Supplementary Information

p-Bromoaryl- and ω-Bromoalkyl-VA-PNBs: Suitable Starting Materials for the Functionalization of Vinylic Addition Polynorbornenes via Palladium-Catalyzed Cross-Coupling Reactions

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1- Tables with additional experimental data.

2- IR and NMR spectra of the polymers.

1- Tables with additional experimental data.

Table S1. Suzuki reactions on polymer **3**: Screening of reaction conditions to synthesize **5**.[a]

Entry	VA-PNB, a/b (mmol Br/g)	**3**:$BPh(OH)_2$:[Pd][b]	[Pd]	Solvent	% Br subst.[c]
1[d]	**3**, 2.4 (2.1)	200:400:1	$[Pd(PPh_3)_4]$	DMF	8
2[e]	**3**, 2.4 (2.1)	100:200:1	$[Pd(PPh_3)_4]$	DMF	34
3[e]	**3**, 1.5 (2.56)	50:200:1	$[PdCl_2dppf]$	DMF	35
4[f]	**3**, 1.5 (2.56)	50:200:1	$[PdCl_2dppf]$	Toluene	90
5[f]	**3**, 1.5 (2.56)	100:200:1	$[PdCl_2dppf]$	Toluene	94
6[f]	**3**, 1.5 (2.56)	100:200:1	$[PdCl_2dppf]$	Dioxane	65

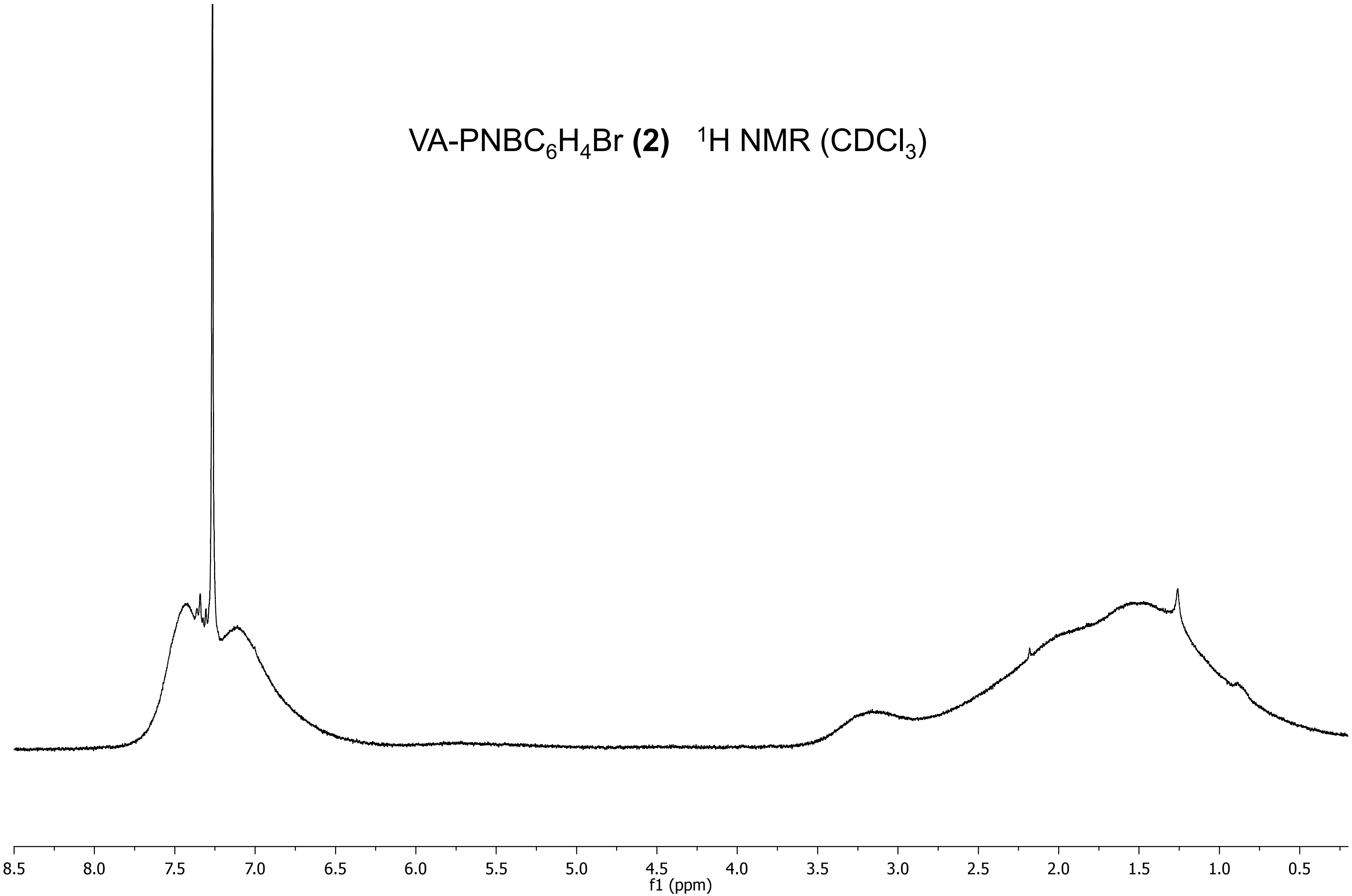
a) The reactions were carried out at 90 ºC for 48 h unless otherwise noted; K_2CO_3 was used as base. b) Molar ratio of reagents. c) Determined by quantitative analyses of the bromine content in the polymer product. d) 120 ºC for 18 h. e) 120 ºC for 48 h. f) 110 ºC for 48 h.

Table S2. Residual palladium content of some polymers before and after the removal procedures tried.

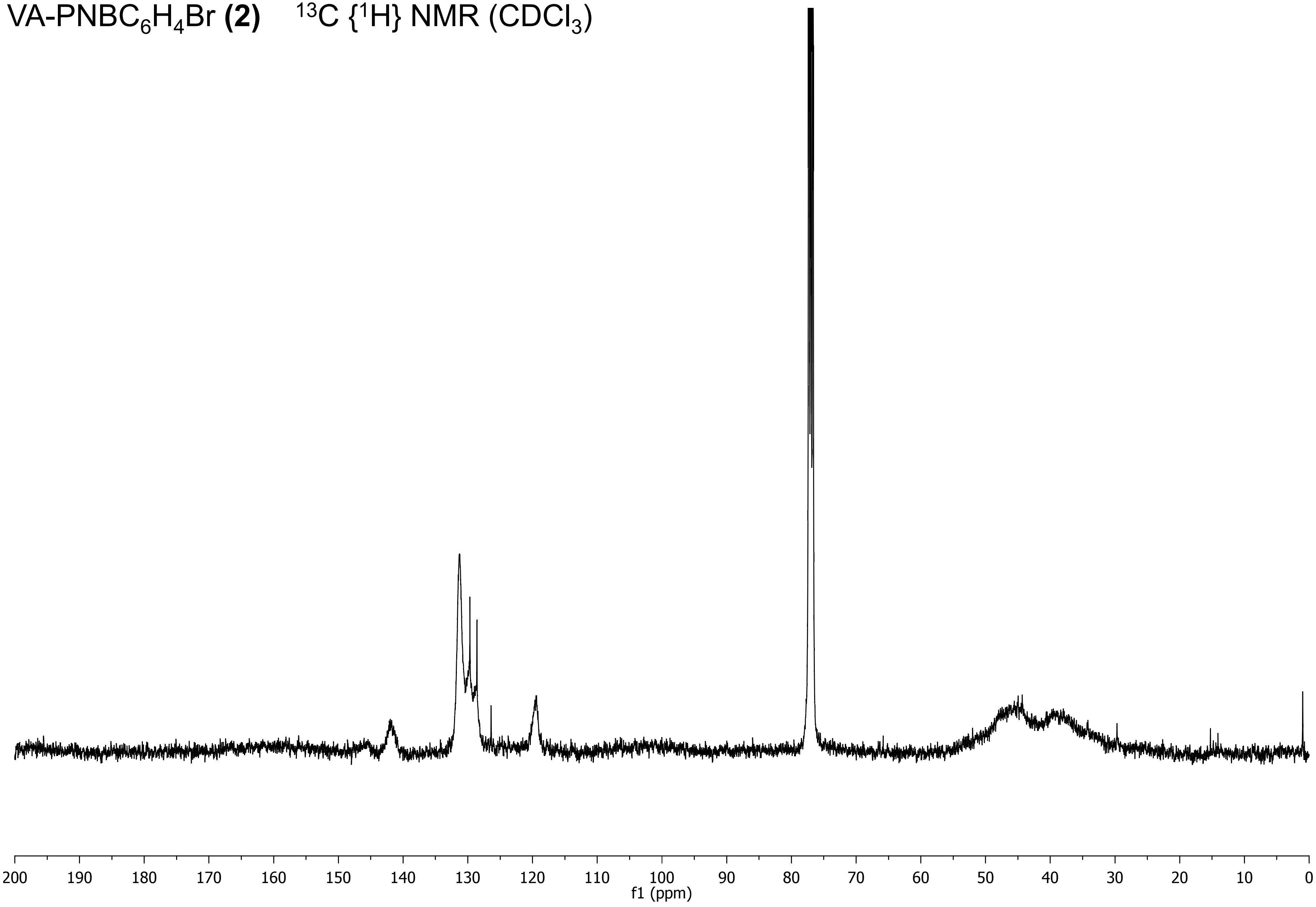
Entry	Polymer, residual Pd	Removal method	Residual Pd after removal
1	**6**,[a] 1.19 mg Pd/g	4-CF_3-C_6H_4I, toluene, reflux, 24 h	1 mg Pd/g
2	**6**,[a] 1.6 mg Pd/g	4-CF_3-C_6H_4I + PPh_3, toluene, reflux, 24 h	0.8 mg Pd/g
3	**20**,[b] 4.6 mg Pd/g	N,N-dimethyl-2-phenyldiazenecarbothioamide, toluene, reflux, 24 h	0.47 mg Pd/g
4	**7**,[c] 9.8 mg Pd/g	N,N-dimethyl-2-phenyldiazenecarbothioamide, toluene, reflux, 24 h	1.47 mg Pd/g

a) Method A, Table 2; 1% mol Pd; b) 5% mol Pd; c) Method B, Table 2; 5% mol Pd.

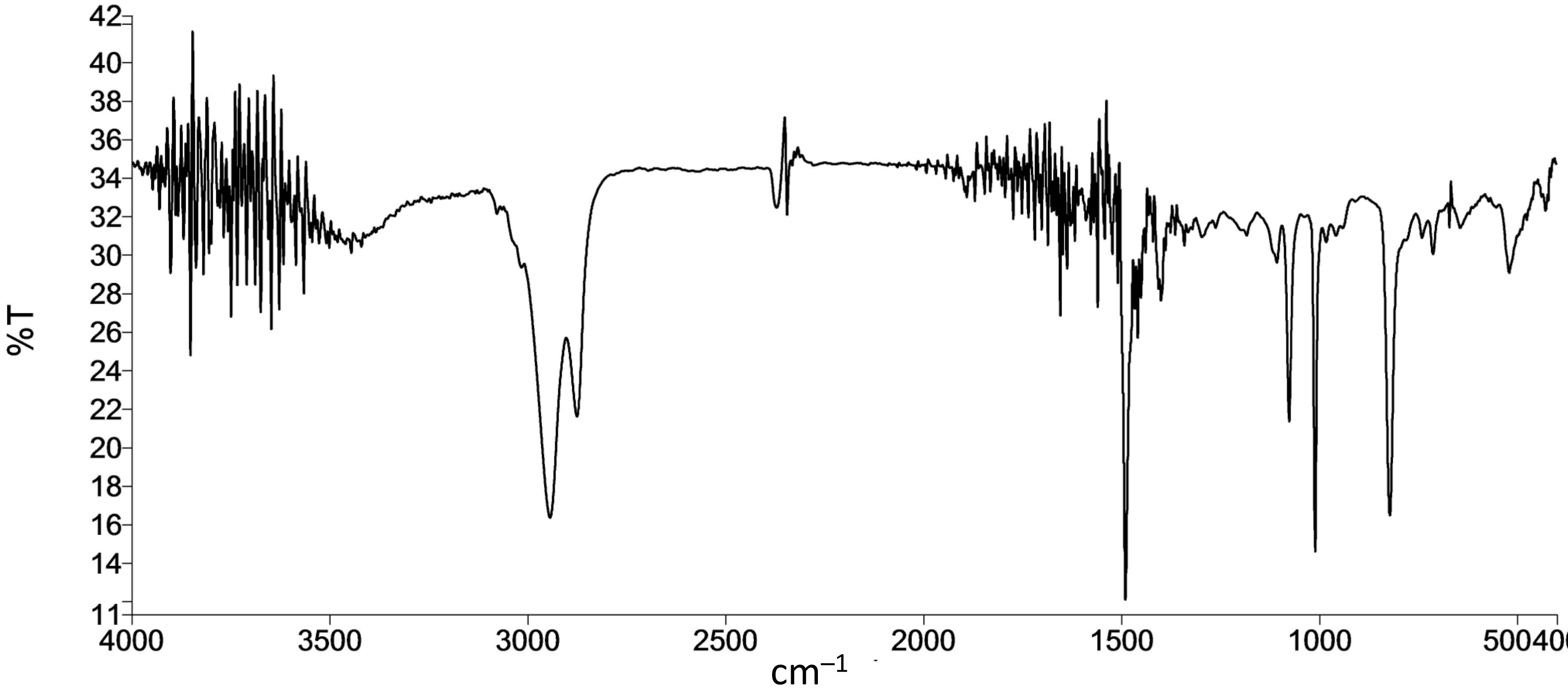
2- IR and MAS-NMR spectra of the polymers.



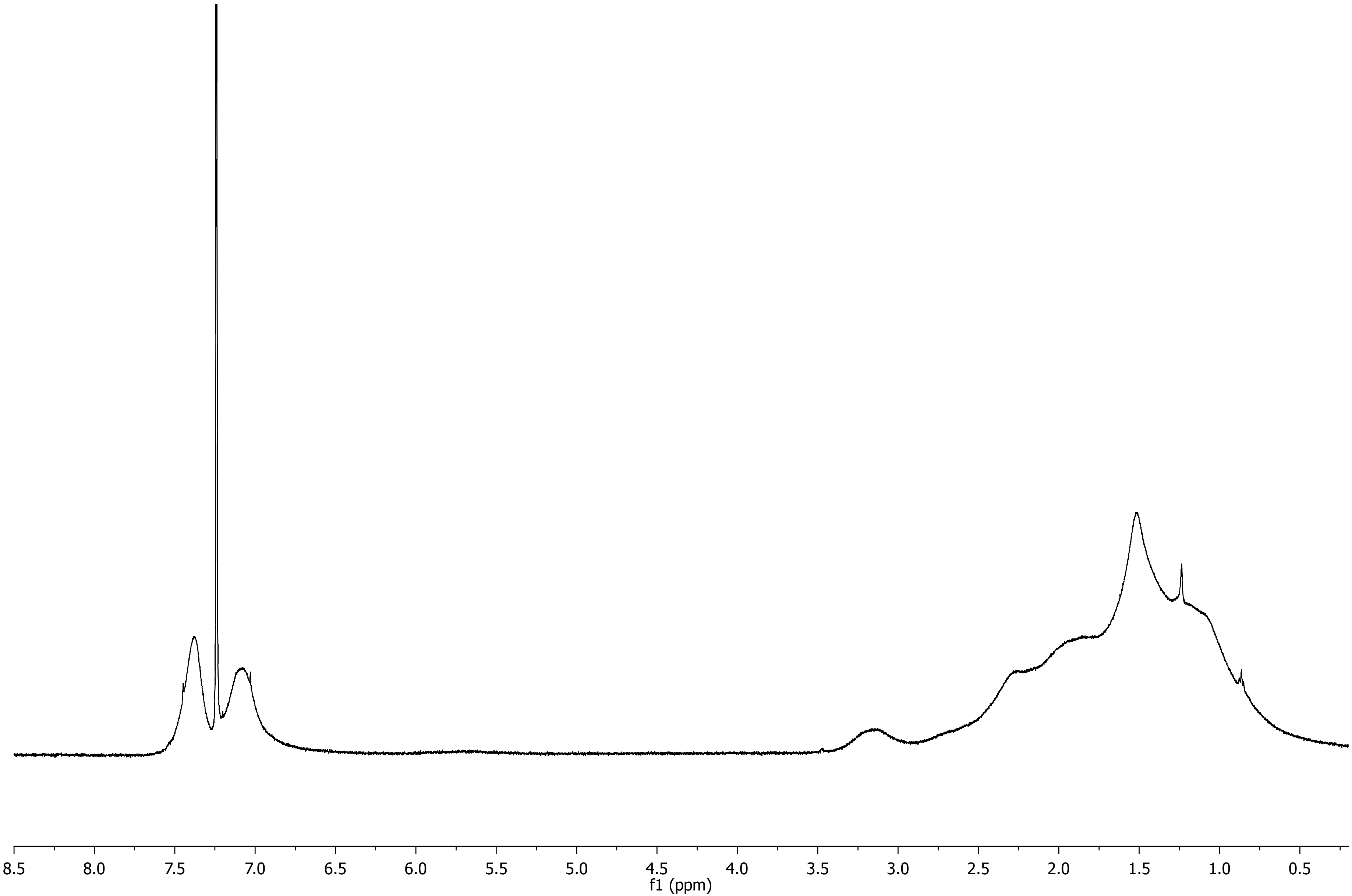
VA-PNBC$_6$H$_4$Br **(2)** ^{13}C {^{1}H} NMR (CDCl$_3$)



