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SUPPORTING INFORMATION

Title: Utilization of the Versatility of Sulfur in C–C Bond Formation and Cleavage: Synthesis of ABC Taxoid Skeletons
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1. Experimental Section:

Starting materials were obtained from commercial sources or prepared using known procedures. All solvents were distilled before use. Petroleum ether refers to the fraction boiling in the range of 60-80 °C. Solvents for anhydrous reaction were prepared according to the standard procedures. TLC analysis was carried out using thin layer plates pre-coated with silica gel 60 F254 (Merck) and visualized by fluorescence quenching or Iodine or by charring after treatment with p-anisaldehyde. In cases where chromatographic purification was done, silica gel (60-120 mesh) was used as the stationary phase or otherwise as stated. IR spectra were recorded on Perkin-Elmer Infrared Spectrophotometer Model 68B or on Perkin-Elmer 1615 FT Infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AC-200 (50 MHz) or Bruker MSL-300 (75 MHz) or Bruker AV-400 (100 MHz) or Bruker DRX-500 (125 MHz). Figures in parentheses refer to ^{13}C frequencies. Tetramethyl silane was used as the internal standard. GCMS were recorded on Shimadzu's GCMS-QP5050-A. Mass spectra were recorded at ionization energy 70eV on Finnigan MAT-1020, automated GC/MS instrument and on API Q STARPULSAR using electron spray ionization [(ESI), solvent medium, a mixture of water, acetonitrile and ammonium acetate] technique and mass values are expressed as m/z.

1. Preparation of 2-(methylsulfinyl)-1-(2,2,4-trimethylcyclohex-3-enyl)ethanone (8): Dimethyl sulfoxide (0.7 mL, 10 mmol) was dissolved in 10 mL of THF in an argon-purged flask, and sodium hydride (0.395 g, 8.24 mmol) as 50 % dispersion in mineral oil, was added all at once. The reaction mixture was refluxed for 2 h at 65 °C, and then cooled to 0 °C. A solution of methyl 2,2,4-trimethylcyclohex-3-enecarboxylate **7** (1 g, 5.5 mmol) in THF (20 mL) was added slowly to above prepared grey coloured sodium dimsyl solution over period of 1 h and left over night at room temperature. The reaction mixture was poured on a mixture of 10 M hydrochloric acid (10 mL) and ice, organic layer was separated and aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed dilute sodium bicarbonate solution and then with brine solution, dried over

anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by the column chromatography (silica gel, 2-5 % methanol/dichloromethane, gradient elution), which provided **8** as a gummy oil (0.870 g, 70 %). R_f=0.3 (MeOH/CH_2Cl_2 1:9); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 5.05 (s, 1H), 4.10 (d, *J* = 15 Hz, 1H), 3.85 (d, *J* = 15 Hz, 1H), 2.76 (s, Me), 2.74 (s, Me), 2.75-2.55 (m, 1H), 2.15-1.70 (m, 2H), 1.63 (s, 3H), 1.15 (s, Me), 1.10 (s, Me), 1.10 (m, 1H), 0.98 (s, 3H), 0.98 (s, 3H) ppm.; ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 206.3, 131.5, 130.6, 65.9, 65.3, 57.1, 38.6, 38.2, 34.6, 29.9, 28.6, 24.2, 22.8, 21.2 ppm; IR (neat): $\tilde{\nu}$=1704 (C=O), 1030 (S=O) cm^{-1}.

2. Preparation of bicyclic unit (5): Trifluoroacetic anhydride (5.45 mL, 39.0 mmol) was added at once to a stirred solution of β-ketosulfoxide **8** (7.500 g, 32.0 mmol) in anhydrous dichloromethane (300 mL) at room temperature under an atmosphere of argon. The reaction mixture was refluxed, after consumption of starting material as indicated by TLC analysis (3 h) it was quenched with slow addition of aqueous saturated sodium bicarbonate solution (50 mL) at 0 °C. The organic layer was separated and aqueous layer was extracted with dichloromethane (3 × 25 mL), combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by flash column chromatography (230-400 mesh size silica gel, 0.5-1.0 % EtOAc/pet. ether gradient elution) afforded fraction-A: R_f=0.50 (EtOAc/pet. ether, 2:8) and fraction-B: R_f=0.45 (EtOAc/pet. ether, 2:8) of **5** respectively. Fraction-A: Yield: 2 g (30%); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 5.17 (s, 1H), 2.9 (s, 1H), 2.35 & 2.40 (s, 3H), 2.40-2.00 (m, 3H), 1.75 (s, 3H), 1.25 and 1.20 (s, 3H), 1.06 and 1.05 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 219.3 (q), 218.8 (q), 147.9 (q), 141.5 (q), 117.2 (s), 108.8 (d), 96.2 (q), 58.1 (s), 55.7 (s), 55.1 (s), 37.0 (q), 28.9 (d), 28.6 (t), 22.9 (t), 21.9 (t), 18.5 ppm (t); IR (neat): $\tilde{\nu}$=1735 cm^{-1} (C=O); MS (70 eV, EI): *m/z*: 210 [M^+], 195, 164, 154, 135, 122, 107, 91, 77. Fraction-B: Yield: 2.0 g (30 %); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 4.84 (m, 1H), 4.74 (m, 1H), 3.57 (m, 2H), 2.29 and 2.27 (s, 3H), 2.25-2.00 (m,

2H), 1.80-1.60 (m, 2H), 1.11 (s, 3H), 1.07 (s, 3H), 1.02 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 218.4 (q), 217.7 (q), 144.1 (q), 137.4 (q), 117.9 (s), 111.4 (d), 57.9 (s), 55.6 (s), 54.9 (s), 53.4 (s), 52.4 (s), 50.7 (s), 37.7 (q), 36.4 (q), 29.4 (d), 27.0 (t), 26.9 (t), 26.1 (d), 24.4 (t), 21.8 (t), 19.4 (t), 15.3 (t), 15.3 (t), 14.9 ppm (t); IR (neat): $\tilde{\nu}$=1735 cm^{-1} (C=O); MS (70 eV, EI): *m/z*: 210 [M$^+$], 195, 164, 154, 135, 122, 107, 91, 77.1.

3. Preparation of 10: The ketosulfide (**5**) (2 g, 9.523 mmol) in THF (20 mL) was to added slowly over a period of 15 min to stirred a solution of NaH (50% dispersion in oil) (0.548 g, 11.4 mmol) in THF (25 mL) at 0 °C under argon atmosphere. The reaction mixture became dark brown in colour after 1 h. 1-(Bromomethyl)-2-iodobenzene **9** (4.242 g, 14.28 mmol) in THF was added slowly (25 min) to sodium enolate and reaction mixture stirred for 3 h at 0 °C and was then left overnight. The reaction was poured in cold dilute hydrochloric acid solution, organic layer was separated, aqueous layer was extracted with ethyl acetate (3 × 25 mL), combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by flash column chromatography (230-400 mesh size silica gel, 0.5-1.0 % EtOAc/pet. ether gradient elution) which provided isomers of **10** as a gummy oil (2.840 g, 70 %). R_f=0.30 (EtOAc/pet. ether 2:8); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 8.04-7.87 (m, aromatics-H), 7.37-7.25 (m, aromatics-H), 6.96-6.66 (m, aromatics-H) 5.36 (s, olefin-H), 4.92 (s, olefin-H), 4.85 (s, olefin-H), 3.54-2.98 (m, benzylic-H), 2.47-2.19 (m, benzylic-H), 1.98 (s, Me), 1.62 and 1.60 (s, Me), 1.43 and 1.40 (s, Me), 1.16 (s, Me), 0.99 ppm (s, Me); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 219.1, 216.5, 146.4, 140.8, 139.9, 139.6, 139.3, 130.4, 129.5, 128.5, 128.1, 127.6, 122.7, 120.4, 112.7, 103.3, 59.7, 59.5, 57.9, 56.0, 55.5, 54.5, 43.4, 42.7, 38.6, 38.0, 31.3, 30.9, 29.7, 27.2, 26.9, 26.2, 24.1, 23.6, 23.3, 13.9, 12.4 ppm ; IR (neat): $\tilde{\nu}$=1735 cm^{-1} (C=O).

4. Preparation of 11: In a two neck 100 mL round bottom flask charged with alkylated compound **10** (0.426 g, 1.0 mmol) and THF (50 mL) was kept at –78 °C under argon atmosphere. nBuLi (1 mL, 1.5

mmol, 1.5 M) was added slowly over a period of 10 min to above stirred solution and the reaction mixture was stirred for 5 h. After completion of the reaction (TLC analysis) it was quenched with saturated aqueous ammonium chloride solution (1 mL), allowed warming to room temperature, organic layer was separated, aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and residue obtained was purified by column chromatography (60-120 mesh size silica gel, 5-15 % EtOAc/pet. ether gradient elution) provided isomers of **11** as a pale yellow solid (0.240 g, 80 %). R_f=0.30 (EtOAc/pet. ether 3:7); m.p. 210-215 °C; ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 7.40-7.00 (m, aromatic-H), 4.79 (m, olefinic-H), 4.64 (m, olefinic-H), 3.9-2.5 (benzylic-H), 2.40-1.75 (m, CH_2), 2.14 and 2.04 (s, SCH_3), 1.71 and 1.65 (s, allylic-CH_3), 1.43 (s), 1.09 (s, CH_3), 0.92 (s, CH_3), 0.68 ppm (s, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 150.8 (q), 150.2 (q), 145.8 (q), 142.0 (q), 141.4 (q), 138.5 (q), 128.7 (d), 127.9 (s), 126.8 (s), 125.2 (s), 124.5 (s), 124.3 (s), 119.7 (s), 110.3 (d), 99.0 (q), 92.3 (q), 77.4 (q), 70.8 (q), 66.4 (s), 66.3 (s), 54.3 (s), 48.9 (d), 44.0 (q), 43.8 (d), 41.8 (q), 30.9 (d), 29.7 (d), 27.9 (t), 27.5 (t), 27.0 (t), 26.0 (t), 25.3 (t), 23.1 (d), 14.2 (q), 13.2 ppm (q); IR ($CHCl_3$): $\tilde{\nu}$=3400 cm^{-1} (O–H); MS (70 eV, EI): *m/z*: 331 [M^++1], 284, 183, 277, 181; elemental analysis calcd (%) for $C_{19}H_{24}OS$ (330): C 75.95, H 8.05, O 5.32, S 10.67; found: C 76.07, H 7.43, S 10.99.

5. Preparation of 12: A 100 mL two-neck RB flask was charged with Lead tetraacetate (0.886 g, 2.0 mmol) along with glacial acetic acid (5 mL) and toluene (20 mL) under argon atmosphere. The mixture was cooled to 0 ^{o}C and β-hydroxy sulfide **11** (0.300 g, 1.0 mmol) in toluene was added slowly and reaction mixture was stirred at 0 °C for 6 h. The reaction was quenched with saturated aqueous ammonium chloride solution (10 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate until neutralization and then with brine solution, dried over anhydrous Na_2SO_4, filtered,

concentrated *in vacuo*, and the residue obtained was purified by column chromatography (silica gel, 5 % EtOAc/pet. ether gradient elution), which provided 1:1 mixture of **12** as a colourless solid (0.223 g, 75 %). R_f=0.35 (EtOAc/pet. ether 3:7); m.p. 150-152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, TMS): δ= 7.35-6.91 (m, 4H, aromatic-H), 6.03 (s, 0.5H), 5.91 (s, 0.5H), 4.83 (m, 0.5H), 4.73 (s, 0.5H), 2.81 (s, 0.5H), 2.60-2.30 (m, 1H), 2.31 (s, 1.5H), 2.29 (s, 1.5H), 2.25-1.50 (m, 1H), 1.44 (s, 1.5H), 1.23 (s, 1.5H), 1.19 (s, 1.5H), 1.14 (s, 1.5H), 1.13 ppm (s, 1.5H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, TMS): δ= 213 (q), 145.5 (q), 142.2 (q), 140.9 (q), 140.6 (q), 139.0 (q), 133.6 (q), 132.7 (q), 132.2 (q), 130.1 (s), 129.5 (s), 128.8 (s), 128.0 (s), 128.0 (s), 127.8 (s), 126.8 (s), 125.8 (s), 125.8 (s), 124.9 (s), 120.2 (q), 119.6 (s), 116.8 (s), 113.9 (q), 113.3 (d), 72.5 (q), 61.3 (s), 56.7 (s), 55.8 (s), 54.5 (s), 34.1 (q), 33.5 (q), 30.8 (t), 30.2 (t), 27.1 (t), 25.3 (d), 23.2 (t), 22.4 (d), 17.1 (t), 16.6 ppm (t); IR ($CHCl_3$): $\tilde{\nu}$=1681 cm^{-1} (C=O); MS (70 eV, EI): *m/z*: 298 [M^+], 270, 283, 251, 223, 201, 174, 165, 153, 115, 77.; elemental analysis calcd (%) for $C_{19}H_{22}OS$ (298): C 76.46, H 7.43, O 5.36, S 10.74; found: C 76.55, H 7.80.

6. C-aromatic ABC skeleton of taxane (13): A mixture of compound **12** (0.298 g 1.0 mmol), $RhCl_3.3H_2O$ (0.023 g, 0.1 mmol) in ethanol (25 mL) was refluxed in 100 mL single-neck RB flask under argon atmosphere. After 24 h (GC analysis) the reaction mixture was quenched by adding triethyl amine (1 mL). The solvent was removed *in vacuo*, solid material was directly adsorbed on silica gel and passed through a column of silica gel (60-120 mesh size) using 5-10 % ethyl acetate/pet. ether as gradient eluent, furnished **13** as a colourless solid (0.238 g, 80%). R_f=0.35 (EtOAc/pet. ether 3:7); m.p. 150-152 °C, ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 7.20 (t, *J* = 6 Hz, 1H), 7.09 (t, *J* = 6 Hz, 1H), 7.18 (d, *J* = 4 Hz, 1H), 7.16 (d, *J* = 6 Hz, 1H), 6.00 (s, 1H), 4.84 (s, 1H), 2.37-2.10 (m, 4H), 2.27 (s, 3H), 1.43 (s, 3H), 1.22 (s, 3H), 1.12 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 211.2 (q), 140.6 (q), 140.0 (q), 132.2 (q), 131.7 (q), 2 × 127 (s), 125.0 (s), 2 × 124.5 (s), 119.4 (s), 56.3 (s), 53.9 (s), 33.0 (q), 29.8 (t), 26.6 (t), 24.8 (d), 21.9 (t), 16.0 ppm (t); IR (neat): $\tilde{\nu}$=1681 cm^{-1} (C=O);

MS (70 eV, EI): *m/z*: 298 [M^+], 270, 283, 251, 223, 201, 174, 165, 153, 115, 77; elemental analysis calcd (%) for $C_{19}H_{22}OS$ (298): C 76.46, H 7.43, O 5.36, S 10.74; found: C 76.74, H 7.79.

7. Preparation of 1-bromo-2-(bromomethyl) cyclohex-1-ene (14):

i. Preparation of 2-bromocyclohex-1-enecarbaldehyde (a): To a dry DMF (44.0 g, 0.6 mol) in chloroform (160 mL) was slowly added a freshly distilled PBr_3 (136.0 g, 0.5 mmol) at 0 °C. To this formylating reagent, was added cyclohexanone (19.6 g, 0.2 mmol) in dry chloroform (80 mL) at 0 ºC. After complete addition, the reaction mixture was refluxed at 60 °C for 3 h. After TLC analysis revealed consumption of starting material the solvent was evaporated *in vacuo*. The residue was carefully decomposed pouring into crushed ice, neutralized with saturated $NaHCO_3$ solution and extracted with hexane (3 × 100 mL). The combine organic extracts were initially washed with saturated aqueous potassium carbonate (2 × 25 mL) and then with brine solution (2 × 50 mL) and finally dried over anhydrous Na_2SO_4. Evaporation of the solvent at room temperature *in vacuo* gave the 2-bromocyclohex-1-enecarbaldehyde **a** as colourless oil. Due to instability of this product it was used as such for the reduction. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 10.0 (s, 1H), 2.73 (m, 2H), 2.25 (m, 2H), 1.72 ppm (m, 4H); IR (neat): $\tilde{\nu}$=2939, 1670 cm^{-1} (CH=O); MS (70 eV, EI): *m/z*: 190 & 188 (1:1) [M^+], 161, 159, 109, 81, 79.

ii. Preparation of (2-bromocyclohex-1-enyl) methanol (b): Solid $NaBH_4$ (1.4 g, 37.5 mmol) was slowly added to a stirred solution of 2-bromocyclohex-1-enecarbaldehyde **a** (14.2 g, 75 mmol) in methanol (100 mL) at 0 °C. The reaction was slightly exothermic. The reaction mixture was further stirred for 6 h, after completion of starting material (TLC analysis) the solvent was evaporated *in vacuo*. The residue was poured into crushed ice, neutralized with 2N HCl solution and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with saturated brine solution (2 × 25 mL), dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent *in vacuo*

furnished the (2-bromocyclohex-1-enyl) methanol **b** as a pale yellow oily liquid (13.0 g, 91 %). R_f=0.35 (EtOAc/pet. ether 3:7); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 4.21 (s, 2H), 2.50 (m, 2H), 2.25 (m, 2H), 1.68 ppm (m, 4H); IR (neat): $\tilde{\nu}$= 3333 cm^{-1} (O-H).

iii. Preparation of 1-bromo-2-(bromomethyl) cyclohex-1-ene (14): To a solution of (2-bromocyclohex-1-enyl)methanol **b** (4.78 g, 25 mmol) in dichloromethane (15 mL) was added pyridine (200 mg) and the reaction mixture was cooled to 0 °C. To this reaction mixture was slowly added phosphorus tribromide (3.39 g, 12.5 mmol). After the addition was over the reaction mixture was further stirred for 3h at room temperature and poured into crushed ice. It was extracted with pet ether (3 × 30 mL) and the combined organic extract was washed with saturated aqueous sodium bicarbonate solution (25 mL) and finally with saturated brine solution (2 × 25 mL). It was dried over anhydrous Na_2SO_4. Evaporation of solvent *in vacuo* yielded crude product which was further distilled under high vacuum (2 Torr, 40-50 °C oil bath temp.) provided a 1-bromo-2-(bromomethyl) cyclohex-1-ene **14** (5.8 g, 92 %). R_f=0.35 (EtOAc/pet. ether 1:9); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 4.1 (s, 2H), 2.51 (m, 2H), 2.28 (m, 2H), 1.69 ppm (m, 4H); MS (70 eV, EI): *m/z*: 254 [M^+], 252 [M^+], 173, 171.

8. Coupling reaction of 14 & 5: preparation of 15: A ketosulfide **5** (0.210 g, 1.0 mmol) in THF (5 mL) was to added slowly over a period of 15 min to stirred solution of NaH (50% dispersion in oil) (0.050 g, 1.1 mmol) in THF (10 mL) at 0 °C under argon atmosphere. The reaction mixture developed a dark brown colour after 1 h. A solution of 1-bromo-2-(bromomethyl)cyclohex-1-ene **14** (0.381 g, 1.5 mmol) in THF was added slowly over a period of 5 min to sodium enolate and reaction mixture stirred for 3 h at 0 °C and then left overnight. The reaction mixture was poured in to a cold dilute hydrochloric acid solution, organic layer was separated, aqueous layer was extracted with ether (3 × 25 mL), combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by flash column chromatography (230-400 mesh size silica gel, 2-3 % EtOAc/pet. ether gradient elution) provided isomers of **15** as a gummy

oil (0.272 g, 70 %). R_f=0.55 (EtOAc/pet. ether 1:9); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 5.33 (s, olefin), 4.66 (s, olefin), 4.59 (s, olefin), 4.53 (s, olefin), 2.54-1.85 (m, methylenes), 2.17 (s, –SC$\underline{H}_3$), 1.85-1.45 (m, methylenes), 1.69 (s, allylic methyl), 1.10 (s, –C$\underline{H}_3$), 1.10 (s, –C$\underline{H}_3$), 0.95 (s, –C$\underline{H}_3$), 0.87 ppm (s, –CH_3); IR (neat): $\tilde{\nu}$= 1731 cm^{-1}; MS (70 eV, ESI): *m/z*: 404.9 [M^++Na], 402.9 [M^++Na], 399, 397, 383, 381, 373.

9. Preparation of 16: In a two neck 100 mL RB flask charged with coupled product **15** (0.384 g, 1.0 mmol) and THF (50 mL) was kept at –100 °C under argon atmosphere. *sec*BuLi (3.3 mL, 5.0 mmol, 1.5 M) was slowly added over a period of 10 min to the above stirred solution and reaction was stirred for 3 h. After completion of starting material (TLC analysis) it was quenched with saturated aqueous ammonium chloride solution (1 mL), allowed warming to room temperature, organic layer was separated, aqueous layer was extracted with ether (3 × 25 mL). Combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by flash column chromatography (230-400 mesh size silica gel, 3-4 % EtOAc/pet. ether gradient elution) which provided isomers of **16** as a gummy oil (0.180 g, 60 %). R_f=0.30 (EtOAc/pet. ether 1:9); ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 4.67 (s, olefin), 4.58 (m, olefin), 3.50 (s, 1H), 3.05 (s, 1H), 2.96 (s, 1H), 2.39 (s, 1H), 2.35 (s, 1H), 2.02 (s, 3H), 2.20-1.50 (m, methylene), 1.01 (s, 3H), 0.89 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 150.2, 141.1, 137.4, 136.9, 136.0, 135.5, 121.0, 119.2, 109.1, 109.0, 100.3, 98.2, 93.8, 68.6, 64.9, 63.8, 58.9, 52.8, 52.1, 51.7, 47.6, 46.7, 46.5, 44.7, 43.7, 41.3, 29.6, 29.4, 29.2, 28.0 , 27.0, 26.4, 26.2, 25.9, 25.6, 25.4, 25.3, 25.0, 24.7, 23.3, 23.1, 22.8, 22.7, 22.5, 22.5, 22.4 , 22.0, 13.5, 13.3, 12.6, 11.9 ppm; IR (neat): $\tilde{\nu}$= 3500 cm^{-1} (O-H); MS (70 eV, EI): *m/z*: 304 [M^+], 289, 271, 256, 241, 227, 213, 200, 182, 123, 105.

