Supporting Information

A Formal Synthesis of (–)-Englerin A by RRCM and Transannular Etherification

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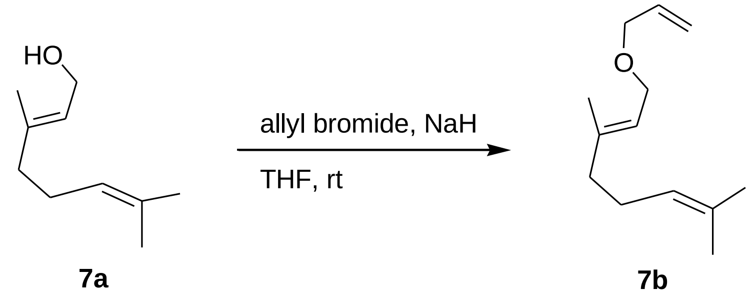
Index of Compounds

Compound No.	Experimental	NMR Spec.
Compound **7b**	S2	**-**
Compound **8**	S3	S 13 (^{1}H), S 14 (^{13}C)
Aldehyde	S3	S 15 (^{1}H), S 16 (^{13}C)
Compound **9**	S4	S 17 (^{1}H), S 18 (^{13}C)
(S) and (R)-MTPA ester of **9**	-	S 19 (^{1}H), S 20 (^{1}H)
Compound **10**	S5	S 21 (^{1}H), S 22 (^{13}C)
Compound **11**	S5	S 23 (^{1}H), S 24 (^{13}C)
Compound **5a** + **13a**	S6	S 25 (^{1}H)
Compound **5a**	S6	S 26 (^{1}H), S 27 (^{13}C)
Compound **13a**	S6	S 28 (^{1}H), S 29 (^{13}C)
Compound **5b** + **13b**	S7	S 30 (^{1}H)
Compound **5b**	S7	S 31 (^{1}H), S 32 (^{13}C)
Compound **13b**	S7	S 33 (^{1}H), S 34 (^{13}C)
Compound **14**	S8	S 35 (^{1}H), S 36 (^{13}C)
Compound **15**	S8	S 37 (^{1}H), S 38 (^{13}C)
Compound **3** (R=H)	S9	S 39 (^{1}H), S 40 (^{13}C)
Compound **3** (R=TBS)	S9	S 41 (^{1}H), S 42 (^{13}C)
Compound **16**	S10	S 43 (^{1}H)
Compound **17**	S10	S 44 (^{1}H), S 45 (^{13}C)
Compound **18**	S10	S 46 (^{1}H), S 47 (^{13}C)
2-(1-methylethyl)-2-propene-1-ol	S11	-

General Information

All air- and moisture sensitive reactions were performed under argon in oven-dried or flame-dried glassware. Unless stated otherwise, commercially available reagents were used as supplied and solvents were dried over molecular sieves prior to use. HPLC grade hexane and HPLC grade ethyl acetate (EtOAc) were used in chromatography. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone ketyl and dichloromethane was distilled from calcium hydride under argon gas. All experiments were monitored by thin layer chromatography (TLC) performed on Whatman precoated AL SIL G/UV 250 μm layer aluminum -supported flexible plates. Flash chromatography was carried out with Sorbent Technologies silica gel (porosity 60 Å, 230-400 mesh, surface area 500-600 m^2/g, bulk density 0.4 g/mL, pH range 6.5-7.5). Infrared spectra were recorded with a Perkin-Elmer 1600 Series FT-IR instrument. Samples were scanned as neat liquids or dissolved in CH_2Cl_2 on sodium chloride (NaCl) salt plates. Frequencies are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were recorded with a Varian Inova-600 (600 MHz for ^1H), a Varian Inova-500 (500 MHz for ^1H and 125 MHz for ^{13}C), Varian Inova-400 (400 MHz for ^1H and 100 MHz for ^{13}C), or Gemini-2300 (300 MHz for ^1H) spectrometer. Chemical shifts for proton NMR spectra are reported in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d.* Chemical shifts for carbon NMR spectra are reported in ppm with the center line of the triplet for chloroform-d set at 77.00 ppm. COSY and NOE experiments were measured on Varian Inova-400 and Varian Inova-600 spectrometer. High-resolution mass spectra were obtained on a Micromass Q-Tof Ultima spectrometer by the Mass Spectrometry Laboratory at the University of Illinois Urbana Champaign.[1]

Experimental Procedures and Characterization of Compounds



Ether 7b. To a stirred solution of geraniol (**7a**, 5.00 g, 32.4 mmol) in THF (50 mL) were added allyl bromide (4.71 g, 38.9 mmol) and slowly NaH (1.43 g, 60 %, 35.7 mmol) under argon.

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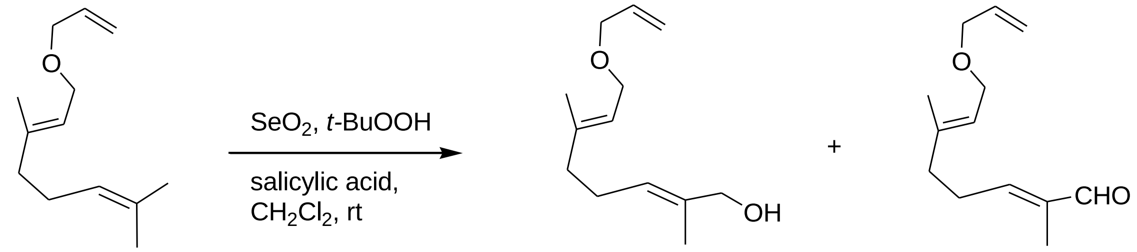
[1] http://www.scs.uiuc.edu/~msweb/instrum/qtof.php

The reaction mixture achieved a gentle reflux and then it was allowed to cool down to room temperature. After stirring for 14 h, the mixture was filtered through Celite to remove a solid and the filter cake was washed with THF. The resulting solution was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with hexane) to give allyl ether **7b** (5.98 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (d, *J* = 0.3 Hz, 3 H), 1.66 (m, 3H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.98 – 2.15 (m, 4H), 3.96 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.99 (dd, *J* = 6.9, 0.9 Hz, 2H), 5.09 (m, 1H), 5.17 (dm, *J* = 10.2 Hz, 1H), 5.27 (ddt, *J* = 17.4, 1.7 Hz, 1H), 5.35 (tdd, *J* = 6.9, 2.4, 1.2 Hz, 1H), 5.93 (ddt, J = 17.4, 10.5, 5.7 Hz, 1H). The ^{1}H NMR data were consistent with the reported values.[2]



7b　**8**　Aldehyde

Alcohol 8. To a stirred solution of SeO_2 (2.3 mg, 0.62 mmol)[3] in CH_2Cl_2 (3 mL) were added salicylic acid (14.2 mg, 0.103 mmol), *t*-BuOOH (477 mg, 70 % in H_2O, 3.71 mmol), and ether **7b** (200 mg, 1.03 mmol). The mixture was stirred for 46 h. Then volatile compounds were removed under reduced pressure and the residue was diluted with Et_2O (10 mL). The organic solution was washed with 10 % NaOH (5 mL X 3) and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by silica gel column chromatography (elution with EtOAc : Hexane = 1:20 to 1:2) to give alcohol **8** (104 mg, 48 %) as an oil, the corresponding aldehyde (17.4 mg, 8 %), and recovered **7b** (42.3 mg, 21 %).

8: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.65 (s, 3H), 1.66 (s, 3H), 2.07 (t, *J* = 7.8 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 3.97 (m, 6H), 5.17 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.26 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.37 (quintet d, *J* = 6.6, 1.2 Hz, 1H), 5.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 16.4, 25.7, 39.1, 66.5, 69.0, 71.0, 117.0, 121.1, 125.6, 135.0, 135.1, 139.7.; IR (neat) ν_{max} 3397, 2918, 2857, 1670, 1647, 1448, 1383 cm^{-1}. HRMS[ES+] calcd for $C_{13}H_{22}O_2$ $[M + Na]^+$ 233. 1517, found 233.1523. .

Aldehyde : ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (m, 3H), 1.70 (dt, *J* = 2.1, 0.9 Hz, 3H), 2.19 (t, 2H), 2.46 (m, 2H), 3.93 (ddd, *J* = 6.0, 1.5 Hz, 2H), 3.95 (dd, *J* = 6.9, 0.9 Hz, 2H), 5.12 (m, 0.5H), 5.16 (m, 0.5H), 5.23 (ddt, *J* = 17.4, 1.5 Hz, 1H), 5.37 (tdd, *J* = 6.6, 2.7, 1.2 Hz, 1H), 5.88 (ddt, *J* = 17.4, 10.5, 5.7 Hz, 1H), 6.43 (tdd, *J* = 7.5, 2.7, 1.2 Hz, 1H), 9.34(s, 1H). NMR (100 MHz, $CDCl_3$) δ 9.1, 16.3, 26.9, 37.7, 66.3, 71.0, 117.0, 121.9, 134.7, 138.3, 139.4, 153.7, 195.1. IR (neat) ν_{max} 2924, 2853, 2711, 1687, 1645, 1447, 1360 cm^{-1}.

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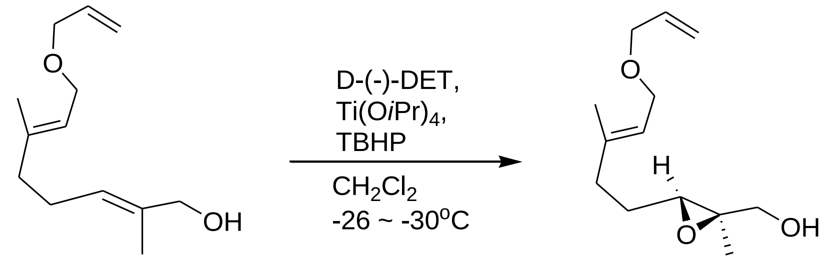
[2] Saburi, H.; Tanaka, S.; Kitamura, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1730

[3] Umbreit, M. S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.



8 **9**

Epoxy Alcohol 9. Regio- and stereoselective epoxidation was accomplished by the catalytic procedure of Sharpless.[4] To a stirred suspension of activated 4 Å molecular sieves (1.6 g) in CH$_2$Cl$_2$ (124 mL) under argon were added alcohol **8** (2.59 g, 12.3 mmol) and D-(-)-DET (381 mg, 1.85 mmol). The resulting mixture was stirred and cooled to - 20 °C. A solution of Ti(O^{i}Pr)$_4$ (350 mg, 1.23 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise and stirred at -20 °C for 30 min. Then TBHP (4.50 mL, 24.7 mmol, 5.5 M in decane with molecular sieves) was added dropwise and the resulting mixture was cooled to -26 to -30 °C. After 2.5 h, it was warmed to 0 °C, water (7 mL) was added, and the solution was allowed to warm to room temperature. A 30% NaOH solution saturated with solid NaCl was prepared. Of this, 1.4 mL was added to the reaction mixture. Vigorous stirring was continued for 30 min. Then the reaction mixture was filtered through Celite and the filter cake was washed with CH$_2$Cl$_2$. The combined organic solution was concentrated under reduced pressure and subjected to silica gel flash column chromatography (elution with EtOAc : Hexane = 1 : 4 to 1 : 1) to afford epoxide **9** (2.42 g, 83 %) as a colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.28 (s, 3H), 1.69 (s, 3H), 1.79 – 1.65 (m, 2H), 1.84 (d, *J* = 5.0 Hz, 1H), 2.20 (m, 1H), 3.03 (t, *J* = 6.5 Hz, 1H), 3.60 (dd, *J* = 12.3, 8.3 Hz, 1H), 3.61 (dd, *J* = 12.5, 4.3 Hz, 1H), 3.98 (t, 4H), 5.18 (d, *J* = 10.5 Hz, 1H), 5.27 (d, *J* = 17.5 Hz, 1H), 5.41 (t, *J* = 6.5 Hz, 1H), 5.92 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.2, 16.3, 26.3, 36.1, 60.0, 60.9, 65.6, 66.4, 71.1, 117.0, 121.5, 134.8, 138.9.; IR (neat) ν_{max} 3441, 2925, 2857, 1741, 1670, 1647, 1449, 1384 cm^{-1}. HRMS[ES+] calcd for $C_{13}H_{22}O_3$ [M + Na]$^+$ 249.1467, found 249.1456. The enantiomeric excess was determined to be 93 % ee by comparison of the ^{1}H NMR of the (*S*)-MTPA and the (*R*)-MTPA ester.

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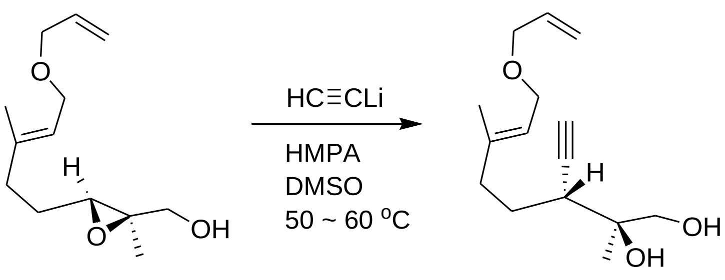
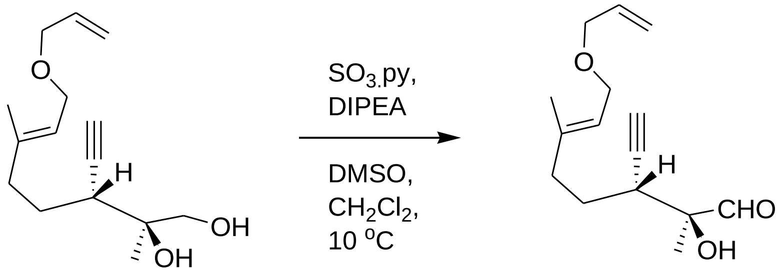
[4] (a) Gao, Y.; Hanson, R.M.; Klunder, J.M.; Ko, S.Y.; Masamune, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (b) Ichige, T.; Okano, Y.; Kanoh, N.; Nakata, M. *J. Org. Chem.* **2009**, *74*, 230. (c) Bravo, F.; McDonald, F. E.; Neiwert, W. A.; Hardcastle, K. I. *Org. Lett.* **2004**, *6*, 4487.



9 **10**

Diol 10. To a stirred solution of epoxide **9** (933 mg, 3.95 mmol) in DMSO (13 mL) and HMPA (13 mL) under argon was added Li-acetylide·ethylenediamine complex (2.02 g, 19.8 mmol, 90 %) at room temperature. The mixture was warmed to 55 °C and stirred for 3.5 h. The reaction was carefully quenched with saturated aq. NH_4Cl (3 mL) at 0 °C and the resulting mixture was diluted with Et_2O (45 mL). Then saturated aq. LiCl was added very carefully. The resulting mixture was separated and the aqueous solution was extracted with Et_2O (20 mL X 5). The combined organic solution was dried over $MgSO_4$, decolorized with activated charcoal, and concentrated under reduced pressure. Silica gel flash column chromatography (elution with EtOAc : Hexane = 1 : 1) provided diol **10** (814 mg, 82 %) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.43 (m, 1H), 1.61 (s, 3H), 1.84 (m, 1H), 2.03 (m, 1H), 2.07 (d, *J* = 2.8 Hz, 1H), 2.28 (m, 1H), 2.43 (dt, *J* = 11.6, 2.6 Hz, 1H), 3.05 (br, 1H), 3.40 (d, *J* = 11.2 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 3.92 (m, 4H), 5.12 (dd, *J* = 10.4, 4.0 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.35 (td, *J* = 7.2, 1.2 Hz, 1H), 5.85 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 19.3, 26.3, 37.5, 38.3, 66.3, 68.4, 70.8, 71.4, 73.9, 84.5, 117.0, 120.9, 134.6, 139.6.; IR (neat) ν_{max} 3418, 3080, 2935, 2110, 1668, 1646, 1455, 1381 cm^{-1}. HRMS[ES+] calcd for $C_{15}H_{24}O_3$ $[M + Na]^+$ 275.1623, found 275.1615.



10 **11**

Aldehyde 11. Oxidation was performed by the Parikh-Doering method.[5] To a stirred solution of diol **10** (200 mg, 0.793 mmol) in CH_2Cl_2 (5.5 mL) were added DMSO (495 mg, 6.34 mmol) and *N,N*-diisopropylamine (DIPEA) (410 mg, 3.17 mmol). Then the reaction mixture was cooled to 0 °C under argon. The SO_3·Py complex (322 mg, 1.98 mmol) was added and the reaction mixture was stirred for 1 h at 0 °C. Then it was warmed to 10 °C andstirred for 2 h. Additional DMSO (0.14 mL, 1.97 mmol), DIPEA (0.10 mL, 0.57 mmol), and SO_3·Py complex (130 mg, 98%, 0.80 mmol) were added and stirring was

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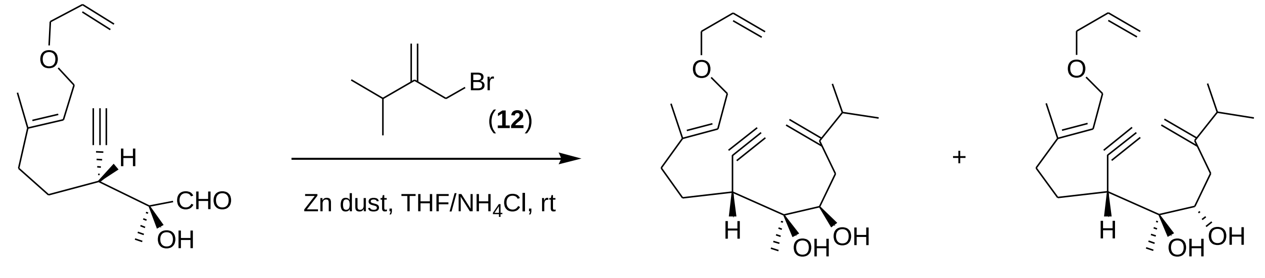
[5] Parikh, J.R.; von Doering, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 5505

continued for 1h. The reaction mixture was quenched with 1*N* HCl (3 mL) and extracted with CH_2Cl_2 (5 mL X 2). The combined organic solution was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (elution with EtOAc : Hexane = 1 : 4) to afford aldehyde **11** as a colorless oil (142 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 3H), 1.59 (s, 3H), 1.61 (m, 1H), 2.01 – 2.10 (m, 1H), 2.18 (d, *J* = 2.4 Hz, 1H), 2.24 – 2.31 (m, 1H), 2.46 (ddd, *J* = 10.4, 4.4, 2.4 Hz, 1H), 3.35 (br, 1H), 3.91 (m, 4H), 5.12 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.34 (td, *J* = 6.4, 0.8 Hz, 1H), 5.86 (m, 1H), 9.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 19.6, 26.8, 36.9, 38.4, 66.2, 70.8, 73.2, 78.0, 81.9, 116.8, 121.7, 134.8, 138.6, 203.3.; IR (neat) ν_{max} 3430, 3295, 3080, 2935, 2859, 1732, 1669, 1646, 1452, 1349 cm^{-1}. HRMS[ES+] calcd for $C_{15}H_{22}O_3$ $[M + H]^+$ 251.1647, found 251.1657.



11 **5a** **13a**

Diols 5a and 13a. The allylation procedure of Luche et al. was used.[6] To a stirred solution of aldehyde **11** (374 mg, 1.43 mmol) in THF (10 mL) and saturated aq. NH_4Cl (5 mL) were added 2-bromo-methyl-3-methyl-1-butene **12** (1.07 g, 6.57 mmol) and activated Zn dust (683 mg, 10.5 mmol). The reaction mixture was stirred for 12 h under argon and diluted with Et_2O (10 mL). The resulting mixture was filtered through Celite and the filter cake was washed with Et_2O. After separation of the layers, the aqueous phase was extracted with Et_2O (10 mL X 3). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was subjected to column chromatography (elution with EtOAc : Hexane = 1 : 4) to afford a mixture of **5a** and **13a** (398 mg, 80 %, d.r. **5a** : **13a** = 1.8 : 1.0)[7].

A sample of the mixture was subjected to additional chromatography and spectroscopic data were obtained for each isomer.

Slower moving isomer, later shown to be 5a (colorless oil) : ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 1.32 (s, 3H), 1.57 (m, 1H), 1.69 (s, 3H), 1.97 (m, 1H), 2.02 (m, 1H), 2.07 – 2.14 (m, 3H), 2.29 (m, 1H), 2.37 (m, 1H), 2.47 (dt, *J* = 11.5, 2.6 Hz, 1H), 2.58 (d, *J* = 13.5 Hz, 1H), 3.79 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.98 (dd, *J* = 11.5, 6.0 Hz, 4H), 4.84 (s, 1H), 4.98 (s,1H), 5.17 (d, *J* = 10.5 Hz, 1H), 5.27 (dd, *J* = 15.5, 1.5, 1H), 5.43 (td, *J* = 5.5, 1.0 Hz, 1H), 5.89 – 5.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 20.7, 21.4, 22.2, 26.9, 33.0, 36.2, 37.7, 38.4, 66.5, 70.9, 71.8, 71.9, 74.7, 84.2, 110.8, 116.9, 121.3, 135.0,

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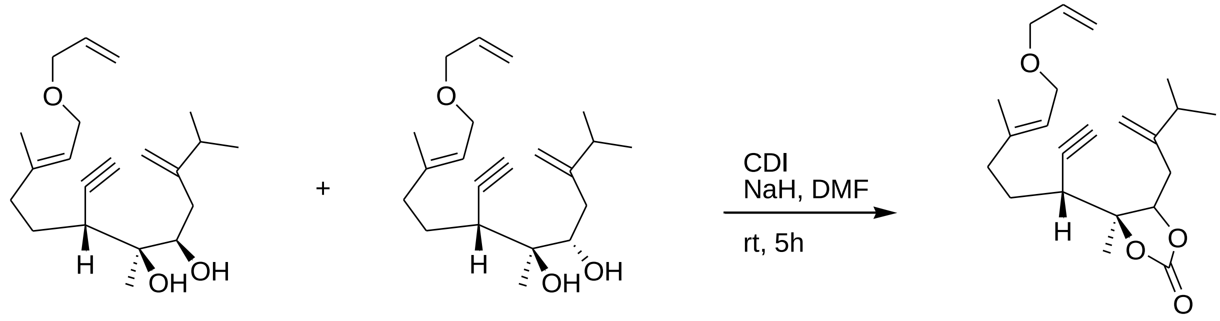
[6] Petrier, C.; Einhorn, J.; Luche, J.L. *Tetraheron Lett.* **1985**, *26*, 1449.

