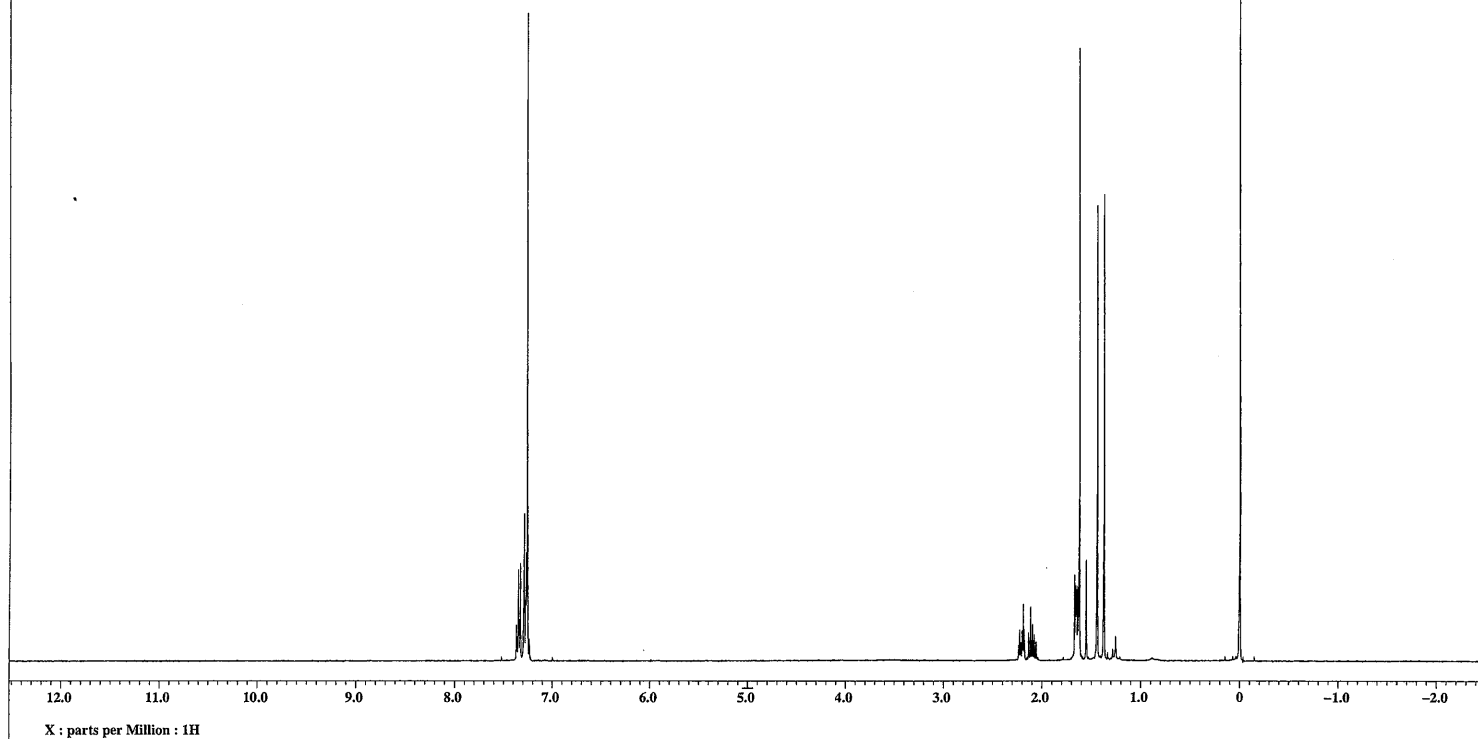
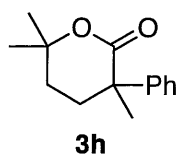


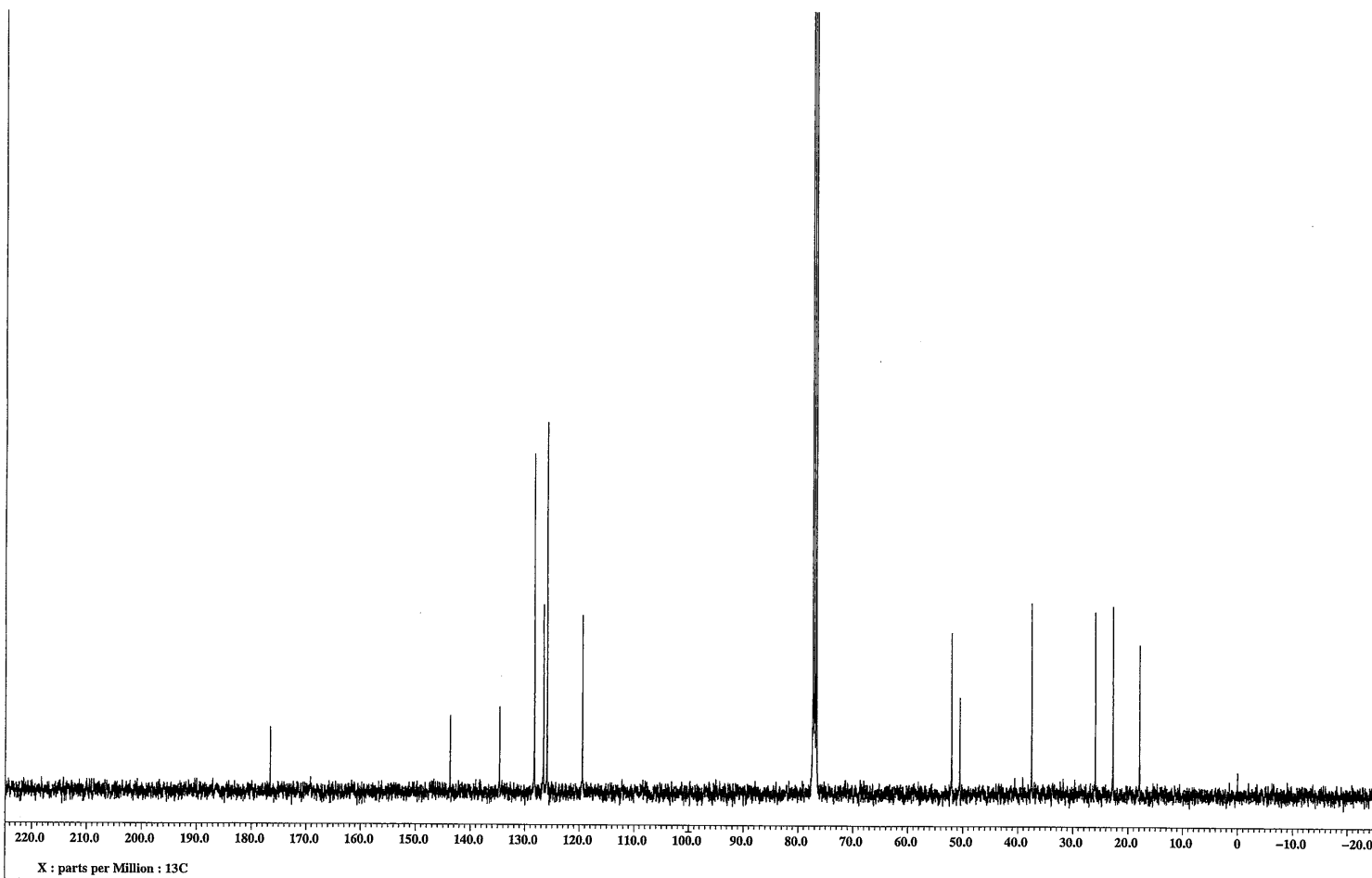
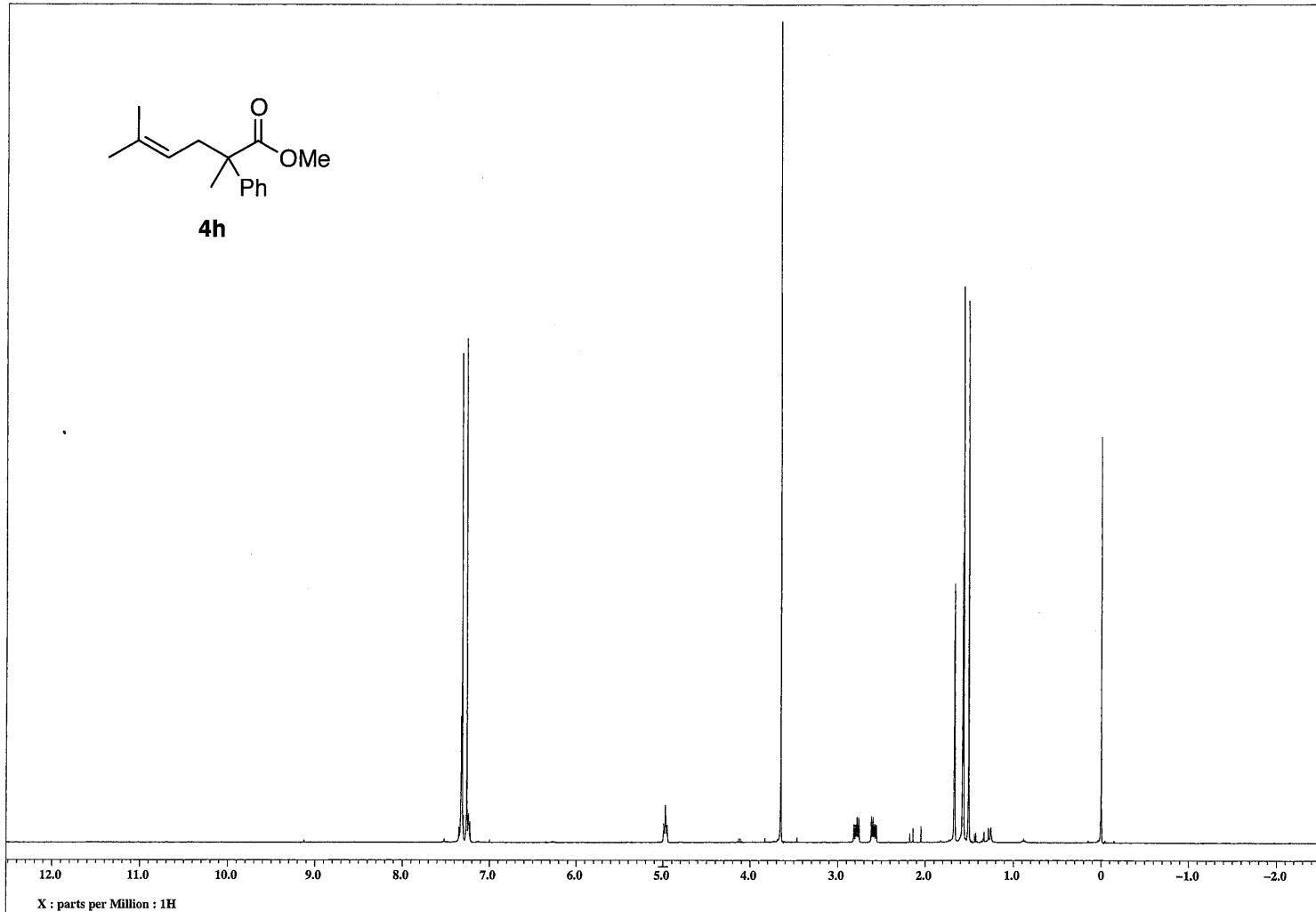
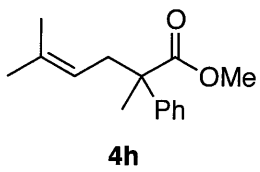


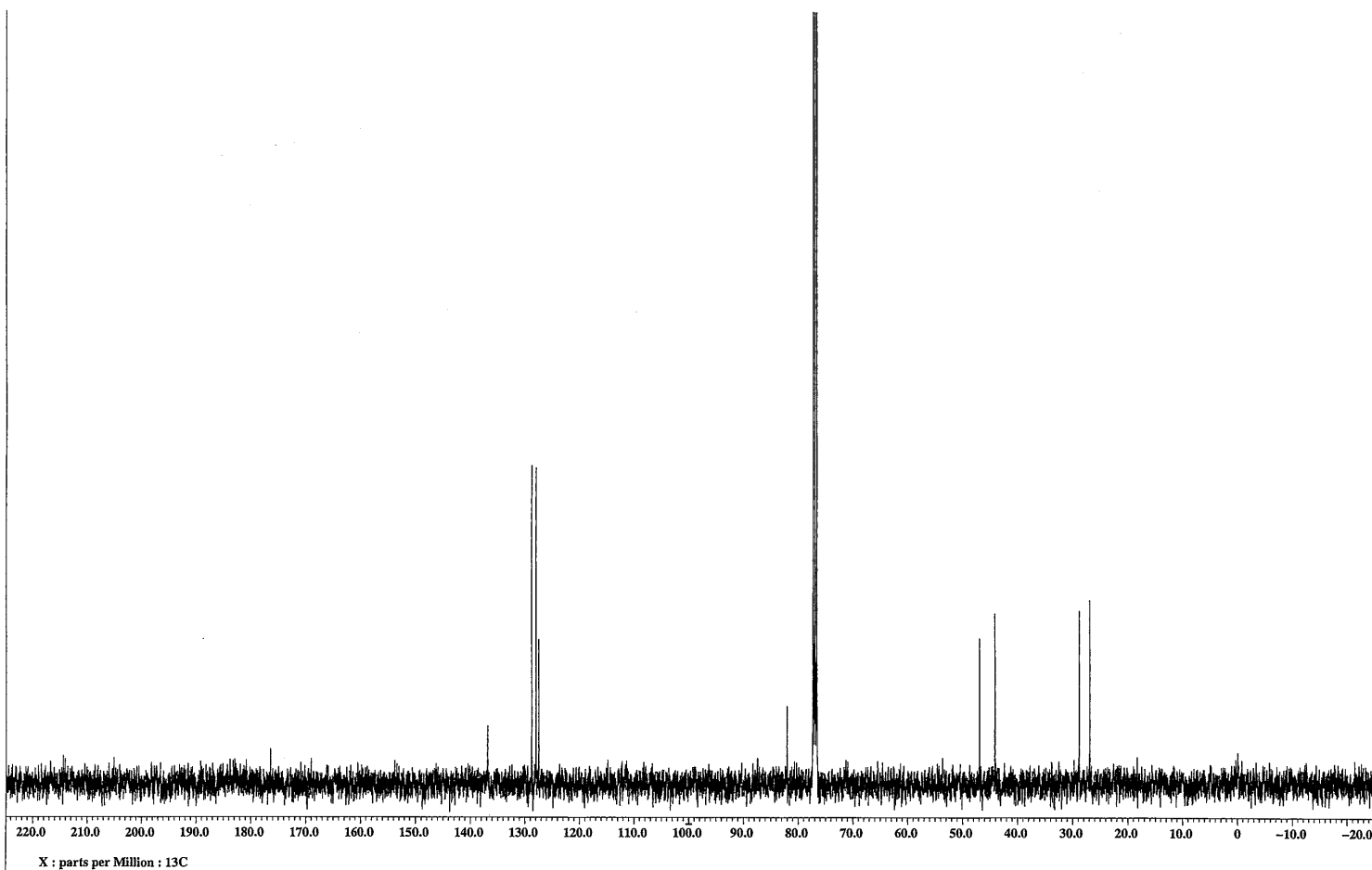
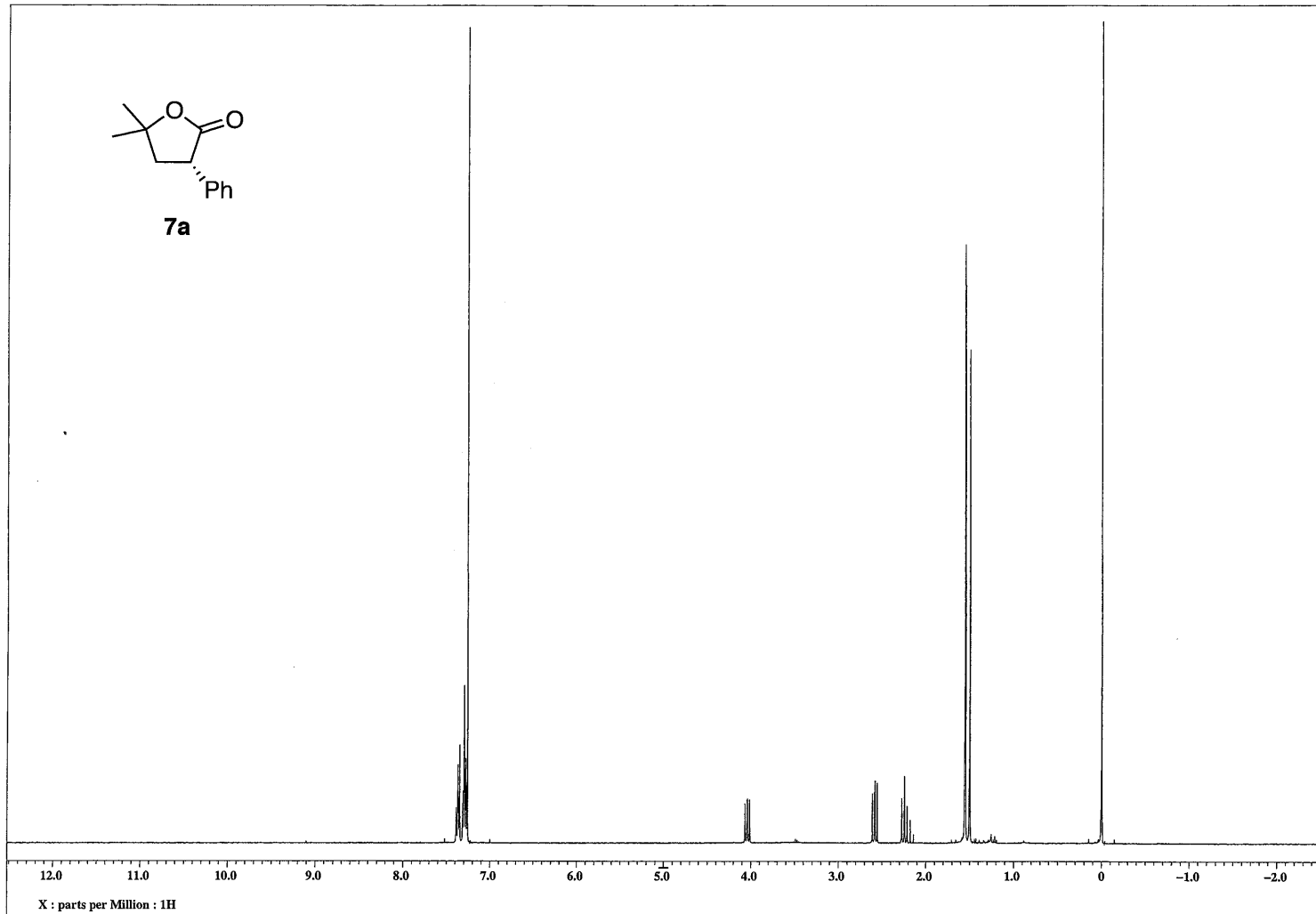
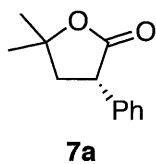


