Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

`

Synthesis of Macrolactone Core of (+)-Neopeltolide by Transannular Cyclization

Gangavaram V. M. Sharma,*[a] Sheri Venkat Reddy[a] and Kallaganti V. S. Ramakrishna[b]

a. Organic and Biomolecular Chemistry Division, b. NMR group, *CSIR-Indian Institute of Chemical Technology, Hyderabad-500 007, India.*

Contents **P. No.**

1. Experimental details S2-S13
2. ^{1}H and ^{13}C Spectra of compounds 3-37 S14-S71
3. ^{1}H , ^{13}C, NOESY and TOCSY Spectra of compound 38 S72-S75
4. ^{1}H , ^{13}C, NOESY and TOCSY Spectra of compound 38a S76-S79
5. ^{1}H , ^{13}C, NOESY and TOCSY Spectra of compound 39 S80-S83
6. ^{1}H and ^{13}C Spectra of compounds 40, 2 S84-S87

`

((2*R*,3*R*)-3-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methyl)oxiran-2-yl)methanol (9)

To a stirred solution of (-)-DIPT (1.90 g, 8.14 mmol) in CH_2Cl_2 (25 mL) at -20 °C containing MS 4 Å (2 g), sequentially $Ti(O^iPr)_4$ (1.17 mL, 4.07 mmol) and cumene hydroperoxide (9.06 mL, 61.05 mmol) were added and stirred for 20 min. A solution of allylic alcohol **8** (7.0 g, 40.70 mmol) in CH_2Cl_2 (25 mL) was added and stirred for 5 h at -20 °C. The reaction mixture was quenched with 10% NaOH solution (3.5 g in 35 mL brine) and stirred for 3 h. It was filtered through a pad of celite and washed with CH_2Cl_2 (50 mL). The organic layer was dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 20% ethyl acetate in pet. ether) to furnish **9** (6.5 g, 85%) as a yellow oil; $[\alpha]_D^{25}$ +42.0 (*c* 0.45, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.19-4.13 (m, 1H), 4.06-4.0 (m, 1H), 3.87-3.82 (m, 1H), 3.62-3.57 (m, 2H), 3.06-3.02 (m, 1H), 2.95-2.91 (m, 1H), 2.07 (br. s, 1H), 1.91-1.81 (m, 2H), 1.39 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.0, 72.8, 68.6, 61.5, 57.8, 52.5, 34.8, 26.6, 25.5; HRMS (ESI): m/z calculated for $C_9H_{16}O_4$ $(M+Na)^+$ 211.1116, found 211.1118.

(*S*)-4-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)butane-1,3-diol (10)

To a stirred solution of epoxide **9** (6.50 g, 34.57 mmol) in dry THF (70 mL), Red-Al (19.56 mL, 69.15 mmol, 70% w/w in toluene) was added at 0 ºC. After 4 h the reaction mixture was quenched with sat. Na_2SO_4 solution (10 mL) and filtered through a pad of celite and washed with EtOAc (2 x 100 mL). Organic layer was dried (Na_2SO_4), solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 40% ethyl acetate in pet. ether) to afford **10** (5.3 g, 80%) as a colourless oil; $[\alpha]_D^{25}$ +2.0 (*c* 0.75, $CHCl_3$); IR (neat): 3401, 2984, 2940, 2878, 1715, 1651, 1419, 1373, 1217, 1159, 1055, 862 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.32-4.22 (m, 1H), 4.14-4.04 (m, 2H), 3.79-3.74 (m,

`

2H), 3.57-3.51 (m, 1H), 1.78-1.63 (m, 4H), 1.41 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 108.7, 74.0, 69.1, 69.0, 59.4, 40.4, 38.5, 26.5, 25.4; HRMS (ESI): m/z calculated for $C_9H_{18}O_4$ $(M+Na)^+$ 213.1106, found 213.1102.

(4*S*)-4-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methyl)-2-(4-methoxyphenyl)-1,3-dioxane (11)

To a stirred solution of **10** (5.20 g, 27.66 mmol) in dry CH_2Cl_2 (90 mL), *p*-anisaldehyde dimethyl acetal (6.05 g, 32.19 mmol) and PTSA (catalytic) were added at 0 ^oC and stirred at room temperature for 3 h. The reaction mixture was neutralized with Et_3N (3 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 10% ethyl acetate in pet. ether) to give **11** (6.7 g, 79%) as a pale yellow oil; $[\alpha]_D^{25}$ +77.7 (*c* 0.50, $CHCl_3$); IR (neat): 2984, 2943, 2861, 1713, 1614, 1520, 1371, 1250, 1105, 1020, 825; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, 2H, *J* = 8.8 Hz), 6.83 (d, 2H, *J* = 8.8 Hz), 5.40 (s, 1H), 4.27-4.21 (m, 2H), 4.08-3.99 (m, 1H), 3.98-3.85 (m, 2H), 3.78 (s, 3H), 3.61-3.54 (m, 1H), 2.05-1.95 (m, 1H), 1.91-1.79 (m, 1H), 1.79-1.70 (m, 1H), 1.56-1.53 (m, 1H), 1.38 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 130.9, 126.9, 113.1, 108.2, 100.6, 73.7, 71.8, 69.0, 66.4, 54.8, 39.0, 30.4, 26.6, 25.4; HRMS (ESI): m/z calculated for $C_{17}H_{24}O_5$ $(M+Na)^+$ 331.1514, found 331.1521.

(*S*)-4-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-3-(4-methoxybenzyloxy)butan-1-ol (12)

DIBAL-H (13.05 mL, 26.10 mmol, 2 M solution in toluene) was added dropwise to a solution of **11** (6.70 g, 21.75 mmol) in dry CH_2Cl_2 (70 mL) at 0 ^oC and stirred for 1 h. Methanol (15 mL) followed by saturated aq. sodium potassium tartarate solution (15 mL) was added, filtered through a pad of celite and washed with EtOAc (2 x 100 mL). The organic layers were dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 15% ethyl acetate in pet. ether) to furnish **12** (5.8 g, 86%) as a light yellow liquid; $[\alpha]_D^{25}$ +22.1 (*c* 0.60, $CHCl_3$); IR (neat): 3339, 2926, 2781, 1717, 1612, 1512, 1406, 1246, 1026, 818 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, 2H, *J* = 8.3 Hz), 6.81 (d, 2H, *J* = 8.3 Hz), 4.49 (d, 1H, *J* = 11.3 Hz), 4.42 (d, 1H, *J* = 11.3 Hz), 4.17-4.06 (m, 1H), 3.99-3.94 (m, 1H), 3.79-3.65 (m, 2H), 3.79 (s,

`

3H), 3.47 (t, 1H, *J* = 7.6 Hz), 2.04-1.67 (m, 4H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 130.0, 129.5, 113.8, 108.6, 74.9, 72.7, 70.5, 69.6, 60.3, 55.2, 37.2, 35.9, 26.9, 25.7; HRMS (ESI): m/z calculated for $C_{17}H_{26}O_5$ $(M+Na)^+$ 333.1727, found 333.1731.

***tert*.-Butyl((*S*)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-methoxybenzyloxy) butoxy) diphenylsilane (13)**

To a stirred solution of **12** (5.40 g, 17.42 mmol) in CH_2Cl_2 (30 mL), imidazole (3.55 g, 52.26 mmol) and TBDPSCl (5.02 mL, 19.16 mmol) were sequentially added at 0 ^oC and stirred at room temperature for 5 h. The reaction mixture was washed with water (40 mL), brine (40 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 5% ethyl acetate in pet. ether) to furnish **13** (8.80 g, 92%) as a pale yellow oil; $[\alpha]_D^{25}$ +23.3 (*c* 0.70, $CHCl_3$); IR (neat): 3314, 3059, 2934, 2864, 1942, 1711, 1607, 1562, 1479, 1435, 1201, 1157, 1095, 1045, 1012, 985, 926, 781, 754, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.60 (m, 4H), 7.41-7.3 (m, 6H), 7.11 (d, 2H, *J* = 8.7 Hz), 6.75 (d, 2H , *J* = 8.7 Hz), 4.35 (s, 2H), 4.15-4.07 (m, 2H), 3.91-3.86 (m, 1H), 3.82-3.65 (m, 2H), 3.77 (s, 3H), 3.44-3.39 (m, 1H), 1.94-1.82 (m, 1H), 1.8-1.62 (m, 3H), 1.35 (s, 3H), 1.30 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 135.5, 133.8, 133.7, 130.6, 129.6, 129.4, 127.6, 113.7, 108.4, 73.0, 72.8, 70.6, 69.6, 60.3, 55.2, 37.6, 36.8, 26.9, 25.7; HRMS (ESI): m/z calculated for $C_{33}H_{44}O_5Si$ $(M+Na)^+$ 571.2855, found 571.2855.

(2*S*,4*S*)-6-[1-(*tert*.-Butyl)-1,1-diphenylsilyl]oxy-4-[(4-methoxybenzyl)oxy]hexane-1,2-diol (14)

To a stirred solution of **13** (8.70 g, 15.87 mmol) in acetonitrile (45 mL), $CuCl_2.2H_2O$ (2.98 g, 17.46 mmol) was added at 0 °C and allowed to stir for 30 min at the same temparature. Reaction mixture was quenched with sat. $NaHCO_3$ (10 mL), filtered through a pad of celite, washed with EtOAc (2 x 100 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 30% ethyl acetate in pet. ether) to afford **14** (6.40 g, 79%) as a colourless oil; $[\alpha]_D^{25}$ +50.1 (*c* 0.0, $CHCl_3$); IR (neat) 3067, 2932, 2857, 2774, 1722, 1612, 1514, 1419, 1250, 1109, 1034, 812, 746, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.61 (m, 4H), 7.41-7.34 (m, 6H), 7.15 (d, 2H, *J* = 8.8 Hz), 6.78 (d, 2H , *J* = 8.8 Hz), 4.48 (d, 1H, *J* = 11.2 Hz), 4.30 (d, 1H, *J* = 11.2 Hz), 3.85-3.80 (m, 1H), 3.78 (s, 3H), 3.78-3.66 (m, 3H), 3.46-3.44 (m, 1H), 3.33-3.27 (m, 1H), 1.96-1.91 (m, 2H), 1.74-1.59 (m, 2H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 135.6,

`

133.6, 129.8, 129.6, 127.8, 113.9, 96.3, 76.3, 71.5, 70.5, 66.7, 60.2, 55.0, 37.4, 36.7, 27.1, 19.3; HRMS (ESI): m/z calculated for $C_{30}H_{40}O_5Si$ $(M+Na)^+$ 531.2524, found 531.2542.

***tert.*-Butyl((*S*)-3-(4-methoxybenzyloxy)-4-((*S*)-oxiran-2-yl)butoxy)diphenylsilane (16)**

To a stirred solution of the diol **14** (6.30 g, 12.40 mmol) in CH_2Cl_2 (63 mL) at 0 °C, Bu_2SnO (62 mg, 0.25 mmol), Et_3N (1.73 mL, 12.40 mmol) and *p*-TsCl (2.37 g, 12.40 mmol) were added and stirred at room temperature. After 1h, the reaction mixture was filtered, and the filtrate was washed with water (50 mL), brine (50 mL) and dried (Na_2SO_4). Solvent was evaporated and the resulting tosylate **15** was directly used for the next reaction.

A solution of **15** (7.8 g, 11.78 mmol) in MeOH (40 mL) was treated with K_2CO_3 (4.88 g, 35.34 mmol) and stirred at room temperature for 30 min. MeOH was evaporated and residue extracted with EtOAc (4 x 50 mL). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 5% ethyl acetate in pet. ether) to furnish **16** (4.80 g, 83%) as a colourless oil; $[\alpha]_D^{25}$ -8.31 (*c* 0.75, $CHCl_3$); IR (neat): 3433, 3073, 3044, 2997, 2932, 2857, 1612, 1587, 1514, 1468, 1427, 1302, 1248, 1173, 1111, 1036, 823, 739, 704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.63-7.59 (m, 4H), 7.41-7.30 (m, 6H), 7.13 (d, 2H, *J* = 8.7 Hz), 6.76 (d, 2H, *J* = 8.7 Hz), 4.43 (d, 1H, *J* = 11.3 Hz), 4.39 (d, 2H, *J* = 11.3 Hz), 3.84-3.69 (m, 3H), 3.77 (s, 3H), 2.97-2.91 (m, 1H), 2.68-2.65 (m, 1H), 2.38 (q, 1H, *J* = 2.6, 5.28 Hz), 1.88-1.64 (m, 4H), 1.38 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 135.5, 133.7, 130.6, 129.6, 129.3, 127.6, 113.7, 73.5, 70.7, 60.3, 55.2, 49.5, 46.7, 37.1, 36.9, 26.8, 19.1; HRMS (ESI): m/z calculated for $C_{30}H_{38}O_4Si$ $(M+Na)^+$ 513.2423, found 513.2437.

(5*R*,7*S*)-5-Allyl-7-(4-methoxybenzyloxy)-12,12-dimethyl-11,11-diphenyl-2,4,10-trioxa-11-silatridecane (18)

To a stirred solution of **17** (3.80 g, 7.33 mmol) in CH_2Cl_2 (30 mL), DIPEA (6.38 mL, 36.68 mmol), methoxymethylchloride (1.17 mL, 14.67 mmol) and DMAP (cat.), were added at 0 ^oC and stirred at room temperature for 6 h. Reaction mixture was extracted with CH_2Cl_2 (2 × 30 mL), and combined organic layers were washed with water (30 mL), brine (30 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue

`

purified by column chromatography (60-120 mesh Silica gel, 10% ethyl acetate in pet. ether) to furnish **18** (3.80 g, 92%) as a colourless oil; $[\alpha]_D^{25}$ -13.77 (*c* 0.4, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.64-7.60 (m, 4H), 7.39-7.29 (m, 6H), 7.13 (d, 2H, *J* = 8.7 Hz), 6.75 (d, 2H, *J* = 8.7 Hz), 5.82-5.68 (m,1H), 5.04-4.99 (m, 2H), 4.57 (d, 1H, *J* = 6.8 Hz), 4.56 (d, 1H, *J* = 6.8 Hz), 4.38 (d, 1H, *J* = 11.3 Hz), 4.33 (d, 1H, *J* = 11.3 Hz), 3.82-3.62 (m, 4H), 3.77 (s, 3H), 3.29 (s, 3H), 2.34-2.14 (m, 2H), 1.88-1.67 (m, 3H), 1.62-1.52 (m, 1H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159, 135.5, 135.5, 134.5, 133.8, 129.5, 129.3, 127.6, 117.3, 113.6, 95.5, 74.2, 72.5, 70.4, 60.4, 55.5, 55.2, 39.0, 39.0, 37.1, 26.8, 19.1; HRMS (ESI): m/z calculated for $C_{34}H_{46}O_5Si$ $(M+Na)^+$ 585.3004, found 585.3012.

(3*S*,5*R*)-3-(4-Methoxybenzyloxy)-5-(methoxymethoxy)oct-7-en-1-ol (19)

To a stirred solution of **18** (3.70 g, 6.58 mmol) in anhydrous THF (4 mL), TBAF (7.90 mL, 7.90 mmol, 1.0 M solution in THF) was added at 0 ^oC and stirred at room temperature for 3 h. The reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (20 mL), brine (20 mL) and dried (Na_2SO_4). Solvent was evaporated and residue purified by column chromatography (60-120 mesh Silica gel, 20% ethyl acetate in pet. ether) to give **19** (1.8 g, 85%) as a colourless oil; $[\alpha]_D^{25}$ -95.5 (*c* 0.7, $CHCl_3$); IR (neat): 3416, 2935, 1711, 1608, 1514, 1441, 1252, 1101, 1034, 916, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, 2H, *J* = 8.7 Hz), 6.83 (d, 2H, *J* = 8.7 Hz), 5.84-5.69 (m,1H), 5.08-5.03 (m, 2H), 4.62 (d, 1H, *J* = 6.8 Hz), 4.55 (d, 1H, *J* = 6.8 Hz), 4.47 (d, 1H, *J* = 11.3 Hz), 4.38 (d, 1H, *J* = 11.3 Hz), 3.77 (s, 3H), 3.75-3.60 (m, 4H), 3.31 (s, 3H), 2.50 (br. s, 1H), 2.29-2.25 (m, 2H), 1.97-1.79 (m, 2H), 1.73-1.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 134.2, 130.2, 129.4, 117.6, 113.7, 95.3, 74.8, 74.0, 70.2, 60.2, 55.5, 55.0, 39.2, 38.2, 36.0; HRMS (ESI): m/z calculated for $C_{18}H_{28}O_5$ $(M+Na)^+$ 347.1826, found 347.1834.

(*S*)-1-(2,2-Dimethyl-1,3-dioxolan-4-yl)pentan-2-ol (21)

To a suspension of magnesium turnings (2.93 g, 122.22 mmol) in dry THF (40 mL) under nitrogen environment, a solution of *n*-propyl bromide (11.10 mL, 122.22 mmol) in THF (20 mL) was added and stirred at room temperature for 30 min. The reaction mixture was cooled to 0 °C, a

`

solution of aldehyde **20** (8.80 g, 61.11 mmol) in dry THF (45 mL) was added and stirred at room temperature for 20 min. It was quenched with sat. NH_4Cl solution (10 mL) at 0 ^oC and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with water (75 mL), brine (75 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 7% ethyl acetate in pet. ether) to afford **21** (7.70 g, 70%) as a colourless oil; $[\alpha]_D^{25}$ -2.16 (*c* 0.5, $CHCl_3$); IR (neat): 3449, 2928, 2868, 1633, 1459, 1374, 1219, 1157, 1059, 861 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.40-4.23 (m, 1H), 4.12-4.06 (m, 1H), 3.84-3.83 (m, 1H), 3.61-3.53 (m, 1H), 1.80-1.25 (m, 6H), 1.42 (s, 3H), 1.37 (s, 3H), 0.96-0.91 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.3, 108.7, 75.9, 73.6, 70.7, 69.7, 69.5, 68.7, 40.4, 39.9, 39.6, 26.8, 26.7, 25.6, 18.8, 18.6, 14.0; HRMS (ESI): m/z calculated for $C_{10}H_{20}O_3$ $(M+Na)^+$ 211.1751, found 211.1732.

(*S*)-1-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)pentan-2-ol (23)

To a stirred solution of oxalyl chloride (5.56 mL, 45.05 mmol) in dry CH_2Cl_2 (30 mL), DMSO (7.03 mL, 90.10 mmol) was added at -78 ^oC and stirred at the same temperature for 0.5 h. A solution of **21** (7.7 g, 40.95 mmol) in CH_2Cl_2 (40 mL) was added at -78 ^oC and stirred for an additional 2 h at the same temperature. Et_3N (34.27 mL, 245.7 mmol) was added at 0 ^oC and stirred for 15 min. The reaction mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (2 x 75 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), evaporated to give **22** which was used as such for the next reaction.

To a stirred solution of **22** (7.62 g, 40.96 mmol) in ether (150 mL), LiI (54.90 g, 409.6 mmol) was added, and the resulting mixture was stirred at -40 °C for 5 min. It was cooled to -78 °C and $LiAlH_4$ (15.56 g, 409.6 mmol) was added to the reaction mixture. The reaction mixture was stirred for 30 min. and quenched with aq. 10% sodium potassium tartrate solution (20 mL). The aq. layer was separated and extracted with ether (3 x 100 mL). The combined organic layers were dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 7% ethyl acetate in pet. ether) to furnish **23** (6.25 g, 81%) as a colourless oil; $[\alpha]_D^{25}$ -8.88 (*c* 0.2, $CHCl_3$); IR (neat): 3447, 2986, 2864, 1645, 1454, 1373, 1217, 1159, 1059, 841, 772 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.23 (q, 1H, *J* = 6.4, 13.2 Hz), 4.04 (dd, 1H, *J* = 6.0, 7.9 Hz), 3.81-3.74 (m, 1H), 3.52 (t, 1H, *J* = 7.5 Hz), 2.91 (br. s, 1H), 1.69-1.55 (m, 2H), 1.54-1.34 (m, 4H), 1.40 (s, 3H), 1.34 (s, 3H), 0.93 (t,

`

3H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.0, 75.5, 70.3, 69.5, 40.2, 39.5, 26.7, 25.5, 18.4, 13.8; HRMS (ESI): m/z calculated for $C_{10}H_{20}O_3$ $(M+Na)^+$ 211.1751, found 211.1727.

***tert*.-Butyl ((*S*)-1-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)pentan-2-yloxy)diphenylsilane (24)**

To a stirred solution of **23** (6.10 g, 32.44 mmol) in CH_2Cl_2 (60 mL), imidazole (7.05 g, 97.3 mmol) and TBDPSCl (9.31 mL, 35.69 mmol) were sequentially added at 0 °C and stirred at room temperature for 1 h. Worked up as described for **13** and purified the residue by column chromatography (60-120 mesh Silica gel, 1% ethyl acetate in pet. ether) to furnish **24** (11.30 g, 82%) as a colourless oil; $[\alpha]_D^{25}$ +2.86 (*c* 0.5, $CHCl_3$); IR (neat): 3449, 3065, 2935, 2862, 1634, 1465, 1429, 1374, 1218, 1108, 1056, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.65 (m, 4H), 7.45-7.34 (m, 6H), 4.16 (q, 1H, *J* = 6.8, 13.2 Hz), 3.85-3.77 (m, 2H), 3.32 (t, 1H, *J* = 7.7 Hz), 1.92-1.83 (m, 1H), 1.65-1.05 (m, 5H), 1.29 (s, 3H), 1.28 (s, 3H), 1.05 (s, 9H), 0.74 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.3, 129.5, 127.4, 108.1, 72.9, 70,5, 69.7, 39.7, 38.6, 27.0, 26.8, 25.7, 19.3, 18.0, 14.0; HRMS (ESI): m/z calculated for $C_{26}H_{38}O_3Si$ $(M+Na)^+$ 449.2487, found 449.2482.

(2*S*,4*S*)-4-(*tert*.-Butyldiphenylsilyloxy)heptane-1,2-diol (25)

To a stirred solution of **24** (11.00 g, 25.82 mmol) in acetonitrile (55 mL), $CuCl_2.2H_20$ (4.84 g, 28.40 mmol) was added at 0 °C and allowed to stir for 30 min. Worked up as described for **14** and purified the residue by column chromatography (60-120 mesh Silica gel, 28% ethyl acetate in pet. ether) to afford **25** (7.50 g, 75%) as a colourless oil; $[\alpha]_D^{25}$ -14.58 (*c* 0.4, $CHCl_3$); IR (neat): 3395, 3070, 2957, 2932, 2856, 1651, 1471, 1427, 1377, 1109, 1039, 821, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.65 (m, 4H), 7.44-7.33 (m, 6H), 3.98-3.90 (m, 1H), 3.85-3.78 (m, 1H), 3.46 (dd, 1H, *J* = 3.4, 11.0 Hz), 3.32-3.26 (m, 1H), 1.67-1.51 (m, 2H), 1.45-1.11 (m, 4H), 1.05 (s, 9H), 0.63 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8, 134.4, 129.7, 129.6, 127.6, 127.4, 70.6, 66.7, 39.2, 39.0, 26.9, 18.0, 13.7; HRMS (ESI): m/z calculated for $C_{23}H_{34}O_3Si$ $(M+Na)^+$ 409.2174, found 409.2174.

(2*S*,4*S*)-4-(*tert*.-Butyldiphenylsilyloxy)-2-hydroxyheptyl benzoate (26)

`

To a solution of **25** (7.30 g, 18.91 mmol) in CH_2Cl_2 (73 mL), Bu_2SnO (0.11 g, 0.38 mmol), Et_3N (2.63 mL, 18.91 mmol) and BzCl (2.19 mL, 18.91 mmol) were added. After 1h, the reaction mixture was filtered, organic layer was washed with water (40 mL), brine (40 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 5% ethyl acetate in pet. ether) to furnish **26** (8.40 g, 94%) as a colourless oil; $[\alpha]_D^{25}$ +5.91 (*c* 0.2, $CHCl_3$); IR (neat): 3067, 2957, 2930, 2856, 1716, 1647, 1539, 1450, 1423, 1388, 1275, 1109, 1024, 706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.01-7.97 (m, 2H), 7.70-7.64 (m, 4H), 7.56-7.30 (m, 1H), 7.44-7.30 (m, 8H), 4.24-4.16 (m, 1H), 4.11-3.94 (m, 3H), 2.46 (br. s, 1H), 1.69 (t, 1H, *J* = 6.0 Hz), 1.52-1.10 (m, 4H), 1.06 (s, 9H), 0.68 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 135.8, 134.3, 133.0, 129.7, 128.3, 127.6, 72.3, 68.9, 68.3, 39.6, 39.1, 27.0, 18.0, 13.8; HRMS (ESI): m/z calculated for $C_{30}H_{38}O_4Si$ $(M+Na)^+$ 513.2437, found 513.2427.

***tert*.-Butyl((*S*)-1-((*R*)-oxiran-2-yl)pentan-2-yloxy)diphenylsilane (28)**

To a cooled (0 °C) solution of **26** (8.20 g, 16.70 mmol) in CH_2Cl_2 (40 mL), Et_3N (4.65 mL, 33.40 mmol) and DMAP (cat.) followed by *p*-TsCl (3.83 g, 16.36 mmol) were added and stirred at room temperature for 12 h. The reaction mixture was washed with water (20 mL), brine (20 mL) and dried (Na_2SO_4). Solvent was evaporated and the resulting **27** was directly used for next reaction.

To a stirred solution of **27** (9.10 g, 14.11 mmol) in MeOH (45 mL), K_2CO_3 (5.84 g, 42.33 mmol) was added at 0 °C and allowed to stir for 30 min. Worked up as described for **16** and purified the residue by column chromatography (60-120 mesh Silica gel, 4% ethyl acetate in pet. ether) to furnish **28** (4.30 g, 83%) as a colourless oil; $[\alpha]_D^{25}$ +7.33 (*c* 0.2, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.67-7.64 (m, 4H), 7.44-7.32 (m, 6H), 3.92-3.91 (m, 1H), 2.89-2.83 (m, 1H), 2.63 (dd, 1H, *J* = 4.2, 5.3 Hz), 2.27 (dd, 1H, *J* = 2.6, 5.3 Hz),1.62-1.57 (m, 2H), 1.46-1.39 (m, 2H), 1.29-1.17 (m, 2H), 1.05 (s, 9H), 0.73 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.4, 129.6, 127.6, 71.4, 49.8, 47.5, 39.8, 39.4, 27.1, 18.1, 14.1; HRMS (ESI): m/z calculated for $C_{23}H_{32}O_2NaSi$ $(M+Na)^+$ 391.2069, found 391.2073.

***tert*.-Butyl((4*S*,6*S*)-6-methoxy-10-(tetrahydro-2H-pyran-2-yloxy)dec-8-yn-4-yloxy) diphen- ylsilane (31)**

`

To a stirred suspension of NaH (0.57 g, 14.17 mmol, 60% w/w dispersion in paraffin oil) in dry THF (5 mL) at 0 °C, a solution of **30** (3.60 g, 7.09 mmol) in dry THF (15 mL) was added and stirred for 30 min. MeI (1.32 mL, 21.26 mmol) was added to the reaction mixture and continued stirring for an additional 4 h. The reaction mixture was quenched with sat. NH_4Cl solution (5 mL) and extracted with EtOAc (2 x 40 mL). The combined organic layers were washed with brine (25 mL), dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 2% ethyl acetate in pet. ether) to afford **31** (3.05 g, 82%) as a colourless oil; $[\alpha]_D^{25}$ +31.0 (*c* 0.35, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68-7.63 (m, 4H), 7.40-7.30 (m, 6H), 4.78 (t, 1H, *J* = 3.0 Hz), 4.24-4.10 (m, 2H), 4.0-3.92 (m, 1H), 3.84-3.76 (m, 1H), 3.53-3.46 (m, 1H), 3.41-3.33 (m, 1H), 3.06 (s, 3H), 2.38-2.17 (m, 2H), 1.88-1.11 (m, 10H), 1.04 (s, 9H), 0.69 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.7, 129.4, 127.4, 96.6, 82.8, 77.6, 75.9, 70.1, 61.9, 56.3, 54.5, 41.9, 39.9, 30.2, 27.0, 25.3, 23.5, 19.1, 17.6, 13.9; HRMS (ESI): m/z calculated for $C_{32}H_{46}O_4Si$ $(M+Na)^+$ 545.3063, found 545.3059.

(5*S*,7*S*)-7-(*tert*.-Butyldiphenylsilyloxy)-5-methoxydec-2-yn-1-ol (32)

To a stirred solution of **31** (3.0 g, 5.75 mmol) in MeOH (15 mL), PPTS(cat.) was added at 0 °C and stirred at room temperature for 2 h. Reaction mixture was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 9% ethyl acetate in pet. ether) to furnish **32** (1.90 g, 75%) as a colourless oil; $[\alpha]_D^{25}$ +55.25 (*c* 0.2, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.68-7.64 (m, 4H), 7.42-7.29 (m, 6H), 4.16-4.15 (m, 2H), 3.98-3.90 (m, 1H), 3.38-3.29 (m, 1H), 3.06 (s, 3H), 2.29-2.26 (m, 2H), 1.75-1.58 (m, 2H), 1.45-1.16 (m, 6H), 1.04 (s, 9H), 0.70 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.6, 129.4, 127.4, 82.3, 80.2, 75.8, 70.2, 56.3, 51.2, 41.8, 39.8, 27.0, 23.2, 17.7, 14.0; HRMS (ESI): m/z calculated for $C_{27}H_{38}O_3NaSi$ $(M+Na)^+$ 461.2487, found 461.2485.

((2*S*,3*S*)-3-((2*S*,4*S*)-4-(*tert*.-Butyldiphenylsilyloxy)-2-methoxyheptyl)oxiran-2-yl) methanol (34)

`

To a stirred solution of (-)-DIPT (0.17 g, 0.72 mmol) in CH_2Cl_2 (5 mL) at -20 ^oC containing MS 4 Å (0.5 g), $Ti(O^iPr)_4$ (0.10 mL, 0.36 mmol) and cumene hydroperoxide (0.81 mL, 5.46 mmol) were added sequentially and stirred for 20 min. A solution of **33** (1.60 g, 3.64 mmol) in CH_2Cl_2 (8 mL) was added and stirred for 5 h at -20 ^oC. Worked up as described for **9** and purified the residue by column chromatography (60-120 mesh Silica gel, 25% ethyl acetate in pet. ether) to furnish **34** (1.25 g, 75%) as a colourless oil; $[\alpha]_D^{25}$ +62.66 (*c* 0.3, $CHCl_3$); IR (neat): 3435, 3071, 2957, 2932, 2862, 1732, 1109, 821, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.69-7.63 (m, 4H), 7.42-7.30 (m, 6H), 3.97-3.88 (m, 1H), 3.85-3.76 (m, 1H), 3.59-3.49 (m, 1H), 3.43-3.31 (m, 1H), 3.02 (s, 3H), 2.88-2.81 (m, 1H), 2.80-2.74 (m, 1H), 1.71-1.48 (m, 4H), 1.43-1.18 (m, 4H), 1.04 (s, 9H), 0.73 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.6, 129.4, 127.4, 75.4, 70.4, 61.7, 58.0, 55.9, 52.6, 42.0, 39.8, 35.2, 27.0, 19.4, 17.7, 14.0; HRMS (ESI): m/z calculated for $C_{27}H_{40}O_4Si$ $(M+Na)^+$ 479.2593, found 479.2609.

(3*R*,5*R*)-(4*R*,6*S*,8*S*)-6-Methoxy-8-methyldec-9-en-4-yl3-(4-methoxybenzyloxy)-5-(methoxym-ethoxy) oct-7-enoate (4)

To a stirred solution of alcohol **5** (0.16 g, 0.80 mmol) in CH_2Cl_2 (3 mL), DCC (0.25 g, 0.88 mmol), DMAP (0.15 g, 0.88 mmol) followed by a solution of acid **6** (0.33 g, 0.96 mmol) in CH_2Cl_2 (5 mL) were added at 0 ^oC. After 12 h, it was diluted with water (2 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (2 mL), dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 7% ethyl acetate in pet. ether) to furnish **4** (0.28 g, 67%) as a colourless oil; $[\alpha]_D^{25}$ +4.10 (*c* 0.5, $CHCl_3$); IR (neat): 3431, 2955, 2928, 1730, 1639, 1614, 1514, 1458, 1375, 1302, 1248, 1172, 1093, 1037, 916, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, 2H, *J* = 8.3 Hz), 6.79 (d, 2H, *J* = 8.3 Hz), 5.81-5.69 (m, 1H), 5.67-5.57 (m, 1H), 5.14-5.02 (m, 3H), 4.95-4.83 (m, 2H), 4.61 (d, 1H, *J* = 6.8 Hz), 4.56 (d, 1H, *J* = 6.8 Hz), 4.45 (d, 1H, *J* = 10.9 Hz), 4.40 (d, 1H, *J* = 10.9 Hz), 4.03-3.92 (m, 1H), 3.78 (s, 3H), 3.73-3.65 (m, 1H), 3.34 (s, 3H), 3.24 (s, 3H), 3.14-3.04 (m, 1H), 2.54-2.43 (m, 2H), 2.32-2.12 (m, 3H), 1.92-1.83 (m, 1H), 1.67-1.43 (m, 5H), 1.36-1.18 (m, 4H), 0.99 (d, 3H, *J* = 6.2 Hz), 0.88 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, CDCl3): δ 171.3, 159.1, 144.2, 134.3, 130.4, 129.4, 117.5, 113.7, 112.9, 95.3, 75.9, 73.7, 72.9, 71.4, 71.0, 56.6, 55.7, 55.2, 40.5, 39.9, 39.4, 38.9, 38.8, 37.2, 34.6, 20.8, 18.5, 13.9; HRMS (ESI): m/z calculated for $C_{30}H_{48}O_7$ $(M+Na)^+$ 543.3297, found 543.3309.

`

(4*R*,6*R*,10*S*,12*S*,14*S*)-12-Methoxy-4-[(4-methoxybenzyl)oxy]-6-(methoxymethoxy)-10-methyl-14-propyl-1-oxa-8-cyclotetradecen-2-one (37)

To a stirred solution of **4** (0.21 g, 0.40 mmol) in anhydrous CH_2Cl_2 (500 mL) under N_2 atmosphere, Grubb's II catalyst (34 mg, 0.04 mmol) was added at room temperature and stirred for 12 h. Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 10% ethyl acetate in pet. ether) to afford **37** (0.13 g, 65%) as a colourless oil; $[\alpha]_D^{25}$ +34.95 (*c* 0.2, $CHCl_3$); IR (neat): 3447, 2986, 2934, 1794, 1745, 1645, 1454, 1373, 1217, 1159, 1059, 841 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 5.50-5.38 (m, 1H), 5.25-5.18 (m, 1H), 5.04-4.96 (m, 1H), 4.69 (d, 1H, *J* = 6.8 Hz), 4.62 (d, 1H, *J* = 6.8 Hz), 4.55 (d, 1H, *J* = 11.3 Hz), 4.33 (d, 1H, *J* = 11.3 Hz), 3.85-3.76 (m, 1H), 3.81 (s, 3H), 3.67-3.55 (m, 1H), 3.42-3.21 (m, 1H), 3.35 (s, 3H), 3.32 (s, 3H), 2.93 (dt, 1H, *J* = 2.3, 10.9 Hz), 2.75 (dd, 1H, *J* = 1.5, 14.4 Hz), 2.56 (dd, 1H, *J* = 8.7, 14.4 Hz), 2.36-1.92 (m, 4H), 1.90-1.39 (m, 6H), 1.37-1.16 (m, 2H), 0.95 (d, 3H, *J* = 6.4 Hz), 0.88 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75MHz, $CDCl_3$): δ 170.7, 137.7, 129.9, 129.8, 124.5, 113.8, 95.1, 75.8, 74.4, 72.0, 71.2, 70.0, 56.6, 55.4, 55.3, 39.5, 39.1, 38.5, 38.3, 37.2, 35.0, 34.9, 29.7, 22.9, 18.4, 13.9; HRMS (ESI): m/z calculated for $C_{28}H_{44}O_7$ $(M+Na)^+$ 515.2984, found 515.2987.

(4*R*,6*R*,10*S*,12*S*,14*S*)-4-Hydroxy-12-methoxy-6-(methoxymethoxy)-10-methyl-14-propyl-1-oxa-8-cyclotetradecen-2-one (3)

To a stirred solution of **37** (0.10 g, 0.20 mmol) in CH_2Cl_2:H_2O (19:1, 4 mL), DDQ (69 mg, 0.31 mmol) was added and stirred at room temperature for 2 h. Sat. $NaHCO_3$ solution (2 mL) was added and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (2 mL), dried (Na_2SO_4), evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 17% ethyl acetate in pet. ether) to furnish **3** (68 mg, 90%) as a colourless oil; $[\alpha]_D^{25}$ -30.2 (*c* 0.35, $CHCl_3$); IR (neat): 3442, 2924, 2853, 1728, 1595, 1474, 1379, 1249, 1188, 1090, 1036, 766 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 5.43-5.15 (m, 3H), 4.77 (d, 1H, *J* = 6.8 Hz), 4.64 (d, 1H, *J* = 6.8 Hz), 4.0-3.92 (m, 1H), 3.75-3.63 (m, 1H), 3.39 (s, 3H), 3.24 (s, 3H), 2.89-2.79 (m, 1H), 2.58-2.38 (m, 2H), 2.24-1.94 (m, 3H), 1.75-1.09 (m, 10H), 1.03 (d, 3H, *J* = 6.4 Hz), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 138.4, 124.7, 94.7, 79.1, 75.5, 70.9, 69.5, 56.7, 55.8, 43.5, 39.8, 39.0, 37.5, 35.3, 34.5, 29.7, 22.5, 18.5, 13.9; HRMS (ESI): m/z calculated for $C_{20}H_{36}O_6$ $(M+Na)^+$ 395.2409, found 395.2420.

(1*R*,5*R*,7*S*,9*S*,11*S*,13*S*)-10-Iodo-7-methoxy-13-(methoxymethoxy)-9-methyl-5-propyl -4,15-dioxa-bicyclo[9.3.1]pentadecan-3-one (38)

`

To a solution of **3** (15 mg, 0.04 mmol) in CH_2Cl_2 (1.0 mL), a solution of NIS (14 mg, 0.06 mmol, dissolved in 0.6 mL of 5:1 CH_2Cl_2/CH_3CN) was added at 0 °C and allowed the reaction mixture to stir at room temperature for 2 h. It was quenched with aq. $Na_2S_2O_3$ solution (1 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with water (3 mL), brine (3 mL) and dried (Na_2SO_4). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh Silica gel, 7% ethyl acetate in pet. ether). First eluted was **38** (5 mg, 24%) as colourless oil; $[\alpha]_D^{25}$ -15.2 (*c* 0.36, $CHCl_3$); IR (neat): 3325, 2916, 2856, 1728, 1622, 1419, 1258, 1103, 1020, 791cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.02-4.94 (m, 1H), 4.69 (d, 1H, *J* = 6.8 Hz), 4.67 (d, 1H, *J* = 6.8 Hz), 4.19-4.11 (m, 1H), 4.12-4.05 (m, 1H), 3.94-3.82 (m, 2H), 3.40 (s, 3H), 3.31 (s, 3H), 2.52 (dd, 1H, *J* = 3.9, 14.1 Hz), 2.45-2.26 (m, 2H), 1.98-1.89 (m, 2H), 1.78-1.68 (m, 4H), 1.61-1.42 (m, 4H), 1.36-1.20 (m, 4H), 1.03 (d, 3H, *J* = 7.3 Hz), 0.91 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz,$CDCl_3$): δ 170.7, 94.9, 77.5, 75.8, 75.4, 70.2, 70.0, 56.2, 55.6, 43.5, 43.2, 39.0, 37.4, 36.3, 36.0, 35.8, 29.7, 23.7, 18.2, 13.9; HRMS (ESI): m/z calculated for $C_{20}H_{35}O_6I$ $(M+Na)^+$ 521.1376, found 521.1371

Second eluted was **38a** (11 mg, 54%)**:** $[\alpha]_D^{25}$ -5.0 (*c* 0.75, $CHCl_3$); IR (neat): 3327, 2918, 2853, 1724, 1628, 1422, 1253, 1113, 1026, 798cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.15-5.07 (m, 1H), 4.81-4.68 (m, 1H), 4.7 (d, 1H, *J* = 7.3 Hz), 4.65 (d, 1H, *J* = 7.3 Hz), 4.39-4.40 (m, 1H), 4.12-4.06 (m, 1H), 4.06-4.0 (m, 1H), 3.39 (s, 3H), 3.32 (s, 3H), 2.63-2.50 (m, 2H), 2.39-2.32 (m, 1H), 2.07-1.88 (m, 2H), 1.84-1.74 (m, 2H), 1.68-1.45 (m, 4H), 1.40-1.22 (m, 6H), 1.06 (d, 3H, *J* = 6.3 Hz), 0.92 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 94.6, 78.3, 73.3, 68.5, 56.6, 55.5, 37.5, 35.5, 33.8, 31.9, 29.7, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 18.6, 13.9; HRMS (ESI): m/z calculated for $C_{20}H_{35}O_6I$ $(M+Na)^+$ 521.1376, found 521.1373.