[7] The diastereomer ratio was determined by ^{1}H NMR.

139.7, 153.2.; IR (neat) ν_{max} 3454, 3307, 3081, 2962, 2871, 1640, 1455, 1379 cm^{-1}. HRMS[ES+] calcd for $C_{21}H_{34}O_3$ [M + Na]$^+$ 357.2406, found 357.2398.

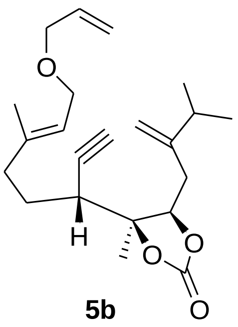
Faster moving isomer, later shown to be 13a (white solid) : ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.07 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.16 (s, 3H), 1.53 (m, 1H), 1.68 (s, 3H), 1.96 (m, 1H), 2.05 – 2.11 (m, 1H), 2.11 (d, *J* = 2.4 Hz, 1H), 2.13 – 2.19 (m, 1H), 2.18 (d, *J* = 2.0 Hz, 1H), 2.25 (s, 1H), 2.25 – 2.30 (m, 1H), 2.33 – 2.40 (m, 1H), 2.41 (d, *J* = 14.0 Hz, 1H), 2.71 (dt, *J* = 11.6, 2.8 Hz, 1H), 3.96 (dt, *J* = 6.0, 1.2 Hz, 2H), 3.99 – 4.02 (m, 3H), 4.85 (s, 1H), 4.99 (s, 1H), 5.17 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.27 (dq, *J* = 17.6, 1.6 Hz, 1H), 5.42 (td, *J* = 6.8, 0.8 Hz, 1H), 5.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.5, 17.6, 21.5, 22.2, 26.7, 33.3, 36.4, 37.9, 39.5, 66.5, 70.8, 70.9, 71.3, 75.2, 85.3, 110.6, 116.9, 121.3, 135.0, 139.8, 153.0.; IR (neat) ν_{max} 3382, 3304, 3229, 2961, 2916, 2850, 1643, 1455, 1391 cm^{-1}. HRMS[ES+] calcd for $C_{21}H_{34}O_3$ [M + Na]$^+$ 357.2406, found 357.2401. mp = 53 - 55 °C.



5a **13a** **5b + 13b**

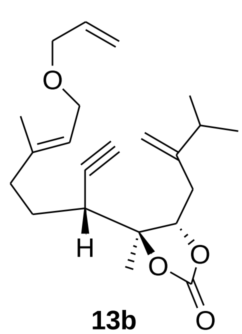
Carbonates 5b+**13b**. To a stirred solution of the mixture of **5a** and **13a** (177 mg, 0.528 mmol) in DMF (1.7 mL) under argon was added NaH (44.3 mg, 60%, 1.11 mmol). The reaction mixture was stirred for 15 min and then 1,1'-carbonyldiimidazole (CDI) (530 mg, 3.17 mmol) was added slowly. The resulting mixture was stirred at room temperature for 4 h. Et_2O and saturated aq. NH_4Cl were added and the resulting mixture was stirred for 10 min. After separation of the two layers, the organic solution was washed with water (1.5 mL X 3) and brine and then dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (elution with EtOAc : hexane = 1 : 4) to provide a mixture of carbonates **5b** and **13b** (175 mg, 92 %) as a colorless oil. Without further purification, the mixture of carbonate **5b** and **13b** was directly used for the next step.

For the purpose of characterization, each carbonate isomer was prepared from the corresponding diol (see above).

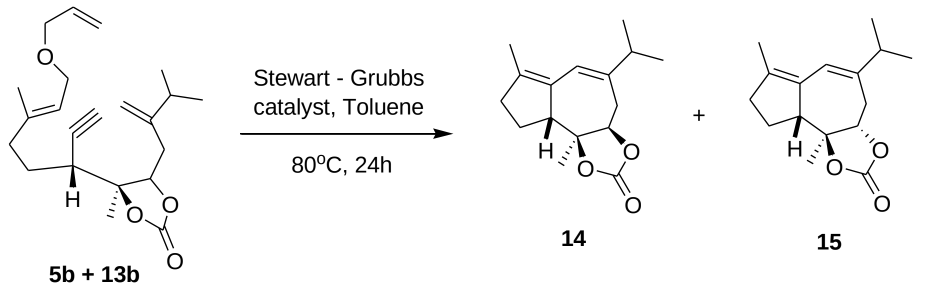


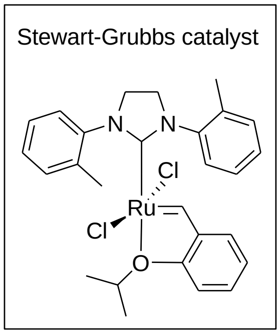
5b

5b : ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.04 (t, J = 6.6 Hz, 6H), 1.56 (s, 3H), 1.65 (m, 1H), 1.66 (s, 3H), 1.87 – 1.94 (m, 1H), 2.11 (m, 1H), 2.24 – 2.37 (m, 4H), 2.69 (d, *J* = 11.4 Hz, 1H), 2.81 (d, *J* = 15.0 Hz, 1H), 3.97 (dd, *J* = 12.6, 6.0 Hz, 4H), 4.46 (d, *J* = 12.0, 1H), 4.85 (s, 1H), 4.93 (s, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.28 (d, *J* = 18.0 Hz, 1H), 5.41 (t, *J* = 6.6 Hz, 1H), 5.87 – 5.94 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 16.3, 20.5, 21.4, 21.6, 27.4, 33.5, 33.7, 35.3, 36.9, 66.3, 71.0, 73.5, 81.9, 84.9, 85.7, 110.6, 116.9, 122.2, 134.8, 138.4, 149.5, 153.4.; IR (neat) ν_{max} 3288, 3083, 2964, 2872, 1808, 1646, 1455, 1384 cm^{-1}. HRMS[ES+] calcd for $C_{22}H_{32}O_4$ [M + Na]$^+$ 383.2198, found 383.2199


13b

13b : ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, *J* = 4.8 Hz, 3H), 1.06 (d, *J* = 4.8 Hz, 3H), 1.43 (s, 3H), 1.59 (m, 1H), 1.67 (s, 3H), 1.86 – 1.94 (m, 1H), 2.12 (m, 1H), 2.22 (d, *J* = 2.4 Hz, 1H), 2.26 – 2.38 (m, 2H), 2.40 (d, *J* = 10.4 Hz, 1H), 2.51 (d, *J* = 15.2 Hz, 1H), 2.65 (dt, *J* = 8.8, 2.4 Hz, 1H), 3.98 (m, 4H), 4.64 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.90 (s, 1H), 4.94 (s, 1H), 5.18 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.28 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.42 (t, *J* = 6.4 Hz, 1H), 5.88 – 5.98 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.7, 16.3, 21.5, 21.6, 27.0, 33.5, 35.4, 36.9, 41.3, 66.5, 71.1, 73.5, 81.2, 83.8, 85.8, 110.5, 117.0, 122.4, 134.9, 138.2, 149.9, 153.2.; IR (neat) ν_{max} 3288, 2962, 2871, 1805, 1646, 1455, 1385 cm^{-1}. HRMS[ES+] calcd for $C_{22}H_{32}O_4$ [M + Na]$^+$ 383.2198, found 383.2194.




Stewart-Grubbs catalyst

Bicyclic Dienes 14 and 15. To a stirred solution of the mixture of carbonates **5b** and **13b** (31.7 mg, 0.088 mmol) in toluene (8.8 mL) under Argon was added 30 mol % Stewart -Grubbs catalyst[8] (15.0 mg, 0.026 mmol). The resulting mixture was stirred at 80 °C for 24 h. After cooling down to room temperature, the reaction mixture was concentrated. The residue was subjected to silica gel flash column chromatography (elution with EtOAc : hexane = 1 : 4) to give diene **14** (10.3 mg, 45 %) as an oil and diene **15** (7.4 mg, 32 %) as an oil.

14 : ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, 3.2 Hz, 1H), 1.35 (d, *J* = 3.6 Hz, 3H), 1.33 (s, 3H), 1.74 (s, 3H), 1.89 – 1.95 (m, 1H), 1.99 – 2.07 (m, 1H), 2.31 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.35 – 2.37 (m, 3H), 2.97 (t, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 8.0 Hz, 1H), 4.27 (dd, *J* = 12.2, 3.8 Hz, 1H), 6.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.9, 20.9, 21.2, 23.3, 30.2, 37.5, 37.8, 50.8, 84.6, 87.1, 120.1, 131.2, 139.3, 139.6, 153.9.; IR (neat) ν_{max} 2960, 2927, 1805, 1466, 1383 cm^{-1}. HRMS[ES+] calcd for $C_{16}H_{22}O_3$ [M + Na]$^+$ 285.1467, found 285.1462.

15 : ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.6 Hz, 6H), 1.17 (s, 3H), 1.73 – 1.78 (m, 1H), 1.77 (s, 3H), 2.03 (m, 1H), 2.38 (sext, 4H), 2.67 (dd, *J* = 17.2, 4.4 Hz, 1H), 3.03 (m, 1H), 4.42 (dd, *J* = 12.0, 4.4 Hz, 1H), 6.19 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 14.5, 21.5, 22.1, 23.8, 28.4, 37.7, 39.0, 54.9, 84.9, 87.5, 118.5,

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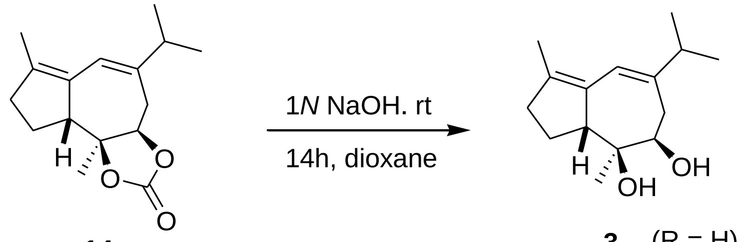
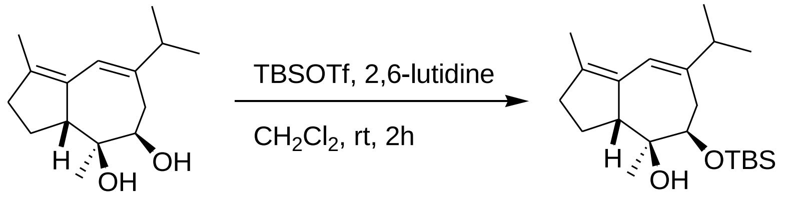
[8] Stewart, I.C.; Ung, T.; Pletnev, A.A.; Berlin, J.M.; Grubbs, R.H.; Schrodi, Y. *Org. Lett.* **2007**, *9*, 1589.

129.4, 137.1, 142.6, 154.9.; IR (neat) ν_{max} 2961, 2930, 1809, 1462, 1382 cm^{-1}. HRMS[ES+] calcd for $C_{16}H_{22}O_3$ [M + Na]$^+$ 285.1467, found 285.1470.



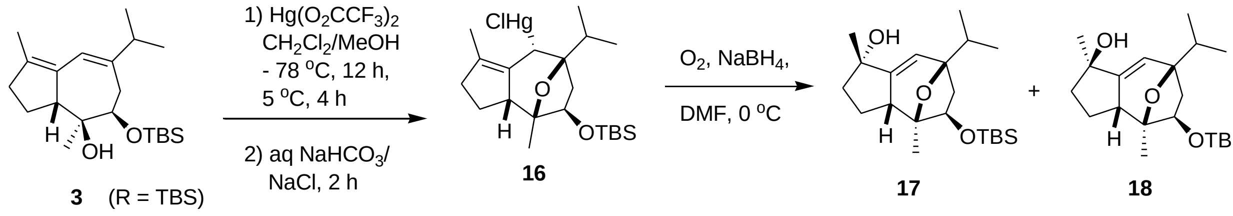
14 → **3** (R = H)

Diol 3 (R = H). To a stirred solution of carbonate **14** (67.2 mg, 0.256 mmol) in dioxane (3.2 mL) was added 1*N* NaOH (0.7 mL) and the resulting mixture was stirred for 14 h at room temperature. The reaction was quenched with saturated aq. NH_4Cl and the resulting mixture was diluted with Et_2O. After separation of layers, the aqueous layer was extracted with Et_2O (5 mL X 2) and the combined organic solution was washed with brine and water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to provide diol **3** (R = H) (58.7 mg, 97 %) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 1.02 (s, 3H), 1.04 (s, 3H), 1.13 (s, 3H), 1.73 (s, 3H), 1.90 – 2.02 (m, 2H), 2.06 (dd, *J* = 16.8, 1.2 Hz, 1H), 2.14 (s, 1H), 2.20 (dd, *J* = 16.8, 9.6 Hz, 1H), 2.33 (quint, *J* = 6.6 Hz, 1H), 2.41 (quint, *J* = 8.4 Hz, 1H), 2.56 (br, 1H), 2.73 (dd, *J* = 16.2, 10.2 Hz, 1H), 3.04 (d, *J* = 9.0 Hz, 1H), 3.45 (d, *J* = 9.0 Hz, 1H), 6.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.7, 21.1, 21.5, 24.3, 34.4, 37.6, 37.8, 53.7, 76.8, 77.2, 119.0, 132.7, 137.2, 144.6.; IR (neat) ν_{max} 3396, 2959, 2924, 1714, 1557, 1463, 1379 cm^{-1}. HRMS[ES+] calcd for $C_{15}H_{24}O_2$ [M + Na]$^+$ 259.1674, found 259.1685.



3 (R = H) → **3** (R = TBS)

Cyclization Substrate 3 (R = TBS). To a stirred solution of diol **3** (R = H) (8.5 mg, 36 μmol) in CH_2Cl_2 (2.0 mL) under argon was added 2,6-lutidine (9.2 mg, 86 μmol). Then TBSOTf (11.4 mg, 43.0 μmol) was added dropwise and the resulting mixture was stirred for 2 h, quenched with water, and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (1 mL X 3) and the combined organic solution was dried over $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel flash column chromatography (elution with EtOAc : hexane = 1 : 20). Alcohol **3** (R = TBS) (11.7 mg, 93 %) was isolated as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.12 (s, 3H), 0.92 (s, 9H), 1.03 (dd, *J* = 6.8, 1.6 Hz, 6H), 1.04 (s, 3H), 1.74 (s, 3H), 1.81 (dd, *J* = 20.8, 1.6 Hz, 1H), 1.90 – 1.98 (m, 1H), 2.02 – 2.07 (m, 1H), 2.17 (dd, J = 16.7, 9.6 Hz, 1H), 2.31 (quint, J = 6.8 Hz, 1H), 2.37 – 2.46 (m, 1H), 2.89 (dd, J = 16.8, 9.6, 1H), 3.03 (d, J = 4.8 Hz, 1H), 3.11 (s, 1H), 3.43 (dd, J = 10.8, 1.6 Hz, 1H), 6.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.8, -3.8, 14.3, 18.0, 21.2, 21.5, 21.9, 24.7, 25.9, 34.3, 37.8, 37.9, 53.1, 76.0, 78.8, 119.1, 133.1, 136.8, 145.2. IR (neat) ν_{max} 3544, 2956, 2930, 2857, 1651, 1472, 1361 cm^{-1}. HRMS[ES+] calcd for $C_{21}H_{38}O_2Si$ [M + Na]$^+$ 373.2539, found 373.2535.



Alcohols 17 and 18. Oxymercuration was carried out according to a hybrid procedure derived from related literature.[9] To a stirred solution of alcohol **3** (R = TBS, 16.0 mg, 45.6 µmol) in CH_2Cl_2 (2 mL) under argon was added MeOH (5.0 mg) at room temperature. The reaction mixture was cooled to -78 °C, $Hg(O_2CCF_3)_2$ (23.8 mg, 54.8 µmol) was added, and stirring was continued for 24 h. Then additional $Hg(O_2CCF_3)_2$ (5.9 mg, 14 µmol) was added and the reaction mixture was slowly warmed to 5 °C over 3.5 h. The reaction was quenched with saturated aq. $NaHCO_3$ (2 mL) and then saturated aq. NaCl (2 mL). The resulting mixture was stirred at room temperature for 2 h, and then extracted with Et_2O (5 mL X 3). The ether solution was washed with brine and then with water, dried over $MgSO_4$, and concentrated under reduced pressure to provide an organomercurial intermediate **16**. Without further purification, the crude product was directly used for the next step. **16**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.02 (s, 3H), 0.30 (s, 3H), 0.88 (s, 9H), 1.2 (d, J = 6.0 Hz, 1H), 1.45 (s, 3H), 1.17 (d, J = 6.6 Hz, 1H), 1.26 – 1.34 (m, 1H),1.81 – 1.96 (m, 4H), 2.00 (s, 3H), 2.31 – 2.40 (m, 2H), 2.71 (m, 1H), 2.93 (s, 1H), 3.99 (dd, J = 7.2, 3.0 Hz, 1H).

Oxidative demercuration was accomplished according to Hill and Whitesides.[10] A stream of oxygen gas was bubbled into a solution of $NaBH_4$ (9.5 mg, 0.11 mmol) in DMF (3.5 mL) at 0°C for 30 min. To the resulting mixture was added dropwise a solution of the alkylmercurial **16** in DMF (0.7 mL) by syringe pump at 0 °C for 1h. During this time, oxygen bubbling was continued. The syringe was filled with DMF (0.2 mL) and this wash was added dropwise (oxygen bubbling continued). When addition was complete, the resulting mixture was warmed slowly to room temperature over 2.5 h (oxygen bubbling continued). The reaction mixture was quenched with 1*N* HCl, diluted with Et_2O (15 mL), and filtered through Celite. Water and Et_2O were added to the filtrate and the layers were separated. The organic solution was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to silica gel

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[9] (a) Broka, C. A.; Lim, Y.-T. *J. Org. Chem.* **1988**, *53*, 5876. (b) Kang, S.H.; Kim, M.; Kang, S. Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 6177 (c) Ushakov, D. B.; Navickas, V.; Ströbele, M.; Maichle-Mössmer, C.; Sasse, F.; Maier, M.E. *Org. Lett.* **2011**, *13*, 2090.

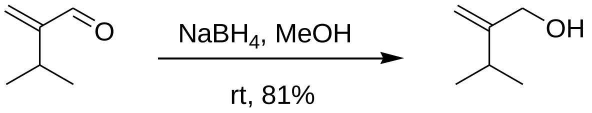
[10] Hill, C. L.; Whitesides, G.M. *J. Am. Chem. Soc.* **1974**, *96*, 870.

Flash column chromatography (elution with EtOAc : hexane = 1 : 3) to afford the known **17** (9.2 mg, 55 % for 2 steps) as an oil and its isomer **18** (6.2 mg, 37 % for 2 steps), also as an oil.

Compound **17** : ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.88 (s, 9H), 0.93 (d, *J* = 6.0 Hz, 3H), 0.97 (d, *J* = 6.0 Hz, 3H), 1.26 (s, 3H), 1.36 (s, 3H), 1.39 – 1.41 (m, 1H), 1.56 – 1.58 (m, 2H), 1.73 – 1.78 (m, 3H), 1.91 (hept, *J* = 6.6 Hz, 1H), 2.30 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.70 (m, 1H), 4.13 (t, *J* = 6.0, 1H), 5.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.5, 17.8, 17.7, 18.0, 20.7, 23.5, 25.8, 28.0, 34.1, 41.0, 50.2, 51.0, 73.4, 77.4, 83.3, 85.1, 119.3, 148.9.; IR (neat) ν_{max} 3419, 2959, 2929, 2857, 1472, 1386 cm^{-1}. ^{1}H NMR and ^{13}C NMR data were consistent with the reported values.[11]

Compound **18** : ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H), 0.02 (s,3H), 0.88 (s, 9H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.17 – 1.24 (m, 1H), 1.26 (s, 3H), 1.37 (s, 3H), 1.60 (m, 1H), 1.70 (m, 1H), 1.84 – 1.97 (m, 1H), 2.26 (dd, *J* = 11.2, 7.2, 1H), 3.07 (td, *J* = 9.2, 2.4 Hz, 1H), 4.01 (m, 1H), 5.65 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) -5.0, -4.5, 17.7, 17.8, 18.0, 20.7, 22.9, 25.5, 25.8, 34.0, 40.8, 49.5, 50.8, 73.4, 77.1, 83.1, 85.2, 120.0, 146.7.; IR (neat) ν_{max} 3373, 2959, 2930, 2857, 1463, 1386 cm^{-1}.

2-(1-Methylethyl)-2-propen-1-ol



2-(1-Methylethyl)-2-propenal, was prepared according to Breit et al.[12] To a stirred solution of this aldehyde (3.04 g, 30.1 mmol) in MeOH (50 mL) was added $NaBH_4$ (1.17 g, 30.1 mmol) at 0 °C. After stirring at room temperature for 1 h, the reaction was quenched with saturated NH_4Cl (8 mL). The resulting mixture was diluted with H_2O (12 mL) and Et_2O (20 mL) then filtered through Celite to remove the white solids. Volatile organic solvent was carefully removed under reduced pressure (note the volatility of the product) and the residue was extracted with CH_2Cl_2 (15 mL X 4). The combined organic solution was concentrated and purified by silica gel column chromatography (elution with EtOAc : Hexane = 1 : 9) to provide 2-(1-methylethyl)-2-propen-1-ol (2.51 g, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.01 (s, 3H), 2.26 (sept, *J* = 6.8 Hz, 1H), 2.43 (br, 1H), 4.05 (s, 2H), 4.82 (m, 1H), 4.94 (m, 1H). ^{1}H NMR data were consistent with the reported values.[13]

2-Bromo-methyl-3-methyl-1-butene (**12**) was prepared from this alcohol according to Barton et al.[13]

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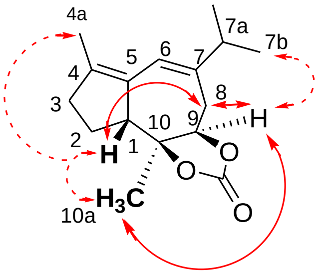
[11] Molawi, K.; Delpont, N; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2010**, *49*, 3517-3519

[12] Breit, B.; Heckmann, G.; Zahn, S. K. *Chem. Euro. J.* **2003**, *9*, 425.

