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Supporting Information

Synthetic Studies of Antitumor Natural Products Superstolides A and B. Construction of C20-C26 Fragment of Superstolide A

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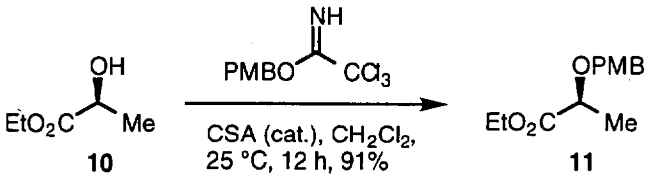
General Procedure

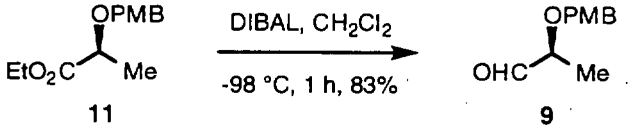
All moisture-sensitive reactions were performed in flame-dried glassware under positive pressure of nitrogen or argon. THF and ether were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Et_3N was distilled from CaH_2. Solvent for TLC and flash column chromatography was hexane with different ratio of ethyl acetate.

Experimental Section:

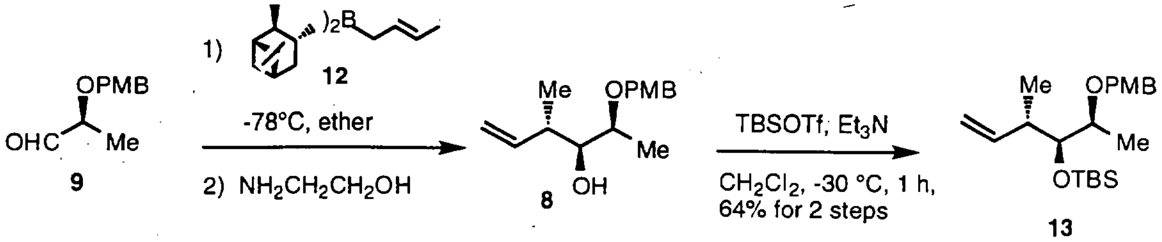


Compound 11. To a solution of ethyl (*S*)-(-)-lactate (5 mL, 44.1 mmol) in anhydrous CH_2Cl_2 (200 mL) was added *para*-methoxy benzyl trichloroacetimidate (57.33 mL, 1M in CH_2Cl_2, containing 3% DBU, 57.33 mmol) under nitrogen. CSA (1.06 g, 4.59 mmol) was added in one portion and the solution was stirred at 25 °C for 2 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (70 mL). The organic layer was separated and the water layer was extracted by CH_2Cl_2 (50 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was

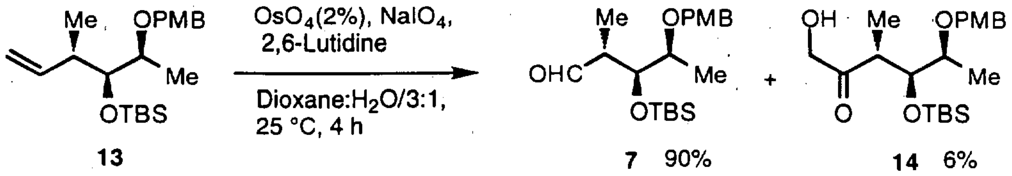
removed and the product was purified with silica gel column chromatography to afford **11** (9.57 g, 91%) as colorless oil. $[\alpha]^{25}_{D}$ -9.36° (*c* 1.1, $CHCl_3$); HR CIMS m/z 256.1552 $(M+NH_4)^+$, calcd for $C_{13}H_{22}NO_4$: 256.1549; ^1H NMR ($CDCl_3$) δ (ppm) 7.30 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.22 (qd, *J* = 6.8, 1.8 Hz, 2H). 4.05 (q, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.30 (q, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 173.3, 159.3, 129.7, 129.6, 113.8, 73.69, 71.6, 60.8, 55.3, 18.7, 14.2.



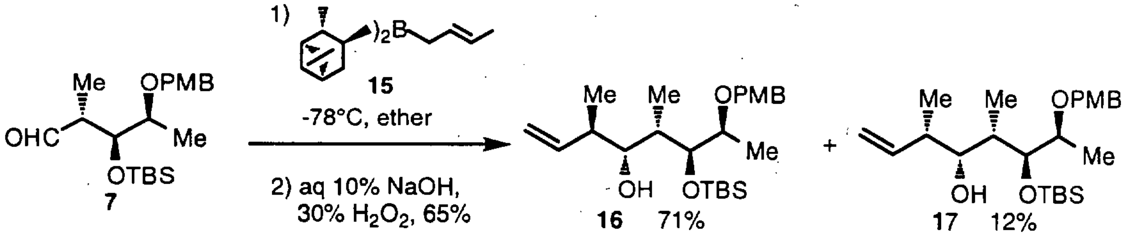
Compound 9. To a solution of **11** (7.1 g, 29.8 mmol) in CH_2Cl_2 (150 mL) was added DIBAL (1 M in CH_2Cl_2, 44.7 mL, 44.7 mmol) under nitrogen at -98 °C (Methanol/dry ice bath). The reaction was stirred at -98 °C for 1 hour and then was quenched with ethyl acetate (5 mL). Saturated aqueous sodium potassium tartrate (150 mL) was added and the reaction was allowed to warm up to room temperature. The organic layer was separated and the water layer was extracted by CH_2Cl_2 (50 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **9** (5.207g, 90%) as colorless oil. $[\alpha]^{24}_{D}$ -38.9 ° (*c* 2.96, $CHCl_3$); HR CIMS m/z 212.1267 $(M+NH_4)^+$, calcd for $C_{11}H_{18}NO_3$: 212.1287; ^1H NMR (C_6D_6) δ (ppm) 9.40 (d, *J* = 1.8 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.76 (d, *J* = 6.8 Hz, 2H), 4.25 (d, *J* = 11.5 Hz, 1H), 4.18 (d, *J* = 11.5 Hz, 1H), 3.44 (qd, *J* = 6.8, 2.2 Hz, 1H). 3.28 (s, 3H), 0.98 (d, *J* = 6.8 Hz); ^{13}C NMR (C_6D_6) δ (ppm) 202.5, 159.9, 130.1, 129.7, 114.1, 79.3, 71.6, 54.7, 15.2.



Compound 13. A balloon was charged with about 800 mL of *trans*-butene and was connected to a 250 mL flame-dried flask merged in dry ice/acetone bath (-78 °C) through a 12 inch needle. The *trans*-butene was released slowly to the flask. After all the *rans*-butene was released, the balloon was removed, and *t*-BuOK (1 M in THF, 27.89 mL) and *n*-BuLi (2.28 M in hexane, 12.2 mL) was added very slowly in -78 °C. The solution was then stirred at -45 °C for 10 min and cooled to -78 °C again. (-)-B-Methoxy-diisopinocampheyborane (8.82 g, 27.89 mmol) in ether (25 mL) was cannulated to the above solution and the reaction was stirred at -78 °C for 30 min. $BF_3 \cdot Et_2O$ (4.7 mL, 37.09 mmol) was added followed by the addition of **9** (3.87 g, 19.9 mmol) in ether (20 mL, washed with 5 mL ether once). After the reaction solution was stirred at -78 °C for three hours, pentane (150 mL) and ethanol amine (3 mL, 41.84 mmol) was added and the reaction was allowed to warmed up to 25 °C. After the reaction was stirred at 25 °C for 2 hours, the stirring was stopped and the reaction solution was allowed to sit for 30 minutes. The reaction solution was filtered through a thin layer of celite and the solid was washed by pentane (30 mL) three times. The solvent was removed and the reaction mixture was separated by silica gel chromatography to give a mixture of **9** and 3-pinanol in the molar ratio of 1:0.6. This mixture was dissolved in anhydrous CH_2Cl_2 (50 mL). Et_3N (5 mL, 36 mmol) and TBSOTf (6.3 mL, 27.47 mmol) was added at -30 °C. The reaction was stirred at -30 °C for 1 hour and was quenched with saturated aqueous $NaHCO_3$ (70 mL). The organic layer was separated and the water layer was extracted by CH_2Cl_2 (10 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **13** (4.72 g, 65% from **9**) as colorless oil. $[\alpha]^{24}_D$ +7.4° (*c* 4.5, $CHCl_3$); HR CIMS m/z 382.2787 $(M+NH_4)^+$, calcd for $C_{21}H_{40}NO_3Si$: 382.2777; ^1H NMR ($CDCl_3$) δ (ppm) 7.26 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.92 (m, 1H), 4.98 (d, *J* = 17.3 Hz, 1H), 4.96 (d, *J* = 10.3 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 3.51 (m, 1H), 3.41 (m, 1H), 2.43 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 1H), 0.90 (s, 9H), 0.03 (s, 3H), -0.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 173.3, 159.3, 129.7, 129.6 (2C), 113.8 (2C), 73.69, 71.6, 60.8, 55.3, 18.7, 14.2.



Compound 7. To a solution of **13** (296.1 mg, 0.812 mmol) in dioxane-water (3:1, 8 mL) was added 2,6-lutidine (0.192 mL, 1.65 mmol), OsO_4 (2.5% in 2-methyl-2-propanol, 162 mg, 0.016 mmol), and $NaIO_4$ (704 mg, 3.29 mmol). The reaction was stirred at 25 °C for 2 hours, and water (10 mL) and CH_2Cl_2 (20 mL) was added. The organic layer was separated and the water layer was extracted by CH_2Cl_2 (10 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **7** (268.1 mg, 90%).as colorless oil. $[\alpha]^{24}_D$ -22.7° (*c* 0.68, $CHCl_3$); HR CIMS m/z 384.2535 $(M+NH_4)^+$, calcd for $C_{20}H_{38}NO_4Si$: 384.2570; ^1H NMR ($CDCl_3$) δ (ppm) 9.77 (d, *J* = 2.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 3.88 (t, *J* = 4.5 Hz, 1H), 3.81 (s, 3H), 3.56 (m, 1H), 2.65 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 3H), -0.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 202.8, 159.7, 131.0, 129.4, 114.0, 77.2, 76.8, 70.8, 54.7, 48.8, 26.0, 18.3, 14.8, 12.4, -4.1, -4.7.



Compounds 16 and 17. A balloon was charged with about 60 mL of *trans*-butene and was connected to a 25 mL flame-dried flask merged in dry ice/acetone bath (-78 °C) through a 12 inch needle. The *trans*-butene was released slowly to the flask. After all the *trans*-butene was released, the balloon was removed and *t*-BuOK (1 M in THF, 1.6 mL) and *n*-BuLi (2.28 M in hexane, 0.7 mL) was added very slowly in -78 °C. The solution was then stirred at -45 °C for 10 min and cooled to -78 °C again. (+)-B-Methoxydiisopinocampheyborane (510 mg, 1.6 mmol) in ether (3 mL) was cannulated to the above solution and it was stirred at -78 °C for 30 min. $BF_3 \cdot Et_2O$ (0.264 mL, 2.08 mmol) was added followed by addition of **13** (370 mg, 1.01 mmol) in ether (2 mL, washed with 0.5 mL ether once). After the reaction solution was stirred at -78 °C for three hours, NaOH (10% in water, 0.64 mL) was added and the reaction was allowed to warm up to 25 °C.[1] H_2O_2 (37%, 1 mL) was added and a condenser was attached. The reaction solution was heated to 40 °C for 12 hours. NaOH (10% in water, 1 mL) was added and the solution was stirred at 25 °C for 30 min. Water (3 mL) and ether (3 mL) was added. The organic layer was separated and the water layer was extracted by ether (5 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **16** (302 mg, 71%) and **17** (50.1 mg, 11%).

16: colorless oil, $[\alpha]^{23}_D$ +16.4° (*c* 0.73, $CHCl_3$); HR ESIMS m/z 445.2719 $(M+Na)^+$, calcd for $C_{24}H_{42}NaO_4Si$: 445.2745; ^1H NMR ($CDCl_3$) δ (ppm) 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.89 (m, 1H), 5.10 (d, *J* = 17.3 Hz, 1H), 5.07 (d, *J* = 10 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 3.71 (dd, *J* = 7.0, 3.2 Hz, 1H), 3.66~3.61 (m, 2H), 2.26 (m, 1H), 1.91 (m, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.064 9s, 3H), 0.003 (s, 3H). 1.14 (d, *J* = 6.2 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 159.0, 142.5, 130.9, 129.0, 114.3, 113.6, 81.0, 77.6, 74.8, 70.6, 55.2, 41.3, 34.8, 26.1, 18.3, 16.3, 15.6, 11.1, -4.0, -4.7.

17: colorless oil, ^1H NMR ($CDCl_3$) δ (ppm) 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.56 (m, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 10.3 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 3.63~3.57 (m, 2H), 3.48 (q, *J* = 7.0 Hz, 1H), 2.27 (m, 1H), 1.89 (m, 1H), 1.10 (m, 6H), 1.03 (d, *J* = 7 Hz, 3H), 0.88 (s, 9H), 0.064 9s, 3H), 0.003 (s, 3H). 1.18 (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 3H), 0.06 (s, 3H).

