Gold (I)-Catalyzed Claisen Rearrangement of Allenyl Vinyl Ethers; Synthesis of Substituted 1,3-Dienes

Marie E. Krafft,* Kassem M. Hallal, Dinesh V. Vidhani, John W. Cran

Supporting Information

General Information

Unless otherwise noted all commercial materials were used without further purification. Dichloromethane (CH_2Cl_2), Tetrahydrofuran (THF), and diisopropyl amine ($i\text{-}Pr_2NH$) were purchased from J.T.Baker and distilled prior to use. Methanol was purchased from EMD and was used without further purification. 1,4-dioxane was obtained from ACROS organics and was used without purification. Ethyl vinyl ether, copper bromide (CuBr), mercuric acetate ($Hg(OAc)_2$), dihydropyran, silverhexafluoroantimonate ($AgSbF_6$), silver triflate (AgOTf), silvertetra-fluoroborate ($AgBF_4$), silvercarbonate (Ag_2CO_3), silverperchlorate ($AgClO_4$). (Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I) (IPrAuCl) was purchased from Strem chemicals and $AuClPPh_3$ and all other gold catalysts were purchased from Aldrich.

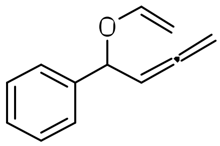
Thin-Layer chromatographic (TLC) analysis of the reaction was performed using Merck silica gel 60 F_{254} TLC plates and was visualized by anisaldehyde staining and UV. Flash column chromatography was performed using Merck 60 silica gel (230-400 mesh) and Alumina (80-200 mesh). ^1H and ^{13}C NMR spectra were recorded with Bruker DRX-500 and 600 spectrometers and referenced to $CDCl_3$ or C_6D_6 . Mass spectral data were obtained via the mass spectrometry lab facility at Florida State University. Infrared (IR) spectra were recorded as thin films on sodium chloride plates using a Perkin-Elmer FT-IR Paragon 1000 Fourier Transform spectrometer with frequencies given in reciprocal centimeters (cm^{-1}).

Propargylic alcohols were prepared by the addition of ethynylmagnesium bromide to the corresponding aldehyde. Allenols were prepared according to Crabbe' homologation method.[1] The allenyl vinyl ethers were prepared according to Yamamoto's procedure.[2] Spectroscopic data for compounds **B**,[3] **D**,[4] were previously reported.

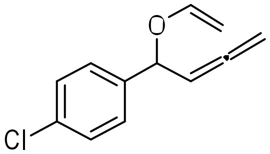
Reported yields refer to isolated yields of pure material as determined by spectroscopic analysis.

General procedure for synthesis of allenyl vinyl ethers

Vinyl ethers were prepared according to the method of Yamamoto,[2] the allenyl alcohol was dissolved in ethyl vinyl ether (0.1M) and then mercuric acetate (0.66 equiv.) was added. The reaction mixture was stirred at room temperature overnight. Potassium carbonate was added to the reaction mixture and the product was extracted with diethyl ether, the organic layer was dried over sodium sulfate and then the product was purified using column chromatography with hexane as an eluent.



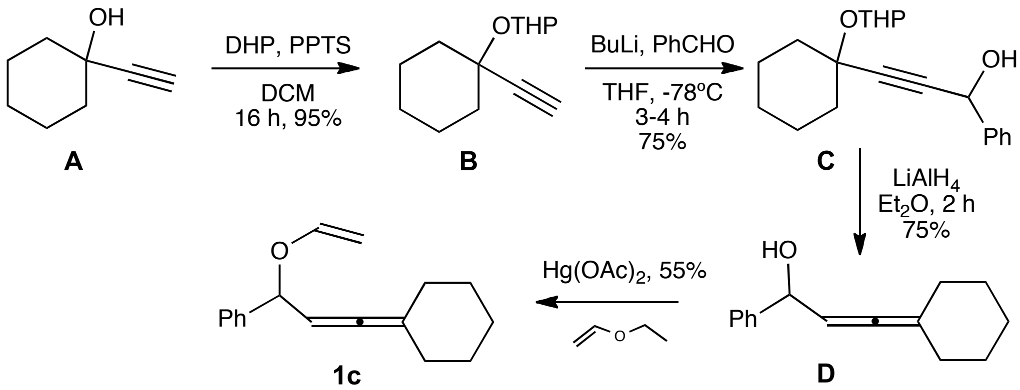
Synthesis of (1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1a). (1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 66% yield as a colorless oil:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 6.44 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.38 (ddd, *J* = 7.8, 6.5, 6.5 Hz, 1H), 5.32 (ddd *J* = 7.8, 1.55, 1.45 Hz, 1H), 4.93 (δ_{obs}) (ABdd, J_{AB} = 11 Hz, *J* = 6.5, 1.55 Hz, Δυ = + 23.5 Hz, 1H; ABdd, J_{AB} = 11 Hz, *J* = 6.5, 1.45 Hz, Δυ = - 23.5 Hz, 1H), 4.39 (dd, *J* = 14.2, 1.8 Hz, 1H), 4.11 (dd, *J* = 6.7, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.72, 150.08, 140.15, 128.64, 128.09, 126.51, 92.52, 90.11, 79.54, 77.35; IR (cm^{-1}) 1617.64, 1636.78, 1956.06, 2894.81, 3031.30, 3064.35; HRMS (EI$^+$) calc'd for $[C_{12}H_{12}O]^+$: m/z 172.08882, found 172.08888.



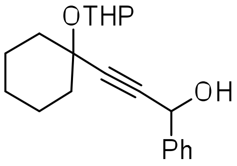
Synthesis of 1-chloro-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1b). 1-chloro-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and the allenyl vinyl ether was obtained in 75% yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.12 – 6.97 (m, 2H), 6.42 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.33 (ddd, *J* = 7.5, 6.3, 6.3 Hz, 1H), 5.28 (d, *J* = 7.5 Hz, 1H), 4.86 (δ_{obs}) (ABdd, J_{AB} = 11.5 Hz, *J* = 6.3, 1.4 Hz, Δυ = + 21.82 Hz, 1H; ABdd, J_{AB} = 11.5 Hz, *J* =

6.3, 1.2 Hz, ⊗{ = - 21.82 Hz, 1H), 4.37 (dd, *J* = 14.2, 1.9 Hz, 1H), 4.11 (dd, *J* = 6.7, 1.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.87, 150.01, 138.87, 133.82, 128.78, 127.90, 92.29, 90.42, 78.76, 77.64; IR (cm^{-1}) 1617.39, 1637.5, 1956.21, 2891.34, 2988.25, 3117.38; HRMS (EI$^+$) calc'd for $[C_{12}H_{11}OCl]^+$: m/z 206.04985, found 206.05019.

Synthesis of (3-cyclohexylidene-1-(vinyloxy)allyl)benzene (1c) from propargyl alcohol A

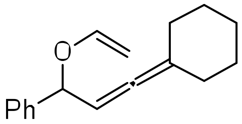


Synthesis of **1c** began with THP protection of propargylic alcohol **A** giving rise to the THP-protected alcohol **B** in 95% yield.[3] Treatment of ether **B** with butyllithium and benzaldehyde led to the formation of the mono-protected diol **C** in 75% yield. Reduction of **C** using lithium aluminum hydride gave allenyl alcohol **D** in 75% yield.[4] Allenyl alcohol **D** was then converted into vinyl ether **1c** using ethyl vinyl ether and mercuric acetate.

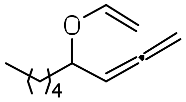


Synthesis of 1-phenyl-3-(1-((tetrahydro-2H-pyran-2-yl)oxy)cyclohexyl)prop-2-yn-1-ol, C. 1-phenyl-3-(1-((tetrahydro-2H-pyran-2-yl)oxy)cyclohexyl)prop-2-yn-1-ol **C** was prepared according to the procedure of Cheung.[5] Treatment of **B** with butyllithium and benzaldehyde led to the formation of the mono-protected diol **C** in 75% yield. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 75 % yield as a yellow oil: ^{1}H NMR (500 MHz, C_6D_6) δ 7.62-7.57 (m, 2H), 7.19-7.14 (m, 2H), 7.09-7.04 (m, 1H), 5.48-5.41(m,2H), 3.96-3.88 (m, 1H), 3.44-3.36 (m, 1H), 2.2(s, 1H), 2.02-1.94 (m, 1H), 1.91-1.81 (m, 1H), 1.8-1.54 (m, 8H), 1.4-1.21 (m,4H), 1.195-1.10 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6)

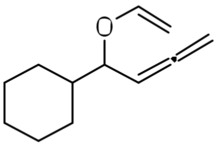
δ128.28, 127.98, 127.80, 126.65, 94.94, 74.61, 64.23, 62.09, 38.81, 31.92, 25.58, 25.37, 23.06, 19.64; HRMS (EI$^+$) calc'd for $[C_{20}H_{25}O_3]^+$: m/z 313.18038, found 313.18201.



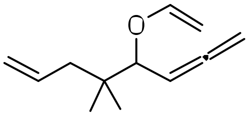
Synthesis of (3-cyclohexylidene-1-(vinyloxy)allyl)benzene (1c). (3-cyclohexylidene-1-(vinyloxy)allyl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 60% yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.17-7.13 (m, 2H), 7.08-7.04 (m, 1H), 6.44 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.38 – 5.34 (m, 1H), 5.25 (d, *J* = 6.76 Hz, 1H), 4.5 (dd, *J* = 14.2, 1.6 Hz, 1H), 4.06 (dd, *J* = 6.6, 1.6 Hz, 1H), 2.06-1.9 (m, 4H), 1.44-1.35 (m, 2H), 1.3-1.17 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.71, 150.8, 141.6, 128.48, 127.71, 126.88, 105.2, 92, 89.7, 80.6, 31.5, 27.3, 26.2 ; IR (cm^{-1}) 1614.55, 1635.19, 1967.28, 2854.24, 2887.73, 2928.33, 3030.09, 3063.90, 3086.76, 3116.01; HRMS (EI$^+$) calc'd for $[C_{17}H_{20}O]^+$: m/z 240.15142, found 240.15116.



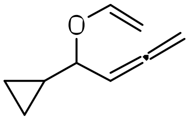
Synthesis of 4-(vinyloxy)nona-1,2-diene (1d). 4-(vinyloxy)nona-1,2-diene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 60% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.35 (dd, *J* = 14.2, 6.6 Hz, 1H), 5.13 (ddd, *J* = 6.7, 6.6, 6.6 Hz, 1H), 4.86 (δ_{obs}) (ABdd, J_{AB} =11, *J* = 6.7, 1.55 Hz, Δυ = + 15.18, 1H; ABdd, J_{AB} =11, *J* = 6.3, 1.55 Hz, Δυ = - 15.18, 1H), 4.3 (dd, *J* = 14.1, 1.5 Hz, 1H), 4.15 (ddd, *J* = 6.7, 1.5, 1.5 Hz, 1H), 4.05 (dd, *J* = 6.6, 1.5 Hz, 1H), 1.74 – 1.61 (m, 1H), 1.51 (tt, *J* = 10.5, 5.7 Hz, 1H), 1.44 – 1.01 (m, 6H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 208.72, 150.92, 92.06, 88.92, 77.77, 76.26, 35.70, 31.90, 25.23, 22.90, 14.18; IR (cm^{-1}) 1614.84, 1635.58, 1957.17, 2346.04, 2372.94, 2733.77, 2861.62, 2932.46, 3024.40, 3046.73, 3119.21; HRMS (EI$^+$) calc'd for $[C_{11}H_{18}O]^+$: m/z 166.13577, found 166.13540.



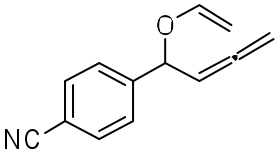
Synthesis of 1-(vinyloxy)buta-2,3-dien-1-yl)cyclohexane (1e). 1-(vinyloxy)buta-2,3-dien-1-yl)cyclohexane was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 65% yield as a colorless oil: ; ^{1}H NMR (500 MHz, C_6D_6) δ 6.37 (dd, J = 14.1, 6.0 Hz, 1H), 5.0 (ddd, J = 8.1, 6.8, 6.6 Hz, 1H), 4.57 (δ_{obs}) (ABdd, J_{AB} = 11 Hz, J = 6.8, 1.3 Hz, Δυ = + 15.8 Hz, 1H; ABdd, J_{AB} = 11 Hz, J = 6.6, 1.4 Hz, Δυ = - 15.8 Hz, 1H), 4.47 (dd, J = 14.1, 1.4 Hz, 1H), 4.06 (ddd, J = 8.1, 1.4, 1.3, 0.75 Hz, 1H), 3.92 (dd, J = 7.9, 1.4 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.74 – 1.44 (m, 5H), 1.19 – 0.91 (m, 5H); ^{13}C NMR (126 MHz, C_6D_6) δ 209.21, 151.30, 90.39, 88.81, 82.63, 75.72, 43.05, 28.83, 26.76, 26.24; IR (cm^{-1})1613.07, 1634.64, 1957.05, 2354.99, 2368.41, 2670.53, 2797.46, 2858.10, 2944.86, 3023.59, 3118.15; HRMS (EI$^+$) calc'd for $[C_{12}H_{18}O]^+$: m/z 178.13577, found 178.13610.



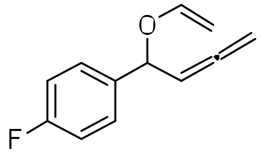
Synthesis of 5,5-dimethyl-4-(vinyloxy)octa-1,2,7-triene (1f). 5,5-dimethyl-4-(vinyloxy)octa-1,2,7-triene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 60% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.33 (dd, J = 14.1, 6.6 Hz, 1H), 5.75 (ddt, J = 16.6, 10.5, 7.5 Hz, 1H), 5.01 (dd, J = 16.6, 2.8 Hz, 1H), 4.98 (dd, J = 10.5, 2.8 Hz, 1H), 4.95 (ddd, J = 8.5, 6.66, 6.6 Hz, 1H), 4.55 (δ_{obs}) (ABdd, J_{AB} = 11 Hz, J = 6.66, 1.2 Hz, Δυ = + 17.5 Hz, 1H; ABdd, J_{AB} = 11 Hz, J = 6.6, 1.3 Hz, Δυ = - 15.8 Hz, 1H), 4.46 (dd, J = 14.1, 1.4 Hz, 1H), 4.05 (dd, J = 6.6, 1.4 Hz, 1H), 3.91 (ddd, J = 8.6, 1.3, 1.1 Hz, 1H), 2.16 (dd, J = 13.5, 7.4 Hz, 1H), 1.99 (dd, J = 13.5, 7.4 Hz, 1H), 0.93 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 209.75, 151.27, 134.89, 117.85, 88.98, 88.60, 84.45, 75.51, 43.56, 38.45, 22.96, 22.72; IR (cm^{-1})1614.41, 1636.51, 1957.44, 2345.85, 2366.55, 2876.89, 2933.43, 2965.27, 3005.78, 3077.76, 3119.69; HRMS (EI$^+$) calc'd for $[C_{12}H_{18}O]^+$: m/z 178.13577, found 178.13556.



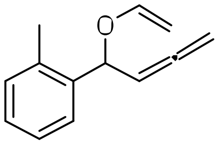
Synthesis of (1-(vinyloxy)buta-2,3-dien-1-yl)cyclopropane (1g). (1-(vinyloxy)buta-2,3-dien-1-yl)cyclopropane was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 55% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.33 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.14 (ddd, *J* = 6.8, 6.4, 6.3 Hz, 1H), 4.58 (δ_{obs}) (ABdd, J_{AB} = 11 Hz, *J* = 6.4, 1.8 Hz, Δυ = + 13.6 Hz, 1H; ABdd, J_{AB} = 11 Hz, *J* = 6.3, 1.6 Hz, Δυ = - 13.6 Hz, 1H), 4.46 (dd, *J* = 14.1, 1.4 Hz, 1H) 4.47 (dd, *J* = 14.1, 1.4 Hz, 1H), 4.05 (dd, *J* = 6.6, 1.4 Hz, 1H), 3.64 (dddd, *J* = 7.3, 6.8, 1.8, 1.6 Hz, 1H), 1.05 – 0.94 (m, 1H), 0.41 – 0.24 (m, 3H), 0.23 – 0.13 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 208.82, 150.88, 91.31, 89.08, 81.18, 76.32, 16.10, 3.51, 2.14; IR (cm^{-1})1614.82, 1635.95, 2345.89, 2367.53, 2888.82, 3010.67, 3084.60, 3118.1; HRMS (EI$^+$) calc'd for $[C_9H_{12}O]^+$: m/z136.08882, found 136.08901.



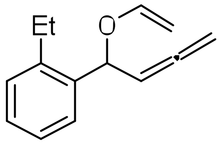
Synthesis of 4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzonitrile (1h). 4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzonitrile was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column (10:1 Hexane : EtOAc) and the allenyl vinyl ether was obtained in 65% yield as a colorless oil: ^{1}H NMR (600 MHz, C_6D_6) δ 7.05 – 7.02 (m, 2H), 6.94 – 6.92 (m, 2H), 6.21 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.08 (d, *J* = 7.6, 1H), 4.96 (ddd, *J* = 7.6, 6.4, 6.3 Hz, 1H), 4.78 (δ_{obs}) (ABdd, J_{AB} = 11.6 Hz, *J* = 6.3, 1.3 Hz, Δυ = + 21.44 Hz, 1H; ABdd, J_{AB} = 11.6 Hz, *J* = 6.2, 1.5 Hz, Δυ= - 21.44 Hz, 1H), 4.33 (dd, *J* = 14.2, 1.9 Hz, 1H), 4.03 (dd, *J* = 6.7, 1.9 Hz, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 208.88, 149.98, 145.12, 132.14, 126.98, 118.61, 112.19, 92.12, 90.51, 78.42, 77.48; IR (cm^{-1}) 1637.88, 1724.79, 1956.20, 2229.28, 2894.09, 2991.65, 3066.97, 3117.88; HRMS (EI$^+$) calc'd for $[C_{13}H_{11}ON]^+$: m/z 197.08407, found 197.08373.



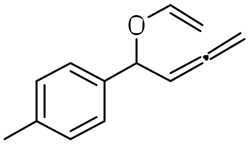
Synthesis of 1-fluoro-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1i). 1-fluoro-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and the allenyl vinyl ether was obtained in 71% yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.07 (ddd, *J* = 8.7, 5.8, 2.4 Hz, 2H), 6.44 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.36 (ddd, *J* = 7.4, 6.5, 6.4 Hz, 2H), 5.29 (d, *J* =7.4 Hz, 1H), 4.86 (δ_{obs}) (ABdd, J_{AB} = 11.4 Hz, *J* = 6.5, 1.6 Hz, Δυ = + 22.26 Hz, 1H; ABdd, J_{AB} = 11.4 Hz, *J* = 6.5, 1.5 Hz, Δυ = - 22.26 Hz, 1H), 4.39 (dd, *J* = 14.2, 1.9 Hz, 1H), 4.13 (dd, *J* = 6.7, 1.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.85, 161.54, 150.08, 136.18, 128.24, 115.41, 92.45, 90.33, 78.85, 77.55; IR (cm^{-1}) 1510.51, 1606.39, 1618.31, 1637.62, 1956.48, 2894.16, 3048, 3118.28; HRMS (EI$^+$) calc'd for $[C_{12}H_{11}OF]^+$: m/z 190.07940., found 190.07965.



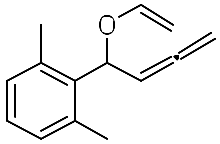
Synthesis of 1-methyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1j). 1-methyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 60 % yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.12 – 7.00 (m, 2H), 6.99 – 6.93 (m, 1H), 6.34 (dd, *J* = 14.3, 6.7 Hz, 1H), 5.41 (d, *J* = 7.4 Hz, 1H), 5.31 (ddd, *J* = 7.4, 6.6, 6.5 Hz, 1H), 4.87 (δ_{obs}) (ABdd, J_{AB} = 11.2 Hz, *J* = 6.6, 1.8 Hz, Δυ = + 30 Hz, 2H; ABdd, J_{AB} = 11.2 Hz, *J* = 6.5, 1.8 Hz, Δυ = - 30 Hz, 1H), 4.03 (dd, *J* = 6.7, 1.7 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209, 150.6, 138.8, 135.3, 130.91,127.92, 126.54, 126.49, 92.11, 89.79, 77.07, 76.95, 19.02; IR (cm^{-1}) 1615.32, 1653.94, 1956.40,. 2929.25, 2955.59, 3026.13, 3067.66, 3116.93; HRMS (EI$^+$) calc'd for $[C_{13}H_{14}O]^+$: m/z 186.10447, found 186.10467.



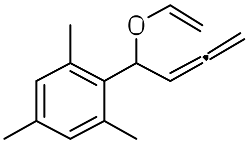
Synthesis of 1-ethyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1k). 1-ethyl-2-(1-(vinyloxy) buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 71 % yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.35 – 7.22 (m, 3H), 6.45 (dd, *J* = 14.2, 6.7 Hz, 1H), 5.41 (d, *J* = 7.5 Hz, 1H), 5.31 (ddd, *J* = 7.5, 6.6, 6.6 Hz, 1H), 4.87 (δ_{obs}) (ABdd, J_{AB} = 11.2 Hz, *J* = 6.6, 1.65 Hz, Δυ = + 30 Hz, 1H; ABdd, J_{AB} = 11.2 Hz, *J* = 6.6, 1.55 Hz, Δυ = - 30 Hz, 1H), 4.39 (dd, *J* = 14.2, 1.7 Hz, 1H), 4.12 (dd, *J* = 6.7, 1.7 Hz, 1H), 2.76 (qd, *J* = 7.6, 2.5 Hz, 2H), 1.29 (dd, *J* = 7.6, 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.78, 150.21, 141.22, 137.69, 128.80, 128.16, 126.49, 126.35, 92.29, 89.96, 77.25, 76.33, 25.39, 15.43; IR (cm^{-1}) 1615.33, 1726.11, 1956.35, 2876.3, 2934.98, 2968.81, 3024.77, 3066.05, 3117.54; HRMS (EI$^+$) calc'd for $[C_{14}H_{16}O]^+$: m/z 200.12012, found 200.12014.



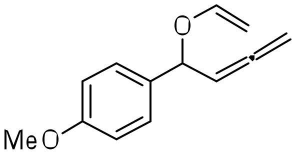
Synthesis of 1-methyl-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1l). 1-methyl-4-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 80% yield as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.47 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.41 (ddd, *J* = 7.6, 6.6, 6.6 Hz, 1H), 5.32 (d, *J* = 7.6 Hz, 1H), 4.9 (δ_{obs}) (ABdd, J_{AB} = 11.2 Hz, *J* = 6.7, 6.5 Hz, Δυ = 29 Hz, 2H), 4.41 (dd, *J* = 14.2, 1.6 Hz, 1H), 4.13 (dd, *J* = 6.6, 1.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.77, 150.25, 137.84, 137.46, 129.32, 126.48, 92.62, 90.02, 79.50, 77.26, 21.30; IR (cm^{-1}) 1514.26, 1617.45, 1626.58, 1956.56, 3868.4, 2922.76, 3025.77, 2988.88, 3050.66, 3117.31; HRMS (EI$^+$) calc'd for $[C_{13}H_{14}O]^+$: m/z 186.10447, found 186.10397.



Synthesis of 1,3-dimethyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1m). 1,3-dimethyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 72% yield as a colorless oil : ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.36 (dd, *J* = 15.0, 5.7 Hz, 1H), 5.78 (ddd, *J* = 6.6, 2.7, 2.5 Hz, 1H), 5.56 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H), 4.83 (δ_{obs}) (ABdd, J_{AB} = 11.3 Hz, *J* = 6.5, 2.6 Hz, $\Delta\upsilon$ = + 28.5 Hz, 1H; ABdd, J_{AB} = 11.3 Hz, *J* = 6.6, 2.6 Hz, $\Delta\upsilon$ = - 28.5 Hz, 1H), 4.29 (dd, *J* = 14.1, 1.7 Hz, 1H), 4.01 (dd, *J* = 6.6, 1.7 Hz, 1H), 2.42 (s, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.55, 149.95, 136.35, 135.91, 129.27, 127.82, 90.58, 89.42, 77.20, 76.33, 20.81; IR (cm^{-1}) 1614.78, 1956.28, 2345.78, 2871.97, 2928.72, 2968.74, 3024.22, 3067.55, 3118.08; HRMS (EI$^+$) calc'd for $[C_{14}H_{16}O]^+$: m/z 200.12012, found 200.12042.



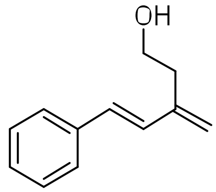
Synthesis of 1,3,5-trimethyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene (1n). 1,3,5-trimethyl-2-(1-(vinyloxy)buta-2,3-dien-1-yl)benzene was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers. The crude mixture was purified by flash chromatography using an alumina column and hexane as an eluent and afforded the allenyl vinyl ether in 70% yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.35 (dd, *J* = 14.1, 6.6 Hz, 1H), 5.75 (ddd, , *J* = 6.7, 2.55, 2.55 Hz 1H), 5.54 (ddd, *J* = 6.7, 6.6, 6.6 Hz, 1H), 4.82 (δ_{obs}) (ABdd, J_{AB} = 11.2 Hz, *J* = 6.6, 2.55 Hz, $\Delta\upsilon$ = + 24.8 Hz, 1H; ABdd, J_{AB} = 11.2 Hz, *J* = 6.6, 2.55 Hz, $\Delta\upsilon$ = - 24.8 Hz, 1H), 4.28 (dd, *J* = 14.1, 1.6 Hz, 1H), 4.00 (dd, *J* = 6.6, 1.6 Hz, 1H), 2.38 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.52, 149.96, 137.38, 136.24, 132.97, 130.08, 90.73, 89.36, 77.16, 76.25, 20.99, 20.70; IR (cm^{-1}) 1578.39, 1612.71, 1634.96, 1956.11, 2864.16, 2921, 2948.02, 2969.48, 3117.03, 3407.42; HRMS (EI$^+$) calc'd for [$C_{15}H_{18}O$]$^+$: m/z 214.13577, found 214.13534.



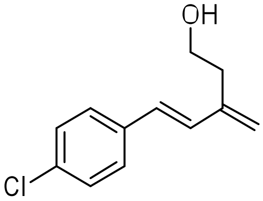
Synthesis of 1-(4-methoxyphenyl)buta-2,3-dien-1-ol (1o). 1-(4-methoxyphenyl)buta-2,3-dien-1-ol was prepared according to the same procedure used for the synthesis of allenyl vinyl ethers The crude mixture was purified by flash chromatography using an alumina column (15:1 Hexane : EtOAc) as an eluent and afforded the allenyl vinyl ether in 65% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 7.25 – 7.19 (m, 2H), 6.79 – 6.73 (m, 2H), 6.39 (dd, J = 14.1, 6.6 Hz, 1H), 5.39 (ddd, J = 7.4, 6.6, 1.8, 1.6 Hz, 1H), 5.21 (ddd, J = 7.4, 1.9, 1.8 Hz, 1H), 4.58 (δ_{obs}) (ABdd, J_{AB} = 11 Hz, J = 6.6, 1.9 Hz, Δυ = + 20.4 Hz, 1H; ABdd, J_{AB} = 11 Hz, J = 6.5, 1.8 Hz, Δυ = - 20.4 Hz, 1H), 4.51 (dd, J = 14.2, 1.6 Hz, 1H), 4.07 (dd, J = 6.7, 1.6 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 208.79, 159.83, 150.61, 132.87, 128.11, 114.11, 93.31, 89.87, 79.40, 77.06, 54.72; IR (cm^{-1}) 1513.54, 1586.29, 1613.18, 1956.25, 2836.92, 2908.12, 2957.61, 2935.63, 3001.14, 3037.71, 3116.36; HRMS (EI$^+$) calc'd for [$C_{13}H_{14}O_2$]$^+$: m/z 202.09938, found 202.10044.

C. General Procedure for the gold (I)-Catalyzed Claisen Rearrangement of Allenyl Vinyl Ethers

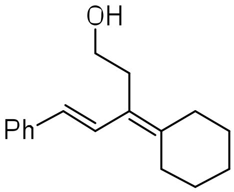
To a solution of $AgSbF_6$ in CH_2Cl_2 (0.01M) was added a solution of IPrAuCl in CH_2Cl_2 (0.01M). After stirring for 5 min at rt, the mixture was filtered through a cotton plug and added to a mixture of the allenyl vinyl ether in CH_2Cl_2 (0.05M). The reaction mixture was stirred at rt until complete consumption of the starting material was observed by TLC. The reaction mixture was then diluted with MeOH (2x CH_2Cl_2) and $NaBH_4$ (1 equiv.) was added. The resulting mixture was stirred for 30 min, concentrated and the product was purified using column chromatography.



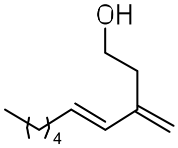
Synthesis of (E)-3-methylene-5-phenylpent-4-en-1-ol (2a). (E)-3-methylene-5-phenylpent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 86% yield as a white solid (m.p = 39 ˚C): ^{1}H NMR (500 MHz, C_6D_6) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.05 (m, 3H), 6.76 (d, *J* = 16.3 Hz, 1H), 6.58 (d, *J* = 16.3 Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.48 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, C_6D_6) δ 143.05, 137.56, 130.95, 128.85, 128.83, 127.77, 126.87, 117.97, 61.32, 35.69; IR (cm^{-1}) 1602.95, 2345.91, 2368.8, 2883.25, 2947.87, 3026.55, 3081.97, 3343.85; HRMS (EI$^+$) calc'd for $[C_{12}H_{14}O]^+$: m/z 174.10447, found 174.10423.



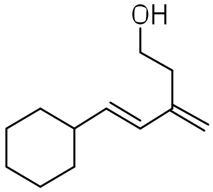
Synthesis of (E)-5-(4-chlorophenyl)-3-methylenepent-4-en-1-ol (2b). (E)-5-(4-chloro phenyl)-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 80% yield as a white solid (m.p = 41 ˚C): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 4H), 6.78 (d, *J* = 16.3 Hz, 1H), 6.55 (d, *J* = 16.3 Hz, 1H), 5.27 (s, 1H), 5.17 (s, 1H), 3.82 (td, *J* = 6.3, 5.8 Hz, 2H), 2.62 (t, *J* = 6.5 Hz, 2H), 1.51 (t, *J* = 5.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.31, 135.67, 133.38, 131.10, 128.95, 127.77, 127.55, 118.89, 61.31, 35.45; IR (cm^{-1}) 1603.93, 2345.78, 2366.84, 28



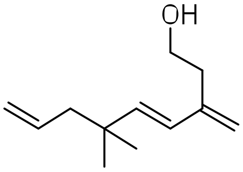
Synthesis of (E)-3-cyclohexylidene-5-phenylpent-4-en-1-ol (2c). (E)-3-cyclohexylidene-5-phenylpent-4-en-1-ol was prepared according to the same procedure used for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the propargylic alcohol in 65% yield as a white solid (m.p = 39 ˚C): ^{1}H NMR (500 MHz, C_6D_6) δ 7.37 – 7.30 (m, 3H), 7.20 – 7.11 (m, 2H), 7.10 – 7.02 (m, 1H), 6.67 (d, J = 16.1 Hz, 1H), 3.58 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 2.31 (d, J = 6.0 Hz, 2H), 2.24 – 2.16 (m, 2H), 1.45 (m, 6H), 1.17 (s, 1H); ^{13}C NMR (126 MHz, C6D6) δ 143.32, 138.93, 128.85, 127.44, 127.16, 126.60, 124.89, 62.04, 32.14, 31.90, 30.78, 28.93, 28.71, 27.13; IR (cm^{-1}) 1447.18, 1494.11, 1594.96, 1619.05, 2852.61, 2926.53, 2969.02, 3022.30, 3045.51, 3078.32, 3335.03; HRMS (EI$^+$) calc'd for $[C_{17}H_{22}O]^+$: m/z 242.16707, found 242.16668.



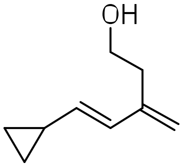
Synthesis of (E)-3-methylenehept-4-en-1-ol (2d). (E)-3-methylenehept-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement for allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 65% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.04 (d, J = 16.4 Hz, 1H), 5.62 (dt, J = 16.4, 7.0 Hz, 1H), 4.94 (d, J = 1.1 Hz, 1H), 4.86 (s, 1H), 3.57 (td, J = 6.7, 5.4 Hz, 2H), 2.35 (td, J = 6.7, 1.1 Hz, 2H), 1.97 (qd, J = 7.4, 1.3 Hz, 2H), 1.34 – 1.16 (m, 6H), 1.03 (t, J = 5.4 Hz, 1H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 143.15, 132.25, 130.85, 115.09, 61.34, 36.08, 33.11, 31.74, 29.37, 22.87, 14.22; IR (cm^{-1}) 1606.80, 1956.31, 2345.72, 2366.08, 2857.01, 2873.64, 2927.84, 2957.85, 3013.16, 3081.85, 3331.41; HRMS (EI$^+$) calc'd for $[C_{11}H_{20}O]^+$: m/z 168.15142, found 168.15099.



