Nazarov Reactions of Vinyl Cyclopropylamines: An Approach to the Imino-Nazarov Problem

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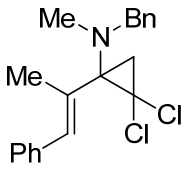
Supporting Information: Experimental procedures, physical data, and NMR spectra for **1a-i**, **3a-e**, **8f-g′**, **10g′**, **11h** and synthetic intermediates, and ORTEP structure for **8f′** (71 pages).

Contents

General Information. Reactions were carried out in flame-dried glassware under an atmosphere of argon. Tetrahydrofuran (Na/benzophenone), diethyl ether

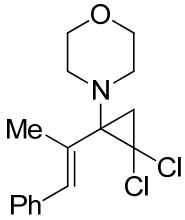
(Na/benzophenone), dichloromethane (CaH_2), acetonitrile (CaH_2), toluene (CaH_2), and triethylamine (CaH_2) were distilled prior to use, and chloroform was filtered through potassium carbonate. Methanol was dried over activated 3Å molecular sieves. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F254 (Merck). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle), or 150 mesh neutral alumina (Sigma-Aldrich). Carbon tetrabromide was dissolved in dichloromethane, dried over magnesium sulfate and filtered prior to use to remove residual water in the commercial reagent. Mercury(II) fluoride and mercury(II) acetate were dried over phosphorus pentoxide under vacuum prior to use. Silver bis(trifluoromethanesulfonyl)imide was prepared from silver carbonate.[1] Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300 MHz, 400 MHz, or 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets, etc. The chemical shifts are reported on the δ scale (ppm) and the spectra are referenced to residual solvent peaks: $CDCl_3$ (7.26 ppm, ^{1}H; 77.26 ppm, ^{13}C), as internal standard. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz, and the chemical shifts are accurate to one decimal place.

Preparation of Substrates



1-(*N*-benzyl-*N*-methylamino)-2,2-dichloro-1-(1-phenyl-[1*E*]-propen-2-yl)cyclopropane (1a). This compound was prepared in a manner analogous to **1b**.

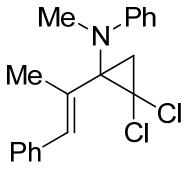
Cyclopropanation time was 35 minutes. FCC (3 % ethyl acetate in hexanes) provided the desired compound as an off-white solid, 180 mg, 42 % over 2 steps; m.p. (decomp.) 85 ºC; IR (dichloromethane cast film) 3061, 3026, 2950, 2945, 1600, 1494, 1447 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (m, 10H), 6.51 (s, 1H), 3.99 (d, *J* = 13.4 Hz, 1H), 3.75 (d, *J* = 13.4 Hz, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 1.85 (d, *J* = 6.9 Hz, 1H), 1.77 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 137.1, 133.4, 131.2, 129.3, 128.6, 128.51, 128.50, 127.2, 127.2, 67.8, 62.4, 59.2, 38.4, 35.9, 20.4; HRMS (ESI, M+H) calculated for $C_{20}H_{22}NCl_2$ m/z 346.1124; found m/z 346.1128.



1,1-dichloro-2-morpholino-2-(1-phenyl-[*2E*]-propen-2-ylcyclopropane (1b). Mercury(II) fluoride (1.26 g, 5.27 mmol), powdered 4 Å molecular sieves (1.4 g), tetrahydrofuran (18 mL), triethylamine (2.5 mL, 17.6 mmol), (*E*)-4-phenyl-3-methyl-3-buten-1-yne [2] (1.00 g, 7.03 mmol), and morpholine (1.23 mL, 14.1 mmol) were sequentially added to a round bottom flask, and the mixture was stirred and heated to reflux for 3 h. The mixture was then cooled to room temperature, and aluminum chloride (9 mg, 0.07 mmol) was added. The mixture was heated to reflux for 19 h, then cooled. Hexane was added, and the mixture was filtered through Celite and concentrated. The resulting oil was dissolved in hexanes, filtered through Celite and concentrated to provide the enamine as a yellow oil, 2.519 g, which was carried on in crude form.

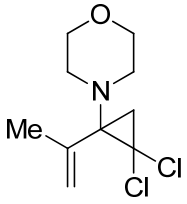
The crude enamine (2.51 mg) was dissolved in 91 mL chloroform. 50 % aqueous sodium hydroxide (157 mL, 1.96 mol) was added followed by benzyltriethylammonium

chloride (745 mg, 3.27 mmol), and the reaction was stirred vigorously for 30 min., and then diluted with water. The layers were separated, and the aqueous was extracted three times with dichloromethane. The combined extract was washed with water then brine, dried over magnesium sulfate, filtered, and concentrated to a brown film. FCC (7 % ethyl acetate in hexanes) provided 1,1-dichloro-2-morpholino-2-(1-phenyl-[*2E*]-propen-2-ylcyclopropane (**1b**) as an off-white solid, 1.021 g, 46 % over 2 steps; IR (thin film) 3024, 2957, 2854, 2828, 1666, 1448, 1266, 1116, 1073, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.39 (m, 3H), 7.24-7.28 (m, 2H), 6.39 (br s, 1H), 3.70 (app t, *J* = 4.8 Hz, 4H), 2.86 (dt, *J* = 10.8, 4.8 Hz, 2H), 2.70 (dt, *J* = 10.8, 4.8 Hz, 2H), 2.12 (d, *J* = 1.6 Hz, 3H), 1.74 (d, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 133.7, 129.9, 129.2, 128.5, 127.3, 67.7, 67.1, 61.6, 50.5, 35.1, 20.5; HRMS (EI, M^+) calculated for $C_{16}H_{19}NOCl_2$ m/z 311.0844, found m/z 311.0847.

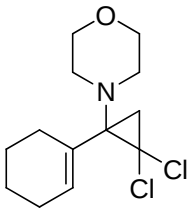


1,1-dichloro-2-(*N*-methyl-*N*-phenylamino)-2-(1-phenyl-[1*E*]-propen-2-yl)cyclopropane (1c). This compound was prepared in a manner analogous to **1b**. Cyclopropanation time was 60 minutes. FCC (15 % dichloromethane in hexanes provided the desired compound as an off-white solid, 324 mg, 14 % over 2 steps; m.p. 76-78 ºC; IR ($CHCl_3$ cast film) 3024, 2892, 2821, 1599, 1500, 1344 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.30-7.22 (m, 5H), 6.92-6.88 (m, 2H), 6.81 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.71 (s, 1H), 3.35 (s, 3H), 2.47 (d, *J* = 8.0 Hz, 1H), 2.08 (d, *J* = 1.3 Hz, 3H), 1.93 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 137.0, 133.5, 131.3,

129.3, 129.1, 128.4, 127.2, 118.0, 114.0, 67.6, 58.3, 40.2, 34.3, 17.9; HRMS (ESI, M+H) calculated for $C_{19}H_{20}NCl_2$ m/z 332.0967; found m/z 332.0965.

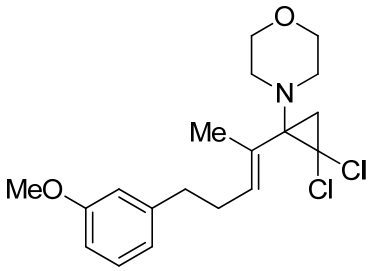


1,1-dichloro-2-morpholino-2-[*E*]-propen-2-ylcyclopropane (1d). This compound was prepared in a manner analogous to **1b**. Cyclopropanation time was 2 minutes. FCC (7 % ethyl acetate in hexanes) provided the desired compound as a shiny white solid, 411 mg, 34 % over 2 steps; m.p. 54-56 ºC; IR (dichloromethane cast film) 2958, 2855, 2828, 1637, 1116 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.26 (app pentet, J = 1.5 Hz, 1H), 4.89-4.88 (m, 1H), 3.67-3.64 (m, 4H), 2.79-2.73 (m, 2H), 2.65-2.60 (m, 2H), 1.93 (dd, J = 1.5, 0.8 Hz, 3H), 1.58 (d, J = 6.8 Hz, 1H), 1.52 (d, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 119.6, 67.7, 66.6, 59.1, 50.4, 34.5, 23.2; HRMS (ESI, M+H) calculated for $C_{10}H_{16}NOCl_2$ m/z 236.0603; found m/z 236.0599.



1,1-dichloro-2-cyclohexen-1-yl-2-morpholinocyclopropane (1e). This compound was prepared in a manner analogous to **1b**. The intermediate enamine was purified by Kugelrohr distillation (100 ºC, 0.5 mmHg) to provide the known enamine **31a**[3] as a colourless liquid, 1.34 g, 69 %. Cyclopropanation time was 15 minutes. The crude cyclopropane was purified by flash column chromatography (20 % ethyl acetate in hexanes) to provide the desired compound as a white solid, 467 mg, 65 %; m.p. 75-77 ºC;

IR (DCM cast film) 2933, 2855, 1655, 1451, 1116; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62-5.59 (m, 1H), 3.67-3.62 (m, 4H), 2.78-2.72 (m, 2H), 2.65-2.60 (m, 2H), 2.26-2.19 (m, 1H), 2.16-2.05 (m, 3H), 1.75-1.64 (m, 2H), 1.58-1.49 (m, 3H), 1.46 (d, *J* = 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.4, 130.8, 67.7, 67.1, 59.4, 50.5, 34.1, 30.3, 25.4, 22.9, 22.5; HRMS (ESI, M+H) calculated for $C_{13}H_{20}NOCl_2$ m/z 276.0916; found m/z 276.0911.



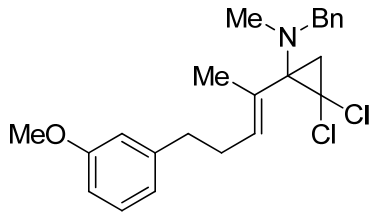
1,1-dichloro-2-morpholino-2-(5-(3-methoxyphenyl)-[2*E*]-penten-2-yl)cyclopropane (1f). 3-(3-Methoxyphenyl)propanal (1.706 g, 10.4 mmol) was dissolved in 100 mL toluene. 2-(Triphenylphosphoranylidene)propanal (3.64 g, 11.4 mmol) was added, and the mixture was heated at reflux for 2 days. The mixture was allowed to cool to room temperature and concentrated. Ether was added, and the flask was placed in a sonicator bath for 1h. Filtration and concentration gave the crude product. FCC (8, 10 % ethyl acetate in hexanes) provided (*E*)-5-(3-methoxyphenyl)-2-methyl-2-pentenal as a pale yellow oil, 1.057 g, 49 %. IR (DCM cast film) 2939, 2835, 2762, 2714, 1685, 1642, 1602, 1585, 1489, 1454, 1262, 1153 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.22 (app t, *J* = 7.9 Hz, 1H), 6.81-6.74 (m, 3H); 6.50 (dq, *J* = 7.2, 1.4 Hz, 1H), 3.80 (s, 3H), 2.82-2.78 (m, 2H), 2.71-2.65 (m, 2H), 1.70 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 160.0, 153.4, 142.5, 140.1, 129.8, 121.0, 114.5, 111.6, 55.4, 34.7, 30.7, 9.4; HRMS (EI, M^+) calculated for $C_{13}H_{16}O_2$ m/z 204.1150; found m/z 204.1146.

A solution of carbon tetrabromide (4.31 g, 13.0 mmol) in 10 mL dichloromethane was added to a stirred solution of triphenylphosphine (6.82 g, 26.0 mmol) in 20 mL dichloromethane at 0 ºC. After 15 minutes of stirring, (*E*)-5-(3-methoxyphenyl)-2-methyl-2-pentenal was added (1.33 g, 6.51 mmol) as a solution in 10 mL dichloromethane. After stirring for 1 h, the reaction was quenched with water, and the resulting layers were separated. The aqueous was extracted once with dichloromethane. Ether was added to the combined extract, the mixture was filtered, and dried over magnesium sulfate then concentrated. Ether was added to the crude mixture, and it was sonicated for 1 hour. The mixture was filtered and concentrated. Hexanes was added, and filtration followed by concentration yielded (3*E*)-1,1-dibromo-6-(3-methoxyphenyl)-3-methyl-1,3-hexadiene as a yellow oil, 1.799 g, 76 %. IR (DCM cast film) 2998, 2936, 2833, 1602, 1584, 1488, 1465, 1262 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.18 (m, 1H), 6.92 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.76-6.73 (m, 2H), 5.70-5.65 (m, 1H), 3.80 (s, 3H), 2.70-2.66 (m, 2H), 2.40 (app q, *J* = 7.6 Hz, 2H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 143.4, 141.0, 134.7, 132.5, 129.6, 121.1, 114.5, 111.4, 86.5, 55.4, 35.4, 30.1, 15.5; HRMS (EI, M-Br) calculated for $C_{14}H_{16}OBr$ m/z 279.0384; found m/z 279.0386.

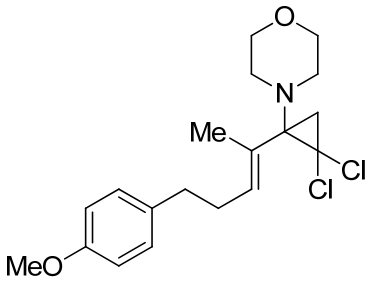
n-Butyllithium (3.9 mL, 2.5 M in hexanes, 9.8 mmol) was added to a solution of (3*E*)-1,1-dibromo-6-(3-methoxyphenyl)-3-methyl-1,3-hexadiene (1.772 g, 4.921 mmol) in 16 mL ether at -78 ºC. The solution was allowed to slowly warm to room temperature and stir 17 h. Water was then added, the layers were separated, and the aqueous was extracted once with hexanes. The combined extract was washed with water then brine, dried over magnesium sulfate and concentrated to provide (*E*)-6-(3-methoxyphenyl)-3-

methylhex-3-en-1-yne as a pale yellow oil, 1.030 g, quantitative. IR (DCM cast film) 3287, 3028, 2938, 2859, 2094, 1585, 1489, 1454, 1437, 1262, 1153, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24-7.16 (m 1H), 6.81-6.71 (m, 3H), 6.02-5.95 (m, 1H), 3.28 (s, 3H), 2.76 (s, 1H), 2.71-2.62 (m, 2H), 2.46-2.35 (m, 2H), 1.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 143.3, 138.8, 129.6, 121.0, 117.8, 114.4, 111.5, 87.0, 74.0, 55.4, 35.3, 30.4, 17.2; HRMS (EI, M^+) calculated for $C_{14}H_{16}O$ m/z 200.1201; found m/z 200.1198.

1,1-Dichloro-2-morpholino-2-(5-(3-methoxyphenyl)-[2*E*]-penten-2-yl)-cyclopropane (**1f**) was prepared from (*E*)-6-(3-methoxyphenyl)-3-methylhex-3-en-1-yne in a manner analogous to **1b**. Cyclopropanation time was 15 minutes. Flash column chromatography (10 % ethyl acetate in hexanes) provided the product as a pale yellow solid, 136 mg, 48 % over 2 steps; m.p. 56-59ºC; IR (dichloromethane cast film) 3008, 2953, 2852, 2833, 1609, 1581, 1489, 1454, 1265 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22-7.17 (m, 1H), 6.78 (br d, *J* = 7.5 Hz, 1H), 6.75-6.72 (m, 2H), 5.38-5.34 (m, 1H), 3.80 (s, 3H), 3.67-3.59 (m, 4H), 2.70-2.63 (m, 4H), 2.53-2.47 (m, 2H), 2.41 (app q, *J* = 7.6 Hz, 2H); 1.79 (s, 3H), 1.53-1.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 143.5, 134.1, 129.6, 128.6, 121.1, 114.6, 111.3, 67.6, 66.9, 60.8, 55.4, 50.4, 35.7, 34.8, 29.8, 18.4; HRMS (ESI, M+H) calculated for $C_{19}H_{26}NO_2Cl_2$ m/z 370.1335; found m/z 370.1337.



1-(*N*-benzyl-*N*-methylamino)-2,2-dichloro-1-(5-(3-methoxyphenyl)-[2*E*]-penten-2-yl)cyclopropane (1g). This compound was prepared from (*E*)-6-(3-methoxyphenyl)-3-methylhex-3-en-1-yne (see **1f**) in a manner analogous to **1b**. Cyclopropanation time was 12 minutes. FCC (2 % ethyl acetate in hexanes) provided **1g** as a pale yellow thick oil, 284 mg, 37 % over two steps; IR (neat) 2938, 2795, 1663, 1601, 1585, 1492, 1454 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H), 7.24-7.19 (m, 2H), 6.81 (br d, *J* = 7.7 Hz, 1H), 6.77-6.74 (m, 2H), 5.45 (br t, *J* = 7.2 Hz, 1H), 3.82-3.76 (m, 4H), 3.52 (d, *J* = 13.4 Hz, 1H), 2.78-2.67 (m, 2H), 2.53-2.42 (m, 2H), 2.13 (s, 3H), 1.87 (s, 3H), 1.63-1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 143.6, 139.5, 133.7, 129.5, 129.2, 128.6, 128.4, 127.2, 121.2, 114.6, 111.3, 67.7, 61.6, 59.1, 55.4, 38.3, 35.7, 35.6, 29.8, 18.4; HRMS (ESI, M+H) calculated for $C_{23}H_{28}Cl_2NO$ m/z 404.1542, found m/z 404.1538.

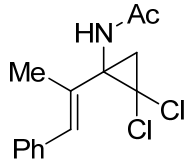


1,1-dichloro-2-(5-(3-methoxyphenyl)-[2*E*]-penten-2-yl)-2-morpholinocyclopropane (1h). (*E*)-5-(4-methoxyphenyl)-2-methyl-2-pentenal was synthesized in a manner analogous to (*E*)-5-(3-methoxyphenyl)-2-methyl-2-pentenal (see **1f**). FCC (7 % ethyl acetate in hexanes) provided (*E*)-5-(4-methoxyphenyl)-2-methyl-2-pentenal as a colourless oil, 755 mg, 72 %; IR (neat) 2997, 2934, 2835, 2714, 1686, 1644, 1612, 1513, 1247 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.13-7.09 (m, 2H), 6.86-6.82 (m, 2H), 6.49 (tq, *J* = 7.2, 1.4 Hz, 1H), 3.80 (s, 3H), 2.79-2.74 (m, 2H), 2.67-2.62 (m, 2H), 1.70-1.67 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 158.4, 153.6, 140.1, 132.9,

129.5, 114.2, 55.5, 33.8, 31.2, 9.4; HRMS (EI, M^+) calculated for $C_{13}H_{16}O_2$ m/z 204.1150, found m/z 204.1143.

(*E*)-6-(4-Methoxyphenyl)-3-methylhex-3-en-1-yne was synthesized from (*E*)-5-(4-methoxyphenyl)-2-methyl-2-pentenal in a manner analogous to (*E*)-6-(3-methoxyphenyl)-3-methylhex-3-en-1-yne (see **1f**), and was isolated as a pale yellow oil, 584 mg, 81 % over 2 steps. IR ($CDCl_3$ cast film) 3287, 2932, 2856, 2093, 1612, 1584, 1513, 1465, 1247 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12-7.07 (m, 2H), 6.85-6.81 (m, 2H), 5.98 (tq, *J* = 7.4, 1.5 Hz, 1H), 3.79 (s, 3H), 2.76 (s, 1H), 2.65-2.61 (m, 2H), 2.40-2.35 (m, 2H), 1.74-1.73 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 138.9, 133.7, 129.5, 117.7, 114.1, 87.1, 73.9, 55.5, 34.4, 30.8, 17.2; HRMS (EI, M^+) calculated for $C_{14}H_{16}O$ m/z 200.1201; found m/z 200.1203.

This compound was prepared from (*E*)-6-(4-methoxyphenyl)-3-methylhex-3-en-1-yne in a manner analogous to **1b**. Cyclopropanation time was 16 minutes. FCC (10 % ethyl acetate in hexanes) provided **1h** as an off-white powder, 275 mg, 26 % over two steps; m.p. 61-65 ºC; IR (neat) 2967, 2852, 1612, 1512, 1453 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.11-7.07 (m, 2H), 6.84-6.81 (m, 2H), 5.36 (br t, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 3.69-3.60 (m, 4H), 2.72-2.60 (m, 4H), 2.56-2.47 (m, 2H), 2.42-2.33 (m, 2H), 1.78 (s, 3H), 1.54-1.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 134.2, 134.0, 129.5, 128.5, 114.0, 67.6, 67.0, 60.8, 55.5, 50.3, 34.8, 34.7, 30.1, 18.4; HRMS (ESI, M+H) calculated for $C_{19}H_{26}Cl_2NO_2$ m/z 370.1335, found m/z 370.1330.



1-acetamido-2,2-dichloro-3-(1-phenyl-[1*E*]-propen-2-yl)cyclopropane (1i). Hydroxylamine hydrochloride (477 mg, 6.86 mmol) was dissolved in 3.1 mL methanol. Sodium acetate (563 mg, 6.86 mmol) was added, and the resulting mixture was stirred for 30 minutes. (*E*)-2-methyl-1-phenyl-1-buten-3-one (1.00 g, 6.24 mmol) was added in one portion, and the reaction was allowed to stir 4 hours. Water was added, and the product was removed by filtration. No further purification was necessary. 2-Methyl-1-phenyl-1-buten-3-one oxime was provided as a white powder, 1.030 g, 94 %. Data for this compound are consistent with that reported in the literature.[4]

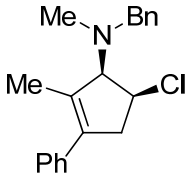
The oxime (993 mg, 5.67 mmol) was dissolved in 16 mL toluene. Acetic anhydride (1.6 mL, 17 mmol) and acetic acid (0.95 mL, 17 mmol) were added, followed by iron powder (697 mg, 12.5 mmol). The mixture was heated at 75 ºC for 8 hours, then allowed to cool and filtered. The filtrate was washed twice with 2M aqueous sodium hydroxide, then dried over magnesium sulfate and concentrated to a white solid. 1.20 g of the acetylated oxime was isolated, 97 %. IR (neat) 3068, 2971, 2859, 1767, 1625, 1575 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.35-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.05 (br s, 1H), 2.25 (s, 3H), 2.25 (s, 3H), 2.16 (d, J = 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 164.6, 136.8, 134.2, 134.2, 129.6, 128.5, 127.8, 20.2, 14.7, 12.8; HRMS (ESI, M+Na) calculated for $C_{13}H_{15}NO_2Na$ m/z 240.0995, found m/z 240.0993.

The material was resubjected to the above conditions with the following reagent purification: the acetic anhydride was freshly distilled over phosphorus pentoxide, some acetic anhydride was added to the acetic acid and then the acetic acid was distilled, and freshly prepared Rieke iron was used. The reaction was worked up after two hours, and

FCC (40 %, 50 % ethyl acetate in hexanes) provided the desired enamide (**6**) as a white solid, 310 mg, 45 %; m.p. 97-100ºC; IR (neat) 3231, 3140, 3026, 2923, 2822, 1659, 1613, 1546, 1446 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H), 6.69 (br s, 1H), 6.61 (br s, 1H), 5.66 (br s, 1H), 5.21 (br s, 1H), 2.16 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 141.9, 137.4, 134.6, 129.4, 128.5, 127.2, 127.0, 106.0, 30.0, 15.9; HRMS (EI, M+Na) calculated for $C_{13}H_{15}NONa$ m/z 224.1046, found m/z 224.1041.

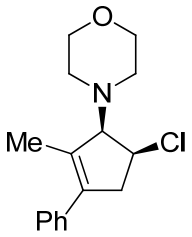
Enamide **6** was subjected to the standard cyclopropanation conditions (see **1b**, 15 min.) and FCC (40 % ethyl acetate in hexanes) to provide **1i** as a tan solid, 184 mg, 49 %; m.p. (decomposed) 142 ºC; IR (neat film) 3241, 3200, 3038, 2860, 1661, 1549, 1447 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.27-7.24 (m, 2H), 7.23-7.18 (m, 1H), 6.67 (s, 1H), 6.35 (br s, 1H), 2.38 (d, J = 8.8 Hz, 1H), 2.01 (d, J = 1.1 Hz, 3H), 2.00 (s, 3H), 1.93 (d, J = 8.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 136.9, 132.5, 131.8, 129.3, 128.4, 127.2, 64.5, 49.2, 33.0, 23.8, 16.2; HRMS (ESI, M+H) calculated for $C_{14}H_{16}Cl_2NO$ m/z 284.0603; found m/z 284.0602.

Imino-Nazarov/Reduction Procedure



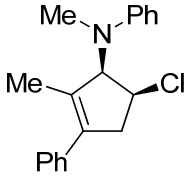
***cis*-3-(*N*-benzyl-*N*-methylamino)-4-chloro-1-phenyl-2-methylcyclopentene (3a).** Cyclopropane **1a** (60 mg, 0.17 mmol) was dissolved in 3.5 mL acetonitrile. Silver triflimide (66 mg, 0.17 mmol) was added, and the solution was heated to reflux for 5h, during which the solution became a raspberry red and white precipitate was formed. The mixture was allowed to cool to room temperature, and then filtered through a pad of

Celite and concentrated to a dark oil. The oil was dissolved in 2 mL methanol, taking no precaution to exclude the ambient atmosphere, and sodium borohydride (13 mg, 0.34 mmol) was added in one portion. The reaction bubbled vigorously, and some black precipitate was formed. After 5 minutes, the reaction mixture was poured into water, and 2 M sodium hydroxide (~ 0.2 mL) was added to ensure the solution was basic. The mixture was extracted three times with dichloromethane. The combined extract was washed with water then brine, dried over magnesium sulfate, filtered, and concentrated. FCC (10 % dichloromethane, 1 % ethyl acetate, 0.5 % triethylamine in hexanes) provided the product as a colourless resin, 28.4 mg, 53 % (54 % BORSM) and 2.0 mg recovered starting material, 3 %. IR (neat) 3060, 2933, 2854, 1600, 1494, 1451 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.22 (m, 10H), 4.73-4.67 (m, 1H), 4.15 (s, 2H), 3.94 (d, J = 7.3 Hz, 1H), 3.16-3.03 (m, 2H), 2.53 (s, 3H), 1.97-1.94 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 137.1, 136.0, 134.9, 128.48, 128.47, 128.43, 128.0, 127.3, 126.9, 75.1, 60.4, 58.7, 46.3, 37.4, 14.6; HRMS (ESI, M+H) calculated for $C_{20}H_{23}NCl$ m/z 312.1514; found m/z 312.1507.

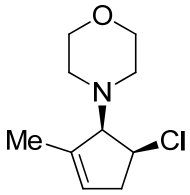


***cis*-4-chloro-1-phenyl-2-methyl-3-morpholinocyclopentene (3b).** Cyclopropane **2b** (100 mg, 0.320 mmol) was subjected to the Imino-Nazarov procedure (8.5 h) followed by reduction and FCC (10 % dichloromethane, 5 % ethyl acetate, 0.5 % triethylamine in hexanes) to provide the product as a thick colourless oil that quickly darkened to a brown oil on standing, 47.1 mg, 53 % (57 % BORSM), and 7.3 mg recovered starting material.

IR (neat) 3055, 2952, 2852, 1600, 1495, 1446, 1115; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.31-7.25 (m, 2H), 4.64-4.58 (m, 1H), 3.72-3.58 (m, 5H), 3.12-3.01 (m, 3H), 3.01-2.89 (m, 3H), 1.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 136.7, 134.1, 128.5, 127.9, 127.5, 75.8, 68.3, 59.4, 49.8, 46.2, 14.9; HRMS (ESI, M+H) calculated for $C_{16}H_{21}NOCl$ m/z 278.1306; found m/z 278.1302.

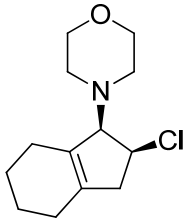


***cis*-4-chloro-1-phenyl-2-methyl-3-(*N*-methyl-*N*-phenylamino)cyclopentene (3c)**. Cyclopropane **1c** (100 mg, 0.301 mmol) was subjected to the Imino-Nazarov procedure (7.5 h) followed by reduction and FCC (15 % dichloromethane in hexanes) to provide the product as a pale yellow solid, 45.4 mg, 50 %; m.p. 69-71 ºC; IR (chloroform cast film) 3057, 2926, 2854, 1597, 1504, 1444 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 -7.24 (m, 7H), 6.90-6.86 (m, 2H), 6.75 (app dt, *J* = 7.3, 0.9 Hz, 1H), 4.98 (d, *J* = 7.5 Hz, 1H), 4.85 (ddd, *J* = 8.0, 7.5, 6.5 Hz, 1H), 3.31 (ddq, *J* = 16.5, 8.0, 1.9 Hz, 1H), 3.16-3.07 (m, 1H), 2.91 (s, 3H), 1.85-1.83 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 136.8, 136.7, 133.4, 129.3, 128.6, 127.9, 127.7, 117.0, 112.9, 70.6, 58.4, 46.7, 33.7, 14.5; HRMS (ESI, M+H) calculated for $C_{19}H_{21}NCl$ m/z 298.1357; found m/z 298.1351.