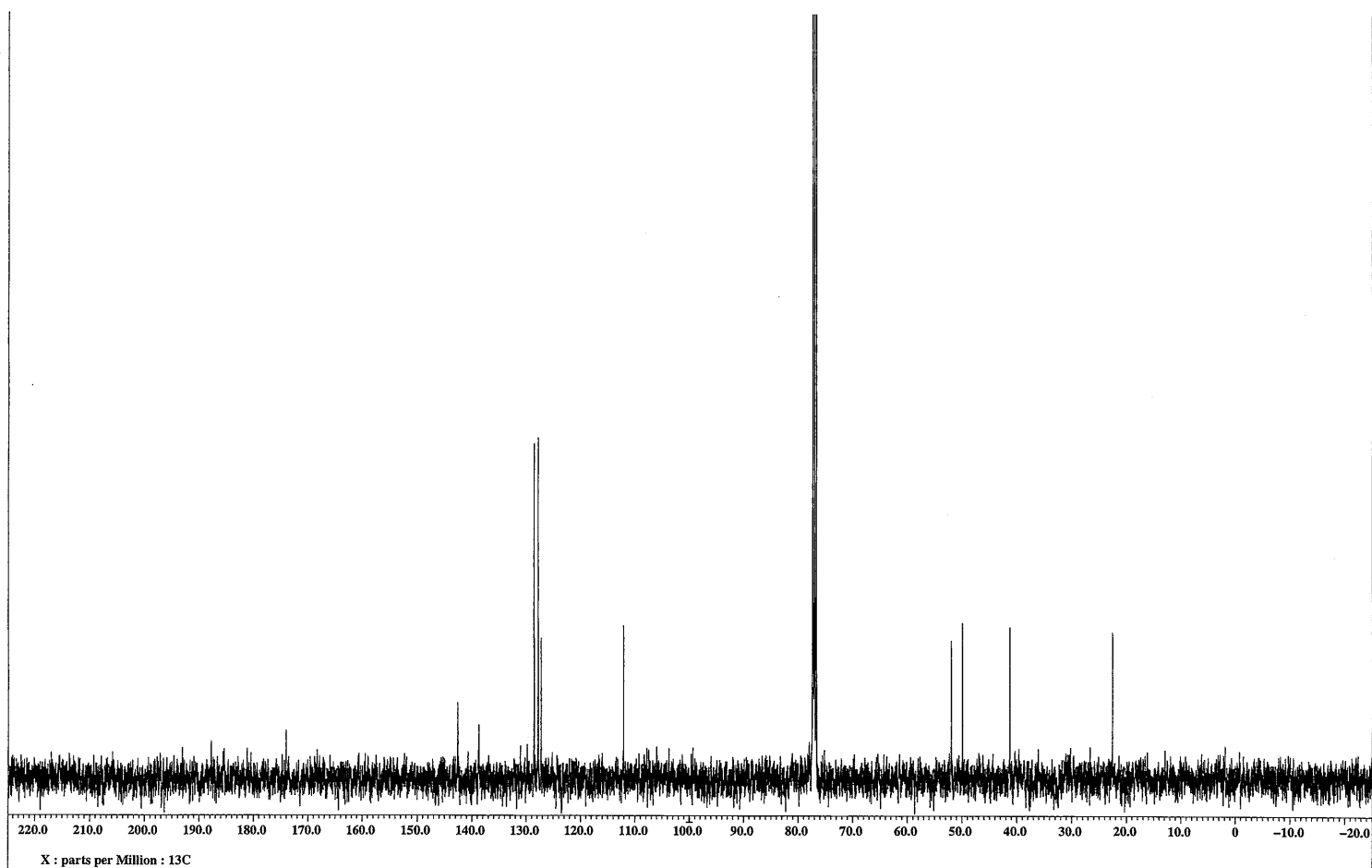
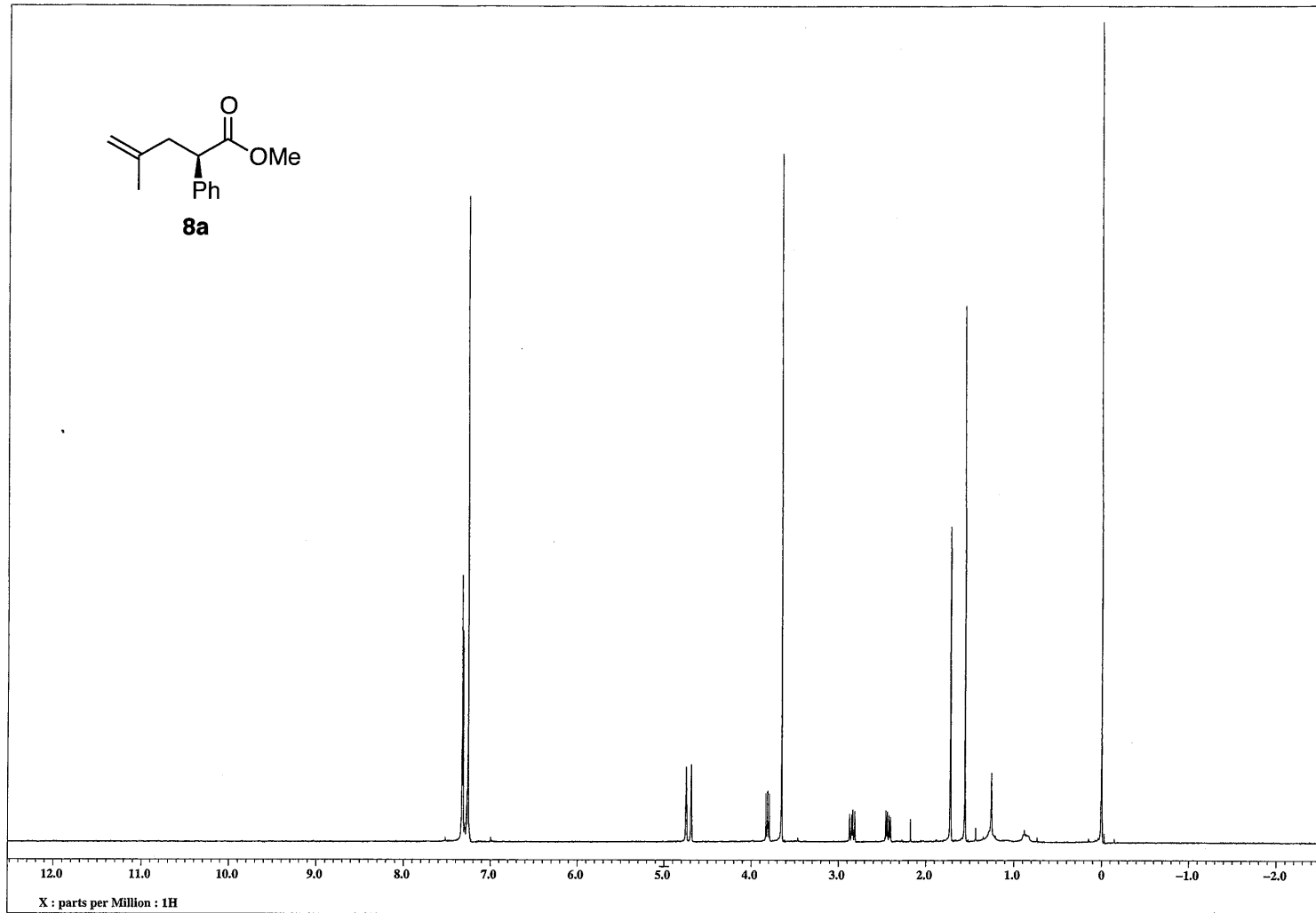
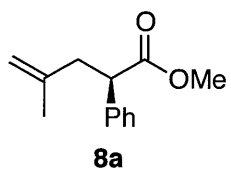


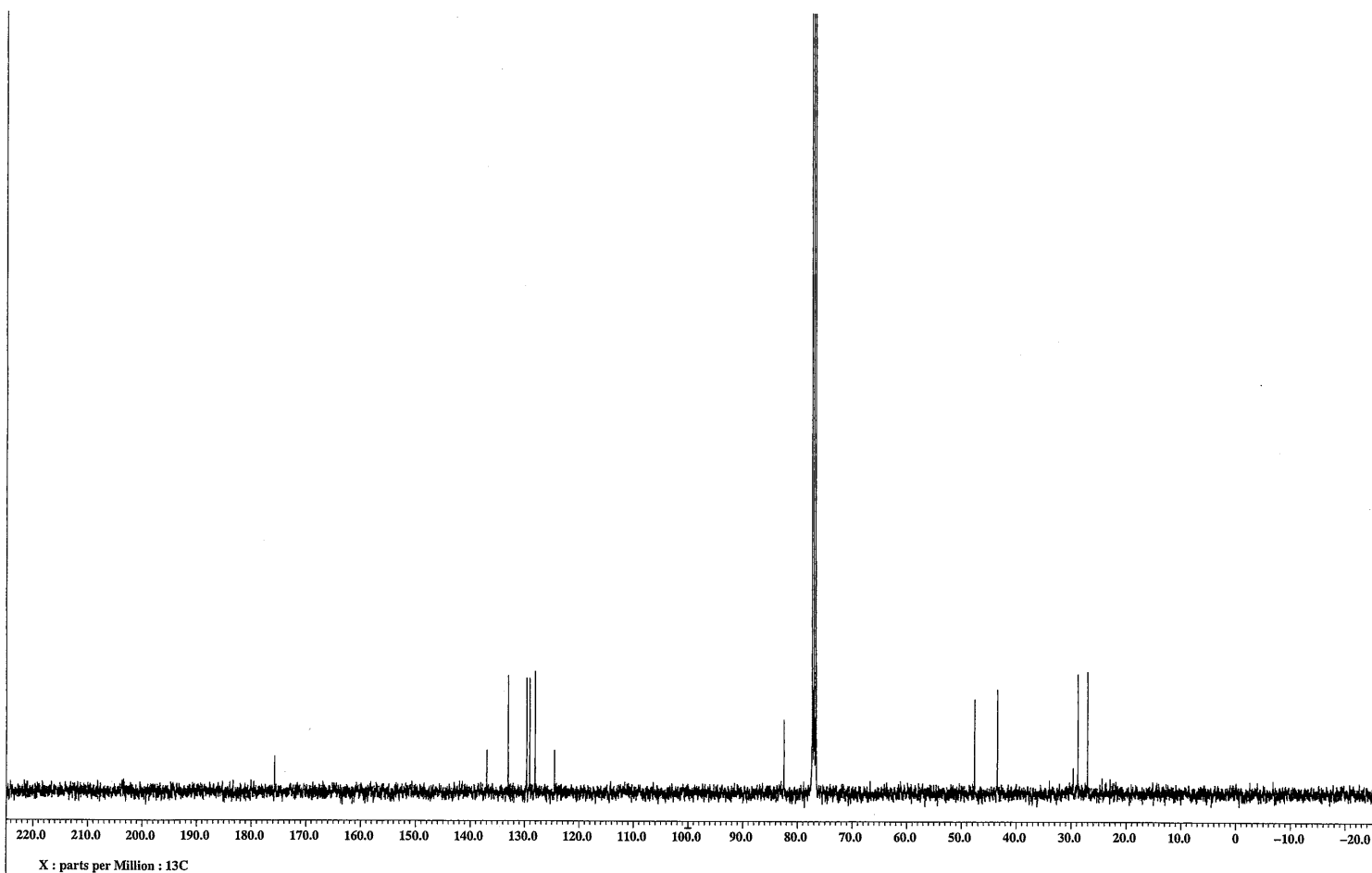
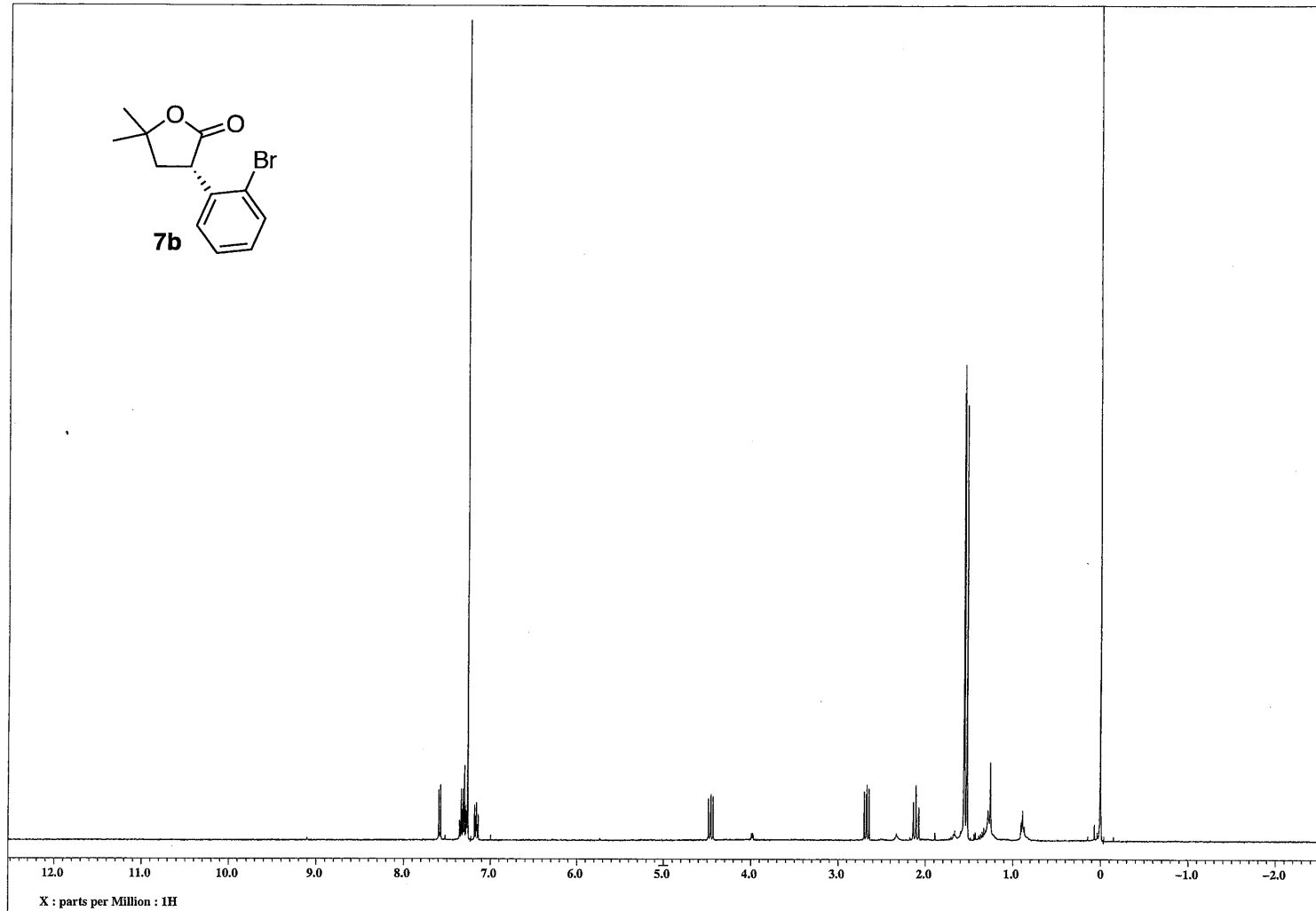
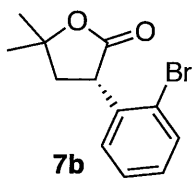