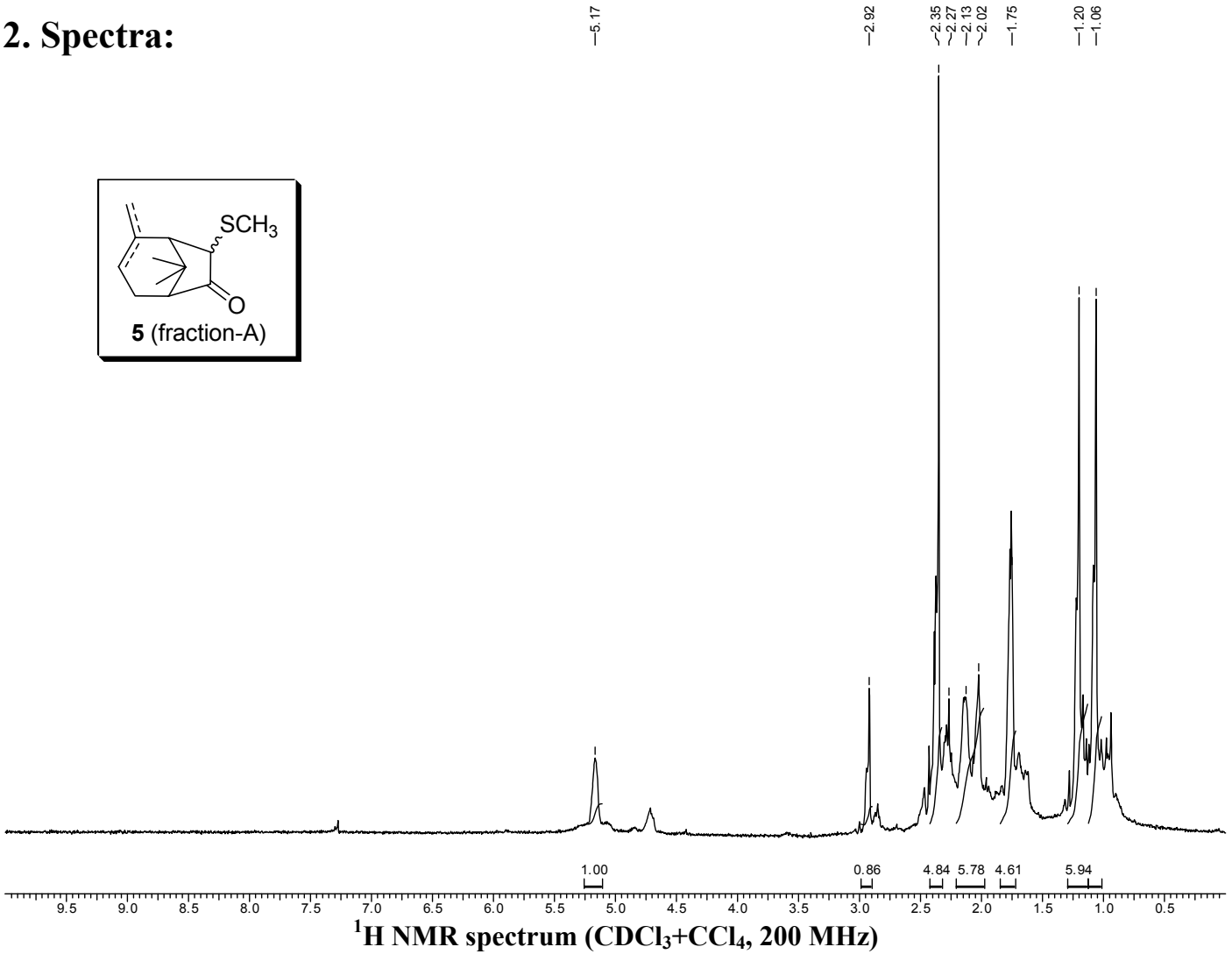
10. Preparation of 17: A 100 mL two-neck RB flask was charged with lead tetraacetate (0.886 g, 2.0 mmol) along with glacial acetic acid (5 mL) and toluene (20 mL) under argon atmosphere. The mixture was cooled to 0 °C and β-hydroxy sulfide **16** (0.304 g, 1.0 mmol) in toluene was slowly added and

reaction mixture was stirred for 6 h at 0 °C. The reaction was quenched with saturated aqueous ammonium chloride solution (10 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic layer were washed with saturated aqueous sodium bicarbonate solution until neutralization and further with brine solution, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo*, and the residue obtained was purified by column chromatography (silica gel, 5-6 % ethyl acetate/pet. ether gradient elution) which provided **17** as a yellowish solid (0.226 g,75 %). R_f=0.30 (EtOAc/pet. ether 3:7); m.p. 175-180 ºC; ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 5.70 (m, olefin), 5.50 (s, olefin), 5.40 (bs, olefin), 5.10 (s, olefin) 4.95 (s, olefin) 4.75 (s, olefin), 2.65 (s, 1H), 2.18 (s, S-CH_3), 2.16 (s, S-CH_3), 2.15 (s, S-CH_3), 2.13 (s, S-CH_3), 2.25-1.40 (m, -CH_2-), 1.58 (s, allylic-CH_3), 1.57 (s, allylic-CH_3), 1.18 (s, Me), 1.03 (s, Me), 1.02 (s, Me), 1.00 (s, Me), 0.97 (s, Me), 0.95 (s, Me), 0.88 (s, Me), 0.76 ppm (s, Me); ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C, TMS): δ= 213.3 (q), 213.1 (q), 145.7 (q), 138.9 (q), 137.2 (q), 135.4 (q), 135.1 (q), 131.0 (q), 130.0 (q), 127.8 (q), 120.7 (s), 118.9 (s), 118.0 (s), 112.5 (d), 60.4 (s), 56.4 (s), 54.8 (s), 53.4 (s), 33.0 (q), 32.0 (q), 30.7 (d), 29.9 (t), 29.7 (d), 29.5 (d), 29.4 (t), 29.3 (d), 27.5 (d), 26.4 (t), 23.9 (d), 22.4 (d), 22.3 (d), 22.1 (s), 21.9 (t), 21.5 (d), 16.2 (t), 15.9 ppm (t); IR ($CHCl_3$): $\tilde{\nu}$= 1674 cm^{-1} (C=O); MS (70 eV, EI): *m/z*: 302 [M^+], 287, 274, 255, 227, 191, 157, 144, 129, 83.

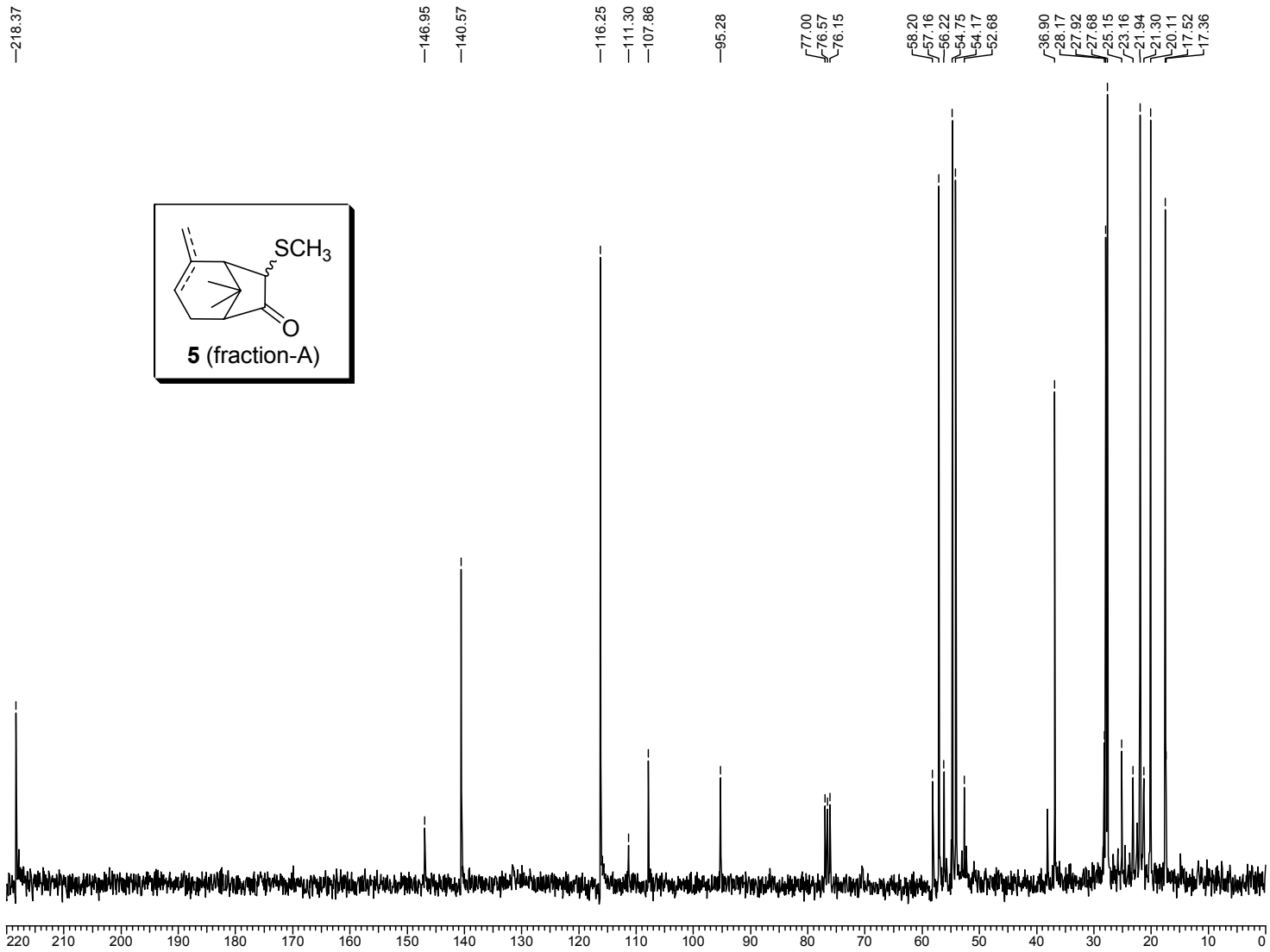
11. C-alicyclic ABC skeleton of taxane (18): A mixture of compound **17** (0.302 g, 1.0 mmol), $RhCl_3.3H_2O$ (0.025 g, 0.1 mmol), and *p*TSA.H_2O (0.019 g, 1 mmol) in ethanol (25 mL) was refluxed in 100 mL single-neck RB flask under argon atmosphere. After 24 h (GC analysis) the reaction mixture was quenched by adding triethyl amine (1 mL). The solvent was removed *in vacuo*, solid material obtained was directly absorbed on silica gel and passed through a column of silica gel using 5-7 % EtOAc/pet.ether as eluent, furnished 18 as a yellowish solid (0.235 g, 80%). R_f=0.30 (EtOAc/pet. ether 3:7); m.p. 175-180 ºC; ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, TMS): δ= 5.40 (s, 1H), 5.12 (s, 1H), 2.21-2.10 (m, 4H), 2.14 (s, 3H), 1.75-1.80 (m, 4H), 1.58 (s, 3H), 1.40-1.55 (m, 4H), 1.03 (s, 3H), 1.00 ppm

(s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C, TMS): δ= 213.7 (q), 137.3 (q), 135.1 (q), 130.5 (q), 127.9 (q), 120.8 (s), 118.9 (s), 56.4 (s), 53.5 (s), 32.3 (q), 30.0 (d), 29.6 (t), 29.4 (d), 26.4 (t), 24.0 (d), 22.4 (t), 22.1 (d), 21.9 (d), 15.9 ppm (t); IR ($CHCl_3$): $\tilde{\nu}$= 1674 cm^{-1} (C=O); MS (70 eV, EI): *m/z*: 302 [M^+], 287, 274, 255, 227, 191, 157, 144, 129, 83; elemental analysis calcd (%) for $C_{19}H_{26}OS$ (302): C 75.45, H 8.66, O 5.29, S 10.60; found C 75.16, H 8.75.

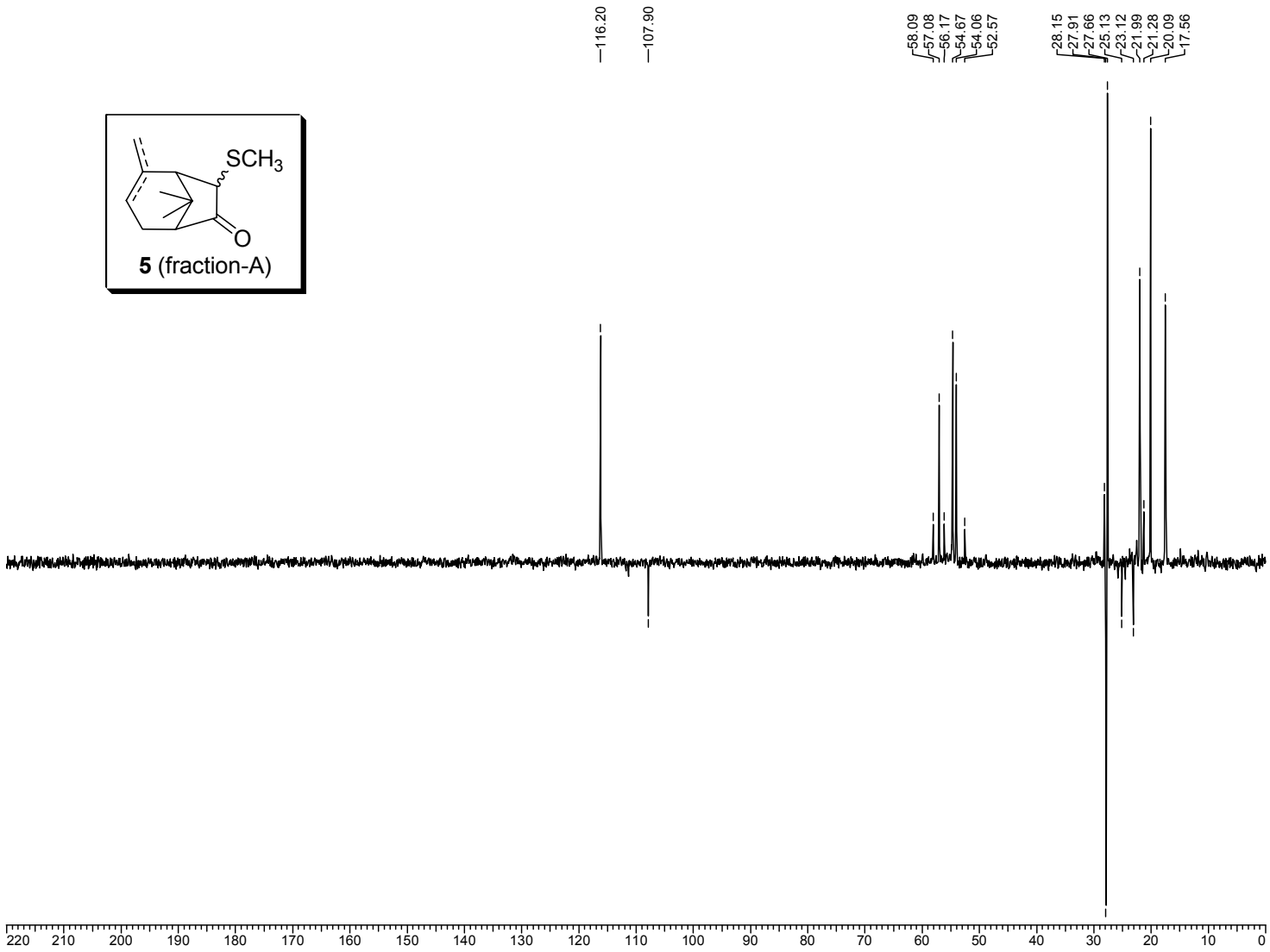
2. Spectra:



^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)

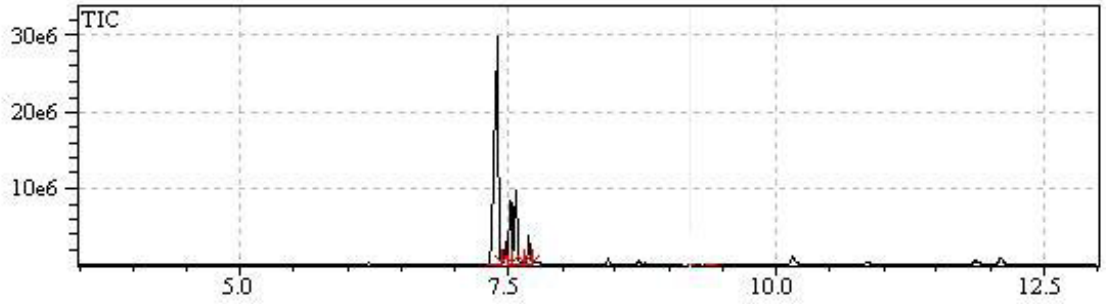


^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)

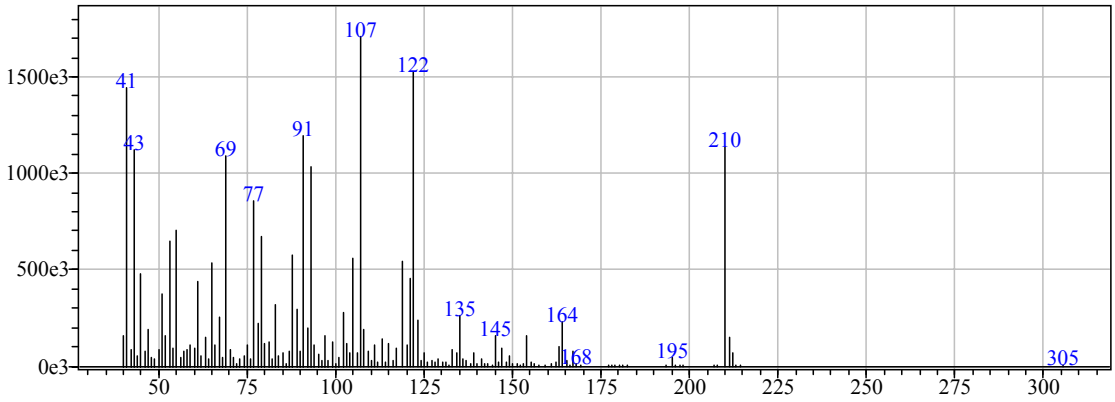


DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)

