Organo-Manganese η^2-Auxiliary Directed Reactions: A Diastereoselective Approach to 2,3-Allenols

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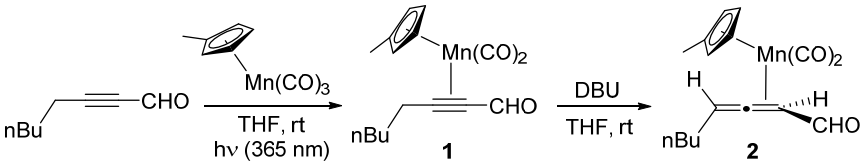
General Information. Reactions were carried out under an argon atmosphere (unless otherwise stated) in oven dried glassware with magnetic stirring. Purification of reaction products was carried out using flash silica gel 40-63μ. Analytical thin layer chromatography was performed on 200 micron silica gel 60 F-254 plates. Visualization of TLC plates was accomplished with UV light, followed by staining with vanillin or potassium permanganate and drying with a heat gun. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet; coupling constant(s) in hertz (Hz). ^{13}C{1H} NMR were recorded on 100 MHz spectrometer. Chemical shifts are reported in ppm, with solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). High-resolution mass spectra were recorded by an ESI-TOF MS spectrometer (DART ion source).[1]

Materials. All reagents were purchased from commercially available sources and were used without further purification. All solvents were dried over activated alumina or 3Å molecular sieves.

General procedure for complexing MMT with alkynyl aldehyde and subsequent isomerization to allene:[2]



Complex 2 ($C_{15}H_{19}MnO_3$): Tricarbonyl(2-methylcyclopentadienyl)manganese (MMT) (3.80 mL, 24.2 mmol) and 2-octynal (2.00 mL, 16.1 mmol) were added to a glass reactor (see page S6) containing THF (0.1 M in 2-octynal) followed by irradiation with UV light (365 nm). The reactor was covered with aluminum foil and irradiated with stirring for 20 h at room temperature under constant flow of argon to produce complex **1** which was used in the next step without purification: IR (ATR) 1638 nm^{-1} (aldehyde carbonyl), 1908 nm^{-1} (MMD CO), 1976 nm^{-1} (MMD CO). To the reactor containing **1** was added DBU (2 eq) followed by stirring at room temperature. Isomerization was complete within 45 minutes. Solvent was evaporated and the reaction mixture was purified by flash chromatography to afford complex **2** (2.8 g, 53%, 2-step yield) as yellow gummy material. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 6.19-6.15 (dt, *J* = 8.0 Hz, 4.0Hz 1H), 4.73-4.68 (m, 2H), 4.54 (m, 1H), 2.87-2.85 (d, *J* = 8.0 Hz, 1H), 2.42- 2.37 (m, 2H), 1.87 (s, 3H), 1.49-1.24 (m, 6H), 0.91, 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 159.9, 129.0, 127.0, 103.2, 87.5, 86.4, 85.6, 84.9, 37.4, 32.2, 27.8, 22.2, 14.0, 12.8.

Notes:

(1) THF is required for MMT complexation. For some substrates, a mixture of THF/Et_2O (1:3) sometimes affords better yield. A continuous flow of argon is also important.

(2) When complexed alkynes are isomerized with DBU at room temperature, a minor product (< 5%) is observed by TLC (R_f close to major product). This product is likely the endo isomer.[2]

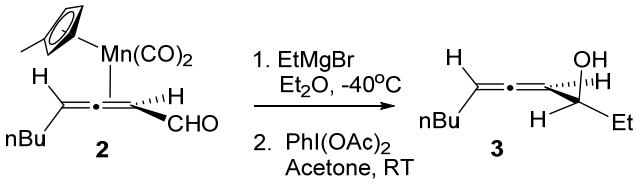
(3) Product **2** should be isolated immediately following isomerization for optimal yields. Complex **2** and related compounds are best stored under argon and with limited light exposure at lower temperatures (< 5 ºC).

(4) Complex **2** was effectively characterized using NMR after a rapid filtration through a plug of silica gel (in a Pasteur pipette) followed by immediate transfer to an NMR tube which was previously charged with argon.

(5) Literature evidence indicates that MMD bonds with the allene α,β-double bond an η^2 fashion and that such a bond possesses metallocyclopropane character.[3] For simplicity the MMD-allene bond will be represented as a single bond as in structure **2**.

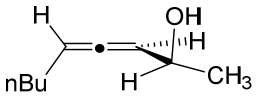
[1] Some allenols proved too unstable for HRMS analysis.
[2] Prepared using a procedure slightly modified from: M. Frank-Neumann, D. Martina, D. Neff, *Tetrahedron: Asymmetry* **1998**, *9*, 697.
[3] Bhowmick, M.; Lepore, S. D. *Org. Lett.* **2010**, *12*, 5078.

General procedure for Grignard additions to MMD complexed allenyl aldehydes followed by decomplexation:

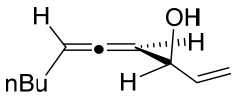


Rel-(3R, 5R)-deca-4,5-dien-3-ol (**3**): MMD-coordinated octa-2,3-dienal **2** (0.558 g, 1.6 mmol) was dissolved in dry ether (16.0 mL, 0.1 M) and cooled to -40 °C (acetonitrile /dry ice bath) for 10 minutes. To this solution, ethyl magnesium bromide (1.20 mL, 3.5 mmol, 3M) was added drop wise (over 5 min) and the resulting reaction mixture was allowed to stir at -40 °C. The reaction was monitored by TLC. After completion (~1 h), the reaction was quenched with saturated aqueous NH_4Cl solution (5 mL) and extracted with diethyl ether (3 × 30 mL). The combined ether layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was dissolved again in dry acetone (20 mL) under an argon atmosphere and treated with $PhI(OAc)_2$ (1.03 g, 3.20 mmol). After ~2.0 h (completion of reaction determined by TLC), the solvent was removed by evaporation. The crude product (now decomplexed) was purified by silica gel flash chromatography using 10% EtOAc/hexanes to afford (0.165 g, 67%) as a light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 - 5.27 (m, 1H), 5.21 - 5.17 (m, 1H), 4.09- 4.03 (m, 1H), 2.05-1.99 (m, 2H), 1.63-1.55 (m, 2H), 1.43 -1.30 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 95.5, 94.1, 71.7, 31.4, 30.5, 28.6, 22.3, 14.0, 9.9 ; HRMS calc. for $C_{10}H_{18}O$ $[M+H]^+$: 155.1430. Found 155.1424.

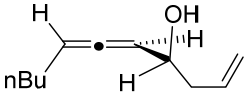
Rel-(2R,4R)-nona-3,4-dien-2-ol (**4**): Prepared according to the general procedure; (0.150 g, 67%) as a light yellow viscous liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 - 5.24 (m, 2H), 4.35 - 4.31 (m, 1H), 2.05 - 2.00 (m, 2H), 1.41 -1.34 (m, 4H), 1.30 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 97.0, 94.5, 66.3, 31.3, 28.5, 23.6, 22.3, 14.0.; HRMS calc. for $C_9H_{16}O$ [M+H]+: 141.1274. Found: 141.1269



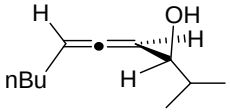
Rel-(3R,5R)-deca-1,4,5-trien-3-ol (**5**): Prepared according to the general procedure; (0.166 g, 68%) as a light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 - 5.87 (m, 1H), 5.36 - 5.29 (m, 2H), 5.27 - 5.22 (m, 1H), 5.15 - 5.12 (m, 1H), 4.68 - 4.58 (m, 1H), 2.05-1.99 (m, 2H), 1.42 - 1.31 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 139.7, 115.0, 94.9, 94.6, 71.2, 31.2, 28.4, 22.2, 14.0.



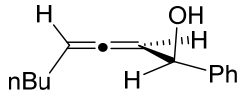
Rel-(4R,6R)-undeca-1,5,6-trien-4-ol (**6**): Prepared according to the general procedure; (0.192 g, 72%) as a light yellow viscous liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.79 (m, 1H), 5.33 - 5.28 (m, 1H), 5.25 - 5.20 (m, 1H), 5.17 - 5.12 (m, 2H), 4.20 - 4.13 (m, 1H), 2.40 - 2.28 (m, 2H), 2.05-1.99 (m, 2H), 1.43 - 1.29 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 134.4, 118.2, 95.1, 94.5, 69.3, 42.1, 31.3, 28.5, 22.3, 14.0; HRMS calc. for $C_{11}H_{18}O$ [M+H]+: 167.14, Found: 167.00



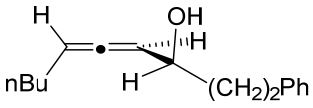
Rel-(3R,5R)-2-methyldeca-4,5-dien-3-ol (**7**): Prepared according to the general procedure; (0.113 g, 42%) as a light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 - 5.27(m, 1H), 5.23 - 5.16(m, 1H), 3.91 - 3.88 (m, 1H), 2.05 - 1.99 (m, 2H), 1.81-1.71 (m, 1H), 1.43 – 1.30 (m, 4H), 0.96 - 0.93 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 94.1, 93.9, 75.3, 74.5, 34.3, 31.4, 28.6, 22.3, 18.2, 18.0, 14.0.



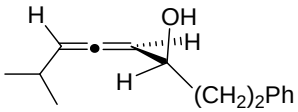
Rel-(1R,3R)-1-phenylocta-2,3-dien-1-ol (**8**): Prepared according to the general procedure; (0.246 g, 76%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 5.38-5.34 (m, 1H), 5.33 - 5.21 (m, 1H), 5.20 -5.22 (m, 1H), 2.02 - 1.98 (m, 2H), 1.36 - 1.29 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 143.3, 128.4, 127.6, 126.1, 96.1, 94.7, 72.5, 31.2, 28.4, 22.2, 14.0; HRMS calc. for $C_{14}H_{18}O$ [M+H]+: 203.14. Found: 203.1430



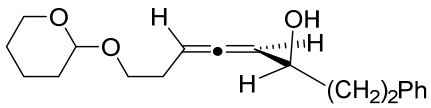
Rel-(3R,5R)-1-phenyldeca-4,5-dien-3-ol (**9**): Prepared according to the general procedure; (0.251 g, 68%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.15 (m, 5H), 5.33 - 5.28 (m, 1H), 5.28 - 5.22 (m, 1H), 4.16 - 4.12 (m, 1H), 2.81 - 2.66 (m, 2H), 2.06 - 2.00 (m, 2H), 1.90-1.84 (m, 2H), 1.43 - 1.30 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 142.1, 128.6, 128.4, 125.9, 95.7, 94.7, 69.2, 39.2, 31.8, 31.3, 28.5, 22.3, 14.0.



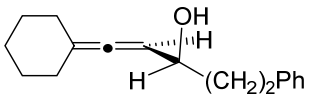
Rel-(3R,5R)-7-methylocta-4,5-dien-3-ol (**10**): Prepared according to the general procedure; (0.256 g, 74%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.16 (m, 5H), 5.36 - 5.27 (m, 2H), 4.18 - 4.13 (m, 1H), 2.81 - 2.67 (m, 2H), 2.37 - 2.28 (m, 1H), 1.92 - 1.85 (m, 2H), 1.03 (d, *J* = 6.7 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 142.0, 128.6, 128.50, 125.9, 102.0, 96.9, 69.6, 39.2, 31.9, 28.1, 22.6; HRMS calc. for $C_{15}H_{20}O$ $[M+H^+]^+$: 217.1514 Found: 217.1609, $[M+H-H_2O^+]^+$:199.1514, Found: 199.1490



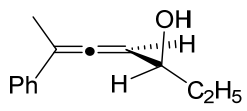
Rel-(3R,5R)-1-phenyl-8-((tetrahydro-2H-pyran-2-yl)oxy)octa-4,5-dien-3-ol (**11**):[4] Prepared according to the general procedure; (0.242 g, 50%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.16 (m, 5H), 5.37- 5.31 (m, 1H), 5.30 - 5.24 (m, 1H), 4.60 - 4.56 (m, 1H), 4.18 - 4.12 (m, 1H), 3.89 - 3.73 (m, 2H), 3.51 - 3.41 (m, 2H), 2.79 - 2.69 (m, 3H), 2.16 - 2.09 (m, 3H), 1.90 - 1.84 (m, 2H), 1.76 - 1.68 (m, 2H), 1.60 - 1.51 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 142.0, 128.6, 128.5, 125.9, 99.0, 98.8, 96.2, 93.9, 69.3, 69.1, 66.7, 66.6, 62.6, 62.3, 39.1, 31.90, 30.8, 29.0, 28.9, 25.5, 25.4, 19.8, 19.6.



1-cyclohexylidenepent-1-en-3-ol (**12**): Prepared according to the general procedure; (0.194 g, 50%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.16 (m, 5H), 5.15 - 5.12 (m, 1H), 4.14 - 4.09 (m, 1H), 2.79 - 2.69 (m, 2H), 2.16 - 2.13 (m, 4H), 1.89 - 1.84 (m, 2H), 1.63 - 1.51 (m, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 142.2, 128.6, 128.4, 125.9, 106.4, 93.6, 69.6, 39.2, 31.8, 31.7, 27.5, 26.1.

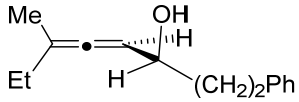


Rel-(3R,5R)-6-phenylhepta-4,5-dien-3-ol (**13**): Prepared according to the general procedure; (0.072 g, 24%) as a light yellow viscous liquid. [1]H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.20 (m, 5H), 5.57 - 5.55 (m, *J* = 5.8, 2.9 Hz, 1H), 4.22 - 4.18 (m, 1H), 2.14 (d, *J* = 2.9 Hz, 3H), 1.71 - 1.64 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 136.7, 128.5, 127.0, 125.8, 103.5, 97.6, 71.7, 30.5, 17.3, 9.9.

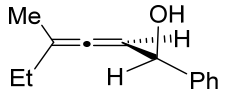


[4] Diastereomeric ratio is 1:1 due to the anomeric center of THP group.

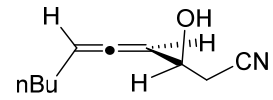
Rel-(3R,5R)-6-methy-1-phenylocta-4,5-dien-3-ol (**14**): Prepared according to the general procedure; (0.156 g, 45%) as a light yellow viscous liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.17 (m, 5H), 5.26 - 5.22 (m, 1H), 4.15 - 4.10 (m, 1H), 2.81 - 2.67 (m, 2H), 2.02 - 1.95 (m, 2H), 1.89 - 1.84 (m, 2H), 1.74 (d, *J* = 2.8 Hz, 3H), 1.03-0.99 (m, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 142.2, 128.6, 128.5, 125.9, 105.5, 95.8, 69.6, 39.4, 31.9, 27.1, 19.4, 12.5.



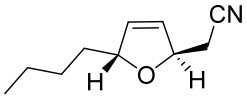
Rel-(1R,3R)-4-methyl-1-phenylhexa-2,3-diene-1-ol (**15**): Prepared according to the general procedure; (0.165 g, 55%) as a light yellow viscous liquid. [1]H NMR (400 MHz, CDCl3) δ 7.42-7.24(m, 6H),5.39-5.37 (m, 1H),5.19 (d, *J*=8.0 Hz, 1H), 2.00-1.95 (m,2H),1.75(d, *J*=2.8 Hz, 3H),0.97 (t, *J* = 7.2 Hz, 3H).;^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 143.6, 128.5, 127.6, 126.2, 106.4, 96.4,72.6, 27.1, 19.3, 12.4.



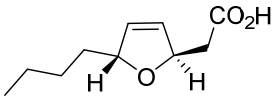
Rel-(3R,5R)-3-hydroxydeca-4,5-dienenitrile (**16**): The acetonitrile metal reagent used here was prepared according a literature procedure.[5] Iodoacetonitrile (0.12 mL, 1.25 mmol) and MMD-complexed allene aldehyde **2** (0.50 g, 1.3 mmol) were dissolved in Et_2O and cooled to -78 ºC for 10 min. At this point, the respective concentrations of ^{i}PrMgCl and ICH_2CN were 0.11 M and 0.05 M. ^{i}PrMgCl (1.42 mL, 2.80 mmol, 2 M THF) was then added. After the consumption of allenyl aldehyde starting material (~20 min, determined by TLC), NH_4Cl (10 mL) was added. The aqueous layer was then extracted with EtOAc (3 x 10 mL). The combined ether layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was dissolved in dry acetone (10 mL) under an argon atmosphere and treated with $PhI(OAc)_2$ (0.65 g, 2.03 mmol). After reaction completion (~ 2 h, determined by TLC), solvent was evaporated and the resulting crude product (now decomplexed) was purified by silica gel column chromatography using 10% EtOAc/hexanes to afford (0.080 g, 60%) of pure product as a clear viscous liquid. [1]H NMR (400 MHz, $CDCl_3$) δ 5.47-5.42 (m, 1H), 5.33-5.28(m, 1H), 4.48-4.45(m, 1H), 2.69-2.56 (m, 2H), 2.08-2.05 (m, 2H), 1.40-1.33 (m, 4H), 0.91(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 117.3, 96.5, 93.2, 65.9, 31.2, 28.3, 26.2, 22.3, 14.0; HRMS calc. for $C_{10}H_{15}NO$ [M+H]+: 166.1226, $[M+NH_4]$+:183.1492 Found:166.1232, 183.1492.



Rel-2-((2R,5R) -5-butyl-2,5-dihydrofuran-2-yl)acetonitrile (**17**): To a solution of allenol **17** (0.050 g, 0.30 mmol) in acetone:water (3:2, v/v) (2.0 mL) was added $AgNO_3$ (10 mg, 0.06 mmol, 0.2 equiv) and the reaction mixture was stirred at room temperature for about 24 h. After the reaction was compete (confirmed by TLC) the solvent was removed under reduced pressure and the crude reaction mixture was subjected to silica gel flash chromatography using hexane/EtOAc to give pure **18** (0.043 g, 86% yield) as clear viscous liquid. [1]H NMR (400 MHz, $CDCl_3$) δ 7.27, 6.06-6.03 (m, 1H), 5.84-5.82 (m,1H), 5.10-5.05 (m, 1H), 5.03-5.01 (m, 1H), 2.69-2.54 (m, 2H), 1.56-1.53 (m, 2H), 1.34-1.31 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 126.6, 117.2, 87.2, 80.9, 35.6, 27.4, 25.2, 22.8, 14.2.



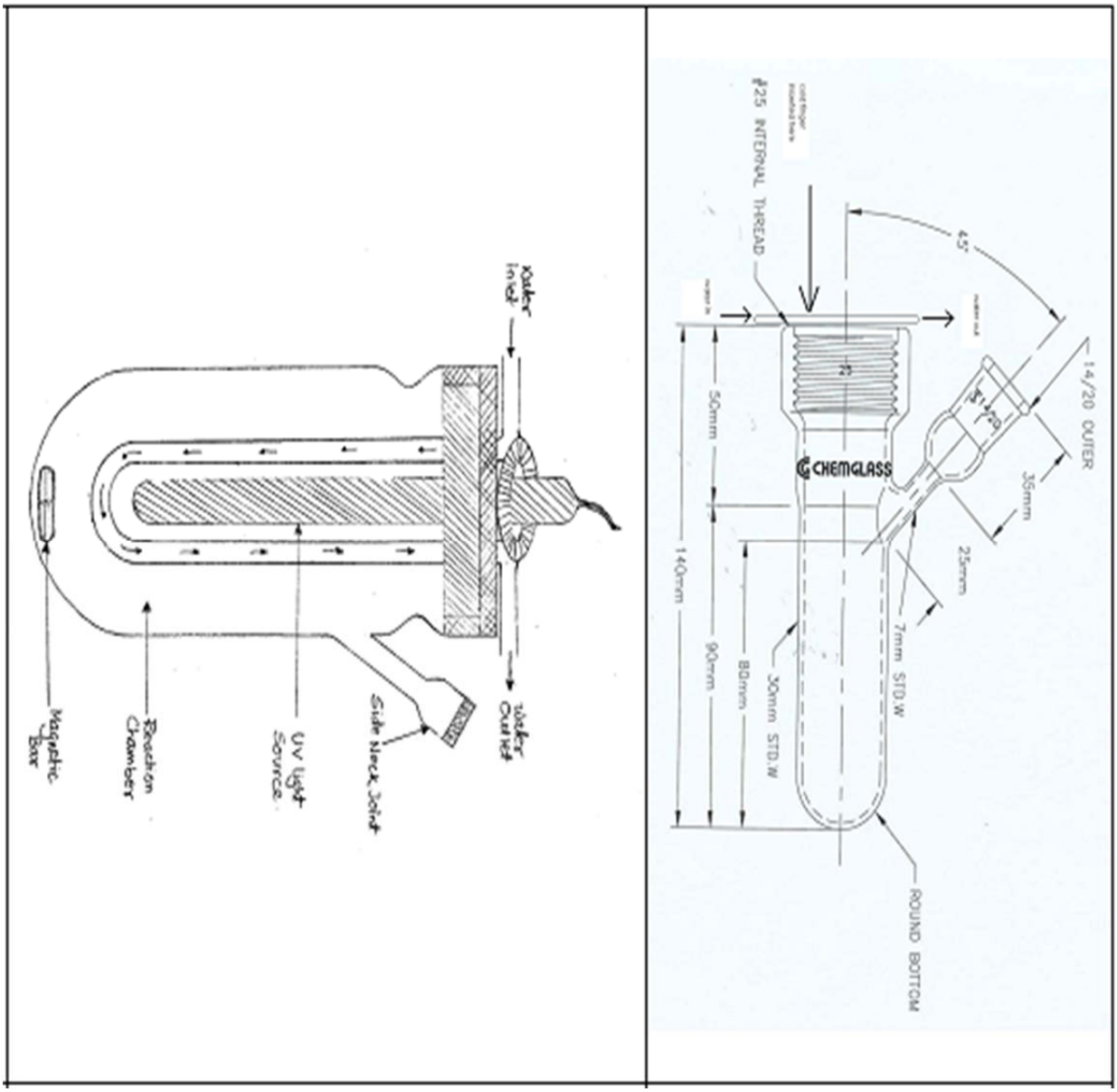
Rel-2-((2R, 5R)-5-butyl-2,5-dihydrofuran-2-yl)acetic acid (**18**): A solution of **18** (0.03 g, 0.18 mmol) dissolved in acetic acid:HCl mixture (4:1, v/v) (2 mL) was heated at 100 °C for 6 hours. After reaction completion (determined by TLC), the reaction mixture was partitioned between water and ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane/EtOAc to give pure **19** (0.025 g, 75%) as clear liquid. [1]H NMR (400 MHz, $CDCl_3$) δ 5.89-5.84 (m, 2H), 5.23-5.18 (m, 1H), 4.94-4.90 (m, 1H), 2.65-2.54 (m, 2H), 1.59-1.56 (m, 2H), 1.34-1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 131.4, 128.5, 86.3, 81.7, 41.0, 35.6, 27.3, 22.9, 14.2. HRMS calc. for $C_{10}H_{16}O_3$, $[M-H]^-$:183.1027, found:183.1036