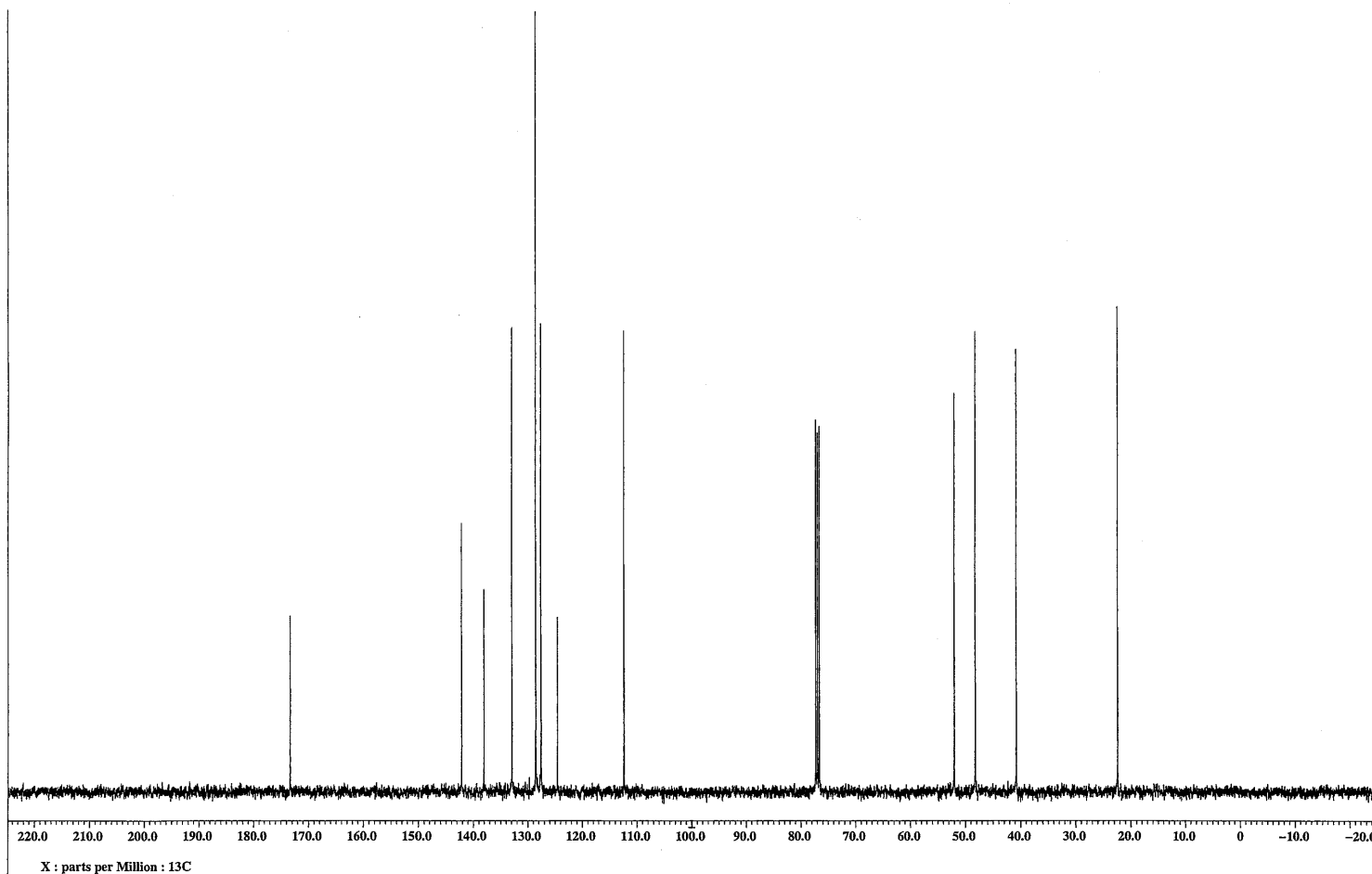
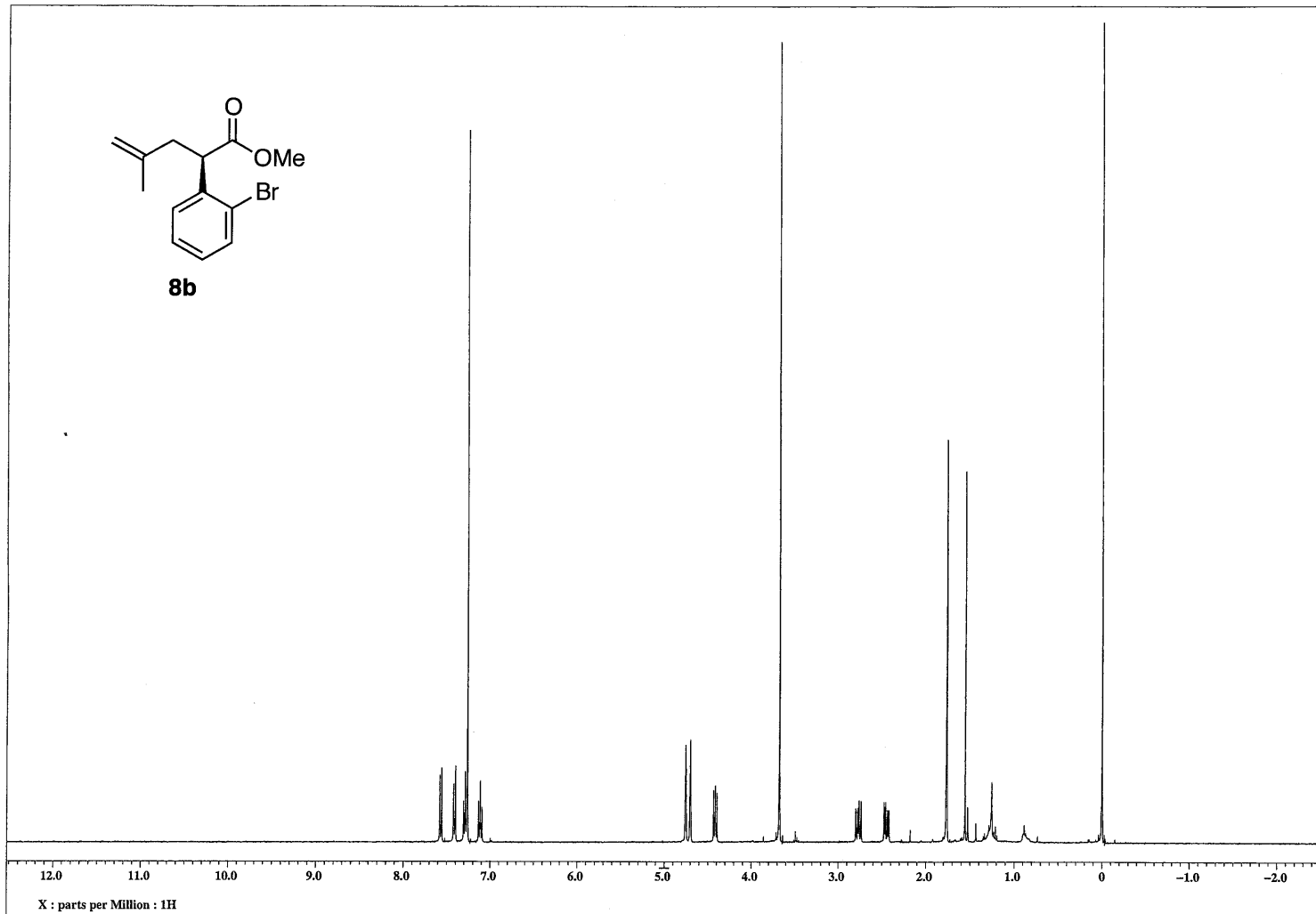
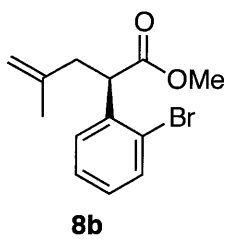


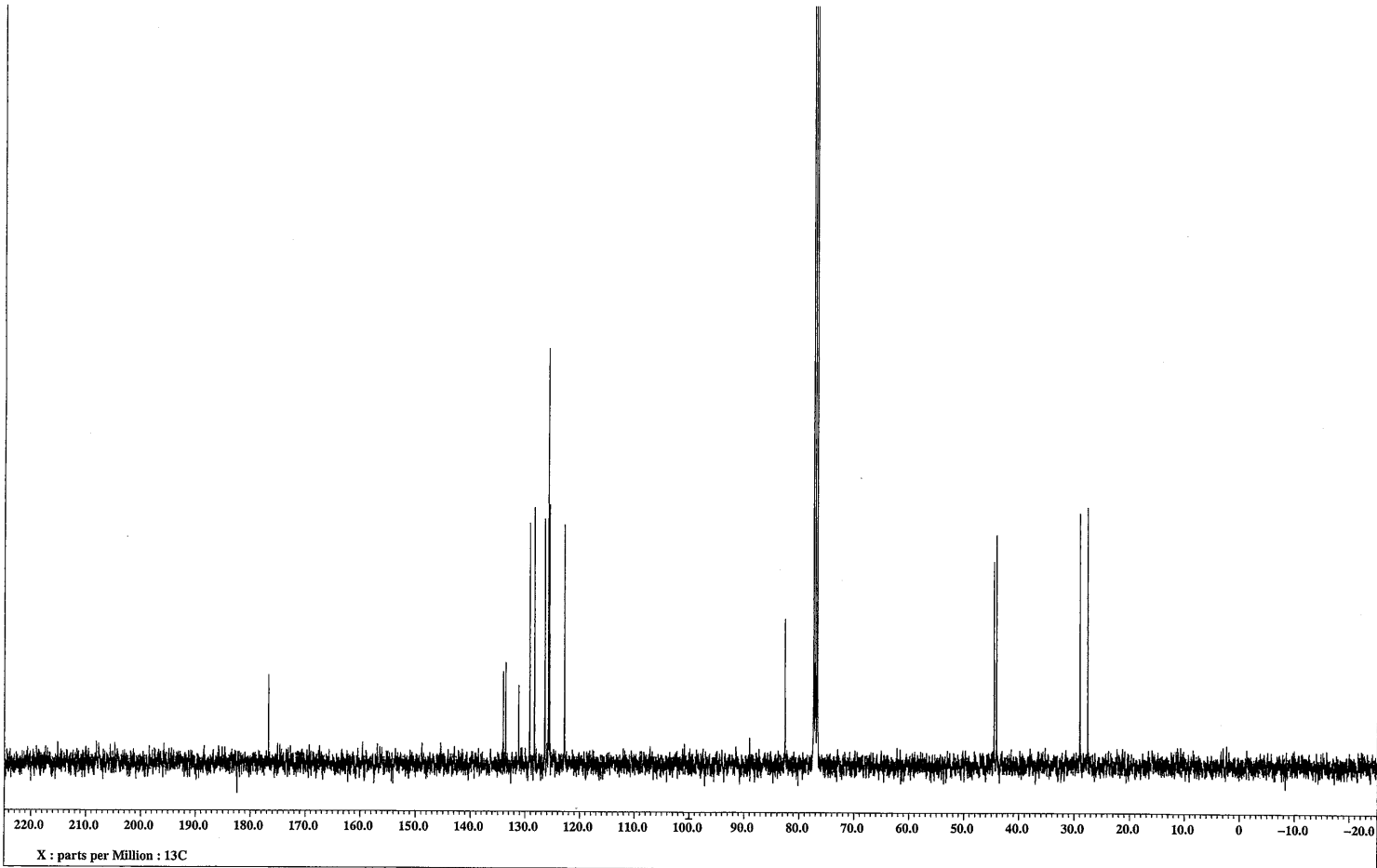
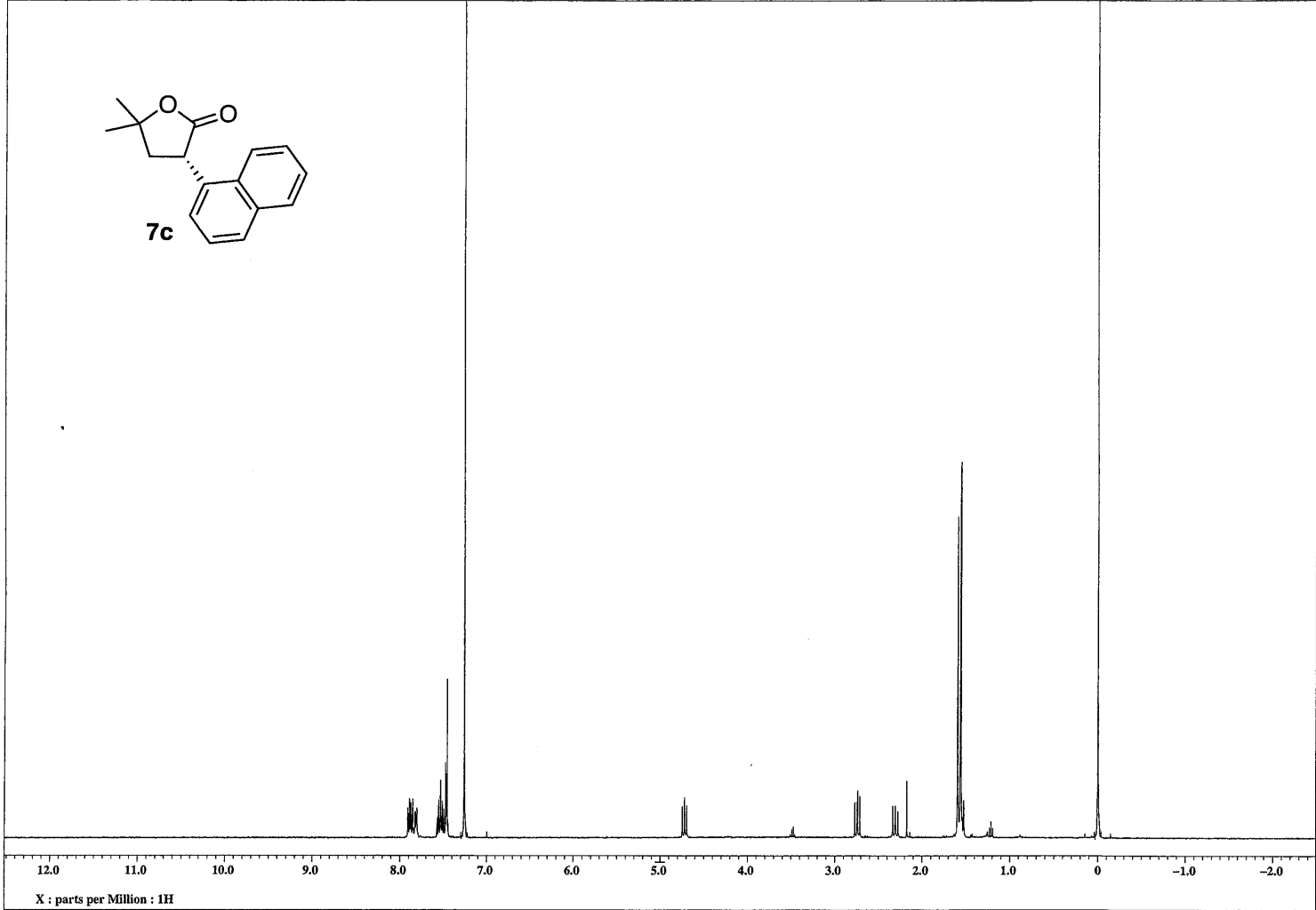
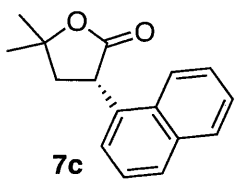


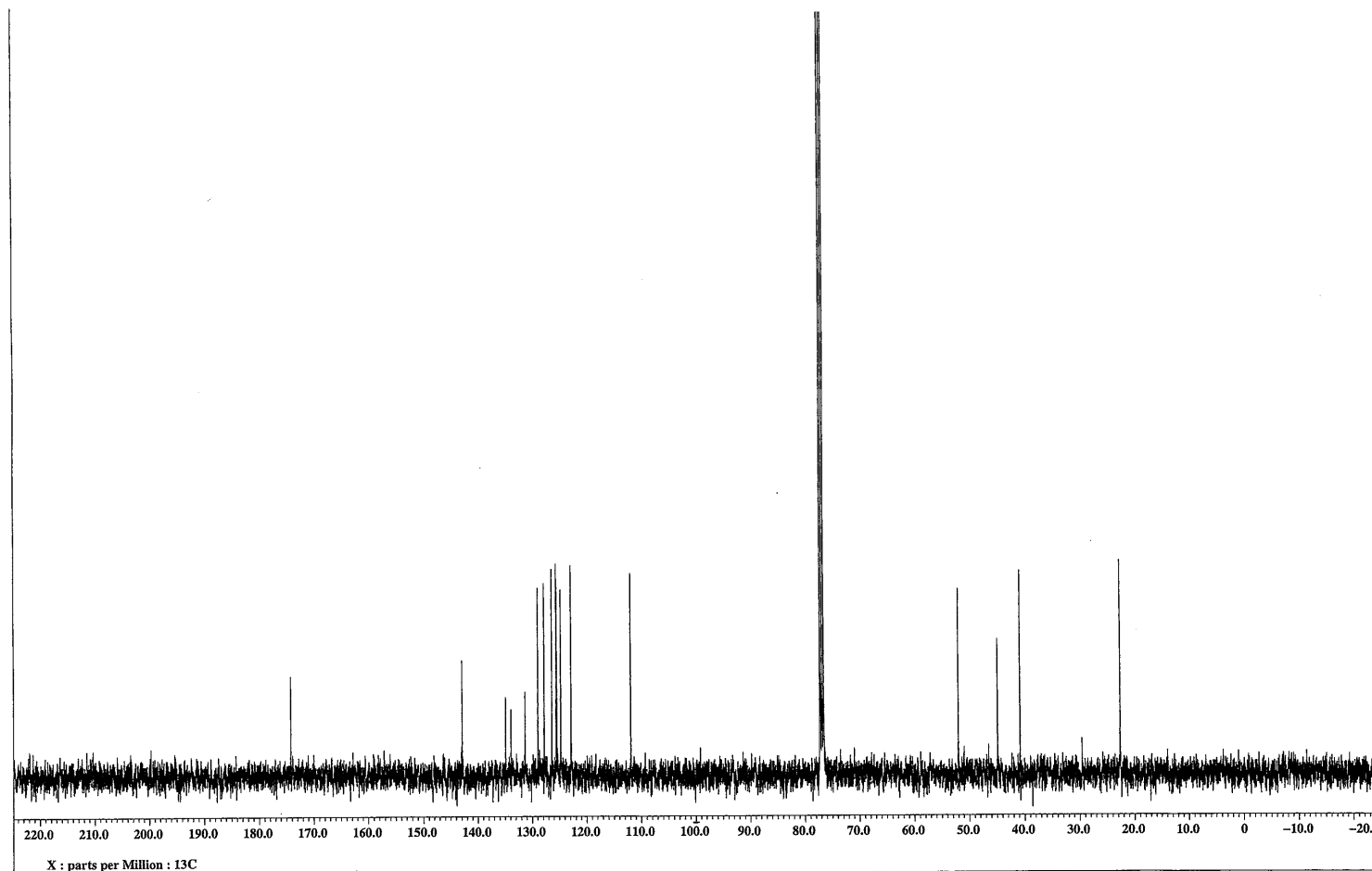
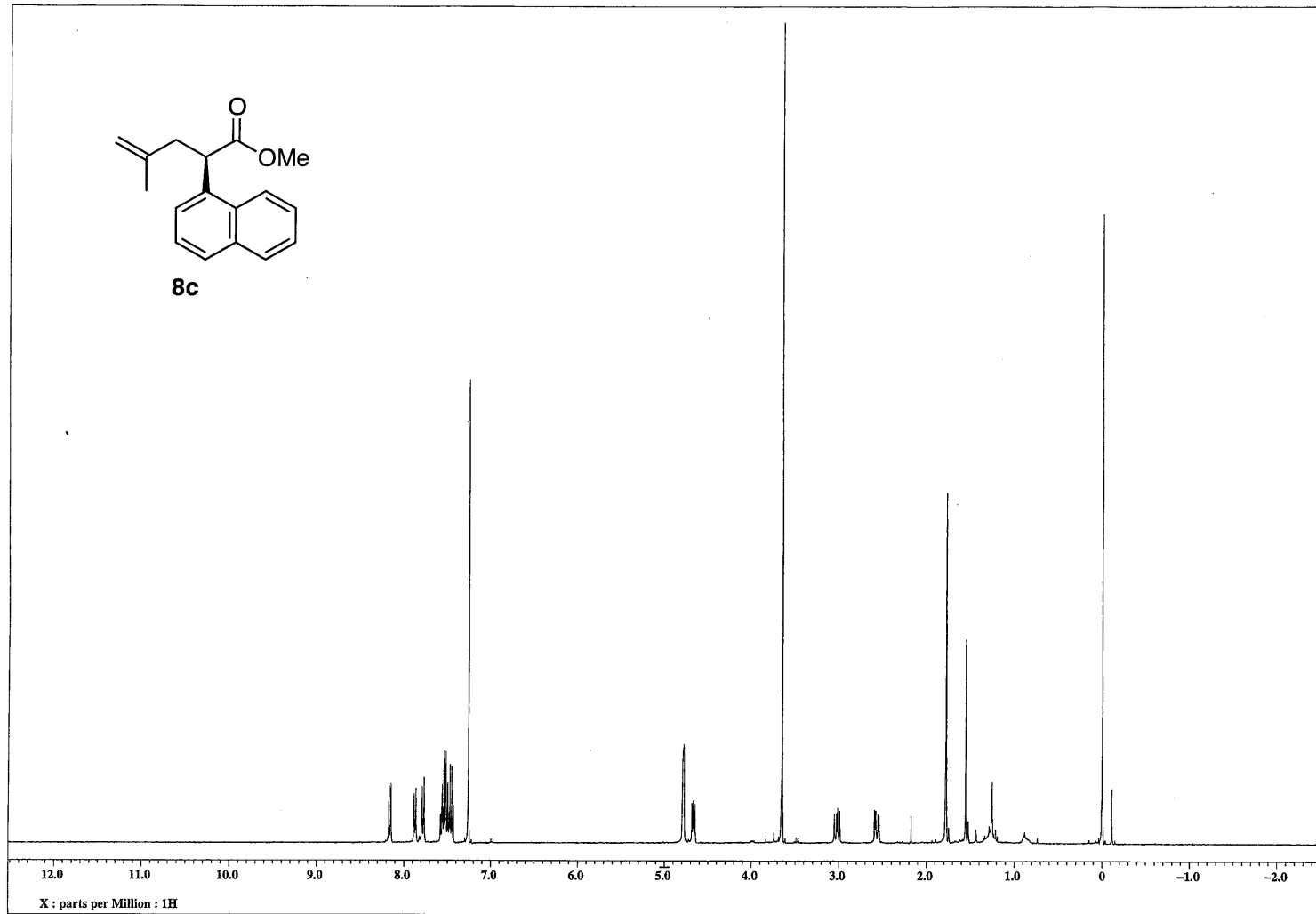
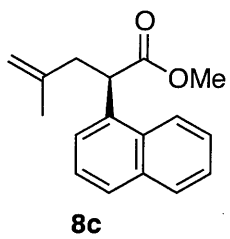


