Supplementary Information.

Poly(ω-Bromoalkylnorbornenes-*co*-norbornene) by ROMP-Hydrogenation: a Robust Support Amenable to Post-Polymerization Functionalization

*Rodrigo García-Loma and Ana C. Albéniz**

1- Additional experimental data.

2- Figures showing NMR spectra of polymers.

3- Figures showing IR spectra of polymers.

4- SEM Images for polymers **4a** and **4b**.

1- Additional experimental data.

Determination of reactivity ratios.

Copolymerizations of norbornene and **1** were carried out at the monomer feed ratios f = NB/**1** shown in Tables S1 and S2, using 0.72 mmol of **1a** and 0.55 mmol of **1b** in each experiment and following the conditions of Table 1 in the text. After 60 min the reactions were quenched by pouring the mixture onto methanol (80-100% conversion). The composition of the copolymers (F) was determined by quantitative analysis of the bromo content in the material. The composition data of the copolymers (F) obtained for the copolymerization at different monomer feed ratios (f) were fitted to the Finemann-Ross equation $f(1-F)/F = r_2 - (f^2/F)\, r_1$ (Figures S1 and S2).[1]

a) Copolymerization **1a** and norbornene (NB):

Table S1

f (NB/**1a**)	F (NB/**1a**)	f(1-F)/F	f^2/F
0.94	1.36	-0.25	0.650
1.87	3.08	-1.26	1.135
3.8	6.03	-3.17	2.395
7.61	11.97	-6.97	4.838

$r_{\mathbf{1a}} = 0.65$ $r_{NB} = 1.58$.

[1] J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*: Chapman & Hall: Cheltenham, 1991.

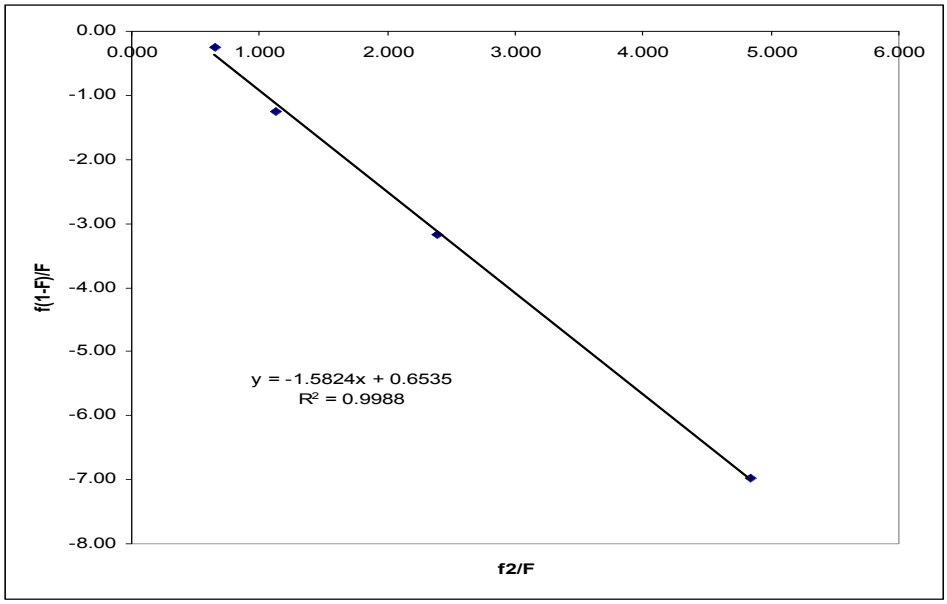

Figure S1.

b) Copolymerization **1b** and norbornene (NB):

Table S2.

f (NB/**1b**)	F (NB/**1b**)	f(1-F)/F	f^2/F
1	1.60	-0.38	0.625
2	3.16	-1.37	1.266
4	6.50	-3.38	2.462
8	13.87	-7.42	4.614

$r_{\mathbf{1b}} = 0.84$ y $r_{NB} = 1.78$.

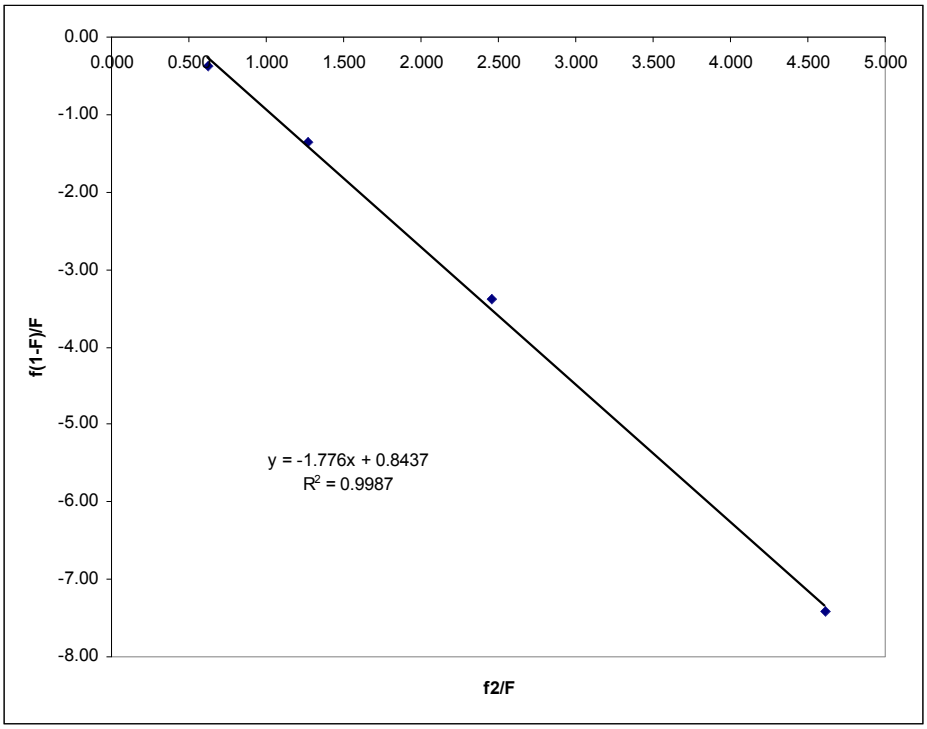

Figure S2.

Reaction of homopolymer 3a (x/y = 0) with 2nd generation Grubbs' catalyst 2.

Homopolymer ROMP-PNBCH$_2$Br (**3a**, 80 mg, 0.43 mmol of Br) was dissolved in CH_2Cl_2 (4.8 mL) under a nitrogen atmosphere. A solution of **2** in CH_2Cl_2 (0.49 mL, 8.84 x 10^{-3} M, 4.3 x 10^{-3} mmol) was added dropwise. The reaction mixture was stirred for 24 h at room temperature. The reaction mixture was poured onto MeOH (30 mL), the CH_2Cl_2 was evaporated and the remaining solid was filtered, washed with MeOH (3 x 10 mL) and air-dried. Off-white powder, 48.7 mg, 61 % yield.

The reaction with the homopolymer ROMP-PNB$(CH_2)_4$Br **3b** (x/y = 0) was carried out in the same way.

The polymer properties before and after exposure to Grubbs' catalyst are shown in Table S3. After 24 h the polymers recovered were shorter and more polydisperse, showing that secondary metathesis is taking place.[2]

Table S3.

Polymer	**M_n**	**M_w/M_n**	**Trans:cis ratio**
3a, before	20291	2.04	2.31
3a, after exposure	3125	2.84	3.69
3b, before	39398	2.17	2.15
3b, after exposure	6591	3.13	2.26

Reaction of copolymer 3a (x/y = 1.1) with [PdBr$(C_6F_5)(NCMe)_2$].

ROMP copolymer **3a** (x/y = 1.1, 0.006 g, 0.043 alkene equivalents) and [PdBr$(C_6F_5)(NCMe)_2$],[3] (0.002 g, 0.0046 mmol) were dissolved in $CDCl_3$ (0.6 mL) in a 5 mm NMR tube. The reaction was monitored at room temperature by ^{19}F NMR. Figure 3 in the text shows the spectra obtained at 10 min, 2 h, and 24 h.

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[2] H. D. Maynard, R. H. Grubbs, *Macromolecules*, 1999, **32**, 6917.

[3] A. C. Albeniz, P. Espinet, C. Foces-Foces, F. H. Cano, *Organometallics* 1990, **9**, 1079.

Determination of the % of Br substitution in Table 4.

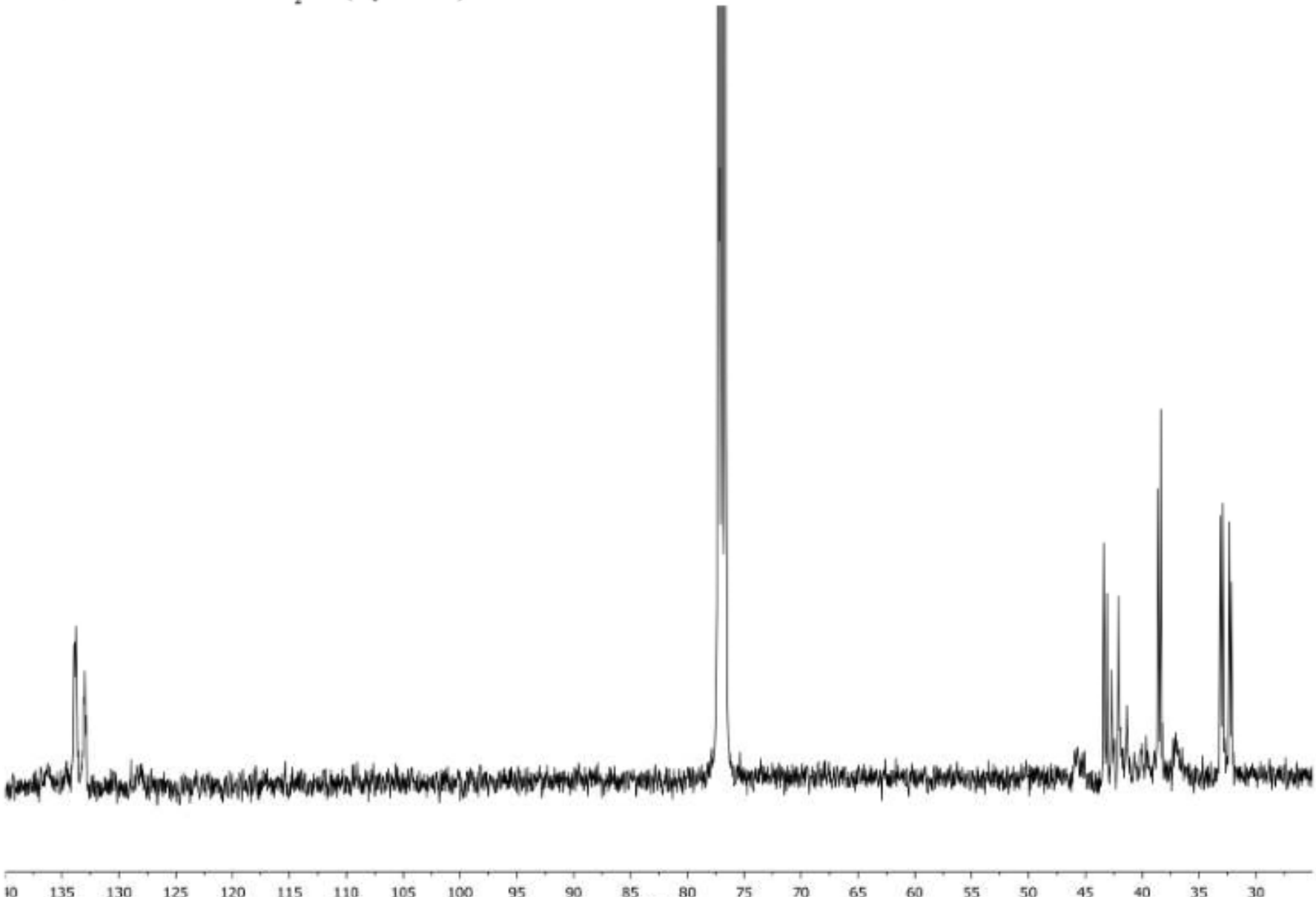
The maximum Nu functionalization in polymers **5-9** (mmol Nu/g) is given by the formula: Max mmolNu/g = $1000\alpha/\{1000 + \alpha\ (M_w(Nu)–79.904)\}$ where α = mmol Br/g of the starting polymer **4**.

Since the Br substitution is high in all cases, the % can be estimated by the ratio: {(residual mmol Br/g in the polymer)/ Max mmolNu/g}100.

2- NMR spectra of polymers.

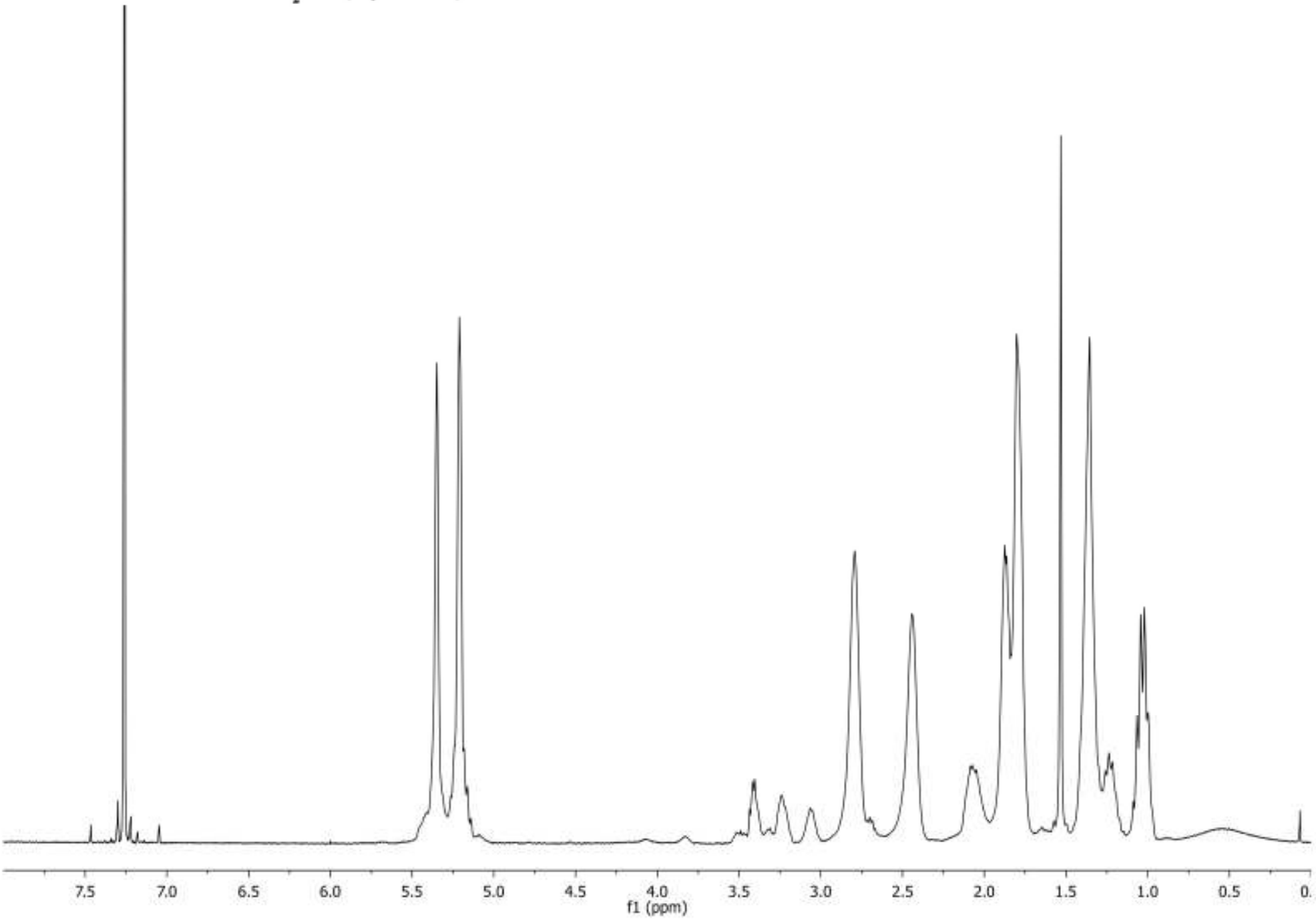
^{13}C NMR 500 MHz

3a : ROMP-PNB-NBCH$_2$Br (x/y = 4.29)



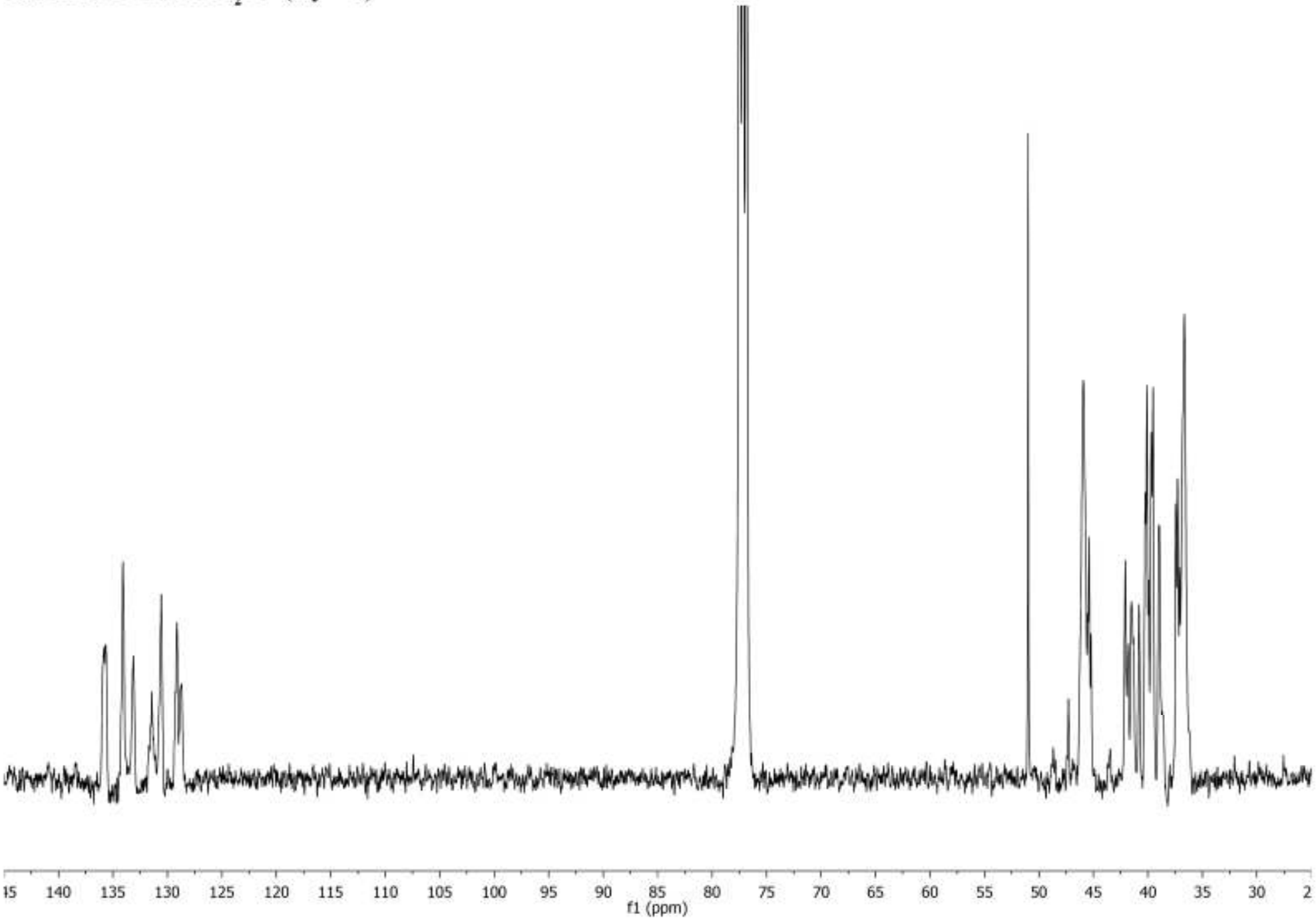
^{1}H NMR 500 MHz

3a : ROMP-PNB-NBCH$_2$Br (x/y = 4.29)



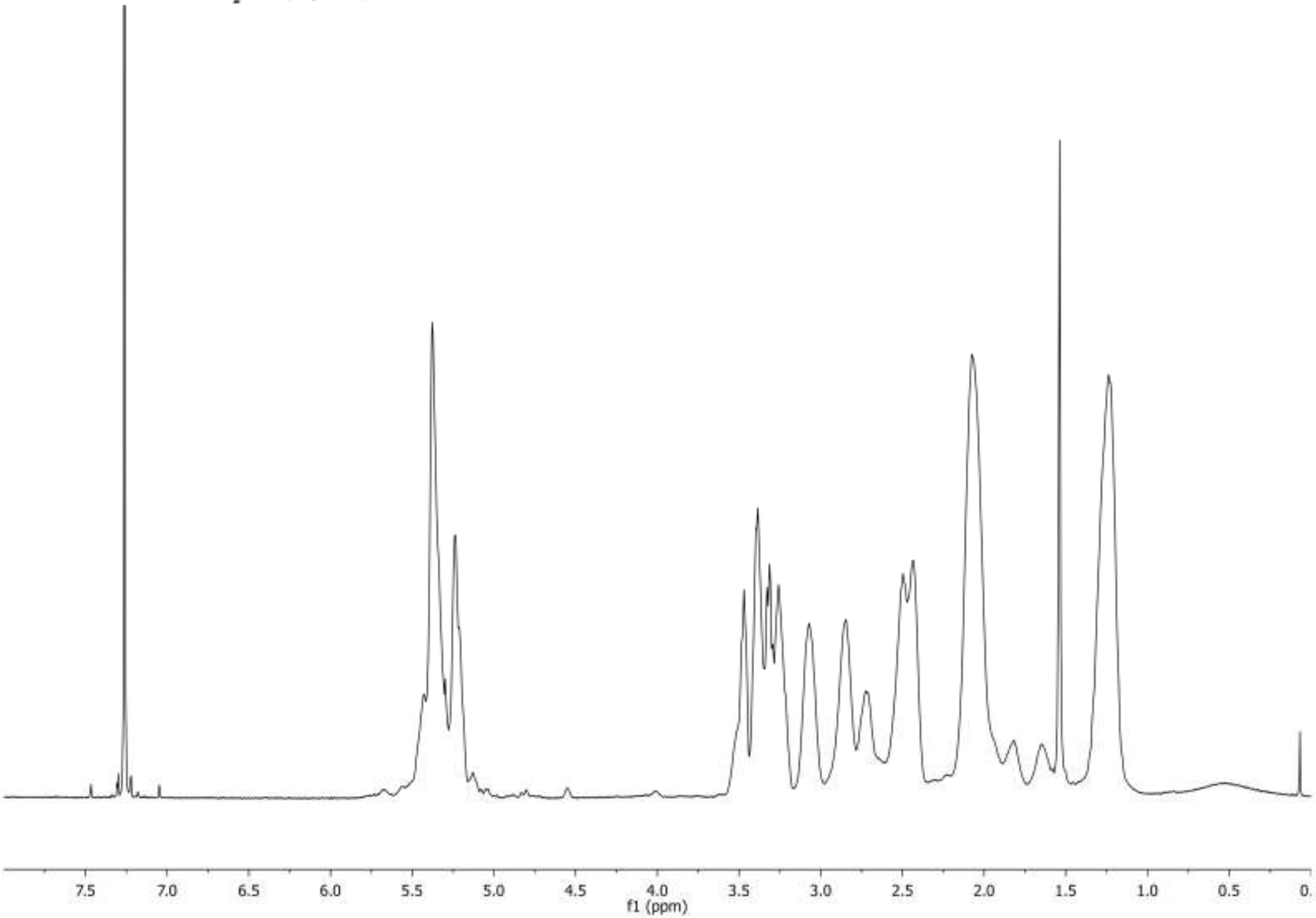
^{13}C NMR 500 MHz

3a : ROMP-PNBCH$_2$Br (x/y = 0)



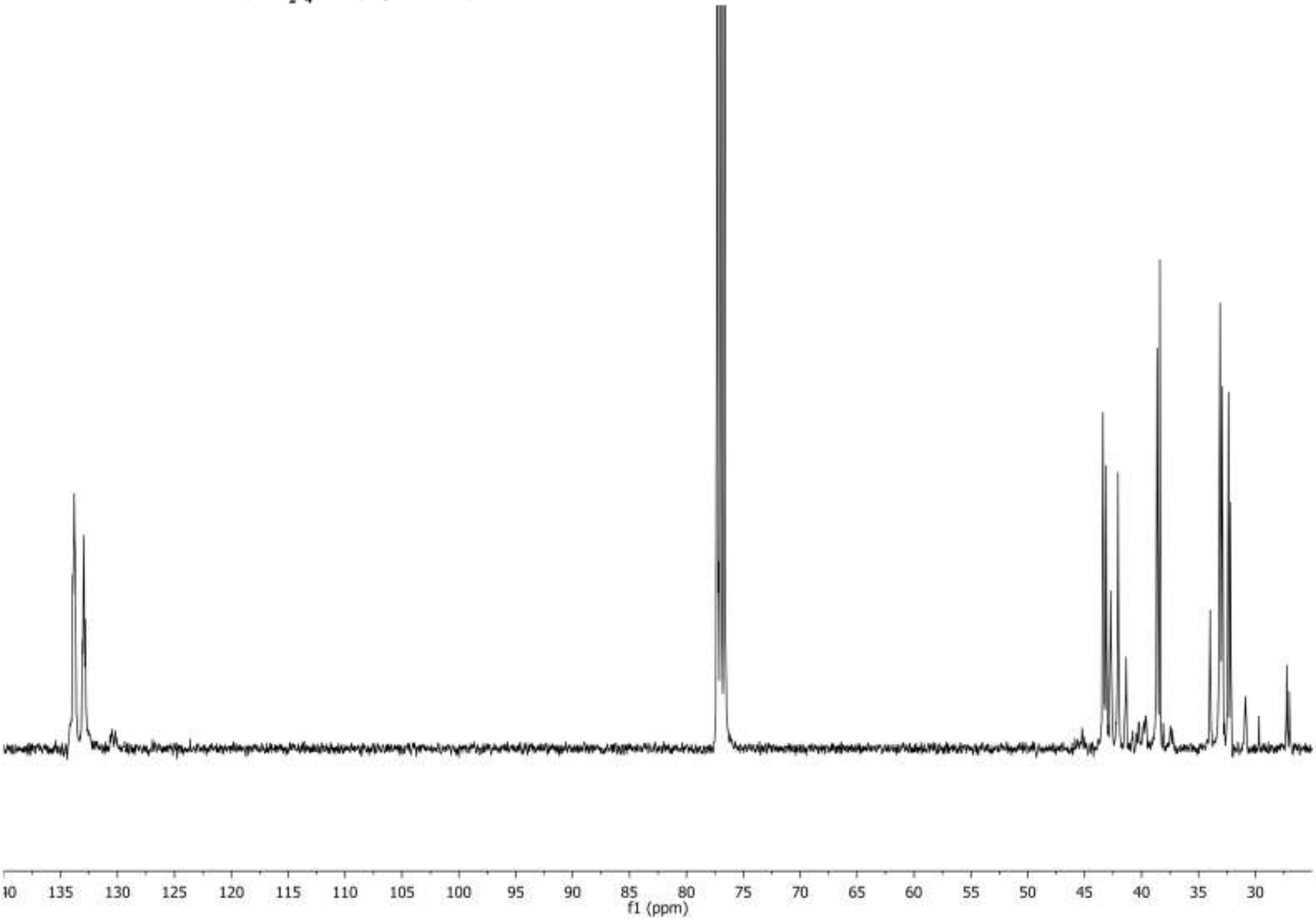
^{1}H NMR 500 MHz

3a : ROMP-PNBCH$_2$Br (x/y = 0)