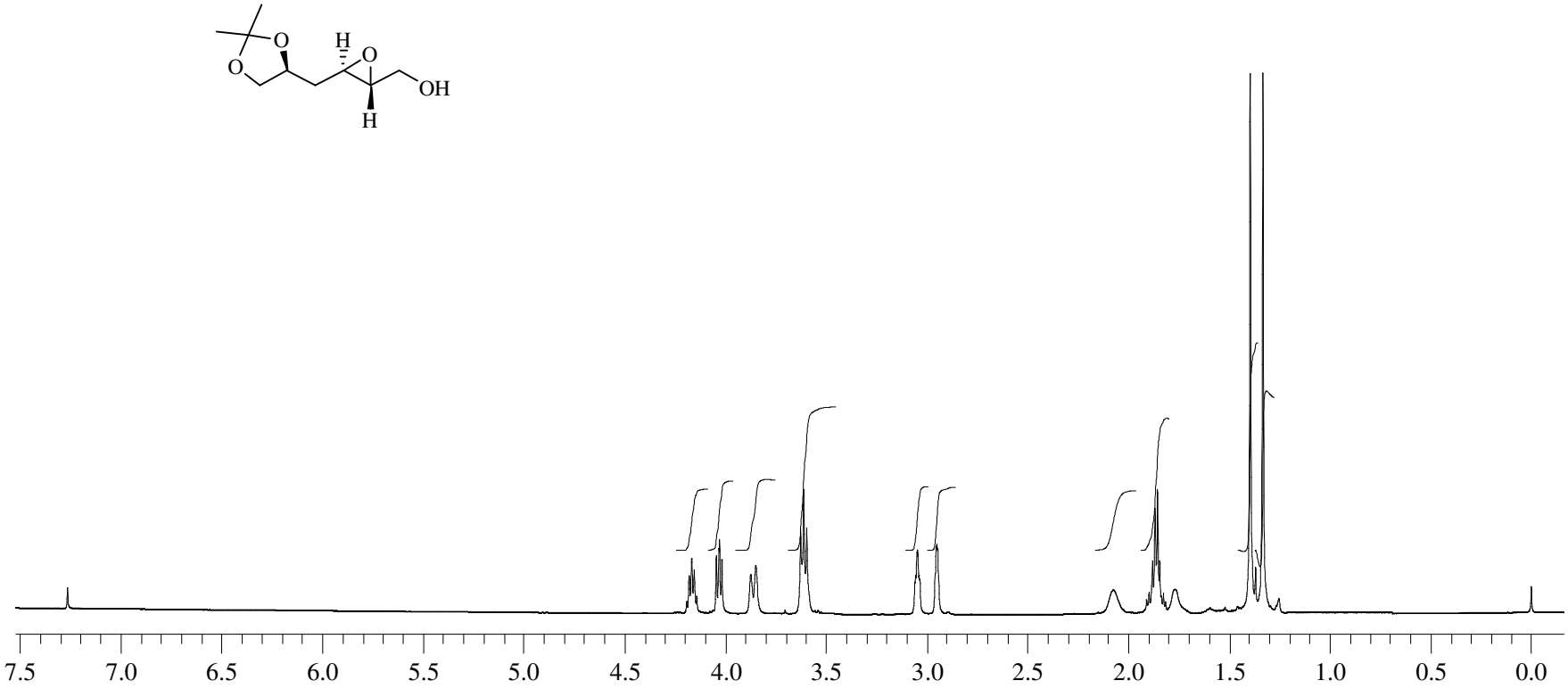

Figure 1: ^{1}H NMR Spectrum of compound **9** ($CDCl_3$, 500 MHz).

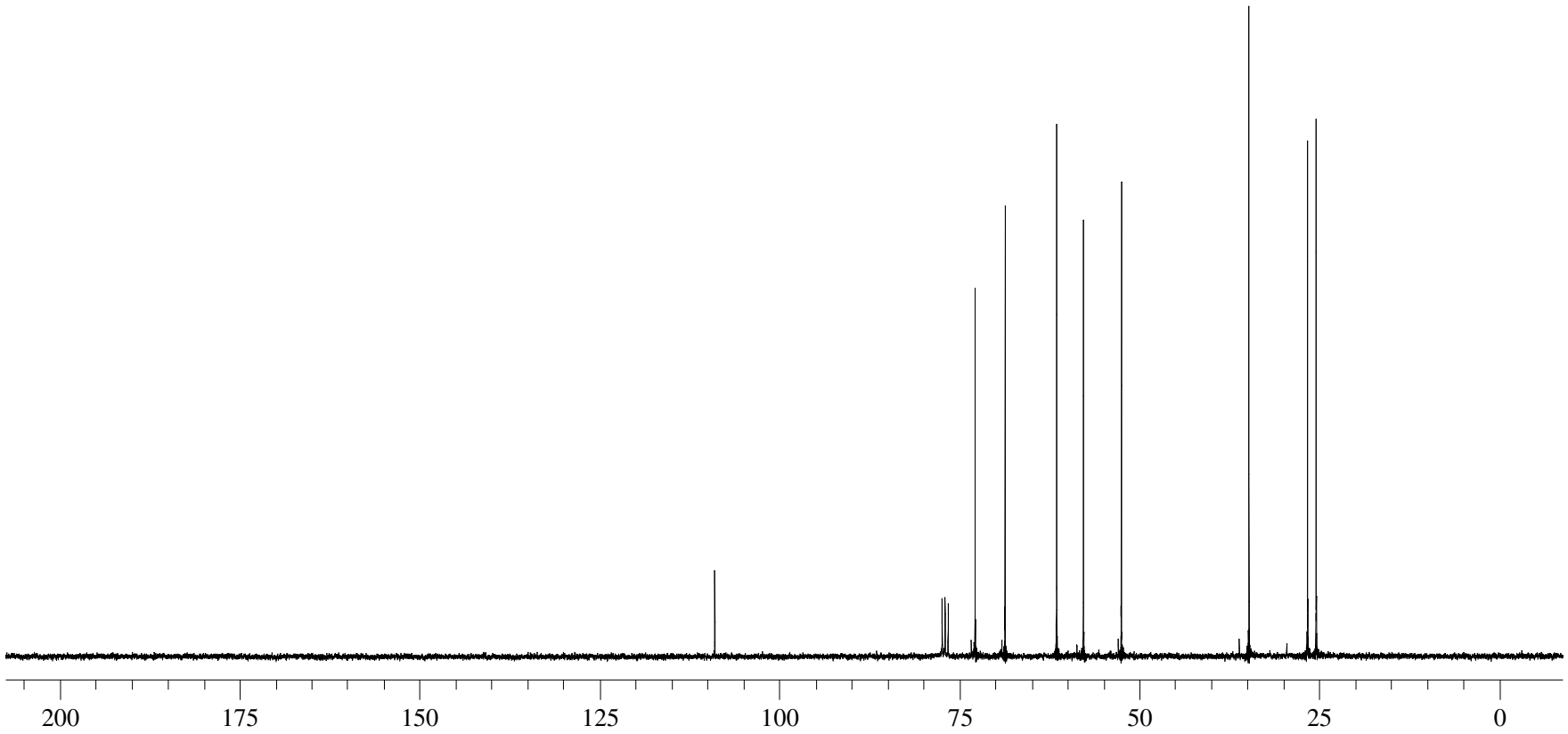

Figure 2: ^{13}C NMR Spectrum of compound **9** ($CDCl_3$, 75 MHz).

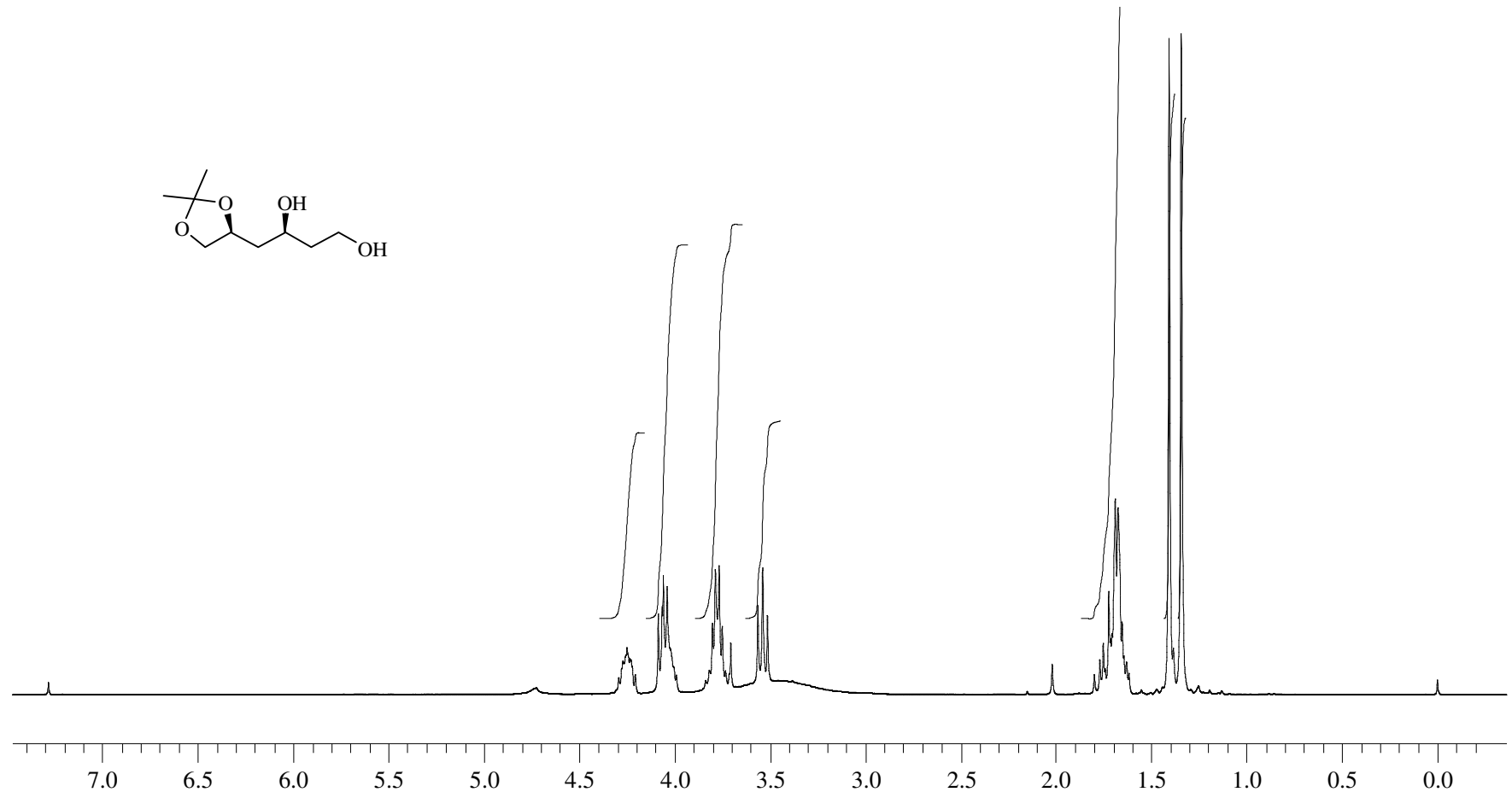

Figure 3: ^{1}H NMR Spectrum of compound **10** ($CDCl_3$, 300 MHz).

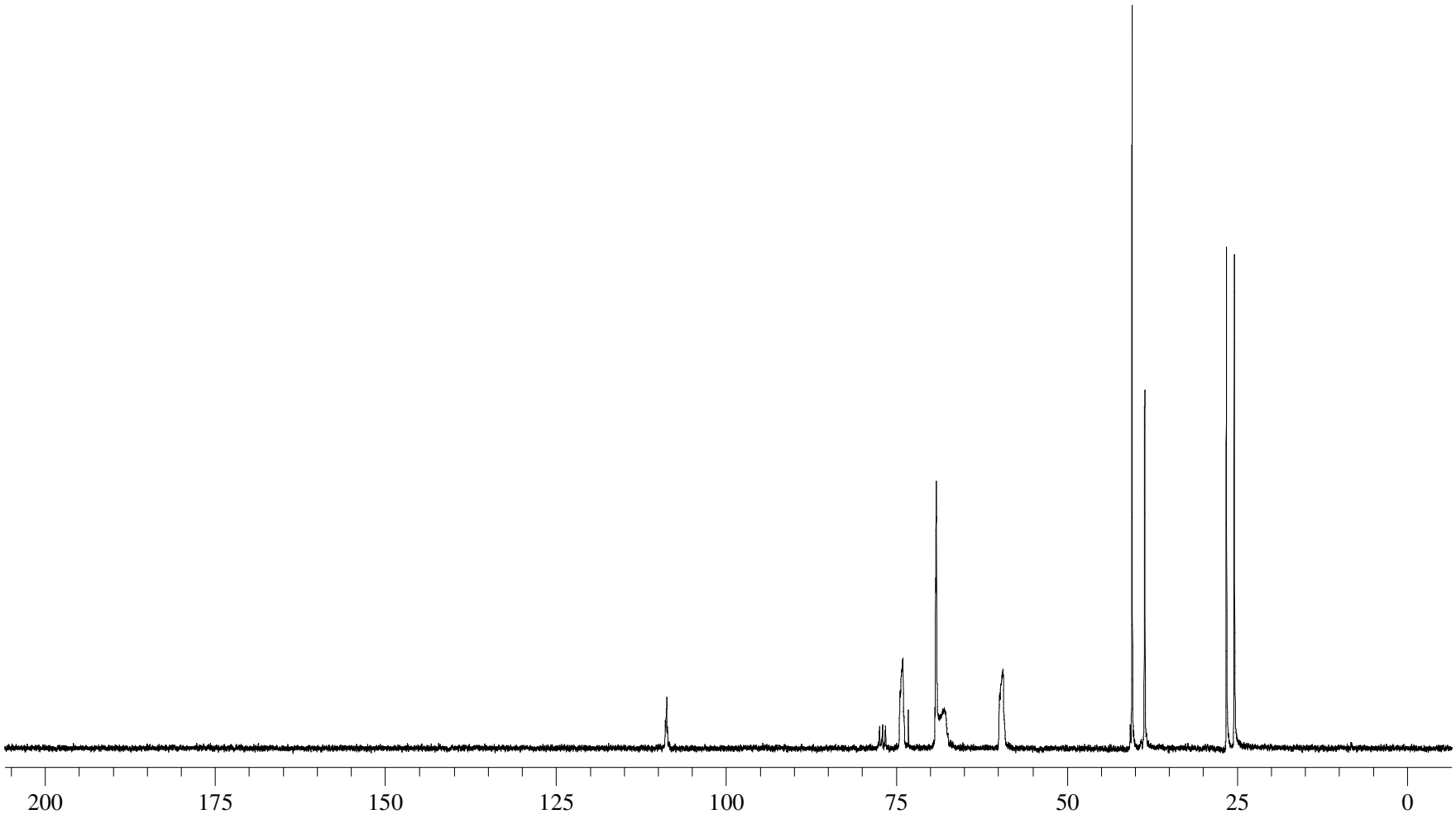

Figure 4: ^{13}C NMR Spectrum of compound **10** ($CDCl_3$, 75 MHz).

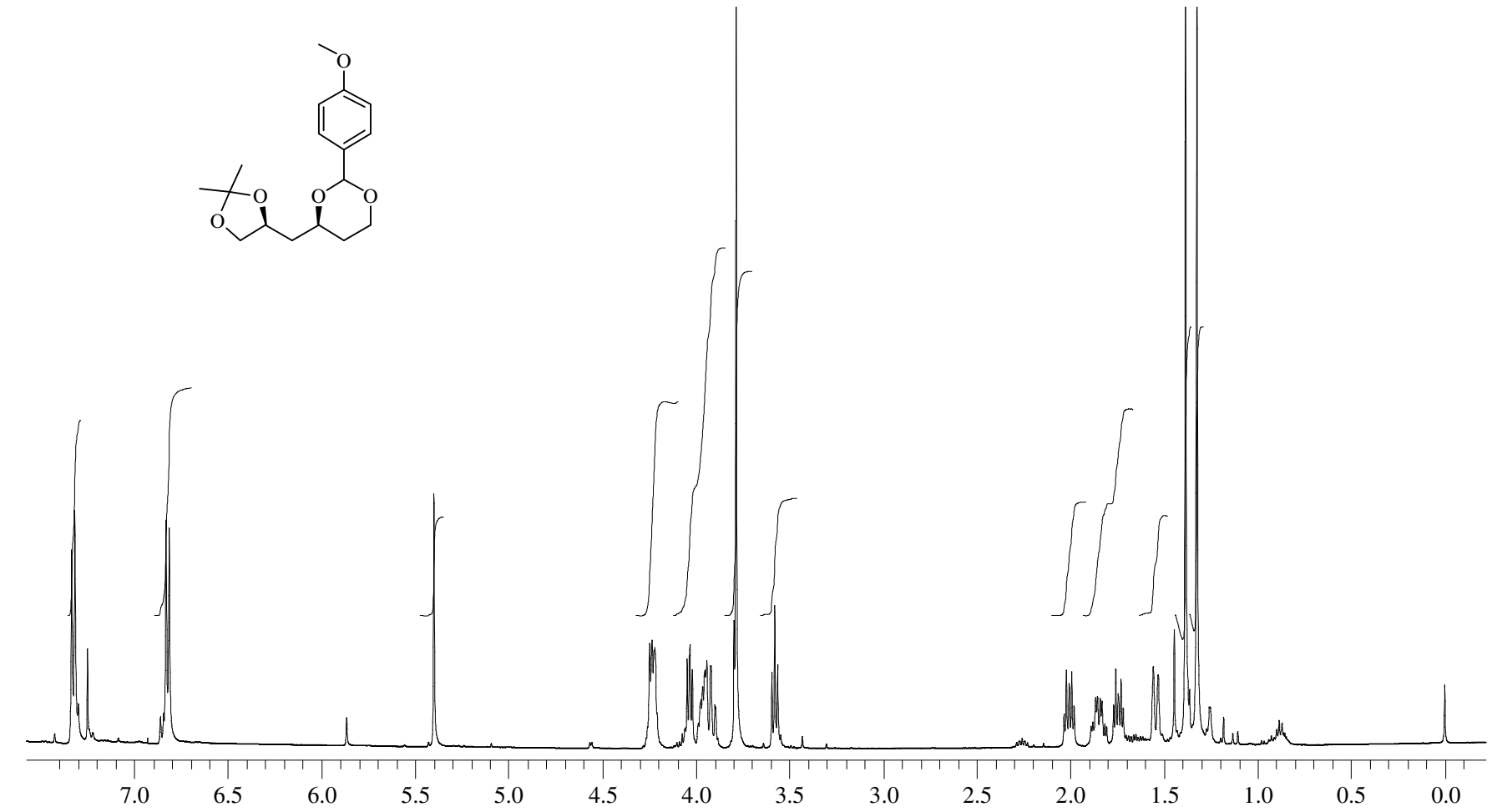

Figure 5: ^{1}H NMR Spectrum of compound **11** ($CDCl_3$, 500 MHz).

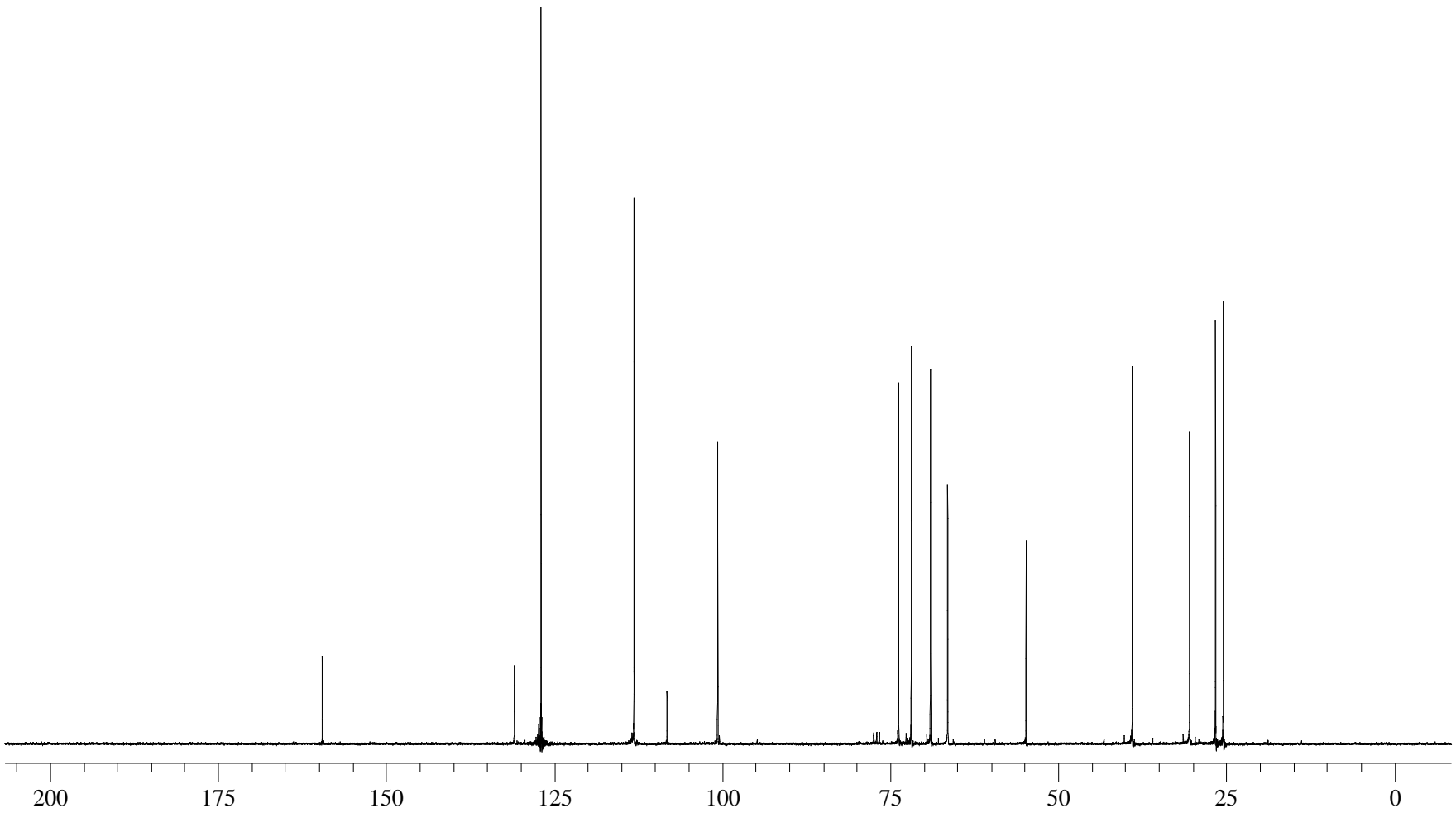

Figure 6: ^{13}C NMR Spectrum of compound **11** ($CDCl_3$, 75 MHz).

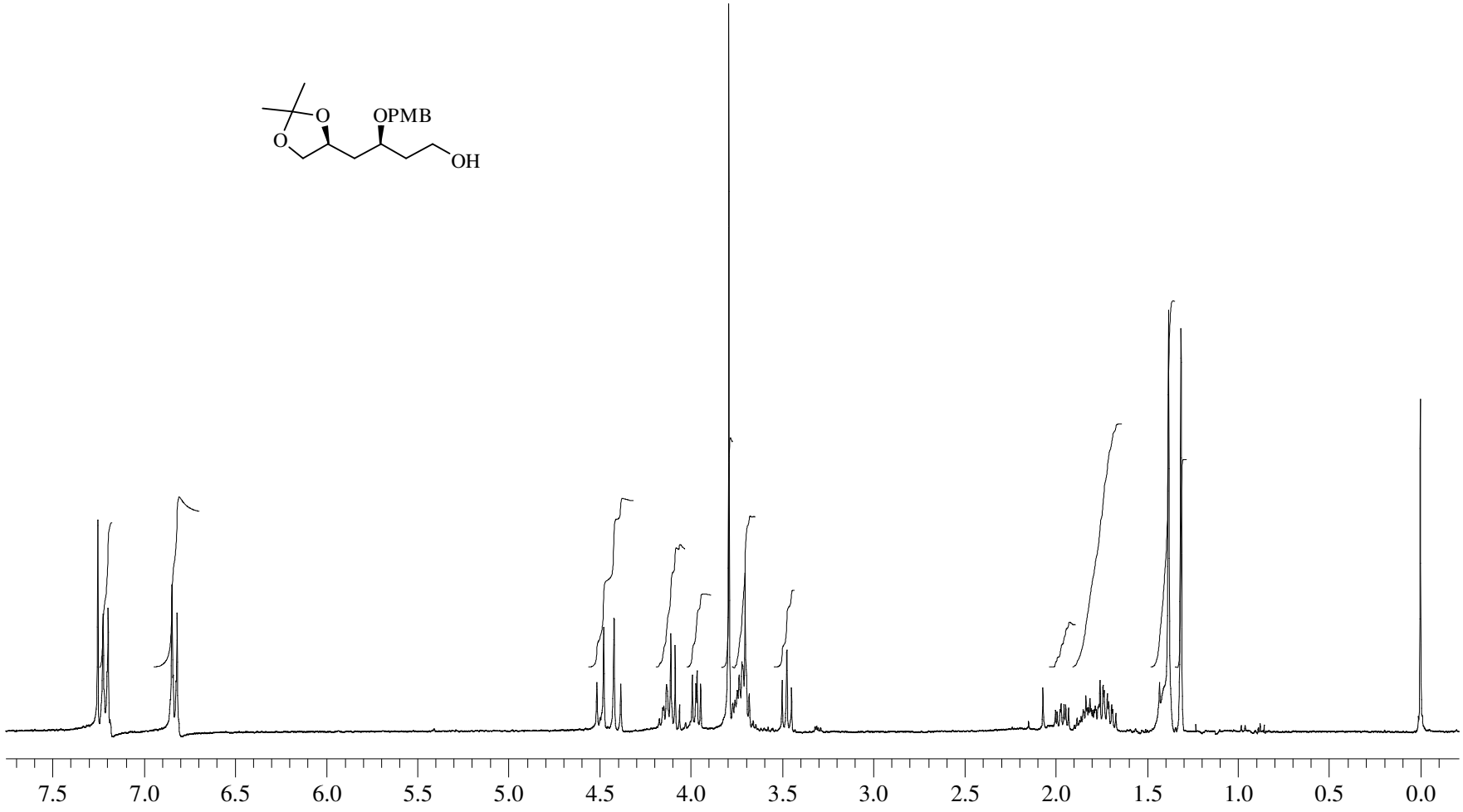

Figure 7: ^{1}H NMR Spectrum of compound **12** ($CDCl_3$, 500 MHz).

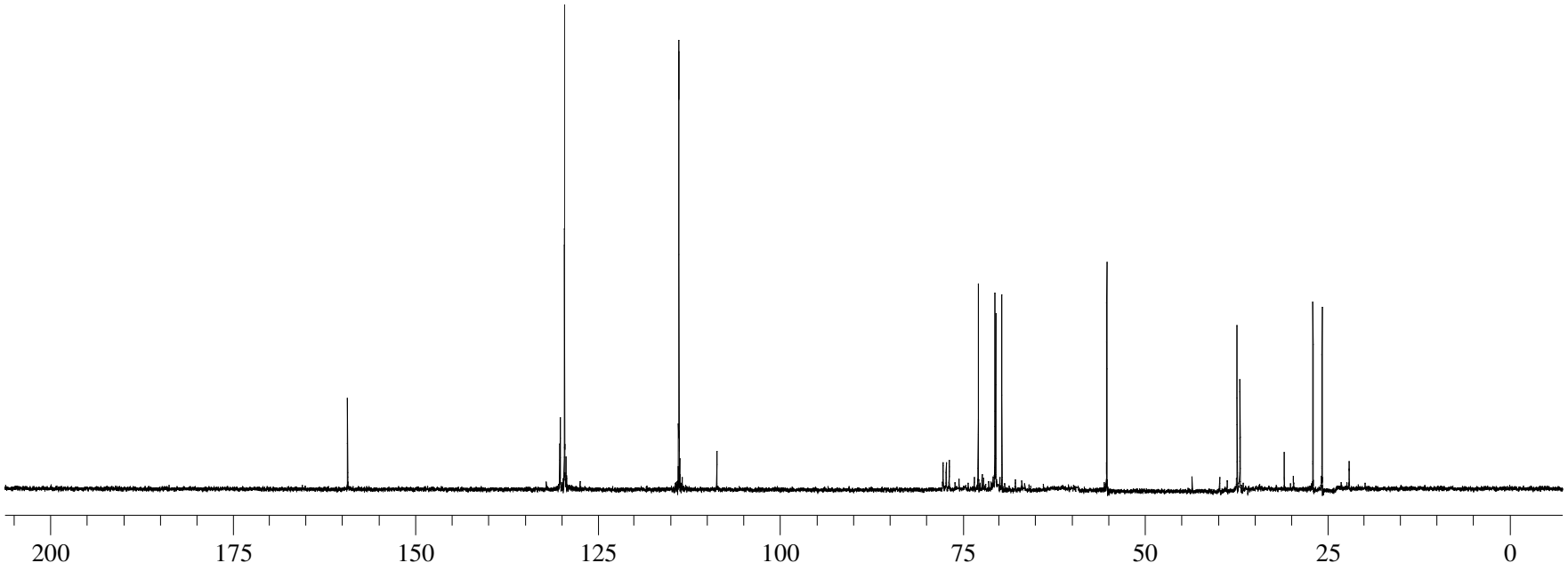

Figure 8: ^{13}C NMR Spectrum of compound **12** ($CDCl_3$, 75 MHz).

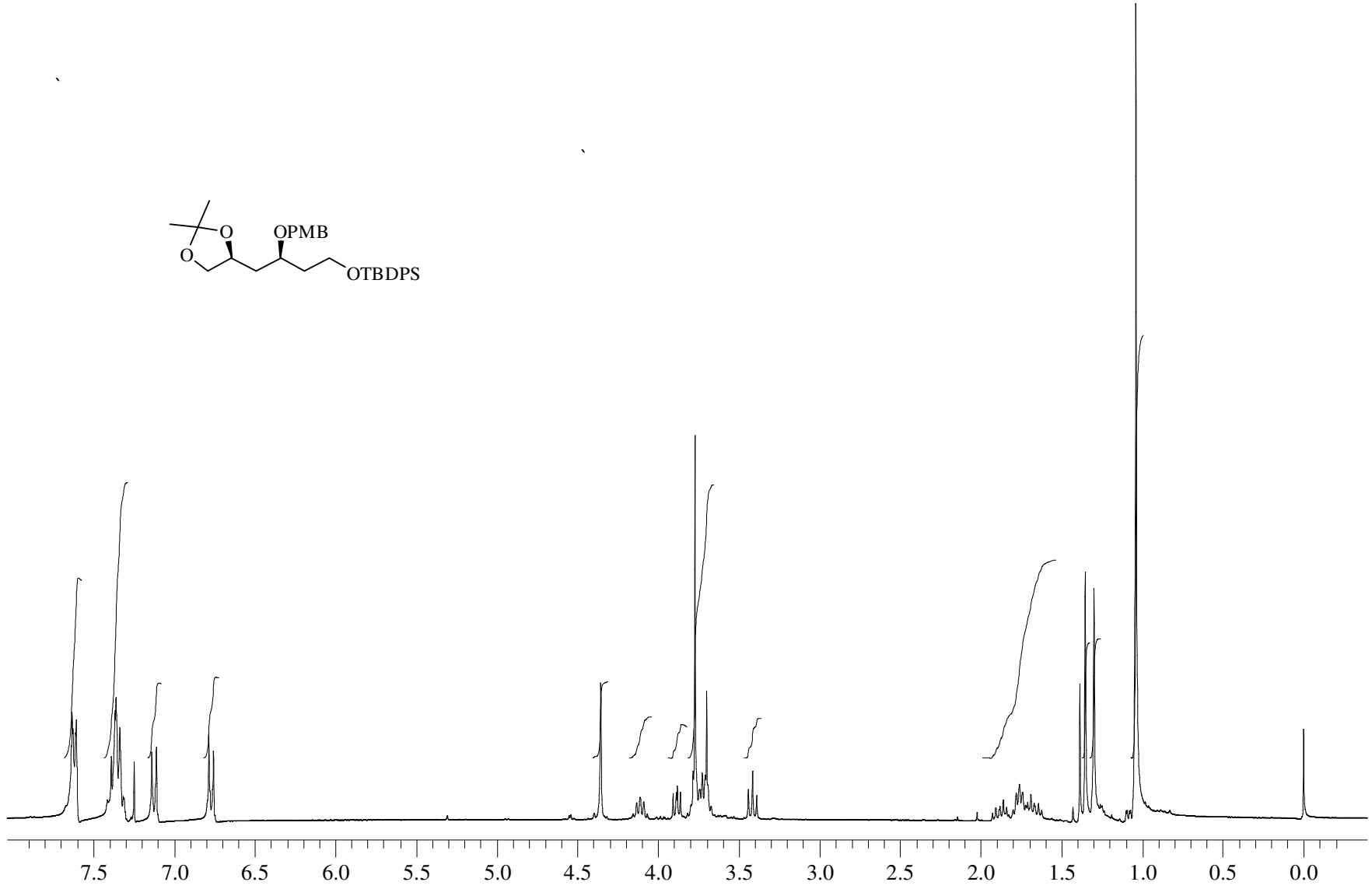

Figure 9: ^{1}H NMR Spectrum of compound **13** ($CDCl_3$, 500 MHz).

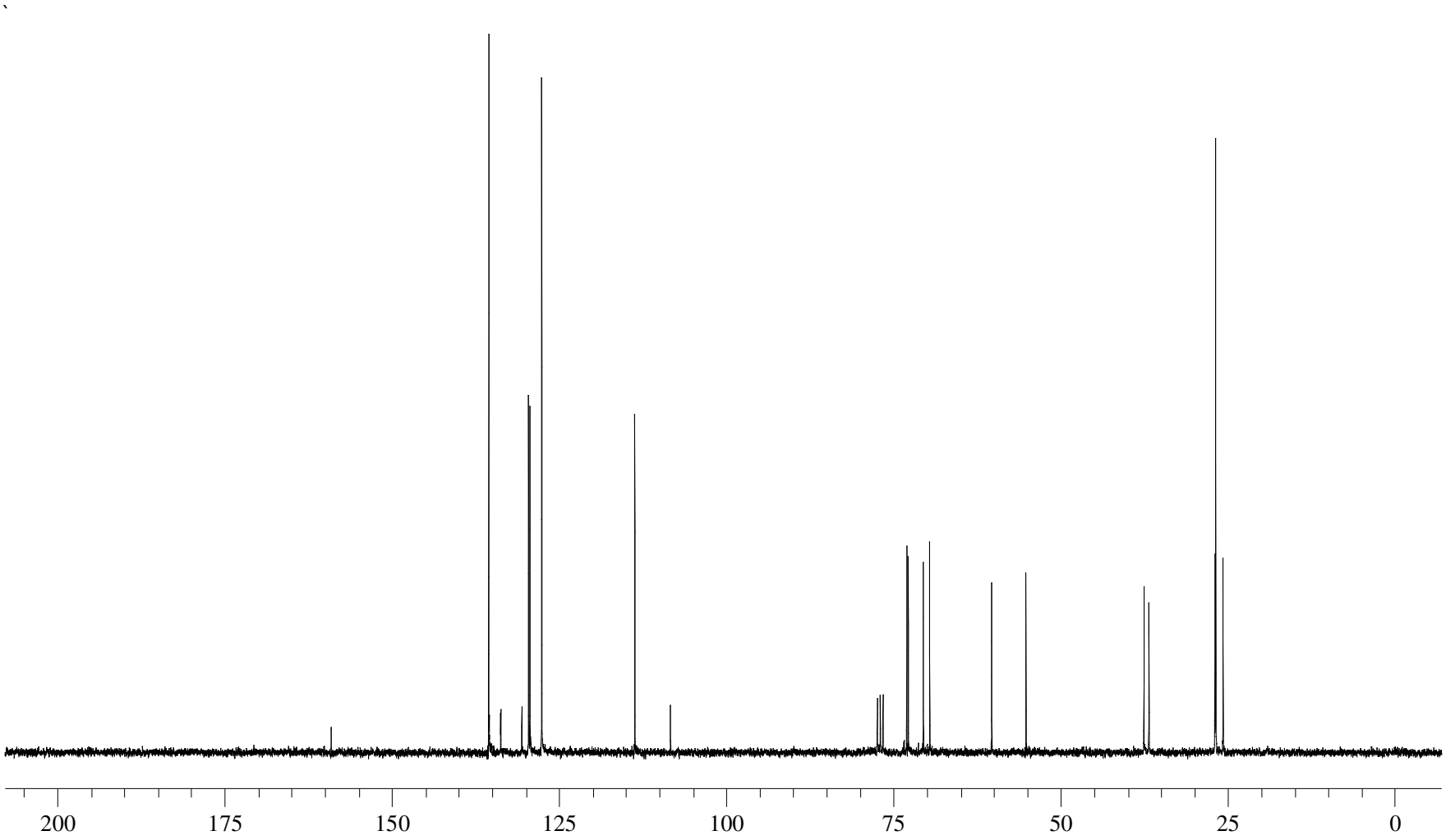

Figure 10: ^{13}C NMR Spectrum of compound **13** ($CDCl_3$, 75 MHz).