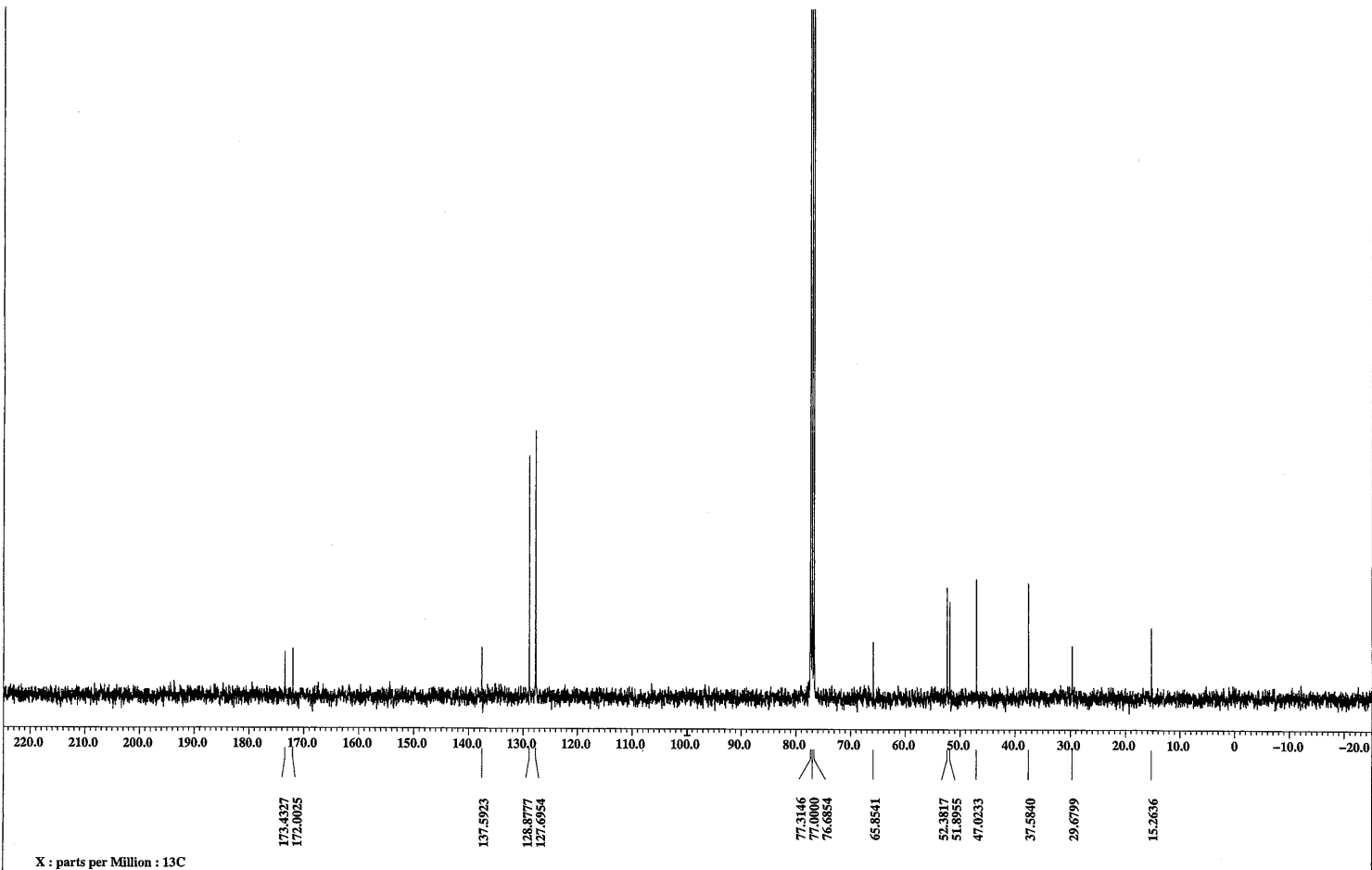
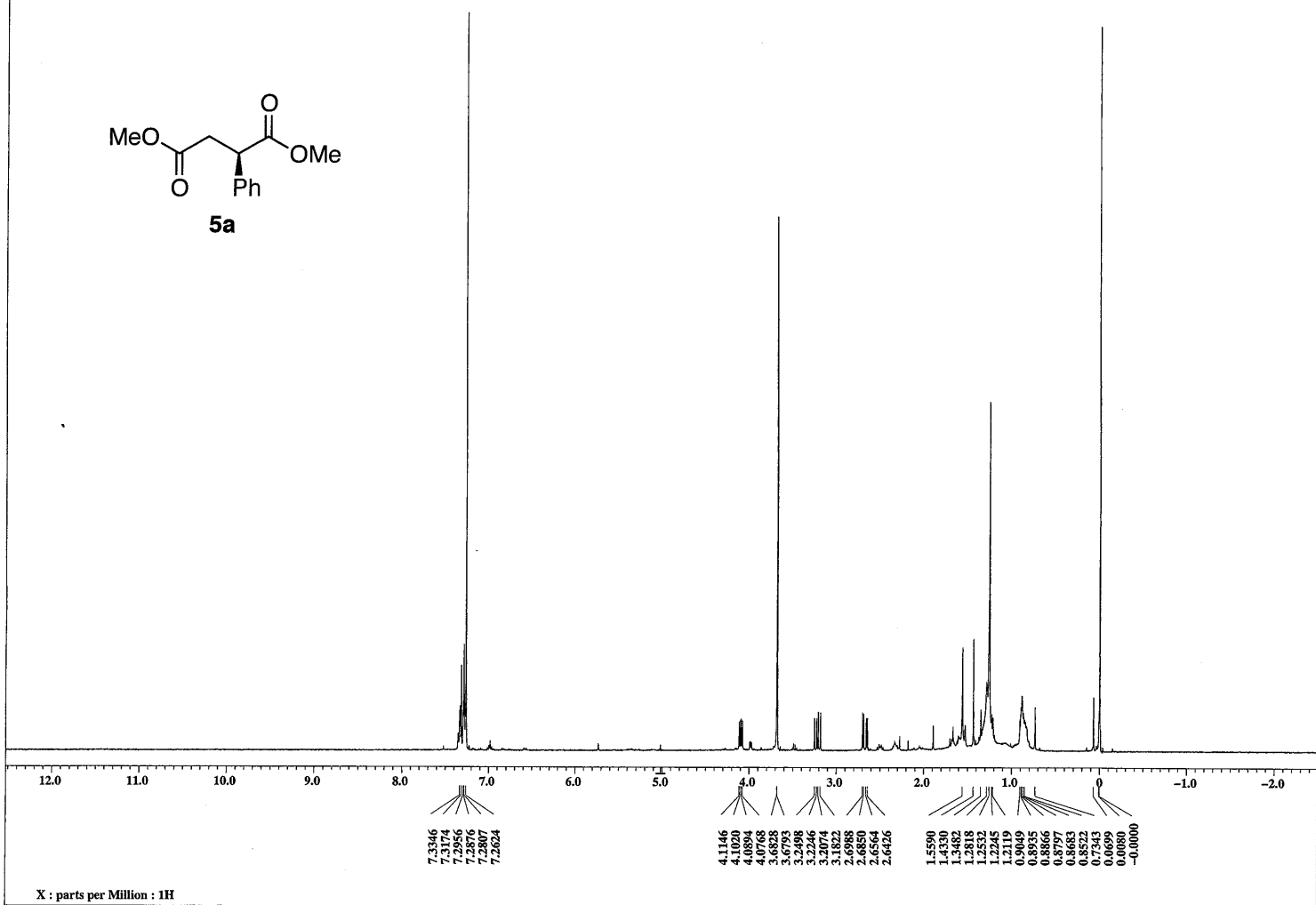
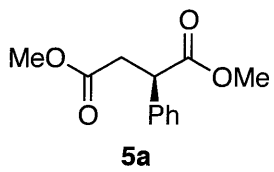


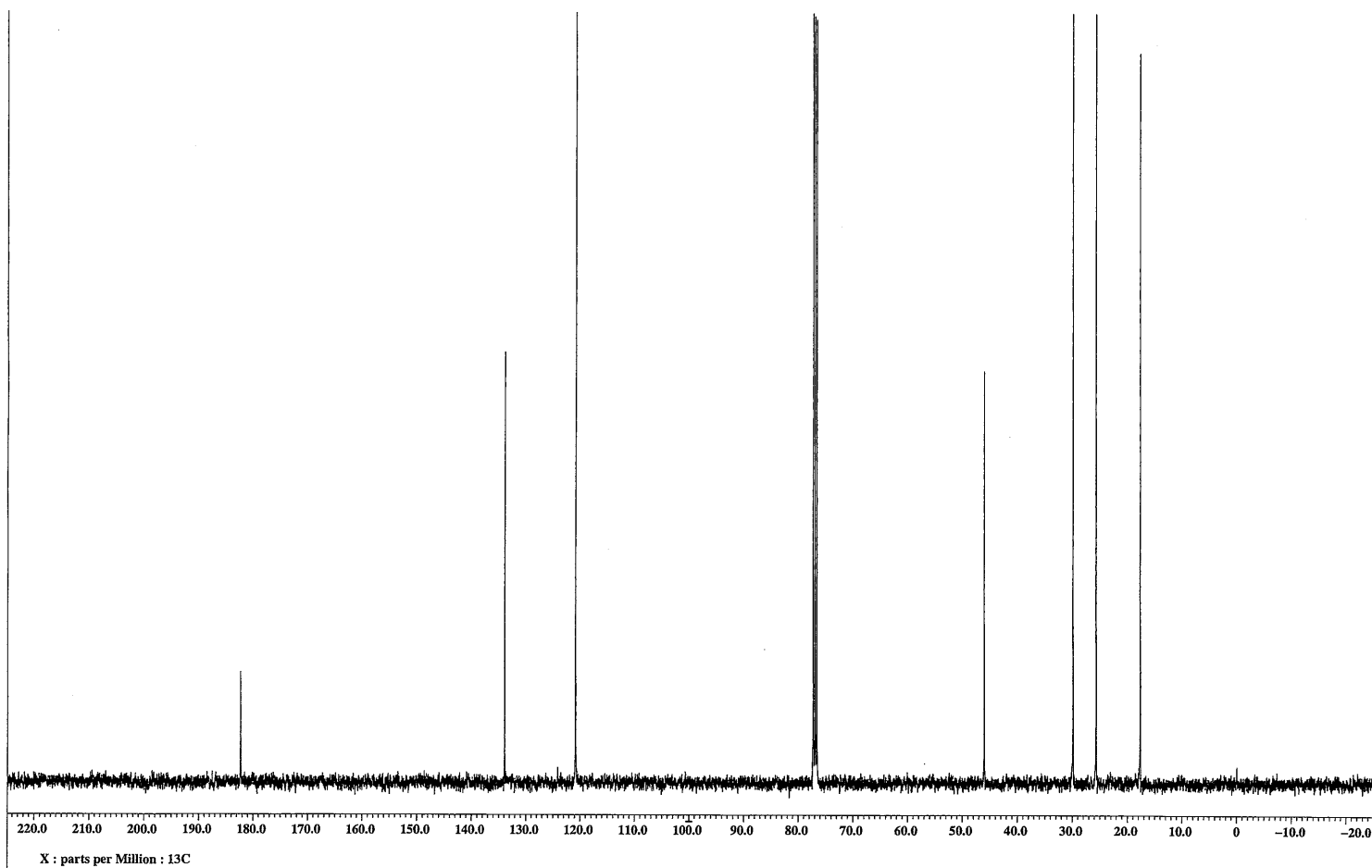
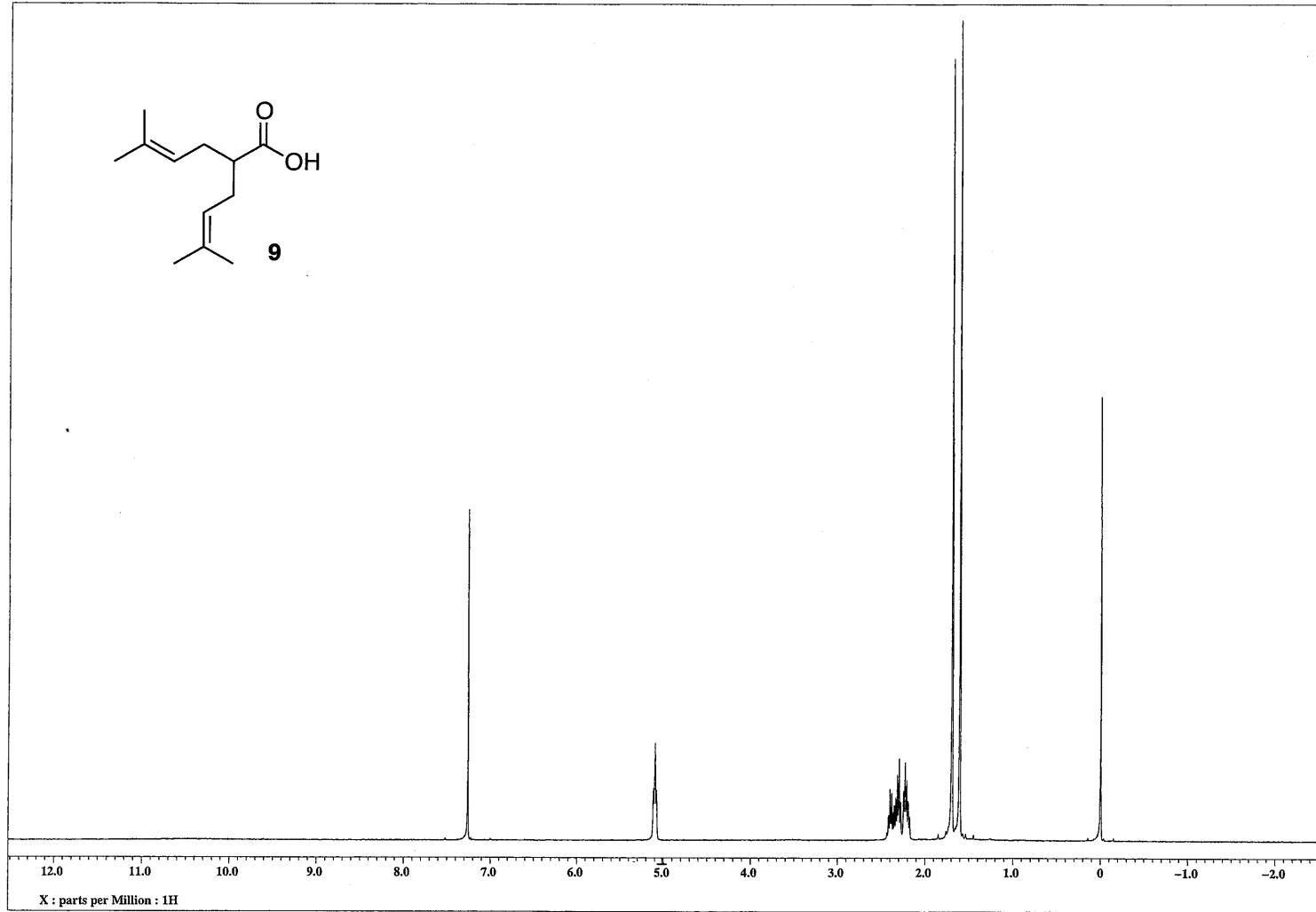
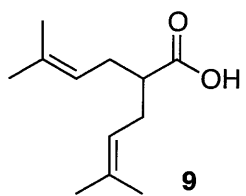


