Nickel–Catalyzed, Carbonyl–Ene–Type Reactions: Selective for Alpha Olefins and More Efficient with Electron–Rich Aldehydes

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Supporting Information

Experimental Procedures, Analytical and Spectroscopic Data for Compounds.

General Aspect.

Unless otherwise indicated, all reactions were performed under an oxygen–free atmosphere of nitrogen or argon with rigid exclusion of moisture from reagents and glassware. Bis(cyclooctadienyl)nickel(0) ($Ni(cod)_2$) and triphenylphosphine were purchased from Strem Chemicals, Inc., stored under nitrogen atomosphere and used without further purification. Ethyl diphenylphosphinite was purchased from Aldrich Chemical Co. and was used as received. All alkenes and aldehydes were used as received without further purification. Triethylsilyl trifluoromethanesulfonate (TESOTf), triethylamine and toluene were distilled over calcium hydride before use.

Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silicycle Silica Gel (230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz or Varian 500 MHz spectrometers in $CDCl_3$. Chemical shifts in ^1H NMR spectra are reported in ppm on the δ scale from an internal

standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. Infrared (IR) spectra were recorded on a Perkin–Elmer 2000 FT–IR. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer by Dr. Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrument Facility.

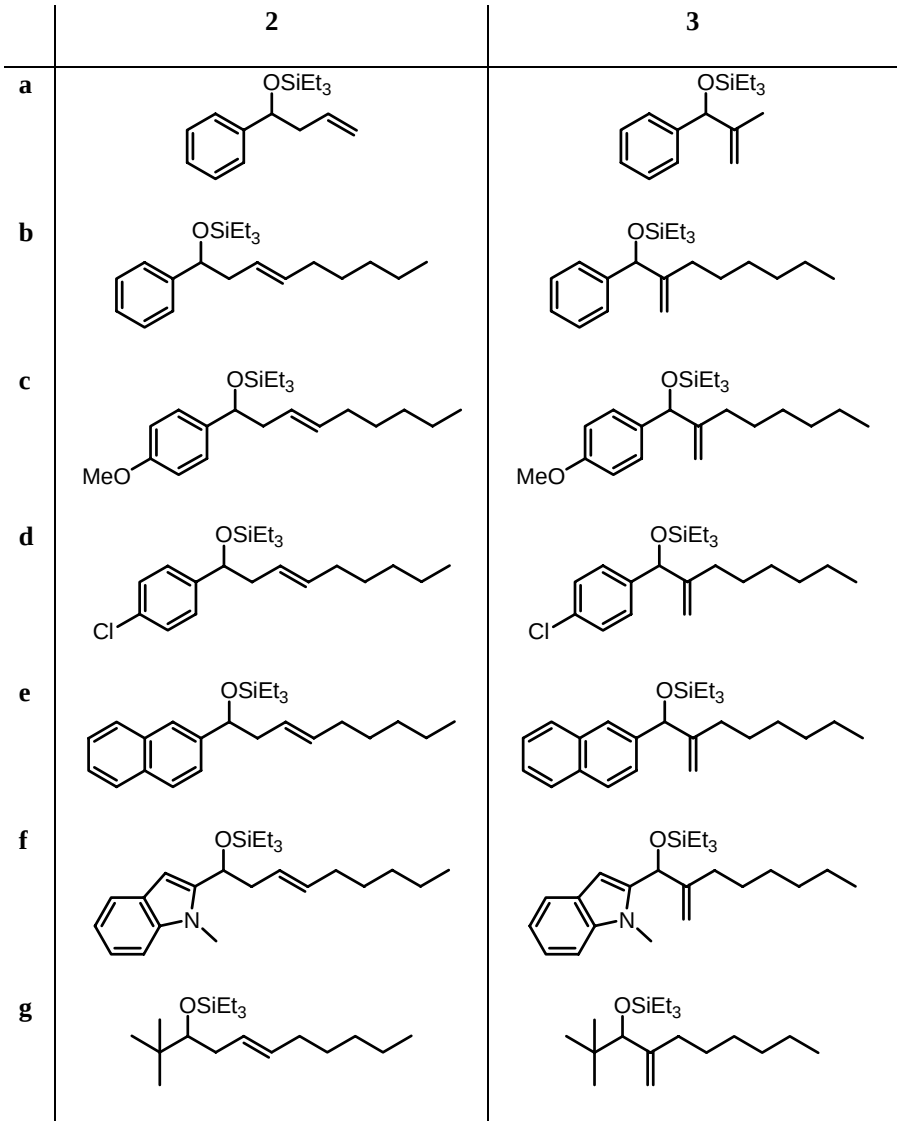
General Procedure for the Nickel–Catalyzed Coupling Reaction.

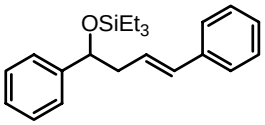
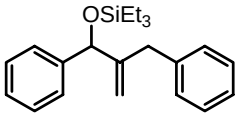
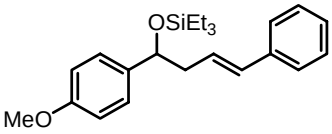
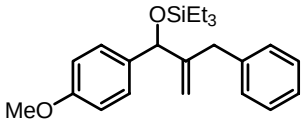
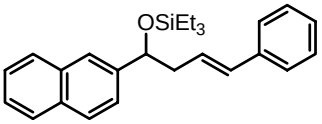
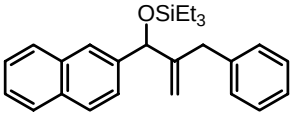
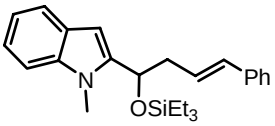
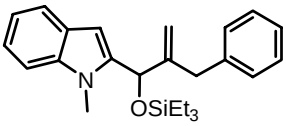
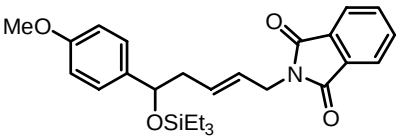
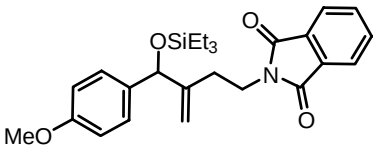
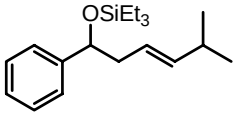
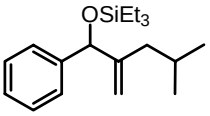
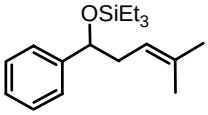
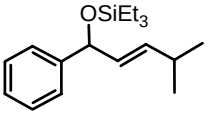
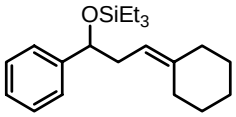
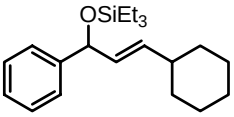
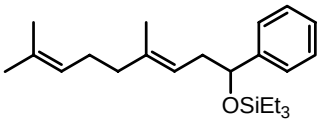
A 10 mL test tube and a stir bar were oven–dried and brought into a glove box. $Ni(cod)_2$ (0.1 mmol, 20 mol%) and phosphine ligand (0.2 mmol, 40 mol%) were added to the tube. The tube was sealed with a septum, and was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in degassed toluene (2.5 mL) under argon and stirred at room temperature. The alkene (1.5 mmol, 300 mol% to 0.5 mL), triethylamine (3 mmol, 600 mol%), aldehyde (0.5 mmol, 100 mol%) were added sequentially to the reaction mixture. Triethylsilyltriflate (0.875 mmol, 175 mol%) was added finally to the reaction mixture in dropwise fraction and the mixture was stirred at room temperature or at indicated temperature for 48 h. The mixture was diluted with ether and filtered through a plug of silica gel. Solvent was removed under reduced pressure. Purification via flash chromatography on silica gel (1% ethyl acetate in hexane, unless otherwise indicated) afforded the coupling product.

In some cases, the coupling product overlapped with the starting materials,

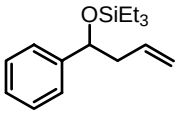
characterization data of the corresponding alcohol was reported instead. The corresponding alcohol product was obtained by treating the mixture with 1 M TBAF in THF at 0 °C and allowed to stir at room temperature for 2 hours, followed by flash column chromatography on silica (15% ethyl acetate in hexane, unless otherwise indicated). E:Z selectivity for the compound **2** was determined by comparing the TES group deprotected alcohol product with the literature.[1,2]

Figure 1. Structures of the Coupling Products



h		
i		
j		
k		
l		
m		
n		
o		
p		

Compound Characterization

Table 1, entry 1: **2a**: 

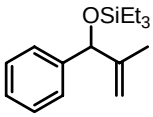
The standard procedure was followed, except that a balloon filled with propene (**1a**, 1 atm) was used in place of Ar. Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.27–7.38 (m, 5H); 5.78–5.89 (m, 1H); 5.05–5.10 (m, 2H); 4.74 (dd, J = 7.2, 5.5 Hz, 1H); 2.42–2.59 (m, 2H); 0.94 (t, J = 7.9 Hz, 9H); 0.59 (dq, J = 2.6, 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ):145.3, 135.4, 128.2, 127.2, 126.1, 117.0, 75.1, 45.6, 7.0, 5.0.

IR (NaCl, thin film): 3029, 2956, 2912, 2877, 1641, 1493, 1454, 1414, 1239, 1089, 1068, 1006, 914, 839, 744, 699.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{26}OSiNa$, 285.1651; found, 285.1633.

Table 1, entry 1: **3a**: 

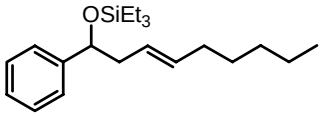
The standard procedure was followed, except that a balloon filled with propene (**1a**, 1 atm) was used in place of Ar. Yield: 8%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24–7.39 (m, 5H); 5.15 (m, 2H); 4.86 (s, 1H); 1.56 (s, 3H); 0.94 (t, J = 7.8 Hz, 9H); 0.61 (q, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.1, 143.5, 128.1, 127.0, 126.3, 111.0, 78.4, 17.4, 7.0, 5.0.

IR (NaCl, thin film): 2955, 2913, 2877, 1451, 1237, 1091, 1066, 1005, 899, 853, 740, 698.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{26}OSiNa$, 285.1645; found, 285.1651.

Table 1, entry 2 and 3: **2b**[1]



The standard procedure was followed (entry 2). Yield: 81%. Isolated as a 75:25 mixture of E and Z isomers, respectively.

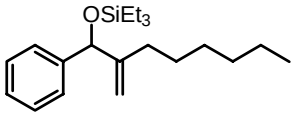
The standard procedure was followed, except that the reaction time was 18 h (entry 3). Yield: 68%. Isolated as a 75:25 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.20–7.40 (m, 5H); 5.30–5.50 (m, 2H); 4.63 (dd, *J* = 5.6, 7.2 Hz, 1H); 2.45 (quintet, *J* = 6.1 Hz, 1H); 2.35 (quintet, *J* = 5.9 Hz, 1H); 1.33 (m, 2H); 0.92 (t, *J* = 7.8 Hz, 12H); 0.56 (dq, *J* = 2.4, 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.6, 133.3, 128.1, 127.1, 126.6, 126.2, 75.6, 44.5, 32.8, 31.6, 29.3, 22.8, 14.2, 7.0, 5.1.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{21}H_{36}OSi$, 355.243; found, 355.244.

Table 1, entry 2 and 3: **3b**[1]



The standard procedure was followed (entry 2). Yield: 4%.

The standard procedure was followed, except that the reaction time was 18 h (entry 3). Yield: 4%.

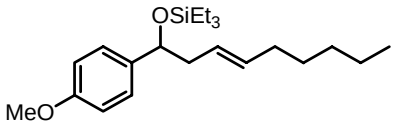
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 (d, *J* = 7.0 Hz, 2H); 7.31 (t, *J* = 7.1 Hz, 2H); 7.24 (t, *J* = 7.2, 1H); 5.22 (brs, 1H); 5.15 (brs, 1H); 5.25 (d, *J* = 5.9 Hz, 1H); 4.87 (s, 1H); 1.96 (pentet, *J* = 7.8 Hz, 1H); 1.76 (pentet, *J* = 8.0 Hz, 1H); 1.15–1.40 (m, 8H); 0.93 (t, *J* = 8.0

Hz, 9H); 0.87 (t, J = 6.8 Hz, 3H); 0.60 (dq, J = 1.6, 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.3, 143.8, 128.1, 127.1, 126.6, 109.5, 78.3, 32.0, 30.8, 29.4, 28.0, 22.8, 14.3, 7.0, 5.1.

IR (NaCl, thin film): 2956, 2876, 1647, 1456, 1089, 1066, 742.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{21}H_{36}OSi$, 355.243; found, 355.242.

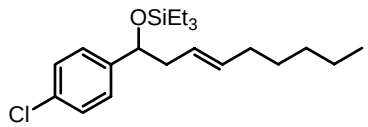
Table 1, entry 4: **2c**: 

The standard procedure was followed, except that the reaction time was 18 h. Yield: 81%. Isolated as a 75:25 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.22 (d, J = 8.6 Hz, 2H); 6.84 (d, J = 8.6 Hz, 2H); 5.33–5.43 (m, 2H); 4.58 (dd, J = 6.1 Hz, 6.1 Hz, 1H); 3.81 (s, 3H); 2.27–2.42 (m, 2H); 1.93–1.98 (m, 2H); 1.22–1.60 (m, 6H); 0.95 (t, J = 8.0 Hz, 3H); 0.88 (t, J = 7.8 Hz, 9H); 0.53 (q, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.7, 137.9, 133.2, 127.3, 126.7, 113.4, 75.2, 55.4, 44.5, 32.8, 31.6, 29.3, 22.8, 14.3, 7.0, 5.0.

IR (NaCl, thin film): 2955, 2876, 1613, 1512, 1459, 1302, 1247, 1172, 1078, 1005, 972, 830, 742.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{22}H_{38}O_2SiNa$, 385.2539; found, 385.2537.

Table 1, entry 5: **2d**: 

The standard procedure was followed, except that the reaction time was 18 h. Yield: 35%. Isolated as a 74:26 mixture of E and Z isomers, respectively.

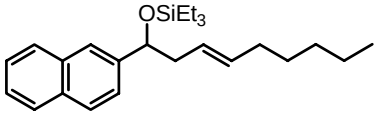
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.28–7.24 (m, 4H); 5.30–5.41 (m, 2H); 4.61 (dd, *J* = 6.1 Hz, 6.1 Hz, 1H); 2.26–2.40 (m, 2H); 1.89–1.97 (m, 2H); 1.21–1.59 (m, 6H); 0.94 (t, *J* = 8.0 Hz, 3H); 0.89 (t, *J* = 7.8 Hz, 9H); 0.54 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.1, 133.7, 132.5, 128.2, 127.5, 126.0, 74.8, 44.4, 32.8, 31.5, 29.2, 22.7, 14.3, 7.0, 4.9.

IR (NaCl, thin film): 2956, 2876, 1490, 1458, 1412, 1238, 1080, 1014, 971, 741.

HRMS–ESI (m/z): $[M+Na–C_6H_{15}SiOCl]^+$ calcd for $C_{15}H_{20}Na$, 223.1463; found, 223.1305.

Table 1, entry 6: **2e**:



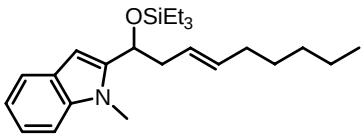
The standard procedure was followed, except that the reaction was heated at 35 °C. Yield: 84%. Isolated as a 70:30 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83–7.92 (m, 3H); 7.80 (s, 1H); 7.48–7.59 (m, 3H); 5.43–5.53 (m, 2H); 4.89 (dd, *J* = 6.9, 13.2 Hz, 1H); 2.45–2.68 (m, 2H); 1.98–2.05 (m, 2H); 1.26–1.39 (m, 6H); 0.97 (t, *J* = 8.0 Hz, 9H); 0.94 (t, *J* = 7.6 Hz, 3H); 0.63 (q, *J* = 4.1, 8.0 Hz 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.1, 133.4, 133.0, 132.3, 128.1, 127.9, 126.5, 126.0, 125.6, 125.6, 124.7, 124.7, 75.7, 44.4, 32.8, 31.7, 29.3, 22.8, 14.3, 7.0, 5.1.

IR (NaCl, thin film): 2956, 2929, 2875, 1458, 1414, 1377, 1239, 1086, 1005, 972, 744.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{25}H_{38}OSiNa$, 405.2590; found, 405.2584

Table 1, entry 7: **2f**: 

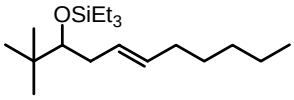
The standard procedure was followed, except that the product was purified with 10% ethyl acetate in hexane buffered with 1% triethylamine. Yield: 53%. Isolated as a 83:17 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.65 (d, *J* = 7.8 Hz, 1H); 7.37 (d, *J* = 8.2 Hz, 1H); 7.27 (t, *J* = 7.1 Hz, 1H); 7.17 (t, *J* = 7.1 Hz, 1H); 6.40 (s, 1H); 5.43–5.59 (m, 2H); 4.96 (dd, *J* = 6.5, 7.4 Hz, 1H); 3.92 (s, 3H); 2.56–2.71 (m, 2H); 2.01–2.07 (m, 2H); 1.29–1.42 (m, 6H); 0.97 (t, *J* = 8.0 Hz, 9H); 0.95 (t, *J* = 4.0 Hz, 3H); 0.63 (dq, *J* = 1.1, 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 142.3, 138.4, 133.7, 127.7, 126.2, 121.3, 120.7, 119.4, 109.1, 100.2, 70.6, 42.2, 32.8, 31.6, 31.0, 29.3, 22.8, 14.3, 7.0, 5.0.

IR (NaCl, thin film): 2954, 2927, 2874, 1466, 1339, 1236, 1072, 1010, 731.

HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{24}H_{39}ONSiNa$, 408.2693; found, 408.2695.

Table 1, entry 8: **2g**: 

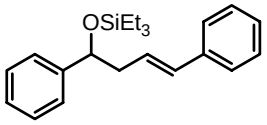
The standard procedure was followed, except that the reaction was heated at 35 °C. Yield: 61%. Isolated as a 78:22 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.37–5.53 (m, 2H); 3.37 (dd, *J* = 3.8, 7.4 Hz, 1H); 2.30–2.36 (m, 1H); 1.99–2.12 (m, 3H); 1.27–1.42 (m, 6H); 0.99 (t, *J* = 8.0 Hz, 9H); 0.92 (t, *J* = 6.8 Hz, 3H); 0.90 (s, 9H); 0.63 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 130.6, 128.5, 81.2, 36.2, 31.8, 31.4, 29.5, 27.6, 26.5, 22.8, 14.2, 7.3, 5.7.

IR (NaCl, thin film): 2956, 2876, 1466, 1238, 1096, 1009, 737.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{40}OSiNa$, 335.2746; found, 335.2741.

Table 1, entry 9: **2h**: 

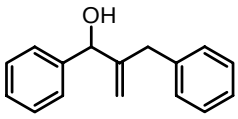
The standard procedure was followed. Yield: 79%. Isolated as a 95:5 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30–7.50 (m, 10H); 6.51 (d, *J* = 15.9 Hz, 1H); 6.34 (dt, *J* = 7.2, 15.9 Hz 1H); 4.89 (dd, *J* = 5.3, 7.2 Hz, 1H); 2.64–2.81 (m, 2H); 1.03 (t, *J* = 7.9 Hz, 9H); 0.68 (dq, *J* = 2.0, 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.5, 138.0, 132.4, 128.8, 128.4, 127.4, 127.4, 127.2, 126.3, 126.2, 75.5, 45.0, 7.1, 5.2.

IR (NaCl, thin film): 3062, 3028, 2955, 2911, 2876, 1600, 1494, 1453, 1414, 1239, 1088, 1070, 1006, 965, 830, 742, 700.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{22}H_{30}OSiNa$, 361.1964; found, 361.1974.

Table 1, entry 9: **3h** (TES group deprotected): 

The standard procedure was followed, except that the coupling product was first purified with 1% ethyl acetate in hexane, followed by TES group deprotection of the coupling product **3h** with TBAF and finally purified with 10% ethyl acetate in hexane in order to separate it from the starting materials. Yield 7%.

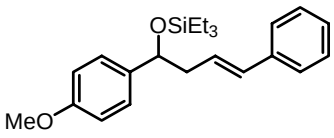
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39 (m, 4H), 7.29–7.35 (m, 3H), 7.22–7.24 (m, 1H),

7.13–7.15 (m, 2H), 5.37 (s, 1H); 5.15 (s, 1H); 4.93 (s, 1H); 3.38 (d, J = 15.5 Hz, 1H); 3.13 (d, J = 15.5 Hz, 1H); 1.24 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.6, 142.0, 139.3, 129.4, 128.7, 128.5, 128.1, 127.0, 126.4, 112.4, 76.7, 39.2.

IR (NaCl, thin film): 3377, 3061, 3028, 2919, 1494, 1453, 1025, 909, 750, 699.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{16}ONa$, 247.1099; found, 247.1101.

Table 1, entry 10 and 11: **2i**: 

The standard procedure was followed (entry 10). Yield: 91%. Isolated as a 95:5 mixture of E and Z isomers, respectively.

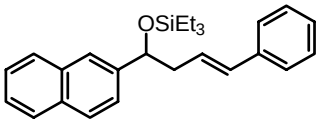
The standard procedure was followed, except that the reaction was carried out in five fold larger scale at reaction was heated at 35 °C and using 9 mL toluene (entry 11). Yield: 90%. Isolated as a 95:5 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.29–7.49 (m, 7H); 7.00 (d, J = 8.6 Hz, 2H); 6.52 (d, J = 15.9 Hz, 1H); 6.35 (dt, J = 7.2, 15.9 Hz, 1H); 4.85 (dd, J = 6.4, 6.4 Hz, 1H); 3.89 (s, 3H); 2.63–2.81 (m, 2H); 1.04 (t, J = 7.8 Hz, 9H); 0.70 (q, J = 7.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.0, 138.1, 137.7, 132.3, 128.7, 127.5, 127.3 127.2, 126.3, 113.7, 75.0, 55.4, 45.1, 7.1, 5.2.

IR (NaCl, thin film): 3027, 2954, 2910, 2875, 1612, 1511, 1414, 1302, 1248, 1171, 1081, 1005, 966, 836, 743, 693.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{23}H_{32}O_2SiNa$, 391.2069; found, 391.2057.

Table 1, entry 12: **2j**: 

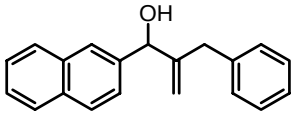
The standard procedure was followed, except that the reaction was heated at 35 °C. Yield: 84%. Isolated as a 95:5 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90–7.96 (m, 4H); 7.67 (d, *J* = 1.6 Hz, 1H); 7.60–7.65 (m, 2H); 7.30–7.59 (m, 5H); 6.54 (d, *J* = 15.9 Hz, 1H); 6.36 (dt, *J* = 7.2, 15.9 Hz, 1H); 5.05 (dd, *J* = 5.4, 7.2 Hz, 1H); 2.74–2.89 (m, 2H); 1.03 (t, *J* = 8.0 Hz, 9H); 0.70 (dq, *J* = 2.9, 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 142.9, 137.9, 133.4, 133.1, 132.4, 128.7, 128.1, 128.1, 127.9, 127.1, 126.2, 126.1, 125.7, 124.6, 75.5, 44.9, 7.0, 5.1.

IR (NaCl, thin film): 3026, 2954, 2910, 2875, 1507, 1496, 1457, 1239, 1123, 1083, 1005, 965, 819, 744.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{32}OSiNa$, 411.2120; found, 411.2167.

Table 1, entry 12: **3j** (TES group deprotected): 

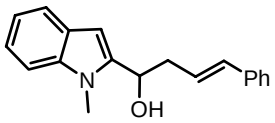
The standard procedure was followed, except that the coupling product was first purified with 1% ethyl acetate in hexane, followed by TES group deprotection of the coupling product **3j** with TBAF and finally purified with 10% ethyl acetate in hexane in order to separate it from the starting materials. Yield 4%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.86–7.88 (m, 4H); 7.48–7.55 (m, 3H); 7.20–7.36 (m, 3H); 7.13–7.16 (m, 2H); 5.43 (s, 1H); 5.32 (s, 1H); 4.97 (s, 1H); 3.41 (d, *J* = 15.6 Hz, 1H), 3.16 (d, *J* = 15.6 Hz, 1H), 2.02 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.5, 149.2, 139.4, 139.3, 133.4, 133.3, 129.4, 128.6, 128.2, 127.9, 126.4, 126.4, 126.2, 126.0, 124.9, 112.8, 77.4, 39.2.

IR (NaCl, thin film): 3365, 3058, 2923, 1495, 1453, 1031, 908, 819, 745, 700.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{20}H_{18}ONa$, 297.1255; found, 297.1260.

Table 1, entry 13: **2k** (TES group deprotected): 

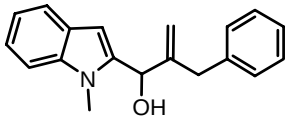
The standard procedure was followed, except that the coupling product was first purified with 10% ethyl acetate in hexane buffered with 1% triethylamine, followed by TES group deprotection of the coupling product **2k** with TBAF and finally purified with 25% ethyl acetate in hexane buffered with 1% triethylamine in order to separate it from the starting materials. Yield: 54%. Isolated as a 95:5 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (d, J = 7.8 Hz, 1H); 7.20–7.41 (m, 8H); 7.14 (t, J = 7.8 Hz, 1H); 6.62 (d, J = 15.8 Hz, 1H); 6.55 (s, 1H); 6.34 (dt, J = 7.3, 15.8 Hz, 1H); 5.01 (m, 1H); 3.86 (s, 3H); 2.93–2.99 (m, 2H); 1.93 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.2, 141.3, 138.1, 137.2, 133.8, 128.7, 127.6, 126.4, 125.7, 122.1, 121.0, 119.8, 109.3, 99.4, 66.9, 40.2, 30.4.

IR (NaCl, thin film): 3640, 3026, 2953, 2910, 2875, 1467, 1339, 1237, 1073, 1006, 966, 744.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{19}ONNa$, 300.1364; found, 300.1365.

Table 1, entry 13: **3k** (TES group deprotected): 

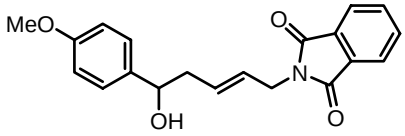
The standard procedure was followed, except that the coupling product was first purified with 10% ethyl acetate in hexane buffered with 1% triethylamine, followed by TES group deprotection of the coupling product **3k** with TBAF and finally purified with 25% ethyl acetate in hexane buffered with 1% triethylamine in order to separate it from the starting materials. Yield 3%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (d, 2H); 7.12–7.38 (m, 10H); 6.49 (s, 1H); 5.38 (s, 1H); 5.31 (s, 1H); 5.14 (s, 1H); 3.70 (s, 3H); 3.54 (d, J = 15.3 Hz, 1H); 3.33 (d, J = 15.3 Hz, 1H); 1.98 (d, J = 5.1Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.7, 139.6, 139.1, 138.4, 129.3, 128.6, 127.3, 126.6, 122.0, 121.0, 119.7, 113.2, 109.3, 101.5, 69.6, 40.2, 30.3.

IR (NaCl, thin film): 3349, 3059, 3027, 2923, 1649, 1601, 1494, 1468, 1453, 1318, 1234, 1030, 968, 907, 751, 737, 700.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{19}NONa$, 300.1364; found, 300.1369.

Table 1, entry 14: **2l** (TES group deprotected): 

The standard procedure was followed, except that the reaction was carried out at 35 °C and the coupling product was first purified with 40% hexane in CH_2Cl_2, followed by TES group deprotection of the coupling product **2l** with TBAF and finally purified with 15% hexane in CH_2Cl_2. Yield: 72%. Isolated as a 83:17 mixture of E and Z isomers, respectively.

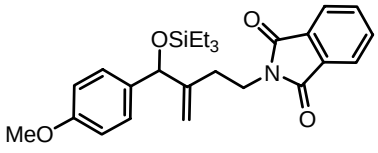
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.86 (dd, *J* = 3.1, 5.4 Hz, 2H); 7.73 (dd, *J* = 3.1, 5.4 Hz, 2H); 7.25 (d, *J* = 8.7 Hz, 2H); 6.84 (d, *J* = 8.7 Hz, 2H); 5.73(dt, *J* = 6.0, 15.4 Hz, 1H); 5.62 (dt, *J* = 6.0, 15.4 Hz, 1H); 4.68 (dd, *J* = 6.4, 6.4 Hz, 1H); 4.25–4.33 (m, 2H); 3.78 (s, 3H); 2.46 (m, 2H), 2.09 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 168.2, 159.1, 136.1, 134.1, 132.3, 130.8, 127.2, 127.1, 123.5, 113.9, 73.1, 55.4, 42.3, 39.7.

