The Stereochemistry of the Thermal Cheletropic Decarbonylation of 3-Cyclopentenone as Determined by Multiphoton Infrared Photolysis/Thermolysis

Supporting Information

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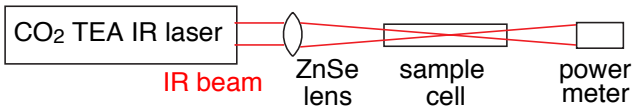
Experimental

NMR spectra were obtained either on an IBM AF-200 or AF-300 spectrometer in acetone-d_6 (^{1}H at 200 MHz, and ^{13}C at 50 MHz) using acetone-d_5 as an internal standard (2.06 ppm) unless otherwise noted. ^{1}H – ^{13}C HETCOR spectra were obtained on the AF-300 for **9c** and **12c.** Chemical shifts are reported in ppm, couplings in Hz. Infrared spectra were measured as neat films on a Perkin-Elmer 1600 Series FTIR. Analytical gas chromatography (GC) was performed on a Hewlett-Packard 5890 gas chromatograph equipped with both flame ionization and thermal conductivity. Stationary phases were either Carbowax 6000 or Carbopack 80/120. THF was distilled from Na prior to use. Preparative GC was performed using a Gow-Mac Model 550 GC, with 20% Carbowax 20M columns. Pentane and HMPA were distilled from CaH_2 prior to use. Other reagents were used as received. All reactions were run under nitrogen. Products were purified by flash chromatography on silica gel, neutral alumina or florisil with eluents as noted.

Flash vacuum pyrolysis (FVP) was carried out between 520° C and 580° C at 0.5 torr using a horizontal quartz pyrolysis tube. The reactant was subjected to four freeze-pump-thaw cycles prior to pyrolysis. The pyrolysate was trapped in a cold finger in a dry ice/ether bath at –100° C. The cold finger was warmed to room temperature and the pyrolysate was taken up in 0.5 mL pentane for GC analysis. The isomeric hexadiene products were identified by comparison to commercial samples whose structure and purity were confirmed by ^{1}H NMR.

Multi-photon Infrared (MPIR) Photolysis/Thermolysis. All of the MPIR experiments were performed using a Lumonics 840 Series infrared laser. This is a transversely excited, atmospheric pressure (TEA) carbon dioxide pulsed laser. The pulse has a 200 ns peak with a low energy tail lasting approximately 4 μs. The output is tunable to a variety of carbon dioxide rotational bands

from approximately 900 cm^{-1} to 1100 cm^{-1}, with a pulse energy of up to 50 J. The output wavelength was calibrated to the rotational spectrum of carbon dioxide. The pulse power was measured with a Scientech Model 380102 power transducer which also served as a beam stop. The laser pulse was focused through a ZnSe lens (converging, 30.5 cm focal length) at the center of an 11 cm long, 2 cm diameter gas cell with NaCl windows epoxied in place. The cell was charged with **2** using standard vacuum manifold techniques. The cell was transferred from the laser to the IR spectrometer for IR analysis. The product was recovered for GC analysis as described above for FVP.



Preparation of 3-Methyl-4-thianone

A solution of 80 mL of anhydrous THF and 56.11 mL of 2M LDA in THF (112.0 mmol) was cooled to -78˚C. A solution of 4-thianone (**8**, 10.0 g, 86.1 mmol), HMPA (20 g, 112 mmol) and 100 mL of dry THF were added dropwise over 1 hr. The solution was allowed to stir for 20 minutes at -78˚C, then methyl iodode (24.0 g, 169 mmol) in 60 mL of THF was added dropwise over 1 hr. This solution was stirred for 2 hr. at -78˚C and then allowed to warm to room temperature and quenched with 100 mL of saturated NH_4Cl. The organic layer was washed twice with 100 mL saturated NH_4Cl, once with 100 mL pH = 7.00 buffer and dried over anhydrous $MgSO_4$/celite/charcoal for 24 hr. This solution was then filtered, concentrated in vacuo and chromatographed on silica gel using 85:15 pentane:acetone yielding 6.8 g (52.2 mmol, 60.71%) of 3-methyl-4-thianone, as a clear, colorless oil.

^{1}**H NMR** δ 2.97 – 2.67 (m, 4 H), 2.73 – 2.59 (m, 3 H), 1.03 (d, J = 6.1 Hz, 3 H).

IR 2931, 1709, 1423, 1318, 1243, 1044, 978, 931, 750, 499 cm^{-1}.

Elemental analysis calc for $C_6H_{10}OS$: C55.35, H 7.74 S 24.63 Found: C 54.94, H 7.67, S 23.98

Preparation of *cis*- and *trans*-3,5-Dimethyl-4-thianone (**9c**) and (**9t**)

A solution of 80 mL of anhydrous THF and 44.9 mL of 2M LDA in THF (9.59 g, 89.6 mmol) was cooled to -78˚C and a solution of 3-methyl-4-thianone (8.0 g, 61.4 mmol), HMPA (18 g, 100.6 mmol) in 100 mL of dry THF were added dropwise over 1 hr. Addition of methyl iodide (19.2 g, 135.2 mmol) in 60 mL of THF and work up as above gave 5.75 g (39.9 mmol, 64.9%) of a mixture of **9c** and **9t**. These were separated by column chromatography.

(9c) ^{1}**H NMR** (300 MHz) δ 2.93 – 2.87 (d of m, J = 8.4, 2H), 2.84 – 2.72 (m, 2H), 2.70 – 2.62 (dd, J = 8.4, 7.5, 2H), 1.01 (d, J = 6.0 Hz, 6 H). The multiplets at 2.93 – 2.87 and 2.70 – 2.62 were shown to be diasterotopic hydrogens on the same carbon by HETCOR (see supporting information). ^{13}C (75 MHz) 211.1, 48.7, 38.8, 15.0
Elemental analysis calc for $C_7H_{12}OS$: C 58.29, H 8.39, S 22.23, Found: C 59.65, H 8.60, S 19.58

(9t) ^{1}**H NMR** 3.10 – 2.55 (m, 6H), 0.98 (d, J = 6.6 Hz, 6H).
IR (**9c** and **9t**) 2978, 2932, 1702, 1454, 1377, 1339, 12989, 1230, 1060, 984, 835, 699 cm^{-1}.

Preparation of *cis*- and *trans*-6,10-Dimethyl-1,4-dioxa-8-thiaspiro[4.5]decane (**10c**) and (**10t**)

In a flask equipped with a Dean-Stark trap were placed 1.0 g (6.9 mmol) of a mixture of *cis*- and *trans*-3,5-dimethyl-4-thianone **(9c)** and **(9t)**, 20 mg of p-TSOH, 0.95 g (17.2 mmol) anhydrous ethylene glycol and 100 mL of anhydrous benzene. After azeotropic removal of water was complete, the reaction was diluted with 100 mL of ether. The ether was filtered, and washed with 2x100 mL 5% $NaHCO_3$ and dried for 24 hr. over anhydrous $MgSO_4$/celite/charcoal. The ether was then filtered, concentrated in vacuo and chromatographed on neutral alumina with 95:5 hexane:EtOAc affording 0.8 g of **(10c)** and 0.1 g of **(10t)** (4.8 mmol, 70% overall).
(10c) ^{1}**H NMR** δ 4.02 (s, 4 H), 2.64 (t, J = 12.2, 2H), 2.34 (d, J = 12.2, 2H), 1.9 (m, 2H), 0.89 (d, J = 6.7 Hz, 6H)
IR 2964, 1465, 1366, 1223, 954, 740 cm^{-1}.
Elemental analysis calc for $C_9H_{16}O_2S$: C, 57.41; H, 8.57; O, 16.99; S, 17.03, Found: C 60.82, H 8.82, S 15.56

(10t) ^{1}**H NMR** δ 4.02 (narrow m, 4 H), 2.9 – 2.8 (m, 2H), 2.7 – 2.5 (m, 2H), 2.35 – 2.15 (m, 2H), 0.84 (d, J = 6.5, 6H).
IR 2964, 1466, 1359, 1218, 916, 723, 716 cm^{-1}.

Preparation of *cis*- and *trans*-6,10-Dimethyl-1,4-dioxa-8-thiaspiro[4.5]decane-8,8-dioxide (**11c**) and (**11d**)

A mixture of 1.0 g (5.3 mmol) of the ketal **(10c)**, 25 mL of MeOH, 15 mL H_2O and 3.0 g (14 mmol) $NaIO_4$ was stirred for 30 minutes at room temperature, then refluxed for 16 hr. The resulting mixture was cooled, filtered and the excess MeOH/H_2O removed in vacuo. The residue was taken up in 50 mL of $CHCl_3$ and filtered a second time to remove the precipitated sodium

iodate. The solids were washed with 50 mL of $CHCl_3$ and the combined $CHCl_3$ portions were dried for 24 hr over anhydrous $MgSO_4$/celite/charcoal. The solution was filtered and concentrated in vacuo affording a white solid which was recrystallized from 95% ethanol, yielding 0.8g **(11c)** (3.6 mmol, 68.9%) of white crystals, mp 158-161°C. A similar reaction of 1.0 g (5.3 mmol) **10t** gave **11t** as a white solid which was recrystallized from 100% ethanol-ether (75:25), yielding 0.4 g (1.58 mmol, 34.5%) of white crystals, mp 164-166°C.

(11c) ^{1}**H NMR** δ 4.12 (s, 4 H), 3.1 – 2.9 (m, 4 H), 2.5 – 2.3 (m, 2 H) 0.97 (d, J = 6.7, 6 H).
^{13}C δ 68.8, 68.0, 56.2, 40.6, 14.3.

IR (Diffuse Reflectance) 2964, 1427, 1322, 1144, 916, 602.3 cm^{-1}.

Elemental Analysis calc for $C_9H_{16}O_4S$: C, 49.07; H, 7.32; O, 29.05; S, 14.56, Found: C 51.06, H 7.11, S 12.40

(11t) ^{1}**H NMR** δ 4.13 (m, 4 H), 3.2 – 2.7 (m, 6 H), 0.96 (d, J = 6.6, 6 H).

IR (Diffuse Reflectance) 2952, 1418, 1316, 1138, 915, 600 cm^{-1}.

Preparation of *cis*- and *trans*-1,4-Dioxa-6,9-dimethylspiro[4.4]non-7-ene (**12c**) and (**12t**)

In a flask equipped with a powder addition funnel were placed 1.8 g (8.2 mmol) of **11c**, 149 mL of anhydrous CCl_4 and 75 mL of anhydrous t-BuOH. To this solution, at room temperature, were slowly added 19.8 g (162.4 mmol) of t-BuOK via the powder addition funnel, maintaining a temperature of 50˚C or below in the reaction vessel. The reaction mixture was then maintained at 50˚C in an oil bath for 24 hr, cooled and poured into a 500 mL beaker containing 200 mL of ice water. The aqueous layer was extracted with 3x70 mL ether. The combined ether extracts were washed with 3x70 mL H_2O, 2x70 mL saturated NaCl and 1x70 mL pH = 7.00 buffer and dried for 24 hr over anhydrous Na_2SO_4/celite/charcoal. The ether solution was filtered, concentrated and chromatographed on florisil using 98:2 pentane:ether as eluent affording 1.1 g **12c** (7.1 mmol, 87.3%) as an oil. A similar reaction using 1.8 g **11t** gave 0.83 g **12t** (5.3 mmol, 65.5%) as an oil.