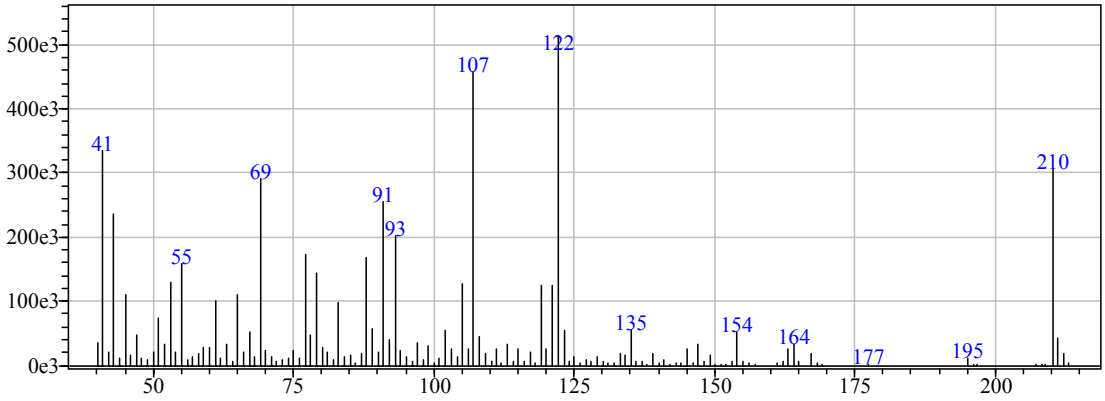
GCMS spectrum of fraction-A



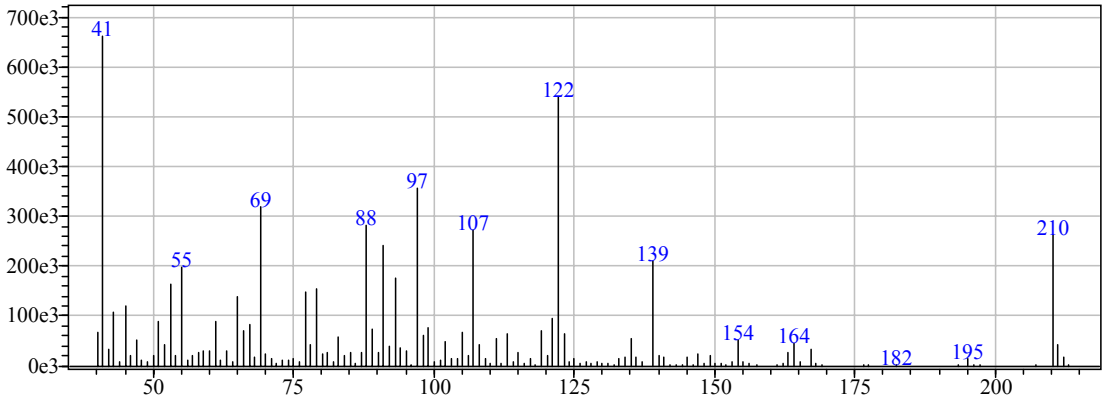
MS at retention time 7.4



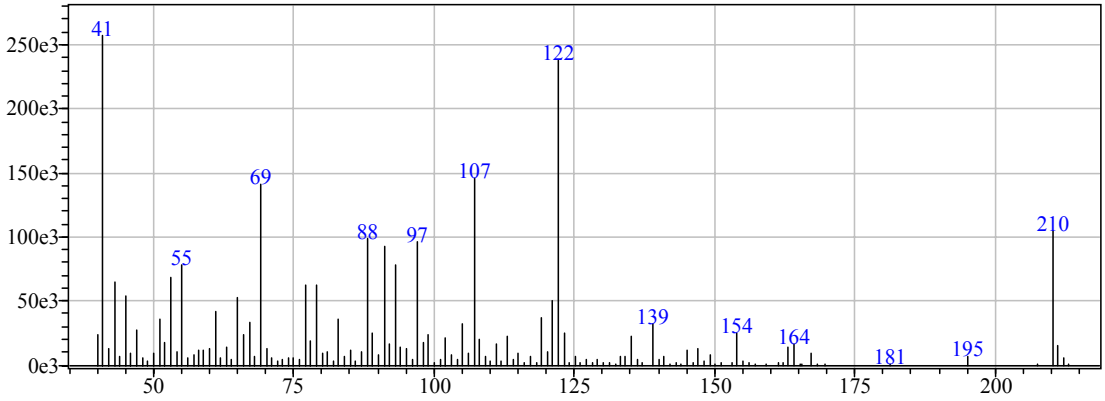
MS at retention time 7.5

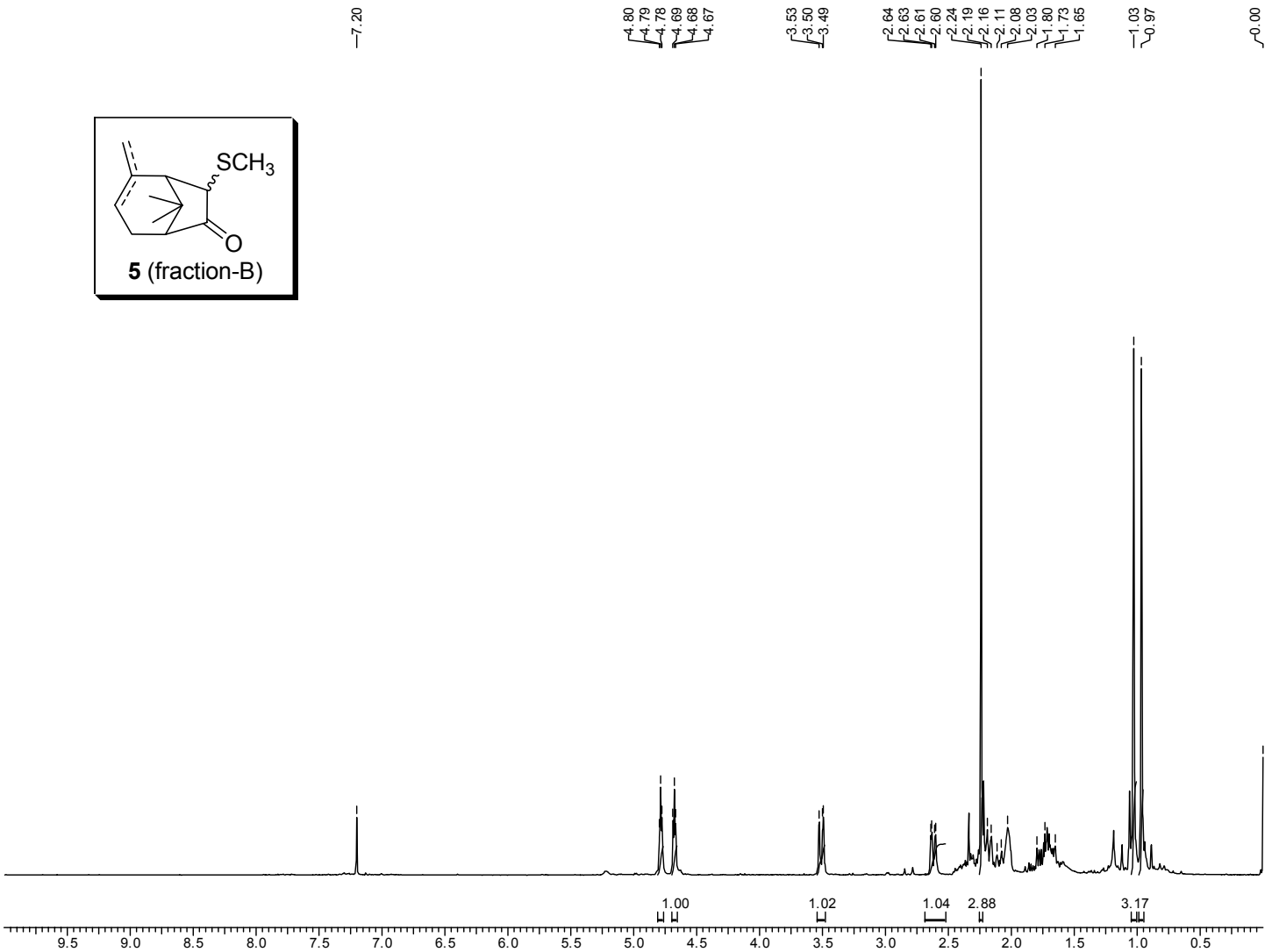


MS at retention time 7.6

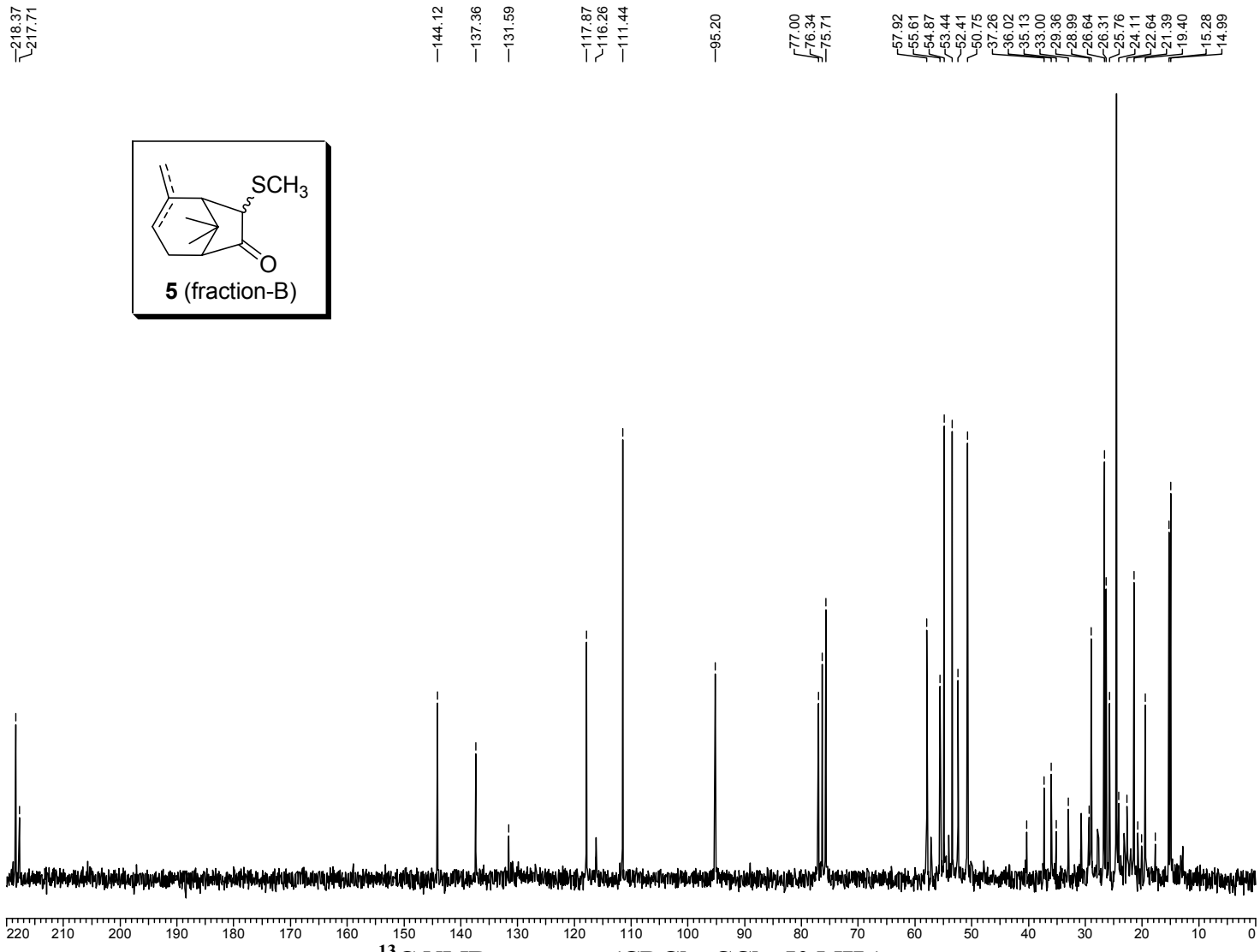


MS at retention time 7.7

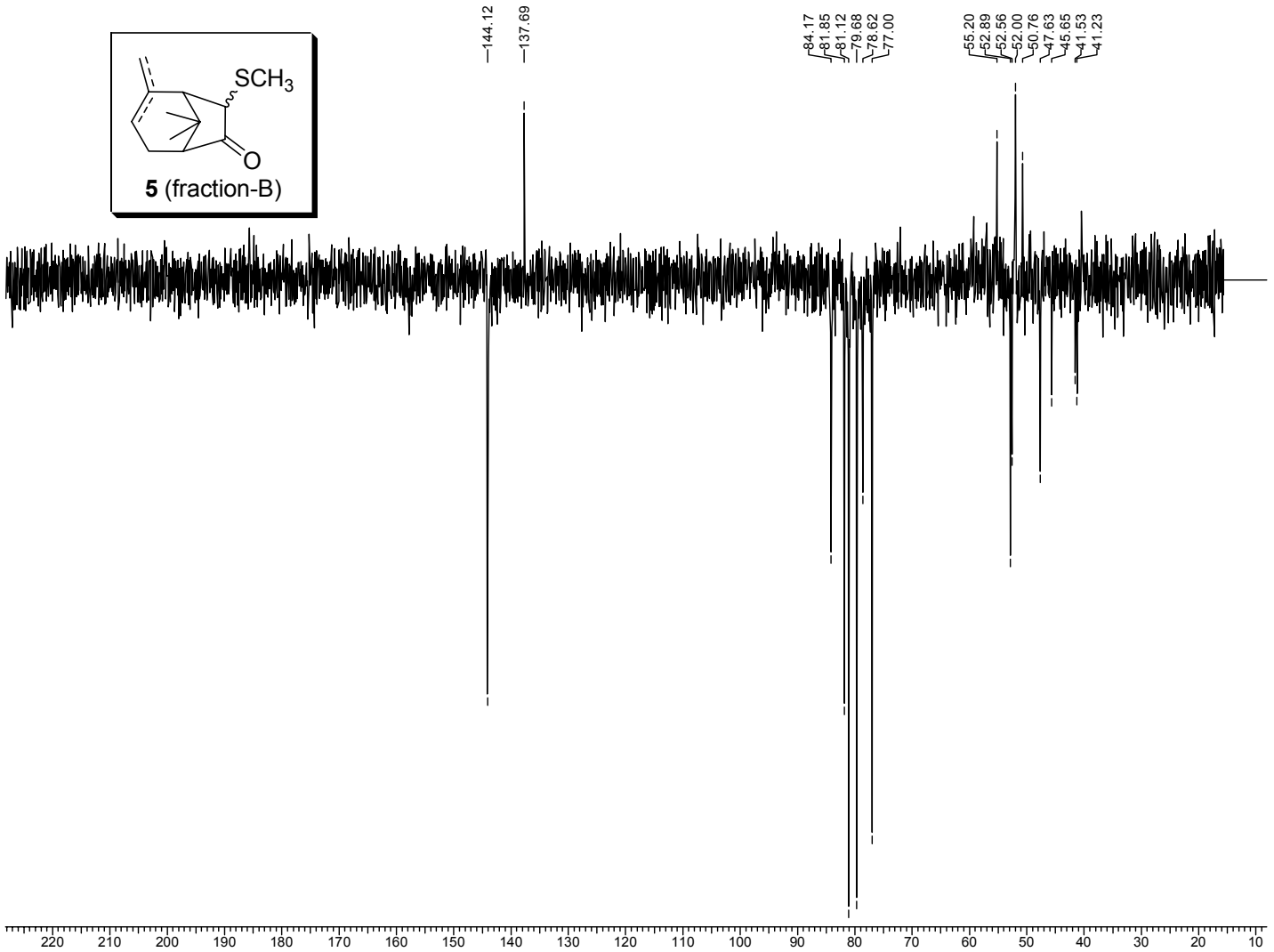




^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)

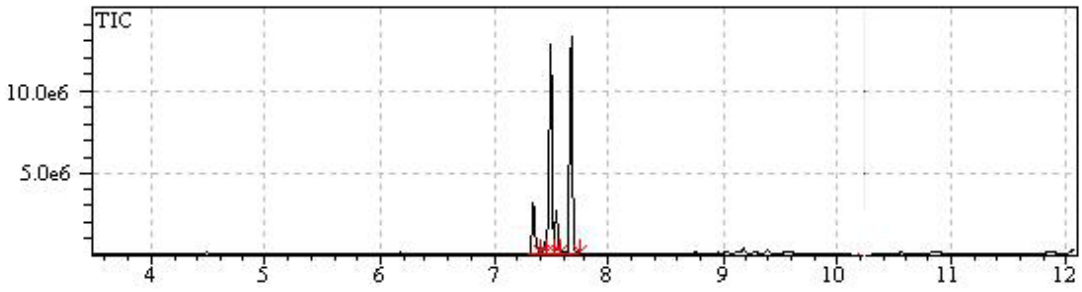


^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)

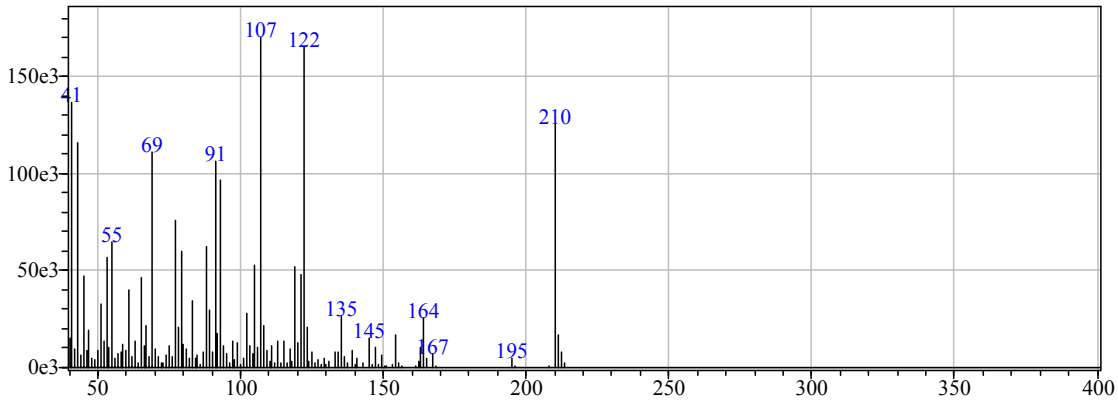


DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)

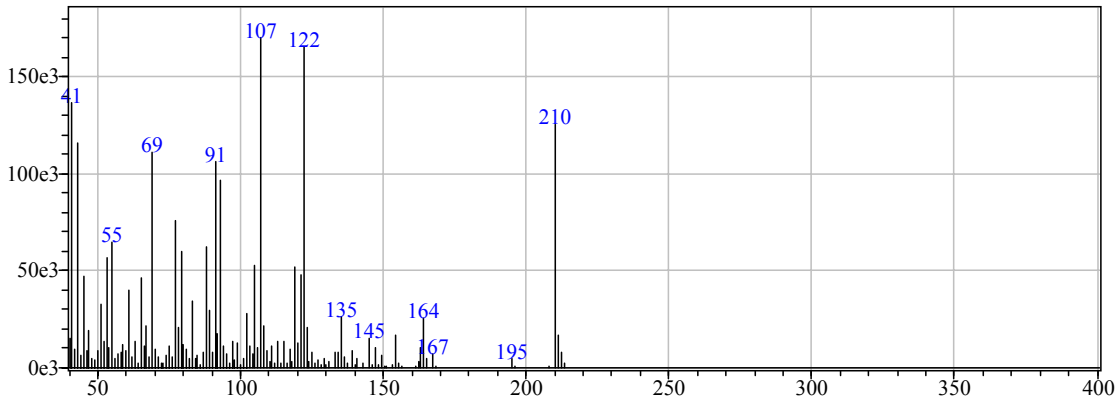
GCMS spectrum of Fraction B:



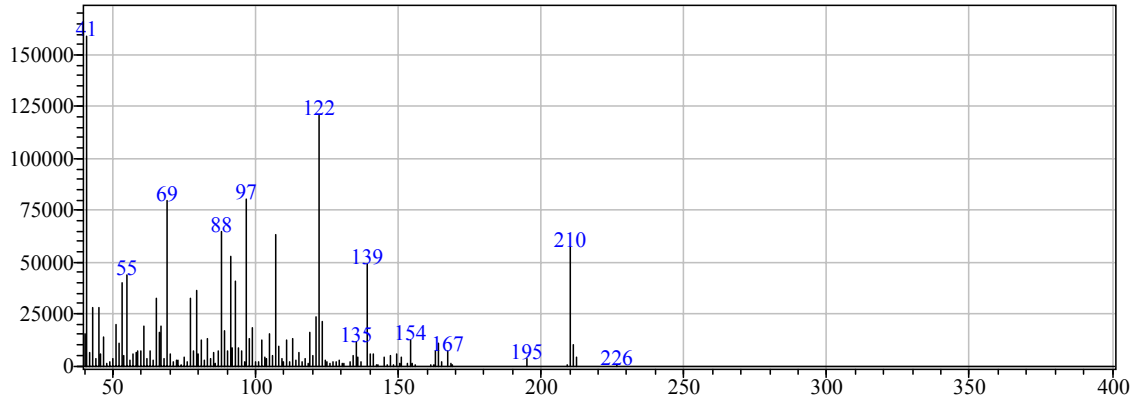
MS at retention time 7.4



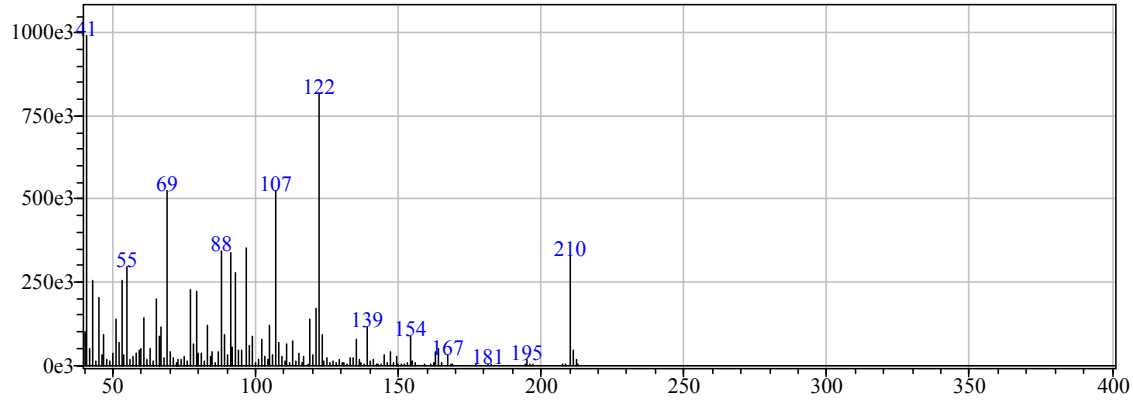
MS at retention time 7.5

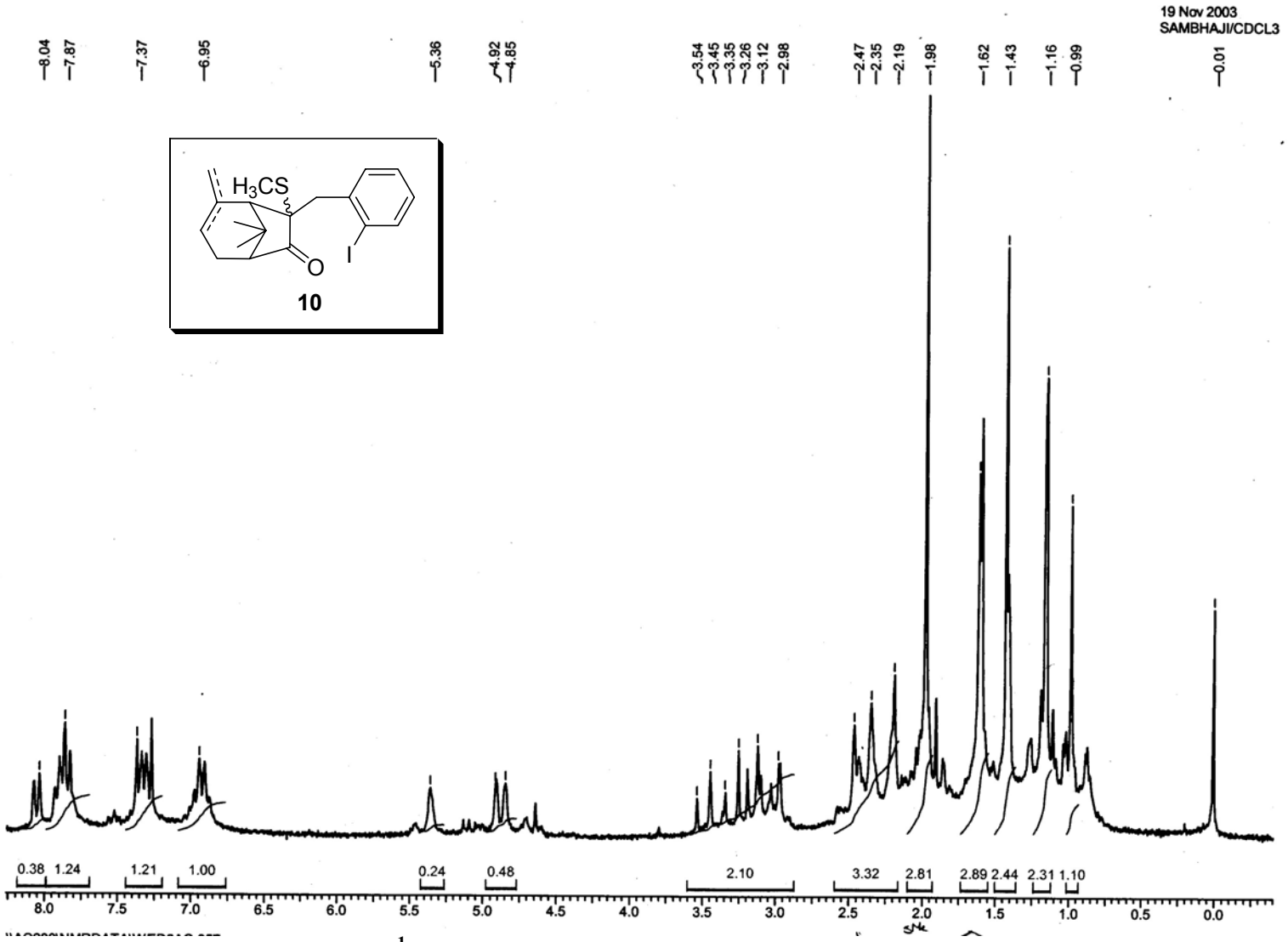


MS at retention time 7.6

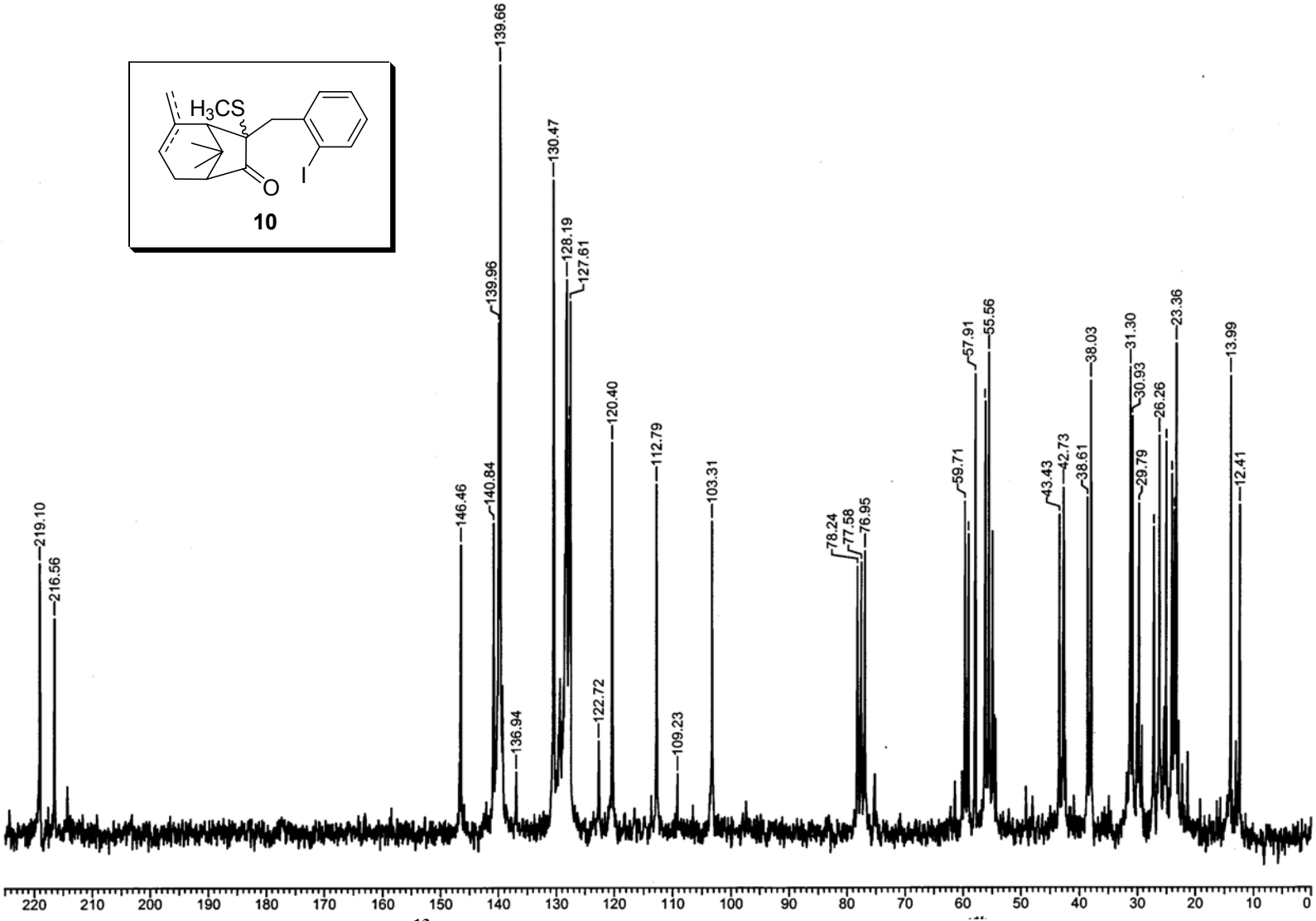


MS at retention time 7.7

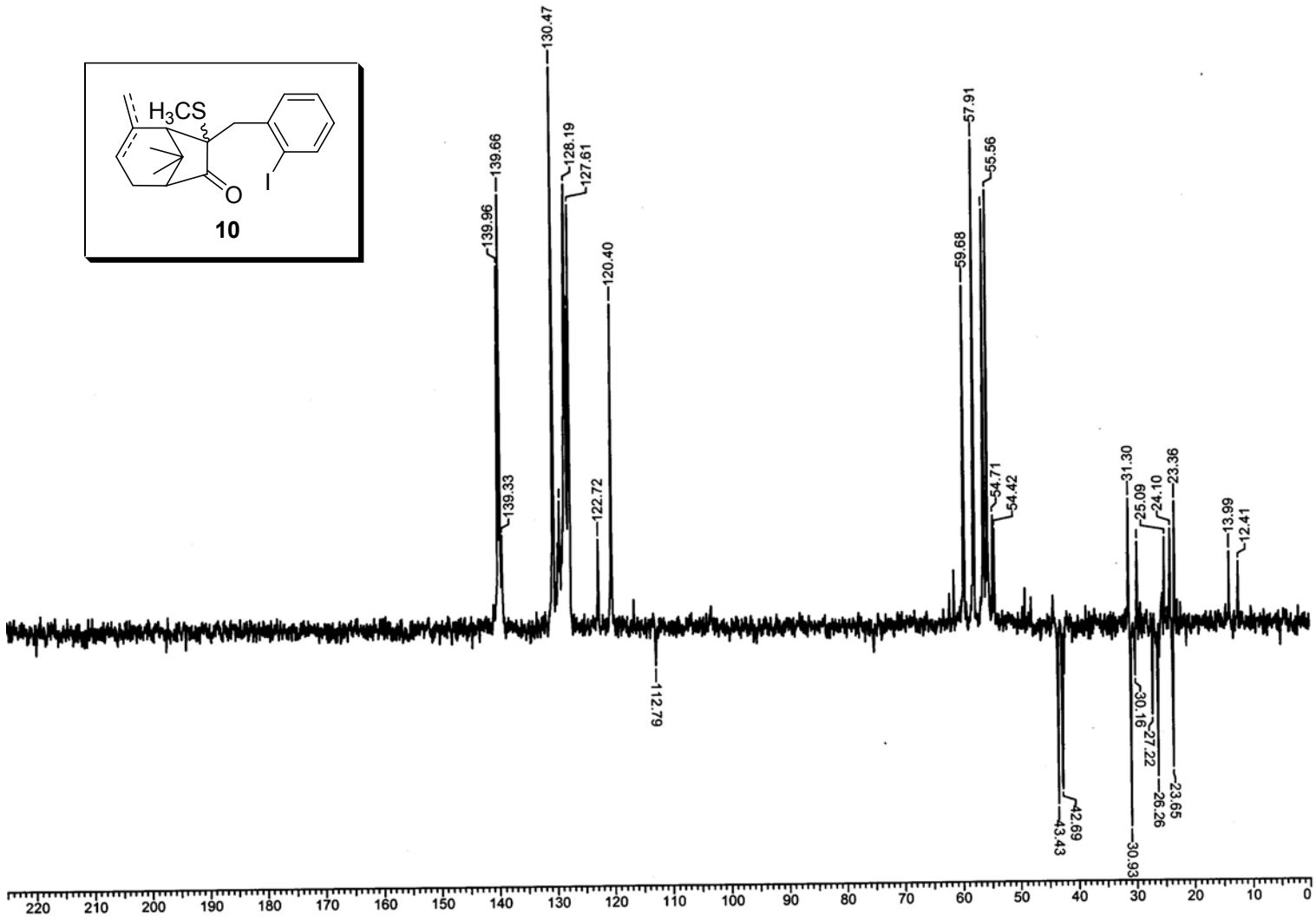




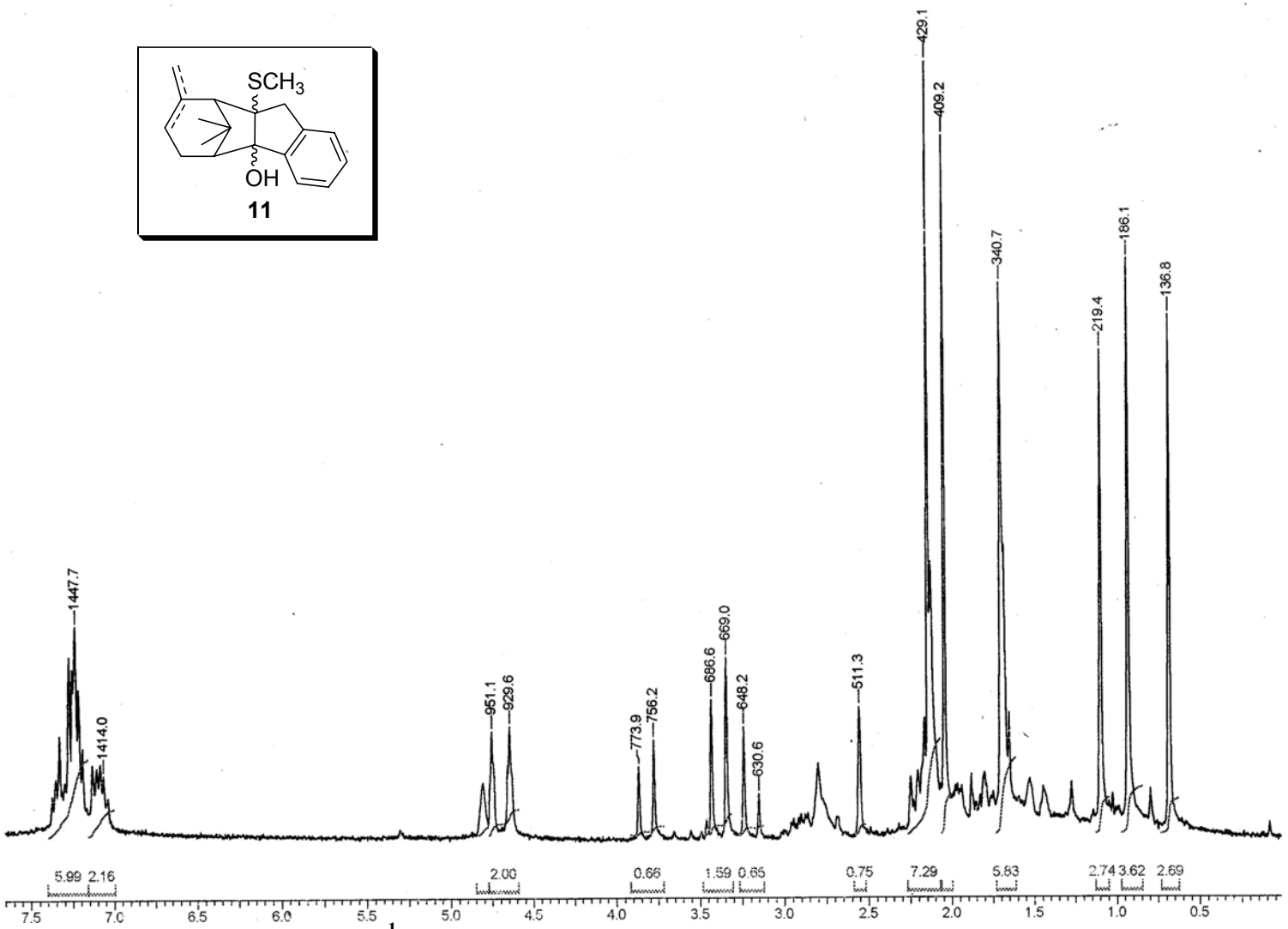
^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



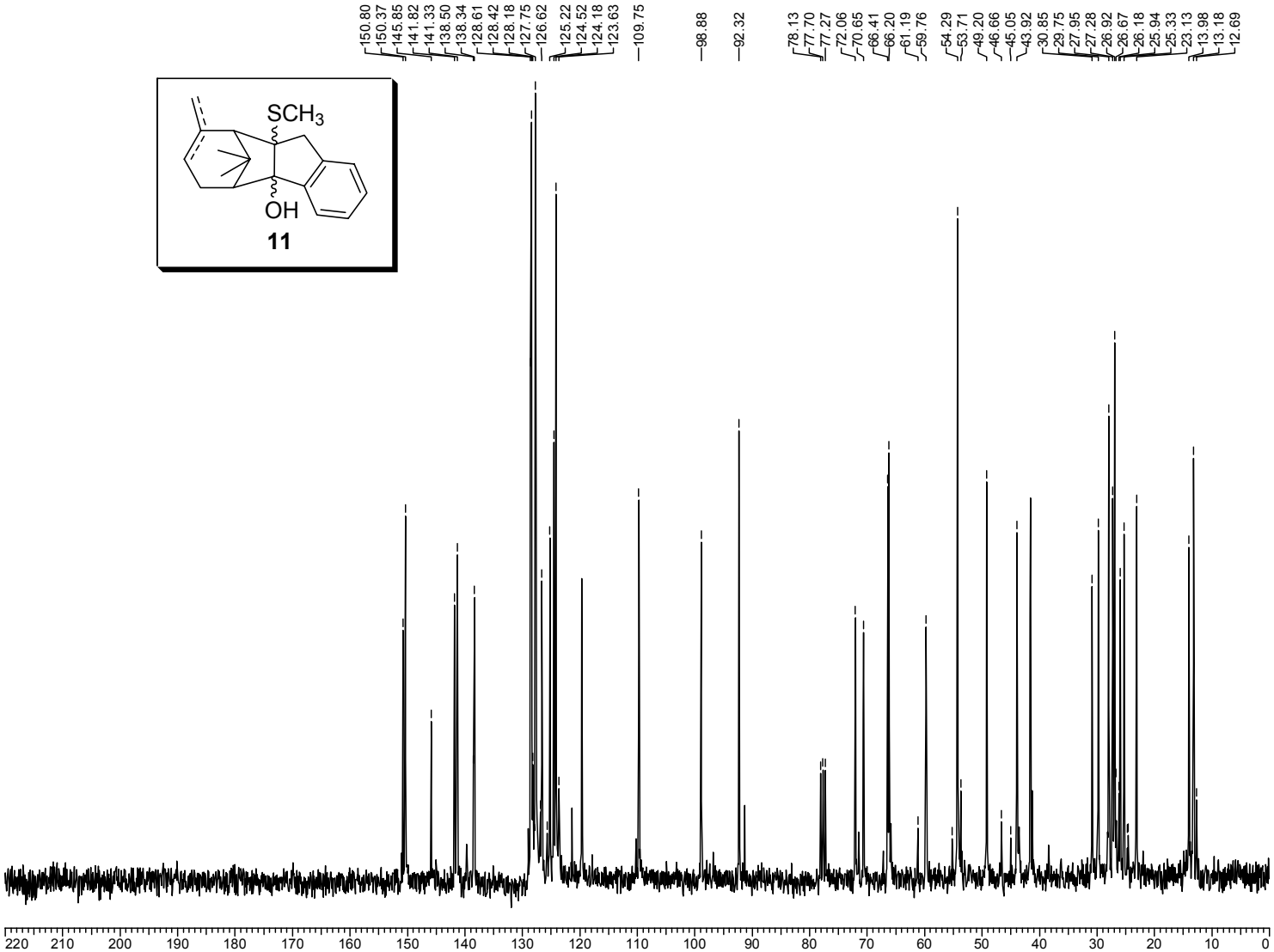
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



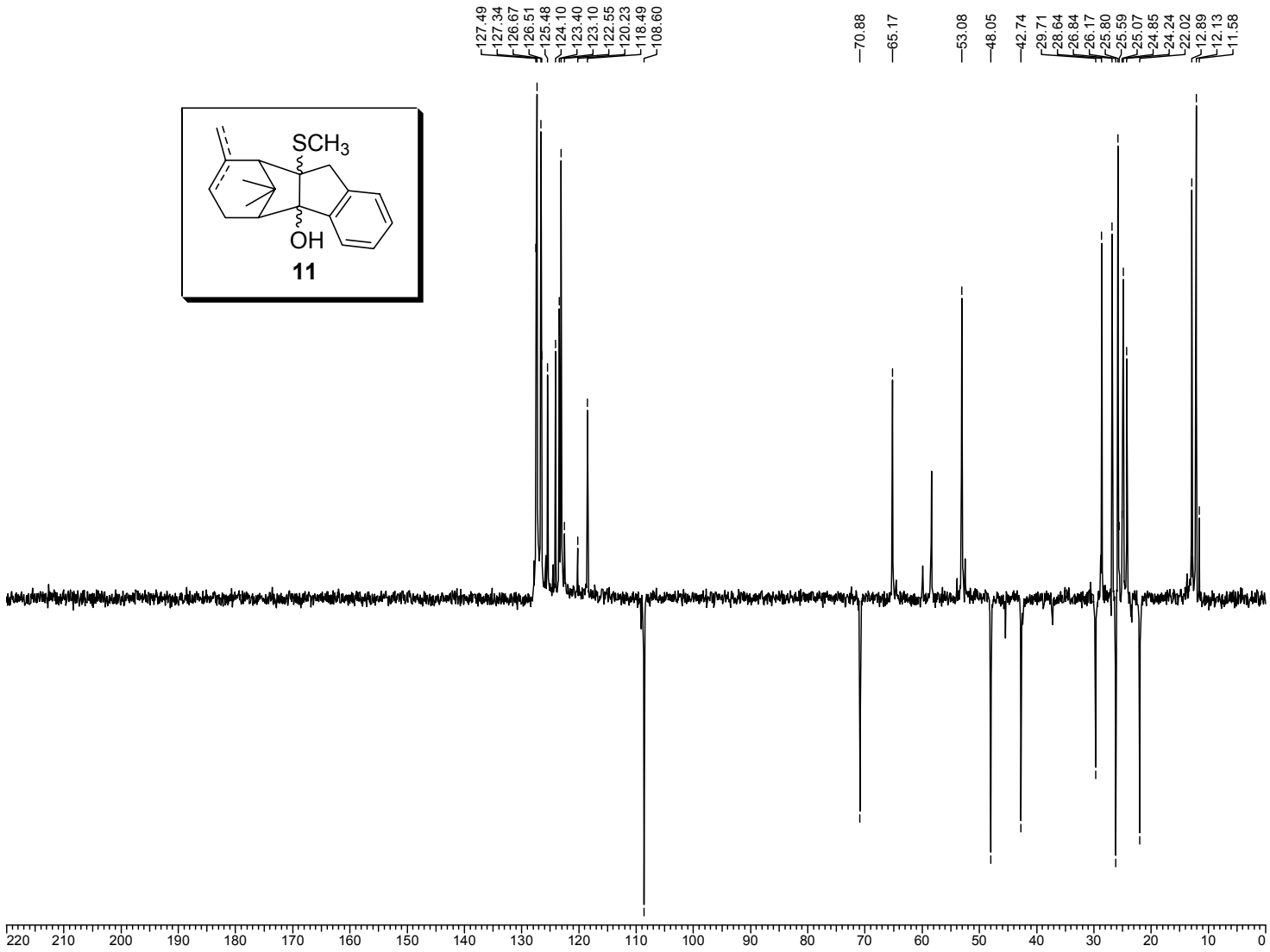
DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)