Synthesis of (E)-5-cyclohexyl-3-methylenepent-4-en-1-ol (2e). (E)-5-cyclohexyl-3-methylene pent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 75% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.03 (d, *J* = 16.8 Hz, 1H), 5.61 (dd, *J* = 16.0, 7.1 Hz, 1H), 4.96 (d, *J* = 2.0 Hz, 1H), 4.87 (d, *J* = 1 Hz, 1H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.35 (td, *J* = 6.7, 1.0 Hz, 2H), 1.95 – 1.82 (m, 1H), 1.71 – 1.54 (m, 5H), 1.26 – 0.96 (m, 5H); ^{13}C NMR (126 MHz, C_6D_6) δ 143.30, 136.42, 129.81, 115.21, 61.36, 41.22, 36.04, 33.13, 26.41, 26.30; IR (cm^{-1}) 1605.78, 1647.3, 2668.58, 2852.18, 2925.65, 3002.27, 3081.4, 3337.51; HRMS (EI$^+$) calc'd for $[C_{12}H_{20}O]^+$: m/z 180.15142, found 180.15135.

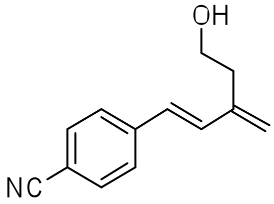


Synthesis of (E)-6,6-dimethyl-3-methylenenona-4,8-dien-1-ol (2f). (E)-6,6-dimethyl-3-methylenenona-4,8-dien-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 60% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.01 (d, *J* = 16.2 Hz, 1H), 5.78 – 5.63 (m, 2H), 5.05 – 4.94 (m, 3H), 4.90 (s, 1H), 3.61 (s, 2H), 2.46 – 2.36 (m, 2H), 1.99 – 1.93 (m, 2H), 0.94 (s, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 143.13, 139.79, 135.60, 128.25, 117.15, 115.61, 61.40, 47.70, 36.08, 26.98; IR (cm^{-1}) 1606.26, 1639.73, 2345.71, 2365.92, 2961.87, 3004.25, 3078.41, 3345.14; HRMS (EI$^+$) calc'd for $[C_{12}H_{20}O]^+$: m/z 180.15142, found 180.15143.

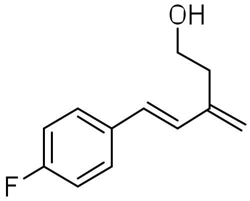


Synthesis of (E)-5-cyclopropyl-3-methylenepent-4-en-1-ol (2g). (E)-5-cyclopropyl-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed

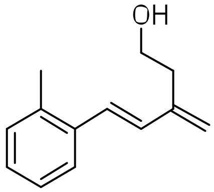
Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 77% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 6.13 (d, *J* = 15.7 Hz, 1H), 5.13 (dd, *J* = 15.7, 8.8 Hz, 1H), 4.92 (s, 1H), 4.82 (d, *J* = 0.9 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.32 (td, *J* = 6.7, 0.9 Hz, 2H), 1.27 – 1.16 (m, 1H), 0.57 – 0.48 (m, 2H), 0.28 – 0.21 (m, 2H); ^{13}C NMR (126 MHz, C_6D_6) δ 142.88, 134.55, 129.95, 114.23, 61.22, 35.93, 14.56, 7.91, 7.37; IR (cm^{-1}) 1605.29, 1644.79, 2345.92, 2371.48, 2883.32, 2947.7, 3006.7, 3082.94, 3357.67; HRMS (EI$^+$) calc'd for $[C_9H_{14}O]^+$: m/z 138.10447, found 138.10417.



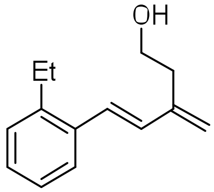
Synthesis of (E)-4-(5-hydroxy-3-methylenepent-1-en-1-yl)benzonitrile (2h). (E)-4-(5-hydroxy-3-methylenepent-1-en-1-yl)benzonitrile was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (2:1 Hexane:EtOAc) and afforded the alcohol in 93% yield as a white solid (m.p = 42 °C): ^{1}H NMR (500 MHz, C_6D_6) δ 7.04 – 6.95 (m, 2H), 6.74 – 6.69 (m, 2H), 6.48 (d, *J* = 16.2 Hz, 1H), 6.19 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 1H), 5.00 (d, *J* = 0.9 Hz, 1H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.31 (td, *J* = 6.7, 0.9 Hz, 2H), 0.95 (s,1H); ^{13}C NMR (126 MHz, C_6D_6) δ 142.68, 141.26, 134.05, 132.24, 126.01, 126.83, 119.00, 118.98, 111.11, 61.19, 35.36; IR (cm^{-1}) 1603.82, 2226.22, 2345.89, 2367.79, 2941.66, 3397.56; HRMS (EI$^+$) calc'd for $[C_{13}H_{13}ON]^+$: m/z 199.09972, found 199.09905.



Synthesis of (E)-5-(4-fluorophenyl)-3-methylenepent-4-en-1-ol (2i). (E)-5-(4-fluorophenyl)-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 75% yield as a white solid (m.p. = 42°C): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.06 – 6.97 (m, 2H), 6.73 (d, *J* = 16.3 Hz, 1H), 6.57 (d, *J* = 16.3 Hz, 1H), 5.26 (s, 1H), 5.15 (d, *J* = 1.0 Hz, 1H), 3.85 – 3.78 (t, *J* = 6.5 Hz, 2H), 2.62 (td, *J* = 6.5, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.34, 133.34, 130.28, 128.12, 127.61, 118.41, 115.82, 115.65, 61.30, 35.47; IR (cm^{-1}) 1508.59, 1558.72, 1865.46, 2344.28, 2363.14, 2879.65, 2958.65, 3301.65; HRMS (EI$^+$) calc'd for $[C_{12}H_{13}OF]^+$: m/z 192.09505, found 192.09496.

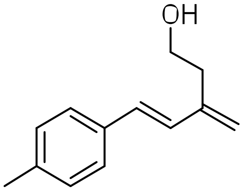


Synthesis of (E)-3-methylene-5-(o-tolyl)pent-4-en-1-ol (2j). (E)-3-methylene-5-(o-tolyl)pent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 84% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 7.41 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.81 (d, *J* = 16.2 Hz, 1H), 6.63 (d, *J* = 15.7 Hz, 1H), 5.08 (s, 1H), 4.99 (d, *J* = 1.0 Hz, 1H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.45 (td, *J* = 6.7, 1.0 Hz, 2H), 2.13 (s, 3H), 1.38 (s, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 143.44, 136.63, 135.85, 132.23, 130.58, 127.78, 126.72, 126.48, 125.74, 117.76, 61.37, 35.88, 19.70; IR (cm^{-1}) 1601.21, 1627.82, 2345.89, 2369.46, 2773.87, 2882.59, 2947.51, 3020.38, 3056.53, 3346.93; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O]^+$: m/z 188.12012, found 188.11968.

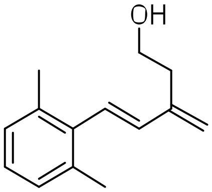


Synthesis of (E)-5-(2-ethylphenyl)-3-methylenepent-4-en-1-ol (2k). (E)-5-(2-ethylphenyl)-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 79% yield as a colorless oil: ^{1}H NMR (500 MHz, C_6D_6) δ 7.46 – 7.41 (m, 1H), 7.11 – 7.01 (m, 3H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 16.1 Hz, 1H), 5.09 (s, 1H), 5.01 (d, *J* = 1.0 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.55 (q, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 6.5 Hz, 2H), 1.59 (s, 1H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126

MHz, C_6D_6) δ 143.39, 142.01, 135.88, 132.30, 129.02, 128.03, 126.51, 126.40, 126.03, 117.81, 61.37, 35.89, 26.73, 15.49; IR (cm^{-1}) 1601.01, 1794.25, 1809.59, 1918.68, 1945.30, 2345.93, 2372.53, 2729.93, 2875.15, 2934.22, 2966.18, 3027.44, 3062.01, 3081.55, 3347.44; HRMS (EI$^+$) calc'd for $[C_{14}H_{18}O]^+$: m/z 202.13577, found 202.13589.

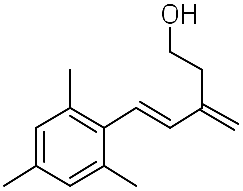


Synthesis of (E)-3-methylene-5-(p-tolyl)pent-4-en-1-ol (2l). (E)-3-methylene-5-(p-tolyl) pent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement for allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 70% yield as a white solid (m.p = 41 ˚C):: ^{1}H NMR (600 MHz, C_6D_6) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 16.3 Hz, 1H), 6.57 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 1H), 4.99 (s, 1H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.44 (td, *J* = 6.7, 1.0 Hz, 2H), 2.12 (s, 3H), 1.32 (s, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 143.24, 137.44, 134.93, 130.06, 129.59, 128.92, 126.89, 117.33, 61.39, 35.85, 21.15; IR (cm^{-1}) 1512.38, 1601.8, 2345.95, 2374.7, 2590.93, 2733.19, 2883.20, 2922.24, 2946.69, 3024.24, 3047.92, 3083.81, 3359.95; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O]^+$: m/z 188.12012, found 188.12032.

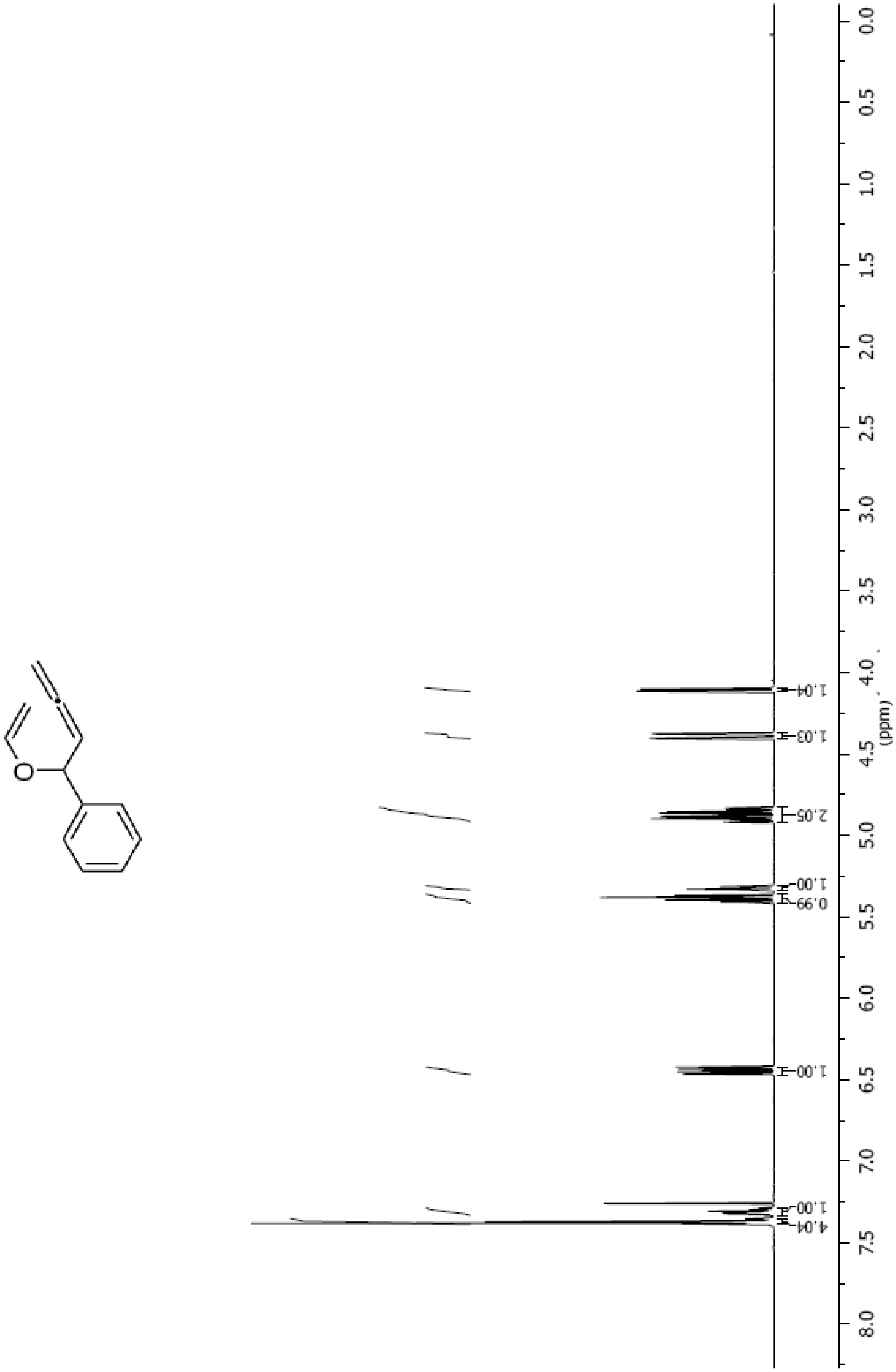


Synthesis of (E)-5-(2,6-dimethylphenyl)-3-methylenepent-4-en-1-ol (2m). (E)-5-(2,6-dimethyl phenyl)-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 82% yield as a white solid (m.p. = 42 ˚C): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 – 7.01 (m, 3H), 6.64 (d, *J* = 16.7 Hz, 1H), 6.31 (d, *J* = 16.7 Hz, 1H), 5.20 (s, 1H), 5.16 (d, *J* = 0.8 Hz, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.70 (td, *J* = 6.4, 0.8 Hz, 2H), 2.33 (s, 6H), 1.77 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.58, 136.86, 136.06, 135.65, 127.91, 127.13, 126.79, 117.54, 61.30, 35.47, 21.07; IR (cm^{-1})

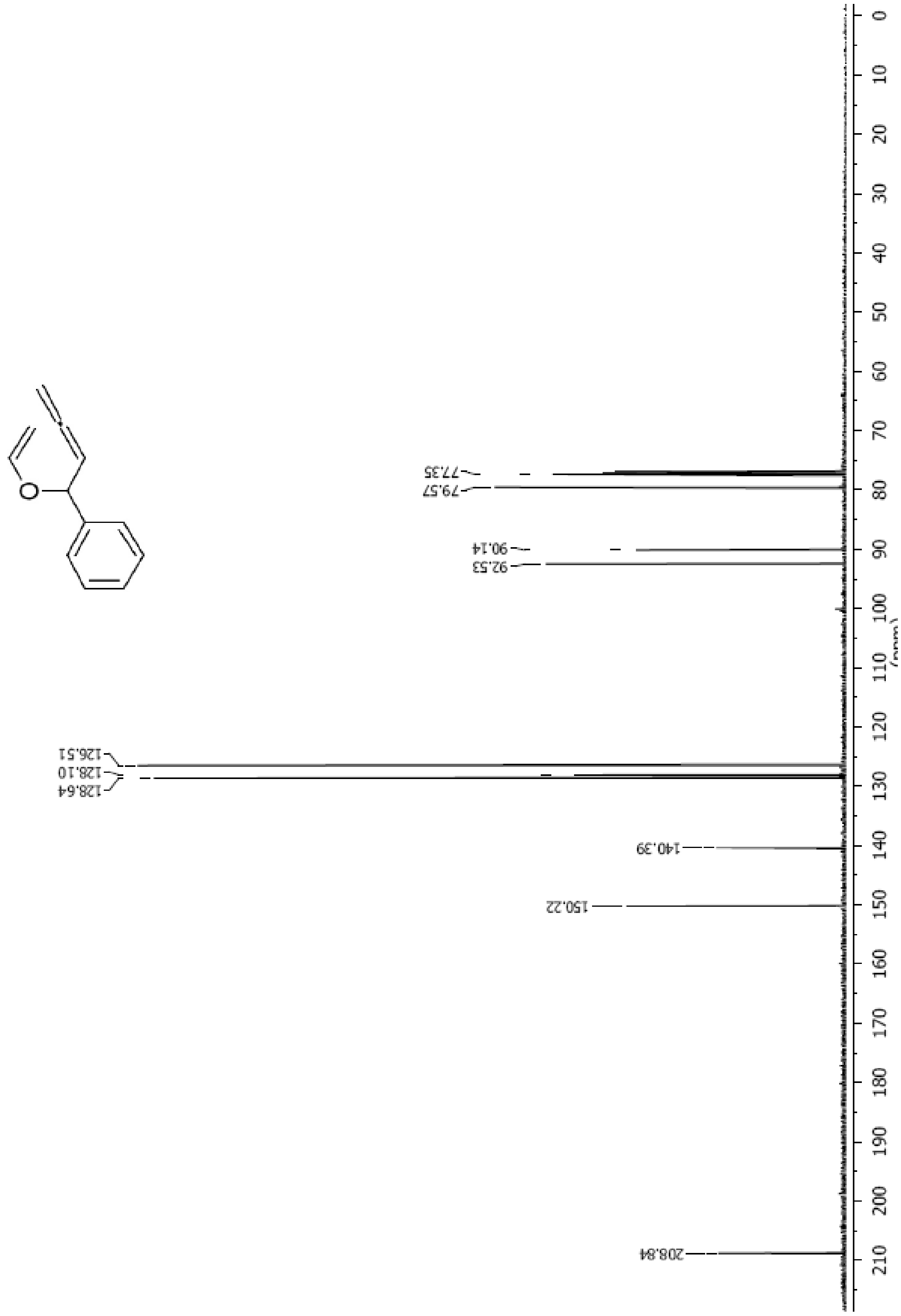
1605.48, 2345.96, 2370.39, 2734.37, 2948.56, 3019.26, 3064.46, 3361.28, HRMS (EI$^+$) calc'd for $[C_{14}H_{18}O]^+$: m/z 202.13577, found 202.13586.



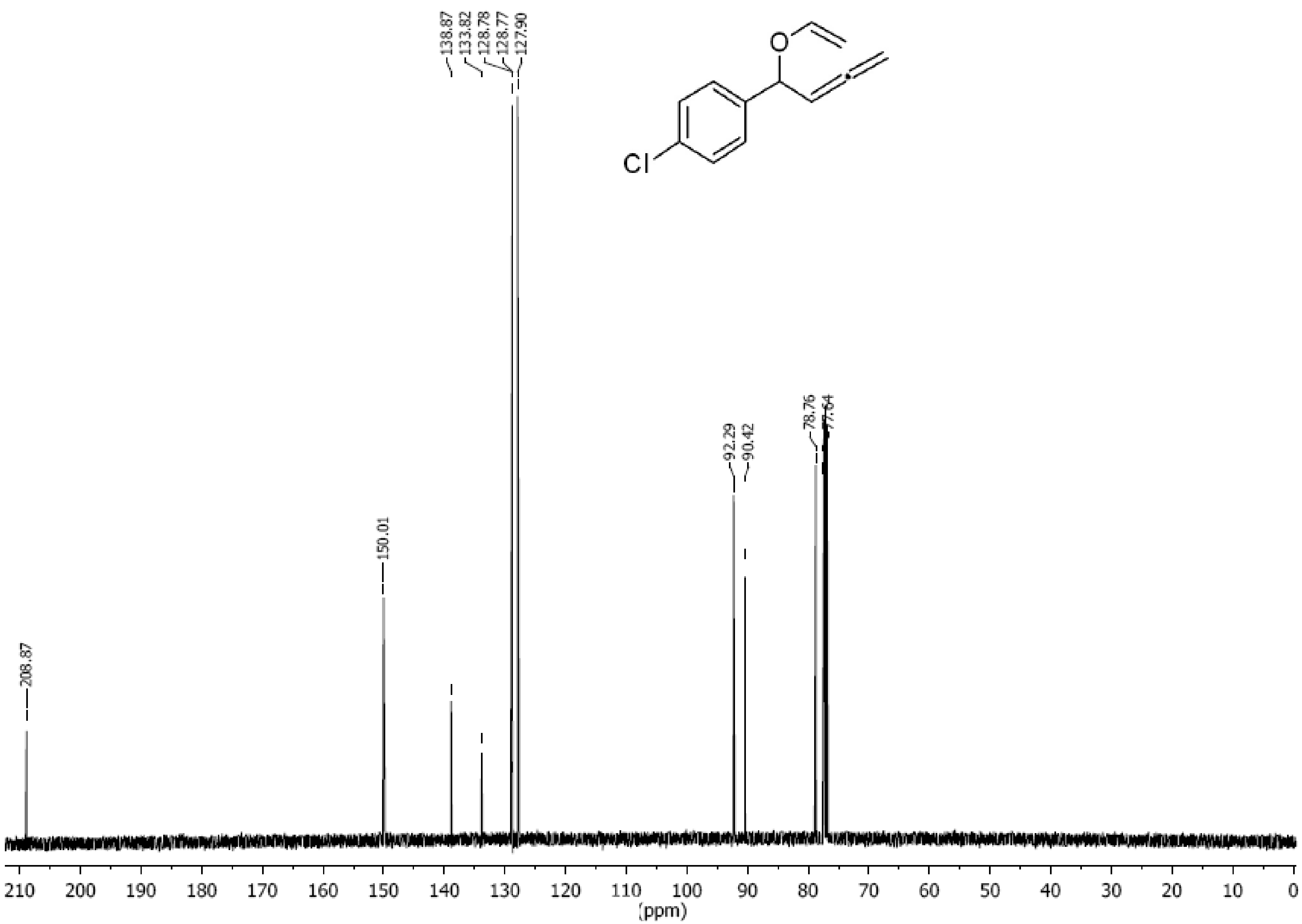
Synthesis of (E)-5-mesityl-3-methylenepent-4-en-1-ol (2n). (E)-5-mesityl-3-methylenepent-4-en-1-ol was prepared according to the general procedure for the gold-catalyzed Claisen rearrangement of allenyl vinyl ethers. The crude mixture was purified by flash chromatography (5:1 Hexane:EtOAc) and afforded the alcohol in 70% yield as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 2H), 6.61 (d, *J* = 16.7 Hz, 1H), 6.28 (d, *J* = 16.7 Hz, 1H), 5.17 (s, 1H), 5.13 (d, *J* = 0.9 Hz, 1H), 3.88 (td, *J* = 6.3, 5.9 Hz, 2H), 2.68 (td, *J* = 6.4, 0.9 Hz, 2H), 2.29 (s, 9H), 1.63 (t, *J* = 5.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.66, 136.44, 136.04, 135.33, 133.91, 128.79, 127.17, 117.38, 61.32, 35.51, 21.07, 21.06; IR (cm^{-1}) 1604.44, 2342.99, 2361.06, 2731.48, 2882.16, 2917.02, 2947.36; HRMS (EI$^+$) calc'd for $[C_{15}H_{20}O]^+$: m/z 216.15142 found 216.15185.



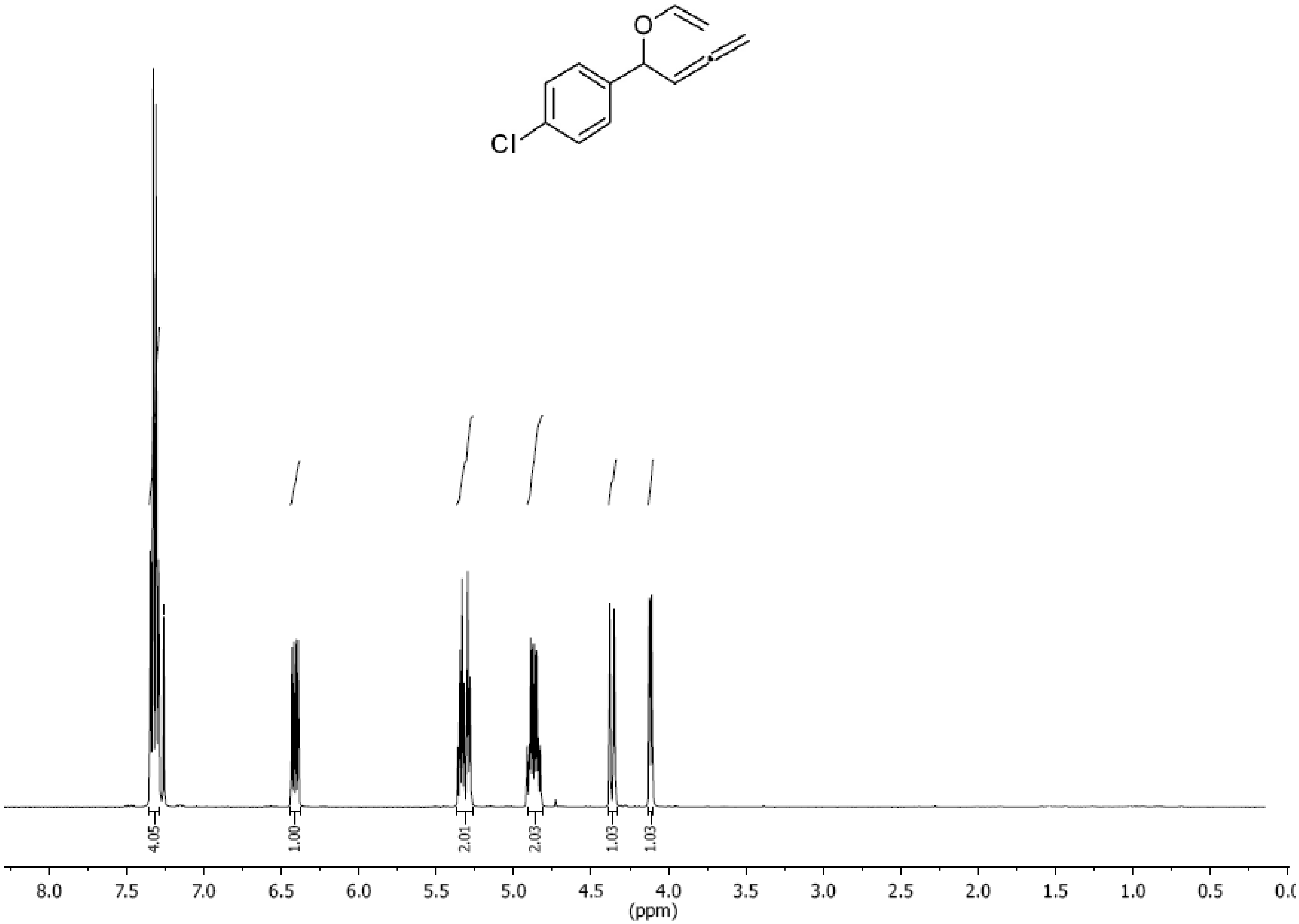
^{1}H NMR of allenyl vinyl ether 1a.



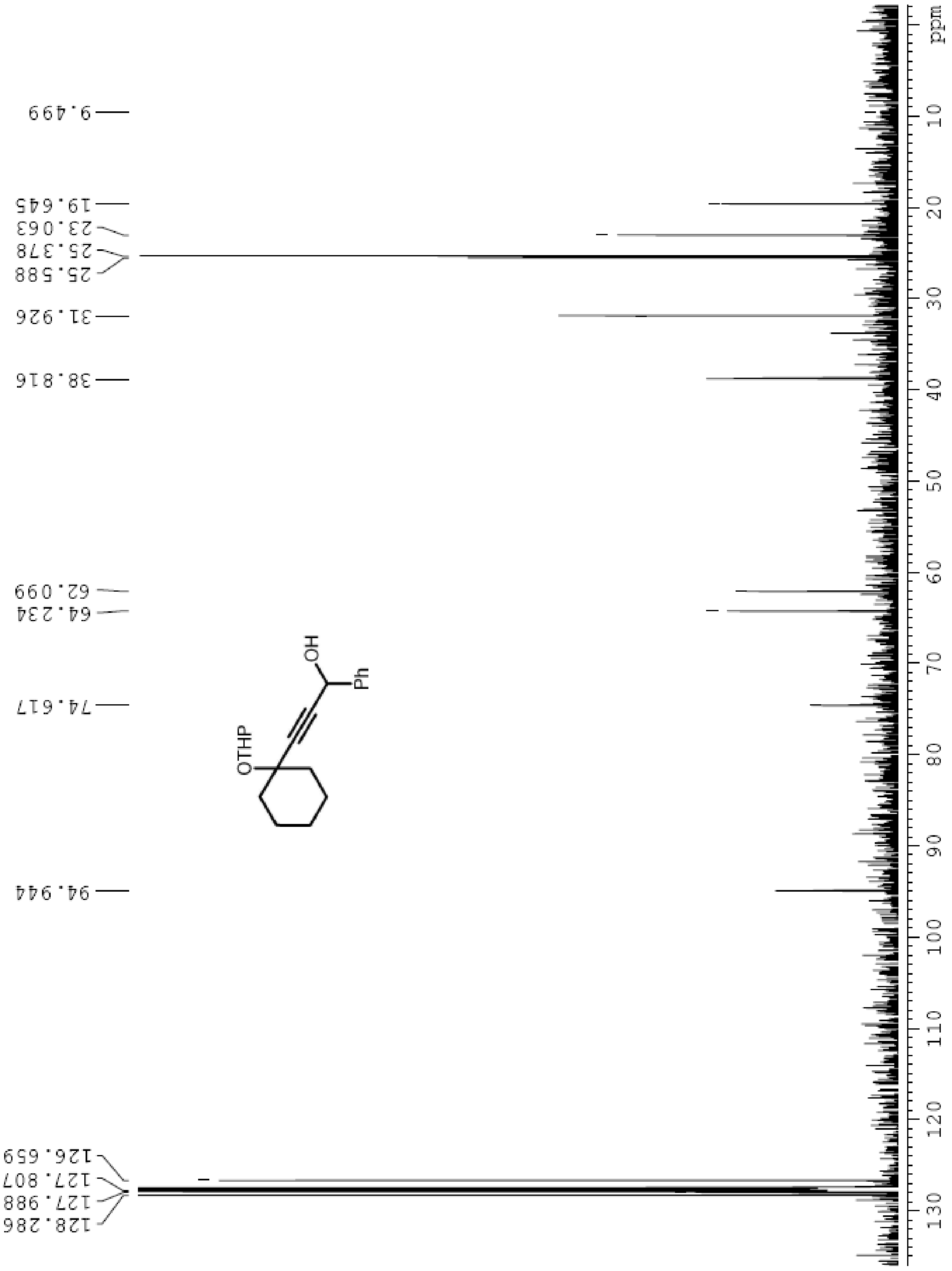
^{13}C NMR of allenyl vinyl ether **1a.**



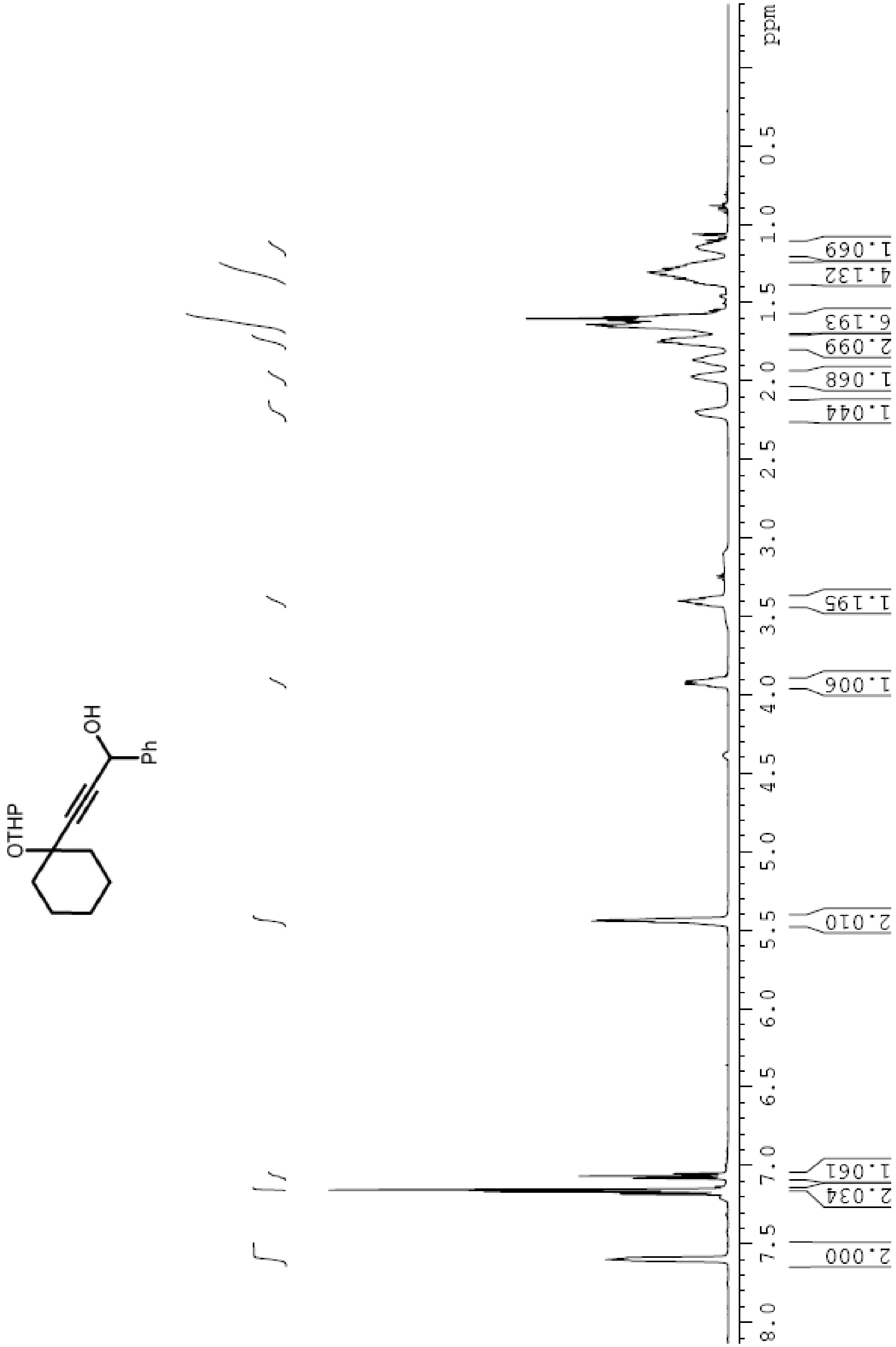
^{13}C NMR of allenyl vinyl ether **1b.**



