Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A Facile Microwave-Assisted Diels-Alder Reaction of Vinylboronates

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Supporting Information

List of contents:

Experimental procedures

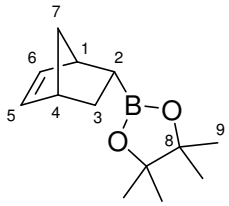
General Experimental Procedures. All reagents and solvents were used directly as purchased or purified according to standard procedures. Microwave heating was performed in a CEM Discover® System using septum-sealed 10 mL vials for high-pressure reaction conditions with stirring and IR-monitored temperature control. Analytical thin layer chromatography was carried out using commercial silica gel plates (Merck, Silica Gel 60 F254) and visualization was effected with short wavelength UV light (254 nm) and a p-anysaldehyde solution (2.5 mL of p-anysaldehyde + 2.5 mL of H_2SO_4 + 0.25 mL of AcOH + 95 mL of EtOH). Column chromatography was performed with silica gel 60 H (Merck), slurry packed, run under low pressure of nitrogen. The Diels-Alder reactions were monitored using ^{11}B NMR analysis in $CDCl_3$. NMR spectra were recorded at 300 MHz for ^1H, 75 MHz for ^{13}C and 96 MHz for ^{11}B on a Bruker Avance-300 DPX spectrometer with $CDCl_3$ as solvent and $(CH_3)_4Si$ (^1H) and $CDCl_3$ (^{13}C, 76.9 ppm) as internal standards. ^{11}B NMR spectra were externally referenced to $BF_3 \cdot Et_2O$. Chemical shifts are reported in delta (δ) units in parts per million (ppm) and splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Coupling constants are recorded in Hertz (Hz). Isomeric ratios were determined by ^1H and ^{13}C NMR integration. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer using sodium chloride plates pellets. Absorbance frequencies are recorded in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS) were obtained at the UCR Mass Spectrometry Facility, Department of Chemistry, University of California. Low resolution mass spectra (MS-EI) were recorded on a Shimadzu GCMS-QP2010 plus mass spectrometer. The structure of the products were determined by a combination of spectroscopic methods such as IR, 1D and 2D NMR (including NOE, DEPT, COSY, HSQC and HMBC experiments) and HRMS. In some cases, conformational analysis and molecular modeling were also performed to corroborate the regiochemistry and/or the stereochemistry. In addition, we confirmed the structure of the Diels-Alder products by oxidation of the boronates to the alcohols, most of which were described in the literature. An example follows to show how we assigned the structure of the major isomer and how we deduced the product ratio. Products **3h** were isolated as a mixture after column chromatography, which prevented complete characterisation of all the isomers. The less polar fractions were enriched in the major isomer though, as shown in the ^1H and ^{13}C NMR spectra. After analysis of the 1D and 2D NMR spectra (including DEPT, COSY, HSQC and HMBC spectra), the major product was characterized as the ortho *exo* isomer **3h-OX**. The pattern and coupling constants of the signal corresponding to the hydrogen on the carbon attached to the boron atom was crucial to determine the regio- and stereochemistry of this product (doublet of doublet of doublet at 0.80 ppm with $J_{1,2}$ = 12.1, $J_{1,6a}$ = 9.7 and $J_{1,6b}$ = 2.6 Hz). Full assignment of signals for **3h-OX** was carried out with the aid of the COSY, HSQC and HMBC spectra. The ratio of the products **3h** was determined based on integration of the methyl signals at *ca.* 1 ppm in the ^1H NMR spectra of the different fractions. The ratio was identical to the one obtained for the mixture generated after oxidation (**4e**) and the major alcohol was, again, the ortho *exo* isomer since the carbinol proton appeared as a doublet of doublet of doublet at 3.44 ppm with $J_{1,6a}$ = 10.0, $J_{1,2}$ = 6.9 and $J_{1,6b}$ = 3.3 Hz. Assuming that oxidation proceeded with complete retention of stereochemistry, we propose that the proportion of each of the other three isomers was maintained too. The structural assignment of the four different alcohols (**4e**) was based on spectroscopic data reported in the literature, together with a set of experiments run in our laboratory (mono- and bidimensional spectra and molecular modelling followed by theoretical calculations of ^{13}C NMR chemical shifts using a methodology developed in our group).[1]

1. Sarotti, A. M.; Pellegrinet, S. C. *J. Org. Chem.*, **2009**, *74*, 7254-7260.

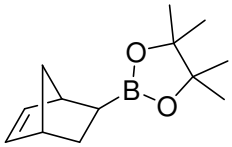
Microwave-assisted Diels-Alder reaction of vinylboronates: synthesis of boronates[2]

General procedure A: To an oven-dried 10 mL pressure-rated reaction vial equipped with a stirring bar were added dry toluene (0.5 mL), vinylboronate **1** (typically 0.5 mmol) and diene **2** (0.75-7.5 mmol) under argon atmosphere. The resulting reaction mixture was stirred at the temperature reported (150-220 ºC) in the microwave until complete conversion (1-6 h). The solvent was removed under reduced pressure, and the crude was purified by column chromatography (hexane/AcOEt) to afford the corresponding boronate.

2-Bicyclo[2.2.1]hept-5-en-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3b)[2]



3b-N



3b-X

Boronate **3b** was obtained as a mixture of diastereomers according to the general procedure A, using vinylboronate **1b** (0.5 mmol) and diene **2a** (1.5 mmol). To avoid polymerization, the diene was added in portions (3 x 0.5 mmol, one portion per run). A small fraction of each diastereomer could be separated and characterized.

Reaction conditions: 60 min at 150 ºC (3 x 20 min).

Yield: 100% (106 mg), *endo/exo* 38:62.

HRMS calcd for $C_{13}H_{25}BNO_2$ $(M+NH_4)^+$: 238.1973, found: 238.1980.

Boronate 3b-N

IR (film) ν_{max}: 3058, 2976, 2934, 2874, 1412, 1371, 1310, 1273, 1146, 979, 856, 719, 690, 502.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.00 (br s, 2H, H-5 and H-6), 3.02 (br s, 1H, H-1), 2.86 (br s, 1H, H-4), 1.83 (ddd, $J_{3n,3x}$ = 10.8, $J_{2,3x}$ = 10.0, $J_{3x,4}$ = 3.6 Hz, 1H, H-3x), 1.40-1.32 (m, 2H, H-2 and H-7), 1.19 (s, 12H, H-9), 1.15-1.08 (m, 2H, H-3n and H-7).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 135.8 (CH, C-5), 134.4 (CH, C-6), 82.7 (2C, C-8), 50.3 (CH_2, C-7), 44.2 (CH, C-1), 42.3 (CH, C-4), 27.7 (CH_2, C-3), 24.6 ($4CH_3$, C-9), C-2 signal missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.4.

Boronate 3b-X

IR (film) ν_{max}: 3056, 2975, 2931, 2871, 1370, 1313, 1232, 1146, 976, 858, 719.

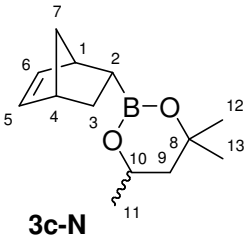
2. Boronates **3b**, **3f** and **3i** have been previously synthezised by Diels-Alder reactions of dichlorovinylborane and the corresponding

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.09 (dd, $J_{5,6}$ = 5.4, $J_{1,6}$ = 2.9 Hz, 1H, H-6), 5.95 (dd, $J_{5,6}$ = 5.4, $J_{4,5}$ = 3.0 Hz, 1H, H-5), 2.88 (br s, 2H, H-1 and H-4), 1.71 (ddd, $J_{3n,3x}$ = 11.1, $J_{2,3x}$ = 4.2, $J_{3x,4}$ = 4.2 Hz, 1H, H-3x), 1.25-1.06 (m, 15H, H-3n, H-7 and H-9), 0.68 (ddd, $J_{2,3n}$ = 9.7, $J_{2,3x}$ = 4.9, $J_{1,2}$ = 1.3 Hz, 1H, H-2).

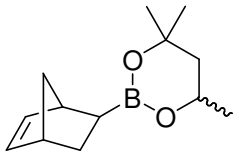
^{13}C NMR (75 MHz; $CDCl_3$) δ: 137.0 (CH, C-6), 134.2 (CH, C-5), 82.8 (2C, C-8), 47.4 (CH_2, C-7), 44.0 (CH, C-1), 42.2 (CH, C-4), 27.6 (CH_2, C-3), 24.6 ($4CH_3$, C-9), C-2 signal missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 34.1.

2-Bicyclo[2.2.1]hept-5-en-2-yl-4,4,6-trimethyl-[1,3,2]dioxaborinane (3c)[3]



3c-N



3c-X

Boronate **3c** was obtained as a mixture of diastereomers according to the general procedure A, using vinylboronate **1c** (0.55 mmol) and diene **2a** (5.5 mmol). To avoid polymerization, the diene was added in portions (3 x 1.8 mmol, one portion per run, three first runs).

Reaction conditions: 80 min at 150 ºC (4 x 20 min).

Yield: 95% (115 mg), *endo/exo* 49:51.

IR (film) ν_{max}: 3055, 2972, 2873, 1445, 1384, 1340, 1198, 1173, 768, 715, 684.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.08 (dd, $J_{5,6}$ = 5.5, $J_{4,5}$ = 2.7 Hz, 1H, H-5X), 5.95-5.90 (m, 3H, H-5N, H-6N and H-6X), 4.20-4.03 (m, 2H, H-10N and H-10X), 2.95 (br s, 1H, H-1N), 2.81 (br s, 3H, H-1X, H-4N and H-4X), 1.79-1.65 (m, 4H, H-3xN, H-3xX, H-9aN and H-9aX), 1.46-0.97 (m, 27H, H-2N, H-3nN, H-3nX, H-7N, H-7X, H-9bN, H-9bX, H-11N, H-11X, H-12N, H-12X, H-13N and H-13X), 0.57-0.50 (m, 1H, H-2X).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 137.4 (2CH, C-5X), 135.2 (2CH, C-5N), 134.4 (CH, C-6N), 134.3 (CH, C-6N), 134.1 (2CH, C-6X), 70.1 (2C, C-8X), 70.0 (2C, C-8N), 64.4 (CH, C-10X), 64.3 (CH, C-10X), 64.2 (CH, C-10N), 64.1 (CH, C-10N), 50.3 (CH, C-7N), 50.2 (CH, C-7N), 46.9 (2CH, C-7X), 45.9 ($4CH_2$, C-9N and C-9X), 44.5 (CH, C-1N), 44.3 (2CH, C-1N and C-1X), 44.2 (CH, C-1X), 42.4 (2CH, C-4N), 42.1 (2CH, C-4X), 31.2 ($4CH_3$, C-13)*, 27.9 ($4CH_3$, C-11)*, 27.5 (CH_2, C-3X), 27.4 (CH_2, C-3X), 27.3 (CH_2, C-3N), 27.2 (CH_2, C-3N), 23.1 ($4CH_3$, C-12), C-2 signals missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 29.9.

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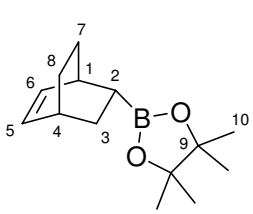
dienes followed by hydrolysis and esterification with pinacol: Noiret, N.; Youssofi, A.; Carboni, B., Vaultier, M. *J. Chem. Soc., Chem. Commun.* **1992**, *16*, 1105-1107.

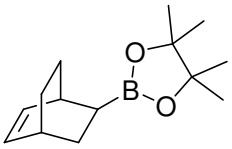
3. Boronates **3c** have been previously synthezised by Diels-Alder reaction of vinylboronate **1c** and diene **2a** with conventional heating: Woods, W. G.; Bengelsdorf, I. S. *J. Org. Chem.* **1966**, *31*, 2769-2772.

HRMS calcd for $C_{13}H_{22}BO_2$ $(M+H)^+$: 221.1713, found: 221.1710.

2-Bicyclo[2.2.2]oct-5-en-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3e)



3e-N



3e-X

Boronate **3e** was obtained as a mixture of diastereomers according to the general procedure A, using vinylboronate **1b** (0.475 mmol) and diene **2b** (1.5 mmol). To avoid polymerization, the diene was added in portions (3 x 0.5 mmol, one portion per run, three first runs).

Reaction conditions: 4 h at 220 ºC (4 x 1h).

Yield: 93% (104 mg), *endo/exo* 75:25.

IR (film) ν_{max}: 3040, 2977, 2936, 2864, 1467, 1375, 1312, 1235, 1146, 969, 861, 687.

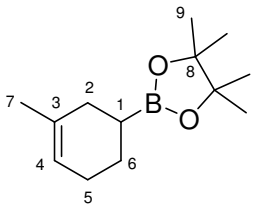
^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.30 (ddd, $J_{5,6}$ = 7.4, $J_{1,6}$ = 7.4, $J_{4,6}$ = 1.1 Hz, 1H, H-6X), 6.21-6.09 (m, 3H, H-5N, H-5X and H-6N), 2.63-2.55 (m, 1H, H-1N), 2.54-2.48 (m, 1H, H-1X), 2.48-2.39 (m, 2H, H-4N and H-4X), 1.66-1.00 (m, 37H, H-2N, H-3N, H-3X, H-7N, H-7X, H-8N, H-8X, H-10N and H-10X), 0.90-0.80 (m, 1H, H-2X).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 136.2 (CH, C-6X), 134.7 (CH, C-6N), 133.7 (CH, C-5N), 133.0 (CH, C-5X), 82.8 (2C, C-9X), 82.7 (2C, C-9N), 31.3 (CH, C-1N), 30.8 (CH, C-1X), 29.7 (CH, C-4N), 29.6 (CH, C-4X), 28.3 (CH_2, C-3N), 27.6 (CH_2, C-3X), 27.5 (CH_2, C-7N), 25.7 (CH_2, C-8X), 25.3 (CH_2, C-8N), 24.7 ($4CH_3$, C-10X), 24.6 ($2CH_3$, C-10N), 24.5 ($2CH_3$, C-10N), 23.9 (CH_2, C-7X), C-2 signals missing.

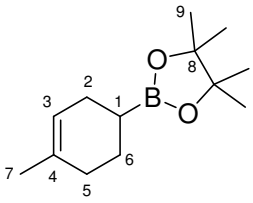
^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.7.

HRMS calcd for $C_{14}H_{24}BO_2$ $(M+H)^+$: 235.1864, found: 235.1855.

4,4,5,5-Tetramethyl-2-(3-methyl-cyclohex-3-enyl)-[1,3,2]dioxaborolane (3f-M) and 4,4,5,5-tetramethyl-2-(4-methyl-cyclohex-3-enyl)-[1,3,2]dioxaborolane (3f-P)[2]



3f-M



3f-P

Boronate **3f** was obtained as a mixture of regioisomers according to the general procedure A, using vinylboronate **1b** (0.5 mmol) and diene **2c** (1.5 mmol).

Reaction conditions: 3 h at 220 ºC.

Yield: 92% (102 mg), meta/para 33:67.

IR (film) ν_{max}: 2978, 2915, 2834, 1672, 1452, 1413, 1386, 1317, 1229, 1146, 1109, 971, 908, 856, 806, 670, 635, 579.

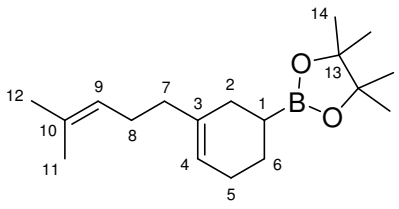
^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.45-5.32 (m, 2H, H-3P and H-4M), 2.12-1.84 (m, 8H, H-2P, H-2M, H-5P and H-5M), 1.84-1.66 (m, 2H, H-6aP and H-6aM), 1.61 (br s, 6H, H-7P and H-7M), 1.57-1.31 (m, 2H, H-6bP and H-6bM), 1.30-1.02 (m, 2H, H-1P and H-1M), 1.22 (br s, 12H, H-9M), 1.21 (br s, 12H, H-9P).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 134.3 (C, C-3M), 133.7 (C, C-4P), 121.3 (CH, C-3P), 120.8 (CH, C-4M), 82.7 (4C, C-8P and C-8M), 31.0 (CH_2, C-5M), 30.0 (CH_2, C-5P), 26.4 (CH_2, C-2P), 25.5 (CH_2, C-2M), 24.6 ($8CH_3$, C-9P and C-9M), 24.2 (CH_2, C-6P), 23.8 ($2CH_3$, C-7P and C-7M), 23.6 (CH_2, C-6M), C-1 signals missing.

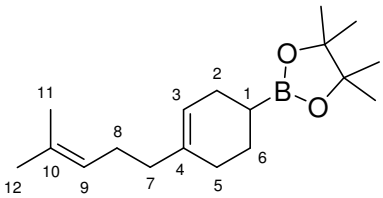
^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.9.

HRMS calcd for $C_{13}H_{24}BO_2$ $(M+H)^+$: 223.1864, found: 223.1866.

4,4,5,5-Tetramethyl-2-[3-(4-methyl-pent-3-enyl)-cyclohex-3-enyl]-[1,3,2]dioxaborolane (3g-M) and 4,4,5,5-tetramethyl-2-[4-(4-methyl-pent-3-enyl)-cyclohex-3-enyl]-[1,3,2]dioxaborolane (3g-P)



3g-M



3g-P

Boronate **3g** was obtained as a mixture of regioisomers according to the general procedure A, using vinylboronate **1b** (0.59 mmol) and diene **2d** (2 mmol).

Reaction conditions: 2 h at 220 ºC (2 x 1h).

Yield: 94% (152.8 mg), meta/para 35:65.

IR (film) ν_{max}: 2977, 2916, 2856, 1452, 1386, 1315, 1229, 1145, 971, 855.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.39-5.33 (br s, 1H, H-3P), 5.33-5.28 (br s, 1H, H-4M), 5.10-4.97 (m, 2H, H-9M and H-9P), 2.08-1.79 (m, 16H, H-2M, H-2P, H-5M, H-5P, H-7M, H-7P, H-8M and H-8P), 1.78-1.67 (m, 2H, H-6aM and H-6aP), 1.60 (s, 6H, H-12M and H-12P), 1.52 (s, 6H, H-11M and H-11P), 1.50-1.29 (m, 2H, H-6bM and H-6bP), 1.16 (s, 24H, H-14M and H-14P), 1.11-0.99 (m, 2H, H-1M and H-1P).

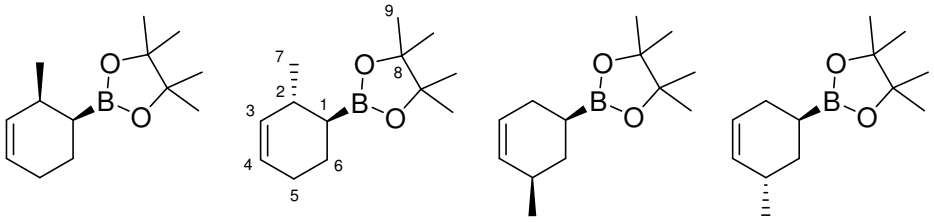
^{13}C NMR (75 MHz; $CDCl_3$) δ: 138.0 (C, C-3M), 137.3 (C, C-4P), 131.0 (C, C-10P), 130.9 (C, C-10M), 124.5 (2CH, C-9M and C-9P), 121.0 (CH, C-3P), 120.5 (CH, C-4M), 82.7 (4C, C13M and C-13P), 38.0 ($2CH_2$, C-7M and C-7P), 29.4 (CH_2, C-

2M), 28.3 (CH_2, C-2P), 26.5 (CH_2, C-8M), 26.4 ($3CH_2$, C-8P, C-5P, C-5M), 25.6 (CH_3, C-12P), 25.4 (CH_3, C-12M), 24.6 ($8CH_3$, C14M and C-14P), 24.2 (CH_2, C-6P), 23.8 (CH_2, C-6M), 17.5 ($2CH_3$, C11M and C-11P), C-1 signals missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.8.

HRMS calcd for $C_{18}H_{32}BO_2$ $(M+H)^+$: 291.2490, found: 291.2498.

4,4,5,5-Tetramethyl-2-(2-methyl-cyclohex-3-enyl)-[1,3,2]dioxaborolane (3h-O) and 4,4,5,5-tetramethyl-2-(5-methyl-cyclohex-3-enyl)-[1,3,2]dioxaborolane (3h-M)



3h-ON **3h-OX** **3h-MN** **3h-MX**

Boronate **3h** was obtained as a mixture of isomers according to the general procedure A, using vinylboronate **1b** (0.6 mmol) and diene **2e** (2.4 mmol).

Reaction conditions: 4 h at 220 ºC.

Yield: 83% (110 mg), *endo*/*exo* 39:61, ortho/meta 54:46.

IR (film) ν_{max}: 2977, 2955, 2929, 2871, 1649, 1457, 1379, 1314, 1272, 1214, 1145, 971, 858, 695, 675, 579.

HRMS calcd for $C_{13}H_{24}BO_2$ $(M+H)^+$: 223.1864, found: 223.1869.

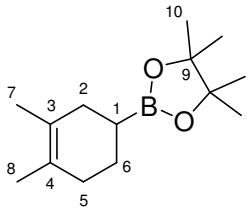
Boronate 3h-OX (major compound)

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.71-5.45 (m, 2H, H-3 and H-4), 2.31-2.12 (m, 1H, H-2), 2.07-1.85 (m, 2H, H-5), 1.83-1.41 (m, 2H, H-6), 1.24 (br s, 12H, H-9), 0.97 (d, 3H, $J_{2,7}$ = 7.1 Hz, H-7), 0.80 (ddd, 1H, $J_{1,2}$ = 12.1, $J_{1,6a}$ = 9.7 and $J_{1,6b}$ = 2.6 Hz, H-1).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 134.1 (CH, C-3), 125.9 (CH, C-4), 82.9 (2C, C-8), 31.4 (CH, C-2), 25.2 (CH_2, C-5), 24.6 ($4CH_3$, C-9), 23.6 (CH_2, C-6), 22.1 (CH_3, C-7), C-1 signal missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.5.

2-(3,4-Dimethyl-cyclohex-3-enyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3i)[2]



3i

Boronate **3i** was obtained according to the general procedure A, using vinylboronate **1b** (0.5 mmol) and diene **2f** (1.5 mmol).

Reaction conditions: 3 h at 200 ºC (3 x 1h).

Yield: 98% (115 mg).

IR (film) ν_{max} : 2978, 2914, 2829, 1450, 1413, 1387, 1313, 1232, 1147, 970, 853, 753, 669, 579.

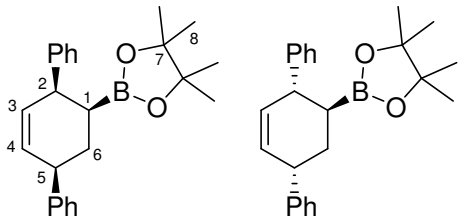
^{1}H NMR (300 MHz; $CDCl_3$) δ: 2.06-1.82 (m, 4H, H-2 and H-5), 1.81-1.68 (m, 1H, H-6a), 1.58 (br s, 6H, H-7 and H-8), 1.52-1.35 (m, 1H, H-6b), 1.28-1.05 (m, 1H, H-1), 1.22 (br s, 12H, H-10).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 125.9 (C, C-3), 125.2 (C, C-4), 82.7 (2C, C-9), 32.7 (CH_2, C-2), 31.9 (CH_2, C-5), 24.7 (CH_2, C-6), 24.6 ($4CH_3$, C-10), 19.0 (CH_3, C-7), 18.9 (CH_3, C-8), C-1 signal missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.9.

