Highly Enantioselective and Regioselective Nickel-Catalyzed Coupling of Allenes, Aldehydes, and Silanes

Ng, S.-S.; Jamison, T. F. *
Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA 02139

Supporting Information

Experimental Procedures, Analytical and Spectroscopic Data for Compounds **1a** – **5d**.
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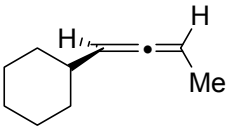
General Information.

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of nitrogen or argon with rigid exclusion of moisture from reagents and glassware. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Triethylsilane, *tert*-butyl-dimethylsilane and dimethylphenylsilane were purchased from Aldrich Chemical Co. and were saturated with nitrogen before use. Benzaldehyde was purchased from Aldrich Chemical Co., distilled by bulb to bulb distillation and then saturated with nitrogen before storage under nitrogen. Other aromatic aldehydes were purchased from Aldrich Chemical Co. and were used without further purification. Bis(cyclooctadienyl)nickel(0) ($Ni(cod)_2$) and tricyclopentylphosphine were purchased from Strem Chemicals, Inc., stored under nitrogen atomosphere and used without further purification. 1,3-Bis-(2,6-di-isopropylphenyl)imidazol-2-ylidene (NHC-IPr) was prepared according to literature procedure.[1] Triethylsilane-d was prepared according to literature procedure.[2] Cyclohexanecarboxaldehyde, methyl lithium, Amano lipase, vinylacetate, acetaldehyde, methyl-(*R*)-mandelate, cyclohexaneacetic acid and Mosher's acid were purchased from Aldrich Chemical Co. and used as received (unless otherwise noted). Carbon tetra-bromide, triphenylphosphine and 4-(dimethylamino)-pyridine were purchased from Alfa Aesar and used as received. *t*ert-butylacetylene and 1-pentyne were purchased from GFS and used as received. Diethylazodicarboxylate was purchased from Lancaster and used as received. Dicyclohexylcarbodiimide was purchased from Pierce and used as received.

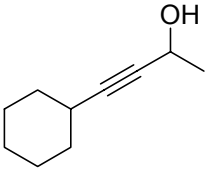
Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F_{254} plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silicycle Silica Gel (230 – 400 mesh). ^1H and ^{13}C NMR spectra were recorded on Varian 300 MHz, Varian 500 MHz or Bruker 400 MHz spectrometer in $CDCl_3$ or C_6D_6, unless otherwise noted. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm) or residual benzene (7.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = 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. Chiral GC analysis was performed on a Varian CP-3800 gas chromatograph fitted with Chiraldex B-PH, B-DA, and G-TA capillary columns. Chiral HPLC analysis was performed on a Hewlett-Packard 1100 chromatograph equipped with a variable wavelength detector and Chiralcel OD or OD-H columns. Specific Rotations ($[\alpha]_D$) were measured on a Perkin-Elmer 241 polarimeter at 589 nm.

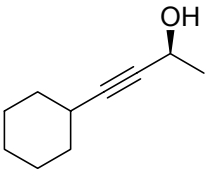
Preparation of 1,3-disubstituted allenes.



(a*S*)-buta-1,2-dienyl-cyclohexane (2b).



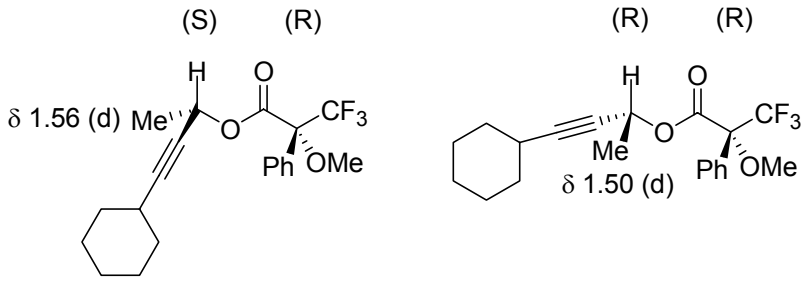
a. Preparation of **(+/-)-4-cyclohexyl-but-3-yn-2-ol**. Carbon-tetrabromide (73 g, 220 mmol) was dissolved in anhydrous dichloromethane (150 mL). The solution was cooled to 0 ºC, triphenylphosphine (115 g, 440 mmol) was added. The mixture was stirred 30 min at 0 ºC. Cyclohexanecarboxaldehyde (10 mL, 110 mmol) was added and the reaction mixture was slowly warmed to room temperature and stirred 12 h. The brown precipitate was removed by filtering the CH_2Cl_2 solution through silica gel and the silica gel was washed with hexane. Evaporation of the solvents gave an oil with white precipitate. The crude was diluted with hexane and filtered through silica gel to yield a colorless oil (2,2-dibromo-vinyl)-cyclohexane (21.62 g, 74% yield). It was used without further purification. (2,2-Dibromo-vinyl)-cyclohexane (9.18 g, 34 mmol) was dissolved in anhydrous THF (40 mL) and was cooled to -78 ºC. Methyllithium (55 mL, 88 mmol, 1.6 M in ether) was added to the solution over 5 min and the mixture was stirred 2.5 h at -78 ºC. Acetaldehyde was added in one portion and the mixture was stirred 1.5 h and was warmed to room temperature. The reaction was quenched with water and extracted with diethylether (1 x 80 mL), which was washed with water and dried with $MgSO_4$. Column chromatography afforded a yellow oil (+/-)-4-cyclohexyl-but-3-yn-2-ol (4.9 g, 94% yield).



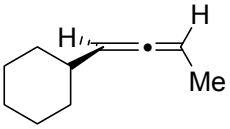
b. Preparation of enantiomerically enriched **(*S*)-4-cyclo-hexyl-but-3-yn-2-ol** by lipase resolution.[3] In an oven-dried round bottom flask, (+/-)-4-cyclohexyl-but-3-yn-2-ol (2.28 g, 15 mmol) was dissolved in anhydrous pentane (50 mL) at room temperature. 4Å molecular sieves (approximately half the volume of the solvent), Amano lipase AK from *pseudomonas fluorescens* (2 g) followed by freshly distilled vinyl acetate (4 mL, 40 mmol) were added. The slurry was stirred 5 h at room temperature. NMR of the crude reaction mixture indicated that the ratio of acetate to alcohol was approximately 1:1. The mixture was stirred for 30 more minutes, filtered through celite and washed with pentane. Column chromatography afforded (*S*)-4-cyclo-hexyl-but-3-yn-2-ol (1.1 g, 99% yield based on 50% conversion) that was at least 98% *ee* according to Mosher's ester analysis. The absolute configuration was determined by Mosher's ester analysis.[4] It was consistent with the specific rotations of similar compounds prepared from the same method.[3]

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.53 (m, 1H), 2.42 – 2.30 (m, 1H), 1.9 – 1.2 (m, 10H), 1.43 (d, J = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 89.0, 82.3, 58.8, 32.8, 29.1, 26.0, 25.1.
IR (NaCl, thin film): 3333, 2931, 2854, 2240, 1449, 1158, 1078, 897.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{10}H_{16}O$, 175.109; found, 175.109.
$[\alpha]^{20}_D$ -23.0 ° (c 1.00, $CHCl_3$)

Mosher's ester analysis: (+/-)-4-cyclohexyl-but-3-yn-2-ol was converted into a pair of diastereomers of (*R*)-Mosher's esters (DCC, DMAP, (*R*)-Mosher's acid, CH_2Cl_2)[5]. The methyl doublets (δ 1.50 and 1.56 ppm) of the two diastereomers were well resolved by ^{1}H NMR and were assigned according to the method of Mosher.[4]

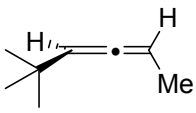


The enantiomerically-enriched alcohol was then converted to (*R*)-Mosher's ester, and a doublet was observed at δ 1.56 ppm. Therefore, 4-cyclo-hexyl-but-3-yn-2-ol prepared from lipase resolution had an absolute configuration of (*S*).

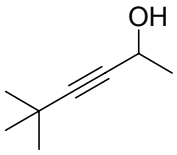


c. Preparation of **(a*S*)-buta-1,2-dienyl-cyclohexane by the method of Myers[6] (2b)**. Triphenylphosphine (5 g, 15 mmol) was dissolved in THF (20 mL). The solution was cooled in a MeOH / ice bath, and diethylazodicarboxylate (DEAD) (2.4 mL, 15 mmol) was added to the solution over 1 min. The solution was stirred 10 min below -10 ºC. (*S*)-4-cyclohexyl-but-3-yn-2-ol (1.52 g, 10 mmol) in THF (10 mL) was added. THF (5 mL) was used to rinse the rest of the alcohol into the reaction mixture. The mixture was stirred 10 min, and *o*-nitrobenzenesulfonyl- hydrazine[7] (3.3 g, 15 mmol in 20 mL THF) was added. The mixture was kept below 0 ºC for 2 h and was allowed to warm to room temperature and stirred 16 h. The reaction was cooled to 0 ºC, diluted with pentane (200 mL) and washed 10 times with ice cold water to remove THF. Column chromatography in pentane afforded (a*S*)-buta-1,2-dienyl-cyclohexane (0.95 g, 70% yield, 98% *ee* based on chiral GC analysis). The absolute configuration of the allene was determined[6] based on the absolute configuration of the alcohol and was consistent with Lowes-Brewster rule.[8] The spectral data are consistent with literature values.[9]

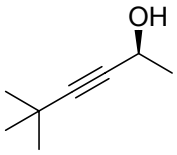
^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.09 (m, 1H), 5.04 (m, 1H), 2.00 – 1.91 (m, 1H), 1.80 – 1.00 (m, 10H), 1.65 (dd, J = 3.4, 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 203.7, 96.7, 86.5, 37.4, 33.3, 26.4, 26.3, 15.0.
IR (NaCl, thin film): 2924, 2852, 1965, 1448, 960, 869, 711.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{10}H_{16}$, 136.125; found, 136.125.
$[\alpha]^{20}_D + 76.7^\circ$ (c 1.46, $CHCl_3$)
Chiral GC analysis: (Chiraldex B-DA, 60 ºC isotherm, 1.5 mL/min): t_R(a*S*) = 21.1 min; t_R(a*R*) = 22.6 min.



(a*S*)-5,5-dimethyl-hexa-2,3-diene (2c).



a. Preparation of (+/-)-**5,5-dimethyl-hex-3-yn-2-ol**. THF (80 mL) was cooled to -78 ºC. *tert*-butylacetylene (7.35 mL, 60 mmol) was added. MeLi (56 mL, 90 mmol, 1.6 M in diethylether) was added via a syringe pump over 10 min. The mixture was stirred 1 h at -78 ºC. Acetaldehyde (6.7 mL, 120 mmol) was added. The mixture was stirred at -78 ºC for one more hour and warmed to room temperature. The reaction was cooled to 0 ºC and quenched with water. The cold mixture was diluted with diethylether (150 mL) and washed two times with water. The ether solution was dried by $MgSO_4$ and was filtered through silica gel. The silica gel was washed with diethyl ether. The NMR of the crude reaction mixture indicated 5,5-dimethyl-hex-3-yn-2-ol along with some cyclotrimer of acetaldehyde. (53.4 mmol alcohol based on NMR integration, 89% yield). The crude product was used without further purification.

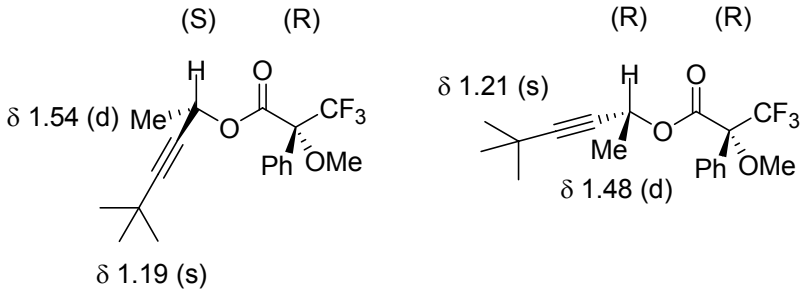


b. Preparation of **(*S*)-5,5-dimethyl-hex-3-yn-2-ol** by lipase resolution. Prepared using the same lipase resolution procedure as described above (lipase, 4Å MS, vinylacetate, pentane, room temperature, 5.5 h. 88.5% isolated yield. > 98% *ee* based on chiral GC analysis and Mosher's ester analysis).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.49 (q, J = 6.5 Hz, 1H), 2.1 (bs, 1H), 1.39 (d, J = 6.5 Hz, 3H), 1.19 (s, *9*H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 92.9, 80.9, 68.1, 58.6, 31.2, 25.0.
IR (NaCl, thin film): 3336, 2971, 2237, 1363, 1263, 1125, 1050, 973, 882.
$[\alpha]^{20}_D$ -27.3 ° (c 1.06, $CHCl_3$)

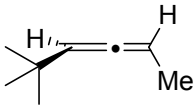
Mosher's ester analysis: (+/-)-5,5-dimethyl-hex-3-yn-2-ol was converted into a pair of diastereomers of (*R*)-Mosher's esters (DCC, DMAP, (*R*)-Mosher's acid, CH_2Cl_2)[5]. The methyl doublets (δ 1.48 and 1.54 ppm) and *t*-Bu singlets (δ 1.19 and 1.21 ppm) of the two diastereomers were well resolved by ^{1}H NMR and were assigned according to the

method of Mosher.[4]



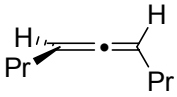
The enantiomerically-enriched alcohol was converted to (*R*)-Mosher's ester. A doublet was observed at δ 1.54 ppm, and a singlet was observed at δ 1.19 ppm. Therefore, 5,5-dimethyl-hex-3-yn-2-ol prepared from lipase resolution had an absolute configuration of (*S*).

Chiral GC analysis: (Chiraldex B-PH, 60 ºC isotherm, 0.3 mL/min): t_R(*S*) = 69.0 min; t_R(*R*) = 72.3 min.



c. Preparation of **(a*S*)-5,5-dimethyl-hexa-2,3-diene (2c)**. Prepared using the same method as described above for **2b**. After the removal of THF by an aneous workup, the pentane solution was filtered through a pad of silica gel to remove most of the by-products. The pentane was removed by rotavap at atmospheric pressure, and the last traces of pentane were removed by fractional distillation. Finally, the product was separated from the crude mixture by distilling under high vacuum at room temperature, collecting in a cooled flask, affording 60% of (a*S*)-5,5-dimethyl-hexa-2,3-diene. The absolute configuration of the allene was assigned[6] based on the absolute configuration of the alcohol and was consistent with Lowes-Brewster rule.[8]

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.12 (quintet , *J* = 6.8 Hz, 1H), 5.06 (dq, *J* = 3.3, 6.42 Hz, 1H), 1.67 (dd, *J* = 3.3, 6.9 Hz, 3H), 1.04 (s, *9*H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 202.1, 102.6, 87.4, 31.9, 30.4, 15.1.
IR (NaCl, thin film): 2962, 1962, 1462, 1363, 1192, 873, 725.
$[\alpha]^{20}_D$ +67.7 ° (c 1.24, $CHCl_3$) (consistent with similar compounds[10])



(a*S*)-nona-4,5-diene (2a). Prepared using the same method as **2b** and **2c** from (*S*)-non-5-yn-4-ol, which was prepared by lipase resolution using the procedure described above (60% yield from (*S*)-non-5-yn-4-ol, 95% *ee*). The absolute configuration was assigned by comparing the specific rotation of **2a** with the literature value [11] and is also consistent with the Lowes-Brewster rule.[8]

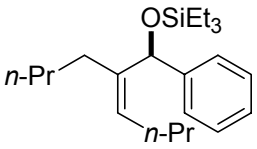
^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.07 (m, 2H), 1.97 (m, 4H), 1.44 (sextet, J = 7.3 Hz, 4H), 0.94 (t, J = 7.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 204.2, 90.8, 31.4, 22.7, 13.9.
IR (NaCl, thin film): 2960, 2931, 1963, 1464, 879.
$[\alpha]^{20}_D$ +64.0 ° (c 1.00, $CHCl_3$)
$[\alpha]^{20}_D$ +84.7 ° (c 0.72, EtOH)
Literature[11] $[\alpha]^{20}_D$ +80.0 ° (c 0.69, EtOH)

Chiral GC analysis: (Chiraldex B-PH, 35 ºC isotherm, 0.1 mL/min): t_R(a*R*) = 74.7 min; t_R(a*S*) = 81.2 min.

Nickel-catalyzed reductive couplings of allenes and aldehdyes.

General procedure. A 25 mL round bottom flask and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (28 mg, 0.1 mmol, 20 mol%) and NHC-IPr (78 mg, 0.2 mmol, 40 mol%) were added to the round bottom flask, the flask was sealed with a septum, and the sealed flask was brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in THF (7.5 mL) under argon and stirred 10 min at room temperature. The solution was cooled to -78 ºC in a dry ice / acetone bath. After 10 min of cooling, triethylsilane (240 μL, 1.5 mmol, 300 mol%), *tert*-butyldimethylsilane (250 μL, 1.5 mmol, 300 mol%), or dimethylphenylsilane (233 μL, 1.5 mmol, 300 mol%), as specified below, was added in one portion. Next the aldehyde (1.5 mmol, 300 mol%) was added in one portion. The mixture was stirred 5 min at -78 ºC. The allene (0.5 mmol, 100 mol%) was added to the reaction mixture in one portion. The reaction was kept in the dry ice / acetone bath and the bath was allowed to warm to room temperature over 6 h. The reaction was stirred an additional 12 h at room temperature. ^{1}H NMR of an aliquot of the crude (after filtering through a plug of silica) indicated the allylic alcohol was the

major coupling product along with minor impurities assigned as various homoallylic alcohols. The ratio of the allylic to homoallylic products was determined by the ^{1}H NMR integration of spectrum of the crude mixture (Refer to ***Table 1*** for the ratio). THF and excess silane were removed under reduced pressure and the crude mixture was diluted in hexane. Purification via flash chromatography on silica afforded the allylic alcohol coupling product.



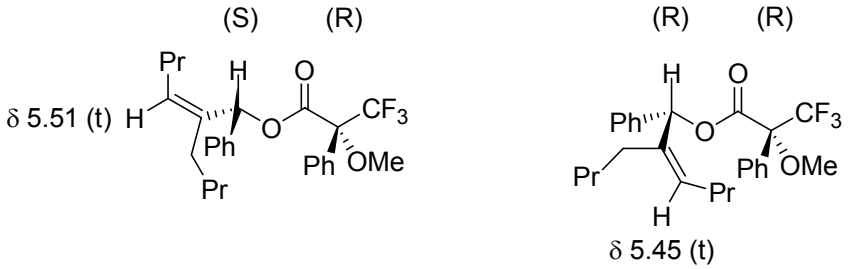
(2-Butyl-1-phenyl-hex-2-enyloxy)-triethyl-silane (3a). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3a** in 77% isolated yield and 95% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was determined by Mosher's ester analysis to be *R*. The olefin geometry was determined to be Z by a nOe experiment (see below).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.16 – 7.40 (m, 5H); 5.76 (s, 1H); 5.24 (t, *J* = 7.3 Hz, 1H); 2.27 (q, *J* = 7.5 Hz, 2H); 2.02 (m, 1H); 1.74 (m, 1H); 1.51 (sextet, *J* = 7.5 Hz, 2H); 1.14 – 1.34 (m, 4H); 1.01 (t, *J* = 6.7 Hz, 3H); 0.97 (t, *J* = 7.6 Hz, 9H); 0.81 (t, *J* = 7.0 Hz, 3H); 0.64 (q, *J* = 7.9 Hz).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.5, 141.9, 128.0, 126.5, 125.6, 125.4, 71. 3, 31.0, 30.4, 29.6, 23.6, 22.9, 14.34, 14.26, 7.11, 7.07.
IR (NaCl, thin film): 2957, 2875, 1458, 1063, 742, 698.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{22}H_{38}OSi$, 369.258; found, 369.259.
$[\alpha]^{20}_D$ -75.2 ° (c 1.07, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3a** (TBAF, THF): (Chiralcel OD, hexanes: 2-propanol, 99:1, 1.0 mL/min): t_R(*S*) = 9.7 min; t_R(*R*) = 10.8 min.