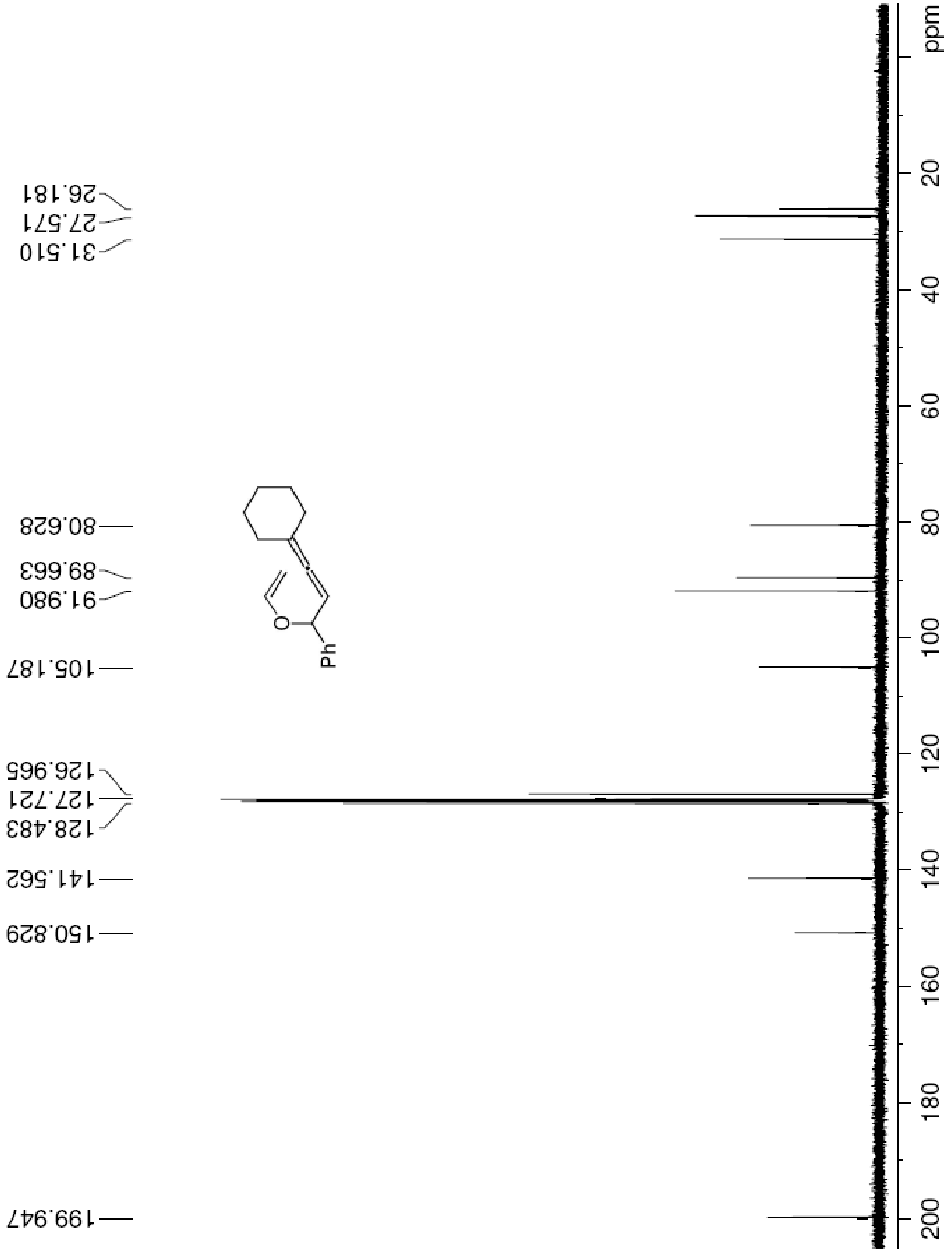
^{1}H NMR of allenyl vinyl ether **1b.**



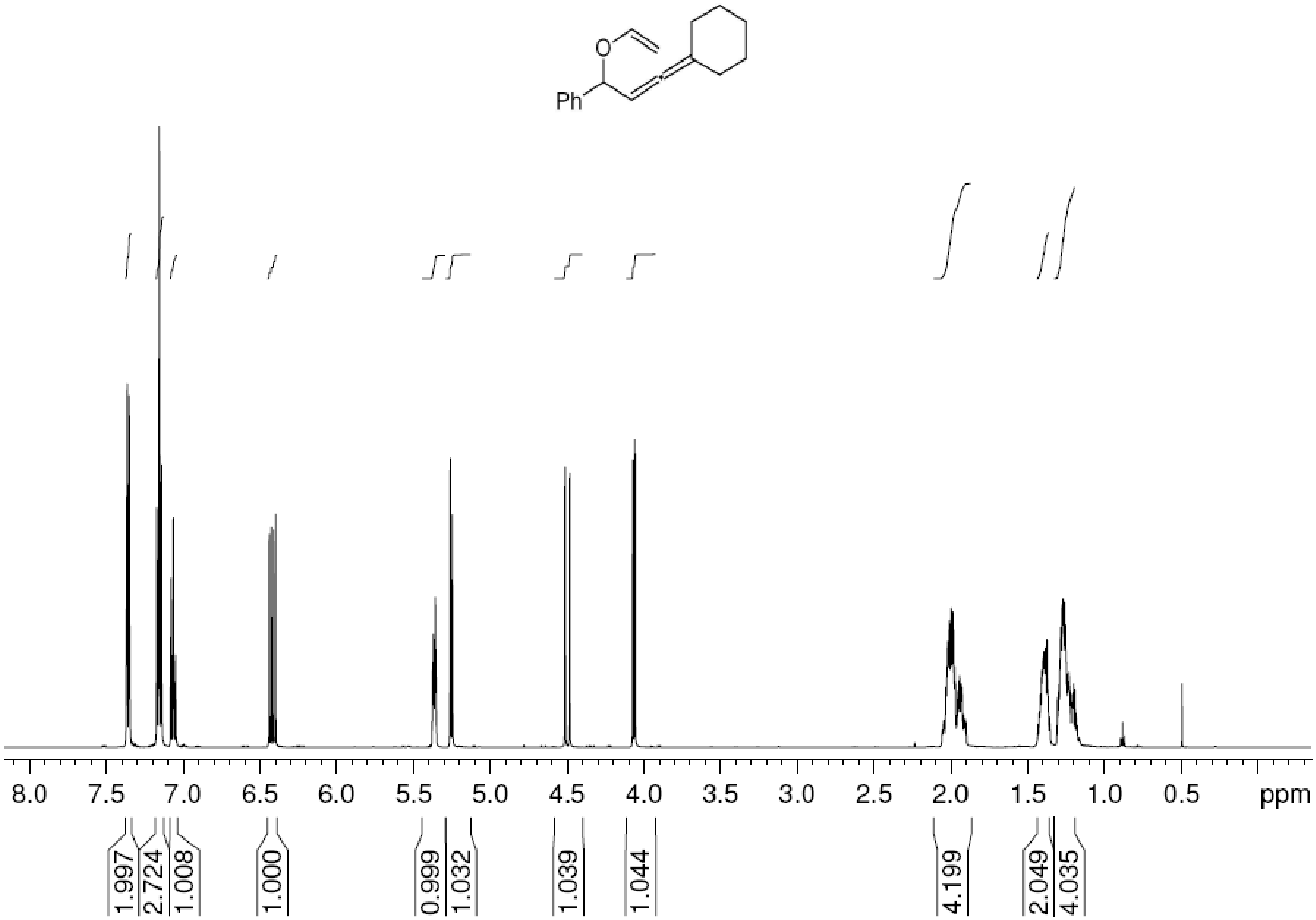
^{13}C NMR of alcohol C.



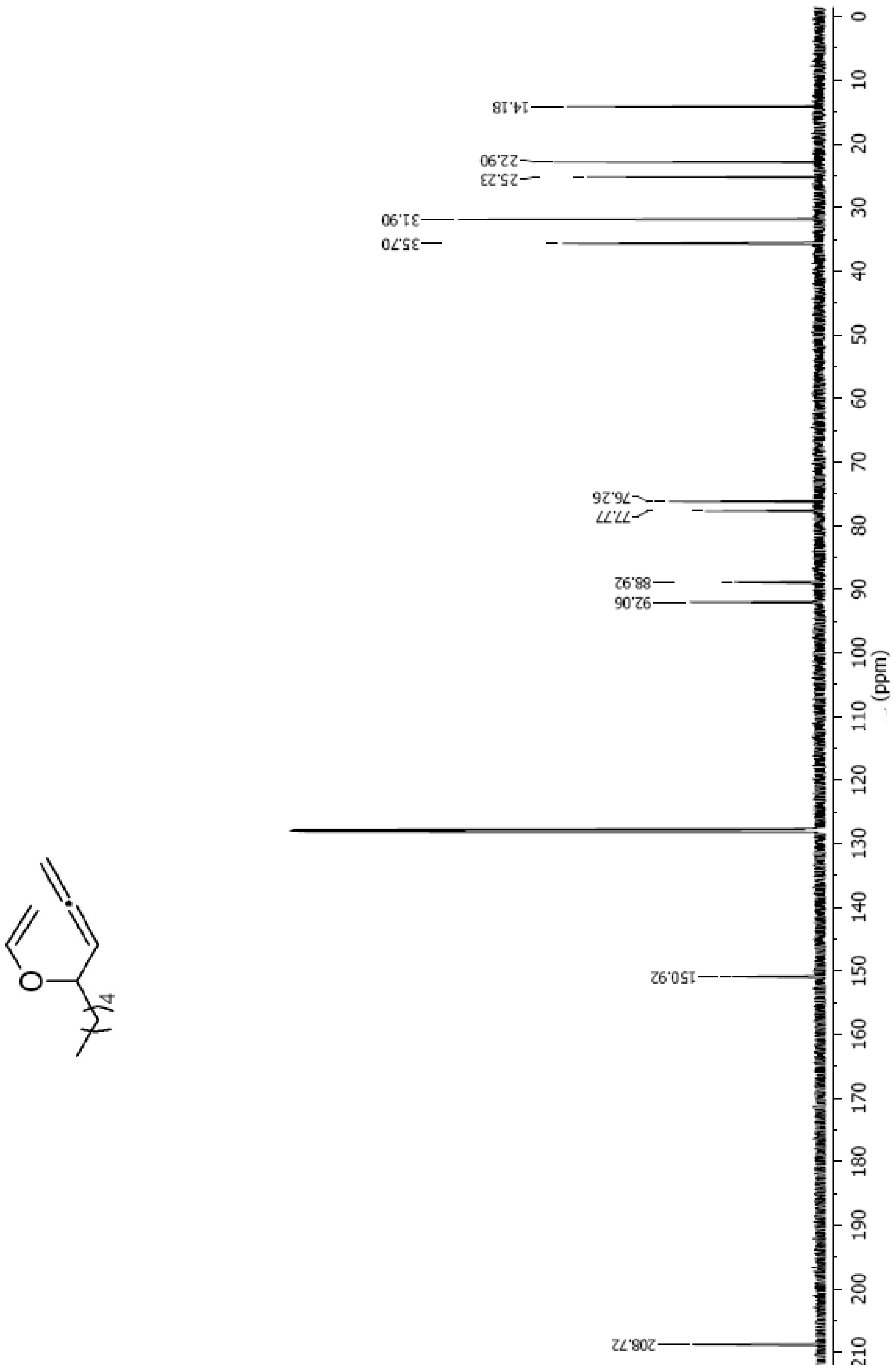
^{1}H NMR of alcohol C.



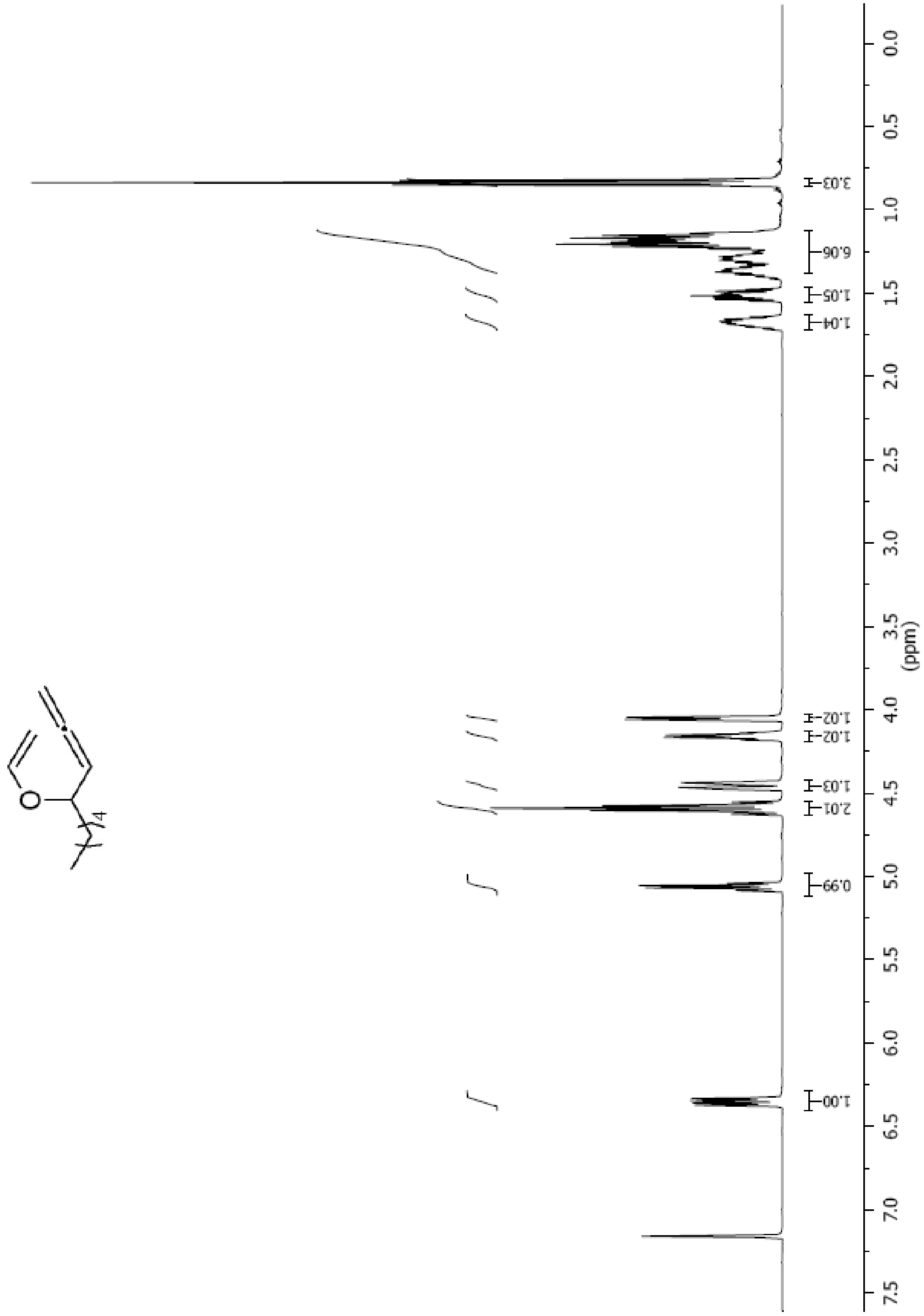
^{13}C NMR of allenyl vinyl ether **1c.**



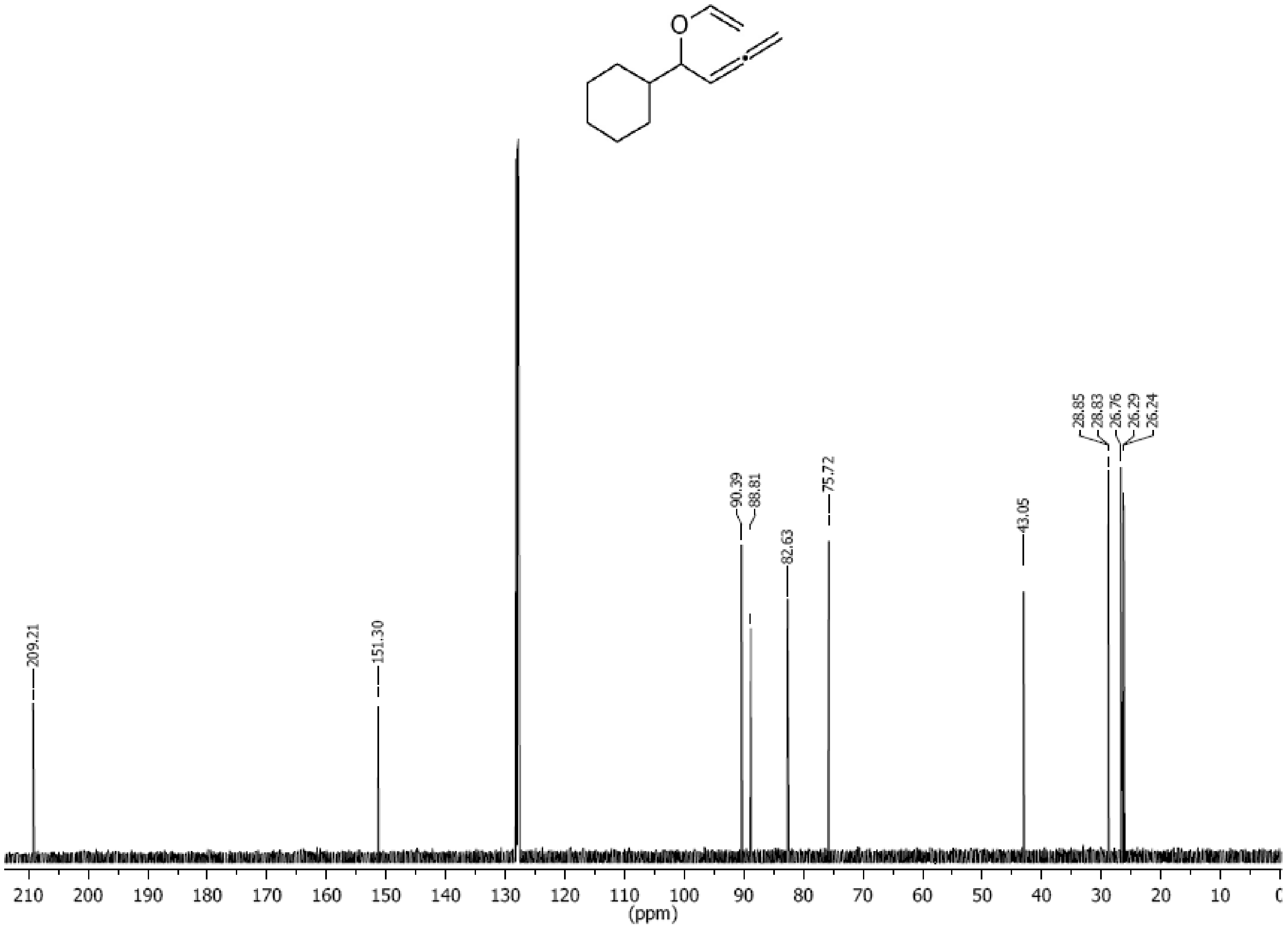
^{1}H NMR of allenyl vinyl ether 1c.



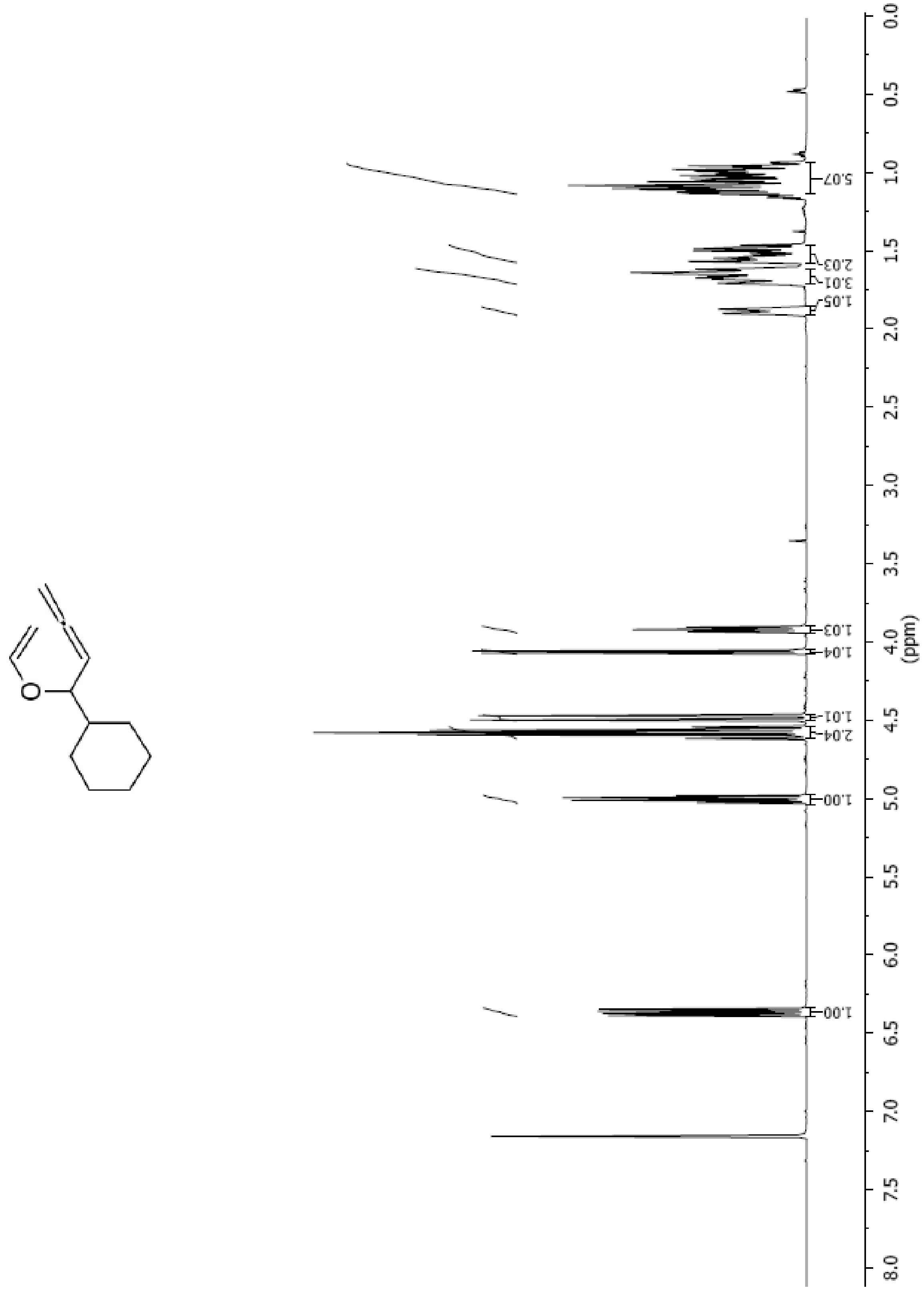
^{13}C NMR of allenyl vinyl ether **1d.**



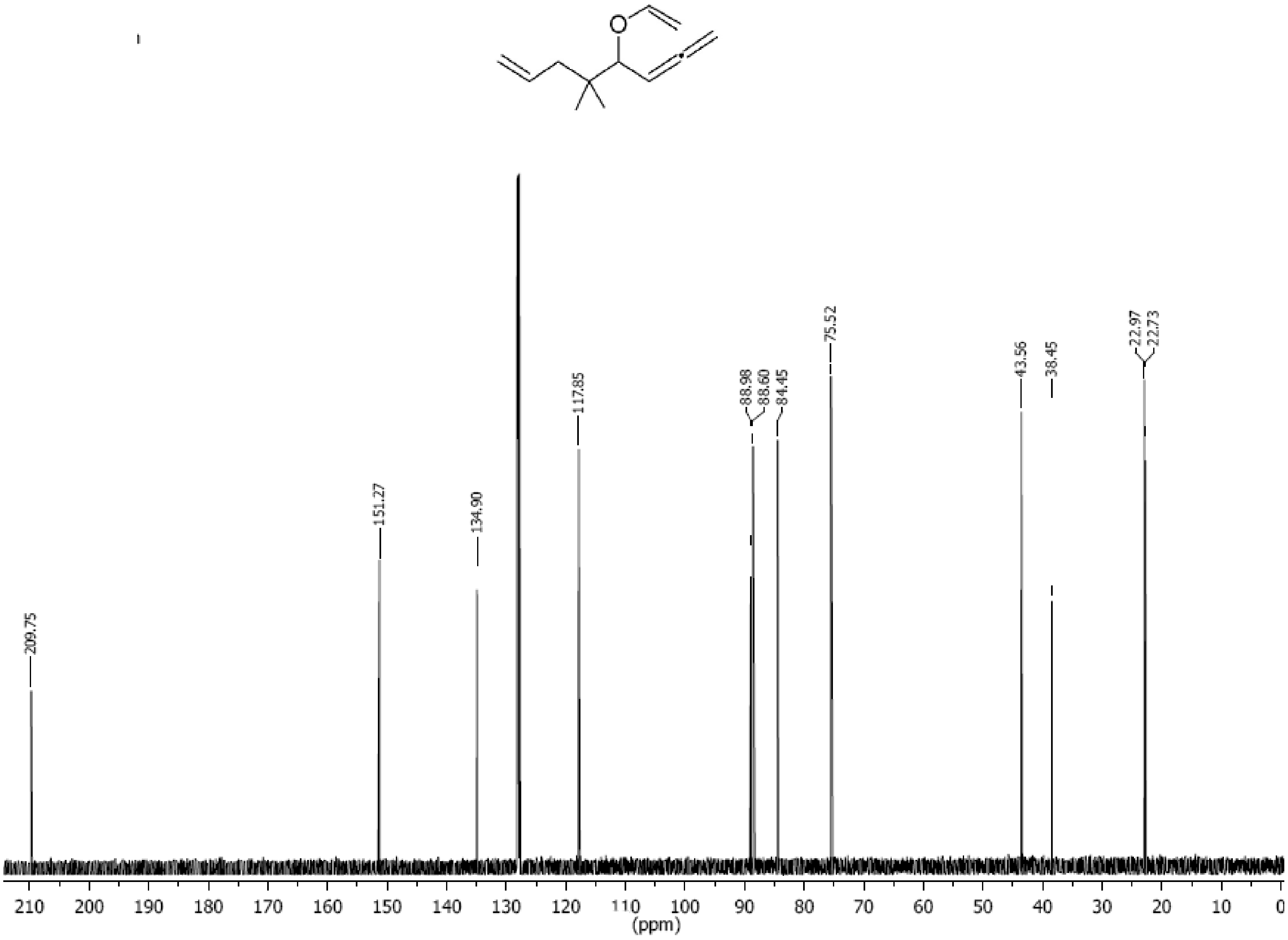
^{1}H NMR of allenyl vinyl ether 1d.



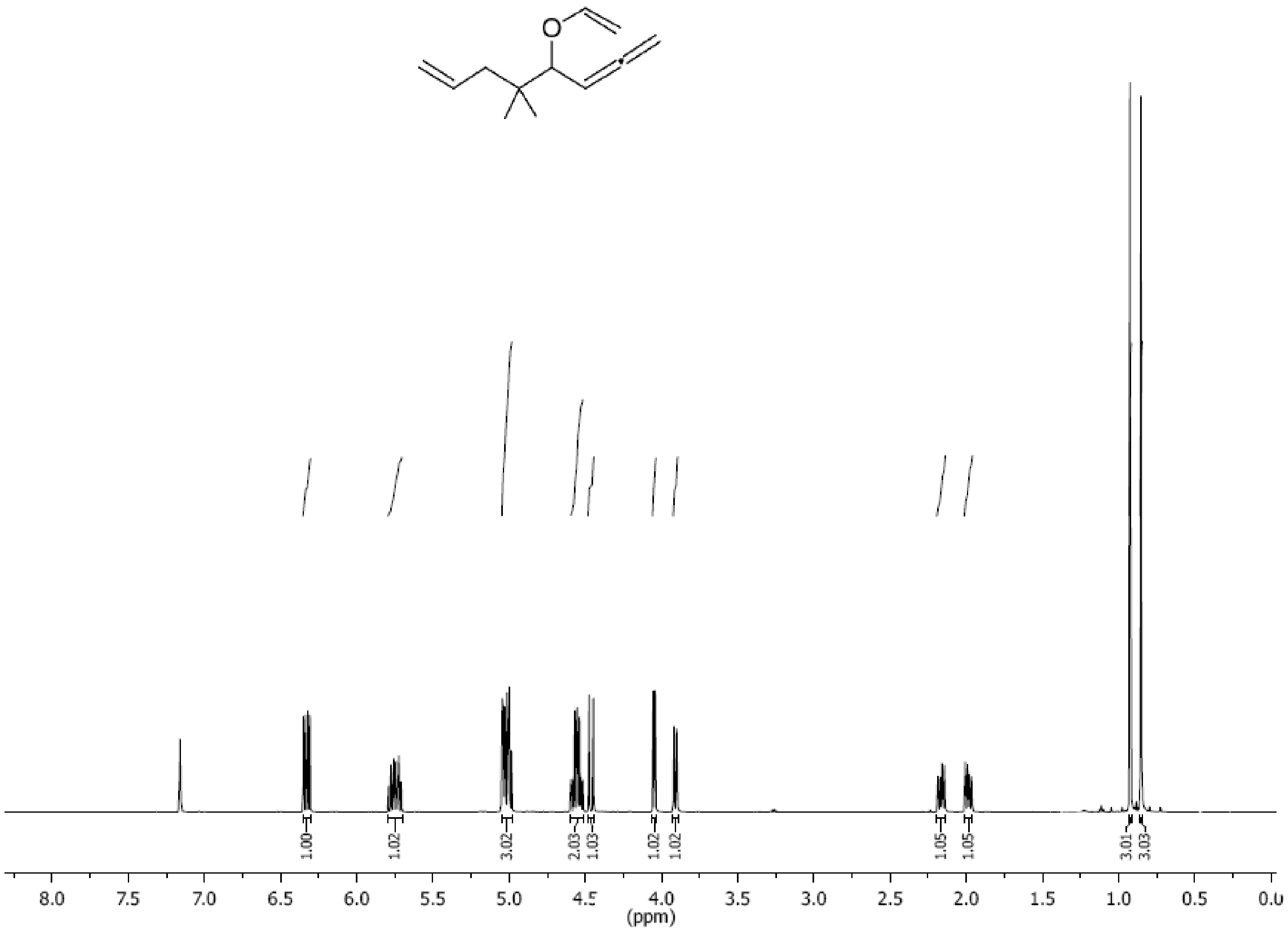
^{13}C NMR of allenyl vinyl ether 1e.