HRMS calcd for $C_{14}H_{26}BO_2$ $(M+H)^+$: 237.2020, found: 237.2026.

2-(2,5-Diphenyl-cyclohex-3-enyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3j)



3j-N **3j-X**

Boronate **3j** was obtained as a mixture of diastereomers according to the general procedure A, using vinylboronate **1b** (0.475 mmol) and diene **2g** (1.5 mmol).

Reaction conditions: 6 h at 220 ºC (6 x 1h).

Yield: 92% (157.6 mg), *endo/exo* 45:55.

IR (film) ν_{max}: 3025, 2977, 2865, 1601, 1493, 1451, 1378, 1320, 1143, 968, 855, 754, 699.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 7.45-7.12 (m, 20H, ArN and ArX), 6.01-5.84 (m, 4H, H-3N, H-3X, H-4N and H-4X), 3.73-3.65 (m, 1H, H-2N), 3.63-3.56 (m, 1H, H-2X), 3.56-3.48 (m, 1H, H-5X), 3.46-3.36 (m, 1H, H-5N), 2.11 (ddd, $J_{6anti\text{-}6syn}$ =

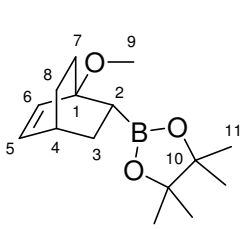
13.1, $J_{1\text{-}6anti}$ = 10.5, $J_{5\text{-}6anti}$ = 6.0 Hz, 1H, H-6_{anti}X), 1.99-1.90 (m, 1H, H-6_{syn}N), 1.84-1.70 (m, 3H, H-1N, H-6_{anti}N and H-6_{syn}X), 1.42-1.32 (m, 1H, H-1X), 1.14 (s, 6H, H-8X), 1.10 (s, 6H, H-8X), 1.04 (s, 6H, H-8N), 0.90 (s, 6H, H-8N).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 146.4 (C, Ar), 146.0 (C, Ar), 145.5 (C, Ar), 143.6 (C, Ar), 132.4 (CH, C3X), 131.2 (CH, C4N), 131.0 (CH, C-3N), 129.6 (CH x 2, Ar), 129.4 (CH, C4X), 128.3 (2CH, Ar), 128.1 (4CH, Ar), 128.0 (4CH, Ar), 127.7 (2CH, Ar), 127.3 (2CH, Ar), 126.2 (CH, Ar), 125.9 (3CH, Ar), 82.9 (2C, C-7N), 82.8 (2C, C-7X), 43.0 (CH, C-5N), 42.8 (CH, C-2X), 40.9 (CH, C-2N), 39.5 (CH, C-5X), 31.2 (CH_2, C-6X), 29.5 (CH_2, C-6N), 24.9 ($2CH_3$, C-8N), 24.5 ($2CH_3$, C-8X), 24.5 ($2CH_3$, C-8X), 24.4 ($2CH_3$, C-8N), C-1 signals missing.

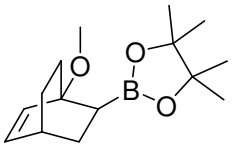
^{11}B NMR (96 MHz; $CDCl_3$) δ: 32.8.

HRMS calcd for $C_{24}H_{30}BO_2$ $(M+H)^+$: 361.2333, found: 361.2343.

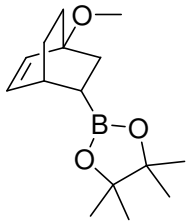
2-(1-Methoxy-bicyclo[2.2.2]oct-5-en-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3k-O) and 2-(4-methoxy-bicyclo[2.2.2]oct-5-en-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3k-M)



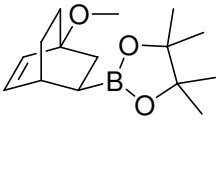
3k-ON



3k-OX



3k-MN



3k-MX

Boronate **3k** was obtained as a mixture of isomers according to the general procedure A, using vinylboronate **1b** (0.56 mmol) and diene **2h** (1.76 mmol).

Reaction conditions: 4 h at 220 ºC.

Yield: 87% (129.1 mg), *ortho/meta* >80:20, ortho *endo*/ortho *exo* 44:56.

IR (film) ν_{max}: 3046, 2940, 2827, 1470, 1373, 1321, 1219, 1147, 862, 678.

HRMS calcd for $C_{15}H_{26}BO_3$ $(M+H)^+$: 265.1975, found: 265.1966.

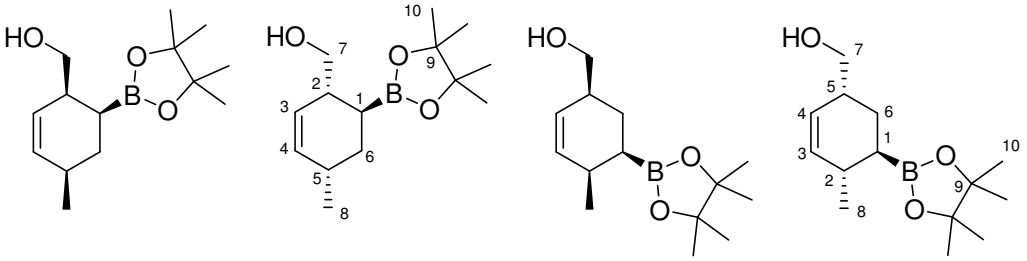
Boronates 3k-ON and 3k-OX (major compounds)

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.46 (d, $J_{5\text{-}6}$ = 8.8 Hz, 1H, H-6OX), 6.30-6.10 (m, 3H, H-5ON, H-5OX and H-6ON), 3.38 (s, 3H, H-9OX), 3.33 (s, 3H, H-9ON), 2.51-2.43 (m, 2H, H-4ON and H-4OX), 2.02-1.29 (m, 14H, H-2ON, H-2OX, H-3ON, H-3OX, H-7ON, H-7OX, H-8ON and H-8OX), 1.25 (s, 12H, H-11OX), 1.20 (s, 12H, H-11ON).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 136.5 (CH, C-6OX), 134.7 (CH, C-6ON), 131.9 (CH, C-5ON), 131.5 (CH, C-5OX), 82.8 (2C, C-10OX), 82.6 (2C, C-10ON), 79.4 (2C, C-1ON and C-1OX), 51.0 (CH_3, C-9OX), 50.4 (CH_3, C-9ON), 30.4 (CH_2, C-3ON), 30.3 (CH_2, C-7ON), 29.8 (CH, C-4OX), 29.6 (CH, C-4ON), 28.7 (CH_2, C-3OX), 27.8 (CH_2, C-7OX), 26.4 (CH_2, C-8OX), 24.8 (CH_2, C-8ON), 24.7 ($2CH_3$, C-11OX), 24.5 ($6CH_3$, C-11ON and C-11OX), C-2 signals missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 33.1.

[4-Methyl-6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-cyclohex-2-enyl]-methanol (3l-O) and [4-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-cyclohex-2-enyl]-methanol (3l-M)



3l-ON **3l-OX** **3l-MN** **3l-MX**

Boronate **3l** was obtained as a mixture of isomers according to the general procedure A, using vinylboronate **1b** (0.53 mmol) and diene **2i** (0.84 mmol).

Reaction conditions: 3 h at 220 ºC.

Yield: 75% (100.6 mg), *endo/exo* 12:88, ortho *exo/*meta *exo* 47:53.

IR (film) ν_{max}: 3436, 2926, 2869, 1455, 1380, 1317, 1145, 1028, 853, 726.

HRMS calcd for $C_{14}H_{26}BO_3$ $(M+H)^+$: 253.1970, found: 253.1975.

Boronates 3l-OX and 3l-MX (major compounds)

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.74-5.64 (m, 2H, H-4OX and H-3MX), 5.59-5.47 (m, 2H, H-3OX and H-4MX), 3.62-3.38 (m, 4H, H-7OX and H-7MX), 2.46-2.33 (m, 1H, H-2OX), 2.33-2.16 (m, 3H, H-2MX, H-5OX and H-5MX), 2.07 (br s, 2H, OH OX and MX), 1.80-1.60 (m, 3H, H-6aOX and H-6MX), 1.51-1.42 (m, 1H, H-6bOX), 1.24 (br s, 24H, H-10OX and H-10MX), 1.20-1.10 (m, 1H, H-1OX), 0.98 (d, $J_{5\text{-}8MX}$ = 7.8 Hz, 3H, H-8MX), 0.98 (d, $J_{2\text{-}8OX}$ = 7.8 Hz, 3H, H-8OX), 0.94-0.84 (m, 1H, H-1MX).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 136.4 (CH, C-3MX), 134.9 (CH, C-4OX), 126.9 (CH, C-3OX), 125.9 (CH, C-4MX), 83.0 (C, C-9OX), 82.9 (C, C-9MX), 67.5 (CH_2, C-7OX), 65.8 (CH_2, C-7MX), 39.6 (CH, C-2OX), 36.5 (CH, C-5MX), 31.2 (CH, C-2MX), 29.6 (CH_2, C-6OX), 28.6 (CH, C-5OX), 24.6 ($4CH_3$, C-10OX and C-10MX), 24.5 ($4CH_3$, C-10OX and C-10MX), 24.4 (CH_2, C-6MX), 21.7 (CH_3, C-8MX), 20.9 (CH_3, C-8OX) , C-1 signals missing.

^{11}B NMR (96 MHz; $CDCl_3$) δ: 34.0.

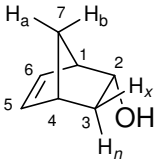
Tandem microwave-assisted Diels-Alder reaction of vinylboronates - oxidation: synthesis of alcohols[4]

General procedure B: To an oven-dried 10 mL pressure-rated reaction vial equipped with a stirring bar were added dry toluene (0.5 mL), vinylboronate **1** (typically 0.5 mmol) and diene **2** (1.5-7.5 mmol) under argon atmosphere. The resulting reaction mixture was stirred at the temperature reported (150-220 ºC) in the microwave until complete conversion (1-6 h).

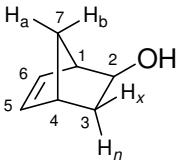
4. Alcohols **4a** - **4f** have been previously synthezised by other methods, including the Diels-Alder reactions of vinylboranes and the corresponding dienes followed by oxidation: (a) Singleton, D. A.; Martinez, J. P.; Watson, J. V.; Ndip, G. M. *Tetrahedron* **1992**, *48*, 5831-5838. (b) Singleton, D. A.; Martinez, J. P.; Ndip, G. M. *J. Org. Chem.* **1992**, *57*, 5768-5771. (c) Zaidlewicz, M.; Binkul, J. R.; Sokól, W. *J. Organomet. Chem.* **1999**, *580*, 354-362.

Once the microwave-assisted Diels-Alder reaction was completed, the reaction mixture was diluted with THF (3 mL), and transferred to a 25 mL round-bottom flask. After the addition of Et_3N (1 mL) the solution was cooled to 0 ºC and treated alternately with 3N NaOH (3 mL) and 30% H_2O_2 (3 mL) under argon atmosphere, and then allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with water (10 mL) and extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with saturated NH_4Cl (15 mL) and brine (15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure at 0 ºC, and the crude was purified by column chromatography (pentane/Et_2O) to afford the corresponding alcohol (**4a-h**).

Bicyclo[2.2.1]hept-5-en-2-ol (4a)[4]



4a-N



4a-X

Alcohol **4a** was obtained as a mixture of diastereomers according to the general procedure B, using:

a) vinylboronate **1a** (0.50 mmol) and diene **2a** (5.0 mmol) in dichloromethane.

Reaction conditions: 60 min at 150 ºC.

Yield: 91% (49.9 mg), *endo/exo* 41:59.

b) vinylboronate **1b** (0.48 mmol) and diene **2a** (1.44 mmol).

Reaction conditions: 60 min at 150 ºC (3 x 20 min).

Yield: 92% (48.3 mg), *endo/exo* 37:63.

c) vinylboronate **1c** (0.55 mmol) and diene **2a** (5.5 mmol).

Reaction conditions: 80 min at 150 ºC (4 x 20 min).

Yield: 86% (52.2 mg), *endo/exo* 44:56.

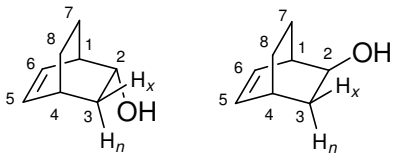
IR (film) ν_{max}: 3334, 3059, 2966, 2939, 2866, 1440, 1336, 1234, 1118, 1056, 987, 920, 752, 705.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.45 (dd, 1H, $J_{5,6}$= 5.7 and $J_{4,5}$= 3.1 Hz, H-5N), 6.17 (dd, 1H, $J_{5,6}$= 5.7 and $J_{5X,4X}$= 2.9 Hz, H-5X), 6.06 (dd, 1H, $J_{5,6}$= 5.7 and $J_{1,6}$= 2.9 Hz, H-6N), 5.95 (dd, 1H, $J_{5,6}$= 5.7 and $J_{1,6}$= 3.2 Hz, H-6X), 4.55-4.39 (m, 1H, H-2N), 3.90 (br d, 1H, $J_{2,3}$= 6.7 Hz, H-2X), 3.00 (br s, 1H, H-1N), 2.81 (br s, 2H, H-4N and H-4X), 2.71 (br s, 1H, H-1X), 2.10 (ddd, 1H, $J_{3n,3x}$= 12.1, $J_{3x,4}$ = 8.2 and $J_{2,3x}$ = 3.9 Hz, H-3$_x$N), 1.73 (br d, 1H, $J_{7a,7b}$= 8.5 Hz, H-7aX), 1.65 (ddd, 1H, $J_{3n,3x}$= 12.1, $J_{3n,4}$ = 6.7 and $J_{2,3n}$ = 2.6 Hz, H-3$_n$X), 1.69-1.52 (m, 1H, H-7bX), 1.51-1.44 (m, 1H, H-7aN), 1.32-1.21 (m, 2H, H-7bN and H-3$_x$X), 0.76 (ddd, 1H, $J_{3n,3x}$= 12.4, $J_{3n,4}$ = 3.2 and $J_{2,3n}$ = 3.1 Hz, H-3$_n$N).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 140.4 (CH, C-5N), 140.1 (CH, C-5X), 133.2 (CH, C-6X), 130.7 (CH, C-6N), 72.5 (CH, C-2X), 72.4 (CH, C-2N), 50.1 (CH, C-1X), 48.2 (CH_2, C-7N), 48.0 (CH, C-1N), 45.4 (CH_2, C-7X), 42.8 (CH, C-4N), 40.6 (CH, C-4X), 37.7 (CH_2, C-3N), 37.1 (CH_2, C-3X).

MS-EI *m/z* (%): 110 (5.42), 91 (2.09), 81 (1.82), 79 (5.03), 66 (100), 53 (2.25), 40 (4.07).

Bicyclo[2.2.2]oct-5-en-2-ol (4b)[4c]



4b-N **4b-X**

Alcohol **4b** was obtained as a mixture of diastereomers according to the general procedure B, using:

a) vinylboronate **1a** (0.50 mmol) and diene **2b** (7.5 mmol).

Reaction conditions: 1 h at 150 ºC and 3 h at 220 ºC.

Yield: 77% (47.7 mg), *endo/exo* 73:27.

b) vinylboronate **1b** (0.48 mmol) and diene **2b** (1.44 mmol).

Reaction conditions: 4 h at 220 ºC (4 x 1h).

Yield: 96% (56.5 mg), *endo/exo* 73:27.

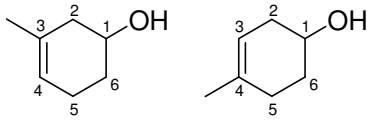
IR (film) ν_{max}: 3338, 3043, 2939, 2864, 1446, 1323, 1093, 1055, 1033, 906, 856, 731, 709, 696.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.45 (t, 1H, $J_{5,6}$= 7.1 Hz, H-5N), 6.25 (t, 1H, $J_{5,6}$= 7.2 Hz, H-5X), 6.17 (t, 1H, $J_{5,6}$= 7.1 Hz, H-6X), 6.12 (t, 1H, $J_{5,6}$= 7.2 Hz, H-6N), 3.93 (br d, 1H, $J_{2,3}$= 7.1 Hz, H-2N), 3.87-3.77 (m, 1H, H-2X), 2.78-2.68 (m, 1H, H-1N), 2.62-2.44 (m, 3H, H-1X, H-4N and H-4X), 2.11-1.90 (m, 2H, H-3$_x$N and H-7aX), 1.89-1.76 (m, 1H, H-3$_n$X), 1.70-1.56 (m, 1H, H-8aX), 1.56-1.04 (m, 10H, H-3$_n$N, H-3$_x$X, H-7N, H-7bX, H-8N, H-8bX, OH N and OH X).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 136.7 (CH, C-5N), 135.3 (CH, C-5X), 131.8 (CH, C-6X), 129.5 (CH, C-6N), 70.4 (CH, C-2N), 69.2 (CH, C-2X), 39.1 (CH_2, C-3N), 37.6 (2CH, C-1N and C-1X), 35.6 (CH_2, C-3X), 30.0 (CH, C-4N), 29.9 (CH, C-4X), 25.8 (CH_2, C-8X), 23.9 (CH_2, C-8N), 21.7 (CH_2, C-7N), 17.1 (CH_2, C-7X).

MS-EI *m/z* (%): 124 (1.63), 106 (0.52), 91 (2.04), 80 (100), 67 (2.06), 51 (3.13), 41(3.47).

3-Methyl-cyclohex-3-enol (4c-m) and 4-methyl-cyclohex-3-enol (4c-P)[4,5]



4c-M **4c-P**

Alcohol **4c** was obtained as a mixture of regioisomers according to the general procedure B, using vinylboronate **1b** (0.6 mmol) and diene **2c** (1.8 mmol).

Reaction conditions: 3 h at 220 ºC.

Yield: 99% (66.9 mg), meta/para 34:66.

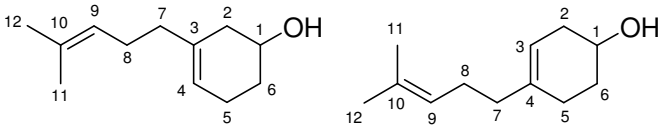
IR (film) ν_{max}: 3333, 2963, 2924, 2840, 1456, 1440, 1368, 1078, 1058, 1039, 1020, 915, 797.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.40-5.32 (m, 1H, H-4M), 5.30-5.21 (m, 1H, H-3P), 4.01-3.85 (m, 2H, H-1P and H-1M), 2.38-1.73 (m, 10H, H-2P, H-2M, H-5P, H-5M, H-6aP and H-6aM), 1.71-1.59 (m, 1H, H-6bP), 1.64 (br s, 6H, H-7P and H-7M), 1.58-1.47 (m, 1H, H-6bM).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 133.8 (C, C-4P), 131.2 (C, C-3M), 120.4 (CH, C-4M), 117.9 (CH, C-3P), 67.2 (CH, C-1M), 66.8 (CH, C-1P), 39.0 (CH_2, C-2M), 34.3 (CH_2, C-2P), 30.9 (CH_2, C-6P), 30.4 (CH_2, C-6M), 28.0 (CH_2, C-5P), 23.4 (CH_3, C-7M), 23.2 (CH_3, C-7P), 23.0 (CH_2, C-5M).

MS-EI *m/z* (%): 112 (7.95), 94 (72.17), 79 (61.4), 68 (100), 53 (23.23), 41 (18.98).

3-(4-Methyl-pent-3-enyl)-cyclohex-3-enol (4d-M) and 4-(4-methyl-pent-3-enyl)-cyclohex-3-enol (4d-P)[4a-b]



4d-M **4d-P**

Alcohol **4d** was obtained as a mixture of regioisomers according to the general procedure B, using vinylboronate **1b** (0.56 mmol) and diene **2d** (1.96 mmol).

Reaction conditions: 2 h at 220 ºC (2 x 1h).

Yield: 90% (90.9 mg), meta/para 33:67.

IR (film) ν_{max}: 3334, 2965, 2921, 2842, 1456, 1447, 1437, 1375, 1362, 1103, 1071, 1052, 827.

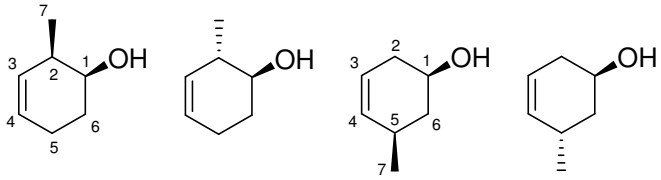
^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.38 (br s, 1 H, H-4M), 5.29 (br s, 1 H, H-3P), 5.14-5.05 (m, 2 H, H-9M and H-9P), 4.00-3.87 (m, 2 H, H-1P and H-1M), 2.40-1.57 (m, 32 H, H-2, H-5, H-6, H-7, H-8, H-11 and H-12).

5. (a) Friedrich, E. C.; De Lucca, G. *J. Org. Chem.* **1983**, *48*, 4563-4567. (b) Danheiser, R. L., Martinez-Davila, C., Sard, H. *Tetrahedron* **1981**, *37*, 3943-3950.

^{13}C NMR (75 MHz; $CDCl_3$) δ: 137.4 (C, C-4P), 134.8 (C, C-3M), 131.4 (2C, C-10P and C-10M), 124.0 (CH, C-9P), 124.0 (CH, C-9M), 120.0 (CH, C-4M), 117.5 (CH, C-3P), 67.3 (CH, C-1M), 66.9 (CH, C-1P), 37.2, 34.2, 30.9, 26.4, 26.3 (CH_2, C-2P, C-5P, C-6P, C-7P and C-8P), 37.4, 37.3, 30.5, 26.2, 23.1 (CH_2, C-2M, C-5M, C-6M, C-7M and C-8M), 25.5 ($2CH_3$, C-11P and C-11M)*, 17.5 ($2CH_3$, C-12P and C-12M)*.

MS-EI *m/z* (%): 180 (0.41), 162 (22.01), 147 (26.46), 119 (18.00), 93 (23.74), 79 (19.87), 69 (100).

2-Methyl-cyclohex-3-enol (4e-O) and 5-methyl-cyclohex-3-enol (4e-M)[4a,5b]



4e-ON **4e-OX** **4e-MN** **4e-MX**

Alcohol **4e** was obtained as a mixture of isomers according to the general procedure B, using vinylboronate **1b** (0.6 mmol) and diene **2e** (2.4 mmol).

Reaction conditions: 4 h at 220 ºC.

Yield: 68% (46 mg), *endo*/*exo* 39:61, ortho/meta 54:46.

IR (film) ν_{max}: 3334, 3023, 2955, 2905, 1457, 1339, 1073, 1058, 991, 923, 678.

MS-EI *m/z* (%): 112 (0.19), 94 (74.48), 91 (5.88), 79 (93.37), 68 (100), 53 (19.36), 41 (23.17).