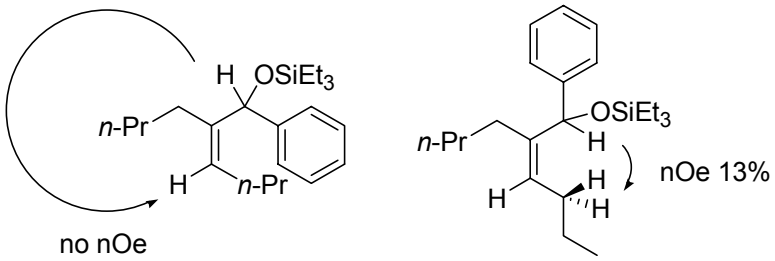
Mosher's ester analysis: (+/-)-**3a** was first converted into the free alcohol (TBAF, THF) and was then converted into a pair of diastereomers of (*R*)-Mosher's esters (DCC, DMAP, (*R*)-Mosher's acid, CH_2Cl_2)[5]. The vinyl triplets (δ 5.45 and 5.51 ppm) of the two

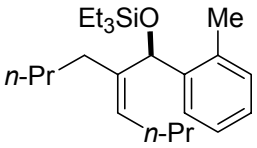
diastereomers were well resolved by ^{1}H NMR and were assigned according to the method of Mosher.[4]



The enantiomerically-enriched **3a** was then converted to (*R*)-Mosher's ester using the same procedure.[5] The vinyl triplet was observed at δ 5.46 ppm. Therefore **3a** had an absolute configuration of (*R*).

NOE DIFF experiment: Pre-saturation of the carbinol proton of **3a** gave no nOe to the vinylic proton (δ 5.24 ppm), but 13% nOe was observed for the allylic protons indicated (δ 2.27 ppm). These results supported a Z olefin geometry.



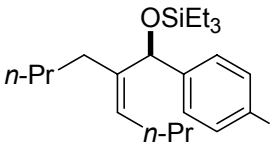


(2-Butyl-1-*o*-tolyl-hex-2-enyloxy)-triethyl-silane (3b). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and *o*-tolualdehyde (174 μL, 1.5 mmol) with Ni(cod)$_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3b** in 66% yield and 95% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configurations were established by Mosher's ester analysis.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 (bd, *J* = 7.6 Hz, 1H), 7.21 (bt, *J* = 7.4 Hz, 1H), 7.13

(dt, J = 1.4, 7.4 Hz, 1H), 7.04 (bd, J = 7.4 Hz, 1H), 5.75 (s, 1H), 5.20 (t, J = 6.6 Hz, 1H), 2.38 – 2.22 (dq, J = 7.5, 14.8 Hz, 2H), 2.20 (s, 3H), 1.91 (ddt, J = 1.1, 5.4, 10.32 Hz, 1H), 1.65 (ddt, J = 1.0, 6.7, 9.8 Hz, 1H), 1.49 (sextet, J = 6.9 Hz, 2H), 1.16 (m, 3H), 1.03 (t, J = 5.6 Hz, 4H), 0.94 (t, J = 8.0 Hz, 9H), 0.77 (t, J = 7.1 Hz, 3H), 0.60 (q, J = 7.5 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 142.2, 139.1, 134.2, 129.8, 126.9, 126.7, 126.5, 125.6, 69.1, 31.7, 30.6, 30.5, 23.5, 22.8, 19.6, 14.4, 14.2, 7.1, 5.2.
IR (NaCl, thin film): 2957, 2875, 1462, 1061, 1006, 744.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{23}H_{40}OSi$, 383.274; found, 383.274.
$[\alpha]^{20}_D$ -75.2 ° (c 1.25, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3b** (TBAF, THF) (Chiralcel OD, hexanes: 2-propanol, 99:1, 1.0 mL/min): t_R(*S*) = 11.4 min; t_R(*R*) = 14.1 min.

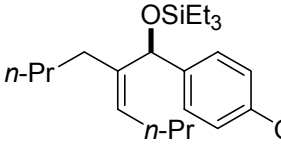


(2-Butyl-1-*p*-tolyl-hex-2-enyloxy)-triethyl-silane (3c). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and *p*-tolualdehyde (177 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3c** in 74% yield and 95% enantiomeric excess as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.24 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 5.74 (s, 1H), 5.22 (t, J = 7.0 Hz, 1H), 2.34 (s, 3H), 2.27 (q, J = 7.3 Hz, 2H), 2.03 (m, 1H), 1.74 (m, 1H), 1.50 (sextet, J = 7.3 Hz, 2H), 1.38 – 1.18 (m, 4H), 1.00 (t, J = 7.3 Hz, 3H), 0.97 (t, J = 7.9 Hz, 9H), 0.82 (t, J = 7.0 Hz, 3H), 0.63 (q, J = 7.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 142.0, 141.5, 136.0, 128.7, 125.6, 125.1, 71.2, 31.0, 30.3, 29.6, 23.6, 22.9, 21.3, 14.33, 14.28, 7.1, 5.1.
IR (NaCl, thin film): 2957, 2875, 1458, 1073, 1006, 741.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{23}H_{40}OSi$, 383.274; found, 383.275.
$[\alpha]^{20}_D$ -83.8 ° (c 1.05, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3c** (TBAF, THF): (Chiralcel OD, hexanes: 2-propanol,

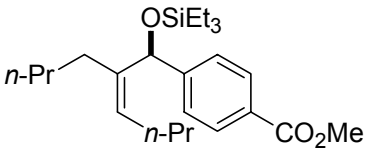
100:0, 1.5 mL/min): $t_R(R)$ = 37.7 min; $t_R(S)$ = 49.1 min.



2-Butyl-1-(4-methoxy-phenyl)-hex-2-enyloxy]-triethyl-silane (3d). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and *p*-anisaldehyde (183 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3d** in 75% yield and 95% enantiomeric excess as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.28 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.73 (s, 1H), 5.23 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 2.26 (q, *J* = 7.6 Hz, 2H), 2.05 (m, 1H), 1.76 (m, 1H), 1.50 (sextet, *J* = 7.2 Hz, 2H), 1.40 – 1.15 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.84 (t, *J* = 7.0, 3H), 0.64 (q, *J* = 7.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.3, 142.1, 136.7, 126.7, 125.1, 113.4, 71.0, 55.4, 31.0, 30.3, 29.6, 23.6, 22.9, 14.33, 14.28, 7.1, 5.1.
IR (NaCl, thin film): 2956, 2875, 1510, 1464, 1246, 1071, 741.
$[\alpha]^{20}_D$ -67.5 ° (c 1.14, $CHCl_3$)

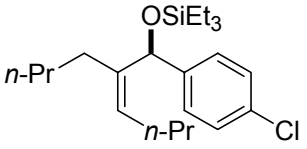
Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3d** (TBAF, THF): (Chiralcel OD, hexanes: 2-propanol, 99:1, 1.0 mL/min): $t_R(R)$ = 14.3 min; $t_R(S)$ = 17.0 min.



4-(2-Butyl-1-triethylsilanyloxy-hex-2-enyl)-benzoic acid methyl ester (3e). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and methyl 4-formylbenzoate (246 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3e** in 56% yield (co-eluted with a small amount of homoallylic alcohol minor products) and 95% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.98 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.0, 2H), 5.79 (s, 1H), 5.26 (t, *J* = 7.0 Hz, 1H), 3.90 (s, 3H), 2.28 (q, *J* = 7.1 Hz, 2H), 1.95 (m, 1H), 1.72 (m, 1H), 1.55 (sextet, *J* = 7.0 Hz, 2H), 1.30 – 1.10 (m, 4H), 1.01 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 9H), 0.79 (t, *J* = 7.3 Hz, 3H), 0.63 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 167.4, 150.1, 141.3, 129.4, 128.5, 126.1, 125.6, 71.2, 52.2, 31.0, 30.4, 29.6, 23.5, 22.8, 14.3, 14.2, 7.06, 5.01.
IR (NaCl, thin film): 2956, 1727, 1277, 1075, 1018, 743.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{24}H_{40}O_3Si$, 427.264; found, 427.266.
$[\alpha]^{20}_D$ -108.6 ° (c 1.28, $CHCl_3$)

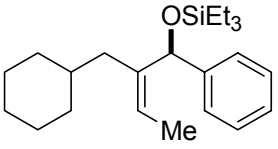
Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3e** (TBAF, THF): (Chiralcel OD, hexanes: 2-propanol, 95:5, 1.0 mL/min): t_R(*R*) = 7.5 min; t_R(*S*) = 19.7 min.



[2-Butyl-1-(4-chloro-phenyl)-hex-2-enyloxy]-triethyl- silane (3f). The reaction of (a*S*)-nona-4,5-diene (**2a**) (82 μL, 0.5 mmol) and *p*-chlorobenzaldehyde solution (211 μL aldehyde, 1.5 mmol in 1mL THF) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above yielded **3f** in 65% yield and 1% of dechlorinated product, ie, **3a** (total 66% isolated yield, ratio of **3f** : **3a** in crude NMR is 94:6) and 95% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 7.2 (m, 4H), 5.73 (s, 1H), 5.26 (t, *J* = 7.0 Hz, 1H), 2.27 (q, J = 7.3 Hz, 2H), 2.00 (m, 1H), 1.72 (m, 1H), 1.51 (sextet, *J* = 7.4 Hz, 2H), 1.40 – 1.10 (m, 4H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.83 (t, *J* = 7.3 Hz, 3H), 0.64 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.2, 141.5, 132.2, 128.1, 127.1, 125.8, 70.9, 31.0, 30.4, 29.6, 23.6, 22.9, 14.3, 14.2, 7.1, 5.1.
IR (NaCl, thin film): 2957, 1488, 1074, 1014, 726.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{22}H_{37}OClSi$, 403.219; found, 403.220.
$[\alpha]^{20}_D$ -88.9 ° (c 1.17, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3f** (TBAF, THF): (Chiralcel OD-H, hexanes: 2-propanol, 99:1, 1.0 mL/min): $t_R(S)$ = 7.4 min; $t_R(R)$ = 8.6 min.

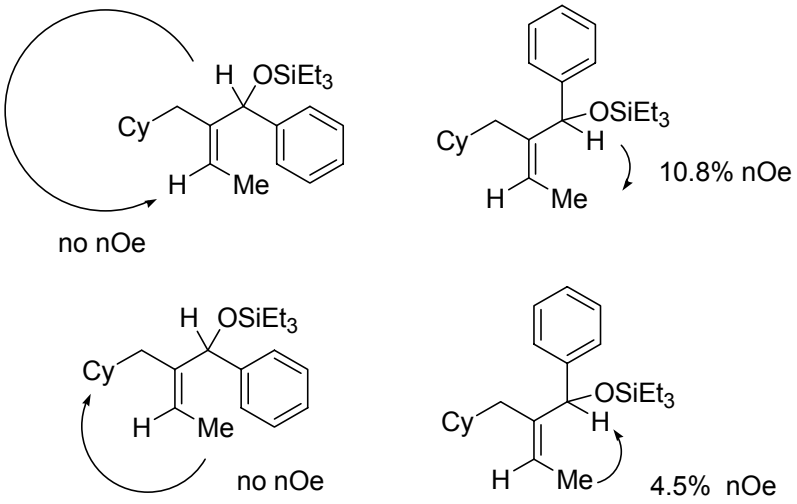


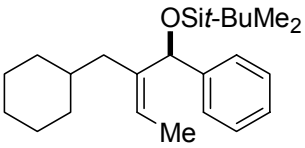
(2-Cyclohexylmethyl-1-phenyl-but-2-enyloxy)-triethyl- silane (3g). The reaction of **2b** (68 mg, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3g** in 76% isolated yield and 98% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis. The olefin geometry was determined to be Z by a nOe experiment (see below).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.79 (s, 1H), 5.30 (q, *J* = 7.0 Hz, 1H), 1.88 (d, *J* = 6.7 Hz, 3H), 1.80 (dd, *J* = 6.5, 14.5 Hz, 1H), 1.68 (dd, *J* = 7.0, 14.5 Hz), 1.64 – 1.54 (m, 6H), 1.28 – 1.18 (m, 1H), 1.12 – 1.00 (m, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.76 – 0.58 (m, 1H), 0.64 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.6, 140.8, 128.0, 126.5, 125.6, 120.4, 70.9, 39.2, 36.1, 33.8, 33.5, 27.0, 26.7, 13.9, 7.1, 5.1.
IR (NaCl, thin film): 2954, 2921, 1449, 1091, 1064, 863, 737.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{23}H_{38}OSi$, 381.258; found, 381.259.
$[\alpha]^{20}_D$ -58.0 ° (c 1.12, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3g** (TBAF, THF): (Chiralcel OD-H, hexanes: 2-propanol, 99:1, 1.0 mL/min): $t_R(S)$ = 11.3 min; $t_R(R)$ = 17.4 min.

NOE DIFF experiment: Pre-saturation of the carbinol proton (δ 5.79 ppm) of **3g** gave no nOe to the vinylic proton (δ 5.30 ppm). A 10.7% nOe to the methyl group, however, was observed. Similarly, pre-saturation of the methyl protons (δ 1.88 ppm) did not show any nOe to the cyclohexyl protons. A 4.5% nOe to the carbinol proton (δ 5.79 ppm), however, was observed. (see below).



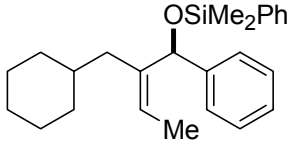


***tert*-Butyl-(2-cyclohexylmethyl-1-phenyl-but-2-enyloxy)-dimethyl-silane (3h)**. The reaction of **2b** (68 mg, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and *tert*-butyldimethyl- silane in THF following the general procedure described above afforded **3h** in 68% isolated yield and 98% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.10 (m, 5H), 5.80 (s, 1H), 5.31 (q, *J* = 7.0 Hz, 1H), 1.88 (d, *J* = 7.0 Hz, 3H), 1.77 (dd, *J* = 7.1, 14.8 Hz, 1H), 1.66 (dd, *J* = 7.0, 14.6 Hz, 1H), 1.57 (m, 6H), 1.30 – 0.50 (m, 5H), 0.96 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.5, 140.5, 127.9, 126.5, 125.6, 120.5, 71.1, 39.1, 35.9, 33.8, 33.5, 26.9, 26.6, 26.2, 18.6, 13.8, -4.6, -4.8.
IR (NaCl, thin film): 2926, 2854, 1449, 1252, 1090, 1064, 876, 835, 775, 698.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{23}H_{38}OSi$, 381.258; found, 381.260.
$[\alpha]^{20}_D$ -55.9 ° (c 1.11, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed **3h** without the deprotection of the silane protected alcohol: (Chiralcel OD-H, hexanes: 2-propanol, 100:0, 0.8 mL/min): $t_R(R)$ = 4.1

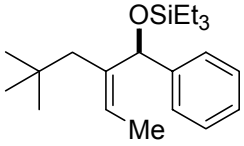
min; $t_R(S)$ = 4.4 min.



(2-Cyclohexylmethyl-1-phenyl-but-2-enyloxy)-dimethyl-phenyl-silane (**3i**). The reaction of **2b** (68 mg, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and dimethylphenylsilane in THF following the general procedure described above afforded **3i** in 65% isolated yield and 98% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was assigned as *R* in analogy to **3a** and **3j** whose configuration were established by Mosher's ester analysis.

^{1}H NMR (500 MHz, C_6D_6, δ): 7.66 – 7.61 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 5H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.89 (s, 1H), 5.25 (q, *J* = 6.7 Hz, 1H), 2.02 (dd, *J* = 7.0, 14.7 Hz, 1H), 1.93 (dd, *J* = 7.0, 14.7 Hz, 1H), 1.74 – 1.58 (m, 5H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.35 (m, 1H), 1.10 (m, 3H), 0.82 – 0.60 (m, 2H), 1.57 (s, 3H), 1.55 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.0, 139.9, 138.2, 133.8, 129.7, 127.99, 127.96, 126.6, 125.6, 121.1, 71.4, 39.1, 36.1, 33.8, 33.5, 26.9, 26.6, 13.6, -0.9, -1.0.
IR (NaCl, thin film): 2921, 2850, 1449, 1428, 1251, 1118, 1088, 1057, 881, 829, 785, 737, 698.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{25}H_{34}OSi$, 401.227; found, 401.227.
$[\alpha]^{20}_D$ -19.0 ° (c 1.00, $CHCl_3$)

Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3i** (TBAF, THF): (Chiralcel OD-H, hexanes: 2-propanol, 99:1, 1.0 mL/min): $t_R(S)$ = 11.3 min; $t_R(R)$ = 17.4 min.

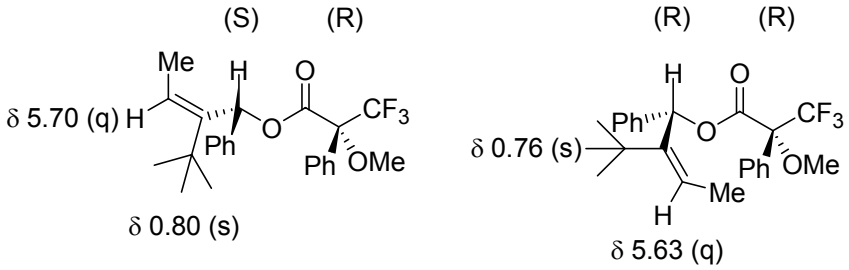


Triethyl-(2-ethylidene-4,4-dimethyl-1-phenyl-pentyloxy)- silane (3j). The reaction of **2c** (55 mg, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane in THF following the general procedure described above afforded **3j** in 40% isolated yield (co-eluted with a homoallylic alcohol minor product) and 98% *ee* as determined by chiral HPLC. The absolute configuration of the stereocenter was determined by Mosher's ester analysis to be *R*.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.72 (s, 1H), 5.46 (q, *J* = 7.0 Hz, 1H), 1.91 (d, *J* = 7.0 Hz, 3H), 1.86 (d, *J* = 14.6 Hz, 1H), 1.77 (d, *J* = 14.6 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9 H), 0.80 (s, 9H), 0.61 (qd, *J* = 2.4, 7.6 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.7, 140.5, 127.8, 126.4, 125.9, 122.9, 71.7, 43.3, 30.7, 22.7, 14.0, 6.9, 4.9.
IR (NaCl, thin film): 2954, 1463, 1091, 1065, 1006, 742.
$[\alpha]^{20}_D$ -29.8 ° (c 1.14, $CHCl_3$)

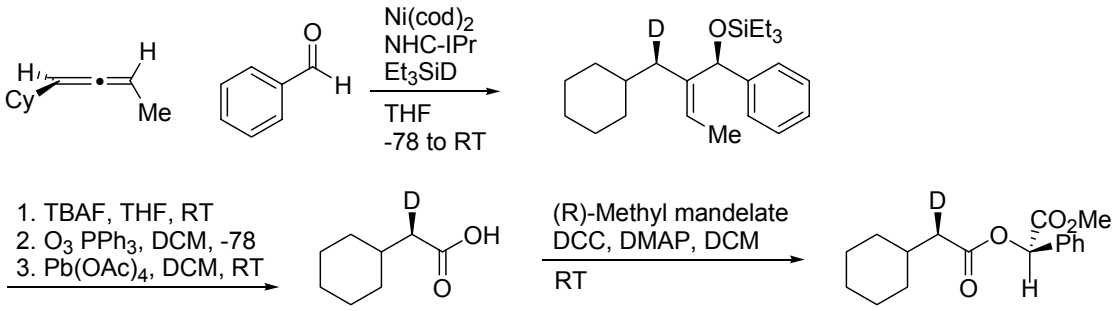
Chiral HPLC analysis: Analysis was performed on the corresponding free alcohol, obtained by the deprotection of **3j** (TBAF, THF): (Chiralcel OD-H, hexanes: 2-propanol, 99:1, 1.0 mL/min): t_R(*S*) = 10.4 min; t_R(*R*) = 13.3 min.