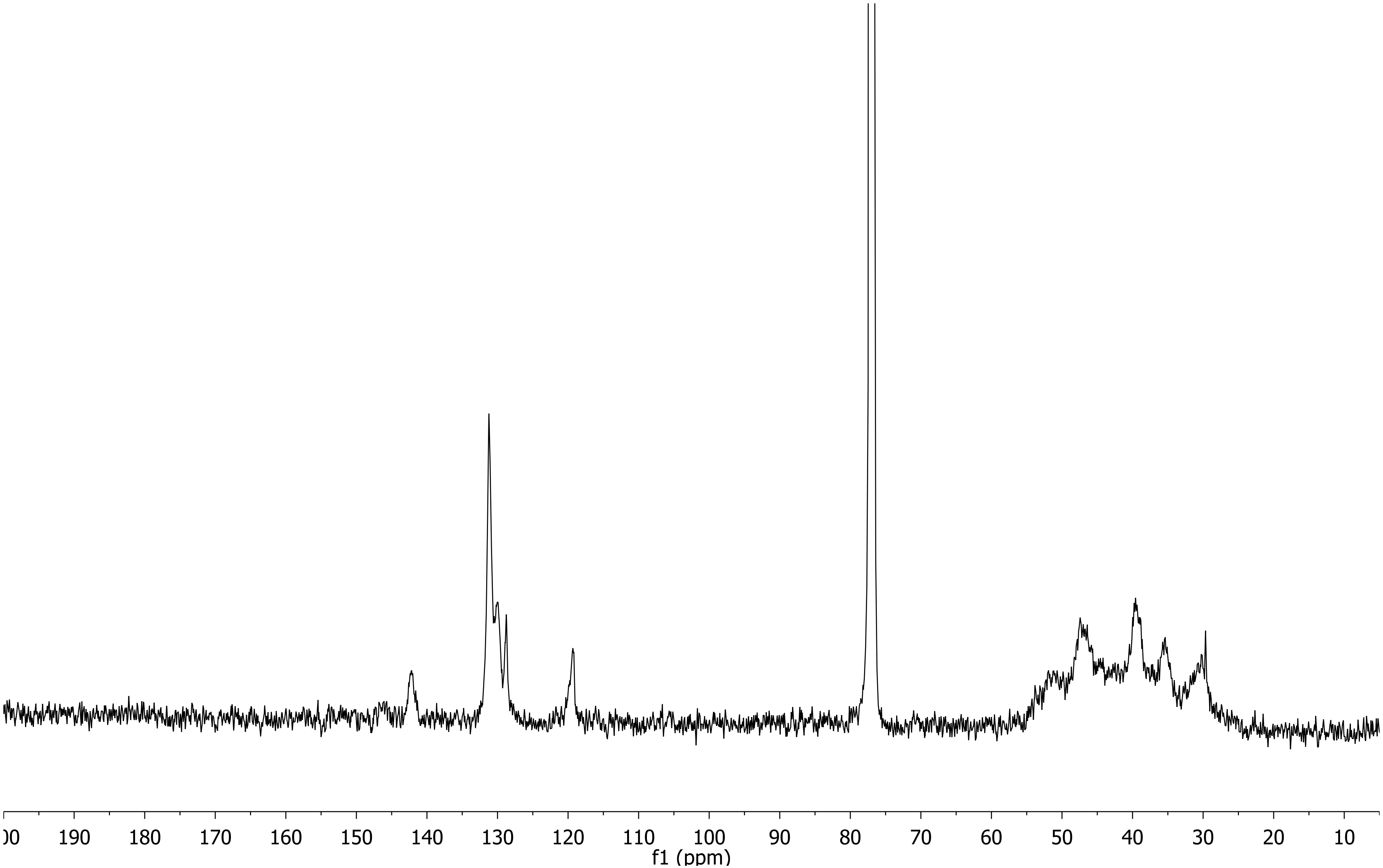
VA-PNBC$_6$H$_4$Br **(2)** IR



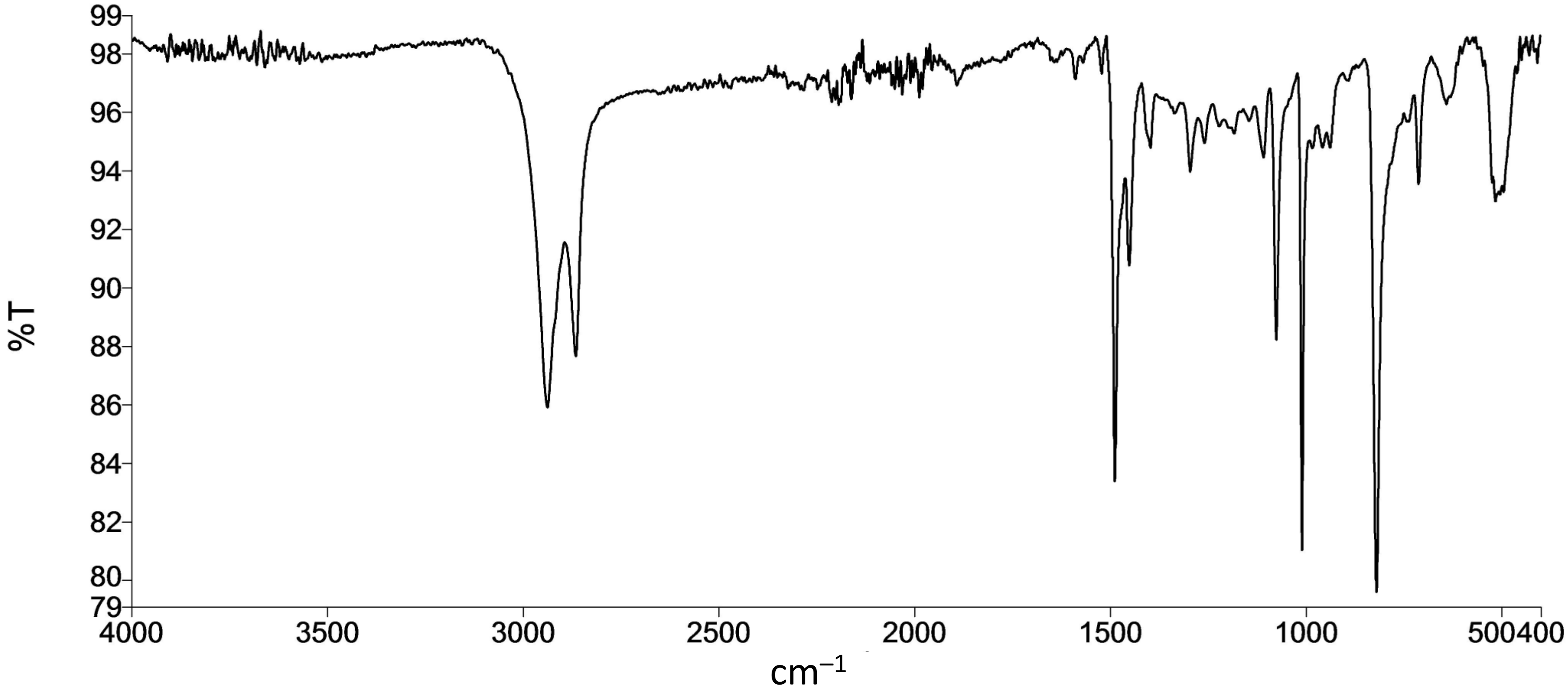
VA-PNBNBC$_6$H$_4$Br **(3)** (a/b = 1.8) ^{1}H NMR (CDCl$_3$)



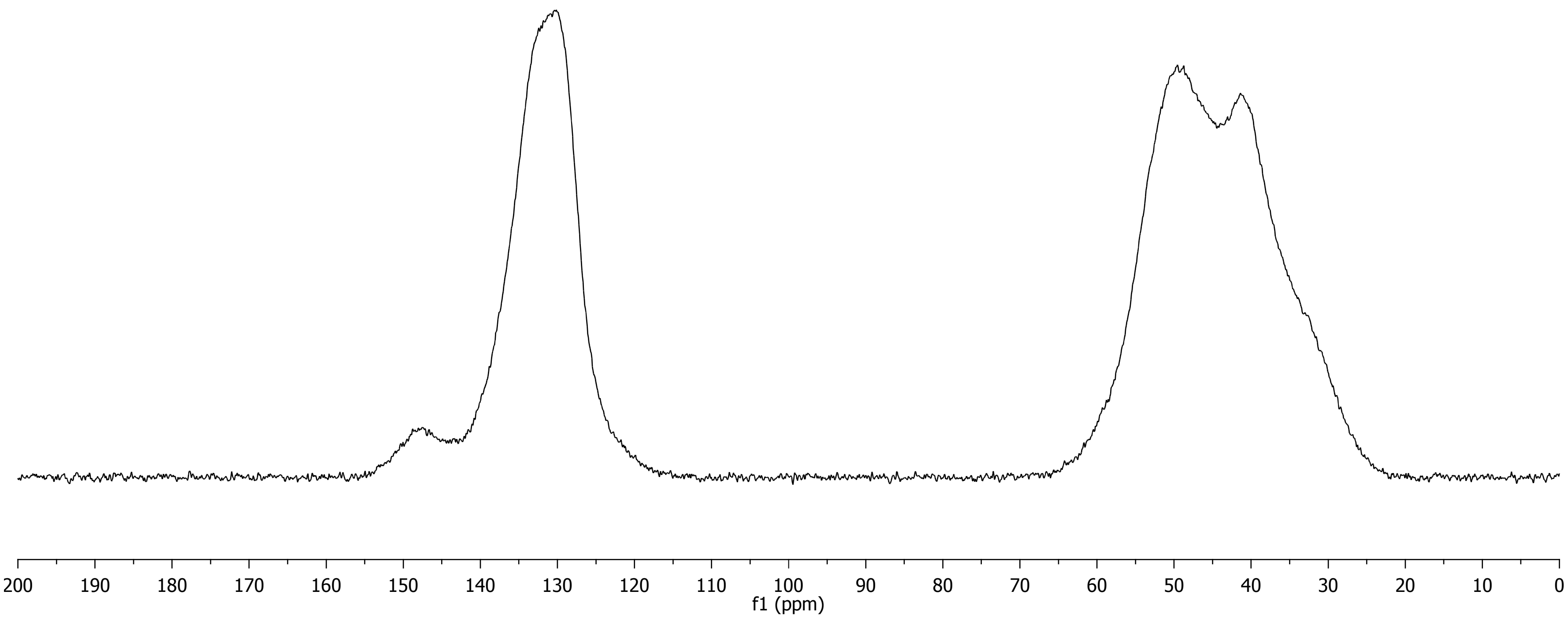
VA-PNBNBC$_6$H$_4$Br **(3)** (a/b = 1.8) ^{13}C {^{1}H} NMR (CDCl$_3$)



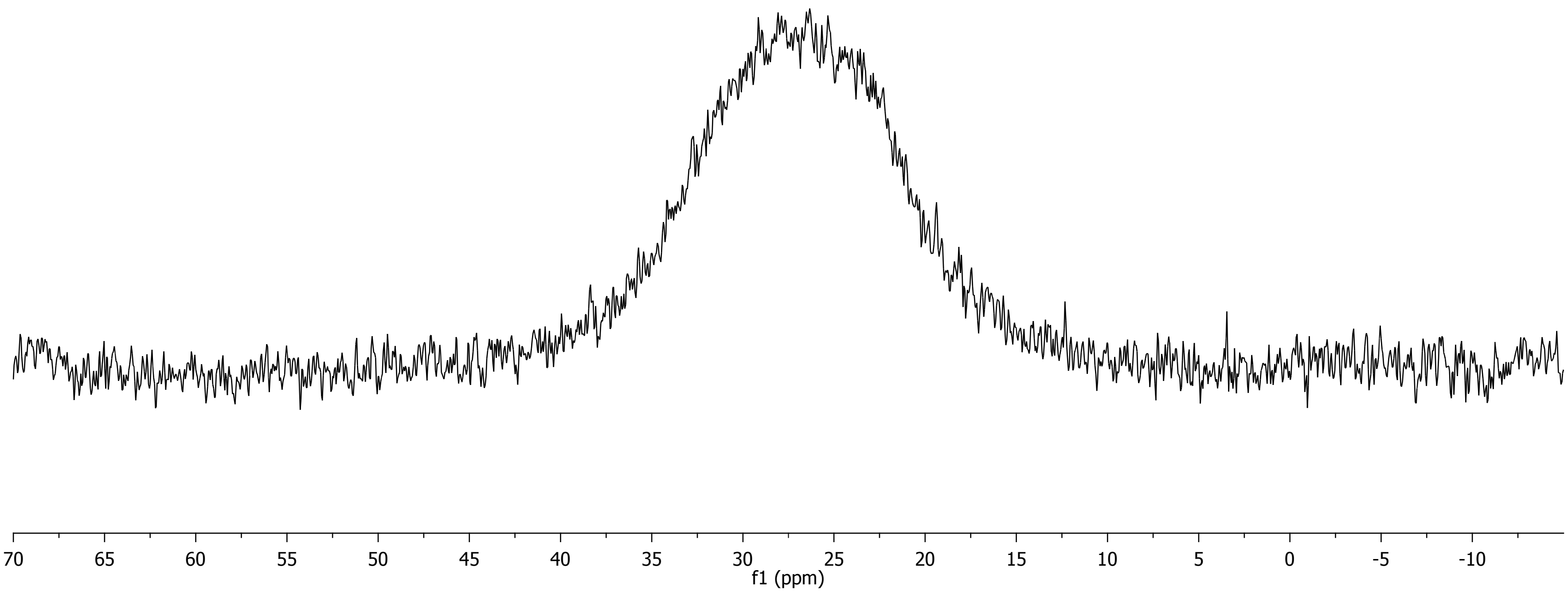
VA-PNBNBC$_6$H$_4$Br **(3)** (a/b = 1.8) IR



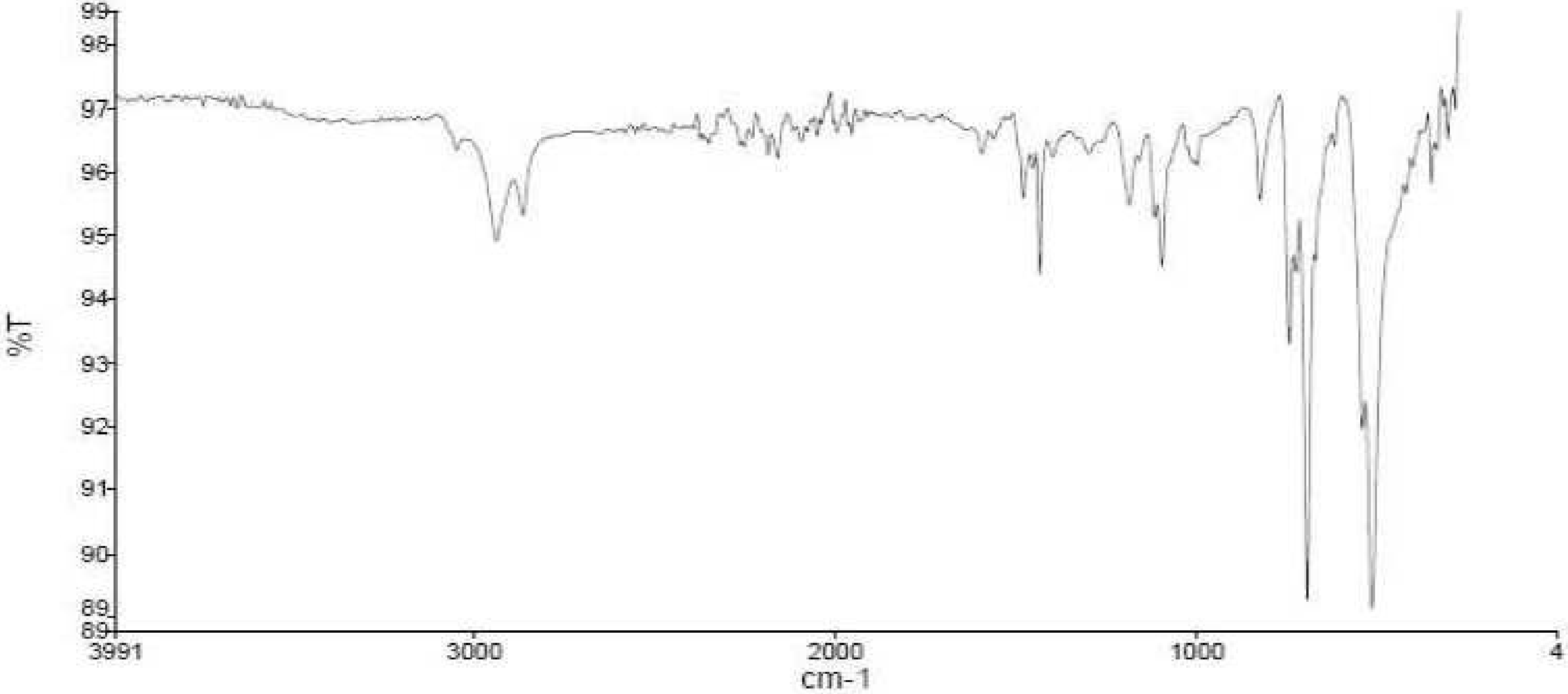
[VA-PNBNBC$_6$H$_4$-PdBr(PPh$_3$)$_2$] **(4)** ^{13}C CP-MAS NMR



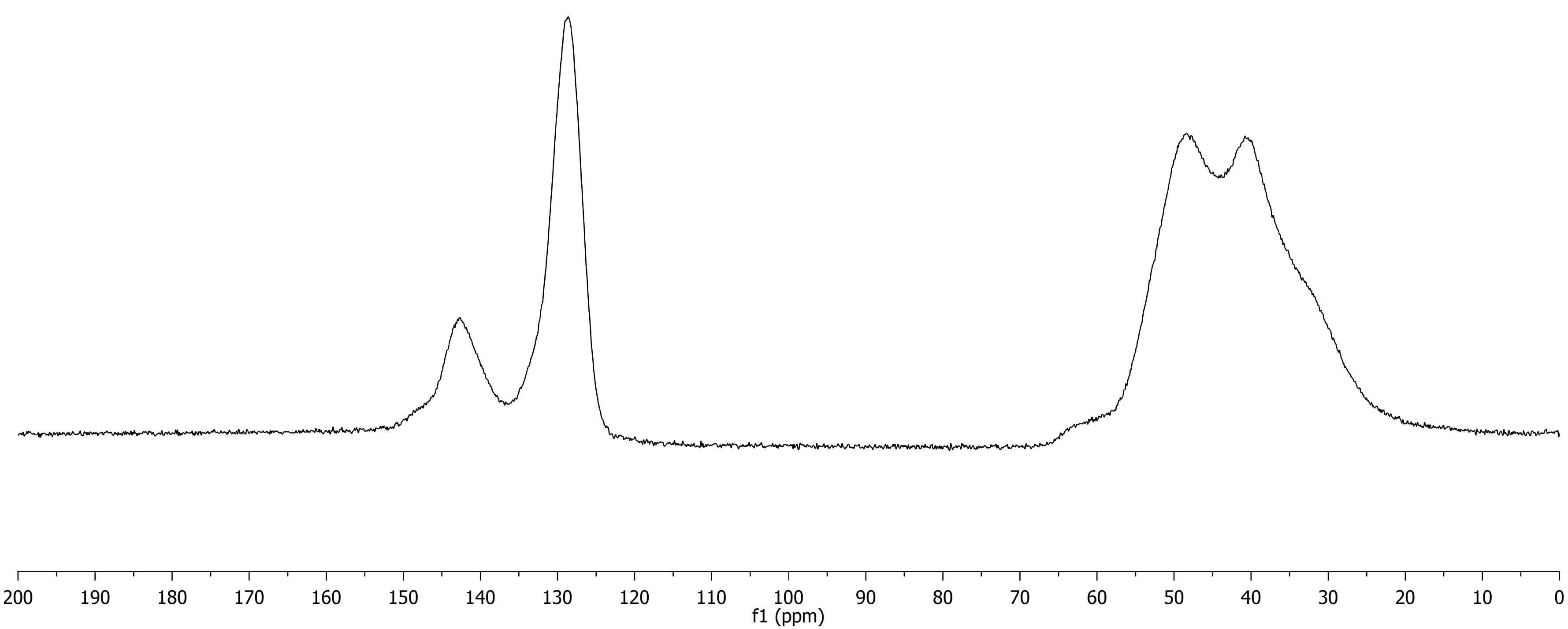
[VA-PNBNBC$_6$H$_4$-PdBr(PPh$_3$)$_2$] **(4)** ^{31}P MAS NMR