Alcohols 4e-ON and 4e-OX (major compounds)

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.69-5.54 (m, 2H, H-4OX and H-4ON), 5.49-5.36 (m, 2H, H-3OX and H-3ON), 3.97-3.86 (m, 1H, H-1ON), 3.44 (ddd, 1H, $J_{1,6a}$= 10.0, $J_{1,2}$= 6.9 and $J_{1,6b}$= 3.3 Hz, H-1OX), 2.44-2.30 (m, 1H, H-2ON), 2.24-1.96 (m, 5H, H-2OX, H-5OX and H-5ON), 1.94-1.45 (m, 4H, H-6OX and H-6ON), 1.07 (d, 3H, $J_{2,7}$= 6.9 Hz, H-7OX), 1.02 (d, 3H, $J_{2,7}$= 7.3 Hz, H-7ON).

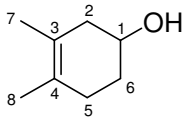
^{13}C NMR (75 MHz; $CDCl_3$) δ: 130.7 (CH, C-3OX), 130.2 (CH, C-3ON), 125.9 (CH, C-4ON), 125.6 (CH, C-4OX), 73.4 (CH, C-1OX), 69.0 (CH, C-1ON), 38.7 (CH, C-2OX), 34.8 (CH, C-2ON), 29.9 (CH_2, C-6OX), 27.6 (CH_2, C-6ON), 24.1 (CH_2, C-5OX), 22.0 (CH_2, C-5ON), 18.7 (CH_3, C-7OX), 15.5 (CH_3, C-7ON).

Alcohols 4e-MN, 4e-MX and 4e-OX

^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.69-5.37 (m, 6H, H-3MN, H-3MX, H-3OX, H-4MN, H-4MX and H-4OX), 4.15-4.00 (m, 1H, H-1MX), 3.98-3.81 (m, 1H, H-1MN), 3.44 (ddd, 1H, $J_{1,6a}$= 10.0, $J_{1,2}$= 6.9 and $J_{1,6b}$= 3.3 Hz, H-1OX), 2.52-2.24 (m, 4H, H-2aMN, H-2aMX, H-5MN and H-5MX), 2.24-1.75 (m, 8H, H-2bMN, H-2bMX, H-2OX, H-5OX, H-6aMN, H-6aMX and H-6aOX), 1.46 (dddd, 1H, $J_{6a,6b}$= 12.9, $J_{5,6b}$= 7.2, $J_{1,6}$= 2.7, $J_{2a,6b}$= 0.9 Hz, H-6bMX), 1.18 (dd, 1H, $J_{6a,6b}$= 22.6, $J_{1,6b}$= 11.6, H-6bMN), 1.07 (d, 3H, $J_{2,7}$= 6.9 Hz, H-7OX), 1.03 (d, 3H, $J_{5,7}$= 7.0 Hz, H-7MX), 1.01 (d, 3H, $J_{5,7}$= 7.0 Hz, H-7MN).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 133.1 (CH, C-4MN), 132.9 (CH, C-4MX), 130.7 (CH, C-3OX), 125.6 (CH, C-4OX), 123.1 (CH, C-3MN), 122.4 (CH, C-3MX), 73.4 (CH, C-1OX), 67.9 (CH, C-1MN), 64.8 (CH, C-1MX), 41.2 (CH_2, C-6MN), 38.8 (CH, C-2OX), 37.9 (CH_2, C-6MX), 34.6 (CH_2, C-2MN), 33.8 (CH_2, C-2MX), 31.2 (CH, C-5MN), 29.9 (CH_2, C-6OX), 27.2 (CH, C-5MX), 24.1 (CH_2, C-5OX), 21.4 ($2CH_3$, C-7MX and C-7MN), 18.7 (CH_3, C-7OX).

3,4-Dimethyl-cyclohex-3-enol (4f)[4b,6]



4f

Alcohol **4f** was obtained according to the general procedure B, using vinylboronate **1b** (0.5 mmol) and diene **2f** (1.5 mmol).

Reaction conditions: 3 h at 200 ºC (3 x 1h).

Yield: 92% (58 mg).

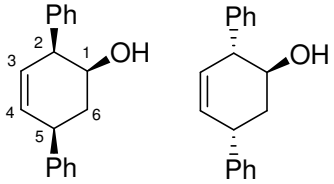
IR (film) ν_{max}: 3332, 2985, 2911, 2859, 2834, 1442, 1363, 1293, 1227, 1128, 1042, 947.

^{1}H NMR (300 MHz; $CDCl_3$) δ: 3.97-3.85 (m, 1H, H-1), 2.31-2.16 (m, 1H, H-2a), 2.10-1.88 (m, 3H, H-2b, H-5), 1.87-1.76 (m, 1H, H-6a), 1.70-1.49 (m, 1H, H-6b), 1.60 (br s, 6H, H-7 and H-8).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 125.3 (C, C-4), 122.7 (C, C-3), 67.5 (CH, C-1), 40.6 (CH_2, C-2), 31.4 (CH_2, C-6), 29.7 (CH_2, C-5), 19.1 (CH_3, C-7), 18.6 (CH_3, C-8).

MS-EI *m/z* (%): 126 (18.59), 108 (49.63), 93 (100), 82 (36.33), 77 (10.73), 67 (95.56), 41 (18.25).

2,5-Diphenyl-cyclohex-3-enol (4g)



4g-N **4g-X**

Alcohol **4g** was obtained as a mixture of diastereomers according to the general procedure B, using vinylboronate **1b** (0.475 mmol) and diene **2g** (1.5 mmol).

Reaction conditions: 6 h at 220 ºC (6 x 1h).

Yield: 92% (109.8 mg), *endo/exo* 47:53.

IR (film) ν_{max}: 3392, 3059, 3025, 2924, 2873, 1601, 1492, 1451, 1073, 746, 700.

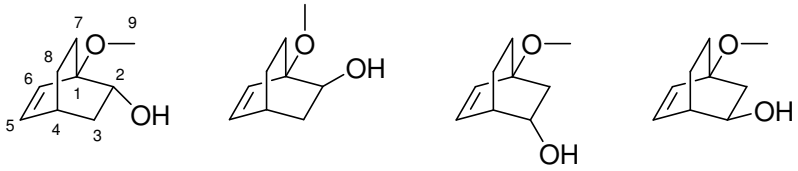
^{1}H NMR (300 MHz; $CDCl_3$) δ: 7.38-7.20 (m, 10H, ArN and ArX), 6.00-5.94 (m, 2H, H-4N and H-4X), 5.89-5.81 (m, 2H, H-3N and H-3X), 4.19-4.12 (m, 1H, H-1N), 3.82-3.73 (m, 3H, H-1X, H-2N and H-5X), 3.65-3.57 (m, 1H, H-5N), 3.39-3.34 (m, 1H, H-2X), 2.07 (ddd, $J_{1,6a}$ = 9.2, $J_{5,6a}$ = 6.2, $J_{6a,6b}$ = 13.0 Hz, 1H, H-6aX), 1.97-1.90 (m, 3H, H-6aN, H-6bX and OH), 1.52 (ddd, $J_{1,6a} = J_{5,6a} = J_{6a,6b}$ = 12.3 Hz, 1H, H-6bN).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 144.8 (C, Ar), 144.7 (C, Ar), 142.3 (C, Ar), 137.7 (C, Ar), 132.0 (CH, C-4N), 130.6 (2CH, Ar), 129.9 (CH, C-4X), 129.1 (CH, C-3X), 128.5 (CH, C-3N), 128.5 (3CH, Ar), 128.3 (4CH, Ar), 128.1 (2CH, Ar), 128.0 (CH, Ar), 127.8 (2CH, Ar), 127.1 (3CH, Ar), 126.7 (CH, Ar), 126.3 (CH, Ar), 126.2 (CH, Ar), 70.1 (CH, C-1X), 69.2 (CH, C-1N), 50.7 (CH, C-2X), 46.6 (CH, C-2N), 43.3 (CH, C-5N), 39.8 (CH, C-5X), 36.6 (CH_2, C-6X), 36.2 (CH_2, C-6N).

MS-EI *m/z* (%): 250 (1.32), 232 (26.62), 206 (100), 191 (18.02), 128 (25.68), 115 (17.90), 91 (52.07).

HRMS calcd for $C_{28}H_{22}NO$ $(M+NH_4)^+$: 268.1696, found: 268.1702.

1-Methoxy-bicyclo[2.2.2]oct-5-en-2-ol (4h-O) and 4-Methoxy-bicyclo[2.2.2]oct-5-en-2-ol (4h-M)



4h-ON **4h-OX** **4h-MN** **4h-MX**

Alcohol **4h** was obtained as a mixture of isomers according to the general procedure B, using vinylboronate **1b** (0.59 mmol) and diene **2h** (1.77 mmol).

Reaction conditions: 4 h at 220 ºC.

Yield: 51% (46.0 mg), ortho/meta > 95:5, ortho *endo*/ortho *exo* 49:51

IR (film) ν_{max}: 3459, 3047, 2942, 2868, 1666, 1464, 1372, 1180, 1100, 688.

MS-EI *m/z* (%): 154 (0.07), 136 (0.04), 126 (2.05), 110 (100), 95 (21.13), 79 (9.43), 67 (12.79).

HRMS calcd for $C_9H_{13}O_2$ $(M-H)^+$: 153.0916, found: 153.0908.

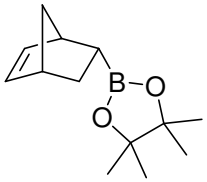
Alcohols 4h-ON and 4h-OX (major compounds)

^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.39-6.10 (m, 4H, H-5ON, H-5OX, H-6ON and H-6OX), 3.92 (br d, $J_{2,3n}$ = 8.7 Hz, 1H, H-2ON), 3.81-3.74 (m, 1H, H-2OX), 3.41 (s, 3H, H-9ON), 3.38 (s, 3H, H-9OX), 2.55-2.43 (m, 2H, H-4ON and H-4OX), 2.06-1.18 (m, 12H, H-3ON, H-3OX, H-7ON, H-7OX, H-8ON and H-8OX).

^{13}C NMR (75 MHz; $CDCl_3$) δ: 135.0 (CH, C-5OX), 134.1 (CH, C-5ON), 131.2 (CH, C-6OX), 130.1 (CH, C-6ON), 80.8 (C, C-1OX), 80.4 (C, C-1ON), 71.5 (CH, C-2ON), 69.9 (CH, C-2OX), 51.2 (CH_3, C-9OX), 50.7 (CH_3, C-9ON), 37.0 (CH_2, C-

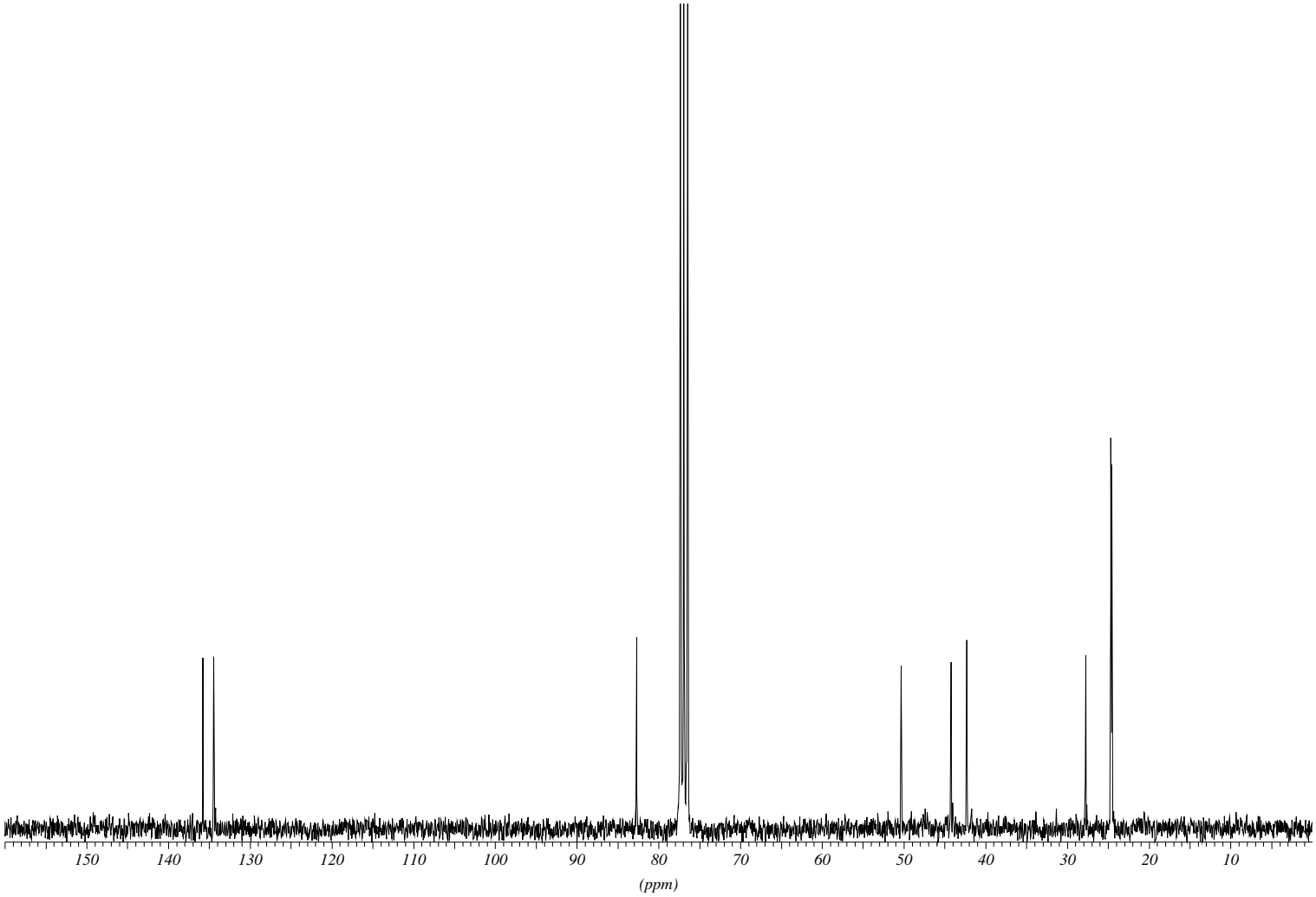
6. (a) Clarke, T. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96,* 7934-7944. (b) Lambert, J. B.; Marko, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 7978-7982.

3ON), 34.2 (CH_2, C-3OX), 29.6 (CH, C-4OX), 29.5 (CH, C-4ON), 25.7 (CH_2, C-8ON), 25.6 (CH_2, C-8OX), 24.0 (CH_2, C-7ON), 20.8 (CH_2, C-7OX).

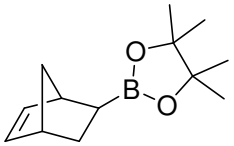


3b-N

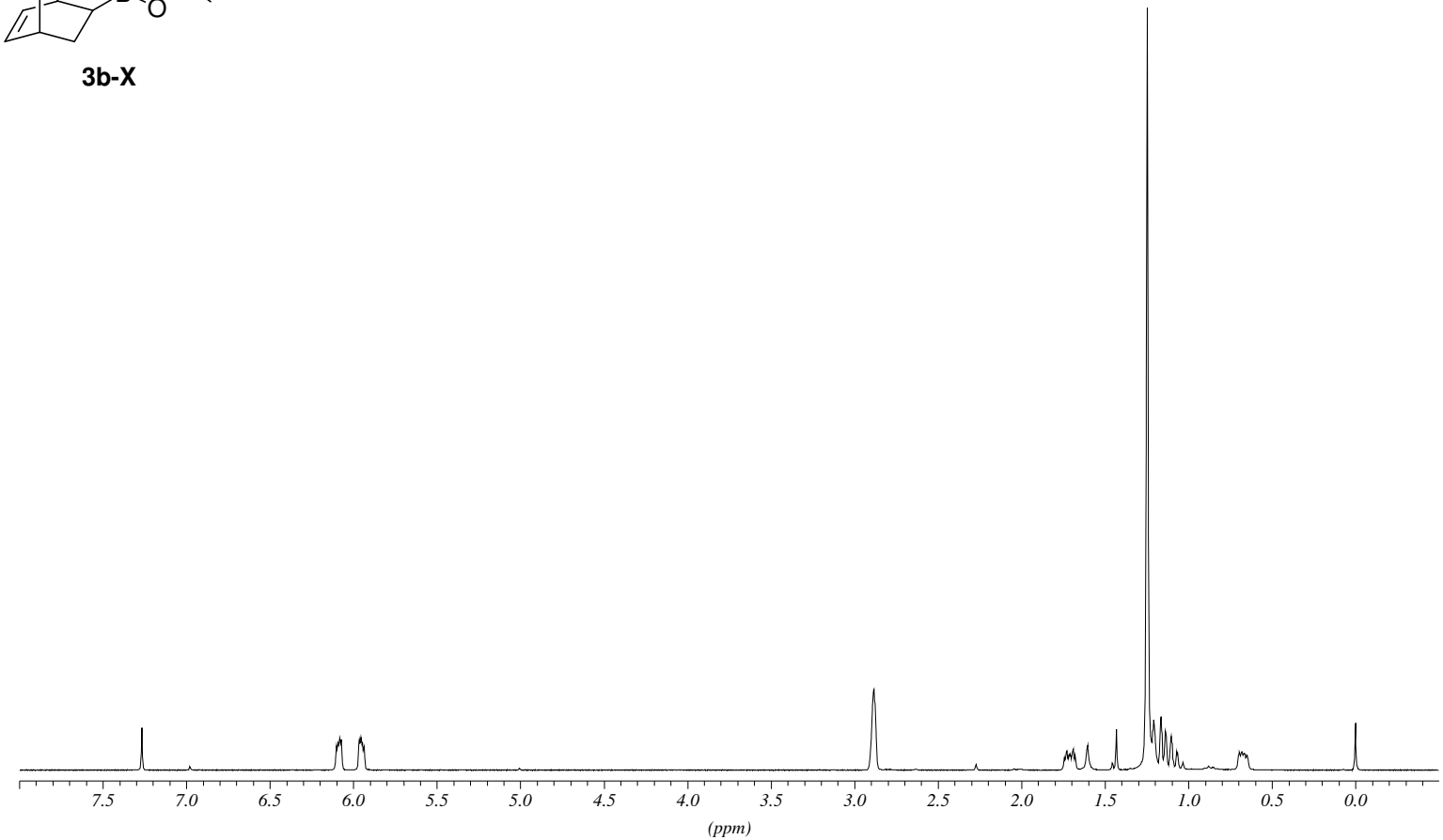
^{1}H NMR spectra of **3b-N** at 300 MHz in $CDCl_3$



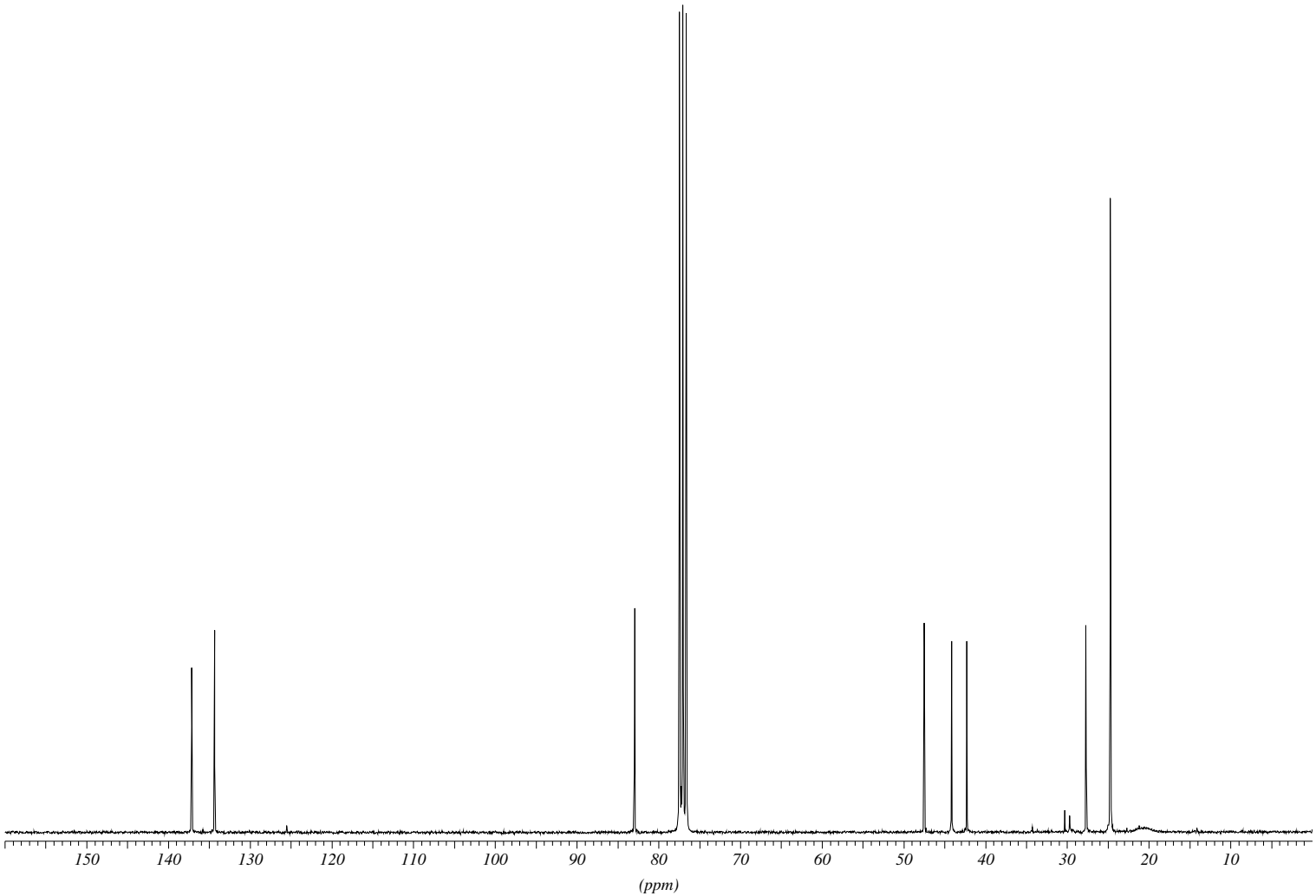
^{13}C NMR spectra of **3b-N** at 75 MHz in $CDCl_3$