Mosher's ester analysis: (+/-)-**3j** was first converted into the free alcohol (TBAF, THF) and then into a pair of diastereomers of (*R*)-Mosher's esters (DCC, DMAP, (*R*)-Mosher's acid, CH_2Cl_2)[5]. The vinylic quartets (δ 5.63 and 5.70 ppm) and the *t*-Bu singlets (δ 0.76 and 0.80 ppm) of the two diastereomers were well resolved by ^{1}H NMR and were assigned according to the method of Mosher.[4]

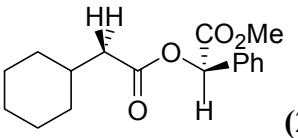


The enantiomerically-enriched **3j** was then converted to (*R*)-Mosher's ester using the same procedure.[5] The vinylic quartet was observed at δ 5.64 ppm, and the t-Bu singlet was observed at δ 0.75 ppm. Therefore, **3a** had an absolute configuration of (*R*).

Deuterium label experiment.



^{2}H-3g (ie, **5a**) can be derivatized to a mandelic acid derivative **4** to determine the absolute configuration of the deuterated stereocenter using ^{1}H NMR by Parker's method.[12] The same mandelic acid derivative was also prepared by Fleming[13] and was also analyzed by the method of Parker.[12]



(2-Cyclohexyl-acetoxy)-phenylacetic acid methyl ester (^{1}H-4). Cyclohexylacetic acid (31.3 mg, 0.22 mmol), methyl-(*R*)-mandelate (33.2 mg, 0.2 mmol), dicyclohexylcarbodiimide (61.9 mg, 0.3 mmol) and 4-(dimethylamino)-pyridine (2.4 mg, 0.02 mmol) were mixed together and dissolved in anhydrous CH_2Cl_2 (2 mL). The mixture was stirred 6 h at room temperature. The CH_2Cl_2 solution was filtered through a plug of silica, the silica was washed with CH_2Cl_2. The filtrate was concentrated and column chromatography afforded **^{1}H-4** (45.1 mg, 78% yield).

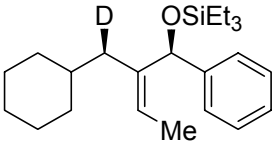
^{1}H NMR (400 MHz, C_6D_6, δ): 7.46 (d, *J* = 7.2 Hz, 2H), 7.10 – 7.00 (m, 3H), 6.09 (s, 1H), 3.18 (s, 3H), 2.22 (dd, *J* = 7.1, 14.9 Hz, 1H), 2.12 (dd, *J* = 7.1, 14.9 Hz, 1H), 1.86 (m, 1H), 1.73 (m, 2H), 1.60 – 1.40 (m, 3H), 1.22 – 1.10 (m, 2H), 1.10 – 0.90 (m, 1H), 0.90 – 0.75 (m, 2H).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.50 – 7.35 (m, 5H), 5.93 (s, 1H), 3.73 (s, 3H), 2.37 (dd, *J* = 7.0, 15.0 Hz, 1H), 2.31 (dd, *J* = 7.0, 14.9 Hz, 1H), 1.92 – 1.61 (m, 6H), 1.36 – 0.60 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.6, 169.6, 134.1, 129.4, 128.9, 127.7, 74.4, 52.7, 41.9, 35.0, 33.1, 26.3, 26.2.

IR (NaCl, thin film): 2925, 2852, 1760, 1743, 1450, 1216, 1159, 1114, 1044, 734.

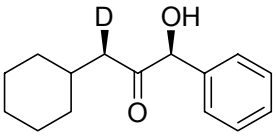
$[\alpha]^{20}_{D}$ -90.3 ° (c 1.03, $CHCl_3$)



(2-Cyclohexylmethyl-2-deuterio-1-phenyl-but-2-enyloxy)-triethyl-silane (5a / ^{2}H-3g). The reaction of **2b** (68 mg, 0.5 mmol) and benzaldehyde (152 μL, 1.5 mmol) with $Ni(cod)_2$, NHC-IPr and triethylsilane-d (239 μL, 1.5 mmol) in THF, following the general procedure described above afforded **5a / ^{2}H-3g** (111 mg, 64% yield) in 98% *ee* as determined by chiral HPLC and >95:5 *dr* as determined by ^{1}H NMR.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.78 (s, 1H), 5.28 (q, *J* = 6.9 Hz, 1H), 1.87 (d, *J* = 7.0 Hz, 3H), 1.76 (bd, *J* = 6.6 Hz, 1H), 1.62 – 1.52 (m, 6H), 1.26 – 1.16 (m, 1H), 1.12 – 1.00 (m, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.76 – 0.58 (m, 1H), 0.62 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.6, 140.7, 127.9, 126.5, 125.6, 120.4, 70.9, 38.8 (t, *J* = 19.5 Hz), 36.0, 33.8, 33.5, 26.9, 26.6, 13.9, 7.1, 5.1.
IR (NaCl, thin film): 2920, 1448, 1090, 1064, 731.
HRMS-ESI (m / z): $[M + Na]^+$ calcd for $C_{23}H_{37}DOSi$, 382.265; found, 382.264.
$[\alpha]^{20}_{D}$ -57.8 ° (c 1.02, $CHCl_3$)

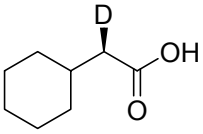
Chiral HPLC analysis: Analysis was performed on the deprotected **5a / ^{2}H-3g** (TBAF, THF): (Chiralcel OD-H, hexanes: 2-propanol, 99:1, 1.0 mL/min): t_R(*S*) = 11.1 min; t_R(*R*) = 17.3 min.



3-Cyclohexyl-3-deuterio-1-hydroxy-1-phenyl-propan-2-one (5b). **5a** / **^{2}H-3g** (96 mg, 0.27 mmol) was stirred 30 min in TBAF (1 mL, 0.5 mmol, 0.5M in THF). The mixture was diluted in diethylether and washed with water. The ether solution was dried in $MgSO_4$, and the solvent was removed under reduced pressure. The crude was dissolved in CH_2CL_2 (5 mL) and was cooled to -78 ºC. Ozone was bubbled through the solution for 20 min, and the solution turned blue. After purging with oxygen

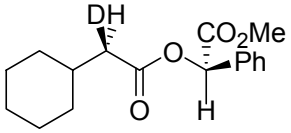
(2 min) triphenylphosphine (157 mg, 0.6 mmol in 5 mL CH_2Cl_2) was added in one portion at -78 ºC, stirred 5 min, and warmed to room temperature. CH_2Cl_2 was removed under reduced pressure. Column chromatography first with 20% CH_2Cl_2 / hexane removed triphenylphosphine. A gradient of 10 – 20 % EtOAc / Hexane afforded **5b** (62 mg, 99% yield) in > 95:5 *dr* as determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.27 (m, 5H), 5.04 (d, J = 4.4 Hz, 1H), 4.43 (d, J = 4.5 Hz, 1H), 2.14 (dt, J = 2.0, 6.9 Hz, 1H), 1.90 – 0.55 (m, 11H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 209.3, 138.1, 129.1, 128.8, 127.7, 80.2, 45.2 (t, J = 19.0 Hz), 34.0, 33.2, 26.2, 26.1, 26.0.
IR (NaCl, thin film): 3458, 2923, 2851, 1711, 1450, 756, 670.
$[\alpha]^{20}_D$ +231.7 ° (c 1.23, $CHCl_3$)

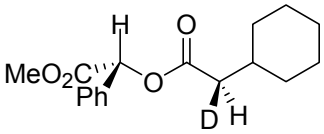


2-Cyclohexy-(2*R*)-deuterio-acetic acid (5c). A 7 mL glass vial was charged with **5b** (60 mg, 0.26 mmol) and lead tetraacetate (115 mg, 0.26 mmol). The vial was purged with nitrogen, CH_2Cl_2 (2.5 mL, saturated with nitrogen) was added. The reaction mixture was stirred 8 h at room temperature, and the CH_2Cl_2 solution was passed through a dry silica gel column (purged with argon) and eluted with CH_2Cl_2 (saturated with argon) under argon to remove benzaldehyde and other low polarity byproducts. **5c** and a minor impurity were eluted with 30% ethylacetate / hexane. Column chromatography with a gradient of 5% - 30% EtOAc / hexane afforded **5c** (14 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 12.2 – 11.0 (bs, 1H), 2.21 (bd, J = 6.5 Hz, 1H), 1.85 – 1.65 (m, 6H), 1.40 – 0.80 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 180.0, 41.8 (t, J = 19.5 Hz), 34.8, 33.2, 33.1, 26.3, 26.2.
IR (NaCl, thin film): 2925, 2852, 1705, 1414, 1295.



(2-Cyclohexyl-(2*R*)-2-deuterio-acetoxy)-phenyl-acetic acid methyl ester (4). **5c** (12 mg, 0.084 mmol), methyl-(*R*)-mandelate (21 mg, 0.09 mmol), dicyclohexylcarbodiimide (26 mg, 0.126 mmol), 4-(dimethyl)-aminopyridine (2 mg, 0.016 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and stirred 12 h at room temperature. The crude reaction mixture was filtered through a plug of silica, and the silica was washed with CH_2Cl_2. Column chromatography in 1% - 5% EtOAc / hexane afforded **4** (15.6 mg, 52% yield). ^{1}H NMR indicated slight erosion of *dr* (>90:10) at the deuterated stereocenter as compared to **5a** / **^{2}H-3g** before derivatization to **4**. The deuterated stereocenter was assigned to be of the *R* configuration, according to the method of Parker,[12] and the analysis was consistent with Fleming's result[13].



(*R*)

(Refer to ^{1}H NMRs of **^{1}H-4**, **4** and **5d** for chemical shifts).

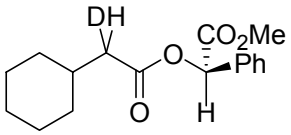
^{1}H NMR (400 MHz, C_6D_6, δ): 7.48 (d, *J* = 6.9 Hz, 2H), 7.07 (t, *J* = 6.0 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.10 (s, 1H), 3.18 (s, 3H), 2.20 (dt, *J* = 1.7, 6.9 Hz, 1H), 1.92 – 1.80 (m, 1H), 1.80 – 1.68 (m, 2H), 1.61 – 1.42 (m, 3H), 1.22 – 1.07 (m, 2H), 1.07 – 0.91 (m, 1H), 0.90 – 0.75 (m, 2H).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 – 7.40 (m, 2H), 7.44 – 7.37 (m, 3H), 5.93 (s, 1H), 3.73 (s, 3H), 2.35 (bd, *J* = 6.9 Hz, 1H), 1.90 – 1.60 (m, 6H), 1.55 – 0.90 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 172.7, 169.6, 134.1, 129.4, 129.0, 127.8, 74.4, 52.8, 41.6 (t, *J* = 20.0 Hz), 35.0, 33.11, 33.08, 26.3, 26.2.

IR (NaCl, thin film): 2924, 2851, 1760, 1743, 1450, 1436, 1216, 1163.

$[\alpha]^{20}_D$ +112.0 ° (c 1.25, $CHCl_3$)



(2*R*)-(2-Cyclohexyl-(2)-deuterio-acetoxy)-phenyl-acetic acid methyl ester and (2*S*)-(2-Cyclohexyl-(2)-deuterio-acetoxy)-phenyl-acetic acid methyl ester (5d). Prepared using the same method as **4** except that (+/-)-**2b** was used to give a mixture of 1:1 diastereomers of **5d**.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.48 (d, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.0 Hz, 2H), 7.04 (t, *J* = 7.1 Hz, 1H), 6.11 (s, 2H), 3.18 (s, 6H), 2.20 (dt, *J* = 1.8, 6.9 Hz, 1H), 2.12 (dt, *J* = 1.8, 7.1 Hz, 1H), 1.92 – 1.80 (m, 1H), 1.80 – 1.68 (m, 2H), 1.61 – 1.42 (m, 3H), 1.22 – 1.07 (m, 2H), 1.07 – 0.91 (m, 1H), 0.90 – 0.75 (m, 2H).
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 – 7.40 (m, 2H), 7.44 – 7.37 (m, 3H), 5.93 (s, 1H), 3.73 (s, 3H), 2.35 (dt, *J* = 1.9, 6.9 Hz, 1H), 2.30 (bd, *J* = 1.8, 7.0 Hz, 1H), 1.90 – 1.60 (m, 6H), 1.55 – 0.90 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 172.7, 169.6, 134.1, 129.4, 129.0, 127.8, 74.4, 52.8, 41.6 (t, *J* = 20.0 Hz), 35.0, 33.11, 33.08, 26.3, 26.2.
IR (NaCl, thin film): 2923, 1850, 1760, 1742, 1215, 1163.

References

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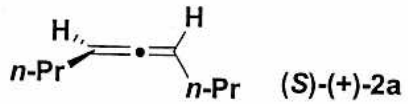

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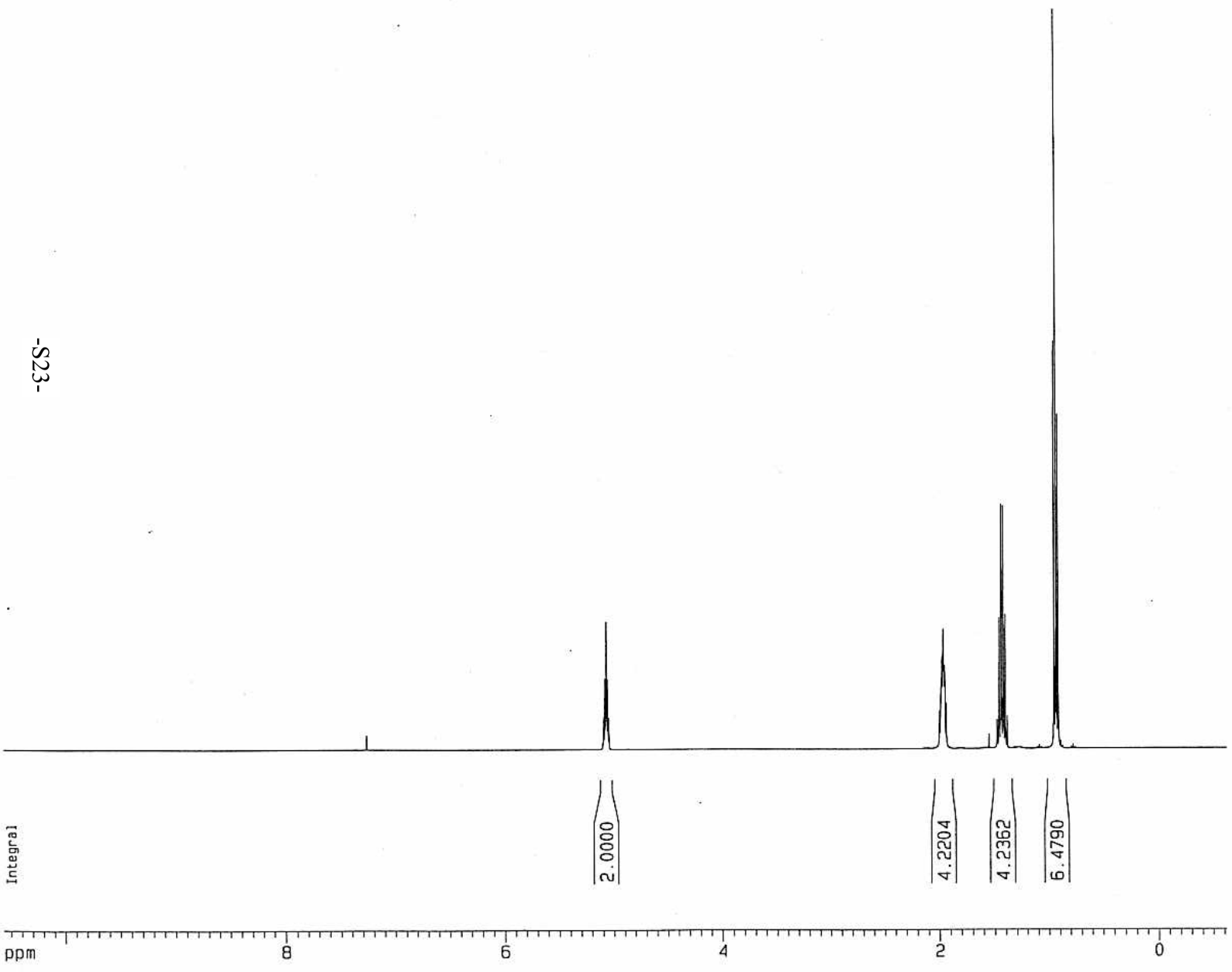


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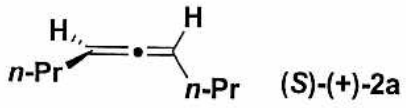

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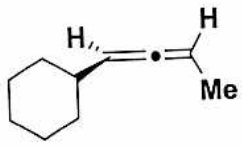

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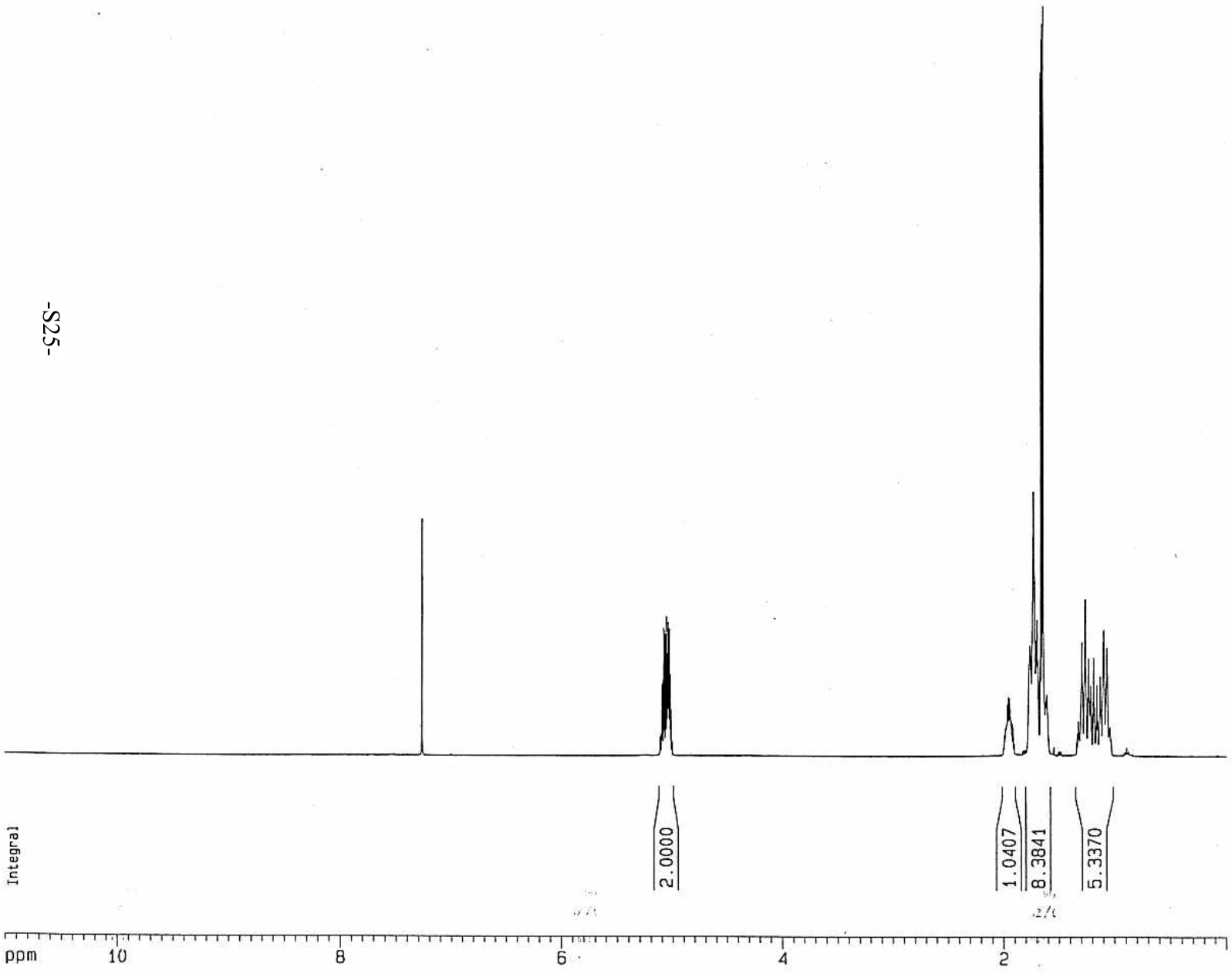


