Report Number BETC-001-1
Distribution Category UC-92b

CHARACTERIZATION OF HIGH BOILING FOSSIL FUEL DISTILLATES VIA ^{1}H AND ^{13}C NMR ANALYSIS

MASTER

Quarterly Report for the Period
July 1, 1973 through September 30, 1978

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Prepared for the United States
Department of Energy
Bartlesville Energy Research Center

Under Contract EW-78-A-19-001

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I. SUMMARY OF TASK-OBJECTIVES AND SCOPE

A major objective was to obtain ^{1}H and ^{13}C NMR spectra of a group of high-boiling (535-675°C) of distilled crude oils supplied by the Bartlesville Energy Center. Assigned samples were:

GACH SARAN Crude Distillates:

(1) Monoaromatic GPC 206: Fractions 14, 18, 22
(2) Diaromatic GPC 207: Fractions 15, 21, 24
(3) Polyaromatic-Polar GPC 208: Fractions 15, 20, 25
(4) Adsorption Chromatography concentrates: saturates, monoaromatics, polyaromatic-polar (ca. 12 samples)

WILMINGTON Crude Distillates:

(1) Monoaromatic GPC 209: Fractions 15, 19, 23
(2) Diaromatic GPC 211: Fractions 16, 19, 24
(3) Polyaromatic-Polar 210: Fractions 16, 21, 26
(4) Adsorption chromatography concentrates: saturates, monoaromatics, diaromatics, polyaromatic-polar (Ca 12 samples)

In addition, it was proposed to evaluate the use of ^{1}H and ^{13}C NMR analysis, along with the use of relaxation agents, to determine in the samples: (a) the ratio of aromatic carbon/aliphatic carbon; (Ar-$\underline{C}$/Aℓ-$\underline{C}$): (b) the average alkyl chain lengths; (c) the level of naphthenic material present; and (d) the content of condensed ring aromatic compounds in a sample. If possible, it was also an objective to evaluate the efficiency of the fractionation of the distillates via NMR analysis. Some exploratory work was needed to determine the scope of using gated-decoupling to minimize Nuclear Overhauser Effects (NOE) which can cause a disproportionate relationship between line intensities, especially in the ^{13}C NMR spectra. Without the elimination of the NOE, it is not possible to easily determine the Ar-C/Aℓ-C and other properties of the fractions.

It was also an objective to develop at least a semi-quantitative approach regarding the best weight ratio of fraction:relaxation agent (RA) to provide the maximum signal accumulation with minimum NOE within 15, 24, and 84 hours. This type of information would be very instructive with regard to the capability of the 100 MHz NMR spectrometer to examine small fractions (less than 5 mg) which would have a large number of individual ^{13}C NMR signals. Moreover, the use of a proper RA in the correct fraction:RA should provide the most accurate Ar-C/Aℓ-C with best confidence limits from a statistical viewpoint. All other generalizations or deductions made from the ^{13}C NMR analysis would also be placed on a more reliable basis.

II. ABSTRACT OF PROGRESS TO DATE

The progress to date under the orginal contract centers around the acquisition and analyses of ^{1}H and ^{13}C NMR spectra of the monoaromatic concentrates and GPC (gel permeation chromatography) fractions of Wilmington 209-76 #15, 19, 23 and Gach Saran 206-76 #14, 18, 22 distillates (535-675°C). In addition, the analyses of diaromatic GPC fractions from Wilmington 211-76 #19 and Gach Saran 207-76 #21 distillates (535-675°C) have also been initiated. The completion of these objectives has been slowed somewhat by additional requests by DOE for immediate analyses of fractions isolated from recovered lubricating oils. The results of the investigation of these lubricating oil fractions has also been included in this report, though not strictly a part of the original contract. Completion of these additional requests will now allow the smooth continuation of the original tasks.

III. DETAILED REPORT OF ACCOMPLISHMENTS TO DATE

a. Glossary of Symbols and Terms

NMR - nuclear magnetic resonance.

PFT - pulse Fourier transform.

a. Glossary of Symbols and Terms (continued)

NOE - nuclear Overhauser effect (an enhancement-addition or subtraction-to the intensity of an NMR signal).

FD - Full decoupling-a term used to describe the removal of of magnetic interactions of one nuclei with another; in our system, the interactions of a proton with carbon is eliminated.

GD - Gated decoupling-a technique used in a PFT experiment in which decoupler power is removed and, in our work, the ^{13}C atom is allowed to relax to its ground state and the NOE effect on the signal intensity is eliminated.

RA - Relaxation agent; an additive used to cause the ^{13}C atom to return to its ground state after a single PFT experiment; in our work $Cr(AcAc)_3$ was used.

FID - Free induction decay; the pattern of precession frequencies of each nucleus detected in the receiver of the NMR spectrometer. A FID corresponding to absorption of one frequency (such as a singlet absorption for $^{13}C\{^{1}H\}$ spectrum) is an exponential decaying sine wave. In the work in progress it is necessary to "build up" a well shaped FID as quickly as possible to obtain the maximum signal accumulations in a specified time.

P2 - Pulse width in μsec-time the sample is exposed to the RF pulse.

D5 - Delay time in sec-time between pulses.

Ar-$\underline{C}$ - Aromatic carbons expressed as a per cent of the total carbon integral.

Ar-$\underline{H}$ - Aromatic protons expressed as a per cent of the total proton integral.

Aℓ-$\underline{C}$ - Aliphatic carbons expressed as a per cent of the total carbon integral

Aℓ-$\underline{H}$ - Aliphatic protons expressed as a per cent of the total proton integral.

α-$\underline{H}$(α to Ar) - Protons on carbons alpha to an arene ring expressed as a per cent of the total proton integral.

β-$\underline{H}$(β or greater to Ar) - Protons on carbons beta (or greater) from an arene ring expressed as a per cent of the total proton integral.

Term $C\underline{H}_3$ - Protons on carbons which are the terminus of alkyl chains, side chains and branching chains expressed as a per cent of the total proton integral.

b. Techniques Employed in the NMR Analysis

Although ^{13}C NMR analysis of coal and fossil fuels and the aromatic qualities of such have been in use for some time,[1] recent developments[2] as late as 1978 point to the use of several techniques to provide improved S/N, to minimize the NOE and to enhance the total signal accumulations in overnight runs in particular with a PFT experiment, especially in ^{13}C NMR analysis. Quantitative applications of ^{13}C NMR have been slower in development[3] because of the weak ^{13}C signal (due to its low material abundance and small magnetic moment) and long relaxation time after a PFT experiment as well as the NOE cited previously.

In the work to date, all spectra have been recorded on a Varian XL-100(15) NMR spectrometer with observing ^{1}H at 100.1 MHz and ^{13}C at 25.2 MHz with tetramethylsilane (TMS) as the standard and using a Nicolet TT-100 PFT unit. A sweep width of 6024 Hz with a memory for acquisition of 16K was employed for all ^{13}C experiments. A sweep width of 1400 Hz was used for all ^{1}H work with a 16K memory for acquisition. The P2 variation (^{13}C) was dependent upon quantity of sample available but was within the range of 8.8 to 15.5 μsec (the 15.5 μsec pulse width for a 90° tilt angle was used when a large quantity of sample was available). Values of D5 varied also with the amount of sample but fell in the range of 0.7-1.7 sec. Without $Cr(acac)_3$ but with GD, the D5 was usually 7.5-8 sec. The chromium salt of acetyl acetonate, $Cr(acac)_3$, (0.03 to 0.05 M in the sample solution) was employed to minimize the NOE. GD was also used in all ^{13}C experiments to also minimize the NOE.

The best overall results was obtained when the GD and RA combination was utilized expecially with small quantities of samples so that a large number of acquisitions could be obtained overnight or within 24 hours.

The solvent used for ^1H and ^{13}C spectral analysis was $DCC\ell_3$ (100% atom D) which was necessary to dissolve all samples and also to provide a medium from which no signals would appear which interfered with signals from the sample. Dioxane-d_8 has finally been acquired and appears to be the medium of choice for some future work as one major peak from this solvent occurs approximately midway between the Ar-C and Aℓ-C.

c. Discussion and Evaluation of Data

The initial focus of the investigation is on the ^1H and ^{13}C NMR spectral analyses of the monoaromatic fractions of both the Gach Saran and Wilmington distillates. In addition, a series of saturate fractions from motor oils, which were sent to us after the contract had been initiated, have also been analyzed by both ^1H and ^{13}C NMR spectroscopy. Finally, our analysis of the diaromatic fractions has also been started. Because of the time-consuming nature of the ^{13}C NMR analysis by PFT methods and the urgency for completion of the analysis of the saturates from the motor oils, the ^{13}C NMR investigation of the monoaromatic fractions has been postponed to the second quarter of the contract.

(1) Analysis of Monoaromatic Fractions

Table I summarizes the data abtained from the spectra of the Wilmington monoaromatic fractions. An evaluation of the data for each of the fractions follows:

Concentrate: The concentrate is interesting in that it should display spectral characteristics which are an average of the further refined GPC fractions #15, #19 and #23. As can be seen from Table I, the concentrate does in fact closely resemble fraction #19, the middle or median fraction of the three GPC fractions listed in Table I. The aromatic signal in the ^1H NMR spectrum of the concentrate extends well beyond δ 7.2, indicating

TABLE I
Wilmington Crude (535-675°C) Distillate
GPC 209-76 (Monoaromatic Fractions)

		Mole% of Total H		
	Concentrate	#15	#19	#23
Ar-H	5.3	3.4	5.4	8.3
Aℓ-H	94.7	96.6	94.6	91.7
Ar-H/Aℓ-H	5.3/94.7 (1:17.9)	3.4/96.6 (1:28.4)	5.4/94.6 (1:17.5)	8.3/91.7 (1:11.0)
α-H(α to Ar)	12.4	7.8	13.8	15.9
β-H(β and greater to Ar)	82.3	88.8	80.8	75.8
Term CH_3	28.1	23.6	27.7	30.7
α-H(α to Ar)/ Total Aℓ-H	12.4/94.7 (1:7.6)	7.8/96.6 (1:12.4)	13.8/94.6 (1:6.8)	15.9/91.7 (1:5.8)
Term-CH_3/Total Aℓ-H	28.1/94.7 (1:3.4)	23.6/96.6 (1:4.1)	27.7/94.8 (1:3.4)	30.7/91.7 (1:3.0)
α-H(α to Ar)/Term CH_3	12.4/28.1 (1:2.3)	7.8/23.6 (1:3.0)	13.8/27.7 (1:2.0)	15.9/30.7 (1:1.9)
Apparent Side Chain Length	>7	>12	>6	>5
Apparent Branches per Chain	0.5	1.0	0.33	0.29
Approx. Diaromatic (mole% of total H)	2.0	0.3	1.7	4.1
Ar-C/Aℓ-C (mole% of total C)	27.4/72.6†	*	29.2/70.8†	*
Ar-H/Ar-C	1/5.2†	*	1/5.4†	*
Aℓ-H/Aℓ-C	1.3/1†	*	1.3/1†	*
Side Chain Length (from C peak ratios); estimated	C_{11}-C_{14}†	*	C_{10}-C_{12}†	*

* To be completed

† Sample contain 0.03 M $Cr(acac)_3$

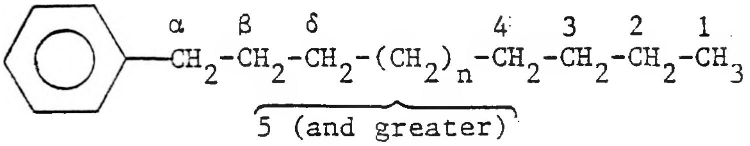
possible contamination by condensed ring aromatic and/or heterocyclic compounds. This observation is supported by the presence of a broad band of aromatic signals extending from δ 136 to δ 148 in the ^{13}C NMR spectrum of the concentrate. The apparent side chain length, as determined from the ^{1}H NMR spectra by the ratio of α-H(α to Ar)/Total Aℓ-H,[1a] is greater than 7 carbons. This estimate is considerably less than the 11 to 14 carbon chains predicted by the ratio of the α-carbon signal (∿δ 14) and β-carbon signal (∿δ 22.5) to the ε-carbon signal (∿δ 29.5) in the ^{13}C NMR spectrum.[1e] This discrepancy arises primarily from an overlap in the ^{1}H NMR spectrum of the naphthenic band with signals corresponding to protons in the side chain which are on carbons alpha to the aromatic ring [α-H(α to Ar)]. Since the α-H(α to Ar) region is used in estimating the side chain length, this overlap of signals artifically lowers the estimate. The approximation of chain length from the carbon spectrum, as outlined by Pugmire,[1e] is probably more acurate since the signals used to determine the chain length are sharp and well defined.

Fraction #15: The aliphatic region (δ 0.0-4.0) of the ^{1}H NMR spectrum of fraction #15 is dominated by a strong, sharp signal at δ 1.29 which corresponds to resonances from methylene groups in side chains and naphthenic rings. While the presence of naphthenic compounds is confirmed by the downfield extension of the broad signal arising from protons on groups alpha to an arene [α-H(α to Ar)], the low intensity of this signal implies a low concentration of naphthenic material. The aromatic portion of the spectrum verifies the predominance of monoaromatic species in this fraction, in view of the presence of signals at δ 6.34, 6.53 and 6.64 and the lack of signals further downfield (>δ 7.2). The broad, but distinctly separate signals in the aromatic region, suggests a variety of mono-, di-, tri- and multi-substituted monoaromatic systems. The ^{13}C NMR analysis of fraction #15 has as yet to be recorded.

Fraction #19: The sharpness of the ^{1}H NMR signals at δ 0.87, 0.90 and 1.27 and the relative intensities associated with these signals suggests aliphatic side chains 6 to 8 carbons long [estimated from the ratio of α-$\underline{H}$(α to Ar) to total $A\ell$-$\underline{H}$] (Table I).

Comparison of the ^{1}H NMR spectrum of #19 with the ^{1}H NMR spectrum of fraction #15 shows a reduction of the intensity of the peak at δ 1.27 relative to the signals between 0.0 and 1.0 ppm and a corresponding reduction in the area of the δ1.27 signal. The notable broad band centered at δ 2.65 and extending to ~δ 3.0 supports ths supposition that naphthenic compounds may be present. These compounds would be expected to increase the ratio of protons on carbons alpha to an arene ring to the total aliphatic protons. Since it is this ratio which is used to predict the side chain length,[1a] such a change would make the predicted chain length too low. For the same reasons, the degree of branching would also be expected to be higher than predicted from the raw ratio of protons on carbons alpha to an arene ring compared to the terminal CH_3 protons.

The ^{13}C NMR spectrum of fraction #19 has also been recorded. Sharp resonances at δ 14.1, 22.7, 32.7, 29.4 and 29.7 have been assigned to the C(1), C(2), C(3), C(4) and C(5) (and greater) atoms (numbering from the



terminal CH_3), respectively. Signals at δ 37.3, 31.9 and 30.0 could be assigned to carbons α, β, and δ to an arene ring, respectively. It is also possible that these latter signals could be partially explained by the presence of naphthenic compounds, as well as branched aliphatic chains. The relative ratios of the C(1) and C(2) peaks to the C(5) (and greater) signal in the ^{13}C NMR spectrum suggest an average side chain length of 10 to 12 carbons.[1e] An aromatic-C/aliphatic-C (Ar-C/Aℓ-C) ratio of 29.2/70.8 (Table I) obtained from the integration of this spectrum indicates that the aromatic rings in this fraction are most likely multi-substituted.

Fraction #23: The peak at δ 1.27 in the ^{1}H NMR spectrum of fraction #23 is further reduced in intensity when compared to the corresponding signal in the spectrum of fraction #19. The broadness of this peak as well as the peak at δ 0.87 would seem to indicate a variety of shorter side chains. This conclusion is further supported by the relative increase in the aromatic proton integral as well as the integral for protons on carbons alpha to an arene ring. An increase in the amount of naphthenic material is also very likely.

The general trend in this series (Fractions #15, 19, and 23) shows variation from longer side chains to shorter chains, respectively. A general increase in the amount of naphthenic material is also indicated/in the same direction. A very marked downfield shift in the broad ^{1}H aromatic signal in the series implies an increase in possible contamination by diaromatic compounds and/or a decrease in the average substitution. The extension of the aromatic proton band beyond δ 7.2 would seem to support the presence of diaromatics, however.

Comparison of this series of GPC fractions with the series of monoaromatic GPC fractions isolated from lower boiling (370-535°C) distillates {Hydrocarbon Processing, **53** (7), 141(1974)} of Wilmington crude oil show very distinct similarities. Both series of GPC fractions show a marked decline in the apparent side chain length in the latter fractions. An increase in the integral of protons on carbons alpha to an arene ring was interpreted to indicate an increase in naphthenic compounds in the lower boiling fractions, an interpretation which cannot be ruled out in the case of the higher boiling (535-675°C) fractions. The principle difference between the lower boiling distillates and the higher boiling distillates in the monaromatic GPC fractions is the sharp peak occuring at $\sim\delta$ 2.6 in the ^{1}H NMR spectra of the higher boilers, indicating a higher initial concentration of naphthenic compounds in the eariest GPC fractions of the high boilers.

Table II summarizes the data obtained from the spectra of the Gach Saran monoaromatic fractions. An appraisal of the data for each of the fractions follows:

Concentrate: The concentrates of the monoaromatics of the Gach Saran distillates should have spectral properties which are an average of the GPC fractions #14, #18 and #22 in a fashion similar to the trends observed in the spectra of the monoaromatic concentrate and fractions (#15, 19, and 23) of the Wilmington distillate. As can be observed from the values in Table II, the data obtained from the ^{1}H NMR spectra of the Gach Saran MA concentrate again most closely resembles the data obtained from the spectrum of the middle or median fraction (#18) of the three fractions (#14, #18 and #22) investigated. The greatest deviations in this trend of closely matched spectral data between the concentrate and fraction #18 involve the estimation of the terminal $C\underline{H}_3$ content. It should be noted, however, that while all the other parameters listed in Table II display clear-cut trends in the ^{1}H NMR spectra over the three fractions, the terminal $C\underline{H}_3$ parameter does not (i.e. there is no steady increase or decrease shown in this parameter going from fraction #14 to fraction #22). Thus, the deviation observed between the terminal $C\underline{H}_3$ value for the concentrate and that for fraction

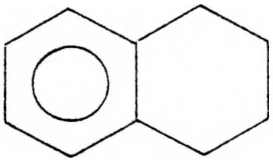
TABLE II
Gach Saran (535-675°C) Distillate
GPC 206-76 (Monoaromatic Fractions)

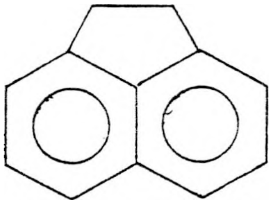
		Mole% of Total H		
	Concentrate	#14	#18	#22
Ar-H	5.0	3.1	4.1	7.2
Aℓ-H	95.0	96.9	95.9	92.8
Ar-H/Aℓ-H	5.0/95.0 (1:19.0)	3.1/96.9 (1:31.2)	4.1/95.9 (1:23.4)	7.2/92.8 (1:12.9)
α-H(α to Ar)	11.2	6.2	12.5	16.2
β-H(β and greater to Ar)	83.8	90.7	83.4	76.6
Term CH_3	23.1	20.3	19.4	23.7
α-H(α to Ar)/ Total Aℓ-H	11.2/95.0 (1:8.5)	6.2/96.9 (I:15.6)	12.5/95.9 (1:7.7)	16.2/92.8 (1:5.7)
Term CH_3/ Total Aℓ-H	23.1/95.0 (1:4.1)	20.3/96.9 (1:4.8)	19.4/95.9 (1:4.9)	23.7/92.8 (1:3.9)
α-H(α to Ar)/ Term CH_3	11.2/23.1 (1:2.1)	6.2/20.3 (1:3.3)	12.5/19.4 (1:1.6)	16.2/23.7 (1:1.5)
Apparent Side Chain Length	>8	>1	>7	>5
Apparent Branches per Chain	0.38	1.2	0.0	0.0
Approx. Diaromatic (mole% of total H)	1.6	0.0	2.1	3.6

#18 could be attributed to a distinct characteristic of the fraction (e.g. less average branching) which differentiates #18 from the other fractions and from the whole concentrate.