(12c) ^{1}**H NMR** (200 MHz) δ 5.57 (s, 2 H), 3.90 (s, 4 H), 2.63 (q, J = 7.3 Hz, 2 H) 0.95 (d, J = 7.3 Hz, 6 H) ppm.

^{13}**C NMR** (50 MHz) 134.1, 118.8, 66.0, 64.7, 49.5, 15.6. A HETCOR spectrum (300 and 75 MHz) showed that the ^{13}C peaks at 66.0 and 64.7 ppm were associated with the ^{1}H singlet at 3.90 ppm (see supporting information).

IR 2980, 2930,1644, 1550, 1469, 1365, 1179, 928, 643, 518 cm^{-1}.

(12t) ^{1}**H NMR** δ 5.46 (m, 2 H), 3.90 (m, 4 H), 2.7 (m, 2 H) 0.96 (d, J = 7.3, 6 H).

Preparation of *cis*--2,5-Dimethyl-3-cyclopentenone (**4**)

A solution of 1.0 g (6.5 mmol) of the ketal **12c**, 50 mg of pyridinium p-toluenesulfonate, 10 mL of H_2O and 20 mL of acetone was refluxed for 6 hr, cooled and poured into a 75 mL of saturated NaCl. This solution was extracted with 3x50 mL ether which were combined and washed with 2x50 mL pH = 7.00 buffer. The ether solution was dried for 24 hr over anhydrous $MgSO_4$/celite/ charcoal, filtered, concentrated and chomatographed on florisil using 98:2 pentane:ether as the eluent. Yield 0.59 g (5.4 mmol, 82.6%) of **4** as a colorless oil. Samples for analysis and for MP-IR and pyrolysis experiments were further purified by preparative GC.
(4) ^{1}**H NMR** δ 6.00 (s, 2 H), 2.90 (q, J = 7.5 Hz, 2 H) 1.12 (d, J = 7.5 Hz, 6 H).
IR (gas phase) 2980, 2950,1724, 1587, 1462, 1454, 1376, 1247, 1146, 1005, 895, 711, 700 cm^{-1}.

Searches of the Cambridge Structural Database.
The substructure **13** was searched against the Cambridge Structural Database. The only constraints were that C2 and C4 were required to have four bonds and the C2-C3 bond could be either double or aromatic. The structures obtained were then grouped as described in the text, into **13**, **14**, **15**, and **16**. The CSD refcodes and the corresponding distances, angles and dihedral angles are recorded in Table S1, along with the averages for each item. Individual references for these structures can be located through the CSD. The average angles are presented below.

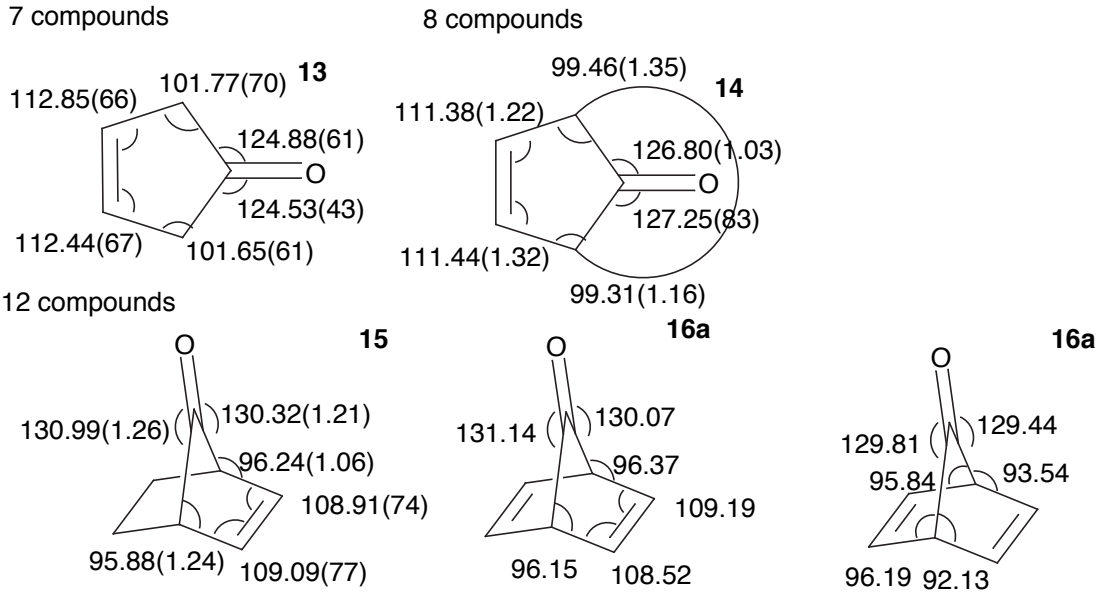


TABLE S1

Refcode	ANGLES					
	O-C1-C2	***C1-C2-C3***	***C2-C3-C4***	***C3-C4-C5***	***C4-C5-C1***	***C5-C1-O***
13						
BEMKUZ	124.37	100.50	113.97	113.80	100.40	124.33
CEHBOG	125.11	101.37	112.41	112.31	102.36	125.85
DONKIA	124.76	102.11	112.03	112.84	101.74	124.32
DONKIA	123.94	101.50	112.44	112.17	102.46	125.41
DONKIA10	124.74	102.06	112.06	112.85	101.71	124.31
DONKIA10	123.93	101.50	112.44	112.17	102.45	125.40
RUWRAC	124.84	102.53	111.71	113.81	101.24	124.51
averages	124.53	101.65	112.44	112.85	101.77	124.88
standard deviation	0.43	0.61	0.67	0.66	0.70	0.61
combined average	124.70	101.71	112.64			
14						
ACNPTH	126.53	98.27	112.32	112.39	98.41	126.13
ACNPTH10	126.53	98.27	112.32	112.39	98.41	126.13
BUDECN	129.10	97.23	113.56	108.57	99.82	126.69
EBEQOR	126.89	100.12	109.34	112.59	97.07	128.89
HAJMEK	127.38	100.54	110.20	111.75	100.95	126.33
HAJMEK	127.48	100.07	110.96	111.16	100.45	126.14
MEWYUI	126.43	100.52	112.37	111.39	101.27	125.94
NKAUON	127.68	99.49	110.48	110.81	99.32	128.15
averages	127.25	99.31	111.44	111.38	99.46	126.80
standard deviation	0.83	1.16	1.32	1.22	1.35	1.03
combined average	127.03	99.39	111.41			
15						
BIYWAH	128.89	93.62	110.33	110.16	94.02	128.83
CIQVAZ	131.14	96.11	108.55	108.68	96.26	131.67
DITMOI	131.54	97.33	108.31	109.07	96.78	129.22
ETHPTB	129.58	96.04	108.56	108.78	96.45	130.81
HOXJIN	130.10	94.60	110.73	109.93	95.09	129.63
JITMEE	130.99	97.71	108.56	108.71	97.73	132.13
JITNIJ	131.38	97.41	108.78	108.51	97.63	131.39
KAFBEY	129.84	95.68	108.45	109.81	96.90	131.00
KUBDAM	132.49	96.93	109.00	108.67	96.92	130.27
PIGSED	130.34	95.06	108.68	108.96	94.95	129.96
TIBGUG	132.15	94.55	109.87	107.33	96.36	131.04
ZEBXOT	133.44	95.49	109.24	108.31	95.83	127.85
averages	130.99	95.88	109.09	108.91	96.24	130.32
standard deviation	1.26	1.24	0.76	0.74	1.06	1.21
combined average	130.65	96.06	109.00			
16						
ZADQOK	130.07	96.37	109.19	108.52	96.15	131.14
		95.35	107.94	108.83	95.08	
ECUMUK	129.44	93.54	108.04	107.65	92.13	129.81
		95.84	113.39	108.53	96.19	

TABLE S1

Refcode	ANGLES					
	O-C1-C2	***C1-C2-C3***	***C2-C3-C4***	***C3-C4-C5***	***C4-C5-C1***	***C5-C1-O***
17						
CIQSIE	132.62	99.34	103.88	104.48	98.73	129.13
		99.99	104.09	104.31	98.71	
FUVTEV	129.66	98.04	103.76	103.08	98.31	131.52
		98.72	103.28	103.94	98.65	
JUKSAJ	129.73	103.84	103.38	103.89	103.42	130.08
		96.53	103.85	103.54	96.51	
JUKSAJ	130.04	103.77	103.38	104.03	103.00	129.95
		96.95	103.74	103.73	96.78	
XAYGOT	129.82	103.12	103.82	103.81	103.59	130.45
		96.41	104.25	103.79	96.64	
averages	130.37	99.67	103.74	103.86	99.43	130.22
standard deviation	1.13	2.79	0.30	0.37	2.69	0.78
combined average	130.30	99.55	103.80			
18						
BEVSOK	131.30	99.07	107.87	108.27	98.89	131.60
BIVBUD20	132.73	100.48	107.44	108.51	99.43	132.63
BIVBUD20	133.95	99.70	107.05	107.63	98.34	129.61
DEPYEC	131.16	97.52	108.34	108.13	97.85	131.81
DEPYOM	132.08	99.24	107.78	107.78	99.24	132.08
DEYTOQ	133.05	100.58	108.01	107.96	100.06	130.29
IBONUI	132.08	98.05	107.54	107.91	98.14	131.86
IBOPAQ	130.11	97.19	108.08	107.83	96.82	133.26
NILLUP	132.96	99.08	107.68	108.43	99.46	130.88
PEWROY	132.80	100.30	107.79	108.21	100.50	129.59
averages	132.22	99.12	107.76	108.07	98.87	131.36
standard deviation	1.06	1.15	0.34	0.28	1.04	1.18
combined average	131.79	99.00	107.91			