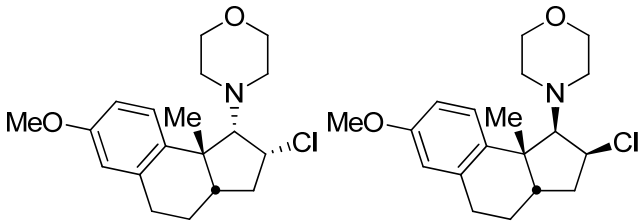


***cis*-4-chloro-2-methyl-3-morpholinocyclopentene (3d).** Cyclopropane **1d** (70.1 mg, 0.297 mmol) was subjected to the Imino-Nazarov procedure (2 h) followed by reduction

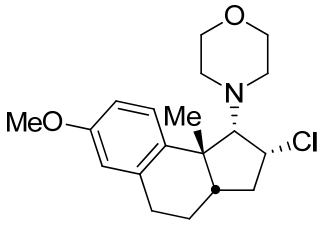
and FCC (10 % dichloromethane, 5 % ethyl acetate, 0.5 % triethylamine in hexanes) to provide the product as a colourless oil which darkened to brown, 13.9 mg, 23 % (29 % BORSM) and 16.4 mg recovered starting material, 23 %; IR (chloroform cast film) 2953, 2852, 1584, 1116 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (br s, 1H), 4.46-4.50 (m, 1H), 3.70-3.61 (m, 4H), 3.49 (d, *J* = 7.1 Hz, 1H), 3.01-2.94 (m, 2H), 2.87-2.81 (m, 2H), 2.72 (dddq, *J* = 16.3, 8.2, 3.5, 1.7 Hz, 1H), 2.46 (dddq, *J* = 16.2, 8.1, 4.6, 2.6 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 126.4, 73.2, 68.1, 60.3, 49.7, 42.3, 16.6; HRMS (ESI, M+H) calculated for $C_{10}H_{17}NOCl$ m/z 202.0993; found m/z 202.0989.



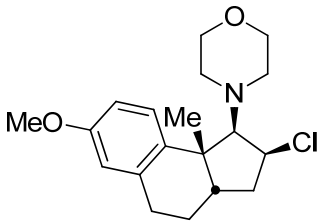
$\Delta^{1,6}$-8-chloro-7-mopholinobicyclo[4.3.0]nonene (3e). Cyclopropane **1e** (25.9 mg, 0.0938 mmol) was subjected to the Imino-Nazarov procedure (10 min) followed by reduction and FCC (10 % dichloromethane, 5 % ethyl acetate, 0.5 % triethylamine in hexanes) to provide the product as a colourless oil which darkened to brown, 3.3 mg, 14 % (16 % BORSM) and 3.2 mg recovered starting material, 12 %. IR ($CDCl_3$ cast film) 2927, 2853, 1448, 1116 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.50-4.45 (m, 1H), 3.69-3.61 (m, 4H), 3.48 (d, *J* = 7.4 Hz, 1H), 2.89-2.84 (m, 2H), 2.81-2.76 (m, 2H), 2.61 (dd, *J* = 15.9, 8.2 Hz, 1H), 2.50-2.43 (m, 1H), 2.15-1.88 (m, 4H), 1.72-1.51 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 133.8, 73.4, 68.1, 59.6, 50.0, 45.7, 25.9, 25.8, 23.1 (one of the aliphatic cyclohexenyl carbons is missing due to incidental overlap); HRMS (ESI, M+H) calculated for $C_{13}H_{21}ClNO$ m/z 242.1306; found m/z 242.1302.



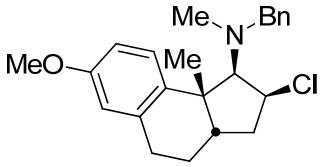
2-chloro-7-methoxy-9b-methyl-1-morpholino-2,3,3a,4,5,9b-hexahydro-cyclopenta[a]naphthalenes (8f) and (8f′). Cyclopropane **1f** (50.1 mg, 0.135 mmol) was subjected to the Imino-Nazarov procedure (2 h) followed by reduction and FCC (10 % ethyl acetate, 0.5 % triethylamine in hexanes). The first compound to elute was **8f′**, 13.2 mg white solid, 30 % followed by **8f**, 15.7 mg white solid that quickly turned pale pink, 38 %.



8f: mp 84-90 ºC; IR (dichloromethane cast film) 3001, 2958, 2855, 2805, 1609, 1572, 1499, 1462, 1169 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.51 (td, *J* = 7.2, 5.6, Hz, 1H), 3.78 (s, 3H), 3.58-3.52 (m, 2H), 3.44-3.38 (m, 2H), 2.93 (d, *J* = 5.6 Hz, 1H), 2.87-2.78 (m, 5H), 2.60 (dt, *J* = 16.1, 5.1 Hz, 1H), 2.43 (ddd, *J* = 13.6, 8.5, 7.2 Hz, 1H), 2.07-1.91 (m, 3H), 1.68-1.62 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 138.4, 133.4, 132.4, 112.5, 111.6, 79.1, 67.4, 61.4, 55.3, 52.5, 46.5, 44.2, 39.8, 36.3, 27.2, 24.8; HRMS (ESI, M+H) calculated for $C_{19}H_{27}NO_2Cl$ m/z 336.1725; found m/z 336.1726.

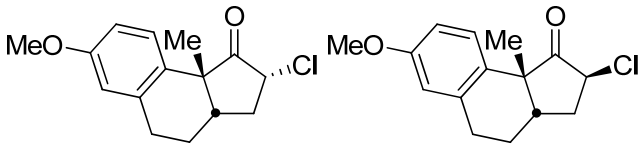


8f′: mp 108-110 ºC; IR (dichloromethane cast film) 3001, 2964, 2857, 1609, 1499, 1470, 1139 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 1H), 6.74 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 4.26-4.21 (m, 1H), 3.80-3.66 (m, 7H), 3.21 – 3.16 (m, 2H), 3.02 (d, *J* = 5.2 Hz, 1H), 2.99-2.93 (m, 2H), 2.79-7.71 (m, 1H), 2.60-2.54 (m, 2H), 2.17 (ddd, *J* = 13.9, 10.1, 7.2 Hz, 1H), 2.12-2.05 (m, 1H), 1.88-1.80 (m, 1H), 1.69 (ddd, *J* = 13.3, 7.9, 3.8 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 137.8, 137.6, 128.9, 113.1, 113.0, 79.6, 68.3, 61.1, 55.4, 52.9, 47.5, 42.8, 39.1, 27.8, 25.8, 24.3; HRMS (ESI, M+H) calculated for $C_{19}H_{27}NO_2Cl$ m/z 336.1725; found m/z 336.1719.



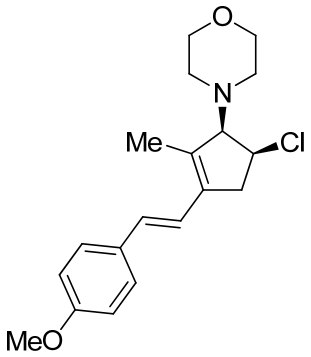
1-(*N*-benzyl-*N*-methylamino)-2-chloro-7-methoxy-9b-methyl-2,3,3a,4,5,9b-hexahydro-cyclopenta[a]naphthalene (8g′). Cyclopropane **1g** (35.4 mg, 0.0875 mmol) was subjected to the imino-Nazarov procedure (2h) followed by reduction and FCC (10 % DCM, 5 % toluene, 0.5 % triethylamine in hexanes on neutral alumina). The major isomer could not be recovered. Compound **8g′** was provided as a colourless film, 10.5 mg, 32 %; IR (neat) 3026, 2925, 2855, 1736, 1608, 1584, 1498, 1453 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.37-7.33 (m, 2H), 7.29-7.25 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.51 (d, *J* = 2.7 Hz, 1H), 4.23-4.14 (m, 3H), 3.75 (s, 3H), 3.37 (d, *J* = 5.8 Hz, 1H), 2.84-2.75 (m, 1H), 2.70 (s, 3H), 2.66-2.60 (m, 1H),

2.59-2.53 (m, 1H), 2.38-2.29 (m, 1H), 2.20-2.13 (m, 1H), 1.87-1.80 (m, 1H), 1.75-1.68 (m, 1H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 141.3, 137.8, 137.6, 129.1, 128.8, 128.5, 127.0, 113.2, 112.9, 62.4, 61.6, 55.4, 48.9, 43.0, 39.4, 39.3, 27.8, 25.4, 24.0 (one aliphatic carbon is missing due to incidental overlap); HRMS (EI, M^+) calculated for $C_{23}H_{29}NOCl$ m/z 369.1859, found m/z 369.1856.



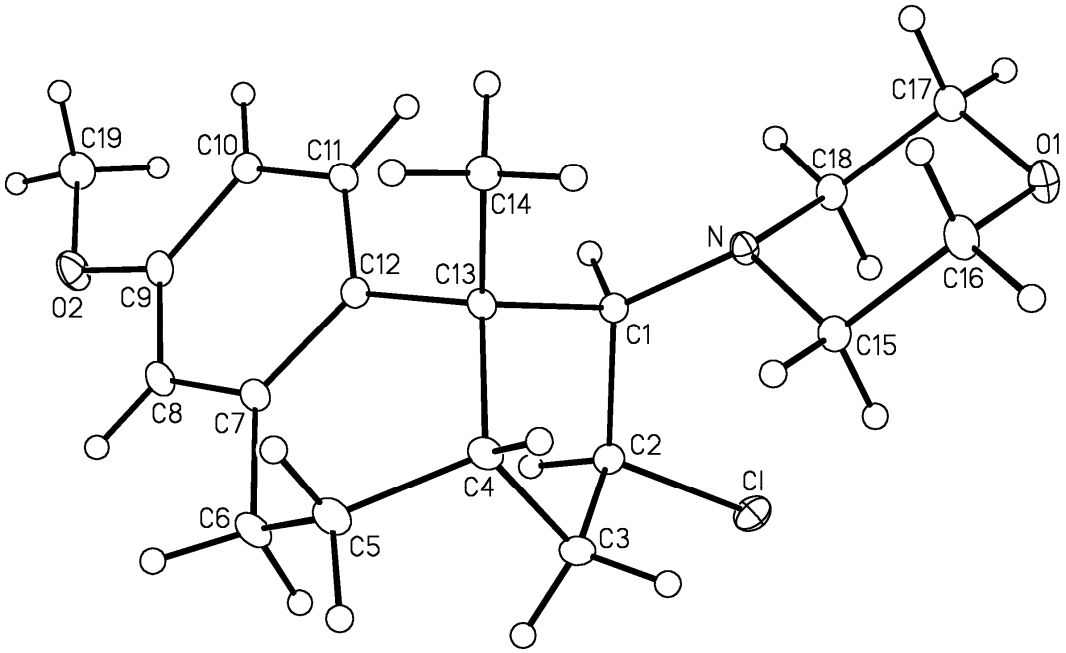
2-chloro-7-methoxy-9b-methyl-2,3,3a,4,5,9b-hexahydro-cyclopenta[a]naphthalen-1-ones (10g) and (10g′). Cyclopropane **1g** (20 mg, 0.049 mmol) was subjected to the Imino-Nazarov procedure (2h), and then 1 mL acetonitrile and 1 mL water was added. The solution was allowed to stand overnight, then it was transferred to a separatory funnel and water was added. The solution was extracted three times with dichloromethane. The combined extract was washed with water then brine, dried over magnesium sulfate and concentrated to a brown film. FCC (10 % DCM, 2 % ethyl acetate in hexanes) provided the products, 10 mg, 76 % in a 1.2 : 1 ratio. Data for **10g** is consistent with that previously reported.[5]

10g′: IR (neat) 2927, 2859, 1750, 1608, 1575 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl^3$) δ 7.45 (d, J = 8.8 Hz, 1H), 6.76 (dd, J = 8.8, 2.8 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 4.25 (dd, J = 7.6, 4.4 Hz, 1H), 3.76 (s, 3H), 2.86 – 2.73 (m, 2H), 2.63-2.57 (m, 1H), 2.33 (ddd, J = 14.2, 9.0, 7.8 Hz, 1H), 2.18 (ddd, J = 14.2, 6.8, 4.4 Hz, 1H), 1.79 (ddd, J = 13.9, 11.1, 5.6 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.8, 158.5, 137.3, 130.1, 127.1, 114.0, 113.2, 57.1, 55.4, 50.3, 40.3, 34.1, 28.1, 26.3, 22.8; HRMS (EI, M^+) calculated for $C_{15}H_{17}O_2Cl$ m/z 264.0917; found m/z 264.0916.



1-(4-methoxycinnamyl)-2-methyl-3-morpholinocyclopentene (11h). Cyclopropane **1h** (30.0 mg, 0.0810 mmol) was subjected to the imino-Nazarov procedure (2h) followed by reduction. FCC (10 % acetone, 1 % triethylamine in hexanes) provided **11h** as a white solid, 8.2 mg, 33 %; m.p. 93-95 ºC; IR (chloroform cast film) 3030, 2849, 2811, 1604, 1511, 1453, 1247 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.88-6.84 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.83-3.77 (m, 4H), 3.73-3.64 (m, 4H), 2.58-2.45 (m, 2H), 2.45-2.40 (m, 4H), 2.00-1.93 (m, 1H), 1.85 (s, 3H), 1.79-1.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 137.4, 136.9, 131.0, 128.9, 127.7, 121.5, 114.3, 75.4, 67.8, 55.6, 48.8, 31.6, 19.8, 12.7; HRMS (ESI, M+H) calculated for $C_{19}H_{26}NO_2$ m/z 300.1958; found m/z 300.1954.

ORTEP Structure for Compound **8f′**.



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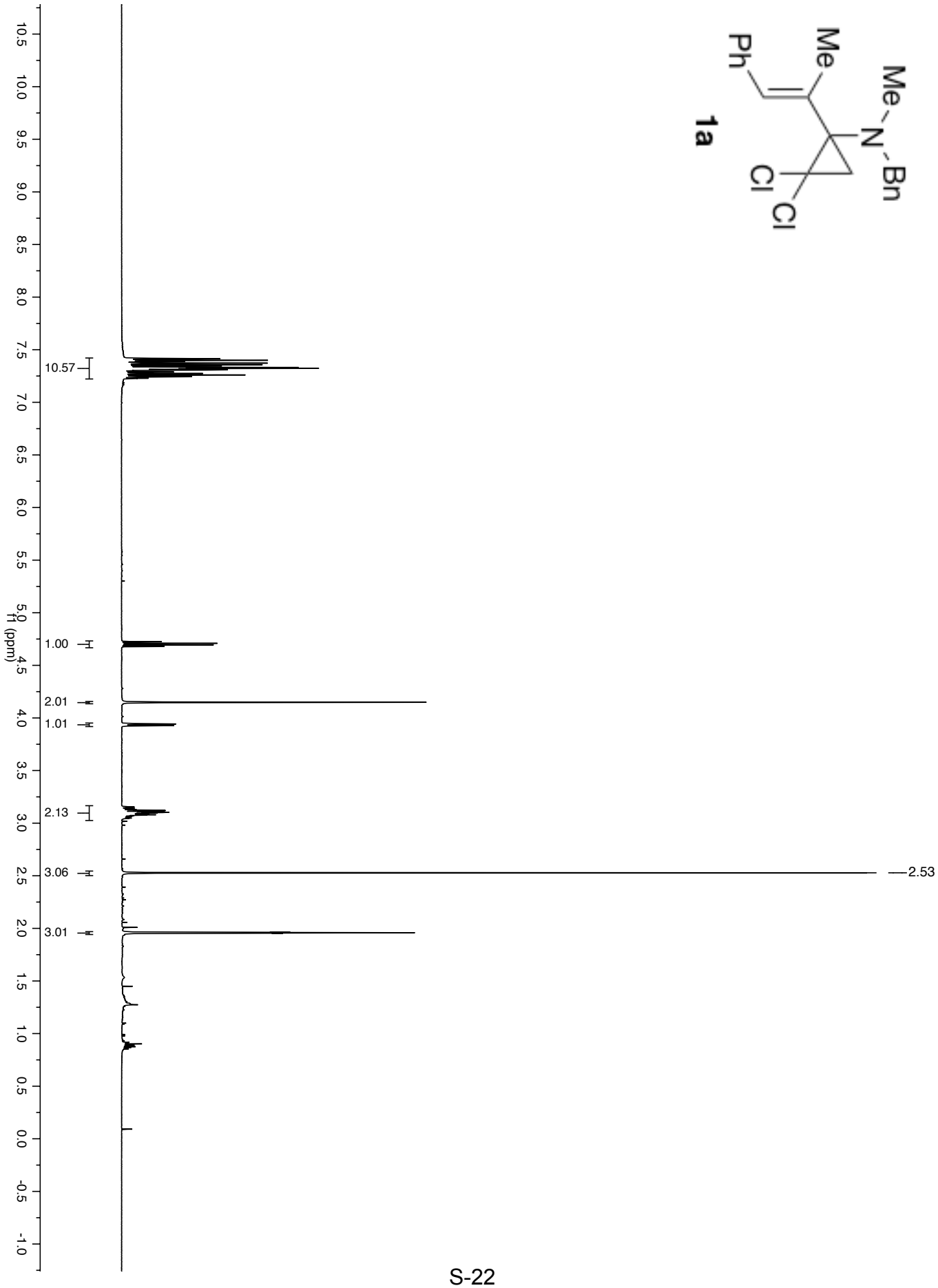
5. Grant, T. N.; West, F. G. *Org. Lett.* **2007**, *9*, 3789.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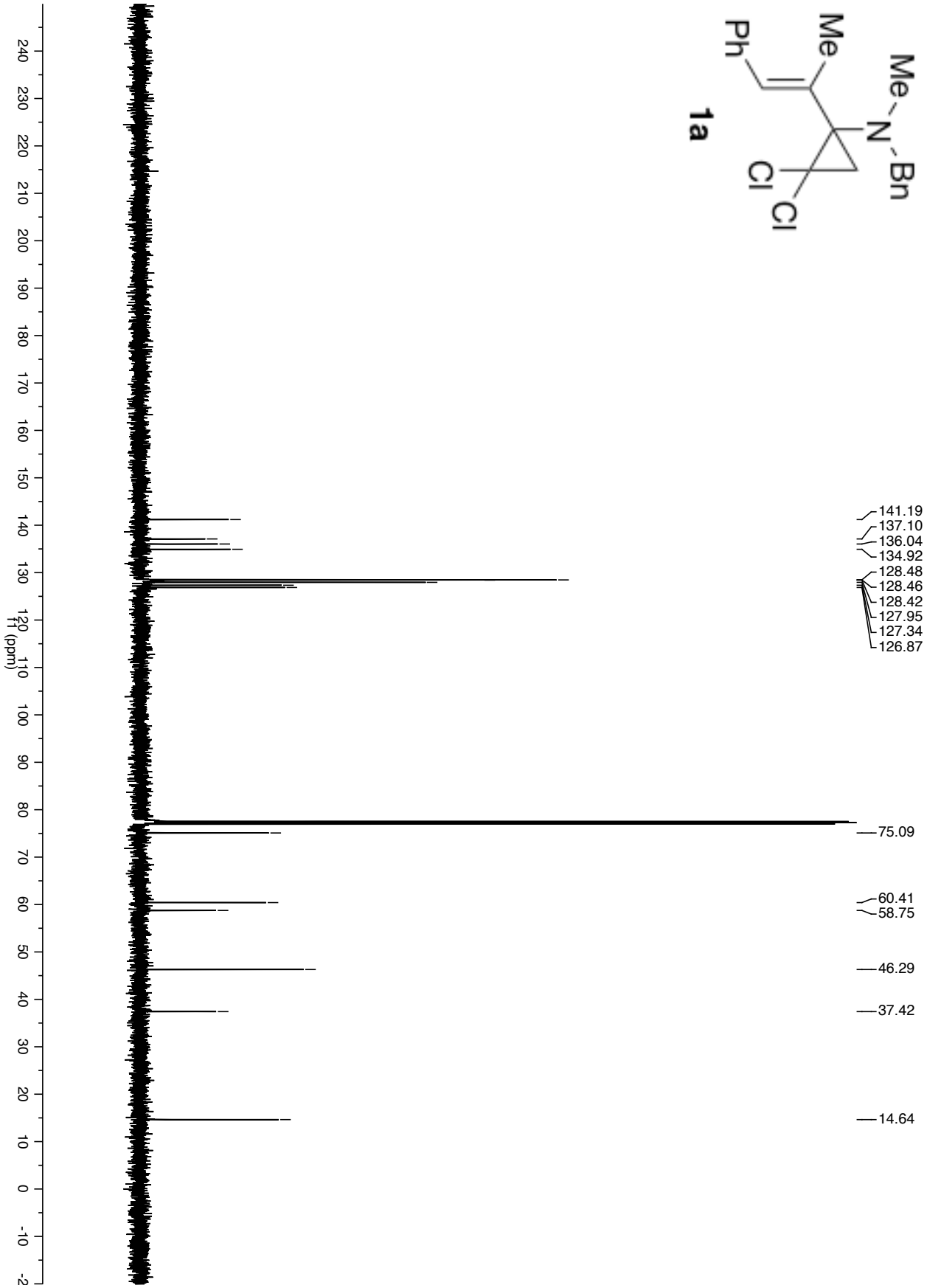
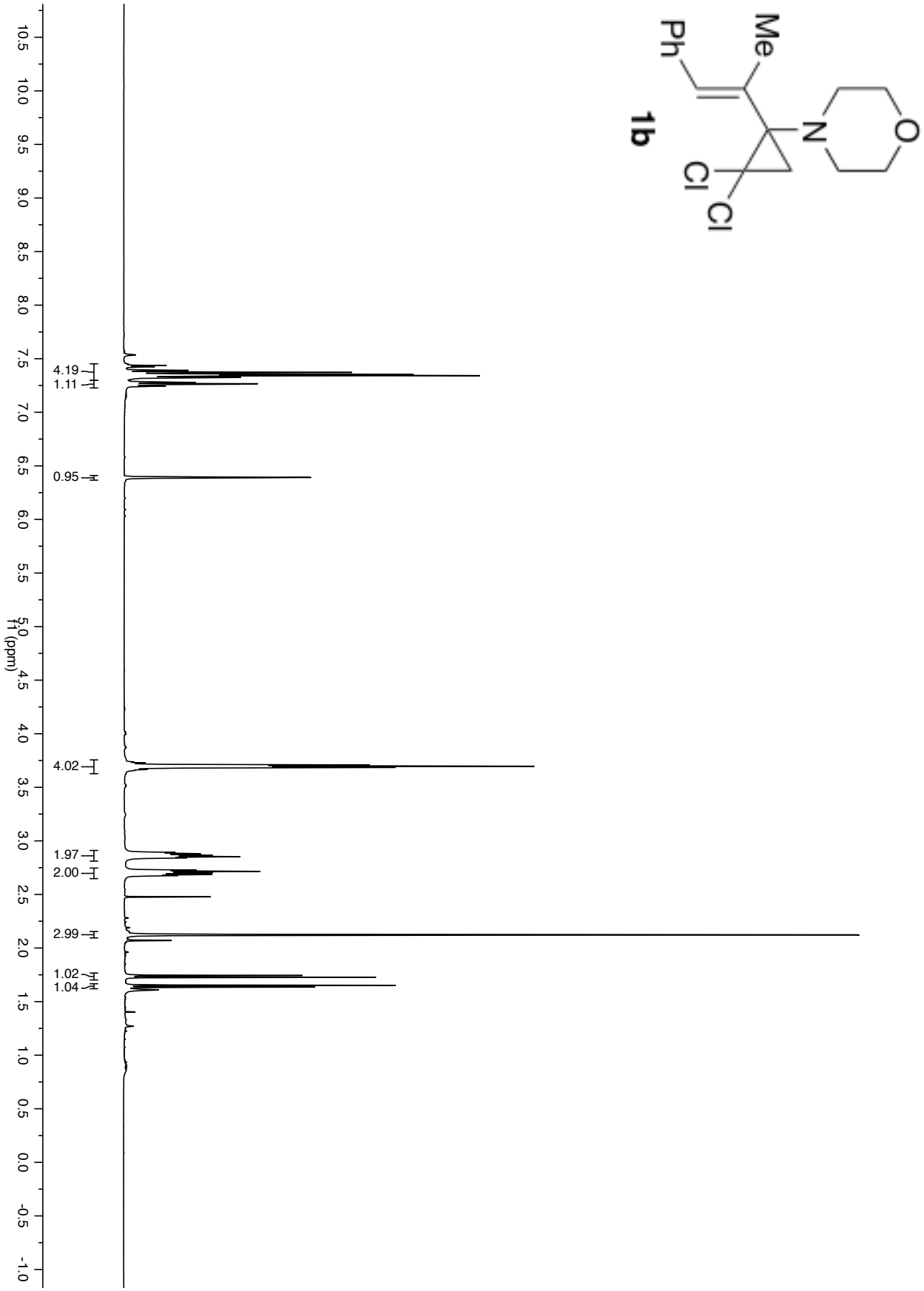
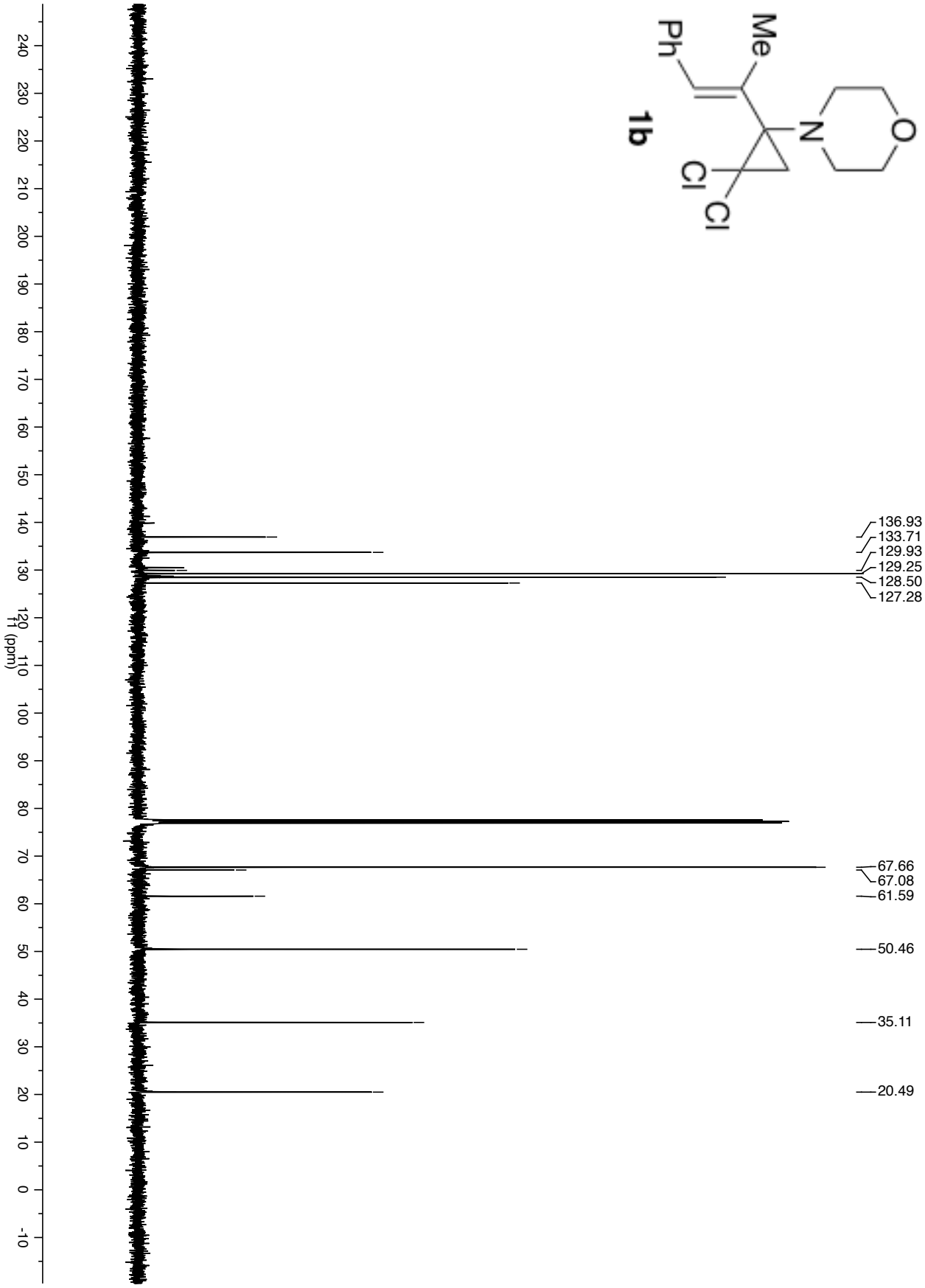
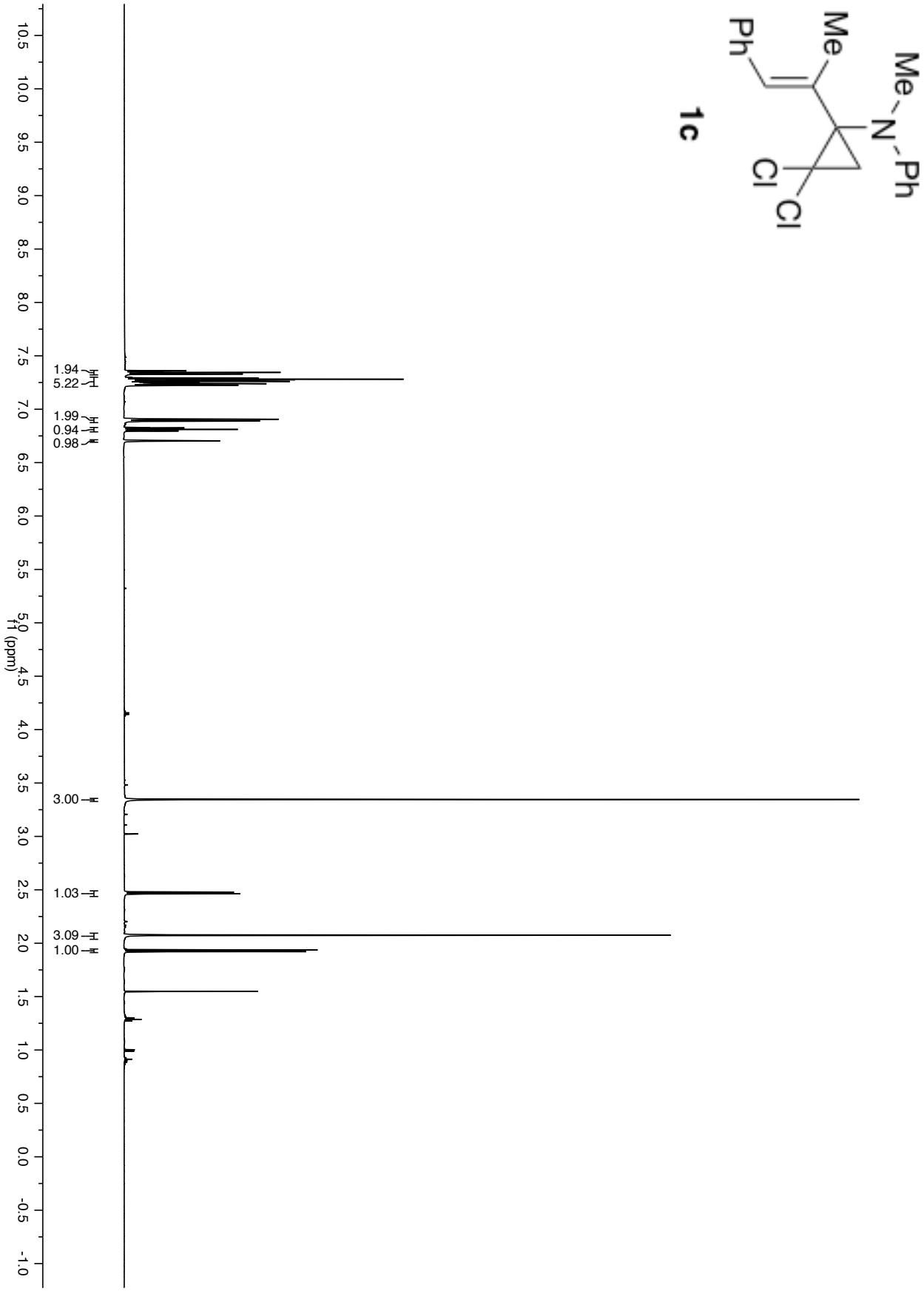
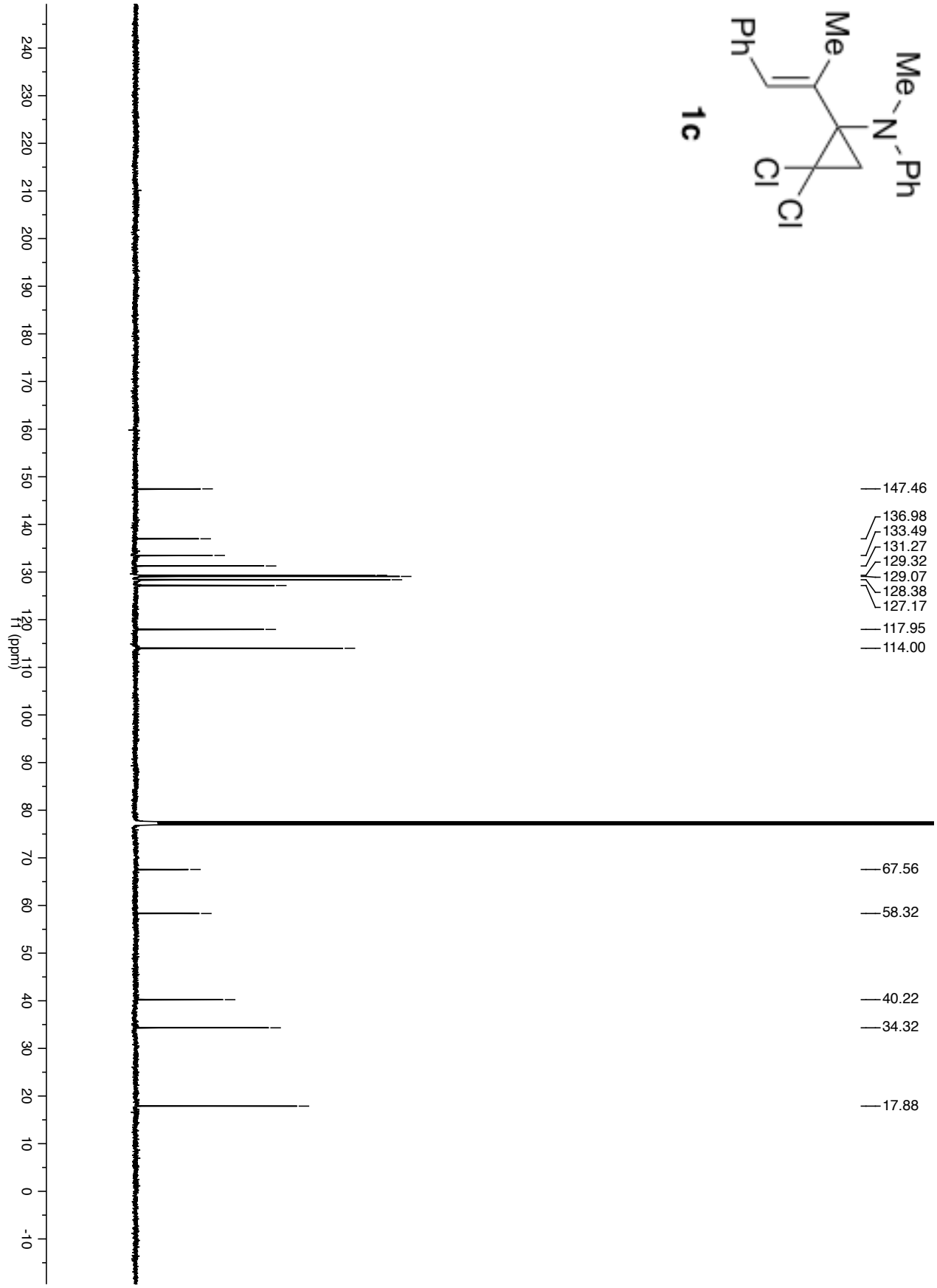
N
Bn
Ph
Cl
Cl
1a
10.57
1.00
2.01
1.01
2.13
3.06
3.01
2.53
f1 (ppm)


