Supporting Information

N-Heterocyclic Carbene Ligands in Cobalt-Catalyzed Sequential Cyclization/Cross-Coupling Reactions of 6-Halo-1-hexene Derivatives with Grignard Reagents

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Instrumentation and Chemicals

^{1}H NMR (300 and 500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian Mercury 300 and UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to $CHCl_3$ at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous $CoCl_2$ was purchased from Wako Pure Chemicals and was used after removal of water. Specifically, in each experiment, $CoCl_2$ was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair dryer for 2 min immediately before use. SIEt·HCl (**1**) and SIMes·HCl (**3**) were prepared according to the literature.[1] IMes·HCl (**2**) and IPr·HCl (**4**) were purchased from Strem Chemicals. Trialkylsilylmethylmagnesium chloride was prepared from magnesium metal and the corresponding (chloromethyl)trialkylsilane in diethyl ether. Diethyl ether was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Dioxane was dried over slices of sodium. All reactions were carried out under argon atmosphere.

Experimental Section

Typical procedure for NHC/cobalt-catalyzed coupling reaction of 6-halo-1-hexene derivative with trialkylsilylmethylmagnesium chloride: The reaction of **5** with allyldimethylsilylmethylmagnesium chloride (Scheme 1) is representative. Anhydrous cobalt(II) chloride (3.2 mg, 0.025 mmol) was placed in a 20-mL reaction flask and was heated with a hair dryer in vacuo for 2 min. After the color of the cobalt salt became blue, anhydrous dioxane (2 mL), SIEt·HCl (**1**, 9.3 mg, 0.025 mmol) and substrate **5** (182 mg, 0.50 mmol) were sequentially added under argon. Allyldimethylsilylmethylmagnesium chloride (1.0 M diethyl ether solution, 1.5 mL, 1.5 mmol) was then added over 5 s to the reaction mixture at 25 ˚C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 30 min at 25 ˚C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane/ethyl acetate = 10:1) of the crude product provided the corresponding cyclization/coupling product **6** (140 mg, 0.40 mmol) in 81% isolated yield.

Oxidation of cyclization/coupling product 6: A solution of **6** (88 mg, 0.25 mmol) in $CHCl_3$ (5 mL) was placed in a 30-mL flask. Potassium hydrogenfluoride (82 mg, 1.05 mmol) and trifluoroacetic acid (0.09 mL, 1.25 mmol) were sequentially added to the

reaction mixture. After being stirred for 18 h at room temperature, the solvent was evaporated under a reduced pressure to give a yellow oil. The crude product was dissolved in methanol-THF (8 mL, 1:1 mixture). Potassium hydrogencarbonate (115 mg, 1.15 mmol) and 30% H_2O_2 aq (0.52 mL) were successively added. After being stirred at room temperature for 18 h, the reaction mixture was poured into saturated sodium thiosulfate solution. The product was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate = 1:1) provided the alcohol **7** (50 mg, 0.18 mmol) in 74% yield.

General procedure for NHC/cobalt-catalyzed coupling reaction of 6-halo-1-hexene derivative with 1-alkynyl Grignard reagent: The reaction of **5** with 1-hexynylmagnesium bromide (eq. 1) is representative.

Preparation of 1-hexynylmagnesium bromide: Isopropylmagnesium bromide (1.0 M diethyl ether solution, 1.25 mL, 1.25 mmol) was placed in a 30-mL reaction flask under argon. 1-Hexyne (134 mg, 1.63 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature.

NHC/cobalt-catalyzed coupling reaction: Anhydrous cobalt(II) chloride (3.2 mg, 0.025 mmol) was placed in a 20-mL reaction flask and was heated with a hair dryer in vacuo for 2 min. After the color of the cobalt salt became blue, anhydrous dioxane (1 mL)

and IMes·HCl (**2**, 8.5 mg, 0.025 mmol) were sequentially added under argon. Substrate **5** (91 mg, 0.25 mmol) was added. 1-Hexynylmagnesium bromide (1.0 M diethyl ether solution, 1.25 mL, 1.25 mmol) was then added over 5 s to the reaction mixture at 25 ˚C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 30 min at 25 ˚C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated to provide a yellow oil. Silica gel column purification (hexane/ethyl acetate = 10:1) furnished **22a** (64 mg, 0.20 mmol) in 80% yield.

Characterization Data

The substrates **5, 8, 9, 10, 11** and **12** were prepared according to the literature.[2]

1-(*p*-Toluenesulfonyl)-3-[2-(allyldimethylsilyl)ethyl]pyrrolidine (6): oil. IR (neat) 663, 1099, 1162, 1248, 1346, 2916, 2952 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.06 (s, 6H), 0.37–0.47 (m, 2H), 1.13–1.25 (m, 2H), 1.39 (m, 1H), 1.42–1.48 (dm, *J* = 8.0 Hz, 2H), 1.89–1.99 (m, 2H), 2.44 (s, 3H), 2.80 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.20 (ddd, *J* = 10.0, 8.5, 7.5 Hz, 1H), 3.32 (ddd, *J* = 10.0, 8.5, 4.5 Hz, 1H), 3.43 (dd, *J* = 10.0, 7.5 Hz, 1H), 4.79–4.84 (m, 2H), 5.73 (dddd, *J* = 17.5, 13.5, 9.5, 8.0 Hz, 1H), 7.32–7.34 (dm, *J* = 8.5 Hz, 2H) , 7.71–7.73 (dm, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –3.72 (× 2C), 13.36, 21.73, 23.20, 27.47, 31.25, 42.17, 47.79, 53.29, 113.13, 127.77, 129.80, 134.29, 135.02, 143.45; Found: C, 61.21; H, 8.09%. Calcd for $C_{18}H_{29}NO_2SSi$: C, 61.49; H, 8.31%.

2-[1-(*p*-Toluenesulfonyl)-3-pyrrolidinyl]ethanol (7): oil. IR (neat) 1043, 1160, 1340, 2880, 2930, 3566 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 (m, 1H), 1.52 (q, *J* = 6.5 Hz, 2H), 1.62 (brs, 1H), 1.96 (m, 1H), 2.16 (septet, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.83 (t, *J* =9.0 Hz, 1H), 3.17 (m, 1H), 3.36 (m, 1H), 3.46 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.56–3.64 (m, 2H), 7.31 –7.33 (dm, *J* = 8.5 Hz, 2 H), 7.70–7.72 (dm, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.72, 31.65, 35.88, 35.91, 47.62, 53.38, 61.42, 127.69, 129.84, 133.99, 143.58; Found: C, 58.12; H, 7.30%. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11%.

Allyl{2-(2,9-dioxa-4-bicyclo[4.3.0]nonanyl)ethyl}dimethylsilane (13, Major isomer): oil. IR (neat) 898, 1147, 1251, 1629, 1773, 2877, 2921 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.01 (s,

6H), 0.41–0.54 (m, 2H), 1.28 (m, 1H), 1.34–1.40 (m, 2H), 1.51–1.53 (dm, *J* = 8.5 Hz, 2H), 1.50–1.63 (m, 3H), 1.97 (m, 1H), 2.73 (m, 1H), 3.62 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.65 (m, 1H), 3.75 (m, 1H), 3.95 (t, *J* = 8.0 Hz, 1H), 4.81–4.86 (m, 2H), 5.28 (d, *J* = 4.0 Hz, 1H), 5.76 (dddd, *J* =18.5, 16.5, 10.5, 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.65 (× 2C), 13.62, 19.29, 21.29, 23.28, 23.49, 36.51, 44.57, 61.21, 70.20, 102.30, 113.14, 135.11; Found: C, 66.11; H, 10.51%. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30%.

Allyl[2-(4-butoxy-2,2-dimethyl-3-oxacyclopentyl)ethyl]dimethylsilane (14) (67:33 mixture of diastereomers): oil. IR (neat) 893, 1097, 1250, 1558, 2932, 2960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.01 (s, 6H), 0.40–0.60 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.01 (s, 0.67×3H), 1.13 (s, 0.33×3H), 1.14–1.21 (m, 1H), 1.23 (s, 0.33×3H), 1.32 (s, 0.67×3H), 1.33–1.41 (m, 4H), 1.49–1.64 (m, 4H), 1.72 (m, 0.33×1H), 2.04–2.11 (m, 0.67×2H), 2.45 (ddd, *J* = 13.0, 8.0, 6.0 Hz, 0.33×1H), 3.30–3.37 (m, 1H), 3.64–3.72 (m, 1H), 4.81–4.85 (m, 2H), 4.95 (d, *J* = 4.5 Hz, 0.67×1H), 5.04 (dd, *J* = 6.0, 4.5 Hz, 0.33×1H), 5.77 (dddd, *J* = 18.0, 16.5, 10.0, 8.0, Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.63 (× 2C), 14.11 (× 2C), 14.22, 14.30, 19.64, 19.66, 23.31, 23.33 (× 2C), 23.35 (× 2C), 23.76, 24.22, 24.41, 28.51, 30.32, 32.14, 32.19, 39.33, 39.54, 49.23, 51.98, 66.68, 67.87, 82.92, 83.64, 102.01, 103.20, 113.01 (× 2C), 135.23 (× 2C) ; Found: C, 68.31; H, 11.45%. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48%.

Allyl[2-(4-butoxy-2-pentyl-3-oxacyclopentyl)ethyl]dimethylsilane (15) (54:46 mixture of diastereomers): oil. IR (neat) 893, 1097, 1250, 1458, 1631, 2957 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ –0.01 (s, 6H), 0.43–0.58 (m, 2H), 0.89–0.94 (m, 6H), 1.19 (m, 0.54×1H), 1.26–1.65 (m, 17H), 1.99 (m, 0.46×1H), 2.11 (dd, *J* = 17.5, 7.5 Hz, 0.54×1H), 2.27 (ddd, *J* = 13.0, 9.5, 5.5 Hz, 0.46×1H), 3.31–3.39 (m, 1H), 3.56–3.62 (m, 1H), 3.65–3.70 (m, 1H), 4.81–4.86 (m, 2H), 5.02 (d, *J* = 5.0 Hz, 0.54×1H), 5.07 (dd, *J* = 5.0, 2.5 Hz, 0.46×1H), 5.73–5.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –3.64 (× 2C), –3.62 (× 2C),13.54, 13.60, 14.08, 14.12, 14.27, 14.30, 19.66, 19.69, 22.89 (× 2C), 22.31, 23.35, 26.26, 26.47, 27.38, 27.75, 32.11, 32.18, 32.19, 32.26, 34.89, 37.25, 39.27, 39.95, 45.94, 47.04, 66.89, 67.26, 82.85, 85.58, 103.61, 103.71, 112.95, 113.00, 135.23, 135.29; Found: C, 70.54; H, 11.93%. Calcd for $C_{20}H_{40}O_2Si$: C, 70.52; H, 11.84%.

Allyl(2-cyclopentylethyl)dimethylsilane (16): oil. IR (neat) 893, 1150, 1250, 1630, 2910, 2952 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.02 (s, 6H), 0.50–0.55 (m, 2H), 1.03–1.10 (m, 2H), 1.25–1.31 (m, 2H), 1.46–1.62 (m, 6H), 1.67–1.78 (m, 3H), 4.80–4.86 (m, 2H), 5.79 (dddd, *J* = 18.0, 16.5, 10.0, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.59, 13.93, 23.44, 25.49, 30.22, 32.57, 43.59, 112.69, 135.59.

1-(*p*-Toluenesulfonyl)-3-[2-(dimethylphenylsilyl)ethyl]pyrrolidine (17): oil. IR (neat) 815, 1113, 1163, 1345, 2919, 2953 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 6H), 0.61–0.69 (m, 2H), 1.17–1.27 (m, 2H), 1.35 (m, 1H), 1.89–1.98 (m, 2H), 2.44 (s, 3H), 2.77 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.18 (ddd, *J* = 10.0, 8.5, 7.5 Hz, 1H), 3.31 (ddd, *J* = 10.0, 8.5, 4.0 Hz, 1H), 3.42 (dd, *J* = 10.0, 7.5 Hz, 1H), 7.31–7.33 (dm, *J* = 8.5 Hz, 2H), 7.34–7.37 (m, 3H), 7.45–7.47 (m, 2H), 7.70–7.72 (dm, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –3.14, –3.08,

14.32, 21.70, 27.45, 31.13, 42.05, 47.77, 53.22, 127.68, 127.97, 129.15, 129.77, 133.62, 134.00, 138.96, 143.44; Found: C, 65.08; H, 7.39%. Calcd for $C_{21}H_{29}SNO_2Si$: C, 65.07; H, 7.39%.

(2-Iodocyclopentyloxy)dimethylvinylsilane (18) : oil. IR (neat) 698, 787, 836, 884, 959, 1017, 1074, 1252, 1407, 2958 cm^{-1}; ^1H NMR (C_6D_6) δ 0.14 (s, 3H), 0.15 (s, 3H), 1.38–1.57 (m, 3H), 1.78–1.95 (m, 2H), 2.08 (m, 1H), 3.96 (m, 1H), 4.43 (m, 1H), 5.71 (dd, *J* = 20.1, 3.9 Hz, 1H), 5.91 (dd, *J* = 14.7, 3.9 Hz, 1H), 6.12 (dd, *J* = 20.1, 3.9 Hz, 1H); ^{13}C NMR (C_6D_6) δ –1.16, –1.15, 22.80, 32.78, 34.85, 36.39, 83.23, 133.76, 138.08; Found: C, 36.27; H, 5.48%. Calcd for $C_9H_{17}OSiI$: C, 36.49; H, 5.78%.

Diol 20 (Major isomer): oil. IR (neat) 700, 838, 1114, 1248, 1427, 2955, 3337 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 6H), 0.67 (ddd, *J* = 14.0, 13.0, 4.5 Hz, 1H), 0.88 (ddd, *J* = 14.0, 13.0, 4.5 Hz, 1H), 1.40–1.88 (m, 9H), 2.44 (brs, 1H), 2.83 (brs, 1H), 3.97 (m, 1H), 4.30 (m, 1H), 7.34–7.36 (m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (C_6D_6) δ –3.00, –2.88, 11.98, 21.22, 22.06, 30.82, 36.22, 47.95, 74.42, 77.37, 128.00, 129.13, 133.76, 139.32. ; Found: C, 69.13; H, 9.28%. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41%. **(Minor isomer):** ^1H NMR (C_6D_6) δ 0.28 (s, 6H), 0.72 (ddd, *J* = 14.0, 13.0, 4.5 Hz, 1H), 0.97 (ddd, *J* = 14.0, 13.0, 4.5 Hz, 1H), 1.45–1.86 (m, 9H), 2.19 (brs, 1H), 2.24 (brs, 1H), 3.64 (m, 1H), 4.40 (m, 1H), 7.34–7.36 (m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (C_6D_6) δ –2.92, _2.89, 11.37, 22.66, 26.57, 30.80, 35.36, 50.06, 74.54, 75.09, 128.02, 129.15, 133.76, 139.29.

1-(*p*-Toluenesulfonyl)-3-(2-heptynyl)pyrrolidine (22a): oil. IR (neat) 664, 1039, 1094,

1162, 1346, 2872, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.5 Hz, 3H), 1.32–1.44 (m, 4H), 1.57 (m, 1H), 1.92 (m, 1H), 2.05–2.12 (m, 4H), 2.22 (septet, *J* = 7.0 Hz, 1H), 2.43 (s, 3H), 2.98 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.23 (dt, *J* = 10.0, 8.5 Hz, 1H), 3.31 (m, 1H), 3.42 (dd, *J* = 10.0, 7.5 Hz, 1H), 7.31–7.33 (dm, *J* = 8.5 Hz, 2H), 7.71–7.73 (dm, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.77, 18.44, 21.70, 22.07, 22.17, 30.57, 31.17, 38.19, 47.60, 52.59, 77.11, 81.95, 127.74, 129.77, 133.81, 143.51; Found: C, 67.78; H, 8.06%. Calcd for $C_{18}H_{25}NO_2S$: C, 67.67; H, 7.89%.

1-(*p*-Toluenesulfonyl)-3-(4,4-dimethyl-2-pentynyl)pyrrolidine (22b): white solid. IR (nujol) 665, 1160, 1340, 2854, 2923 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 1.57 (m, 1H), 1.90 (m, 1H), 2.05 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.10 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.22 (septet, *J* = 7.0 Hz, 1H), 2.43 (s, 3H), 2.94 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.22–3.30 (m, 2H), 3.42 (dd, *J* = 10.0, 7.5 Hz, 1H), 7.31–7.33 (dm, *J* = 8.5 Hz, 2H), 7.71–7.72 (dm, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.70, 21.96, 27.48, 30.45, 31.39, 38.16, 47.69, 52.51, 75.48, 90.83, 127.80, 129.82, 134.00, 143.52; Found: C, 67.38; H, 7.82%. Calcd for $C_{18}H_{25}NO_2S$: C, 67.67; H, 7.89%. m.p. 76–80 °C.

1-(*p*-Toluenesulfonyl)-3-[7-(trimethylsilyloxy)-2-heptynyl]pyrrolidine (22c): oil. IR (neat) 664, 842, 1094, 1162, 1251, 1346, 2866, 2952 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 1.46–1.60 (m, 5H), 1.91 (m, 1H), 2.05–2.12 (m, 4H), 2.22 (septet, *J* = 7.0 Hz, 1H), 2.43 (s, 3H), 2.97 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.22 (dt, *J* = 10.0, 7.5 Hz, 1H), 3.31 (m, 1H), 3.41 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.58 (t, *J* = 6.0 Hz, 2H), 7.31–7.33 (dm, *J* = 8.5 Hz, 2H),

7.70–7.72 (dm, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –0.26, 18.66, 21.73, 22.32, 25.59, 30.71, 32.05, 38.31, 47.63, 52.68, 62.30, 77.48, 81.73, 127.81, 129.82, 134.13, 143.52; Found: C, 62.15; H, 8.22%. Calcd for $C_{21}H_{33}NO_3SSi$: C, 61.87; H, 8.16%.

