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Organogel formation rationalized by Hansen solubility parameters: influence of gelator structure

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ELECTRONIC SUPPLEMENTARY INFORMATION

Gelation data

Table S1 Gelation tests for LMWG **C4** to **C18**. First step: pure liquids.[a-c]

Liquid	δ_d^s (MPa$^{1/2}$)	δ_p^s (MPa$^{1/2}$)	δ_h^s (MPa$^{1/2}$)	**C4**	**C8**	**C12**	**C18**
acetonitrile	15.3	18	6.1	G	G	I	I
benzyl alcohol	18.4	6.3	13.7	S	I	I	I
1-butanol	16	5.7	15.8	S	I	I	I
t-butyl acetate	15	3.7	6	G	G	G	I
1-chloropentane	16	6.9	1.9	G	G	G	G
chlorobenzene	19	4.3	2	G	G	G	G
cyclohexane	16.8	0	0.2	G	G	G	I
cyclohexanone	17.8	8.4	5.1	G	G	G	I
diacetone alcohol	15.8	8.2	10.8	G	G	I	I
dimethylformamide (DMF)	17.4	13.7	11.3	I	G	I	G
dimethylsulfoxide (DMSO)	18.4	16.4	10.2	I	I	I	G
1,4-dioxane	17.5	1.8	9	G	G	G	I
ethanolamine	17	15.5	21	I	I	I	I
hexadecane	16.3	0	0	G	I	I	I
methanol	14.7	12.3	22.3	S	I	I	I
methylethylketone (MEK)	16	9	5.1	G	G	G	I
N,N-diethyl acetamide	16.4	11.3	7.5	S	I	I	I
propylene carbonate	20	18	4.1	G	I	I	G
propylene glycol	16.8	10.4	21.3	S	I	I	I
toluene	18	1.4	2	G	G	G	G
water	15.5	16	42.3	I	I	I	I

[a] Gelation is tested by introducing 20 mg of gelator and 1 mL of liquid in a screw-cap vial, heating until dissolution and leaving the vial to cool on the bench.

[b] G: gel; S: soluble; I: insoluble or formation of a precipitate after cooling.

[c] Minor differences can be noted between these data and previous data reported for LMWG **C12**[1] because several samples initially formed homogeneous solutions (one or two days after preparation) but turned out to precipitate slowly over time. The present solubility data was established several weeks after preparation, while taking care to avoid evaporation. Whether the gelation data is determined after one day or after a few weeks, does not change the trends and conclusions described in the article.

Table S2 Gelation tests for LMWG **C4** to **C18**. Second step: mixtures.[a-c]

Liquid 1	Liquid 2	Composition	**C4**	**C8**	**C12**	**C18**
chlorobenzene	t-butyl acetate	0/100	G	G	G	I
		20/80	G	G	G	I
		40/60	G	G	G	I
		60/40	G	G	G	I
		80/20	G	G	G	I
		100/0	G	G	G	G
1-chloropentane	DMSO	0/100	I	I	I	G
		20/80	I	G	I	I
		40/60	S	I	I	I
		60/40	S	S	I	I
		80/20	S	I	I	I
		100/0	G	G	G	G
1-chloropentane	t-butyl acetate	0/100	G	G	G	I
		20/80	G	G	G	I
		40/60	G	G	G	I
		60/40	G	G	G	I
		80/20	G	G	G	I
		100/0	G	G	G	G
cyclohexanone	benzyl alcohol	0/100	S	I	I	I
		20/80	S	I	I	I
		40/60	S	G	I	I
		60/40	I	G	I	I
		80/20	I	G	I	I
		100/0	G	G	G	I
cyclohexanone	butanol	0/100	S	I	I	I
		20/80	S	I	I	I
		40/60	S	I	I	I
		60/40	S	I	I	I
		80/20	S	I	I	I
		100/0	G	G	G	I
cyclohexanone	ethanolamine	0/100	I	I	I	I
		20/80	I	I	I	G
		40/60	I	G	I	G
		60/40	I	G	I	I
		80/20	I	G	I	I
		100/0	G	G	G	I
1,4-dioxane	1-chloropentane	0/100	G	G	G	G
		20/80	G	G	G	I
		40/60	G	G	G	I
		60/40	G	G	G	I
		80/20	G	G	G	I
		100/0	G	G	G	I

DMSO	ethanolamine	0/100	I	I	I	I
		20/80	I	I	I	I
		40/60	I	I	I	I
		60/40	I	I	I	G
		80/20	I	I	I	G
		100/0	I	I	I	G
DMSO	propylene glycol	0/100	S	I	I	I
		20/80	I	I	I	G
		40/60	I	I	I	G
		60/40	I	I	I	G
		80/20	I	I	I	G
		100/0	I	I	I	G
MEK	DMSO	0/100	I	I	I	G
		20/80	I	G	I	G
		40/60	I	G	I	G
		60/40	I	G	I	I
		80/20	I	I	I	I
		100/0	G	G	G	I
MEK	propylene carbonate	0/100	G	I	I	G
		20/80	G	G	G	G
		40/60	G	G	G	G
		60/40	G	G	G	G
		80/20	G	G	G	I
		100/0	G	G	G	I
propylene carbonate	t-butyl acetate	0/100	G	G	G	I
		20/80	G	G	G	I
		40/60	G	G	G	I
		60/40	G	G	G	G
		80/20	G	G	G	G
		100/0	G	I	I	G
propylene carbonate	DMSO	0/100	I	I	I	G
		20/80	I	I	I	G
		40/60	I	G	I	G
		60/40	I	G	I	G
		80/20	I	I	I	G
		100/0	G	I	I	G
propylene carbonate	toluene	0/100	G	G	G	G
		20/80	G	G	G	I
		40/60	G	G	G	I
		60/40	G	G	G	I
		80/20	G	G	G	G
		100/0	G	I	I	G
toluene	benzyl alcohol	0/100	S	I	I	I
		20/80	S	S	I	I
		40/60	S	S	S	I
		60/40	S	S	S	I
		80/20	S	S	I	I
		100/0	G	G	G	G

toluene	butanol	0/100	S	I	I	I
		20/80	S	S	I	I
		40/60	S	S	S	I
		60/40	S	S	S	I
		80/20	S	G	I	I
		100/0	G	G	G	G
toluene	diacetone alcohol	0/100	G	G	I	I
		20/80	I	G	I	I
		40/60	I	G	I	I
		60/40	G	G	I	I
		80/20	G	G	I	G
		100/0	G	G	G	G

[a] Gelation is tested by introducing 20 mg of gelator and 1 mL of liquid in a screw-cap vial, heating until dissolution and leaving the vial to cool on the bench.

[b] G: gel; S: soluble; I: insoluble or formation of a precipitate after cooling.

[c] Minor differences can be noted between these data and previous data reported for LMWG **C12**[1] because several samples initially formed homogeneous solutions (one or two days after preparation) but turned out to precipitate slowly over time. The present solubility data was established several weeks after preparation, while taking care to avoid evaporation. Whether the gelation data is determined after one day or after a few weeks, does not change the trends and conclusions described in the article.

Table S3 Hansen solubility parameters for LMWG **C4** to **C18** estimated by Hoy's group contribution method.[2]

	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
C4	17.4	8.5	6.8
C8	17.5	7.4	5.7
C12	17.6	6.6	5.1
C18	17.7	5.8	4.4

Table S4 Centroid of the solubility domain for LMWG **C4** to **C12**. The centroid is defined as $\delta_d = \frac{1}{n}\sum_{i=1}^{n}(\delta_d^s)_i$, $\delta_p = \frac{1}{n}\sum_{i=1}^{n}(\delta_p^s)_i$, $\delta_h = \frac{1}{n}\sum_{i=1}^{n}(\delta_h^s)_i$ where δ_d^s, δ_p^s and δ_h^s are the solubility parameters of the liquids in which the gelator is soluble.