Me
N
Bn
Ph
Cl
Cl
1a
141.19
137.10
136.04
134.92
128.48
128.46
128.42
127.95
127.34
126.87
75.09
60.41
58.75
46.29
37.42
14.64
f1 (ppm)


Ph
Me
N
O
Cl
Cl
1b
4.19
1.11
0.95
4.02
1.97
2.00
2.99
1.02
1.04
f1 (ppm)


Ph
Me
N
O
Cl
Cl
1b
136.93
133.71
129.93
129.25
128.50
127.28
67.66
67.08
61.59
50.46
35.11
20.49
f1 (ppm)


Me
N
Ph
Cl
Cl
Ph
1c
1.94
5.22
1.99
0.94
0.98
3.00
1.03
3.09
1.00
f1 (ppm)


Me
N
Ph
Ph
Cl
Cl
1c
147.46
136.98
133.49
131.27
129.32
129.07
128.38
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114.00
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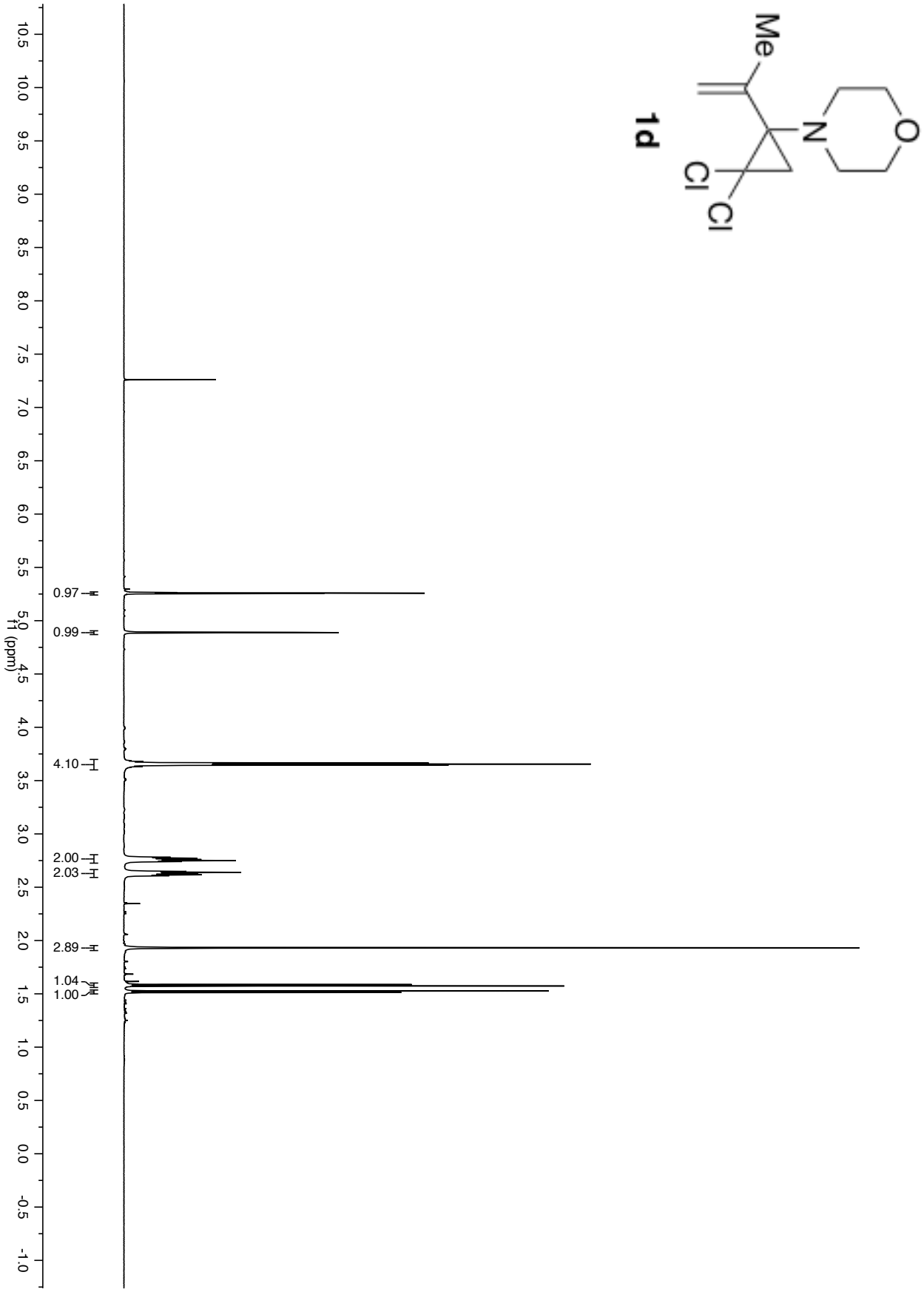
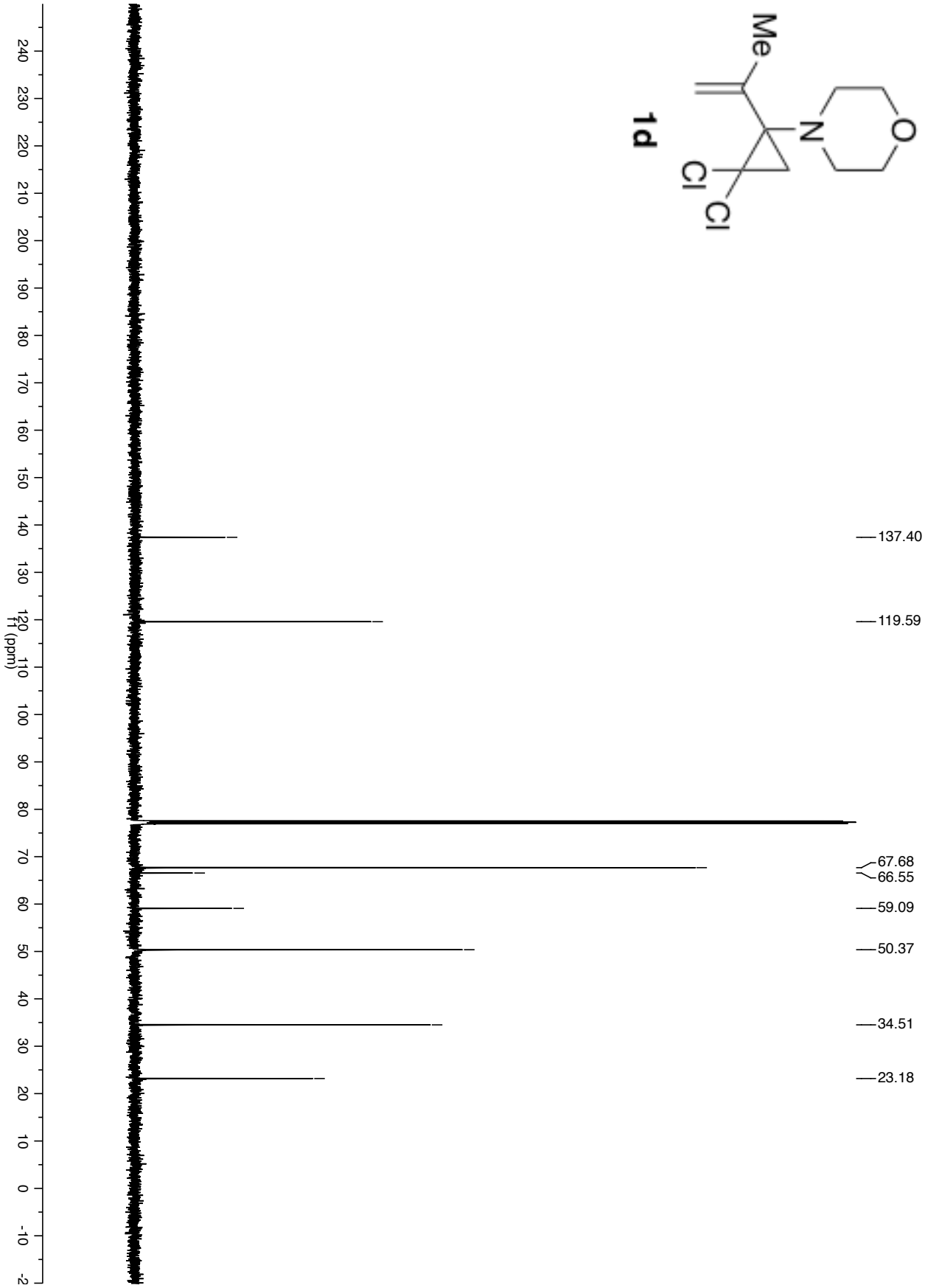
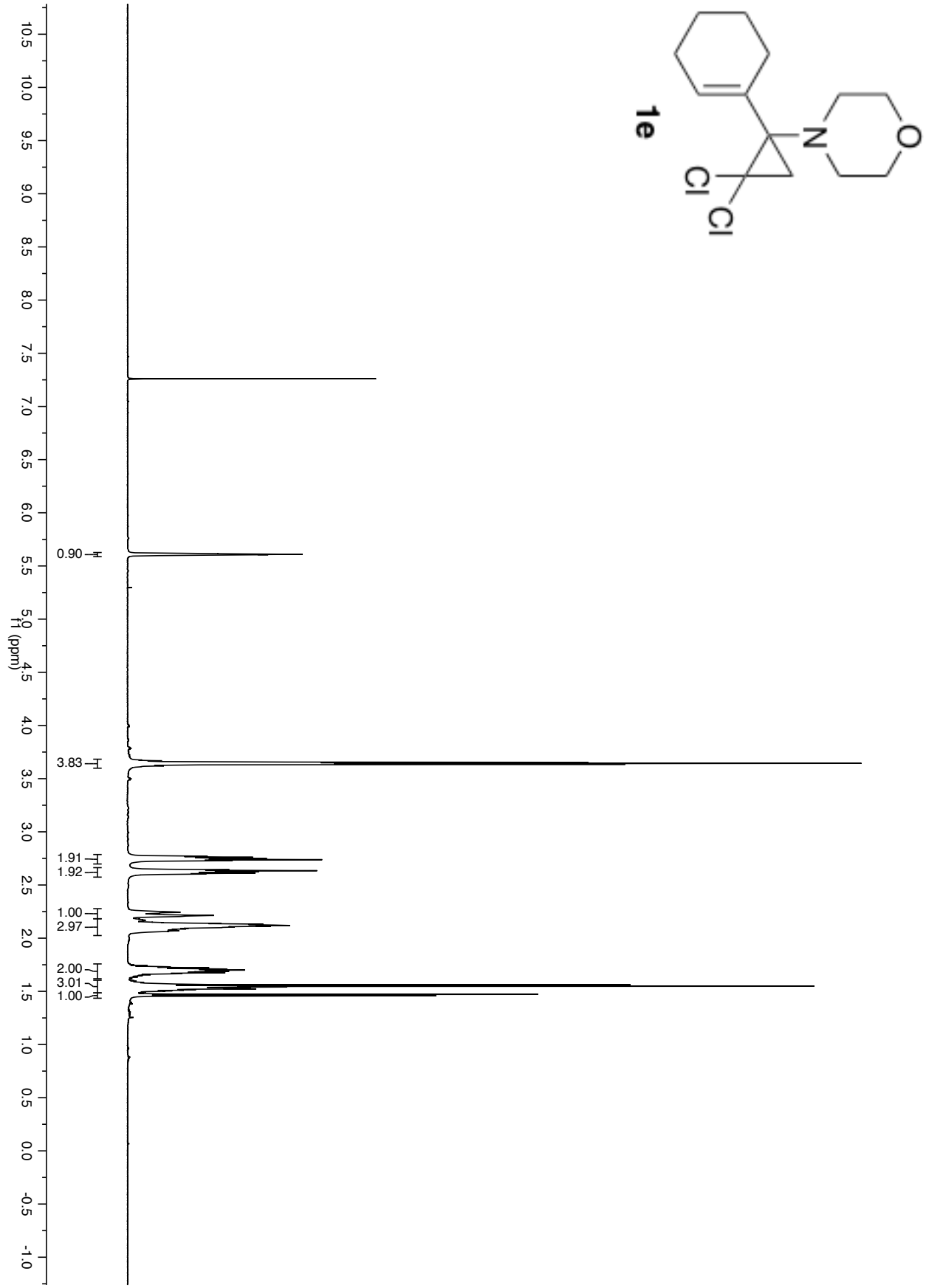
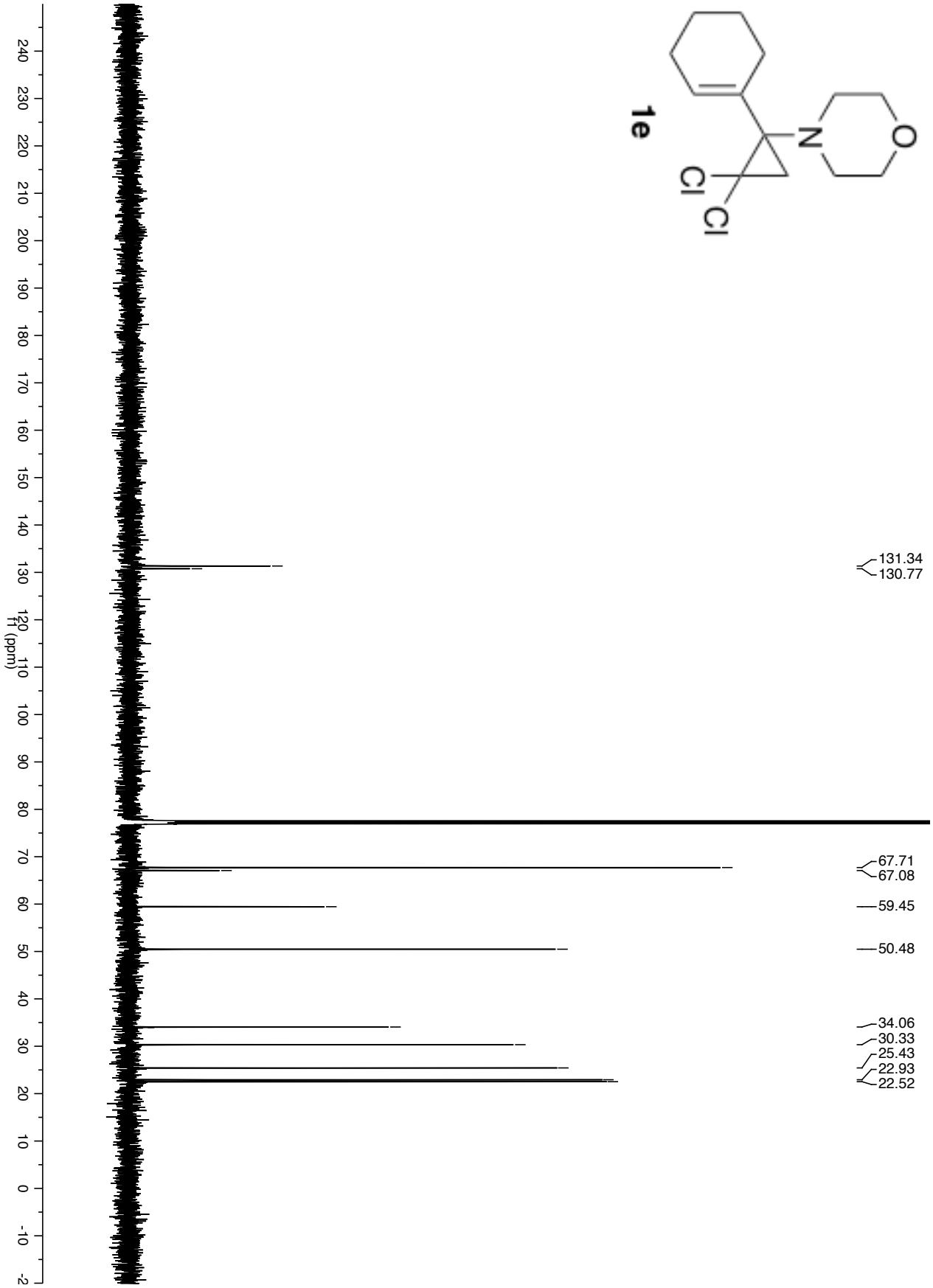
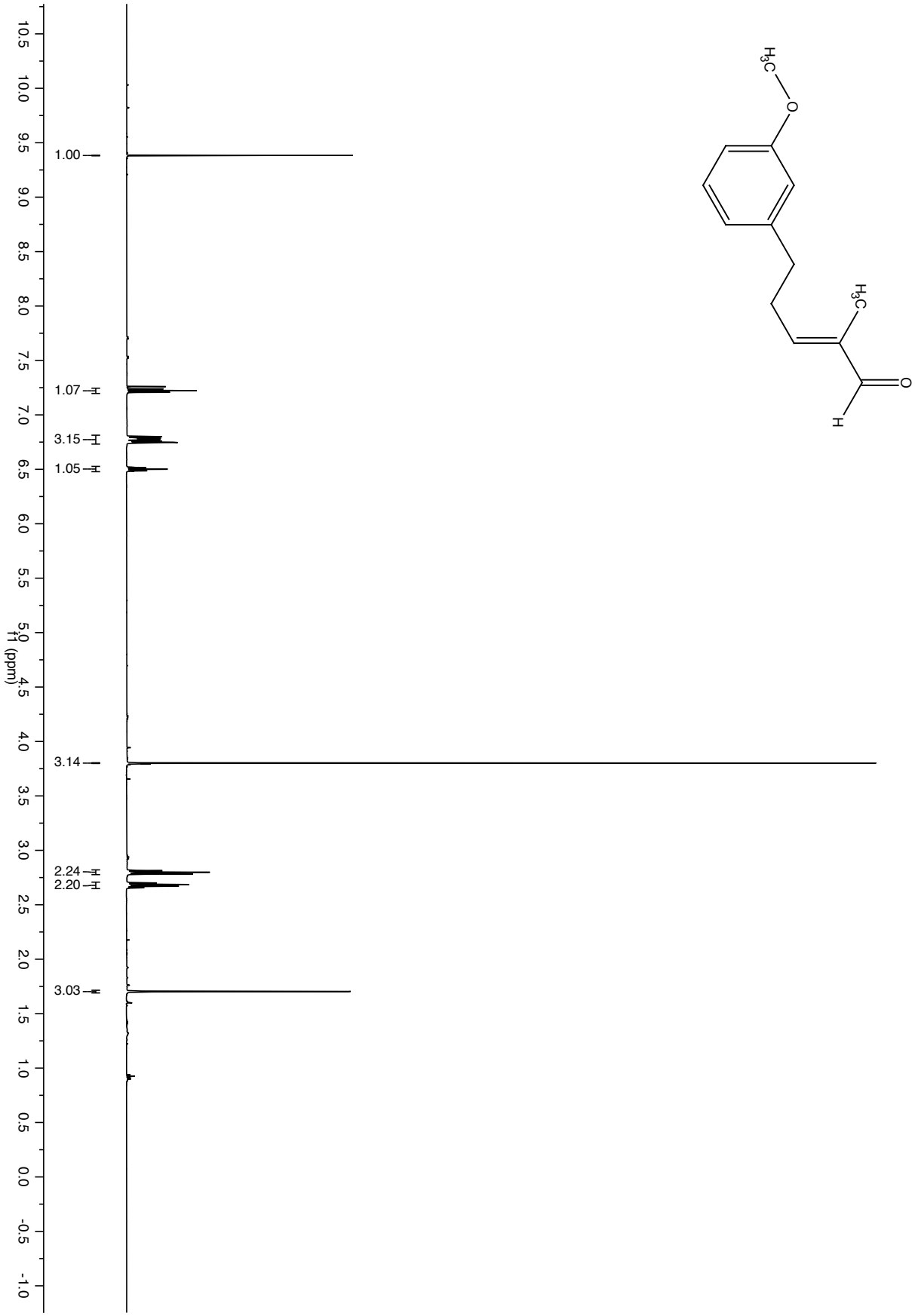
58.32
40.22
34.32
17.88
f1 (ppm)