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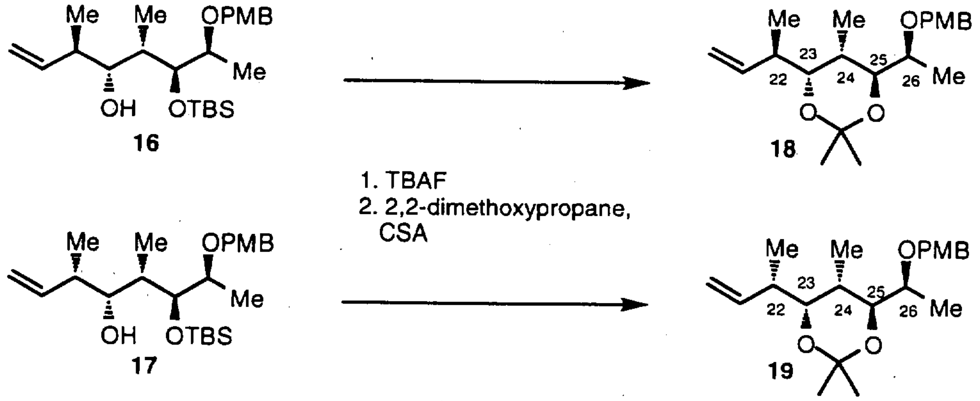
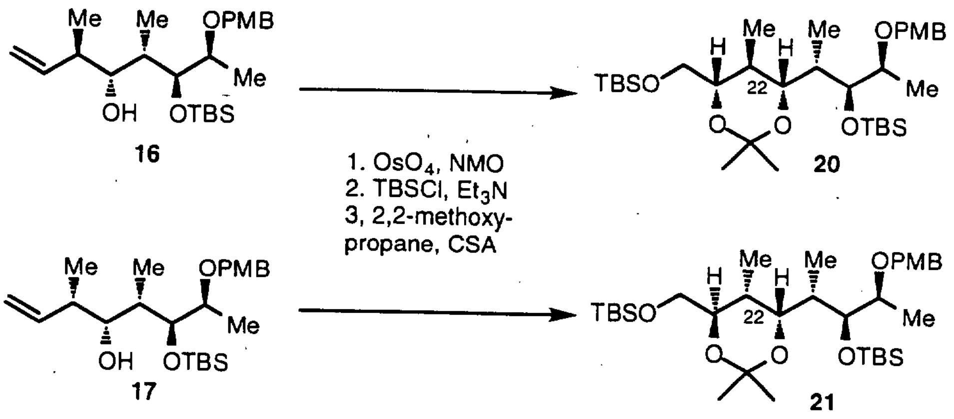
[1] Addition of excess base leaded to the vigorous decomposition of H_2O_2, therefore lead to low yield of the product.



Compounds 18 and 19. To a solution of **16** (20 mg) or **17** (20 mg) in THF was added TBAF in THF (1M in THF, 1.2 equiv.) at 25 °C and the reaction was stirred at 25 °C for 2 hours. Solvent was removed and the products were purified with silica gel column chromatography to afford the corresponding alcohol in about 85% yield. The alcohol was dissolved in CH_2Cl_2. 2,2-Methoxypropane (3 equiv.) and CSA (catalytic amount) were added. After the reaction was stirred at 25 °C for 30 min, the solvent was removed and the product was purified with silica gel column chromatography to afford **18** (from **16**) and **19** (from **17**) in about 80% yield for two steps.

18: colorless oil, ^{1}H NMR ($CDCl_3$) δ (ppm) 7.27 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.86 (m, 1H), 5.06 (d, *J* = 17.3 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 3.80 (s, 3H), 3.57 (m, 1H), 3.45 (dd, *J* = 10.4, 4 Hz, 1H), 3.31 (dd, *J* = 7.2, 3.3 Hz, 1H), 2.25 (m, 1H) 2.03 (m, 1H), 1.31 (s, 3H), 1.33 (s, 3H), 1.20 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 159.1, 142.2, 130.9, 129.3, 113.6, 113.3, 100.8, 74.4, 73.4, 70.9, 55.3, 37.0, 33.2, 25.2, 23.5, 15.7, 15.3, 12.1.

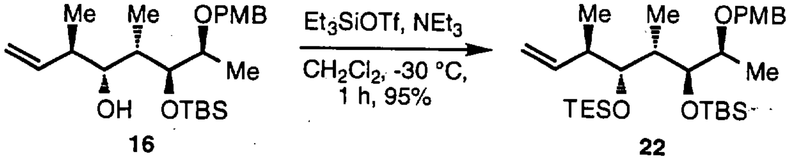
19: colorless oil, ^{1}H NMR ($CDCl_3$) δ (ppm) 7.25 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.65 (m, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.46 (d, *J* = 11.7 Hz, 1H), 3.80 (s, 3H), 3.54 (m, 1H), 3.45 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.31 (dd, *J* = 7.1, 4.3 Hz, 1H), 2.27 (m, 1H) 1.98 (m, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 159.1, 140.2, 131.0, 129.3, 115.0, 113.6, 100.7, 77.6, 74.6, 73.2, 71.0, 55.3, 38.2, 33.8, 25.3, 23.5, 17.8, 15.4, 12.4.



Compounds 20 and 21. To a solution of **16** (20 mg) or **17** (20 mg) in acetone-water (10:1) was added OsO_4 (2.5% in 2-methyl-2-propanol, 3%) and NMO (6 equiv.). The reaction was stirred at 25 °C for 3 hours (for **16**) or 12 hours (for **17**). Water and CH_2Cl_2 was added. The organic layer was separated. The water layer was extracted by CH_2Cl_2 for three times. The combined organic layer dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford the corresponding triol (in the case of **16**, two isomers were obtained in a ration of about 2:1. The major isomer was used in the next step. In the case of **17**, one isomer is by far the main product and the minor isomer was not obtained). To the triol was added anhydrous CH_2Cl_2, imidazole (1.5 equiv.) and TBSCl (1.3 equiv.) at 0 °C. After the reaction was stirred at 0 °C for 1 hour, $NaHCO_3$ was added. After standard work up with CH_2Cl_2, the product was purified with silica gel column chromatography to afford the corresponding diol in about 90% yields. The diols were dissolved in anhydrous CH_2Cl_2. 2,2-Methoxypropane (3 equiv.) and CSA (catalytic amount) was added. After the reaction was stirred at 25 °C for 30 min, the solvent was removed and the product was purified with silica gel column chromatography to afford **20** (from **16**) and **21** (from **17**) in about 90% yields.

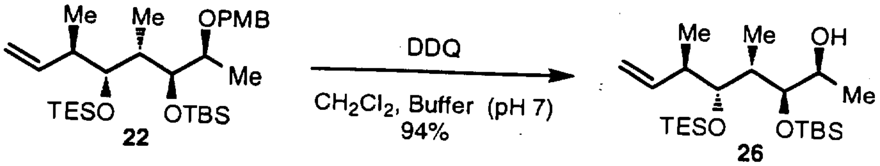
20: colorless oil, ^1H NMR ($CDCl_3$) δ (ppm) 7.27 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 4.47 (s, 2H), 3.80 (s, 3H), 3.79~3.61 (m, 5H), 3.50 (m, 1H), 1.83 (m, 1H), 1.62 (m, 1H), 1.40 (s, 3H), 1.35 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.78 (d, *J* = 6.6 Hz, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), -0.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 159.0, 131.2, 129.0, 113.7, 97.3, 75.6, 73.0, 72.6, 70.4, 65.7, 55.3, 37.2, 30.6, 30.0, 26.1, 26.0, 20.5, 18.3, 13.8. 12.6, 9.0, -3.6, -4.2, -5.1.

21: colorless oil, ^{1}H NMR ($CDCl_3$) δ (ppm) 7.25 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 3.75 (dd, *J* = 4.2, 9.9 Hz, 1H), 3.61~3.47 (m, 4H), 3.32 (m, 1H), 1.91 (m, 1H), 1.74 (m, 1H), 1.33 (s, 3H), 1.30 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 18H), 0.05 (s, 9H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 158.9, 131.2, 129.0, 113.6, 100.6, 76.9, 76.4, 75.0, 70.2, 65.6, 55.2, 38.3, 35.4, 26.0, 25.9, 23.8, 20.5, 18.4, 18.2, 16.2, 13.1, 12.5, -4.3, -4.4, -5.1, -5.2.

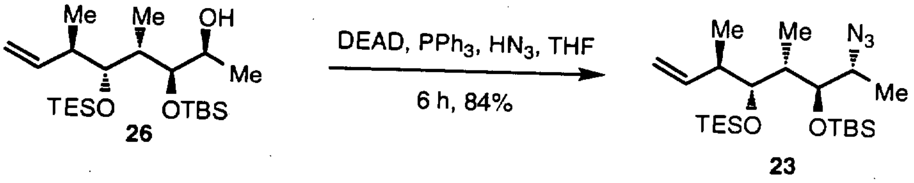


16 **22**

Compound 22. To a solution of **16** (1.12 g, 2.65 mmol) in anhydrous CH_2Cl_2 (15 mL) was added Et_3N (0.6 mL, 4.24 mmol) and TESOTf (0.78 mL, 3.44 mL) in -50 °C. The reaction was gradually warm up to -30 °C and stirred at -30 °C for one hour. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated and the water layer was extracted by CH_2Cl_2 (10 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **22** (1.348 g, 95%) as colorless oil. $[\alpha]^{26}_{D}$ -4.17° (*c* 2.6, $CHCl_3$). HR FABMS m/z 559.3570 $(M+Na)^+$, calcd for $C_{30}H_{56}NaO_4Si_2$: 559.3615; ^{1}H NMR ($CDCl_3$) δ (ppm) 7.26 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.88 (m, 1H), 5.00 (d, *J* = 15.1 Hz, 1H), 4.99 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 3H), 3.81 (overlap, 1H), 3.68 (dd, *J* = 7.6, 3.4 Hz, 1H), 3.57 (m, 1H), 2.34 (m, 1H), 1.83 (m, 1H), 1.19 (d, *J* = 6.5 Hz), 1.00~0.95 (m, 15H), 0.89 (s, 9H), 0.63(q, *J* = 8.0, 6H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 158.9, 141.5, 131.2, 129.0, 114.3, 113.6, 77.1, 76.5, 75.2, 55.2, 43.5, 40.5, 26.0, 18.3, 17.8, 14.8, 11.9, 7.2, 5.8, -3.9, -4.0.



Compound 26. To a solution of **22** (306.5 mg, 0.571 mmol) in a mixture of CH_2Cl_2 (4 mL) and buffer (pH=7, 4 mL) was added DDQ (197 mg, 0.87 mmol). The reaction was stirred at 25 °C for 4 hours and then was quenched with saturated aqueous Na_2SO_3 (3 mL). The organic layer was separated and the water layer was extracted by CH_2Cl_2 (5 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **26** (223 mg, 94%) as colorless oil; $[\alpha]^{23}_{D}$ 12.2° (*c* 1.0, $CHCl_3$). HR FABMS m/z 417.3225 $(M+H)^+$, calcd for $C_{22}H_{49}O_3Si_2$: 417.3220; ^1H NMR ($CDCl_3$) δ (ppm) 5.89 (m, 1H), 5.06 (d, *J* = 17.4 Hz, 1H), 5.03 (d, *J* = 9.4 Hz, 1H), 3.71 (m, 1H), 3.55~3.51 (m, 2H), 2.46(d, *J* = 8.7 Hz, 1H), 2.26 (m, 1H), 1.77 (m, 1H), 1.13 (d, *J* = 6.4 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H),0.98 (t, *J* = 7.7 Hz, 9H), 0.92 (s, 9H), 0.65(q, *J* = 7.7 Hz, 6H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 140.2, 115, 78.0, 75.3, 66.1, 42.7, 42.6, 25.9, 22.7, 18.1, 17.5, 11.6, 7.1, 5.6, -3.9, -4.8.



Compound 23. To a solution of PPh_3 (196 mg, 0.749 mmol) and HN_3 (1.6 mL) in THF (1 mL) was added DEAD (0.118 mL, 0.749 mmol) dropwise at 25 °C water bath.[2] Then **26** (132 mg, 0.32 mmol) in THF (1 mL) was cannulated to the

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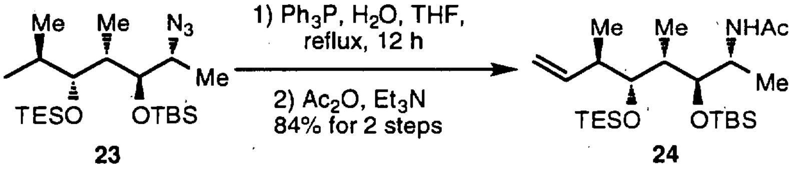
[2] HN_3 was prepared in the day before. It was dried over Na_2SO_4 overnight in a sealed flask and was dried further over MS3A for 30 min. before use. HN_3 which was not prepared according to

above solution.[3] The reaction was stirred at 25 °C for 5 hours and the solvent was removed. The product was purified with silica gel column chromatography to afford **23** (116.3 mg, 84%) as colorless oil. $[\alpha]^{24}_D$ -3.8° (*c* 1.7, $CHCl_3$). HR FABMS m/z 442.3283 $(M+H)^+$, calcd for $C_{22}H_{48}N_3O_2Si_2$: 442.3285; ^1H NMR ($CDCl_3$) δ (ppm) 5.88 (m, 1H), 5.04 (d, *J* = 15.5 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 3.73(dd, *J* = 5.8, 3.2 Hz, 1H), 3.62 (m, 1H), 3.55 (m, 1H), 2.35 (m, 1H), 1.72 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H),0.98 (t, *J* = 7.9 Hz, 9H), 0.98 (overlap, 3H), 0.90 (s, 9H), 0.64(q, *J* = 7.9, 6H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 140.9, 115.2, 77.3, 75.8, 59.1, 43.7, 42.8, 26.2, 18.5, 17.9, 14.1, 11.5, 7.4, 6.1, -4.0.