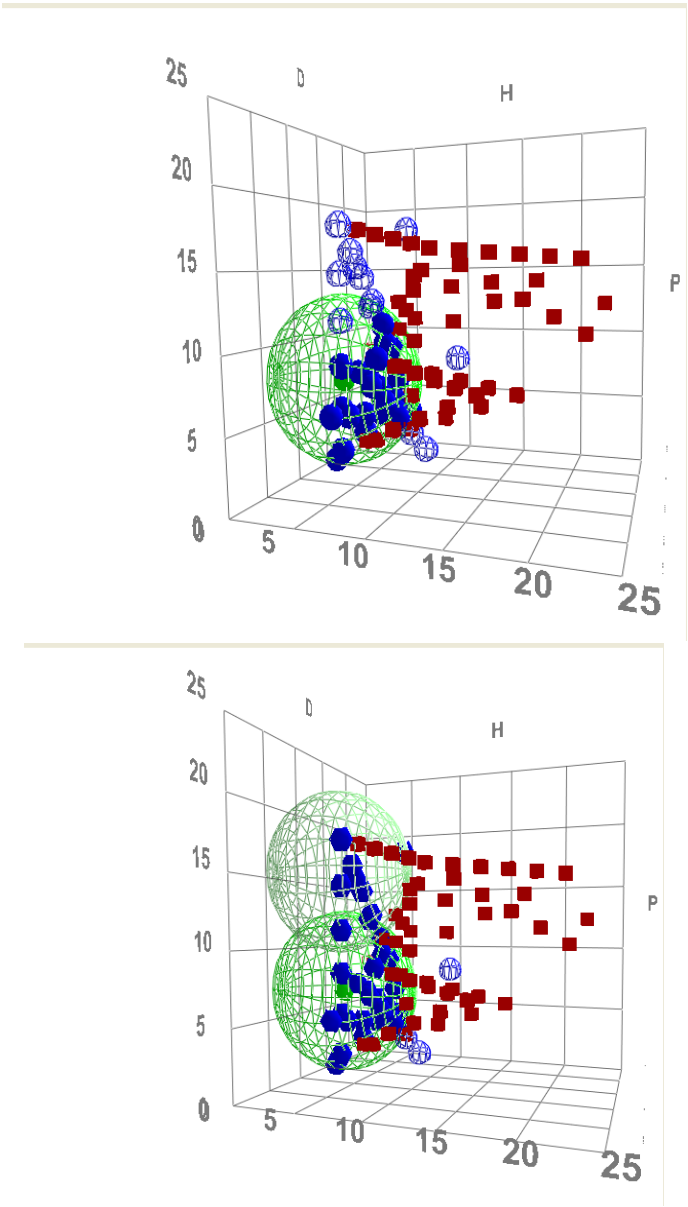
	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
C4	17.2	6.8	10.3
C8	17.5	4.8	8.4
C12	17.6	3.7	8.4

Table S5 Centroid of the gelation domain for LMWG **C4** to **C18**. The centroid is defined as $\delta_d = \frac{1}{n}\sum_{i=1}^{n}(\delta_d^s)_i$, $\delta_p = \frac{1}{n}\sum_{i=1}^{n}(\delta_p^s)_i$, $\delta_h = \frac{1}{n}\sum_{i=1}^{n}(\delta_h^s)_i$ where δ_d^s, δ_p^s and δ_h^s are the solubility parameters of the gelled liquids.

	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
C4	17.2	7.3	4.4
C8	17.3	8.3	5.8
C12	17.2	7.1	4.2
C18	18.2	13.3	8.5

Table S6 Centre and radius of the gelation sphere for LMWG **C4** to **C18** determined with HSPiP software.[1,3]

	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	R ($MPa^{1/2}$)
C4	15.8	6.2	0.3	6.9
C8	16.3	11.2	2.6	9.6
C12	16.4	9.0	0.0	7.5
C18	21.3	16.8	12.4	10.3



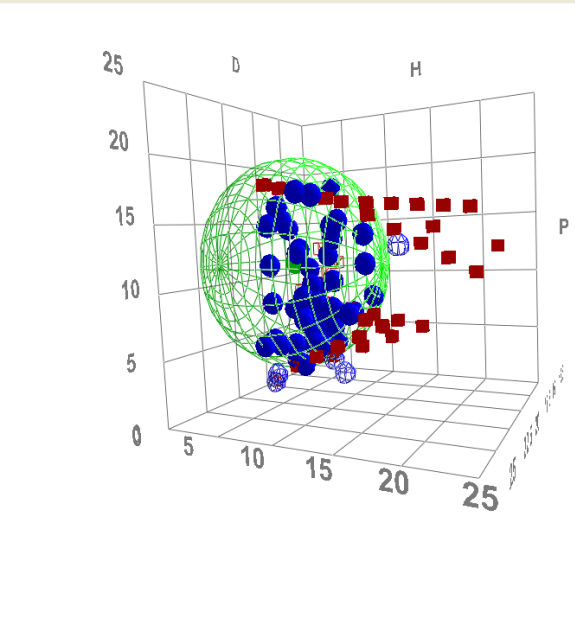
$\delta_d = 15.8, \delta_p = 6.2, \delta_h = 0.3$
R= 6.9

Wrong In= 1
Chloropentane:DMSO 80:20
Wrong Out= 12
Acetonitrile
Diacetone alcohol
1,4-Dioxane
Propylene carbonate (Pc)
Methylethylketone (MEK):Pc 60:40
MEK:Pc 40:60
MEK:Pc 20:80
Chloropentane:1,4-Dioxane 20:80
Pc:*t*-butylacetate (tBA) 80:20
Pc:tBA 60:40
Pc:Toluene 80:20
Pc:Toluene 60:40

$\delta_{d1} = 15.8, \delta_{p1} = 6.2, \delta_{h1} = 0.4$
$R_1 = 6.9$
$\delta_{d2} = 17.2, \delta_{p2} = 16.1, \delta_{h2} = 1.3$
$R_2 = 6.5$

Wrong In= 1
Chloropentane:DMSO 80:20
Wrong Out= 3
Diacetone alcohol
1,4-Dioxane
Chloropentane:1,4-Dioxane 20:80

Fig. S1 Gelation data for amide **C4** (20g/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. Upper figure: a single gelation sphere is used. Lower figure: two gelation spheres are used. The plots are generated with the HSPiP software.[1,3]

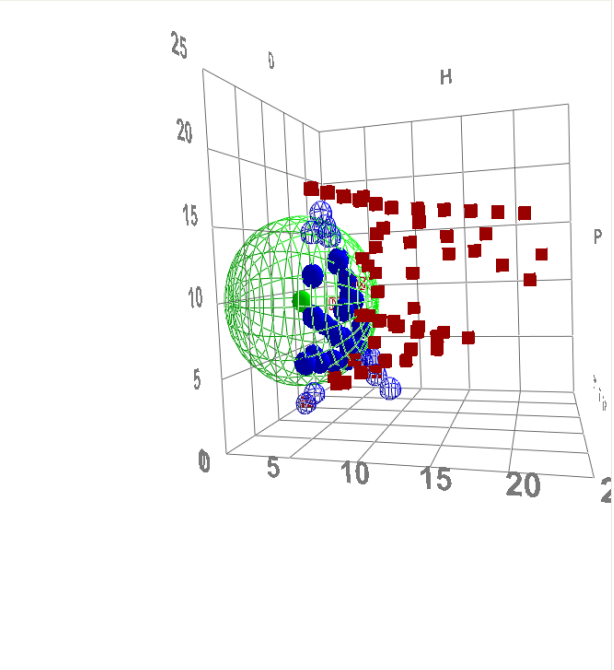


δ_d = 16.3, δ_p = 11.2, δ_h = 2.6
R= 9.6

Wrong In= 7
N,N-Diethyl acetamide
Chloropentane:DMSO 80:20
Chloropentane:DMSO 60:40
Chloropentane:DMSO 40:60
MEK:DMSO 80:20
Cyclohexanone:Butanol 80:20
Cyclohexanone:Butanol 60:40

Wrong Out= 5
Cyclohexane
1,4-Dioxane
Toluene
Chloropentane:1,4-Dioxane 20:80
Cyclohexanone:Ethanolamine 40:60

Fig. S2 Gelation data for amide **C8** (20g/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. A single gelation sphere (green) is used. The plots are generated with the HSPiP software.[1,3]