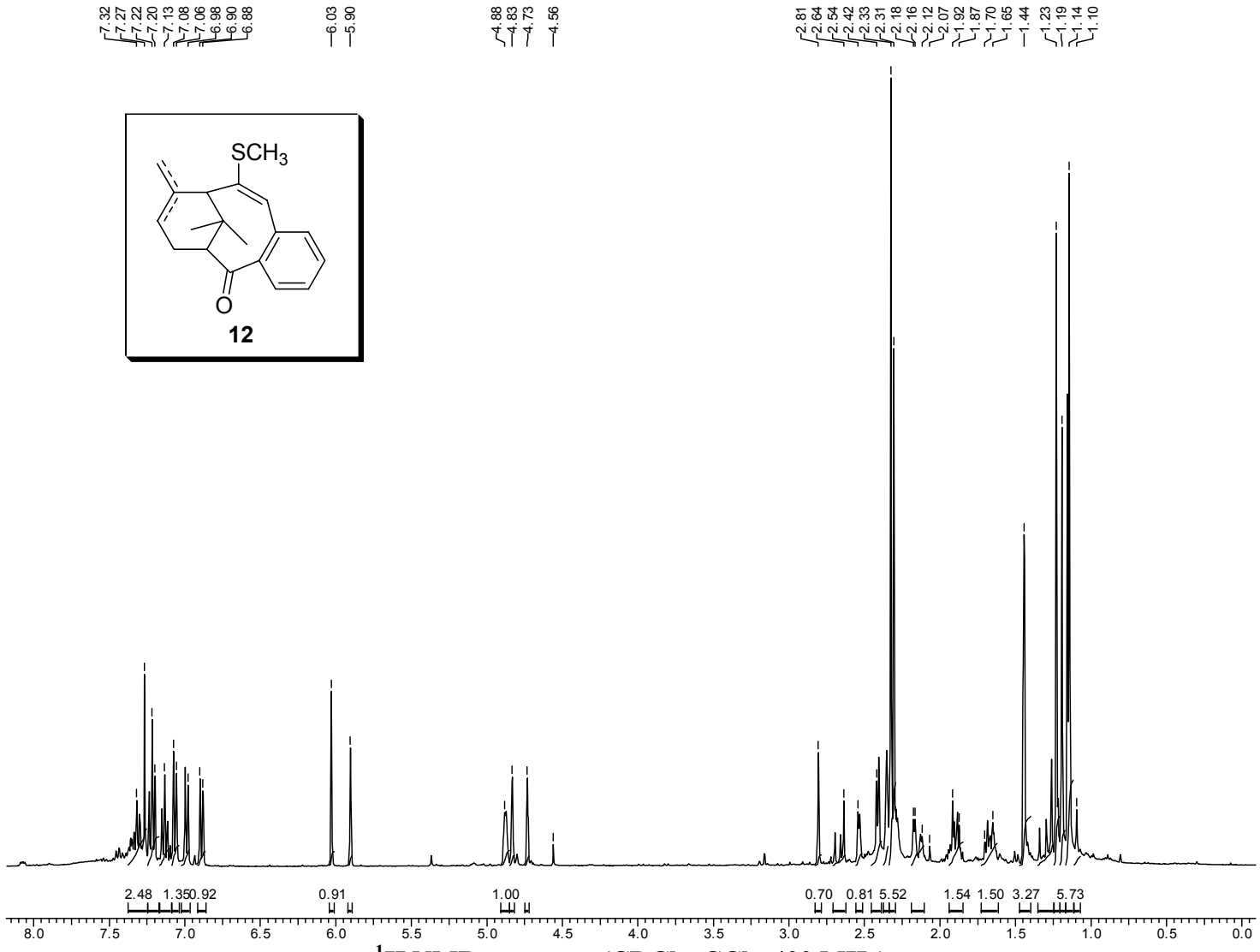
^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



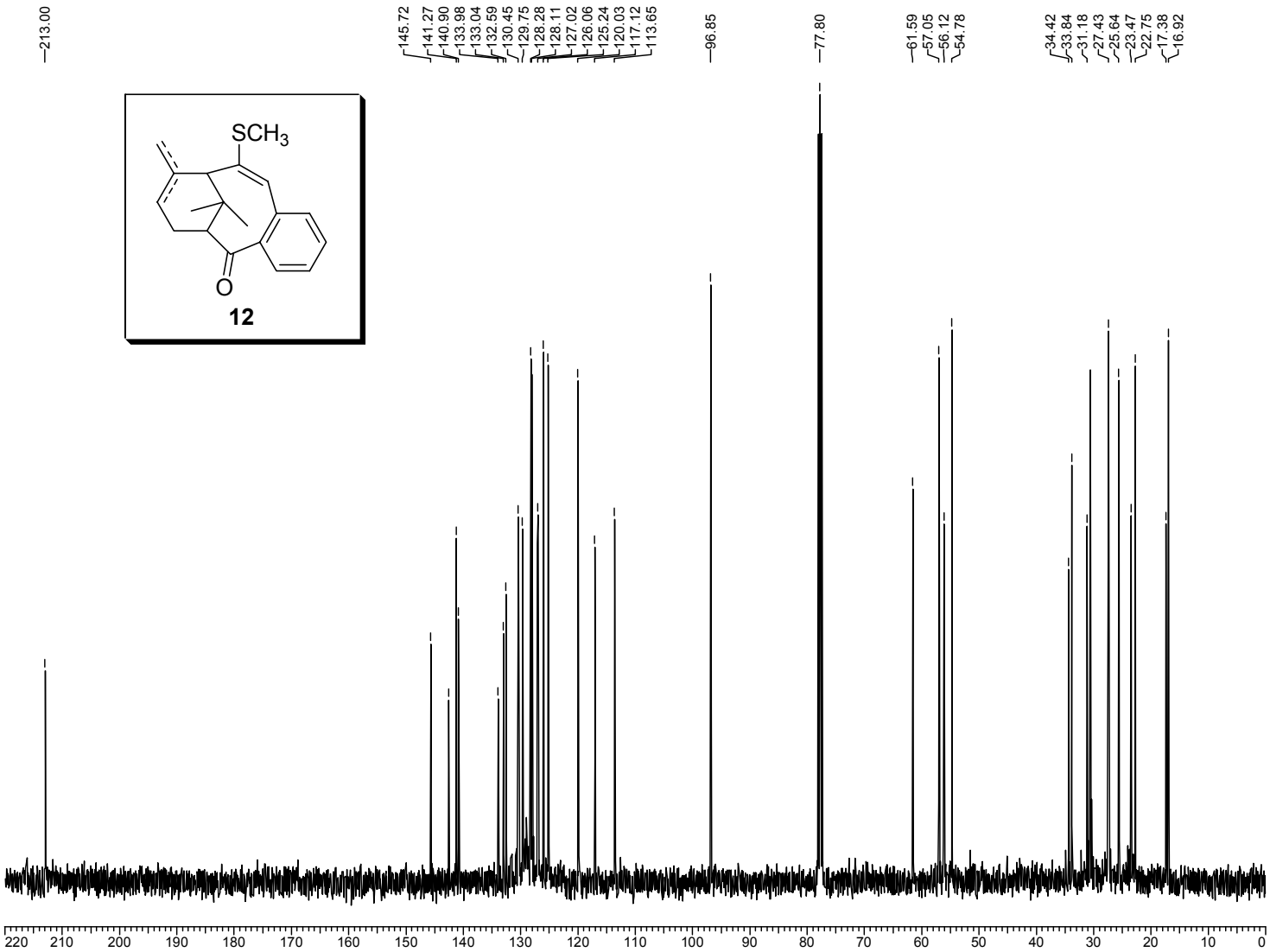
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



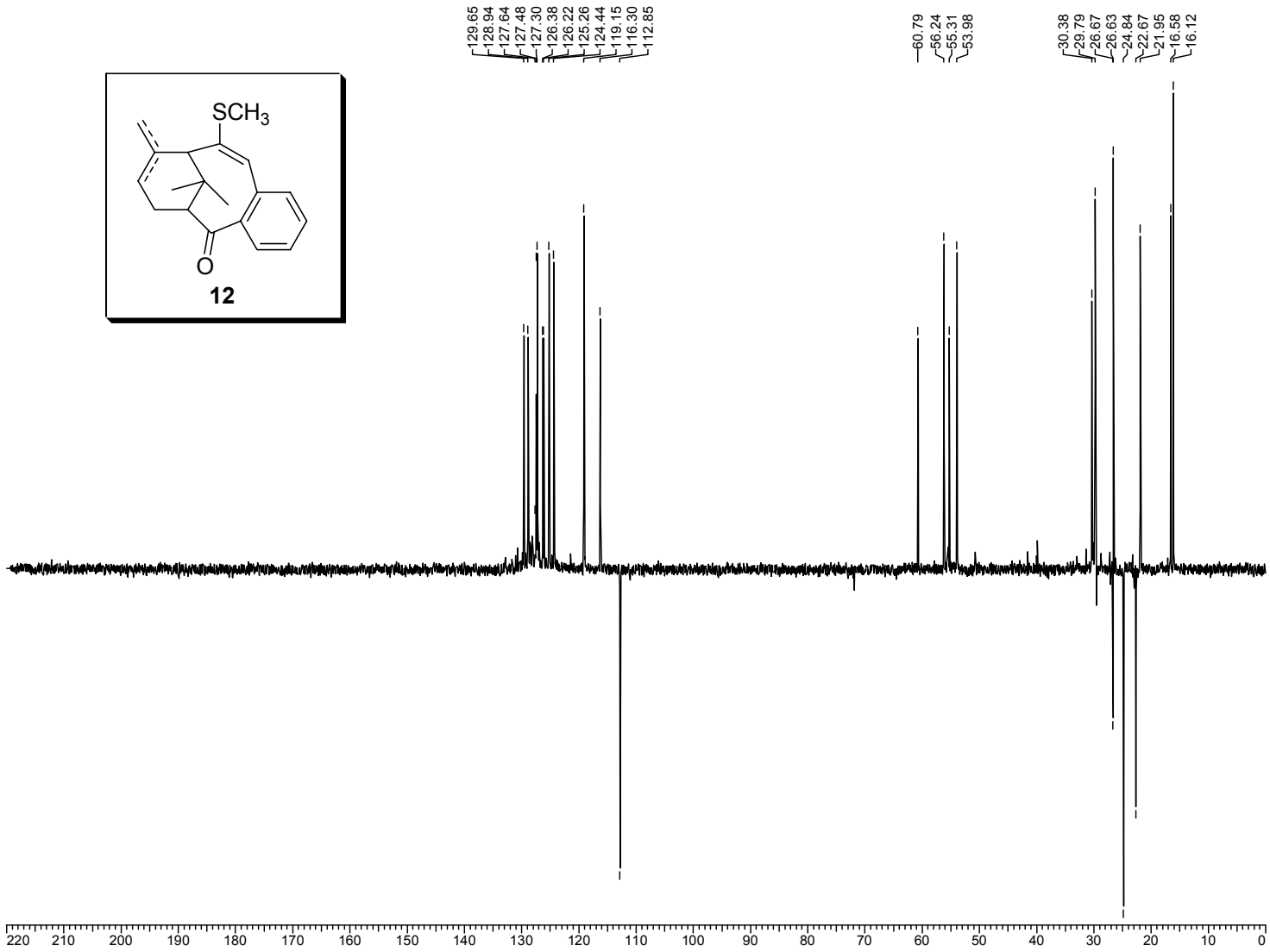
DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)



^{1}H NMR spectrum ($CDCl_3$+CCl_4, 400 MHz)



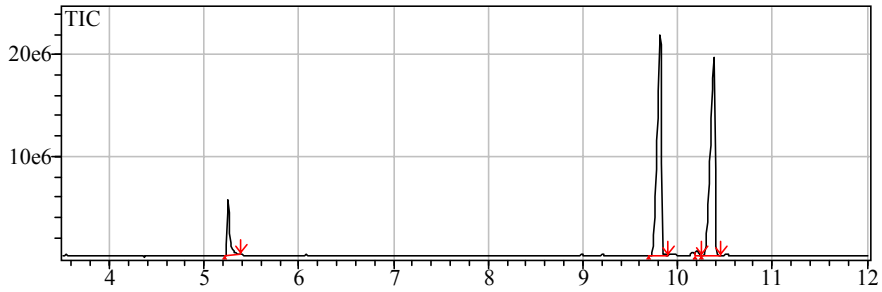
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 100 MHz)



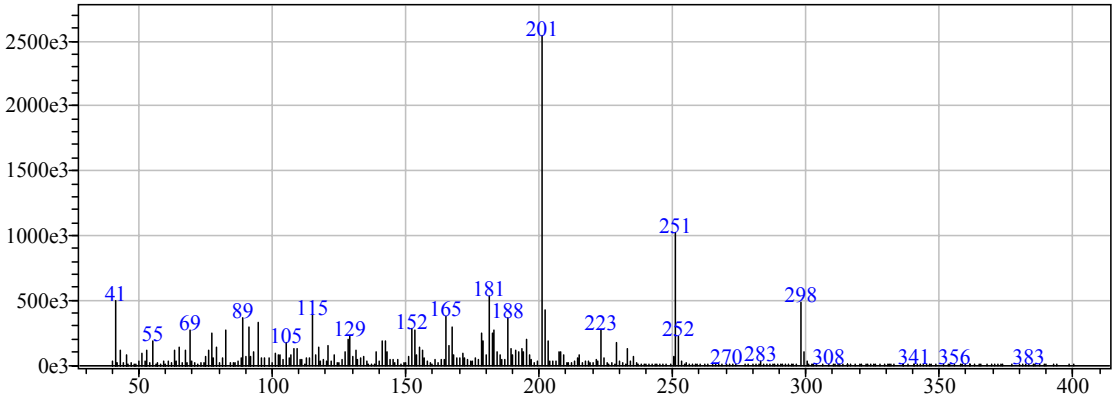
DEPT spectrum ($CDCl_3$+CCl_4, 100 MHz)

