

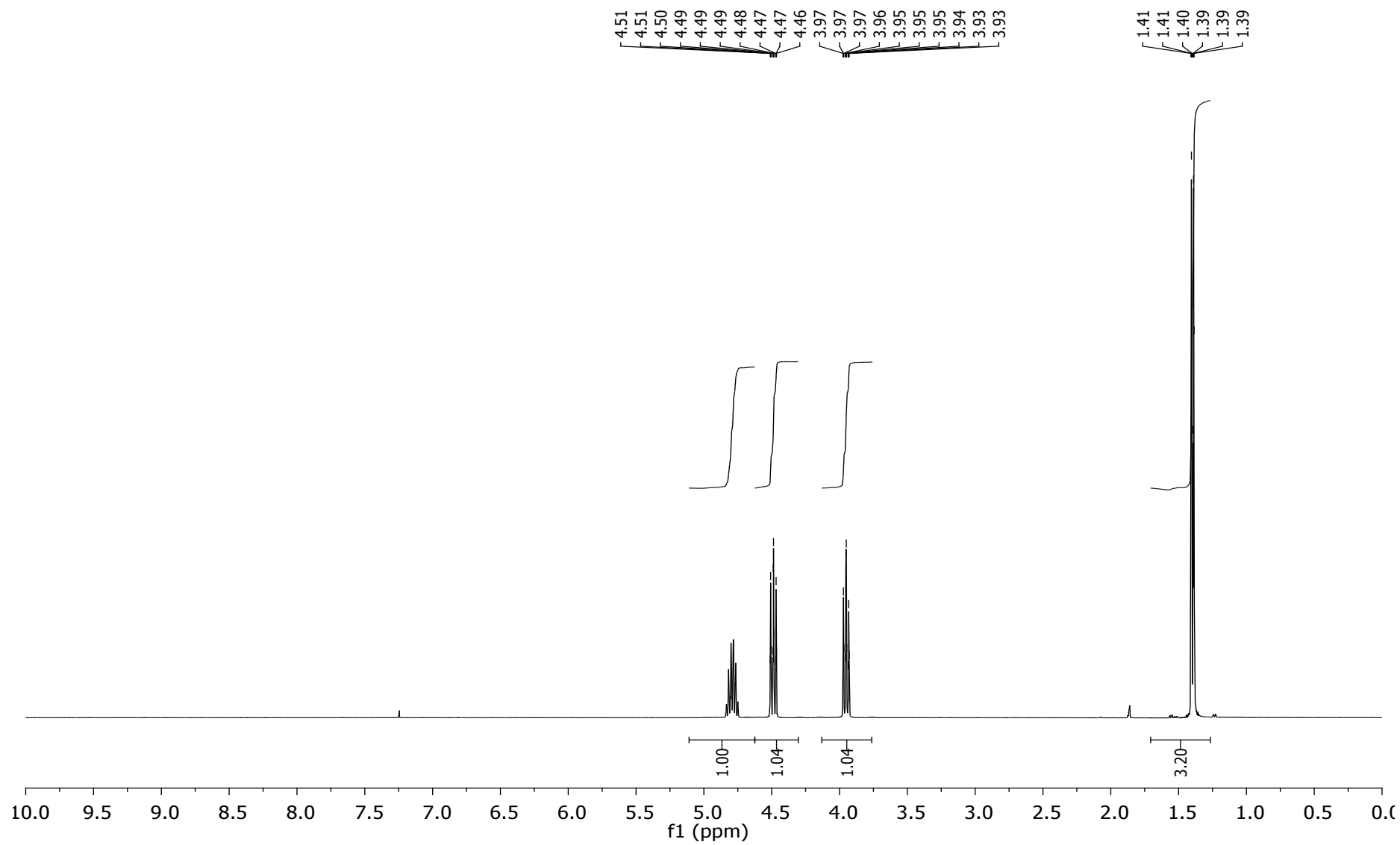
Homogeneous and silica-supported zinc complexes for the synthesis of propylene carbonate from propane-1,2-diol and carbon dioxide.

James W. Comerford, Sam J. Hart, Michael North* and Adrian Whitwood

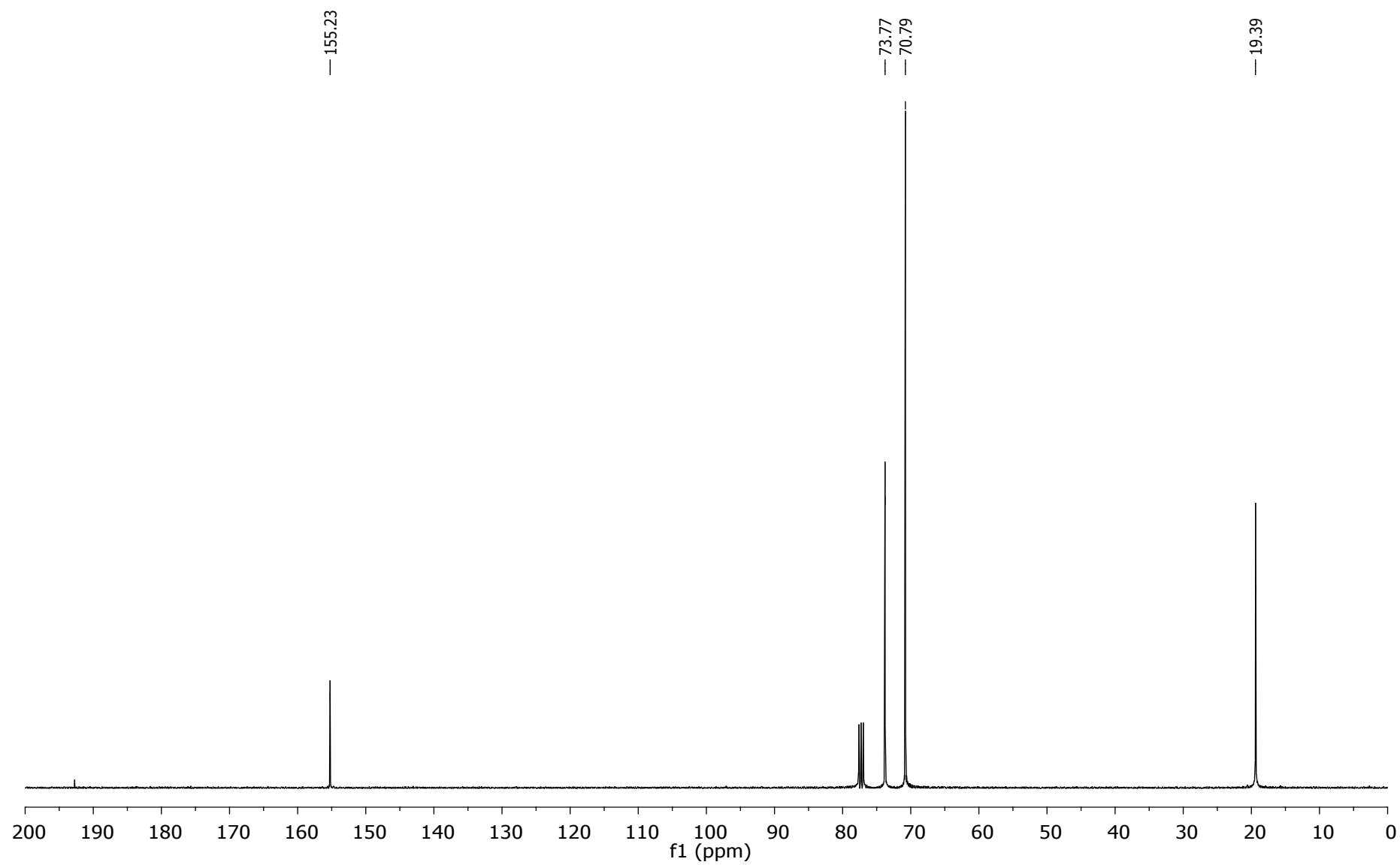
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¹H NMR spectrum of propylene carbonate 2 in CDCl₃.



^{13}C NMR spectrum of propylene carbonate 2 in CDCl_3 .

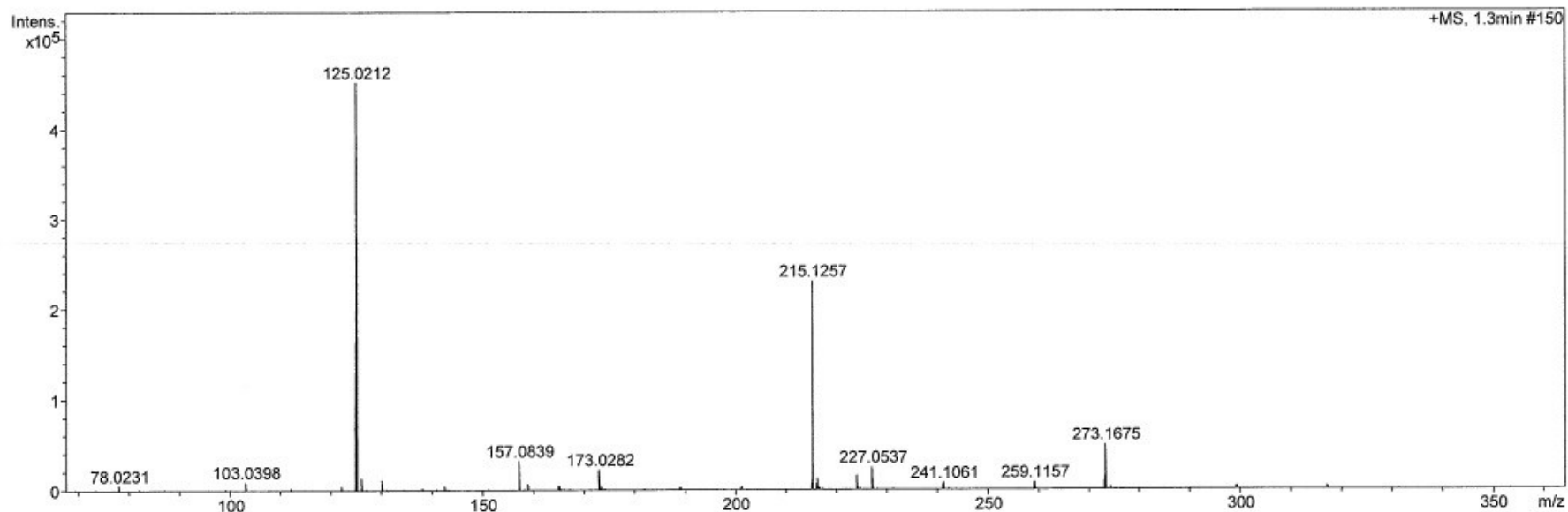


High Resolution Mass Spectrum (ESI-TOF) of propylene carbonate 2.