[13] Barton, D. H.; Shioiri, T.; Widdowson, D. A.; *J. Chem. Soc. C*, **1971**, 1968

Difference NOE for compound **14**



Difference NOE chart for compound **14**

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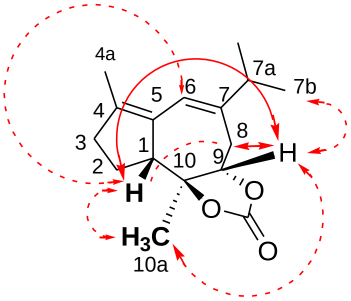
CH (1, 3.64)	CH_3 (10a, 1.33), CH_3 (4a, 1.74), CH_2 (1.89 – 1.95), CH_2 (2, 1.99 – 2.07), CH_2 (2.35 – 2.37), CH_2 (8, 2.97)
CH (9, 4.27)	CH3 (7b, 1.04), CH_3 (10a, 1.33), CH_2 (2.31), CH_2 (8, 2.97)

Difference NOE for compound **15**



Difference NOE chart for compound **15**

Inverted peak (C_{number}, ppm)	Enhanced peaks (C_{number}, ppm)
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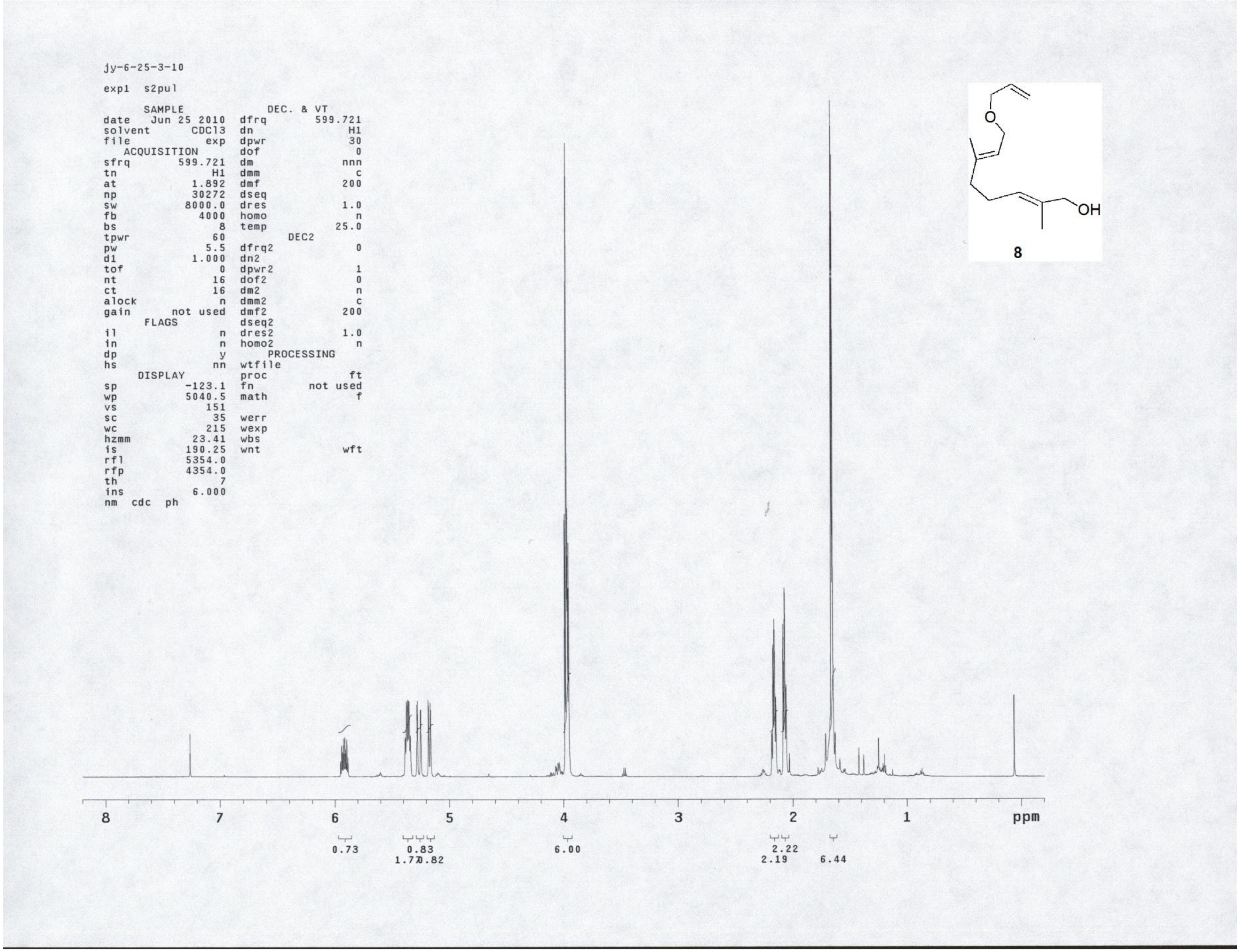
CH (1, 3.03)	CH (10a, 1.17), CH_2 (1.73 – 1.78), CH_2 (2.38), CH_2 (2, 2.03), CH (9, 4.42), CH (6, 6.19)
CH (9, 4.42)	CH3 (7b, 1.04), CH (10a, 1.17), CH_2 (2.38), CH_2 (8, 2.67), CH (1, 3.03), CH (6, 6.19)



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tn              H1  dmm              c
at           1.892  dmf            200
np           30272  dseq
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bs               8  temp          25.0
tpwr            60          DEC2
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ct              16  dm2              n
alock            n  dmm2             c
gain      not used  dmf2           200
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il               n  dres2          1.0
in               n  homo2            n
dp               y       PROCESSING
hs              nn  wtfile
     DISPLAY        proc            ft
sp          -123.1  fn        not used
wp          5040.5  math             f
vs             151
sc              35  werr
wc             215  wexp
hzmm         23.41  wbs
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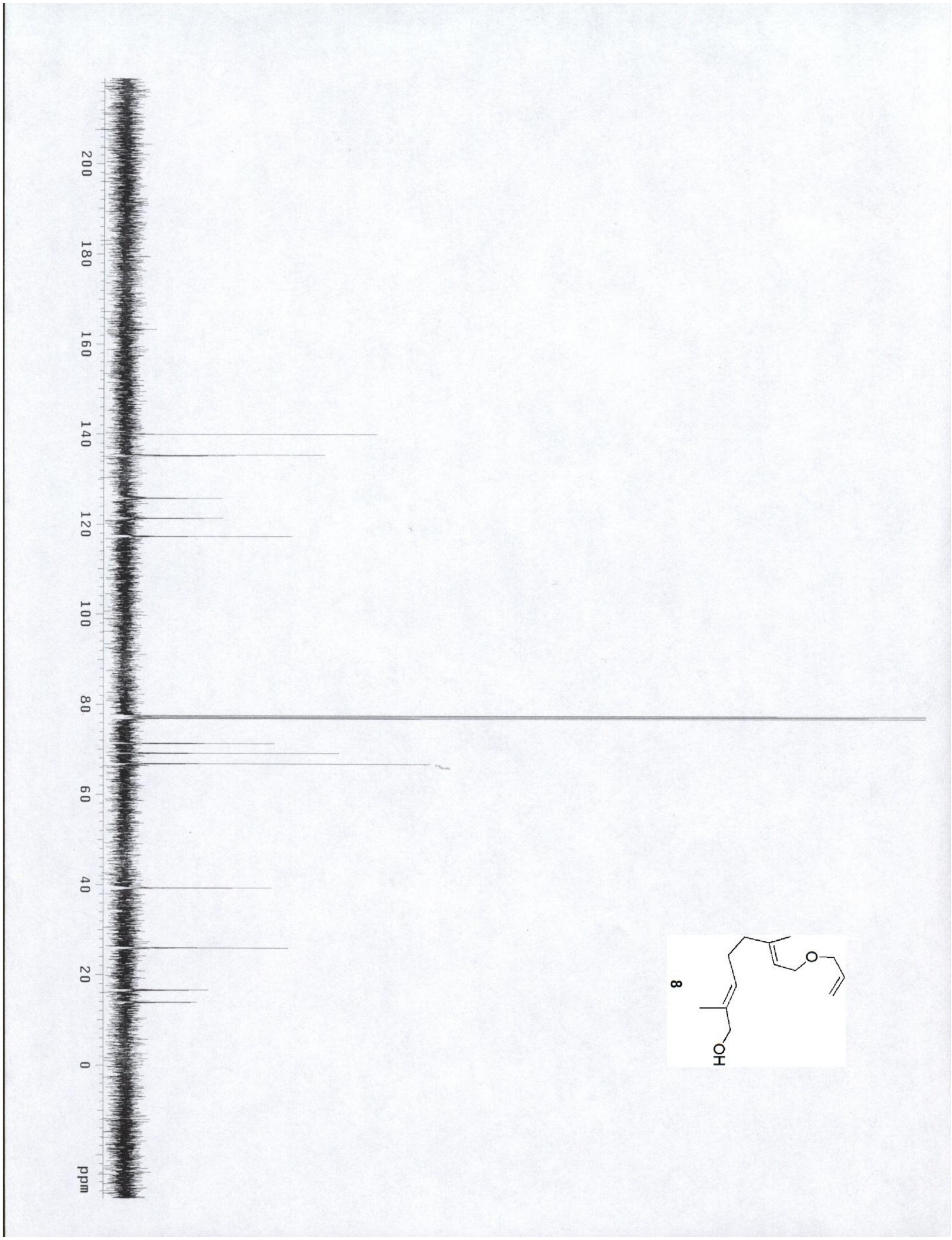
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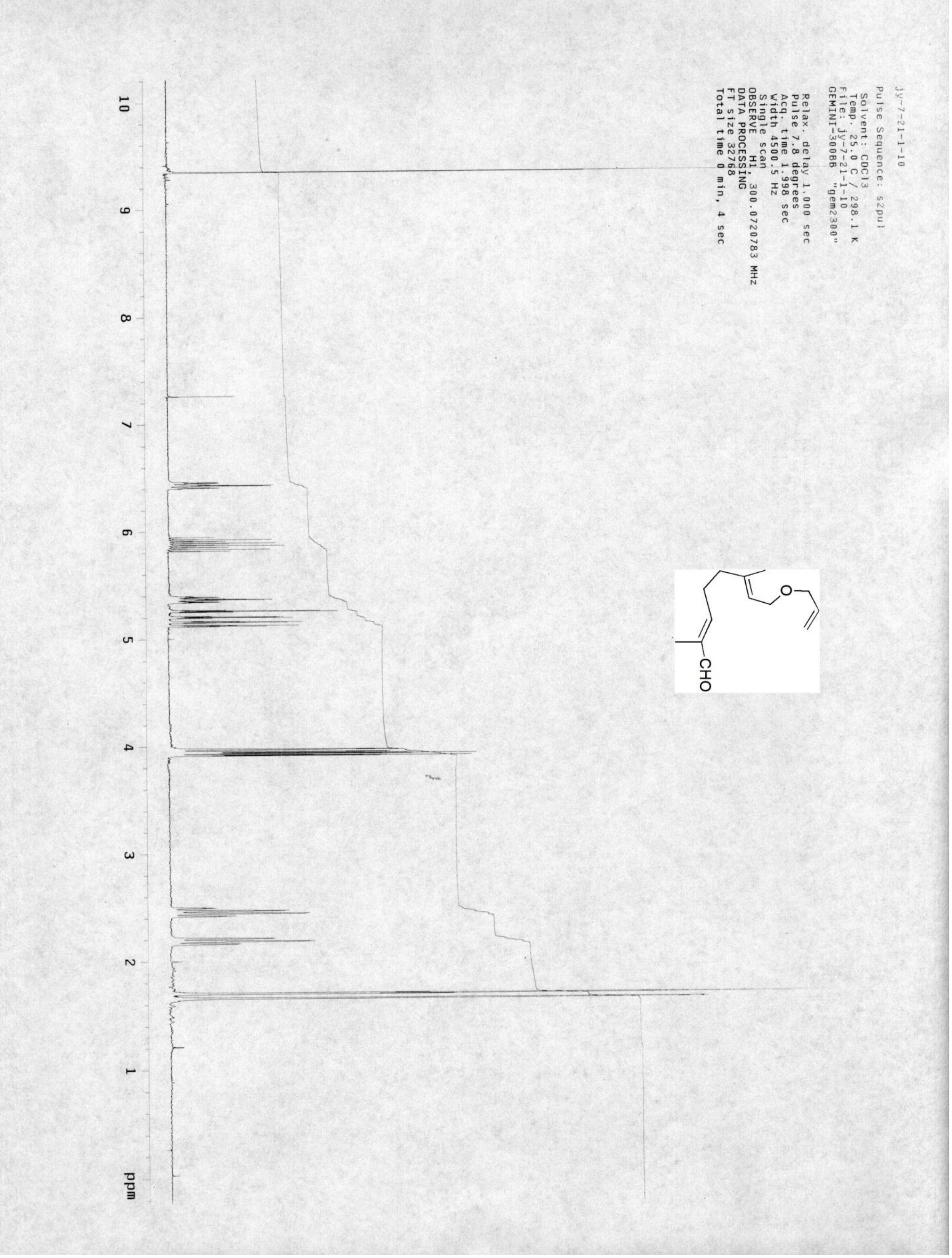
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Single scan
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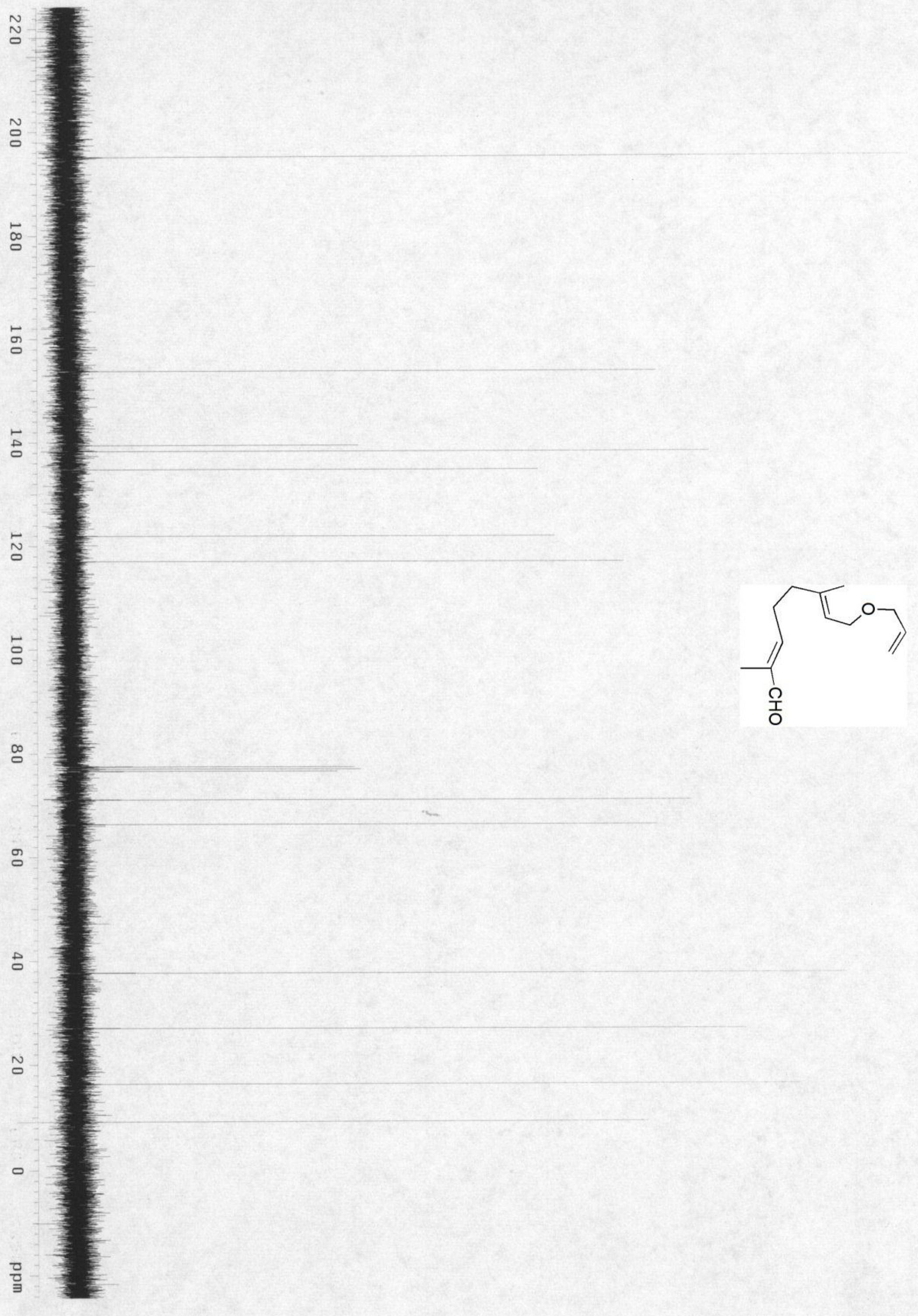
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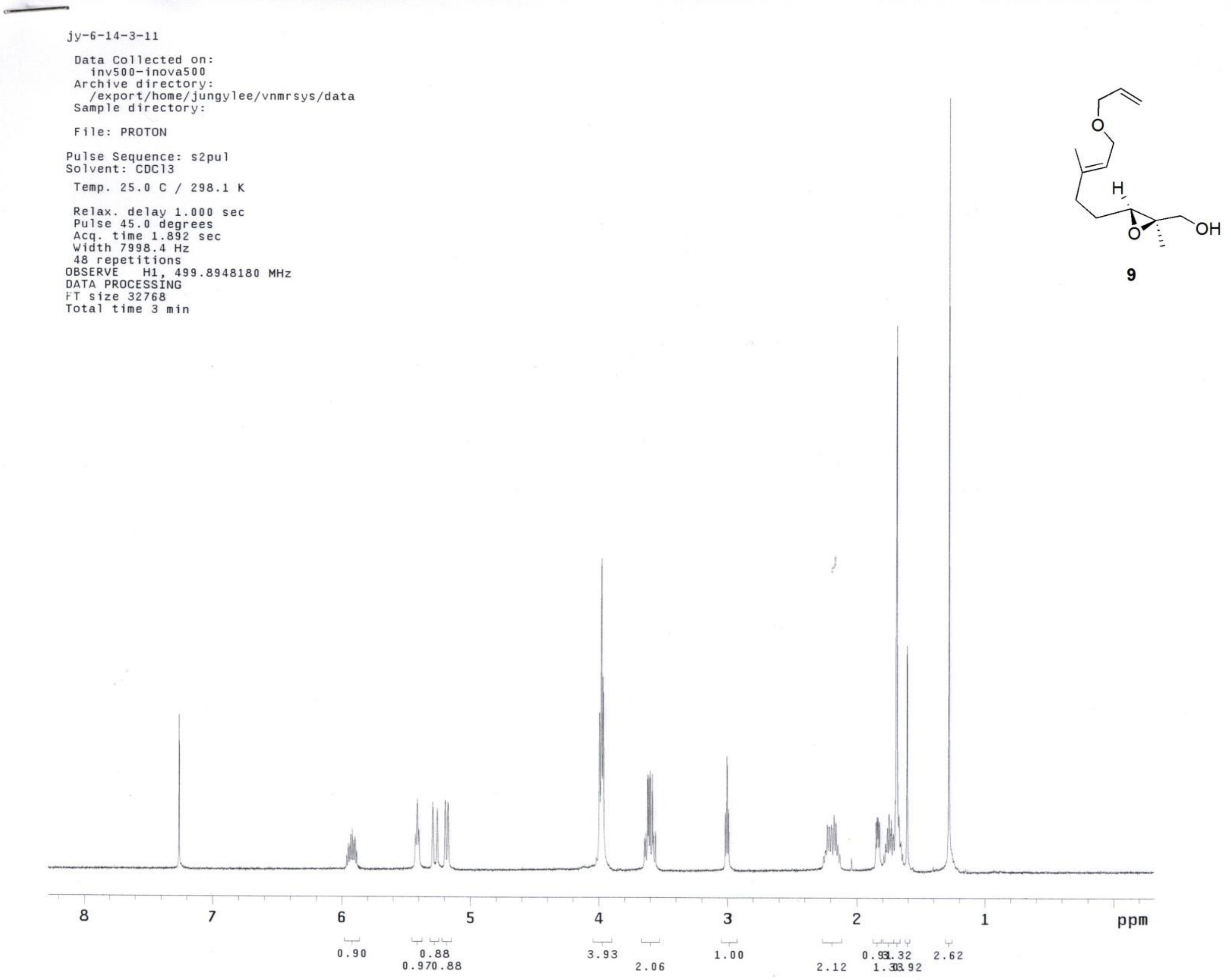

9

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Sample directory:

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JY-6-14-3-11 (#623).