GCMS spectrum of 12

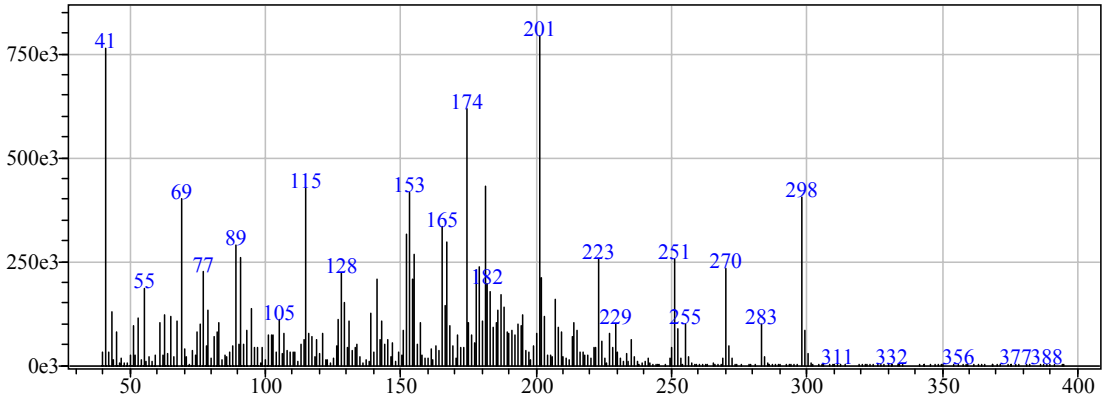
GC chromatogram

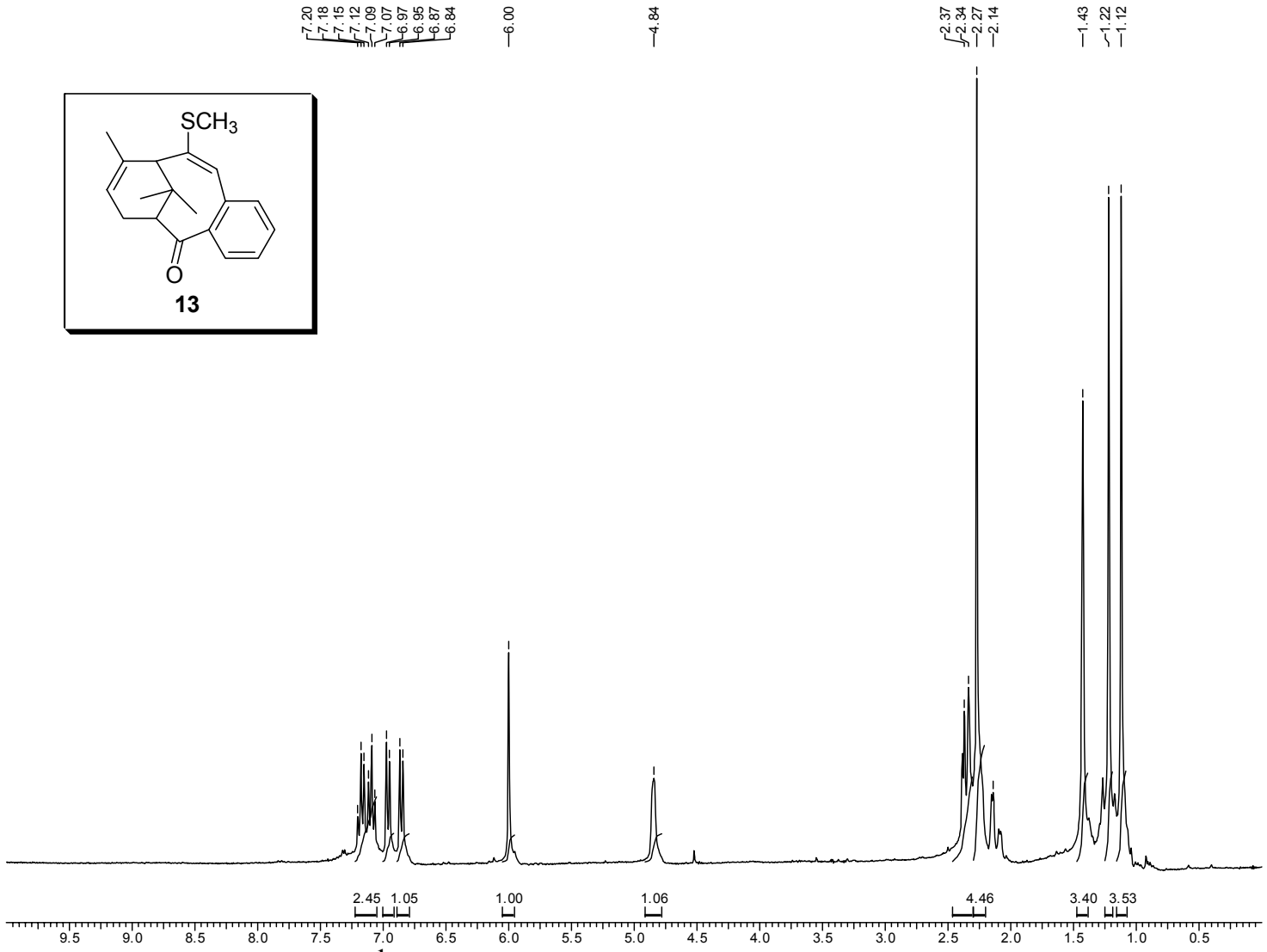


MS at retention time 9.9

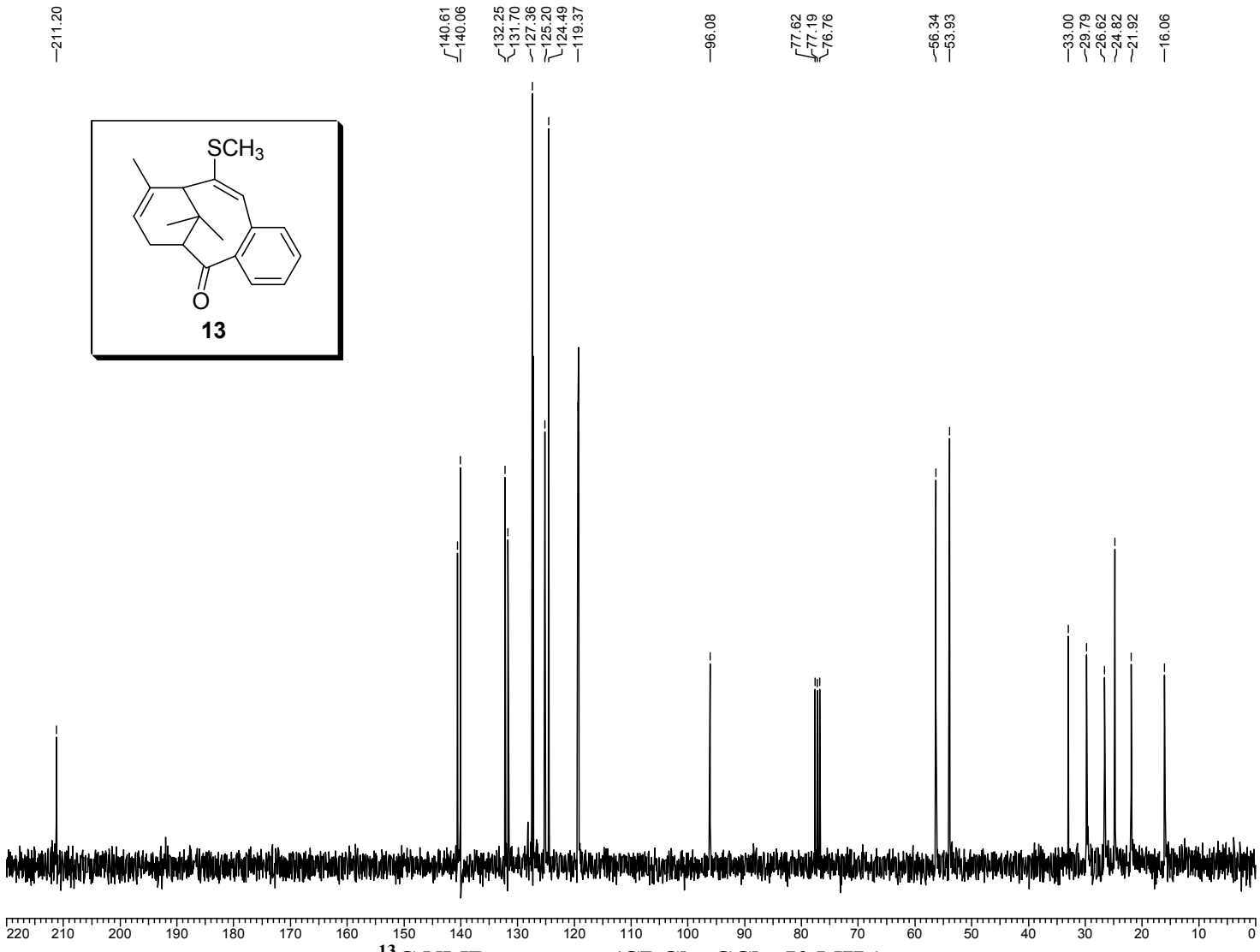


MS at retention time 10.2

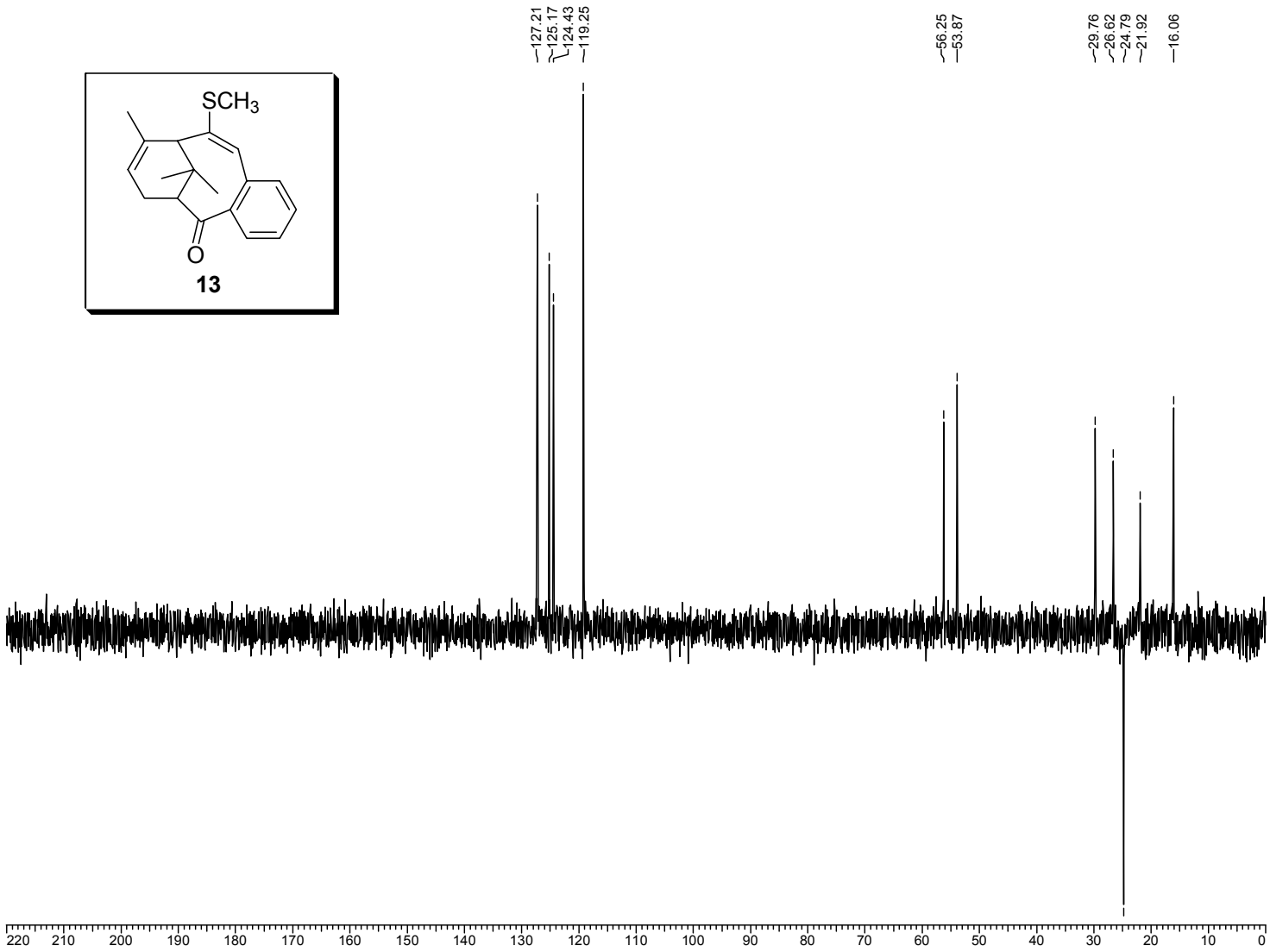




^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



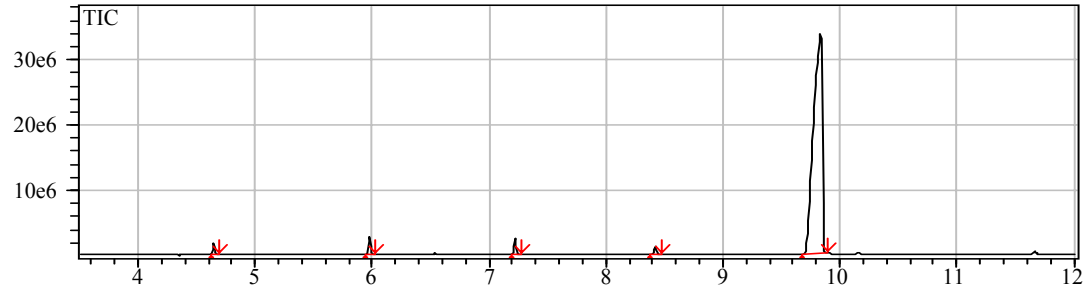
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



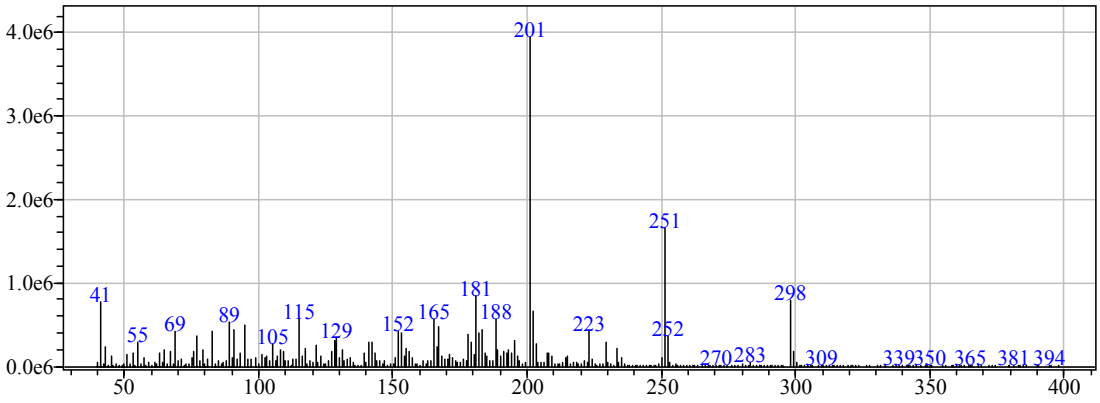
DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)

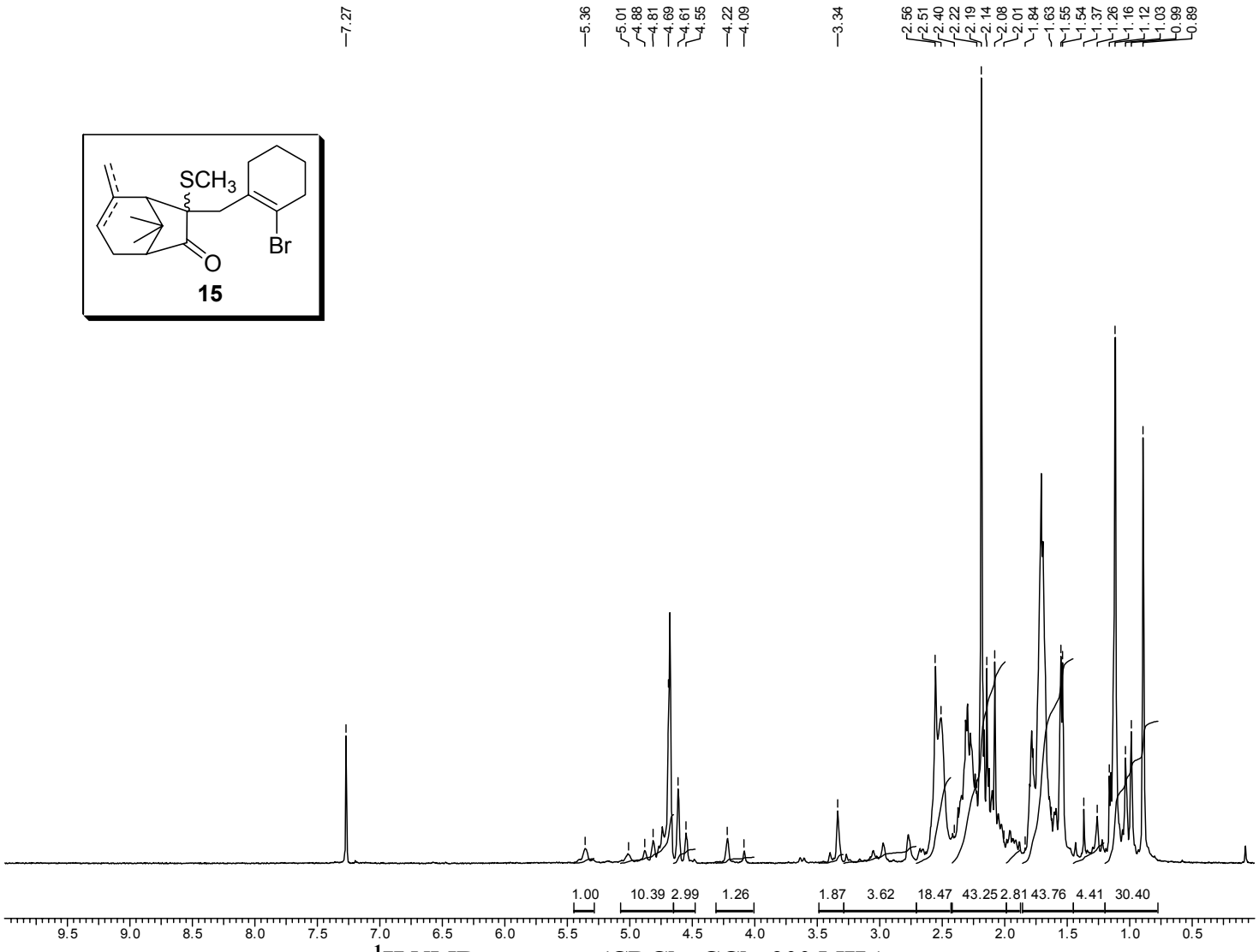
GCMS spectrum of 13

GC chromatogram

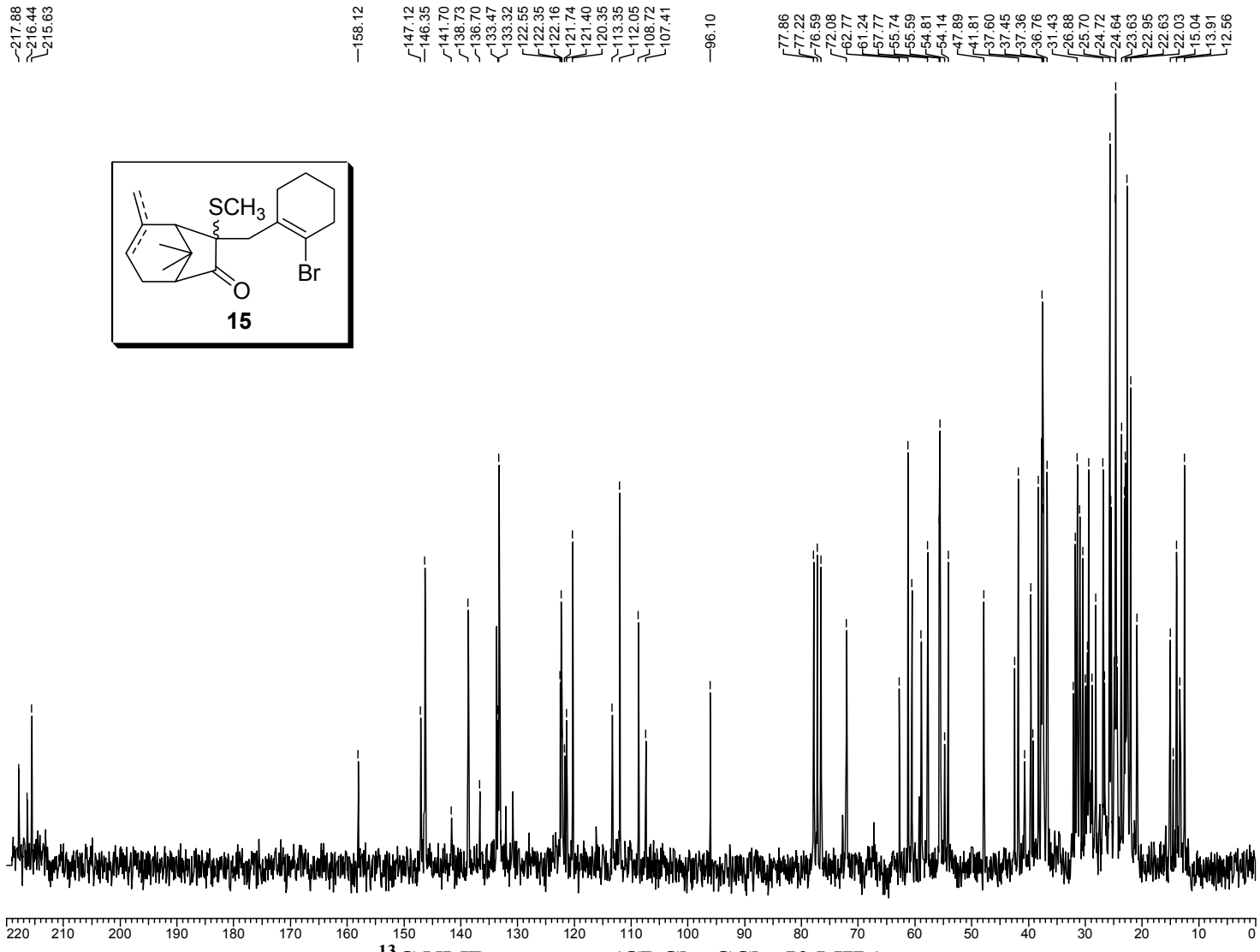


Mass spectrum at retention time 9.9

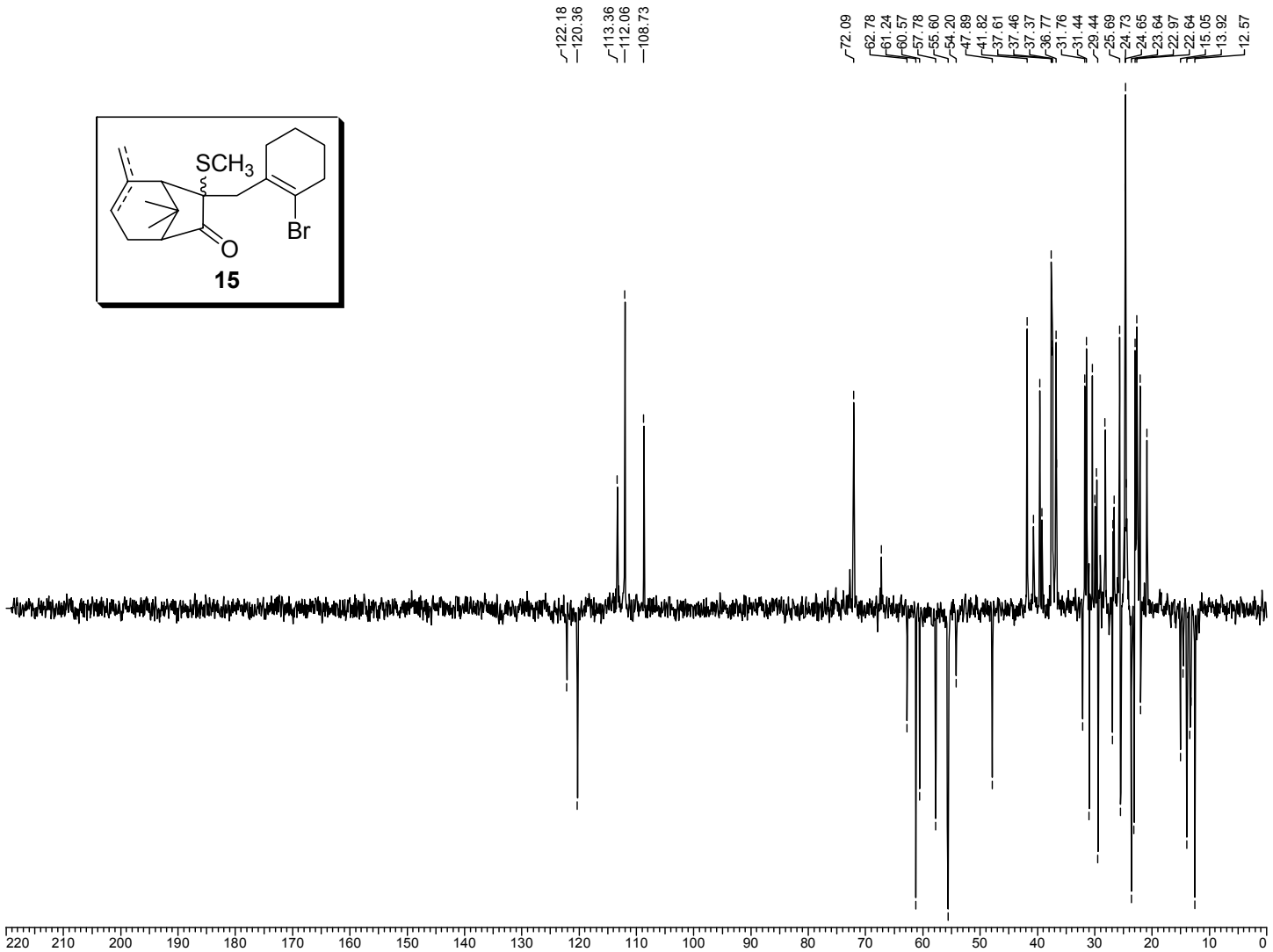




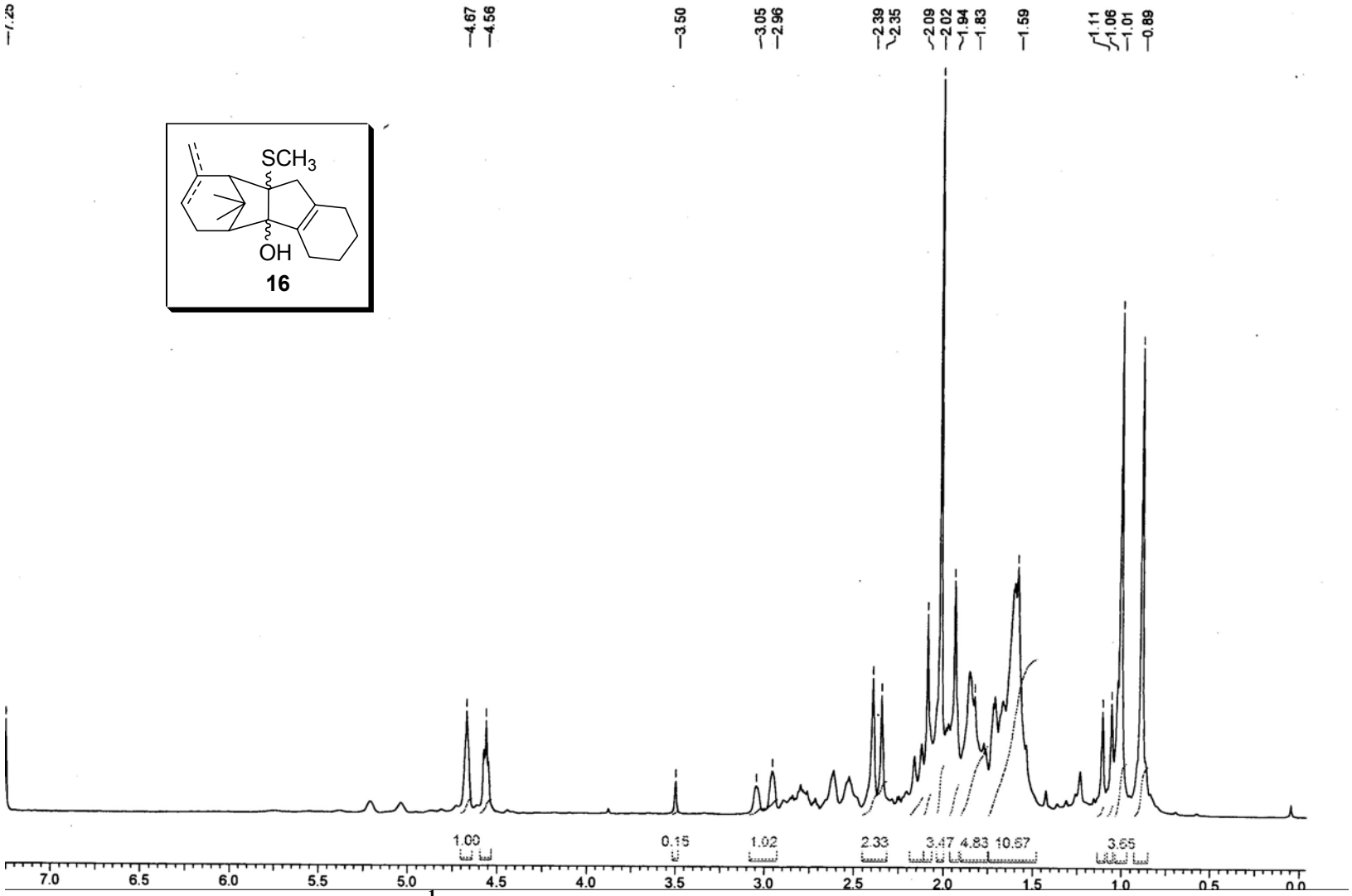
^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