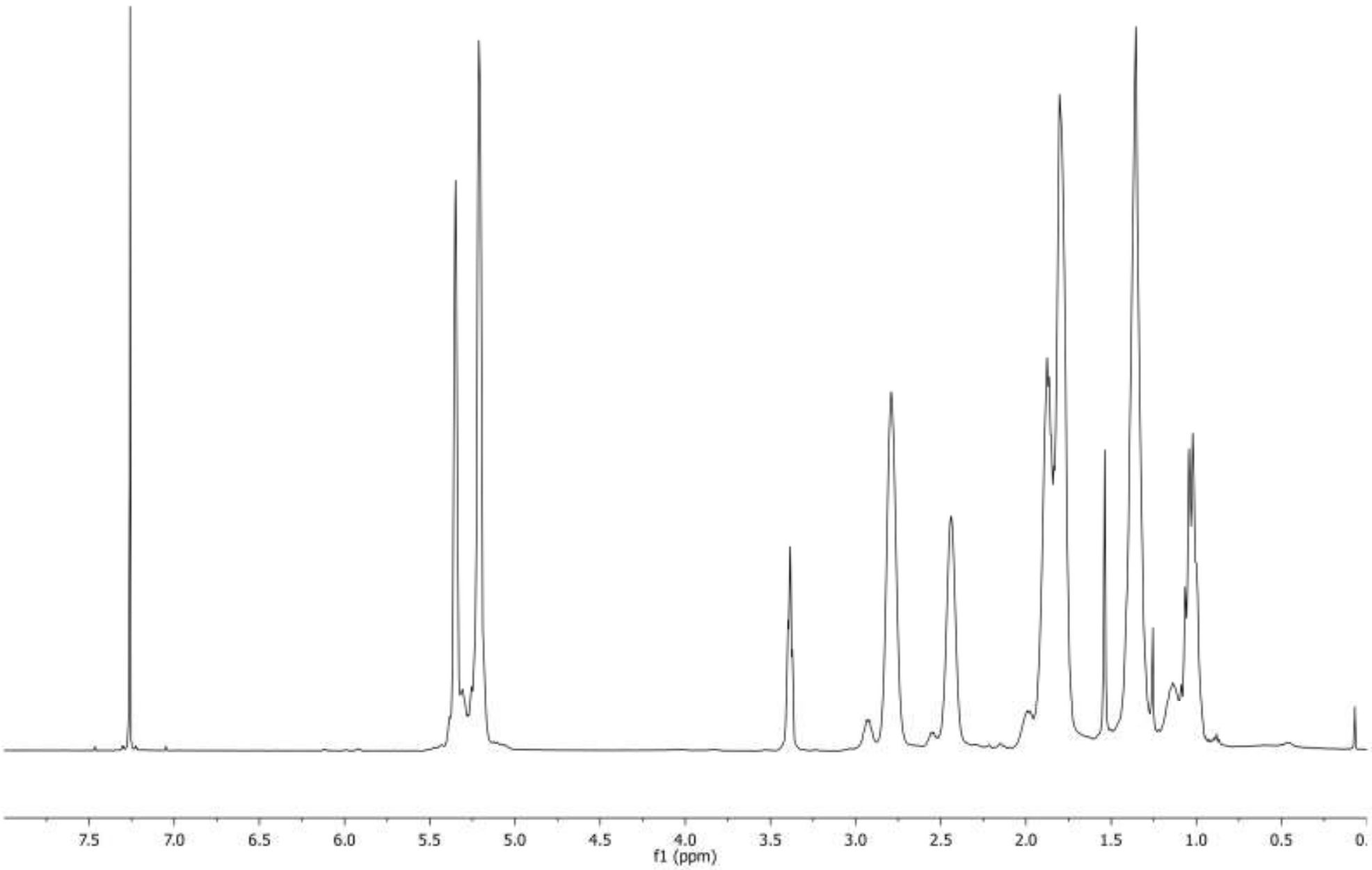
^{13}C NMR 500 MHz

3b : ROMP-PNB-NB$(CH_2)_4$Br (x/y = 7.09)



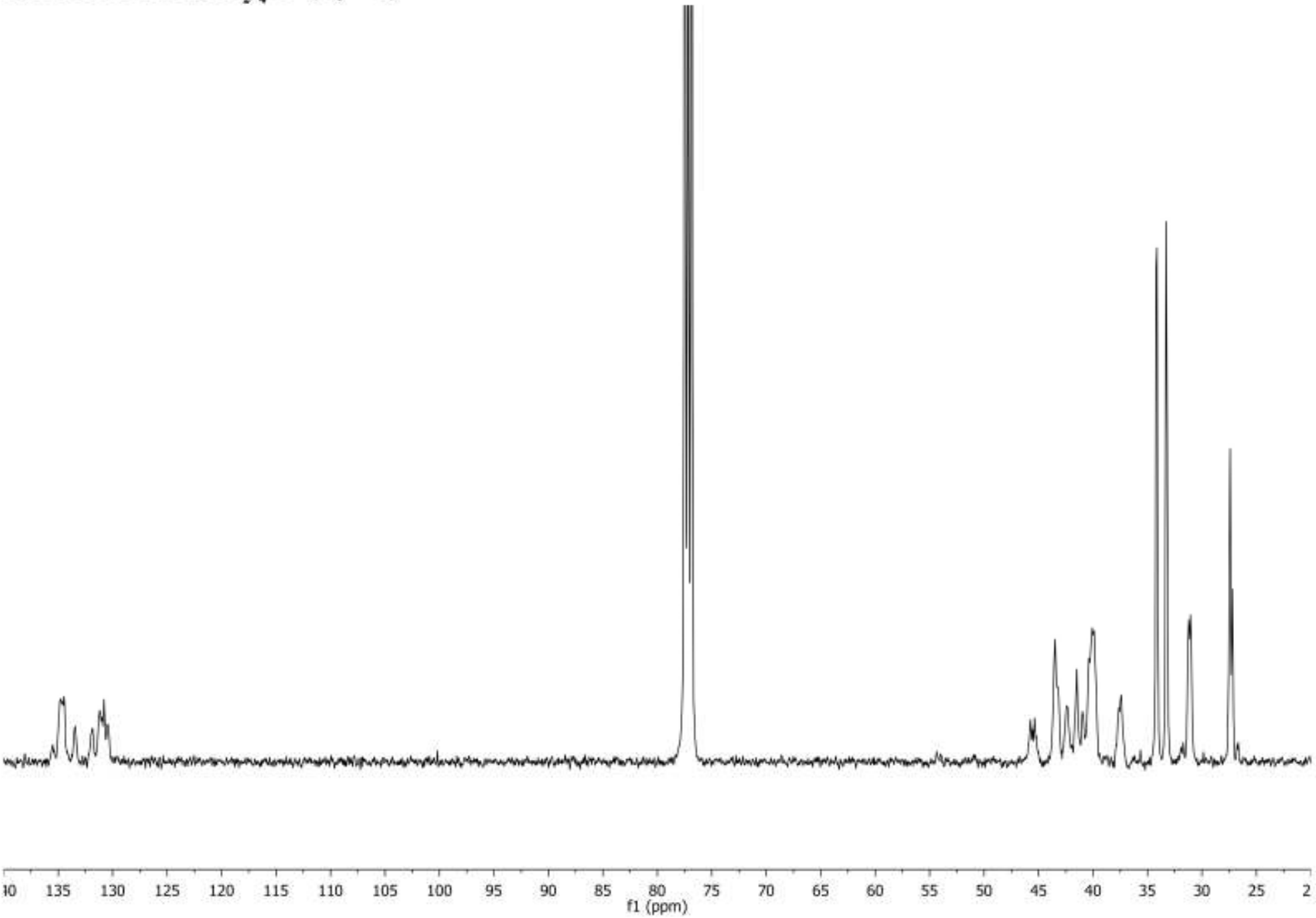
^{1}H NMR 500 MHz

3b : ROMP-PNB-NB$(CH_2)_4$Br (x/y = 7.09)



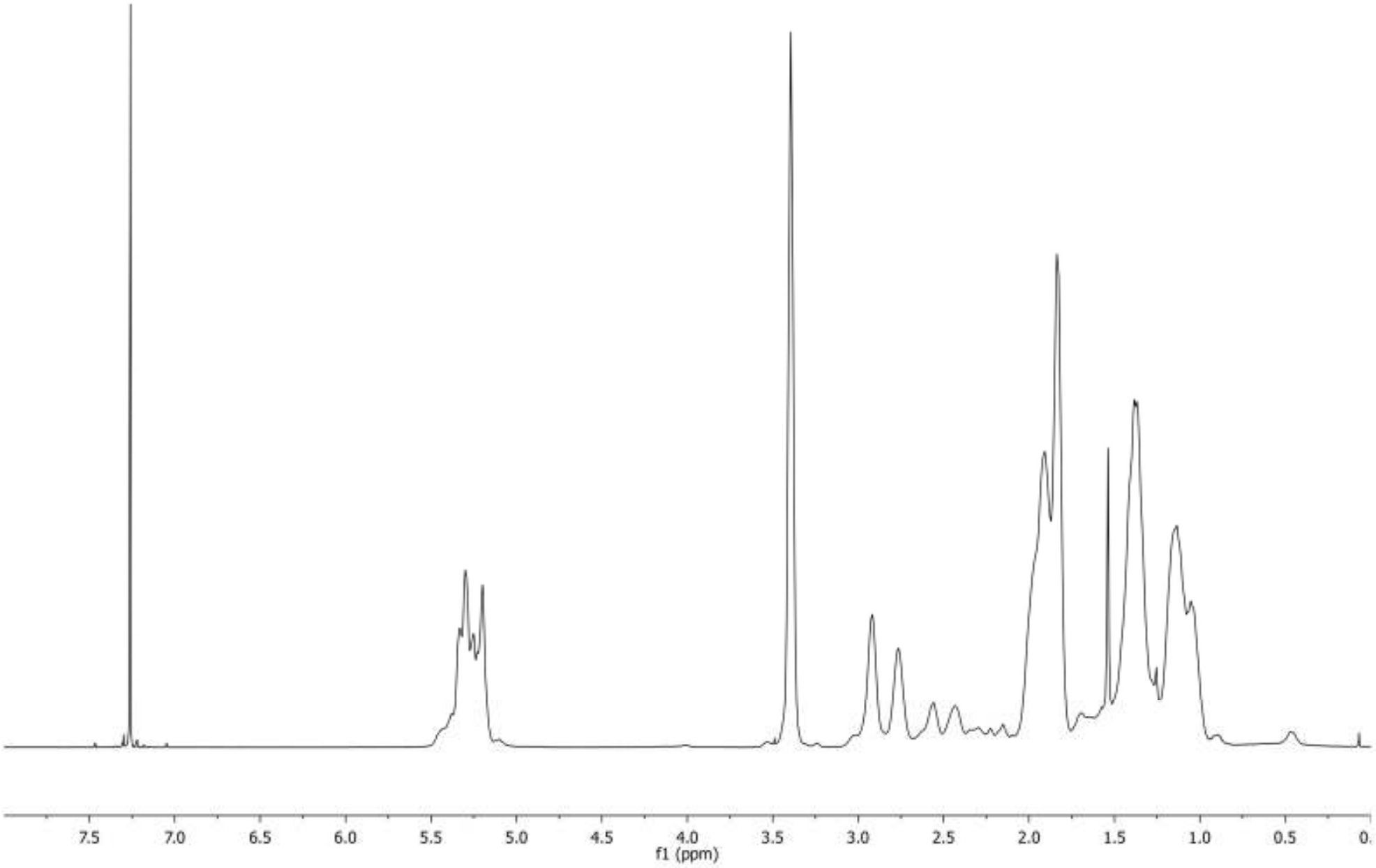
^{13}C NMR 500 MHz

3b : ROMP-PNB$(CH_2)_4$Br (x/y = 0)



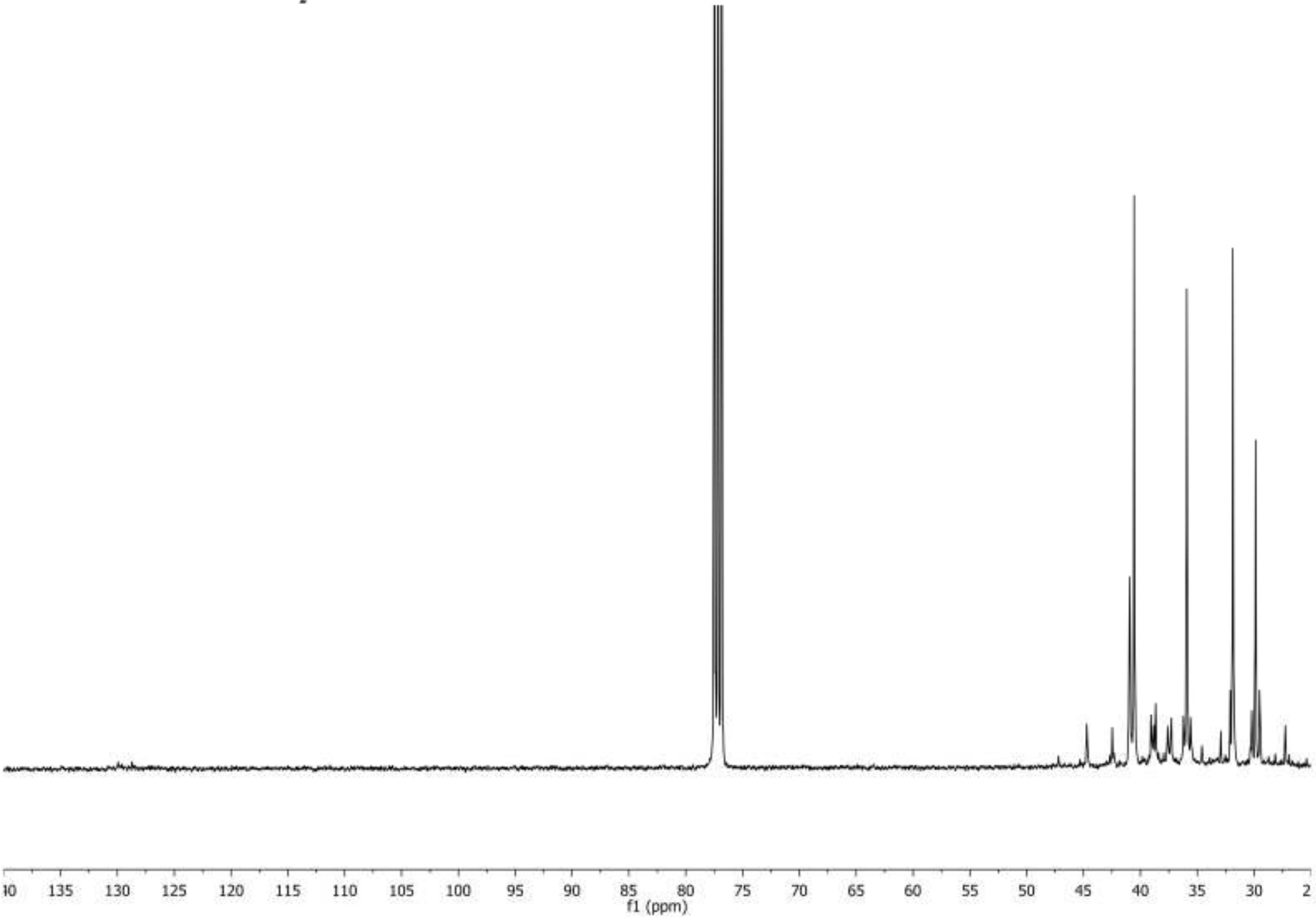
^{1}H NMR 500 MHz

3b : ROMP-PNB$(CH_2)_4$Br (x/y = 0)



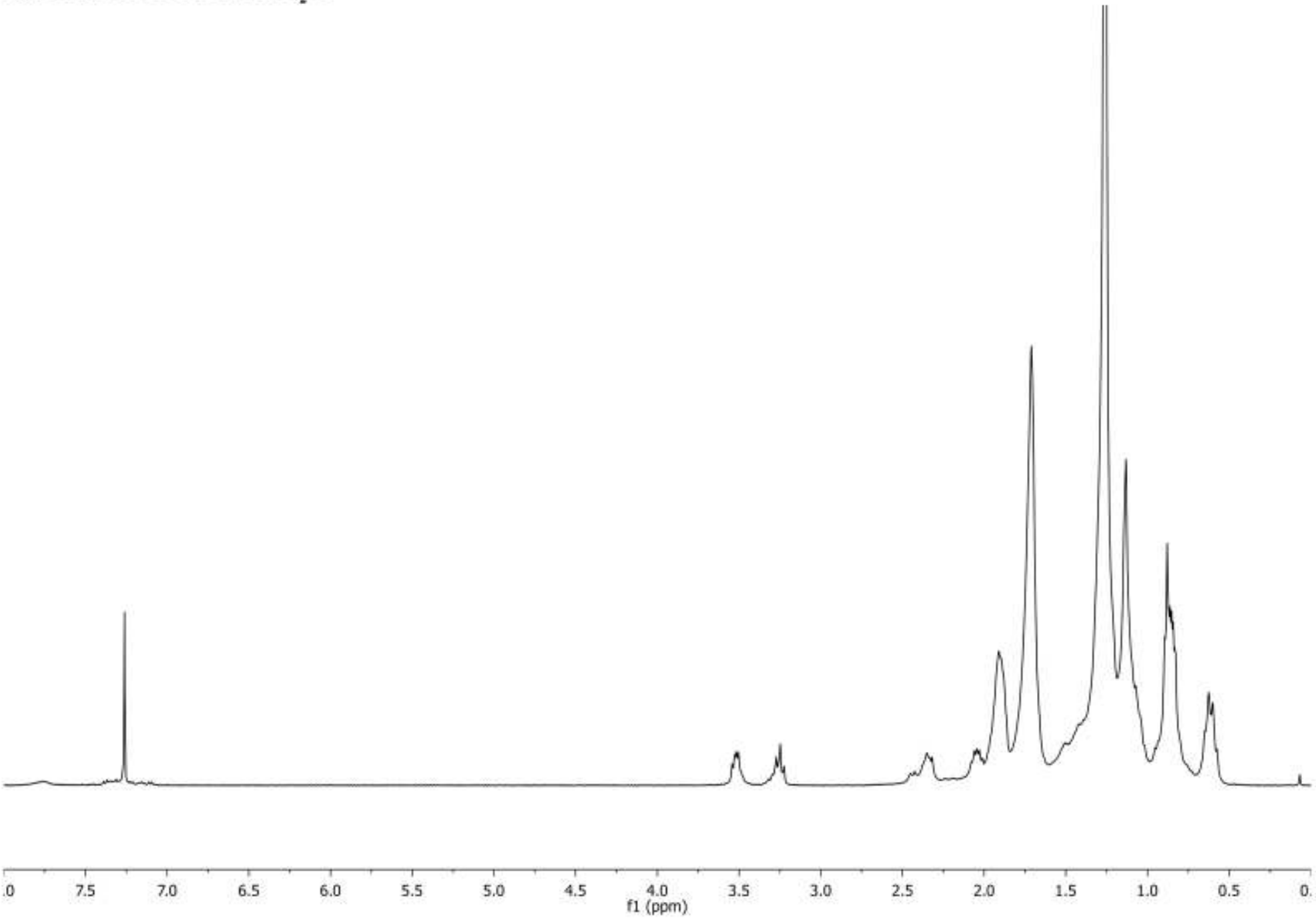
^{13}C NMR 400 MHz

4a : ROMPH-PNB-NBCH$_2$Br



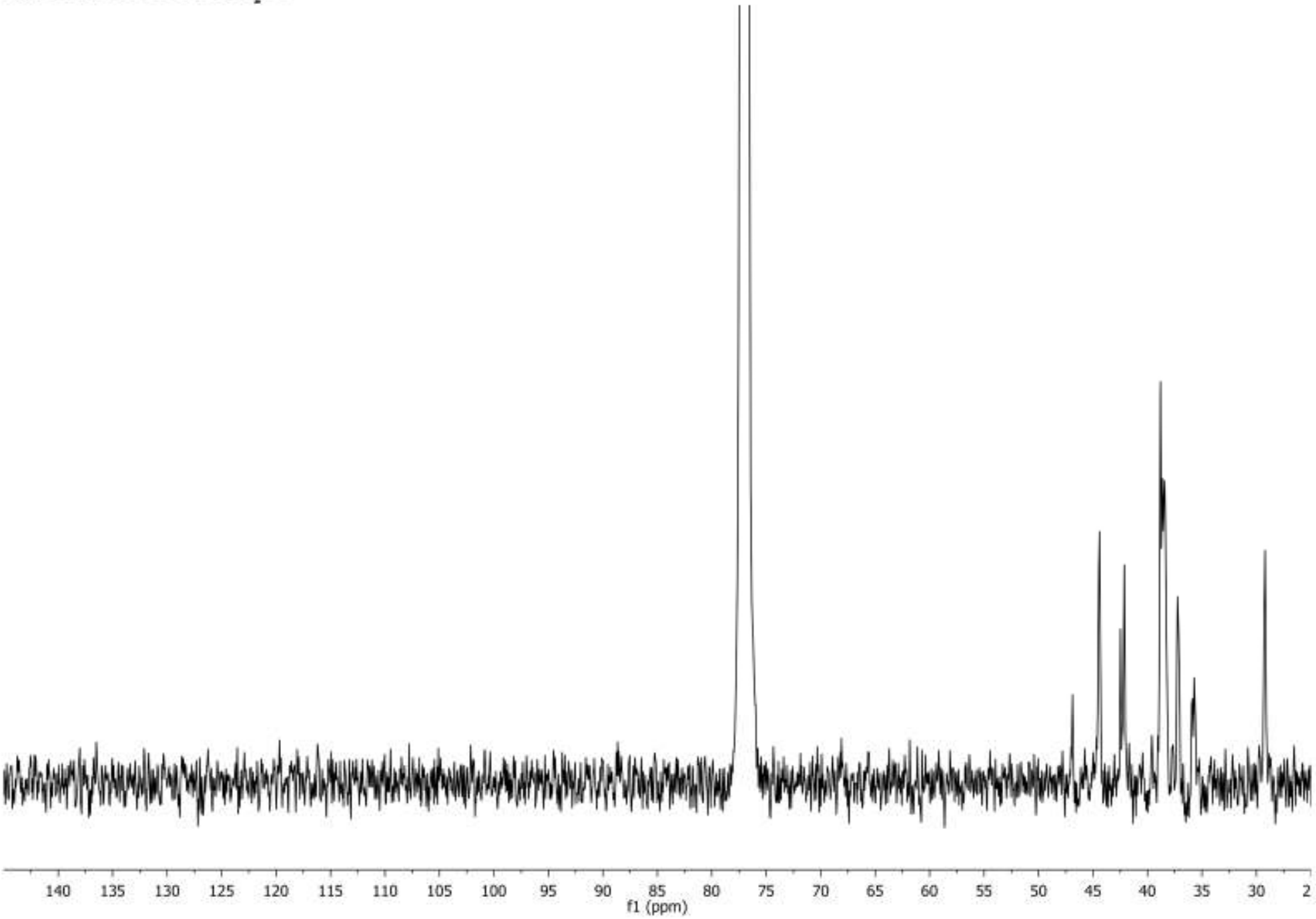
^{1}H NMR 400 MHz

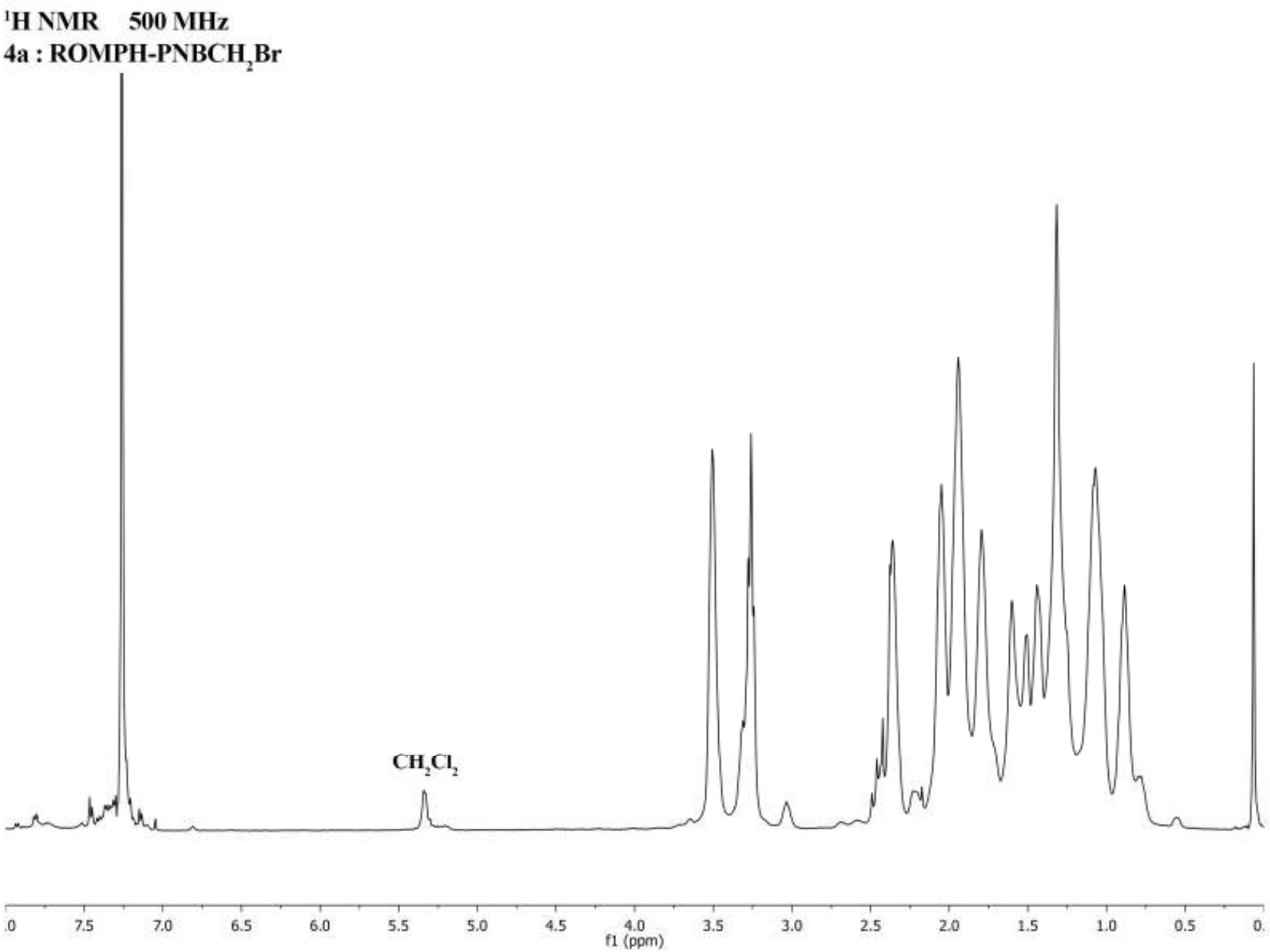
4a : ROMPH-PNB-NBCH$_2$Br



^{13}C NMR 400 MHz

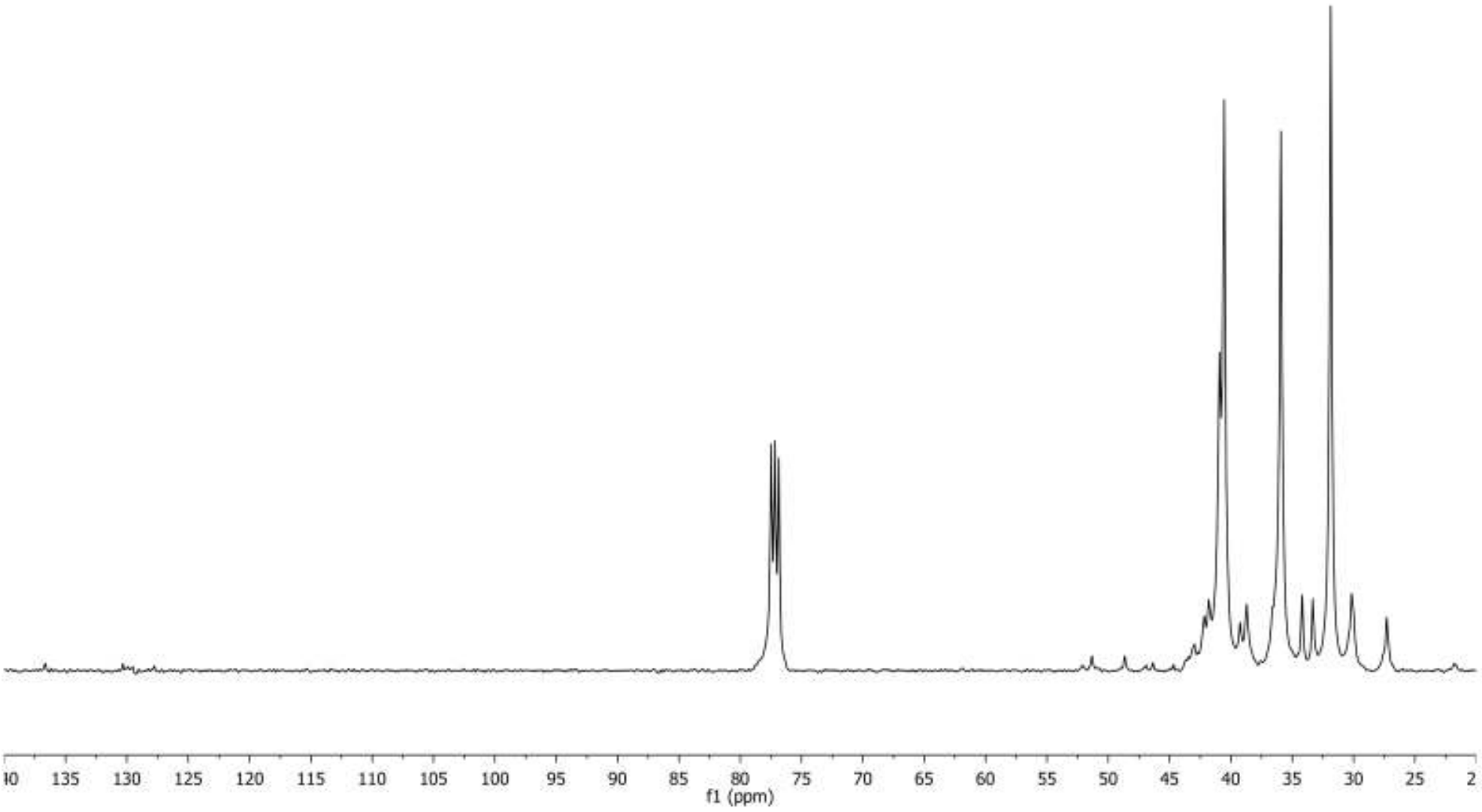
4a : ROMPH-PNBCH$_2$Br




1H NMR 500 MHz
4a : ROMPH-PNBCH2Br
CH2Cl2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

