Catalytic Enantioselective Allylation of Dienals Through the Intermediacy of Unsaturated π-Allyl Complexes

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Supporting Information

Table of Contents

General Information

^{1}H NMR spectra were recorded on either a Varian Gemini-400 (400 MHz), or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on either a Varian Gemini-400 (100 MHz), or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.23 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA) in ethanol, or potassium permanganate ($KMnO_4$) in water. Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supleco β-Dex 120 column with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Berger Instruments Supercritical Chromatograph equipped with an Alcott auto sampler and a Knauer UV detector with methanol as the modifier. Analytical high performance liquid chromatography (HPLC) was performed on a Shimadzu chromatograghy equipped with two LC-10APvp pumps, SPD-10AVvp UV detector and SIL-10ADvp injector. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF) and dichloromethane (DCM) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. Bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$] and tricyclohexylphosphine (PCy_3) were purchased from Strem Chemicals, Inc. Acetic acid and dimethyl malonate were distilled under reduced pressure. Hoveyda-Grubbs catalyst second generation (HG-II) refers to [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(*o*-isopropoxyphenylmethylene)ruthenium.[1] All other reagents were purchased from either Fisher or Aldrich and used without further purification. (*R*,*R*)-^{t}BuTADDOLPPh (**L1**)[2], (*R*,*R*)-xylylTADDOLPPh (**L2**)[1], (*R*,*R*)-TADDOLPPh (**L3**)[1], (*R*,*R*)-

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[1] Garber, S.B.; Kingsbury, J.S.; Gray, B.L.; Hoveyda, A.H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

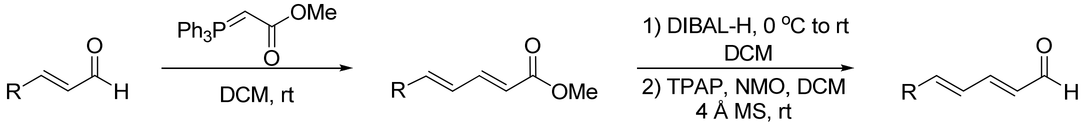
[2] Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.

TADDOLPN(C_4H_8) (**L4**)[3] and (*R,R*)-TADDOLPN(C_4H_8) (**L5**)[2] were prepared according to literature procedures.

Experimental Procedures

Preparation of Dienals

Representative Procedure for the Synthesis of Dienals

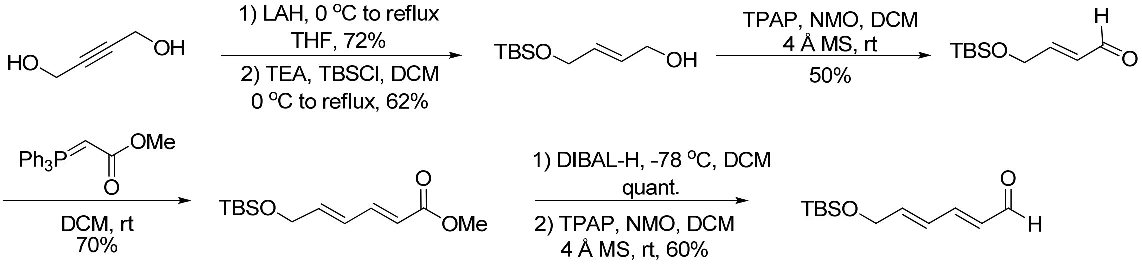


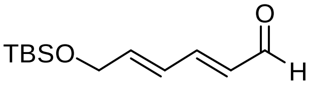
The following dienals were prepared from commercially available α,β-unsaturated aldehydes: (2*E*,4*E*)-deca-2,4-dienal (Table 2, entries 3 and 4)[4] and (2*E*,4*E*)-phenylpenta-2,4-dienal (Table 2, entry 5)[3]. Spectral data are in accordance with the literature references.

(2*E*,4*E*)-5-cyclohexylpenta-2,4-dienal was prepared from (*E*)-3-cyclohexylacrylaldehyde (Table 2, entry 8), which was originally synthesized from cyclohexanecarboxaldehyde according to general procedure. Spectral data are in accordance with the literature reference.[3]

(2*E*,4*E*)-5-(furan-2-yl)penta-2,4-dienal (Table 2, entry 9) was prepared according to the literature procedure.[5] Spectral data are accordance with the literature reference.

Preparation of (2E,4E)-6-(tert-butyldimethylsilyloxy)hexa-2,4-dienal





(2*E*,4*E*)-6-(*tert*-butyldimethylsilyloxy)hexa-2,4-dienal (Table 2, entry 7). A light yellow oil. R_f= 0.48 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz,

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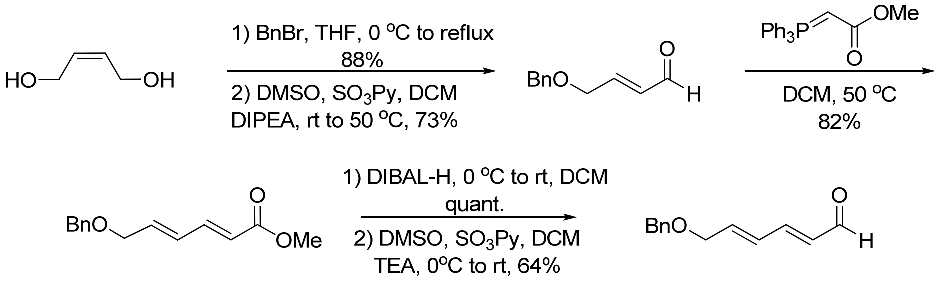
[3] Burks, H. E.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 8766.

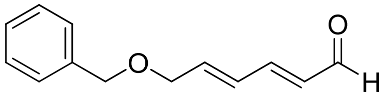
[4] Rein, T.; Kann, N.; Åkermark, B.; Helquist, P. *J. Org. Chem.* **1990**, *55*, 5312.

[5] Bellassoued, M.; Salemkour, M. *Tetrahedron.* **1996**, *52*, 4507.

CDCl$_3$): δ 0.09 (6H, s, Si(C**H**$_3$)$_2$), 0.93 (9H, s, SiC(C**H**$_3$)$_3$), 4.34 (2H, dd, *J* = 4.2 Hz, 1.8 Hz, SiOC**H**$_2$CH=CH), 6.15 (1H, dd, *J* = 15.2 Hz, 8.0 Hz, C(O)HC**H**=CH), 6.32 (1H, dt, *J* = 15.2 Hz, 4.0 Hz, SiOCH$_2$C**H**=CH), 6.56 (1H, ddt, *J* = 15.2 Hz, 10.8 Hz, 2.0 Hz, SiOCH$_2$CH=C**H**), 7.13 (1H, dd, *J* = 15.4 Hz, 11.0 Hz, C(O)HCH=C**H**), 9.57 (1H, d, *J* = 8.4 Hz, C(O)**H**); ^{13}C NMR (100 Hz, CDCl$_3$): δ 193.9, 151.7, 144.4, 131.5, 127.0, 63.1, 26.1, 18.7, -5.05 ppm; IR (neat): 2954.7 (m), 2930.0 (m), 2886.1 (w), 2856.8 (w), 2728.7 (m), 1684.6 (s), 1645.7 (s), 1602.7 (w), 1643.4 (w), 1362.1 (w), 1264.2 (m), 1161.5 (m), 1131.98 (s) cm^{-1}; HRMS (ESI+) for $C_{12}H_{23}O_2Si$ [M+H]: calculated 227.1467, found: 227.1475.

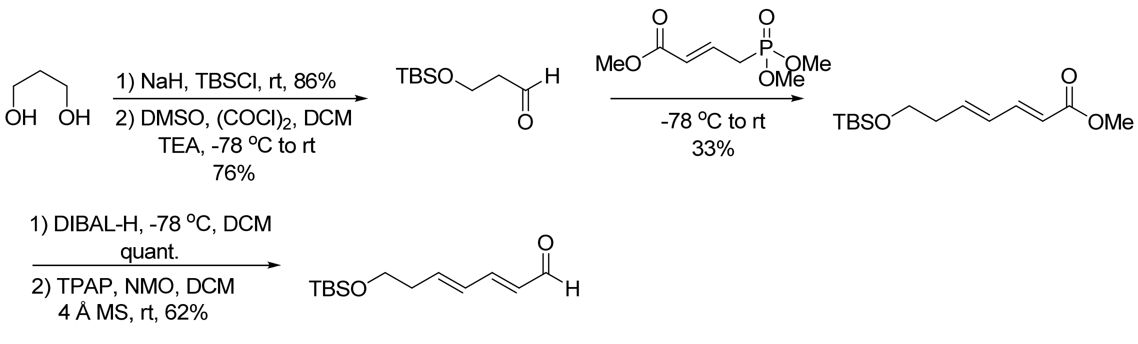
Preparation of (2E,4E)-6-(benzyloxy)hexa-2,4-dienal

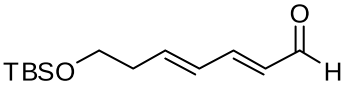




(2*E*,4*E*)-6-(benzyloxy)hexa-2,4-dienal (Table 2, entry 6). A yellow oil. R$_f$ = 0.37 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, CDCl$_3$): δ 4.18 (2H, d, *J* = 5.2 Hz, OC**H**$_2$CH=CH), 4.57 (2H, s, PhC**H**$_2$O), 6.16 (1H, dd, *J* = 15.2 Hz, 8.0 Hz, C(O)HC**H**=CH), 6.32 (1H, dt, *J* = 15.2 Hz, 5.2 Hz, OCH$_2$C**H**=CH), 6.58 (1H, ddm, *J* = 15.2 Hz, 10.8 Hz, OCH$_2$CH=C**H**), 7.13 (1H, dd, *J* = 15.4 Hz, 11.0 Hz, C(O)HCH=C**H**), 7.31-7.36 (5H, m, Ph-H), 9.58 (1H, d, *J* = 8.0 Hz, C(O)**H**); ^{13}C NMR (125 Hz, CDCl$_3$): δ 194.0, 151.4, 141.2, 137.9, 132.0, 126.2, 128.7, 128.1, 128.0, 73.1, 69.7 ppm; IR (neat): 3030.9 (w), 2845.9 (br), 2735.3 (w), 1678.8 (s), 1643.4 (s), 1602.1(w), 1469.6 (w), 1453.3 (m), 1391.1 (w), 1360.4 (m), 1161.9 (m), 1101.9 (s) cm^{-1}; HRMS (ESI+) for $C_{13}H_{15}O_2$ [M+H]: calculated 203.1072, found: 203.1082.

Preparation of (2E,4E)-7-(tert-butyldimethylsilyloxy)hepta-2,4-dienal





(2*E*,4*E*)-7-(*tert*-butyldimethylsilyloxy)hepta-2,4-dienal (Table 2, entry 10). A yellow oil. R_f= 0.65 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, CDCl$_3$): δ 0.05 (6H, s, Si(C**H$_3$**)$_2$), 0.89 (9H, s, SiC(C**H$_3$**)$_3$), 2.43 (2H, q, *J* = 6.4 Hz, CH$_2$C**H$_2$**CH=CH), 3.73 (2H, t, *J* = 6.4 Hz, C**H$_2$**CH$_2$CH=CH), 6.09 (1H, dd, *J* = 15.2 Hz, 8.0 Hz, C(O)HC**H**=CH), 6.26-6.41 (2H, m, CH$_2$C**H**=CH and CH$_2$CH=C**H**), 7.09 (1H, dd, *J* = 15.2 Hz, 10.0 Hz, C(O)HCH=C**H**), 9.55 (1H, d, *J* = 7.6 Hz, C(O)**H**); ^{13}C NMR (100 Hz, CDCl$_3$): δ 194.0, 152.6, 143.7, 130.6, 130.4, 62,1, 36.9, 26.1, 18.6, -5.0 ppm; IR (neat): 2953.4 (m), 2928.7 (m), 2885.7 (w), 2856.8 (m), 2738.5 (w), 1685.1 (s), 1640.9 (s), 1600.3 (w), 1471.1 (w), 1289.1 (w), 1254.8 (m), 1098.7 (s), 936.7 (m) cm^{-1}; HRMS (ESI+) for $C_{13}H_{25}O_2Si$ [M+H]: calculated 241.1624, found: 241.1633.

Procedure for Non-Catalyzed Allylation (Scheme 1)

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 33.7 mg (0.351 mmol) of sorbic aldehyde in a dry-box under an argon atmosphere, followed by 0.70 mL of THF and 70.7 mg (0.421 mmol) of allylboronic acid pinacol ester, sequentially. The vial was capped, taped with electrical tape, removed from the dry-box, and allowed to stir at ambient temperature for 15 hours. After this time period, deionized water was added and the mixture was allowed to stir for another 10 minutes. The aqueous layer was washed with CH$_2$Cl$_2$ (×3), and the combined organic layers were dried with Na$_2$SO$_4$ and concentrated in vacuo. Analysis of the unpurified reaction mixture using ^{1}H NMR was used to determine [*E*,*Z*]:[*E*,*E*] ratio.

Representative Procedure for Ni-Catalyzed Allylation at Ambient Temperature (Scheme 1 and Table 1)

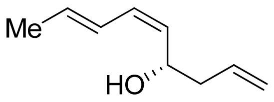
An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 9.6 mg (0.0351 mmol) of bis(1,5-cyclooctadiene)nickel, 20.1 mg (0.0351 mmol) of chiral ligand **L3**, and 0.70 mL of THF in a dry-box under an argon atmosphere. The vial was capped and stirred for 5 minutes. Next, 33.7 mg (0.351 mmol) of sorbic aldehyde was added, followed by 70.7 mg (0.421 mmol) of allylboronic acid pinacol ester. The vial was capped, taped with electrical tape, removed from the dry-box, and allowed to stir at ambient temperature for 18 hours. After this time period, deionized water was added and the mixture was allowed to stir for another 10 minutes. The aqueous layer was washed with CH$_2$Cl$_2$ (×3), and the combined organic layers were dried with Na$_2$SO$_4$ and concentrated in vacuo. Analysis of the unpurified reaction mixture using ^{1}H NMR was used to determine [*E*,*Z*]:[*E*,*E*] ratio. Silica gel chromatography (10:1 hexane:EtOAc) afforded 37.0 mg (77%) of a light yellow oil of the allylation product as a mixture of isomers.

Representative Procedure for Ni-Catalyzed Allylation at -35 °C (Table 2)

In a dry-box freezer: An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 9.6 mg (0.0351 mmol) of bis(1,5-cyclooctadiene)nickel, 20.1 mg (0.0351 mmol) of chiral ligand **L3**, and 0.70 mL of THF in a dry-box under an argon atmosphere. The vial was capped and stirred for 5 minutes. Next, 33.7 mg (0.351 mmol) of sorbic aldehyde was added, and the vial was capped and put into the freezer (temperature: -35 °C) inside the dry-box without stirring. Meanwhile, a syringe containing 70.7 mg (0.421 mmol) of allylboronic acid pinacol ester was put into the same freezer. After 30 minutes, the allylboronic acid pinacol ester was quickly transferred to the reaction vial and the vial resealed. The reaction was kept in the dry-box freezer for 18 hours, and deionized water was added. After stirring for another 10 minutes, the aqueous layer was washed with CH_2Cl_2 (×3), and the combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. Analysis of the unpurified reaction mixture using ^{1}H NMR was used to determine [*E,Z*]:[*E,E*] ratio. Silica gel chromatography (10:1 hexane:EtOAc) afforded 27.1 mg (56%) of a light yellow oil of the allylation product as a mixture of isomers.

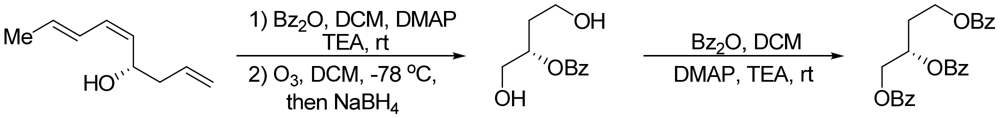
In a cryo-cool: An oven-dried 6-dram vial equipped with a magnetic stir-bar was charged with 9.6 mg (0.035 mmol) of bis(1,5-cyclooctadiene)nickel, 20.1 mg (0.035 mmol) of chiral ligand **L3**, and 0.70 mL of THF in a dry-box under an argon atmosphere. The vial was capped and stirred for 5 minutes. To a separate oven-dried 1-mL vial was added 33.7 mg (0.351 mmol) of sorbic aldehyde. To a third oven-dried 1-mL vial was added 117 mg (0.701 mmol) of allylboronic acid pinacol ester. After removal of the magnetic stir-bar from the 6-dram vial, the two uncapped 1-mL vials were transferred carefully into the 6-dram vial without mixing the reaction with the two reagents. The vial was capped, taped with electrical tape, removed from the dry-box, and cooled in a cryo-cool at -35 °C. After 30 minutes, the vial was gently shaken to mix the contents of the three vials and then put back to the cryo-cool for another 18 hours. After this time period, 0.6 mL (1.2 mmol) of acetaldehyde was added, followed by warming to ambient temperature over 30 minutes. Deionized water was added, and the mixture was lightly shaken for another 10 minutes. The aqueous layer was washed with CH_2Cl_2 (×3), and the combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. Analysis of the unpurified reaction mixture using ^{1}H NMR was used to determine [*E,Z*]:[*E,E*] ratio. Silica gel chromatography (10:1 hexane:EtOAc) afforded 33.9 mg (70%) of a light yellow oil of the allylation product as a mixture of isomers.

Characterization and Proof of Stereochemistry

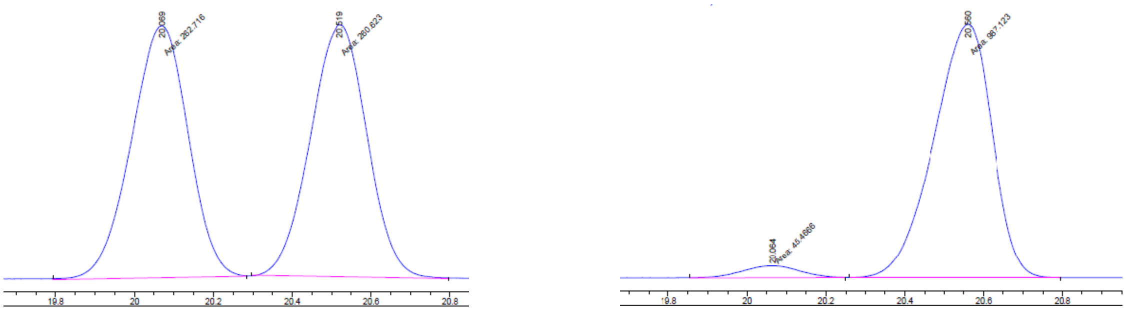


(*S*,5*Z*,7*E*)-nona-1,5,7-trien-4-ol. A light yellow oil. Single isomer. R_f= 0.42 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, $CDCl_3$): δ 1.60 (1H, d, *J* = 3.6 Hz, O**H**), 1.79 (3H, dd, *J* = 6.4 Hz, 1.6 Hz, C**H$_3$**), 2.32 (2H, ddt, *J* = 6.8, 6.0, 1.2 Hz, C**H$_2$**CH=CH$_2$), 4.63 (1H, dddd, *J* = 8.8, 6.0, 6.0, 3.2 Hz, C**H**OH), 5.12-5.18 (2H, m, CH$_2$CH=C**H$_2$**), 5.30 (1H, dd, *J* = 10.8, 8.8 Hz, CH=C**H**CHOH), 5.73-5.88 (2H, m, CH$_2$C**H**=CH$_2$ and CH$_3$C**H**=CH), 6.04 (1H, dd, *J* = 11.2, 10.8 Hz, C**H**=CHCHOH), 6.35 (1H, ddq, *J* = 14.8, 11.4, 1.2 Hz, CH$_3$CH=C**H**); ^{13}C NMR (100 Hz, $CDCl_3$): δ 134.3, 132.1, 130.7, 130.4, 126.6, 118.3, 67.3, 42.3, 18.5 ppm; IR (neat): 3349.4 (br), 3076.5 (w), 3021.8 (m), 2978.7 (w), 2914.2 (m), 2852.4 (m), 1654.9 (m), 1641.0 (m), 1433.7 (m), 1376.2 (m), 1306.3 (m), 1019.6 (s), 982.2 (s), 946.3 (s), 912.7 (s) cm^{-1}; HRMS (ESI+) for C_9H_{13} [M+H-H$_2$O]: calculated 121.1017, found: 121.1017; $[\alpha]_D^{20}$ = -2.3 (*c* = 0.42, $CHCl_3$).

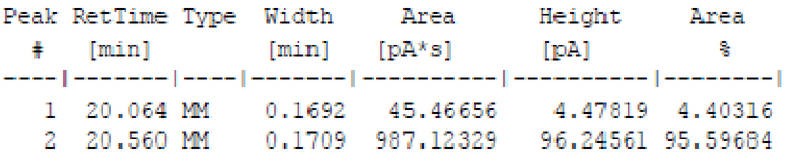
Proof of Stereochemistry: Enantioselectivies were determined by comparison of the acylated product with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. Absolute stereochemistry was determined by converting the allylation product to benzoate, followed by ozonolysis/reduction, and converting the corresponding diol to tribenzoate, as shown bellow. The resulting tribenzoate was compared on chiral SFC to butane-1,2,4-triyl tribenzoate and (*S*)- butane-1,2,4-triyl tribenzoate which were derived from commercially available butane-1,2,4-triol and (*S*)-1,2,4-triol respectively.



Chiral GLC (β-dex, supelco, 100 °C, 20 psi) - analysis of the acetate of (5Z,7E)-nona-1,5,7-trien-4-ol



racemic allylation product



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   2  20.560 MM    0.1709  987.12329   96.24561 95.59684
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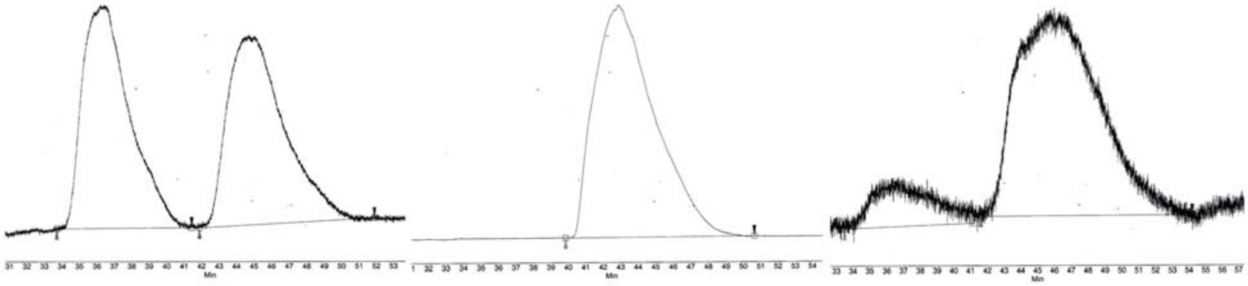
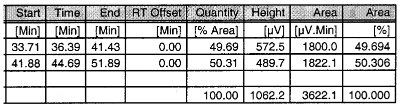
Chiral SFC (OD-H, Chiralpak, 220 nm, 3.0 mL/min, 3.0% MeOH, 150 psi, 50 °C) – analysis of butane-1,2,4-triyl tribenzoate



racemic tribenzoate

S-tribenzoate

tribenzoate derived from allylation product



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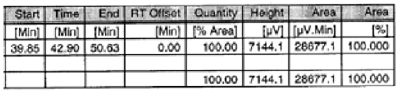
				100.00	1062.2	3622.1	100.000



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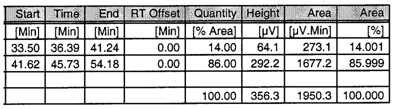
				100.00	7144.1	28677.1	100.000



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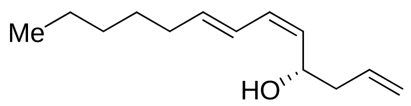
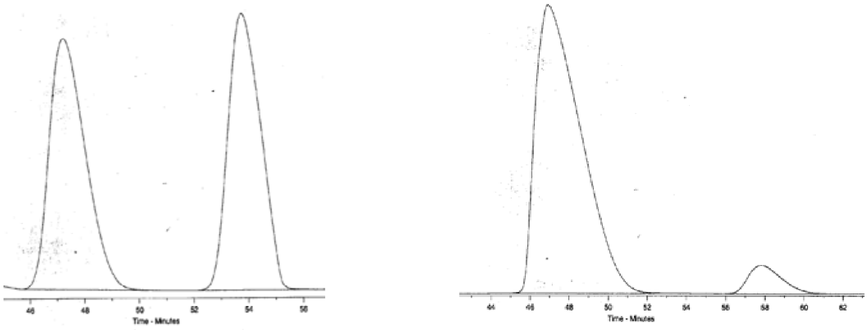
33.50	36.39	41.24	0.00	14.00	64.1	273.1	14.001
41.62	45.73	54.18	0.00	86.00	292.2	1677.2	85.999
				100.00	356.3	1950.3	100.000



(*S*,5*Z*,7*E*)-trideca-1,5,7-trien-4-ol. A colorless oil. Mixture of isomers (24:1 [*E,Z*]:[*E,E*]). R_f = 0.59 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.8 Hz, C**H$_3$**), 1.26-1.41 (6H, m, CH_3(**CH$_2$**)$_3$), 1.71 (1H, s, O**H**), 2.10 (2H, q, *J* = 7.2 Hz, C**H$_2$**CH=CH), 2.32 (2H, t, *J* = 6.8 Hz, C**H$_2$**CHOH), 4.62 (1H, dt, *J* = 8.0, 6.4 Hz, C**H**OH), 5.11-5.17 (2H, m, CH_2CH=C**H$_2$**), 5.30 (1H, dd, *J* = 10.4, 9.2 Hz, CH=C**H**CHOH), 5.71-5.87 (2H, m, CH_2C**H**=CH_2 and CH_2C**H**=CH), 6.03 (1H, t, *J* = 11.0 Hz, C**H**=CHCHOH), 6.31 (1H, ddt, *J* = 14.8, 11.2, 0.8 Hz, CH_2CH=C**H**); ^{13}C NMR (100 Hz, $CDCl_3$): δ 137.8, 134.3, 130.9, 130.5, 125.2, 118.3, 67.3, 42.3, 33.0, 31.7, 29.1, 22.7, 14.3 ppm; IR (neat): 3367.7 (br), 3076.4 (m), 2956.4 (s), 2925.4 (m), 2856.7 (m), 1692.3 (m), 1641.0 (m), 1458.8 (m), 1433.1 (m), 1378.4 (m), 1307.7 (m), 1021.2 (s), 984.4 (s), 946.9 (s), 912.2 (s) cm^{-1}; HRMS (ESI+) for $C_{13}H_{21}$ [M+H-H_2O]: calculated 177.1643, found: 177.1639; $[\alpha]_D^{20}$ = -1.2 (*c* = 1.41, $CHCl_3$).