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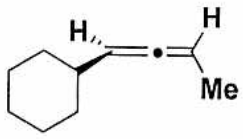

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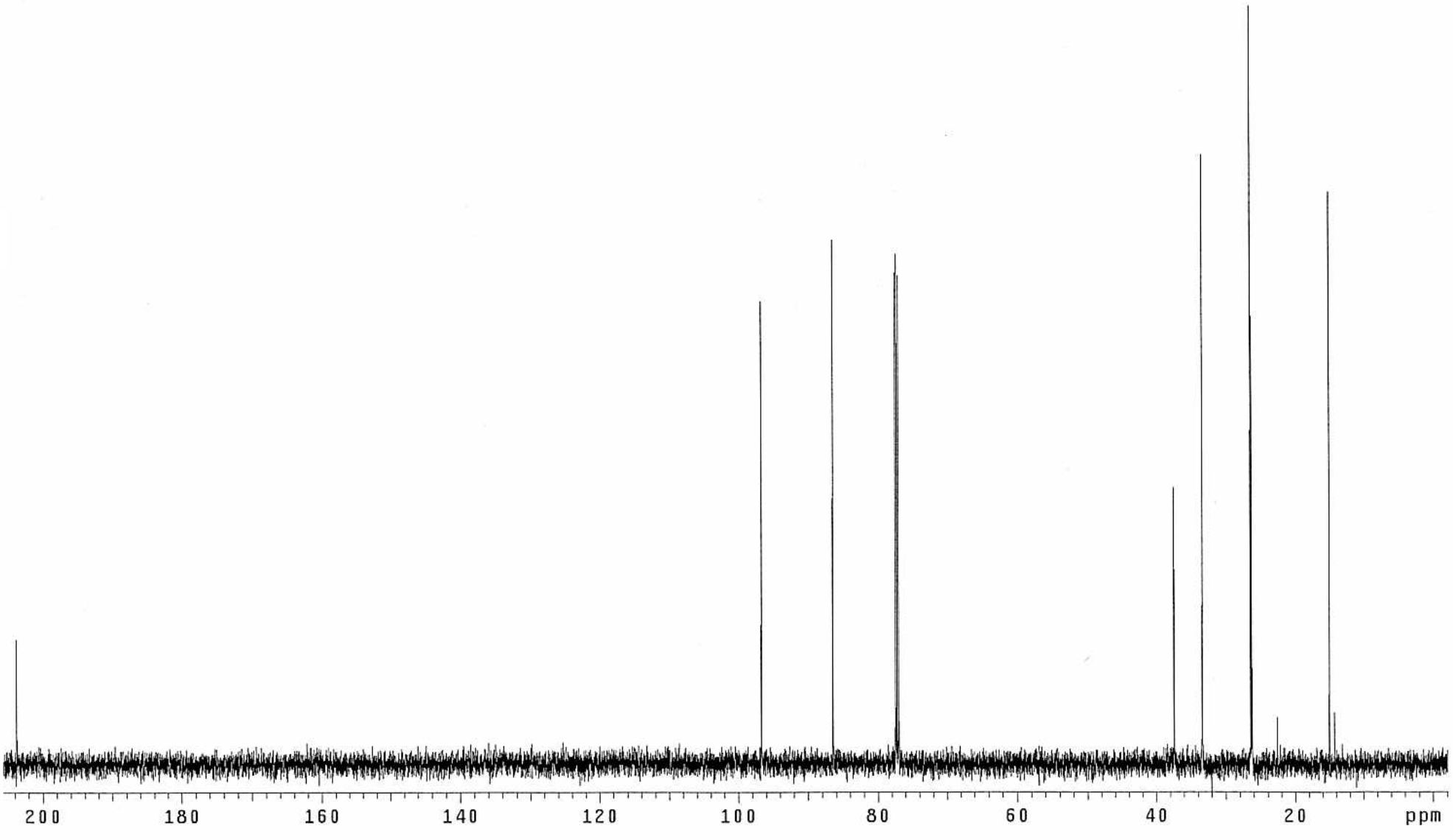

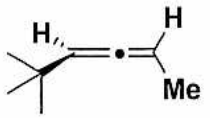

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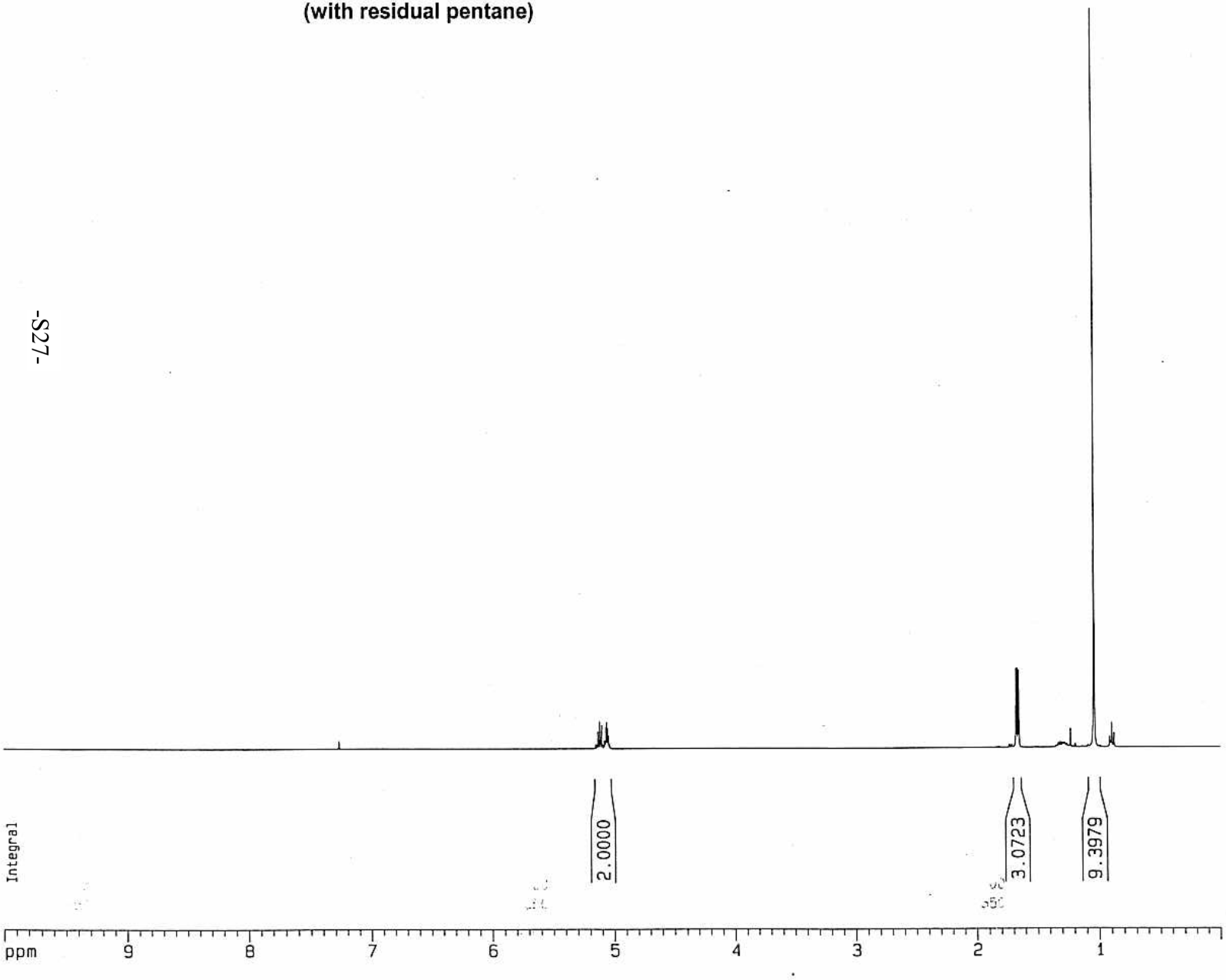


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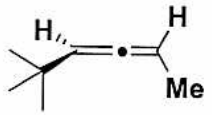
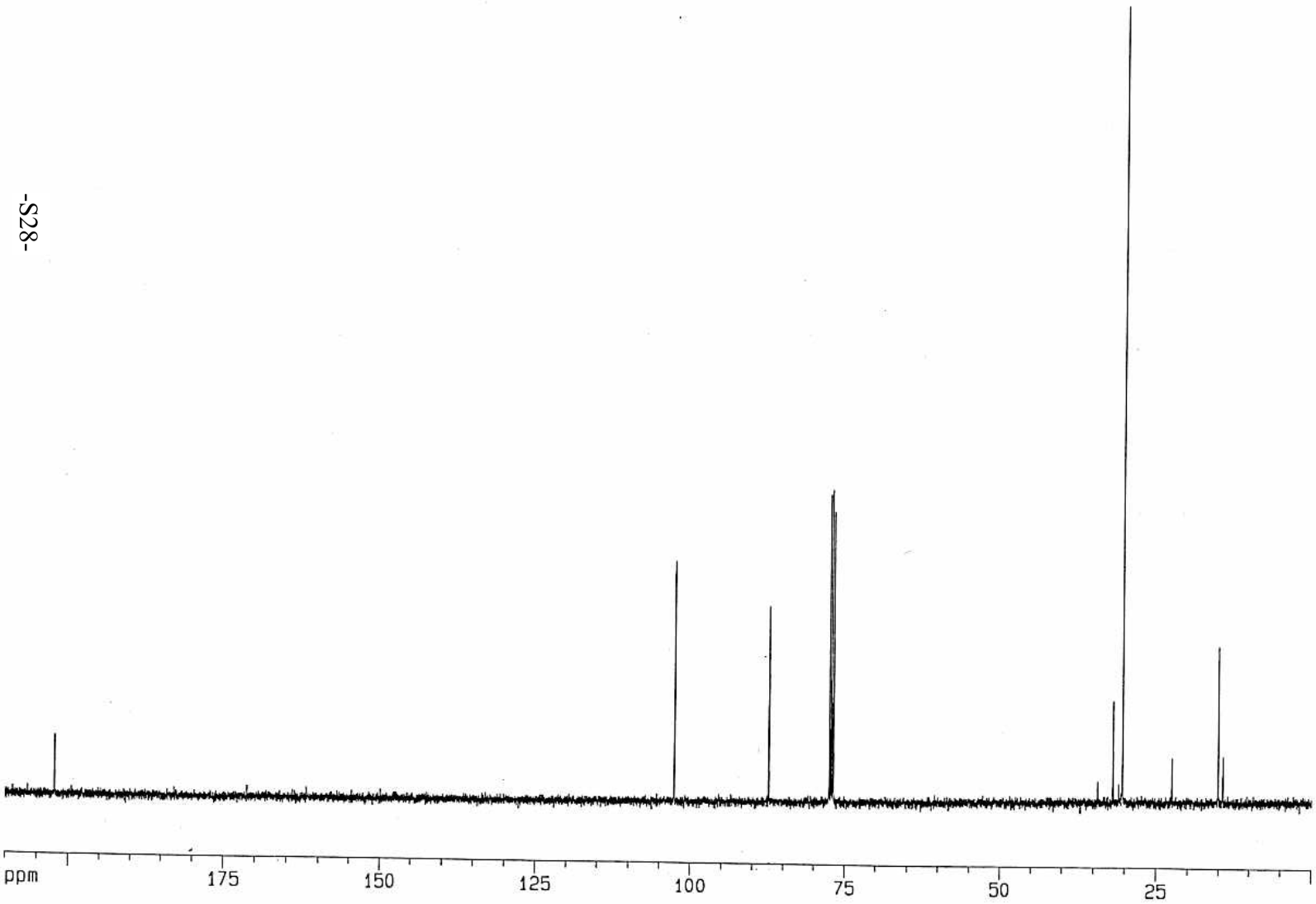


(*S*)-(+)-2c
(with residual pentane)



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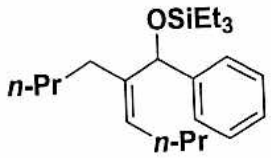
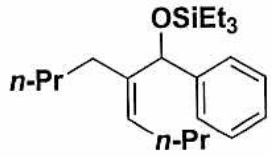
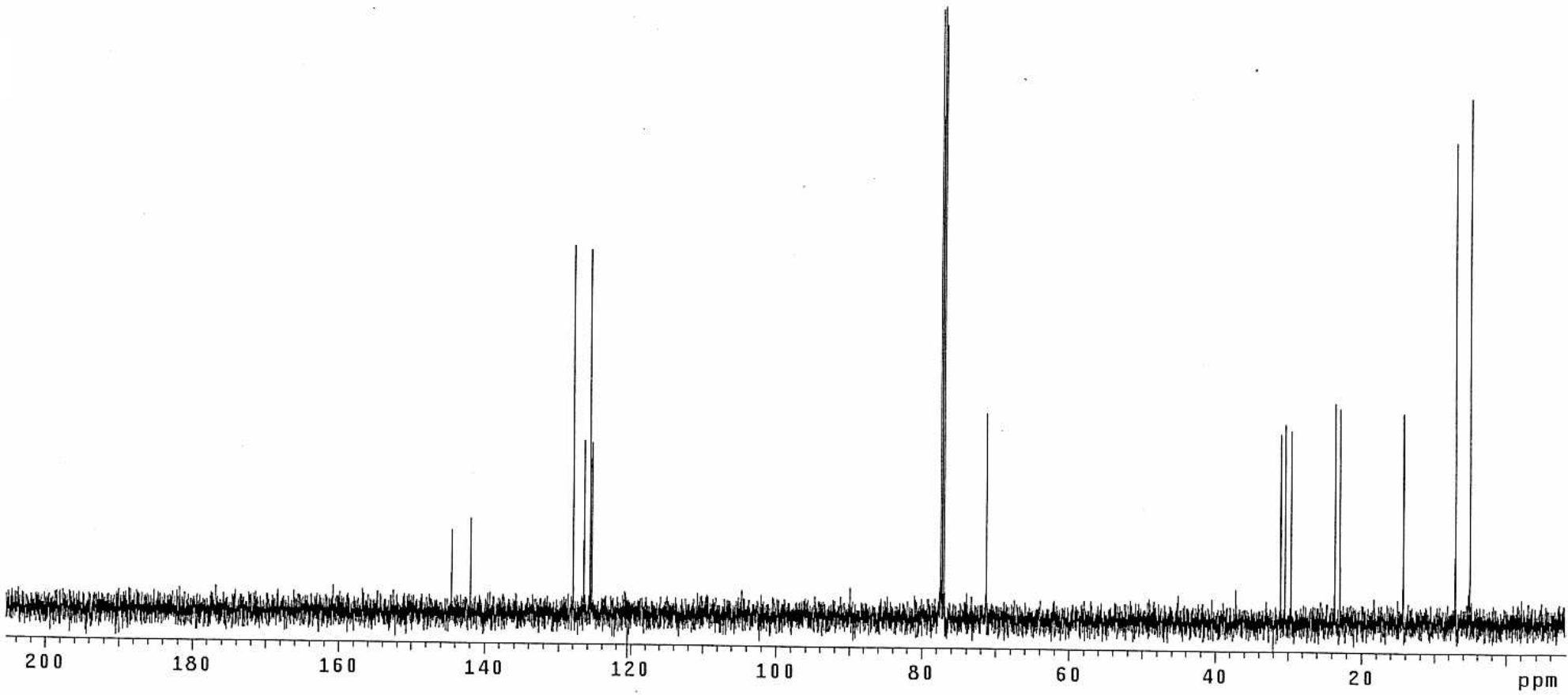
PPMCM	10.50000 ppm/cm
HZCM	1056.43384 Hz/cm