Compound 24. A mixture of **23** (84.3 mg, 0.191 mmol), triphenylphosphine (73 mg, 0.277 mmol) and water (two drops) in THF (2 mL) was heated to reflux for 12 hours. Then the solvent was removed. the water was carefully removed by adding 0.5 mL benzene and removing the benzene under rotary evaporator. This process was repeated twice. Anhydrous CH_2Cl_2 (2 mL) was added and followed by addition of Et_3N (0.3 mL, 2.13 mmol) and Ac_2O (0.03 mL, 0.32 mmol). The reaction was stirred at 25 °C for 30 min. The solvent was removed and the product was purified with silica gel column chromatography to afford **24** (74.3 mg, 85%) as white solid. $[\alpha]^{25}_D$ +24.0° (*c* 1.7, $CHCl_3$). HR FABMS m/z 480.3286 $(M+H)^+$, calcd for $C_{24}H_{51}NO_3Si_2$: 480.3305; ^1H NMR ($CDCl_3$) δ (ppm) 5.87 (m, 1H), 5.50 (d. *J* = 7.6 Hz, 1H), 5.03 (d, *J* = 16.6 Hz, 1H), 5.02 (d, *J* = 11.5 Hz, 1H), 4.02 (m, 1H), 3.75(dd, *J* = 6.3, 2.1 Hz, 1H), 3.62 (dd, *J* = 6.8, 2.9 Hz, 1H), 2.51 (m, 1H), 1.94 (s, 3H), 1.78 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H),0.98 (t, *J* = 7.9 Hz, 9H), 0.95 (overlap, 3H), 0.92 (s, 9H),

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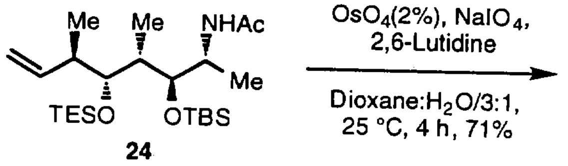
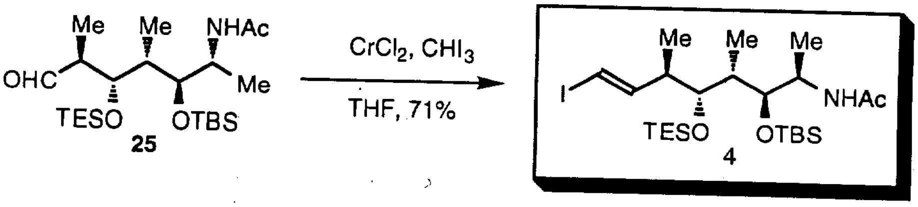
this procedure will give uncertain results, either lead to the significant formation of the intramolecular silyl transfer product or lead to no reaction.

[3] Premixing the alcohol with PPh_3 and HN_3 before the addition of DEAD give slightly higher ratio of intramolecular silyl transfer product.

0.65(q, J = 7.9, 6H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 168.3, 140.5, 114.9, 74.9, 46.9, 42.6, 41.7, 25.9, 23.5, 18.3, 17.7, 15.5, 11.6, 7.1, 5.7, -3.9, -4.7.

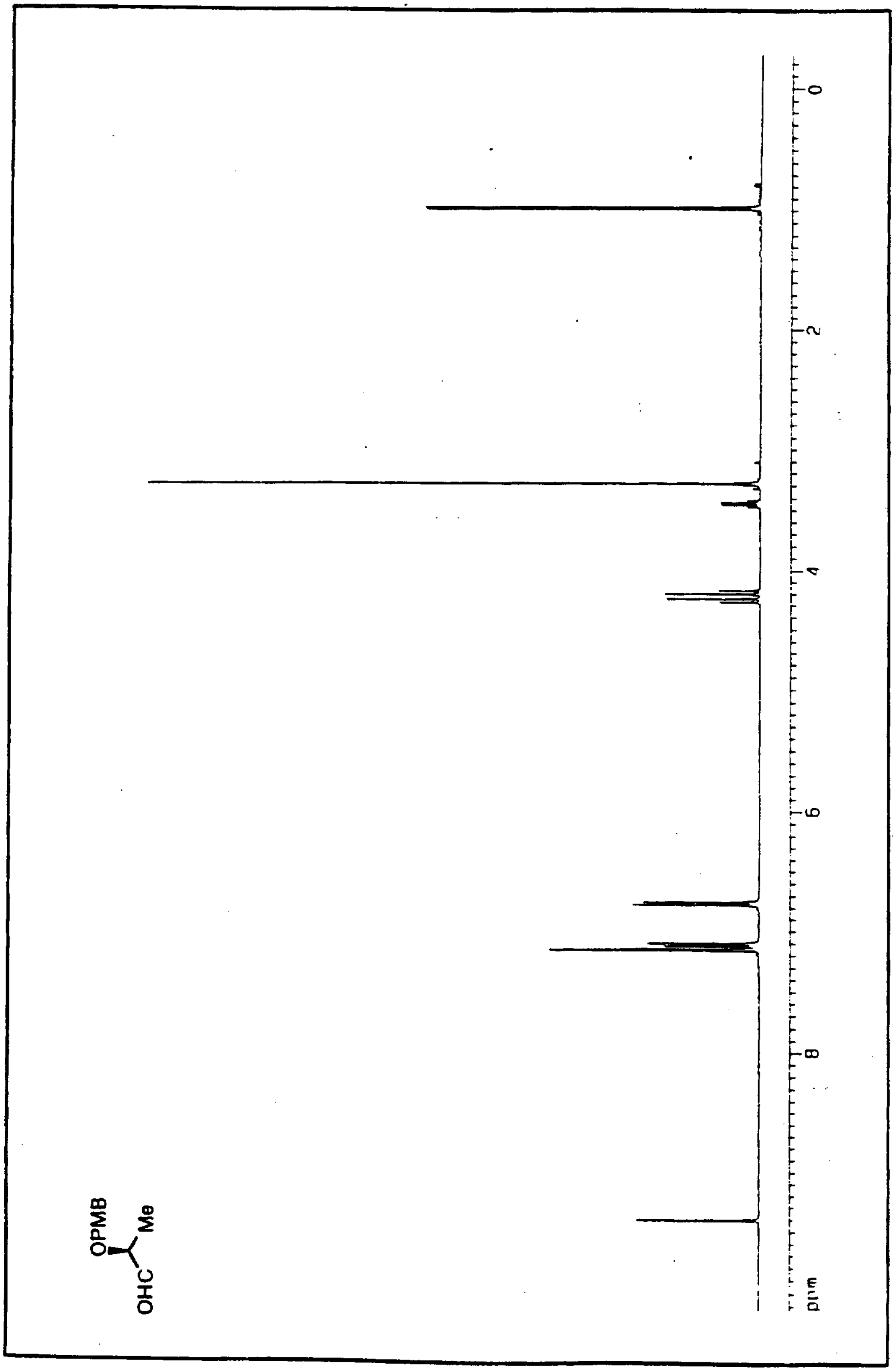


Compound 25. To a solution of **24** (32.3 mg, 0.07 mmol) in 1,4 dioxane-water (3:1,1.5 mL) was added 2,6-lutidine (0.016 mL, 0.14 mmol), OsO_4 (2.5% in 2-methyl-2-propanol, 28 μL, 0.003 mmol), and $NaIO_4$ (75 mg). The reaction was stirred at 25 °C for 7 hours and then water (2 mL) and CH_2Cl_2 (3 mL) was added. The organic layer was separated and the water layer was extracted by CH_2Cl_2 (3 mL) for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the product was purified with silica gel column chromatography to afford **25** (23.1 mg, 71 %) as white solid. $[\alpha]^{26}_D$ +26.0° (c 1.6, $CHCl_3$). HR FABMS m/z 482.3139 $(M+Na)^+$, calcd for $C_{23}H_{49}NO_4Si_2$: 482.3098; ^{1}H NMR ($CDCl_3$) δ (ppm) 9.79 (d, J = 2 Hz, 2H), 5.01 (d, J = 7.6 Hz, 1H), 4.15 (m, 1H), 4.06(dd, J = 6.8, 3.2 Hz, 1H), 3.96 (dd, J = 5.6, 2.3 Hz, 1H), 2.77 (m, 1H), 1.97 (m, 1H), 1.58 (s, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H), 0.99 (t, J = 7.9 Hz, 9H), 0.95 (overlap, 3H), 0.94 (s, 9H), 0.66(q, J = 7.9, 6H), 0.11 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 204.1, 167.9, 76.4, 75.8, 50.7, 47.0, 43.1, 26.2, 23.1, 18.5, 12.3, 12.1, 7.3, 5.9, -4.0, -4.4.



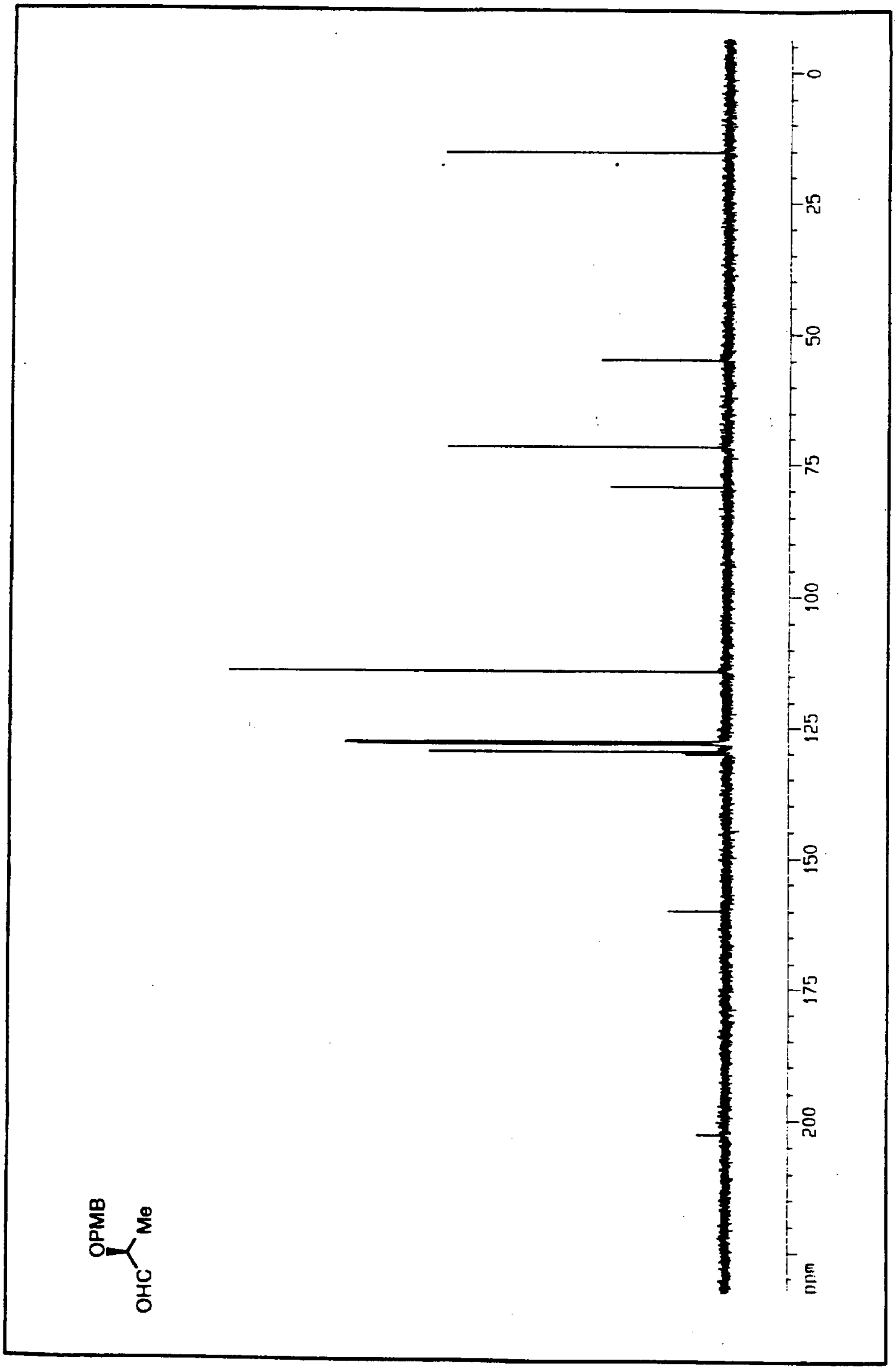
Compound 4. A 10 mL flask was charged with $CrCl_2$ (28.7 mg, 0.22 mmol) under nitrogen gas (passed through two columns filled with P_2O_5 and pyrogallol respectively) and the flask was gently flame dried with heat gun under high

vacuum. After cooling down, it was filled with nitrogen, THF (0.3 mL) was added. Carefully dried **25** (17.0 mg, 0.037 mmol) was dissolved in THF (0.5 mL) and to this solution was added CHI_3 (29 mg, 0.074 mmol). This solution was cannulated to the $CrCl_2$ solution at 0 °C. The reaction was stirred at 0 °C for 1 hour and the solvent was removed. The product was purified with silica gel column chromatography to afford **4** (15.4 mg, 71%) as white solid. $[\alpha]^{26}_{D}$ +33.3° (*c* 0.5, $CHCl_3$). HR FABMS m/z 606.2258 $(M+Na)^+$, calcd for $C_{24}H_{50}INO_3Si_2$: 606.2272; ^1H NMR ($CDCl_3$) δ (ppm) 6.82 (dd, *J* = 16, 10 Hz, 1H), 6.12 (d, *J* = 16Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.04~3.97 (m, 2H), 3.66 (dd, *J* = 8.4, 3.2Hz, 1H), 2.90 (m, 1H), , 1.91(q, *J* = 7.6 Hz, 1H), 1.54 (s, 3H), 1.10 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.96 (s, 9H), 0.94 (overlap, 3H), 0.65(q, *J* = 7.9, 6H), 0.11 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 167.8, 148.5, 128.6, 77.7, 76.3, 74.2, 47.2, 45.0, 43.0, 26.2, 23.1, 18.5, 17.9, 15.3, 12.1, 7.4, 6.0, -3.7, -4.5.