TABLE S1

Refcode	DISTANCES					
	C1-O	***C1-C2***	***C2-C3***	***C3-C4***	***C4-C5***	***C1-C5***
13						
BEMKUZ	1.202	1.537	1.501	1.320	1.506	1.537
CEHBOG	1.208	1.532	1.505	1.333	1.502	1.512
DONKIA	1.215	1.509	1.524	1.330	1.518	1.515
DONKIA	1.217	1.519	1.526	1.333	1.514	1.505
DONKIA10	1.214	1.508	1.523	1.329	1.517	1.515
DONKIA10	1.216	1.518	1.524	1.332	1.513	1.504
RUWRAC	1.212	1.534	1.499	1.367	1.499	1.539
averages	1.212	1.522	1.515	1.335	1.510	1.518
standard deviation	0.005	0.011	0.011	0.014	0.007	0.013
combined average		1.520	1.512			
14						
ACNPTH	1.191	1.548	1.503	1.347	1.497	1.543
ACNPTH10	1.191	1.548	1.503	1.347	1.497	1.543
BUDECN	1.200	1.540	1.517	1.323	1.524	1.521
EBEQOR	1.207	1.513	1.515	1.333	1.527	1.546
HAJMEK	1.202	1.515	1.523	1.341	1.503	1.516
HAJMEK	1.201	1.513	1.528	1.337	1.519	1.526
MEWYUI	1.214	1.529	1.522	1.335	1.509	1.525
NKAUON	1.201	1.523	1.522	1.330	1.514	1.520
averages	1.201	1.529	1.517	1.337	1.511	1.530
standard deviation	0.007	0.014	0.009	0.008	0.011	0.011
combined average		1.529	1.514			
15						
BIYWAH	1.203	1.535	1.512	1.324	1.511	1.531
CIQVAZ	1.200	1.521	1.499	1.326	1.490	1.520
DITMOI	1.198	1.532	1.545	1.355	1.527	1.542
ETHPTB	1.200	1.531	1.529	1.344	1.534	1.512
HOXJIN	1.199	1.548	1.527	1.321	1.517	1.551
JITMEE	1.204	1.515	1.500	1.318	1.494	1.527
JITNIJ	1.197	1.526	1.500	1.325	1.503	1.521
KAFBEY	1.199	1.532	1.537	1.338	1.483	1.526
KUBDAM	1.205	1.567	1.502	1.352	1.514	1.532
PIGSED	1.200	1.528	1.537	1.350	1.527	1.534
TIBGUG	1.203	1.544	1.525	1.336	1.514	1.542
ZEBXOT	1.196	1.539	1.540	1.351	1.526	1.544
averages	1.200	1.535	1.521	1.337	1.512	1.532
standard deviation	0.003	0.013	0.017	0.013	0.016	0.011
combined average		1.533	1.516			
16						
ZADQOK	1.191	1.562	1.536	1.368	1.541	1.551
			1.536	1.393	1.541	
ECUMUK	1.197	1.540	1.559	1.432	1.570	1.567
			1.511	1.338	1.583	

TABLE S1

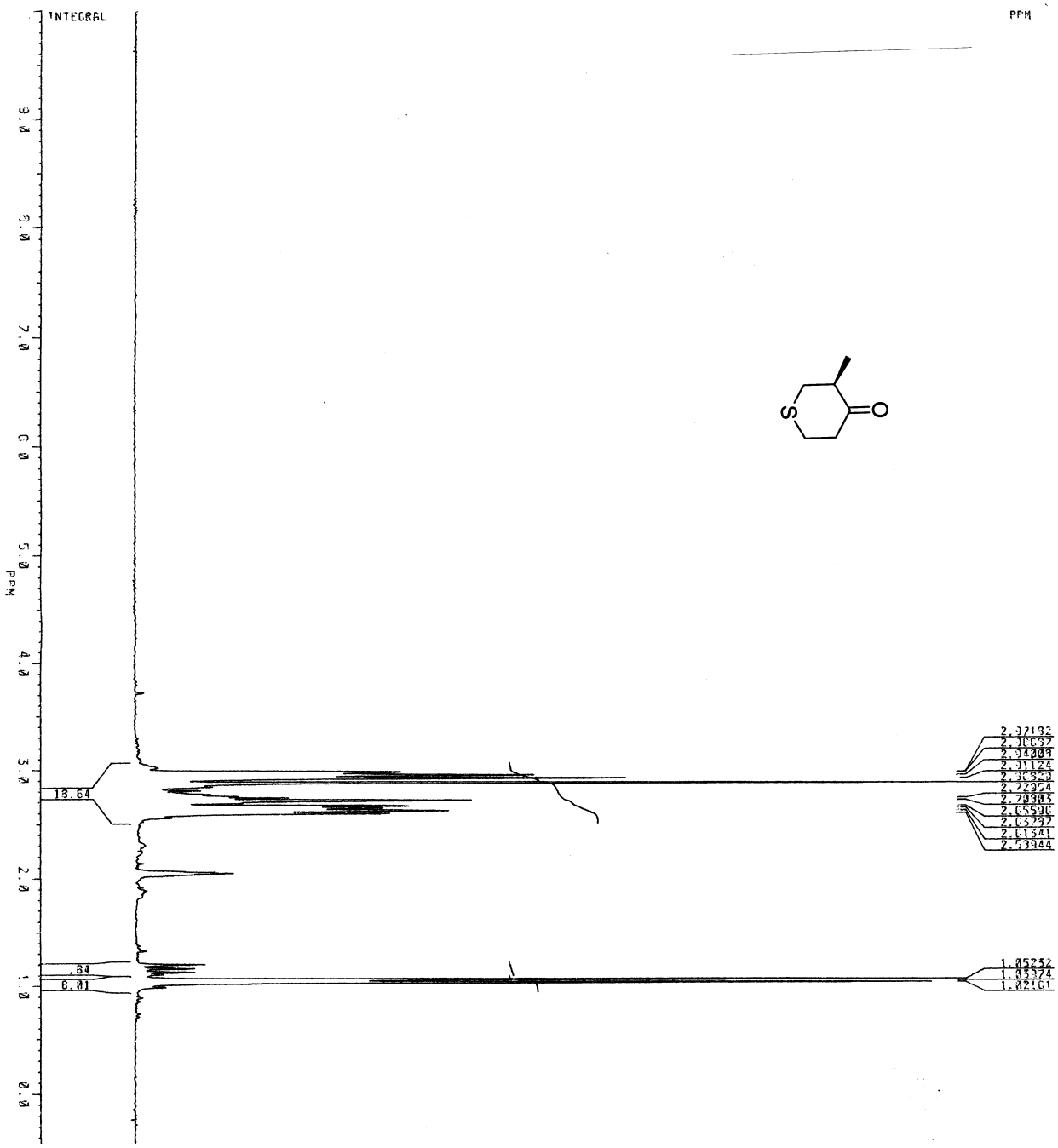
Refcode	DISTANCES					
	C1-O	***C1-C2***	***C2-C3***	***C3-C4***	***C4-C5***	***C1-C5***
17						
CIQSIE	1.193	1.506	1.527	1.550	1.532	1.535
			1.521	1.552	1.527	
FUVTEV	1.217	1.514	1.537	1.571	1.549	1.498
			1.537	1.562	1.542	
JUKSAJ	1.214	1.522	1.533	1.586	1.531	1.524
			1.550	1.575	1.550	
JUKSAJ	1.214	1.524	1.530	1.590	1.537	1.529
			1.547	1.581	1.551	
XAYGOT	1.210	1.526	1.532	1.577	1.538	1.525
			1.548	1.562	1.544	
averages	1.210	1.518	1.536	1.571	1.540	1.522
standard deviation	0.009	0.007	0.009	0.013	0.008	0.013
combined average		1.520	1.538			
18						
BEVSOK	1.312	1.517	1.530	1.322	1.526	1.515
BIVBUD20	1.315	1.532	1.520	1.342	1.513	1.566
BIVBUD20	1.339	1.501	1.544	1.339	1.542	1.533
DEPYEC	1.328	1.521	1.517	1.331	1.518	1.524
DEPYOM	1.306	1.526	1.510	1.341	1.510	1.526
DEYTOQ	1.323	1.522	1.509	1.334	1.517	1.523
IBONUI	1.316	1.515	1.526	1.320	1.519	1.520
IBOPAQ	1.320	1.514	1.521	1.315	1.526	1.523
NILLUP	1.329	1.517	1.510	1.319	1.509	1.515
PEWROY	1.321	1.520	1.514	1.320	1.515	1.511
averages	1.321	1.519	1.520	1.328	1.520	1.526
standard deviation	0.009	0.008	0.010	0.010	0.009	0.015
combined average		1.522	1.520			

TABLE S1 TORSIONS

Refcode	***C1-C2-C5-C4***	**absolute value**	***C1-C5-C2-C4***	**absolute value**	***O-C2-C5-C4***	**absolute value**	***O-C5-C2-C4***	**absolute value**
13								
BEMKUZ	178.35	178.35	-179.02	179.02	-179.20	179.20	178.53	178.53
CEHBOG	163.13	163.13	-165.04	165.04	-164.91	164.91	163.00	163.00
DONKIA	-173.93	173.93	173.58	173.58	173.40	173.40	-173.76	173.76
DONKIA	-171.19	171.19	170.75	170.75	170.67	170.67	-171.10	171.10
DONKIA10	-173.93	173.93	173.58	173.58	173.40	173.40	-173.76	173.76
DONKIA10	-171.18	171.18	170.75	170.75	170.66	170.66	-171.10	171.10
RUWRAC	179.24	179.24	-177.93	177.93	-177.83	177.83	179.14	179.14
averages	-24.22	172.99	23.81	172.95	23.74	172.87	-24.15	172.91
standard deviation		4.98		4.39		4.45		5.02
combined average		172.97				172.89		
14								
ACNPTH	-145.66	145.66	145.09	145.09	143.51	143.51	-144.08	144.08
ACNPTH10	-145.66	145.66	145.09	145.09	143.51	143.51	-144.08	144.08
BUDECN	-138.99	138.99	138.83	138.83	139.03	139.03	-139.19	139.19
EBEQOR	-139.52	139.52	139.07	139.07	139.36	139.36	138.92	138.92
HAJMEK	-147.01	147.01	148.27	148.27	147.51	147.51	-146.26	146.26
HAJMEK	145.84	145.84	-147.07	147.07	-146.48	146.48	145.26	145.26
MEWYUI	152.77	152.77	154.26	154.26	152.37	152.37	-153.87	153.87
NKAUON	-140.70	140.70	139.69	139.69	139.58	139.58	-140.59	140.59
averages	-69.87	144.52	107.90	144.67	107.30	143.92	-72.99	144.03
standard deviation		4.31		5.02		4.40		4.54
combined average		144.59				143.98		
15								
BIYWAH	123.96	123.96	-124.36	124.36	-119.64	119.64	119.25	119.25
CIQVAZ	123.73	123.73	-123.40	123.40	-121.99	121.99	122.32	122.32
DITMOI	-127.36	127.36	126.03	126.03	127.39	127.39	-128.73	128.73
ETHPTB	-124.97	124.97	125.63	125.63	125.77	125.77	-125.11	125.11
HOXJIN	125.96	125.96	-125.48	125.48	-124.57	124.57	125.04	125.04
JITMEE	126.34	126.34	-126.49	126.49	-127.47	127.47	127.31	127.31
JITNIJ	-126.14	126.14	126.40	126.40	-126.81	126.81	127.07	127.07
KAFBEY	-126.22	126.22	125.53	125.53	126.10	126.10	-126.79	126.79
KUBDAM	-125.88	125.88	125.05	125.05	124.77	124.77	-125.59	125.59
PIGSED	123.38	123.38	-122.84	122.84	-121.49	121.49	122.03	122.03
TIBGUG	121.79	121.79	-122.09	122.09	-120.40	120.40	120.10	120.10
ZEBXOT	-124.34	124.34	123.20	123.20	122.14	122.14	-123.29	123.29
averages	-0.81	125.00	0.60	124.71	-19.68	124.05	19.47	124.39
standard deviation		1.52		1.43		2.67		2.87
combined average		124.86				124.22		
16								
ZADQOK	-125.68	125.68	124.63	124.63	125.08	125.08	-126.12	126.12
	122.16	122.16	-122.49	122.49	-122.04	122.04	121.71	121.71
ECUMUK	128.24	128.24	127.37	127.37	129.44	129.44	128.57	128.57
	-117.36	117.36	-118.77	118.77	116.16	116.16	117.57	117.57