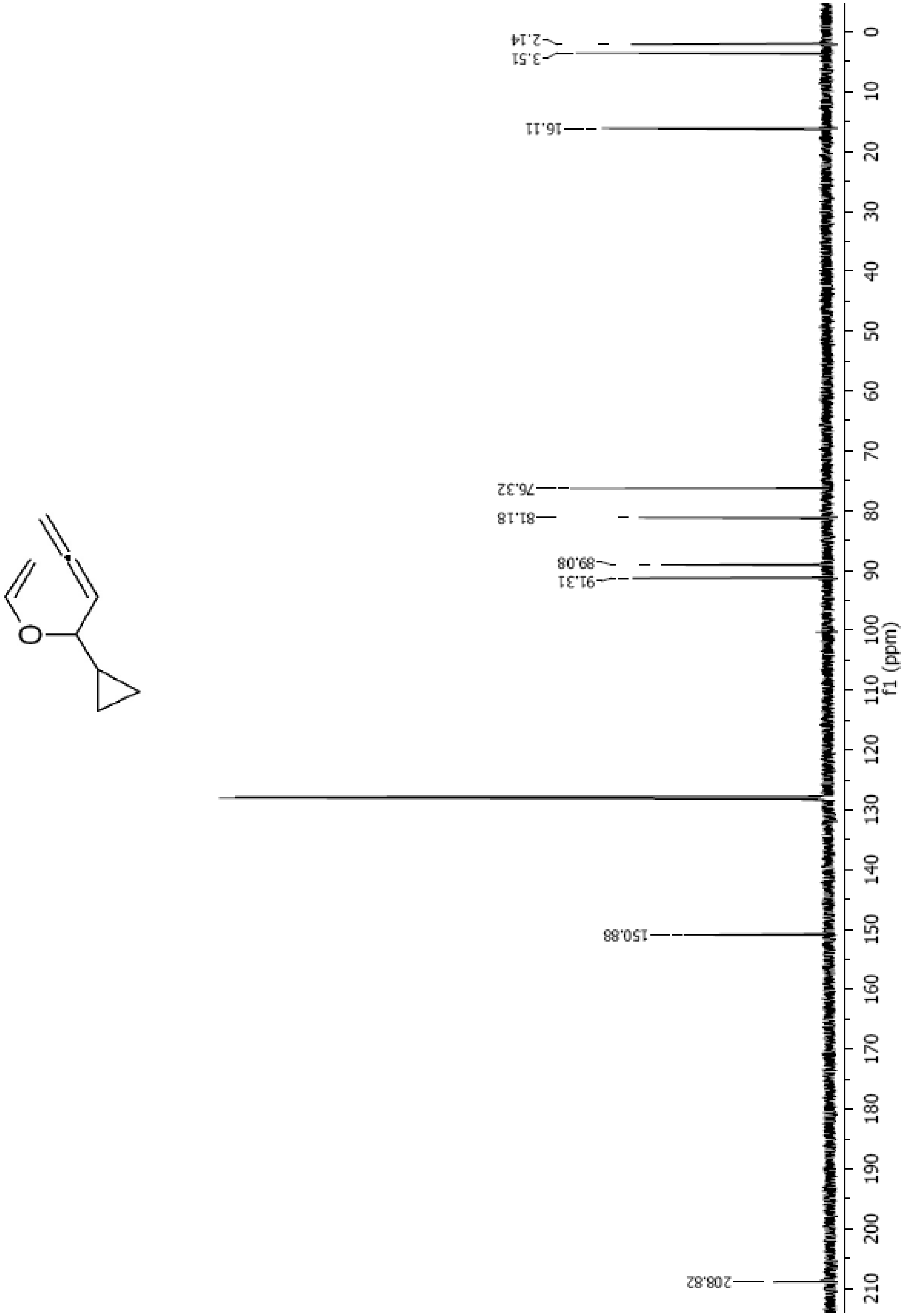
^{1}H NMR of allenyl vinyl ether 1e.



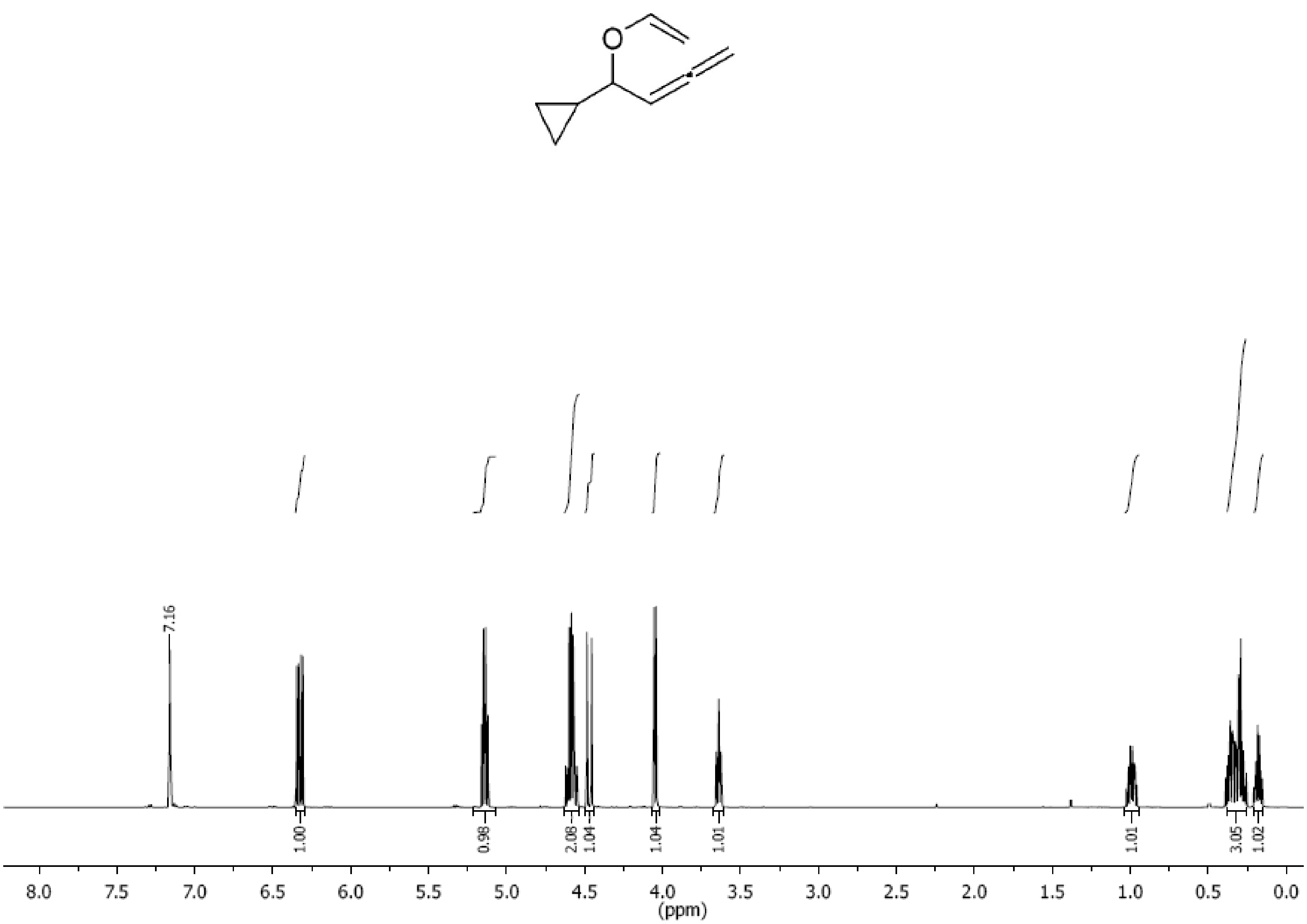
^{13}C NMR of allenyl vinyl ether **1f.**



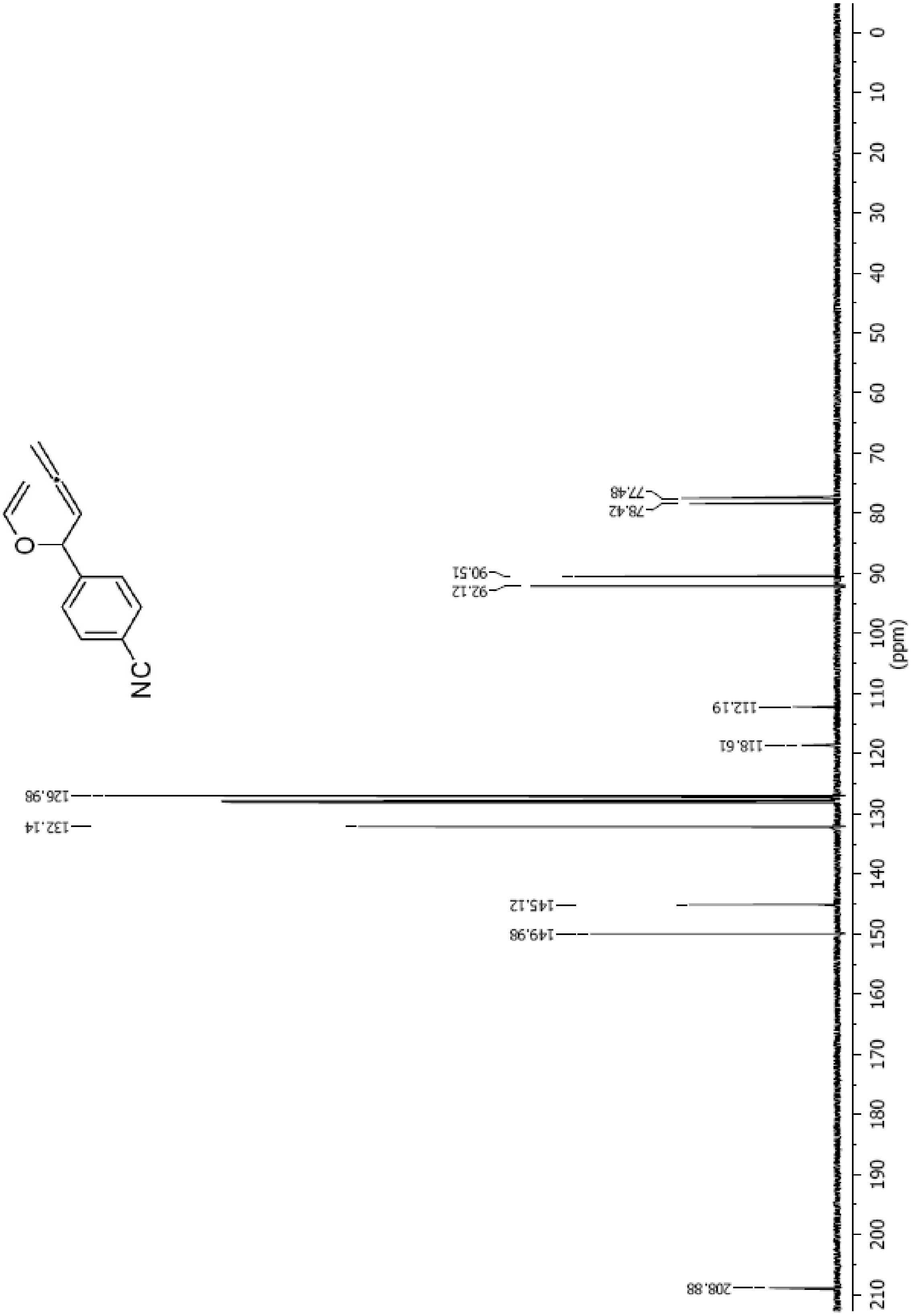
^{1}H NMR of allenyl vinyl ether **1f.**



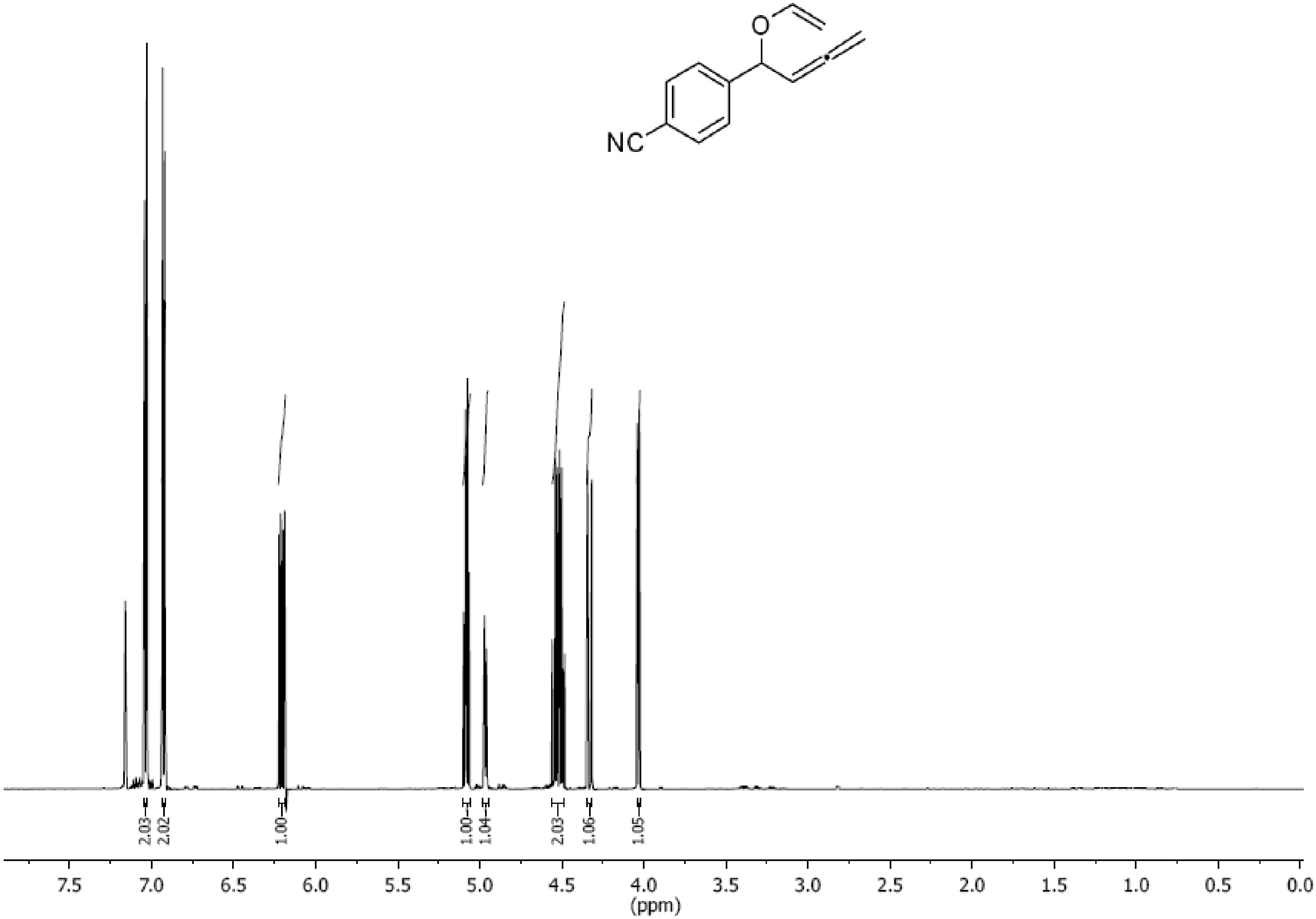
^{13}C NMR of allenyl vinyl ether **1g.**



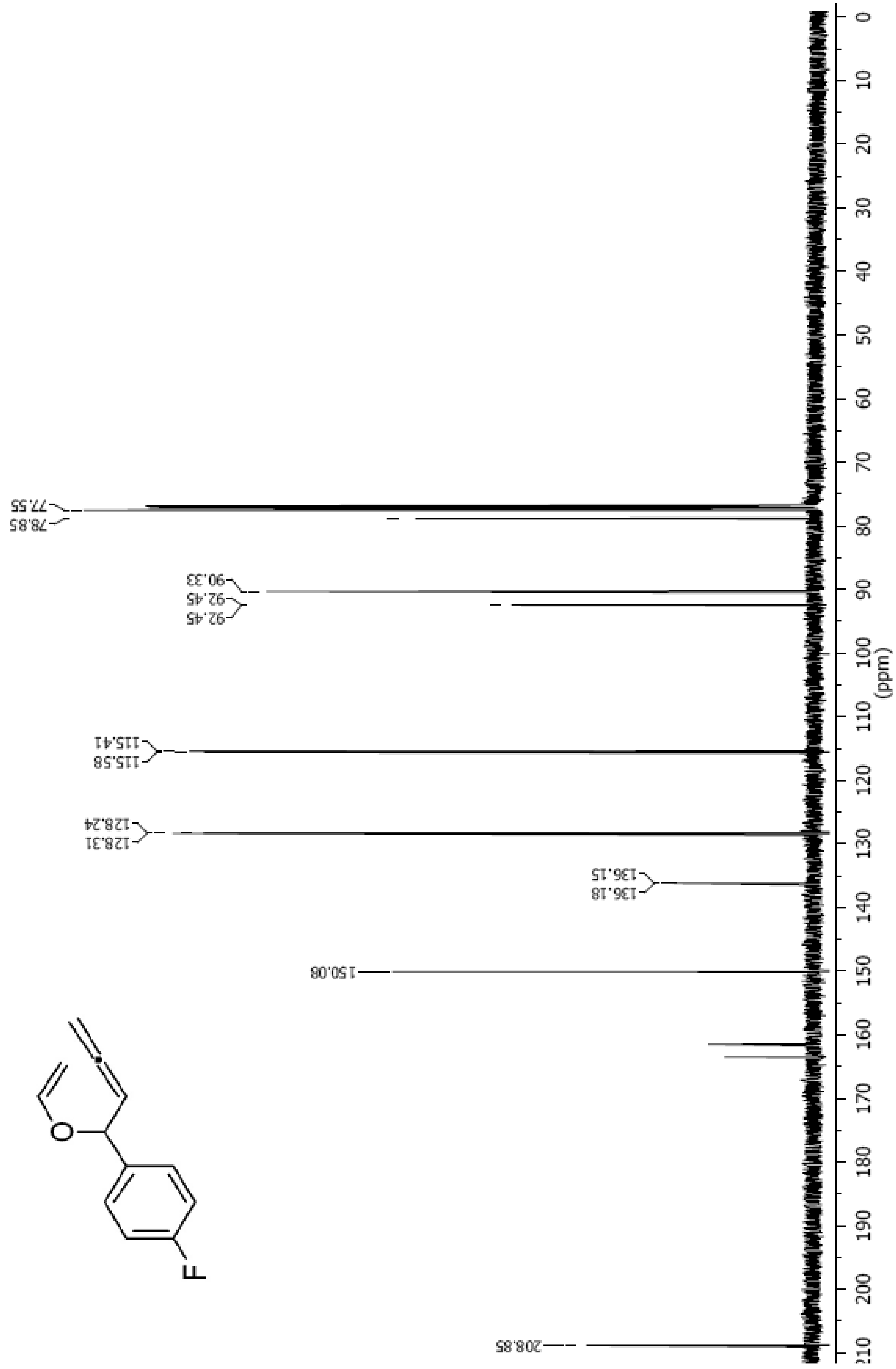
^{1}**H NMR of allenyl vinyl ether 1g.**



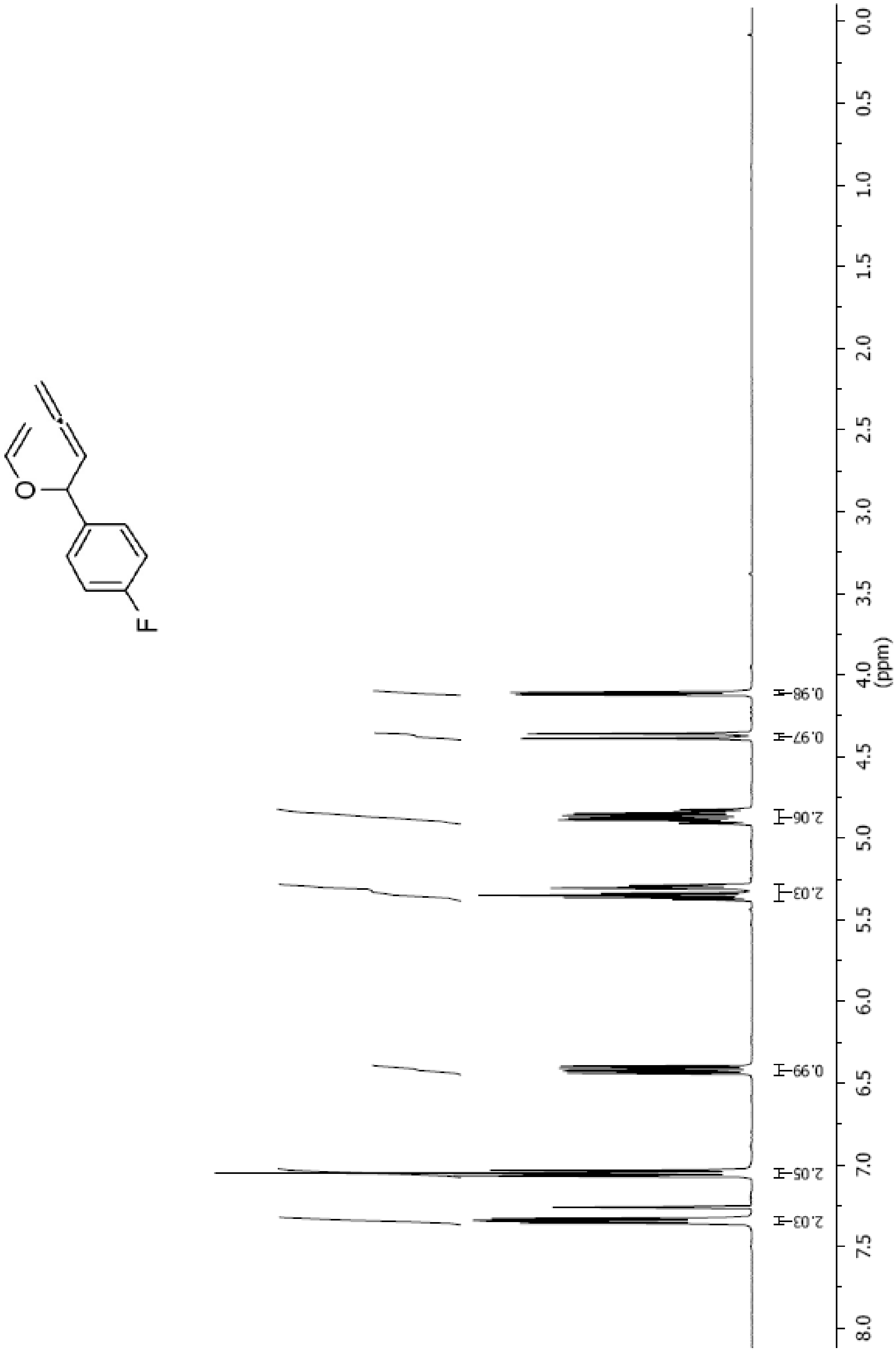
^{13}C NMR of allenyl vinyl ether **1h.**



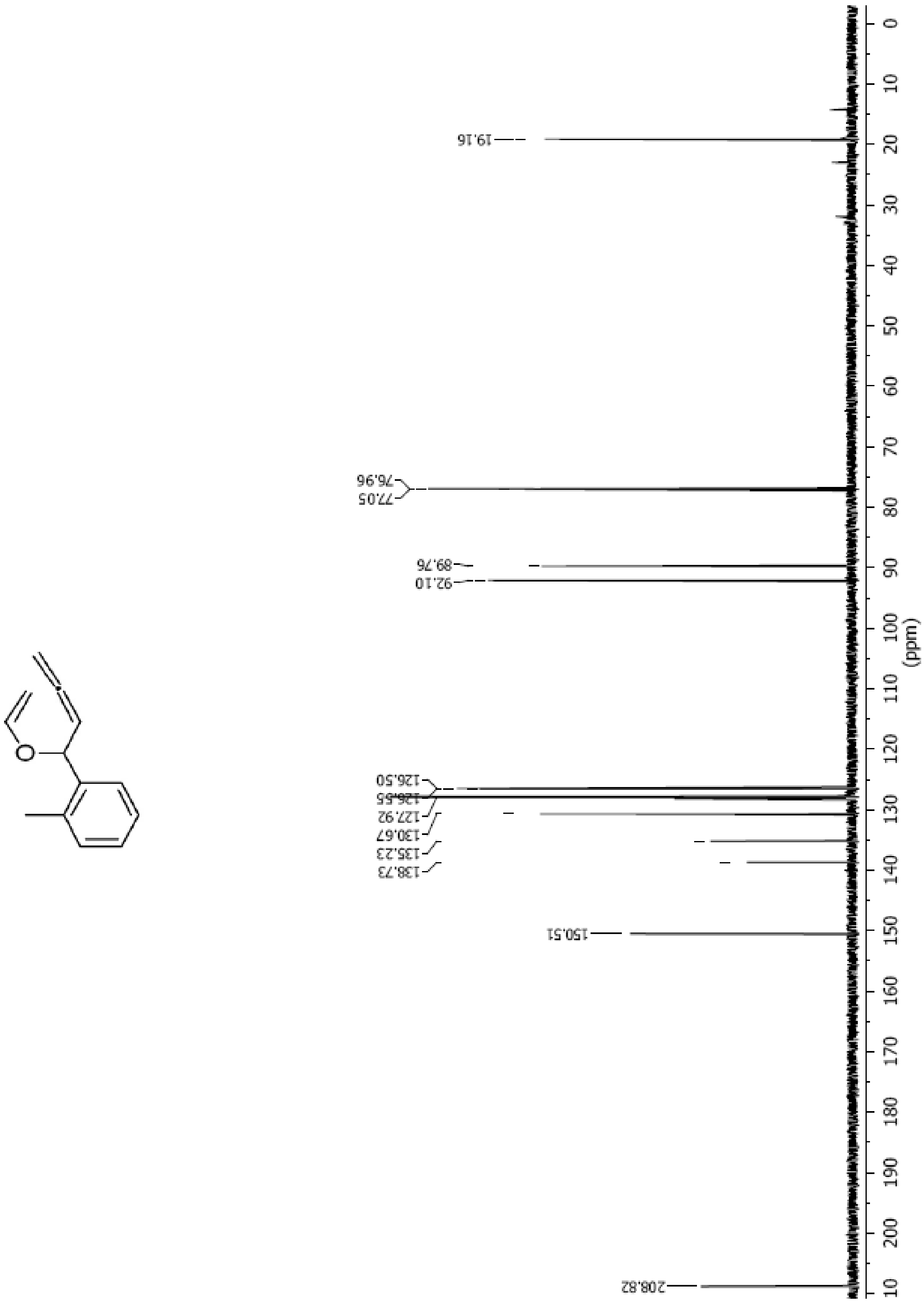
^{1}H NMR of allenyl vinyl ether **1h.**



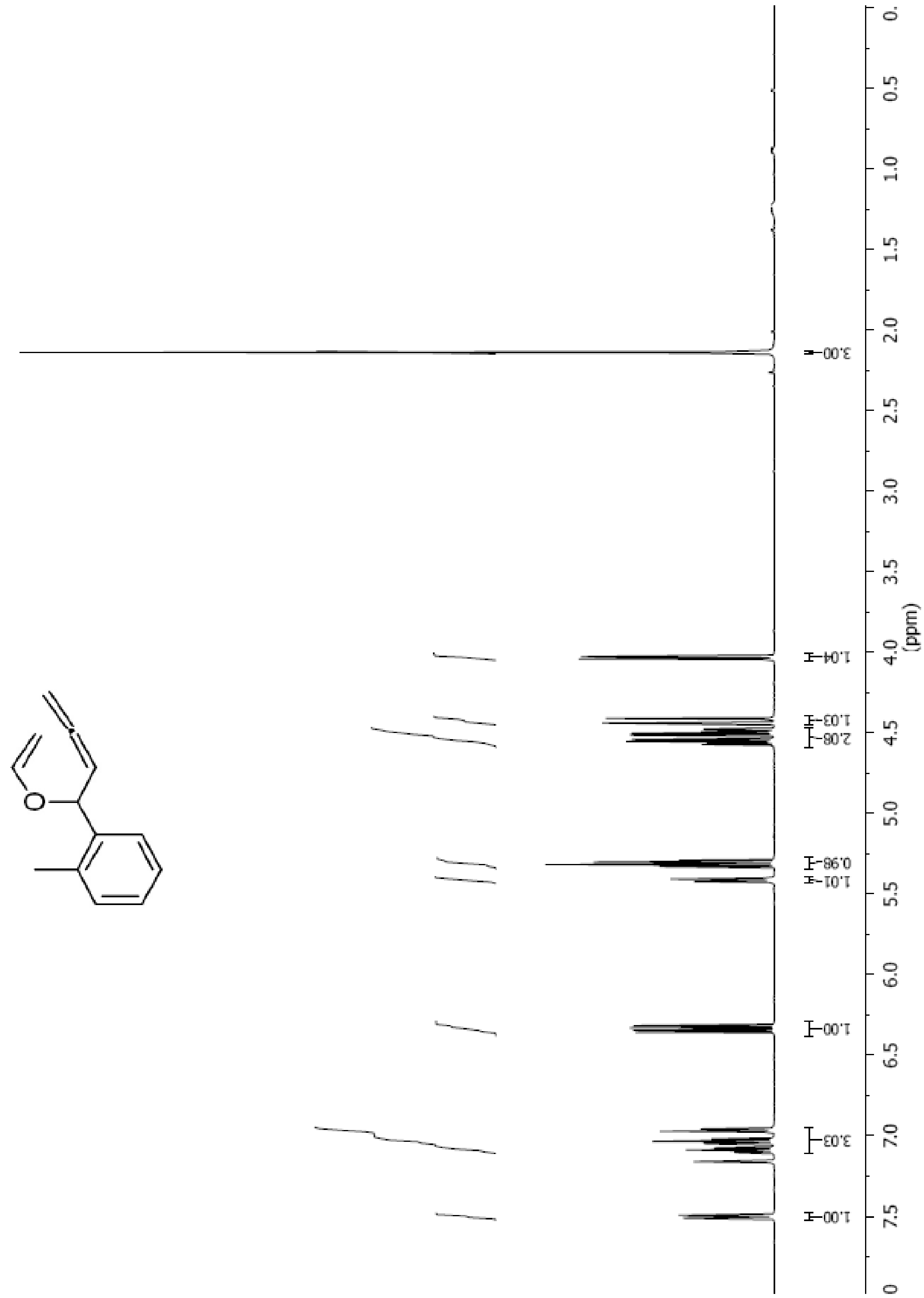
^{13}C NMR of allenyl vinyl ether **1i.**



^{1}H NMR of allenyl vinyl ether **1i.**

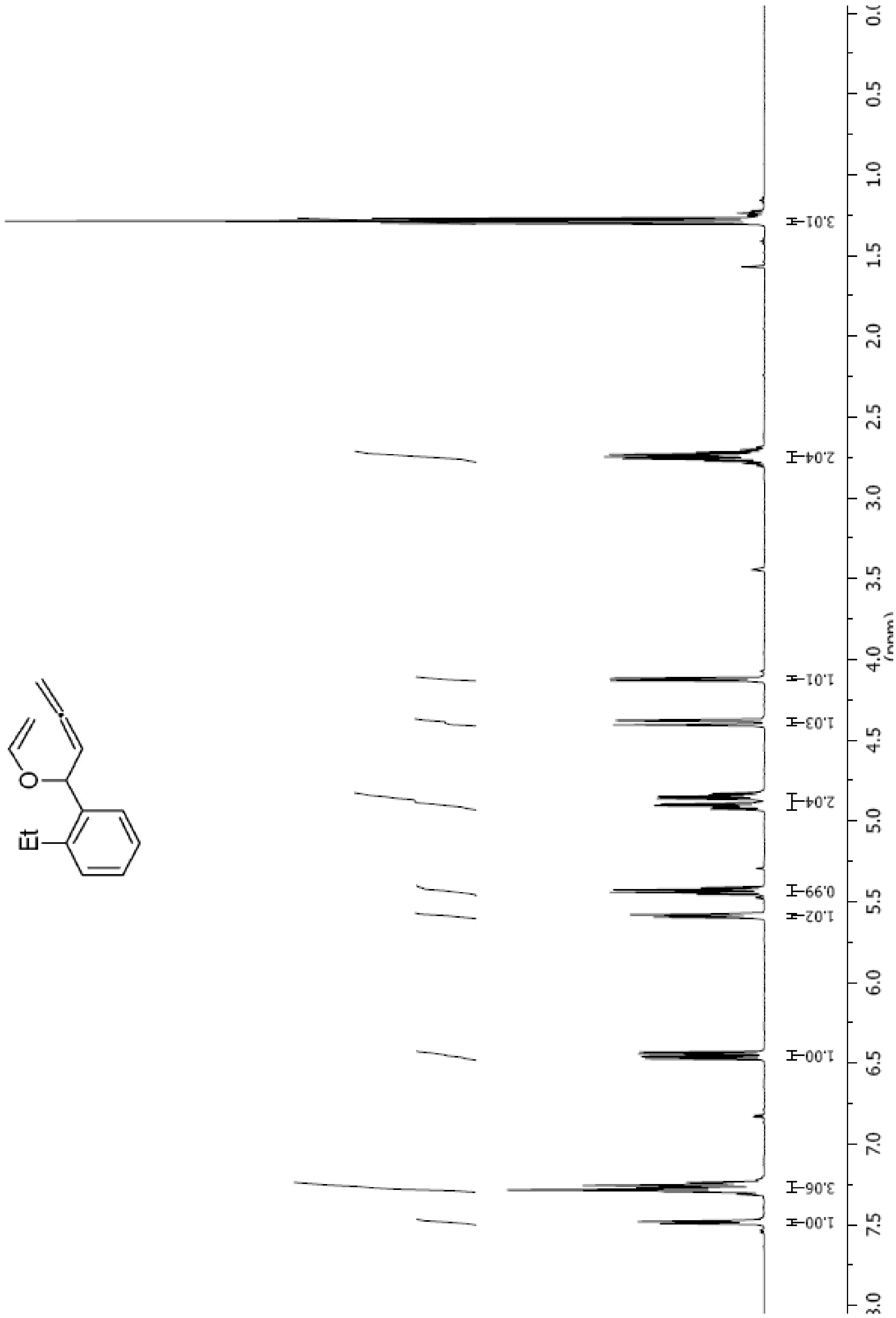


^{13}C NMR of allenyl vinyl ether **1j.**

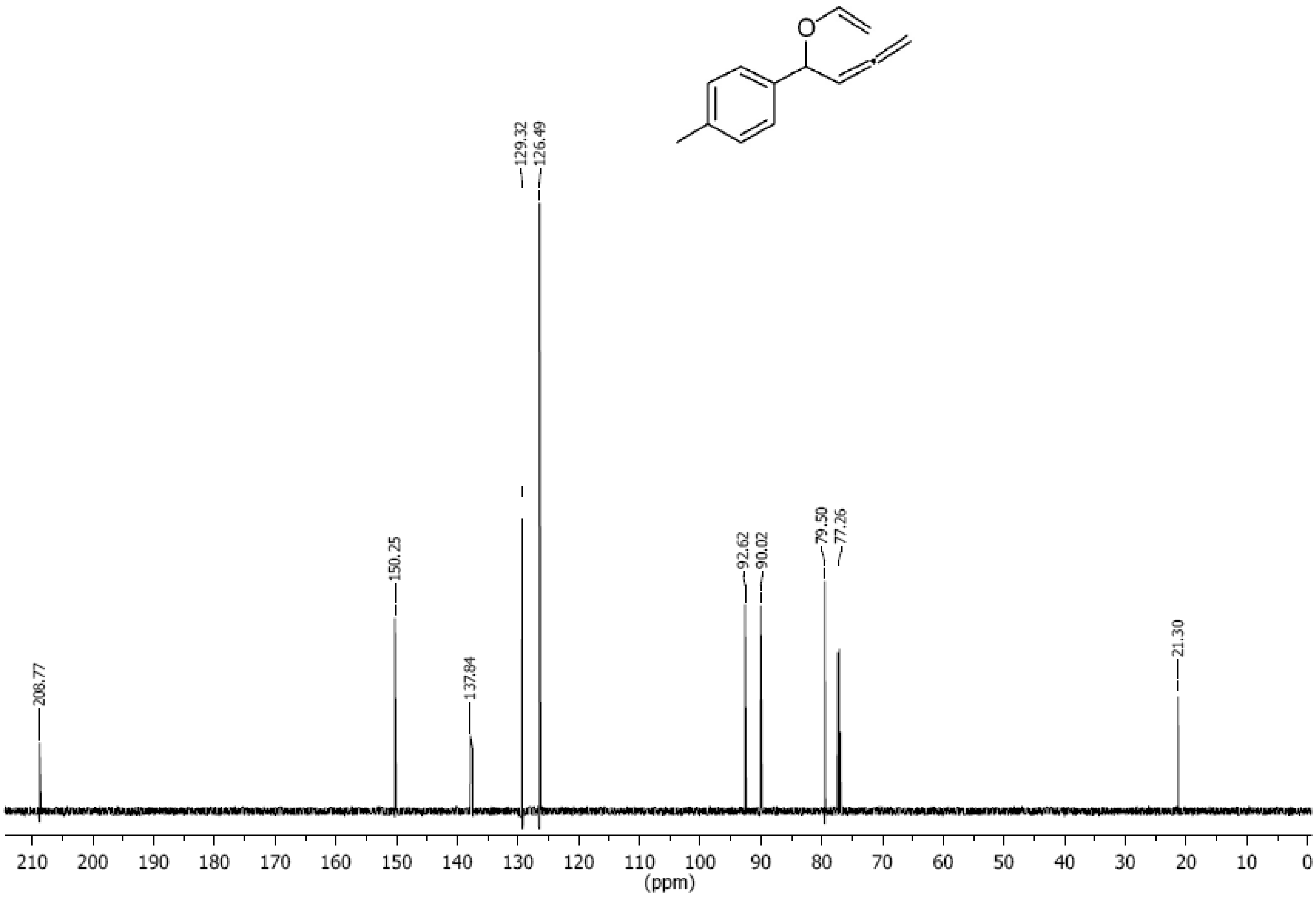


^{1}H NMR of allenyl vinyl ether 1j.