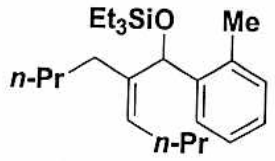


3a



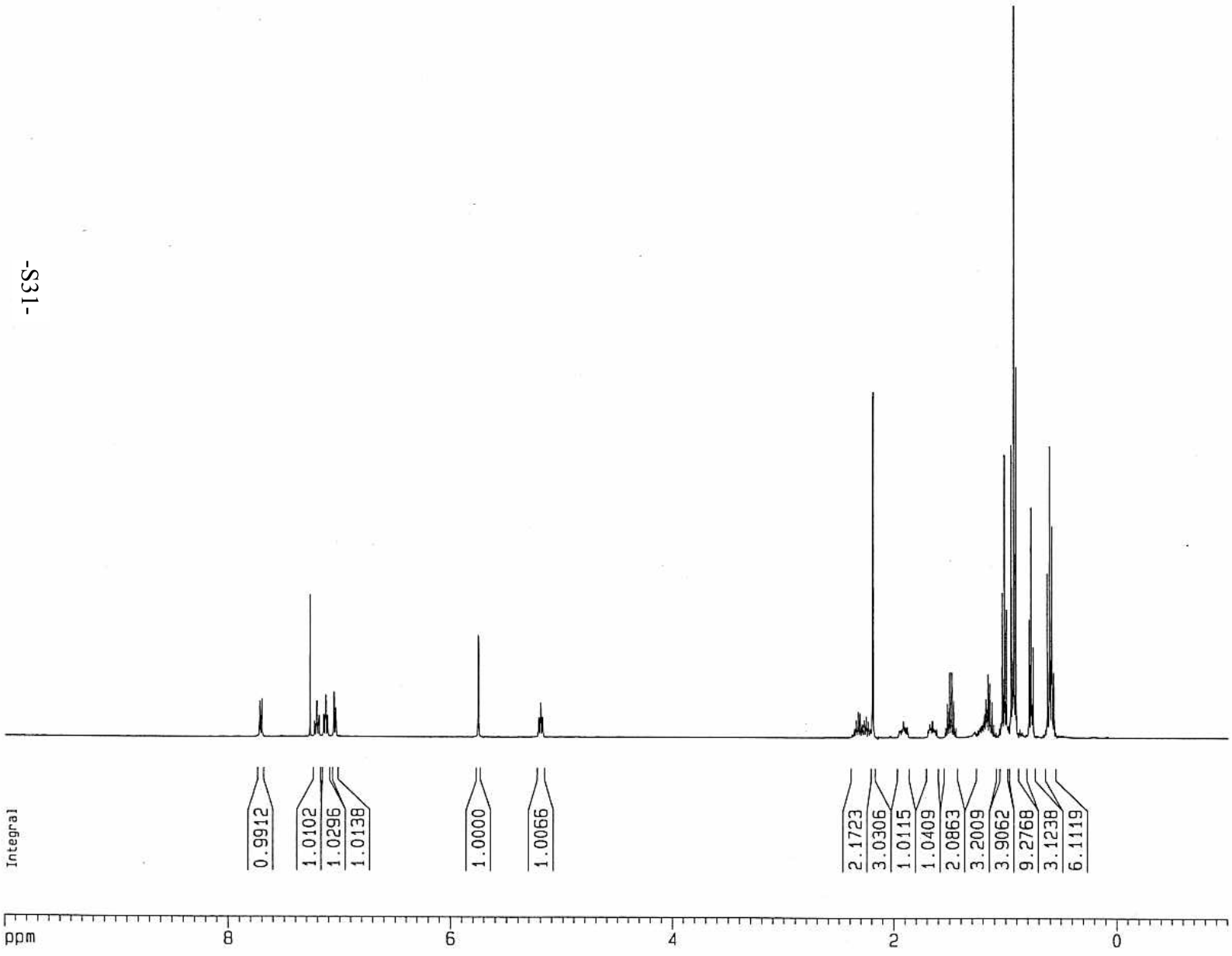
3a



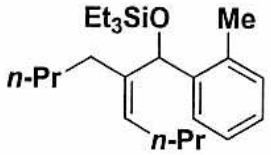


3b

SN050454

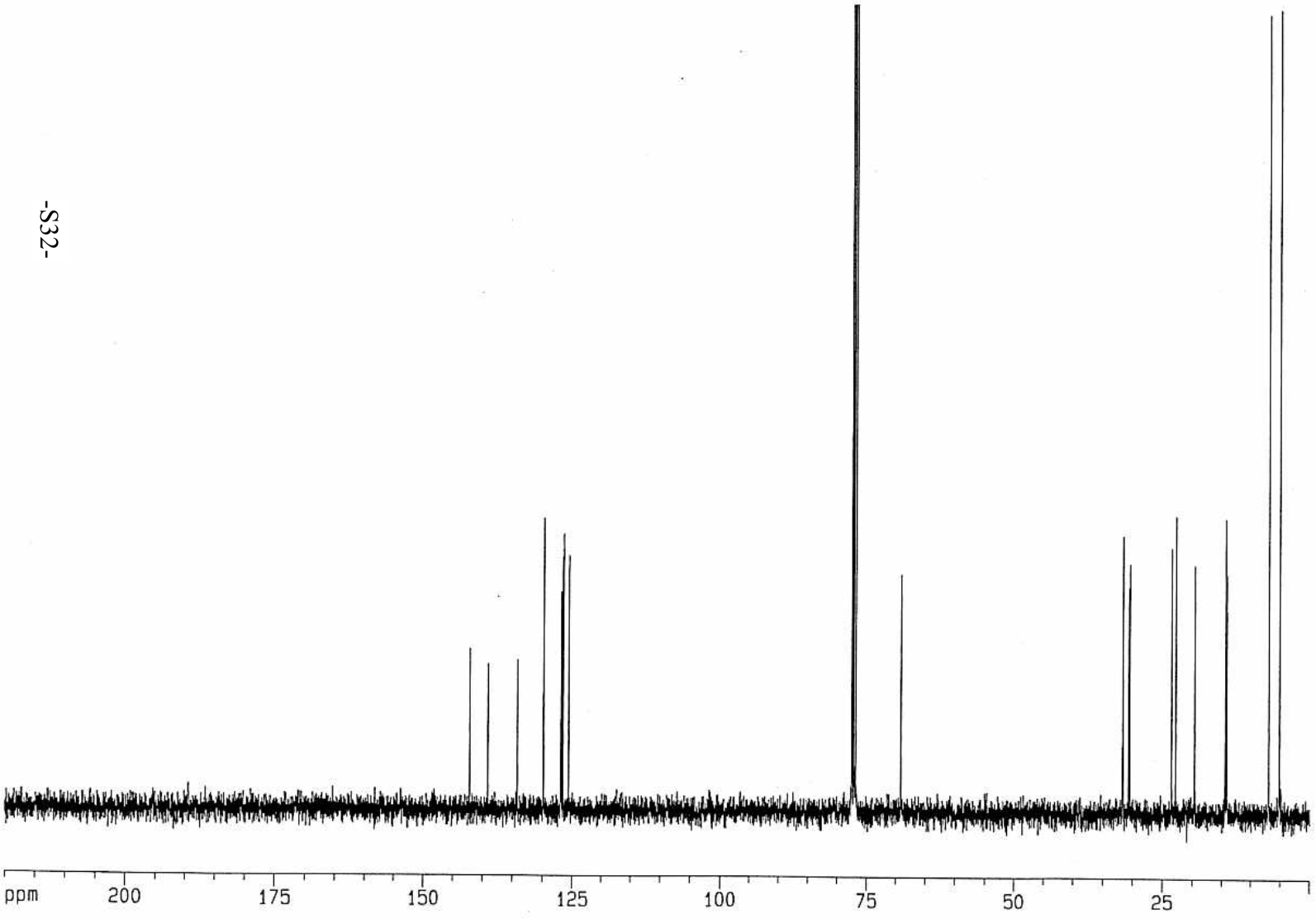



```
Current Data Parameters
NAME                  SN454-H
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20050124
Time                  16.24
INSTRUM               spect
PROBHD      5mm BBO BB-1
PULPROG               zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                       57
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             400.1300056 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                -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.55000 ppm/cm
HZCM             220.07152 Hz/cm
```



3b

SN050454



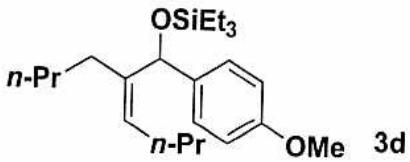

```
Current Data Parameters
NAME                  SN454-C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20050124
Time                  16.43
INSTRUM               spect
PROBHD     5mm BBO BB-1
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      136
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                220.000 ppm
F1                22134.80 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM             11.00000 ppm/cm
HZCM           1106.74023 Hz/cm
```


Et3SiO
n-Pr
n-Pr
Me

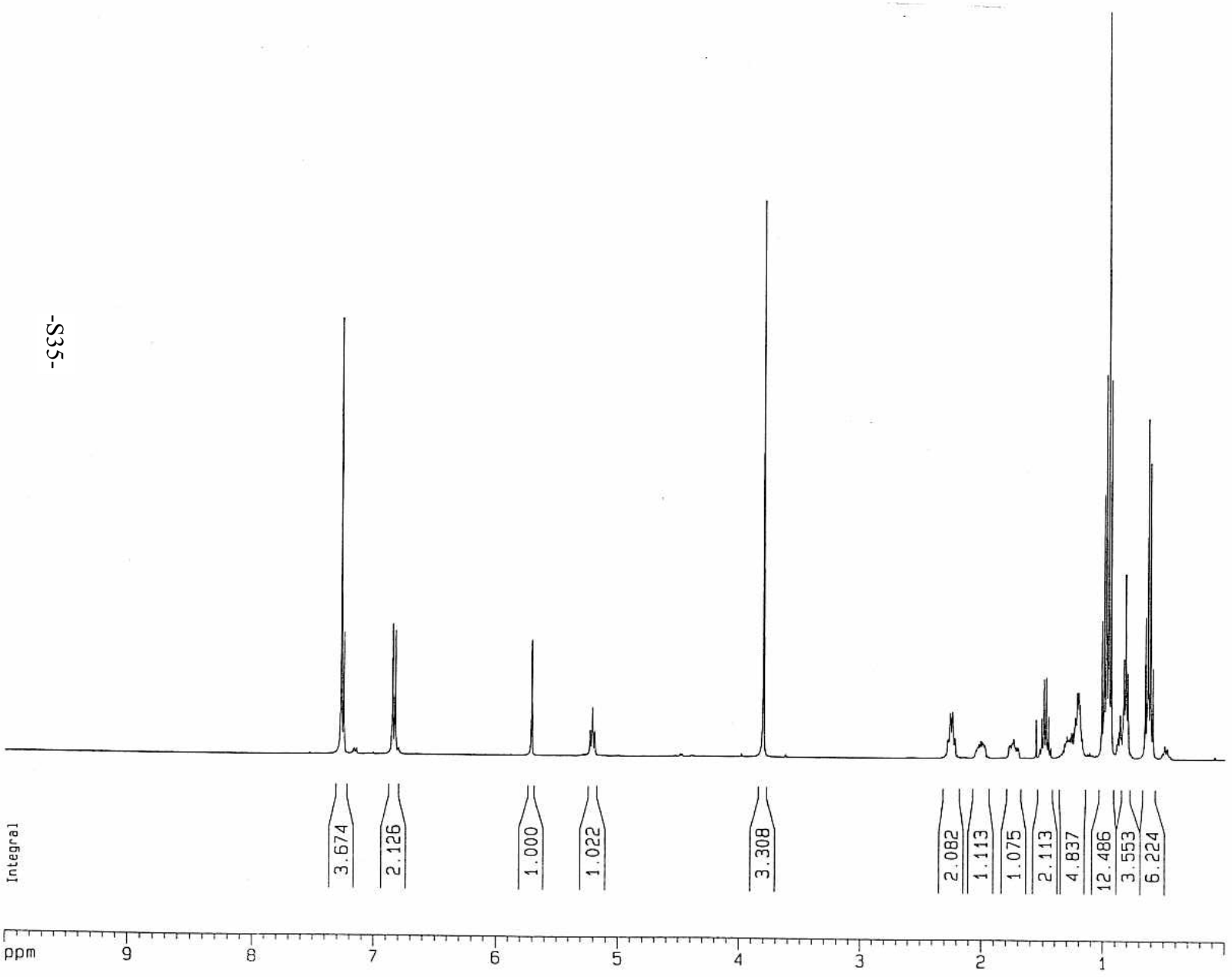
3c

11
10
9
8
7
6
5
4
3
2
1
ppm
1.77
1.72
1.00
1.00
2.92
2.00
1.06
1.06
1.94
4.13
10.00
2.75
5.31

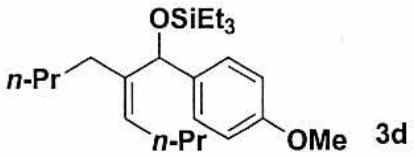
3c



3d

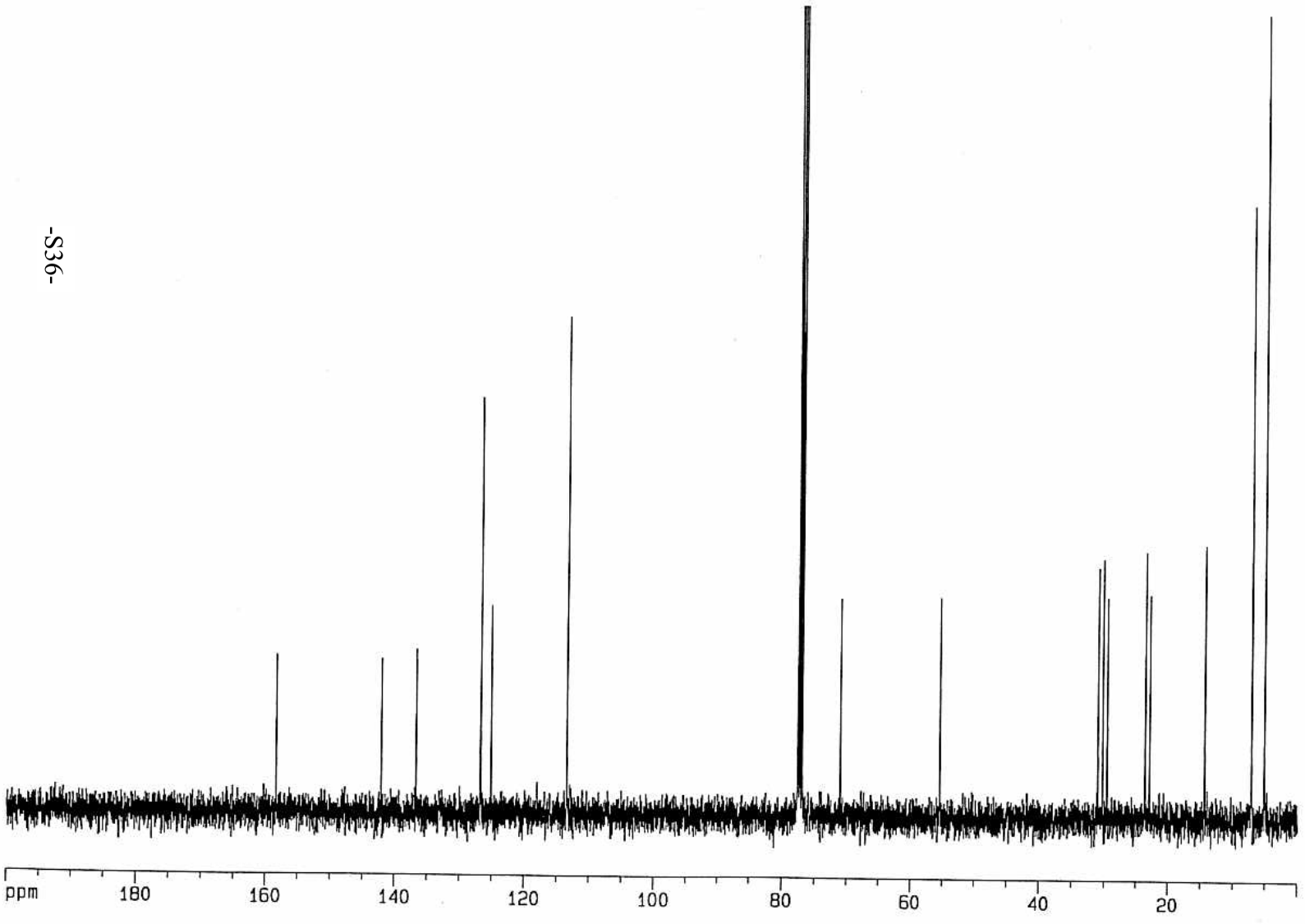



```
Current Data Parameters
NAME                  SN450-H
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20050120
Time                  21.21
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG               zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                    203.2
DW                 60.400 usec
DE                  6.00 usec
TE                  293.7 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                   12.50 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
```



3d

SN050468



Current Data Parameters	
NAME	SN468-C
EXPNO	1
PROCNO	1

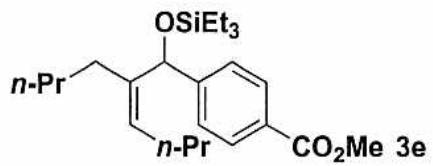
F2 - Acquisition Parameters	
Date_	20050219
Time	9.51
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	108
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	16384
DW	19.900 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

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

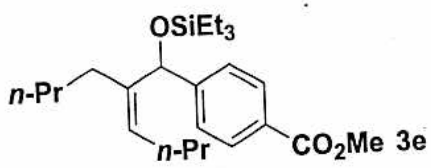
========== CHANNEL f2 ==========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	107.50 usec
PL2	0.00 dB
PL12	24.00 dB
PL13	24.00 dB
SFO2	400.1316005 MHz

F2 - Processing parameters	
SI	32768
SF	100.6127492 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

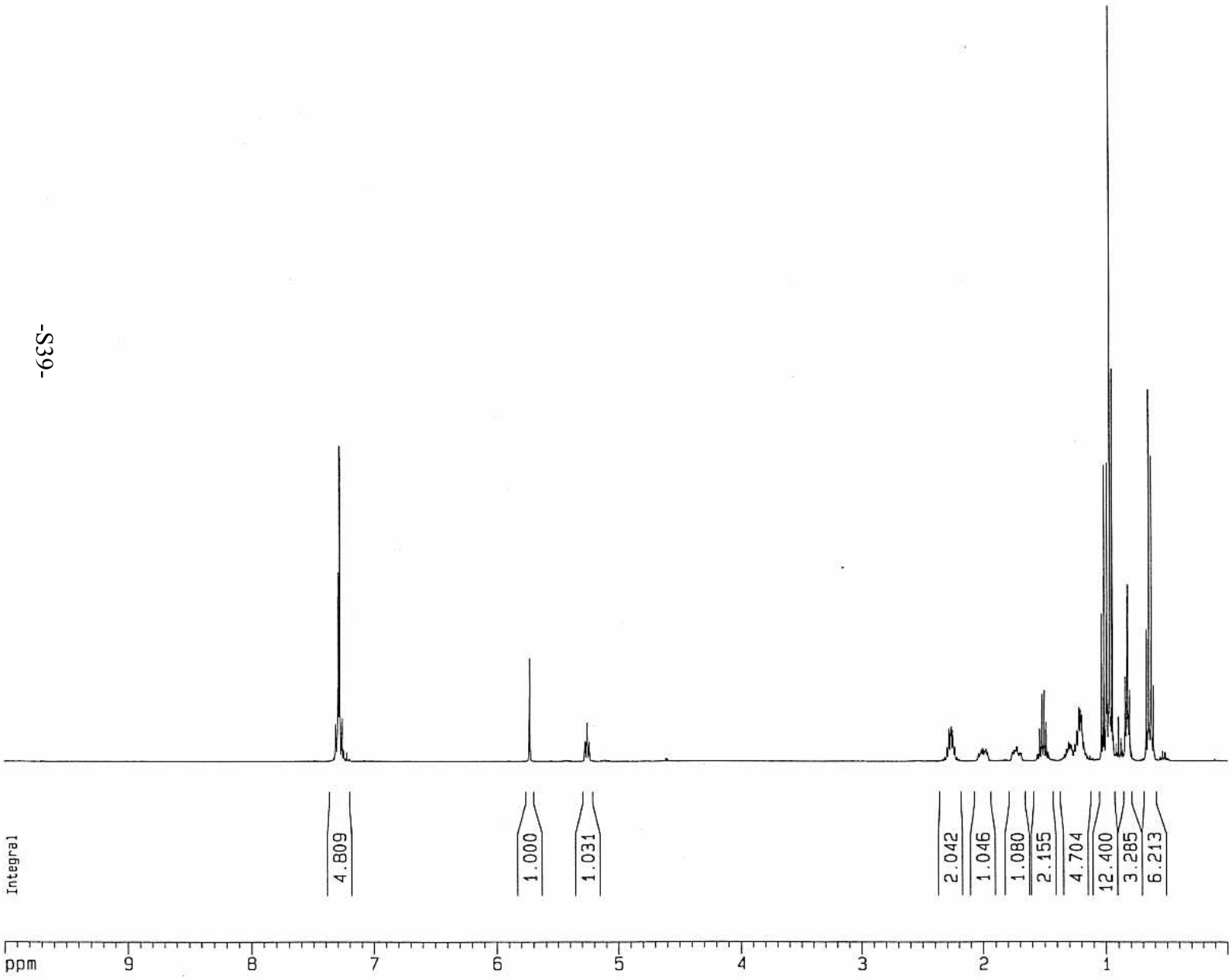

OSiEt3
n-Pr
n-Pr
CO2Me 3e

10
9
8
7
6
5
4
3
2
1
ppm
1.87
1.90
1.00
1.00
3.47
2.00
1.36
1.06
2.32
4.75
8.91
2.72
2.95
6.17


OSiEt3
n-Pr
n-Pr
CO2Me 3e

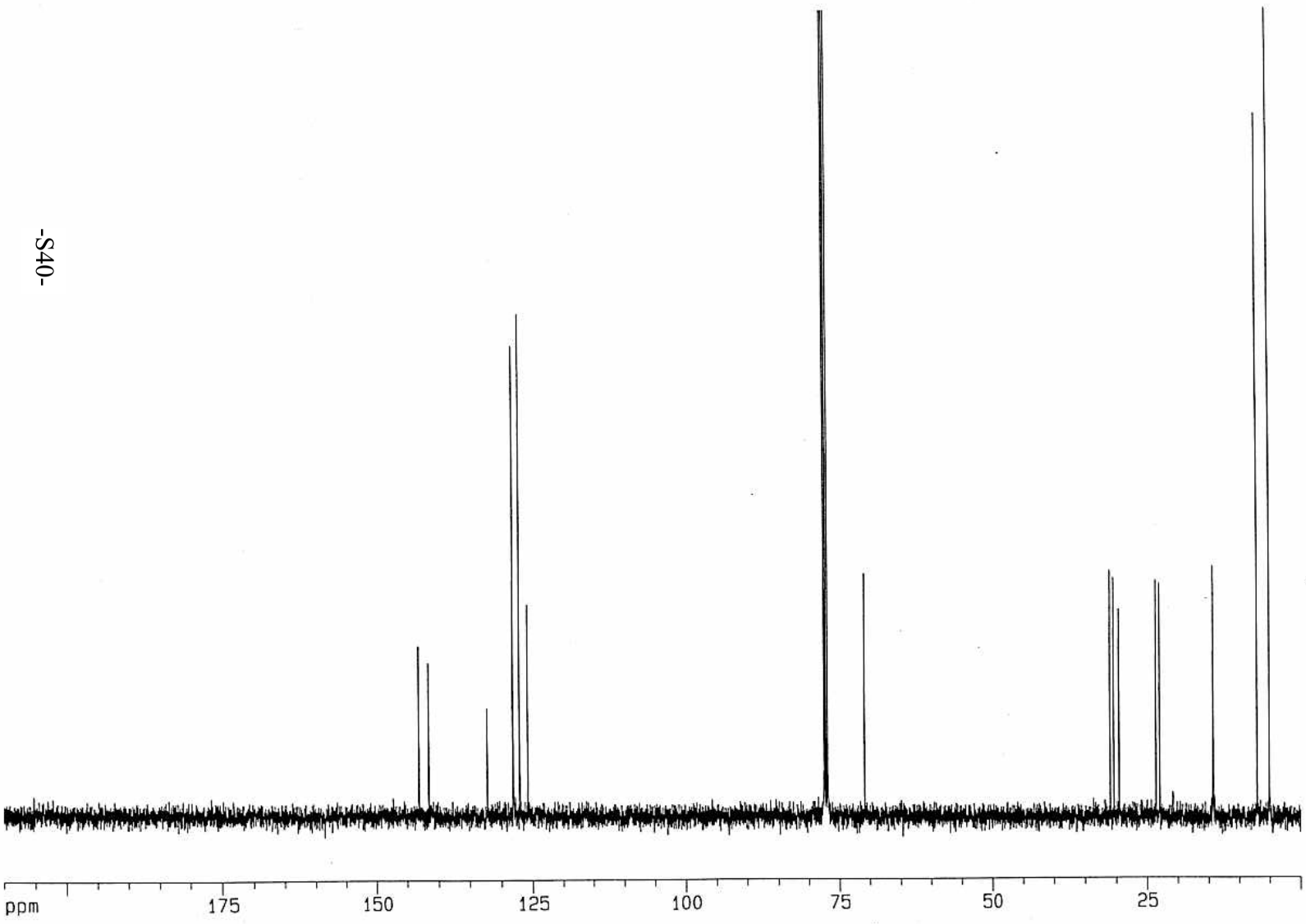
200
180
160
140
120
100
80
60
40
20
ppm

3f

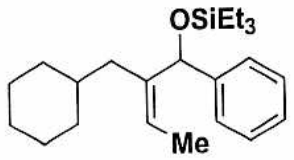



```
Current Data Parameters
NAME                  SN455-H
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20050124
Time                  16.51
INSTRUM               spect
PROBHD      5mm BBO BB-1
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      57
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             400.1300000 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
```

