

Supplement

Experimental Part

Synthesis

General

All final ^1H and ^{13}C NMR (300 MHz and 600 MHz) spectra were obtained on a Varian Unity Plus 300 or a Varian Unity Plus 500. Deuteriochloroform (99.98% in CDCl_3) and deuterobenzene (99+% in C_6D_6) were used as solvents and the chemical shifts were assigned using tetramethylsilane, CHCl_3 , $\text{C}_6\text{H}_5\text{D}$ as internal references.

The mass spectral analyses were carried out on a Finningan-Mat 8430 mass spectrometer equipped with a Varian 3400 gas chromatograph. TLC analyses were carried out on a commercially available 0.2 mm thick silica gel 60 PF254 containing gypsum as a binder. Column chromatographic separations were carried out using 230-400 mesh silica gel purchased from Aldrich company.

Synthesis of the tertiary alcohol **6**:

To an open flask containing 20mL of saturated ammonium chloride solution, 40 mmol of zinc dust and 200 mmol of acetone, were added 40 mmol of the allyl halide while stirring at room temperature. Ultrasonic and magnetic stirring were alternatively applied in the respective periods of 25 min and 5 min for a minimum of 3 hours or until the total disappearance of the zinc dust. To facilitate the work-up it is better to leave the solution stirring for at least 12 hours. Ether (25 mL) was added to the flask and the reaction mixture was filtered under vacuum and the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. 2-methyl-3-phenyl-4-penten-2-ol (**6**) was prepared in 91% yield from cinnamyl chloride following the general procedure described above. Yellow oil: ^1H NMR (CDCl_3) 1.17 (s, 3H), 1.21 (s, 3 H), 3.28 (d, J = 9.6 Hz, 1 H), 5.15 (dd, J = 16.9, 1 Hz, 1 H), 5.2 (dd, J = 8.5, 1 Hz, 1 H), 6.31 (ddd, J = 16.8, 10, 10 Hz, 1 H), 7.25 (m, 5 H).

2) Synthesis of the epoxy *t*-alcohol (**7**):

3 mmol of *t*-alcohol was dissolved in 10 mL of dry methylene chloride at 0°C. 5.5 mmol (1.8 equiv.) of *m*-chloroperbenzoic acid (*m*-CPBA, 85%) in 5 mL of dry methylene chloride were added at 0°C. The reaction mixture was allowed to reach room temperature, then it was refluxed for 2 hours. The reaction mixture was then allowed to cool down to room temperature. The solution was transferred to a separatory funnel. Excess peracid was destroyed with 10% sodium sulfite solution, until a starch-iodide test was negative. The organic layer was washed with saturated aqueous sodium chloride solution (2 x 30 mL), dried over MgSO₄, and concentrated under reduced pressure. The epoxy *t*-alcohol was purified by Medium Pressure Liquid Chromatography using an eluent system composed of a gradient of Skellysolve B and ether.

4,5-epoxy-2-methyl-3-phenyl-pentan-2-ol (**7**) was prepared in 82% from using the general procedure described above. A mixture of two diastereoisomers was obtained (ratio 2.5:1) as the crude product. One diastereoisomer was isolated as a yellow oil: ¹H NMR (CDCl₃) 1.22 (s, 3 H), 1.36 (s, 3 H), 2.22 (d, *J* = 8.8 Hz, 1 H), 2.38 (dd, *J* = 4.9, 2.8 Hz, 1 H), 2.74 (dd, *J* = 4.8, 4.2 Hz, 1 H), 3.55 (m, 1 H), 7.25-7.4 (m, 5 H). ¹³C NMR (CDCl₃) 28.1, 28.13, 45.8, 52.6, 59.4, 72.5, 126.8, 128.1, 129.0, 139.0. IR (neat): 702, 741, 866, 898, 951, 1153, 1373, 1453, 1493, 2974, 3467. MS (CI) calculated for [M+H⁺]: 193.1229 observed: 193.1225.

The other diastereoisomer was isolated as a yellow oil: ¹H NMR (CDCl₃) 1.20 (s, 3 H), 1.35 (s, 3 H), 2.42 (d, *J* = 8 Hz, 1 H), 2.59 (dd, *J* = 5, 2.6 Hz, 1 H), 2.93 (dd, *J* = 5, 3.9 Hz, 1 H), 7.25-7.4 (m, 5 H). ¹³C NMR (CDCl₃) 28.3, 28.7, 48.7, 52.3, 58.7, 72.3, 127.0, 128.2, 129.5, 138.2.

Synthesis of the sulfenates **4** and **5**:

To a 50 mL three-neck flask containing the alcohol (5mmol) and 15 mL of anhydrous methylene chloride under an argon atmosphere in a darkened hood was added at -30°C 1.6 mL (11.5 mmol) of freshly distilled triethylamine. After the addition, the mixture was stirred for 10 min. 10 mL of a methylene chloride solution of 4-nitrobenzenesulfonyl chloride was then added slowly via a dropping funnel. After the reaction, the mixture was stirred for 15 min and was then allowed to warm to room temperature for 30 min. The reaction mixture was washed with cold

5% hydrochloric acid (2 x 10 mL) and cold water (3 x 10 mL), and the extract was dried over magnesium sulfate, keeping the light exposure to a minimum. The solvent was removed under reduced pressure in an aluminum-wrapped flask giving the sulfenates in a crude form. Analysis of the crude products by ^1H NMR showed the presence of unreacted alcohol, 4-nitrobenzene disulfide and the corresponding sulfinates, presumably formed by air/light oxidation of the sulfenates during the work-up, as the major side products. The sulfenates were purified by flash chromatography with silica gel using an eluent system composed of hexanes and methylene chloride in a 3:1 ratio.

4,5-epoxy-2-methyl-3-phenyl-2-pentyl 4-nitrobenzenesulfenate (4) was prepared from 4,5-epoxy-2-methyl-3-phenyl-pentan-2-ol in 39% yield after purification as a single diastereoisomer. Dark yellow oil: ^1H NMR (CDCl_3) 1.29 (s, 3H), 1.47 (s, 3H), 2.37 (dd, $J = 4.9, 2.7$ Hz, 1H), 2.43 (d, $J = 8.8$ Hz, 1H), 2.77 (t, $J = 4.6$ Hz, 1H), 3.61 (ddd, $J = 2.7, 4.15, 8.55$ Hz, 1H), 7.03 (d, $J = 8.8$ Hz, 2H), 7.25-7.4 (m, 5H), 8.02 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (CDCl_3) 23.6, 24.6, 45.8, 52.1, 59.2, 87.5, 120.0, 123.8, 127.4, 128.3, 129.7, 138.2, 144.8, 153.8. IR (neat): 735, 840, 909, 1087, 1336, 1516, 1577, 1594. MS (CI) calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{S}$: 346.1113, found 346.1112.