TABLE S1 TORSIONS

Refcode	***C1-C2-C5-C4***	**absolute value**	***C1-C5-C2-C4***	**absolute value**	***O-C2-C5-C4***	**absolute value**	***O-C5-C2-C4***	**absolute value**
17								
CIQSIE	-123.12	123.12	122.22	122.22	-123.10	123.10	122.20	122.20
	122.90	122.90	-123.65	123.65	122.92	122.92	-123.67	123.67
FUVTEV	-120.26	120.26	120.14	120.14	-119.75	119.75	119.63	119.63
	121.60	121.60	-121.23	121.23	122.11	122.11	-121.73	121.73
JUKSAJ	130.64	130.64	-131.00	131.00	136.35	136.35	-136.71	136.71
	-117.40	117.40	117.70	117.70	-111.69	111.69	111.99	111.99
JUKSAJ	130.52	130.52	-130.55	130.55	135.66	135.66	-135.68	135.68
	-118.32	118.32	118.23	118.23	-113.18	113.18	113.10	113.10
XAYGOT	131.25	131.25	-129.83	129.83	136.30	136.30	-134.89	134.89
	-117.81	117.81	118.13	118.13	-112.76	112.76	113.07	113.07
averages	4.00	123.38	-3.98	123.27	7.29	123.38	-7.27	123.27
standard deviation		5.21		5.04		9.24		9.06
combined average		123.32				123.32		
18								
BEVSOK	127.86	127.86	-128.22	128.22	129.59	129.59	-129.94	129.94
BIVBUD20	128.30	128.30	-128.34	128.34	128.31	128.31	-128.35	128.35
BIVBUD20	126.06	126.06	-126.90	126.90	128.08	128.08	-128.93	128.93
DEPYEC	-126.18	126.18	125.49	125.49	-125.85	125.85	125.16	125.16
DEPYOM	127.31	127.31	-127.31	127.31	126.21	126.21	-126.21	126.21
