

Supporting Information:

Kinetics of a Fast Reversible Alkene Radical Cation Cyclization Reaction

John H. Horner, Martin Newcomb

The University of Illinois at Chicago, 845 West Taylor St. Chicago IL 60607

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General Procedures and Instrumentation: Reactions involving water-sensitive reagents were performed under a nitrogen atmosphere. THF and dichloromethane were purified using a commercial column purification apparatus^{S1, S2}. Diisopropylamine and triethylamine were purified prior to use by distillation after stirring over calcium hydride. Column chromatography was carried out using Silicycle Ultra Pure Silica Gel (200-425 mesh) (60 Å). α,α,α -Trifluorotoluene (anhydrous), methanol, acetonitrile, diethyl ether, benzene, thiophenol, and other reagents were purchased from Aldrich Chemical Company and used as received. ^1H NMR spectra were recorded at 300 or 500 MHz with CDCl_3 solutions unless specified otherwise. Chemical shifts are reported in ppm (δ) downfield from internal TMS at 0.00 ppm. ^{13}C NMR spectra were recorded at 75 or 125 MHz with chemical shifts referenced to internal TMS at 0.00 ppm or to the solvent peak at 77.00 ppm. ^{13}C multiplicities (C), (CH), (CH_2), (CH_3) were obtained from DEPT-135 and DEPT-90 spectra. High resolution mass spectra were recorded by the University of Illinois at Chicago Research Resources Center. HPLC analyses were carried out on an Agilent 1100 HPLC system equipped with a photodiode array detector and using a Supelcosil LC-18 column (25 mm \times 4.6 mm) (5 μm). GCMS analyses were carried out on an Agilent 6890N gas chromatograph equipped with a DB1701 capillary column (30.0 m \times 0.25 mm \times 0.25 μm), interfaced to an Agilent 5973 mass selective detector running in scan mode with electron impact ionization (70 eV).

Laser flash photolysis studies of 1 were carried out on an Applied Photophysics LKS-50 laser kinetic spectrometer. The third harmonic (355 nm, 7 ns duration, 40 to 60 mJ / pulse) from a Continuum Surelite 1 laser was used in all LFP studies. Data from the photomultiplier was digitized using an Agilent Infinium oscilloscope (Model 54845a). When possible, oversampling (64 / 1) was used to improve S/N. Samples of **1** were prepared in the appropriate solvent, and the concentration of **1** was adjusted to give an absorbance of 0.2 to 0.5 at 355 nm. The samples (typically 250 mL) were placed in a jacketed addition funnel and deoxygenated by a slow flow of helium. The temperature of the solution was adjusted by circulating a temperature regulated methanol / water mixture through the external jacket with a circulating pump. The sample was equilibrated at the desired temperature for 10 to 20 min and then allowed to flow through a flow cuvette at a rate of 5 to 20 mL / min. Sample temperatures were measured by a thermocouple inserted into the cuvette just above the laser and analyzing light paths. For low temperature data the sample and cuvette were enclosed in a box equipped with quartz windows that was purged with nitrogen in order to minimize water condensation on optical surfaces.

Reactions of 1 and Analysis for 9, 10, 11, 12, and 13: Photolyses of PTOC ester **1** were carried out in 8 mm (i.d.) pyrex reaction tubes, capped with a rubber septum. The tube was purged for at least 5 min with a continuous flow of N_2 . The solvent (TFT, DCM, benzene, or ACN), thiophenol, and, in some cases, TFE, was added to the reaction tube to make a volume of 700 μL . The solution was deoxygenated for 2 to 4 min. by agitating the solution while passing a gentle stream of N_2 through the solution using a syringe needle. The solution was then shielded from light, the PTOC ester **1** solution (300 μL , 0.033M) was added, and the solution was further deoxygenated for 2 to 3 min as described above. The syringe needle was withdrawn, and the solution was then irradiated with a 150 W tungsten floodlamp at a distance of ca. 24 inches for 1 to 1.5 h. The reaction mixtures were analyzed directly by HPLC. Mixtures of methanol, acetonitrile, and water were used as eluant (typically 70:20:10, respectively) for 10 min., followed by a gradient (1 min) to a 70:30 mixture of methanol:acetonitrile, followed by further elution to 30 min.

Calibration curves for **9** and **10** were constructed by injecting samples (2 μL and 5 μL) of known concentration (1, 2, 3, 4, 5 and 10 mM). Chromatograms were extracted from the PDA data at 250, 260, 270, and 280 nm. Plots of peak area vs sample concentration typically yielded straight lines with $r^2 > 0.999$. For reactions in TFT, TFT / 0.5%TFE, TFT / 1%TFE, and DCM, the yields of **9** and **10** from each reaction were determined by comparison of the calibration curves with peak areas for **9** and **10** from chromatograms at 250, 260, 270, and 280 nm of quadruplicate injections (2 \times 2 μL and 2 \times 5 μL). In the benzene and acetonitrile cases, single or

duplicate injections were used (2, 5 or 10 μL). The cyclic products **11** and **12** coeluted on HPLC and absorbed weakly beyond 240 nm. Since calibration curves prepared for **11** and **12** at 222 nm were similar and GC studies showed the **11** to be the major cyclic component (>90%), the calibration curve for **11** was used to quantitate the yield of cyclic product.

The identities of the hydrocarbon products **10**, **11**, **12**, and **13** were further verified by GCMS. Reactions run in DCM (PhSH = 0.1, 0.3, 0.5 and 0.7 M) as described above were analyzed by HPLC, and then chromatographed on silica (Hexanes) to remove **9** and other polar components. The solvent was removed by rotary evaporator, and the resulting material was taken up in DCM and analyzed by GCMS. The major component (approximately 75%) of this hydrocarbon mixture was established to be **10** as determined by identical retention times and mass spectra with an authentic sample of **10**. Identical retention times as verified by coinjection, and identical mass spectra with independently prepared authentic samples of, **11**, **12**, and **13** established the presence these cyclic compounds in the product mixture. The acyclic diene **10** and the cyclic alkene products **11** and **12** comprised 88% of the hydrocarbon fraction when PhSH = 0.1 M and 96% when PhSH = 0.5 M.

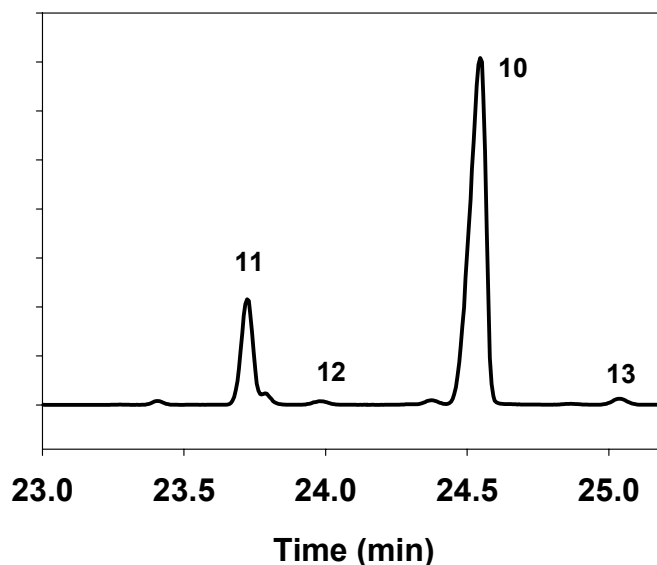


Figure S1. Portion of the GCMS chromatogram of the hydrocarbon fraction from the photolysis of **1** in DCM with PhSH = 0.5 M.

Table S1. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in TFT.

[PhSH]	9	10	11
3.0000	45.9300	31.2800	3.3500
3.0000	45.5500	30.8600	3.3500
3.0000	45.1200	31.8200	3.0600
3.0000	46.0800	31.7600	3.0600
2.5000	46.3500	31.8600	3.1400
2.5000	47.7500	32.9300	3.1800
2.5000	46.3600	31.9000	3.4600
2.5000	44.7600	30.6800	3.4500
2.0000	49.4000	33.9200	4.7700
2.0000	47.7600	32.0400	4.4200
2.0000	48.3100	32.7400	4.4500
2.0000	48.2500	33.3900	4.7100
1.5000	44.8600	34.6400	4.4600
1.5000	44.3700	33.5400	4.2000
1.5000	43.9500	33.9300	4.4300
1.5000	43.5100	32.9600	4.2000
1.0000	42.3700	34.4300	5.7700
1.0000	42.5900	33.7100	5.8000
1.0000	41.9700	35.5700	5.0900
1.0000	41.9500	33.8100	5.7600
0.9000	41.0900	38.4400	4.5900
0.9000	40.3000	36.8000	5.1800
0.9000	40.7000	38.0500	4.5500
0.9000	41.0000	37.6100	5.3090
0.8000	41.2000	38.4000	5.9800
0.8000	40.2600	38.2200	6.0000
0.8000	41.3900	38.6000	6.1200
0.8000	40.5900	38.6900	6.2800
0.7000	39.4600	41.1200	6.0000
0.7000	39.1400	40.7600	5.3200
0.7000	40.4500	41.3100	6.3000
0.7000	40.5400	41.5300	6.4500
0.6000	35.9200	40.7000	6.1900
0.6000	35.6400	39.5900	5.9600
0.6000	34.6000	38.3700	6.0100
0.6000	33.6000	37.2000	5.9900
0.5000	35.7100	45.0300	8.2100
0.5000	33.7700	42.5800	7.6000
0.5000	34.6100	43.5100	6.9500
0.5000	31.1300	41.1500	6.1500
0.4000	29.7400	44.5300	6.1900
0.4000	28.9800	42.9600	6.2200
0.4000	29.4000	42.3500	6.8600
0.4000	28.2900	40.6500	6.9100
0.3000	27.1200	48.4700	7.9000
0.3000	26.6000	47.3900	7.9200
0.3000	25.5100	45.8900	7.5700
0.3000	24.7700	44.2500	7.5600
0.2000	20.9500	51.6500	8.8000
0.2000	20.6300	50.9600	8.7900
0.2000	19.8100	50.3200	7.7100
0.2000	19.3100	49.0000	8.9000
0.1000	13.0100	55.2700	11.1900
0.1000	13.3400	54.8200	10.8000
0.1000	13.2500	54.4100	11.4900
0.1000	13.0700	55.5800	11.3200
0.0500	6.9100	53.1100	11.1100
0.0500	7.0600	53.6000	11.3400
0.0500	7.2900	54.2900	11.3800
0.0500	7.3700	53.9600	11.3700

Table S2. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in TFT / 0.5% TFE.

[PhSH]	9	10	11
2.0000	26.6500	52.1900	6.4000
2.0000	27.3300	51.8400	6.6600
2.0000	27.3900	51.7100	7.1700
2.0000	27.4200	51.4900	7.0700
1.7500	33.0600	69.5000	9.3600
1.7500	33.6200	69.9800	9.5800
1.7500	33.9300	68.9000	10.2800
1.7500	34.0500	68.8600	10.2300
1.7500	29.4700	67.8400	9.4500
1.7500	30.4200	67.9400	8.8100
1.7500	30.4900	68.1000	8.8000
1.7500	29.5000	68.0200	9.1900
1.5000	23.1200	55.6000	8.4100
1.5000	22.9800	55.1300	8.3400
1.5000	23.6700	55.2400	9.1700
1.5000	23.9400	55.2500	9.1600
1.5000	23.5400	54.7800	9.1500
1.5000	24.7500	53.2400	11.7800
1.5000	25.5600	53.2000	10.0400
1.5000	25.5000	53.0400	9.6900
1.2500	31.0800	67.2700	12.7700
1.2500	30.1500	65.6300	14.1300
1.2500	31.0500	65.3500	12.7800
1.2500	30.4100	66.3100	10.4100
1.2500	27.4300	68.6800	10.2200
1.2500	26.4600	69.2300	9.5200
1.2500	26.3200	69.3400	9.3000
1.2500	27.4100	69.1400	10.3200
1.0000	23.1800	57.0400	13.6600
1.0000	23.8500	60.5100	9.9900
1.0000	27.1600	65.2300	12.5500
1.0000	27.1700	65.1900	12.4400
1.0000	22.7500	58.6200	10.0900
1.0000	26.5200	66.1700	11.6800
1.0000	26.3700	65.7400	11.0100
1.0000	28.6700	67.0100	12.1800
1.0000	29.3600	67.0100	13.2300
1.0000	28.6700	67.0100	12.1800
1.0000	22.8500	56.2200	10.7300
1.0000	28.2300	66.5300	11.9800
1.0000	29.3100	66.9500	13.1800
0.9000	21.8300	58.5800	10.3100
0.9000	22.4800	58.0000	10.3100
0.9000	22.7500	58.2000	11.2300
0.9000	22.7600	58.1600	11.2400
0.8000	22.9900	67.5400	12.4100
0.8000	22.8700	66.8300	12.6400
0.8000	23.4700	67.8400	13.5200
0.8000	25.0300	68.2200	13.9300
0.7000	20.7500	59.2800	13.0200
0.7000	20.1600	59.2200	12.3800
0.7000	20.8900	59.2500	13.4400
0.7000	21.0000	59.3300	13.4100
0.6000	19.6600	60.9800	14.1900
0.6000	19.7000	61.2500	14.2400
0.6000	19.2200	60.8800	13.0200
0.6000	18.8500	60.9800	13.1200
0.5000	17.5200	60.9900	13.5100
0.5000	17.5800	61.0100	13.5200
0.5000	17.8100	61.0200	14.8600
0.5000	17.8600	61.0500	14.6100
0.4000	14.8800	68.4700	15.8400

0.4000	14.8600	68.0100	15.6100
0.4000	15.5100	68.3200	16.7200
0.4000	15.5100	68.3700	16.8000
0.3000	11.7100	69.8700	18.1000
0.3000	11.7100	69.3000	18.0800
0.3000	12.2800	69.7200	19.5600
0.3000	12.2100	69.6100	19.5500
0.2000	9.3100	66.9700	19.4800
0.2000	9.1400	66.7300	19.2500
0.2000	9.3500	66.5200	20.4200
0.2000	9.4100	66.6400	20.4600
0.1000	4.9100	61.5600	19.4100
0.1000	4.9900	61.4200	20.0900
0.1000	5.5600	61.5400	20.9200
0.1000	5.5700	61.4900	21.5700

Table S3. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in TFT / 1.0 % TFE.

[PhSH]	9	10	11
2.0000	12.8600	68.2000	7.0600
2.0000	12.7800	67.5200	6.8100
2.0000	13.3400	67.5700	7.3700
2.0000	13.4100	67.5600	7.4700
2.0000	14.6400	85.3000	7.5500
2.0000	14.6000	84.5500	7.5600
2.0000	15.2700	83.4500	8.2400
2.0000	15.2600	83.2800	8.1800
1.7500	12.6900	79.5300	9.6400
1.7500	12.6600	79.0400	9.6500
1.7500	13.3300	78.7900	10.3400
1.7500	13.5400	79.4000	10.4200
1.5000	10.0000	66.2500	7.3500
1.5000	10.0300	65.7600	7.7000
1.5000	10.5100	65.7300	8.3800
1.5000	10.5300	67.1100	8.4700
1.5000	12.9300	83.3500	9.8100
1.5000	12.8400	82.4300	9.7300
1.5000	13.4100	82.0700	10.7000
1.5000	13.4600	81.9200	10.6900
1.0000	10.7700	81.3600	13.9300
1.0000	10.6700	81.2500	12.2600
1.0000	11.0300	79.9900	13.0300
1.0000	11.1100	79.4600	13.0500
0.9000	10.6000	81.6600	13.1100
0.9000	10.3800	81.4200	13.2400
0.9000	10.5400	80.4400	14.2900
0.9000	10.6800	80.4300	14.4000
0.8000	11.3500	77.4900	15.4300
0.8000	11.3500	77.3700	15.5200
0.8000	10.7400	77.3100	14.4300
0.8000	10.8200	77.4300	14.3100
0.7000	10.8000	78.2400	16.2400
0.7000	10.5700	78.1500	16.2100
0.7000	10.0900	78.2900	14.9000
0.7000	9.9800	78.8100	14.9000
0.6000	9.0600	77.7900	15.8200
0.6000	9.3700	77.9400	17.6400
0.6000	9.2000	77.9400	18.2300
0.6000	9.1500	78.5700	12.2100
0.5000	8.3800	76.7900	16.9800
0.5000	8.3700	76.9600	17.0600
0.5000	8.8000	76.8000	18.3700
0.5000	8.7900	76.8700	20.3500
0.4000	7.9700	78.6700	18.9000
0.4000	8.0100	78.9100	18.7900
0.4000	8.3700	78.7000	20.3500
0.4000	8.3000	78.9400	20.6700
0.3000	4.2400	68.9200	17.0400
0.3000	4.2400	67.9400	19.1000
0.3000	4.4300	69.2800	17.8900
0.3000	4.4500	69.1000	17.1700
0.2000	3.2200	65.1100	19.1000
0.2000	3.2300	65.0100	19.0900
0.2000	3.4800	64.9600	20.2000
0.2000	3.4700	65.1000	20.3100

Table S4. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in Dichloromethane.

[PhSH]	9	10	11
3.0000	35.6000	57.5000	10.0000
3.0000	35.7000	56.9000	10.8000
3.0000	36.0000	57.1000	10.8000
3.0000	34.7200	56.7800	9.8900
2.5000	28.7000	51.8000	11.3200
2.5000	28.9000	51.8000	11.2000
2.5000	28.6000	52.4000	10.0000
2.5000	28.4000	52.3000	10.9000
2.0000	25.5000	57.6000	14.3000
2.0000	25.5000	57.5000	13.8000
2.0000	25.5000	56.7000	13.6000
2.0000	27.0000	56.5000	13.9000
1.7500	22.8200	54.8800	13.4200
1.7500	22.8700	55.0000	13.4400
1.7500	22.0900	55.0800	12.4600
1.7500	22.5400	55.6800	12.5400
1.5000	20.2000	57.6100	14.0200
1.5000	20.4000	56.4800	15.4700
1.5000	20.3800	56.5400	15.4000
1.5000	20.1500	57.4300	15.1800
1.0000	15.7800	61.1700	18.1100
1.0000	15.7900	61.3800	18.0800
1.0000	15.9800	59.9300	18.1200
1.0000	15.9400	60.1600	18.2200
0.8100	13.4900	59.0600	19.5700
0.8100	13.2000	58.8900	19.5600
0.8100	13.1800	59.8200	18.3700
0.8100	13.1100	59.5400	18.3000
0.7000	12.4100	59.6300	20.1900
0.7000	13.2900	64.3900	20.0000
0.7000	12.2700	61.4100	19.1100
0.7000	12.4700	60.1300	20.2600
0.6000	10.4300	59.8600	21.3200
0.6000	10.6200	61.8500	21.3900
0.6000	10.6300	61.8200	21.0200
0.6000	10.5400	61.7100	21.3400
0.5000	8.1400	53.9200	17.7900
0.5000	8.7800	54.4300	18.0100
0.5000	8.2400	54.3400	22.3100
0.5000	8.4200	52.8500	17.8800
0.4000	7.3700	60.0900	23.4400
0.4000	7.3000	61.7600	23.0800
0.4000	7.2600	61.4300	23.0100
0.4000	7.2600	59.4800	23.3100
0.3000	6.0200	60.3100	24.2400
0.3000	5.9000	58.2900	24.5400
0.3000	5.7900	58.1100	24.1000
0.3000	5.6200	59.0500	23.5400
0.2000	3.3500	44.8800	22.1100
0.2000	3.2700	48.6200	21.5900
0.2000	3.0800	45.7800	19.2500
0.2000	3.3800	44.7300	22.0100
0.1000	2.4200	71.7800	36.8600
0.1000	2.4300	72.2000	31.3400
0.1000	2.9100	74.1100	35.0000
0.1000	2.4800	69.8700	32.7700

Table S5. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in Benzene.

[PhSH]	9	10	11
3.0000	51.8600	27.6900	3.3800
3.0000	55.3500	30.3900	3.9000
2.5000	37.8600	15.7500	5.0200
2.5000	41.1600	22.4000	5.6500
2.5000	51.4600	30.9400	4.2000
2.5000	55.5900	30.2000	3.9700
2.0000	63.4100	41.4400	3.5200
2.0000	62.9800	37.6100	3.4500
1.5000	57.5400	41.4100	4.5600
1.5000	61.0400	45.6700	3.4500
1.0000	48.8100	49.0600	3.7900
1.0000	54.0500	54.4800	4.0500
1.0000	62.6600	58.4900	4.5000
1.0000	62.4000	54.3300	5.4000
0.5000	49.9900	64.2800	5.2200
0.5000	57.1100	76.4400	5.1500
0.1000	16.8400	71.6600	9.4800
0.1000	16.7400	70.5200	9.3000
0.0800	11.8700	49.9200	5.9100
0.0800	11.9100	49.0500	6.0400
0.0600	8.3600	59.6900	9.2700
0.0600	8.3300	59.4300	9.2800
0.0420	5.2700	53.1500	4.0300
0.0420	5.3500	53.3000	3.5500
0.0200	2.8100	58.9600	4.3300
0.0200	2.9300	58.9000	4.1000

Table S6. Yields of **9**, **10**, and **11** determined by HPLC for photolysis of PTOC **1** in Acetonitrile.

[PhSH]	9	10	11
2.0000	12.5400	75.2600	9.8300
2.0000	10.9600	64.9200	9.7200
1.5000	9.3000	63.6600	10.9000
1.5000	10.4500	72.0400	11.4900
1.2500	10.1900	80.8400	12.5500
1.2500	9.3700	73.9400	12.3100
1.0000	9.3300	82.8000	14.0200
1.0000	8.8500	77.3500	13.6400
0.7700	6.9800	70.8100	10.7900
0.7700	6.9800	71.1200	10.7600
0.5000	5.2100	74.7100	14.5200
0.5000	5.2900	75.6800	14.2900
0.5000	4.5700	74.5500	14.2200
0.4000	4.3000	70.9600	14.0600
0.4000	4.4300	70.6200	13.8000

Table S7. Observed Rate Constants as a function of Temperature for LFP of **1** in TFT.^a

Temperature (°C)	k_{obs}
-0.8	1.18 ± 0.05
-0.8	1.15 ± 0.04
9.8	1.65 ± 0.04
9.8	1.61 ± 0.04
18.9	2.20 ± 0.05
19.5	2.26 ± 0.02
19.5	2.15 ± 0.02
30.5	3.28 ± 0.03
30.5	3.29 ± 0.04
39.4	4.73 ± 0.11
39.4	5.03 ± 0.14
49.1	6.77 ± 0.27
49.1	7.31 ± 0.11

^aRate constants in units of 10^5 s^{-1} .**Table S8.** Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.5 % TFE.^a

Temperature (°C)	k_{obs}
10.5	18.7 ± 0.6
10.5	22.1 ± 1.5
19.8	27.0 ± 1.6
19.8	24.9 ± 1.2
29.8	30.6 ± 1.7
29.8	29.0 ± 1.4
39.5	36.2 ± 3.1
39.5	32.5 ± 3.0
49.3	40.8 ± 0.9
49.3	39.0 ± 0.9

^aRate constants in units of 10^5 s^{-1} .

Table S9. Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.0125 M 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanol.^a

Temperature (°C)	k_{obs}
-29.0	2.00 ± 0.09
-29.0	2.03 ± 0.1
-20.7	2.40 ± 0.07
-20.7	2.45 ± 0.08
-9.7	3.02 ± 0.04
-9.7	2.97 ± 0.05
-1.5	3.47 ± 0.07
-1.5	3.59 ± 0.03
7.6	4.28 ± 0.05
7.6	4.29 ± 0.05
9.5	4.83 ± 0.04
9.5	5.00 ± 0.09
18.8	5.23 ± 0.02
18.8	5.35 ± 0.06
20.2	6.43 ± 0.07
20.2	6.13 ± 0.05
30.1	7.53 ± 0.12
30.1	7.62 ± 0.15
38.6	9.10 ± 0.23
38.6	8.94 ± 0.17
47.6	11.1 ± 0.34
47.6	10.8 ± 0.41

^aRate constants in units of 10^5 s^{-1} .