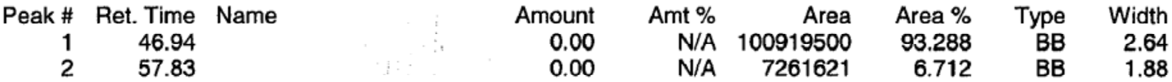
Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. Absolute stereochemistry was determined by converting the allylation product to butane-1,2,4-triyl tribenzoate as described for (*S*,5*Z*,7*E*)-nona-1,5,7-trien-4-ol. The resulting tribenzoate was compared on chiral SFC to butane-1,2,4-triyl tribenzoate and (*S*)- butane-1,2,4-triyl tribenzoate derived from commercially available butane-1,2,4-triol and (*S*)-1,2,4-triol, respectively.

Chiral HPLC (AS, Chiralcel, 0.5 mL/min, 0% Isopropanol, 220 nm) – analysis of (5Z,7E)-trideca-1,5,7-trien-4-ol



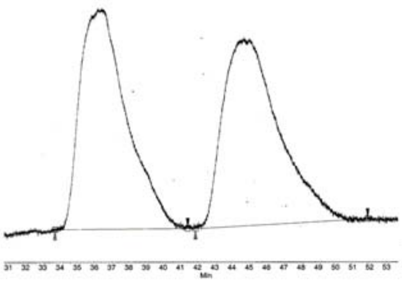
Racemic

allylation product

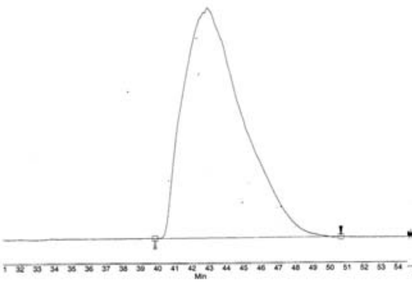


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	46.94		0.00	N/A	100919500	93.288	BB	2.64
2	57.83		0.00	N/A	7261621	6.712	BB	1.88

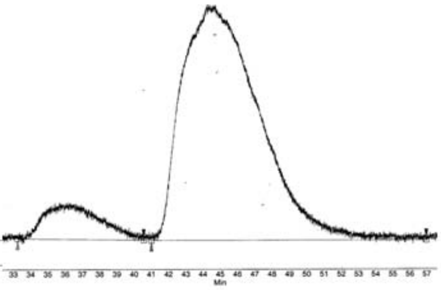
Chiral SFC (OD-H, Chiralpak, 220 nm, 3.0 mL/min, 3.0% MeOH, 150 psi, 50 ^{o}C) – analysis of butane-1,2,4-triyl tribenzoate



racemic tribenzoate



S-tribenzoate

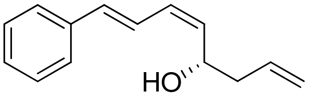


tribenzoate derived from allylation product

Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
33.71	36.39	41.43	0.00	49.69	572.5	1800.0	49.694
41.88	44.69	51.89	0.00	50.31	489.7	1822.1	50.306
				100.00	1062.2	3622.1	100.000

Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
39.85	42.90	50.63	0.00	100.00	7144.1	28677.1	100.000
				100.00	7144.1	28677.1	100.000

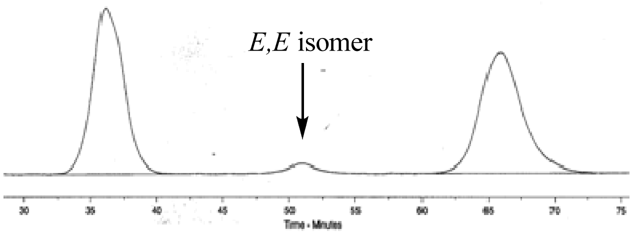
Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
33.25	35.94	40.55	0.00	9.83	130.9	516.3	9.829
41.01	44.37	56.98	0.00	90.17	903.5	4736.3	90.171
				100.00	1034.4	5252.6	100.000



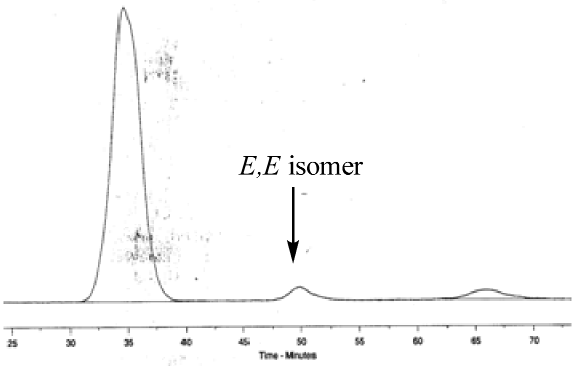
(*S*,5*Z*,7*E*)-8-phenylocta-1,5,7-trien-4-ol. A yellow oil. Mixture of isomers (24:1 [*E*,*Z*]:[*E*,*E*]). R_f = 0.33 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, $CDCl_3$): δ 1.87 (1H, s, O**H**), 2.38 (2H, t, *J* = 6.8 Hz, C**H₂**CH=CH₂), 4.76 (1H, dt, *J* = 8.0, 6.8 Hz, C**H**OH), 5.14-5.21 (2H, m, CH₂CH=C**H₂**), 5.51 (1H, dd, *J* = 10.8, 8.8 Hz, CH=C**H**CHOH), 5.85 (1H, ddt, *J* = 17.2, 10.0, 7.2 Hz, CH₂C**H**=CH₂), 6.24 (1H, t, *J* = 11.2 Hz, C**H**=CHCHOH), 6.59 (1H, d, *J* = 15.2, PhC**H**=CH), 7.07 (1H, dd, *J* = 15.6, 11.2 Hz, PhCH=C**H**), 7.25 (1H, t, *J* = 7.2 Hz, para-Ph-H), 7.33 (2H, dd, *J* = 8.0, 7.2 Hz, meta-Ph-H), 7.42 (2H, dd, *J* = 8.0, 0.8 Hz, ortho-Ph-H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 137.1, 134.6, 134.1, 133.3, 130.6, 128.8, 128.0, 128.6, 123.8, 118.5, 67.5, 42.3 ppm; IR (neat): 3361.3 (br), 3077.1 (m), 3027.4 (m), 2978.4 (m), 2906.9 (m), 1638.9 (m), 1597.4 (w), 1493.4 (m), 1448.8 (m), 1306.3 (m), 989.2 (s), 946.1 (s), 916.2 (s), 858.4 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{15}$ [M+H-H_2O]: calculated 183.1174, found: 183.1177; $[\alpha]_D^{20}$ = +3.22 (*c* = 1.41, $CHCl_3$).

Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. Absolute stereochemistry was determined by converting the allylation product to butane-1,2,4-triyl tribenzoate as described for (*S*,5*Z*,7*E*)-nona-1,5,7-trien-4-ol. The resulting tribenzoate was compared on chiral SFC to butane-1,2,4-triyl tribenzoate and (*S*)- butane-1,2,4-triyl tribenzoate derived from commercially available butane-1,2,4-triol and (*S*)-1,2,4-triol, respectively.

Chiral HPLC (OD, Chiralcel, 1.0 mL/min, 1.0% Isopropanol, 220 nm) – analysis of (5Z,7E)-8-phenylocta-1,5,7-trien-4-ol



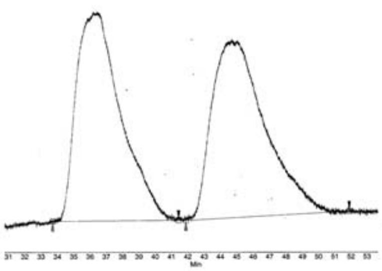
racemic



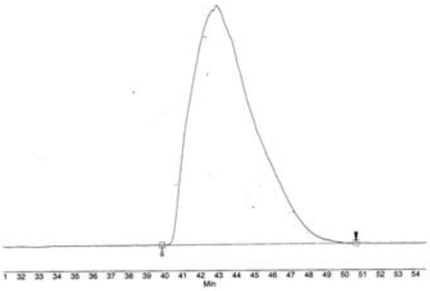
allylation product

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	34.73		0.00	N/A	9043018	96.063	BB	2.68
2	65.83		0.00	N/A	370651	3.937	BB	3.31

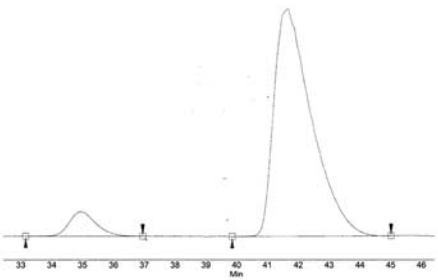
Chiral SFC (OD-H, Chiralpak, 220 nm, 3.0 mL/min, 3.0% MeOH, 150 psi, 50 °C) – analysis of butane-1,2,4-triyl tribenzoate



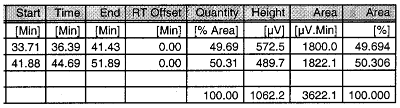
racemic tribenzoate



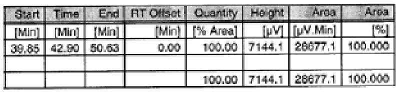
S-tribenzoate



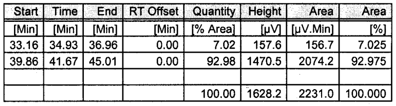
tribenzoate derived from
allylation product



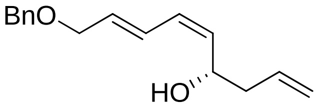
Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
33.71	36.39	41.43	0.00	49.69	572.5	1800.0	49.694
41.88	44.69	51.89	0.00	50.31	489.7	1822.1	50.306
				100.00	1062.2	3622.1	100.000



Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
39.85	42.90	50.63	0.00	100.00	7144.1	28677.1	100.000
				100.00	7144.1	28677.1	100.000



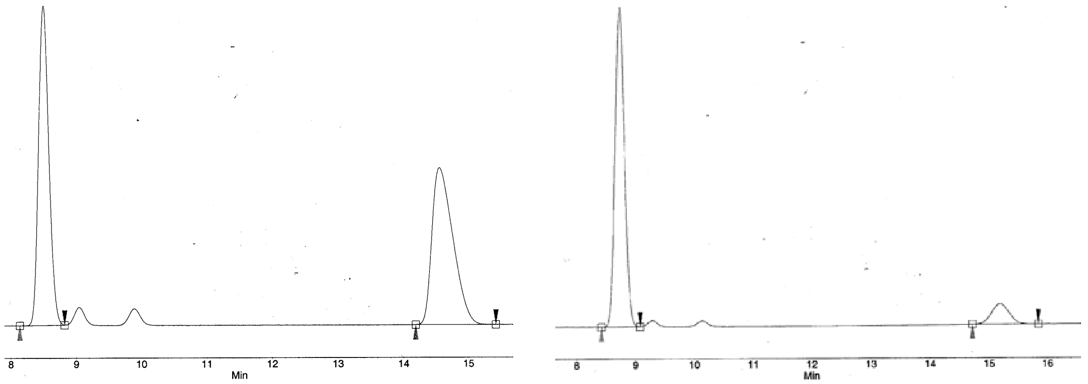
Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
33.16	34.93	36.96	0.00	7.02	157.6	156.7	7.025
39.86	41.67	45.01	0.00	92.98	1470.5	2074.2	92.975
				100.00	1628.2	2231.0	100.000



(*S*,5*Z*,7*E*)-9-(benzyloxy)nona-1,5,7-trien-4-ol. A yellow oil. Mixture of isomers (18:1 [*E*,*Z*]:[*E*,*E*]). R_f= 0.24 (3:1 hexane:EtOAc); ^{1}H NMR (500 Hz, $CDCl_3$): δ 1.67 (1H, d, *J* = 2.5 Hz, O**H**), 2.32 (2H, tt, *J* = 7.0, 0.5 Hz, C**H₂**CH=CH₂), 4.09 (2H, d, *J* = 4.5 Hz, OC**H₂**CH=CH), 4.53 (1H, s, PhC**H₂**O), 4.63 (1H, m, C**H**OH), 5.13-5.18 (2H, m, CH₂CH=C**H₂**), 5.44 (1H, dd, *J* = 10.5, 9.5 Hz, CH=C**H**CHOH), 5.77-5.88 (2H, m, OCH₂C**H**=CH and CH₂C**H**=CH₂), 6.09 (1H, t, *J* = 11.5 Hz, C**H**=CHCHOH), 6.58 (1H, ddd, *J* = 15.5, 12.0, 1.5 Hz, OCH₂CH=C**H**), 7.28-7.36 (5H, m, Ph-H); ^{13}C NMR (125 Hz, $CDCl_3$): δ 138.3, 134.1, 133.3, 132.2, 129.8, 128.6, 180.0, 127.9, 127.4, 118.6, 72.5, 70.4, 67.2, 42.2 ppm; IR (neat): 3390.1 (br), 3066.2 (m), 3027.8 (m), 292.8 (m), 2853.4 (m), 1640.5 (m), 143.8 (m), 1358.5 (m), 1305.9 (w), 1206.6 (w), 1102.2 (s), 1046.5 (s), 1027.1 (s), 989.5 (s), 915.6 (s), 737.5 (s) cm^{-1}; HRMS (ESI+) for $C_{16}H_{19}O$ [M+H-H_2O]: calculated 227.1436, found: 227.1438; $[\alpha]_D^{20}$ = -4.32 (*c* = 0.66, $CHCl_3$).

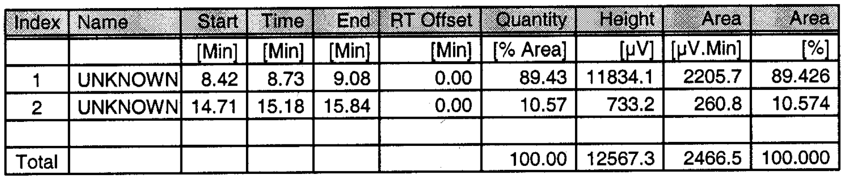
Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (AD-H, Chiralpak, 220 nm, 3.0 mL/min, 3.0% MeOH, 150 psi, 50 °C) – analysis of (5Z,7E)-9-(benzyloxy)nona-1,5,7-trien-4-ol

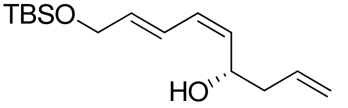


racemic

allylation product



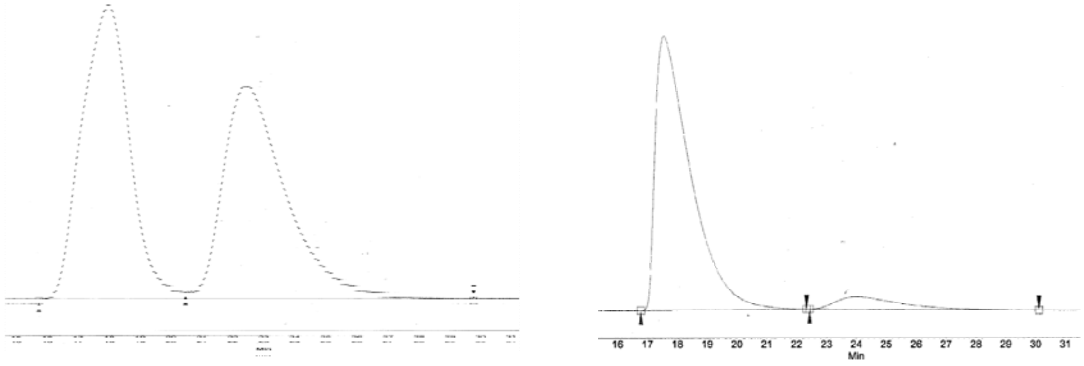
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.42	8.73	9.08	0.00	89.43	11834.1	2205.7	89.426
2	UNKNOWN	14.71	15.18	15.84	0.00	10.57	733.2	260.8	10.574
Total						100.00	12567.3	2466.5	100.000



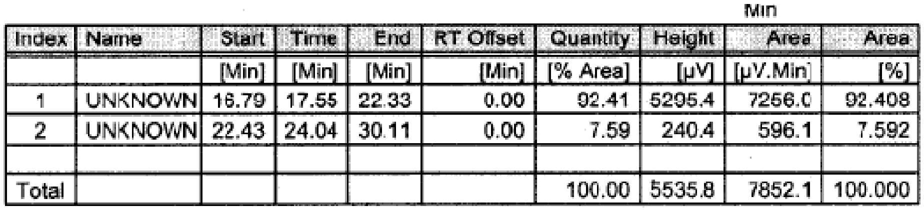
(S,5Z,7E)-9-(*tert*-butyldimethylsilyloxy)nona-1,5,7-trien-4-ol. A light yellow oil. Single isomer. R_f= 0.43 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, CDCl$_3$): δ 0.08 (6H, s, Si(C**H**$_3$)$_2$), 0.92 (1H, s, SiC(C**H**$_3$)$_3$), 1.63 (1H, d, J = 3.2 Hz, O**H**), 2.32 (2H, t, J = 6.8 Hz, C**H**$_2$CH=CH$_2$), 4.24 (2H, dd, J = 4.4, 1.6 Hz, SiOC**H**$_2$CH=CH), 4.64 (1H, dddd, J = 8.8, 6.4, 6.0, 2.4 Hz, C**H**OH), 5.12-5.18 (2H, m, CH$_2$CH=C**H**$_2$), 5.40 (1H, dd, J = 10.8, 8.8 Hz, CH=C**H**CHOH), 5.76-5.86 (2H, m, CH$_2$C**H**=CH$_2$ and SiOCH$_2$C**H**=CH), 6.08 (1H, dd, J = 11.2, 10.8 Hz, C**H**=CHCHOH), 6.54 (1H, ddq, J = 14.0, 11.2, 1.2 Hz, SiOCH$_2$CH=C**H**); ^{13}C NMR (100Hz, CDCl$_3$): δ 135.2, 134.2, 132.5, 129.8, 124.4, 118.4, 67.5, 63.5, 42.3, 26.2, 18.7, -4.93, -4.94 ppm; IR (neat): 3380.1 (br), 3077.2 (w), 3009.9 (m), 2954.4 (m), 2895.7 (m), 2856.4 (m), 1641.2 (w), 1471.5 (m), 1362.4 (m), 1253.7 (m), 1100.9 (br), 1007.2 (br), 831.9 (s), 744.2 (s) cm^{-1}; HRMS (ESI+) for $C_{15}H_{27}OSi$ [M+H-H$_2$O]: calculated 251.1831, found: 251.1821; $[\alpha]_D^{20}$ = -5.94 (c = 0.83, CHCl$_3$).

Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. Absolute stereochemistry was determined by converting the allylation product to butane-1,2,4-triyl tribenzoate as described for (S,5Z,7E)-nona-1,5,7-trien-4-ol. The resulting tribenzoate was compared on chiral SFC to butane-1,2,4-triyl tribenzoate and (S)- butane-1,2,4-triyl tribenzoate derived from commercial available butane-1,2,4-triol and (S)-1,2,4-triol, respectively.

Chiral SFC (AD-H, Chiralpak, 220 nm, 1.0 mL/min, 1.5% MeOH, 150 psi, 50 °C) – analysis of (S,5Z,7E)-9-(tert-butyldimethylsilyloxy)nona-1,5,7-trien-4-ol

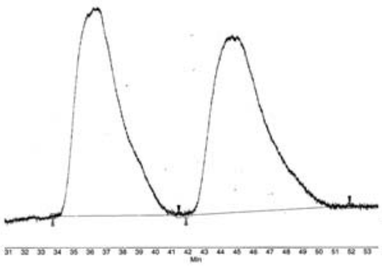


racemic allylation product

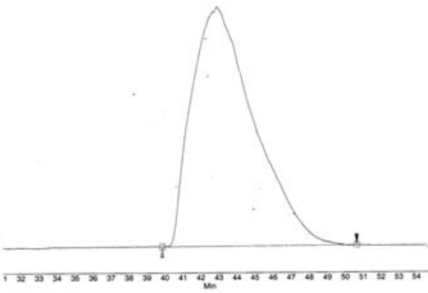


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	16.79	17.55	22.33	0.00	92.41	5295.4	7256.0	92.408
2	UNKNOWN	22.43	24.04	30.11	0.00	7.59	240.4	596.1	7.592
Total						100.00	5535.8	7852.1	100.000

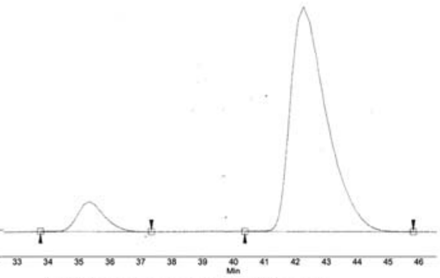
Chiral SFC (OD-H, Chiralpak, 220 nm, 3.0 mL/min, 3.0% MeOH, 150 psi, 50 ^{o}C) – analysis of butane-1,2,4-triyl tribenzoate



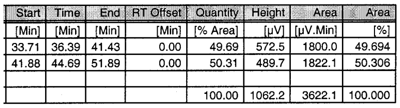
racemic tribenzoate



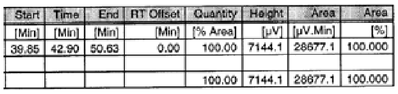
S-tribenzoate



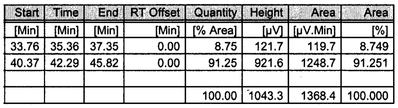
tribenzoate derived from allylation product



Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
33.71	36.39	41.43	0.00	49.69	572.5	1800.0	49.694
41.88	44.69	51.89	0.00	50.31	489.7	1822.1	50.306
				100.00	1062.2	3622.1	100.000



Start	Time	End	RT Offset	Quantity	Height	Area	Area
[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
39.85	42.90	50.63	0.00	100.00	7144.1	28677.1	100.000
				100.00	7144.1	28677.1	100.000



Start	Time	End	RT Offset	Quantity	Height	Area	Area
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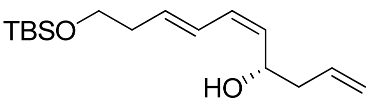
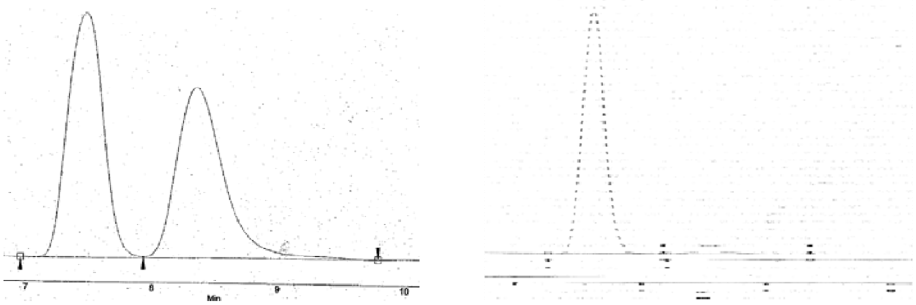
33.76	35.36	37.35	0.00	8.75	121.7	119.7	8.749
40.37	42.29	45.82	0.00	91.25	921.6	1248.7	91.251
				100.00	1043.3	1368.4	100.000



(*S*,5*Z*,7*E*)-10-(*tert*-butyldimethylsilyloxy)deca-1,5,7-trien-4-ol. A yellow oil. Single isomer. R_f = 0.51 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, $CDCl_3$): δ 0.05 (6H, s, Si(C**H**$_3$)$_2$), 0.89 (9H, s, SiC(C**H**$_3$)$_3$), 1.61 (1H, d, *J* = 4.2 Hz, O**H**), 2.33 (4H, m, C**H**$_2$CH=CH$_2$ and C**H**$_2$CH=CH), 3.66 (2H, t, *J* = 6.6 Hz, SiOC**H**$_2$), 4.62 (1H, m, C**H**OH), 5.12-5.18 (2H, m, CH$_2$CH=C**H**$_2$), 5.33 (1H, dd, *J* = 10.8, 8.8 Hz, CH=C**H**CHOH), 5.71-5.87 (2H, m, CH$_2$C**H**=CH$_2$ and CH$_2$C**H**=CH), 6.04 (1H, t, *J* = 11.2 Hz, C**H**=CHCHOH), 6.38 (1H, ddt, *J* = 14.8, 11.2, 1.2 Hz, CH$_2$CH=C**H**); ^{13}C NMR (125 Hz, $CDCl_3$): δ 134.3, 133.8, 131.1, 130.7, 127.0, 118.5, 67.3, 62.9, 42.2, 36.6, 26.1, 18.6, -5.1 ppm; IR (neat): 3361.4 (br), 3077.2 (w), 2954.0 (s), 2929.6 (s), 2898.1 (m), 2857.5 (s), 1471.6 (m), 1255.6 (m), 1100.5 (s), 948.7 (m), 836.2 (s) cm^{-1}; HRMS (ESI+) for $C_{16}H_{29}OSi$ [M+H-H$_2$O]: calculated 265.1988, found: 265.1986; $[\alpha]_D^{20}$ = 2.34 (*c* = 1.37, $CHCl_3$).

Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (AD-H, Chiralpak, 220 nm, 1.0 mL/min, 2.0% MeOH, 150 psi, 50 °C) – analysis of (5Z,7E)-10-(tert-butyldimethylsilyloxy)deca-1,5,7-trien-4-ol



racemic allylation product

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
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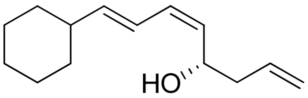
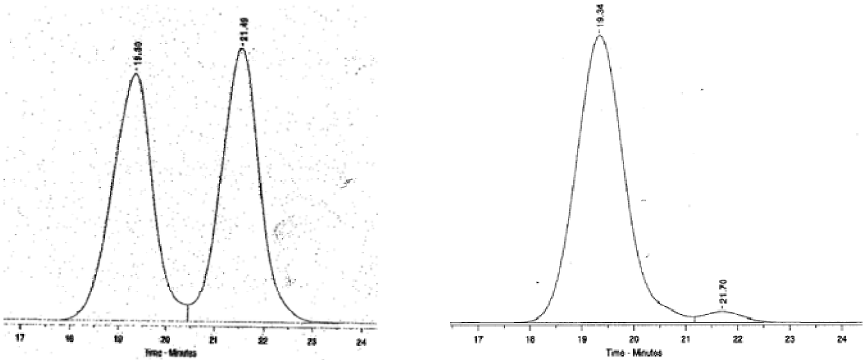
1	UNKNOWN	7.54	7.84	8.41	0.00	94.17	5158.7	1045.1	94.171
2	UNKNOWN	8.46	8.83	9.63	0.00	5.83	206.1	64.7	5.829
Total						100.00	5364.8	1109.8	100.000



(S,5Z,7E)-8-cyclohexylocta-1,5,7-trien-4-ol. A light yellow oil. Mixture of isomers (38:1 [E,Z]:[E,E]). R_f = 0.43 (3:1 hexane:EtOAc); ^{1}H NMR (400 Hz, CDCl$_3$): δ 1.05–1.74 (11H, m, (**CH$_2$**)$_5$ and O**H**), 2.03 (1H, dtt, J = 7.6, 7.2, 3.6 Hz, C**H**CH=CH), 2.32 (2H, t, J = 6.2 Hz, C**H$_2$**CH=CH$_2$), 4.63 (1H, dddd, J = 8.8, 6.4, 6.0, 2.4 Hz, C**H**OH), 5.11-5.18 (2H, m, CH$_2$CH=C**H$_2$**), 5.31 (1H, dd, J = 10.0, 8.8 Hz, CH=C**H**CHOH), 5.70 (1H, dd, J = 15.2, 7.2 Hz, CHC**H**=CH), 5.83 (1H, ddt, J = 17.2, 10.0, 7.2 Hz, CHC**H**=CH$_2$), 6.03 (1H, dd, J = 11.2, 10.8 Hz, C**H**=CHCHOH), 6.27 (1H, ddt, J = 15.2, 11.2, 0.8 Hz, CHCH=C**H**) ppm; ^{13}C NMR (100 Hz, CDCl$_3$): δ 143.4, 134.4, 131.2, 130.7, 122.7, 118.3, 67.4, 42.3, 41.2, 33.02, 32.99, 26.4, 26.2 ppm; IR (neat): 3338.5 (br), 3075.3 (w), 3008.0 (w), 2978.6 (w), 2921.9 (s). 2850.1 (s), 1641.2 (m), 1447.5 (m), 1349.3 (br), 1020.2 (s), 984.0 (s), 947.5 (s), 921.1 (s), 839.9 (m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{21}$ [M+1-H$_2$O]: calculated 189.1643, found: 189.1639; $[\alpha]_D^{20}$ = -0.91 (c = 1.24, CHCl$_3$).

Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. The absolute stereochemistry was assigned by analogy.

Chiral HPLC (AS, Chiralcel, 220 nm, 0.5 mL/min, 0.5% Isopropanol) – analysis of (5Z,7E)-8-cyclohexylocta-1,5,7-trien-4-ol



racemic allylation product

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
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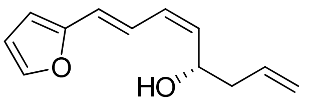
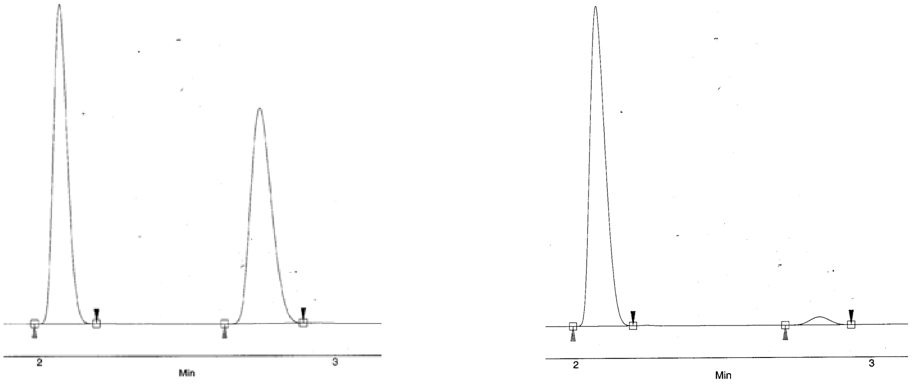
2	21.70		0.00	N/A	1265217	2.965	VB	0.92



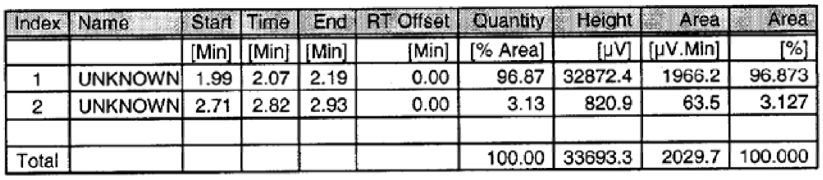
(*S*,5*Z*,7*E*)-8-(furan-2-yl)octa-1,5,7-trien-4-ol. A yellow oil. Mixture of isomers (18:1 [*E*,*Z*]:[*E*,*E*]). R_f = 0.28 (3:1 hexane:EtOAc); ^{1}H NMR (400Hz, $CDCl_3$): δ 1.76 (1H, d, *J* = 3.2 Hz, O**H**), 2.36 (2H, ddt, *J* = 7.2, 6.4, 1.2 Hz, C**H₂**CH=CH₂), 4.75 (1H, dddd, *J* = 9.6, 6.4, 6.0, 3.2 Hz, C**H**OH), 5.13-5.21 (2H, m, CH₂CH=C**H₂**), 5.49 (1H, dd, *J* = 10.0, 9.6 Hz, CH=C**H**CHOH), 5.85 (1H, ddt, *J* = 17.2, 10.4, 7.2 Hz, CH₂C**H**=CH₂), 6.16 (1H, ddt, *J* = 12.0, 10.4, 0.8 Hz, C**H**=CHCHOH), 6.29-6.40 (3H, m, ArC**H**=CH, ortho-Ar and meta-Ar), 6.96 (1H, dd, *J* = 15.6, 11.6 Hz, ArCH=C**H**), 7.38 (1H, d, *J* = 1.6 Hz, para-Ar); ^{13}C NMR (100Hz, $CDCl_3$): δ 153.1, 142.6, 134.2, 133.6, 130.2, 122.4, 122.0, 118.6, 111.9, 109.4, 67.4, 42.3 ppm; IR (neat): 3381.7 (br), 3118.2 (w), 3076.0 (w), 3010.9 (m), 2978.2 (w), 2929.4 (m), 1676.1 (w), 1638.5 (m), 1609.6 (w), 1483.7 (m), 1152.1 (m) 1014.4 (s), 984.1 (s), 942.4 (s), 925.2 (s), 735.8 (s) cm^{-1}; HRMS (ESI+) for $C_{12}H_{13}O$ [M+1-H_2O]: calculated 173.0966, found: 173.0971; $[\alpha]_D^{20}$ = 0.65 (*c* = 1.12, $CHCl_3$).

Proof of Stereochemistry: Enantioselectivies were determined by comparison with authentic racemic material prepared using tricyclohexylphospine as the achiral ligand in the allylation reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (AD-H, Chiralpak, 220 nm, 5.0 mL/min, 5.0% MeOH, 150 psi, 50 °C) – analysis of (5Z,7E)-8-(furan-2-yl)octa-1,5,7-trien-4-ol

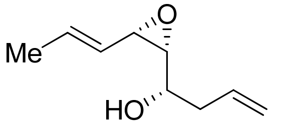


Racemic allylation product

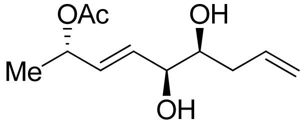


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	1.99	2.07	2.19	0.00	96.87	32872.4	1966.2	96.873
2	UNKNOWN	2.71	2.82	2.93	0.00	3.13	820.9	63.5	3.127
Total						100.00	33693.3	2029.7	100.000

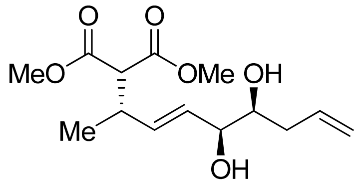
Procedure for Functionalization of (*S*,5*Z*,7*E*)-nona-1,5,7-trien-4-ol (Scheme 2)



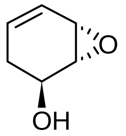
(*S*)-1-((2*R*,3*S*)-3-((*E*)-prop-1-enyl)oxiran-2-yl)but-3-en-1-ol. A flame-dried 25-mL round-bottom-flask equipped with a magnetic stir-bar was charged with 221 mg (1.60 mmol) of (*S*,5*Z*,7*E*)-nona-1,5,7-trien-4-ol, 8.01 mL of THF, and 336 mg (4.01 mmol) of $NaHCO_3$. The flask was sealed with septum and cooled in a cryo-cool to -20 °C under N_2. After 30 minutes, mCPBA (77%) was added as a white powder, and the mixture was allowed to stir at this temperature for another 4 hours. Then, the reaction was filtered through a plug of silica gel (prewashed with 5% triethylamine in ether), washed with ether, and concentrated under reduced pressure. The crude material was purified by silica gel (prewashed with 5% triethylamine in ether) chromatography (3:1 pentane:ether) to afford 195.0 mg (79%) of the title compound as light yellow oil and as a mixture of diastereomers (40:1 *d.r.*). R_f = 0.59 (1:1 hexane/EtOAc, stain in $KMnO_4$). ^{1}H NMR (400 Hz, $CDCl_3$): δ 1.76 (3H, dd, *J* = 6.8, 1.6 Hz, C**H₃**), 2.12 (1H, s, O**H**), 2.33 (2H, m, C**H₂**CH=CH₂), 3.06 (1H, dd, *J* = 8.0, 4.4 Hz, CHOC**H**CHOH), 3.49 (1H, dd, *J* = 8.0, 4.4 Hz, C**H**OCHCHOH), 3.60 (1H, dtd, *J* = 7.6, 6.0, 4.0 Hz, C**H**OH), 5.12-5.18 (2H, m, CH₂CH=C**H₂**), 5.33 (1H, ddd, *J* = 15.2, 8.0, 1.2 Hz, CH₃CH=C**H**), 5.82 (1H, ddt, *J* = 17.2, 10.4, 6.8 Hz, CH₂C**H**=CH₂), 5.97 (1H, dq, *J* = 15.2, 6.4 Hz, CH₃C**H**=CH); ^{13}C NMR (100Hz, $CDCl_3$): δ 133.9, 133.5, 124.9, 118.4, 69.4, 61.8, 58.0, 38.7, 18.3 ppm; IR (neat): 3415.0 (br), 3077.0 (w), 3003.5 (m), 2970.6 (m), 2919.7 (m), 2857.1 (w), 1668.3 (w), 1641.9 (m), 1436.2 (m), 1378.2 (w), 1295.1 (br), 1047.3 (m), 963.5 (s), 914.4 (s), 873.4 (m) cm^{-1}; HRMS (ESI+) for $C_9H_{13}O$ [M+H-H_2O]: calculated: 137.0966, found: 137.0973; $[\alpha]_D^{20}$ = +1.53 (*c* = 0.70, $CHCl_3$).



(2*S*,5*S*,6*S*,*E*)-5,6-dihydroxynona-3,8-dien-2-yl acetate. An oven-dried 2-dram vial was charged with 7.5 mg (0.0065 mmol) of tetrakis(triphenylphosphine)palladium, 0.20 mL of THF, and 5.8 mg (0.098 mmol) of acetic acid in a dry-box under an argon atmosphere. The vial was capped with a septum, taped with electrical tape, and removed from the dry-box. The reaction mixture was cooled in a ice-water bath for 30 minutes, and then 10.0 mg (0.0650 mmol) of (*S*)-1-((2*R*,3*S*)-3-((*E*)-prop-1-enyl)oxiran-2-yl)but-3-en-1-ol was added dropwise to the reaction vial as a solution in 0.14 mL of THF. The reaction was allowed to stir at 0 °C for 1 hour, followed by another 3 hours at ambient temperature. After this time period, the reaction was cooled to 0 °C again, followed by addition of about 10 μL of H_2O_2 (30% in water). Saturated $NaHCO_3$ and ether were added and stirring continuously for 5 minutes, and the layers were separated. The aqueous layer was extracted with ether (×3), and the organic layers were filtered through a plug of $MgSO_4$ (top) and silica gel (bottom). Solvent was evaporated *in vacuo*. The crude material was purified by silica gel chromatography (1:1 pentane:ether) to afford 8.1 mg (58%) of the title compound (10:1 *1,4*:*1,2*) as a colorless oil. R_f = 0.2 (1:1 hexane/EtOAc, stain in $KMnO_4$). ^{1}H NMR (500 Hz, $CDCl_3$): δ 1.32 (3H, d, *J* = 6.5 Hz, C**H₃**CHOAc), 2.05 (3H, s, C**H₃**C(O)), 2.15-2.38 (4H, m, C**H₂**CH=CH₂ and 2 O**H**s), 3.55 (1H, ddt, *J* = 8.0, 6.0, 4.0 Hz, C**H**OHCH₂), 3.98 (1H, m, CH=CHC**H**OH), 5.13-5.17 (2H, m, CH₂CH=C**H₂**), 5.36 (1H, p, *J* = 6.5 Hz, CH₃C**H**OAc), 5.77-5.89 (3H, m, C**H**=C**H** and CH₂C**H**=CH₂); ^{13}C NMR (125 Hz, $CDCl_3$): δ 170.5, 134.3, 133.2, 130.9, 118.7, 74.9, 73.6, 70.4, 37.8, 21.6, 20.4 ppm; IR (neat): 3387.1 (br), 3114.3 (w), 2979.2 (w), 2930.9 (w), 2033.3 (w), 2005.8 (w), 1735.7 (s), 1641.5 (w), 1432.0 (w), 1372.4 (m), 1242.5 (s), 1043.2 (m) cm^{-1}; HRMS (ESI+) for $C_{11}H_{17}O_3$ [M+H-H_2O]: calculated: 197.1178, found: 197.1181; $[\alpha]_D^{20}$ = -31.85 (*c* = 0.43, $CHCl_3$).

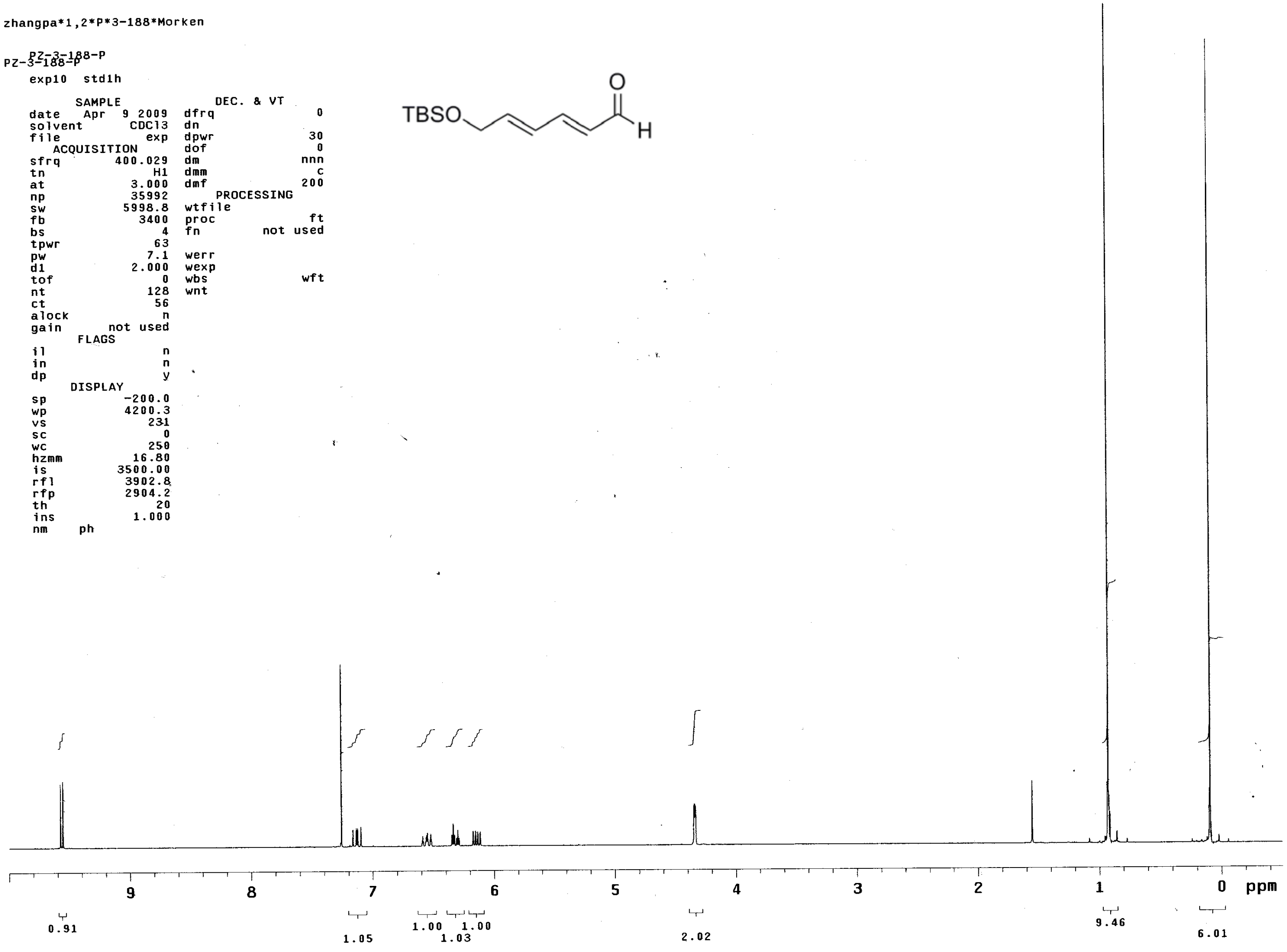


Dimethyl 2-((2*S*,5*S*,6*S*,*E*)-5,6-dihydroxynona-3,8-dien-2-yl)malonate. An oven-dried 2-dram vial was charged with 7.5 mg (0.0065 mmol) of tetrakis(triphenylphosphine)palladium, 0.20 mL of THF, and 12.9 mg (0.0975 mmol) of dimethylmalonate in a dry-box under an argon atmosphere. The vial was capped with septum, taped with electrical tape, and removed from the dry-box. Next, 10.0 mg (0.0650 mmol) of (*S*)-1-((2*R*,3*S*)-3-((*E*)-prop-1-enyl)oxiran-2-yl)but-3-en-1-ol was added to the reaction vial as a solution in THF (0.14 mL). The reaction was allowed to stir at ambient temperature for 14 hours. After this time period, the reaction was cooled to 0 °C, followed by addition of about 10 μL of H_2O_2 (30% in water). Saturated $NaHCO_3$ and ether were added and stirring continuously for 5 minutes, and the layers were separated. The aqueous layer was extracted with ether (×3), and the organic layers were filtered through a plug of $MgSO_4$ (top) and silica gel (bottom). Solvent was evaporated *in vacuo*. The crude material was purified by silica gel chromatography (3:1 hexane:EtOAc) to afford 16.0 mg (86%) of the title compound (17:1 *d.r.*) as a colorless oil. $R_f = 0.2$ (1:1 hexane:EtOAc, stain in $KMnO_4$). ^{1}H NMR (500 Hz, $CDCl_3$): δ 1.11 (3H, d, *J* = 7.0 Hz, CHC**H$_3$**), δ 2.15 (1H, dddt, *J* = 14.5, 7.5, 8.0, 1.0 Hz, C**H$_a$**H$_b$CH=CH$_2$), δ 2.27-2.35 (3H, m, CH$_a$**H$_b$**CH=CH$_2$ and 2 O**H**s), δ 2.99 (1H, ddq, *J* = 8.5, 7.5, 7.0 Hz, C**H**CH$_3$), δ 3.33 (1H, d, *J* = 8.5 Hz, C(O)C**H**C(O)), δ 3.51 (1H, ddd, *J* = 8.0, 6.0, 4.0 Hz, CHOHC**H**OHCH$_2$), δ 3.70 (3H, s, (OC**H$_3$**)$_a$), δ 3.73 (3H, s, (OC**H$_3$**)$_b$), δ 3.92 (1H, dd, *J* = 6.5, 4.5 Hz, C**H**OHCHOHCH$_2$), δ 5.12-5.17 (2H, m, CH$_2$CH=C**H$_2$**), δ 5.55 (1H, ddd, *J* = 15.5, 7.0, 1.0 Hz, CH=C**H**CHOH), δ 5.72 (1H, ddd, *J* = 16.0, 8.5, 1.0 Hz, C**H**=CHCHOH), δ 5.84 (1H, dddd, *J* = 17.5, 10.5, 7.5, 6.5Hz, CH$_2$C**H**=CH$_2$); ^{13}C NMR (125 Hz, $CDCl_3$):
δ 168.78, 168.76, 135.2, 134.5, 130.8, 118.4, 75.2, 73.6, 57.6, 52.7, 52.6, 37.6, 37.0, 18.3 ppm; IR (neat): 3433.4 (br), 2955.5 (m), 1734.9 (s), 1641.3 (w), 1534.7 (m), 1243.5 (br), 1159.9 (m), 1062.7 (m), 1018.7 (m), 976.3 (m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{21}O_5$ [M+H-H_2O]: calculated: 269.1389, found: 269.1382; $[\alpha]_D^{20} = -19.86$ (*c* = 0.88, $CHCl_3$).



(1*R*,2*S*,6*S*)-7-oxabicyclo[4.1.0]hept-4-en-2-ol. A flame-dried round-bottom-flask was charged with 2.0 mg (0.0032 mmol) of Hoveyda-Grubbs II catalyst, 6.0 mL of CH_2Cl_2, and 10.0 mg (0.0650 mmol) of (*S*)-1-((2*R*,3*S*)-3-((*E*)-prop-1-enyl)oxiran-2-yl)but-3-en-1-ol in CH_2Cl_2 (0.5 mL). The reaction was allowed to stir at ambient temperature under N_2 for 2 hours. After this time period, solvent was evaporated *in vacuo*, and the crude material was purified by silica gel chromatography (2:1 pentane:ether) to afford 5.9 mg (81%) of the title compound (17:1 *d.r.*) as a colorless oil. $R_f = 0.23$ (1:1 hexane:EtOAc, stain in $KMnO_4$). ^{1}H NMR (500 Hz, $CDCl_3$): δ 1.53 (1H, d, *J* = 8.5 Hz, O**H**), δ 2.27 (1H, ddt, *J* = 17.5, 6.5, 2.0 Hz,C**H$_a$**H$_b$), δ 2.37 (1H, dddd, *J* = 17.0, 6.0, 3.5, 3.0 Hz, CH$_a$**H$_b$**), δ 3.34 (1H, td, *J* = 4.0, 1.5 Hz, CHOHC**H**OCH), δ 3.51 (1H, ddd, *J* = 4.0, 2.5, 2.0 Hz, C**H**OH), δ 4.43 (1H, m, CHOHCHOC**H**), δ 5.82 (1H, ddm, *J* = 9.5, 6.0 Hz, CH$_2$CH=C**H**), δ 6.06 (1H, dt, CH$_2$C**H**=CH); ^{13}C NMR (125 Hz, $CDCl_3$): δ 129.6, 124.1, 64.1, 55.9, 47.0, 30.6 ppm; IR (neat): 3412.5 (br), 3041.1 (w), 2993.0 (w), 2923.0 (s), 2852.8 (m), 1641.8 (w), 1418.5 (m), 1398.1 (m), 1050.9 (s), 1036.0 (s), 981.1 (s), 952.2 (m), 885.9 (s), 805.2 (s), 771.3 (s) cm^{-1}; HRMS (ESI+) for $C_6H_9O_2$ [M+H]: calculated: 113.0603, found: 113.0597; $[\alpha]_D^{20} = -79.15$ (*c* = 0.42, $CHCl_3$).