3f

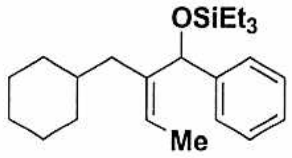



```
Current Data Parameters
NAME                 SN455-C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20050124
Time                 17.06
INSTRUM              spect
PROBHD     5mm BBO BB-1
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     152
DS                       4
SWH              25125.629 Hz
FIDRES           0.383387 Hz
AQ               1.3042164 sec
RG                  3649.1
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                210.000 ppm
F1                21128.68 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43384 Hz/cm
```

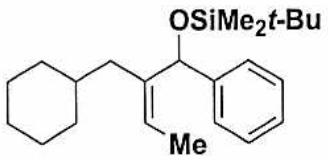

OSiEt3
Me

3g

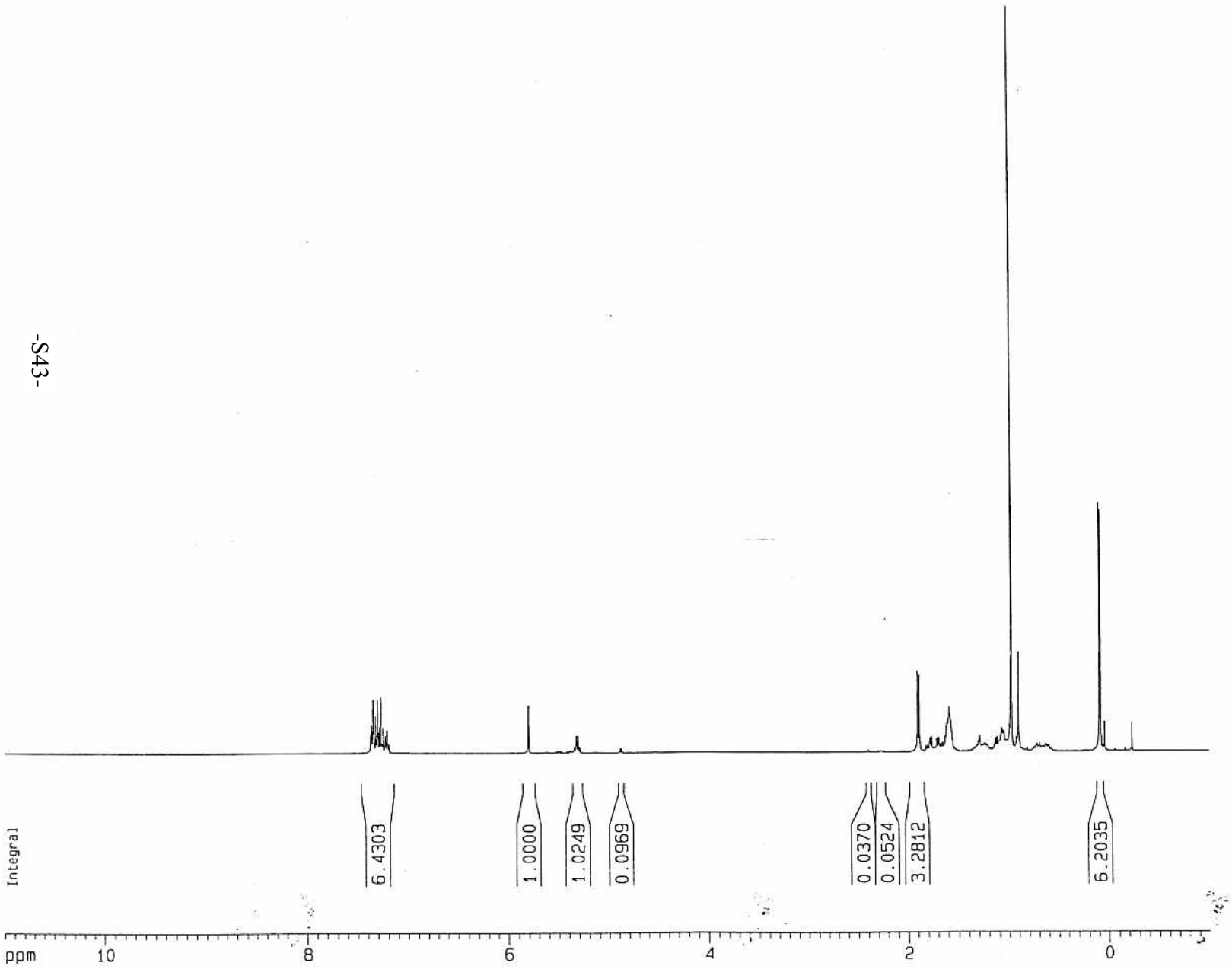
10
9
8
7
6
5
4
3
2
1
0 ppm
1.74
1.83
1.80
1.00
1.04
1.15
5.70
3.11.23
3.40
1.307.58
6.57



3g



3h



Current Data Parameters

NAME	SN461Major-H
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050127
Time	21.48
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	64
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

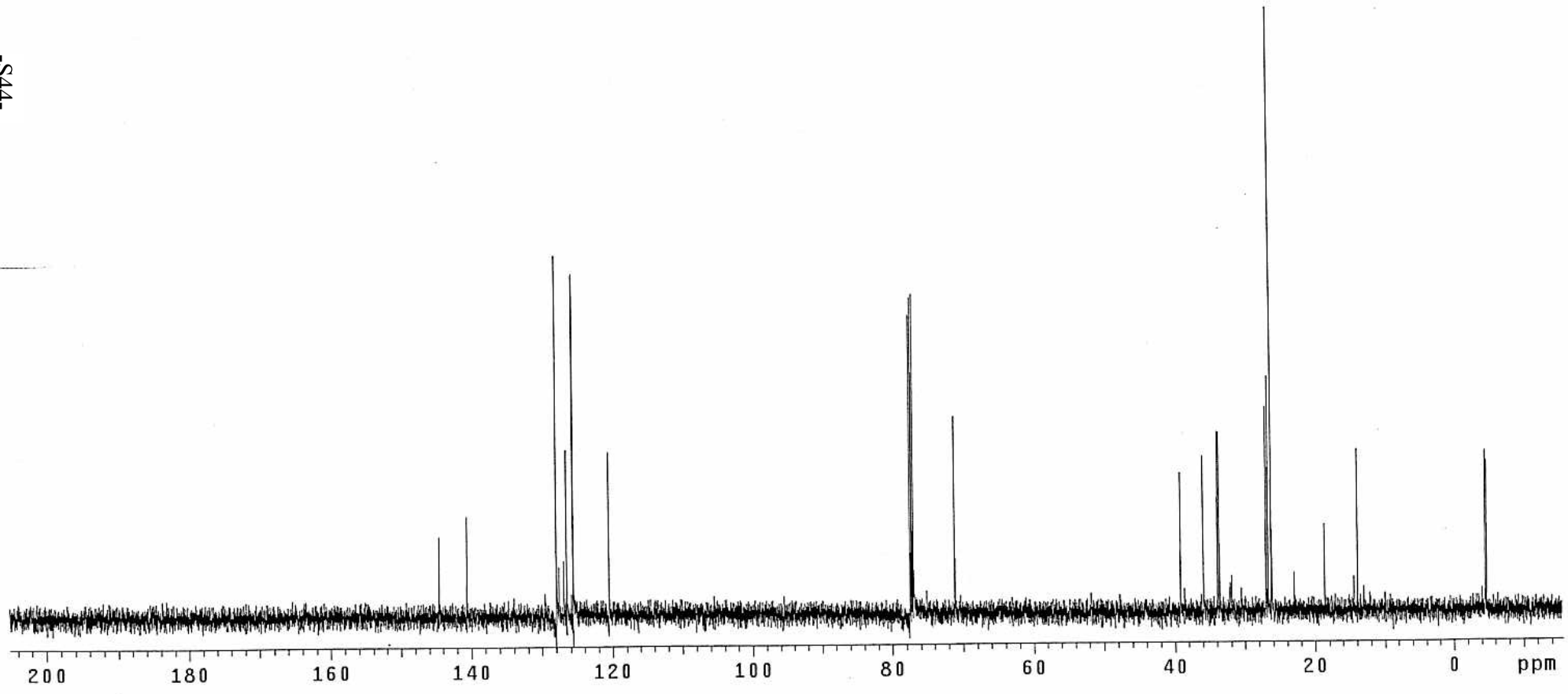
F2 - Processing parameters

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	12.50 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm

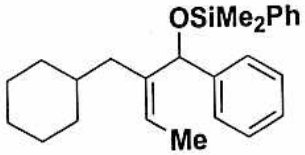
3h



SN050529

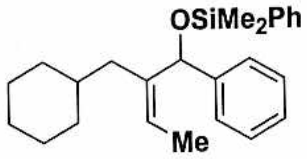
Pulse Sequence: s2pul

Wed Mar 30 17:57:14 EST 2005



3i

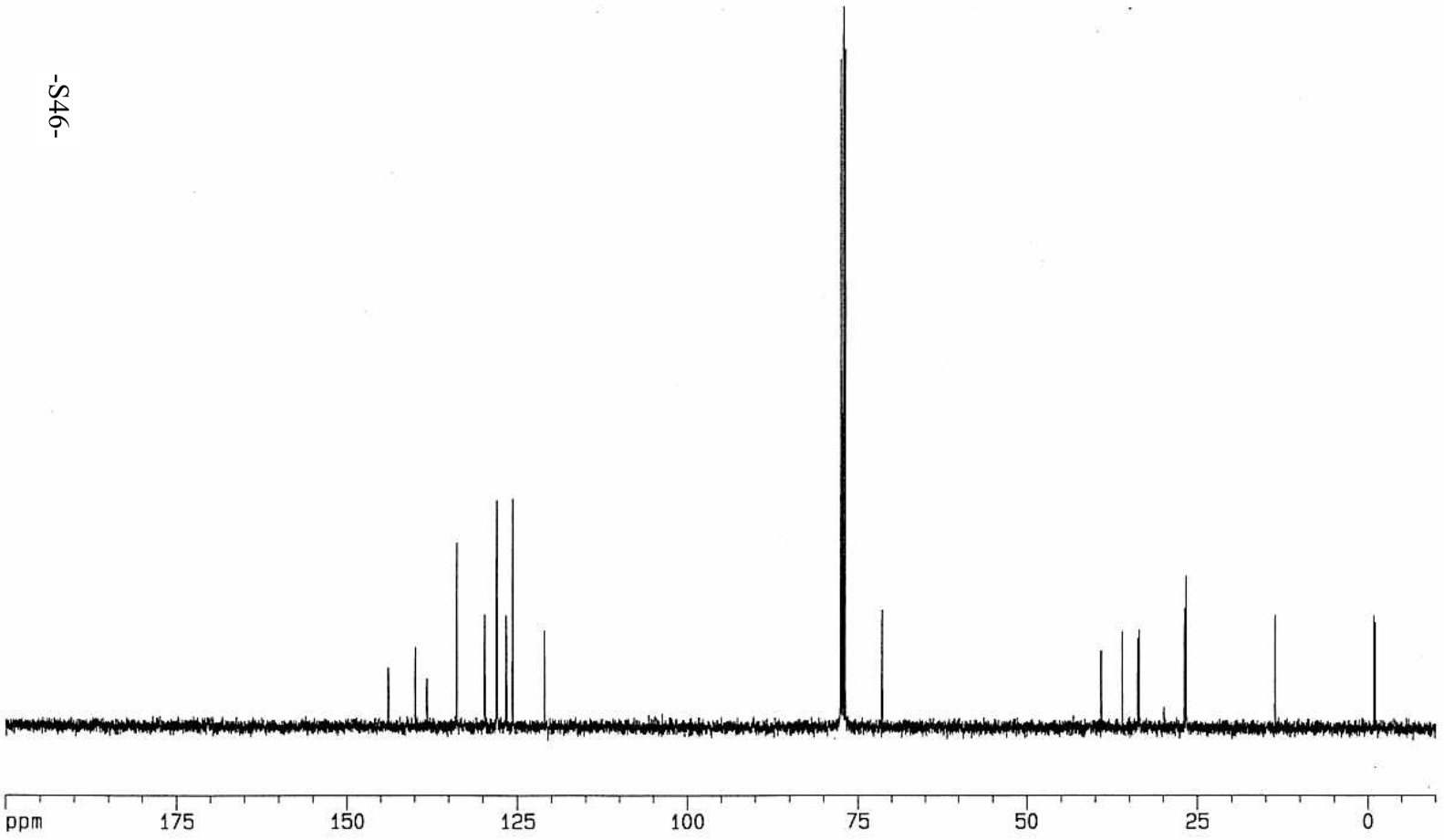
C_6D_6



3i

SN050529

$CDCl_3$

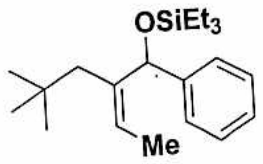



```
Current Data Parameters
NAME                 SN529-C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20050330
Time                  19.34
INSTRUM               spect
PROBHD      5mm BBO BB-1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      225
DS                        4
SWH              25125.629 Hz
FIDRES            0.383387 Hz
AQ                1.3042164 sec
RG                     2048
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             100.6127499 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                 -10.000 ppm
F2                  -1006.13 Hz
PPMCM               10.50000 ppm/cm
HZCM              1056.43384 Hz/cm
```


OSiEt3
Me

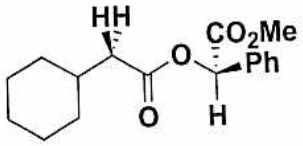
3j

10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.90
0.10
0.09
0.10
0.07
2.28
3.15
1.45
8.10
0.29
0.69



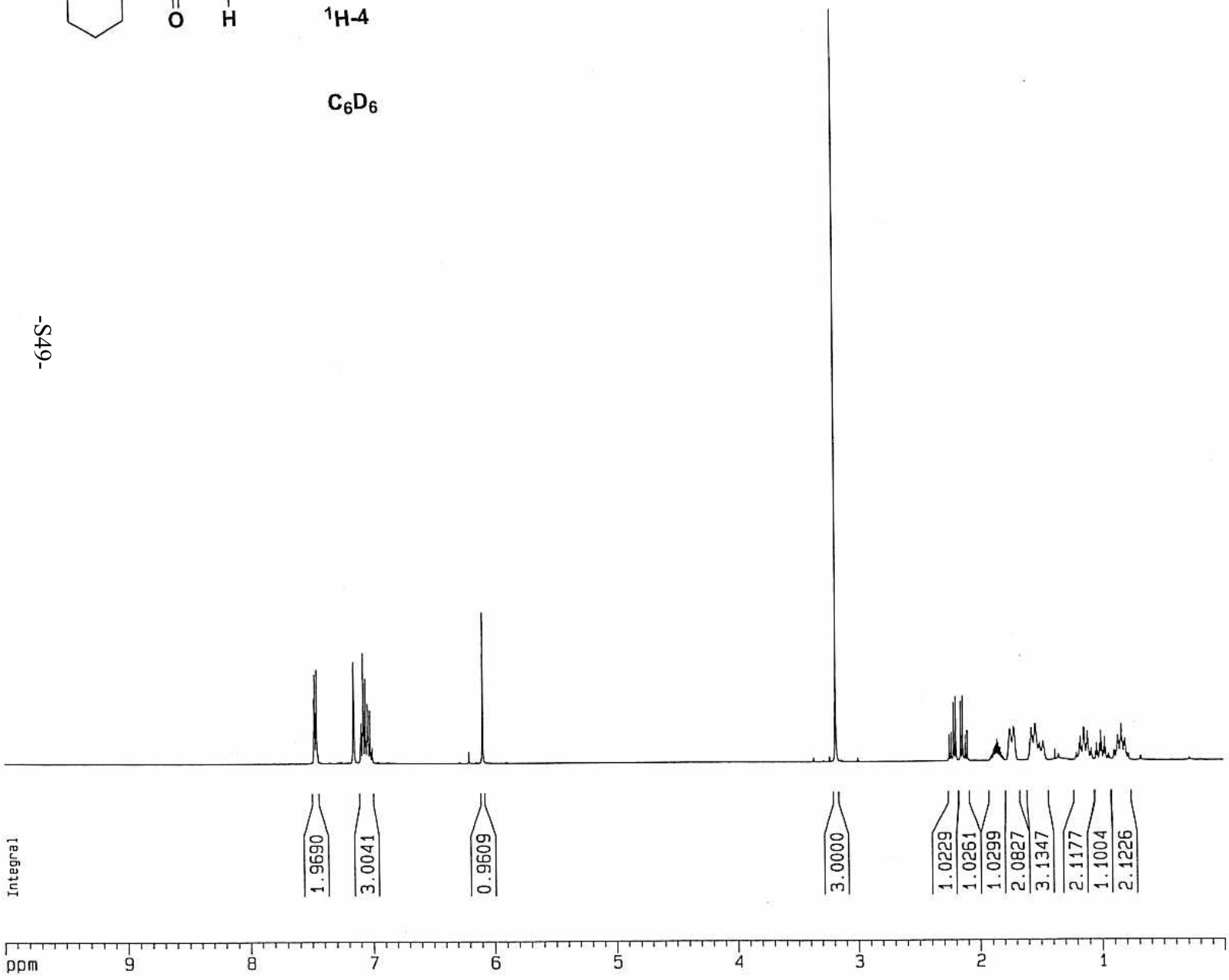
3j

SN050526 ester



^{1}H-4

C_6D_6



Current Data Parameters
NAME SN526-H
EXPNO 2
PROCNO 1

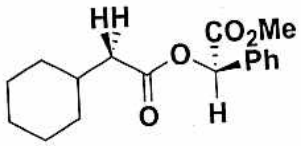
F2 - Acquisition Parameters
Date_ 20050329
Time 21.02
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 712.3 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 400.1300455 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06502 Hz/cm

SN050526



^{1}H-4

$CDCl_3$

Current Data Parameters

NAME	SN526-H
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050324
Time	22.09
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	45.3
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

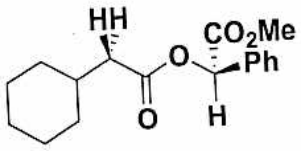
NUC1	1H
P1	7.90 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