Cinnamyl-4-nitrobenzenesulfenate (5) was prepared in 28% yield after purification from cinnamyl alcohol. This compound was found to be sensitive to air oxidation in the presence of light. Pale yellow solid, forming flakes: mp (uncorrected) 64-66°C. ^1H NMR (CDCl_3) 8.22 (d, $J = 9$ Hz, 2 H), 7.34 (m, 5 H), 7.3 (d, $J = 9.2$ Hz, 2 H), 6.7 (d, $J = 15.9$ Hz, 1H), 6.33 (dt, $J = 15.9, 6.8$ Hz, 1 H), 4.54 (d, 6.9 Hz, 2 H). ^{13}C NMR (CDCl_3) 79.6, 120.4, 123.5, 124.5, 127.0 (2 CH), 128.8, 128.9, 136.0, 136.4, 151.7. IR (neat): 1577, 1509, 1333, 1084, 921, 837, 740. MS (CI, $[\text{M}+\text{H}]^+$) calcd: 288.0694, obsd: 288.0714.

Independent Synthesis

1,2-epoxy-3-phenyl-3-propyl-4-nitrobenzene sulfide (8) was isolated from the crude products of the photolysis of 4,5-epoxy-2-methyl-3-phenyl-2-pentyl 4-nitrobenzenesulfenate and also from the crude product of the photolysis of cinnamyl-4-nitrobenzenesulfenate by flash chromatography with a gradient of methylene chloride and hexanes as eluent. A mixture of two

diastereoisomers was obtained. Yellow oil: ^1H NMR (CDCl_3) 2.65 (dd, $J = 2.35, 3.92$ Hz, 1H diastereoisomer 1), 2.70 (dd, $J = 2.57, 4.71$ Hz, 1H diastereoisomer 2), 2.85 (m, 1H), 3.45 (m, 1H), 4.21 (d, $J = 7.07$ Hz, 1H diastereoisomer 2), 4.39 (d, $J = 6.0$ Hz, 1H diastereoisomer 1), 7.25-7.45 (m, 7H), 8.08 (d, $J = 9$ Hz, 2H). ^1H NMR (C_6D_6): 2.12 (dd, $J = 2.56, 5.13$ Hz, 1H diastereoisomer 1 or 2), 2.15 (m, 1H) 2.22 (dd, $J = 3.85, 5.13$ Hz, 1H diastereoisomer 1 or 2), 2.98 (m, 1H), 3.78 (d, $J = 6.64$ Hz, 1H diastereoisomer 2), 3.81 (d, $J = 5.77$ Hz, 1H diastereoisomer 1), 6.78 (d, $J = 9$ Hz, 1H diastereoisomer 1), 6.85 (d, $J =$ (Hz, 1H diastereoisomer 2), 6.9-7.3 (m, 5H), 7.6 (m, 2H). ^{13}C NMR (CDCl_3): 46.6, 46.8, 53.5, 54.1, 54.8, 55.0, 123.8, 123.9, 128.0, 128.2, 128.5 (2 C, a shoulder is present), 128.96, 129.0, 129.2, 129.7, 136.6, 136.9, 144.4, 144.9, 145.9, 146.1. IR (in CCl_4): 699, 742, 789, 853, 1093, 1338, 1511, 1578, 1595, 2920, 3062. MS (FAB, $[\text{M}+\text{H}]^+$) calcd: 288.0694, obsd: 288.0703.

Photolysis

Photolysis of cinnamyl-4-nitrobenzene sulfenate (**5**).

Monitoring of the reaction: 10 mg of cinnamyl-4-nitrobenzene sulfenate were dissolved in 0.6 mL of deuterobenzene and placed in a 5mm NMR tube. The solution was degassed by applying sonication / vacuum for ~ 20 minutes. ^1H NMR analysis was performed on the sample before the thermolysis. The NMR tube was then placed in a Rayonet UV reactor equipped with 350 nm wavelength light bulbs. Periodically, the tube was removed from the reactor and ^1H NMR analysis was performed. Spectra were obtained after 30s, 2 min, 5 min, 10 min, 22 min and 30 min. At that time, the starting material was almost completely disappeared and the photolysis was stopped. The spectra before and after the photolysis are provided in this supporting information. The solvent was removed under reduced pressure. The crude product was dissolved in deuteriochloroform and ^1H NMR analysis was performed.

Larger scale: 80 mg of cinnamyl-4-nitrobenzene sulfenate were dissolved in 4.0 mL of benzene and placed in two 5mm NMR tubes. The solution was degassed by applying sonication / vacuum for ~ 20 minutes. The NMR tubes were then placed in a Rayonet UV reactor equipped with 350 nm wavelength light bulbs for 33 minutes. The solvent was removed under reduced pressure. Flash chromatography was performed on the crude product using a gradient of methylene chloride and hexanes as the eluent. 5 mg of pure 1,2-epoxy-3-phenyl-3-propyl-4-

nitrobenzene sulfide were isolated as a 1:1 mixture of diastereoisomers for characterization purposes.

Photolysis of 4,5-epoxy-2-methyl-3-phenyl-2-pentyl 4-nitrobenzenesulfenate (**4**).

Monitoring of the reaction: 10 mg of 4,5-epoxy-2-methyl-3-phenyl-2-pentyl 4-nitrobenzenesulfenate were dissolved in 0.6 mL of deuterobenzene and placed in a 5mm NMR tube. The solution was degassed by applying sonication / vacuum for ~ 20 minutes. ¹H NMR analysis was performed on the sample before the thermolysis. The NMR tube was then placed in a Rayonet UV reactor equipped with 350 nm wavelength light bulbs. Periodically, the tube was removed from the reactor and ¹H NMR analysis was performed. Spectra were obtained after 30s, 2 min, 5 min, 10 min, 20 min and 30 min. At that time, the starting material was almost completely disappeared and the photolysis was stopped. The spectra before and after the photolysis are provided in this supporting information. The solvent was removed under reduced pressure. The crude product was dissolved in deuteriochloroform and ¹H NMR analysis was performed. Flash chromatography was performed on the crude product using a gradient of methylene chloride and hexanes as the eluent. Three fractions yielded enough product for identification purposes: one contained 4-nitrophenyl disulfide, another 1,2-epoxy-3-phenyl-3-propyl-4-nitrobenzene sulfide and the last one cinnamaldehyde.