IR (NaCl, thin film): 3466, 2929, 1770, 1711, 1611, 1512, 1395, 1249, 1174, 1034, 833, 720.

HRMS–ESI (m/z): $[M–OH]^+$ calcd for $C_{20}H_{18}O_3N$, 320.1287; found, 320.1297.

Table 1, entry 14: **3l**:



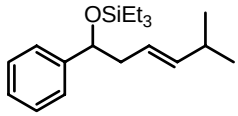
The standard procedure was followed, except that the reaction was carried out at 35 °C and the coupling product was purified with 40% hexane in CH_2Cl_2. Yield 4%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.81 (dd, 2H); 7.70 (dd, 2H); 7.26 (d, *J* = 8.7 Hz, 2H); 6.79 (d, *J* = 8.7 Hz, 2H); 5.27 (s, 1H); 5.15 (s, 1H); 4.99 (s, 1H); 3.66–3.86 (m, 2H); 3.78 (s, 3H); 2.33–2.40 (m, 1H); 2.16–2.23 (m, 1H); 0.90 (t, *J* = 7.9 Hz, 9H); 0.57 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 168.4, 158.8, 148.6, 135.2, 134.0, 132.3, 127.7, 123.3, 113.5, 111.8, 77.6, 55.3, 37.2, 29.8, 7.0, 5.0.

IR (NaCl, thin film): 2954, 2876, 1773, 1715, 1511, 1467, 1431, 1395, 1354, 1247, 1078, 952, 719.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{33}O_4SiNa$, 474.2066; found, 474.2071.

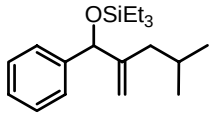
Table 1, entry 15: **2m**[1] 

The standard procedure was followed. Yield: 78%. Isolated as a 81:29 mixture of E and Z isomers, respectively.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.30 (m, 5H); 5.40 (m, 2H); 4.63 (dd, *J* = 5.3, 7.3 Hz, 1H); 2.41 (quintet, *J* = 5.3 Hz, 1H); 2.30 (quintet, *J* = 5.5 Hz, 1H); 2.24 (septet, *J* = 6.7 Hz, 1H); 2.00 (m, 2H); 0.95 (dd, *J* = 6.7, 7.6 Hz, 6H); 0.89 (t, *J* = 7.9 Hz, 9H); 0.62 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 145.6, 140.2, 128.1, 127.0, 126.1, 123.7, 75.7, 44.5, 31.3, 22.6, 7.01, 5.0.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{32}OSi$, 327.212; found, 327.212.

Table 1, entry 15: **3m**[1] 

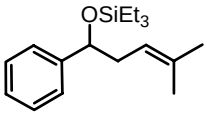
The standard procedure was followed. Yield: 5%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 (d, *J* = 7.8 Hz, 2H); 7.32 (t, *J* = 7.1 Hz, 2H); 7.25 (t, *J* = 7.1, 1H); 5.30 (brs, 1H); 5.12 (brs, 1H); 4.87 (brs, 1H); 1.65–1.85 (m, 3H); 0.93 (t, *J* = 8.0 Hz, 9H); 0.84 (d, *J* = 6.4 Hz, 3H); 0.82 (d, *J* = 6.2 Hz, 3H); 0.60 (dq, *J* = 1.3, 8.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.5, 143.7, 128.1, 127.1, 126.7, 110.7, 77.9, 41.1, 26.3, 23.0, 22.6, 7.0, 5.0.

IR (NaCl, thin film): 2955, 2877, 1646, 1454, 1088, 1067, 743.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{32}OSi$, 327.211; found, 327.212.

Table 1, entry 16: **2n**: 

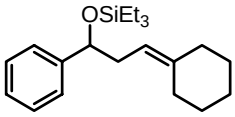
The standard procedure was followed. Yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.27–7.43 (m, 5H); 5.19–5.24 (m, 1H); 4.68 (dd, *J* = 5.8, 7.2 Hz, 1H); 2.36–2.54 (m, 2H); 1.74 (d, *J* = 0.8 Hz, 3H); 1.58 (s, 3H); 0.95 (t, *J* = 7.8 Hz 9H); 0.60 (dq, *J* = 3.4, 7.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.8, 133.6, 128.1, 127.0, 126.1, 121.0, 75.4, 40.0, 26.0, 18.0, 7.0, 5.0.

IR (NaCl, thin film): 3028, 2956, 2877, 2912, 1454, 1414, 1377, 1239, 1089, 1069, 1005, 941, 744, 699.

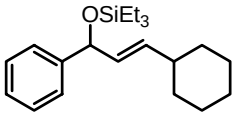
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{30}OSiNa$, 313.1964; found, 313.1966.

Table 1, entry 17: **2o**: 

The standard procedure was followed. Isolated as a mixture of **2o** and **3o**.

2o: Yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24–7.42 (m, 5H); 5.14 (t, *J* = 7.4 Hz, 1H); 4.66 (t, *J* = 6.4 Hz, 1H); 2.37–2.52 (m, 2H); 2.00–2.11 (m, 3H); 1.50–1.78 (m, 3H); 1.03–1.48 (m, 4H); 0.94 (t, *J* = 7.9 Hz, 9H); 0.59 (dq, *J* = 2.8, 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.7, 141.6, 128.0, 127.0, 126.2, 117.5, 75.6, 39.0, 37.5, 29.0, 28.7, 27.8, 27.1, 7.0, 5.0.

Table 1, entry 17: **3o**: 

The standard procedure was followed. Isolated as a mixture of **2o** and **3o**.

3o: Yield 25%.

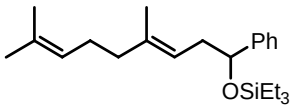
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24–7.42 (m, 5H); 5.69 (dd, *J* = 6.5, 15.4 Hz, 1H); 5.56 (dd, *J* = 7.0, 15.4 Hz, 1H); 5.18 (d, *J* = 7.0 Hz, 1H); 2.00–2.11 (m, 3H); 1.63–1.78 (m, 1H); 1.50–1.78 (m, 3H); 1.03–1.48 (m, 4H); 1.00 (t, *J* = 8.0 Hz, 9H); 0.67 (dq, *J* = 2.3, 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.8, 136.9, 131.2, 128.2, 126.9, 126.1, 75.9, 40.4, 33.0, 32.9, 26.4, 26.2, 7.1, 5.2.

IR (NaCl, thin film): 2954, 2928, 2876, 2853, 1449, 1414, 1238, 1086, 1067, 1007, 969, 829, 744, 699.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{21}H_{34}OSiNa$, 353.2277; found, 353.2267.

Scheme 1: **2p**:



The standard procedure was followed. Yield: 75%. Isolated as a 71:29 mixture of E and Z isomers, respectively.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25–7.36 (m, 5H); 5.18–5.20 (m, 1H); 5.12–5.12 (m, 1H); 4.64–4.68 (m, 1H); 2.37–2.48 (m, 2H); 2.01–2.10 (m, 4H); 1.73 (s, 4H); 1.64 (s, 3H); 1.55 (s, 2H); 0.92 (t, *J* = 6.9 Hz, 9H); 0.57 (dq, *J* = 3.0, 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.8, 145.8, 137.2, 137.1, 131.7, 131.5, 128.1, 128.0, 127.0, 127.0, 126.1, 126.1, 124.6, 124.5, 121.8, 120.7, 75.5, 75.3, 40.0, 39.8, 39.7, 32.3, 26.8, 26.7, 25.9, 25.9, 23.6, 17.8, 17.8, 16.3, 7.0, 7.0, 5.0, 5.0.

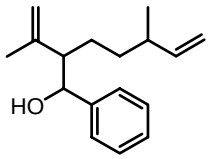
IR (NaCl, thin film): 2955, 2876, 1454, 1376, 1239, 1088, 1068, 1006, 829, 743, 700.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $C_{23}H_{28}OSiNa$, 381.2590; found, 381.2583.

Procedure for the preparation of 4[3]

β–Citronellene (0.5 mmol) in anhydrous CH_2Cl_2 (5 mL) was added Me_2AlCl (1.0 M in hexane, 1.1 mL) at 0 °C and stirred at room temperature for 24 hrs. The reaction was quenched by dilution with ether followed by slow addition of water until gas evolution ceased. The organic layer was separated, and the aqueous layer was extracted with ether twice. The combined organic layers were washed with brine, dried and evaporated in vacuo. Purification via flash chromatography on silica gel afforded the coupling product.

Scheme 1: **4**:



Yield: 40%. Isolated as a mixture of diastereomers.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.28–7.39 (m, 5H); 5.45–5.61 (m, 1H); 5.09 (s, 1H); 5.00 (s, 1H); 4.79–4.94 (m, 2H); 4.38 (dd, J = 0.7, 8.5 Hz, 1H); 2.19–2.35 (m, 1H); 1.89–2.05 (m, 1H); 1.73, 1.75 (two s, 3H); 1.67 (brs, 1H); 0.91–1.27 (m, 4H); 0.87, 0.84 (two d, J = 6.8 Hz, 3H).

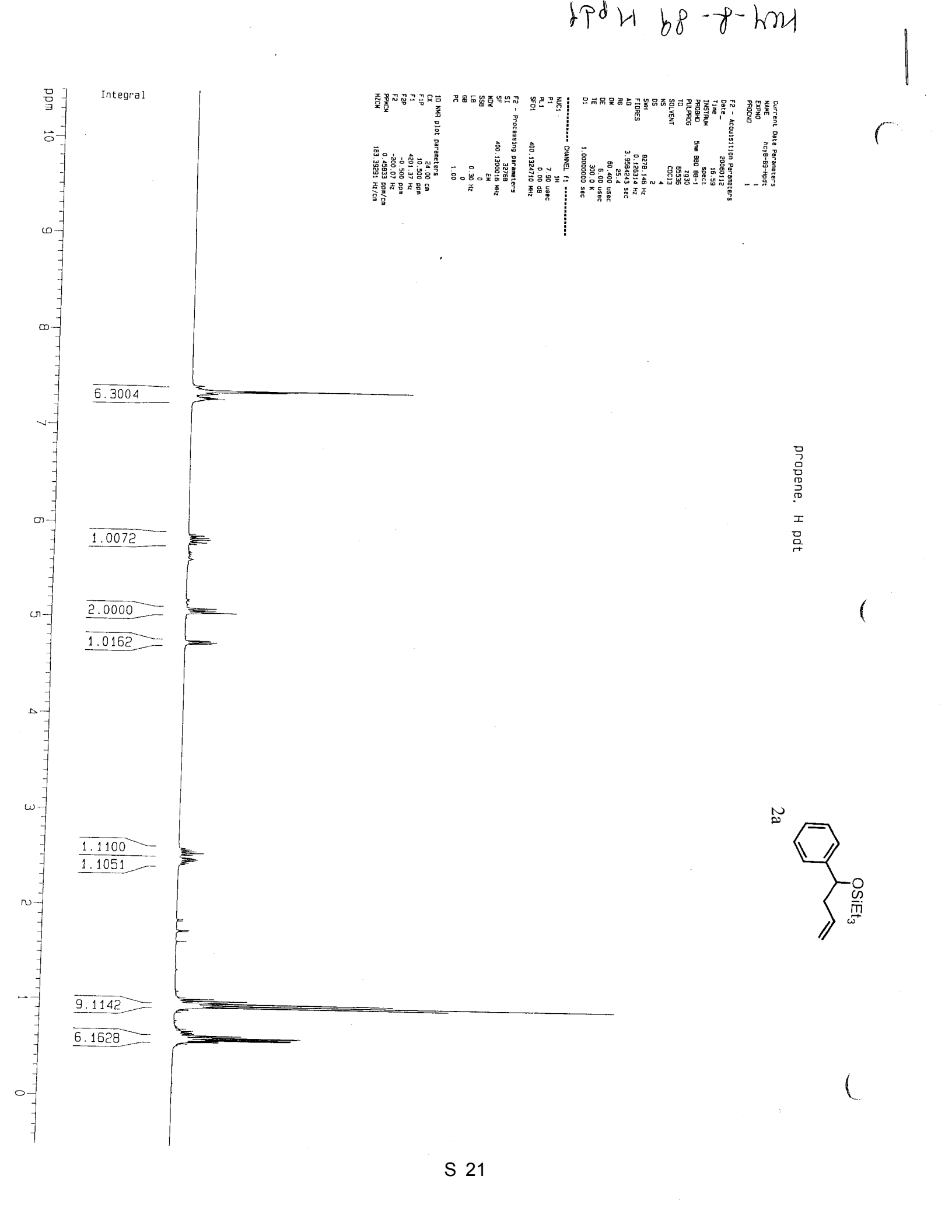
^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.1, 144.3, 142.9, 128.5, 127.9, 127.4, 127.3, 126.0, 116.5, 116.4, 113.1, 112.4, 75.5, 75.4, 56.5, 56.4, 37.8, 37.5, 34.2, 34.2, 31.2, 26.3, 21.0, 19.5, 18.3, 18.1.

References:

1. Ng, S. S.; Jamison, T. F. *J. Am. Chem. Soc.* **2005,** *127*, 14194–14195.

2. E:Z selectivity for the compound **2** was determined by comparing ^{1}H NMR of the TES group deprotected alcohol product with the literature, (a) Padwa, A.; Rodriguez, A.; Tohidi, M.; Fukunaga, T. *J. Am. Chem. Soc.* **1983**, *105*, 933–943. (b) Craig, D.; Smith, A. M. *Tetrahedron Lett.* **1990**, *31*, 2631–2632. (c) Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116,* 6130–6141. (d) Okuma, K.; Tanaka, Y.–i.; Hirabayashi, S. i.; Shioji, K.; Matsuyama, H. *Heterocycles* **1997**, *45*, 1385–1390. (e) Sumida, S. i.; Ohga, M.; Mitani, J.; Nokami, J. *J. Am. Chem. Soc.* **2000**, *122,* 1310–1313. (f) Loh, T. P.; Hu, Q. Y.; Chok, Y. K.; Tan, K. T. *Tetrahedron Lett.* **2001**, *42*, 9277–9280.

3. (a) Snider, B. B.; Rodini, D. J.; Kirk, T. C.; Cordova, R. *J. Am. Chem. Soc.* **1982**, *104,* 555–563. (b) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 464–469.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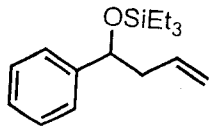
1.0072
2.0000
1.0162
1.1100
1.1051
9.1142
6.1628
propene, H pdt
2a
OSiEt3

propene, H-pdt



2a

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Current Data Parameters
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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time              17.03
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  146
DS                    4
SWH           24875.621 Hz
FIDRES         0.379572 Hz
AQ            1.3173236 sec
RG                 1024
DW               20.100 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

********** CHANNEL f1 **********
NUC1               13C
P1               15.25 usec
PL1               3.00 dB
SFO1        100.6237959 MHz

********** CHANNEL f2 **********
CPDPRG2         waltz16
NUC2               1H
PCPD2           107.50 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127529 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX               24.00 cm
F1P             220.000 ppm
F1             22134.80 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM           9.58333 ppm/cm
HZCM          964.20551 Hz/cm
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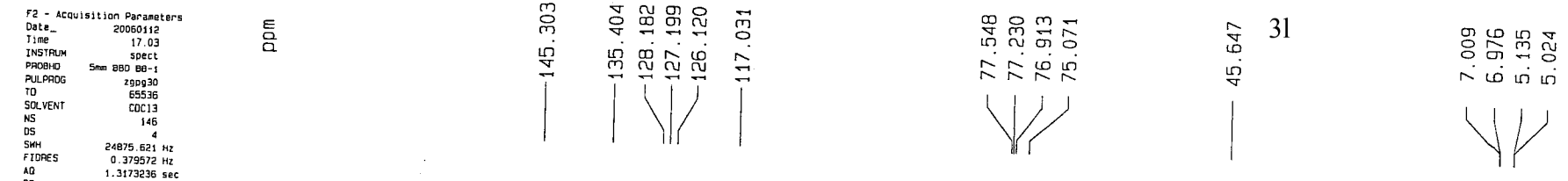
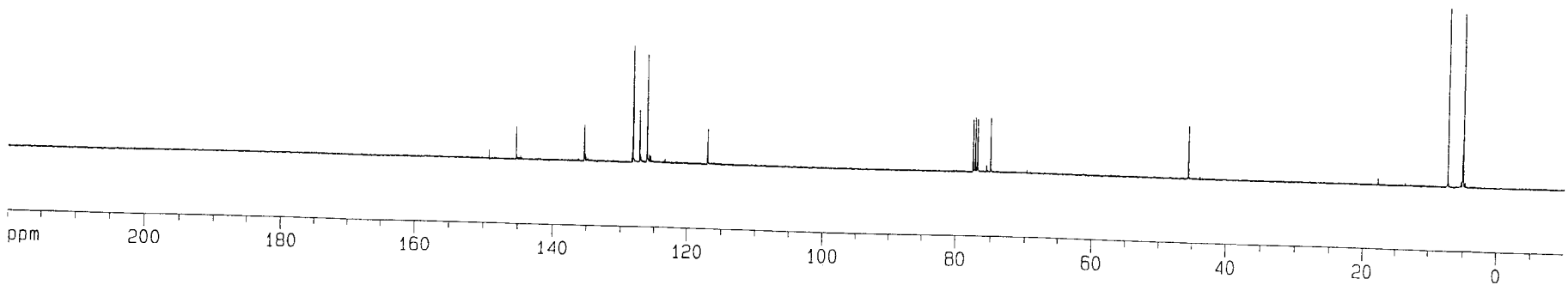
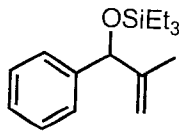




hcy-8-89 Apdt.

propene. A-pdt



3a

```
Current Data Parameters
NAME        hcy8-89-Apdt
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20060112
Time              16.54
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                   4
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG               228.1
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

========== CHANNEL f1 ==========
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI               32768
SF         400.1300016 MHz
WDW                 EM
SSB                  0
LB              0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX              24.00 cm
F1P           10.500 ppm
F1           4201.37 Hz
F2P           -0.500 ppm
F2           -200.07 Hz
PPMCM         0.45833 ppm/cm
HZCM        183.39291 Hz/cm
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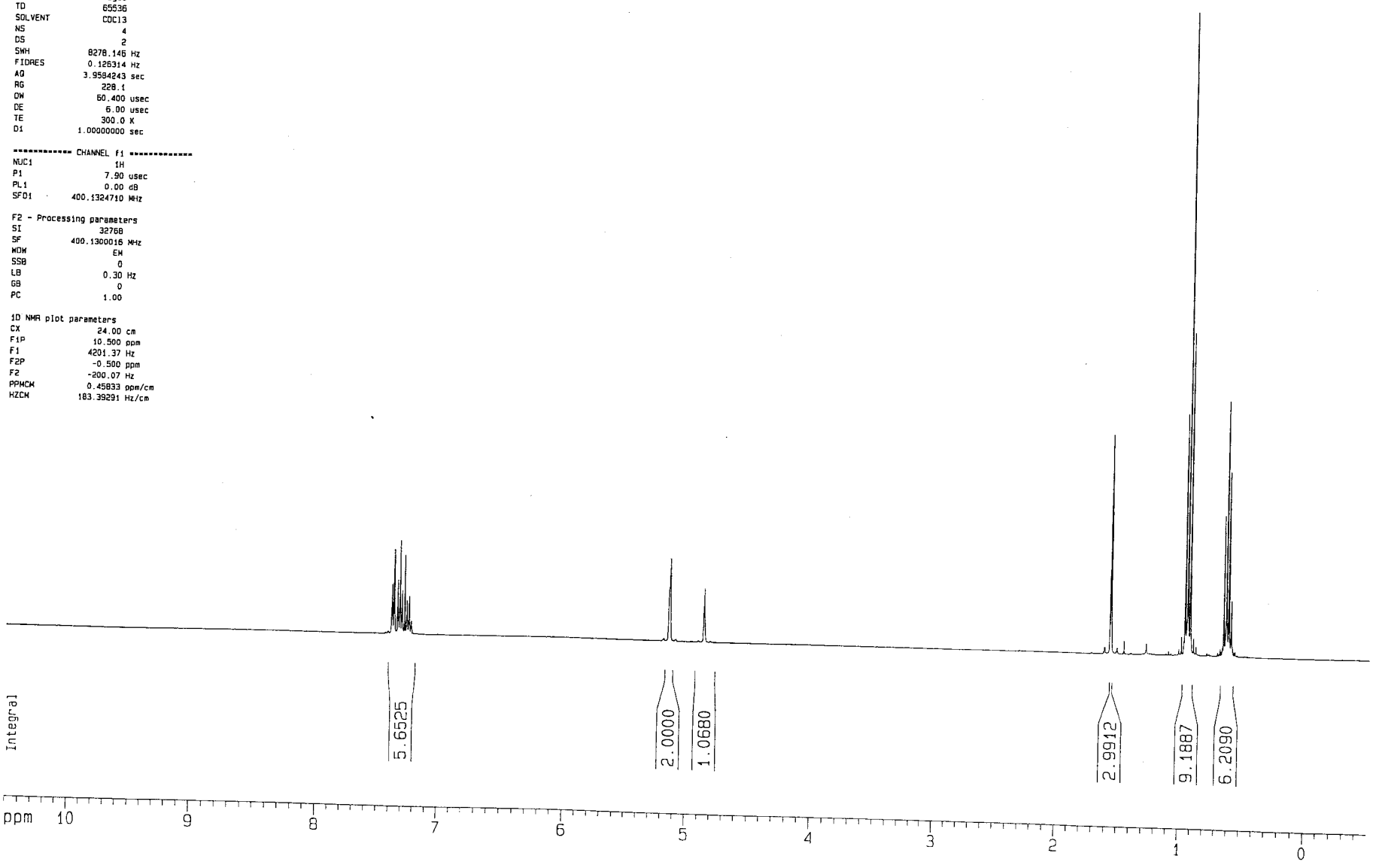

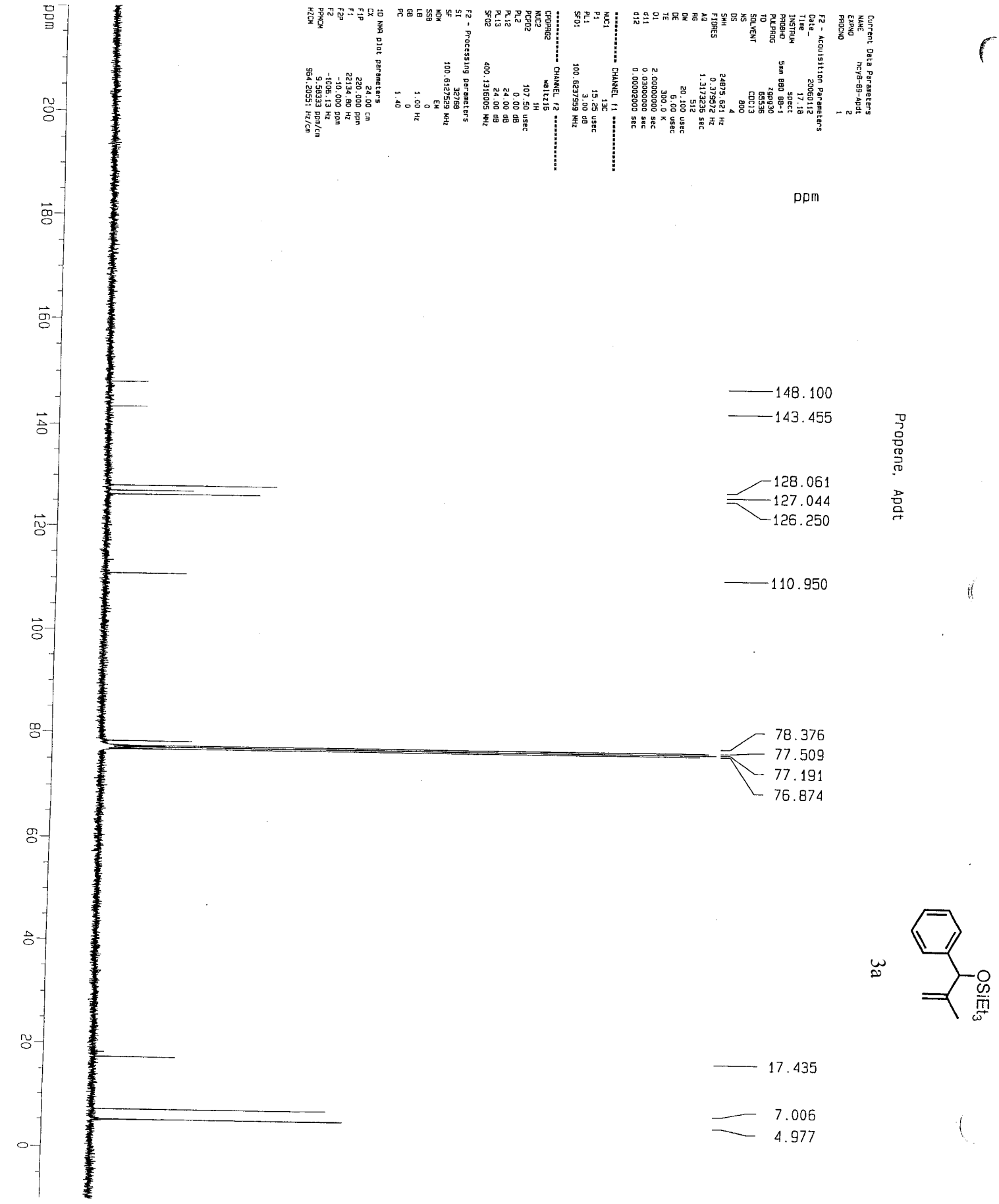
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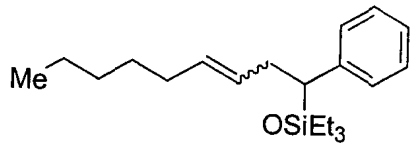
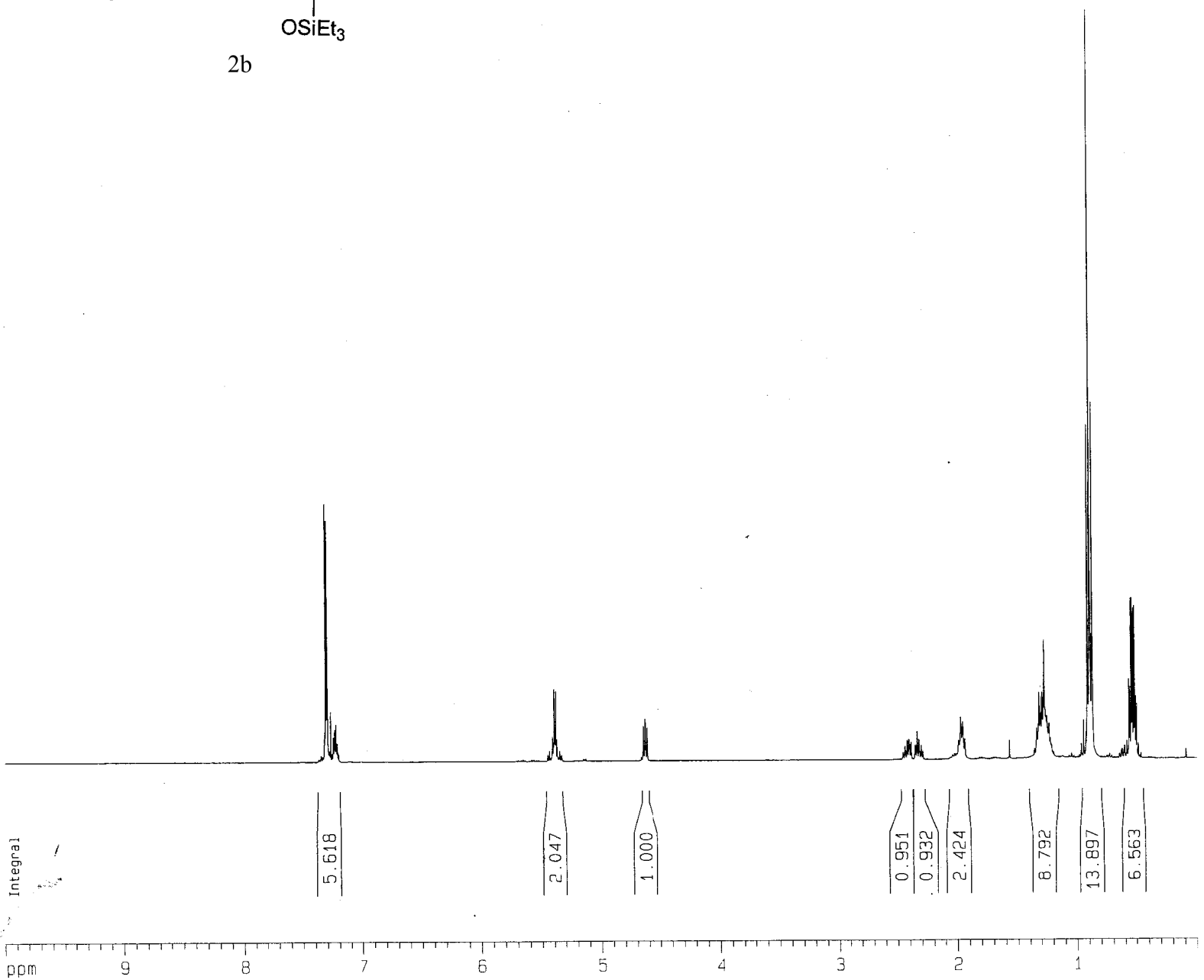
7.006
4.977
Propene, Apdt
3a
OSiEt3
ppm

SN050658 ene product



2b



Current Data Parameters

NAME	SN568ene-H
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050614
Time	19.59
INSTRUM	spect
PROBHD	5 mm GNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	4
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	128
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	9.50 usec
PL1	2.00 dB
SFO1	400.1324710 MHz

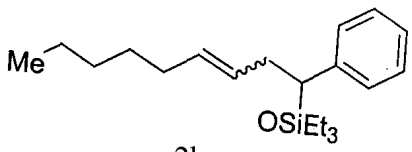
F2 - Processing parameters

SI	32768
SF	400.1300059 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

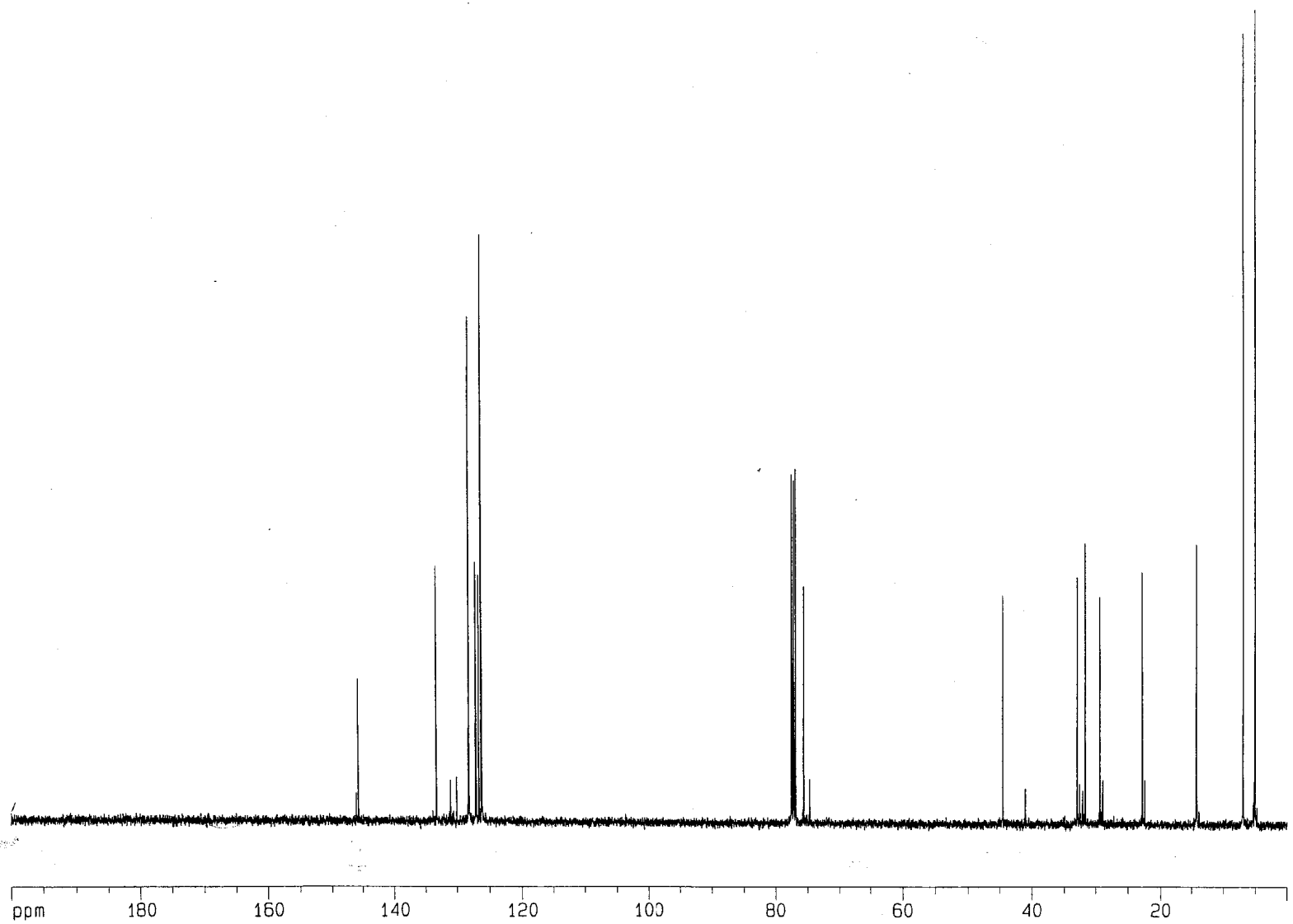
1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	4001.30 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm

octene benzaldehyde TESOTf ene



2b

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Current Data Parameters
NAME        octene-ene-C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20050716
Time              22.11
INSTRUM           spect
PROBHD     5mm BBC BB-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  213
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG               1149.4
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                1H
PCPD2            107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127476 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               200.000 ppm
F1              20122.55 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM          10.00000 ppm/cm
HZCM         1006.12744 Hz/cm
```
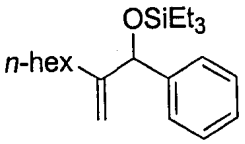
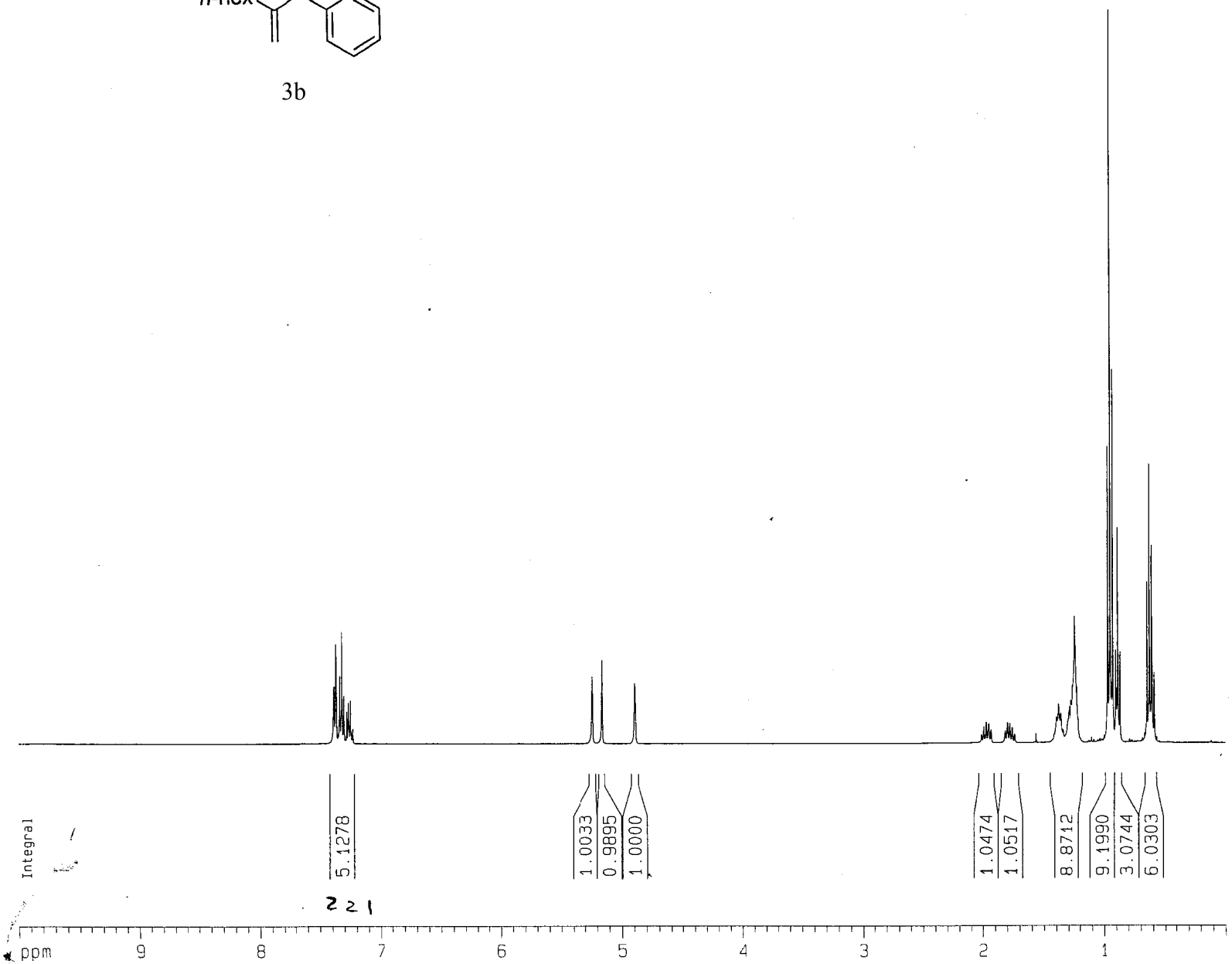