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

1D NMR plot parameters

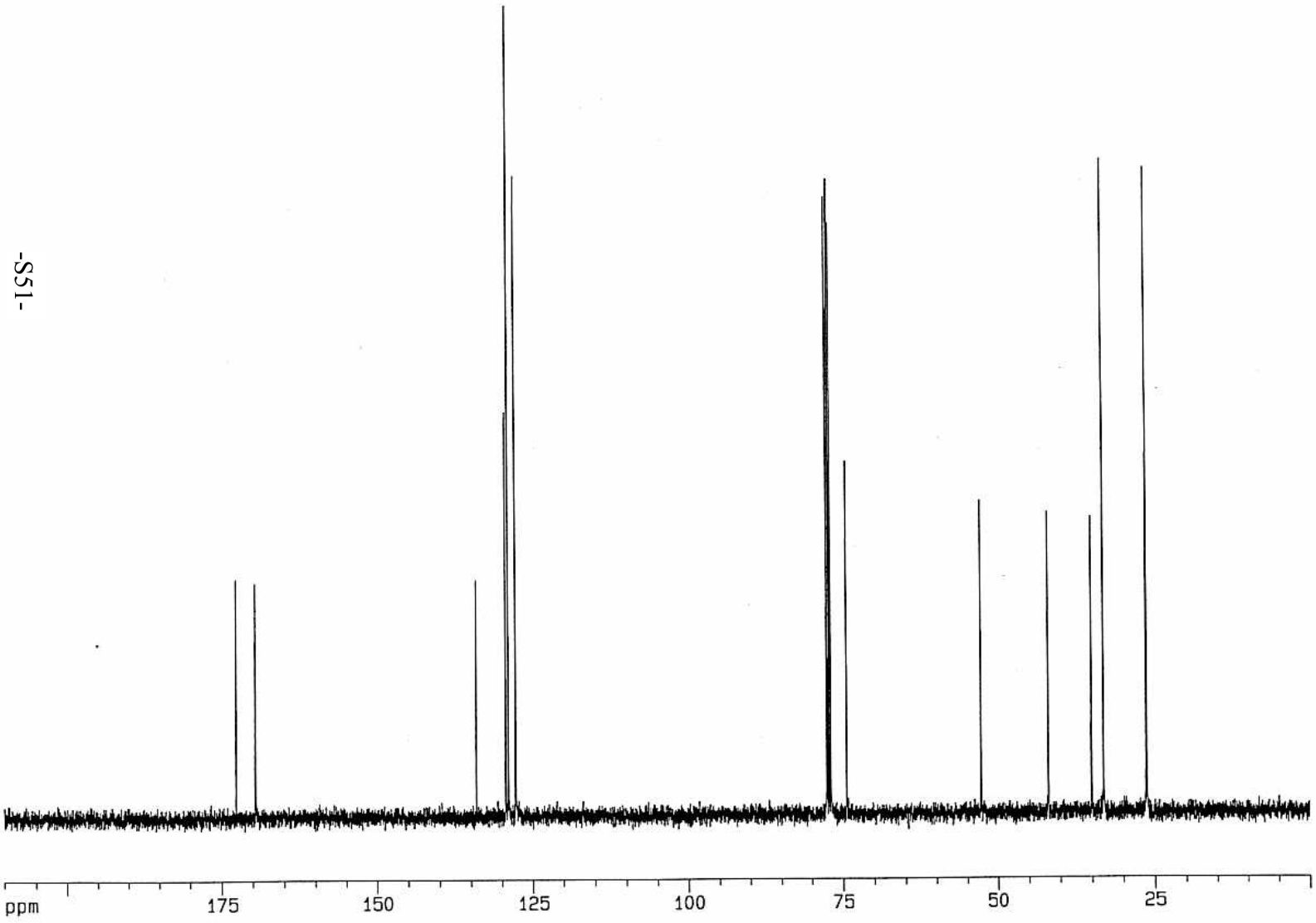
CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.55000 ppm/cm
HZCM	220.07152 Hz/cm



SN050526

^{1}H-4

$CDCl_3$



Current Data Parameters

NAME	SN526-C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050324
Time	22.18
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
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 ==========

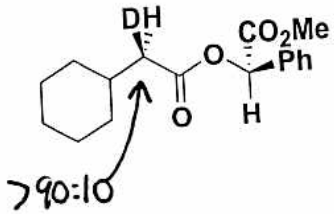
CPDPRG2	waltz16
NUC2	1H
PCPD2	107.50 usec
PL2	0.00 dB
PL12	24.00 dB
PL13	24.00 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127538 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	210.000 ppm
F1	21128.68 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.50000 ppm/cm
HZCM	1056.43396 Hz/cm

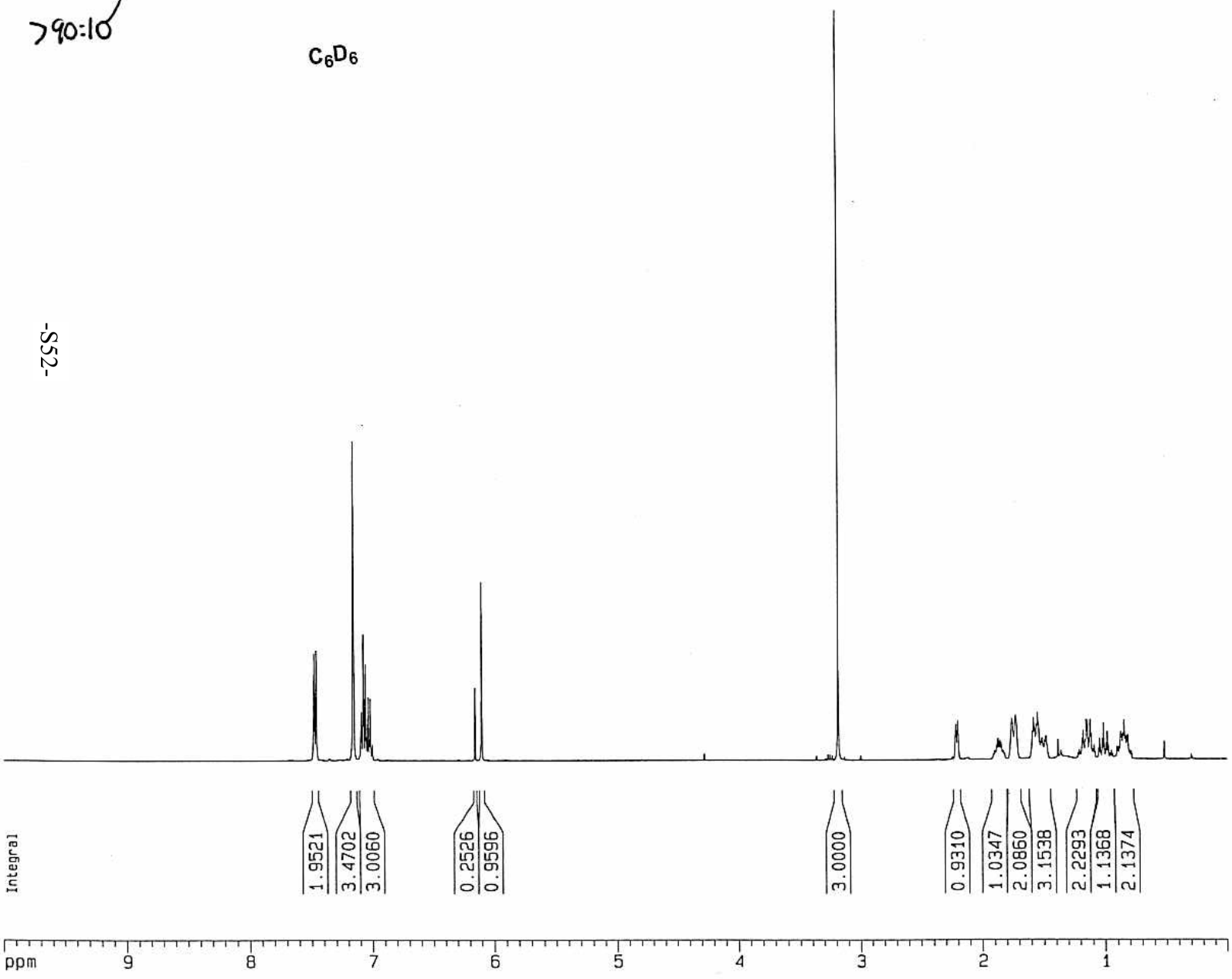


>90:10

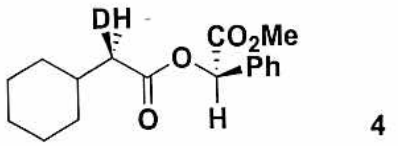
4

C_6D_6

SN050528 ester



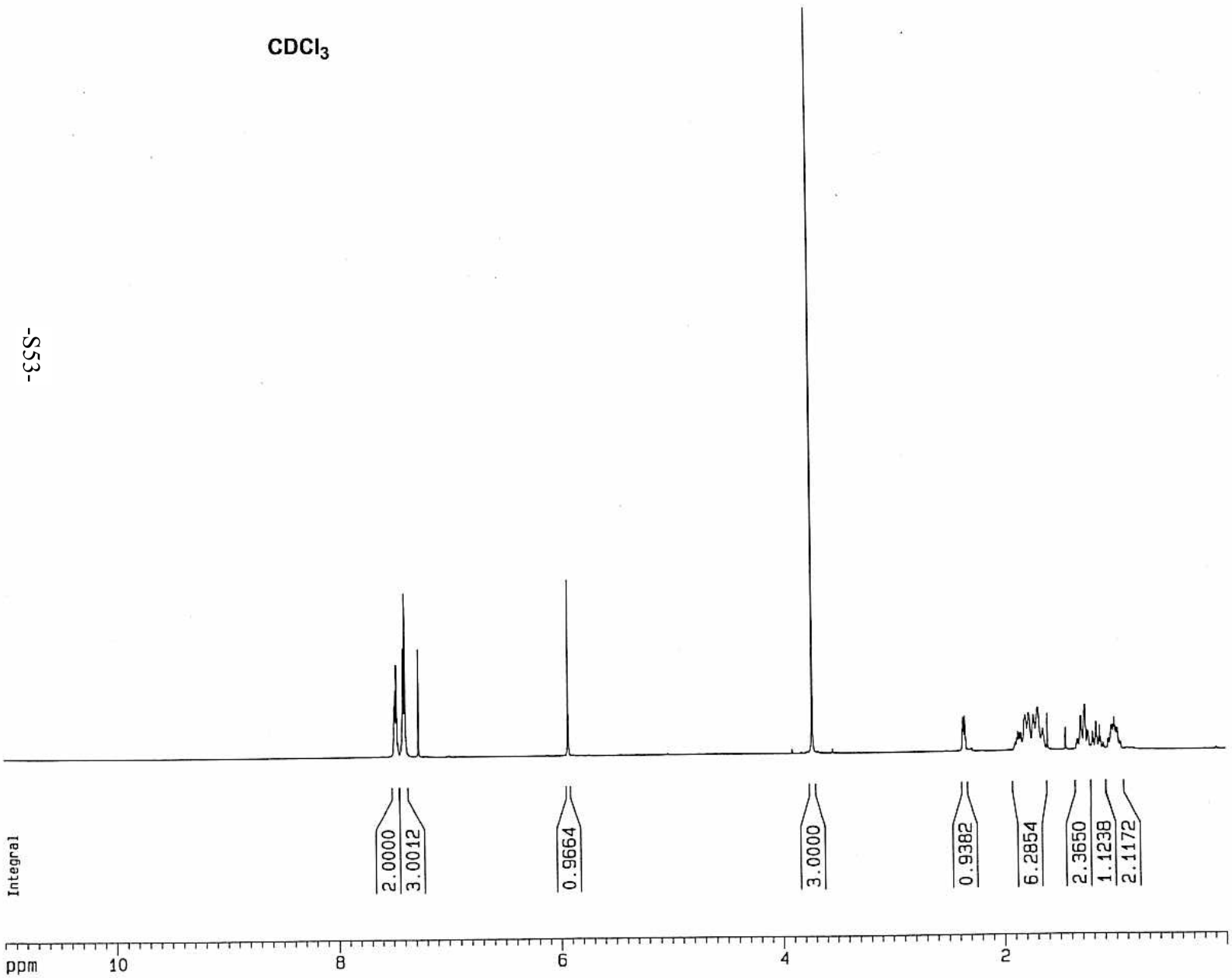

```
Current Data Parameters
NAME        SN528-ester-H
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_          20050329
Time              21.18
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG           zg30
TD               65536
SOLVENT           C6D6
NS                  22
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                203.2
DW               60.400 usec
DE                6.00 usec
TE               712.3 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          400.1300443 MHz
WDW                 EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00

1D NMR plot parameters
CX              20.00 cm
CY              12.50 cm
F1P             10.000 ppm
F1              4001.30 Hz
F2P             0.000 ppm
F2              0.00 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06502 Hz/cm
```



4

SN050528 ester

$CDCl_3$



Current Data Parameters

NAME	SN528-ester-H
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050328
Time	12.07
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	17
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	101.6
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

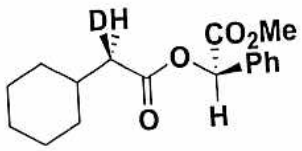
NUC1	1H
P1	7.90 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

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

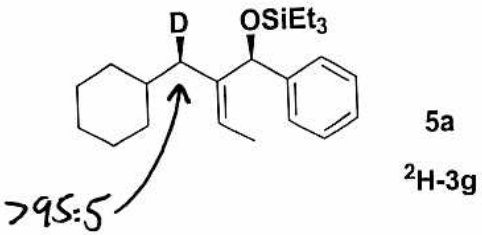
1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.55000 ppm/cm
HZCM	220.07152 Hz/cm



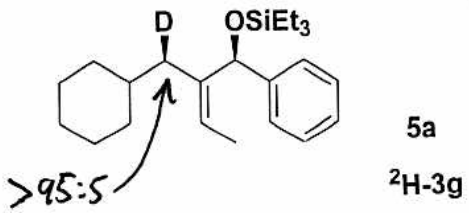
4

$CDCl_3$



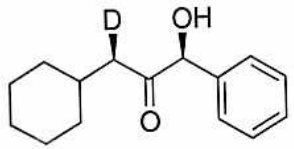
5a

^{2}H-3g



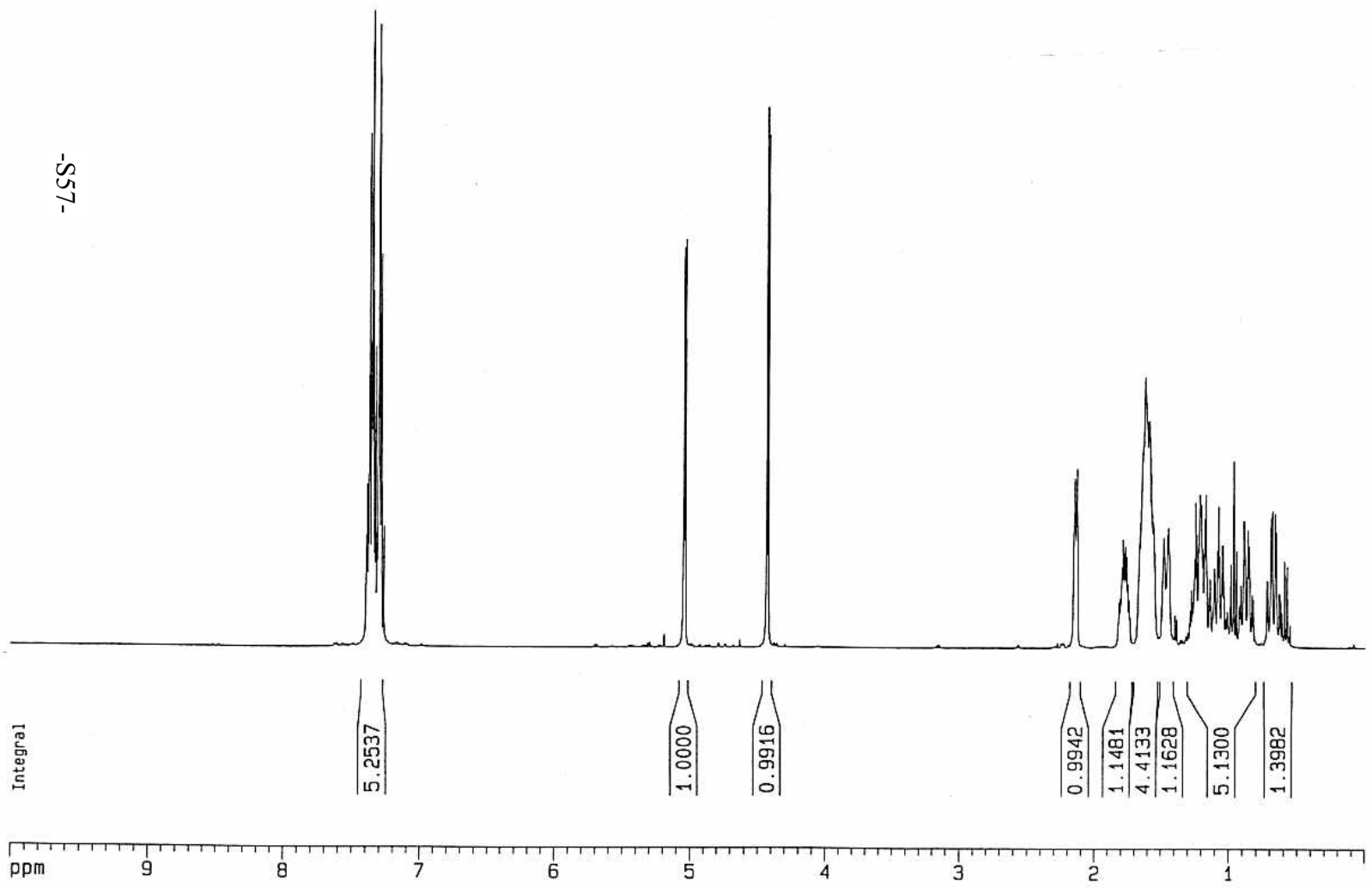
5a

^{2}H-3g

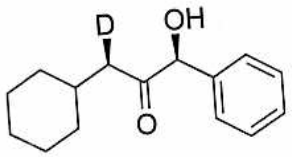


5b

SN050528 ozonolysis

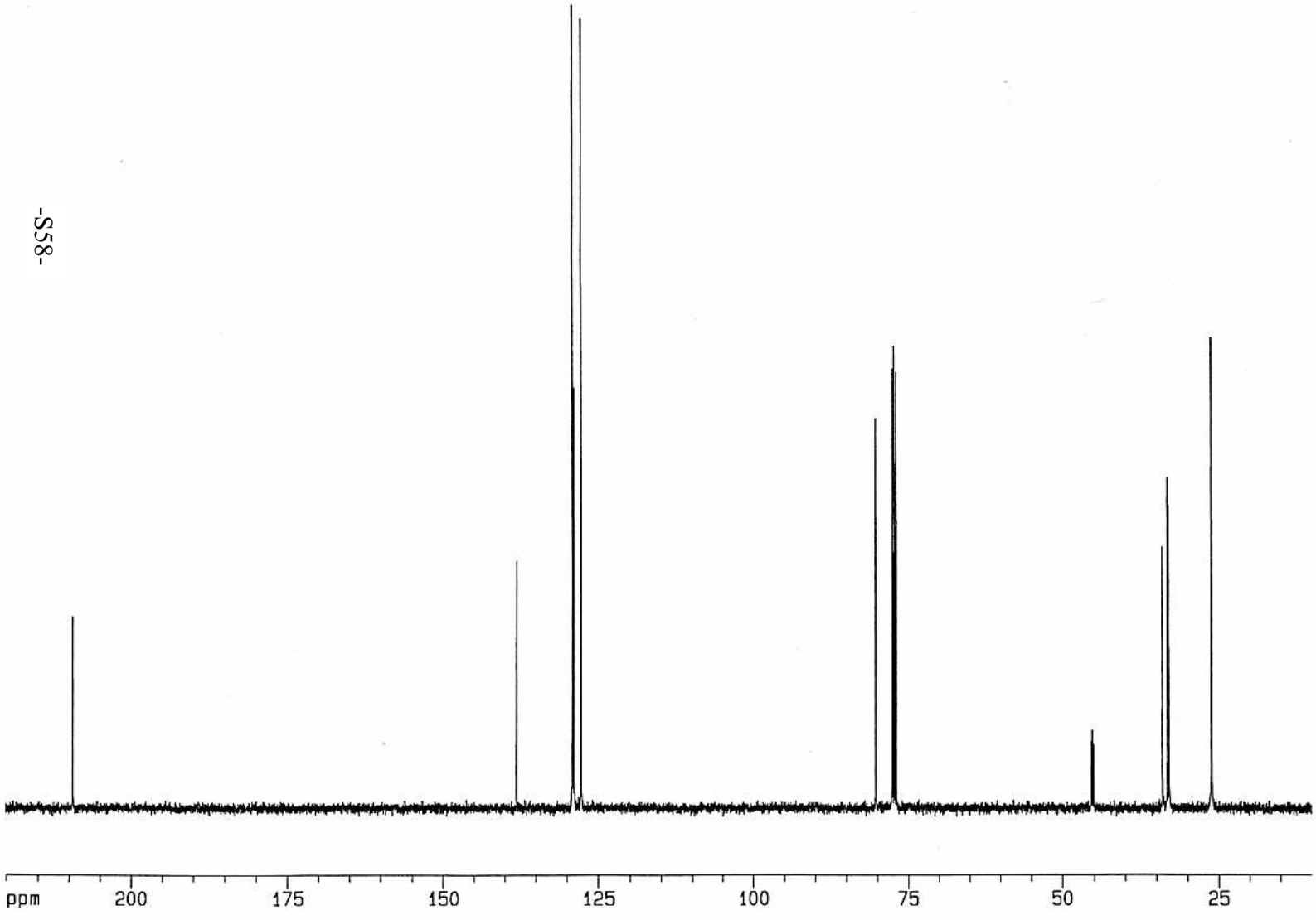



```
Current Data Parameters
NAME          SN528-03-H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050326
Time               21.03
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                35.9
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          400.1300054 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
```