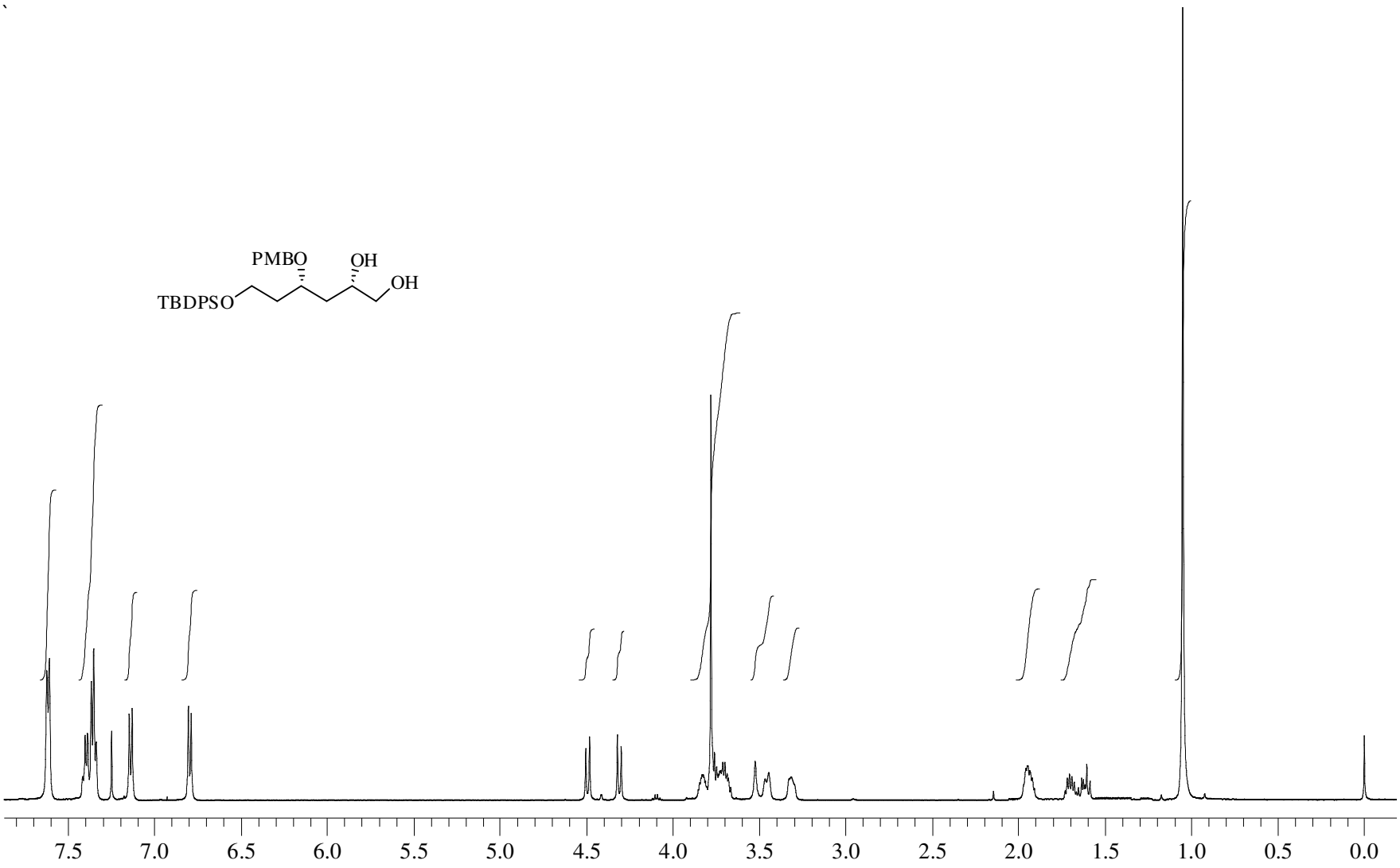

Figure 11: ^{1}H NMR Spectrum of compound **14** ($CDCl_3$, 500 MHz).

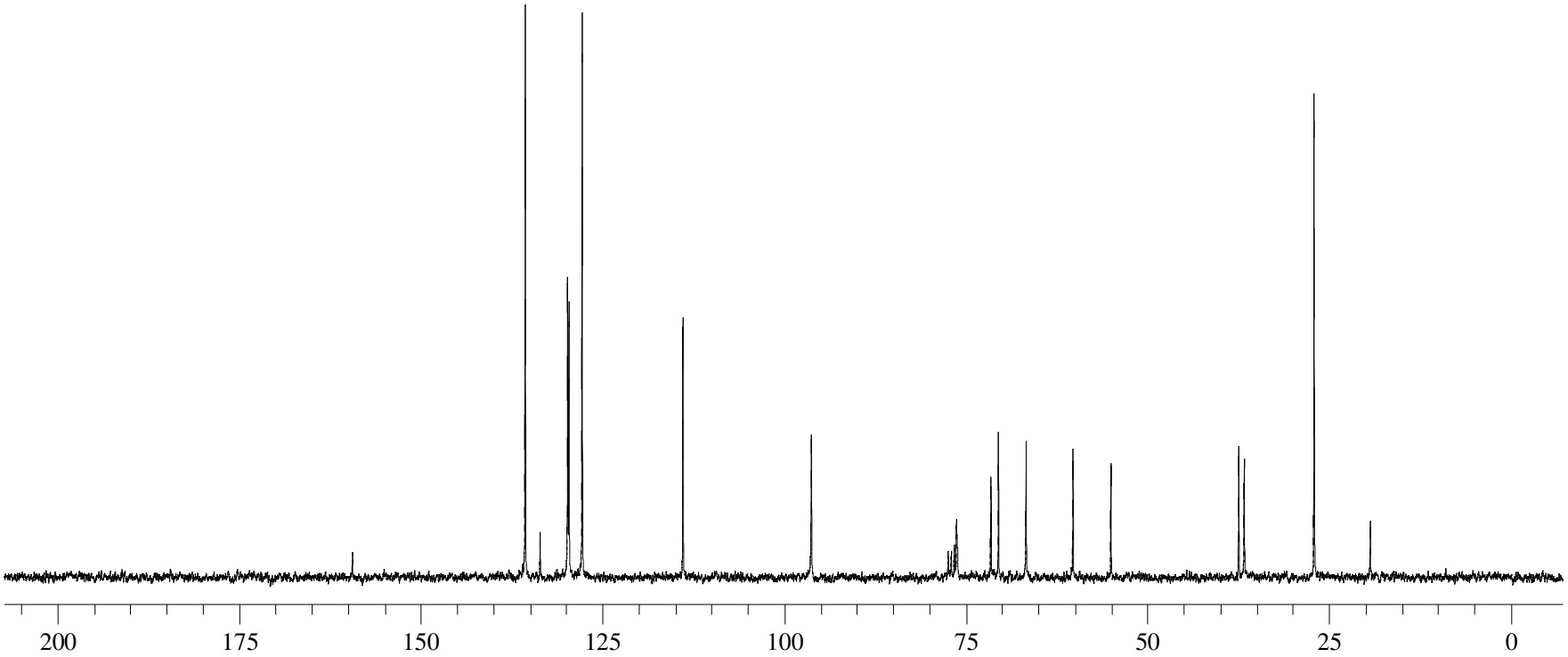

Figure 12: ^{13}C NMR Spectrum of compound **14** ($CDCl_3$, 75 MHz).

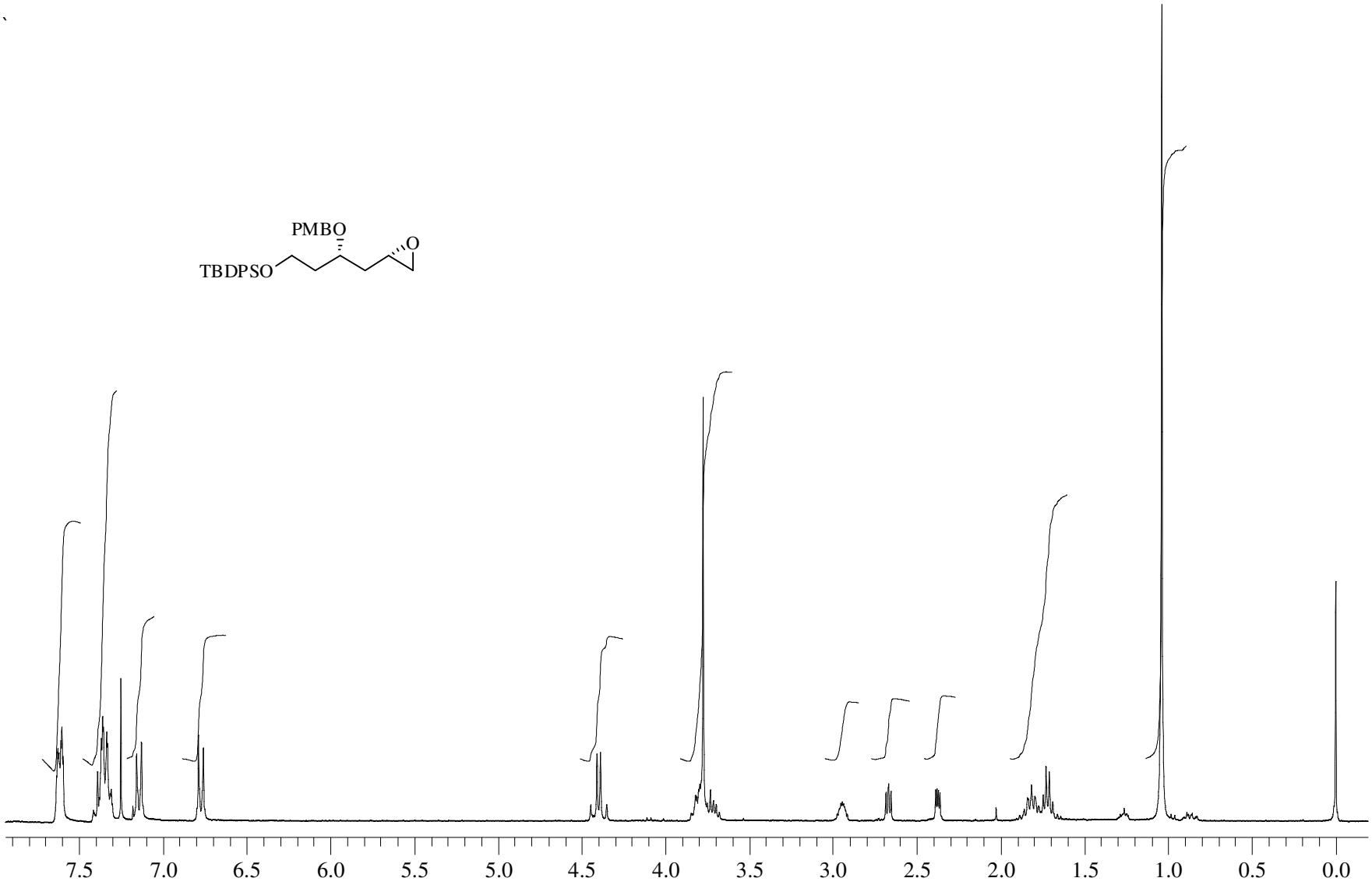

Figure 13: ^{1}H NMR Spectrum of compound **16** ($CDCl_3$, 500 MHz).

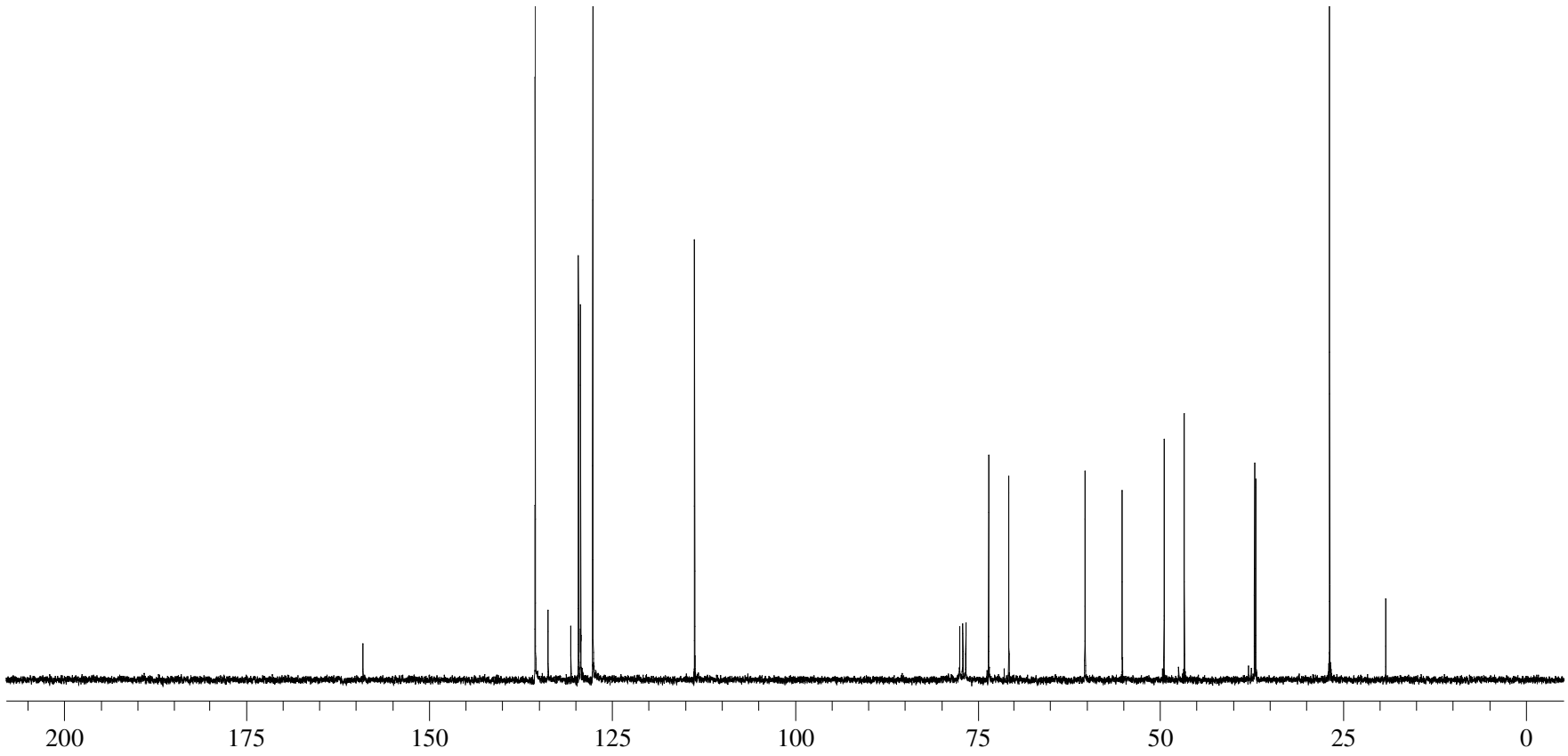

Figure 14: ^{13}C NMR Spectrum of compound **16** ($CDCl_3$, 75 MHz).

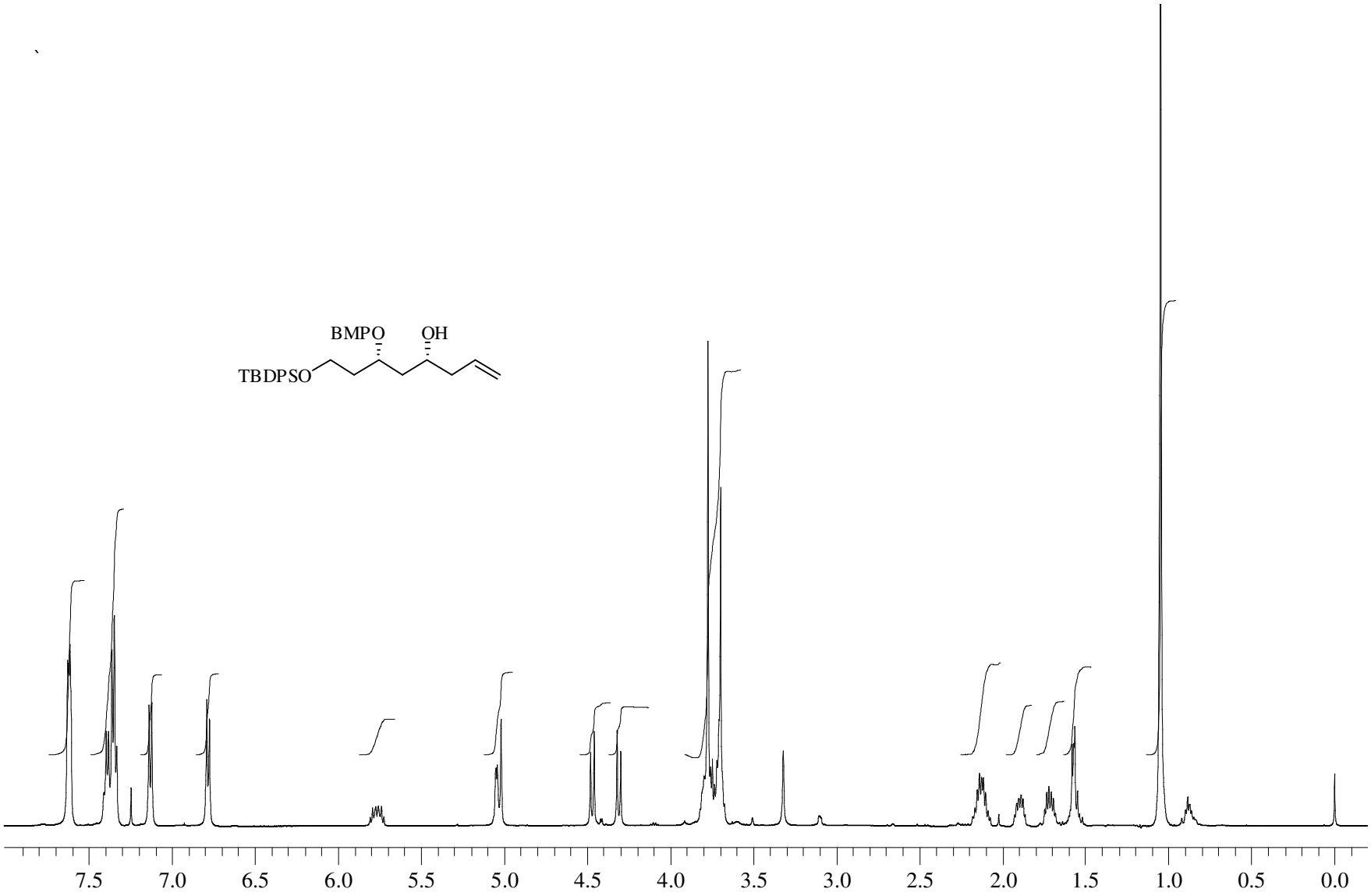

Figure 15: ^{1}H NMR Spectrum of compound **17** ($CDCl_3$, 500 MHz).

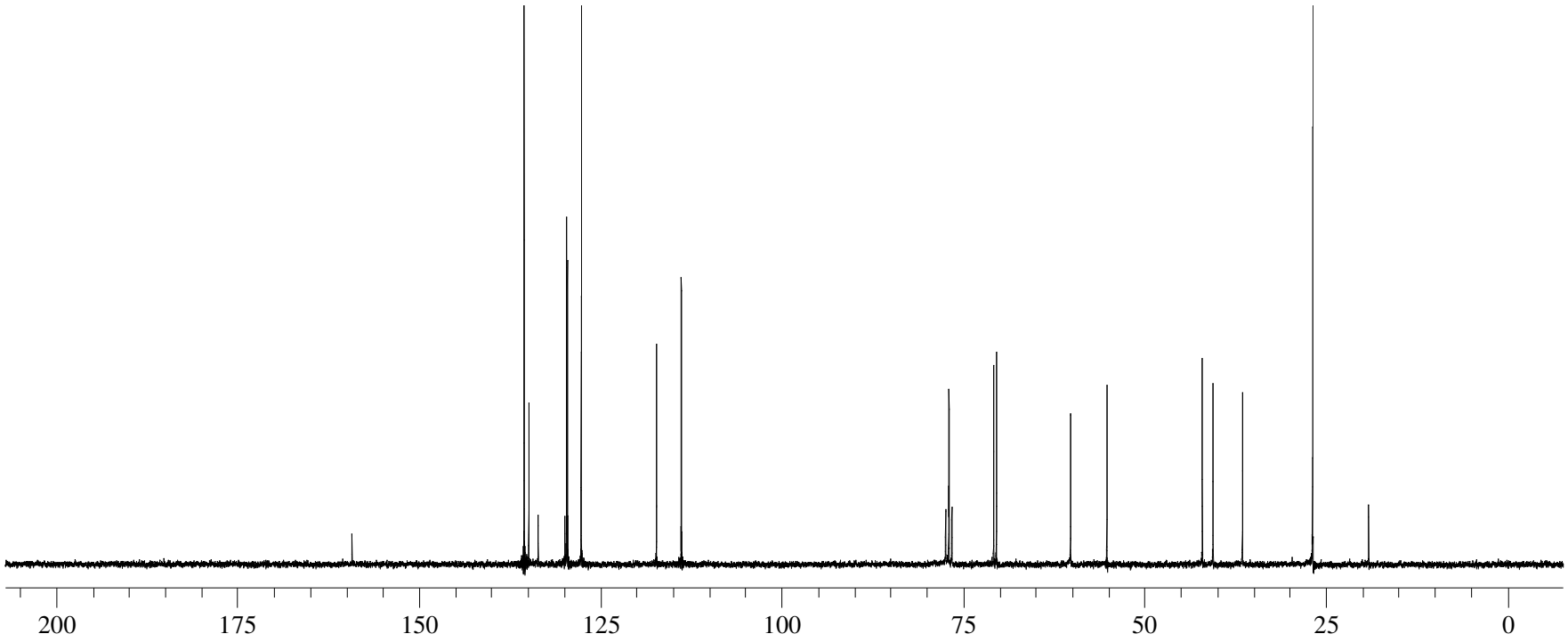

Figure 16: ^{13}C NMR Spectrum of compound **17** ($CDCl_3$, 75 MHz).

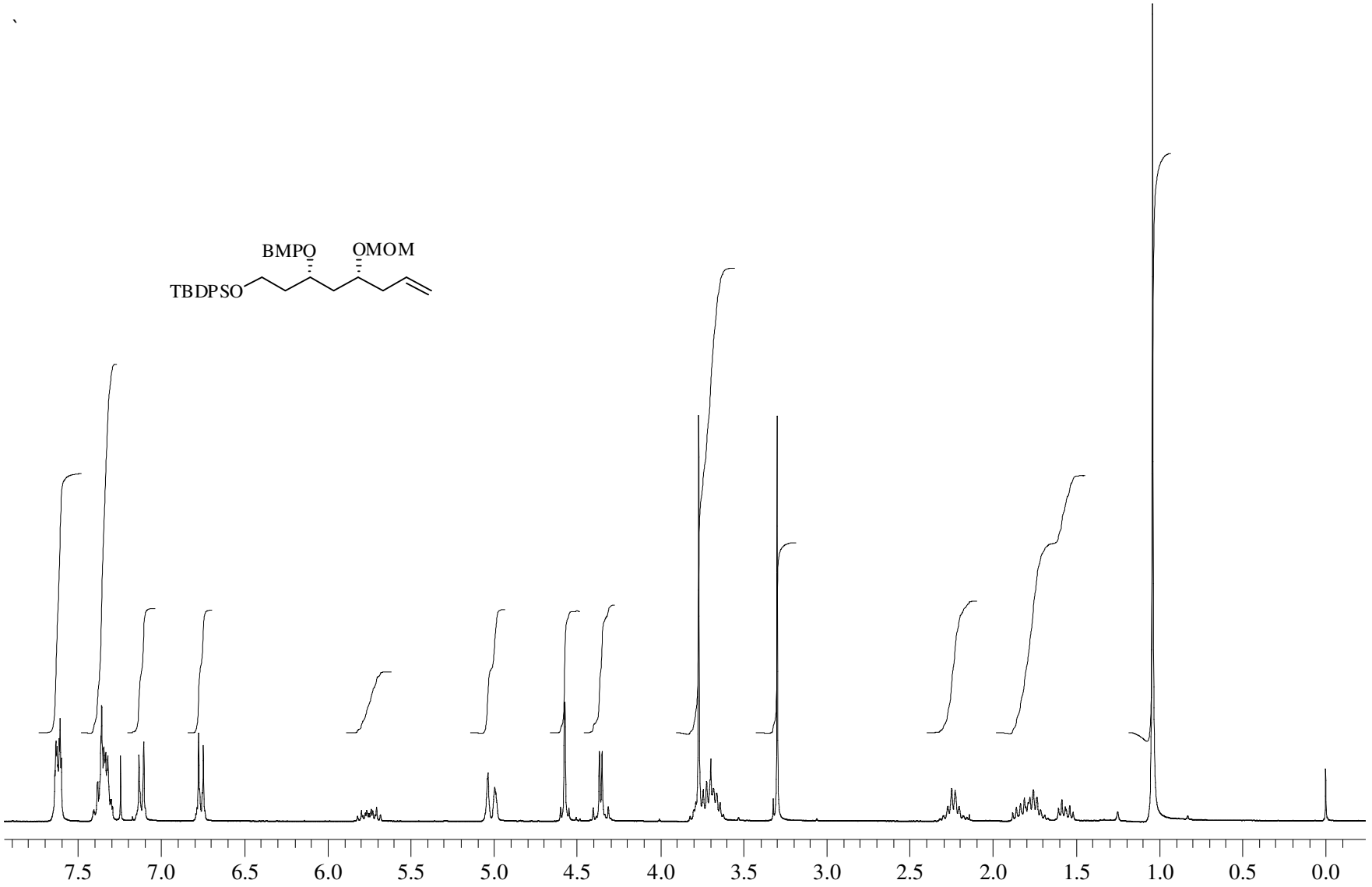

Figure 17: ^{1}H NMR Spectrum of compound **18** ($CDCl_3$, 500 MHz).

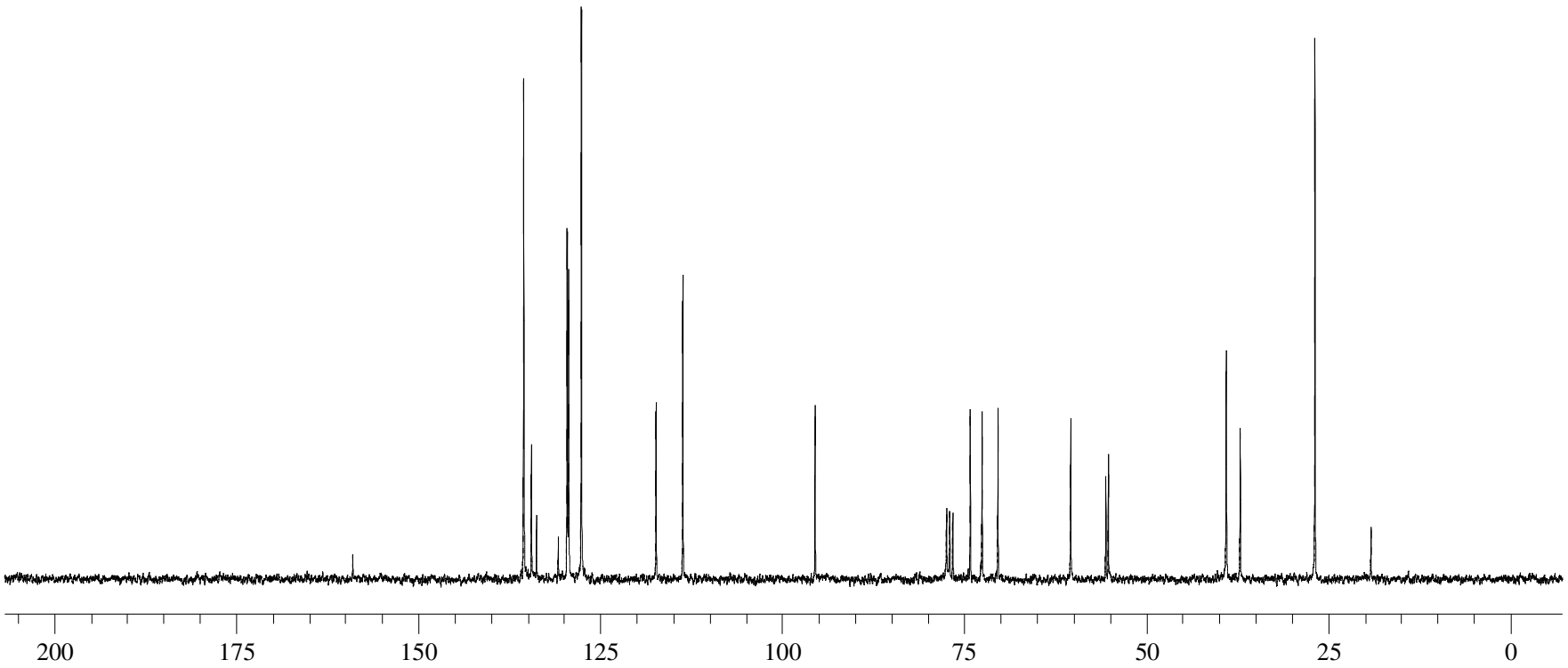

Figure 18: ^{13}C NMR Spectrum of compound **18** ($CDCl_3$, 75 MHz).

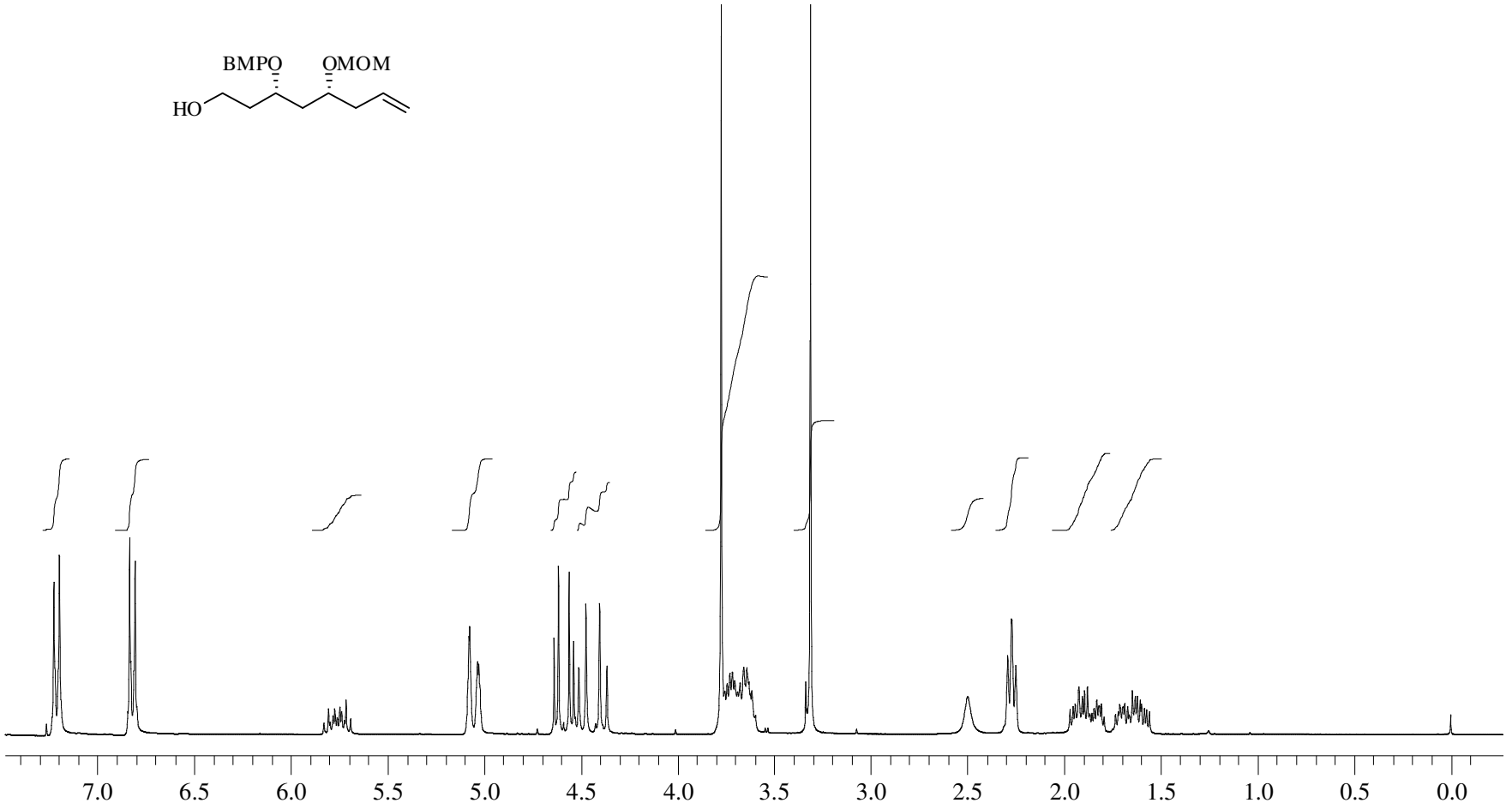

Figure 19: ^{1}H NMR Spectrum of compound **19** ($CDCl_3$, 500 MHz).

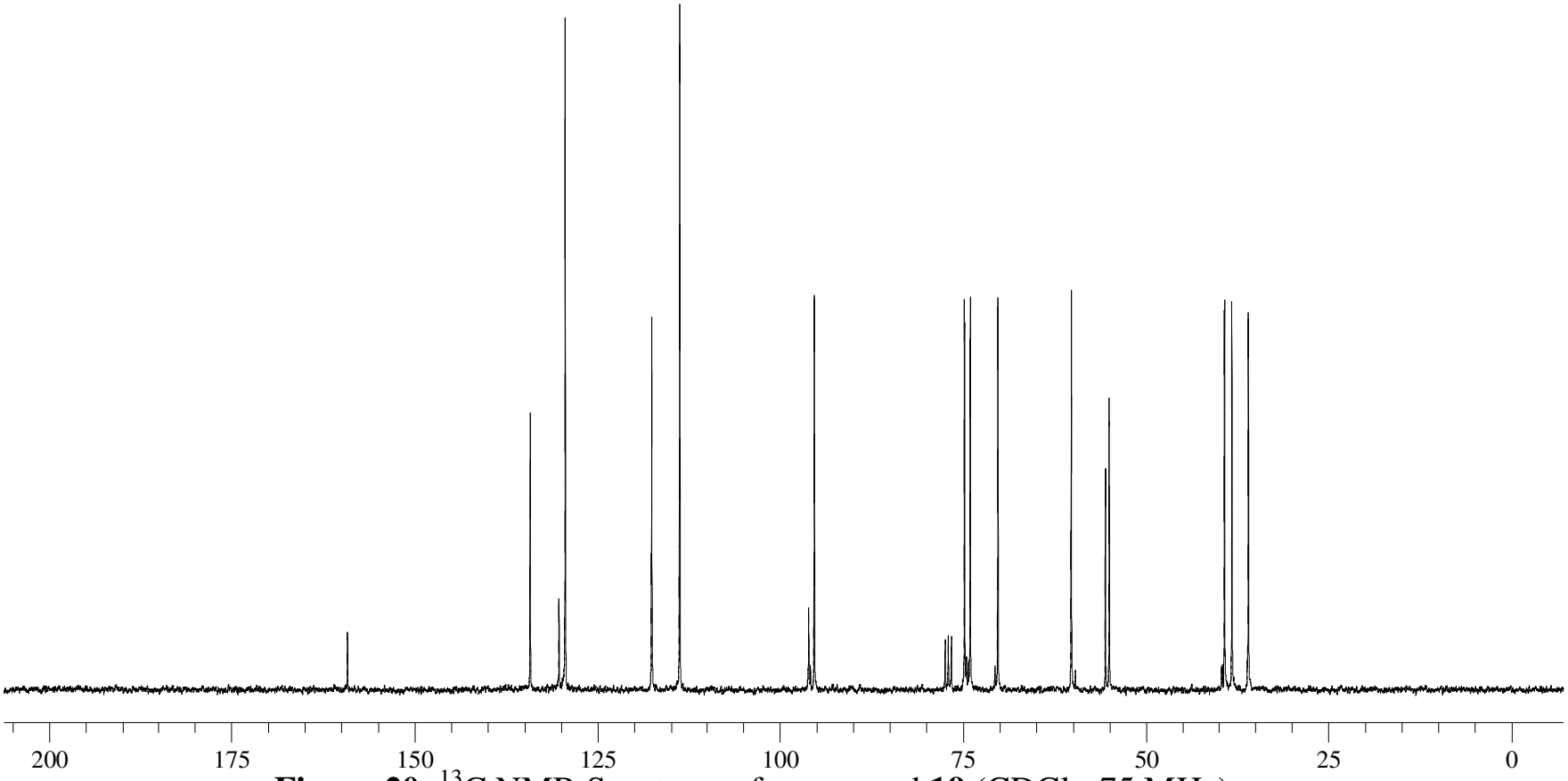

Figure 20: ^{13}C NMR Spectrum of compound **19** ($CDCl_3$, 75 MHz).

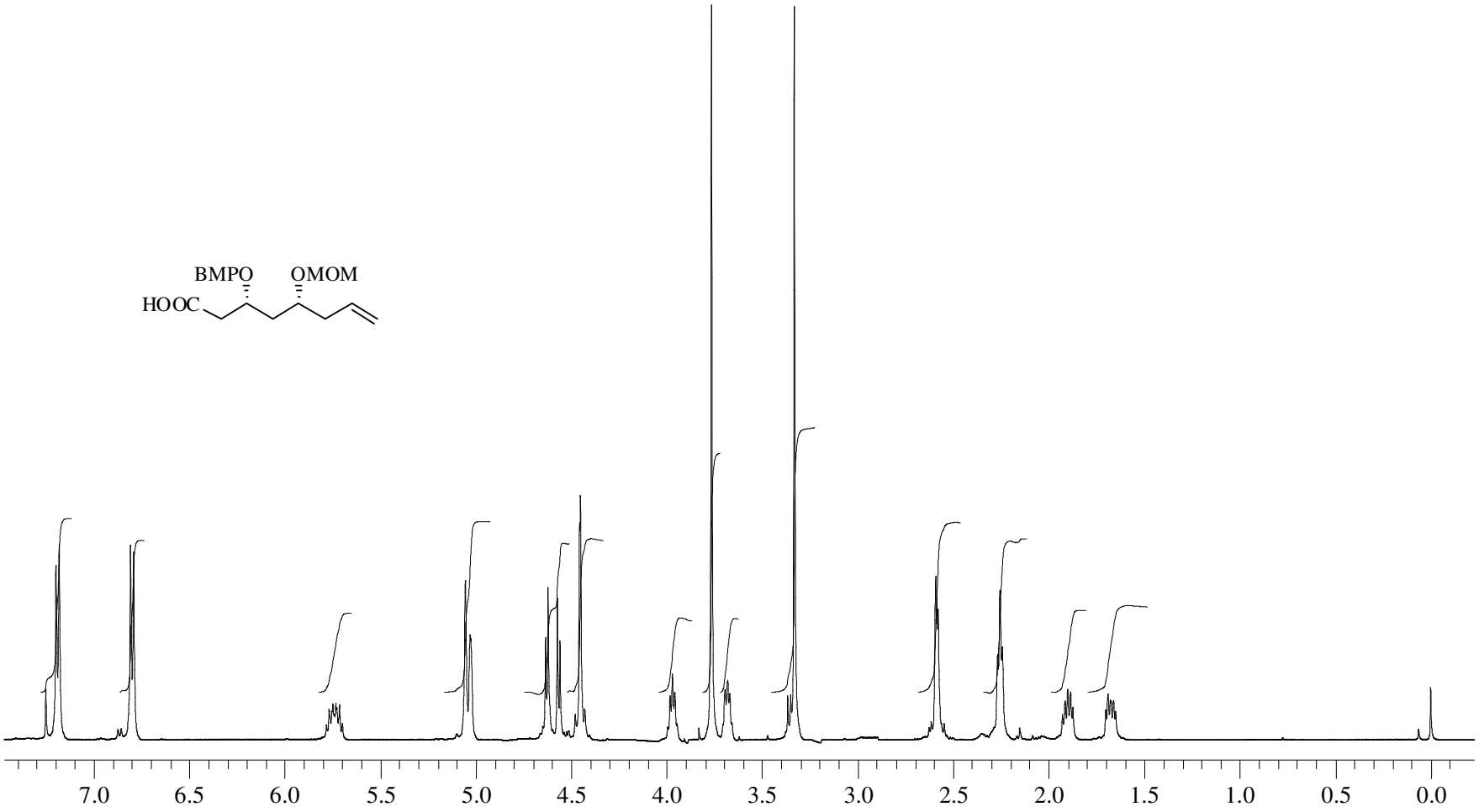

Figure 21: ^{1}H NMR Spectrum of compound **6** ($CDCl_3$, 500 MHz).