SN050658 allylic alcohol



3b

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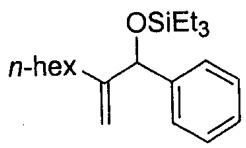
Current Data Parameters
NAME          SN658heck-c
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20050614
Time              19.05
INSTRUM           spect
PROBHD     5 mm QNP  1H
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   4
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  64
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1               9.50 usec
PL1              2.00 dB
SFO1        400.1324710 MHz

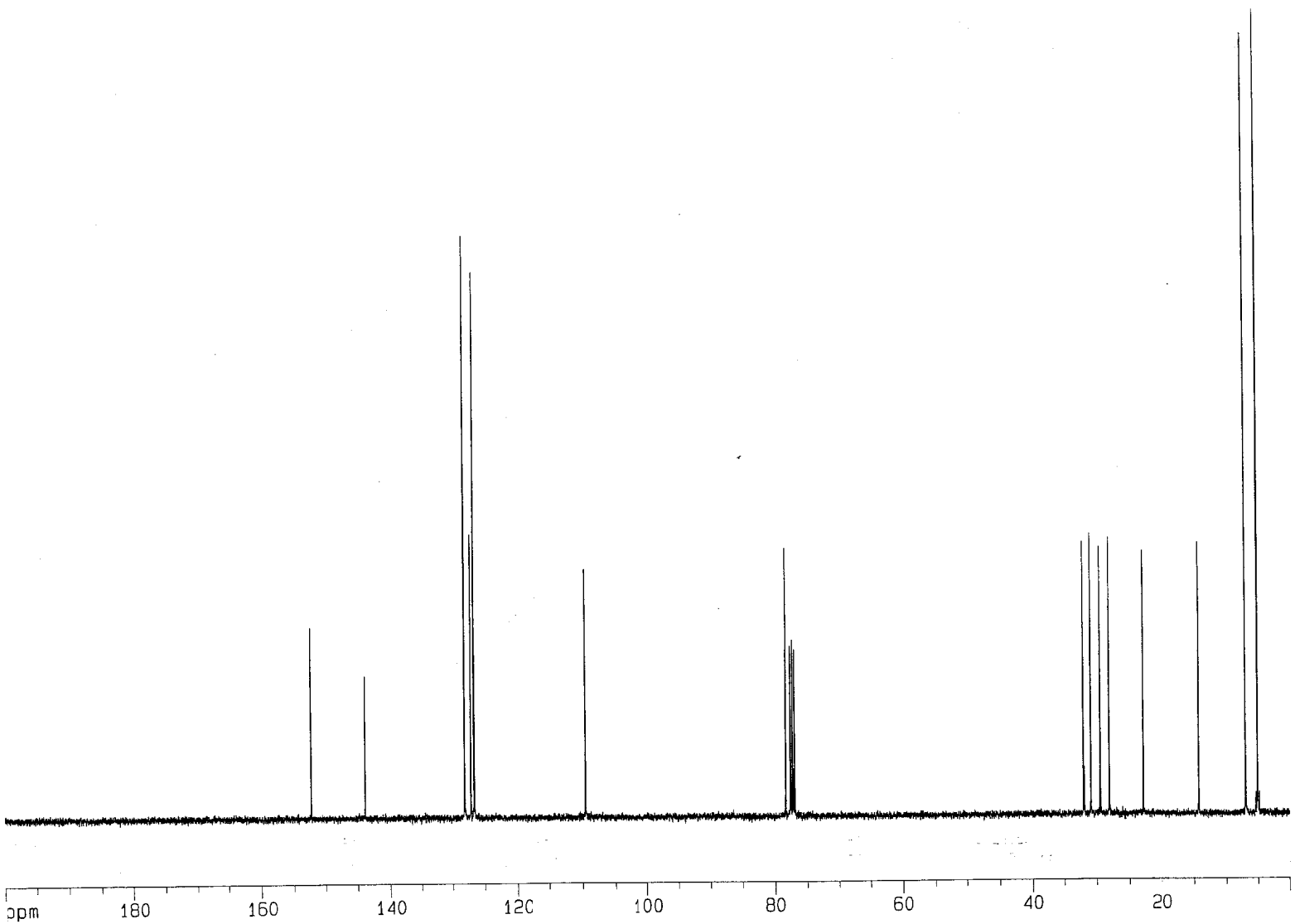
F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00

1D NMR plot parameters
CX              20.00 cm
F1P            10.000 ppm
F1           4001.30 Hz
F2P             0.000 ppm
F2              0.00 Hz
PPMCM        0.50000 ppm/cm
HZCM       200.06500 Hz/cm
```



3b

octene benzaldehyde TESOTf



Current Data Parameters

NAME	octene-al-C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050716
Time	21.50
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	95
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	8192
DW	19.900 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	15.25 usec
PL1	3.00 dB
SFO1	100.6237959 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	107.50 usec
PL2	0.00 dB
PL12	24.00 dB
PL13	24.00 dB
SFO2	400.1316005 MHz

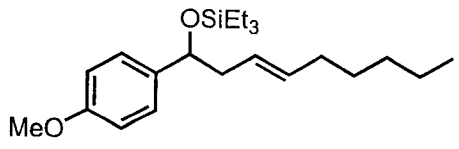
F2 - Processing parameters

SI	32768
SF	100.6127484 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

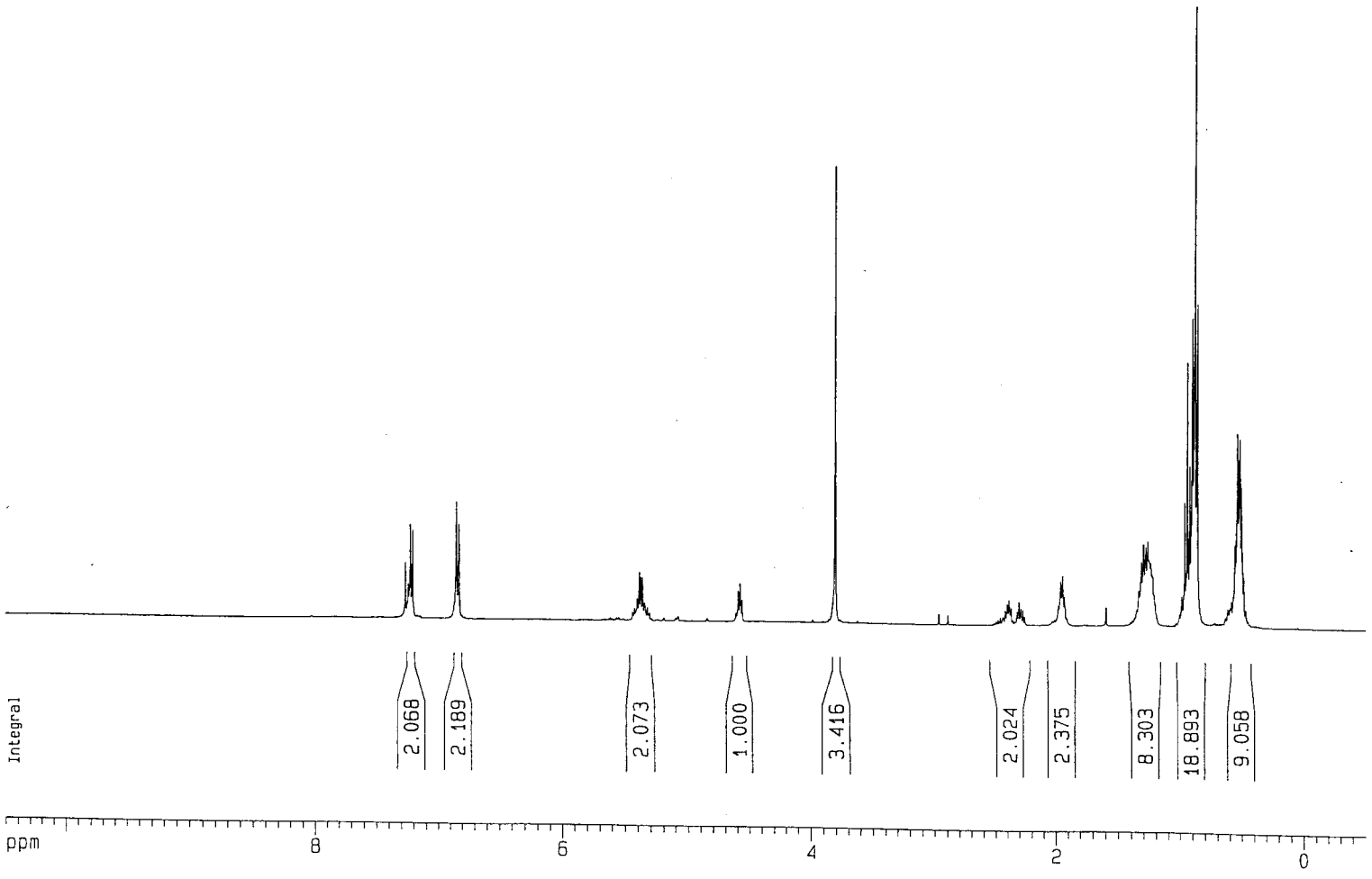
1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	20122.55 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	1006.12744 Hz/cm

OMe



2c



Current Data Parameters

NAME	hcy-8-44p-OMe
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20051028
Time	17.30
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	4
DS	1
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	90.5
DW	60.400 usec
DE	6.00 usec
TE	294.8 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	1H
P1	9.88 usec
PL1	3.00 dB
SFO1	400.1324710 MHz

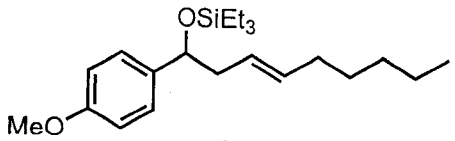
F2 - Processing parameters

SI	32768
SF	400.1300054 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	9.19 cm
F1P	10.500 ppm
F1	4201.37 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.55000 ppm/cm
HZCM	220.07150 Hz/cm

OMe



2c

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76.910
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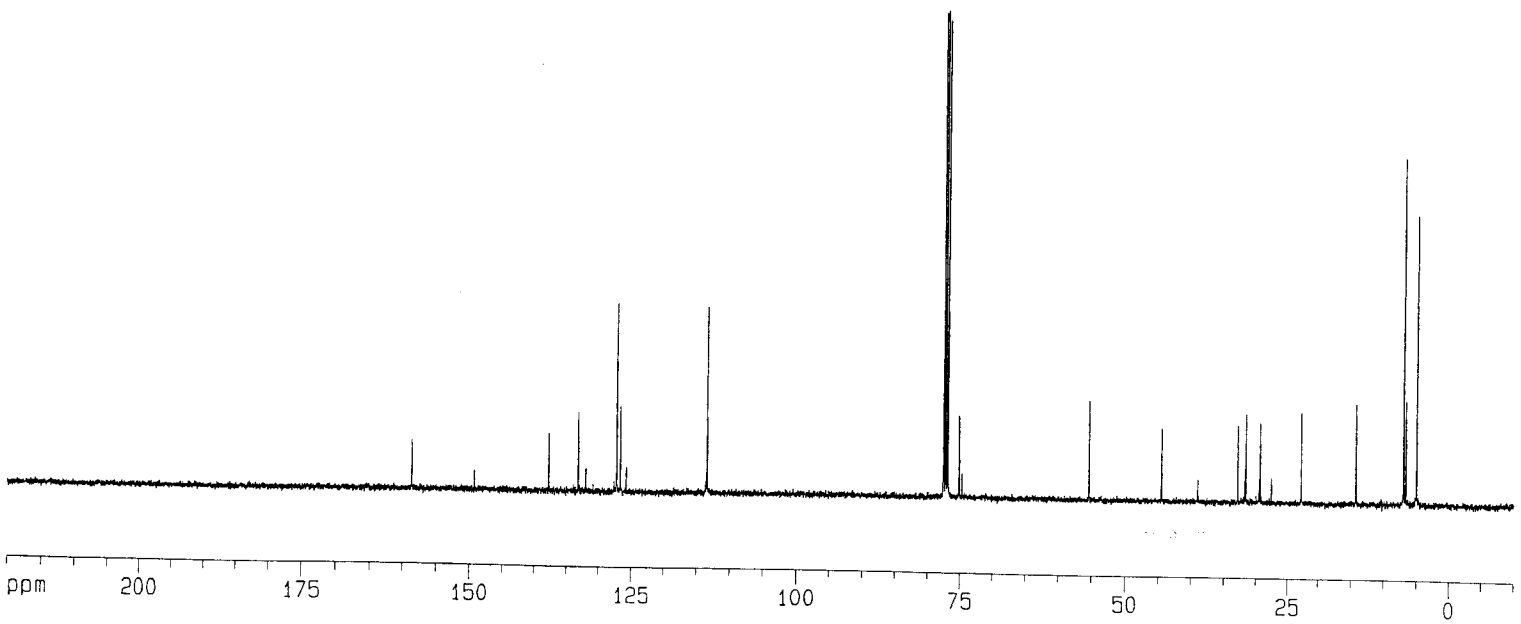
14.273
7.007
6.610
5.024

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Current Data Parameters
NAME            hcy-8-44-OMe
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_           20051028
Time                 16.05
INSTRUM              spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH          24875.621 Hz
FIDRES        0.379572 Hz
AQ            1.3173236 sec
RG                  1024
DW               20.100 usec
DE                6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1               15.25 usec
PL1               3.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2           107.50 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127499 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              220.000 ppm
F1             22134.80 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM          11.50000 ppm/cm
HZCM         1157.04663 Hz/cm
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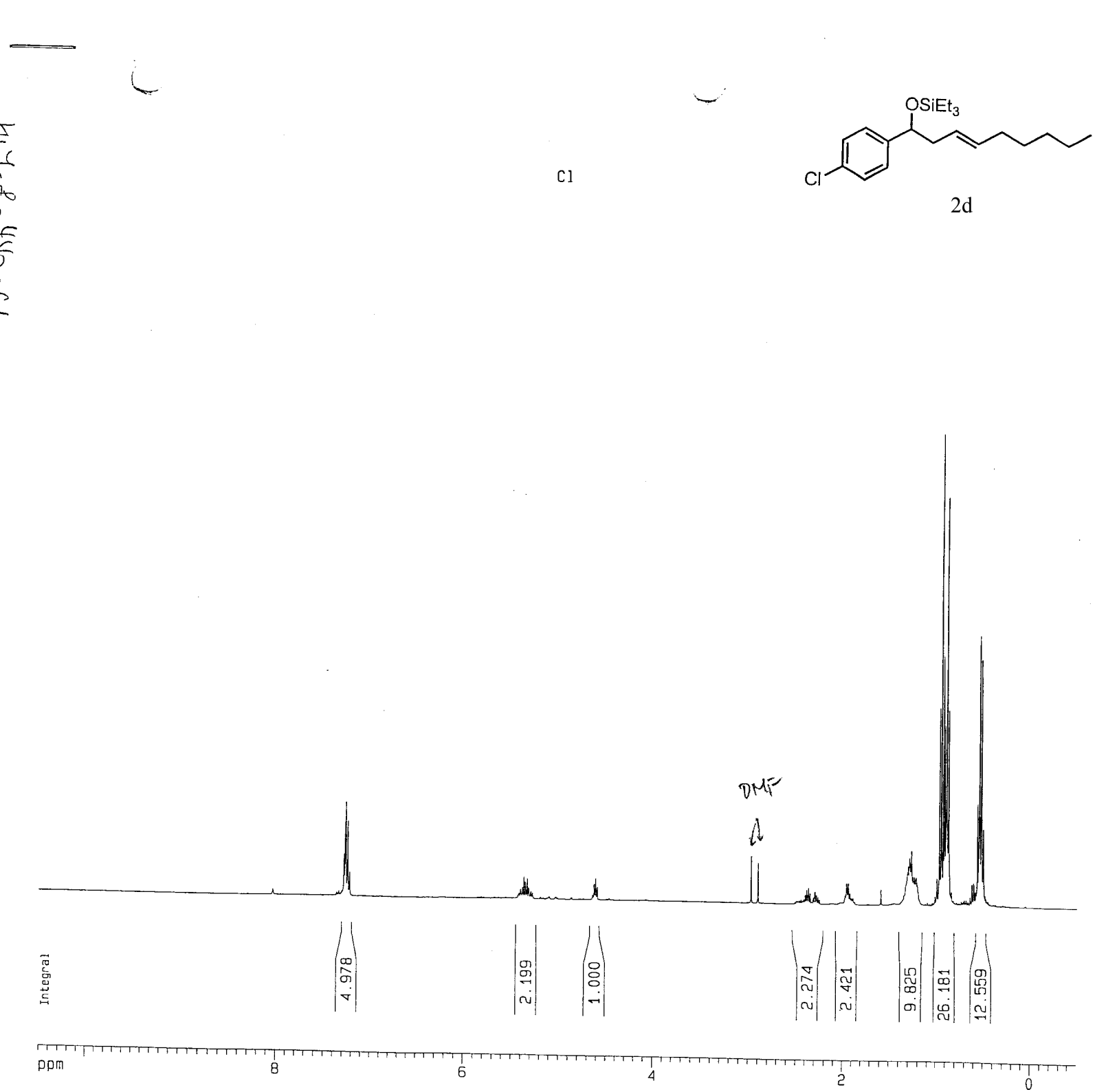


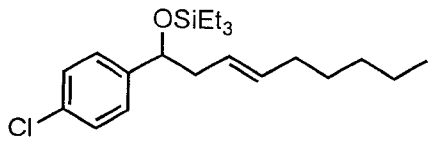
Current Data Parameters
NAME hcy-8-44p-Cl
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051028
Time 17.34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 1
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 294.8 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.88 usec
PL1 3.00 dB
SFO1 400.1324710 MHz

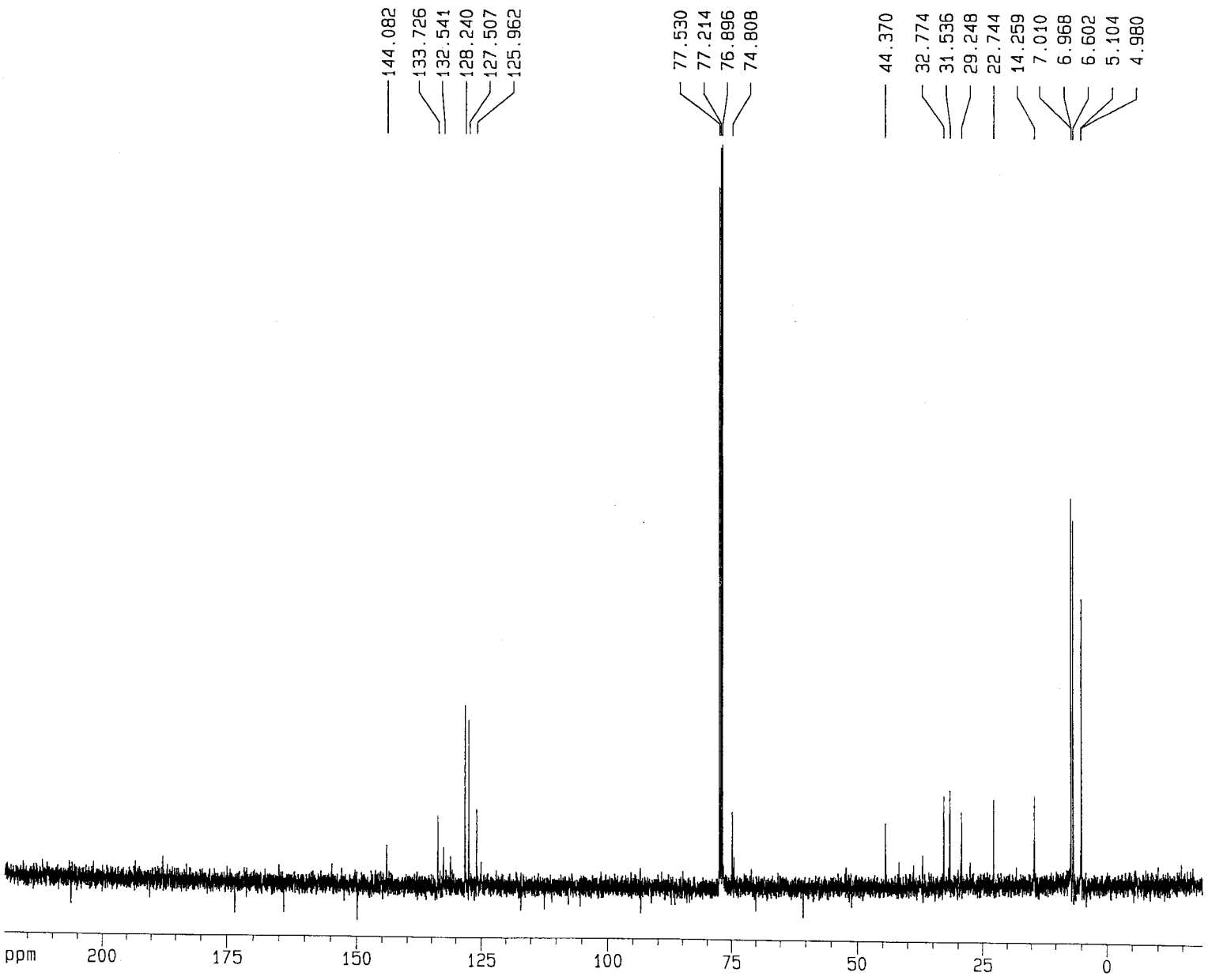
F2 - Processing parameters
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 9.19 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm



Cl

2d