5b

SN050528 ozonolysis



Current Data Parameters	
NAME	SN528-03-C
EXPNO	1
PROCNO	1

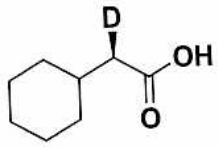
F2 - Acquisition Parameters	
Date_	20050326
Time	21.13
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	193
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	2048
DW	19.900 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== 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

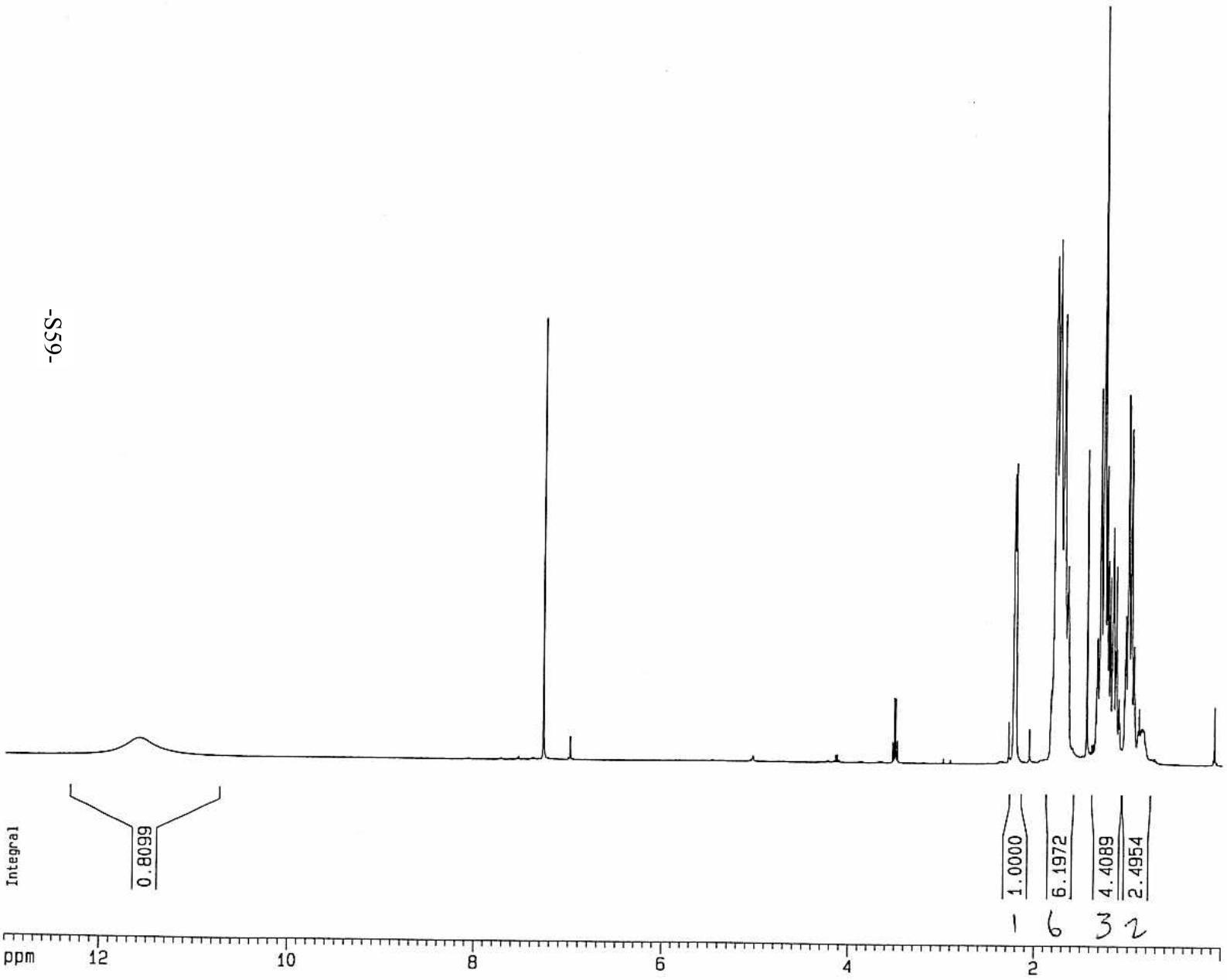
F2 - Processing parameters	
SI	32768
SF	100.6127561 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
F1P	220.000 ppm
F1	22134.81 Hz
F2P	10.000 ppm
F2	1006.13 Hz
PPMCM	10.50000 ppm/cm
HZCM	1056.43396 Hz/cm

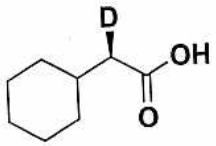


5c

SN050527 acid

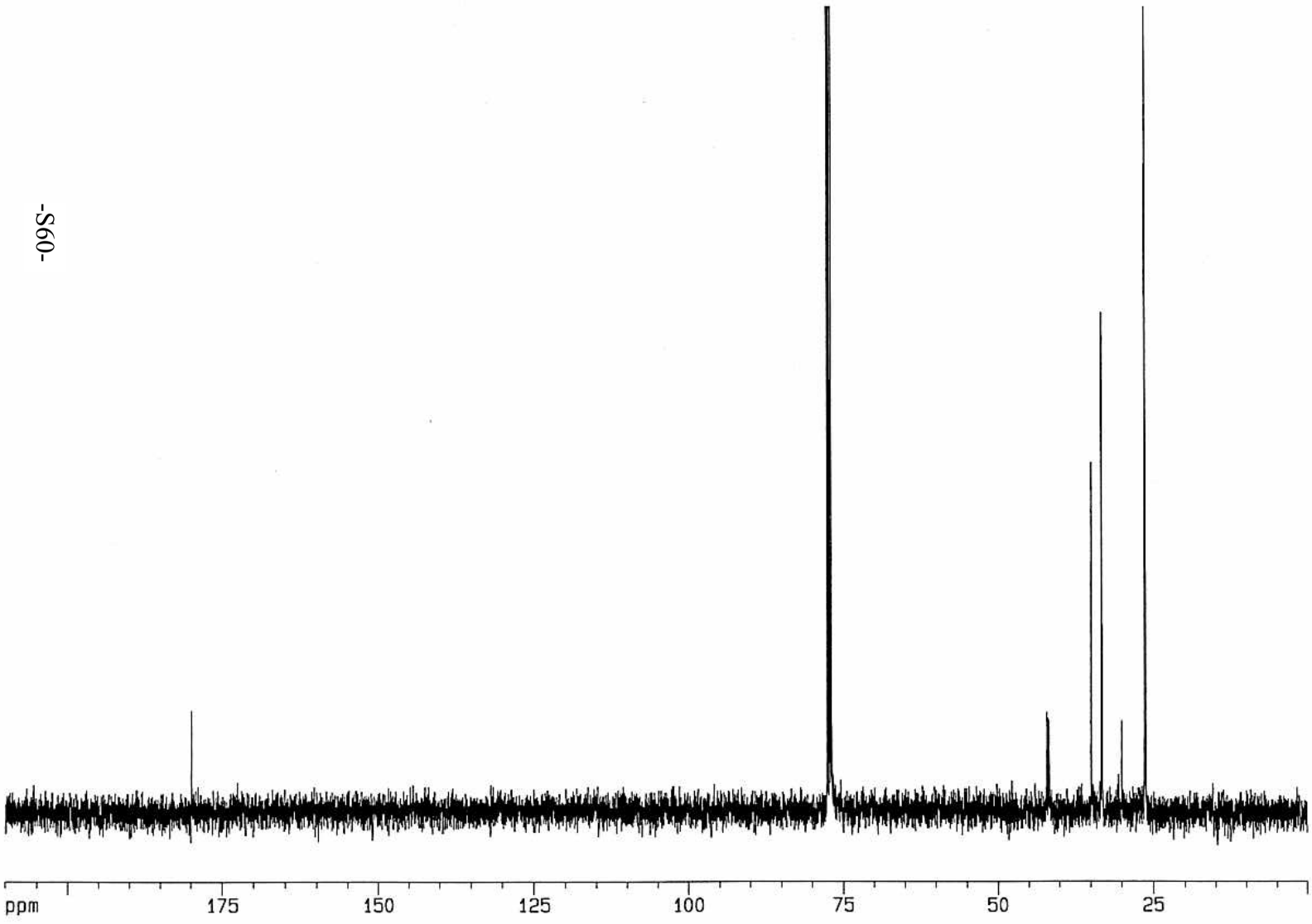



```
Current Data Parameters
NAME        SN527-acid-H
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_         20050326
Time             17.04
INSTRUM          spect
PROBHD     5mm BBO BB-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
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         400.1300056 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX              20.00 cm
F1P            13.000 ppm
F1            5201.69 Hz
F2P            0.000 ppm
F2              0.00 Hz
PPMCM         0.65000 ppm/cm
HZCM        260.08450 Hz/cm
```



5c

SN050527 acid



Current Data Parameters

NAME	SN527-acid-C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050326
Time	17.16
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	223
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	2048
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

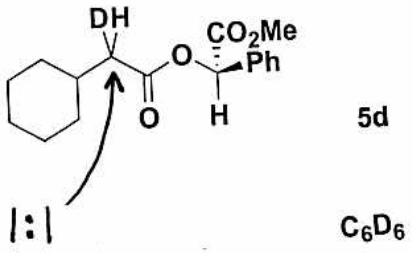
F2 - Processing parameters

SI	32768
SF	100.6127492 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	210.000 ppm
F1	21128.68 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.50000 ppm/cm
HZCM	1056.43384 Hz/cm

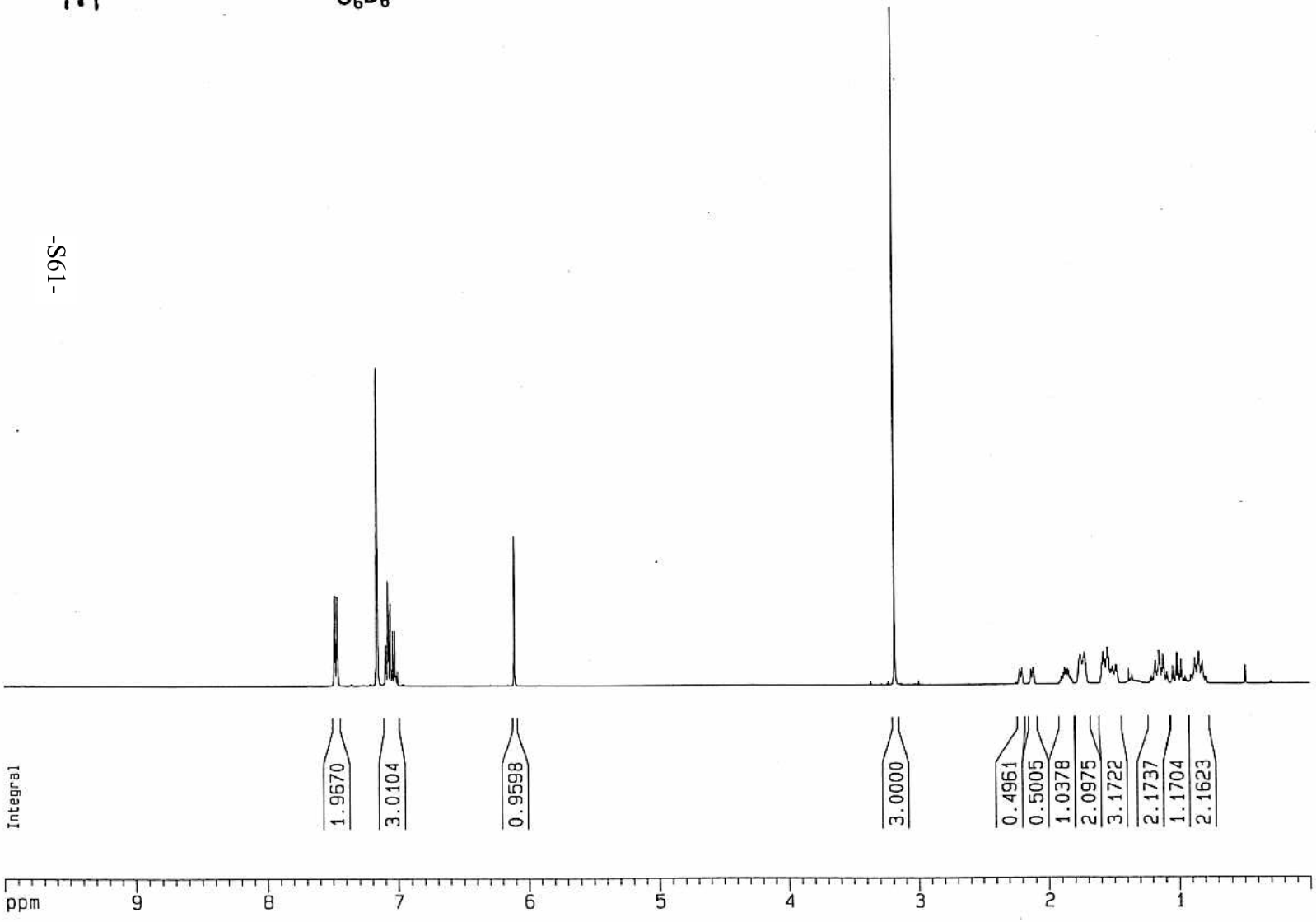
SN050527 ester



5d

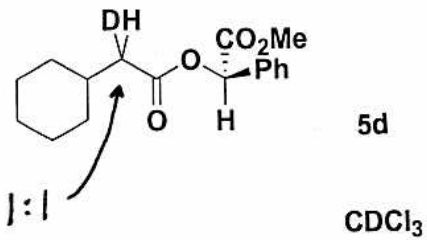
1:1

C_6D_6




```
Current Data Parameters
NAME        SN527-ester-H
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_          20050329
Time              21.11
INSTRUM           spect
PROBHD   5 mm QNP 1H/1
PULPROG           zg30
TD             65536
SOLVENT           C6D6
NS                32
DS                 2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ           3.9584243 sec
RG               256
DW            60.400 usec
DE             6.00 usec
TE            712.3 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        400.1300440 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00

1D NMR plot parameters
CX             20.00 cm
CY             11.00 cm
F1P            10.000 ppm
F1             4001.30 Hz
F2P            0.000 ppm
F2             0.00 Hz
PPMCM          0.50000 ppm/cm
HZCM          200.06502 Hz/cm
```

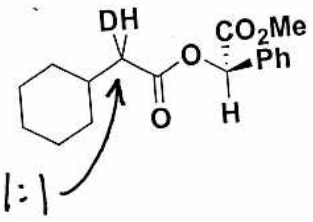
SN050527 ester



5d

$CDCl_3$

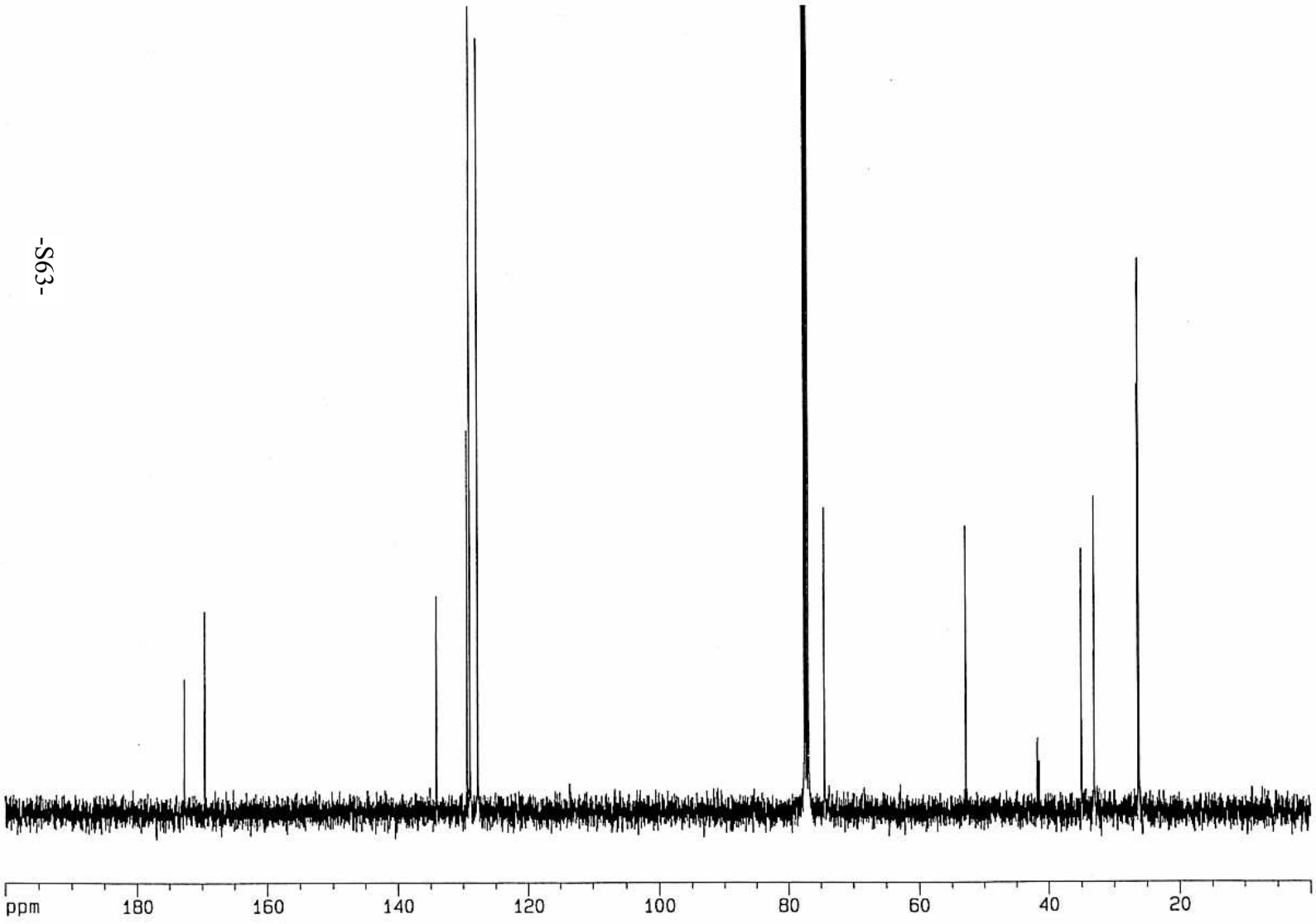

```
Current Data Parameters
NAME        SN527-ester-H
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_          20050327
Time             18.02
INSTRUM          spect
PROBHD     5mm BBO BB-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 20
DS                  2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ           3.9584243 sec
RG                 114
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          400.1300056 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
```



5d

$CDCl_3$

SN050527 ester




```
Current Data Parameters
NAME       SN527-ester-C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20050327
Time              18.08
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG        zgpg30
TD              65536
SOLVENT          CDCl3
NS                 512
DS                   4
SWH          25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG               7298.2
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          100.6127499 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
```