Table S10. Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.025 M 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanol.^a

Temperature (°C)	k_{obs}
-30.2	3.75 ± 0.2
-19.7	5.18 ± 0.4
-19.7	5.11 ± 0.4
-11.8	5.96 ± 0.4
-11.8	5.95 ± 0.4
-2.3	7.34 ± 0.2
-2.3	6.98 ± 0.3
8.5	7.72 ± 0.4
8.5	7.65 ± 0.4
9.2	7.99 ± 0.3
9.2	8.11 ± 0.2
14.6	8.45 ± 0.2
18.7	9.11 ± 0.4
18.7	8.95 ± 0.2
32.1	11.2 ± 0.1
32.1	11.2 ± 0.1
41.2	12.8 ± 0.1
41.2	12.9 ± 0.2
51.3	14.4 ± 0.2
51.3	14.3 ± 0.2

^aRate constants in units of 10^5 s^{-1} .

Table S11. Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.05 M 2,2,3,3,4,4,5,5-octafluoropentanol.^a

Temperature (°C)	k_{obs}
-3.5	16.6 ± 0.9
-3.5	16.8 ± 1.0
6.5	19.7 ± 1.0
6.5	19.8 ± 0.8
9.2	20.8 ± 0.5
9.2	20.2 ± 1.0
19.2	24.0 ± 0.6
19.2	23.4 ± 0.7
31.5	26.3 ± 1.0
31.5	26.8 ± 0.6
41.5	28.6 ± 0.4
41.5	30.1 ± 1.0
51.7	32.8 ± 0.9
51.7	31.1 ± 0.4

^aRate constants in units of 10^5 s^{-1} .

Table S12. Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.1 M 2,2,3,3,4,4,5,5-octafluoropentanol.^a

Temperature (°C)	k_{obs}
9.3	68.9 ± 1.4
9.3	71.3 ± 1.2
19.4	68.7 ± 0.7
19.4	69.6 ± 1.2
31.0	72.2 ± 0.8
31.0	68.6 ± 1.0
41.4	72.4 ± 2.0
41.4	69.2 ± 0.9
52.0	71.4 ± 1.9
52.0	68.5 ± 1.5

^aRate constants in units of 10^5 s^{-1} .

Table S13. Observed Rate Constants as a Function of Temperature for LFP of **1** in TFT / 0.2 M 2,2,3,3,4,4,5,5-octafluoropentanol.^a

Temperature (°C)	k_{obs}
1.4	328 ± 7
1.4	298 ± 6
9.3	238 ± 3
9.3	243 ± 3
19.4	267 ± 7
19.4	209 ± 5
30.9	218 ± 4
30.9	227 ± 3
42.1	202 ± 3
42.1	209 ± 3
52.7	187 ± 3
52.7	192 ± 4

^aRate constants in units of 10^5 s^{-1} .

Table S14. Observed Rate Constants as a Function of Temperature for LFP of **1** in Acetonitrile.^a

Temperature (°C)	k_{obs}
9.8	28.2 ± 1.7
9.8	27.6 ± 1.5
19.6	36.0 ± 1.6
19.6	38.9 ± 2.0
29.1	52.9 ± 1.8
29.1	50.5 ± 2.2
39.2	70.9 ± 2.3
39.2	71.2 ± 2.1
48.0	83.9 ± 1.0
48.0	88.8 ± 3.0

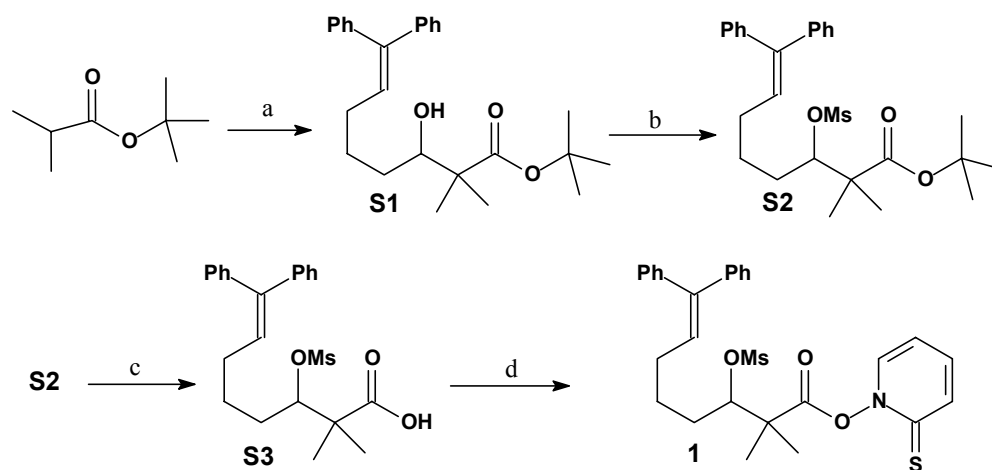
^aRate constants in units of 10^5 s^{-1} .

Table S15. Observed Rate Constants as a Function of Temperature for LFP of **1** in Acetonitrile / 5% TFE.^a

Temperature (°C)	k_{obs}
11.4	42.3 ± 1.6
11.4	39.8 ± 1.4
20.0	60.1 ± 2.9
20.0	59.6 ± 3.3
29.5	81.3 ± 4.1
29.5	82.4 ± 5.5
39.8	105 ± 2.6
39.2	105 ± 2.5
47.5	133 ± 1.4
47.5	133 ± 2.3

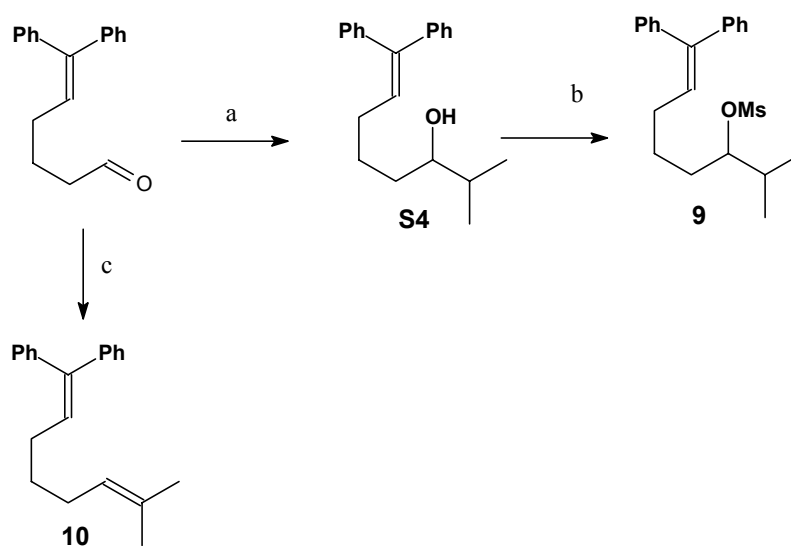
^aRate constants in units of 10^5 s^{-1} .

Scheme S1



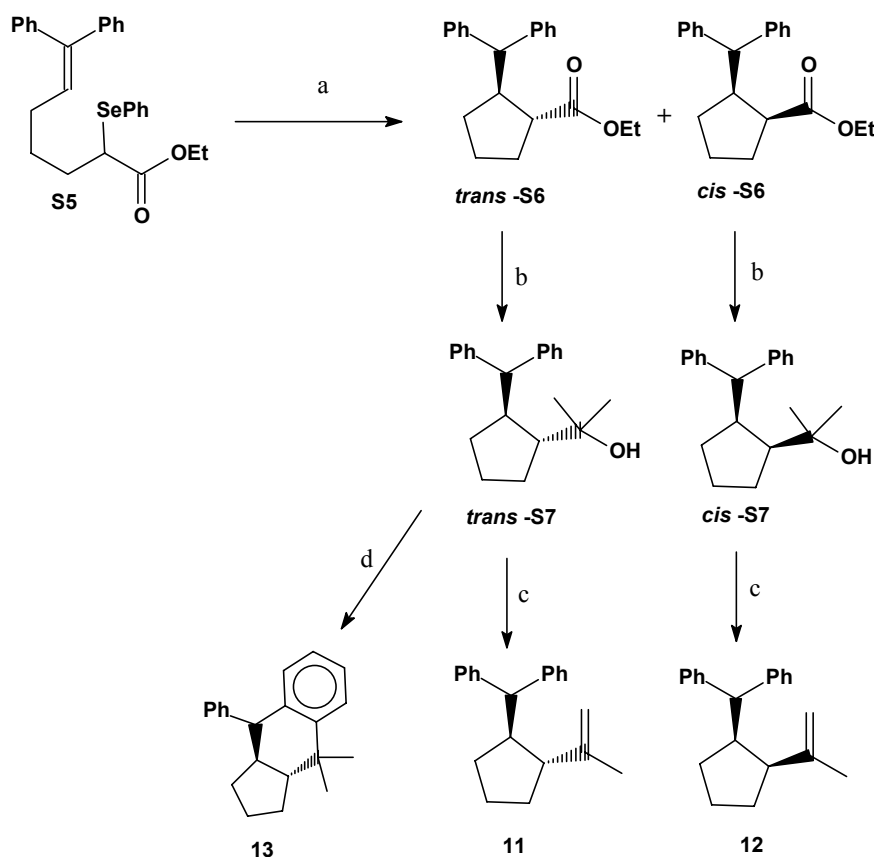
a) LDA/THF (-78 °C), then 6,6-diphenyl-5-hexenal; b) Et₃N / DCM (0 °C), CH₃SO₂Cl;
c) TFA / DCM d) 2,2'-dithio-bis(pyridine *N*-oxide), *n*-Bu₃P

Scheme S2



a) *i*-PrMgBr / THF (0 °C); b) Et₃N / DCM (0 °C), CH₃SO₂Cl;
c) isopropyltriphenylphosphonium iodide / LiHMDS / THF (0 °C).

Scheme S3



a) Bu_3SnH / AIBN / Benzene (reflux); b) MeLi / THF (0 °C); c) Et_3N / DCM (0 °C), $\text{CH}_3\text{SO}_2\text{Cl}$; d) *p*-TsOH/Benzene, (80 °C).

***t*-Butyl 3-hydroxy-2,2-dimethyl-8,8-diphenyl-7-heptenoate (S1).** *t*-Butyl 2-methylpropanoate (1.4 g, 0.01 mol) in THF (10 mL) was added to a cold (-78 °C) solution of LDA (0.012 moles) in THF (25 mL). After stirring at -78 °C for 45 min, 6,6-diphenyl-5-hexenal (2.50 g, 0.01 mol) was added, and the mixture was stirred at -78 °C for 30 min. The reaction mixture was added to water and extracted with diethyl ether. The ether extracts were washed with brine and dried over MgSO_4 . After solvent removal by rotary evaporator, the crude product was chromatographed on silica gel (6 / 1 hexanes / ethyl acetate) to give a clear oil (2.60 g, 67%) ^1H NMR: δ 1.07 (s, 3 H), 1.15 (s, 3 H), 1.25 (m, 1 H), 1.42 (s, 9 H), 1.45 (m, 2 H), 1.77 (m, 1 H), 2.15 (m, 2 H), 2.61 (d, J = 7.0 Hz, 1 H), 3.49 (m, 1 H), 6.07 (t, J = 7.2 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 20.8 (CH_3), 22.2 (CH_3), 27.1 (CH_2), 28.0 (CH_3), 29.6 (CH_2), 31.5 (CH_2), 47.3 (C), 76.6 (CH), 80.8 (C), 126.77 (CH), 126.84 (CH), 127.2 (CH), 128.0 (CH), 128.1 (CH), 129.8 (CH), 129.9 (CH), 140.2 (C), 141.7 (C), 142.8 (C), 177.0 (C). HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{34}\text{O}_3$ $[\text{M} + \text{Na}]^+$, 483.2406; found, 483.2387.

***t*-Butyl 3-methanesulfonyloxy-2,2-dimethyl-8,8-diphenyl-7-heptenoate (S2).** Methanesulfonyl chloride (0.77 mL, 0.01 mol) was added to a cooled (0 °C) solution of S1 (2.6 g, 0.0066 mol) and triethylamine (1.4 mL, 0.01 mol) in dichloromethane (30 mL). The solution was stirred at 0 °C for 2 h. The reaction mixture was washed successively with cold dilute HCl (5%), cold NaHCO_3 (sat. aq), and brine. The resulting solution was dried over MgSO_4 , and

solvent was removed by rotary evaporator. The crude product was chromatographed on silica gel (4:1, hexanes / ethyl acetate) to give an oil (2.7 g, 87%). ^1H NMR: δ 1.10 (s, 3 H), 1.22 (s, 3 H), 1.40 (s, 9 H), 1.45-1.55 (m, 2 H), 1.64 (m, 1 H), 1.74 (m, 1 H), 2.15 (m, 2 H), 3.02 (s, 3 H), 4.94 (dd, J = 9.2, 2.1 Hz, 1 H), 6.06 (t, J = 7.5 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 19.5 (CH₃), 23.1 (CH₃), 26.8 (CH₂), 27.9 (CH₃), 29.5 (CH₂), 31.4 (CH₂), 38.9 (CH₃), 47.6 (C), 81.2 (C), 87.2 (CH), 126.90 (CH), 126.93 (CH), 127.2 (CH), 128.1 (CH), 128.2 (CH), 128.8 (CH), 129.8 (CH), 140.1 (C), 142.3 (C), 142.5 (C), 174.2 (C). HRMS (EI): Calcd for C₂₇H₃₆SO₅ [M]⁺, 472.2283; found: 472.2265.

3-Methanesulfonyloxy-2,2-dimethyl-8,8-diphenyl-7-heptenoic acid (S3). A solution of **S2** (1.22 g, 0.0021 mol) and trifluoroacetic acid (1.4 g, 0.012 mol) in dichloromethane (15 mL) was stirred for 15 h. The solution was washed with water and brine and dried over MgSO₄. Solvent was removed by rotary evaporation to give a viscous oil (0.81 g, 76%). ^1H NMR: δ 1.19 (s, 3 H), 1.27 (s, 3 H), 1.54 (m, 2 H), 1.60-1.78 (m, 2 H), 2.16 (m, 2 H), 2.99 (s, 3 H), 4.95 (d, J = 9.2 Hz, 1 H), 6.05 (t, J = 7.4 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 20.7 (CH₃), 21.5 (CH₃), 26.6 (CH₂), 29.4 (CH₂), 30.7 (CH₂), 38.9 (CH₃), 47.0 (C), 86.7 (CH), 126.95 (CH), 126.98 (CH), 127.2 (CH), 128.1 (CH), 128.2 (CH), 128.8 (CH), 129.9 (CH), 140.1 (C), 142.4 (C), 142.5 (C), 181.2 (C). HRMS (ESI): Calcd for C₂₃H₂₈SO₅ [M + Na]⁺, 439.1555; found, 439.1549.

(1H)-2-Thioxo -1-pyridyl 3-methanesulfonyloxy-2,2-dimethyl-8,8-diphenyl-7-heptenoate (1). Tributylphosphine (0.82 mL, 0.0033 mol) was added to a mixture of **S3** (0.92 g, 0.0022 mol) and 2,2'-dithio-bis (pyridine-*N*-oxide) (0.83 g, 0.0033 mol) in dichloromethane (15 mL), which was cooled to 0 °C and shielded from light. The mixture was stirred at 0 °C for 1 h and then washed with NaHCO₃ (sat. aq) and brine. The solution was dried over MgSO₄. The solvent was removed by rotary evaporator, and the resulting crude product was chromatographed on silica gel (2:1, hexanes / ethyl acetate) to give a yellow solid (1.02 g, 89%). Mp 100-103 °C (dec). ^1H NMR: δ 1.45 (s, 3 H), 1.52 (s, 3 H), 1.55-1.80 (m, 4 H), 2.20 (m, 2 H), 3.04 (s, 3 H), 5.10 (d, J = 9.1 Hz, 1 H), 6.07 (t, J = 7.4 Hz, 1 H), 6.57 (td, J = 6.8, 1.6 Hz, 1 H), 7.10-7.40 (m, 11 H), 7.65 (dd, J = 8.8, 1.4 Hz, 1 H), 7.77 (d, J = 6.7 Hz, 1 H). ^{13}C NMR: δ 19.6 (CH₃), 22.3 (CH₃), 26.5 (CH₂), 29.2 (CH₂), 29.6 (CH₂), 39.0 (CH₃), 47.5 (C), 85.5 (CH), 112.7 (CH), 127.01 (CH), 127.03 (CH), 127.18 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 129.8 (CH), 133.6 (CH), 137.3 (CH), 138.1 (CH), 139.9 (C), 142.4 (C), 142.6 (C), 170.7 (C), 175.9 (C). HRMS (ESI): Calcd for C₂₈H₃₁NO₅S [M + H]⁺, 526.17164; found, 526.17180.

2-Methyl-8,8-diphenyl-7-octen-3-ol (S4). A solution of 6,6-diphenyl-5-hexenal (1.0 g, 0.004 mol) in THF (5 mL) was added to a cooled (0 °C) solution of isopropylmagnesium bromide freshly prepared under a nitrogen atmosphere from 2-bromopropane (1.0 g, 0.0078 mol) and Mg (1.0 g, 0.041 mol) in THF (30 mL). After 2 h, water was added, and the mixture was extracted with diethyl ether. The ether extracts were washed with brine and dried over MgSO₄. The solvent was removed by rotary evaporator. The crude product was chromatographed on silica gel (5:1, hexanes / ethyl acetate) to give a clear oil (0.66 g, 56%). ^1H NMR: δ 0.88 (d, J = 6.9 Hz, 3 H), 0.89 (d, J = 6.90 Hz, 3 H), 1.35 (br s, 1 H), 1.40-1.75 (m, 5 H), 2.13 (q, J = 7.3 Hz, 2 H), 3.30 (m, 1 H), 6.06 (t, J = 7.5 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 17.0 (CH₃), 18.8 (CH₃), 26.3 (CH₂), 29.7 (CH₂), 33.4 (CH₃), 33.6 (CH), 76.3 (CH), 126.58 (CH), 126.64 (CH), 127.0 (CH), 127.8 (CH), 127.9 (CH), 129.6 (CH), 129.7 (CH), 140.0 (CH), 141.5 (C), 142.5 (C). HRMS (EI): Calcd for C₂₁H₂₆O [M]⁺, 294.1984; found, 294.1979.

2-Methyl-3-methanesulfonyloxy-8,8-diphenyl-7-octene (9). Methanesulfonyl chloride (250 μL , 0.0033 mol) was added to a cold (0 °C) solution of **S4** (0.64 g, 0.0033 mol) and triethylamine (460 μL , 0.0033 mol) in dichloromethane (15 mL). The mixture was stirred at 0 °C for 1 h and then washed successively with cold dilute HCl (5%), NaHCO₃ (sat, aq) and brine. After drying over MgSO₄, the solvent was removed by rotary evaporator, and the crude product was chromatographed on silica gel (4:1, hexanes / ethyl acetate) to give an oil (0.44 g, 54%). ^1H

NMR: δ 0.92 (d, J = 6.5 Hz, 3 H), 0.95 (d, J = 7.0 Hz, 3 H), 1.40-1.72 (m, 4 H), 1.97 (septet of doublets, J = 6.8, 4.7 Hz, 1 H), 2.14 (q, J = 7.0 Hz, 2 H), 4.51 (m, 1 H), 6.06 (t, J = 7.5 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 17.4 (CH_3), 17.9 (CH_3), 25.5 (CH_2), 29.4 (CH_2), 30.5 (CH_2), 31.4 (CH), 38.6 (CH_3), 88.3 (CH), 126.76 (CH), 126.82 (CH), 127.0 (CH), 127.9 (CH), 128.0 (CH), 128.8 (CH), 129.7 (CH), 139.9 (CH), 142.1 (C), 142.4 (C). HRMS (EI): Calcd for $\text{C}_{22}\text{H}_{28}\text{SO}_3[\text{M}]^+$, 372.1759; found, 372.1765.

1,1-Diphenyl-7-methyl-1,6-octadiene (10). *n*-BuLi (3.0 mL, 1.6 M in hexanes, 0.0048 mol) was added to a cooled (0 °C) solution of hexamethyldisilazane (0.81 g, 0.005 mol) in THF (20 mL). After stirring for 10 min at 0 °C, isopropyltriphenylphosphonium iodide (2.1 g, 0.0049 mol) was added, and the mixture was stirred at 0 °C for 30 min. 6,6-Diphenyl-5-hexenal (1.1 g, 0.0044 mol) was added, and the mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into hexane and filtered through silica gel. The solvent was removed by rotary evaporator, and the crude product was chromatographed on silica gel (hexanes) to give a clear oil (0.43 g, 35%). ^1H NMR: δ 1.46 (pentet, J = 7.8 Hz, 2 H), 1.50 (br s, 3 H), 1.65 (br s, 3 H), 1.95 (q, J = 7.2 Hz, 2 H), 2.13 (q, J = 7.2 Hz, 2 H), 5.05 (t of septets, J = 7.0, 1.4 Hz, 2 H), 6.08 (t, J = 7.2 Hz, 1 H), 7.10-7.40 (m, 10 H). ^{13}C NMR: δ 17.7 (CH_3), 25.7 (CH_3), 27.7 (CH_2), 29.5 (CH_2), 30.2 (CH_2), 124.4 (CH), 126.72 (CH), 126.78 (CH), 127.2 (CH), 128.03 (CH), 128.05 (CH), 129.9 (CH), 130.1 (CH), 131.6 (CH), 140.3 (CH), 141.6 (C), 142.9 (C). HRMS (EI): Calcd for $\text{C}_{21}\text{H}_{24}[\text{M}]^+$, 276.1878; found, 276.1901.

Ethyl 7,7-diphenyl-2-(phenylselenenyl)-6-heptenoate (S5). A solution of ethyl 7,7-diphenyl-6-heptenoate (3.07 g, 0.01 mol) in THF (15 mL) was added slowly to a cold (-78 °C) solution of LDA (0.012 mol) in THF / hexanes (27 mL). The solution was stirred for 1 h at -78 °C. Diphenyldiselenide (3.7 g, 0.012 mol) in THF (15 mL) was added, and the mixture was stirred as it warmed slowly to room temperature. Water was added, and the mixture was extracted with diethyl ether. The extracts were washed with brine and dried over MgSO_4 . Solvent was removed by rotary evaporator, and the crude product was chromatographed on silica gel (10:1, hexanes / ethyl acetate) to give an oil (4.12 g, 89%). ^1H NMR: δ 1.46 (t, J = 7.2 Hz, 3 H), 1.53 (m, 2 H), 1.74 (m, 1 H), 1.87 (m, 1 H), 2.13 (q, J = 7.2 Hz, 2 H), 3.53 (dd, J = 8.4, 6.7 Hz, 1 H), 4.06 (q, J = 7.2 Hz, 2 H), 6.01 (t, J = 7.4 Hz, 1 H), 7.10-7.40 (m, 13 H), 7.55 (m, 2 H). ^{13}C NMR: δ 14.0 (CH_3), 28.2 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 43.3 (CH), 60.8 (CH_3), 126.72 (CH), 126.76 (CH), 127.0 (CH), 127.7 (C), 127.9 (CH), 128.0 (CH), 128.2 (CH), 128.78 (CH), 128.81 (CH), 129.7 (CH), 135.5 (CH), 139.9 (C), 142.0 (C), 142.4 (C), 172.7 (C). HRMS (EI): Calcd for $\text{C}_{27}\text{H}_{28}\text{SeO}_2[\text{M}]^+$, 464.1255; found, 464.1273.