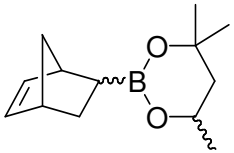
3b-X



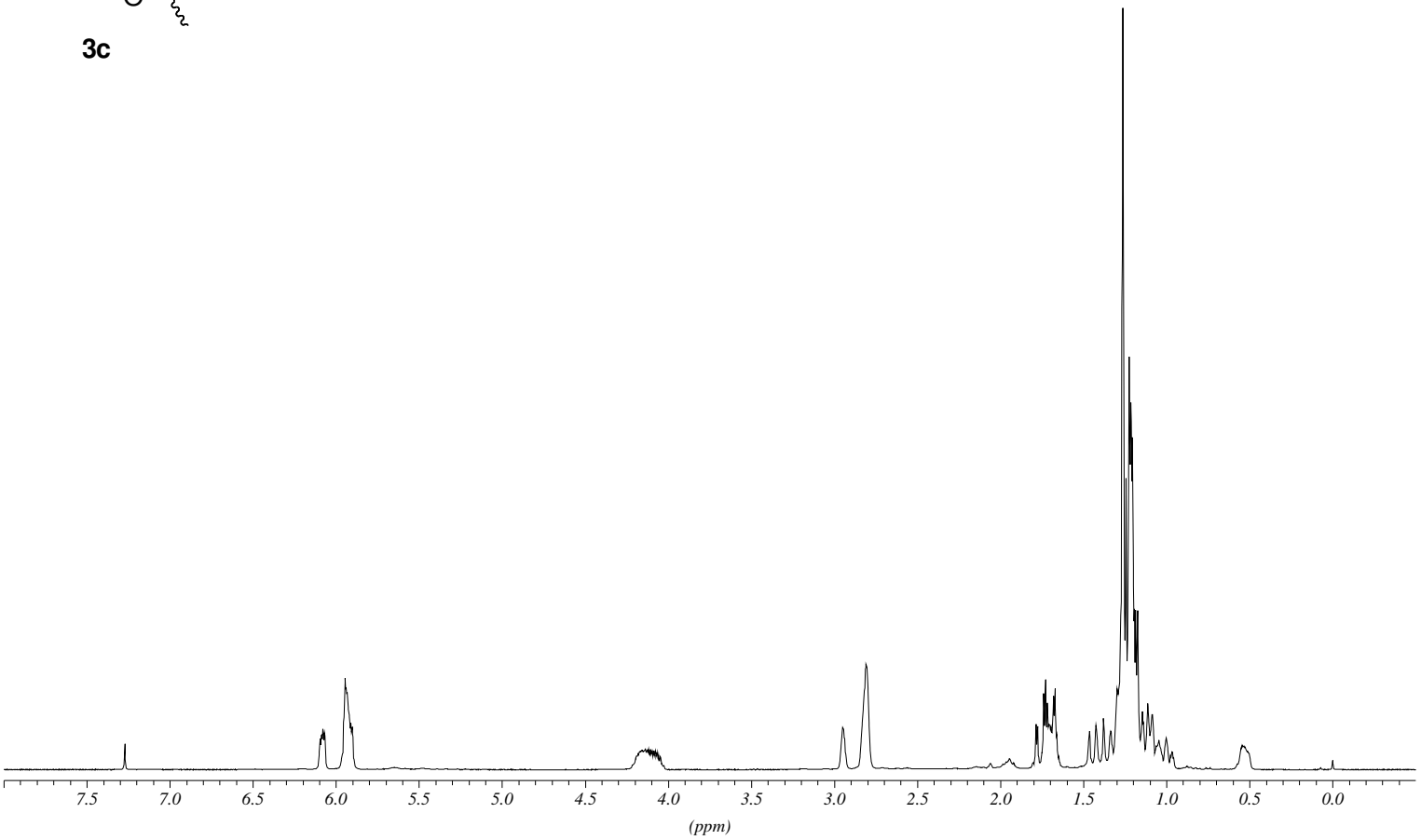
^{1}H NMR spectra of **3b-X** at 300 MHz in $CDCl_3$



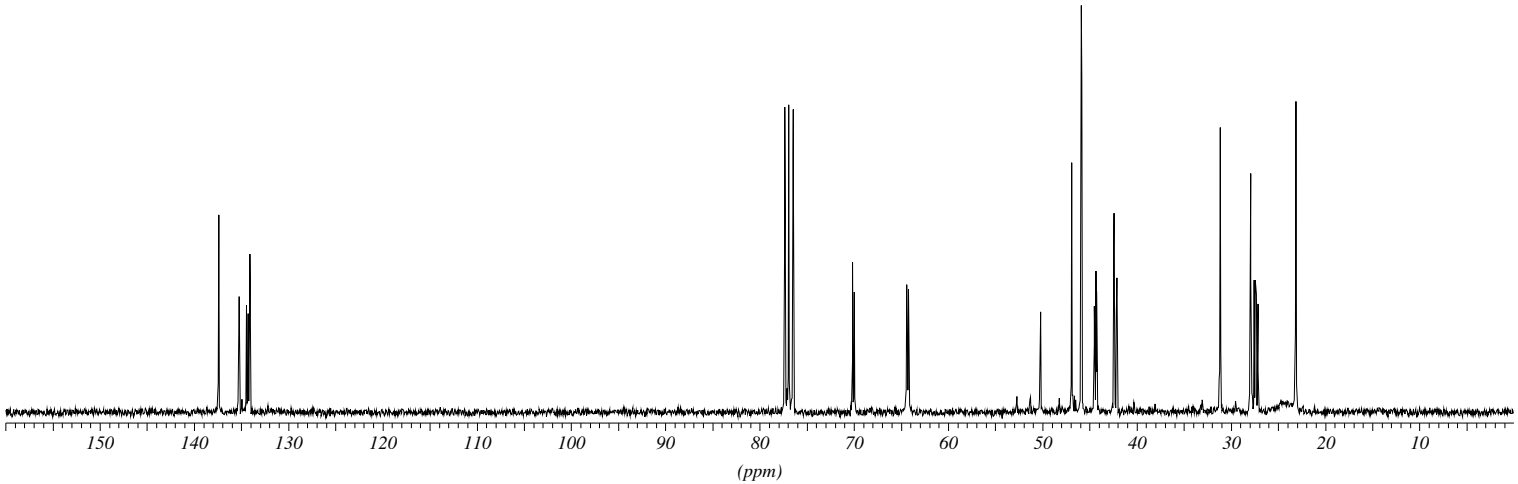
^{13}C NMR spectra of **3b-X** at 75 MHz in $CDCl_3$



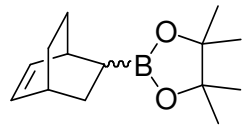
3c



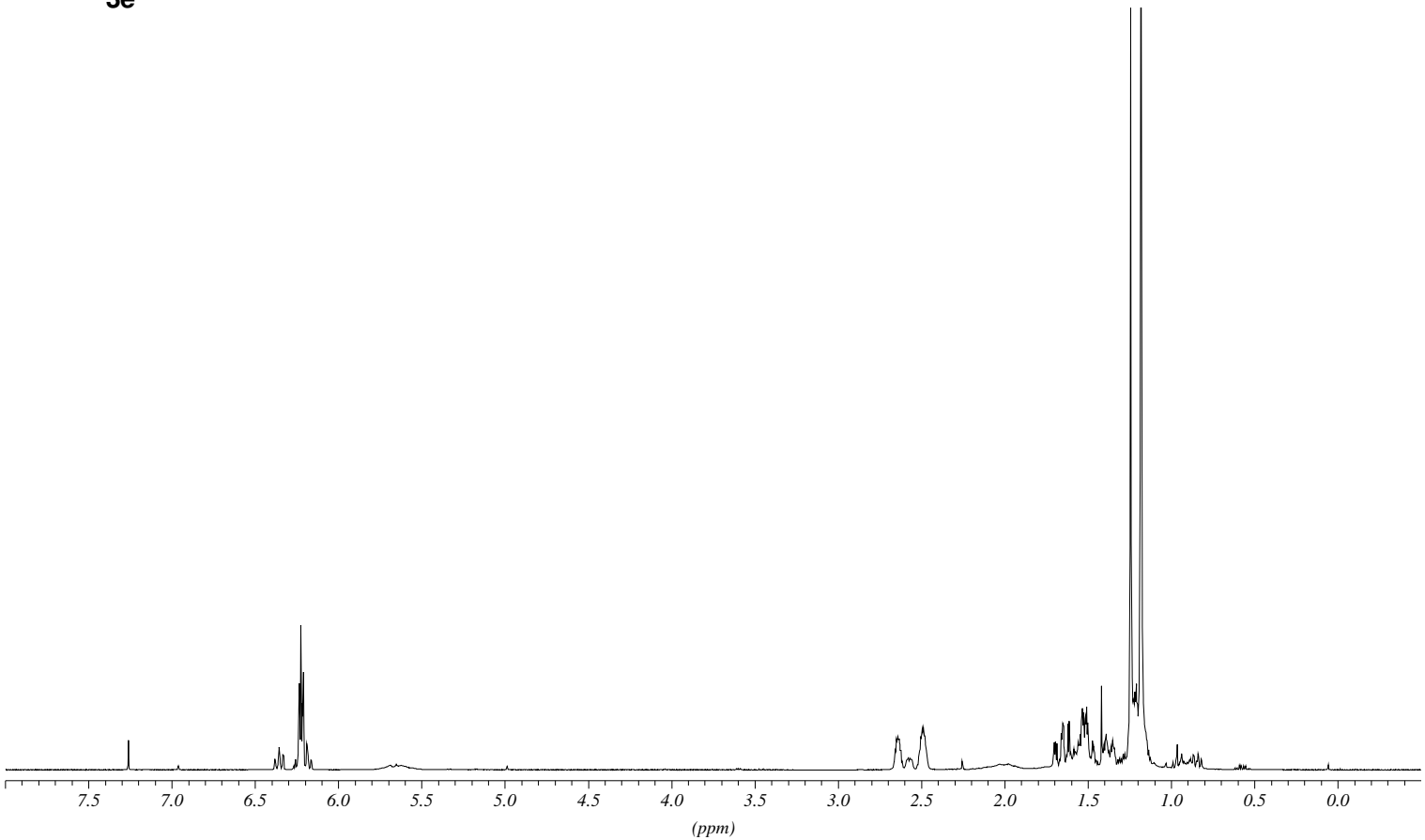
^{1}H NMR spectra of **3c** at 300 MHz in $CDCl_3$



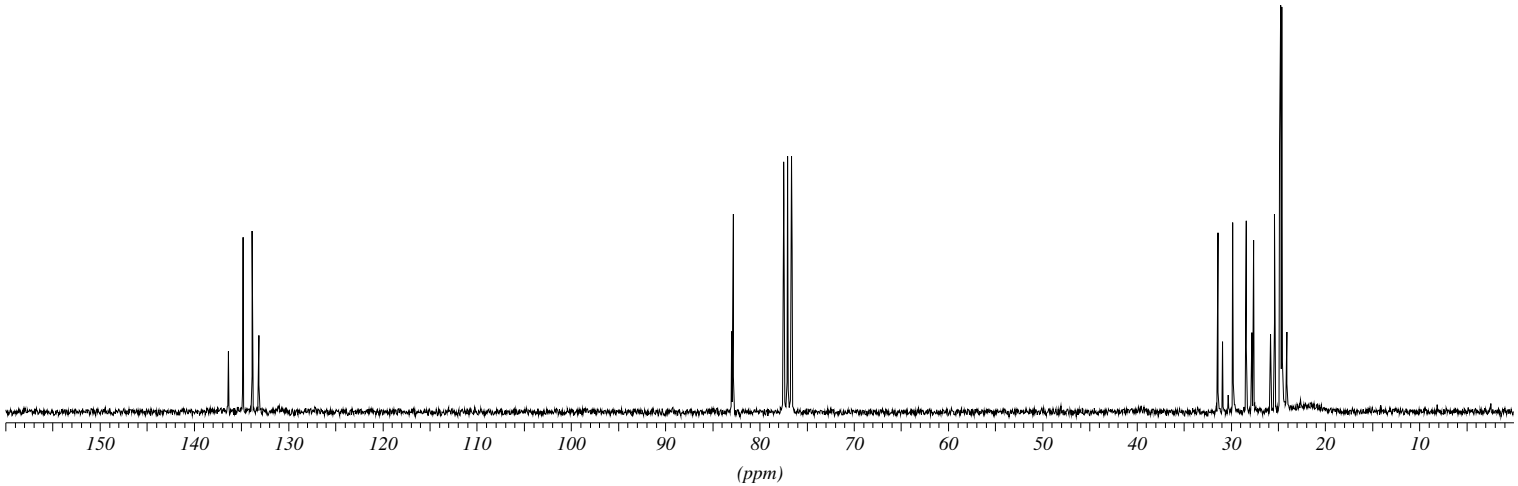
^{13}C NMR spectra of **3c** at 75 MHz in $CDCl_3$



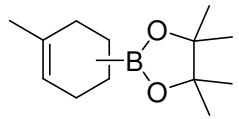
3e



^{1}H NMR spectra of **3e** at 300 MHz in $CDCl_3$

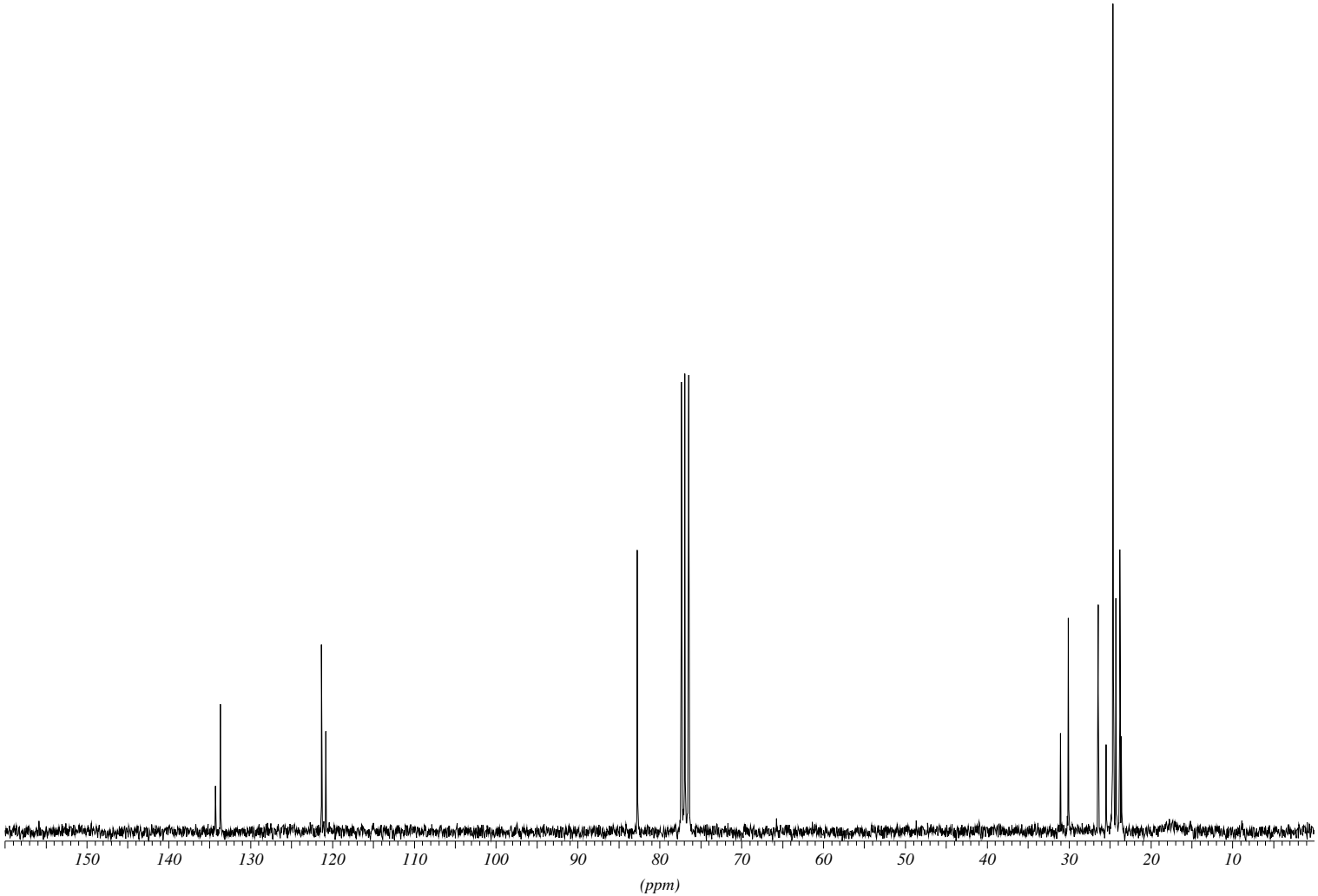


^{13}C NMR spectra of **3e** at 75 MHz in $CDCl_3$

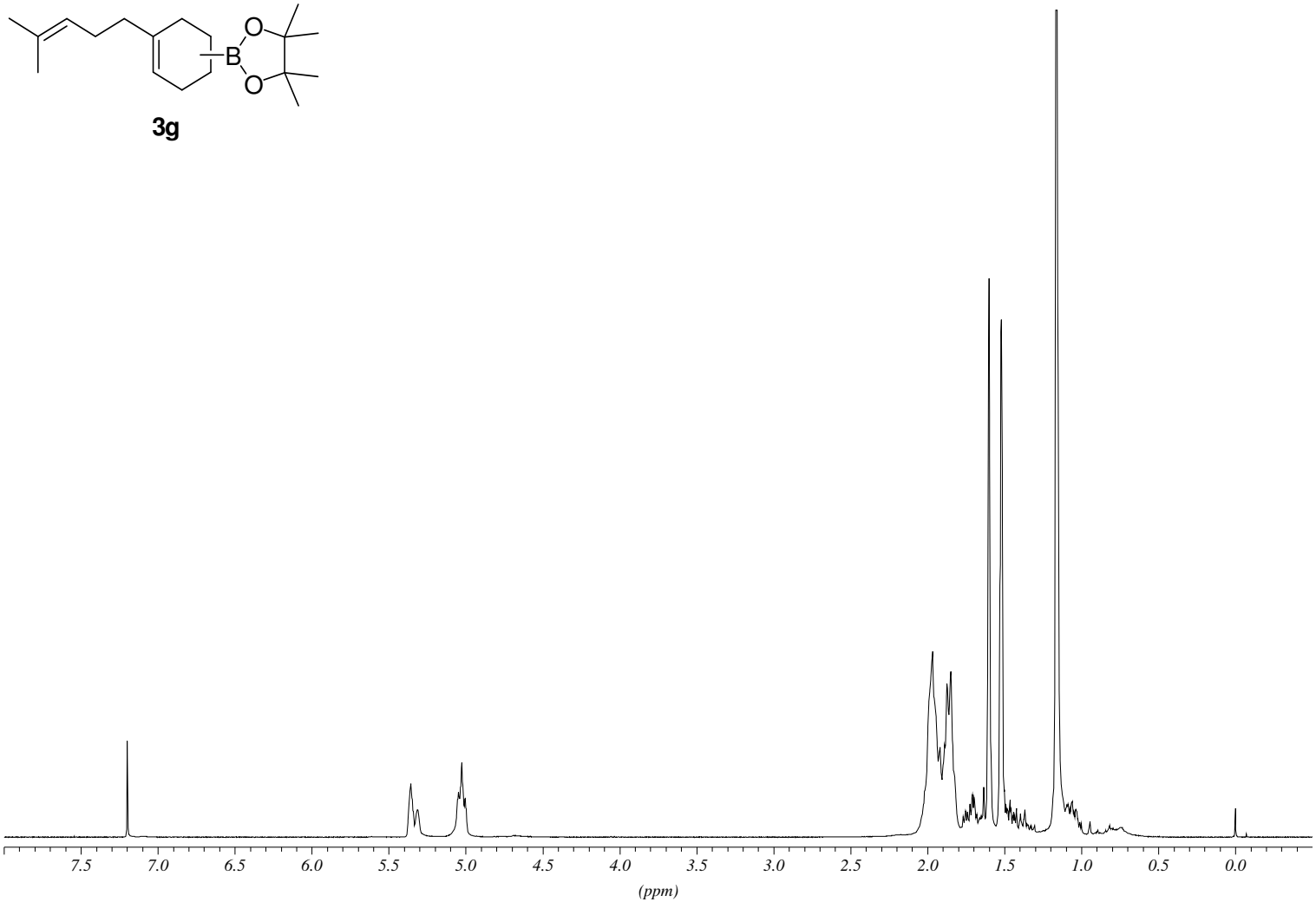


3f

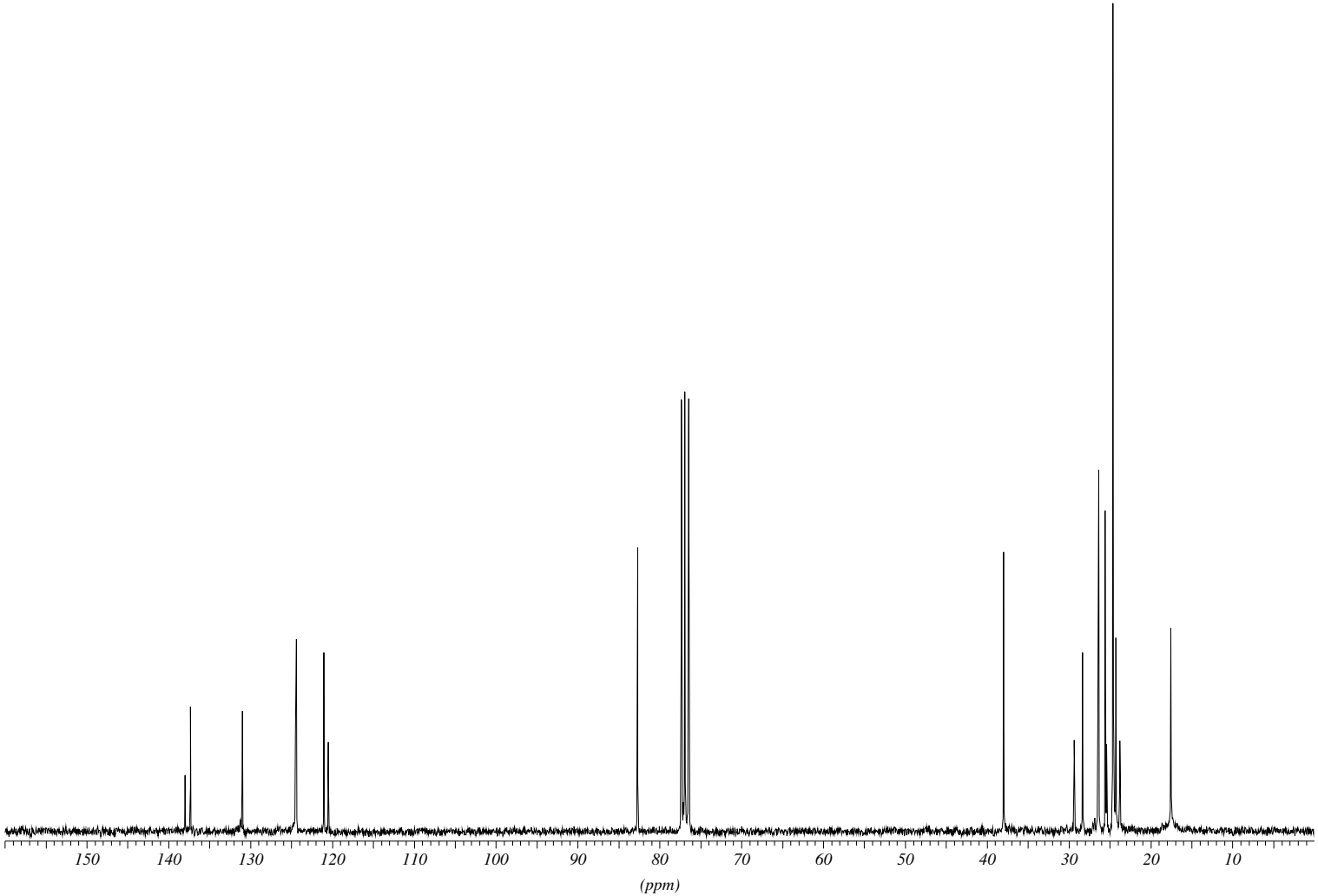
^{1}H NMR spectra of **3f** at 300 MHz in $CDCl_3$