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STANDARD CARBON PARAMETERS

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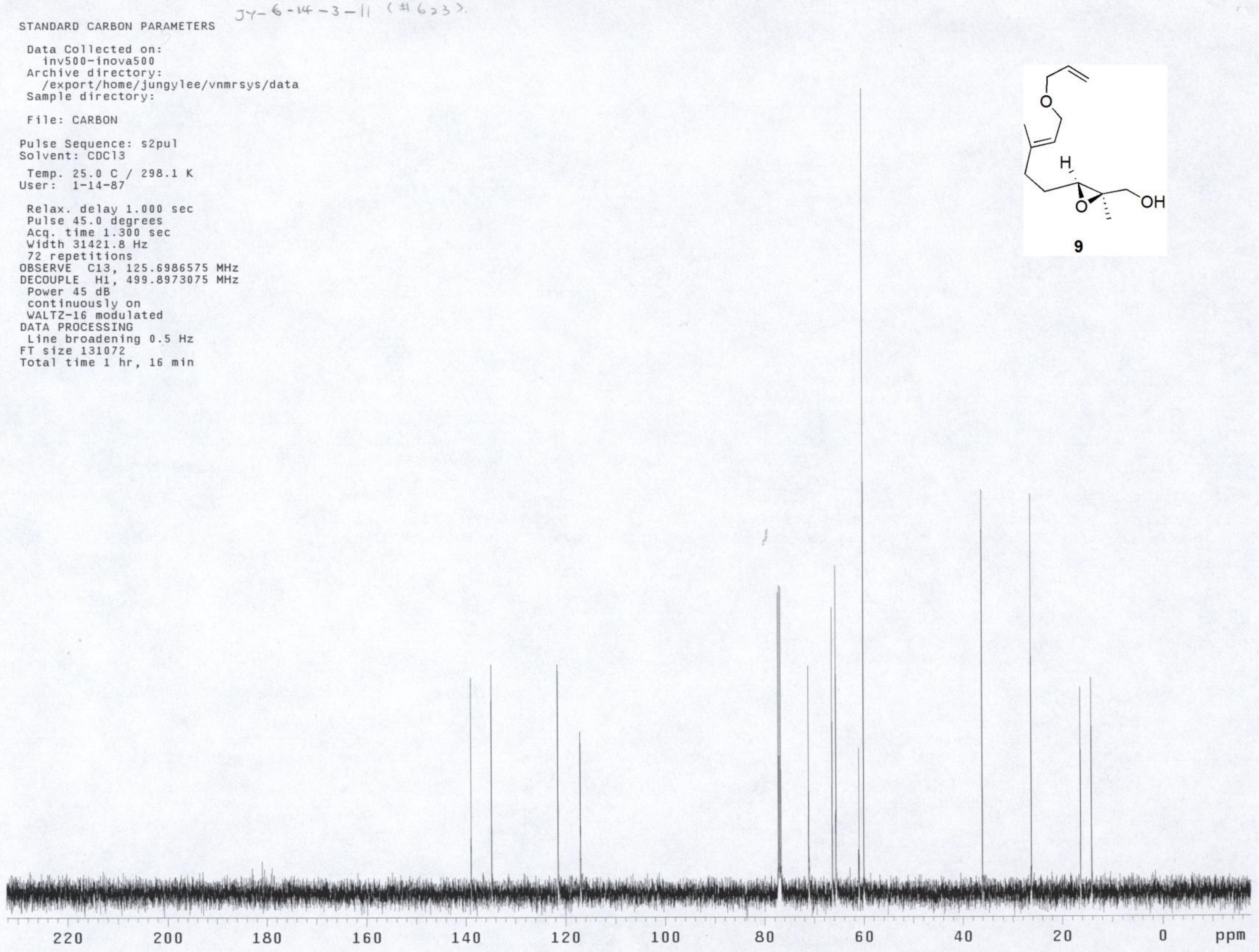

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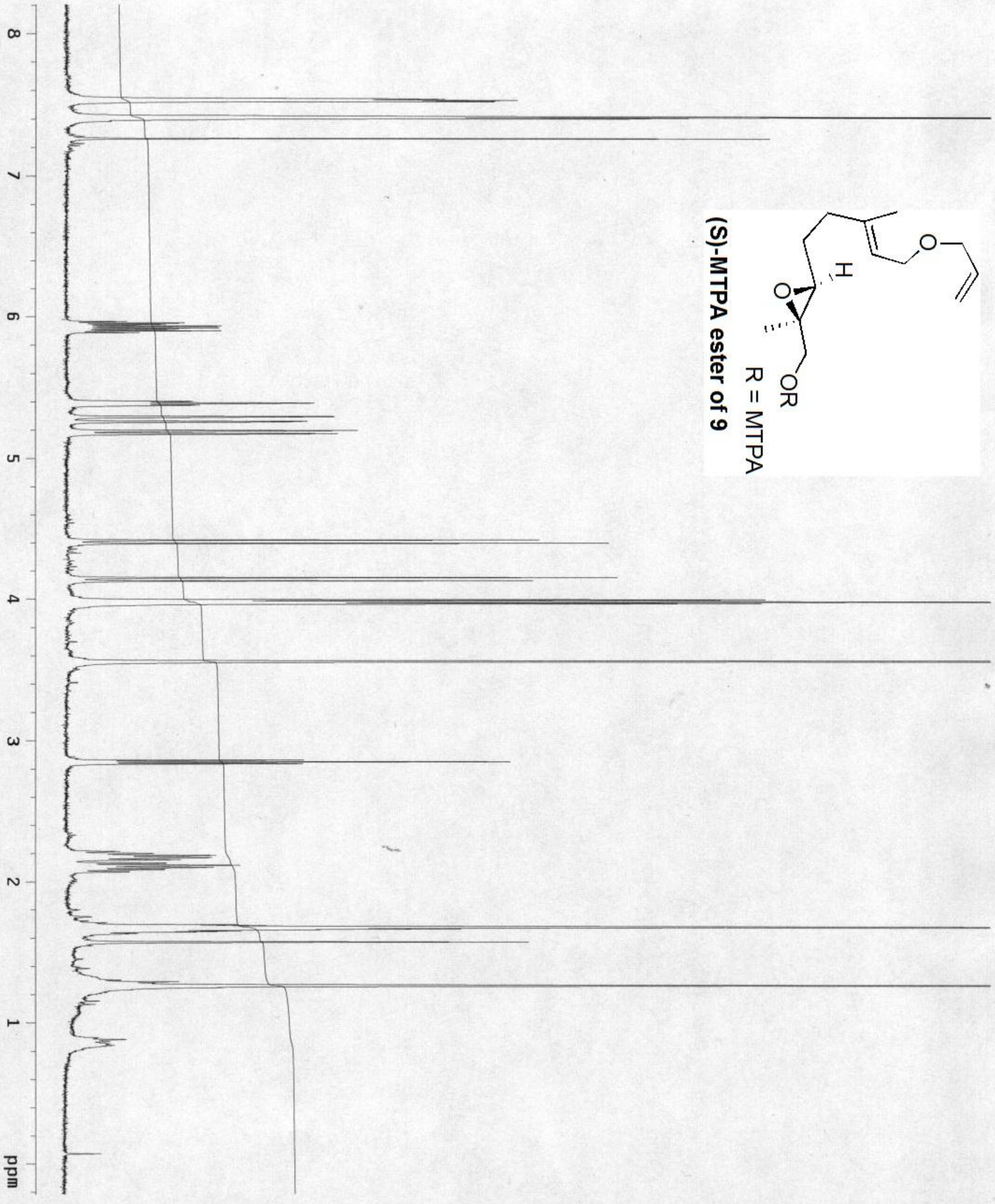
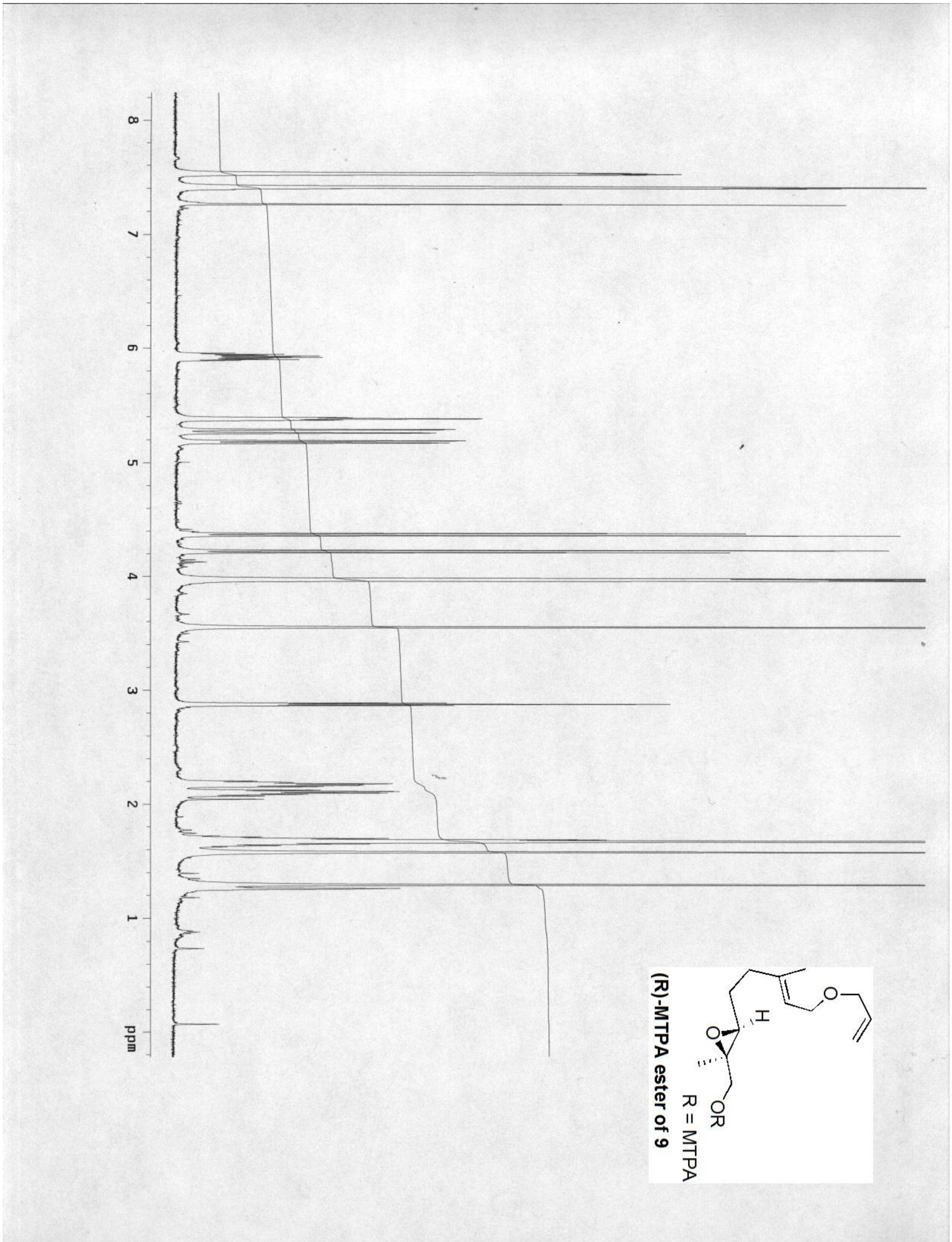
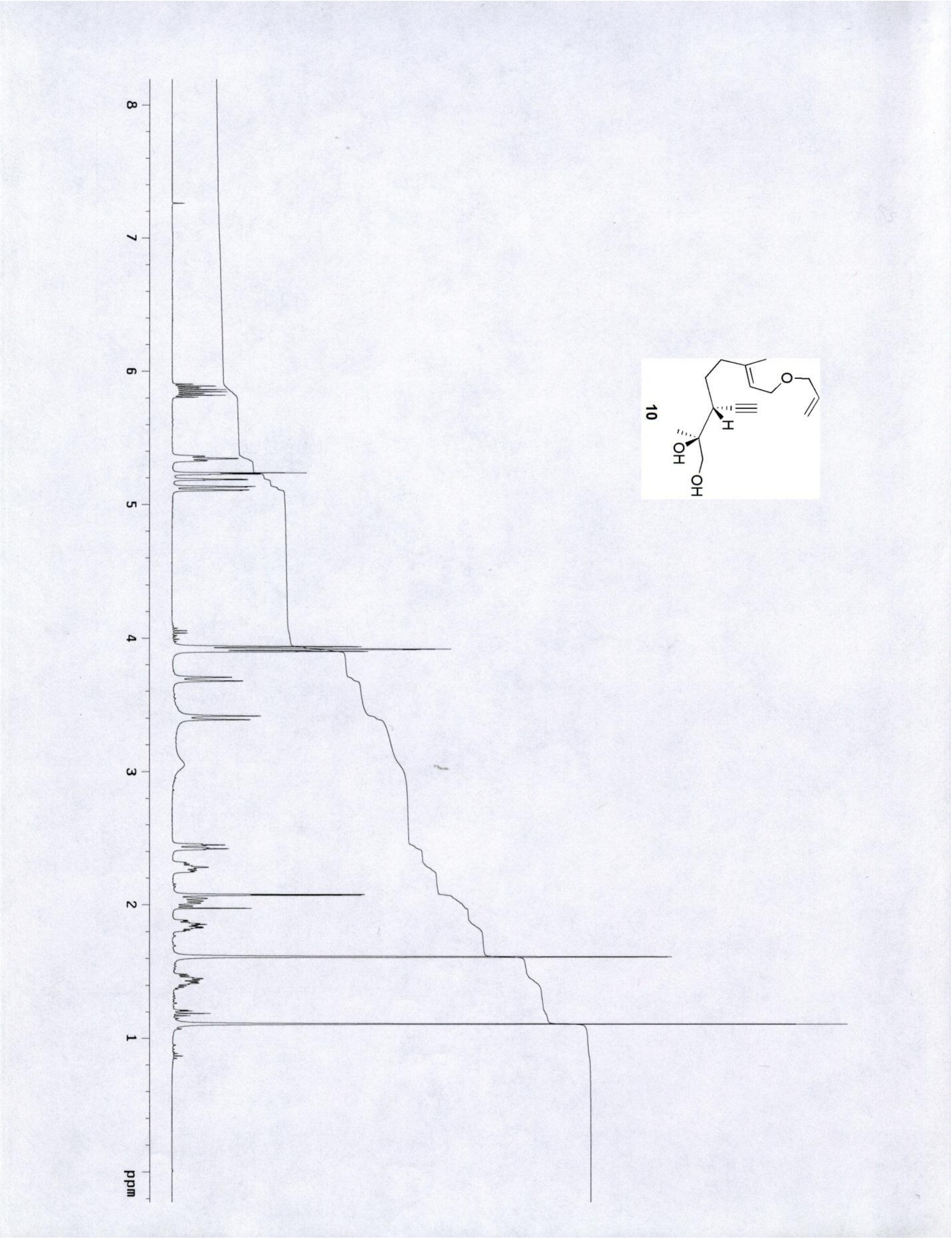
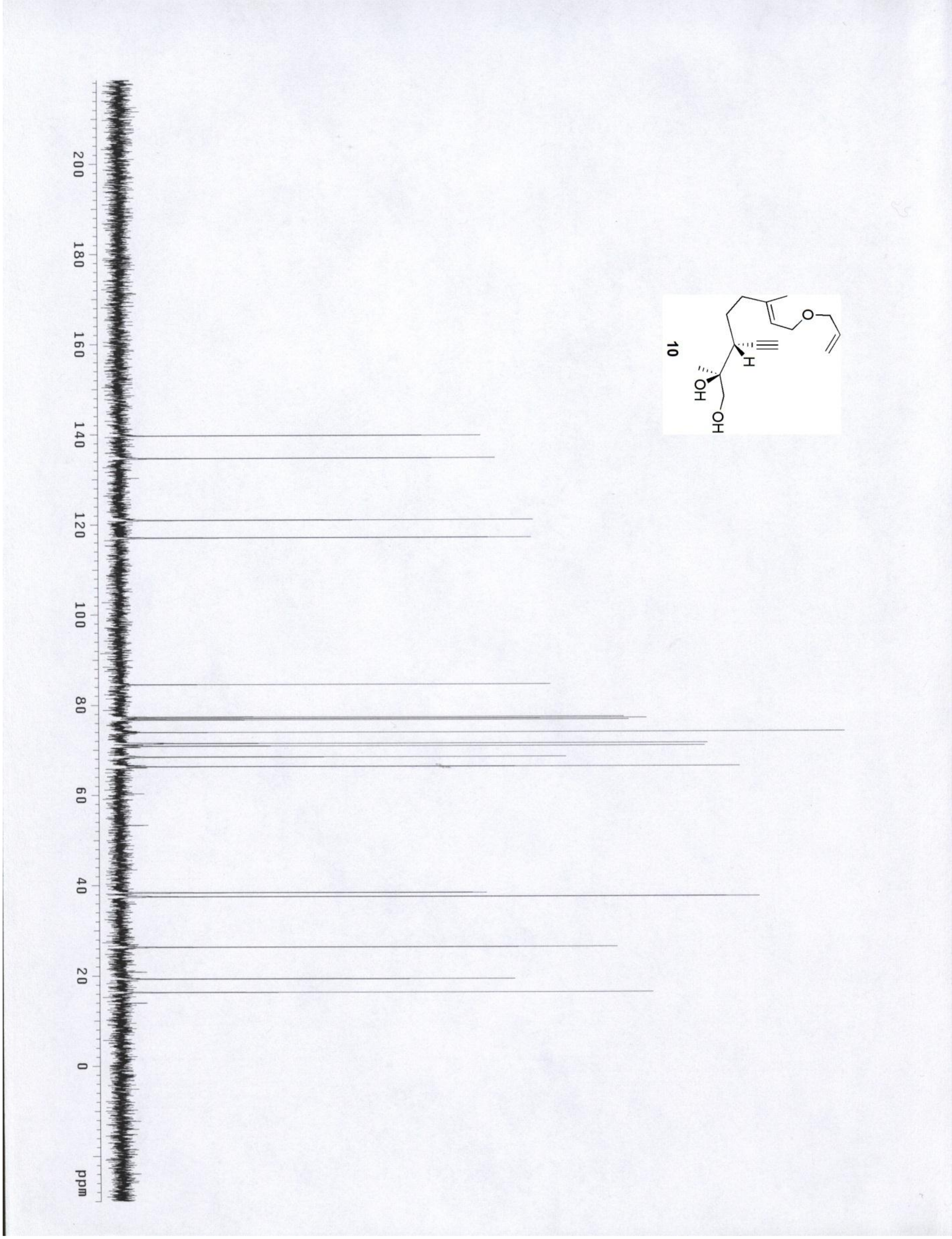