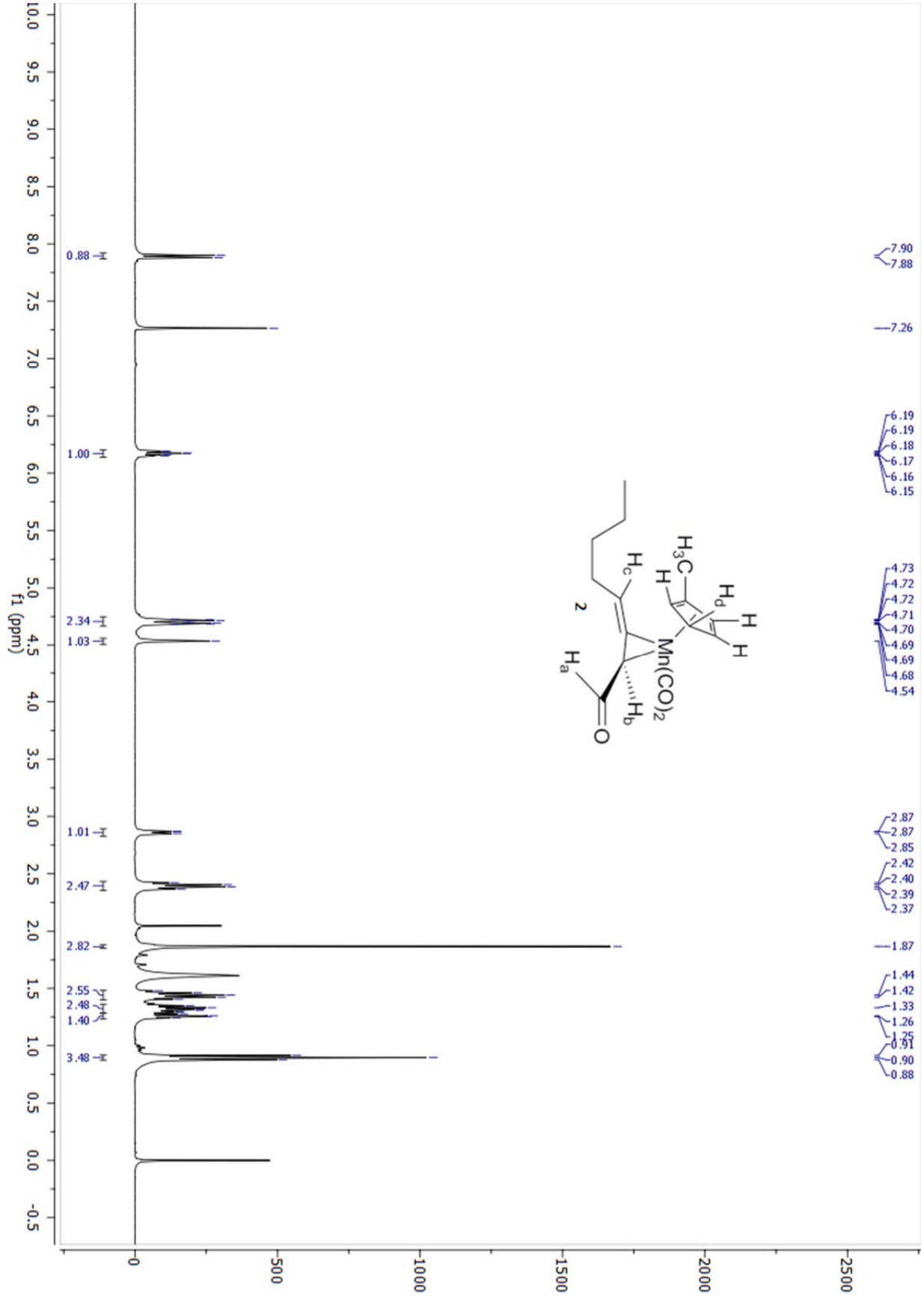


[5] Knochel, P.; Zhang, Z.; Fleming, F. F. *Org. Lett.*, **2004**, 6, 501.

Rel-(3aR,5R,6aR)-5-butyltetrahydrofuro[3,2-b]furan-2(3H)-one (**19**): To a solution of **19** (20 mg, 0.11 mmol) in MeCN (2 mL) was added sequentially $NaHCO_3$ (28 mg, 0.33 mmol, 3.0 eq) and iodine (42 mg, 0.33 mmol, 3.0 eq) at 0 °C and the reaction mixture was stirred for 2 - 3 h at rt. The reaction was quenched with aqueous $Na_2S_2O_3$ and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4. The latter was passed through a short celite pad and solvent evaporated under reduced pressure to give crude iodolactone product which was used for the next reaction without further purification. To a stirred solution of iodolactone (25 mg, 0.08 mmol) in benzene (5 mL) was added *n*-Bu_3SnH (44 mg, 0.16 mmol, 2.0 eq) and AIBN (10 mg, 0.064 mmol, 0.4 eq). The reaction was refluxed for 6 h, cooled to room temperature. and volatiles were evaporated. The residue was purified through silica gel chromatography using hexane/EtOAc to give pure **20** (0.012 g, 60 %, over two steps) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14-5.12 (t, *J* = 4.7 Hz, 1H), 4.83-4.80 (dt, *J* = 6.7, 5.1,1H), 4.11-4.04 (m, 1H), 2.74 (dd, *J* = 18.8, 6.7 Hz, 1H), 2.6 (d, *J* = 18.8 Hz, 1H), 2.41-2.36 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.71-1.60 (m, 2H), 1.56-1.47 (m, 1H), 1.41-1.27 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 85.1, 78.4, 77.5, 38.9, 36.8, 34.5, 28.3, 22.8, 14.1. HRMS calc. for $C_{10}H_{16}O_3$, $[M+NH4]^+$: 202.1438. Found: 202.1436

Schematic diagram of photo reactor glassware and sketch of reaction set up.

