MHSMP-78-60

Dist. Category UC-25

A ^{13}C NMR Characterization of the Halthane Pre-Polymer System

George L. Clink

DEVELOPMENT DIVISION

NOVEMBER 1978

Process Development
Endeavor No. 101

P. O. BOX 30020
AMARILLO, TEXAS 79177
806-335-1581

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant

OPERATED FOR THE
Department of Energy
UNDER
U. S. GOVERNMENT CONTRACT EY-76-C-04-0487

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $4.00 ; Microfiche $3.00

A ^{13}C NMR CHARACTERIZATION OF THE HALTHANE PRE-POLYMER SYSTEM

George L. Clink

DEVELOPMENT DIVISION
(November 1978)

Process Development
Endeavor No. 101

ABSTRACT

A cursory ^{13}C NMR analysis of Halthane pre-polymer components was initiated for the purpose of establishing a data file for potential use as a product qualification base. A ^{13}C analysis of the hydrolysis of 4,4′-diphenylmethane diisocyanate (MDI) was initiated. Chloroform extraction of the cured polymer produced an approximate 1% removal of polymerized Halthane.

EXPERIMENTAL

The pre-polymer admixture components are designated by Bendix as the R component (hardener) and the T component (pre-polymer). The available literature described composition of these systems is as follows:

1. Halthane R Component

   Polymeg 1000 (polytetramethylene ether glycol) (85%)

   1,4-butanediol (10%)

   Quadrol [N,N,N′,N′-tetrakis(2-hydroxypropyl) ethylenediamine (5%)]

2. Halthane T Component

   Polymeg 1000 (polytetramethylene ether glycol) (47.6%)

   Polymeg 2000 (7.4%)

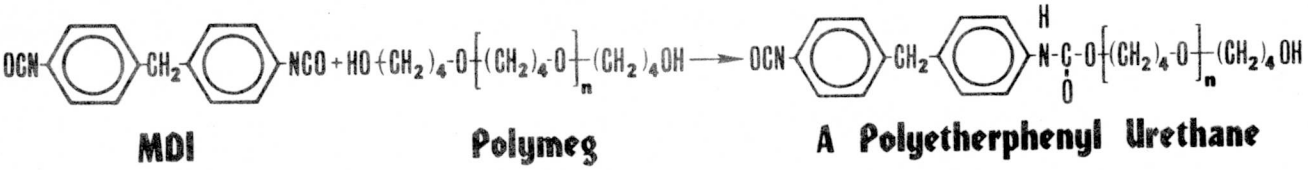
   MDI (4,4′-diphenylmethane diisocyanate) (45.0%)

^{13}C NMR analysis of the R components were run individually for the purpose of shift assignments. The composite R mixture was subsequently run and no problems were encountered with superposed peaks.

The individual materials, and subsequently the composites, were dissolved in deuterochloroform and analyzed in a 12 mm tube on a Nicolet NT-150 FT-NMR at 37.7350 MHz. The ^{13}C spectrum of the R component is presented in Fig. 1, with shift assignments given in Table I. Quadrol, although it has been spectrally analyzed, is not graphically included due to the combination of its lower percentage contribution to the admixture, and the appreciable number of its resonance lines. Upon low attenuation, the Quadrol resonances can be quite clearly seen, but the concomitant noise level generated produces a total spectrum quite poor in quality.

Individually, only the ^{13}C spectral data for MDI were necessarily acquired, as the remaining components of the T mixture are redundant to the R system results. Fresh, relatively unhydrolytically contaminated MDI was obtained from the MOBAY Chemical Corporation under the trade name Mondur M. The resulting spectra along with shift assignments are presented in Fig. 2, 2a and Table II.

The ^{13}C spectrum of the "T" component (20903T) made it immediately obvious that many of the spectral characteristics of the formulated mixture were significantly different from those expected from a spectral composite of Polymeg and MDI (Fig. 3). The single resonance at 153.6 ppm describes an appreciable degree of occurrence in the "T" system following the formulation of Polymeg and MDI. This resonance is due to the formation of the carboxy carbonyl of a urethane linkage, viz



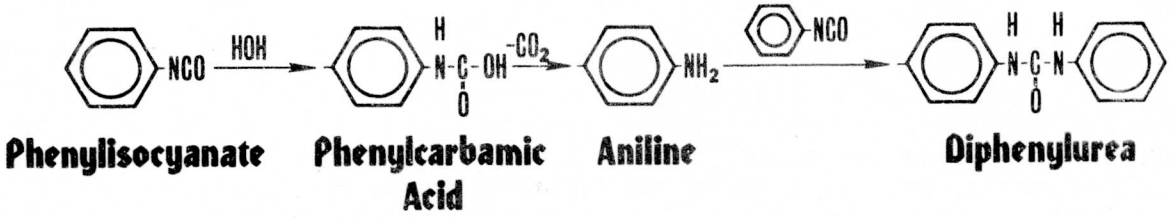
Inspection of the aromatic portion (Fig. 3a) shows proton coupled quaternary ring carbon triplets in two general groups at the following shifts:

(ppm)	(ppm)
138.8	131.3
138.1	131.0
136.6	
136.3	
135.6	
134.9	

The resonance lines from 138.8 to 134.9 describe molecular environment changes taking place at or near the isocyanate substituted quaternary ring carbon. The latter group (131.3, 131.0 ppm) originate with the methylene substituted quaternary ring carbon. The former are more clearly seen in Fig. 3b.

^{13}C analysis of the Bendix "T" component 770920-1B provides essentially identical results (Figs. 4, 4a, and 4b). The reaction effects are also evidenced in the spectral region containing the Polymeg (Fig. 3c).

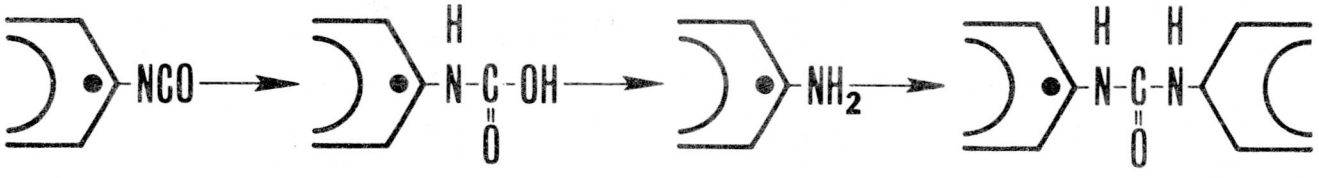
It is well established(*1*) that phenyl isocyanates are quite readily attacked by water, the reaction route being as follows:



Phenylisocyanate **Phenylcarbamic Acid** **Aniline** **Diphenylurea**

It would be expected that MDI, being the symmetric bis-methylene phenyl-p-isocyanate, would follow the same or a quite similar reaction path. Hydrolysis of MDI was effected by the dissolution of MDI in a 1% solution of H_2O/d-6 acetone, and monitoring the resultant system on NMR (see Figs. 5, 5a). In the spectra in Fig. 5, the appearance of additional quaternary ring carbons can be seen at 140.6, 139.0 and 135.6 ppm. These shifts are slightly different from those in the previous figures due to a solvent shift resulting from the use of d-6 acetone rather than chloroform as a solvent. A subsequent run on MDI in wet chloroform produced the same results but at a significantly slower rate and at slightly different shifts from those in acetone. Peak growth can be more clearly seen in Fig. 5a. Although not shown in the MDI hydrolysis spectra series, upon low attenuation the carbonyl carbons due to the formation of phenylcarbamic acid and diphenyl urea materials were present (180.9 and 163.8 ppm, respectively). Addition of $Cr(acac)_3$ to the solution decreases the carbonyl carbon relaxation time, increases its spectral intensity and is spectrally detectable. The nature of the several nitrogen substituted quaternary ring carbon resonances would be highly speculative at this point as to shift assignment without some addititional work in this area.

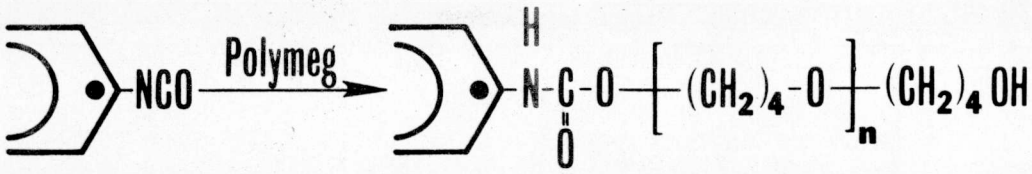
The hydrolysis of MDI, including the unhydrolyzed material itself, does produce four quaternary ring carbons of differing environment;



1 2 3 4

(*1*) *C. R. Noller, Chemistry of Organic Compounds (Saunders, 1966), pp 529, 819.*

The formation of a polyetherphenyl urethane produces additional magnetic and chemical environments.