(S)-MTPA ester of 9



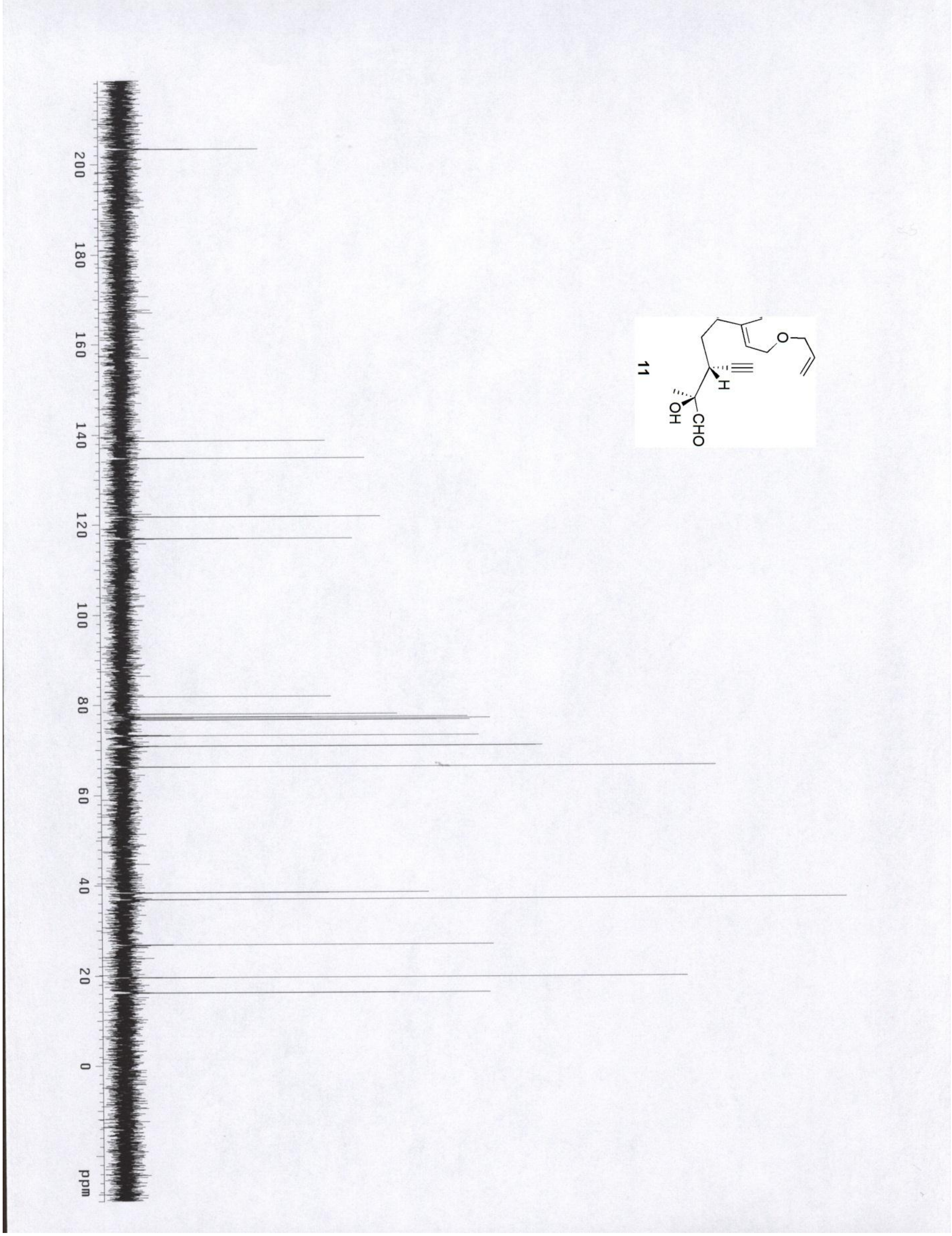
(R)-MTPA ester of 9


8
7
6
5
4
3
2
1
ppm
10
OH
OH
H

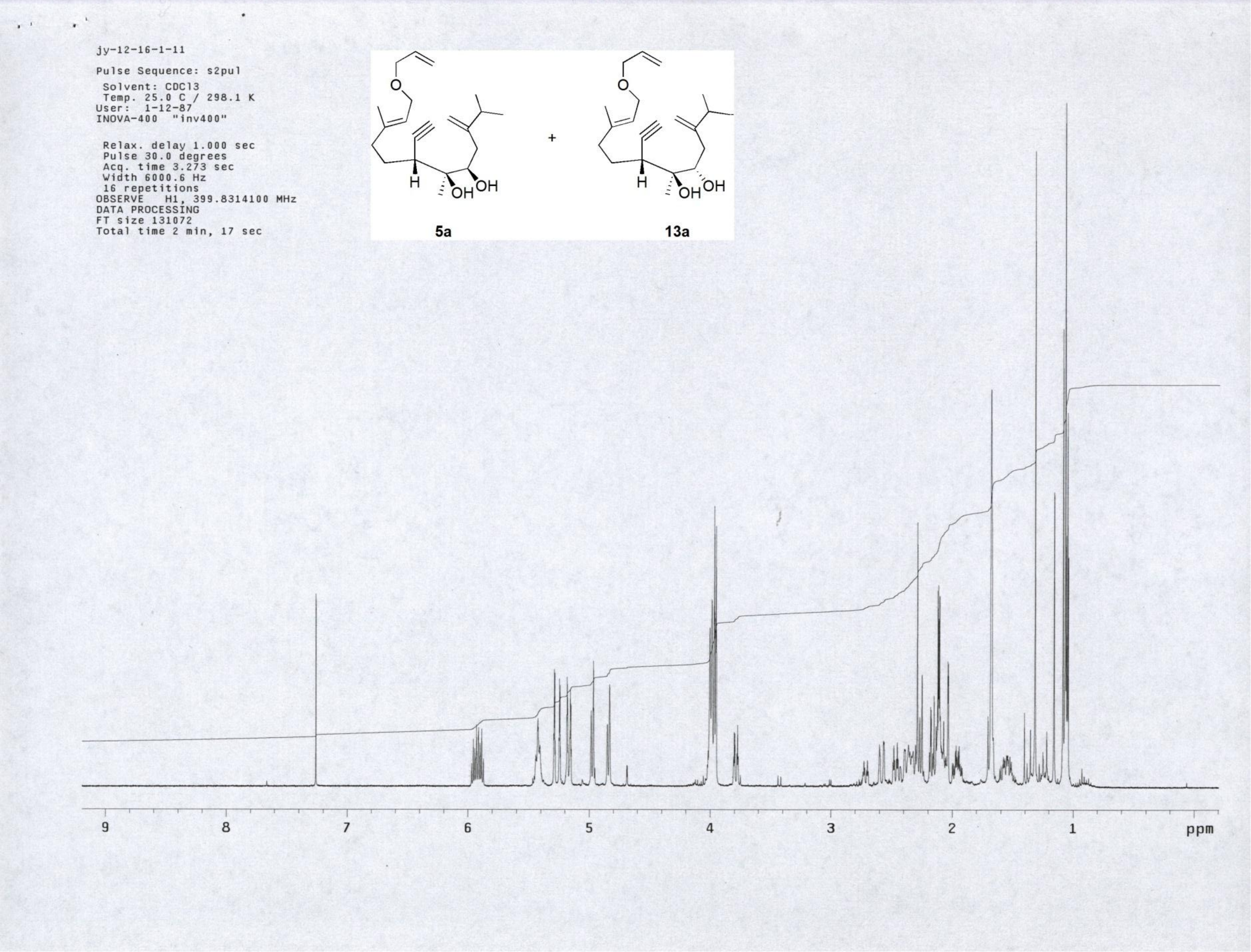


10


12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
CHO
OH
H
O
11



11



jy-12-16-1-11

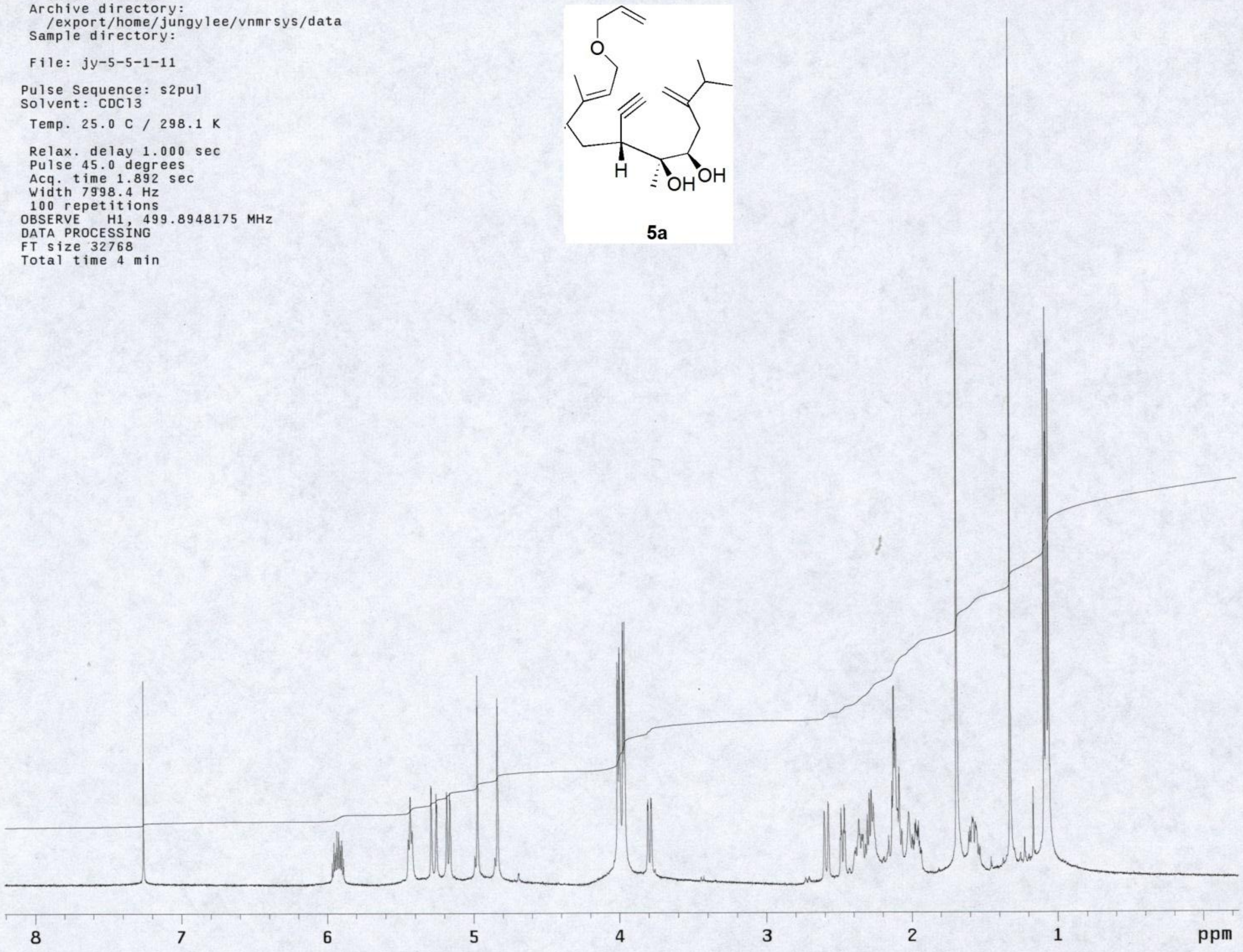
Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
User: 1-12-87
INOVA-400 "inv400"

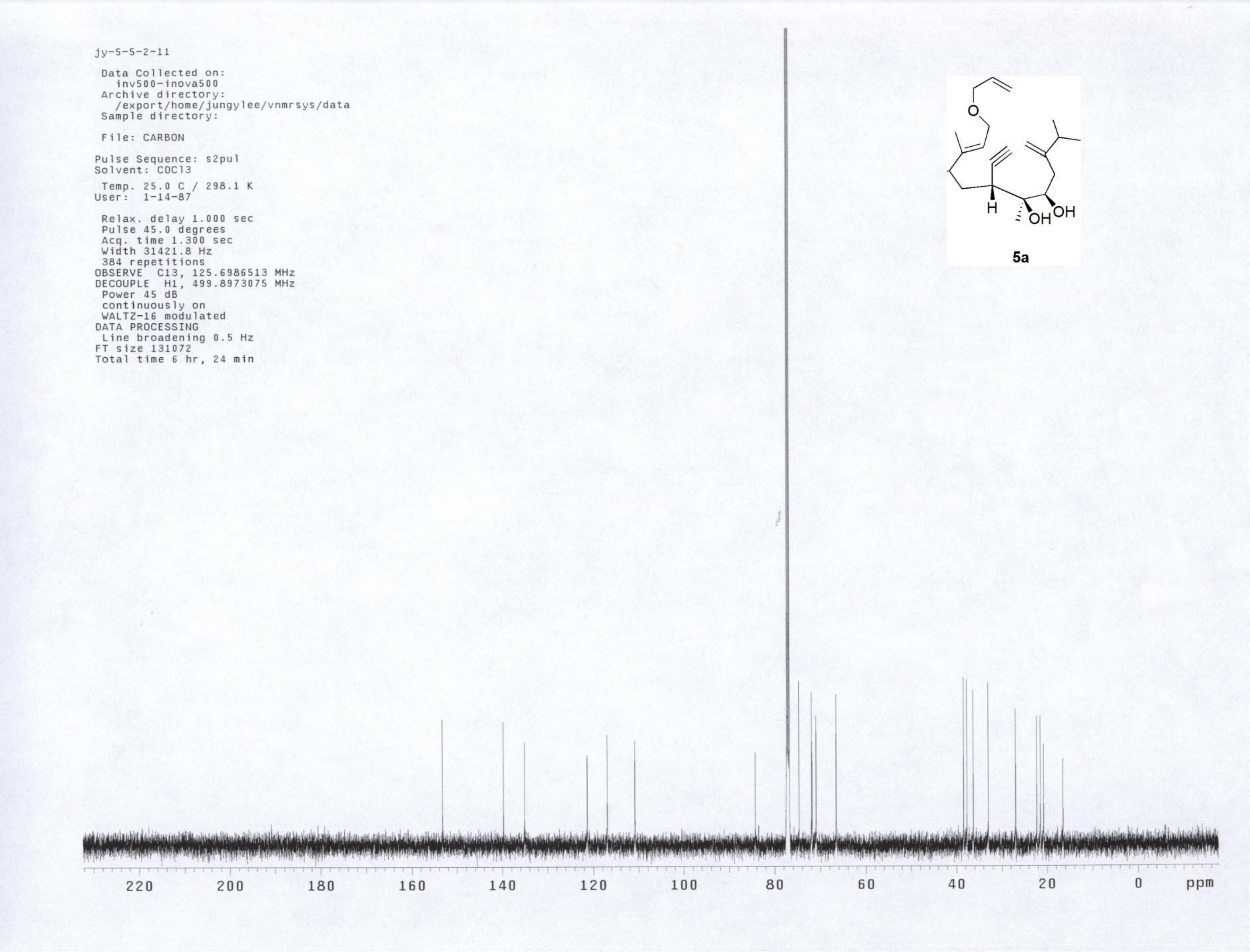
 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 3.273 sec
 Width 6000.6 Hz
 16 repetitions
OBSERVE   H1, 399.8314100 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 17 sec

5a + **13a**

```
jy-5-5-1-11

 Data Collected on:
   inv500-inova500
 Archive directory:
   /export/home/jungylee/vnmrsys/data
 Sample directory:

 File: jy-5-5-1-11

Pulse Sequence: s2pul
Solvent: CDCl3
 Temp. 25.0 C / 298.1 K

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 7998.4 Hz
 100 repetitions
OBSERVE   H1, 499.8948175 MHz
DATA PROCESSING
FT size 32768
Total time 4 min
```

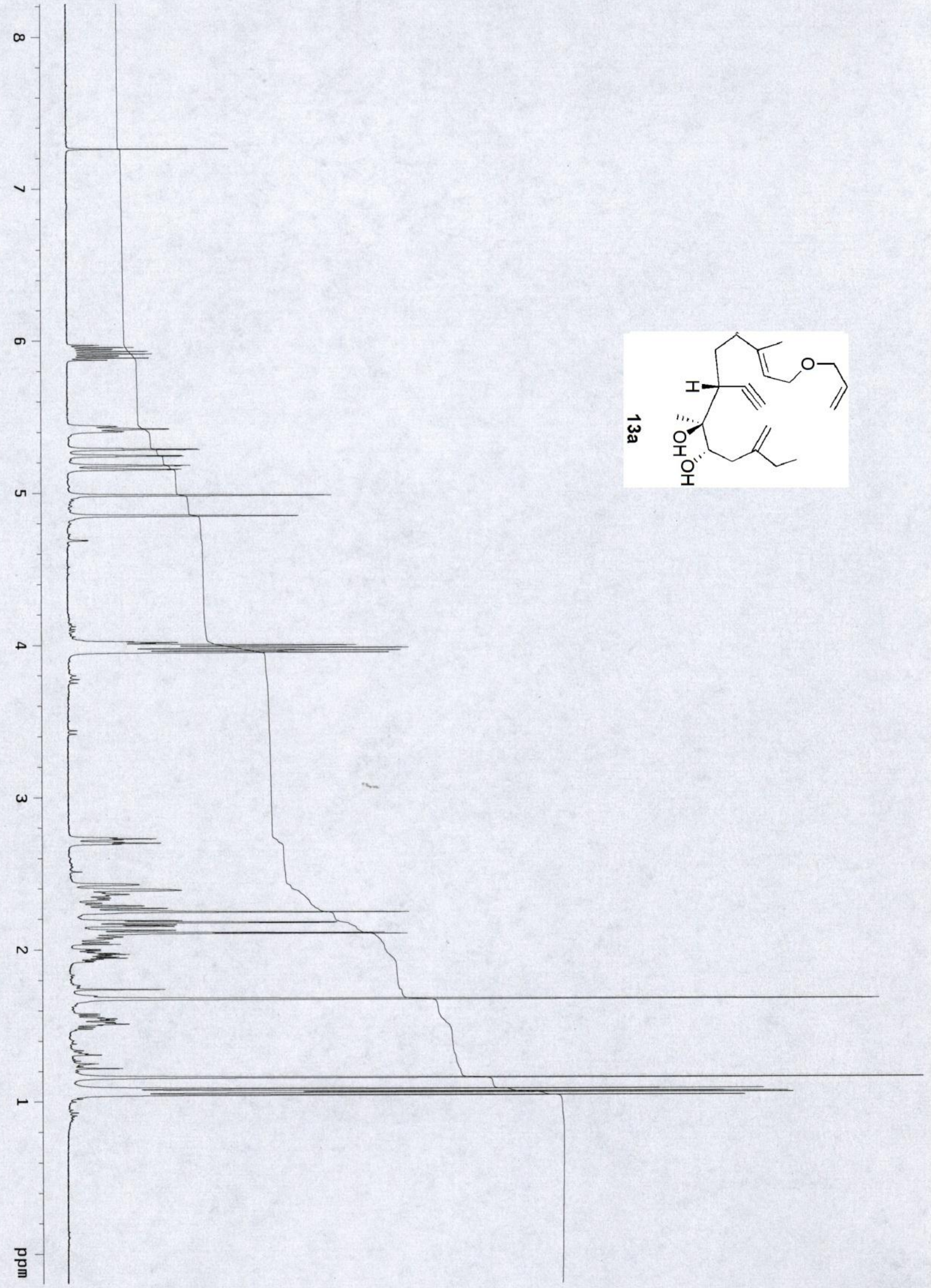
5a

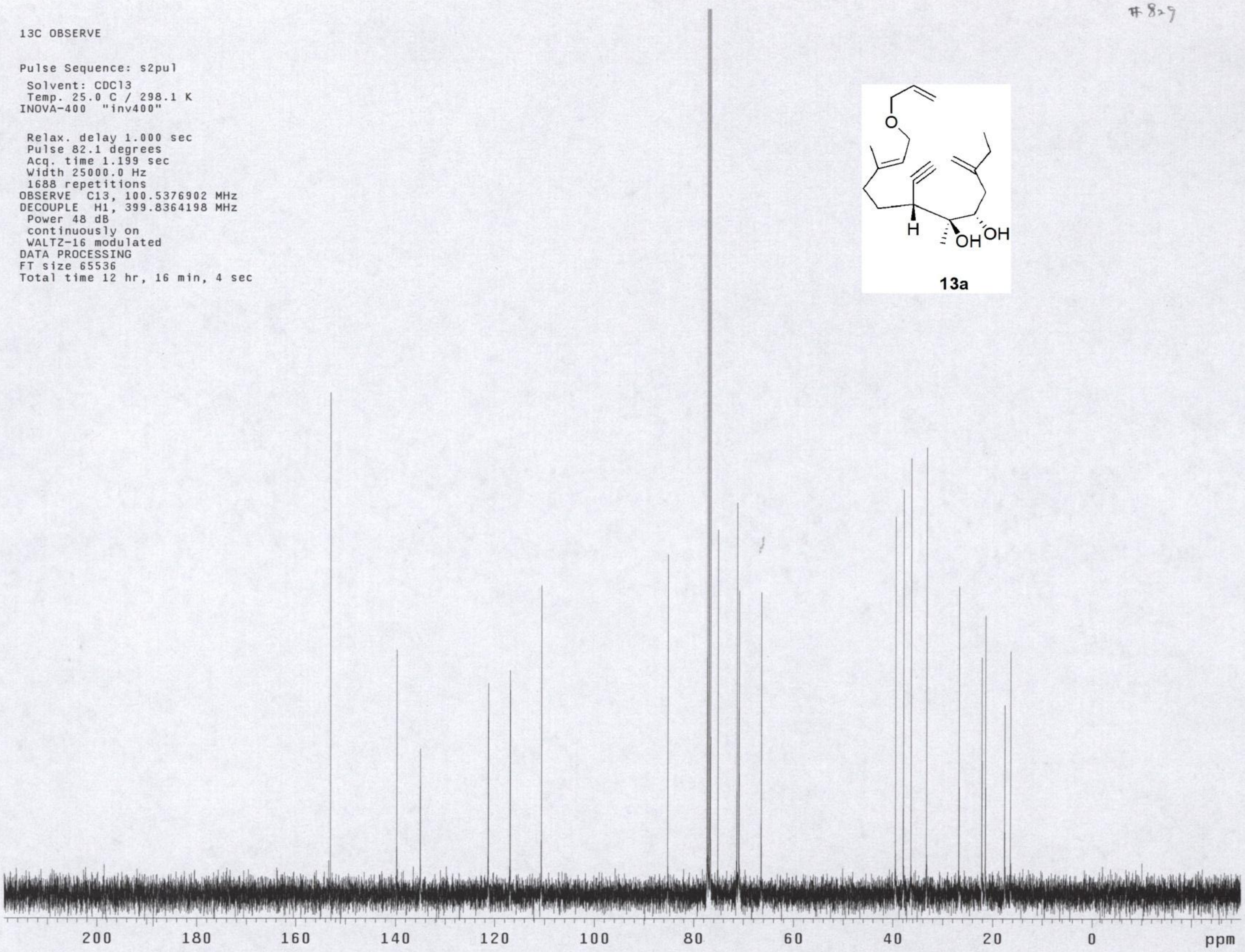




```
jy-5-5-2-11

 Data Collected on:
   inv500-inova500
 Archive directory:
   /export/home/jungylee/vnmrsys/data
 Sample directory:

 File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3

 Temp. 25.0 C / 298.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 31421.8 Hz
 384 repetitions
OBSERVE  C13, 125.6986513 MHz
DECOUPLE  H1, 499.8973075 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 6 hr, 24 min
```

5a

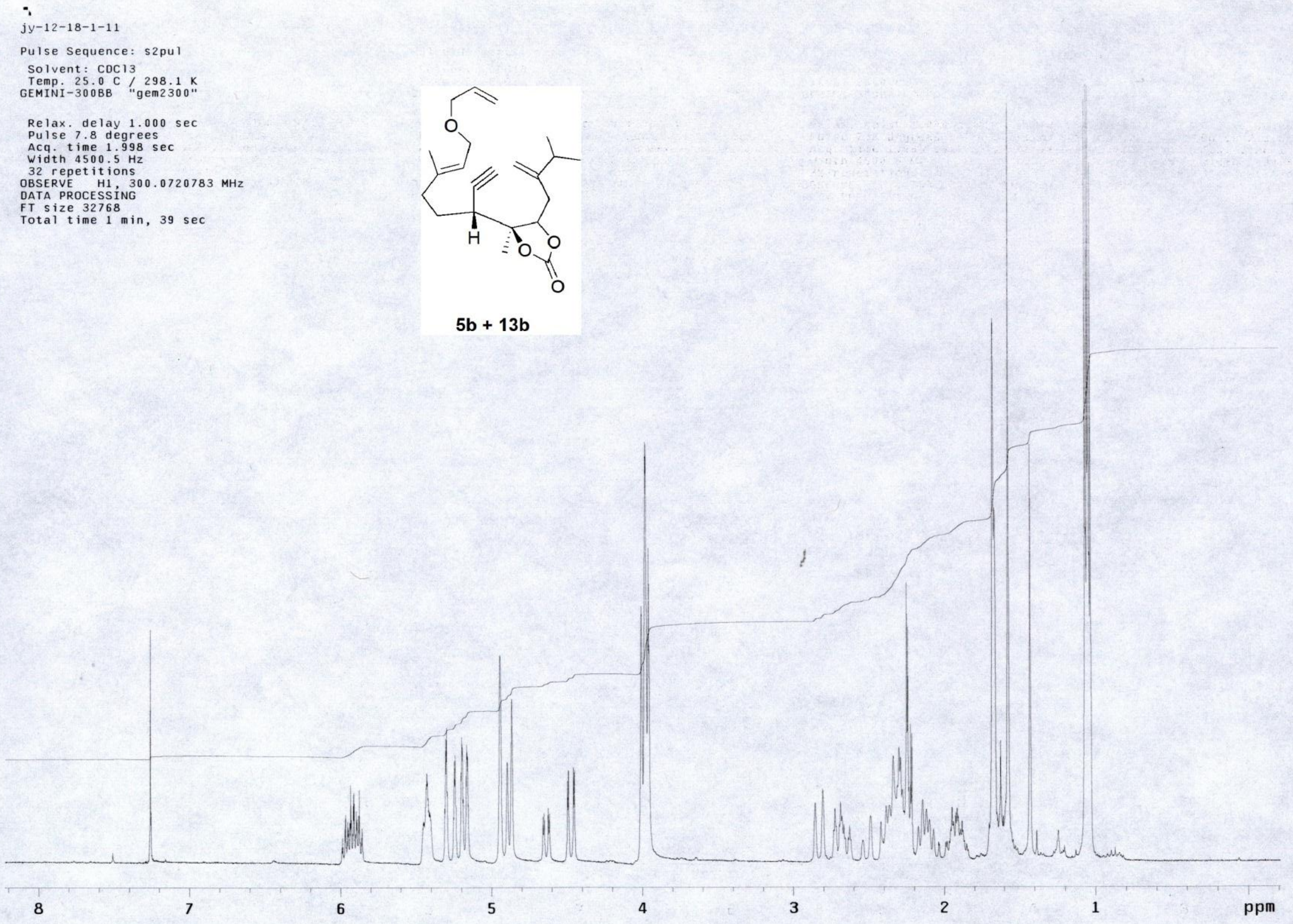

13a
OH
OH
H
O
8
7
6
5
4
3
2
1
ppm



```
13C OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1688 repetitions
OBSERVE  C13, 100.5376902 MHz
DECOUPLE  H1, 399.8364198 MHz
 Power 48 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 12 hr, 16 min, 4 sec
```