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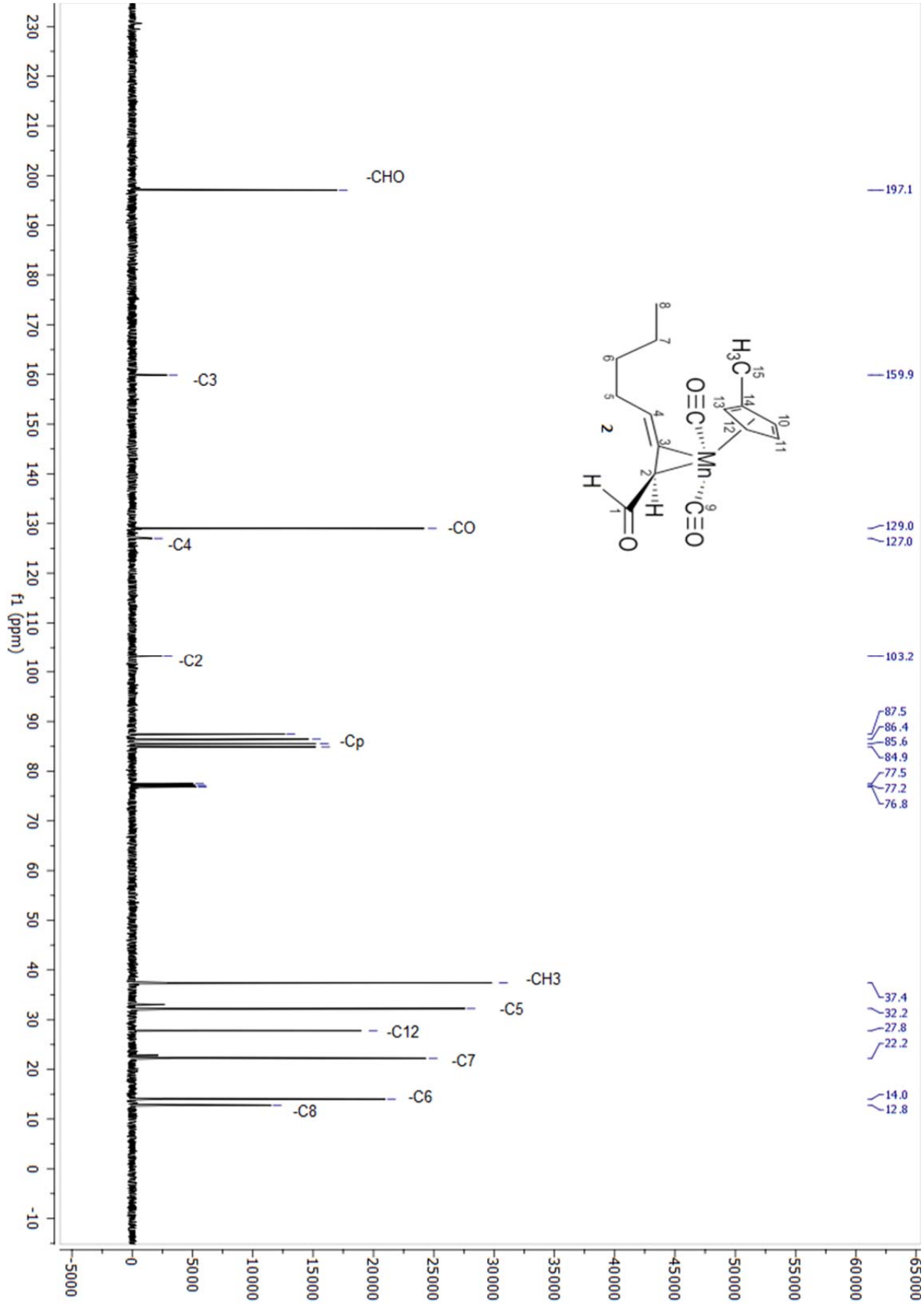
Hc
Hd
H
H
2
Mn(CO)2
Ha
Hb
O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-C2
-Cp
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-C6
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127.0
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76.8
37.4
32.2
27.8
22.2
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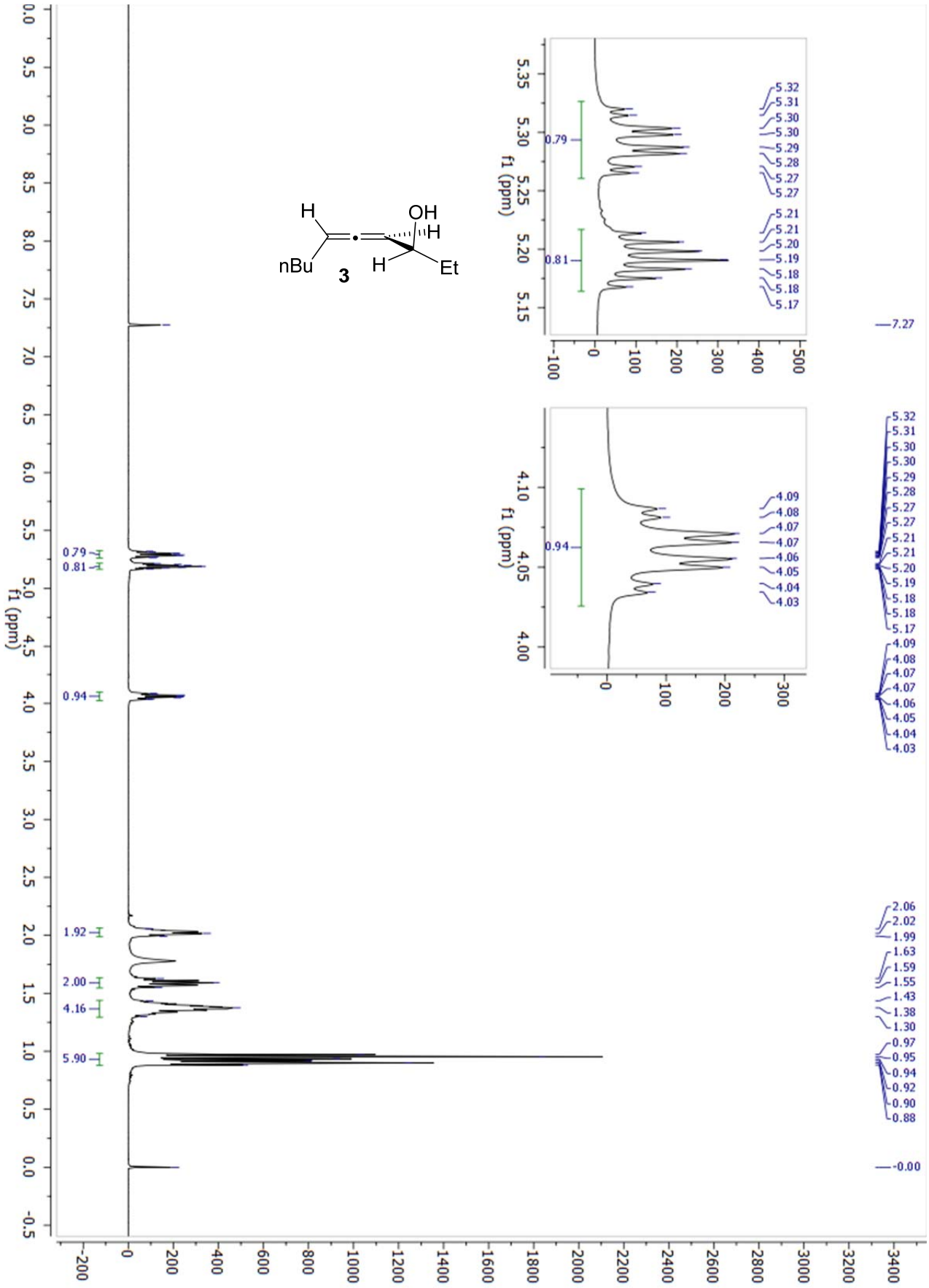
f1 (ppm)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5.30
5.29
5.28
5.27
5.27
5.21
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5.20
5.19
5.18
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5.17
4.09
4.08
4.07
4.07
4.06
4.05
4.04
4.03
7.27
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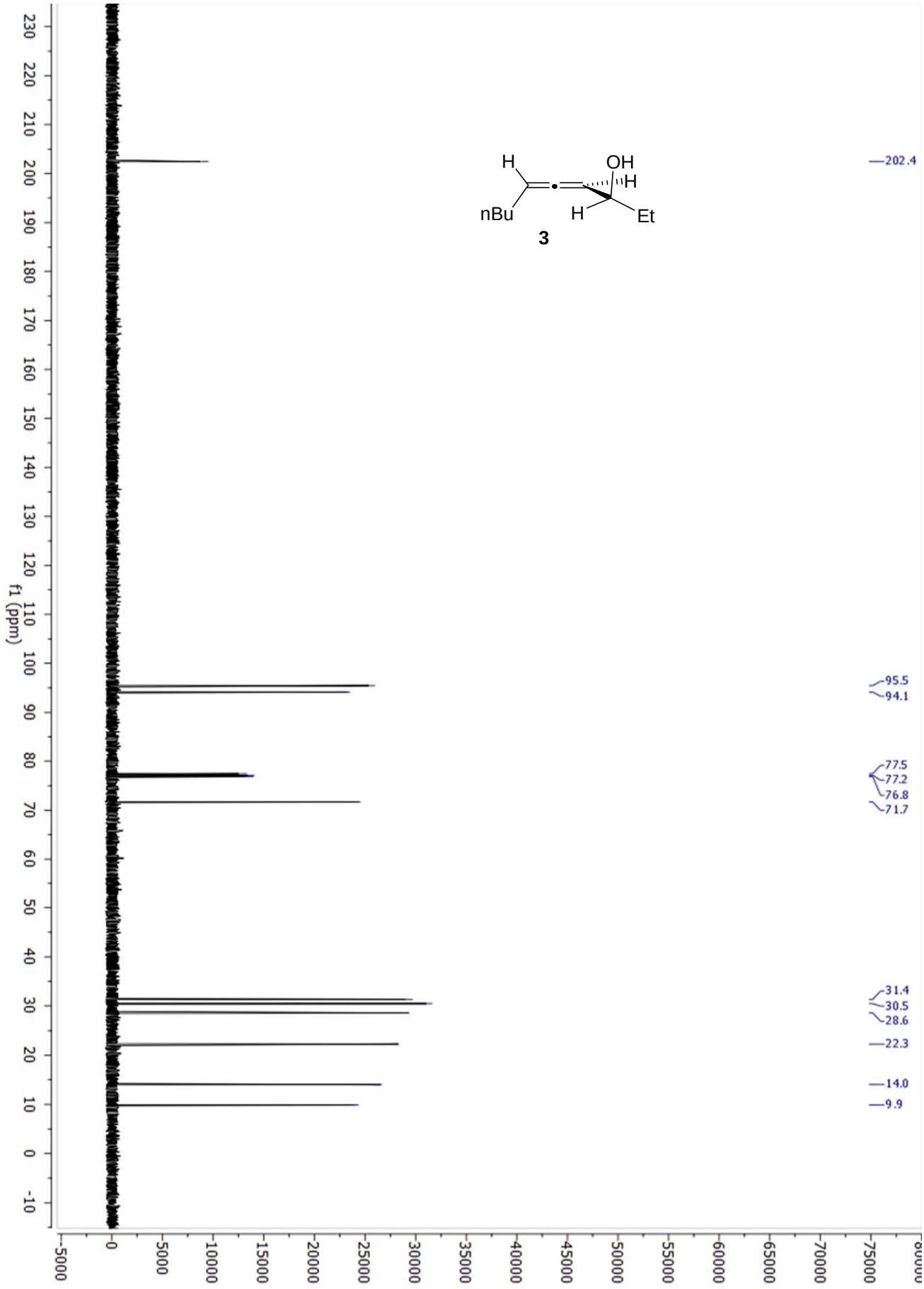
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Et
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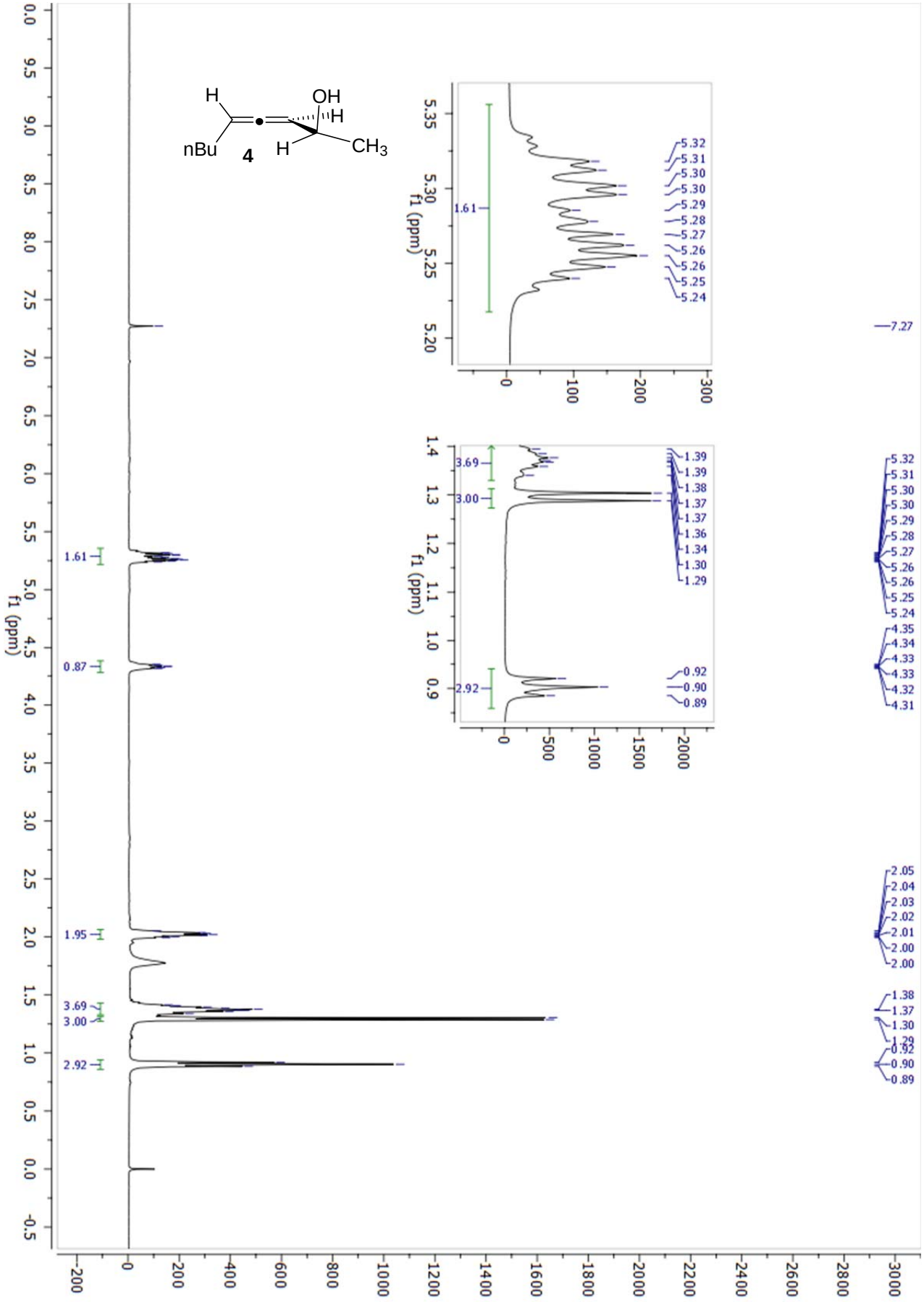
9.9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5.27
5.26
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2.00
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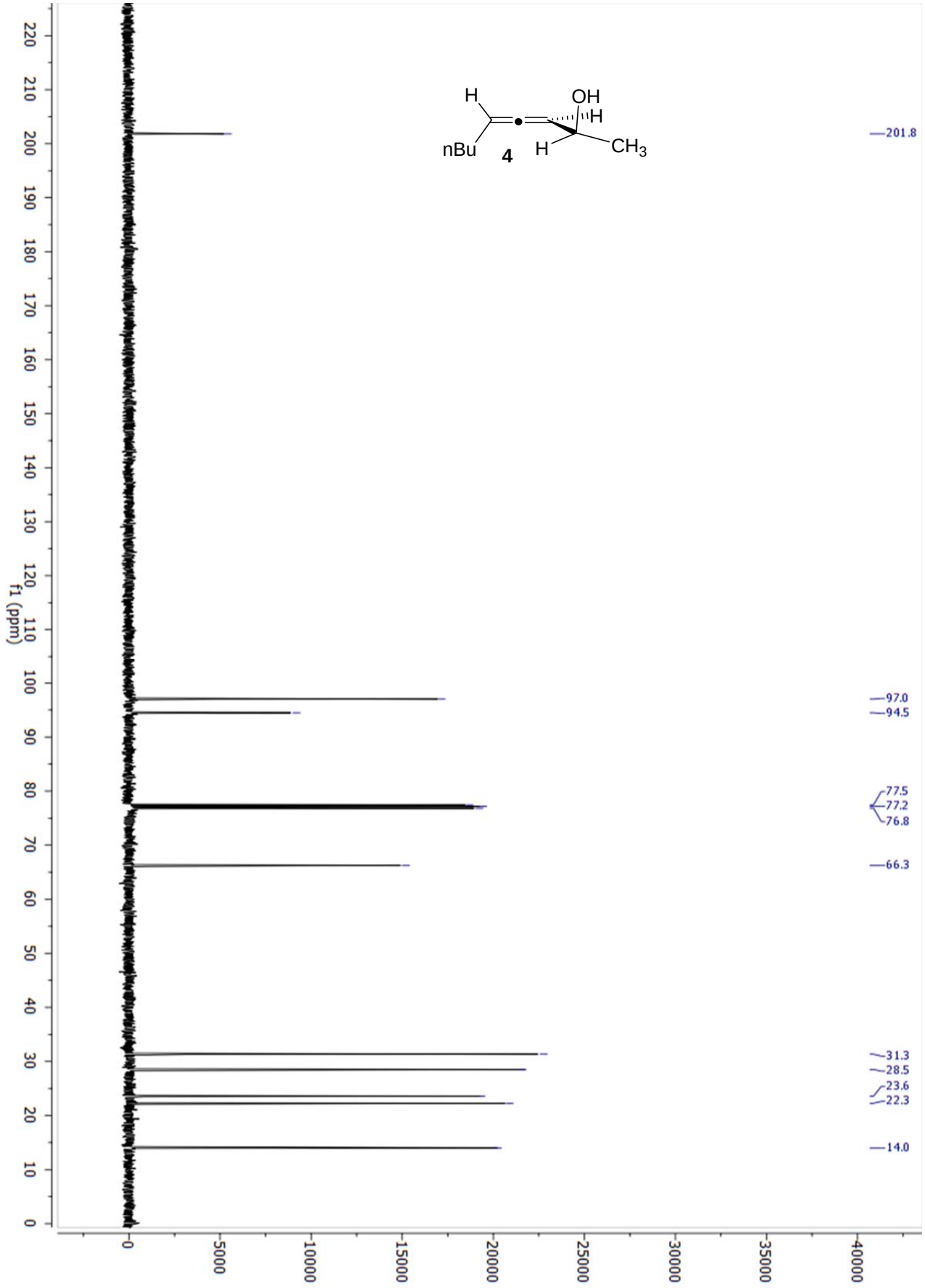