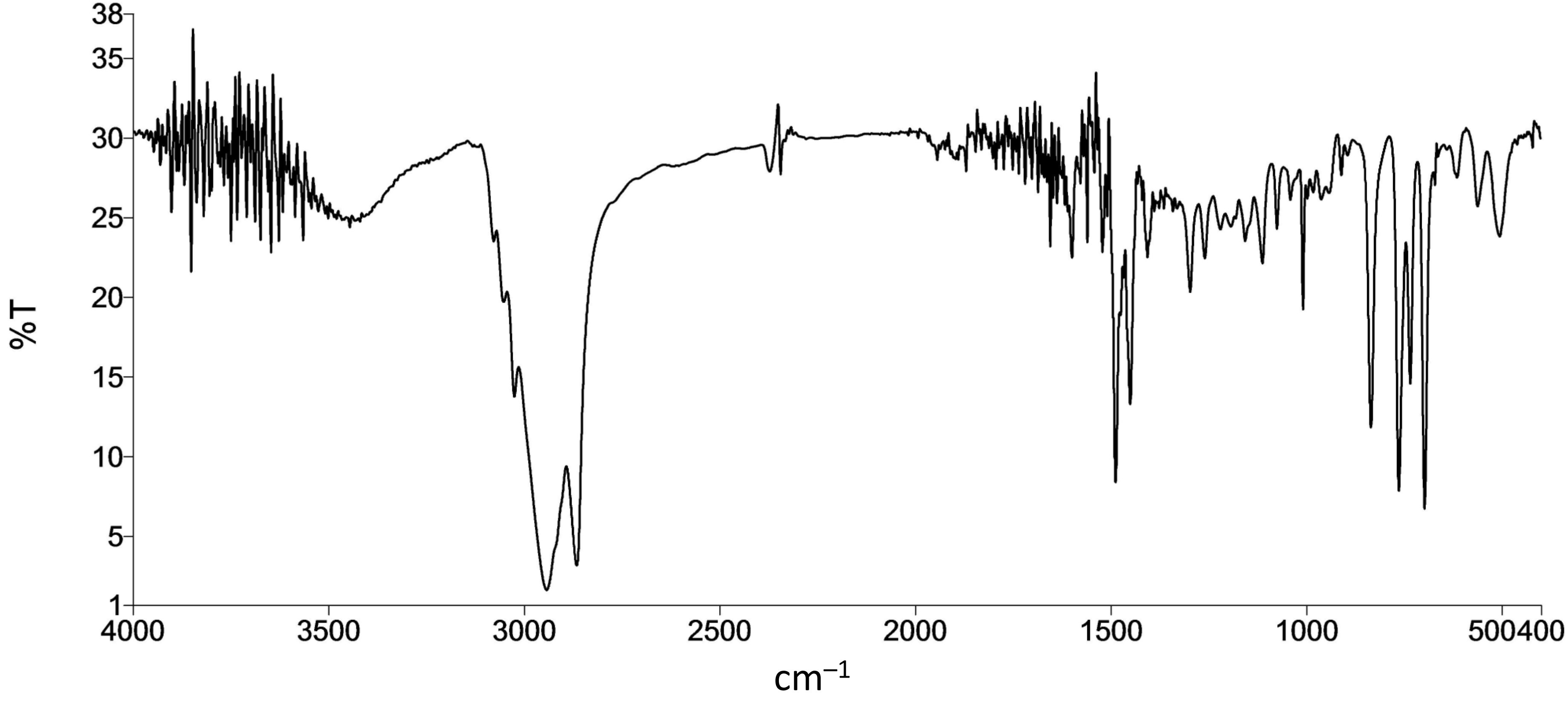
[VA-PNBNBC$_6$H$_4$-PdBr(PPh$_3$)$_2$] **(4)** IR



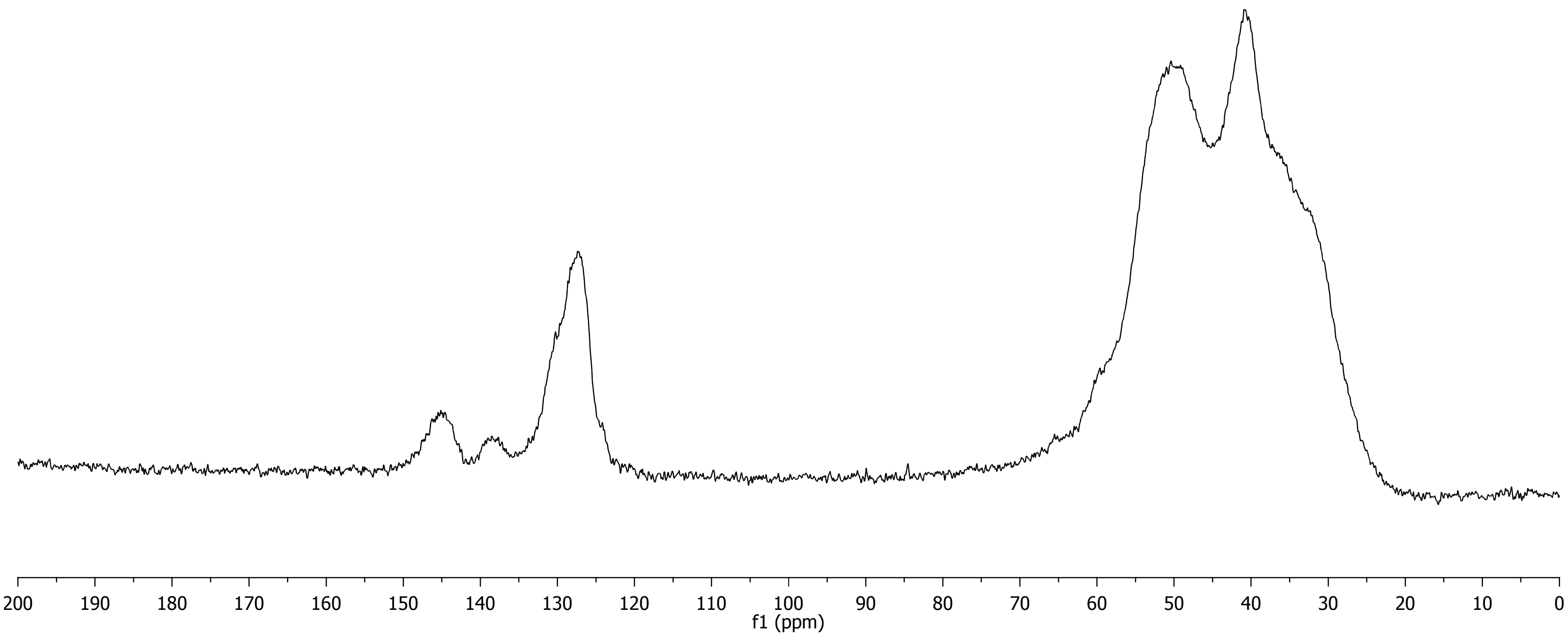
VA-PNBNBC$_6$H$_4$-Ph **(5)** ^{13}C CP-MAS NMR



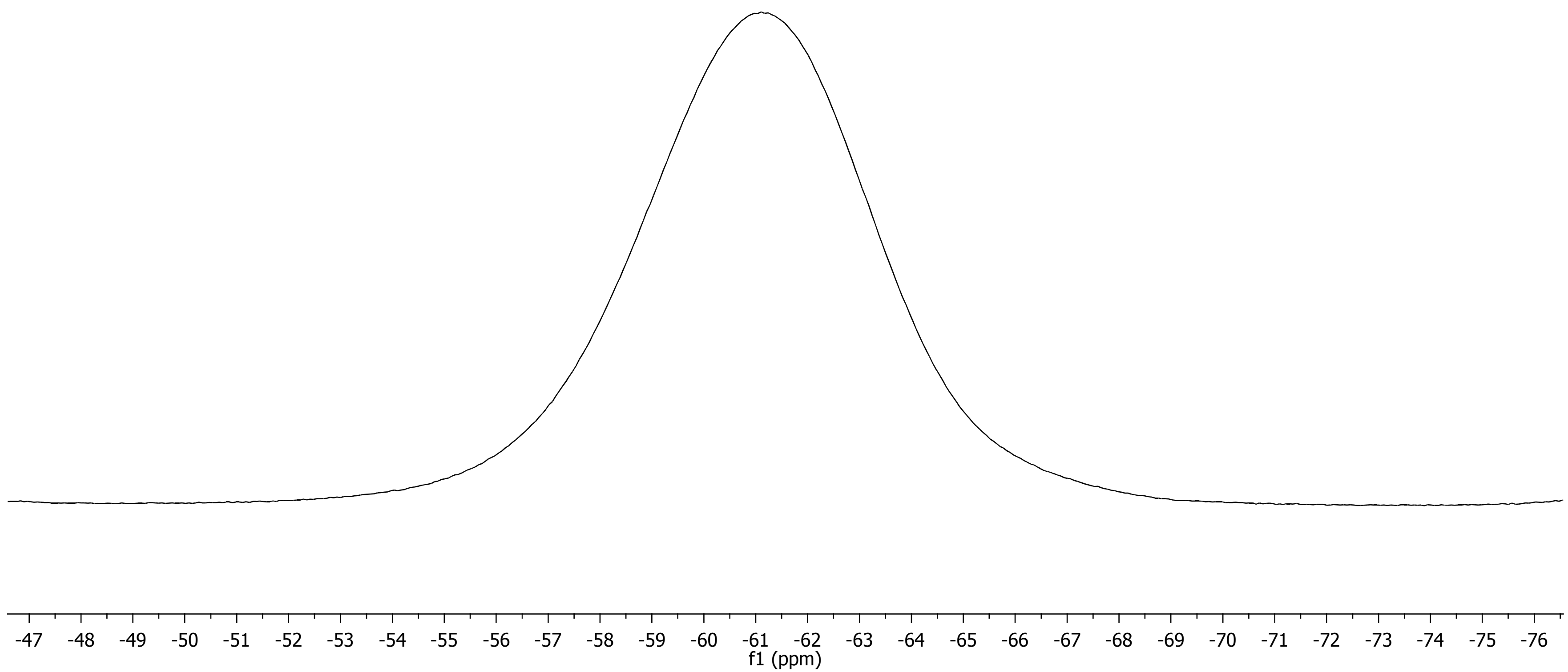
VA-PNBNBC$_6$H$_4$-Ph **(5)** IR



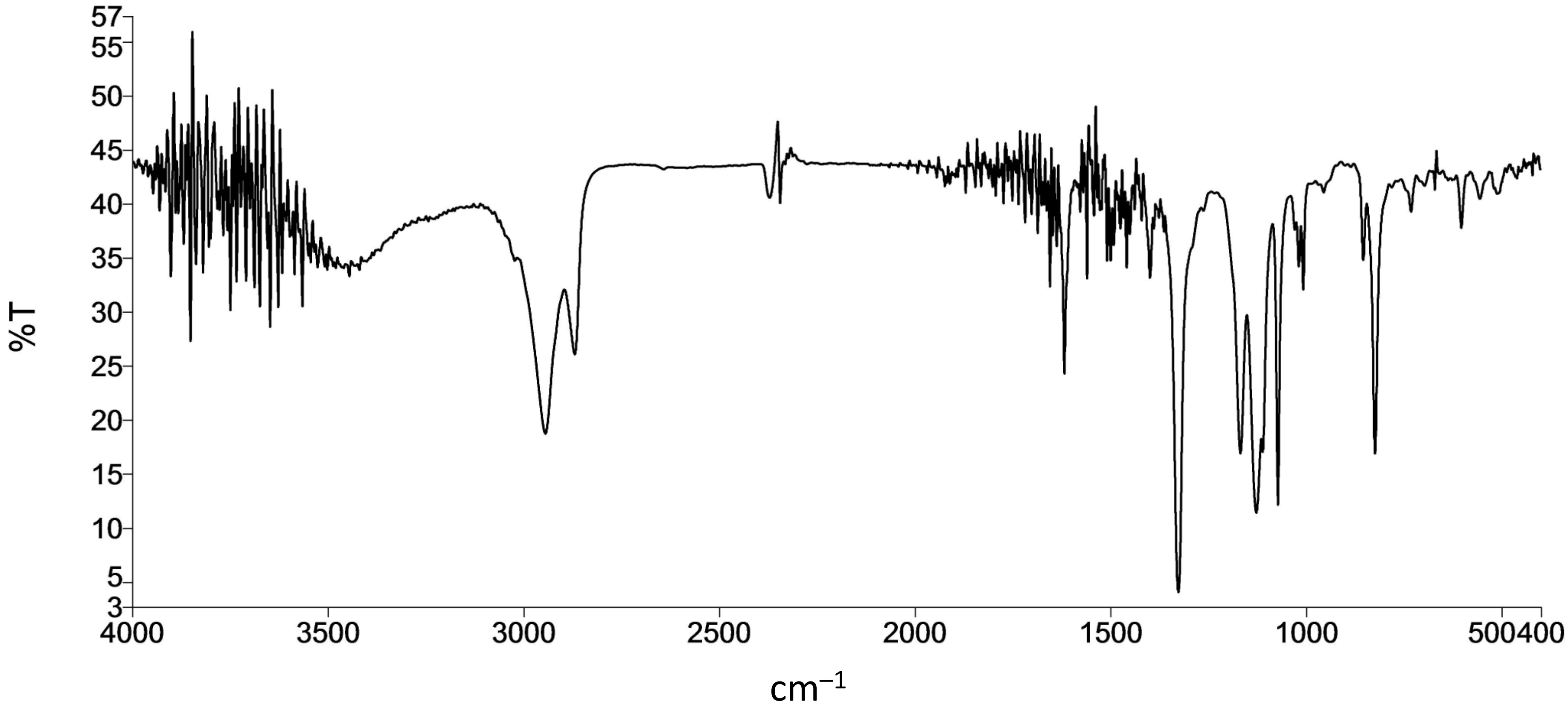
VA-PNBNBC$_6$H$_4$-C$_6$H$_4$-4-CF$_3$ **(6)** ^{13}C CP-MAS NMR



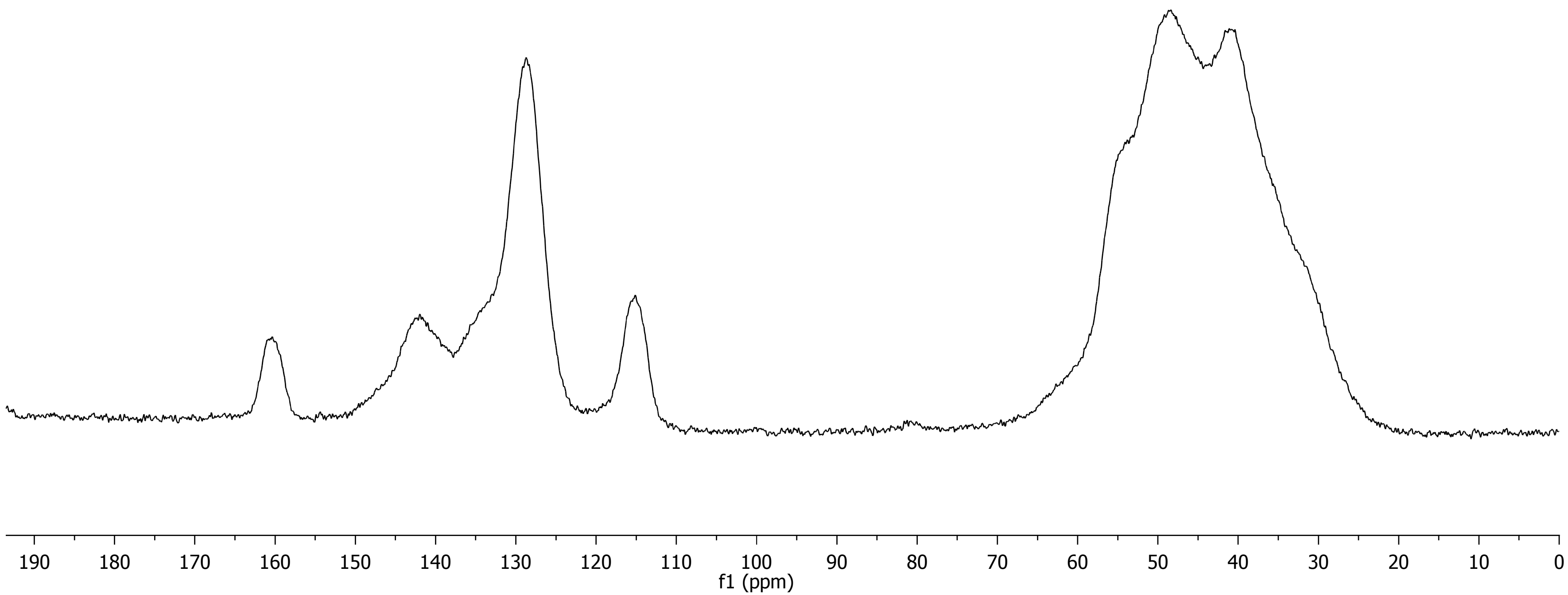
VA-PNBNBC$_6$H$_4$-C$_6$H$_4$-4-CF$_3$ **(6)** ^{19}F MAS NMR