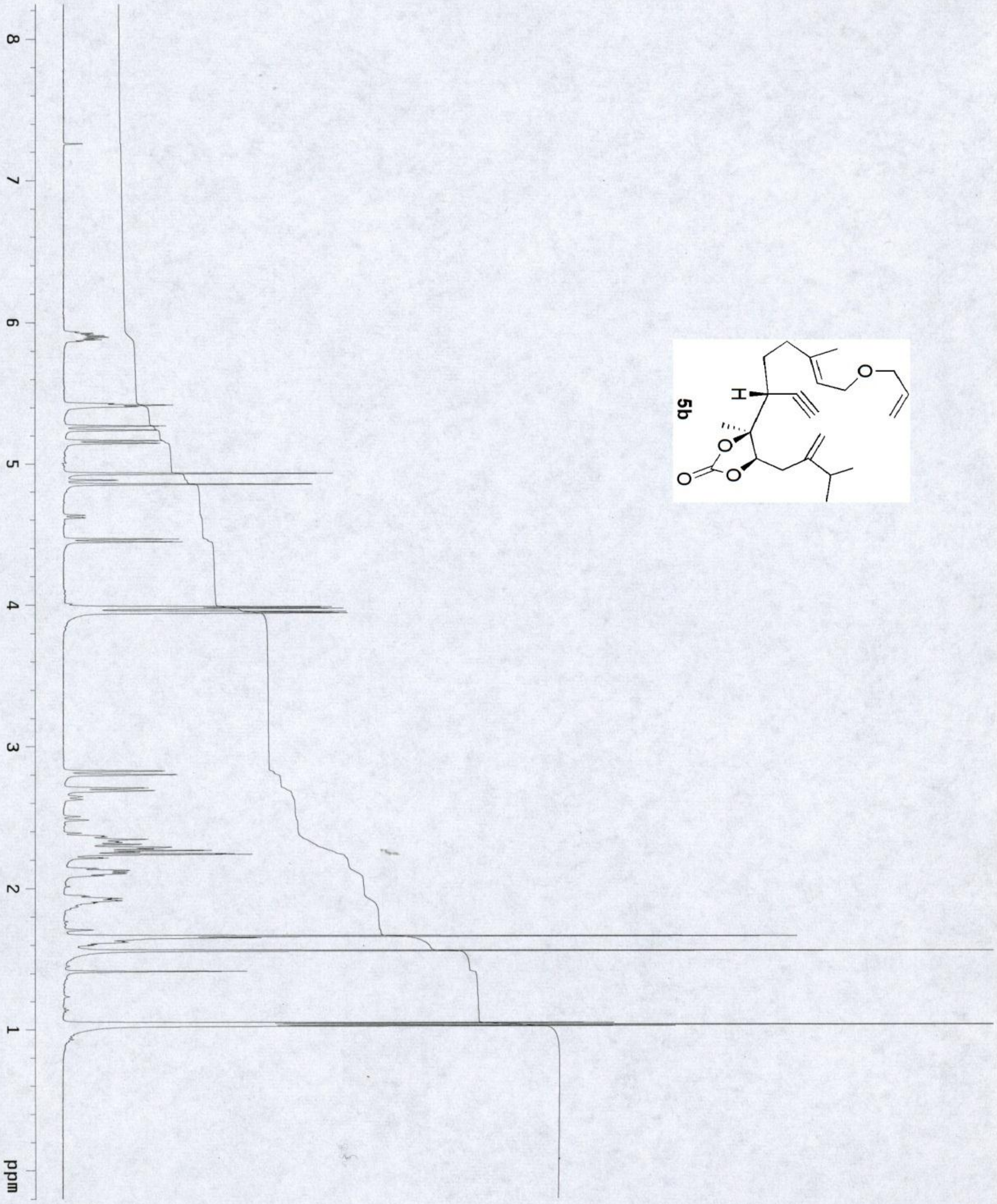
#829

13a

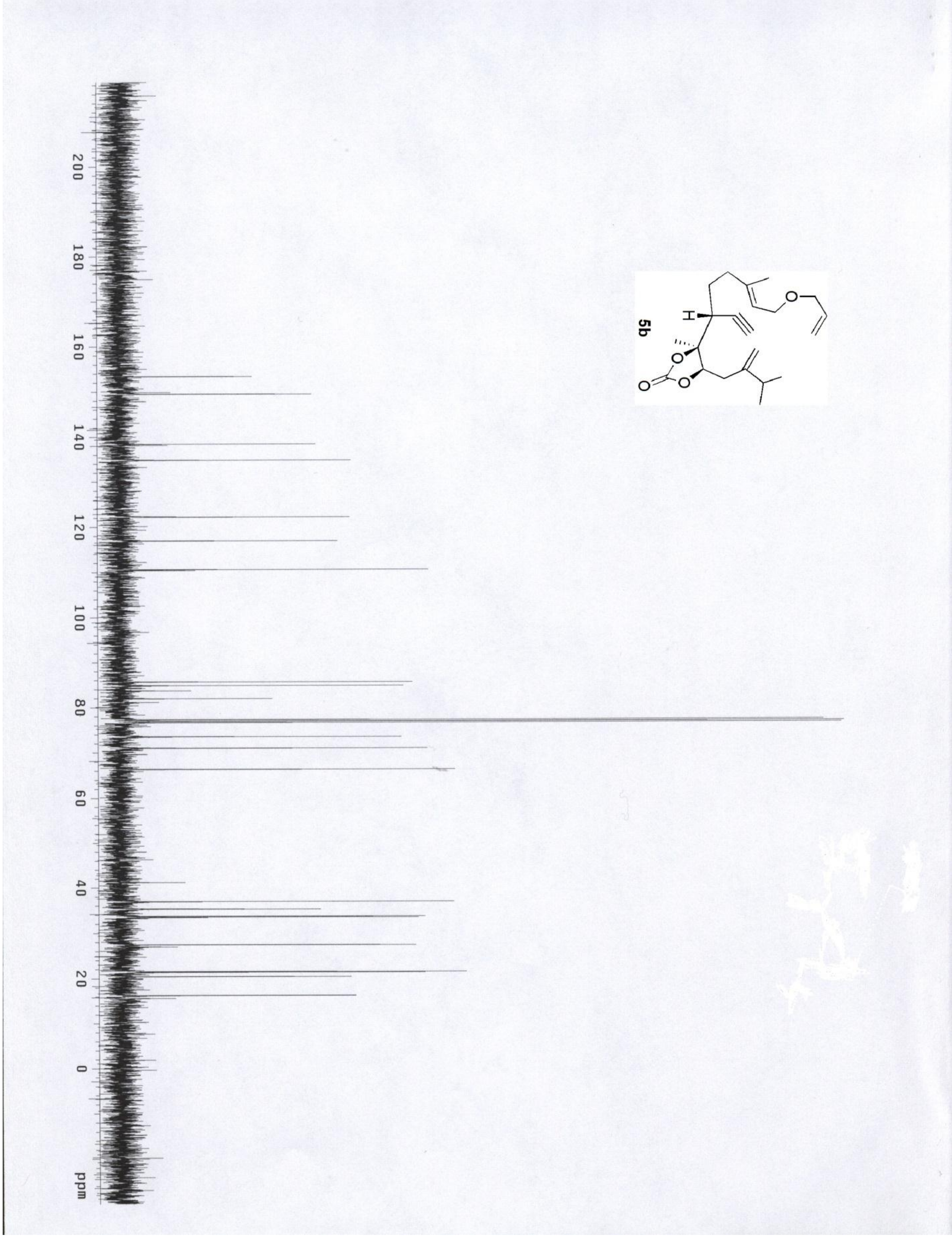


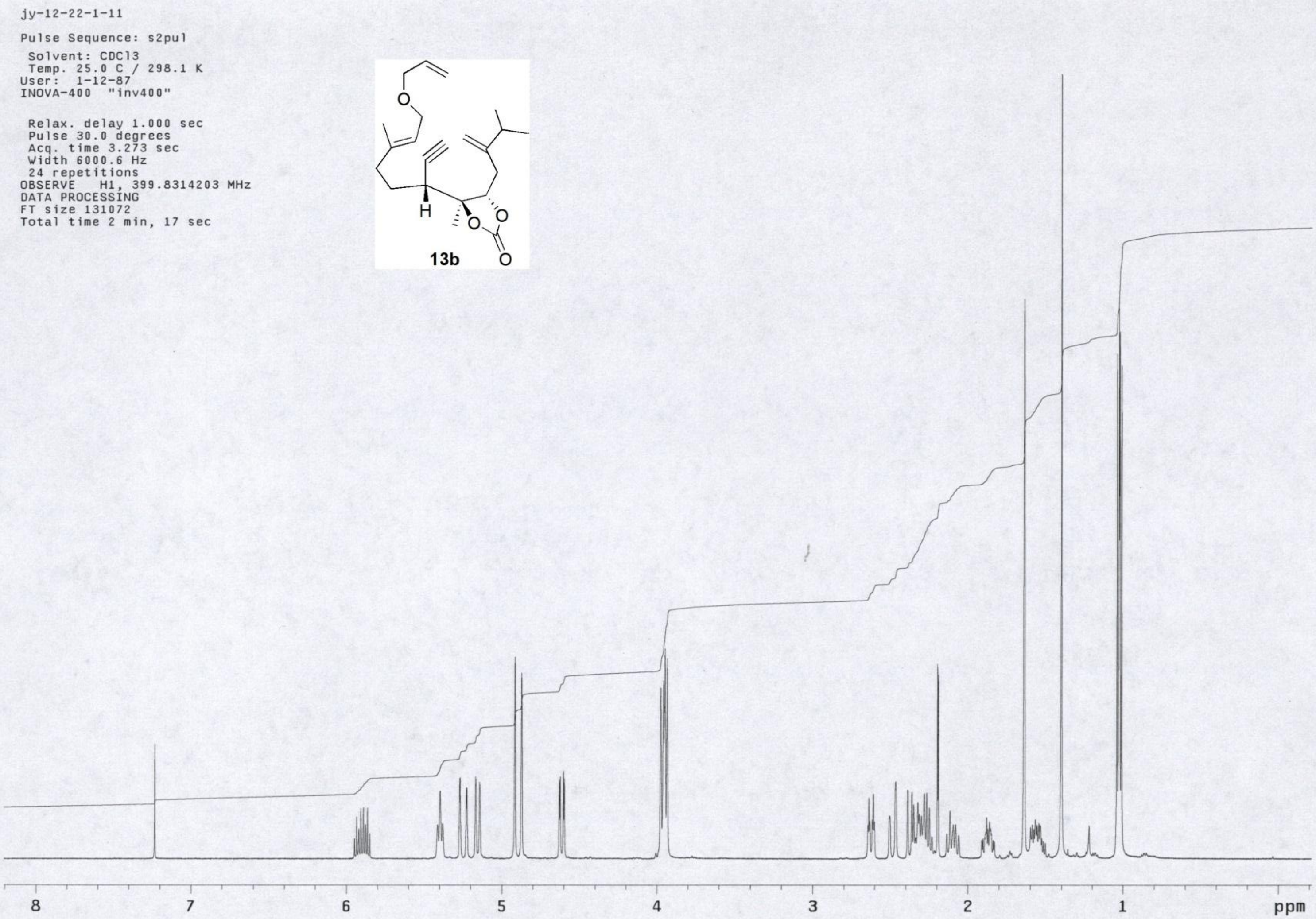
```
jy-12-18-1-11

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
GEMINI-300BB  "gem2300"

 Relax. delay 1.000 sec
 Pulse 7.8 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 32 repetitions
OBSERVE   H1, 300.0720783 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 39 sec
```

5b + 13b



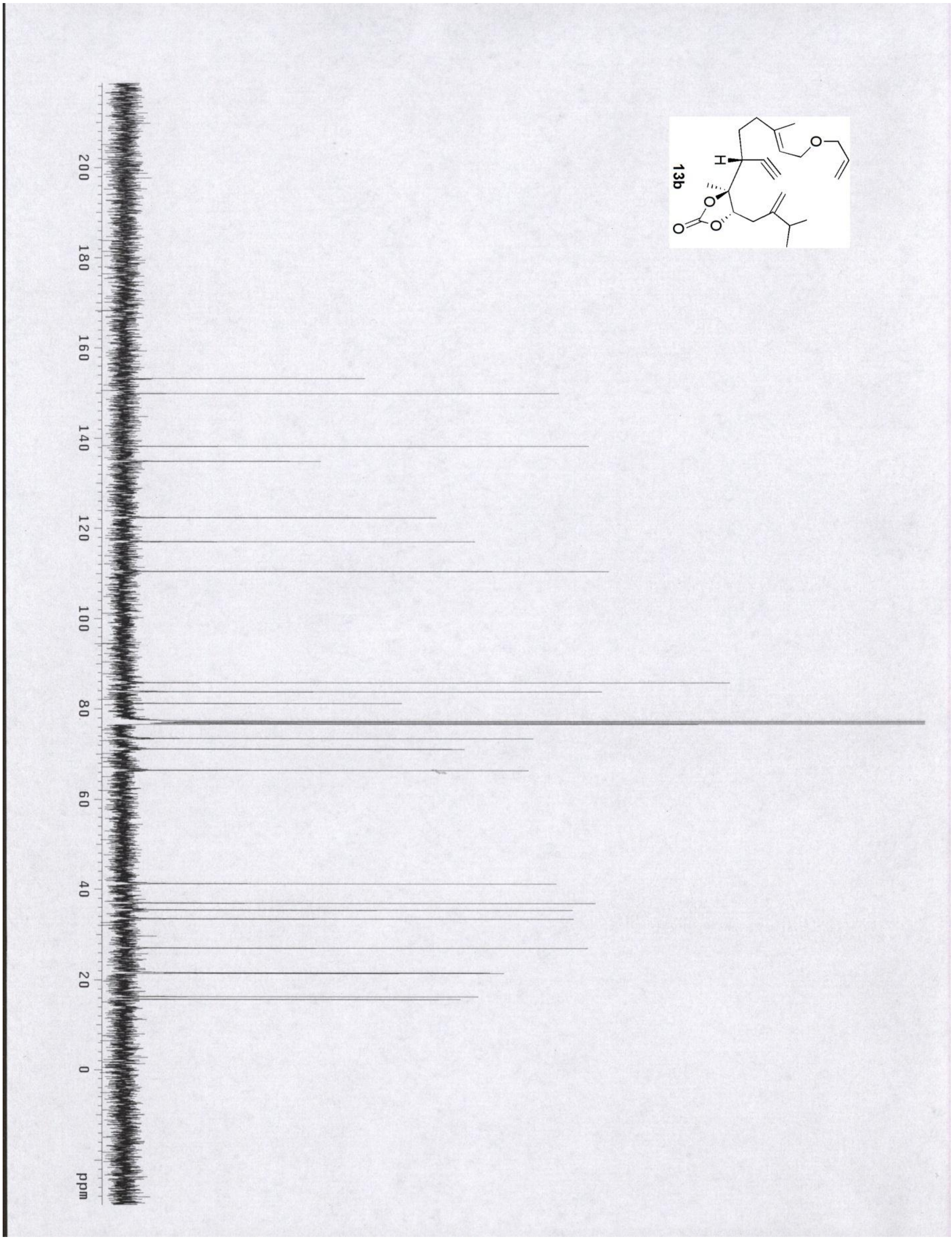
5b


5b

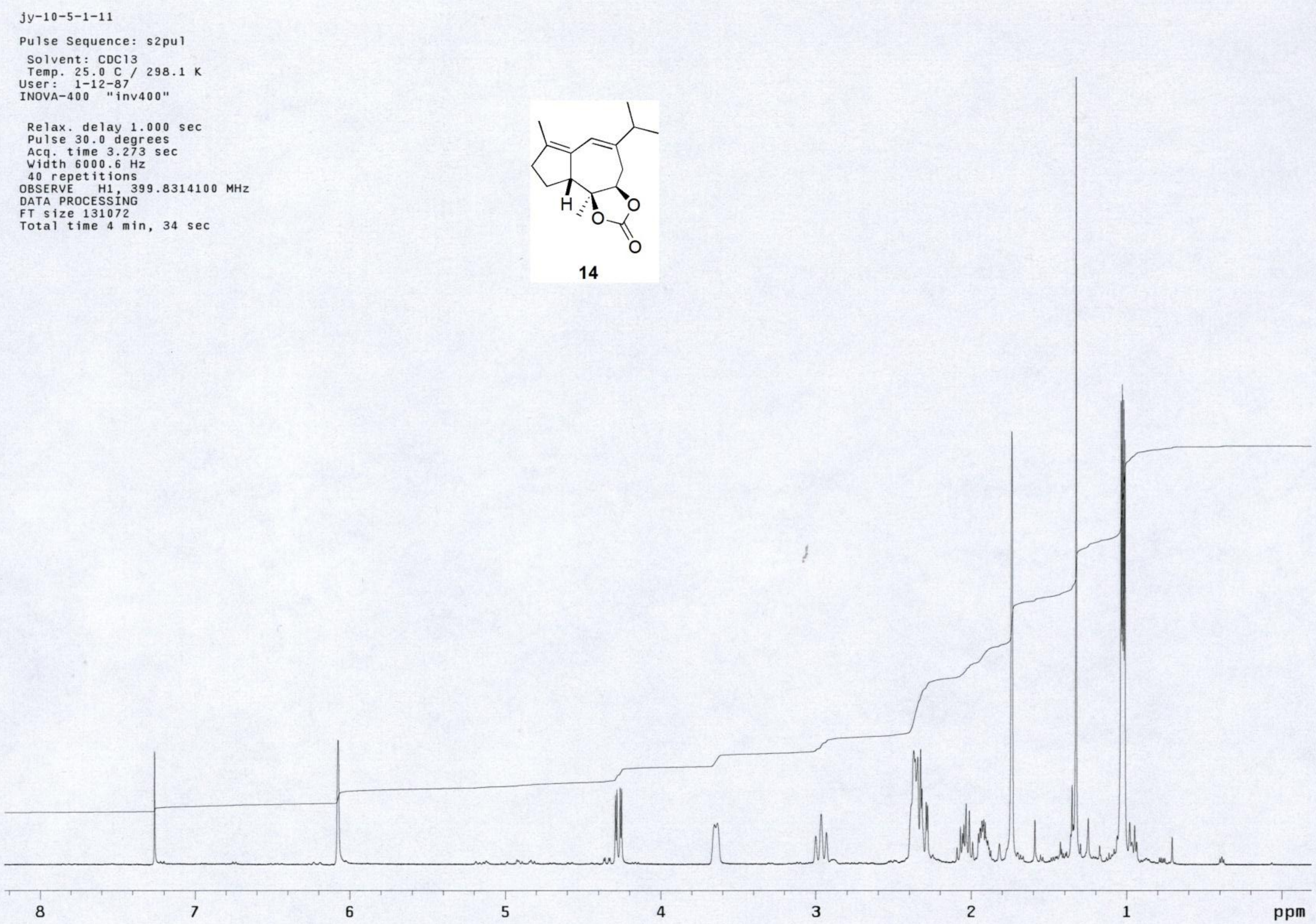


```
jy-12-22-1-11

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
User:  1-12-87
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 3.273 sec
 Width 6000.6 Hz
 24 repetitions
OBSERVE   H1, 399.8314203 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 17 sec
```