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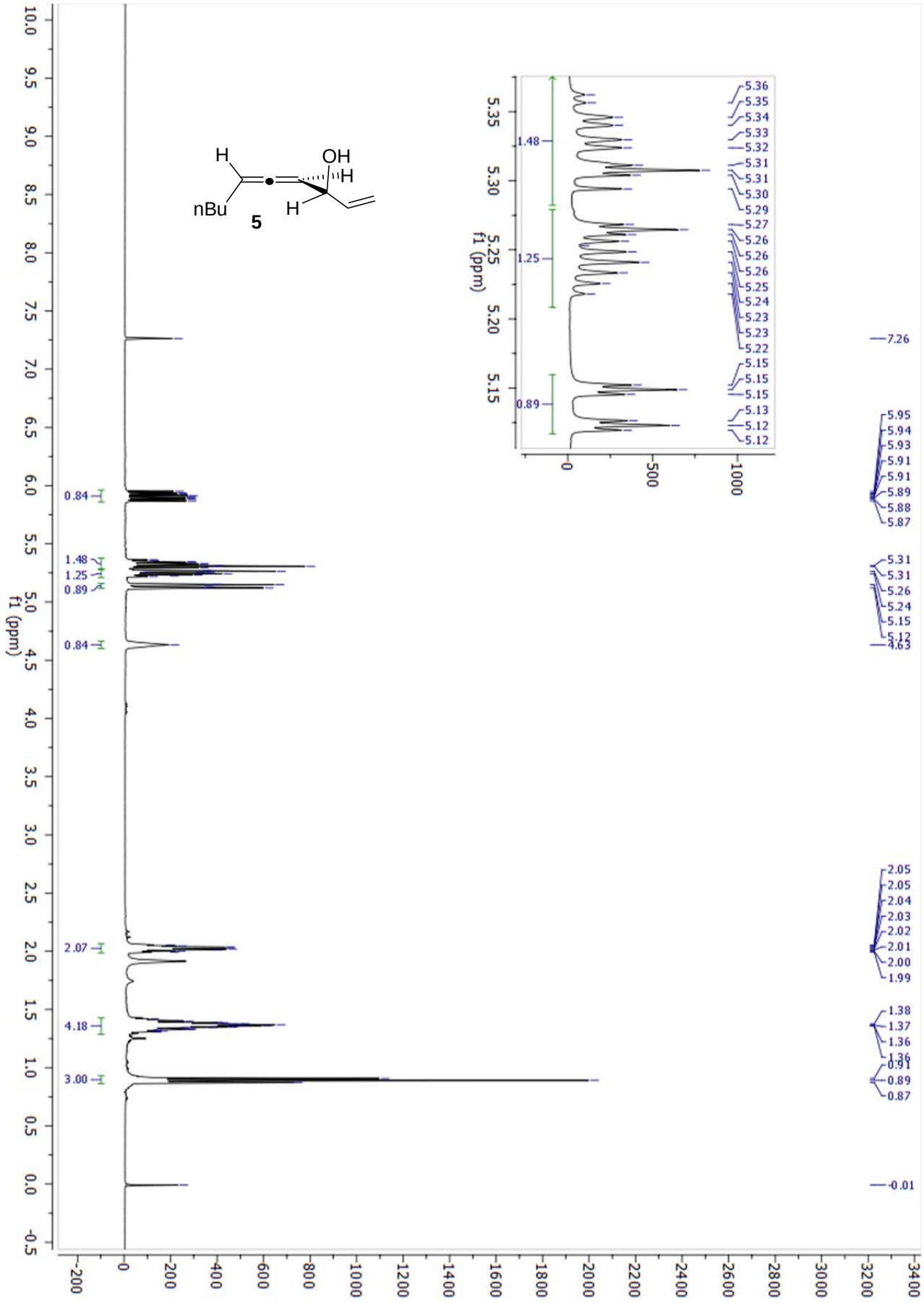
23.6
22.3
14.0
f1 (ppm)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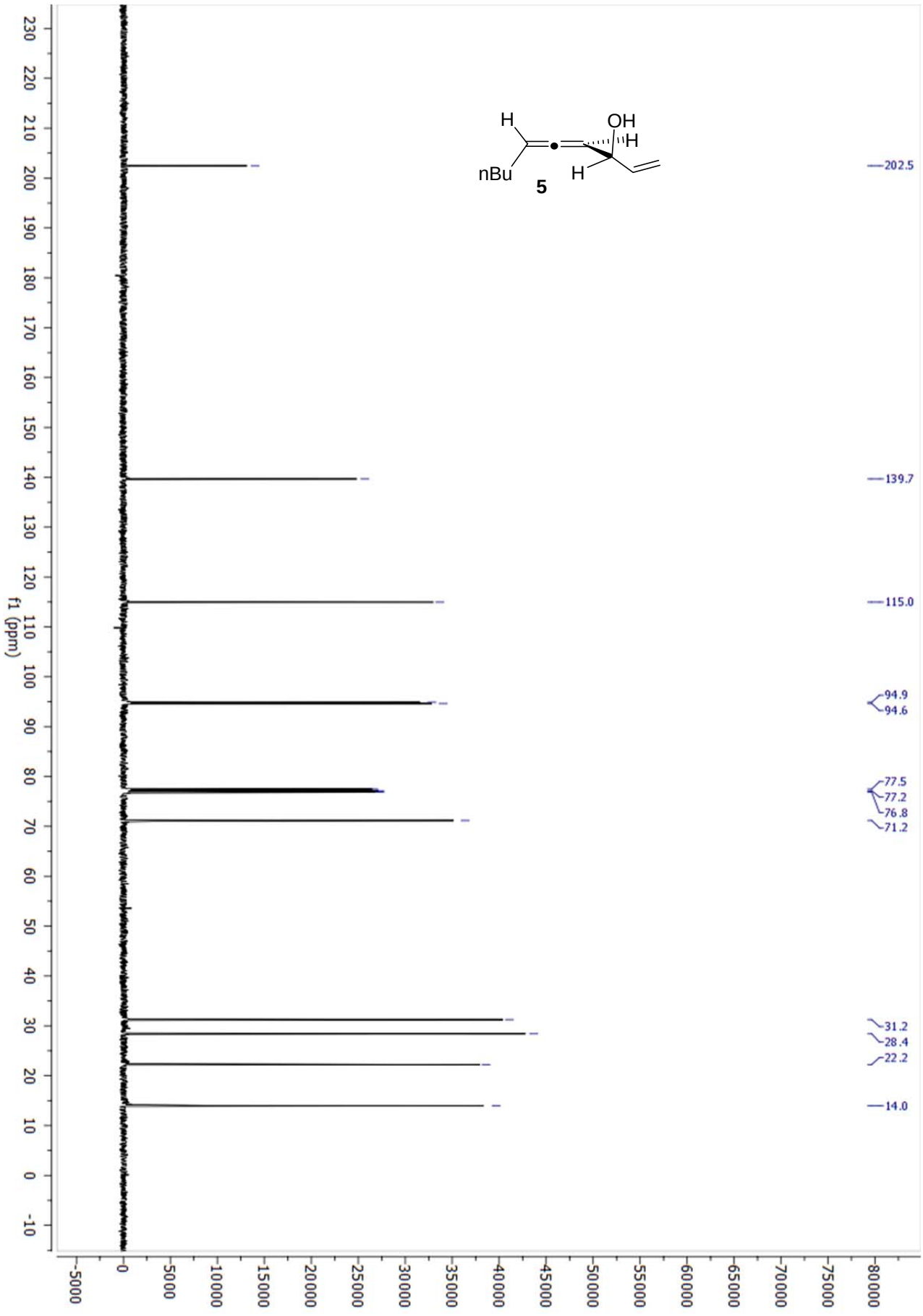
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nBu
H
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77.2
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28.4
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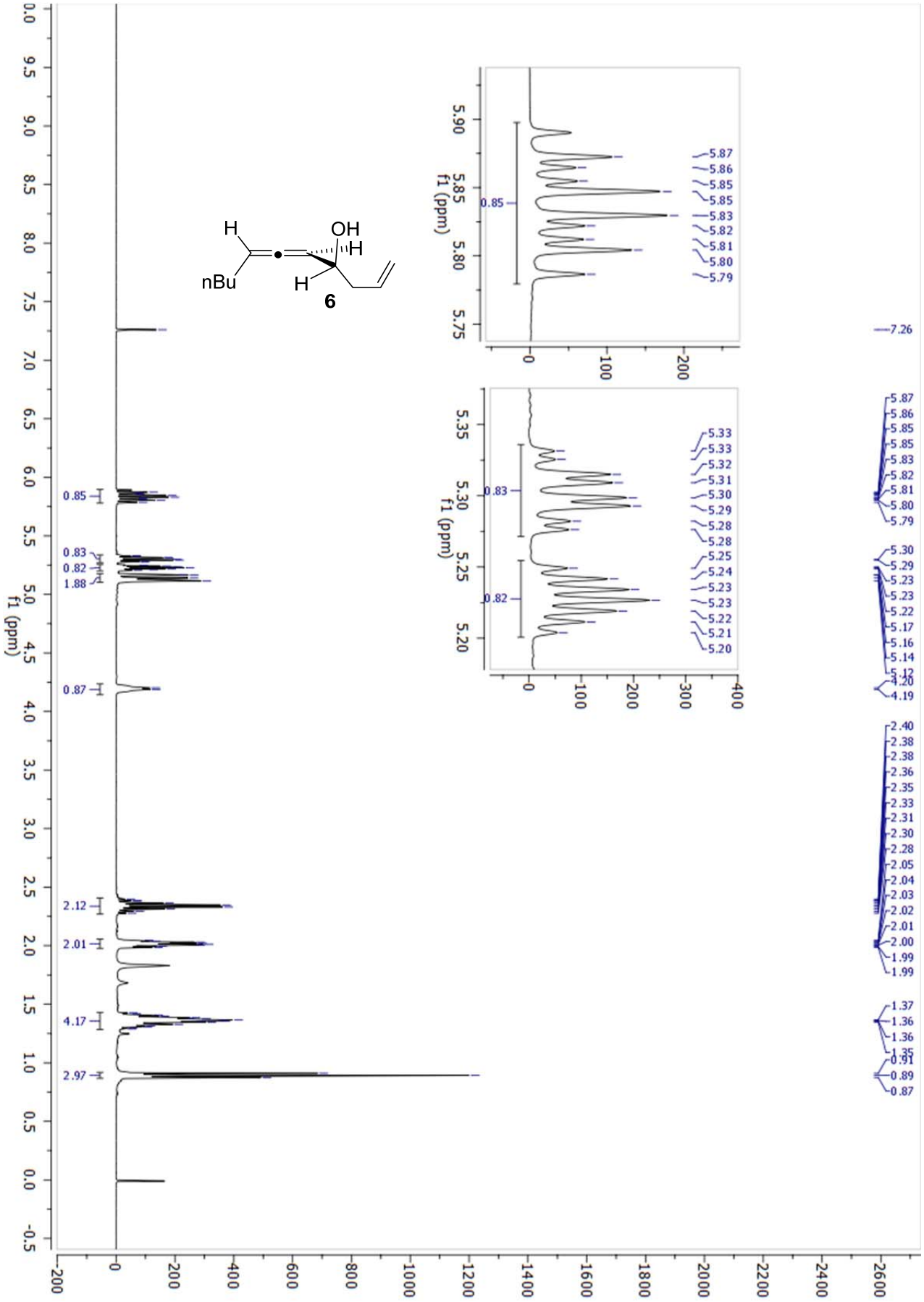
f1 (ppm)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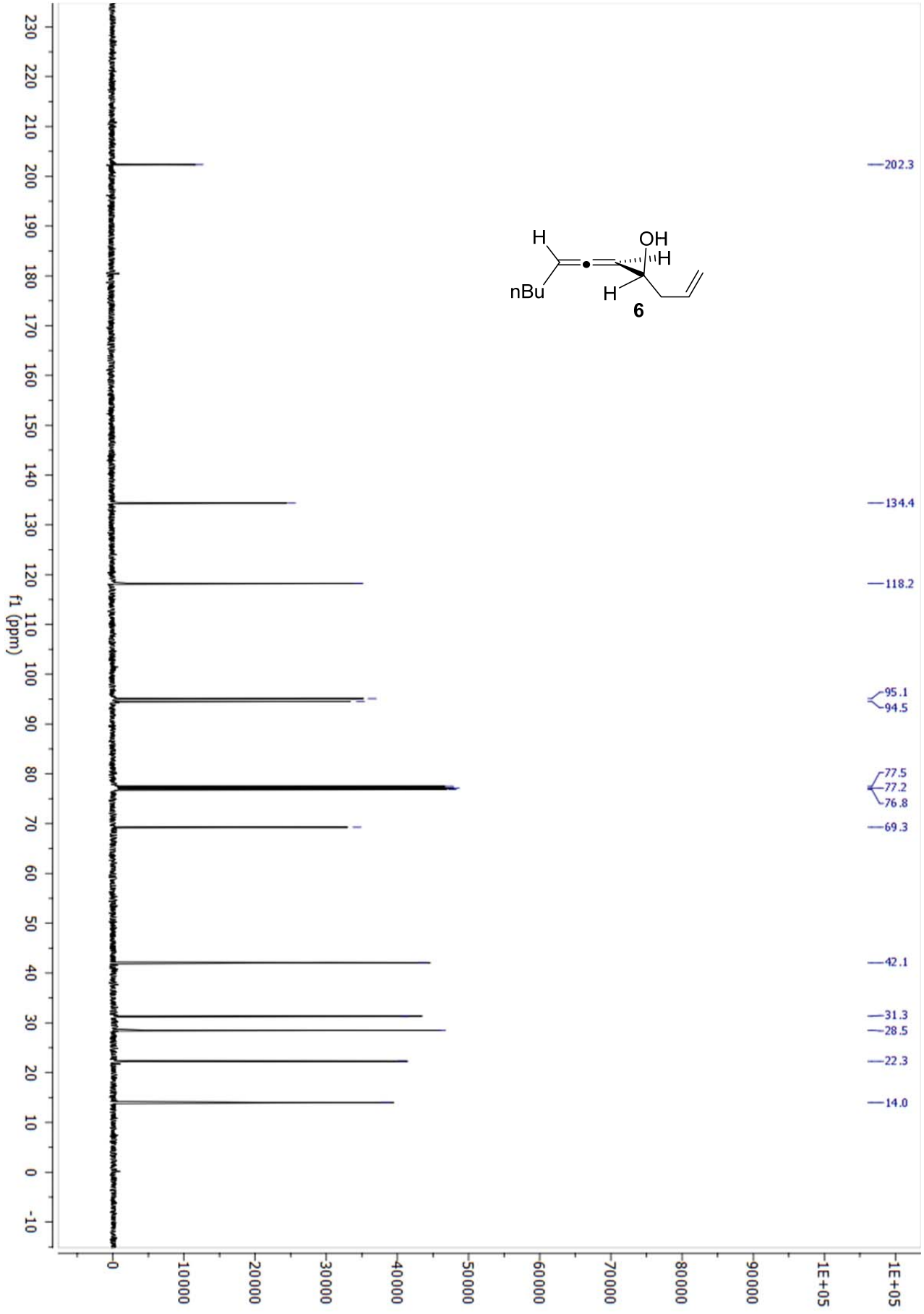
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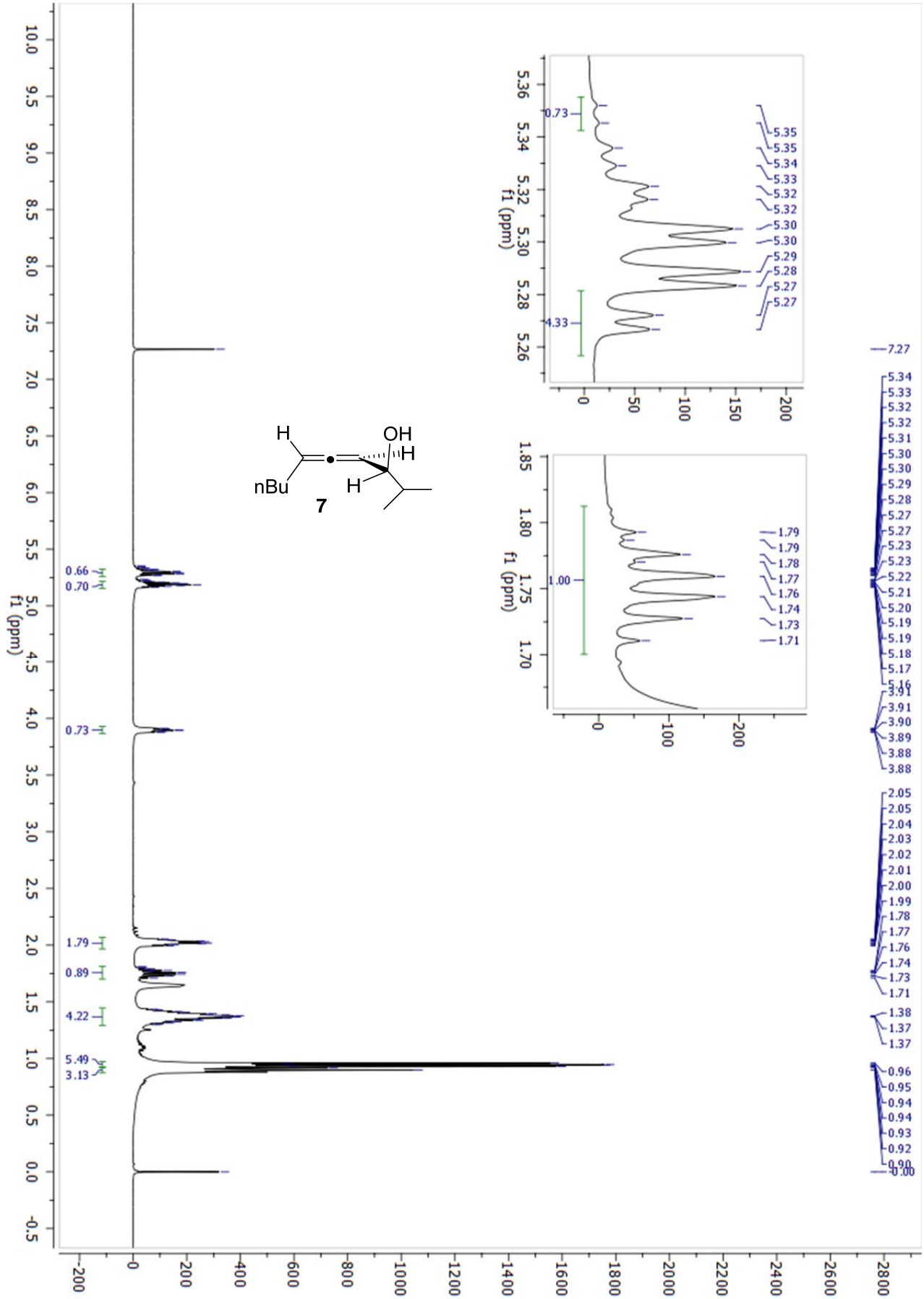
28.5
22.3
14.0
f1 (ppm)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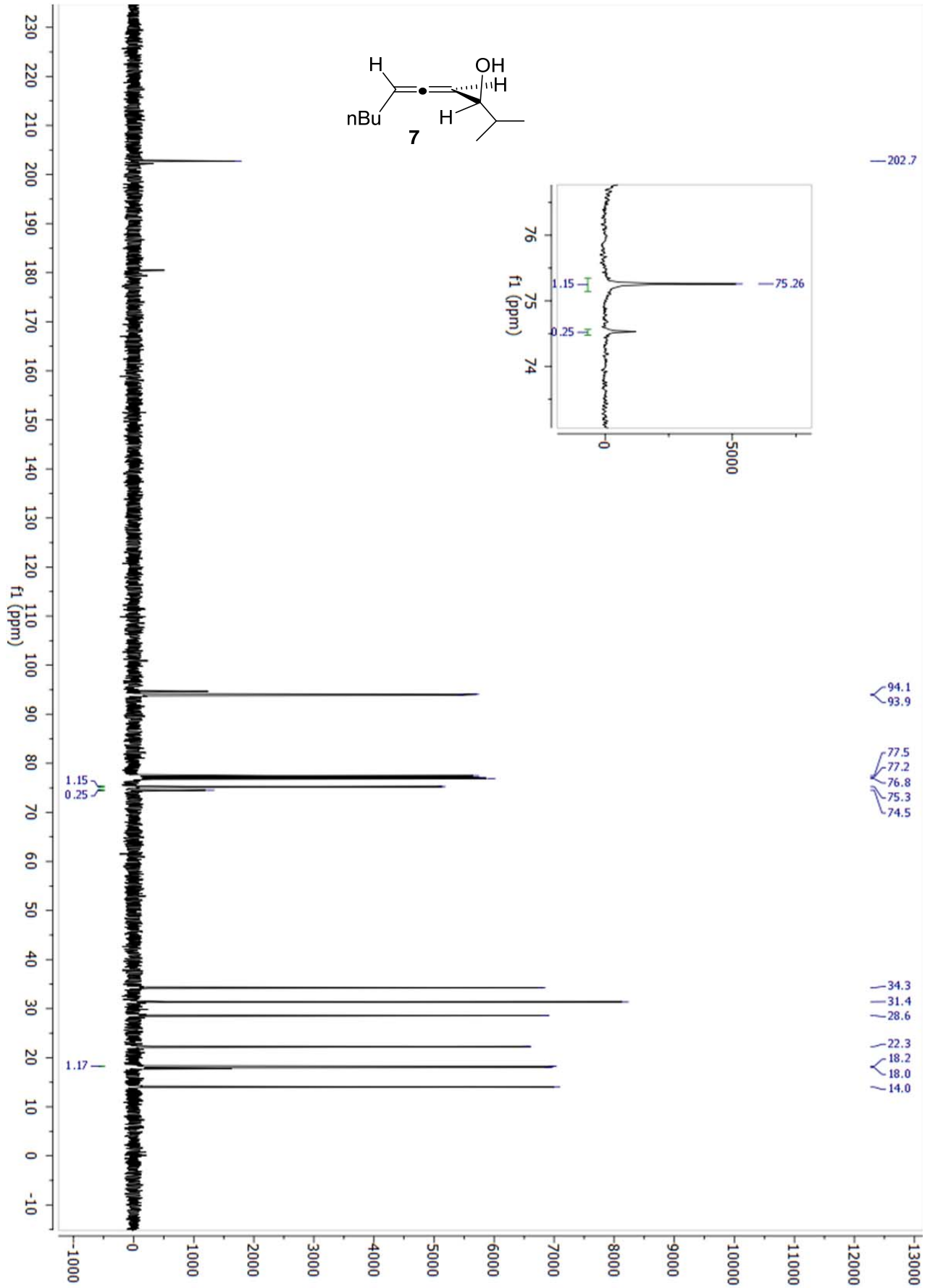
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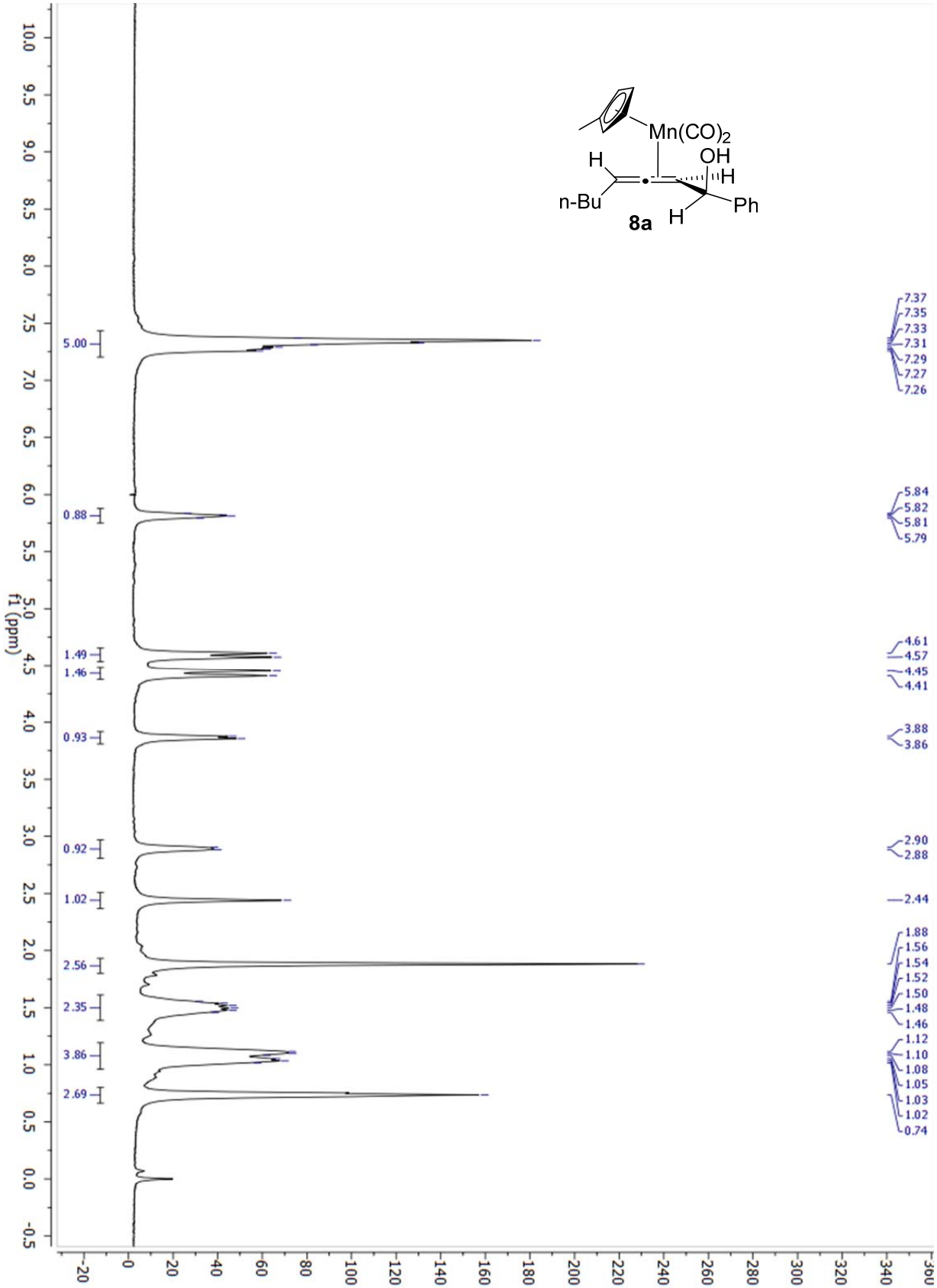
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H
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Ph
H
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2.69
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7.33
7.31
7.29
7.27
7.26