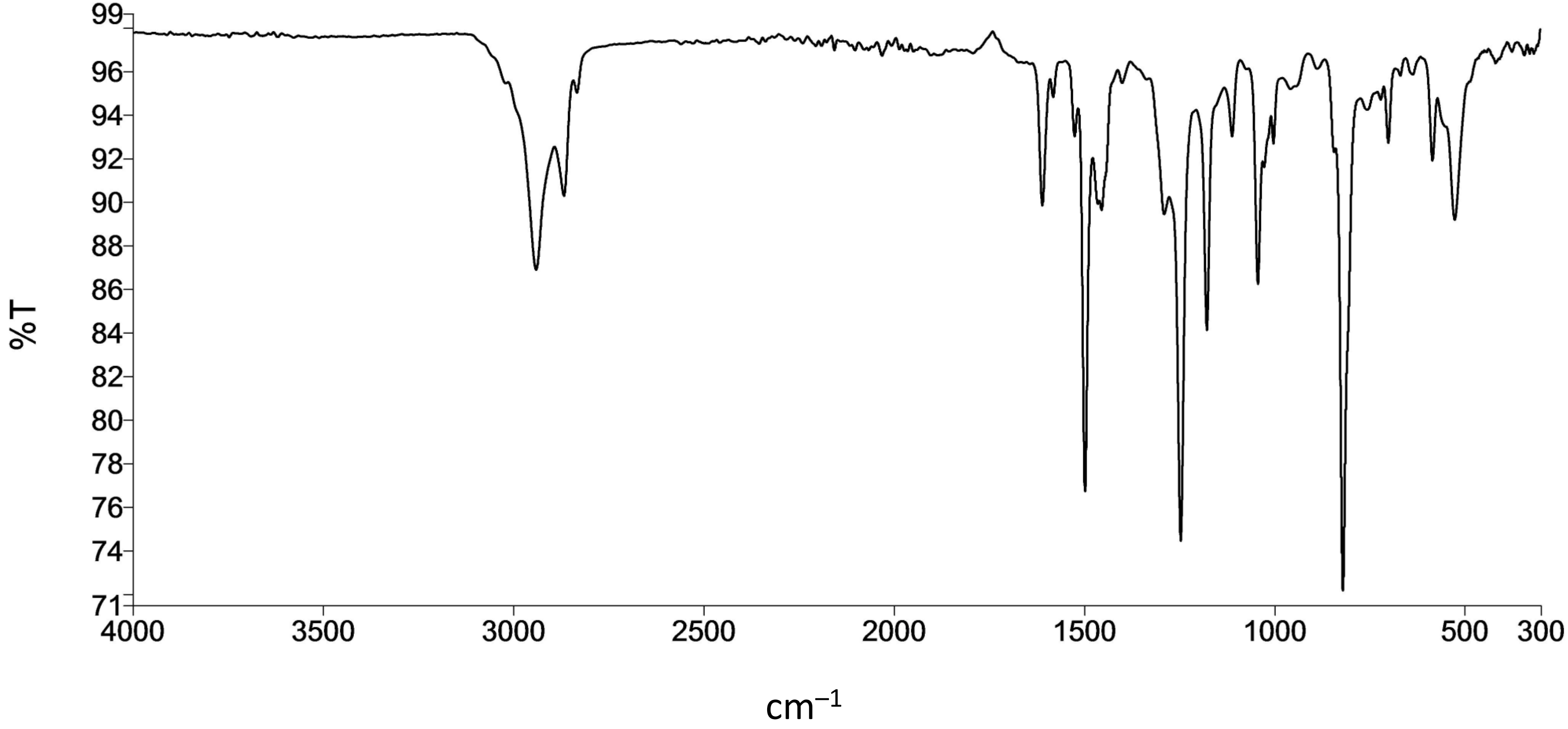
VA-PNBNBC$_6$H$_4$-C$_6$H$_4$-4-CF$_3$ **(6)** IR



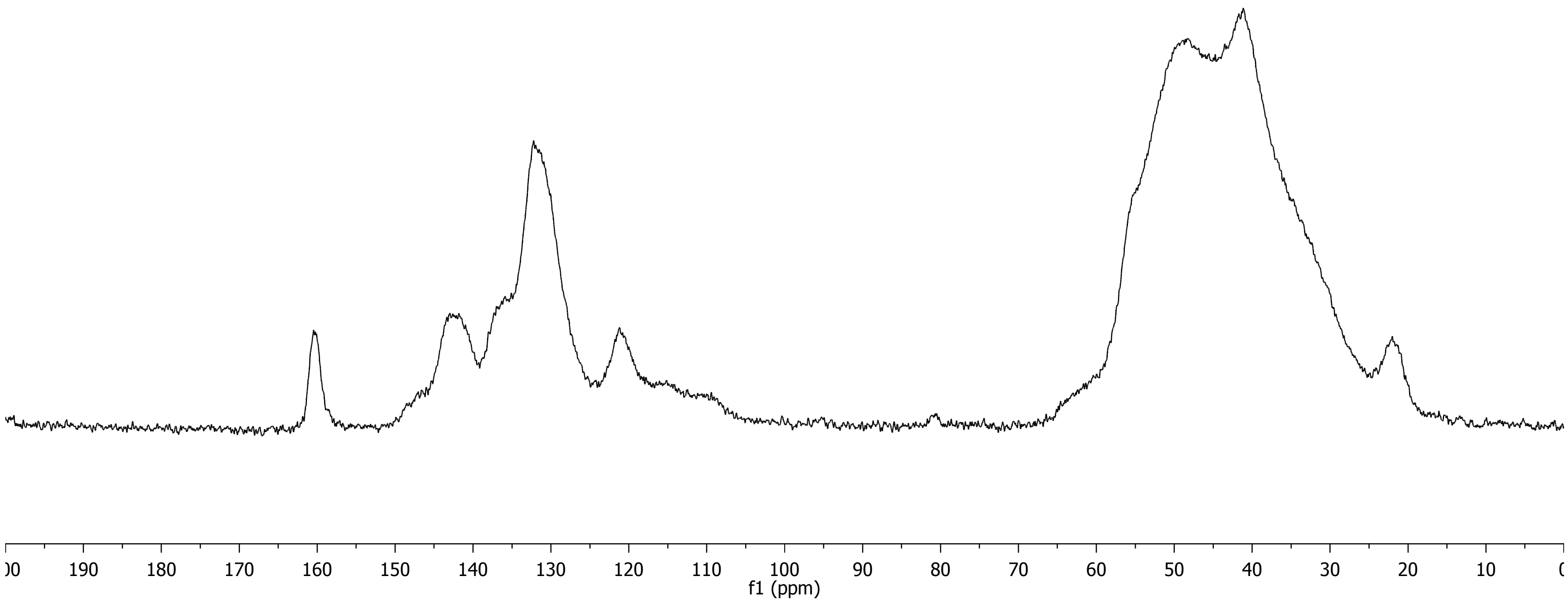
VA-PNBNBC$_6$H$_4$-C$_6$H$_4$-4-OMe **(7)** ^{13}C CP-MAS NMR



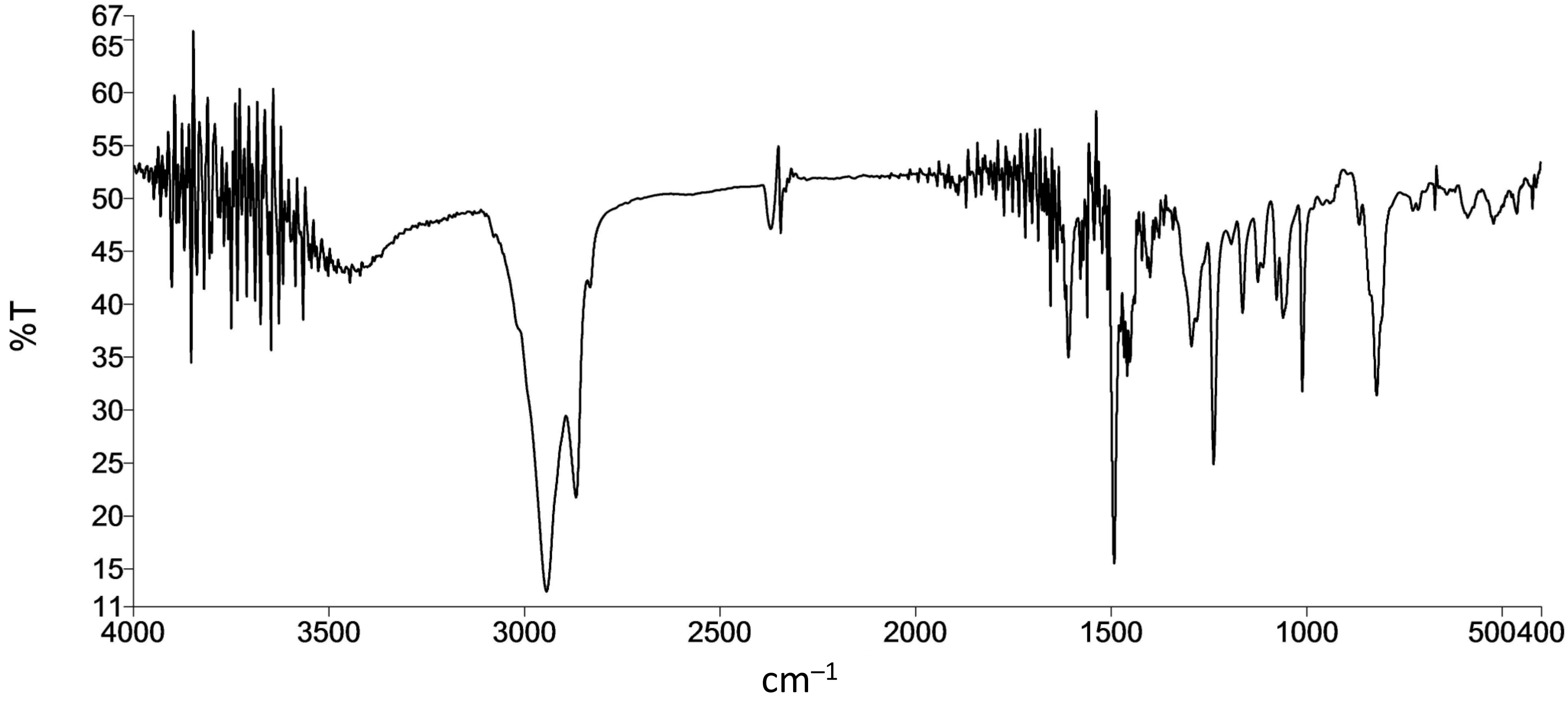
VA-PNBNBC$_6$H$_4$-C$_6$H$_4$-4-OMe **(7)** IR



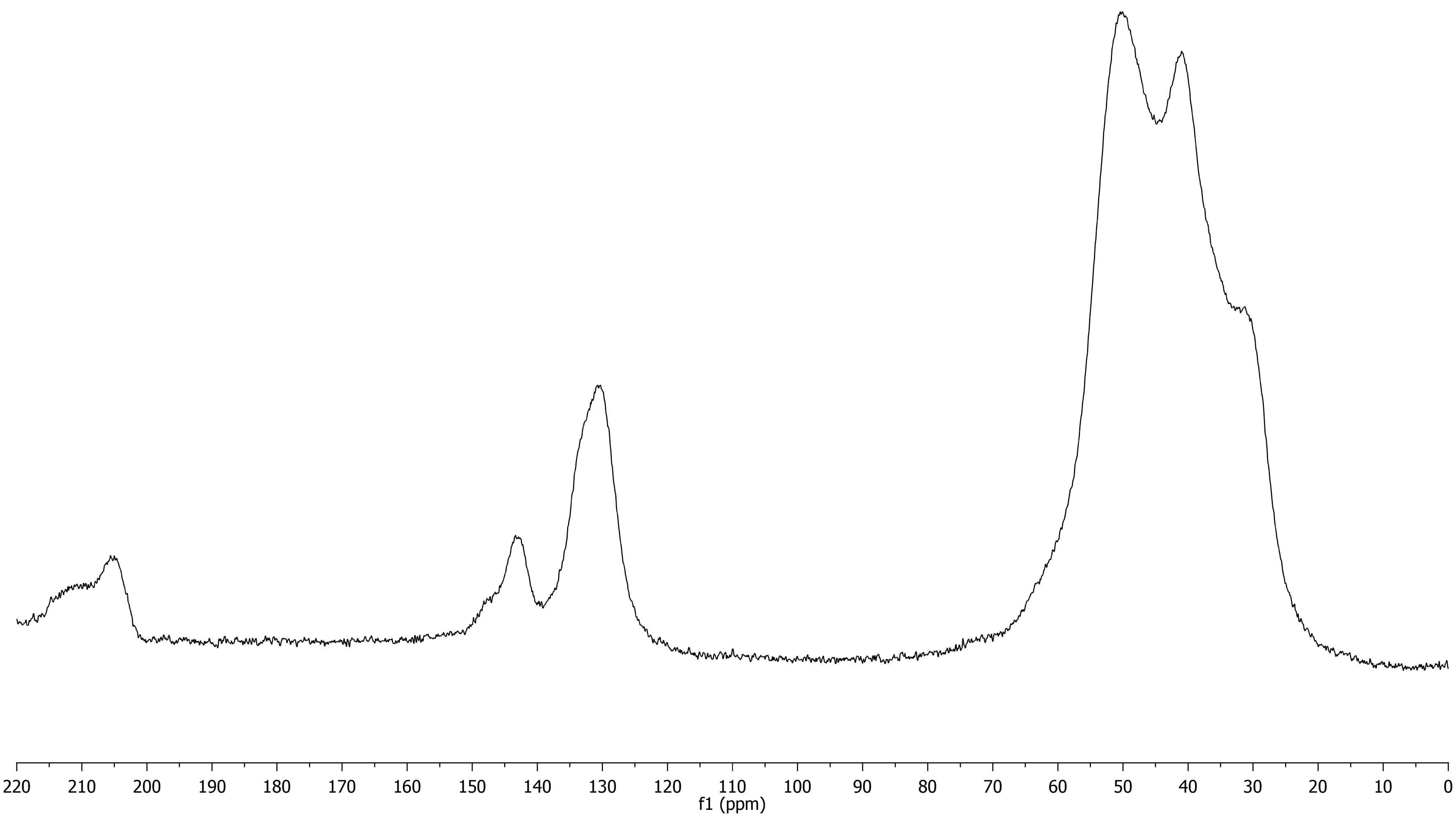
VA-PNBNBC$_6$H$_4$-C$_6$H$_3$-2-Me-4-OMe **(8)** ^{13}C CP-MAS NMR



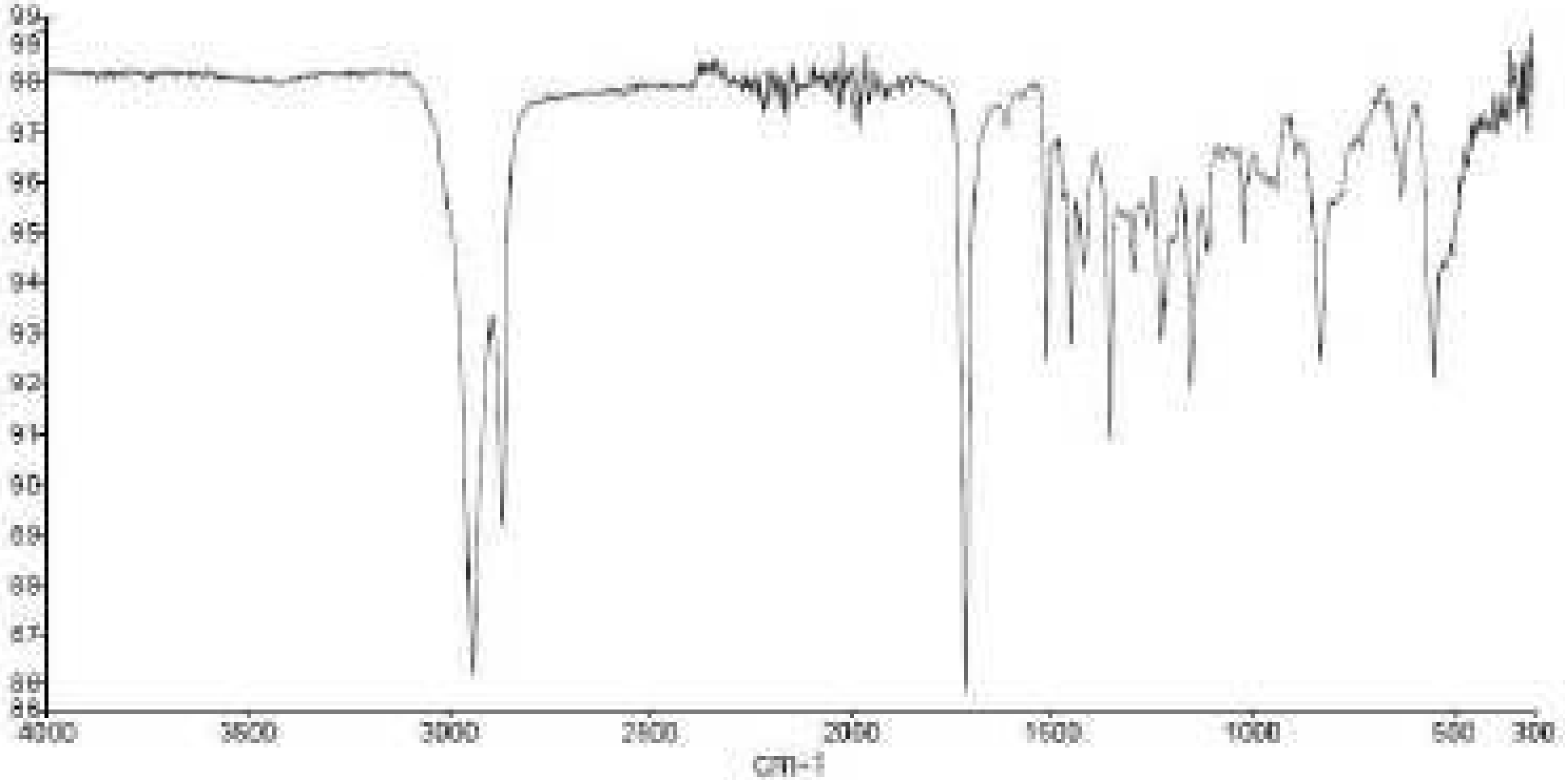
VA-PNBNBC$_6$H$_4$-C$_6$H$_3$-2-Me-4-OMe **(8)** IR