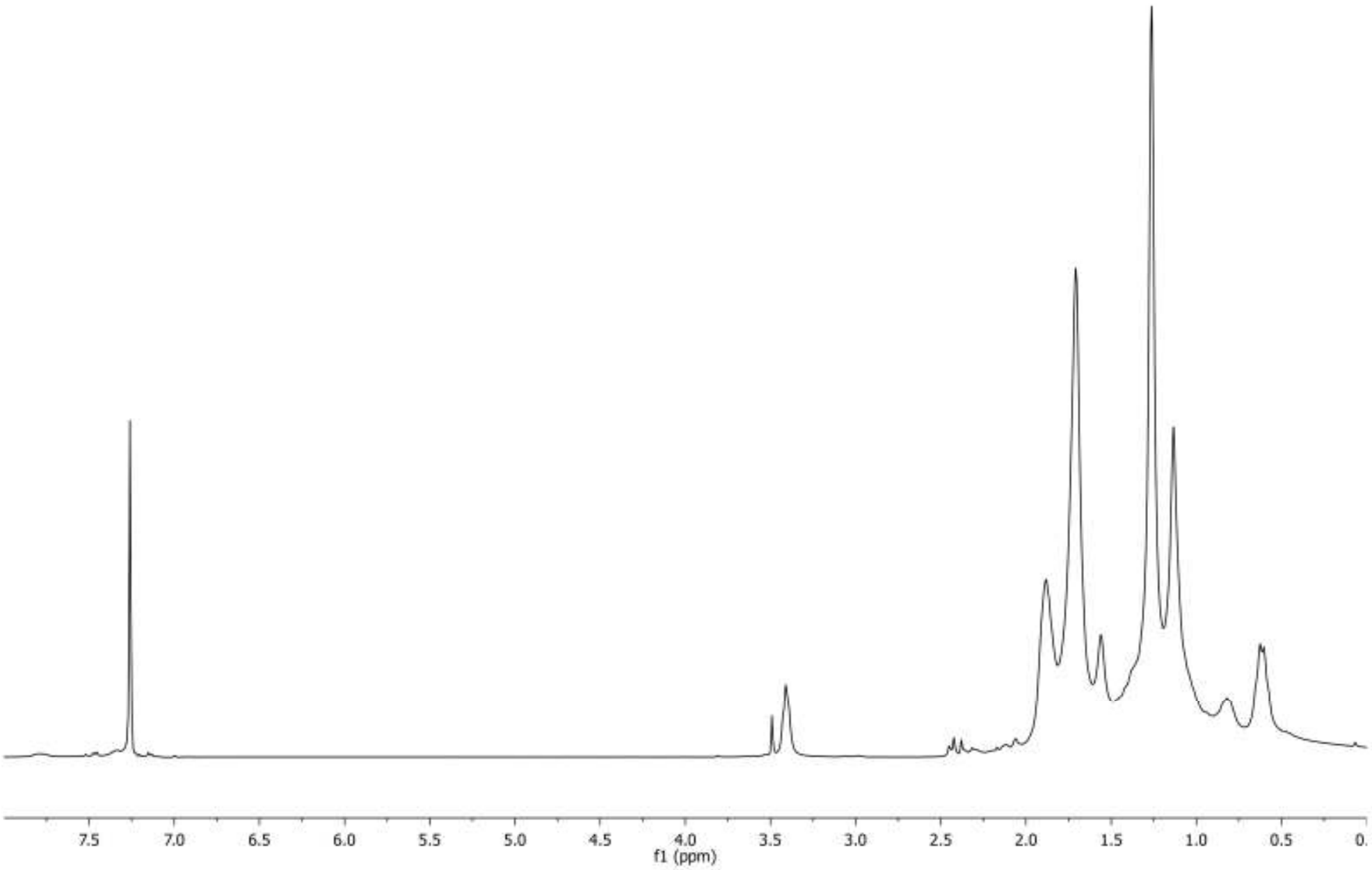
^{13}C NMR 400 MHz

4b : ROMPH-PNB-NB$(CH_2)_4$Br



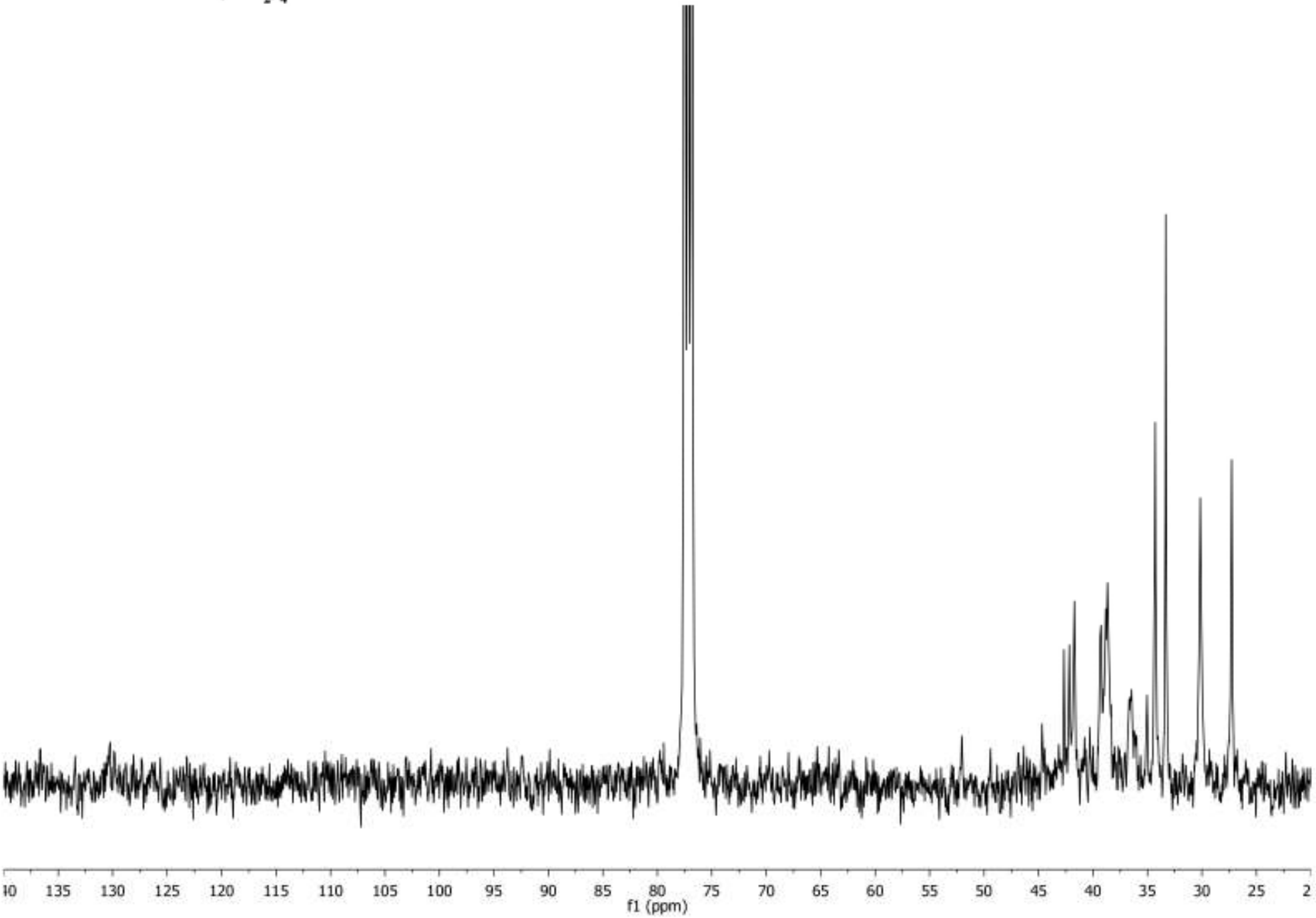
^{1}H NMR 400 MHz

4b : ROMPH-PNB-NB$(CH_2)_4$Br



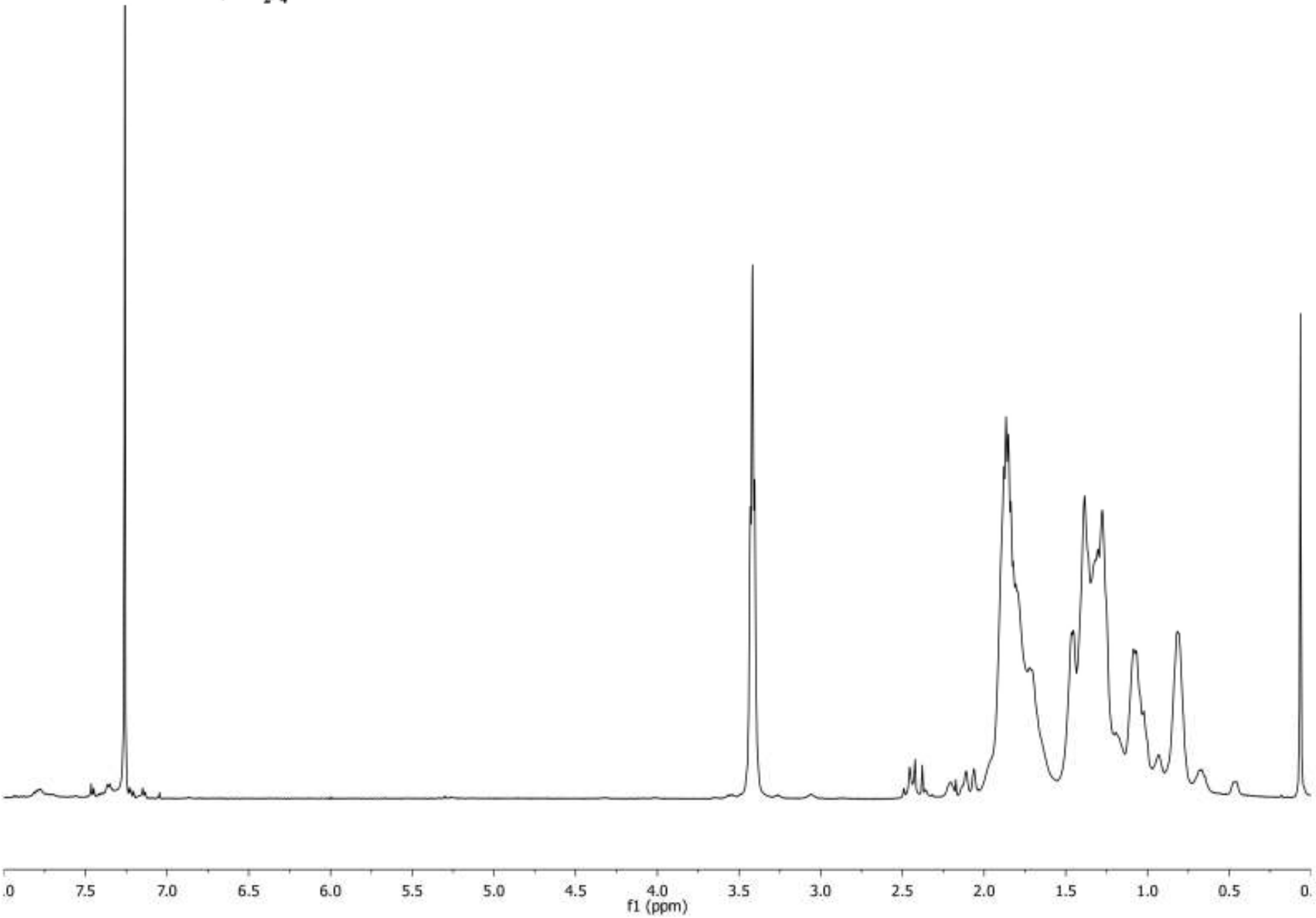
^{13}C NMR 400 MHz

4b : ROMPH-PNB$(CH_2)_4$Br



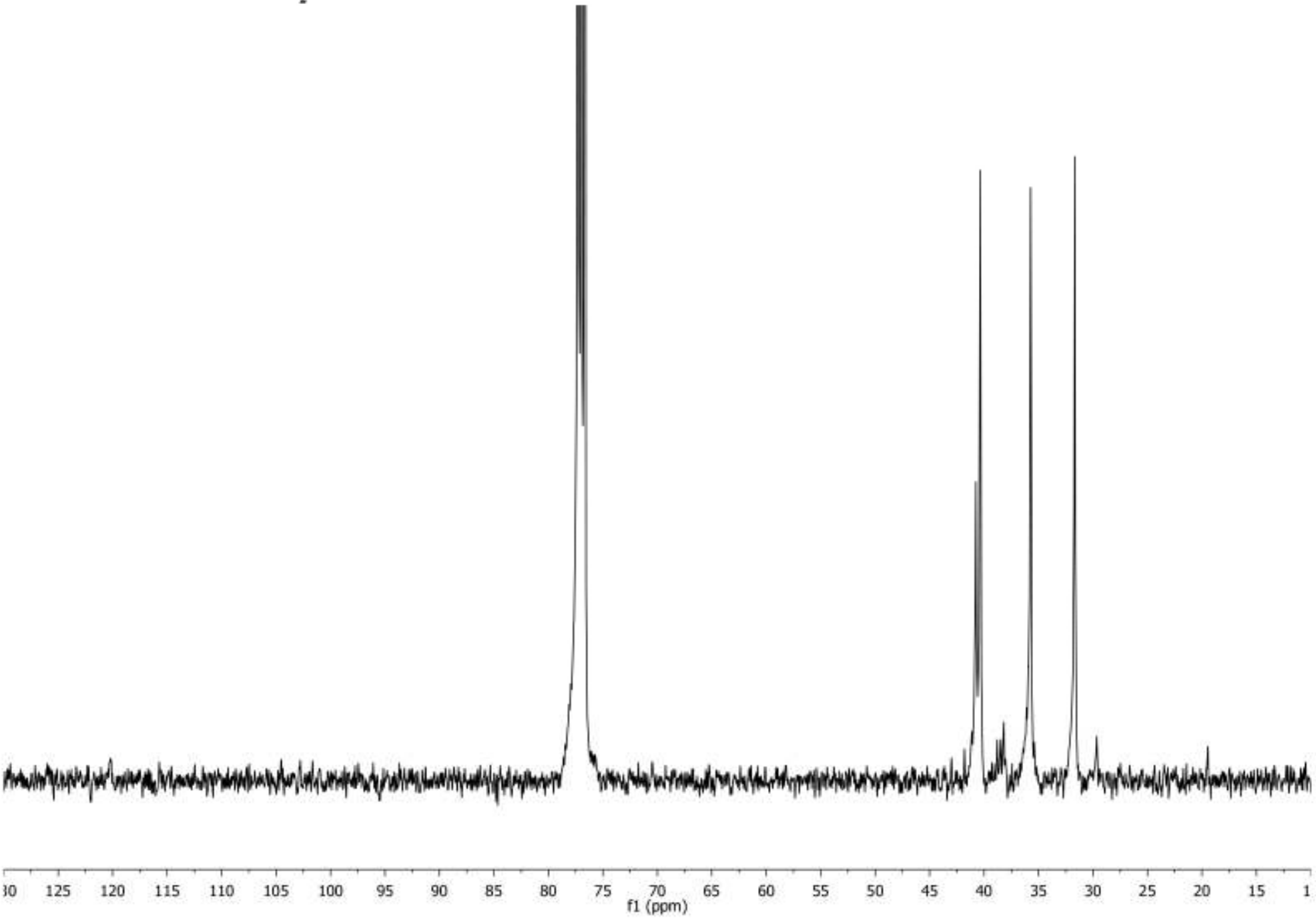
^{1}H NMR 500 MHz

4b : ROMPH-PNB$(CH_2)_4$Br



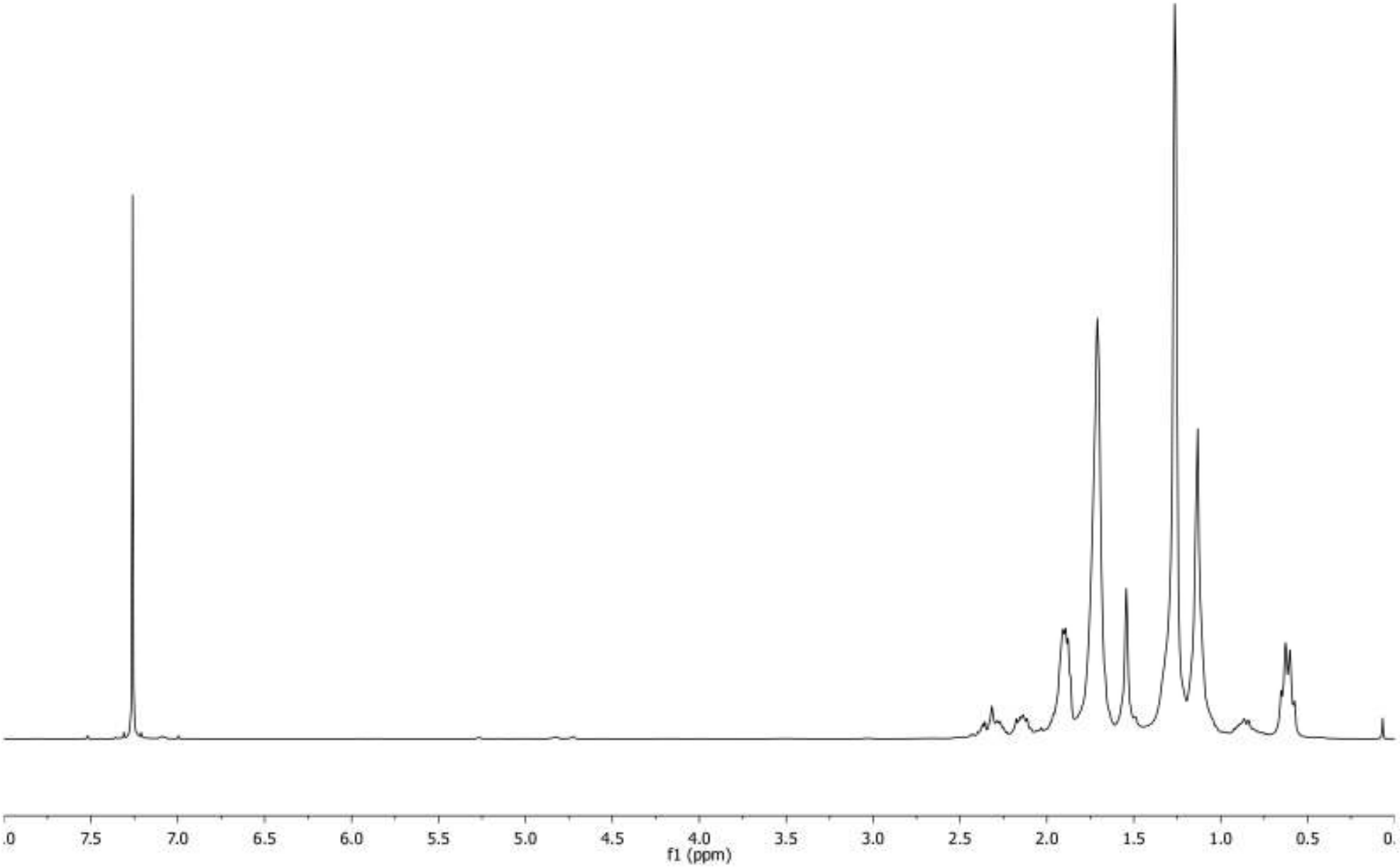
^{13}C NMR 400 MHz

5a : ROMPH-PNB-NBCH$_2$CN



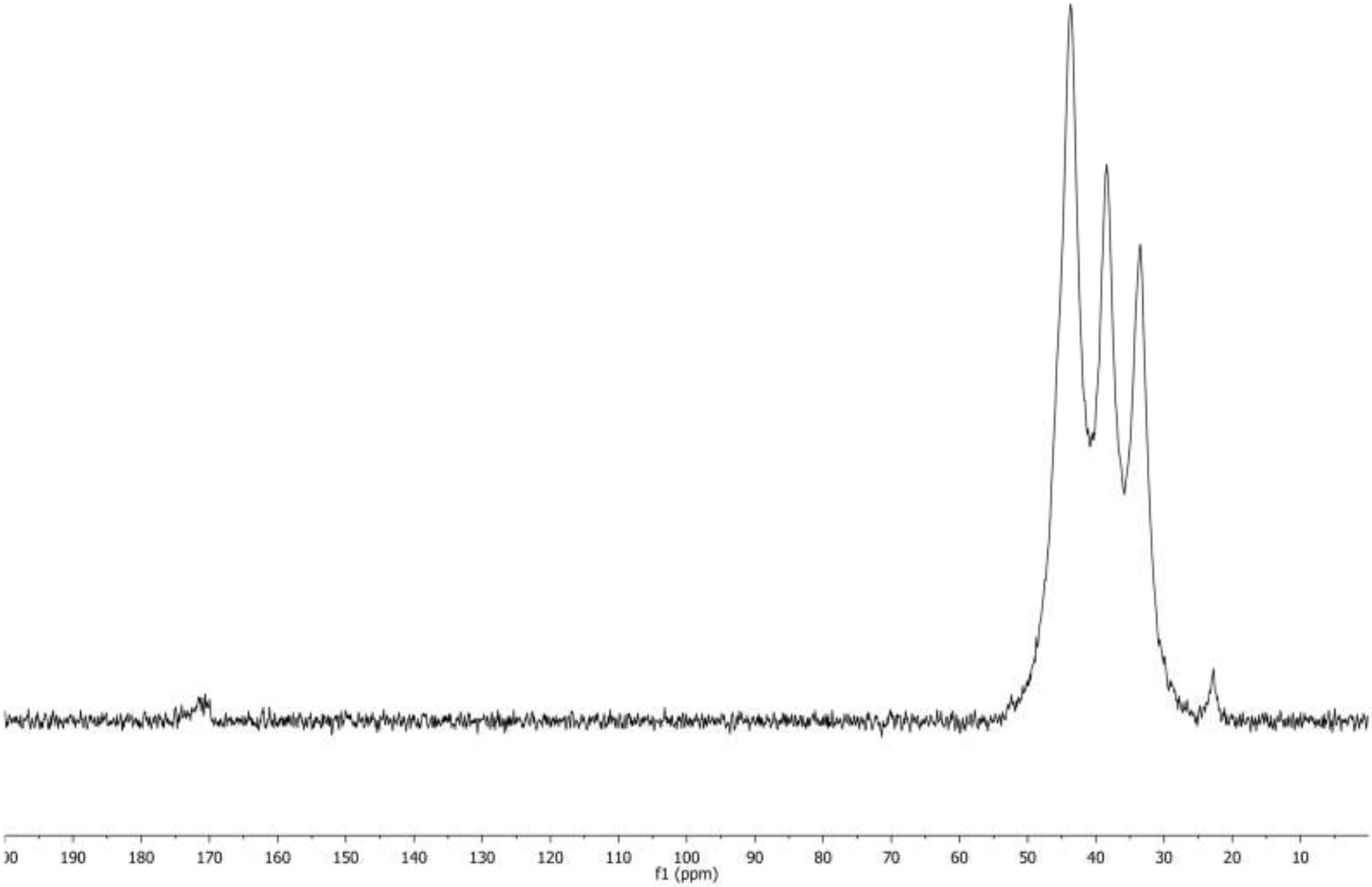
^{1}H NMR 500 MHz

5a : ROMPH-PNB-NBCH$_2$CN



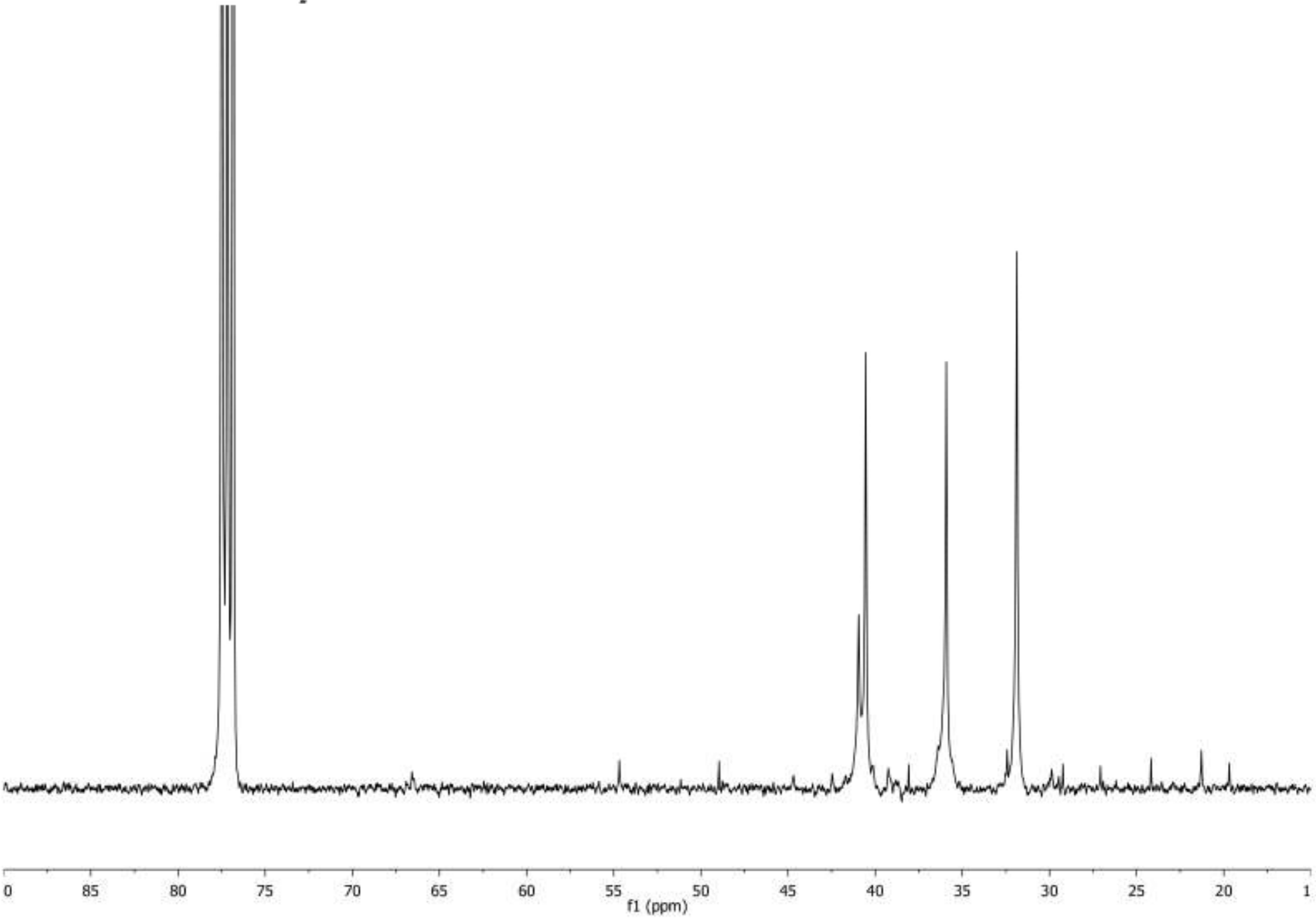
^{13}C CP-MAS NMR 400 MHz

6a : ROMPH-PNB-NBCH$_2$OCOMe



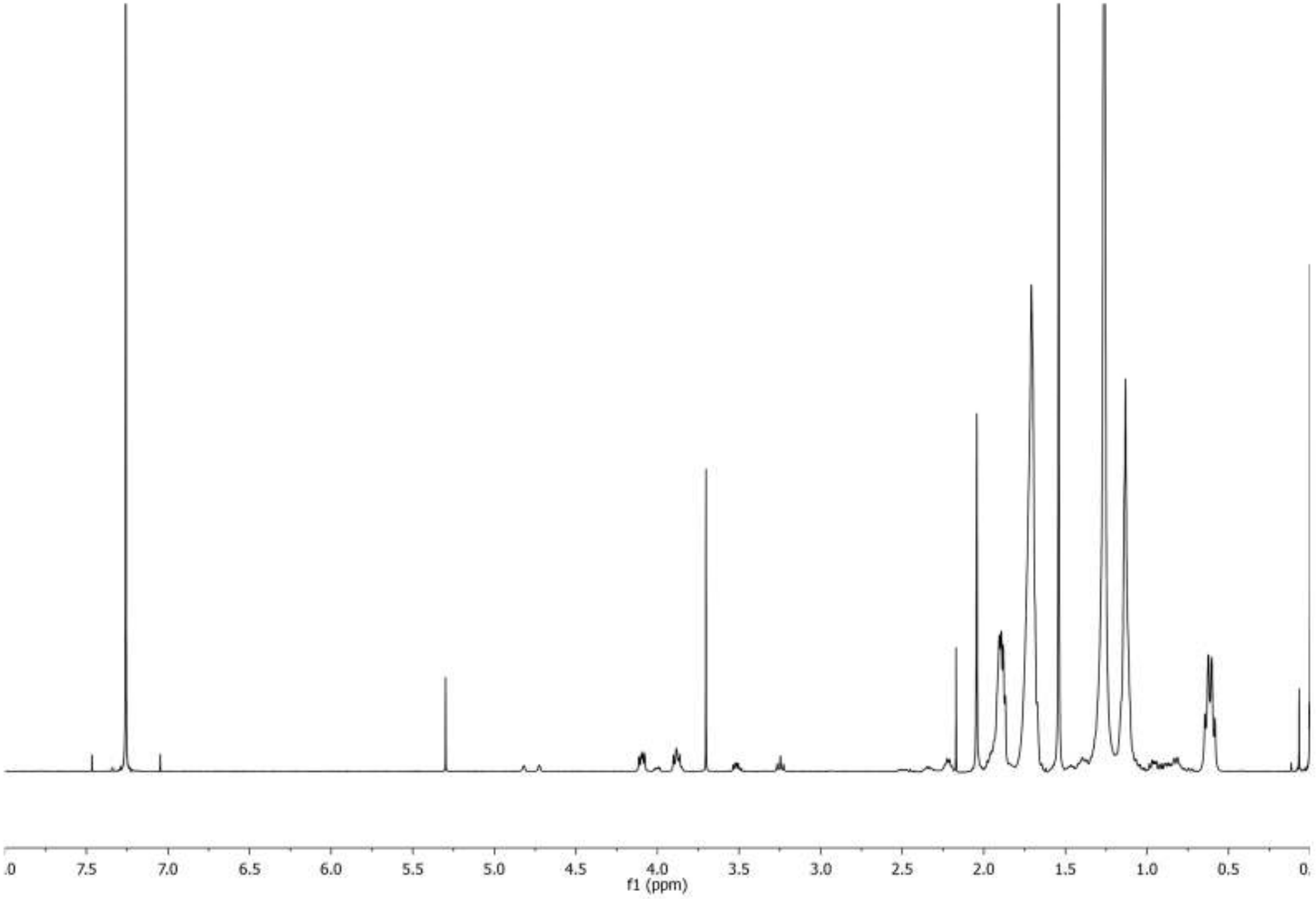
^{13}C NMR 400 MHz