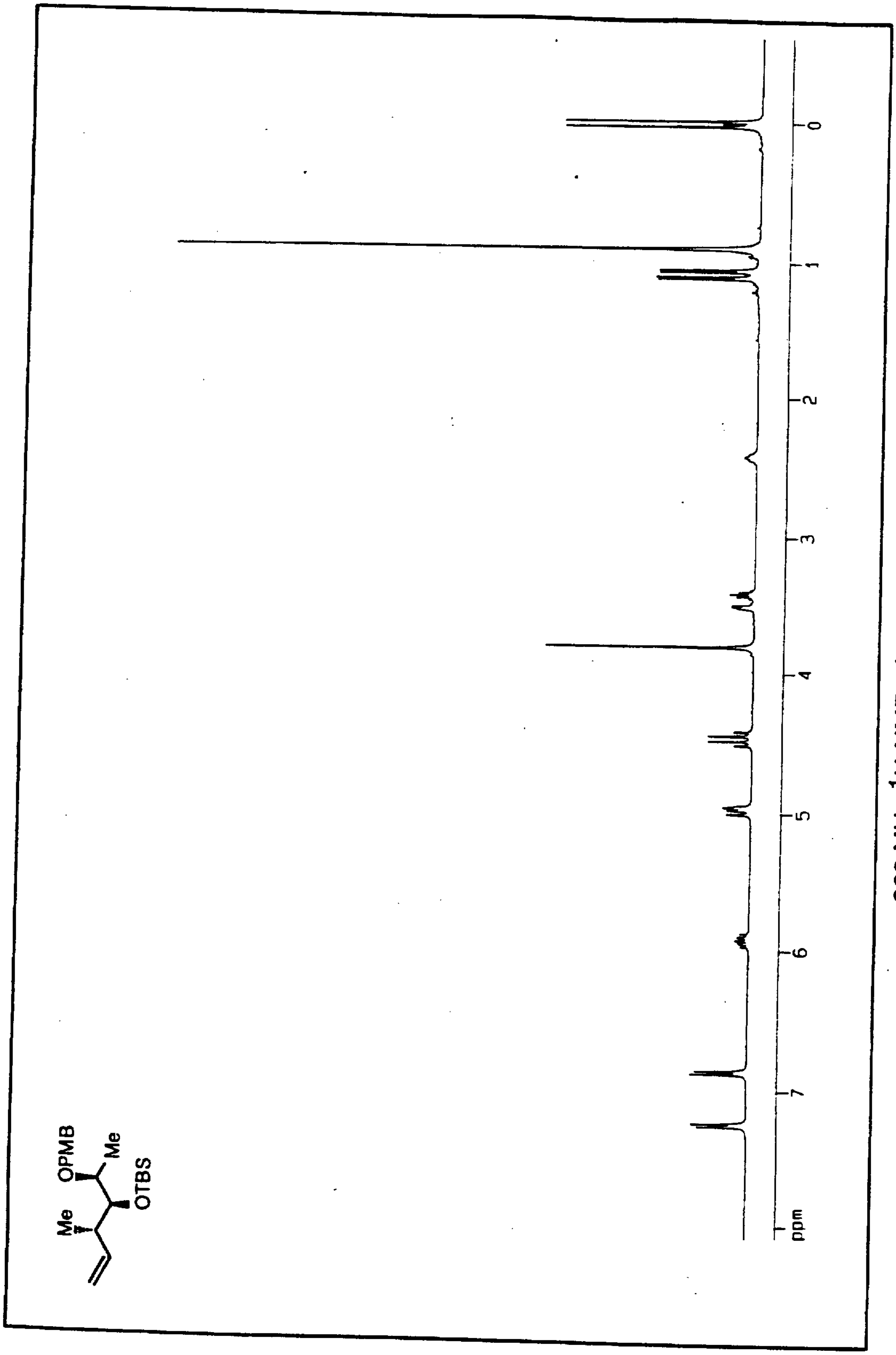
400 MHz ^{1}H NMR of compound 9

2



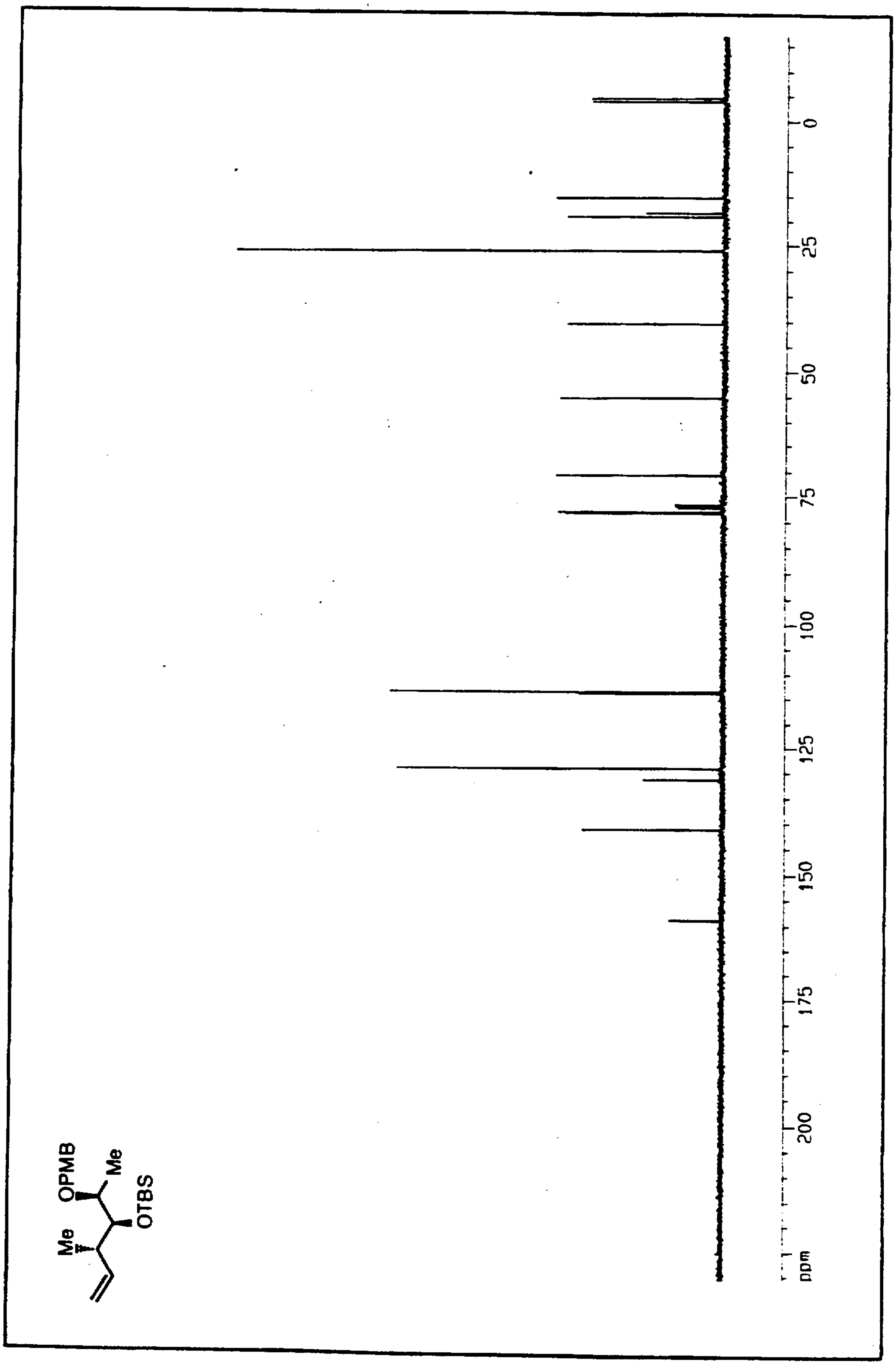
100 MHz ^{13}C NMR of compound **9**

3



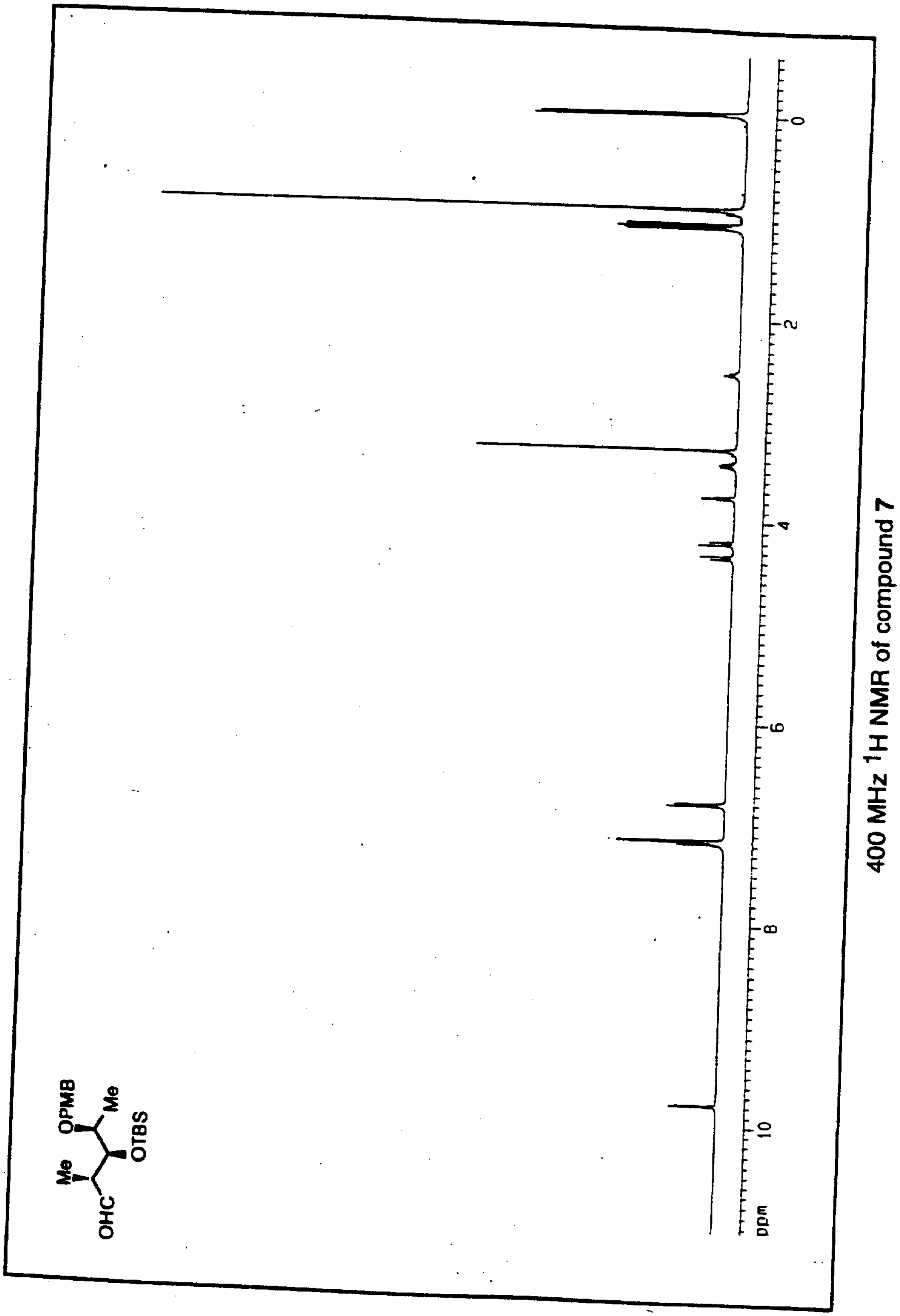
360 MHz ^{1}H NMR of compound **13**

4



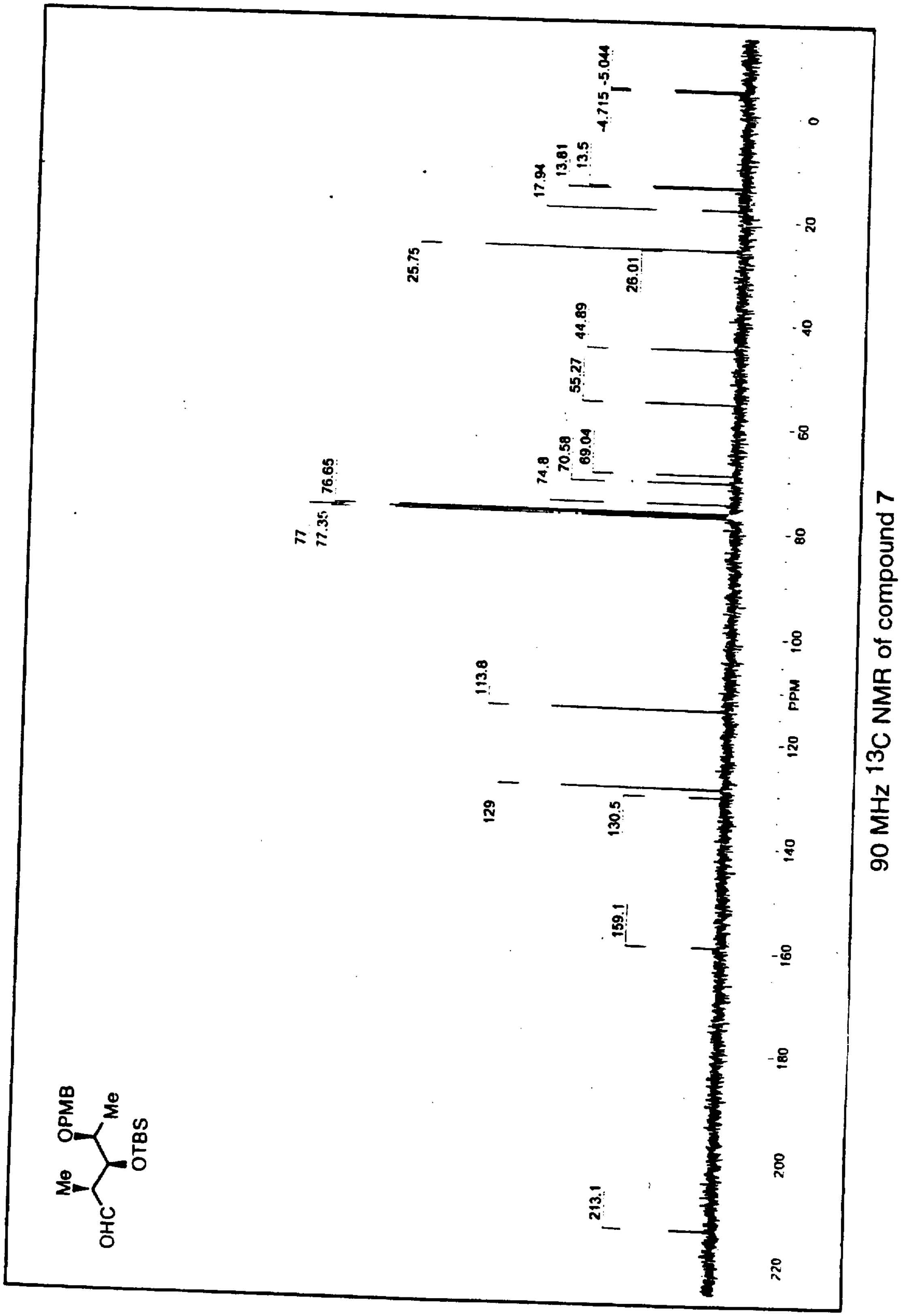
90 MHz 13C NMR of compound 13