Ethyl (*cis*-2-diphenylmethyl)cyclopentanecarboxylate and ethyl (*trans*-2-diphenylmethyl)cyclopentanecarboxylate (*cis*-S6 and *trans*-S6). A solution of S5 (0.96 g, 0.0021 mol) and tributyltin hydride (4.0 g, 0.014 mol) in benzene (100 mL) was heated to reflux. AIBN (50 mg) in benzene (10 mL) was added over 5 min. After 40 min, a second portion of AIBN (70 mg) was added. After heating at reflux for 1 h, the solvent was removed by rotary evaporator, and the crude product was chromatographed on silica gel (hexanes and then 10:1, hexanes / ethyl acetate). Two isomeric cyclic products were isolated, in order of elution, *cis*-S6 (0.18 g, 58%) and *trans*-S6 (0.060 g, 19%).

cis-S6: ^1H NMR: δ 1.01 (t, J = 7.1 Hz, 3 H), 1.57 (m, 2 H), 1.65 (m, 1 H), 1.85 (m, 1 H), 1.85 (m, 2 H), 1.96 (m, 1 H), 2.80 (td, J = 7.7, 3.3 Hz, 1 H), 2.91 (m, 1 H), 3.75 (dq, J = 10.7, 7.2 Hz, 1 H), 3.90 (dq, J = 10.7, 7.2 Hz, 1 H), 3.99 (d, J = 11.8 Hz, 1 H), 7.10-7.30 (m, 10 H). ^{13}C -NMR: δ 13.9 (CH_3), 24.2 (CH_2), 30.8 (CH_2), 31.0 (CH_2), 45.9 (CH), 48.3 (CH), 53.7 (CH), 59.7 (CH_2), 126.07 (CH), 126.15 (CH), 127.7 (CH), 127.9 (CH), 128.3 (CH), 128.4 (CH), 144.2 (C), 145.2 (C), 175.8 (C). HRMS (EI): Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2[\text{M}]^+$, 308.1776; found, 308.1788.

trans-S6: ^1H -NMR: δ 1.00 (t, J = 7.1 Hz, 3 H), 1.27 (dq, J = 13.0, 7.6 Hz, 1 H), 1.62 (m, 1 H), 1.69 (m, 1 H), 1.78 (m, 2 H), 1.84 (m, 1 H), 1.95 (m, 1 H), 2.44 (q, J = 7.2 Hz, 1 H), 3.28 (dq, J = 11.4, 7.6 Hz, 1 H), 3.62 (d, J = 11.5 Hz, 1 H), 3.65 (dq, J = 10.7, 7.1 Hz, 1 H), 3.78 (dq, J = 10.7, 7.2 Hz, 1 H), 7.07-7.32 (m, 10 H). ^{13}C NMR: δ 14.0 (CH_3), 25.3 (CH_2), 32.0 (CH_2),

32.5 (CH₂), 47.4 (CH), 49.7 (CH), 58.5 (CH), 60.1 (CH₂), 126.15 (CH), 126.25 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 144.0 (C), 144.5 (C), 176.7 (C). HRMS (ESI): Calcd for C₂₁H₂₄O₂[M + Na]⁺, 331.1674; found, 331.1687.

Assignment of stereochemistry to *cis* and *trans*-S6. NOE difference spectroscopy was used to assign the relative stereochemistry of the two S6 isomers. Irradiation of H-1 in the second eluting isomer resulted in a >5% enhancement of the diphenylmethyl C-H indicating that these hydrogens are in close proximity. Molecular mechanics (MM2) calculations on *trans*-S6 reveal that these hydrogens are held in a 1,3-diaxial type relationship at an internuclear distance of only ca. 2.5 Å. Based on the observation of the large NOE enhancement between these two hydrogens, the stereochemistry of the second eluting isomer was assigned as *trans*. Similar NOE difference experiments on the first eluting isomer revealed no similar enhancement. Molecular mechanics (MM2) calculations on *cis*-S6 reveal in this isomer that H-1 and the diphenylmethyl C-H are ca 3.5 Å apart, consistent with the absence of any NOE. On this basis, *cis* stereochemistry was assigned to the first eluting isomer. The identities of H-1, H-2, and the diphenylmethyl C-H protons in *cis*-S6 and *trans*-S6 were established by ¹H-COSY experiments.

***trans*-2-(Diphenylmethyl)cyclopentyl-2-propanol (*trans*-S7).** MeLi (4.4 mL, 1.6 M in ether, 0.007 mol) was added to a cooled (0 °C) solution of *trans*-S6 (0.86 g, 0.0028 mol) in THF (20 mL). After 20 min, water was added, and the mixture was extracted with diethyl ether. The ether extracts were dried over MgSO₄, and the solvent was removed by rotary evaporator. The product was chromatographed on silica gel (6:1, hexanes / ethyl acetate) to give an oil (0.58 g, 67%). ¹H NMR: δ 0.54 (br s, 1 H), 0.92 (s, 3 H), 0.98 (s, 3 H), 1.38-1.68 (m, 5 H), 1.85 (m, 2 H), 2.85 (m, 1 H), 3.65 (d, *J* = 11.1 Hz, 1 H), 7.10-7.38 (m, 10 H). ¹³C NMR: δ 25.2 (CH₂), 25.3 (CH₃), 28.9 (CH₂), 29.2 (CH₃), 31.9 (CH₂), 44.4 (CH), 53.5 (CH), 57.2 (CH), 72.9 (C), 126.0 (CH), 126.4 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 129.1 (CH), 144.4 (C), 144.6 (C). HRMS (EI): Calcd for C₂₁H₂₄[M-H₂O]⁺, 276.1878; found, 276.1879.

***cis*-2-(Diphenylmethyl)cyclopentyl-2-propanol (*cis*-S7).** MeLi (4.1 mL, 1.6 M in ether, 0.0065 mol) was added to a cooled (0 °C) solution of *cis*-S6 (0.67 g, 0.0022 mol) in THF (25 mL). After 20 min, water was added, and the mixture was extracted with diethyl ether. The ether extracts were dried over MgSO₄, and the solvent was removed by rotary evaporator. The product was chromatographed on silica gel (6:1, hexanes / ethyl acetate) to give an oil (0.46 g, 72%). ¹H NMR: δ 0.83 (br s, 1 H), 1.08 (s, 3 H), 1.23 (s, 3 H), 1.20-1.36 (m, 1 H), 1.40-1.65 (m, 4 H), 1.85 (m, 1 H), 2.14 (m, 1 H), 2.86 (tt, *J* = 11.3, 6.3 Hz, 1 H), 4.42 (d, *J* = 11.8 Hz, 1 H), 7.10-7.40 (m, 10 H). ¹³C NMR: δ 22.3 (CH₂), 26.2 (CH₃), 28.6 (CH₂), 31.0 (CH₂), 32.0 (CH₃), 47.9 (CH), 51.0 (CH), 52.4 (CH), 74.3 (C), 125.6 (CH), 125.9 (CH), 127.5 (CH), 127.7 (CH), 128.1 (CH), 128.5 (CH), 145.1 (C), 146.3 (C). HRMS (EI): Calcd for C₂₁H₂₄[M-H₂O]⁺, 276.1878; found, 276.1888.

***trans*-2-Diphenylmethyl-1-(2-propenyl)cyclopentane (11).** A solution of *trans*-S7 (0.50 g, 0.0017 mol) and triethylamine (0.4 mL, 0.0028 mol) in dichloromethane (10 mL) was cooled to 0 °C. Methanesulfonyl chloride (0.32 mL, 0.0041 mol) was added, and the mixture was stirred for 2 h at 0 °C. The reaction mixture was washed successively with cold dilute HCl (5%), cold NaHCO₃ (sat. aq), and brine. The resulting solution was dried over MgSO₄, and solvent was removed by rotary evaporator. The crude product was chromatographed on silica gel (hexanes) to give an oil (0.17 g, 36%). ¹H NMR: δ 1.00 (sextet, *J* = 6.8 Hz, 1 H), 1.48-1.63 (m, 3 H), 1.54 (s, 3 H), 1.79 (m, 2 H), 2.28 (q, *J* = 6.8 Hz, 1 H), 2.77 (m, 1 H), 3.73 (d, *J* = 9.6, 1 H), 4.43 (br s, 1 H), 4.51 (br s, 1 H), 7.10-7.30 (m, 10 H). ¹³C NMR: δ 20.3 (CH₃), 24.6 (CH₂), 31.2 (CH₂), 32.1 (CH₂), 46.6 (CH), 51.4 (CH), 56.9 (CH), 109.7 (CH₂), 125.90 (CH), 125.94 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 144.6 (C), 144.9 (C), 148.8 (C). HRMS (EI): Calcd for C₂₁H₂₄[M]⁺, 276.1878; found, 276.1873.

cis-2-Diphenylmethyl-1-(2-propenyl)cyclopentane (12). A solution of *cis*-**S7** (0.46 g, 0.0016 mol) and triethylamine (0.35 mL, 0.0024 mol) in dichloromethane (20 mL) was cooled to 0 °C. Methanesulfonyl chloride (0.19 mL, 0.0024 mol) was added, and the mixture was stirred for 1 h at 0 °C. The reaction mixture was washed successively with cold dilute HCl (5%), cold NaHCO₃ (sat. aq), and brine. The resulting solution was dried over MgSO₄, and solvent was removed by rotary evaporator. The crude product was chromatographed on silica gel (hexanes) to give an oil (0.15 g, 36%). ¹H NMR: δ 1.35-1.48 (m, 3 H), 1.51 (s, 3 H), 1.61-1.68 (m, 2 H), 1.70-1.77 (m, 1 H), 1.86-1.93 (m, 1 H), 2.62 (td, *J* = 7.3, 1.9 Hz, 1 H), 2.86 (tt, *J* = 11.6, 7.3 Hz, 1 H), 3.76 (d, *J* = 11.7, 1 H), 4.28 (br s, 1 H), 4.67 (br s, 1 H), 7.08-7.14 (m, 2 H), 7.18-7.26 (m, 6 H), 7.30-7.36 (m, 2 H). ¹³C NMR: δ 23.4 (CH₂), 23.6 (CH₃), 30.7 (CH₂), 31.8 (CH₂), 47.8 (CH), 48.5 (CH), 53.7 (CH), 112.3 (CH₂), 125.8 (CH), 125.9 (CH), 127.8 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 144.9 (C), 146.0 (C), 147.4 (C). HRMS (EI): Calcd for C₂₁H₂₄[M]⁺, 276.1878; found, 276.1866.

3a,9a-trans-9,9a-trans-4,4-dimethyl-2,3,3a,4,9,9a-hexahydro-9-phenylbenz[f]indene (13). A solution of *trans*-**S7** (0.2 g, 0.00041 mol) and *p*-toluenesulfonic acid (0.2 g) in benzene was heated at reflux for 20 min. The mixture was washed with NaHCO₃ (sat. aq), and brine. The resulting solution was dried over MgSO₄, and the solvent was removed by rotary evaporator. The crude product was chromatographed on silica gel (hexanes) to give a white solid (0.105 g, 92%).^{S3} The physical and spectroscopic properties were in agreement with literature reported data.

Computational Studies: All structures were fully optimized at the B3LYP/6-31G(d) level of theory using Gaussian 98.^{S4} Zero point calculations were carried out at the B3LYP/6-31G(d) level on the optimized structures. The calculated energies and Cartesian coordinates of the final structures for species **10**, **5**, **14+•**, **14**, **15+•**, **15**, **16+**, **16**, **17+**, and **17** are given in tables S16 to S27.

The accuracy of using B3LYP/6-31G* level DFT calculations combined with isodesmic reactions for estimating enthalpies of radical cations was evaluated using simple alkenes with accurately known ionization energies. The enthalpies of formation of the radical cations of propene, 2-methylpropene, 2-methyl-2-butene, and styrene were estimated using the isodesmic reactions of the alkene plus ethylene radical cation going to the alkene radical cation plus ethylene. The structure of each alkene and its corresponding radical cation was minimized at the B3LYP/6-31G* level of theory, and the enthalpy change was calculated using Eq S1, where ΔH(rxn) is the calculated enthalpy change for the reaction in kcal/mole and the values of H are the sum of electronic and thermal enthalpies for each species from the Gaussian 98 output. The enthalpy of formation for the radical cation was then calculated using Eq S2. The results are given in table S28.

$$\Delta H(\text{rxn}) = 627.5095 \times [\text{H}(\text{ethene}) + \text{H}(\text{Alkene}+\bullet) - \text{H}(\text{Alkene}) - \text{H}(\text{Ethene}+\bullet)] \quad (\text{S1})$$

$$\Delta H_f(\text{alkene}+\bullet) = \Delta H(\text{rxn}) - \Delta H_f(\text{ethane}) + \Delta H_f(\text{ethene}+\bullet) + \Delta H_f(\text{alkene}) \quad (\text{S2})$$

Table S16. B3LYP/6-316(d) Energies and Cartesian Coordinates for **10**:

E (RB+HF-LYP)				-814.672615716
Zero-point correction				0.390650
Thermal correction to Energy				0.411280
Thermal correction to Enthalpy				0.412224
Thermal correction to Gibbs Free Energy				0.337435
Sum of electronic and zero-point Energies				-814.281966
Sum of electronic and thermal Energies				-814.261336
Sum of electronic and thermal Enthalpies				-814.260392
Sum of electronic and thermal Free Energies				-814.335181
Atom Type	X	Y	Z	
C	2.1512	-2.4973	0.3654	
C	3.1356	-3.4751	0.5014	
C	2.4588	-1.2237	-0.1449	
H	1.1332	-2.7114	0.6784	
C	4.4556	-3.1995	0.1401	
C	3.7962	-0.9572	-0.4885	
C	1.4013	-0.1868	-0.3307	
H	2.8726	-4.4501	0.9040	
C	4.7810	-1.9344	-0.3532	
C	1.7838	1.2308	-0.0532	
C	0.1647	-0.5445	-0.7394	
H	5.2245	-3.9594	0.2510	
H	4.0602	0.0225	-0.8756	
C	1.5913	2.2412	-1.0091	
C	2.3653	1.5830	1.1772	
C	-1.0623	0.3142	-0.8738	
H	5.8058	-1.7068	-0.6357	
H	5.1170e-3	-1.5979	-0.9722	
C	2.7161	2.9037	1.4515	
C	1.9481	3.5634	-0.7382	
C	-2.2490	-0.2450	-0.0633	
H	1.1721	1.9811	-1.9770	
H	2.5355	0.8115	1.9231	
H	-0.8564	1.3423	-0.5587	
H	-1.3614	0.3658	-1.9332	
C	2.5077	3.9002	0.4946	
C	-3.5355	0.5862	-0.2376	
H	3.1545	3.1557	2.4137	
H	1.7938	4.3285	-1.4949	
H	-1.9739	-0.2789	0.9997	
H	-2.4482	-1.2832	-0.3623	
C	-4.6654	0.0915	0.6253	
H	2.7860	4.9291	0.7067	
H	-3.3116	1.6307	0.0302	
H	-3.8155	0.5979	-1.2973	
C	-5.8491	-0.4192	0.2519	
H	-4.4671	0.1529	1.6975	
C	-6.8537	-0.8735	1.2851	
C	-6.3059	-0.5915	-1.1765	
H	-6.4849	-0.7284	2.3055	
H	-7.8012	-0.3249	1.1851	
H	-7.0981	-1.9380	1.1598	
H	-5.5643	-0.2698	-1.9112	
H	-7.2286	-0.0231	-1.3603	
H	-6.5465	-1.6442	-1.3812	

Table S17. B3LYP/6-316(d) Energies and Cartesian Coordinates for 5:

E (UB+HF-LYP)				-814.417478481
Zero-point correction				0.390509
Thermal correction to Energy				0.411224
Thermal correction to Enthalpy				0.412168
Thermal correction to Gibbs Free Energy				0.336976
Sum of electronic and zero-point Energies				-814.026970
Sum of electronic and thermal Energies				-814.006255
Sum of electronic and thermal Enthalpies				-814.005310
Sum of electronic and thermal Free Energies				-814.080503
Atom Type	X	Y	Z	
C	1.9042	-2.5516	0.1590	
C	2.8304	-3.5536	0.3997	
C	2.3265	-1.2366	-0.1664	
H	0.8460	-2.7677	0.2652	
C	4.2036	-3.2791	0.3093	
C	3.7205	-0.9780	-0.2397	
C	1.3649	-0.1653	-0.4386	
H	2.4929	-4.5503	0.6661	
C	4.6431	-1.9898	-0.0132	
C	1.7475	1.2192	-0.1108	
C	0.1363	-0.4822	-1.0064	
H	4.9260	-4.0700	0.4877	
H	4.0630	0.0130	-0.5168	
C	1.5572	2.2795	-1.0253	
C	2.3404	1.5032	1.1423	
C	-1.0493	0.3858	-1.1995	
H	5.7052	-1.7818	-0.0968	
H	-0.0142	-1.5233	-1.2863	
C	2.6952	2.8047	1.4786	
C	1.9396	3.5736	-0.6942	
C	-2.1788	-0.0748	-0.2191	
H	1.1568	2.0716	-2.0126	
H	2.4838	0.6998	1.8581	
H	-0.8364	1.4413	-1.0229	
H	-1.4307	0.2748	-2.2239	
C	2.4991	3.8422	0.5618	
C	-3.4736	0.7571	-0.4340	
H	3.1256	3.0126	2.4534	
H	1.8117	4.3755	-1.4149	
H	-1.8292	0.0379	0.8134	
H	-2.3982	-1.1379	-0.3716	
C	-4.5134	0.3736	0.5691	
H	2.7856	4.8571	0.8209	
H	-3.2247	1.8201	-0.3180	
H	-3.8205	0.6183	-1.4627	
C	-5.6081	-0.4093	0.3778	
H	-4.3496	0.7611	1.5748	
C	-6.5594	-0.6727	1.5128	
C	-5.9796	-1.0477	-0.9316	
H	-6.2449	-0.1880	2.4409	
H	-7.5686	-0.3178	1.2632	
H	-6.6527	-1.7516	1.6988	
H	-5.2659	-0.8560	-1.7354	
H	-6.9659	-0.6937	-1.2611	
H	-6.0728	-2.1353	-0.8102	

Table S18. B3LYP/6-316(d) Energies and Cartesian Coordinates for **14+•**:

E (UB+HF-LYP)				-619.069505543
Zero-point correction				0.272092
Thermal correction to Energy				0.286216
Thermal correction to Enthalpy				0.287160
Thermal correction to Gibbs Free Energy				0.229681
Sum of electronic and zero-point Energies				-618.797414
Sum of electronic and thermal Energies				-618.783290
Sum of electronic and thermal Enthalpies				-618.782345
Sum of electronic and thermal Free Energies				-618.839824
Atom Type	X	Y	Z	
C	3.2482	-1.2791	-0.7126	
C	3.1527	-2.2743	0.2727	
C	2.2328	-0.3460	-0.8609	
H	4.1160	-1.2419	-1.3635	
C	2.0237	-2.3459	1.0957	
C	1.0784	-0.4059	-0.0426	
H	3.9598	-2.9902	0.3961	
H	2.2991	0.3998	-1.6459	
C	0.9889	-1.4344	0.9323	
C	-0.0196	0.5529	-0.1817	
H	1.9568	-3.1086	1.8649	
C	-1.3940	0.0653	-0.1241	
C	0.2022	1.9252	-0.3668	
H	0.1243	-1.4730	1.5869	
C	-2.4546	0.8721	0.3728	
C	-1.7043	-1.2438	-0.5896	
C	1.4741	2.6904	-0.3161	
H	-0.6833	2.5347	-0.5401	
C	-3.0084	-1.7138	-0.5658	
C	-3.7506	0.3884	0.4109	
C	1.3414	3.9456	0.5805	
H	-2.2435	1.8579	0.7739	
H	-0.9171	-1.8565	-1.0147	
H	2.3122	2.0722	0.0118	
H	1.7020	3.0332	-1.3401	
C	-4.0346	-0.9035	-0.0633	
H	-3.2348	-2.7033	-0.9500	
H	-4.5477	1.0056	0.8127	
H	1.1449	3.6683	1.6205	
H	2.2756	4.5128	0.5497	
H	0.5348	4.6010	0.2362	
H	-5.0562	-1.2714	-0.0465	

Table S19. B3LYP/6-316(d) Energies and Cartesian Coordinates for **14**:

E (RB+HF-LYP)				-619.332235281
Zero-point correction				0.272179
Thermal correction to Energy				0.286221
Thermal correction to Enthalpy				0.287165
Thermal correction to Gibbs Free Energy				0.230111
Sum of electronic and zero-point Energies				-619.060056
Sum of electronic and thermal Energies				-619.046014
Sum of electronic and thermal Enthalpies				-619.045070
Sum of electronic and thermal Free Energies				-619.102125
Atom Type	X	Y	Z	
C	3.1386	-1.4371	-0.8098	
C	3.1514	-2.2772	0.3040	
C	2.1120	-0.5053	-0.9743	
H	3.9246	-1.5094	-1.5571	
C	2.1260	-2.1844	1.2484	
C	1.0799	-0.3934	-0.0288	
H	3.9500	-3.0030	0.4329	
H	2.0968	0.1335	-1.8529	
C	1.0983	-1.2585	1.0793	
C	-0.0244	0.5992	-0.1937	
H	2.1258	-2.8364	2.1181	
C	-1.4214	0.0778	-0.1233	
C	0.1977	1.9144	-0.4054	
H	0.3001	-1.1963	1.8138	
C	-2.4478	0.8189	0.4883	
C	-1.7519	-1.1707	-0.6798	
C	1.5052	2.6588	-0.3981	
H	-0.6771	2.5439	-0.5738	
C	-3.0616	-1.6467	-0.6490	
C	-3.7580	0.3432	0.5202	
C	1.4578	3.8865	0.5290	
H	-2.2071	1.7666	0.9617	
H	-0.9742	-1.7655	-1.1497	
H	2.3256	1.9994	-0.0986	
H	1.7381	3.0026	-1.4181	
C	-4.0721	-0.8913	-0.0508	
H	-3.2934	-2.6105	-1.0951	
H	-4.5322	0.9328	1.0048	
H	1.2789	3.5873	1.5678	
H	2.4028	4.4401	0.4929	
H	0.6551	4.5744	0.2366	
H	-5.0921	-1.2652	-0.0216	

Table S20. B3LYP/6-316(d) Energies and Cartesian Coordinates for **15+•**:

E (UB+HF-LYP)				-314.190142211
Zero-point correction				0.220745
Thermal correction to Energy				0.232038
Thermal correction to Enthalpy				0.232982
Thermal correction to Gibbs Free Energy				0.182505
Sum of electronic and zero-point Energies				-313.969398
Sum of electronic and thermal Energies				-313.958104
Sum of electronic and thermal Enthalpies				-313.957160
Sum of electronic and thermal Free Energies				-314.007637
Atom Type	X	Y	Z	
C	3.7826	0.1680	-0.7032	
C	2.7057	0.1120	0.3886	
H	4.7408	0.4586	-0.2584	
H	3.9187	-0.8058	-1.1855	
H	3.5369	0.9035	-1.4769	
C	1.3487	-0.3006	-0.2077	
H	2.9930	-0.6057	1.1663	
H	2.6118	1.0909	0.8743	
C	0.2413	-0.3359	0.9435	
H	1.4155	-1.2917	-0.6689	
H	1.0362	0.4069	-0.9835	
C	-1.0092	-0.7859	0.3380	
H	0.5896	-1.0630	1.6856	
H	0.1761	0.6526	1.4034	
C	-2.1024	0.0261	-0.0543	
H	-1.0970	-1.8511	0.1229	
C	-3.3405	-0.6138	-0.5648	
C	-2.0675	1.5080	0.0550	
H	-3.3750	-1.6931	-0.4019	
H	-3.4052	-0.4275	-1.6517	
H	-4.2339	-0.1399	-0.1383	
H	-1.0626	1.9313	-5.2140e-3	
H	-2.7150	1.9768	-0.6922	
H	-2.4813	1.7897	1.0398	

Table S21. B3LYP/6-316(d) Energies and Cartesian Coordinates for **15**:

E (RB+HF-LYP)		-314.484530296	
Zero-point correction		0.222939	
Thermal correction to Energy		0.233726	
Thermal correction to Enthalpy		0.234670	
Thermal correction to Gibbs Free Energy		0.186277	
Sum of electronic and zero-point Energies		-314.261591	
Sum of electronic and thermal Energies		-314.250804	
Sum of electronic and thermal Enthalpies		-314.249860	
Sum of electronic and thermal Free Energies		-314.298253	
Atom Type	X	Y	Z
C	-3.9616	-0.1476	-0.5885
C	-2.7933	0.3142	0.2885
H	-4.9014	0.3297	-0.2878
H	-3.7862	0.0972	-1.6433
H	-4.1031	-1.2333	-0.5211
C	-1.4559	-0.3297	-0.0982
H	-2.7001	1.4080	0.2275
H	-3.0129	0.0870	1.3416
C	-0.2778	0.1354	0.7806
H	-1.2286	-0.1060	-1.1500
H	-1.5471	-1.4240	-0.0337
C	1.0125	-0.5615	0.4404
H	-0.1775	1.2239	0.7010
H	-0.5291	-0.0706	1.8332
C	2.1588	-0.0365	-0.0198
H	0.9843	-1.6444	0.5807
C	3.3481	-0.9202	-0.3162
C	2.3952	1.4311	-0.2827
H	3.1365	-1.9740	-0.1086
H	4.2215	-0.6245	0.2826
H	3.6525	-0.8356	-1.3692
H	1.5230	2.0552	-0.0753
H	3.2284	1.8055	0.3288
H	2.6840	1.5950	-1.3304

Table S22. B3LYP/6-316(d) Energies and Cartesian Coordinates for **16+**:

E (RB+HF-LYP)				-815.033535223
Zero-point correction				0.404754
Thermal correction to Energy				0.424184
Thermal correction to Enthalpy				0.425128
Thermal correction to Gibbs Free Energy				0.356274
Sum of electronic and zero-point Energies				-814.628782
Sum of electronic and thermal Energies				-814.609352
Sum of electronic and thermal Enthalpies				-814.608407
Sum of electronic and thermal Free Energies				-814.677261
Atom Type	X	Y	Z	
C	-0.7166	3.6280	-0.7663	
C	-1.9592	2.9655	-0.1479	
C	0.4720	2.7362	-0.3440	
H	-0.6179	4.6658	-0.4337	
H	-0.8185	3.6482	-1.8568	
C	-1.6381	1.4339	-0.3599	
C	-0.1271	1.3536	0.0552	
H	-2.0264	3.1862	0.9227	
H	-2.9012	3.2574	-0.6211	
H	1.0130	3.1664	0.5033	
H	1.1989	2.6263	-1.1541	
C	0.5679	0.1310	-0.5946	
C	-2.5827	0.5951	0.3828	
H	-1.7270	1.2228	-1.4311	
H	-0.0838	1.2491	1.1436	
C	-0.2311	-1.1468	-0.3681	
C	2.0367	-7.4100e-4	-0.1739	
C	-3.5807	-0.2304	-0.3203	
C	-2.7198	0.6968	1.8579	
H	0.5680	0.3140	-1.6771	
C	-0.4982	-1.6327	0.9279	
C	-0.7414	-1.8618	-1.4633	
C	2.9878	-0.3331	-1.1479	
C	2.4675	0.1703	1.1490	
H	-3.6969	0.0409	-1.3719	
H	-4.5461	-0.2323	0.1986	
H	-3.2264	-1.2812	-0.2923	
H	-1.8470	1.1082	2.3651	
H	-3.5709	1.3745	2.0450	
H	-3.0011	-0.2646	2.2974	
C	-1.5199	-3.0028	-1.2752	
C	-1.2736	-2.7778	1.1210	
C	3.8120	8.5850e-3	1.4876	
C	4.3318	-0.4964	-0.8120	
H	-0.0597	-1.1375	1.7895	
H	-0.5264	-1.5196	-2.4726	
H	2.6742	-0.4684	-2.1806	
H	1.7644	0.4390	1.9335	
C	-1.7998	-3.4595	0.0212	
C	4.7482	-0.3265	0.5089	
H	-1.9053	-3.5429	-2.1353	
H	-1.4535	-3.1461	2.1271	
H	4.1269	0.1486	2.5177	
H	5.0518	-0.7531	-1.5836	
H	-2.3979	-4.3543	0.1664	
H	5.7942	-0.4497	0.7731	

Table S23. B3LYP/6-316(d) Energies and Cartesian Coordinates for **16**:

E (RB+HF-LYP)				-814.673045350
Zero-point correction				0.393924
Thermal correction to Energy				0.412796
Thermal correction to Enthalpy				0.413740
Thermal correction to Gibbs Free Energy				0.345207
Sum of electronic and zero-point Energies				-814.279122
Sum of electronic and thermal Energies				-814.260249
Sum of electronic and thermal Enthalpies				-814.259305
Sum of electronic and thermal Free Energies				-814.327839
Atom Type	X	Y	Z	
C	-0.0614	1.3419	-0.3215	
C	-0.0446	1.8673	0.9783	
C	0.3035	2.1854	-1.3784	
C	-0.4719	-0.1052	-0.6018	
C	0.3356	3.1873	1.2132	
C	0.6844	3.5097	-1.1493	
C	-1.9225	-0.3499	-0.1749	
C	0.5277	-1.1514	-0.0382	
H	-0.3395	1.2421	1.8166	
H	0.2881	1.8014	-2.3964	
H	-0.4483	-0.2263	-1.6938	
C	0.7039	4.0152	0.1500	
C	-2.9543	-0.1105	-1.0935	
C	-2.2776	-0.7699	1.1150	
C	0.1328	-2.6064	-0.3979	
C	1.9975	-0.9670	-0.5814	
H	0.3427	3.5722	2.2299	
H	0.9622	4.1439	-1.9874	
H	0.5506	-1.0563	1.0541	
C	-4.2931	-0.2806	-0.7415	
C	-3.6161	-0.9420	1.4732	
C	1.4591	-3.3746	-0.4381	
C	2.4143	-2.3777	-1.1110	
C	2.9775	-0.4052	0.4383	
H	0.9985	5.0450	0.3340	
H	-2.7024	0.2188	-2.0993	
H	-1.5063	-0.9766	1.8517	
H	-0.5962	-3.0314	0.2986	
H	-0.3321	-2.6242	-1.3940	
H	1.9781	-0.2647	-1.4212	
C	-4.6304	-0.6976	0.5471	
C	3.2724	-1.2233	1.6756	
C	3.5887	0.7667	0.2337	
H	-5.0720	-0.0897	-1.4753	
H	-3.8644	-1.2713	2.4791	
H	1.7954	-3.6013	0.5823	
H	1.3871	-4.3278	-0.9742	
H	3.4724	-2.5957	-0.9308	
H	2.2663	-2.4115	-2.1978	
H	-5.6720	-0.8338	0.8253	
H	4.0003	-0.7172	2.3170	
H	3.6795	-2.2107	1.4213	
H	2.3701	-1.4030	2.2748	
H	3.3867	1.3739	-0.6445	
H	4.3016	1.1712	0.9486	

Table S24. B3LYP/6-316(d) Energies and Cartesian Coordinates for 17+:

E (RB+HF-LYP)				-815.054289352
Zero-point correction				0.407315
Thermal correction to Energy				0.426415
Thermal correction to Enthalpy				0.427359
Thermal correction to Gibbs Free Energy				0.359722
Sum of electronic and zero-point Energies				-814.646974
Sum of electronic and thermal Energies				-814.627875
Sum of electronic and thermal Enthalpies				-814.626931
Sum of electronic and thermal Free Energies				-814.694567
Atom Type	X	Y	Z	
C	-2.5525	-0.3485	2.3855	
C	-3.1350	-0.8954	1.0750	
C	-1.0237	-0.5627	2.2742	
H	-2.9592	-0.8399	3.2746	
H	-2.7832	0.7199	2.4805	
C	-2.1127	-0.4649	3.7890e-3	
C	-0.7490	-0.7523	0.7109	
H	-3.2016	-1.9891	1.1230	
H	-4.1406	-0.5170	0.8688	
H	-0.4497	0.2582	2.7120	
H	-0.7015	-1.4737	2.7856	
C	0.4603	6.9140e-3	0.2719	
C	-2.2471	-1.0984	-1.4041	
H	-2.2087	0.6193	-0.1294	
H	-0.5291	-1.8137	0.5928	
C	1.7130	-0.7036	0.1282	
C	0.4299	1.4314	0.0206	
C	-3.4574	-0.5097	-2.1490	
C	-2.3184	-2.6350	-1.4106	
H	-1.3473	-0.8042	-1.9685	
C	2.9380	-0.0678	0.4773	
C	1.7620	-2.0554	-0.3104	
C	1.2974	1.9870	-0.9622	
C	-0.4771	2.3072	0.6787	
H	-4.3989	-0.7705	-1.6517	
H	-3.4003	0.5834	-2.2098	
H	-3.5086	-0.8986	-3.1716	
H	-2.2859	-3.0073	-2.4398	
H	-1.4905	-3.1094	-0.8685	
H	-3.2512	-2.9964	-0.9643	
C	2.9740	-2.7173	-0.4257	
C	4.1416	-0.7540	0.3999	
C	-0.4818	3.6634	0.3967	
C	1.2592	3.3418	-1.2643	
H	2.9207	0.9419	0.8715	
H	0.8548	-2.5585	-0.6249	
H	1.9508	1.3326	-1.5271	
H	-1.1373	1.9272	1.4469	
C	4.1646	-2.0744	-0.0609	
C	0.3796	4.1843	-0.5794	
H	2.9988	-3.7365	-0.7979	
H	5.0621	-0.2661	0.7042	
H	-1.1566	4.3229	0.9330	
H	1.9081	3.7410	-2.0372	
H	5.1087	-2.6066	-0.1310	
H	0.3566	5.2457	-0.8085	

Table S25. B3LYP/6-316(d) Energies and Cartesian Coordinates for **17**:

E (RB+HF-LYP)				-814.684657011
Zero-point correction				0.393551
Thermal correction to Energy				0.412716
Thermal correction to Enthalpy				0.413660
Thermal correction to Gibbs Free Energy				0.345054
Sum of electronic and zero-point Energies				-814.291106
Sum of electronic and thermal Energies				-814.271941
Sum of electronic and thermal Enthalpies				-814.270997
Sum of electronic and thermal Free Energies				-814.339603
Atom Type	X	Y	Z	
C	0.1734	1.3969	-0.1506	
C	-0.3756	2.1030	-1.2334	
C	0.5503	2.1252	0.9908	
C	0.4190	-0.0800	-0.2261	
C	-0.5681	3.4839	-1.1681	
C	0.3524	3.5035	1.0609	
C	1.8517	-0.4827	-0.0430	
C	-0.5538	-0.9854	-0.4705	
H	-0.6362	1.5645	-2.1403	
H	1.0017	1.6001	1.8284	
C	-0.2103	4.1890	-0.0183	
C	2.2477	-1.3264	1.0072	
C	2.8450	0.0173	-0.9011	
C	-0.3102	-2.4674	-0.7492	
C	-2.0579	-0.6922	-0.5822	
H	-0.9906	4.0095	-2.0209	
H	0.6425	4.0443	1.9582	
C	3.5872	-1.6765	1.1821	
C	4.1833	-0.3364	-0.7327	
C	-1.7000	-3.1269	-0.7256	
C	-2.6562	-2.0024	-1.1618	
C	-2.6931	-0.2127	0.7611	
H	-0.3598	5.2642	0.0338	
H	1.4962	-1.6987	1.6986	
H	2.5604	0.6896	-1.7063	
H	0.1371	-2.5638	-1.7503	
H	0.3944	-2.9363	-0.0585	
H	-2.2298	0.1255	-1.2897	
C	4.5600	-1.1864	0.3094	
C	-4.1219	0.3086	0.5414	
C	-2.6613	-1.2539	1.8893	
H	3.8709	-2.3274	2.0053	
H	4.9339	0.0551	-1.4146	
H	-1.7585	-4.0068	-1.3754	
H	-1.9406	-3.4603	0.2899	
H	-2.6700	-1.9399	-2.2577	
H	-3.6893	-2.1777	-0.8438	
H	-2.0856	0.6399	1.0892	
H	5.6036	-1.4582	0.4444	
H	-4.1437	1.1029	-0.2144	
H	-4.5314	0.7212	1.4713	
H	-4.8009	-0.4869	0.2101	
H	-3.2978	-2.1188	1.6652	
H	-3.0311	-0.8133	2.8229	
H	-1.6449	-1.6183	2.0760	

Table S26. Enthalpies of Formation of Neutral Precursors ($\Delta H_f^{298}(\text{Neutral})$), B3LYP/ 6-31G(d) Isodesmic Reaction Enthalpies ($\Delta H^{298}(\text{Rxn})$), and Enthalpies of Formation of Alkene Radical Cations **5**, **4**, **3**, **14+**, and **15+**. All values are in kcal / mole.

Neutral + $\text{C}_2\text{H}_4+\bullet^a$	Radical Cation + C_2H_4^a	$\Delta H_f^{298}(\text{Neutral})^b$	$\Delta H^{298}(\text{Rxn})^c$	$\Delta H_f^{298}(\text{Radical Cation})^{d,e}$
10 + $\text{C}_2\text{H}_4+\bullet$	5 + C_2H_4	46.1	-72.1	217
10 + $\text{C}_2\text{H}_4+\bullet$	4 + C_2H_4	46.1	f	221
10 + $\text{C}_2\text{H}_4+\bullet$	3 + C_2H_4	46.1	f	240
14 + $\text{C}_2\text{H}_4+\bullet$	14+ + C_2H_4	46.0	-67.9	221
15 + $\text{C}_2\text{H}_4+\bullet$	15+ + C_2H_4	-25.2	-48.5	169

(a) Energies and ZPE values calculated by us for ethylene and the ethylene radical cation are in agreement with those reported by Carsky and Bally (ref. S5). (b) S.E. Stein, and R.L. Brown, "Structures and Properties Group Additivity Model" in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>). (c) $\Delta H^{298}(\text{Rxn}) = 627.5095 [\text{H}(\text{radical cation}) + \text{H}(\text{C}_2\text{H}_4) - (\text{H}(\text{Neutral}) - \text{H}(\text{C}_2\text{H}_4+\bullet))]$, where the values of H are the sum of electronic and thermal enthalpies (298 K). (d) $\Delta H_f^{298}(\text{Radical Cation}) = \Delta H(\text{Rxn}) - \Delta H_f(\text{C}_2\text{H}_4) + \Delta H_f(\text{Neutral}) + \Delta H_f(\text{C}_2\text{H}_4+\bullet)$, where all ΔH values are at 298 K. (e) Use of this methodology on a test set of simple alkenes with known ionization potentials (propene, isobutene, 2-methyl-2-butene, 2-methyl-2-pentene, and styrene gave an average error of ± 2 Kcal/mole. (f) Substitution of $\Delta H(\text{Rxn})$ for ionization of **15** and **14** gives estimates of ΔH_f for the localized radical cations **3** and **4** respectively.

Table S27. Enthalpies of formation of Neutral Precursors, B3LYP/ 6-31G(d) Isodesmic Reaction Enthalpies, and Enthalpies of Formation of Cations **16+**, and **17+**, plus Estimated Enthalpies of Formation for Distonic Radical Cations **6** and **7**. All values are in kcal/mol.

Neutral + Me_3C^+	Ion + Isobutene	BDE → Distonic Radical Ion	$\Delta H_f(\text{Neutral})^a$	$\Delta H^{298}(\text{Rxn})^b$	$\Delta H_f(\text{Ion})^c$	$\Delta H_f(\text{Distonic Radical Ion})$
16 + Me_3C^+	16+ + Isobutene	BDE → 6	35.9	-20.0	191	219 ^d
17 + Me_3C^+ ---> 17+ + Me_3CH			30.4	-23.6	181	225 ^e
BDE ---> 7						

(a) Cohen, N.; Benson S.W, *Chem. Rev.* **1993**, 93, 2419-2438. (b) $\Delta H_{298}(\text{Rxn}) = 627.5095 [(\text{H}_{298}(\text{ion}) + \text{H}_{298}(\text{isobutene}) - (\text{H}_{298}(\text{neutral}) + \text{H}_{298}(\text{Me}_3\text{C}^+))]$, where the H_{298} values are the thermally corrected enthalpies. (c) Isodesmic reaction Enthalpy calculated from $\Delta H_f^{298}(\text{ion}) = \Delta H_{298}(\text{Rxn}) - \text{H}(\text{isobutene}) + \text{H}(\text{Neutral}) + \text{H}(\text{Me}_3\text{C}^+)$, where the values of H are the sum of electronic and thermal enthalpies (298 K). (d) Calculated assuming a bond dissociation energy of 80 kcal/mole for conversion of **16+** to **6**. (e) Calculated assuming a bond dissociation energy of 96 kcal/mole for the conversion of **17+** to **7**.

Table S28. Comparison of Experimental and Calculated Enthalpies of Formation for Simple Alkenes as a Test of the DFT / Isodesmic Methodology used in Scheme 3 to Estimate the Enthalpies of Formation of Species **3**, **4**, and **5**.

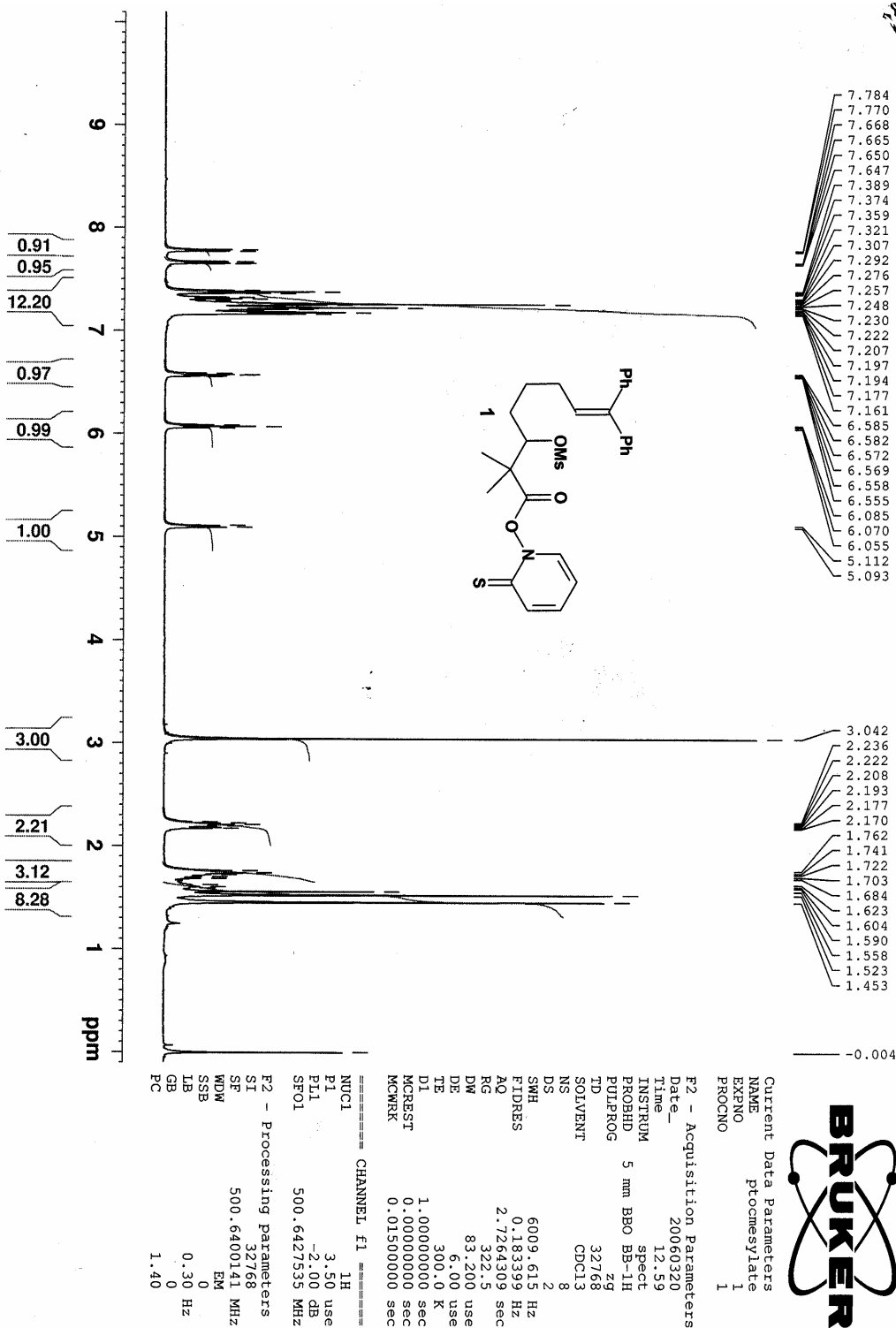
Alkene	IE ^a	ΔH_f (kcal/mole) ^b	$\Delta H(\text{rxn})^c$ (kcal/mole)	ΔH_f (alkene+●) ^d (kcal/mole)	Error (kcal/mole)
Ethene	10.51	254.9		-----	-----
Propene	9.73	229.3	-18.7	228.5	-0.7
2-methylpropene	9.22	208.3	-31.1	207.3	-1.0
2-methyl-2-butene	8.69	190.5	-44.0	188.8	-1.7
Styrene	8.46	230.3	-50.6	226.9	-3.4

(a) IE values were taken from P.J. Linstrom and W.G. Mallard, Eds., **NIST Chemistry WebBook**, **NIST Standard Reference Database Number 69**, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>). (b) Values for the experimental enthalpies of formation of the alkene radical cations were derived from the IE values with the following relationship $\Delta H_f(\text{alkene}+\bullet) = (23.06 \times \text{IE}) + \Delta H_f(\text{alkene})$. (c) $\Delta H(\text{rxn})$ calculated from Eq. S1 (d) Enthalpy of formation calculated using Eq. S2.