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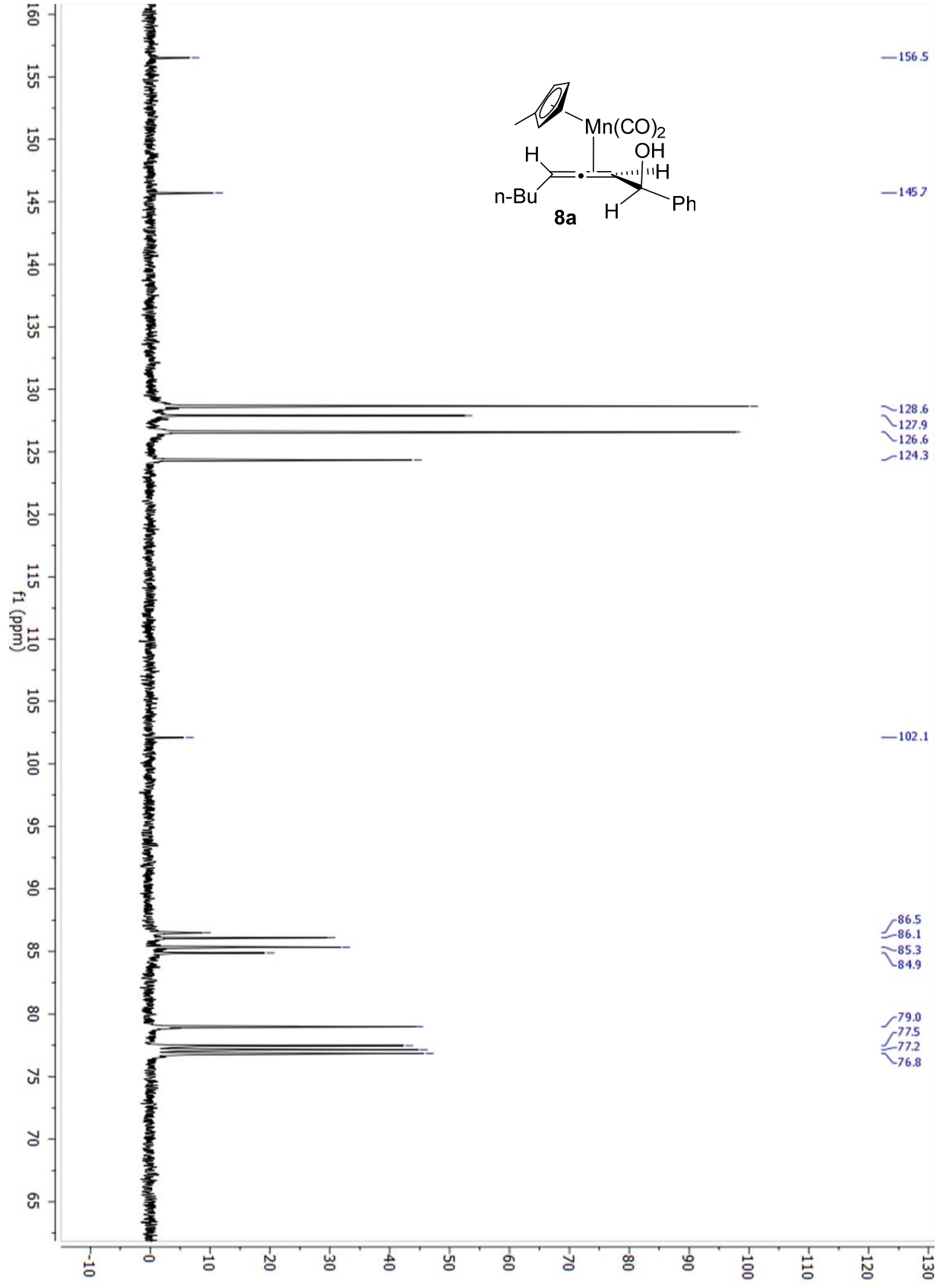
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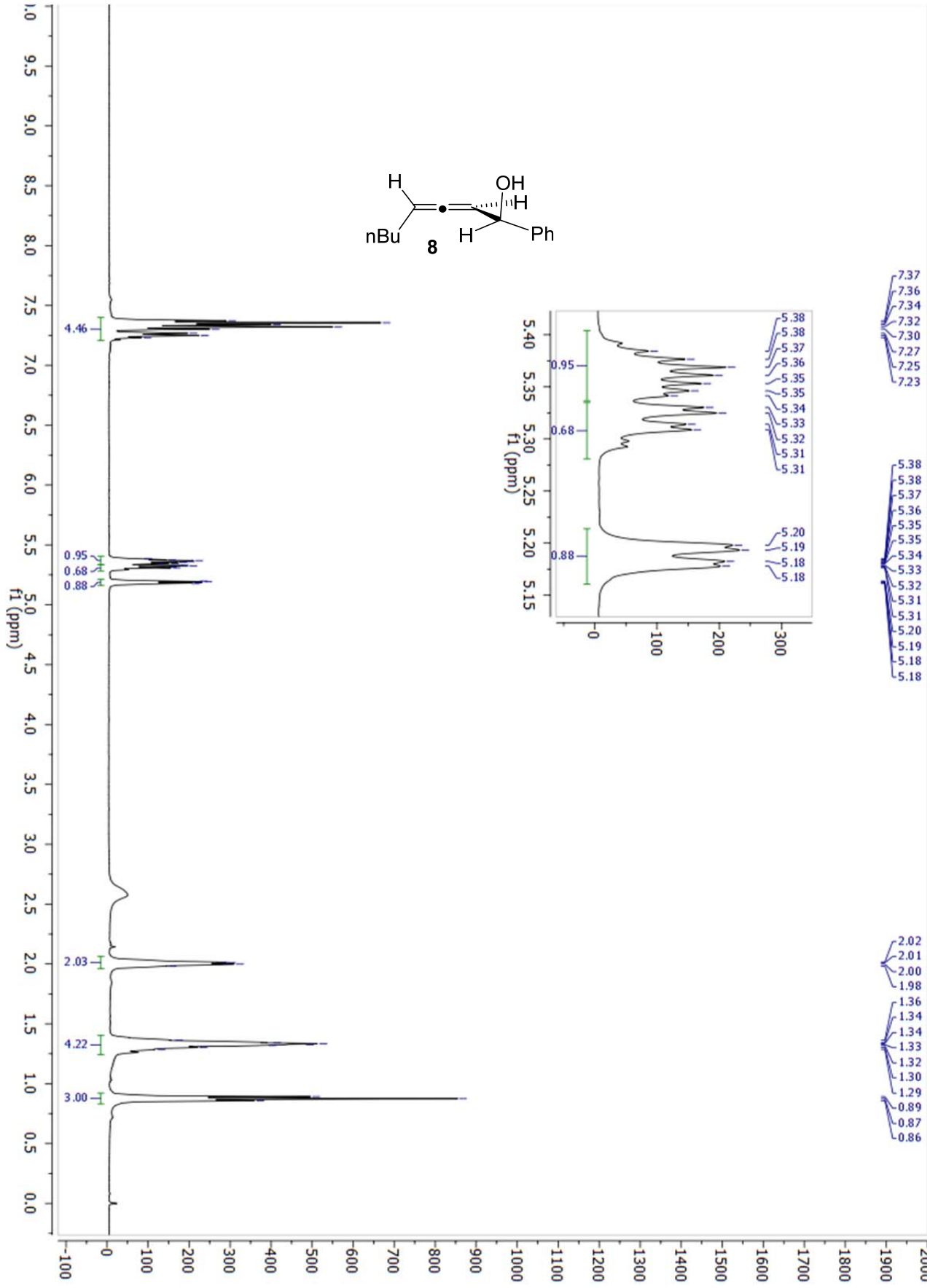
OH
H
n-Bu
H
Ph
8a
f1 (ppm)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5.36
5.35
5.35
5.34
5.33
5.32
5.31
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5.20
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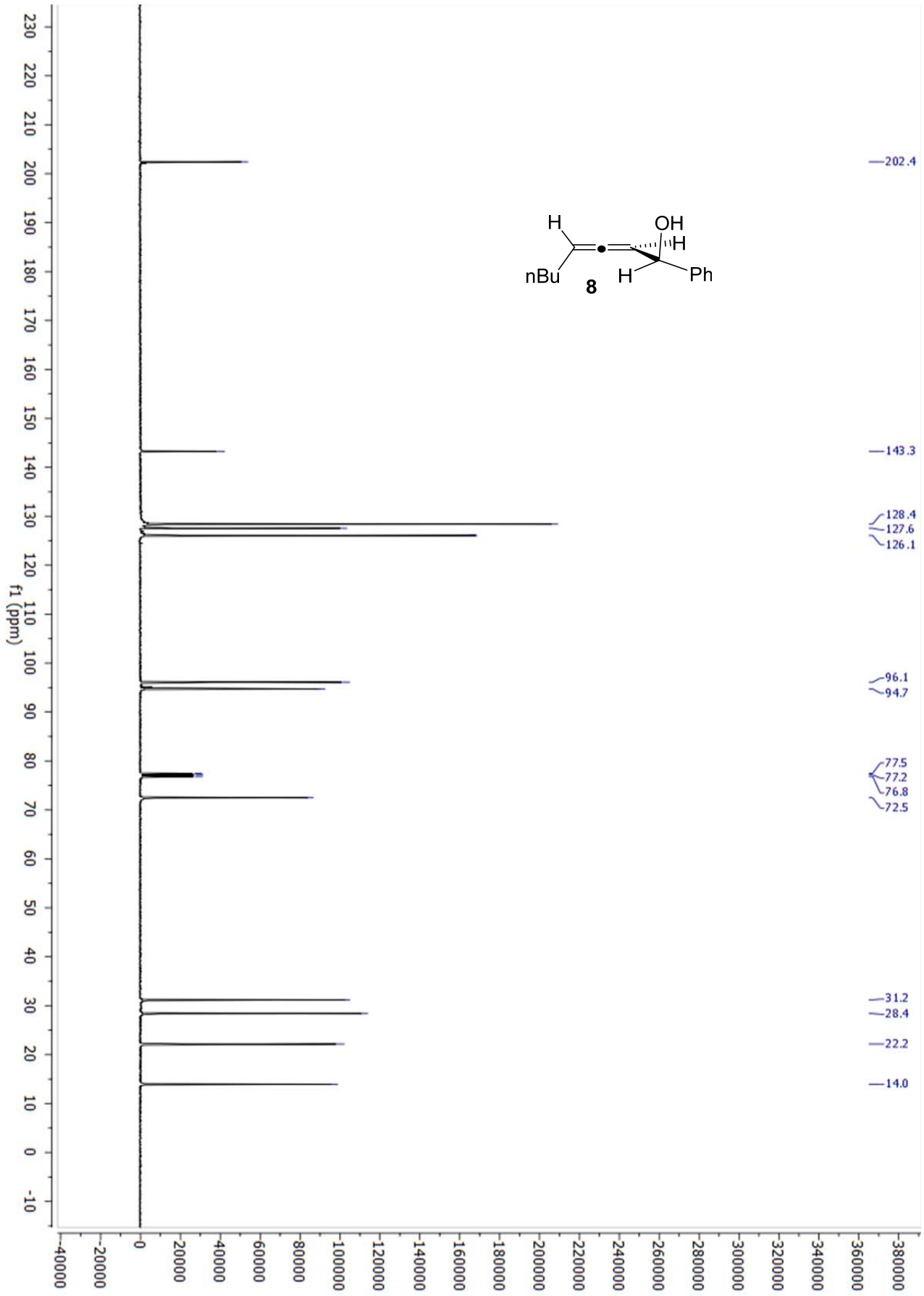
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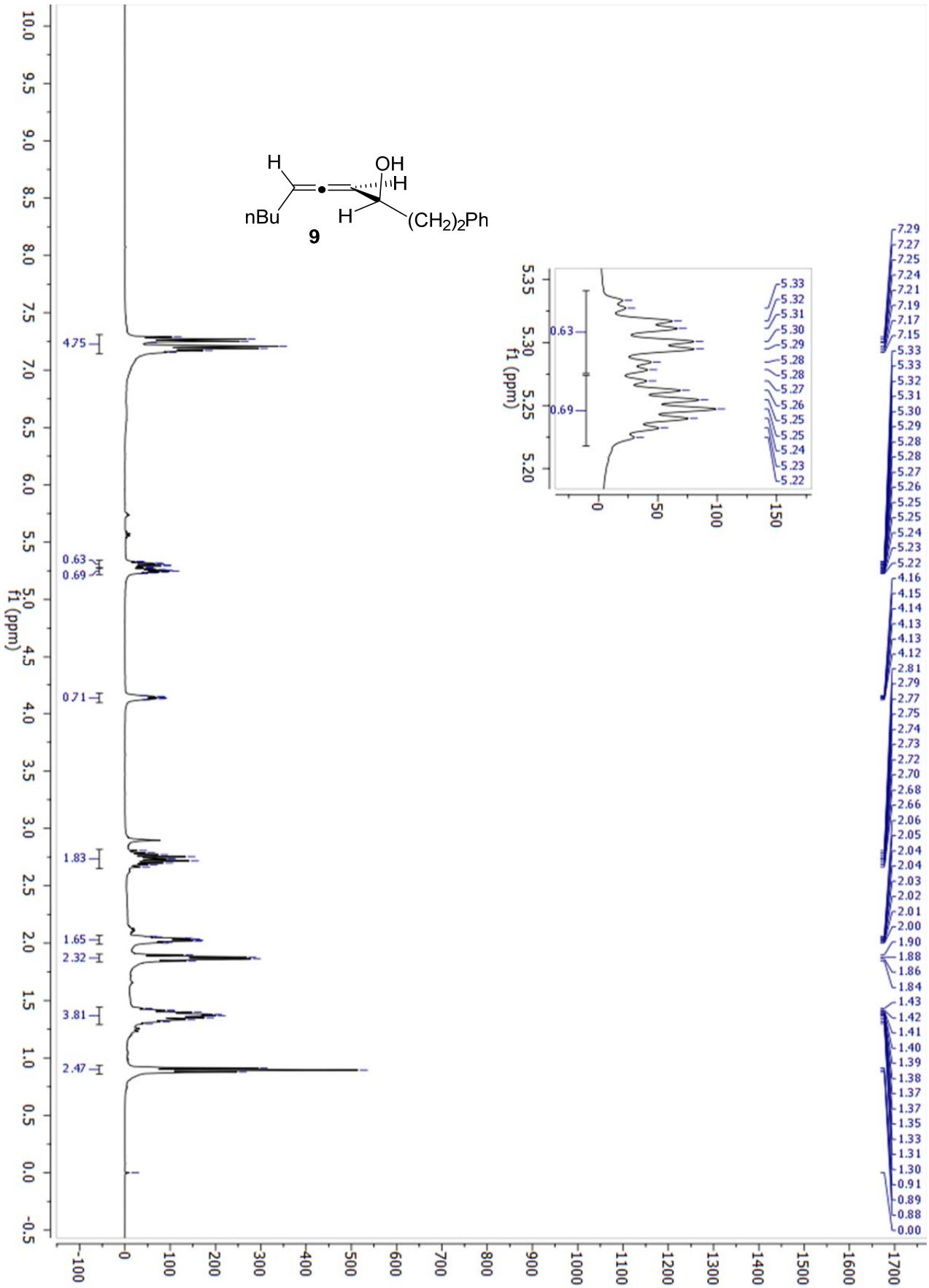
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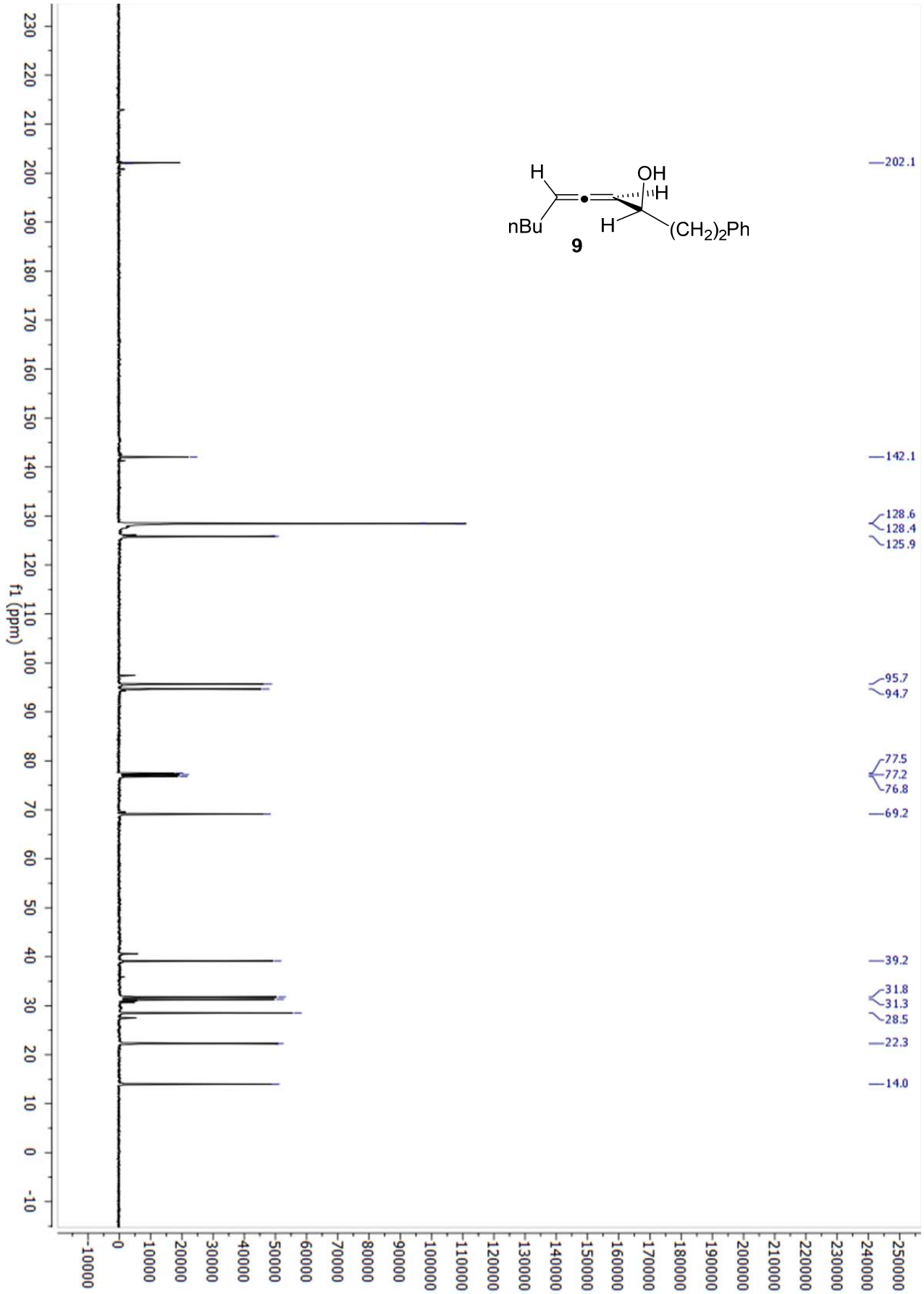
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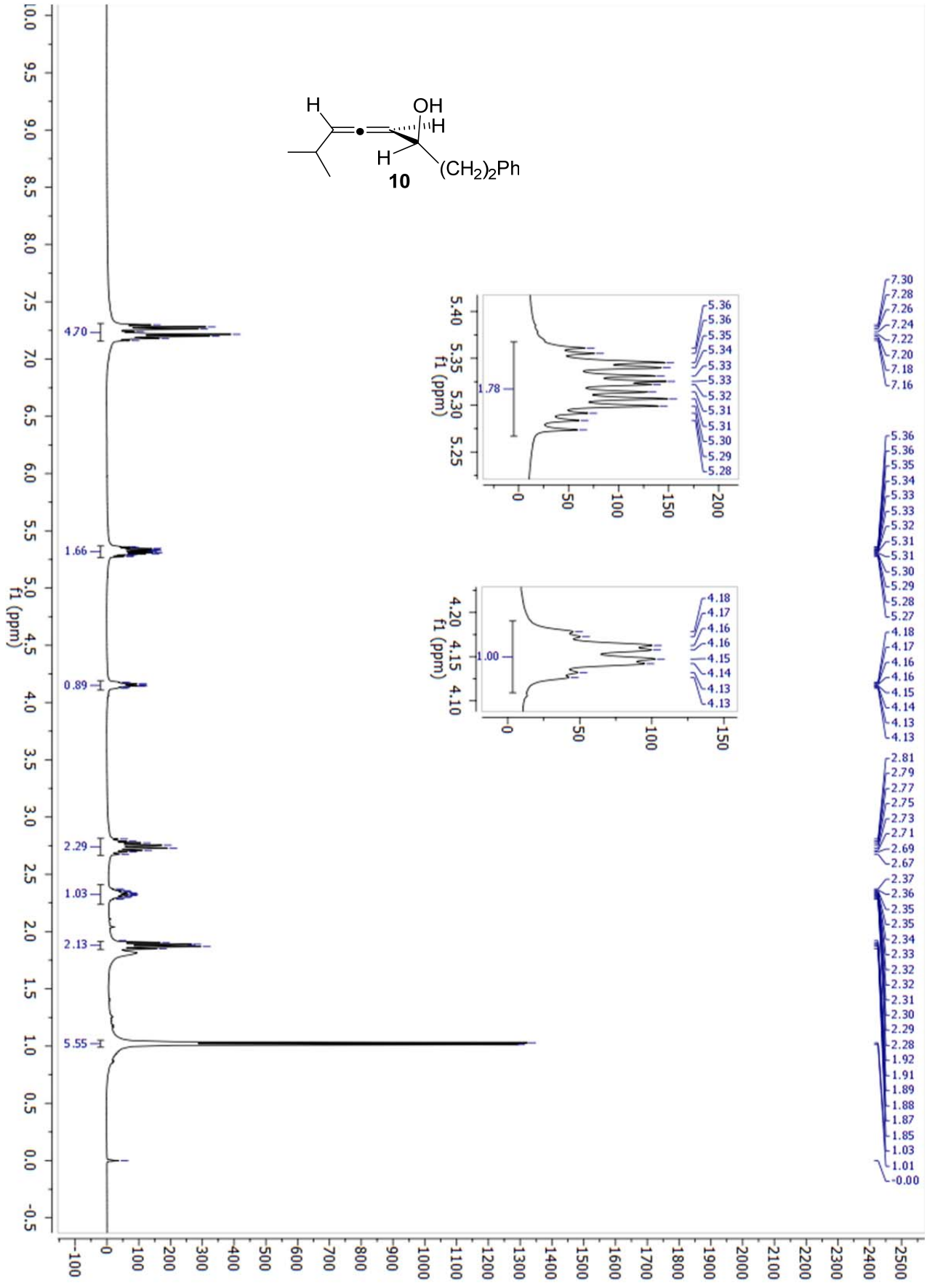
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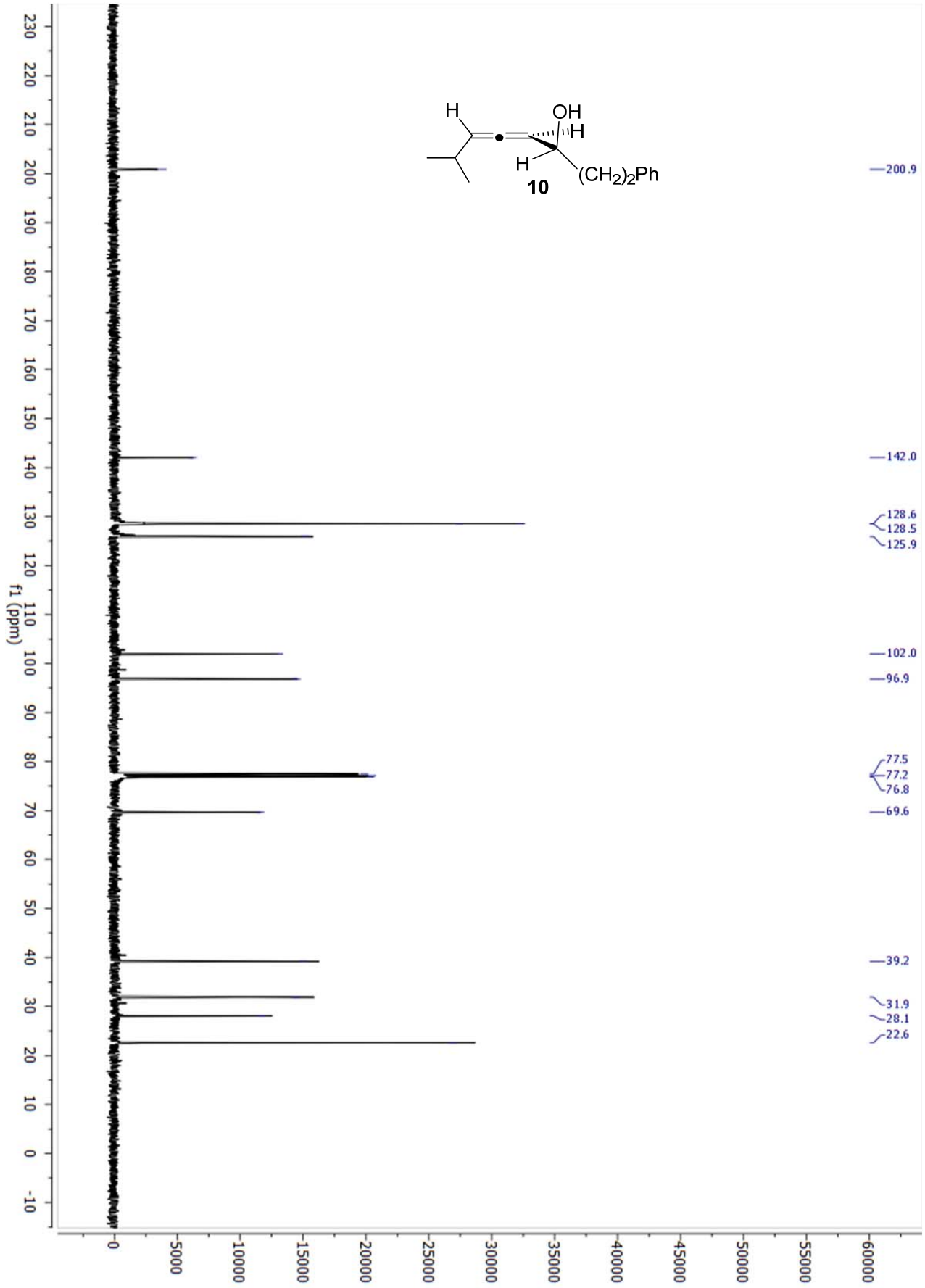
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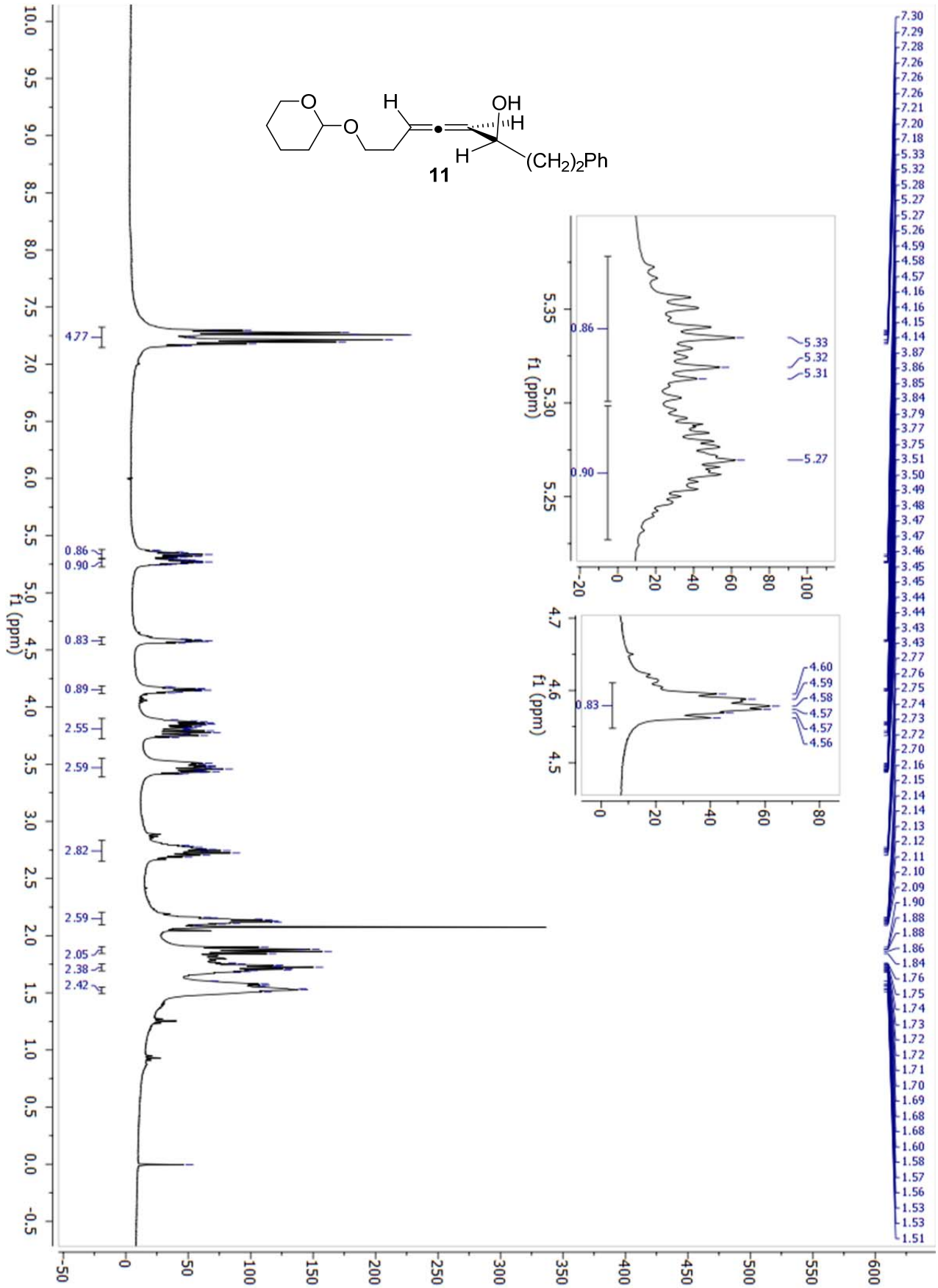
28.1
22.6
f1 (ppm)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O
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2.59
2.82
2.59
2.05
2.38
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5.27
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4.59