Computational Studies

Cinnamyl-benzyl sulfenate
 B3LYP/6-31G*

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	-1.064616	-1.310653	0.091344
2	6	-1.278601	-2.479068	1.426199
3	6	-1.764517	-4.328358	3.467347
4	6	-0.399135	-3.551338	1.620965
5	6	-2.398843	-2.330731	2.254708
6	6	-2.645404	-3.265203	3.261058
7	6	-0.639392	-4.461239	2.649912
8	1	0.464478	-3.659540	0.973244
9	1	-3.069289	-1.485724	2.119168
10	1	-3.518044	-3.147554	3.898108
11	1	0.050560	-5.286885	2.804405
12	1	-1.950829	-5.045740	4.261597
13	8	0.610886	-1.390071	-0.147085
14	6	1.375238	-0.443052	0.618901
15	6	1.429417	0.934239	0.018942
16	1	2.383304	-0.880796	0.658480
17	1	1.001662	-0.401944	1.651283
18	6	1.025247	1.244705	-1.220183
19	1	1.860528	1.690794	0.674279
20	6	1.063340	2.565725	-1.865180
21	1	0.632693	0.439199	-1.838826
22	6	1.125017	5.045334	-3.212701
23	6	1.379386	3.754004	-1.180519
24	6	0.768437	2.655587	-3.236841
25	6	0.801156	3.878463	-3.905328
26	6	1.411890	4.975823	-1.846021
27	1	1.590214	3.724386	-0.115210
28	1	0.515219	1.749420	-3.782410
29	1	0.571876	3.918873	-4.966958
30	1	1.656441	5.880639	-1.295541
31	1	1.148737	6.001222	-3.728880

E(RB+HF-LYP) = -1053.38897624 A.U. after 15 cycles
 Convrg = 0.8528D-08 -V/T = 2.0074
 S**2 = 0.0000

Zero-point correction= .248868 (Hartree/Particle)
 Thermal correction to Energy= 0.264217
 Thermal correction to Enthalpy= 0.265161
 Thermal correction to Gibbs Free Energy= 0.201979
 Sum of electronic and zero-point Energies= -1053.140108
 Sum of electronic and thermal Energies= -1053.124760
 Sum of electronic and thermal Enthalpies= -1053.123815
 Sum of electronic and thermal Free Energies= -1053.186997

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1-2epoxy-3-phenyl-3-propyl-phenyl sulfide
 B3LYP/6-31G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.666888	2.536214	0.281927
2	6	0	-0.587010	2.841432	0.909731
3	1	0	-0.680554	2.512573	1.945133
4	6	0	-0.501016	1.842305	-0.166094
5	1	0	-0.988674	3.832662	0.699010
6	6	0	-0.587015	0.357327	0.132251
7	1	0	-0.835226	2.133042	-1.163188
8	6	0	-2.022251	-0.125947	0.113123
9	1	0	-0.143324	0.173021	1.114674
10	16	0	0.399392	-0.667258	-1.091492
11	6	0	-4.700404	-0.987307	0.118712
12	6	0	-2.810544	-0.020545	-1.043001
13	6	0	-2.596068	-0.672820	1.268182
14	6	0	-3.924364	-1.099205	1.273339
15	6	0	-4.138071	-0.448622	-1.039877
16	1	0	-2.382628	0.387185	-1.955265
17	1	0	-1.996043	-0.765937	2.170438
18	1	0	-4.351523	-1.520240	2.179678
19	1	0	-4.732910	-0.362315	-1.945282
20	1	0	-5.734819	-1.320017	0.120660
21	6	0	2.070731	-0.598563	-0.430934
22	6	0	4.704228	-0.609259	0.521388
23	6	0	2.568067	-1.712362	0.260245
24	6	0	2.903179	0.507364	-0.650482
25	6	0	4.211996	0.501223	-0.168015
26	6	0	3.881622	-1.716815	0.732491
27	1	0	1.923602	-2.571526	0.420443
28	1	0	2.522230	1.370613	-1.184330
29	1	0	4.849489	1.365242	-0.335671
30	1	0	4.259925	-2.585137	1.265659
31	1	0	5.726595	-0.611981	0.890150

E(RB+HF-LYP) = -1053.38881192 A.U. after 15 cycles
 Convg = 0.7184D-08 -V/T = 2.0073
 S**2 = 0.0000

Zero-point correction= 0.249710 (Hartree/Particle)
 Thermal correction to Energy= 0.264698
 Thermal correction to Enthalpy= 0.265642
 Thermal correction to Gibbs Free Energy= 0.203577
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 Sum of electronic and thermal Energies= -1053.124114
 Sum of electronic and thermal Enthalpies= -1053.123169
 Sum of electronic and thermal Free Energies= -1053.185235

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Cinnamyloxy radical
 B3LYP/6-31G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	2.397775	-0.007361	-2.733197
2	6	0	1.380908	0.055478	-2.355157
3	6	0	-1.221038	0.203283	-1.378442
4	6	0	1.155956	0.050023	-0.982740
5	6	0	0.306871	0.135860	-3.247611
6	6	0	-0.996104	0.208496	-2.753472
7	6	0	-0.152409	0.126555	-0.466614
8	1	0	2.001490	-0.023288	-0.305342
9	1	0	0.486659	0.138002	-4.319139
10	1	0	-1.837707	0.267836	-3.438240
11	6	0	-0.450264	0.126402	0.968703
12	1	0	-2.238131	0.259163	-0.997441
13	6	0	0.426444	0.186382	1.987962
14	1	0	-1.511306	0.100433	1.218293
15	1	0	1.500466	0.173391	1.826887
16	6	0	-0.017056	0.133541	3.438310
17	1	0	0.630720	0.779055	4.056382
18	8	0	0.171559	-1.204015	3.719411
19	1	0	-1.064323	0.464759	3.540869

E(UB+HF-LYP) = -423.505100029 A.U. after 33 cycles
 Convg = 0.8404D-08 -V/T = 2.0096
 S**2 = 0.7567

Zero-point correction= 0.153928 (Hartree/Particle)
 Thermal correction to Energy= 0.162999
 Thermal correction to Enthalpy= 0.163944
 Thermal correction to Gibbs Free Energy= 0.117671
 Sum of electronic and zero-point Energies= -423.351172
 Sum of electronic and thermal Energies= -423.342101
 Sum of electronic and thermal Enthalpies= -423.341157
 Sum of electronic and thermal Free Energies= -423.387429

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Oxiranyl benzyl radical
 B3LYP/6-31G*