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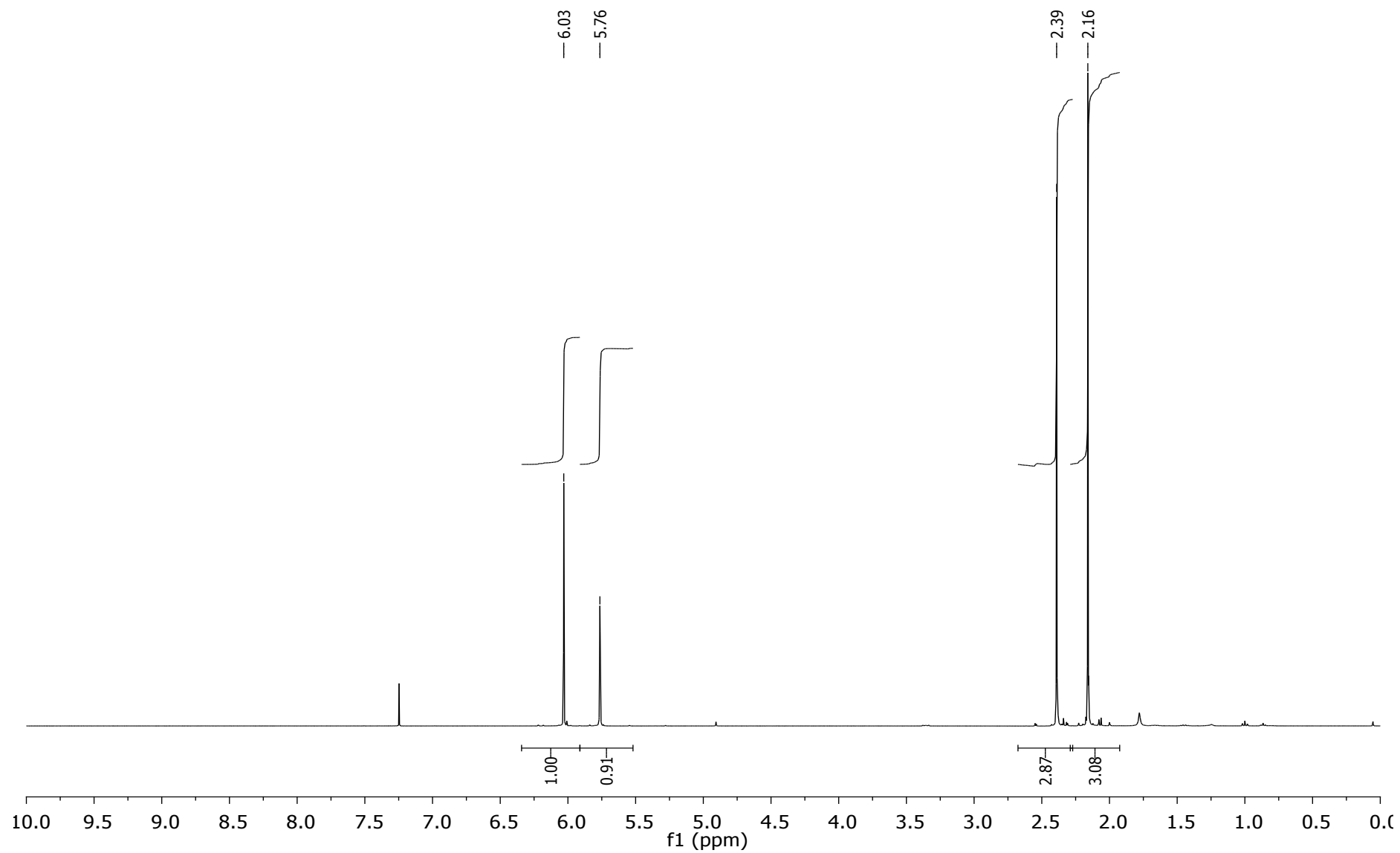
Analysis Information

Analysis Filename mn56477jc_P1-D-9_01_63093.d
Method 200p_meah1260_2c1s.m
Submission Name mn56477jc
Instrument micrOTOF
ESI Positive

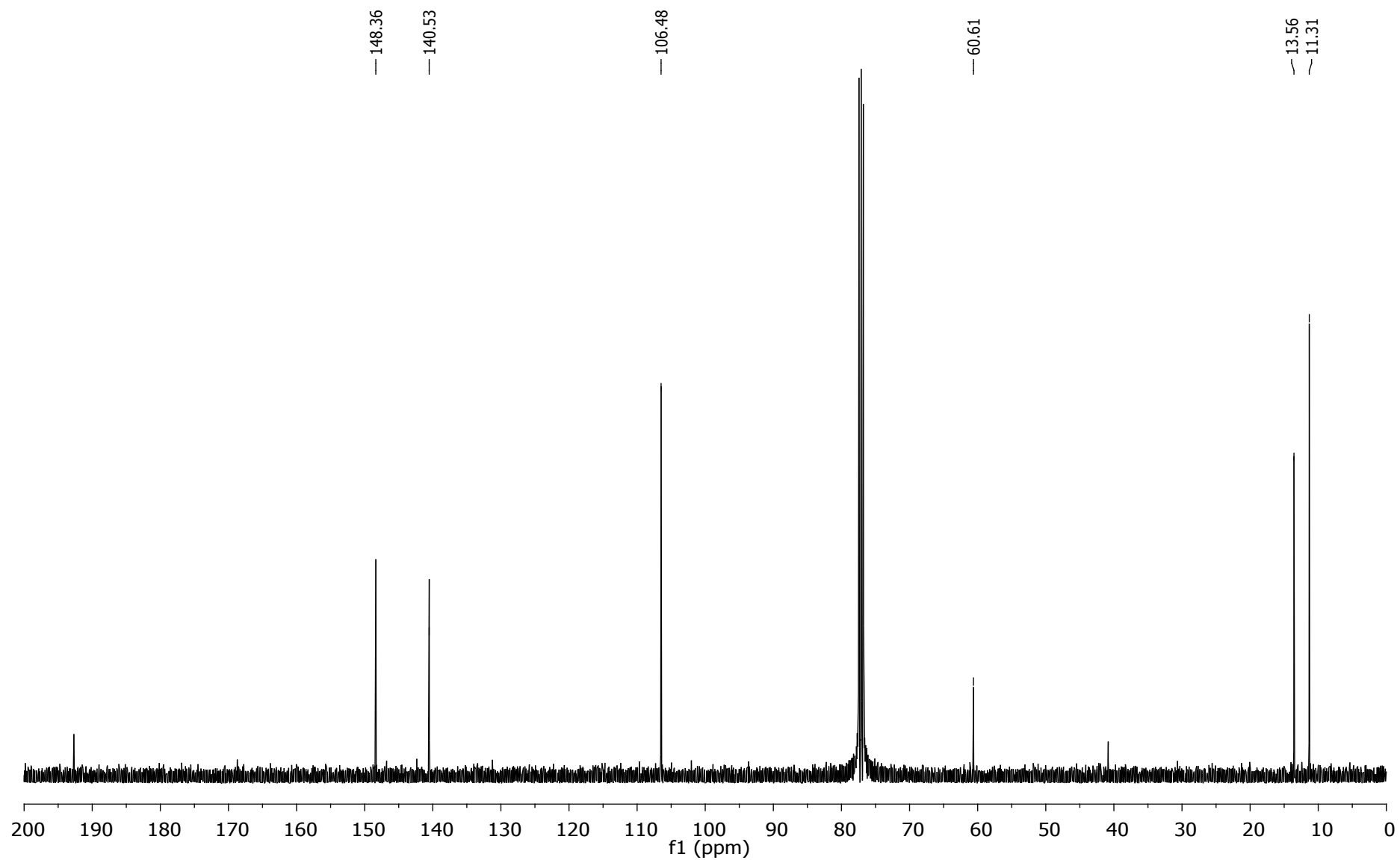


Meas. m/z	#	Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
125.0212	1	C ₄ H ₆ NaO ₃	125.0209	-1.9	-0.2	8.3	-2.0