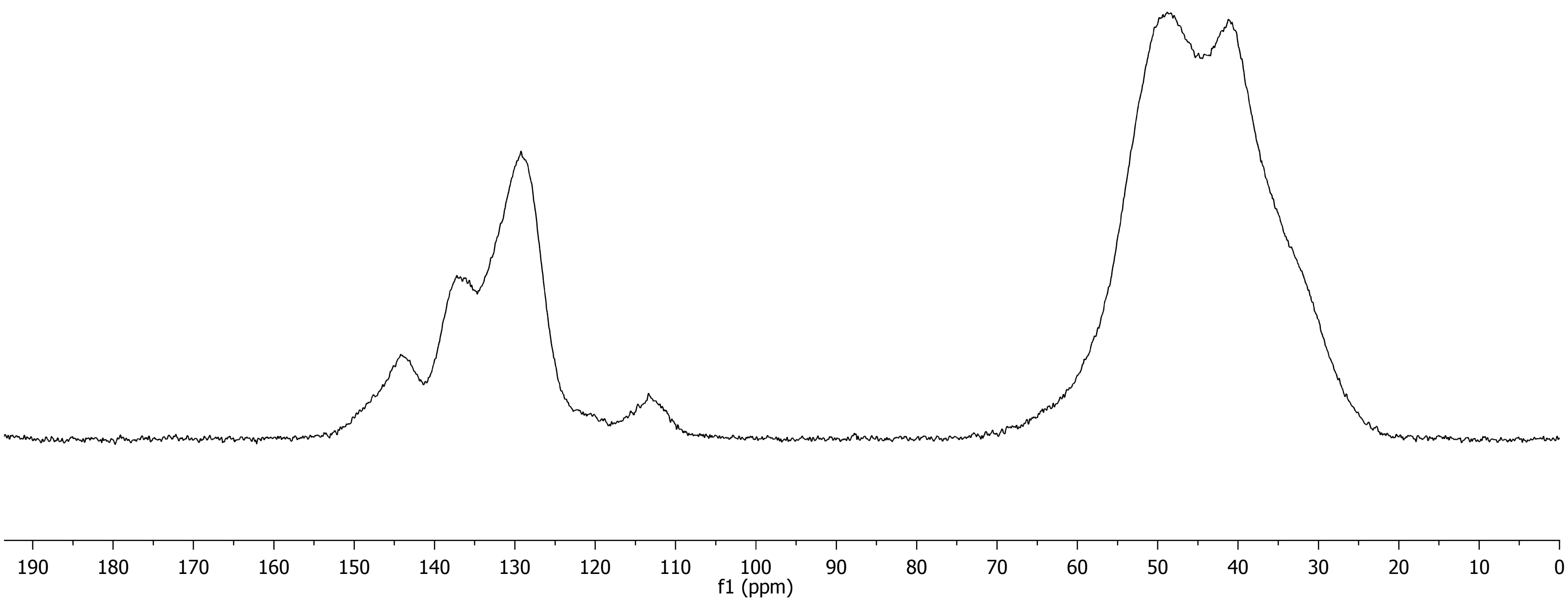
VA-PNBNBC$_6$H$_4$-CH$_2$C(O)CH$_3$ **(9)** ^{13}C CP-MAS NMR



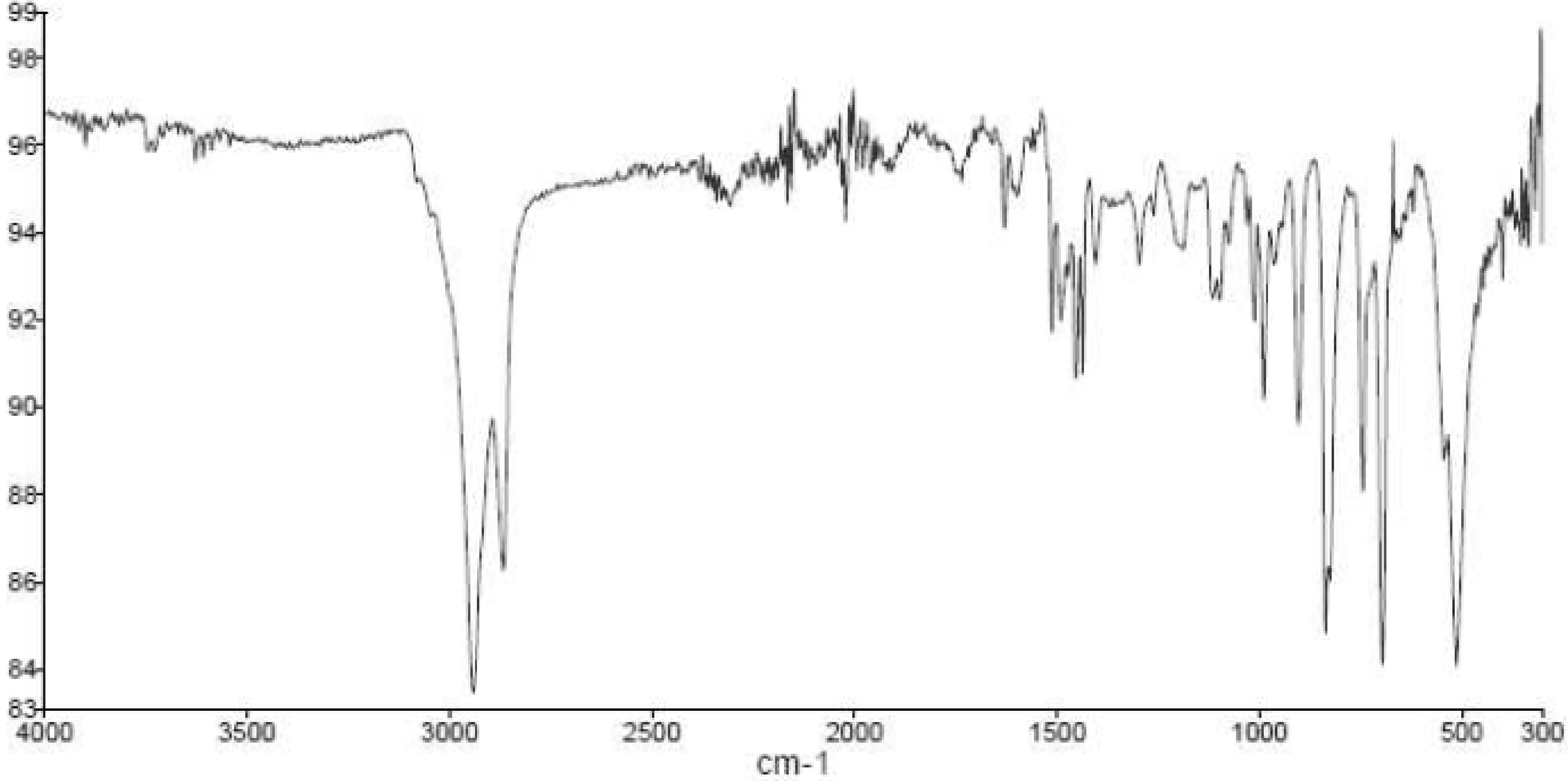
VA-PNBNBC$_6$H$_4$-CH$_2$C(O)CH$_3$ **(9)** IR



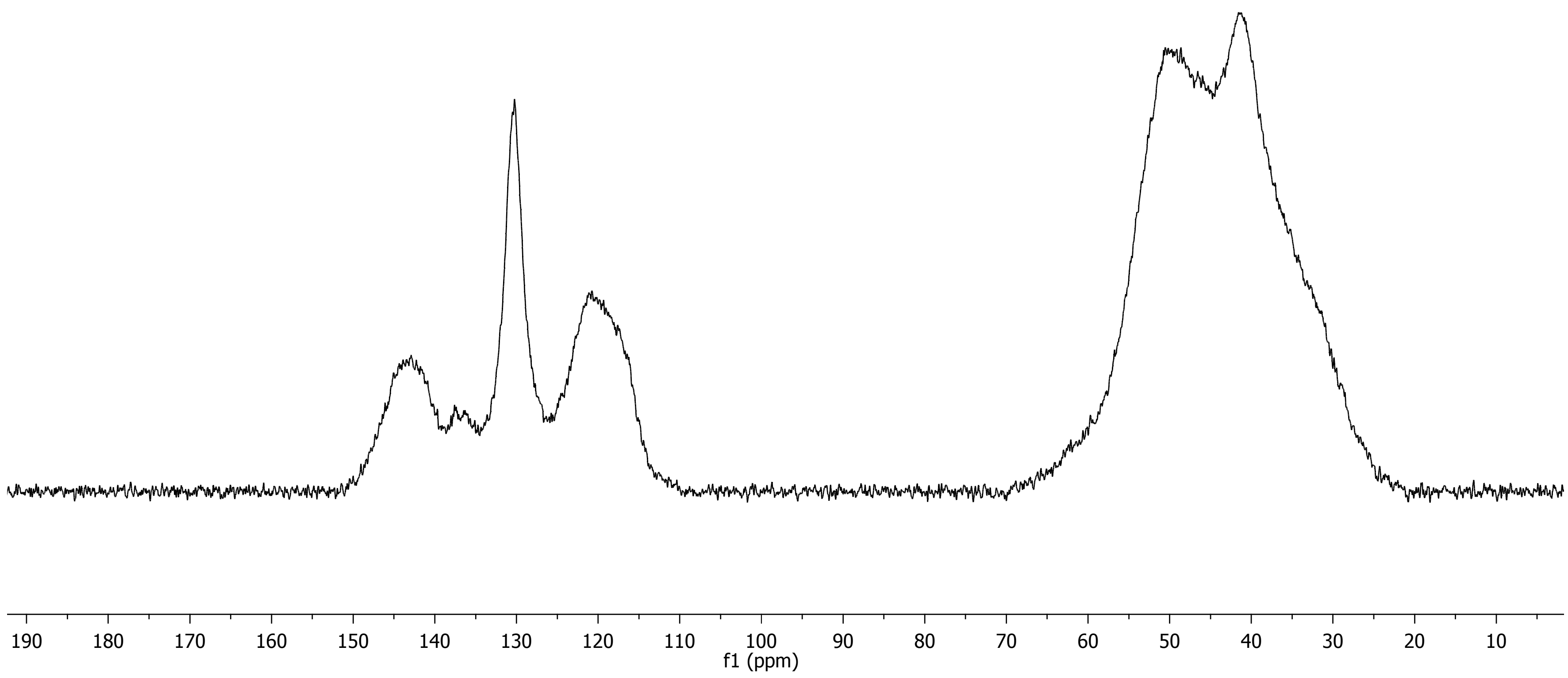
VA-PNBNBC$_6$H$_4$-CH=CH$_2$ **(10)** ^{13}C CP-MAS NMR



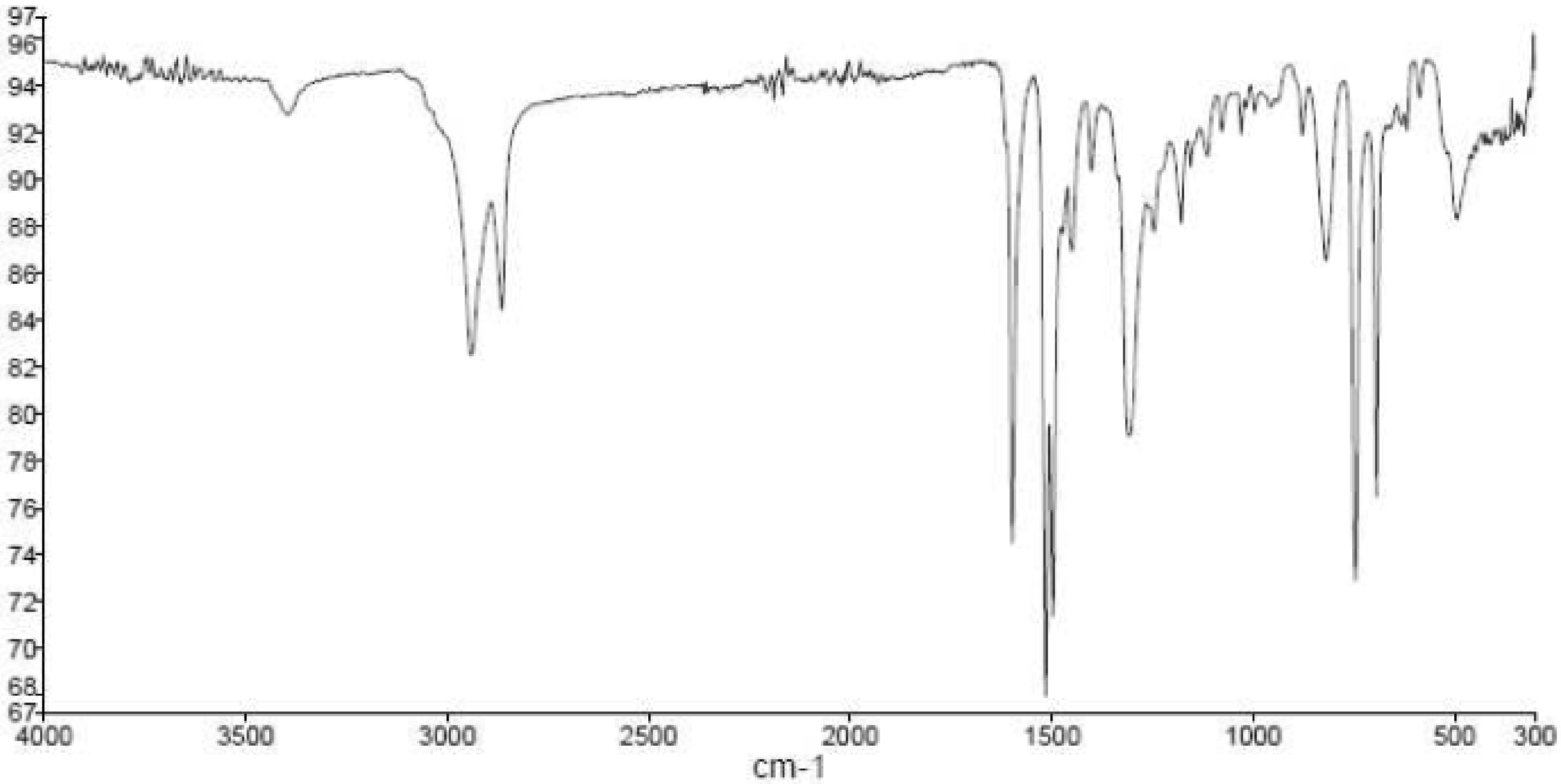
VA-PNBNBC_6H_4-CH=CH_2 **(10)** IR



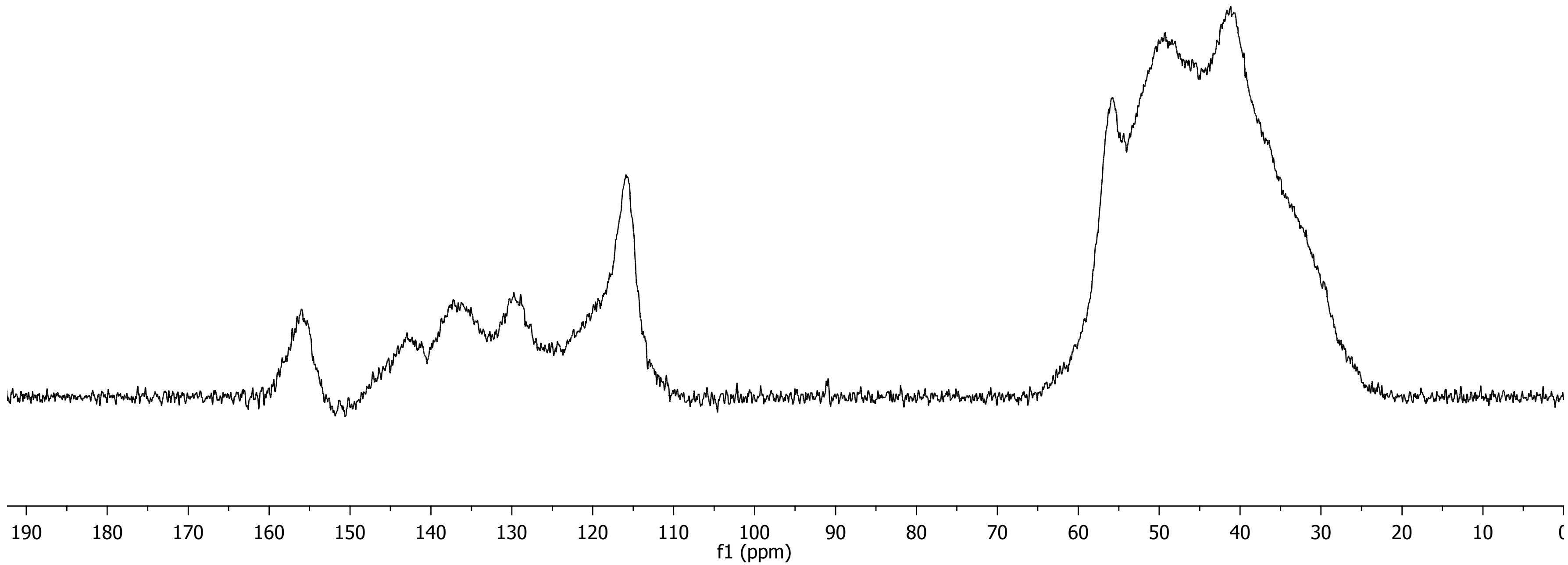
VA-PNBNBC$_6$H$_4$-NHPh **(11)** ^{13}C CP-MAS NMR



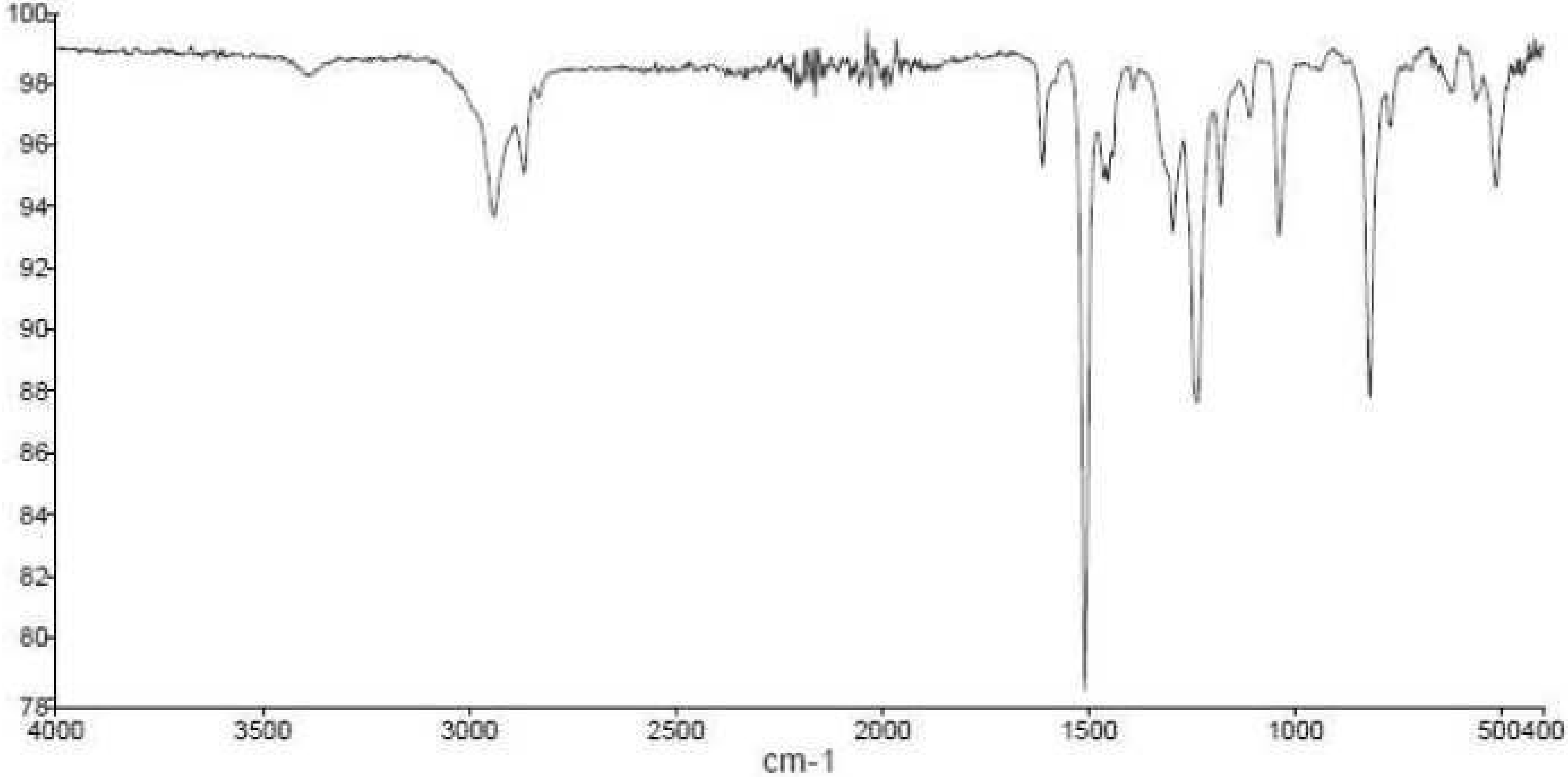
VA-PNBNBC_6H_4-NHPh **(11)** IR



VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_4$-4-OMe) **(12)** ^{13}C CP-MAS NMR



VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_4$-4-OMe) **(12)** IR



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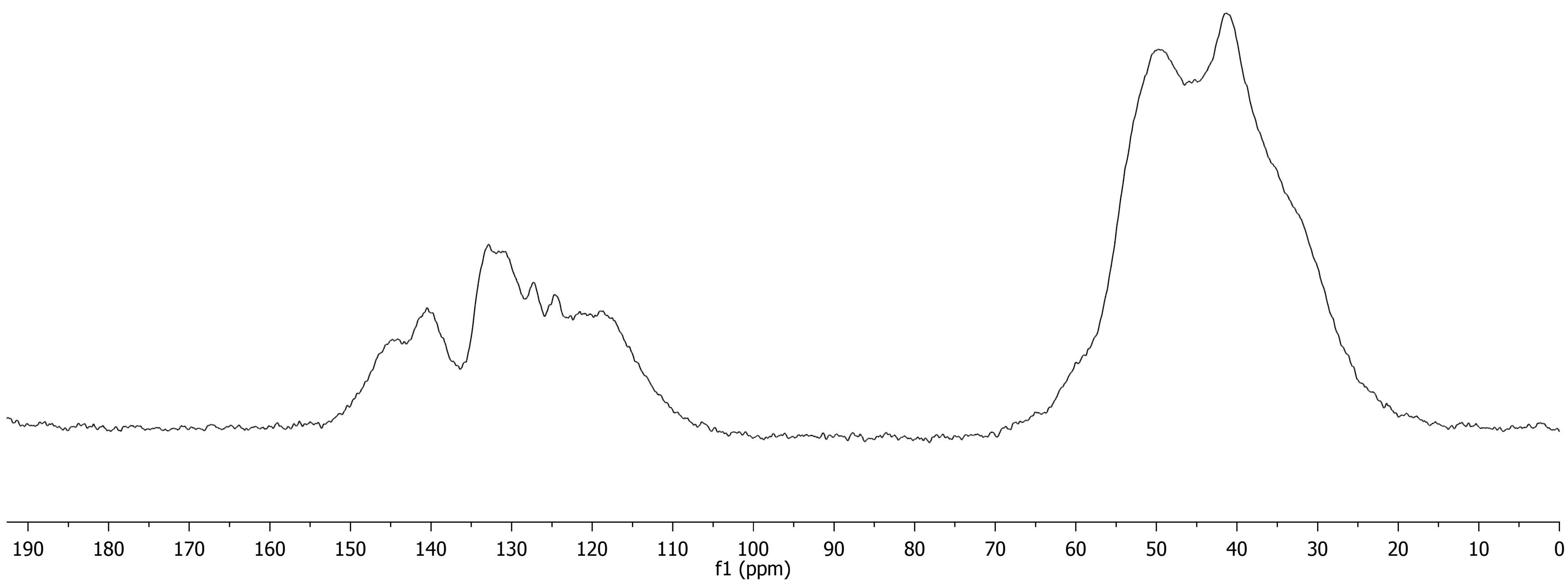
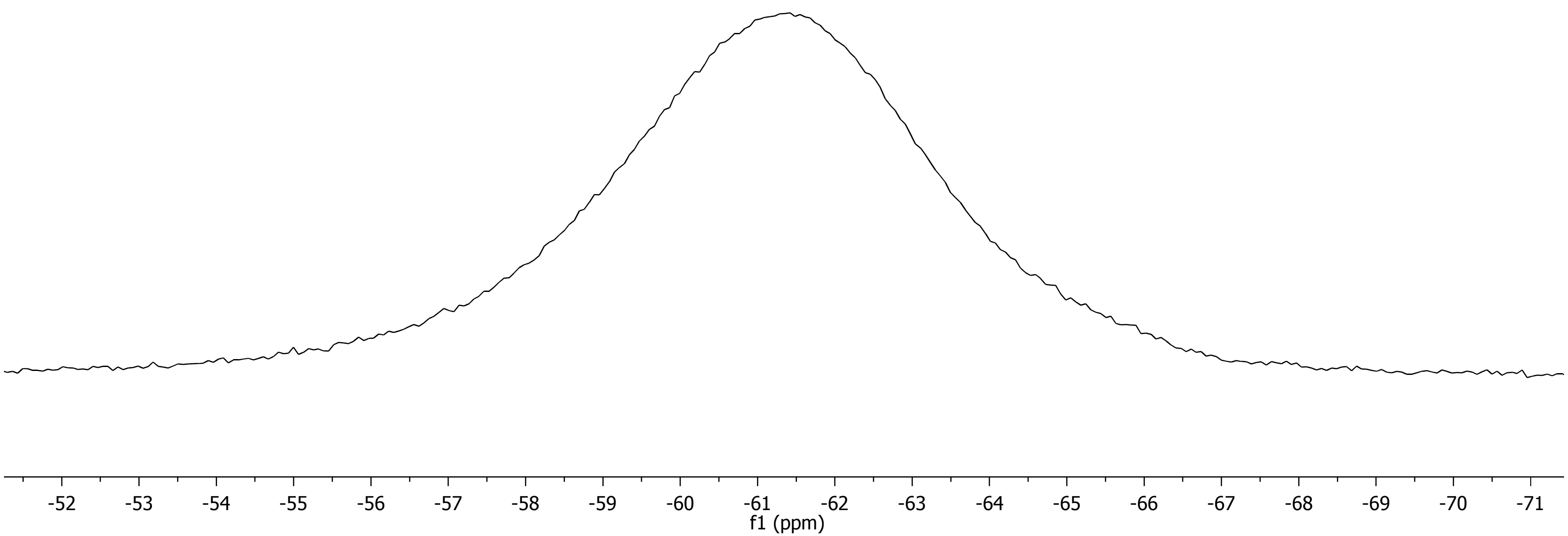
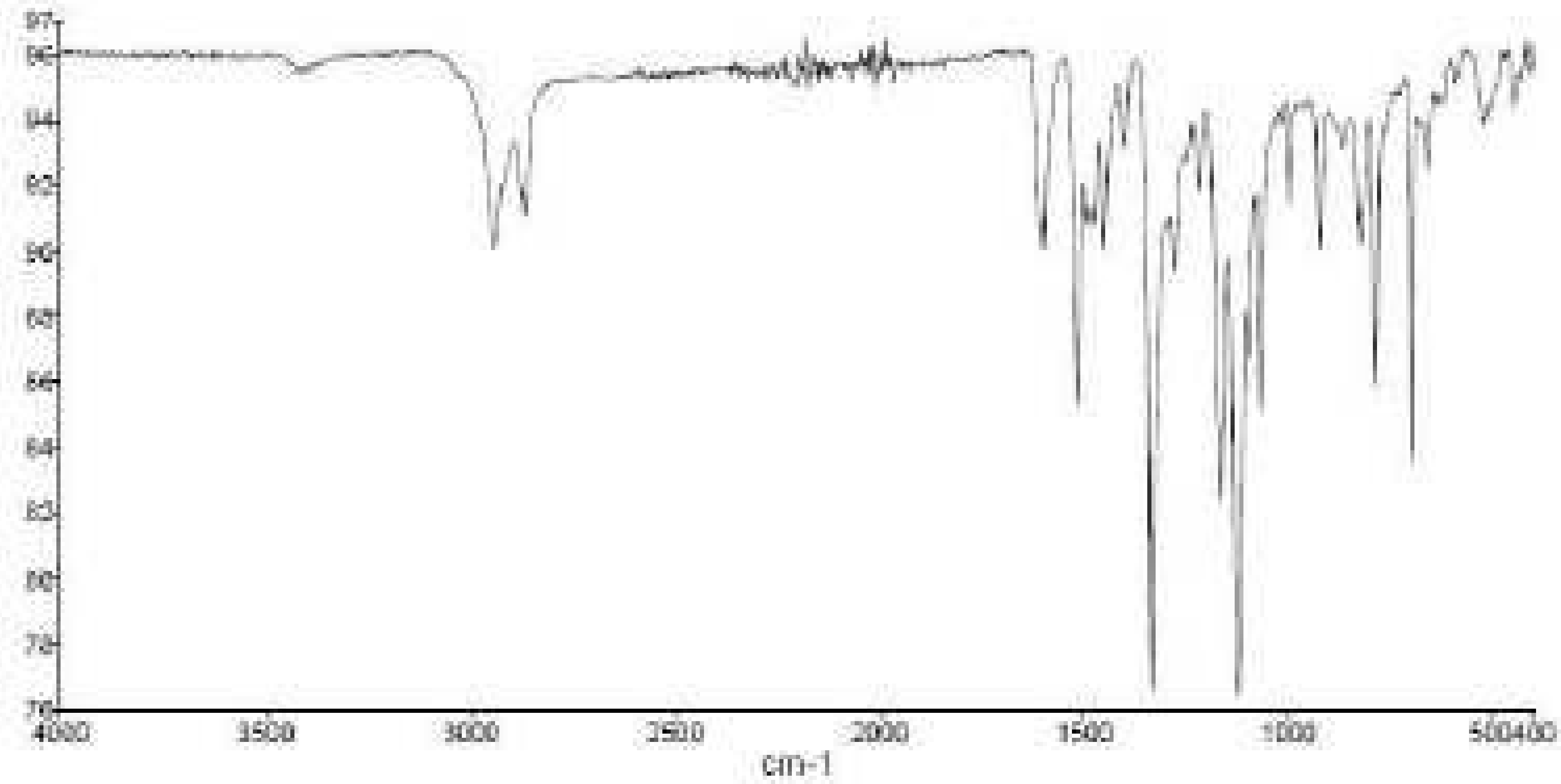


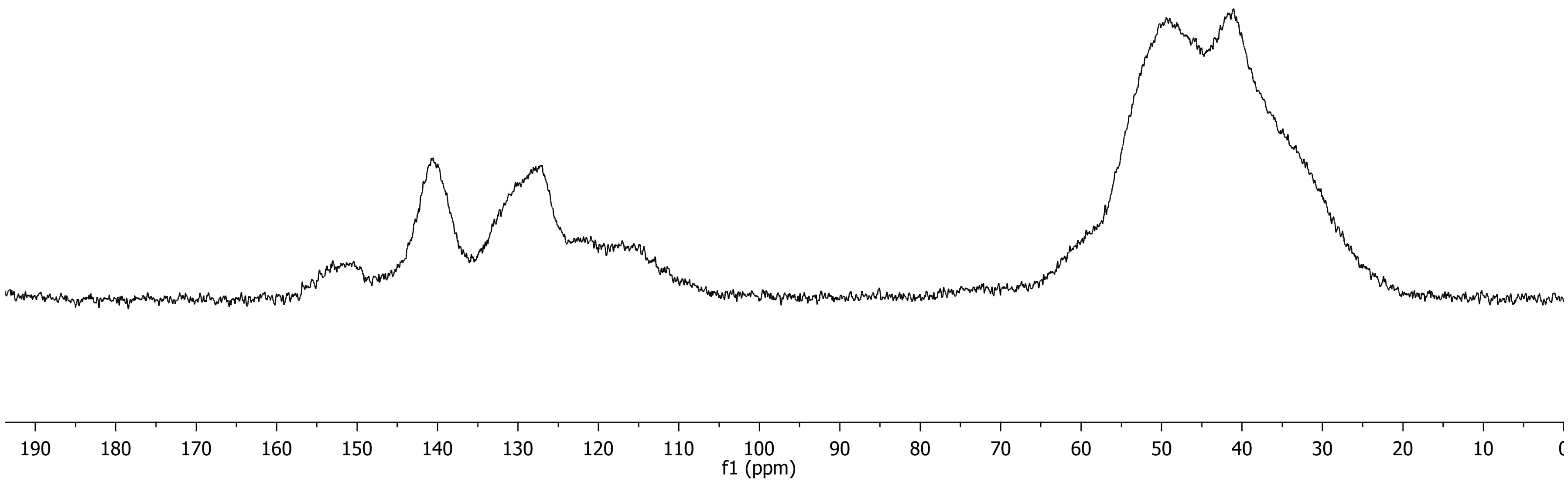
VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_4$-3-CF$_3$) **(13)** ^{19}F MAS NMR



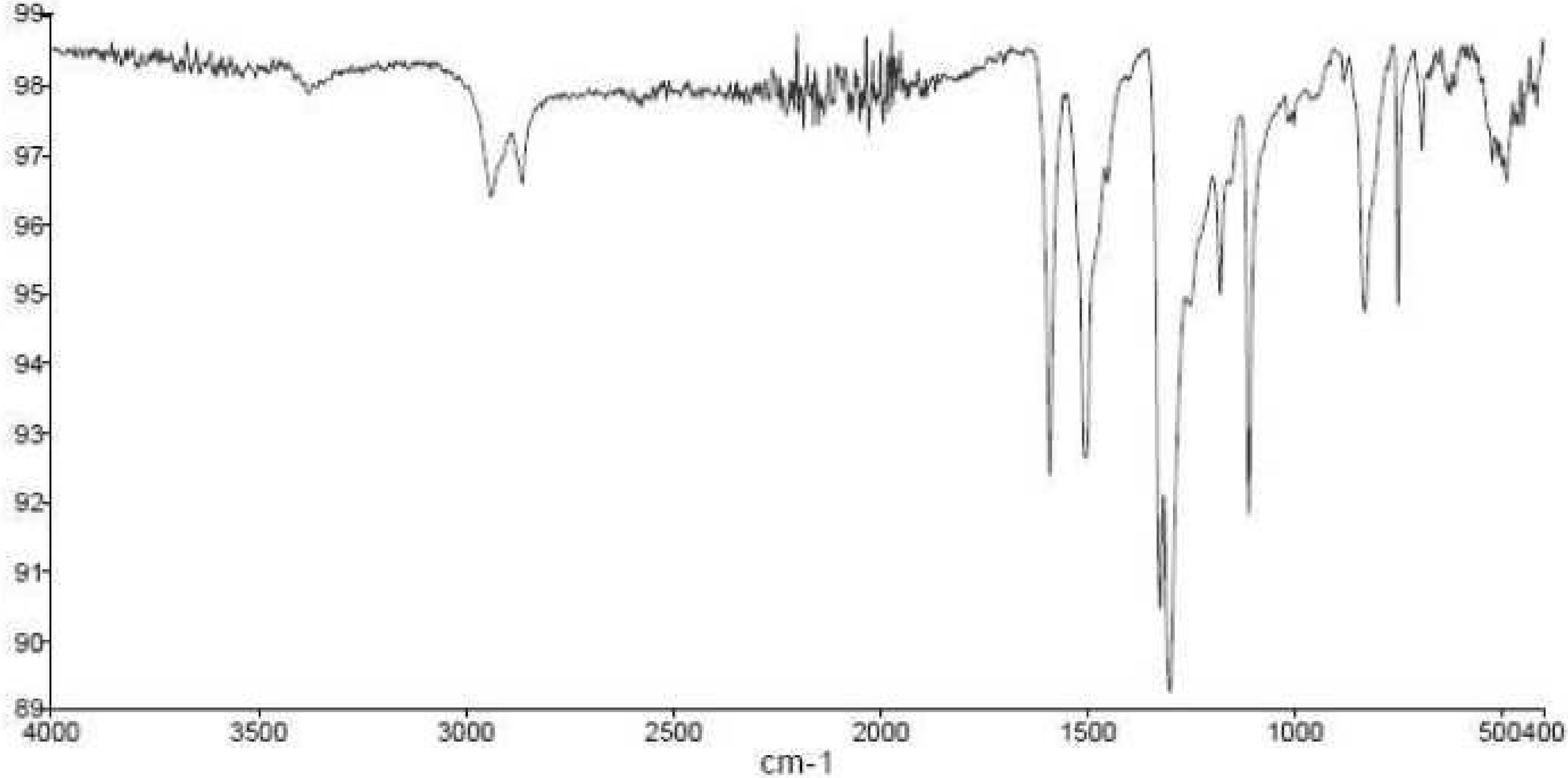
VA-PNBNBC_6H_4-NH(C_6H_4-3-CF_3) **(13)** IR