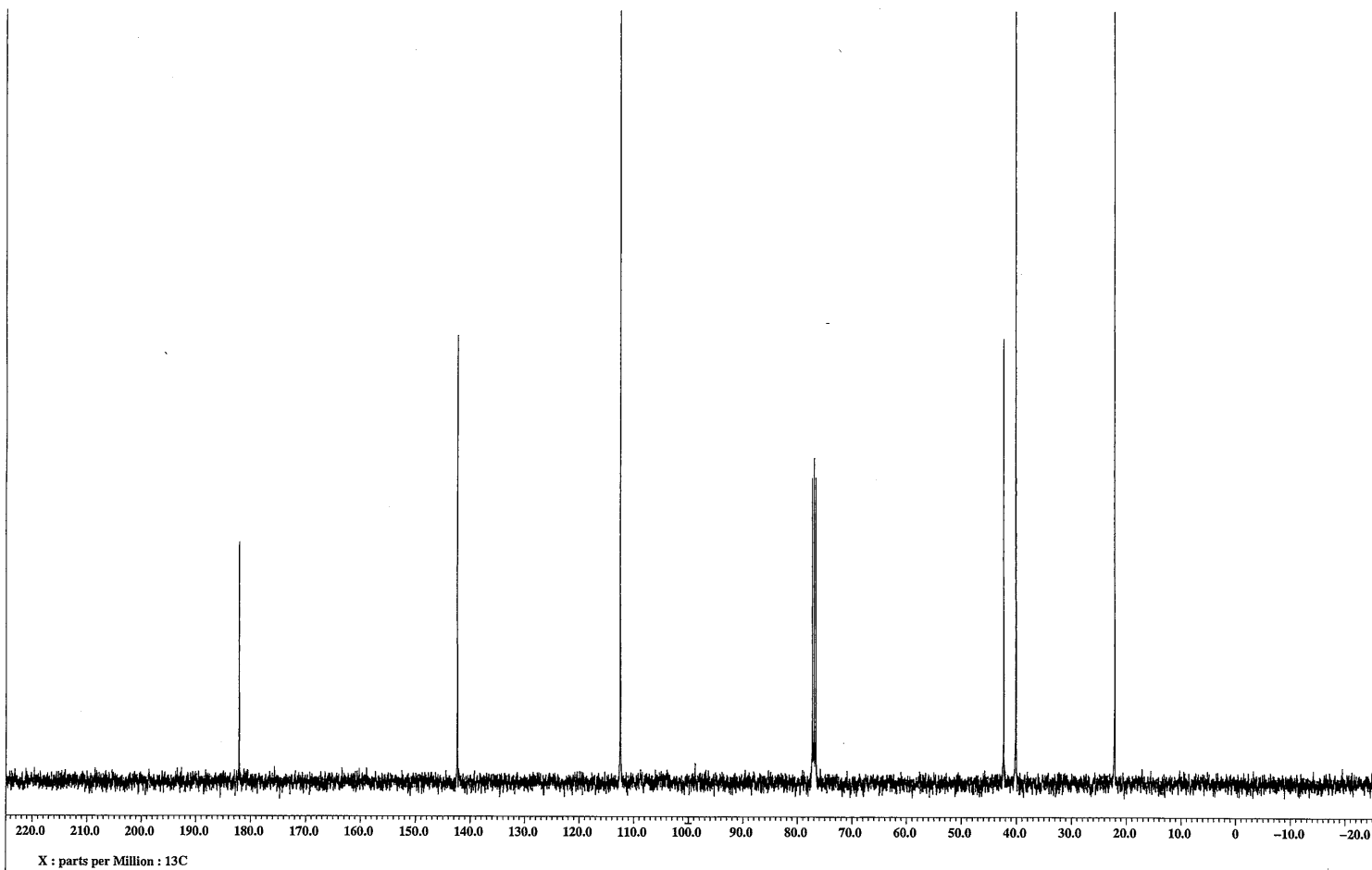
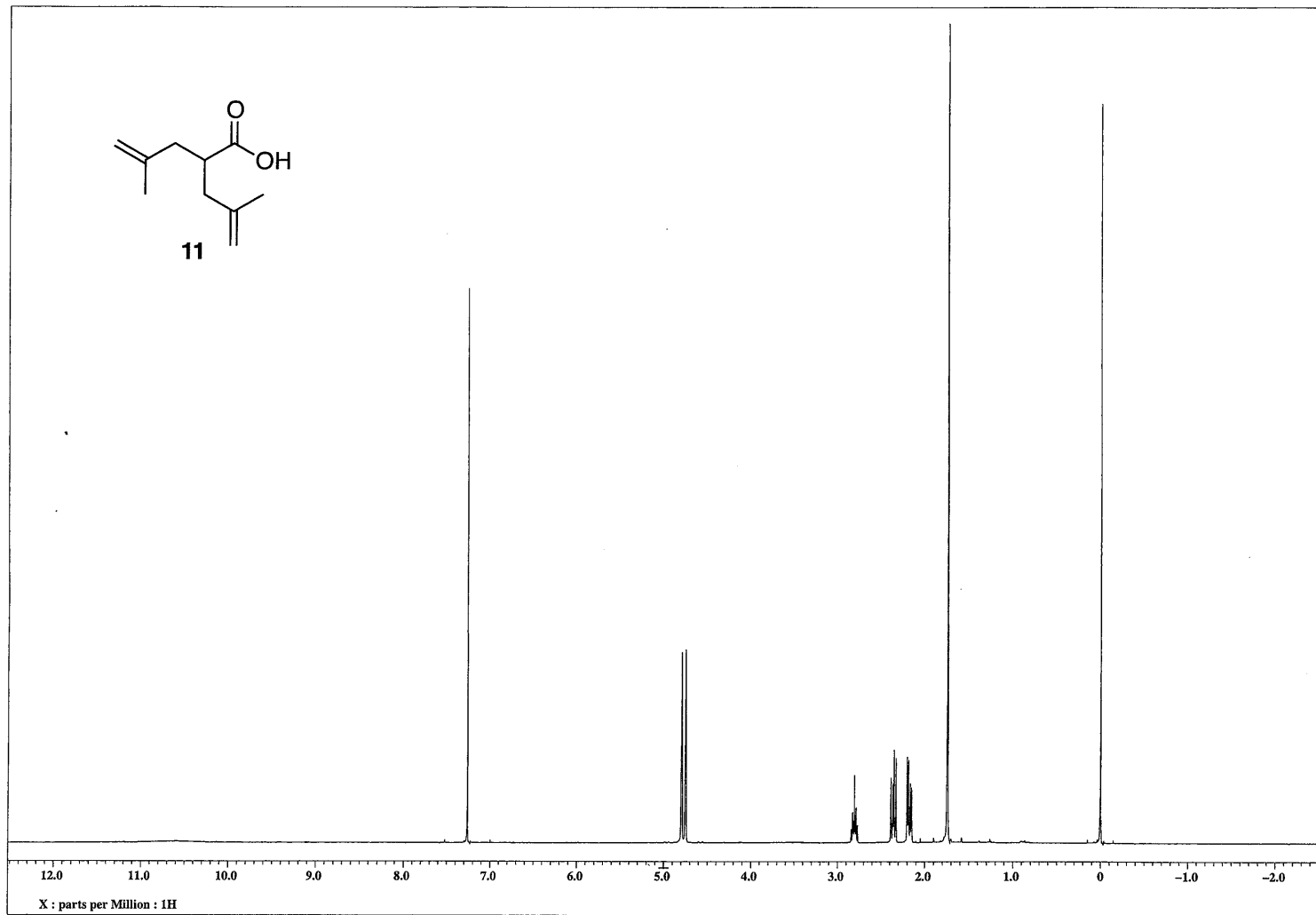
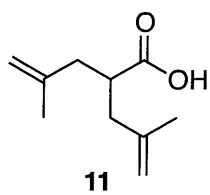


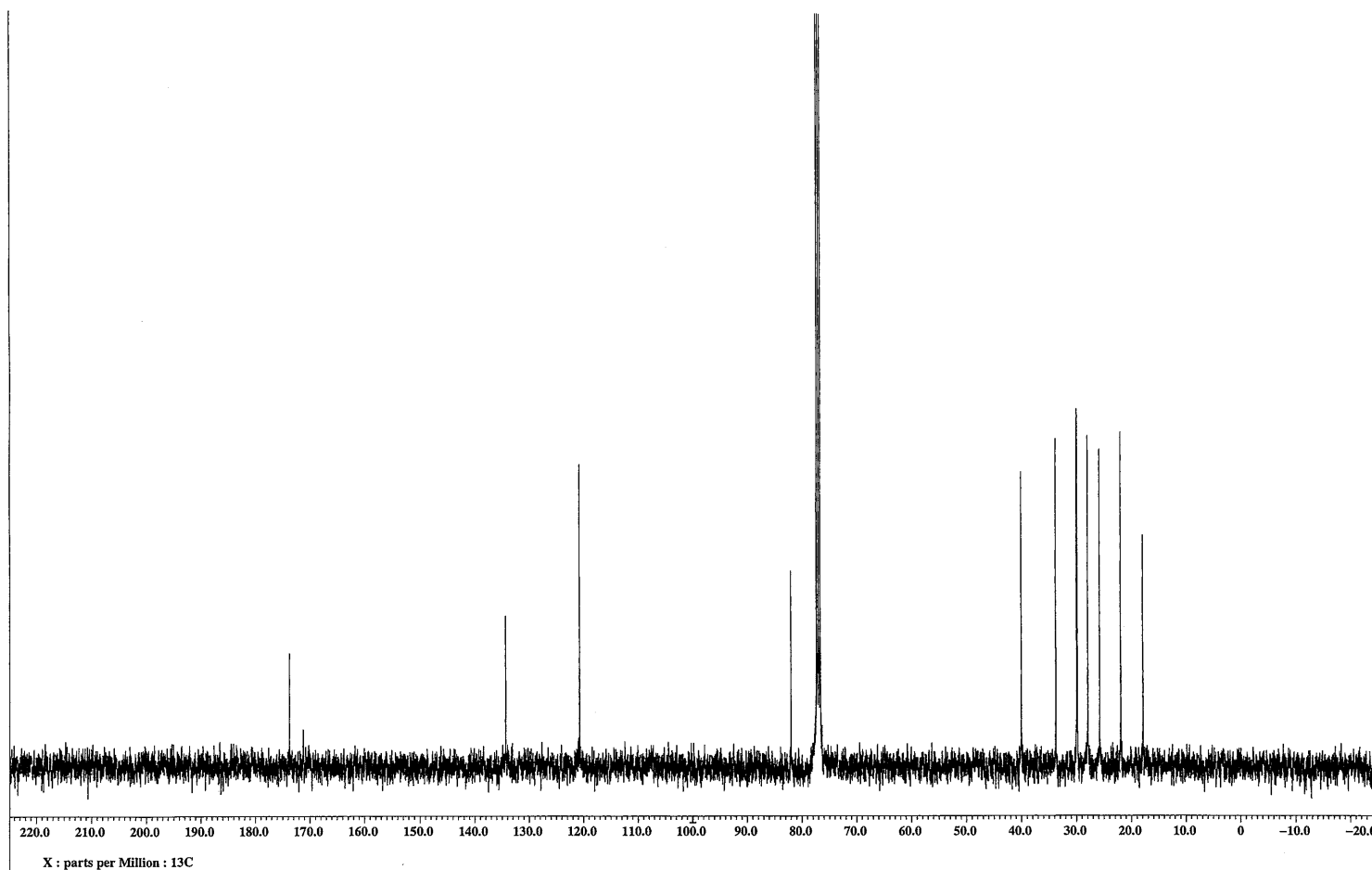
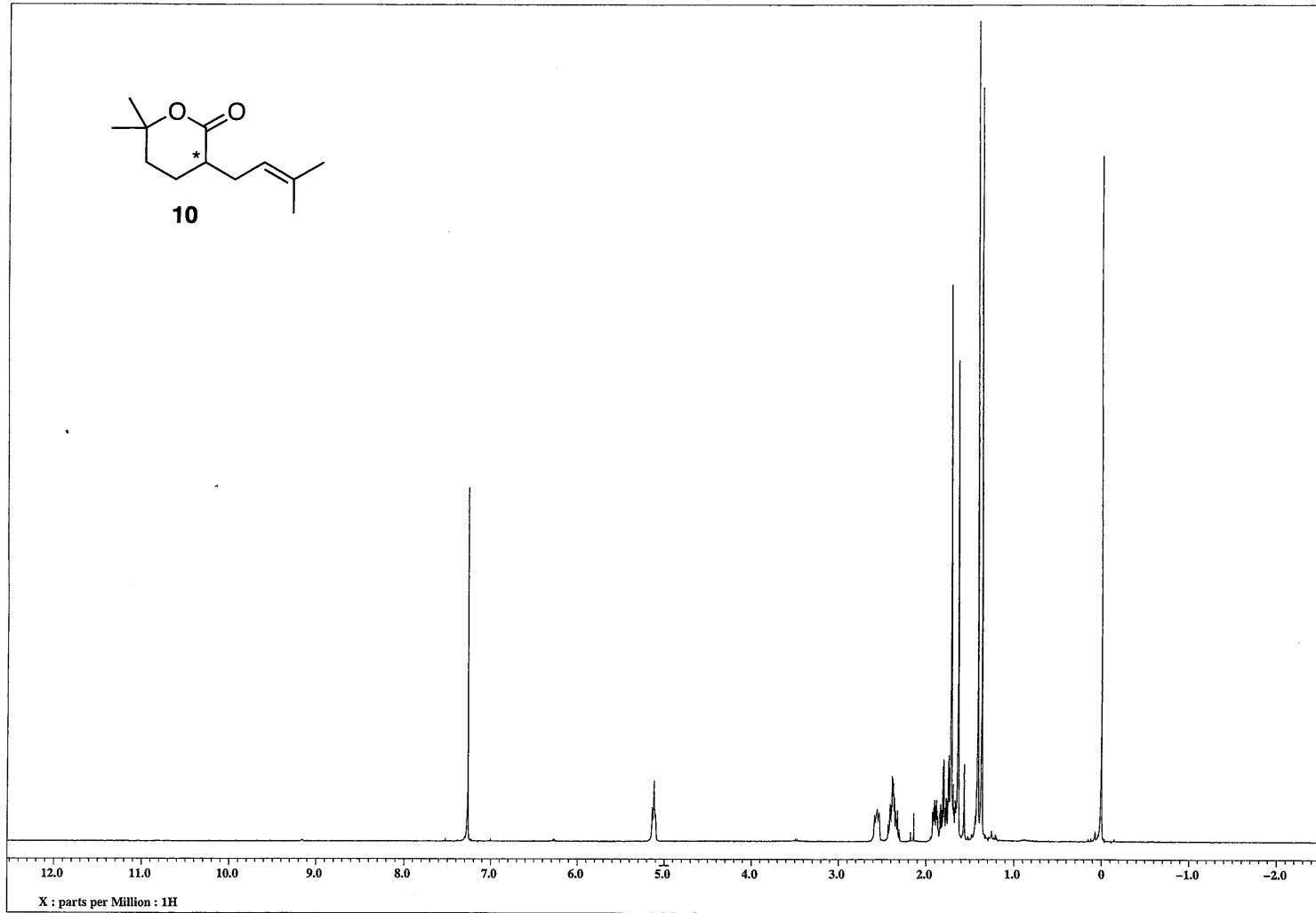
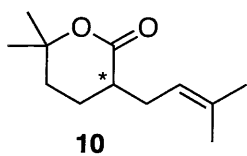


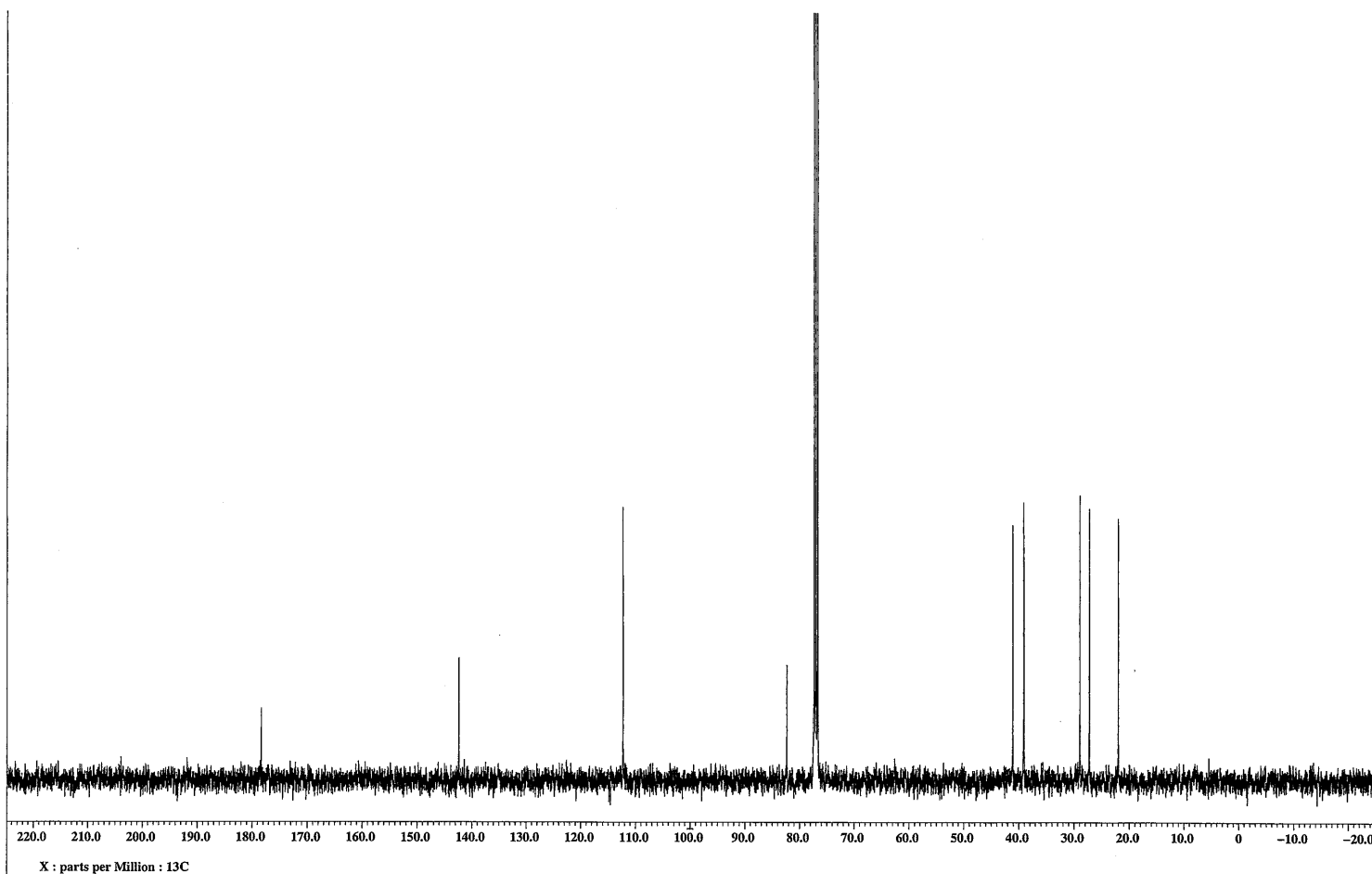
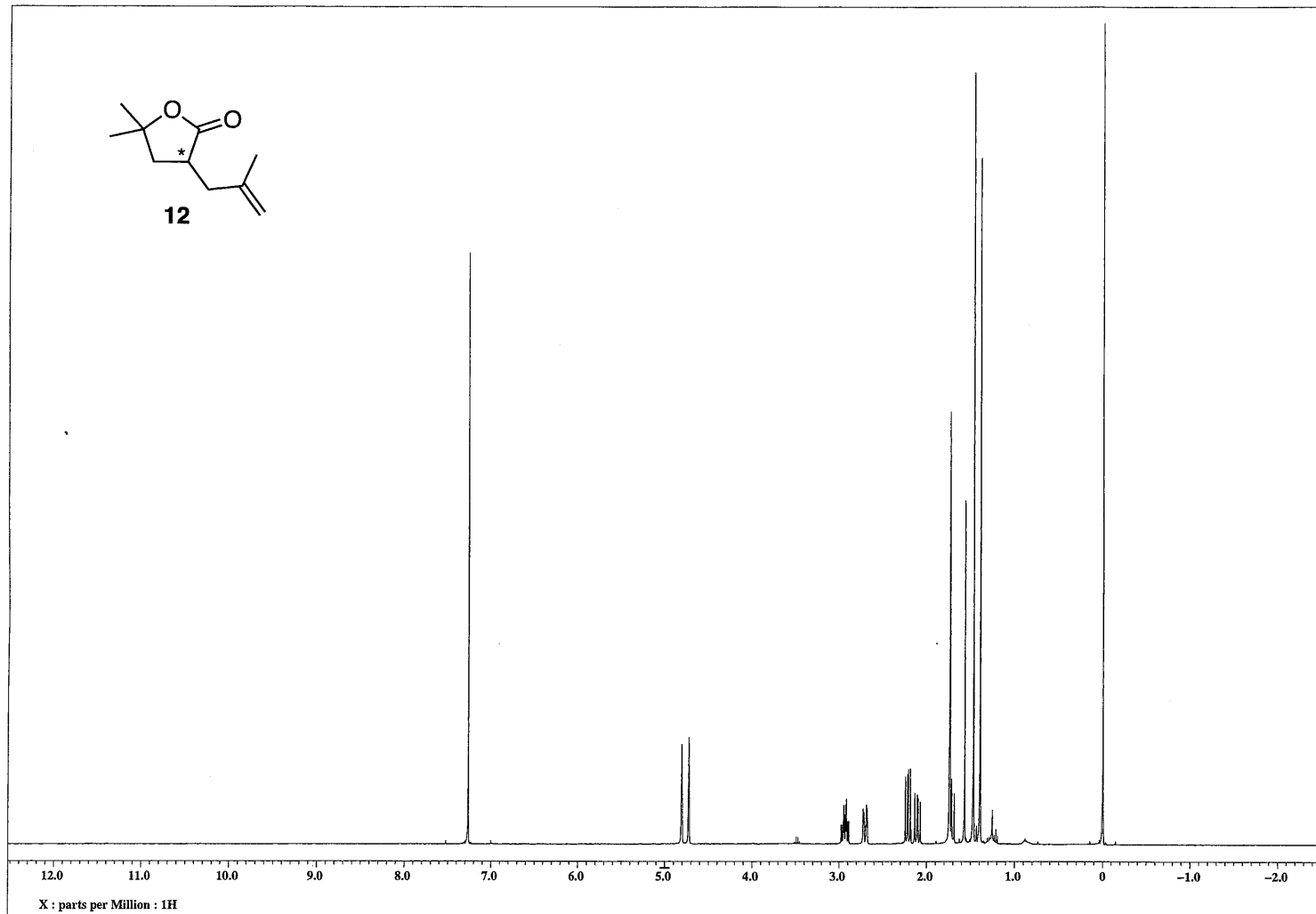
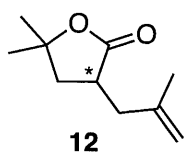