4-(2-Heptynyl)-4,5-dihydro-5,5-dimethyl-2(3*H*)-furanone (23): oil. IR (neat) 960, 1123, 1272, 1388, 1773, 2959 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.5 Hz, 3H), 1.33 (s, 3H), 1.35–1.48 (m, 4H), 1.50 (s, 3H), 2.12–2.17 (m, 2H), 2.29 (dt, J = 6.5, 2.5 Hz, 2H), 2.39–2.46 (m, 2H), 2.71 (q, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.77, 18.50, 19.79, 22.06, 22.15, 28.35, 31.10, 35.18, 44.62, 76.67, 82.79, 86.45, 175.32; Found: C, 74.70; H, 9.60%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

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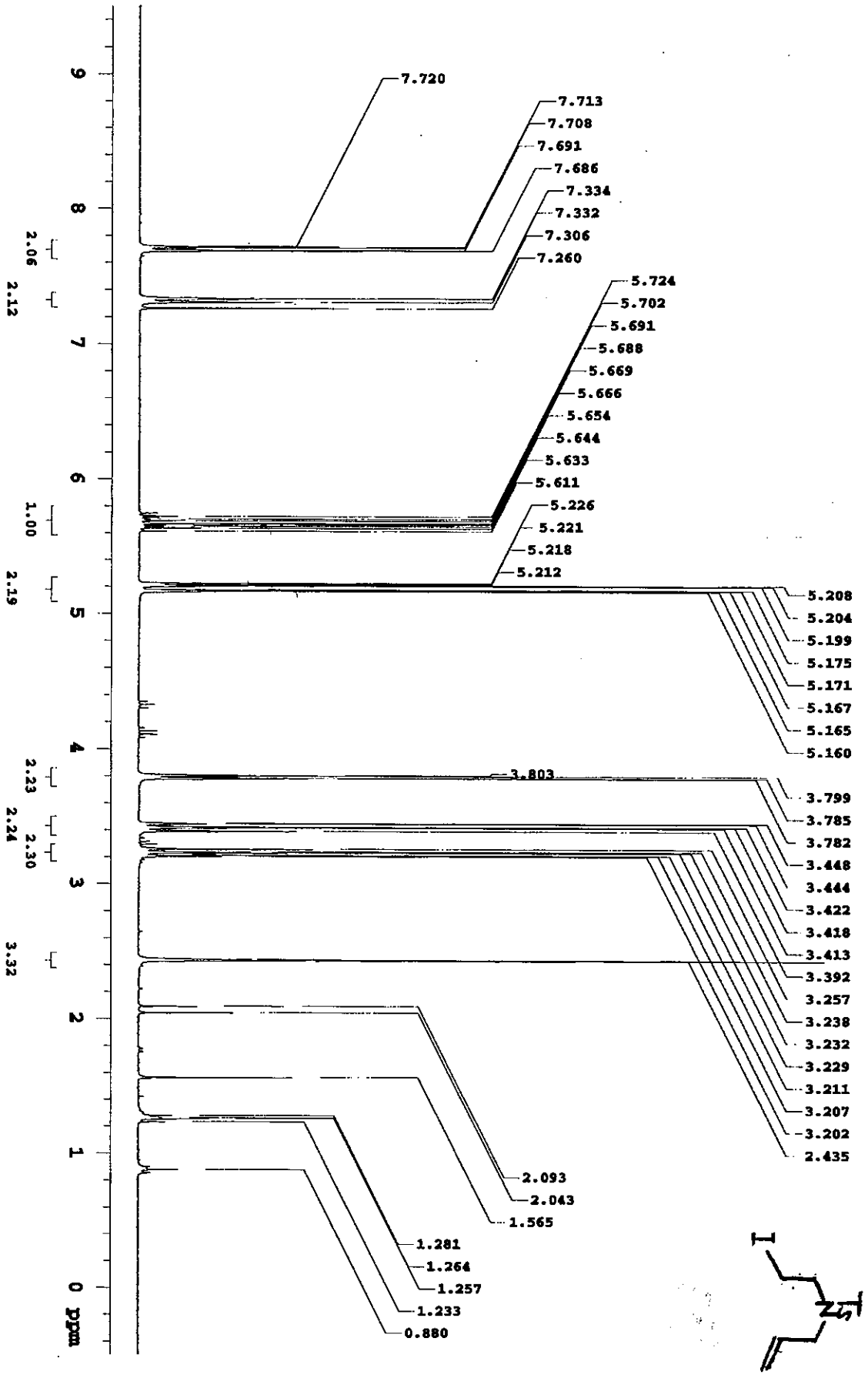
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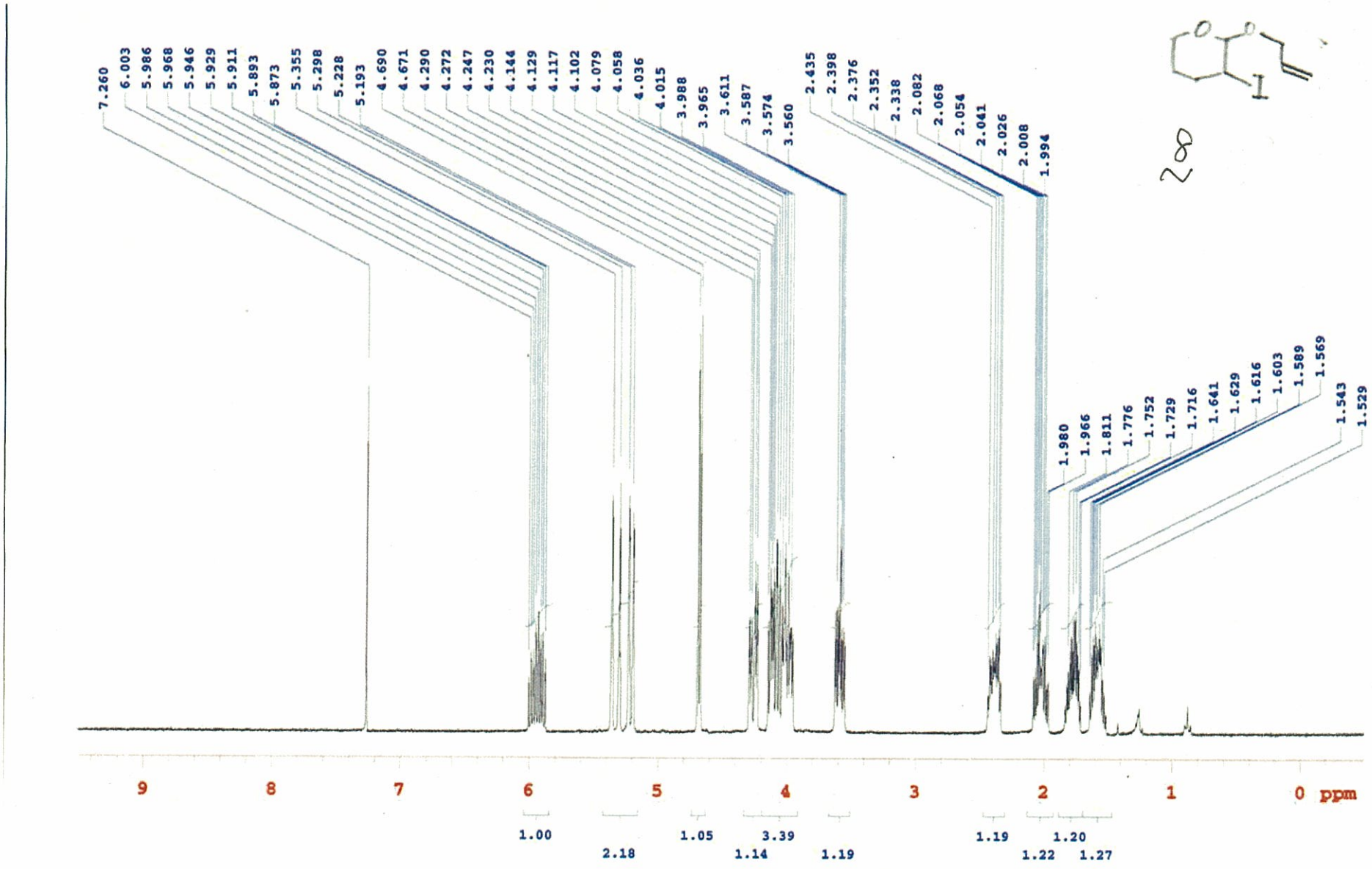
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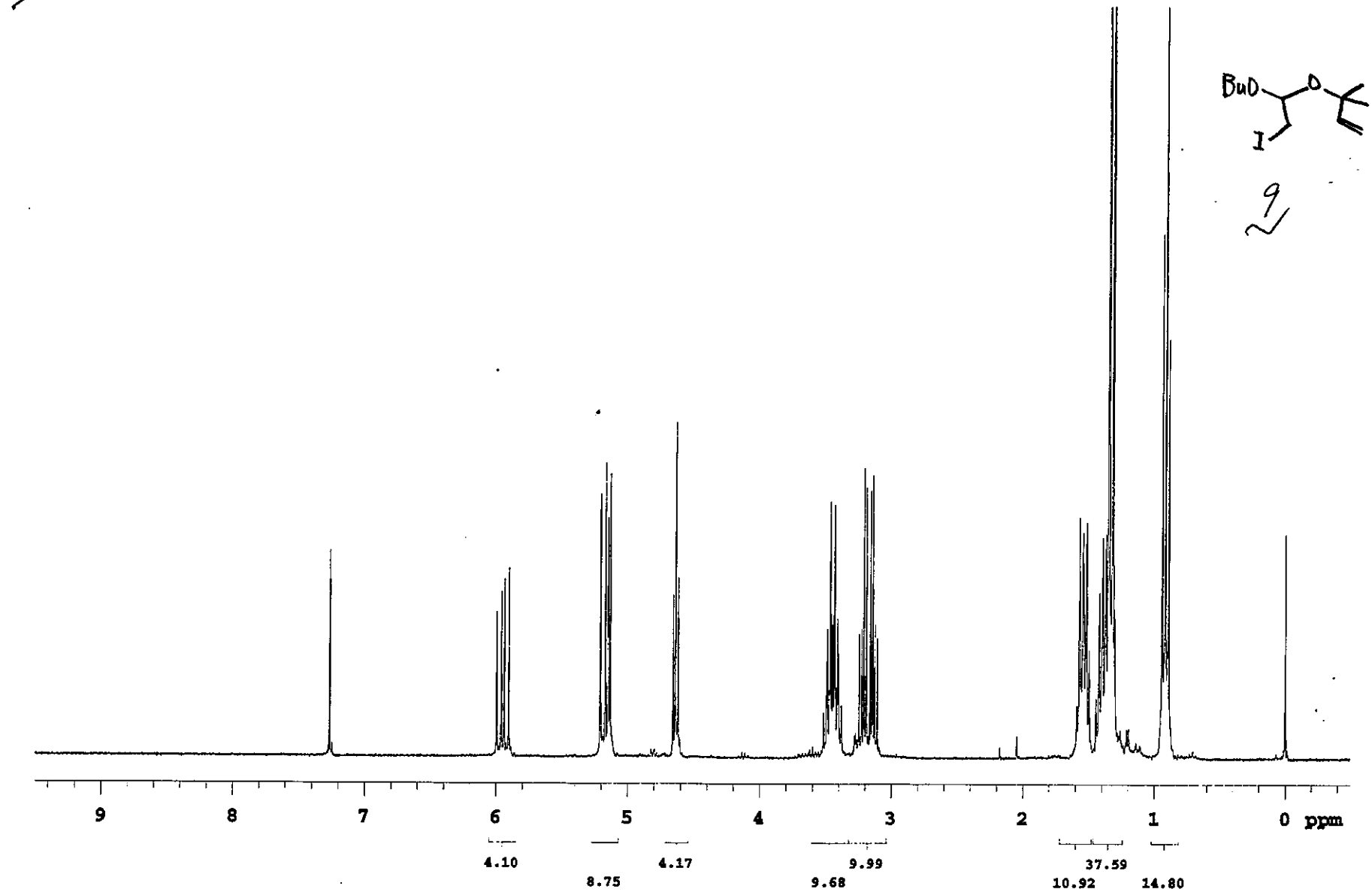
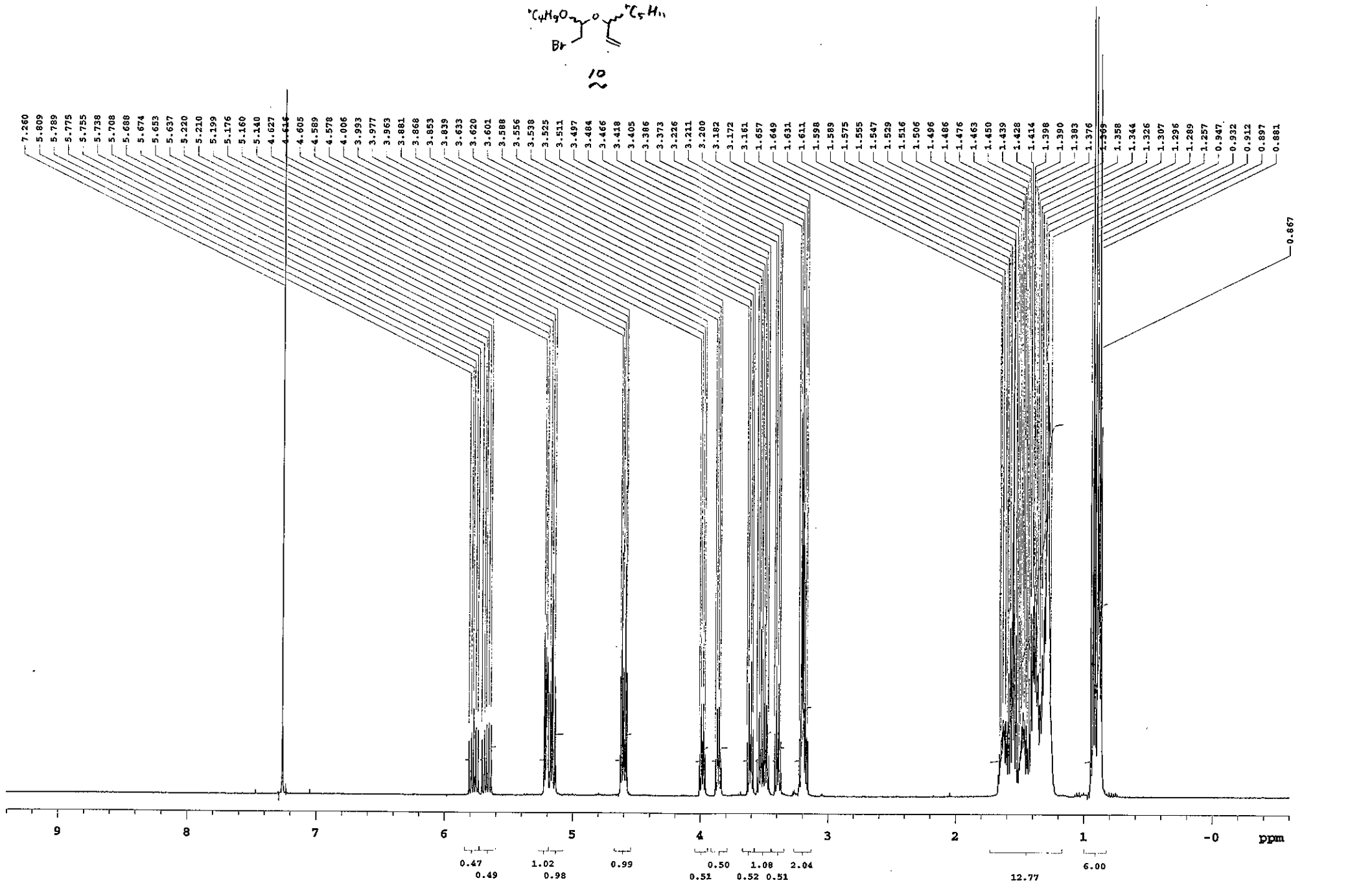
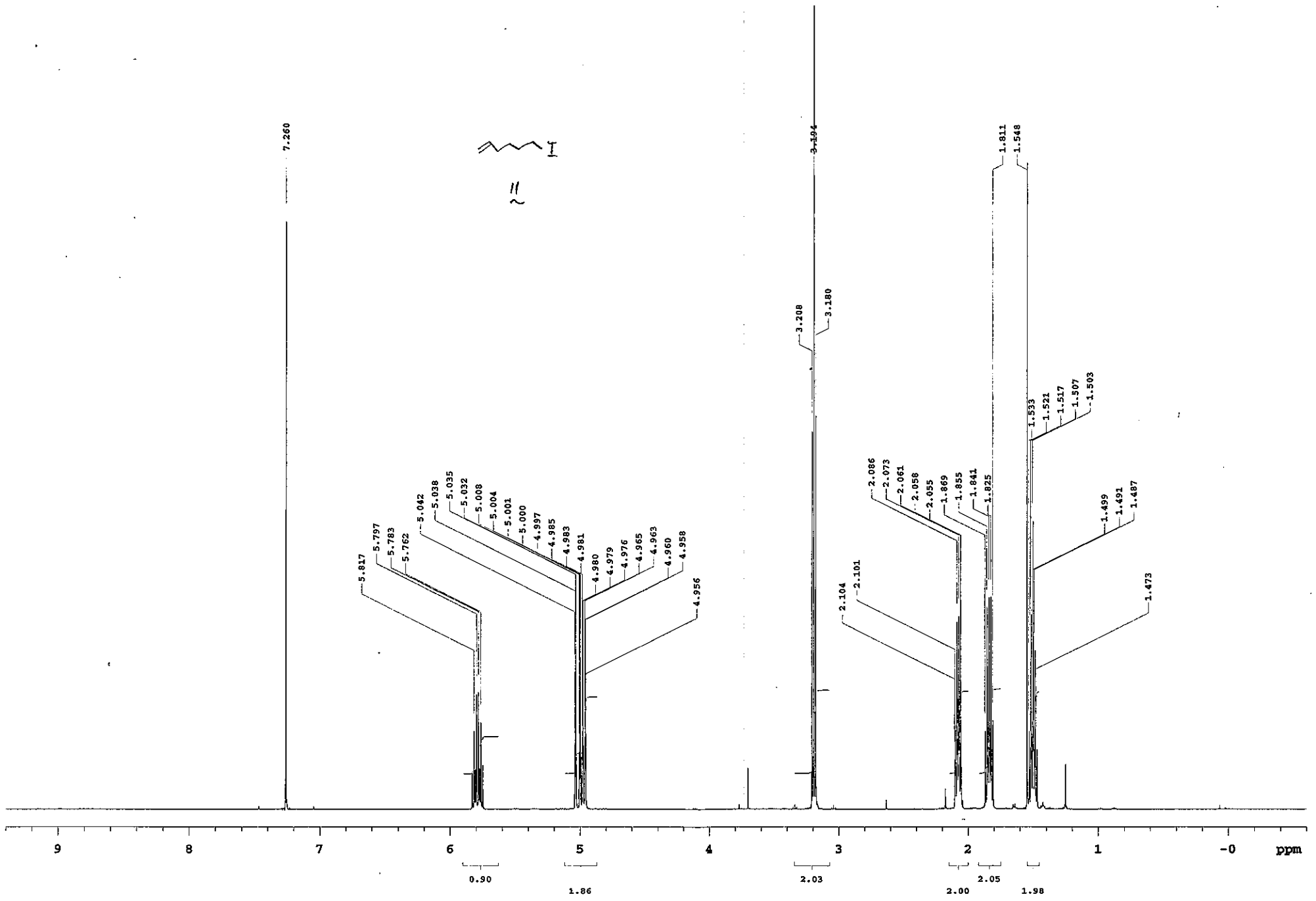
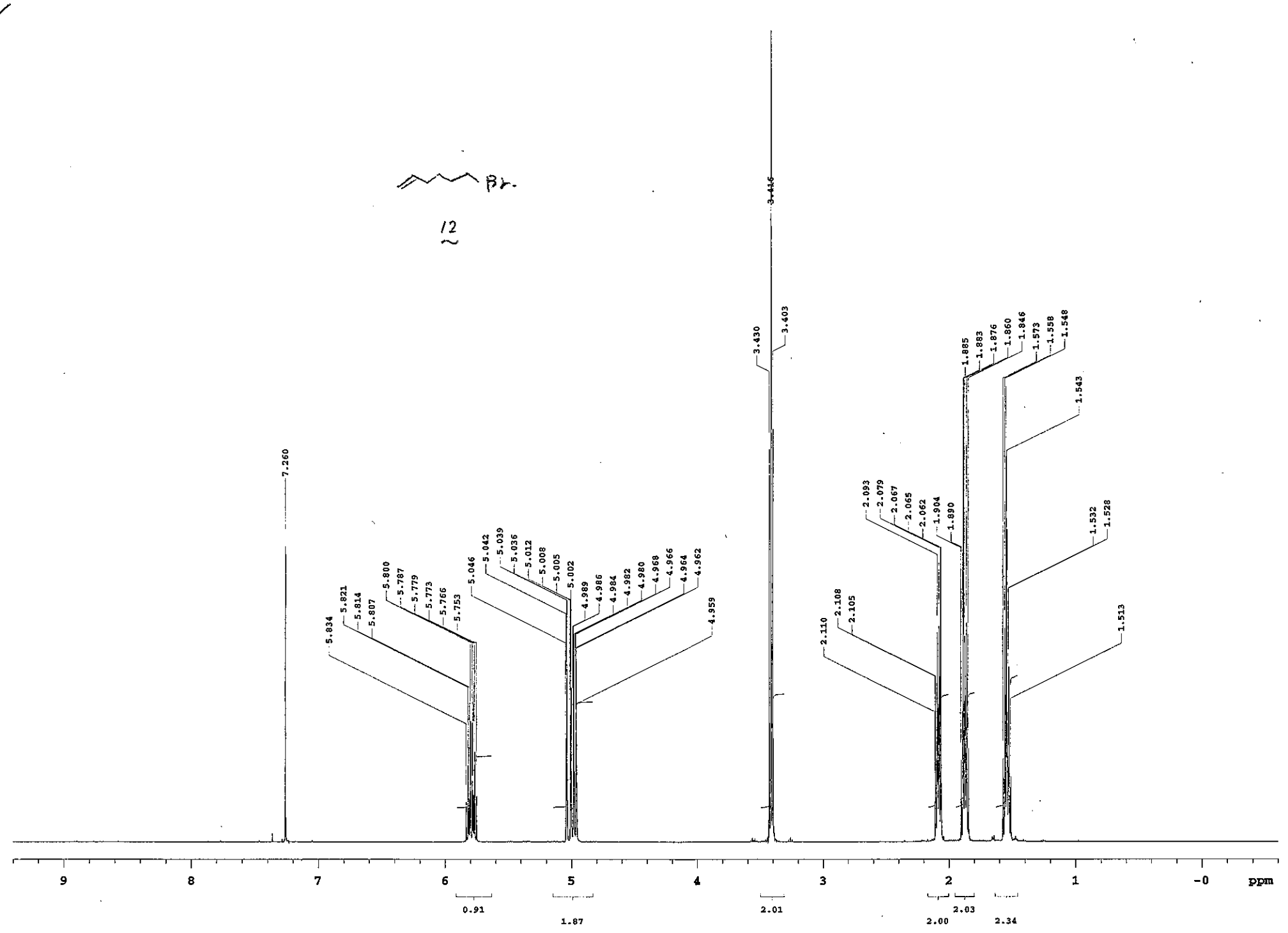
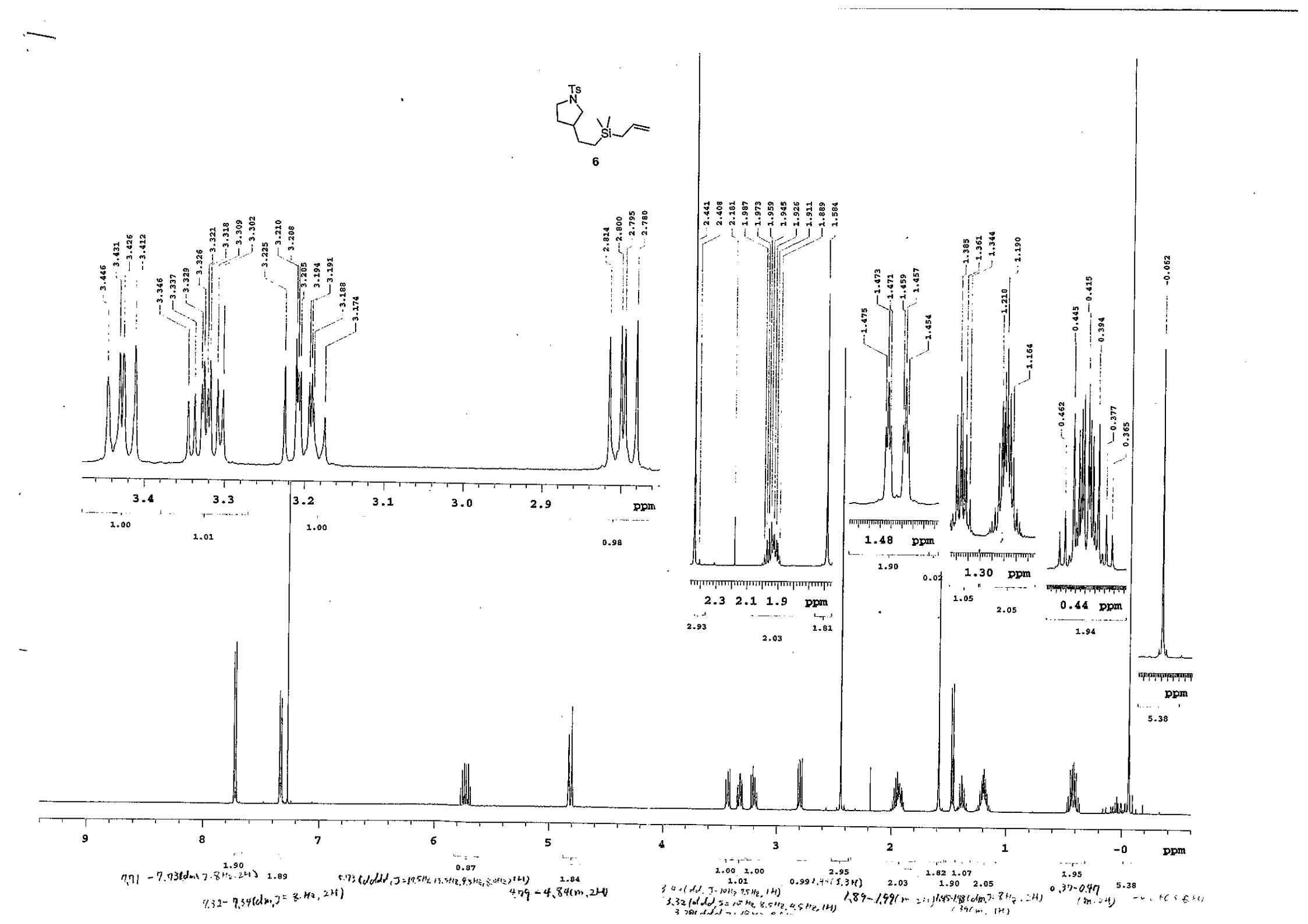
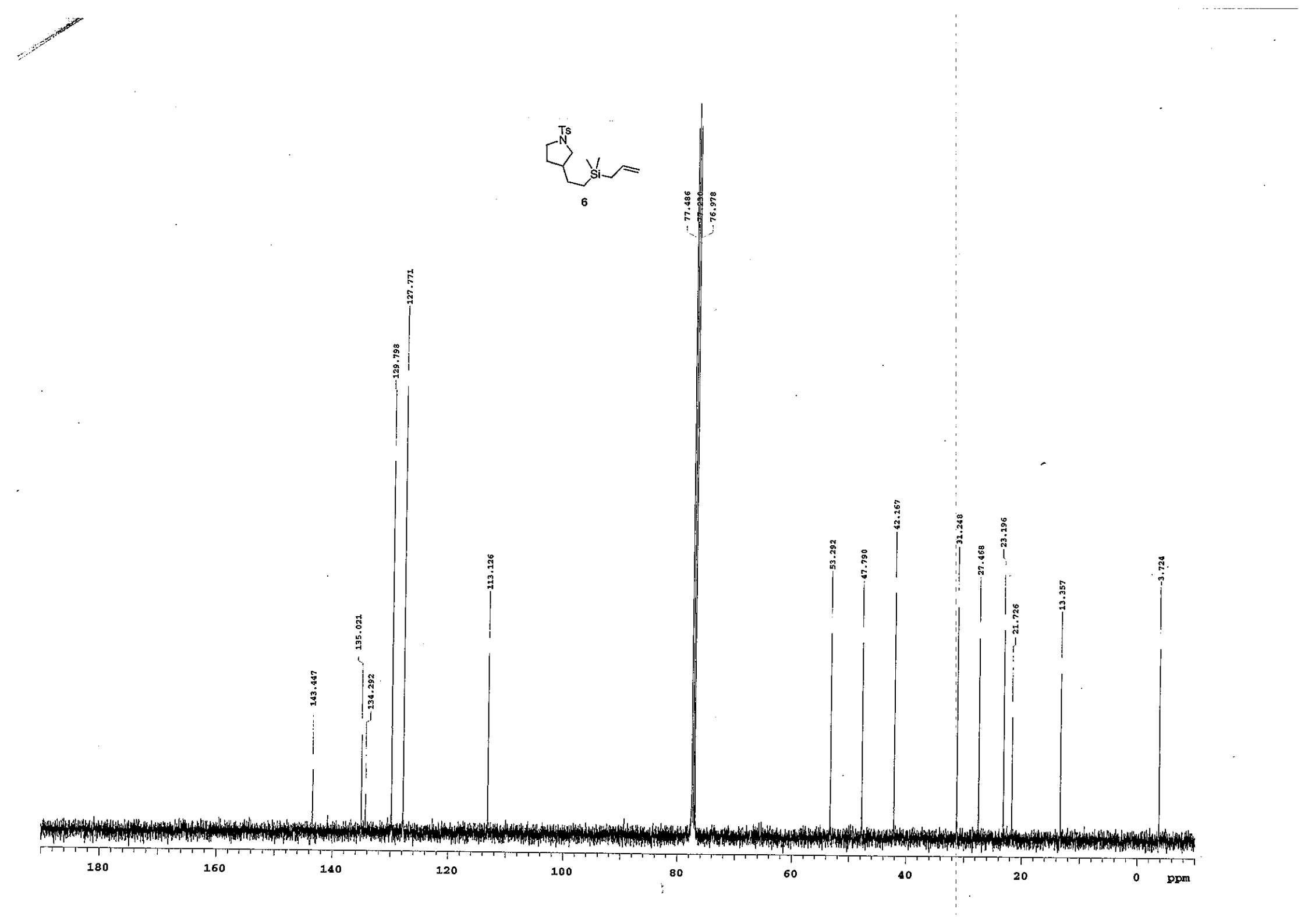