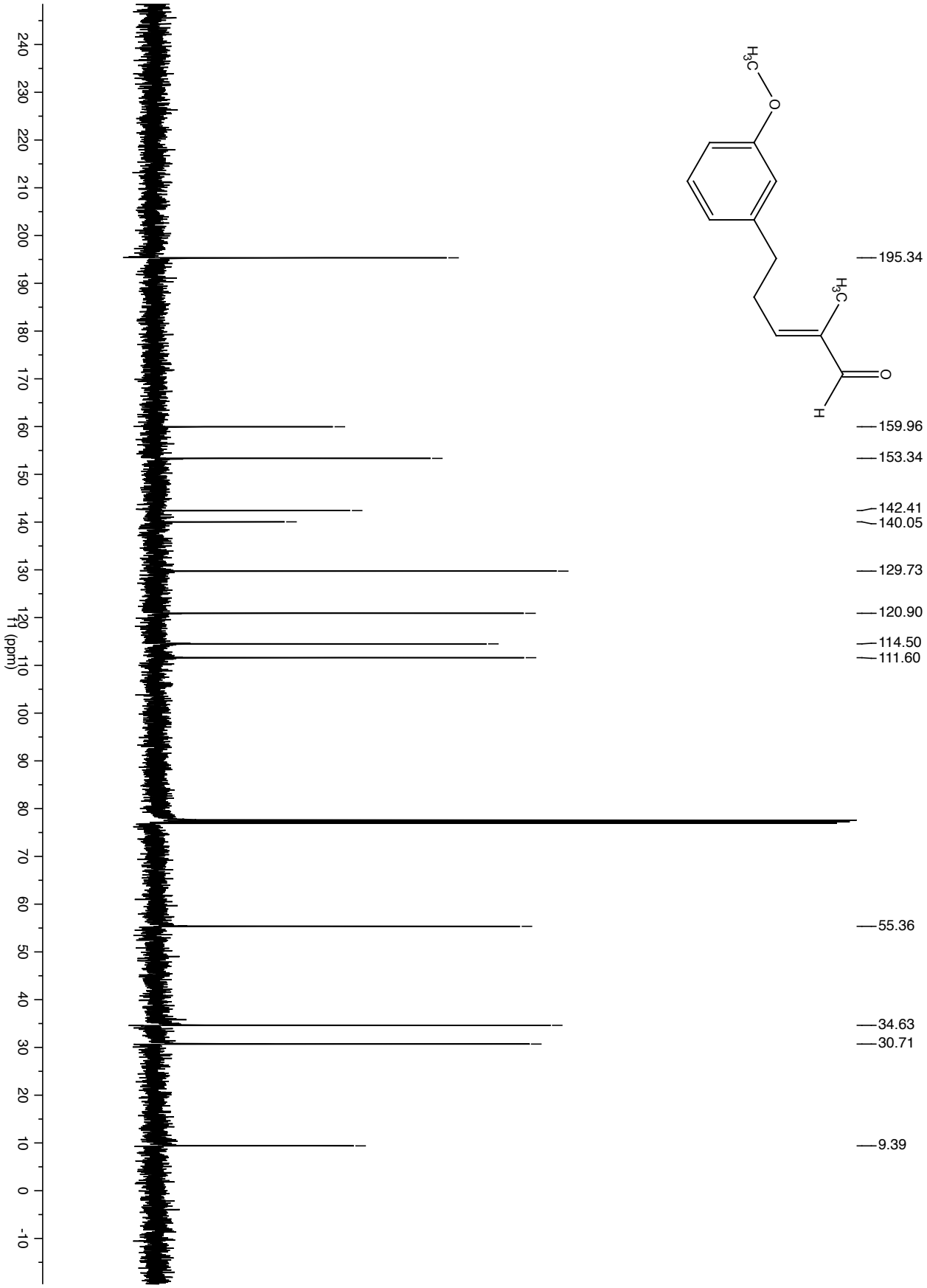

Me
N
O
Cl
Cl
1d
0.97
0.99
4.10
2.00
2.03
2.89
1.04
1.00
f1 (ppm)

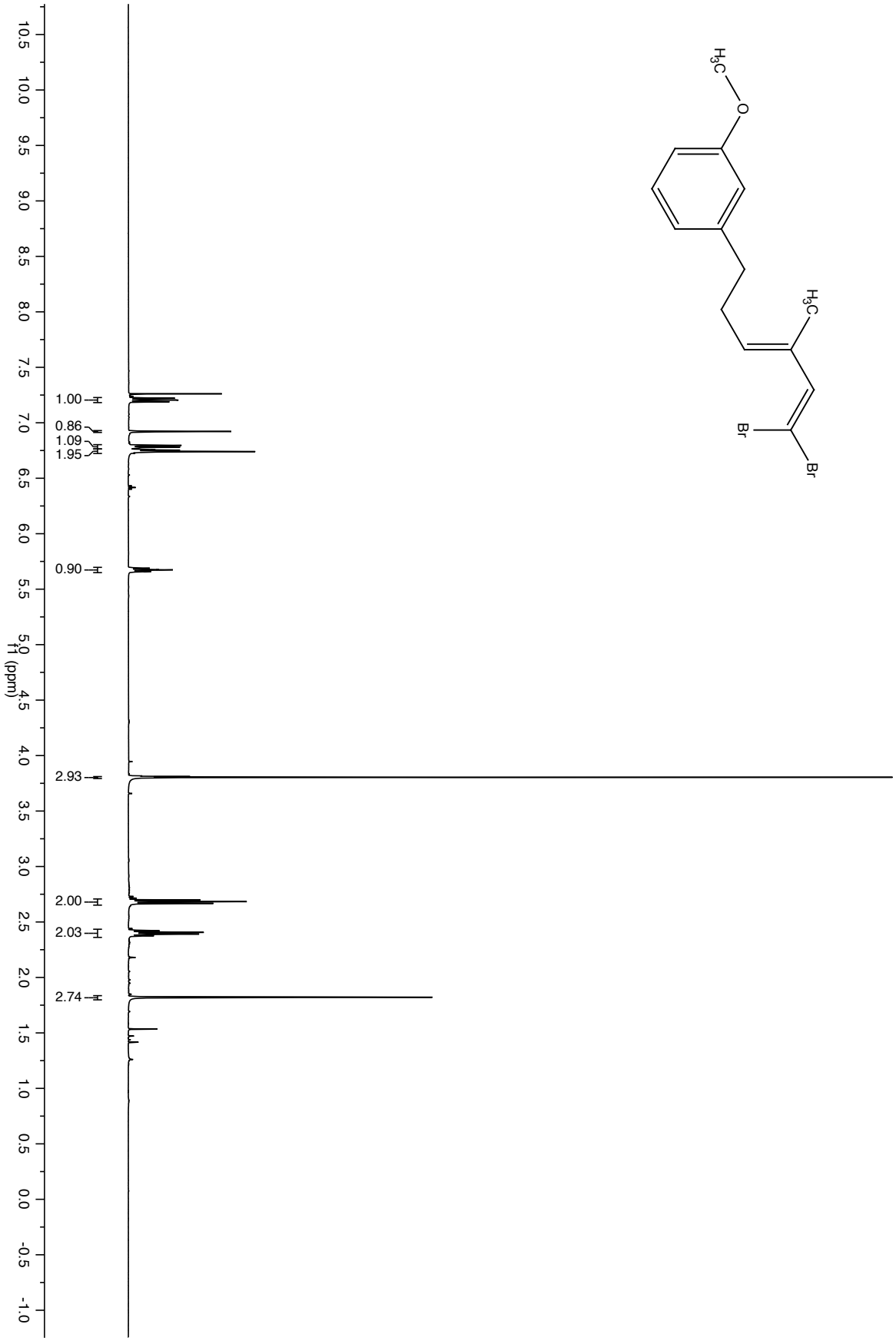

Me
N
O
Cl
Cl
1d
137.40
119.59
67.68
66.55
59.09
50.37
34.51
23.18
f1 (ppm)

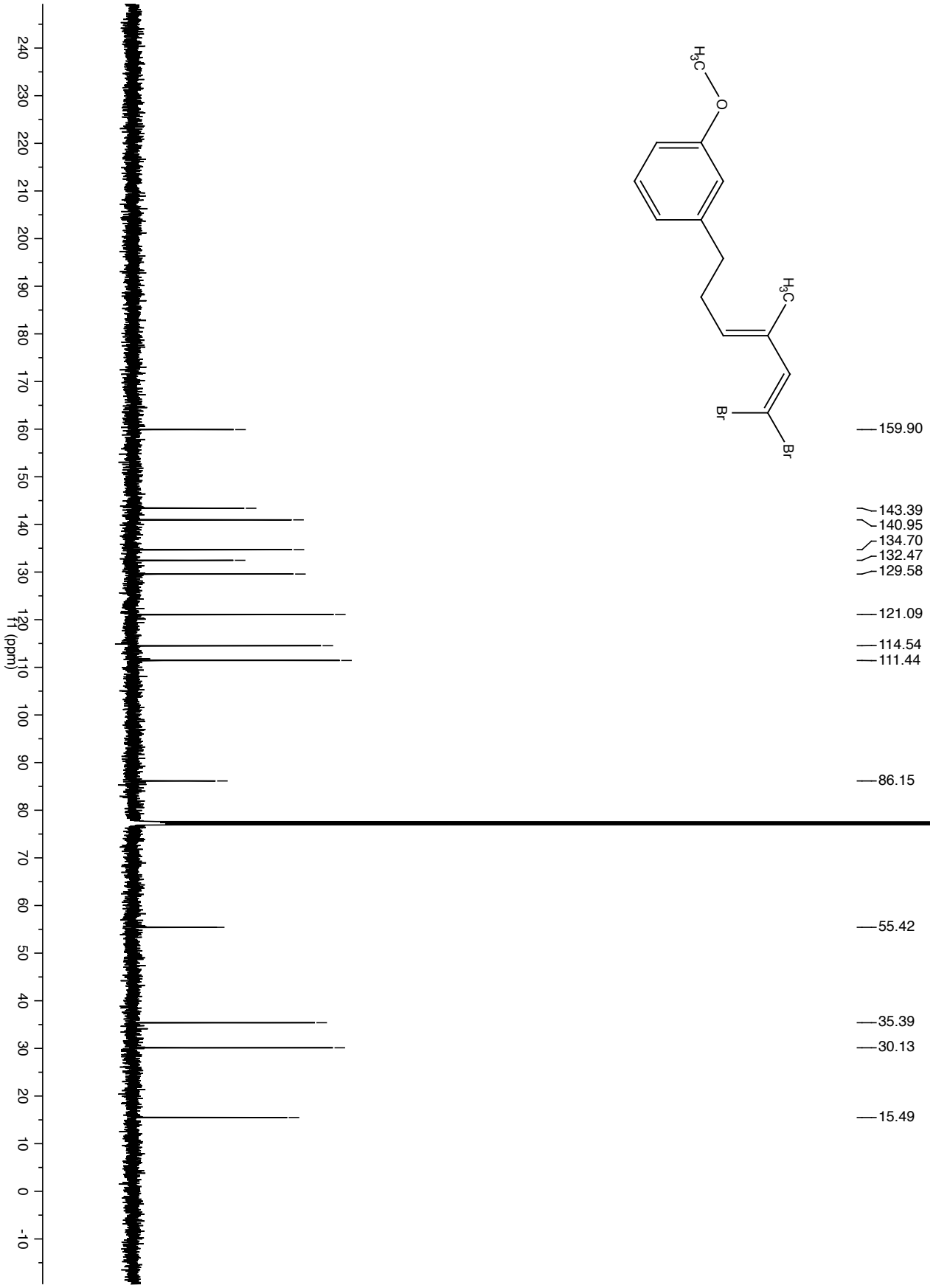

1e
Cl
Cl
N
O
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
0.90
3.83
1.91
1.92
1.00
2.97
2.00
3.01
1.00

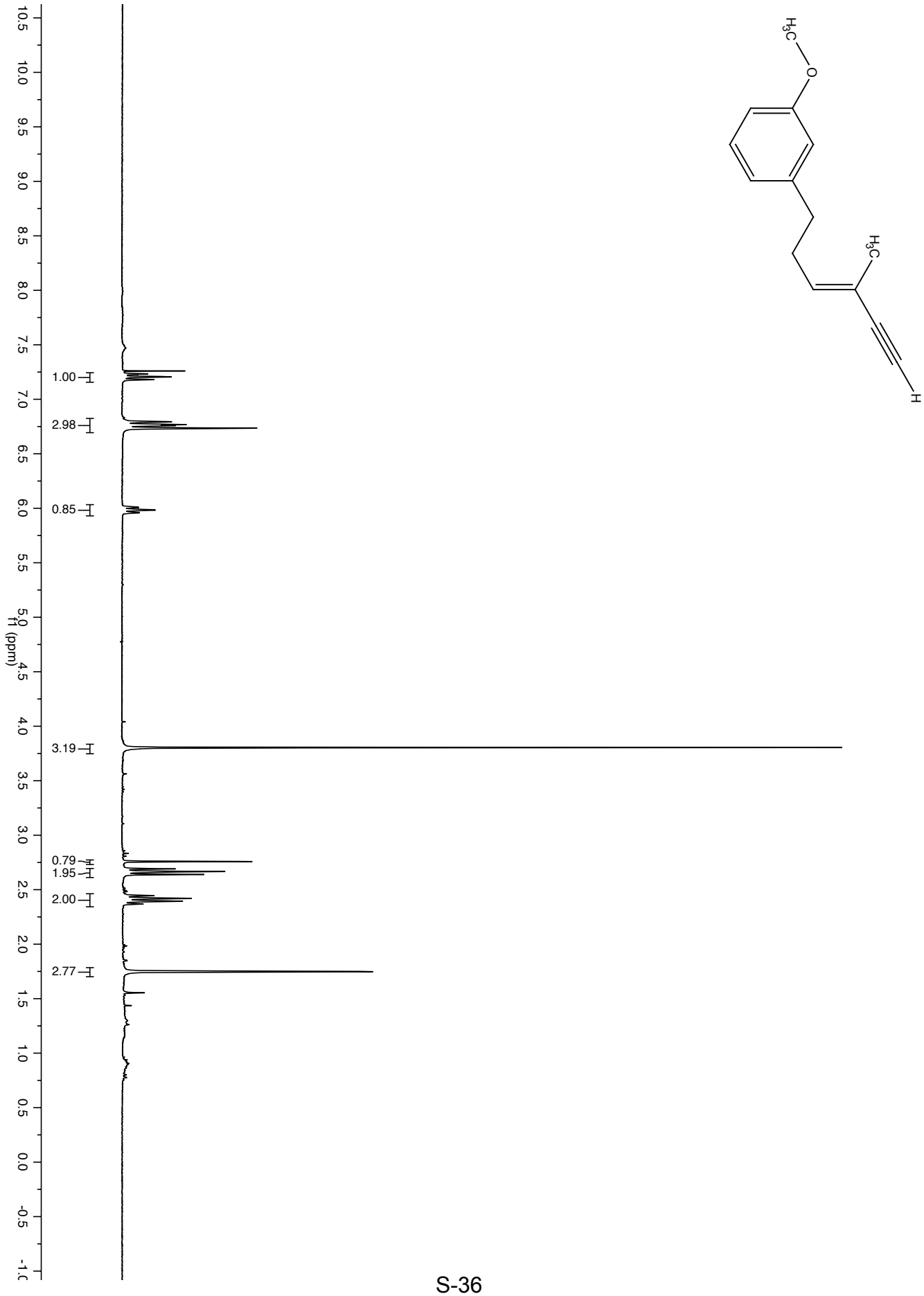

1e
N
O
Cl
Cl
131.34
130.77
67.71
67.08
59.45
50.48
34.06
30.33
25.43
22.93
22.52
f1 (ppm)

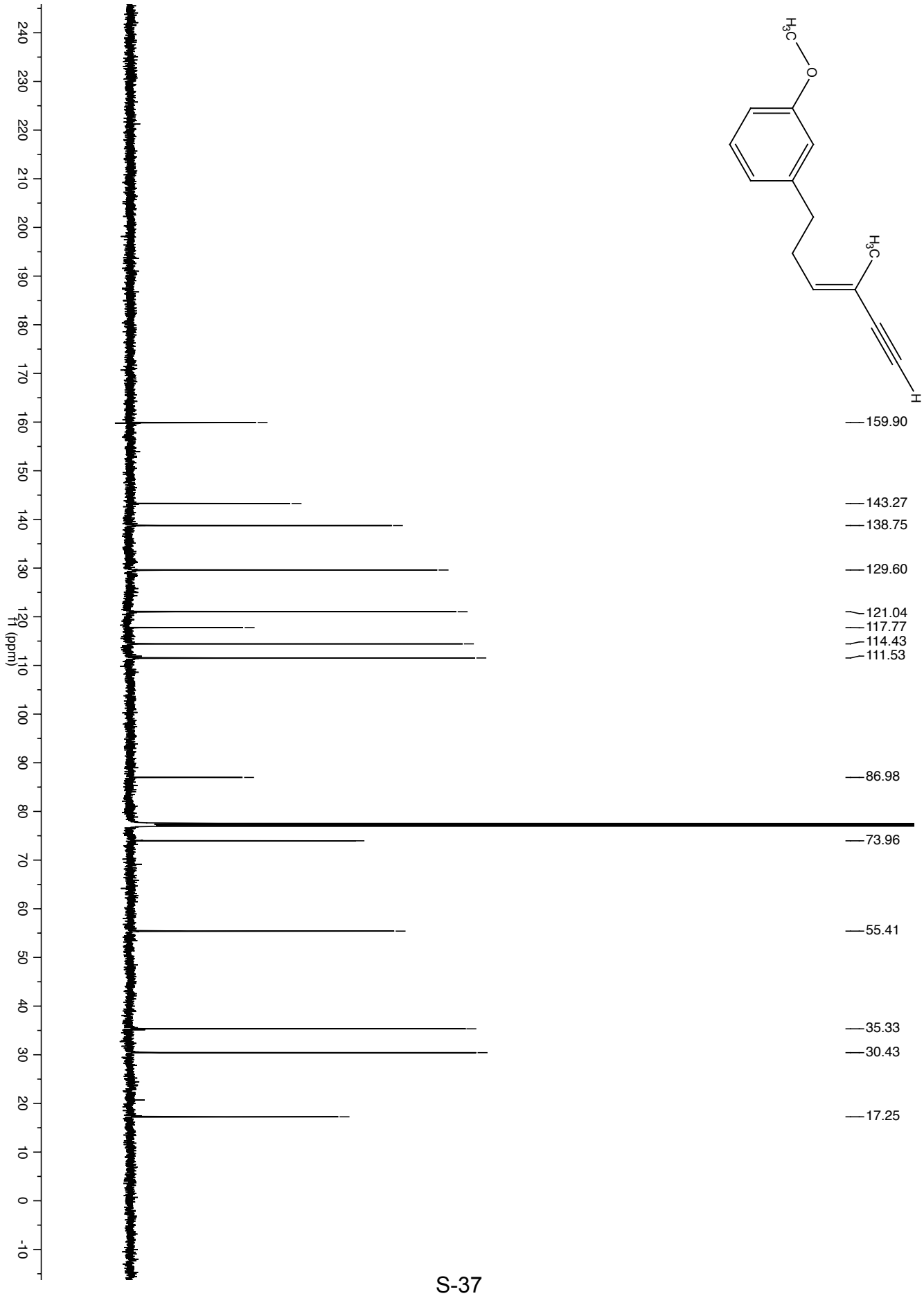

1.00
1.07
3.15
1.05
3.14
2.24
2.20
3.03
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
H3C
O
H3C
O
H

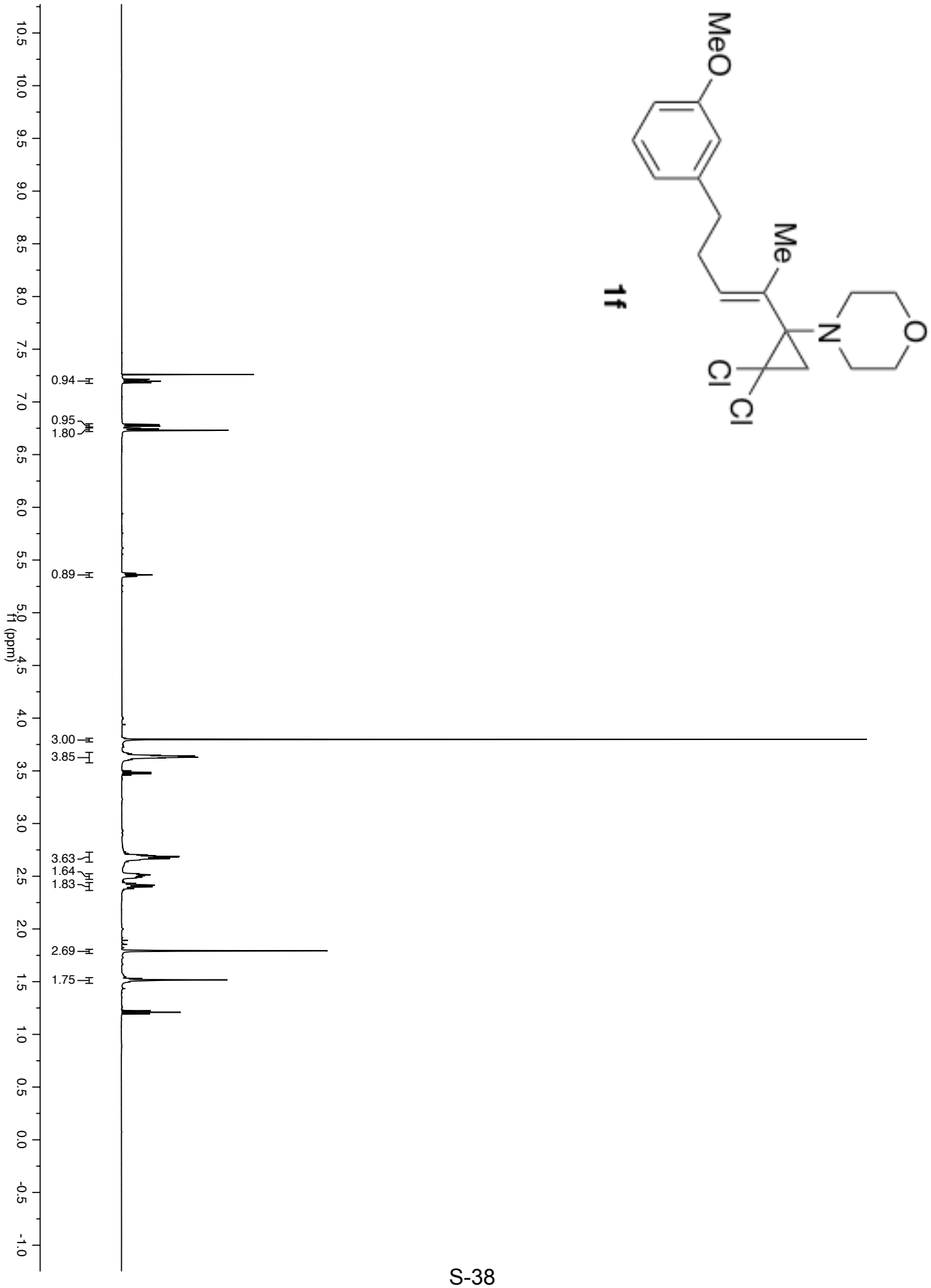

195.34
159.96
153.34
142.41
140.05
129.73
120.90
114.50
111.60
55.36
34.63
30.71
9.39
f1 (ppm)

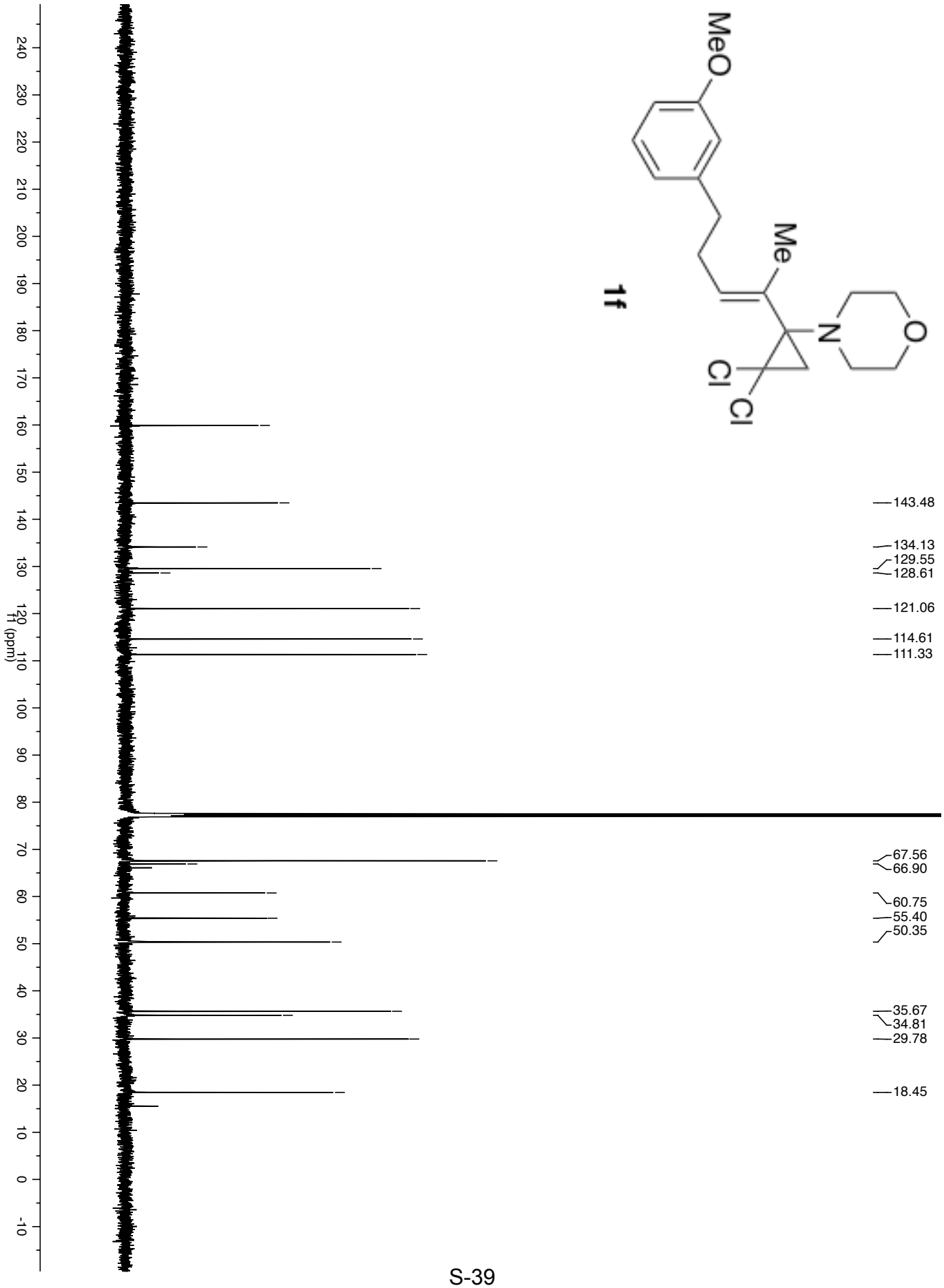

1.00
0.86
1.09
1.95
0.90
2.93
2.00
2.03
2.74
f1 (ppm)
H3C
O
H3C
Br
Br

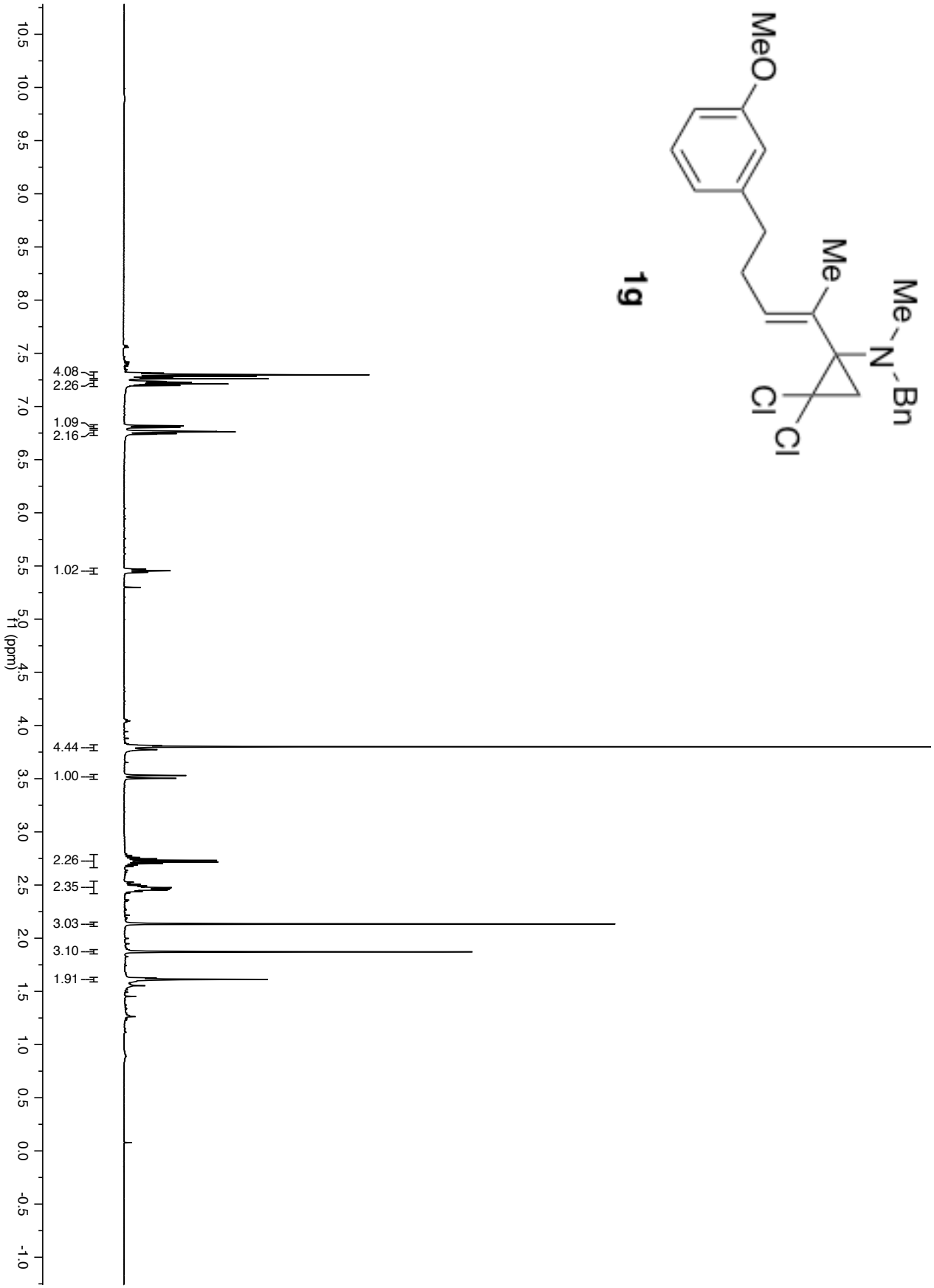

H3C
O
H3C
Br
Br
159.90
143.39
140.95
134.70
132.47
129.58
121.09
114.54
111.44
86.15
55.42
35.39
30.13
15.49
f1 (ppm)