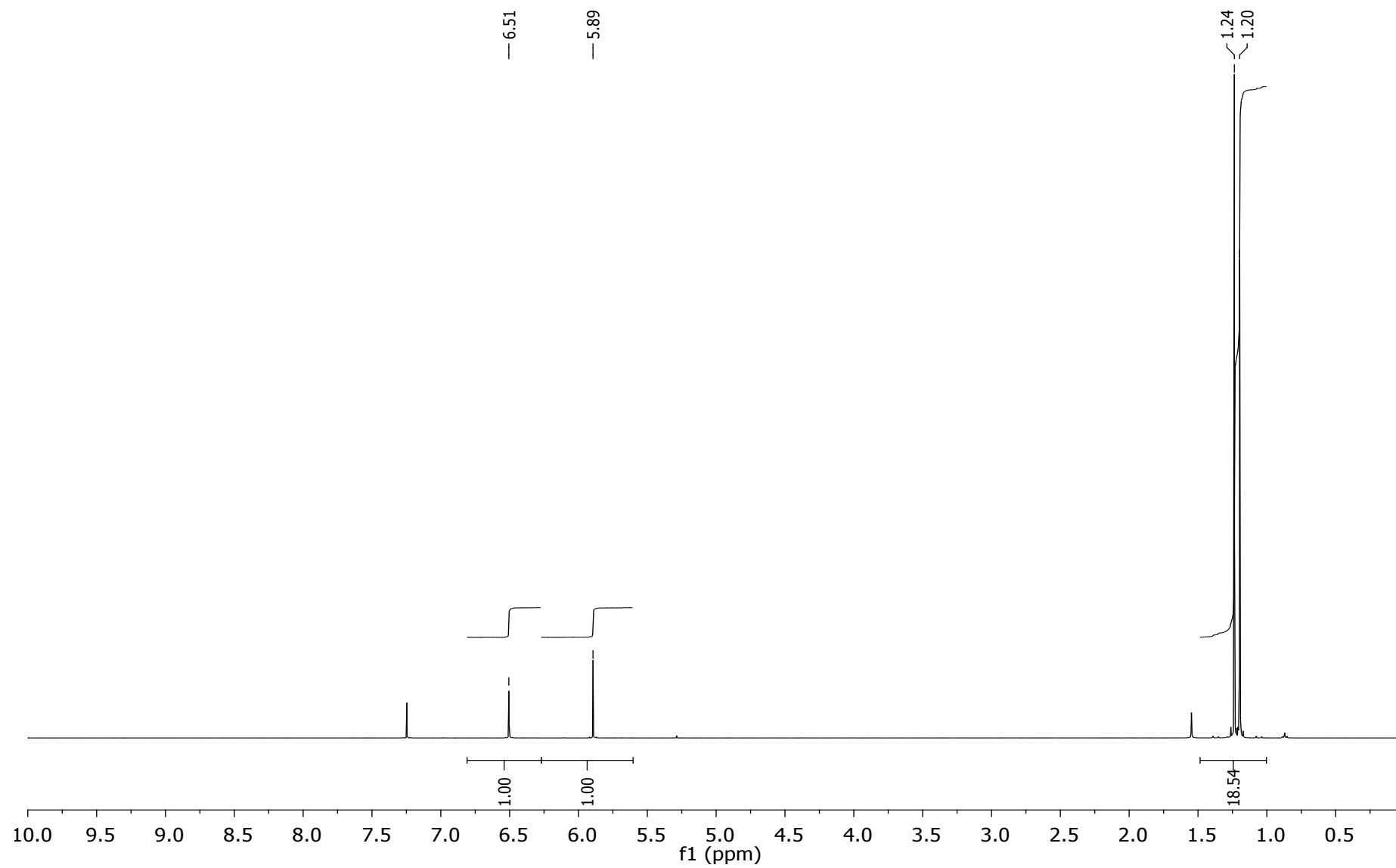
¹H NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl₃.



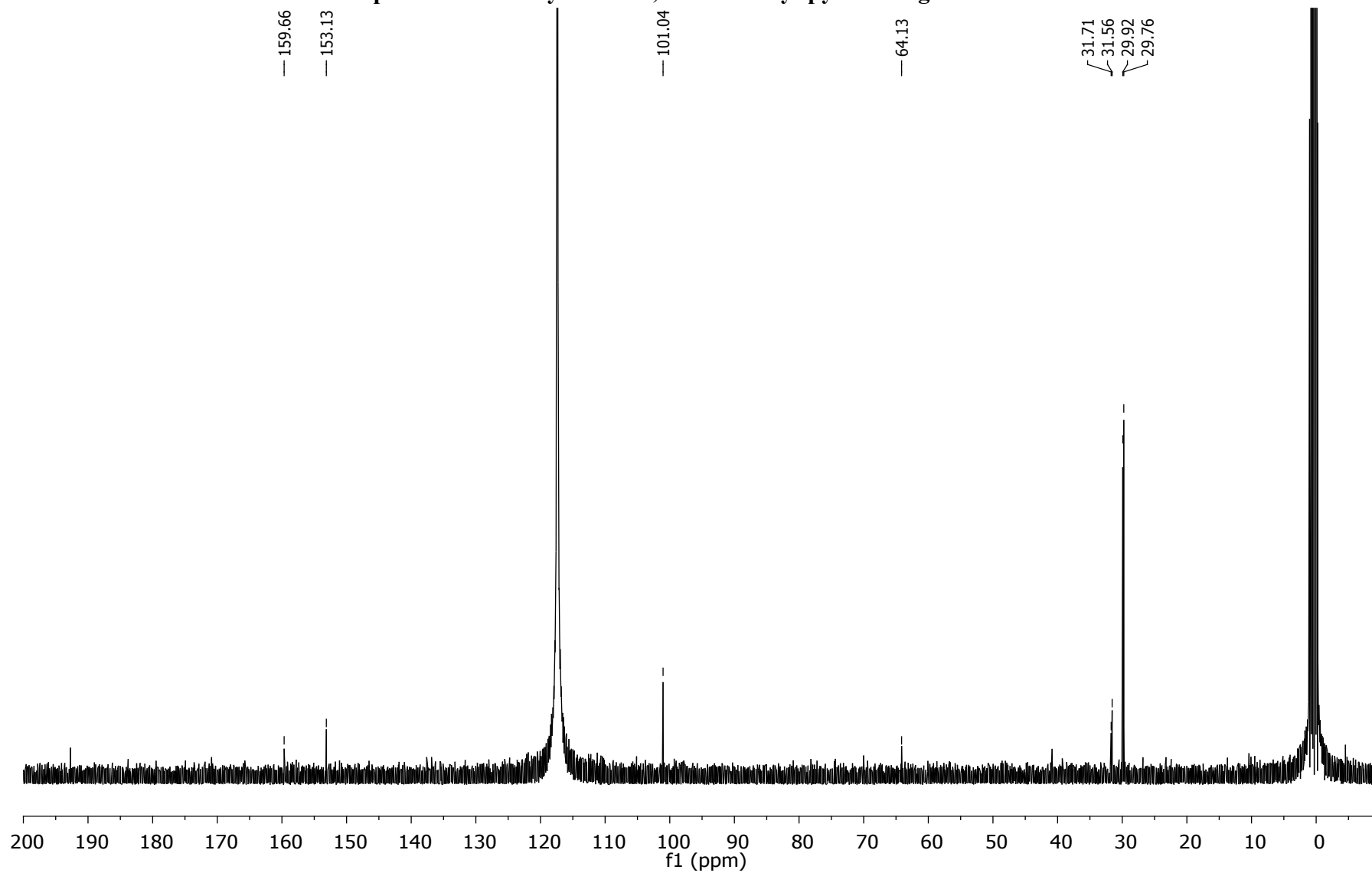
^{13}C NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl_3 .



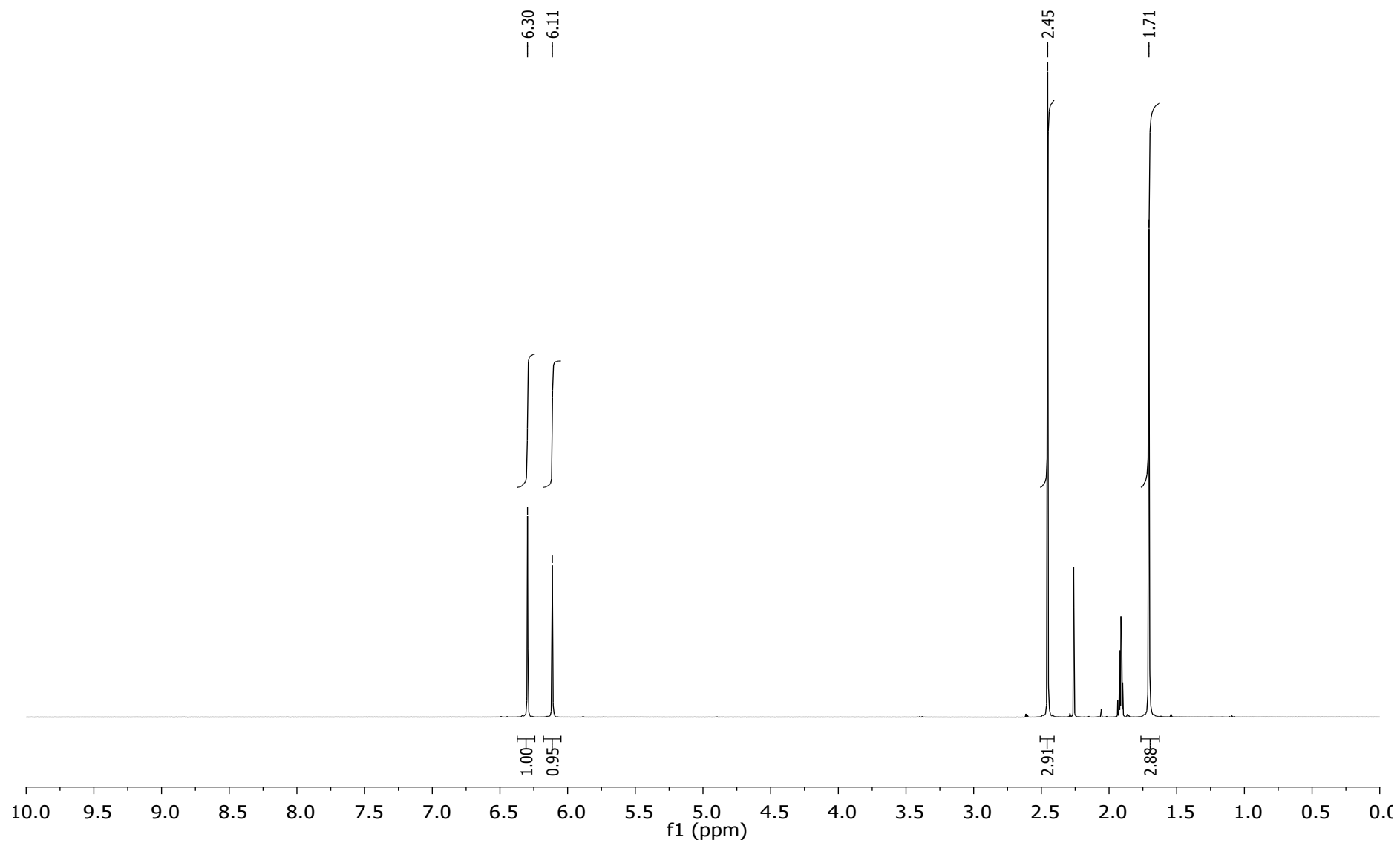
¹H NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in CDCl₃.