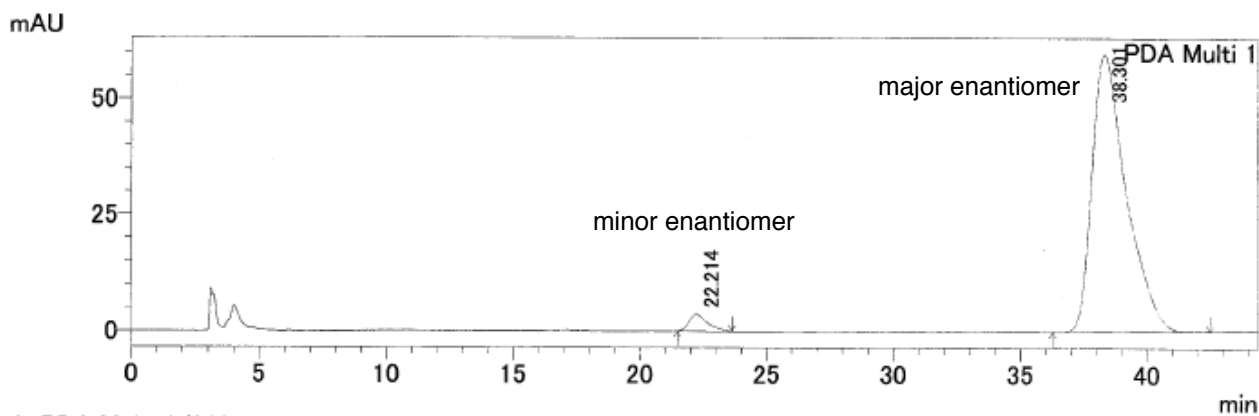
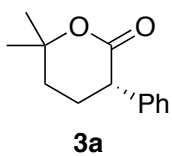






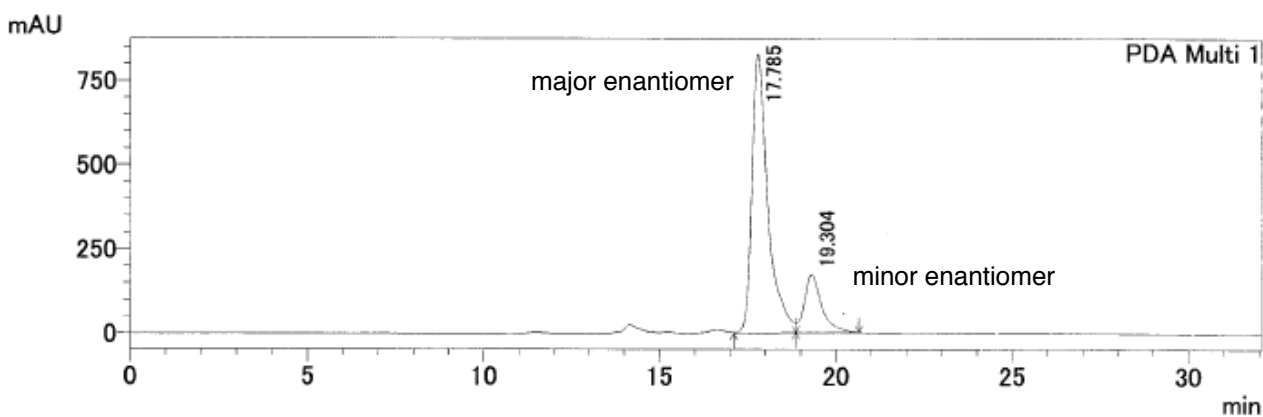
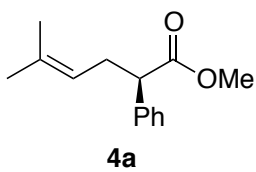






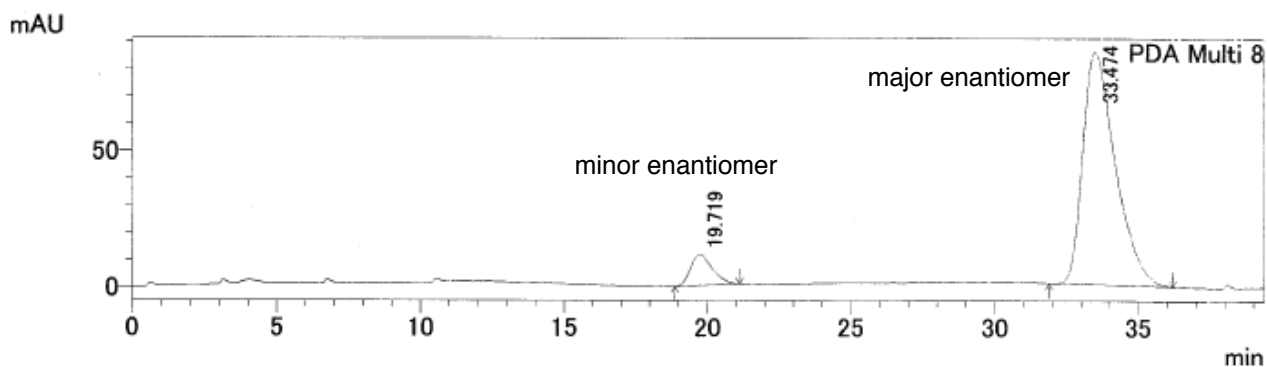
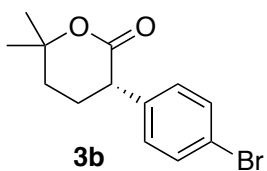
SPD-M20A Ch1 210nm 4nm

	retention time	area	hight	area %
1	22.214	179417	3555	3.077
2	38.301	5651430	59802	96.923
total		5830847	63357	100.000



SPD-M20A Ch1 210nm 4nm

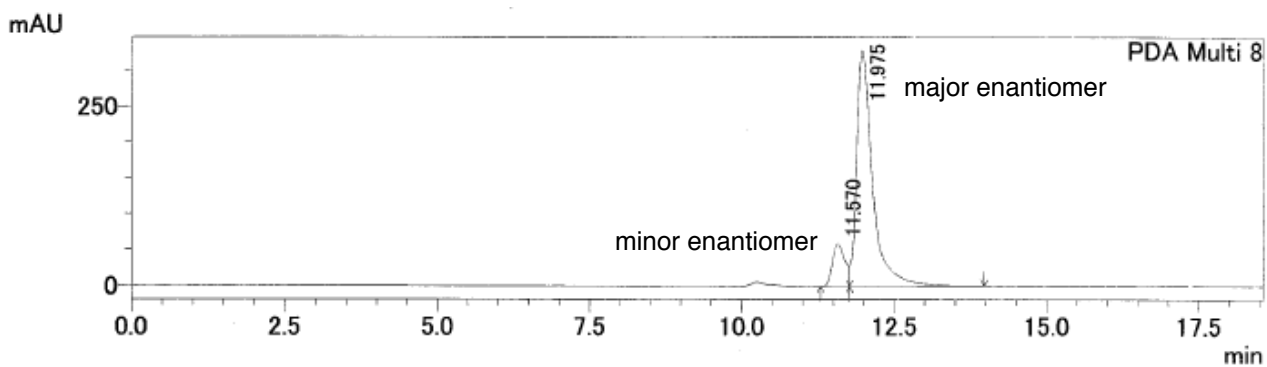
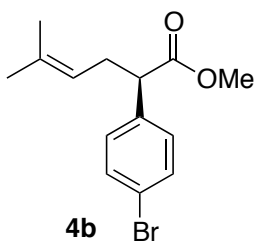
	retention time	area	hight	area %
1	17.785	25967765	826454	81.472
2	19.304	5905422	173252	18.528
total		31873187	999707	100.000



1 PDA Multi 8/220nm 4nm

SPD-M20A Ch8 220nm 4nm

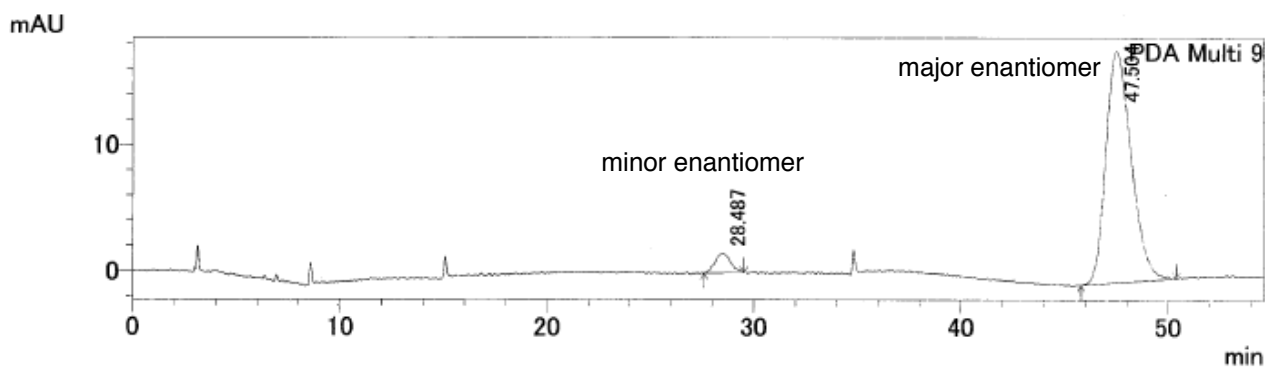
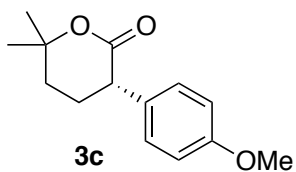
	retention time	area	hight	area %
1	19.719	601497	11295	8.174
2	33.474	6756832	85032	91.826
total		7358330	96327	100.000



1 PDA Multi 8/220nm 4nm

SPD-M20A Ch8 220nm 4nm

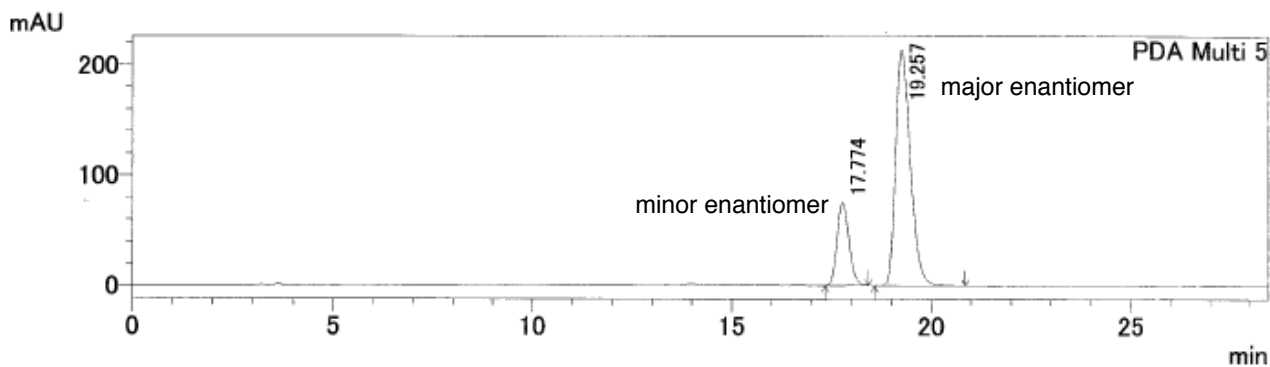
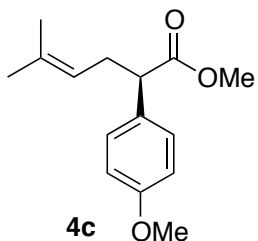
	retention time	area	hight	area %
1	11.570	845950	59392	12.362
2	11.975	5997219	329372	87.638
total		6843169	388763	100.000



1 PDA Multi 9/224nm 4nm

SPD-M20A Ch9 224nm 4nm

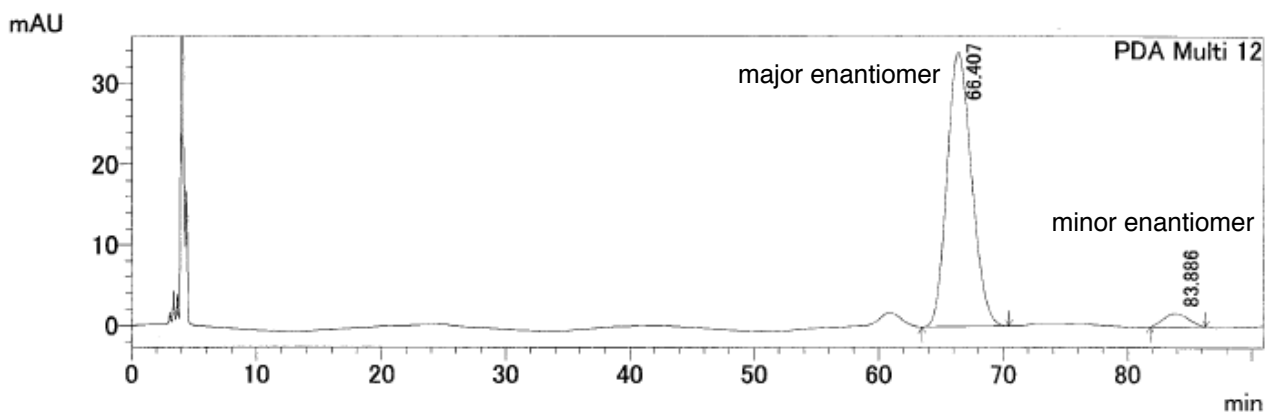
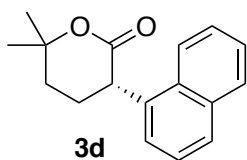
	retention time	area	hight	area %
1	28.487	82601	1579	4.987
2	47.504	1573643	18274	95.013
total		1656243	19854	100.000



1 PDA Multi 5/230nm 4nm

SPD-M20A Ch5 230nm 4nm

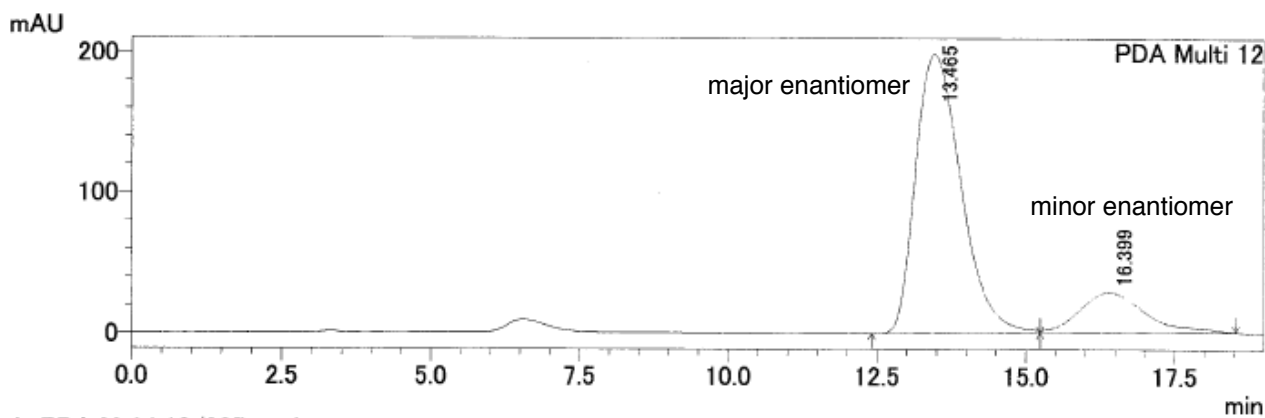
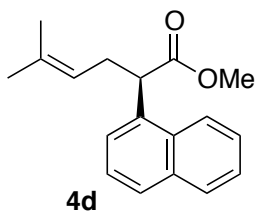
	retention time	area	hight	area %
1	17.774	1570914	75435	22.221
2	19.257	5498715	214228	77.779
total		7069629	289663	100.000