Spectral Data



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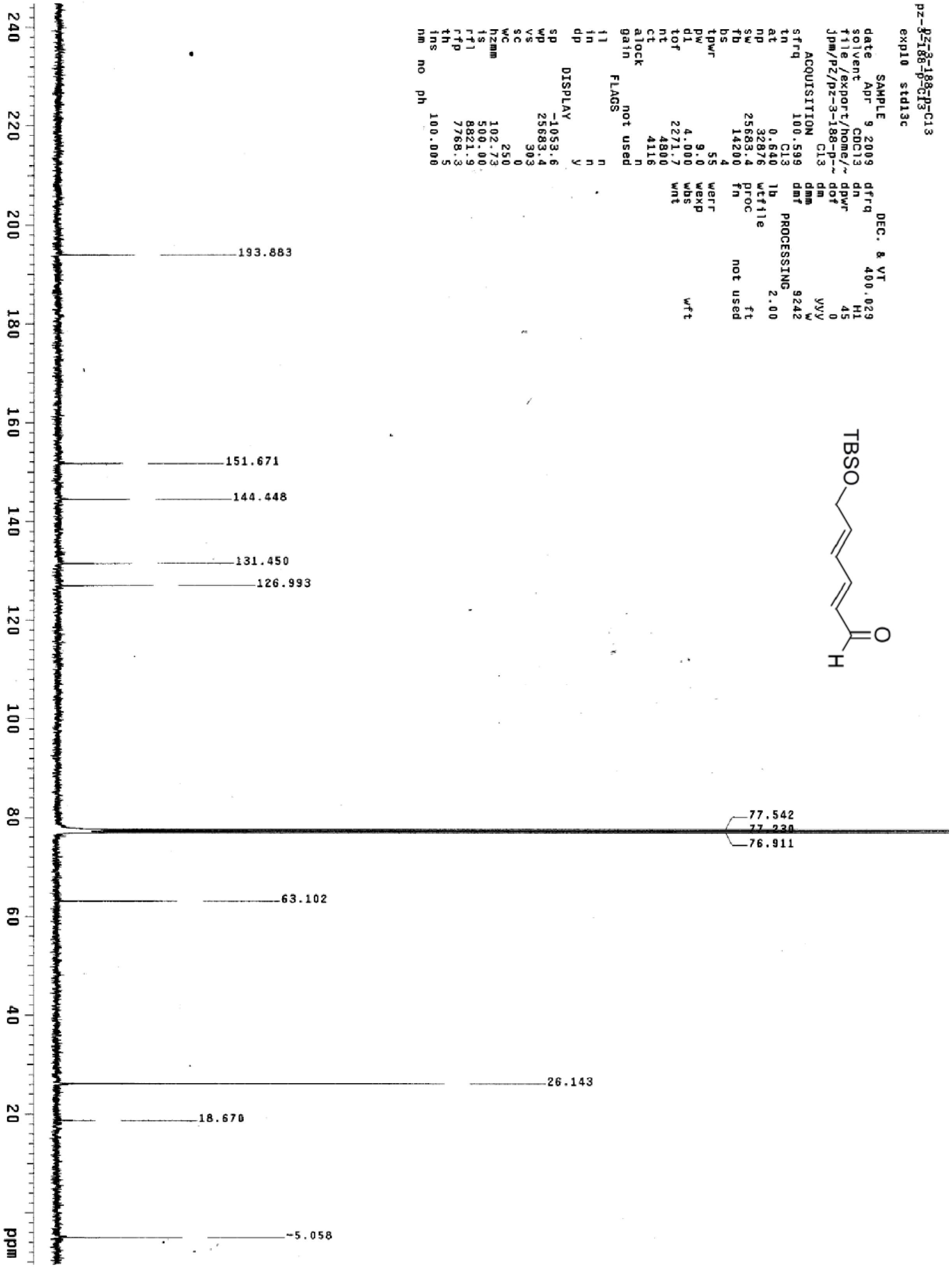
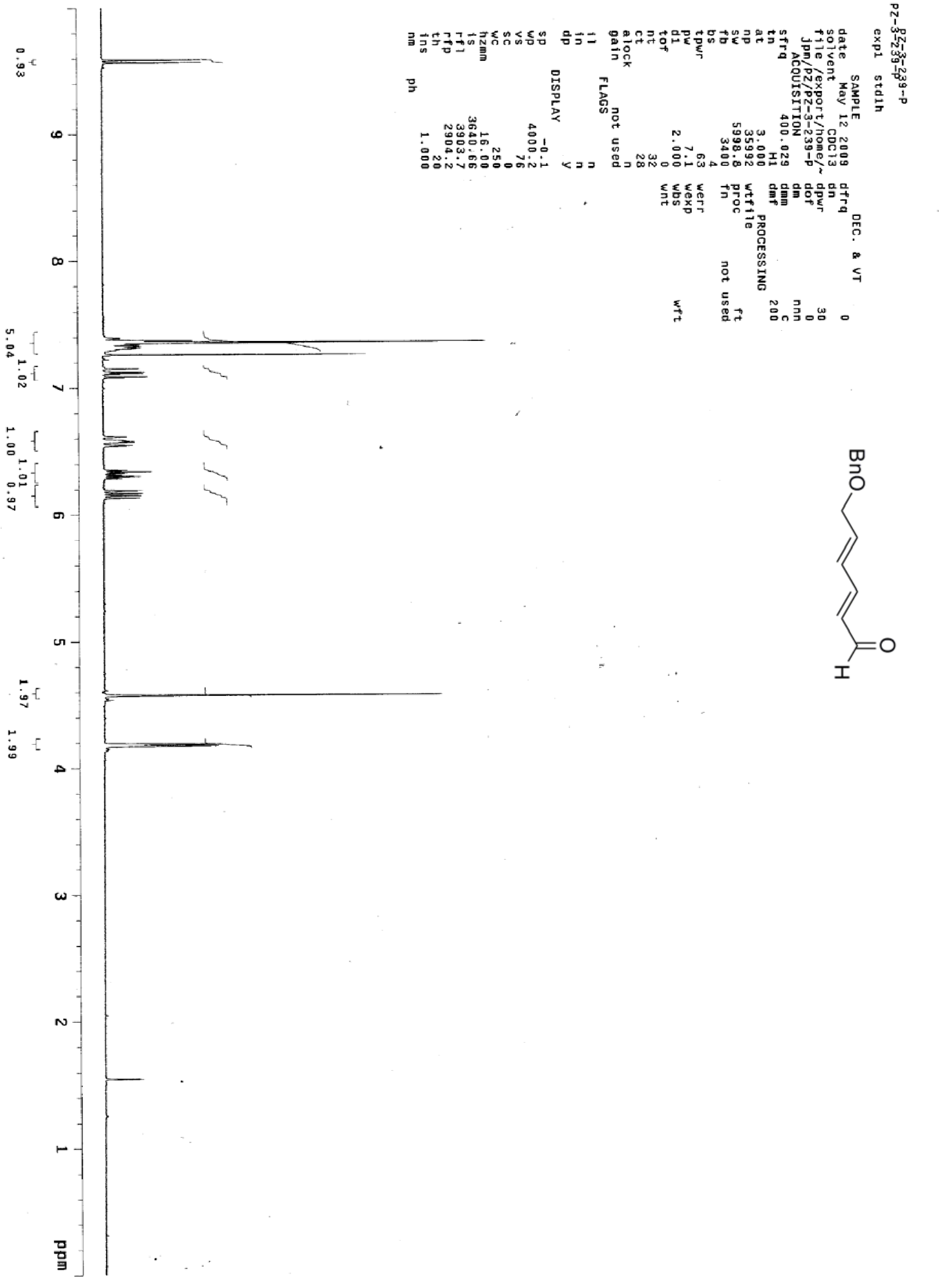
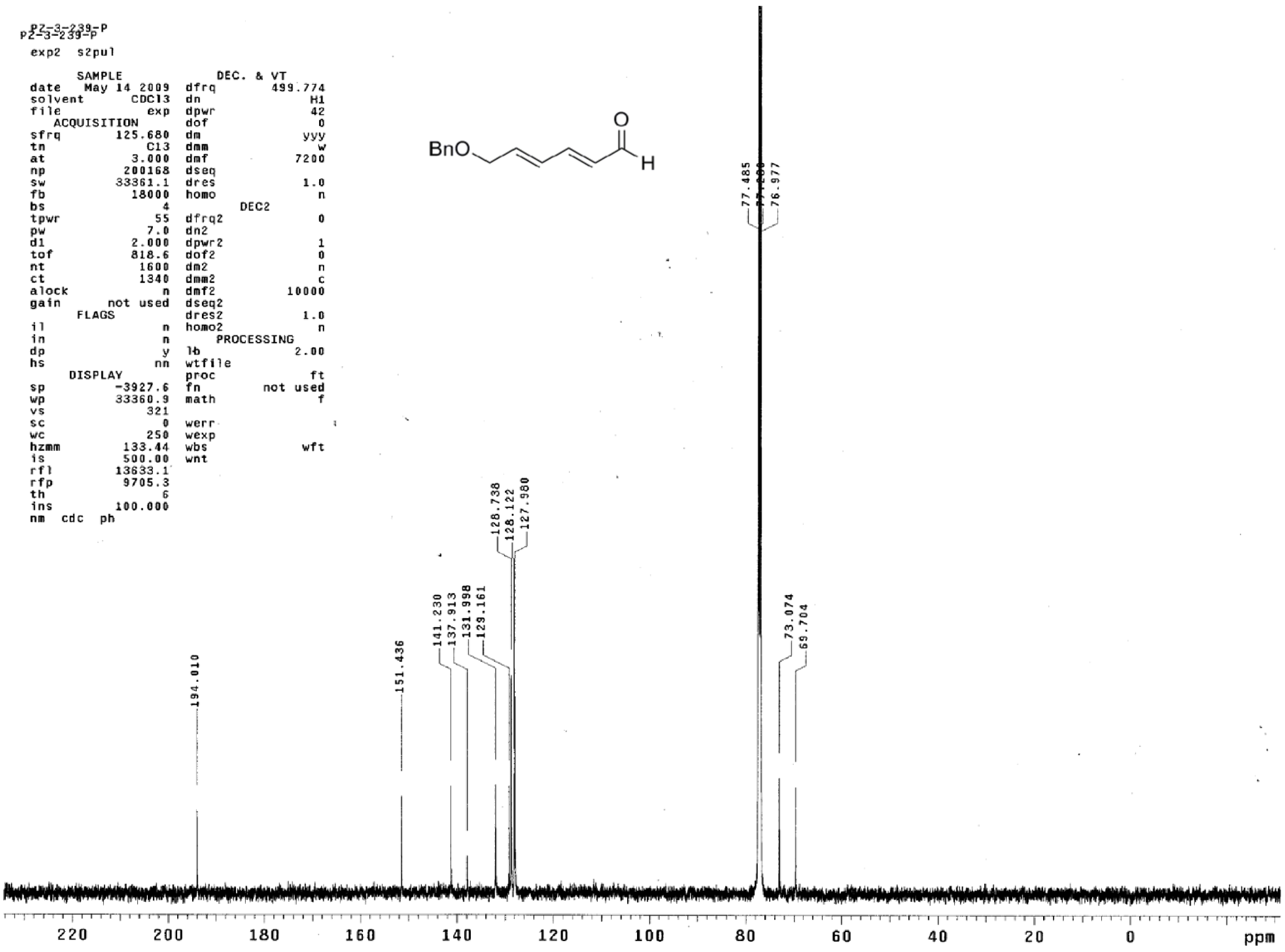
        FLAGS
   il               n
   in               n
   dp               y
       DISPLAY
   sp          -200.0
   wp          4200.3
   vs             231
   sc               0
   wc             250
   hzmm         16.80
   is         3500.00
   rfl         3902.8
   rfp         2904.2
   th              20
   ins          1.000
   nm    ph
```



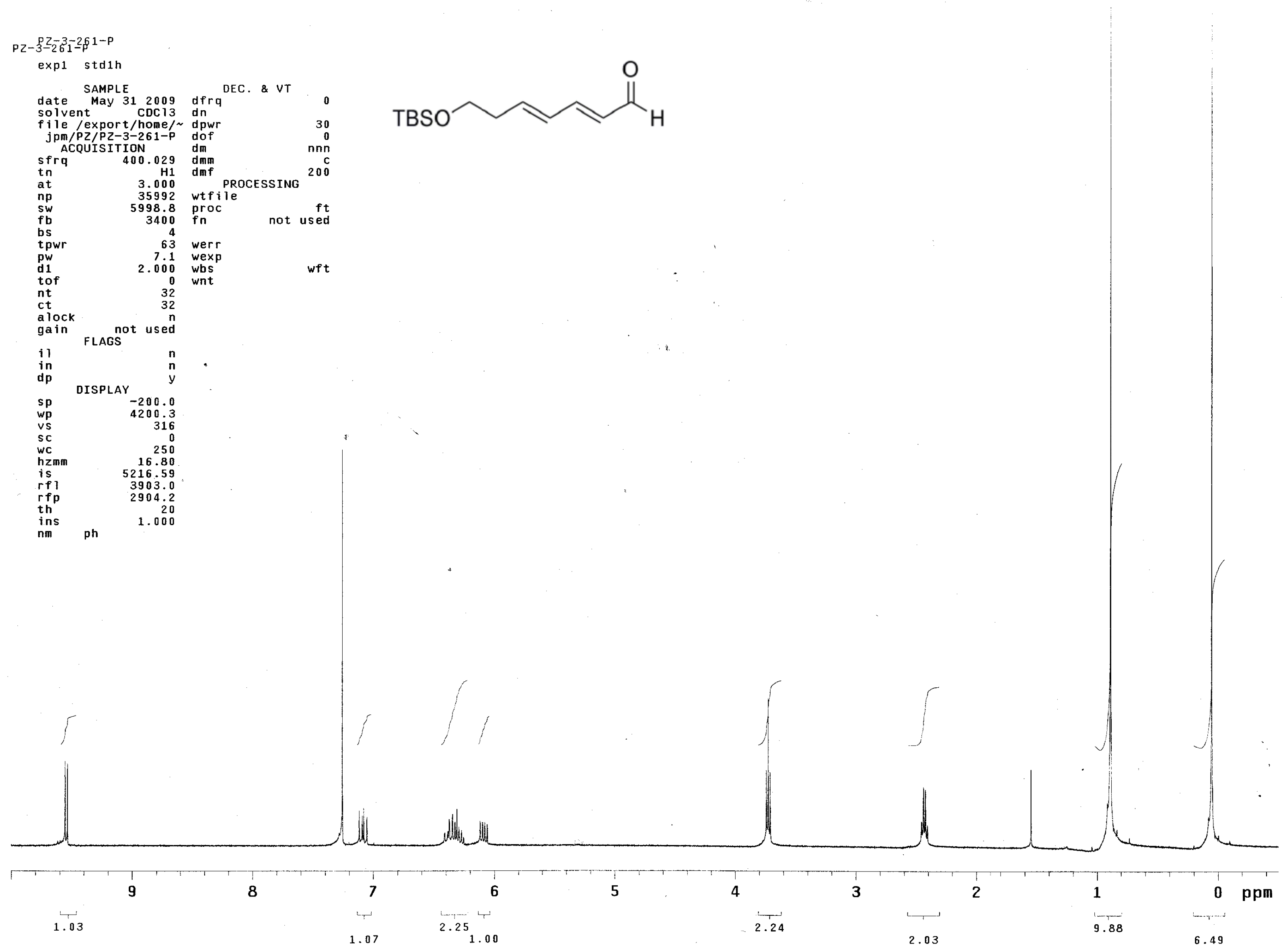
pz-3-188-p-C13
exp10 std13c
SAMPLE DEC. & VT
date Apr 9 2009 dfrq 400.029
solvent CDCl3 dn H1
file /export/home/~ dpwr 45
jpm/PZ/pz-3-188-p-~ dof 0
C13 dm yyy
ACQUISITION dmm w
sfrq 100.599 dmf 9242
tn C13 PROCESSING
at 0.640 lb 2.00
np 32876 wtfile
sw 25683.4 proc ft
fb 14200 fn not used
bs 4
tpwr 55 werr
pw 9.0 wexp
d1 4.000 wbs
tof 2271.7 wnt wft
nt 4800
ct 4116
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -1053.6
wp 25683.4
vs 303
sc 0
wc 250
hzmm 102.73
is 500.00
rfl 8821.9
rfp 7768.3
th 5
ins 100.000
nm no ph
TBSO
O
H
193.883
151.671
144.448
131.450
126.993
77.542
77.230
76.911
63.102
26.143
18.670
-5.058
240
220
200
180
160
140
120
100
80
60
40
20
ppm


PZ-3-239-P
exp1 std1h
SAMPLE
date May 12 2009
solvent CDCl3
file /export/home/~
jpm/PZ/PZ-3-239-p
ACQUISITION
sfrq 400.029
tn H1
at 3.000
np 35992
sw 5998.8
fb 3400
bs 4
tpwr 63
pw 7.1
d1 2.000
tof 0
nt 32
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -0.1
wp 4000.2
vs 76
sc 0
wc 250
hzmm 16.00
is 3640.66
rfl 3903.7
rfp 2904.2
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 0
dn
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt wft
BnO
O
H
0.93
5.04
1.02
1.00
1.01
0.97
1.97
1.99
9
8
7
6
5
4
3
2
1
ppm



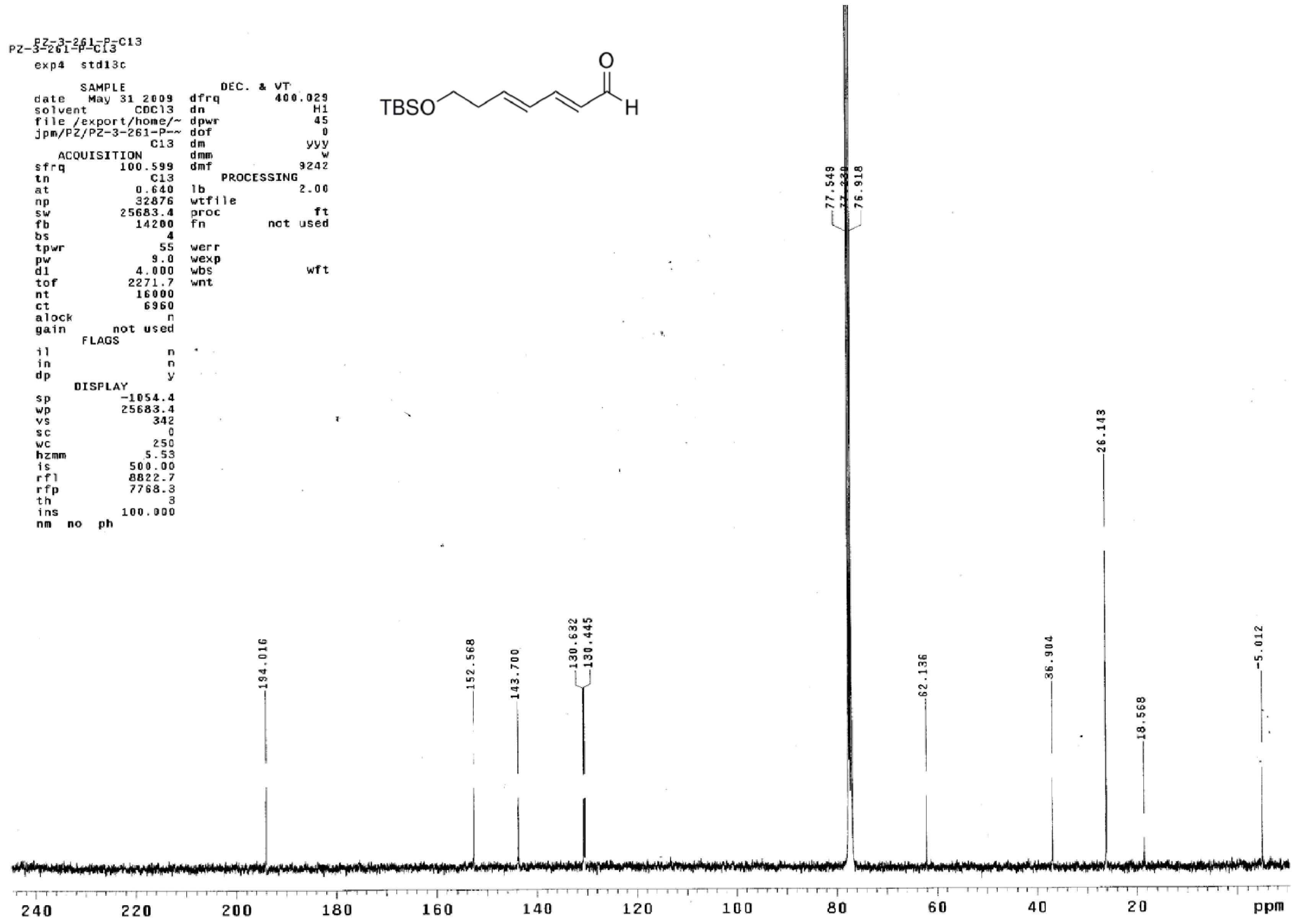
```
PZ-3-239-P
exp2  s2pul

      SAMPLE                DEC. & VT
date   May 14 2009   dfrq        499.774
solvent      CDCl3   dn               H1
file           exp   dpwr             42
   ACQUISITION       dof               0
sfrq       125.680   dm              yyy
tn             C13   dmm               w
at           3.000   dmf            7200
np          200168   dseq
sw         33361.1   dres            1.0
fb           18000   homo              n
bs               4            DEC2
tpwr            55   dfrq2             0
pw             7.0   dn2
d1           2.000   dpwr2             1
tof          818.6   dof2              0
nt            1600   dm2               n
ct            1340   dmm2              c
alock            n   dmf2          10000
gain      not used   dseq2
      FLAGS          dres2           1.0
il               n   homo2             n
in               n        PROCESSING
dp               y   lb             2.00
hs              nn   wtfile
     DISPLAY         proc             ft
sp         -3927.6   fn         not used
wp         33360.9   math              f
vs             321
sc               0   werr
wc             250   wexp
hzmm        133.44   wbs             wft
is          500.00   wnt
rfl        13633.1
rfp         9705.3
th               6
ins        100.000
nm  cdc  ph
```



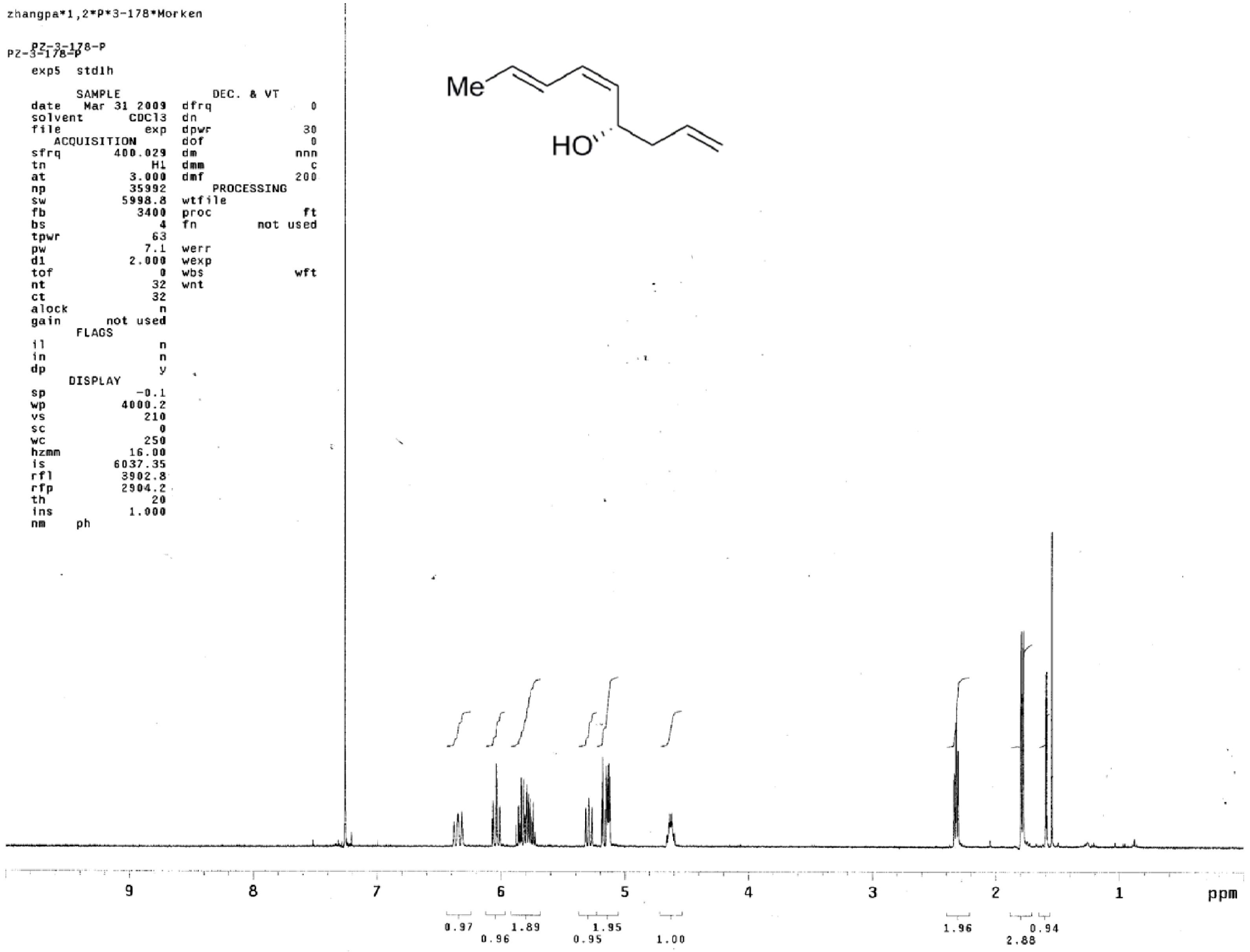
```
PZ-3-261-P
PZ-3-261-P
   exp1  std1h

       SAMPLE              DEC. & VT
date   May 31 2009  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
 jpm/PZ/PZ-3-261-P  dof               0
   ACQUISITION      dm              nnn
sfrq       400.029  dmm               c
tn              H1  dmf             200
at           3.000       PROCESSING
np           35992  wtfile
sw          5998.8  proc             ft
fb            3400  fn         not used
bs               4
tpwr            63  werr
pw             7.1  wexp
d1           2.000  wbs             wft
tof              0  wnt
nt              32
ct              32
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs             316
sc               0
wc             250
hzmm         16.80
is         5216.59
rfl         3903.0
rfp         2904.2
th              20
ins          1.000
nm    ph
```