6a : ROMPH-PNB-NBCH$_2$OCOMe



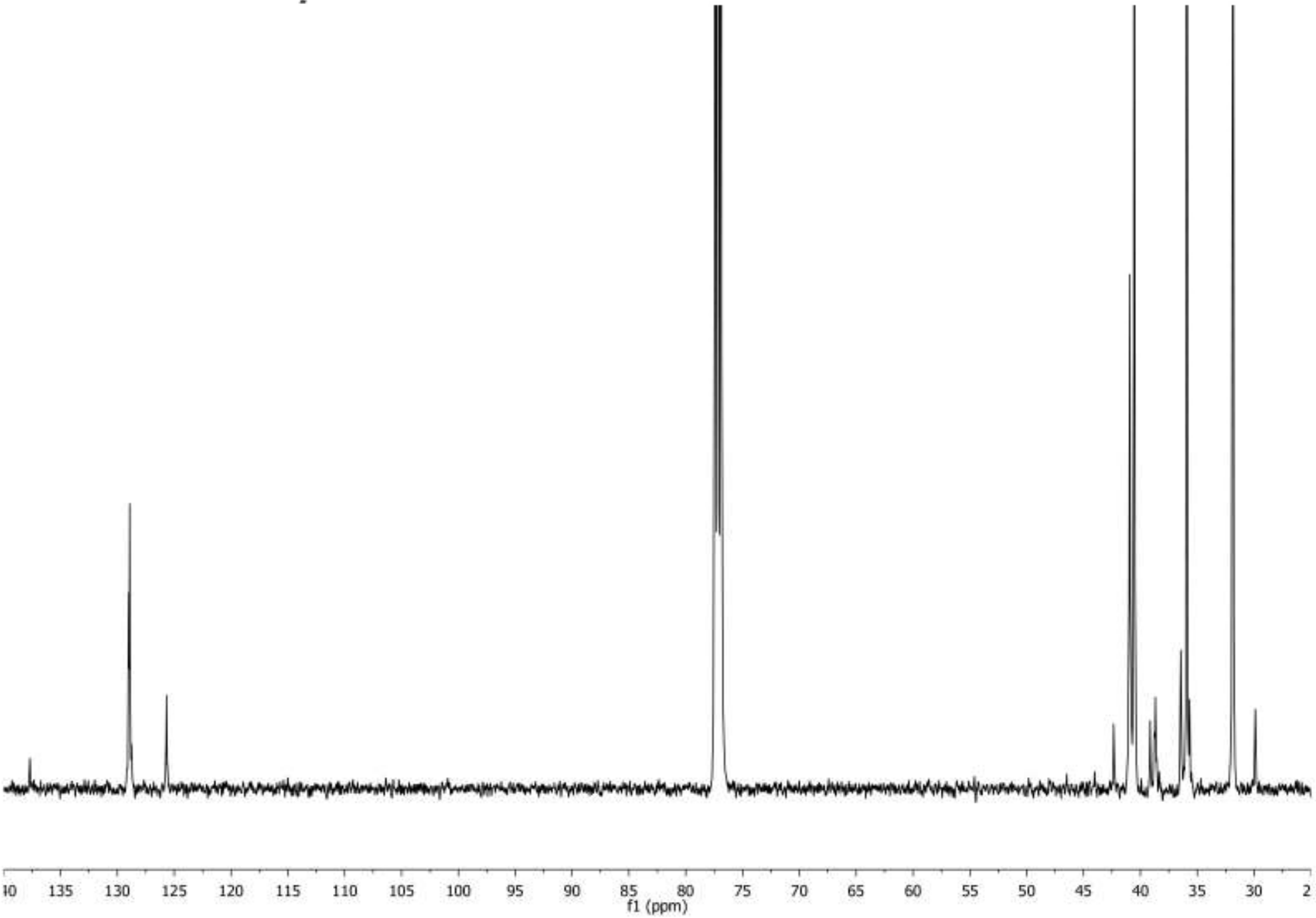
^{1}H NMR 500 MHz

6a : ROMPH-PNB-NBCH$_2$OCOMe



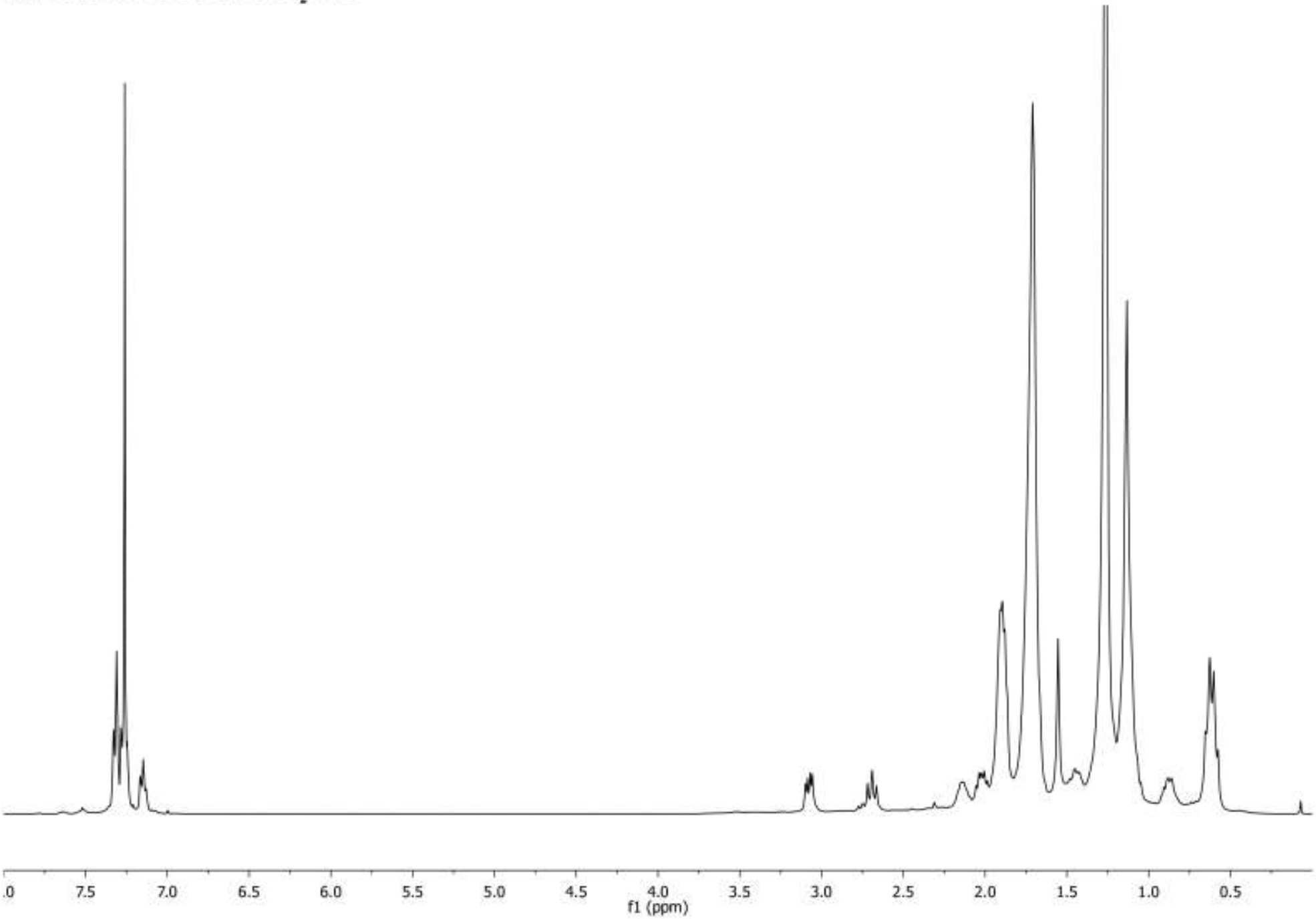
^{13}C NMR 500 MHz

7a : ROMPH-PNB-NBCH$_2$SPh



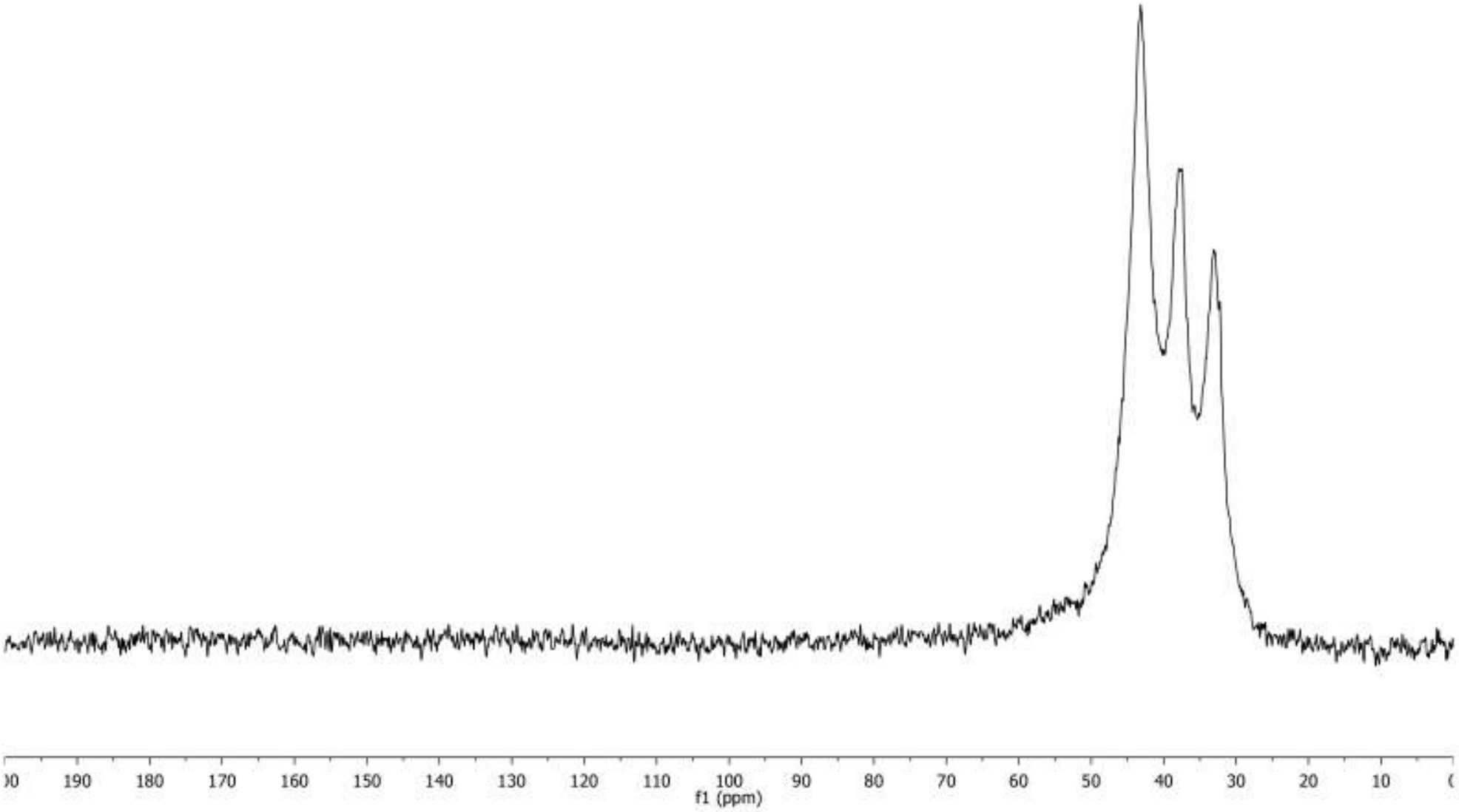
^{1}H NMR 500 MHz

7a : ROMPH-PNB-NBCH$_2$SPh



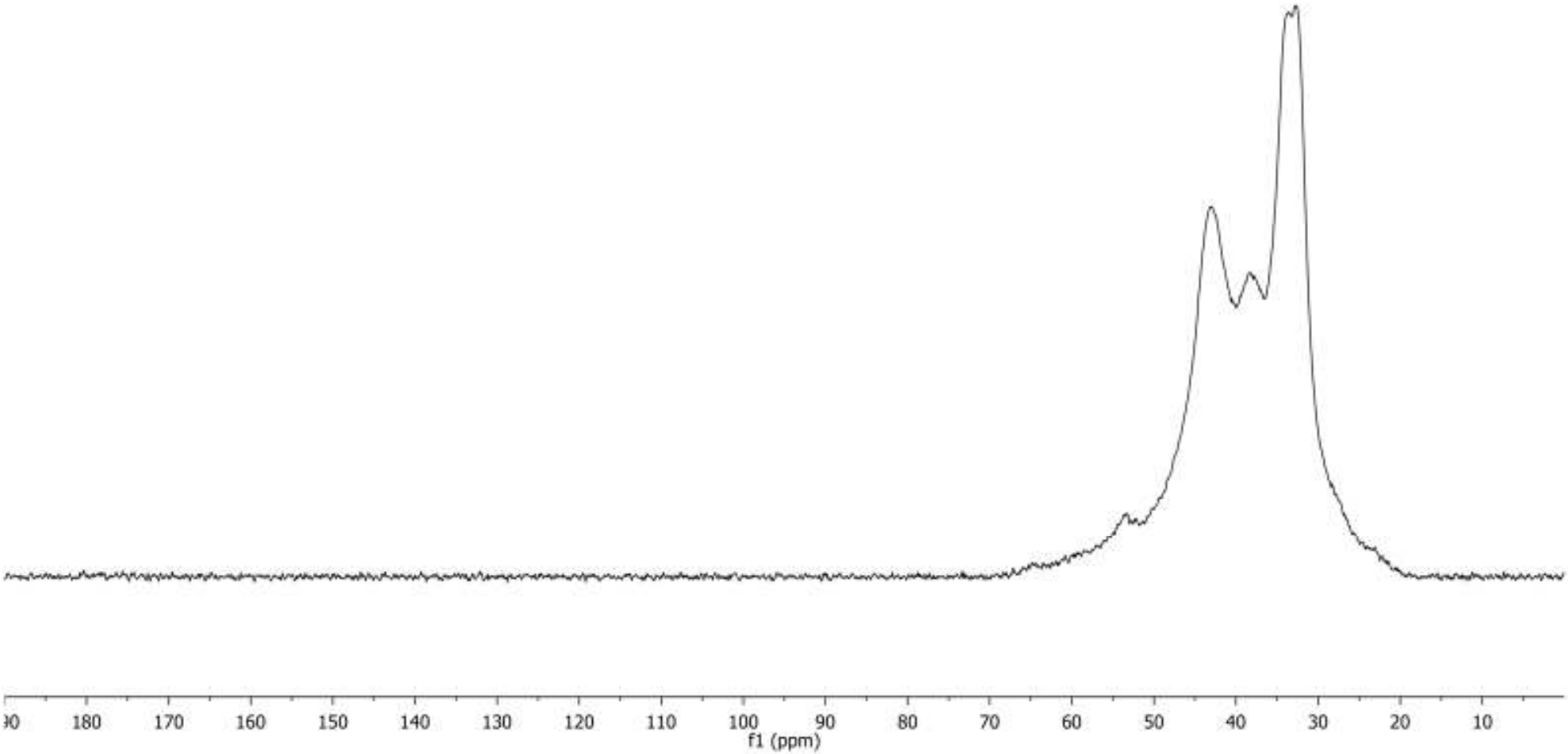
^{13}C CP-MAS NMR 400 MHz

8a : ROMPH-PNB-NBCH$_2$N$_3$



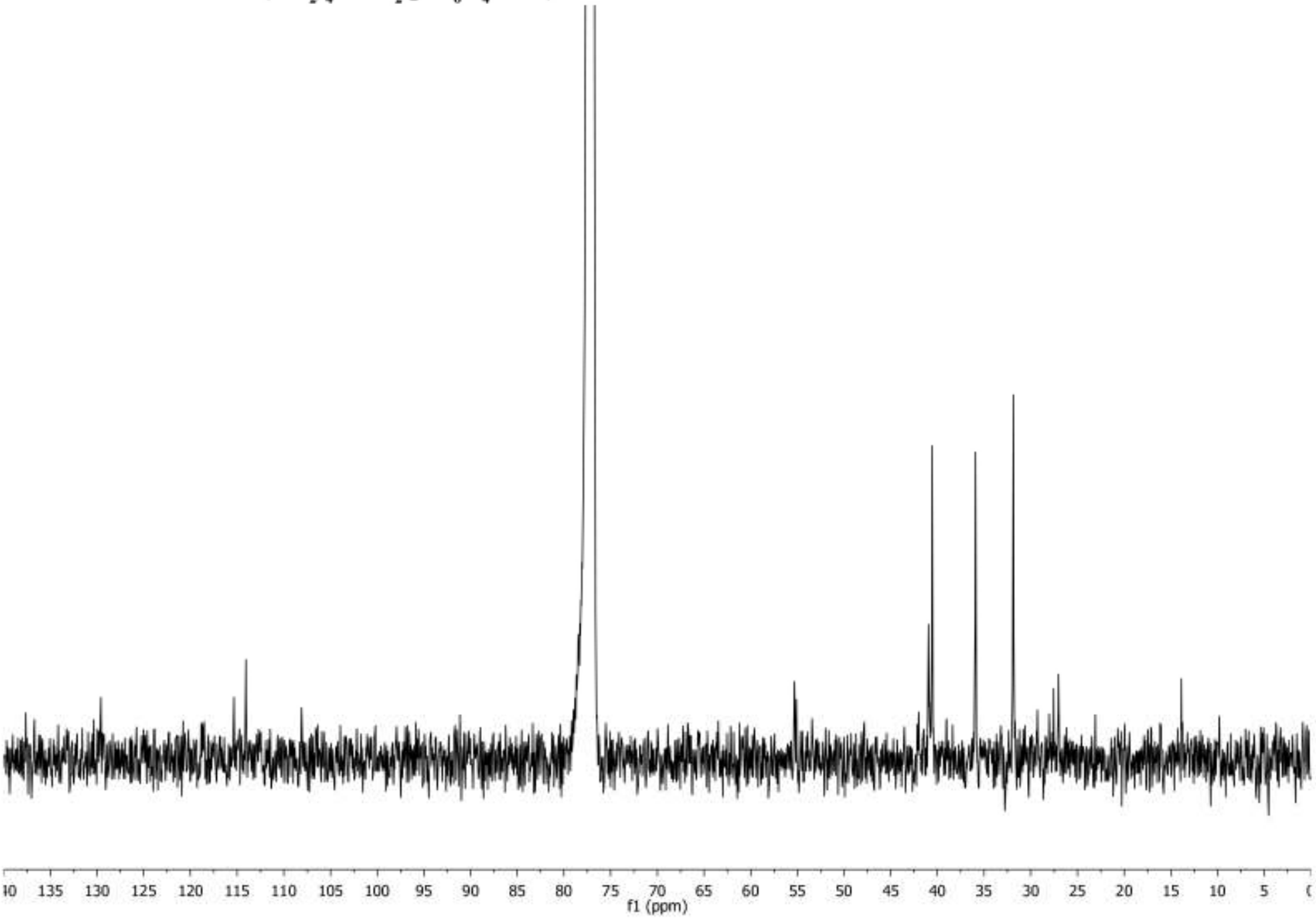
^{13}C CP-MAS NMR 400 MHz

8b : ROMPH-PNB-NB$(CH_2)_4N_3$



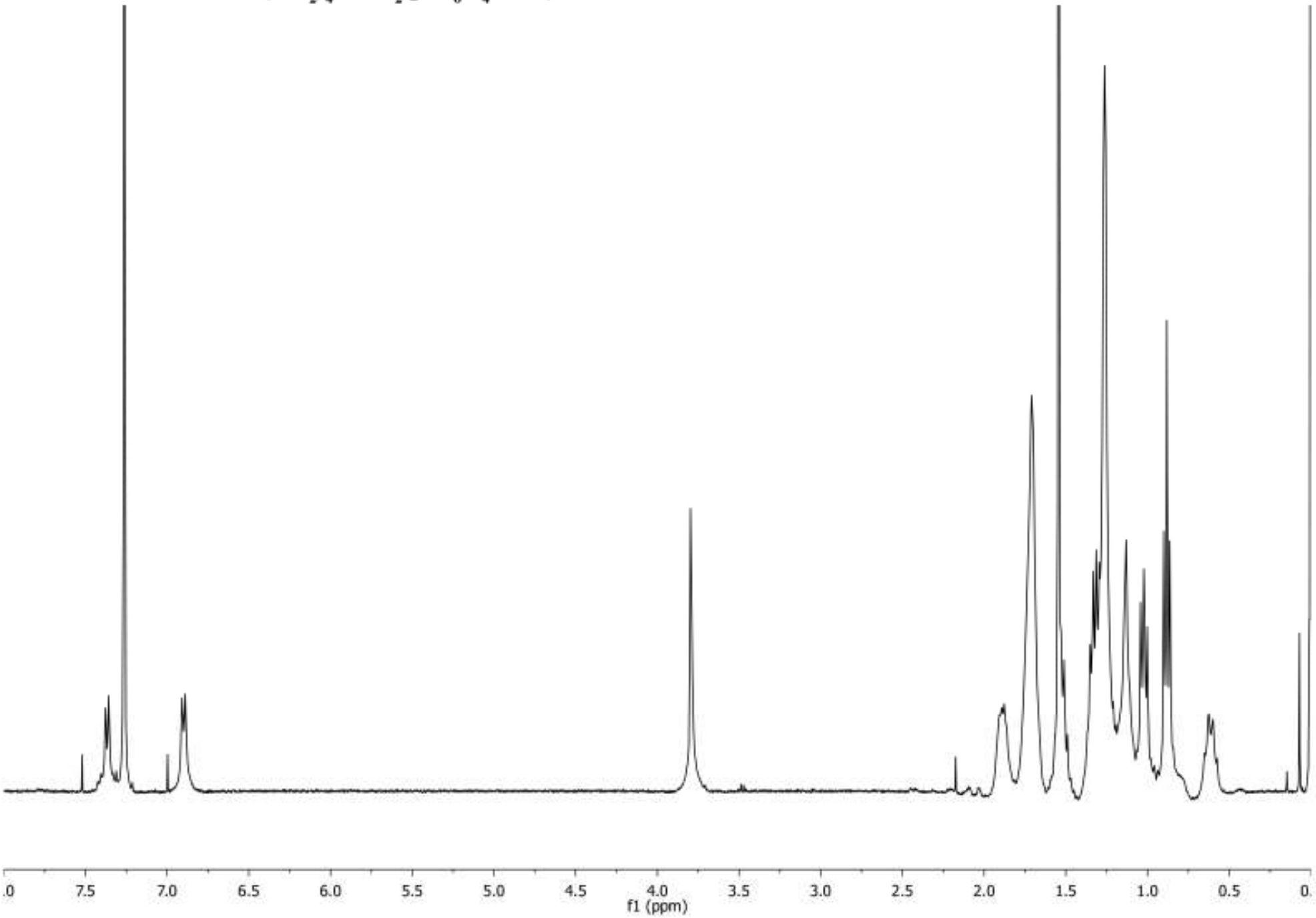
^{13}C NMR 400 MHz

9b : ROMPH-PNB-NB$(CH_2)_4$SnBu$_2$(*p*-C_6H_4OMe)



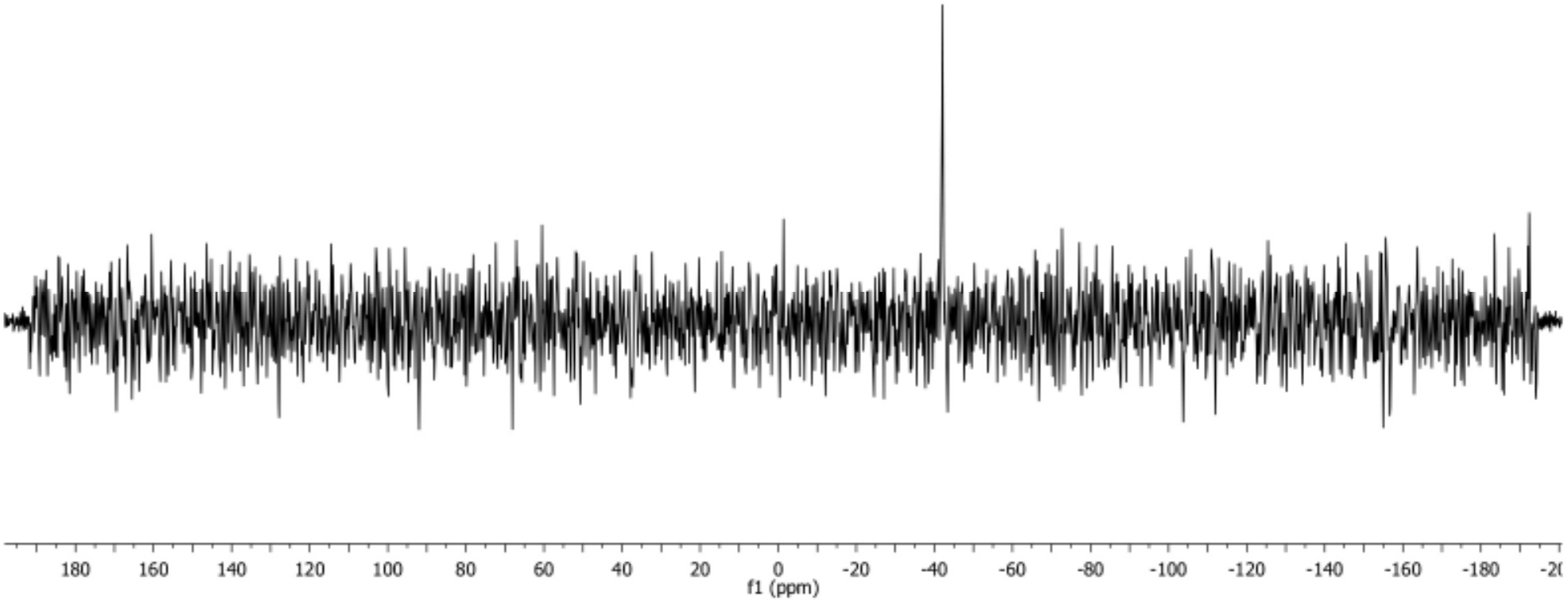
^{1}H NMR 500 MHz

9b : ROMPH-PNB-NB$(CH_2)_4$SnBu$_2$(*p*-C_6H_4OMe)