Fraction #14: The most noticable feature of the ^{1}H NMR spectrum of this fraction is total lack of signals downfield from δ 7.2. This indicates the predominance of substituted monoaromatic compounds. The aromatic region of the spectrum is also dominated by well-defined, broad signals at δ 7.14, 7.10, 7.02, 6.98 and 6.84, which could be indicative of a somewhat homogeneous fraction. The ^{1}H NMR spectrum has an aliphatic region which also seems to indicate a homogeneous material with a very sharp peak at δ 1.29. Almost no signals, appear in the α-H(α to an arene ring) region (δ 2.00-4.00). As indicated in Table II, the average side chain length (calculated from the ratio of α-H(α to Ar) to total Aℓ-H)[1e] is fairly long (>15). The lack of naphthenic signals (δ 2-4) implies that this estimate of the chain length is reasonably accurate. The ^{13}C NMR spectrum has yet to be obtained.

Fraction #18: The signal at δ 1.29 in the ^{1}H NMR spectrum are still sharp and clean, but the aliphatic region also reveals the presence of some naphthenic compounds. The signal at δ 0.90 is more intense relative to the peak at δ 1.29 in the spectrum of this fraction when compared to the same signals in the spectrum of fraction #14. This observation, coupled with the downfield shift of the aromatic band (which is broad and less detailed in the spectrum of #18 compared to that in #14), could result from an increase in the variety of compounds in this fraction as well as from an increase in the naphthenic material. The low broad signal centered at δ 2.50 would seem to confirm these conclusions. The presence of naphthenic materials would result in an artificially low side chain length and low estimation of average branches per chain. Some diaromatic material is also indicated by the downfield





extension of the aromatic band. The ^{13}C NMR spectrum of this fraction will be obtained shortly.

Fraction #22: This last monoaromatic fraction of the Gach Saran distillate displays a dramatic change in the ^{1}H NMR spectrum from the previous two fractions. The peak at δ 1.29 is much broader and, compared to the signal at δ 0.90, is less intense than that in the spectra of the other two fractions (#14 and #18). A broad signal extending to δ 3.0 suggests a higher naphthenic content in this fraction, as well. The broad nature of all the signals in the ^{1}H NMR spectrum most likely arises from a high signal density from a wide variety of monoaromatic compounds with shorter (>5 carbons) side chains. Again, the shift of the aromatic ^{1}H signal to lower field ($>\delta$ 7.2) could be the result of diaromatic compounds contaminating this monoaromatic fraction. It should be possible to provide a more definitive evaluation of the types of aromatic carbon when the ^{13}C NMR spectrum is recorded which is in progress.

(2) Summary of NMR Analysis of Monoaromatics

The general trend in the Gach Saran monoaromatic fractions parallels that in the Wilmington fractions. However, the Gach Saran fractions displayed an overall lower level of aromatic content. In addition, the Gach

Saran fractions have a generally lower level of terminal CH_3. This could arise from either a smaller degree of branching or a higher content of naphthenic material. The indication from the spectra, however, is that the Gach Saran fractions contain less naphthenic material.

(3) Analysis of Diaromaric Fractions

The results from the NMR analysis of the diaromatic fractions investigated to date have been given in Table III. Although only a few fractions have been analyzed thus far, some very interesting observations were made. The Wilmington DA concentrate and the Wilmington GPC fraction #19 are very similar in nearly all of the catagories listed in Table III. Judging from the consistent trends observed in the spectra of the monoaromatic fractions, possibly the GPC fractions to be analyzed (GPC 211-76 #16 and #24) will be similar. If these trends hold, one would predict that the middle or median fraction (#19) of the three fractions to be investigated (#16, #19 and #24) will resemble the average spectral features of the concentrate. This must await the additional work now in progress.

It is interesting that the ^1H NMR data of the Gach Saran fraction #21 also resembles the two Wilmington samples to some extent, but not as closely as the two Wilmington samples resemble each other. Since the remaining Gach Saran diaromatic GPC fractions to be examined (#15 and #24) bracket fraction #21, it will be interesting to determine whether any trends are observed among these fractions to compare with those of the Wilmington fractions.

The calculation of the apparent number of branches per side chain is based on a few basic assumptions. First, it is assumed in the calculation that all of the alkyl protons observed in the ^1H NMR spectra are part of a side chain on an arene ring. Second, all protons on carbons alpha to an

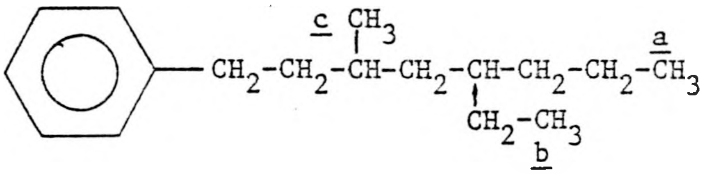
TABLE III
Diaromatic Fractions of Gach Saran (207-76) and Wilmington (211-76) Distillates (570°-635°C)

	Wilmington Concentrate	211-76 #19	207-76 #21
Ar-*H*	8.6	8.4	9.6
Aℓ-*H*	91.4	91.6	90.4
Ar-*H*/Aℓ-*H*	8.6/91.4 (1:10.6)	8.4/91.6 (1:10.9)	9.6/90.4 (1:9.4)
α-*H*(α to Ar)	17.0	17.8	17.2
β-*H*(β and greater to Ar)	74.4	73.8	73.2
Term C*H*$_3$	26.8	24.2	23.9
α-*H*(α to Ar)/Total Aℓ-*H*	17.0/91.4 (1:5.4)	17.8/91.6 (1:5.1)	17.2/90.4 (1:5.2)
Term C*H*$_3$/Total Aℓ-*H*	26.8/91.4 (1:3.4)	24.2/91.6 (1:3.8)	23.9/90.4 (1:3.8)
α-*H*(α to Ar)/Term C*H*$_3$	17.0/26.8 (1:1.6)	17.8/24.2 (1:1.4)	17.2/23.9 (1:1.4)
Apparent Side Chain Length	>5	>5	>5
Apparent Branches per Chains	0.0	-0.1	-0.1
Approx. Diaromatic (mole% of total *H*)	5.0	4.0	6.1
Ar-*C*/Aℓ-*C* (mole% of total C)	37.1/62.9†	39.1/60.9†	*
Ar-*H*/Ar-*C*	1/4.3†	1/4.6†	*
Aℓ-*H*/Aℓ-*C*	1.5/1†	1.5/1†	*

* To be completed.

† Sample contained 0.03 M Cr(acac)$_3$

arene ring are assumed to be part of an alkyl side chain. Third, it is also assumed that the amount of branching at carbons alpha to an arene ring is insignificant. Of these three assumptions, it is the second which is most likely to give rise to artificially low values for the apparent branches per chain. The low values can result from the presence of naphthenic material in the sample which would increase the number of protons on carbons alpha to an arene ring, without a corresponding increase in the number of terminal methyl groups. Here we have defined the apparent number of branches per side chain as the number of alkyl chains branching from the main side chain which terminate in a methyl ($-CH_3$) group. Thus the compound illustrated below would be considered to have two branches, resulting in two terminal



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methyl groups (b and c) and a main side chain terminating in a single methyl group (a). Ignoring the possibility of naphthenic material for the moment, one can see that if the relative amounts of α-$\underline{H}$(α to Ar) and term $C\underline{H}_3$ can be determined and, making the assumptions stated previously, one can calculate the apparent branching per side chain as follows:

$$\frac{2}{3}[\text{Term } C\underline{H}_3/\alpha\text{-H}(\alpha \text{ to Ar})] - 1 = \text{apparent branches per chain.}$$

In the case of the molecule I above, there are 9 protons on terminal methyls (term $C\underline{H}_3$) a, b, and c and 2 protons on carbons alpha to an arene ring [α-H(α to Ar)]. The equation becomes;

$$2/3(9/2) - 1 = 2$$

As the level of naphthenic material increases, the value of the ratio in the brackets in the above equation will diminish, until a level is reached at which the value of the equations becomes negative, a very noticable indicator of a relatively high level of naphthenic material. As can be seen in Table III, this level has been reached for Wilmington fraction #19 and Gach Saran fraction #21.

(4) Summary of Analysis of Diaromatic Fractions

Although the number of diaromatic fractions investigated to date is limited, some interesting correlations and trends are already apparent. The similarities between the Wilmington concentrate and fraction #19 may be useful in the prediction of spectral properties of later related fractions. Specifically, the aromatic content of fraction #19 is very similar to that in the Wilmington concentrate as can be seen from both the ^{1}H and ^{13}C NMR spectral data in Table III. If the trends for the diaromatic fractions parallel those in the monoaromatic fractions (see Table I) one might expect an increase in the aromatic content of the latter diaromatic fraction (#24). Other trends observed in the monoaromatic fractions may also have parallels in the diaromatic fractions. Of course some deviations may occur. Completion of the investigation of the diaromatic fractions will provide the test of any predictions.

(5) Analysis of Saturate Fractions from Oil

In addition to the crude oil distillates investigated as a part of the original contract, several saturate chromatographic fractions of recovered lubricating oils were also analyzed at the request of DOE. The results obtained from this investigation are summarized in Tables IV and V, and discussed below.

Table IV lists the data from a series of four fractions isolated from

TABLE IV
Saturate Fractions of Lubricating Oils

		Mole% of Total H		
	#1465	#1480	#1498	#1570
Ar-H	0.6	0.5	0.6	0.5
Aℓ-H	99.4	99.5	99.4	99.5
Ar-H/Aℓ-H	0.6/99.4 (1:166)	0.5/99.5 (1:199)	0.6/99.4 (1:166)	0.5/99.5 (1:199)
α-H(α to Ar)	3.3	2.1	0.8	1.9
Term CH_3	27.3	27.8	33.1	28.8
α-H(α to Ar/Total Aℓ-H	3.3/99.4 (1:30)	2.1/99.5 (1:47.4)	0.6/99.4 (1:165)	1.9/99.5 (1:52.4)
Term CH_3/Total Aℓ-H	27.3/99.4 (1:3.6)	27.8/99.5 (1:3.6)	33.1/99.4 (1:3.0)	28.8/99.5 (1:3.4)
Ar-C/Aℓ-C (mole% of total C)	†	†	†	5.1/94.9*
Ar-H/Ar-C	†	†	†	1/10.2*
Aℓ-H/Aℓ-C	†	†	†	1.05/1*
Average Chain length (from ^{13}C spectrum)	†	†	†	C_{16}-C_{18}*

* Carbon spectra were obtained from sampled doped with 0.03 M Cr(acac)$_3$

† To be completed

TABLE V
Saturate Fractions from Lubricating Oils

		Mole% of Total H		
	1553	1553 HPLC	#39-1484	Sil-Aℓ355
Ar-H	0.6	0.0†	0.0†	0.0†
Aℓ-H	99.4	100.0	100.0	100.0
Ar-H/Aℓ-H	0.6/99.4 (1:166)	0.0 -	0.0 -	0.0 -
α-H(α to Ar)	0.6	0.0	0.0	0.0
Term CH$_3$	33.1	32.7	30.4	30.5
α-H(α to Ar)/Total Aℓ-H	0.6/99.4 (1:165)	0.0 -	0.0 -	0.0 -
Term CH$_3$/Total Aℓ-H	33.1/99.4 (1:3.0)	32.7/100 (1:3.1)	30.4/100 (1:3.3)	30.5/100 (1:3.3)
Ar-C/Aℓ-C(Mole% of total C)	3.9/96.1*	0.0/100.0*§	0.0/100.0*§	0.0/100.0*§
Ar-H/Ar-C	1/7.8*	0.0*	0.0*	0.0*
Aℓ-H/Aℓ-C	1.03/1*	1.0*	1.0*	1.0*
Average Chain Length (from ^{13}C spectrum)	$C_{16}-C_{17}$*	$C_{14}-C_{16}$*	$C_{14}-C_{16}$*	$C_{14}-C_{16}$*

* Samples contained 0.05M Cr(acac)$_3$

† No dectectable Ar-H.

§ No detectable Ar-C after a minimum of 27,000 pulses.

motor oils. Although all four are similar, some trends are evident. The amount of α-H(α to Ar) detectable in the ^1H NMR spectra decreases from fraction #1465 to #1498, but increases again in fraction #1570. Conversely, the amount of terminal $C\underline{H}_3$ increases from fraction #1465 to #1498, but decreases in fraction #1570. It is possible that fraction #1570 represents a break in the trend, but this cannot be varified on the basis of the information obtained so far. In general, each of the fractions display characteristics typical of long chain alkyl saturates with the possibility that some saturate ring compounds may also be present.

The ^{13}C NMR of fraction #1570 indicates a chain of C_{16}-C_{18}. Signals between δ 16 and 21 indicate the possibility of branching in the chain.

Table V contains ^1H and ^{13}C NMR data from an additional series of four fractions isolated from motor oil. The first fraction, #1553, is taken from the series listed in Table IV. Some aromatic content is indicated in both the ^1H and ^{13}C NMR of this fraction although the level is low. The next fraction, #1553-HPLC, is a HPLC (high pressure liquid chromatography) fraction isolated from #1553. The most obvious difference between these two samples is the absence of any detectable aromatic protons or carbons in the ^1H and ^{13}C NMR spectra of fraction #1553-HPLC, in spite of the use of PFT techniques. It can be assumed that the additional refinement of #1553 by HPLC techniques has greatly reduced the amount of aromatic material in the fraction to a level below detectability with the number of pulses acquired per spectra to date. The remaining fractions listed in Table V as well as fraction #1553-HPLC are remarkable in that the respective ^1H and ^{13}C spectra are nearly identical. From this fact it can only be assumed that the history of these fractions must be similar but this is of course an assumption.

Finally, the data acquired to date is summarized in Table VI. Information gleaned from the ^{13}C and ^{1}H NMR spectra currently being compiled should provide additional insights into the nature of these and other petroleum fractions.

d. References

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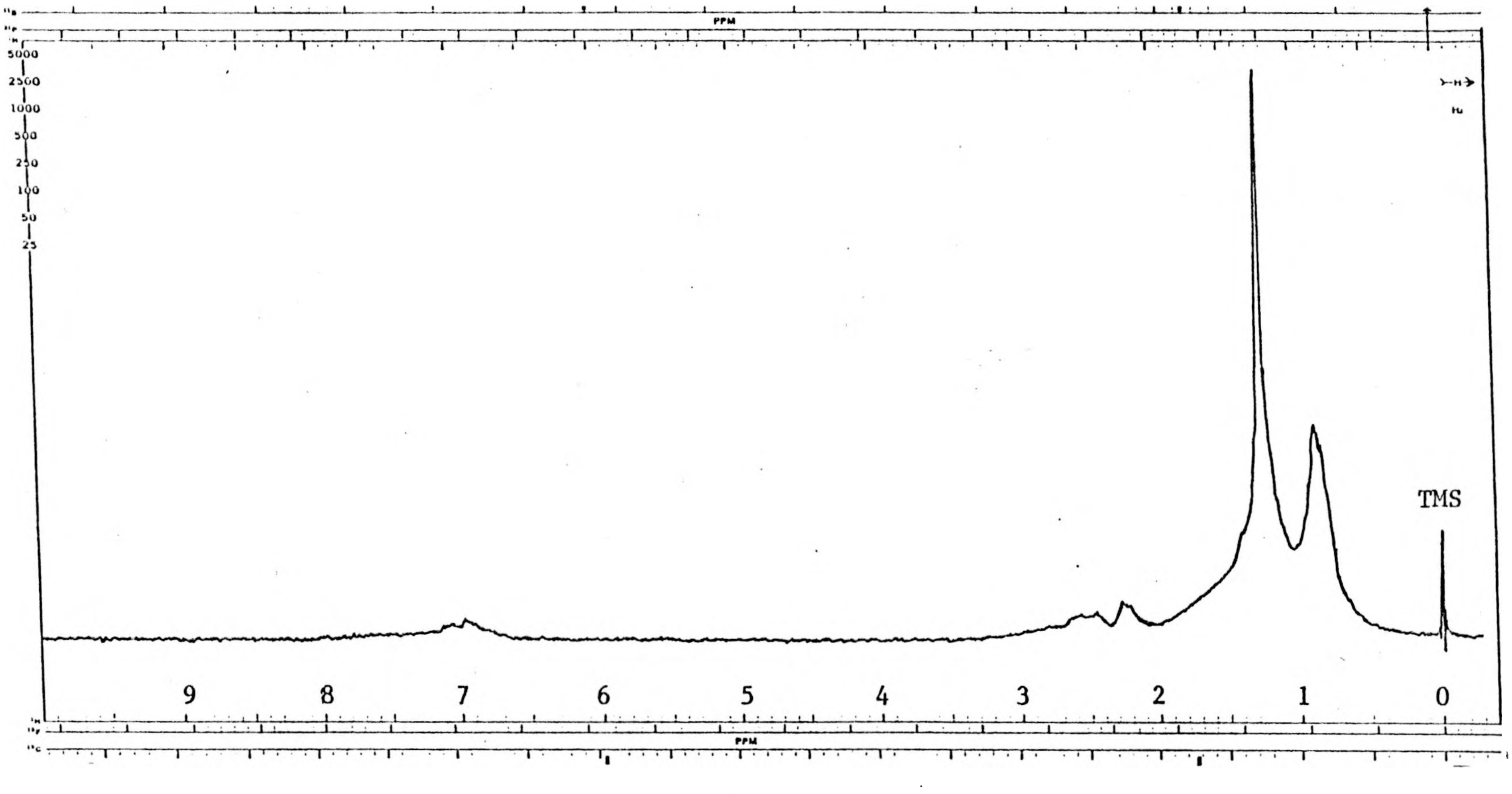
TABLE VI Summary of Data to Date.