1 PDA Multi 12/225nm 4nm

SPD-M20A Ch12 225nm 4nm

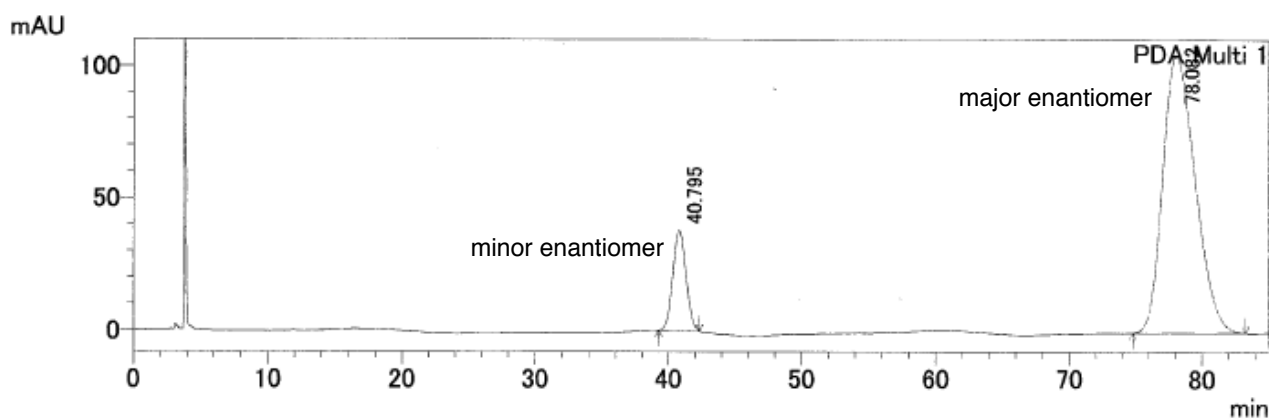
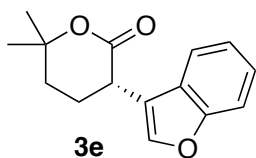
	retention time	area	hight	area %
1	66.407	4672824	34009	95.304
2	83.886	230267	1638	4.696
total		4903091	35647	100.000



1 PDA Multi 12/225nm 4nm

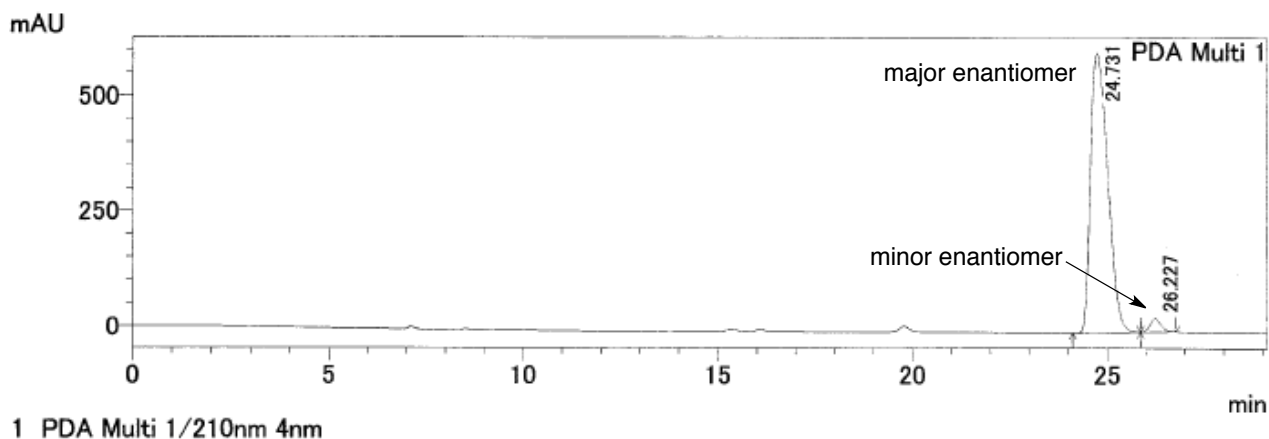
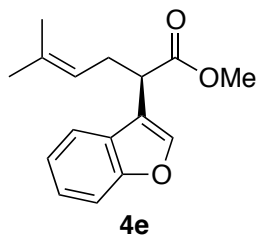
SPD-M20A Ch12 225nm 4nm

	retention time	area	hight	area %
1	13.465	10556047	197942	82.831
2	16.399	2187981	28350	17.169
total		12744028	226292	100.000



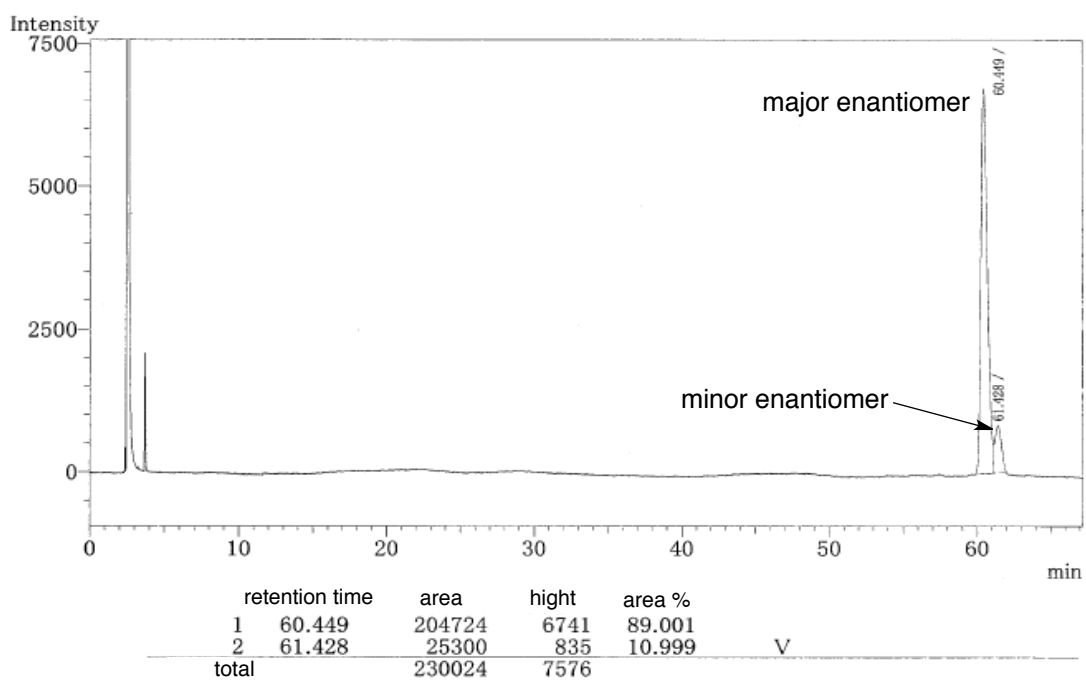
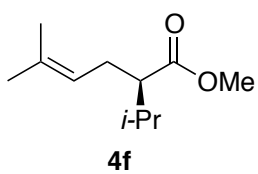
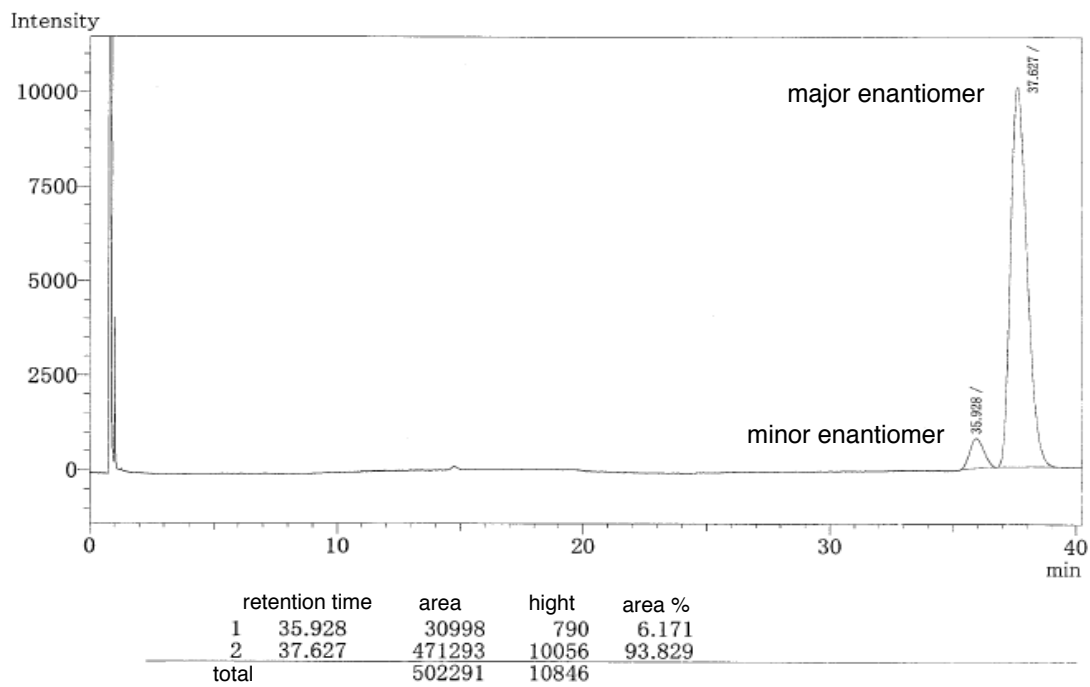
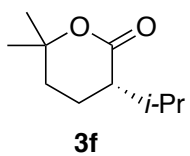
SPD-M20A Ch1 210nm 4nm

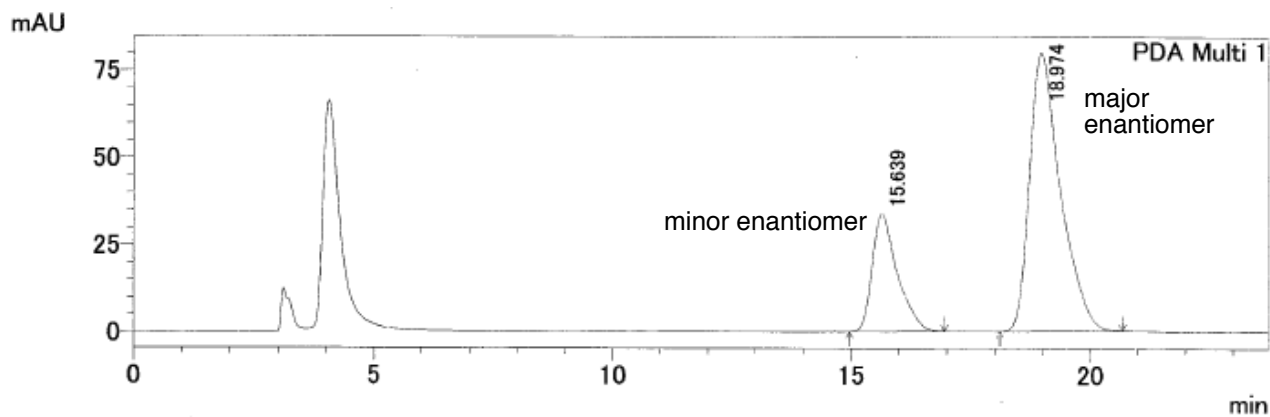
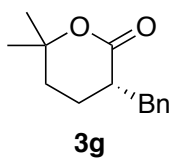
	retention time	area	hight	area %
1	40.795	2598779	37751	12.678
2	78.082	17899388	104880	87.322
total		20498166	142630	100.000



SPD-M20A Ch1 210nm 4nm

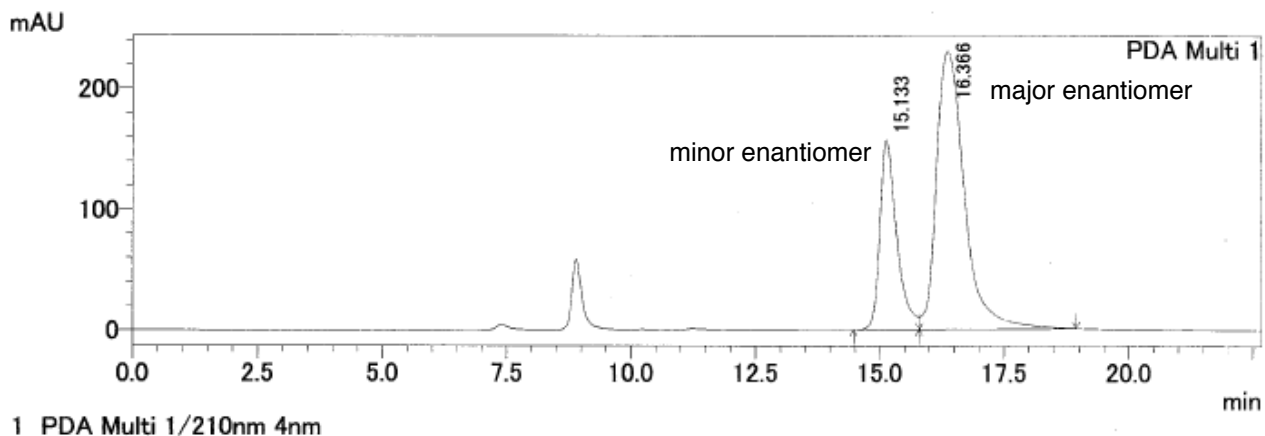
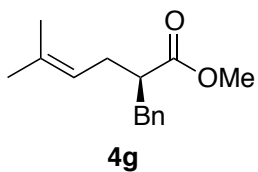
	retention time	area	hight	area %
1	24.731	18503309	605914	97.026
2	26.227	567147	28690	2.974
total		19070457	634604	100.000





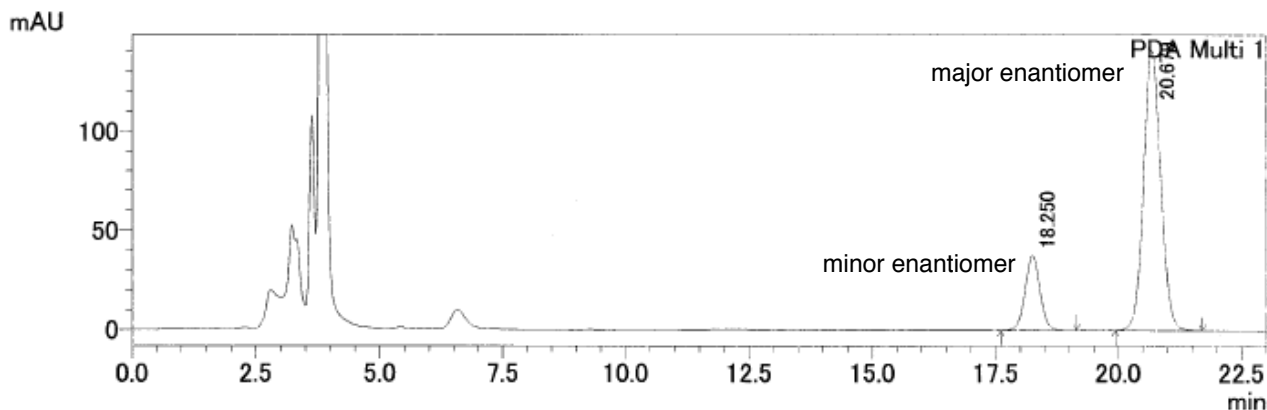
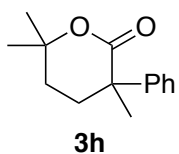
SPD-M20A Ch1 210nm 4nm

	retention time	area	hight	area %
1	15.639	1230073	33715	25.447
2	18.974	3603726	79646	74.553
total		4833799	113361	100.000



SPD-M20A Ch1 210nm 4nm

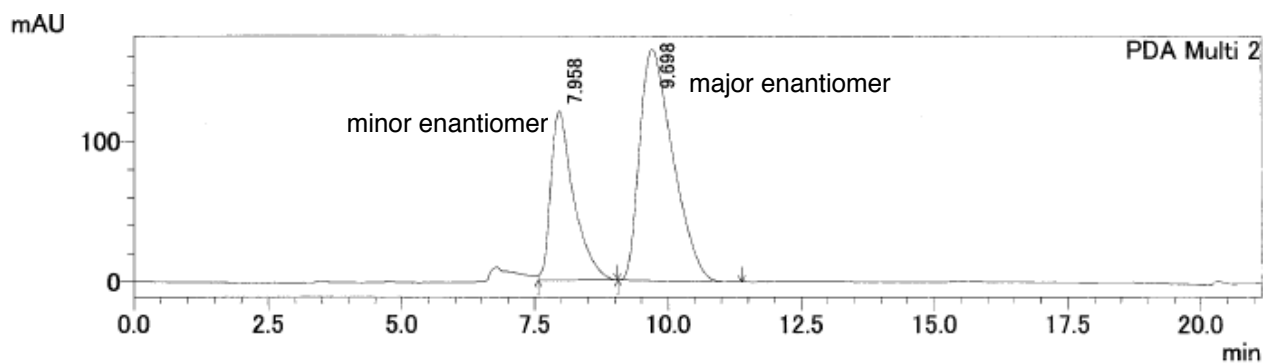
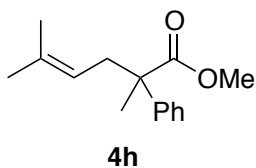
	retention time	area	hight	area %
1	15.133	3724186	156932	29.216
2	16.366	9022689	229728	70.784
total		12746874	386660	100.000



1 PDA Multi 1/210nm 4nm

SPD-M20A Ch1 210nm 4nm

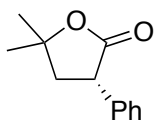
	retention time	area	hight	area %
1	18.250	794691	37635	18.933
2	20.679	3402637	140777	81.067
total		4197329	178412	100.000