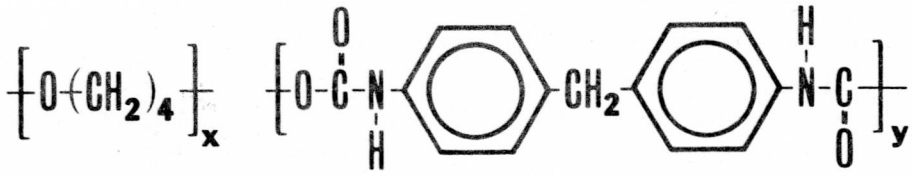
5

The quaternary resonances at 131.3 and 131.0 are due to the methylene substituted quaternary ring carbon. The fact that two resonances are seen would indicate a substantial affect on the ring characteristics being exerted by one (or more) of the resulting MDI and MDI/polymeg products.

A significant change in the character of the protonated ring carbons can be seen in the appearance of peaks at 118.6, 124.4, and 129.0 ppm (Fig. 6).

The compositional consistency among the various lots of the T component can be seen in Fig. 7, a spectral comparison of the isocyanate quaternary ring carbon region. The variance in the chemical shift of the quaternary isocyanate ring carbon of MDI is due to the admixture/solution variation between the T component as opposed to MDI alone in deuterochloroform.

Previous toluene extractions of the cured Halthanes have resulted in yields of approximately 1%(2). A development formulated Halthane, made up of Bendix Lot No. 770920-1B (T component) and Bendix Lot No. 7709192E (R component) was cured at 50 C (122 F) for four hours. The resultant polymer (40 g) was freeze ground and subsequently underwent extraction with 300 mℓ of spectrograde chloroform on a mechanical shaker. The filtered resultant solution was evaporated to dryness (21 C vacuum), taken up in a sufficient amount of deuterochloroform, filtered, and the ^{1}H and ^{13}C NMR information obtained. The resultant spectra show the extract to be Halthane polymer(s). The empirical ratio of the polymer units was approximately 10/1, viz



$$\frac{X}{y} = 9.97$$

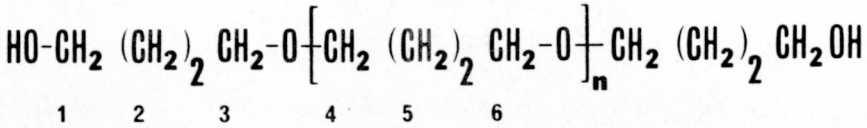
(2) *P. A. Foster, Development Division, Pantex (Unpublished data). This work being reported is in conjunctive support of a Halthane compatibility study by P. A. Foster.*

COMMENTS

Additional work in this area is suggested, predicated on the acquisition of a 20 mm ^{13}C probe and a 16K word data table increase, expected in early fiscal year 1979. The presence of the several quaternary ring carbons, their identification, and the effect of their presence on final product quality could prove to be important. T_1 (spin-lattice) measurements of the Halthane extracts among various lots might also prove informative, should the molecular size of the extract constituent(s) not produce T_1 values below useful measurable values.

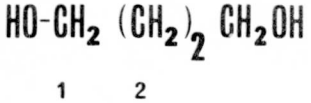
Table I. ^{13}C Shift Assignments for Halthane R Component

Polymeg (Polytetramethylene Ether Glycol)



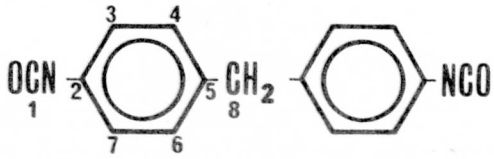
Assignment	Chemical Shift (ppm, TMS)
C_1	61.2
C_2	28.9
$C_{3,4,6}$	69.9
C_5	25.9

1,4-Butanediol



Assignment	Chemical Shift (ppm, TMS)
C_1	61.3
C_2	29.0

Table II. ^{13}C Shift Assignments for 4,4'-diphenylmethane diisocyanate (MDI)



Assignments	Chemical Shift (ppm, TMS)
C_1	124.7*
C_2	138.4
$C_{3,7}$	124.9*
$C_{4,6}$	130.0
C_5	131.6
C_8	40.7

**The isocyanate carbon (C_1) is superposed by the meta methylene ring carbons ($C_{3,7}$) in the proton decoupled spectrum, but upon proton coupling is readily seen at 124.7 ppm.*

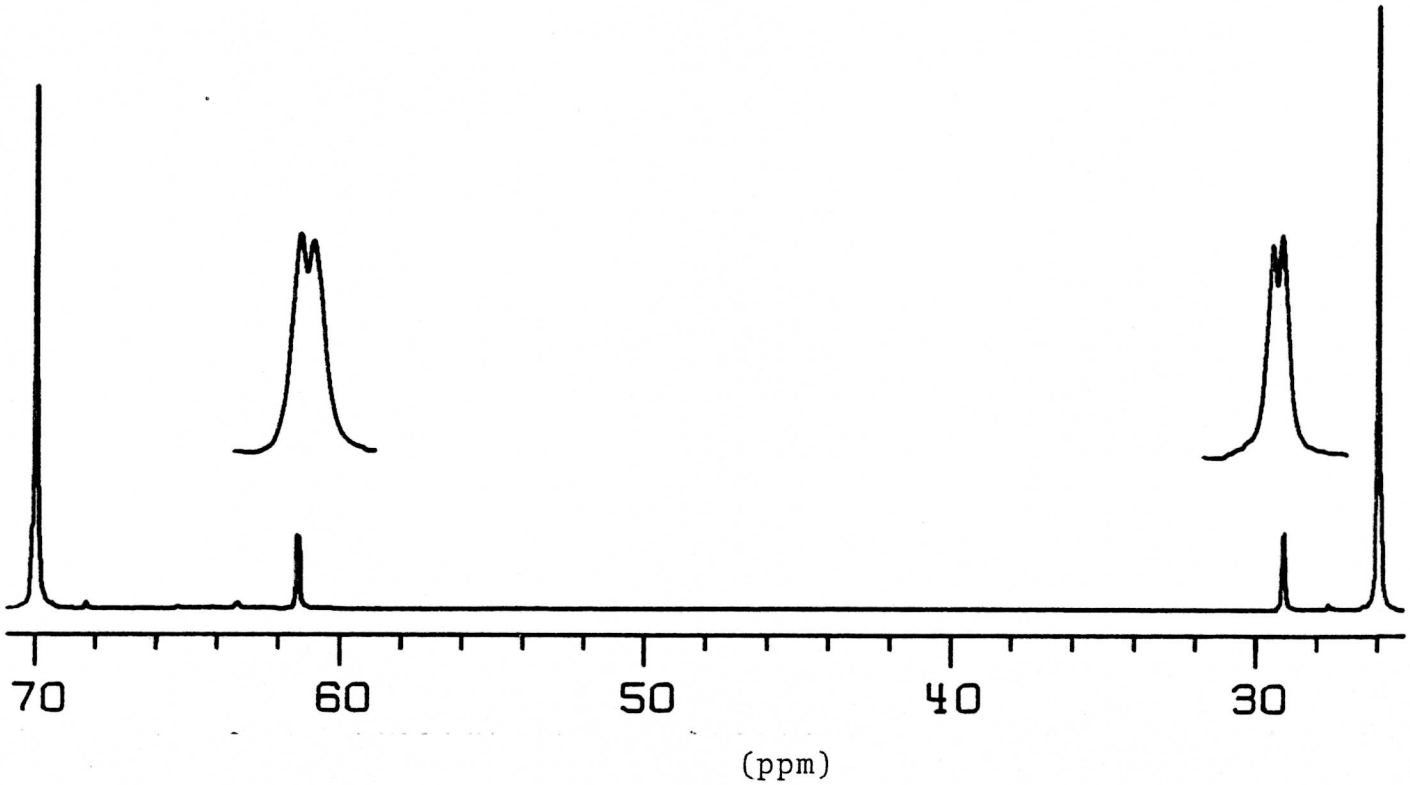


Fig. 1. ^{13}C Spectrum of Halthane 20903R, in $CDCl_3$ (Proton Decoupled)