BuO
O
I
9
9
8
7
6
5
4
3
2
1
0 ppm
4.10
8.75
4.17
9.68
9.99
10.92
37.59
14.80

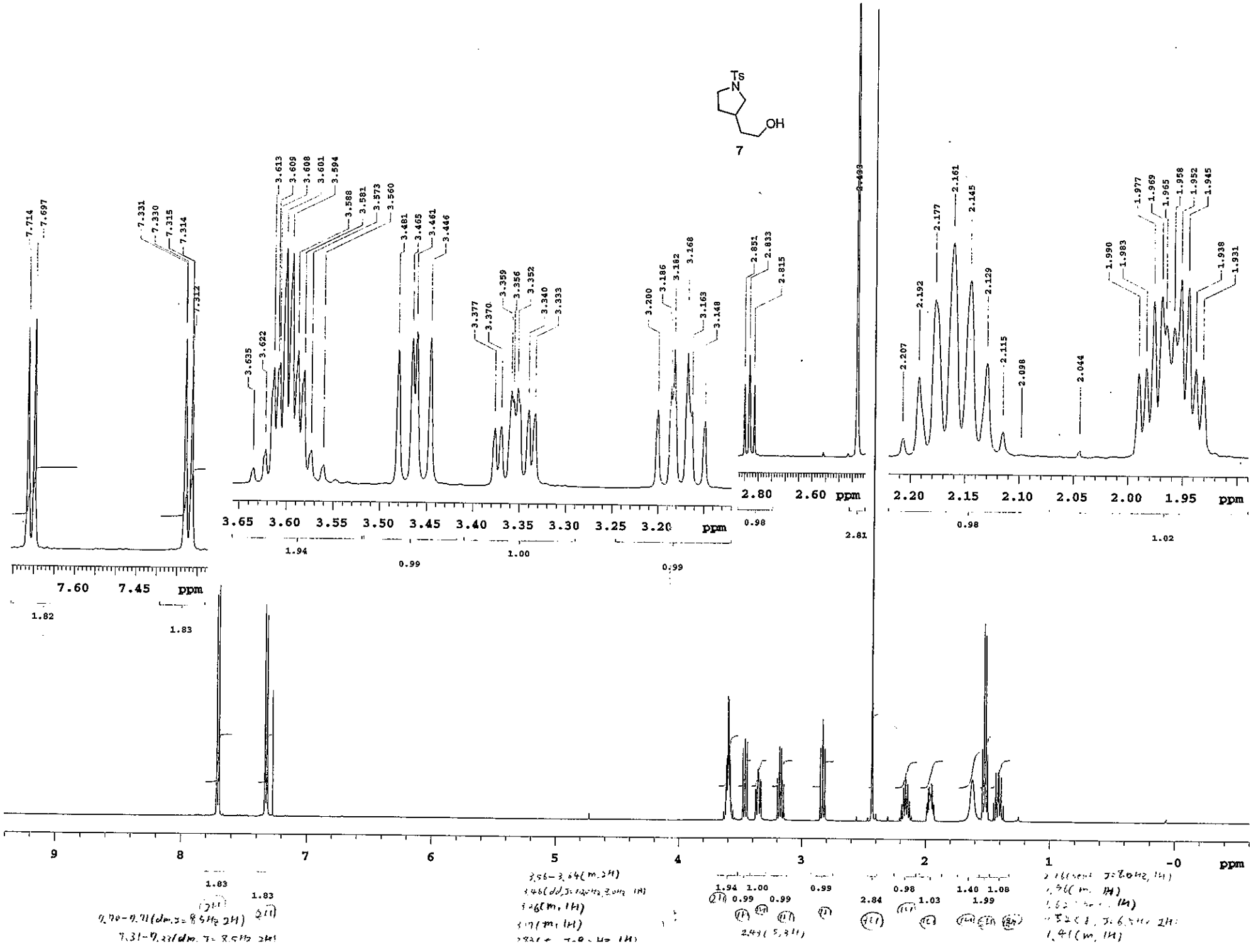

7.260
5.809
5.789
5.775
5.755
5.738
5.708
5.688
5.674
5.653
5.637
5.220
5.210
5.199
5.176
5.160
5.140
4.627
4.616
4.605
4.589
4.578
4.006
3.993
3.977
3.963
3.881
3.868
3.853
3.839
3.633
3.620
3.601
3.588
3.556
3.538
3.525
3.511
3.497
3.484
3.466
3.418
3.405
3.386
3.373
3.226
3.211
3.200
3.182
3.172
3.161
1.657
1.649
1.631
1.611
1.598
1.589
1.575
1.555
1.547
1.529
1.516
1.506
1.496
1.486
1.476
1.463
1.450
1.439
1.428
1.414
1.398
1.390
1.383
1.376
1.369
1.358
1.344
1.326
1.307
1.296
1.289
1.257
0.947
0.932
0.912
0.897
0.881
0.867
9
8
7
6
5
4
3
2
1
-0
ppm
0.47
0.49
1.02
0.98
0.99
0.50
0.51
1.08
0.52
2.04
0.51
12.77
6.00

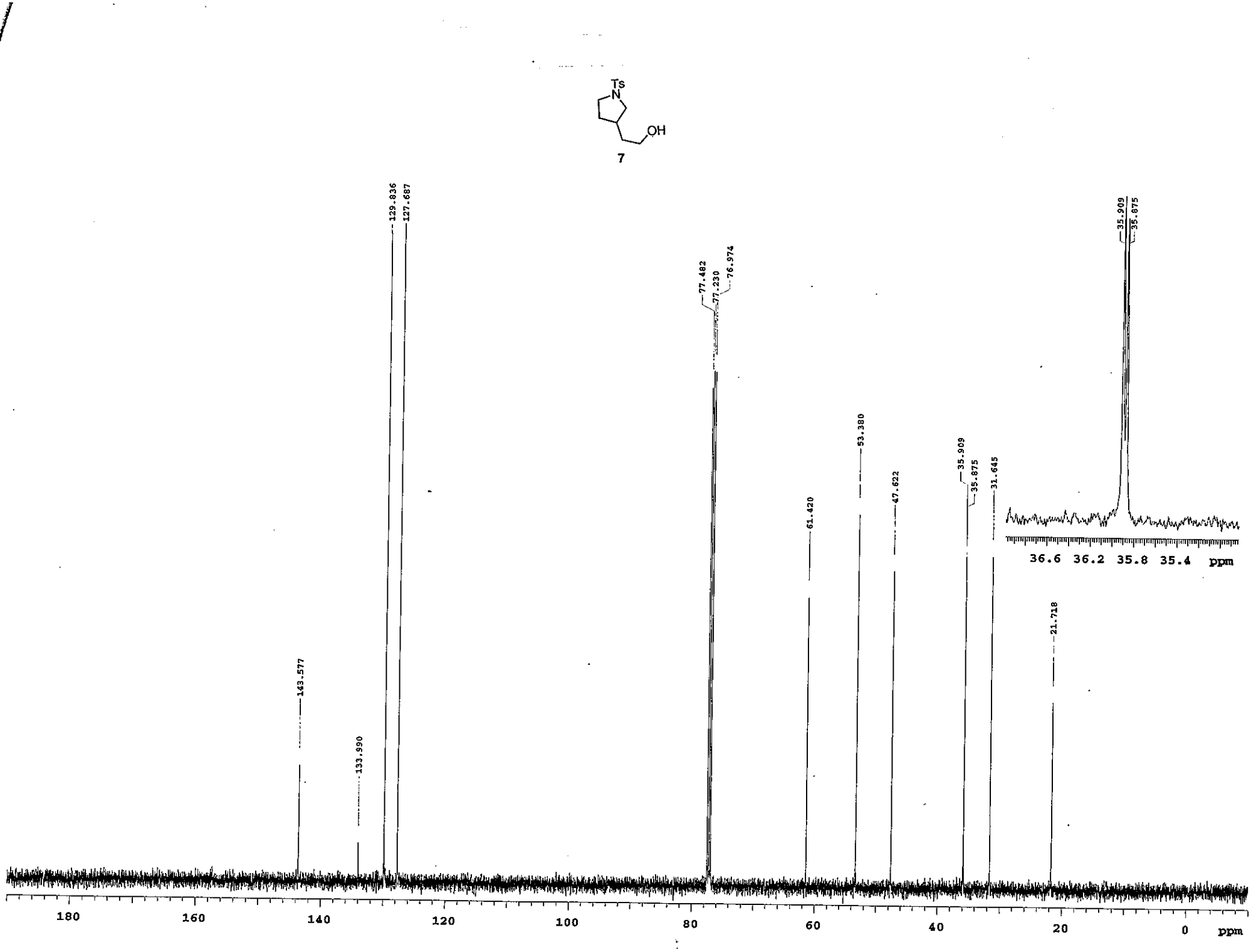

7.260
5.817
5.797
5.783
5.762
5.042
5.038
5.035
5.032
5.008
5.004
5.001
5.000
4.997
4.985
4.983
4.981
4.980
4.979
4.976
4.965
4.963
4.960
4.958
4.956
3.208
3.180
2.104
2.101
2.086
2.073
2.061
2.058
2.055
1.869
1.855
1.841
1.825
1.811
1.548
1.533
1.521
1.517
1.507
1.503
1.499
1.491
1.487
1.473
9
8
7
6
5
4
3
2
1
-0
ppm
0.90
1.86
2.03
2.00
2.05
1.98

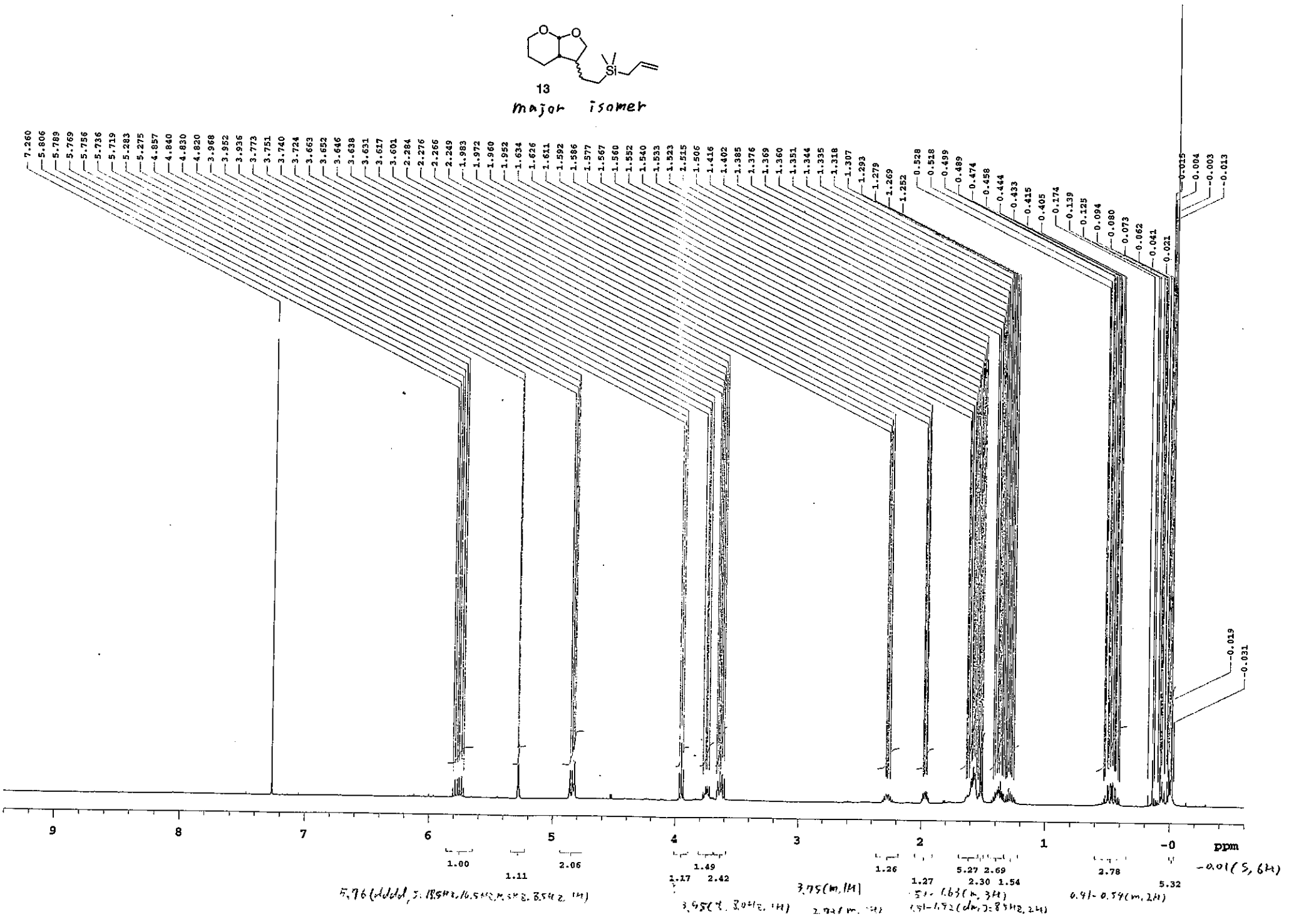

Br.
12
7.260
5.834
5.821
5.814
5.807
5.800
5.787
5.779
5.773
5.766
5.753
5.046
5.042
5.039
5.036
5.012
5.008
5.005
5.002
4.989
4.986
4.984
4.982
4.980
4.968
4.966
4.964
4.962
4.959
3.446
3.430
3.403
2.110
2.108
2.105
2.093
2.079
2.067
2.065
2.062
1.904
1.890
1.885
1.883
1.876
1.860
1.846
1.573
1.558
1.548
1.543
1.532
1.528
1.513
9
8
7
6
5
4
3
2
1
-0
ppm
0.91
1.87
2.01
2.00
2.03
2.34