13b

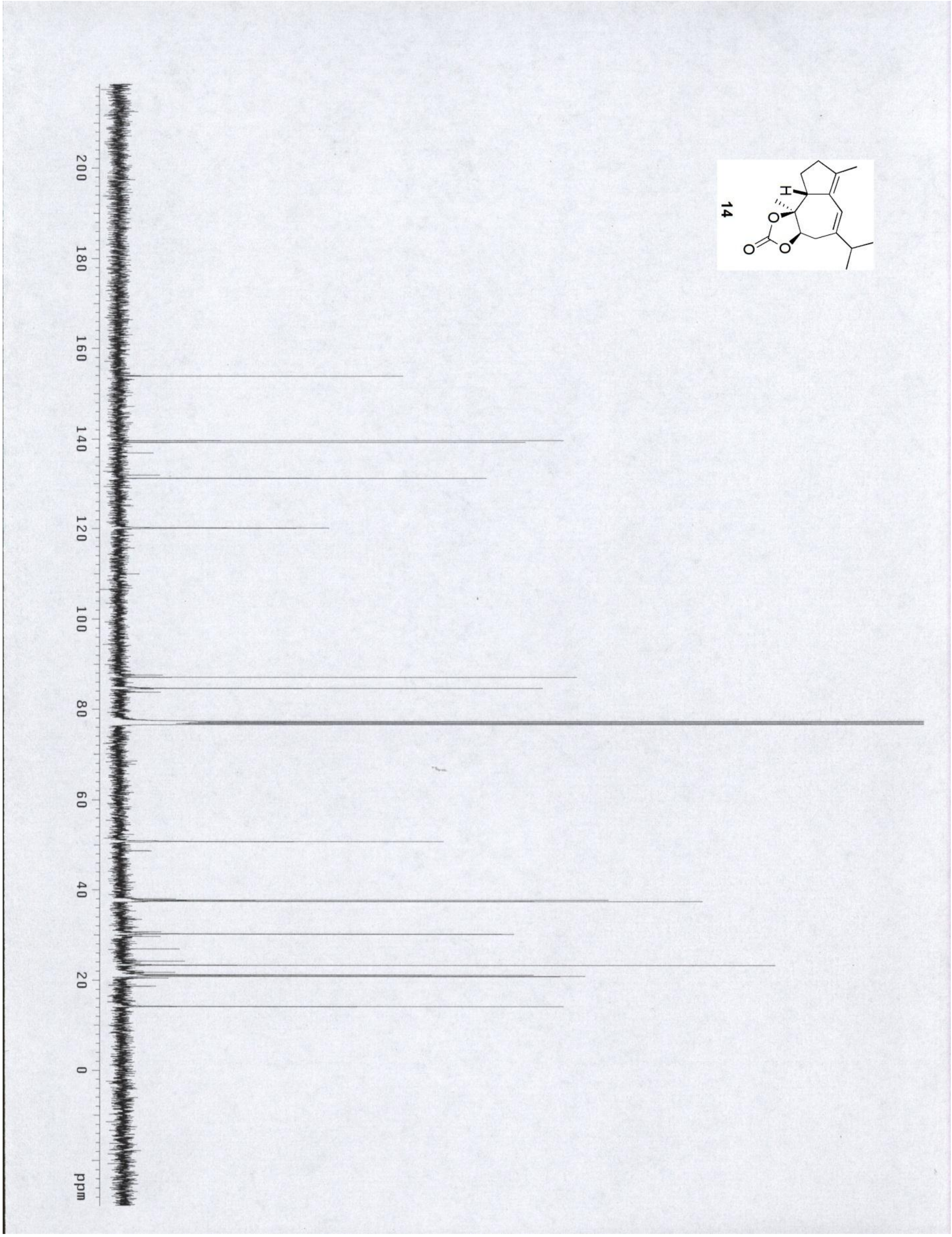


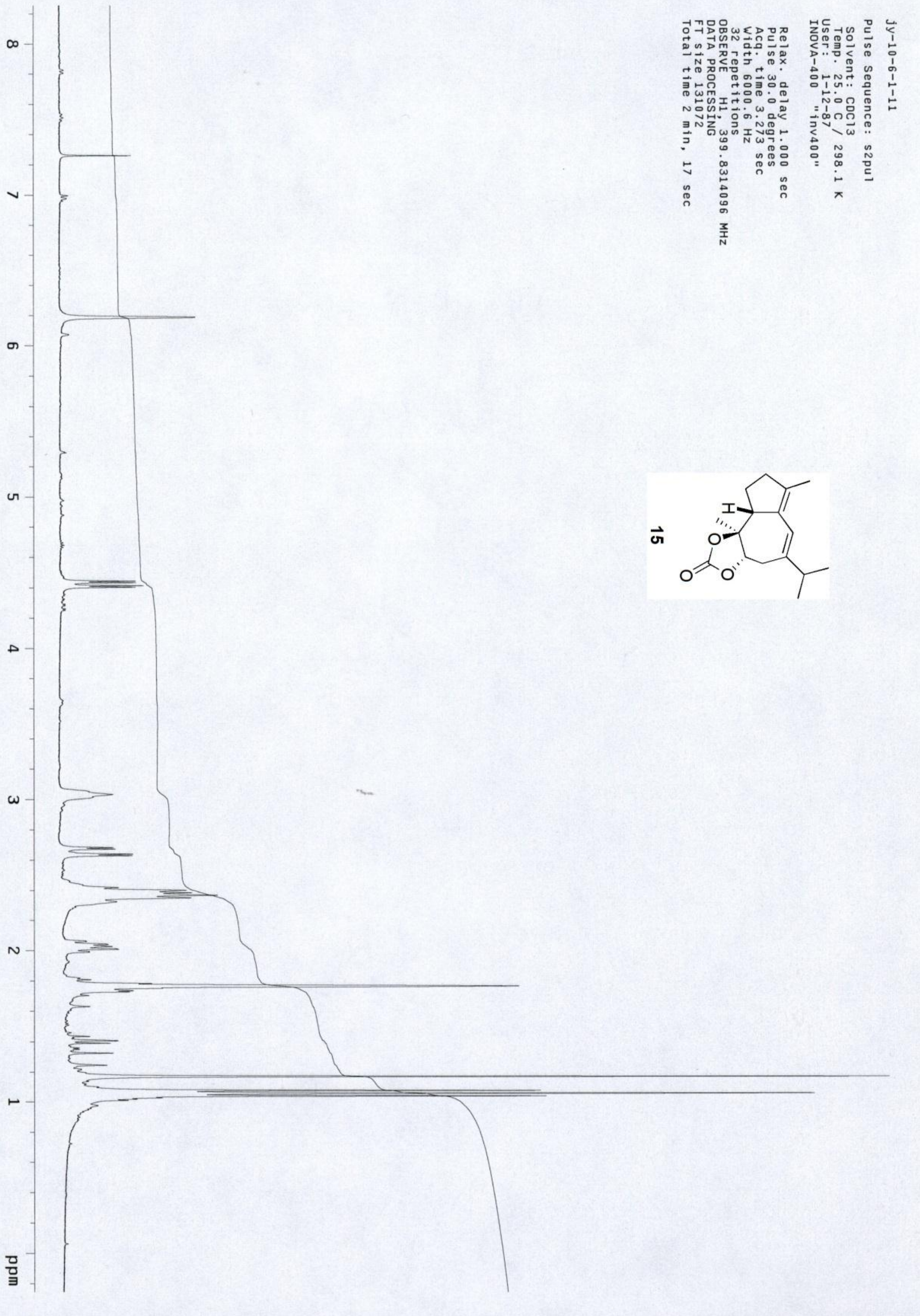
13b



```
jy-10-5-1-11

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
User:  1-12-87
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 3.273 sec
 Width 6000.6 Hz
 40 repetitions
OBSERVE   H1, 399.8314100 MHz
DATA PROCESSING
FT size 131072
Total time 4 min, 34 sec
```

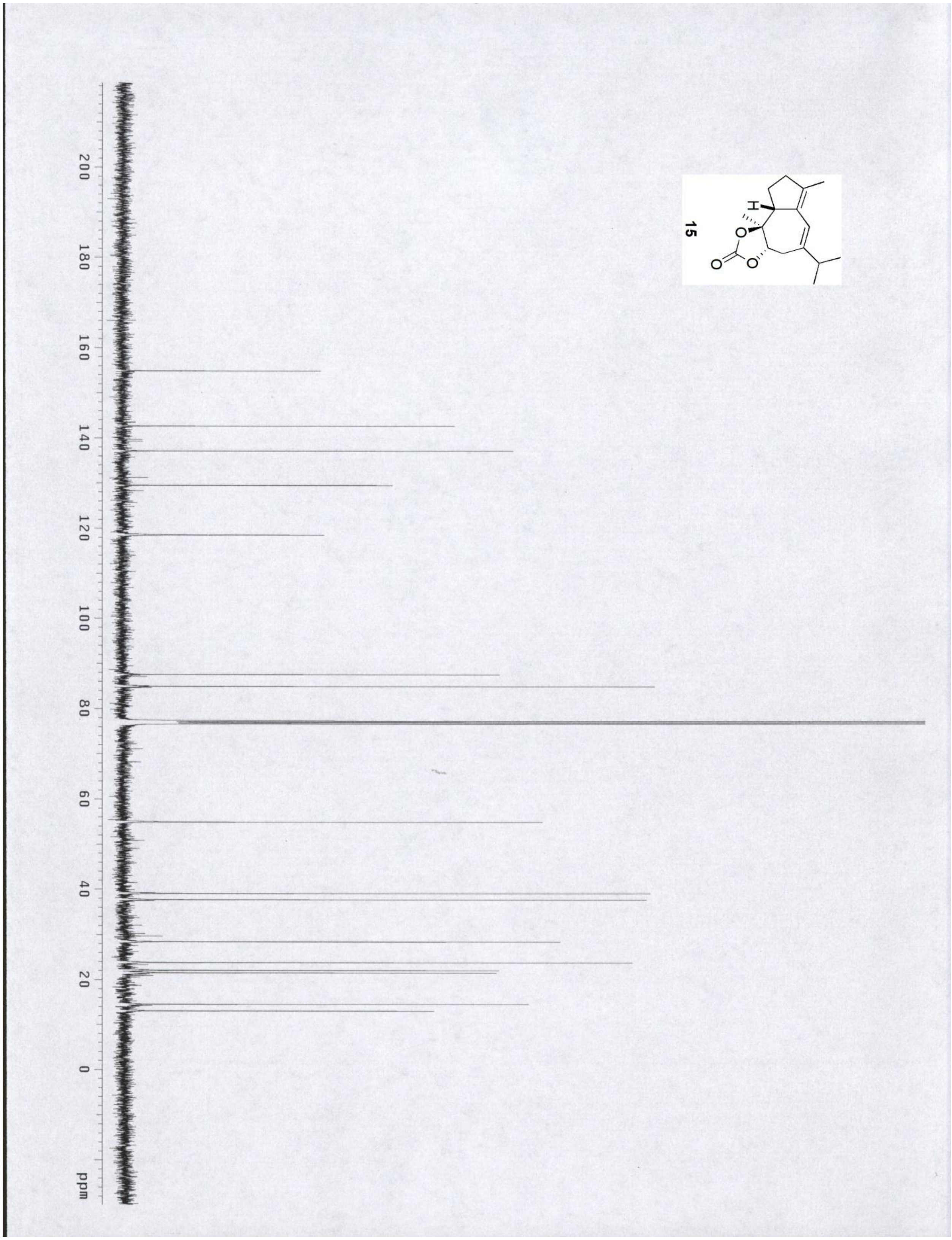
14

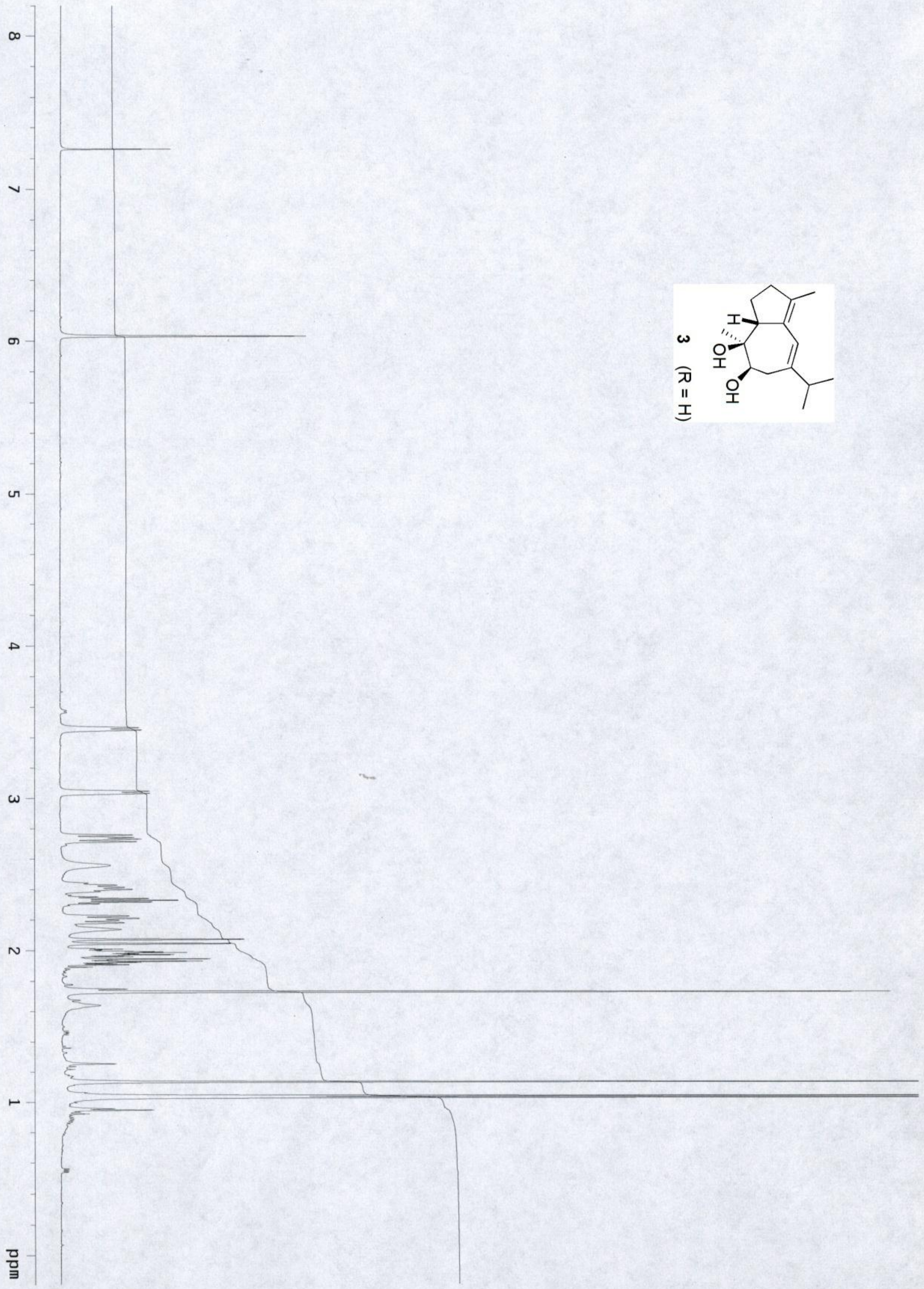

14
200
180
160
140
120
100
80
60
40
20
0
ppm



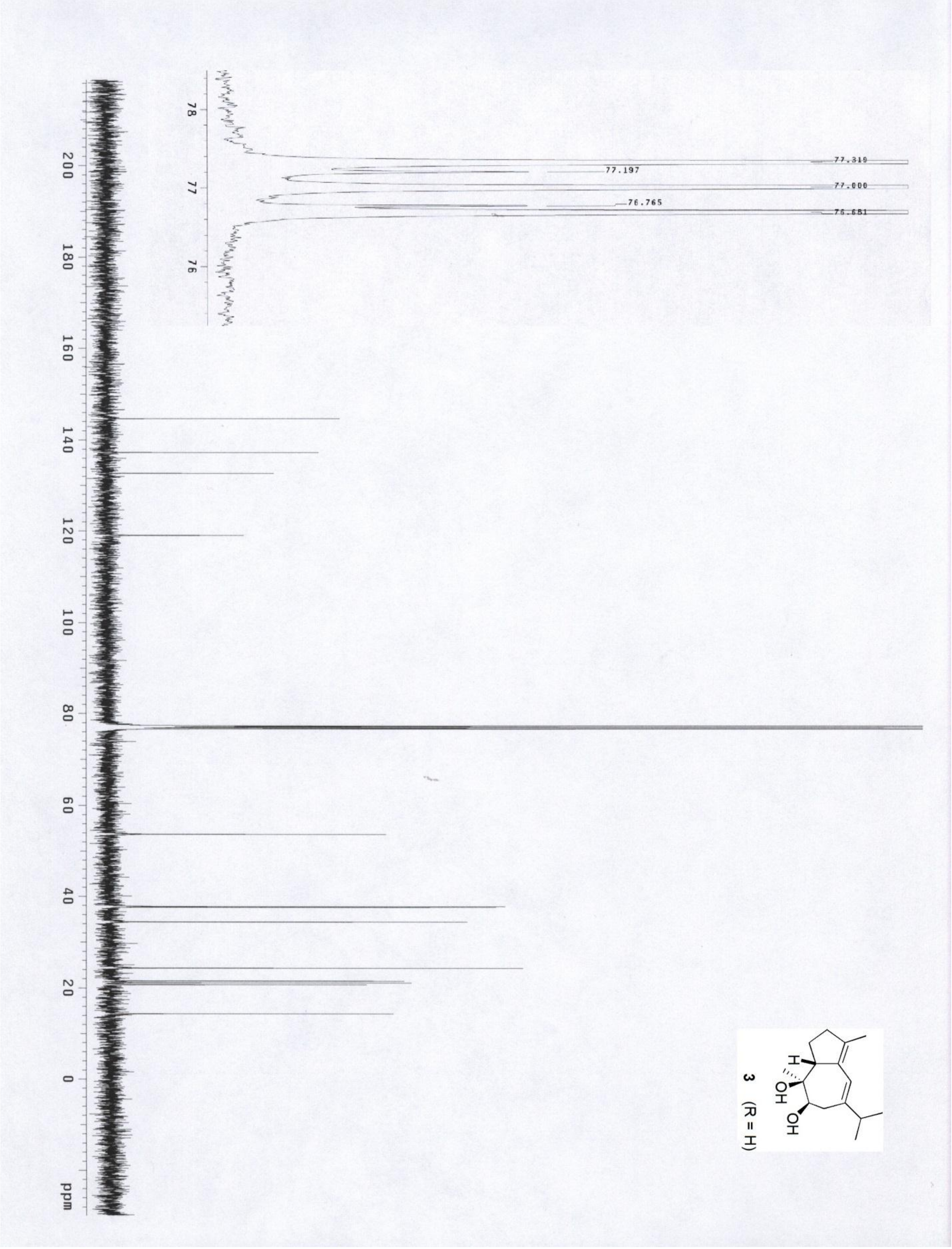
15

```
jy-10-6-1-11

Pulse Sequence: s2pul
  Solvent: CDC13
  Temp. 25.0 C / 298.1 K
User: 1-12-87
INOVA-400  "inv400"

  Relax. delay 1.000 sec
  Pulse 30.0 degrees
  Acq. time 3.273 sec
  Width 6000.6 Hz
  32 repetitions
OBSERVE   H1, 399.8314096 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 17 sec
```

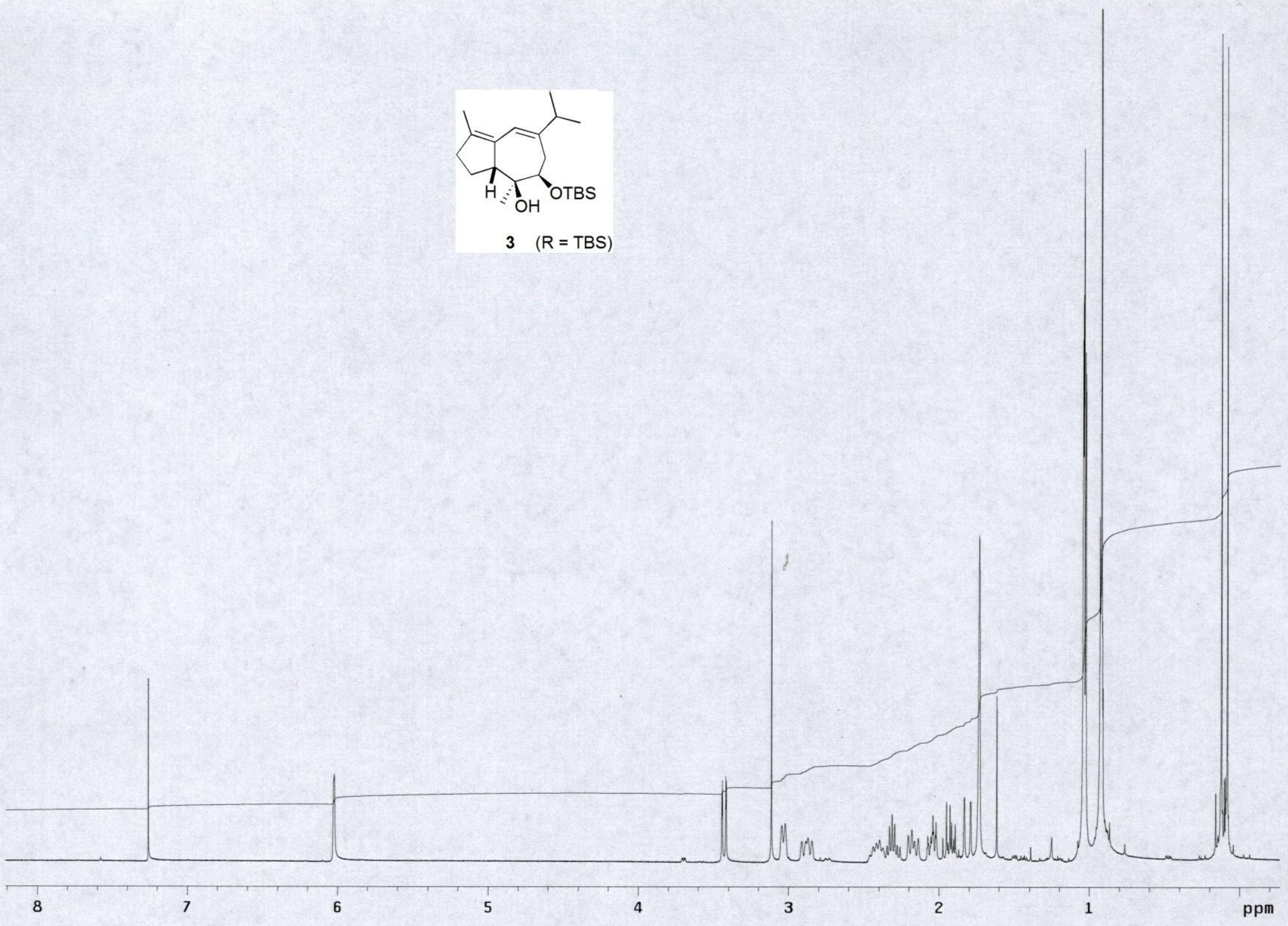

200
180
160
140
120
100
80
60
40
20
0
ppm
15
H
O
O
O

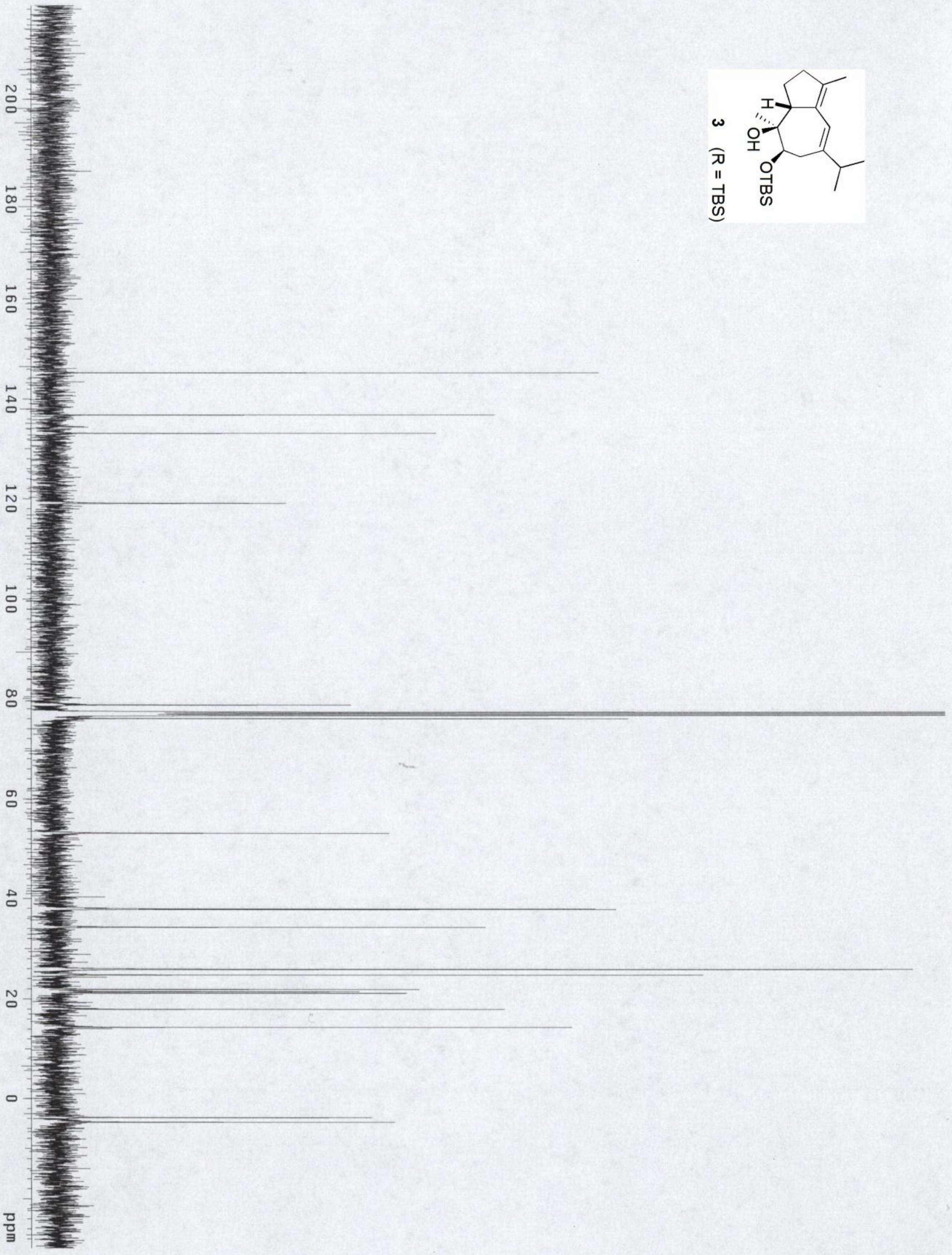


3 (R = H)