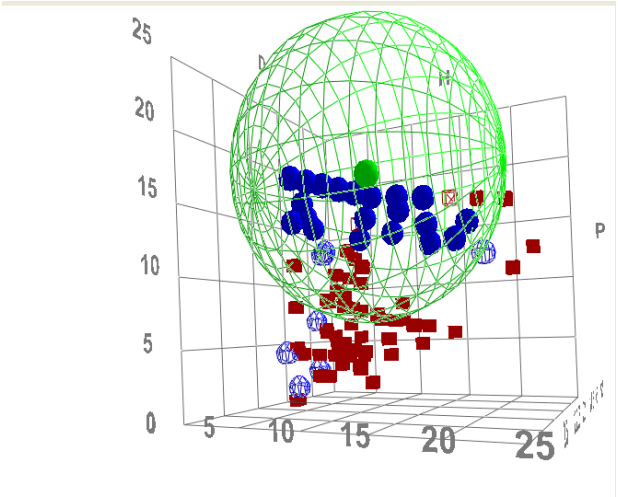


δ_d = 16.4, δ_p = 9.0, δ_h = 0.0
R= 7.5

Wrong In= 3
MEK:DMSO 80:20
Chloropentane:DMSO 80:20
Chloropentane:DMSO 60:40

Wrong Out= 10
t-Butyl acetate
Cyclohexane
1,4-Dioxane
Toluene
Pc:tBA 80:20
Pc:Toluene 80:20
1,4-Dioxane:Chloropentane 80:20
1,4-Dioxane:Chloropentane 60:40
MEK:Pc 40:60
MEK:Pc 20:80

Fig. S3 Gelation data for amide **C12** (20g/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. A single gelation sphere (green) is used. The plots are generated with the HSPiP software.[1,3]



δ_d = 21.3, δ_p = 16.8, δ_h = 12.4
R= 10.3

Wrong In= 2
Chloropentane:DMSO 20:80
DMSO:Ethanolamine 40:60
Wrong Out= 7
Chloropentane
Chlorobenzene
Toluene
DMSO:Propylene glycol 20:80
MEK:Pc 60:40
Pc:tBA 60:40
Toluene:Diacetone alcohol 80:20

Fig. S4 Gelation data for amide **C18** (20g/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. A single gelation sphere (green) is used. The plots are generated with the HSPiP software.[1,3]

Synthesis

The synthesis and characterization of **C12** was previously described.[1]

Mass ESI-TOF:

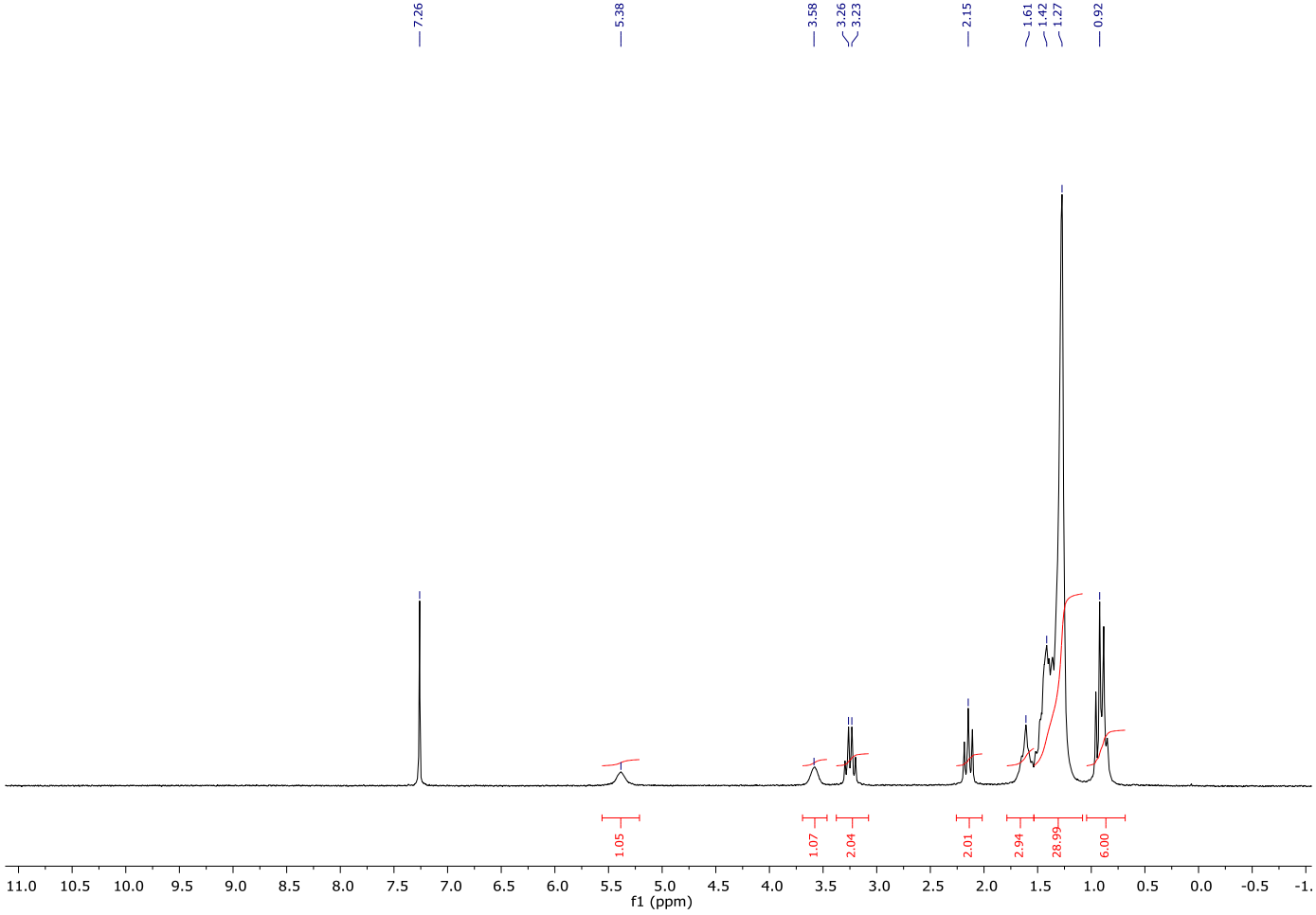
	$[M+Na]^+$	theoretical
C4	378.3341	378.3342
C8	434.3967	434.3968
C18	574.5529	574.5533

FTIR, ^{1}H and ^{13}C NMR: see pages S9-S20.