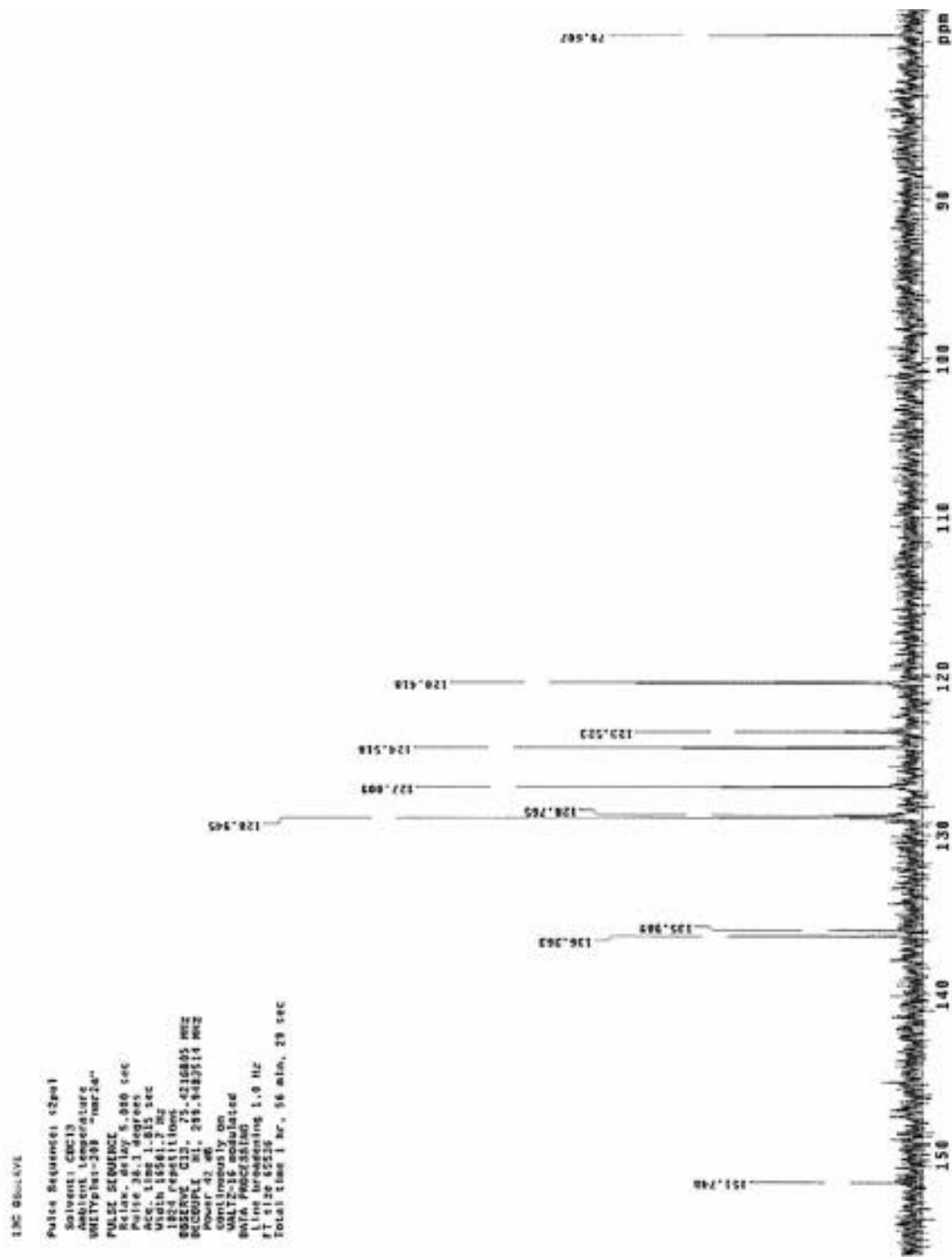
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			X	Y	Z
1	6	0	0.255566	-0.265917	2.344223
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3	1	0	-1.833025	0.277078	2.910961
4	1	0	-0.980293	-0.826944	4.114712
5	8	0	-0.704851	-1.318576	2.052460
6	1	0	1.156223	-0.636607	2.831970
7	6	0	0.415932	0.756482	1.309850
8	1	0	-0.476356	0.969868	0.725226
9	1	0	4.791534	3.557486	0.070568
10	6	0	1.597576	1.478294	1.010481
11	6	0	3.906955	2.982919	0.329739
12	6	0	1.578434	2.443374	-0.039330
13	6	0	2.830226	1.302672	1.705305
14	6	0	3.954327	2.041251	1.366187
15	6	0	2.707346	3.175987	-0.369106
16	1	0	0.651793	2.597282	-0.587008
17	1	0	2.895566	0.582363	2.514825
18	1	0	4.880811	1.885677	1.913005
19	1	0	2.660170	3.903303	-1.175460