```
PZ-3-261-P-C13
PZ-3-261-P-C13
    exp4  std13c

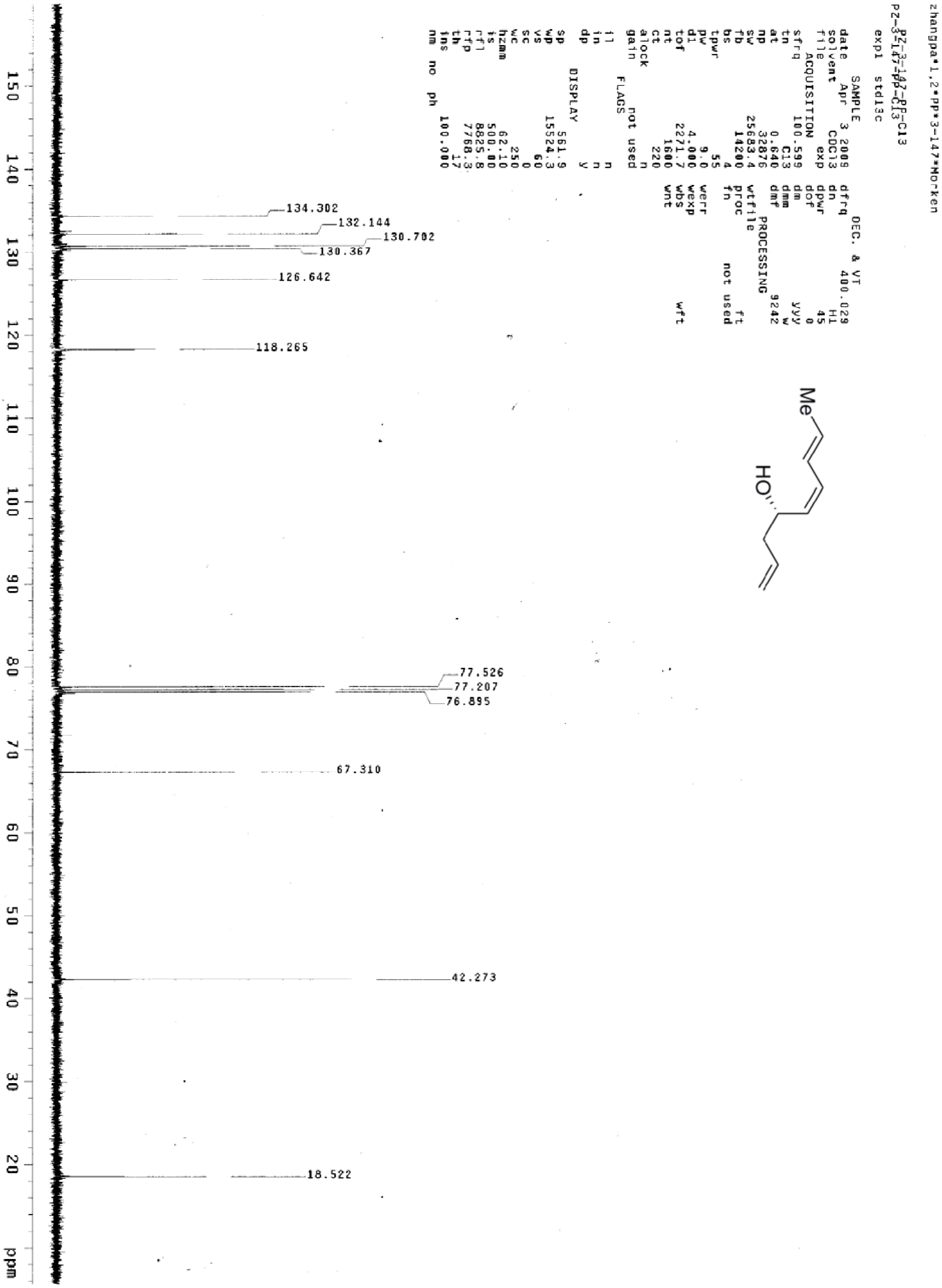
        SAMPLE              DEC. & VT
    date   May 31 2009  dfrq       400.029
    solvent      CDCl3  dn              H1
    file /export/home/~ dpwr            45
    jpm/PZ/PZ-3-261-P-~ dof              0
                   C13  dm             yyy
      ACQUISITION       dmm              w
    sfrq       100.599  dmf           9242
    tn             C13       PROCESSING
    at           0.640  lb            2.00
    np           32876  wtfile
    sw         25683.4  proc            ft
    fb           14200  fn        not used
    bs               4
    tpwr            55  werr
    pw             9.0  wexp
    d1           4.000  wbs            wft
    tof         2271.7  wnt
    nt           16000
    ct            6960
    alock            n
    gain      not used
          FLAGS
    il               n
    in               n
    dp               y
         DISPLAY
    sp         -1054.4
    wp         25683.4
    vs             342
    sc               0
    wc             250
    hzmm          5.53
    is          500.00
    rfl         8822.7
    rfp         7768.3
    th               3
    ins        100.000
    nm  no  ph
```

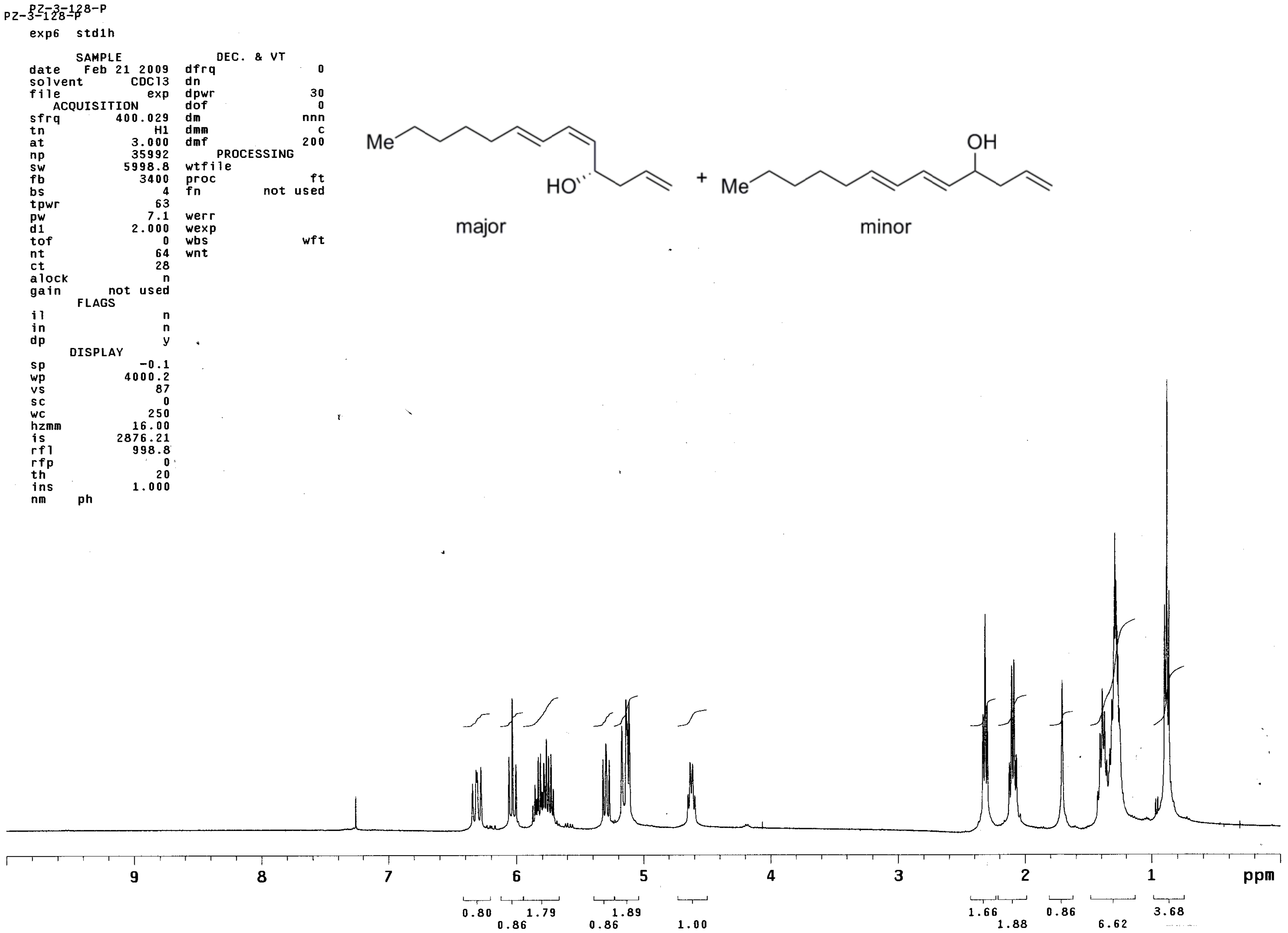


```
zhangpa*1,2*P*3-178*Morken

    PZ-3-178-P
PZ-3-178-P
    exp5  stdlh

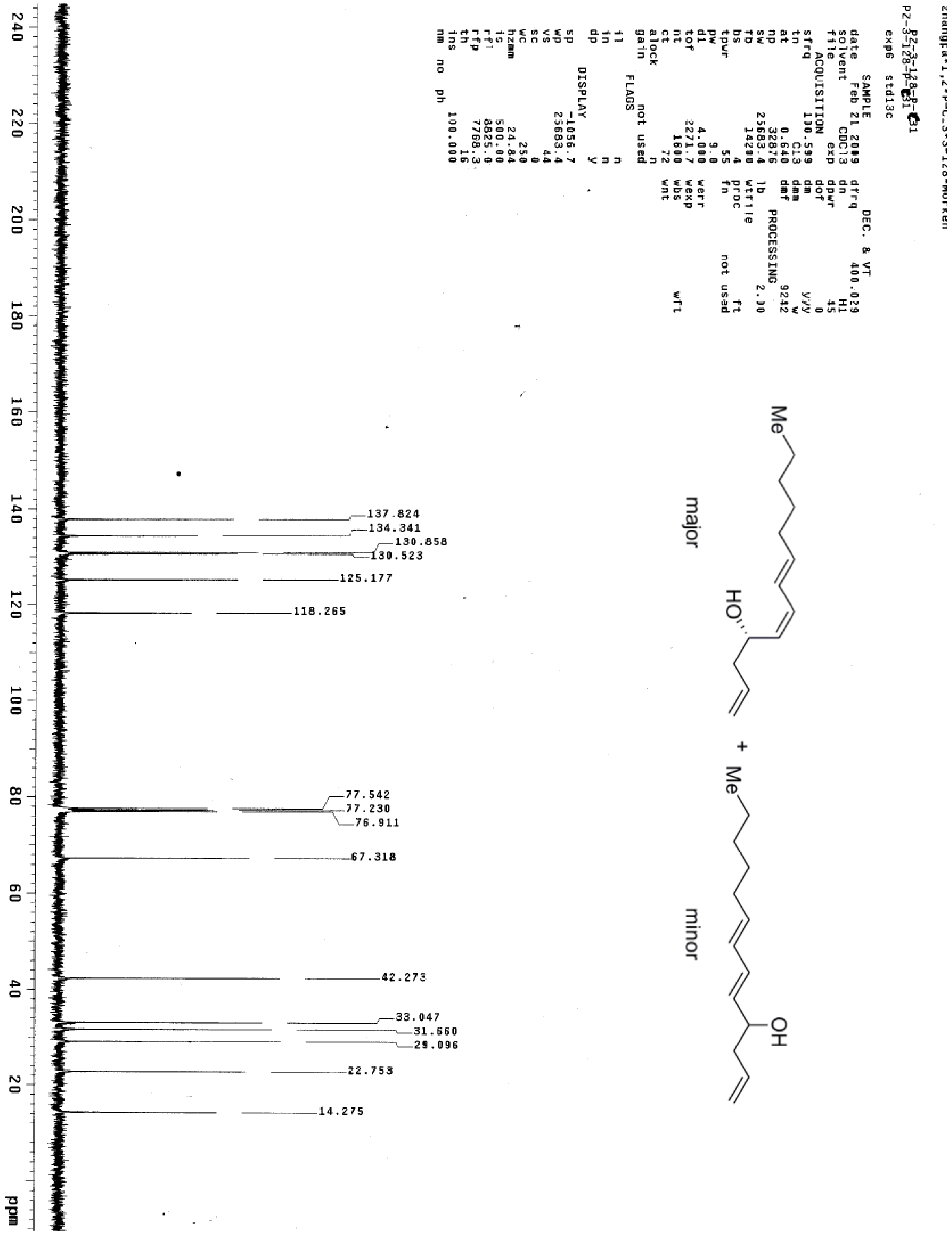
         SAMPLE                DEC. & VT
    date   Mar 31 2009  dfrq              0
    solvent       CDCl3  dn
    file            exp  dpwr             30
       ACQUISITION       dof               0
    sfrq        400.029  dm              nnn
    tn               H1  dmm               c
    at            3.000  dmf             200
    np            35992        PROCESSING
    sw           5998.8  wtfile
    fb             3400  proc             ft
    bs                4  fn         not used
    tpwr             63
    pw              7.1  werr
    d1            2.000  wexp
    tof               0  wbs             wft
    nt               32  wnt
    ct               32
    alock             n
    gain       not used
          FLAGS
    il                n
    in                n
    dp                y
         DISPLAY
    sp             -0.1
    wp           4000.2
    vs              210
    sc                0
    wc              250
    hzmm          16.00
    is          6037.35
    rfl          3902.8
    rfp          2904.2
    th               20
    ins           1.000
    nm     ph
```


zhangpa*1,2*PP*3-147*Morken
PZ-3-147-PP-C13
exp1 std13c
SAMPLE
date Apr 3 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 100.599
tn C13
at 0.640
np 32876
sw 25683.4
fb 14200
bs 4
tpwr 55
pw 9.0
d1 4.000
tof 2271.7
nt 1600
ct 220
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 561.9
wp 15524.3
vs 60
sc 0
wc 250
hzmm 62.10
is 500.00
rfl 8825.8
rfp 7768.3
th 17
ins 100.000
nm no ph
DEC. & VT
dfrq 400.029
dn H1
dpwr 45
dof 0
dm yyy
dmm w
dmf 9242
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt wft
134.302
132.144
130.702
130.367
126.642
118.265
77.526
77.207
76.895
67.310
42.273
18.522
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
Me
HO



```
PZ-3-128-P
PZ-3-128-P
   exp6  std1h

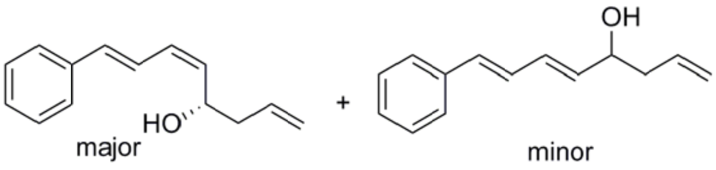
        SAMPLE              DEC. & VT
date   Feb 21 2009  dfrq              0
solvent      CDCl3  dn
file           exp  dpwr             30
    ACQUISITION     dof               0
sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           3.000  dmf             200
np           35992        PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn         not used
tpwr            63
pw             7.1  werr
d1           2.000  wexp
tof              0  wbs             wft
nt              64  wnt
ct              28
alock            n
gain      not used
        FLAGS
il               n
in               n
dp               y
       DISPLAY
sp            -0.1
wp          4000.2
vs              87
sc               0
wc             250
hzmm         16.00
is         2876.21
rfl          998.8
rfp              0
th              20
ins          1.000
nm     ph
```

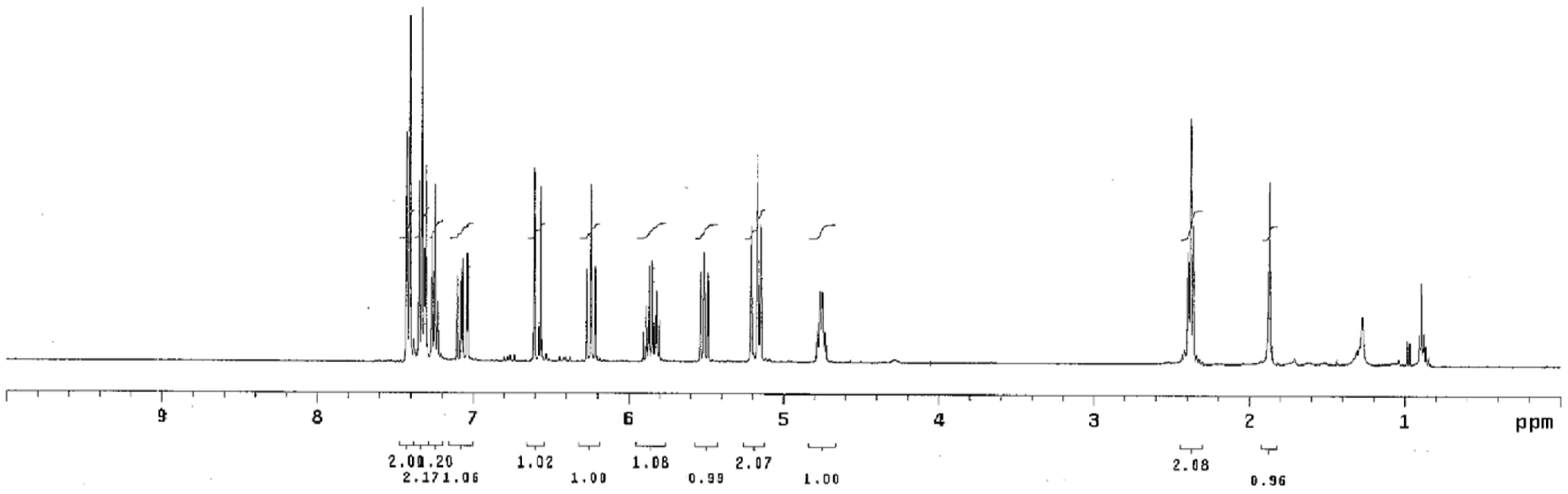

exp6 std13c
SAMPLE
DEC. & VT
date Feb 21 2009
dfrq 400.029
solvent CDCl3
dn H1
file exp
dpwr 45
ACQUISITION
dof 0
sfrq 100.599
dm yyy
tn C13
dmm w
at 0.640
dmf 9242
np 32876
sw 25683.4
PROCESSING
fb 14200
lb 2.00
bs 4
wtfile
tpwr 55
proc ft
pw 9.8
fn not used
d1 4.000
tof 2271.7
werr
nt 1600
wexp
ct 72
wbs
alock n
wnt wft
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -1056.7
wp 25683.4
vs 44
sc 0
wc 250
hzmm 24.84
is 500.00
rfl 8825.0
rfp 7768.3
th 16
ins 100.000
nm no ph
Me
HO
major
+
Me
OH
minor
137.824
134.341
130.858
130.523
125.177
118.265
77.542
77.230
76.911
67.318
42.273
33.047
31.660
29.096
22.753
14.275
240
220
200
180
160
140
120
100
80
60
40
20
ppm

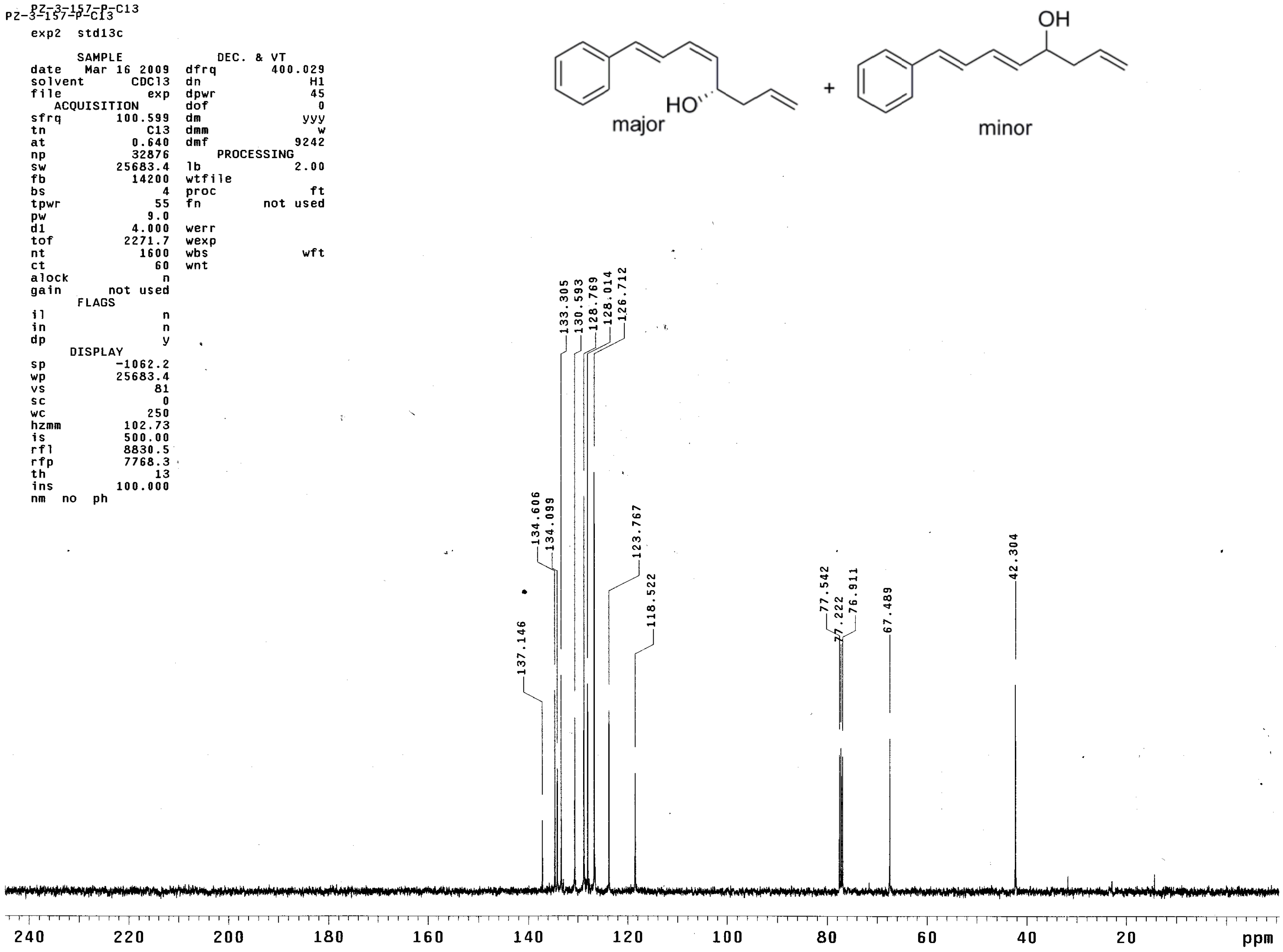
```
PZ-3-157-P
PZ-3-157-P

exp1  stdlh

      SAMPLE                 DEC. & VT
date   Mar 16 2009   dfrq               0
solvent       CDCl3   dn
file /export/home/~  dpwr              30
 jpm/PZ/PZ-3-157-P   dof                0
   ACQUISITION        dm               nnn
sfrq        400.029   dmm                c
tn               H1   dmf              200
at            3.000       PROCESSING
np            35992   wtfile
sw           5998.8   proc              ft
fb             3400   fn          not used
bs                4
tpwr             63   werr
pw              7.1   wexp
d1            2.000   wbs              wft
tof               0   wnt
nt               32
ct               24
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp             -0.1
wp           4000.2
vs               57
sc                0
wc              250
hzmm          16.00
is          1856.21
rfl          1001.1
rfp               0
th                9
ins           1.000
nm     ph
```

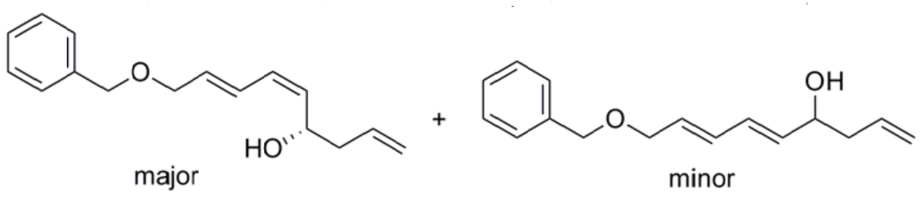






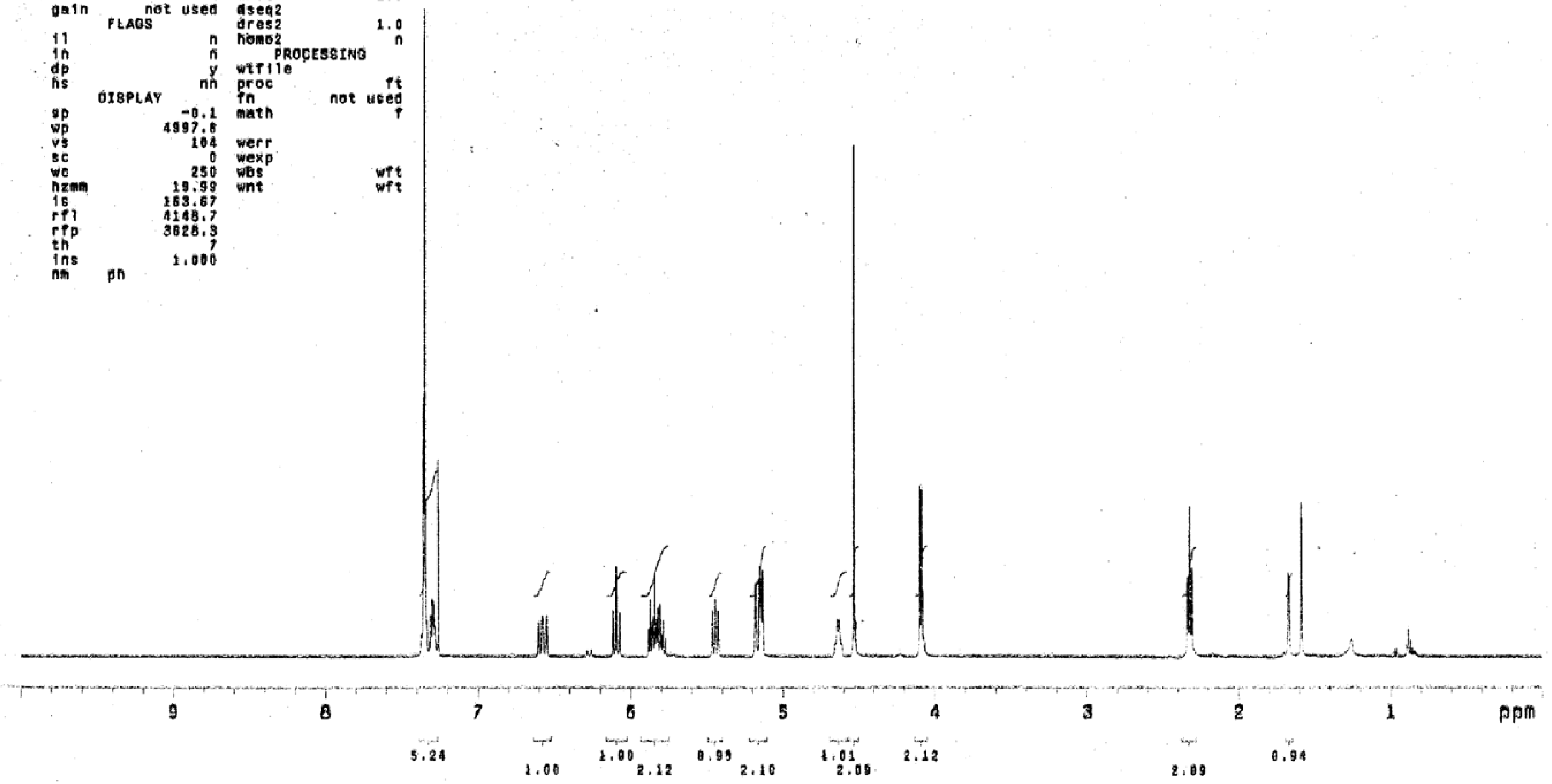
```
PZ-3-157-P-C13
PZ-3-157-P-C13
   exp2  std13c