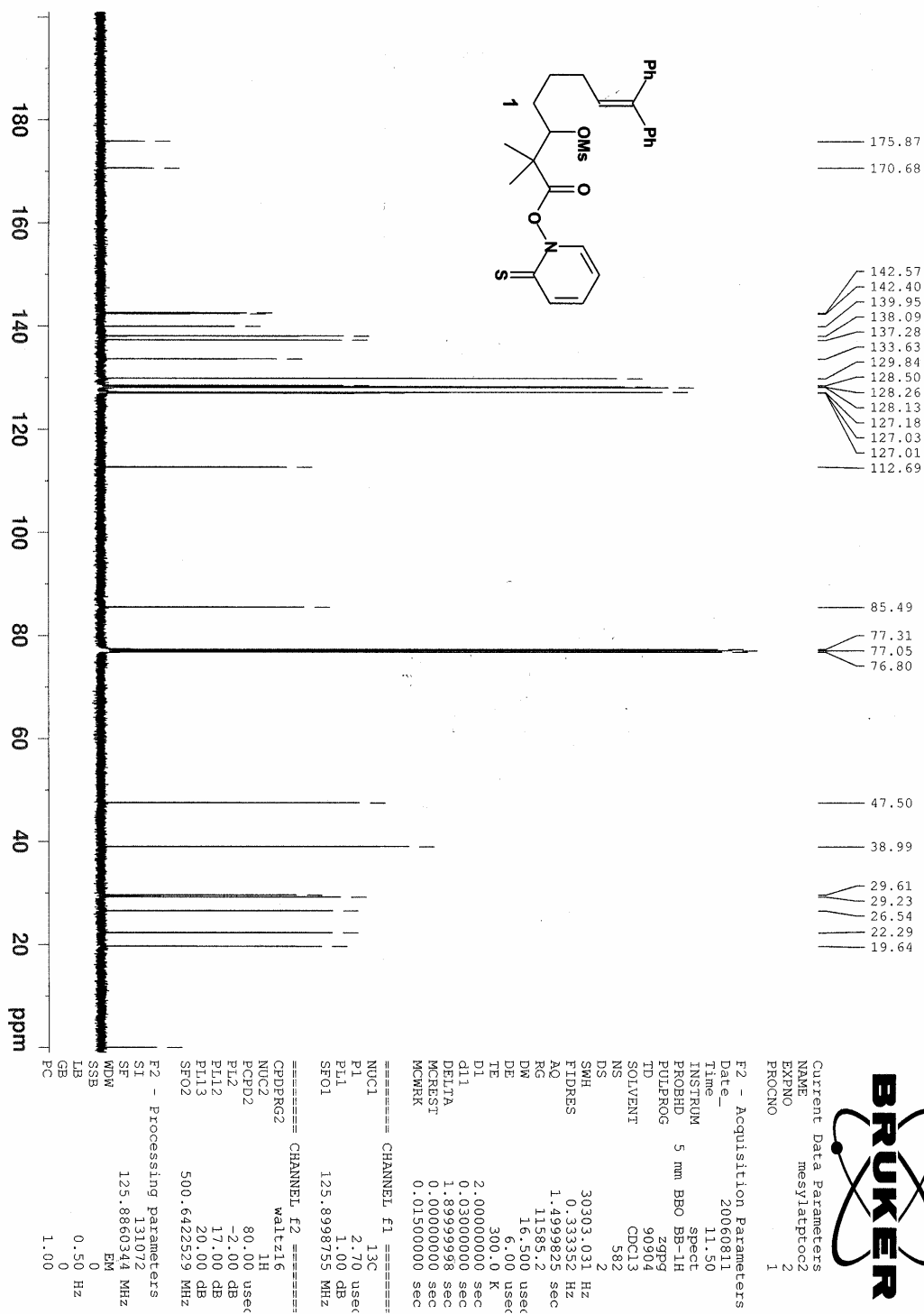
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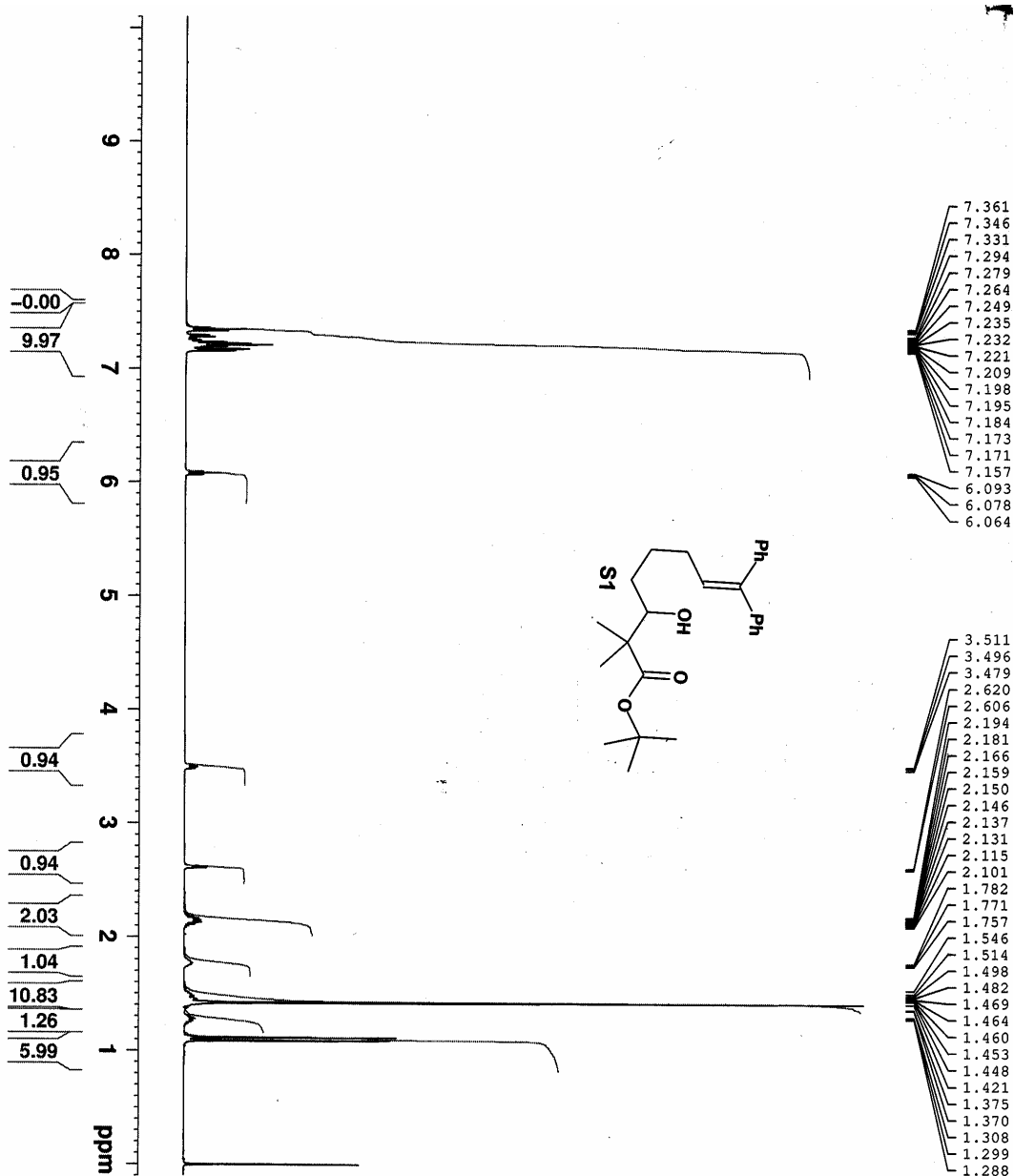
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¹³C-NMR Spectrum of 1.



¹H-NMR Spectrum of S1



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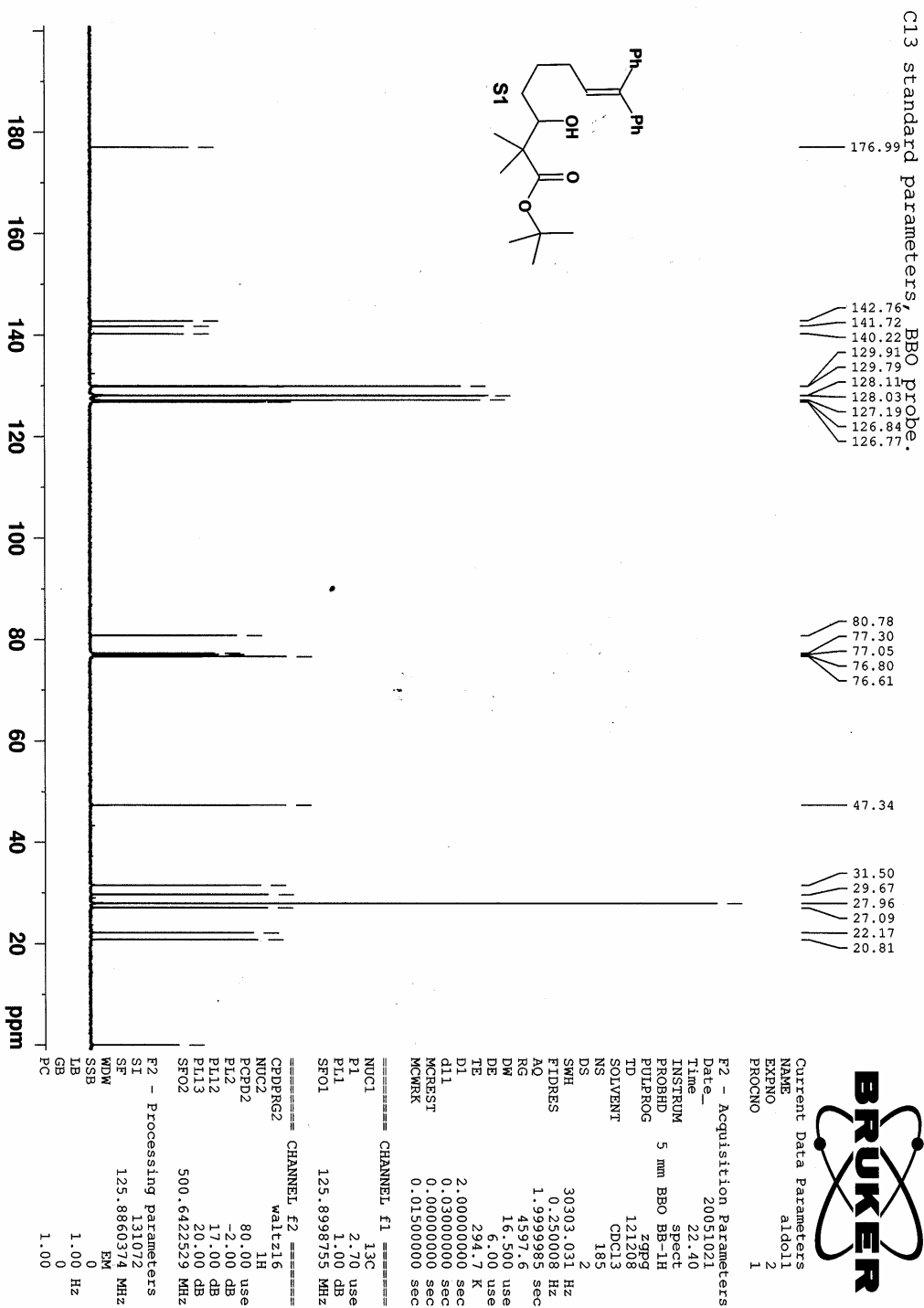
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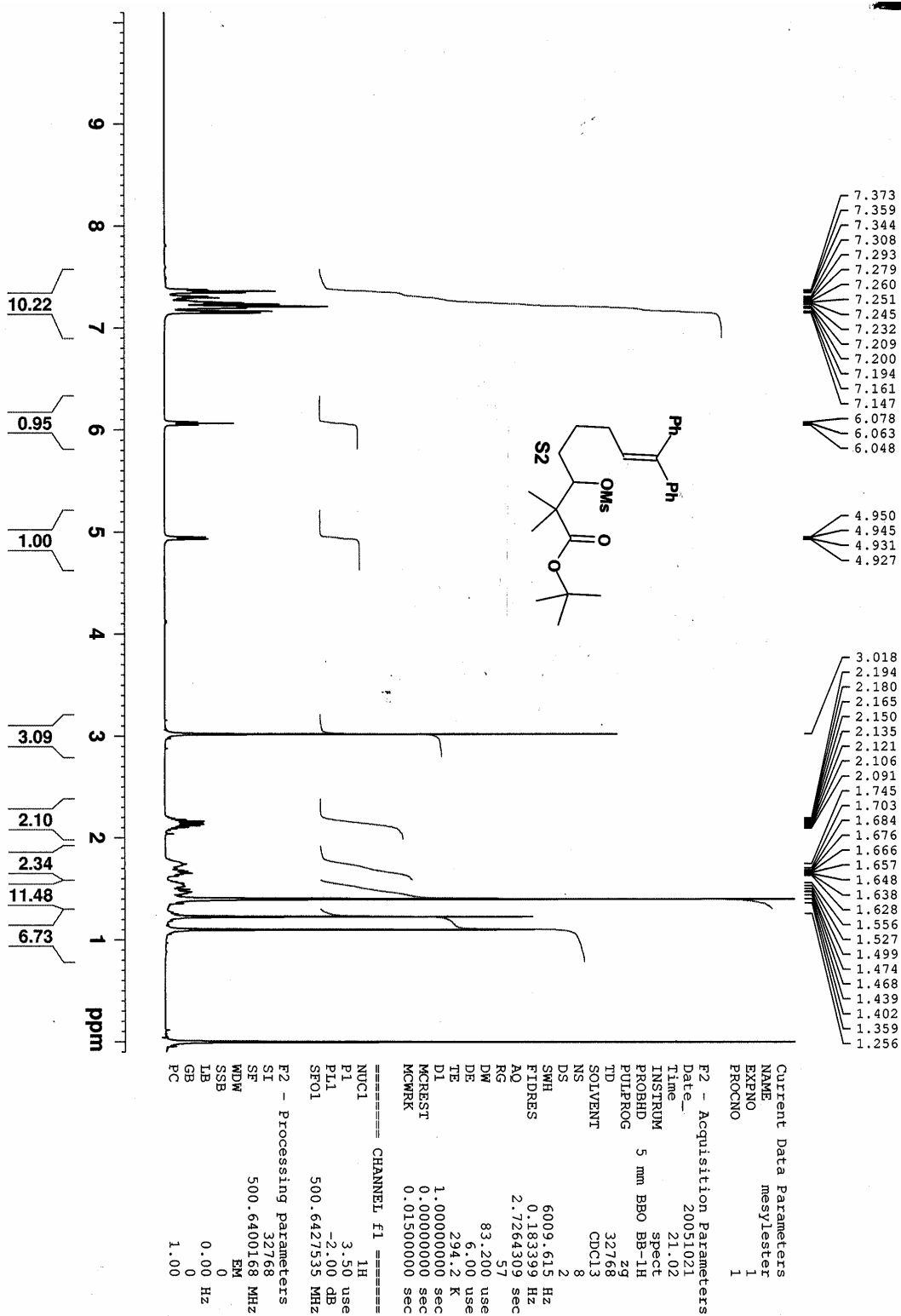
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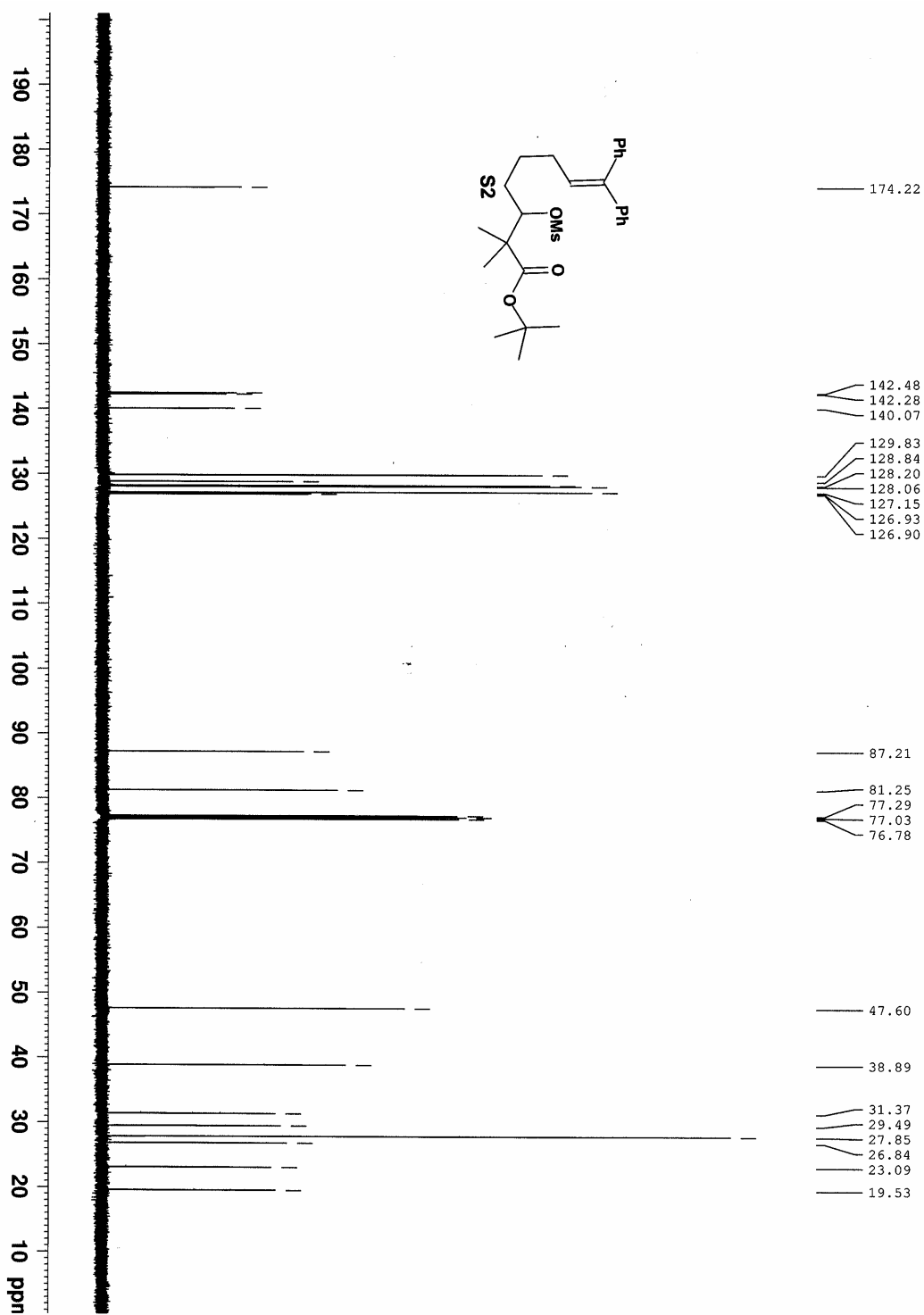
¹³C-NMR Spectrum of S1