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 S**2 = 0.7794

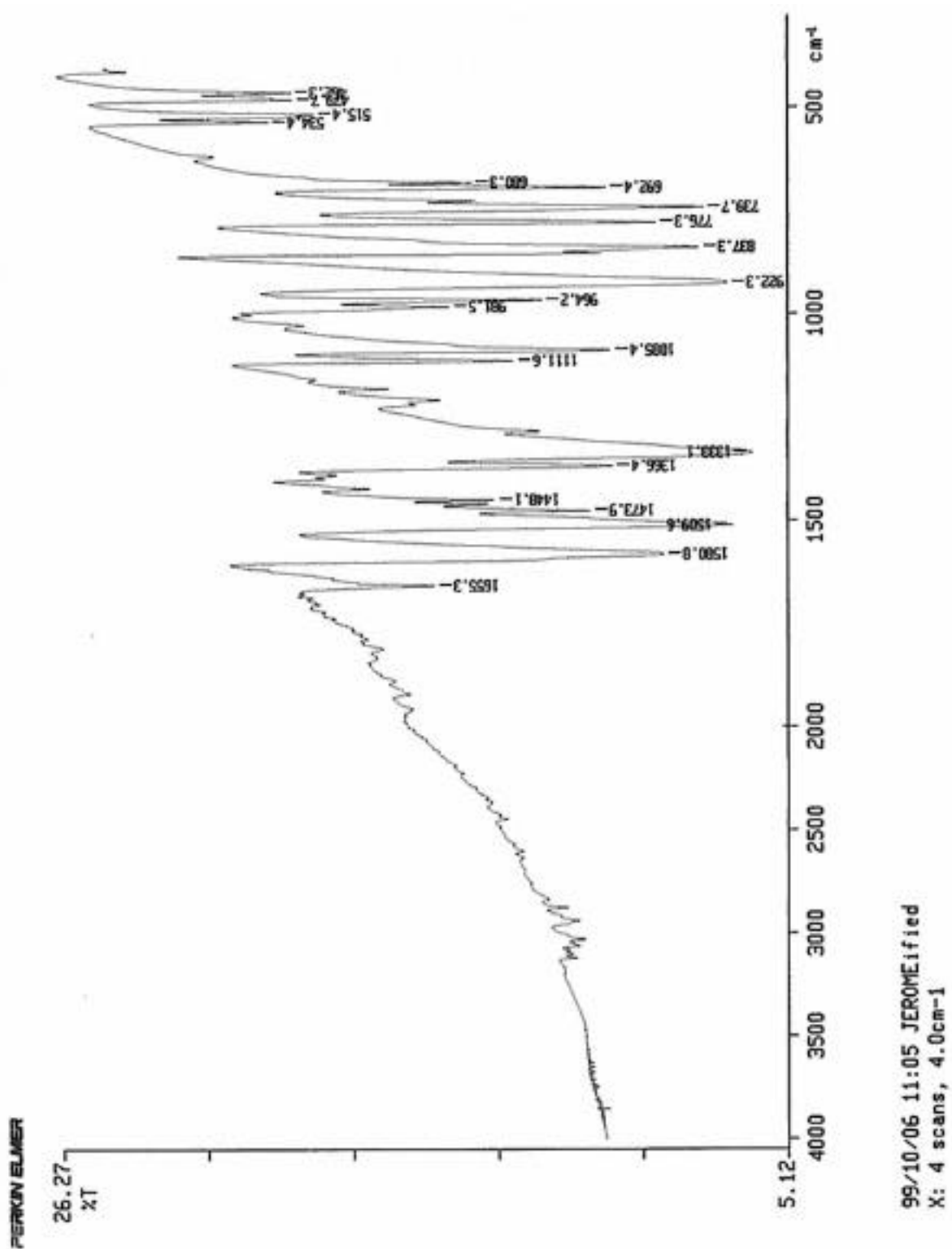
Zero-point correction= 0.154093 (Hartree/Particle)
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 Sum of electronic and thermal Enthalpies= -423.349761
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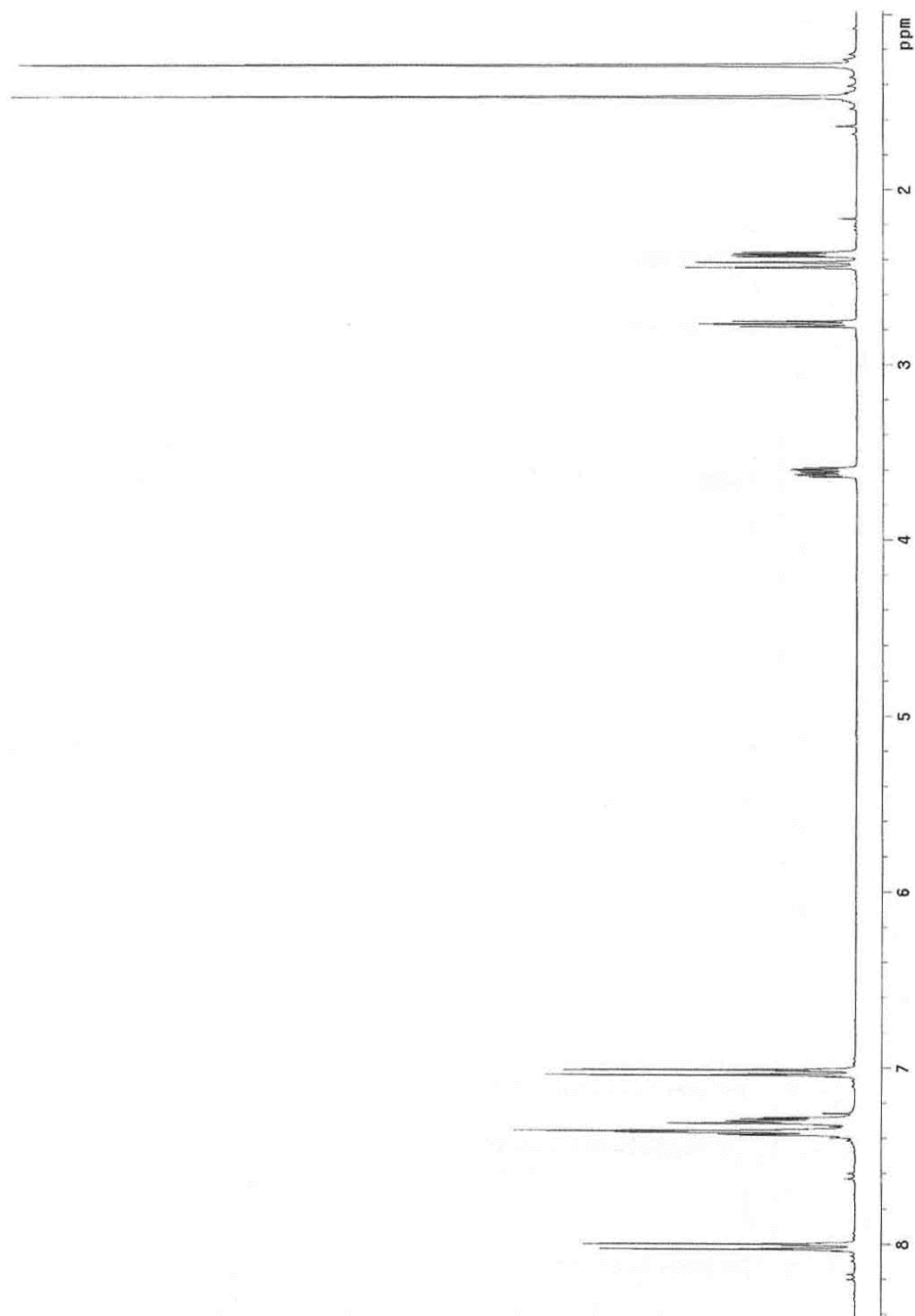
NMR Spectrum 2
Cinnamyl-4-nitrobenzenesulfenate (**5**), ^{13}C NMR in CDCl_3