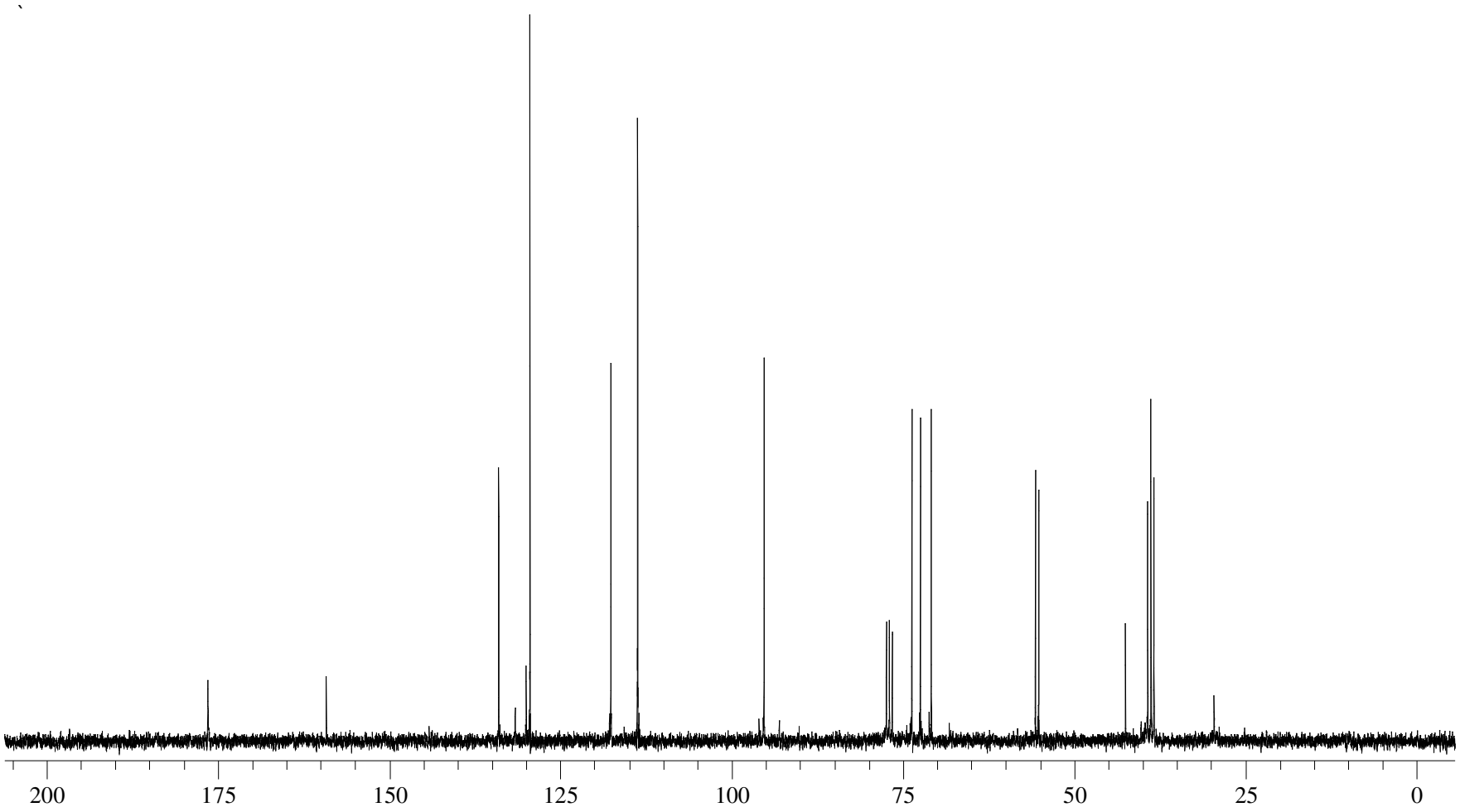

Figure 22: ^{13}C NMR Spectrum of compound **6** ($CDCl_3$, 75 MHz).

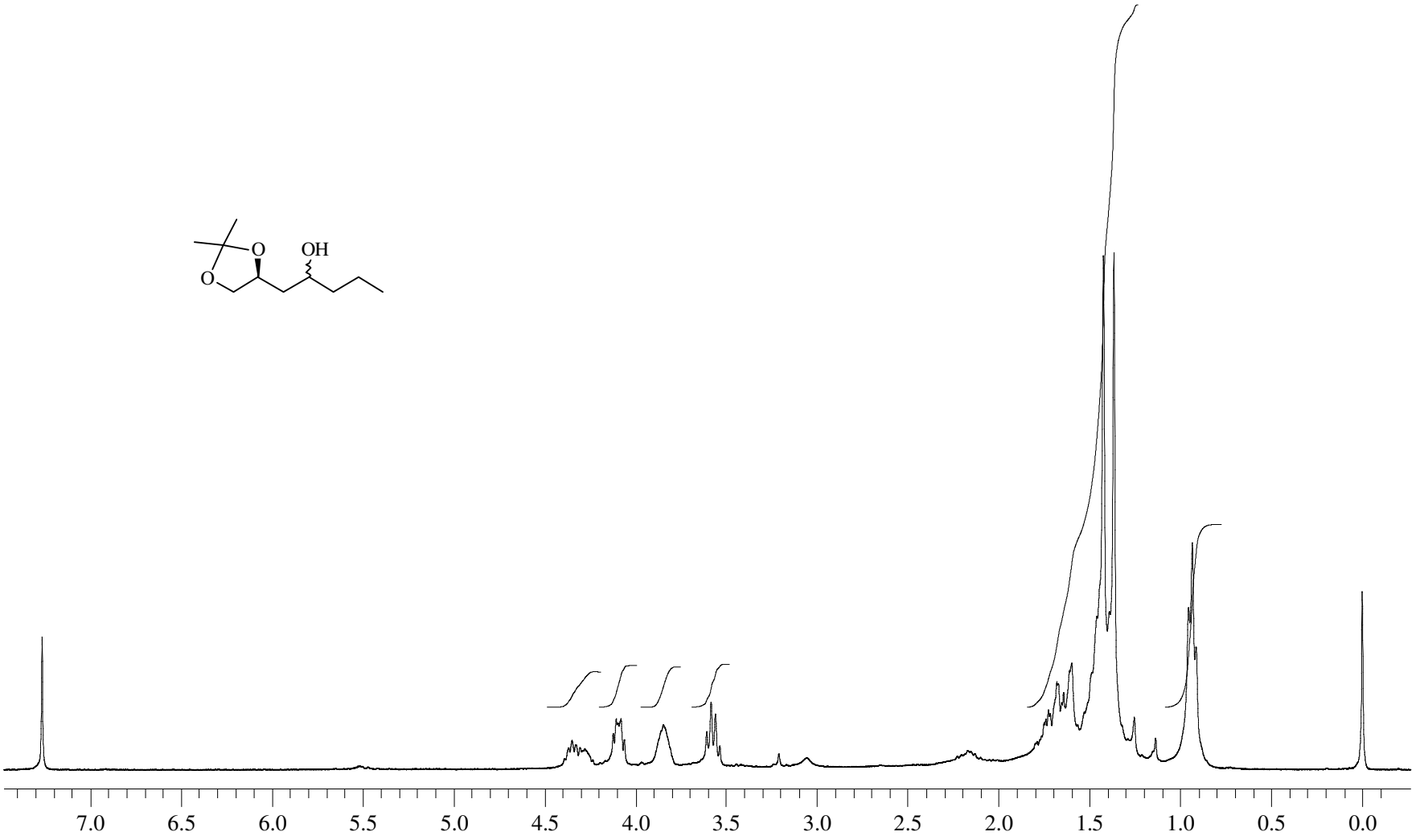

Figure 23: ^{1}H NMR Spectrum of compound **21** ($CDCl_3$, 500 MHz).

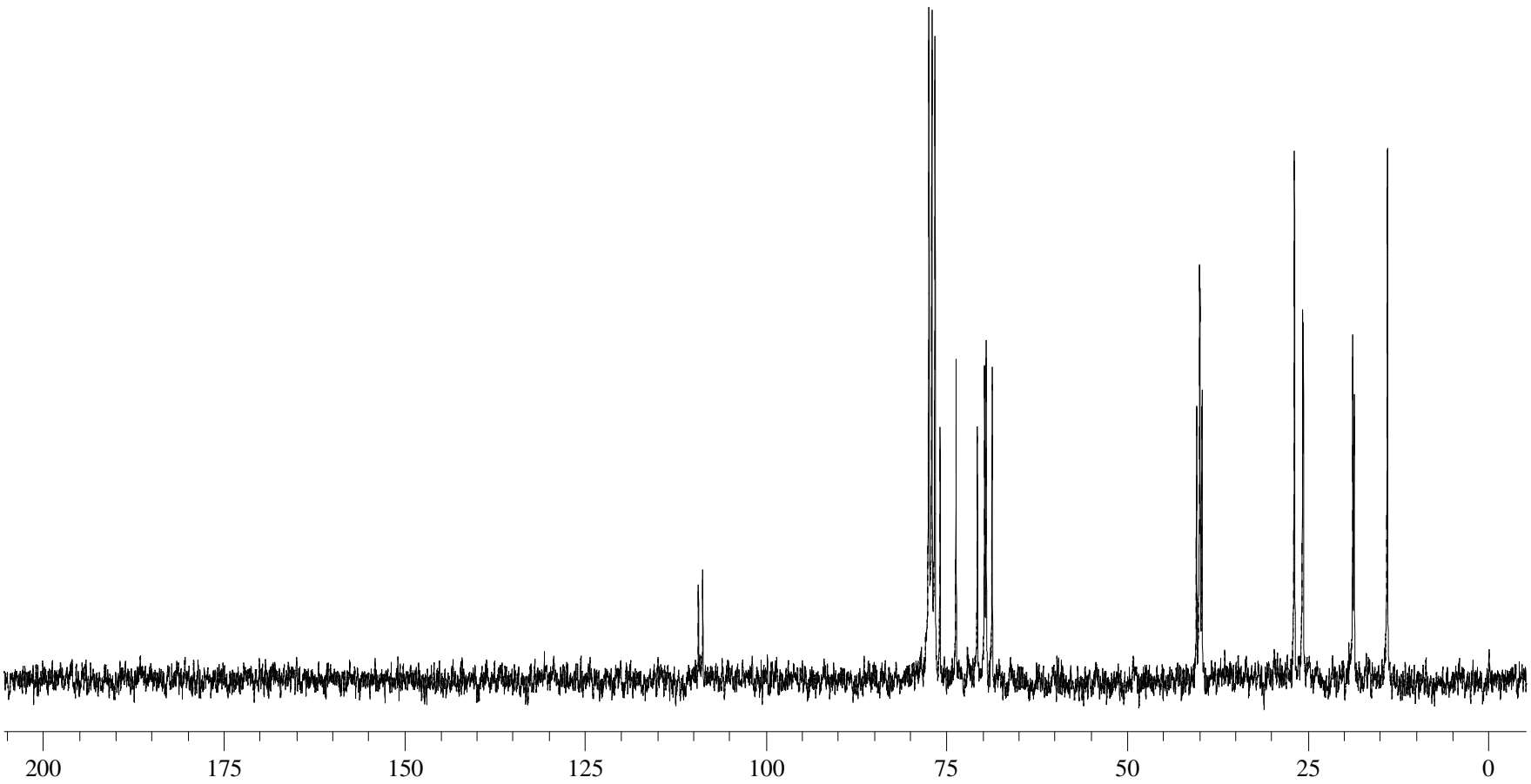

Figure 24: ^{13}C NMR Spectrum of compound **21** ($CDCl_3$, 75 MHz).

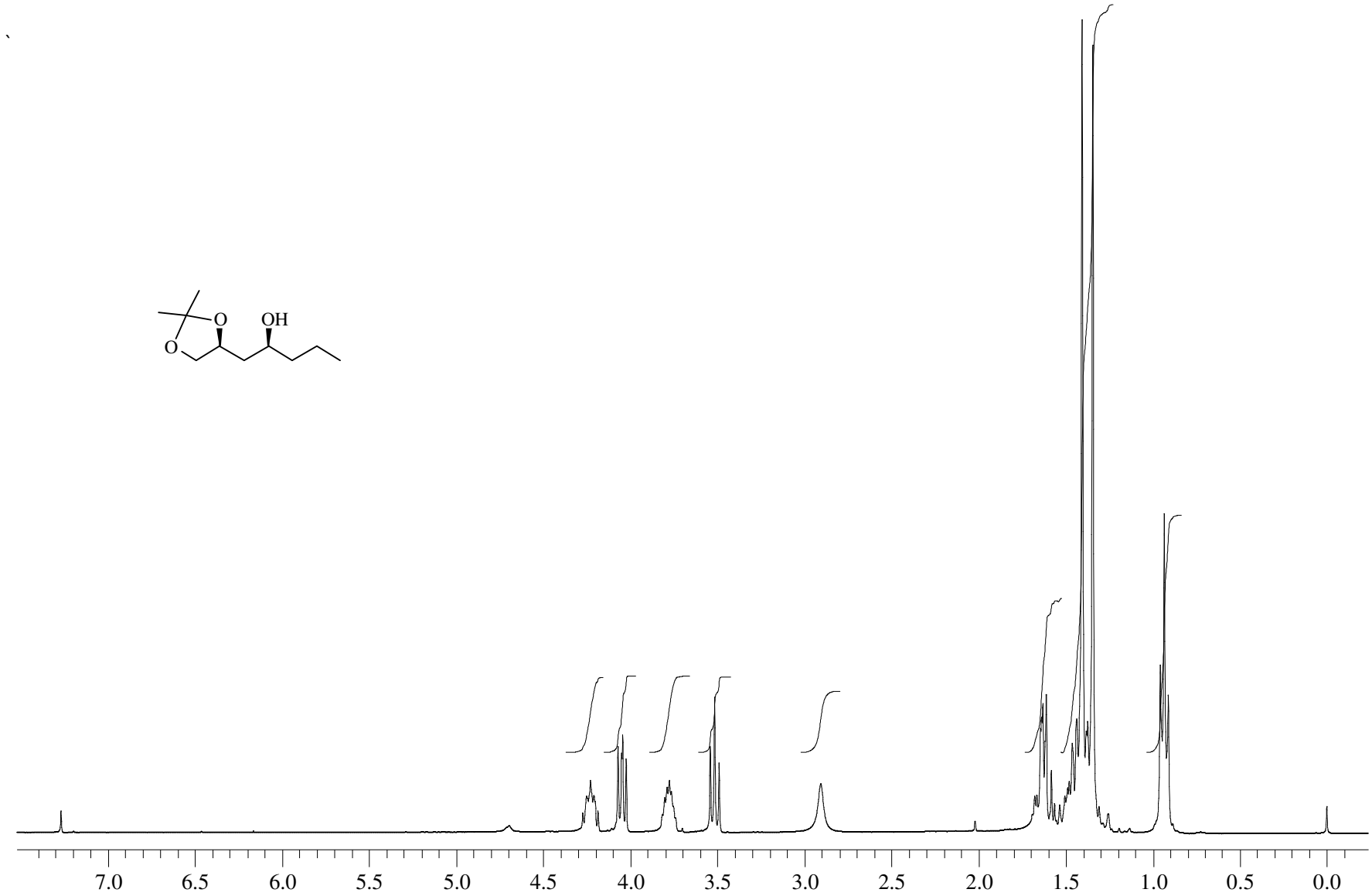

Figure 25: ^{1}H NMR Spectrum of compound **23** ($CDCl_3$, 500 MHz).

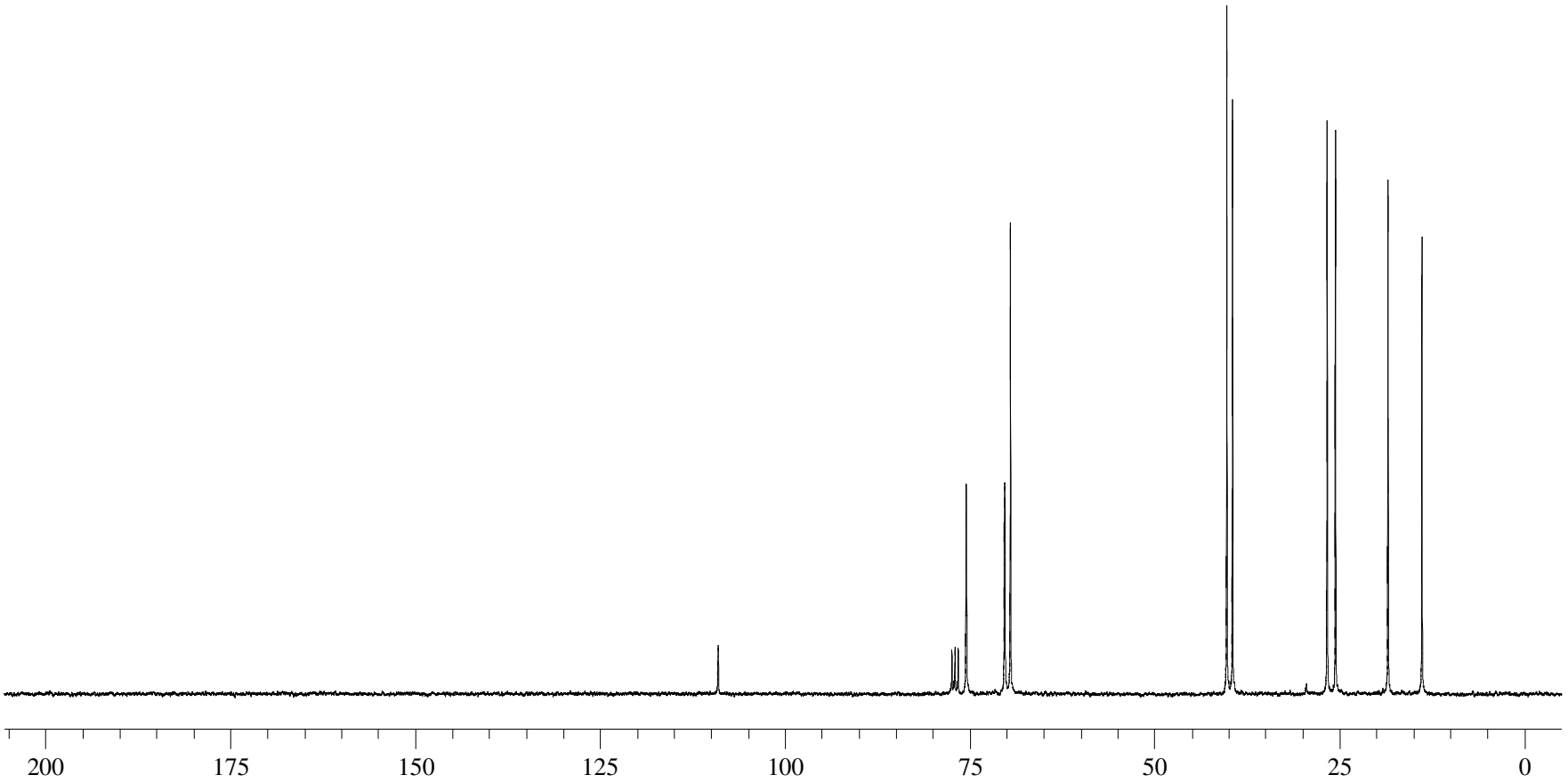

Figure 26: ^{13}C NMR Spectrum of compound **23** ($CDCl_3$, 75 MHz).

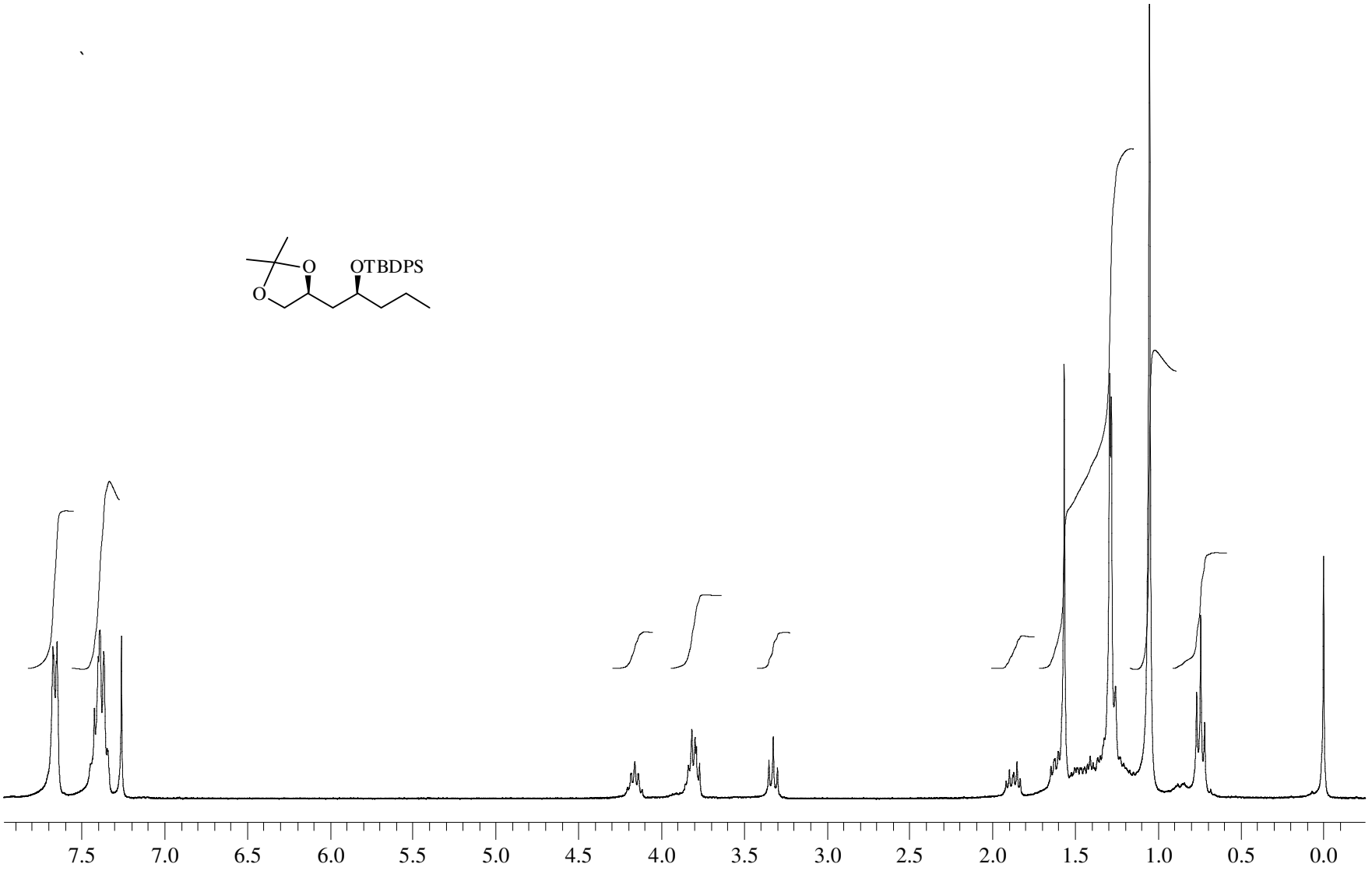

Figure 27: ^{1}H NMR Spectrum of compound **24** ($CDCl_3$, 500 MHz).

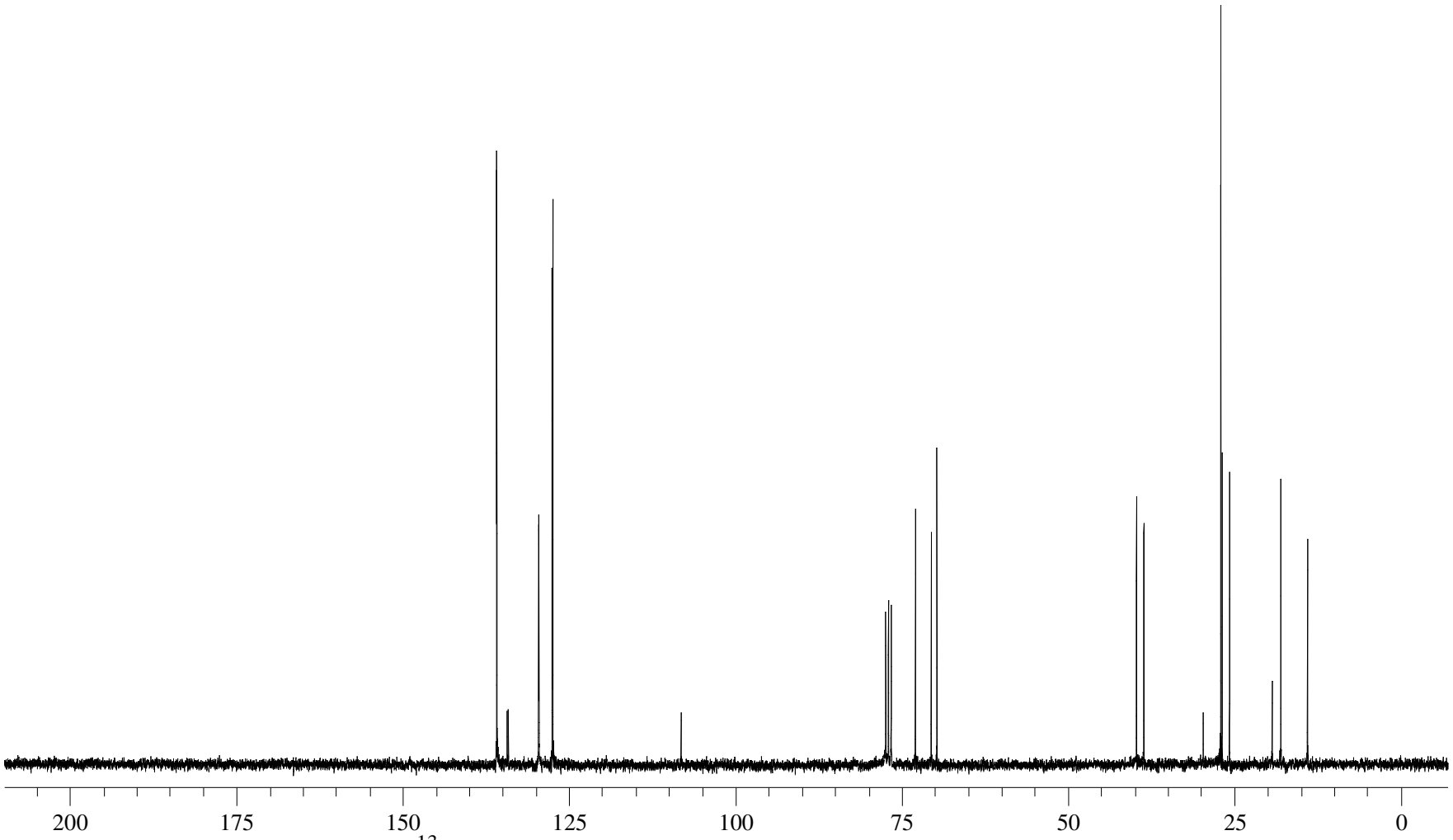

Figure 28: ^{13}C NMR Spectrum of compound **24** ($CDCl_3$, 75 MHz).

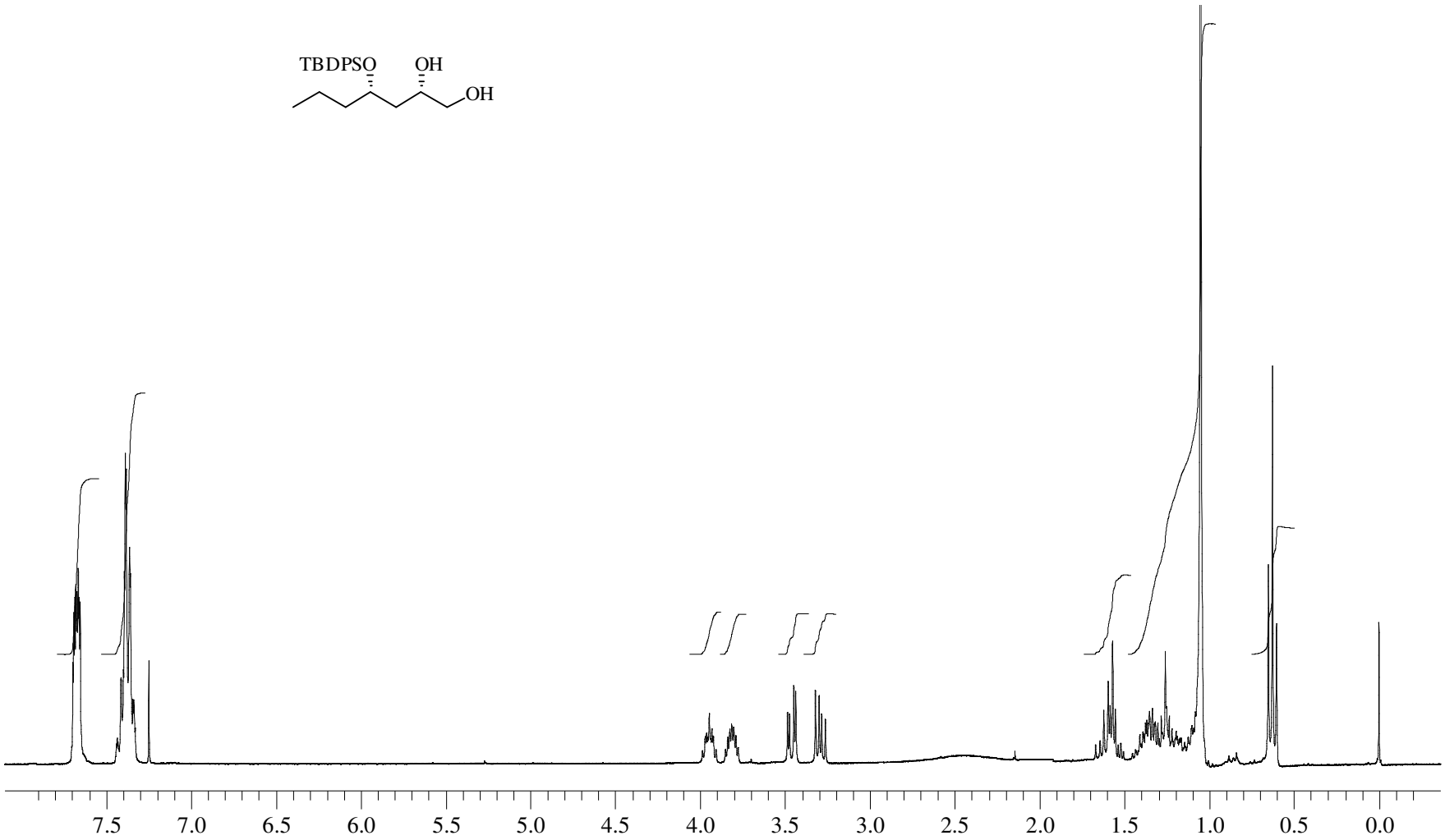

Figure 29: ^{1}H NMR Spectrum of compound **25** ($CDCl_3$, 500 MHz).

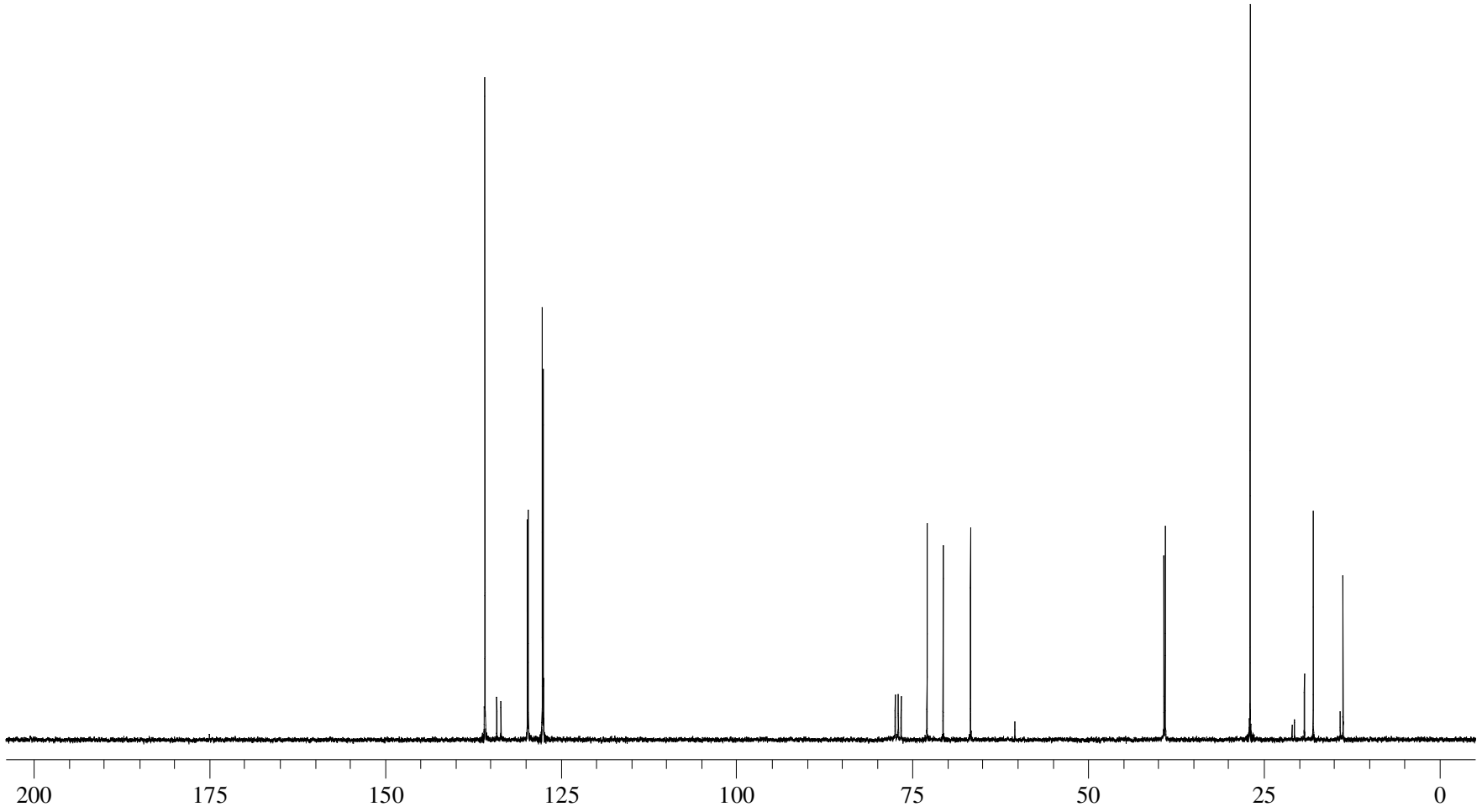

Figure 30: ^{13}C NMR Spectrum of compound **25** ($CDCl_3$, 75 MHz).

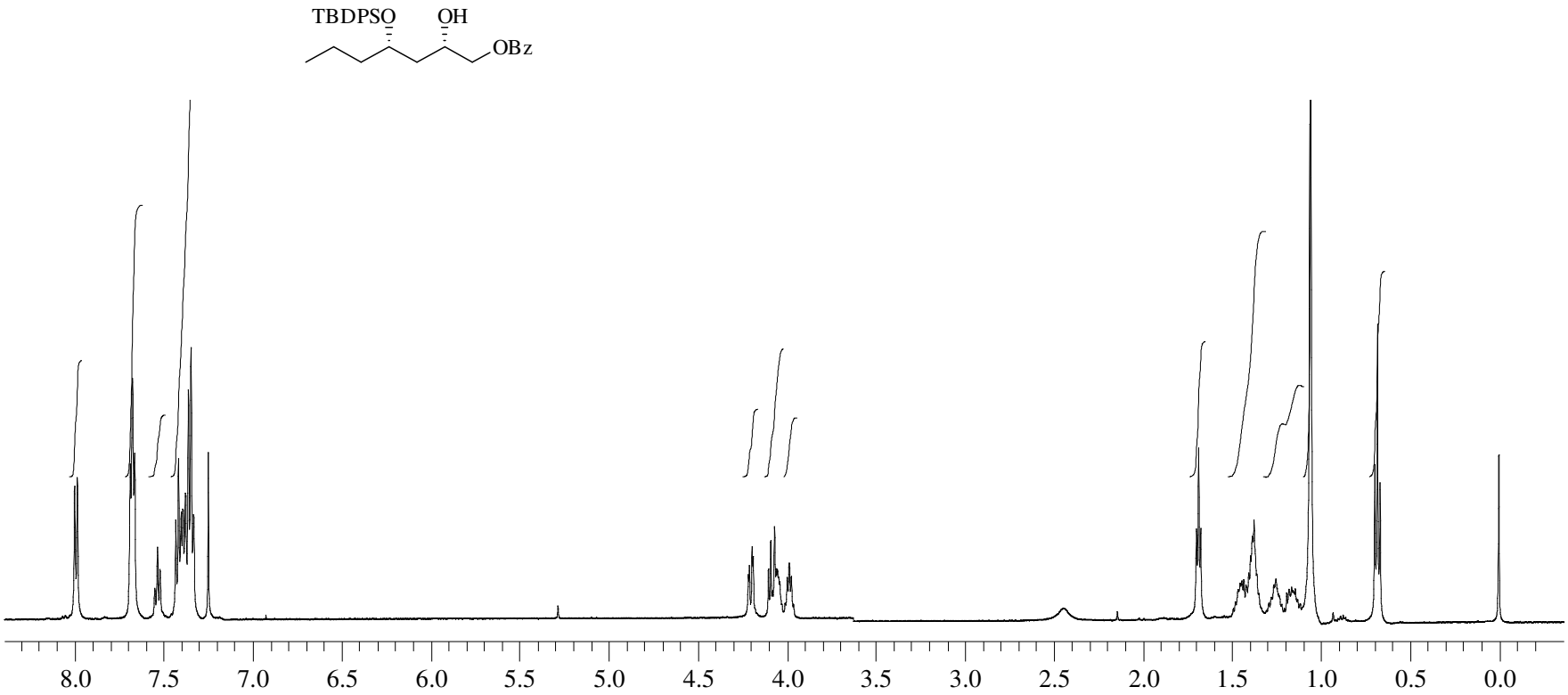

Figure 31: ^{1}H NMR Spectrum of compound **26** ($CDCl_3$, 500 MHz).