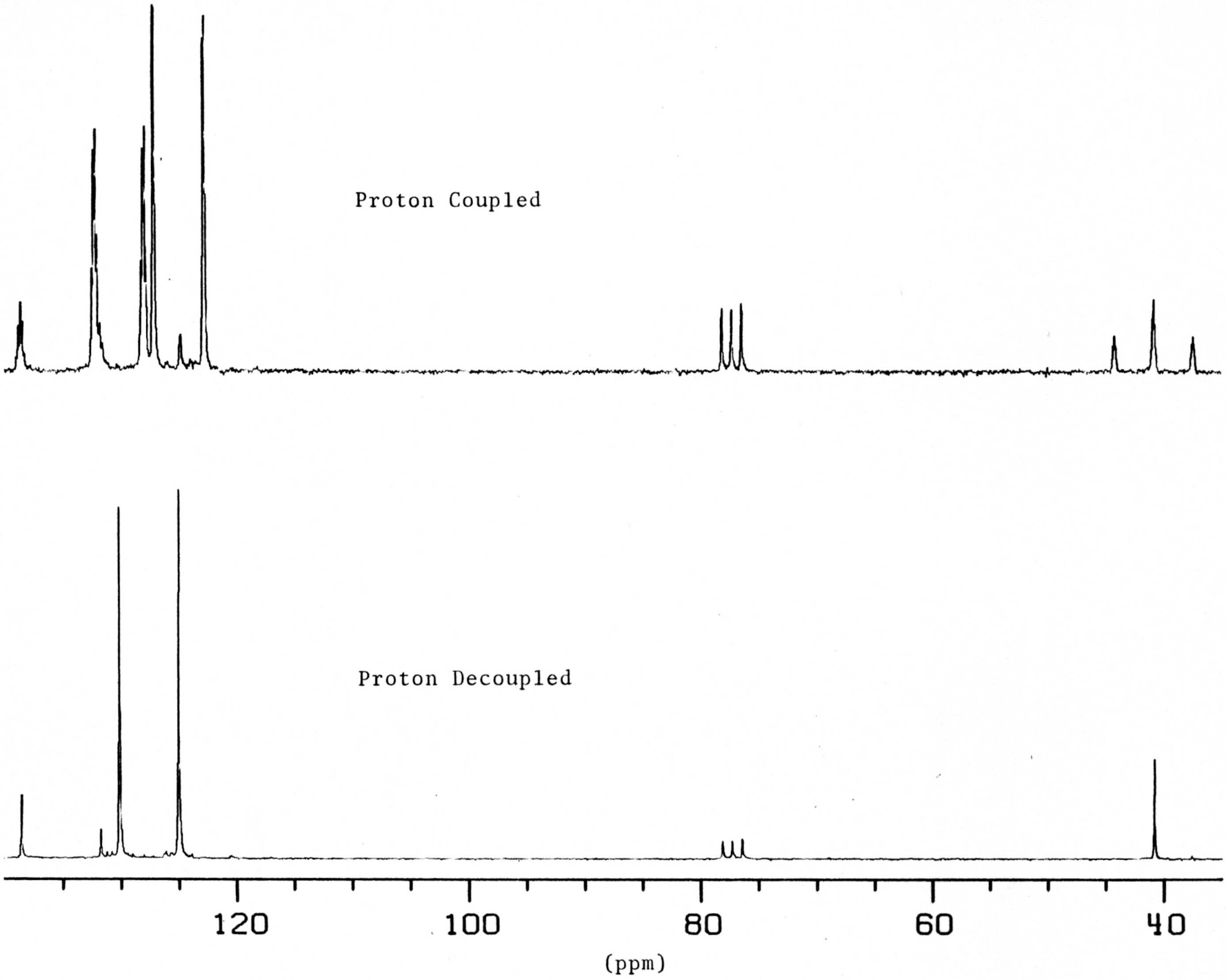


Fig. 2. ^{13}C Spectra of MDI (MOBAY) in $CDCl_3$

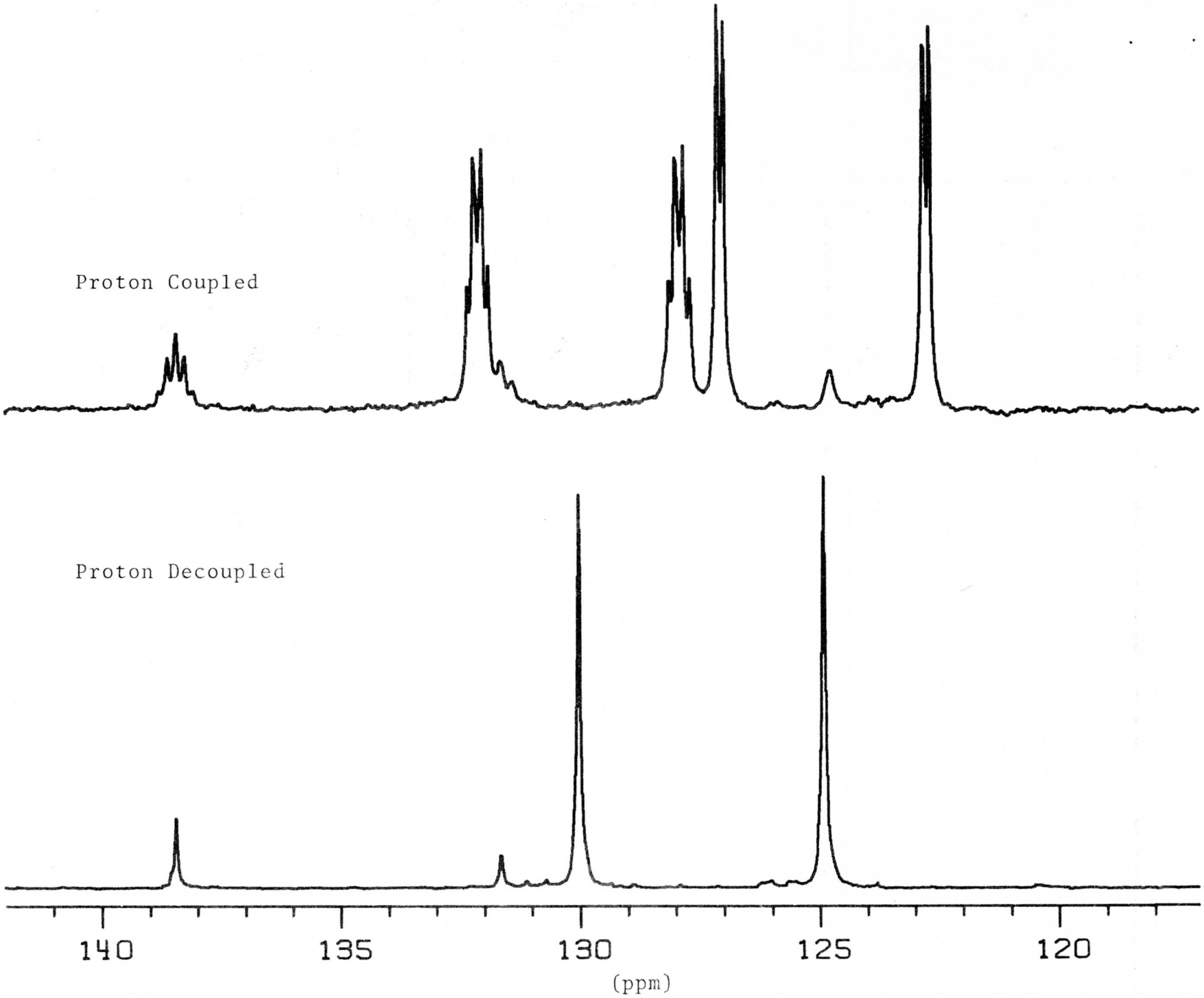


Fig. 2a. ^{13}C Spectra of MDI (Aromatic Region)