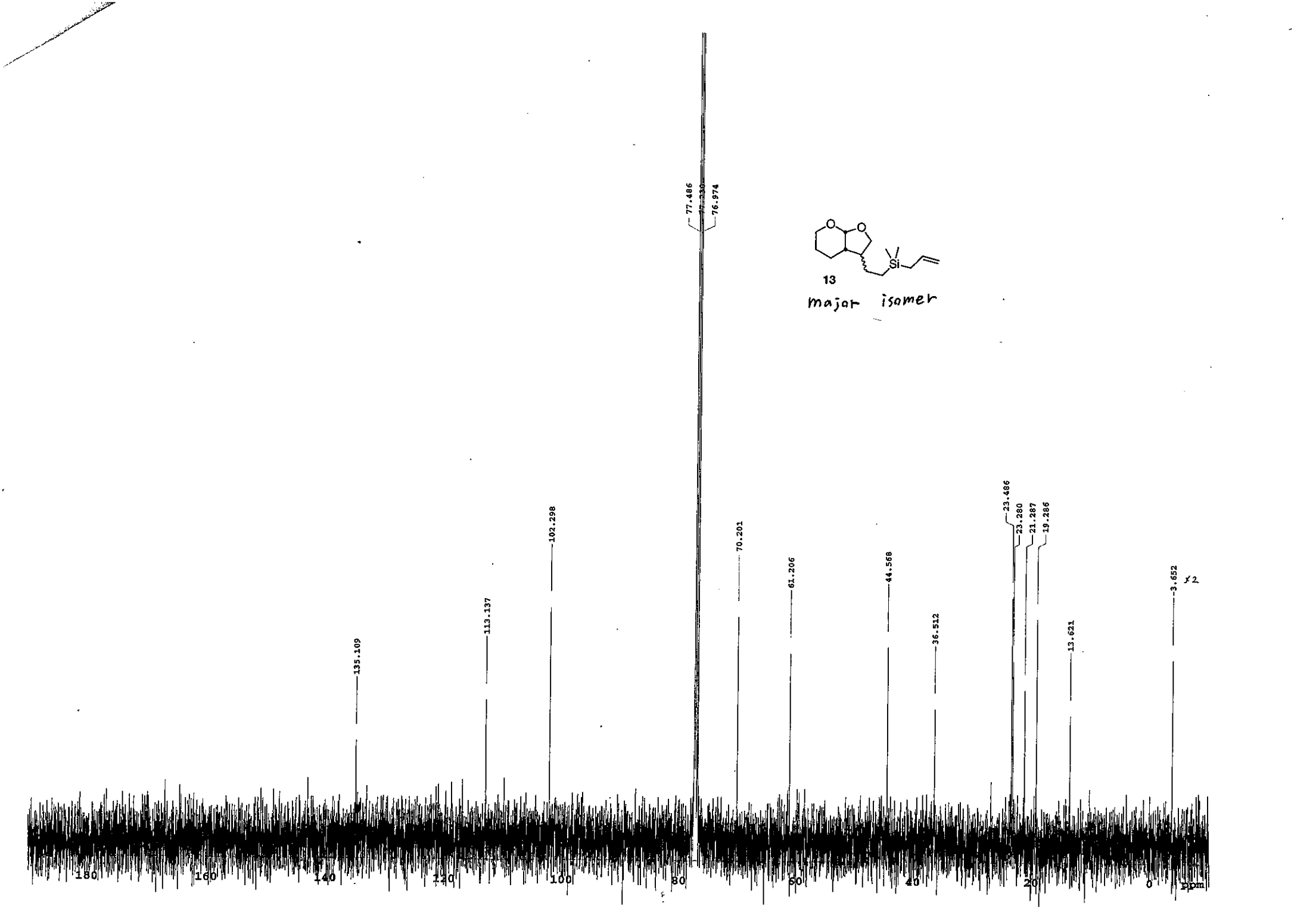

Ts
N
Si
6
3.446
3.431
3.426
3.412
3.346
3.337
3.329
3.326
3.321
3.318
3.309
3.302
3.225
3.210
3.208
3.205
3.194
3.191
3.188
3.174
2.814
2.800
2.795
2.780
3.4
3.3
3.2
3.1
3.0
2.9
ppm
1.00
1.01
1.00
0.98
2.441
2.408
2.181
1.987
1.973
1.959
1.945
1.926
1.911
1.889
1.584
2.3 2.1 1.9 ppm
2.93
2.03
1.81
1.475
1.473
1.471
1.459
1.457
1.454
1.48 ppm
1.90
1.385
1.361
1.344
1.210
1.190
1.164
1.30 ppm
1.05
2.05
0.462
0.445
0.415
0.394
0.377
0.365
0.44 ppm
1.94
-0.062
ppm
5.38
9
8
7
6
5
4
3
2
1
-0
ppm
1.90
0.87
1.84
2.00 1.00
1.01
0.99
2.95
2.03
1.82 1.07
1.90 2.05
1.95
5.38


Ts
N
Si
6
143.447
135.021
134.292
129.798
127.771
113.126
77.486
76.978
53.292
47.790
42.167
31.248
27.468
23.196
21.726
13.357
-3.724
180
160
140
120
100
80
60
40
20
0
ppm


Ts
N
OH
7
7.714
7.697
7.331
7.330
7.315
7.314
7.312
3.635
3.622
3.613
3.609
3.608
3.601
3.594
3.588
3.581
3.573
3.560
3.481
3.465
3.461
3.446
3.377
3.370
3.359
3.356
3.352
3.340
3.333
3.200
3.186
3.182
3.168
3.163
3.148
2.851
2.833
2.815
2.493
2.207
2.192
2.177
2.161
2.145
2.129
2.115
2.098
2.044
1.990
1.983
1.977
1.969
1.965
1.958
1.952
1.945
1.938
1.931
7.60 7.45 ppm
1.82
1.83
3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 ppm
1.94
0.99
1.00
0.99
2.80 2.60 ppm
0.98
2.81
2.20 2.15 2.10 2.05 2.00 1.95 ppm
0.98
1.02
9 8 7 6 5 4 3 2 1 -0 ppm
1.83
1.83
1.94 1.00
0.99
0.99
0.99
2.84
0.98
1.03
1.40 1.08
1.99

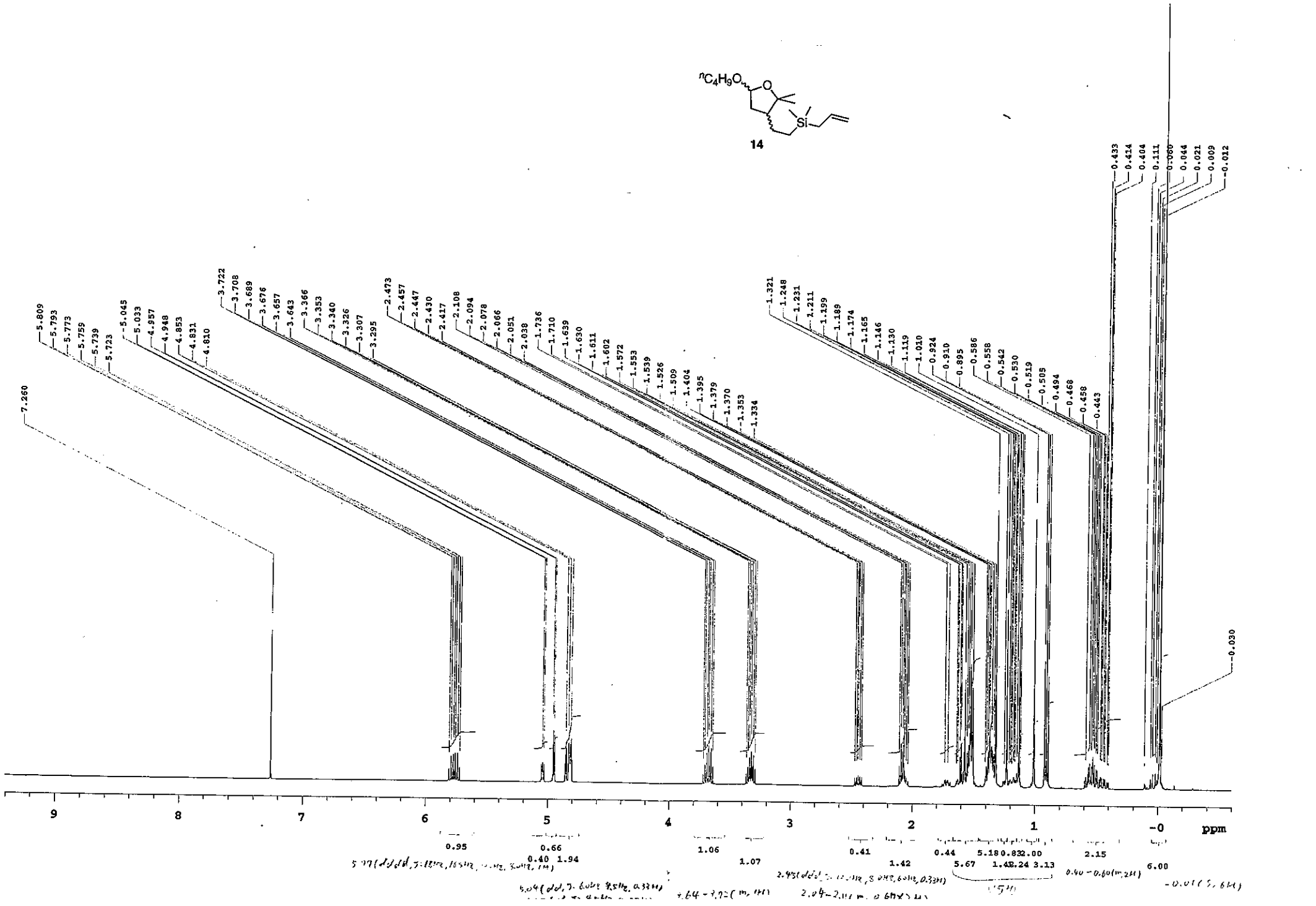

Ts
N
OH
7
143.577
133.990
129.836
127.687
77.482
77.230
76.974
61.420
53.380
47.622
35.909
35.875
31.645
21.718
35.909
35.875
36.6 36.2 35.8 35.4 ppm
180
160
140
120
100
80
60
40
20
0
ppm

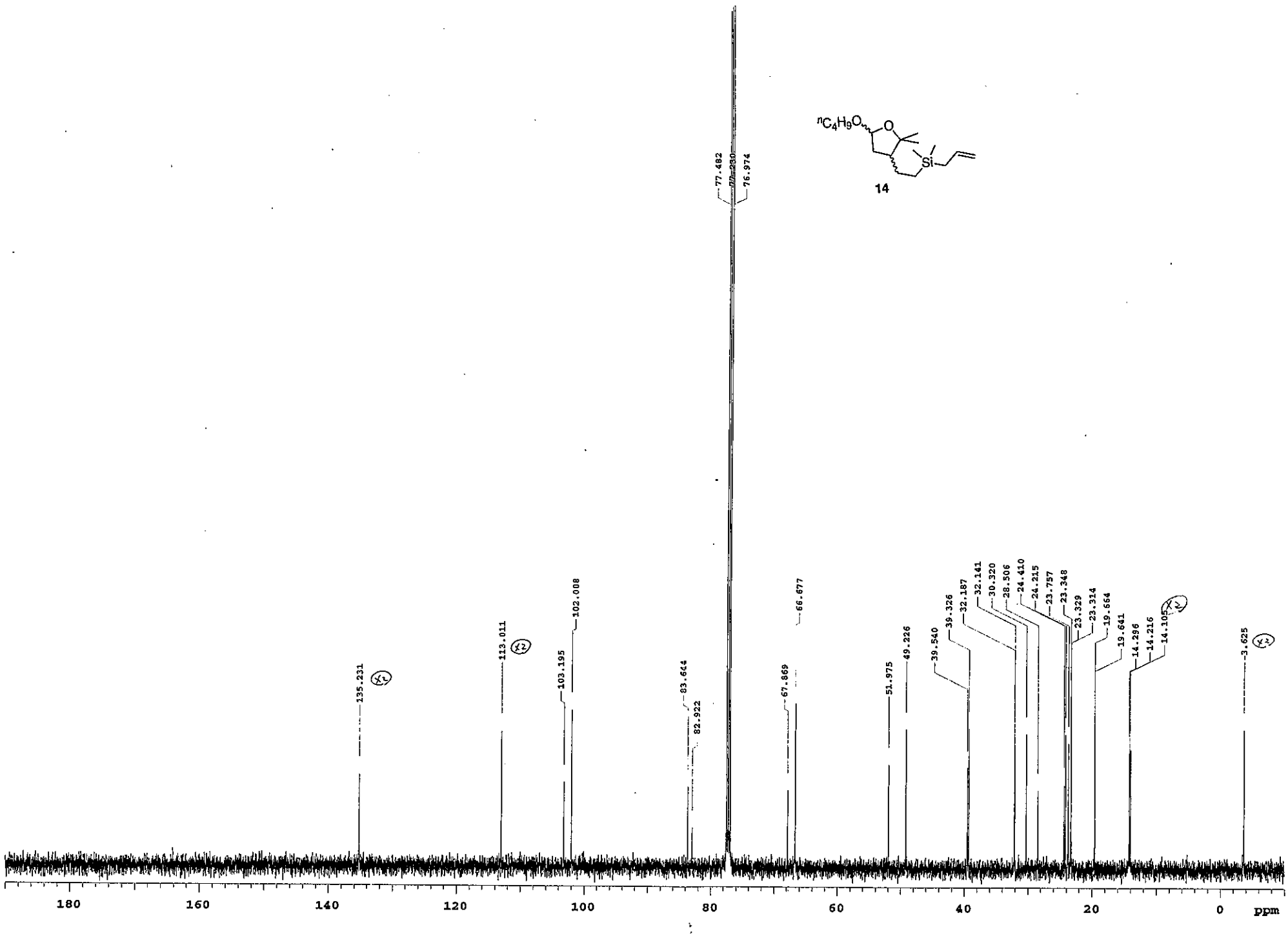

13
major isomer
7.260
5.806
5.789
5.769
5.756
5.736
5.719
5.283
5.275
4.857
4.840
4.830
4.820
3.968
3.952
3.936
3.773
3.751
3.740
3.724
3.663
3.652
3.646
3.638
3.631
3.617
3.601
2.284
2.276
2.266
2.249
1.983
1.972
1.960
1.952
1.634
1.626
1.611
1.592
1.586
1.577
1.567
1.560
1.552
1.540
1.533
1.523
1.515
1.506
1.416
1.402
1.385
1.376
1.369
1.360
1.351
1.344
1.335
1.318
1.307
1.293
1.279
1.269
1.252
0.528
0.518
0.499
0.489
0.474
0.458
0.444
0.433
0.415
0.405
0.174
0.139
0.125
0.094
0.080
0.073
0.062
0.041
0.021
0.015
0.004
-0.003
-0.013
-0.019
-0.031
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.11
2.06
1.49
1.17
2.42
1.26
5.27
2.69
2.30
1.54
1.27
2.78
5.32
5.76(dddd, J=18.5Hz,16.5Hz,8.5Hz,8.5Hz, 1H)
3.95(t, 8.0Hz, 1H)
3.75(m,1H)
0.91-0.54(m,2H)
-0.01(s,6H)