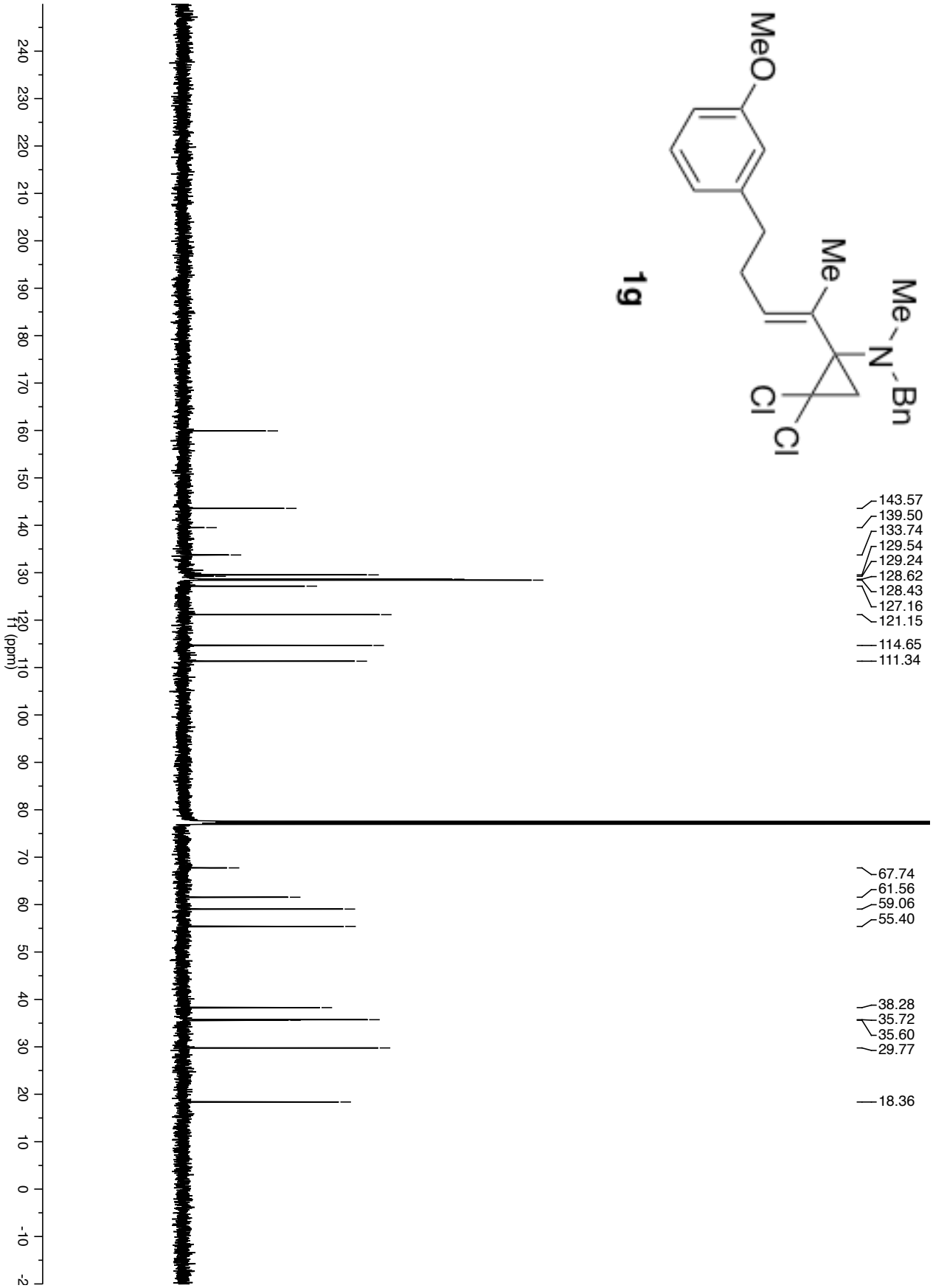

f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
1.00
2.98
0.85
3.19
0.79
1.95
2.00
2.77
H3C
O
H3C
H

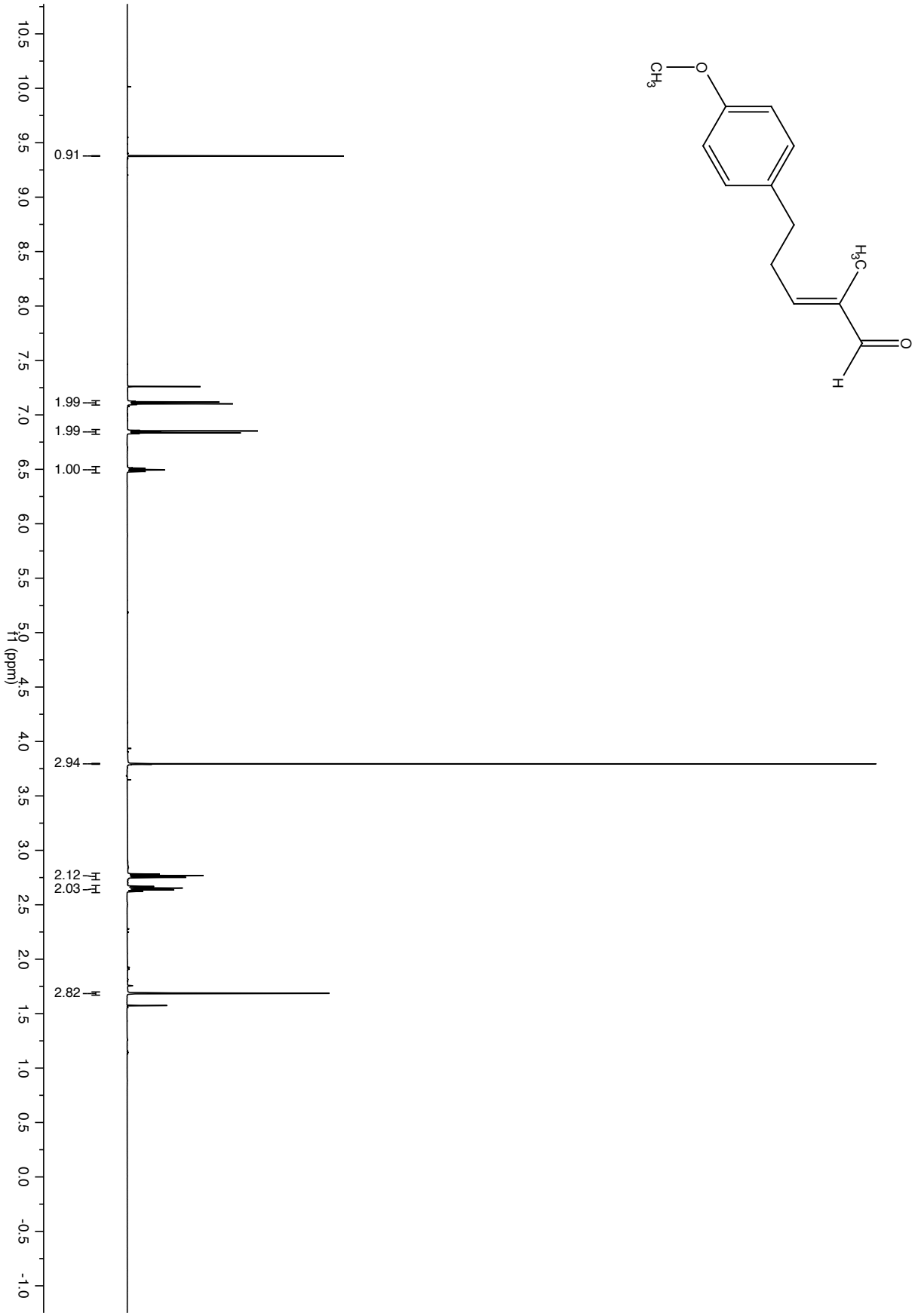

f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
159.90
143.27
138.75
129.60
121.04
117.77
114.43
111.53
86.98
73.96
55.41
35.33
30.43
17.25
H3C
O
H3C
H

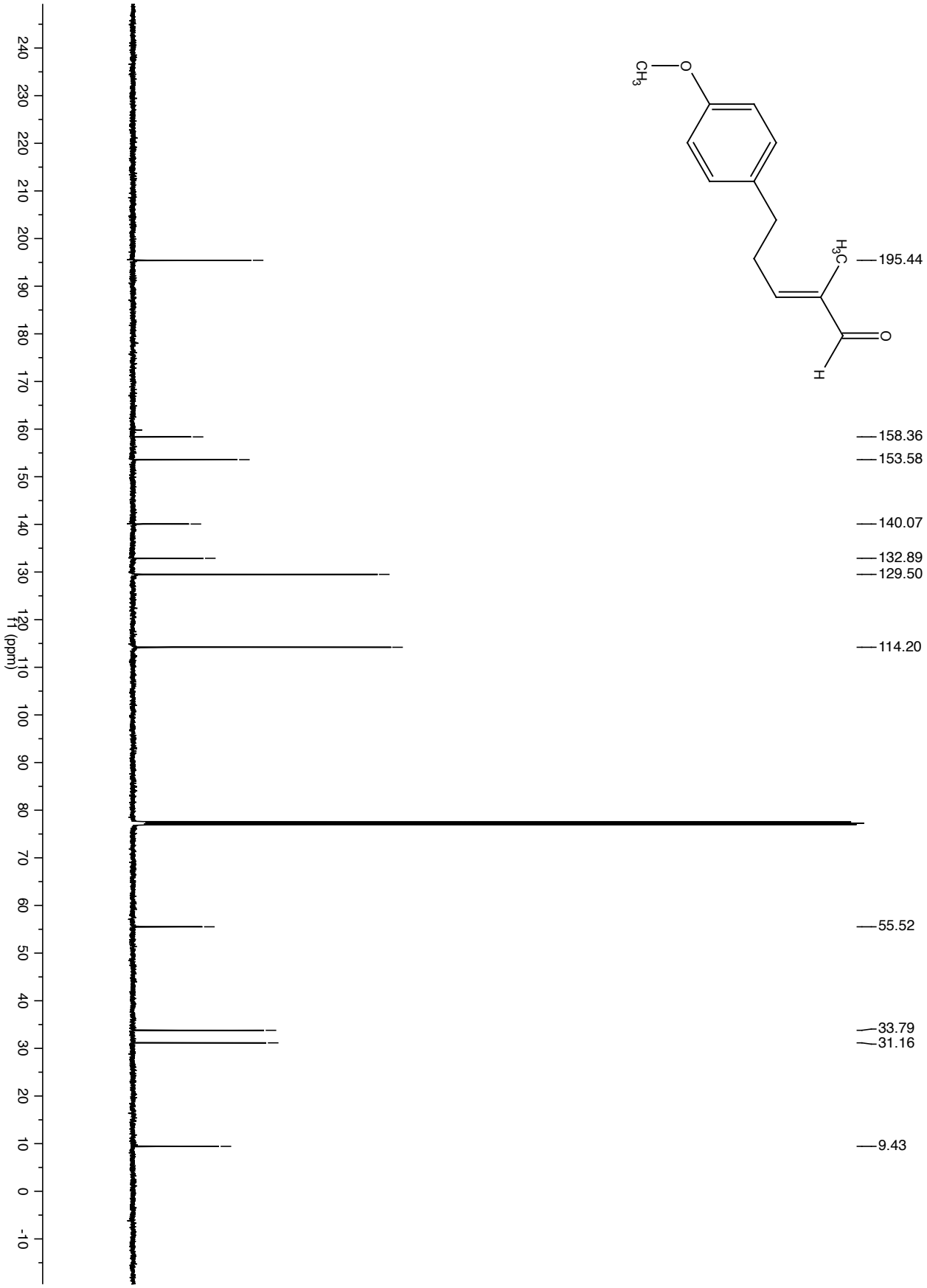

MeO
Me
N
O
Cl
Cl
1f
0.94
0.95
1.80
0.89
3.00
3.85
3.63
1.64
1.83
2.69
1.75
f1 (ppm)

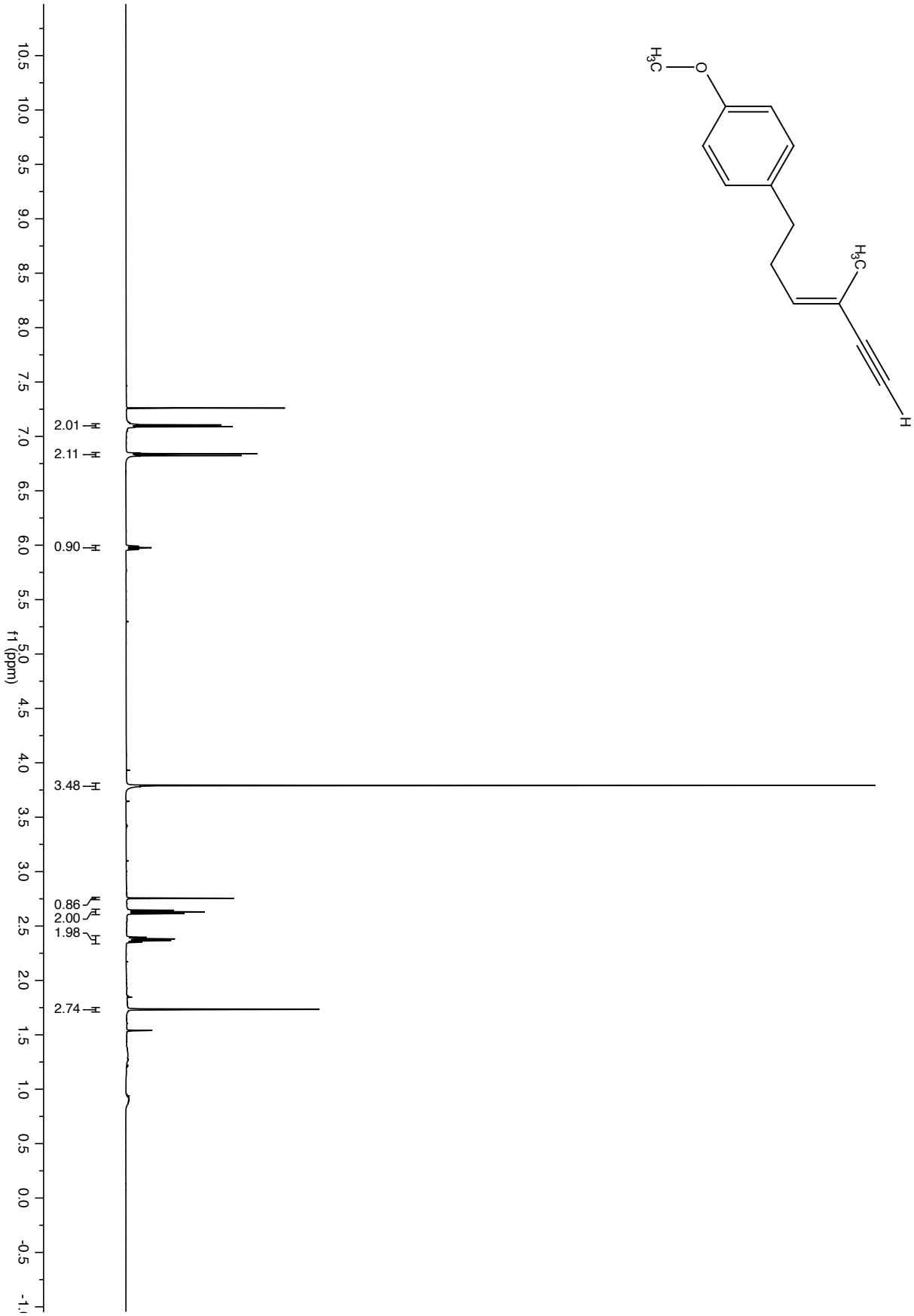

MeO
Me
N
O
Cl
Cl
1f
143.48
134.13
129.55
128.61
121.06
114.61
111.33
67.56
66.90
60.75
55.40
50.35
35.67
34.81
29.78
18.45
f1 (ppm)

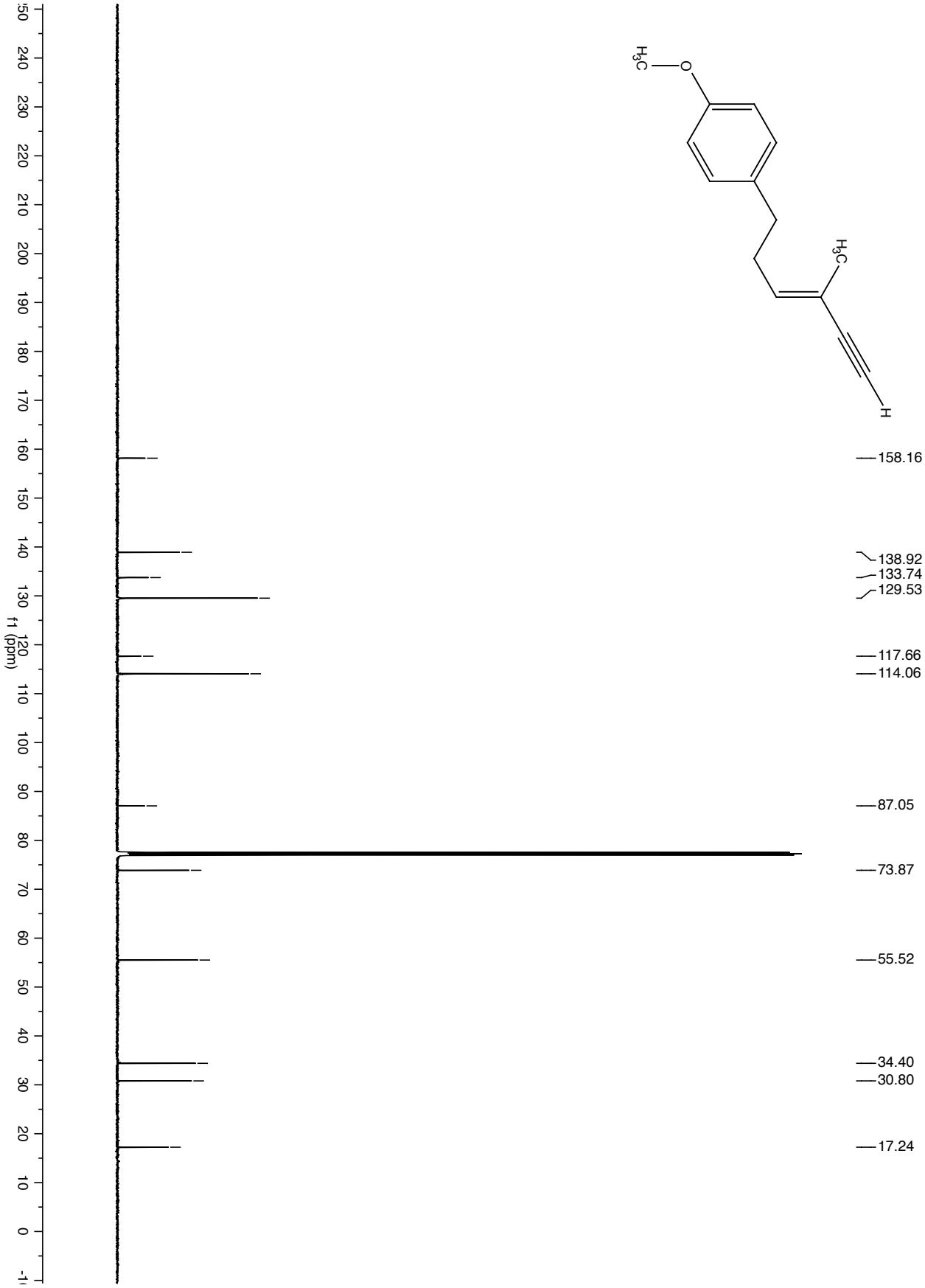

MeO
Me
N
Bn
Cl
Cl
1g
4.08
2.26
1.09
2.16
1.02
4.44
1.00
2.26
2.35
3.03
3.10
1.91
f1 (ppm)

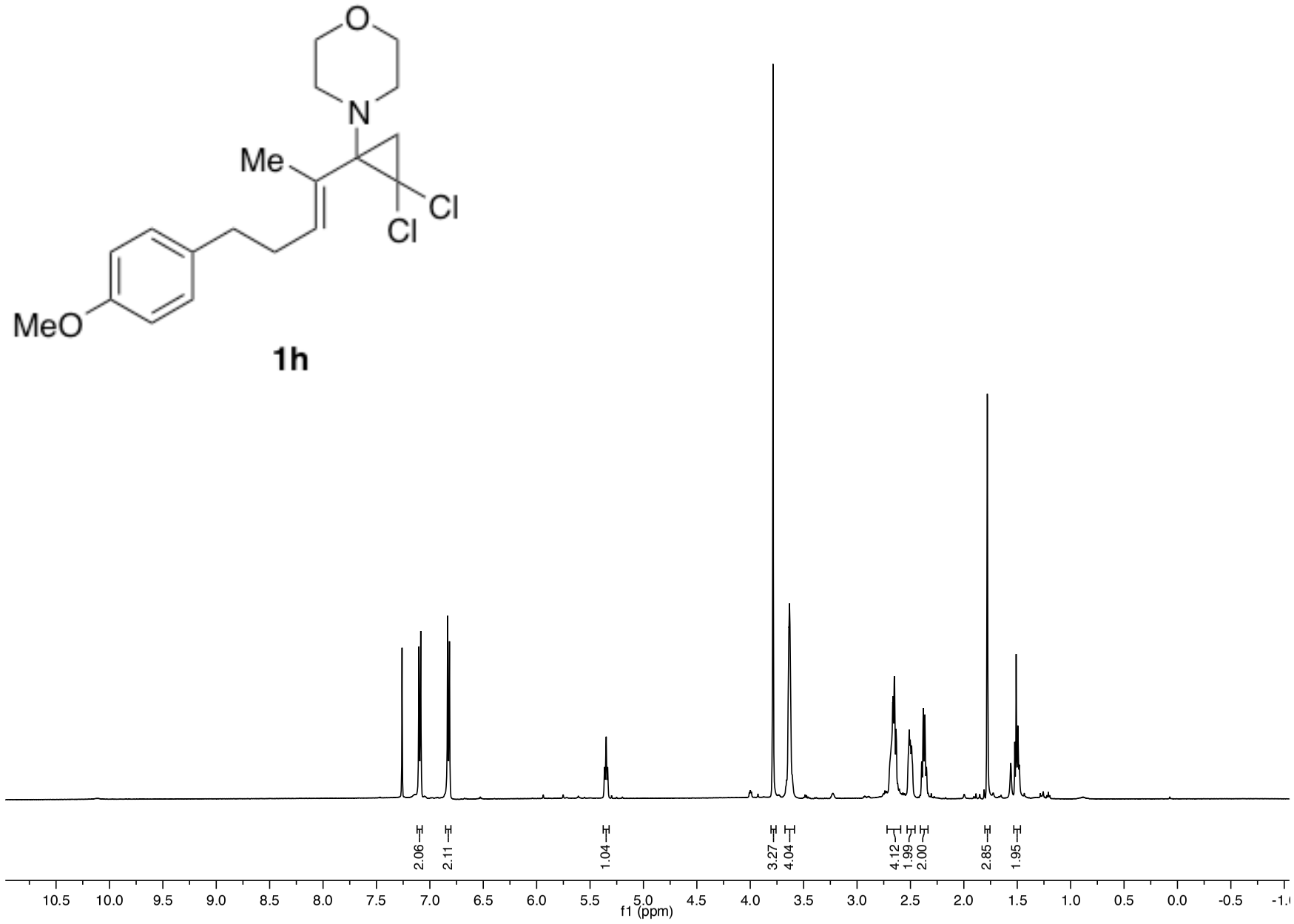

MeO
Me
Me
N
Bn
Cl
Cl
1g
143.57
139.50
133.74
129.54
129.24
128.62
128.43
127.16
121.15
114.65
111.34
67.74
61.56
59.06
55.40
38.28
35.72
35.60
29.77
18.36
f1 (ppm)