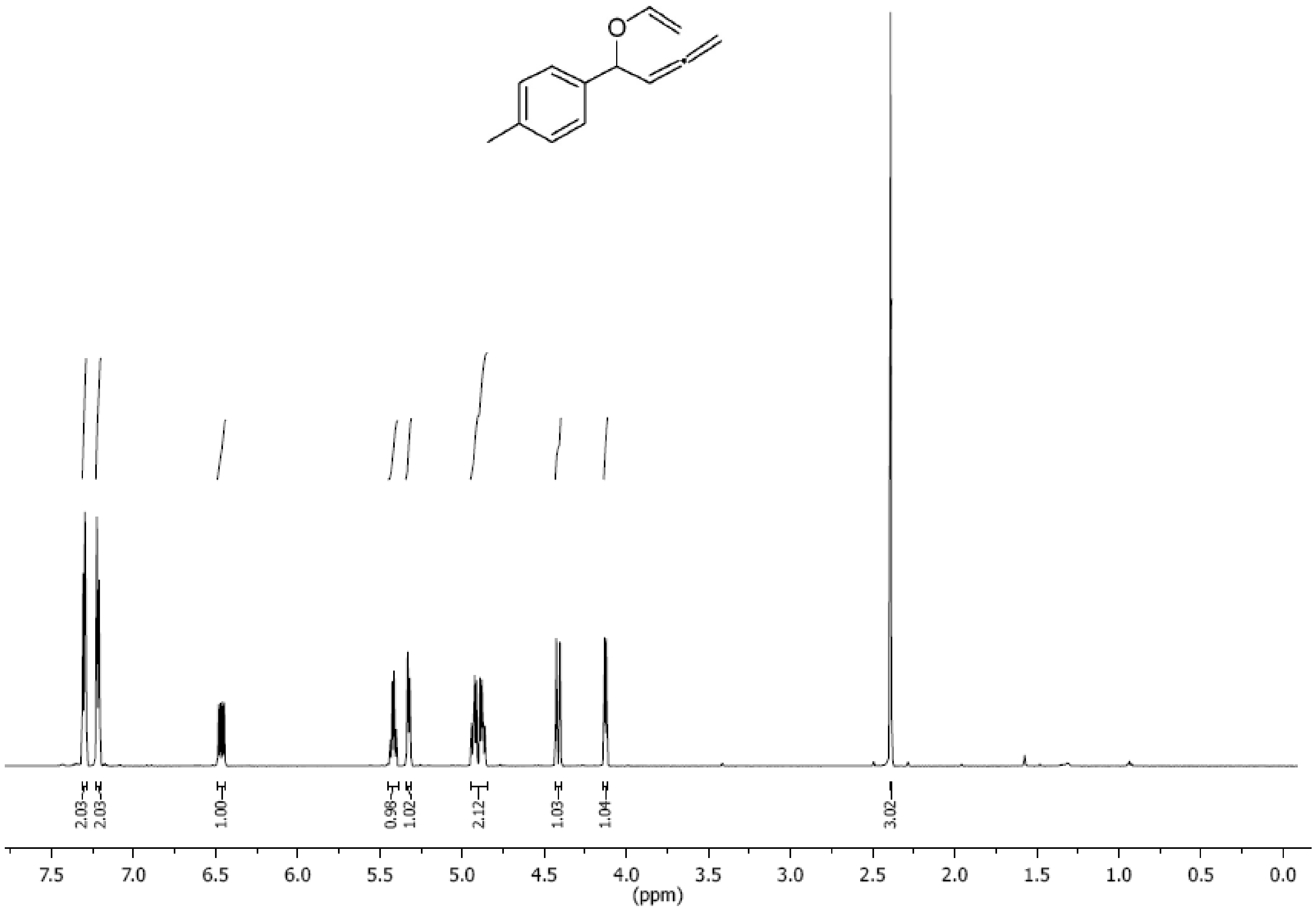
^{13}C NMR of allenyl vinyl ether **1k.**



^{1}H NMR of allenyl vinyl ether **1k**

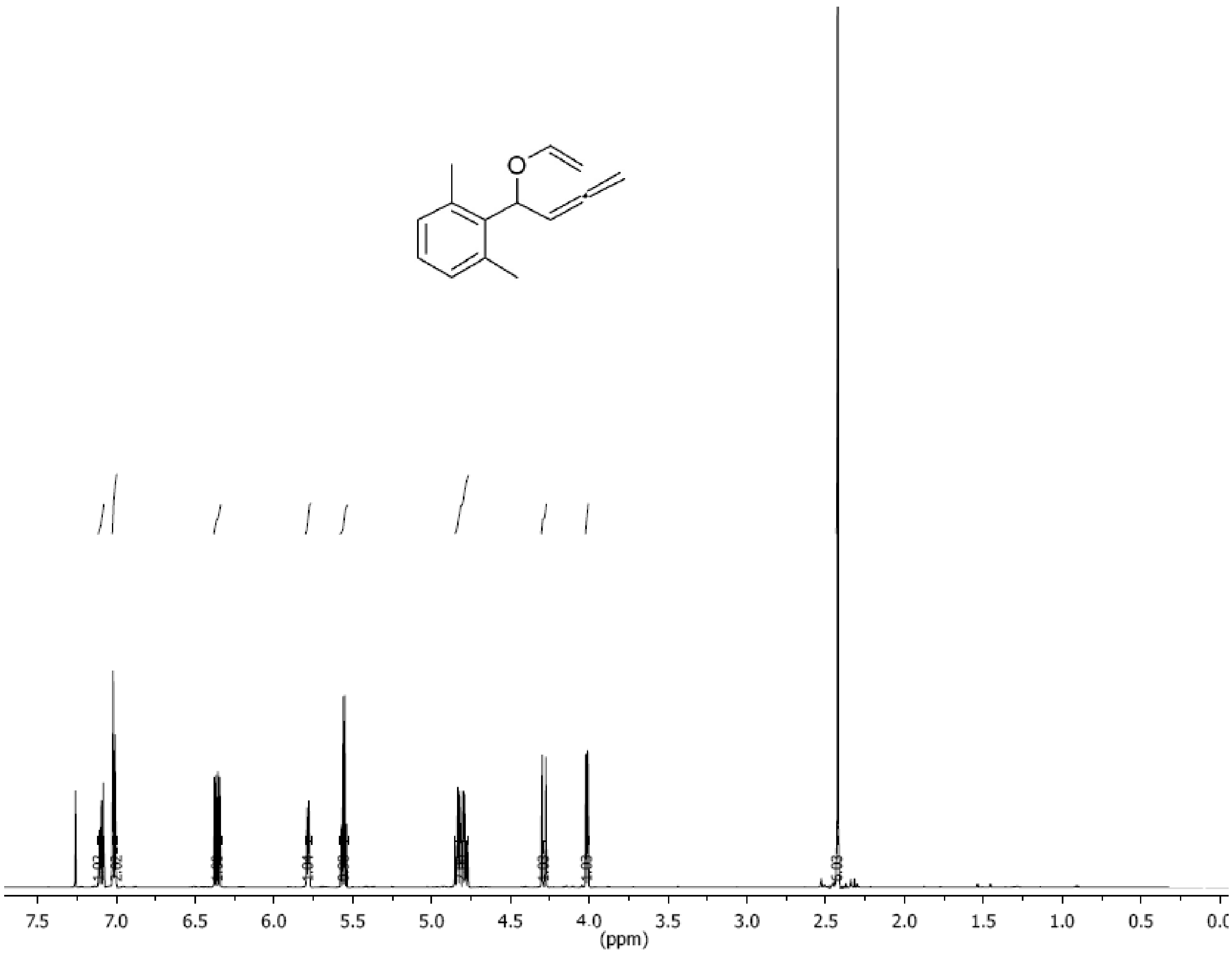


^{13}C NMR of allenyl vinyl ether 1l

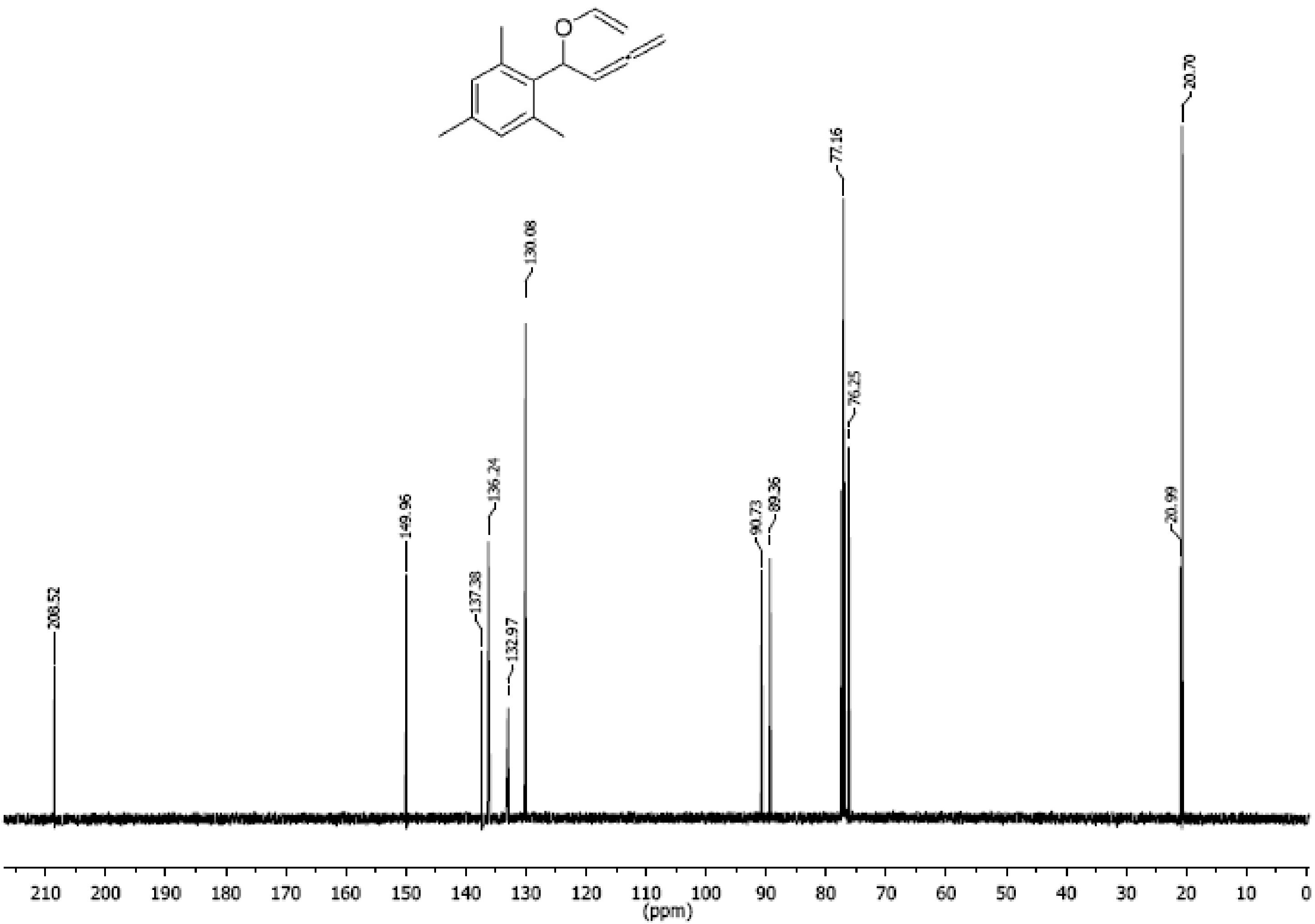


^{1}H NMR of allenyl vinyl ether 1l.

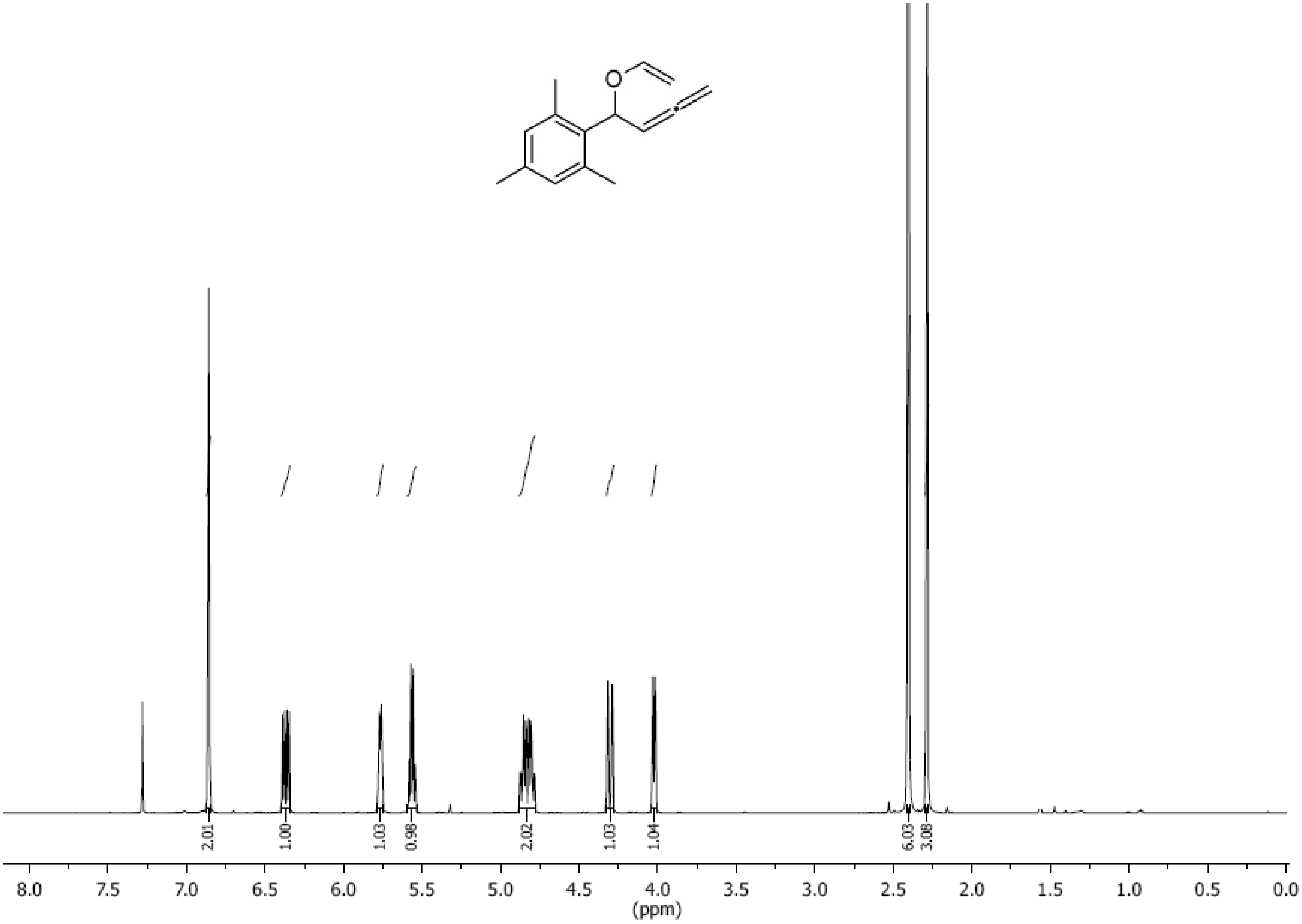
^{13}C NMR of allenyl vinyl ether **1m.**



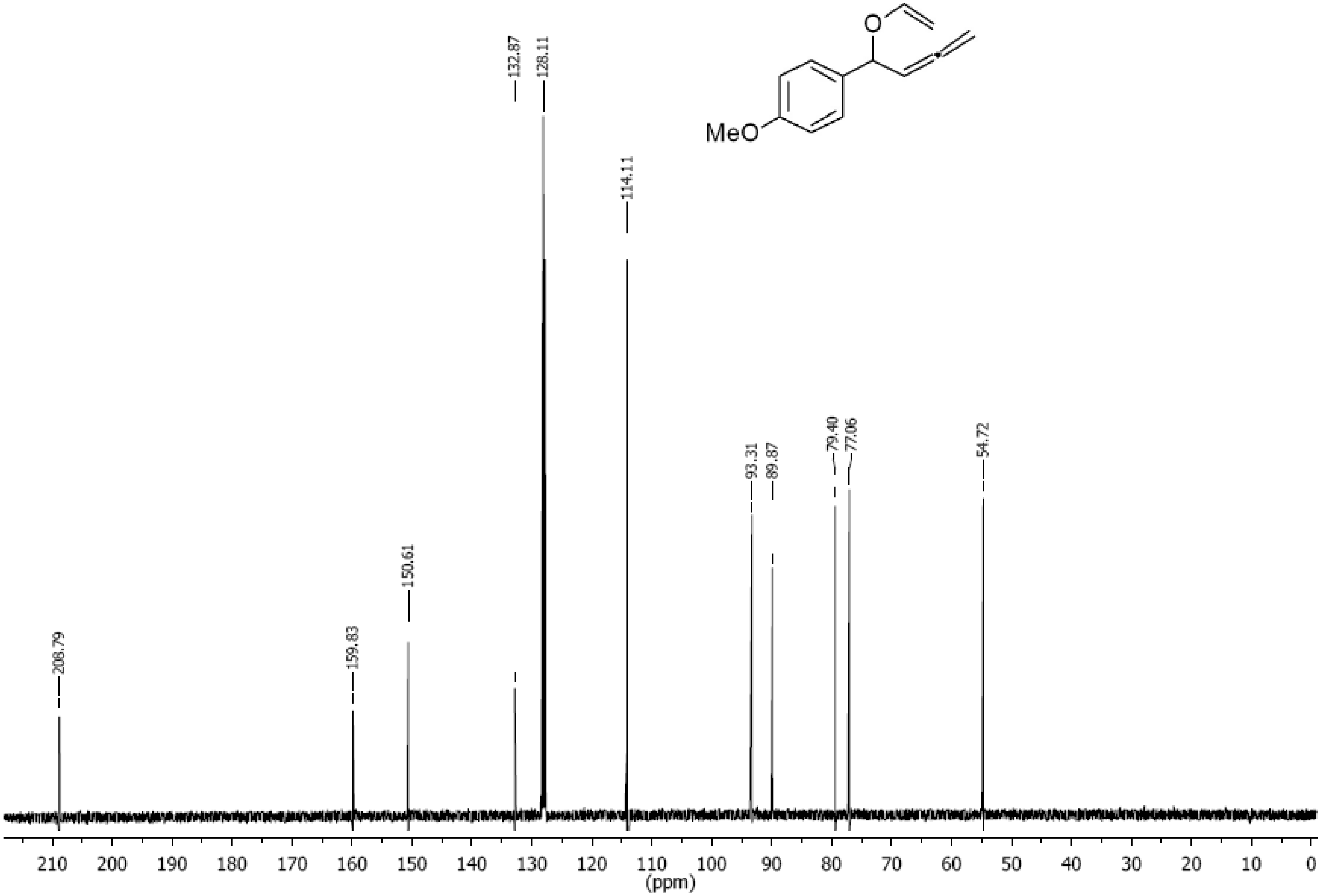
^{1}H NMR of allenyl vinyl ether 1m.



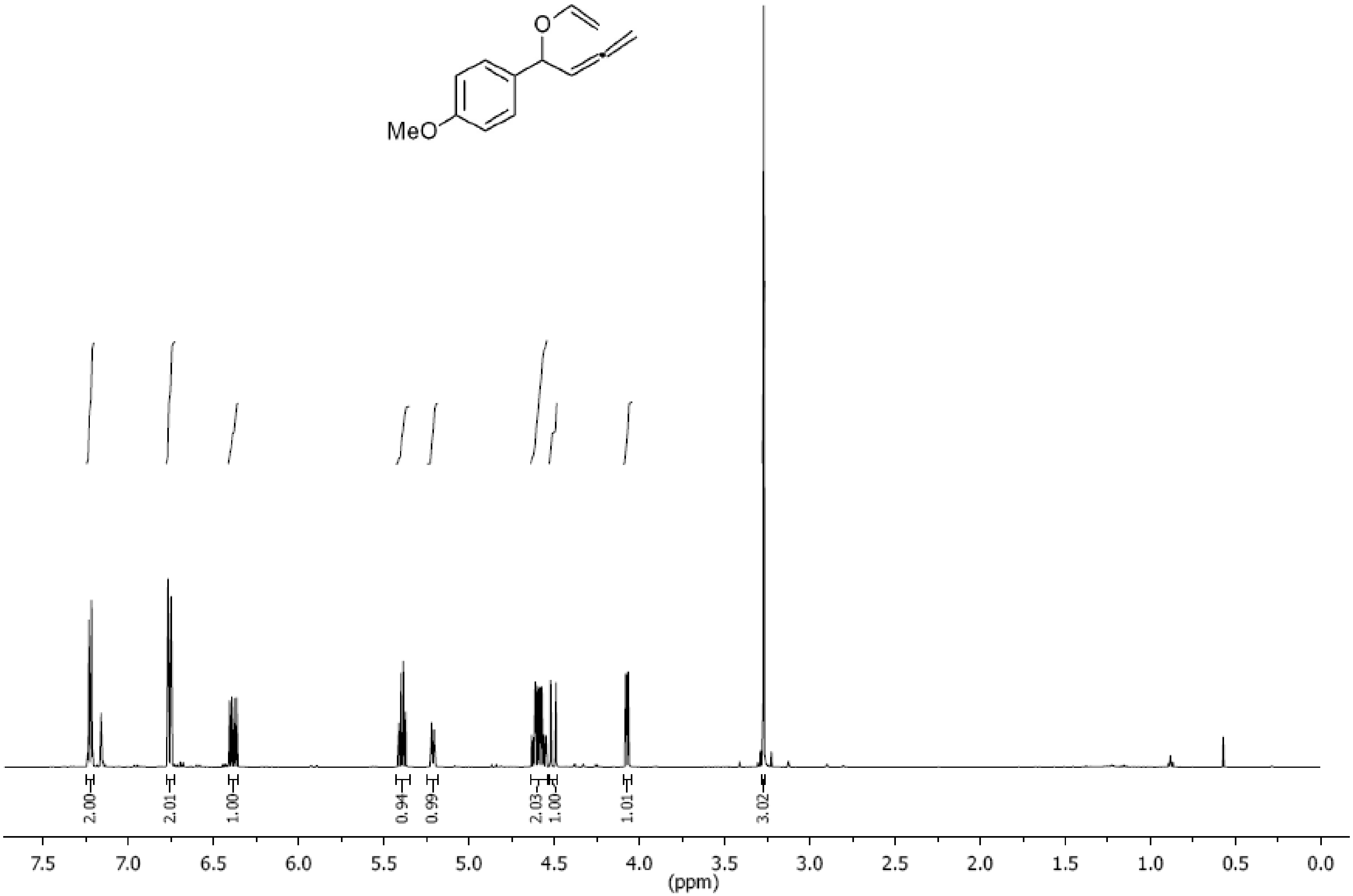
^{13}C NMR of allenyl vinyl ether 1n.



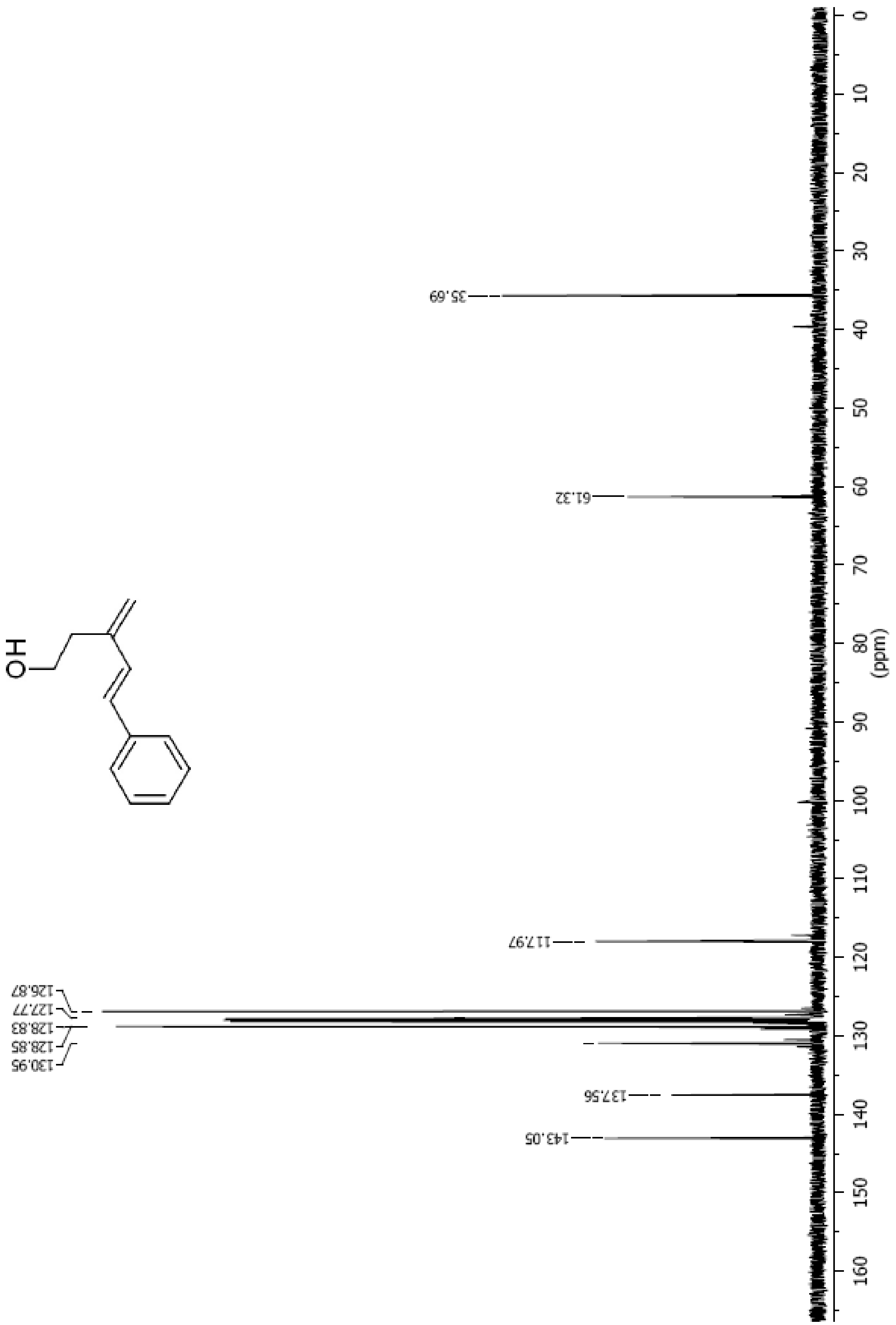
^{1}H NMR of allenyl vinyl ether 1n.