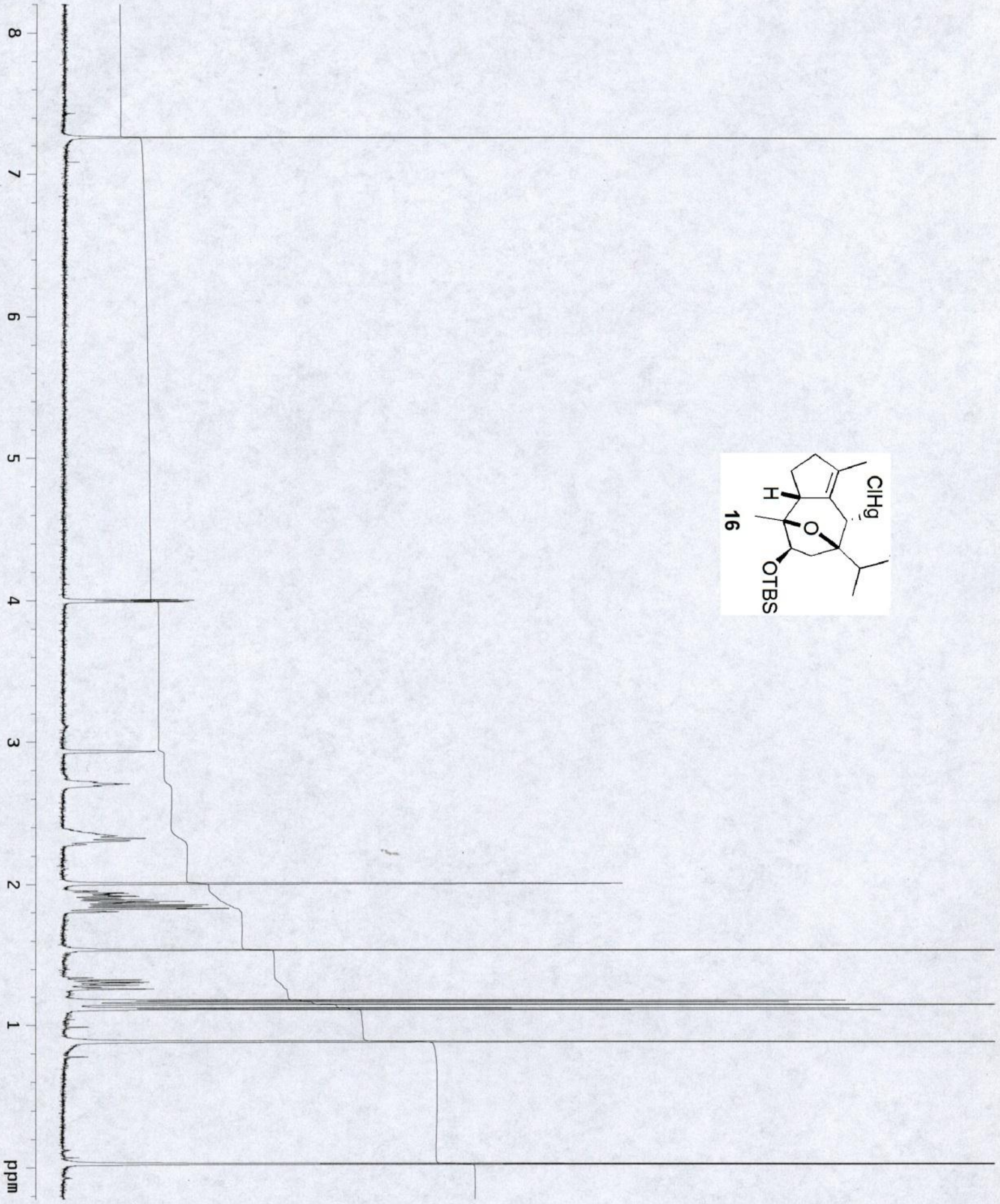

77.319
77.197
77.000
76.765
76.681
78
77
76
200
180
160
140
120
100
80
60
40
20
0
ppm
H
OH
OH

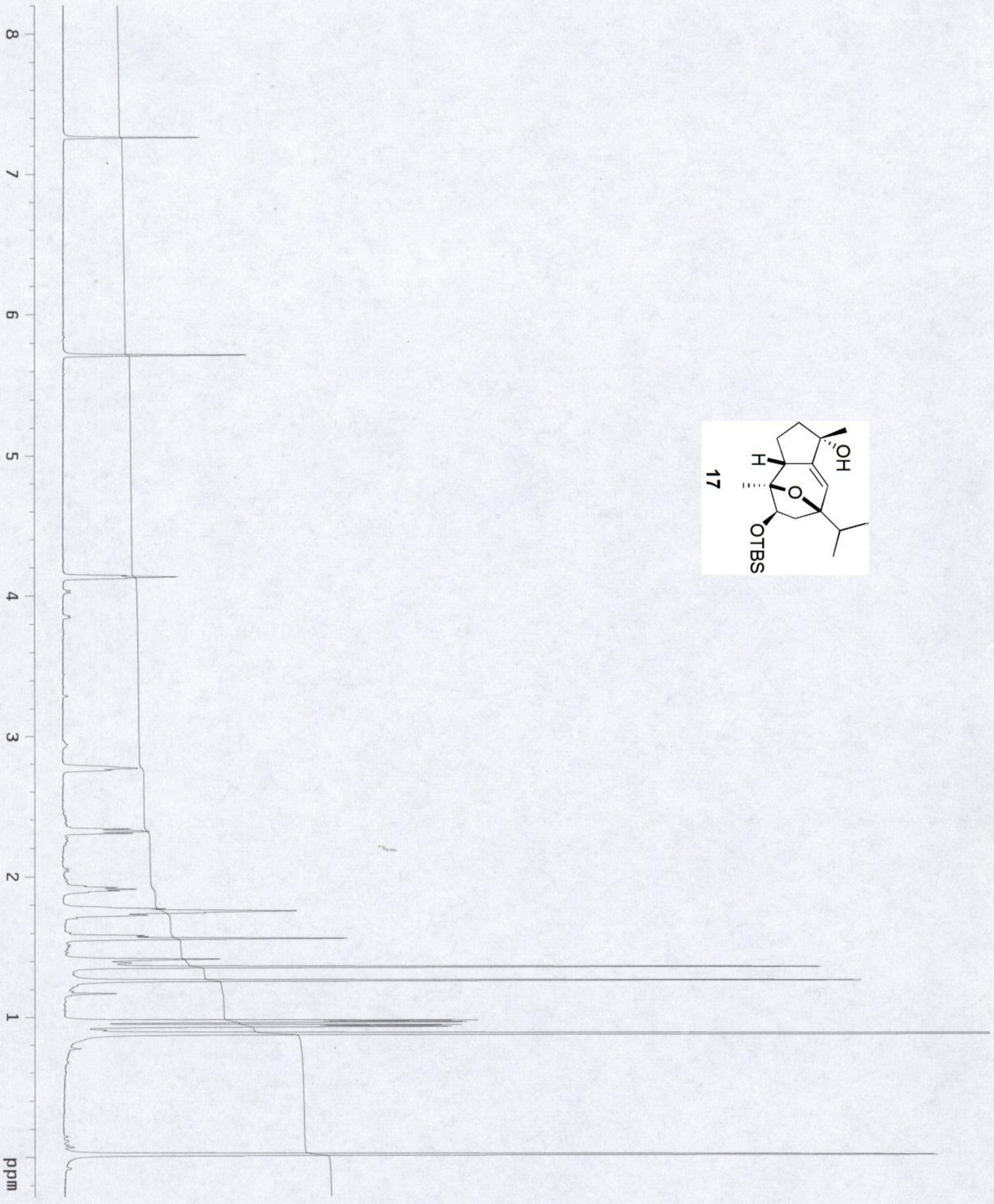
3 (R = H)


OTBS
H
OH
3 (R = TBS)
8
7
6
5
4
3
2
1
ppm

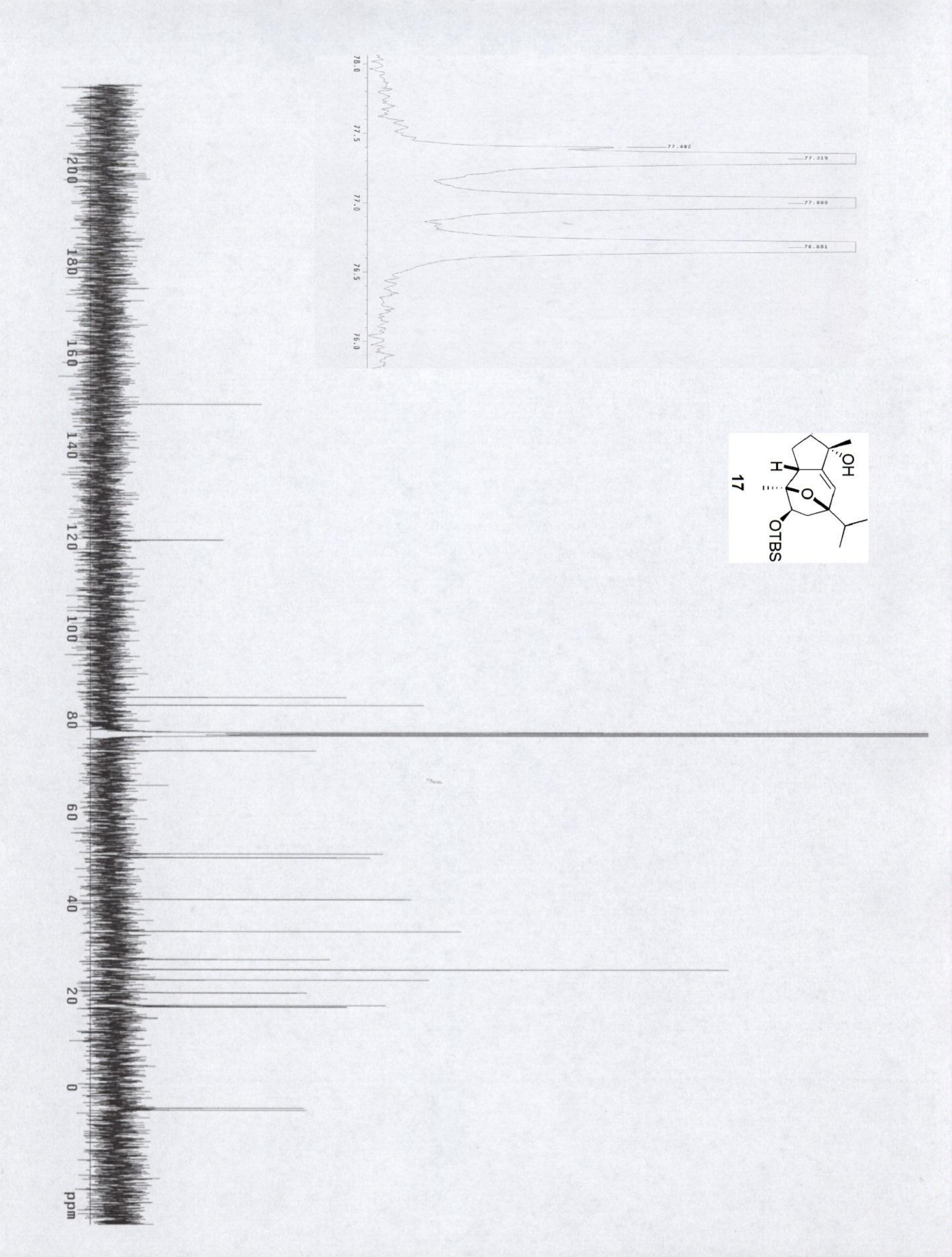


3 (R = TBS)


8
7
6
5
4
3
2
1
ppm
ClHg
H
O
OTBS
16

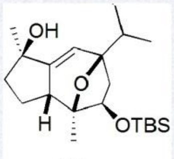


17

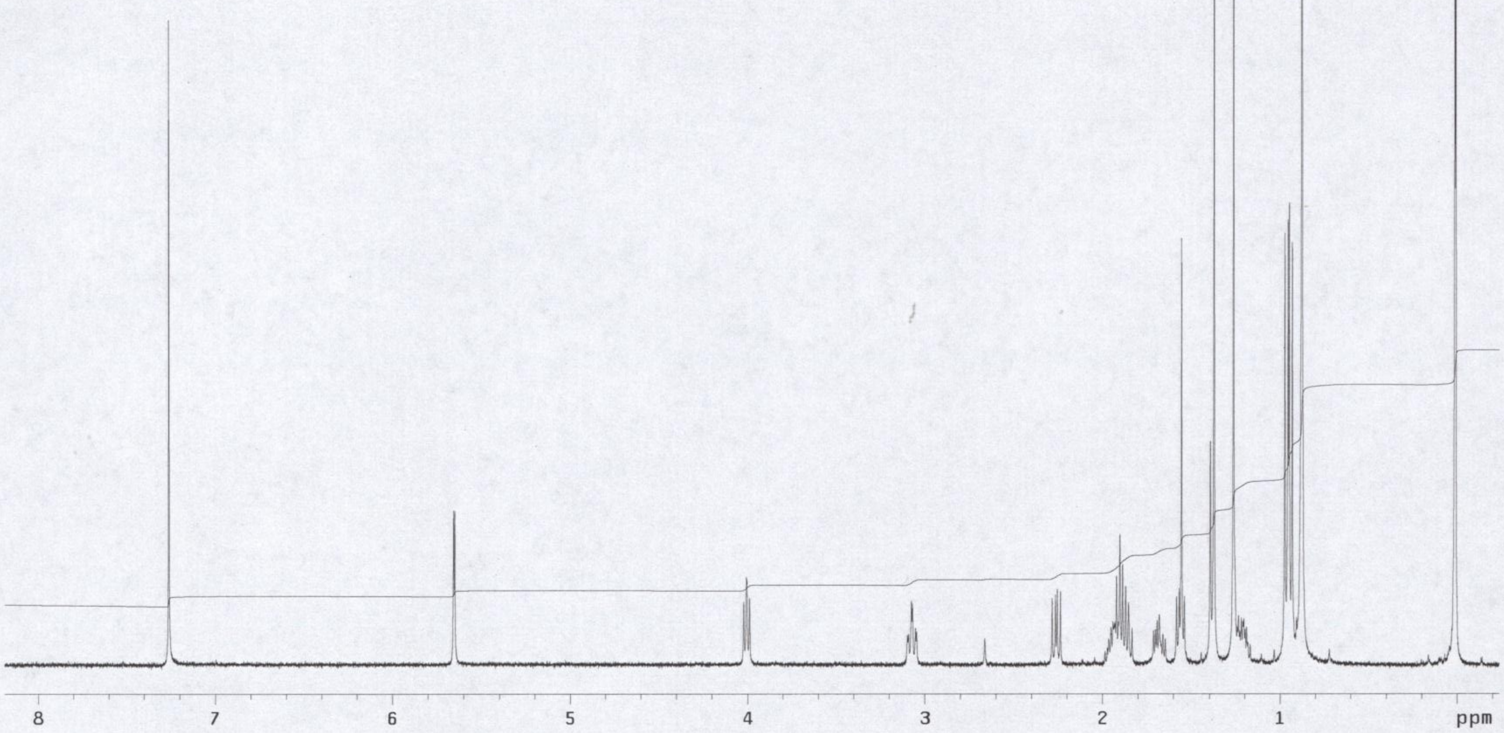


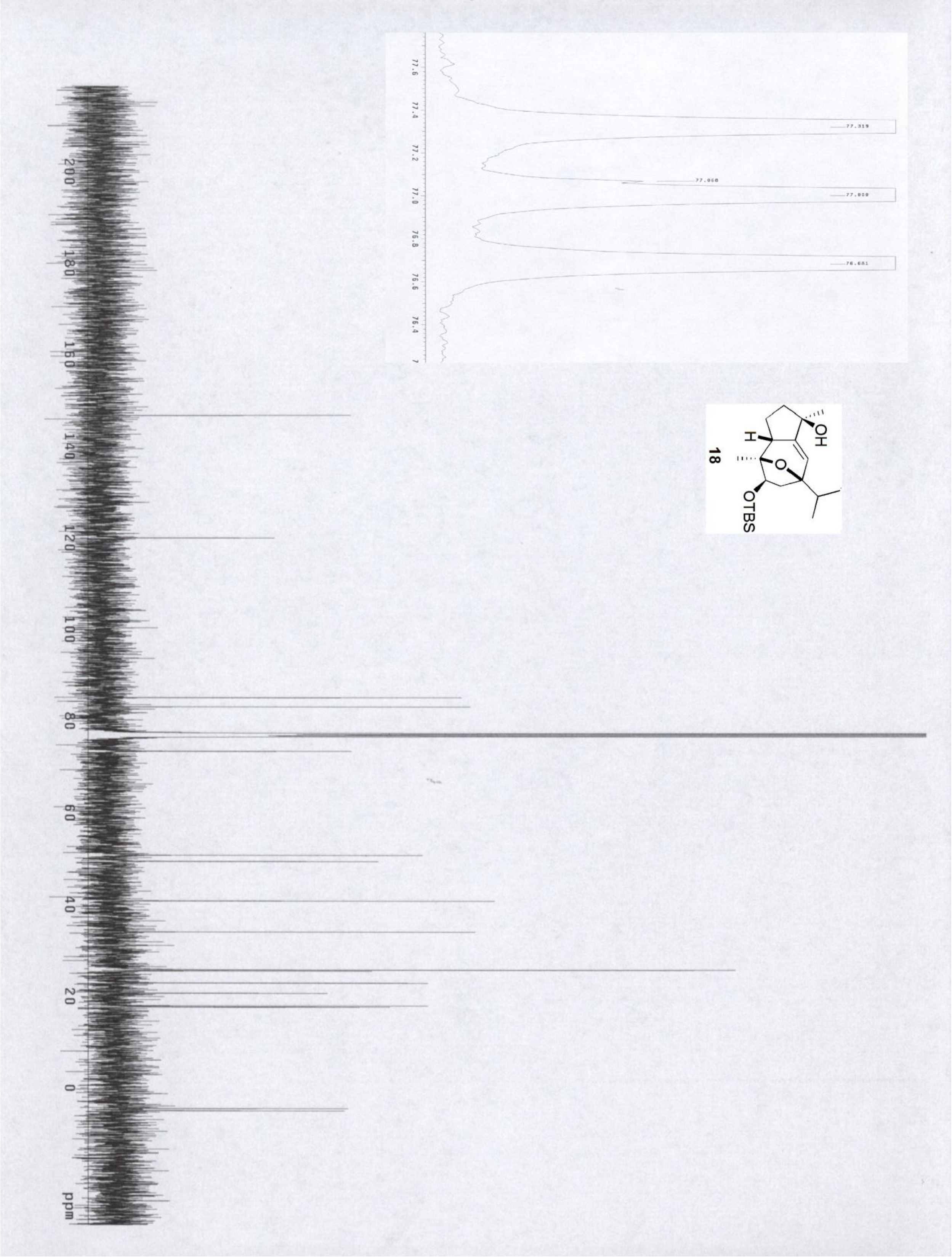
ppm
200
180
160
140
120
100
80
60
40
20
0
78.0
77.5
77.0
76.5
76.0
77.402
77.319
77.000
76.681
OH
H
O
OTBS
17

```
jy-11-19-1-11

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
User:  1-12-87
File: jy-11-19-1-11
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 3.273 sec
 Width 6000.6 Hz
 40 repetitions
OBSERVE   H1, 399.8314095 MHz
DATA PROCESSING
FT size 131072
Total time 4 min, 34 sec
```



18




200
180
160
140
120
100
80
60
40
20
0
ppm
77.6
77.4
77.2
77.0
76.8
76.6
76.4
77.319
77.068
77.000
76.681
OH
H
O
OTBS
18