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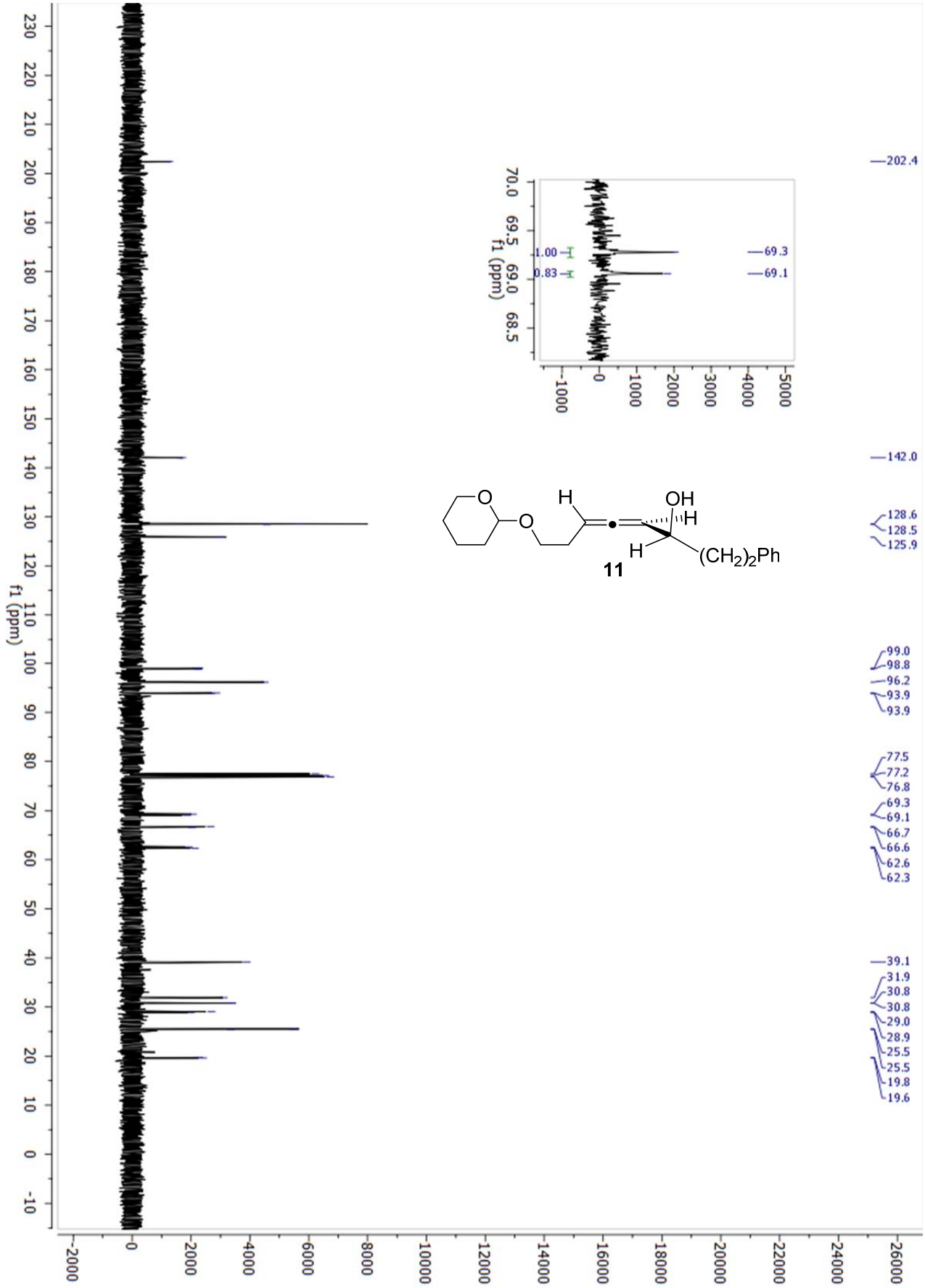
4.57
4.57
4.56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31.9
30.8
30.8
29.0
28.9
25.5
25.5
19.8
19.6
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1.00
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f1 (ppm)
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O
H
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H
H
(CH2)2Ph
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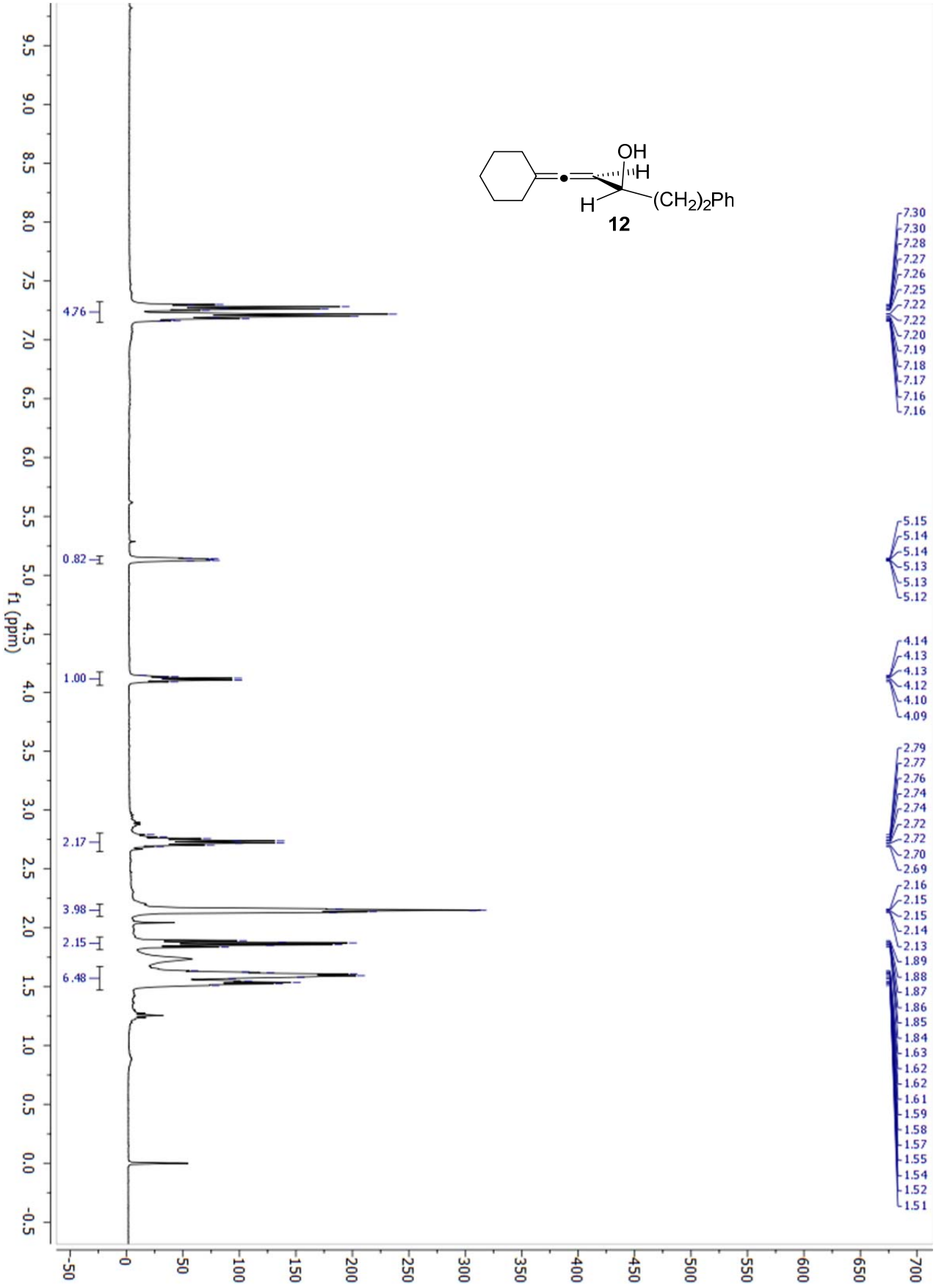
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7.25
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7.22
7.20
7.19
7.18
7.17
7.16
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5.14
5.13
5.13
5.12
4.14
4.13
4.13
4.12
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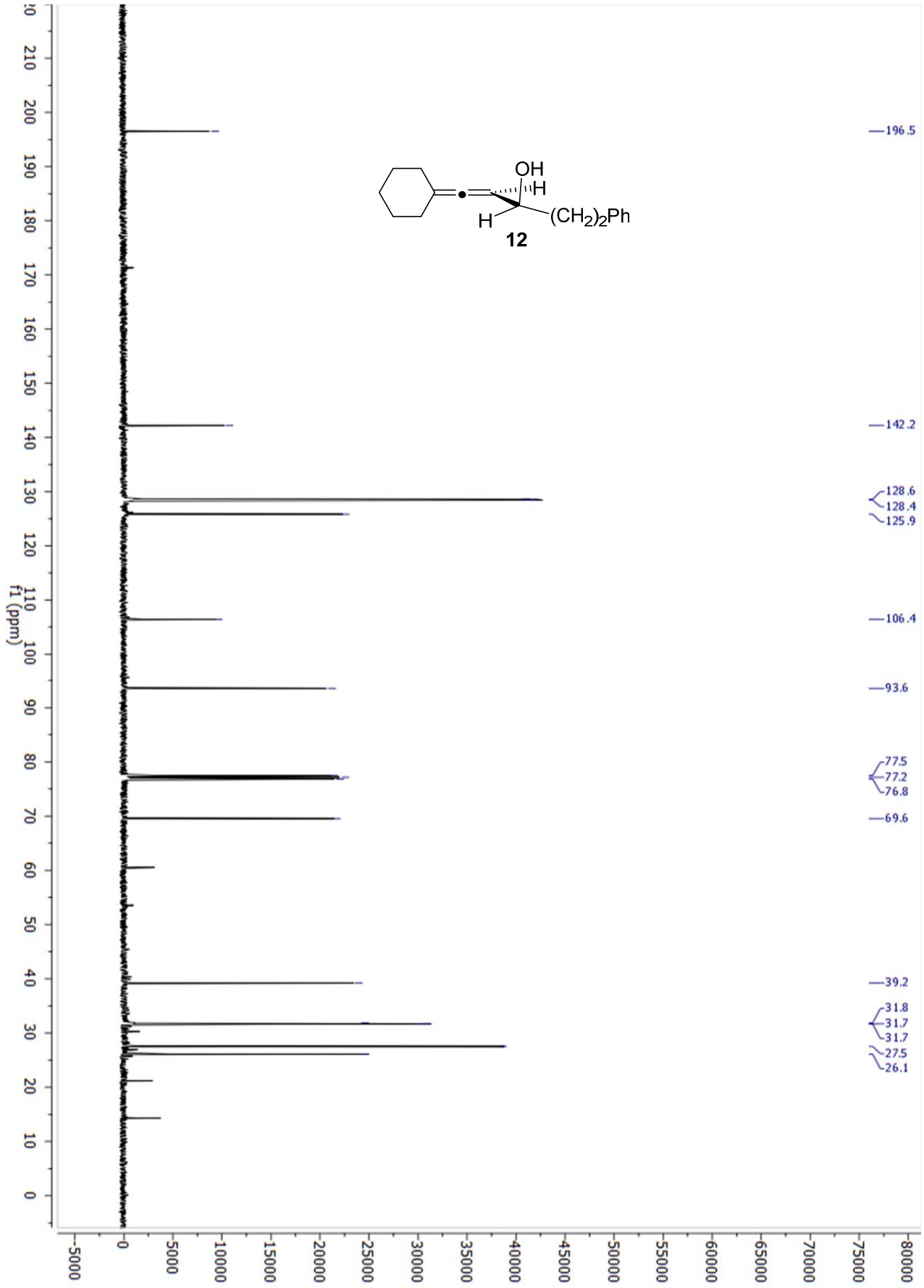
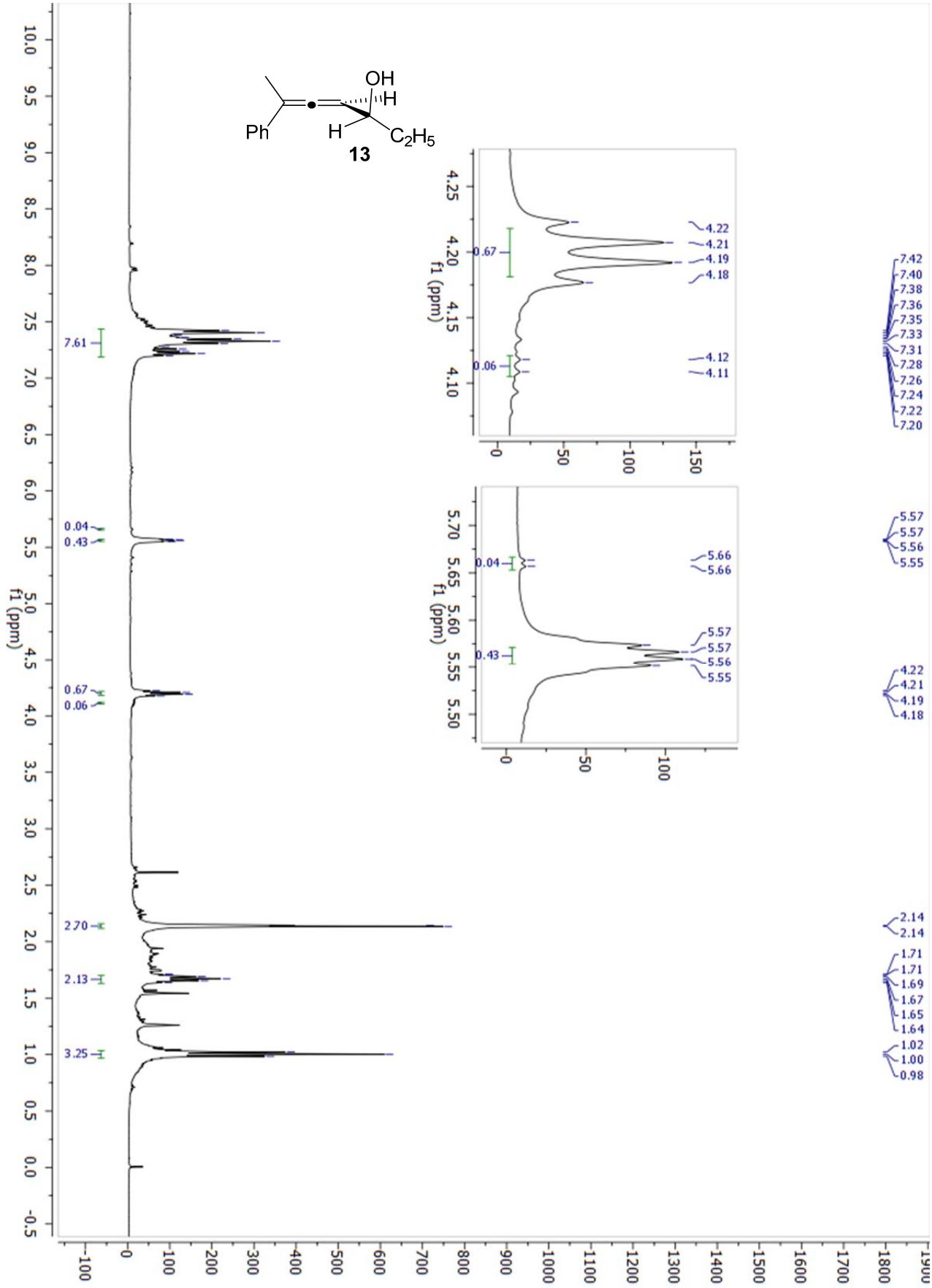
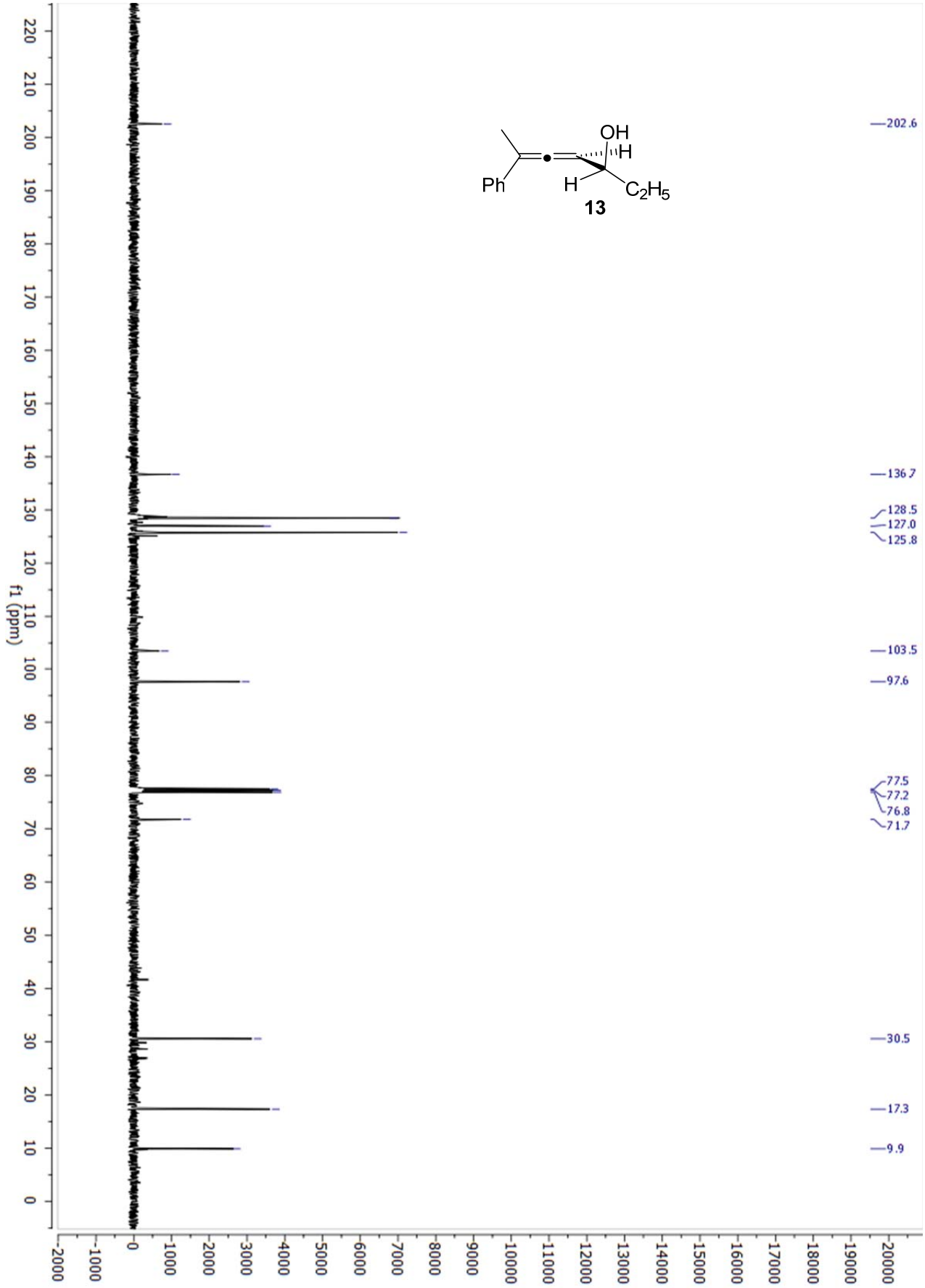
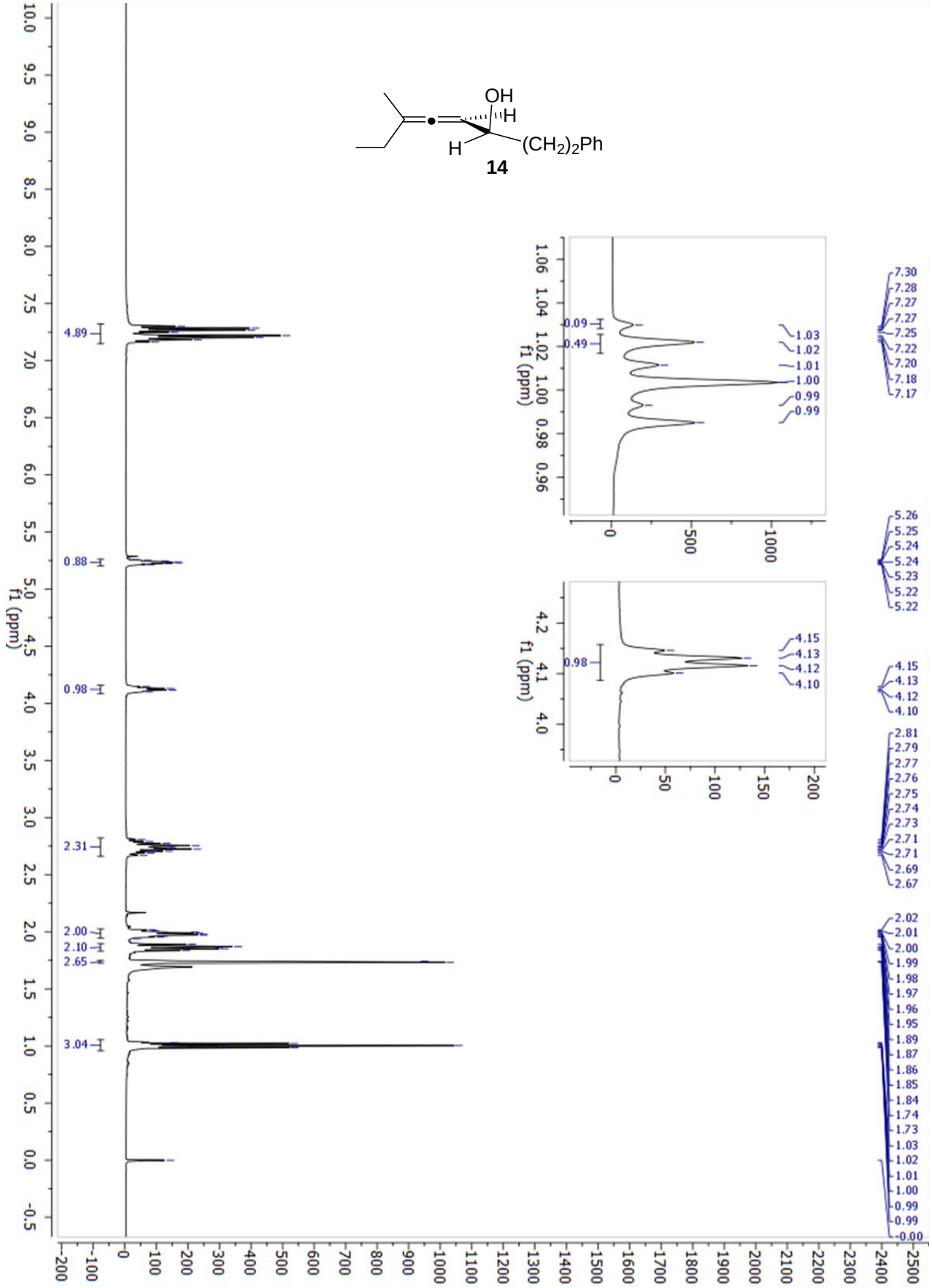
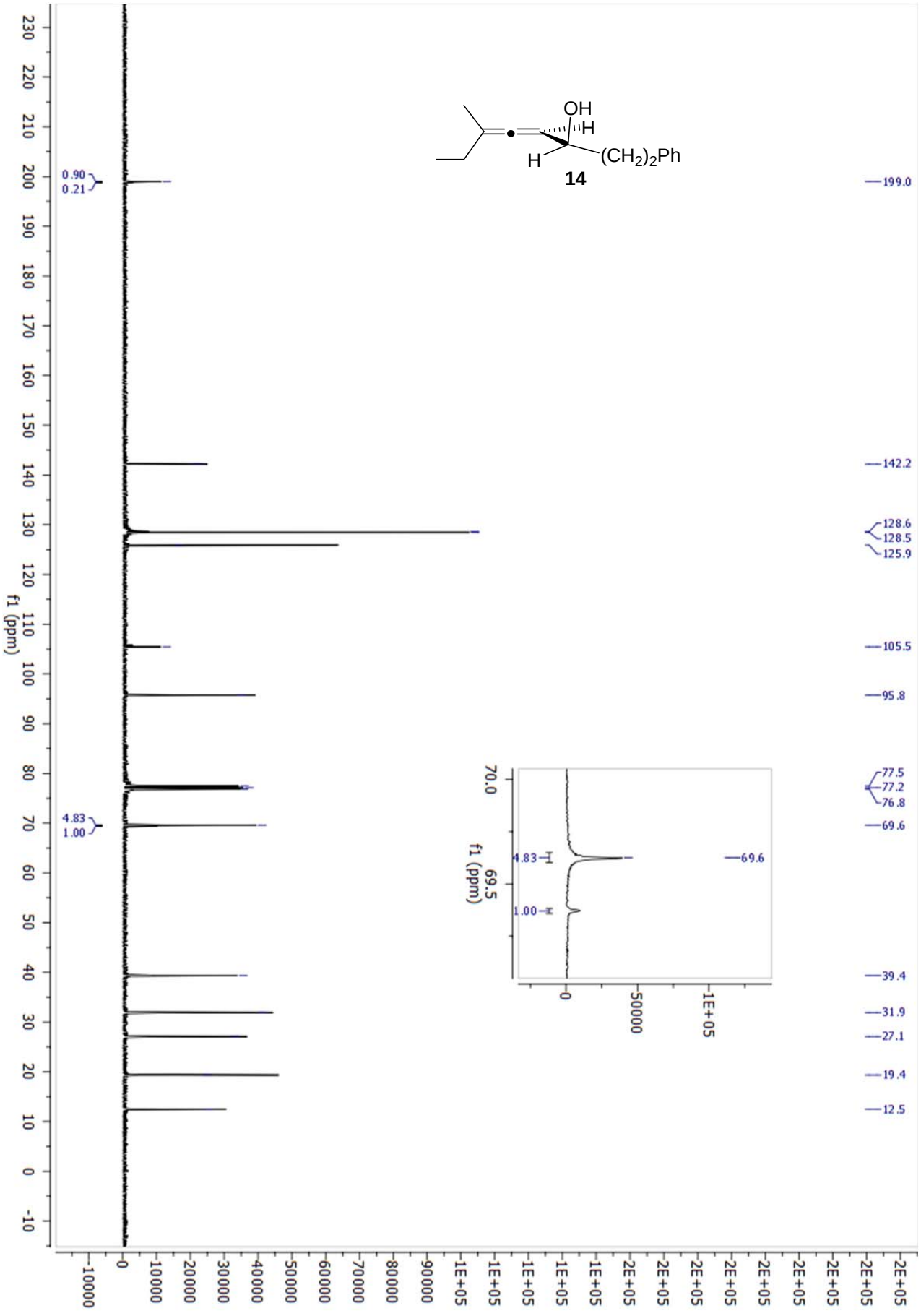
4.09
2.79
2.77
2.76
2.74
2.74
2.72
2.72
2.70
2.69
2.16
2.15
2.15
2.14
2.13
1.89
1.88
1.87
1.86
1.85
1.84
1.63
1.62
1.62
1.61
1.59
1.58
1.57
1.55
1.54
1.52
1.51