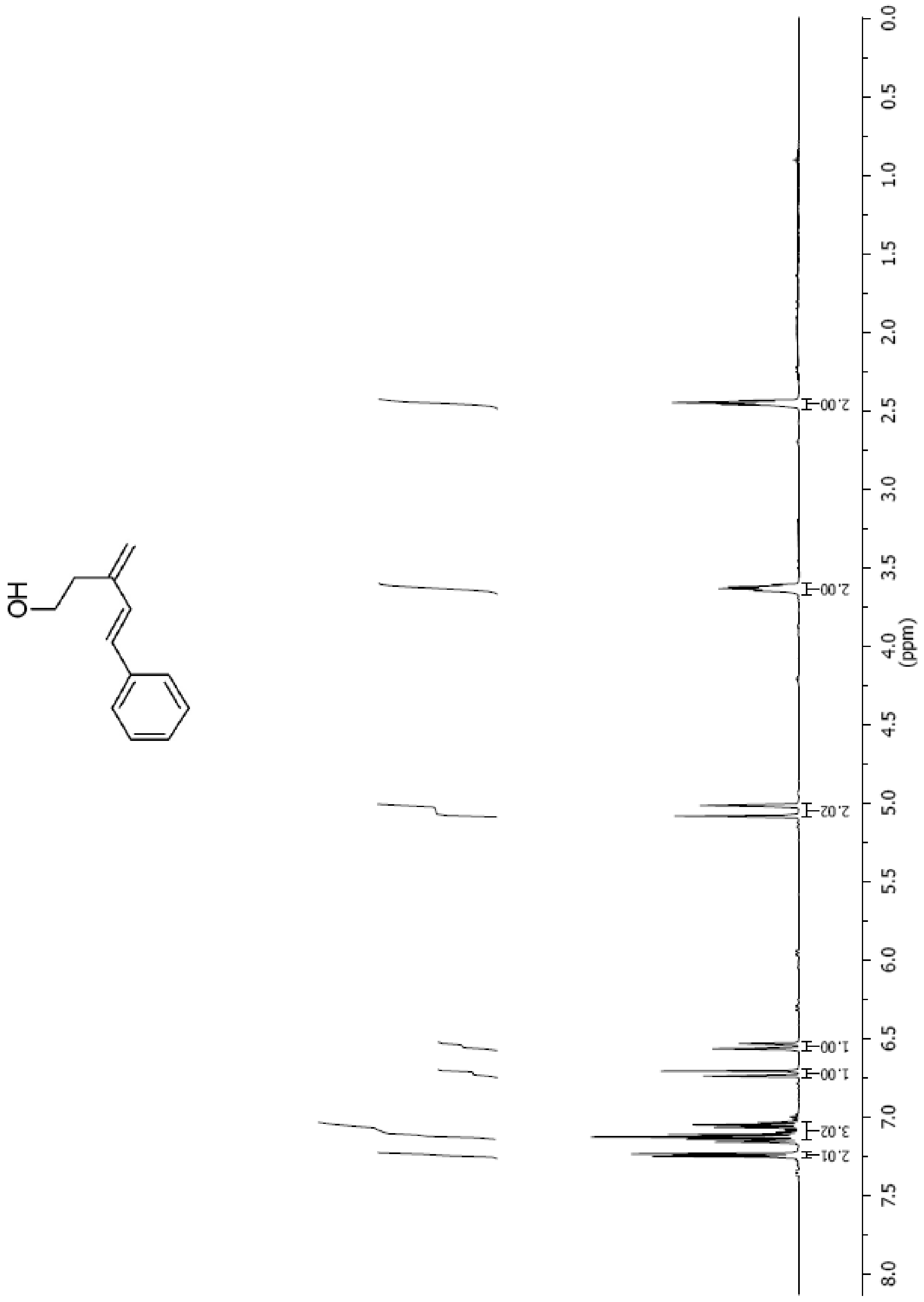
^{13}**C NMR of allenyl vinyl ether 1o.**



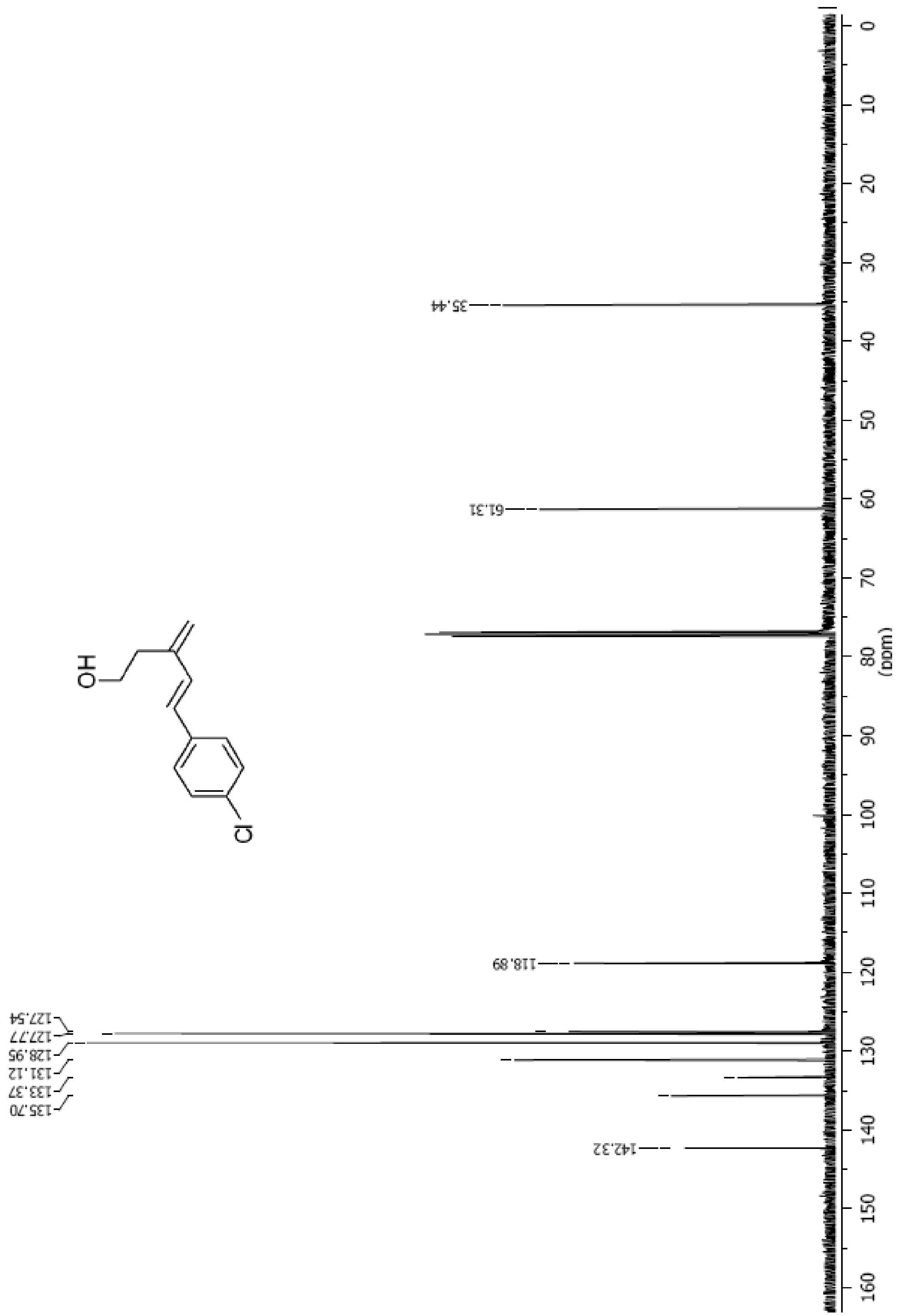
^{1}H NMR of allenyl vinyl ether 1o.



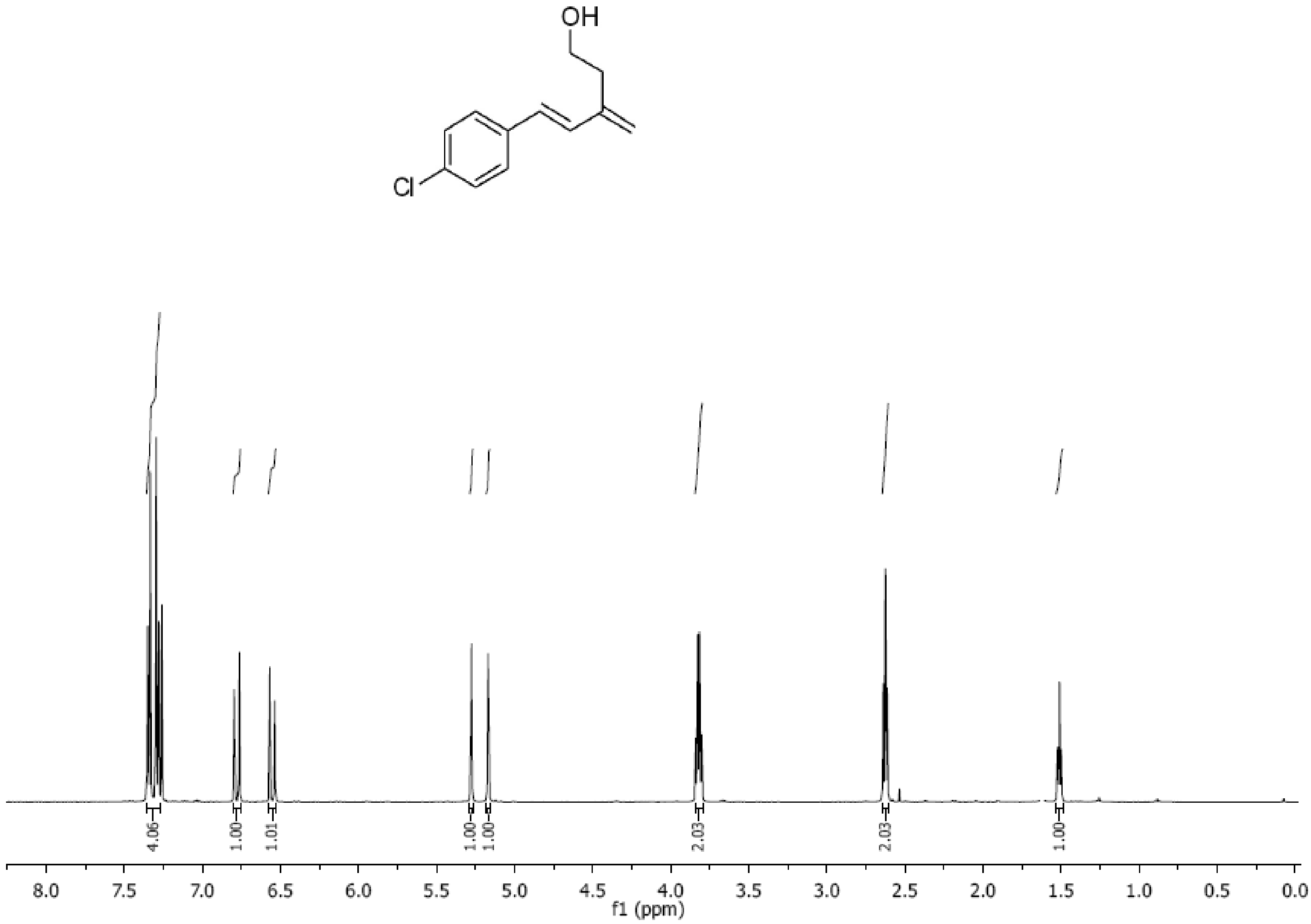
^{13}C NMR of diene 2a.



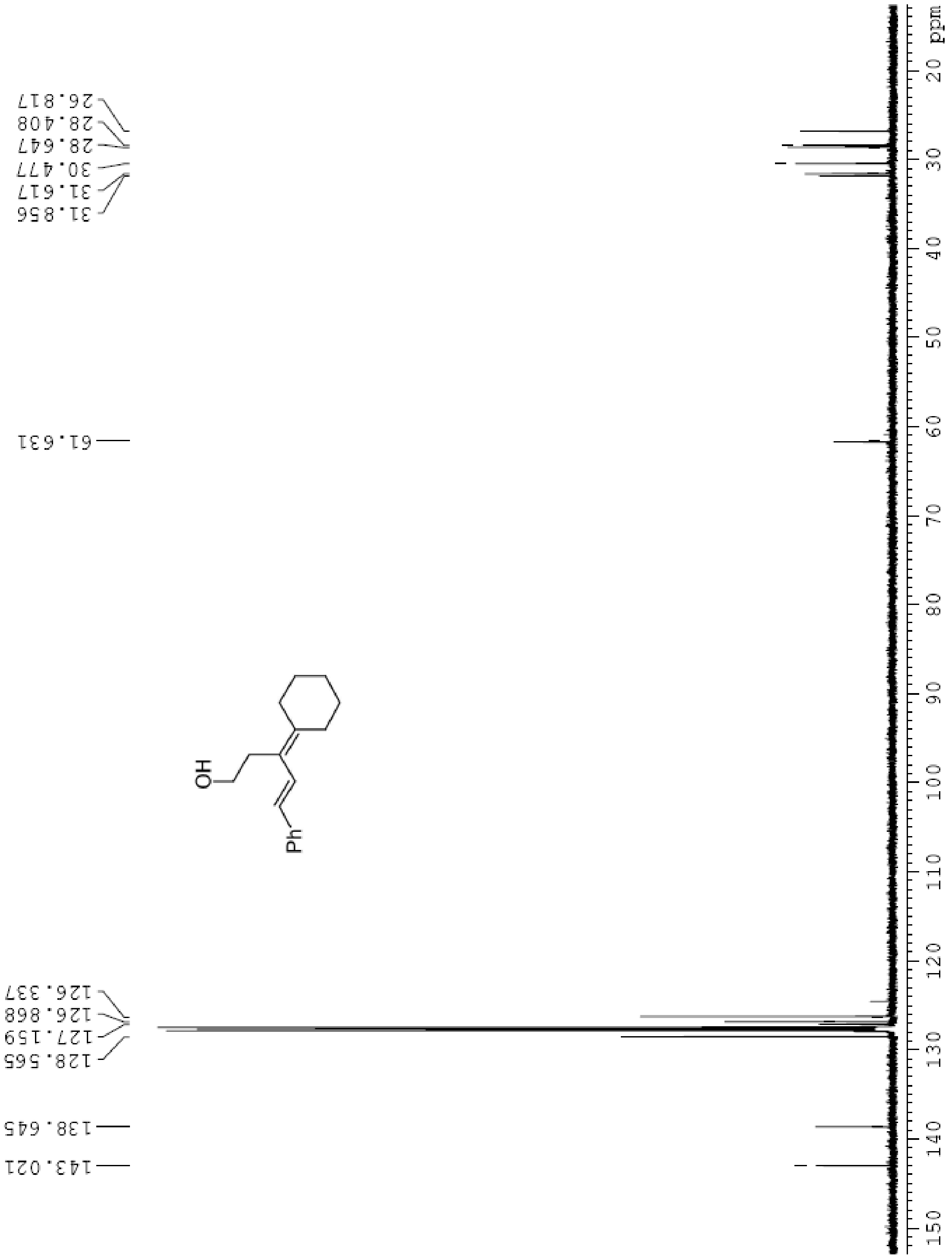
^{1}H NMR of diene **2a.**



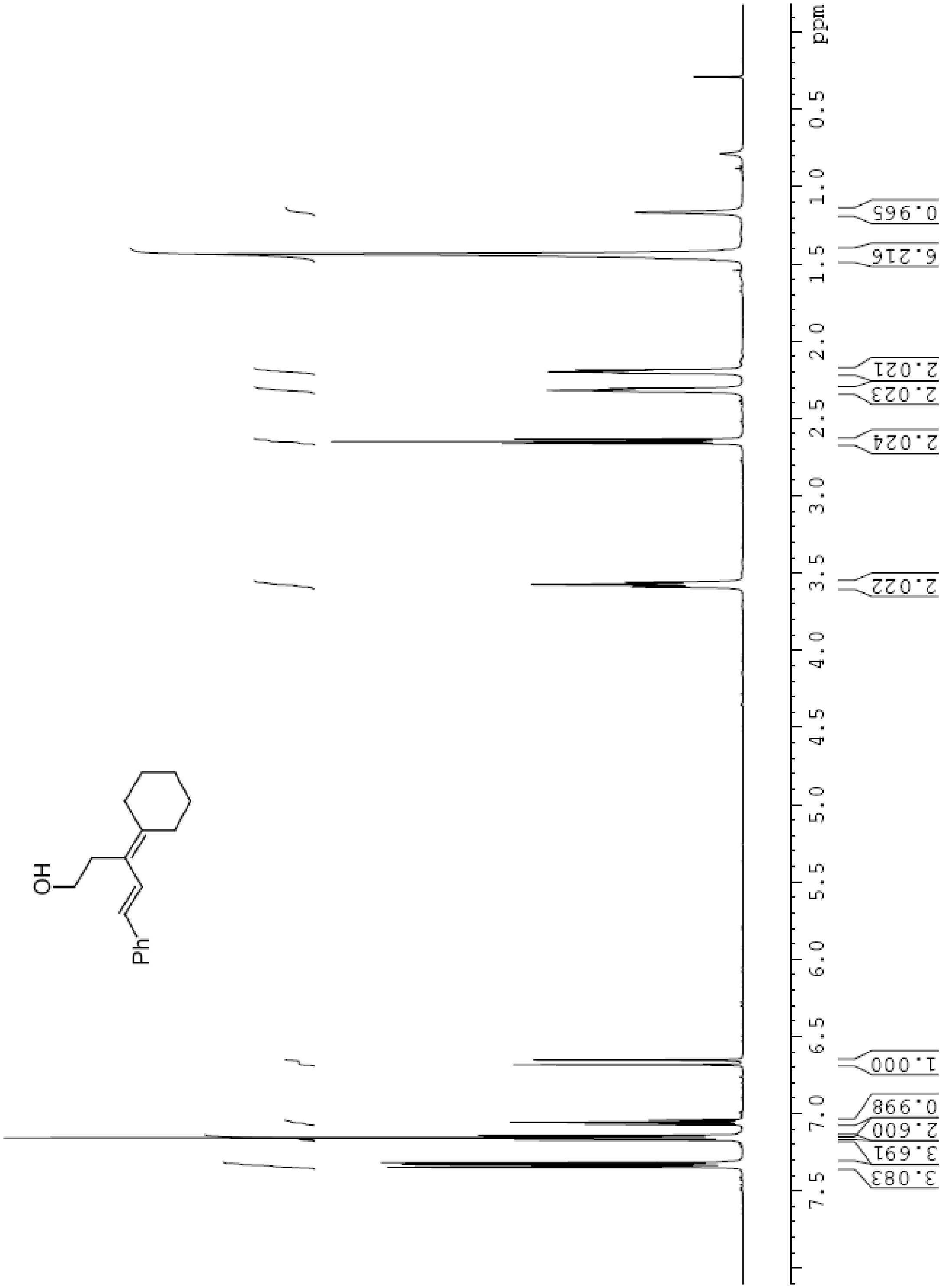
^{13}C NMR of diene 2b.



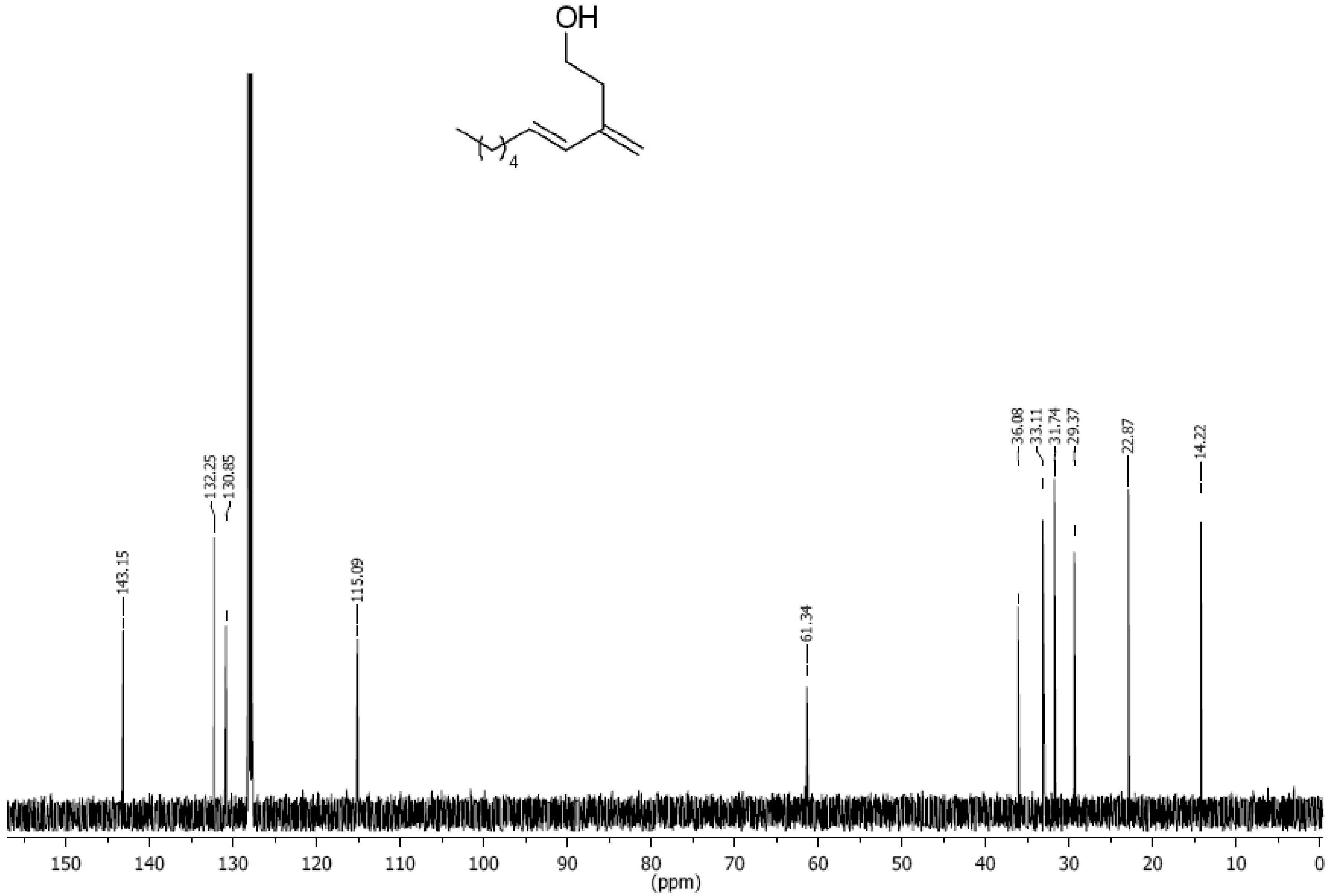
^{1}H NMR of diene 2b.



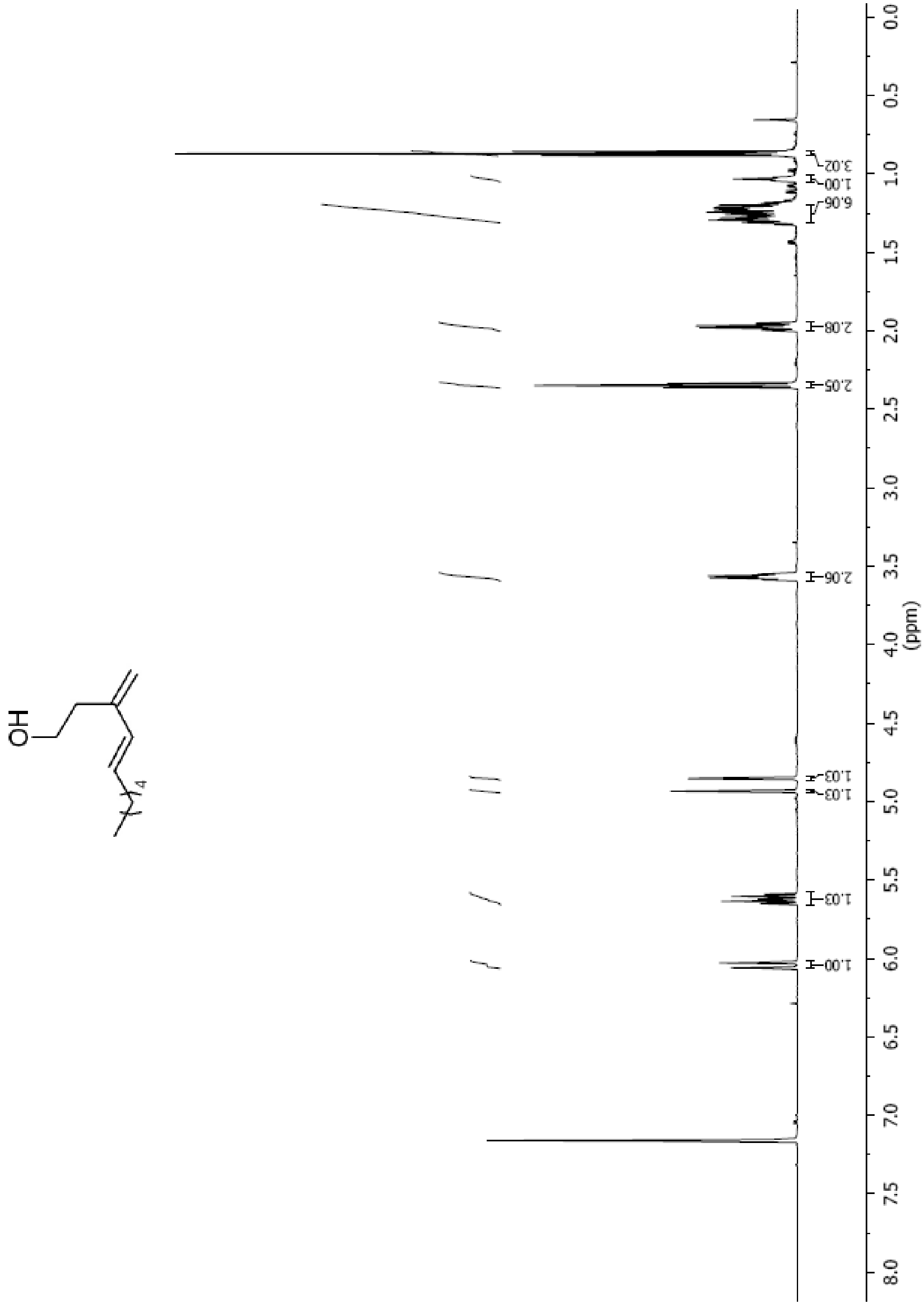
^{13}C NMR of diene 2c.



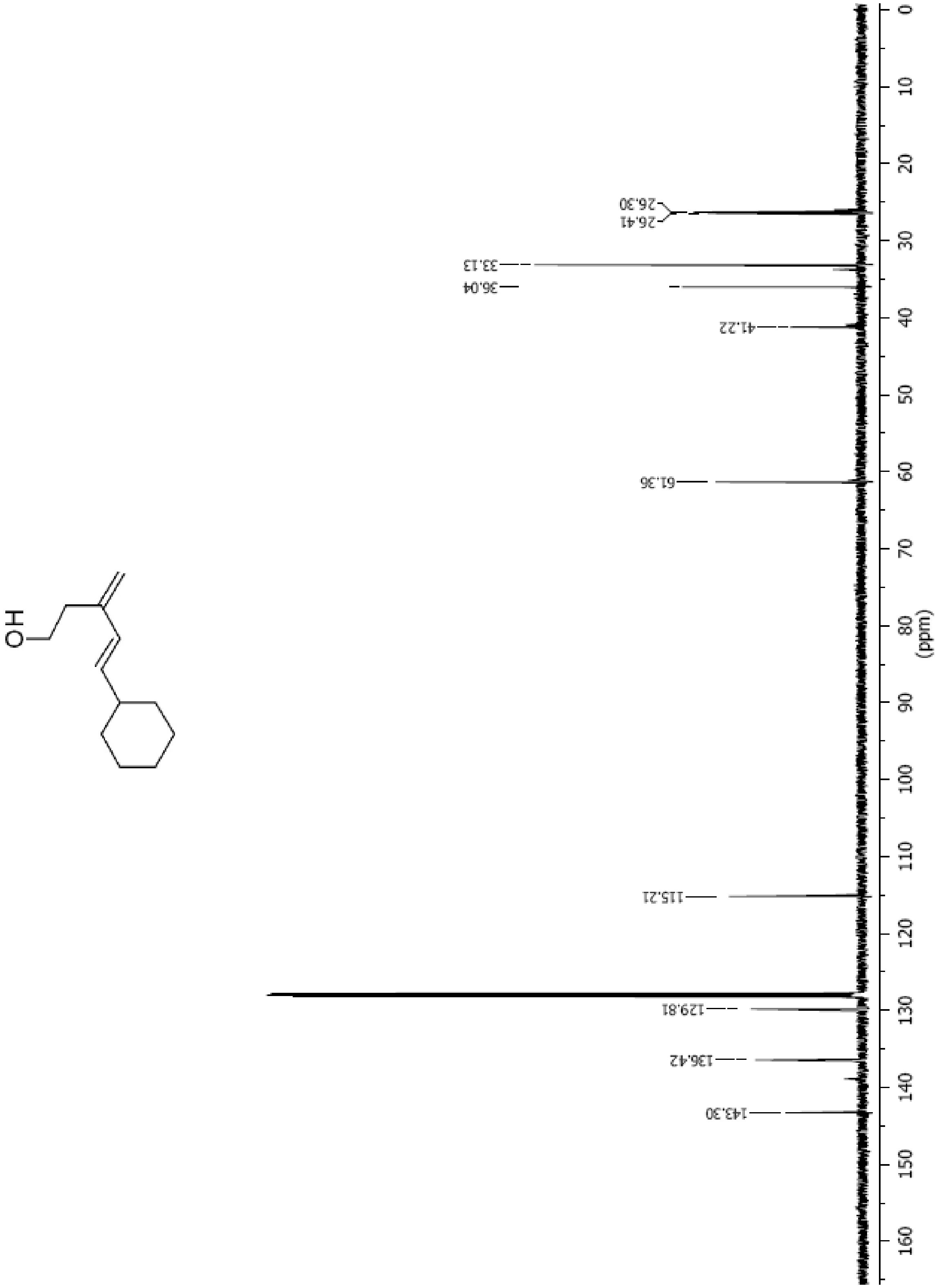
^{1}H NMR of diene 2c.



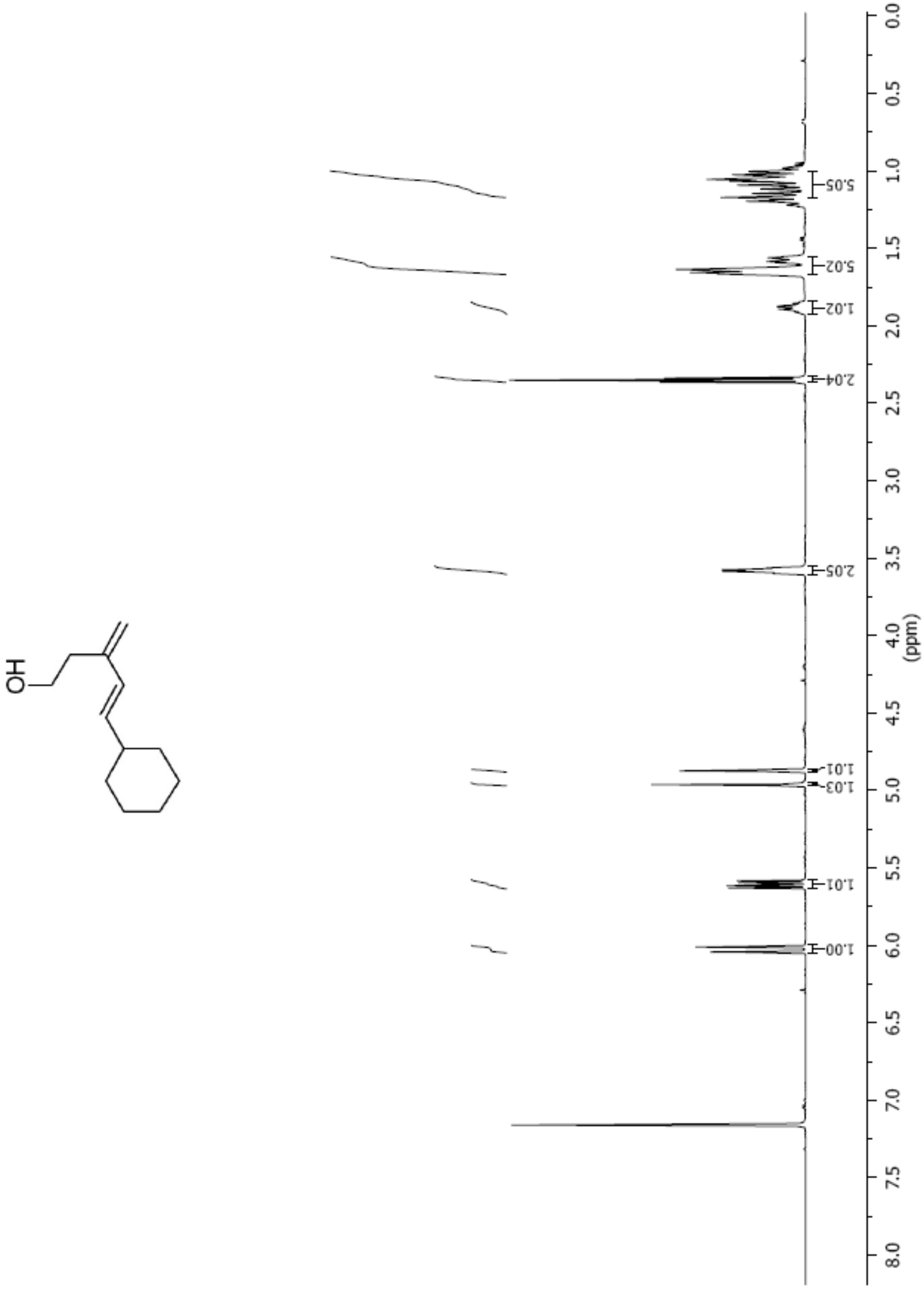
^{13}C NMR of diene 2d.



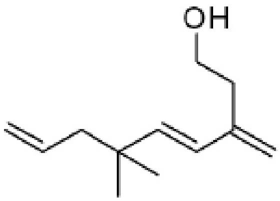
^{1}H NMR of diene 2d.

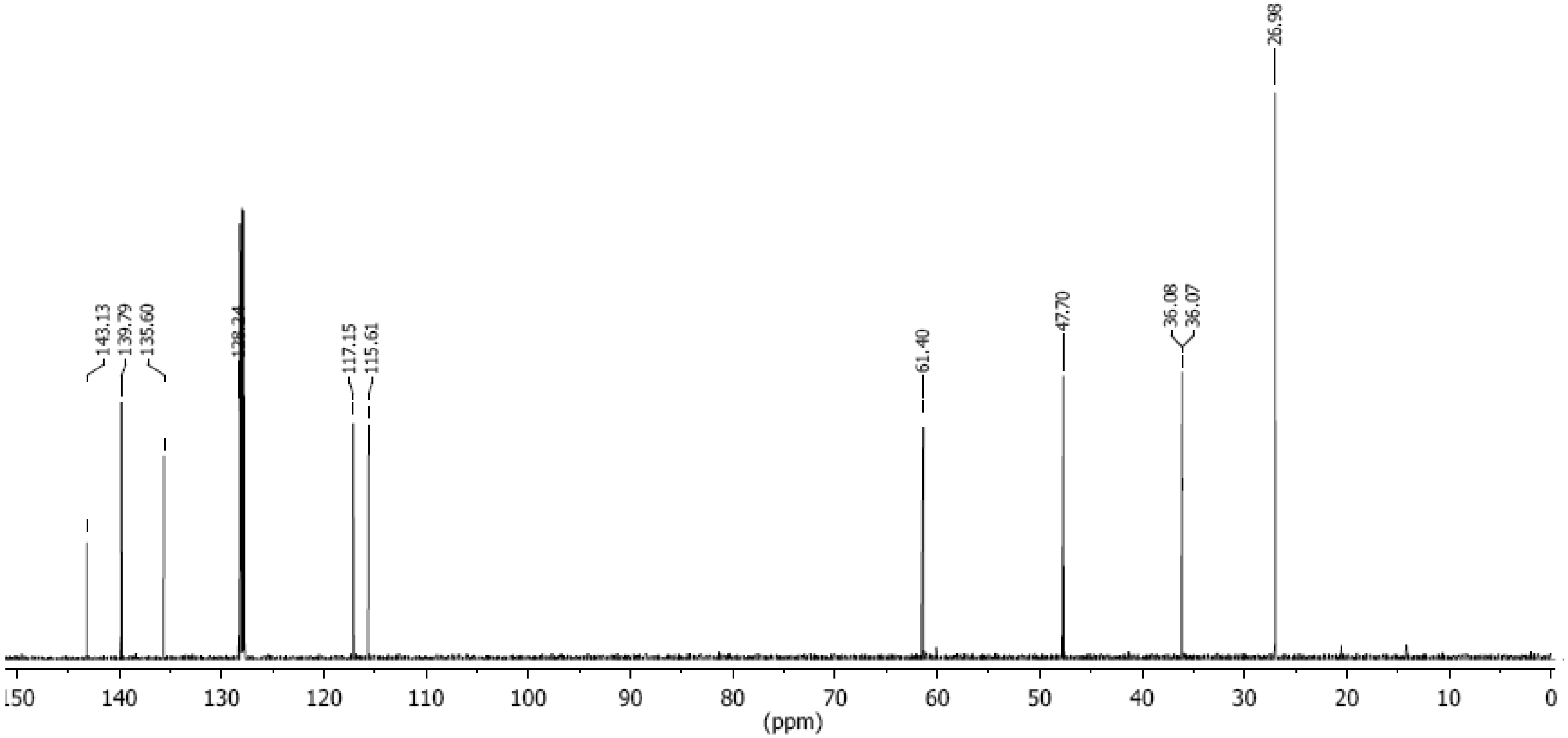


^{13}C NMR of diene 2e.