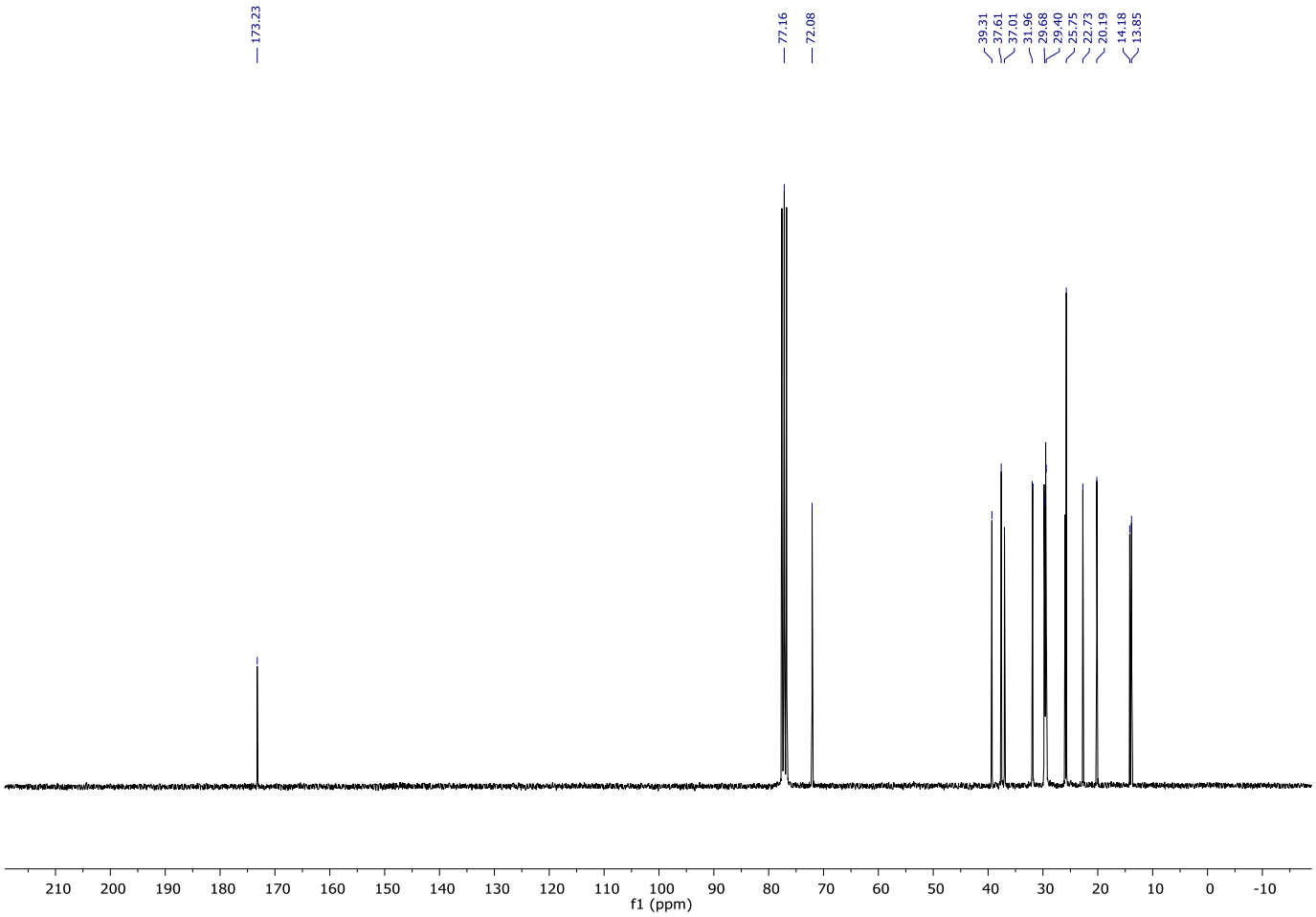
REFERENCES

1. J. Bonnet, G. Suissa, M. Raynal and L. Bouteiller, *Soft Matter*, 2014, **10**, 3154.
2. J. Brandrup, E. H. Immergut and E. A. Grulke, Polymer Handbook, Wiley, New York, fourth edn, 1999.
3. S. J. Abbott, C. M. Hansen, H. Yamamoto, Hansen Solubility Parameters in Practice software, eBook, datasets, www.hansen-solubility.com