Source	Ar-H[a]	Al-H[a]	Ar-H / Al-H	α-H[a,b]	β-H[a,c]	Term. CH_3[a]	α-H[b] / Tot. Al-H	Term. CH_3 / Tot. Al-H	α-H[b] / Term. CH_3	Appar. side ch. len.	Appar. br./ch.	Approx.[a] Diar.	Ar-C[d,f] / Al-C	Ar-H[e,f] / Ar-C	Al-H[e,f] / Al-C
Wilmington Crude Monoaromatic															
Concentrate	5.3	94.7	1/17.9	12.4	82.3	28.1	1/7.6	1/3.4	1/2.3	7	0.5	2.0	1/2.6	1/5.2	1.3/1
GPC 209-76 #15	3.4	96.6	1/28.4	7.8	88.8	23.6	1/12.4	1/4.1	1/3.0	12	1.0	0.3			
GPC 209-76 #19	5.4	94.6	1/17.5	13.8	80.8	27.7	1/6.8	1/3.4	1/2.0	6	0.33	1.7	1/2.4	1/5.4	1.3/1
GPC 209-76 #23	8.3	91.7	1/11.0	15.9	75.8	30.7	1/5.8	1/3.0	1/1.9	5	0.29	4.1			
Diaromatic															
Concentrate	8.6	91.4	1/10.6	17.0	74.4	26.8	1/5.4	1/3.4	1/1.6	5	0.0	5.0	1/1.7	1/4.3	1.5/1
GPC 211-76 #19	8.4	91.6	1/10.9	17.8	73.8	24.2	1/5.1	1/3.8	1/1.4	5	-0.1	4.0	1/1.6	1/4.6	1.5/1
Gach Saran Monoaromatic															
Concentrate	5.0	95.0	1/19.0	11.2	83.8	23.1	1/8.5	1/4.1	1/2.1	8	0.4	1.6			
GPC 206-76 #14	3.1	96.9	1/31.2	6.2	90.7	20.3	1/15.6	1/4.8	1/3.3	15	1.2	0.0			
GPC 206-76 #18	4.1	95.9	1/23.4	12.5	83.4	19.4	1/7.7	1/4.9	1/1.6	7	0.0	2.1			
GPC 206-76 #22	7.2	92.8	1/12.9	16.2	76.6	23.7	1/5.7	1/3.9	1/1.5	5	0.0	3.6			
Diaromatic															
GPC 207-76 #21	9.6	90.4	1/9.4	17.2	73.2	23.9	1/5.2	1/3.8	1/1.4	5	-0.1	6.1			
Sat. Frac. Fr. Oil															
#1465	0.6	99.4	1/166	3.3	96.1	27.3	1/30	1/3.6	-	-	-	-			
#1480	0.5	99.5	1/199	2.1	97.4	27.8	1/47.4	1/3.6	-	-	-	-			
#1498	0.6	99.4	1/166	0.8	98.6	33.1	1/165	1/3.0	-	-	-	-			
#1570	0.5	99.5	1/199	1.9	97.6	28.8	1/52.4	1/3.4	-	-	-	-	1/18.6	1/10.2	1.05/1
#1553	0.6	99.4	1/166	0.6	98.8	33.1	1/165	1/3.0	-	-	-	-	1/24.6	1/7.8	1.03/1
#1553-HPLC	0.0	100.0	0.0	0.0	100.0	32.7	0.0	1/3.1	-	-	-	-	0.0	0.0	1.0
#39-1484	0.0	100.0	0.0	0.0	100.0	30.4	0.0	1/3.3	-	-	-	-	0.0	0.0	1.0
Sil-Aℓ 355	0.0	100.0	0.0	0.0	100.0	30.5	0.0	1/3.3	-	-	-	-	0.0	0.0	1.0

[a] Mole% of total proton integral. [b] Protons on carbons α to arenes. [c] Protons on carbons β or greater to arenes. [d] Expressed in mole % of total carbon integral. [e] Ratio of mole % of the total proton integral vs mole % of total carbon integral. [f] All carbon spectra were recorded using gated decoupled techniques. $Cr(acac)_3$ was used as a relaxation agent when sample size dictated it.

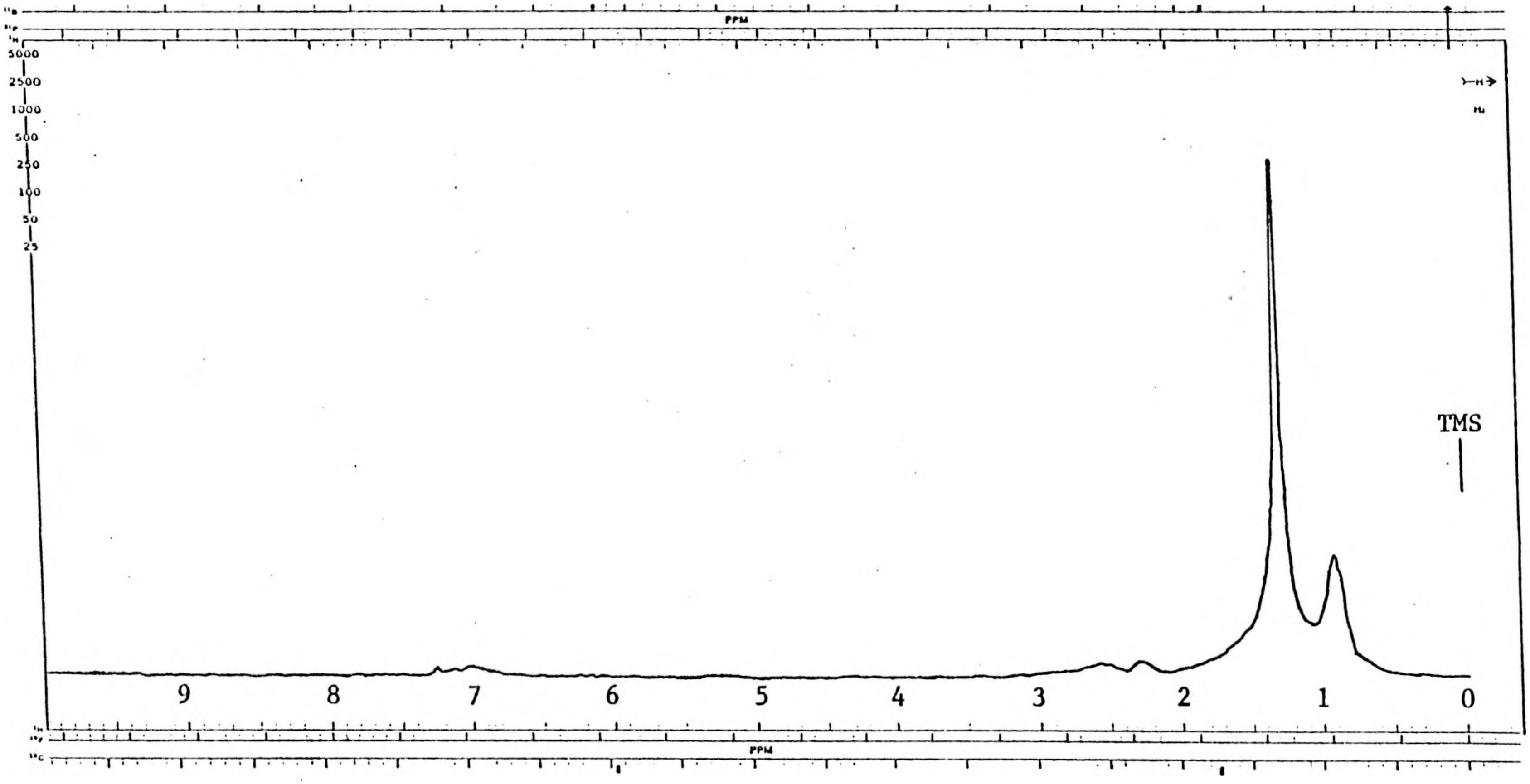
^{1}H NMR Spectrum of Oil, Wilmington MA Concentrate 9-30-76 (see Table I)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.25

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 60 µs/dB; Size. . - K; Lock. . ^{2}H

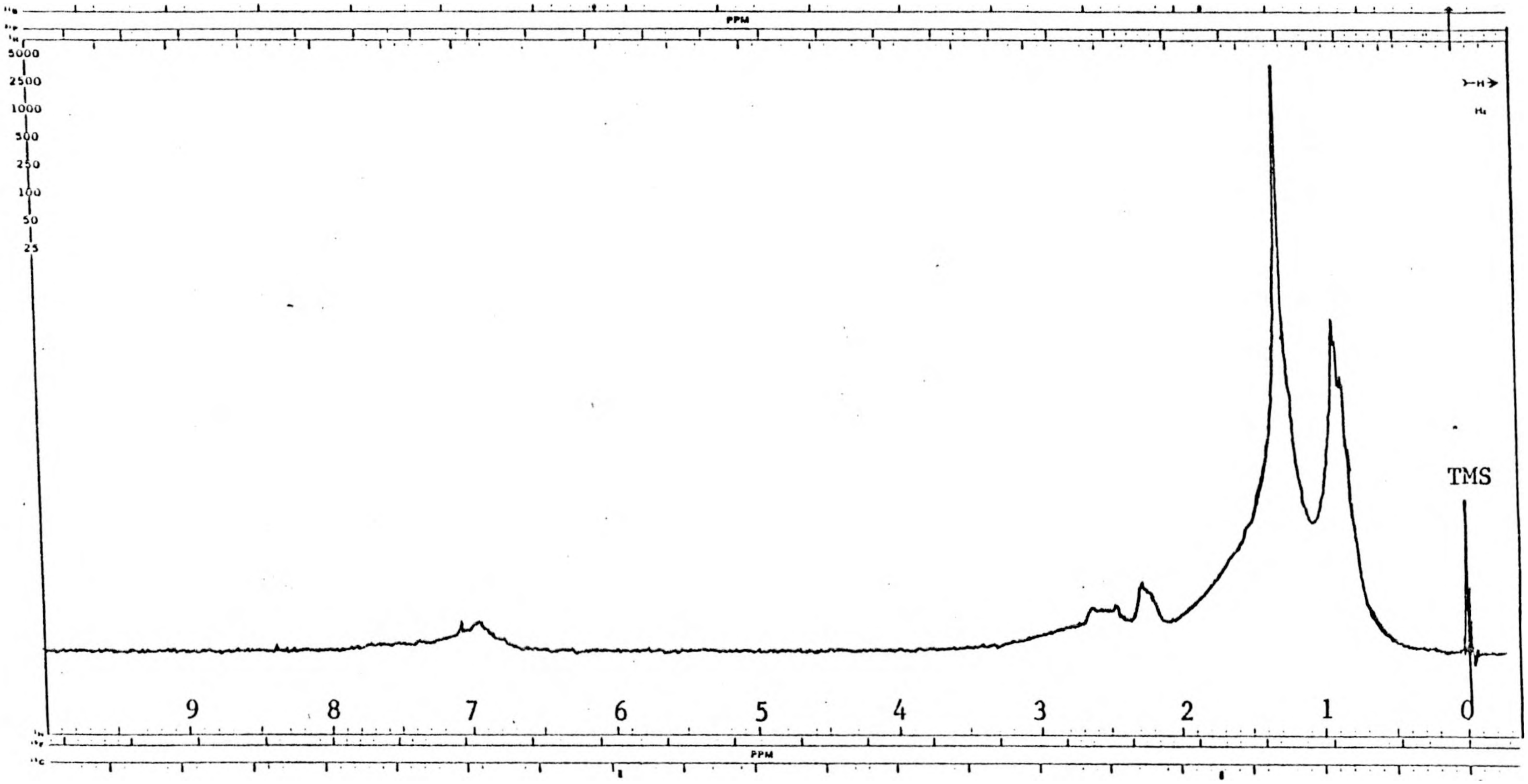
^{1}H NMR Spectrum of Oil, Wilmington MA GPC 209-76 #15 (see Table I)



PFT X CW _; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . ± 700 Hz; Acq/S.A. . 64

D5/S.T. . 2 s; S.O. . 45251 Hz; T. . 37 °C; P2/RF. . 5.7 μs/dB; Size. . 8 K; Lock. . ^{2}H

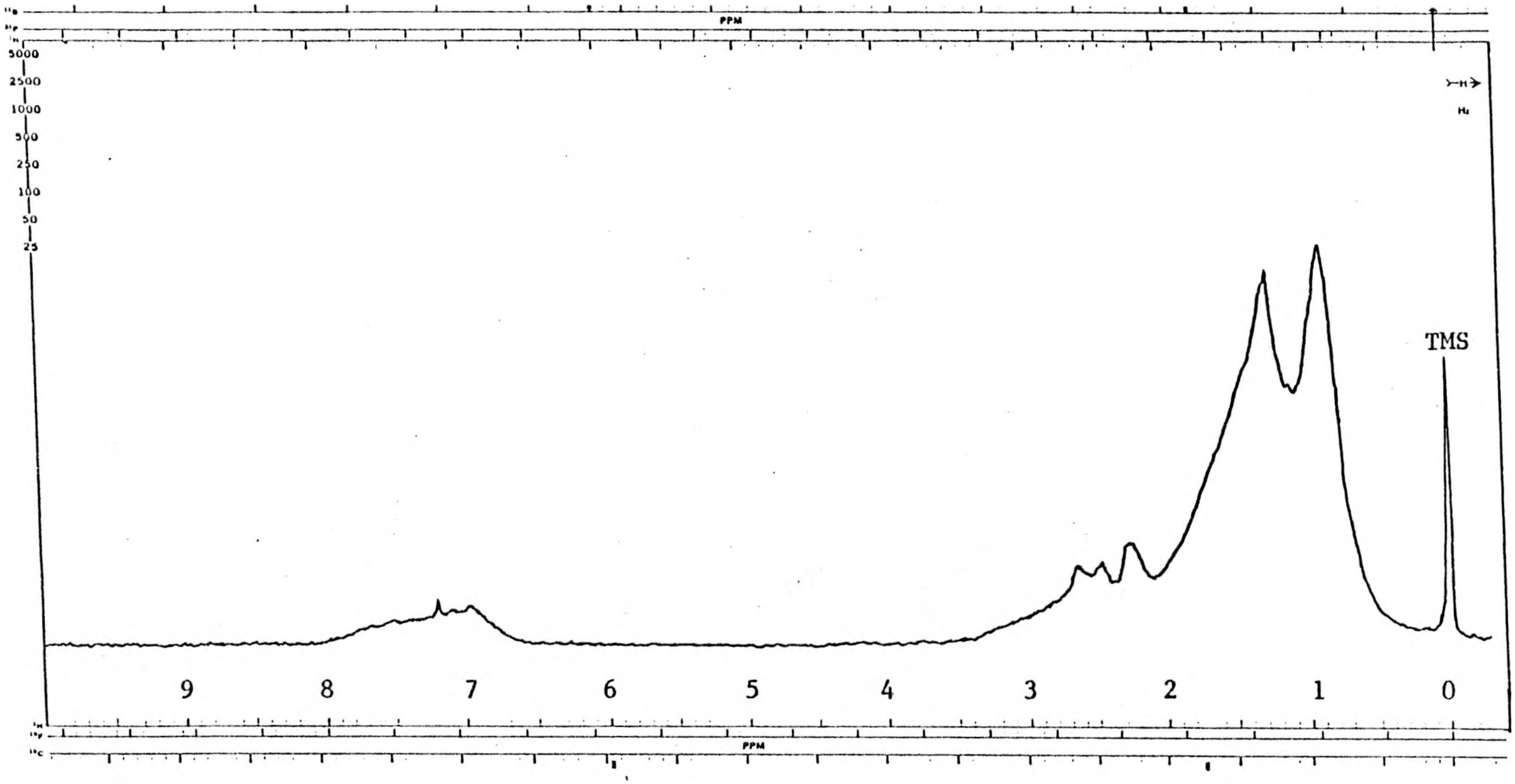
^{1}H NMR Spectrum of Oil, Wilmington MA GPC 209-76 #19 (see Table I)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85789 Hz; T. . 37.°C; P2/RF. . 52 μs/dB; Size. . 8 K; Lock. . ^{2}H

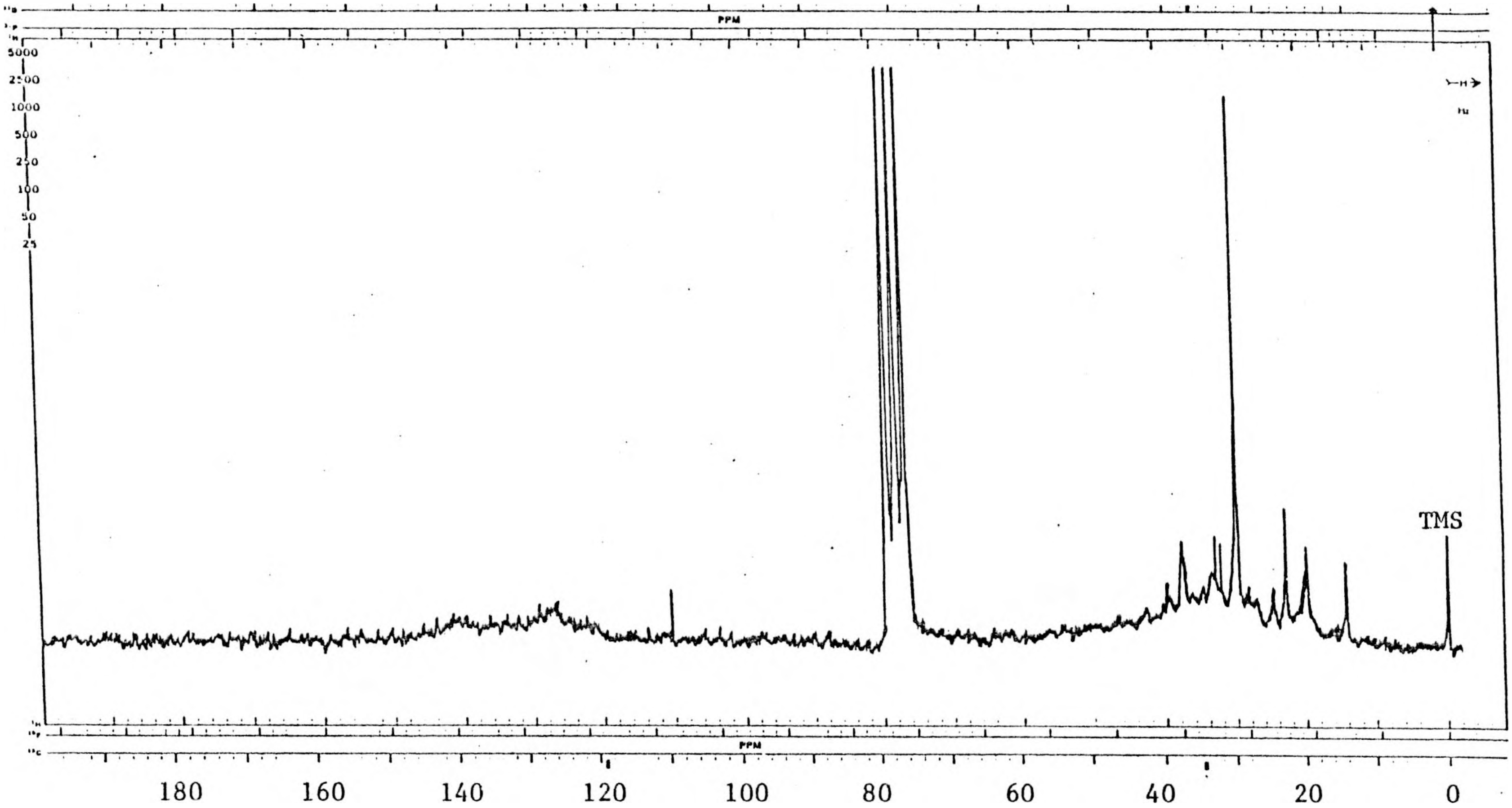
^{1}H NMR Spectrum of Oil, Wilmington MA GPC 209-76 #23 (see Table I)