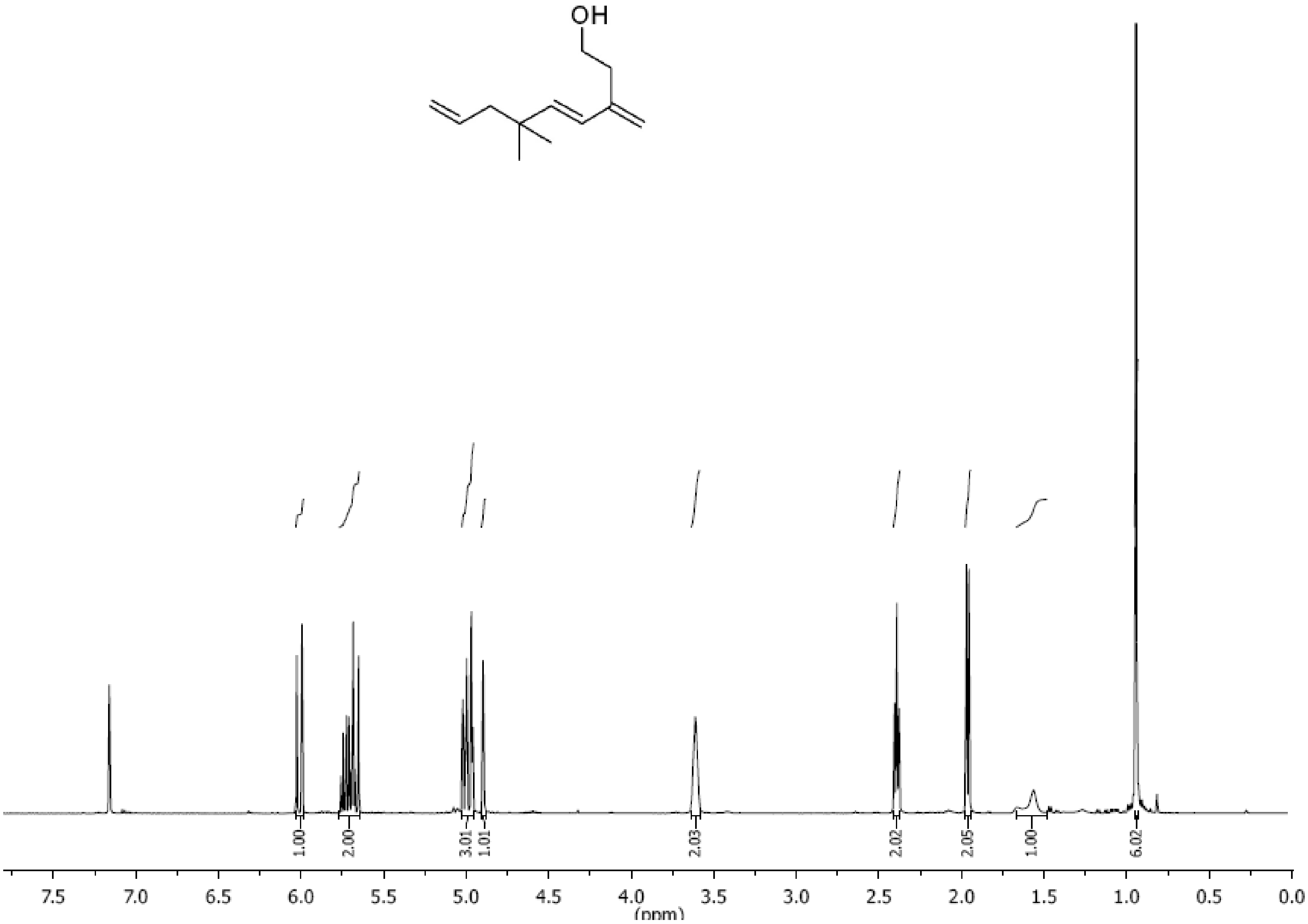


^{1}H NMR of diene 2e.

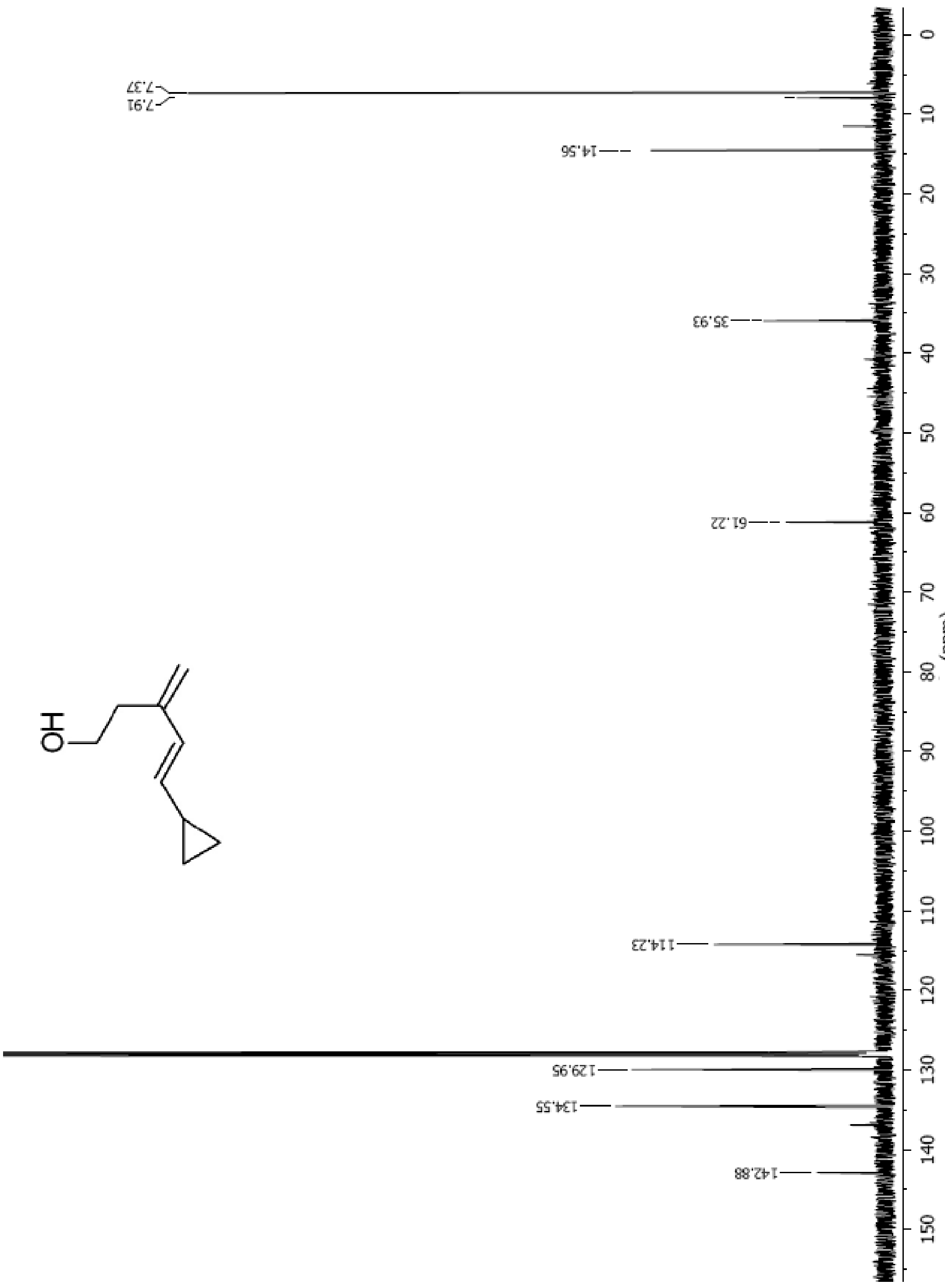




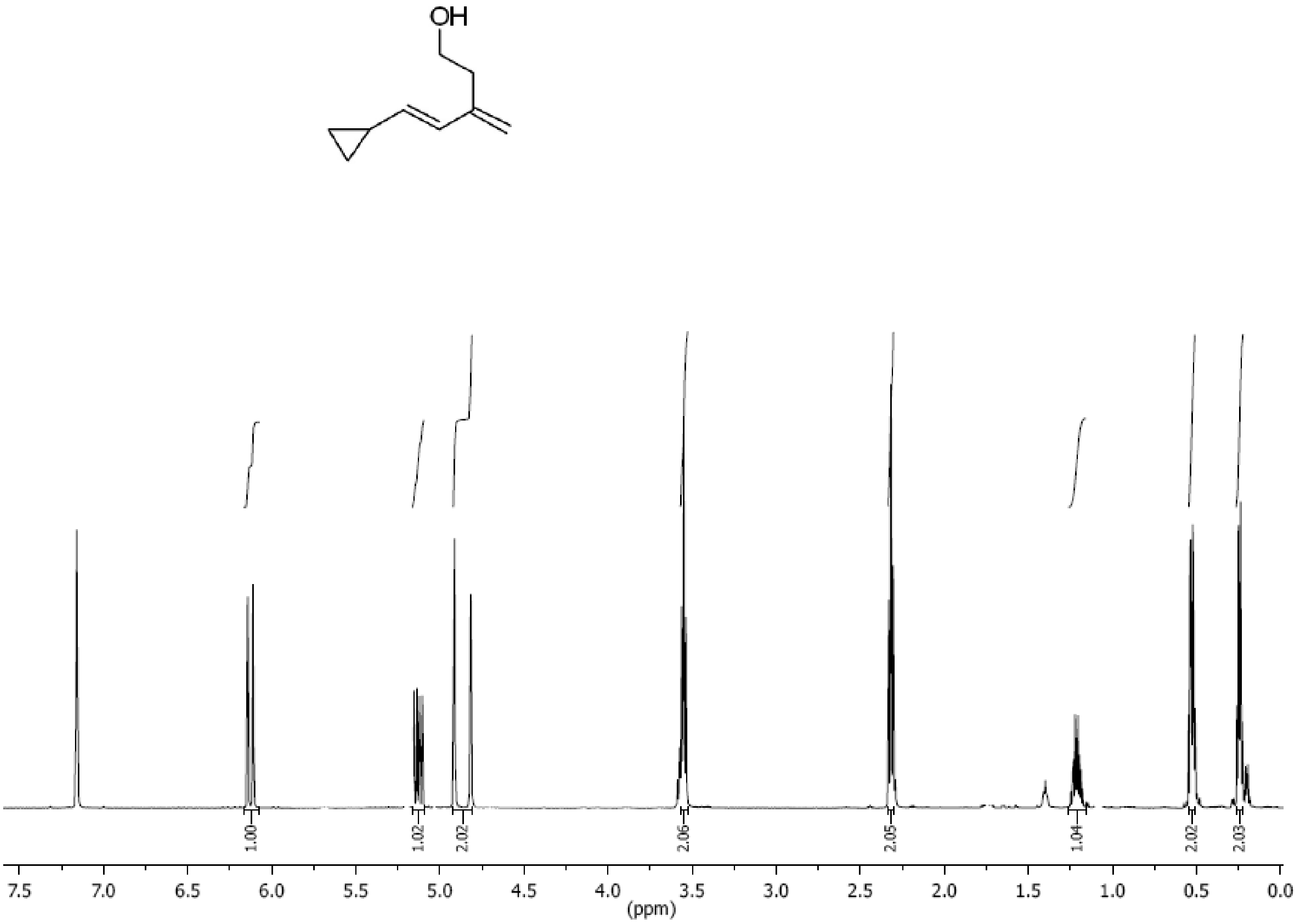
^{13}C NMR of diene 2f.



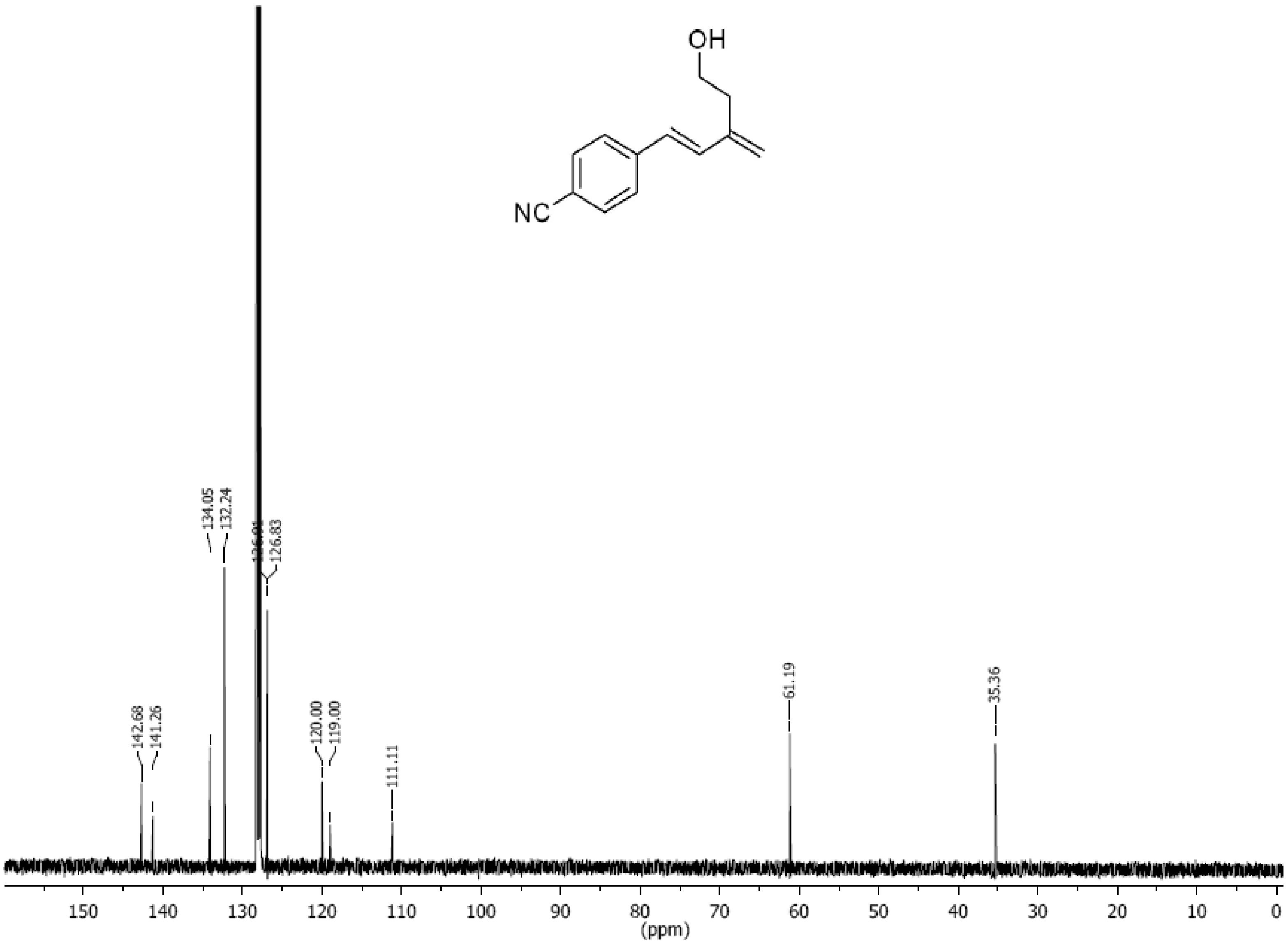
^{1}H NMR of diene 2f



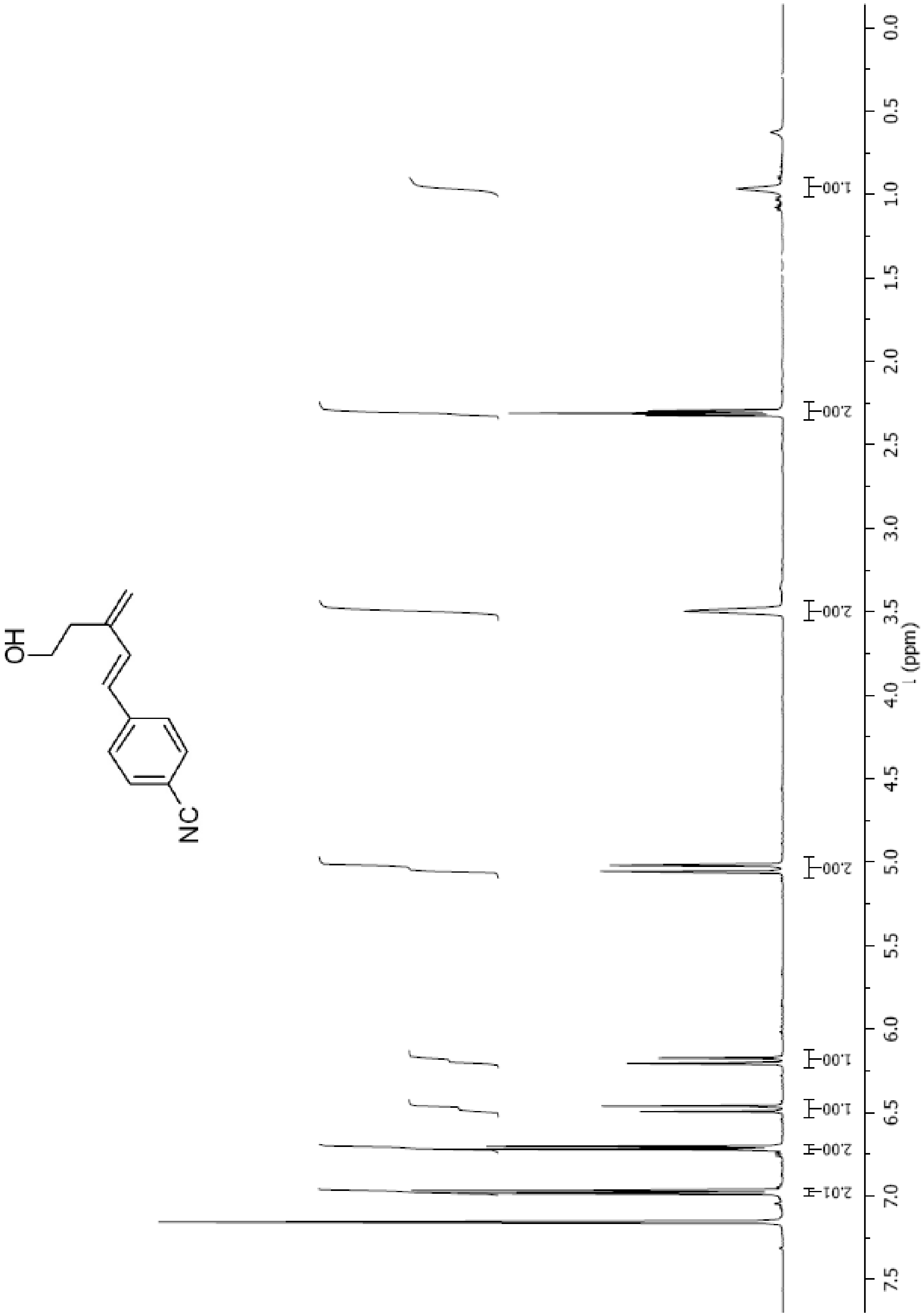
^{13}C NMR of diene 2g.



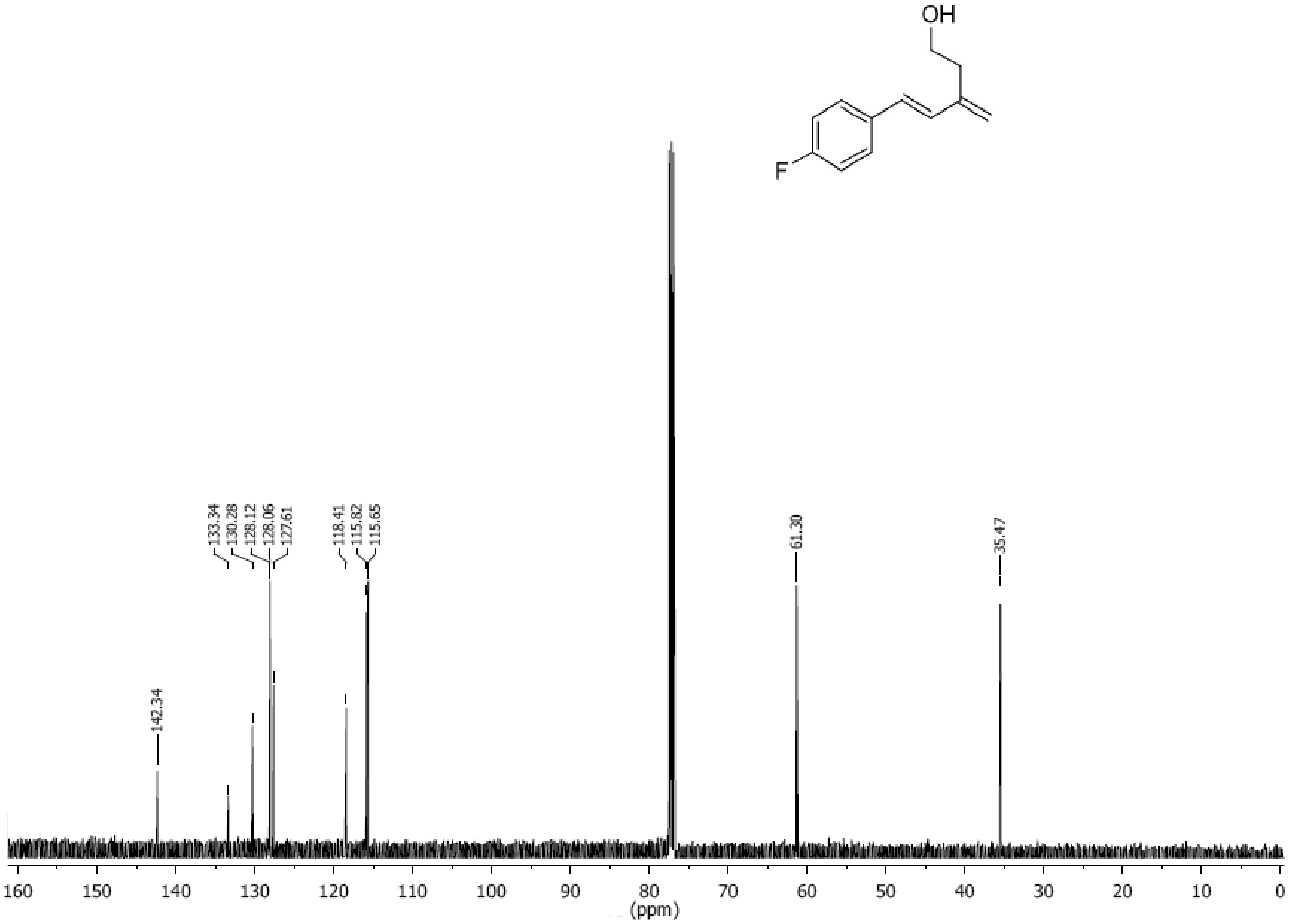
^{1}H NMR of diene 2g.



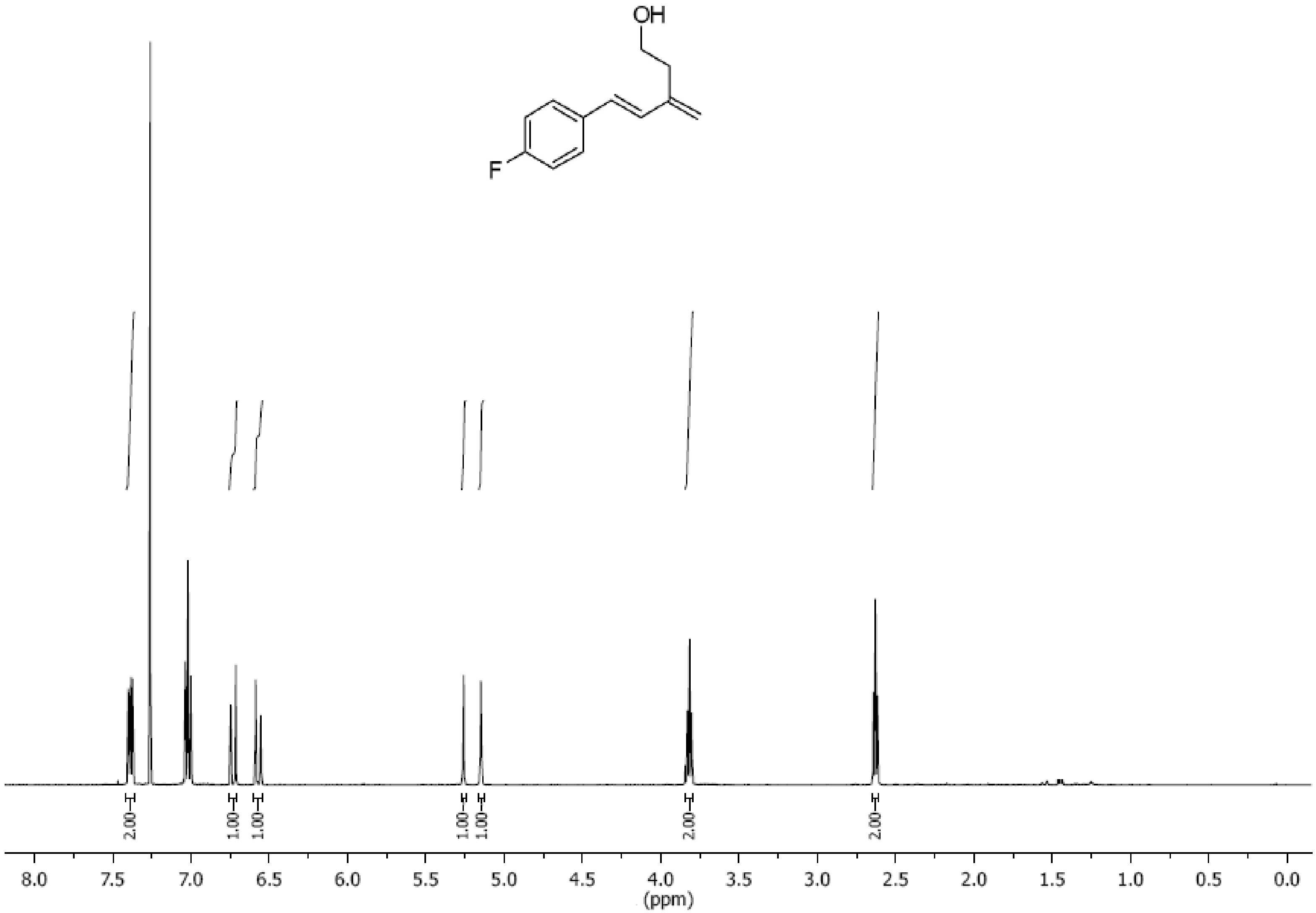
^{13}C NMR of diene 2h.



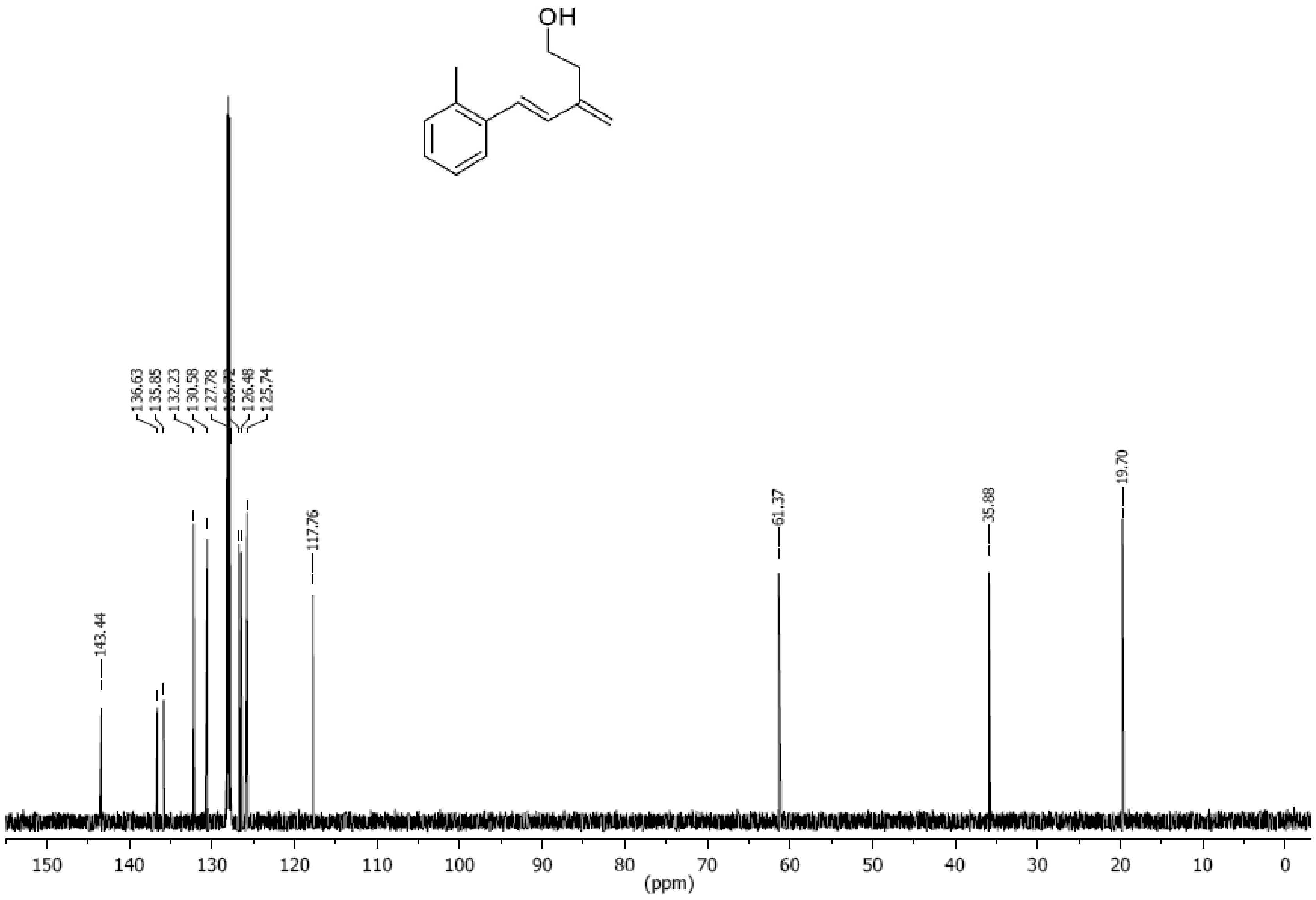
^{1}H NMR of diene **2h.**



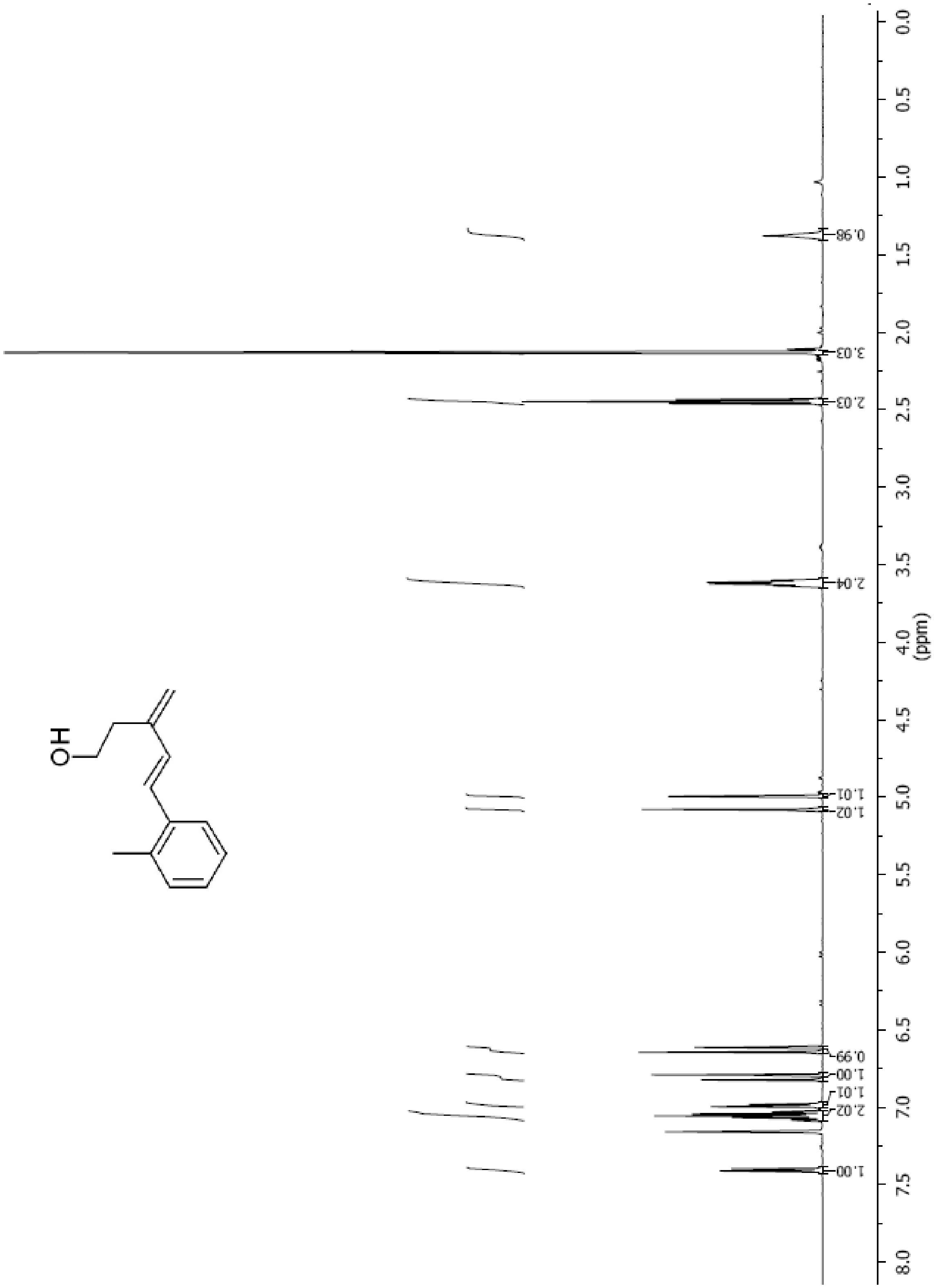
. ^{13}C NMR of diene 2i.