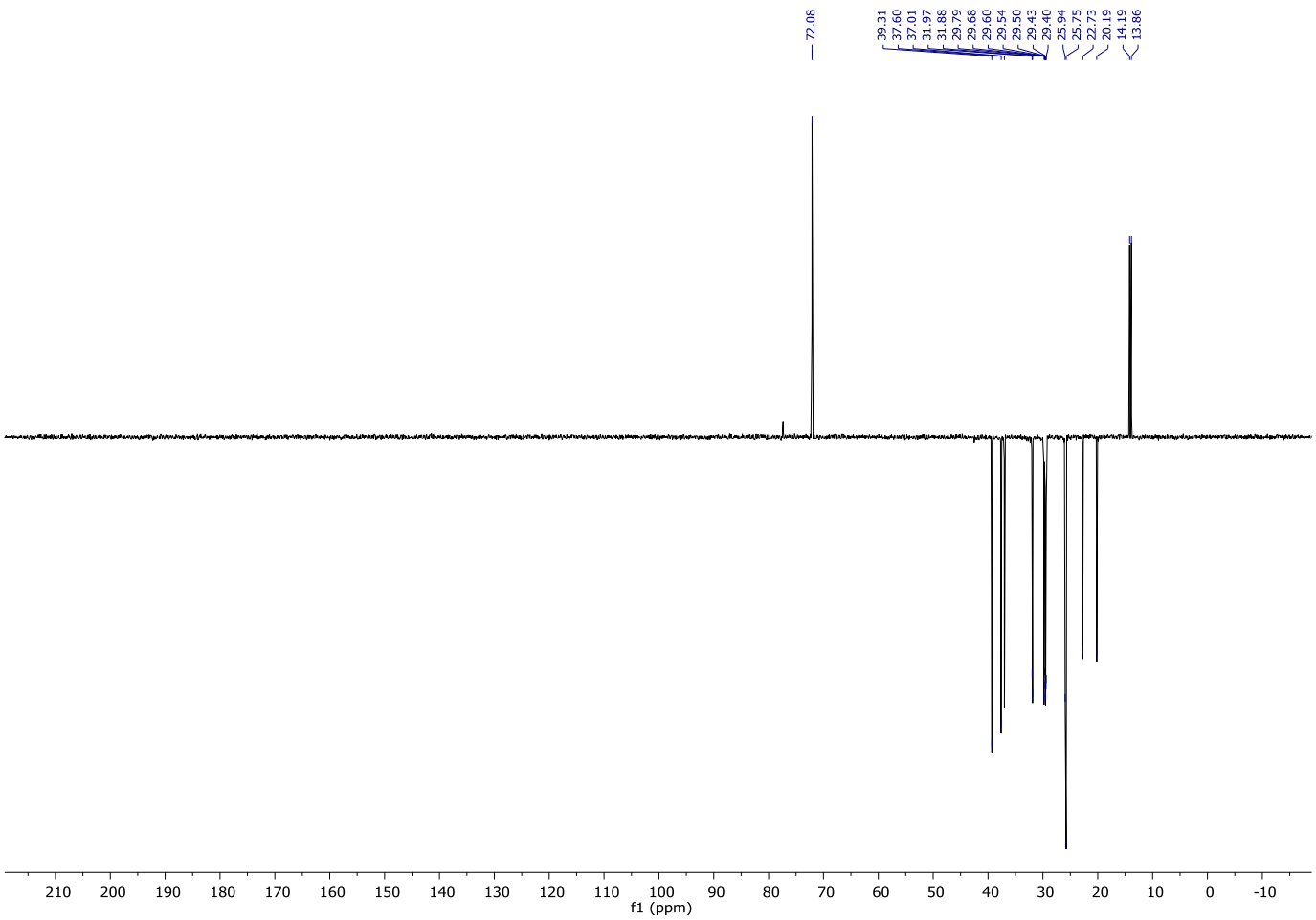
^{1}H-NMR ($CDCl_3$) **C4**



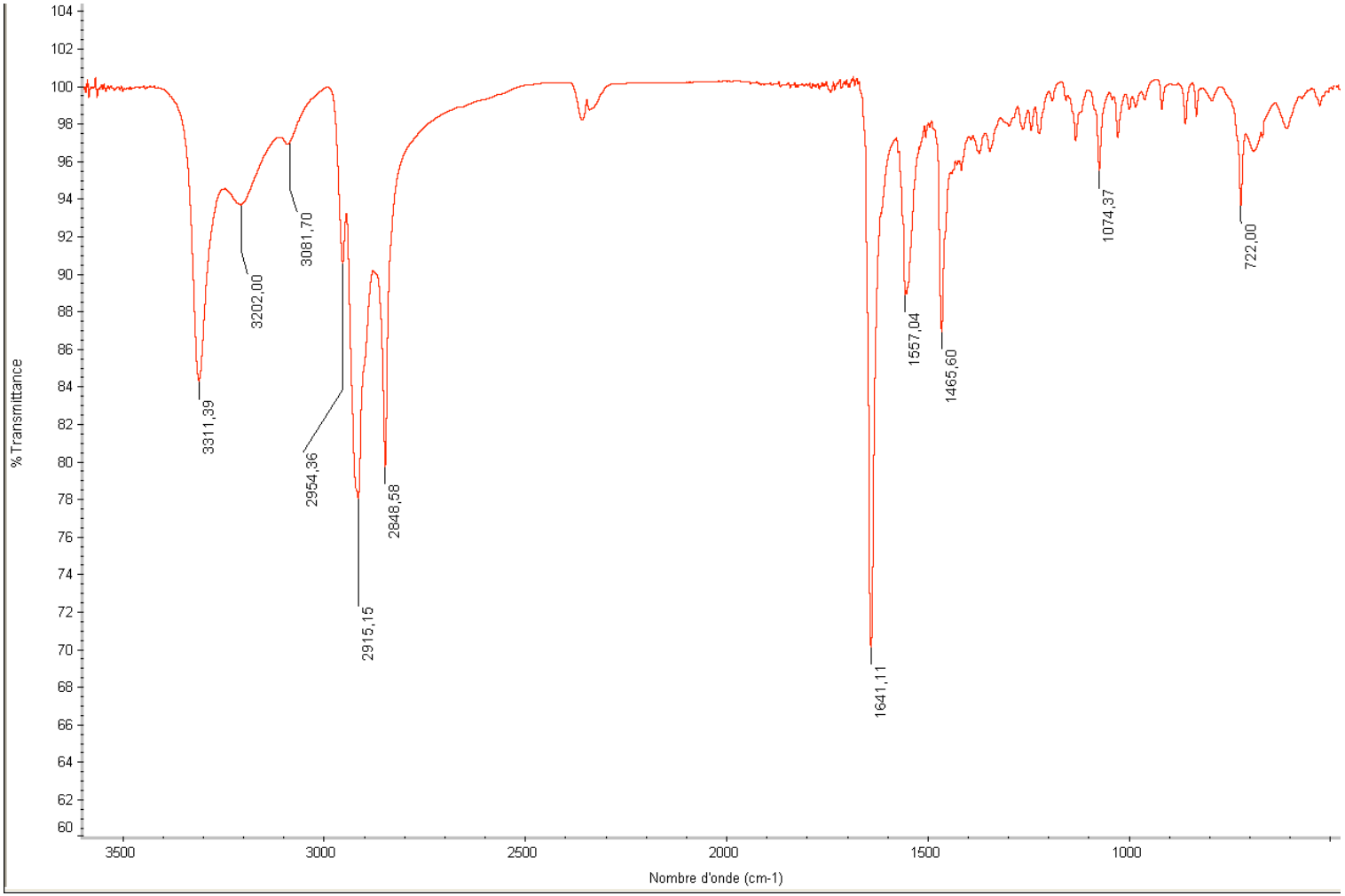
$^{13}C\{^{1}H\}$-NMR ($CDCl_3$) **C4**



DEPT 135 ($CDCl_3$) **C4**