```
Current Data Parameters
NAME          hcy-8-44-Cl
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20051028
Time               12.15
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  800
DS                    4
SWH           23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG               1824.6
DW               20.850 usec
DE                6.00 usec
TE               294.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                3.00 dB
SF01         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             88.01 usec
PL2                3.00 dB
PL12              22.00 dB
PL13              22.00 dB
SF02         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127505 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              219.353 ppm
F1               22069.67 Hz
F2P              -18.995 ppm
F2               -1911.15 Hz
PPMCM            11.91738 ppm/cm
HZCM          1199.04077 Hz/cm
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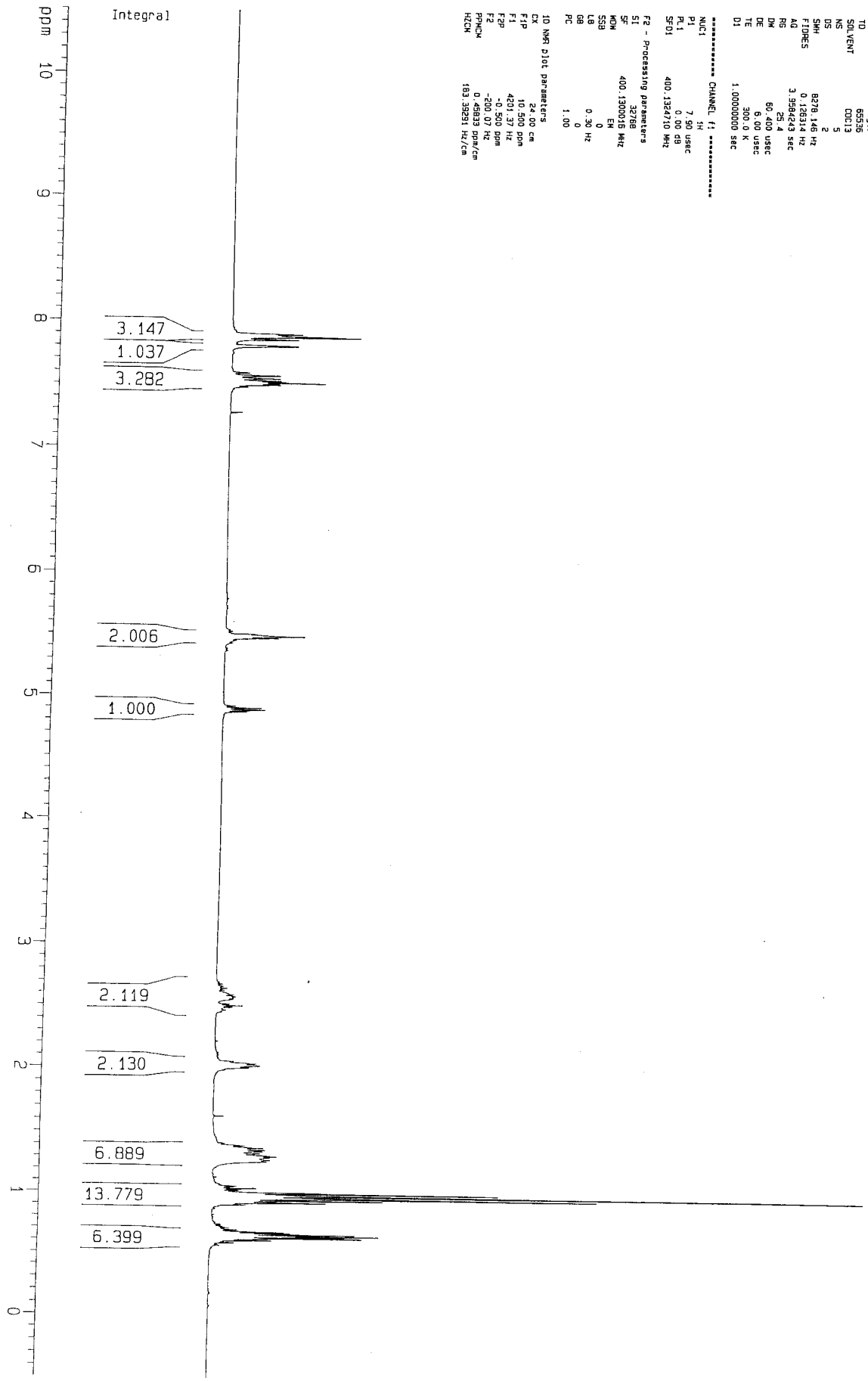


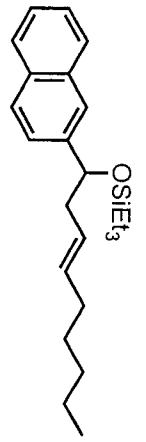
Current Data Parameters
NAME hcje-pht-p
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060109
Time 17.29
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 25.4
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

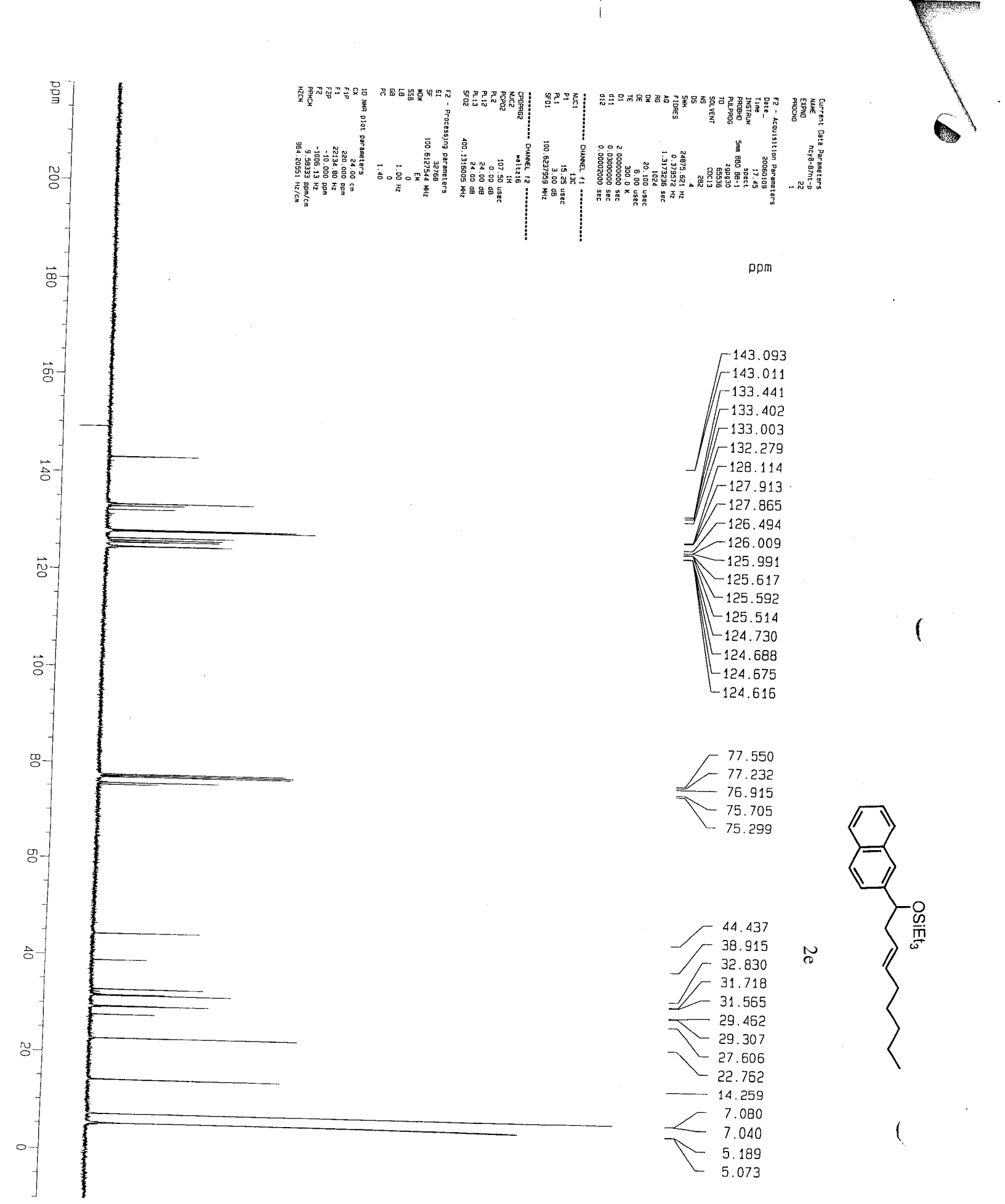
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

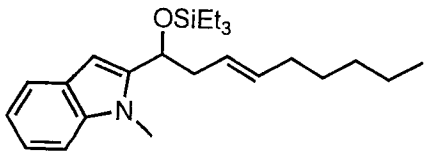
1D NMR plot parameters
CX 24.00 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45833 ppm/cm
HZCM 183.39281 Hz/cm



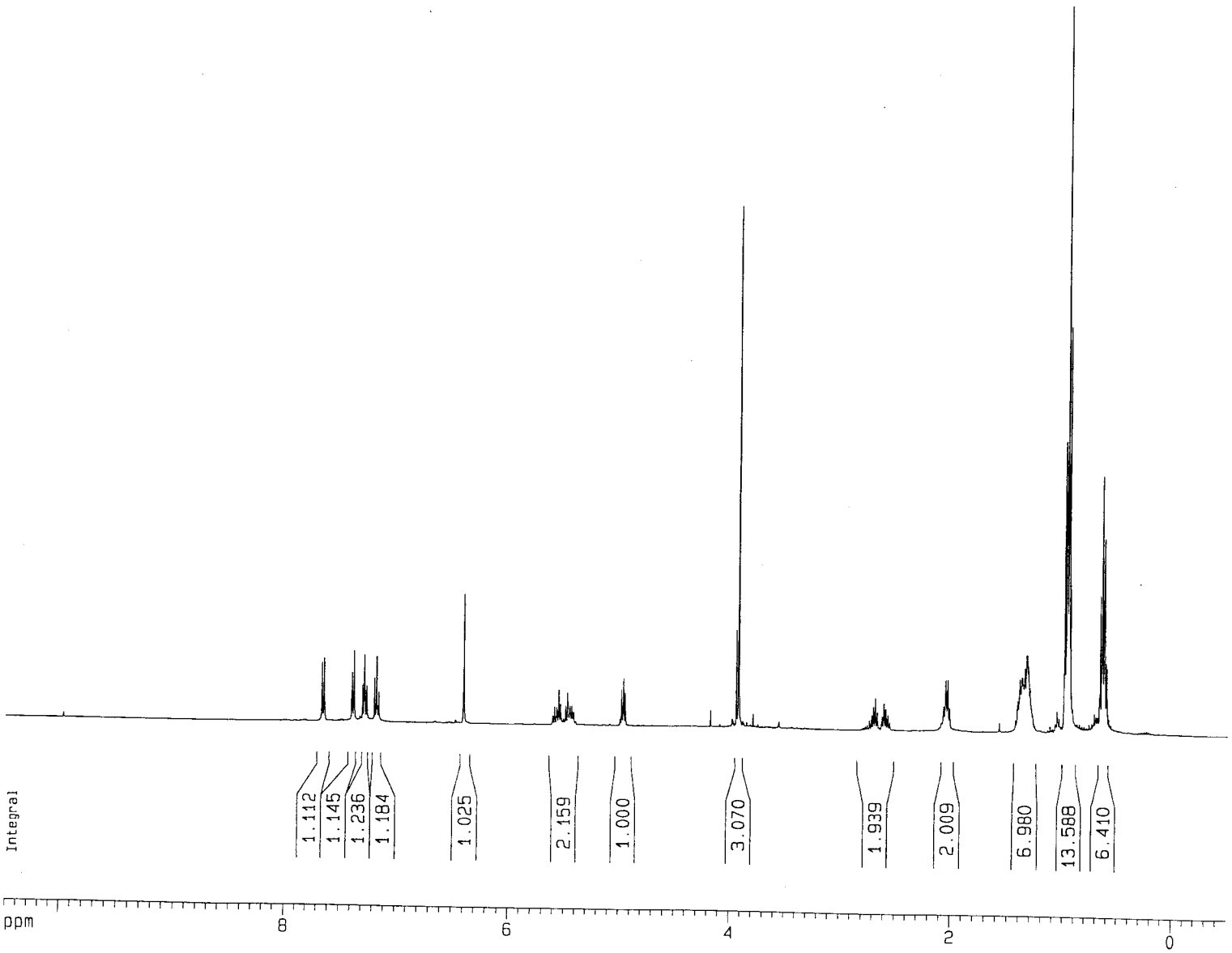
2e


Current Data Parameters
NAME
EXPNO
PROCNO
F2 - Acquisition Parameters
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
d11
d12
CHANNEL f1
NUC1
P1
PL1
SFO1
CHANNEL f2
CPDPRG2
NUC2
PCPD2
PL2
PL12
PL13
SFO2
F2 - Processing parameters
SI
SF
WDW
SSB
LB
GB
PC
1D NMR plot parameters
CX
F1P
F1
F2P
F2
PPMCM
HZCM
ppm
143.093
143.011
133.441
133.402
133.003
132.279
128.114
127.913
127.865
126.494
126.009
125.991
125.617
125.592
125.514
124.730
124.688
124.675
124.616
77.550
77.232
76.915
75.705
75.299
44.437
38.915
32.830
31.718
31.565
29.462
29.307
27.606
22.762
14.259
7.080
7.040
5.189
5.073
OSiEt3
2e

Me-indole-2-CHO, f1



2f



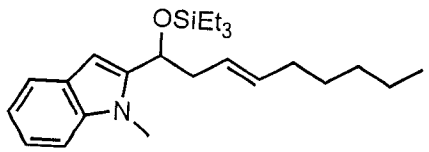
Current Data Parameters
NAME hcy-8-52-ind-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051110
Time 12.10
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 18
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

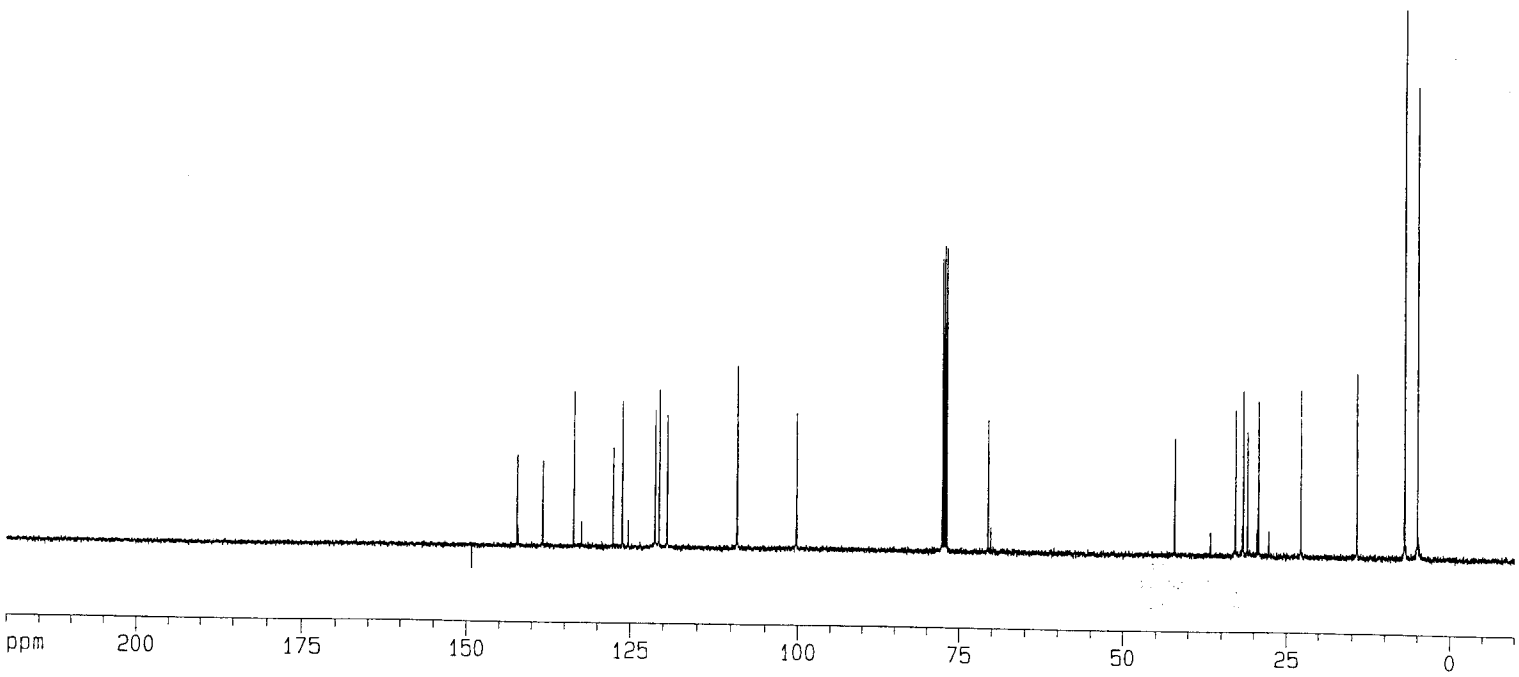
F2 - Processing parameters
SI 32768
SF 400.1300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm



2f

142.280
138.383
133.691
127.670
126.236
121.293
120.677
119.432
109.071
100.181
77.587
77.269
76.952
70.584
42.188
32.818
31.611
31.038
29.295
22.784
14.296
6.999
5.029

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Current Data Parameters
NAME      hcy-8-52-ind-2
EXPNO                 2
PROCNO                1

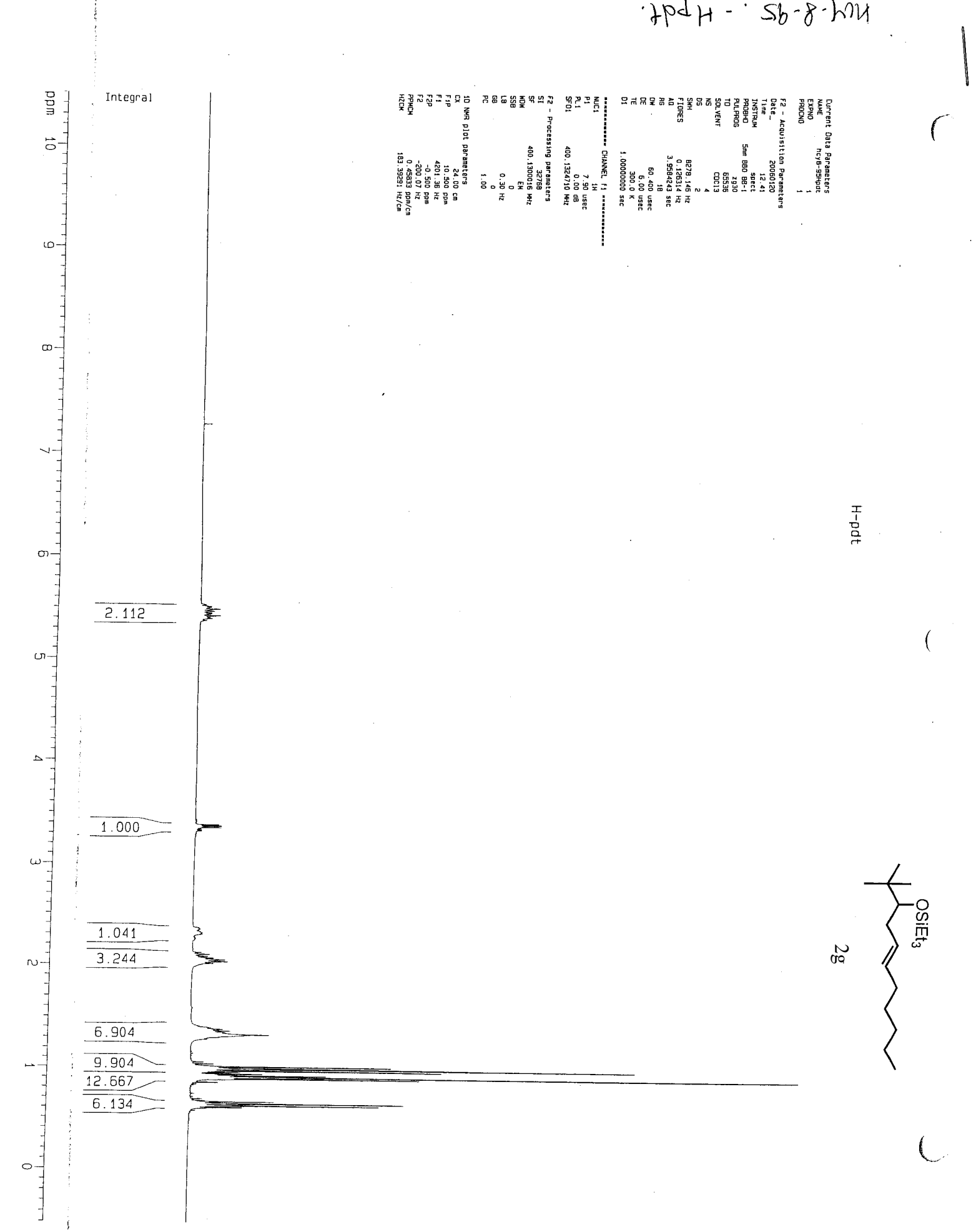
F2 - Acquisition Parameters
Date_          20051110
Time              12.17
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 434
DS                   4
SWH          24875.621 Hz
FIDRES        0.379572 Hz
AQ            1.3173236 sec
RG                1024
DW              20.100 usec
DE               6.00 usec
TE              300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1              15.25 usec
PL1              3.00 dB
SFO1        100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2          107.50 usec
PL2              0.00 dB
PL12            24.00 dB
PL13            24.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127529 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               220.000 ppm
F1              22134.80 Hz
F2P               -10.000 ppm
F2              -1006.13 Hz
PPMCM             11.50000 ppm/cm
HZCM           1157.04663 Hz/cm
```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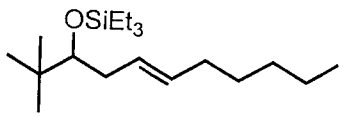
1.041
3.244
6.904
9.904
12.667
6.134
Current Data Parameters
NAME mcy8-95hpdt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060120
Time 12.41
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 18
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 24.00 cm
FIP 10.500 ppm
F1 4201.36 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45833 ppm/cm
HZCM 183.39291 Hz/cm
mcy-8-95 . . Hpdf.
H-pdt
OSiEt3
2g



2g

H-pdt

```
Current Data Parameters
NAME          hcy8-95Hpdt
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20060120
Time              12.55
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  238
DS                    4
SWH           24875.621 Hz
FIDRES         0.379572 Hz
AQ             1.3173236 sec
RG                1149.4
DW               20.100 usec
DE                6.00 usec
TE                300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ============
NUC1                13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

========== CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2           107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127529 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX                24.00 cm
F1P              220.000 ppm
F1             22134.80 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM             9.58333 ppm/cm
HZCM           964.20551 Hz/cm
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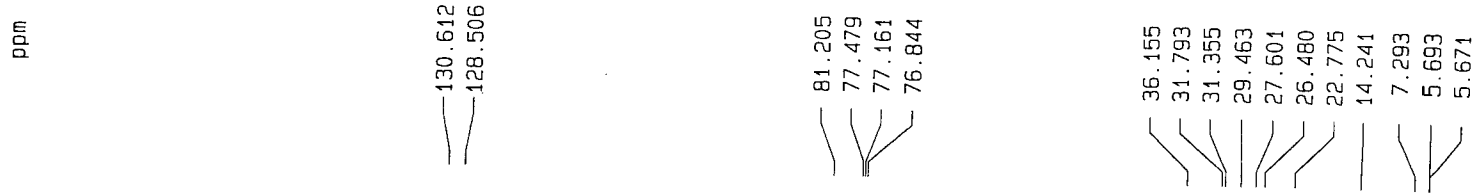