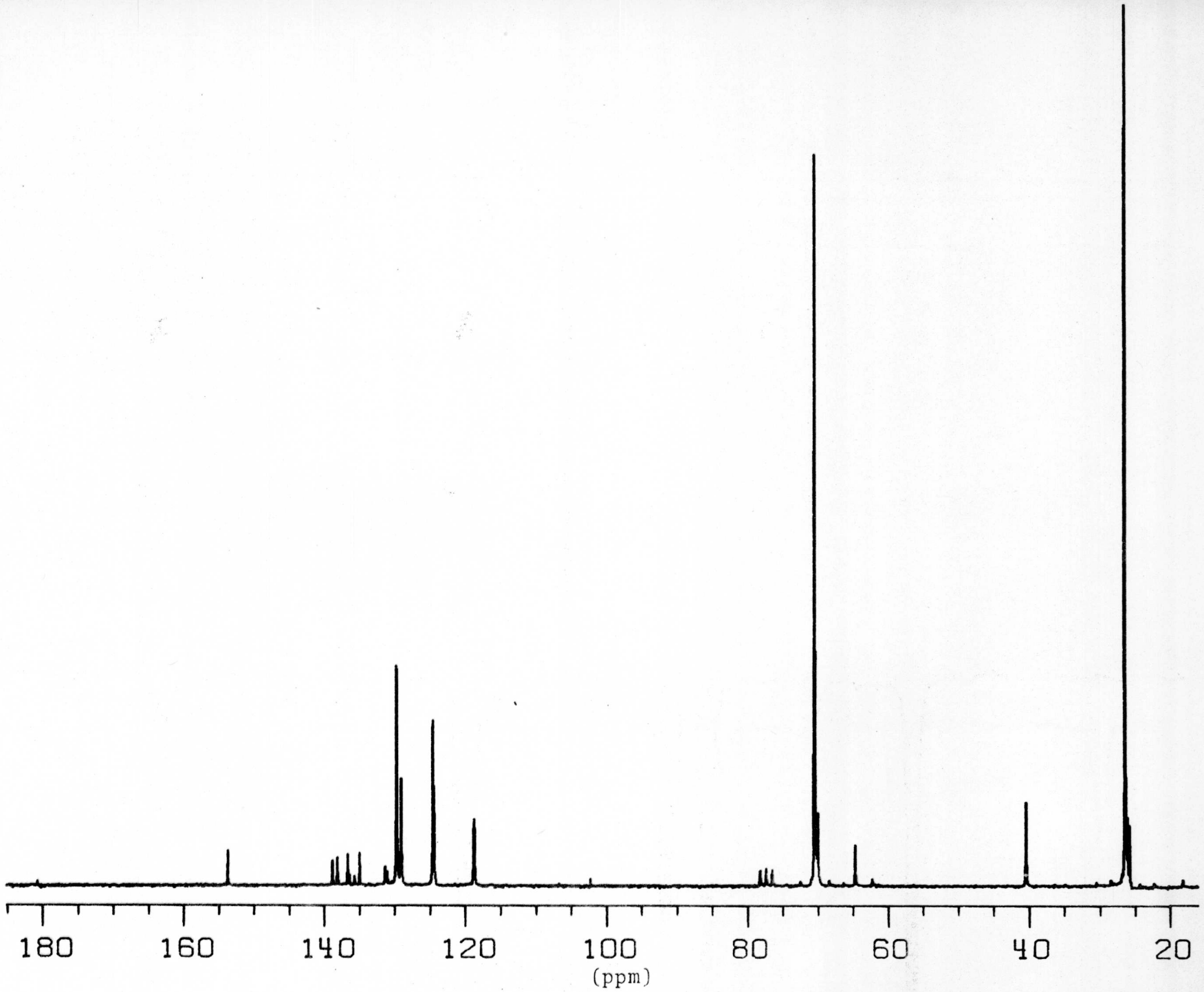


Fig. 3. ^{13}C Spectrum of Halthane, 20903T, in $CDCl_3$ (Proton Decoupled)

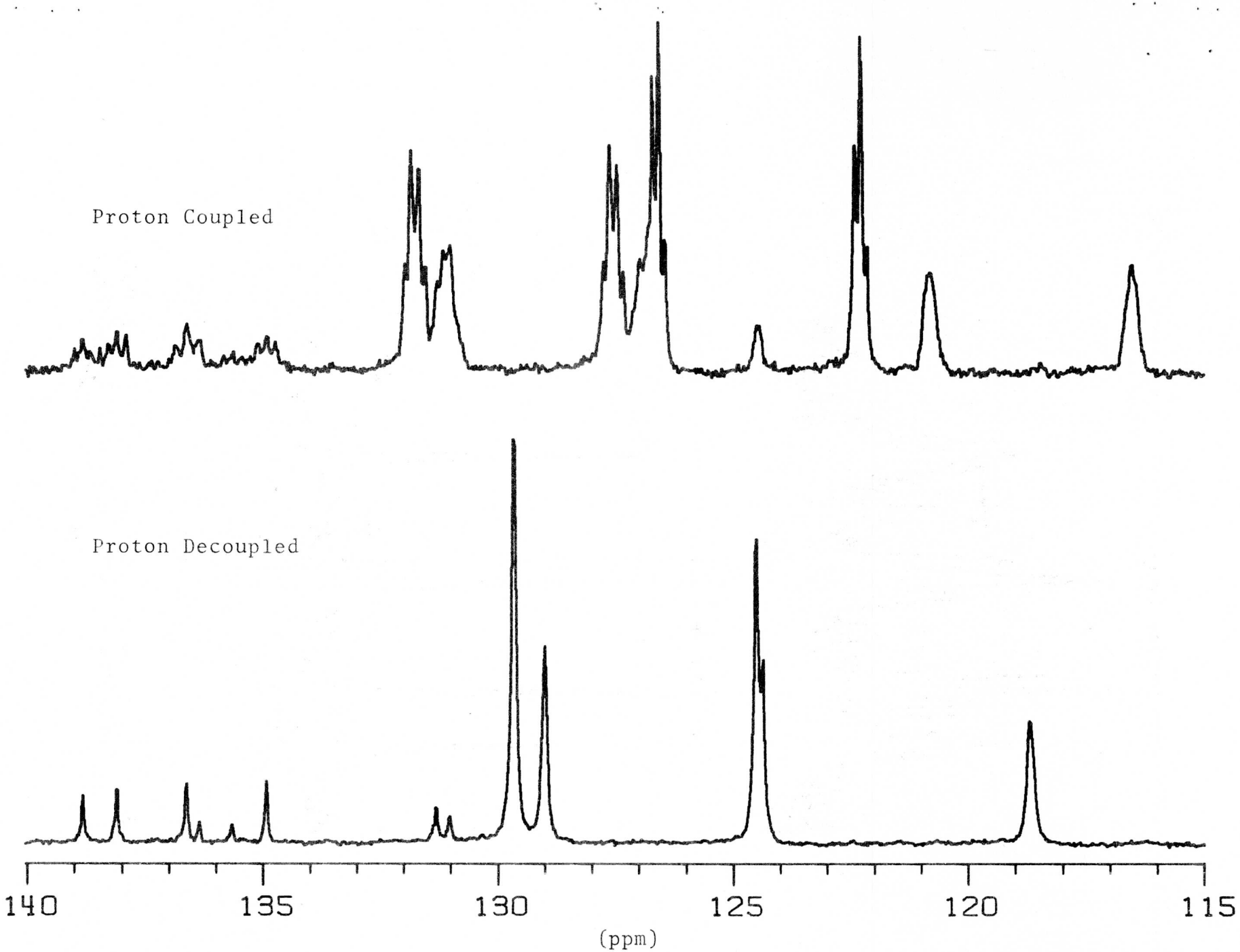


Fig. 3a. ^{13}C Spectra of Halthane 20903T, in $CDCl_3$ (Aromatic Region)