IR Spectrum 1
Cinnamyl-4-nitrobenzenesulfonate (**5**), IR

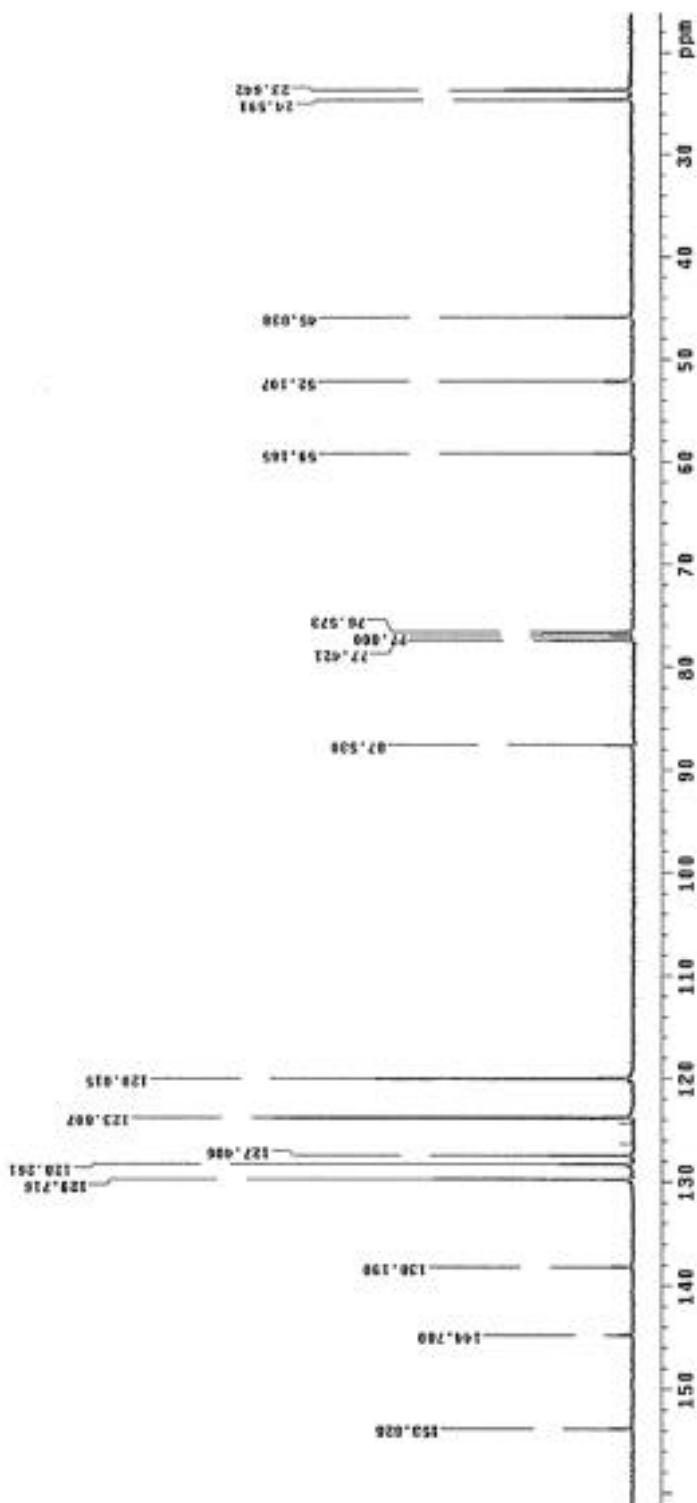


NMR Spectrum 3
 ^1H NMR of sulfenate **4**, in CDCl_3

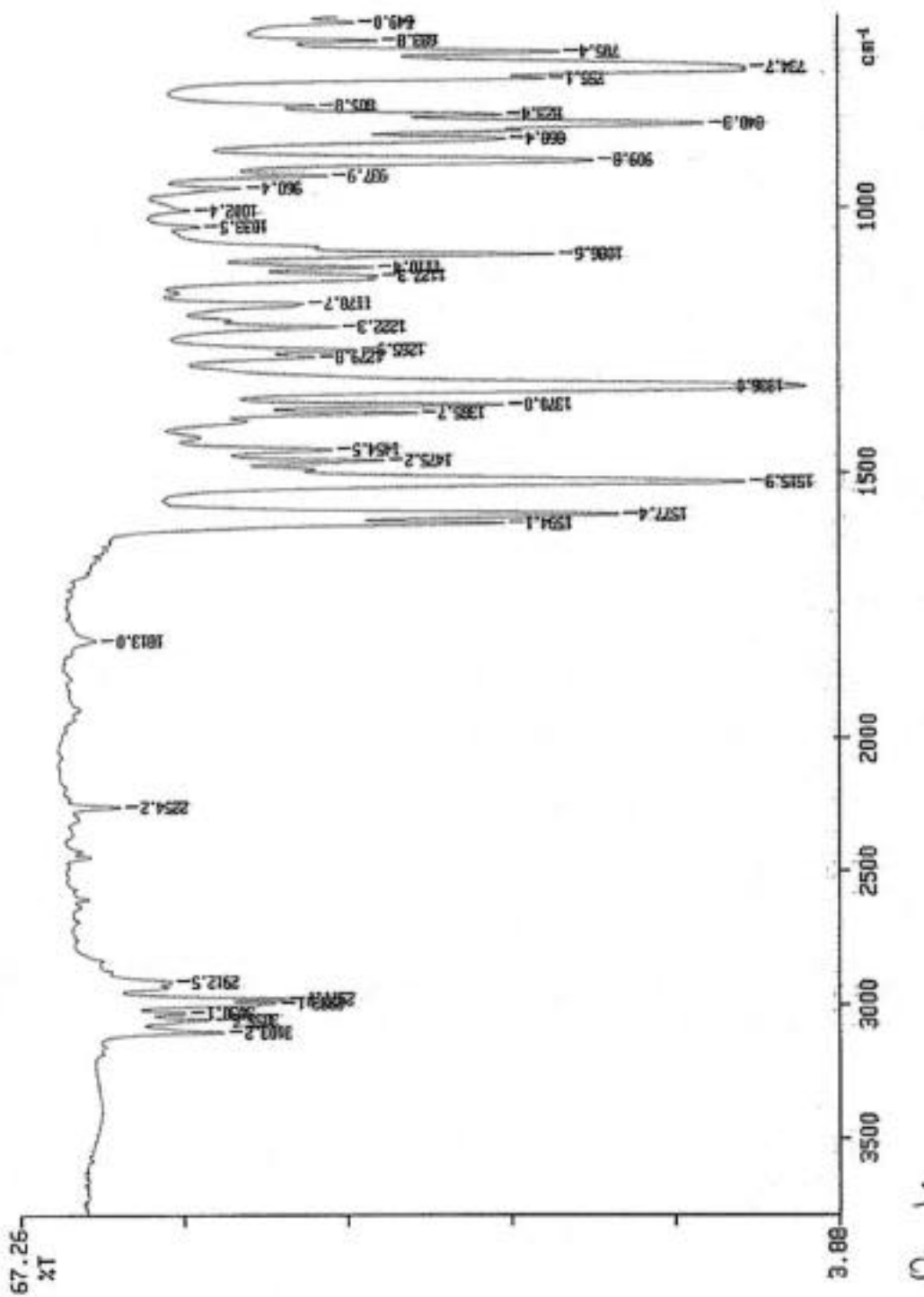


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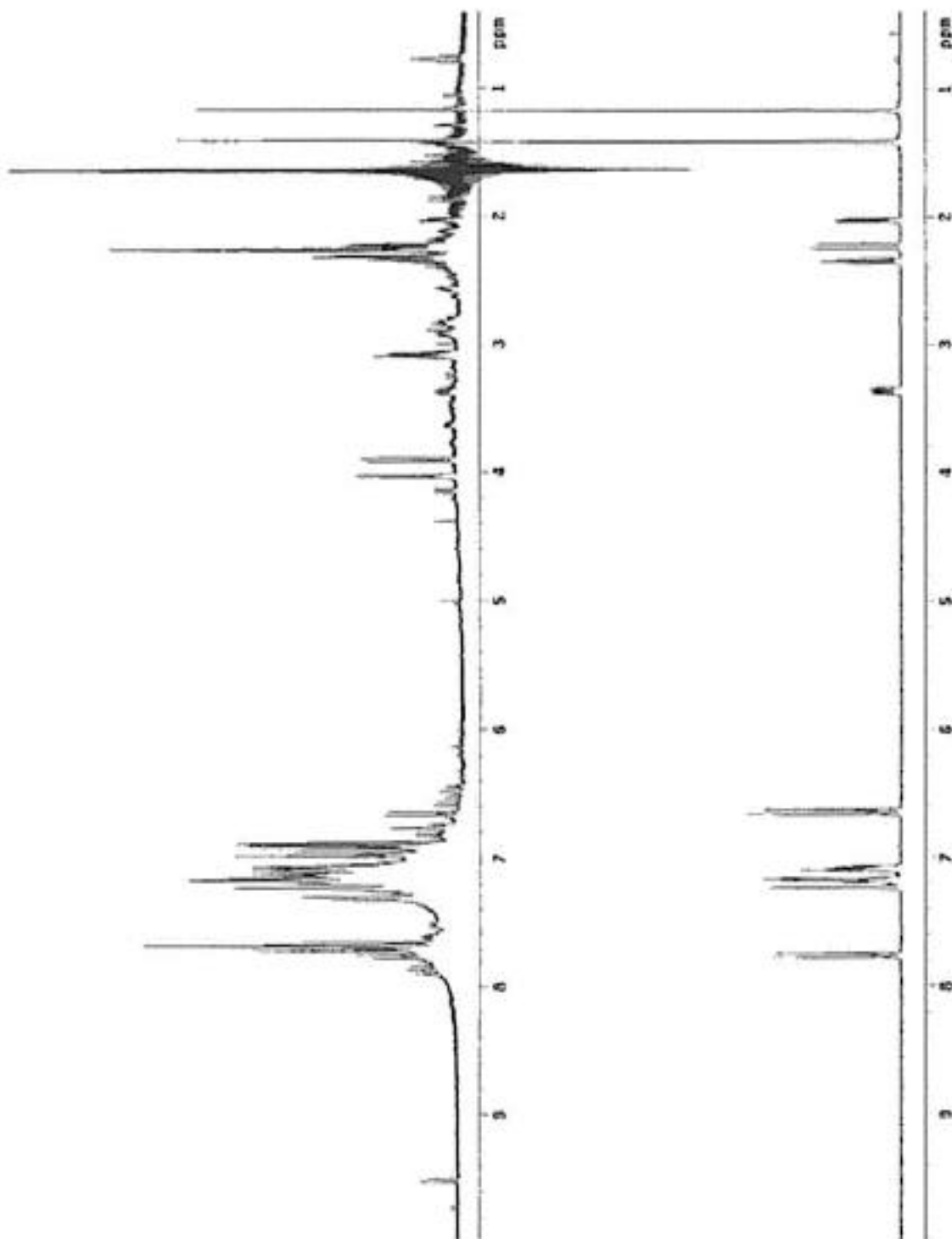
NMR Spectrum 4
 ^{13}C NMR of sulfenate **4**. In CDCl_3