DEYTOQ	-129.91	129.91	130.32	130.32	-132.78	132.78	133.19	133.19
IBONUI	124.96	124.96	-124.80	124.80	121.63	121.63	-121.46	121.46
IBOPAQ	123.29	123.29	-123.51	123.51	119.33	119.33	-119.55	119.55
NILLUP	-128.79	128.79	127.43	127.43	-128.19	128.19	126.83	126.83
PEWROY	-130.57	130.57	130.04	130.04	-135.88	135.88	135.35	135.35
averages	24.23	127.32	-24.58	127.24	23.05	127.58	-23.39	127.50
standard deviation		2.13		2.07		4.58		4.58
combined average		127.28				127.54		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S
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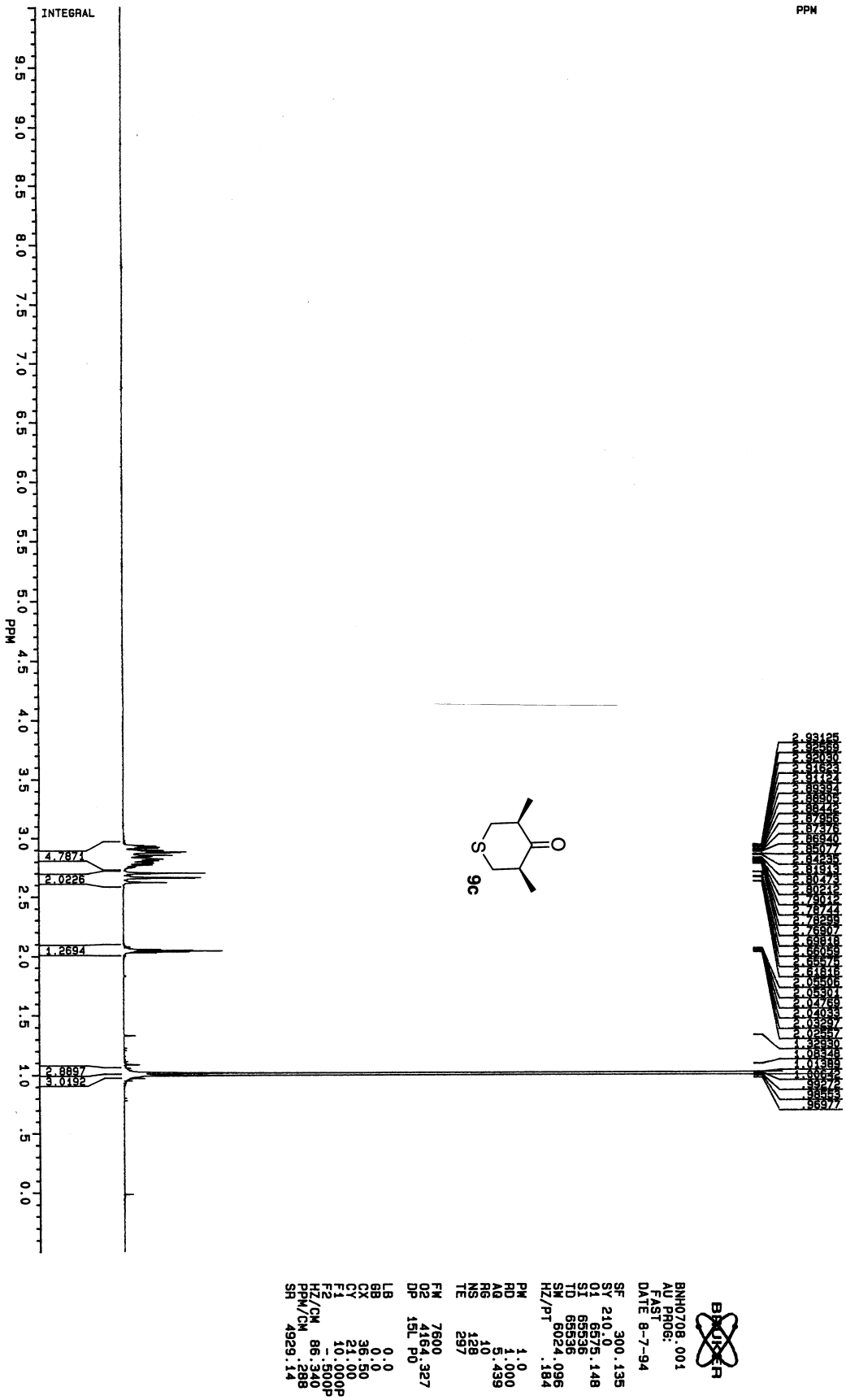