IR **C4**


% Transmittance
Nombre d'onde (cm-1)
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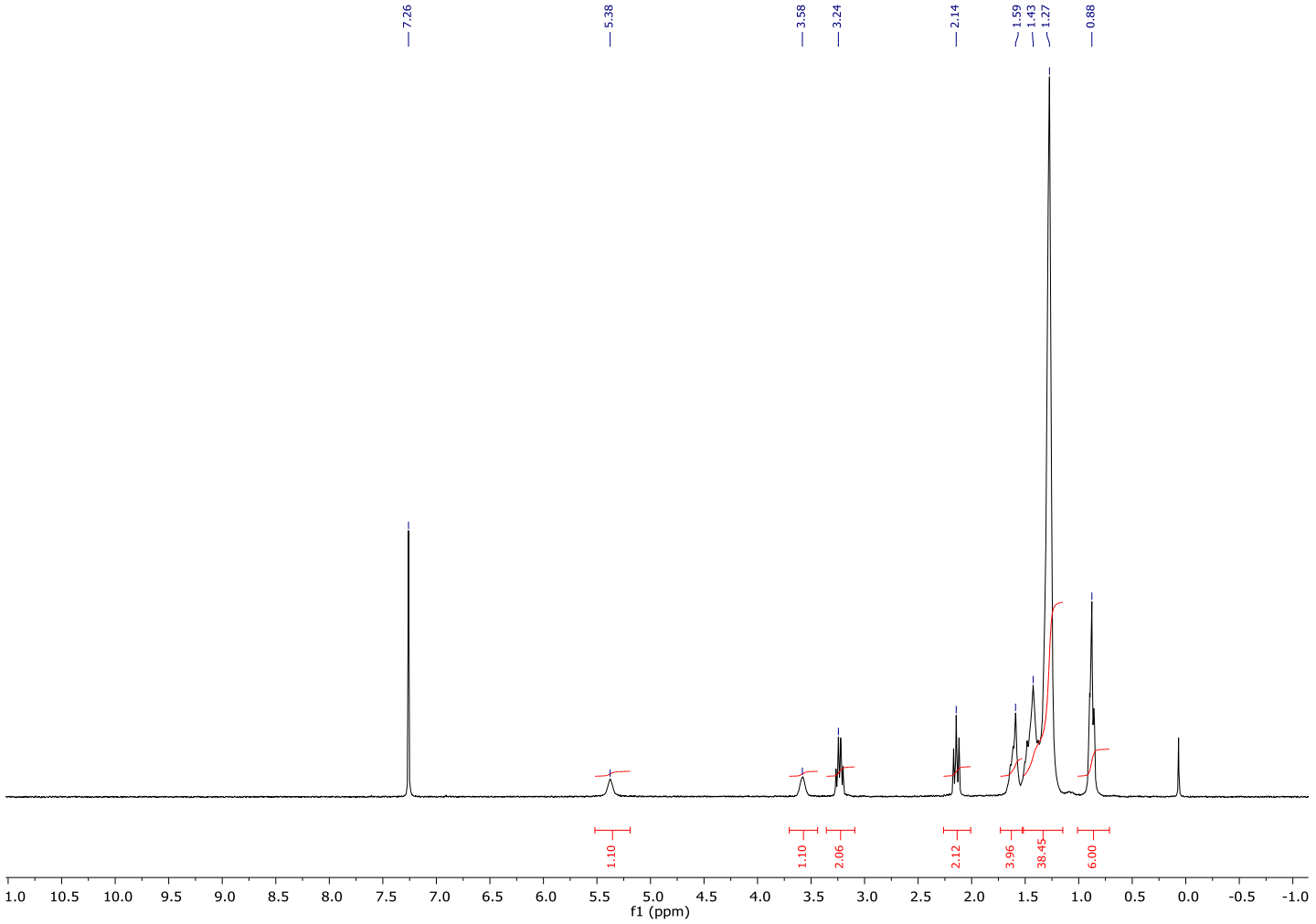
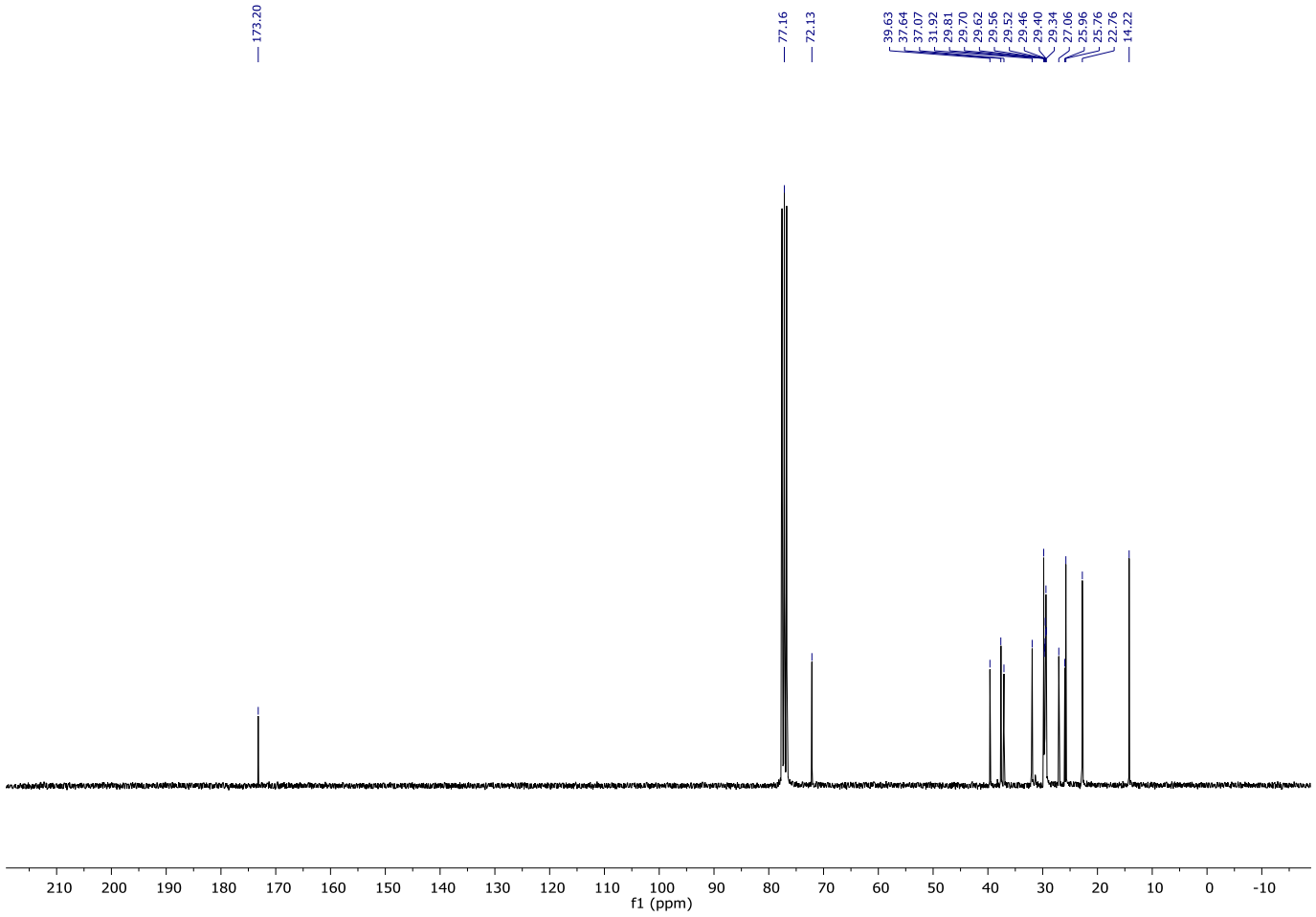
722,00