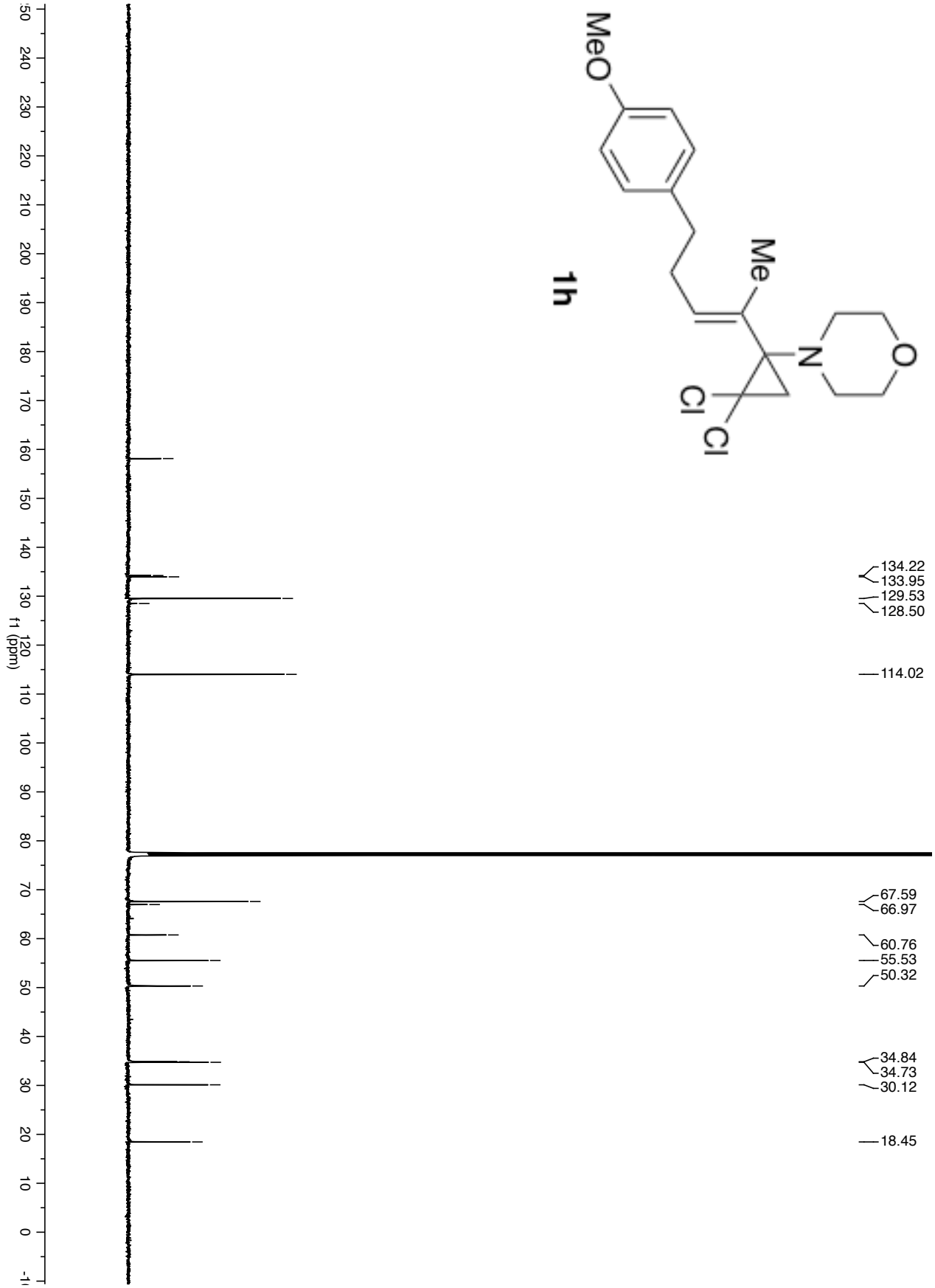

0.91
1.99
1.99
1.00
2.94
2.12
2.03
2.82
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
CH3
O
H3C
O
H

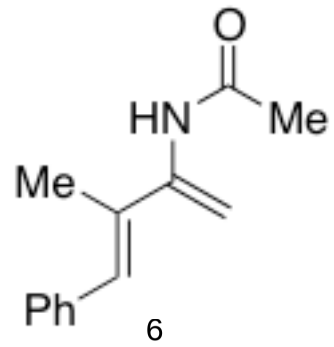

195.44
158.36
153.58
140.07
132.89
129.50
114.20
55.52
33.79
31.16
9.43
f1 (ppm)


H3C
O
H3C
H
2.01
2.11
0.90
3.48
0.86
2.00
1.98
2.74
f1 (ppm)

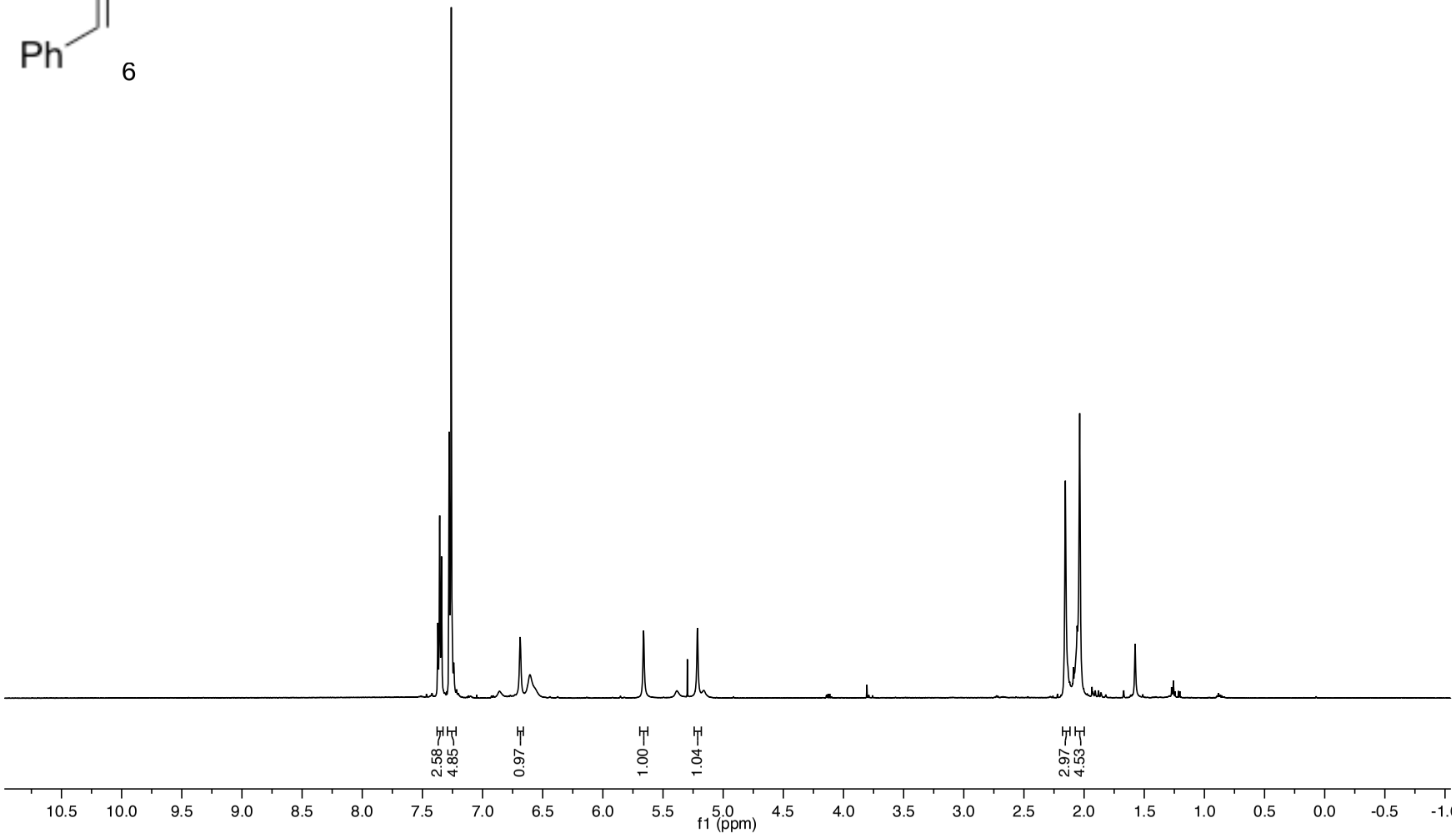

f1 (ppm)
158.16
138.92
133.74
129.53
117.66
114.06
87.05
73.87
55.52
34.40
30.80
17.24

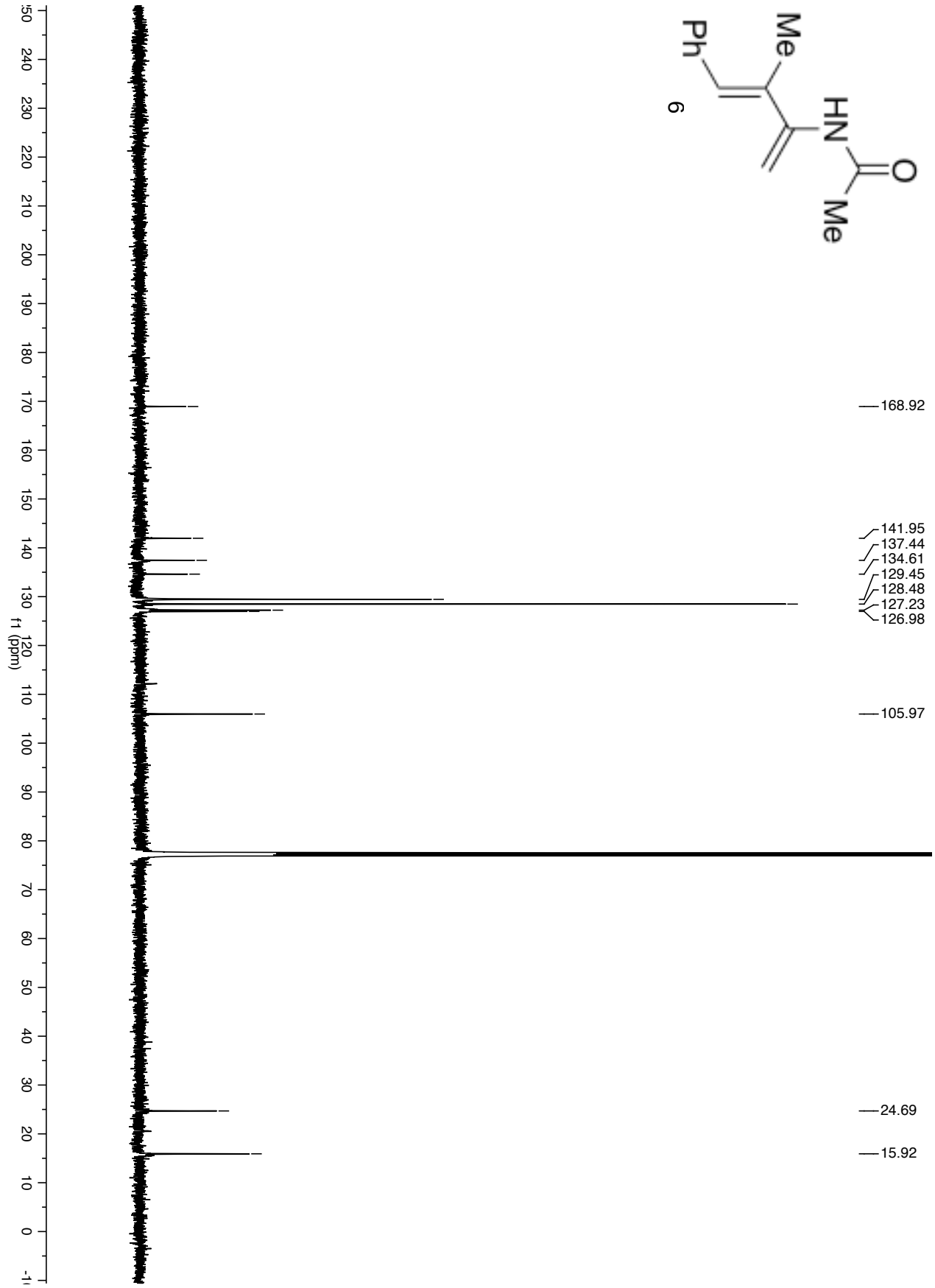

O
N
Me
Cl
Cl
MeO
1h
2.06
2.11
1.04
3.27
4.04
4.12
1.99
2.00
2.85
1.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

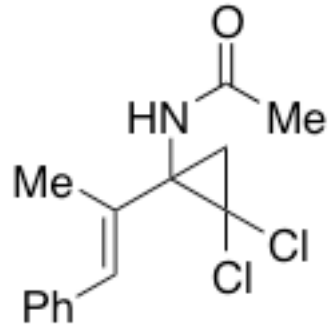

MeO
Me
N
O
Cl
Cl
1h
134.22
133.95
129.53
128.50
114.02
67.59
66.97
60.76
55.53
50.32
34.84
34.73
30.12
18.45
f1 (ppm)


O
HN
Me
Me
Ph

6

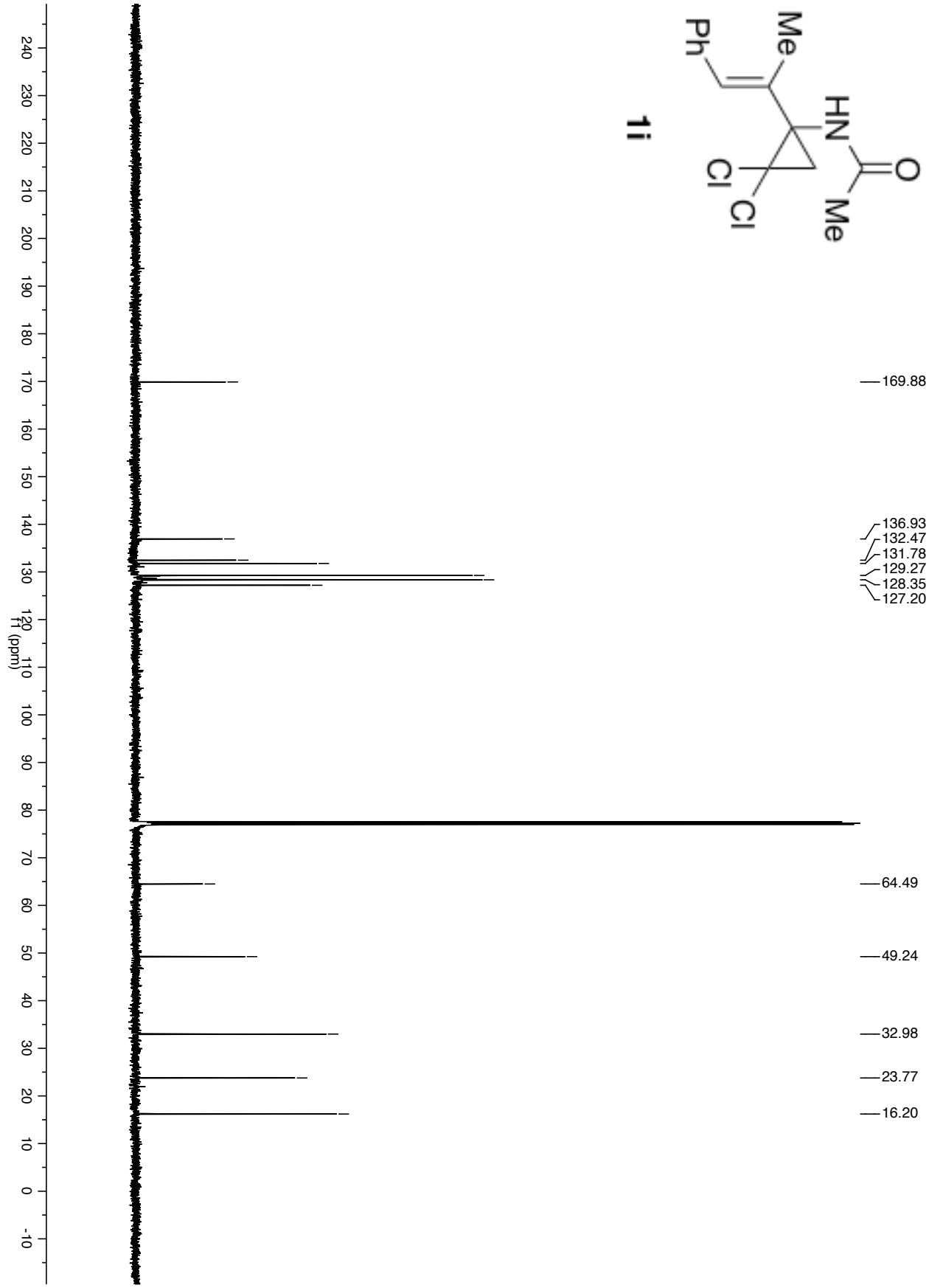

2.58
4.85
0.97
1.00
1.04
2.97
4.53
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

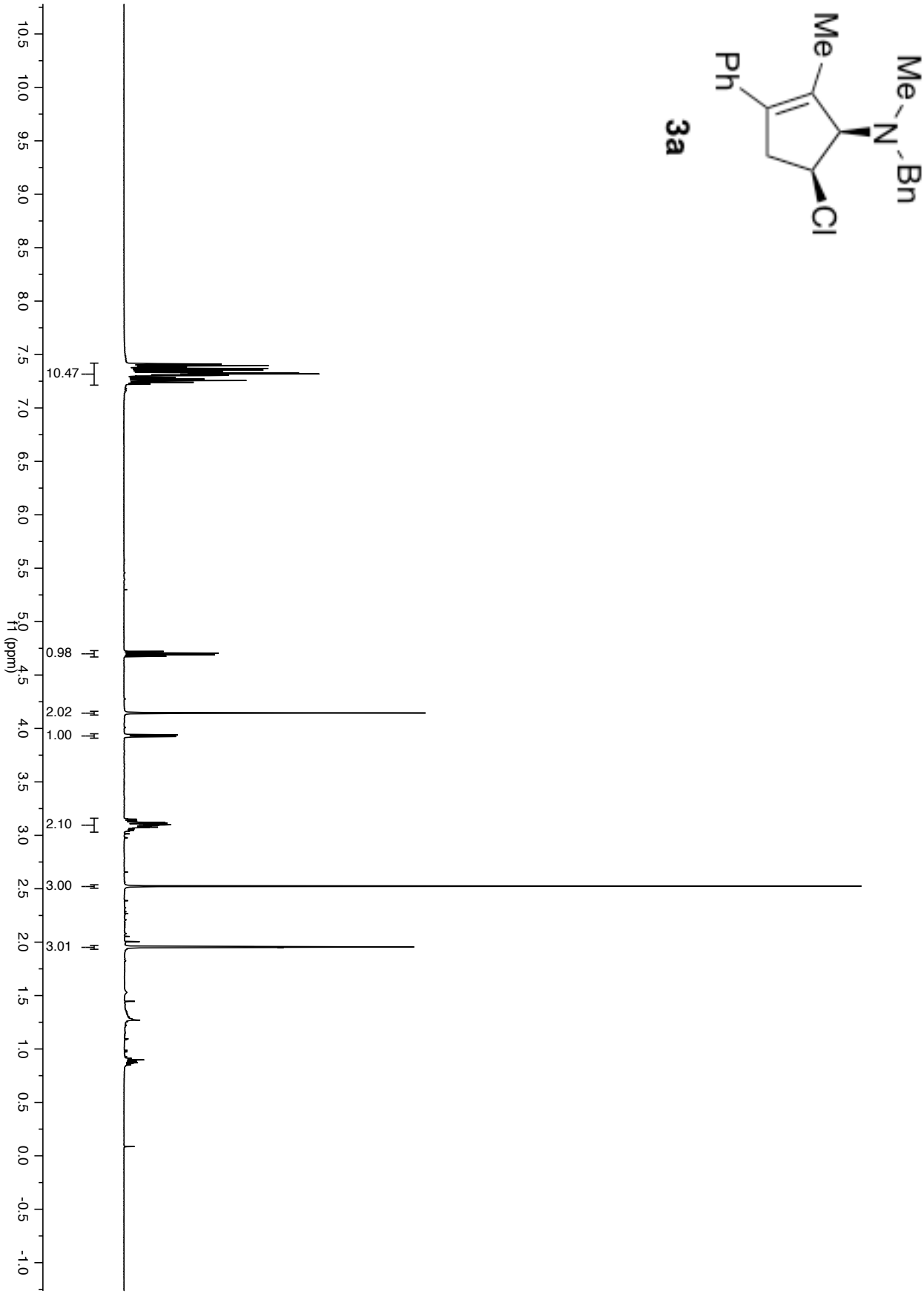

Ph
Me
HN
O
Me
6
168.92
141.95
137.44
134.61
129.45
128.48
127.23
126.98
105.97
24.69
15.92
f1 (ppm)

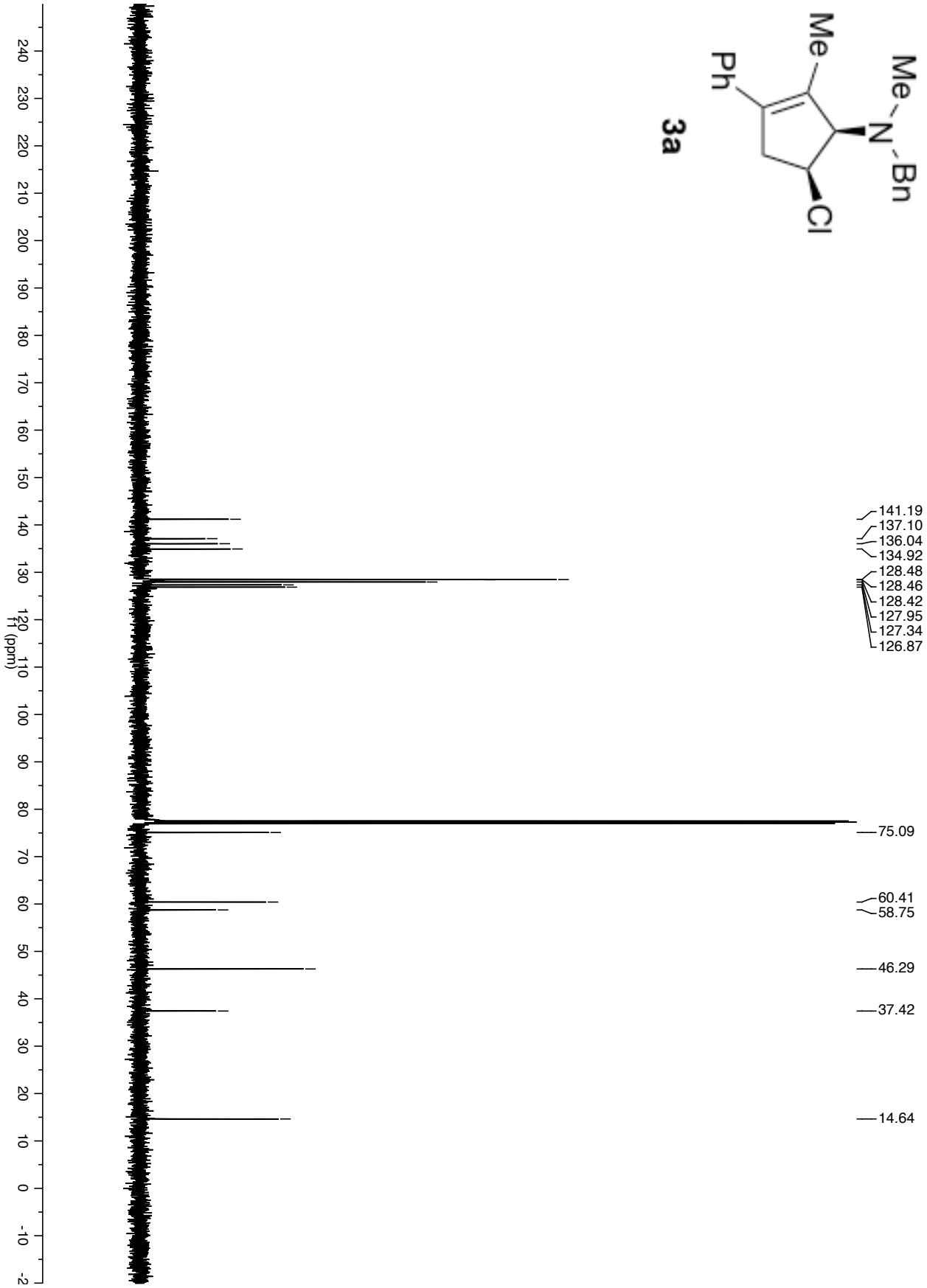

O
HN
Me
Me
Cl
Cl
Ph

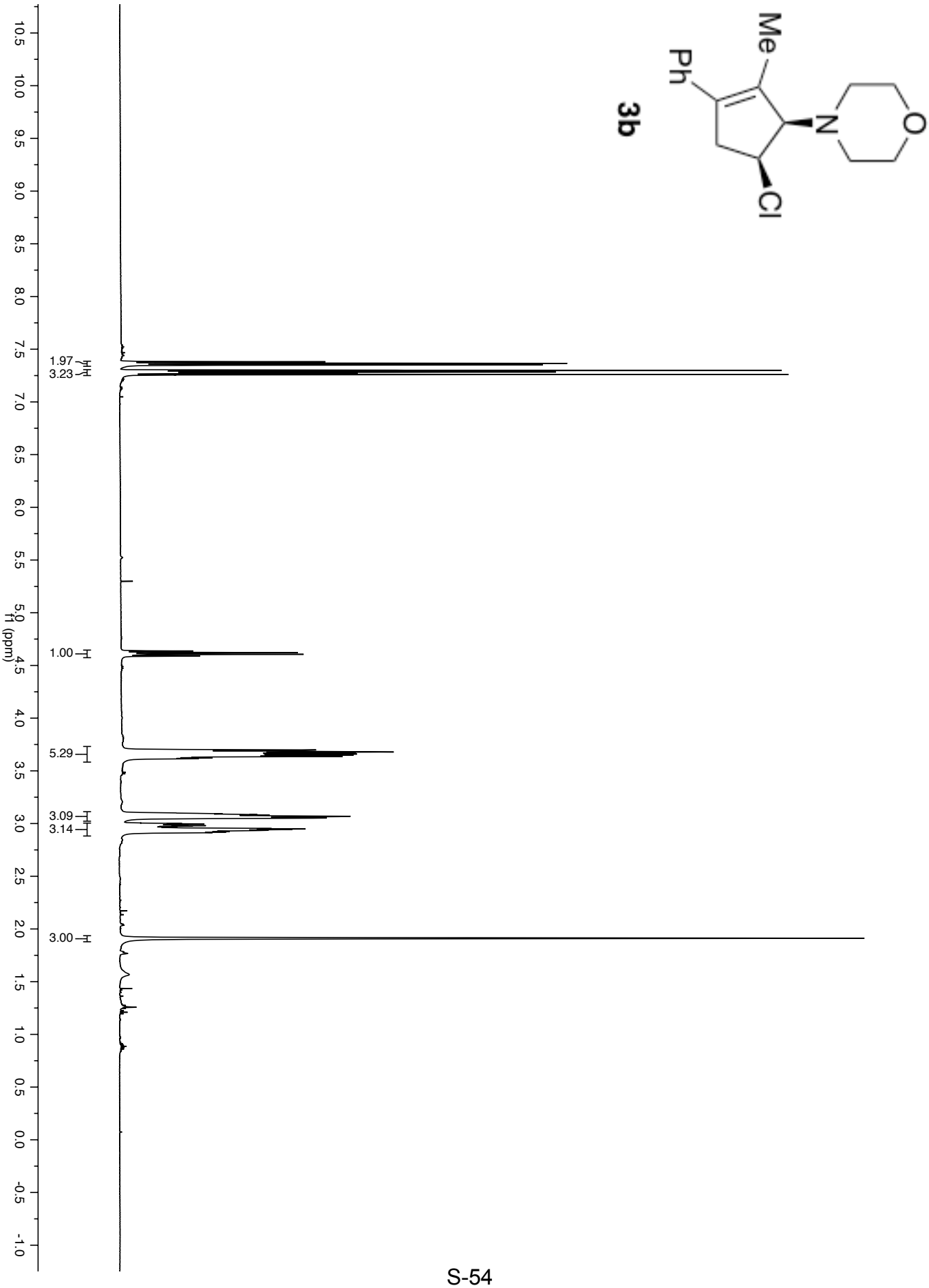
1i

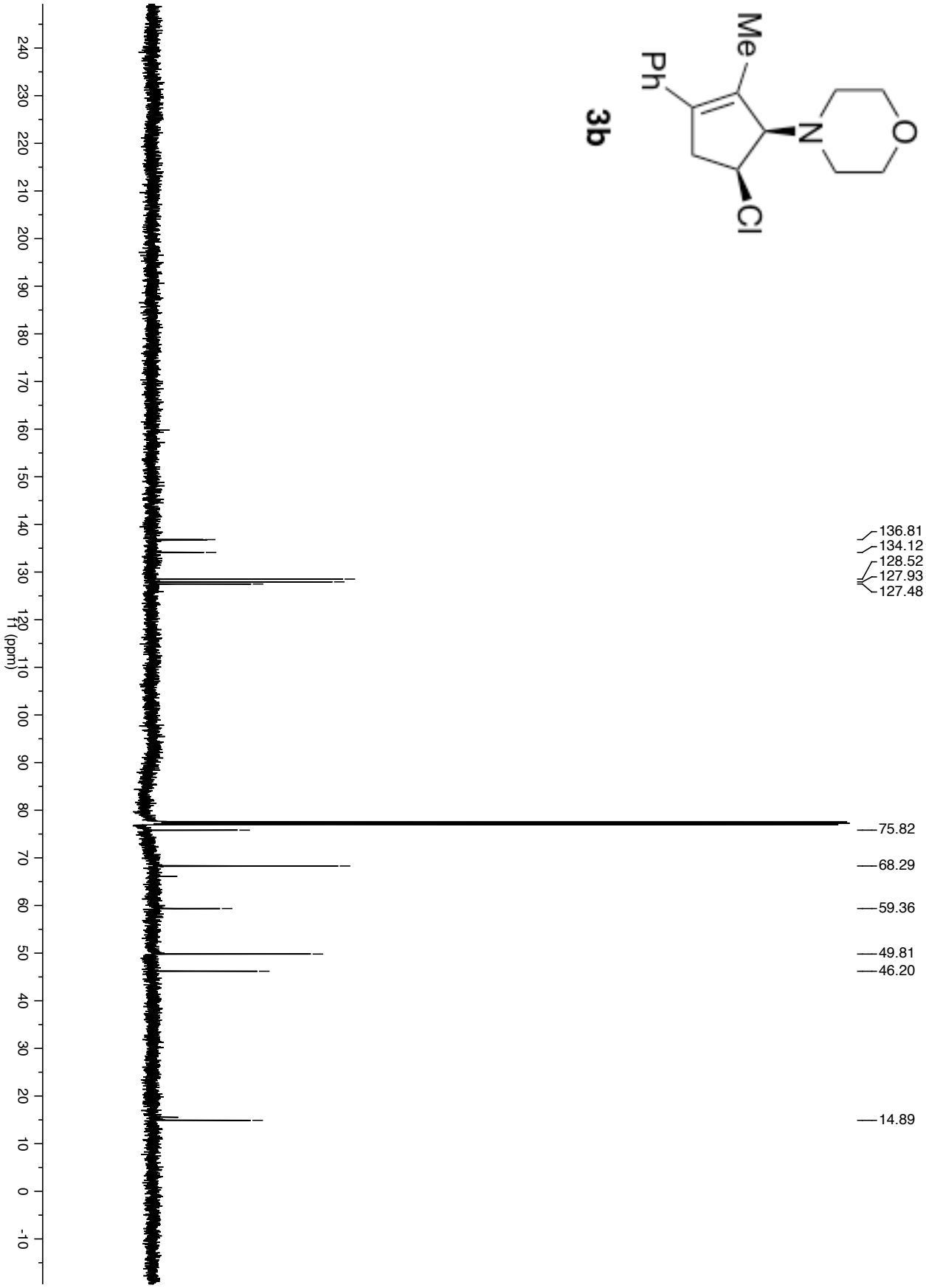
2.02
3.42
0.89
0.95
0.94
2.77
2.77
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