PFT __ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 69 μs/dB; Size. . - K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Wilmington MA Concentrate 9-30-76 (see Table I)

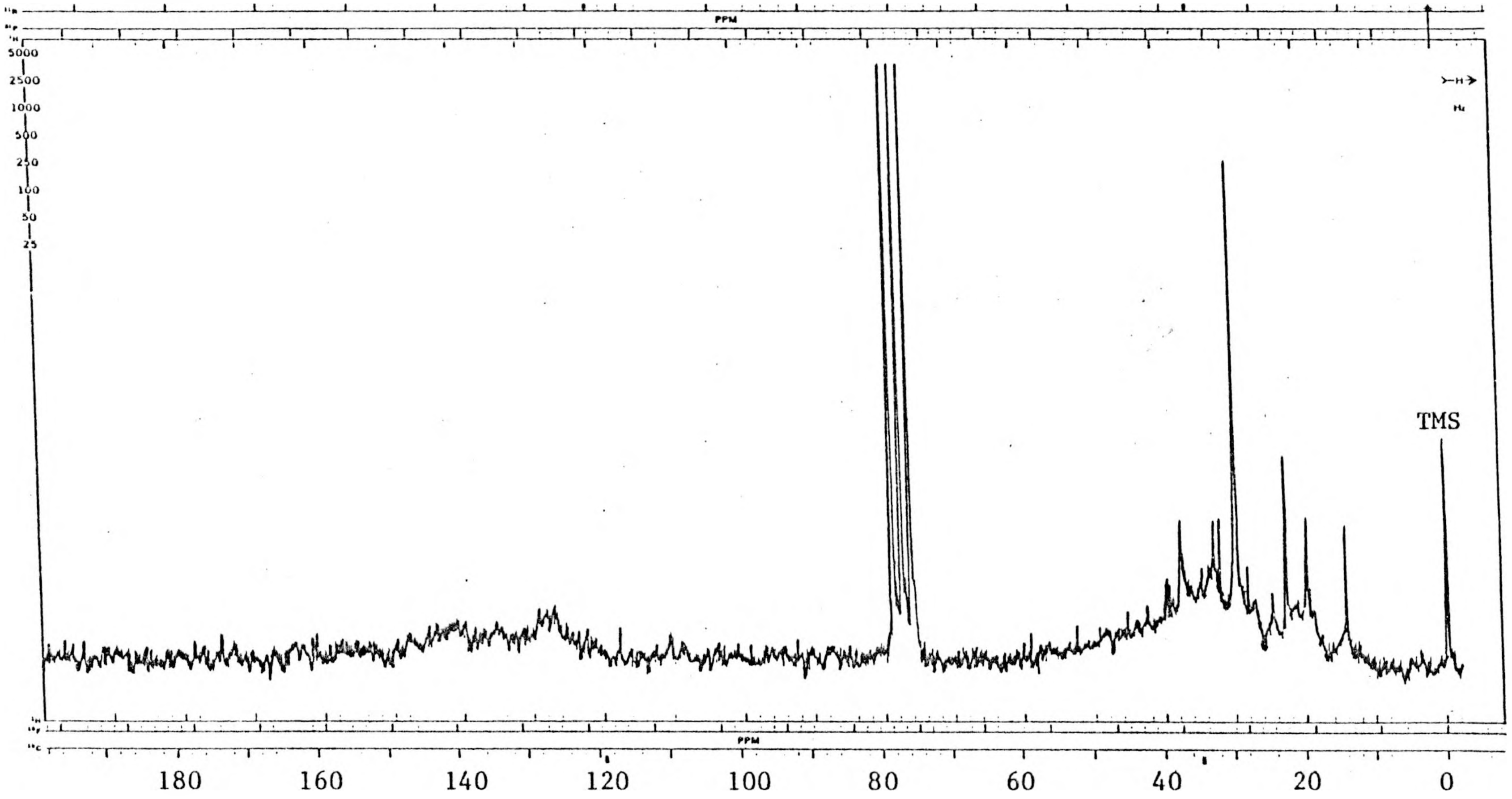


Gated Decoupled (off delay) Sample contained 0.05 M Cr(acac)$_3$

PFT X CW _; Solvent. . $DCCl_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 36,000

D5/S.T. . 0.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 8.8 µs/dB; Size. . 8K; Lock. . ^2H

^{13}C NMR Spectrum of Oil, Wilmington MA GPC 209-76 #19 (see Table I)

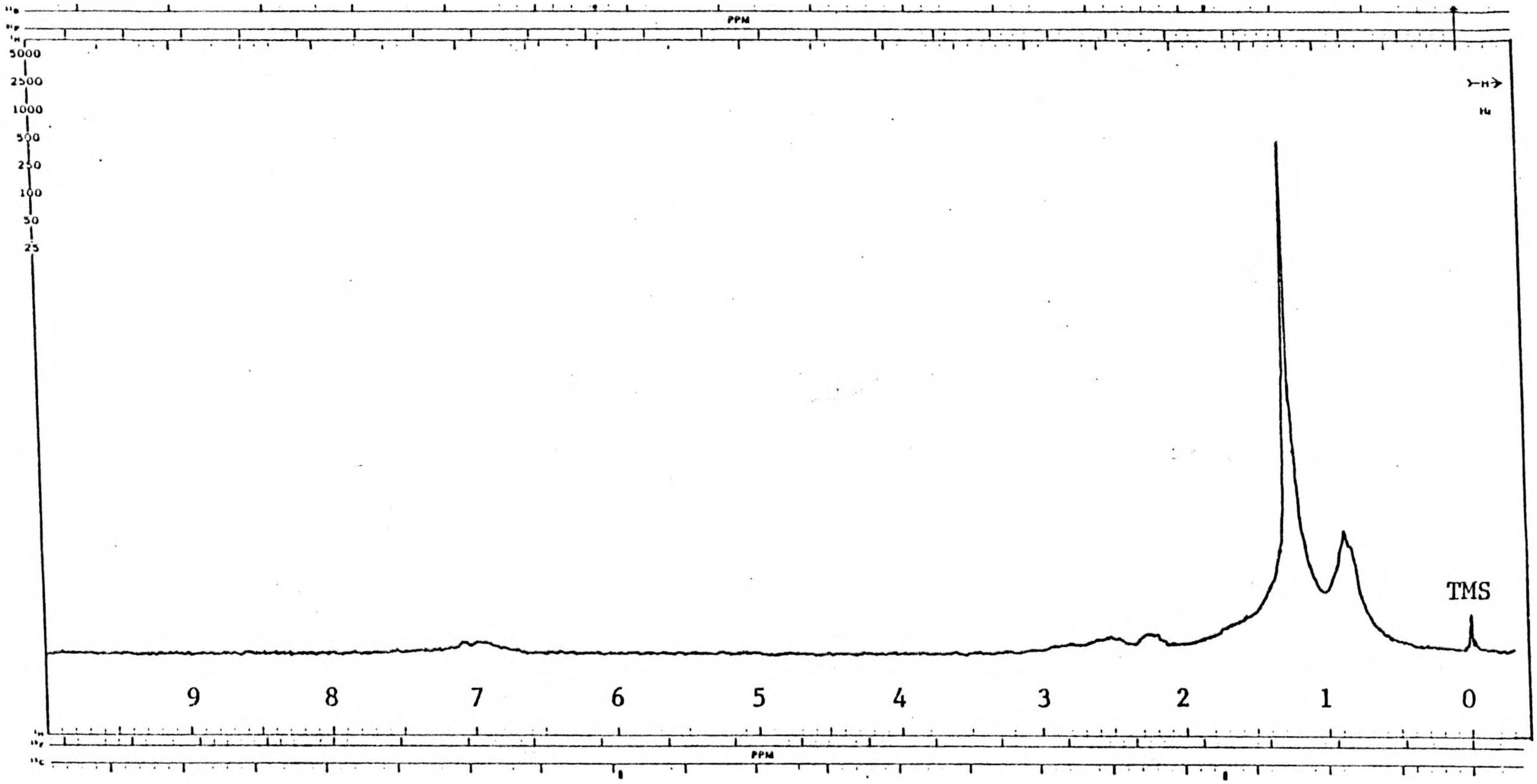


Gated Decouple (off delay) Sample contained 0.03 M Cr(acac)

PFT X CW _; Solvent. . $DCCl_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 6,600

D5/S.T. . 6.9 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 10.0 μs/dB; Size. . 8 K; Lock. . ^2H

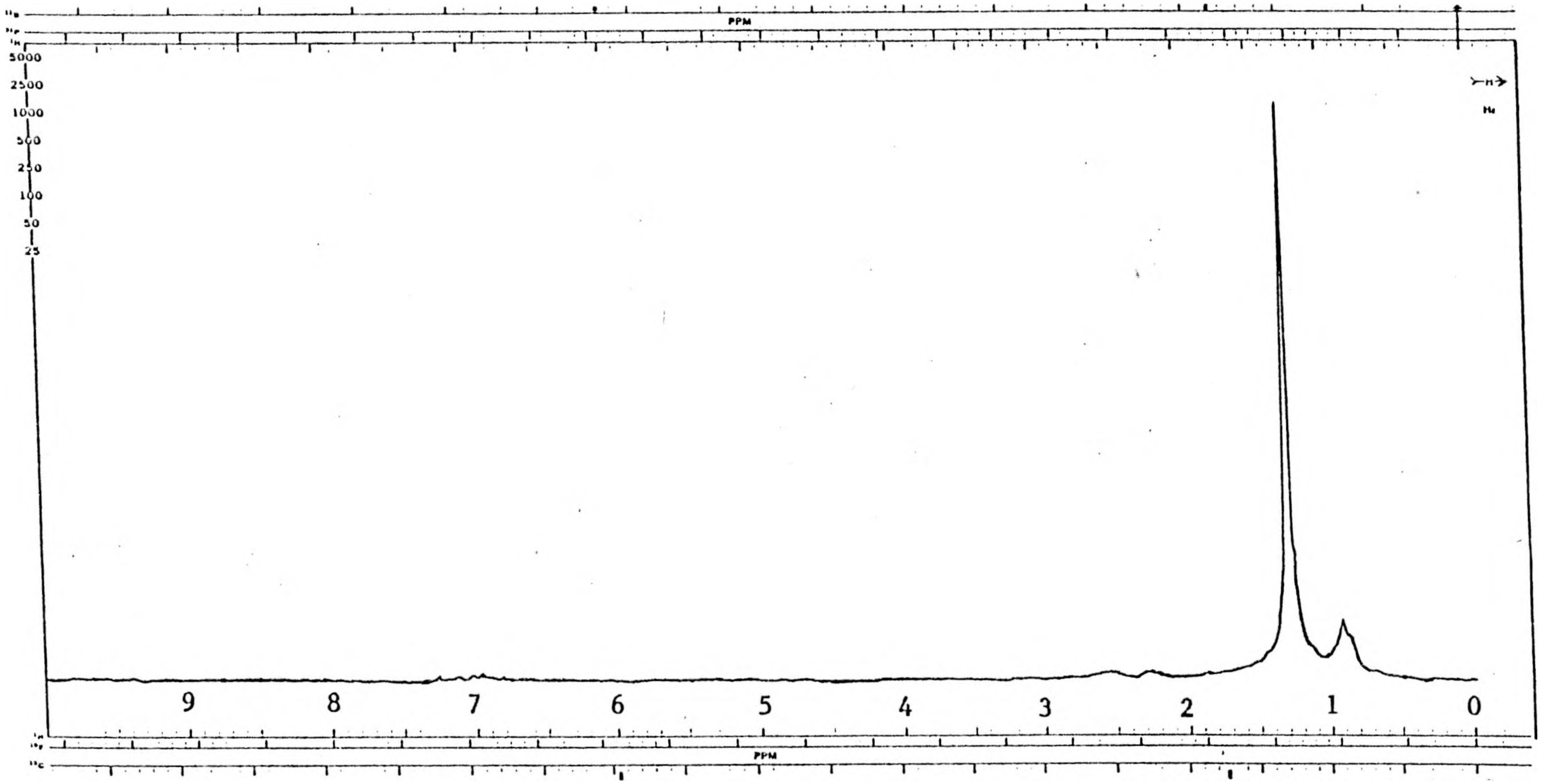
^{1}H NMR Spectrum of Oil, Gach Saran MA Concentrate 9-30-76 (see Table II)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 62 μs/dB; Size. . – K; Lock. . ^{2}H

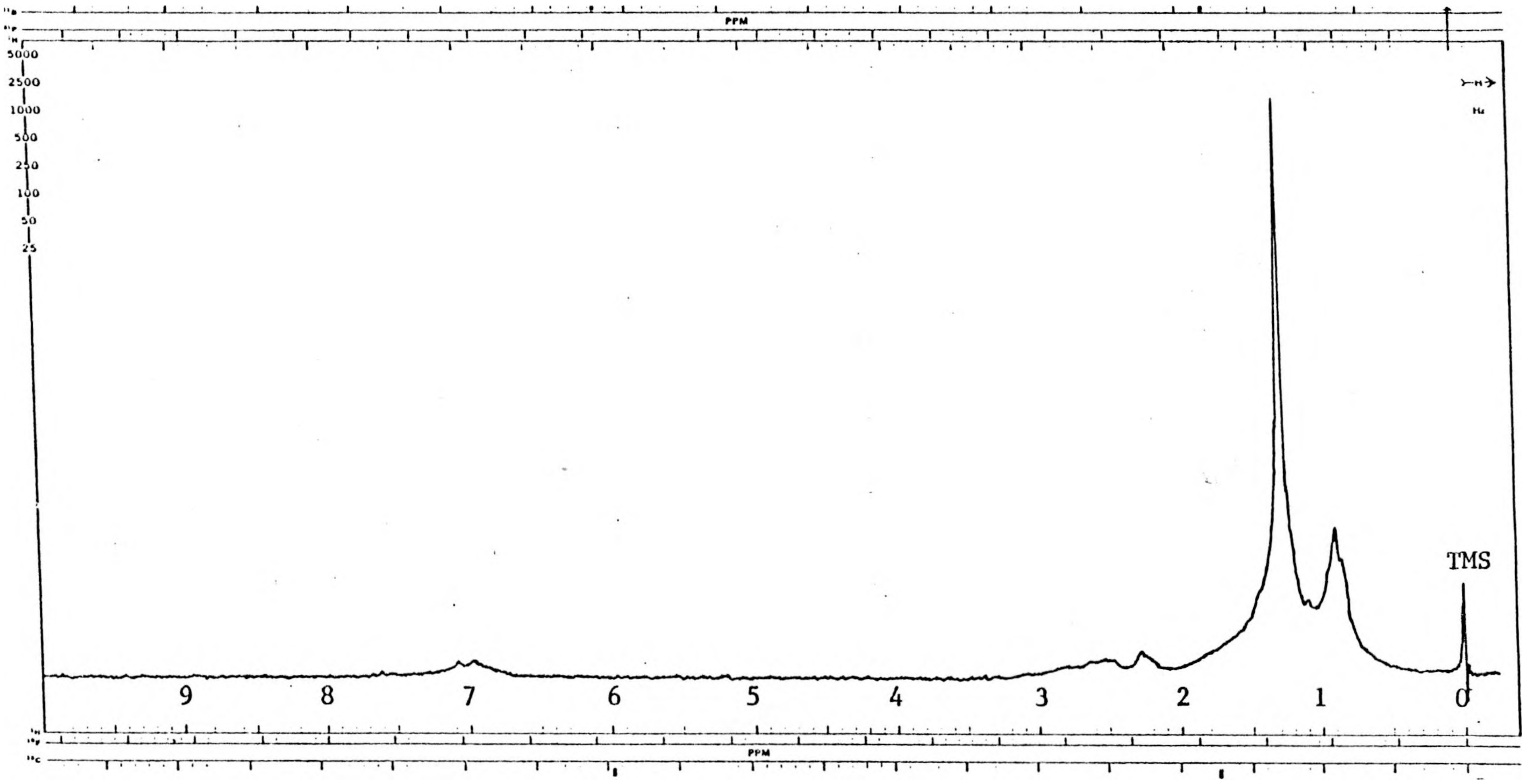
^{1}H NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #14 (see Table II)



PFT X CW _; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . ± 700 Hz; Acq/S.A. . 64

D5/S.T. . 2.0 s; S.O. . 45251 Hz; T. . 37 °C; P2/RF. . 5.7 μs/dB; Size. . 8 K; Lock. . ^{2}H