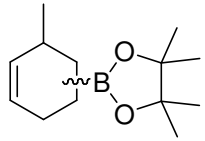
^{13}C NMR spectra of **3f** at 75 MHz in $CDCl_3$



^{1}H NMR spectra of **3g** at 300 MHz in $CDCl_3$

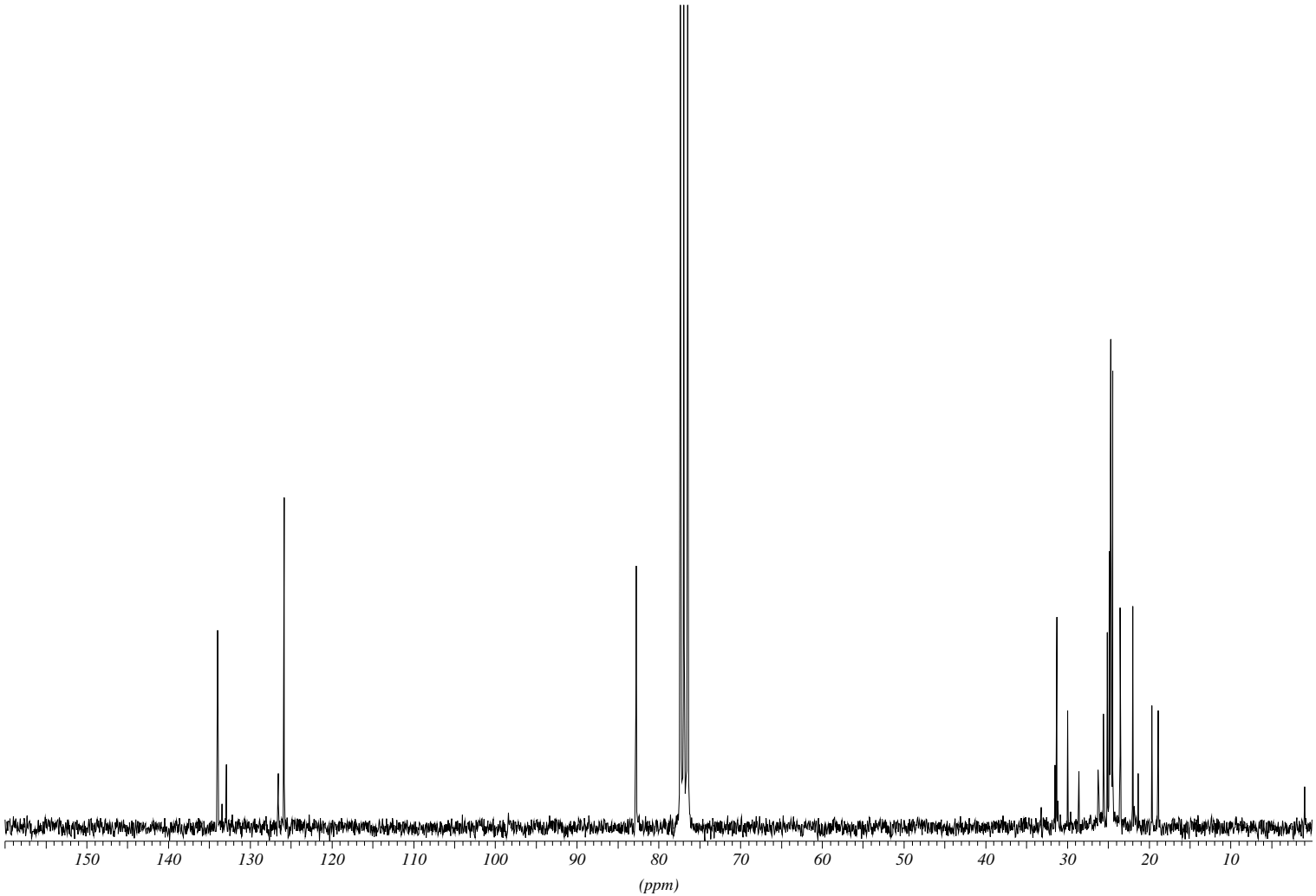


^{13}C NMR spectra of **3g** at 75 MHz in $CDCl_3$

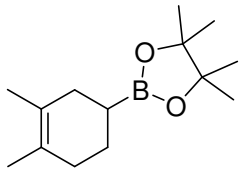


3h

^{1}H NMR spectra of **3h** at 300 MHz in $CDCl_3$

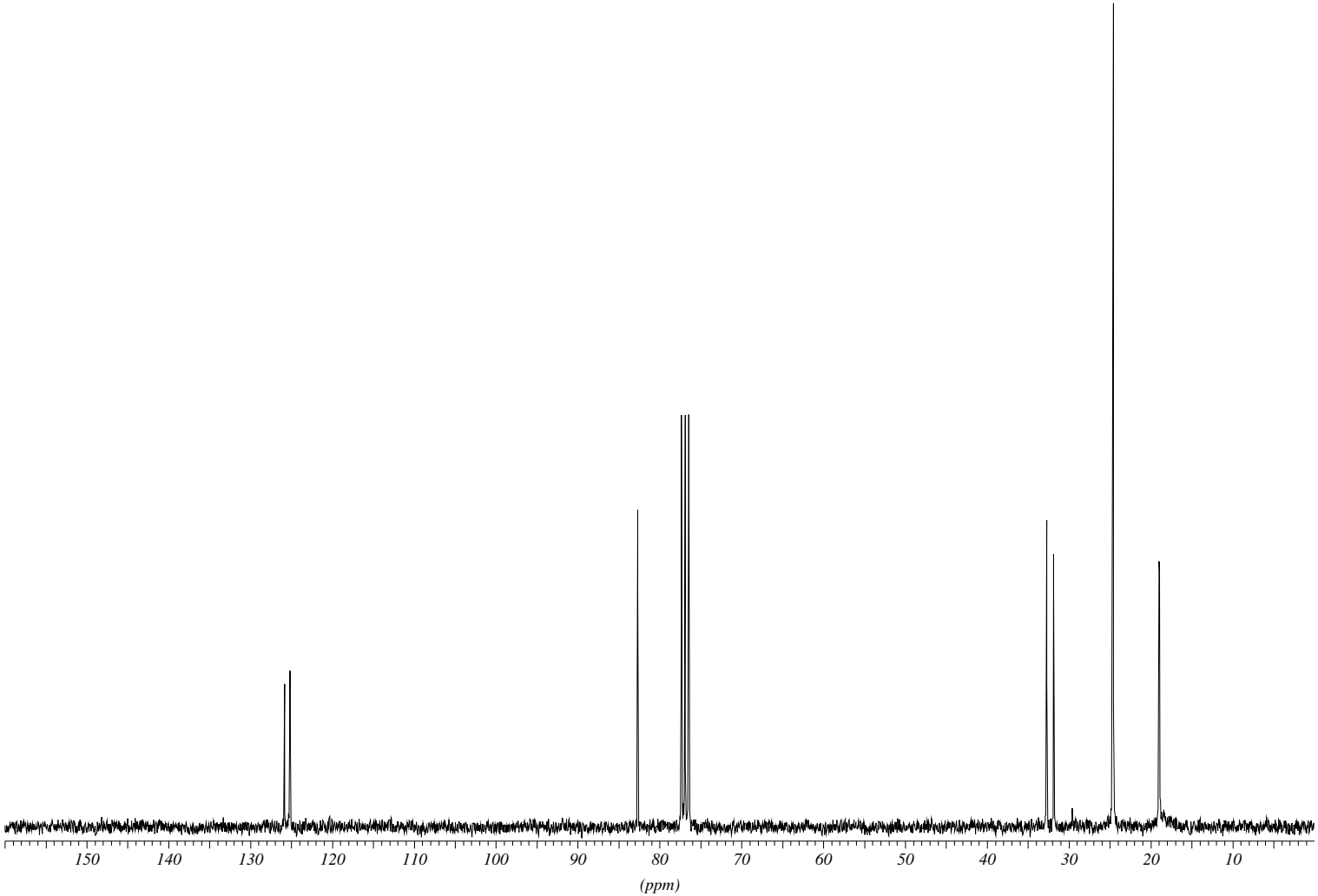


^{13}C NMR spectra of **3h** at 75 MHz in $CDCl_3$

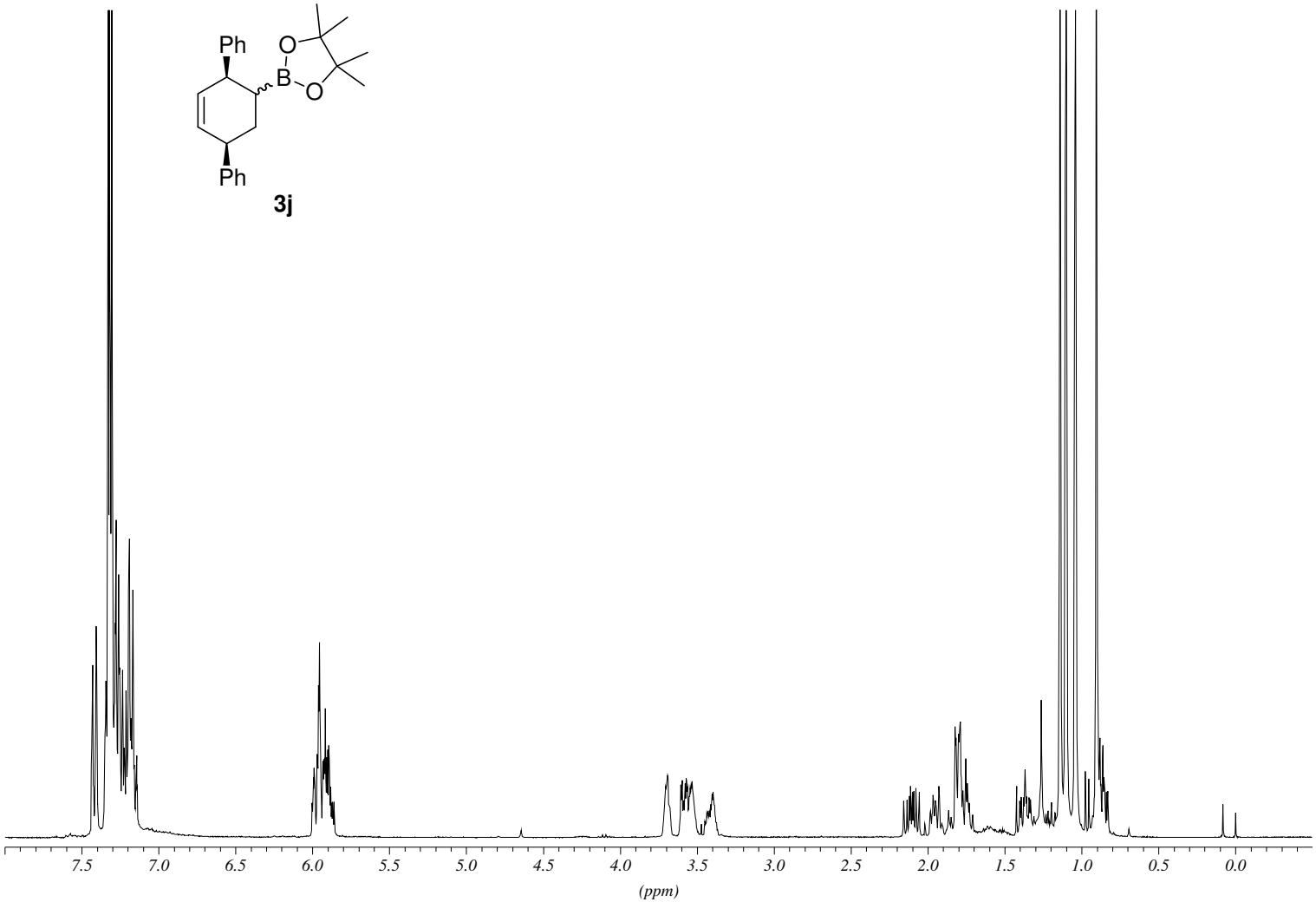


3i

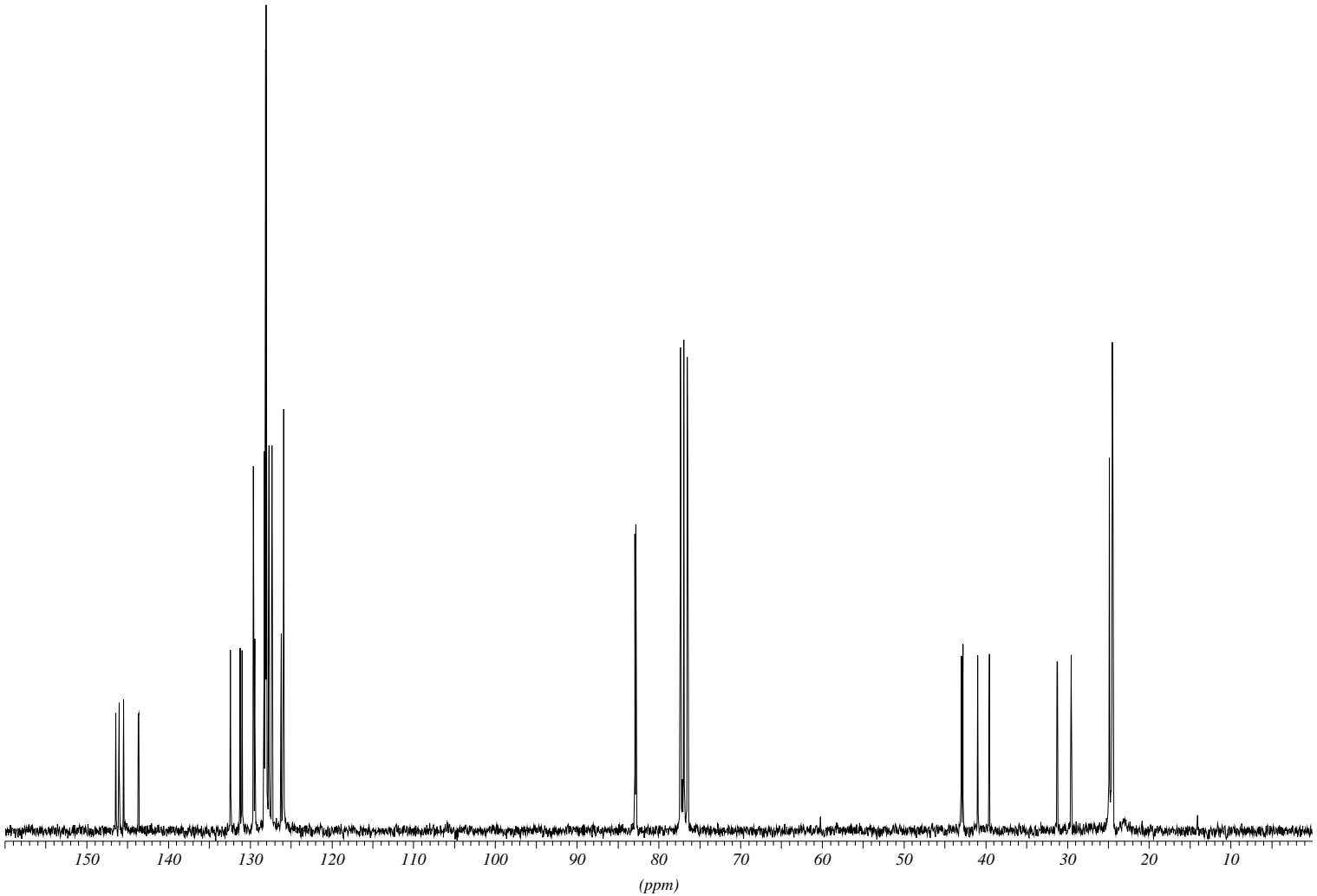
^{1}H NMR spectra of **3i** at 300 MHz in $CDCl_3$



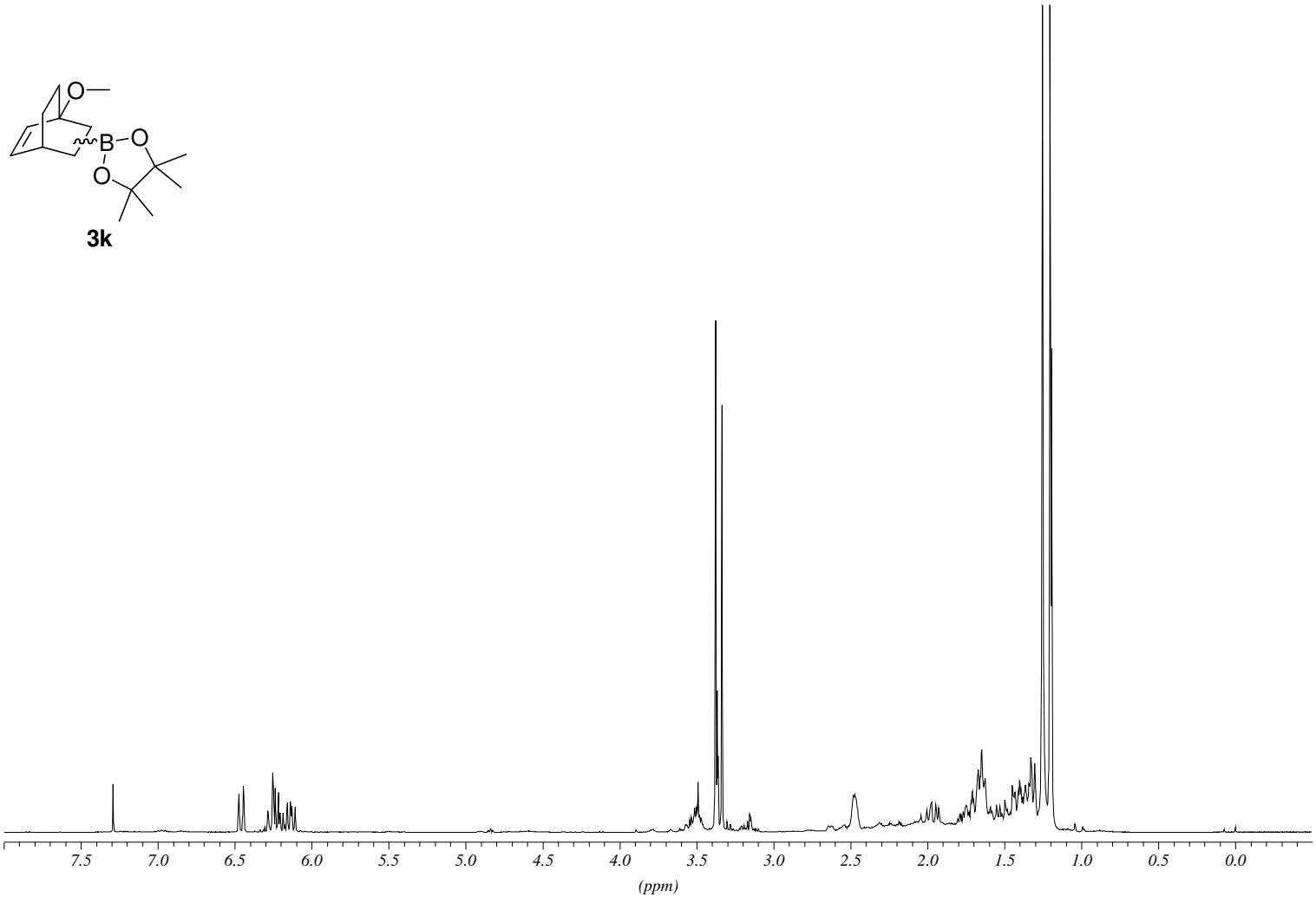
^{13}C NMR spectra of **3i** at 75 MHz in $CDCl_3$



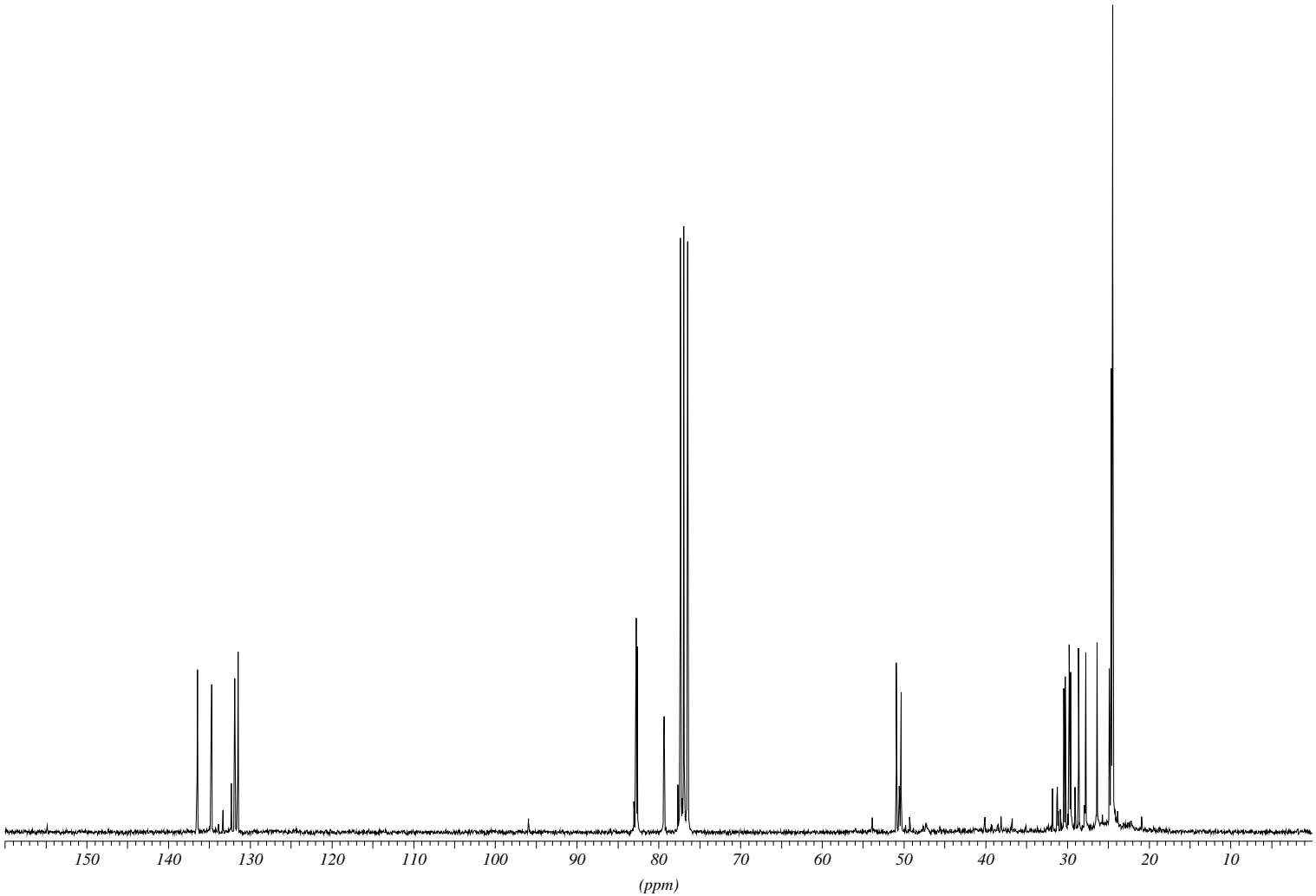
^{1}H NMR spectra of **3j** at 300 MHz in $CDCl_3$