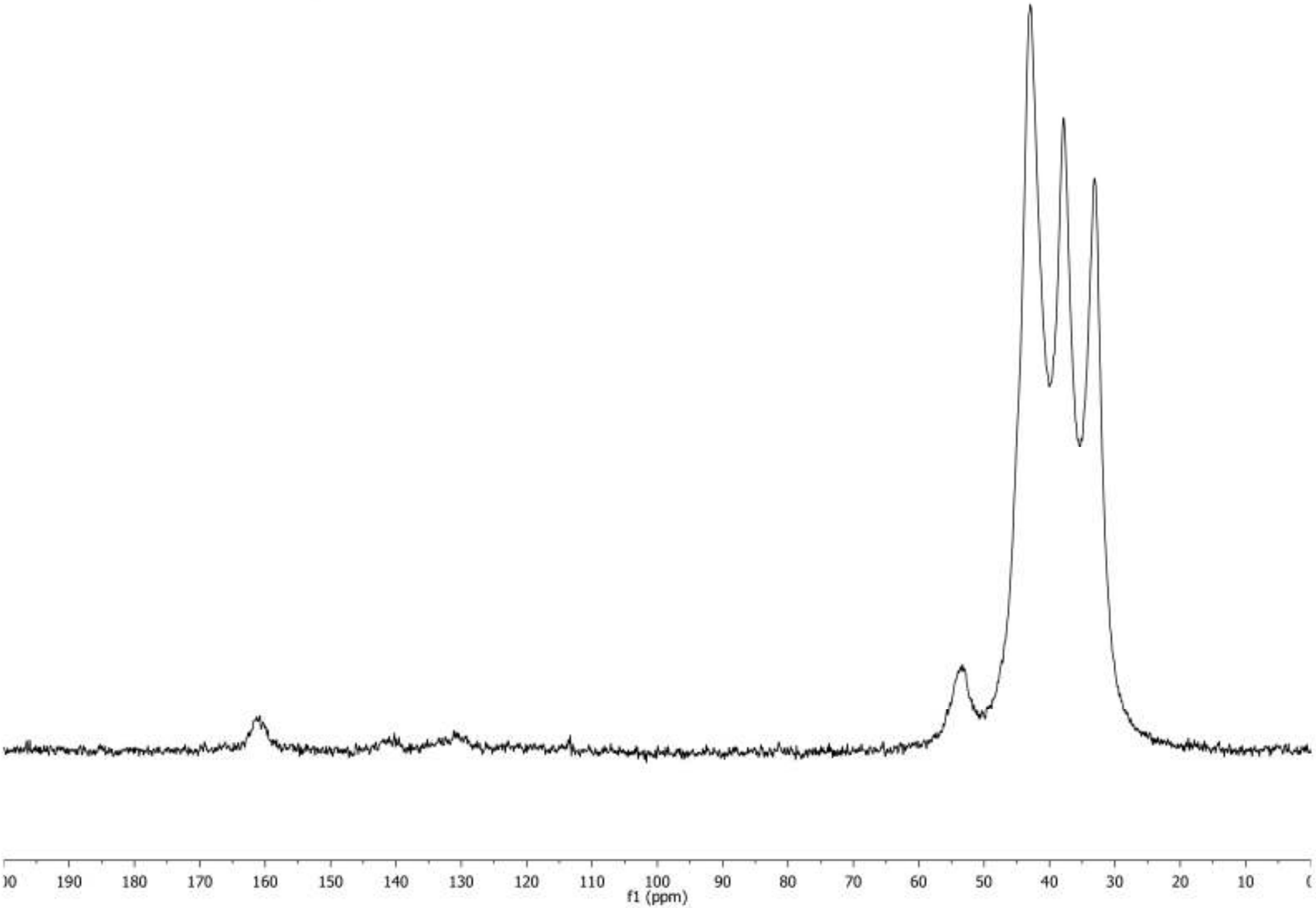
^{119}Sn NMR 400 MHz

9b : ROMPH-PNB-NB$(CH_2)_4$SnBu$_2$(*p*-C_6H_4OMe)



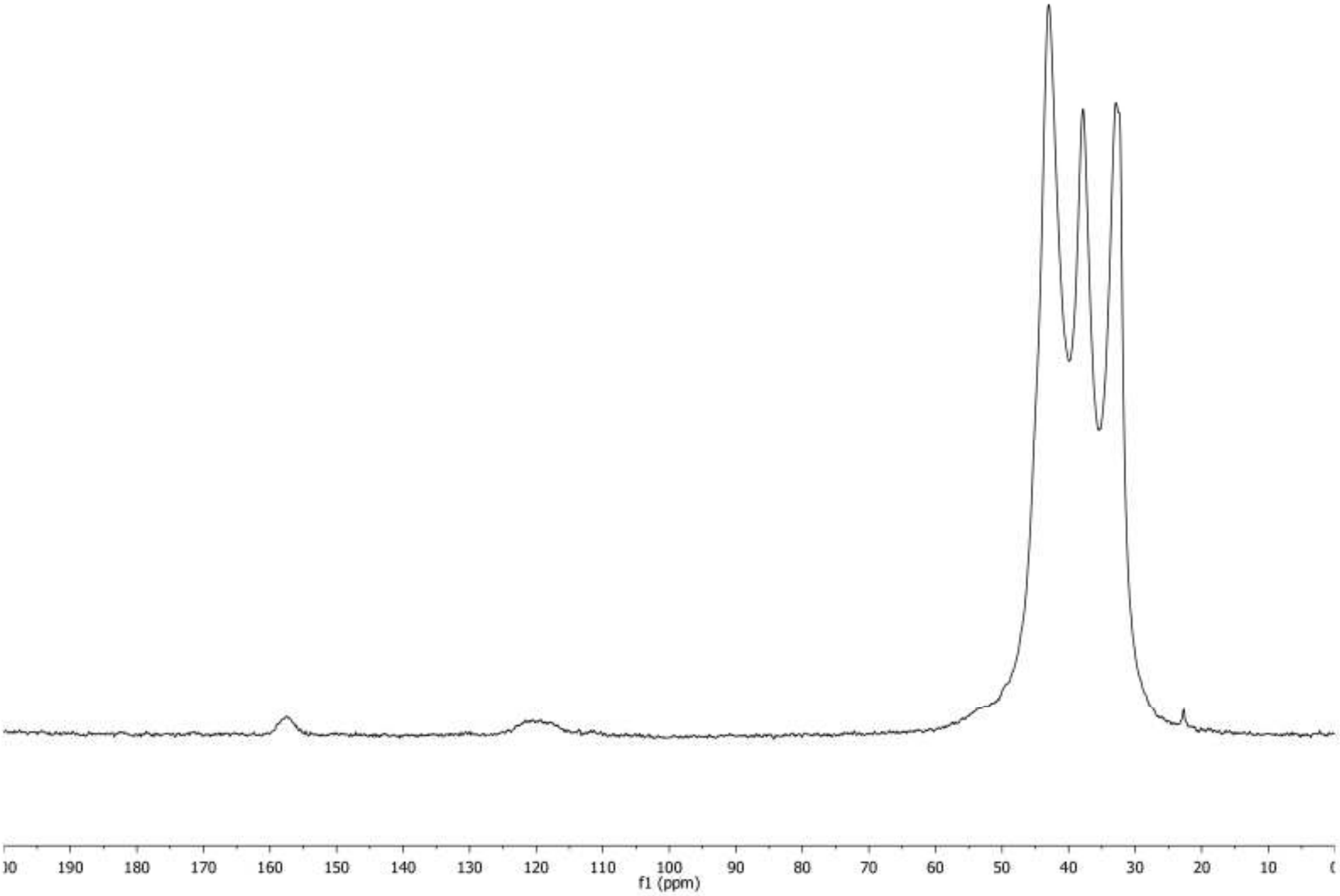
^{13}C CP-MAS NMR 400 MHz

10a : ROMPH-PNB-NBCH$_2$triazole



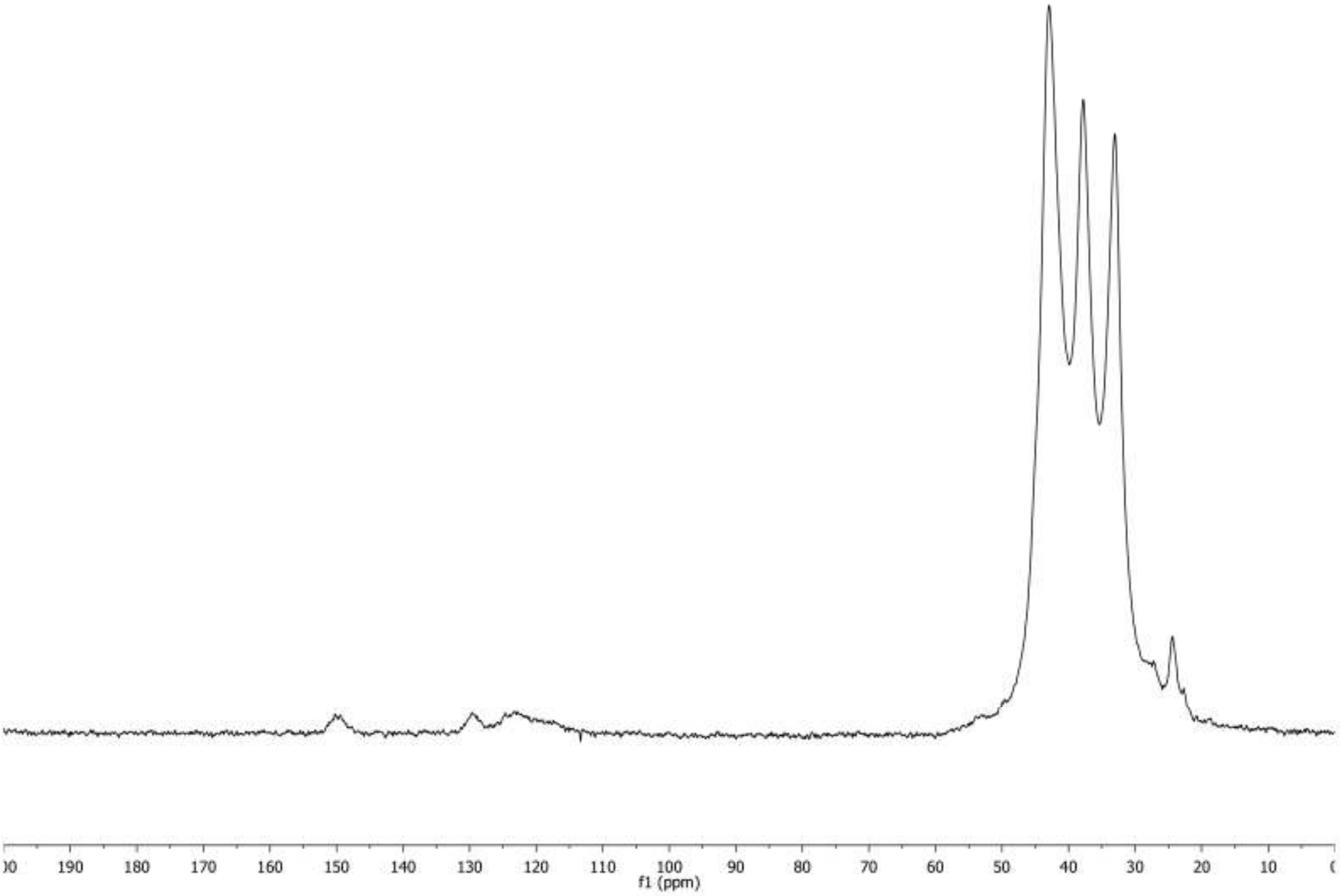
^{13}C CP-MAS NMR 400 MHz

11a : ROMPH-PNB-NBCH$_2$triazole



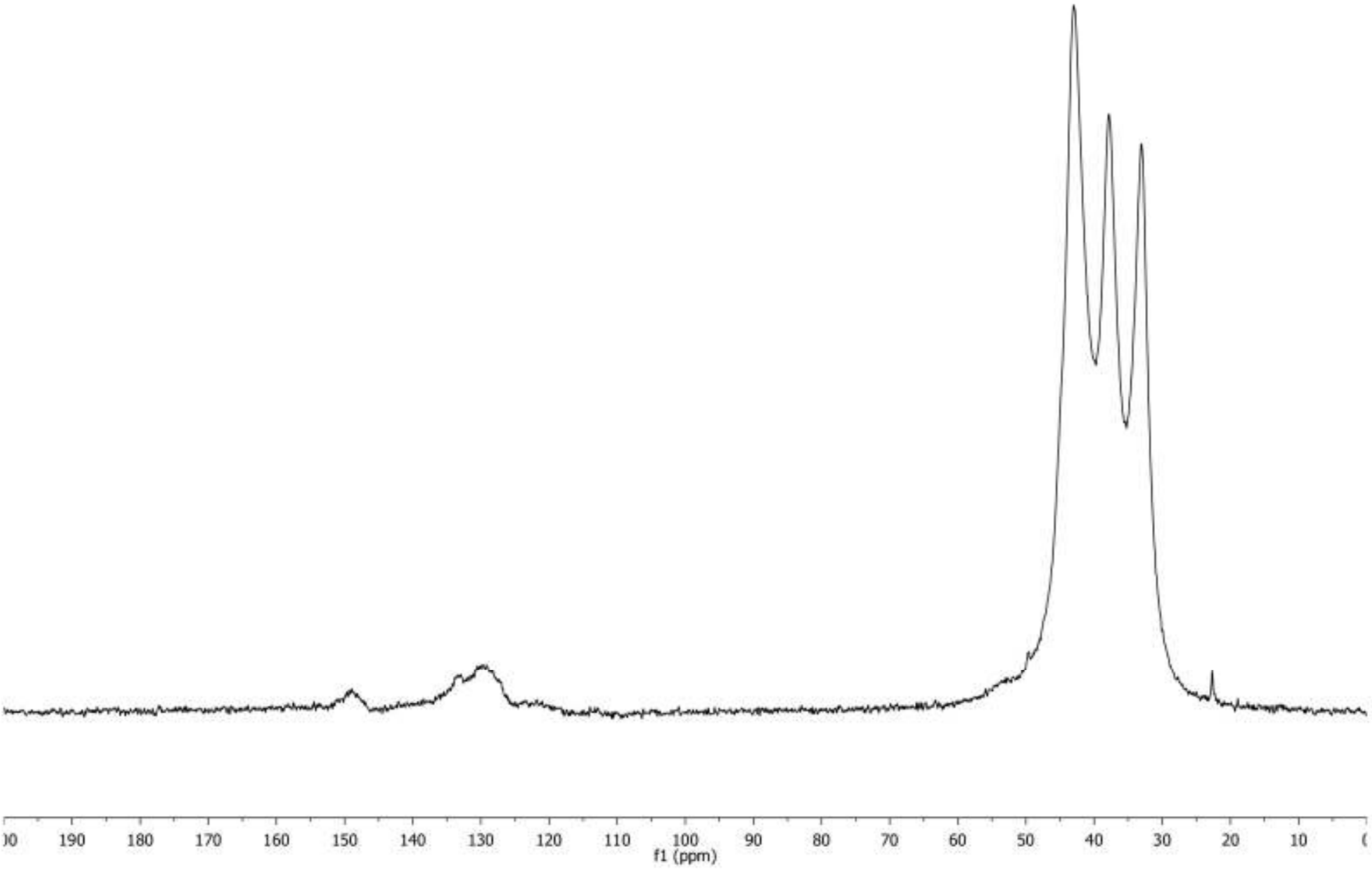
^{13}C CP-MAS NMR 400 MHz

12a : ROMPH-PNB-NBCH$_2$triazole



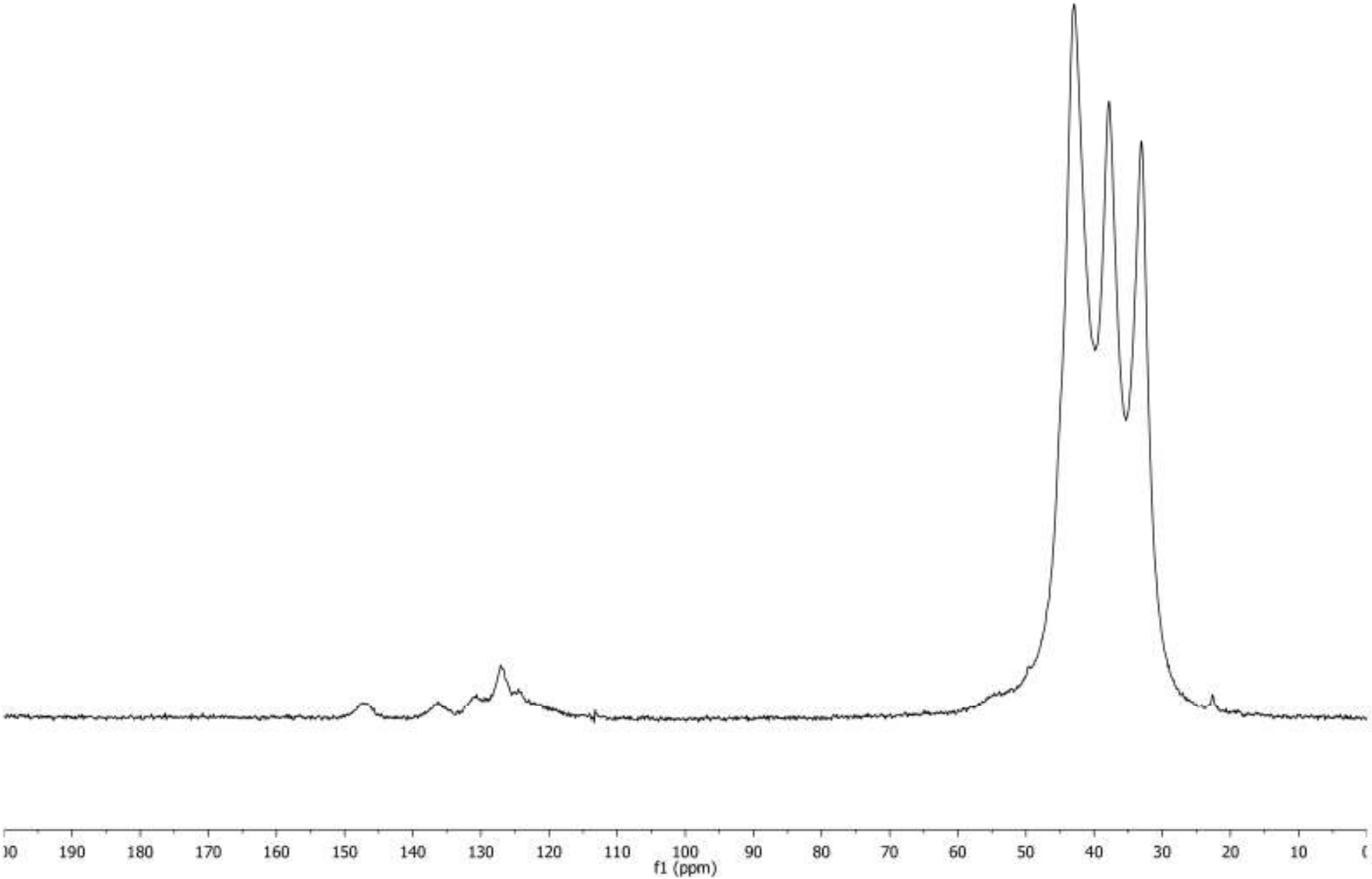
^{13}C CP-MAS NMR 400 MHz

13a : ROMPH-PNB-NBCH$_2$triazole

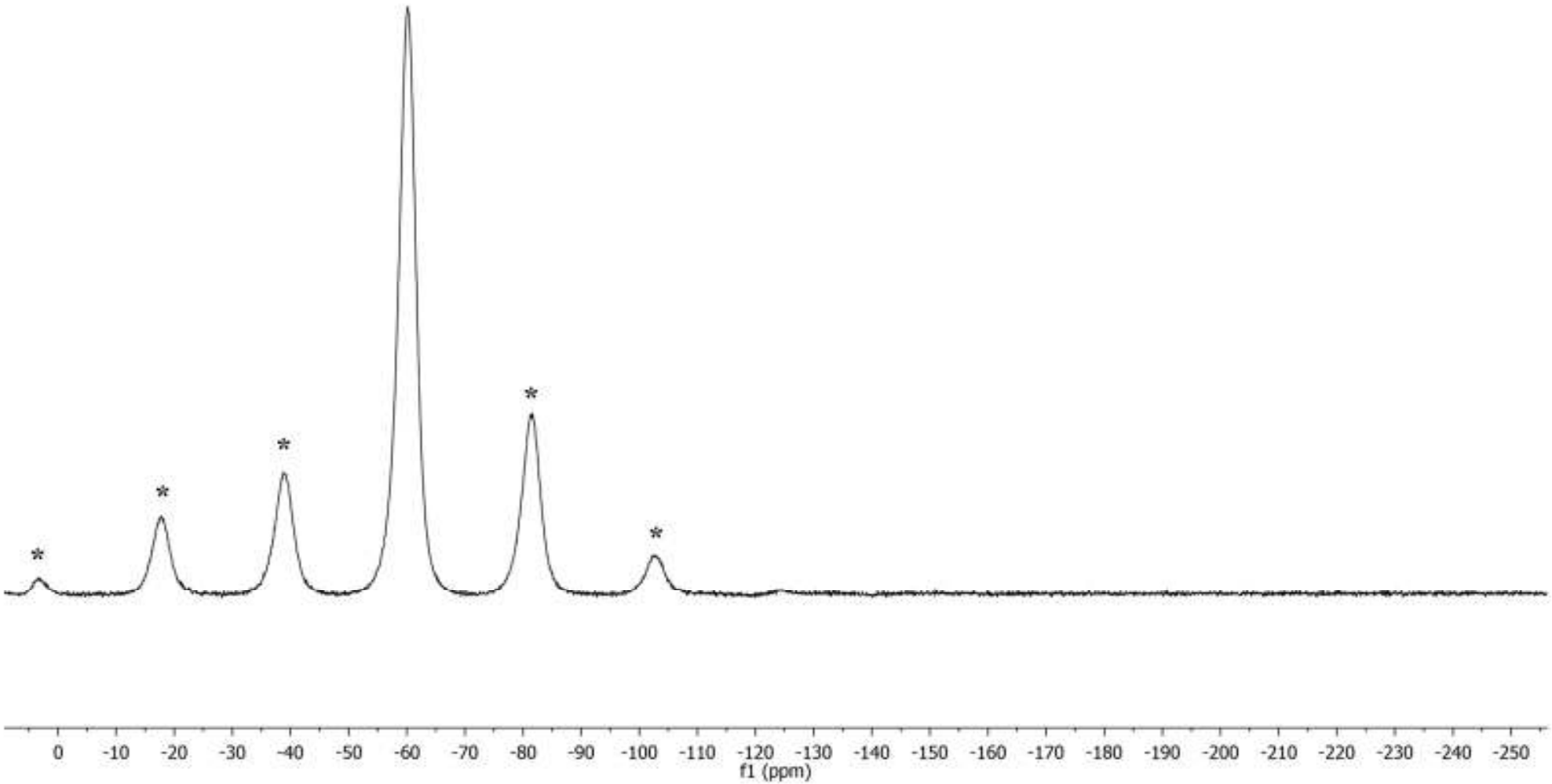


^{13}C CP-MAS NMR 400 MHz

14a : ROMPH-PNB-NBCH$_2$triazole



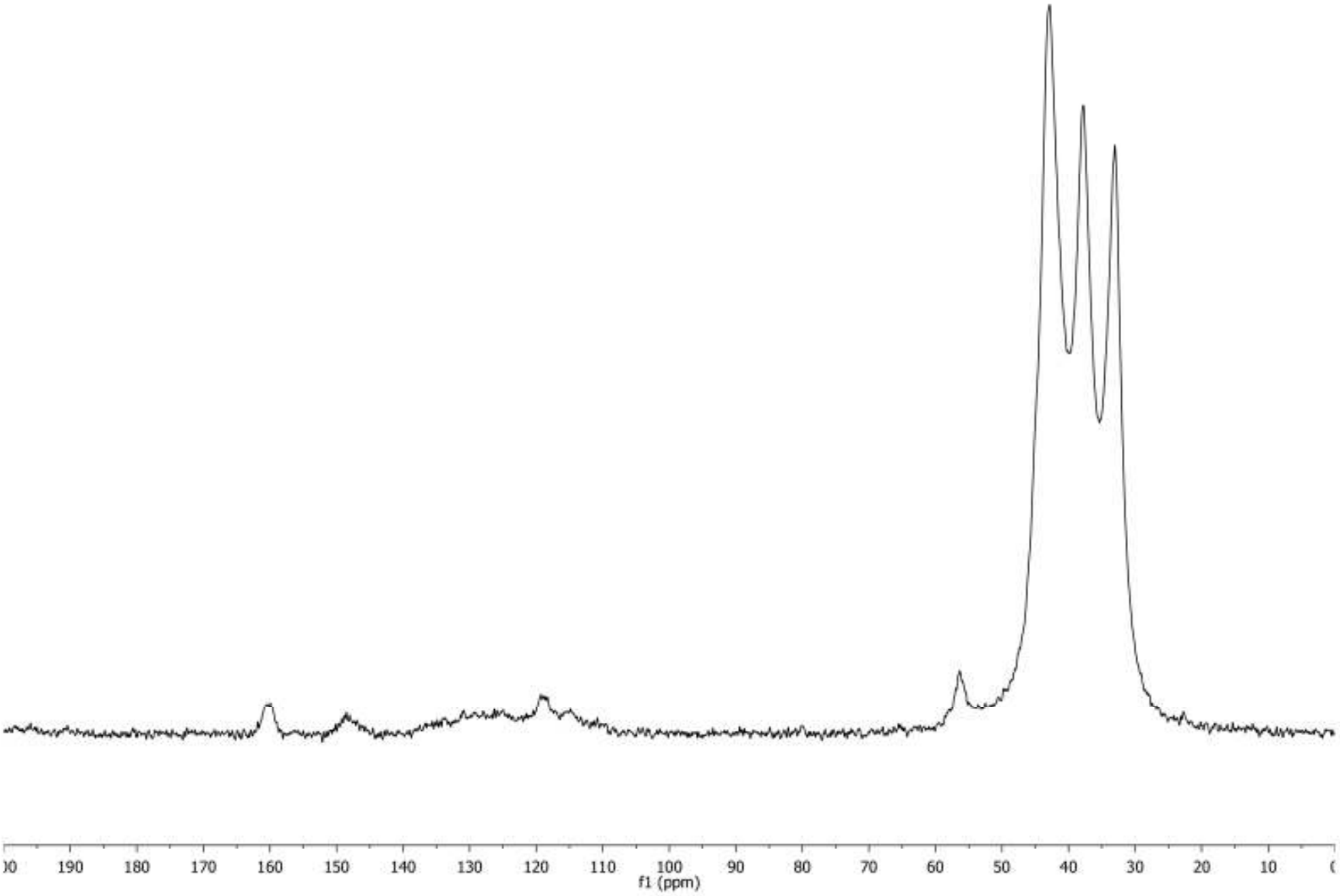
^{19}F CP-MAS NMR 400 MHz
14a : ROMPH-PNB-NBCH$_2$triazole