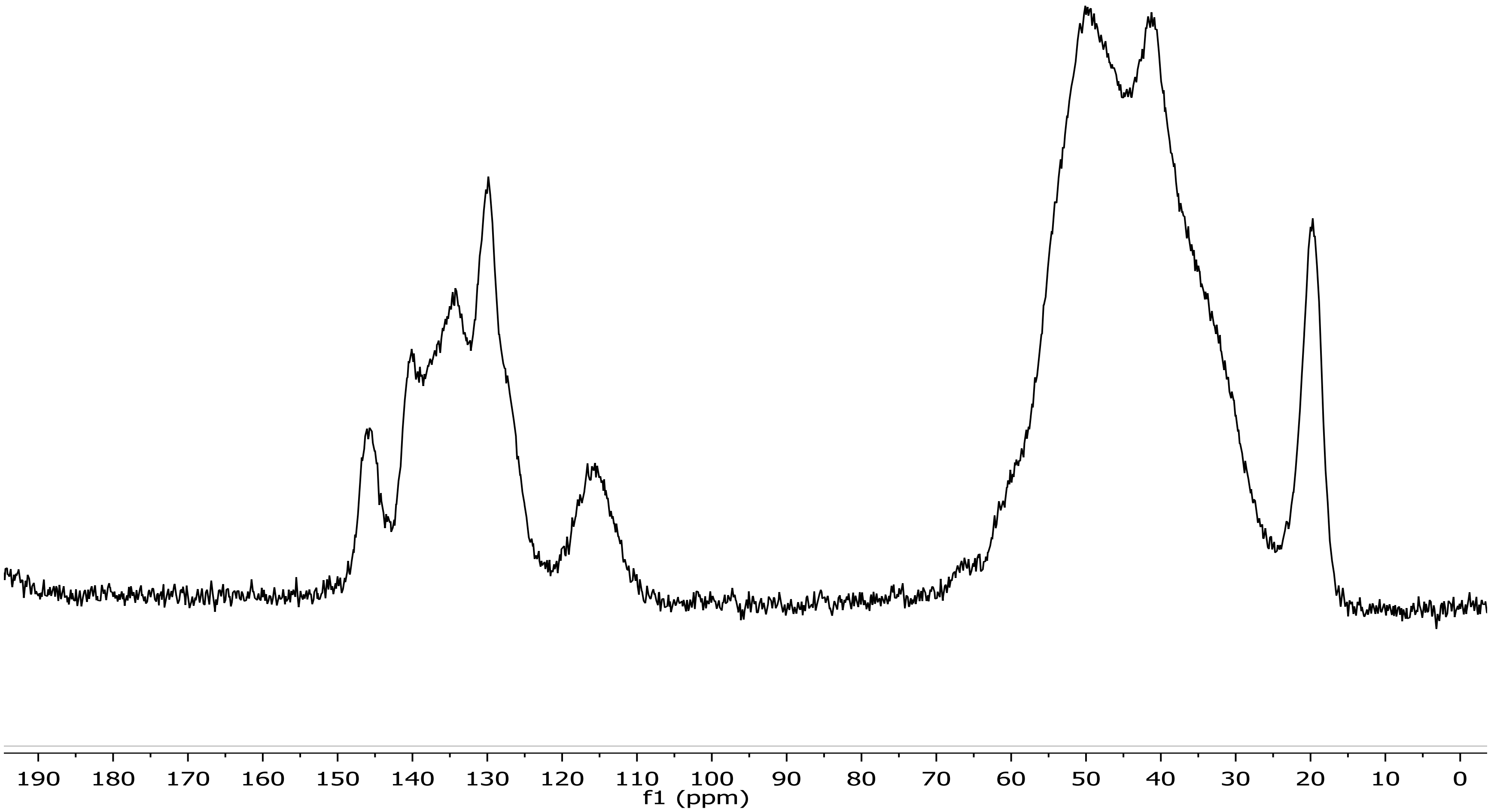
VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_4$-4-NO$_2$) **(14)** ^{13}C CP-MAS NMR



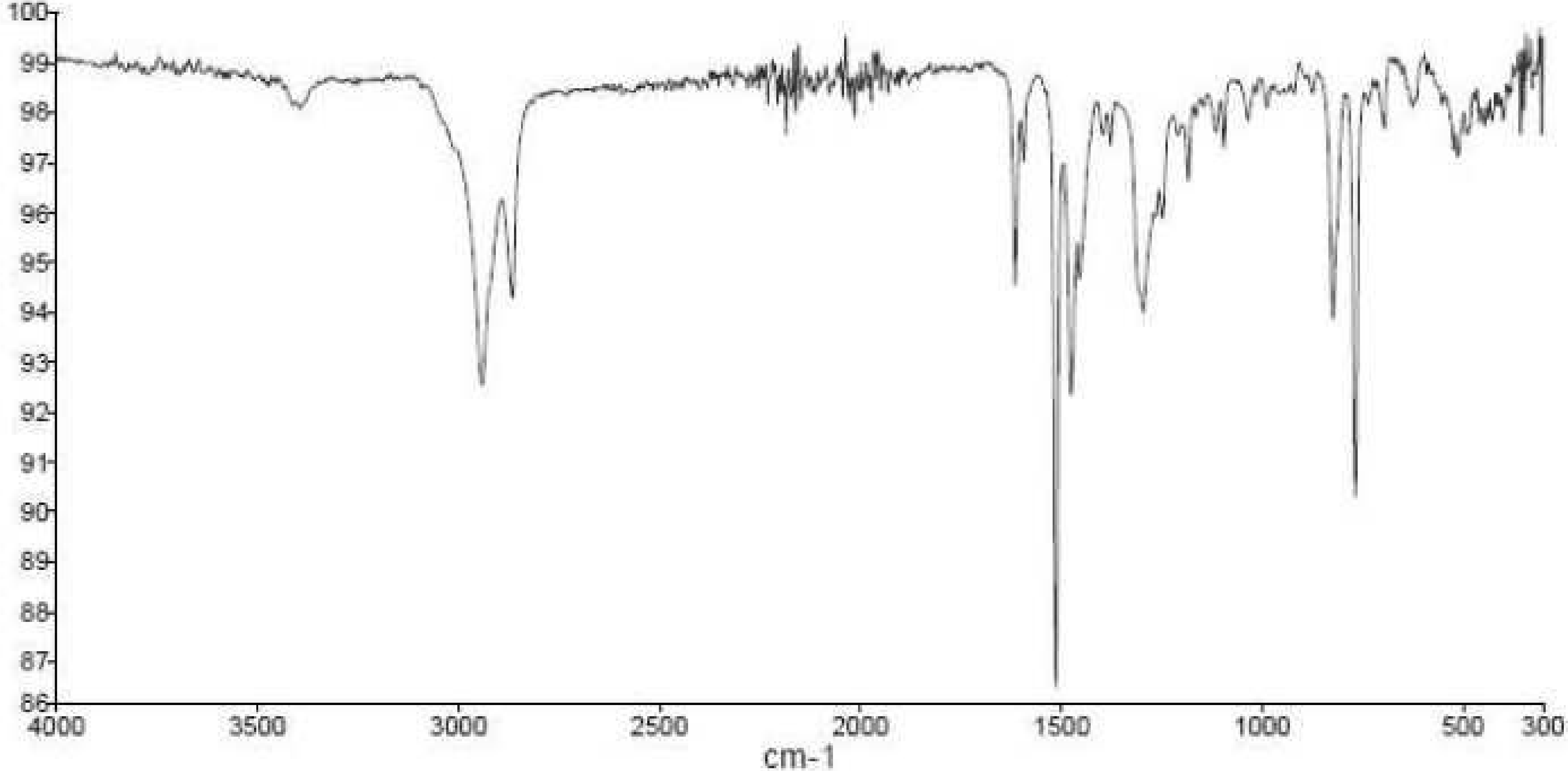
VA-PNBNBC_6H_4-NH(C_6H_4-4-NO_2) **(14)** IR



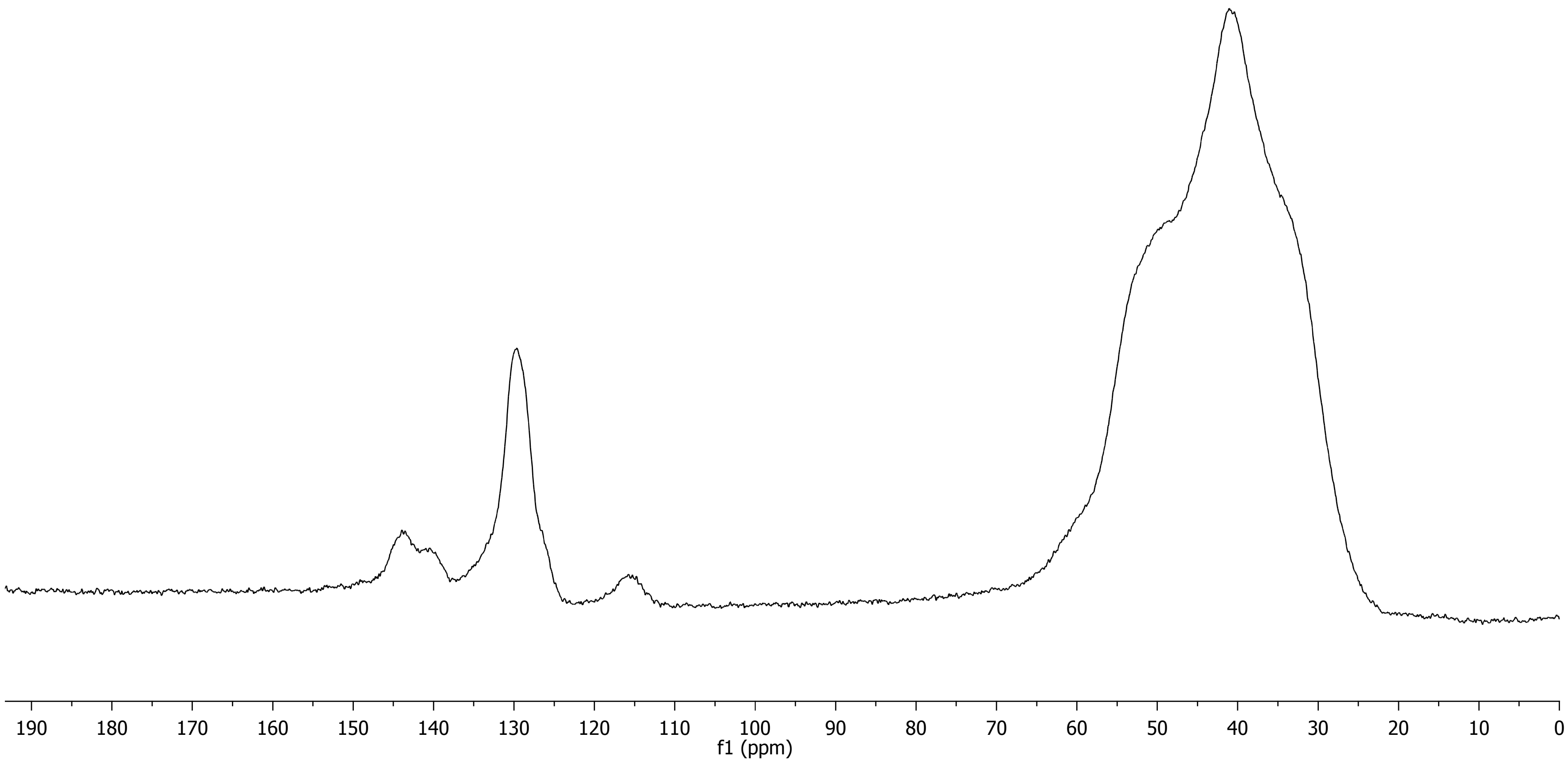
VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_3$-2,6-diMe) **(15)** ^{13}C CP-MAS NMR



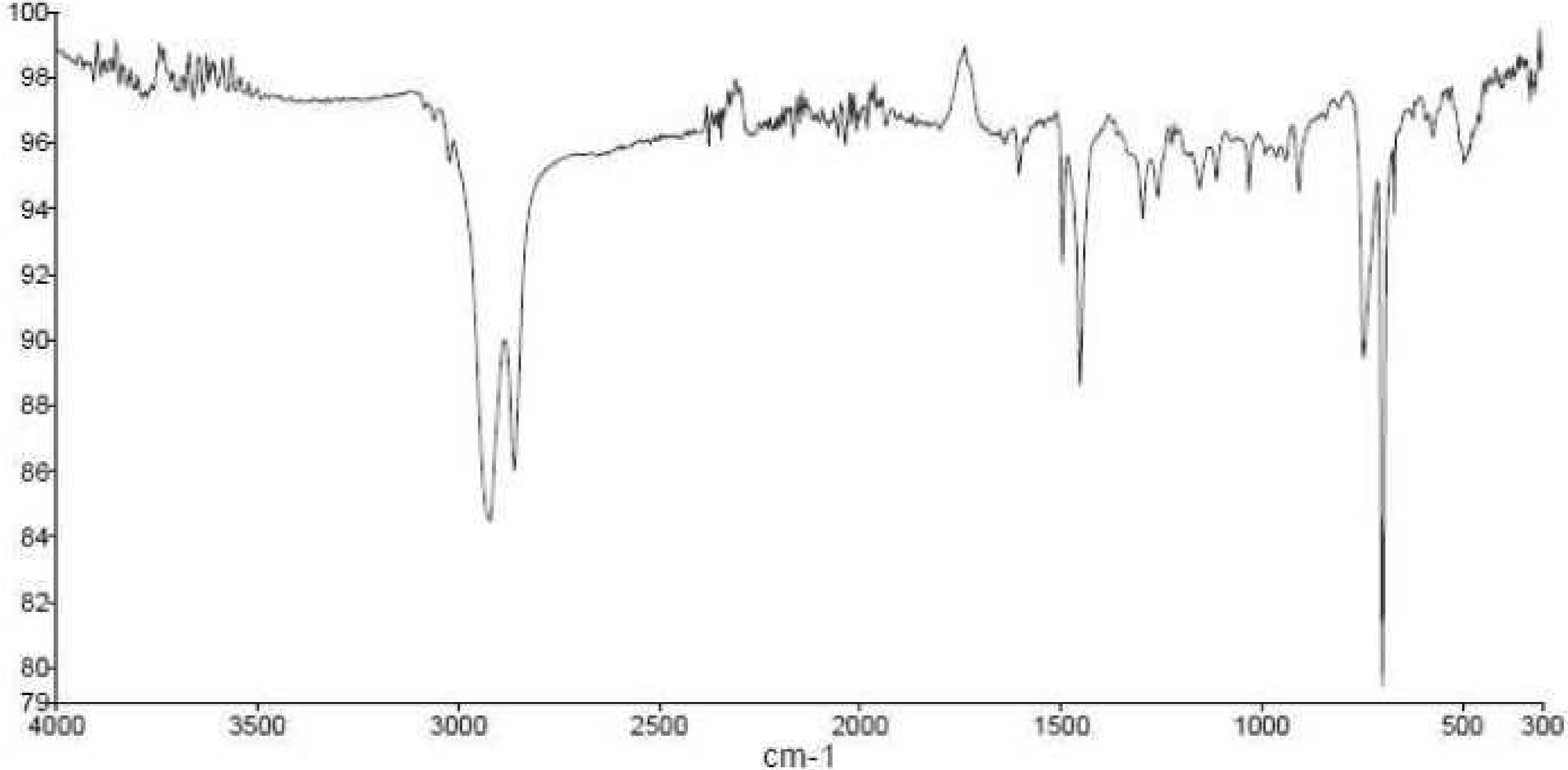
VA-PNBNBC$_6$H$_4$-NH(C$_6$H$_3$-2,6-diMe) **(15)**   IR



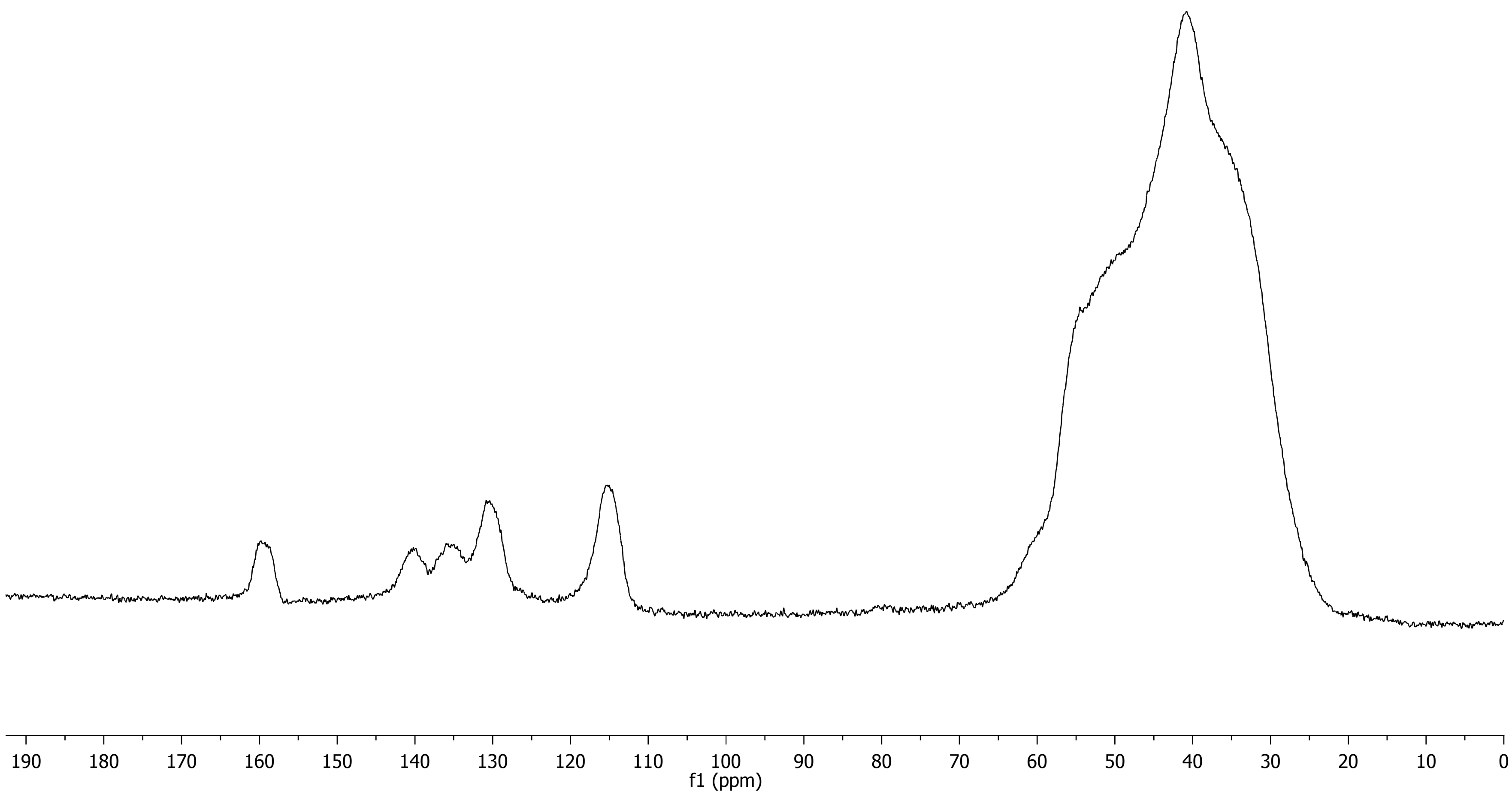
VA-PNBNB$(CH_2)_4$Ph **(17)** ^{13}C CP-MAS NMR