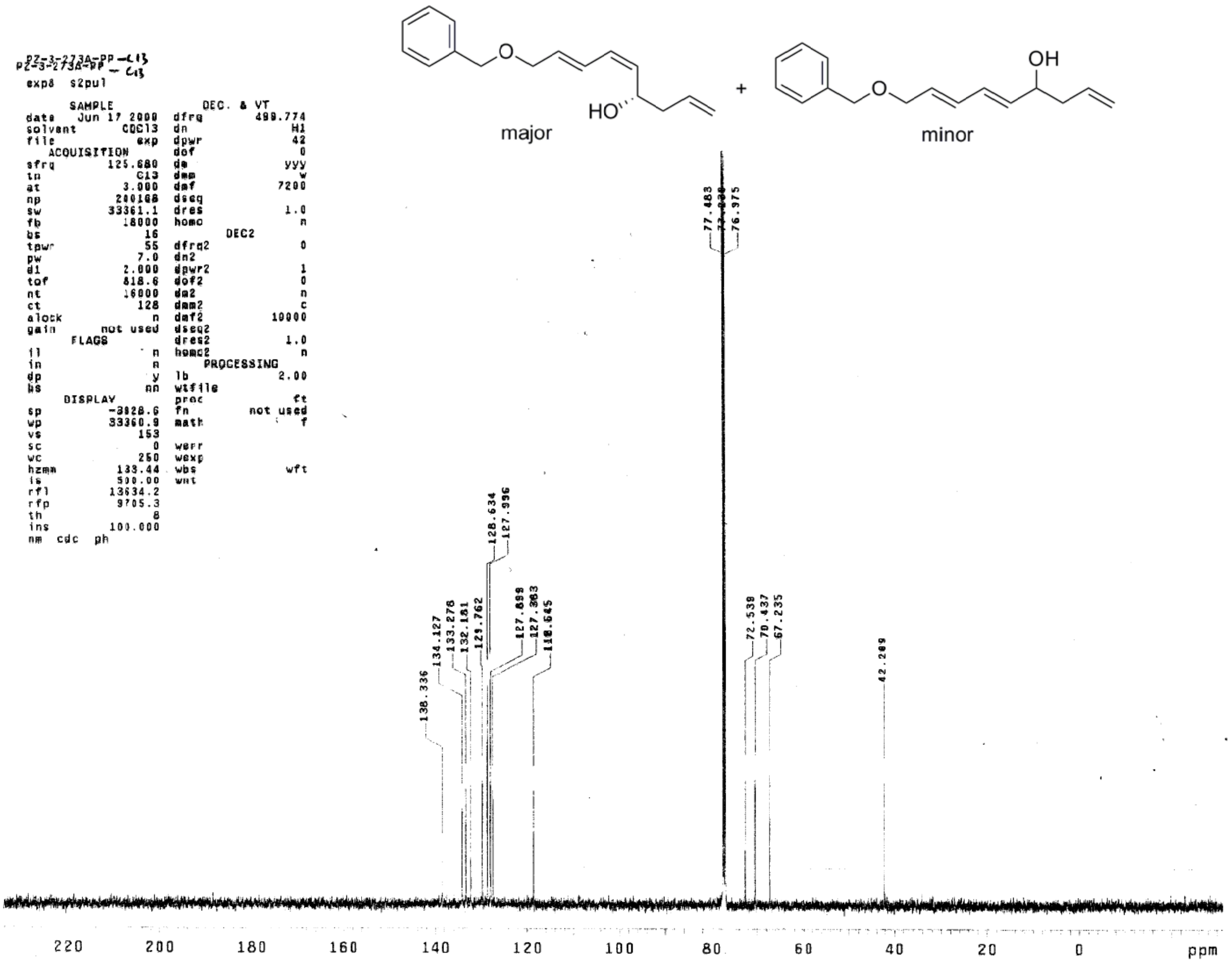
         SAMPLE            DEC. & VT
   date   Mar 16 2009  dfrq       400.029
   solvent      CDCl3  dn              H1
   file           exp  dpwr            45
      ACQUISITION      dof              0
   sfrq       100.599  dm             yyy
   tn             C13  dmm              w
   at           0.640  dmf           9242
   np           32876      PROCESSING
   sw         25683.4  lb            2.00
   fb           14200  wtfile
   bs               4  proc            ft
   tpwr            55  fn        not used
   pw             9.0
   d1           4.000  werr
   tof         2271.7  wexp
   nt            1600  wbs            wft
   ct              60  wnt
   alock            n
   gain      not used
         FLAGS
   il               n
   in               n
   dp               y
        DISPLAY
   sp         -1062.2
   wp         25683.4
   vs              81
   sc               0
   wc             250
   hzmm        102.73
   is          500.00
   rfl         8830.5
   rfp         7768.3
   th              13
   ins        100.000
   nm  no  ph
```



```
pZ-3-273A-pp
pZ-3-273A-pp
 exp8  s2pul

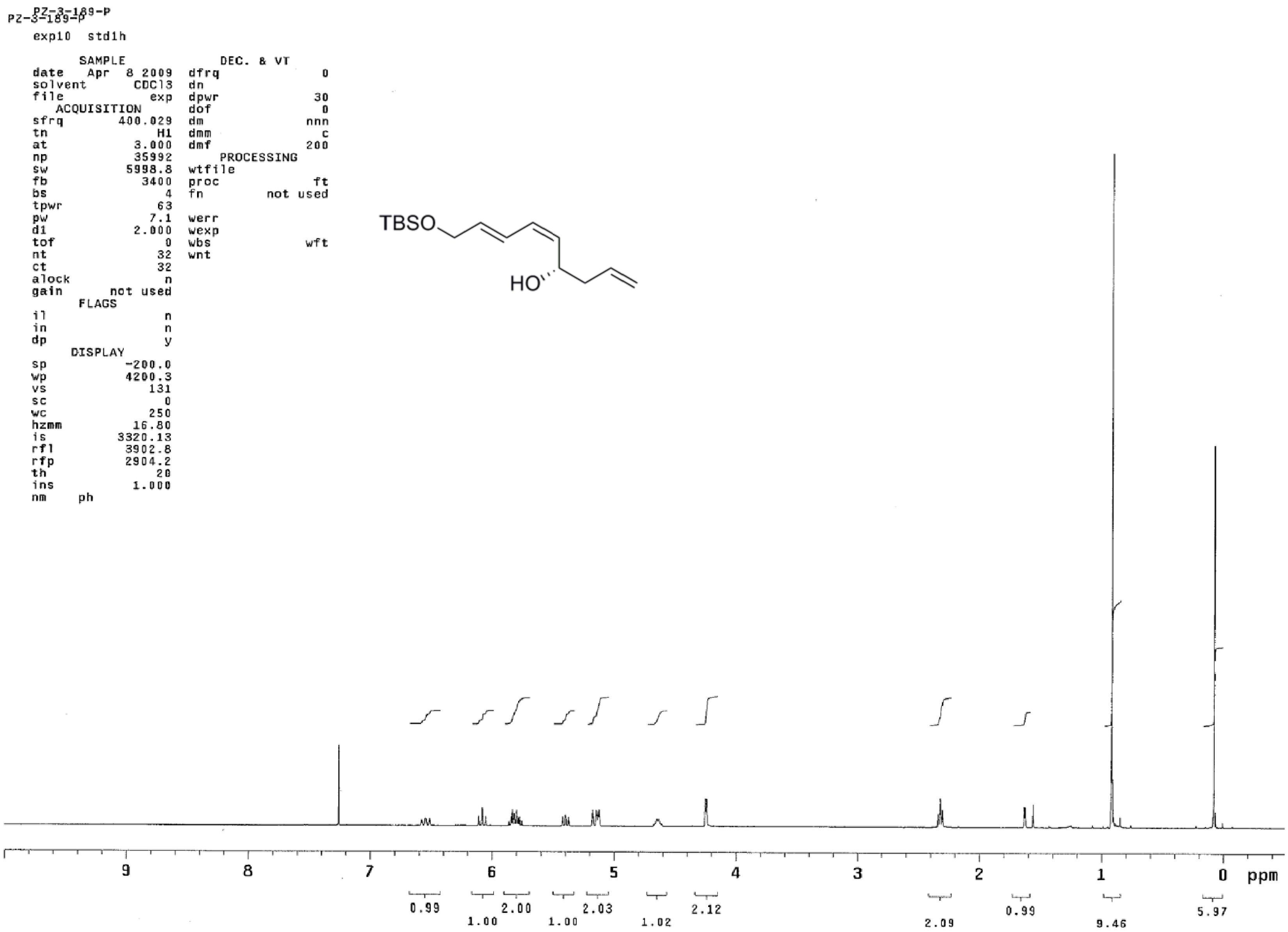
        SAMPLE              DEC. & VT
 date   Jun 17 2009   dfrq          499.774
 solvent      CDCl3   dn                 H1
 file           exp   dpwr               30
    ACQUISITION       dof                 0
 sfrq       499.774   dm                nnn
 tn              H1   dmm                 c
 at           5.000   dmf               200
 np           70058   dseq
 sw          7005.6   dres              1.0
 fb            4000   homo                n
 bs               4             DEC2
 tpwr            57   dfrq2               0
 pw             4.6   dn2
 d1               0   dpwr2               1
 tof          497.6   dof2                0
 nt              32   dm2                 n
 ct              32   dmm2                c
 alock            n   dmf2              200
 gain      not used   dseq2
       FLAGS          dres2             1.0
 il               n   homo2               n
 in               n       PROCESSING
 dp               y   wtfile
 hs              nn   proc               ft
      DISPLAY         fn           not used
 sp            -0.1   math                f
 wp          4997.6
 vs             104   werr
 sc               0   wexp
 wc             250   wbs               wft
 hzmm         19.99   wnt               wft
 is          163.67
 rfl         4148.7
 rfp         3628.9
 th               7
 ins          1.000
 nm     ph
```





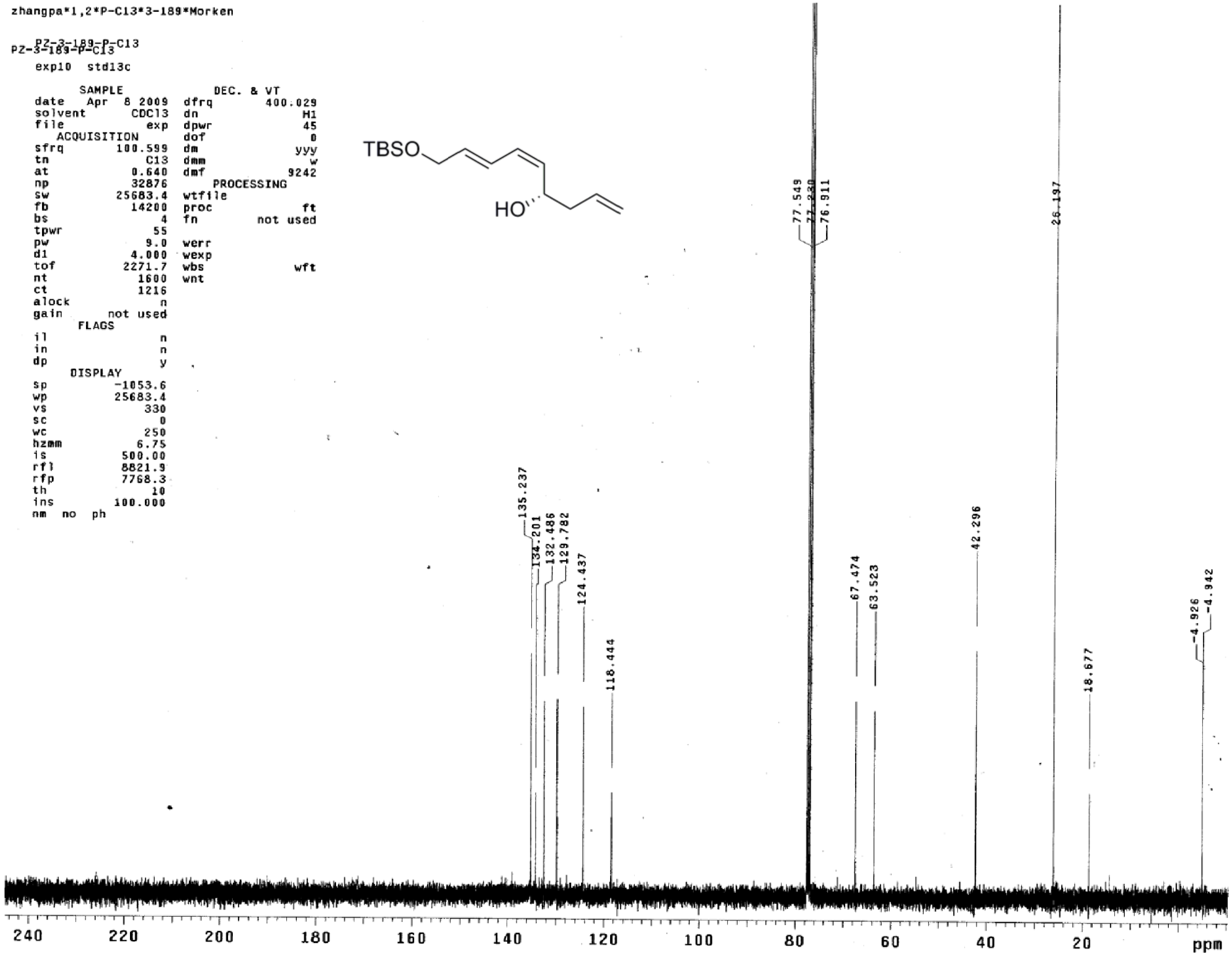
```
PZ-3-273A-PP — C13
PZ-3-273A-PP — C13
exp8  s2pul

      SAMPLE                 DEC. & VT
date   Jun 17 2000   dfrq         499.774
solvent       CDCl3   dn                H1
file            exp   dpwr              42
   ACQUISITION        dof                0
sfrq        125.680   dm               yyy
tn              C13   dmm                w
at            3.000   dmf             7200
np           200168   dseq
sw          33361.1   dres             1.0
fb            18000   homo               n
bs               16            DEC2
tpwr             55   dfrq2              0
pw              7.0   dn2
d1            2.000   dpwr2              1
tof           818.6   dof2               0
nt            16000   dm2                n
ct              128   dmm2               c
alock             n   dmf2           10000
gain       not used   dseq2
      FLAGS           dres2            1.0
il                n   homo2              n
in                n         PROCESSING
dp                y   lb              2.00
hs               nn   wtfile
     DISPLAY          proc              ft
sp          -3828.6   fn          not used
wp          33360.9   math               f
vs              153
sc                0   werr
wc              250   wexp
hzmm         133.44   wbs              wft
is           500.00   wnt
rfl         13634.2
rfp          9705.3
th                8
ins         100.000
nm  cdc  ph
```



```
  PZ-3-189-P
PZ-3-189-P
  exp10  std1h

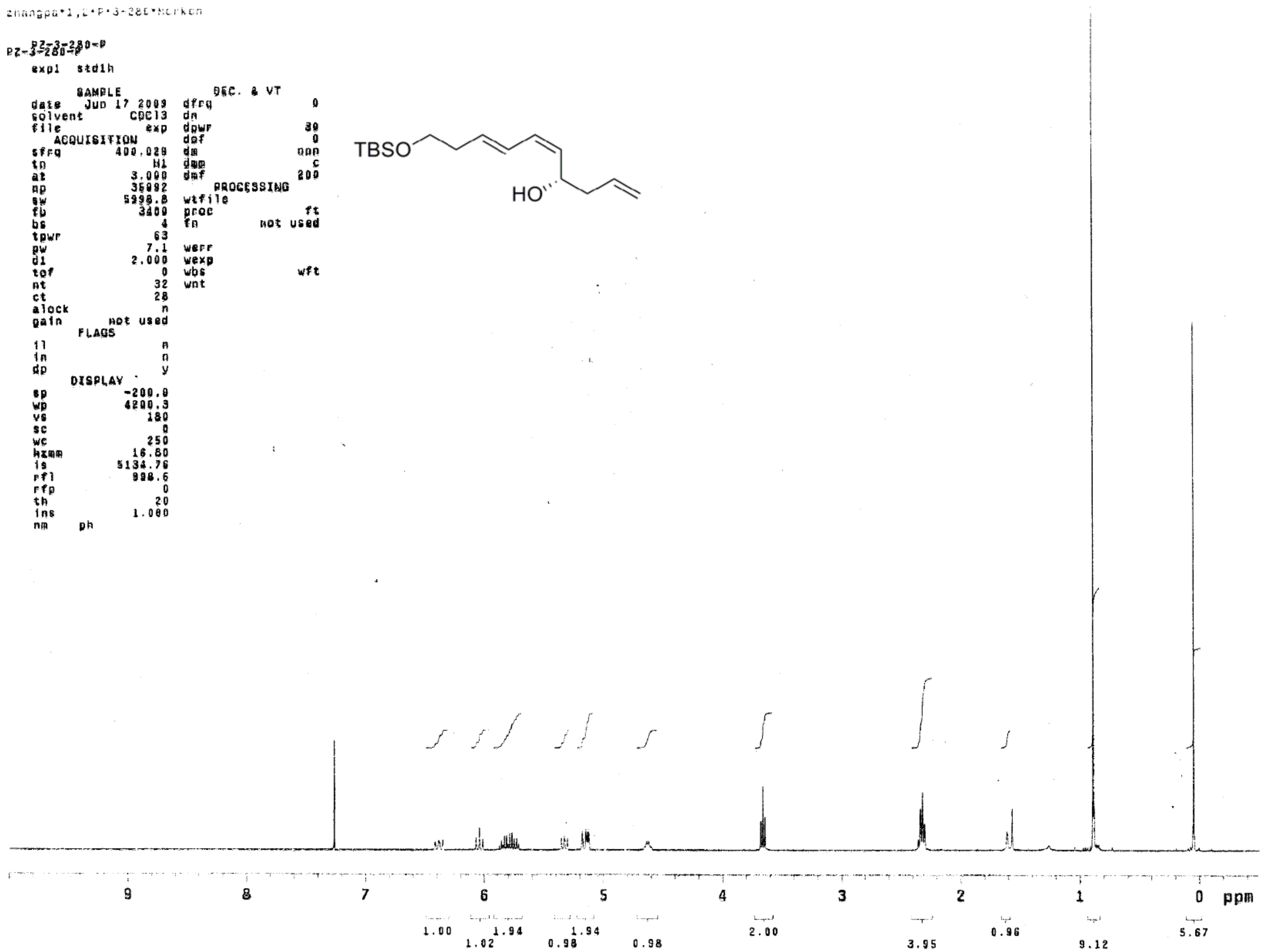
        SAMPLE               DEC. & VT
  date   Apr  8 2009  dfrq              0
  solvent      CDCl3  dn
  file           exp  dpwr             30
     ACQUISITION      dof               0
  sfrq       400.029  dm              nnn
  tn              H1  dmm               c
  at           3.000  dmf             200
  np           35992       PROCESSING
  sw          5998.8  wtfile
  fb            3400  proc             ft
  bs               4  fn         not used
  tpwr            63
  pw             7.1  werr
  d1           2.000  wexp
  tof              0  wbs             wft
  nt              32  wnt
  ct              32
  alock            n
  gain      not used
        FLAGS
  il               n
  in               n
  dp               y
       DISPLAY
  sp          -200.0
  wp          4200.3
  vs             131
  sc               0
  wc             250
  hzmm         16.80
  is         3320.13
  rfl         3902.8
  rfp         2904.2
  th              20
  ins          1.000
  nm     ph
```



```
zhangpa*1,2*P-C13*3-189*Morken

PZ-3-189-P-C13
PZ-3-189-P-C13
   exp10  std13c

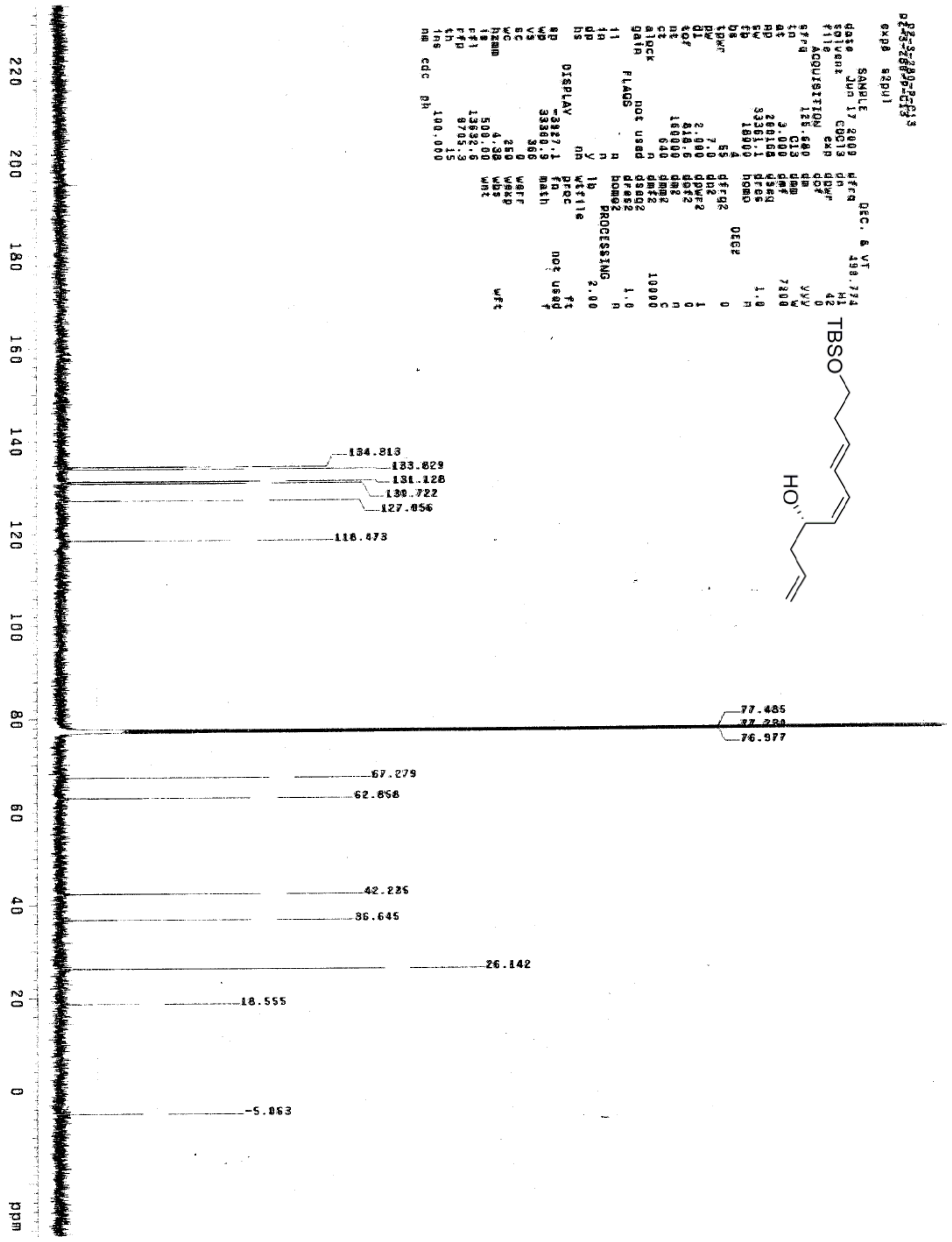
        SAMPLE                DEC. & VT
  date    Apr  8 2009   dfrq        400.029
  solvent      CDCl3    dn               H1
  file           exp    dpwr             45
     ACQUISITION        dof               0
  sfrq       100.599    dm              yyy
  tn             C13    dmm               w
  at           0.640    dmf            9242
  np           32876          PROCESSING
  sw         25683.4    wtfile
  fb           14200    proc             ft
  bs               4    fn         not used
  tpwr            55
  pw             9.0    werr
  d1           4.000    wexp
  tof         2271.7    wbs             wft
  nt            1600    wnt
  ct            1216
  alock            n
  gain      not used
        FLAGS
  il               n
  in               n
  dp               y
       DISPLAY
  sp         -1053.6
  wp         25683.4
  vs             330
  sc               0
  wc             250
  hzmm          6.75
  is          500.00
  rfl         8821.9
  rfp         7768.3
  th              10
  ins        100.000
  nm  no  ph
```

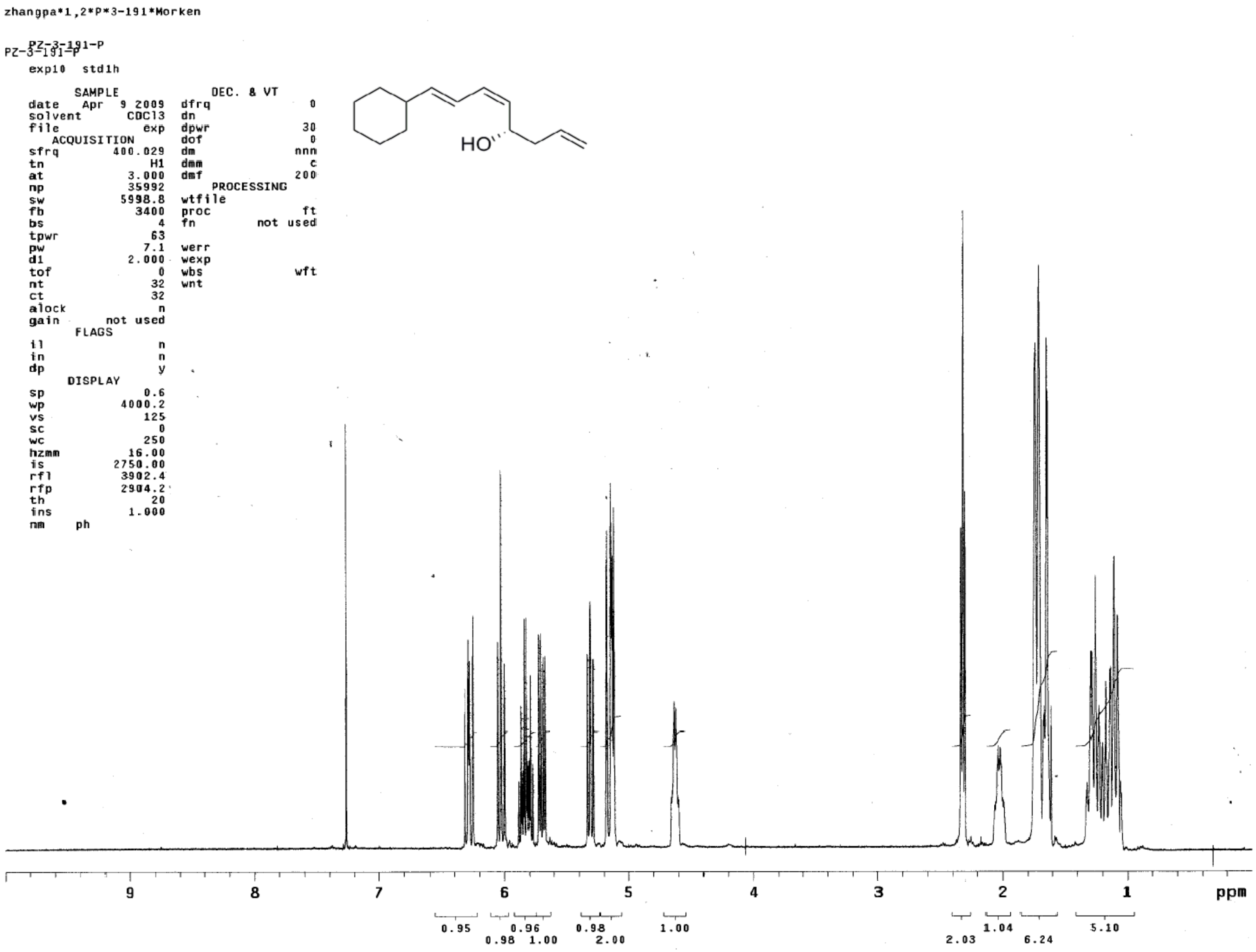


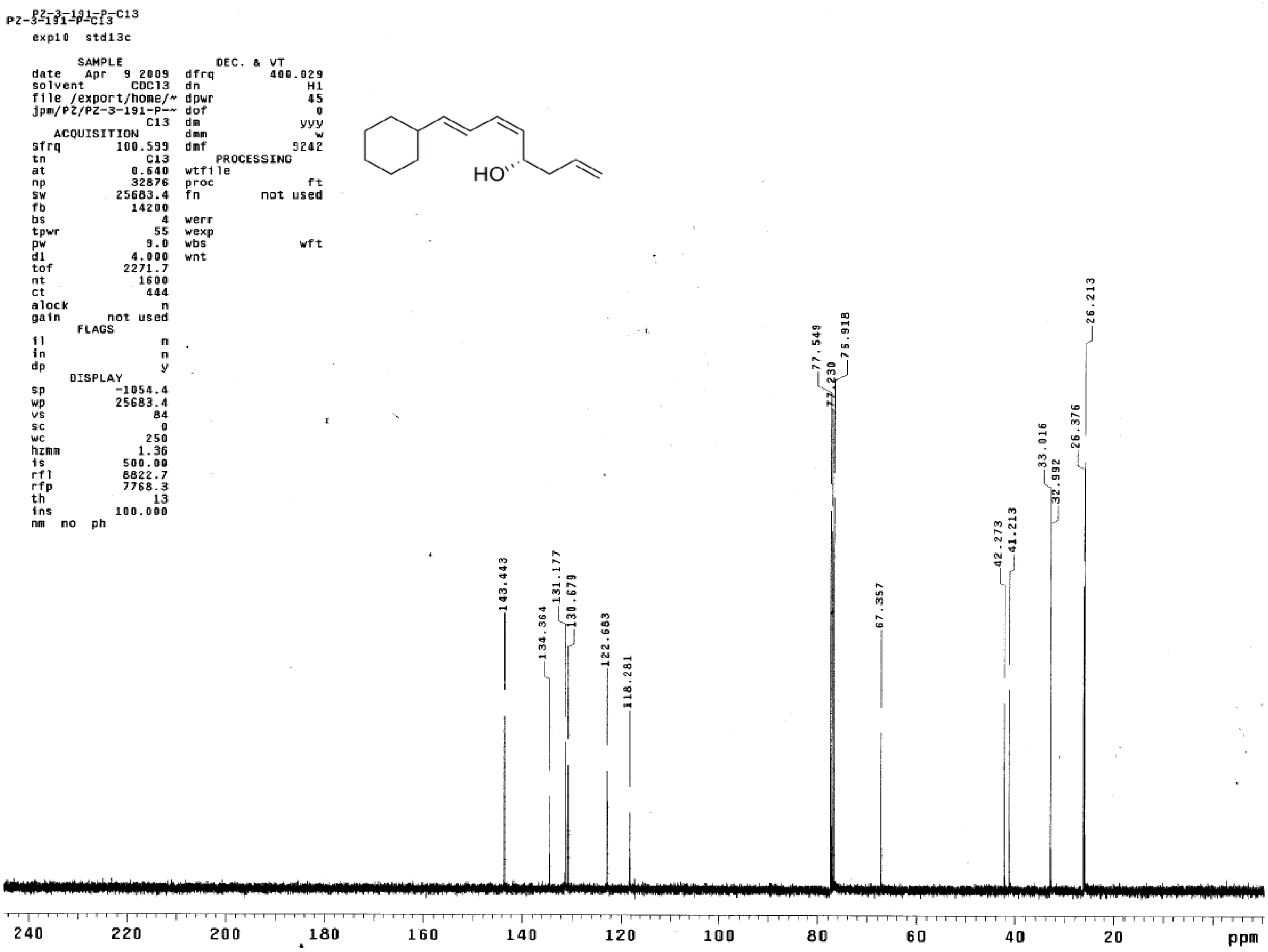
```
zhangpa*1,2*P*3-280*Morken