*** Spinning sidebands are present.**

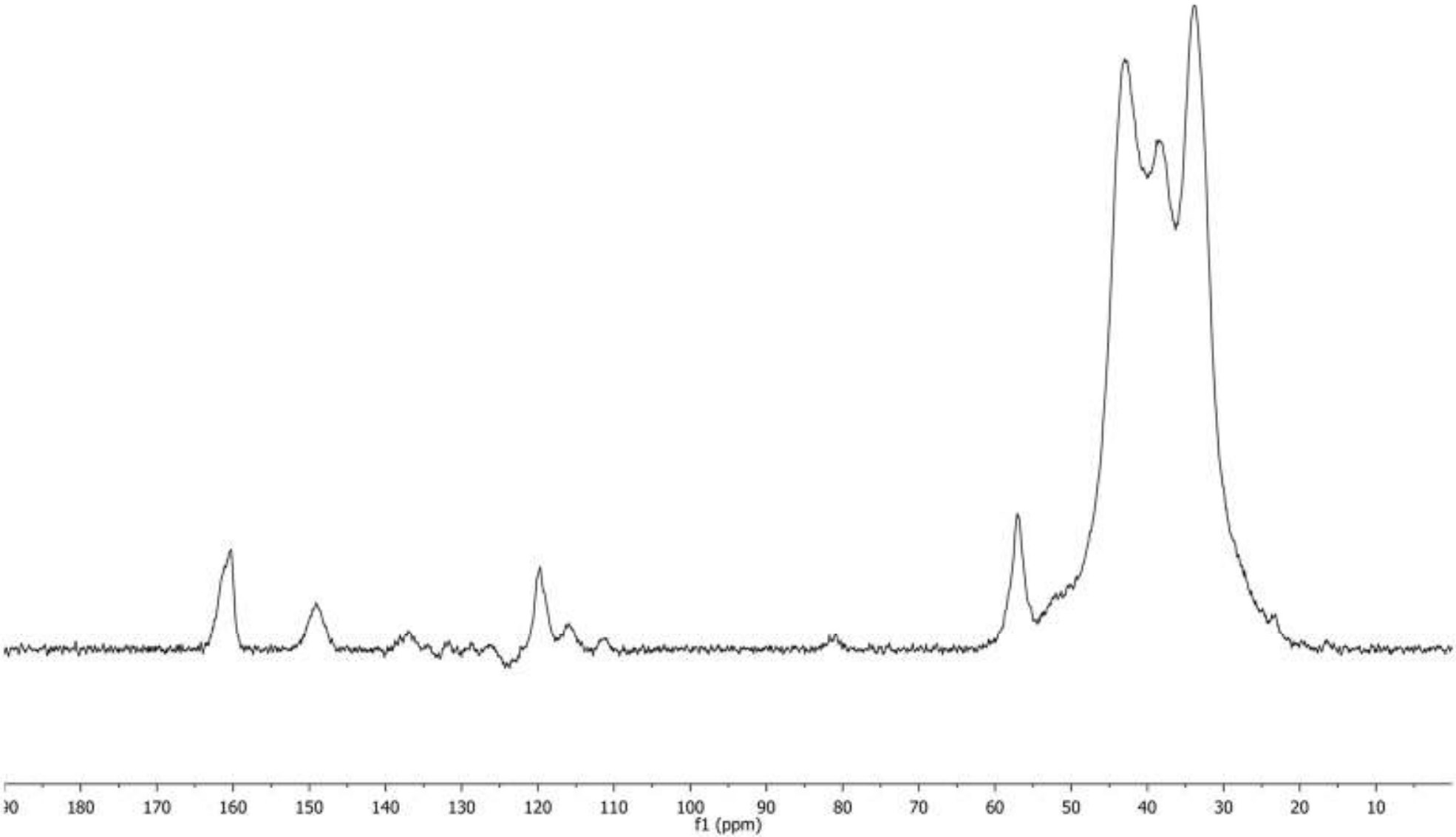
^{13}C CP-MAS NMR 400 MHz

15a : ROMPH-PNB-NBCH$_2$triazole

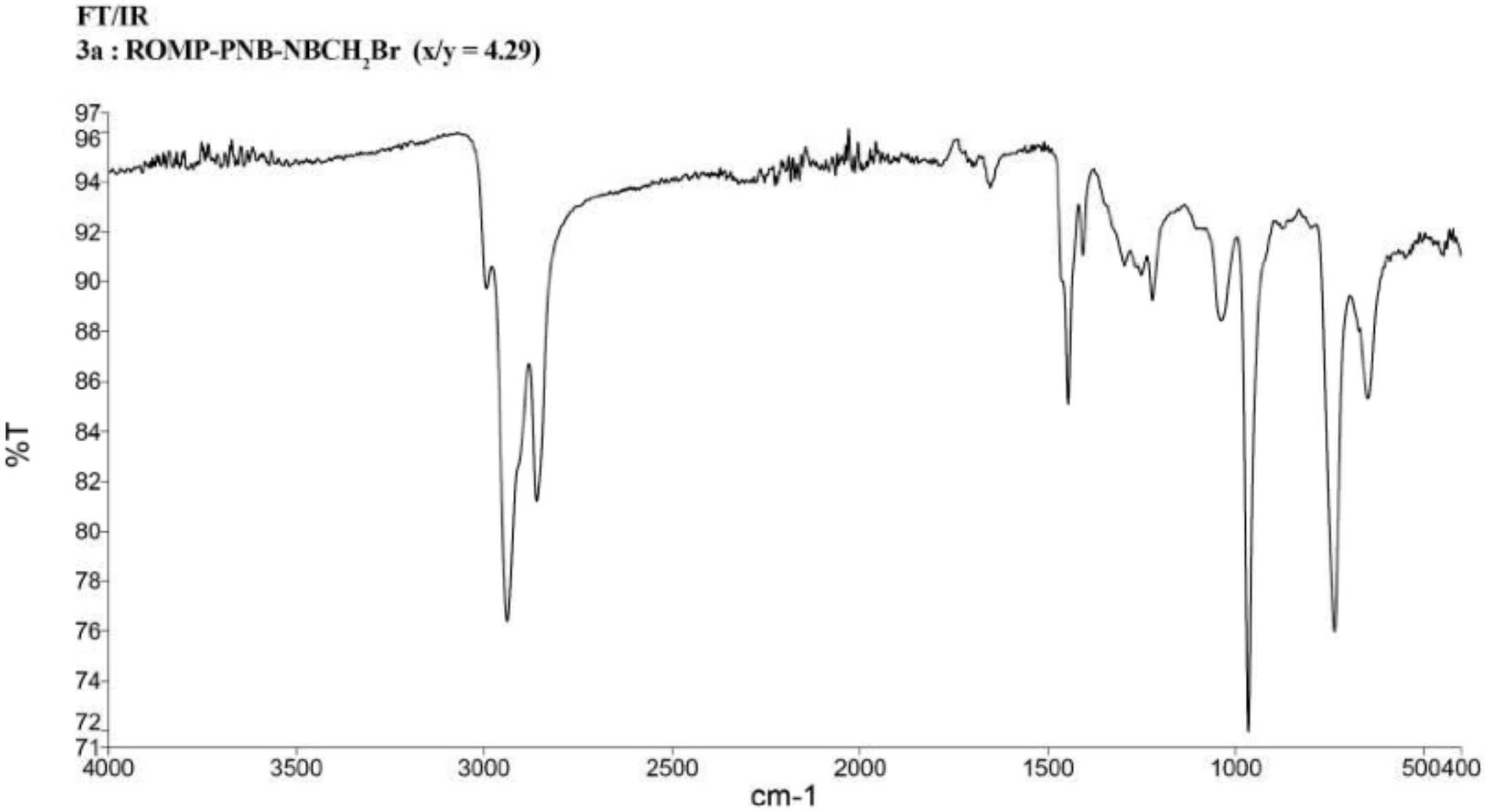


^{13}C CP-MAS NMR 400 MHz

15b: ROMPH-PNB-NB$(CH_2)_4$triazole

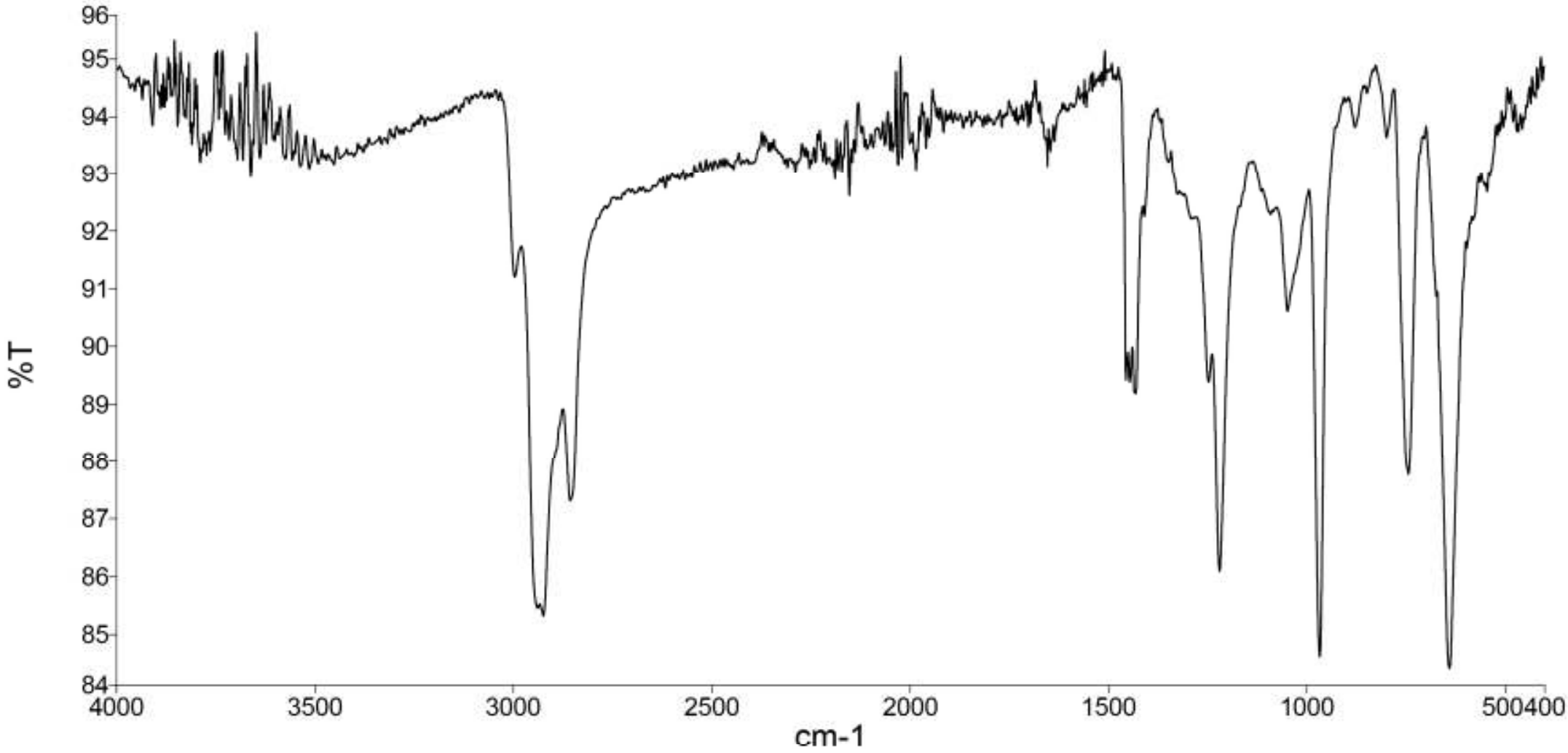


3- IR spectra of polymers



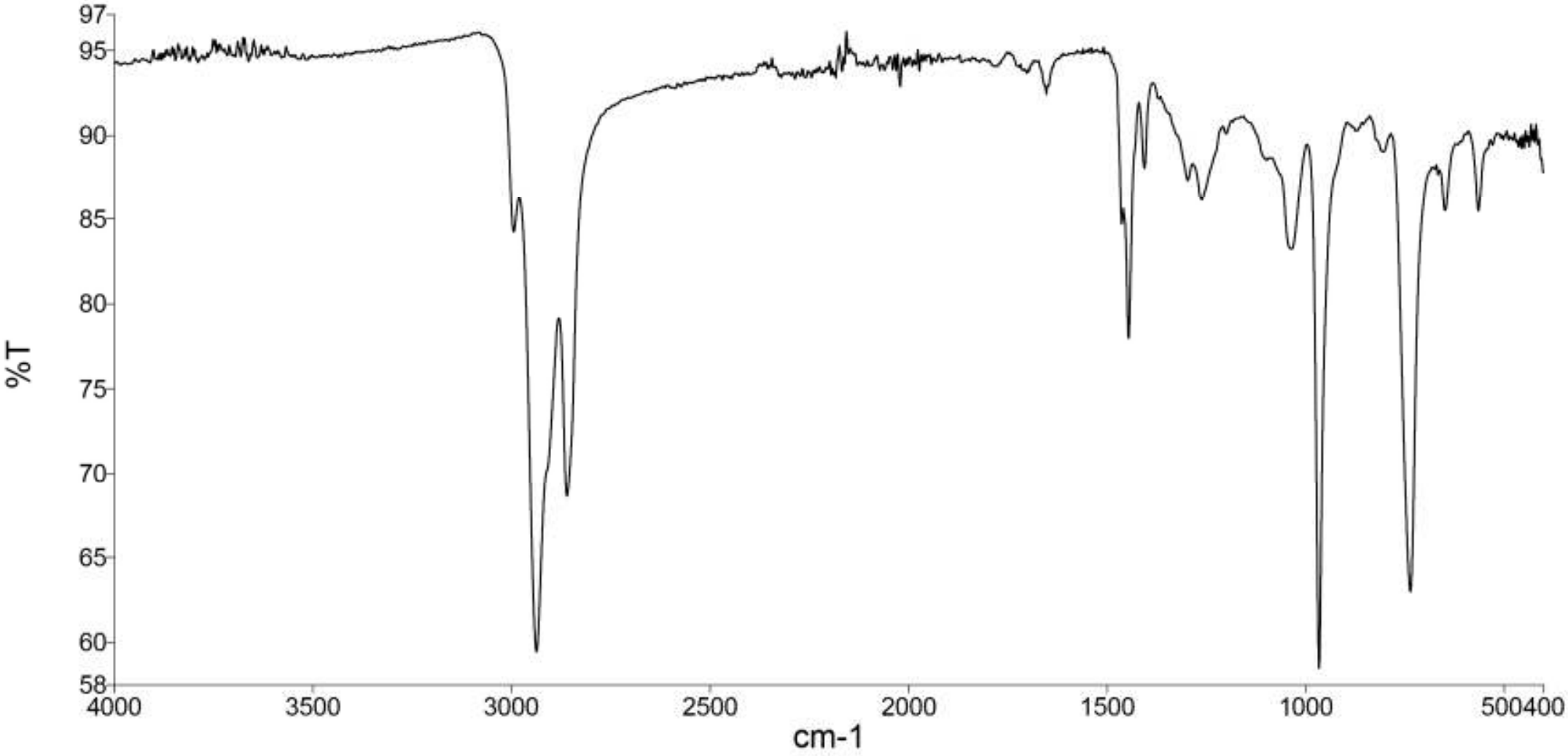
FT/IR

3a : ROMP-PNBCH$_2$Br (x/y = 0)



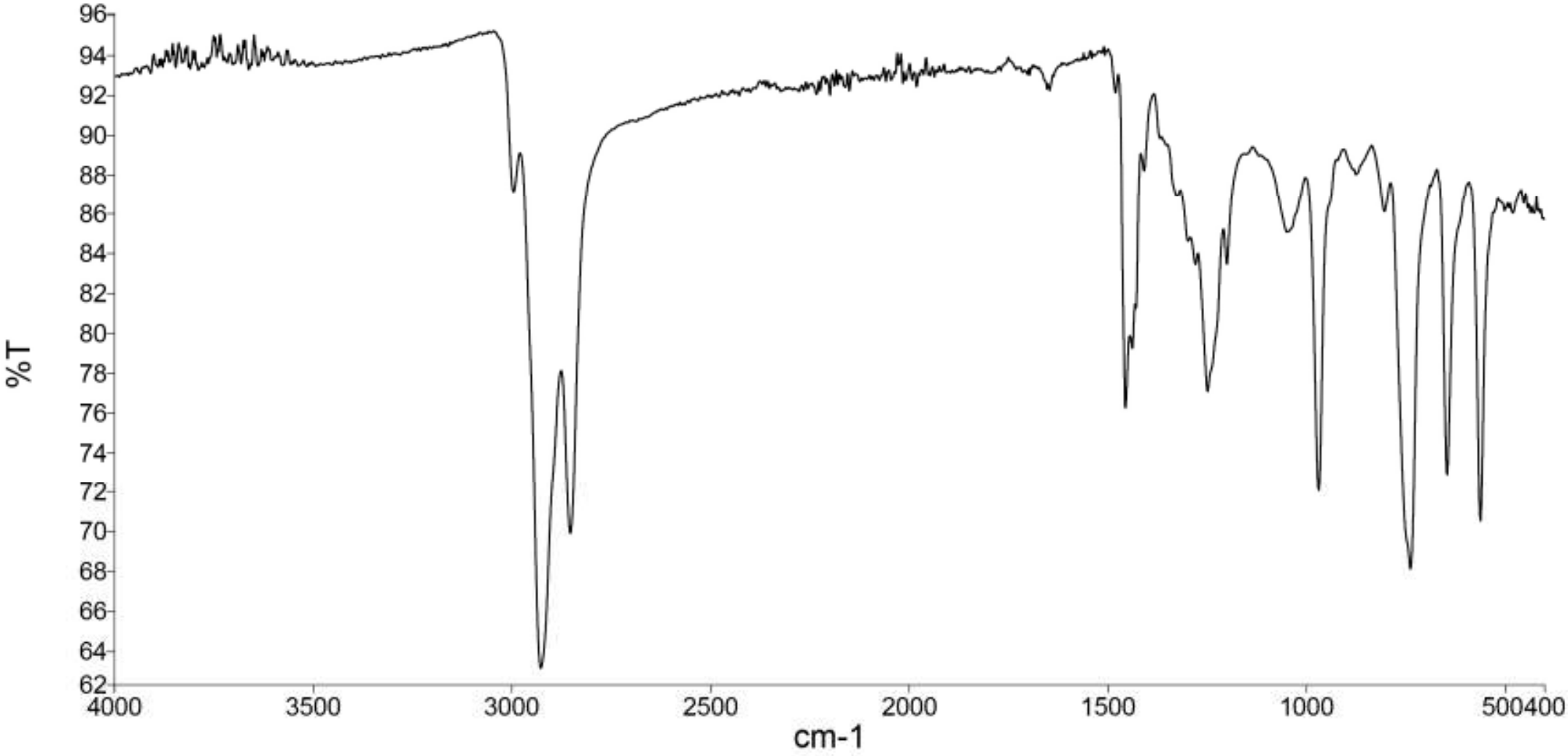
FT/IR

3b : ROMP-PNB-NB(CH_2)$_4$Br (x/y = 7.09)



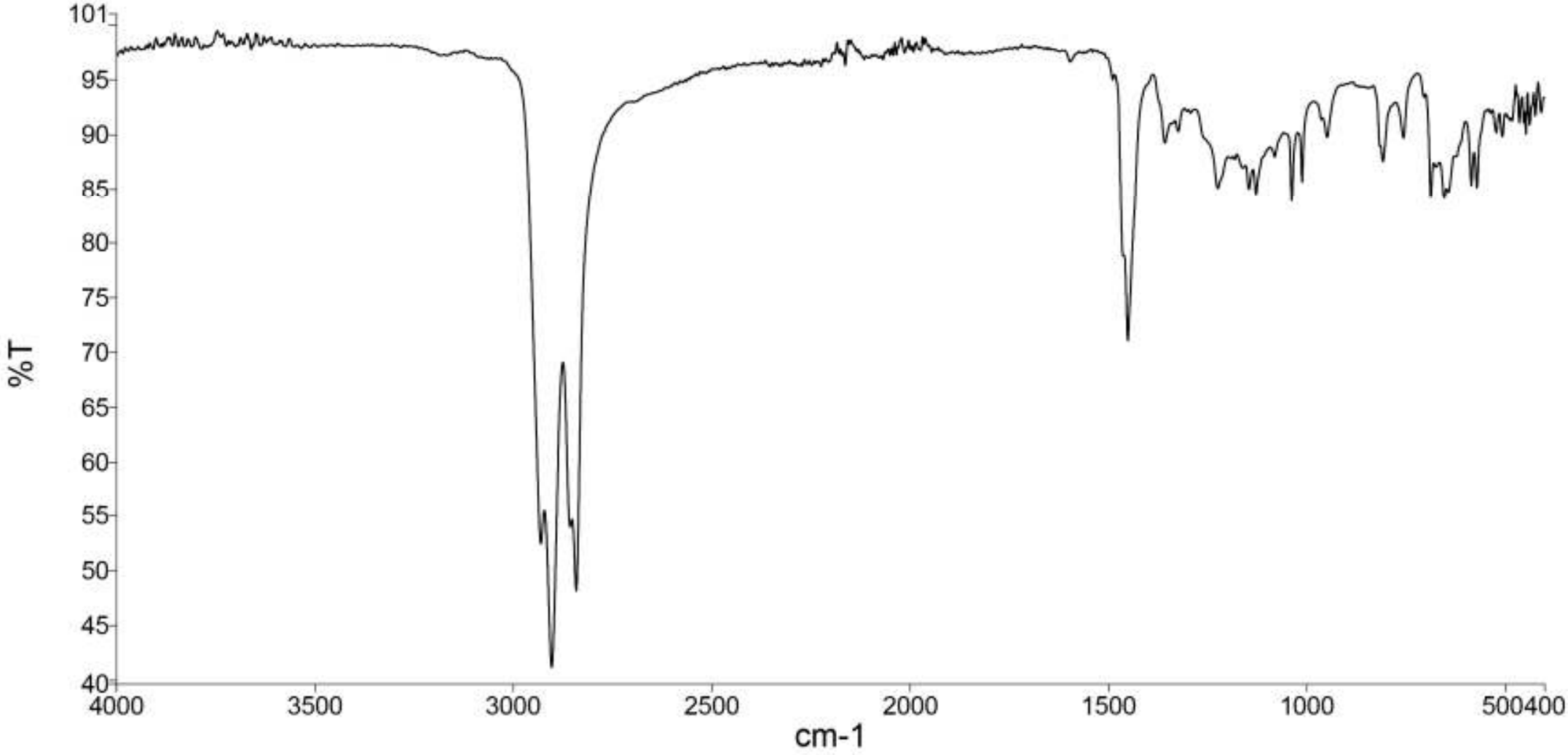
FT/IR

3b : ROMP-PNB$(CH_2)_4$Br (x/y = 0)