5

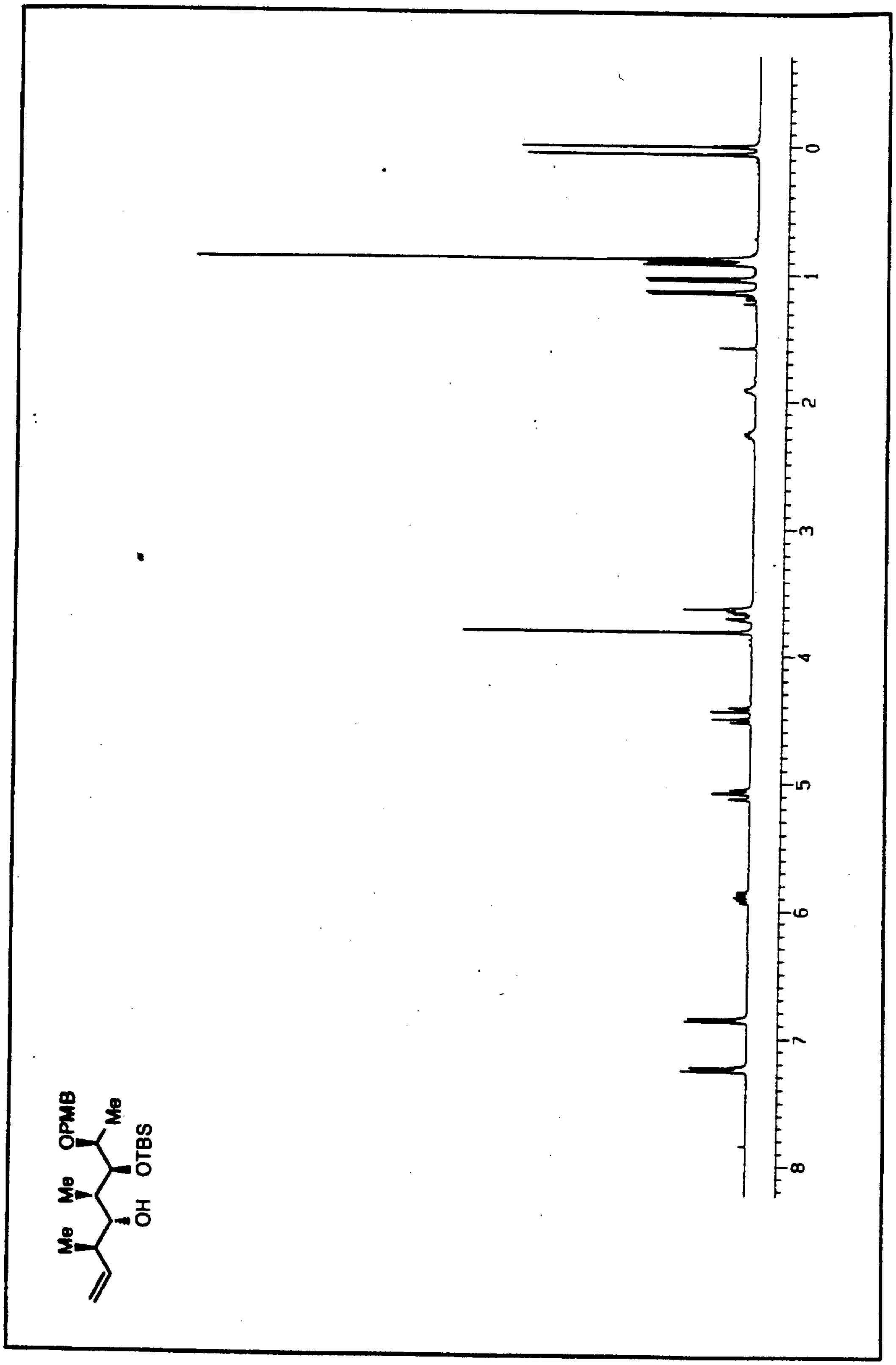


400 MHz ^1H NMR of compound 7

6

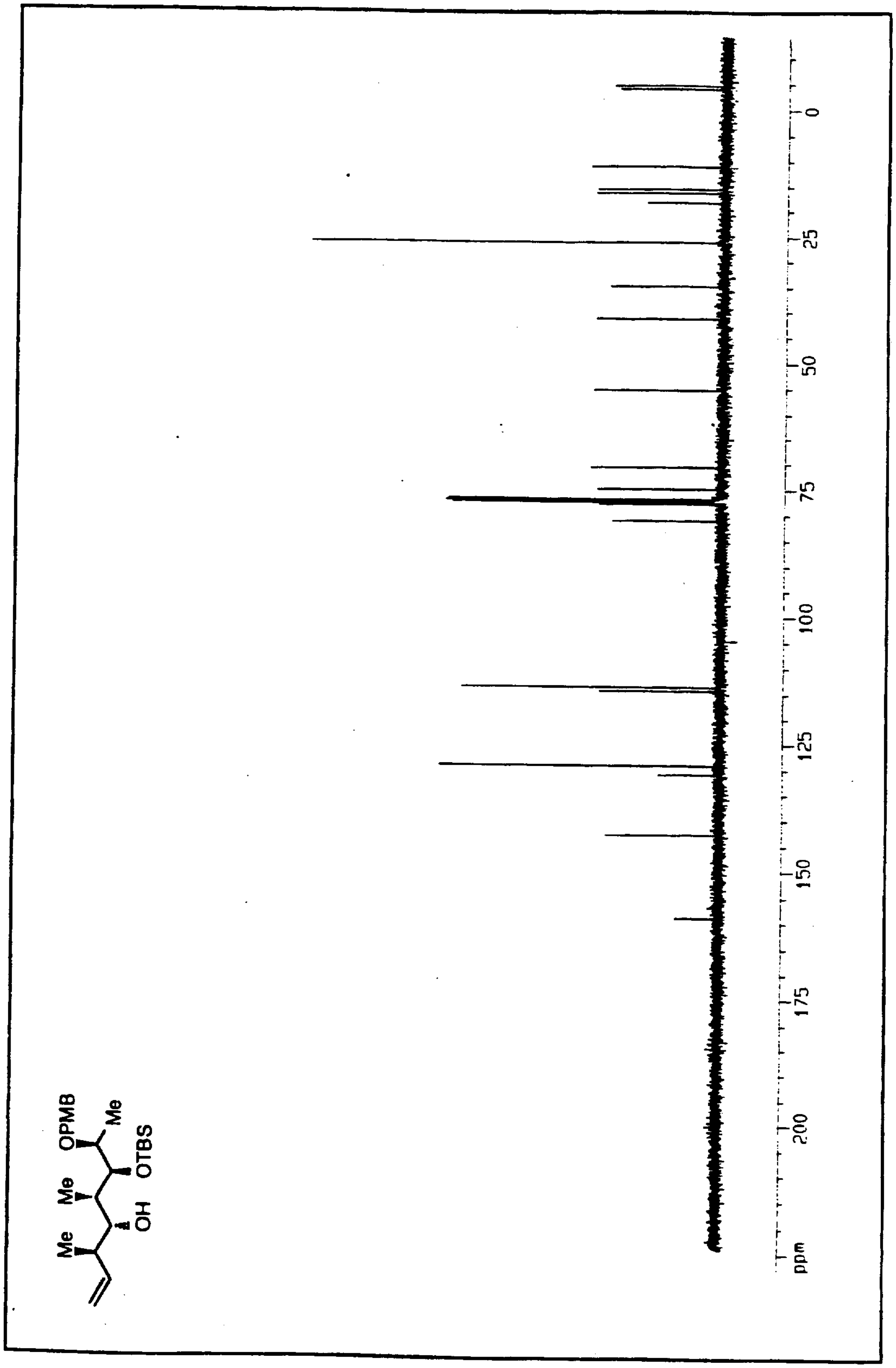


90 MHz 13C NMR of compound 7

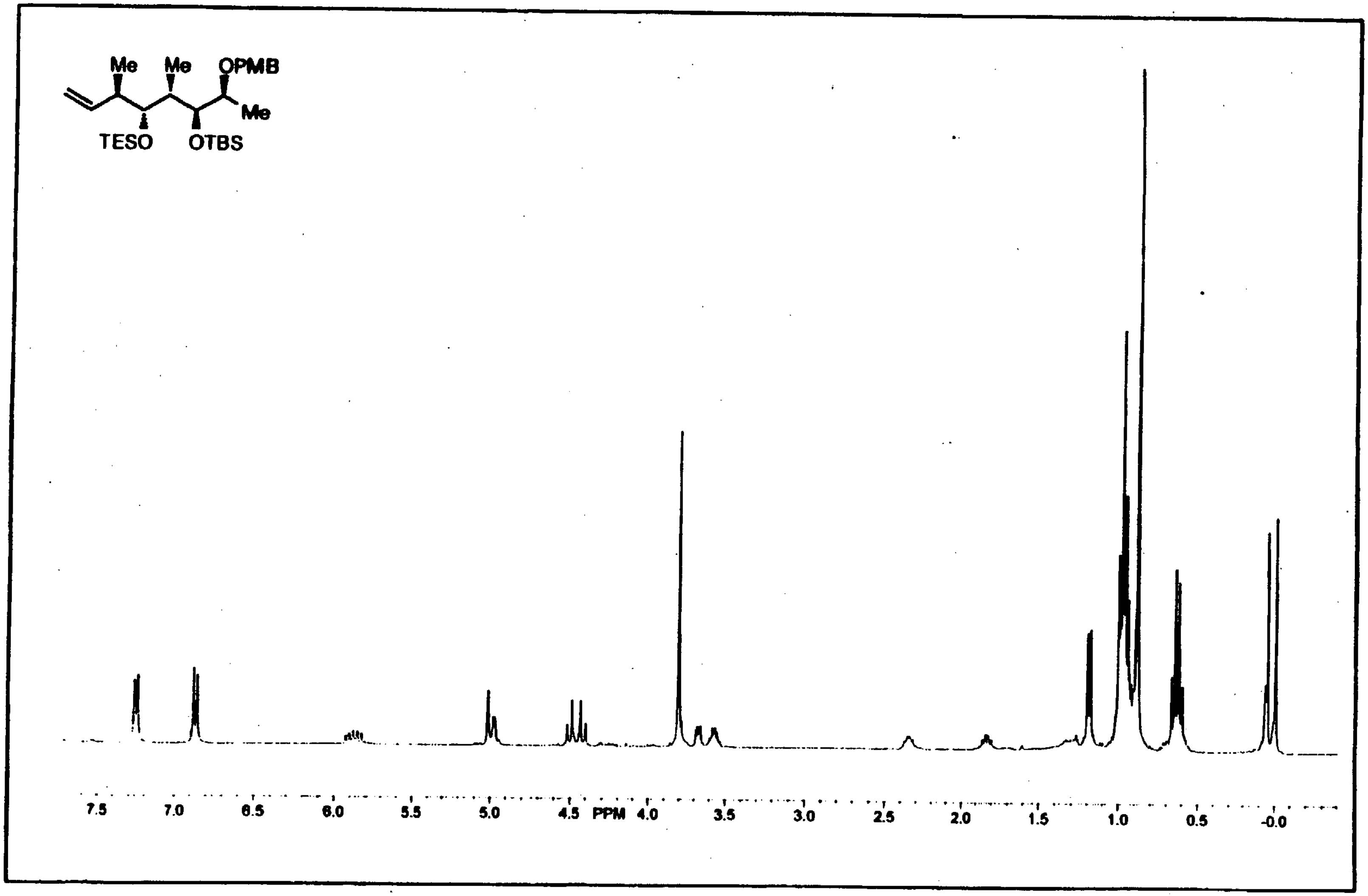


400 MHz ^1H NMR of compound **16**

8

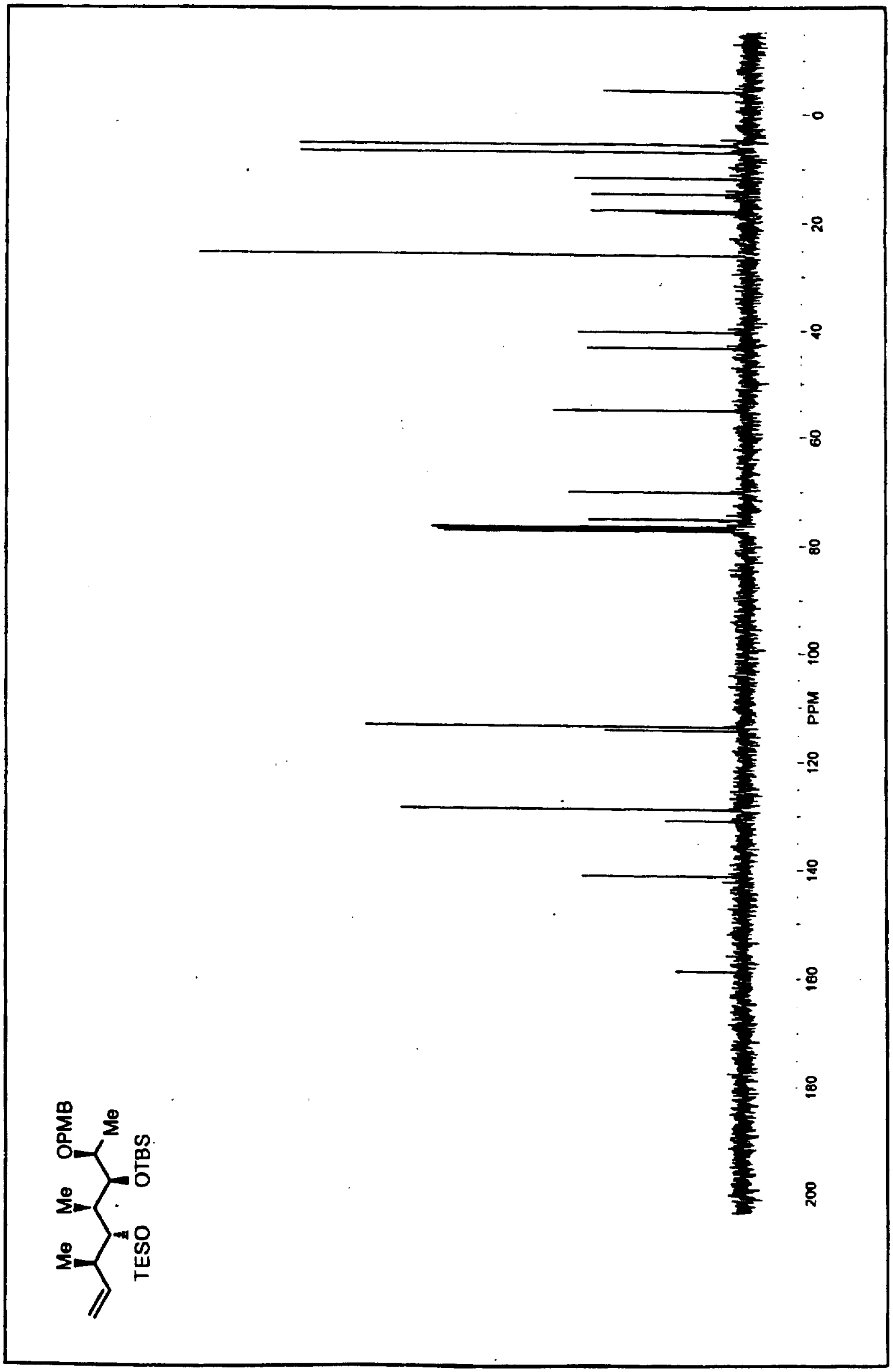