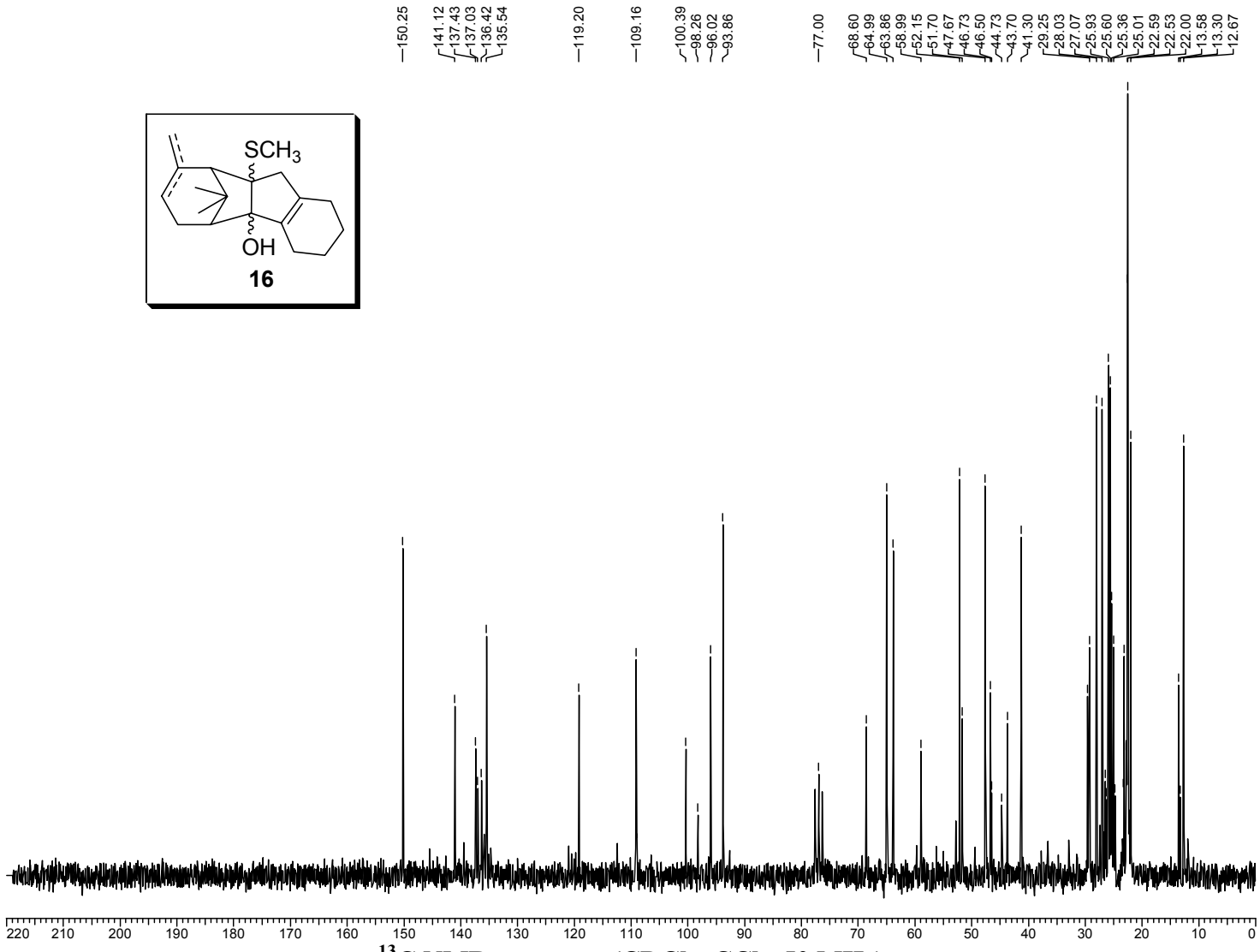
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



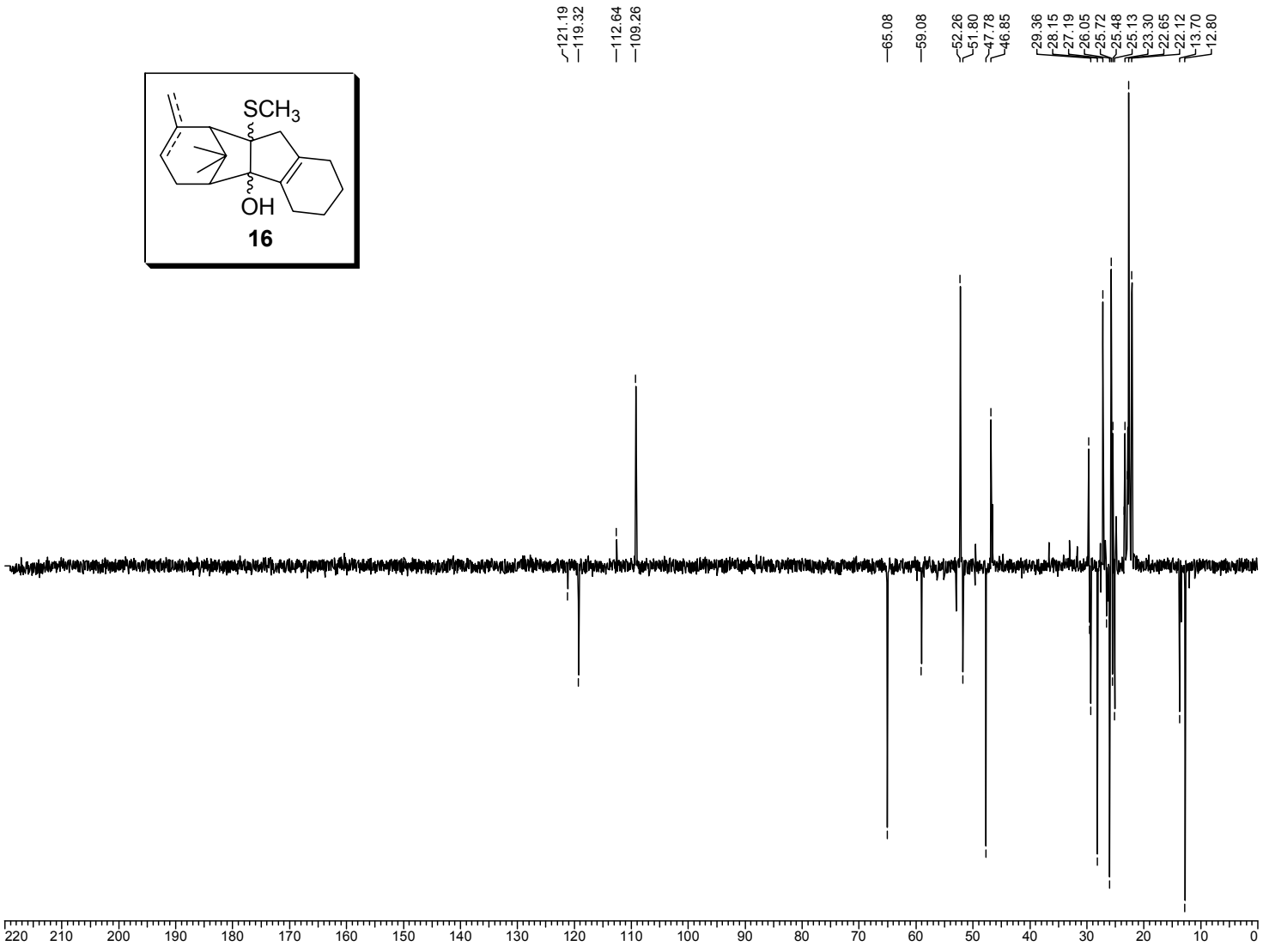
DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)



^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



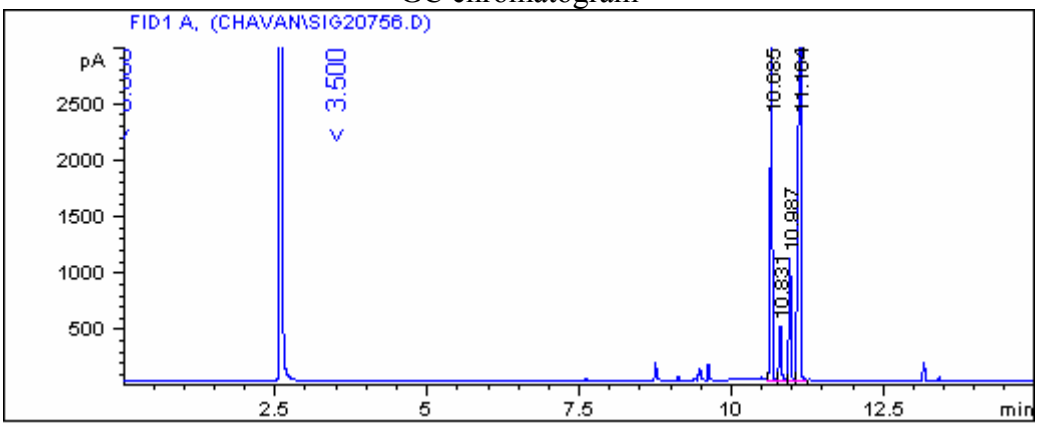
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



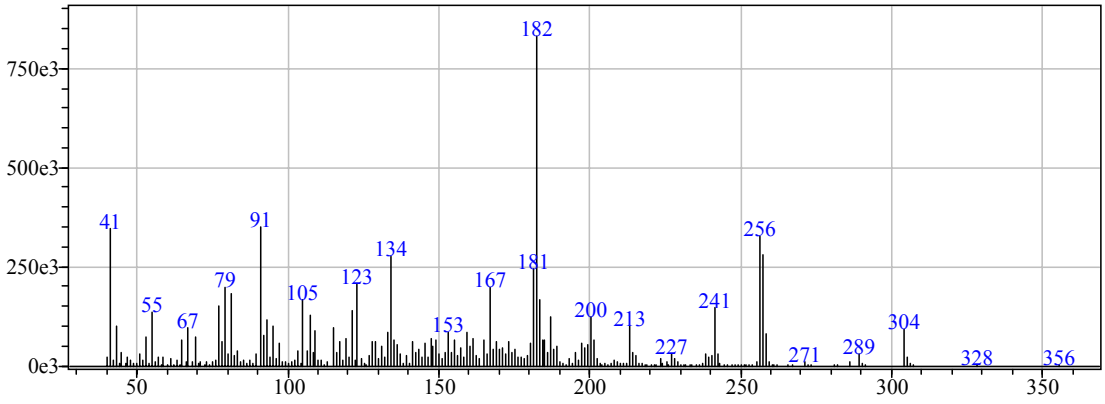
DEPT spectrum ($CDCl_3$, 50 MHz)