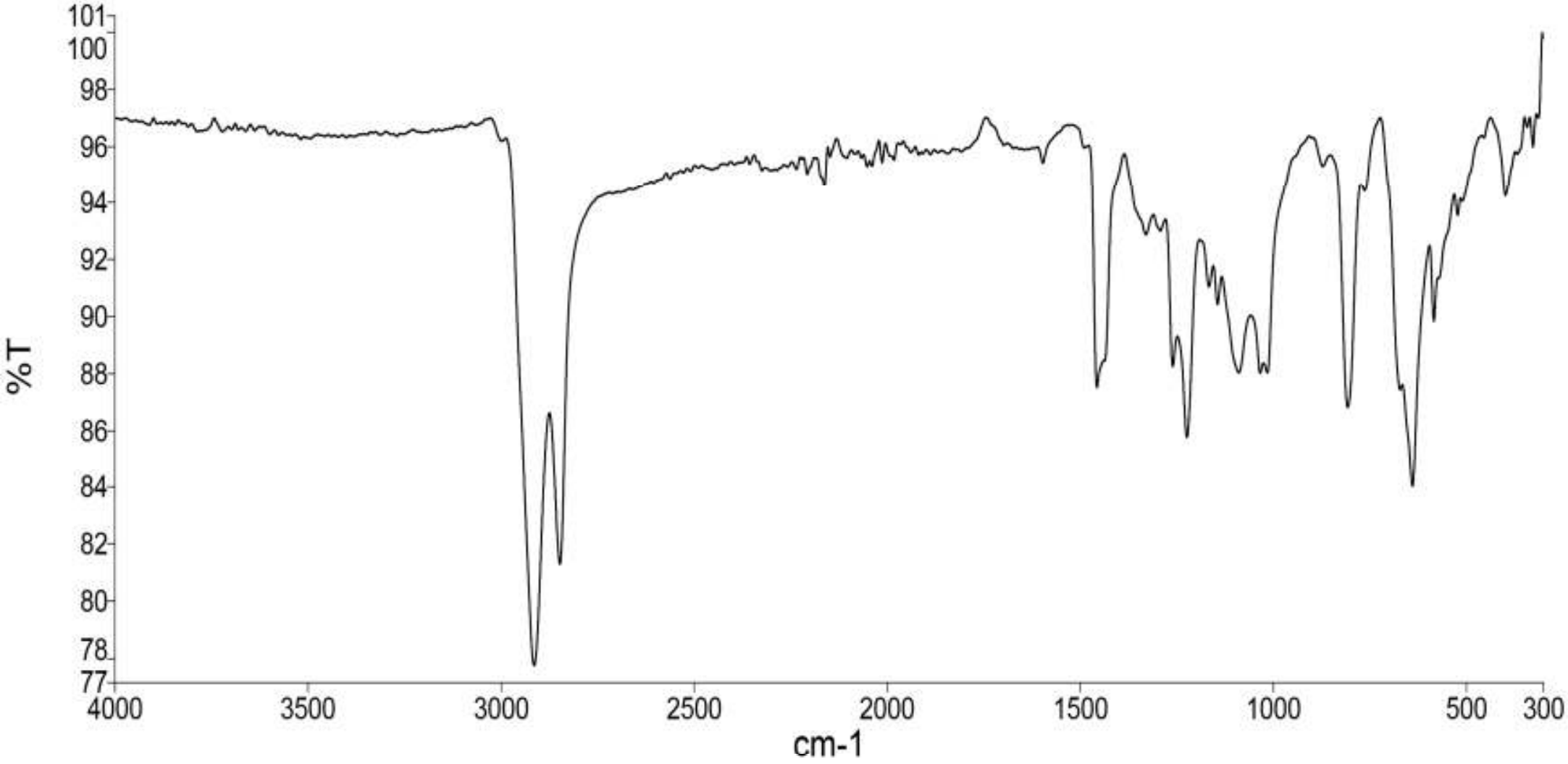
FT/IR

4a : ROMPH-PNB-NBCH$_2$Br



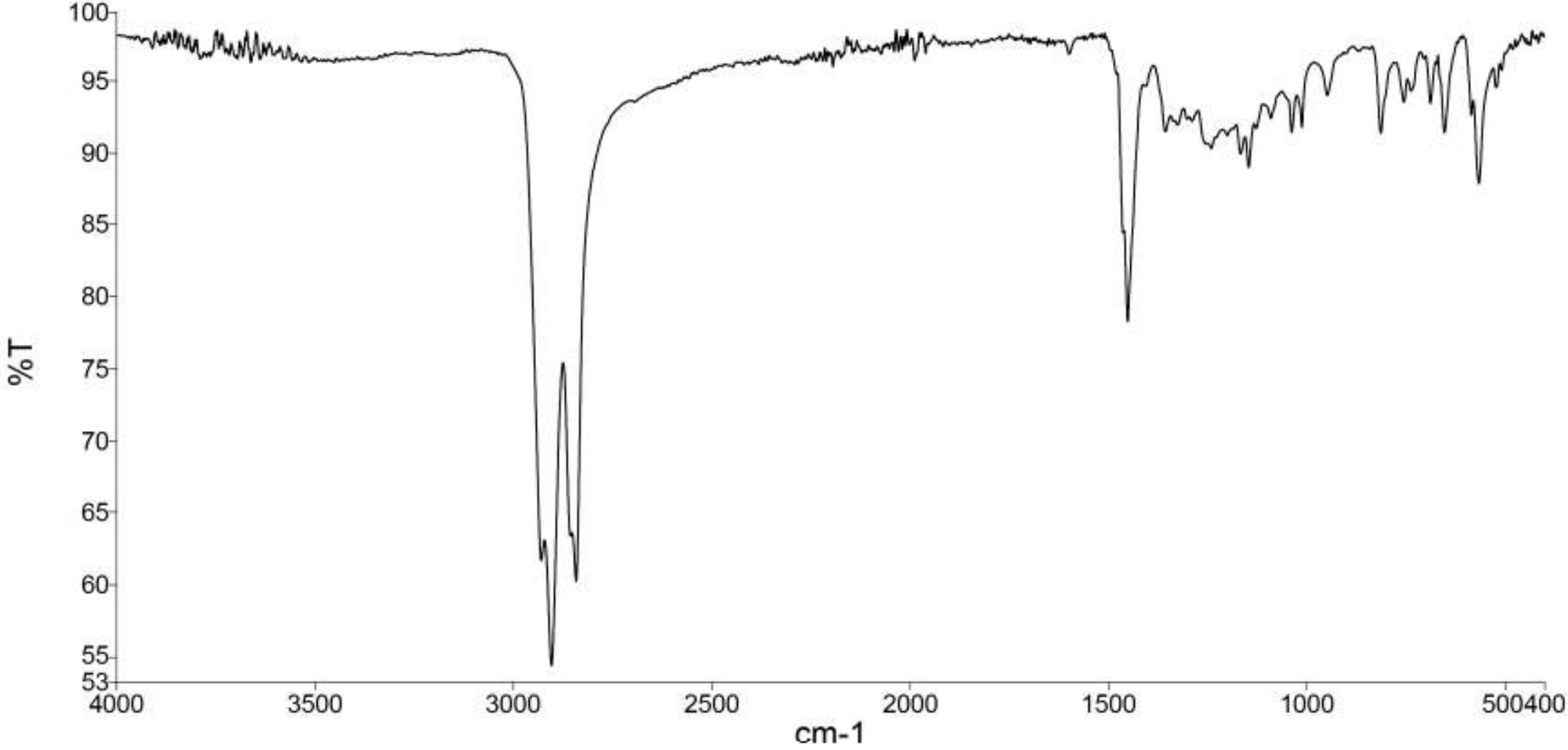
FT/IR

4a : ROMPH-PNBCH$_2$Br



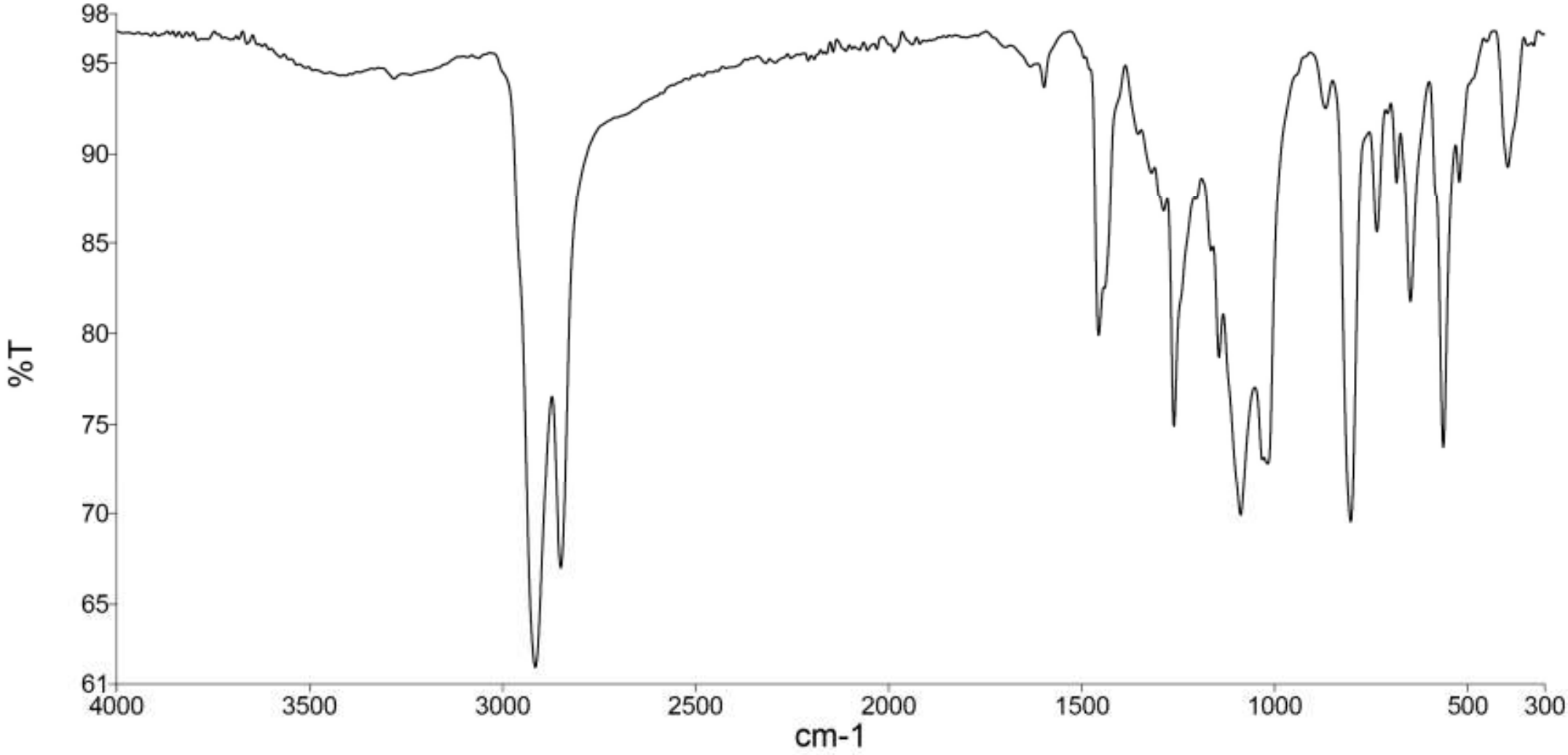
FT/IR

4b : ROMPH-PNB-NB$(CH_2)_4$Br



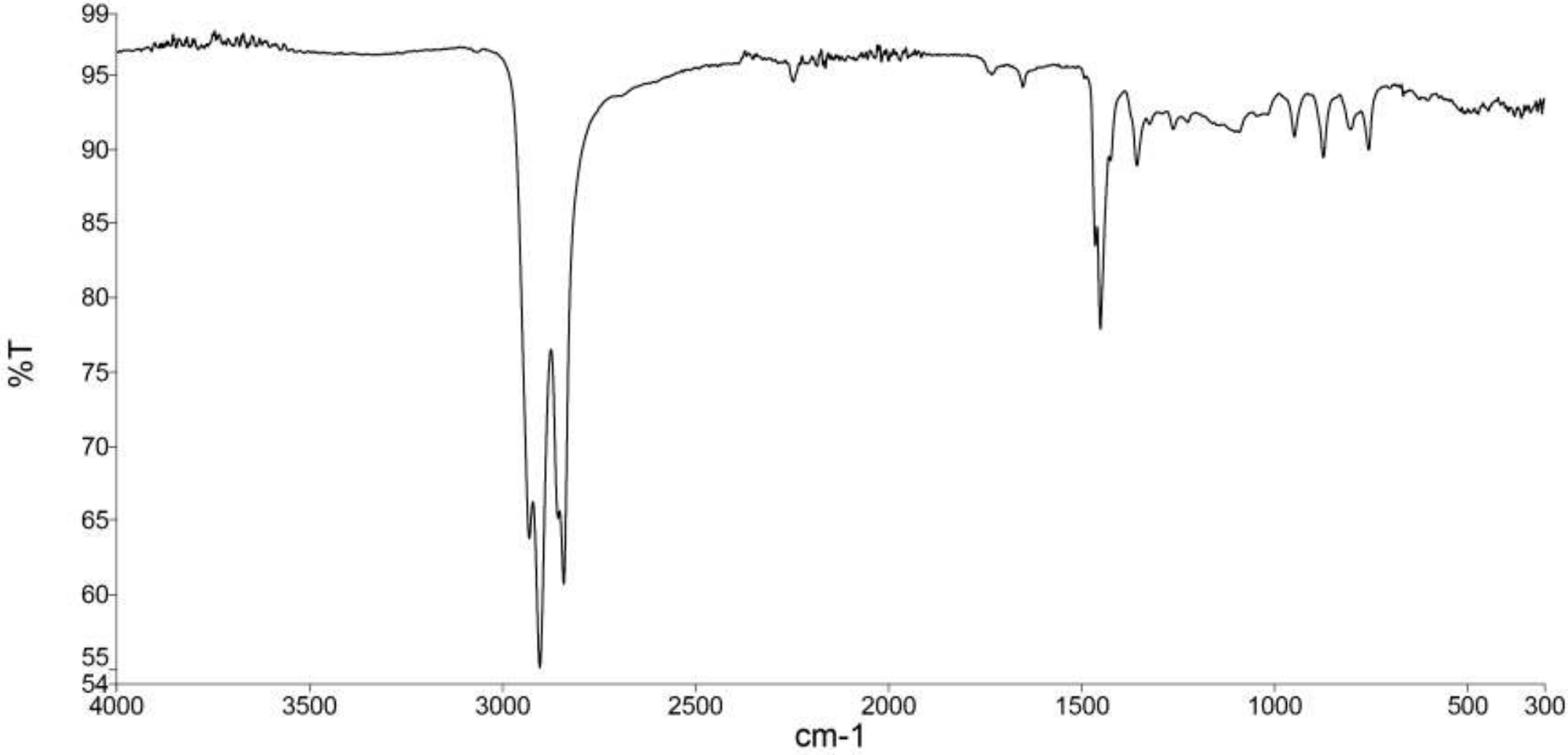
FT/IR

4b : ROMPH-PNB$(CH_2)_4$Br



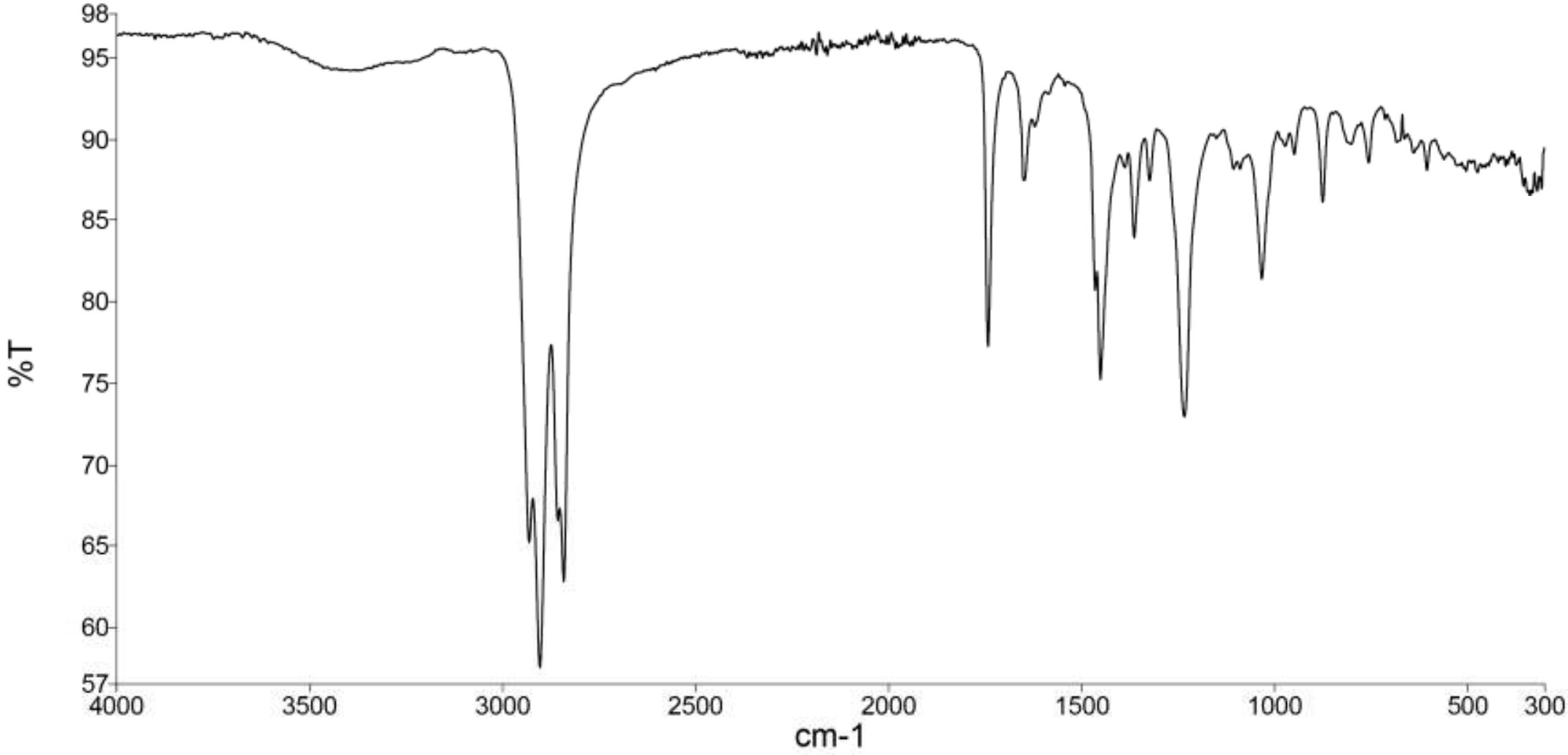
FT/IR

5a : ROMPH-PNB-NBCH$_2$CN



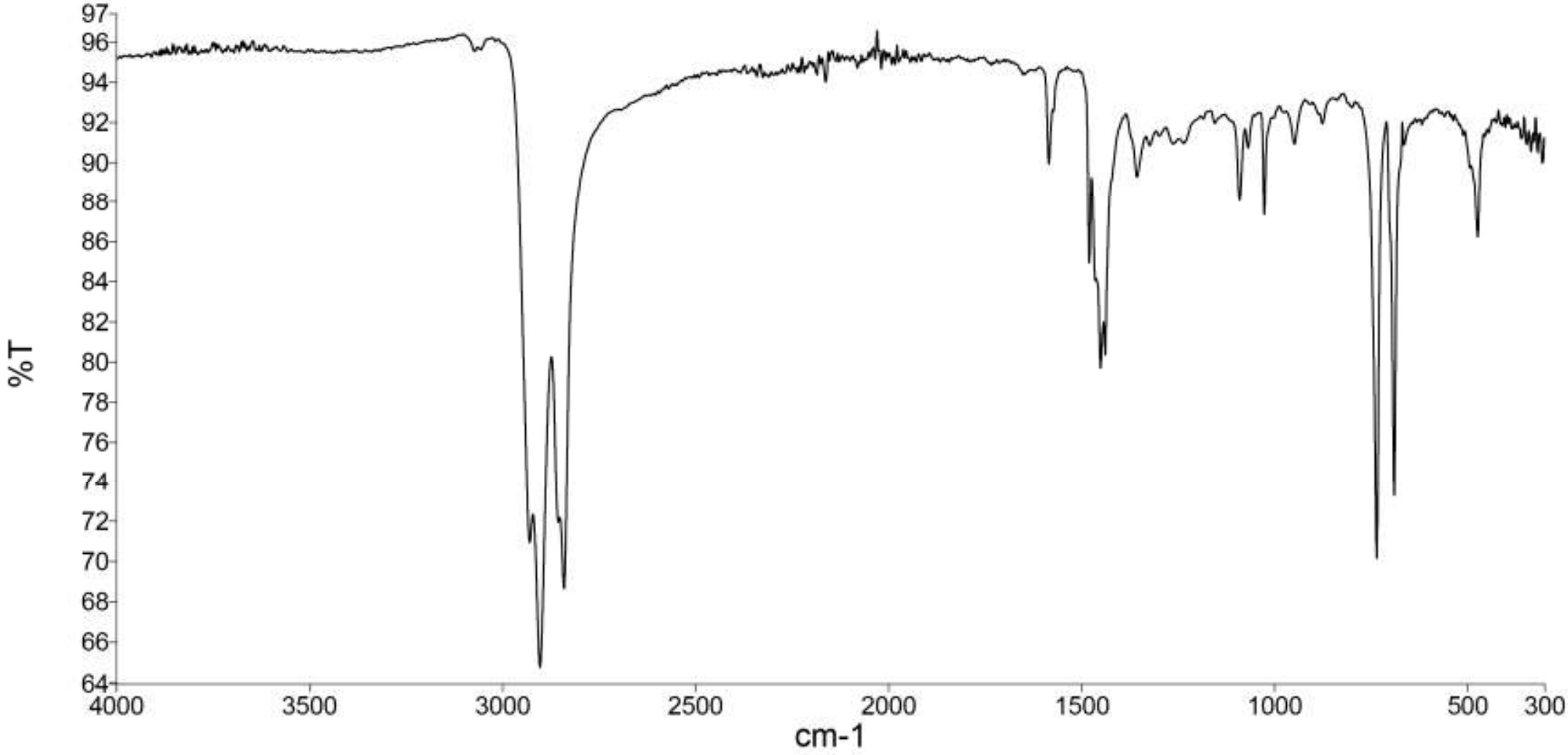
FT/IR

6a : ROMPH-PNB-NBCH$_2$OCOMe



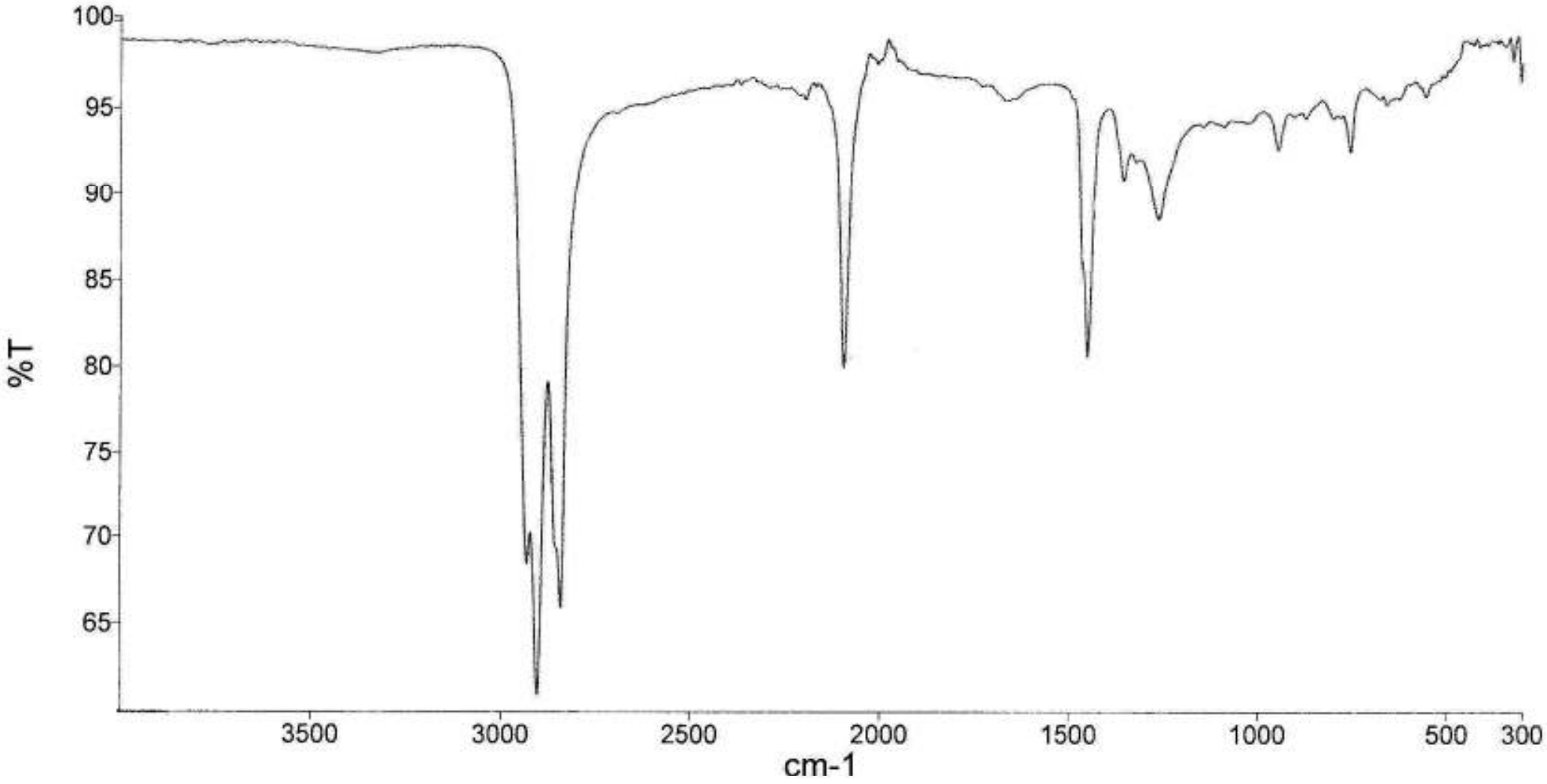
FT/IR

7a : ROMPH-PNB-NBCH$_2$SPh



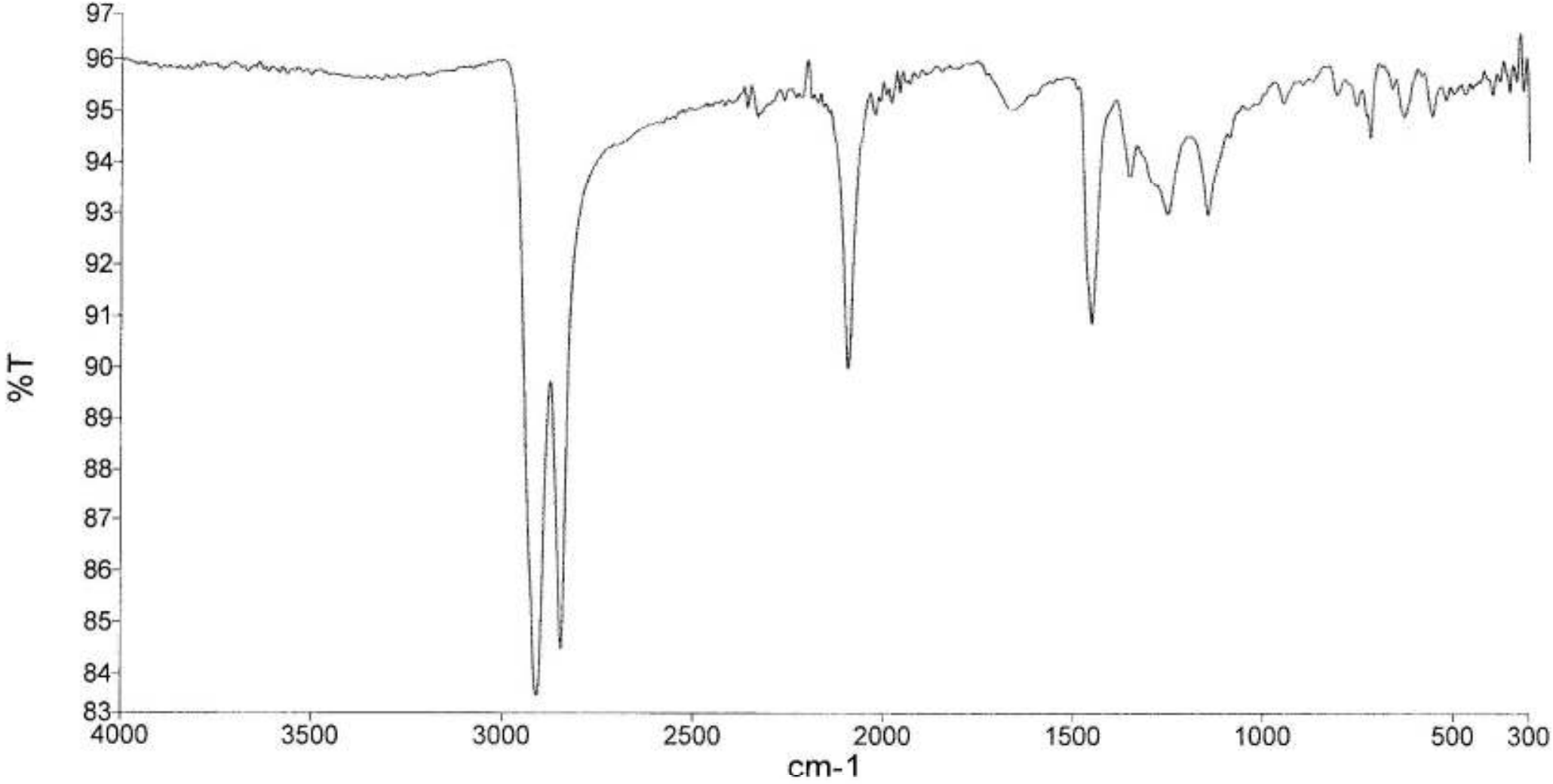
FT/IR

8a : ROMPH-PNB-NBCH$_2$N$_3$



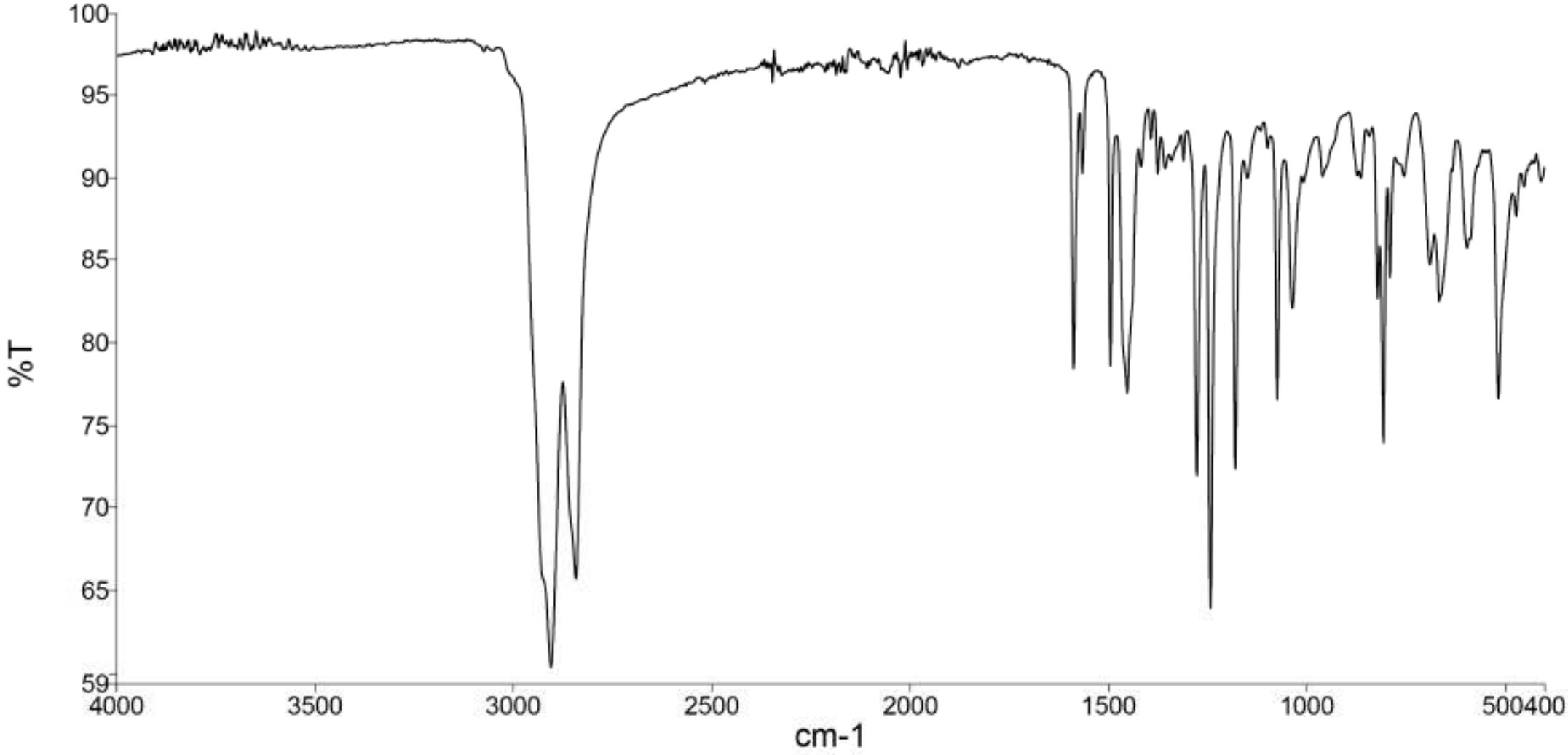
FT/IR

8b : ROMPH-PNB-NB$(CH_2)_4N_3$



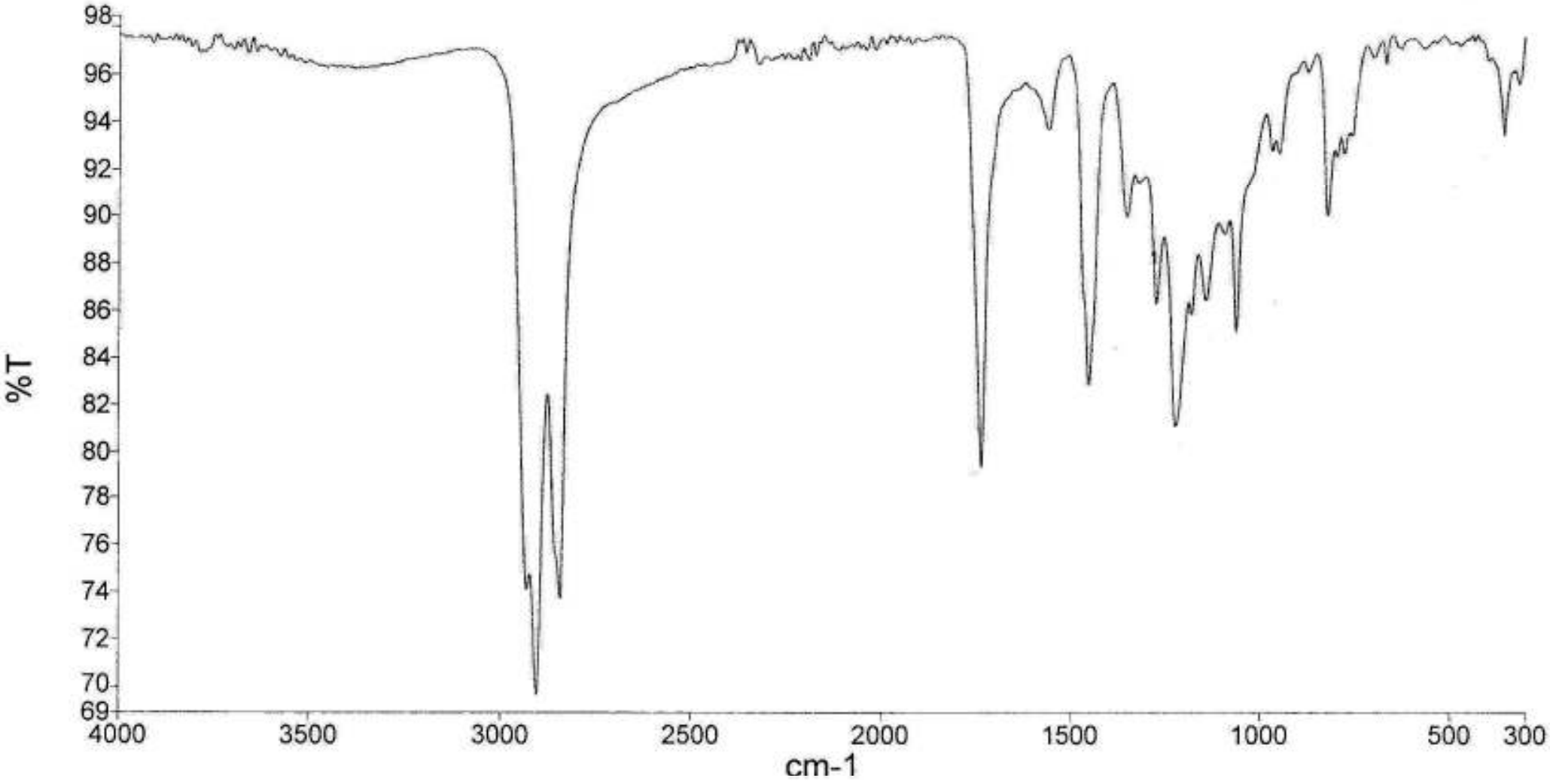
FT/IR

9b : ROMPH-PNB-NB$(CH_2)_4SnBu_2$(*p*-C_6H_4OMe)