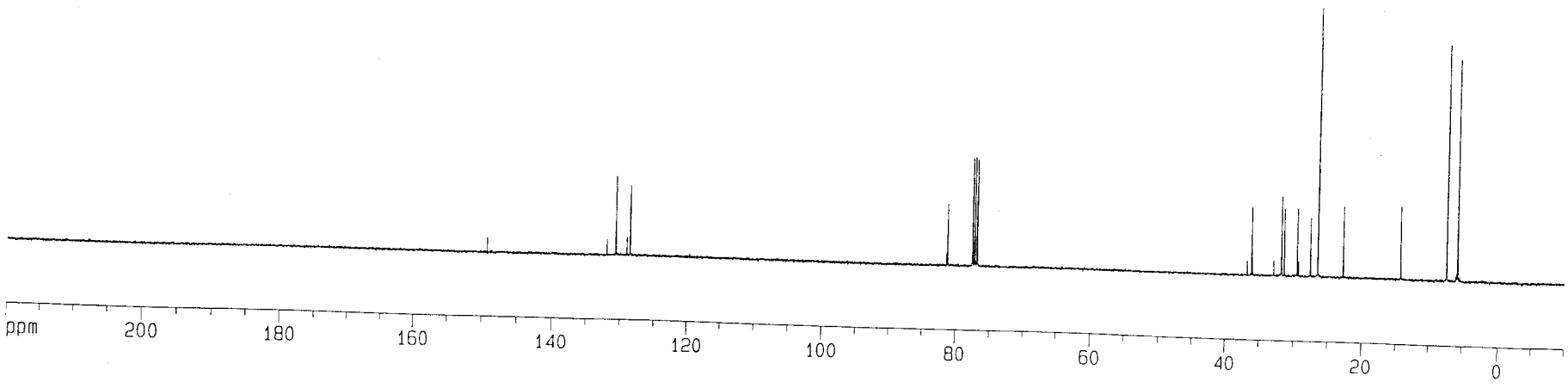

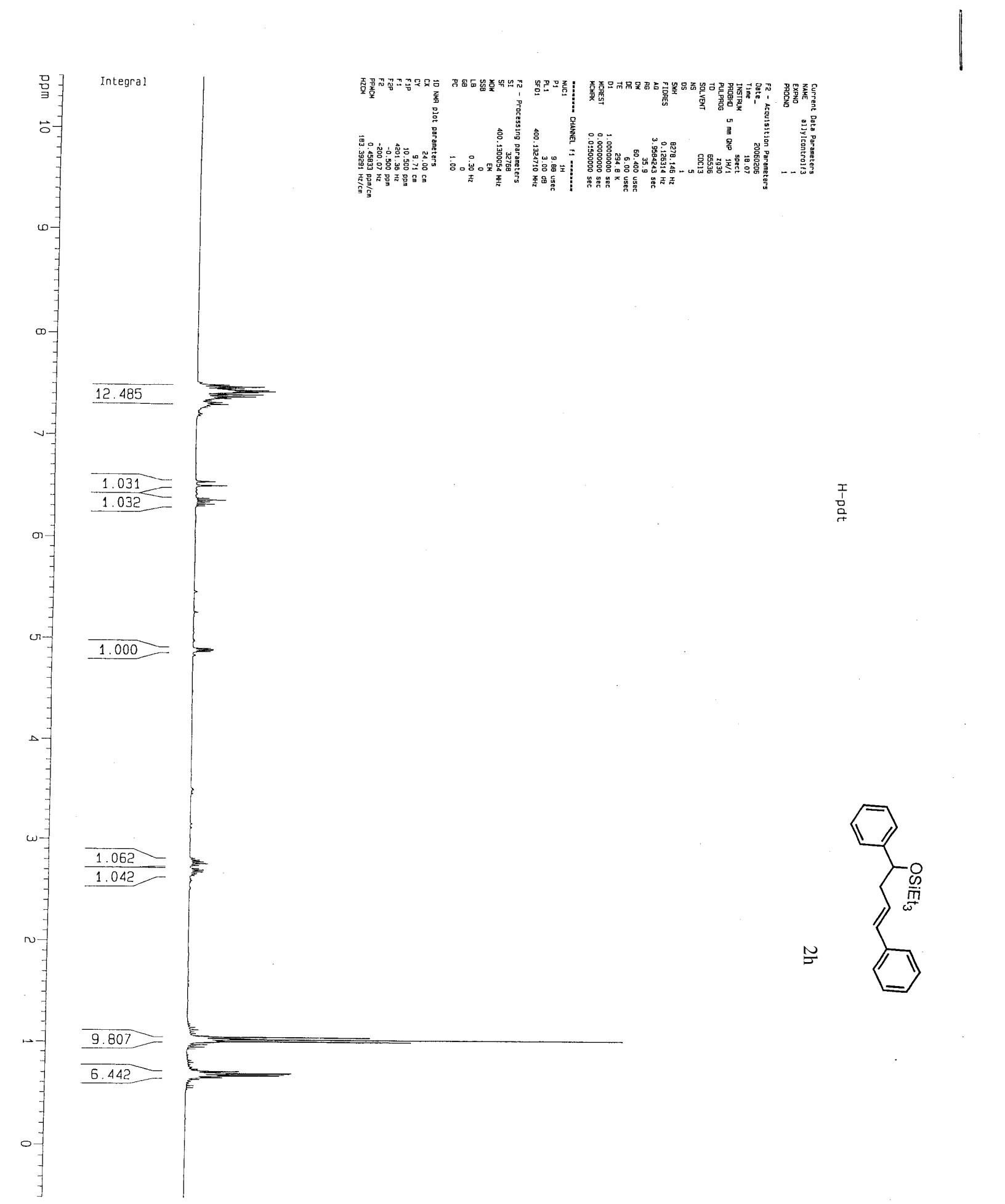
Integral
ppm
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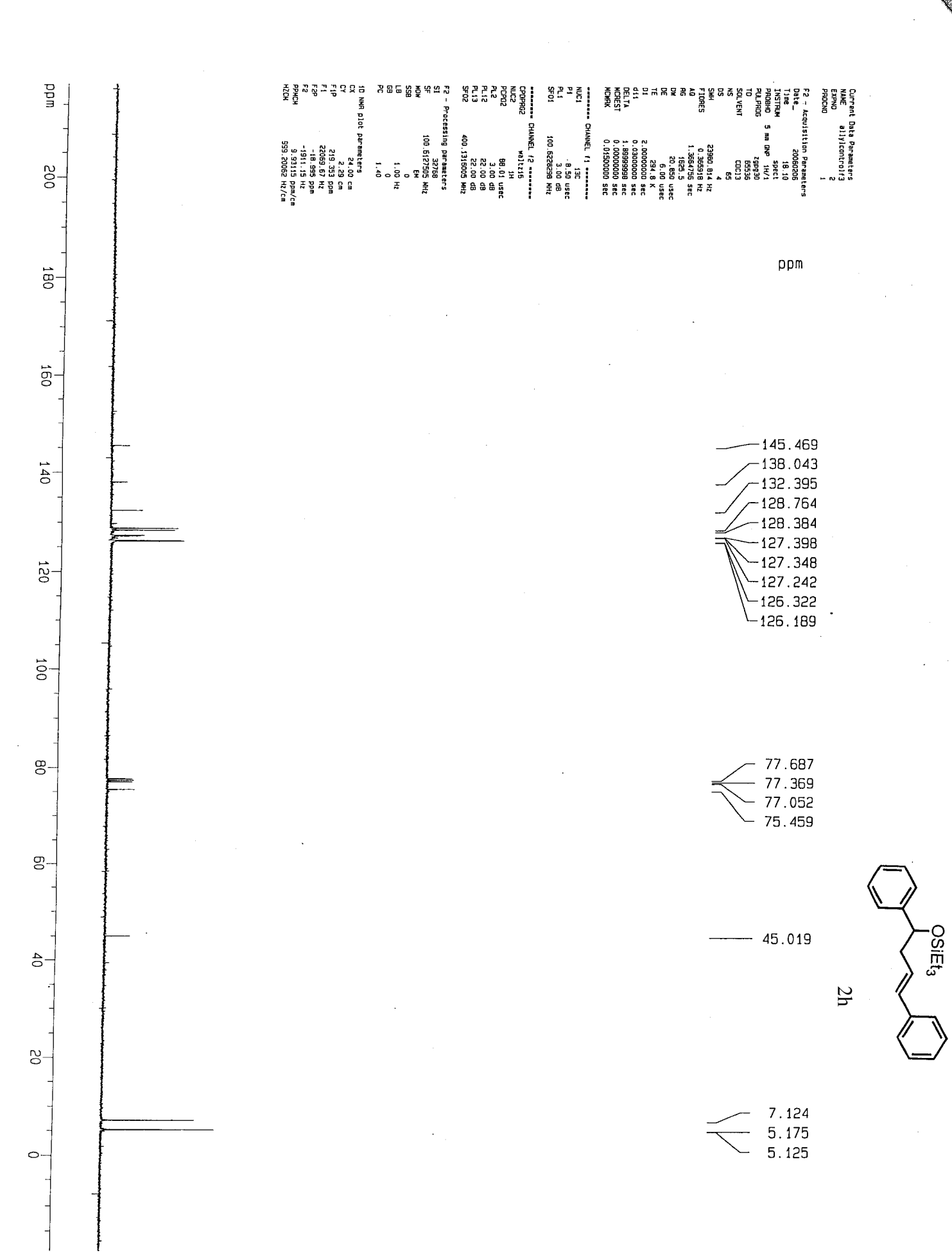
1.031
1.032
1.000
1.062
1.042
9.807
6.442
Current Data Parameters
NAME allylcontrol3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060206
Time 18.07
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 1
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 294.8 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.88 usec
PL1 3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 24.00 cm
CY 9.71 cm
F1P 10.500 ppm
F1 4201.36 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.43683 ppm/cm
HZCM 183.32691 Hz/cm
H-pdt
OSiEt3
2h


Current Data Parameters
NAME allylcontrolf3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060206
Time 18.10
INSTRUM spect
PROBHD 5 mm DNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 65
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664795 sec
RG 1625.5
DW 20.850 usec
DE 6.00 usec
TE 294.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 98.01 usec
PL2 3.00 dB
PL12 22.00 dB
PL13 22.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127505 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
CY 2.29 cm
F1P 219.353 ppm
F1 22069.67 Hz
F2P -18.995 ppm
F2 -1911.15 Hz
PPMCM 9.93115 ppm/cm
HZCM 999.20062 Hz/cm
ppm
145.469
138.043
132.395
128.764
128.384
127.398
127.348
127.242
126.322
126.189
77.687
77.369
77.052
75.459
45.019
7.124
5.175
5.125
OSiEt3
2h
ppm
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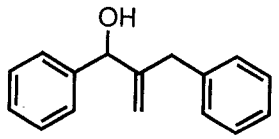
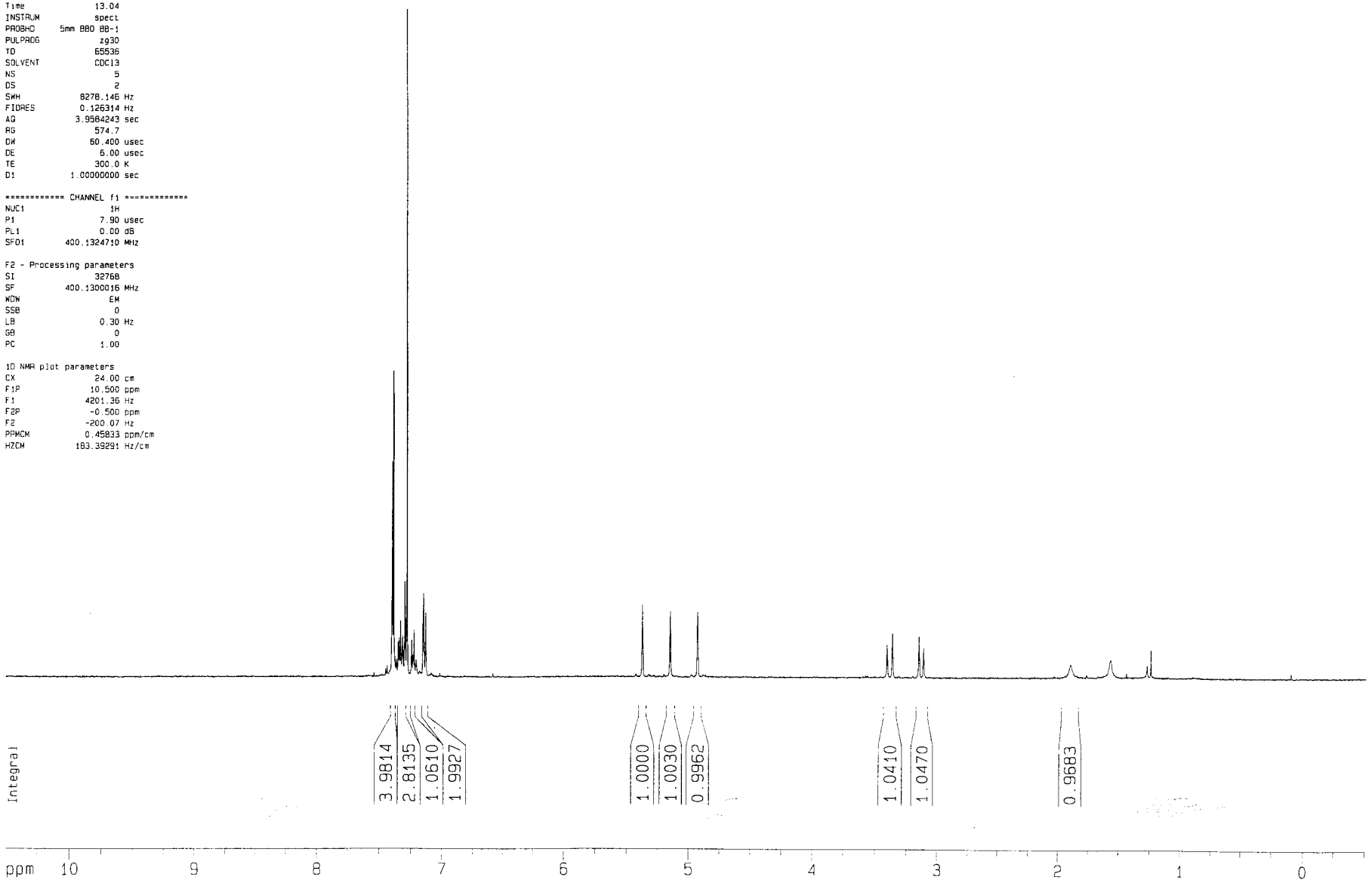
180
160
140
120
100
80
60
40
20
0

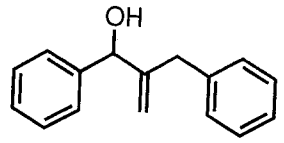


TES deprotection, Apdt

3h (TES group deprotected)

```
Current Data Parameters
NAME      hcy8-32phde-Ap
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060208
Time              13.04
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     5
DS                     2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

========== CHANNEL f1 ============
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300016 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                24.00 cm
F1P              10.500 ppm
F1             4201.36 Hz
F2P               -0.500 ppm
F2              -200.07 Hz
PPMCM           0.45833 ppm/cm
HZCM          183.39291 Hz/cm
```





3h (TES group deprotected)

Current Data Parameters
NAME hcy8-32phde-Ap
EXPNO 2
PROCNO 1

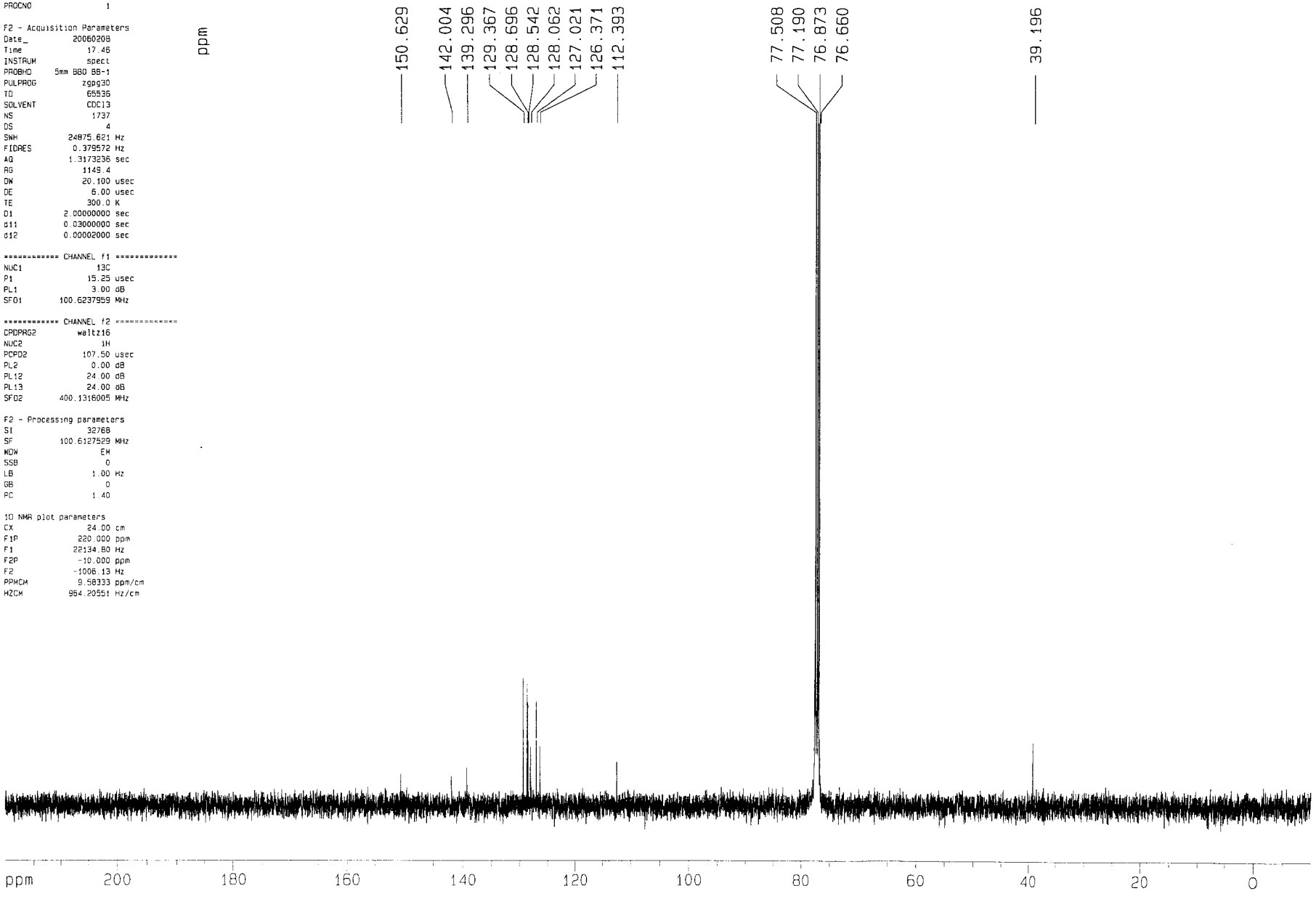
F2 - Acquisition Parameters
Date_ 20060208
Time 17.46
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1737
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1149.4
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz

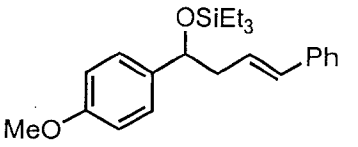
========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20551 Hz/cm

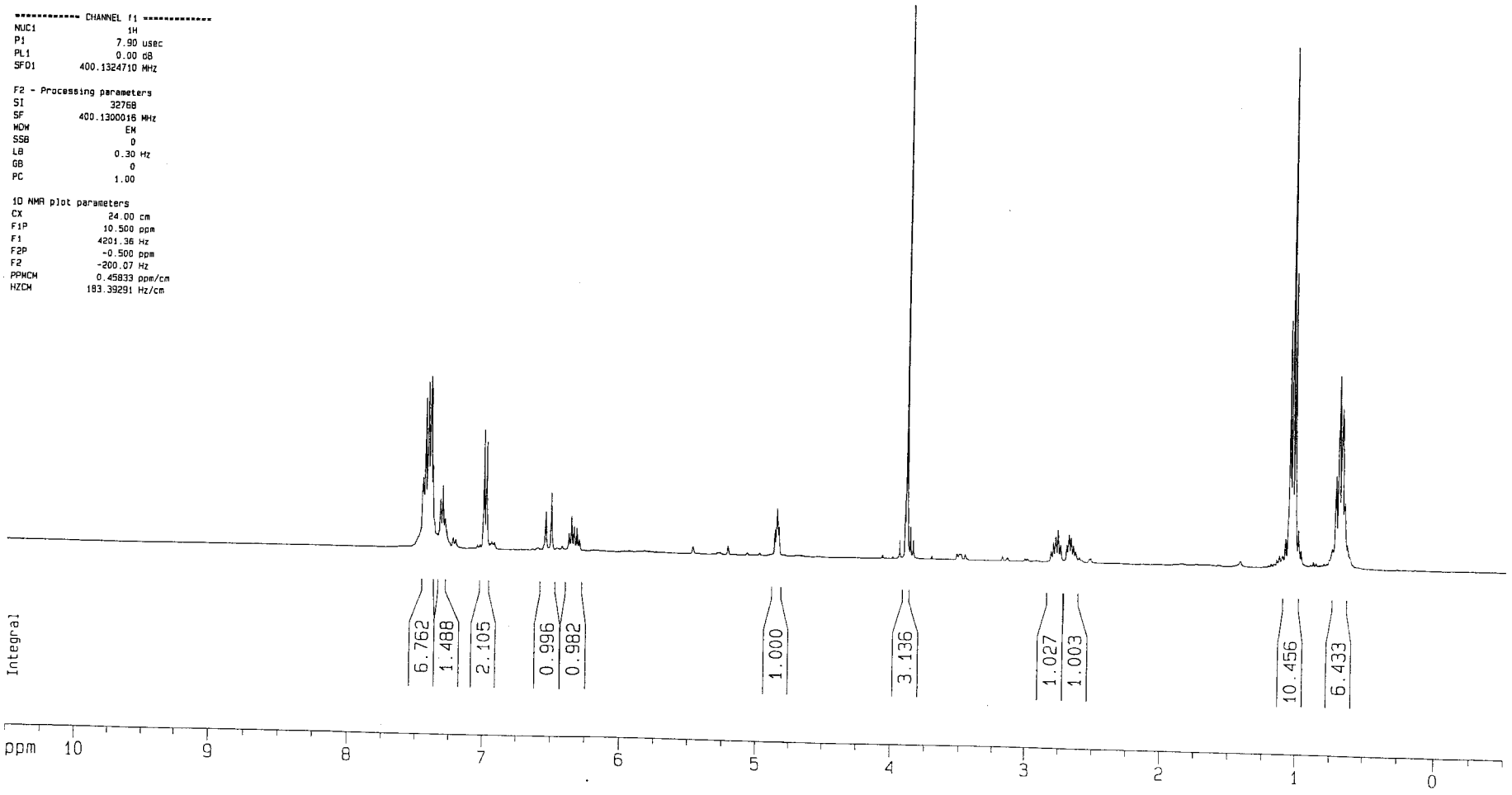


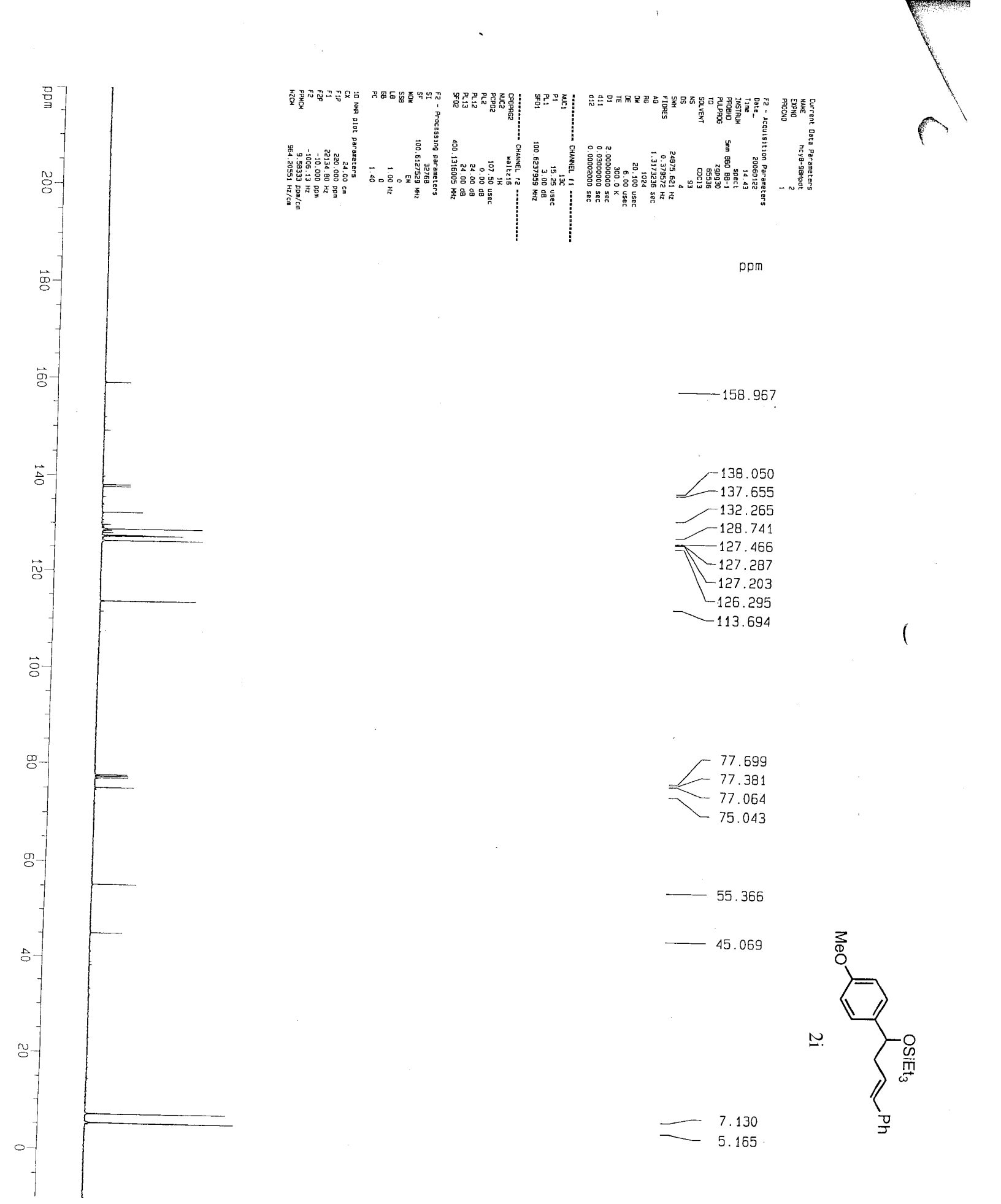
H-pdt

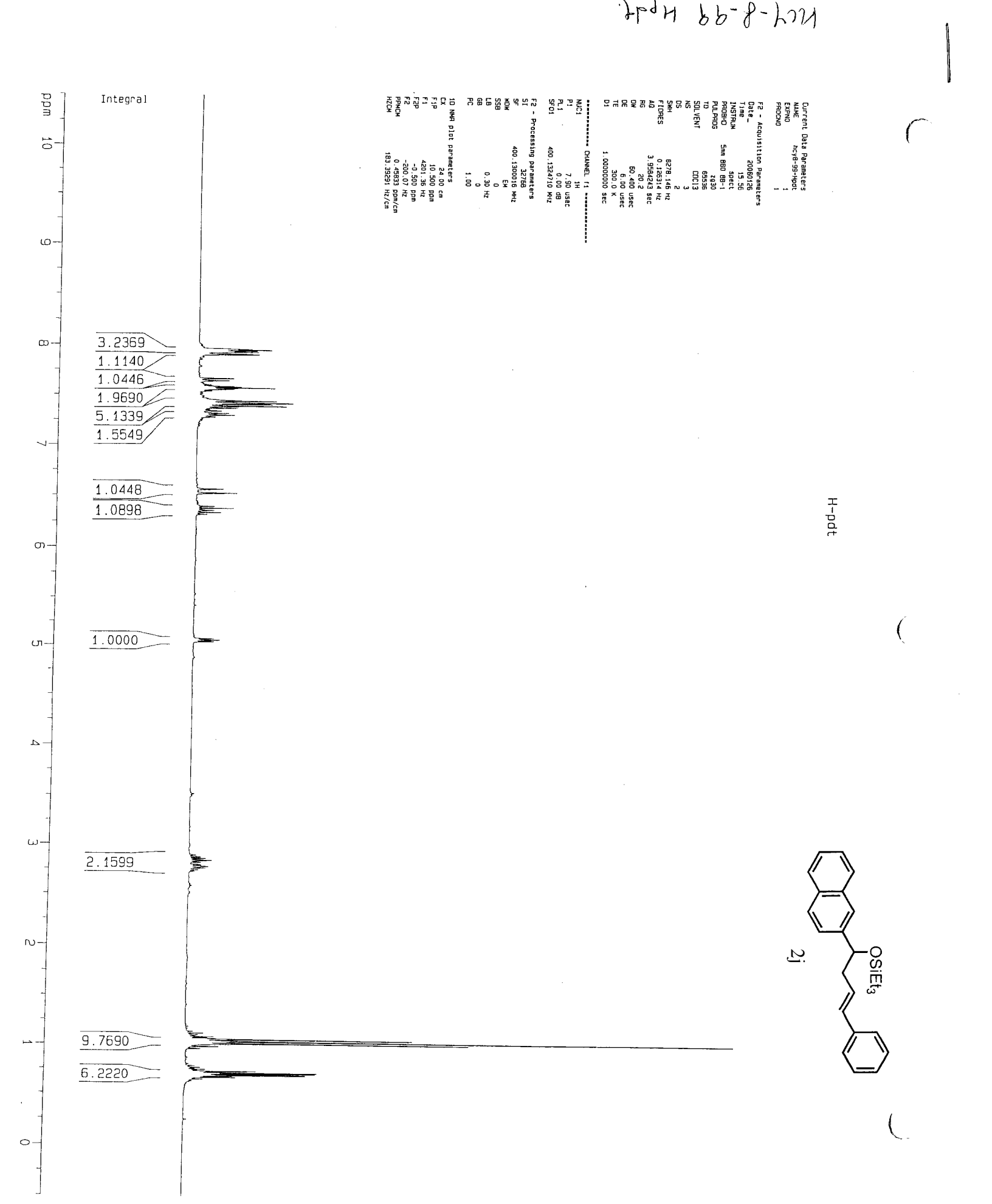


2i

```
Current Data Parameters
NAME          ncy8-98Hpdt
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_          20060122
Time             14.39
INSTRUM          spect
PROBHD     5mm BBO BB-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                   5
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                20.2
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

========== CHANNEL f1 ==========
NUC1                 1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300016 MHz
WDW                  EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               24.00 cm
F1P              10.500 ppm
F1              4201.36 Hz
F2P              -0.500 ppm
F2             -200.07 Hz
PPMCM          0.45833 ppm/cm
HZCM          183.39291 Hz/cm
```