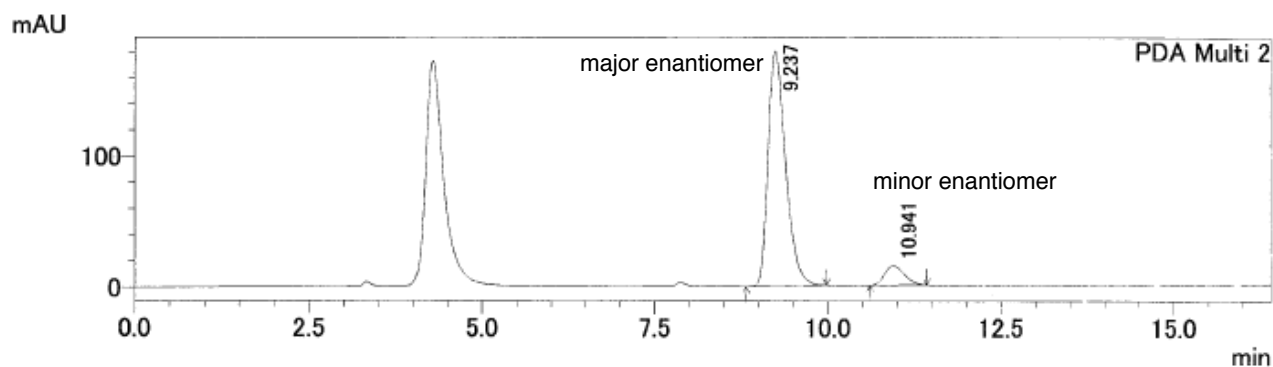
1 PDA Multi 2/210nm 4nm

SPD-M20A Ch2 210nm 4nm

	retention time	area	hight	area %
1	7.958	3611580	120322	33.404
2	9.698	7200110	164797	66.596
total		10811689	285118	100.000



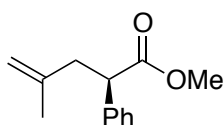
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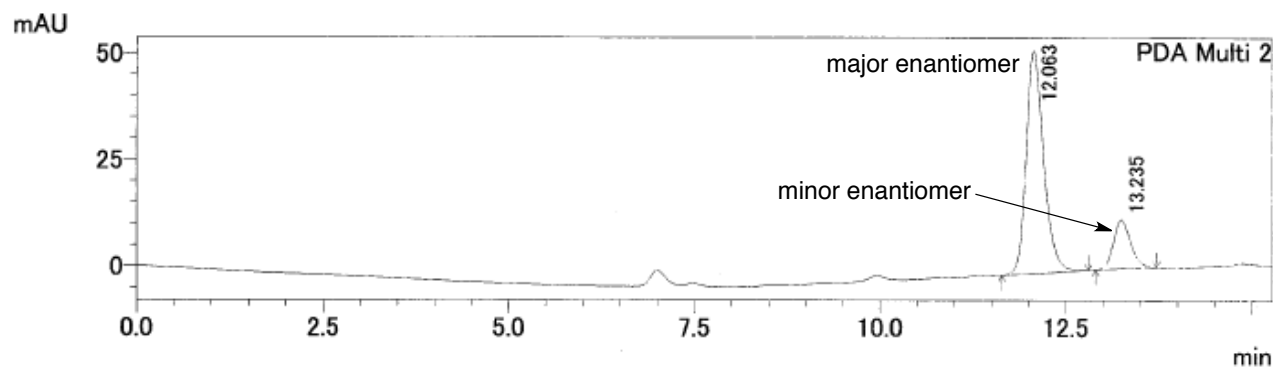
1 PDA Multi 2/210nm 4nm

SPD-M20A Ch2 210nm 4nm

	retention time	area	hight	area %
1	9.237	3165346	179447	91.691
2	10.941	286848	14563	8.309
total		3452194	194010	100.000



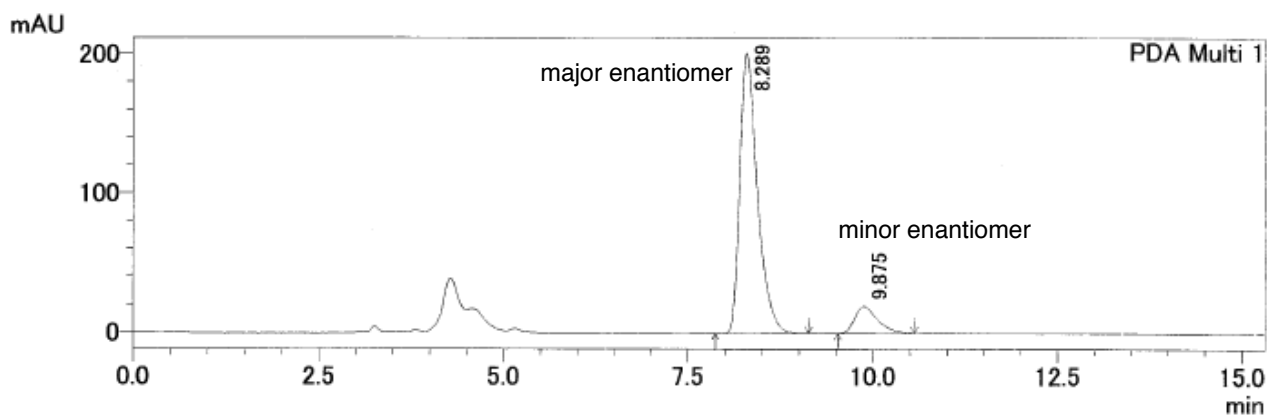
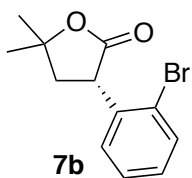
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1 PDA Multi 2/210nm 4nm

SPD-M20A Ch2 210nm 4nm

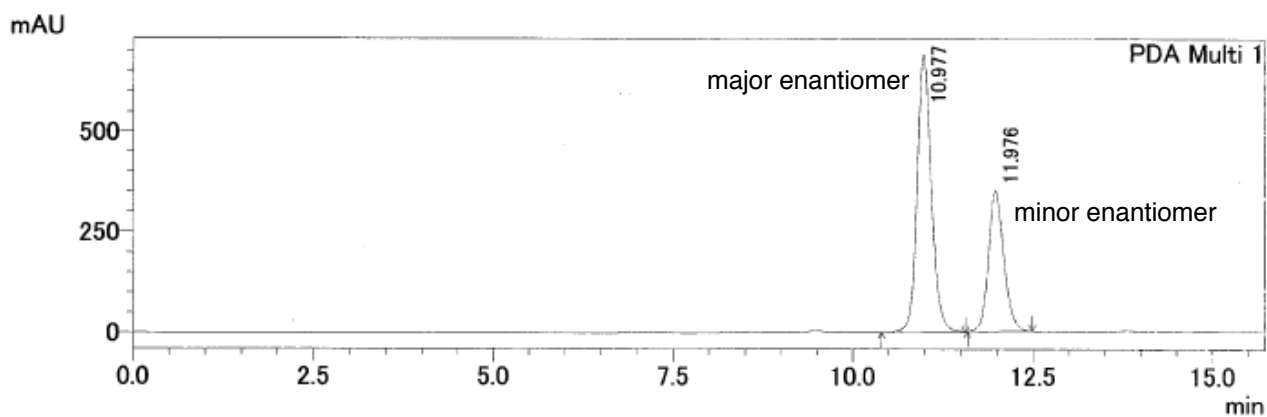
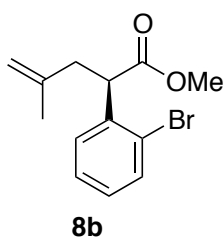
	retention time	area	hight	area %
1	12.063	848661	52239	81.898
2	13.235	187578	11450	18.102
total		1036239	63689	100.000



1 PDA Multi 1/210nm 4nm

SPD-M20A Ch1 210nm 4nm

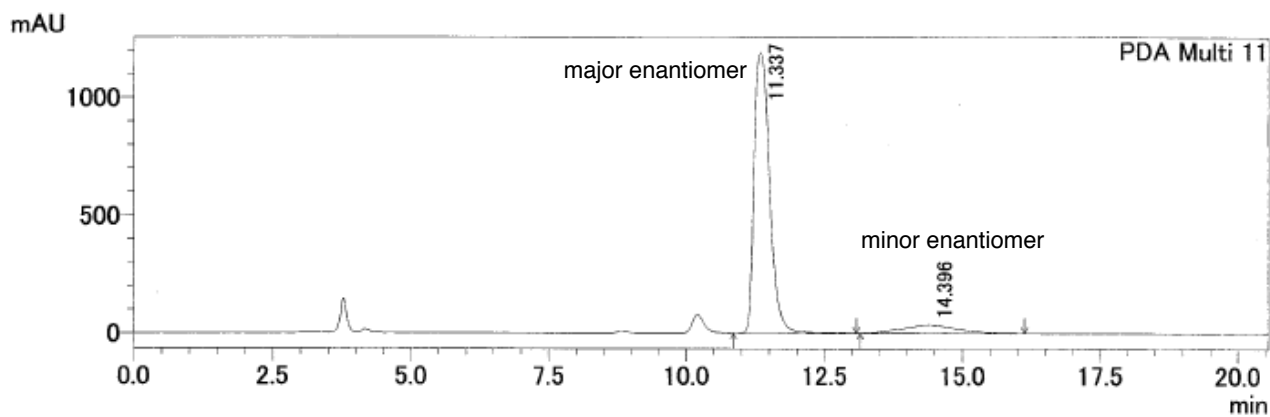
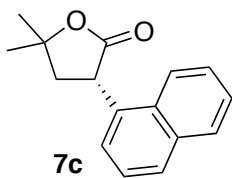
	retention time	area	hight	area %
1	8.289	3300757	200994	88.763
2	9.875	417868	19359	11.237
total		3718625	220353	100.000



1 PDA Multi 1/210nm 4nm

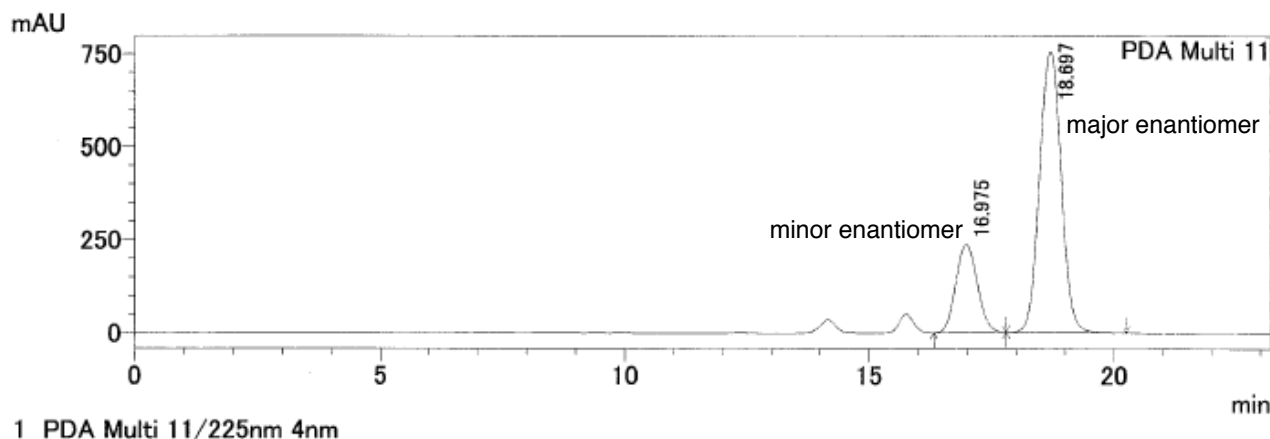
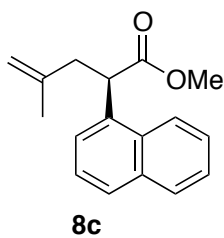
SPD-M20A Ch1 210nm 4nm

	retention time	area	hight	area %
1	10.977	9610197	691388	65.041
2	11.976	5165388	349774	34.959
total		14775585	1041162	100.000



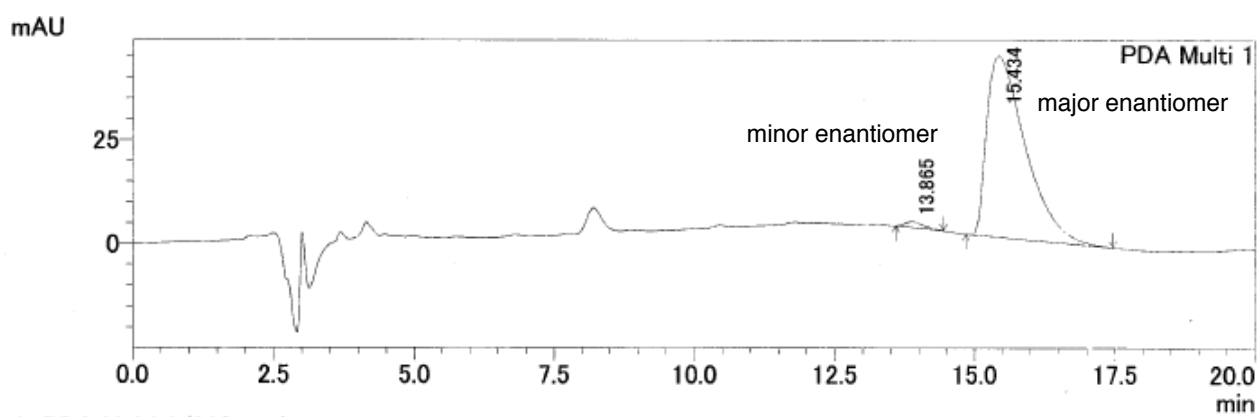
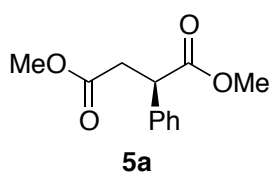
SPD-M20A Ch11 225nm 4nm

	retention time	area	hight	area %
1	11.337	23445573	1191053	90.767
2	14.396	2384844	34836	9.233
total		25830417	1225889	100.000



SPD-M20A Ch11 225nm 4nm

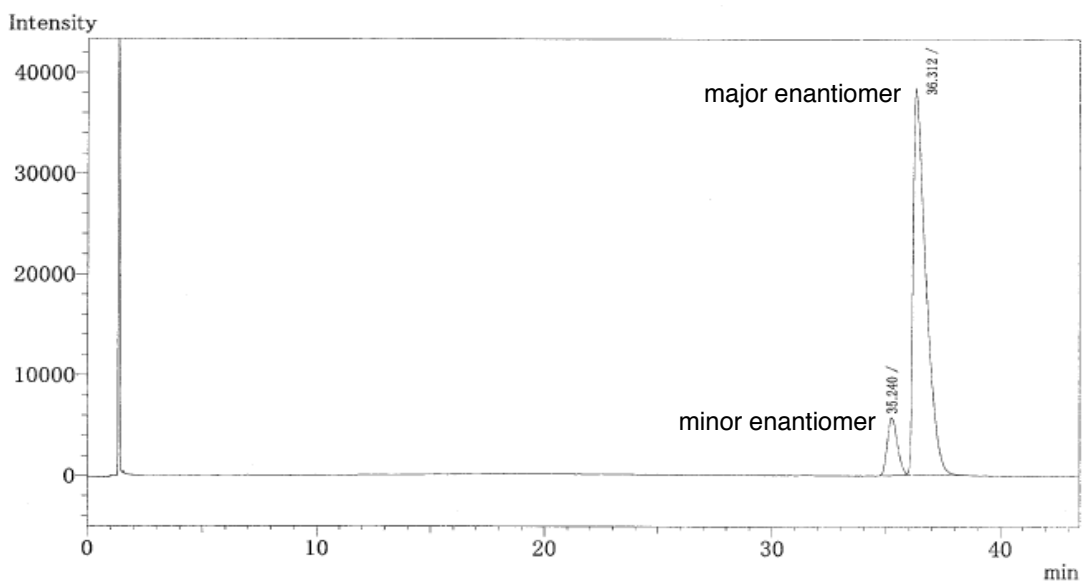
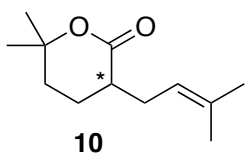
	retention time	area	hight	area %
1	16.975	7210807	236685	23.706
2	18.697	23207085	753074	76.294
total		30417892	989759	100.000



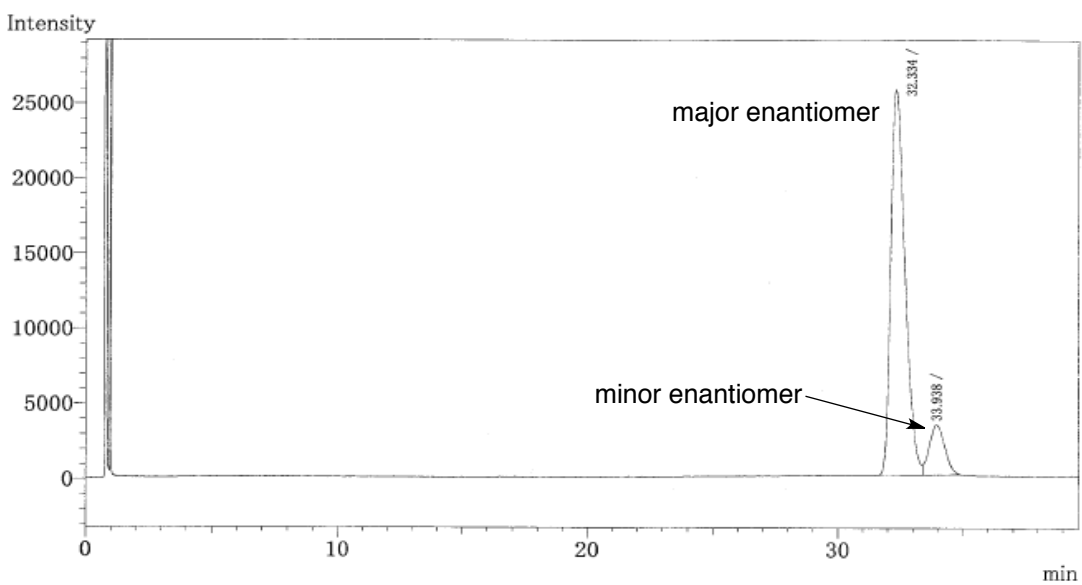
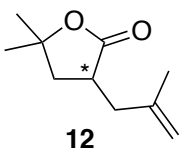
1 PDA Multi 1/210nm 4nm

SPD-M20A Ch1 210nm 4nm

	retention time	area	hight	area %
1	13.865	33063	1354	1.555
2	15.434	2092831	43437	98.445
total		2125894	44791	100.000



	retention time	area	hight	area %	
1	35.240	176916	5737	10.623	
2	36.312	1488472	38380	89.377	V
total		1665388	44117		



	retention time	area	hight	area %	
1	32.334	1006464	25641	87.756	
2	33.938	140425	3289	12.244	V
total		1146889	28930		