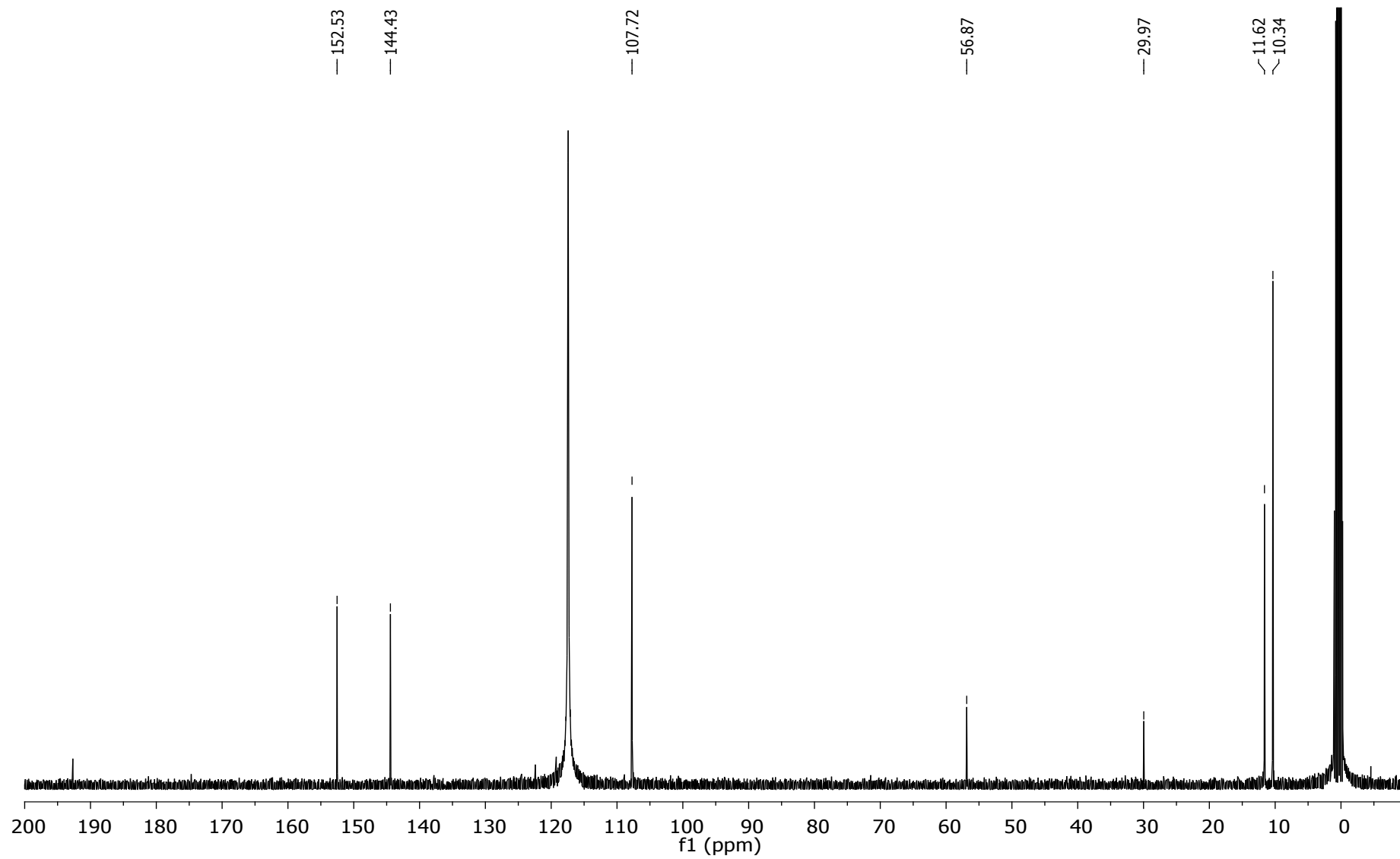
^{13}C NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in MeCN.



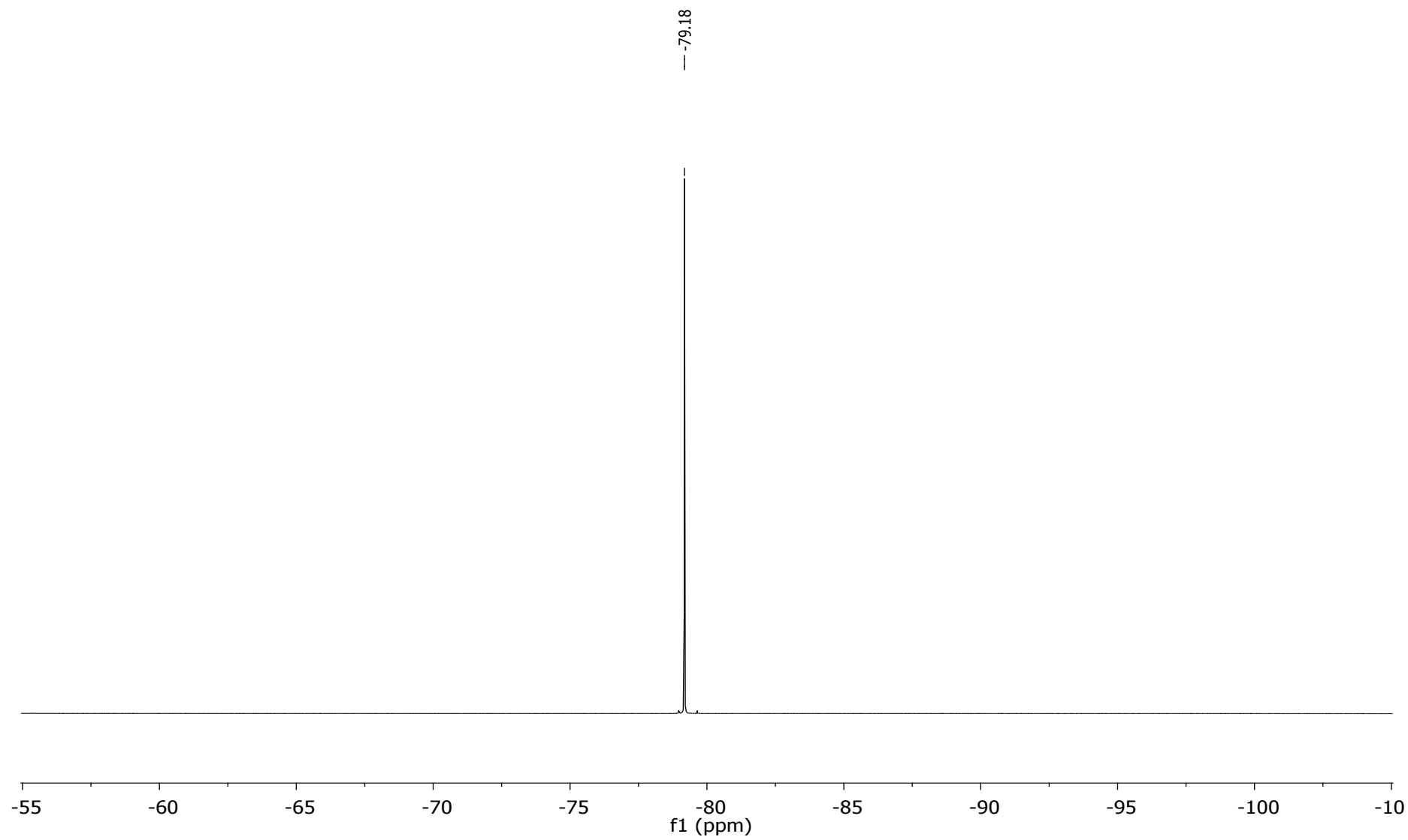
^1H NMR spectrum of $[\text{Zn}(\mathbf{5})_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$ in MeCN.



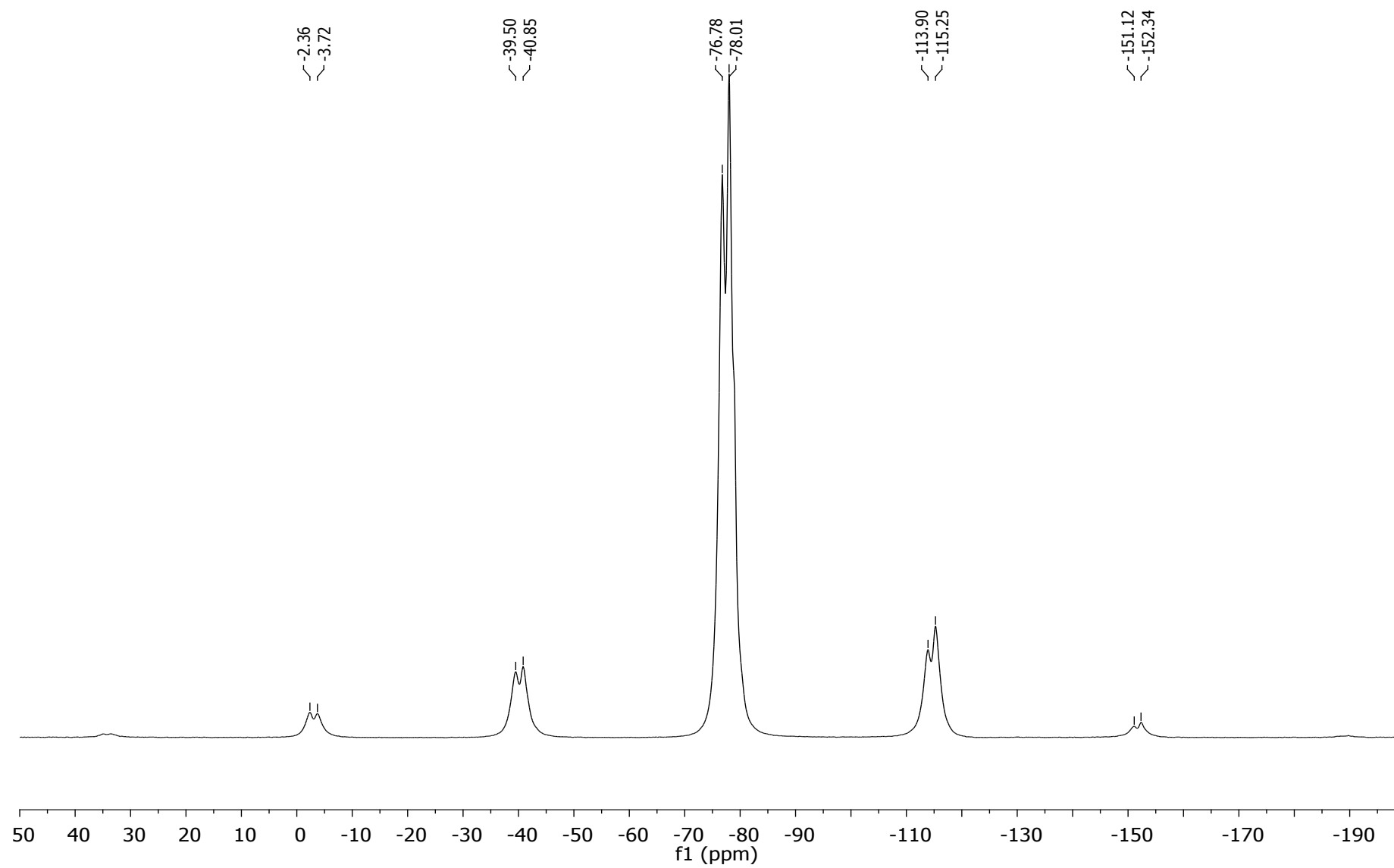
^{13}C NMR spectrum of $[\text{Zn}(\text{S})_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$ in MeCN.