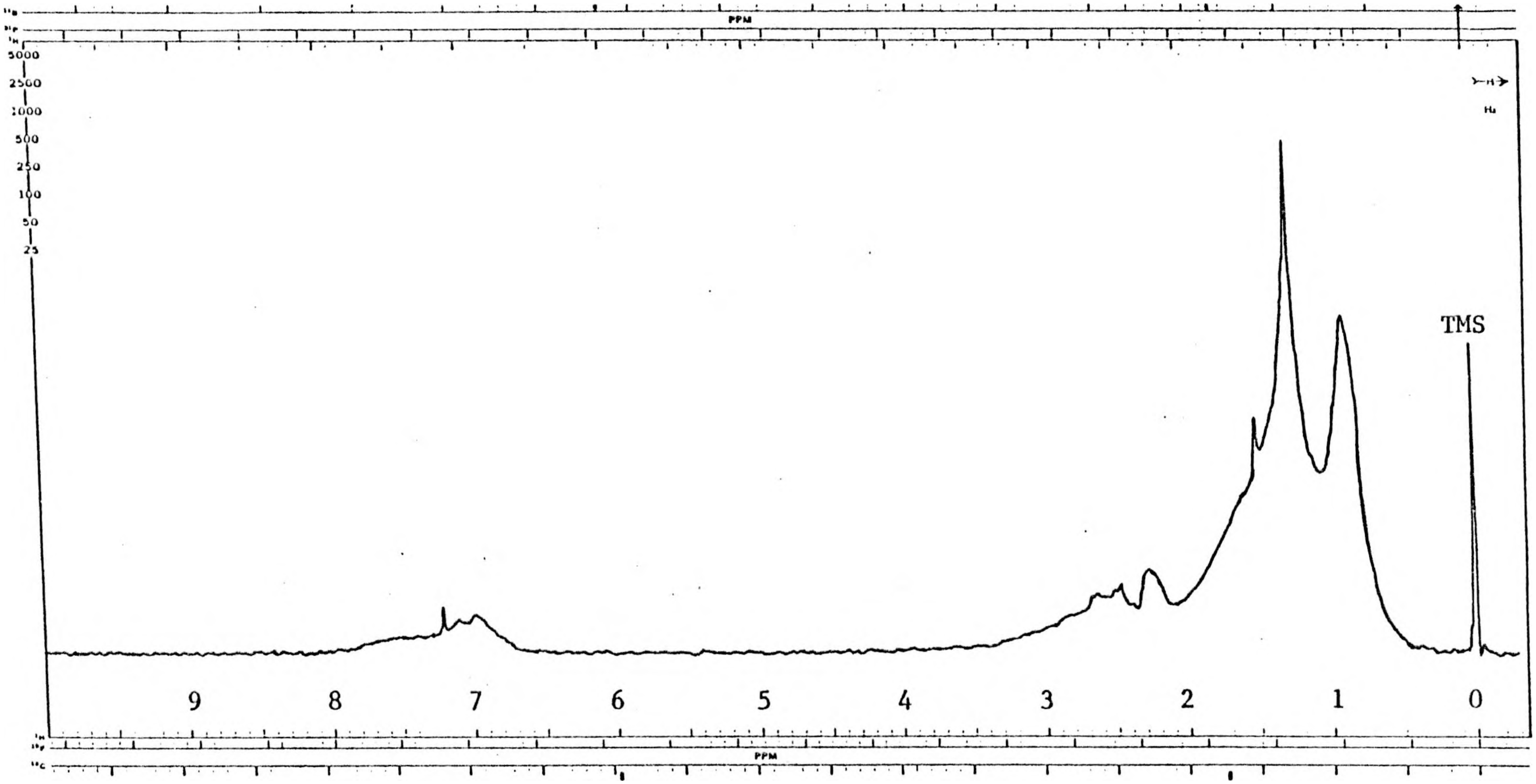
^{1}H NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #18 (see Table II)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37°C; P2/RF. . 57 μs/dB; Size. . -K; Lock. . ^{2}H

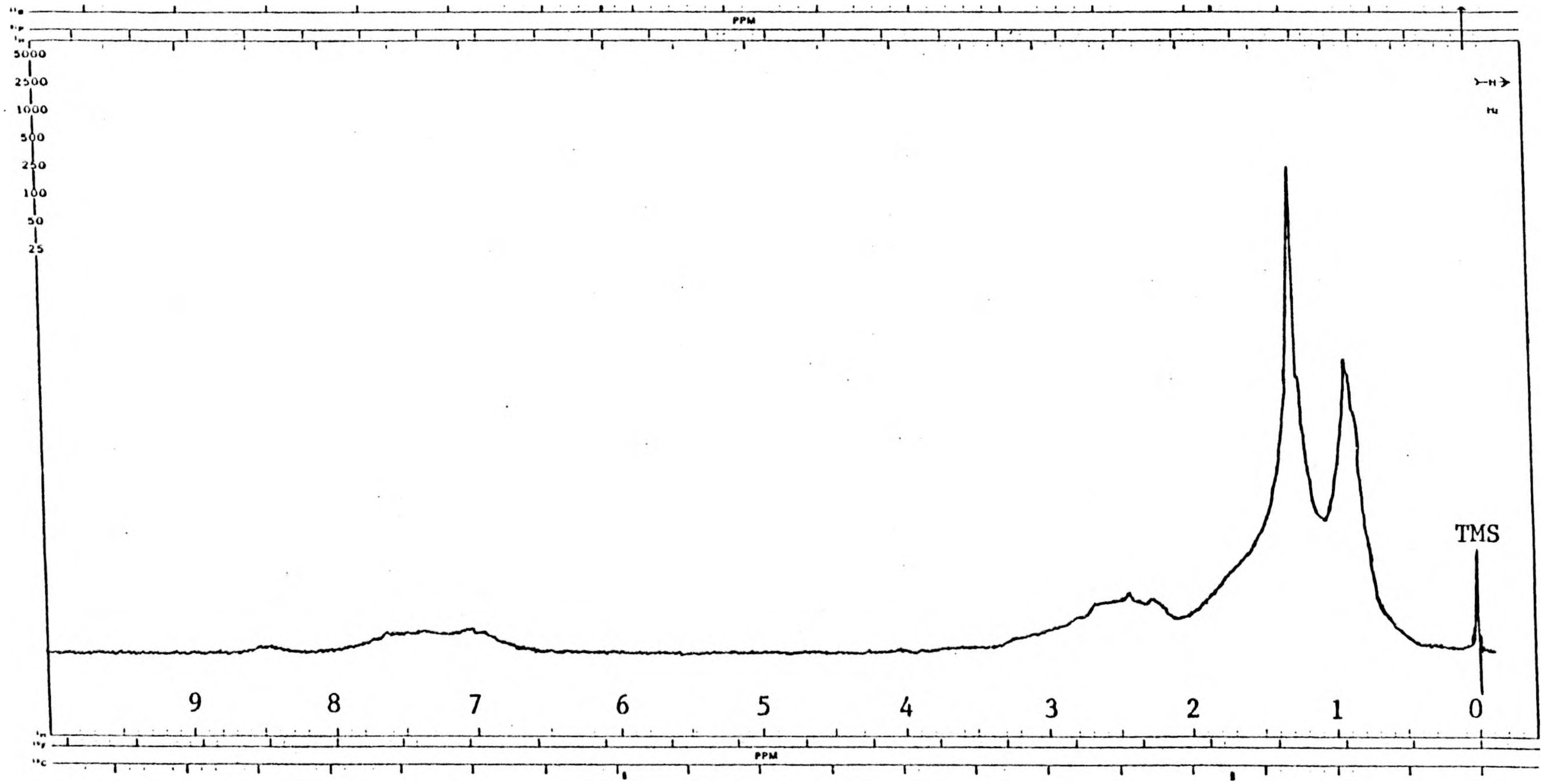
^{1}H NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #22 (see Table II)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

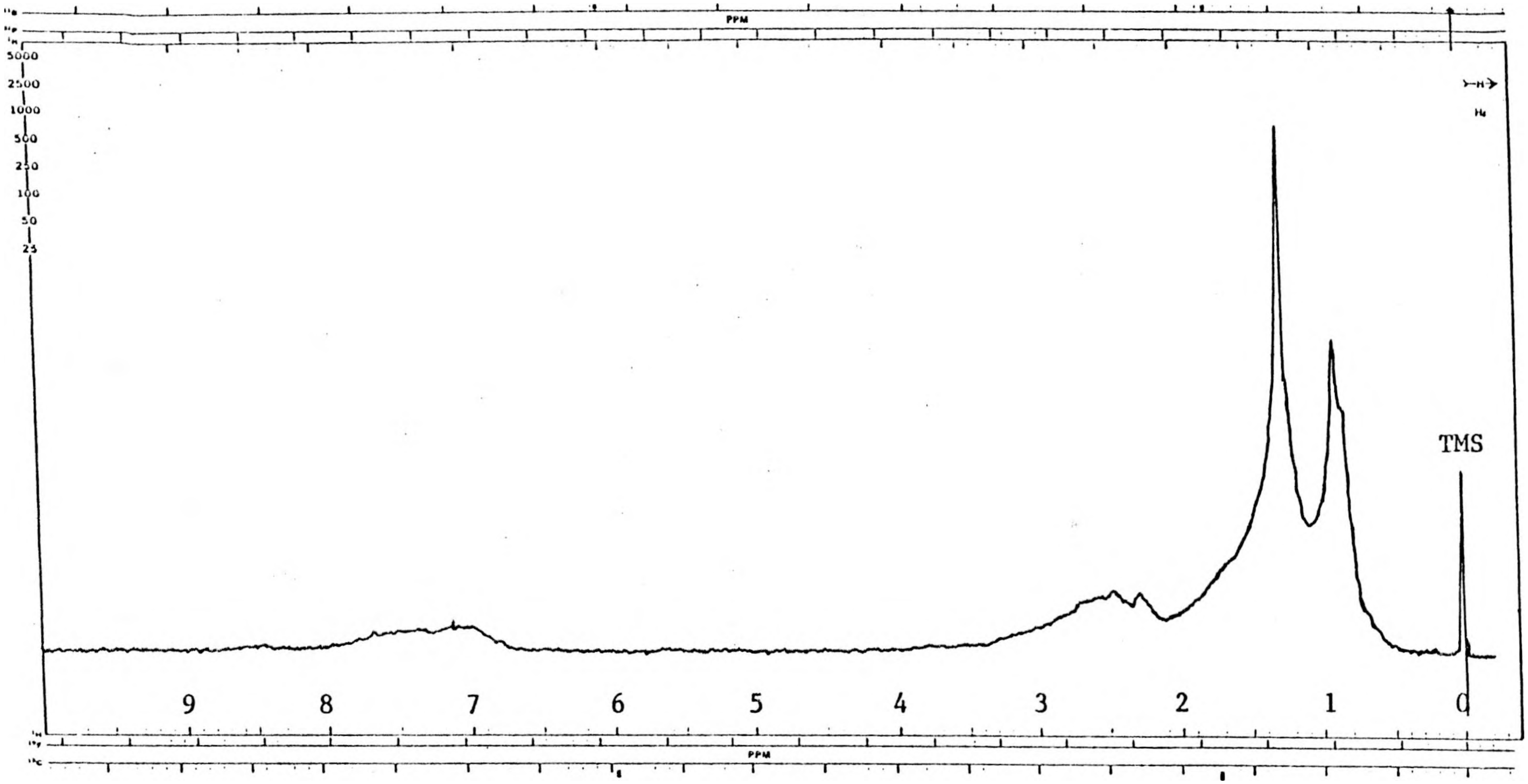
D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 63 μs/dB; Size. . - K; Lock. . ^{2}H

^{1}H NMR Spectrum of Oil, Wilmington DA Concentrates (see Table III)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. .100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0
D5/S.T. . 250 s; S.O. . 85772 Hz; T. . 37 °C; P2/RF. . 52 μs/dB; Size. . - K; Lock. . ^{2}H

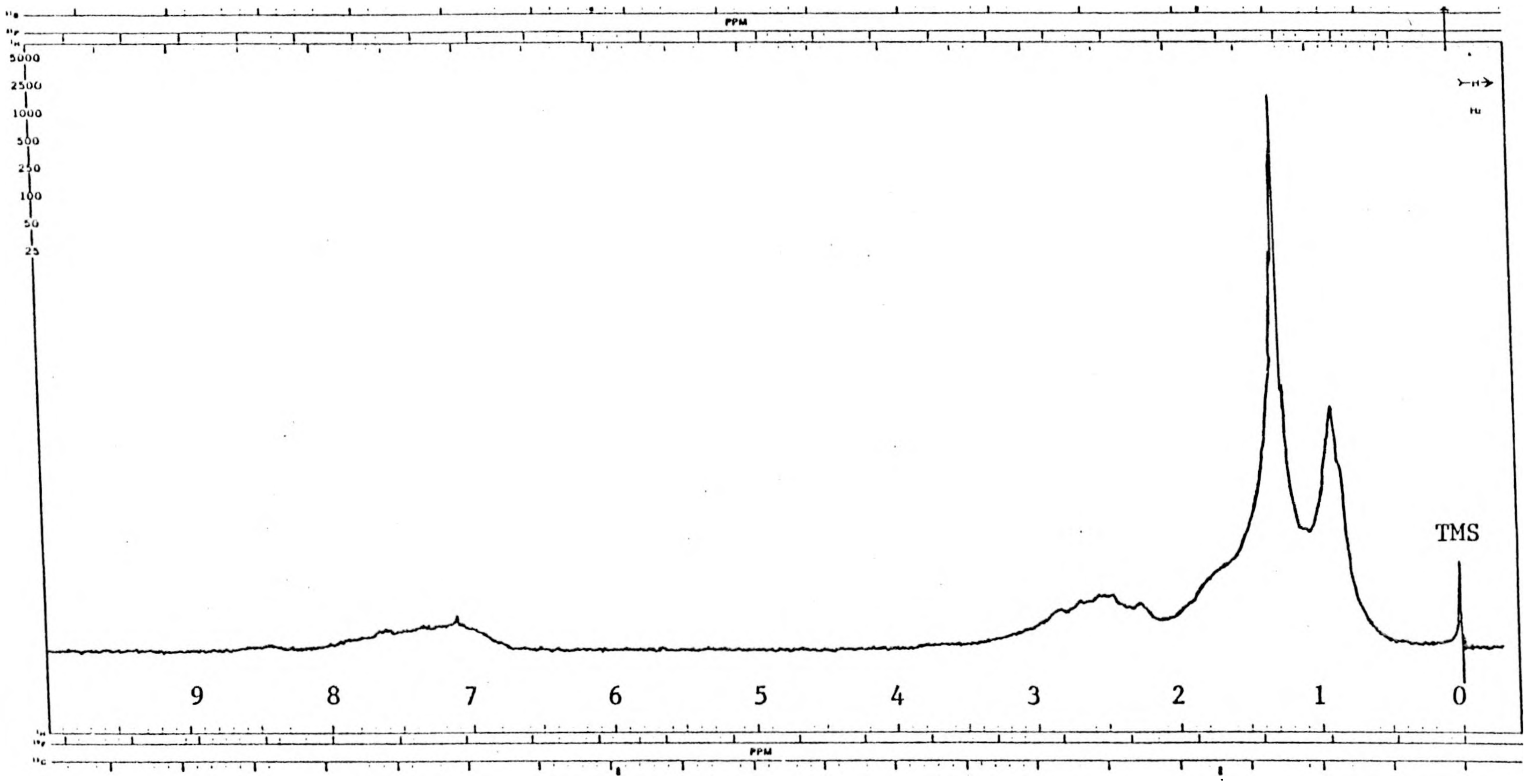
^{1}H NMR Spectrum of Oil, Wilmington DA GPC 211-76 #19 (see Table III)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 56 µs/dB; Size. . - K; Lock. . ^{2}H

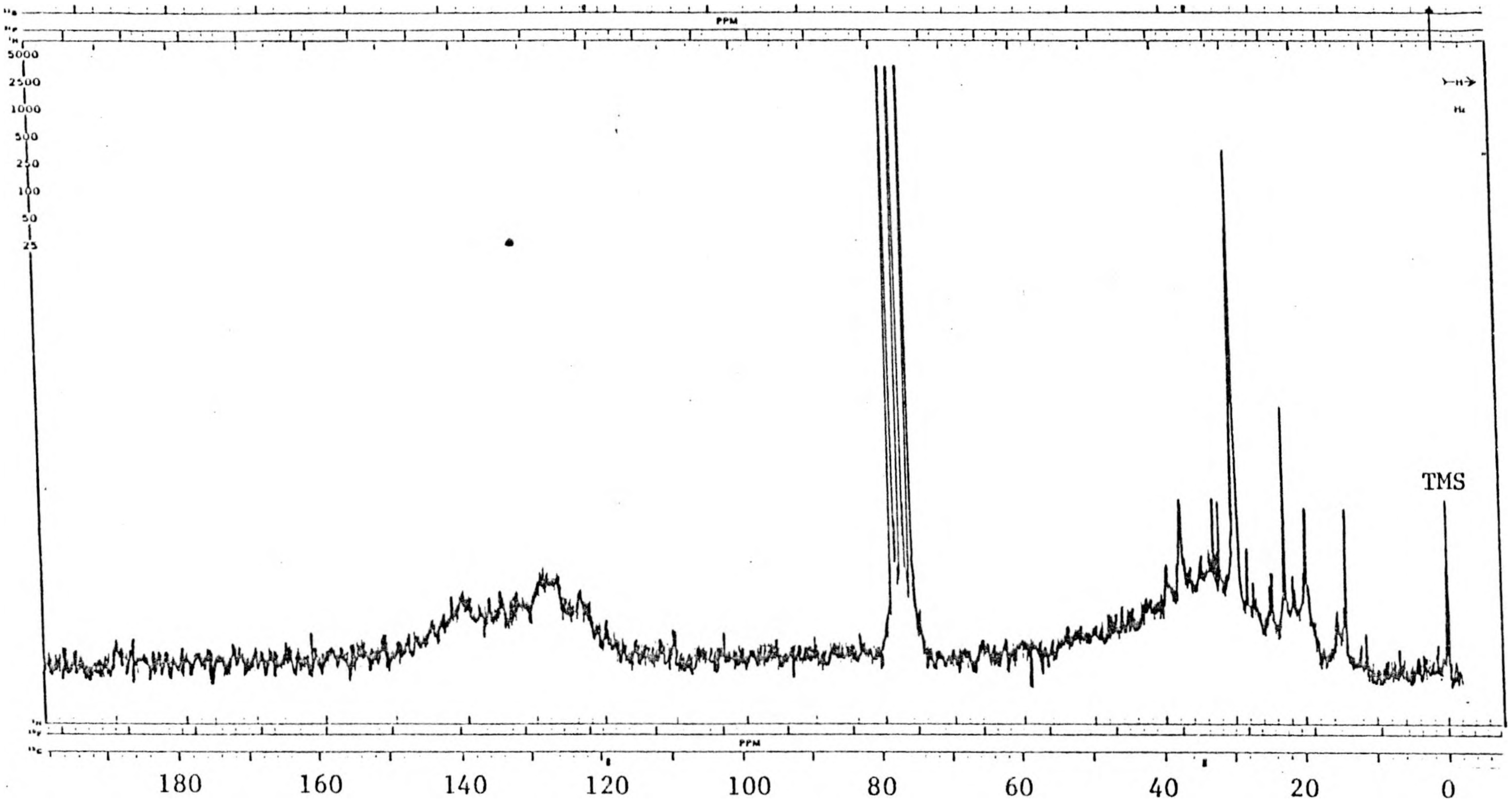
^{1}H NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #21 (see Table III)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 65 μs/dB; Size. . – K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Wilmington DA Concentrate 9-30-76 (see Table III)