`

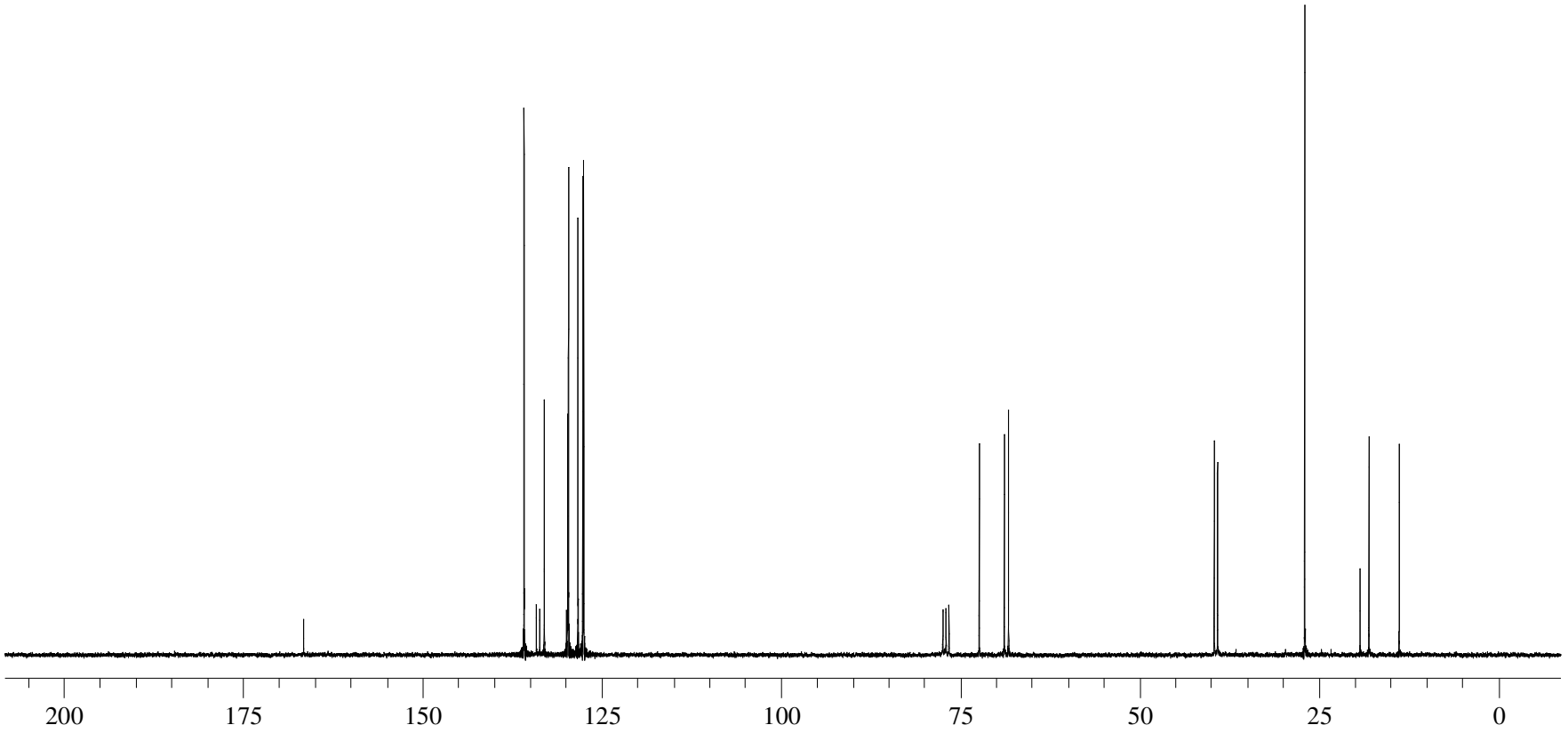

Figure 32: ^{13}C NMR Spectrum of compound **26** ($CDCl_3$, 75 MHz).

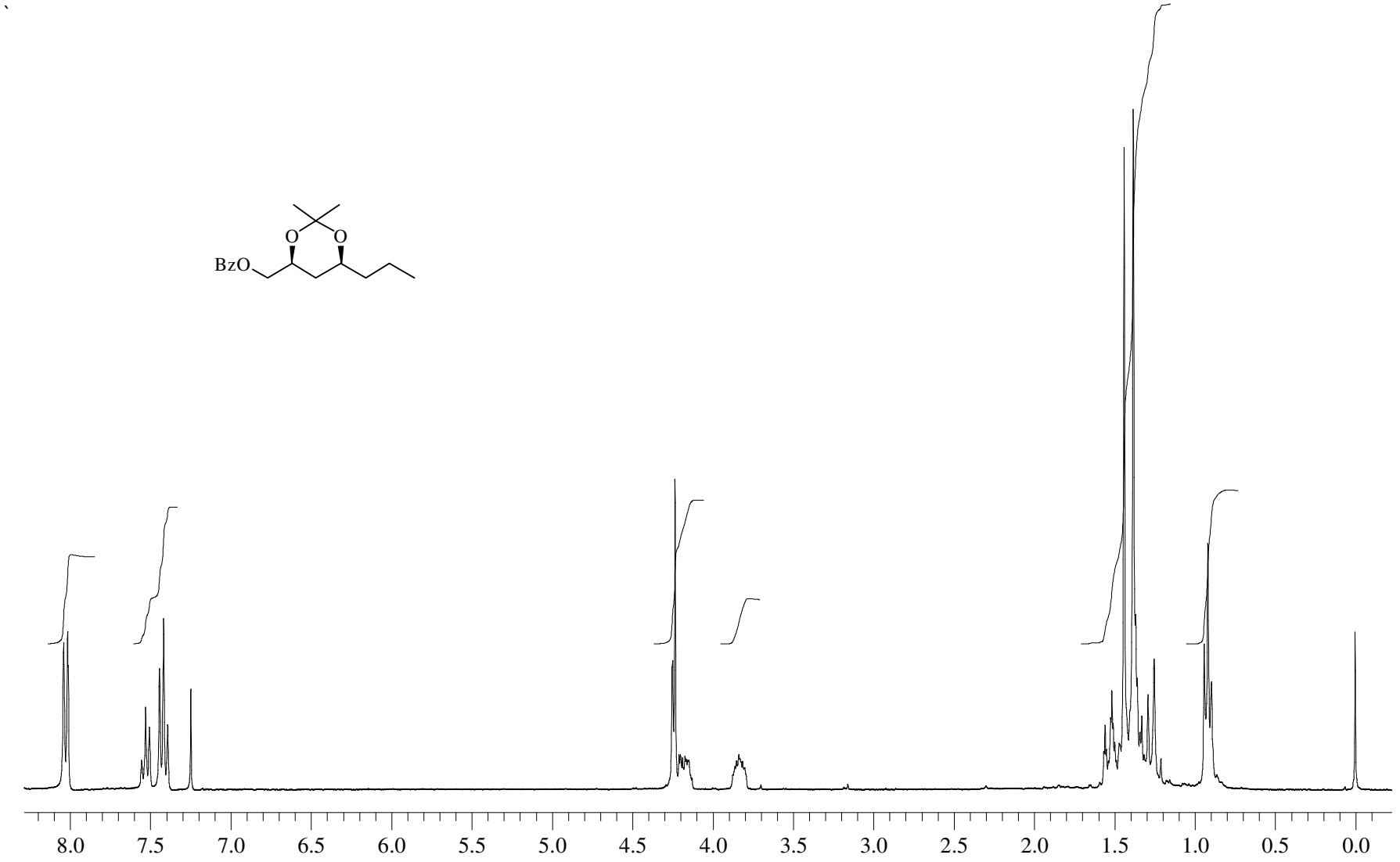

Figure 33: ^{1}H NMR Spectrum of compound **26b** ($CDCl_3$, 500 MHz).

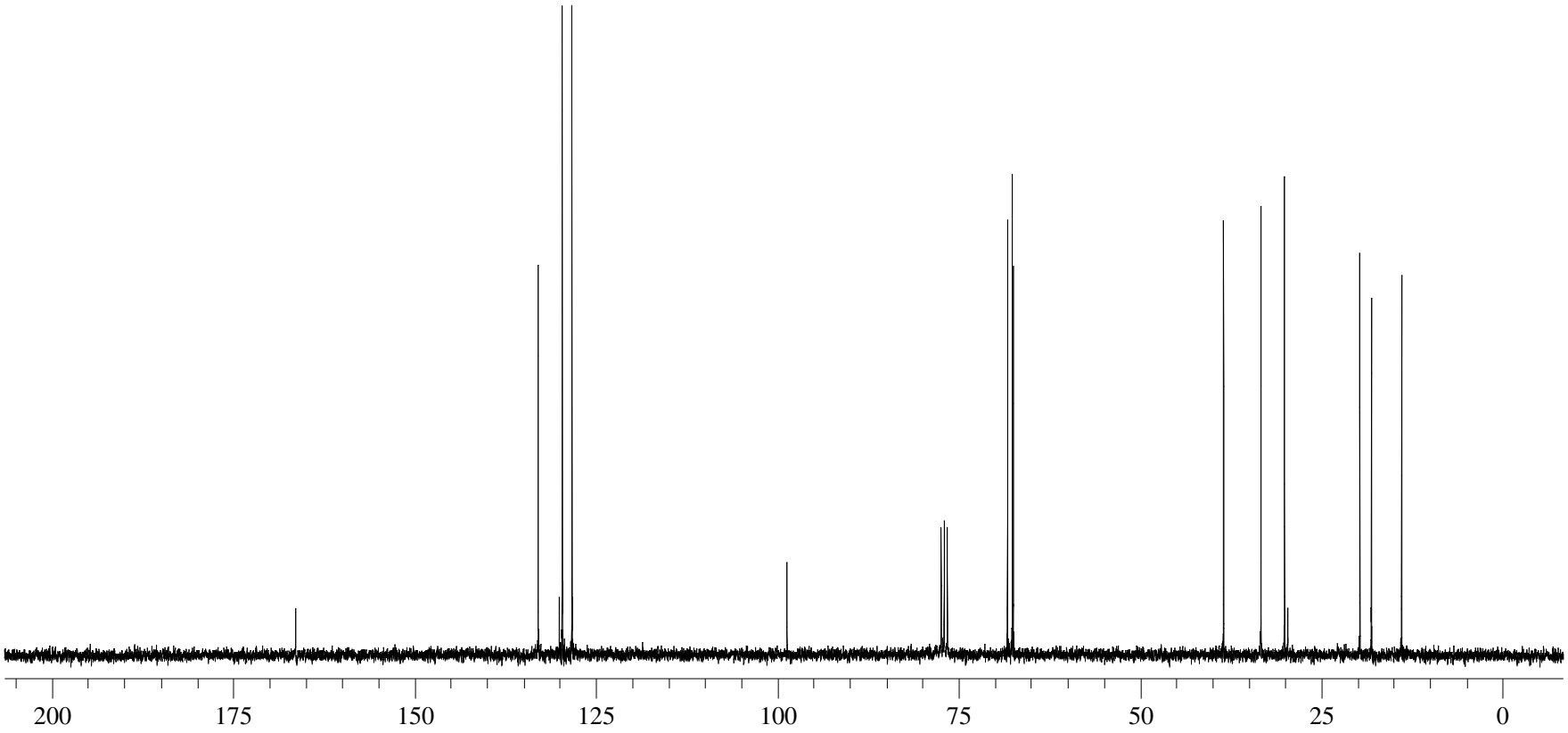

Figure 34: ^{13}C NMR Spectrum of compound **26b** ($CDCl_3$, 75 MHz).

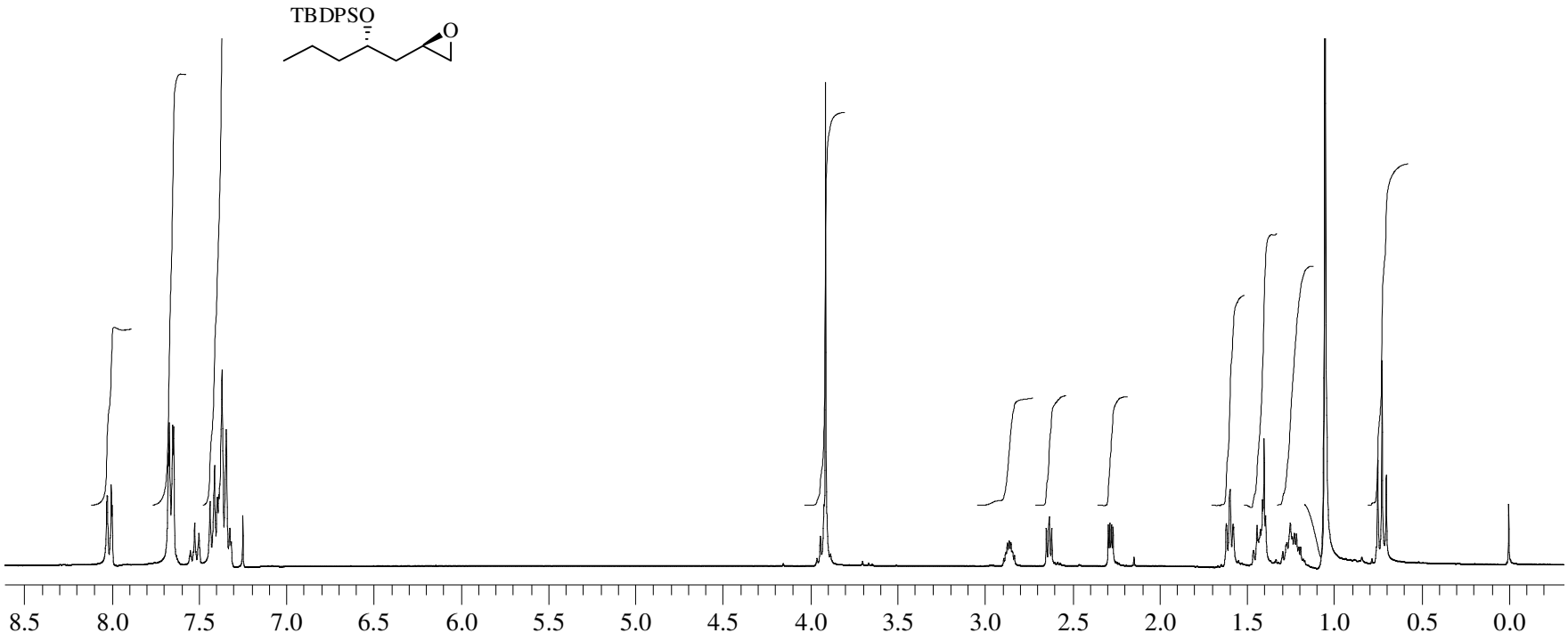

Figure 35: ^{1}H NMR Spectrum of compound **28** ($CDCl_3$, 500 MHz).

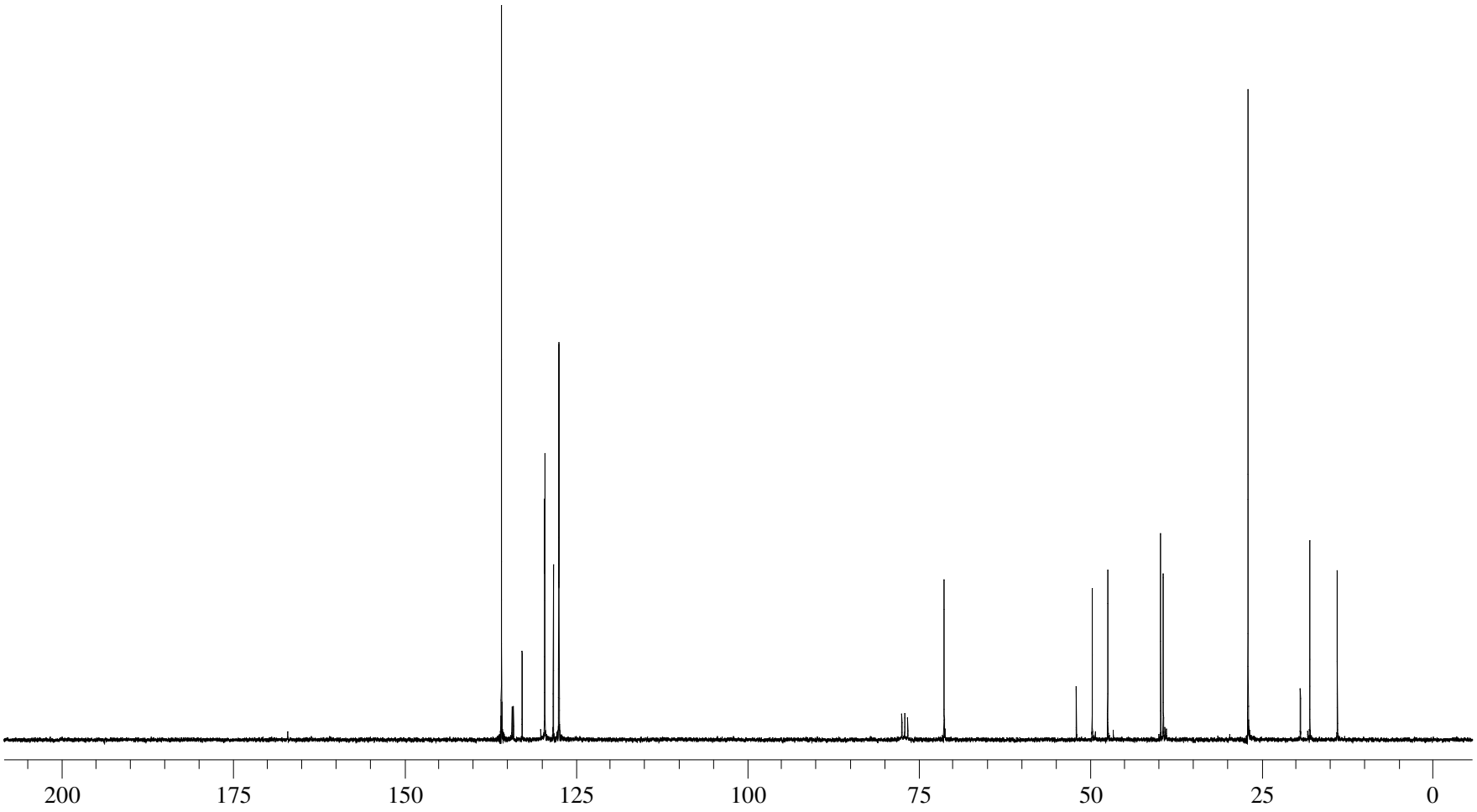

Figure 36: ^{13}C NMR Spectrum of compound **28** ($CDCl_3$, 75 MHz).

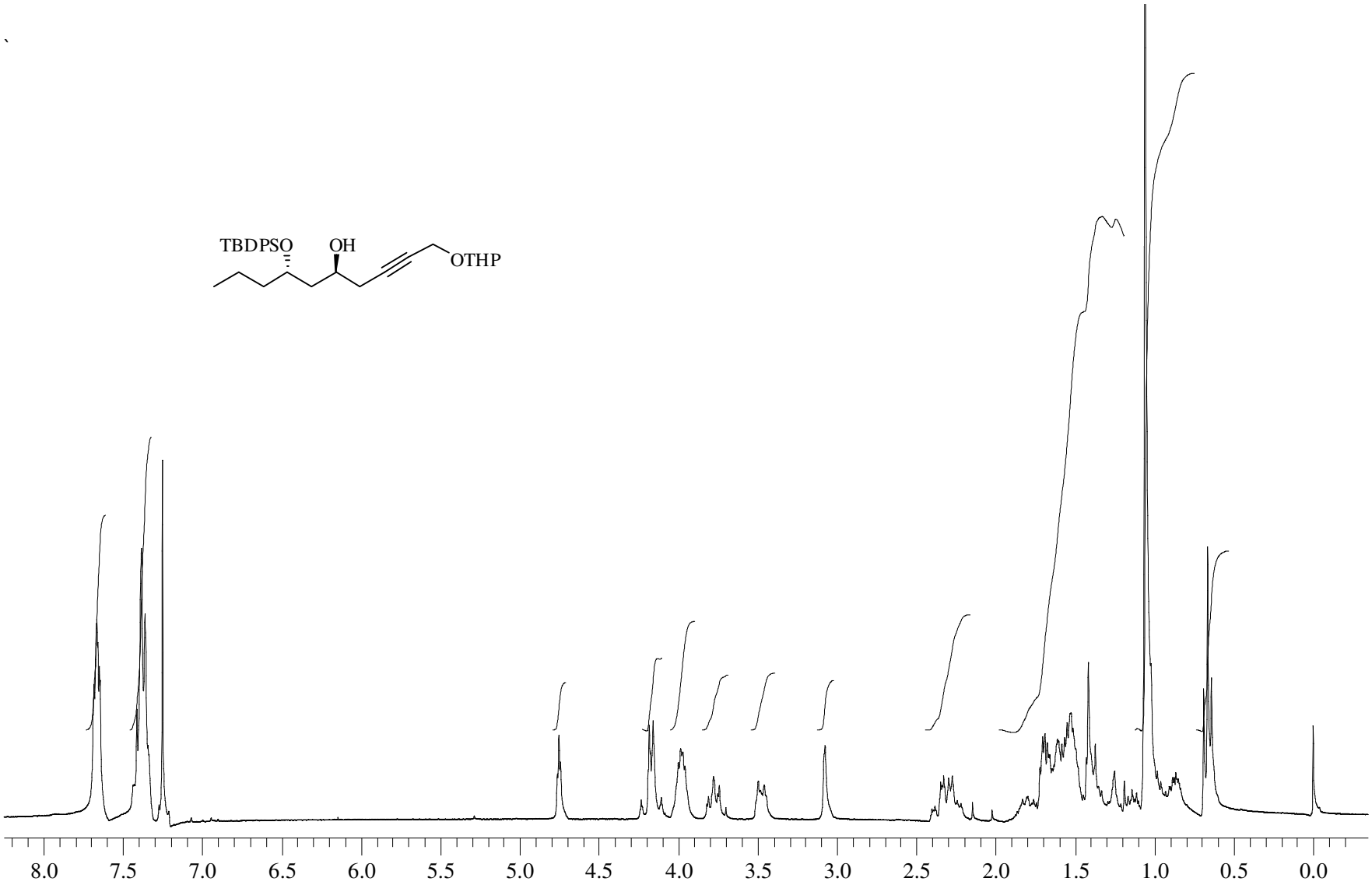

Figure 37: ^{1}H NMR Spectrum of compound **30** ($CDCl_3$, 500 MHz).

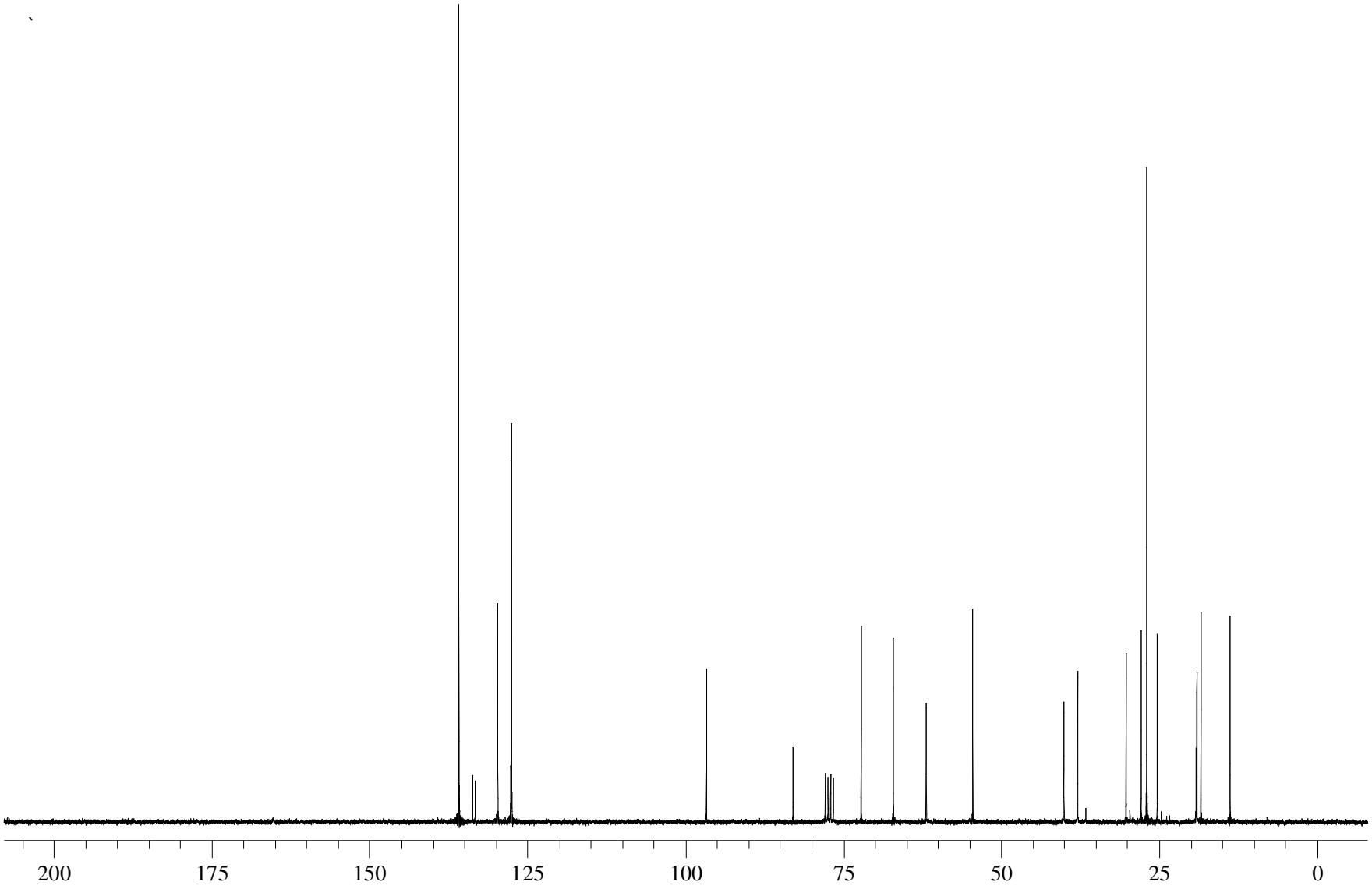

Figure 38: ^{13}C NMR Spectrum of compound **30** ($CDCl_3$, 75 MHz).

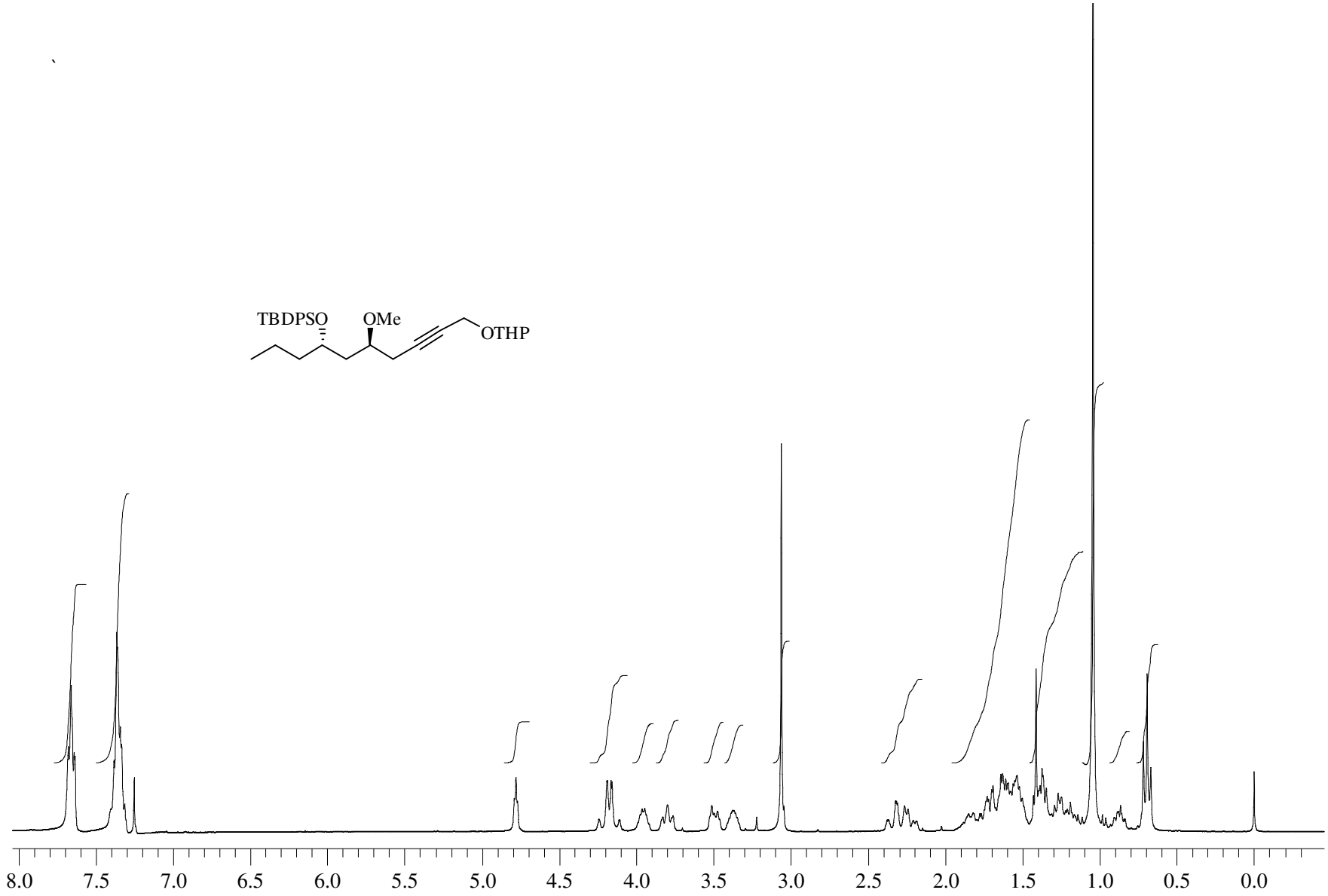

Figure 39: ^{1}H NMR Spectrum of compound **31** ($CDCl_3$, 500 MHz).

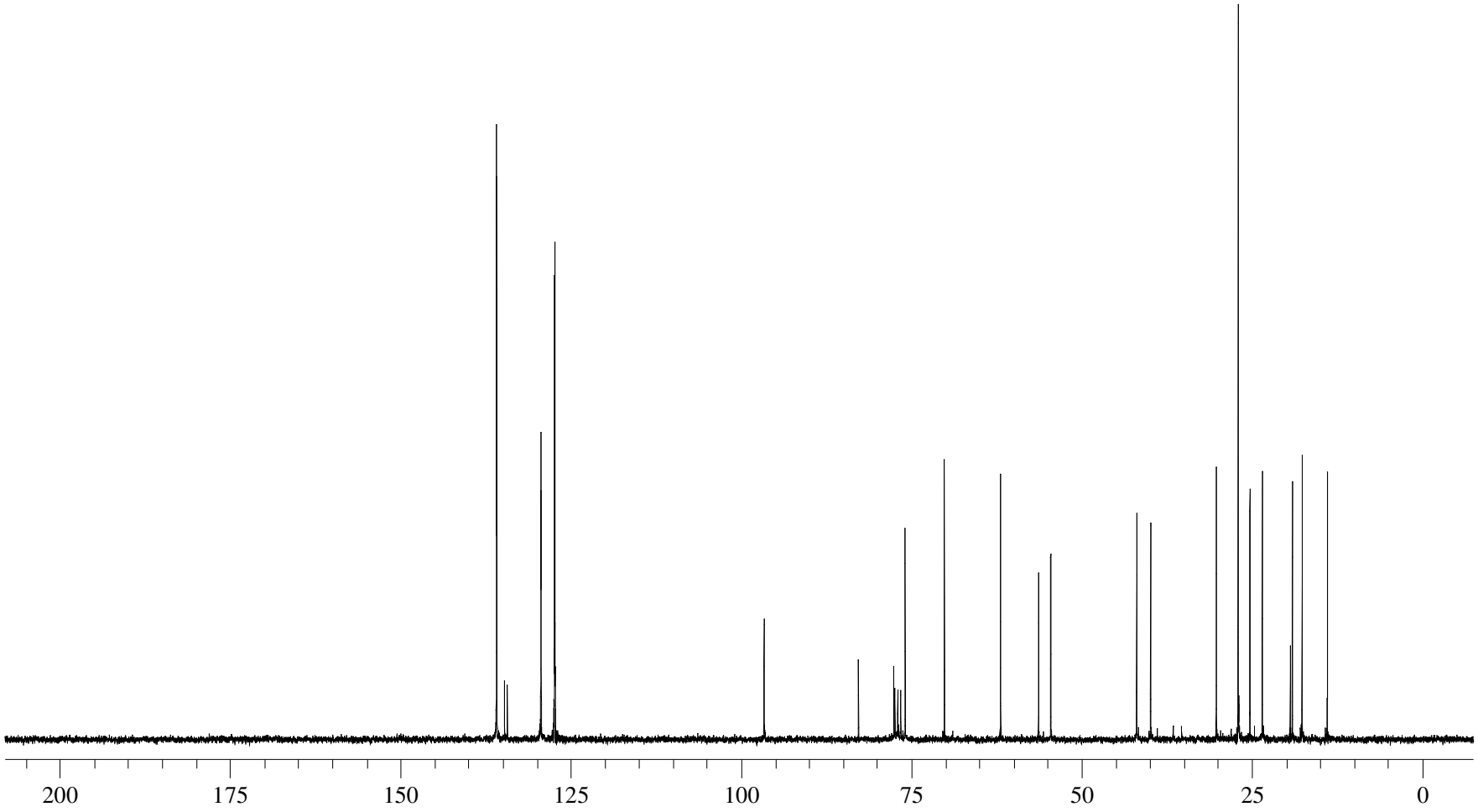

Figure 40: ^{13}C NMR Spectrum of compound **31** ($CDCl_3$, 75 MHz).

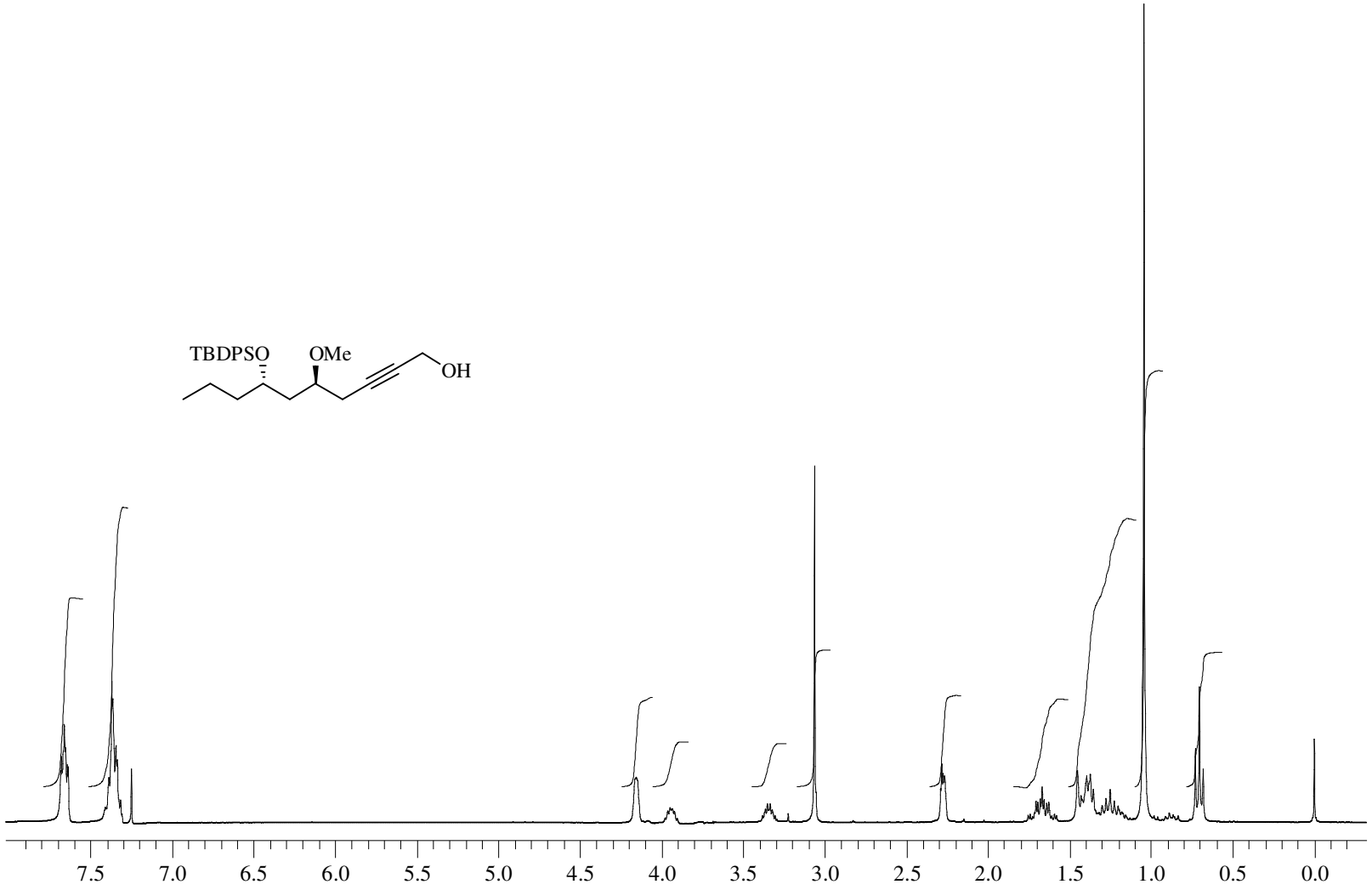

Figure 41: ^{1}H NMR Spectrum of compound **32** ($CDCl_3$, 500 MHz).

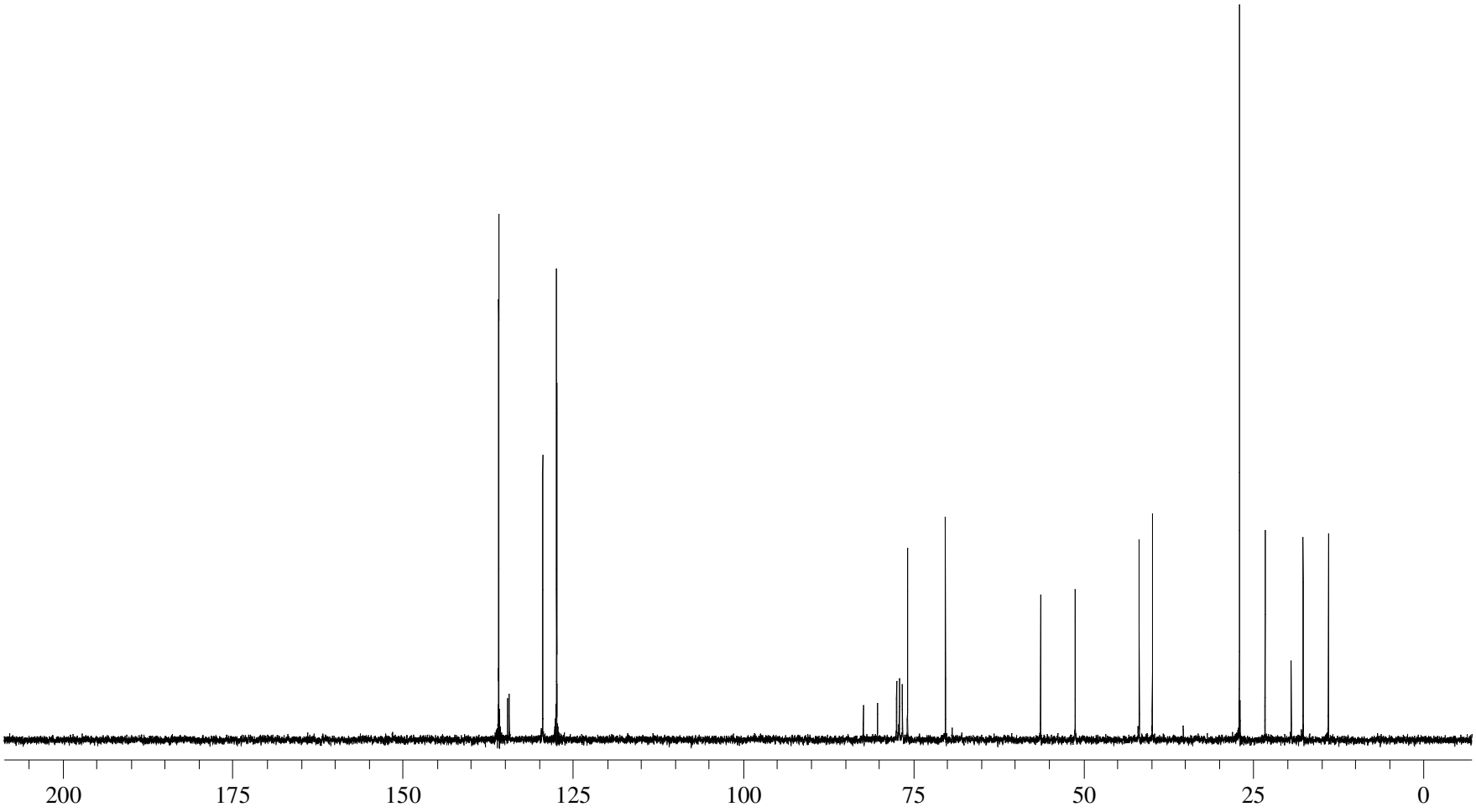

Figure 42: ^{13}C NMR Spectrum of compound **32** ($CDCl_3$, 75 MHz).