^{19}F NMR spectrum of $[\text{Zn}(\mathbf{5})_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$ in CD_3COCD_3 .



Solid state ^{19}F NMR spectrum of $[\text{Zn}(5)_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)$.

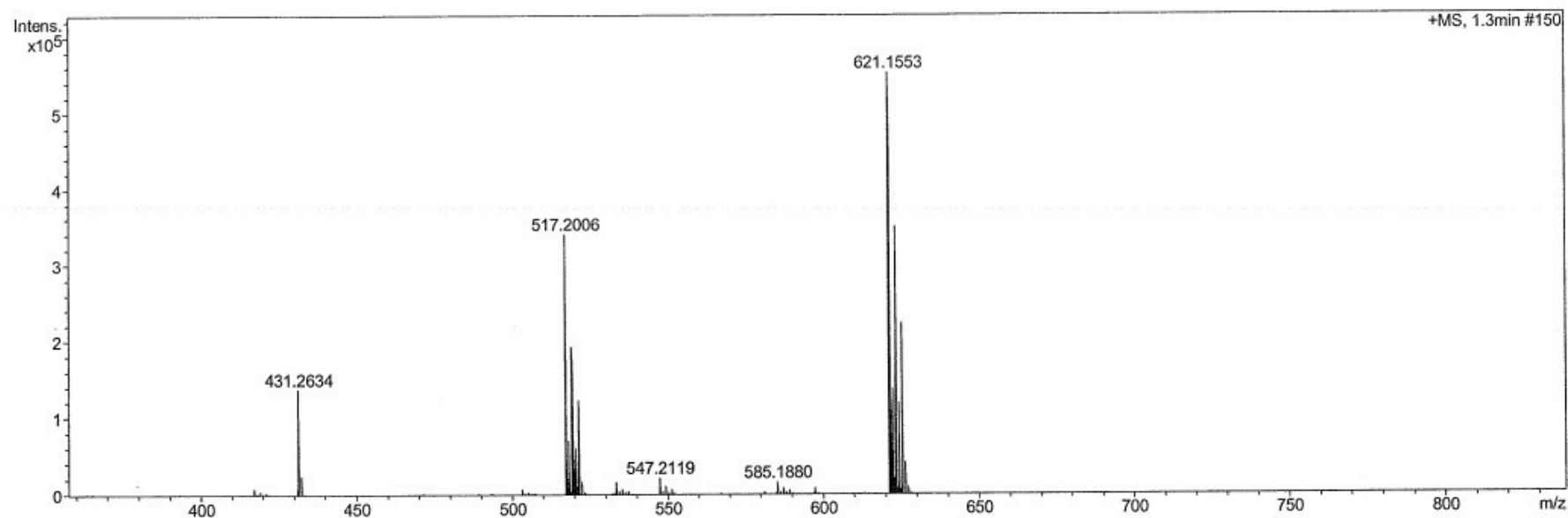


High Resolution Mass Spectrum (ESI-TOF) of $[\text{Zn}(\text{5})_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$.

York - Chemistry - Mass Spectrometry Service Report

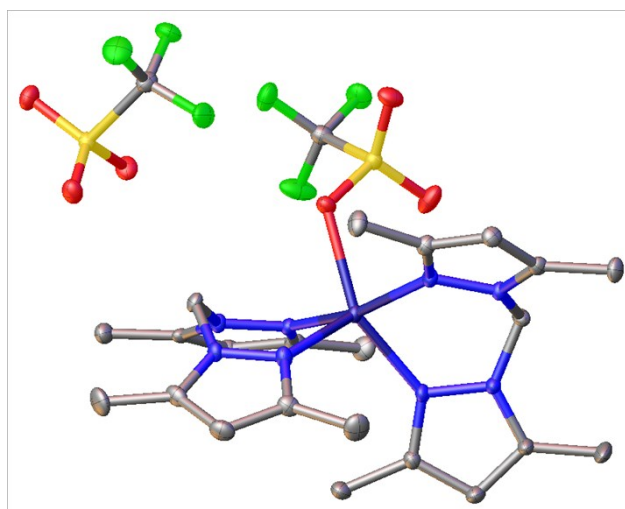
Analysis Information

Analysis Filename mn56369jc_P1-B-9_01_62942.d
Method 800p_meoh1260_2c1s.m
Submission Name mn56369jc
Instrument micrOTOF
ESI Positive



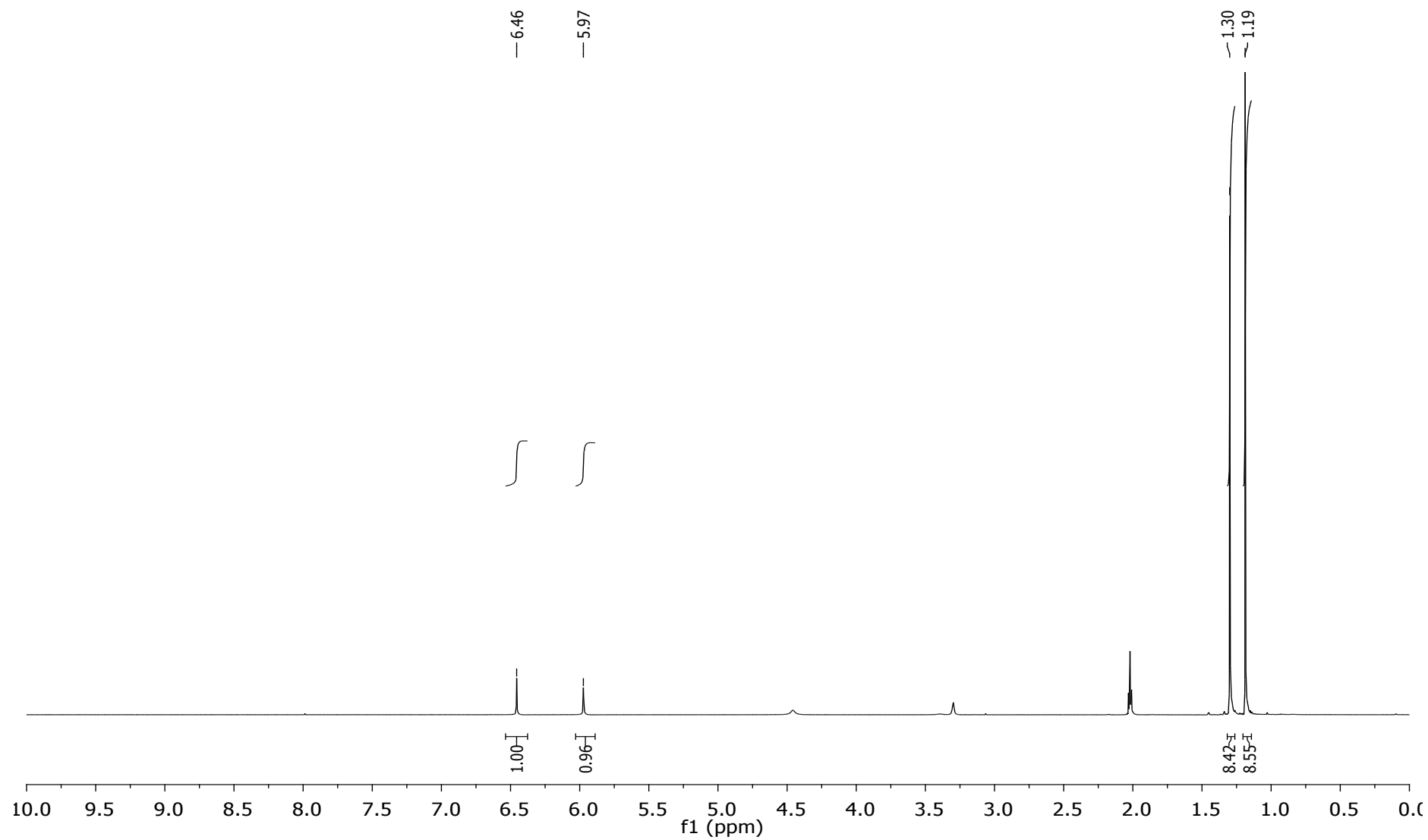
Meas. m/z	#	Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
621.1553	1	C ₂₃ H ₃₂ F ₃ N ₈ O ₃ S Zn	621.1556	0.5	0.3	41.0	1.1

X-Ray Diffraction data for $[\text{Zn}(\mathbf{5})_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$.