100 MHz ^{13}C NMR of compound 16

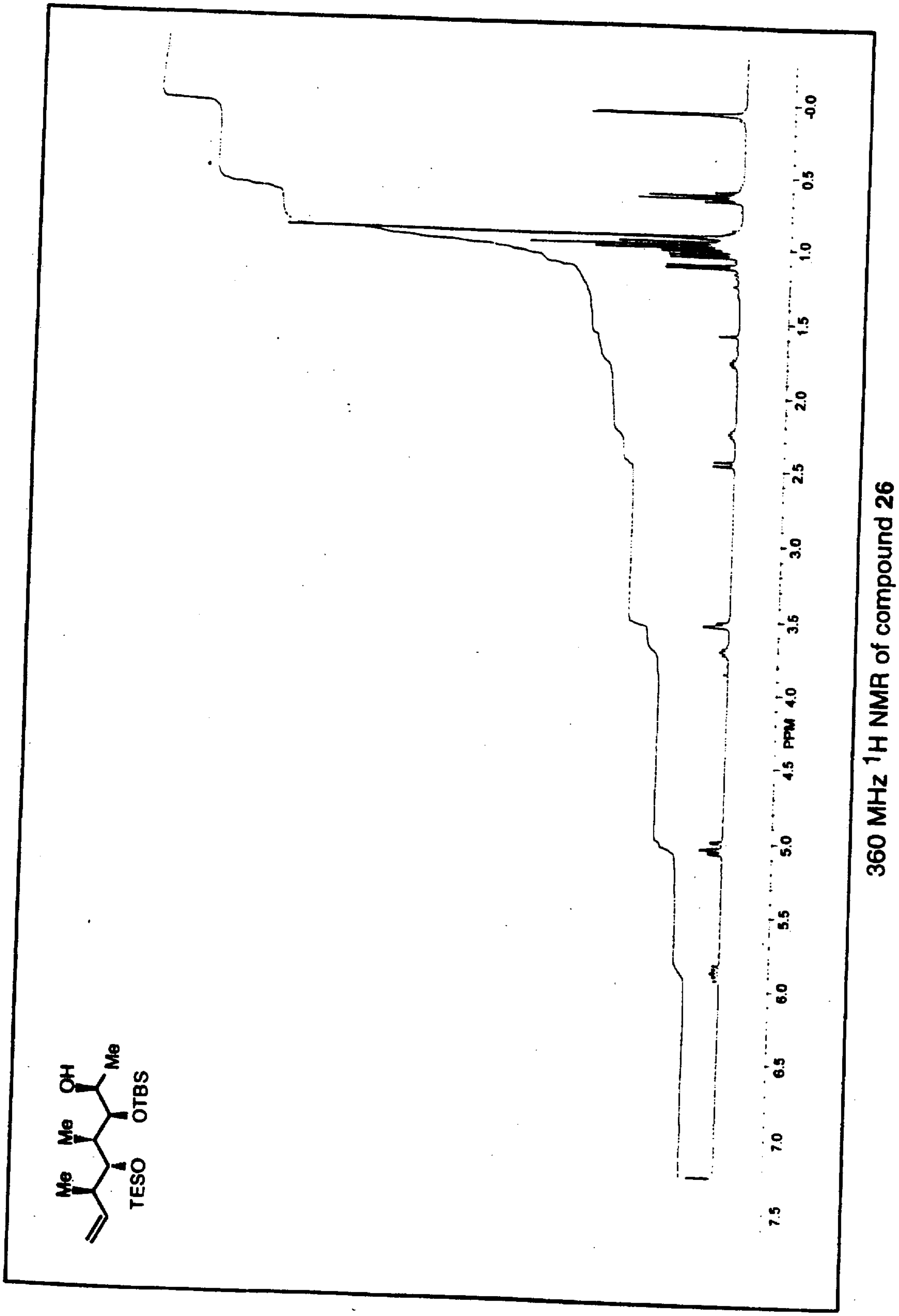


360 MHz ^{1}H NMR of compound **22**

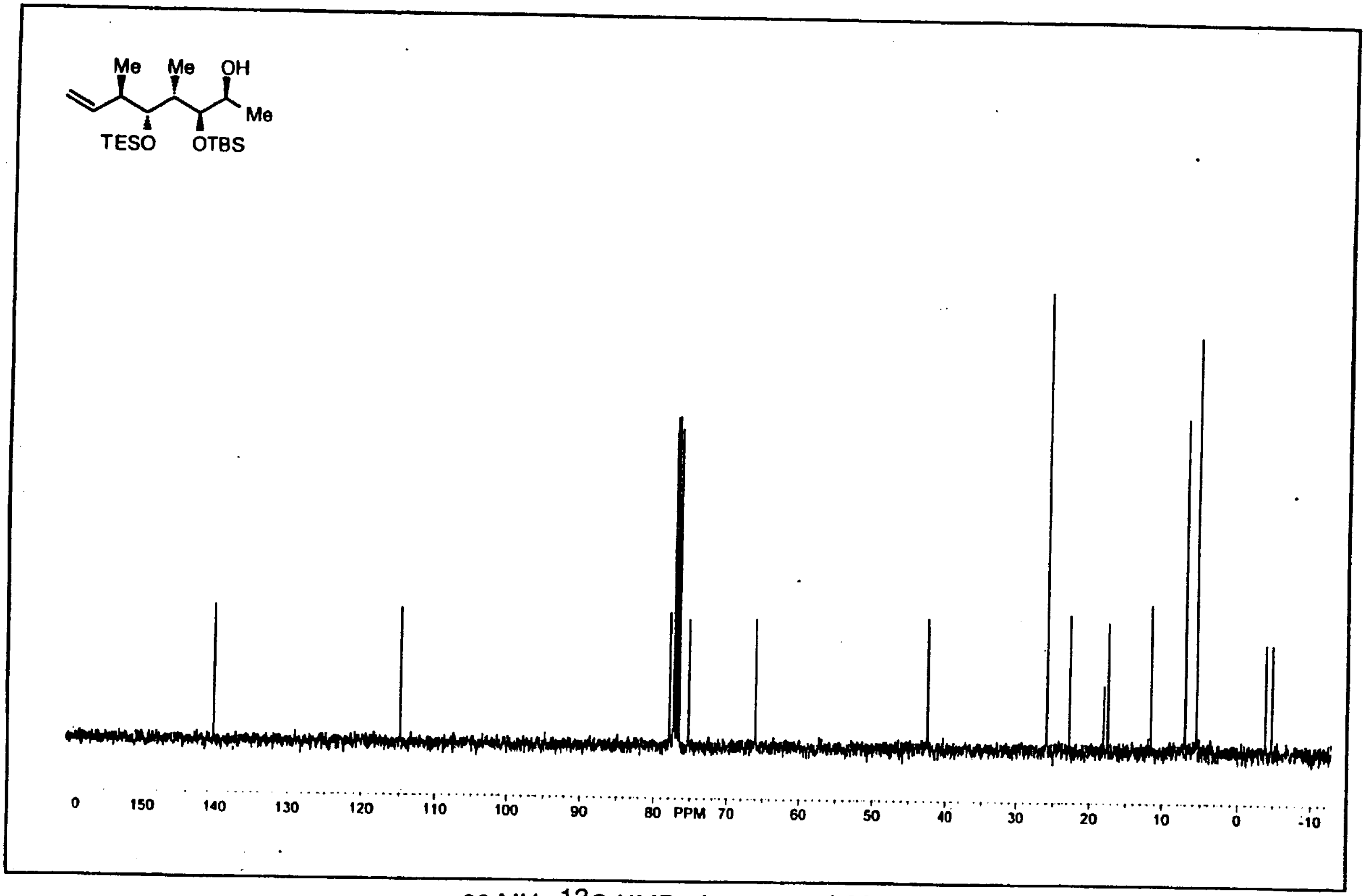
10



90 MHz ^{13}C NMR of compound **22**

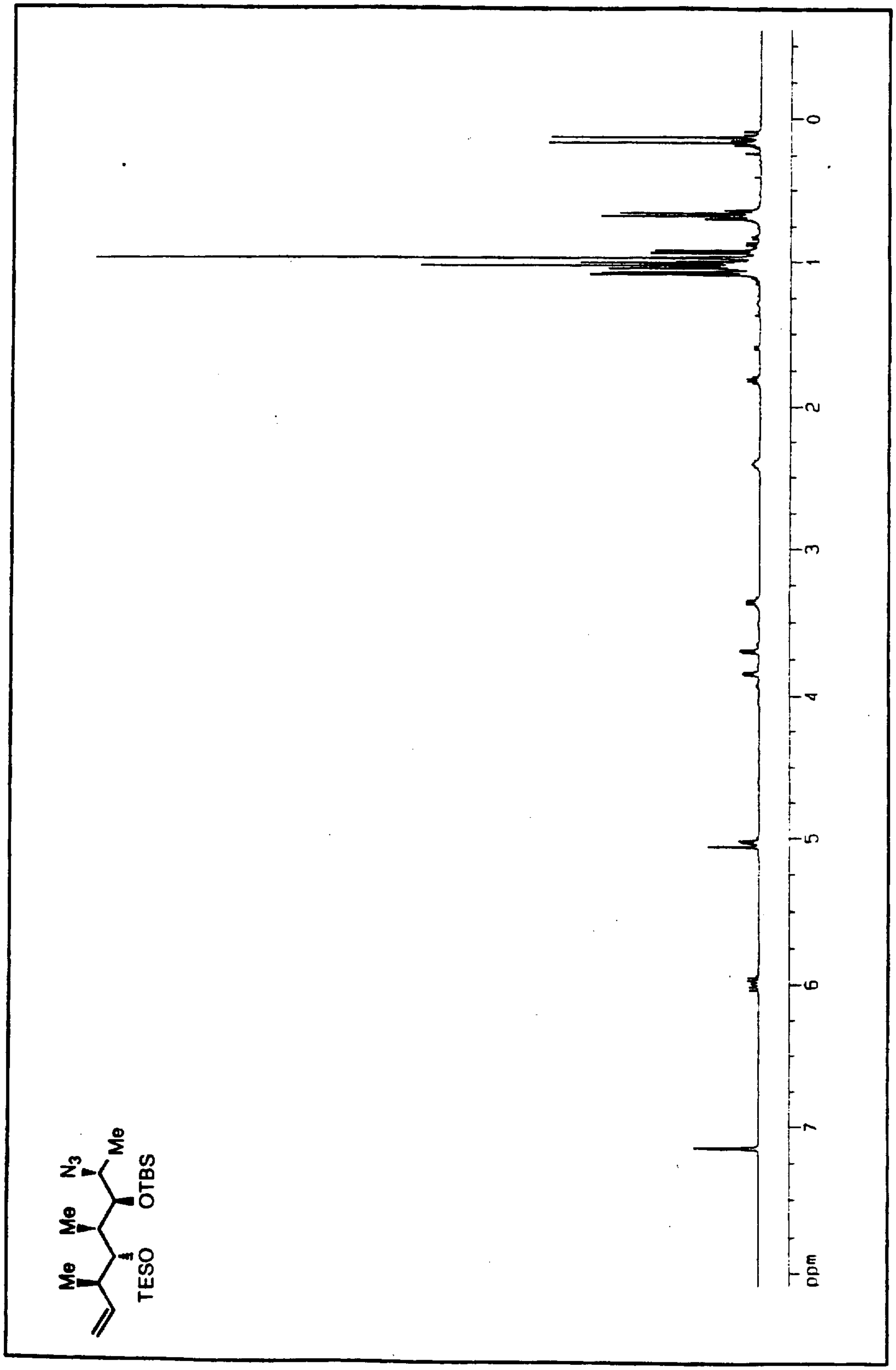


360 MHz ^{1}H NMR of compound 26



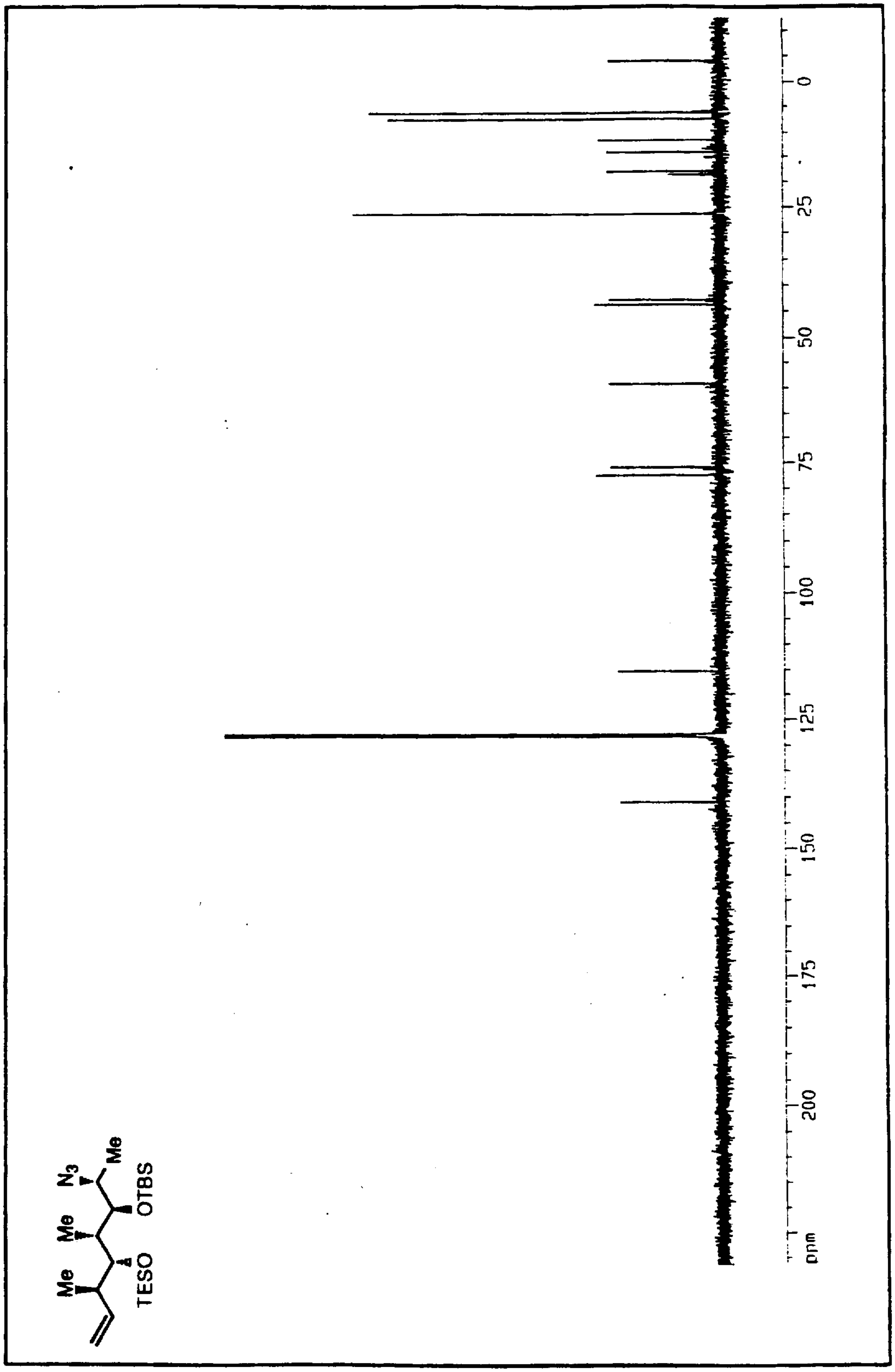