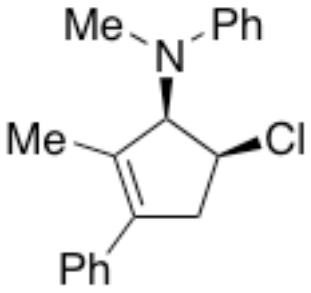

Me
Ph
HN
O
Me
Cl
Cl
1i
169.88
136.93
132.47
131.78
129.27
128.35
127.20
64.49
49.24
32.98
23.77
16.20
f1 (ppm)


Me
Ph
N
Bn
Cl
3a
f1 (ppm)
10.47
0.98
2.02
1.00
2.10
3.00
3.01


Me
Ph
Me
N
Bn
Cl
3a
141.19
137.10
136.04
134.92
128.48
128.46
128.42
127.95
127.34
126.87
75.09
60.41
58.75
46.29
37.42
14.64
f1 (ppm)

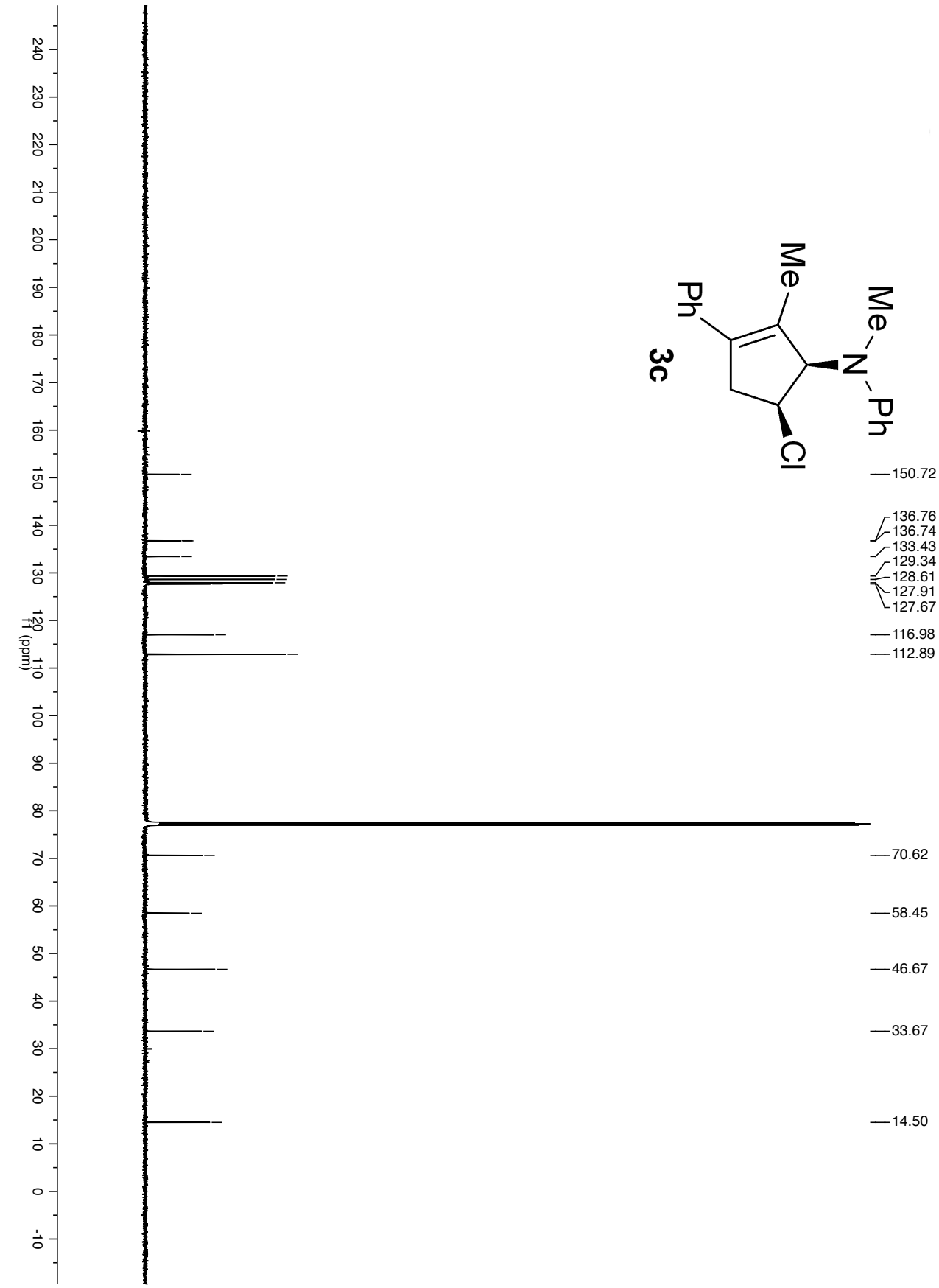

Me
Ph
N
O
Cl
3b
1.97
3.23
1.00
5.29
3.09
3.14
3.00
f1 (ppm)

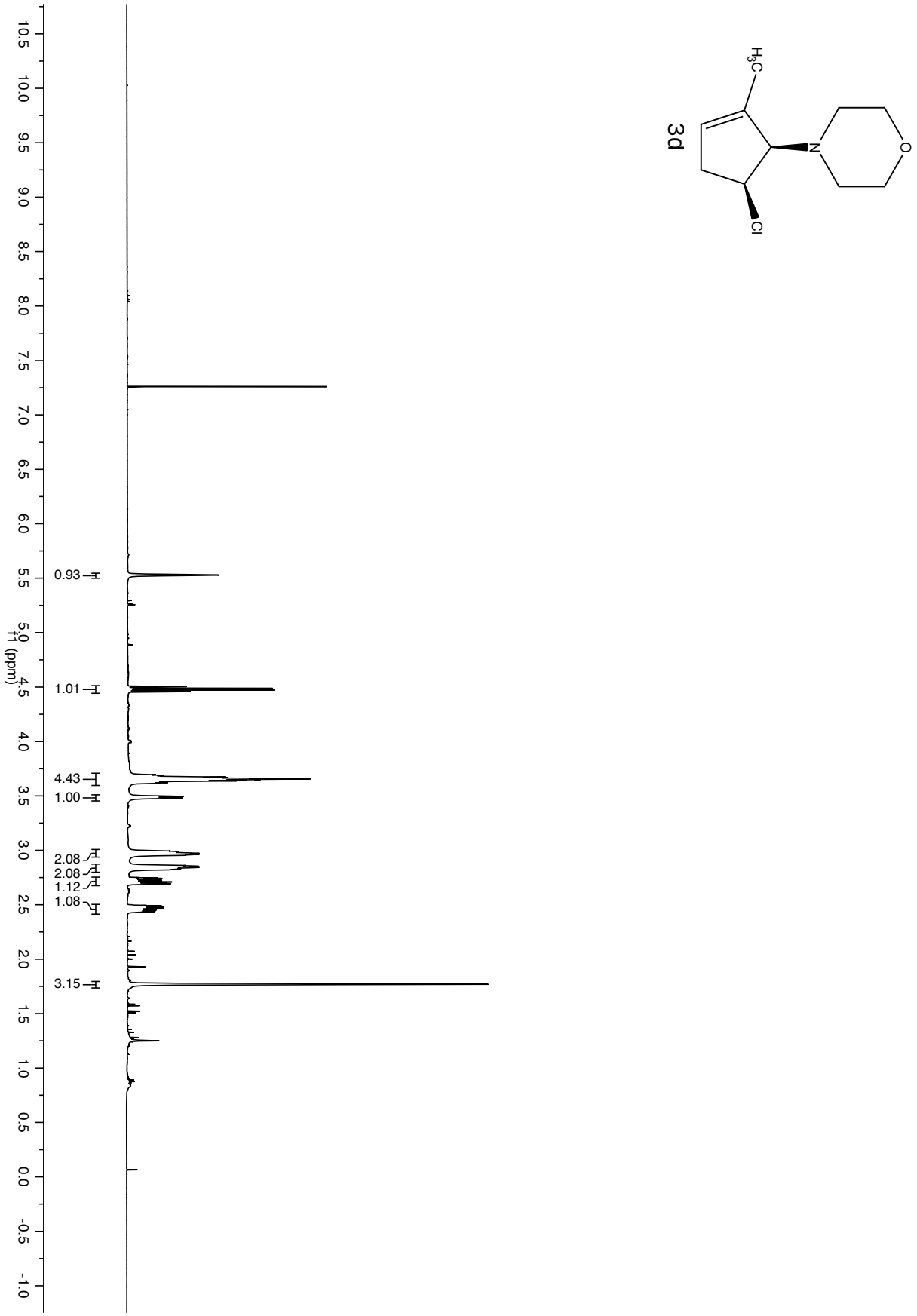

Me
Ph
N
O
Cl
3b
136.81
134.12
128.52
127.93
127.48
75.82
68.29
59.36
49.81
46.20
14.89
f1 (ppm)

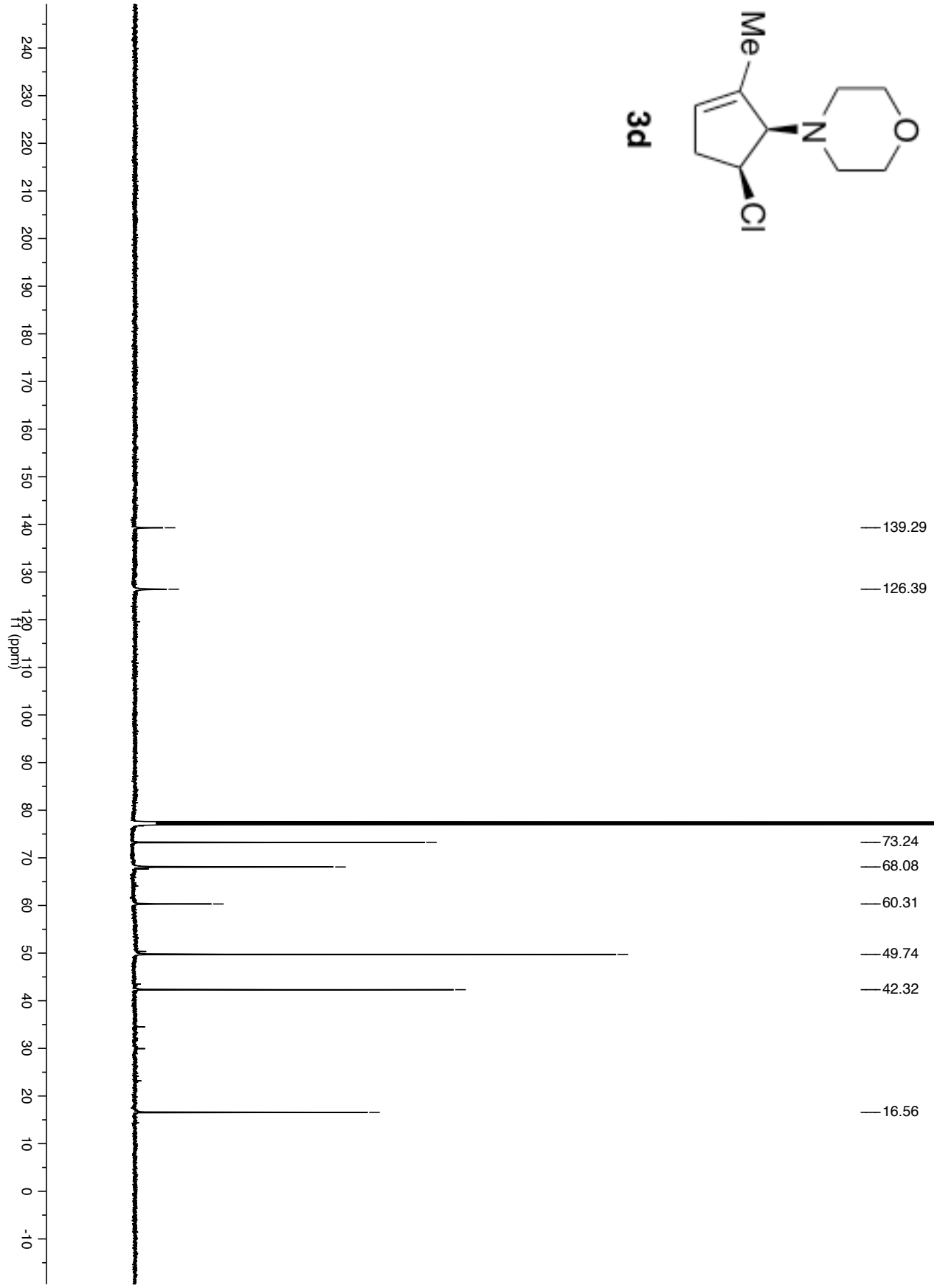

Me
N
Ph
Me
Cl
Ph

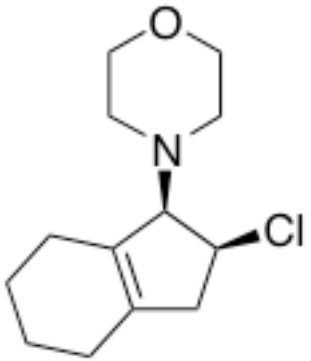
3c

1.93
2.03
3.47
2.01
0.94
1.00
0.98
1.05
1.03
2.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

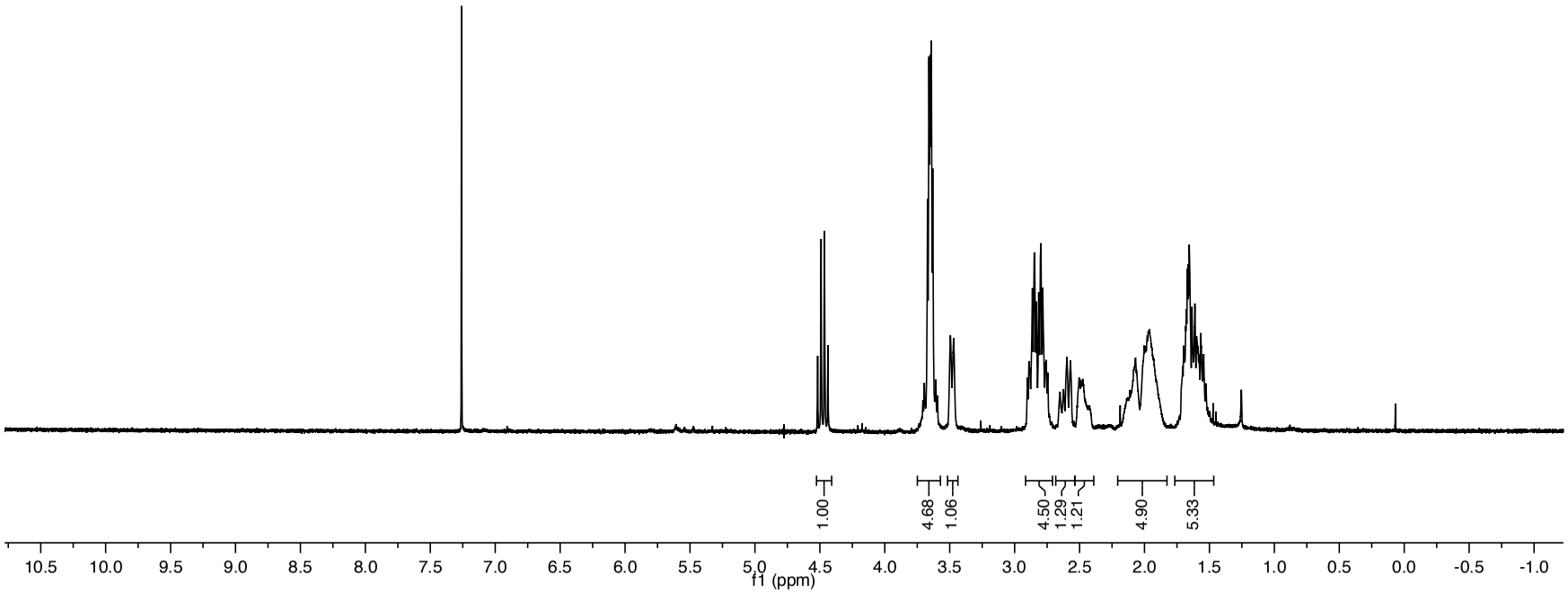

Me
Ph
Me
N
Ph
Cl
3c
150.72
136.76
136.74
133.43
129.34
128.61
127.91
127.67
116.98
112.89
70.62
58.45
46.67
33.67
14.50
f1 (ppm)

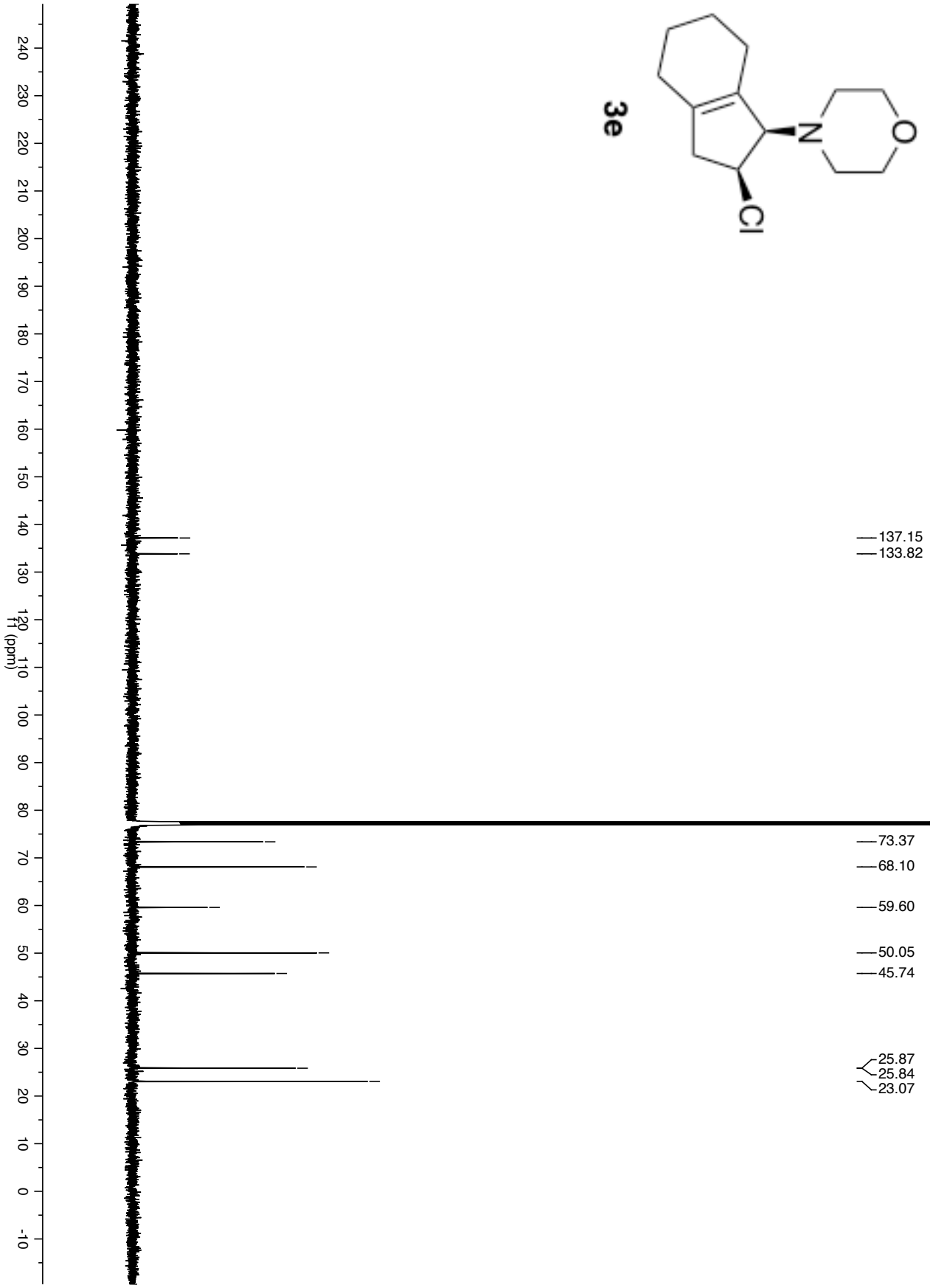

3d
H3C
Cl
N
O
f1 (ppm)
0.93
1.01
4.43
1.00
2.08
2.08
1.12
1.08
3.15

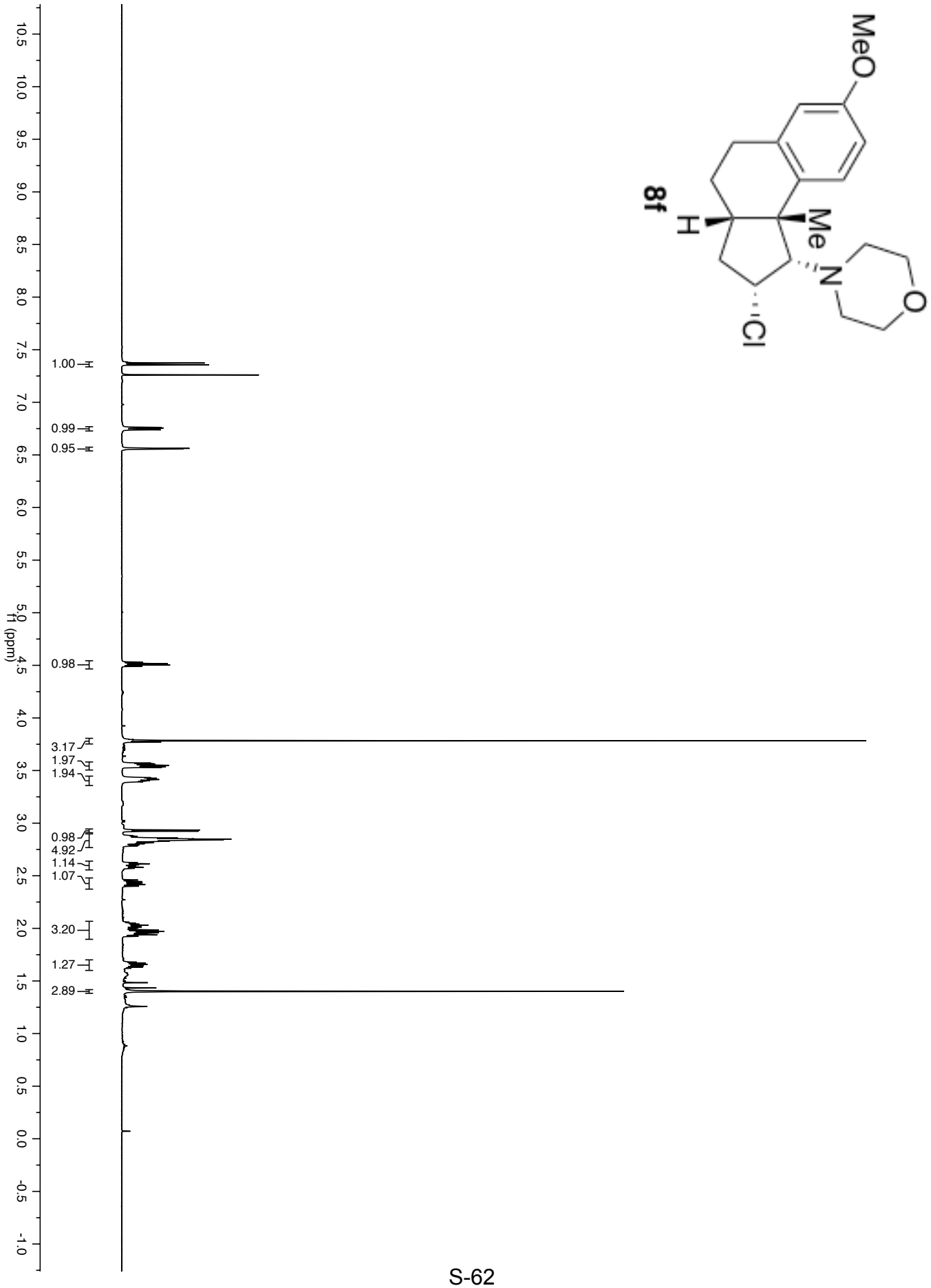

Me
N
O
Cl
3d
139.29
126.39
73.24
68.08
60.31
49.74
42.32
16.56
f1 (ppm)