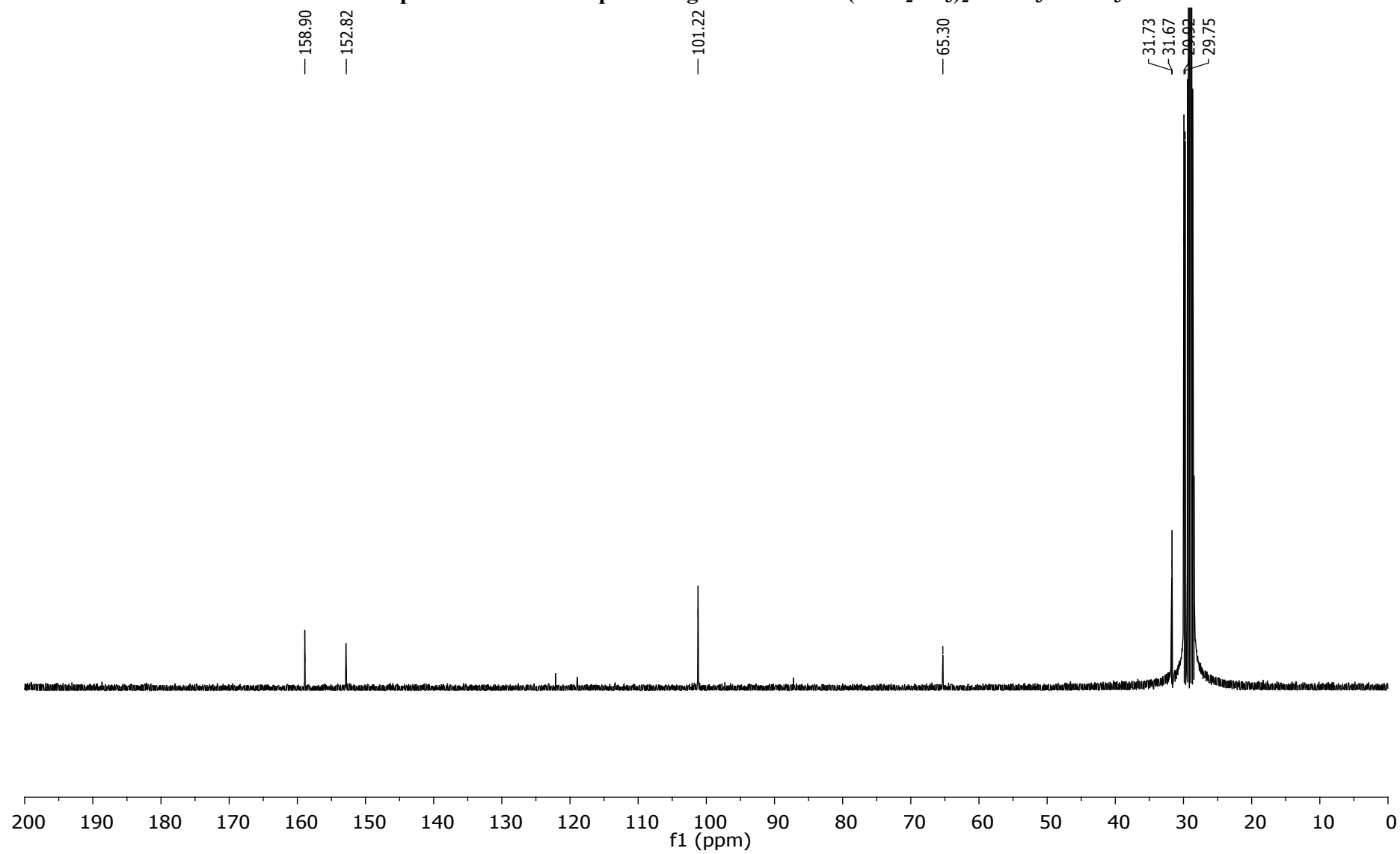


Empirical formula	$\text{C}_{24}\text{H}_{32}\text{F}_6\text{N}_8\text{O}_6\text{S}_2\text{Zn}$
Formula weight	772.06
Temperature/K	110.05(10)
Crystal system	triclinic
Space group	P1
a/Å	8.3731(3)
b/Å	8.6907(3)
c/Å	11.7281(5)
$\alpha/^\circ$	68.851(3)
$\beta/^\circ$	81.968(3)
$\gamma/^\circ$	82.401(3)
Volume/Å ³	785.04(5)
Z	1
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.633
μ/mm^{-1}	1.004
F(000)	396.0
Crystal size/mm ³	$0.2125 \times 0.1858 \times 0.0806$
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	6.516 to 64.184
Index ranges	$-12 \leq h \leq 11, -12 \leq k \leq 12, -17 \leq l \leq 17$
Reflections collected	14482
Independent reflections	8455 [$R_{\text{int}} = 0.0265, R_{\text{sigma}} = 0.0586$]
Data/restraints/parameters	8455/3/432
Goodness-of-fit on F^2	0.966
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0304, wR_2 = 0.0525$
Final R indexes [all data]	$R_1 = 0.0331, wR_2 = 0.0539$
Largest diff. peak/hole / e Å ⁻³	0.38/-0.38
Flack parameter	0.037(4)

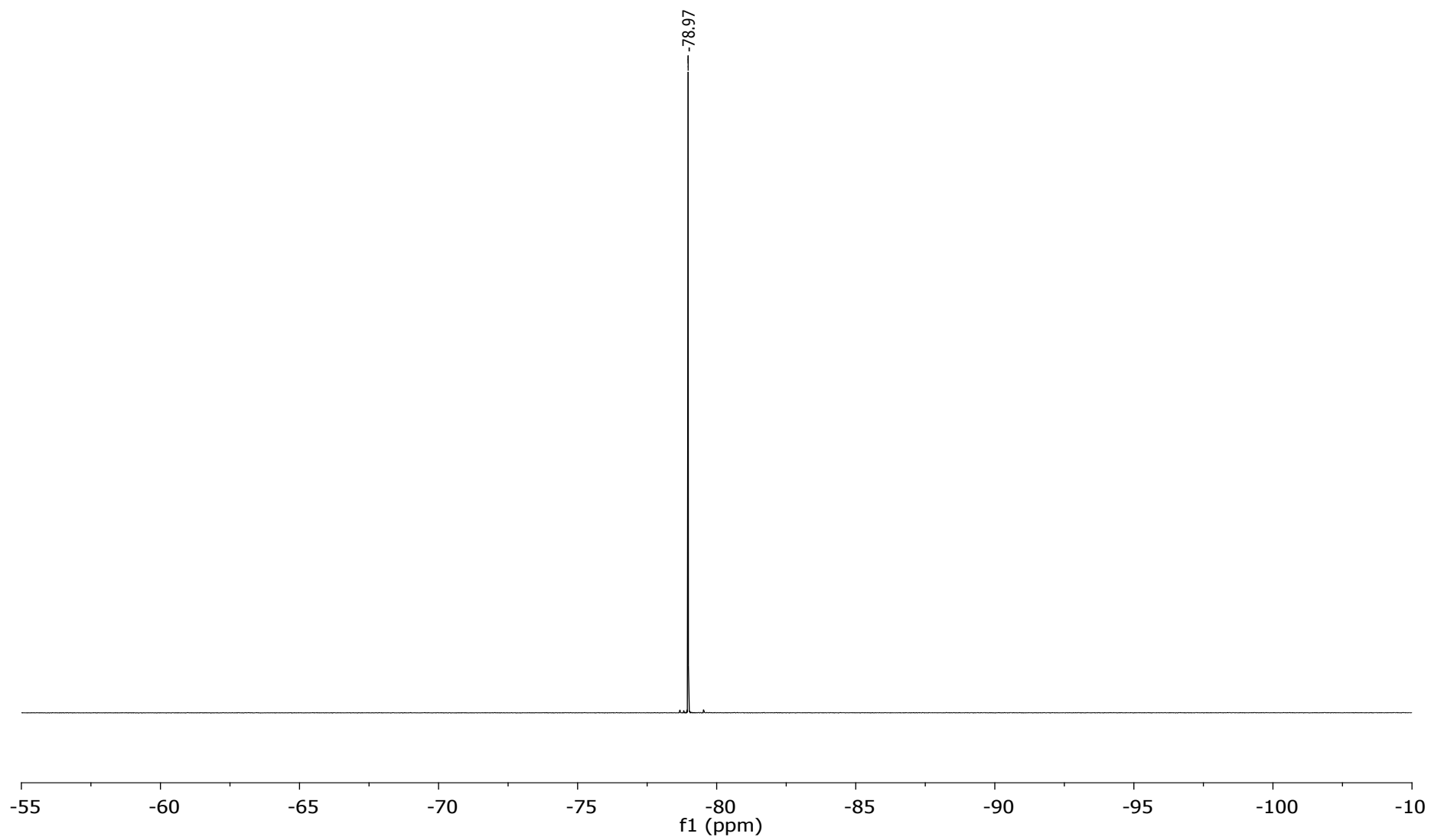
¹H NMR spectrum of the complex of ligand 18 and Zn(OSO₂CF₃)₂ in CD₃COCD₃.