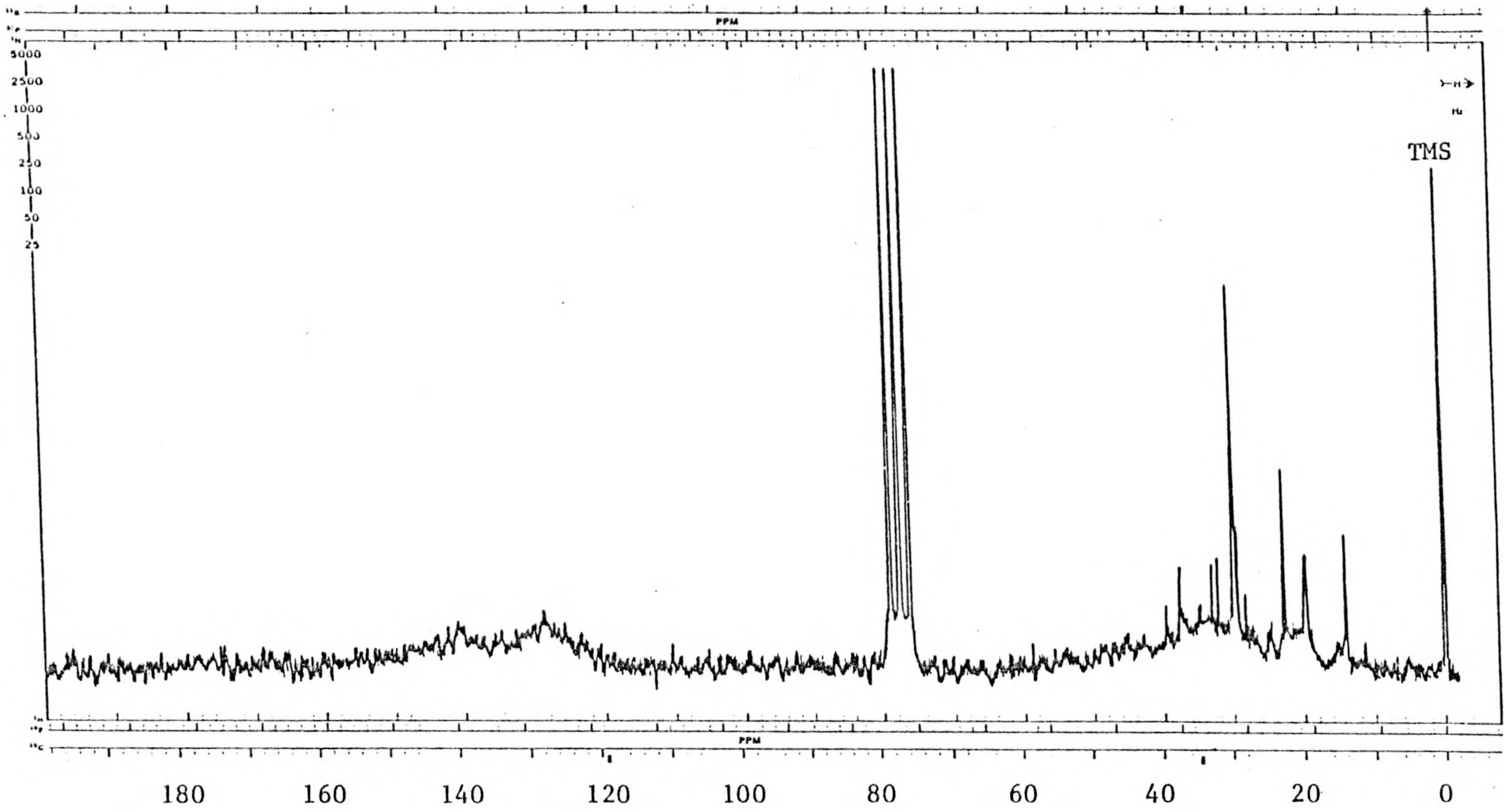


Gated Decouple (off delay) Sample contained 0.03 M Cr(acac)$_3$

PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 21,800

D5/S.T. . 6.0 s; S.O. . 35101 Hz; T. . 37°C; P2/RF. . 5.0 µs/dB; Size. . 8K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Wilmington DA GPC 211-76 #19 (see Table III)

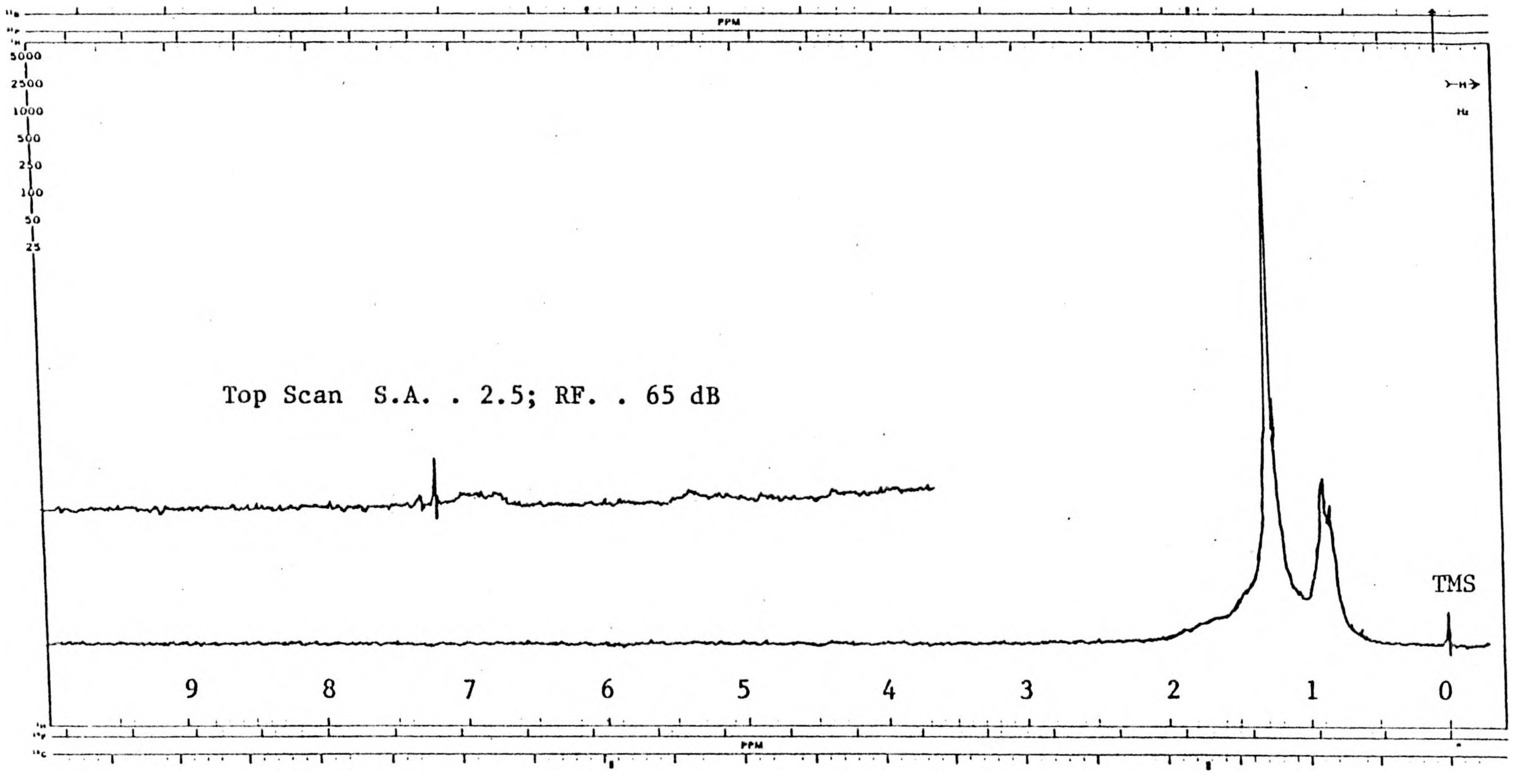


Gated Decoupled (off delay) Sample contained 0.03 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 7000

D5/S.T. . 7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 10 µs/dB; Size. . 8K; Lock. . ^{2}H

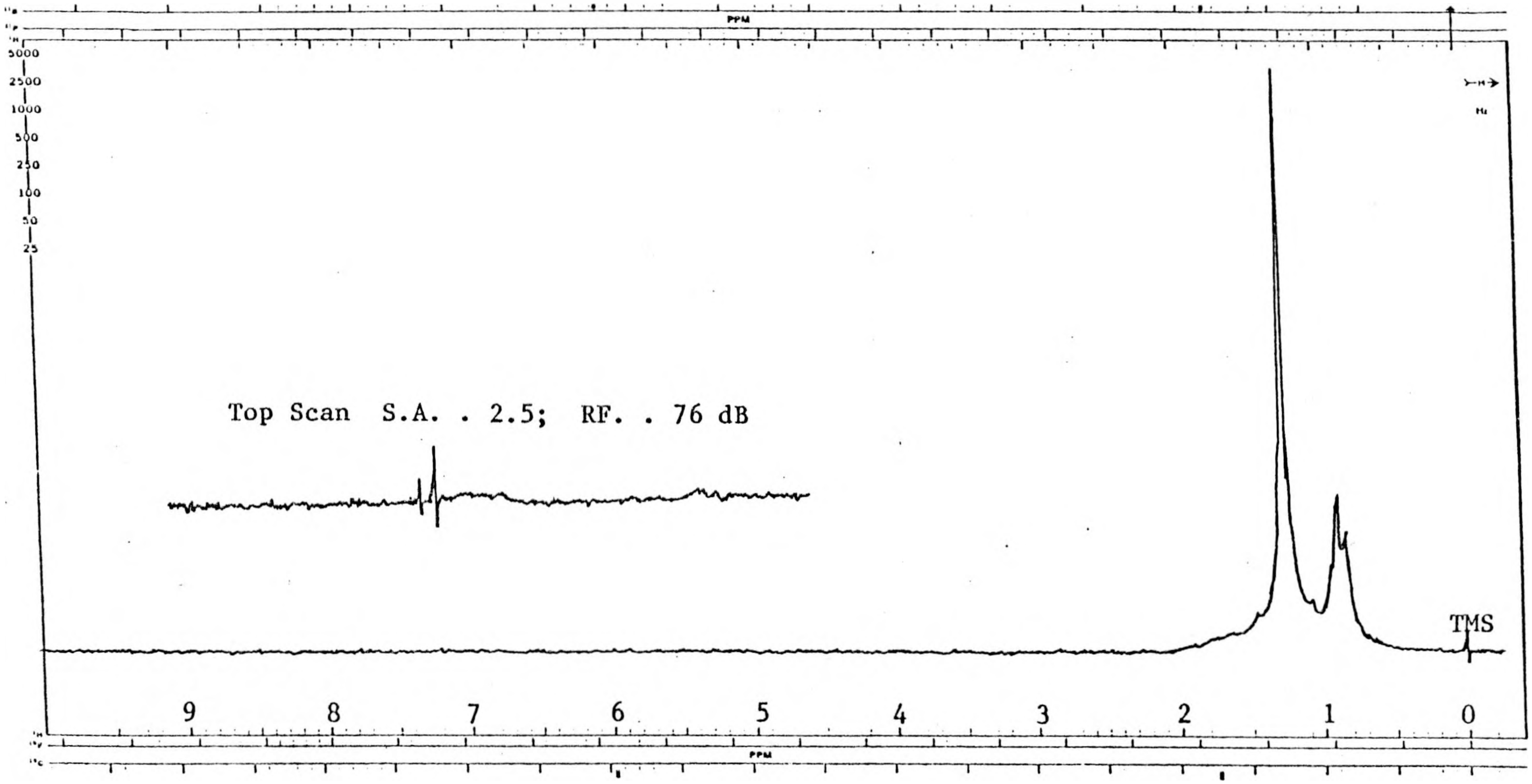
^{1}H NMR Spectrum of Oil, Saturate Fraction #1465 (see Table IV)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 40 μs/dB; Size. . -K; Lock. . ^2H

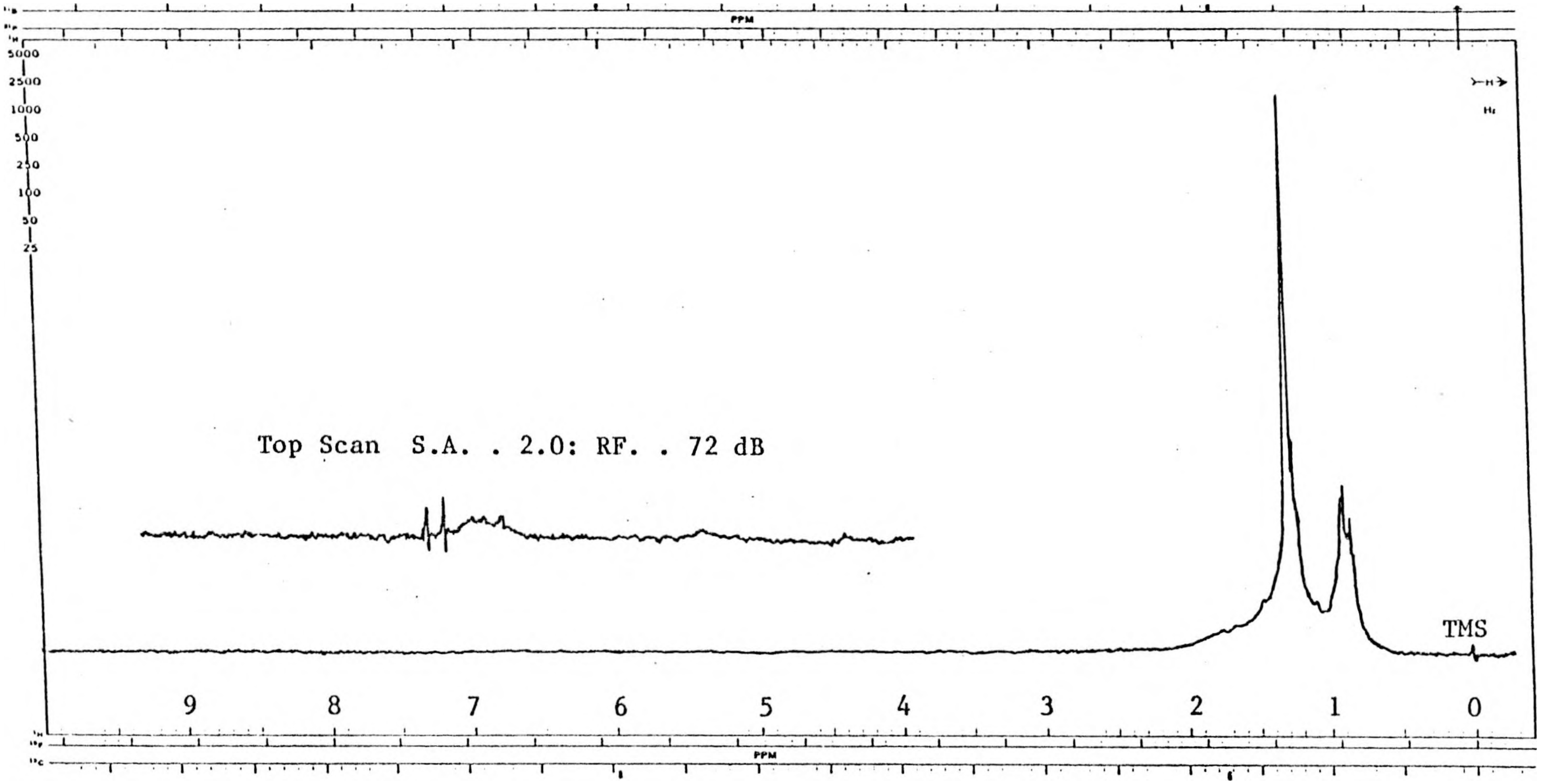
^{1}H NMR Spectrum of Oil, Saturate Fraction #1480 (see Table IV)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 40 μs/dB; Size. . - K; Lock. . ^{2}H

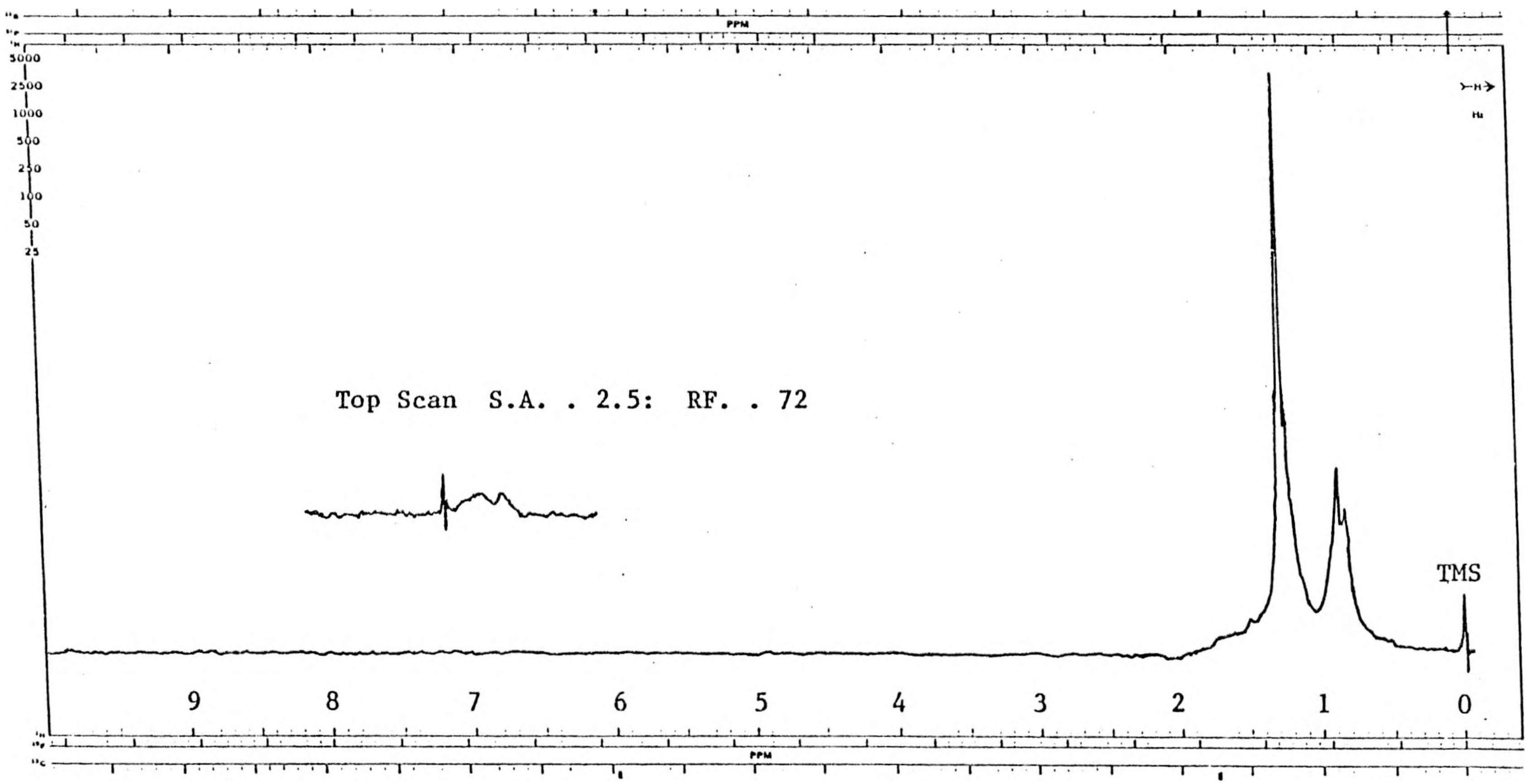
^{1}H NMR Spectrum of Oil, Saturate Fraction #1498 (see Table IV)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