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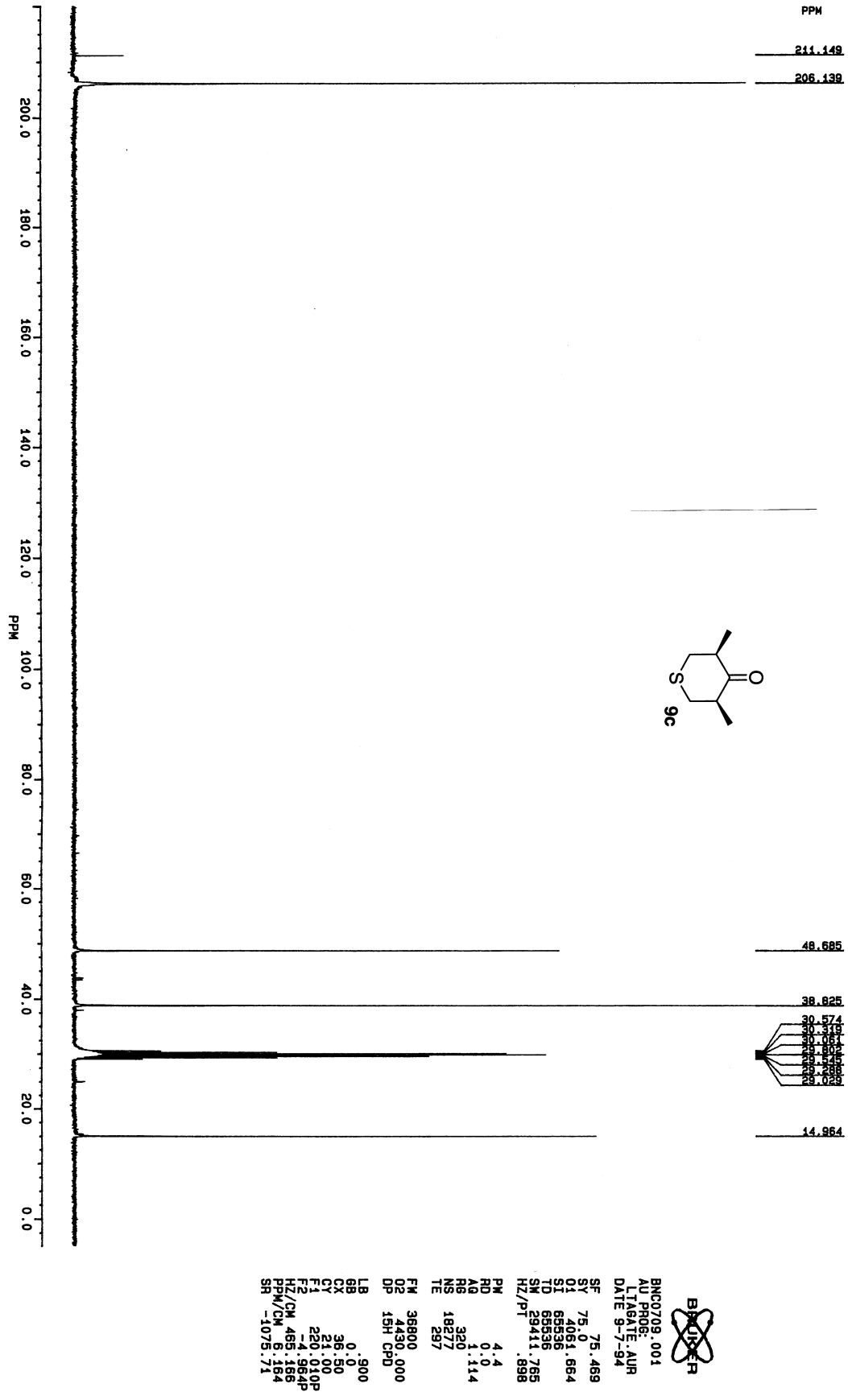
BRUKER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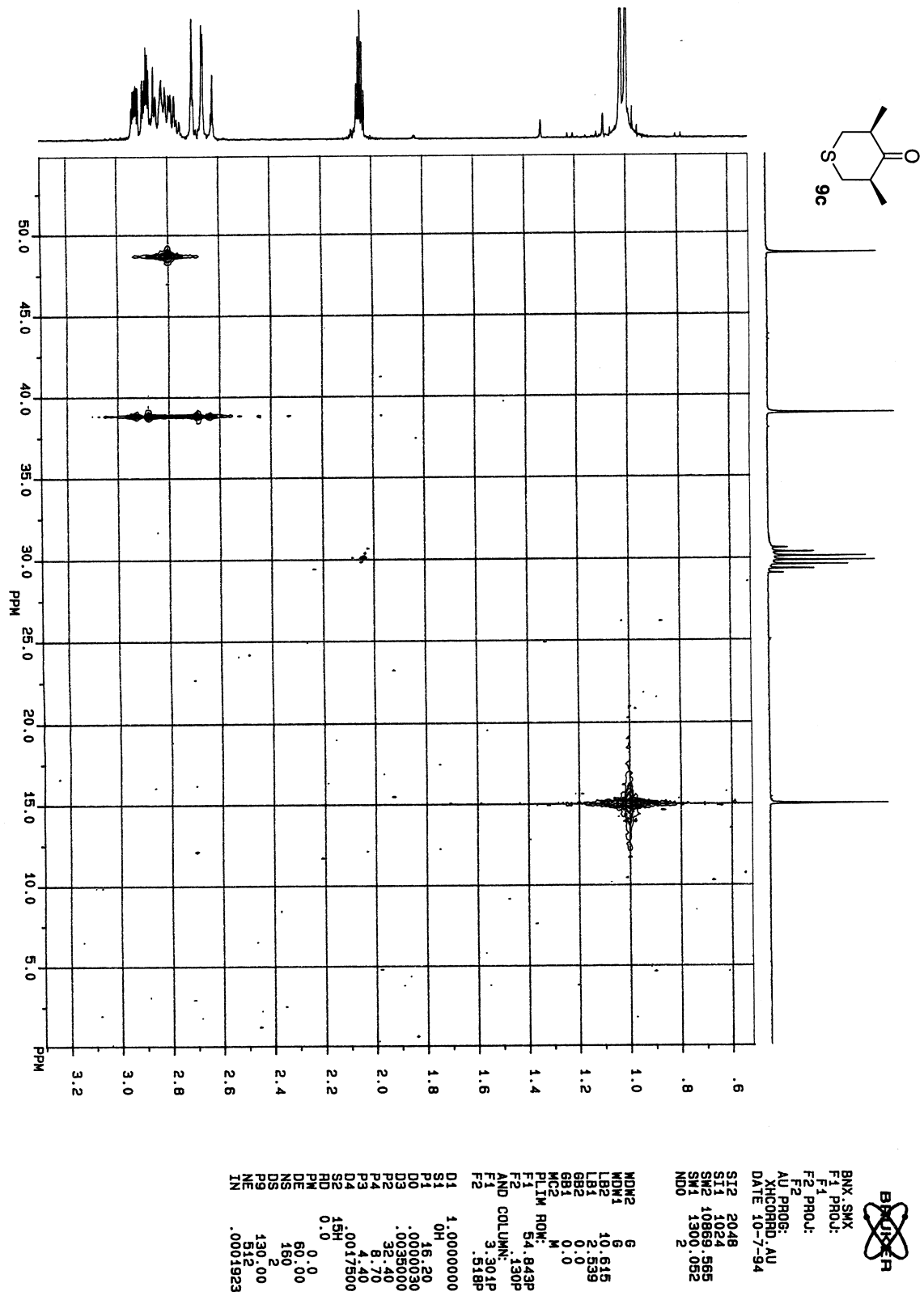
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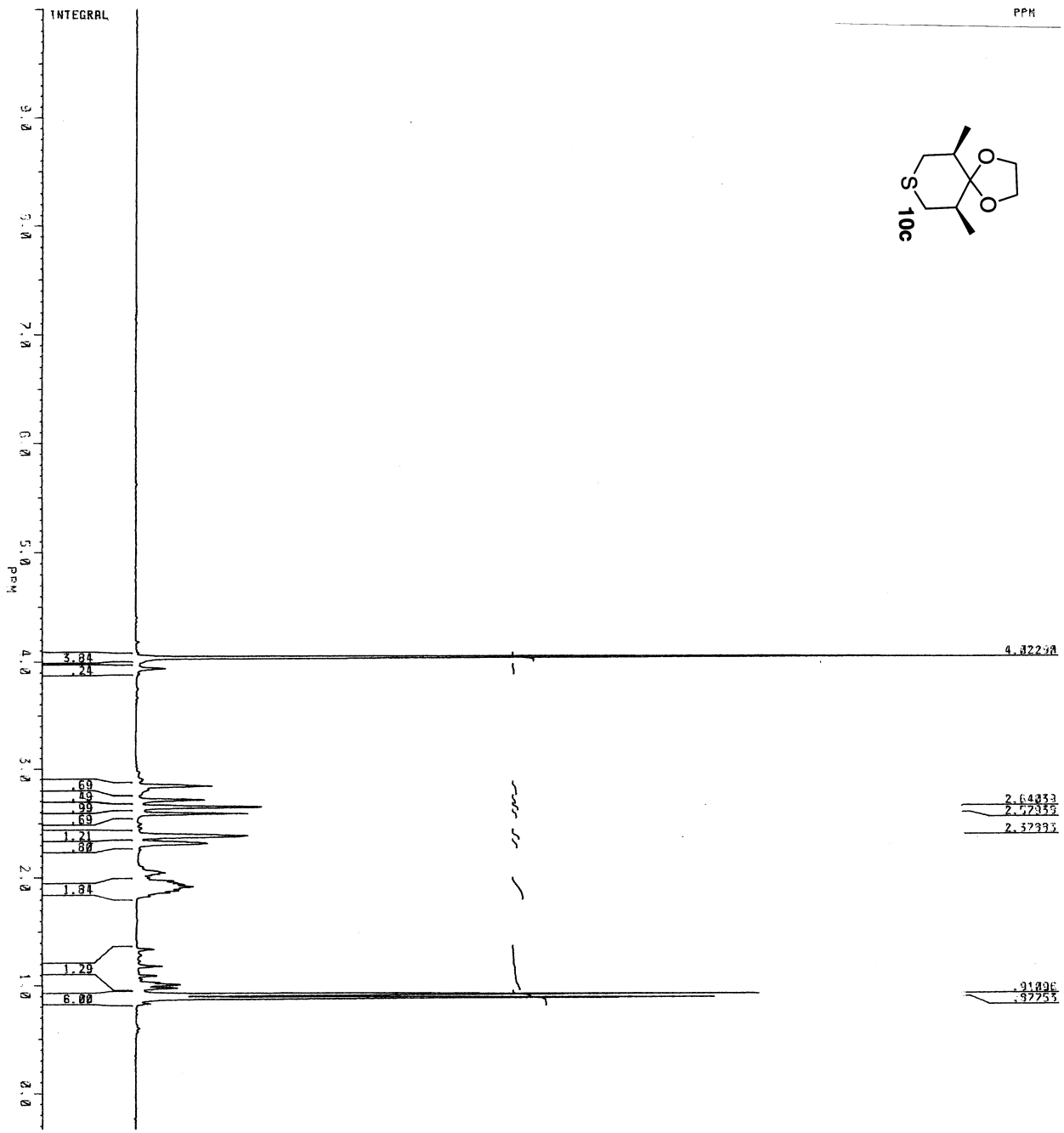
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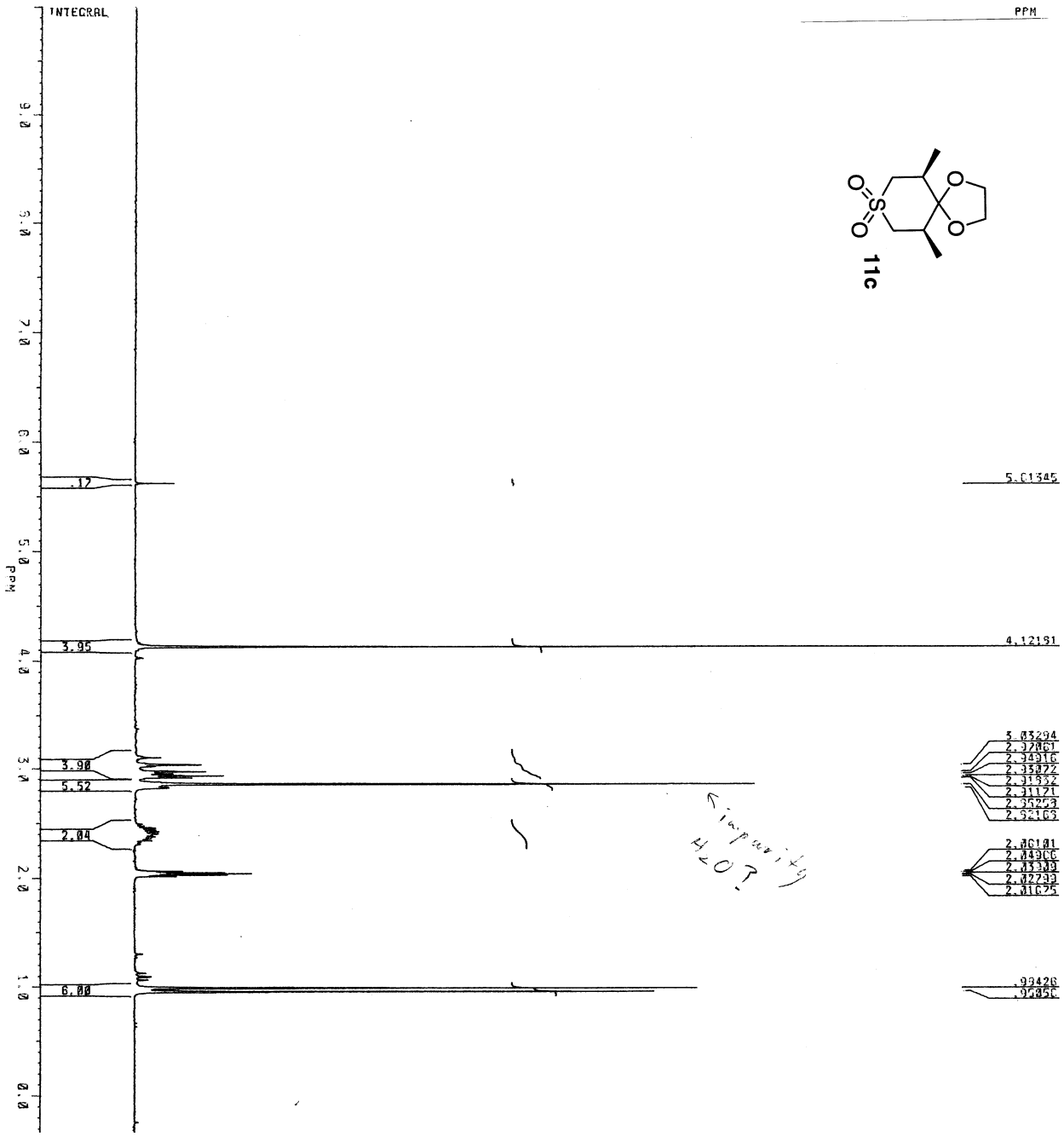
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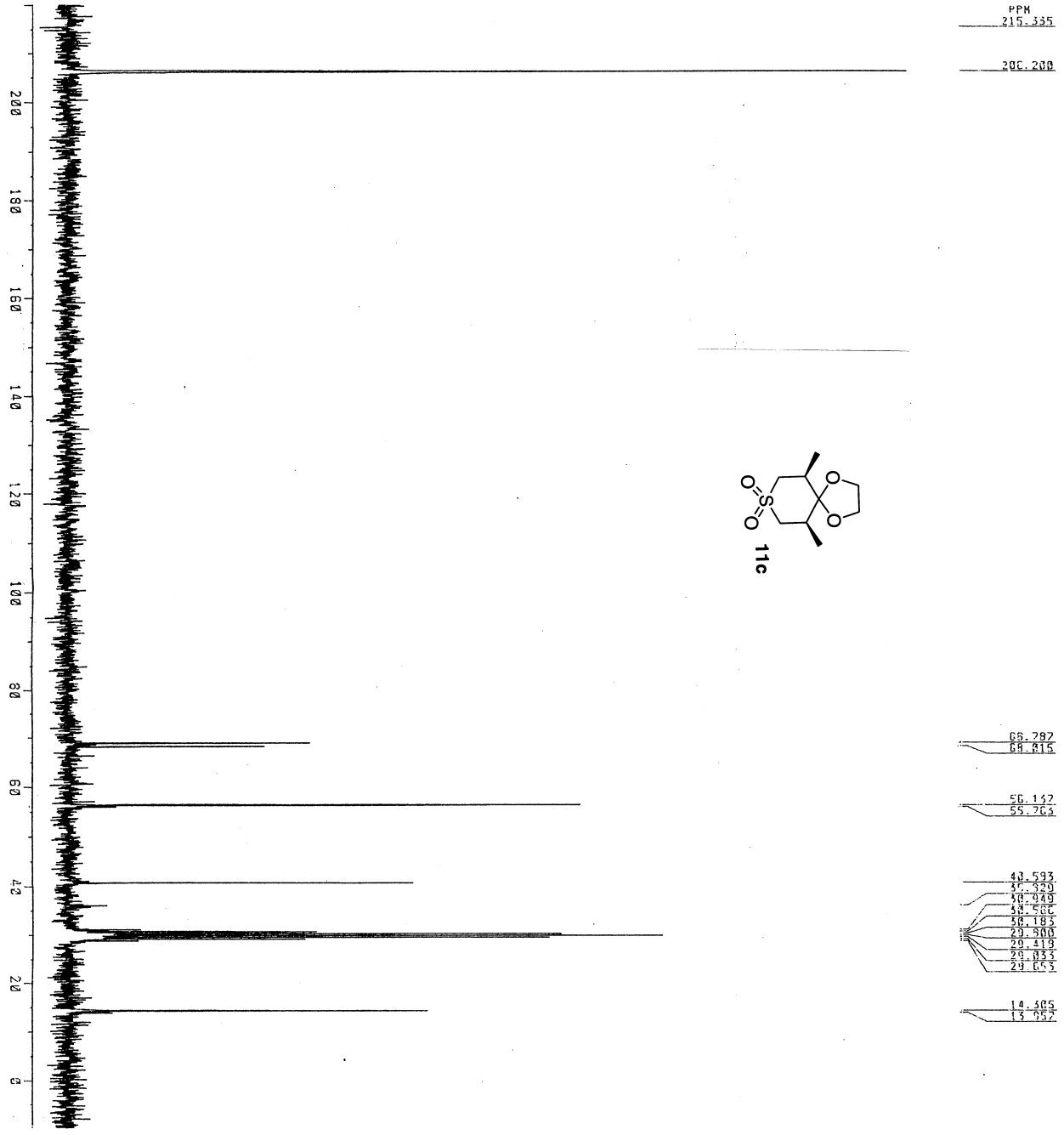
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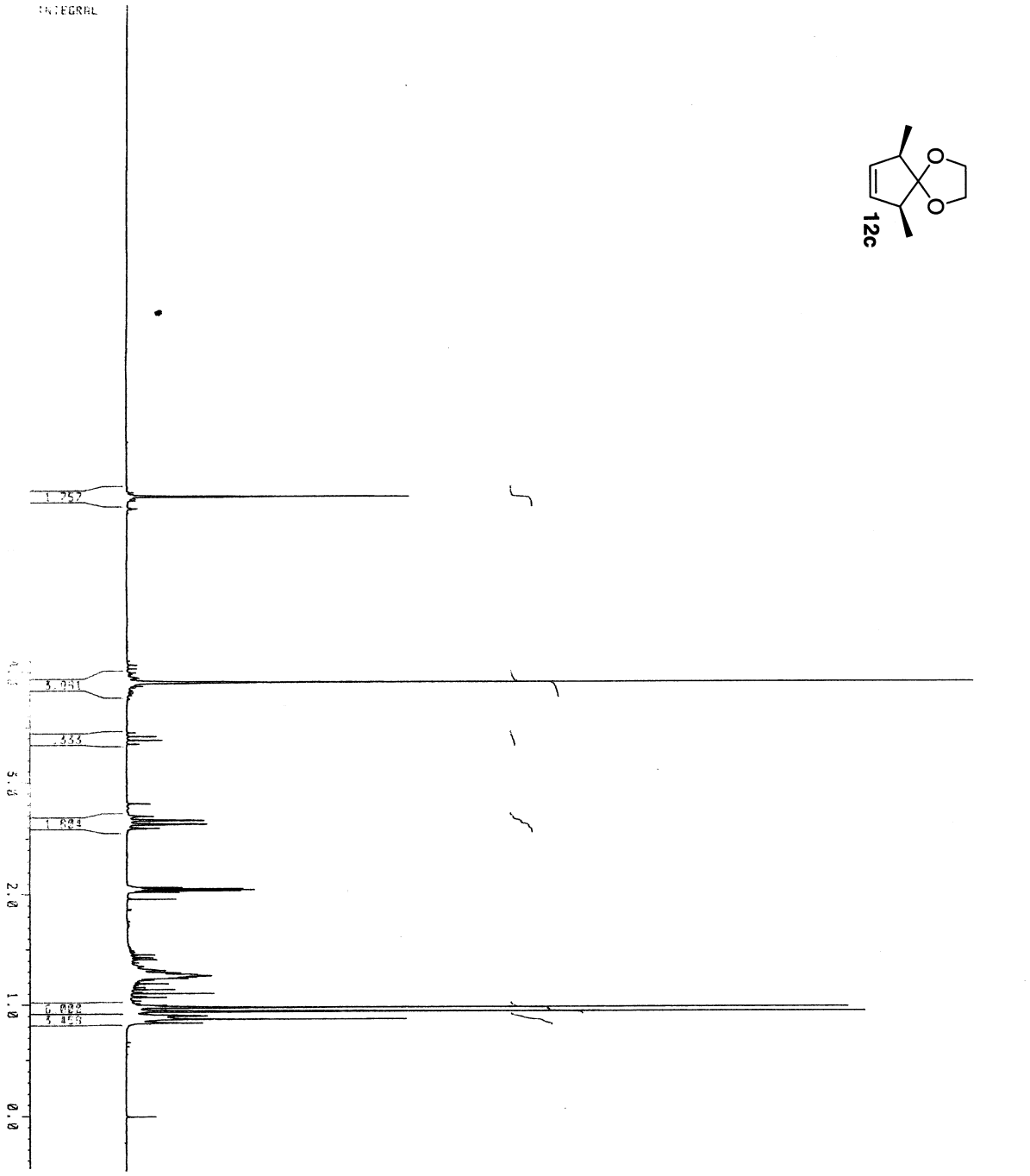
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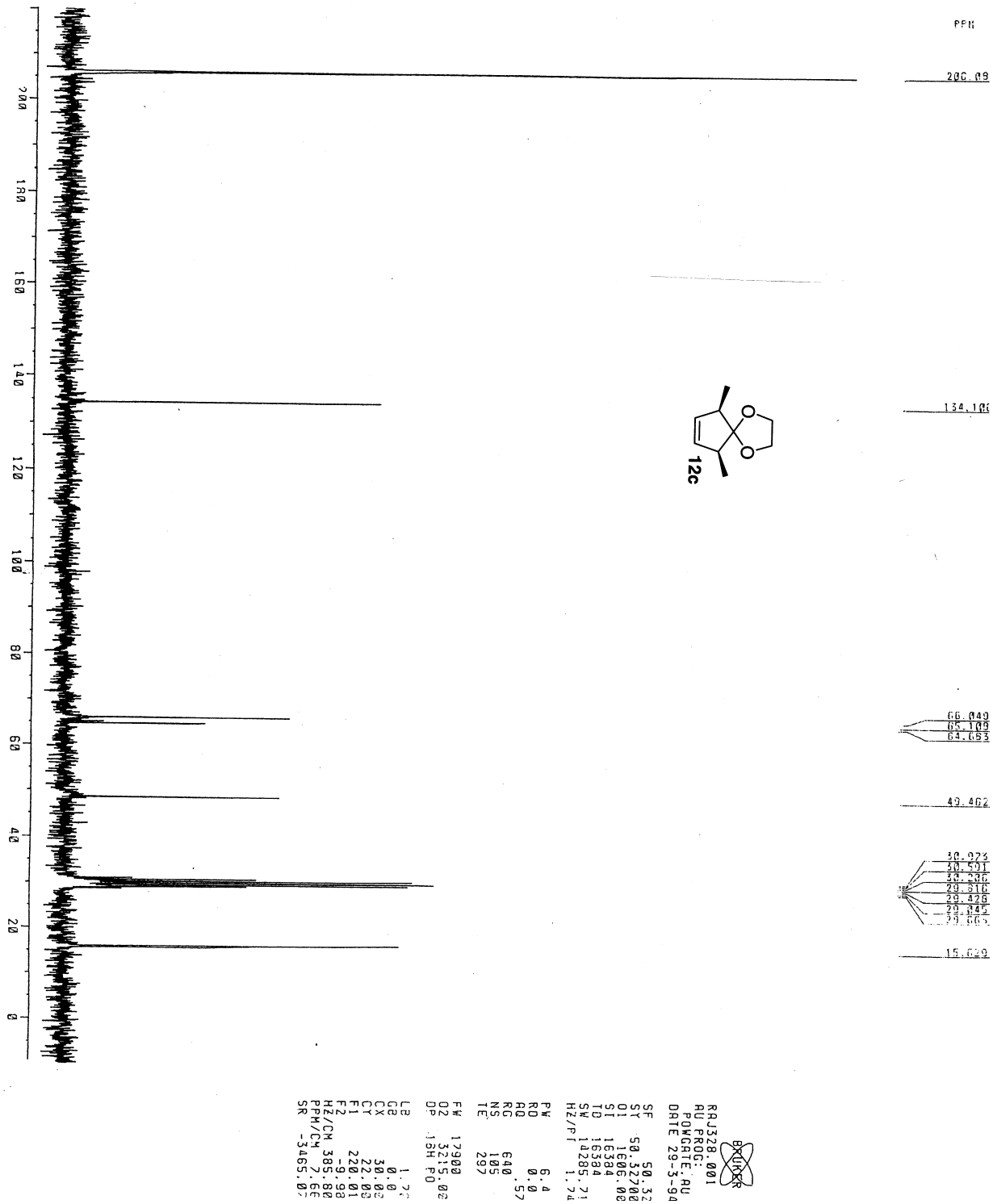