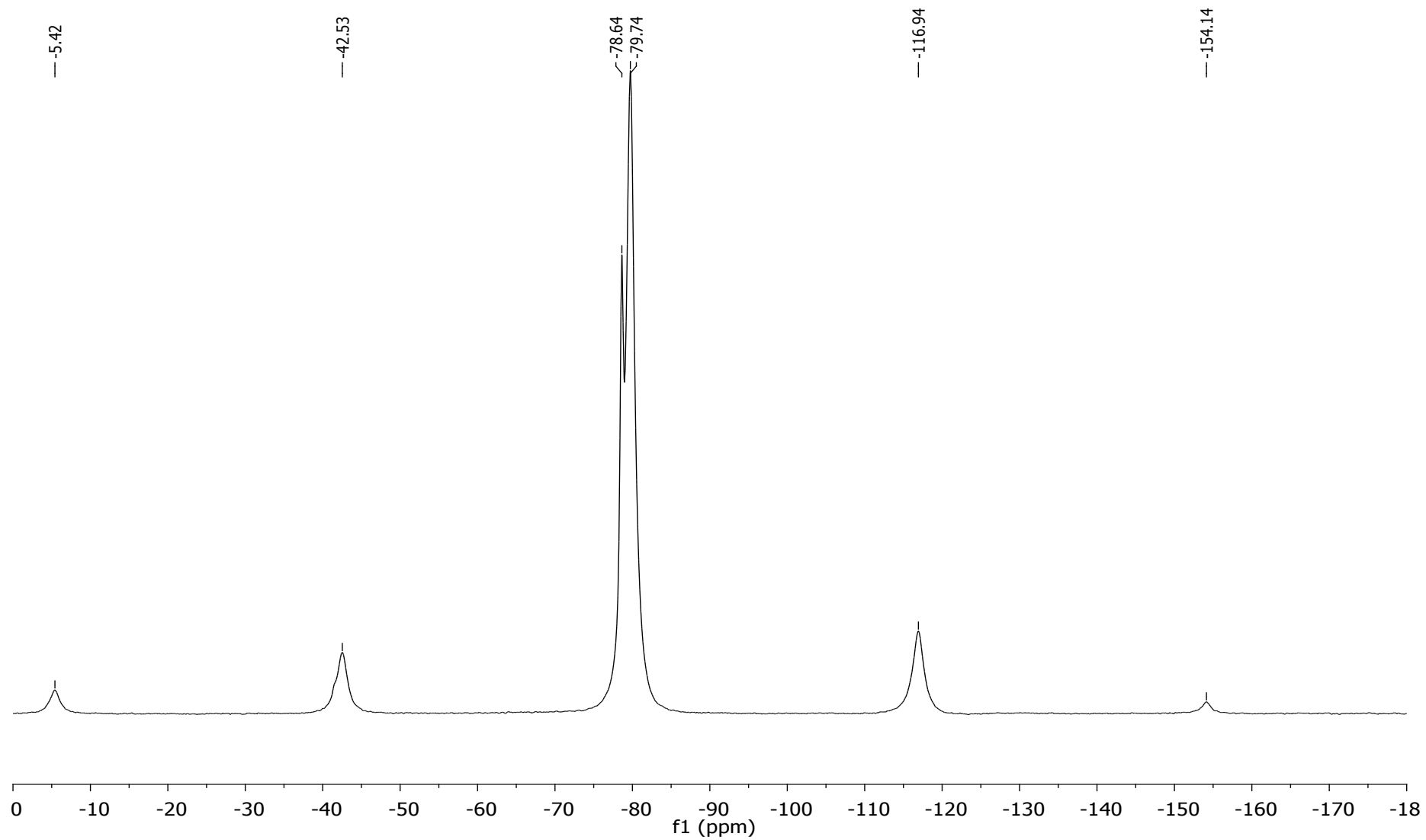
^{13}C NMR spectrum of the complex of ligand 18 and $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$ in CD_3COCD_3 .



^{19}F NMR spectrum of the complex of ligand 18 and $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$ in CD_3COCD_3 .



Solid state ^{19}F NMR spectrum of the complex of ligand 18 and $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$.



Porosimetry data for silica 21a.

Surface Area

Single point surface area at P/Po = 0.238411307:	699.3663 m ² /g.
BET Surface Area:	782.5325 m ² /g.
Langmuir Surface Area:	1142.6012 m ² /g.
t-Plot External Surface Area:	1085.9397 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	610.238 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	144.0534 m ² /g.

Pore Volume

Single point adsorption total pore volume of pores less than 56.6231 nm radius at P/Po = 0.982756180:	0.387883 cm ³ /g.
Single point desorption total pore volume of pores less than 33.3263 nm radius at P/Po = 0.970294573:	0.386017 cm ³ /g.
t-Plot micropore volume:	-0.172779 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.346690 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.117019 cm ³ /g.

Pore Size

Adsorption average pore width (4V/A by BET):	1.98271 nm.
Desorption average pore width (4V/A by BET):	1.97317 nm.
BJH Adsorption average pore radius (2V/A):	1.1362 nm
BJH Desorption average pore radius (2V/A):	1.6247 nm.

Nanoparticle Size - Average Particle Size: 7.6674 nm.

Porosimetry data for silica 21b.

Surface Area

Single point surface area at $P/P_0 = 0.300672136$:	253.7011 m ² /g.
BET Surface Area:	268.2281 m ² /g.
Langmuir Surface Area:	386.0740 m ² /g.
T-Plot External Surface Area:	312.1251 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	274.763 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	302.0997 m ² /g.

Pore Volume

Single point adsorption total pore volume of pores less than 67.8719 nm radius at $P/P_0 = 0.985666084$:	0.712821 cm ³ /g.
Single point desorption total pore volume of pores less than 56.2277 nm radius at $P/P_0 = 0.982632302$:	0.716998 cm ³ /g.
t-Plot micropore volume:	-0.026517 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.717321 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.740051 cm ³ /g.

Pore Size

Adsorption average pore width (4V/A by BET):	10.63007 nm.
Desorption average pore width (4V/A by BET):	10.69236 nm.
BJH Adsorption average pore radius (2V/A):	5.2214 nm.
BJH Desorption average pore radius (2V/A):	4.8994 nm.

Nanoparticle Size - Average Particle Size: 22.3690 nm

Porosimetry data for silica 21c.

Surface Area

Single point surface area at $P/P_0 = 0.300224030$:	157.6600 m ² /g.
BET Surface Area:	166.7211 m ² /g.
Langmuir Surface Area:	241.1675 m ² /g.
t-Plot External Surface Area:	200.1888 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	171.675 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	186.6019 m ² /g.

Pore Volume

Single point adsorption total pore volume of pores less than 60.1425 nm radius at $P/P_0 = 0.983785703$:	0.544113 cm ³ /g.
Single point desorption total pore volume of pores less than 45.9861 nm radius at $P/P_0 = 0.978664887$:	0.555024 cm ³ /g.
t-Plot micropore volume:	-0.019020 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.560722 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.574331 cm ³ /g.

Pore Size

Adsorption average pore width (4V/A by BET):	13.05444 nm.
Desorption average pore width (4V/A by BET):	13.31622 nm.
BJH Adsorption average pore radius (2V/A):	6.5324 nm.
BJH Desorption average pore radius (2V/A):	6.1557 nm.

Nanoparticle Size - Average Particle Size: 35.9882 nm.

Porosimetry data for heterogeneous catalyst 23a

Surface Area

Single point surface area at $P/P_0 = 0.300156167$:	40.6970 m ² /g.
BET Surface Area:	42.5908 m ² /g.
Langmuir Surface Area:	67.5899 m ² /g.
t-Plot External Surface Area:	45.5602 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	22.147 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	6.4356 m ² /g.

Pore Volume

Single point adsorption total pore volume of pores less than 61.1908 nm radius at $P/P_0 = 0.984069088$:	0.037137 cm ³ /g.
Single point desorption total pore volume of pores less than 36.8255 nm radius at $P/P_0 = 0.973197536$:	0.035323 cm ³ /g.
t-Plot micropore volume:	-0.000482 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.031584 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.023260 cm ³ /g.

Pore Size

Adsorption average pore width (4V/A by BET):	3.48781 nm.
Desorption average pore width (4V/A by BET):	3.31747 nm.
BJH Adsorption average pore radius (2V/A):	2.8522 nm.
BJH Desorption average pore radius (2V/A):	7.2286 nm.

Nanoparticle Size - Average Particle Size: 140.8755 nm.

Porosimetry data for heterogeneous catalyst 23b

Surface Area

Single point surface area at $P/P_0 = 0.300152318$:	63.0414 m ² /g.
BET Surface Area:	66.3520 m ² /g.
Langmuir Surface Area:	96.6962 m ² /g.
t-Plot External Surface Area:	76.7784 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	65.089 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	76.7368 m ² /g.

Pore Volume

Single point adsorption total pore volume of pores less than 66.5841 nm radius at $P/P_0 = 0.985383601$:	0.250480 cm ³ /g.
Single point desorption total pore volume of pores less than 46.2219 nm radius at $P/P_0 = 0.978776436$:	0.251914 cm ³ /g.
t-Plot micropore volume:	-0.005783 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.262823 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.268515 cm ³ /g.

Pore Size

Adsorption average pore width (4V/A by BET):	15.10006 nm.
Desorption average pore width (4V/A by BET):	15.18651 nm.
BJH Adsorption average pore radius (2V/A):	8.0758 nm.
BJH Desorption average pore radius (2V/A):	6.9983 nm.

Nanoparticle Size - Average Particle Size: 90.4269 nm

Porosimetry data for heterogeneous catalyst 23c

Surface Area

Single point surface area at $P/P_0 = 0.299874650$:	58.3303 m ² /g.
BET Surface Area:	61.1929 m ² /g.
Langmuir Surface Area:	88.2629 m ² /g.
t-Plot External Surface Area:	69.9641 m ² /g.
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	61.510 m ² /g.
BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	75.1870 m ² /g.