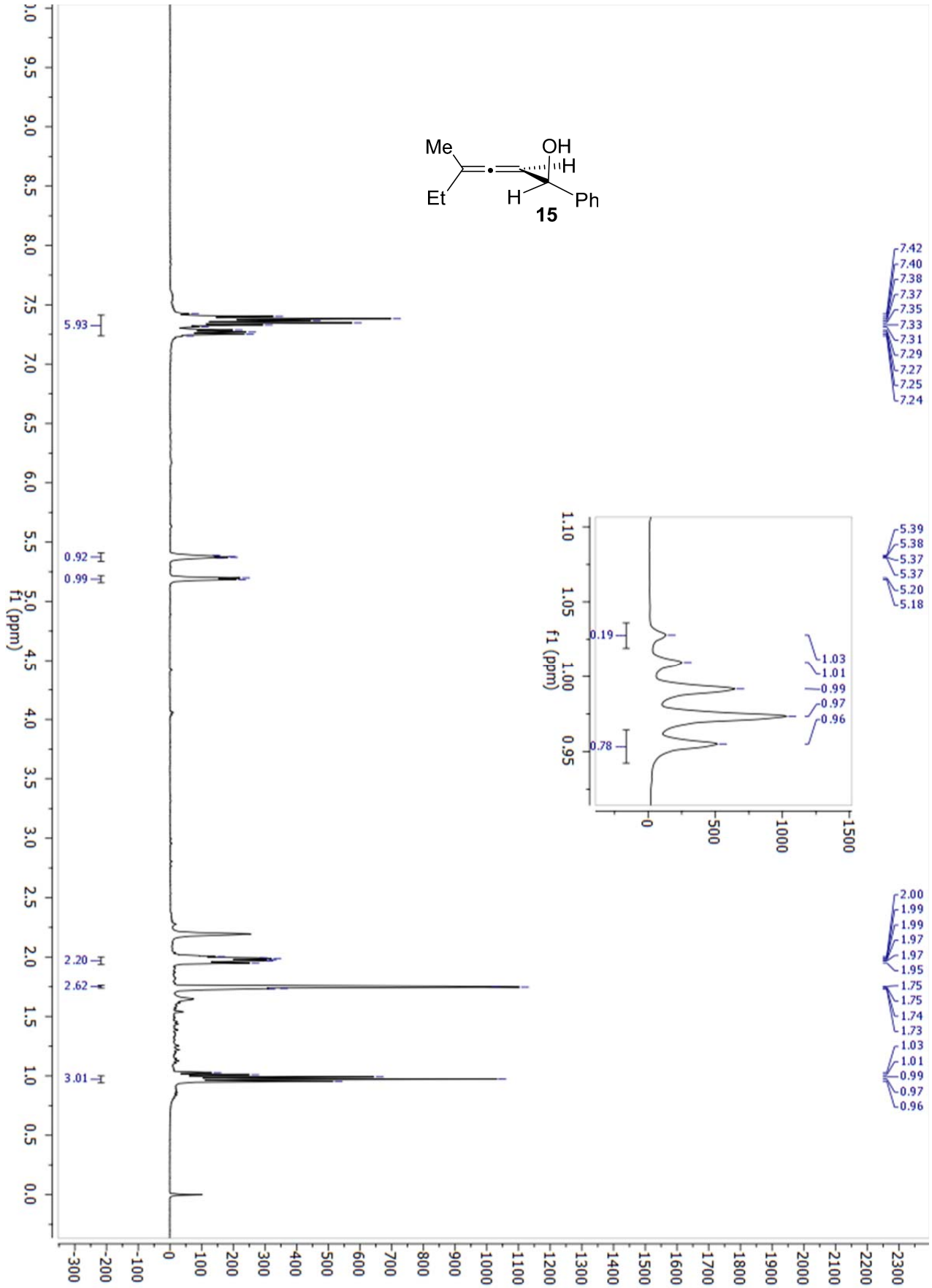

OH
H
H
(CH2)2Ph
12
196.5
142.2
128.6
128.4
125.9
106.4
93.6
77.5
77.2
76.8
69.6
39.2
31.8
31.7
31.7
27.5
26.1
f1 (ppm)

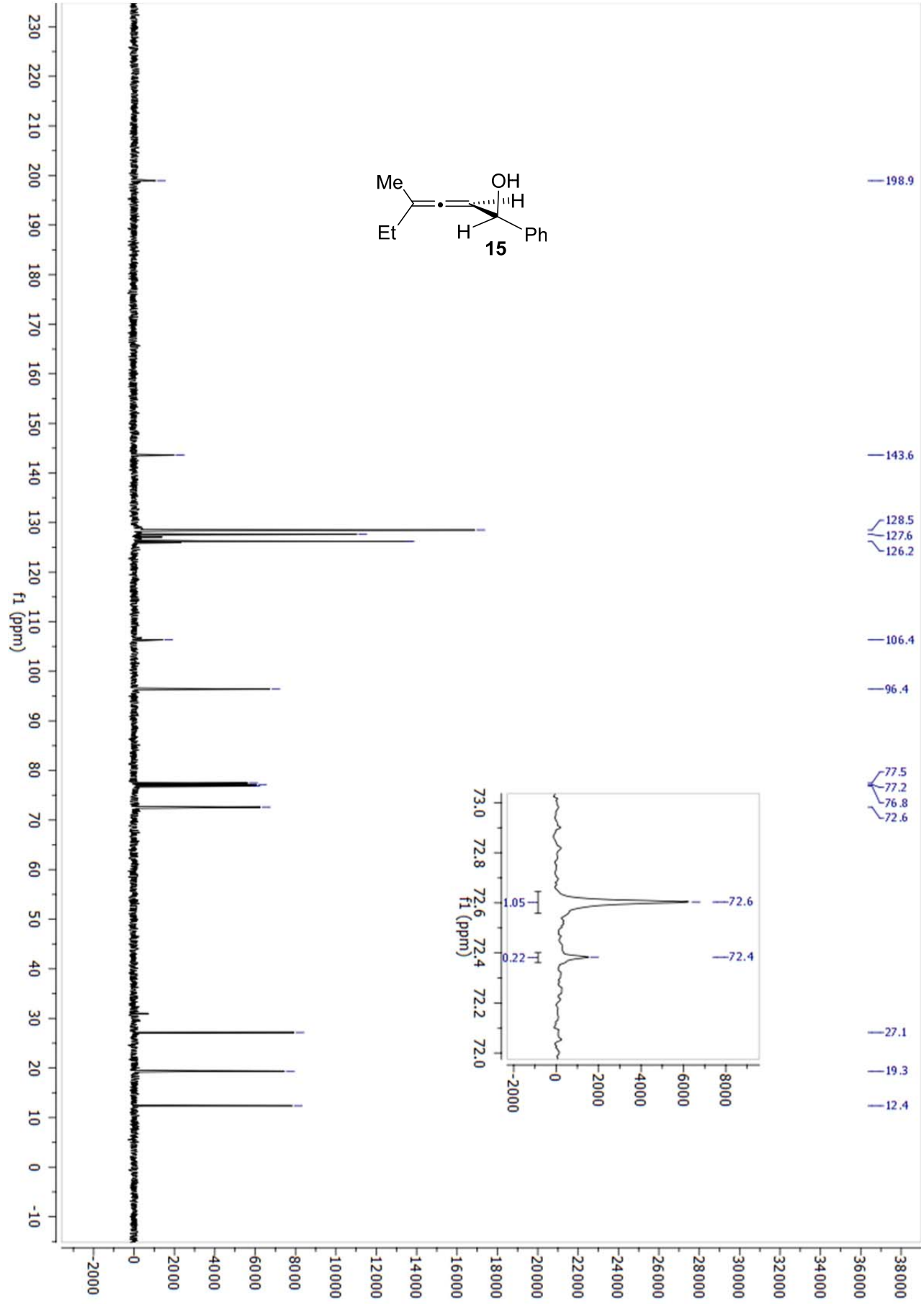

OH
H
Ph
H
C_2H_5
13
f1 (ppm)
7.61
0.04
0.43
0.67
0.06
2.70
2.13
3.25
4.22
4.21
4.19
4.18
4.12
4.11
5.66
5.66
5.57
5.57
5.56
5.55
7.42
7.40
7.38
7.36
7.35
7.33
7.31
7.28
7.26
7.24
7.22
7.20
2.14
2.14
1.71
1.71
1.69
1.67
1.65
1.64
1.02
1.00
0.98

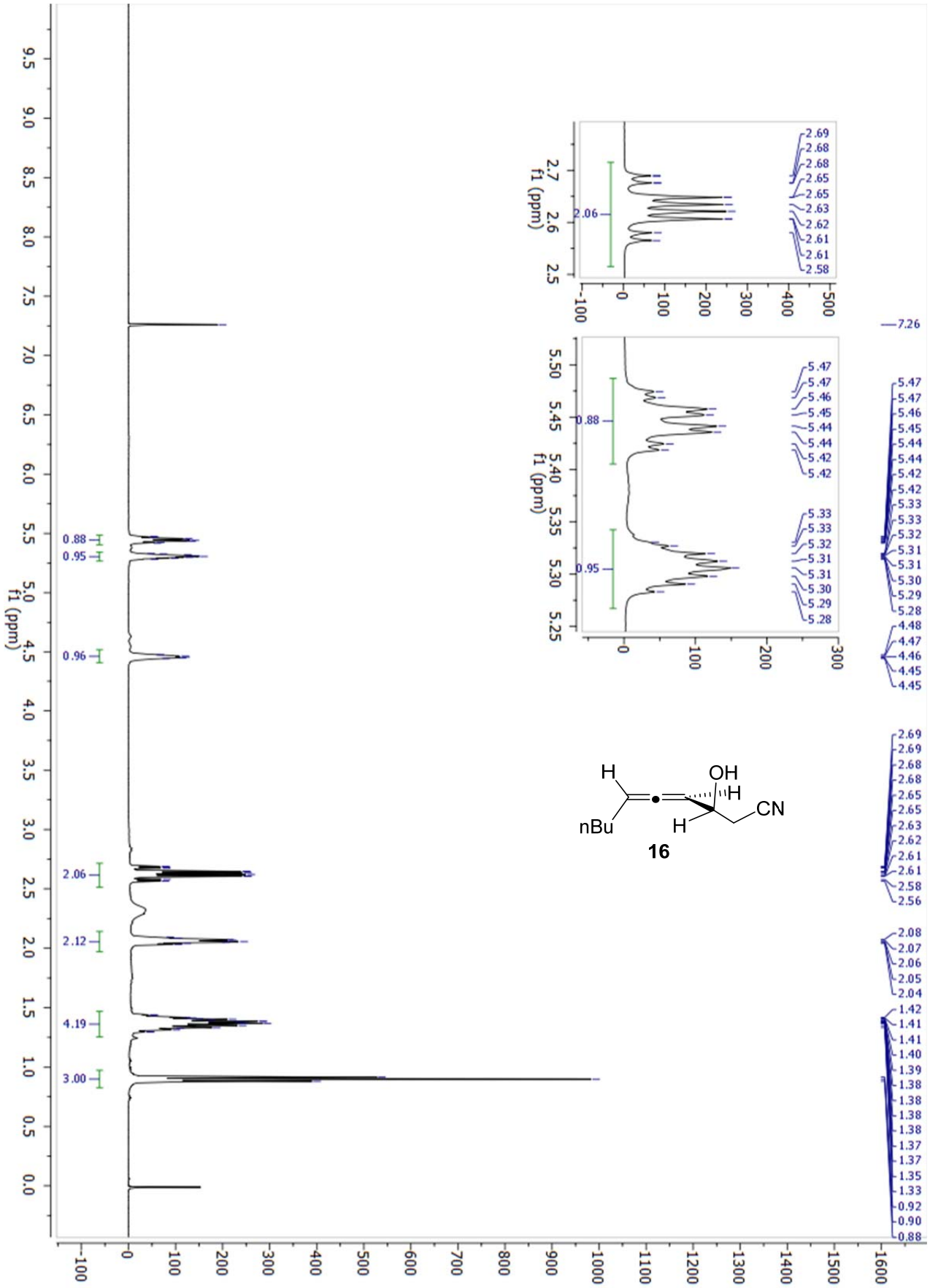

OH
H
Ph
H
C_2H_5
13
202.6
136.7
128.5
127.0
125.8
103.5
97.6
77.5
77.2
76.8
71.7
30.5
17.3
9.9
f1 (ppm)

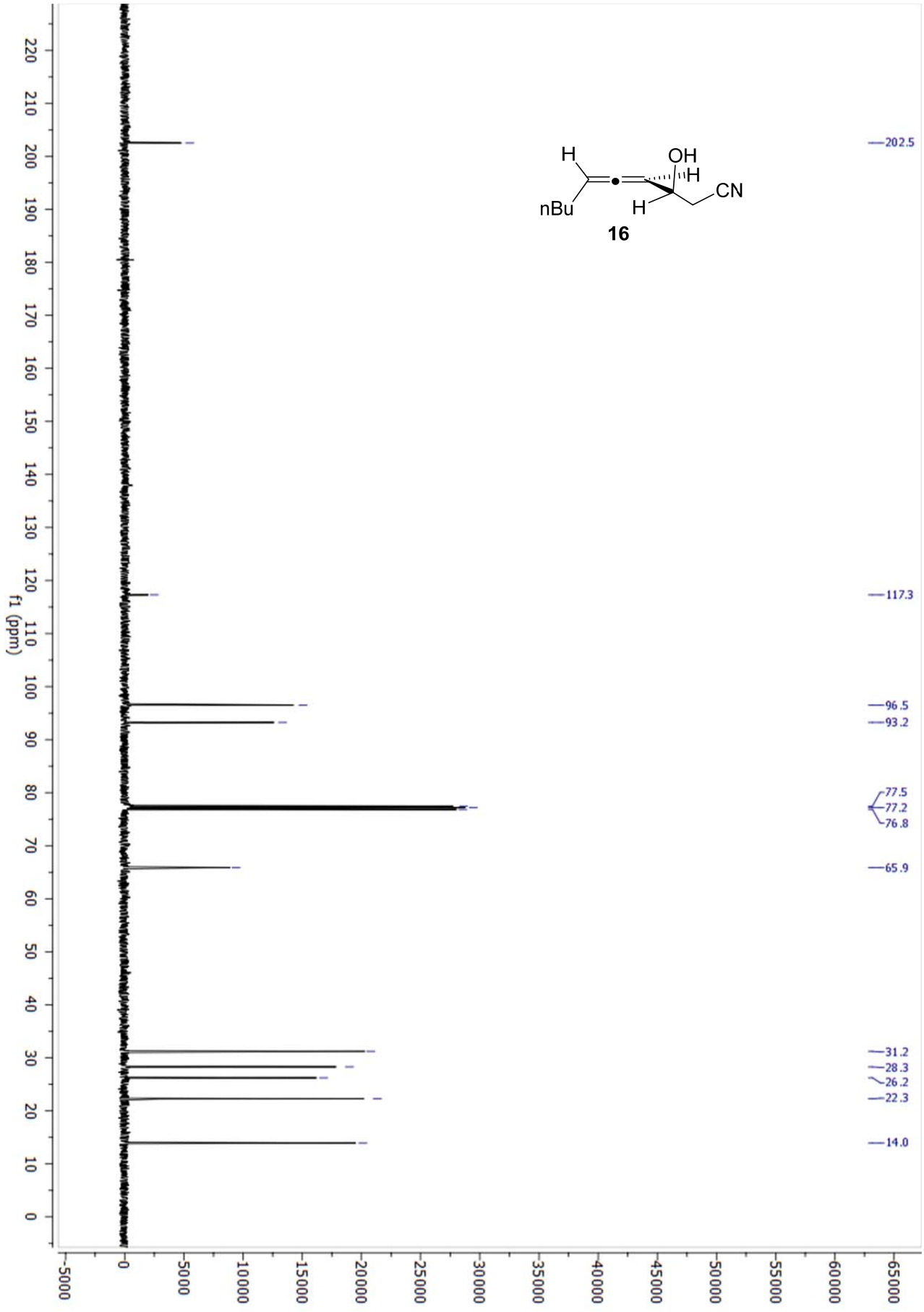

OH
H
H
(CH2)2Ph
14
f1 (ppm)
4.89
0.88
0.98
2.31
2.00
2.10
2.65
3.04
0.09
0.49
1.03
1.02
1.01
1.00
0.99
0.99
0.98
4.15
4.13
4.12
4.10
7.30
7.28
7.27
7.27
7.25
7.22
7.20
7.18
7.17
5.26
5.25
5.24
5.24
5.23
5.22
5.22
4.15
4.13
4.12
4.10
2.81
2.79
2.77
2.76
2.75
2.74
2.73
2.71
2.71
2.69
2.67
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.89
1.87
1.86
1.85
1.84
1.74
1.73
1.03
1.02
1.01
1.00
0.99
0.99
-0.00

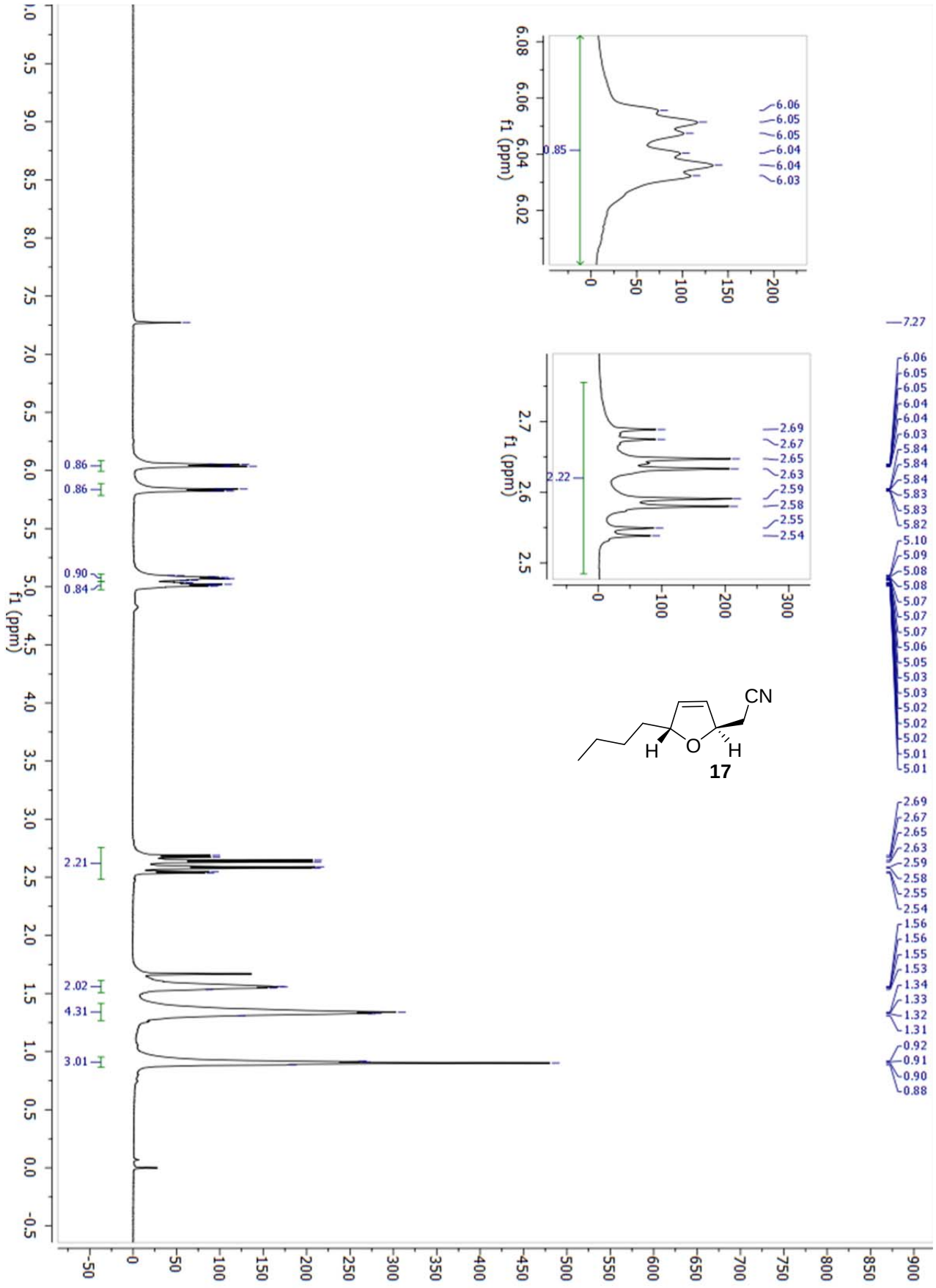

OH
H
H
(CH2)2Ph
14
0.90
0.21
4.83
1.00
199.0
142.2
128.6
128.5
125.9
105.5
95.8
77.5
77.2
76.8
69.6
39.4
31.9
27.1
19.4
12.5
f1 (ppm)
70.0
69.5
4.83
1.00
69.6