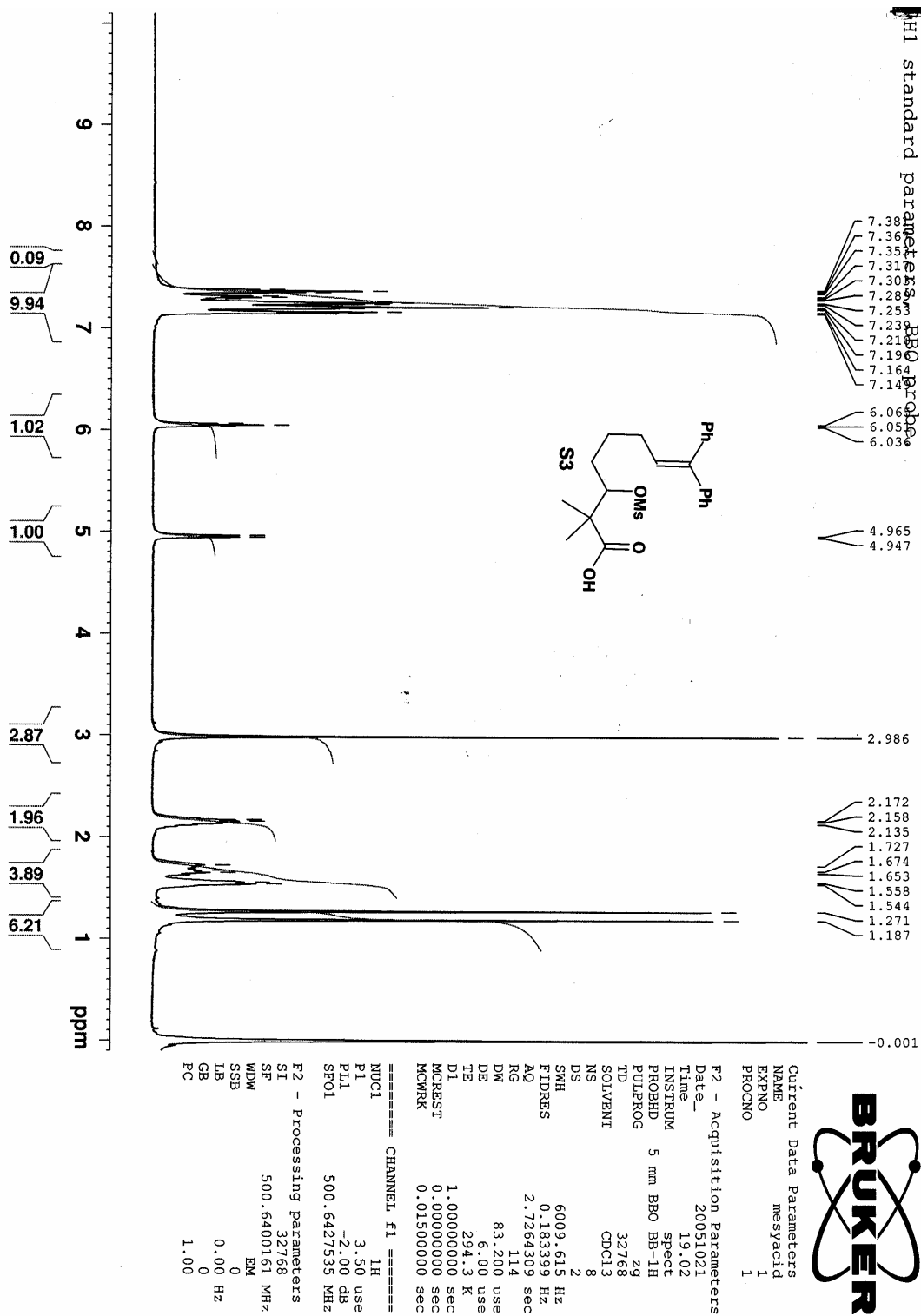
¹H-NMR Spectrum of S2



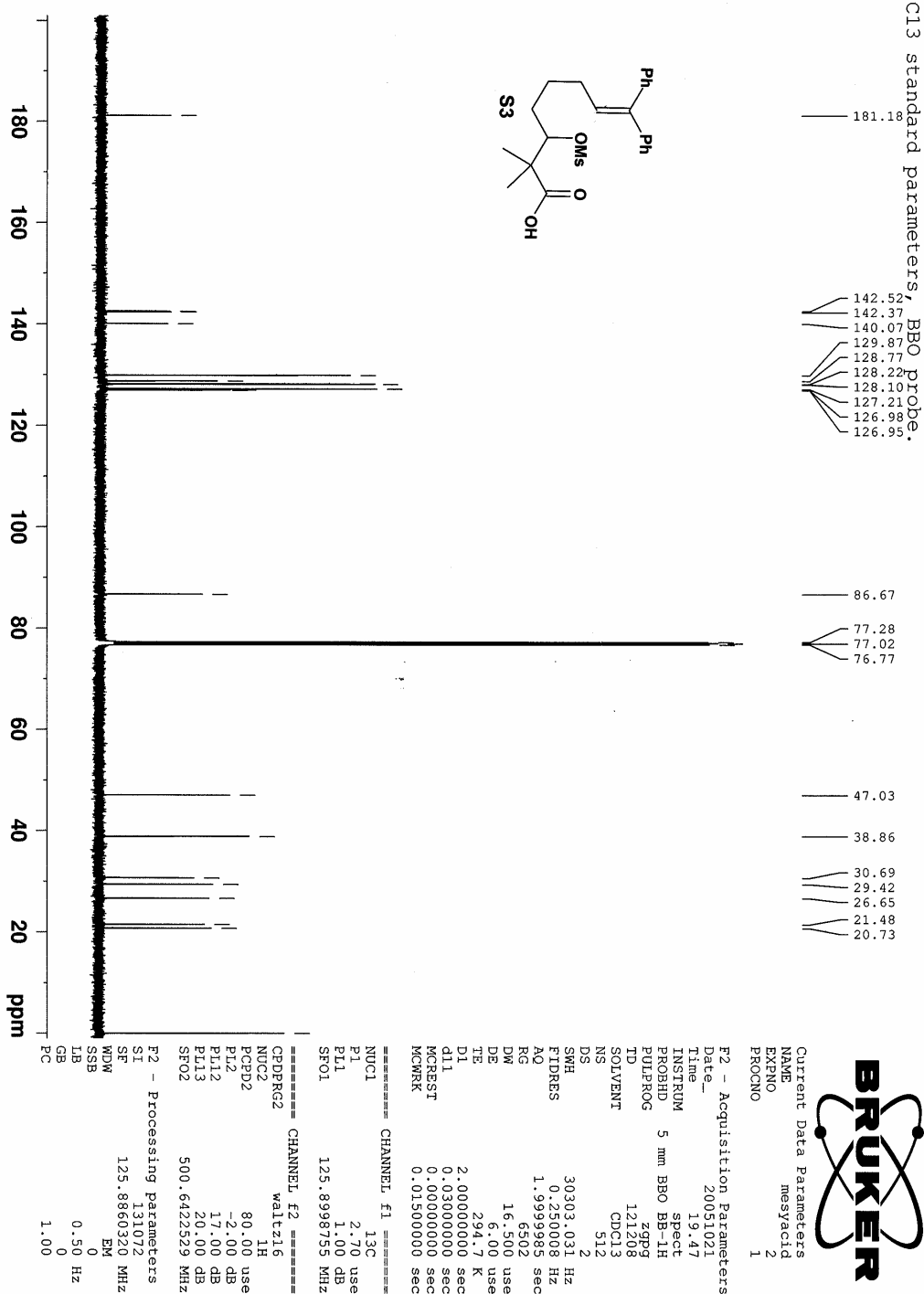
¹³C-NMR Spectrum of S2



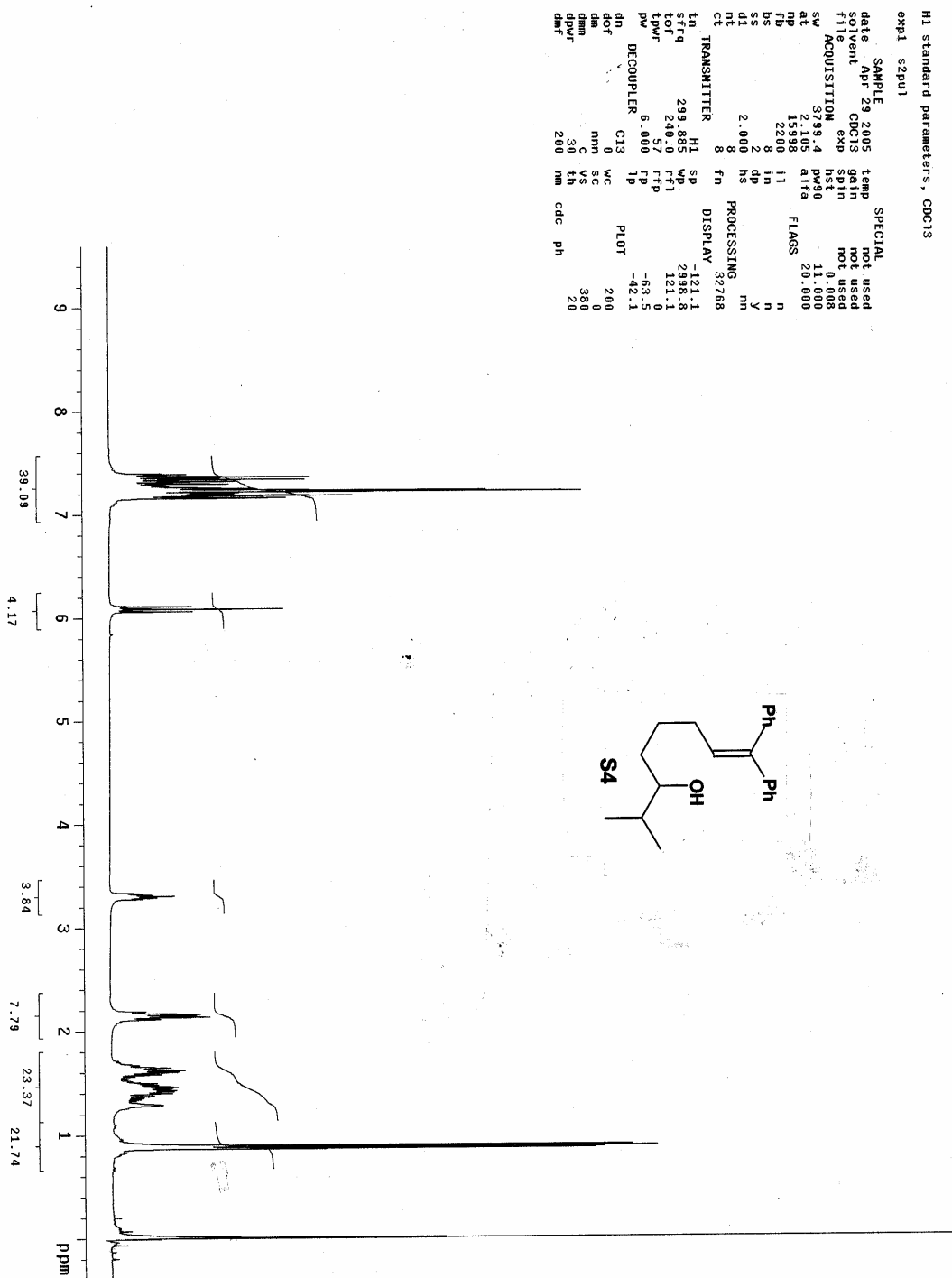
¹H-NMR Spectrum of S3



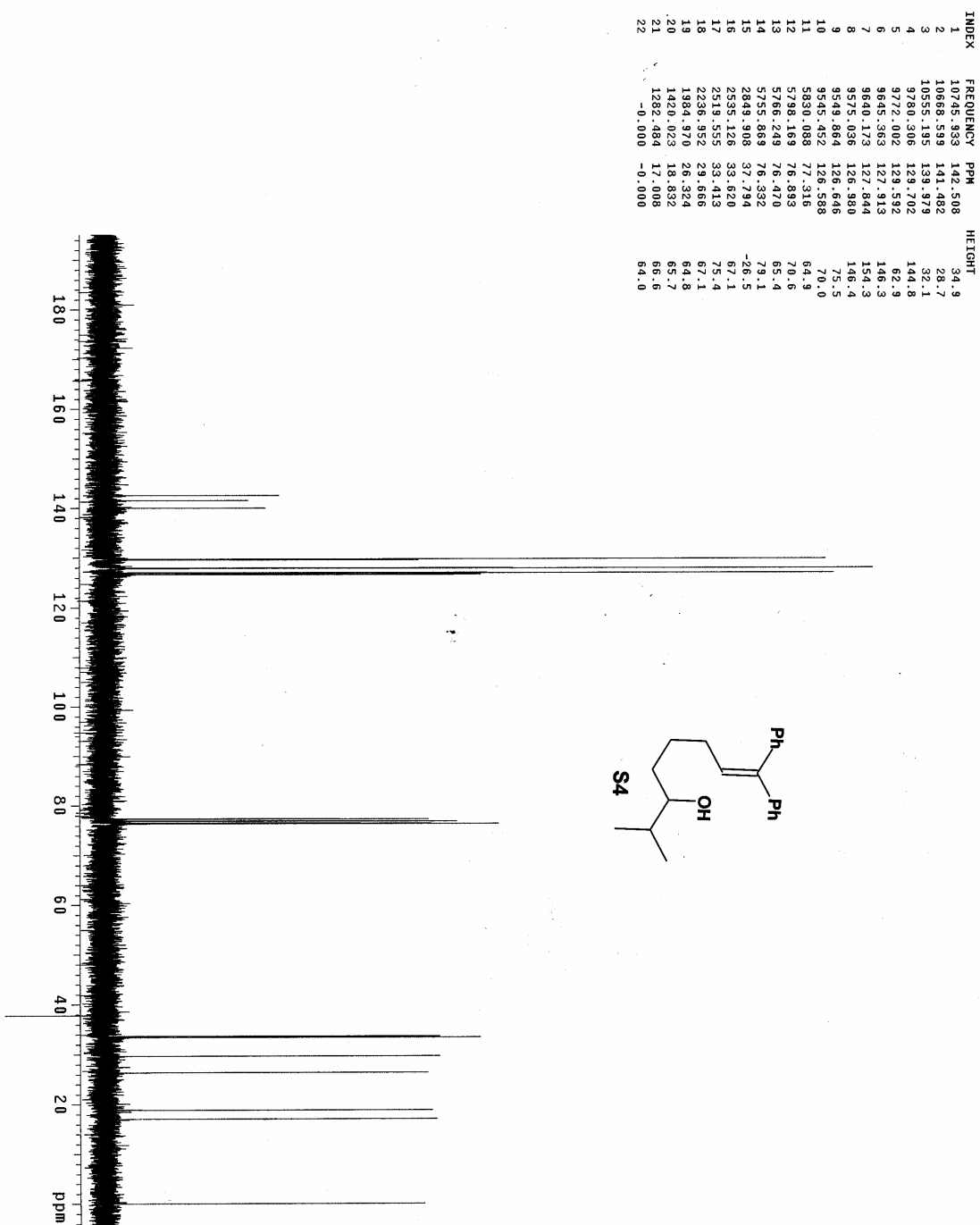
¹³C-NMR Spectrum of S3



¹H-NMR Spectrum of S4.



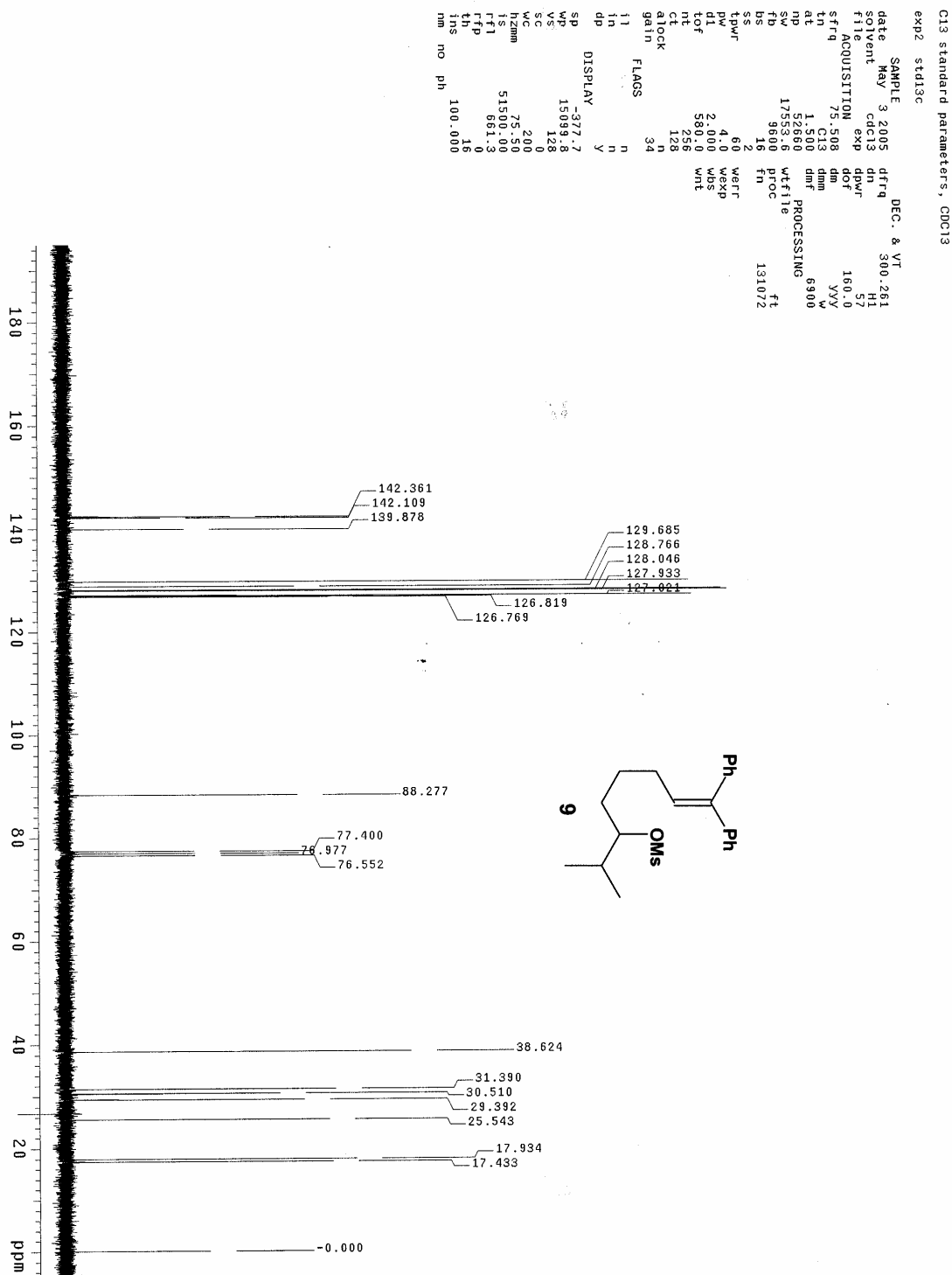
¹H-NMR Spectrum of S4.



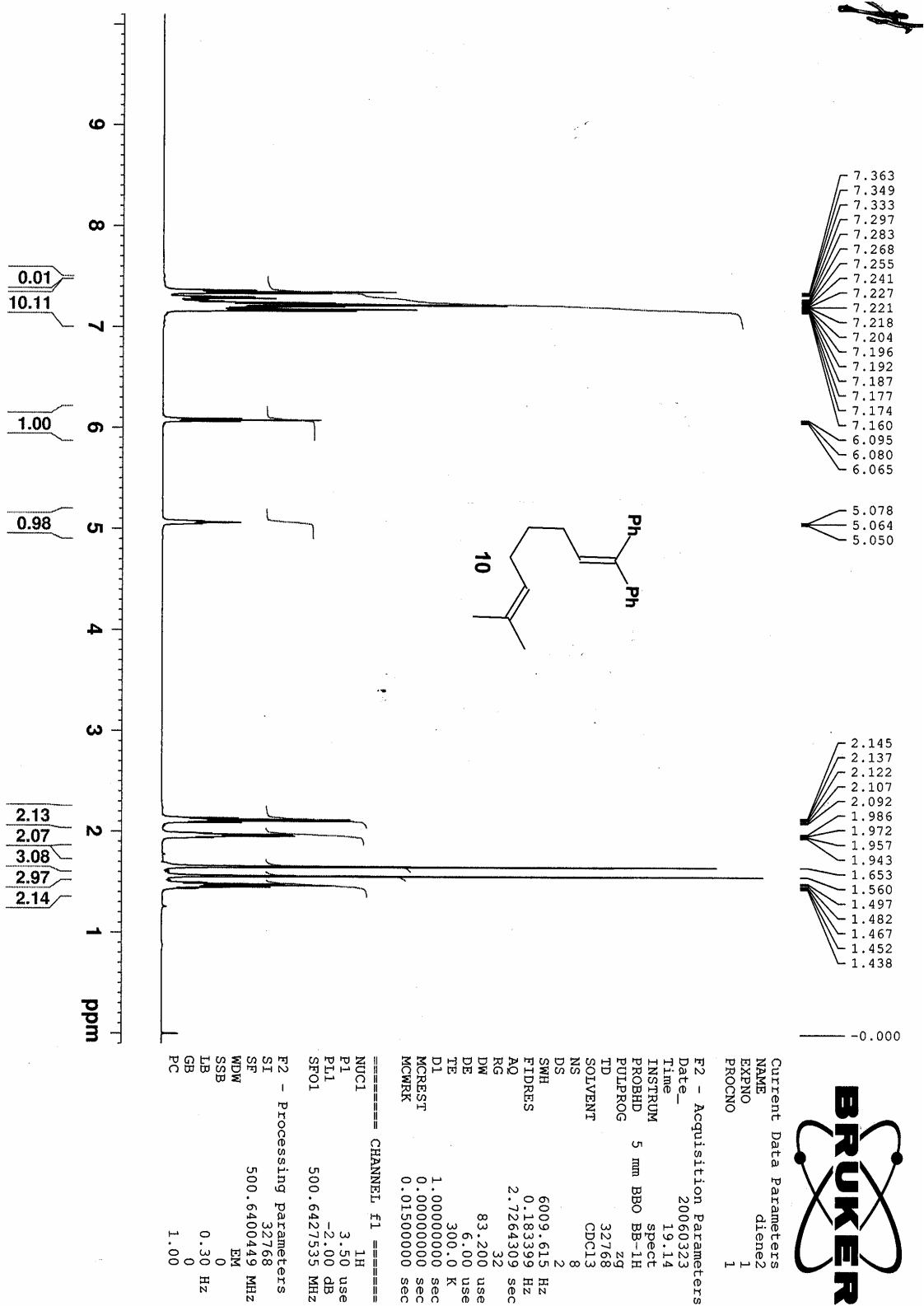
S3



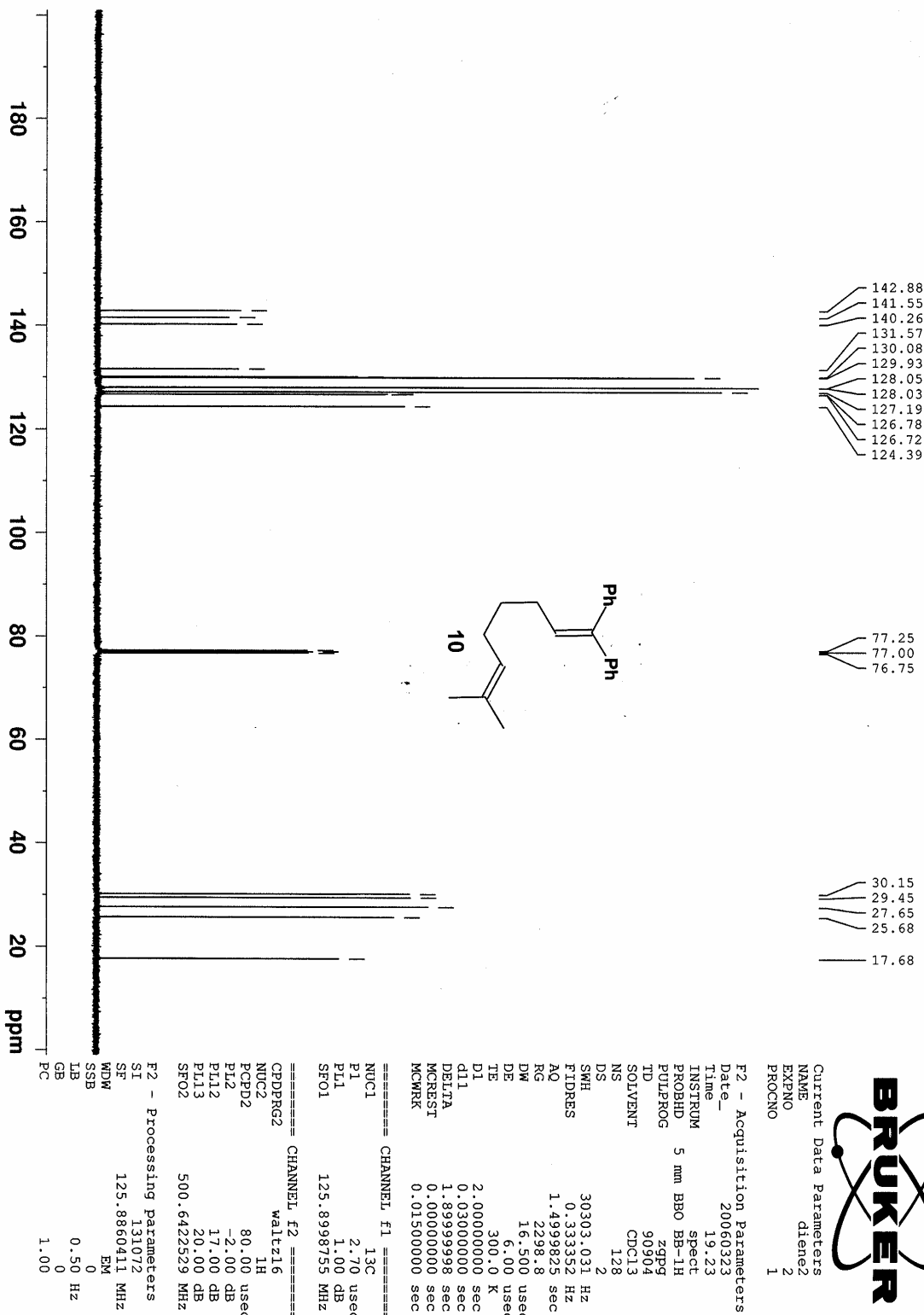
¹³C-NMR Spectrum of 9.



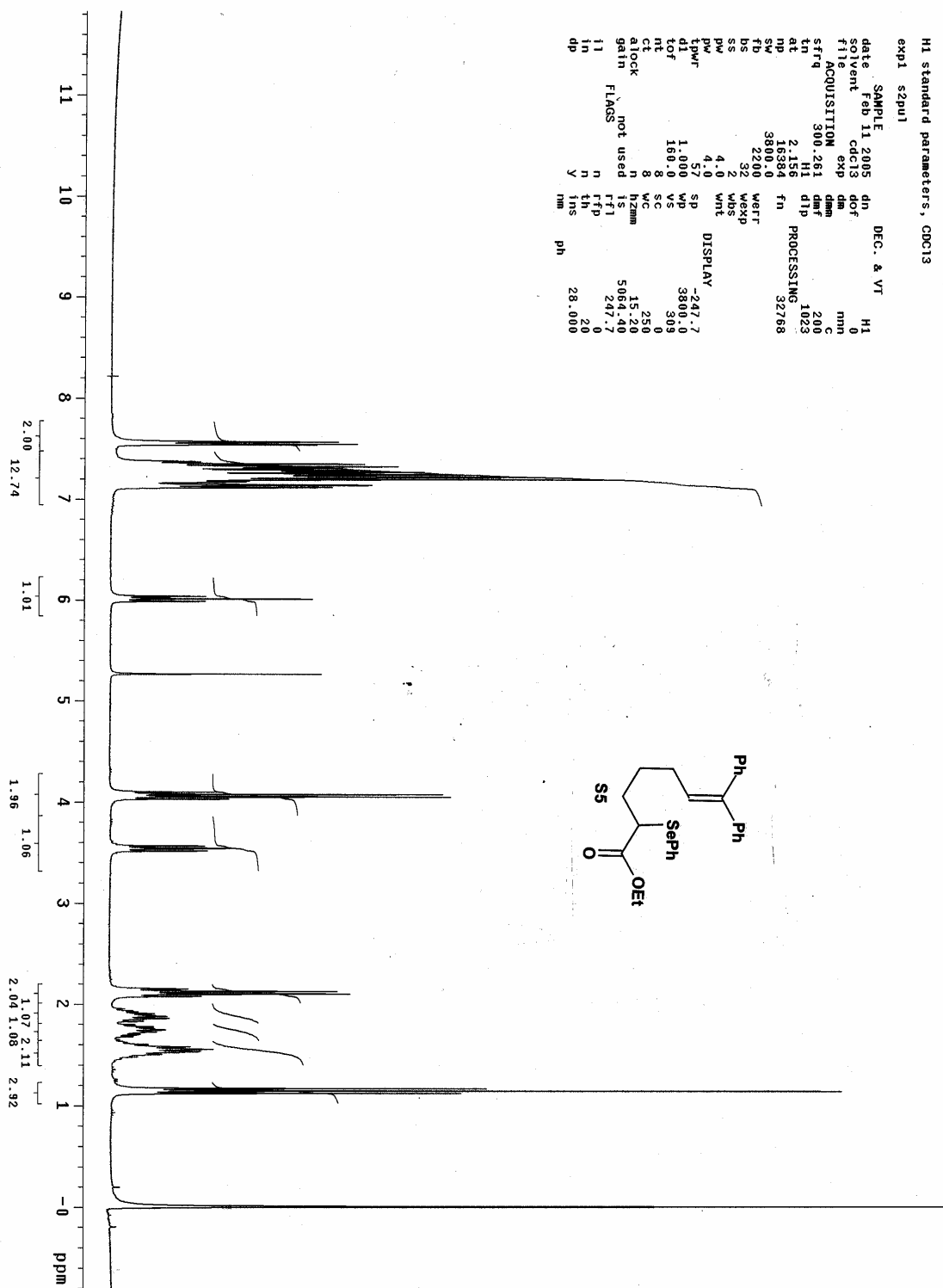
¹H-NMR Spectrum of 10.