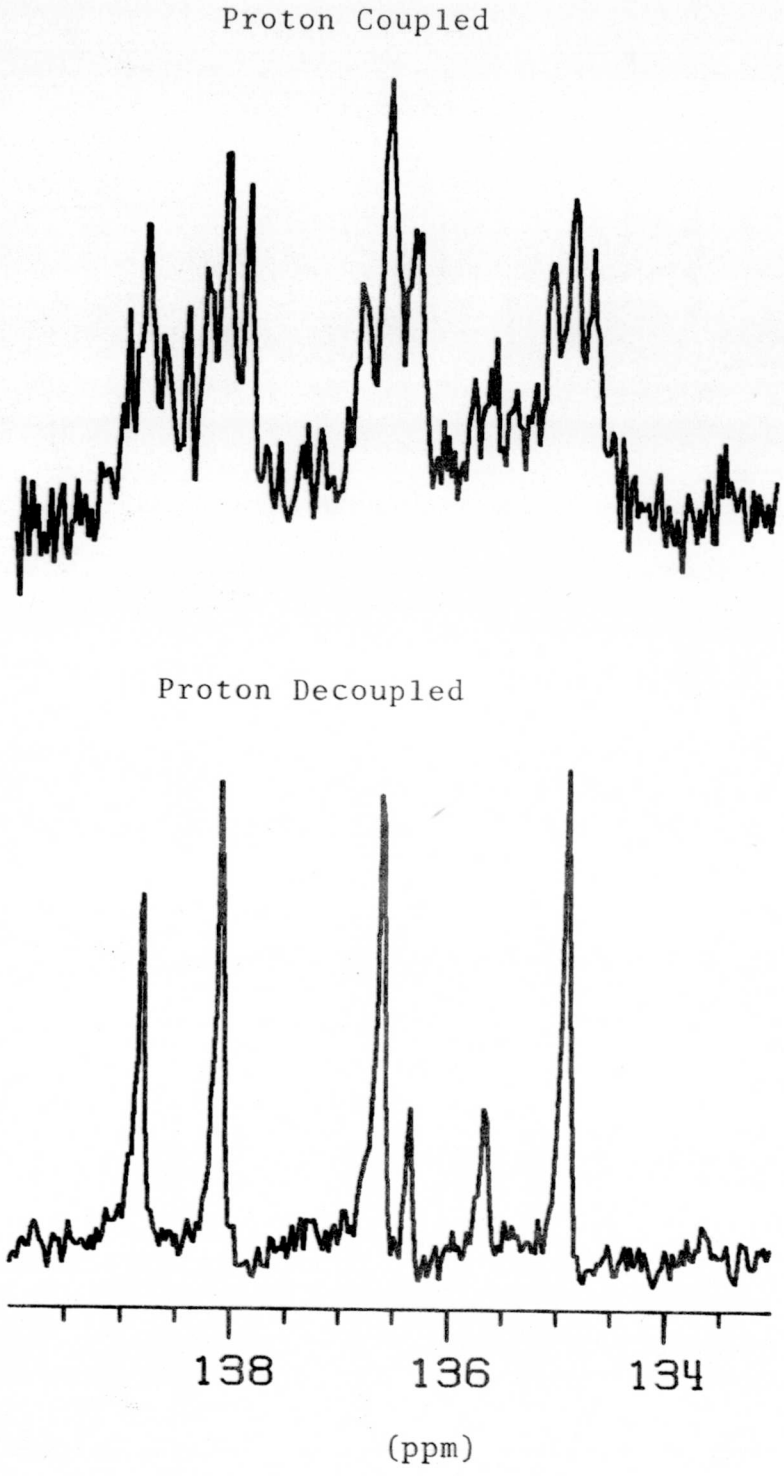


Fig. 3b. ^{13}C Spectra of Halthane 20903T, in $CDCl_3$ (Isocyanate Quaternary Ring Carbon Region)

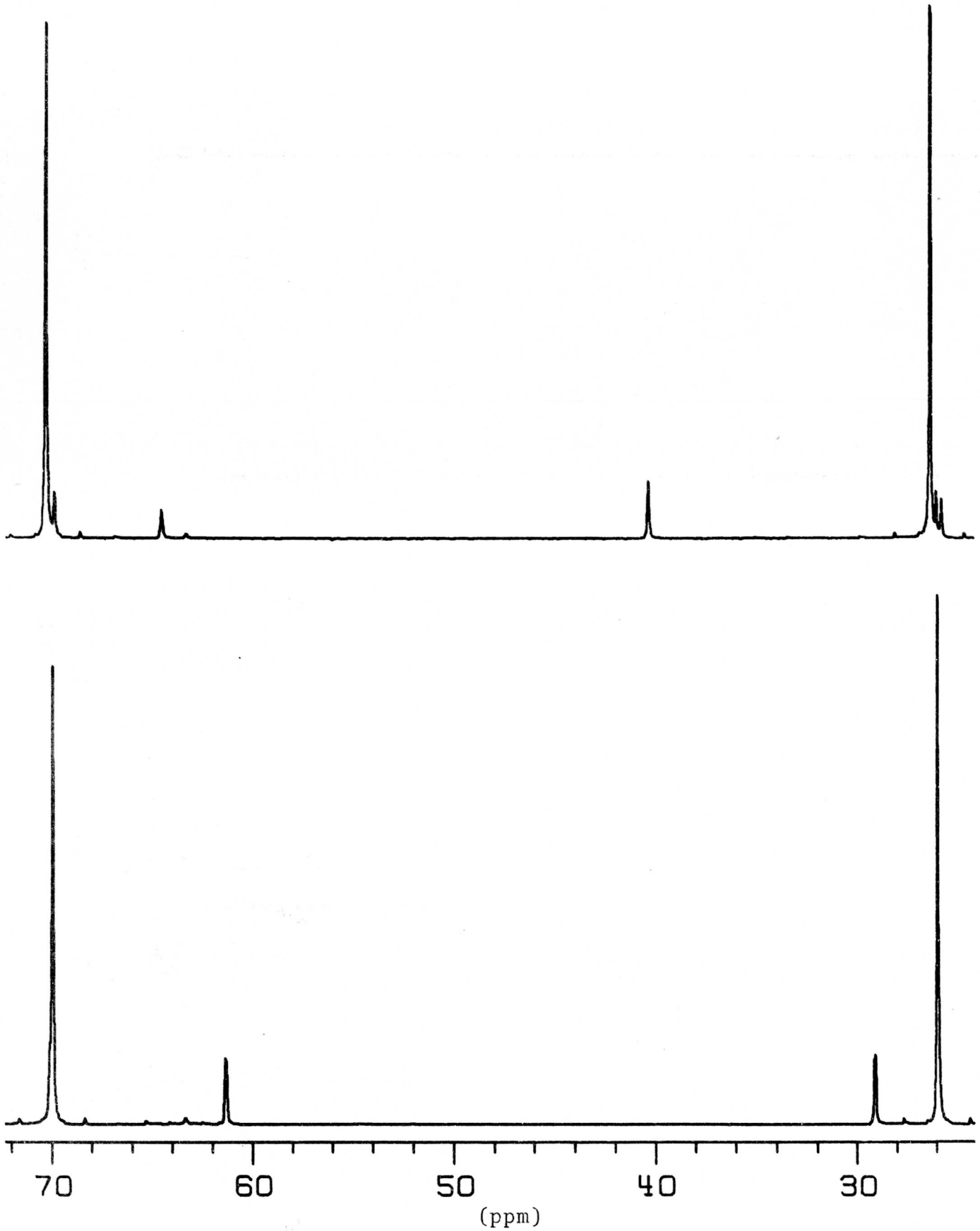


Fig. 3c. ^{13}C Spectral Comparison of Polymeg 1000 in $CDCl_3$ (Lower) With That of Polymeg 1000 in Admixture with MDI (in $CDCl_3$, Proton Decoupled)

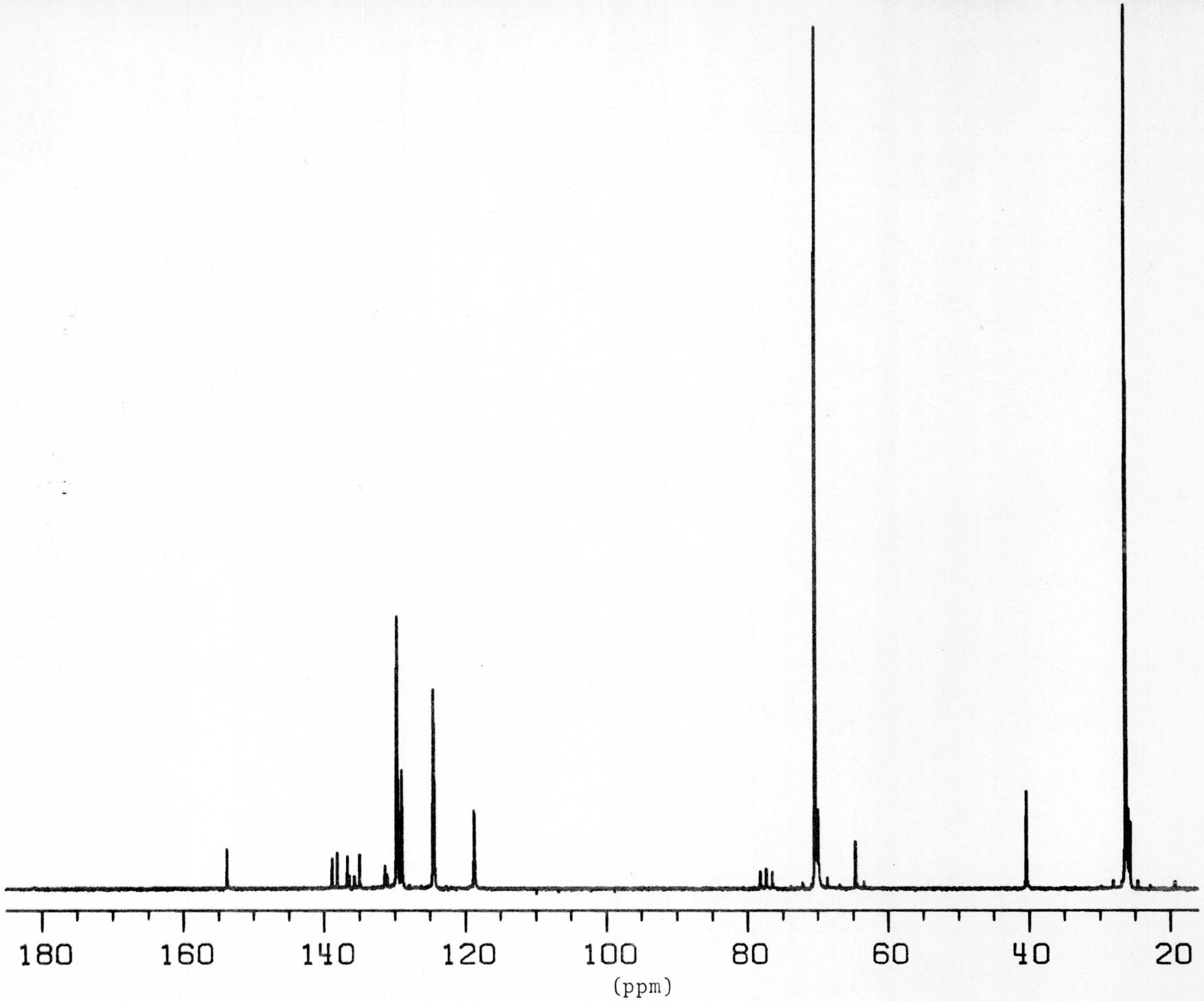


Fig. 4. ^{13}C Spectrum of Halthane Pre-Polymer (770920-1B), in $CDCl_3$ (Proton Decoupled)