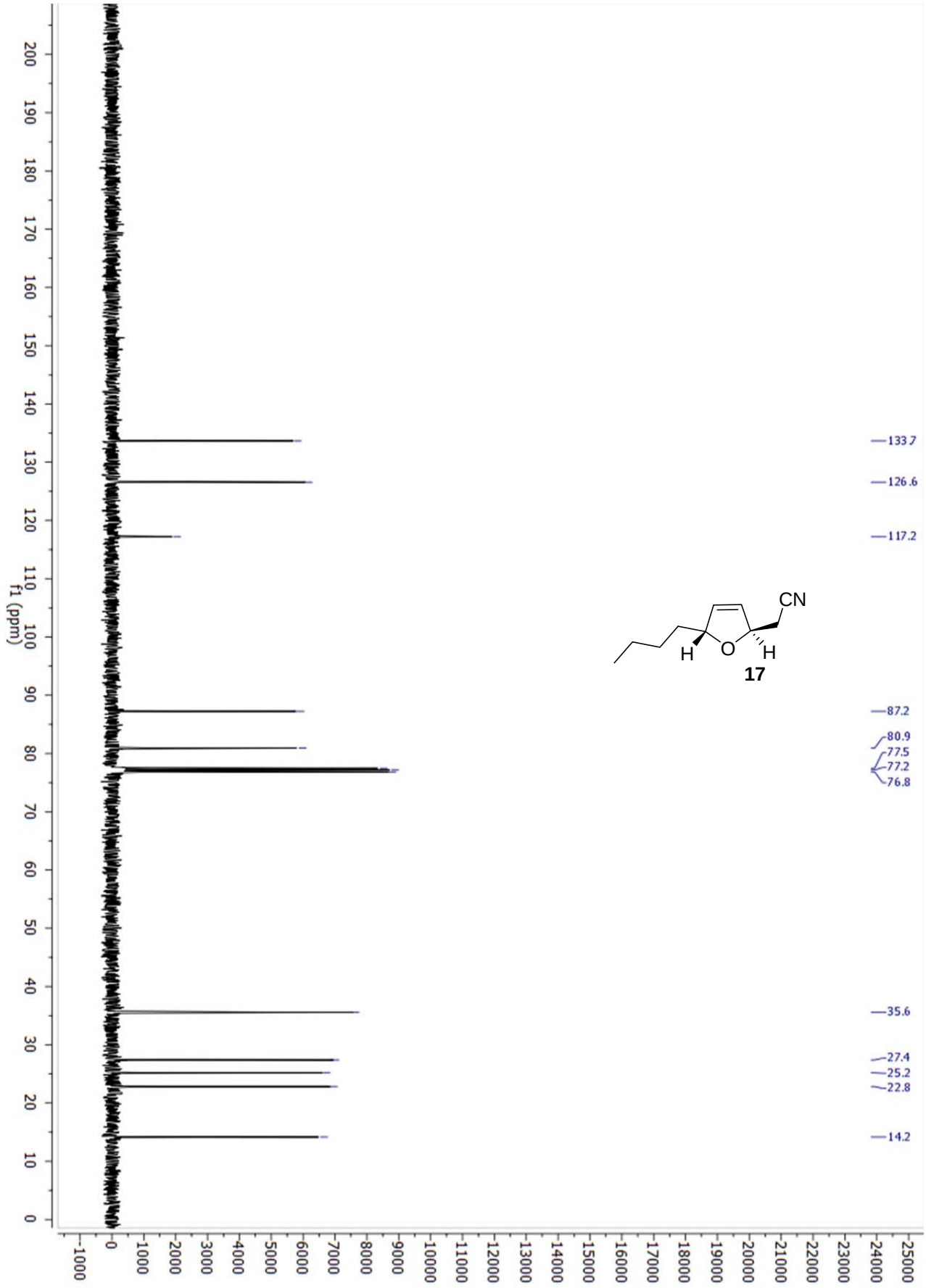

Me
OH
H
Et
H
Ph
15
7.42
7.40
7.38
7.37
7.35
7.33
7.31
7.29
7.27
7.25
7.24
5.39
5.38
5.37
5.37
5.20
5.18
2.00
1.99
1.99
1.97
1.97
1.95
1.75
1.75
1.74
1.73
1.03
1.01
0.99
0.97
0.96
5.93
0.92
0.99
2.20
2.62
3.01
f1 (ppm)
0.19
0.78
1.03
1.01
0.99
0.97
0.96

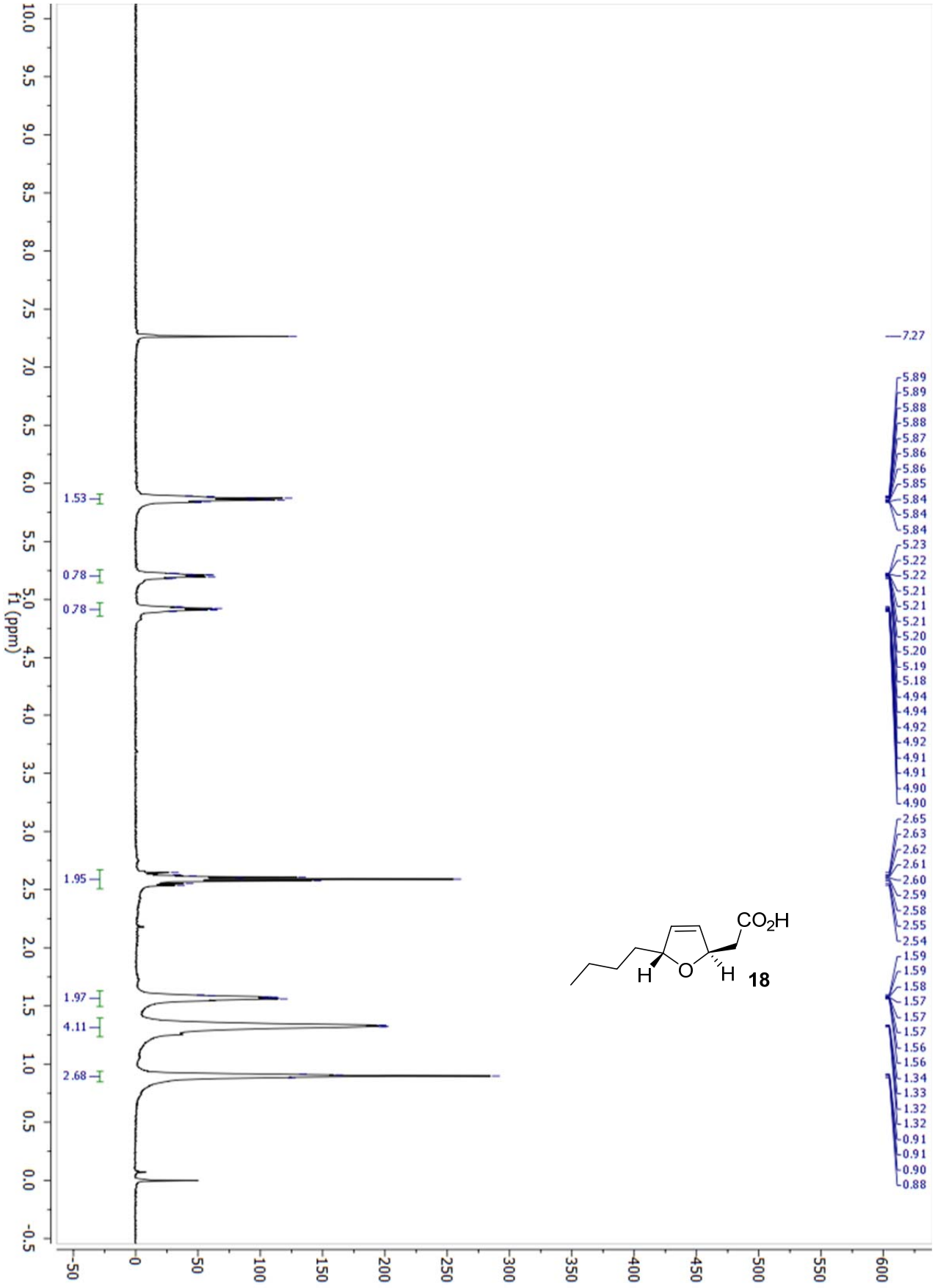

Me
OH
H
Et
H
Ph
15
198.9
143.6
128.5
127.6
126.2
106.4
96.4
77.5
77.2
76.8
72.6
27.1
19.3
12.4
f1 (ppm)
1.05
0.22
72.6
72.4

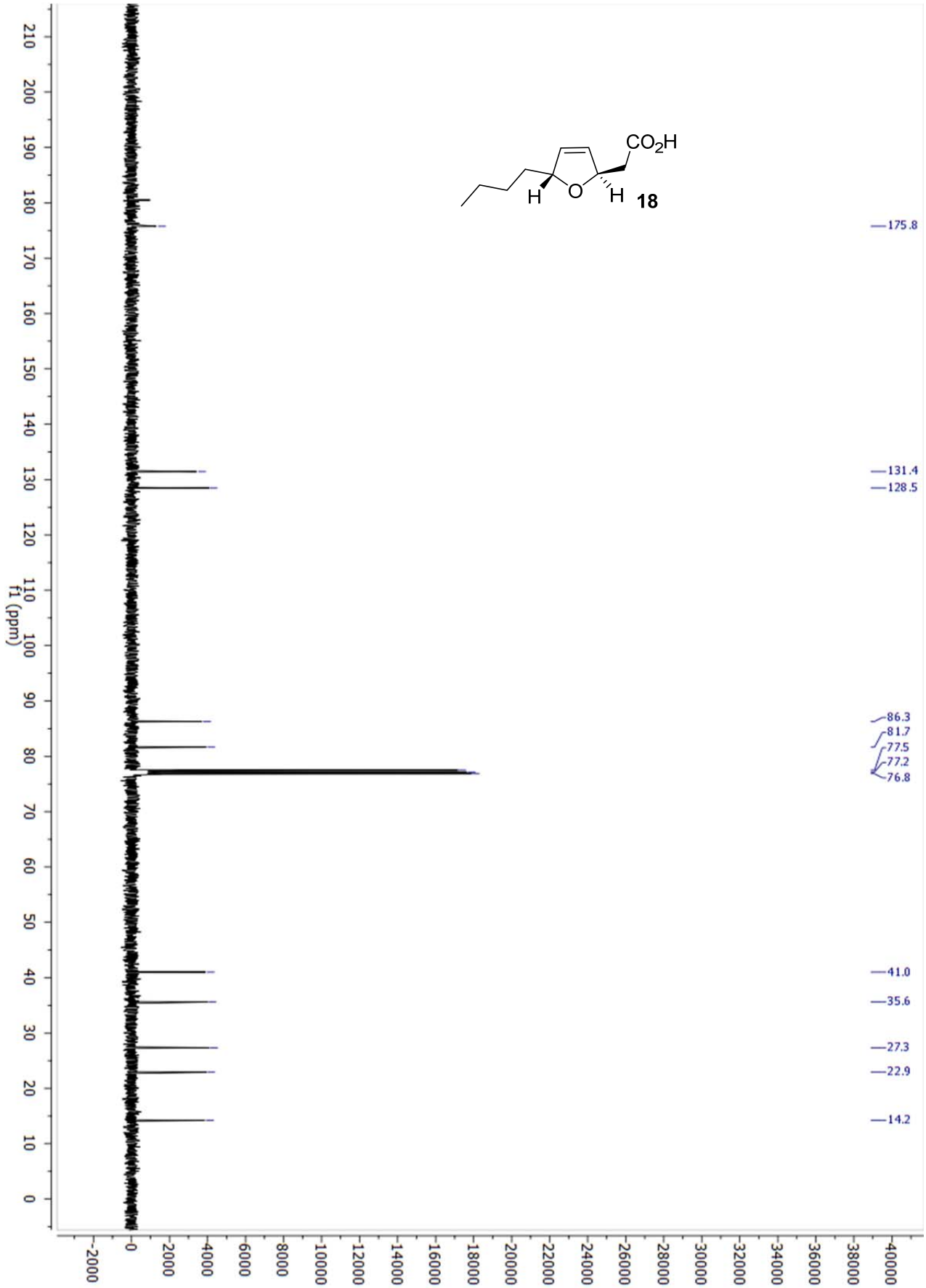

f1 (ppm)
0.88
0.95
0.96
2.06
2.12
4.19
3.00
2.06
0.88
0.95
7.26
H
OH
H
nBu
H
CN
16

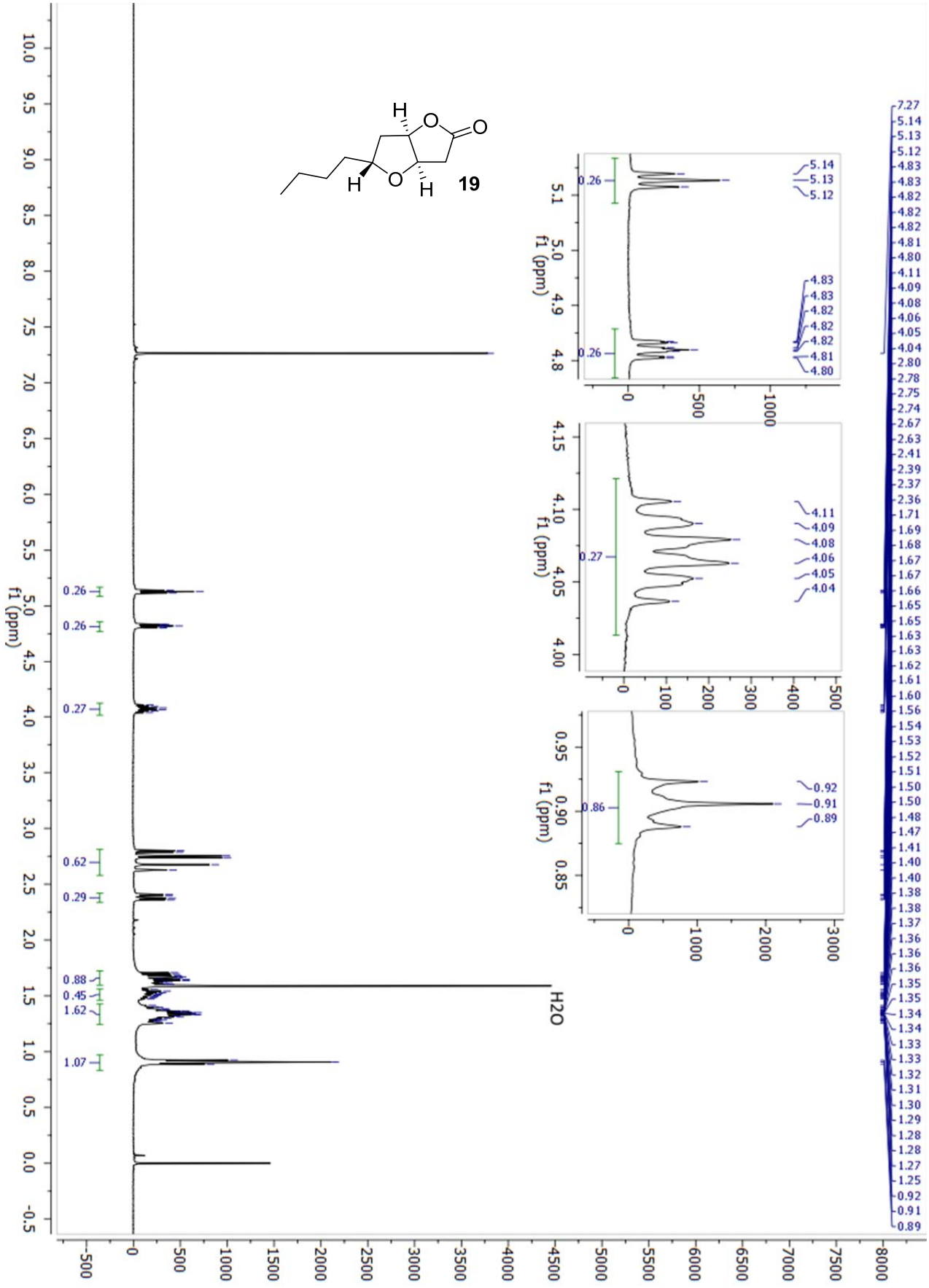

H
OH
H
CN
nBu
H
16
202.5
117.3
96.5
93.2
77.5
77.2
76.8
65.9
31.2
28.3
26.2
22.3
14.0
f1 (ppm)

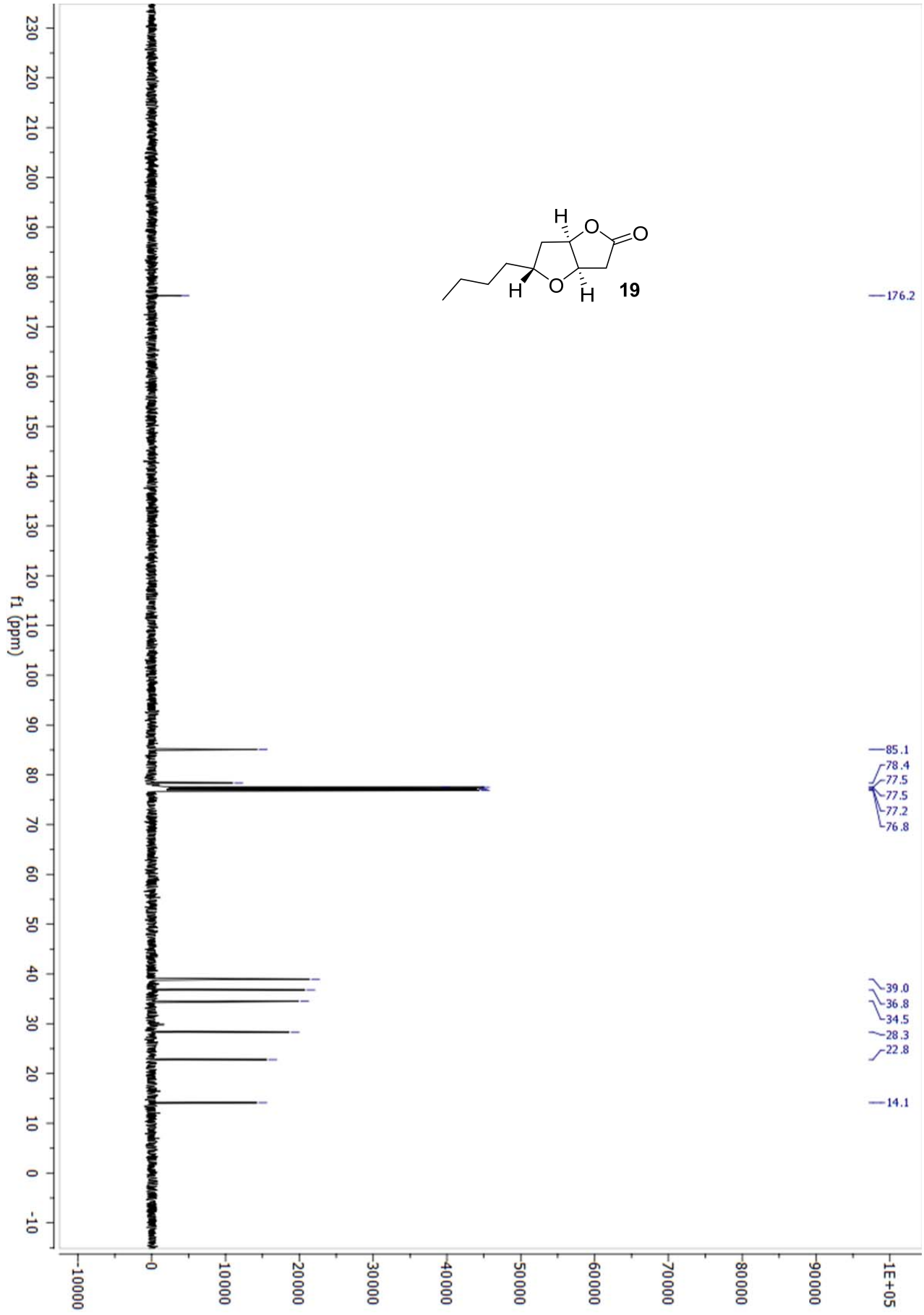

f1 (ppm)
0.86
0.86
0.90
0.84
2.21
2.02
4.31
3.01
0.85
2.22
CN
H
O
H
17


133.7
126.6
117.2
87.2
80.9
77.5
77.2
76.8
35.6
27.4
25.2
22.8
14.2
CN
H
O
H
17
f1 (ppm)


f1 (ppm)
1.53
0.78
0.78
1.95
1.97
4.11
2.68
7.27
5.89
5.89
5.88
5.88
5.87
5.86
5.86
5.85
5.84
5.84
5.84
5.23
5.22
5.22
5.21
5.21
5.21
5.20
5.20
5.19
5.18
4.94
4.94
4.92
4.92
4.91
4.91
4.90
4.90
2.65
2.63
2.62
2.61
2.60
2.59
2.58
2.55
2.54
1.59
1.59
1.58
1.57
1.57
1.57
1.56
1.56
1.34
1.33
1.32
1.32
0.91
0.91
0.90
0.88
CO2H
H
O
H
18


CO2H
H
O
H
18
175.8
131.4
128.5
86.3
81.7
77.5
77.2
76.8
41.0
35.6
27.3
22.9
14.2
f1 (ppm)


19
H2O
f1 (ppm)


H
O
O
H
O
H
19
176.2
85.1
78.4
77.5
77.5
77.2
76.8
39.0
36.8
34.5
28.3
22.8
14.1
f1 (ppm)