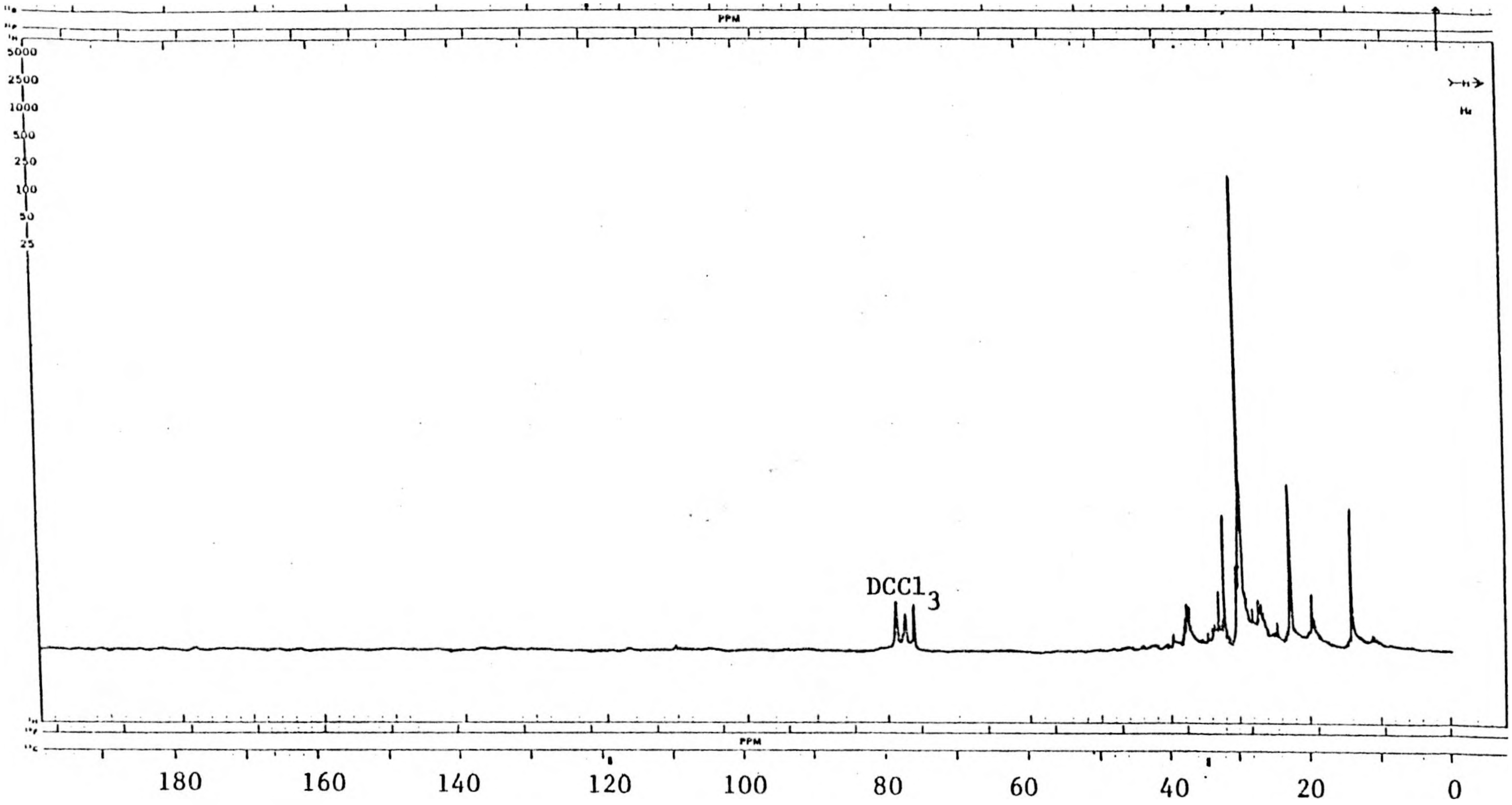
D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 65 µs/dB; Size. . – K; Lock. . ^2H

^{1}H NMR Spectrum of Oil, Satuarate Fraction #1570 (see Table IV)



PFT _ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0
D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 40 μs/dB; Size. . ; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Saturate Fraction #1570 (see Table IV)

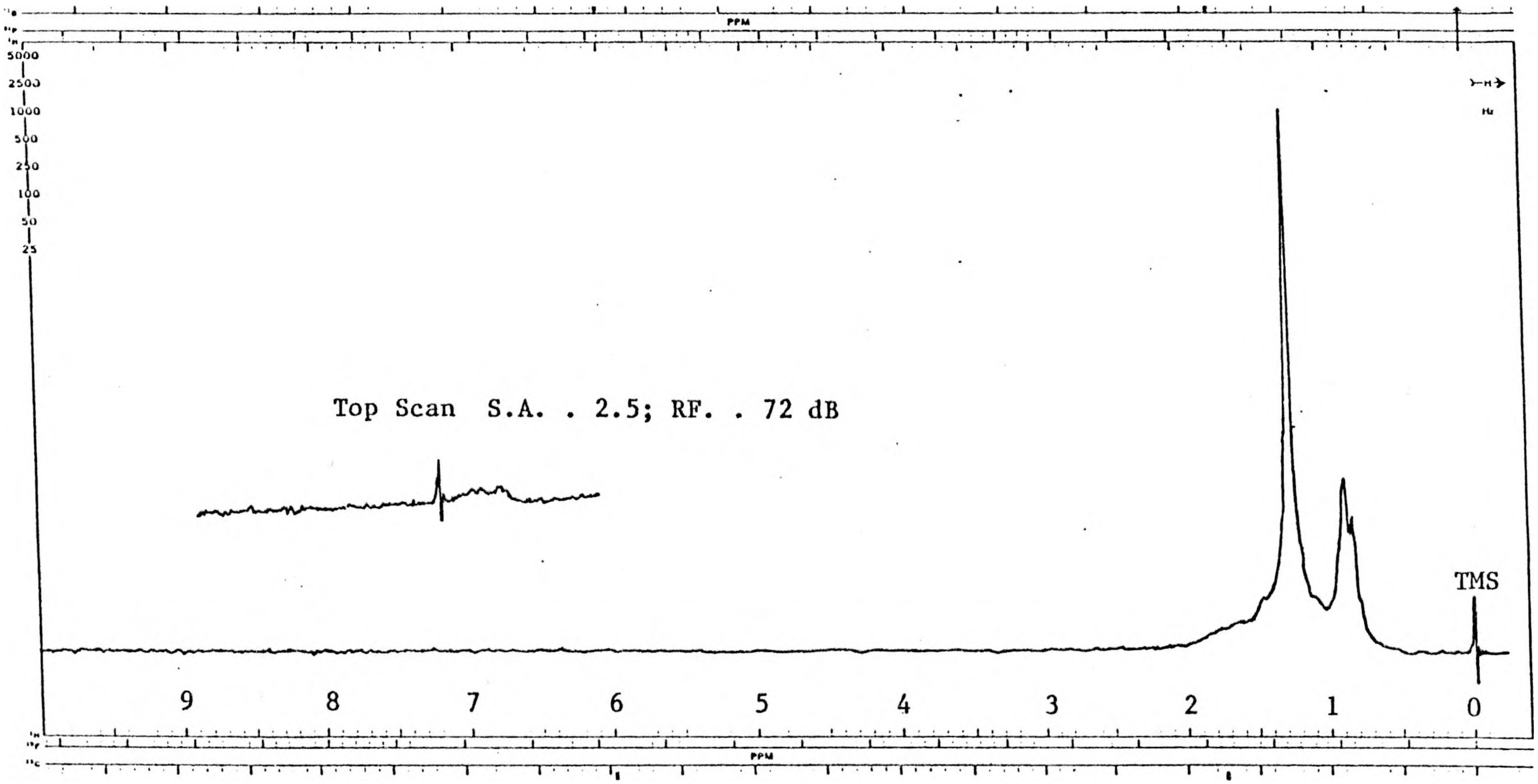


Gated Decoupled (off delay) Sample contained 0.03 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 112,300

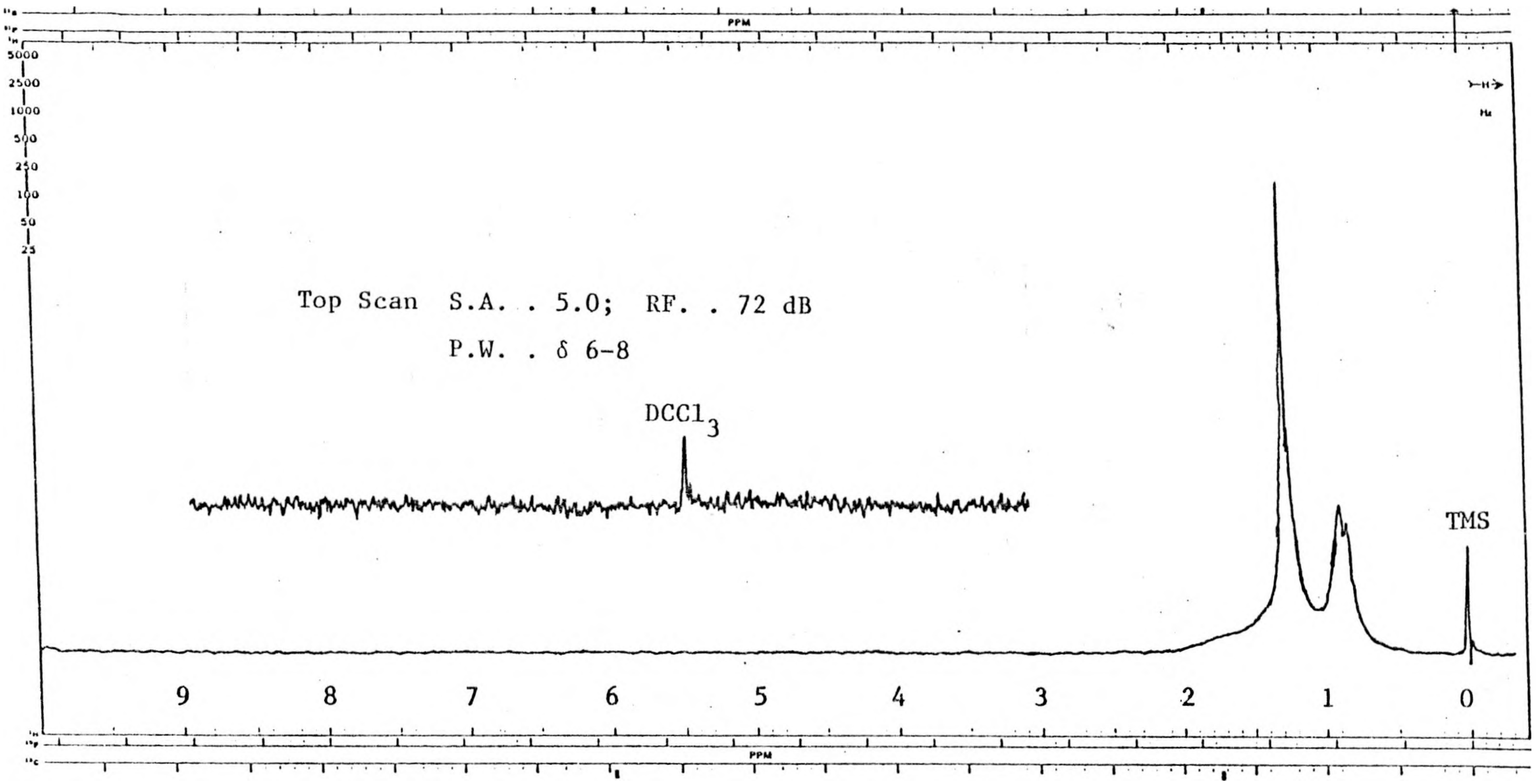
D5/S.T. . 0.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 10.0 µs/dB; Size. . 8K; Lock. . ^{2}H

^{1}H NMR Spectrum of Oil, Saturate Fraction #1553 (see Table V)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 2.0
D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 40 μs/dB; Size. . – K; Lock. . ^{2}H

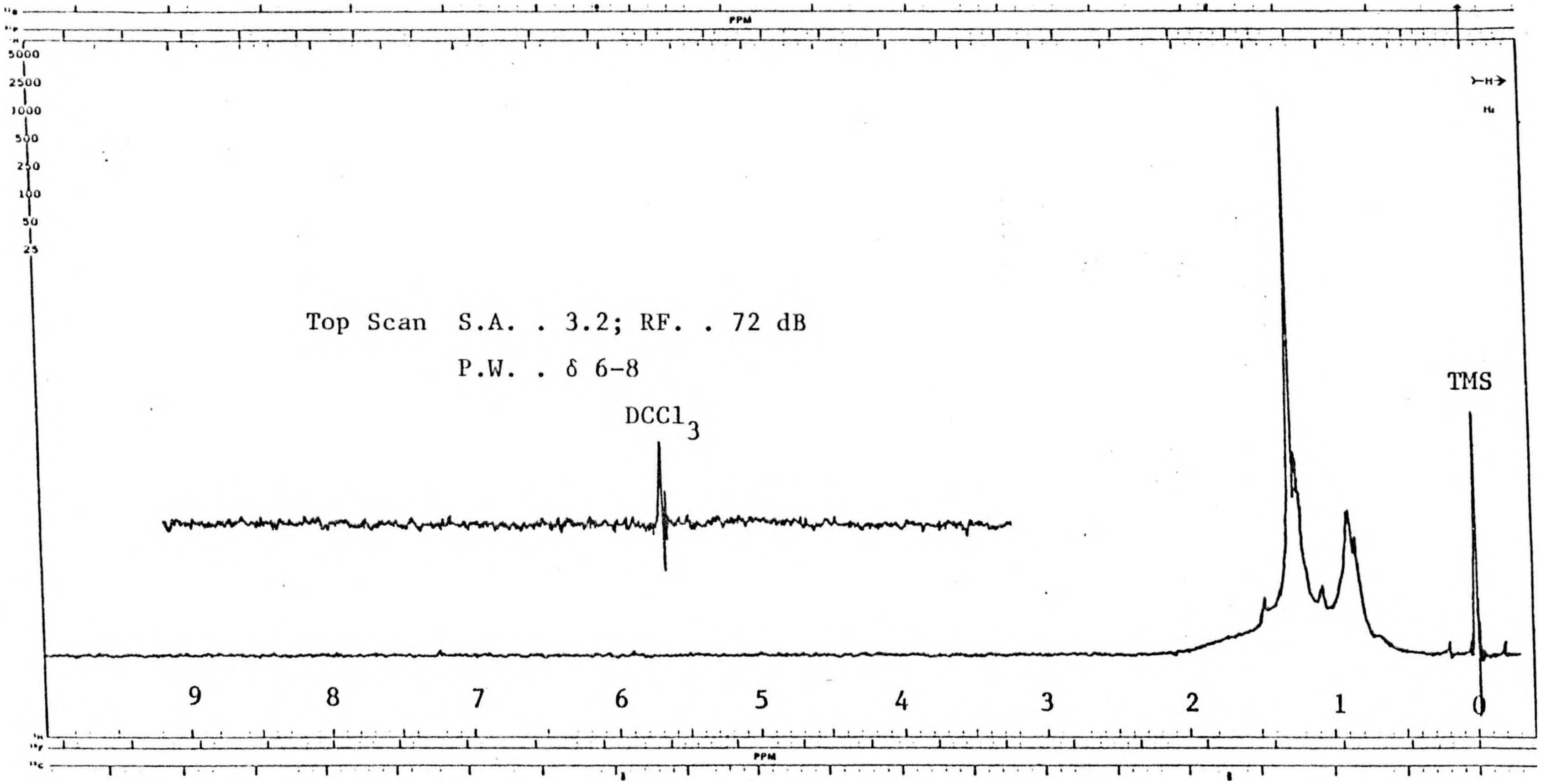
^{1}H NMR Spectrum of Oil, Saturated Fraction #1553-HPLC (see Table V)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 0.16

D5/S.T. . 250 s; S.O. . 85772 Hz; T. . 37 °C; P2/RF. . 64 μs/dB; Size. . - K; Lock. . ^{2}H

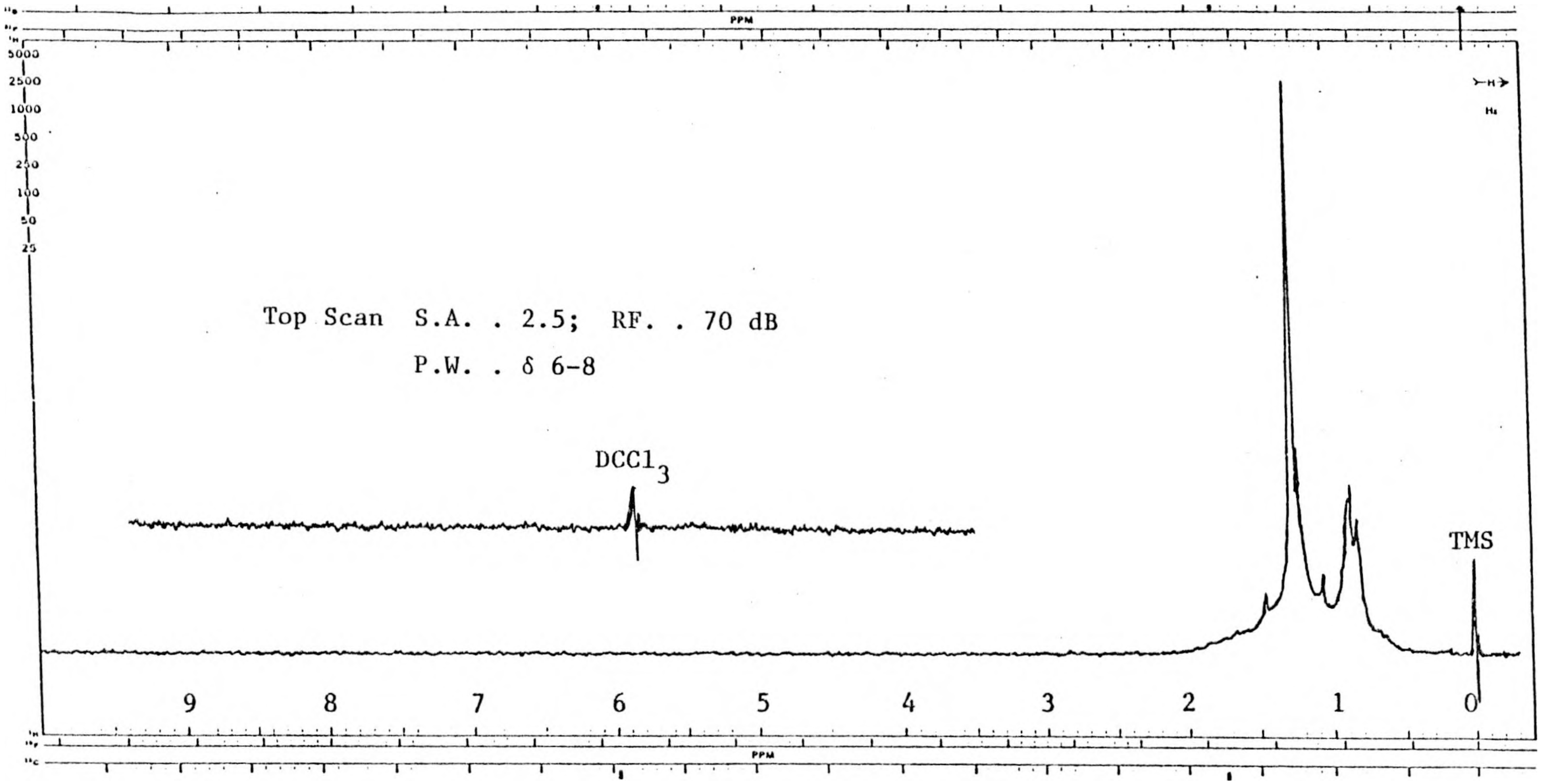
^{1}H NMR Spectrum of Oil, Run #39 1484 Fr. #1 (see Table V)