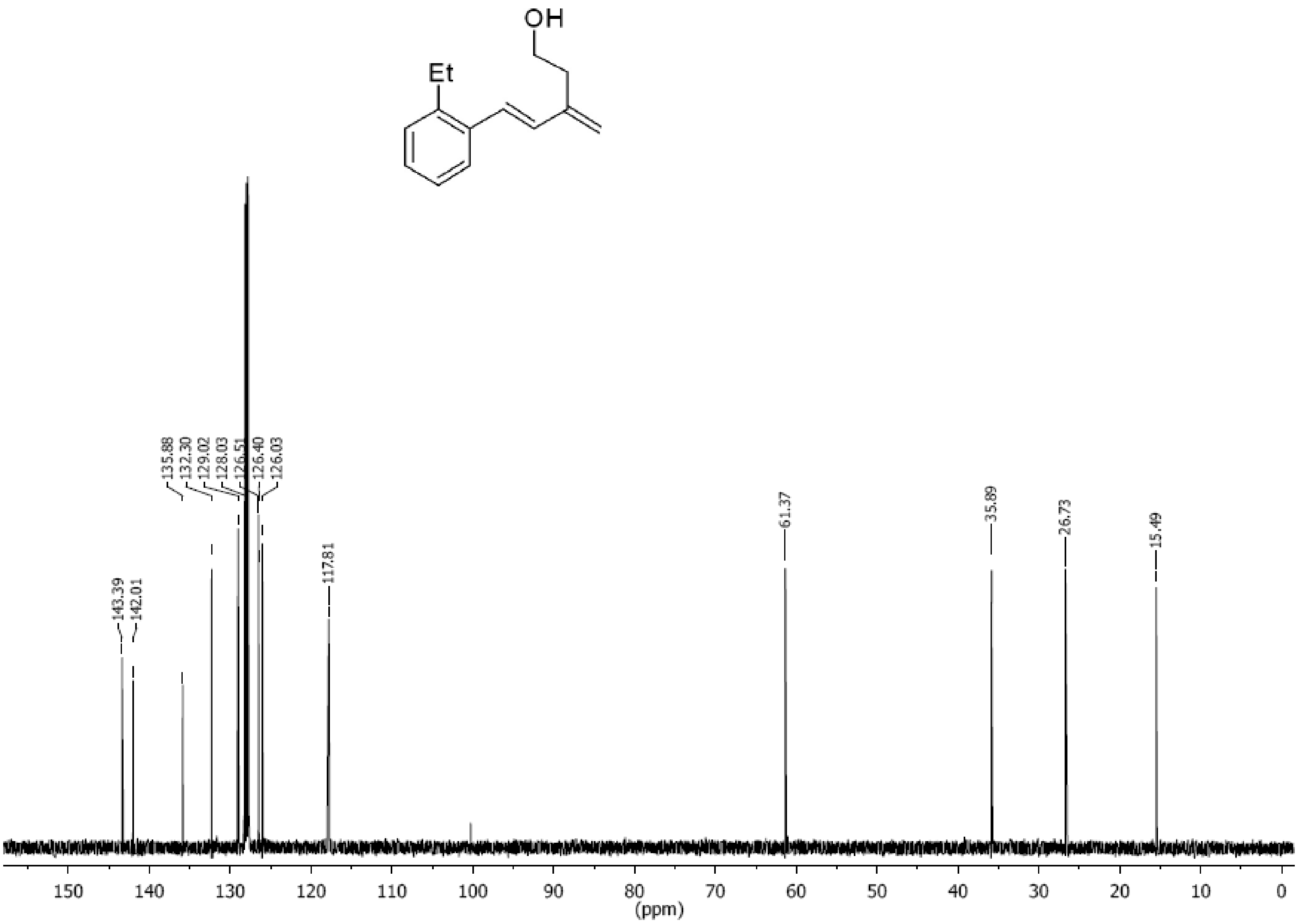
^{1}**H NMR of diene 2i.**



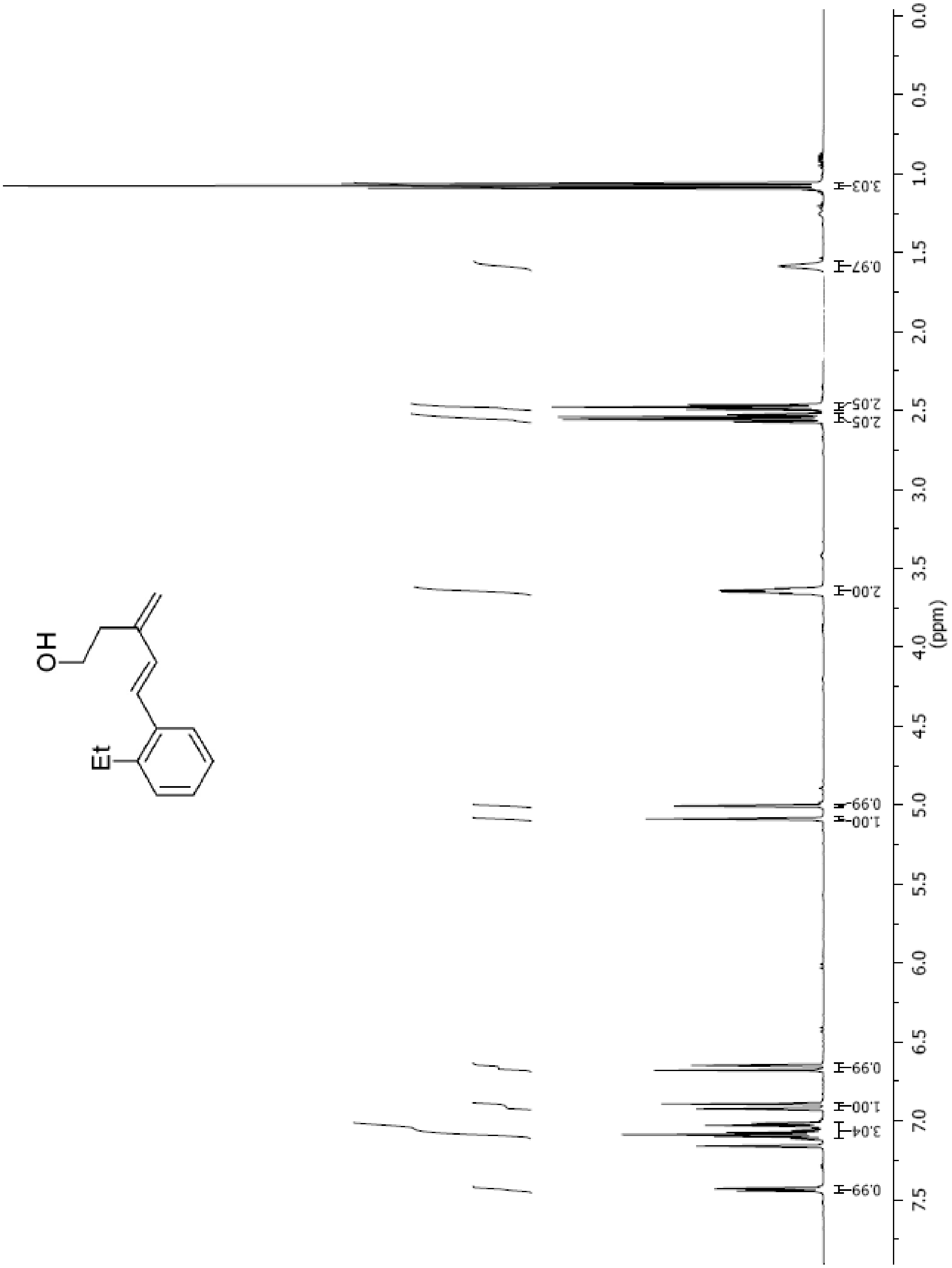
^{13}C NMR of diene 2j.



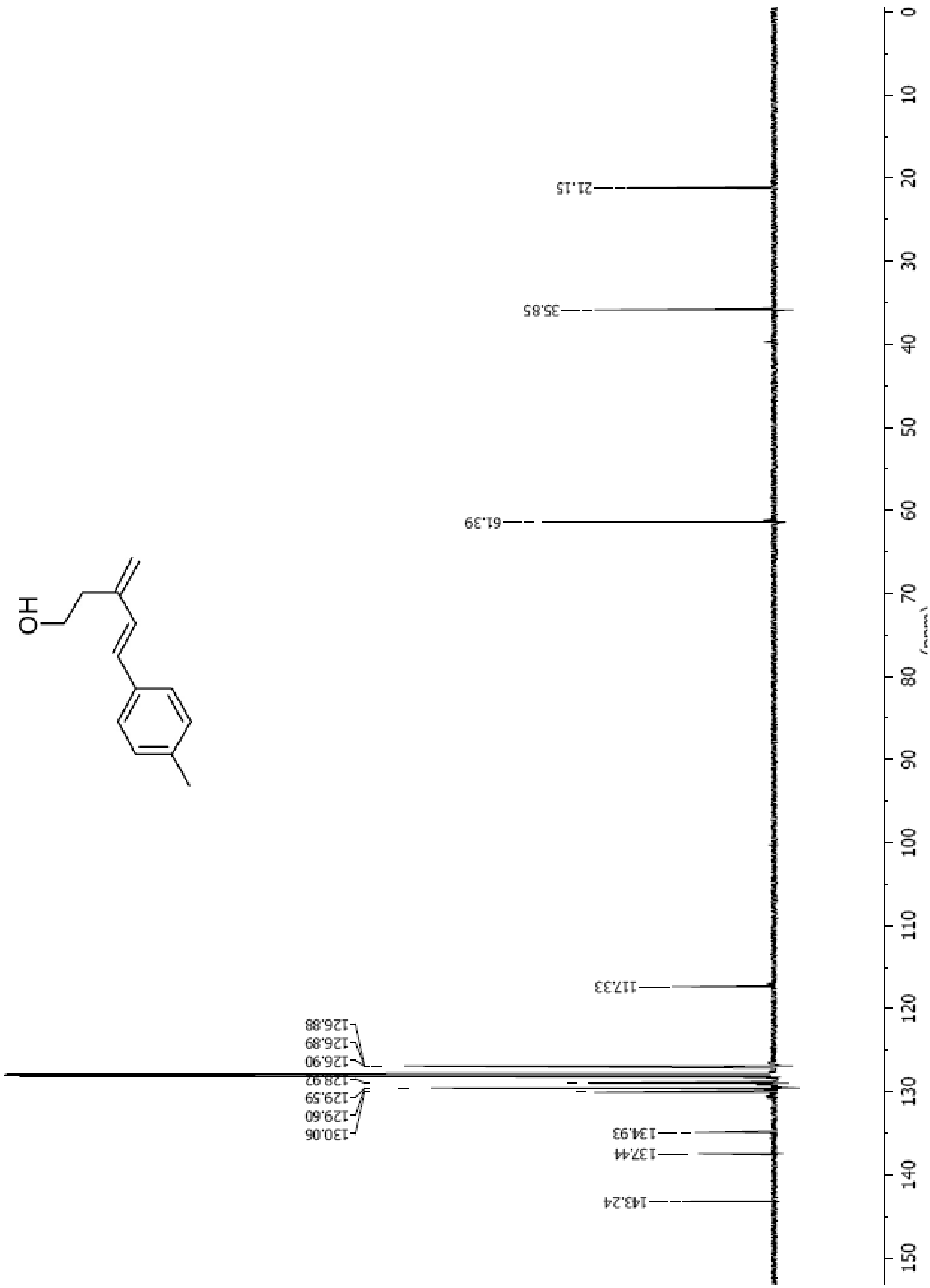
^{1}H NMR of diene **2j.**



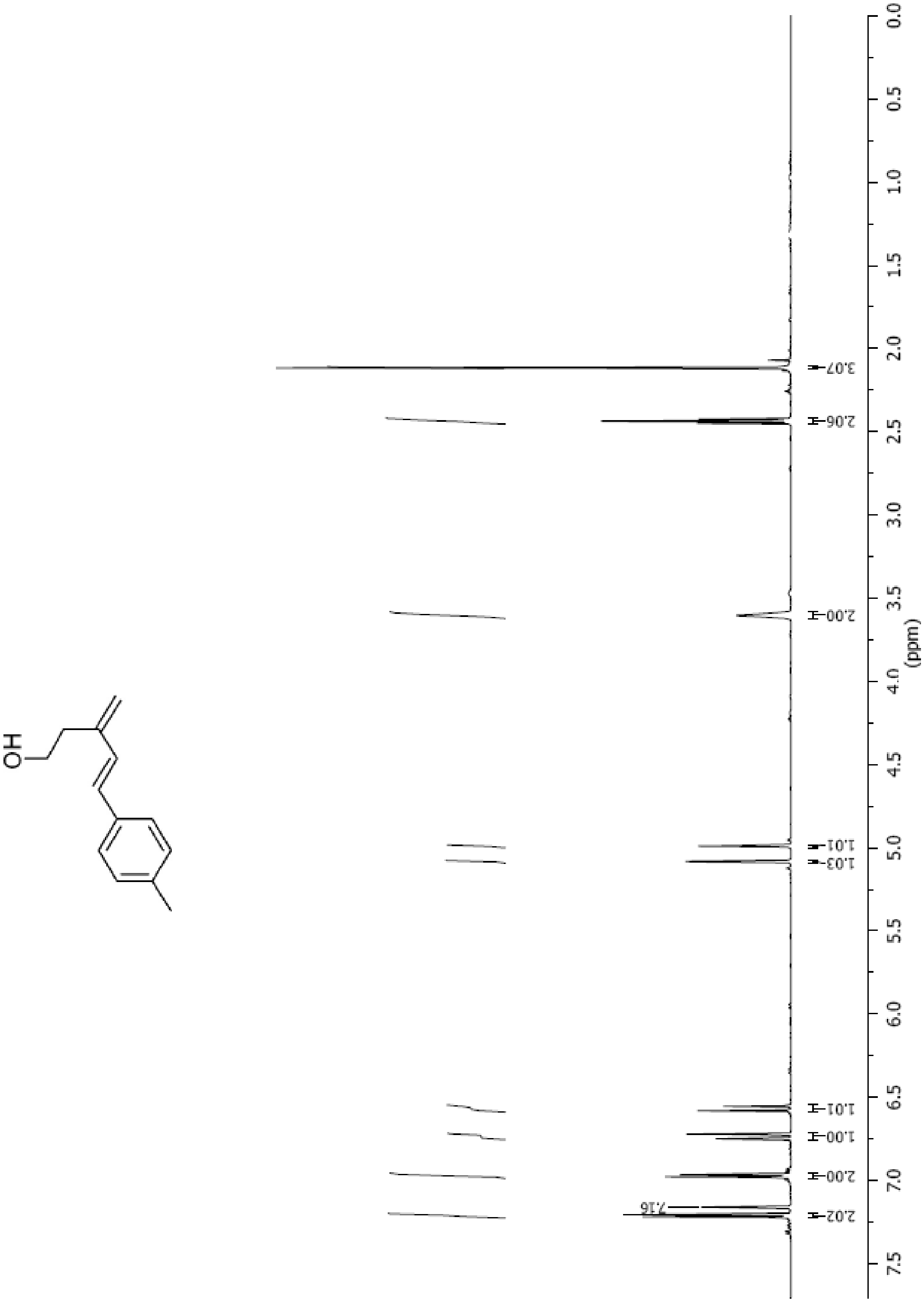
^{13}C NMR of diene 2k.



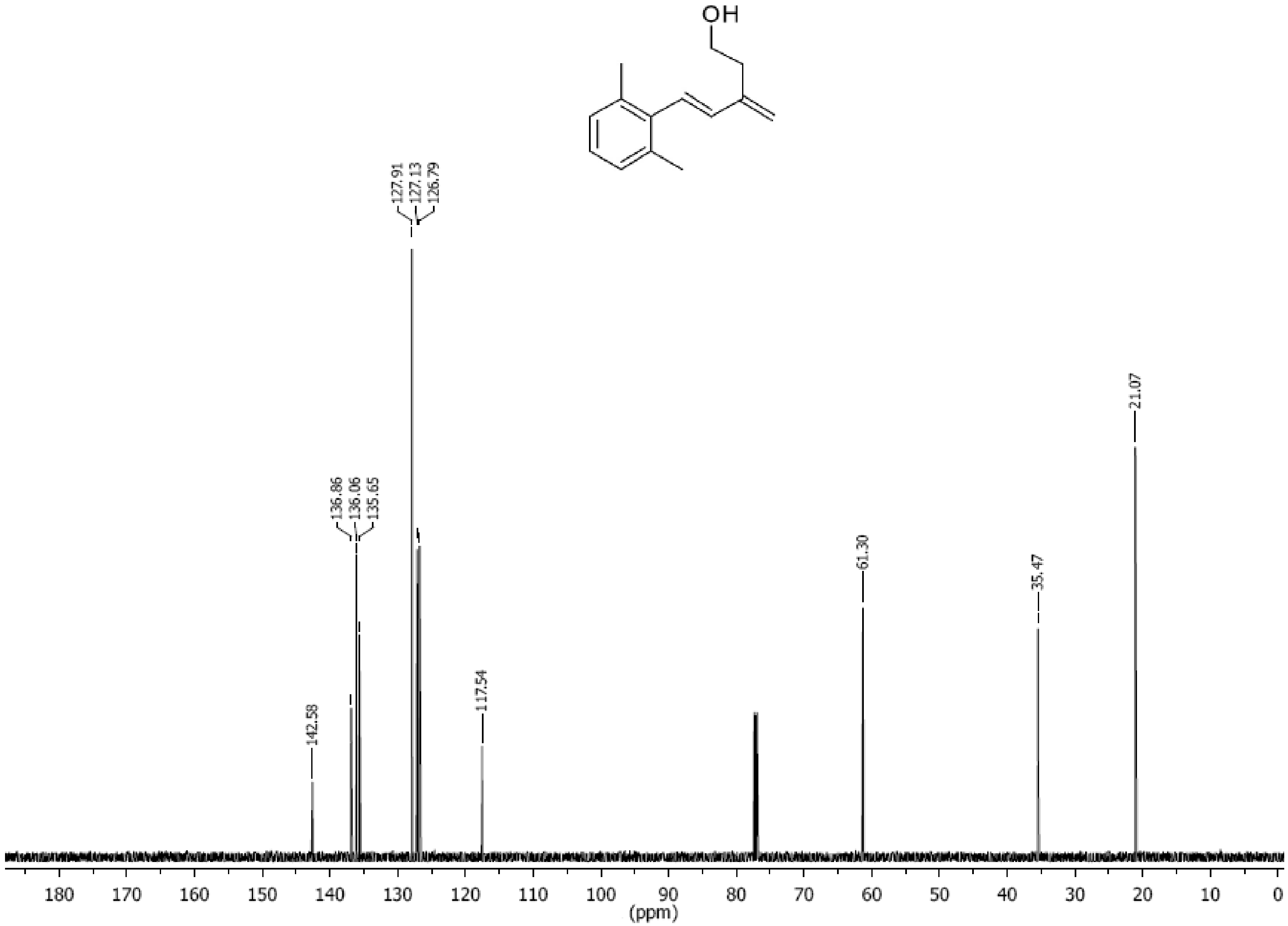
^{1}**H NMR of diene 2k.**



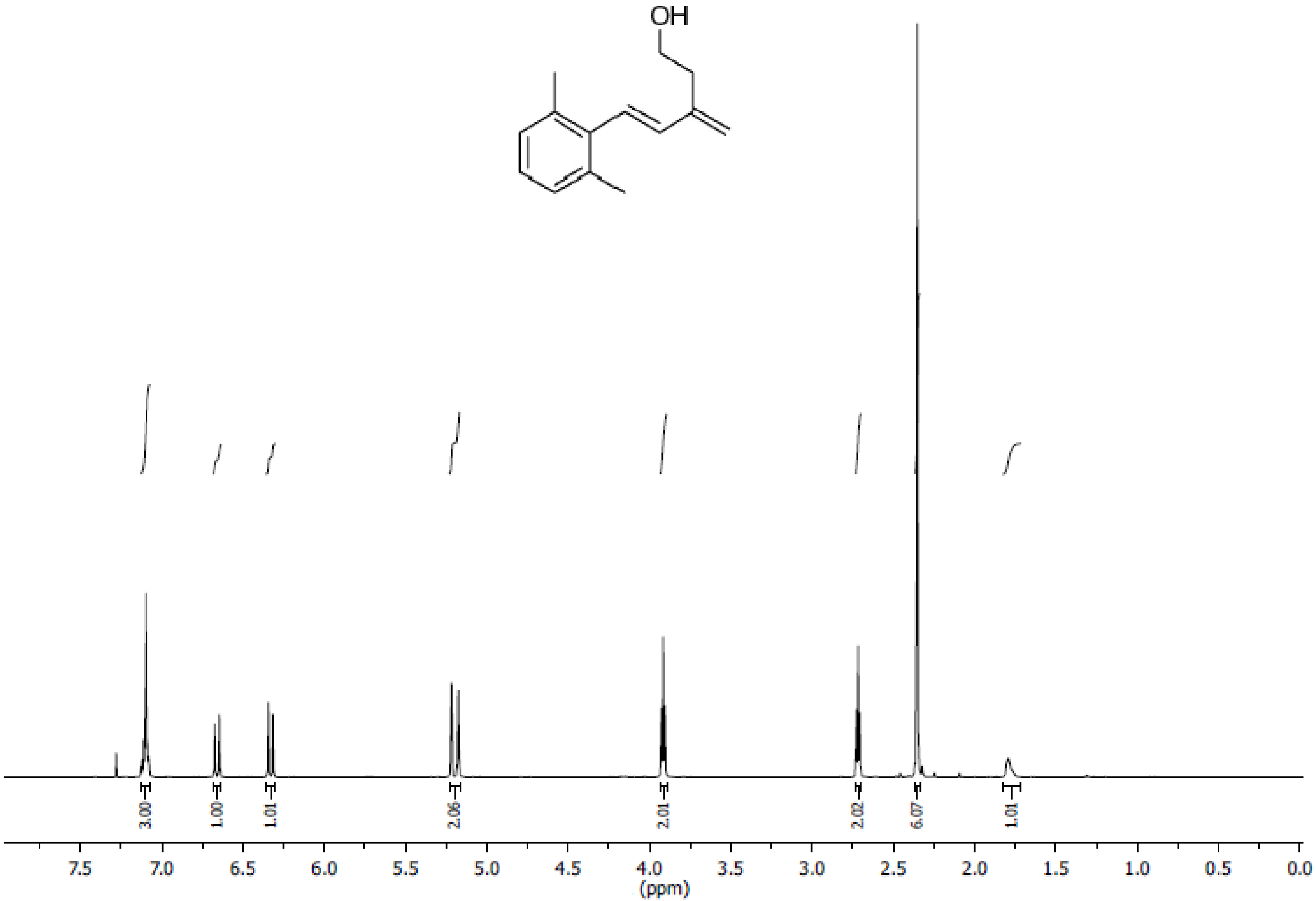
^{13}C NMR of diene **2l.**



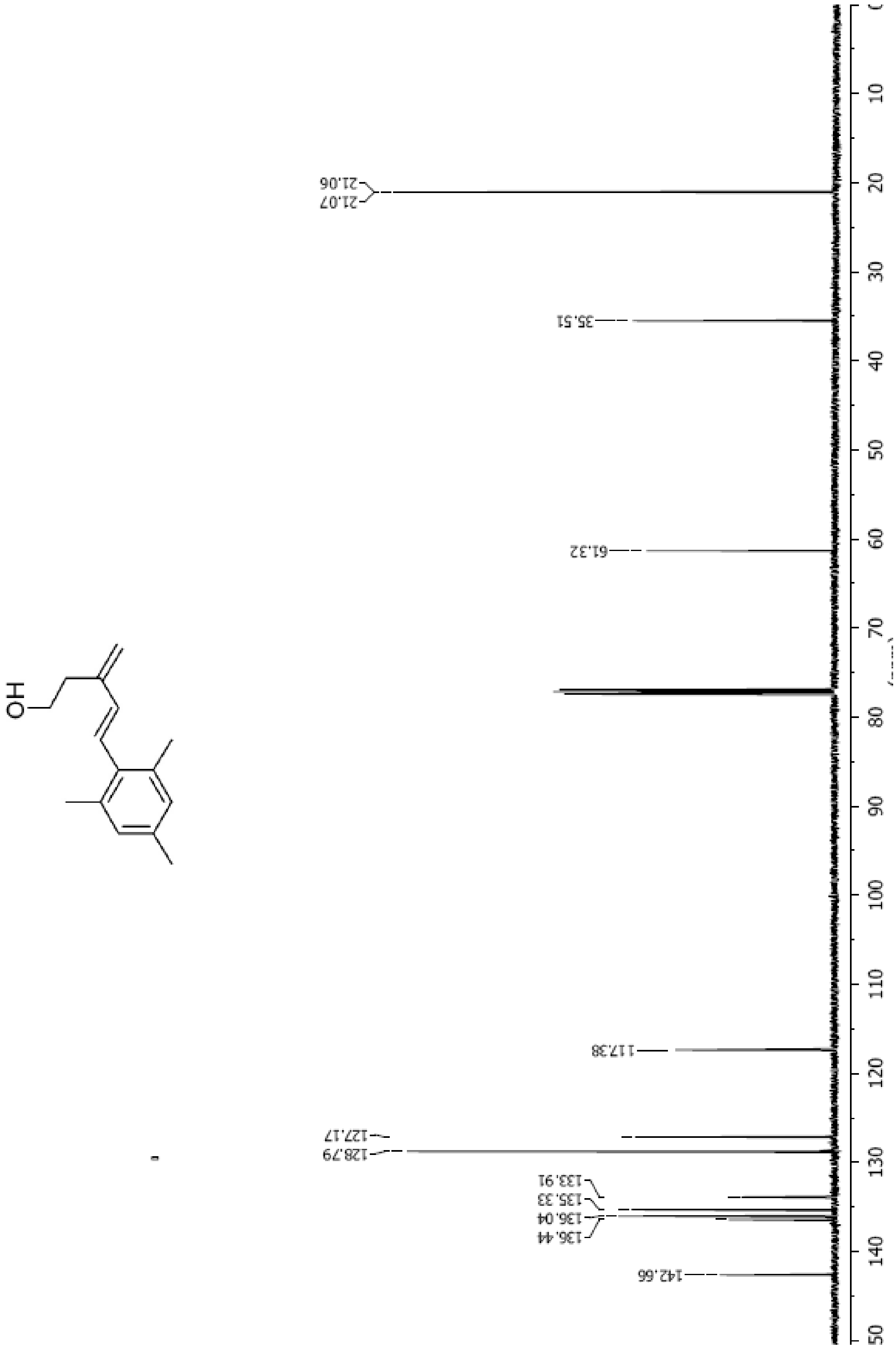
^{1}H NMR of diene 2l.



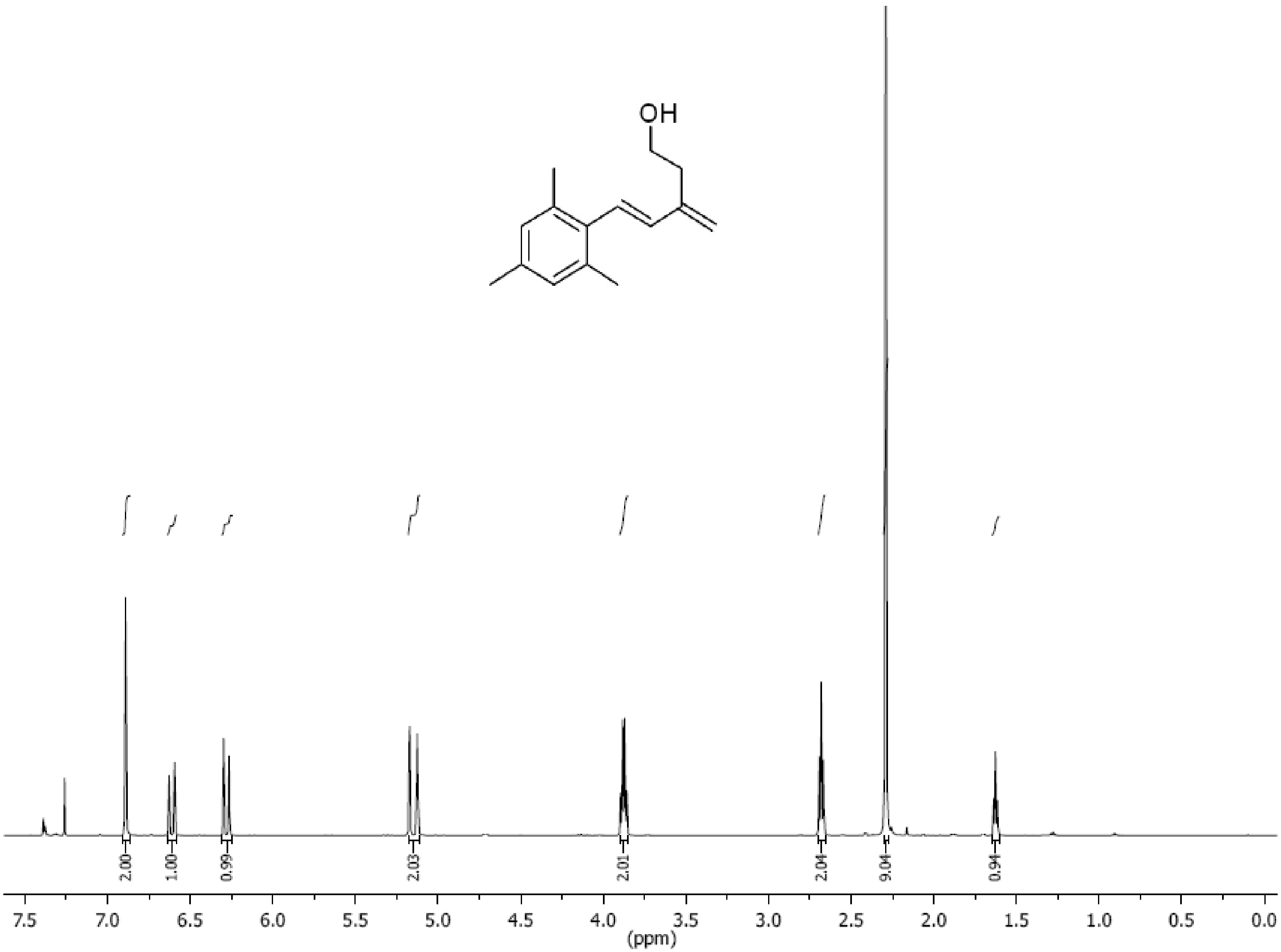
^{13}C NMR of diene 2m.



^{1}**H NMR of diene 2m.**



^{13}C NMR of diene 2n.



^{1}H NMR of diene 2n.

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