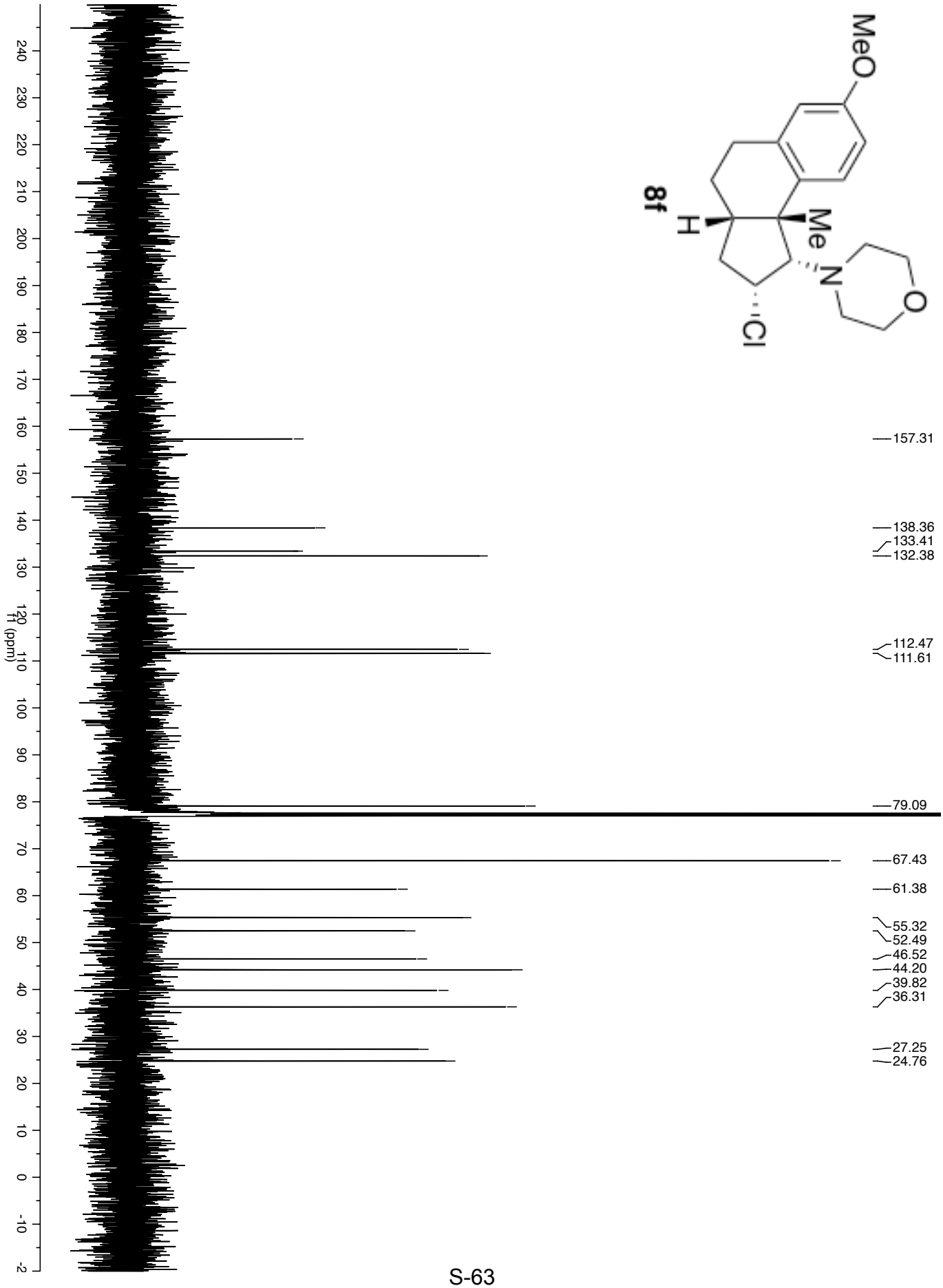

O
N
Cl

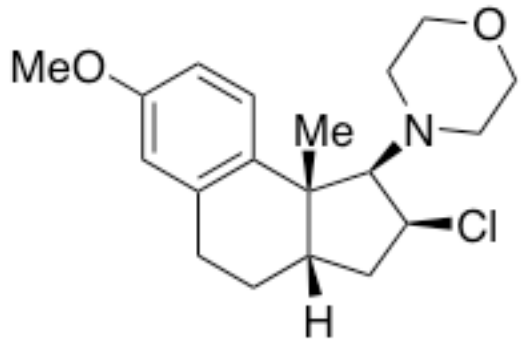
3e


1.00
4.68
1.06
4.50
1.29
1.21
4.90
5.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


3e
N
O
Cl
137.15
133.82
73.37
68.10
59.60
50.05
45.74
25.87
25.84
23.07
f1 (ppm)

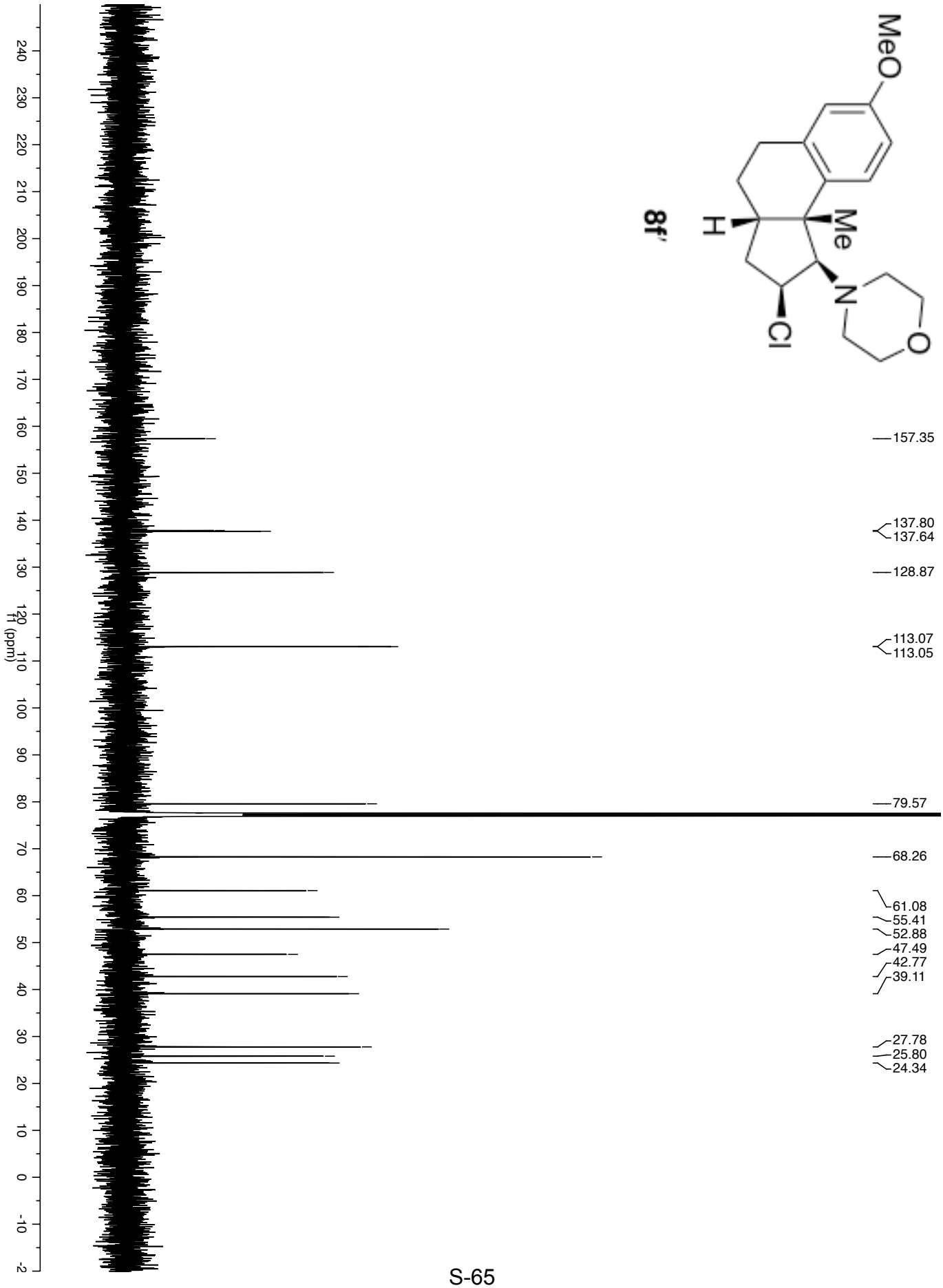

MeO
8f
H
Me
N
O
Cl
1.00
0.99
0.95
0.98
3.17
1.97
1.94
0.98
4.92
1.14
1.07
3.20
1.27
2.89
f1 (ppm)

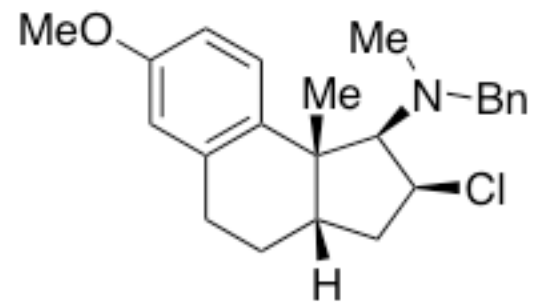

MeO
8f
H
Me
N
O
Cl
157.31
138.36
133.41
132.38
112.47
111.61
79.09
67.43
61.38
55.32
52.49
46.52
44.20
39.82
36.31
27.25
24.76
f1 (ppm)


MeO
Me
N
O
Cl
H

8f′

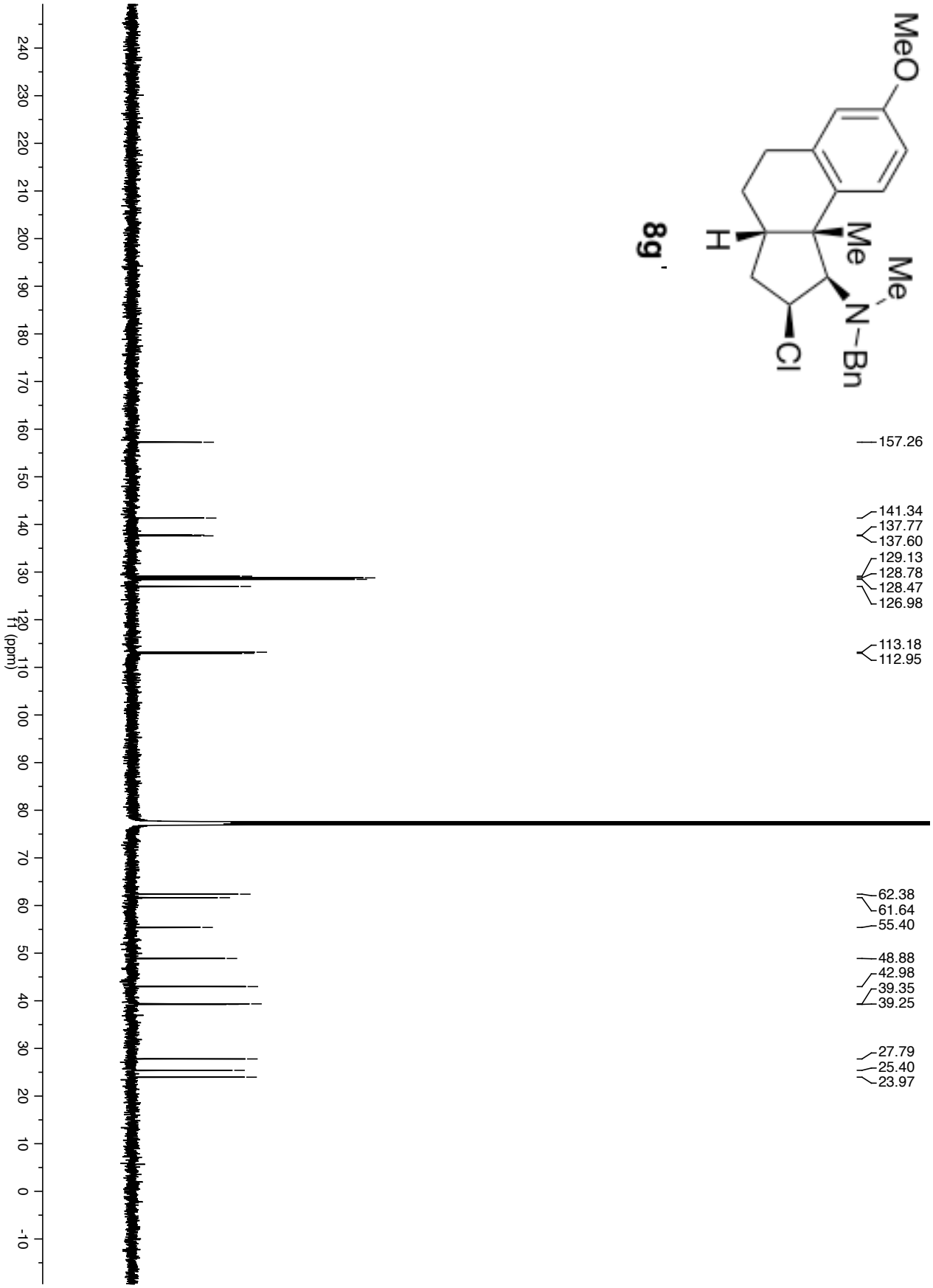
1.00
1.08
0.95
1.02
7.50
2.01
0.96
2.09
1.16
2.19
2.37
1.33
1.34
3.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

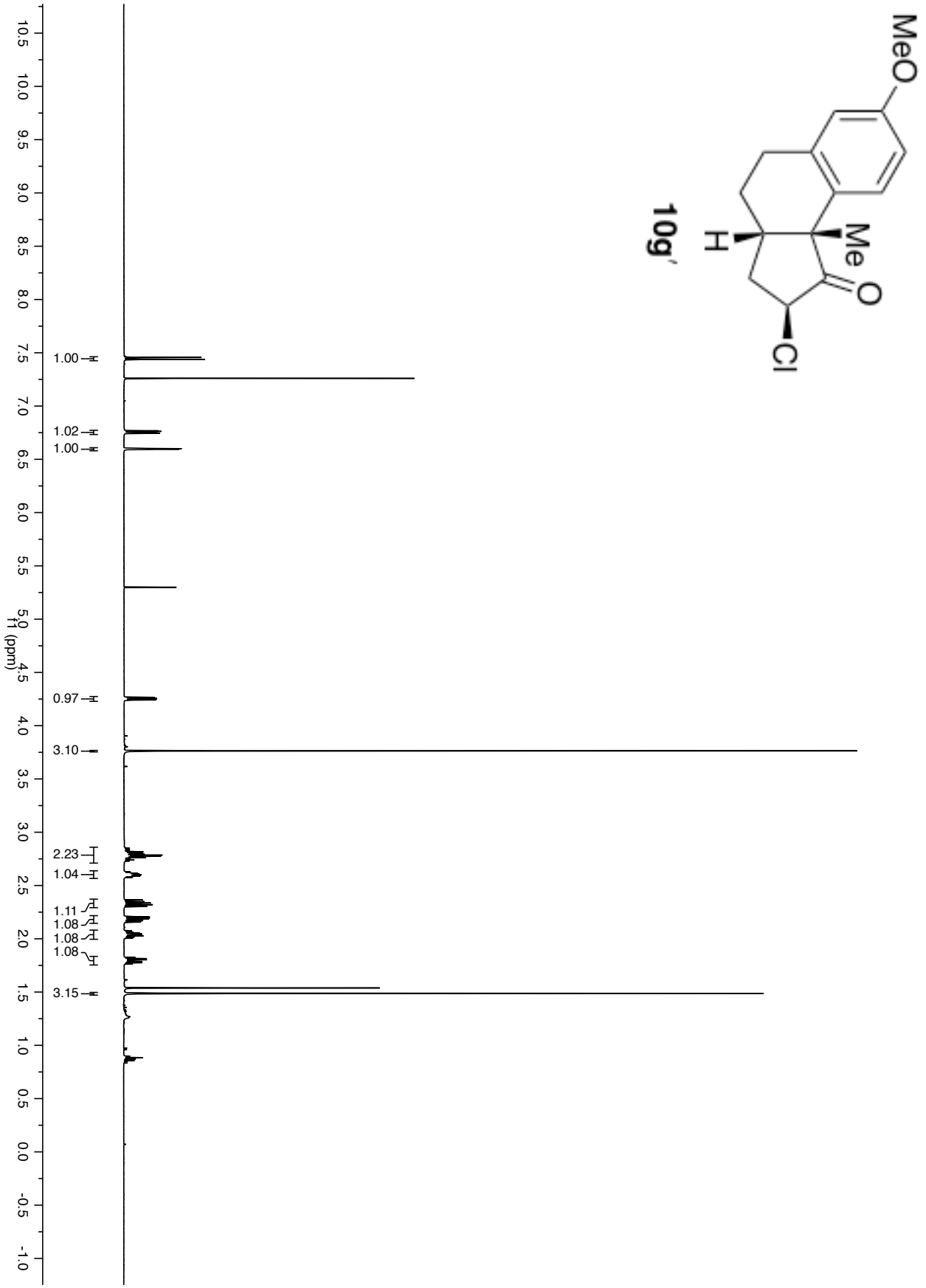

MeO
H
Me
N
Cl
O
8f'
157.35
137.80
137.64
128.87
113.07
113.05
79.57
68.26
61.08
55.41
52.88
47.49
42.77
39.11
27.78
25.80
24.34
f1 (ppm)

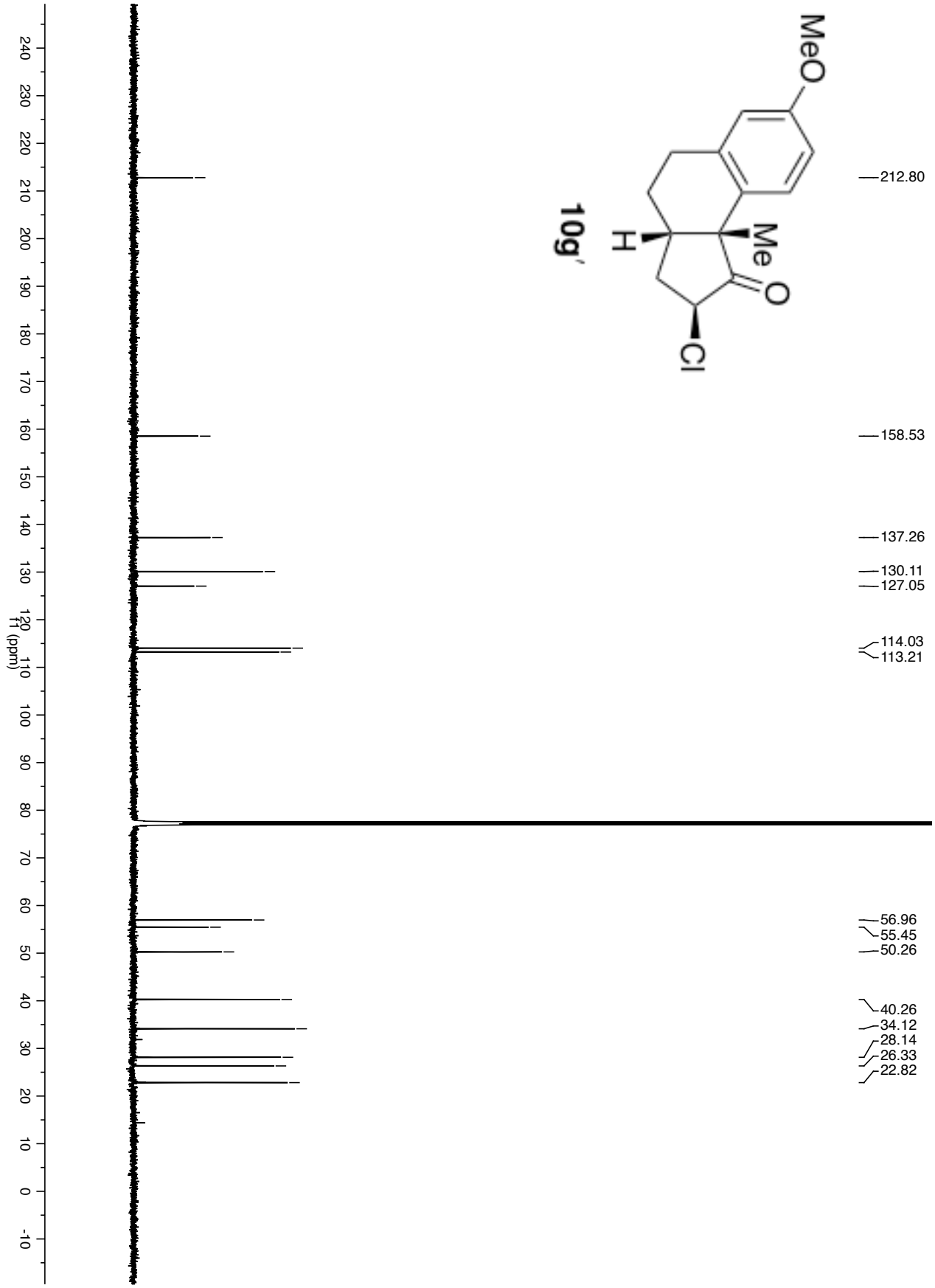

MeO
Me
Me
N–Bn
Cl
H

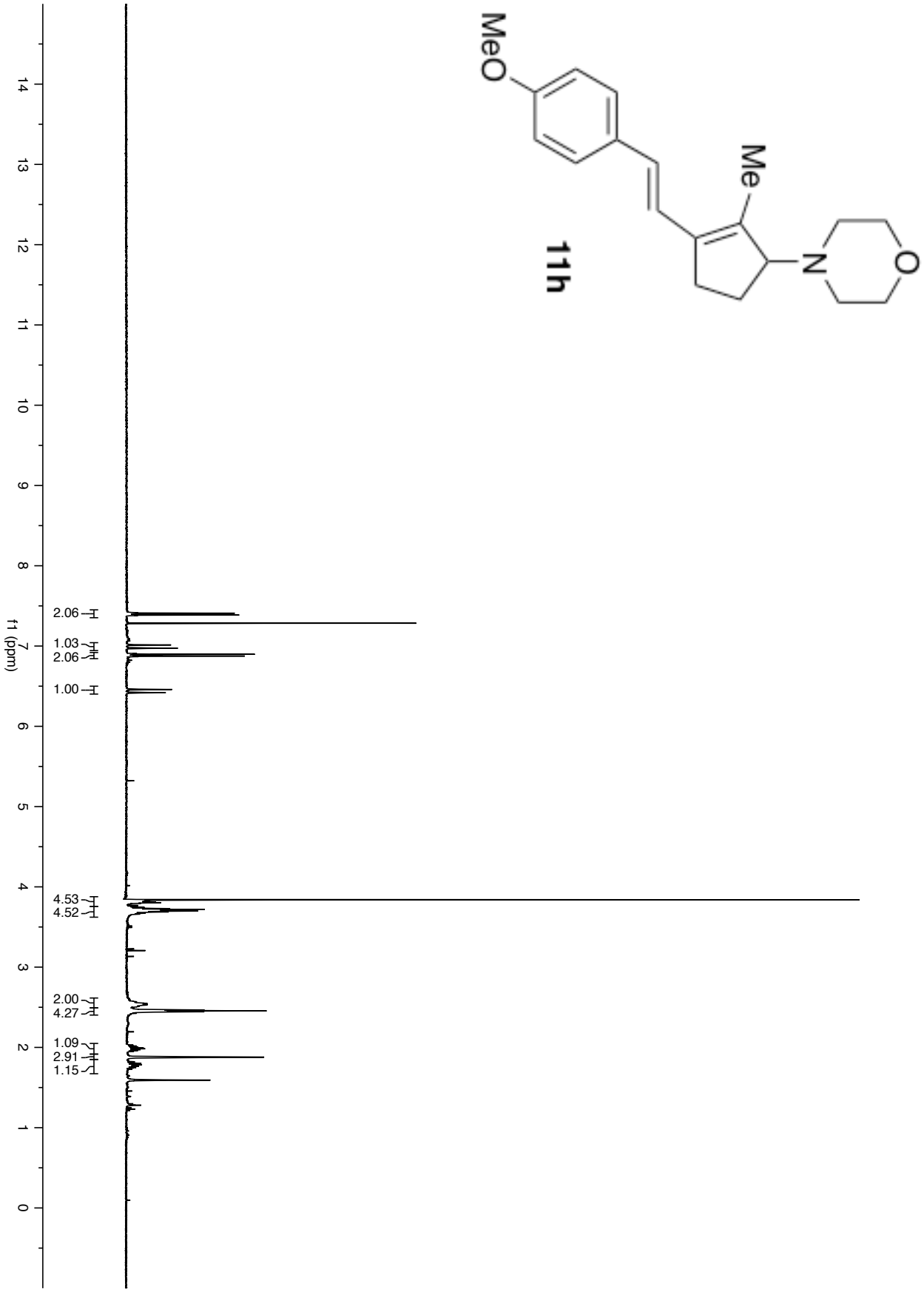
8g'

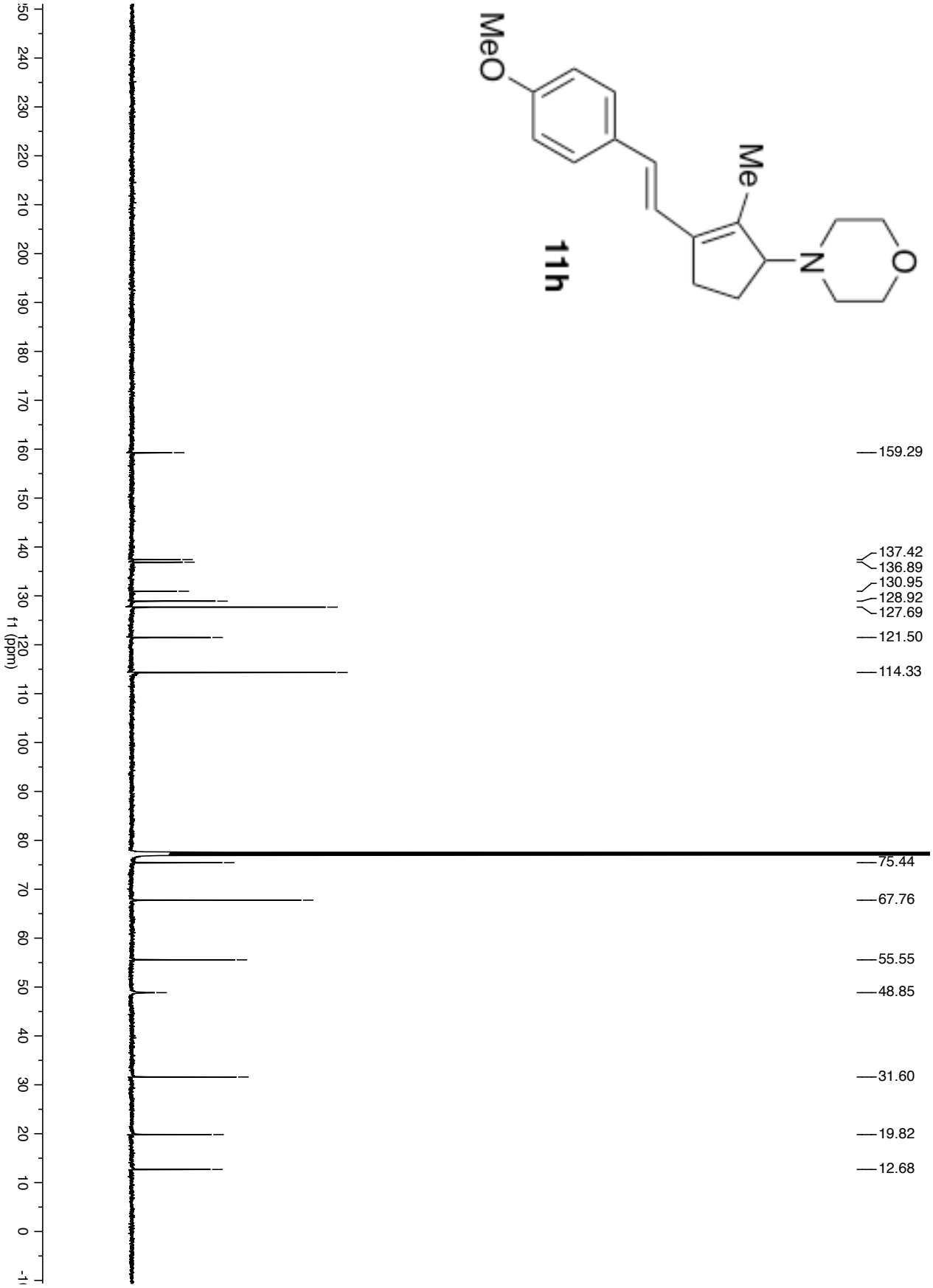
1.91
1.88
0.82
0.96
0.94
0.92
2.98
2.93
0.98
1.06
2.82
1.02
1.00
1.07
1.00
1.00
1.01
2.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


MeO
Me
N–Bn
Me
H
Cl
8g
157.26
141.34
137.77
137.60
129.13
128.78
128.47
126.98
113.18
112.95
62.38
61.64
55.40
48.88
42.98
39.35
39.25
27.79
25.40
23.97
f1 (ppm)


MeO
Me
O
H
Cl
10g′
1.00
1.02
1.00
0.97
3.10
2.23
1.04
1.11
1.08
1.08
1.08
3.15
f1 (ppm)


MeO
Me
O
H
Cl
10g′
212.80
158.53
137.26
130.11
127.05
114.03
113.21
56.96
55.45
50.26
40.26
34.12
28.14
26.33
22.82
f1 (ppm)


MeO
Me
N
O
11h
f1 (ppm)
2.06
1.03
2.06
1.00
4.53
4.52
2.00
4.27
1.09
2.91
1.15


MeO
Me
N
O
11h
159.29
137.42
136.89
130.95
128.92
127.69
121.50
114.33
75.44
67.76
55.55
48.85
31.60
19.82
12.68
f1 (ppm)