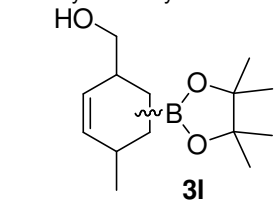
^{13}C NMR spectra of **3j** at 75 MHz in $CDCl_3$



^{1}H NMR spectra of **3k** at 300 MHz in $CDCl_3$

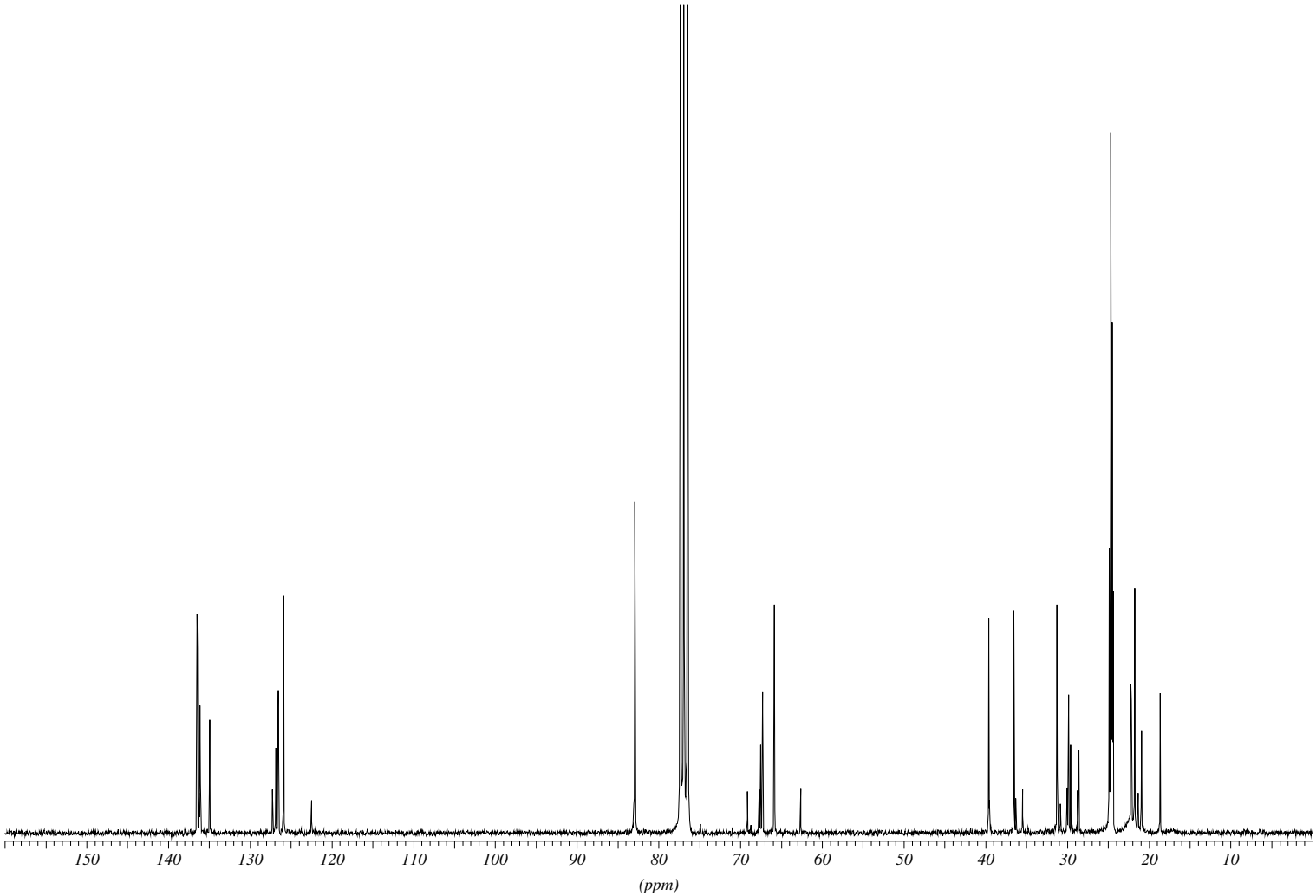


^{13}C NMR spectra of **3k** at 75 MHz in $CDCl_3$



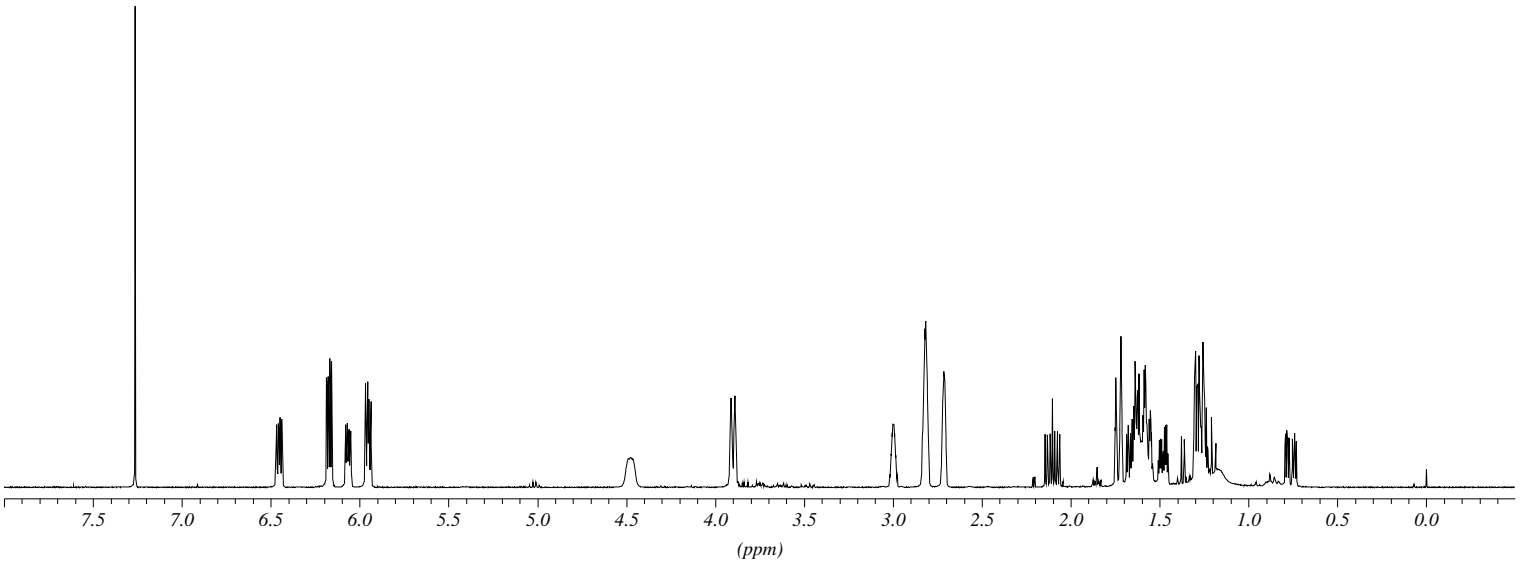
3l

^{1}H NMR spectra of **3l** at 300 MHz in $CDCl_3$

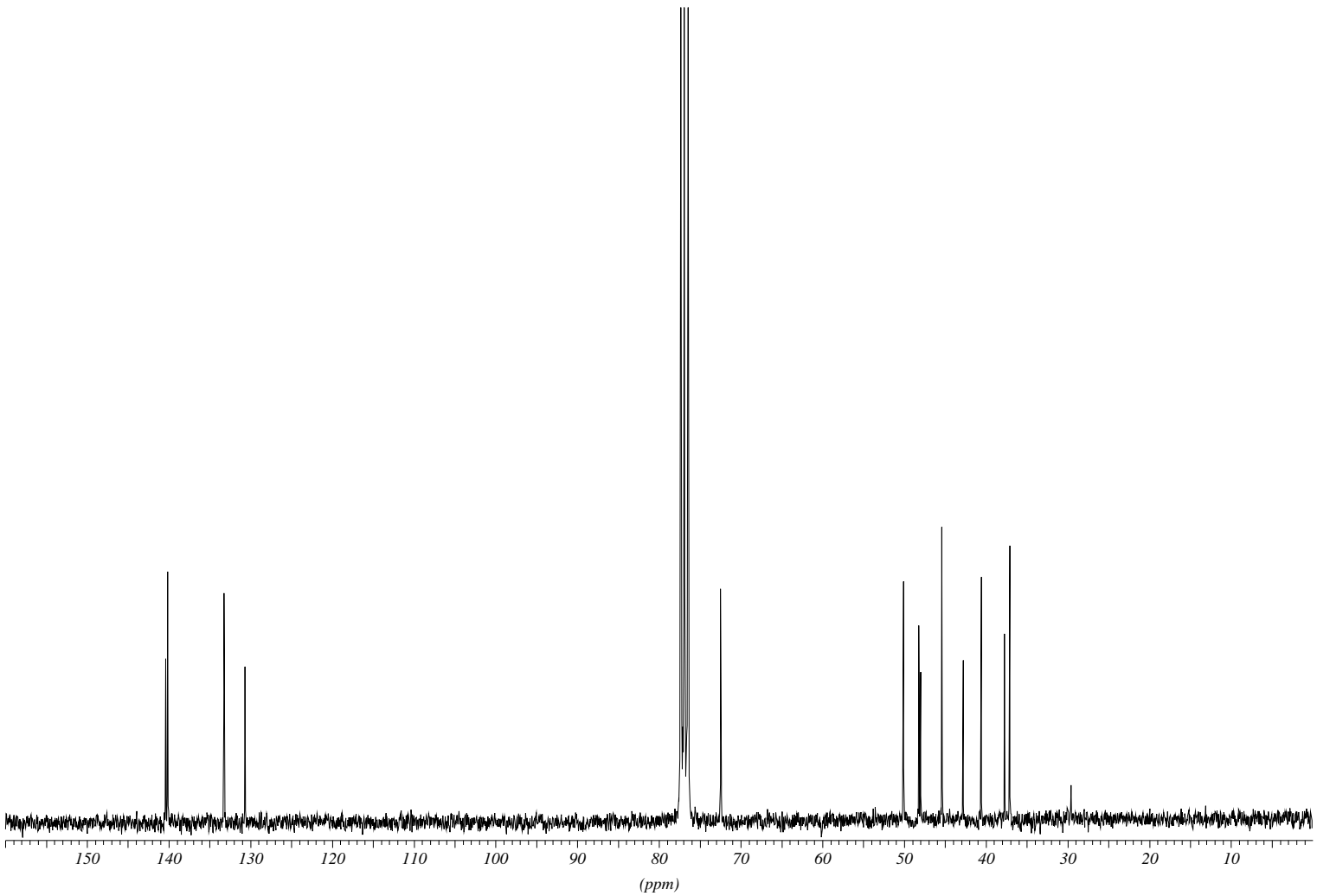


^{13}C NMR spectra of **3l** at 75 MHz in $CDCl_3$

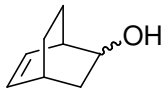
4a



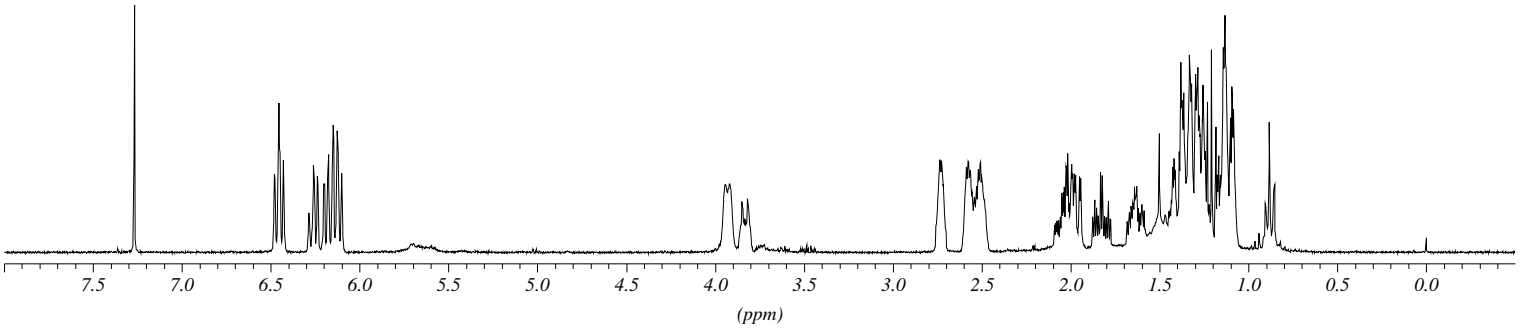
^{1}H NMR spectra of **4a** at 300 MHz in $CDCl_3$



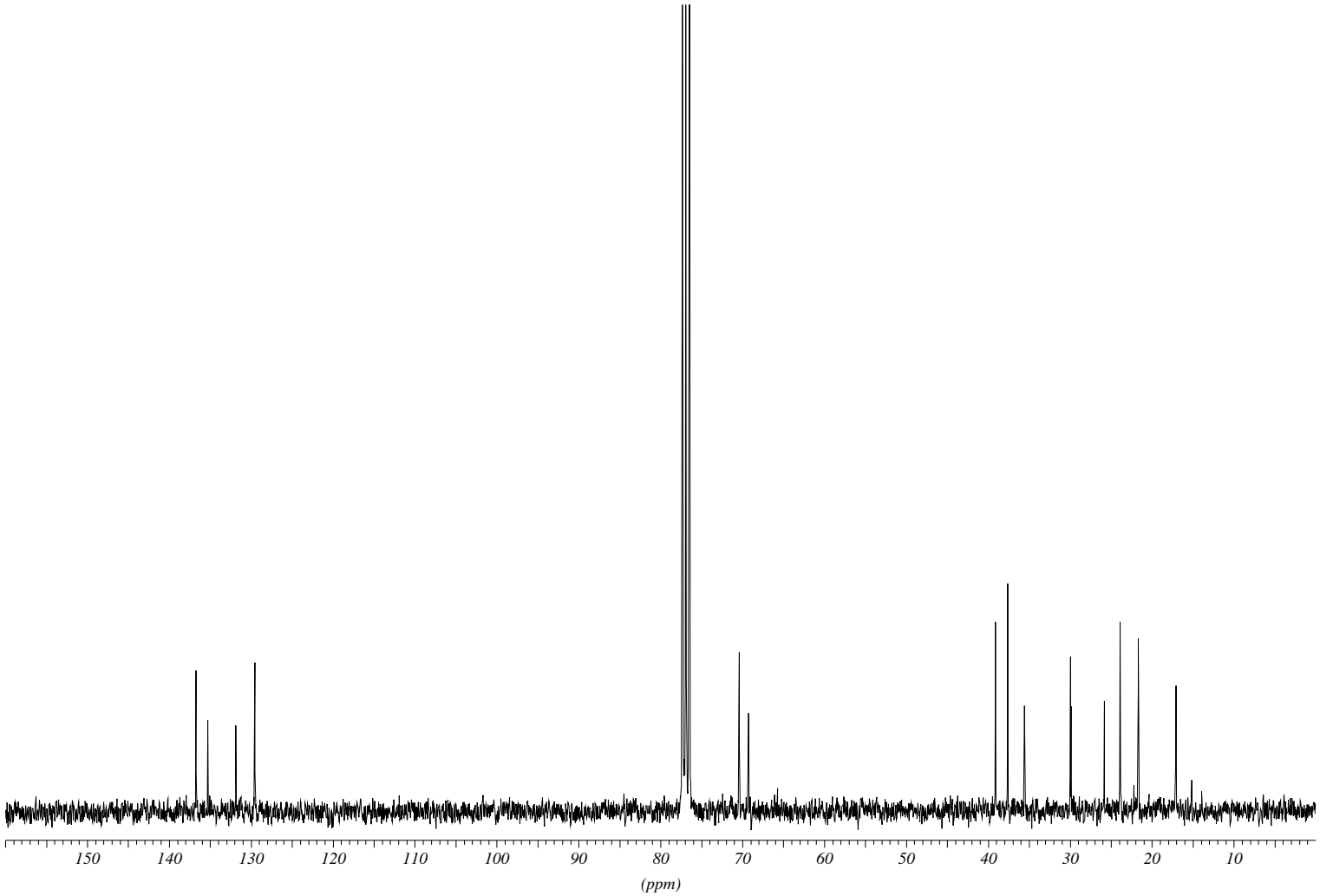
^{13}C NMR spectra of **4a** at 75 MHz in $CDCl_3$



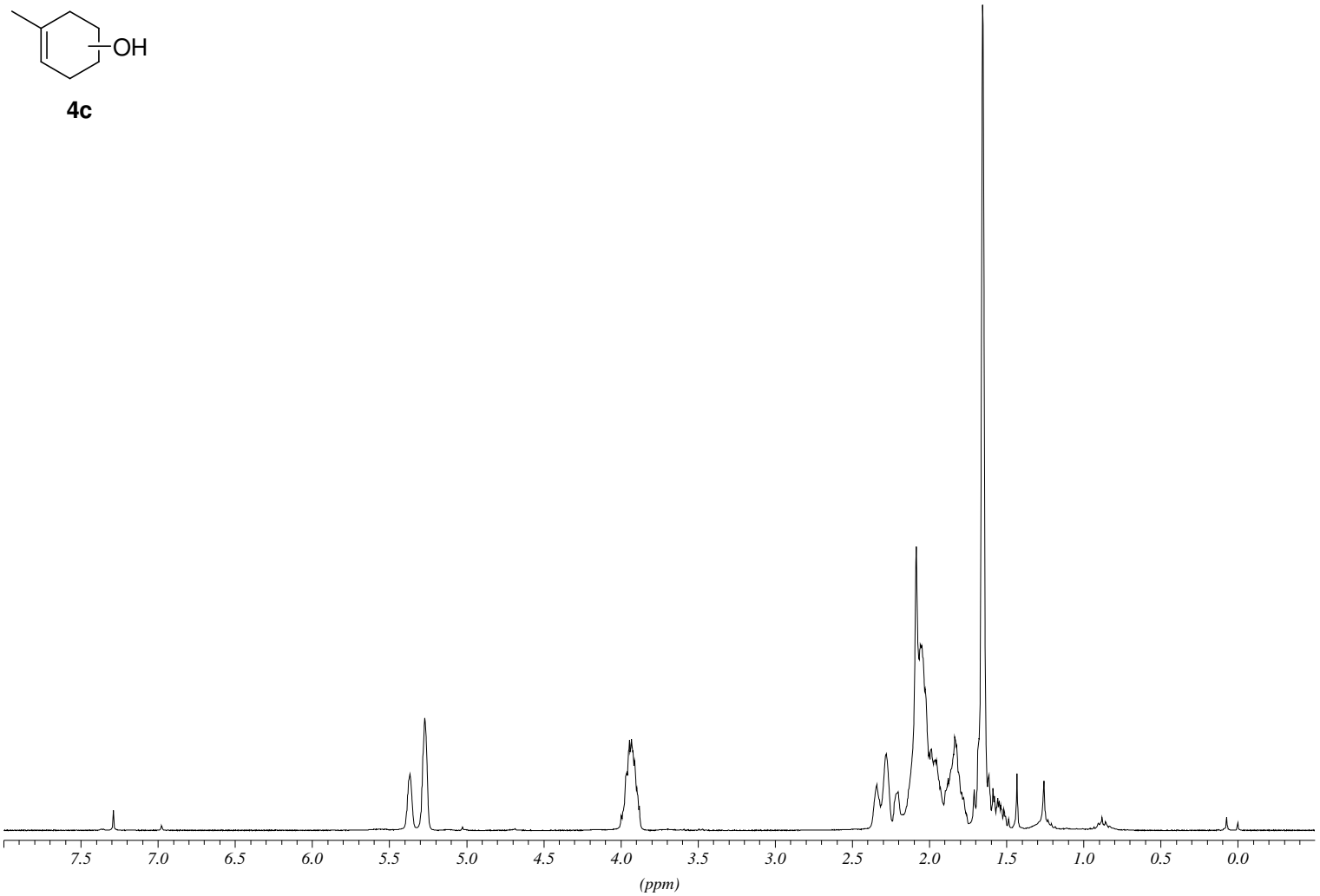
4b



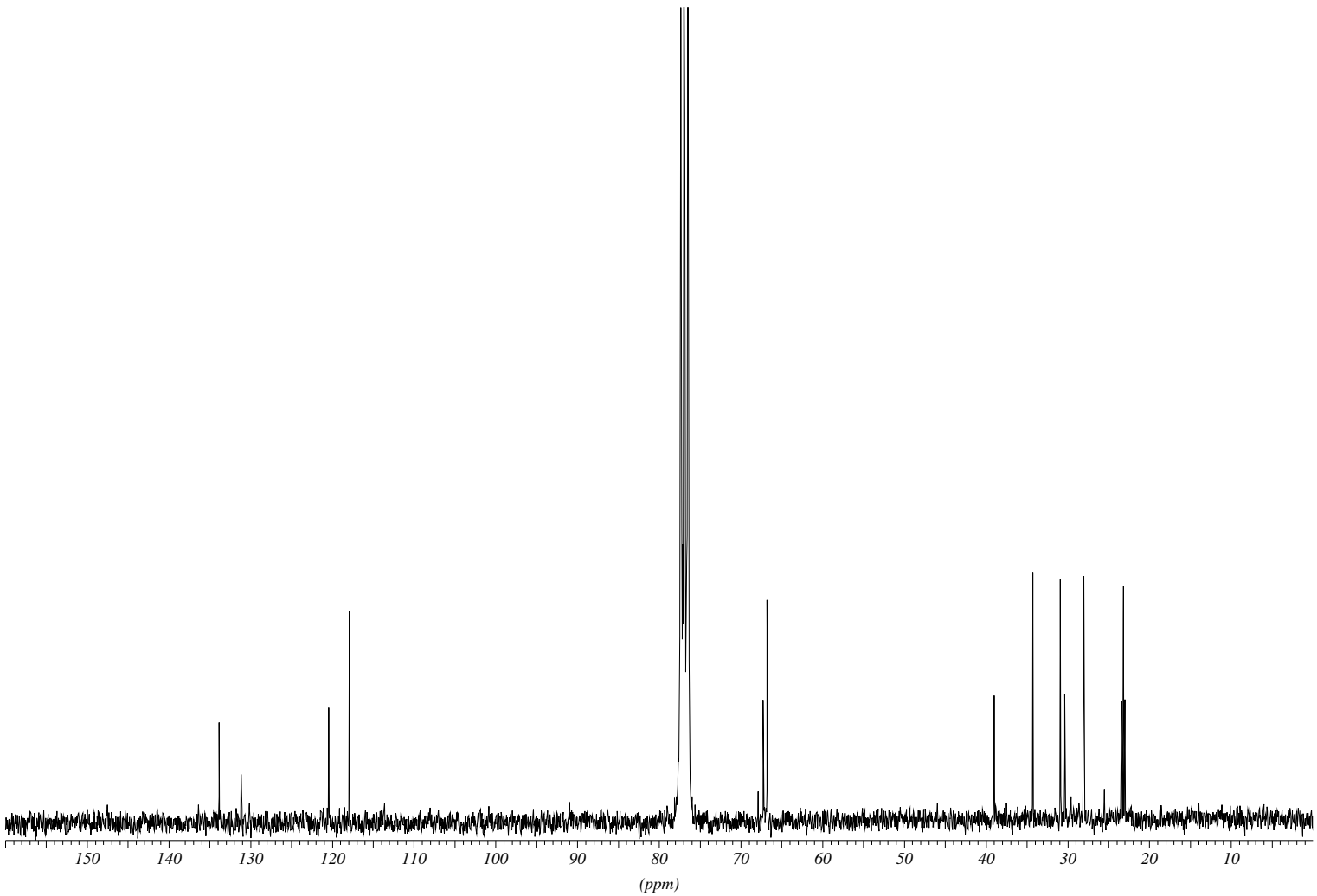
^{1}H NMR spectra of **4b** at 300 MHz in $CDCl_3$