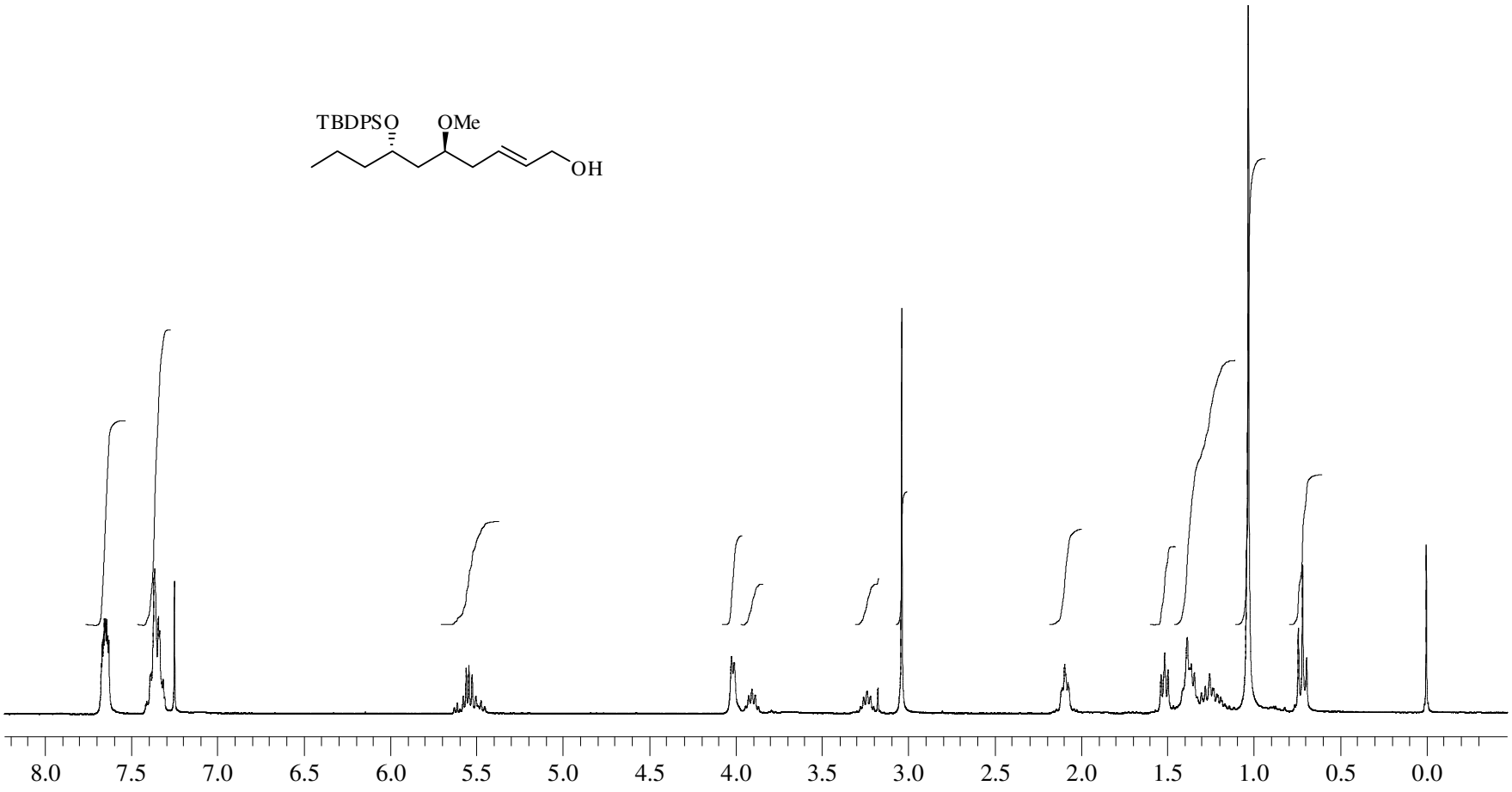

Figure 43: ^{1}H NMR Spectrum of compound **33** ($CDCl_3$, 500 MHz).

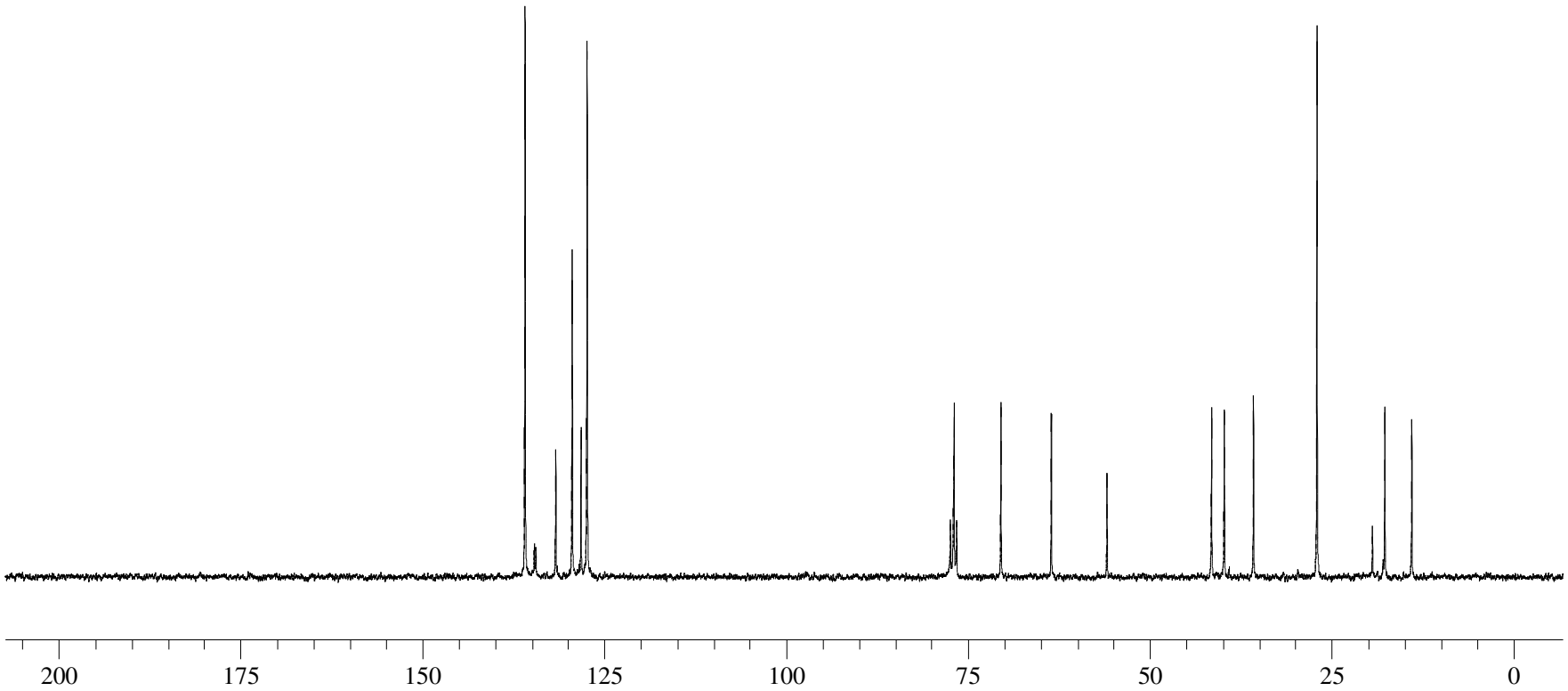

Figure 44: ^{13}C NMR Spectrum of compound **33** ($CDCl_3$, 75 MHz).

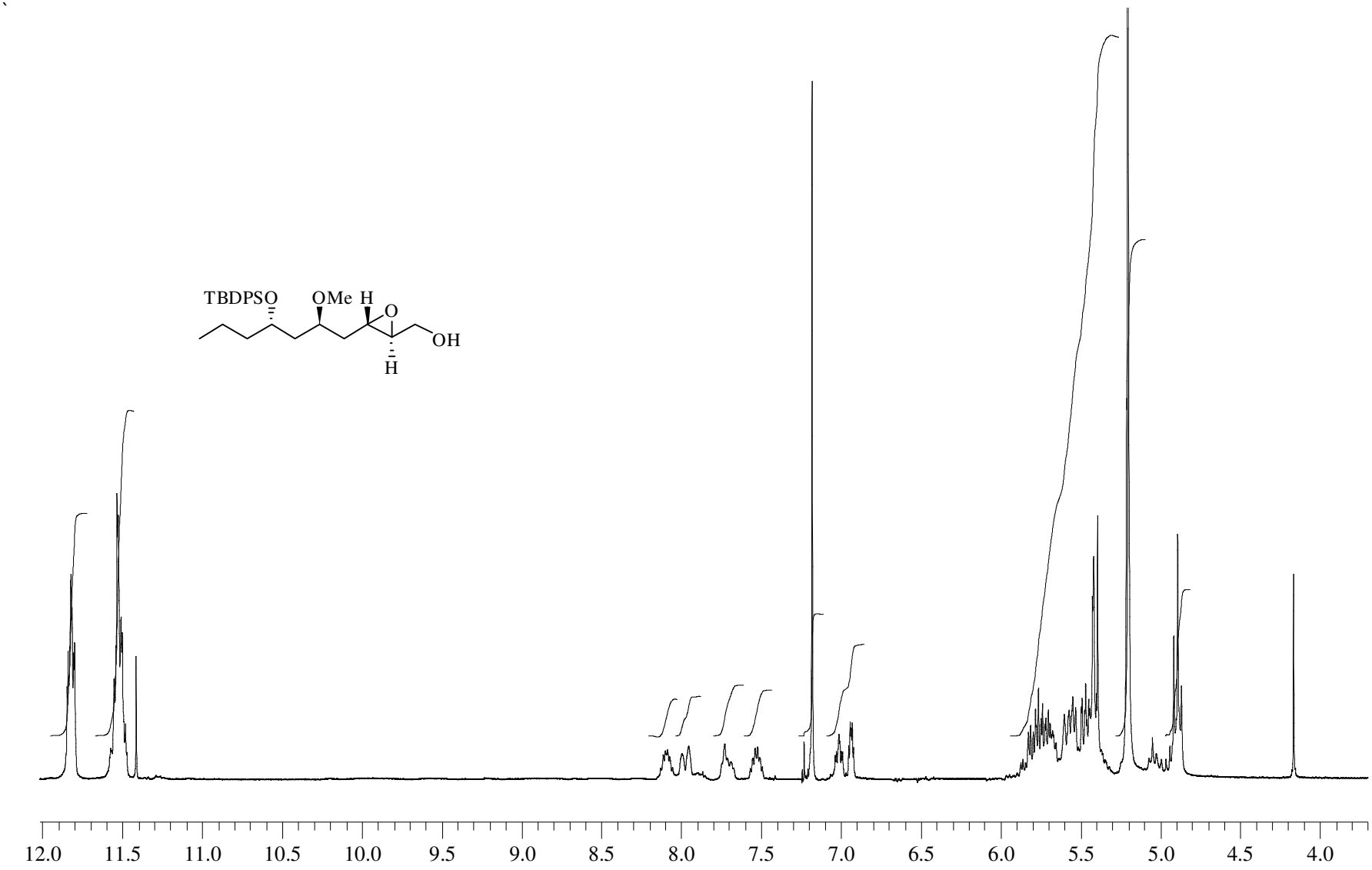

Figure 45: ^{1}H NMR Spectrum of compound **34** ($CDCl_3$, 500 MHz).

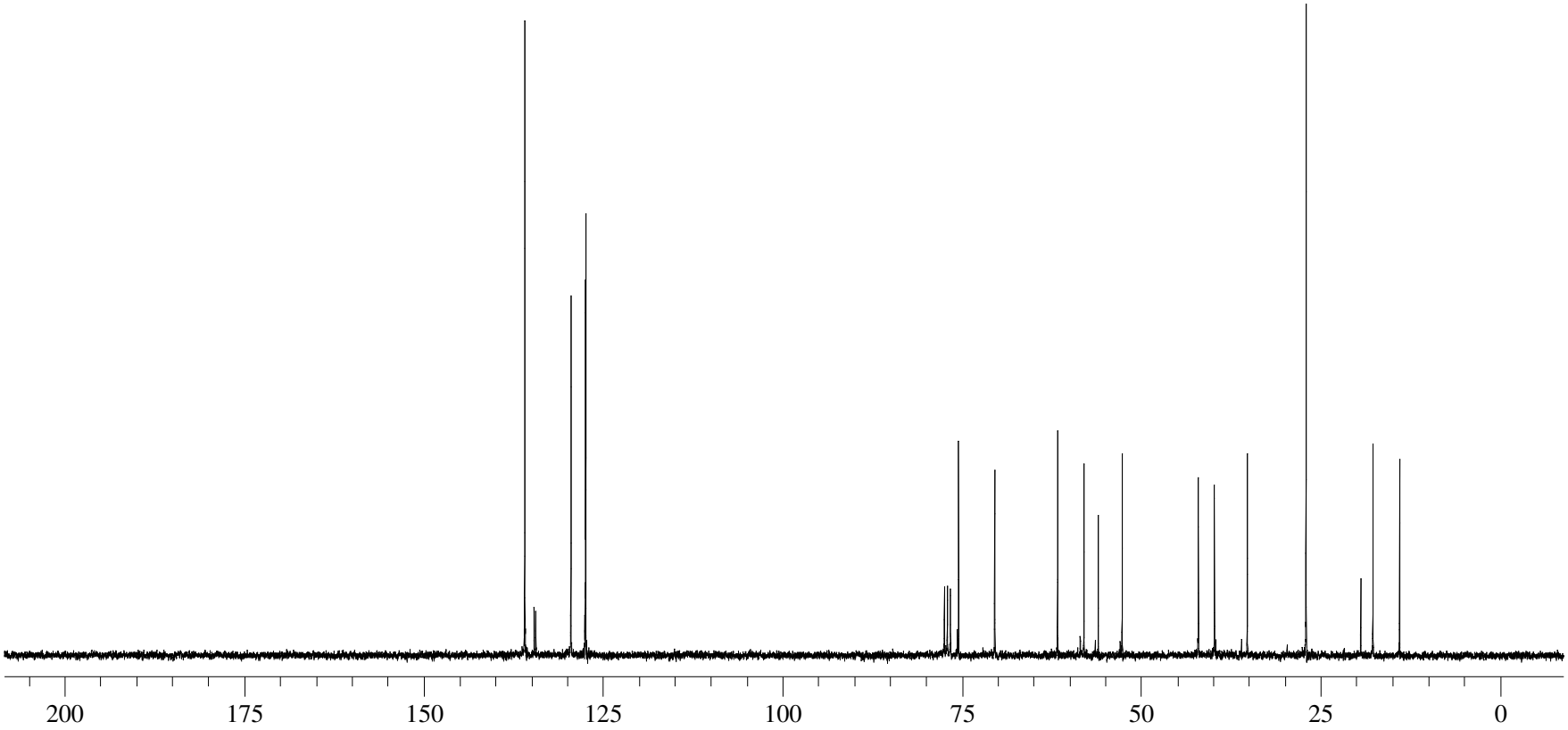

Figure 46: ^{13}C NMR Spectrum of compound **34** ($CDCl_3$, 75 MHz).

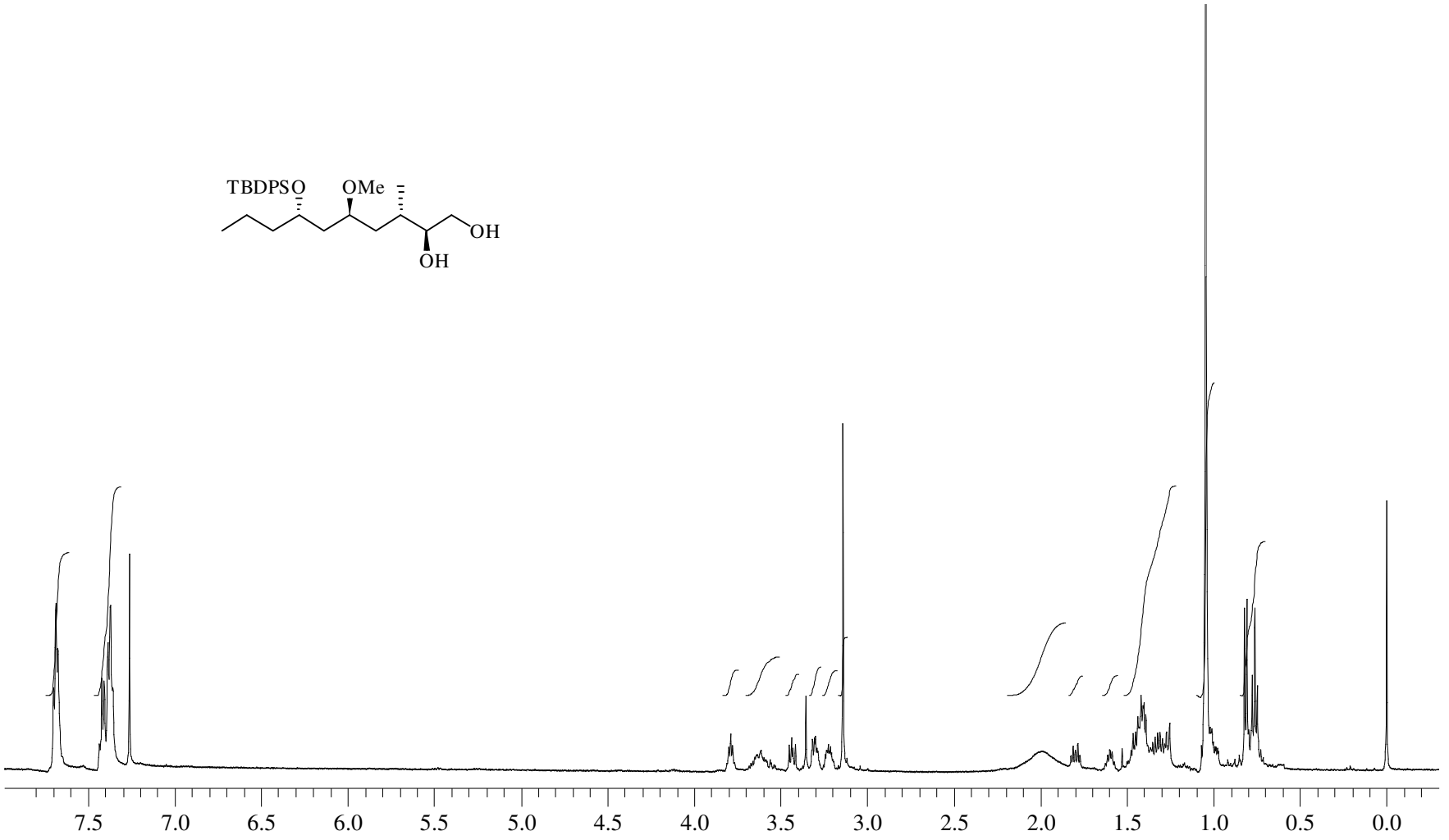

Figure 47: ^{1}H NMR Spectrum of compound **35** ($CDCl_3$, 500 MHz).

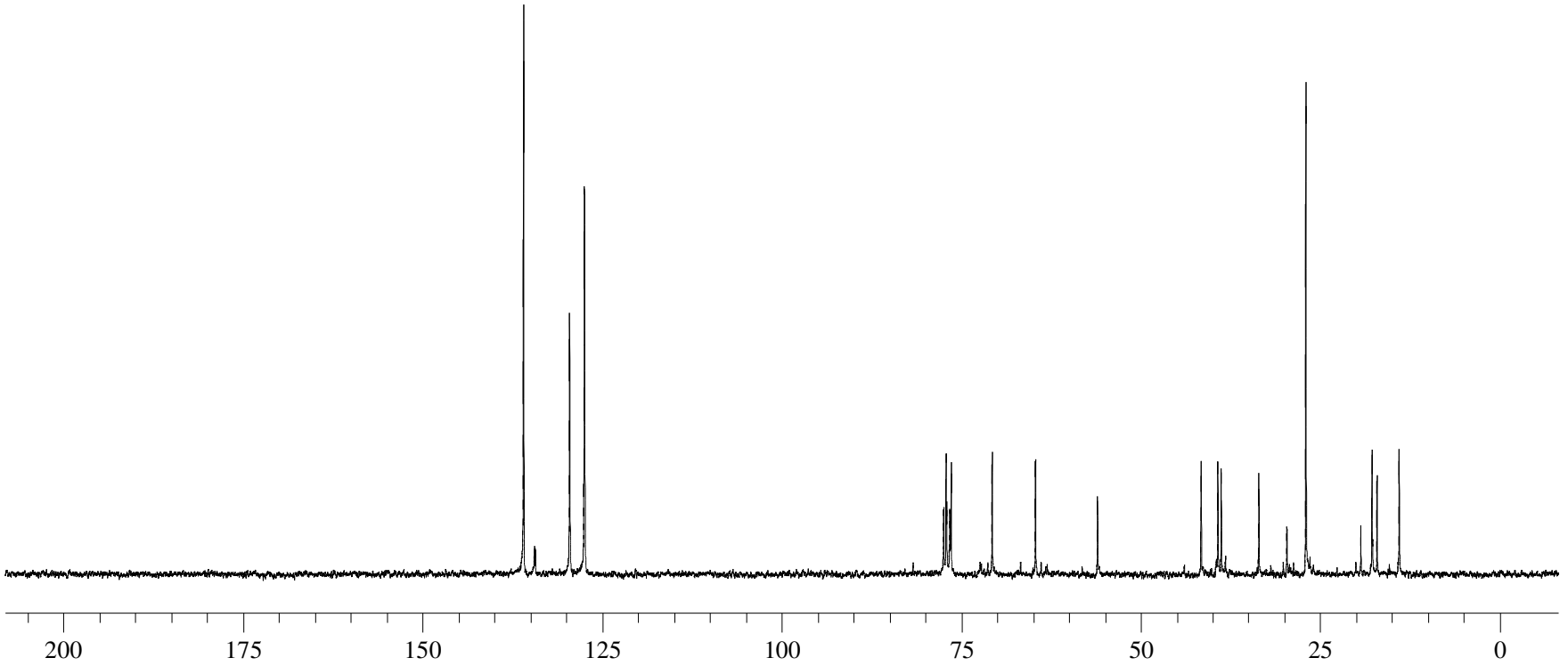

Figure 48: ^{13}C NMR Spectrum of compound **35** ($CDCl_3$, 75 MHz).

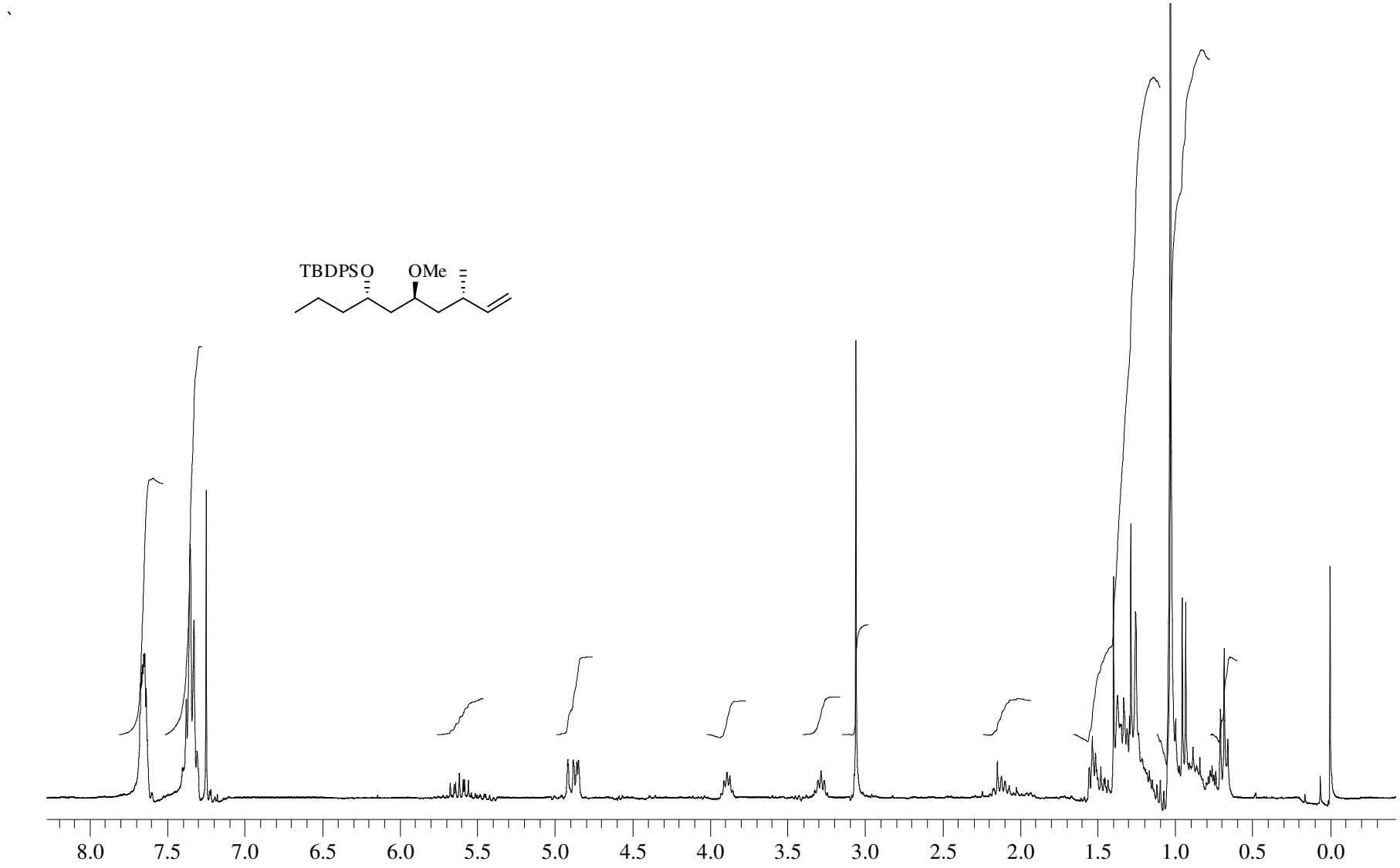

Figure 49: ^{1}H NMR Spectrum of compound **36** ($CDCl_3$, 500 MHz).

`

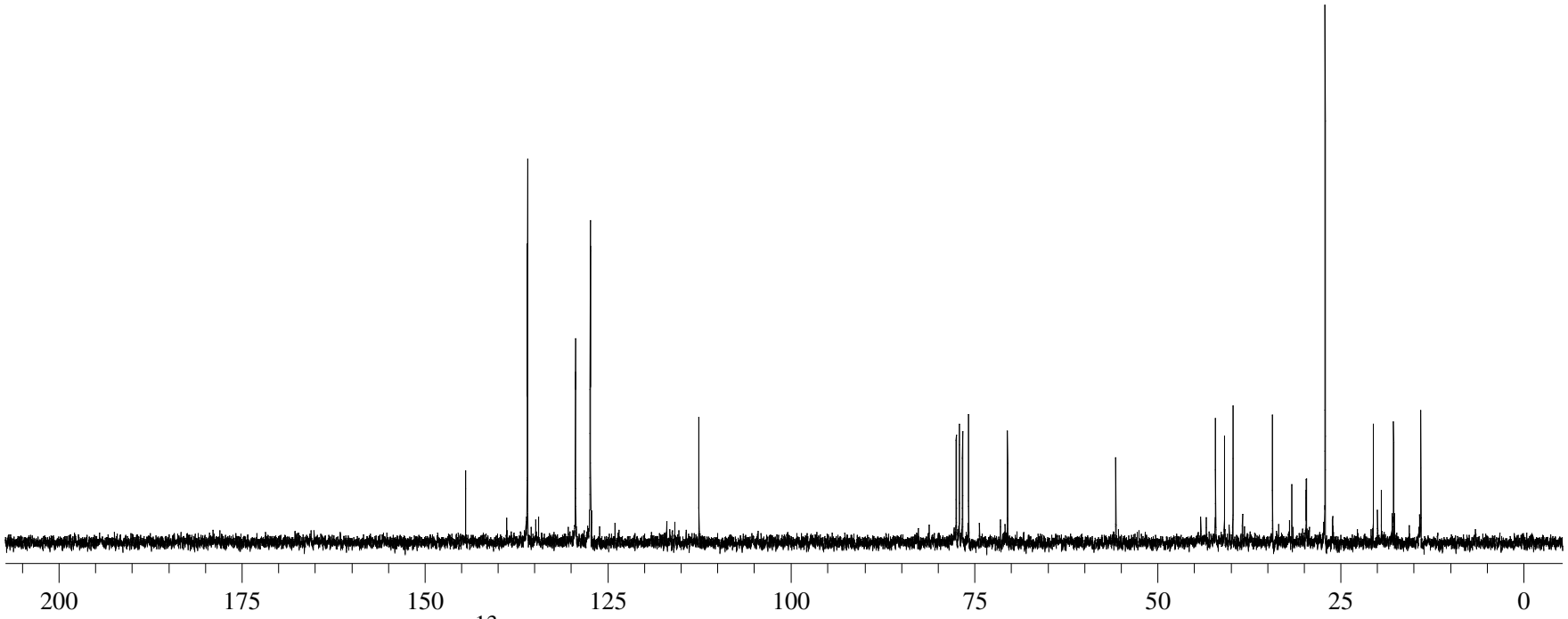

Figure 50: ^{13}C NMR Spectrum of compound **36** ($CDCl_3$, 75 MHz).

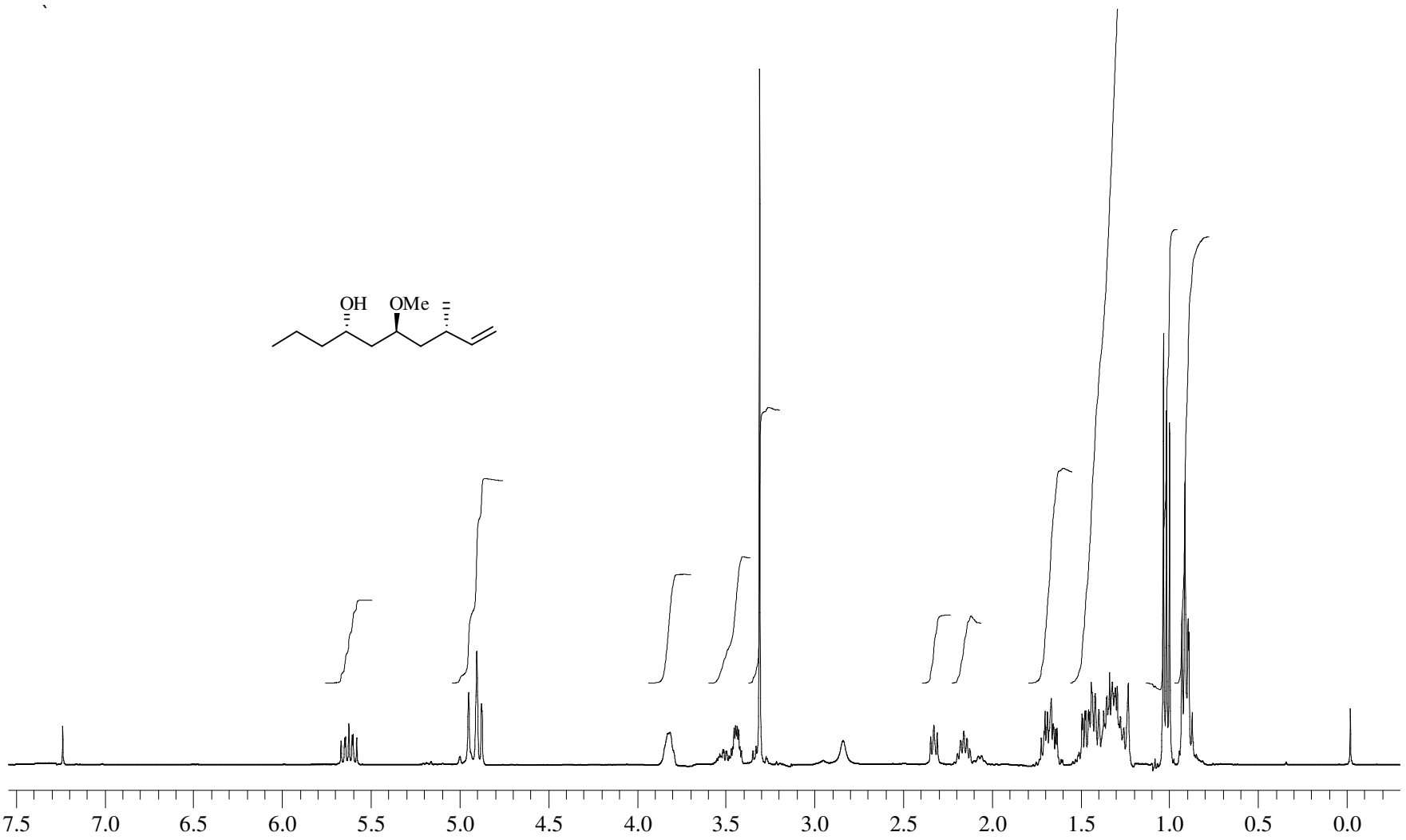

Figure 51: ^{1}H NMR Spectrum of compound **5** ($CDCl_3$, 500 MHz).

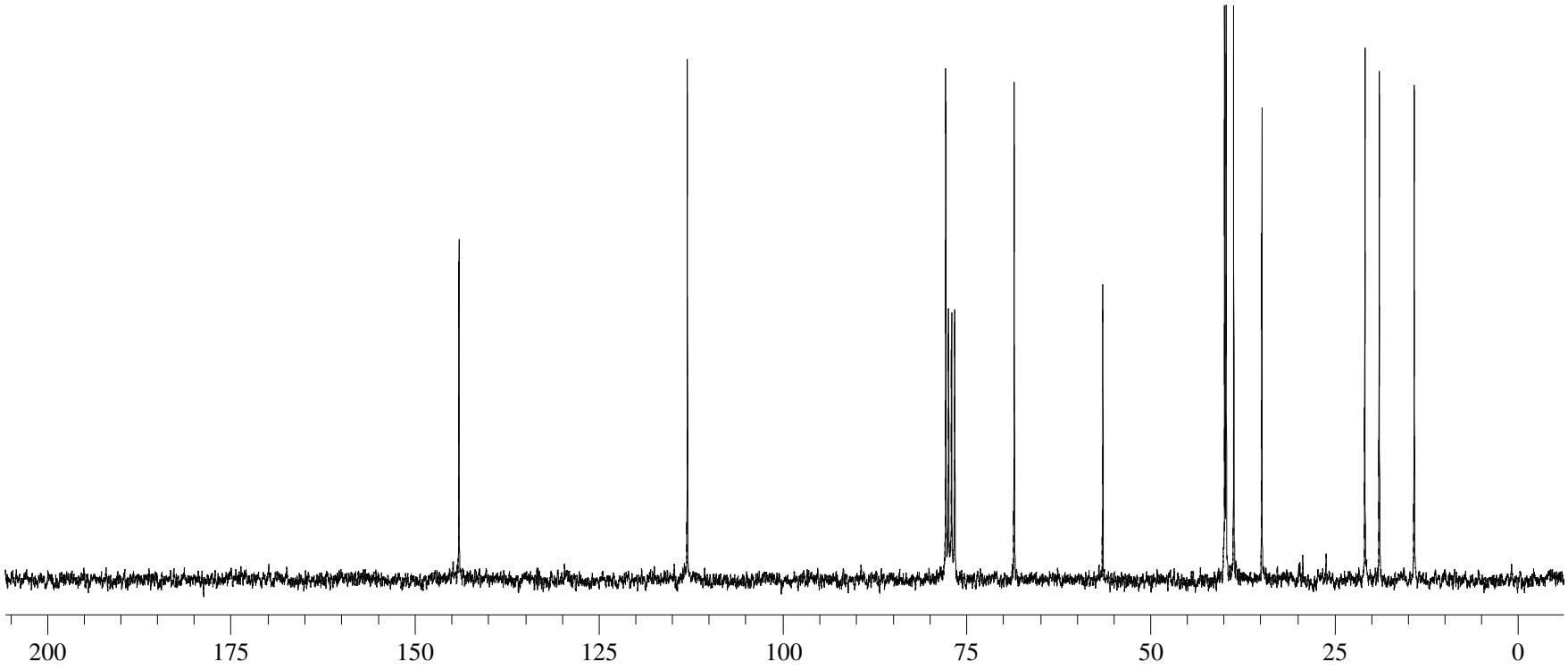

Figure 52: ^{13}C NMR Spectrum of compound **5** ($CDCl_3$, 75 MHz).