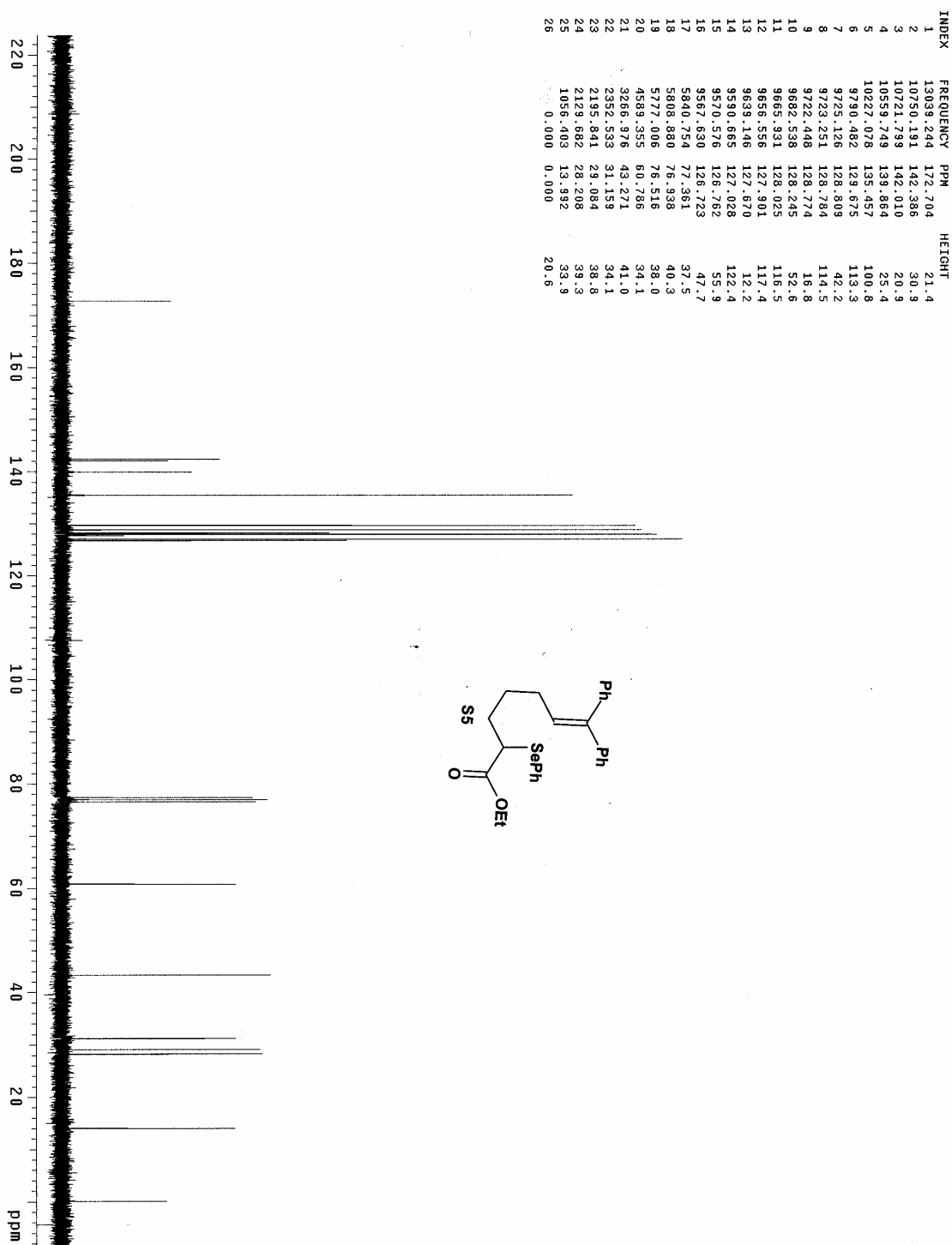
¹³C-NMR Spectrum of 10.



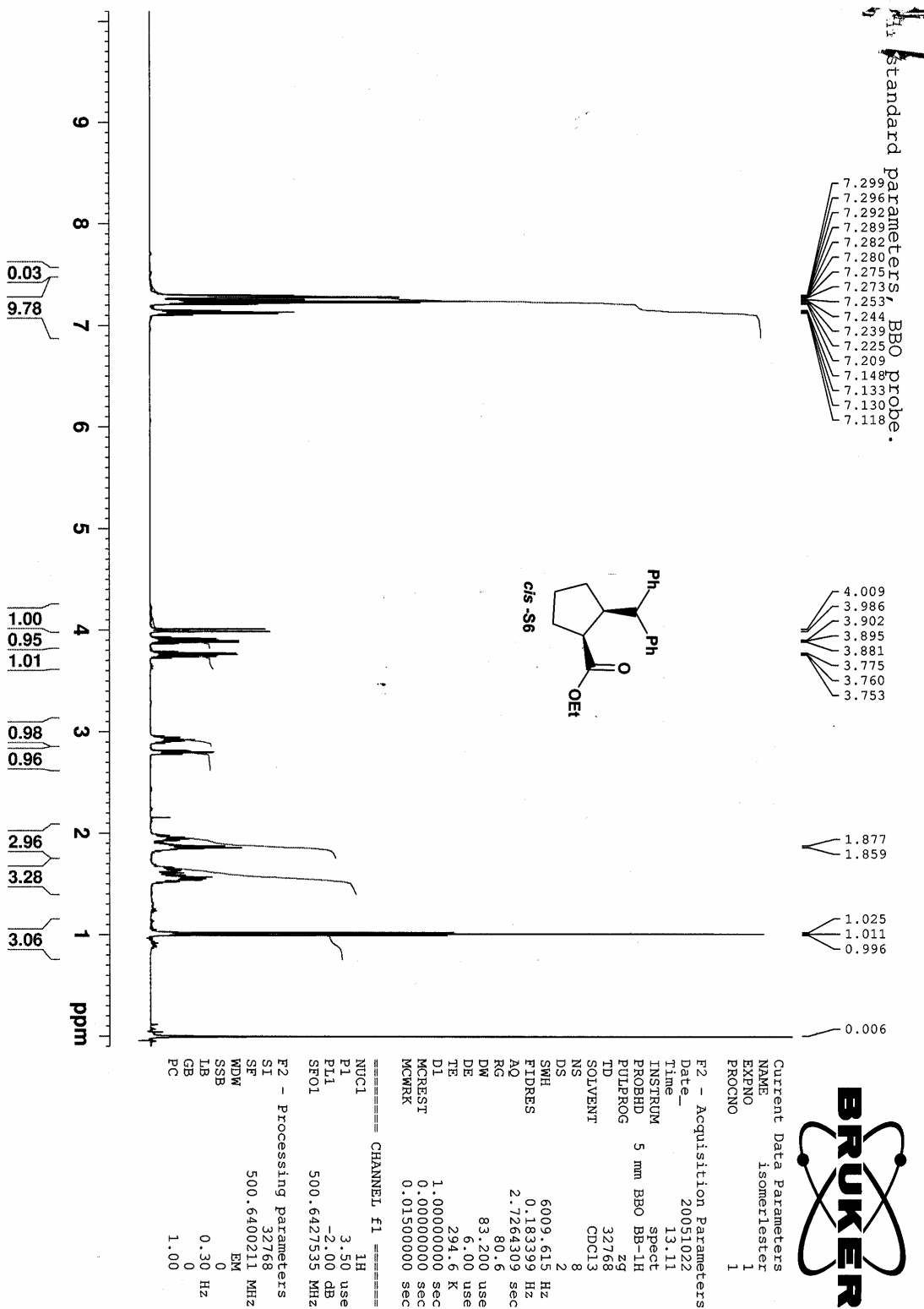
¹H-NMR Spectrum of S5.



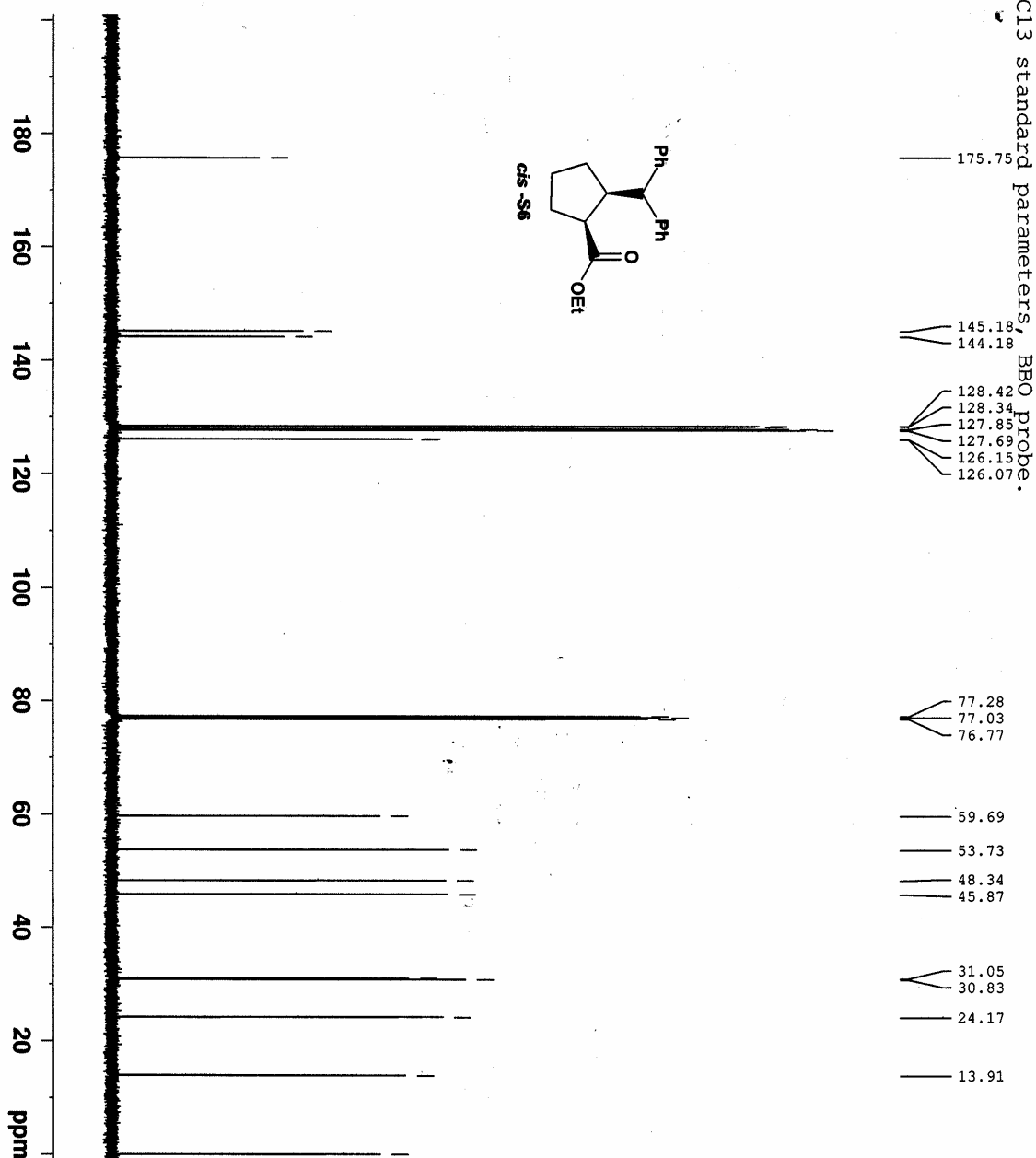
¹³C-NMR Spectrum of S5.



¹H-NMR Spectrum of *cis*-S6.



¹³C-NMR Spectrum of *cis*-S6.



Current Data Parameters
 NAME Isomerlester
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051022
 Time 13.38

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg
 TD 121208
 SOLVENT CDCl3
 NS 128

DS 2
 SWH 30303.031 Hz
 FIDRES 0.250008 Hz
 AQ 1.9999985 sec

RG 7298.2
 DW 16.500 use
 DE 6.00 use
 TE 295.0 K

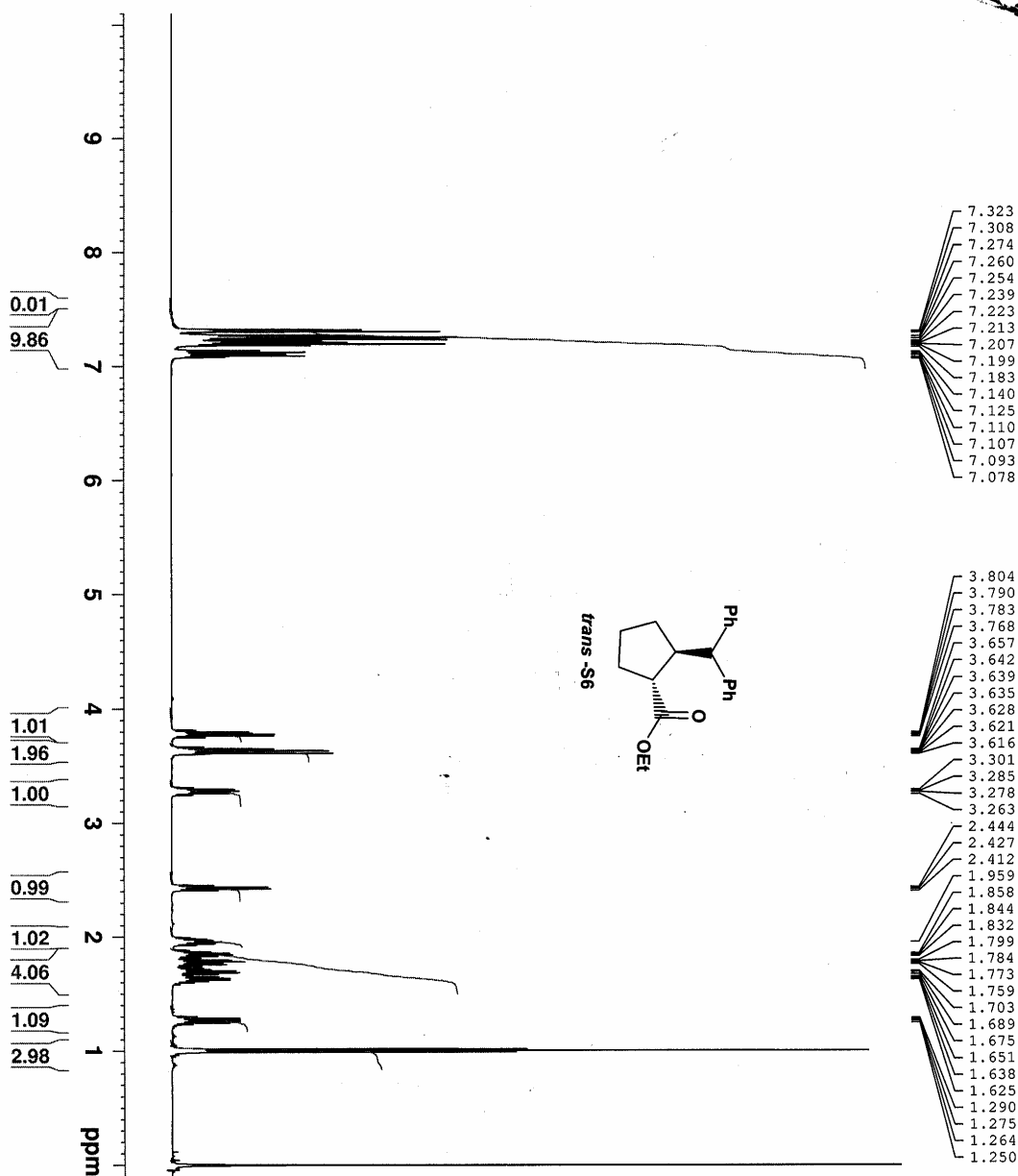
D1 2.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 2.70 use
 PL1 1.00 dB
 SF01 125.8998755 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 use
 PL2 -2.00 dB
 PL12 17.00 dB
 PL13 20.00 dB
 SF02 500.6422529 MHz

F2 - Processing parameters
 SI 131072
 SF 125.8860325 MHz
 WDW EM
 SSB 0
 GB 0
 PC 1.00

¹H-NMR Spectrum of *trans*-S6.



Current Data Parameters
NAME cycloesterisomer2
EXPNO 1
PROCNO 1

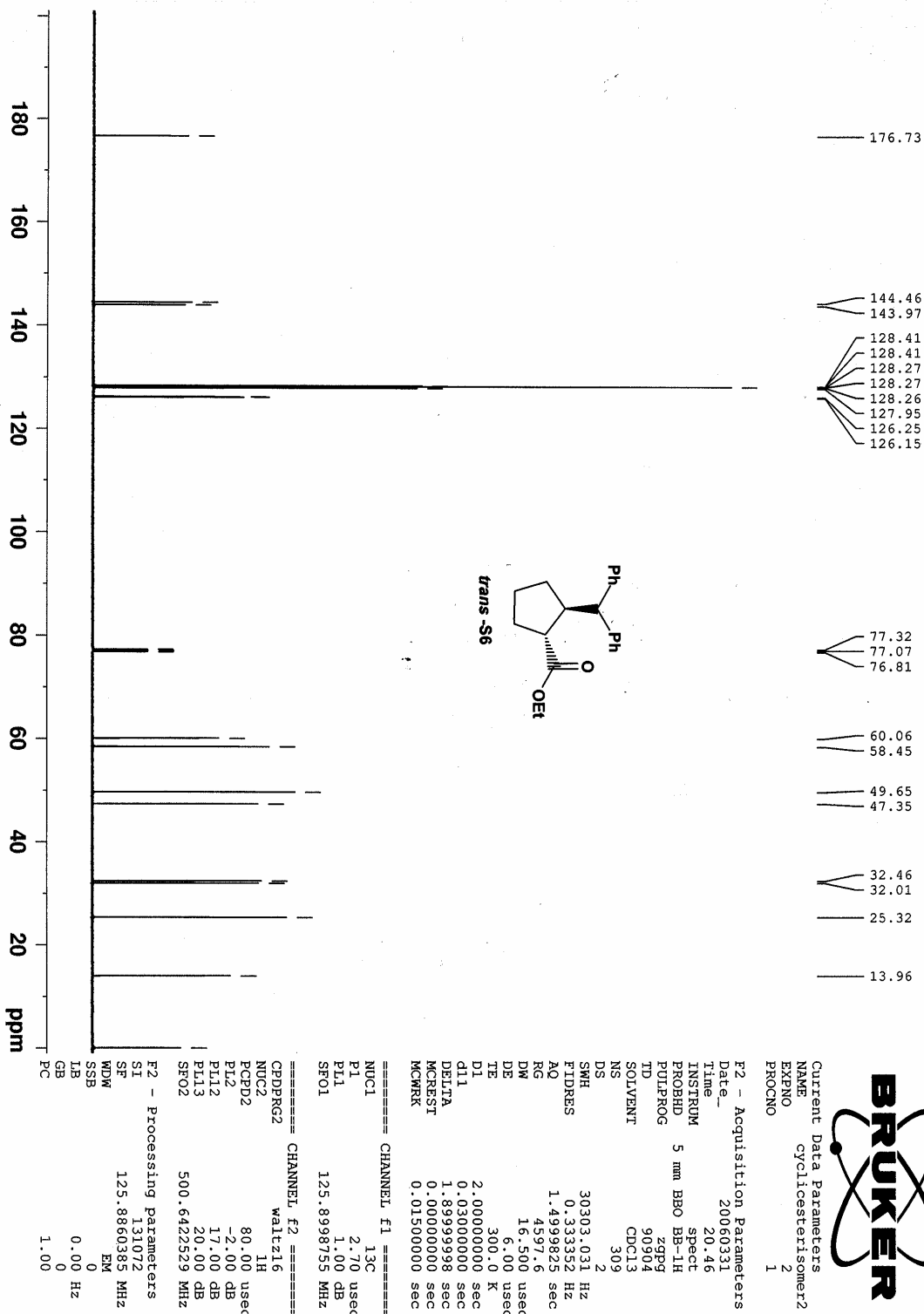
F2 - Acquisition Parameters
Date_ 20060331
Time 20.29
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 32
DW 83.200 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz

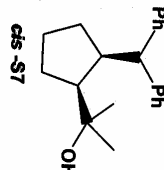
F2 - Processing parameters
SI 32768
SF 500.6400390 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



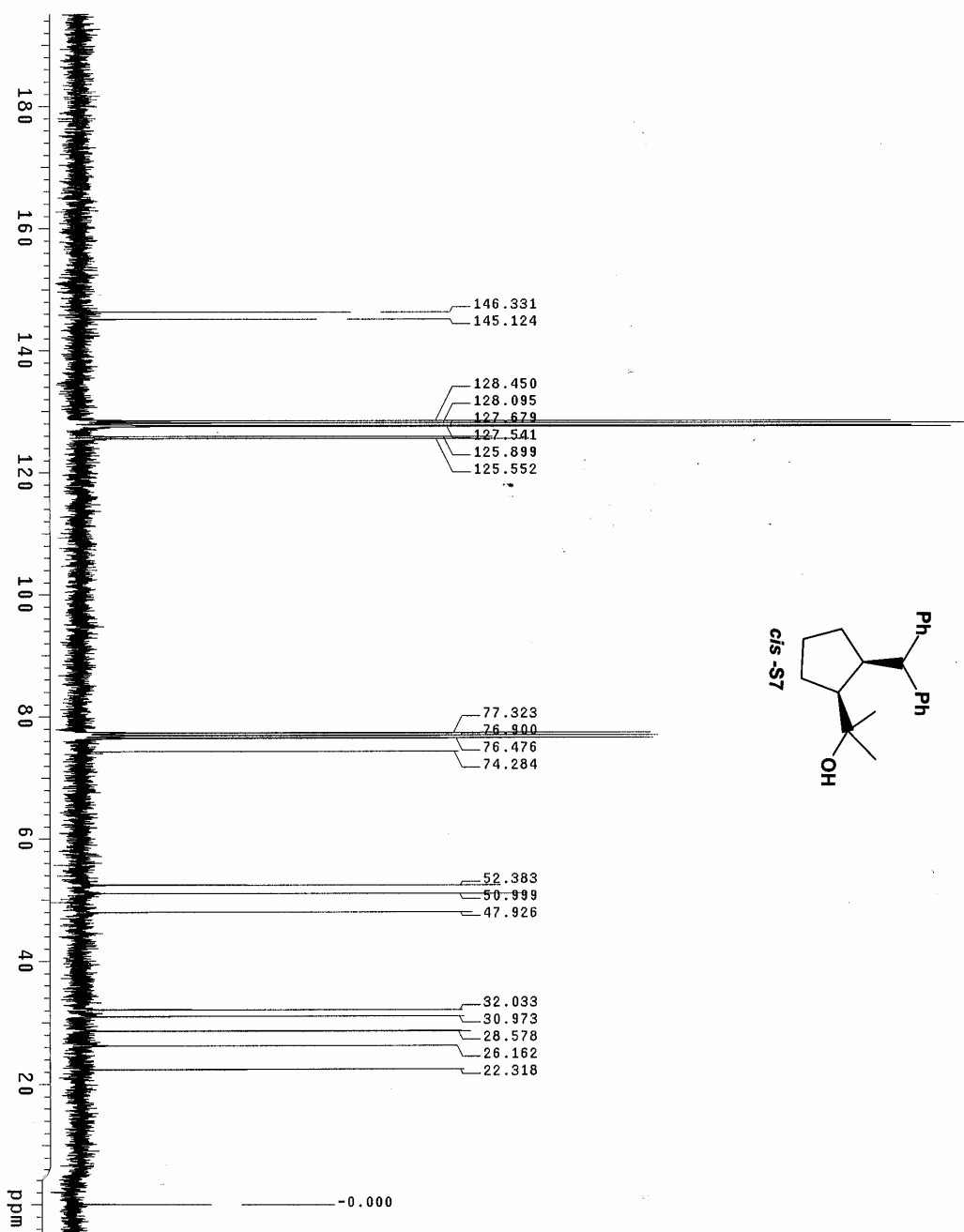
¹³C-NMR Spectrum of *trans*-S6.