Top Scan S.A. . 3.2; RF. . 72 dB
P.W. . δ 6-8

PFT __ CW X; Solvent. . $DCCl_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0
D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 56 μs/dB; Size. . – K; Lock. . ^{2}H

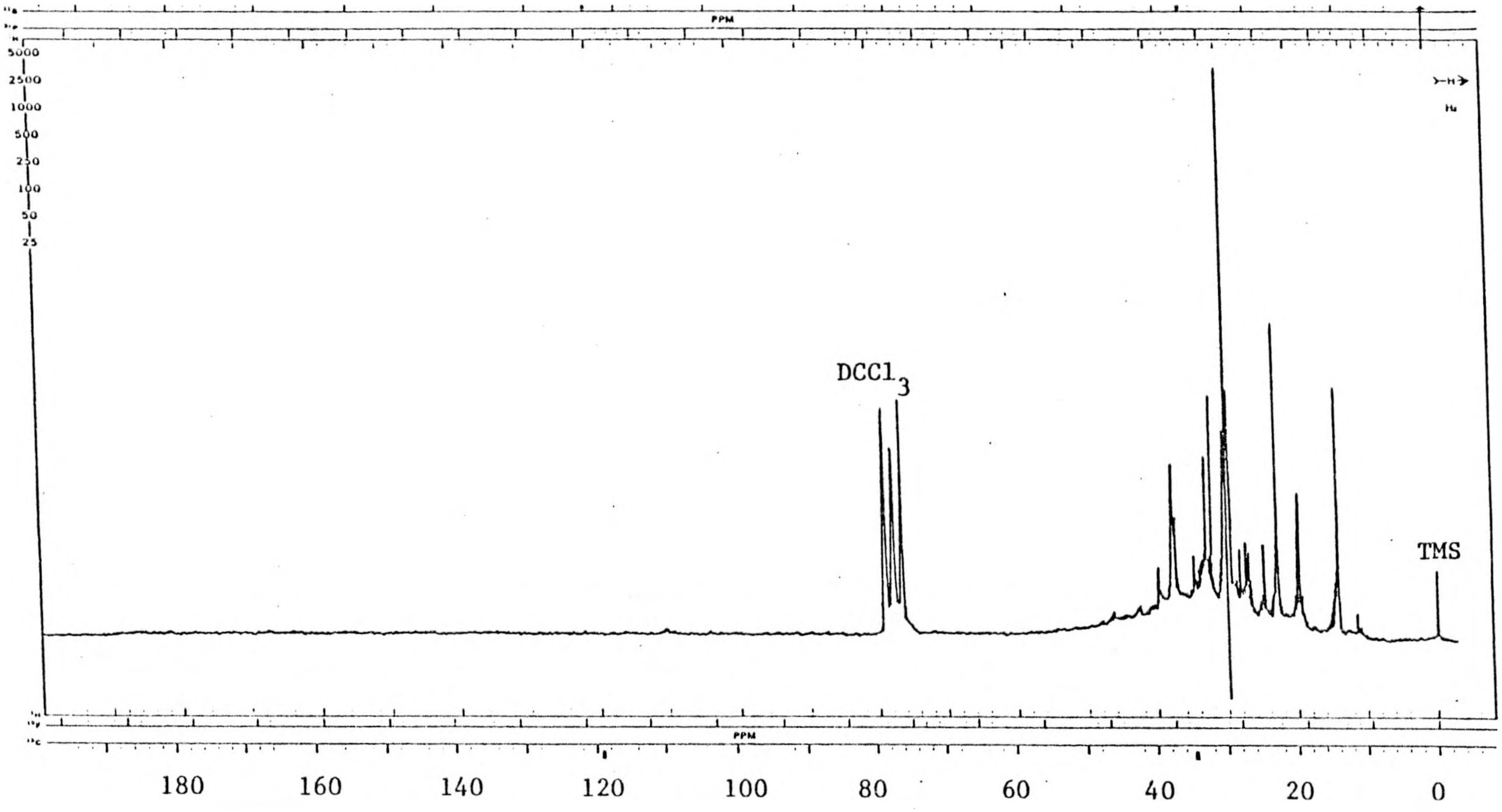
^{1}H NMR Spectrum of Oil, Sil-Al 355 Fr. #1 (PN) 1421 (see Table V)



PFT _ CW X; Solvent. . DCCl$_3$; S.F. . 100.1 Hz; P.W. . 1000 Hz; F.B. . 2 Hz; Acq/S.A. . 1.0

D5/S.T. . 250 s; S.O. . 85771 Hz; T. . 37 °C; P2/RF. . 52 μs/dB; Size. . - K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Saturate Fraction #1553 (see Table V)

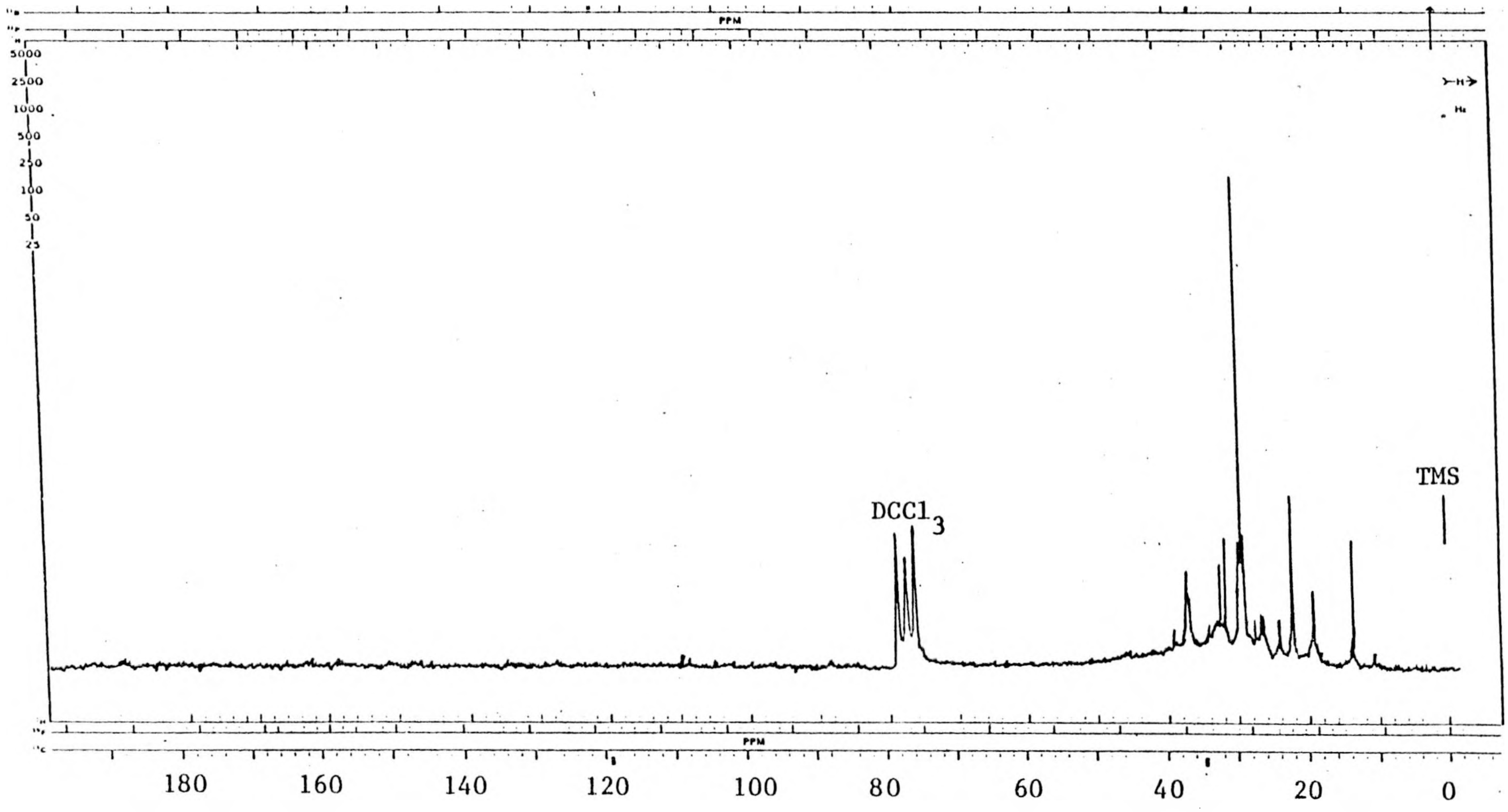


Gated Decoupled (off delay) Sample contained 0.03 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 35,228

D5/S.T. . 1.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 15.5 μs/dB; Size. . 8K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Saturate Fraction #1553-HPLC (see Table V)

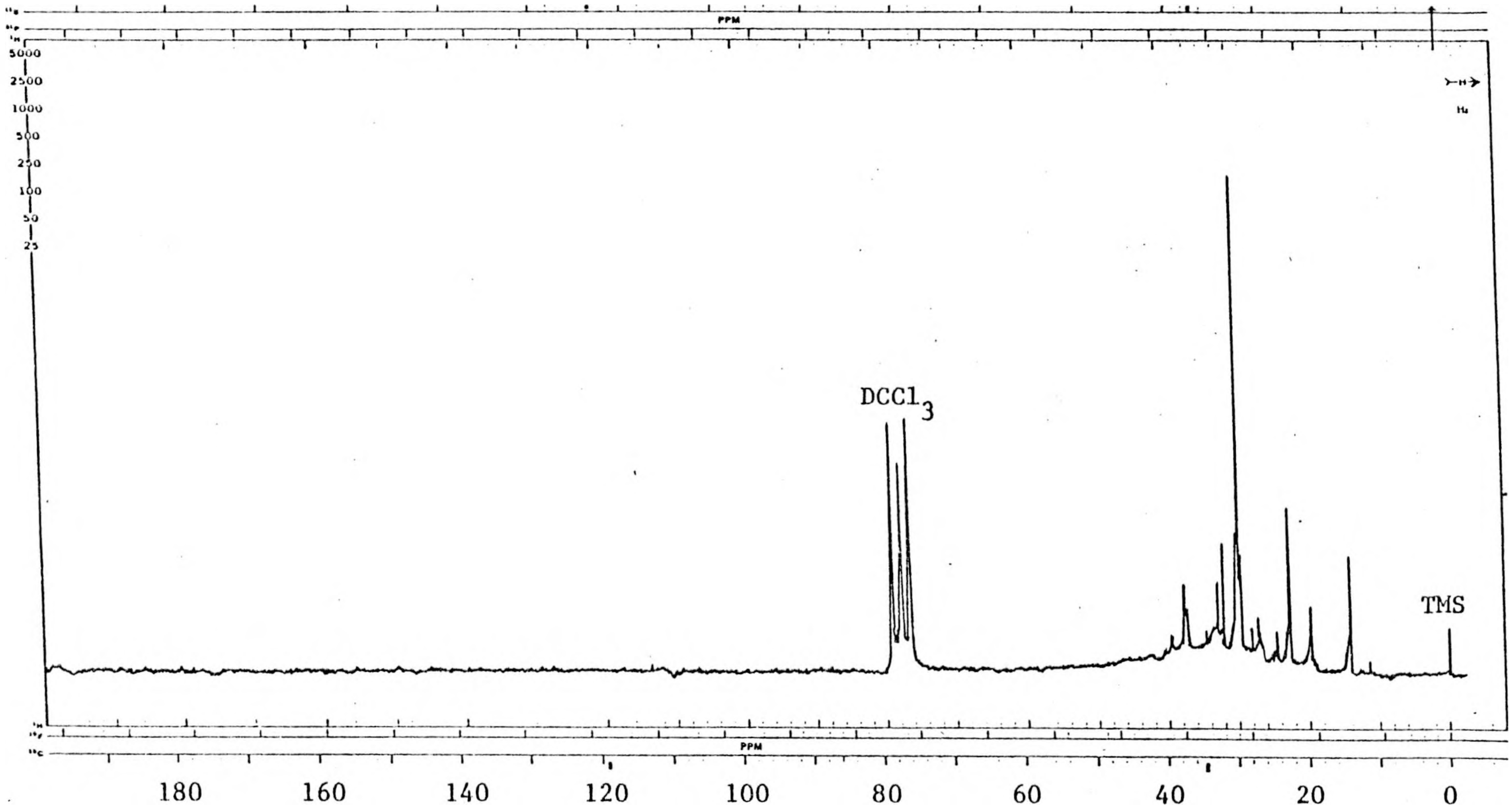


Gated Decoupled (off delay) Sample contained 0.05 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 27,000

D5/S.T. . 0.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 8.8 µs/dB; Size. . 8 K; Lock. . ^{2}H

^{13}C NMR Spectrum of Oil, Run #39 1484 Fr. #1 (see Table V)

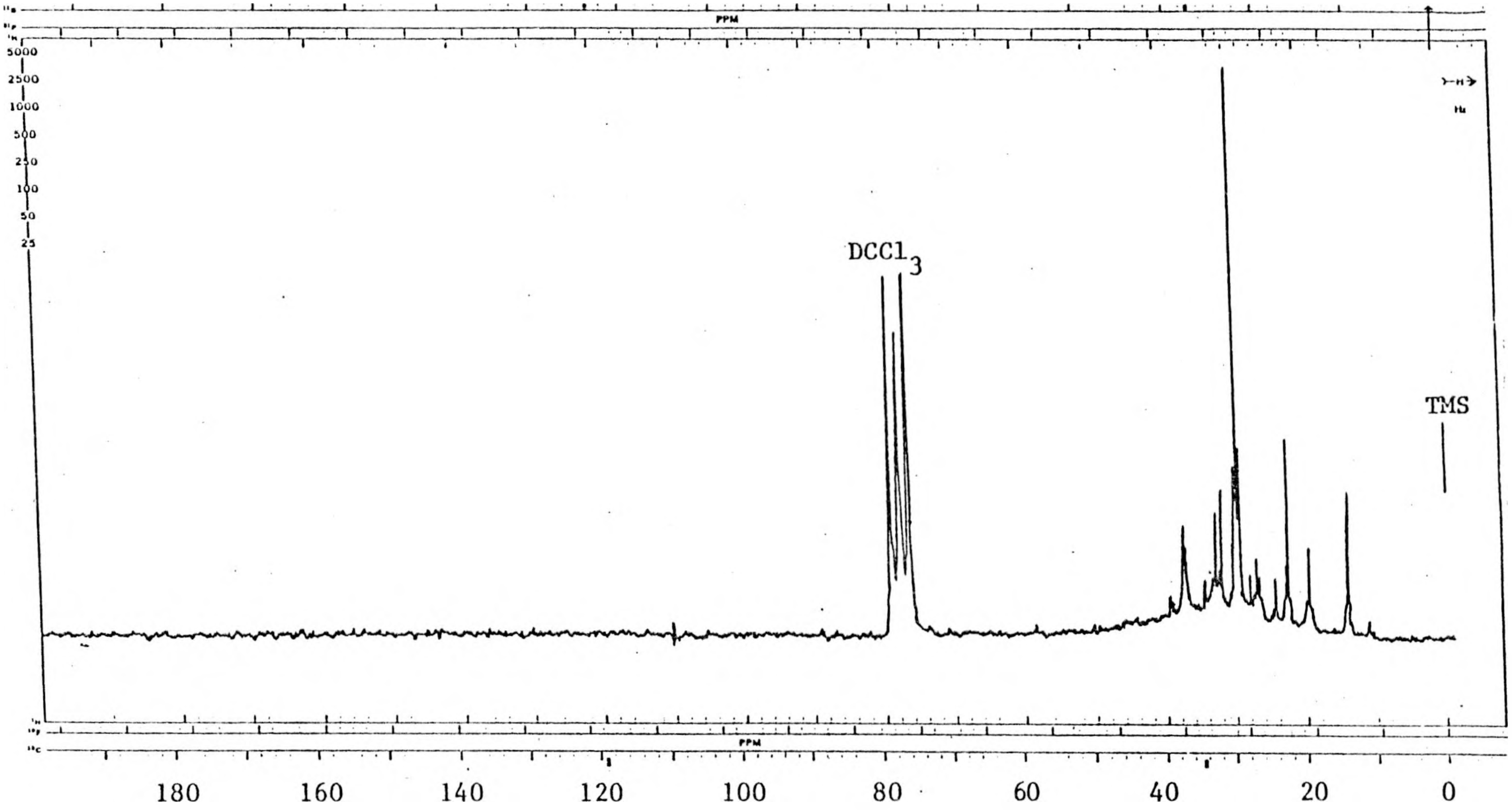


Gated Decoupled (off delay) Sample contained 0.05 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 27,000

D5/S.T. . 0.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 8.8 μs/dB; Size. . 8K; Lock. . ^2H

^{13}C NMR Spectrum of Oil, Sil-Al 355 Fr. #1 (PN) 1421 (see Table V)



Gated Decoupled (off delay) Sample contained 0.05 M Cr(acac)$_3$

PFT X CW _; Solvent. . DCCl$_3$; S.F. . 25.2 Hz; P.W. . 5000 Hz; F.B. . ± 3K Hz; Acq/S.A. . 26,000

D5/S.T. . 0.7 s; S.O. . 35101 Hz; T. . 37 °C; P2/RF. . 8.8 μs/dB; Size. . 8K; Lock. . ^{2}H

IV. WORK PLANNED FOR NEXT QUARTER

The thrust of the work for next quarter will be toward completion of the ^{1}H NMR analysis of the diaromatic fractions from Wilmington (211-76 #16, 19 and 24) and Gach Saran (207-76 #15, 21 and 24) distillates. As time permits, the accumulation of ^{13}C NMR spectra of concentrates and GPC fractions will continue. However, the direction of the 13_C NMR analysis will be somewhat dictated by the availability of instrument time, and the size of the individual fractions. Hence, ^{13}C NMR analyses of the concentrate fractions will progress faster that the analyses of the individual GPC fractions because the analysis time of the concentrates can be reduced by using a higher concentration of the ^{13}C NMR sample. The use of $Cr(acac)_3$ will, of course, aid in reducing the analysis time since it facilitates the relaxations process with carbon. It should be possible to complete most of the ^{13}C NMR analysis of the monoaromatic GPC fractions by the end of the next quarter.

V. ACKNOWLEDGMENTS

We are grateful to the Department of Chemistry at Oklahoma State University for use of the 100 MHz NMR facility and to the College of Arts and Sciences Research office for funds to purchase a 5 mm ^{13}C insert for use on this project. We are also indebted to the Research office of the College of Arts and Science at O.S.U. for the preparations of this report. Of course, special thanks is due the Department of Energy, Bartlesville Research Center, for funding the project including preparation of this report under contract EW-78-A-19-0001.