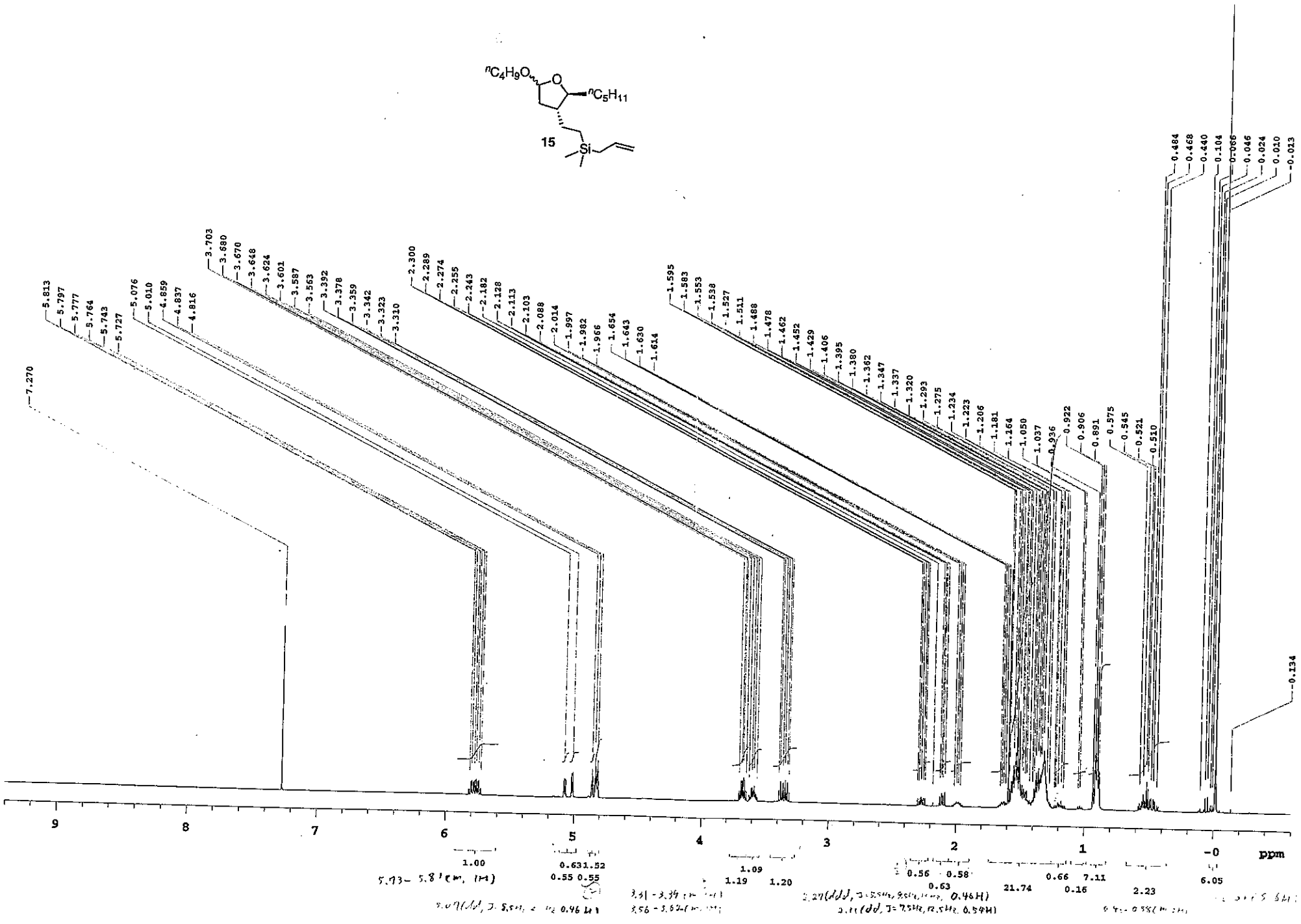


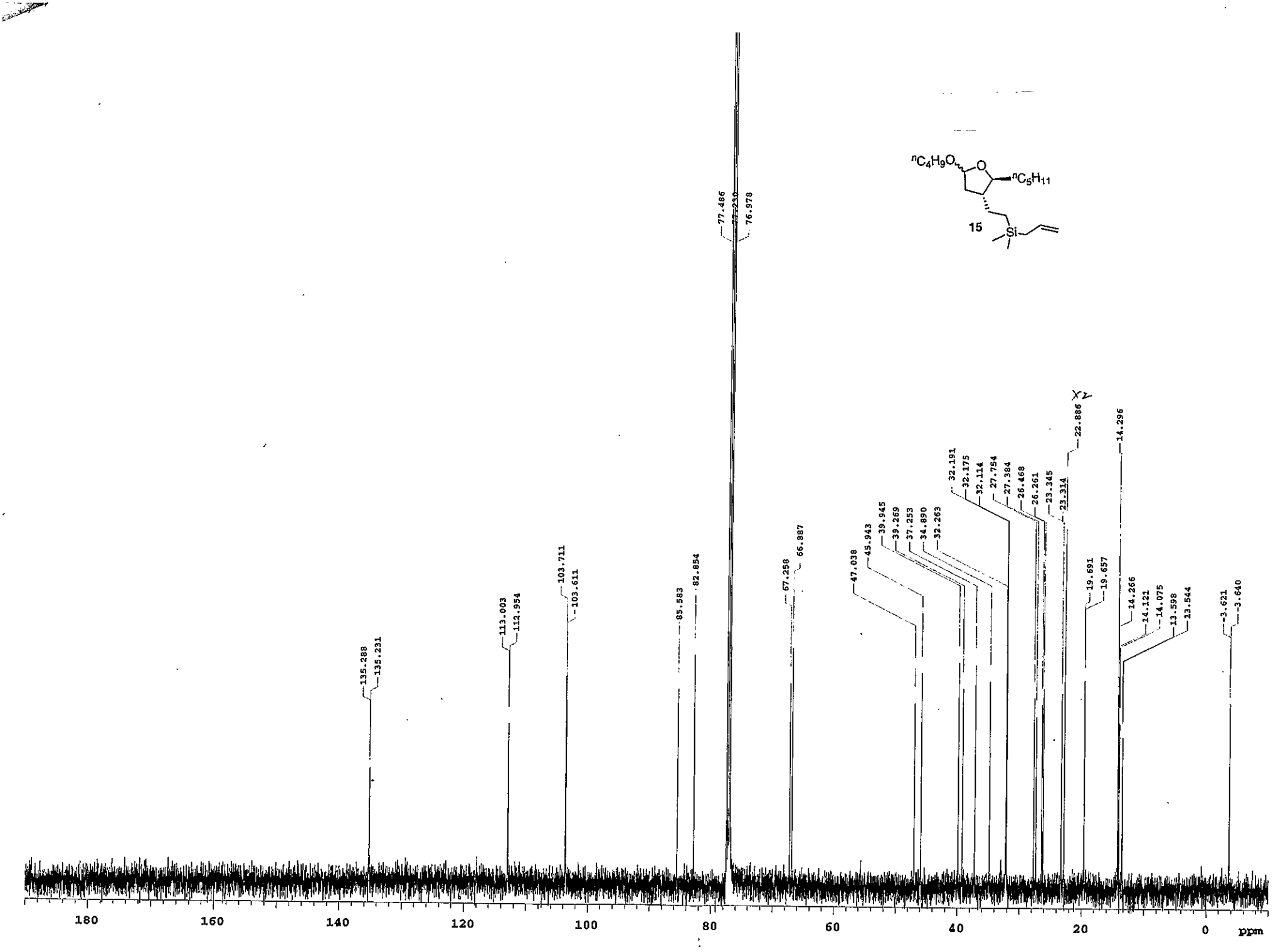
13

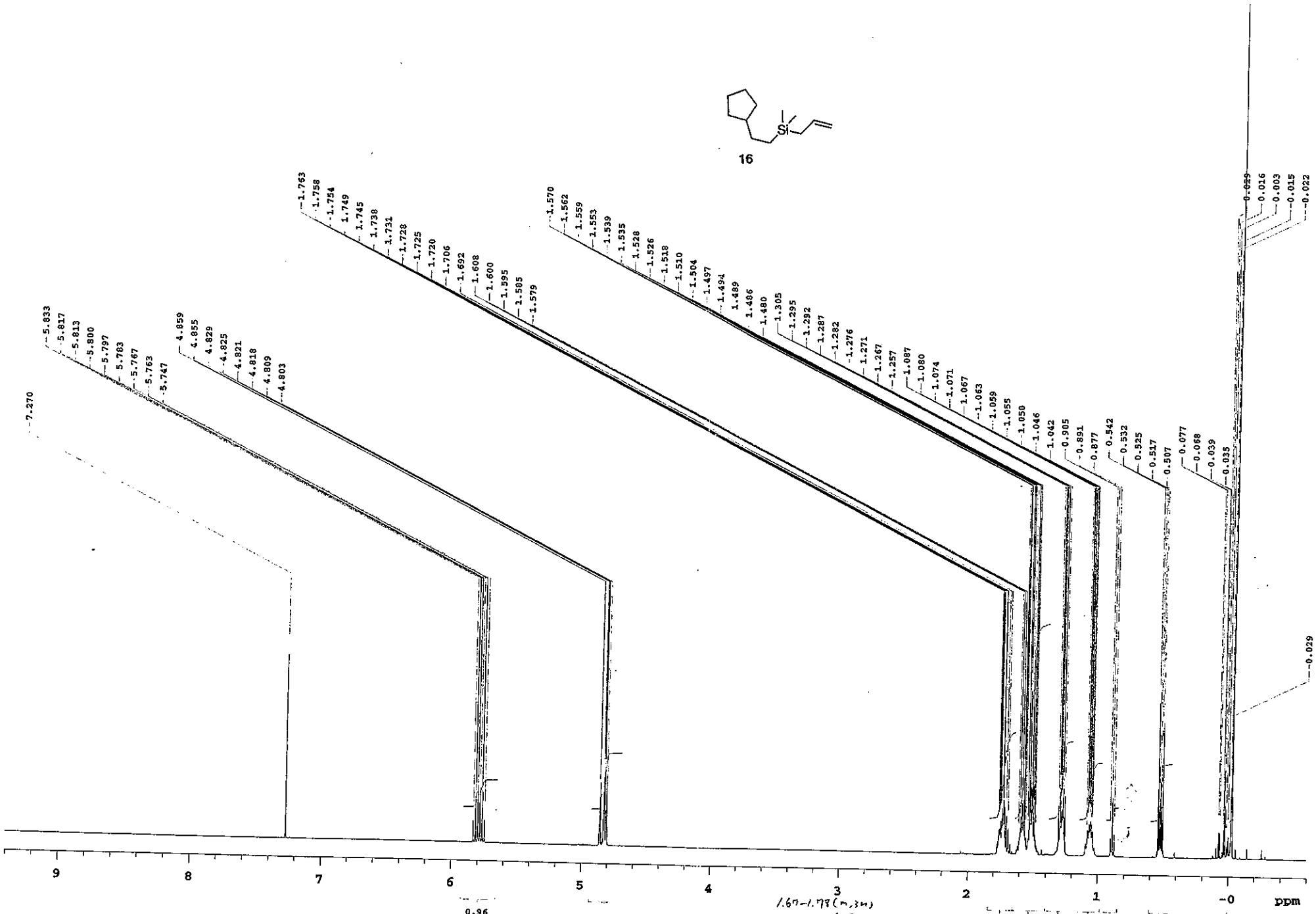
major isomer

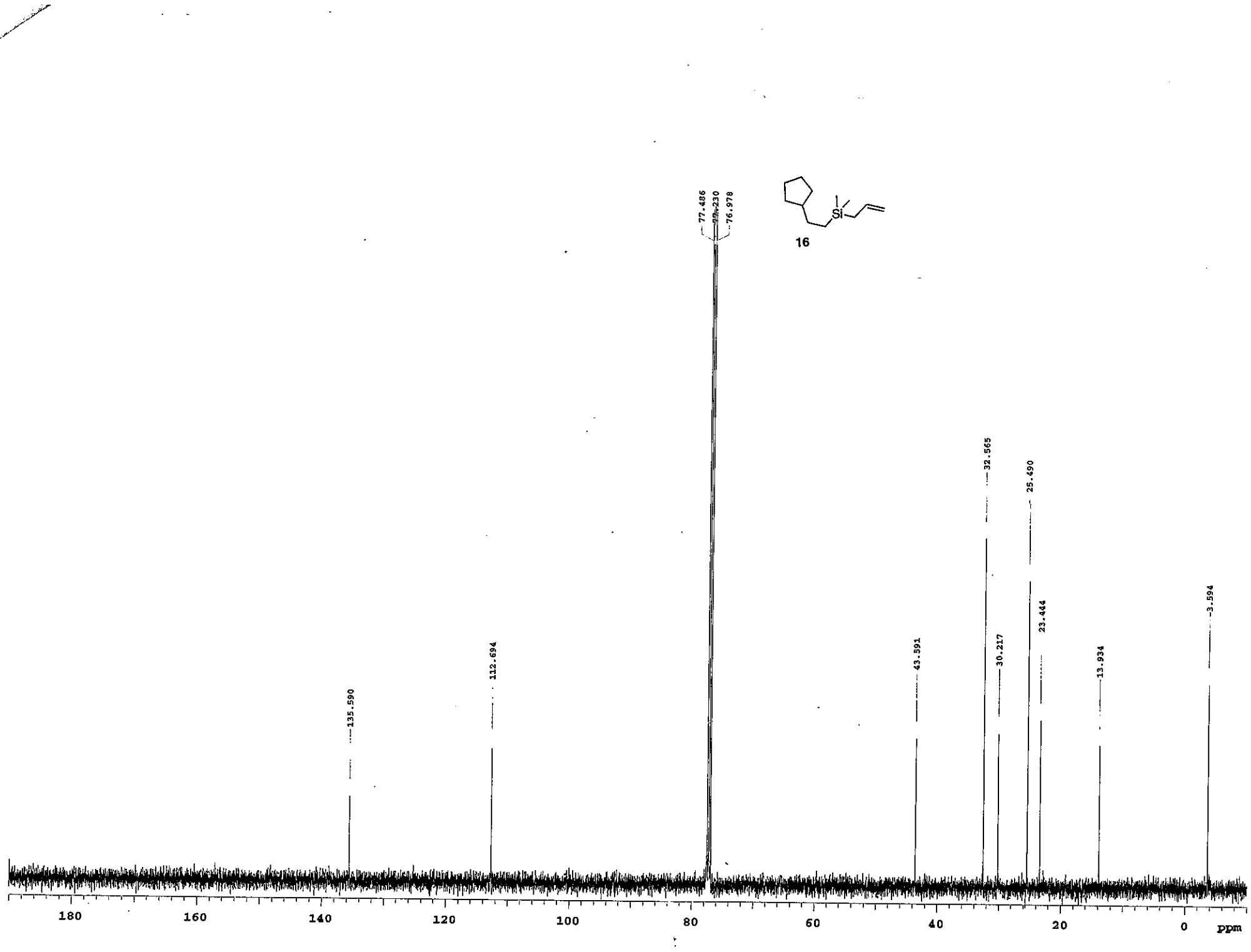

$^nC_4H_9O$
O
Si
14
7.260
5.809
5.793
5.773
5.759
5.739
5.723
5.045
5.033
4.957
4.948
4.853
4.831
4.810
3.722
3.708
3.689
3.676
3.657
3.643
3.366
3.353
3.340
3.326
3.307
3.295
2.473
2.457
2.447
2.430
2.417
2.108
2.094
2.078
2.066
2.051
2.038
1.736
1.710
1.639
1.630
1.611
1.602
1.572
1.553
1.539
1.526
1.509
1.404
1.395
1.379
1.370
1.353
1.334
1.321
1.248
1.231
1.211
1.199
1.189
1.174
1.165
1.146
1.130
1.119
1.010
0.924
0.910
0.895
0.586
0.558
0.542
0.530
0.519
0.505
0.494
0.468
0.458
0.443
0.433
0.414
0.404
0.111
0.000
0.044
0.021
0.009
-0.012
0.030
9
8
7
6
5
4
3
2
1
-0
ppm
0.95
0.66
0.40
1.94
1.06
1.07
0.41
1.42
0.44
5.67
5.18
1.42
0.83
24
2.00
3.13
2.15
6.00

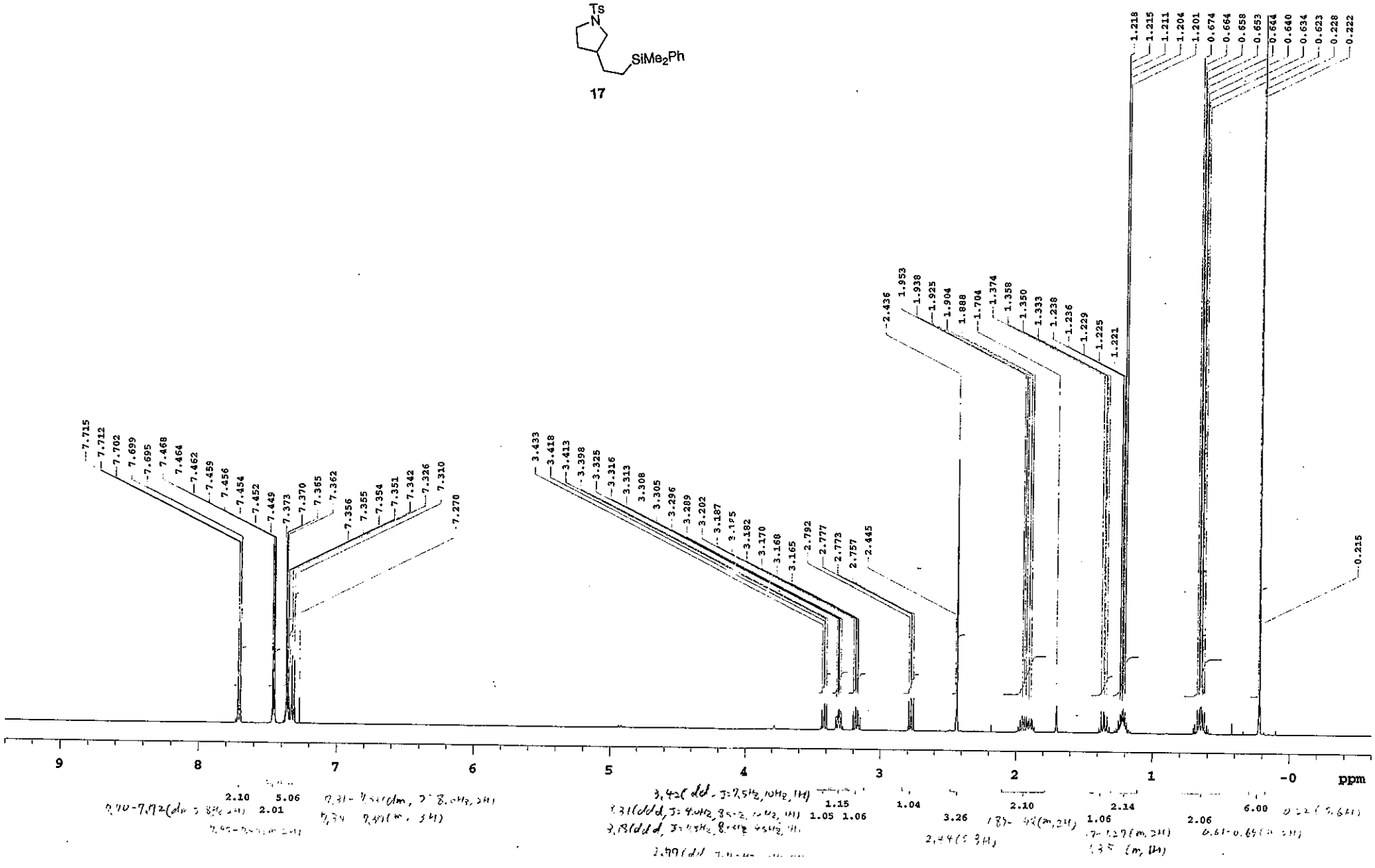

nC4H9O
O
Si
14
77.482
77.230
76.974
135.231
113.011
103.195
102.008
83.644
82.922
67.869
66.677
51.975
49.226
39.540
39.326
32.187
32.141
30.320
28.506
24.410
24.215
23.757
23.348
23.329
23.314
19.664
19.641
14.296
14.216
14.105
3.625
180
160
140
120
100
80
60
40
20
0
ppm

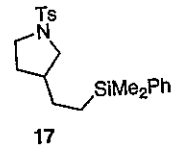

$^{n}C_4H_9O$
O
$^{n}C_5H_{11}$
15
Si
7.270
5.813
5.797
5.777
5.764
5.743
5.727
5.076
5.010
4.859
4.837
4.816
3.703
3.680
3.670
3.648
3.624
3.601
3.587
3.563
3.392
3.378
3.359
3.342
3.323
3.310
2.300
2.289
2.274
2.255
2.243
2.182
2.128
2.113
2.103
2.088
2.014
1.997
1.982
1.966
1.654
1.643
1.630
1.614
1.595
1.583
1.553
1.538
1.527
1.511
1.488
1.478
1.462
1.452
1.429
1.406
1.395
1.380
1.362
1.347
1.337
1.320
1.293
1.275
1.234
1.223
1.206
1.181
1.164
1.050
1.037
0.936
0.922
0.906
0.891
0.575
0.545
0.521
0.510
0.484
0.468
0.440
0.104
0.066
0.046
0.024
0.010
-0.013
-0.134
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
0.63
1.52
0.55
0.55
1.09
1.19
1.20
0.56
0.58
0.63
21.74
0.66
7.11
0.16
2.23
6.05


77.486
77.230
76.978
135.288
135.231
113.003
112.954
103.711
103.611
85.583
82.854
67.258
66.887
47.038
45.943
39.945
39.269
37.253
34.890
32.263
32.191
32.175
32.114
27.754
27.384
26.468
26.261
23.345
23.314
22.886
19.691
19.657
14.296
14.266
14.121
14.075
13.598
13.544
3.621
3.640
180
160
140
120
100
80
60
40
20
0
ppm