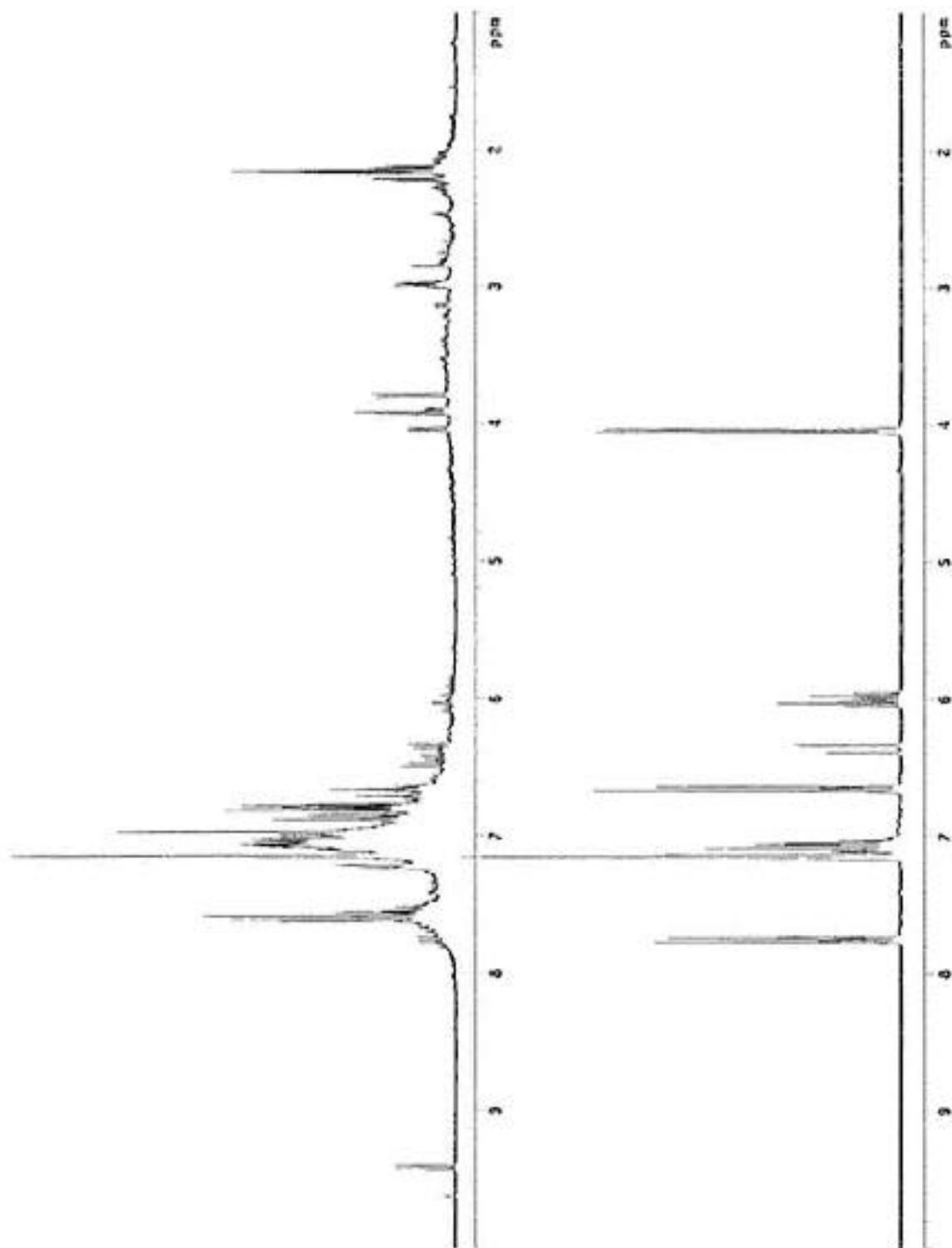
IR Spectrum 2
sulfenate 4, neat



NMR Spectrum 5
Sulfenate **4**, before and after photolysis, in deuterobenzene



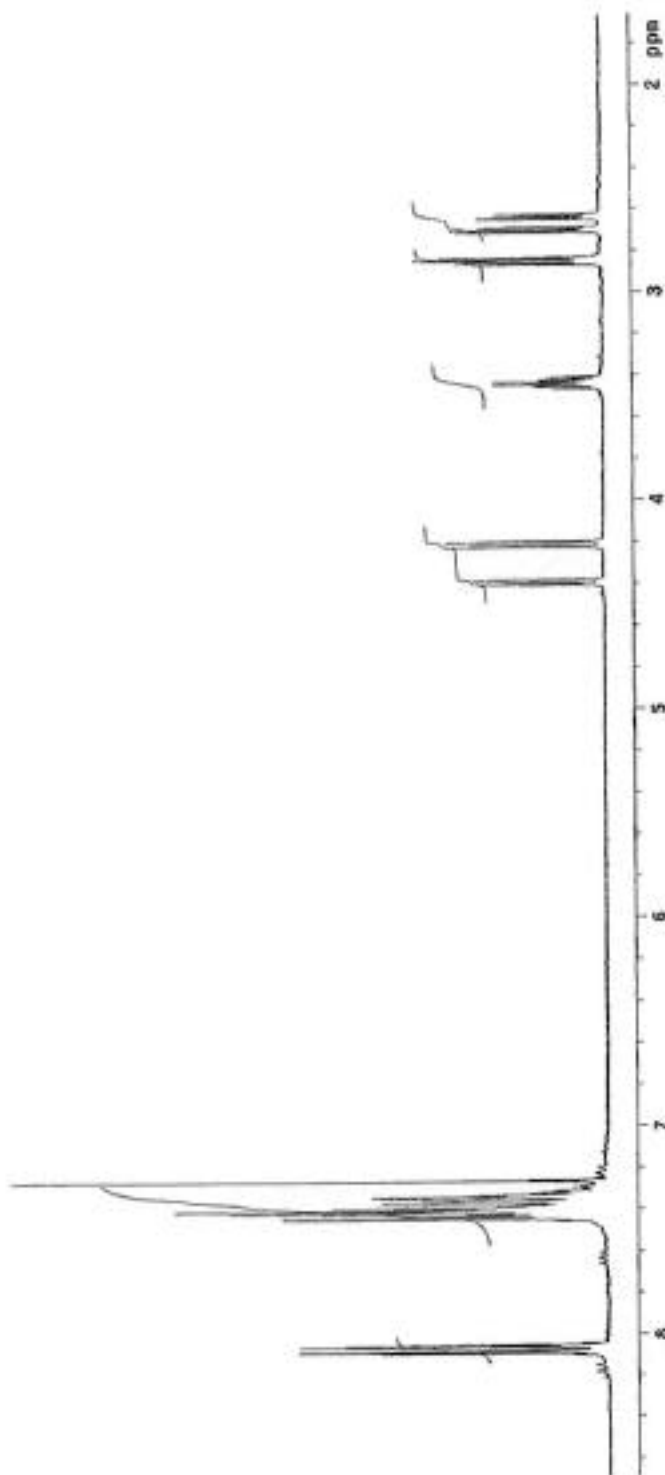
NMR Spectrum 6
cinnamyl-4-nitrobenzenesulfonate (**5**), before and after photolysis, in deuterobenzene



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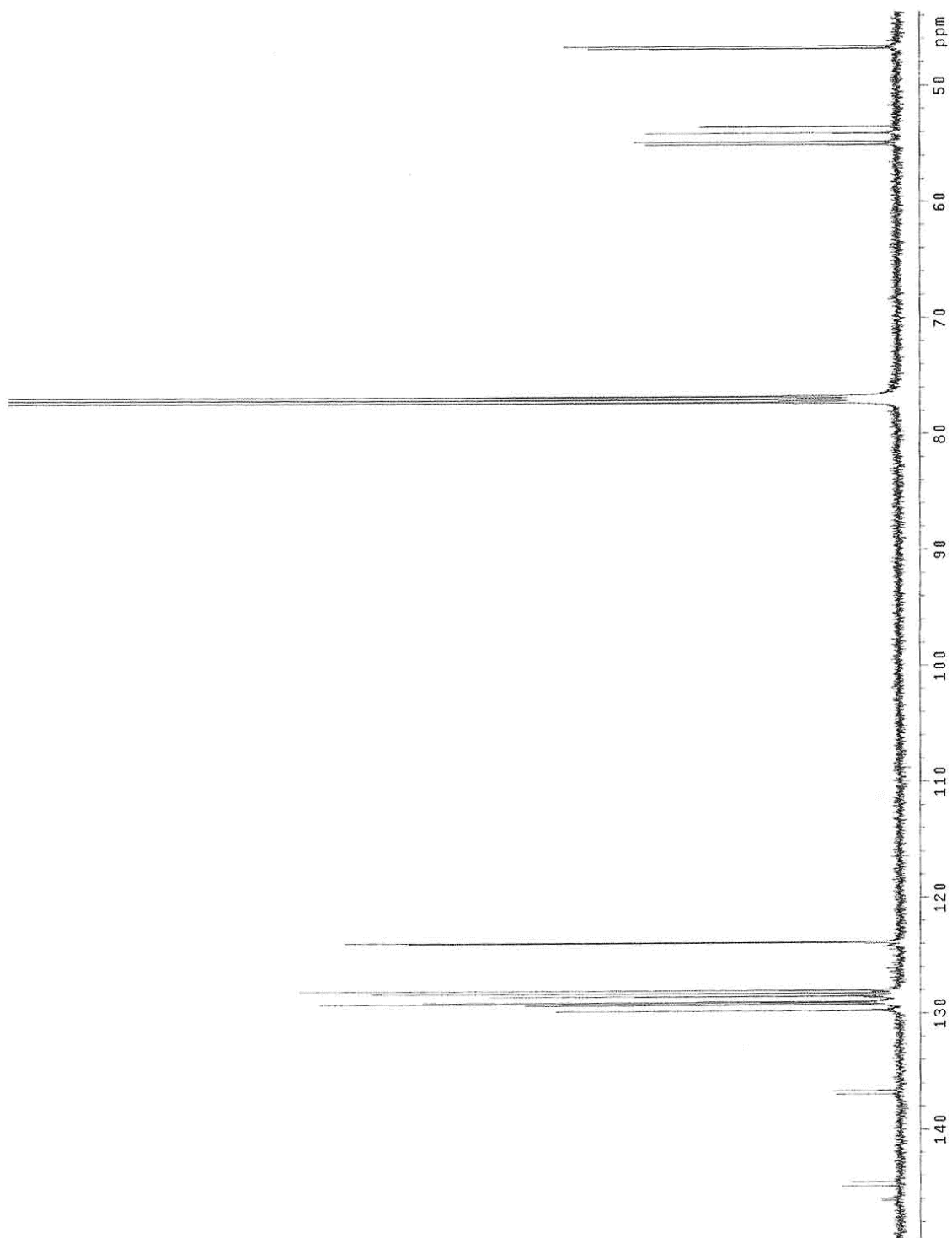
NMR Spectrum 7
epoxi-sulfide **8**, ¹H NMR spectrum in deuteriochloroform.

J2. 1H parameters for nmr03
Pulse sequence: zgpg30
Solvent: CDCl3
Ambient temperature
UNIT: gms-300 "nmr3a"
PULSE SEQUENCE
Relax. delay: 1.000 sec
Pulse: z3-6 degrees
Acq. time: 2.287 sec
Width: 3500.0 Hz
#2 repetitions
NOISE: nmr03
SOLVENT: CDCl3
PT: 1.000 sec
Total time: 7 min, 8 sec



Supporting Information for
" Epoxide formation by ring closure of the cinnamyloxy radical."
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NMR Spectrum 8
epoxi-sulfide **8**, ^{13}C NMR spectrum, in deuteriochloroform.



IR Spectrum 3
epoxi-sulfide **8**, in CCl₄.