90 MHz ^{13}C NMR of compound **26**

13

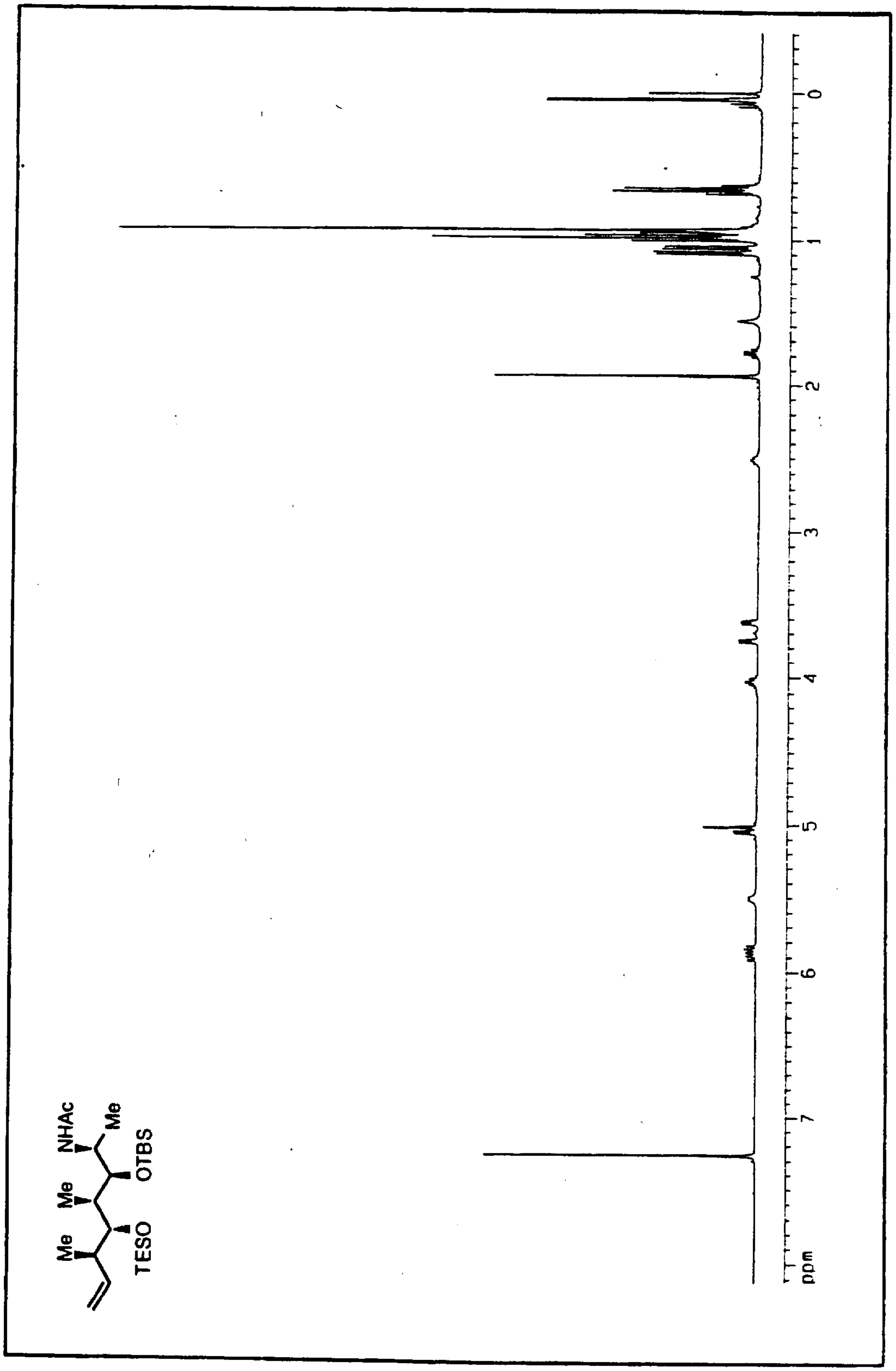


400 MHz ^{1}H NMR of compound **23**

14

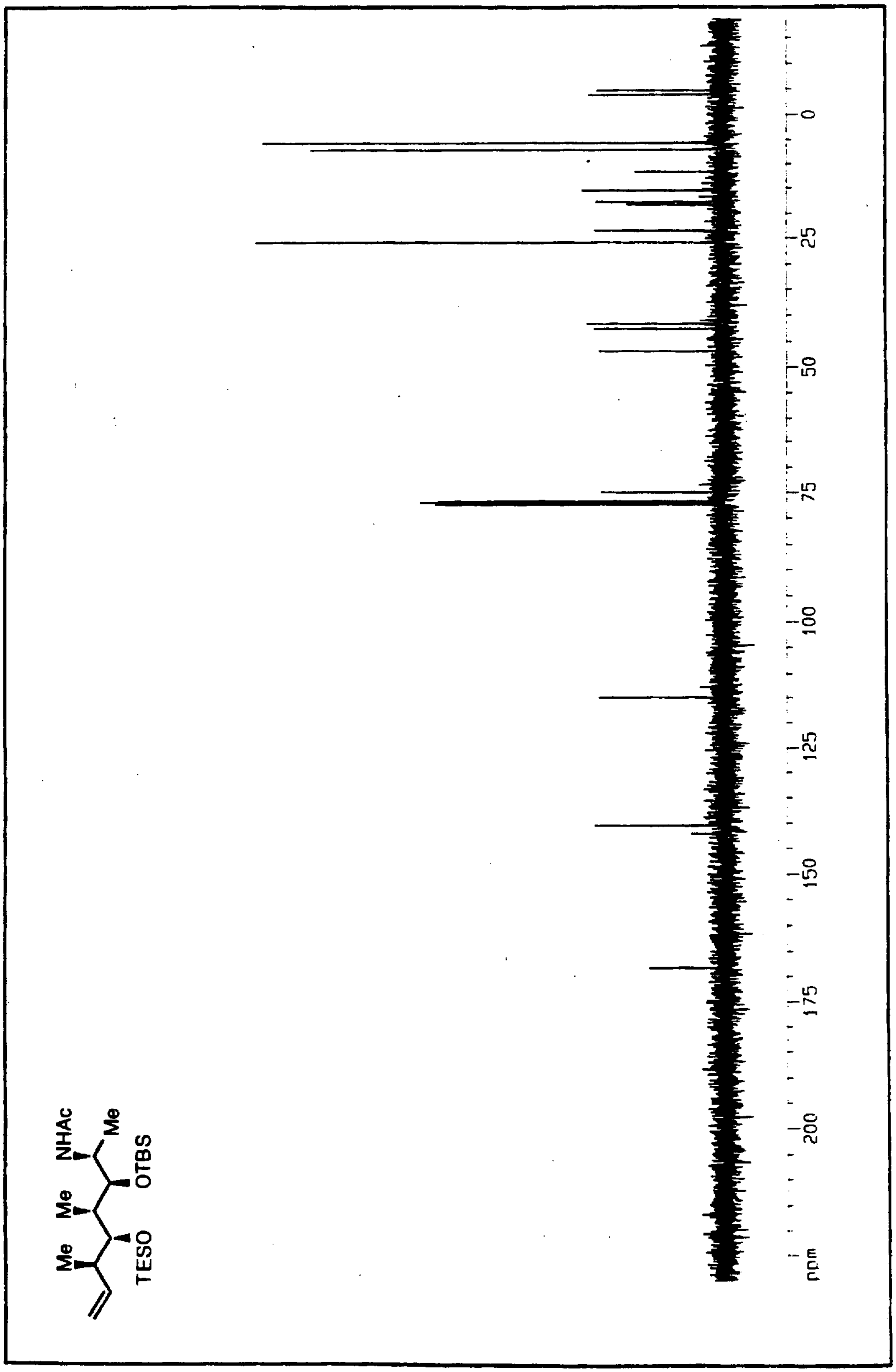


100 MHz ^{13}C NMR of compound **23**



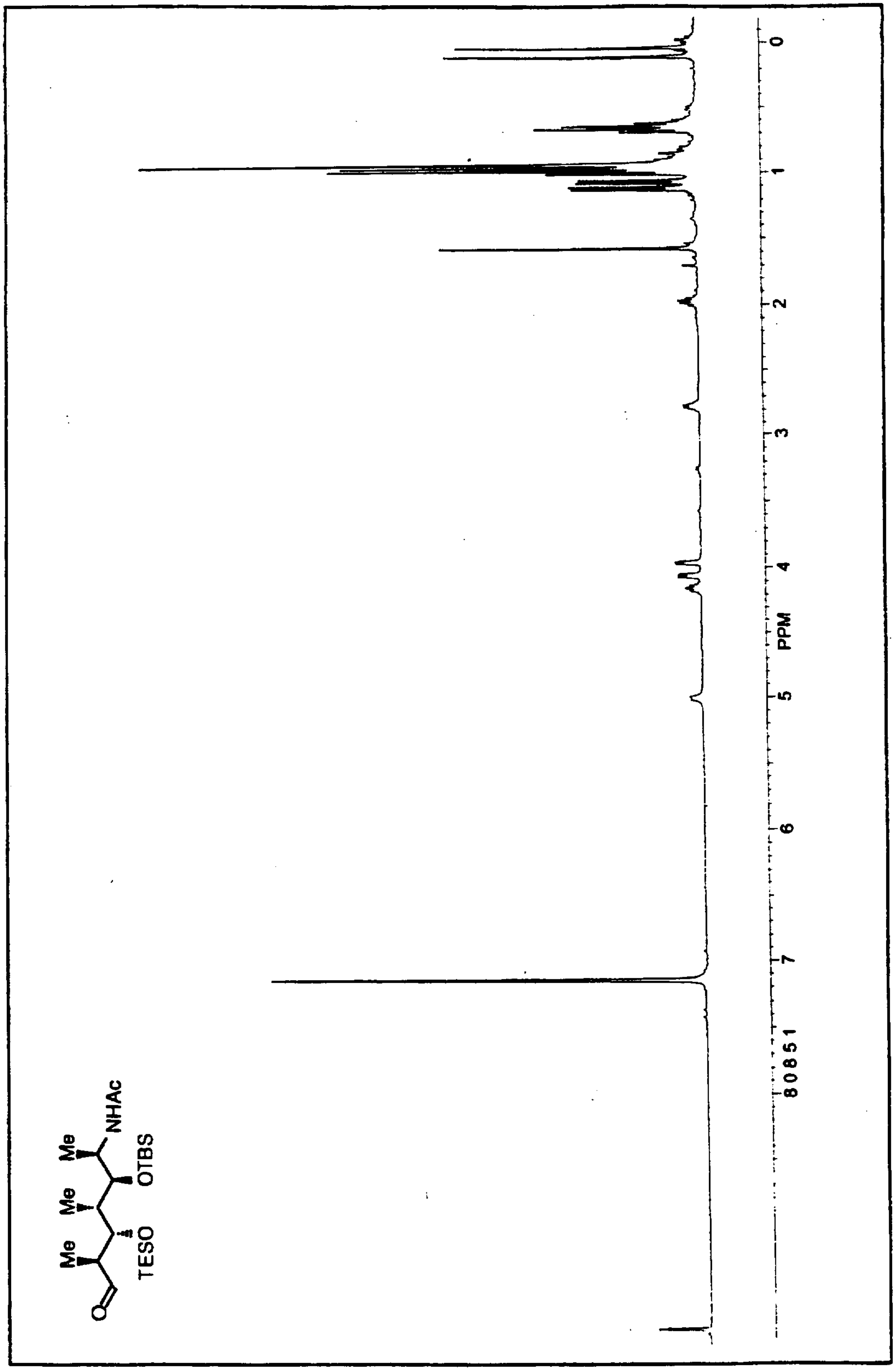
400 MHz ^{1}H NMR of compound **24**

10