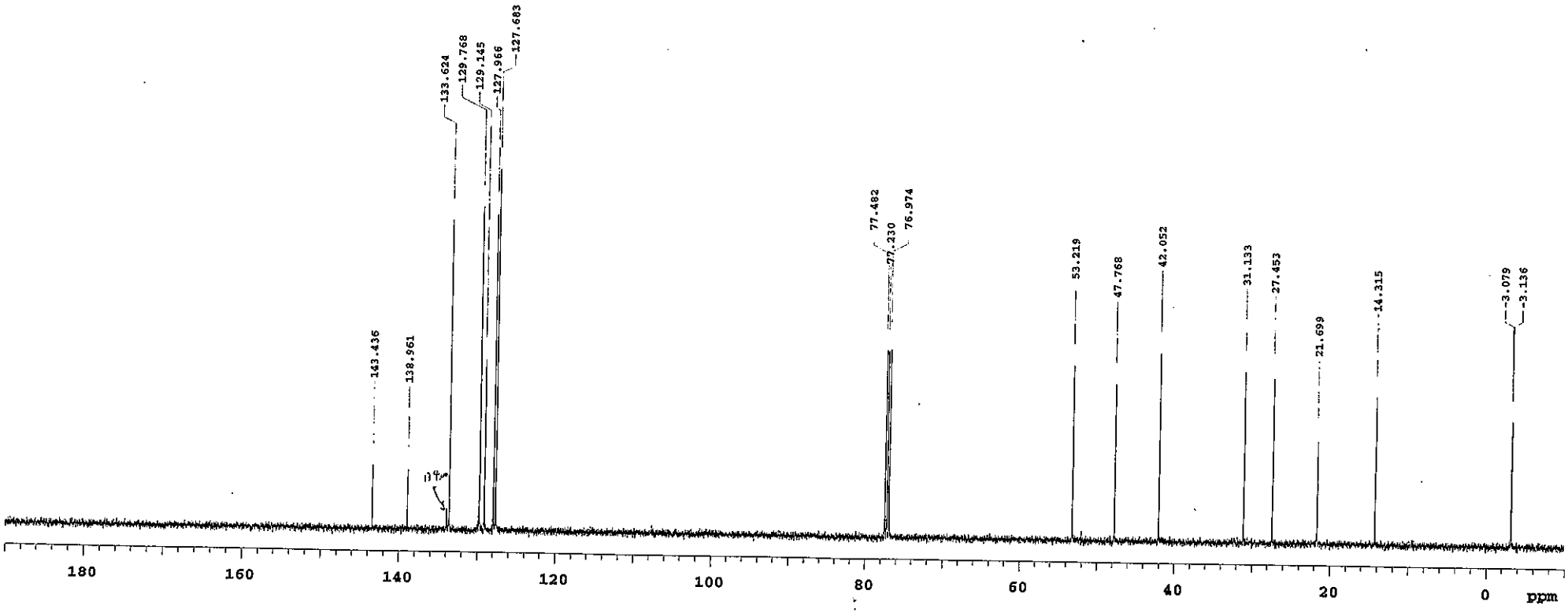

Si
16
5.833
5.817
5.813
5.800
5.797
5.783
5.767
5.763
5.747
4.859
4.855
4.829
4.825
4.821
4.818
4.809
4.803
7.270
1.763
1.758
1.754
1.749
1.745
1.738
1.731
1.728
1.725
1.720
1.706
1.692
1.608
1.600
1.595
1.585
1.579
1.570
1.562
1.559
1.553
1.539
1.535
1.528
1.526
1.518
1.510
1.504
1.497
1.494
1.489
1.486
1.480
1.305
1.295
1.292
1.287
1.282
1.276
1.271
1.267
1.257
1.087
1.080
1.074
1.071
1.067
1.063
1.059
1.055
1.050
1.046
1.042
0.905
0.891
0.877
0.542
0.532
0.525
0.517
0.507
0.077
0.068
0.039
0.035
0.029
0.016
0.003
-0.015
-0.022
-0.029
9
8
7
6
5
4
3
2
1
-0
ppm
0.96
2.00
3.07
2.79
0.48
2.03
2.05
5.57

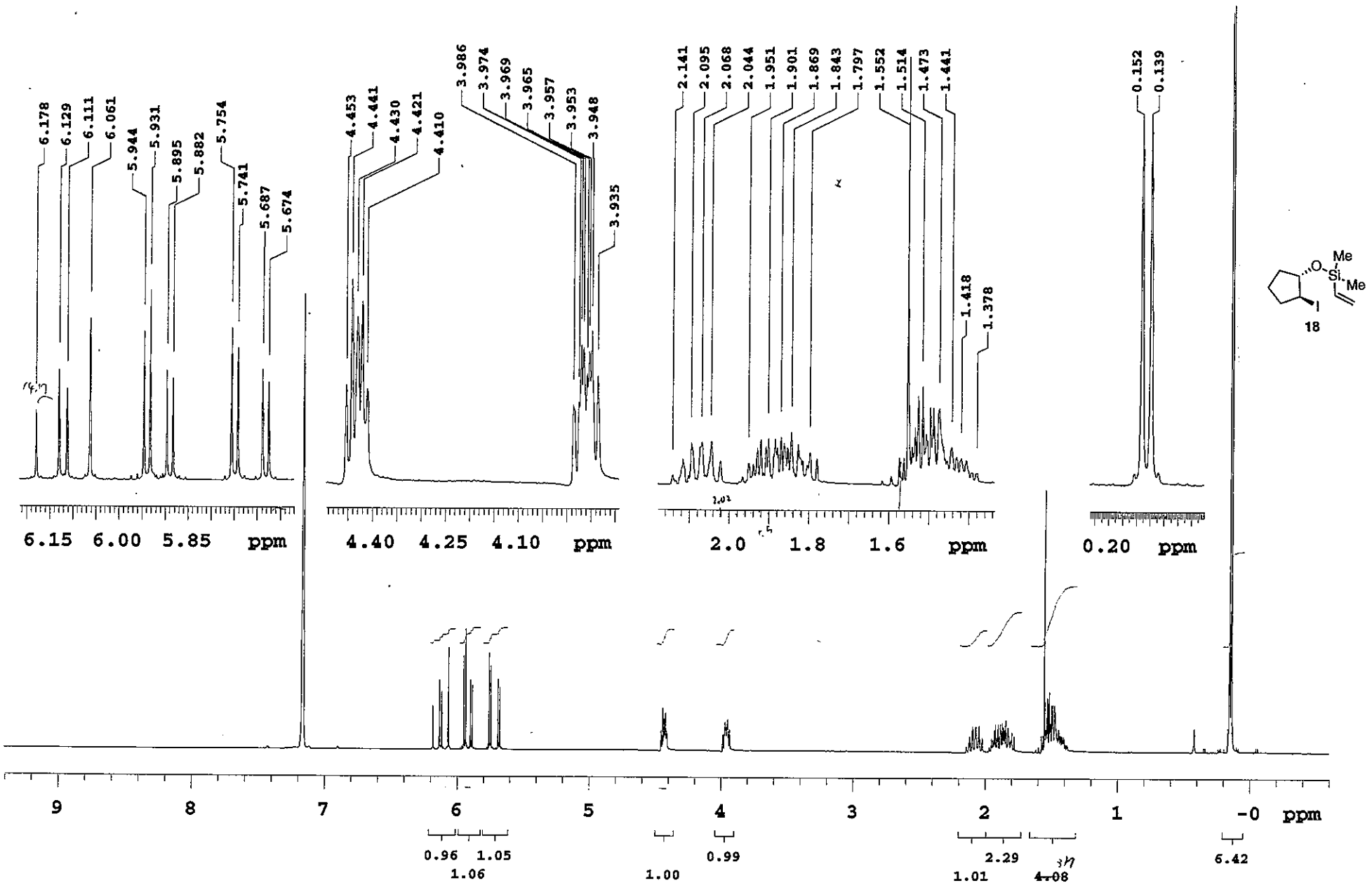

77.486
77.230
76.978
16
Si
135.590
112.694
43.591
32.565
30.217
25.490
23.444
13.934
-3.594
180
160
140
120
100
80
60
40
20
0
ppm

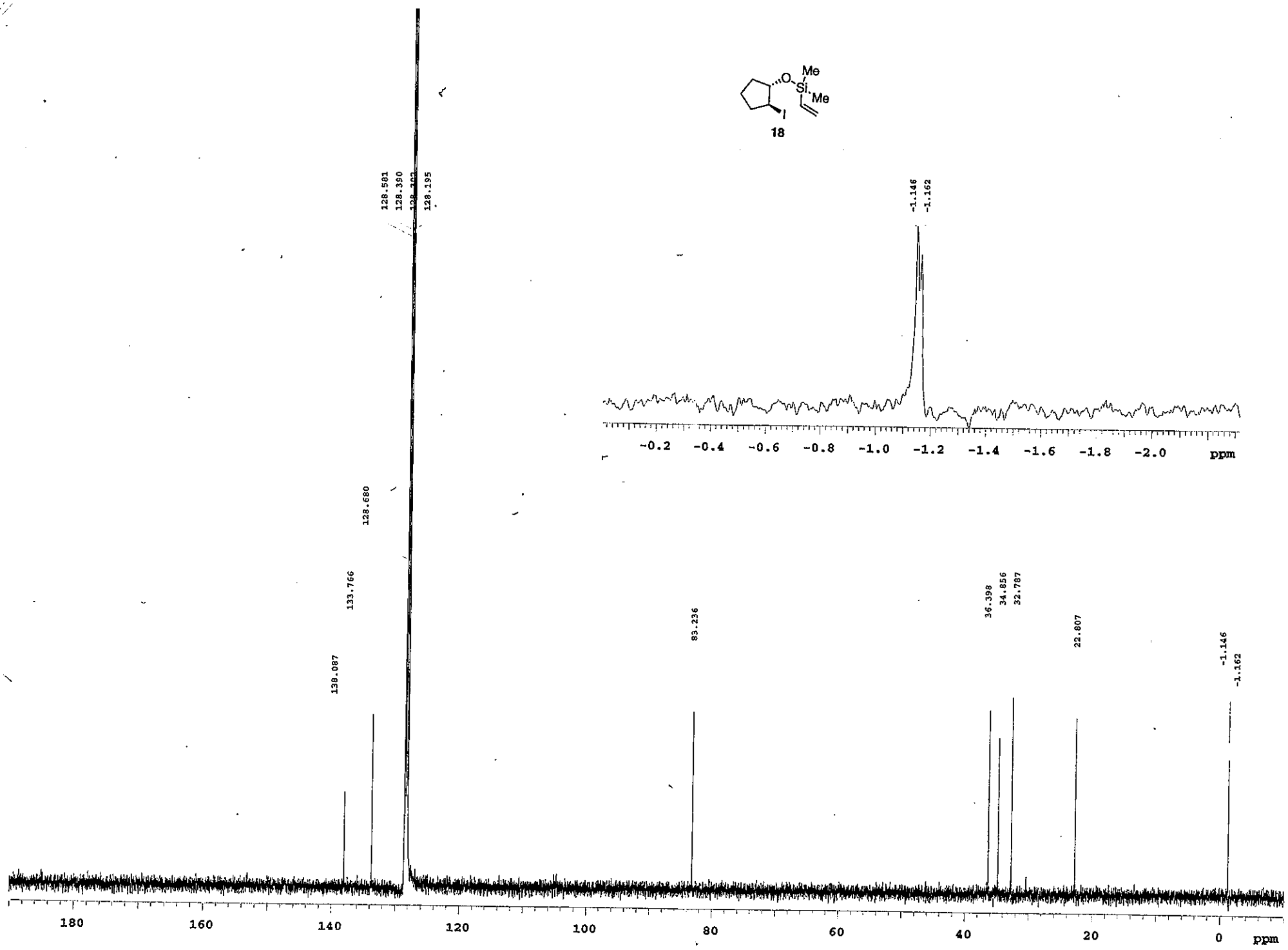

Ts
N
SiMe2Ph
17
7.715
7.712
7.702
7.699
7.695
7.468
7.464
7.462
7.459
7.456
7.454
7.452
7.449
7.373
7.370
7.365
7.362
7.356
7.355
7.354
7.351
7.342
7.326
7.310
7.270
3.433
3.418
3.413
3.398
3.325
3.316
3.313
3.308
3.305
3.296
3.289
3.202
3.187
3.182
3.170
3.168
3.165
2.792
2.777
2.773
2.757
2.445
2.436
1.953
1.938
1.925
1.904
1.888
1.704
1.374
1.358
1.350
1.333
1.238
1.236
1.229
1.225
1.221
1.218
1.215
1.211
1.204
1.201
0.674
0.664
0.658
0.653
0.644
0.640
0.634
0.623
0.228
0.222
0.215
9
8
7
6
5
4
3
2
1
-0
ppm
2.10
5.06
2.01
1.15
1.05
1.06
1.04
3.26
2.10
2.14
1.06
2.06
6.00

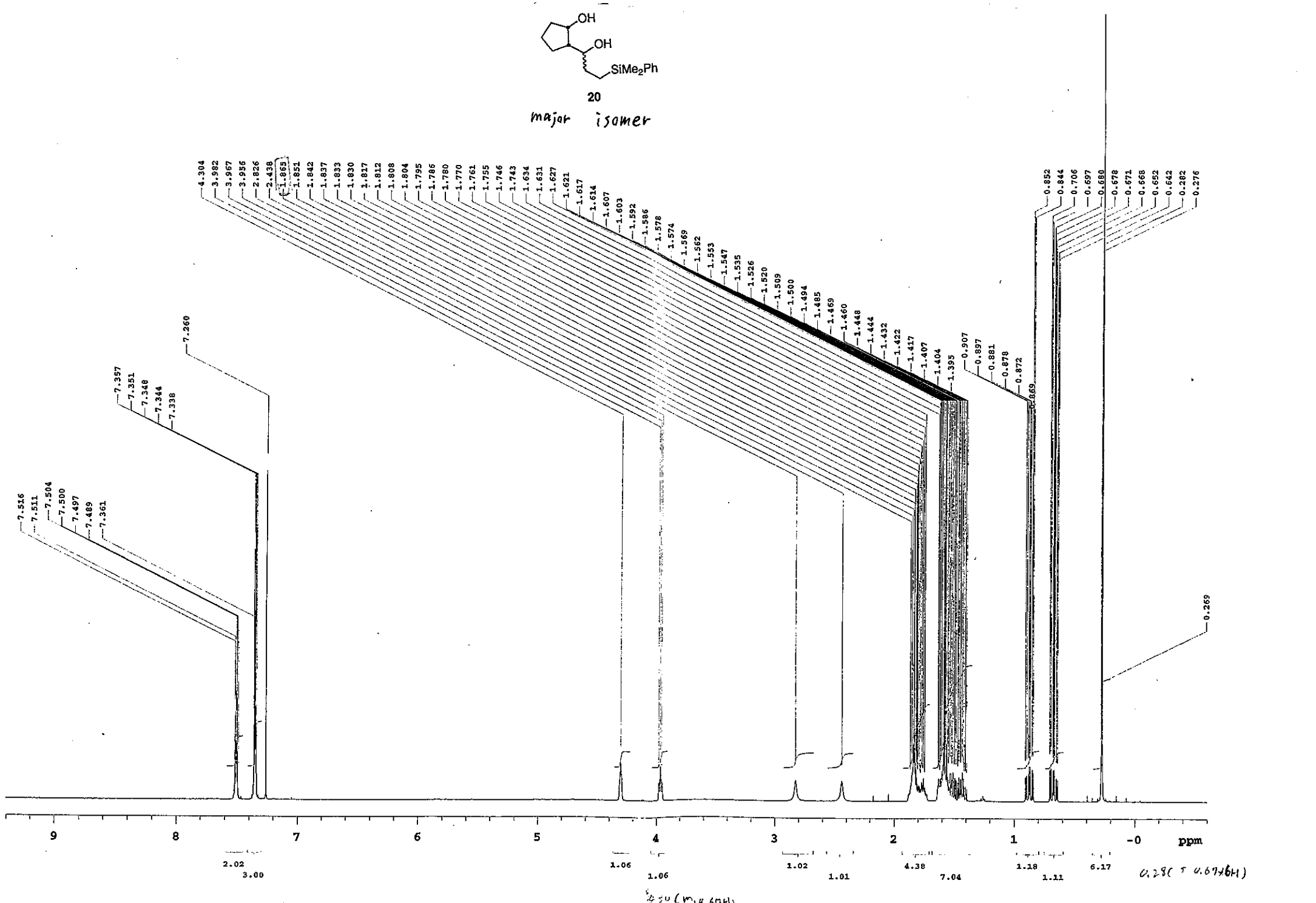

Ts
N
SiMe2Ph

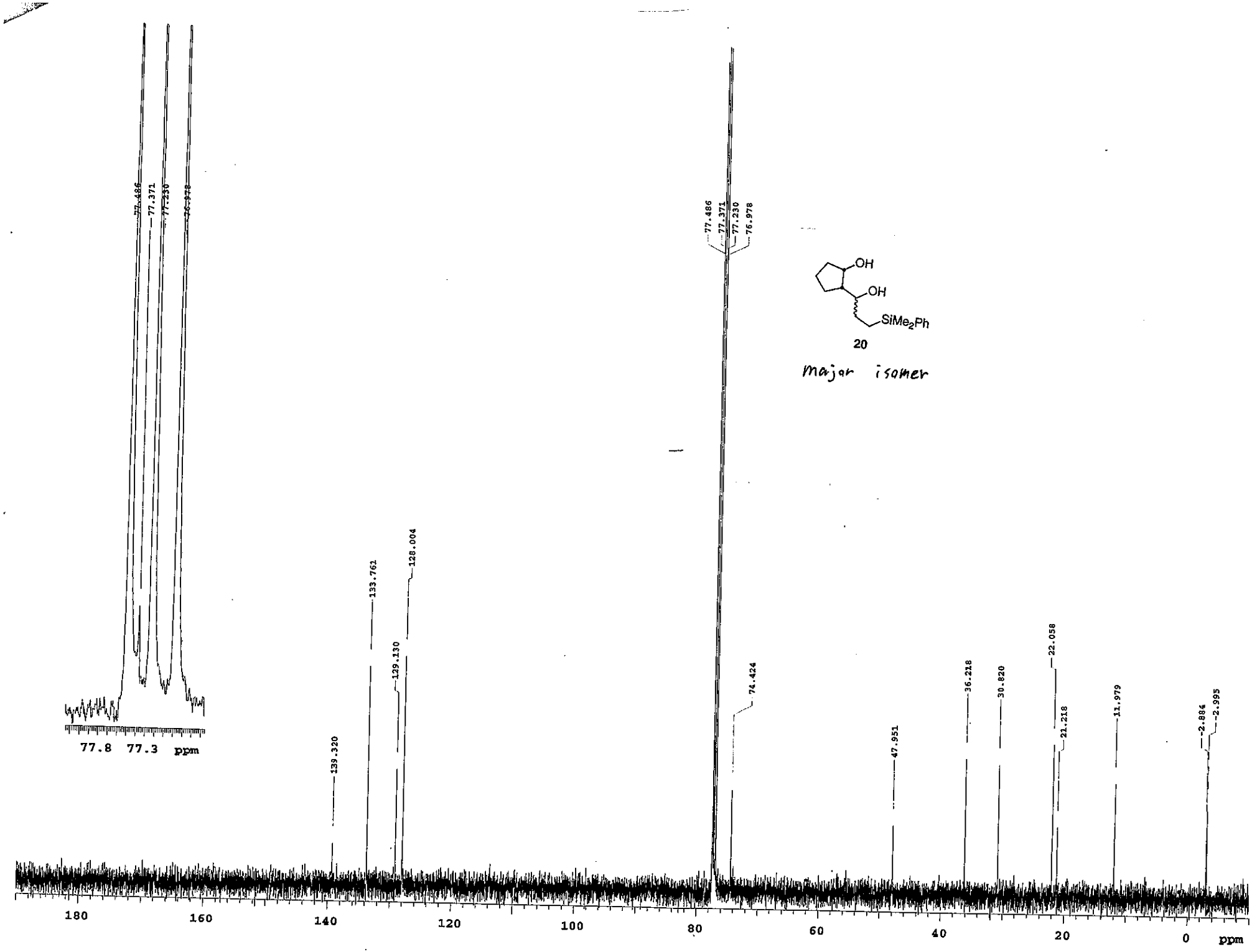
17

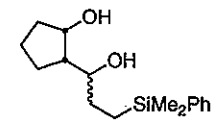

143.436
138.961
133.624
129.768
129.145
127.966
127.683
77.482
77.230
76.974
53.219
47.768
42.052
31.133
27.453
21.699
14.315
-3.079
-3.136
180
160
140
120
100
80
60
40
20
0
ppm


6.178
6.129
6.111
6.061
5.944
5.931
5.895
5.882
5.754
5.741
5.687
5.674
6.15 6.00 5.85 ppm
4.453
4.441
4.430
4.421
4.410
3.986
3.974
3.969
3.965
3.957
3.953
3.948
3.935
4.40 4.25 4.10 ppm
2.141
2.095
2.068
2.044
1.951
1.901
1.869
1.843
1.797
1.552
1.514
1.473
1.441
1.418
1.378
2.0 1.8 1.6 ppm
0.152
0.139
0.20 ppm
Me
Si
Me
O
I
18
9 8 7 6 5 4 3 2 1 -0 ppm
0.96 1.05
1.06
1.00
0.99
2.29
1.01
4.08
6.42