Current Data Parameters
NAME mcyB-98hpot
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060122
Time 14.43
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 93
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20551 Hz/cm
ppm
158.967
138.050
137.655
132.265
128.741
127.466
127.287
127.203
126.295
113.694
77.699
77.381
77.064
75.043
55.366
45.069
7.130
5.165
MeO
OSiEt3
Ph
2i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1.0446
1.9690
5.1339
1.5549
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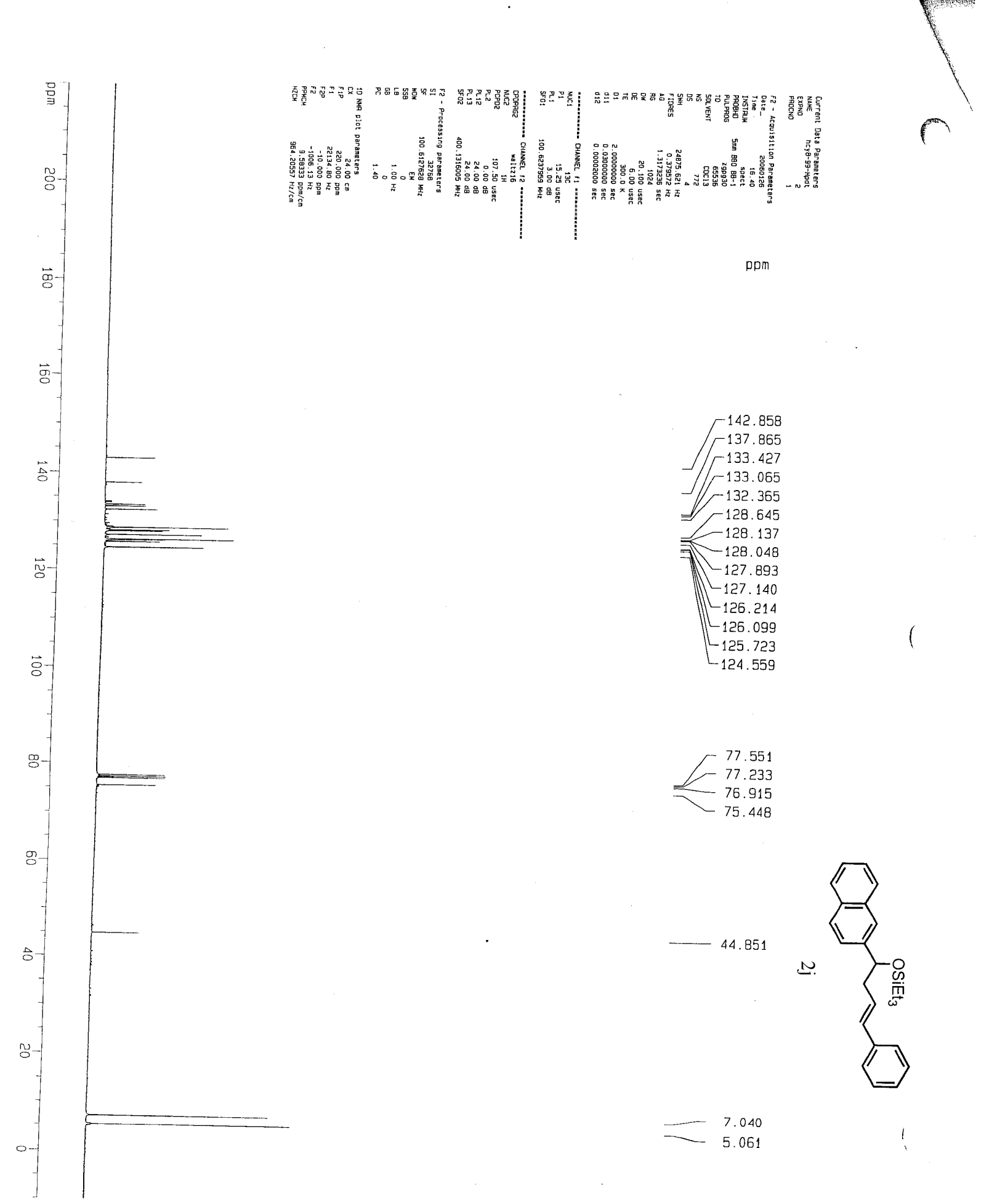
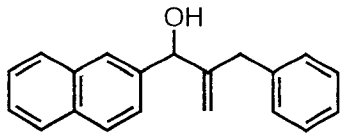
1.0898
1.0000
2.1599
9.7690
6.2220
ppm
H-pdt
OSiEt3
2j

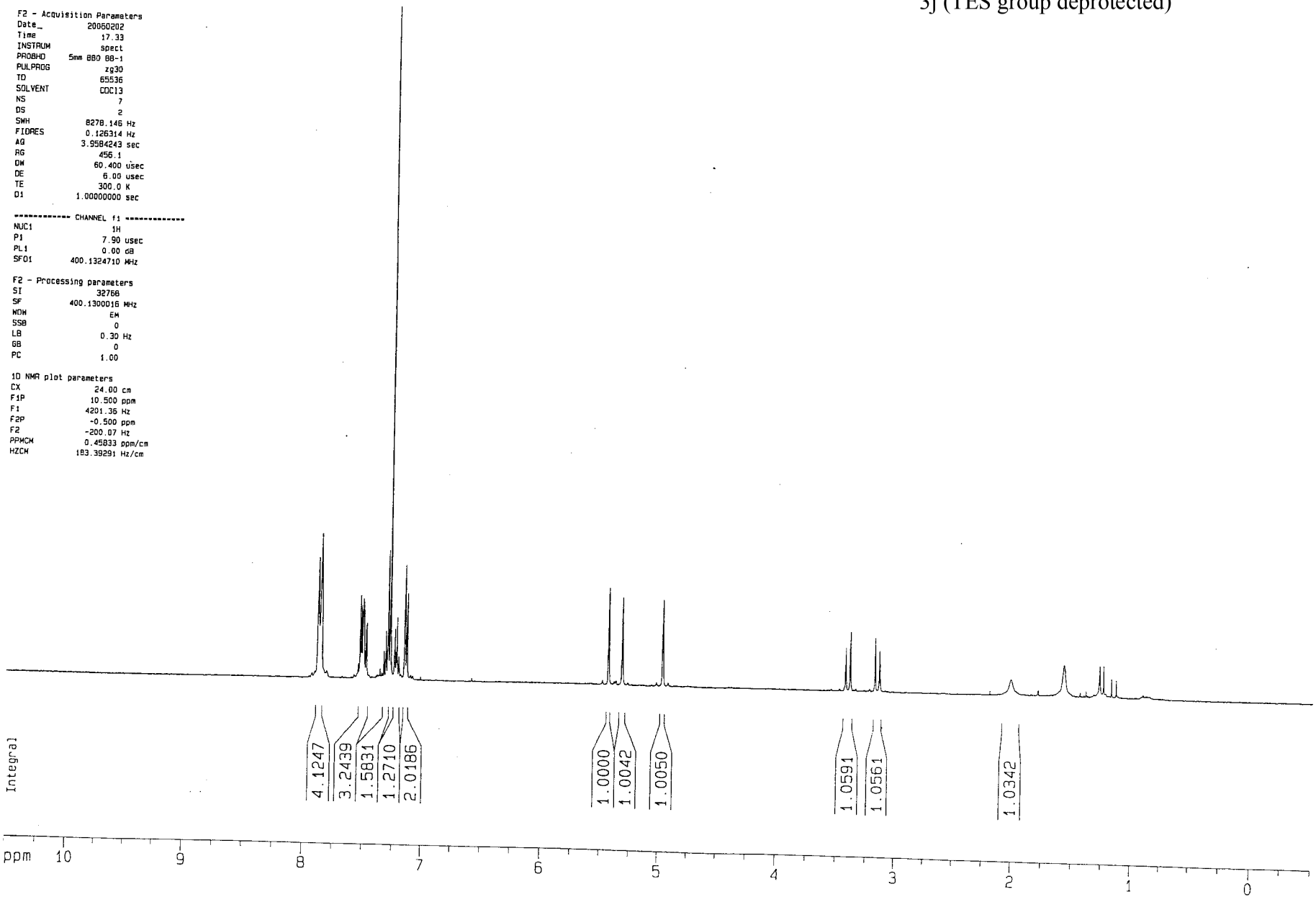

Current Data Parameters
NAME ncy8-99-Hpdt
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060126
Time 16.40
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 772
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127628 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.28557 Hz/cm
ppm
142.858
137.865
133.427
133.065
132.365
128.645
128.137
128.048
127.893
127.140
126.214
126.099
125.723
124.559
77.551
77.233
76.915
75.448
44.851
7.040
5.061
OSiEt3
2j
ppm
200
180
160
140
120
100
80
60
40
20
0

TES deprotection, Apdt

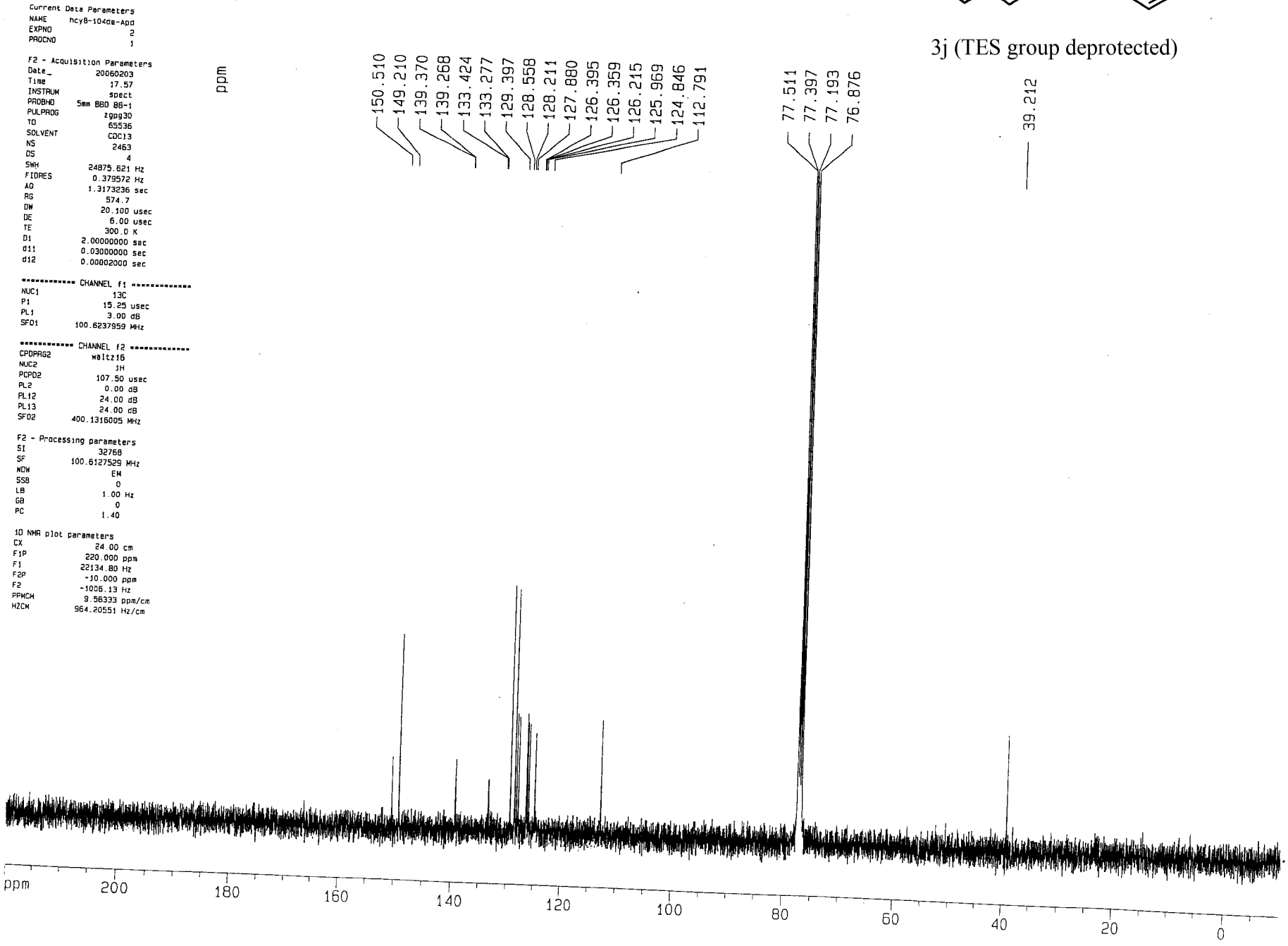


3j (TES group deprotected)

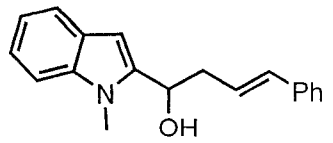
```
Current Data Parameters
NAME      hcy8-104de-Apd
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20060202
Time              17.33
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   7
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                456.1
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec

------------ CHANNEL f1 ------------
NUC1                 1H
P1                7.90 usec
PL1               0.00 dB
SFO1     400.1324710 MHz

F2 - Processing parameters
SI                32768
SF       400.1300016 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX               24.00 cm
F1P             10.500 ppm
F1             4201.36 Hz
F2P             -0.500 ppm
F2             -200.07 Hz
PPMCM          0.45833 ppm/cm
HZCM        183.39291 Hz/cm
```



3j (TES group deprotected)

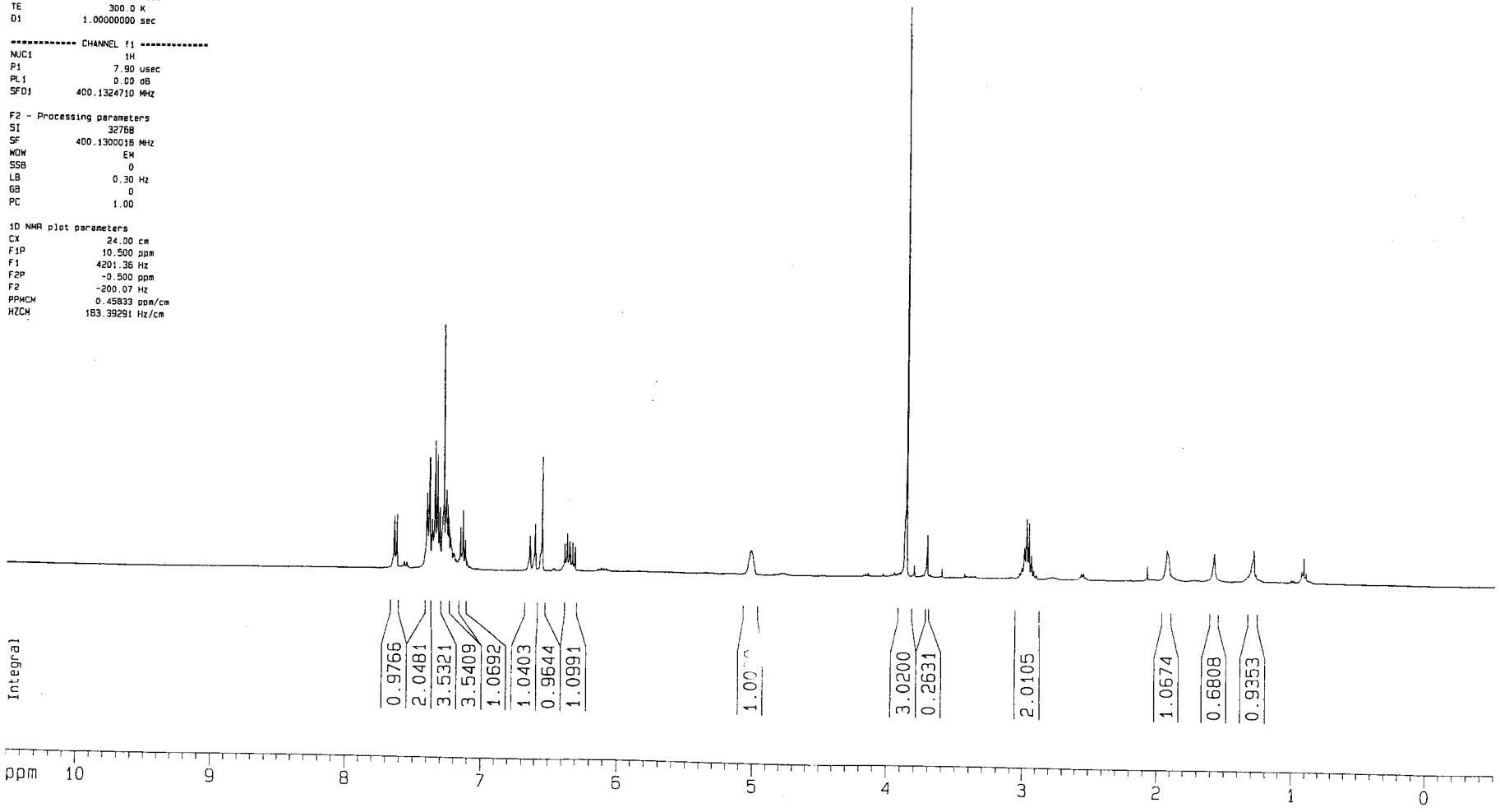


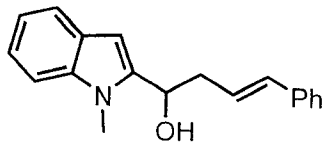
Me-indo-2-CHO AllylPh coupling, H pdt deprotection



2k (TES group deprotected)

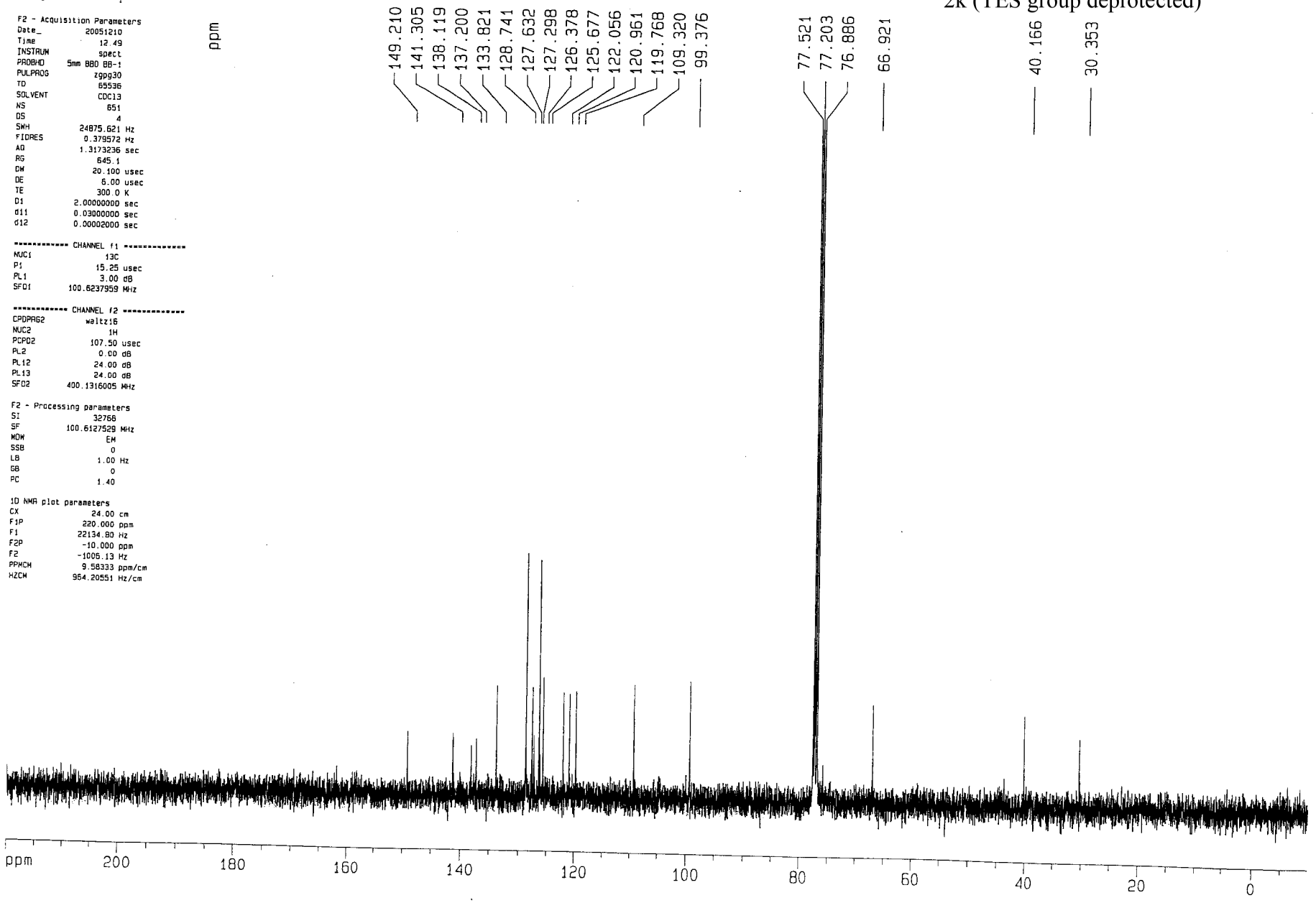
```
Current Data Parameters
NAME      hcyB-70de-Hpdt
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051210
Time               12.45
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
DS                    2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                287.4
DW               60.400 usec
DE                6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                 7.90 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300016 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                24.00 cm
F1P               10.500 ppm
F1               4201.36 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM             0.45833 ppm/cm
HZCM            183.39291 Hz/cm
```

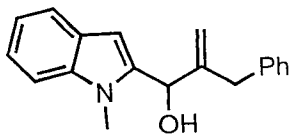




2k (TES group deprotected)

```
Current Data Parameters
NAME      hcyB-70de-Hpdt
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20051210
Time              12.49
INSTRUM           spect
PROBHD   5mm BBO BB-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 651
DS                   4
SWH          24875.621 Hz
FIDRES        0.379572 Hz
AQ            1.3173236 sec
RG                645.1
DW               20.100 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1               13C
P1               15.25 usec
PL1               3.00 dB
SFO1        100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2          107.50 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127529 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                24.00 cm
F1P              220.000 ppm
F1             22134.80 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM          9.58333 ppm/cm
HZCM         964.20551 Hz/cm
```

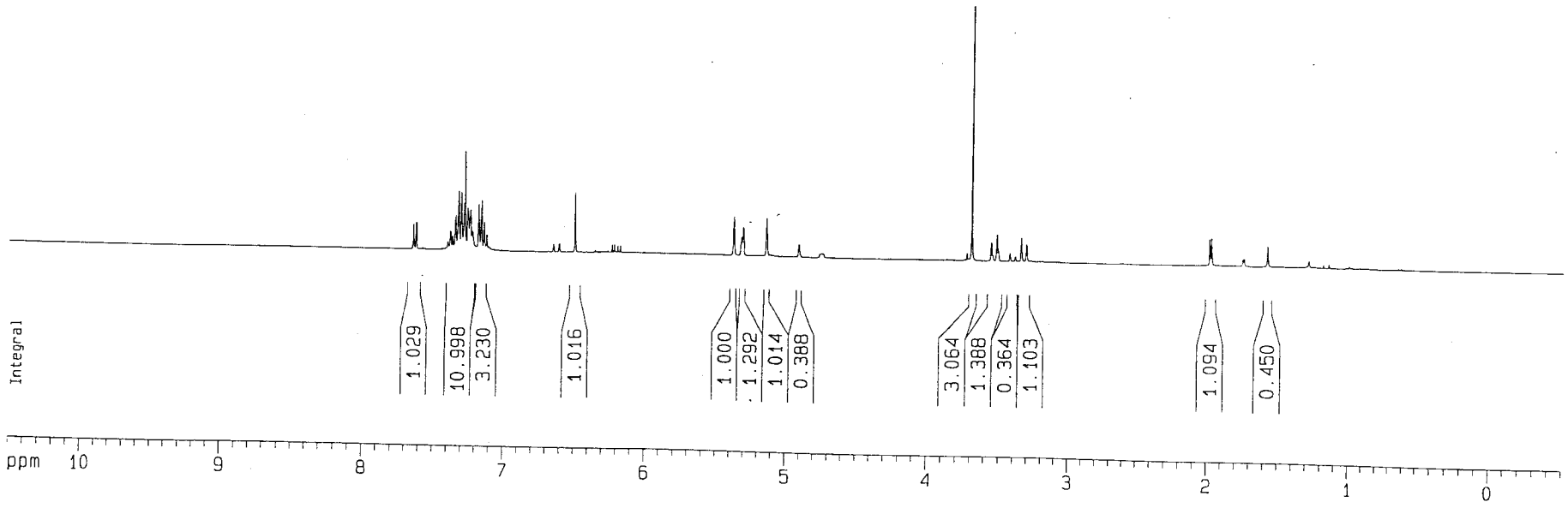


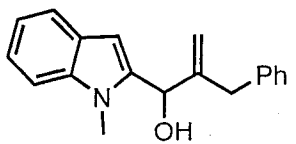


Cy2PPh f9 deprotection, f6

3k (TES group deprotected)

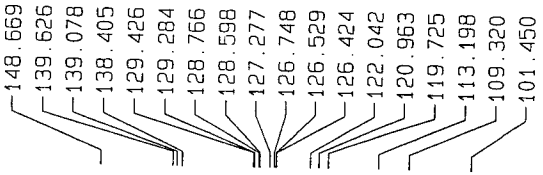
```
Current Data Parameters
NAME      hcy8-70dcyf9-6
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20051212
Time             14.52
INSTRUM          spect
PROBHD     5mm BBO BB-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  12
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 181
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1          1.00000000 sec

------------ CHANNEL f1 -------------
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300016 MHz
WDW                  EM
SSB                   0
LB               0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX              24.00 cm
F1P           10.500 ppm
F1           4201.36 Hz
F2P           -0.500 ppm
F2           -200.07 Hz
PPMCM         0.45833 ppm/cm
HZCM        183.39291 Hz/cm
```

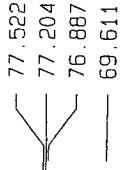


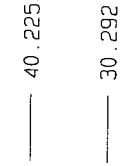


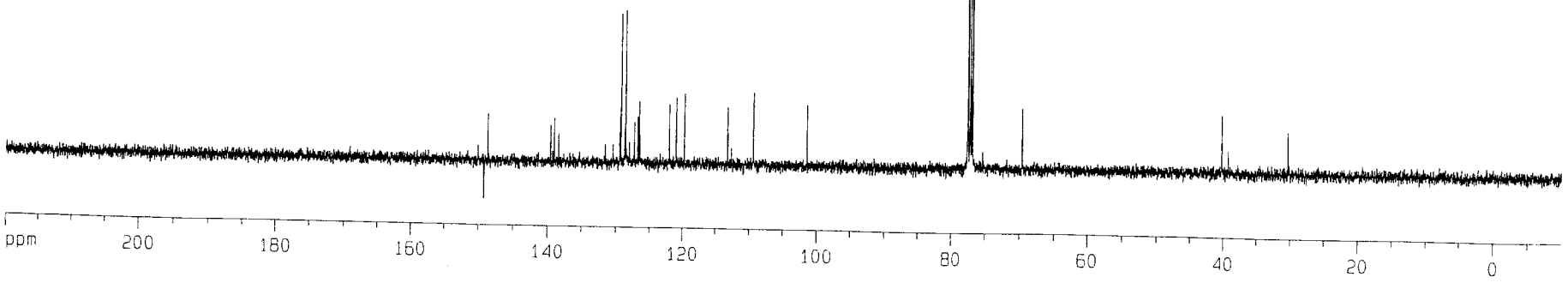
3k (TES group deprotected)

```
Current Data Parameters
NAME      hcy8-70dcyf9-6
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20051212
Time              15.01
INSTRUM             spect
PROBHD   5mm BBO BB-1
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  593
DS                    4
SWH           24875.621 Hz
FIDRES         0.379572 Hz
AQ             1.3173236 sec
RG                1625.5
DW               20.100 usec
DE                6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

********** CHANNEL f1 **********
NUC1                 13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

********** CHANNEL f2 **********
CPDPRG2          waltz16
NUC2                 1H
PCPD2            107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127529 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                24.00 cm
F1P              220.000 ppm
F1             22134.80 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM             9.58333 ppm/cm
HZCM            964.20551 Hz/cm
```