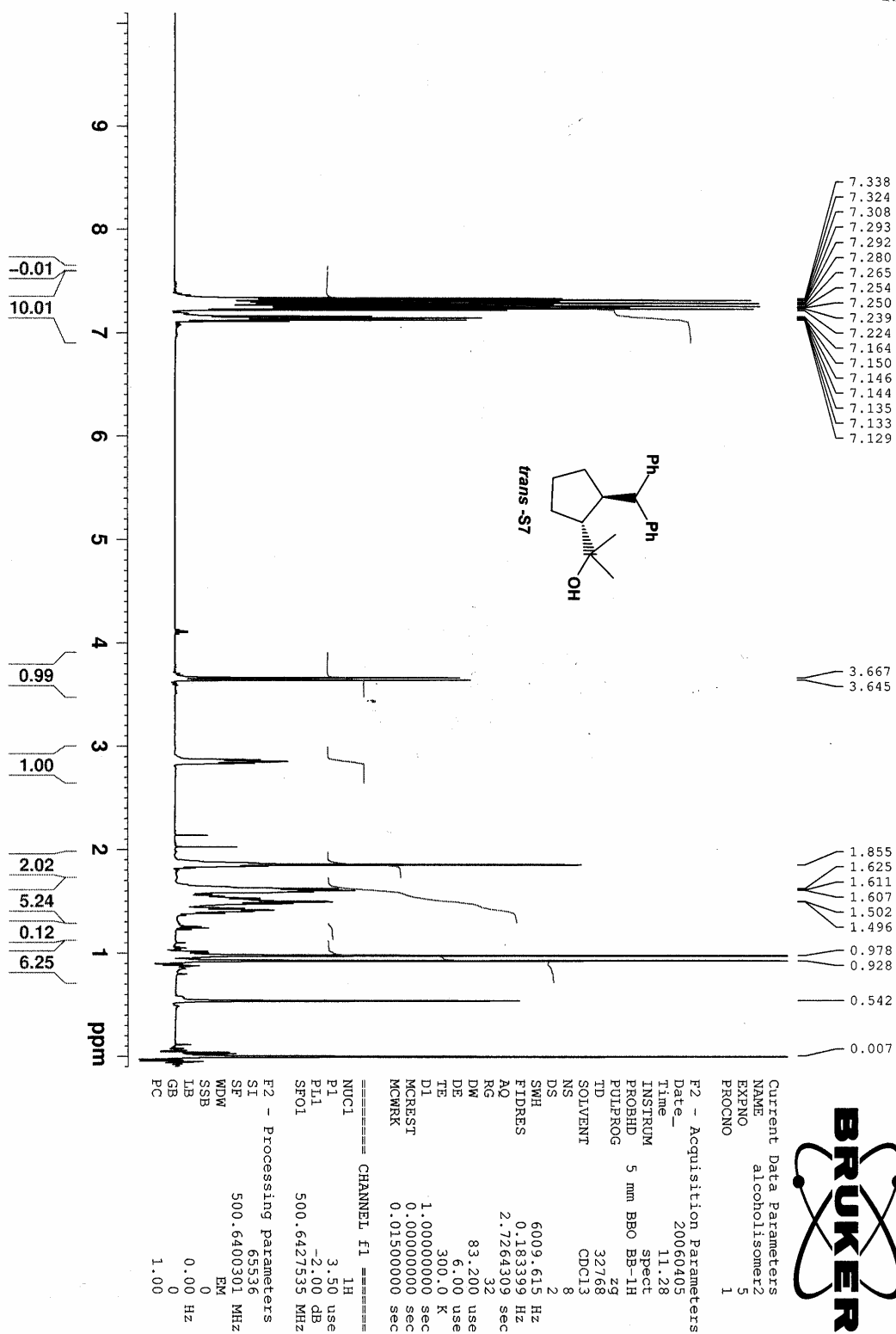
¹H-NMR Spectrum of *cis*-S7.



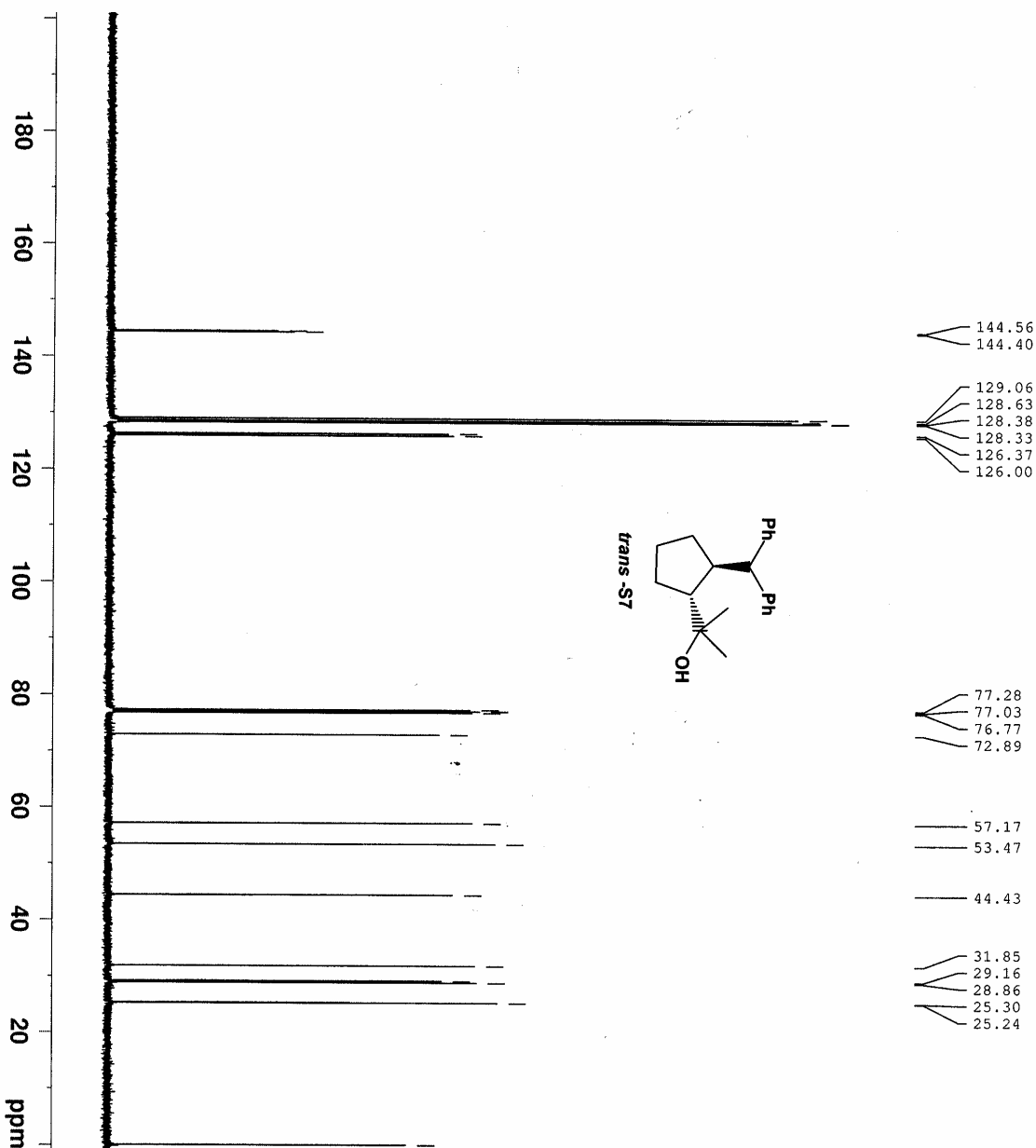
¹³C-NMR Spectrum of *cis*-S7.



¹H-NMR Spectrum of *trans*-S7.



¹³C-NMR Spectrum of *trans*-S7.



Current Data Parameters

NAME	alcoholisomer2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060405
Time	10.49
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg
TD	90904
SOVENT	CDCl3
NS	128
DS	2
SMH	30303.031 Hz
FIDRES	0.333352 Hz
AQ	1.4999825 sec
RG	2580.3
DW	16.500 usec
DE	6.00 usec
TE	300.0 K
D1	2.0000000 sec
d11	0.0300000 sec
DELTA	1.8999998 sec
MCREST	0.0000000 sec
MCWRR	0.0150000 sec

Channel f1

NUC1	¹³ C
P1	2.70 usec
PL1	1.00 dB
SFO1	125.8998755 MHz

Channel f2

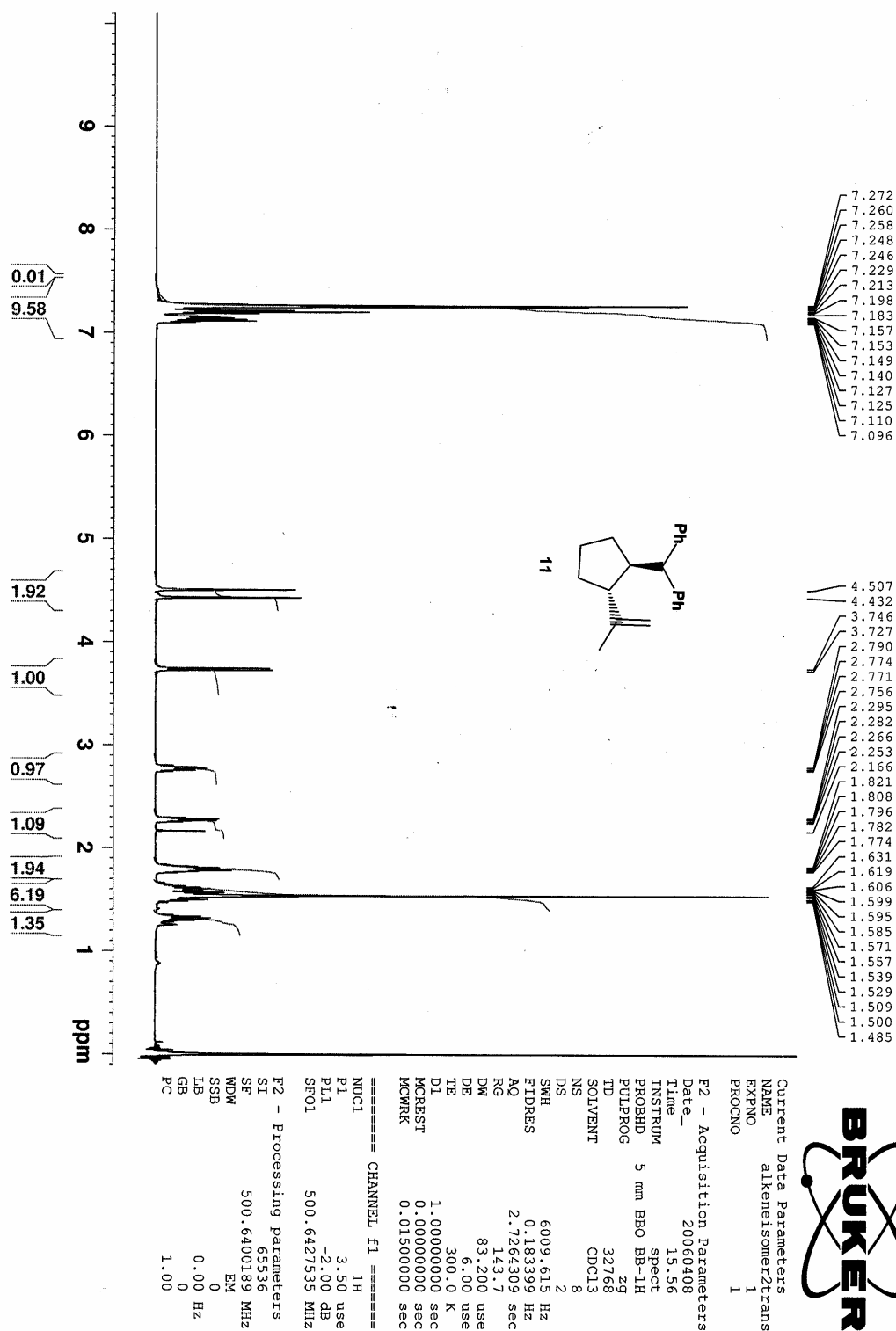
CPDPRG2	waltz16
NUC2	¹ H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	17.00 dB
PL13	20.00 dB
SFO2	500.6422529 MHz

F2 - Processing parameters

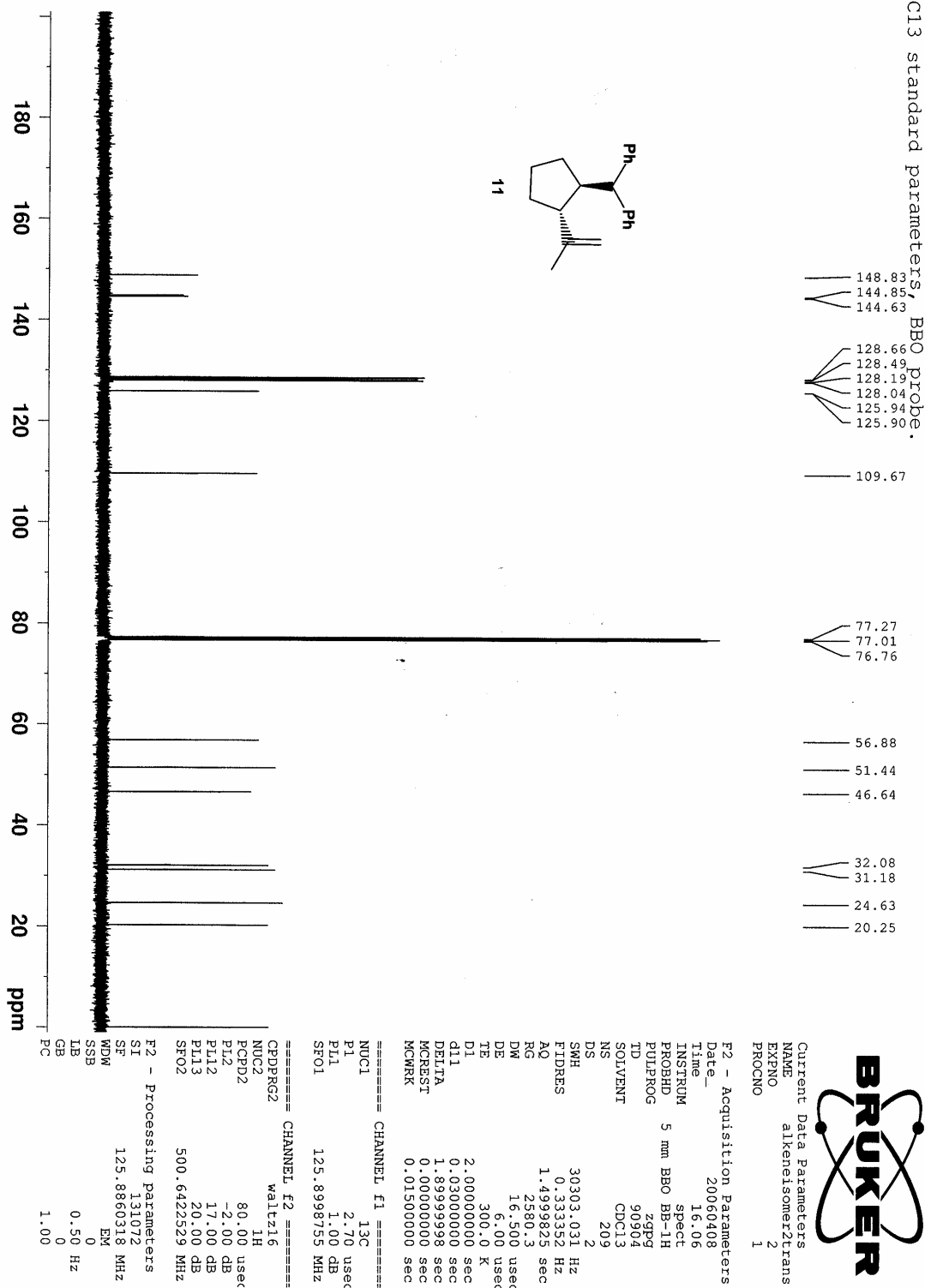
SI	131072
SF	125.8860371 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



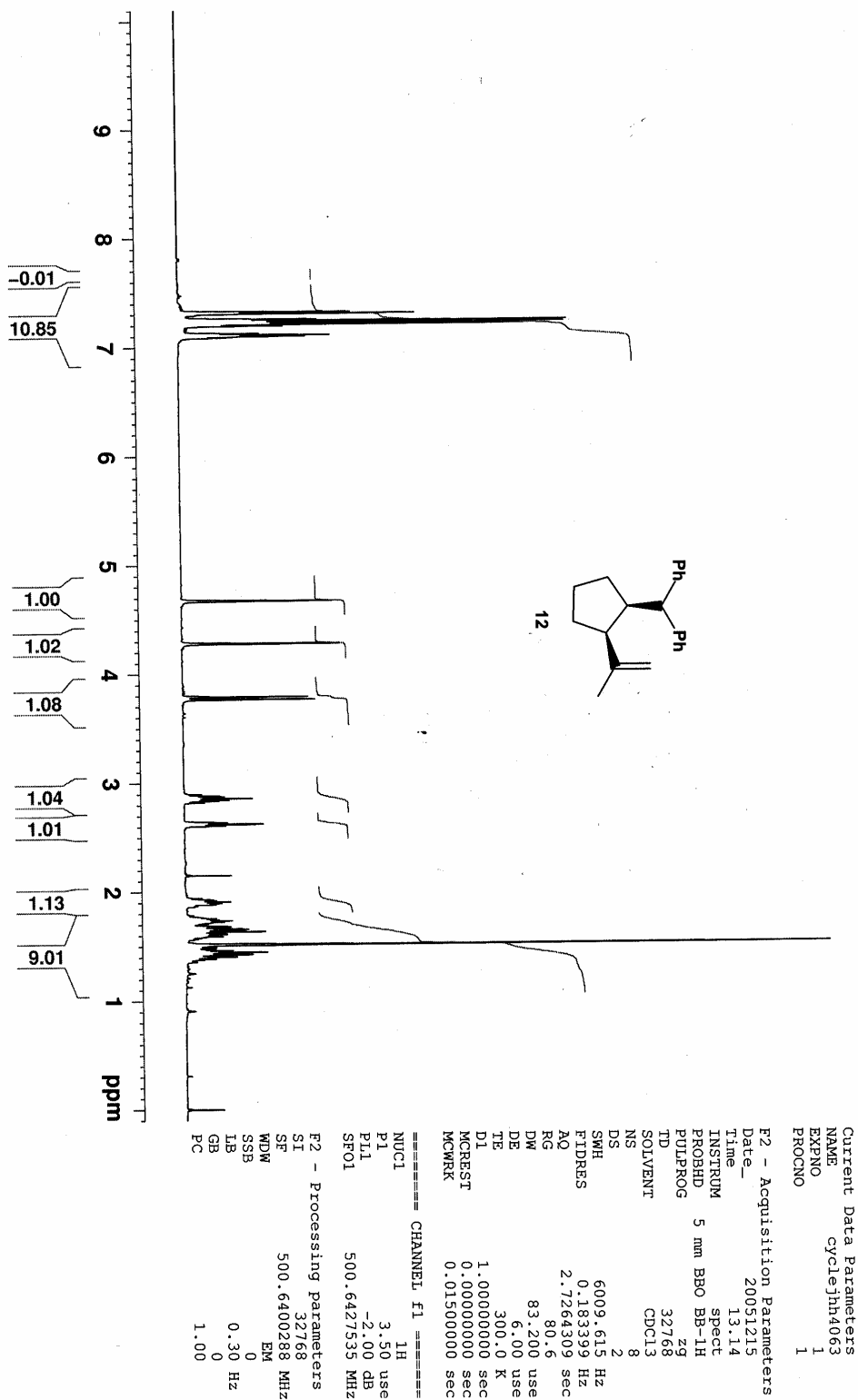
¹H-NMR Spectrum of 11.



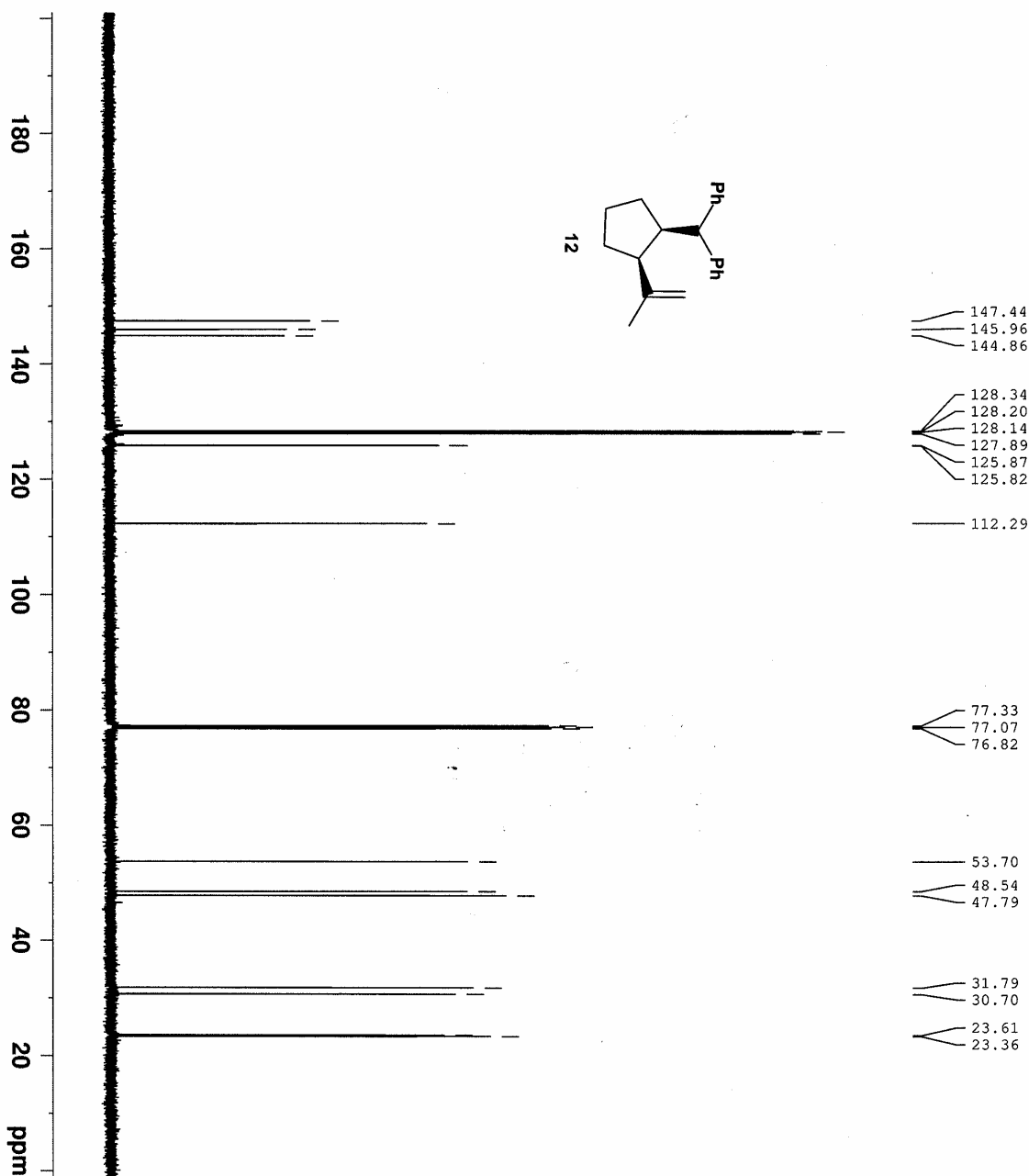
¹³C-NMR Spectrum of 11.



¹H-NMR Spectrum of 12.



¹³C-NMR Spectrum of 12.



Current Data Parameters
 NAME cyclejh4063
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20051215
 Time 13.37
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg
 TD 90904
 SOLVENT CDCl3
 NS 153
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.333352 Hz
 AQ 1.4999825 sec
 RG 4096
 DE 16.500 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWPRK 0.01500000 sec

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

NUC1 13C
 P1 2.70 usec
 PL1 1.00 dB
 SFO1 125.8998755 MHz

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

CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.00 dB
 PL12 17.00 dB
 PL13 20.00 dB
 SFO2 500.6422529 MHz

F2 - Processing parameters

SI 131072
 SF 125.8860280 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00