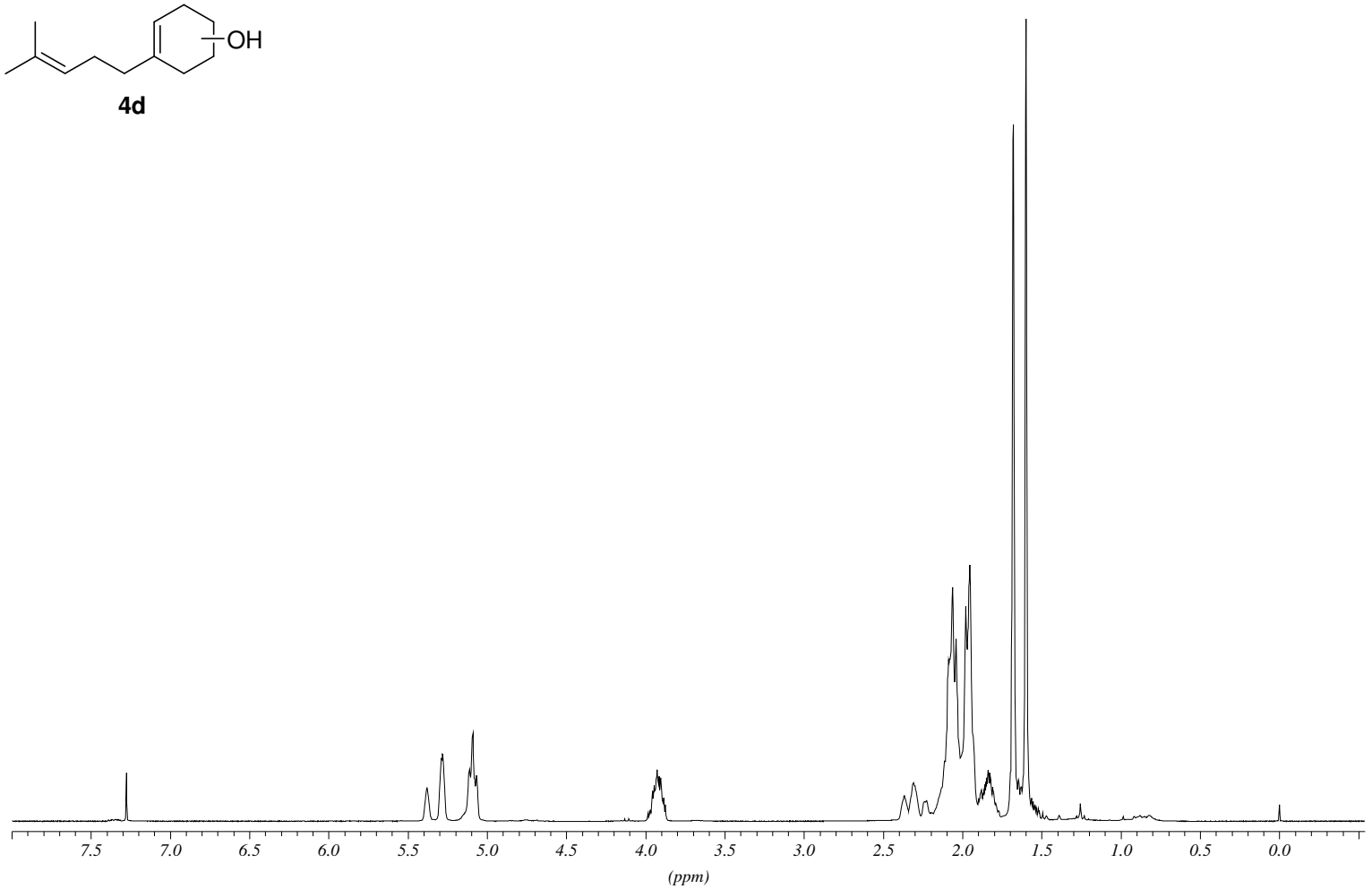
^{13}C NMR spectra of **4b** at 75 MHz in $CDCl_3$



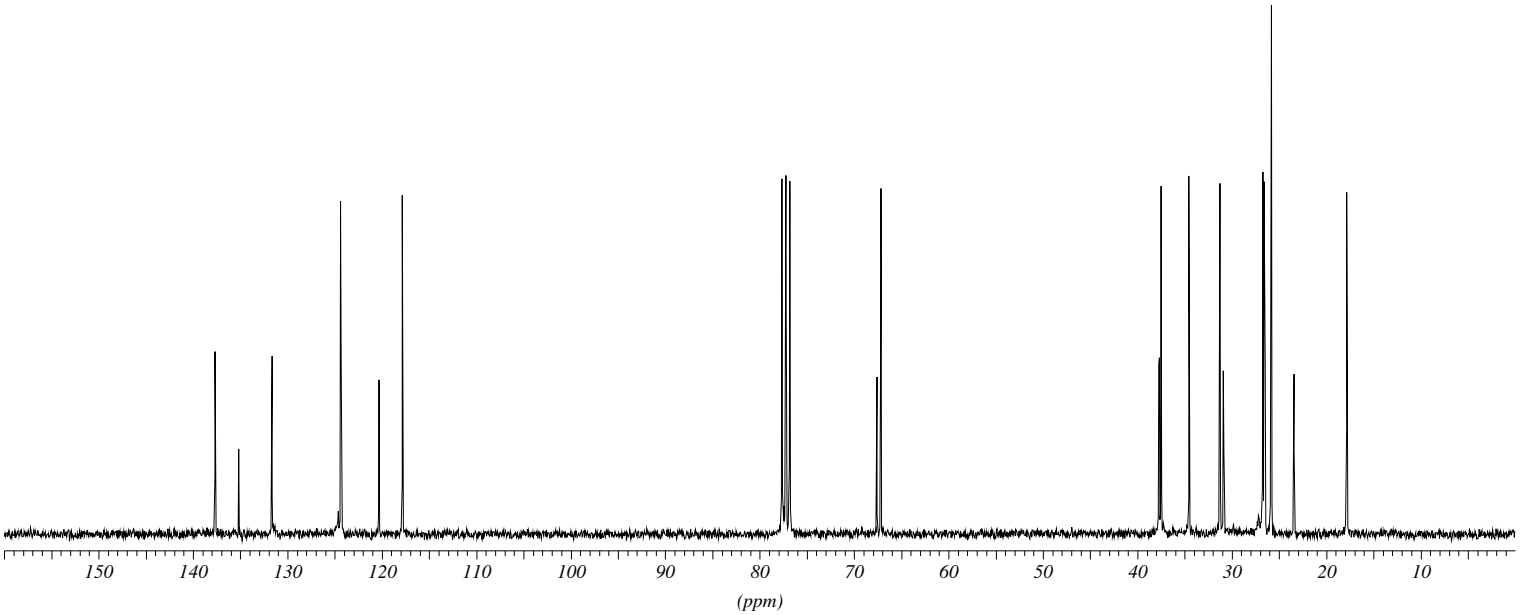
^{1}H NMR spectra of **4c** at 300 MHz in $CDCl_3$



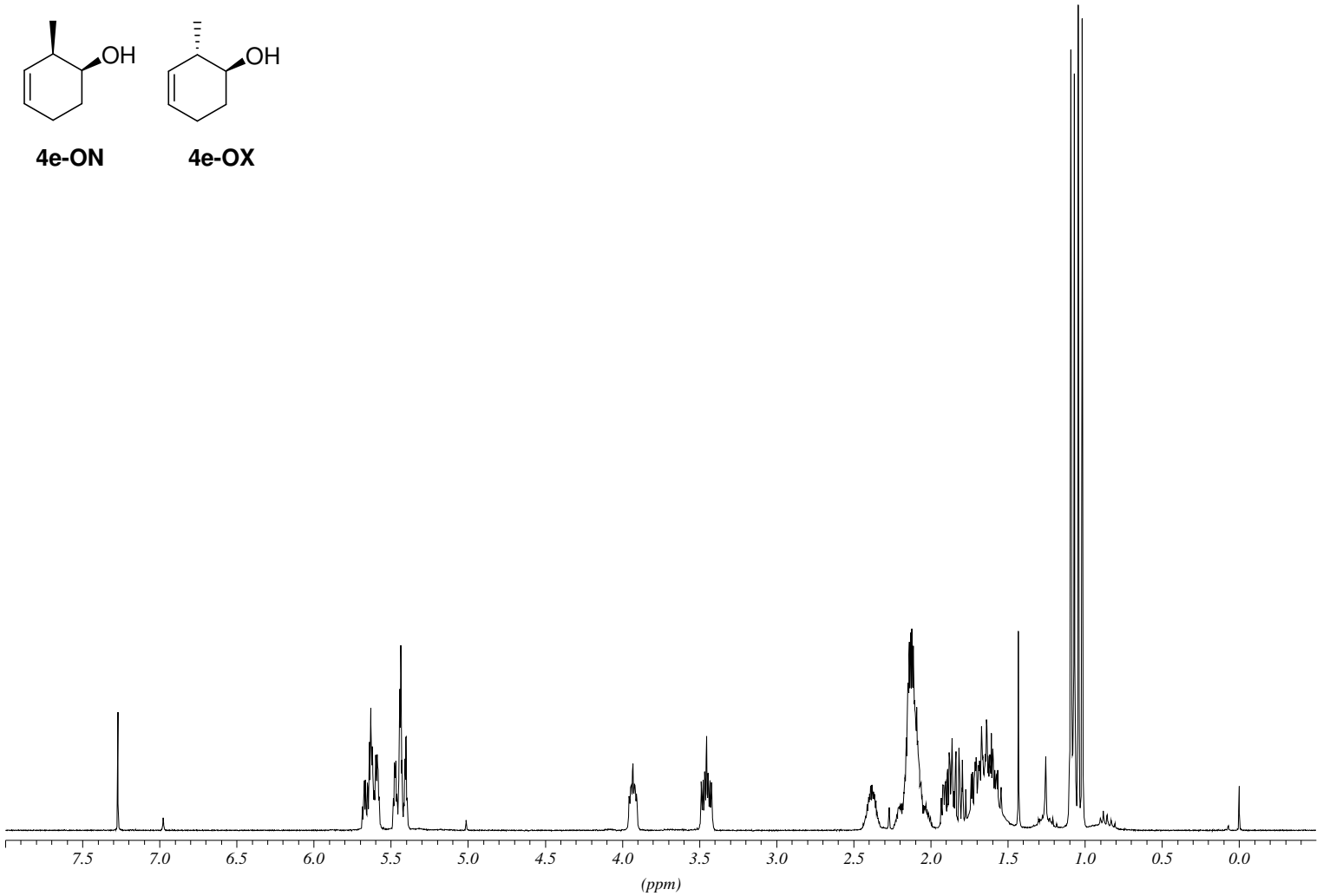
^{13}C NMR spectra of **4c** at 75 MHz in $CDCl_3$



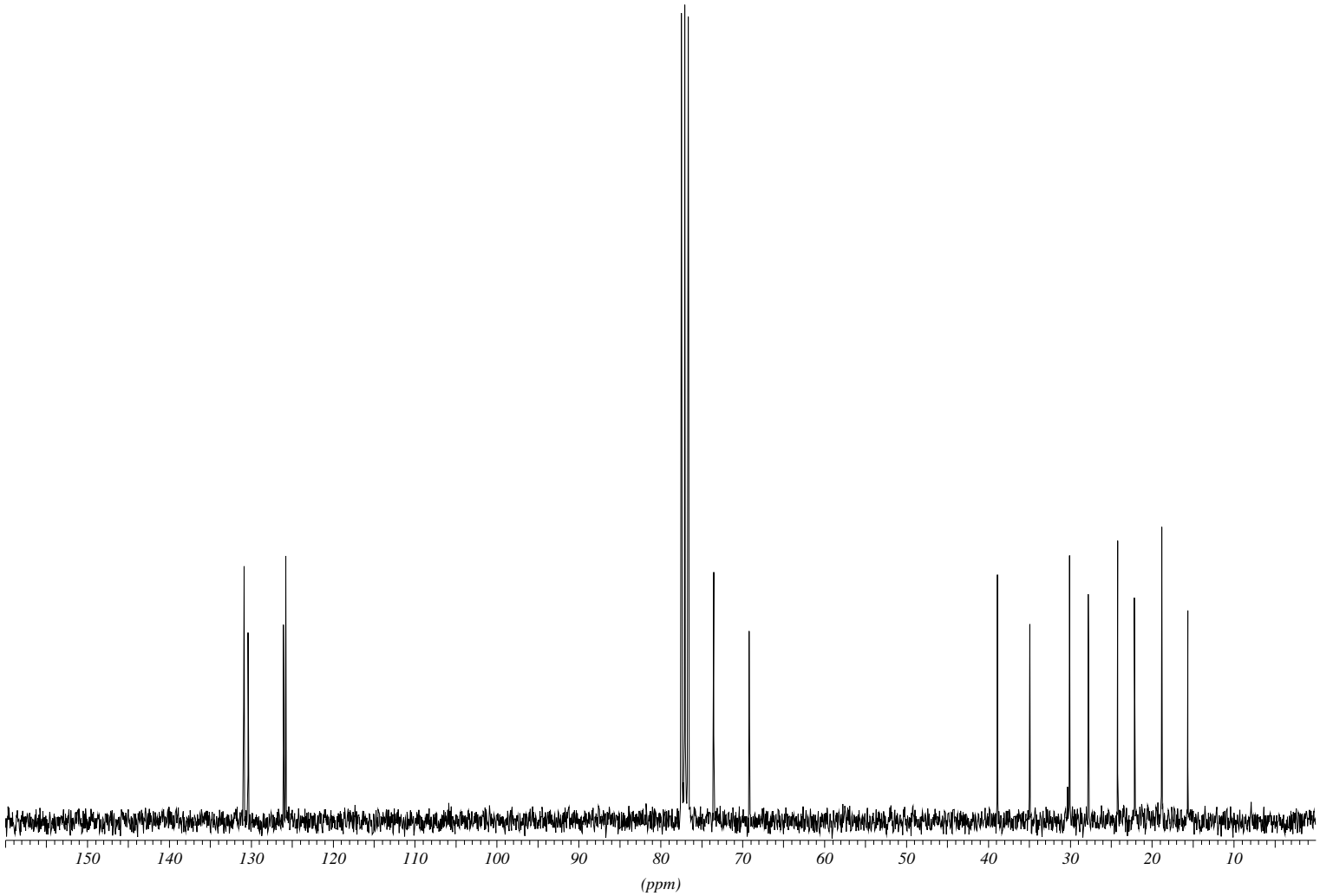
^{1}H NMR spectra of **4d** at 300 MHz in $CDCl_3$



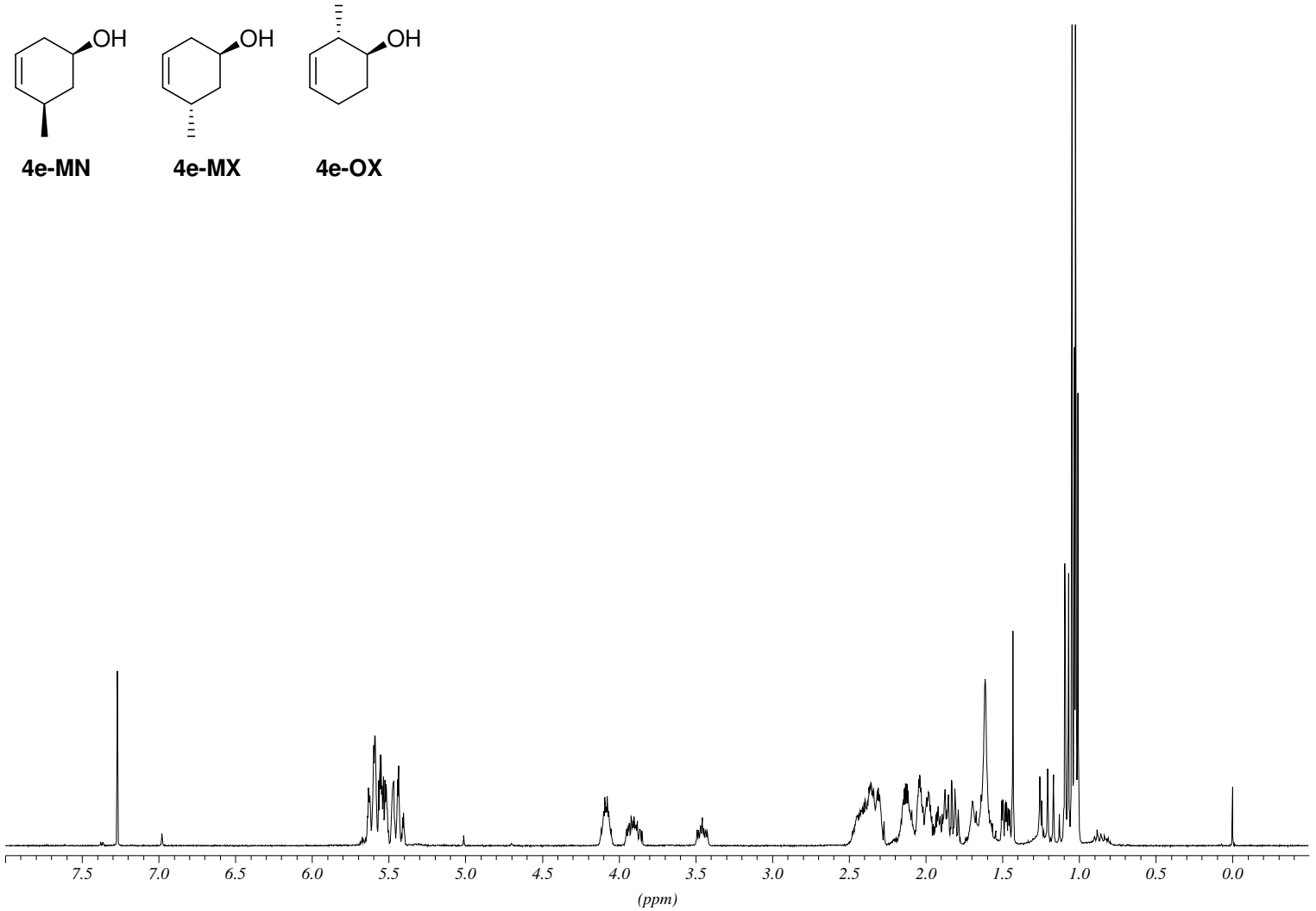
^{13}C NMR spectra of **4d** at 75 MHz in $CDCl_3$



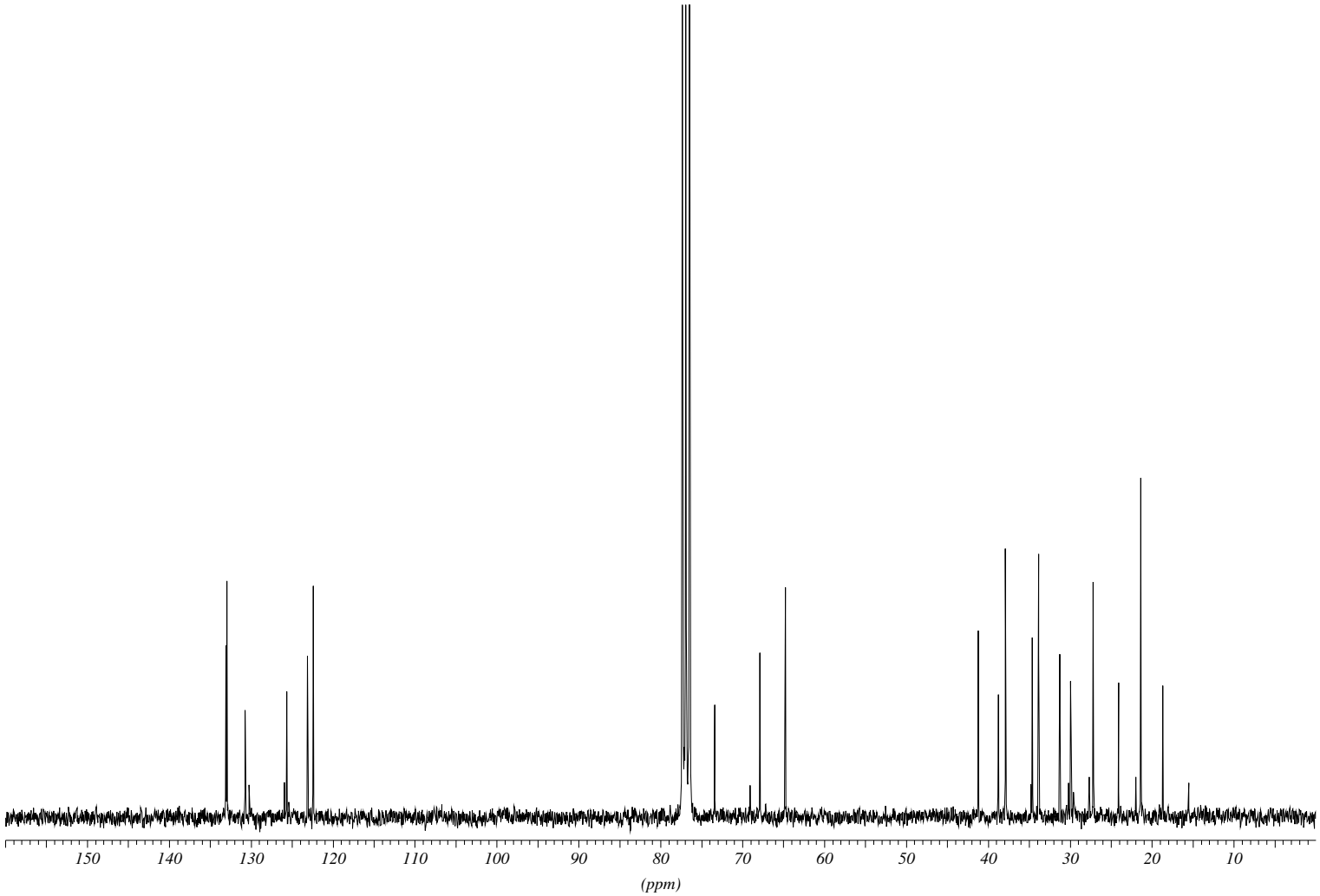
^{1}H NMR spectra of **4e-ON** and **4e-OX** at 300 MHz in $CDCl_3$