Me
O
Si
Me
I
18
-1.146
-1.162
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
ppm
128.581
128.390
128.302
128.195
128.680
133.766
138.087
83.236
36.398
34.856
32.787
22.807
-1.146
-1.162
180
160
140
120
100
80
60
40
20
0
ppm

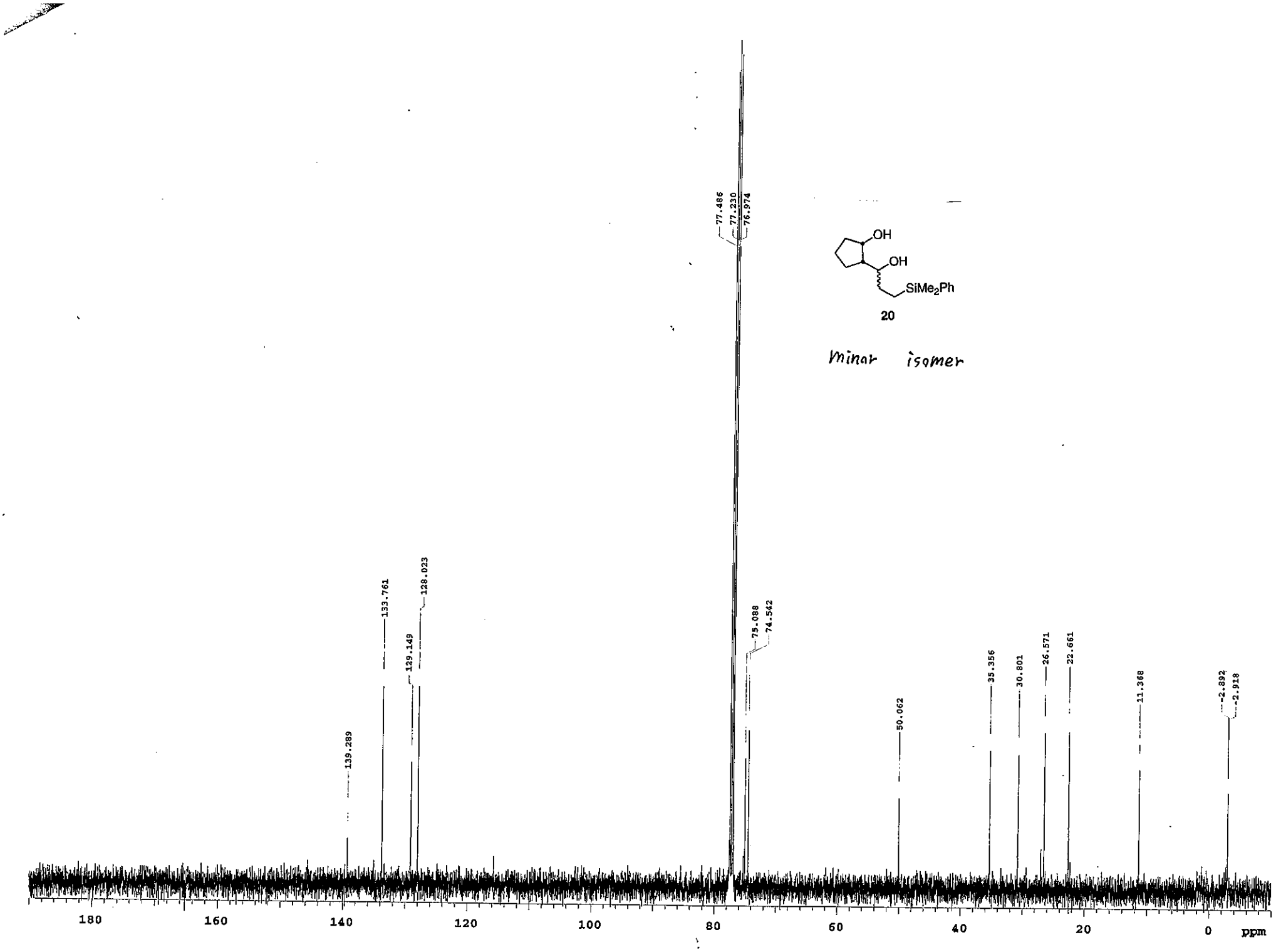

OH
OH
SiMe2Ph
20
major isomer
4.304
3.982
3.967
3.956
2.826
2.438
1.865
1.851
1.842
1.837
1.833
1.830
1.817
1.812
1.808
1.804
1.795
1.786
1.780
1.770
1.761
1.755
1.746
1.743
1.634
1.631
1.627
1.621
1.617
1.614
1.607
1.603
1.592
1.586
1.578
1.574
1.569
1.562
1.553
1.547
1.535
1.526
1.520
1.509
1.500
1.494
1.485
1.469
1.460
1.448
1.444
1.432
1.422
1.417
1.407
1.404
1.395
0.907
0.897
0.881
0.878
0.872
0.852
0.844
0.706
0.697
0.680
0.678
0.671
0.668
0.652
0.642
0.282
0.276
0.269
7.516
7.511
7.504
7.500
7.497
7.489
7.361
7.357
7.351
7.348
7.344
7.338
7.260
9
8
7
6
5
4
3
2
1
-0
ppm
2.02
3.00
1.06
1.06
1.02
1.01
4.38
7.04
1.18
1.11
6.17


77.486
77.371
77.230
76.978
77.8 77.3 ppm
139.320
133.762
129.130
128.004
74.424
47.951
36.218
30.820
22.058
21.218
11.979
-2.884
-2.995
OH
OH
SiMe2Ph
20
major isomer
180
160
140
120
100
80
60
40
20
0
ppm