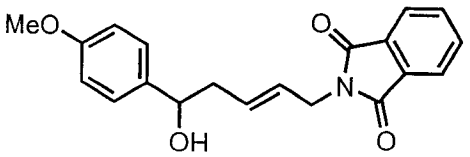






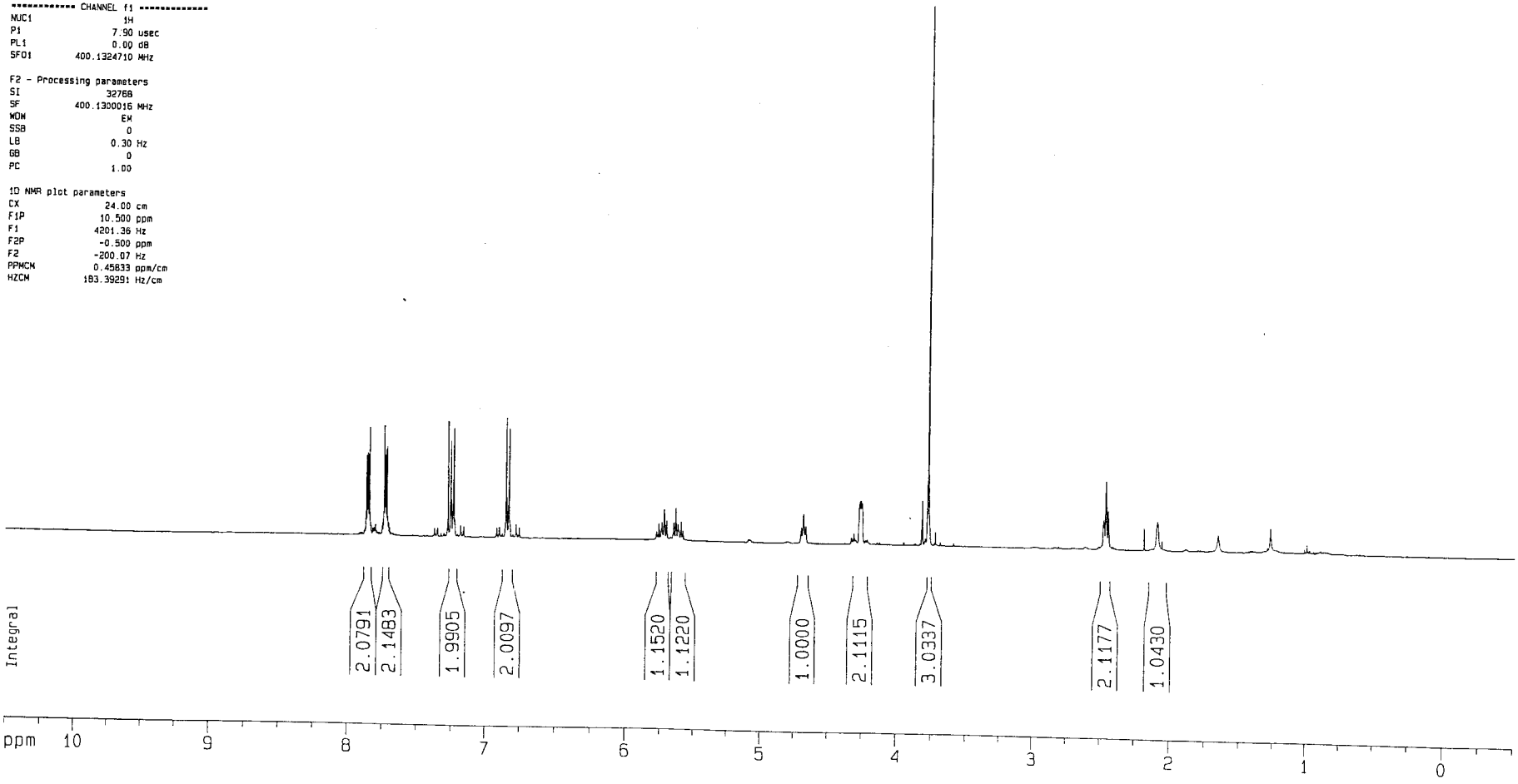


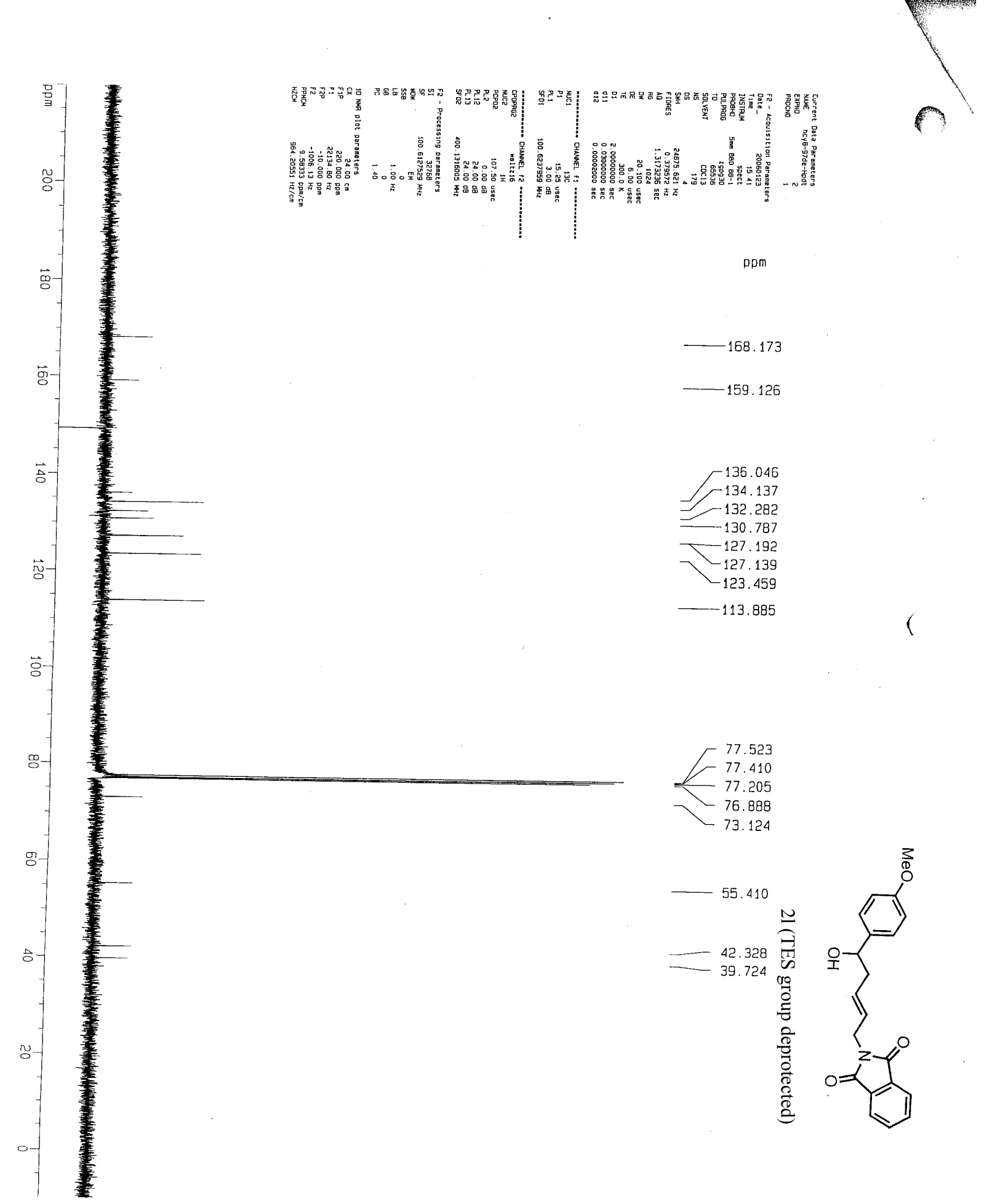
H pdt TES deprotection



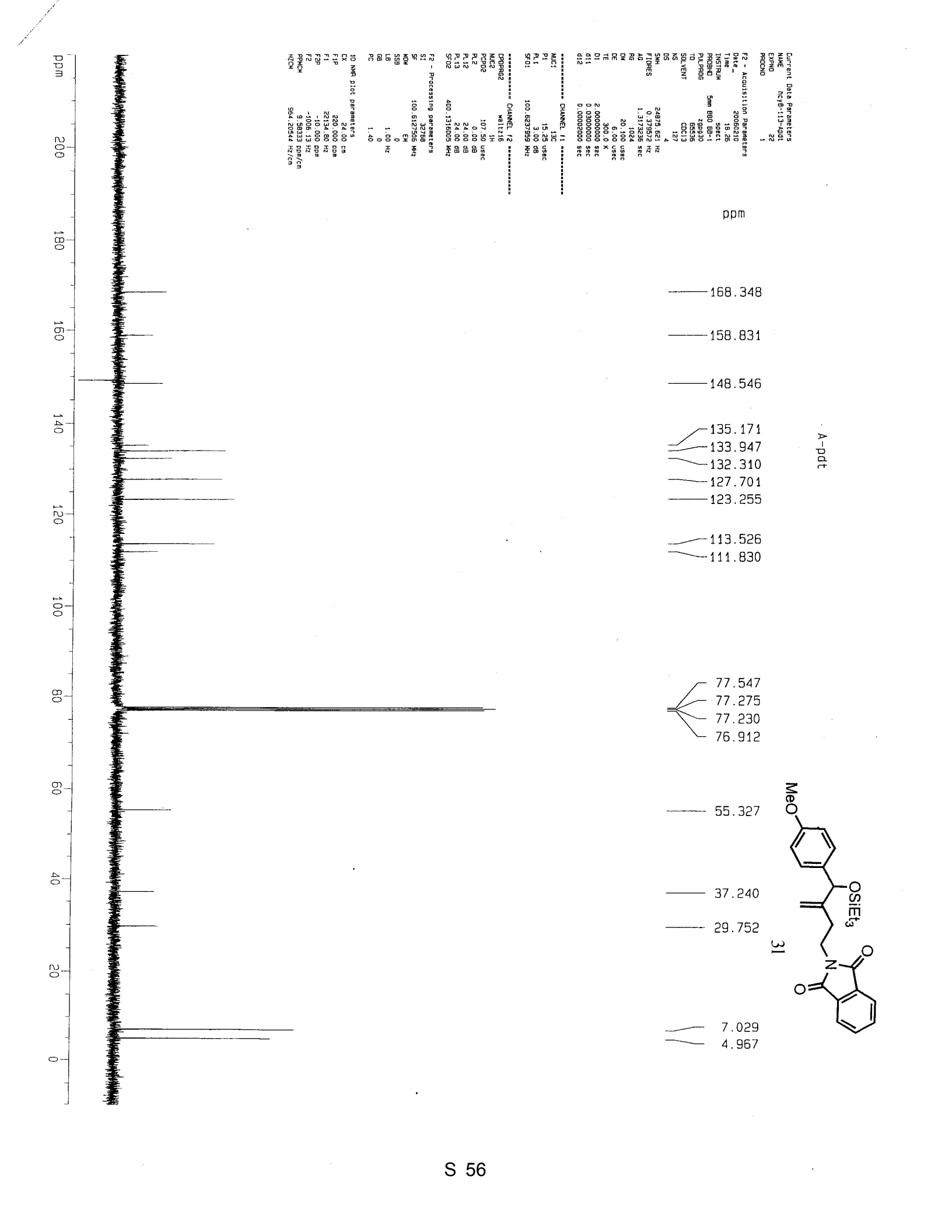
2l (TES group deprotected)

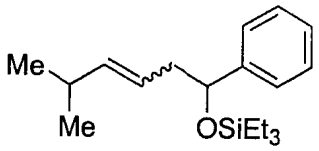
```
Current Data Parameters
NAME      hcy8-97de-Hpdt
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060123
Time               15.38
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
DS                    2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  181
DW               60.400 usec
DE                6.00 usec
TE                300.0 K
D1           1.00000000 sec

========== CHANNEL f1 ==========
NUC1                  1H
P1                 7.90 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300016 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                24.00 cm
F1P               10.500 ppm
F1               4201.36 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.45833 ppm/cm
HZCM           183.39291 Hz/cm
```



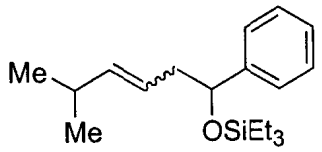

Current Data Parameters
NAME ncy6-97de-1pot
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060123
Time_ 15.41
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 179
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.28551 Hz/cm
ppm
168.173
159.126
136.046
134.137
132.282
130.787
127.192
127.139
123.459
113.885
77.523
77.410
77.205
76.888
73.124
55.410
42.328
39.724
MeO
OH
N
O
O
21 (TES group deprotected)

Integral
ppm
2.0071
2.0475
2.0119
2.0019
1.0000
0.9959
1.0060
4.0305
1.0913
1.0562
1.0771
9.2524
6.1482
A-pdt
MeO
OSiEt3
O
N
O

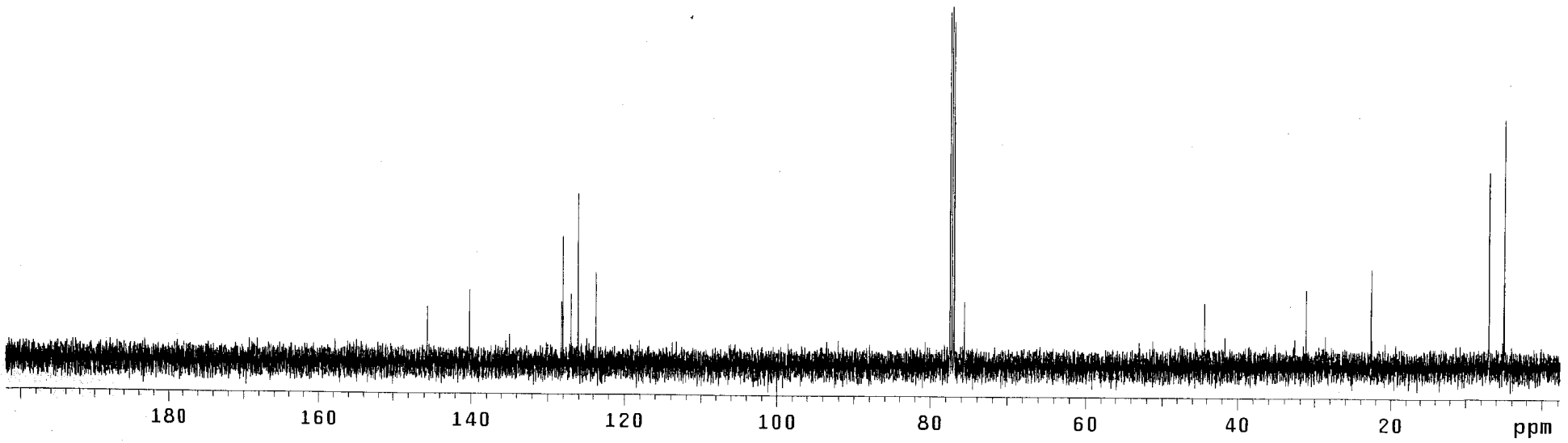

Current Data Parameters
NAME hcy8-113-Apdt
EXPNO 22
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060210
Time_ 15.26
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 127
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127506 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20544 Hz/cm
ppm
168.348
158.831
148.546
135.171
133.947
132.310
127.701
123.255
113.526
111.830
77.547
77.275
77.230
76.912
55.327
37.240
29.752
7.029
4.967
A-pdt
MeO
OSiEt3
N
O
O
31
ppm
200
180
160
140
120
100
80
60
40
20
0



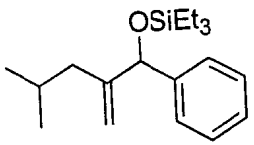
2m



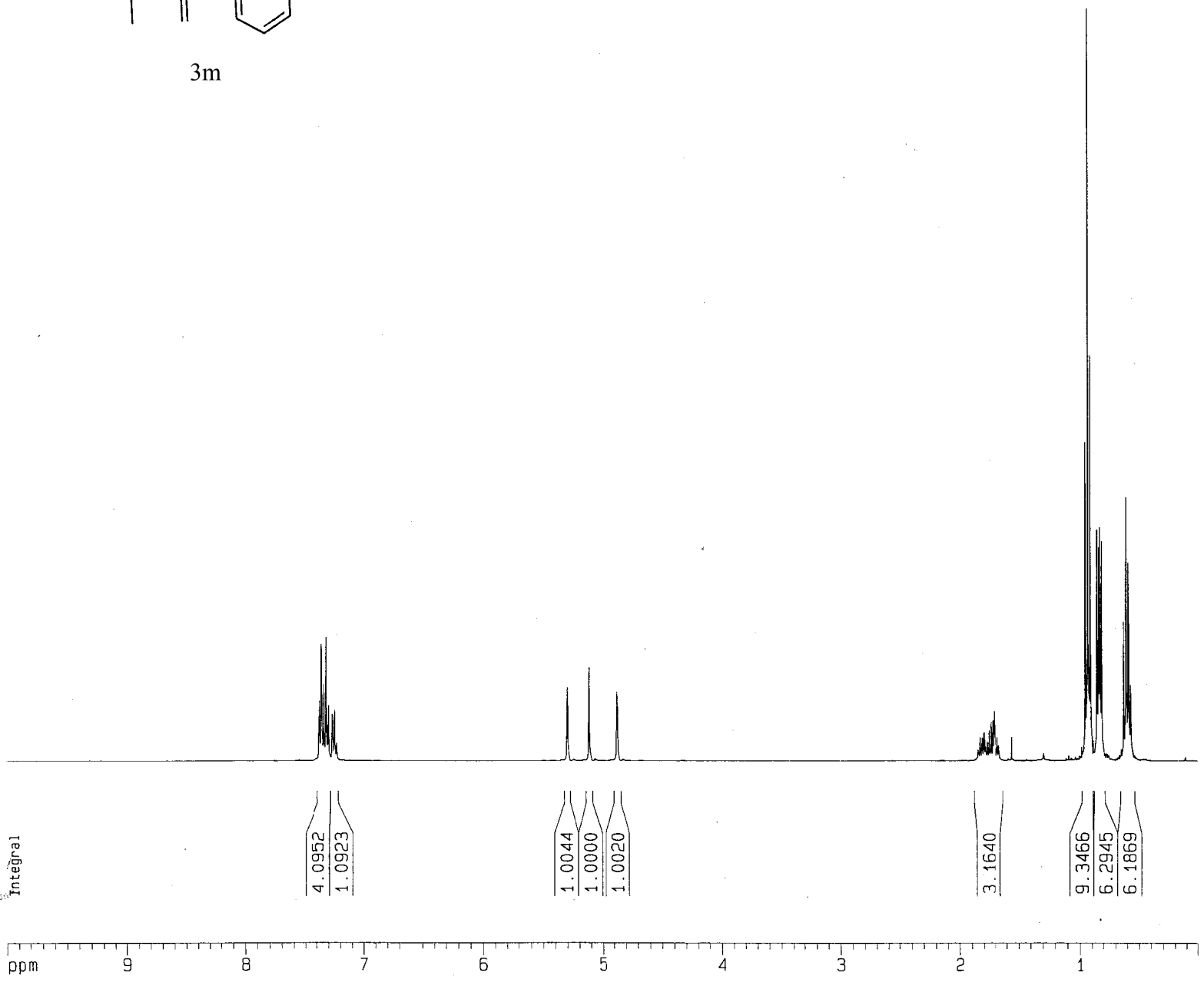
2m



SN050726 allylic alcohol



3m



Current Data Parameters

NAME	SN726-all-H
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050722
Time	21.51
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	32
DW	60.400 use
DE	6.00 use
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

NUC1	1H
P1	7.90 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

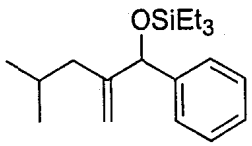
F2 - Processing parameters

SI	32768
SF	400.1300056 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

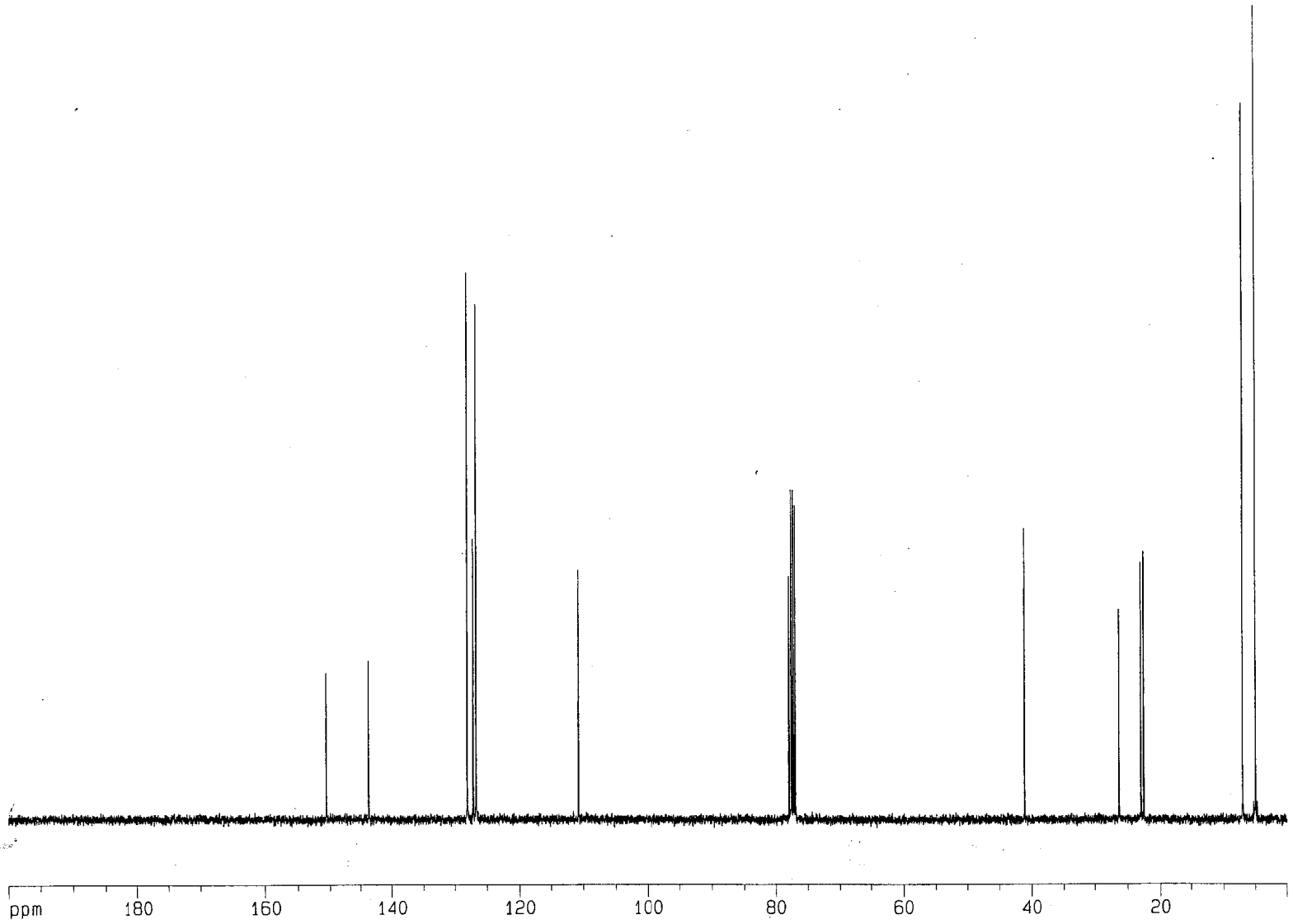
1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	4001.30 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm

SN050726 allylic alcohol



3m



Current Data Parameters
NAME SN726-all-C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050722
Time 21.53
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 159
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