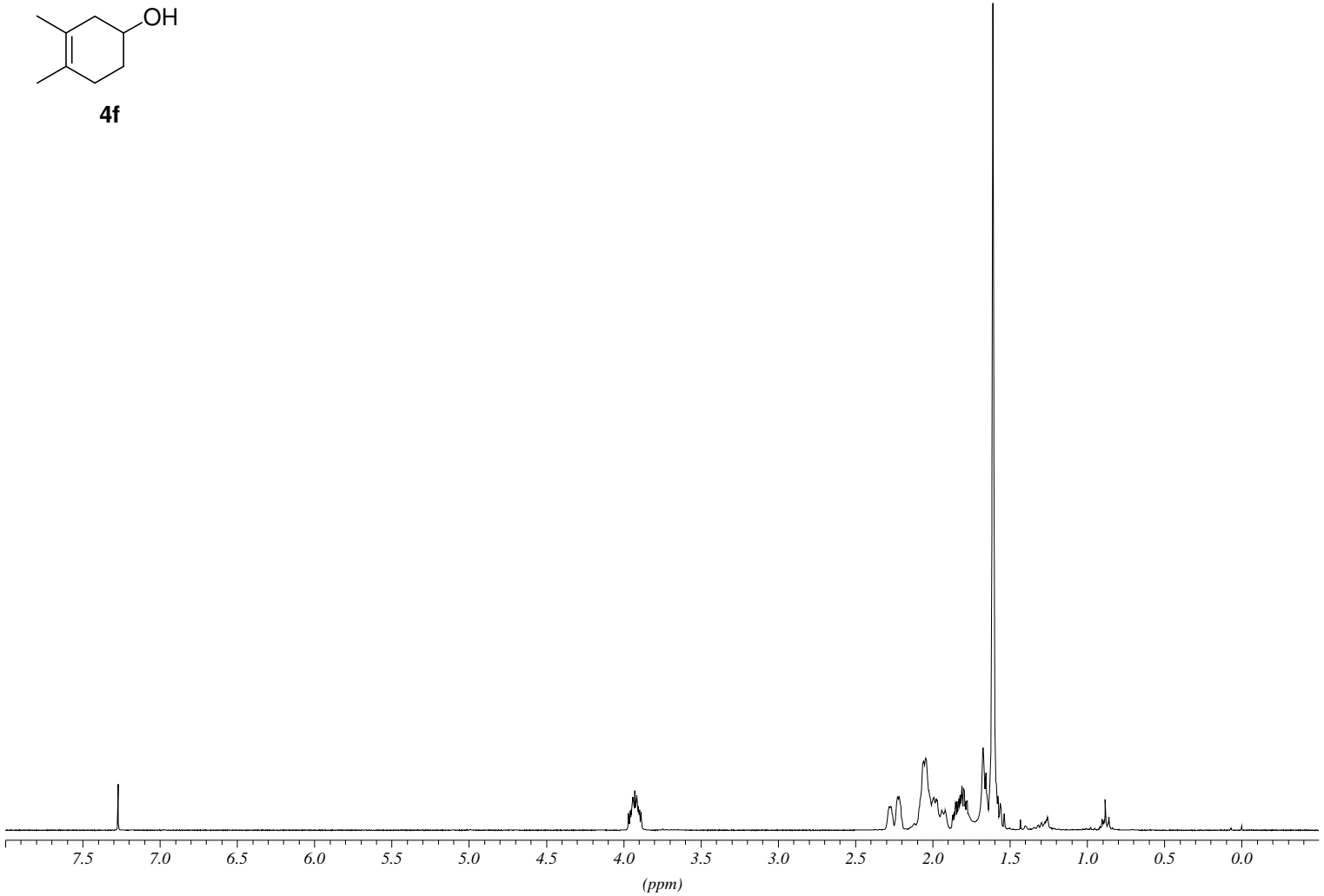
^{13}C NMR spectra of **4e-ON** and **4e-OX** at 75 MHz in $CDCl_3$



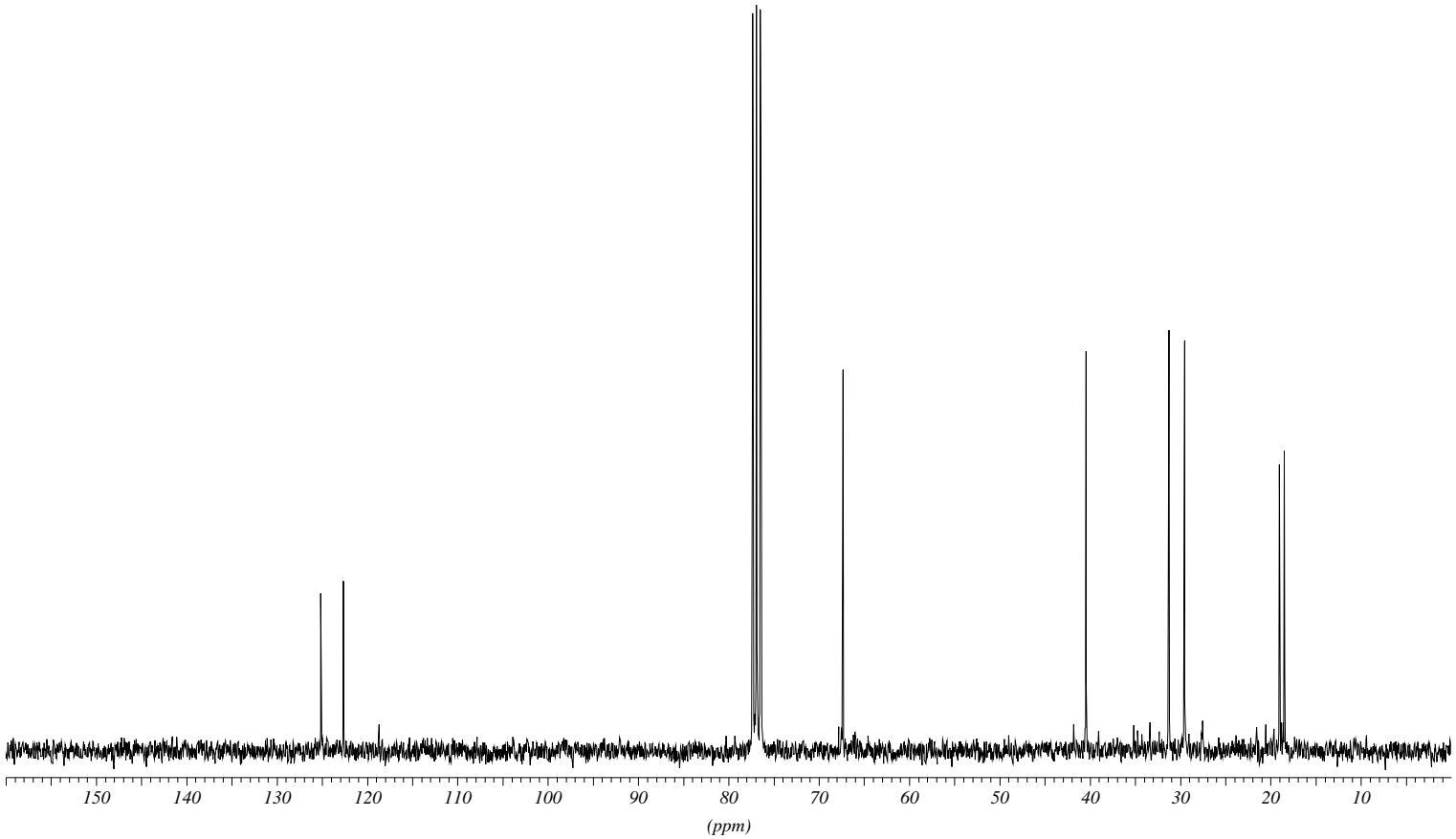
^{1}H NMR spectra of **4e-MN**, **4e-MX** and **4e-OX** at 300 MHz in $CDCl_3$



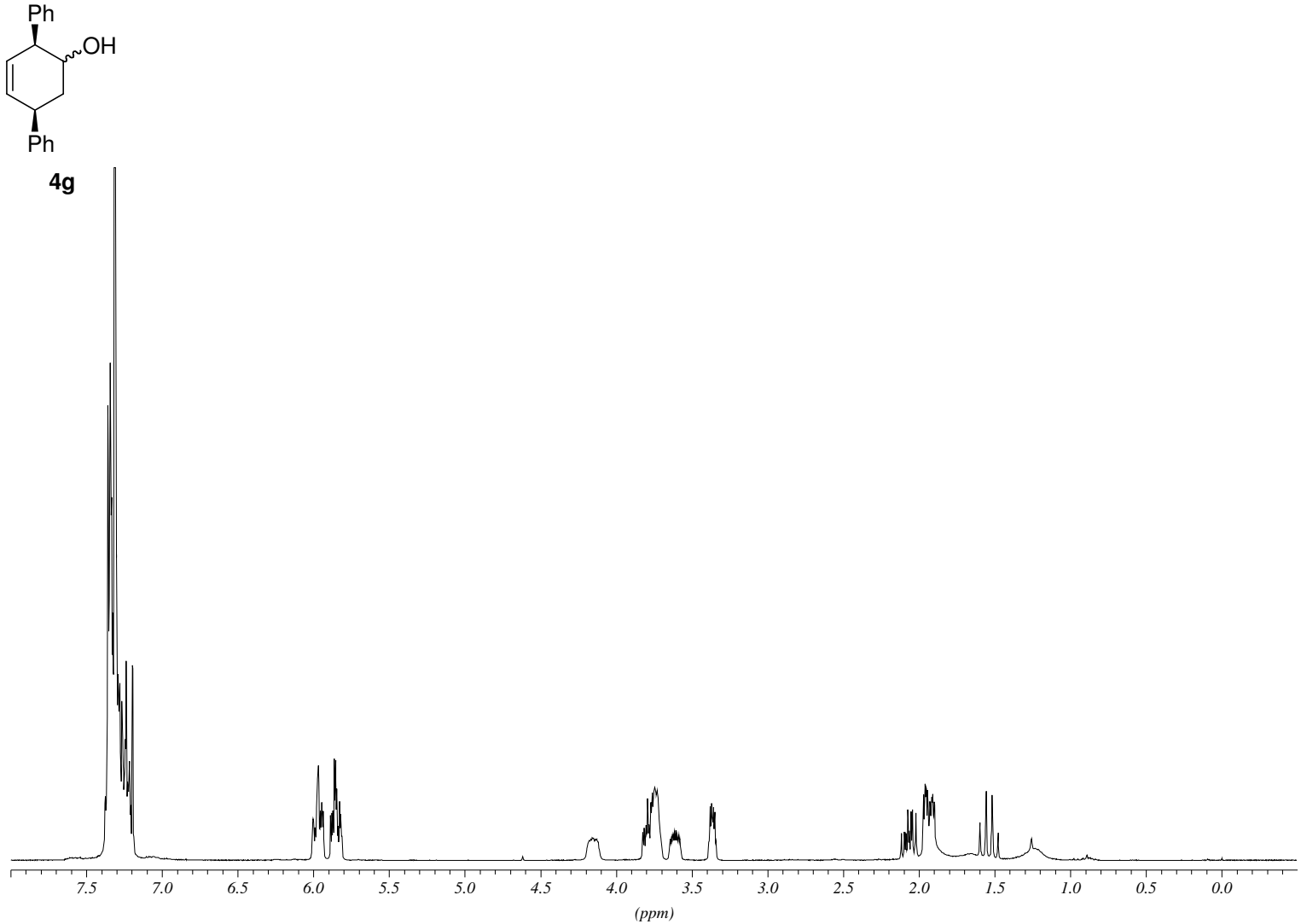
^{13}C NMR spectra of **4e-MN**, **4e-MX** and **4e-OX** at 75 MHz in $CDCl_3$



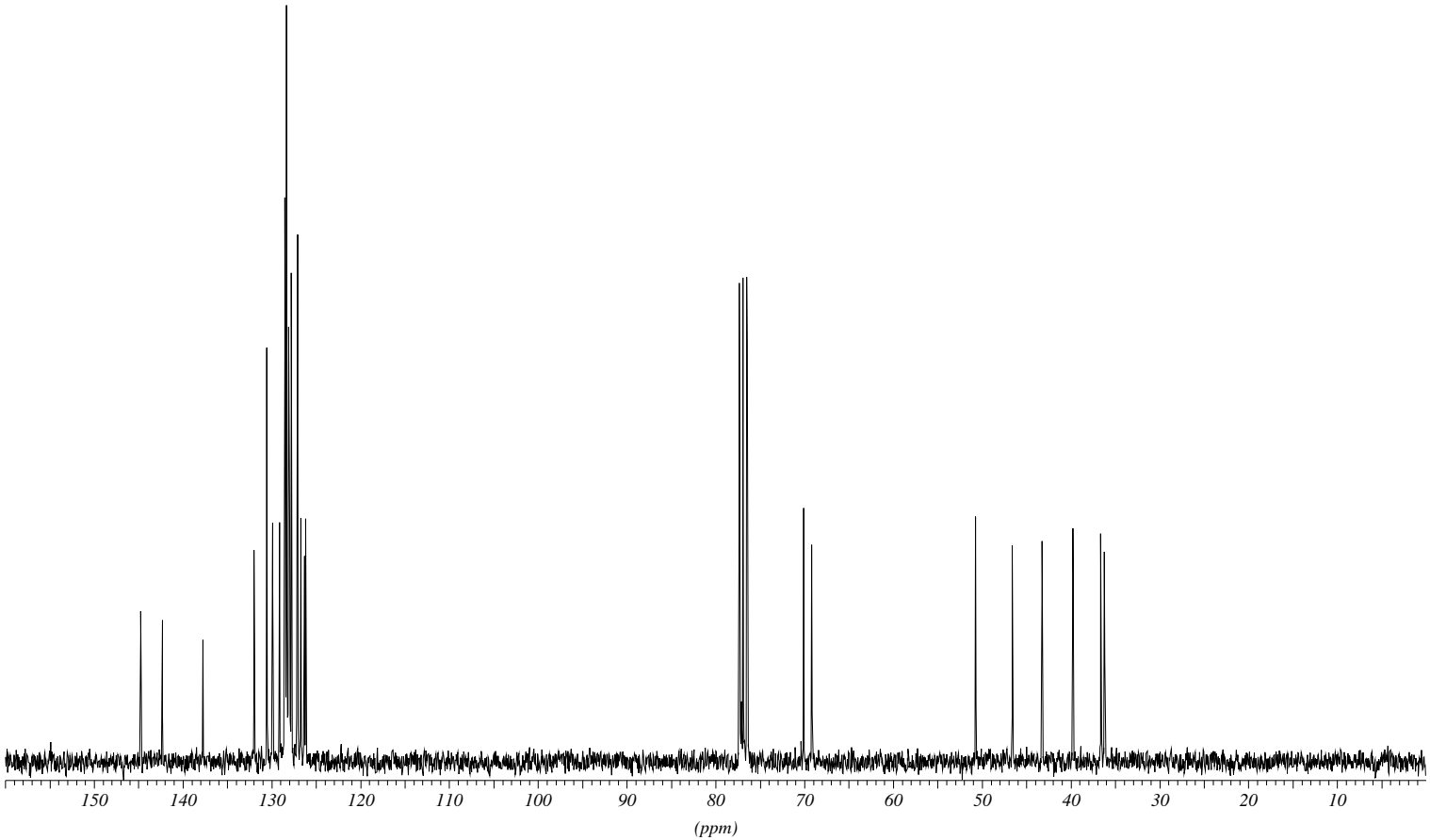
^{1}H NMR spectra of **4f** at 300 MHz in $CDCl_3$



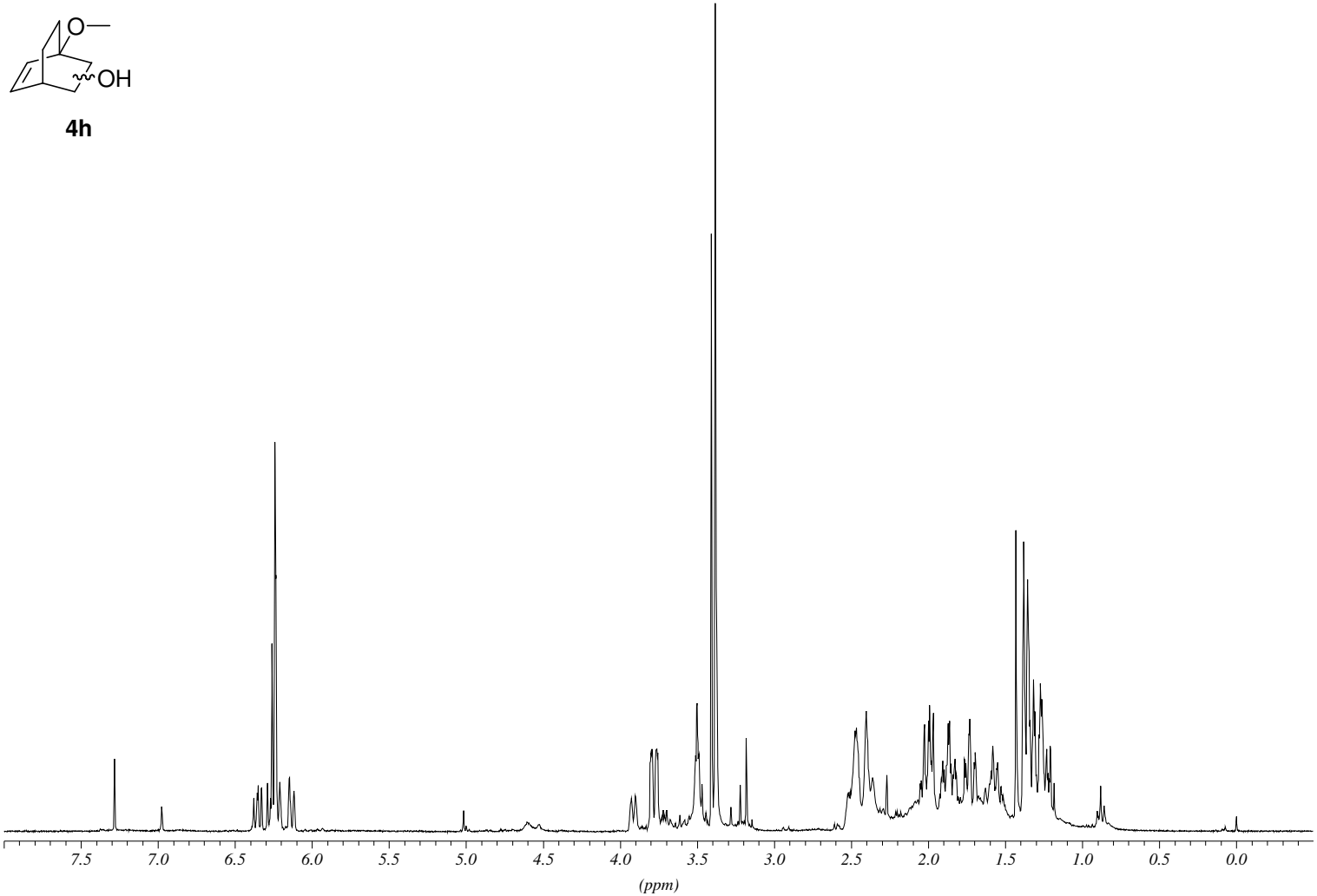
^{13}C NMR spectra of **4f** at 75 MHz in $CDCl_3$



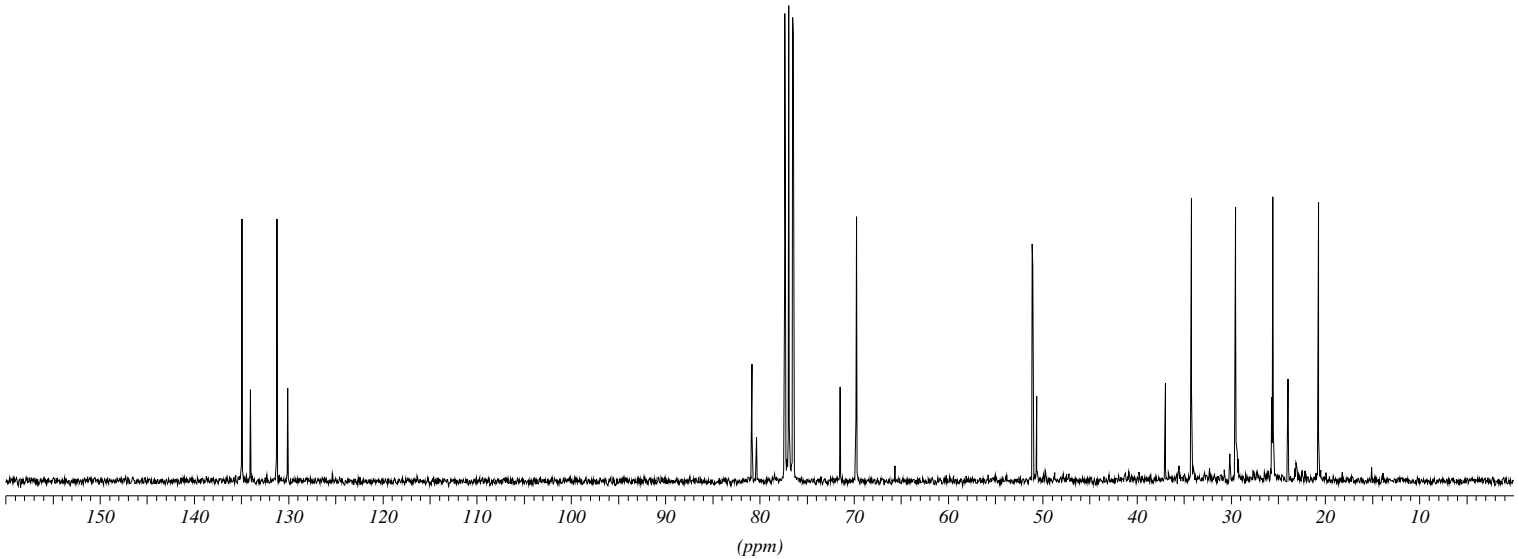
^{1}H NMR spectra of **4g** at 300 MHz in $CDCl_3$



^{13}C NMR spectra of **4g** at 75 MHz in $CDCl_3$



^{1}H NMR spectra of **4h** at 300 MHz in $CDCl_3$



^{13}C NMR spectra of **4h** at 75 MHz in $CDCl_3$