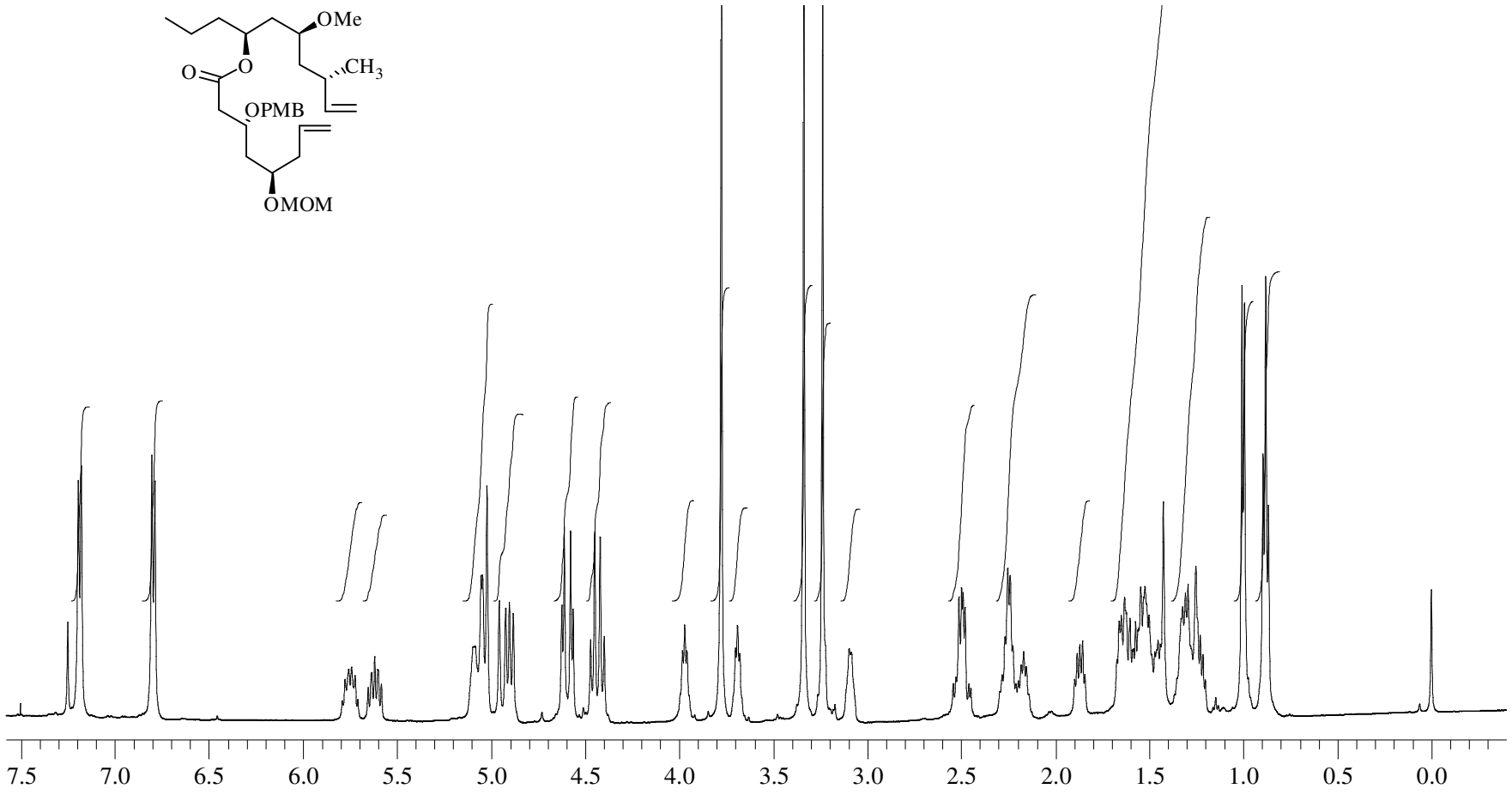

Figure 53: ^{1}H NMR Spectrum of compound **4** ($CDCl_3$, 500 MHz).

`

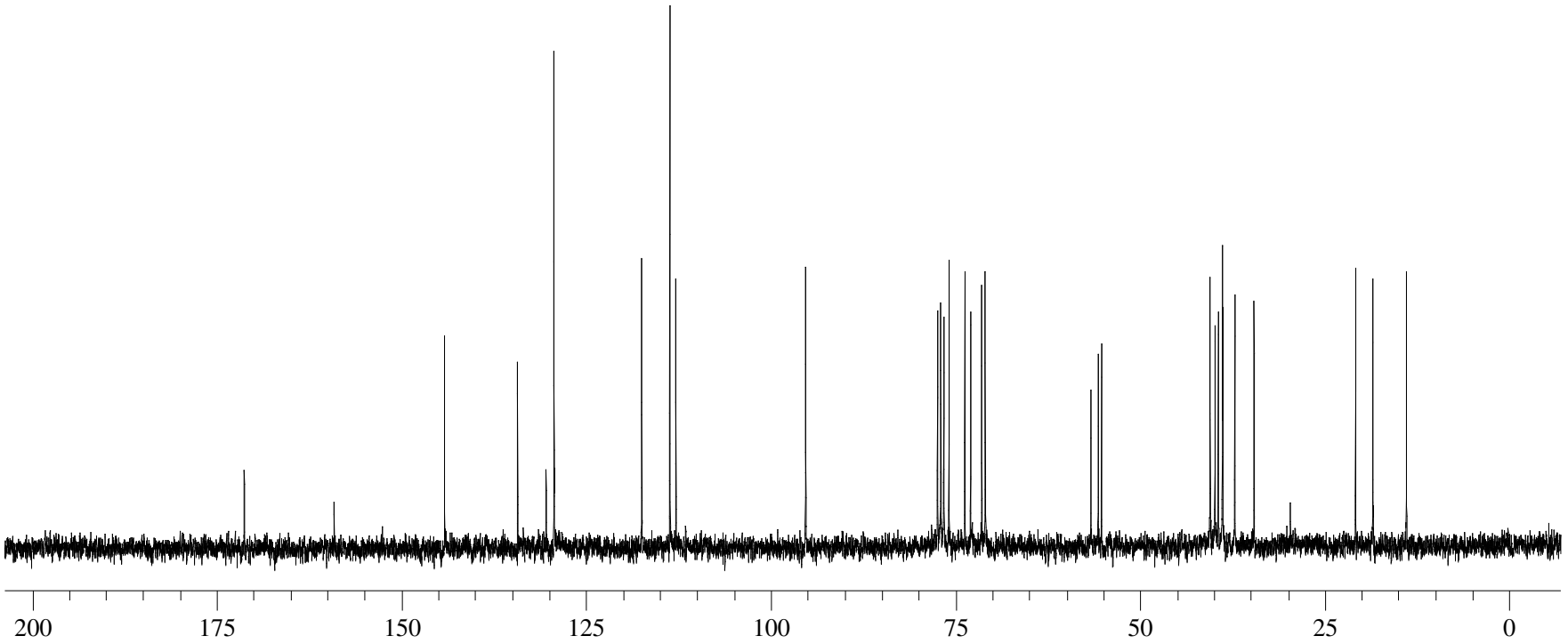

Figure 54: ^{13}C NMR Spectrum of compound **4** ($CDCl_3$, 75 MHz).

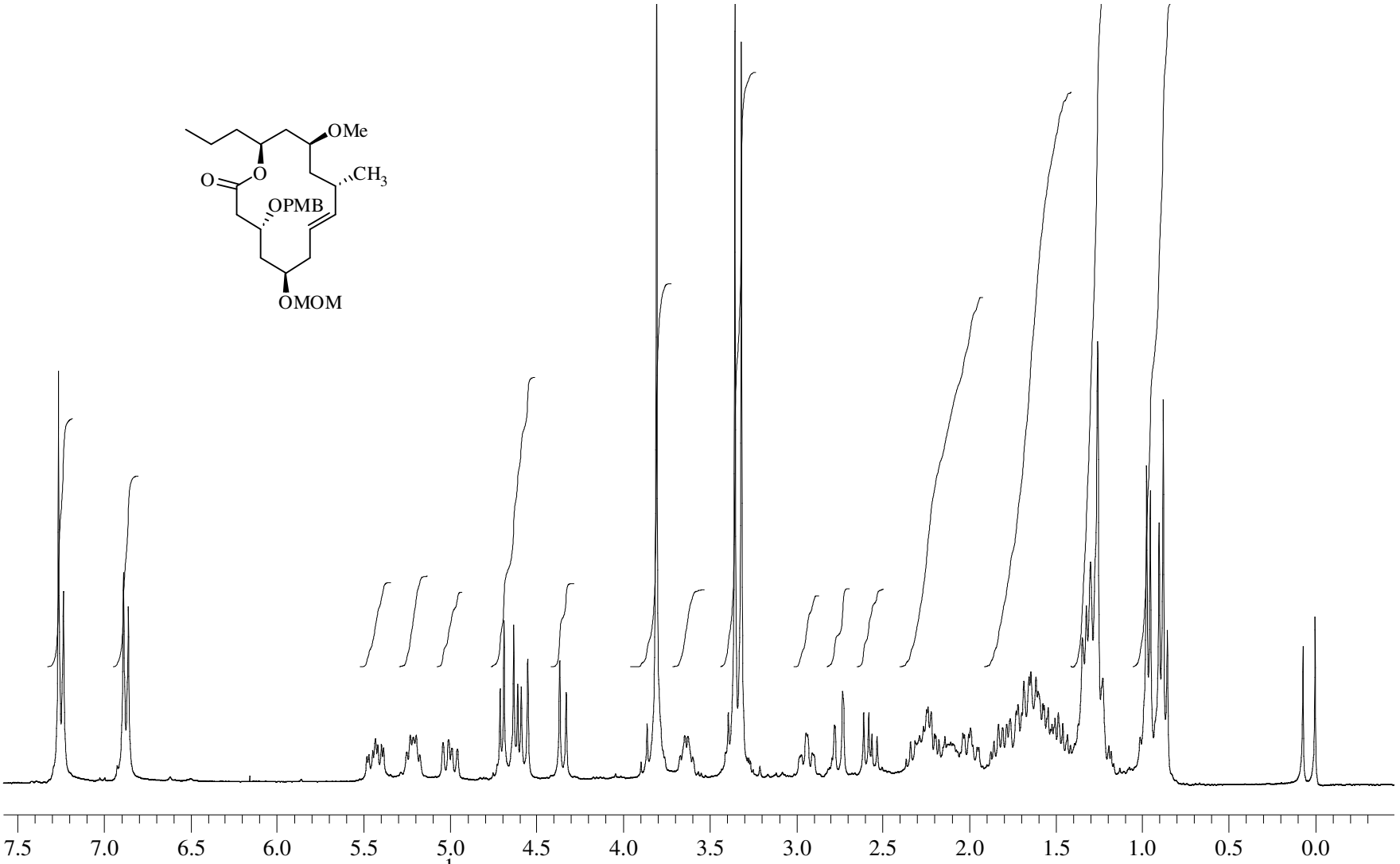

Figure 55: ^{1}H NMR Spectrum of compound **37** ($CDCl_3$, 500 MHz).

`

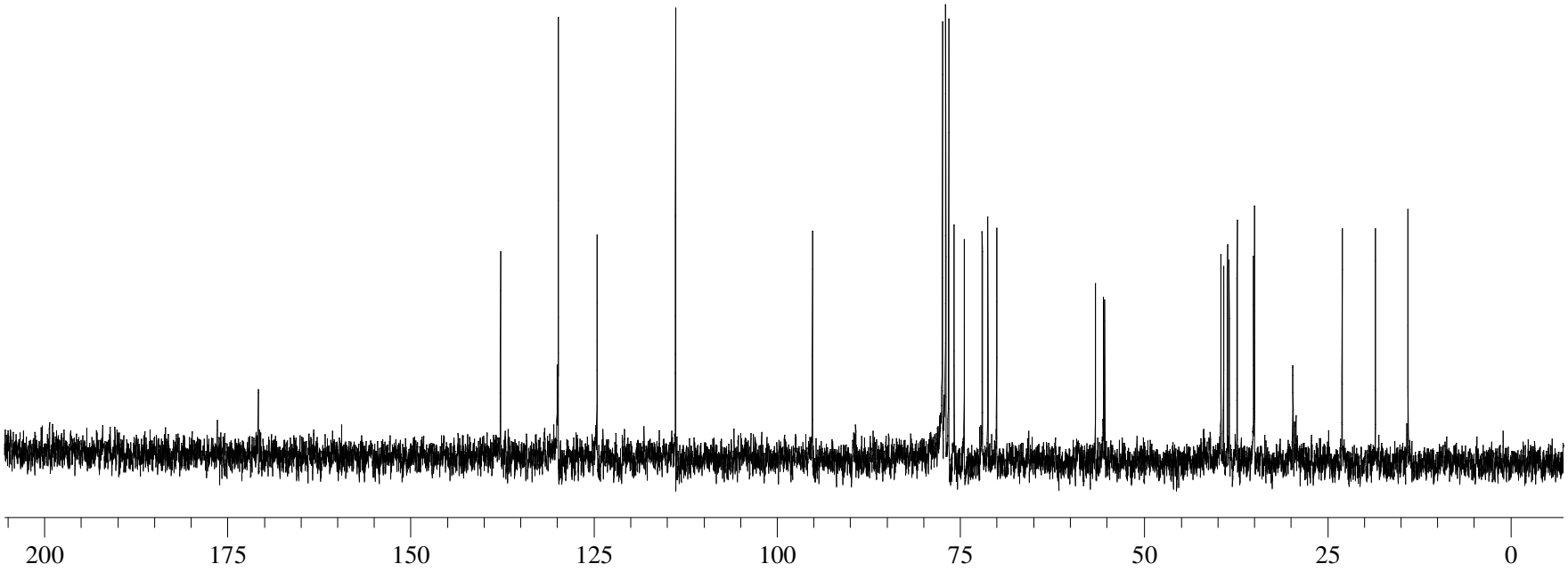

Figure 56: ^{13}C NMR Spectrum of compound **37** ($CDCl_3$, 75 MHz).

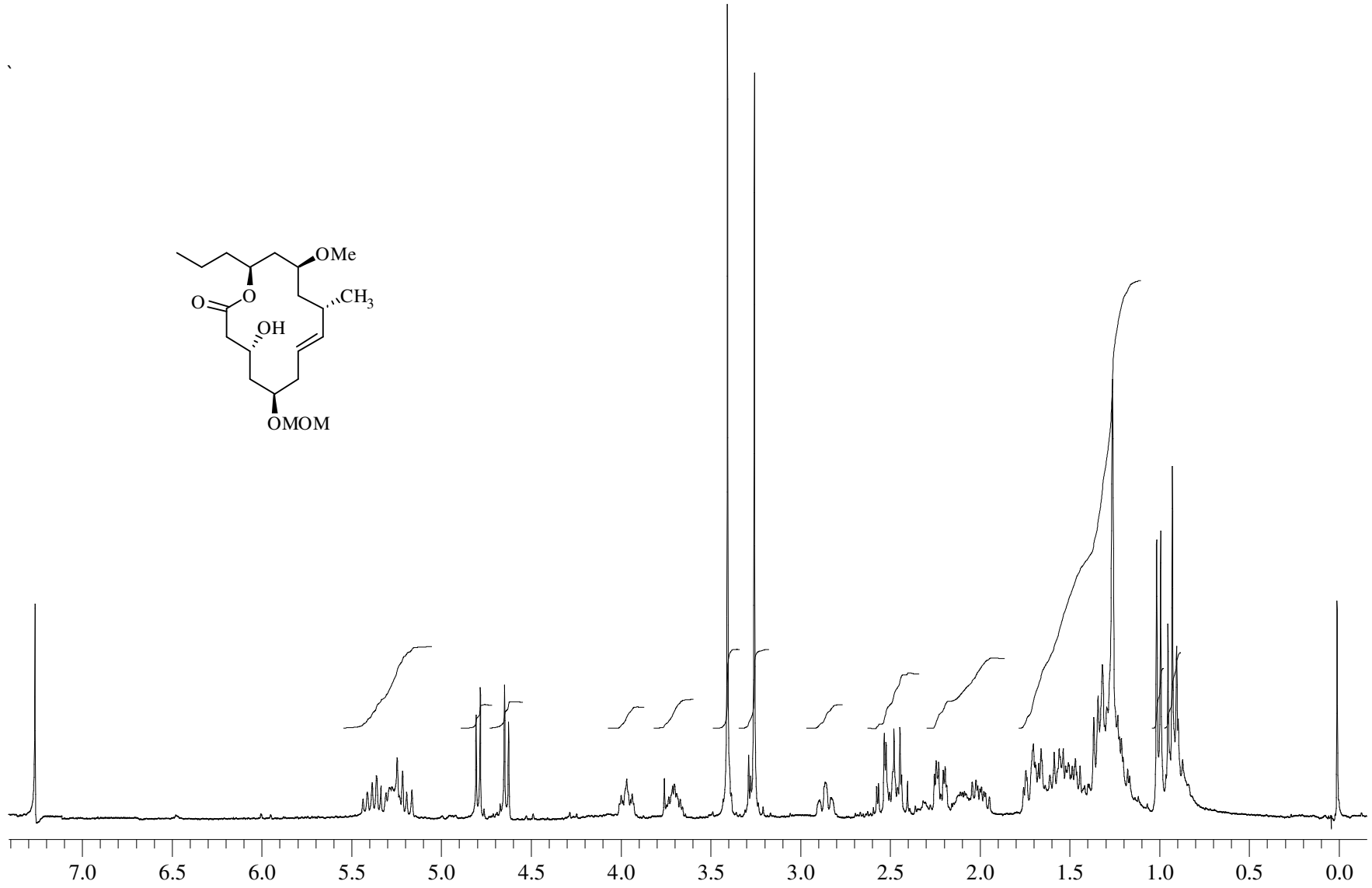

Figure 57: ^{1}H NMR Spectrum of compound **3** ($CDCl_3$, 500 MHz).

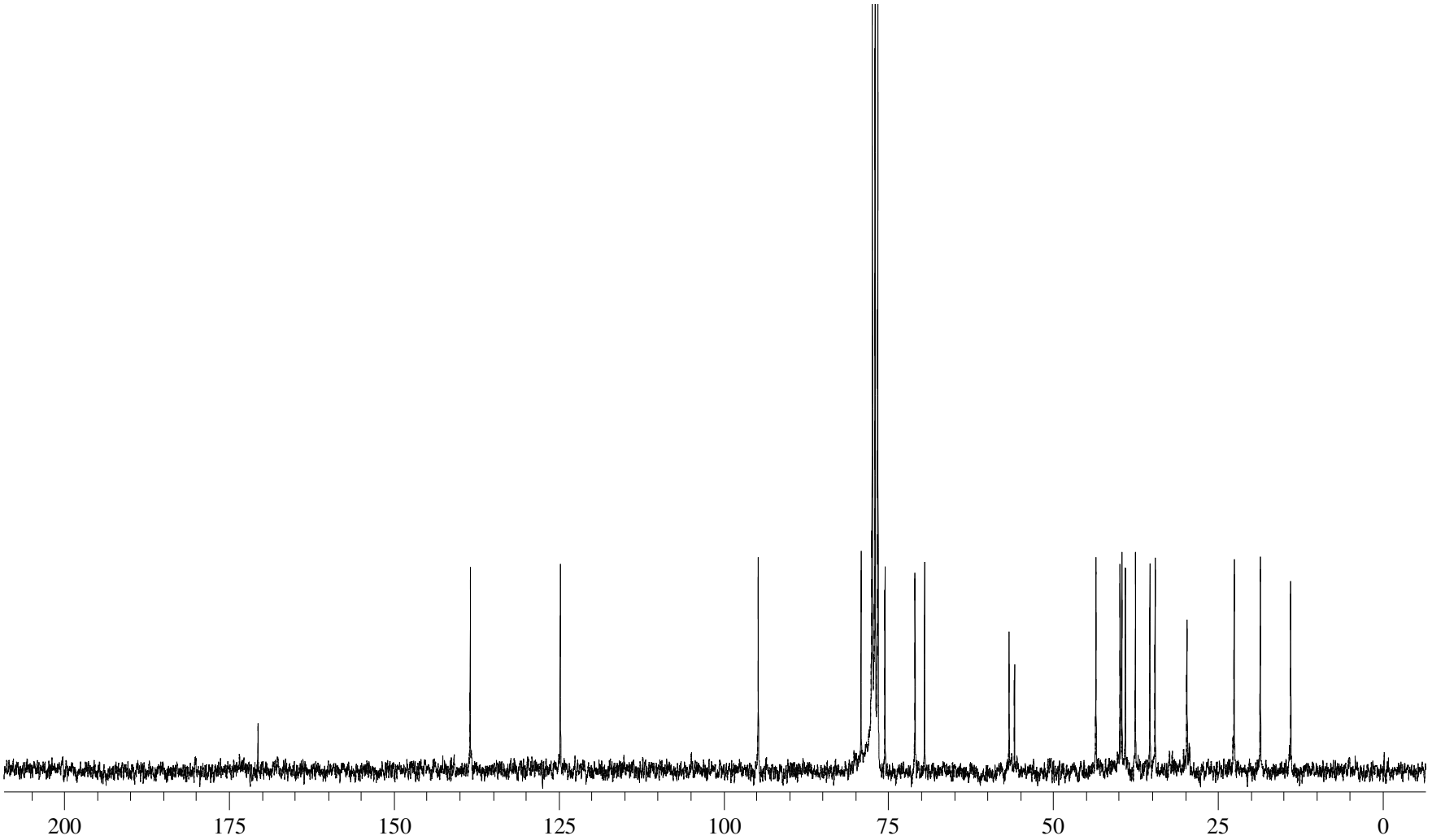

Figure 58: ^{13}C NMR Spectrum of compound **3** ($CDCl_3$, 75 MHz).

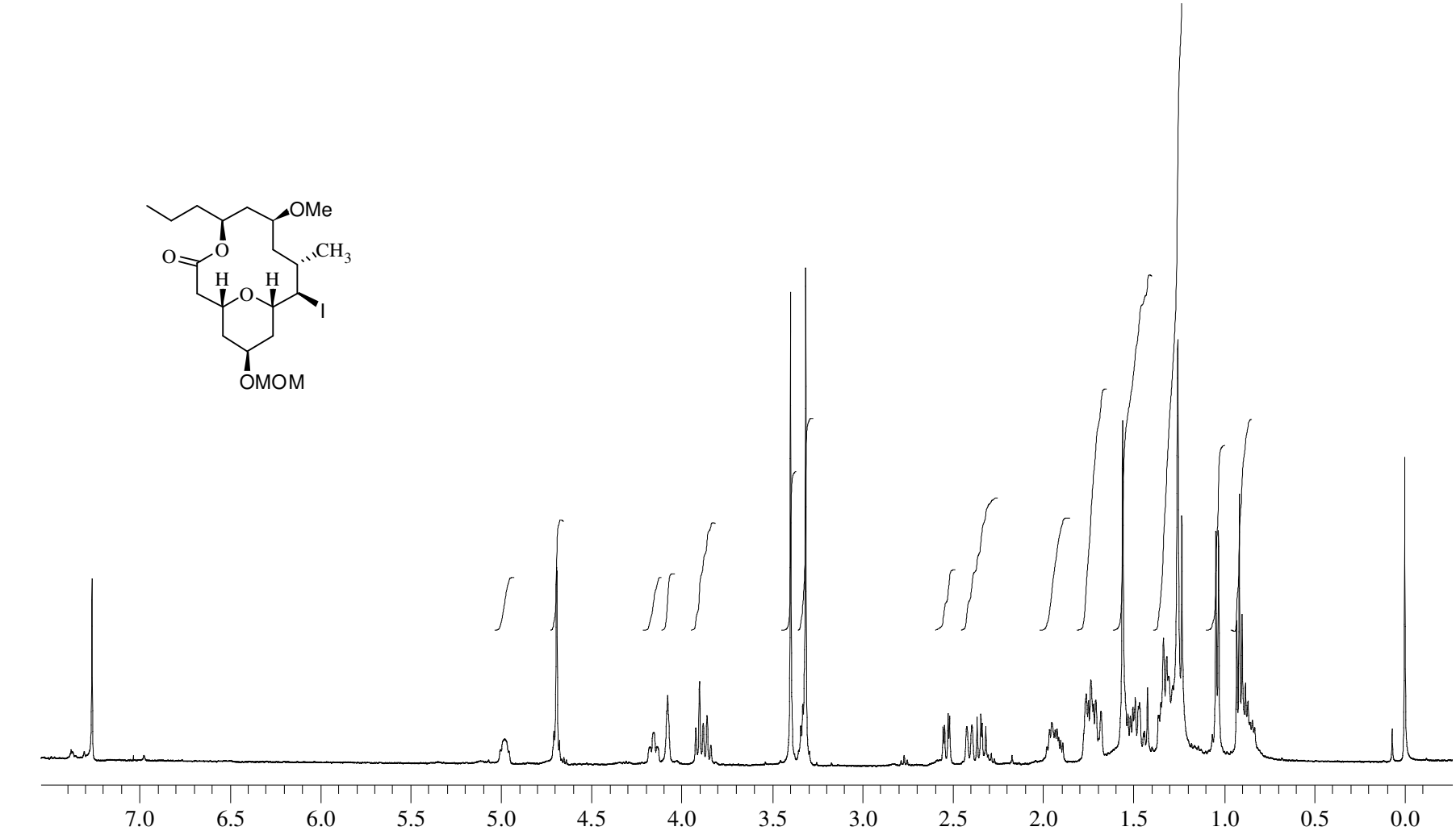

Figure 59: ^{1}H NMR Spectrum of compound **38** ($CDCl_3$, 500 MHz).

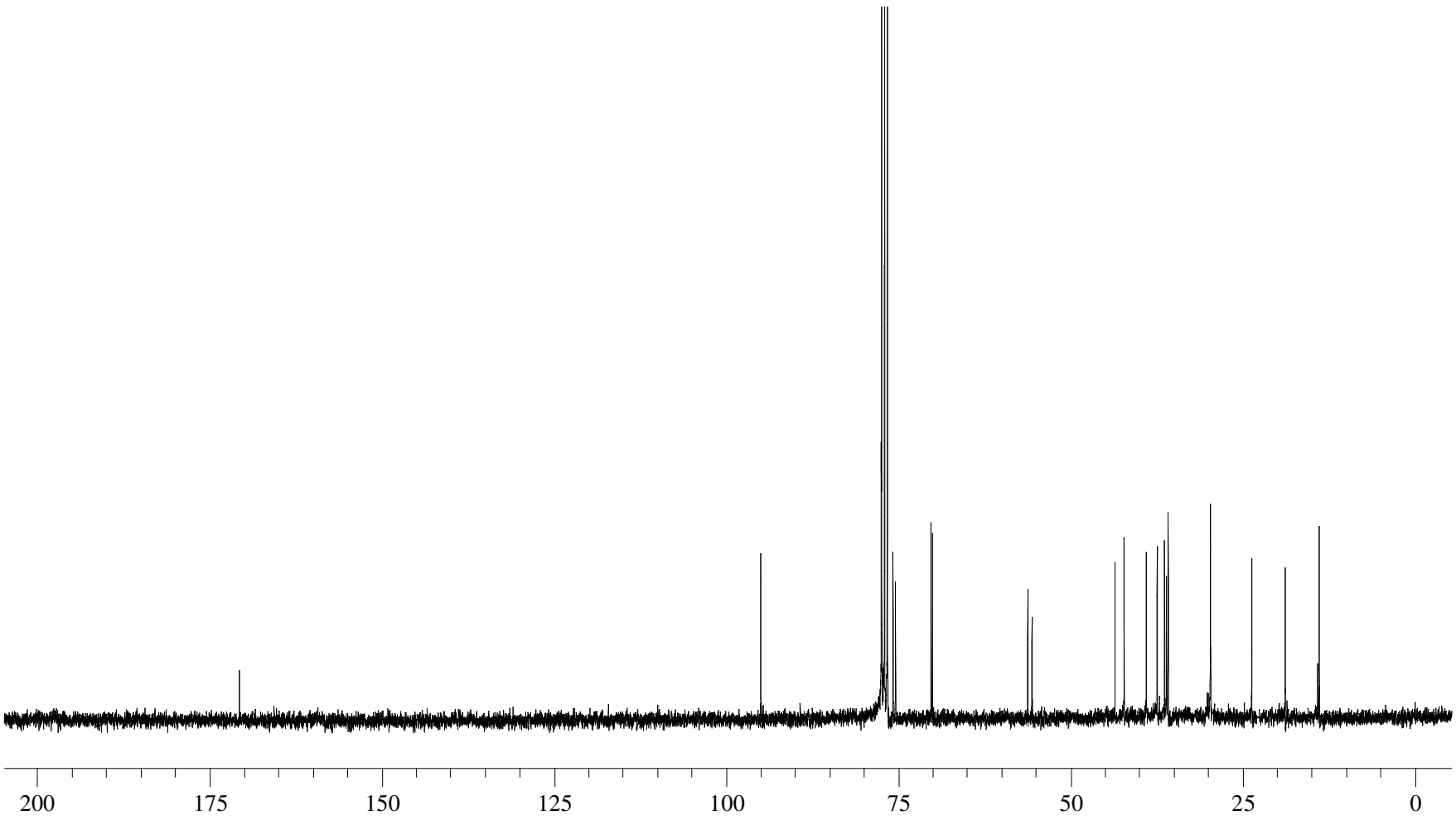

Figure 60: ^{13}C NMR Spectrum of compound **38** ($CDCl_3$, 75 MHz).

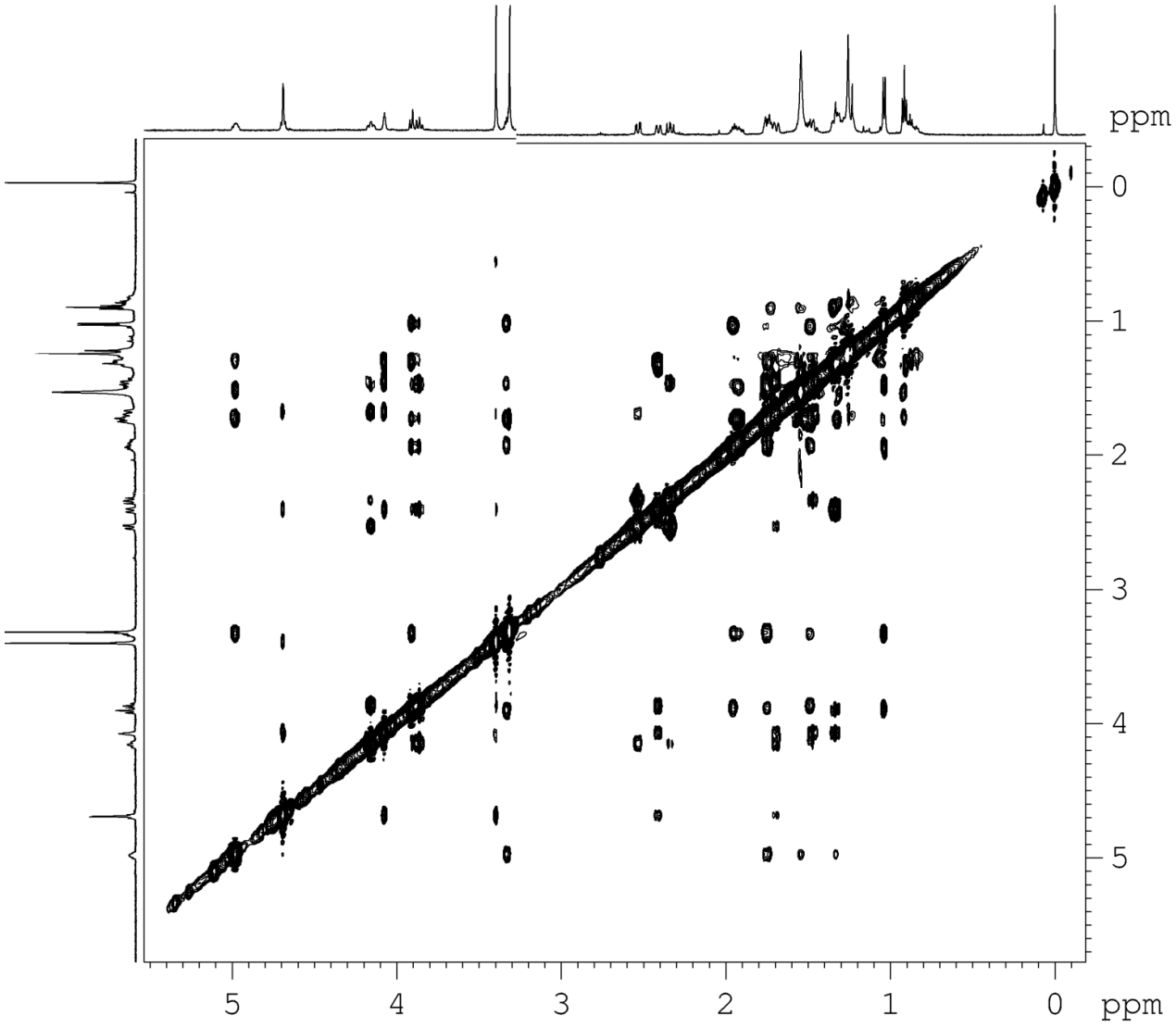

Figure 61: NOESY Spectrum of Compound **38**.

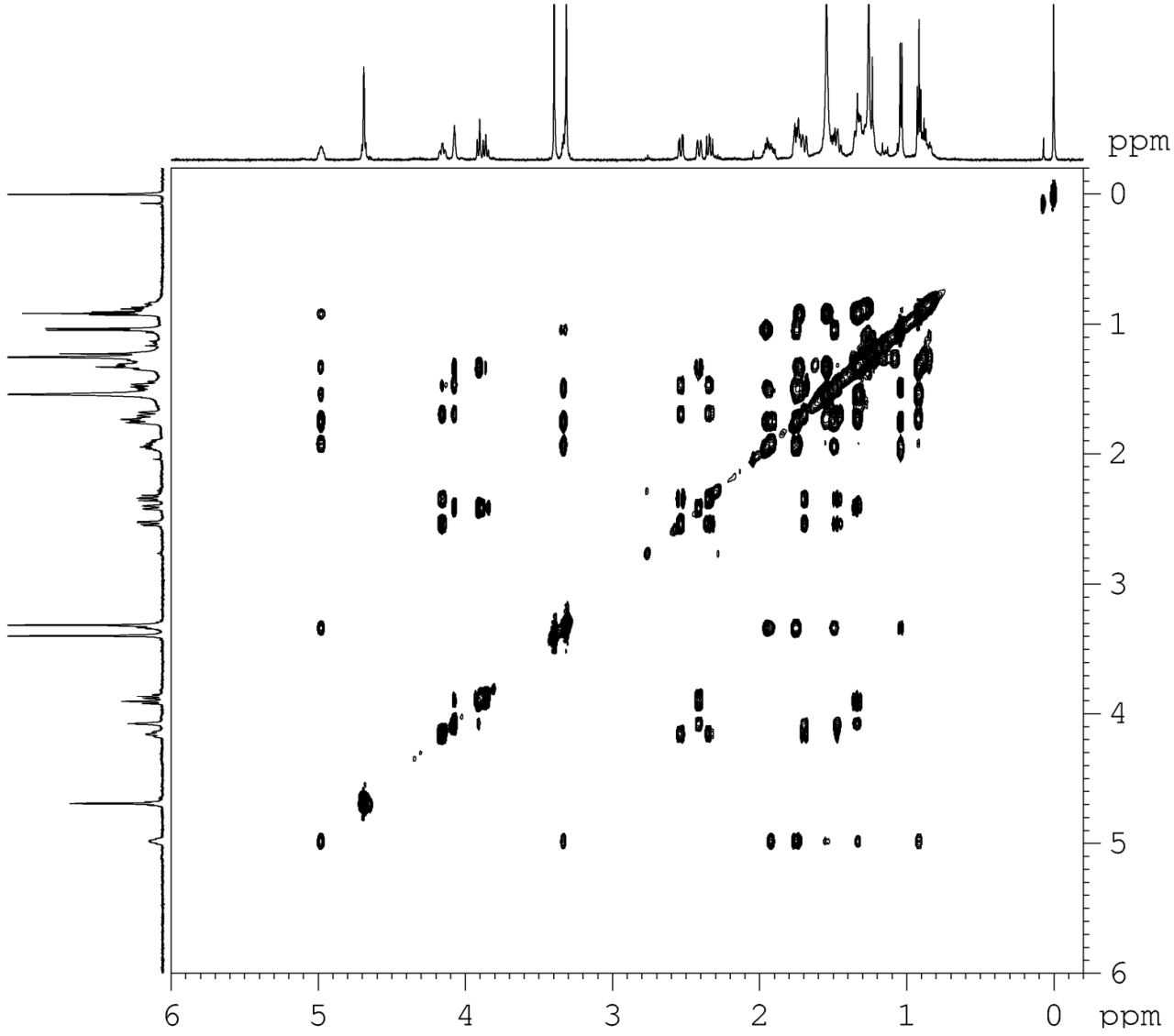

Figure 62: TOCSY Spectrum of compound **38**:

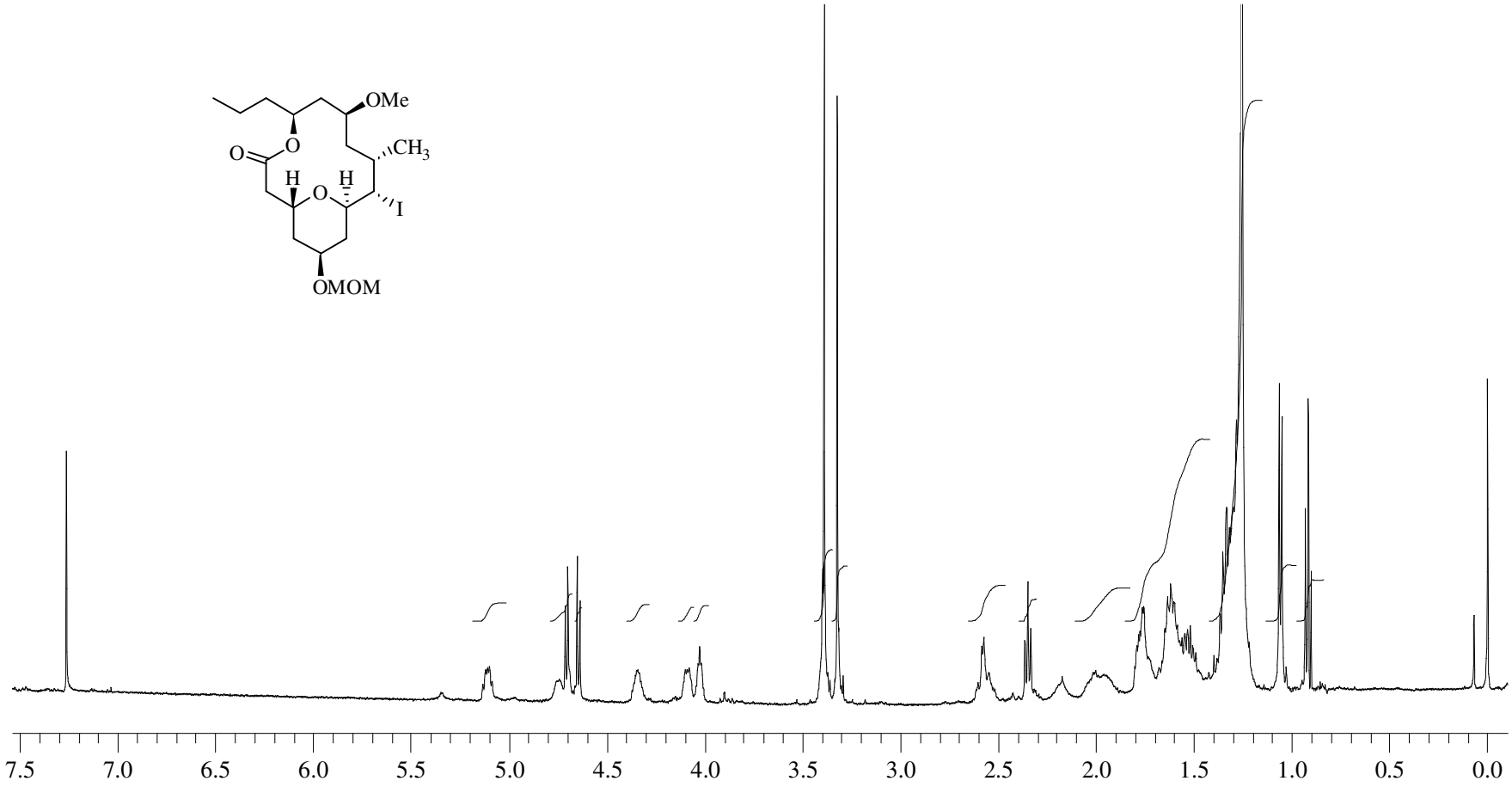

Figure 63: ^{1}H NMR Spectrum of compound **38a** ($CDCl_3$, 500 MHz).