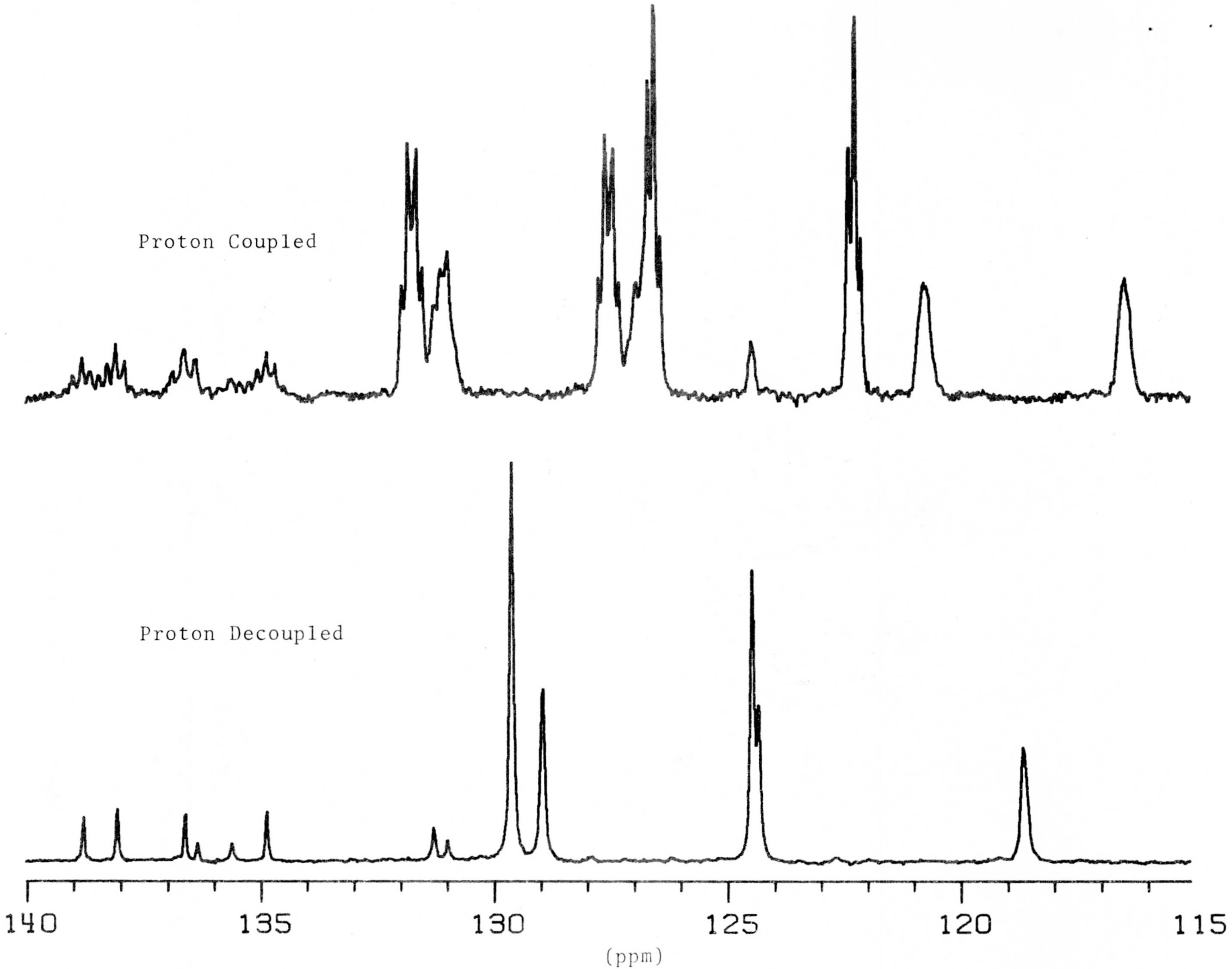


Fig. 4a. ^{13}C Spectra of Halthane 770920-1B, in $CDCl_3$ (Aromatic Region)

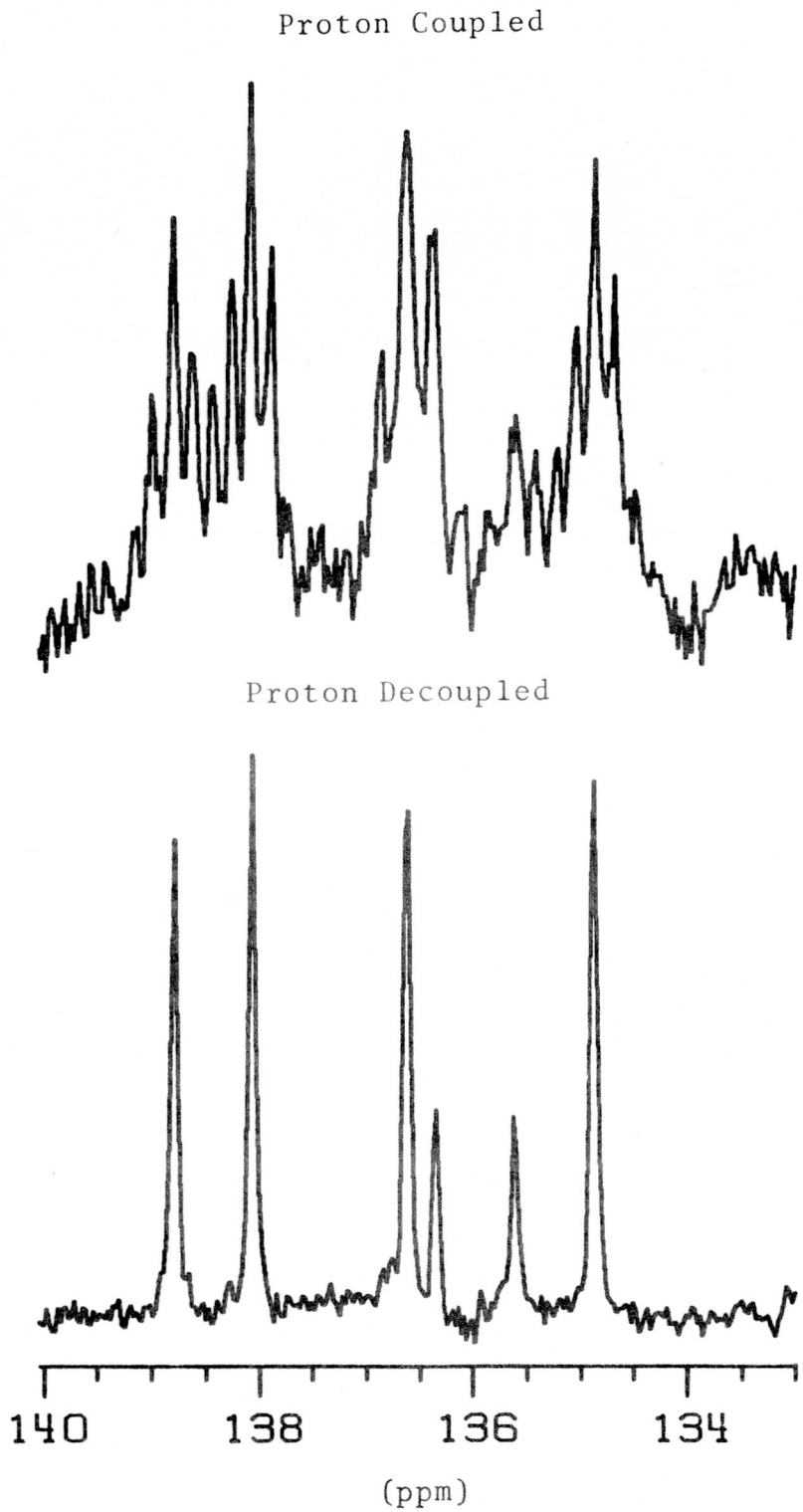


Fig. 4b. ^{13}C Spectra of 770920-1B in $CDCl_3$ (Isocyanate Quaternary Ring Carbon Region)