PZ-3-280-P
PZ-3-280-P
   exp1  stdlh

         SAMPLE              DEC. & VT
   date   Jun 17 2009   dfrq             0
   solvent      CDCl3   dn
   file           exp   dpwr            30
      ACQUISITION       dof              0
   sfrq       400.029   dm             nnn
   tn              H1   dmm              c
   at           3.000   dmf            200
   np           35992        PROCESSING
   sw          5998.8   wtfile
   fb            3400   proc            ft
   bs               4   fn        not used
   tpwr            63
   pw             7.1   werr
   d1           2.000   wexp
   tof              0   wbs            wft
   nt              32   wnt
   ct              28
   alock            n
   gain      not used
         FLAGS
   il               n
   in               n
   dp               y
        DISPLAY
   sp          -200.0
   wp          4200.3
   vs             180
   sc               0
   wc             250
   hzmm         16.80
   is         5134.76
   rfl          998.6
   rfp              0
   th              20
   ins          1.000
   nm     ph
```


TBSO
HO
134.813
133.829
131.128
130.722
127.856
118.473
77.485
77.231
76.977
67.279
62.858
42.235
36.645
26.142
18.555
-5.063
220
200
180
160
140
120
100
80
60
40
20
0
ppm

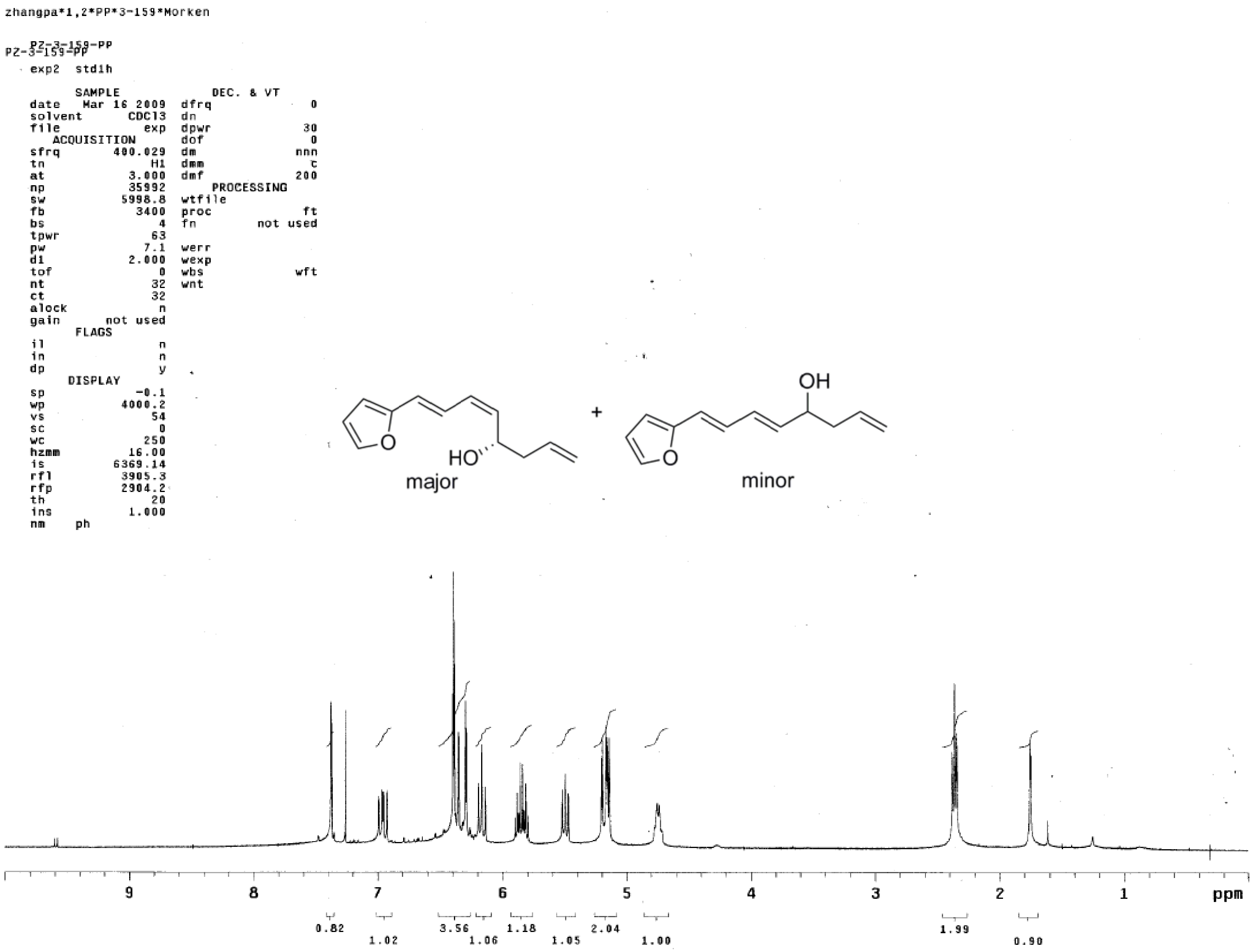

zhangpa*1,2*P*3-191*Morken
PZ-3-191-P
PZ-3-191-P
exp10 std1h
SAMPLE
date Apr 9 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 400.029
tn H1
at 3.000
np 35992
sw 5998.8
fb 3400
bs 4
tpwr 63
pw 7.1
d1 2.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 0.6
wp 4000.2
vs 125
sc 0
wc 250
hzmm 16.00
is 2750.00
rfl 3902.4
rfp 2904.2
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 0
dn
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs wft
wnt
HO
9
8
7
6
5
4
3
2
1
ppm
0.95
0.98
0.96
1.00
0.98
2.00
1.00
2.03
1.04
6.24
5.10



```
PZ-3-191-P-C13
PZ-3-191-P-C13

    exp10  std13c

         SAMPLE                 DEC. & VT
    date   Apr  9 2009   dfrq          400.029
    solvent       CDCl3   dn                 H1
    file /export/home/~ dpwr               45
    jpm/PZ/PZ-3-191-P-~ dof                 0
                   C13   dm               yyy
       ACQUISITION       dmm                w
    sfrq         100.599   dmf             9242
    tn               C13        PROCESSING
    at             0.640   wtfile
    np             32876   proc              ft
    sw           25683.4   fn          not used
    fb             14200
    bs                 4   werr
    tpwr              55   wexp
    pw               9.0   wbs              wft
    d1             4.000   wnt
    tof           2271.7
    nt              1600
    ct               444
    alock              n
    gain        not used
          FLAGS
    il                 n
    in                 n
    dp                 y
         DISPLAY
    sp           -1054.4
    wp           25683.4
    vs                84
    sc                 0
    wc               250
    hzmm            1.36
    is            500.00
    rfl           8822.7
    rfp           7768.3
    th                13
    ins          100.000
    nm  mo  ph
```



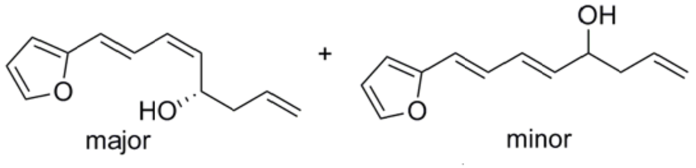
```
zhangpa*1,2*PP*3-159*Morken

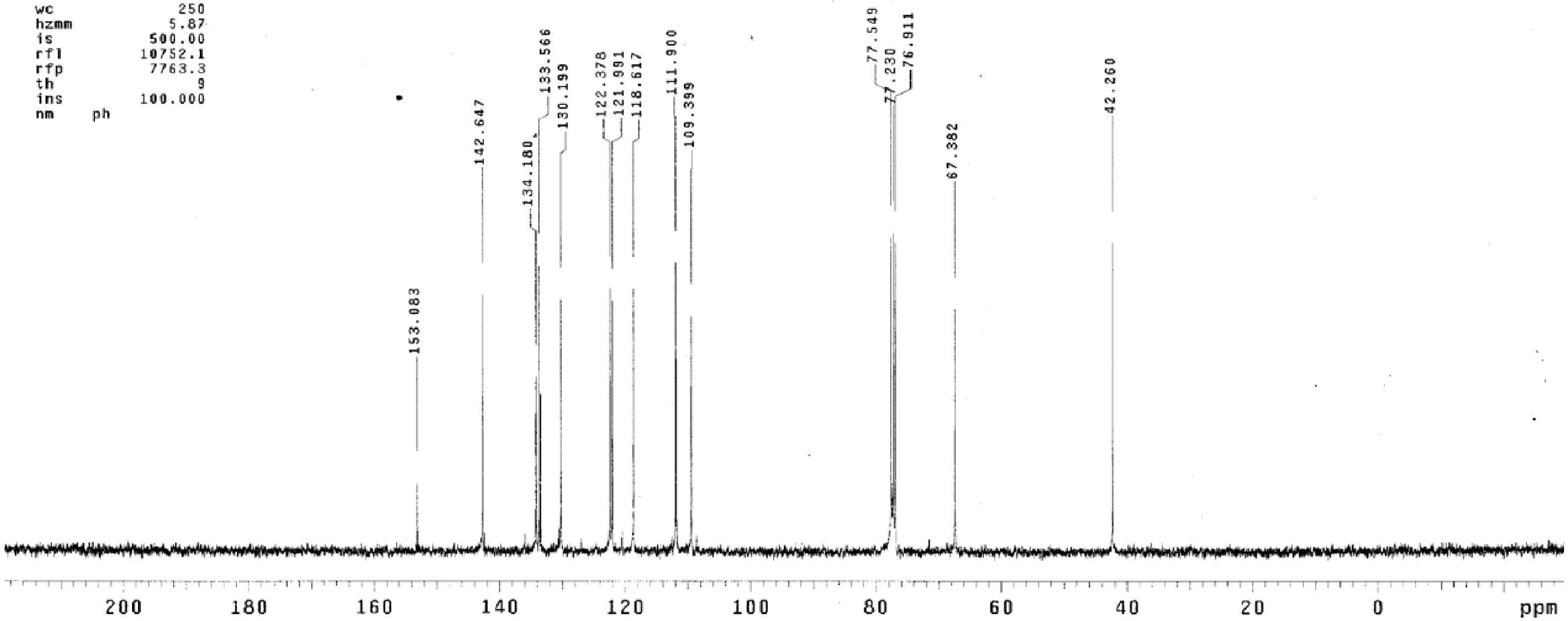

   PZ-3-159-PP
PZ-3-159-PP
   exp2  stdlh

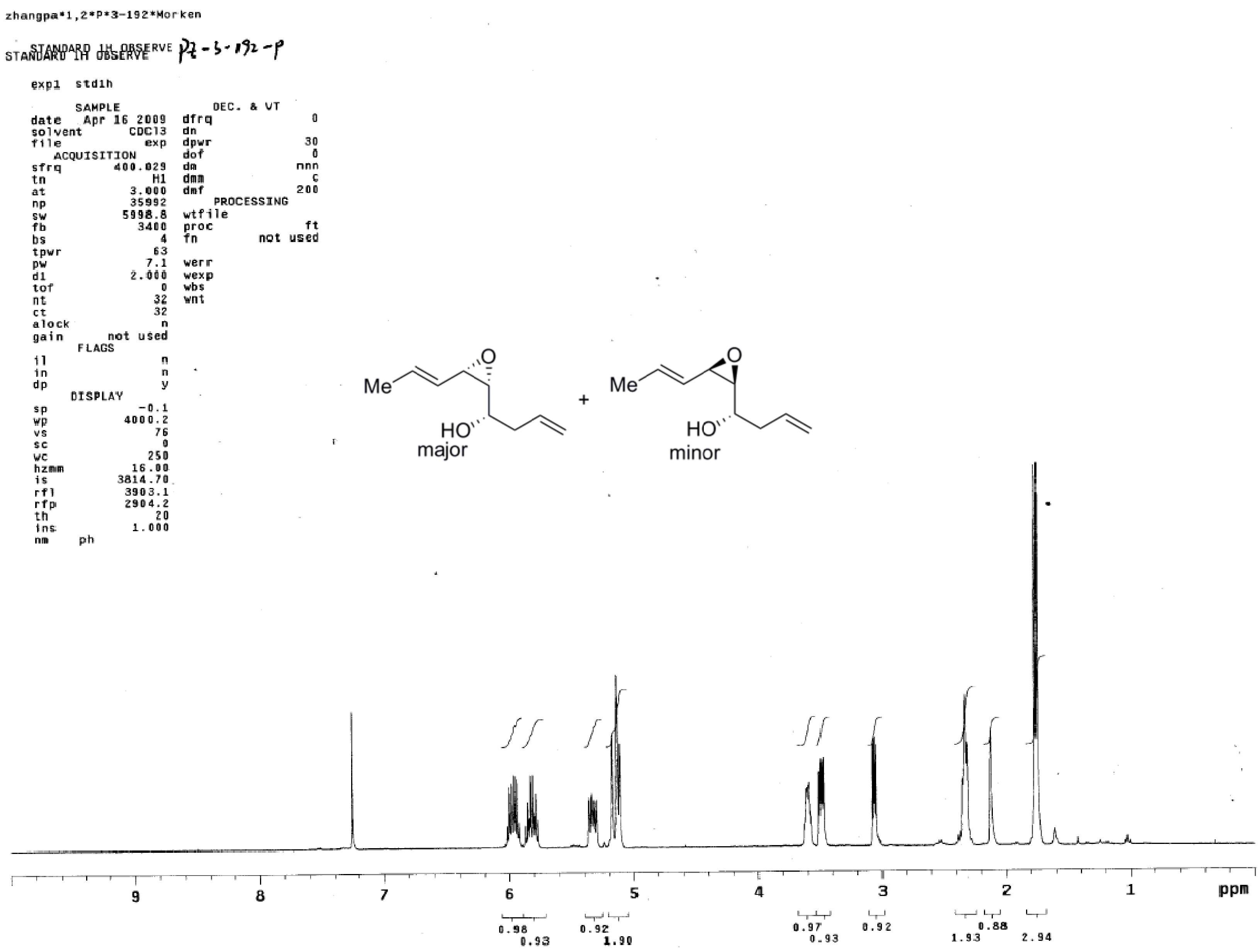
        SAMPLE                 DEC. & VT
   date   Mar 16 2009  dfrq                0
   solvent      CDCl3  dn
   file           exp  dpwr               30
      ACQUISITION      dof                 0
   sfrq       400.029  dm                nnn
   tn              H1  dmm                 c
   at           3.000  dmf               200
   np           35992      PROCESSING
   sw          5998.8  wtfile
   fb            3400  proc               ft
   bs               4  fn           not used
   tpwr            63
   pw             7.1  werr
   d1           2.000  wexp
   tof              0  wbs               wft
   nt              32  wnt
   ct              32
   alock            n
   gain      not used
        FLAGS
   il               n
   in               n
   dp               y
       DISPLAY
   sp            -0.1
   wp          4000.2
   vs              54
   sc               0
   wc             250
   hzmm         16.00
   is         6369.14
   rfl         3905.3
   rfp         2904.2
   th              20
   ins          1.000
   nm    ph
```

```
   PZ-3-159-pdt-13C
PZ-3-159-pdt-13C
   exp1  std13c

        SAMPLE            DEC. & VT
   date   Mar 17 2009   dfrq        399.768
   solvent      CDCl3   dn               H1
   file /export/home/~  dpwr             40
   gaofb/PZ-3-159-pdt~  dof               0
           -13C.fid     dm              yyy
      ACQUISITION       dmm               w
   sfrq       100.531   dmf            9259
   tn             C13   dseq
   at           2.000   dres            1.0
   np          100000   homo              n
   sw         25000.0   temp           25.0
   fb           14000     PROCESSING
   bs               4   lb             2.00
   tpwr            59   wtfile
   pw             9.7   proc             ft
   d1           1.000   fn         not used
   tof              0   math              f
   nt           10000
   ct             992   werr
   alock            s   wexp
   gain     not used    wbs
        FLAGS           wnt
   il               n
   in               n
   dp               y
   hs              nn
        DISPLAY
   sp         -2988.5
   wp         24999.6
   vs              50
   sc               0
   wc             250
   hzmm          5.87
   is          500.00
   rfl        10752.1
   rfp         7763.3
   th               9
   ins        100.000
   nm     ph
```





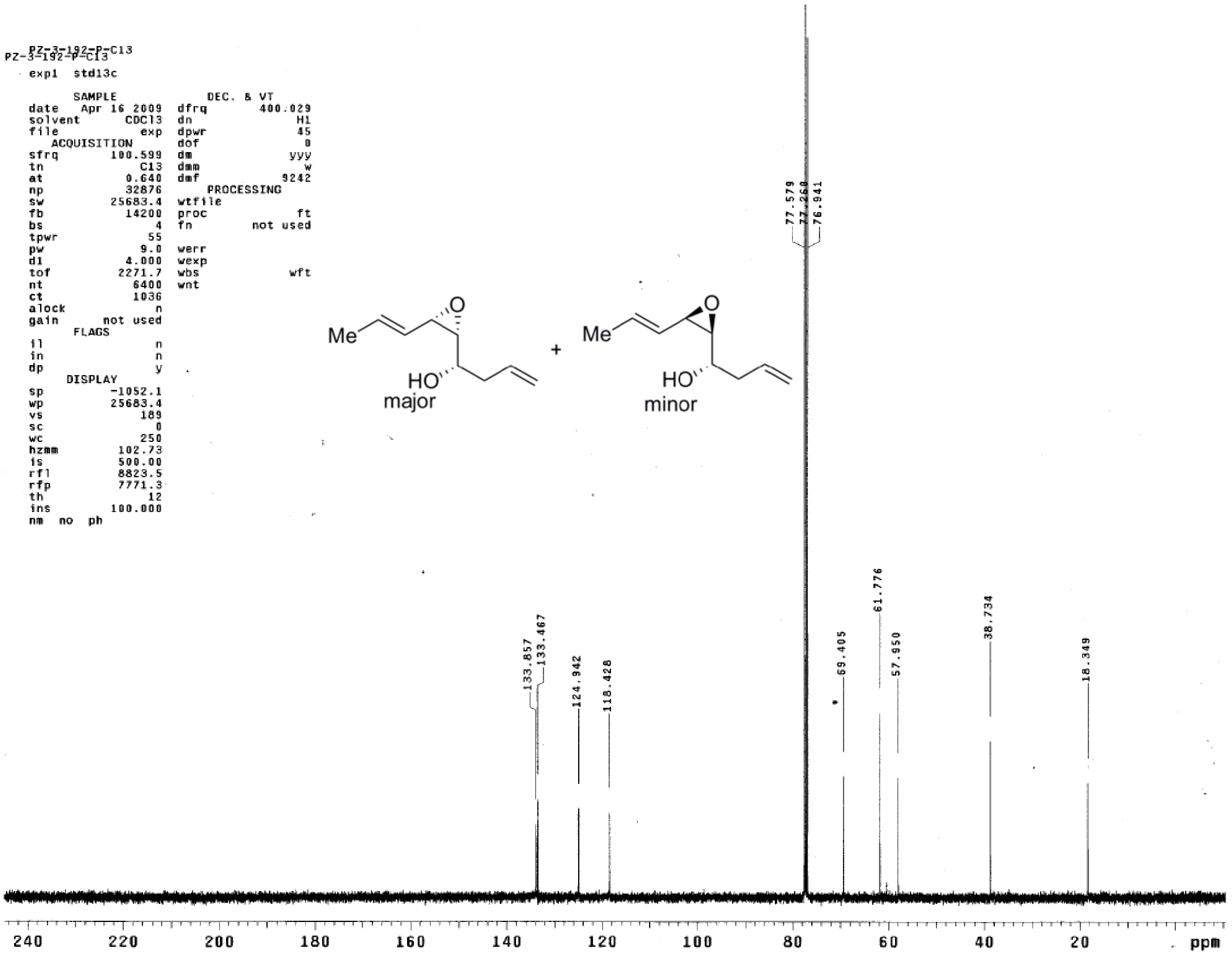


```
zhangpa*1,2*P*3-192*Morken

STANDARD 1H OBSERVE PZ-3-192-P

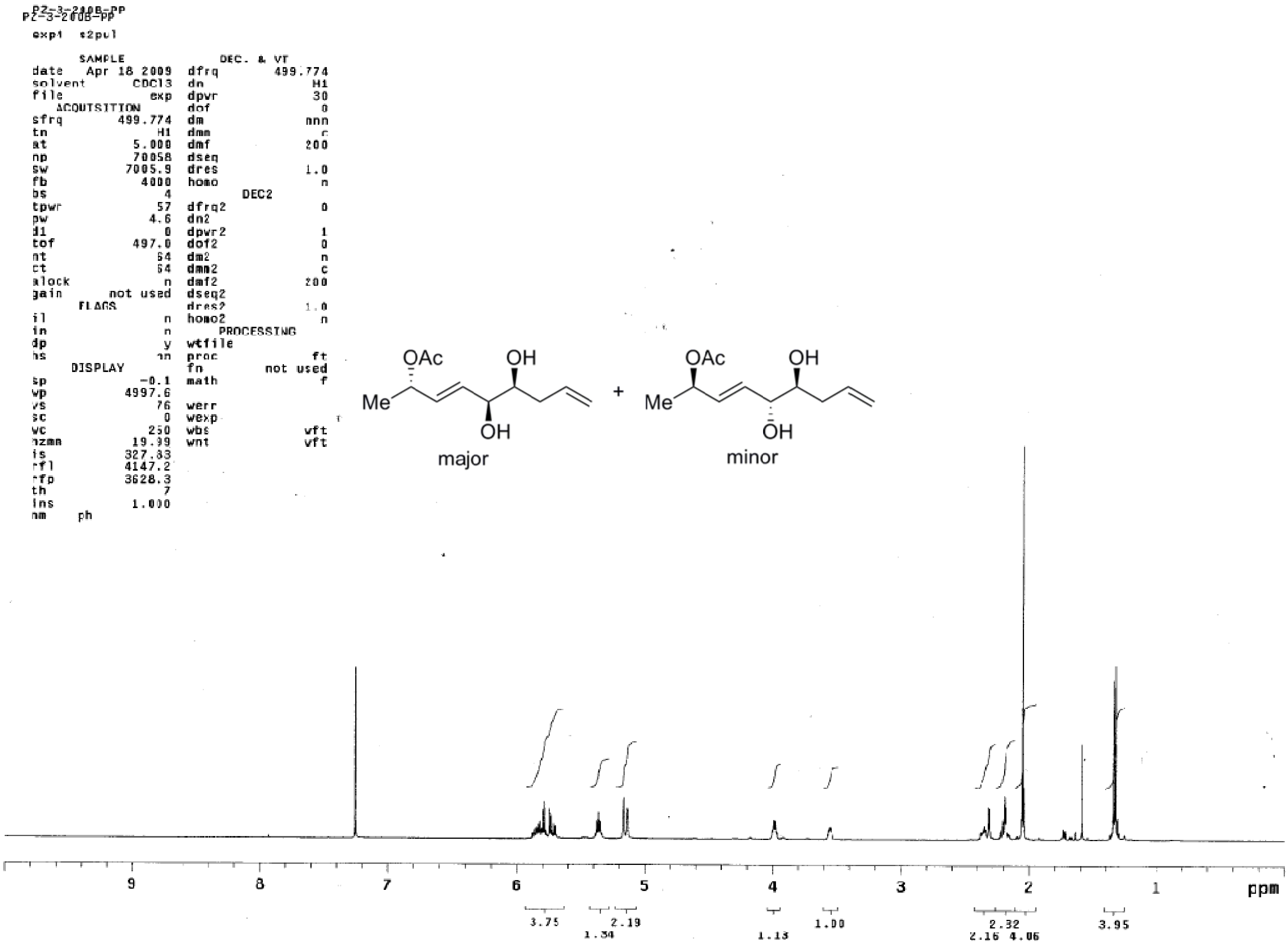
exp1  std1h

      SAMPLE              DEC. & VT
date   Apr 16 2009  dfrq              0
solvent      CDCl3  dn
file           exp  dpwr             30
     ACQUISITION    dof               0
sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           3.000  dmf             200
np           35992       PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn         not used
tpwr            63
pw             7.1  werr
d1           2.000  wexp
tof              0  wbs
nt              32  wnt
ct              32
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp            -0.1
wp          4000.2
vs              76
sc               0
wc             250
hzmm         16.00
is         3814.70
rfl         3903.1
rfp         2904.2
th              20
ins          1.000
nm     ph
```