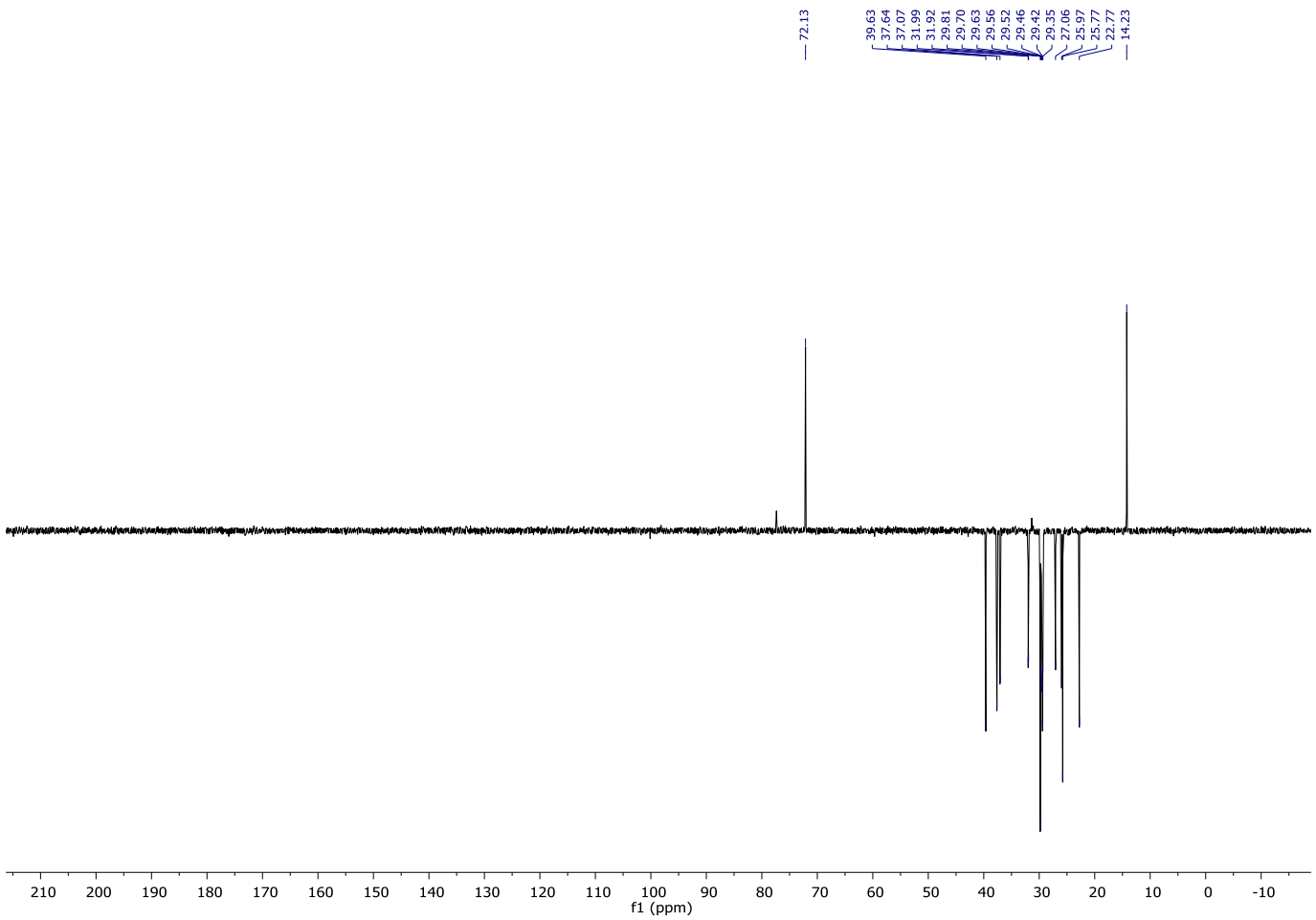
^{1}H-NMR ($CDCl_3$) **C8**



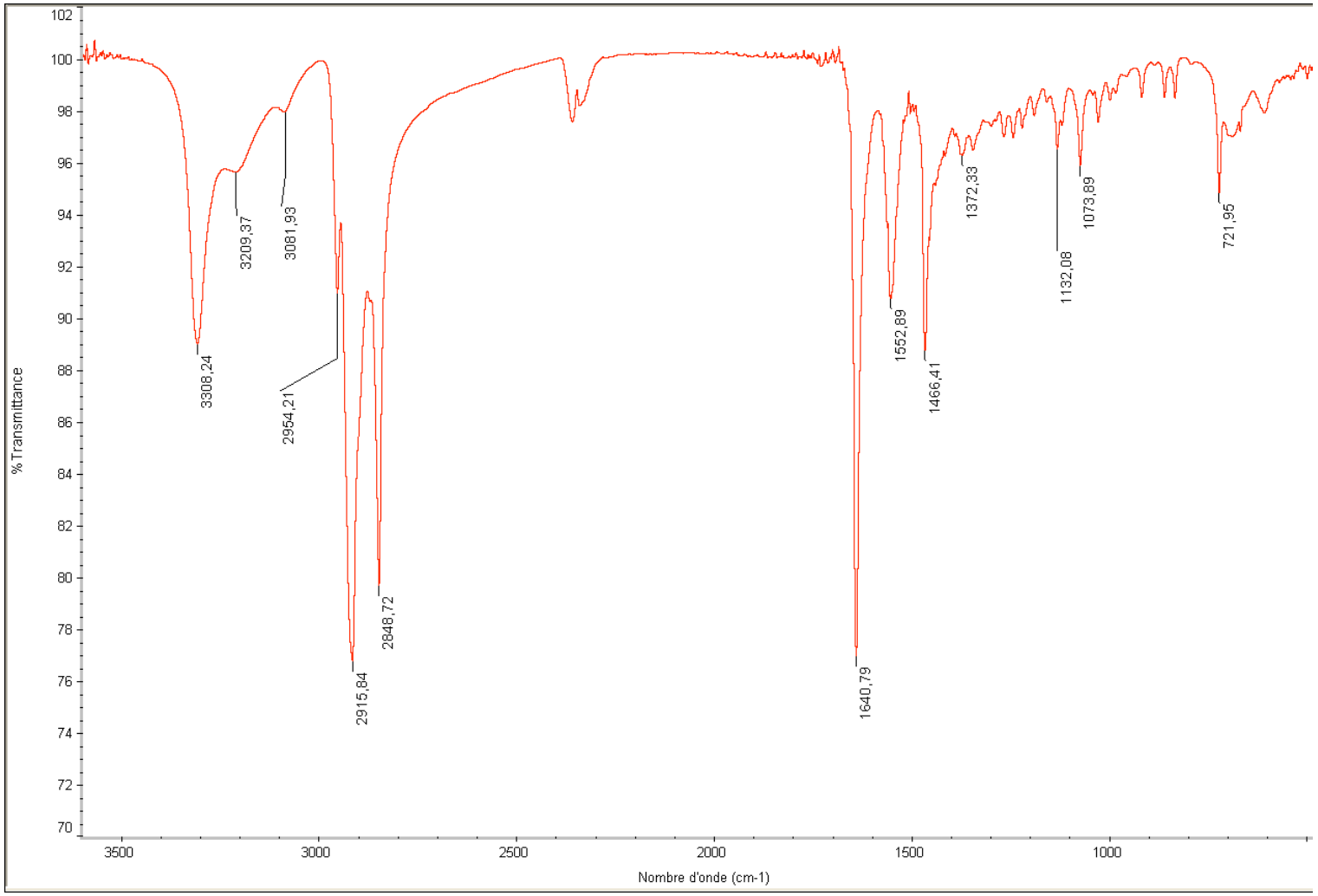
$^{13}C\{^{1}H\}$-NMR ($CDCl_3$) **C8**



DEPT 135 ($CDCl_3$) **C18**



IR **C8**


% Transmittance
Nombre d'onde (cm-1)
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3209,37
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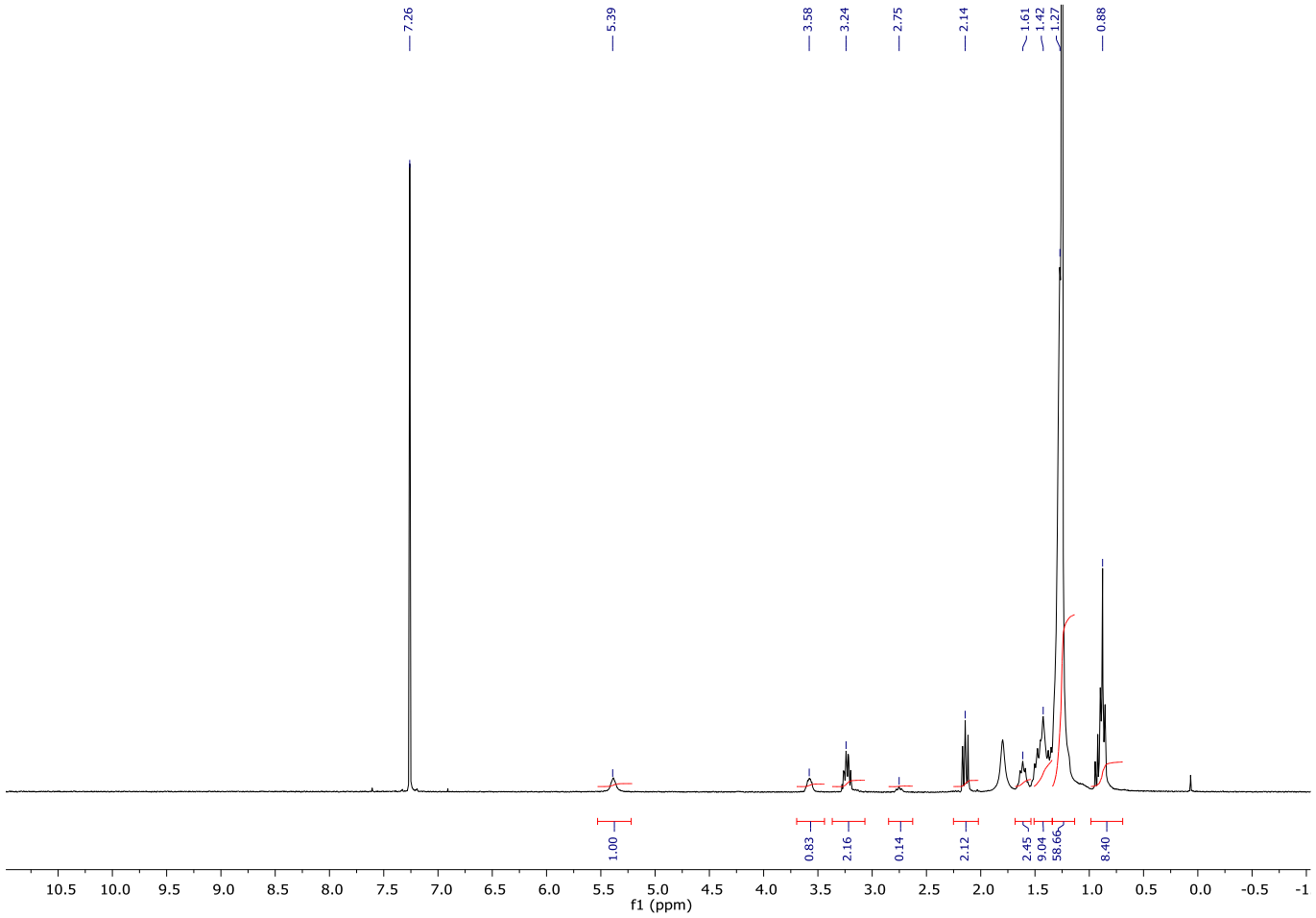
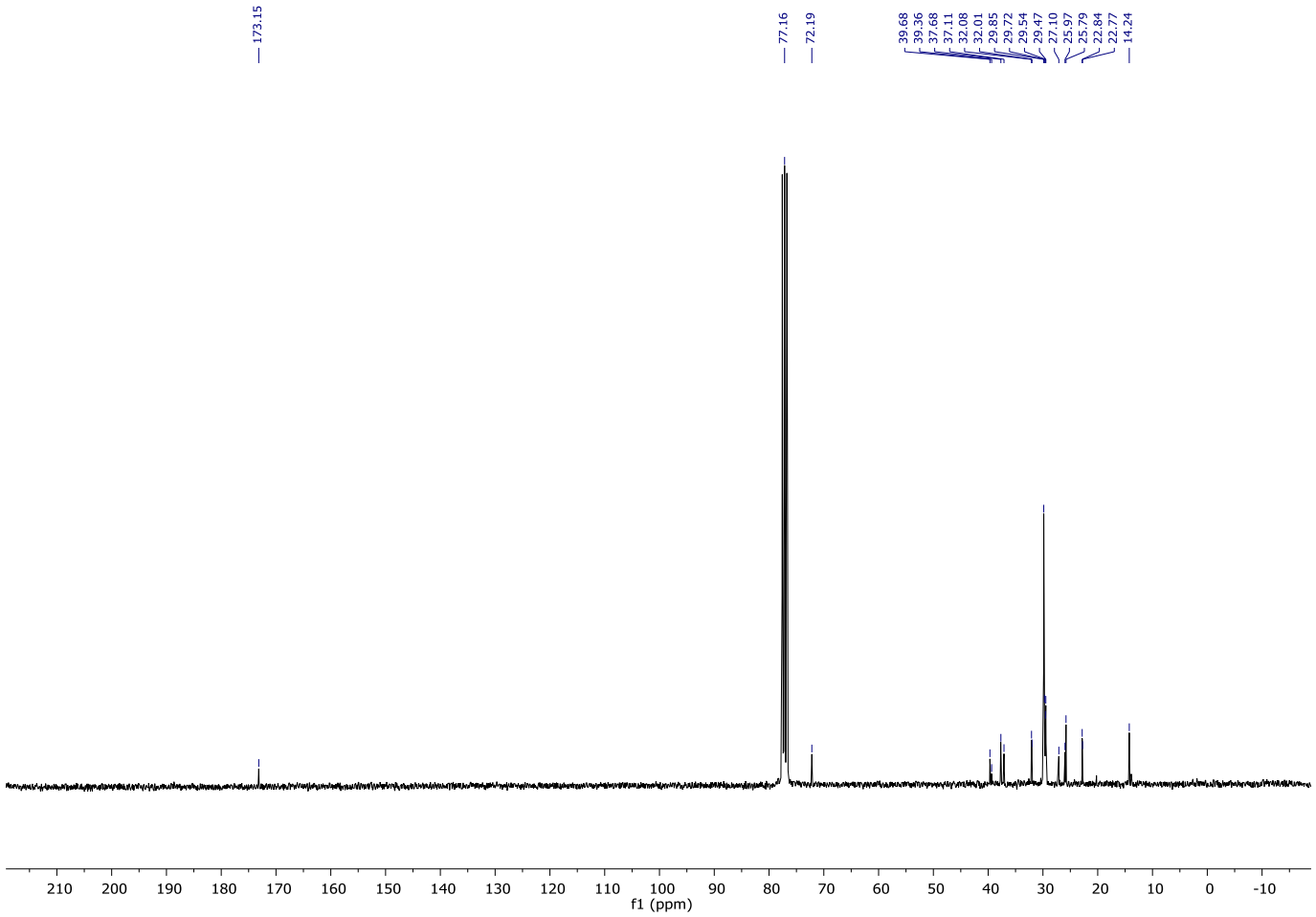
1073,89
721,95