60

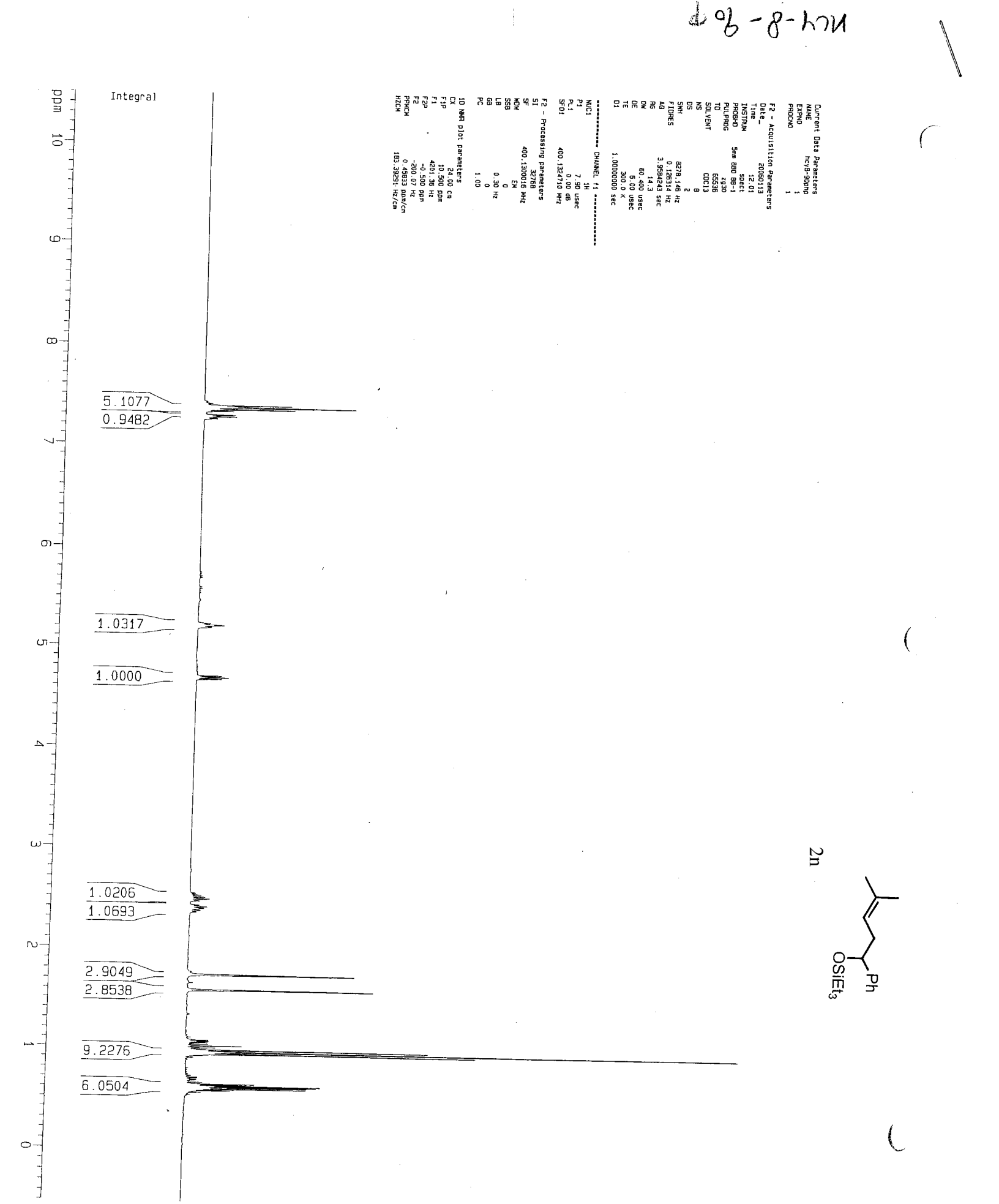
S

========== CHANNEL f1 ==========
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127499 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 10.00000 ppm/cm
HZCM 1006.12744 Hz/cm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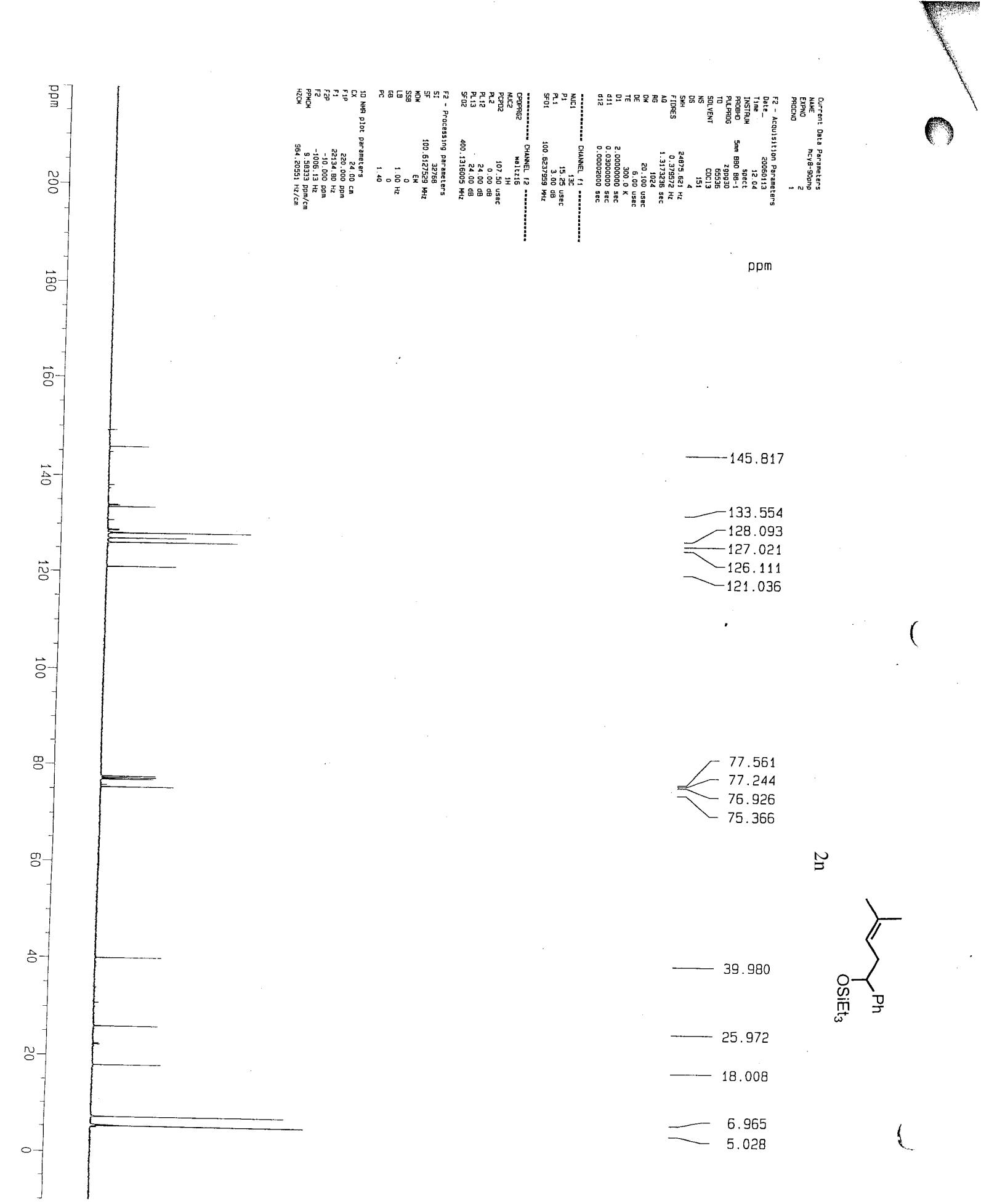
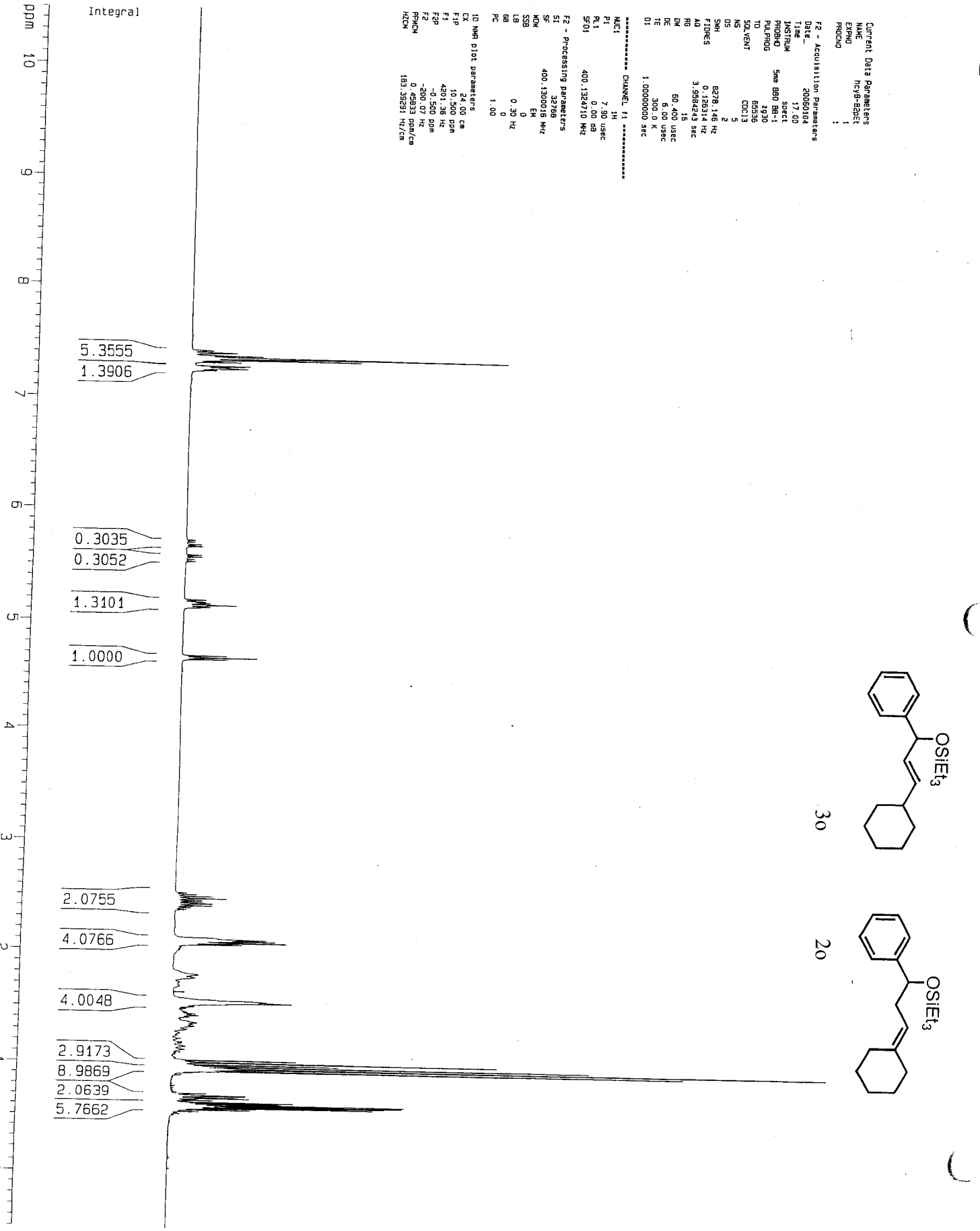
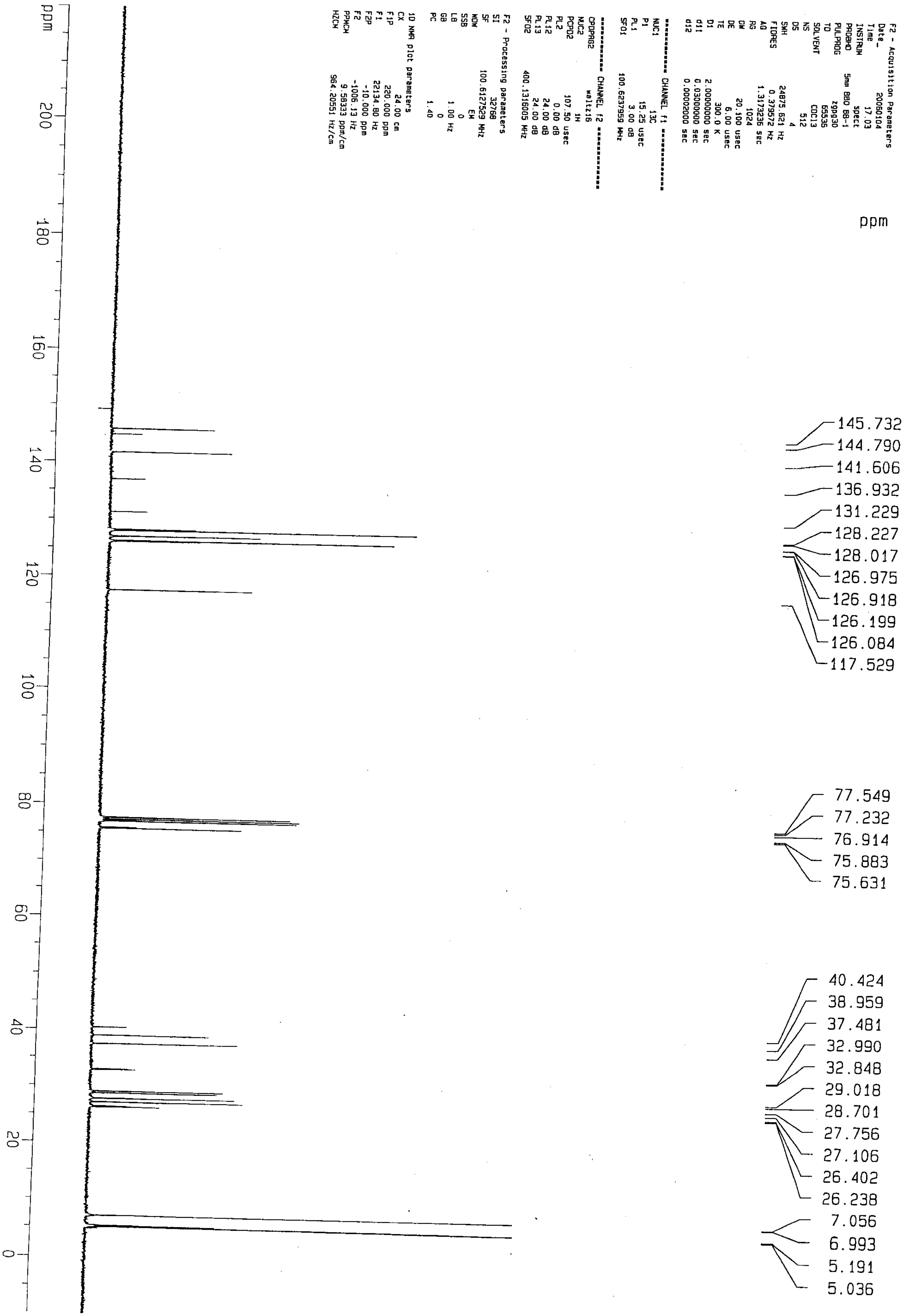
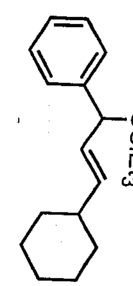
ppm
5.1077
0.9482
1.0317
1.0000
1.0206
1.0693
2.9049
2.8538
9.2276
6.0504
Current Data Parameters
NAME hcy5-90dmq
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060113
Time 12.01
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 14.3
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 24.00 cm
F1P 10.500 ppm
F1 4201.36 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45833 ppm/cm
HZCM 183.39231 Hz/cm
2n
OSiEt3
Ph

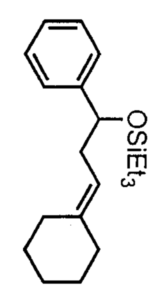

Current Data Parameters
NAME hcy8-90mp
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060113
Time 12.04
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 151
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3172336 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20551 Hz/cm
ppm
145.817
133.554
128.093
127.021
126.111
121.036
77.561
77.244
76.926
75.366
39.980
25.972
18.008
6.965
5.028
2n
Ph
OSiEt3


Integral
ppm
5.3555
1.3906
0.3035
0.3052
1.3101
1.0000
2.0755
4.0766
4.0048
2.9173
8.9869
2.0639
5.7662
OSiEt3
OSiEt3

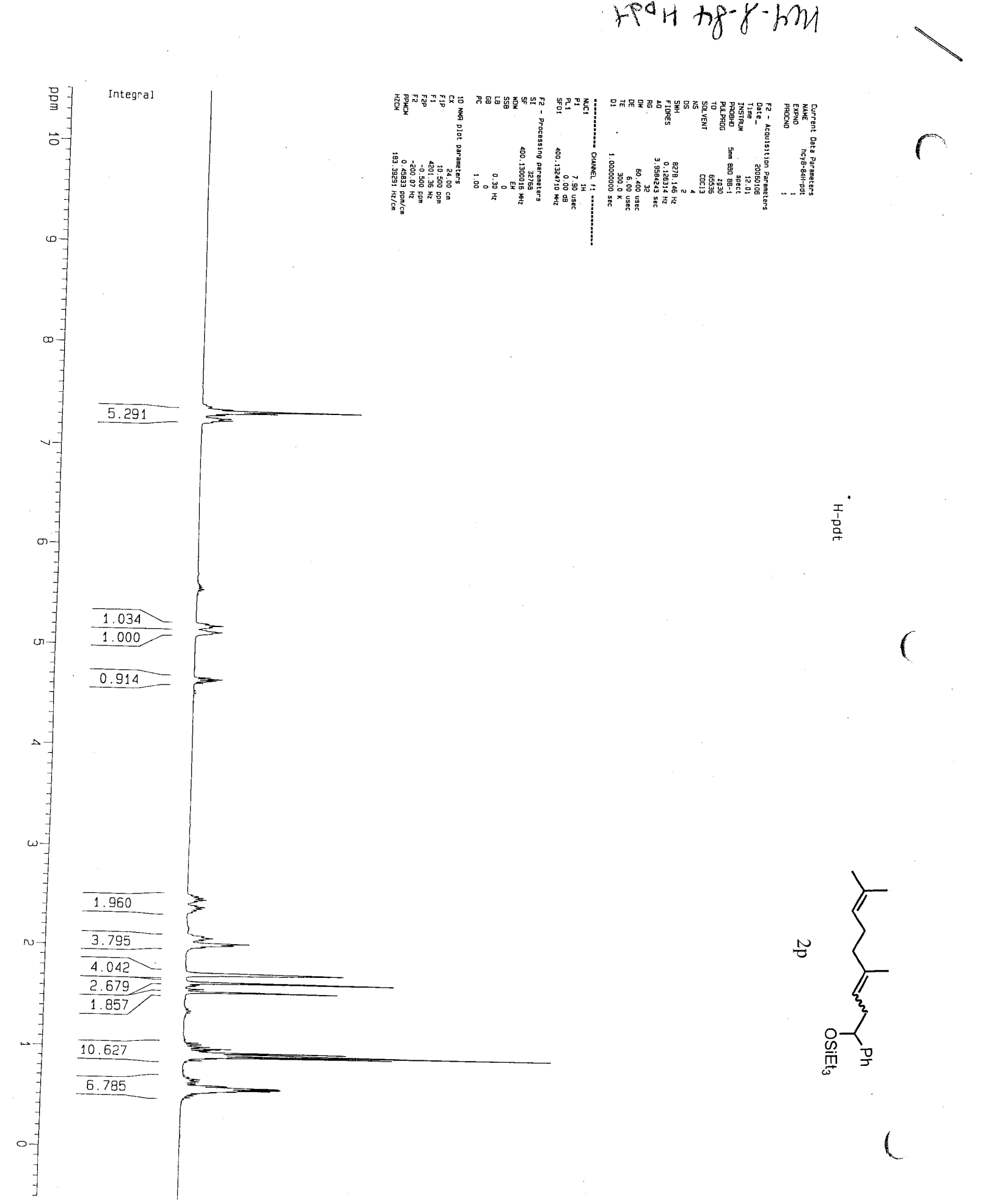

Current Data Parameters
NAME hcy8-82pEt
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060104
Time 17.03
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20551 Hz/cm
ppm
145.732
144.790
141.606
136.932
131.229
128.227
128.017
126.975
126.918
126.199
126.084
117.529
77.549
77.232
76.914
75.883
75.631
40.424
38.959
37.481
32.990
32.848
29.018
28.701
27.756
27.106
26.402
26.238
7.056
6.993
5.191
5.036
ppm
200
180
160
140
120
100
80
60
40
20
0

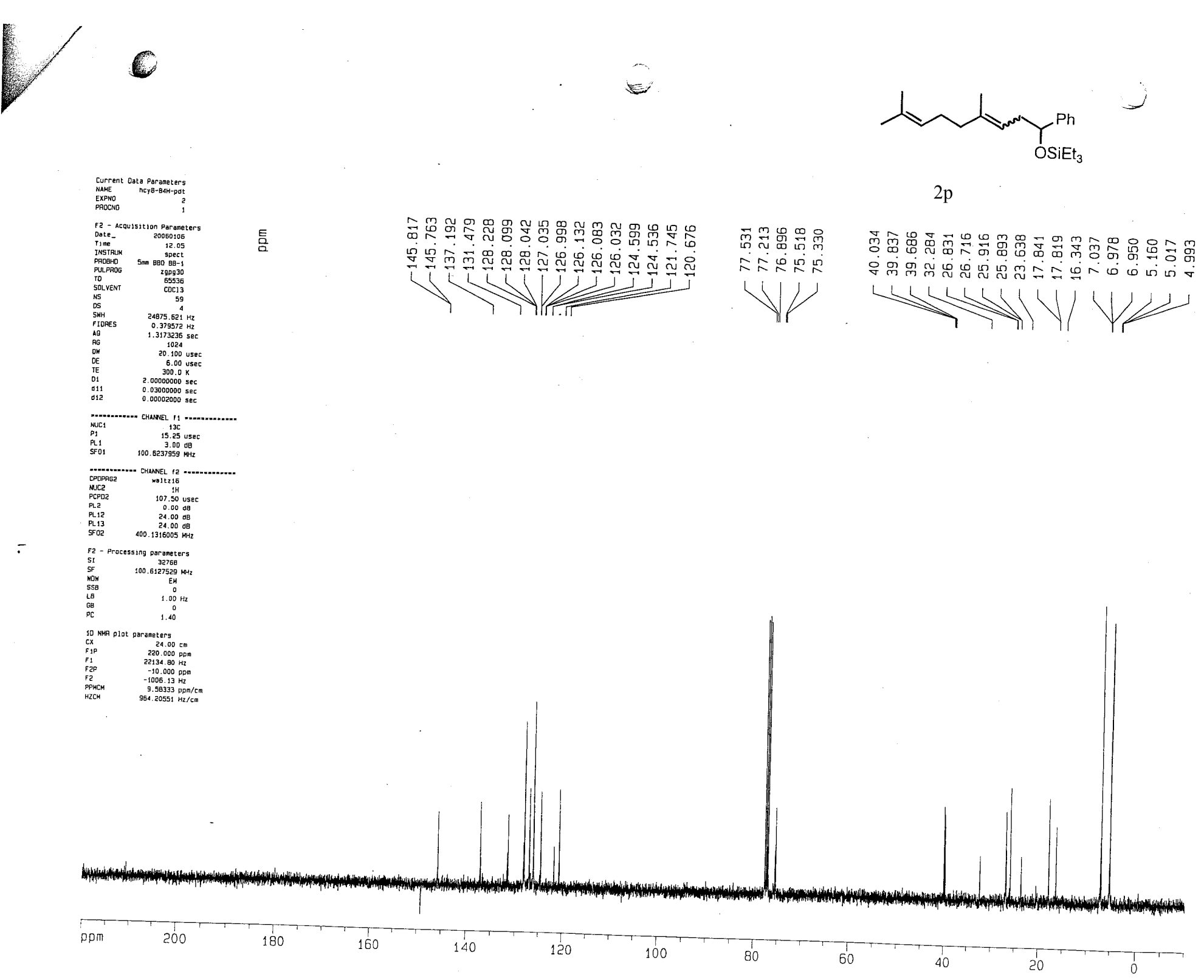

OSiEt3

3o

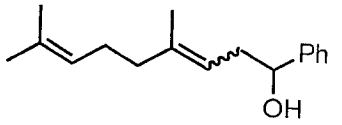

OSiEt3

2o


Integral
ppm
10
9
8
7
6
5
4
3
2
1
0
5.291
1.034
1.000
0.914
1.960
3.795
4.042
2.679
1.857
10.627
6.785
Current Data Parameters
NAME hcy8-64H-pdt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060106
Time 12.01
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.958243 sec
RG 32
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300018 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 24.00 cm
F1P 10.500 ppm
F1 4201.36 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45833 ppm/cm
HZCM 183.39291 Hz/cm
H-pdt
2p
Ph
OSiEt3

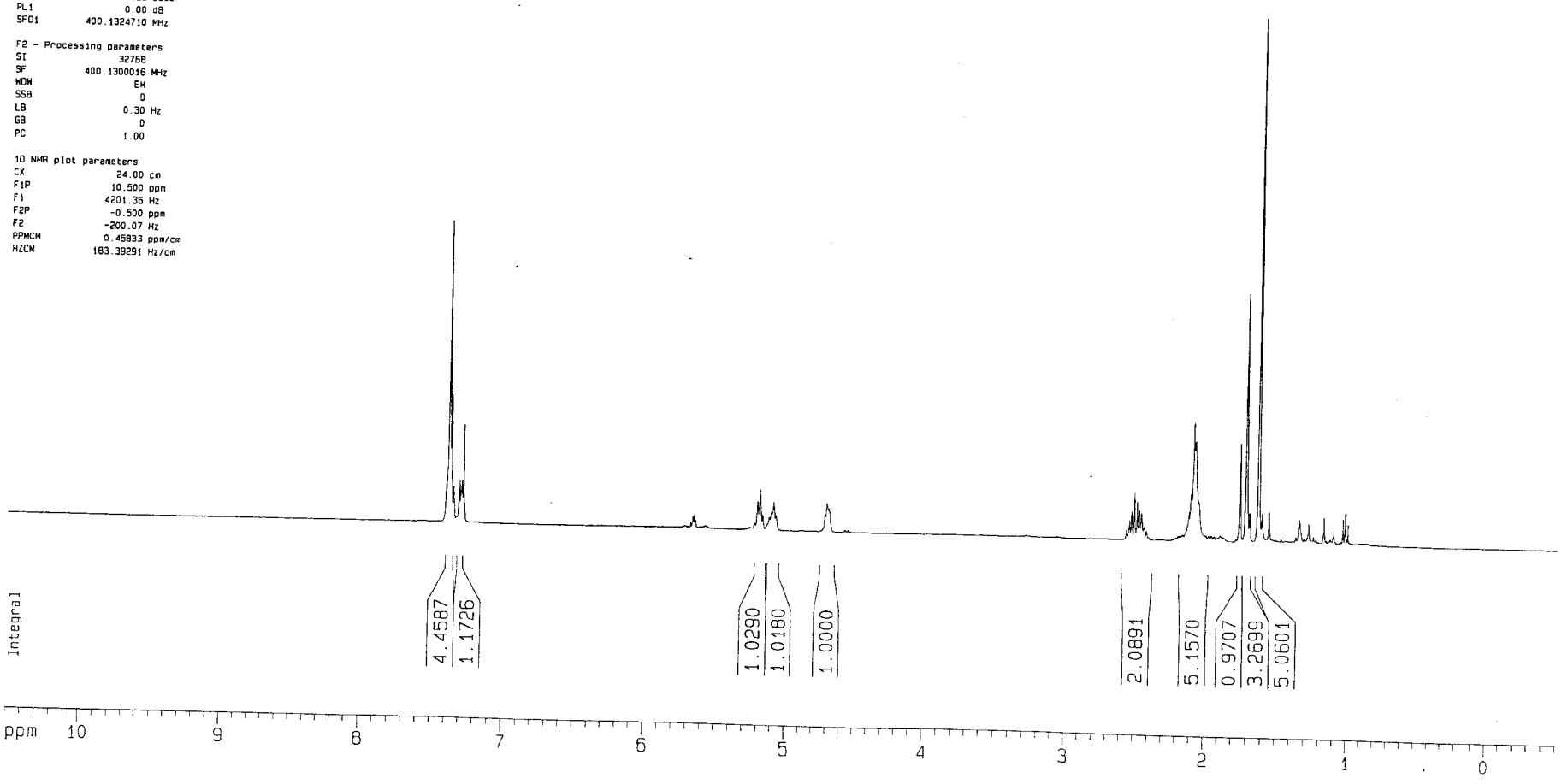

Ph
OSiEt3
2p
Current Data Parameters
NAME hcy8-84H-pdt
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060106
Time 12.05
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 59
DS 4
SWH 24875.621 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 1024
DW 20.100 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SF01 100.6237959 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127529 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 24.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.58333 ppm/cm
HZCM 964.20551 Hz/cm
ppm
145.817
145.763
137.192
131.479
128.228
128.099
128.042
127.035
126.998
126.132
126.083
126.032
124.599
124.536
121.745
120.676
77.531
77.213
76.896
75.518
75.330
40.034
39.837
39.686
32.284
26.831
26.716
25.916
25.893
23.638
17.841
17.819
16.343
7.037
6.978
6.950
5.160
5.017
4.993
ppm
200
180
160
140
120
100
80
60
40
20
0

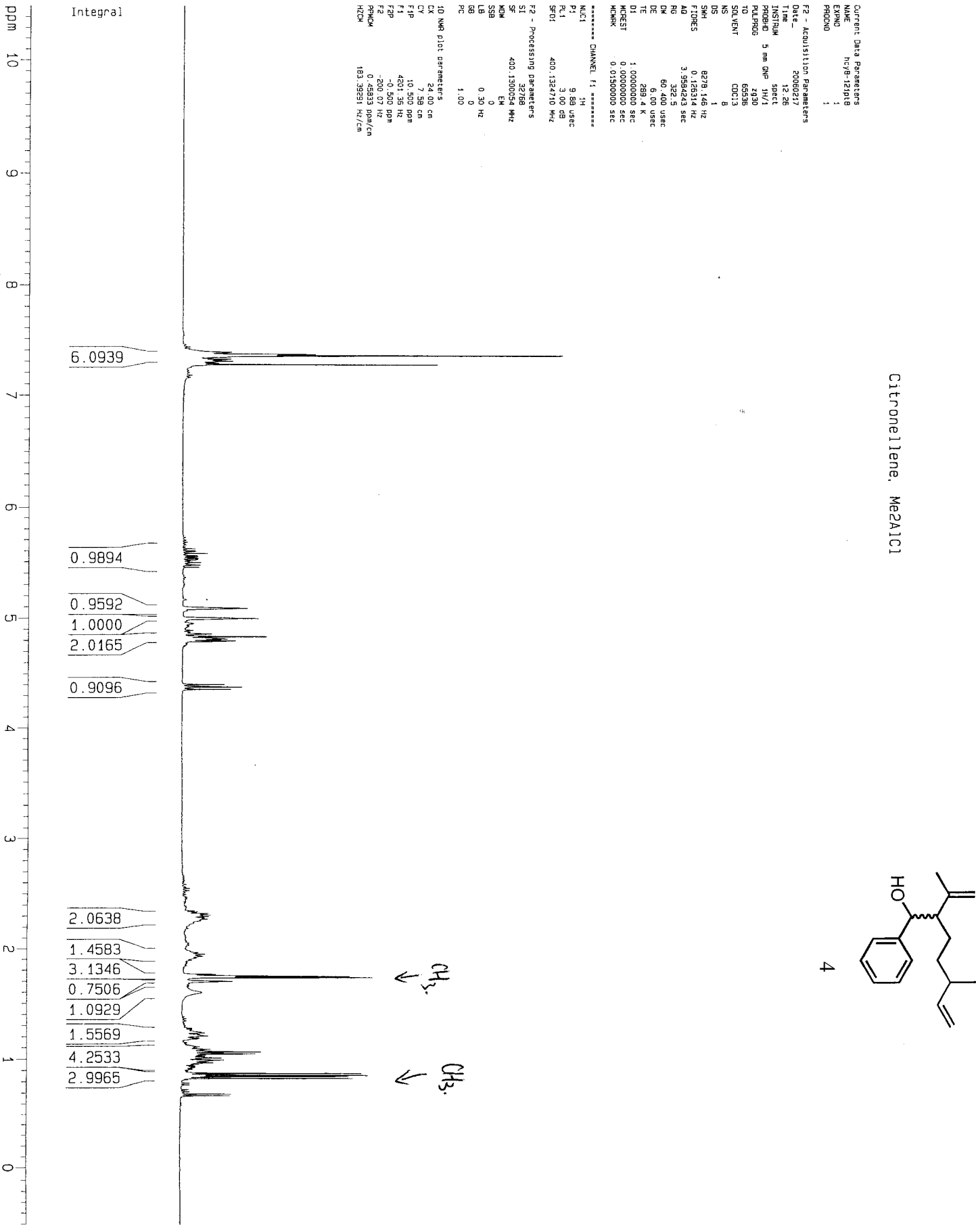
TES deprotection, H-pdt



2p (TES deprotected)

```
Current Data Parameters
NAME          hcy8-84de-p
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060107
Time                13.39
INSTRUM             spect
PROBHD     5mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                      3
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                   90.5
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

========== CHANNEL f1 ==========
NUC1                   1H
P1                  7.90 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300016 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 24.00 cm
F1P               10.500 ppm
F1                4201.36 Hz
F2P               -0.500 ppm
F2                -200.07 Hz
PPMCM             0.45833 ppm/cm
HZCM          183.39291 Hz/cm
```




Citronellene, Me2AlCl
4
HO
Integral
ppm
6.0939
0.9894
0.9592
1.0000
2.0165
0.9096
2.0638
1.4583
3.1346
0.7506
1.0929
1.5569
4.2533
2.9965
CH3.
CH3.
Current Data Parameters
NAME hcy8-12ipt8
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060217
Time 12.26
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 1
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 289.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 24.00 cm
CY 7.58 cm
F1P 10.500 ppm
F1 4201.35 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45833 ppm/cm
HZCM 183.39231 Hz/cm