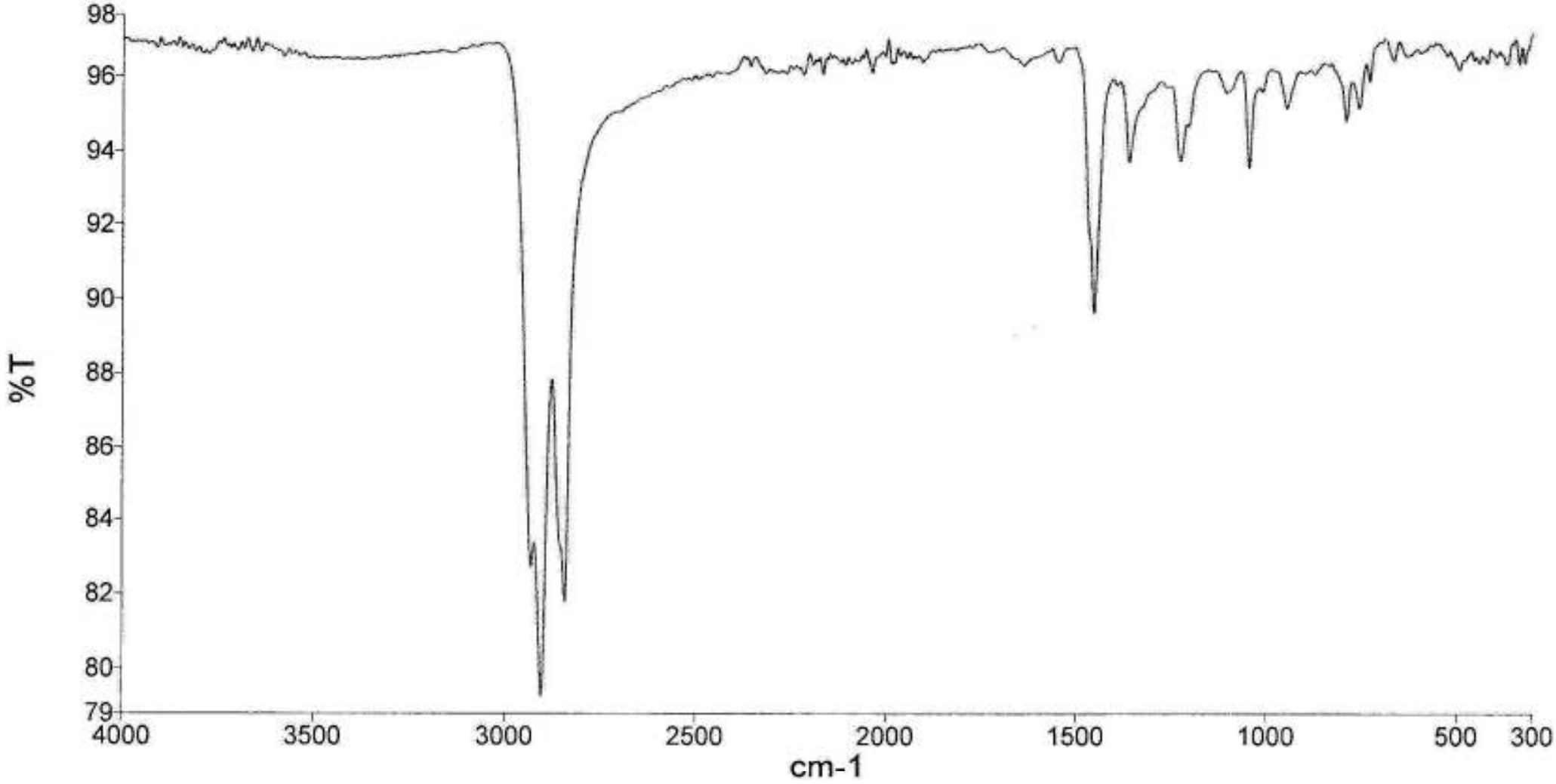
FT/IR

10a : ROMPH-PNB-NBCH$_2$triazole



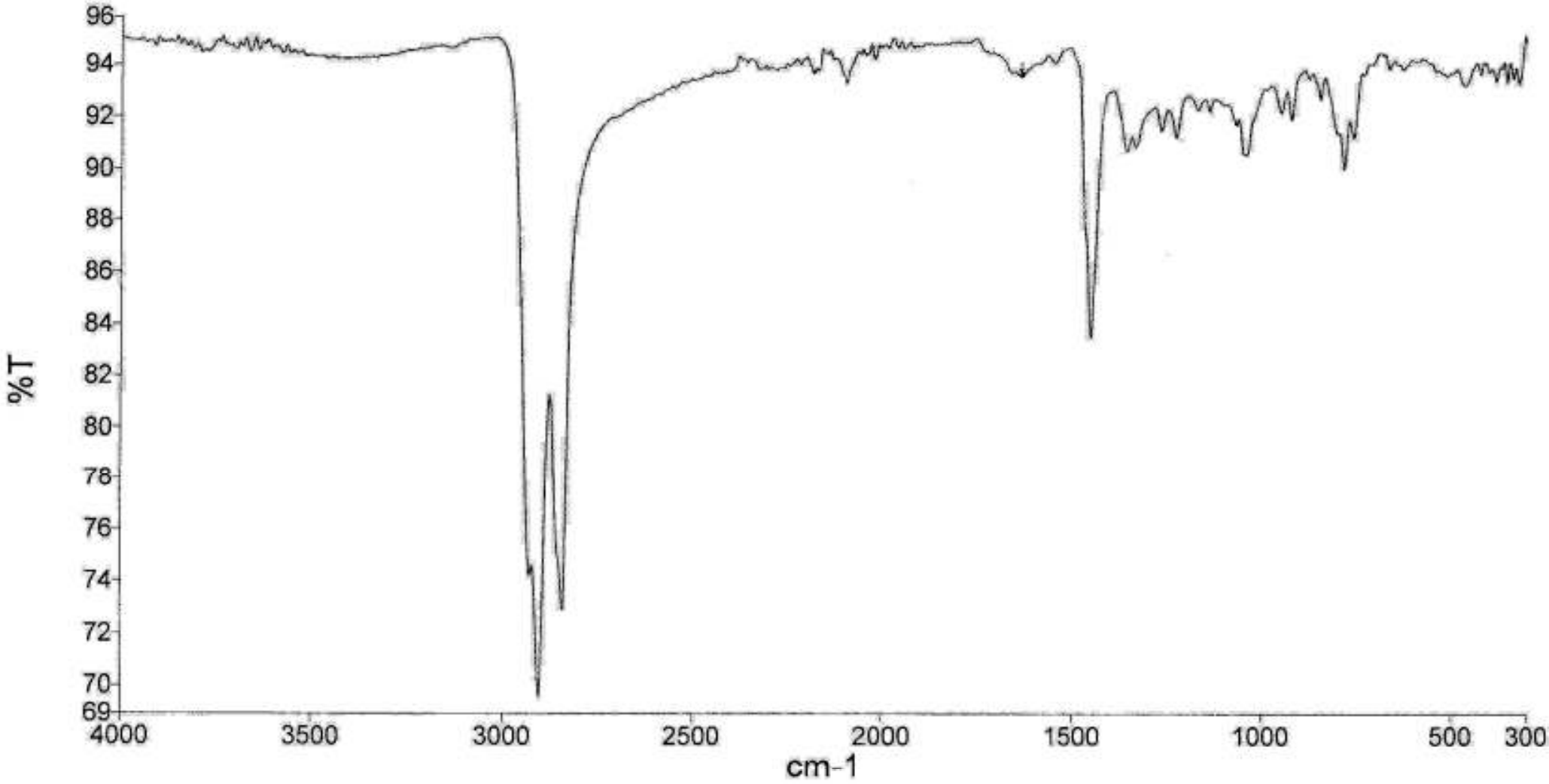
FT/IR

11a : ROMPH-PNB-NBCH$_2$triazole



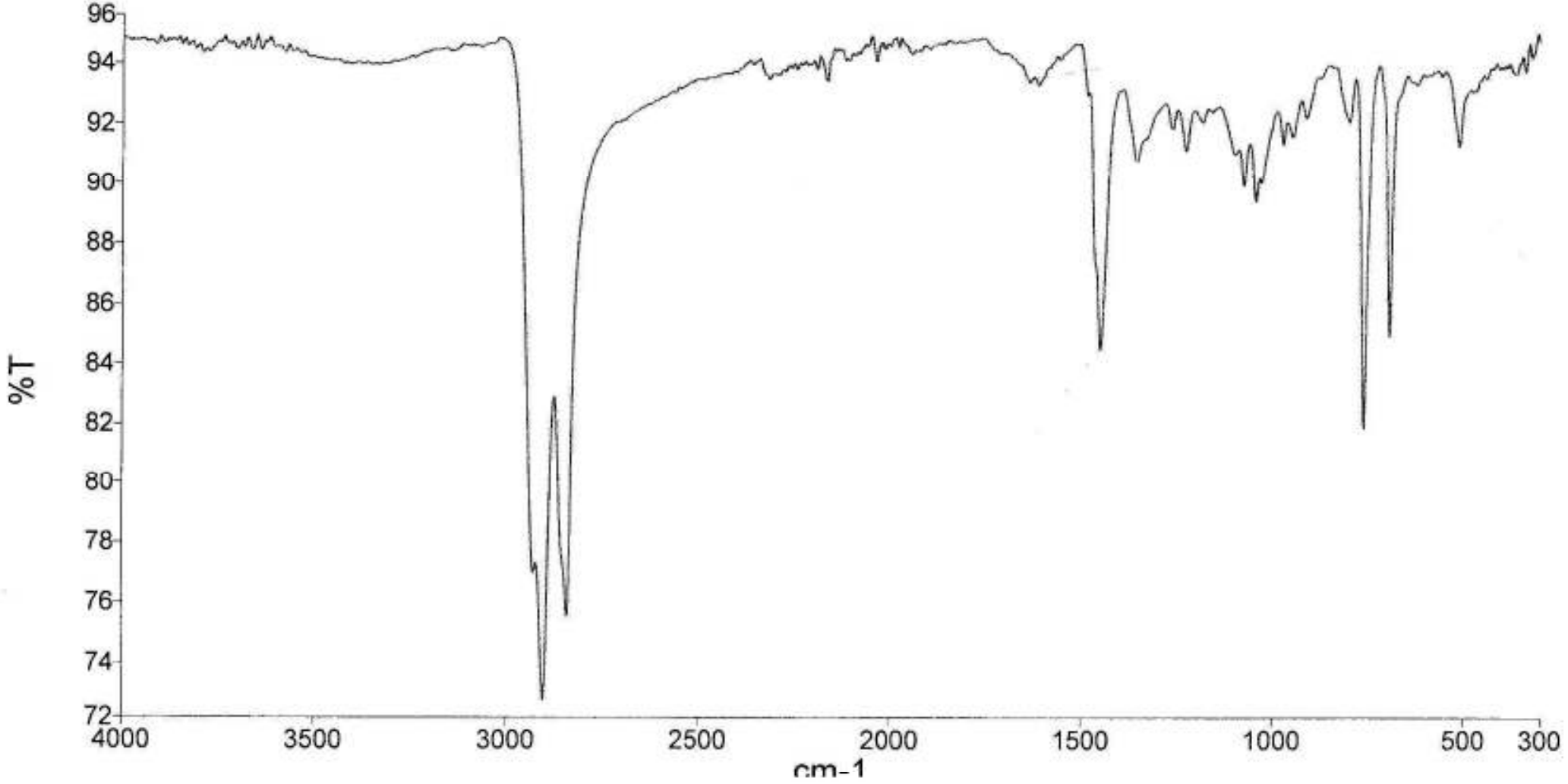
FT/IR

12a : ROMPH-PNB-NBCH$_2$triazole



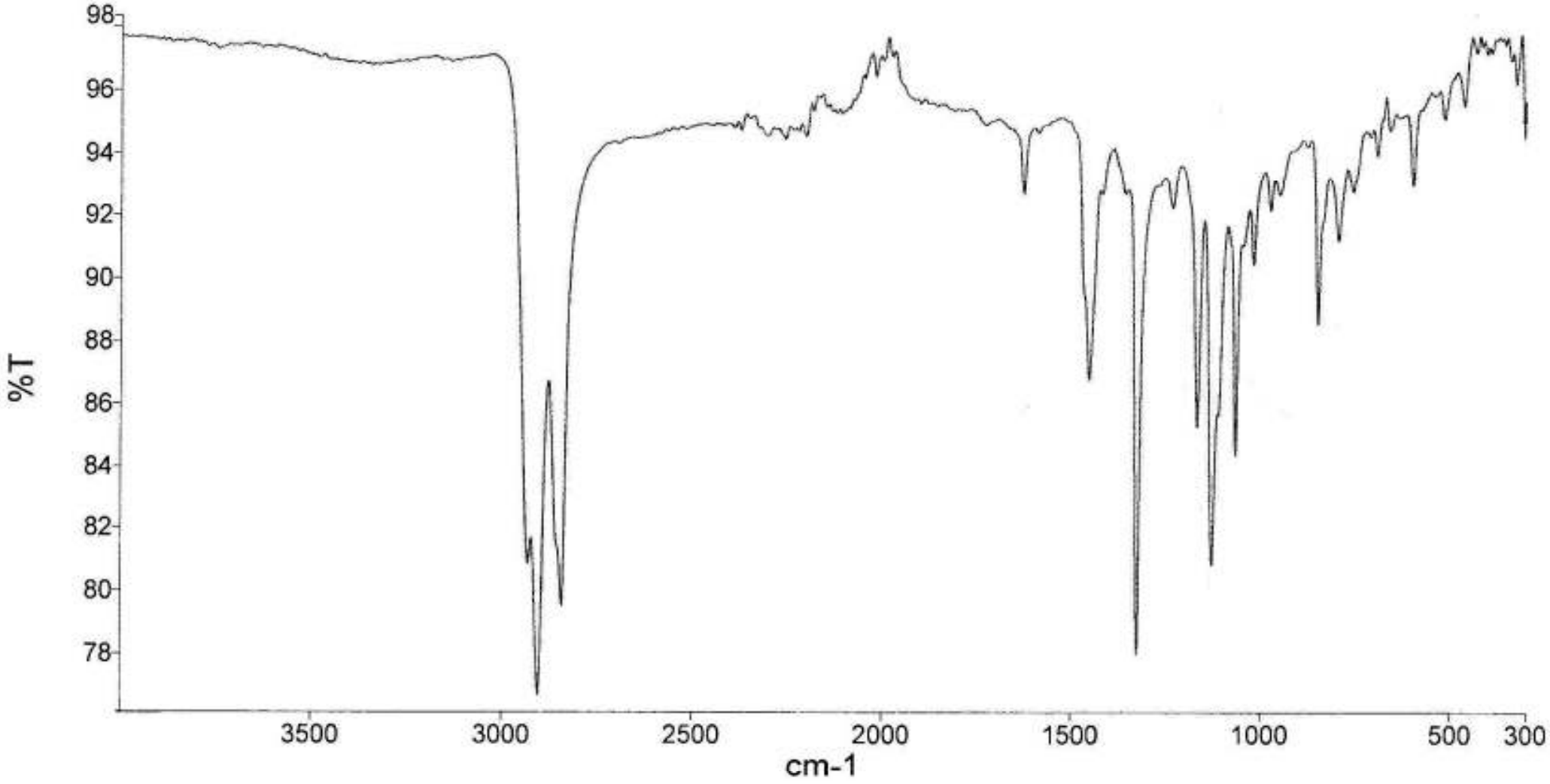
FT/IR

13a : ROMPH-PNB-NBCH$_2$triazole



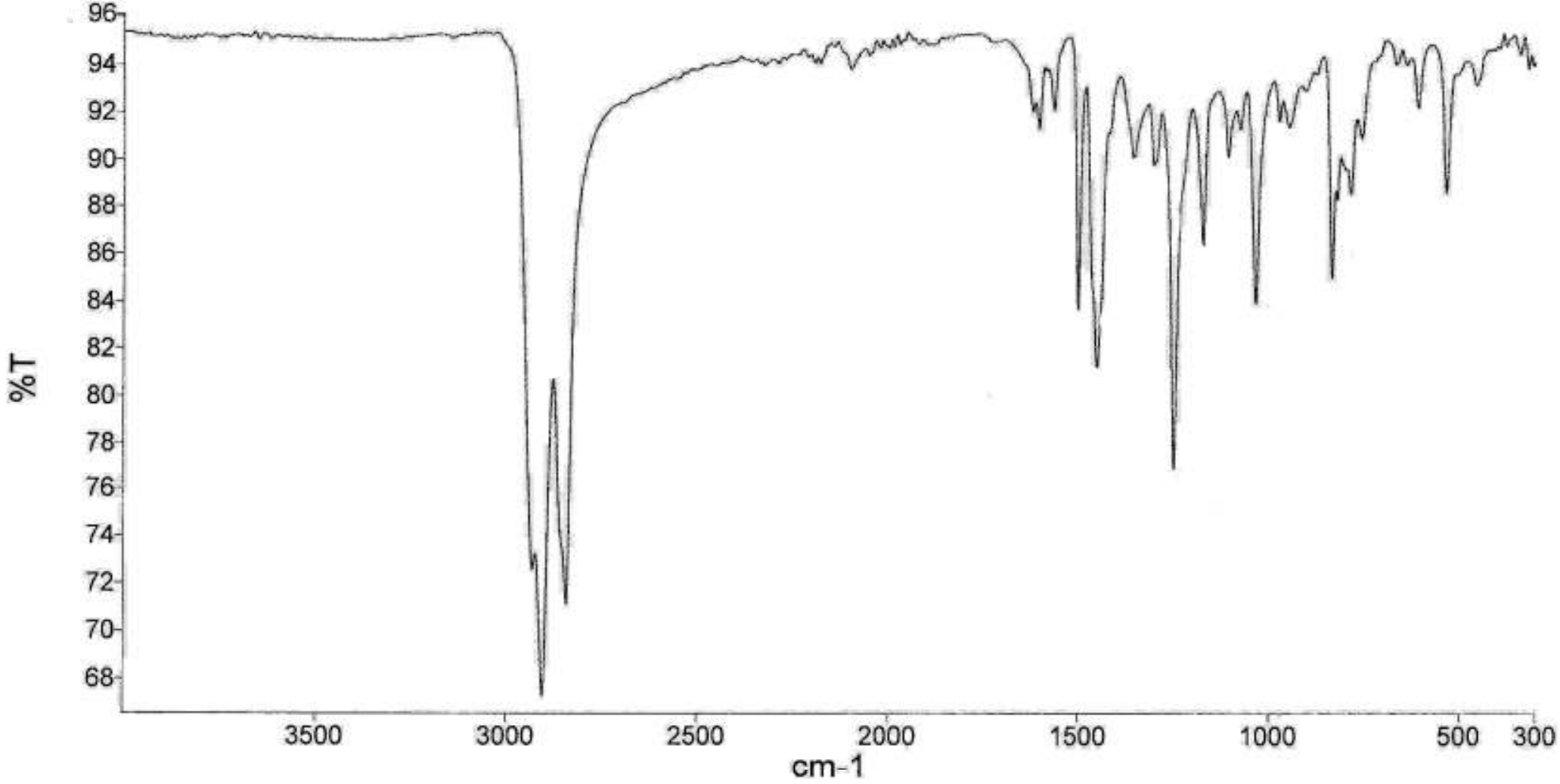
FT/IR

14a : ROMPH-PNB-NBCH$_2$triazole



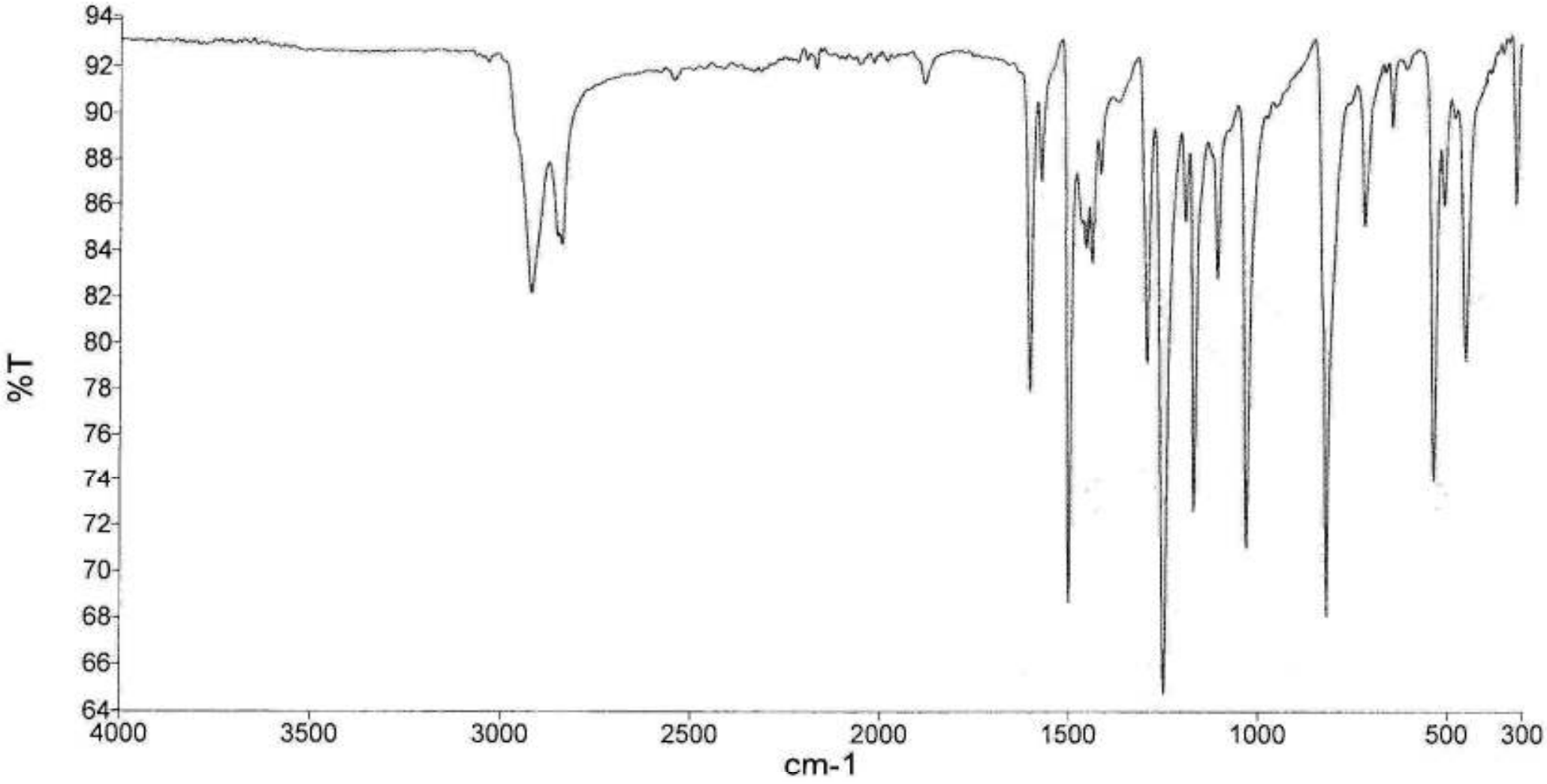
FT/IR

15a : ROMPH-PNB-NBCH$_2$triazole



FT/IR

15b : ROMPH-PNB-NB$(CH_2)_4$triazole



*4- SEM Images for polymers **4a** and **4b**.*

Scanning Electron Microscopy (SEM) measurements have been carried out at the *Unidad de Microscopía Avanzada* of the *Parque Científico UVa* by means of an Environmental Scanning Electron Microscope (ESEM), model FEI-Quanta 200FEG provided with a Schottky-Field Emission filament. The SEM analyses were performed at Low Vacuum Mode using water vapour as auxiliary gas. This imaging mode allows working with non-conductive samples without any specific preparation or metallic coatings. The measurements were performed at a working pressure in the chamber ranging between 0.6-1 Torr (80-133 Pa) and an accelerating voltage of 7kV. The Secondary Electron SEM images were acquired with a Large Field Detector (LFD) which is the suitable one for working at Low Vacuum Mode.

SEM images of the aliphatic polymers show a different surface topography for polymers **4a** and **4b**. Whereas a granular texture is observed for **4a** (Figure S3, a and b), **4b** shows a smoother surface with large pores (Figure S3, c and d).

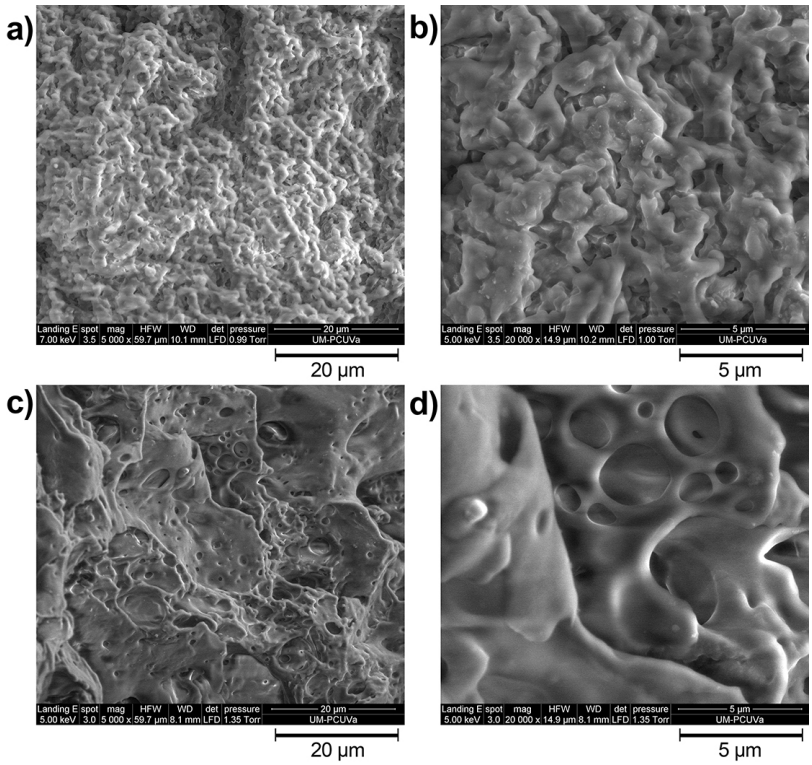


Figure S3. SEM images with different magnification for **4a** (a and b) and **4b** (c and d).