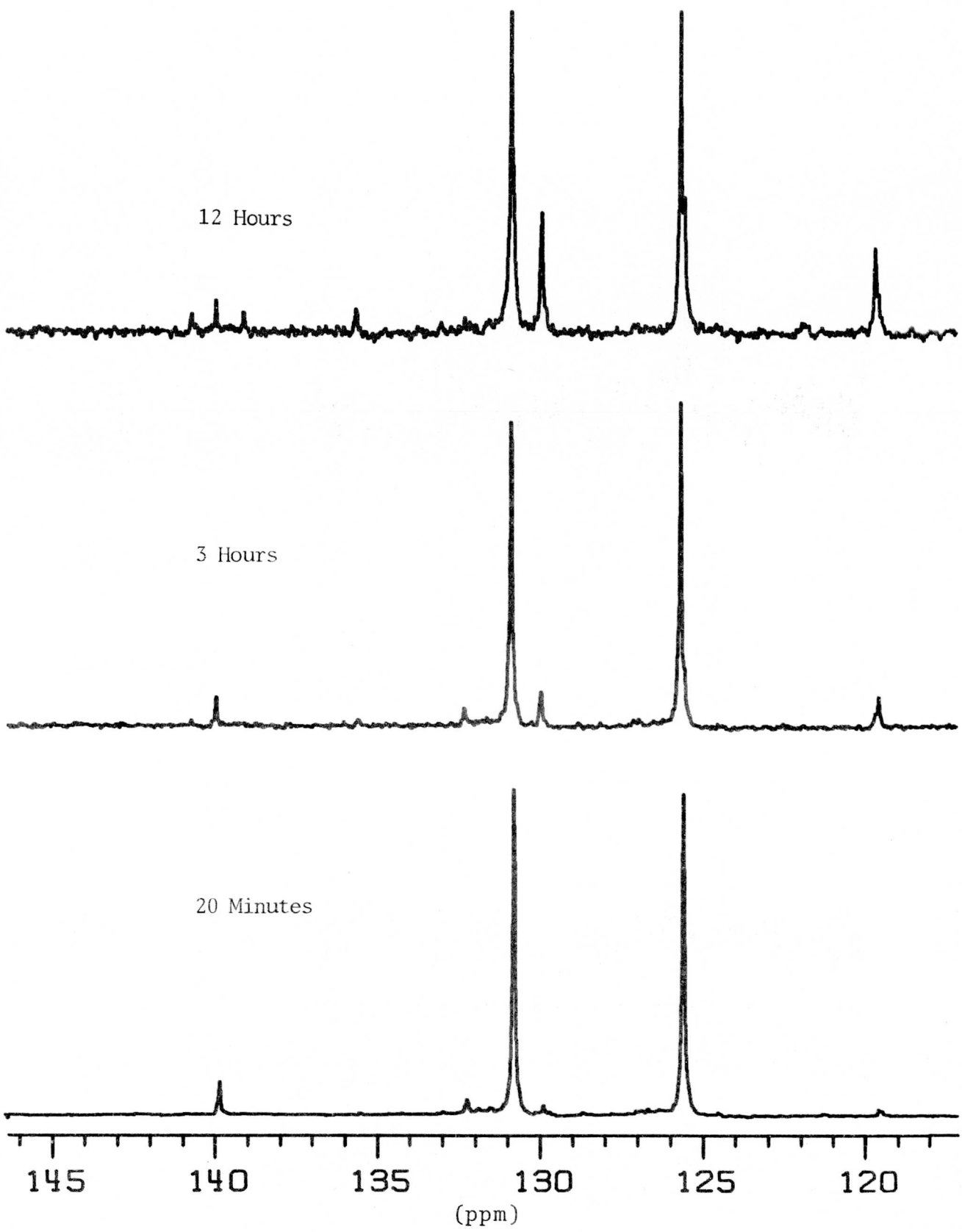


Fig. 5. ^{13}C Proton Decoupled Spectra of MDI (MOBAY) in d-6 Acetone, 1% HOH, 21 C (Aromatic Region)

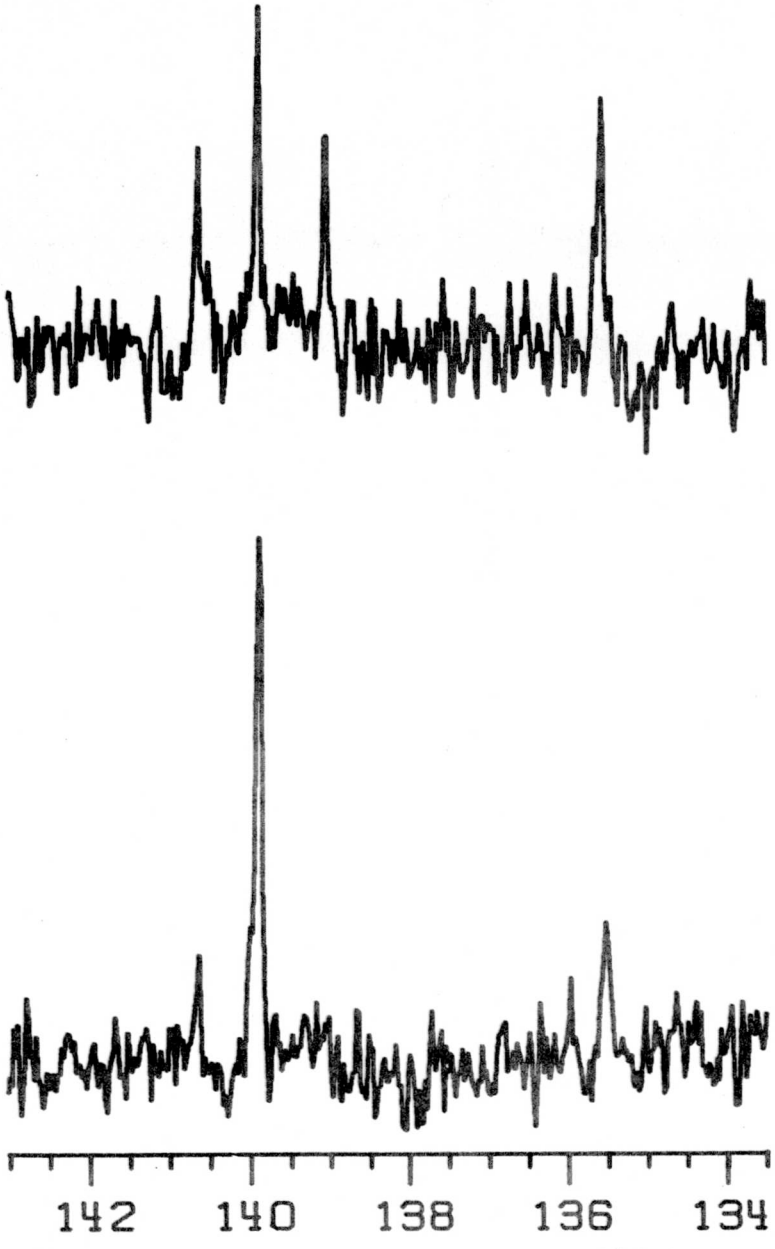


Fig. 5a. ^{13}C Spectral Comparison of Aromatic Region of MDI in 1% HOH/d-6 Acetone