```
PZ-3-192-P-C13
PZ-3-192-P-C13
 exp1  std13c

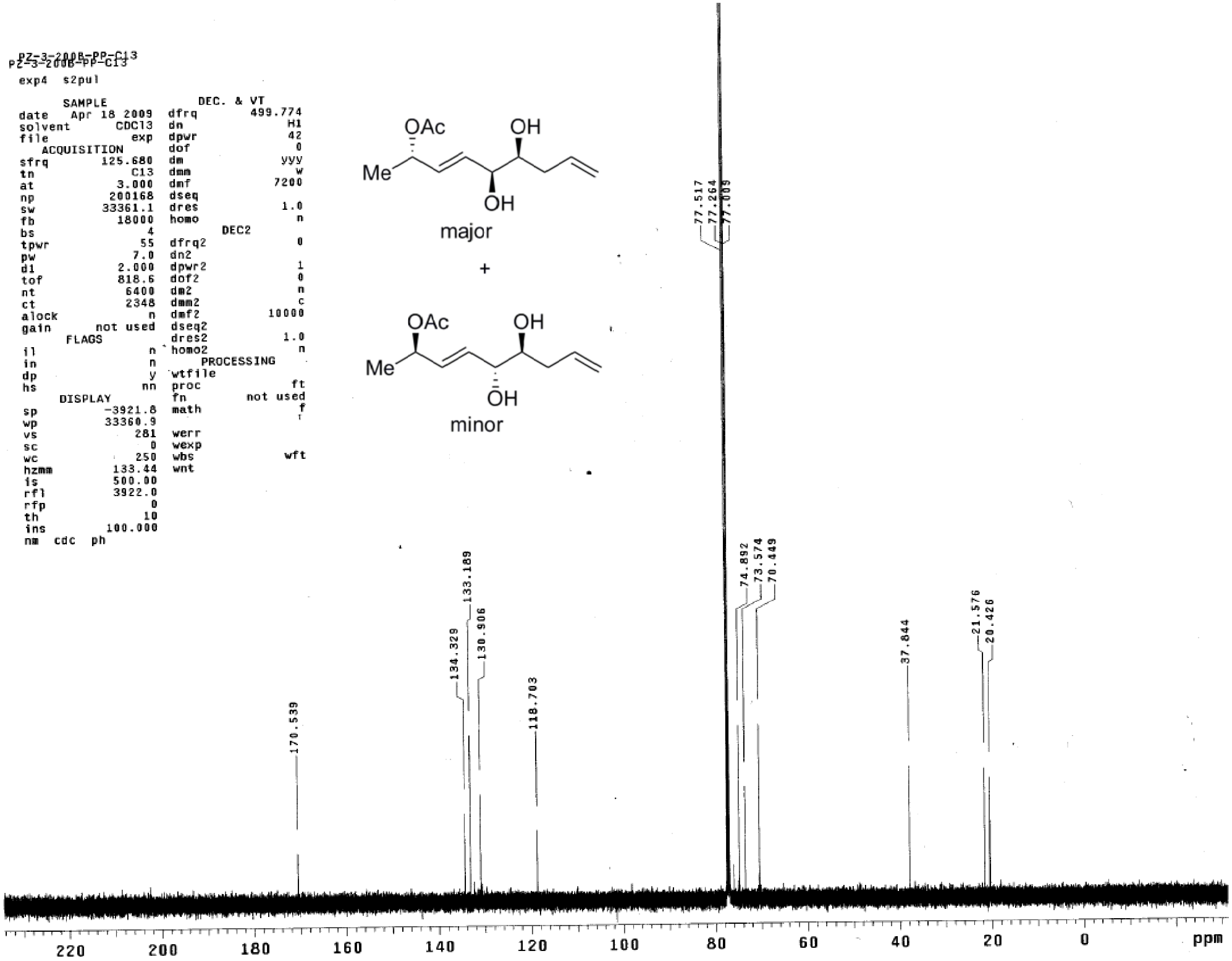
       SAMPLE              DEC. & VT
date   Apr 16 2009   dfrq        400.029
solvent      CDCl3   dn               H1
file           exp   dpwr             45
    ACQUISITION      dof               0
sfrq       100.599   dm              yyy
tn             C13   dmm               w
at           0.640   dmf            9242
np           32876       PROCESSING
sw         25683.4   wtfile
fb           14200   proc             ft
bs               4   fn         not used
tpwr            55
pw             9.0   werr
d1           4.000   wexp
tof         2271.7   wbs             wft
nt            6400   wnt
ct            1036
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp         -1052.1
wp         25683.4
vs             189
sc               0
wc             250
hzmm        102.73
is          500.00
rfl         8823.5
rfp         7771.3
th              12
ins        100.000
nm  no  ph
```



```
PZ-3-240B-PP
PZ-3-200B-PP

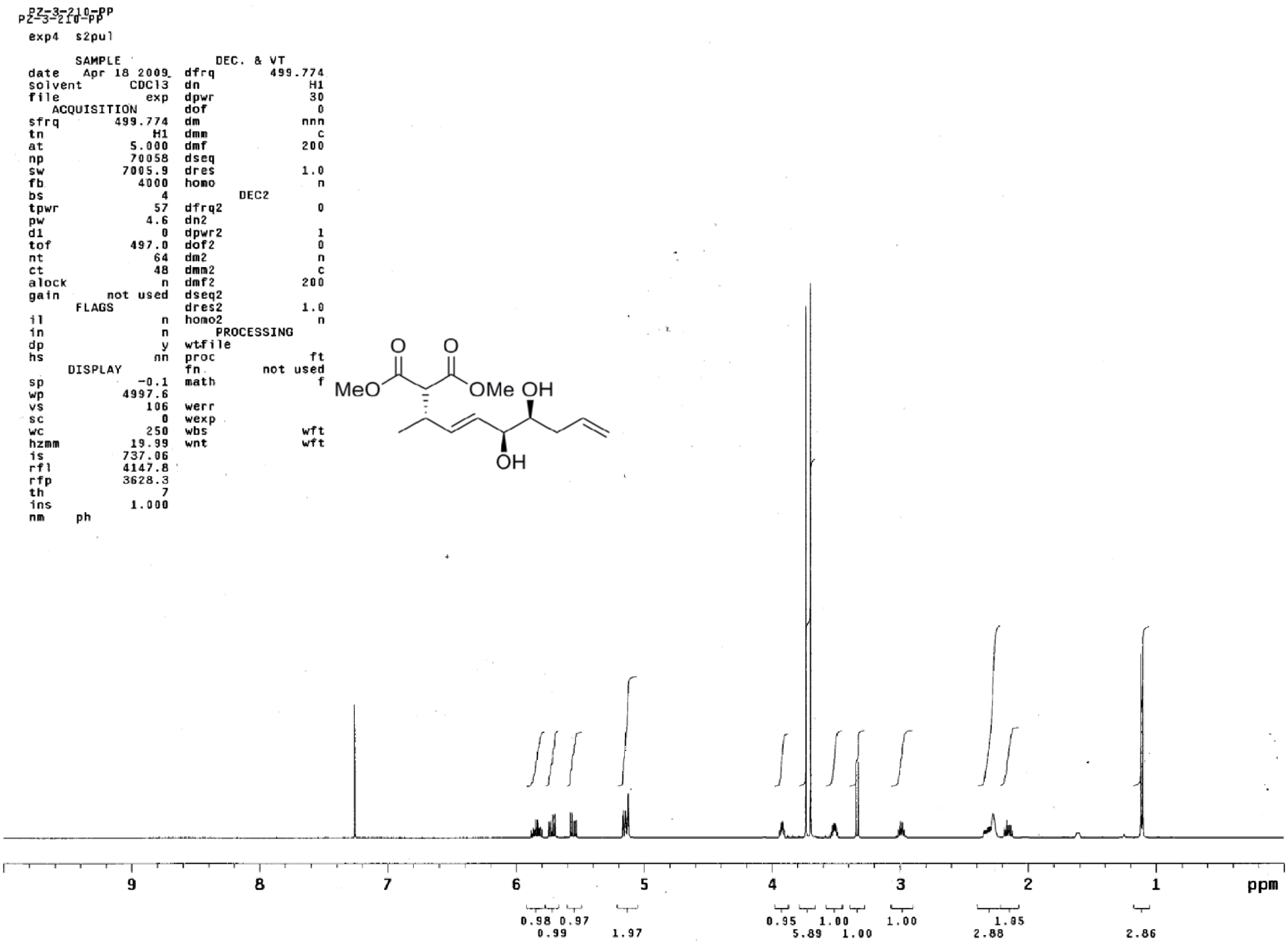
exp1  s2pul

      SAMPLE                 DEC. & VT
date   Apr 18 2009  dfrq          499.774
solvent       CDCl3  dn                 H1
file            exp  dpvr               30
    ACQUISITION      dof                 0
sfrq        499.774  dm                nnn
tn               H1  dmm                 c
at            5.000  dmf               200
np            70058  dseq
sw           7005.9  dres              1.0
fb             4000  homo                n
bs                4          DEC2
tpwr             57  dfrq2               0
pw              4.6  dn2
d1                0  dpwr2               1
tof           497.0  dof2                0
nt               64  dm2                 n
ct               64  dmm2                c
alock             n  dmf2              200
gain       not used  dseq2
      FLAGS          dres2             1.0
il                n  homo2               n
in                n       PROCESSING
dp                y  wtfile
hs               nn  proc               ft
     DISPLAY         fn           not used
sp             -0.1  math                f
wp           4997.6
vs               76  werr
sc                0  wexp
wc              250  wbs               vft
hzmm          19.99  wnt               vft
is           327.83
rfl          4147.2
rfp          3628.3
th                7
ins           1.000
nm     ph
```



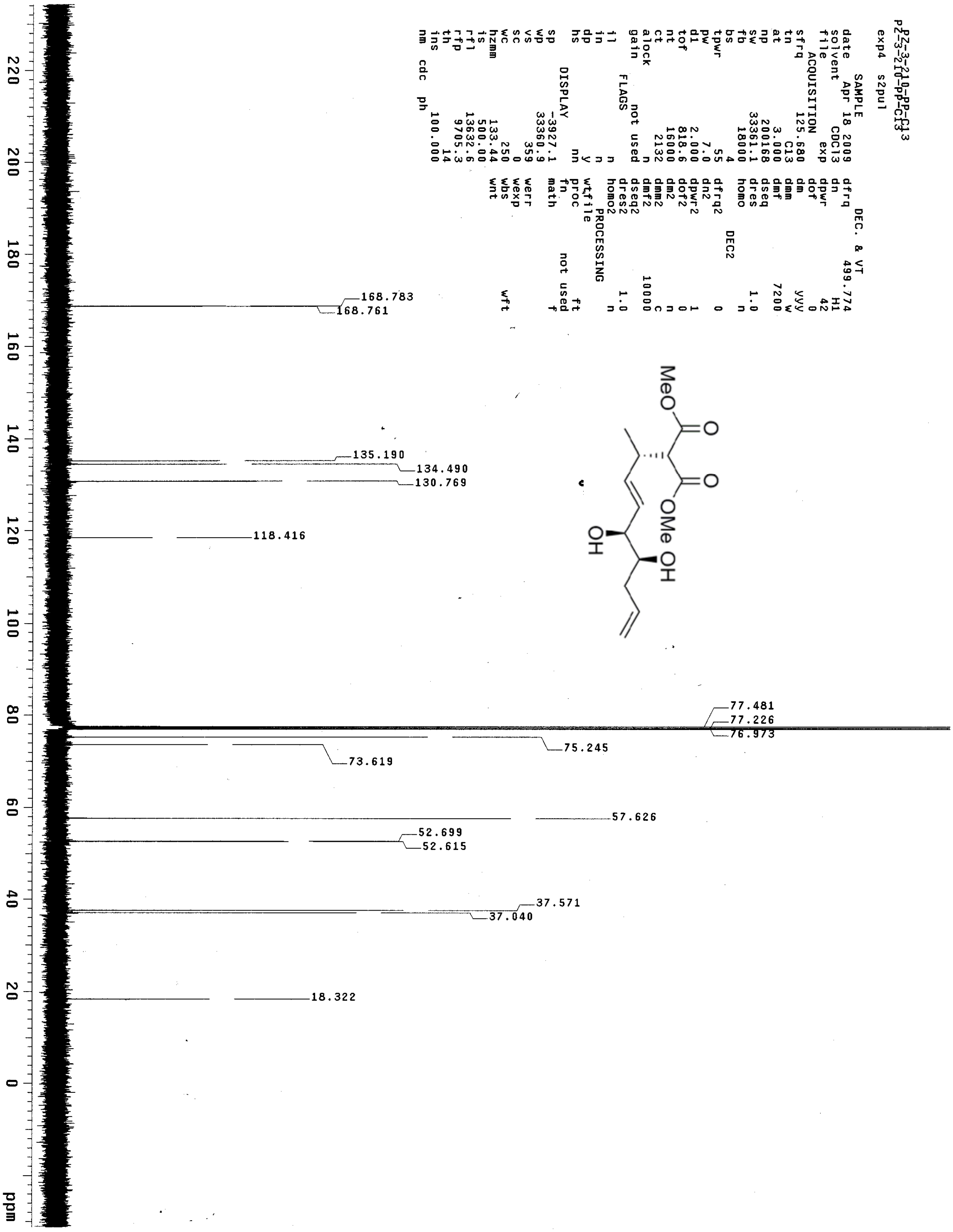
```
PZ-3-200B-PP-C13
PZ-3-200B-PP-C13
exp4  s2pul

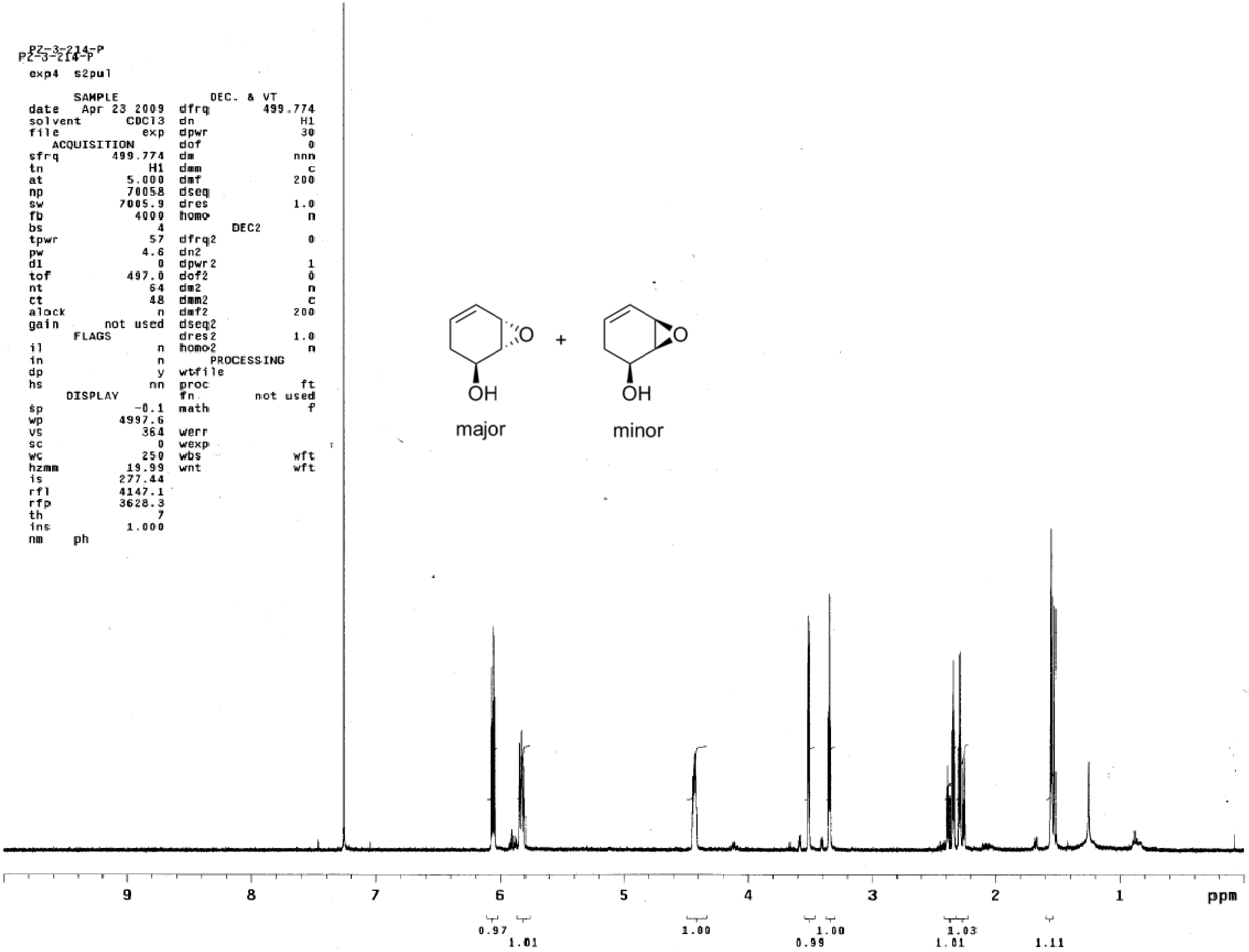
      SAMPLE              DEC. & VT
date   Apr 18 2009  dfrq        499.774
solvent       CDCl3  dn               H1
file            exp  dpwr             42
   ACQUISITION       dof               0
sfrq        125.680  dm              yyy
tn              C13  dmm               w
at            3.000  dmf            7200
np           200168  dseq
sw          33361.1  dres            1.0
fb            18000  homo              n
bs                4         DEC2
tpwr             55  dfrq2             0
pw              7.0  dn2
d1            2.000  dpwr2             1
tof           818.6  dof2              0
nt             6400  dm2               n
ct             2348  dmm2              c
alock             n  dmf2          10000
gain       not used  dseq2
      FLAGS          dres2           1.0
il                n  homo2             n
in                n       PROCESSING
dp                y  wtfile
hs               nn  proc             ft
     DISPLAY         fn         not used
sp          -3921.8  math              f
wp          33360.9
vs              281  werr
sc                0  wexp
wc              250  wbs             wft
hzmm         133.44  wnt
is           500.00
rfl          3922.0
rfp               0
th               10
ins         100.000
nm  cdc  ph
```

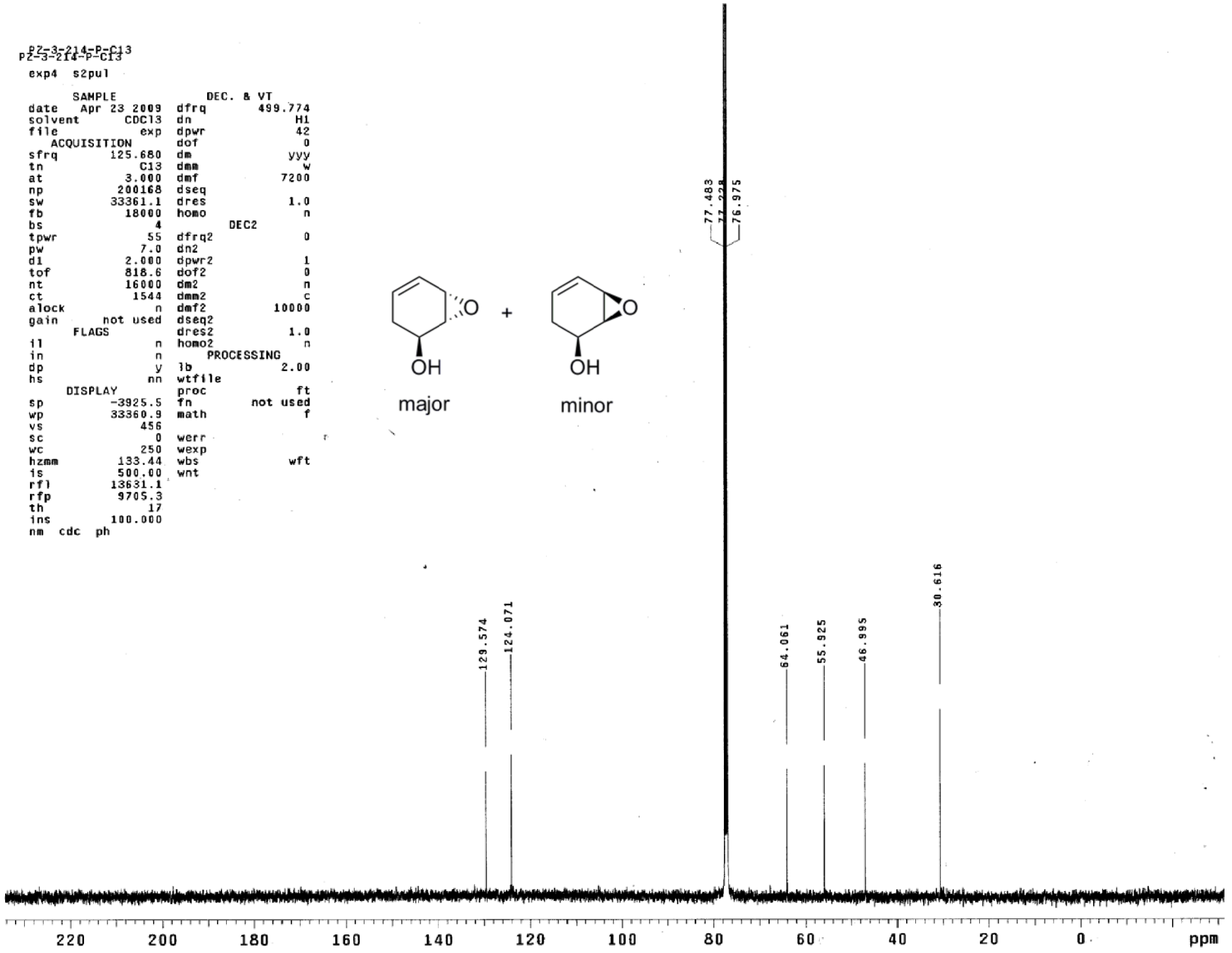


```
PZ-3-210-PP
PZ-3-210-PP
 exp4  s2pul

       SAMPLE              DEC. & VT
 date   Apr 18 2009   dfrq         499.774
 solvent      CDCl3   dn                H1
 file           exp   dpwr              30
    ACQUISITION       dof                0
 sfrq       499.774   dm               nnn
 tn              H1   dmm                c
 at           5.000   dmf              200
 np           70058   dseq
 sw          7005.9   dres             1.0
 fb            4000   homo               n
 bs               4         DEC2
 tpwr            57   dfrq2              0
 pw             4.6   dn2
 d1               0   dpwr2              1
 tof          497.0   dof2               0
 nt              64   dm2                n
 ct              48   dmm2               c
 alock            n   dmf2             200
 gain      not used   dseq2
       FLAGS          dres2            1.0
 il               n   homo2              n
 in               n      PROCESSING
 dp               y   wtfile
 hs              nn   proc              ft
      DISPLAY         fn          not used
 sp            -0.1   math               f
 wp          4997.6
 vs             106   werr
 sc               0   wexp
 wc             250   wbs              wft
 hzmm         19.99   wnt              wft
 is          737.06
 rfl         4147.8
 rfp         3628.3
 th               7
 ins          1.000
 nm    ph
```


PZ-3-210-PP-C13
exp4 s2pul
SAMPLE
date Apr 18 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 125.680
tn C13
at 3.000
np 200168
sw 33361.1
fb 18000
bs 4
tpwr 55
pw 7.0
d1 2.000
tof 818.6
nt 16000
ct 2132
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -3927.1
wp 33360.9
vs 359
sc 0
wc 250
hzmm 133.44
is 500.00
rfl 13632.6
rfp 9705.3
th 14
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.774
dn H1
dpwr 42
dof 0
dm yyy
dmm w
dmf 7200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
MeO
O
O
OMe OH
OH
168.783
168.761
135.190
134.490
130.769
118.416
77.481
77.226
76.973
75.245
73.619
57.626
52.699
52.615
37.571
37.040
18.322
220
200
180
160
140
120
100
80
60
40
20
0
ppm


PZ-3-214-P
exp4 s2pul
SAMPLE
date Apr 23 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 499.774
tn H1
at 5.000
np 70058
sw 7005.9
fb 4000
bs 4
tpwr 57
pw 4.6
d1 0
tof 497.0
nt 64
ct 48
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 4997.6
vs 364
sc 0
wc 250
hzmm 19.99
is 277.44
rfl 4147.1
rfp 3628.3
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.774
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs wft
wnt wft
O
+
O
OH
OH
major
minor
9
8
7
6
5
4
3
2
1
ppm
0.97
1.01
1.00
0.99
1.00
1.01
1.03
1.11



```
PZ-3-214-P-C13
PZ-3-214-P-C13
exp4  s2pul

      SAMPLE             DEC. & VT
date    Apr 23 2009  dfrq        499.774
solvent       CDC13  dn               H1
file            exp  dpwr             42
   ACQUISITION       dof               0
sfrq        125.680  dm              yyy
tn              C13  dmm               w
at            3.000  dmf            7200
np           200168  dseq
sw          33361.1  dres            1.0
fb            18000  homo              n
bs                4         DEC2
tpwr             55  dfrq2             0
pw              7.0  dn2
d1            2.000  dpwr2             1
tof           818.6  dof2              0
nt            16000  dm2               n
ct             1544  dmm2              c
alock             n  dmf2          10000
gain       not used  dseq2
      FLAGS          dres2           1.0
il                n  homo2             n
in                n     PROCESSING
dp                y  lb             2.00
hs               nn  wtfile
     DISPLAY         proc             ft
sp          -3925.5  fn         not used
wp          33360.9  math              f
vs              456
sc                0  werr
wc              250  wexp
hzmm         133.44  wbs             wft
is           500.00  wnt
rfl         13631.1
rfp          9705.3
th               17
ins         100.000
nm  cdc  ph
```