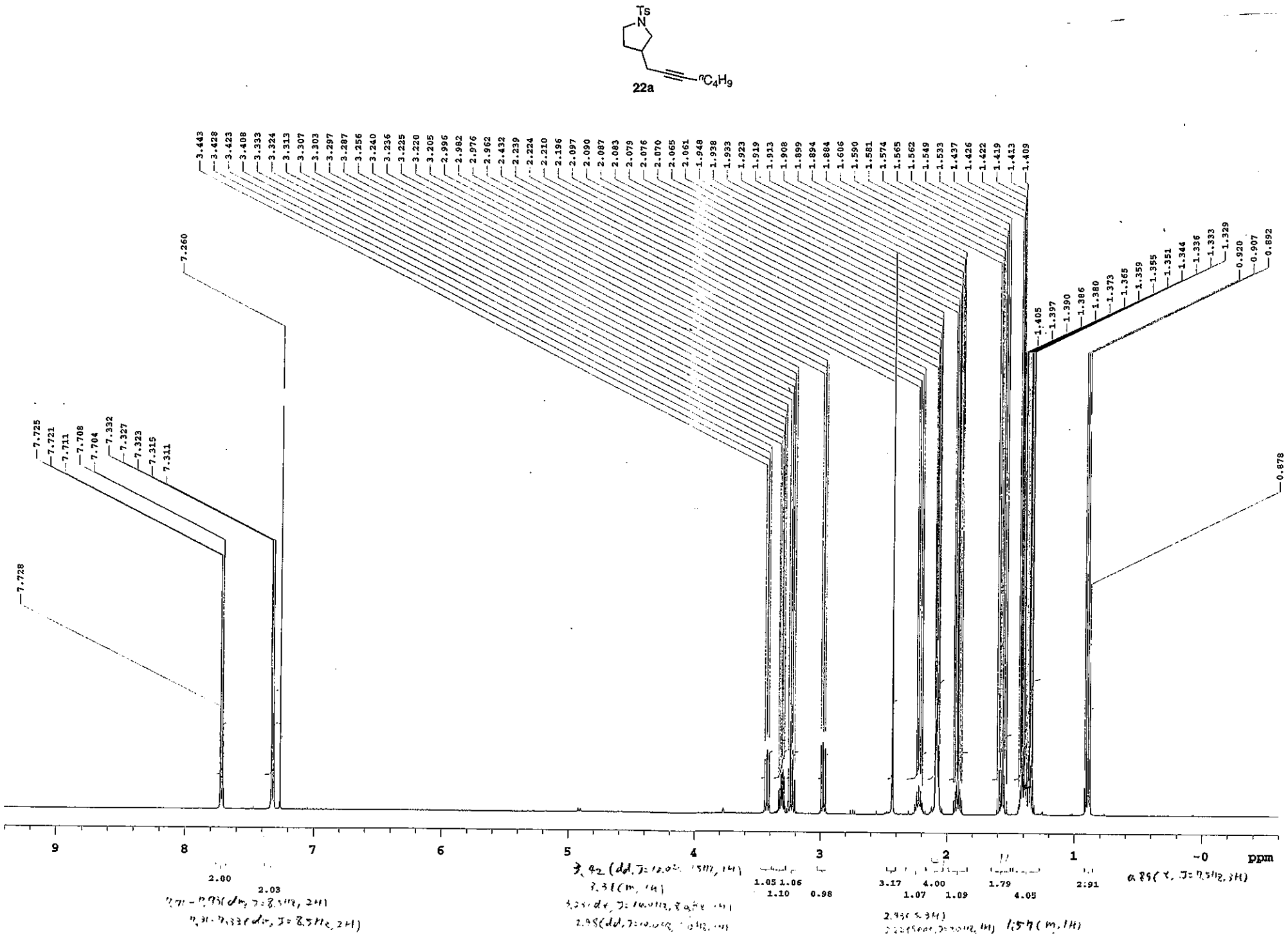
20

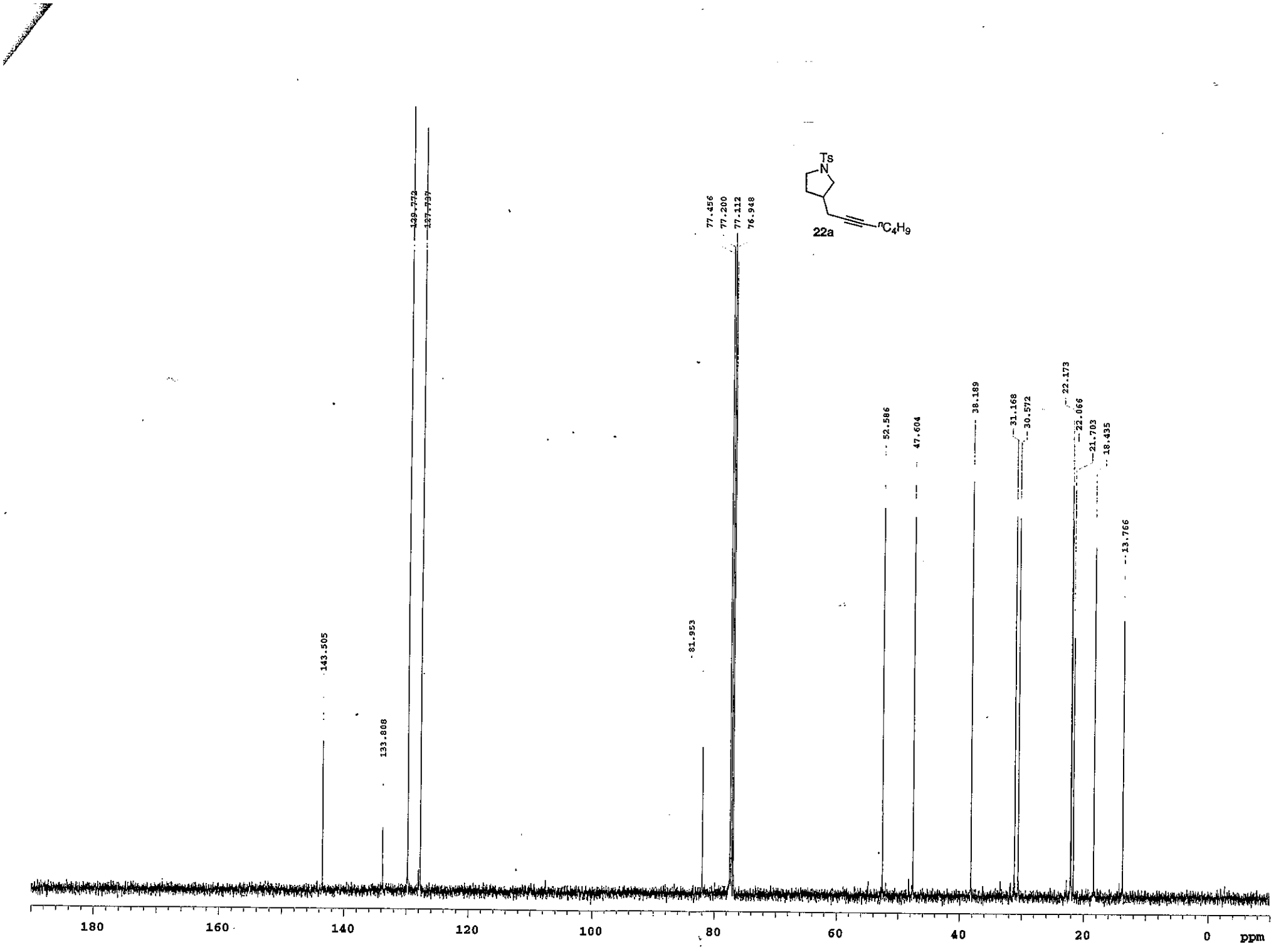
minor isomer

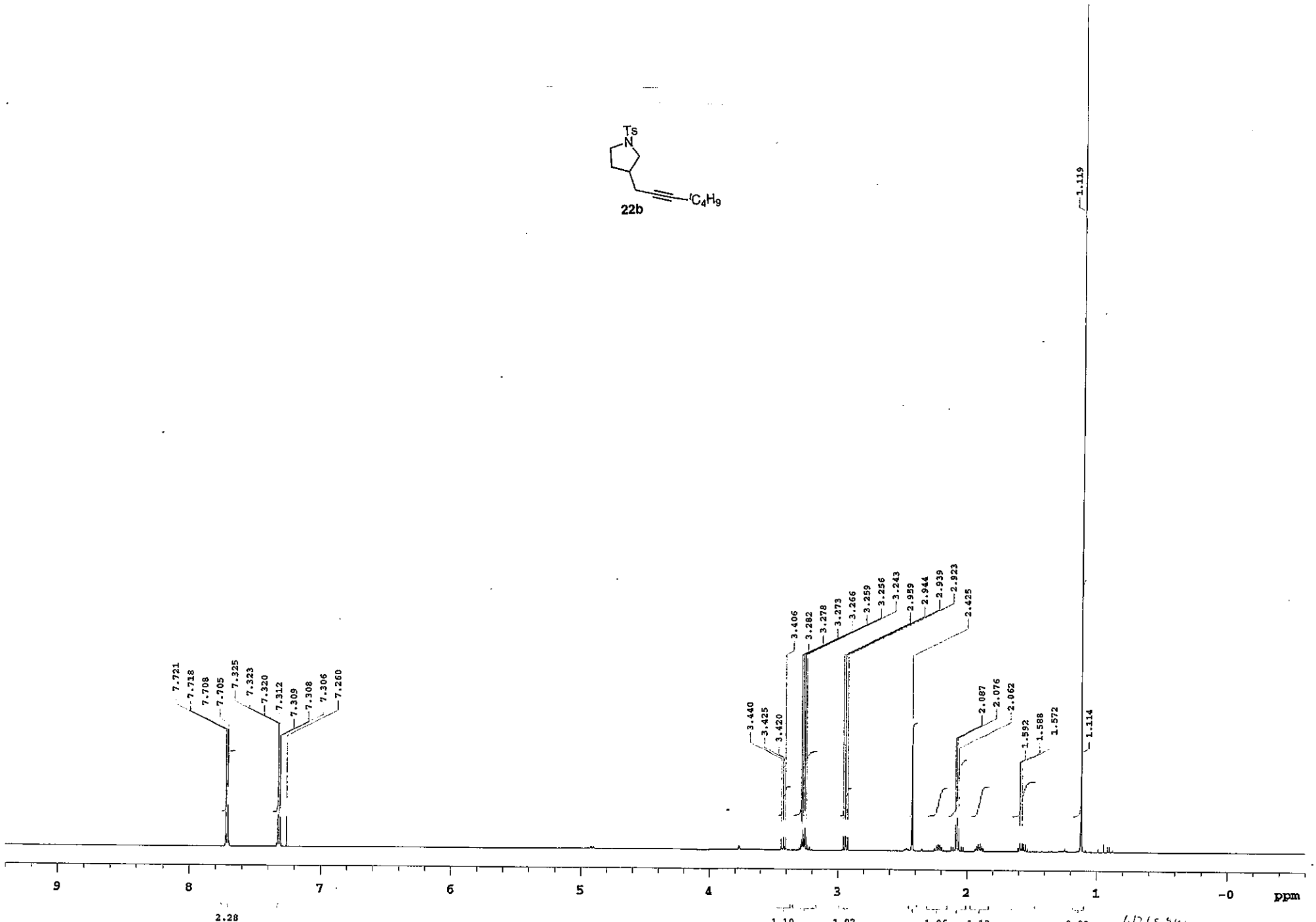


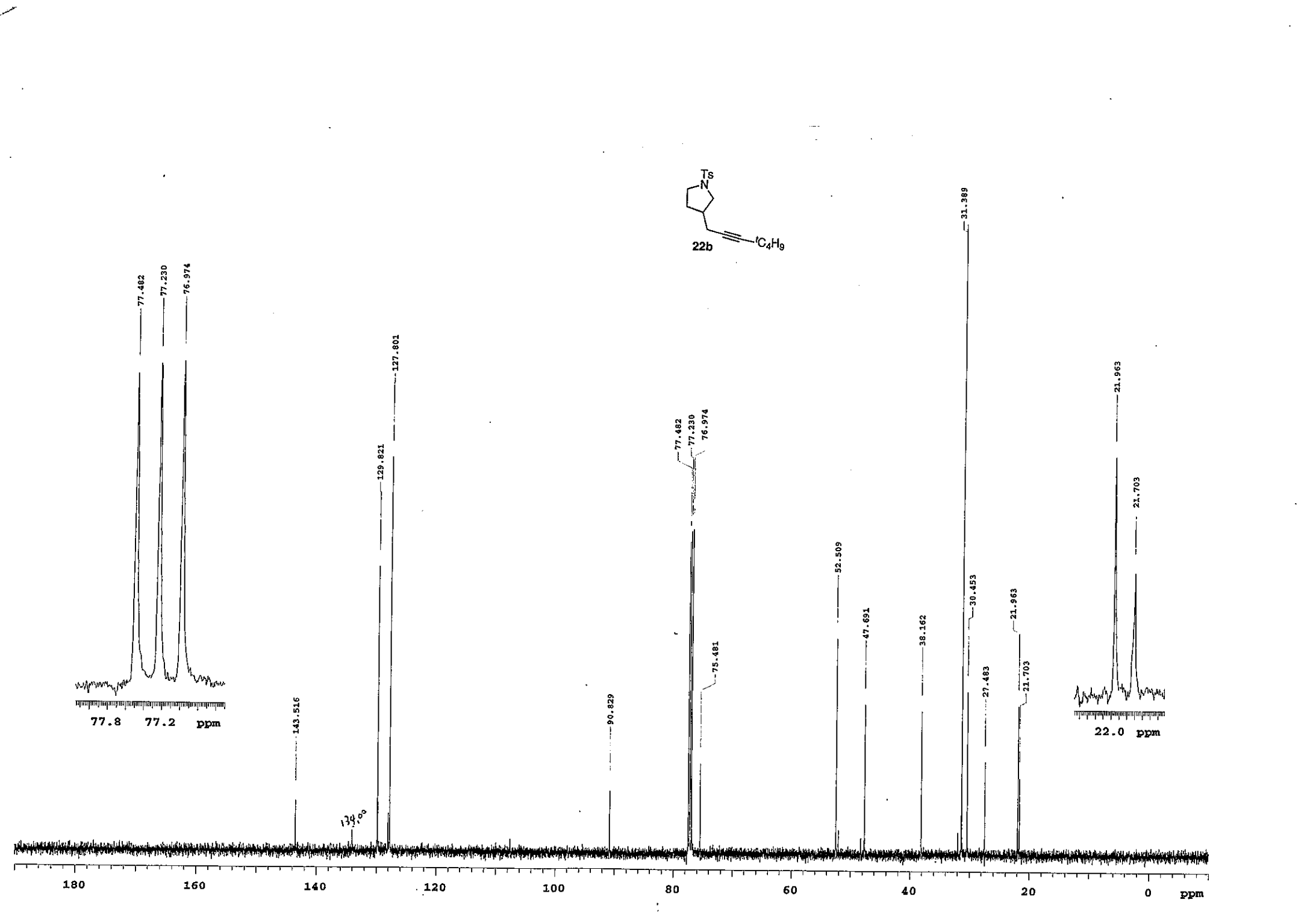
20

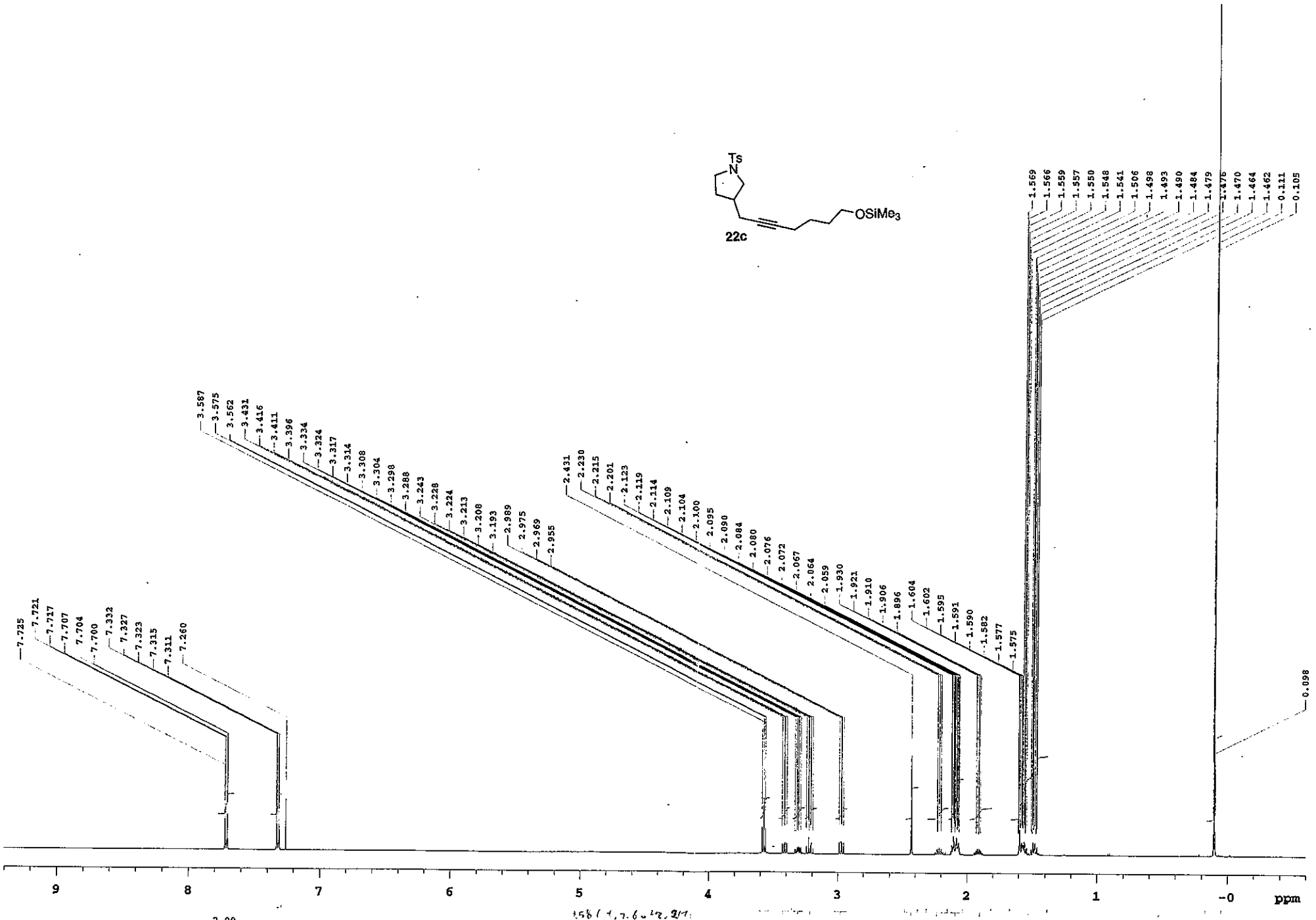
minor isomer

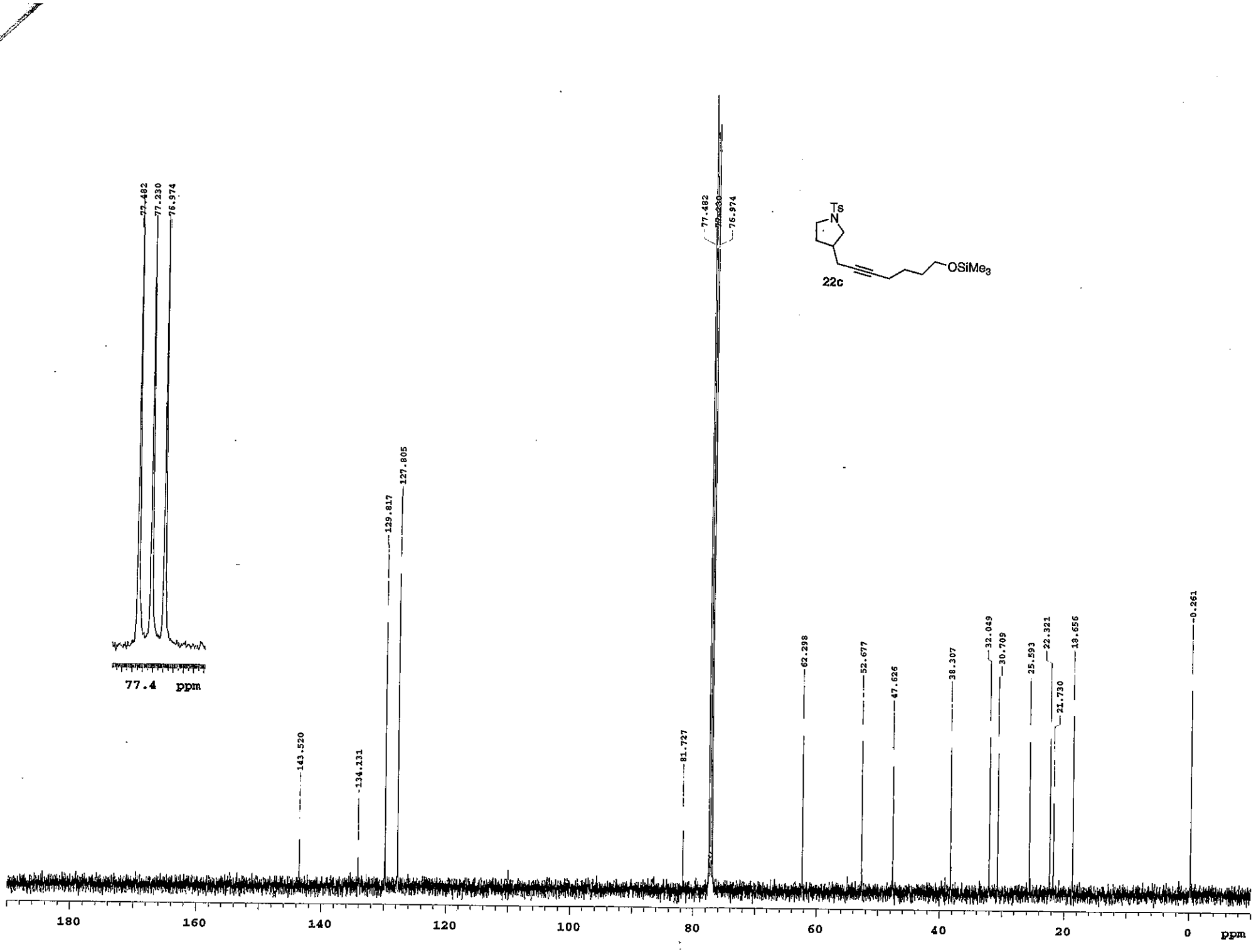

Ts
N
$^nC_4H_9$
22a
7.728
7.725
7.721
7.711
7.708
7.704
7.332
7.327
7.323
7.315
7.311
7.260
3.443
3.428
3.423
3.408
3.333
3.324
3.313
3.307
3.303
3.297
3.287
3.256
3.240
3.236
3.225
3.220
3.205
2.996
2.982
2.976
2.962
2.432
2.239
2.224
2.210
2.196
2.097
2.090
2.087
2.083
2.079
2.076
2.070
2.065
2.061
1.948
1.938
1.933
1.923
1.919
1.913
1.908
1.899
1.894
1.884
1.606
1.590
1.581
1.574
1.565
1.562
1.549
1.533
1.437
1.426
1.422
1.419
1.413
1.409
1.405
1.397
1.390
1.386
1.380
1.373
1.365
1.359
1.355
1.351
1.344
1.336
1.333
1.329
0.920
0.907
0.892
0.878
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.03
1.05 1.06
1.10
0.98
3.17
4.00
1.07
1.09
1.79
4.05
2.91

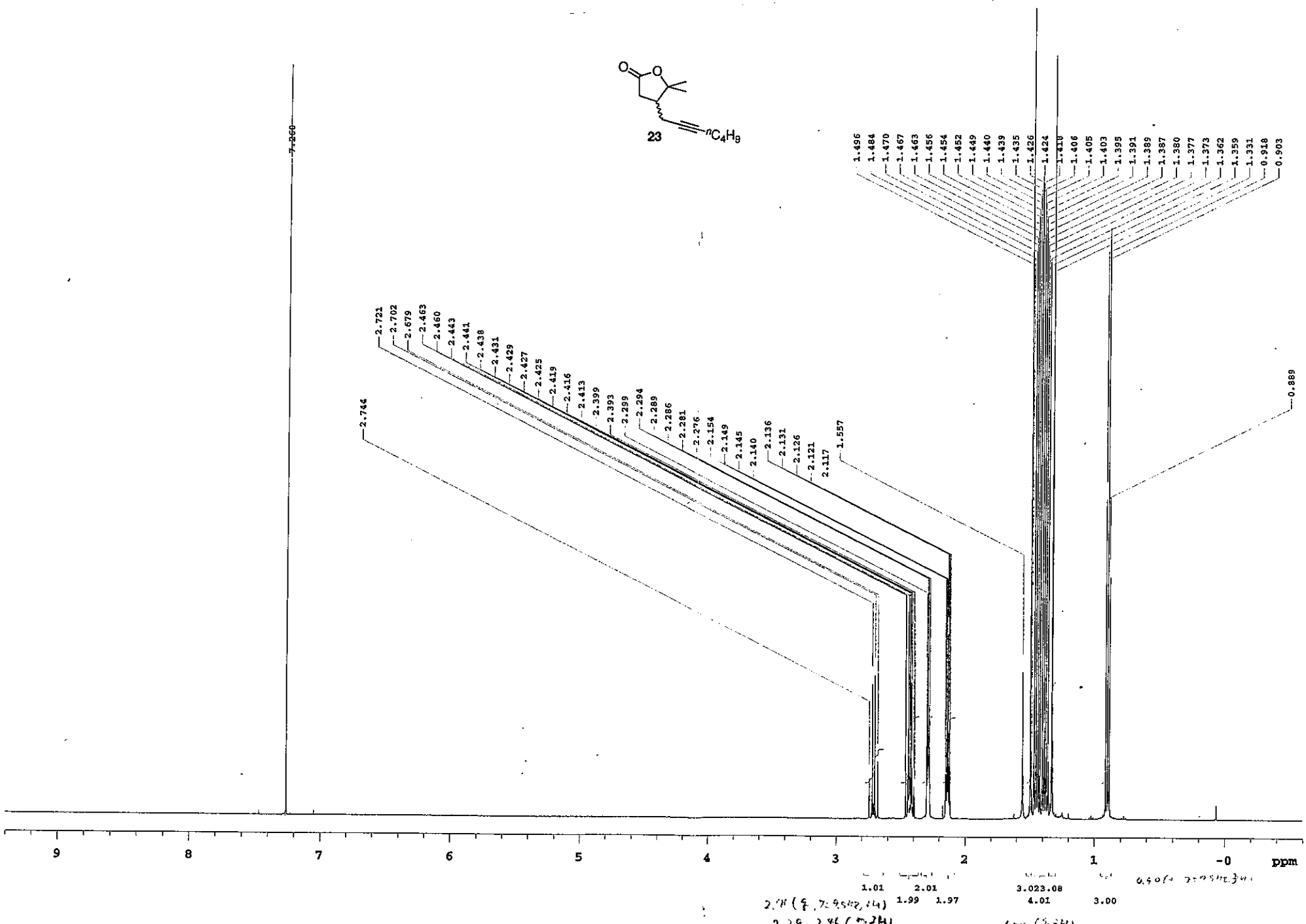

Ts
N
$^{n}C_4H_9$
22a
143.505
133.808
129.772
127.939
81.953
77.456
77.200
77.112
76.948
52.586
47.604
38.189
31.168
30.572
22.173
22.066
21.703
18.435
13.766
180
160
140
120
100
80
60
40
20
0
ppm

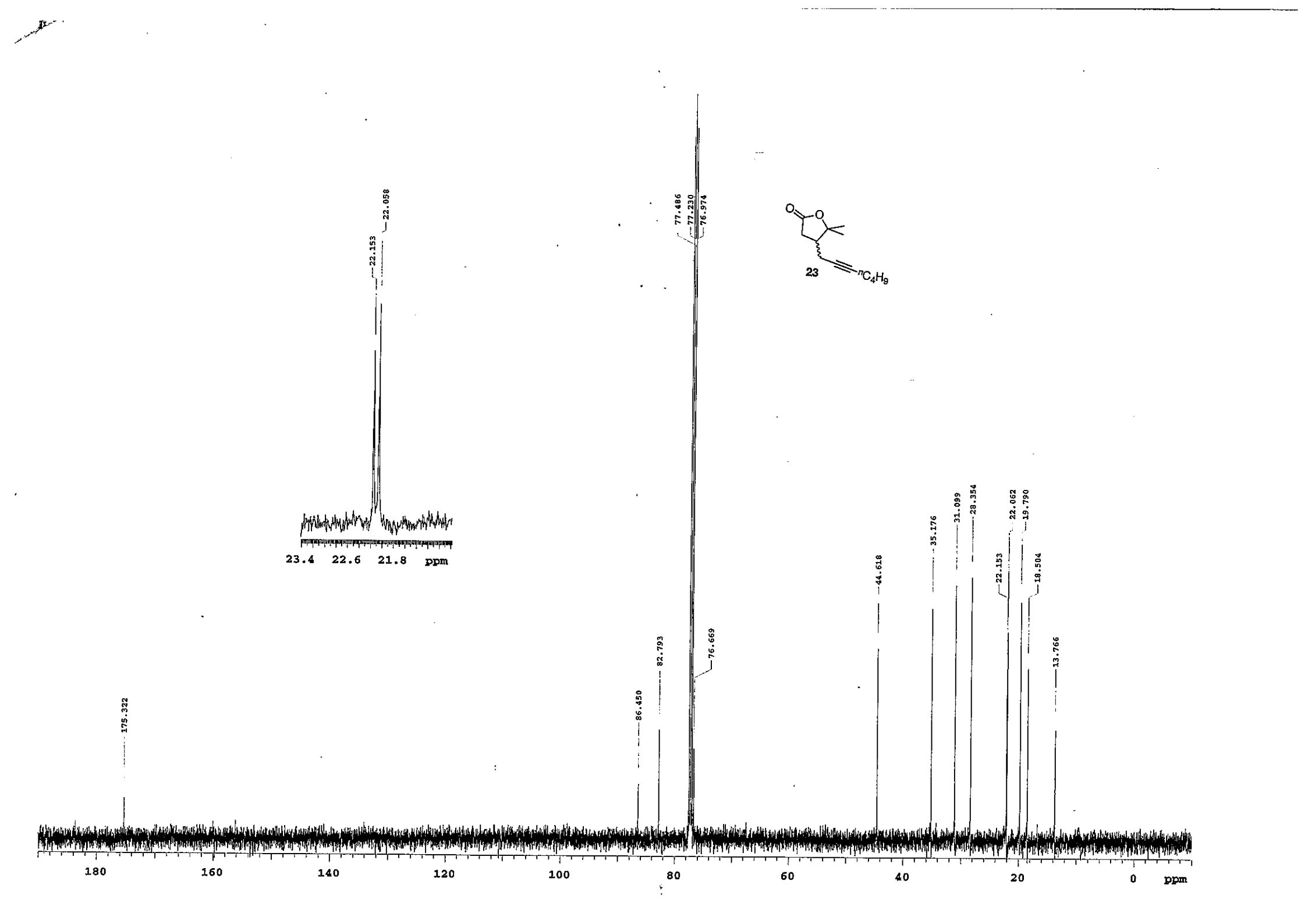

Ts
N
$^tC_4H_9$
22b
7.721
7.718
7.708
7.705
7.325
7.323
7.320
7.312
7.309
7.308
7.306
7.260
3.440
3.425
3.420
3.406
3.282
3.278
3.273
3.266
3.259
3.256
3.243
2.959
2.944
2.939
2.923
2.425
2.087
2.076
2.062
1.592
1.588
1.572
1.119
1.114
9
8
7
6
5
4
3
2
1
-0
ppm
2.28
1.10
2.43
1.02
3.54
1.06
2.13
1.13
1.32
9.00


Ts
N
22b
$^tC_4H_9$
77.482
77.230
76.974
143.516
139.00
129.821
127.801
90.829
77.482
77.230
76.974
75.481
52.509
47.691
38.162
31.389
30.453
27.483
21.963
21.703
77.8
77.2
ppm
21.963
21.703
22.0
ppm
180
160
140
120
100
80
60
40
20
0
ppm


Ts
N
OSiMe3
22c
7.725
7.721
7.717
7.707
7.704
7.700
7.332
7.327
7.323
7.315
7.311
7.260
3.587
3.575
3.562
3.431
3.416
3.411
3.396
3.334
3.324
3.317
3.314
3.308
3.304
3.298
3.288
3.243
3.228
3.224
3.213
3.208
3.193
2.989
2.975
2.969
2.955
2.431
2.230
2.215
2.201
2.123
2.119
2.114
2.109
2.104
2.100
2.095
2.090
2.084
2.080
2.076
2.072
2.067
2.064
2.059
1.930
1.921
1.910
1.906
1.896
1.604
1.602
1.595
1.591
1.590
1.582
1.577
1.575
1.569
1.566
1.559
1.557
1.550
1.548
1.541
1.506
1.498
1.493
1.490
1.484
1.479
1.476
1.470
1.464
1.462
0.111
0.105
0.098
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
2.03
1.09
1.00
1.06
1.04
1.13
1.10
3.16
4.02
6.24
8.44


77.482
77.230
76.974
77.4 ppm
143.520
134.131
129.817
127.805
81.727
62.298
52.677
47.626
38.307
32.049
30.709
25.593
22.321
21.730
18.656
-0.261
Ts
N
OSiMe3
22c
180
160
140
120
100
80
60
40
20
0
ppm


23
nC4H9
7.260
2.744
2.721
2.702
2.679
2.463
2.460
2.443
2.441
2.438
2.431
2.429
2.427
2.425
2.419
2.416
2.413
2.399
2.393
2.299
2.294
2.289
2.286
2.281
2.276
2.154
2.149
2.145
2.140
2.136
2.131
2.126
2.121
2.117
1.557
1.496
1.484
1.470
1.467
1.463
1.456
1.454
1.452
1.449
1.440
1.439
1.435
1.426
1.424
1.418
1.406
1.405
1.403
1.395
1.391
1.389
1.387
1.380
1.377
1.373
1.362
1.359
1.331
0.918
0.903
0.889
9
8
7
6
5
4
3
2
1
-0
ppm
1.01
2.01
3.023.08
1.99
1.97
4.01
3.00


175.322
86.450
82.793
77.486
77.230
76.974
76.669
44.618
35.176
31.099
28.354
22.153
22.062
19.790
18.504
13.766
22.153
22.058
23.4
22.6
21.8
ppm
23
$^{n}C_4H_9$
180
160
140
120
100
80
60
40
20
0
ppm