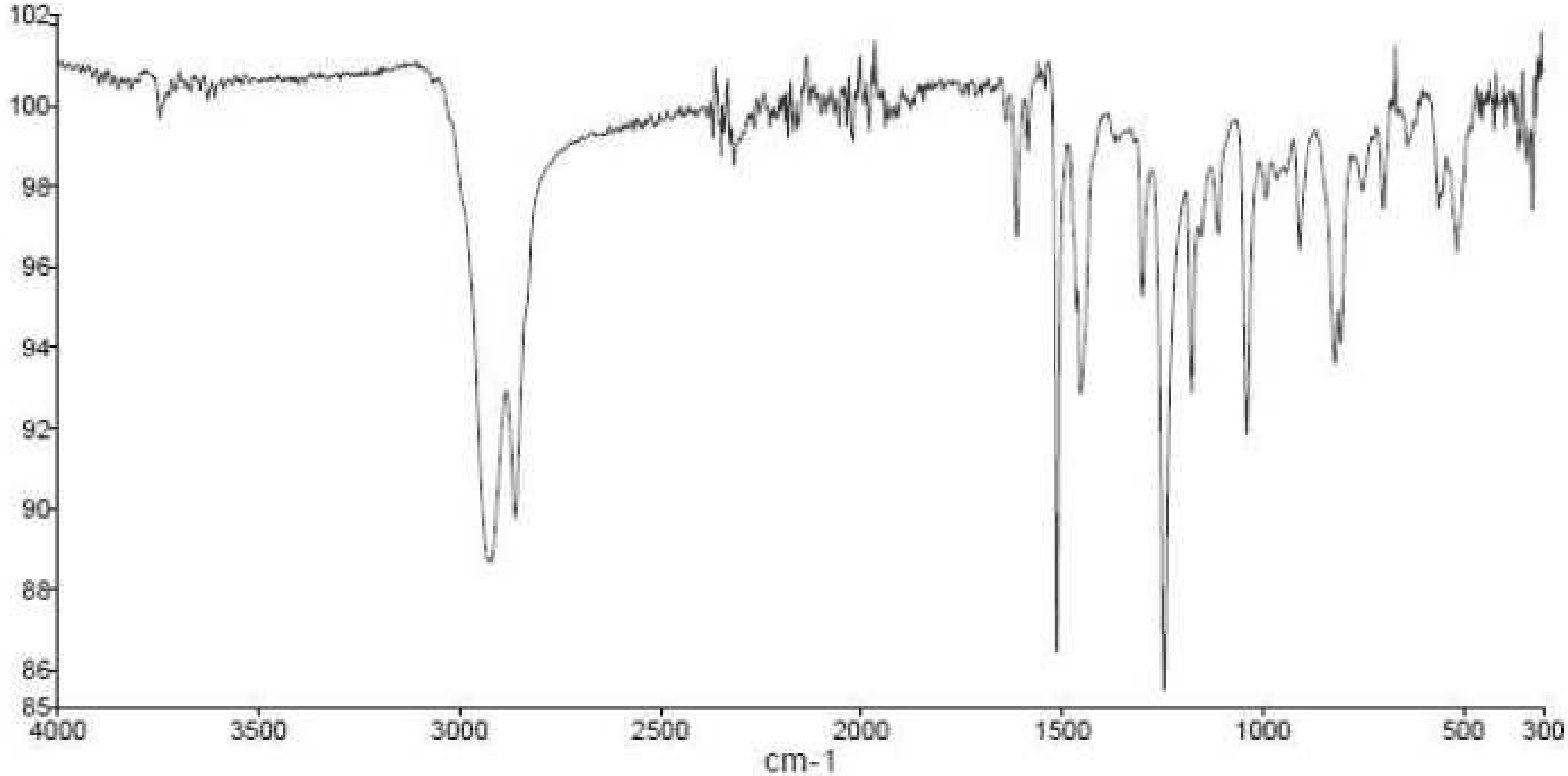
VA-PNBNB(CH_2)$_4$Ph **(17)** IR



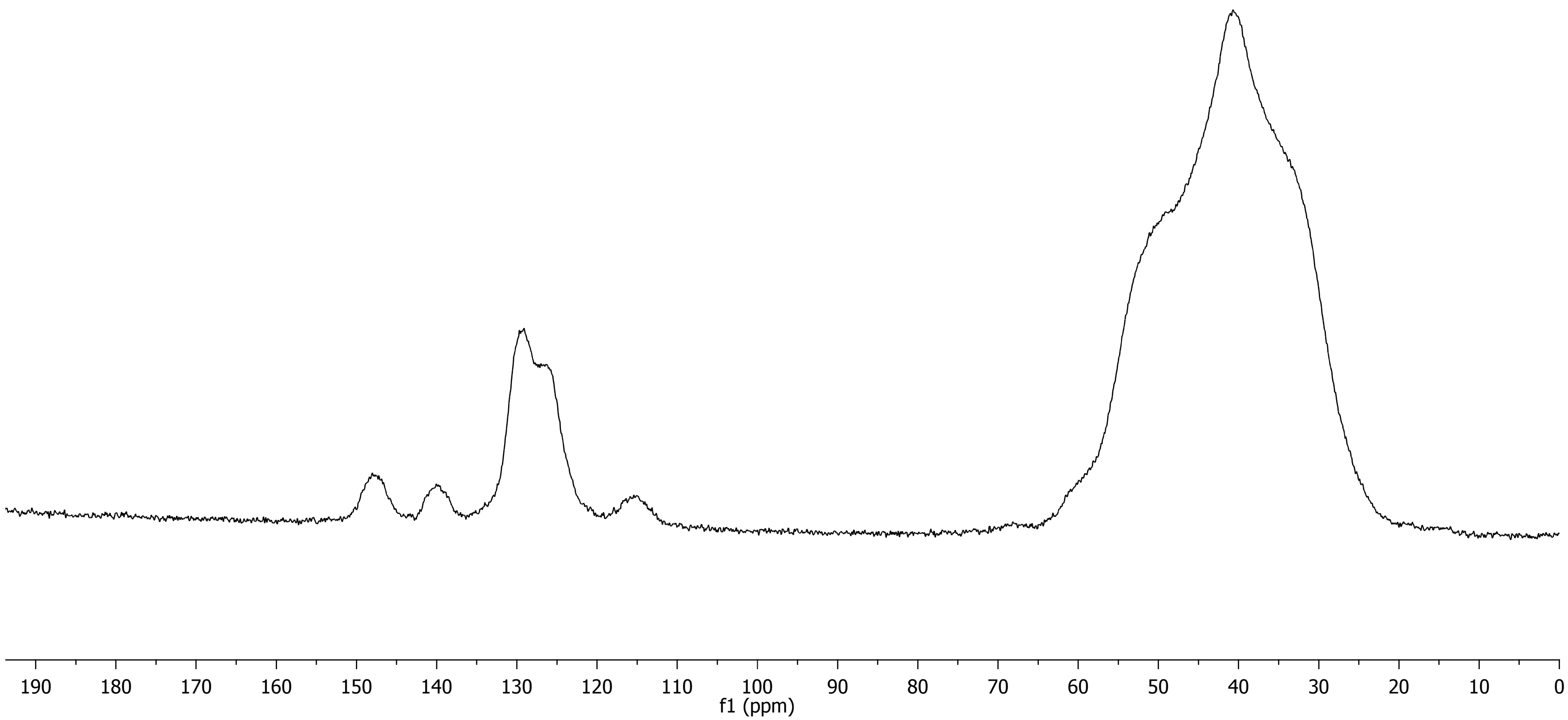
VA-PNBNB$(CH_2)_4$-C_6H_4-4-OMe **(18)** ^{13}C CP-MAS NMR



VA-PNBNB$(CH_2)_4$-C_6H_4-4-OMe **(18)** IR



VA-PNBNB$(CH_2)_4$-C_6H_4-4-CF_3 **(19)** ^{13}C CP-MAS NMR



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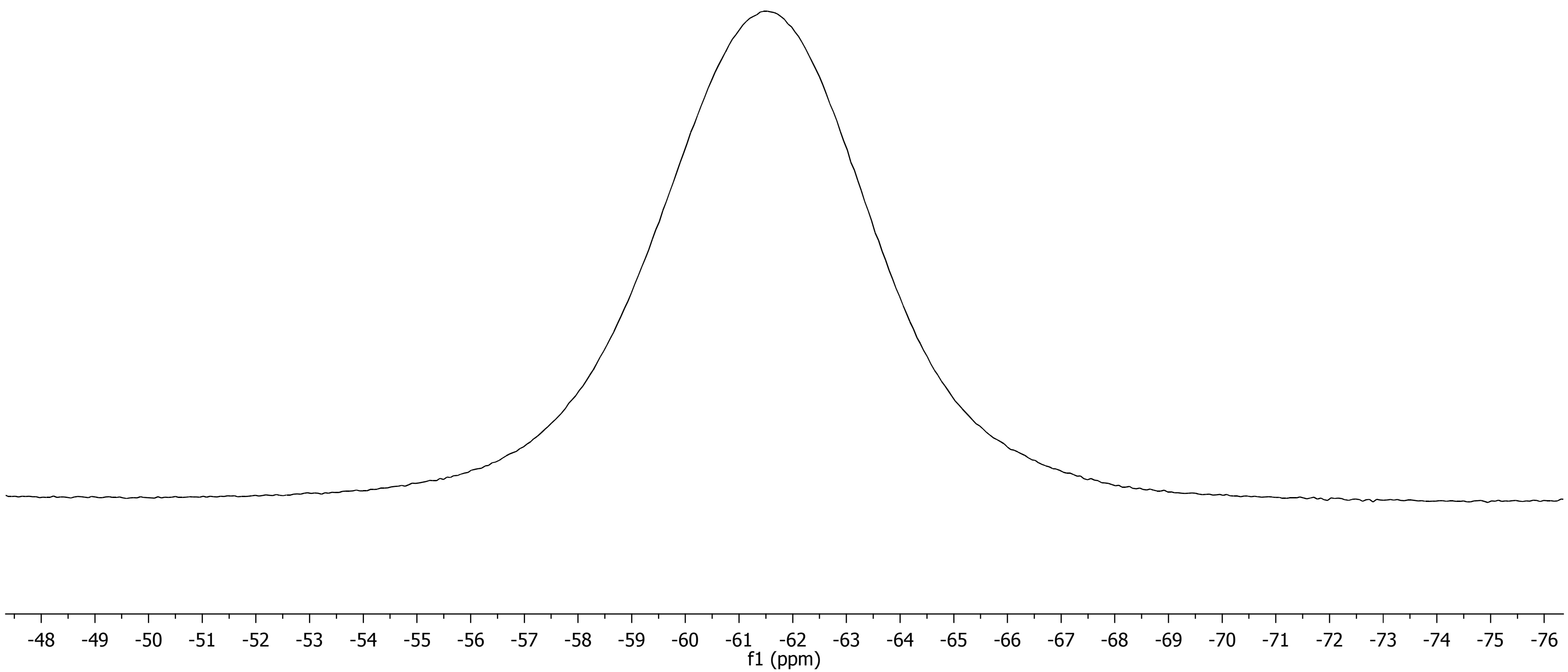
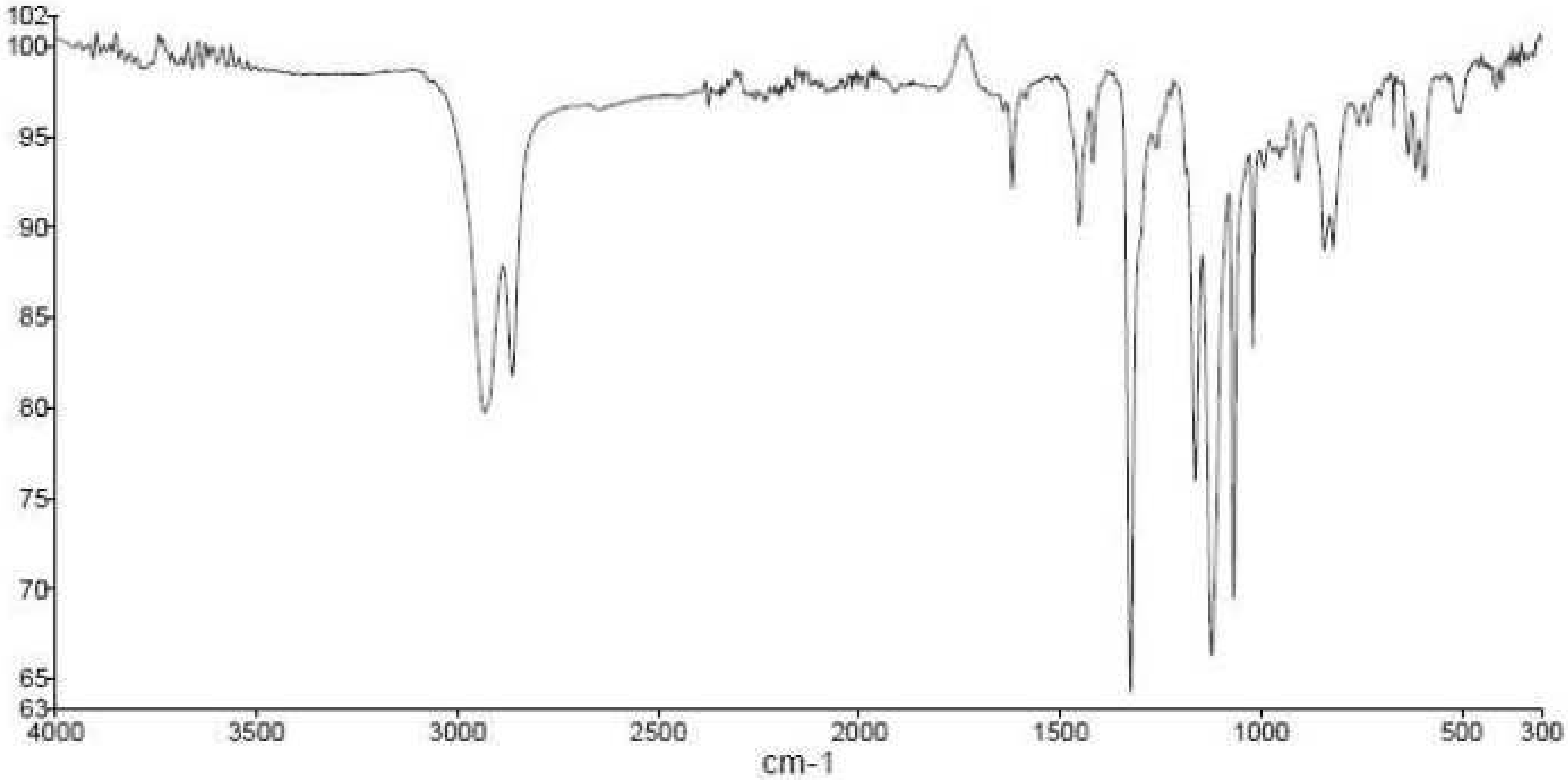
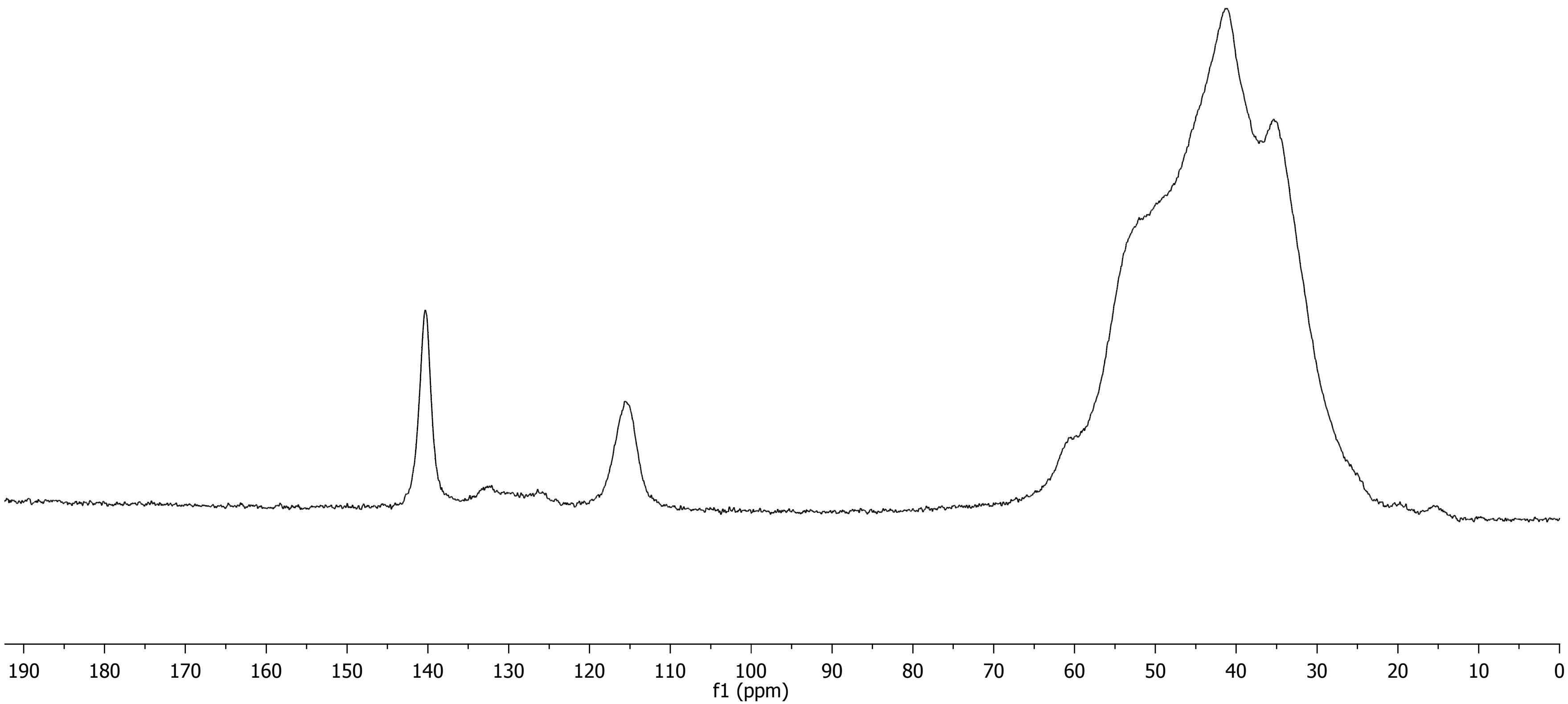


VA-PNBNB$(CH_2)_4$-C_6H_4-4-CF_3 **(19)** IR



VA-PNBNB$(CH_2)_2$-CH=CH_2 **(20)** ^{13}C CP-MAS NMR



VA-PNBNB$(CH_2)_2$-CH=CH_2 **(20)** IR