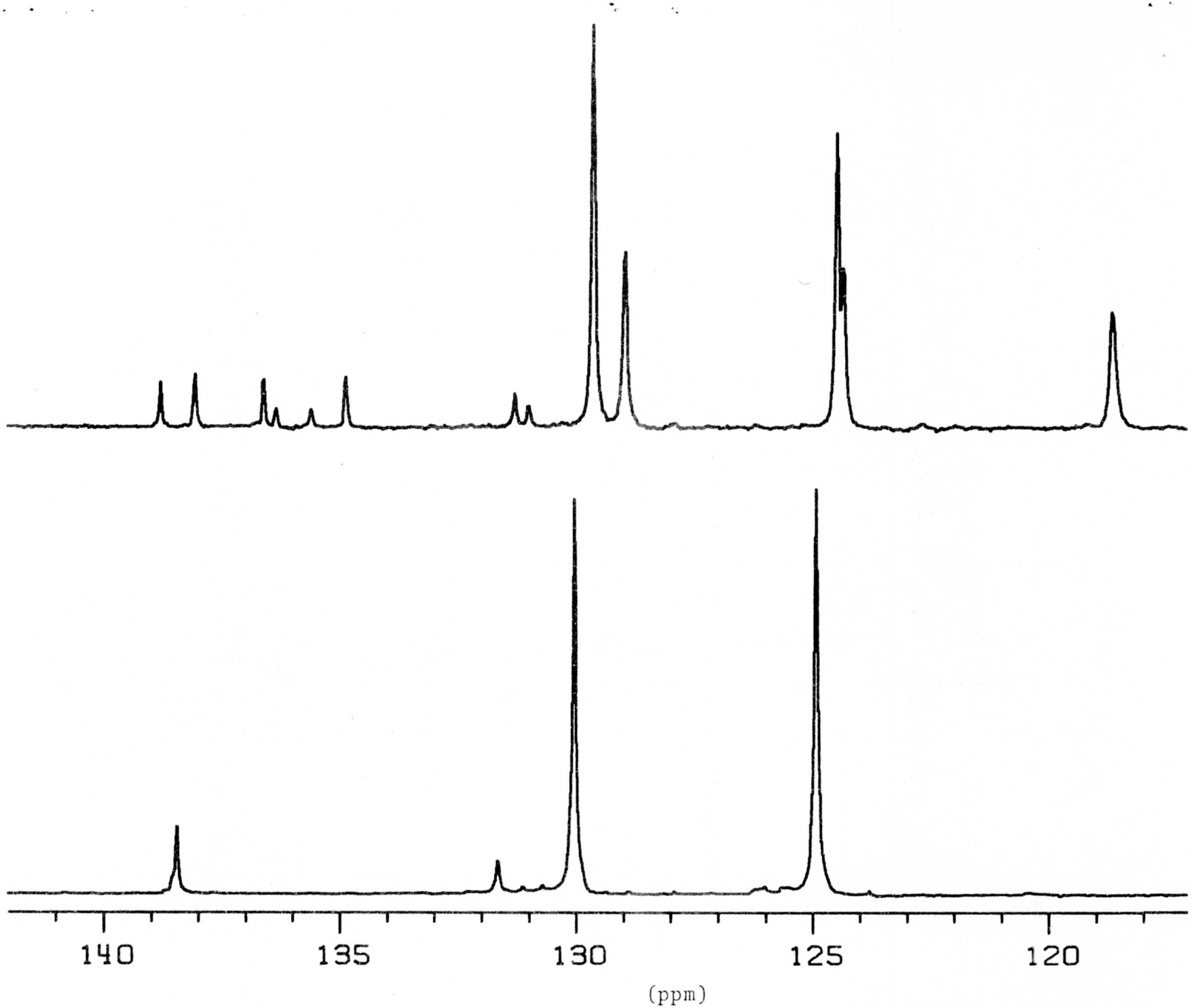


Fig. 6. Spectral Comparison of MDI (MOBAY) and Halthane 20903T (Top)(Proton Decoupled, in $CDCl_3$)

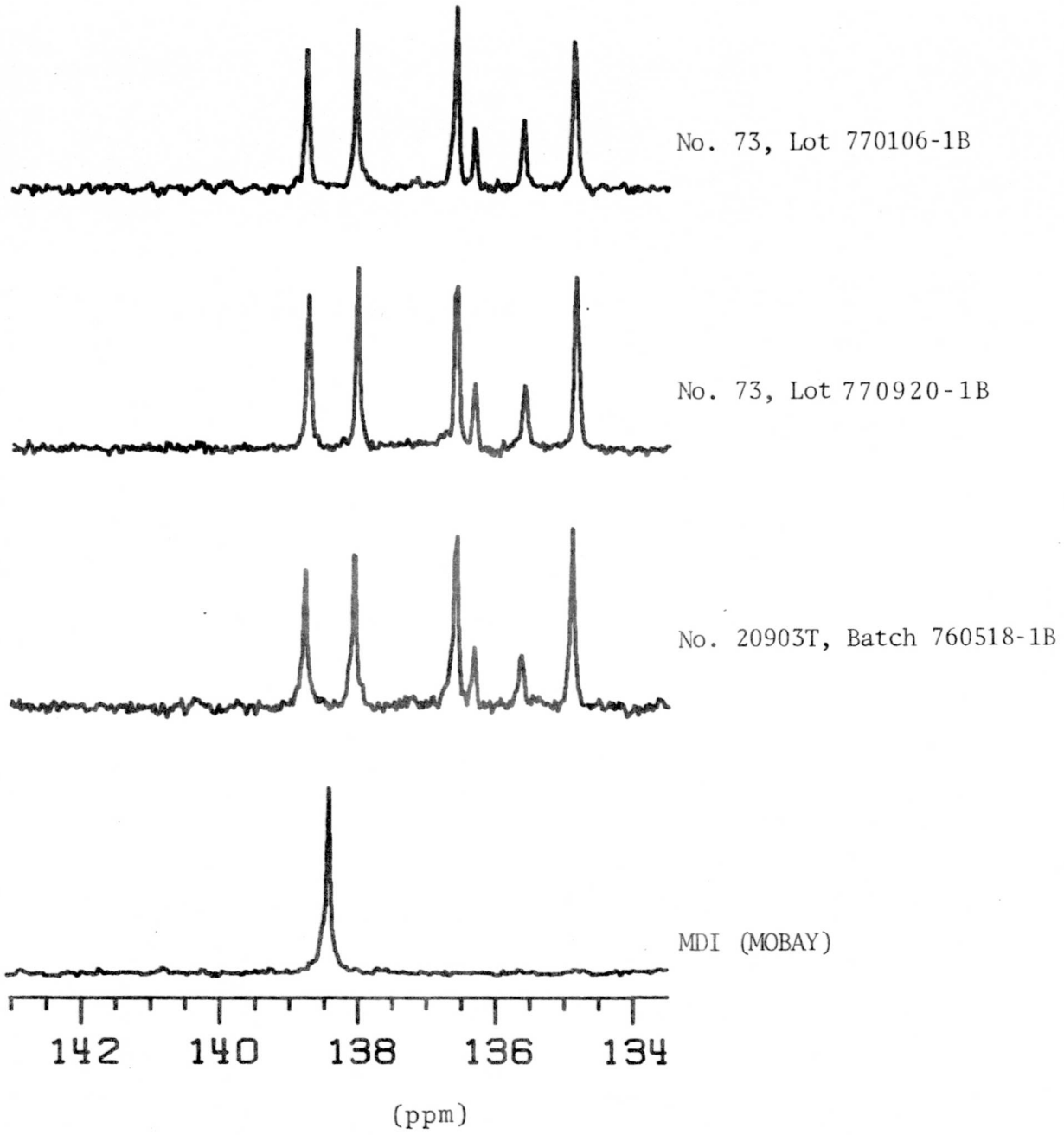


Fig. 7. ^{13}C Spectral Comparison of Several Lots of Halthane "T" Component to that of Unhydrolyzed MDI (MOBAY, Bottom Spectrum)

DISTRIBUTION

DOE

Ralph E. Caudle
Assistant Director of Operations
Military Application
Attn: Robert E. Clough
Washington, DC

ALO

H. N. Meyer, Director
Weapons Development Division

R. R. Fredlund, Jr., Director
Classification & Technical
Information

AAO

P. M. Ramey, Chief,
Operations Branch

Mound Lab

R. T. Braun

SLL

R. D. Cozine - Org. 8180

LLL

G. L. Dittman (10 Copies)
Attn: A. C. Van Dyk

C. T. Brockett
Technical Information Dept.

LASL

E. H. Eyster - WX-DO
Attn: J. J. Wechsler

R. N. Rogers - WX-2
J. Aragon - WX-3
Report Library - ISD-4

SLA

B. E. Arthur - Org. 1570
J. C. Crawford - Org. 2500/
D. H. Anderson - Org. 2510
J. C. King - Org. 2300/
C. B. McCampbell - Org. 2310
Central Technical Files - Org. 3141

TIC

Technical Information Center (27 Copies)
Oak Ridge, TN

UK

Jack Kirkham
Atomic Weapons Research Establishment
Aldermaston, Reading, England

PX

Division Manager, Mfg. Engineering
Division Manager, Quality
Division Manager, Development
Division Manager, Safety & Fire
Protection
Education & Training Center (5 Copies)
Technical Library (5 Copies)

Circulation Copy:

(1) Area Manager, DOE/AAO
(2) Division Manager, Manufacturing
M&H

Circulation Copy:

(1) Asst. Plant Manager
(2) Plant Manager
(3) M&H-SM Co., Inc., Lexington, KY