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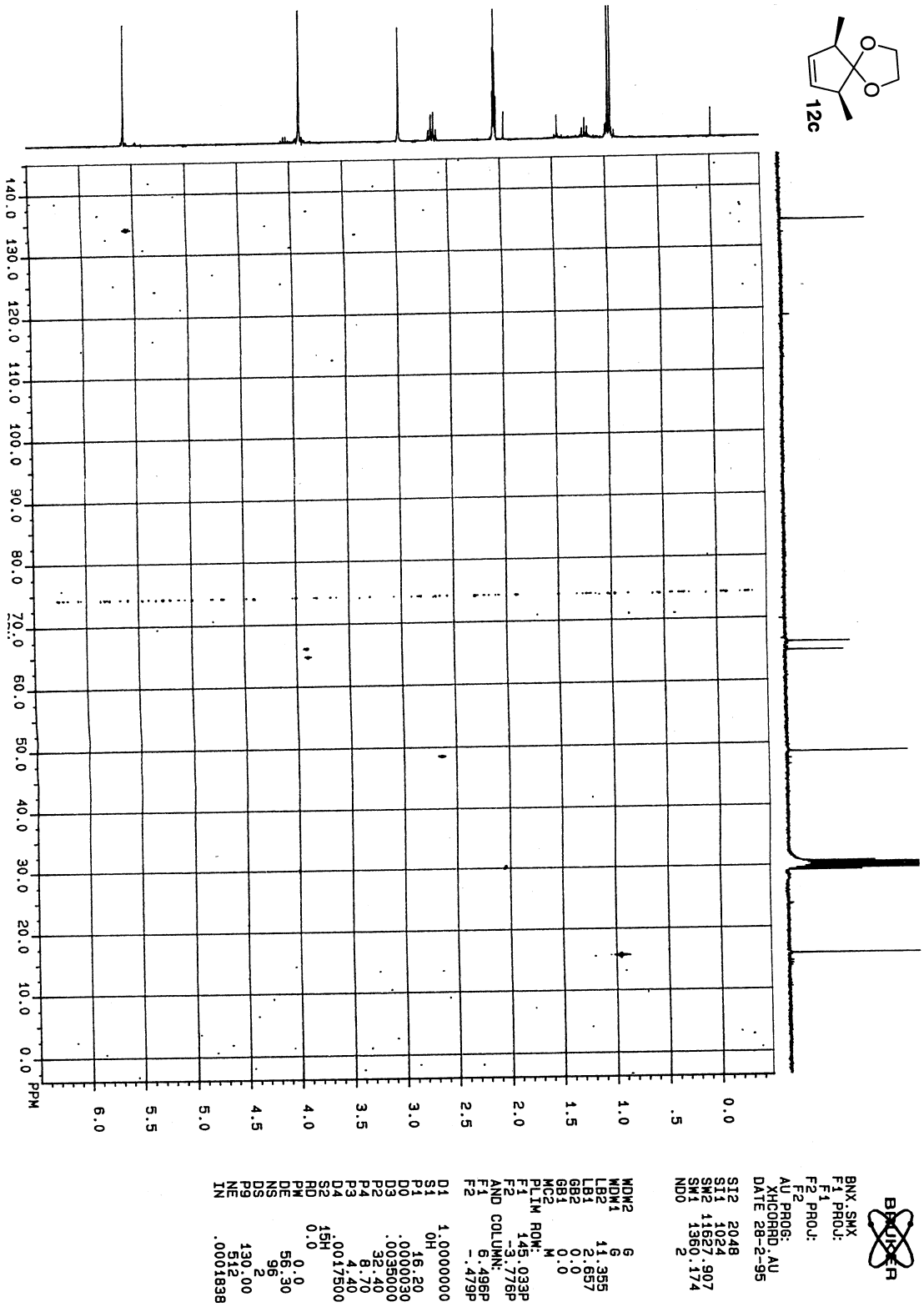
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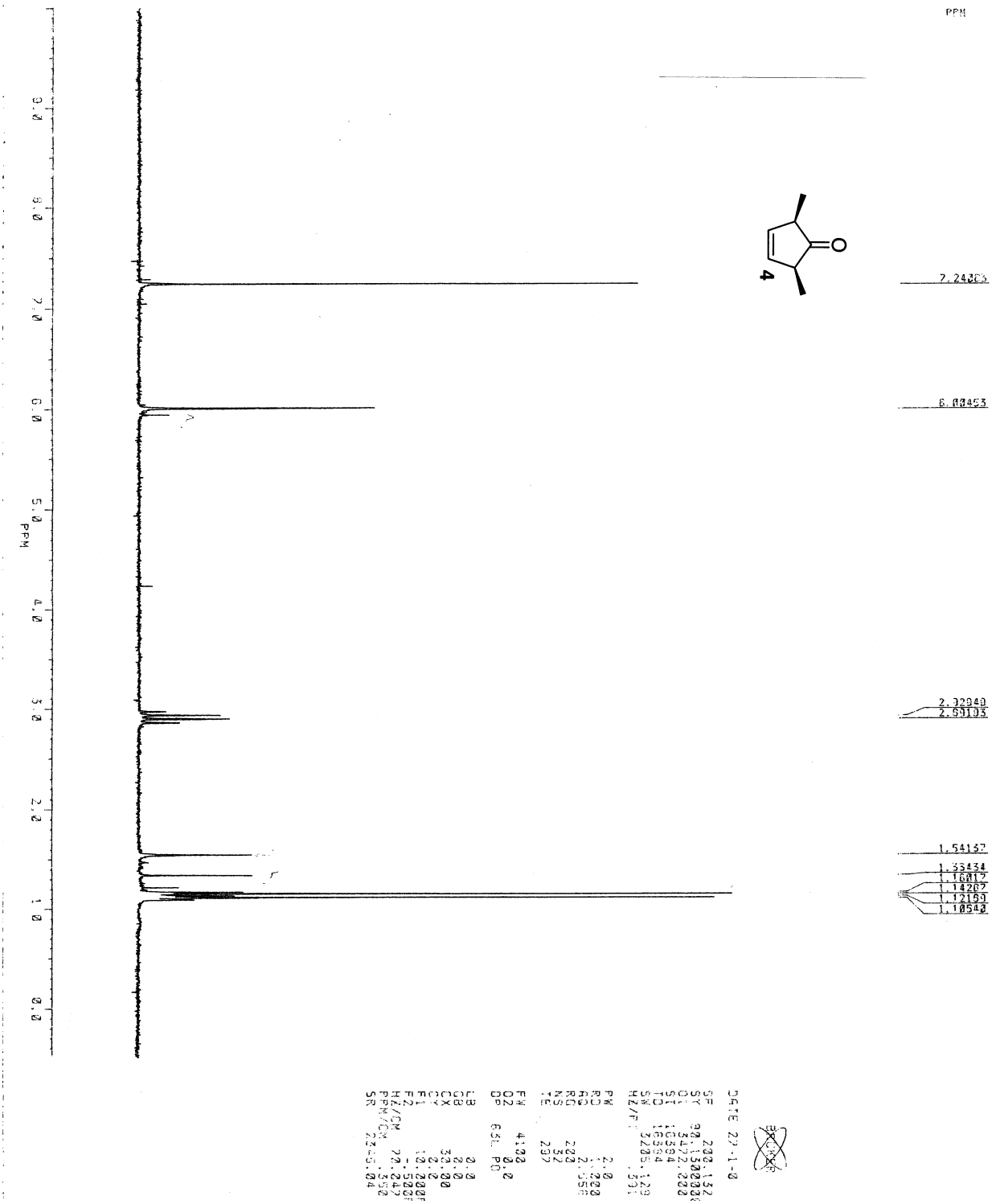
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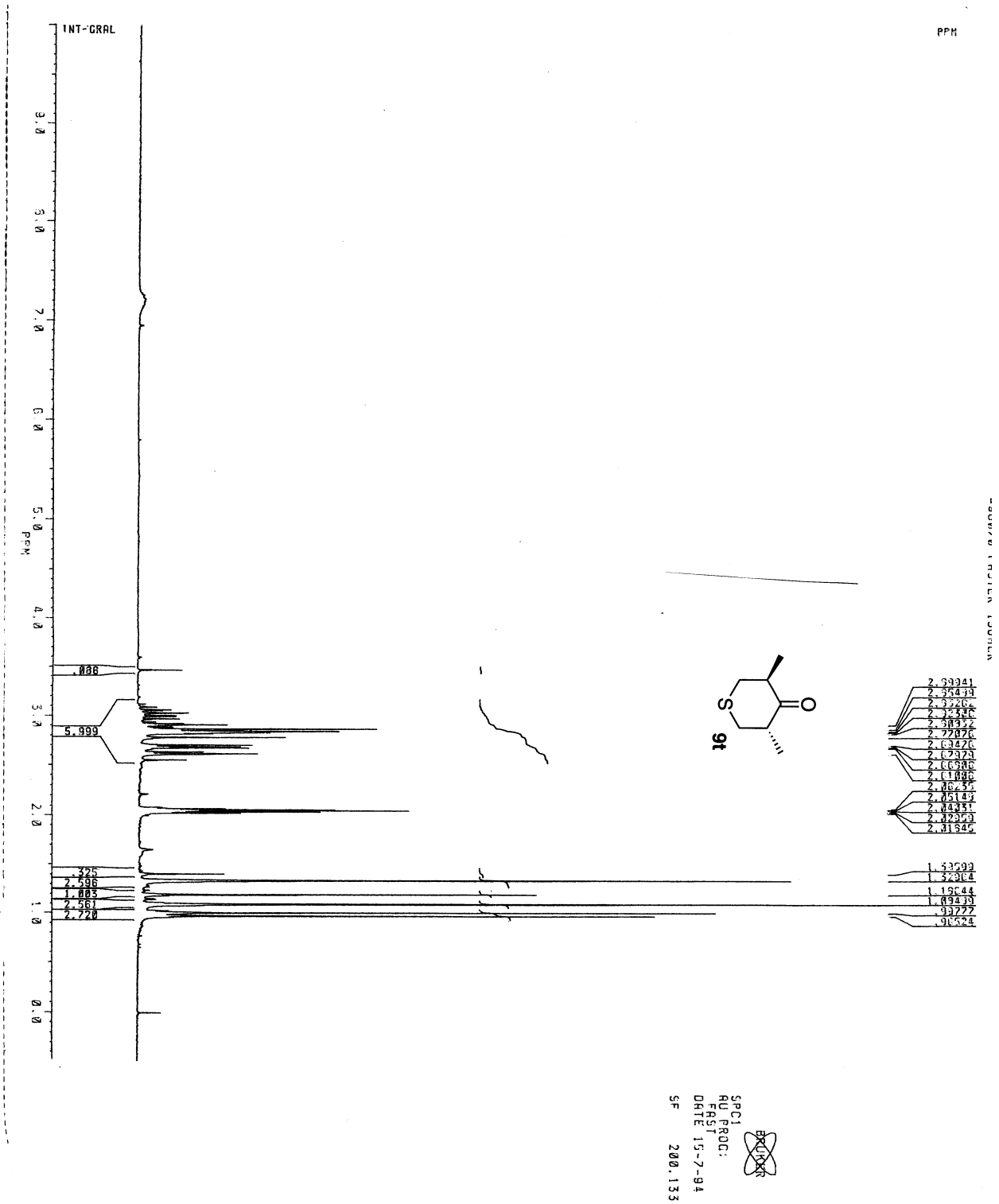
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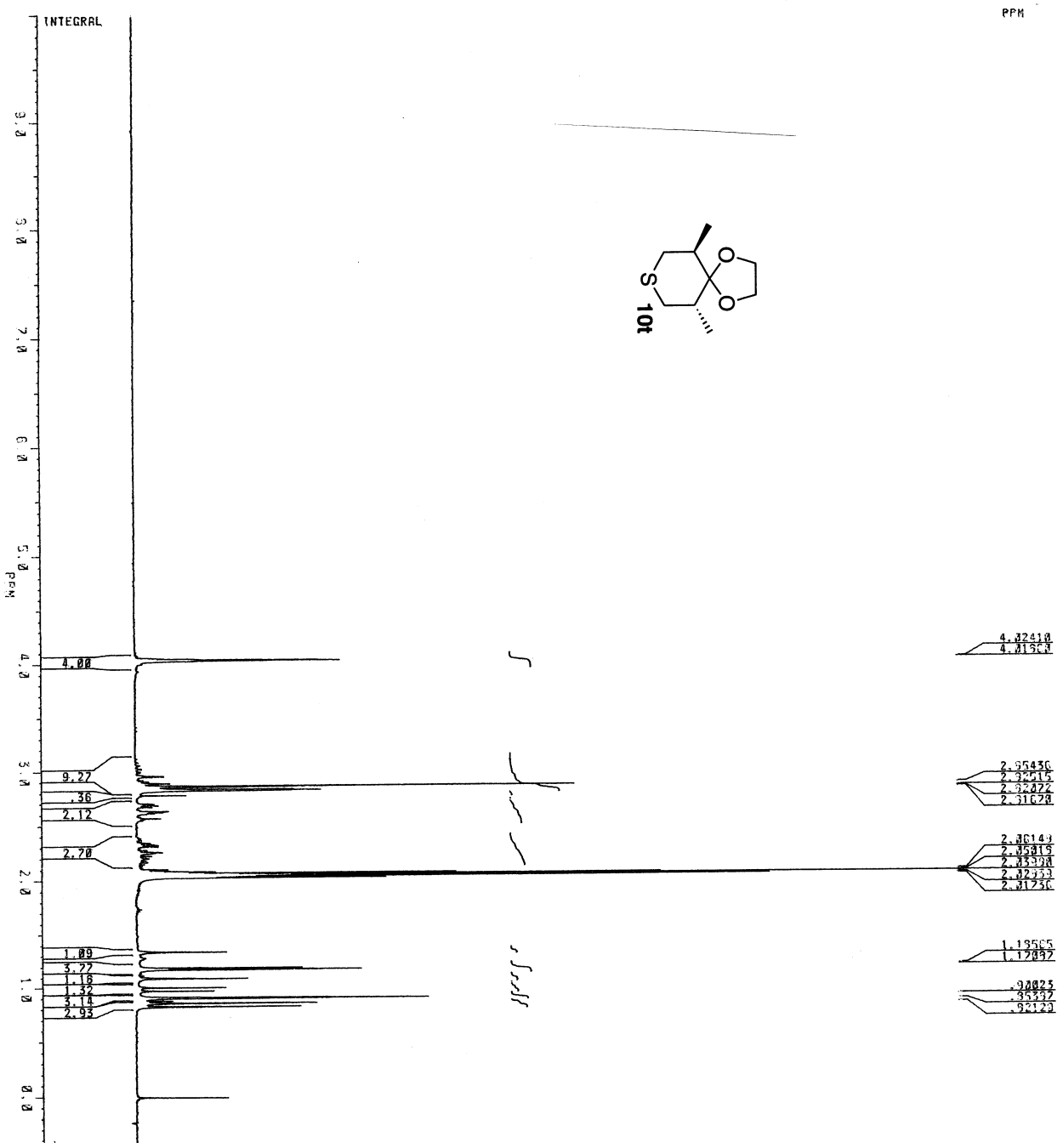
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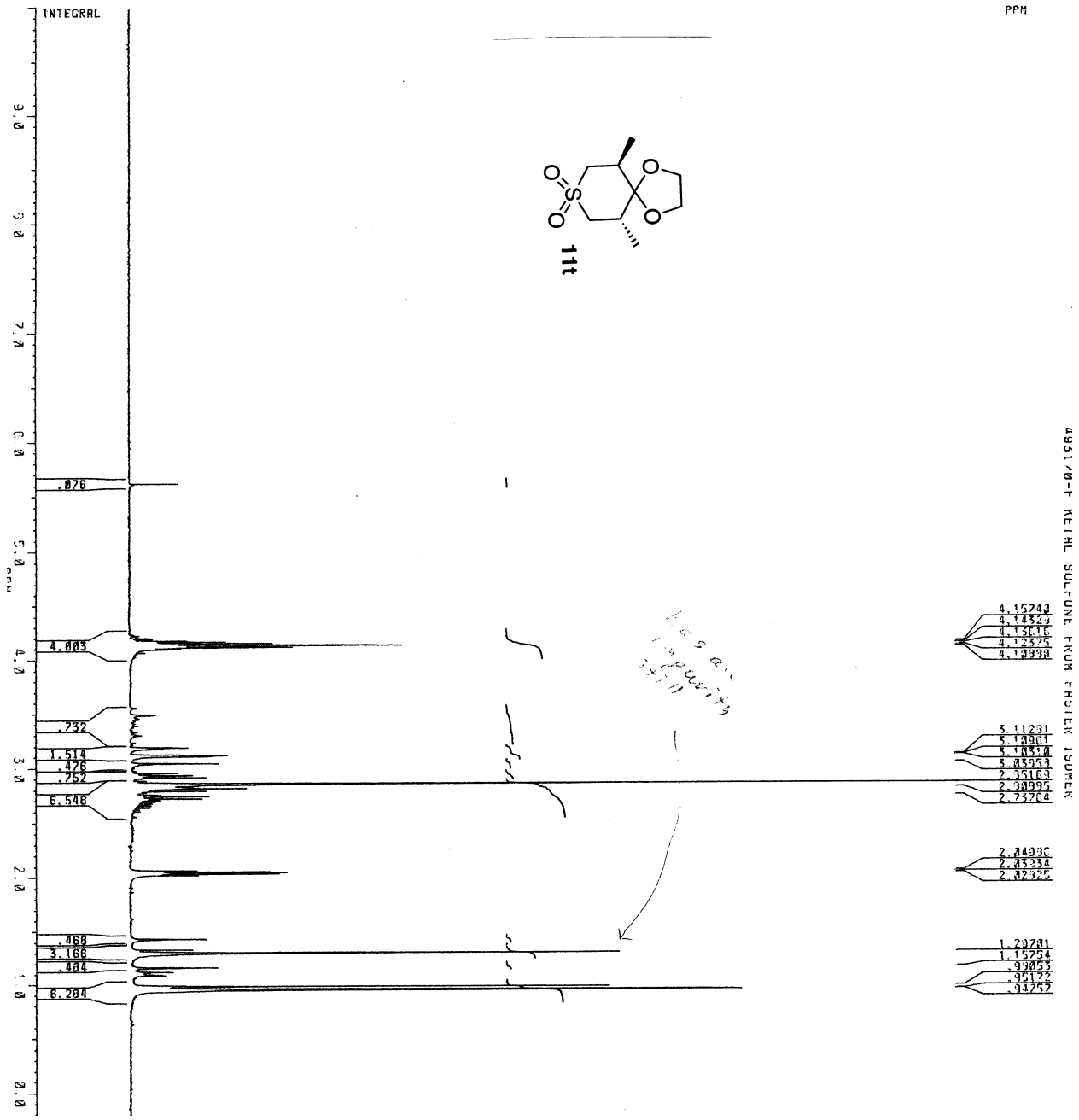
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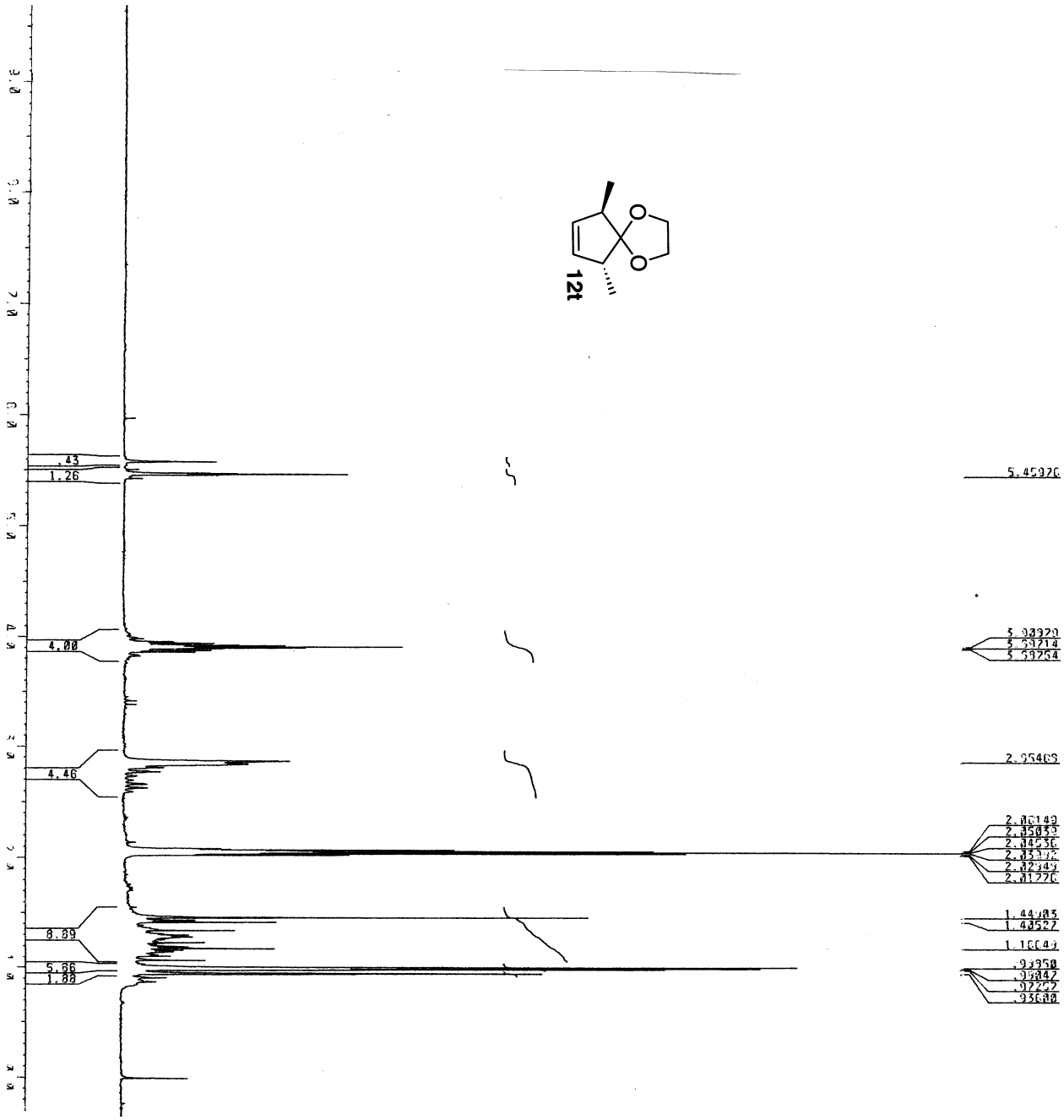
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