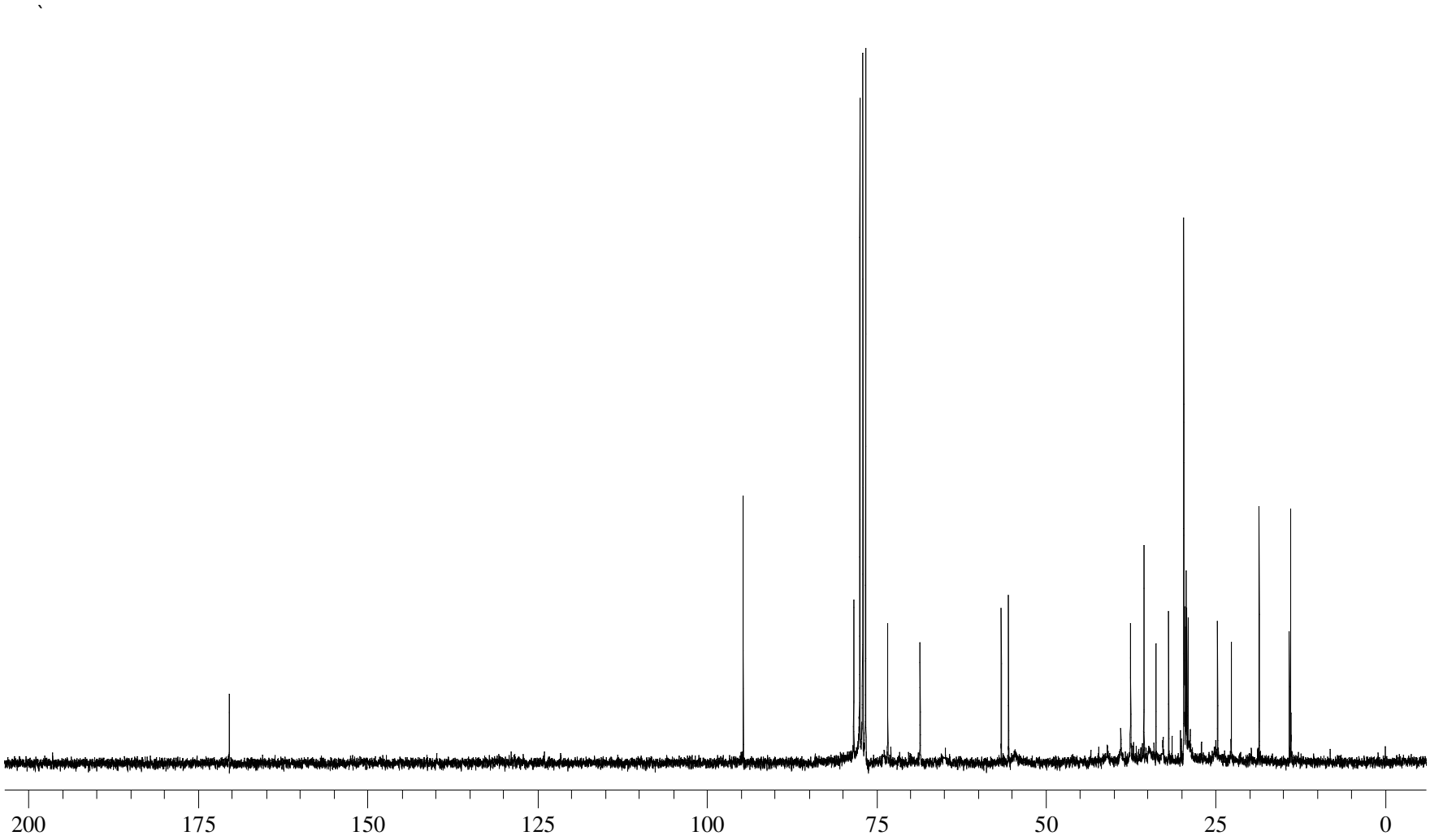

Figure 64: ^{13}C NMR Spectrum of compound **38a** ($CDCl_3$, 75 MHz).

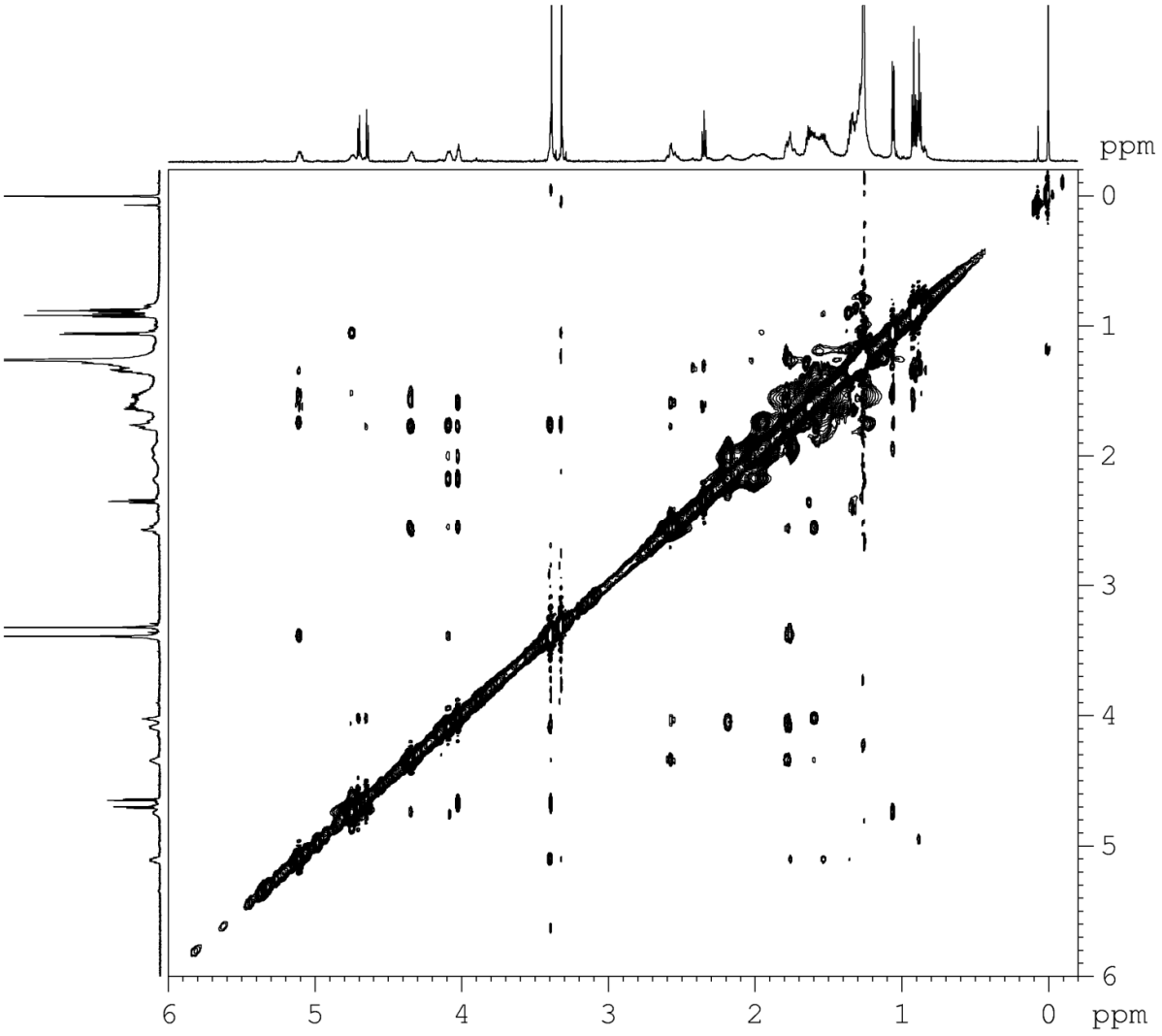

Figure 65: NOESY Spectrum of compound **38a**.

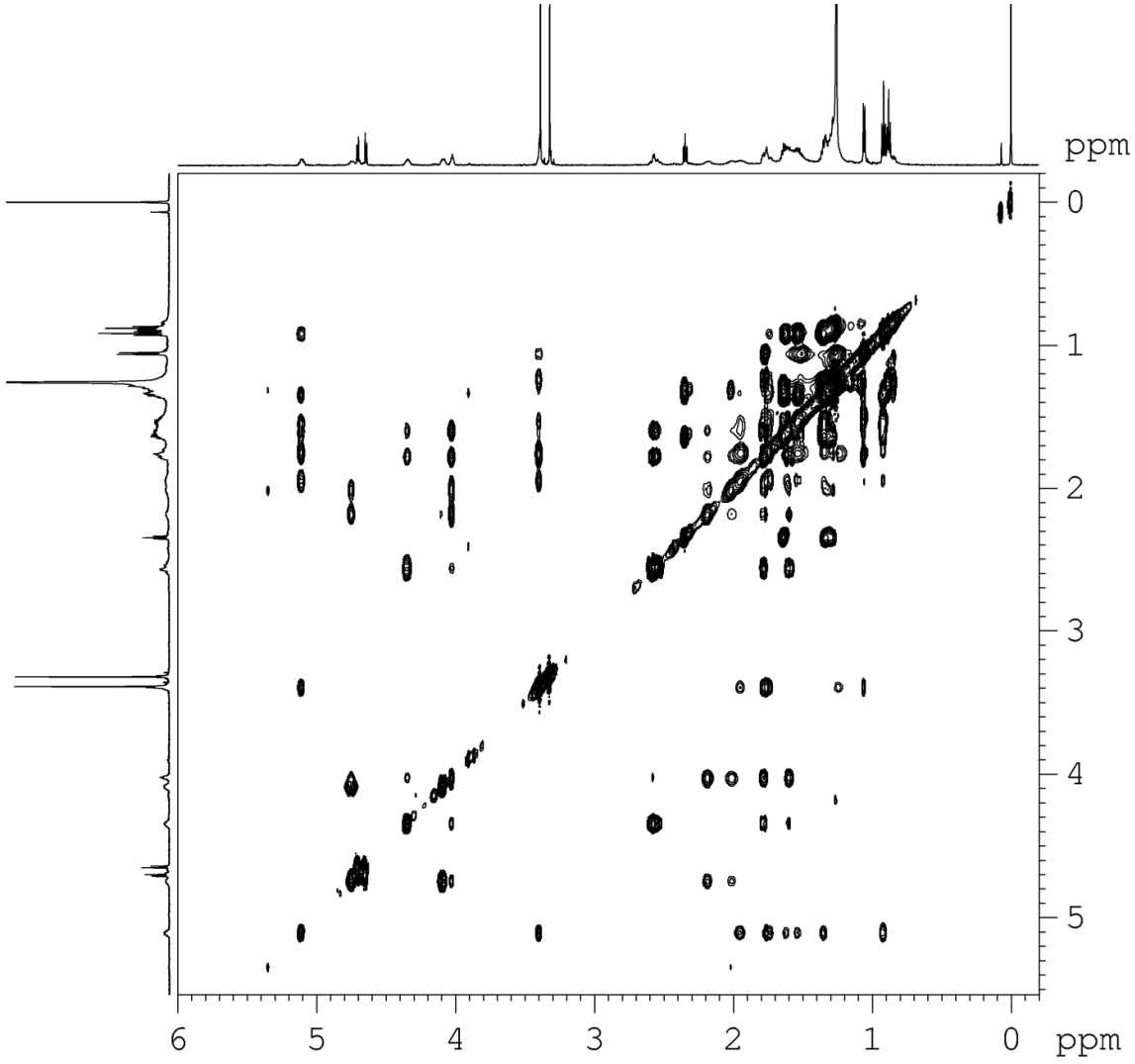

Figure 66: TOCSY Spectrum of compound **38a**.

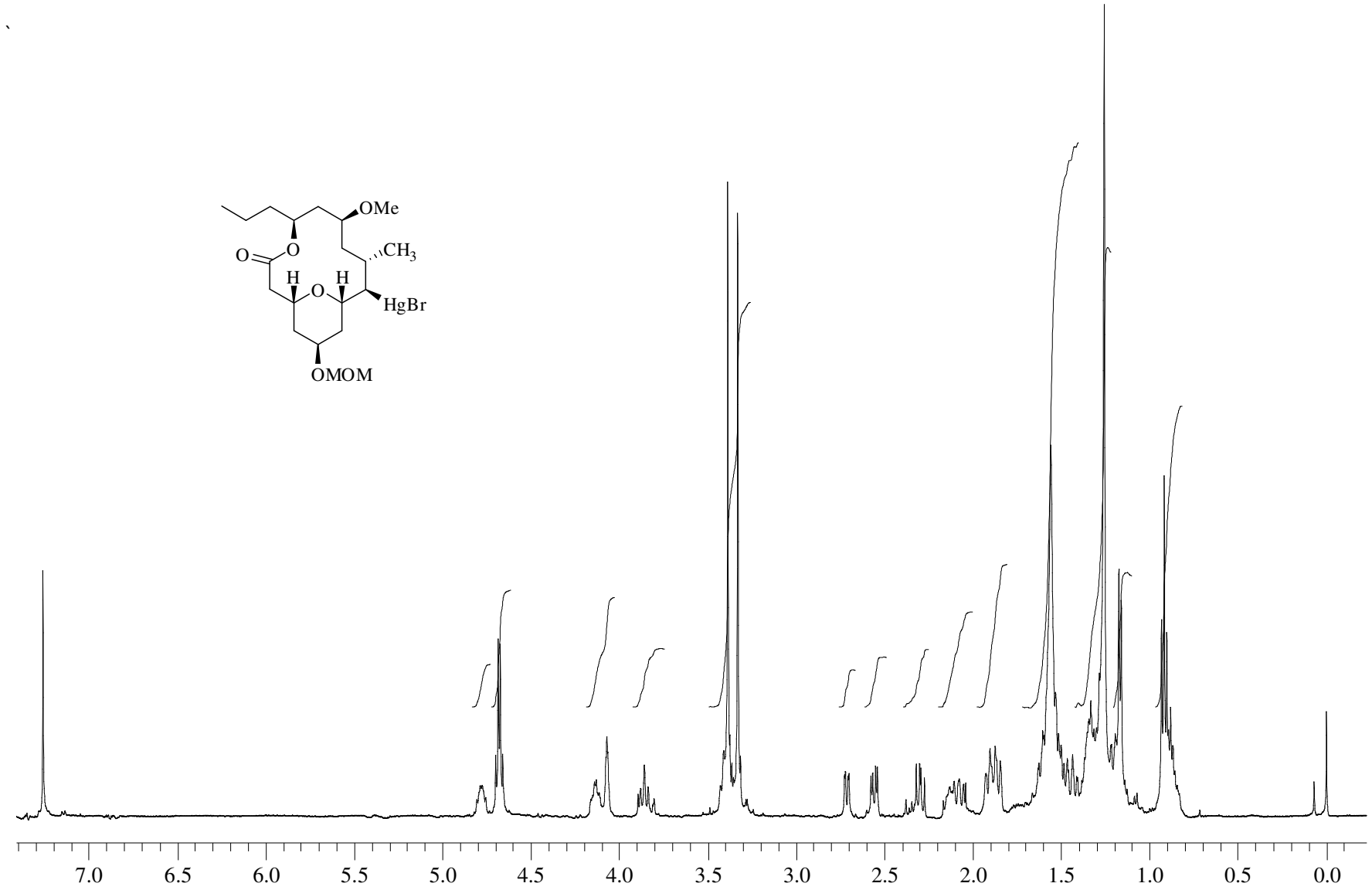

Figure 67: ^{1}H NMR Spectrum of compound **39** ($CDCl_3$, 500 MHz).

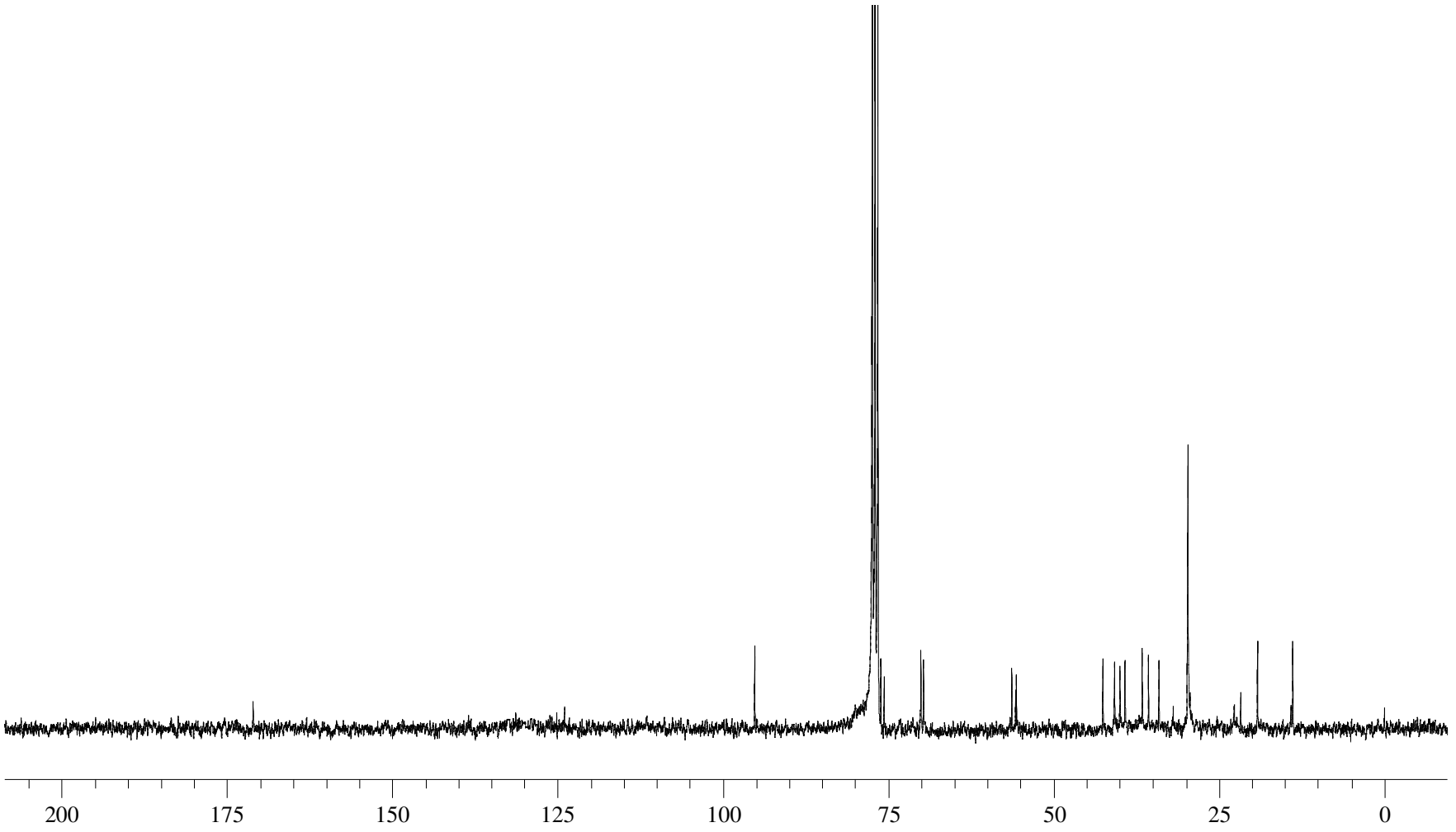

Figure 68: ^{13}C NMR Spectrum of compound **39** ($CDCl_3$, 75 MHz).

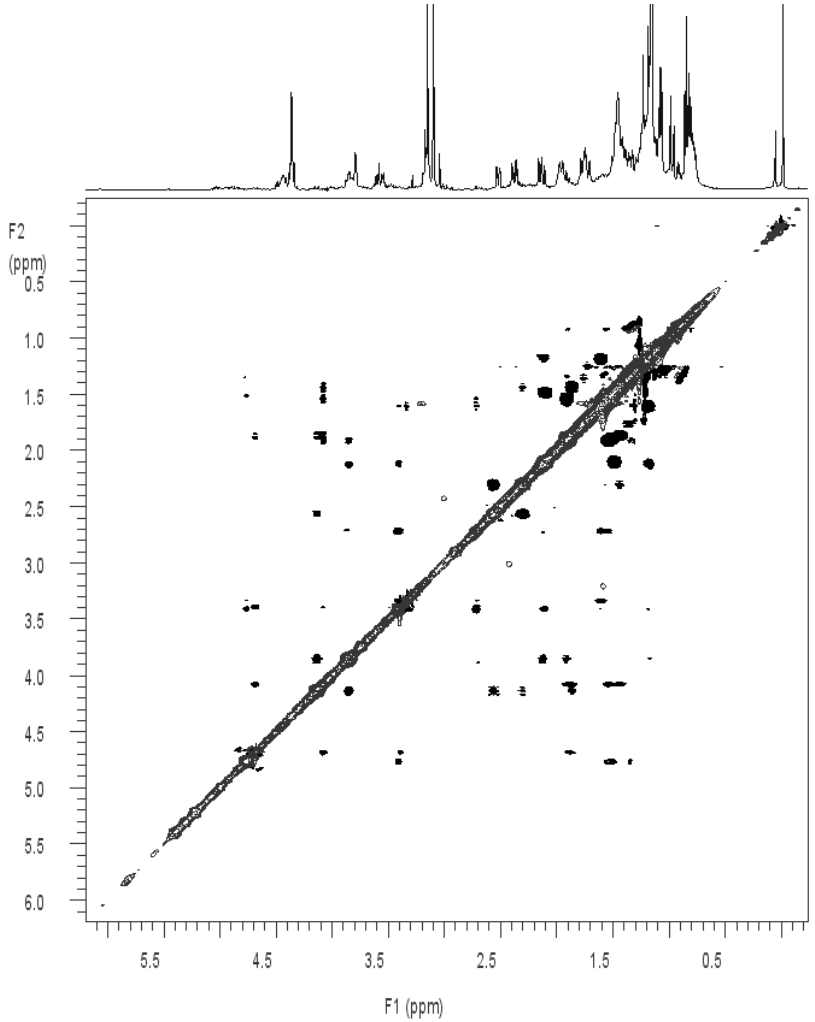

Figure 69: NOESY Spectrum of compound **39**.

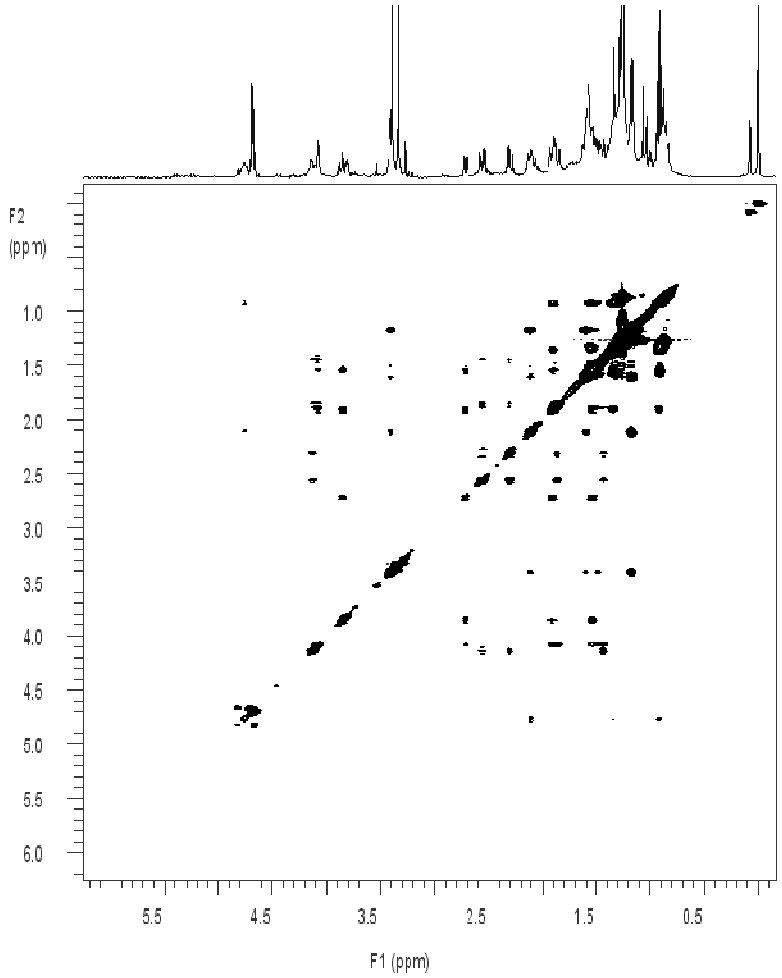

Figure 70: TOCSY Spectrum of compound **39.**

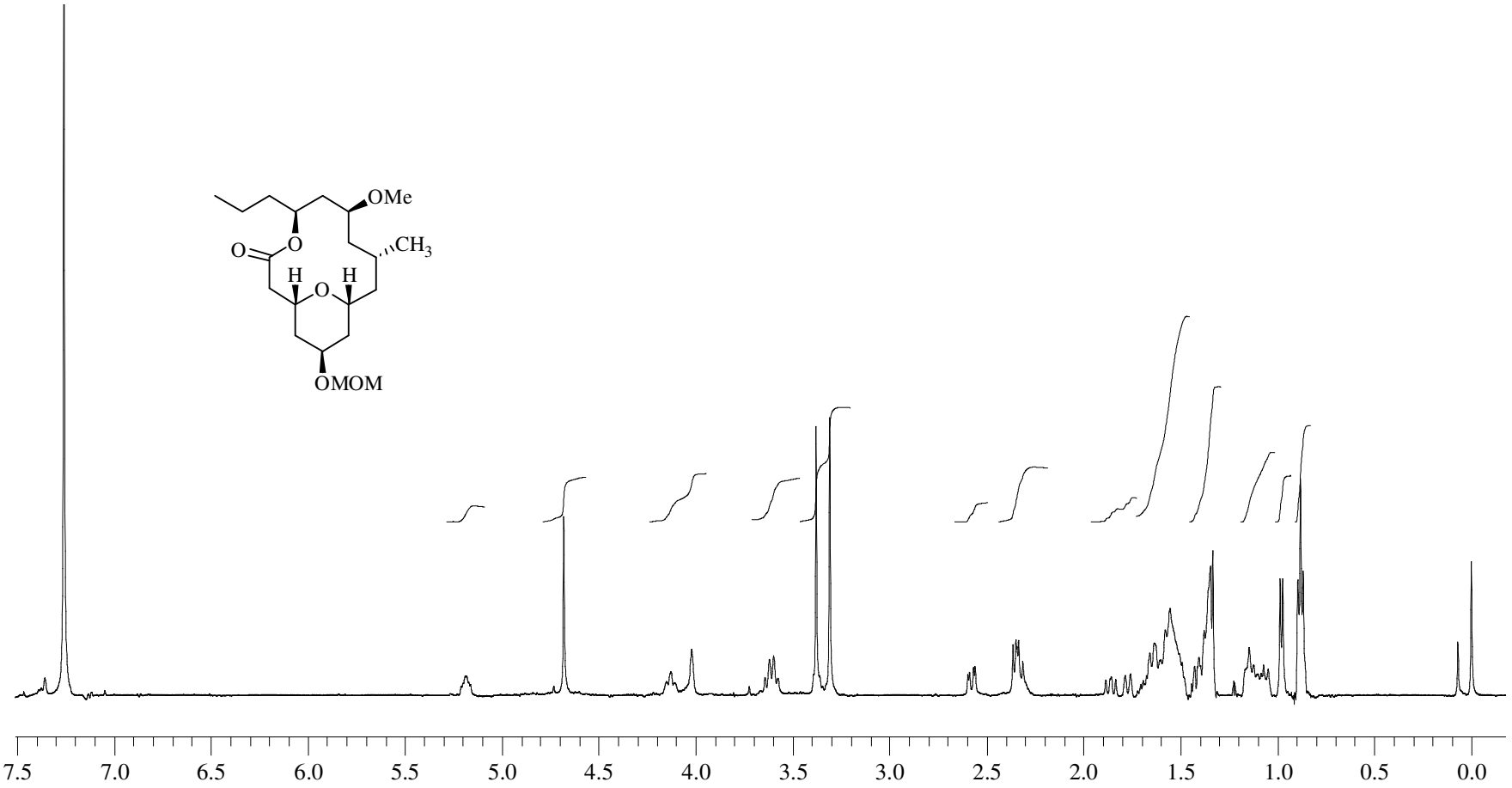

Figure 71: ^{1}H NMR Spectrum of compound **40** ($CDCl_3$, 500 MHz).

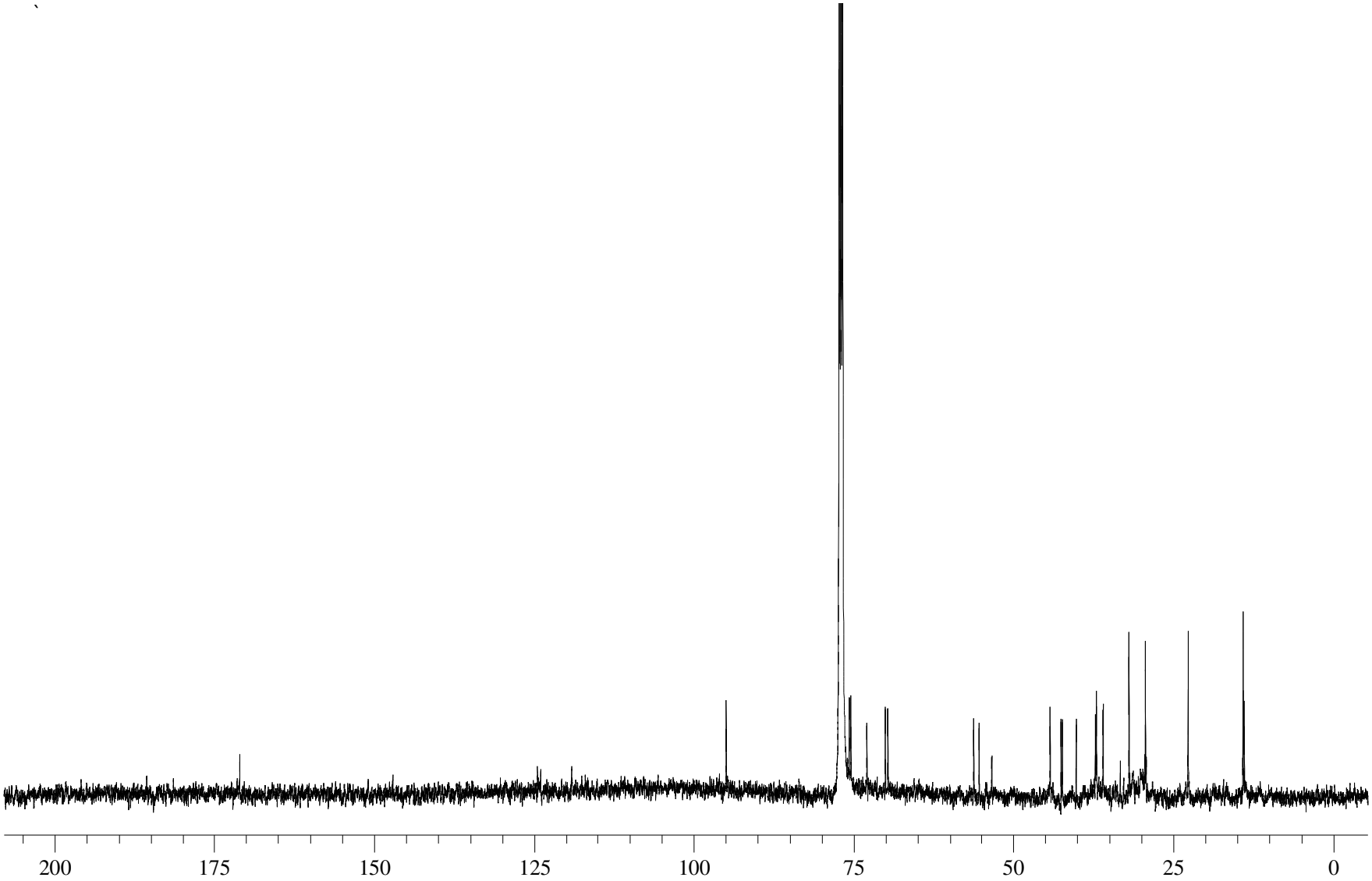

Figure 72: ^{13}C NMR Spectrum of compound **40** ($CDCl_3$, 75 MHz).

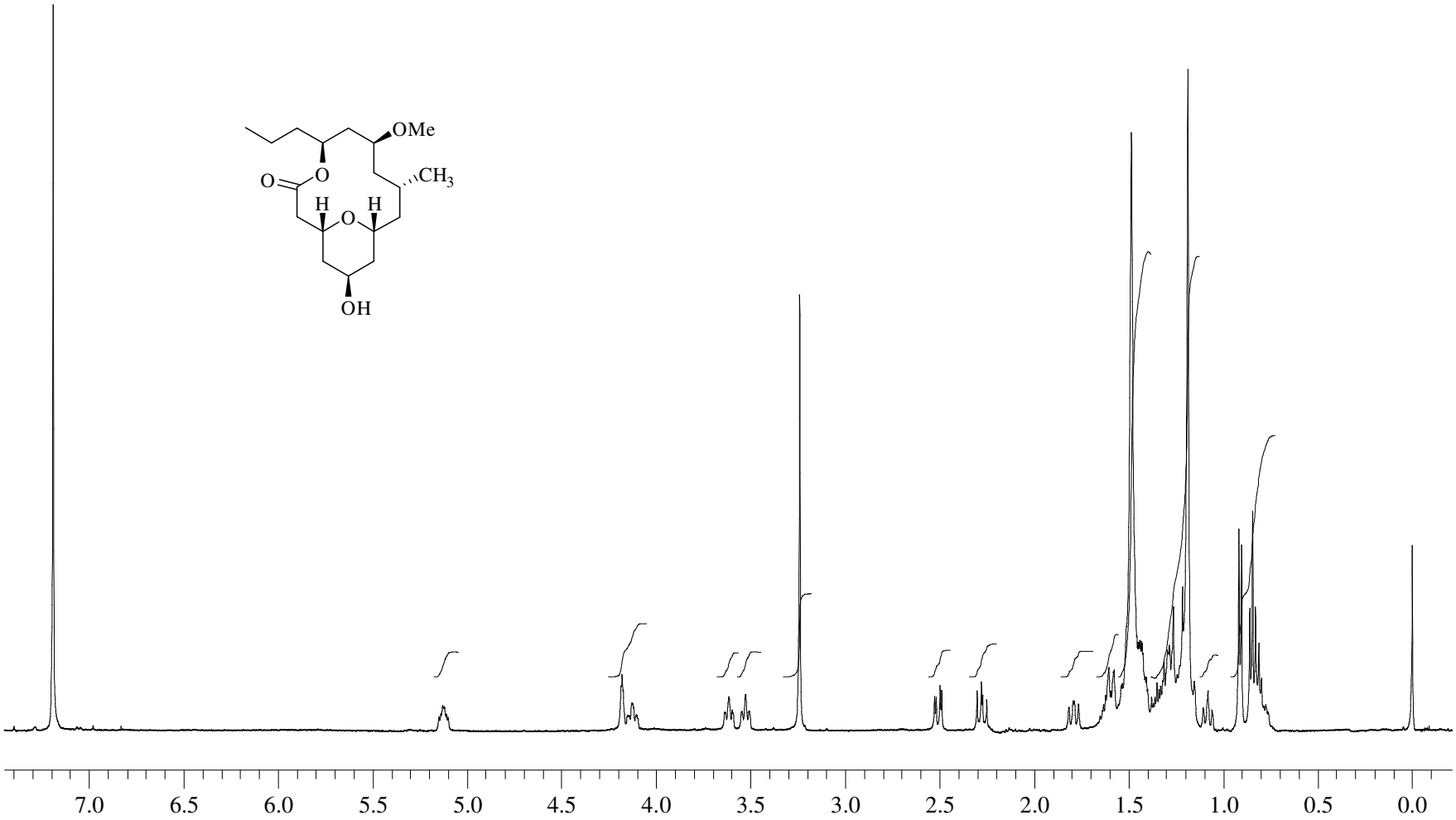

Figure 73: ^{1}H NMR Spectrum of compound **2** ($CDCl_3$, 500 MHz).

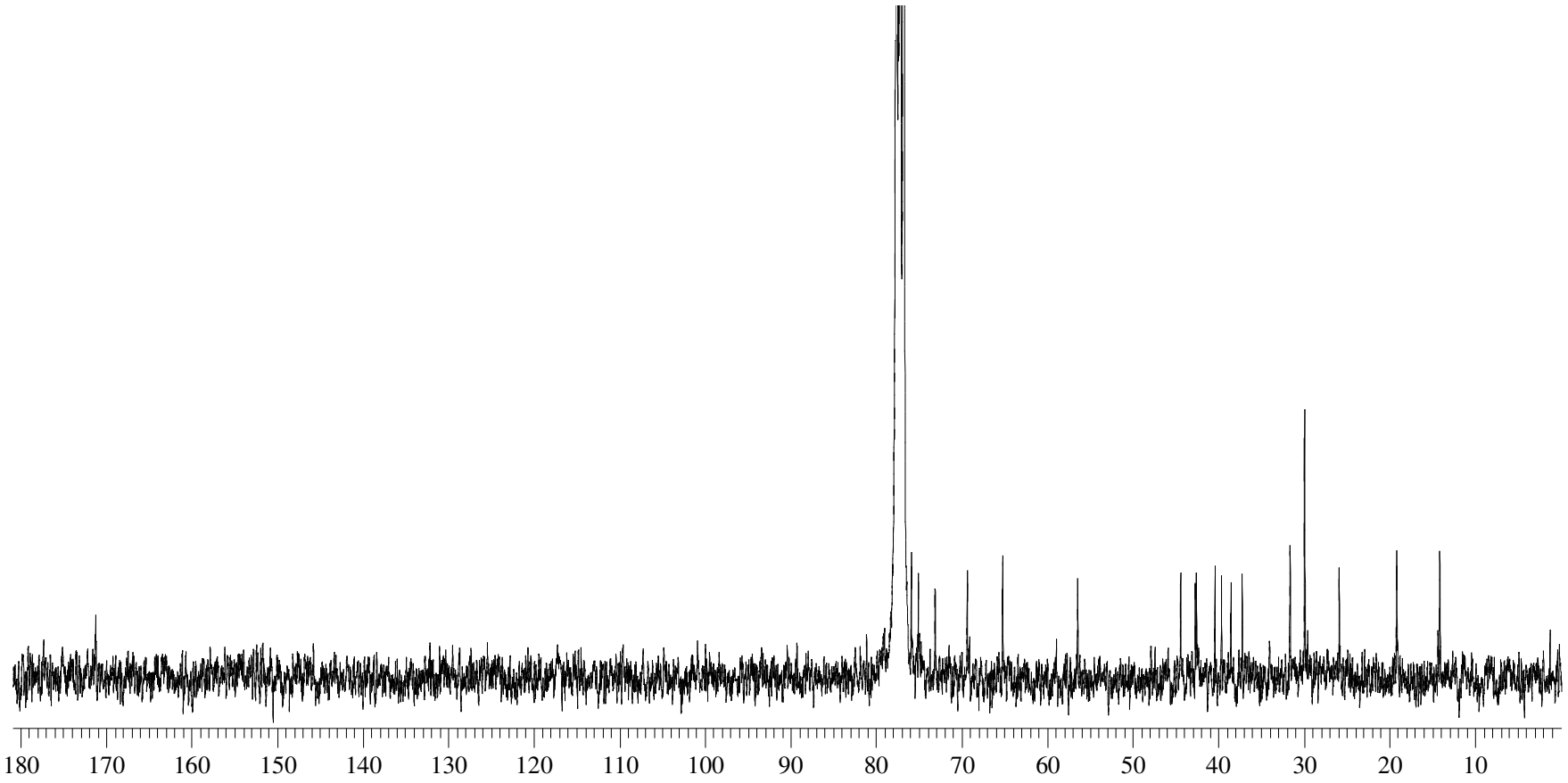

Figure 74: ^{13}C NMR Spectrum of compound **2** ($CDCl_3$, 75 MHz).