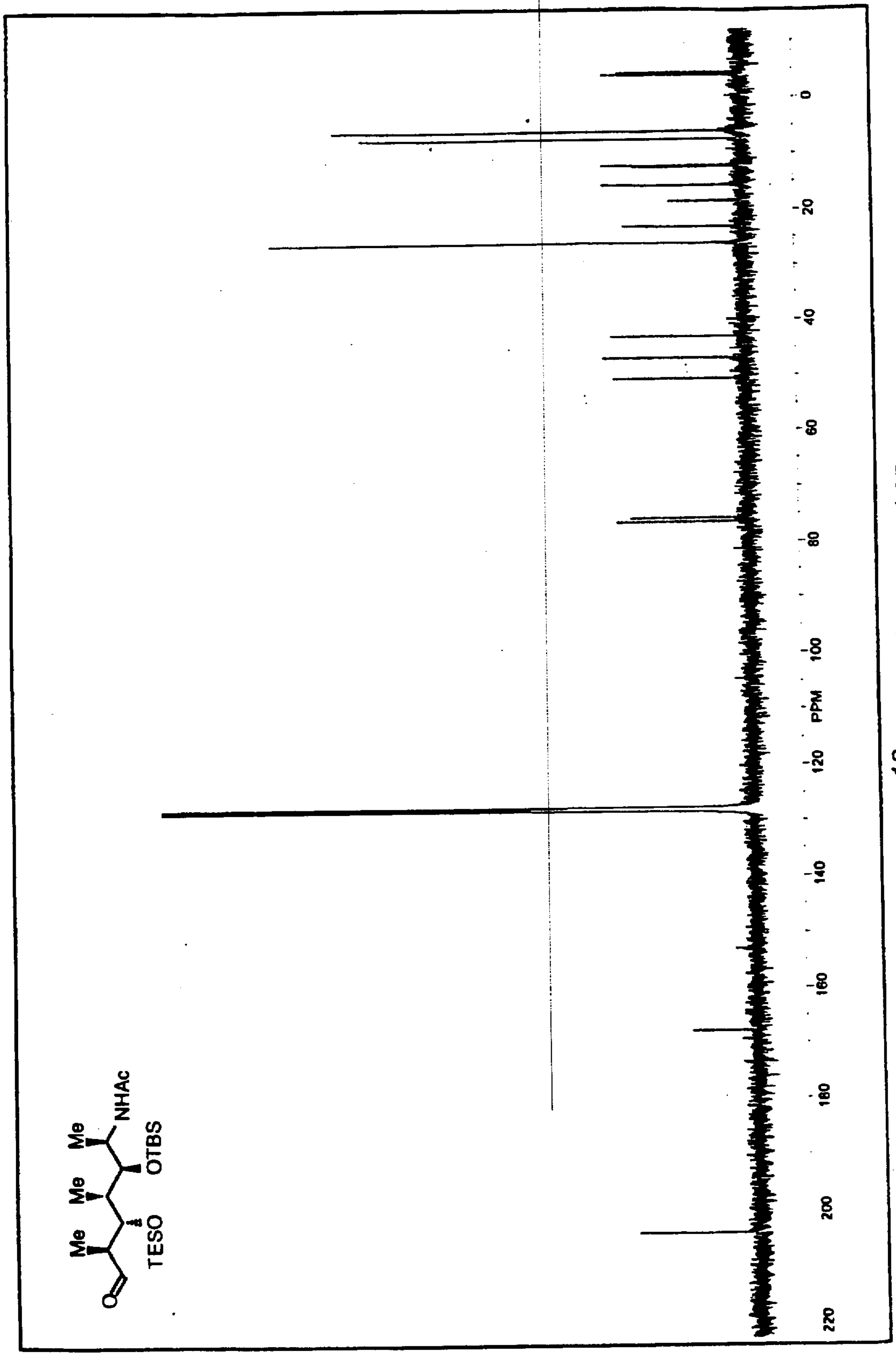
100 MHz ^{13}C NMR of compound **24**

17

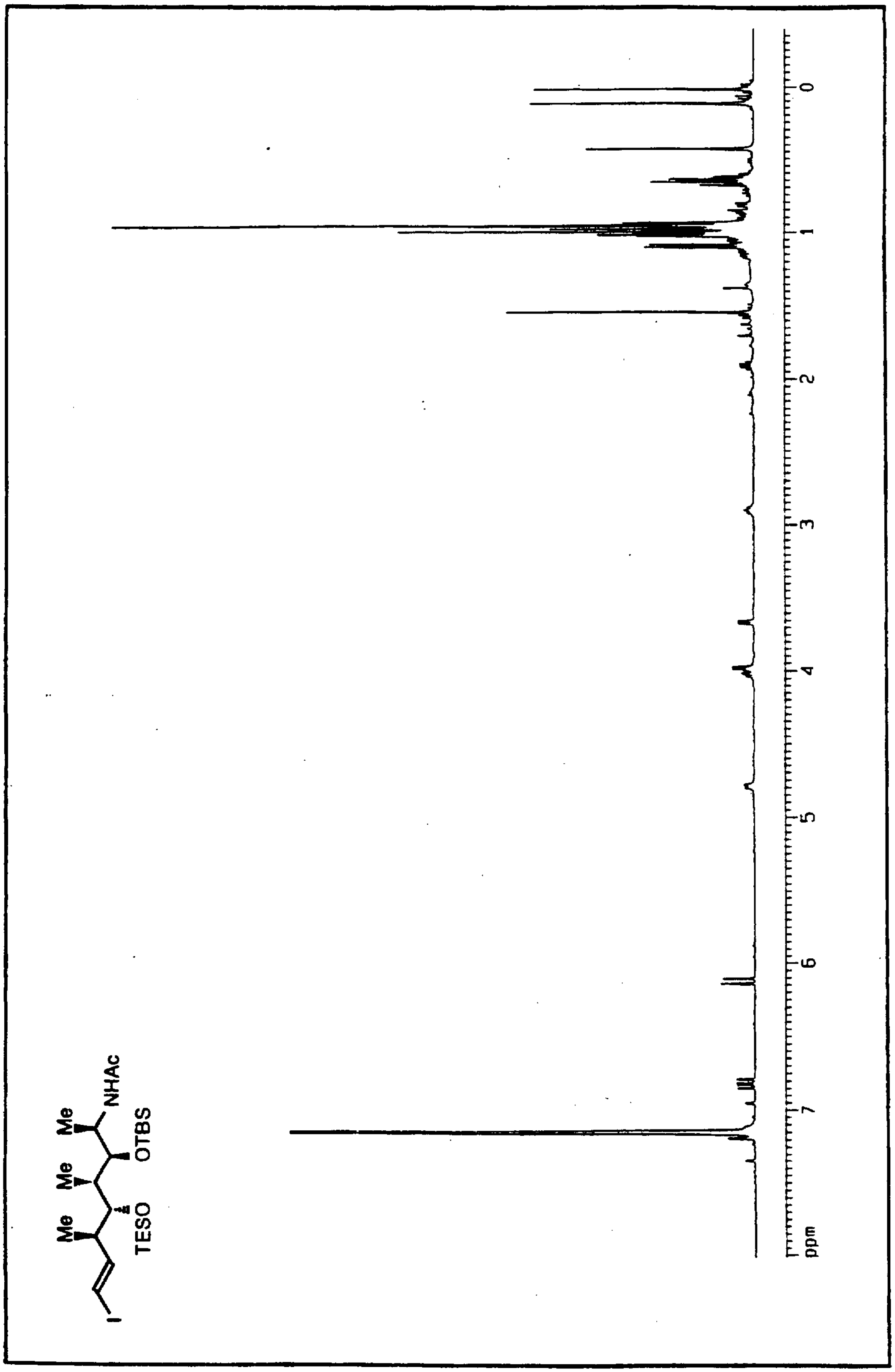


360 MHz ^{1}H NMR of compound **25**

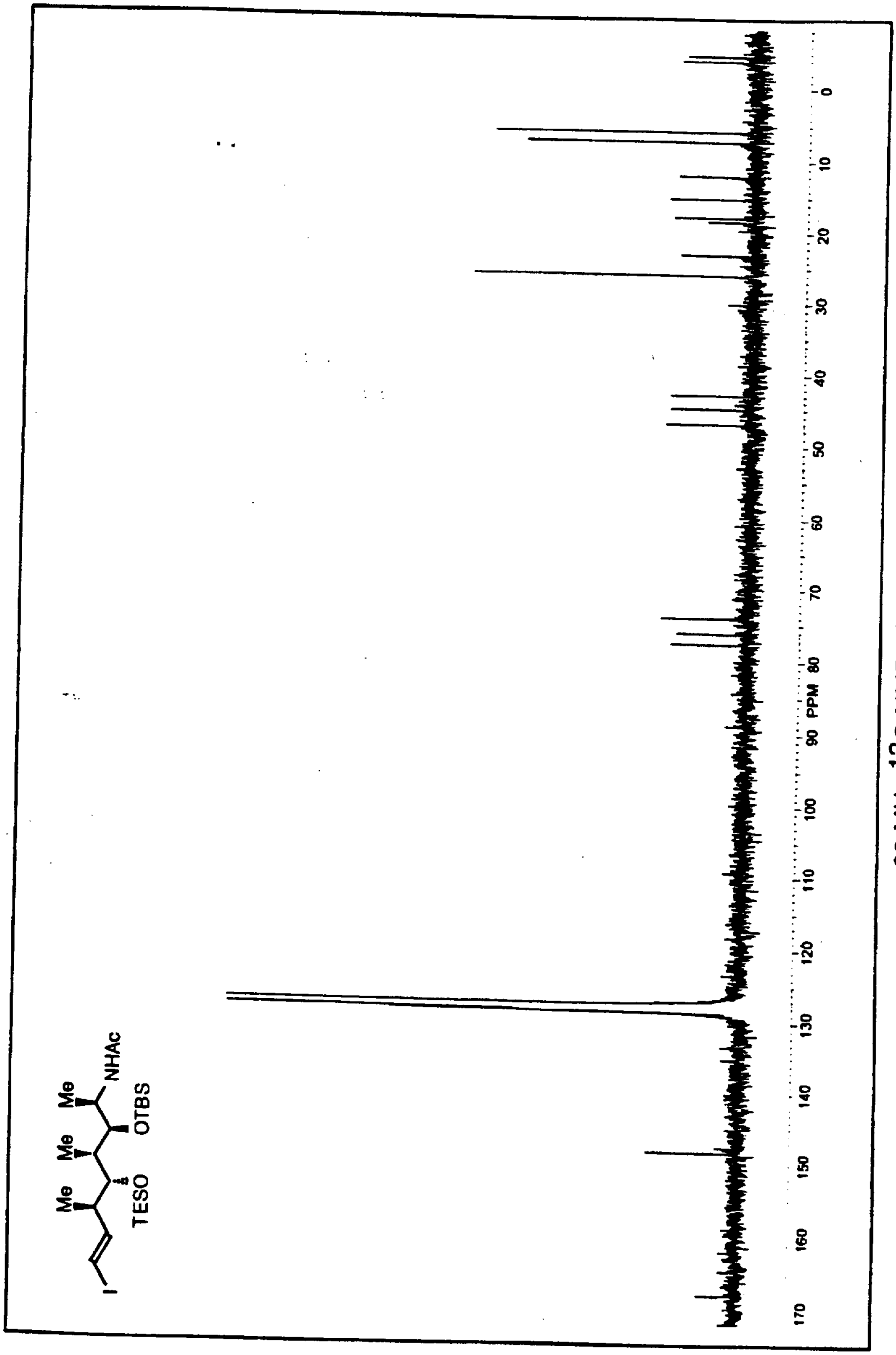
18



90 MHz ^{13}C NMR of compound 25



400 MHz ^{1}H NMR of compound **4**



90 MHz ^{13}C NMR of compound 4