^{1}H-NMR ($CDCl_3$) **C18**

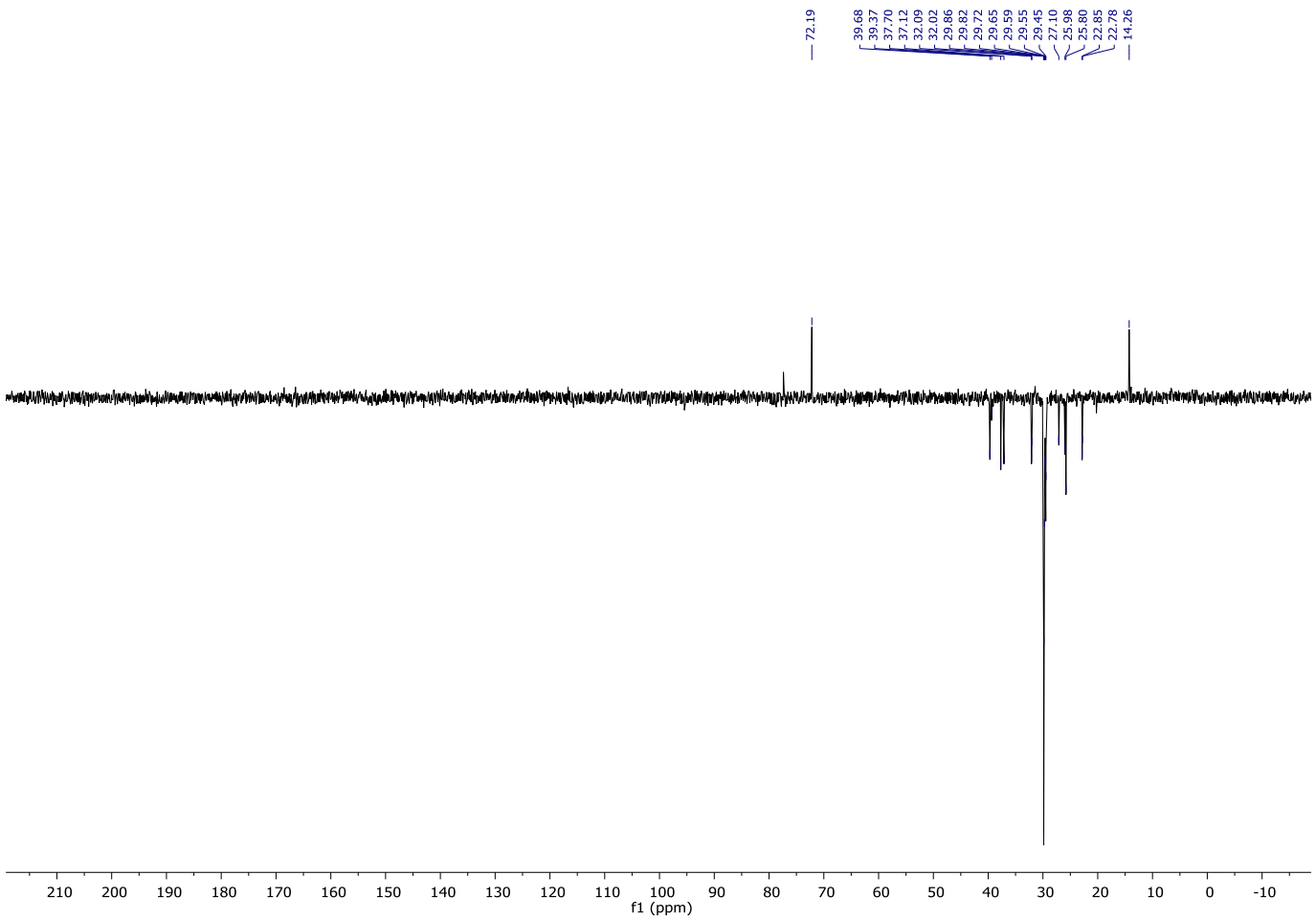


C18 is contaminated by residual amounts of octadecylamine (CH_2NH_2 triplet at δ = 2.75 ppm, approximately 7%).

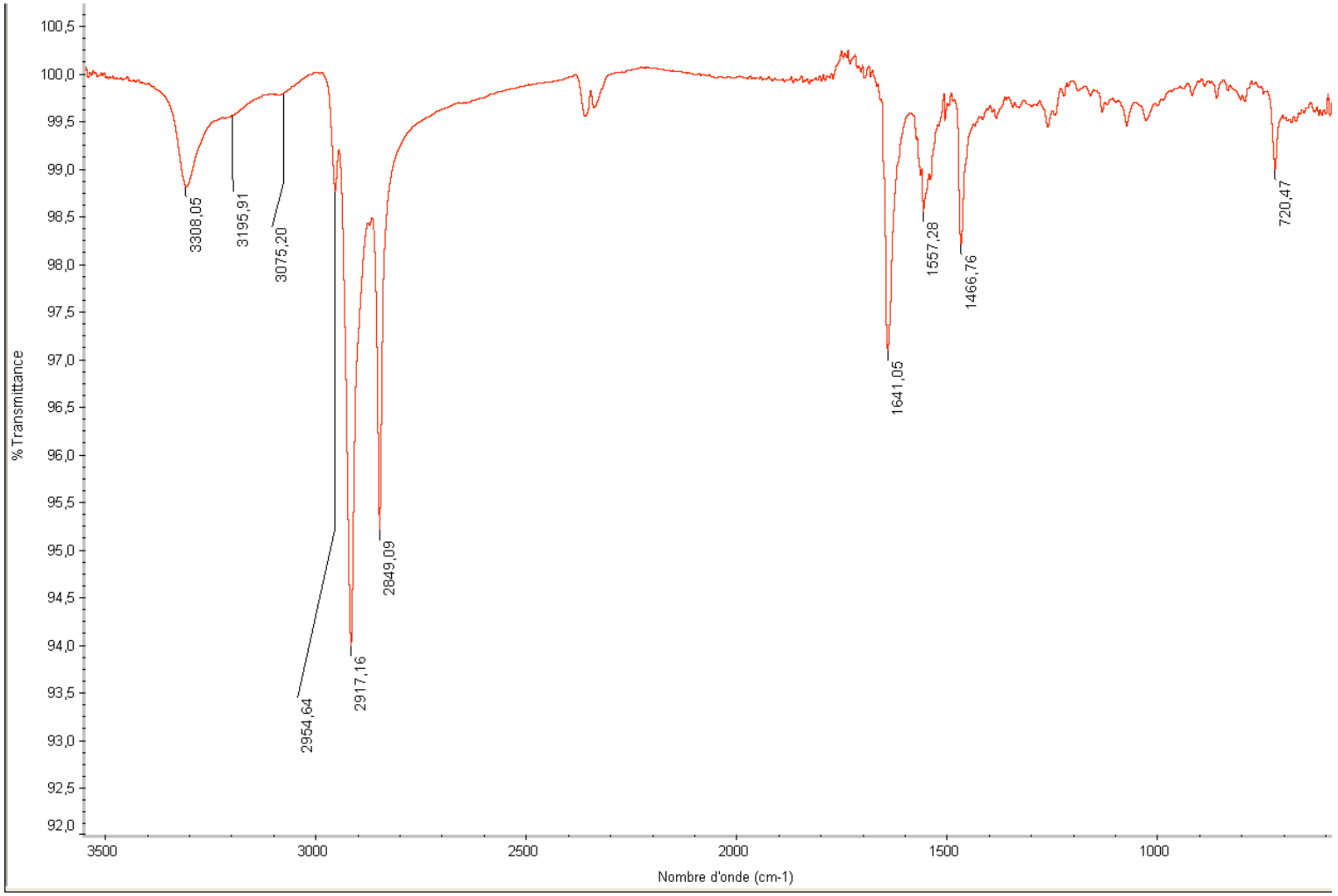
$^{13}C\{^{1}H\}$-NMR ($CDCl_3$) **C18**



DEPT 135 ($CDCl_3$) **C18**



IR **C18**


% Transmittance
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720,47
3500
3000
2500
2000
1500
1000
Nombre d'onde (cm-1)