GCMS of 16

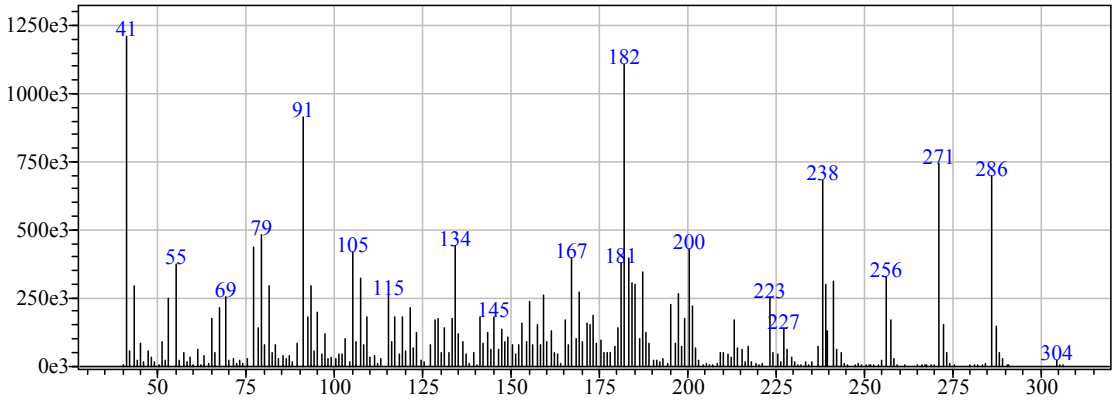
GC chromatogram



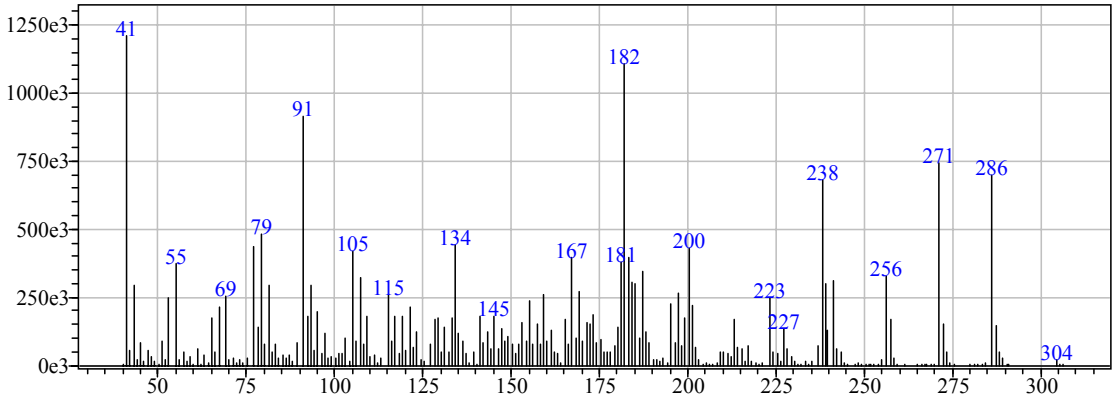
MS at retention time 10.6



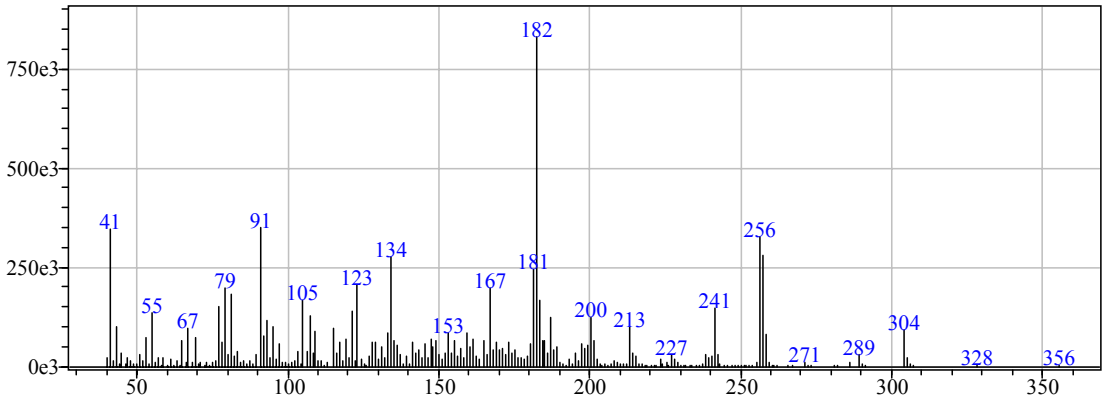
MS at retention time 10.8

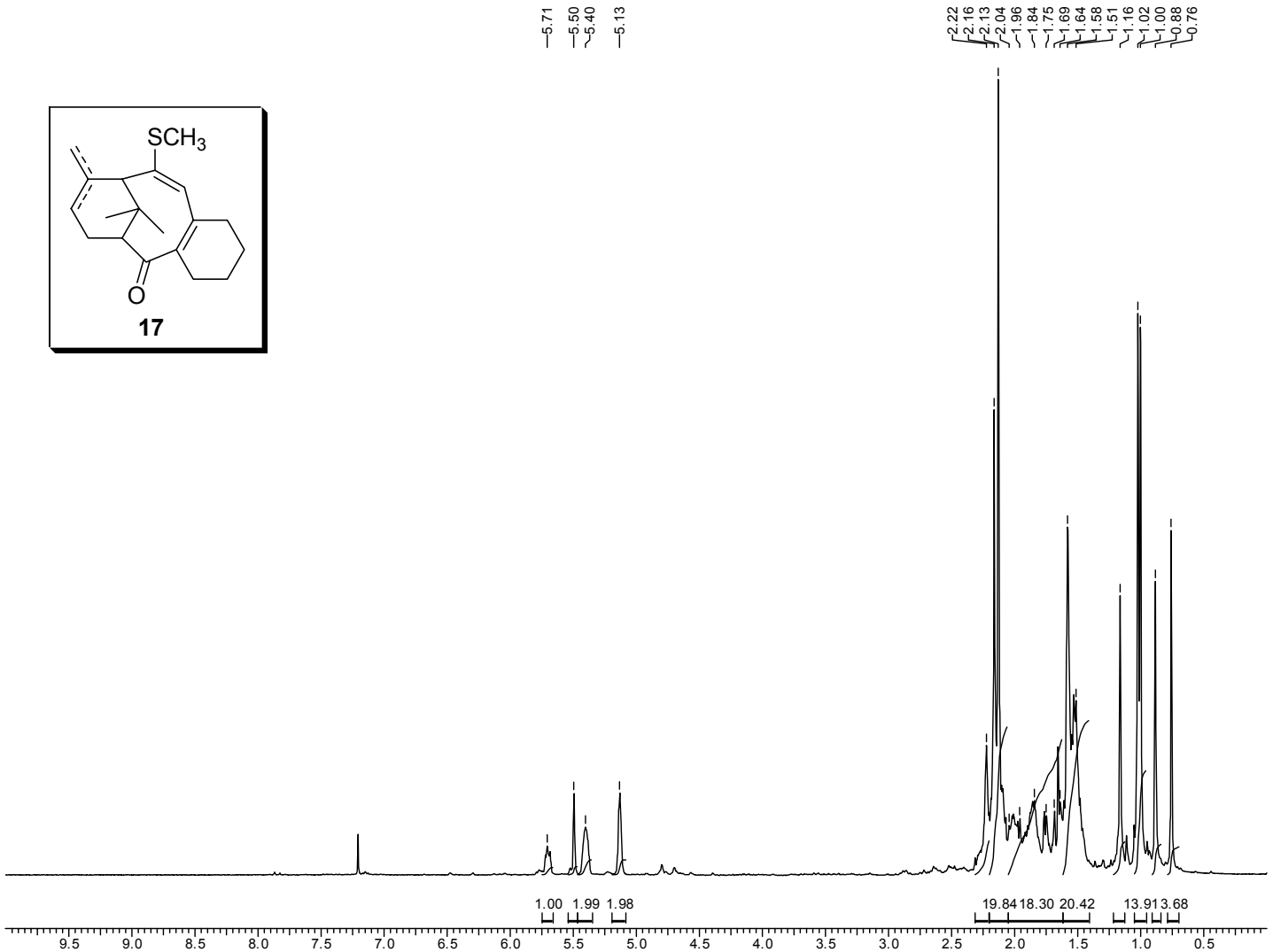


MS at retention time 10.9

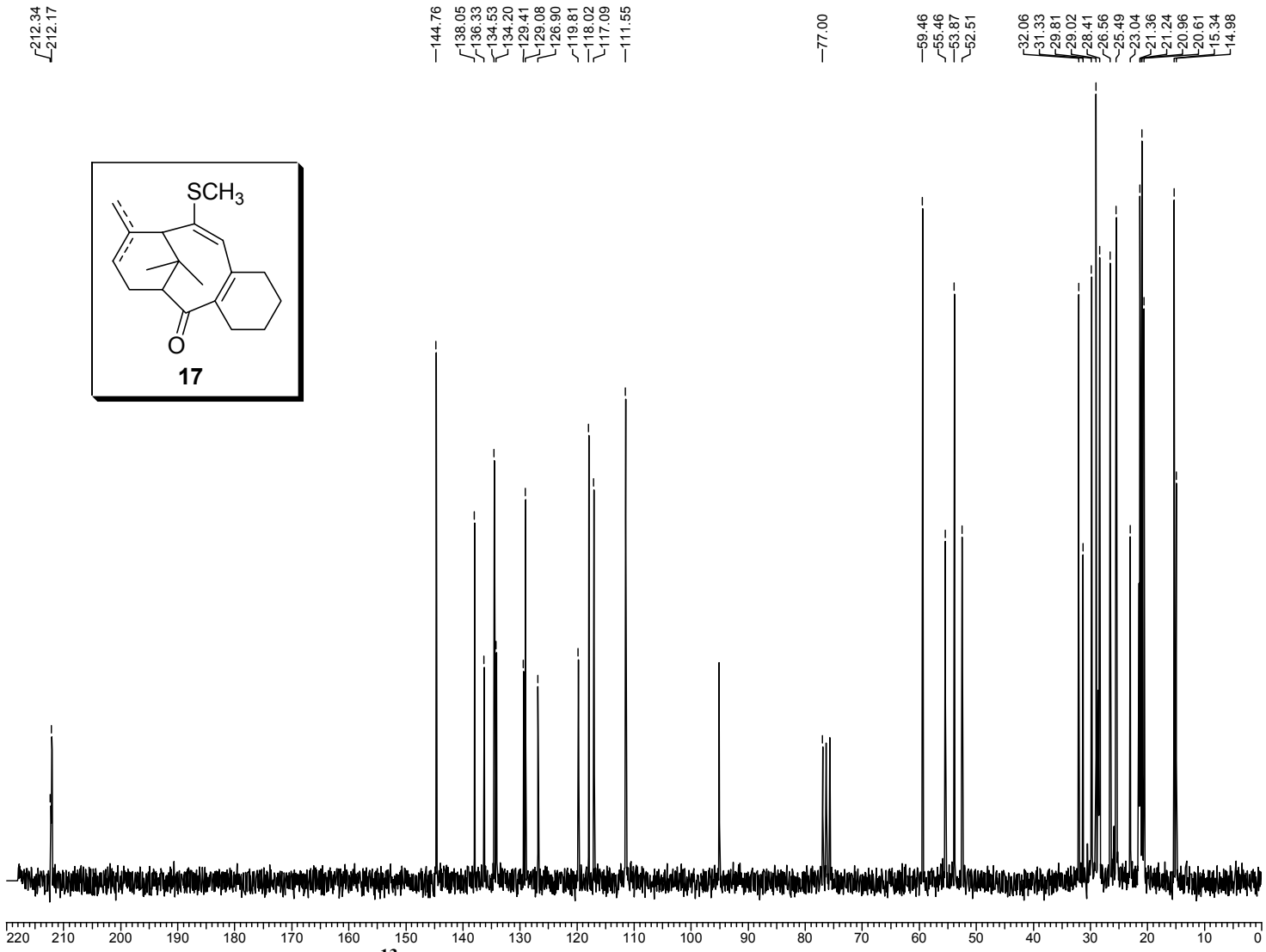


MS at retention time 11.1

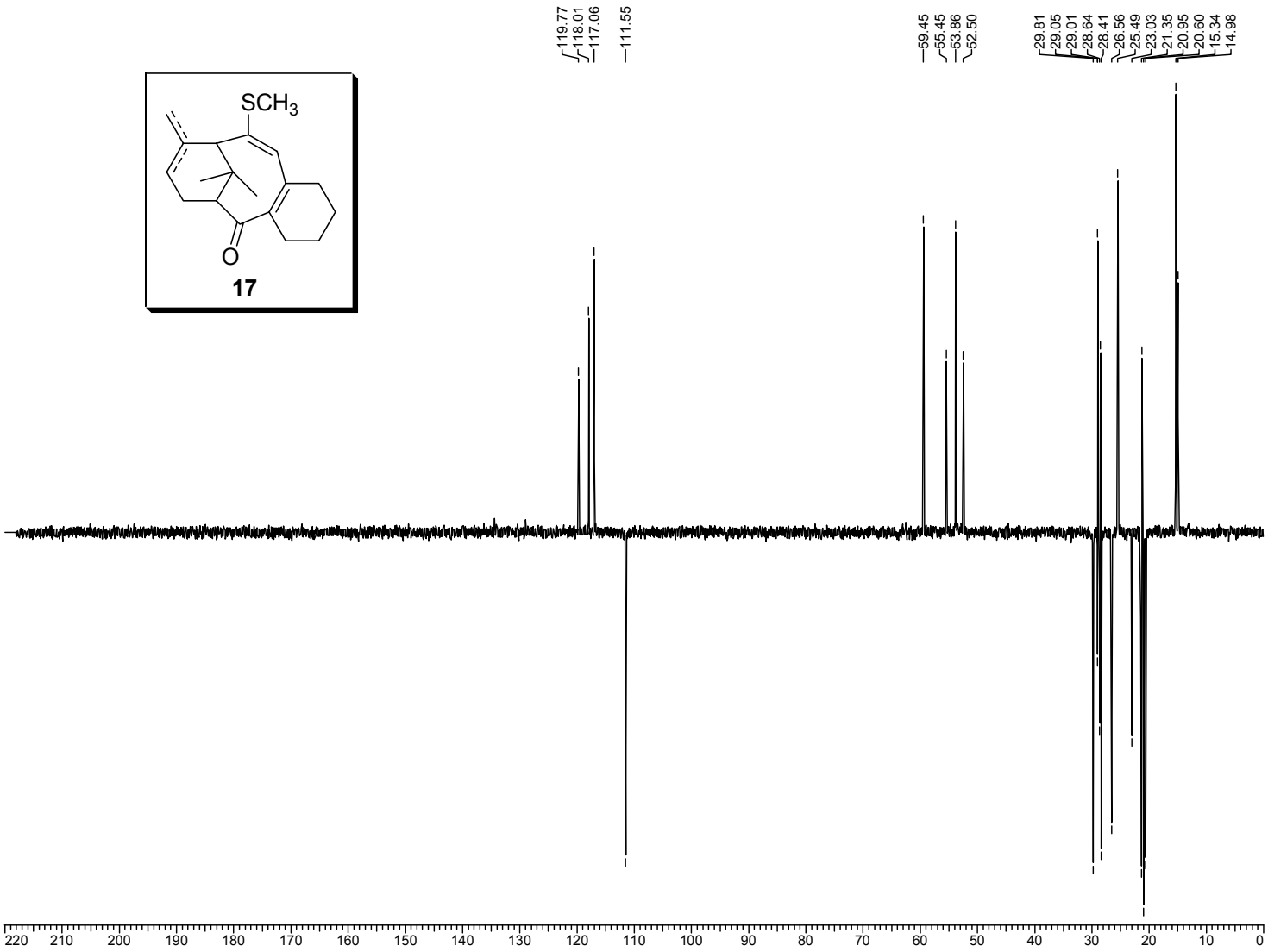




^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



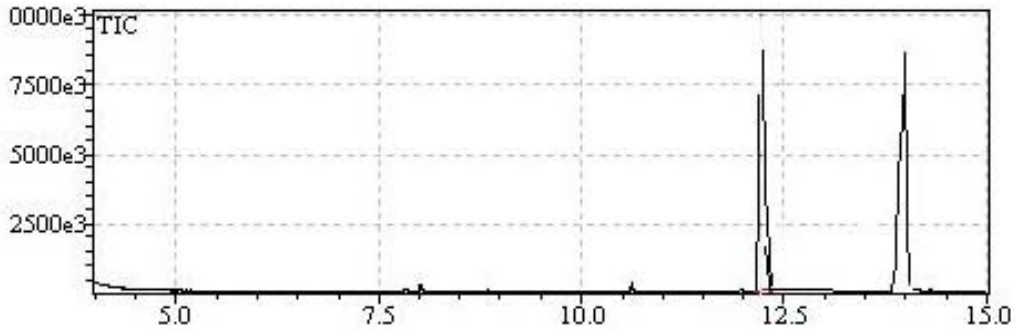
^{13}C NMR spectrum ($CDCl_3$+CCl_4, 50 MHz)



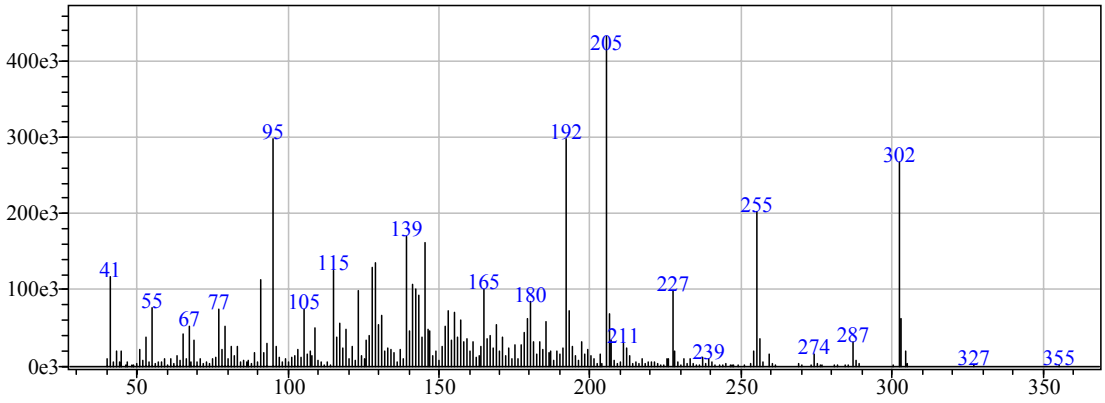
DEPT spectrum ($CDCl_3$+CCl_4, 50 MHz)

GCMS of 17

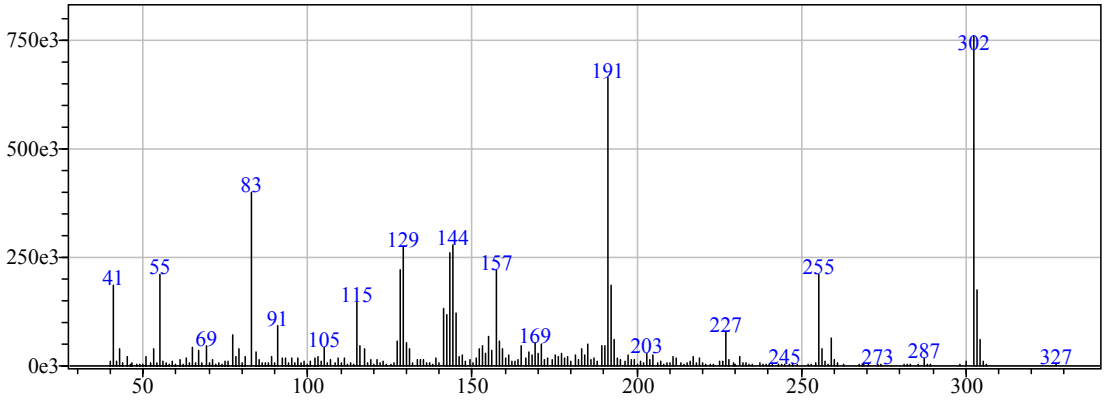
GC chromatogram

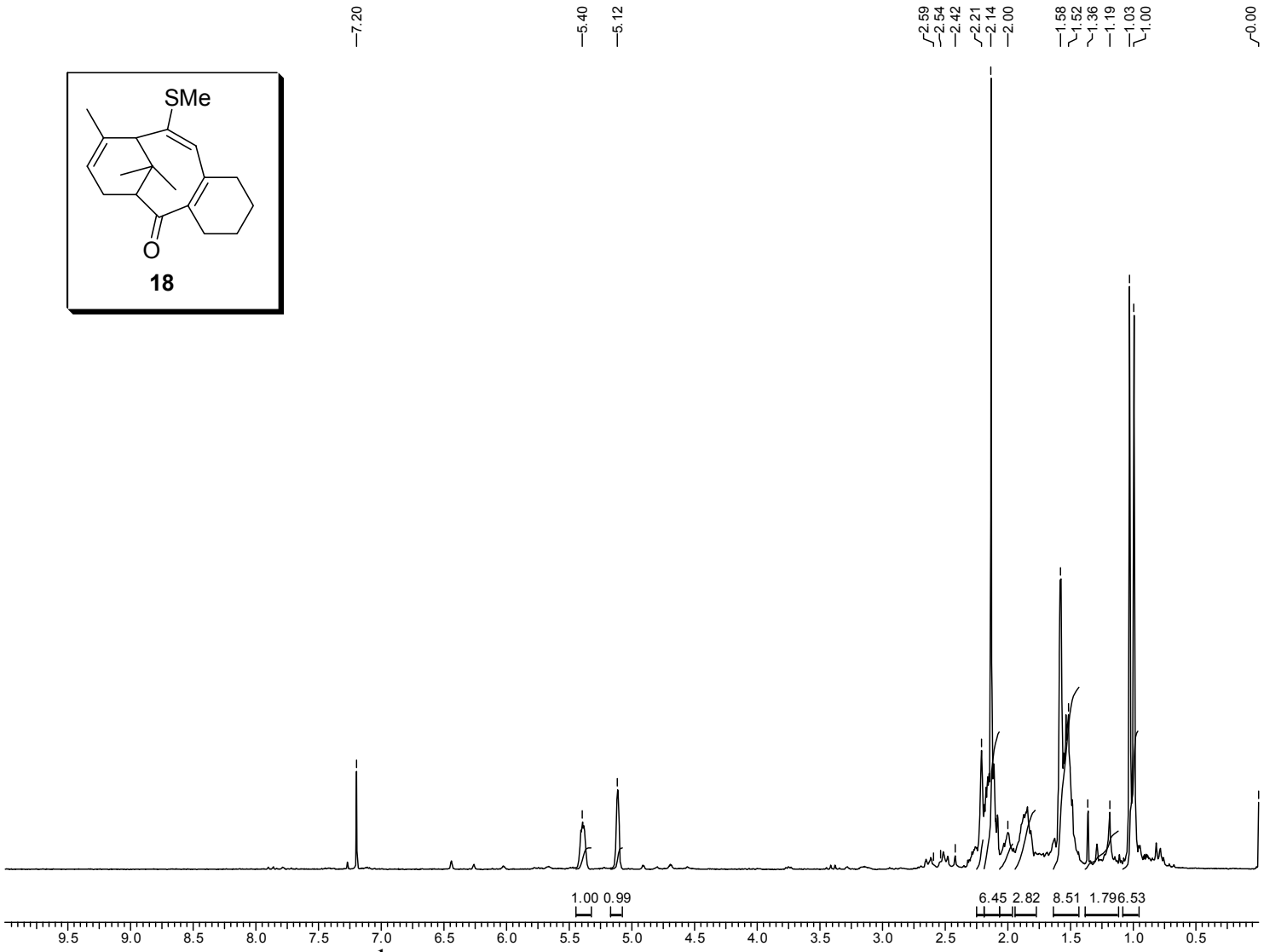


MS at retention time 12.3

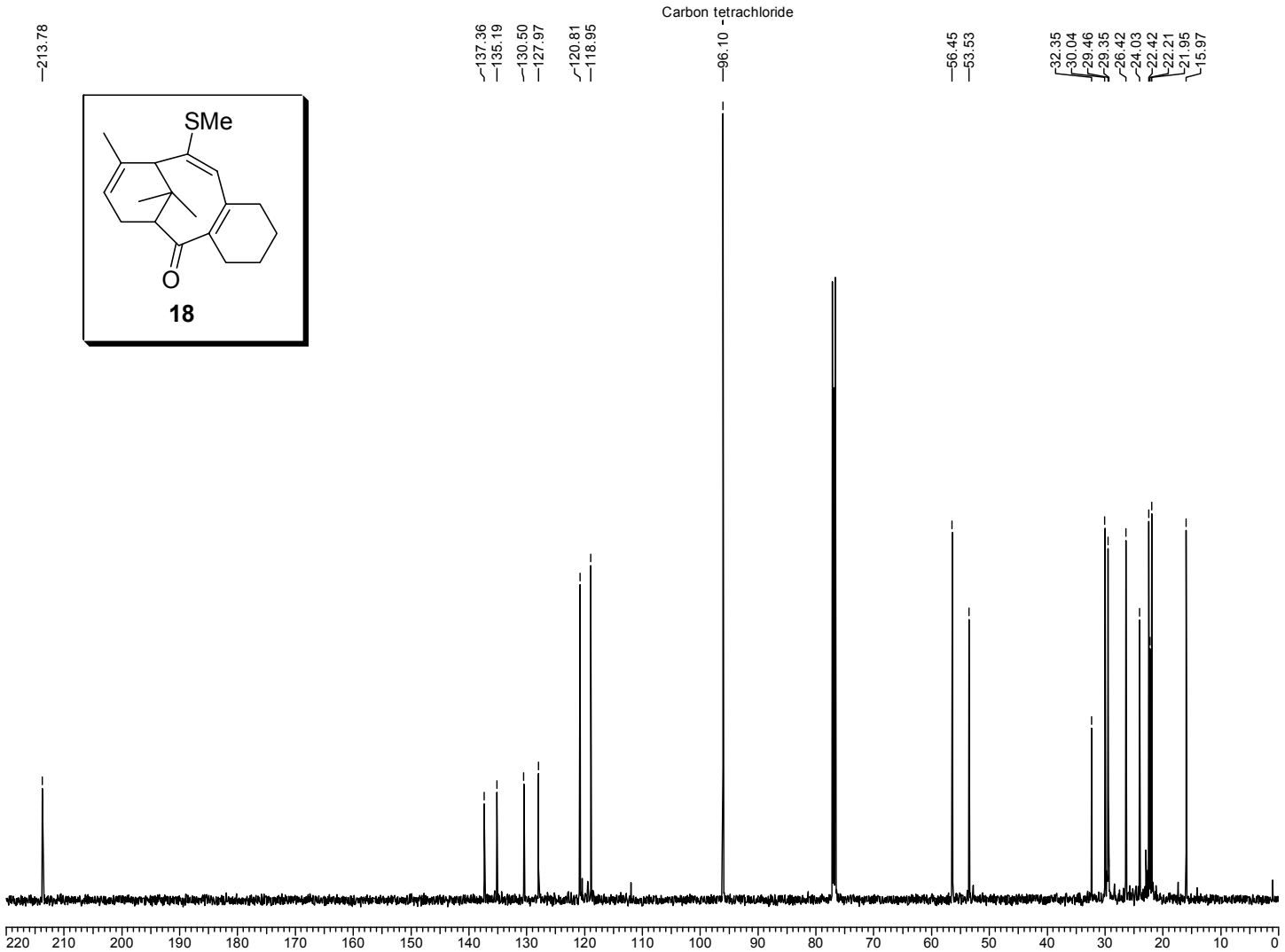


MS at retention time 14

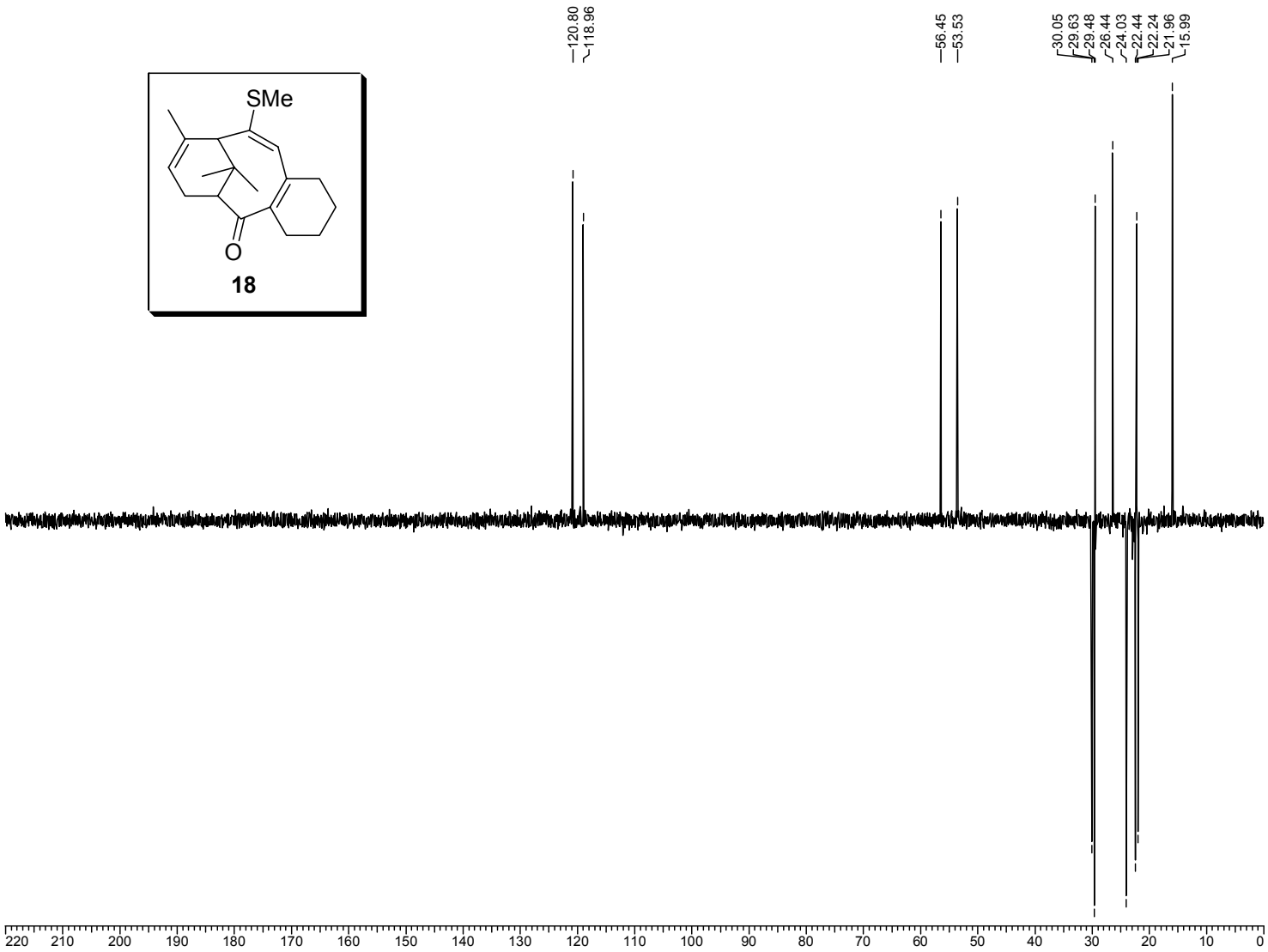




^{1}H NMR spectrum ($CDCl_3$+CCl_4, 200 MHz)



^{13}C NMR spectrum ($CDCl_3$+CCl_4, 125 MHz)



DEPT spectrum ($CDCl_3$+CCl_4, 125 MHz)