Pore Volume

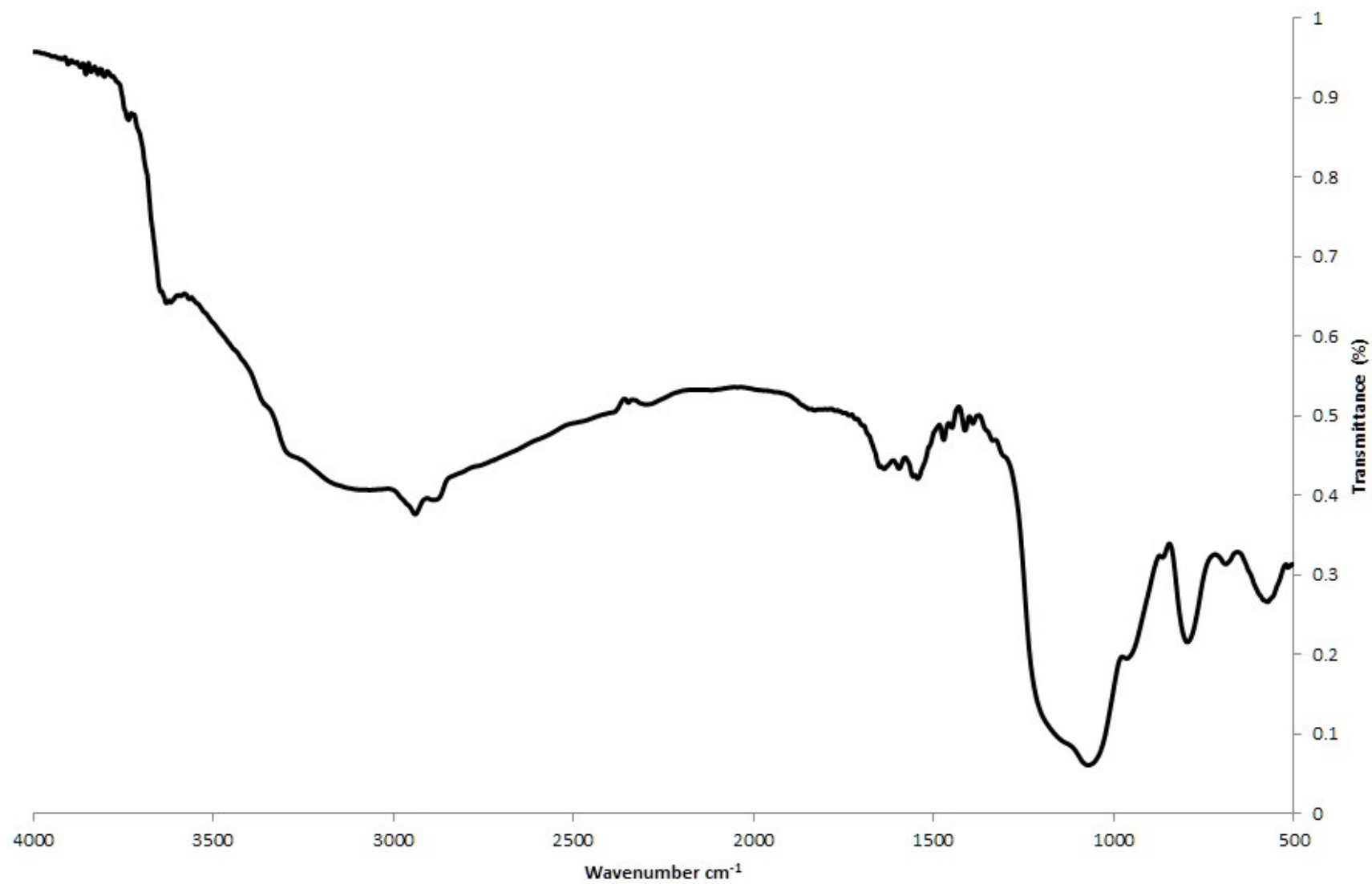
Single point adsorption total pore volume of pores less than 60.8452 nm radius at $P/P_0 = 0.983976764$:	0.286665 cm ³ /g.
Single point desorption total pore volume of pores less than 47.5567 nm radius at $P/P_0 = 0.979386600$:	0.298825 cm ³ /g.
t-Plot micropore volume:	-0.004894 cm ³ /g.
BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.312618 cm ³ /g.
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.316537 cm ³ /g.

Pore Size

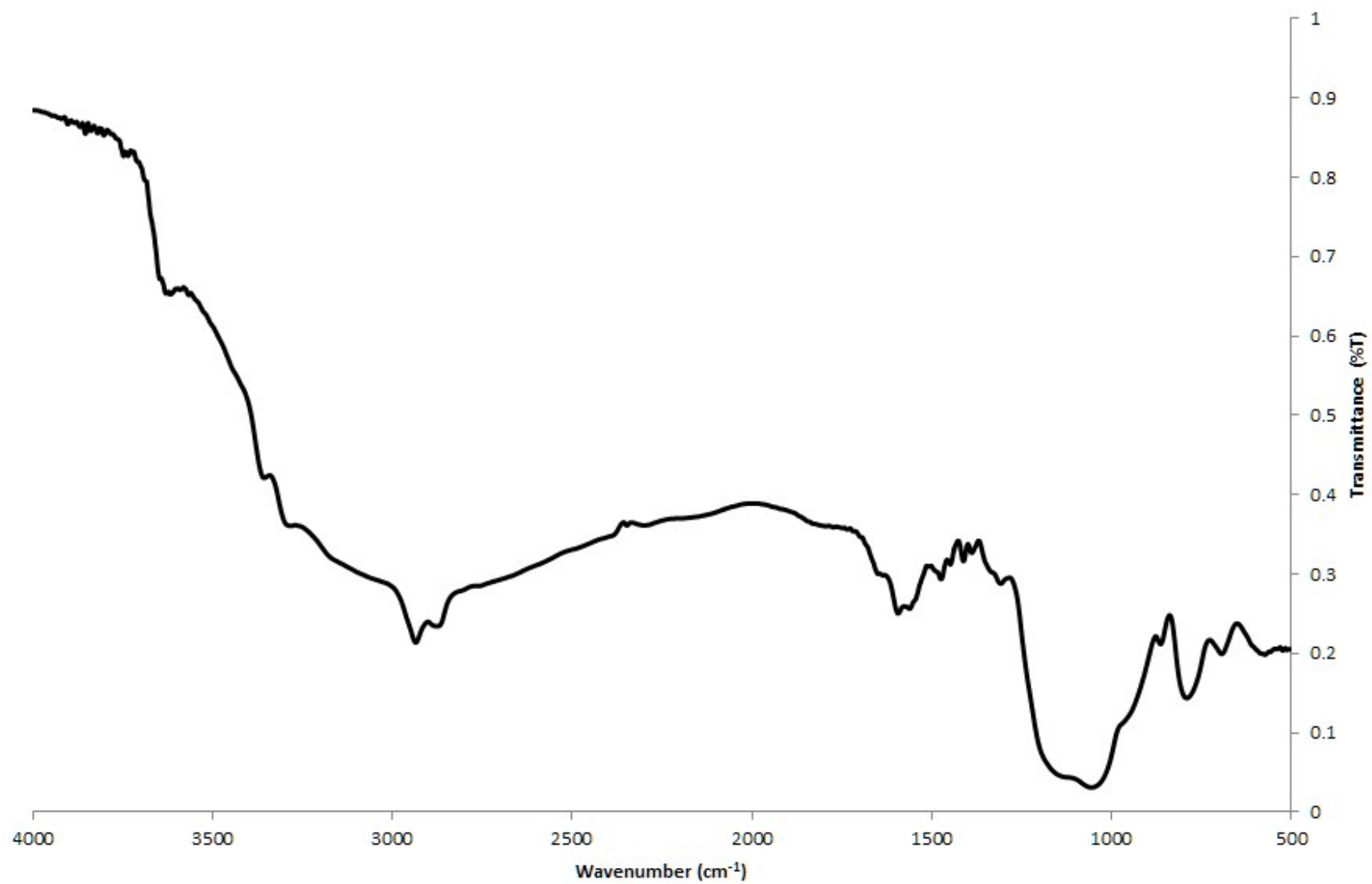
Adsorption average pore width (4V/A by BET):	18.73843 nm.
Desorption average pore width (4V/A by BET):	19.53333 nm.
BJH Adsorption average pore radius (2V/A):	10.1648 nm.
BJH Desorption average pore radius (2V/A):	8.4200 nm.

Nanoparticle Size - Average Particle Size: 98.0507 nm.

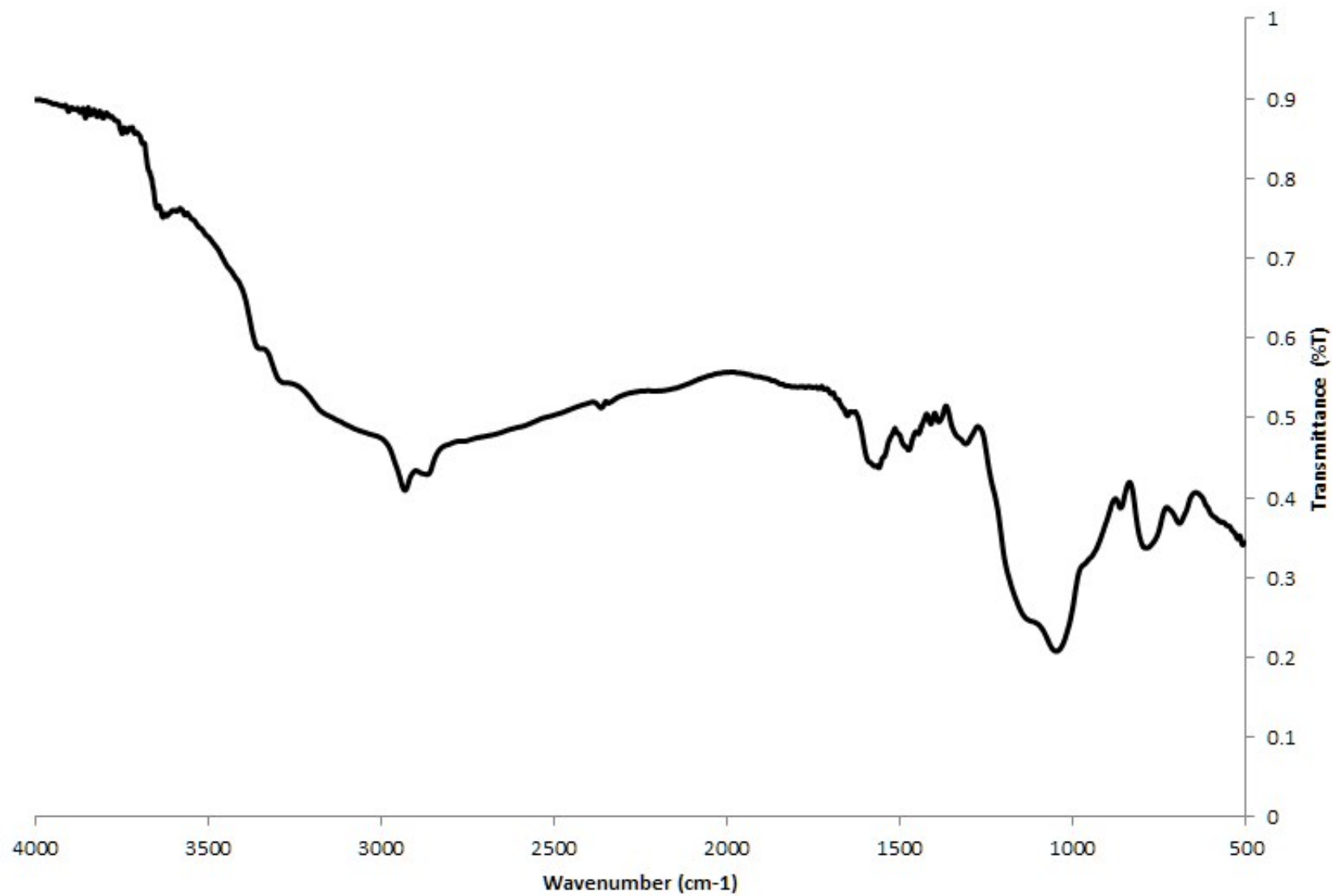
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21a.



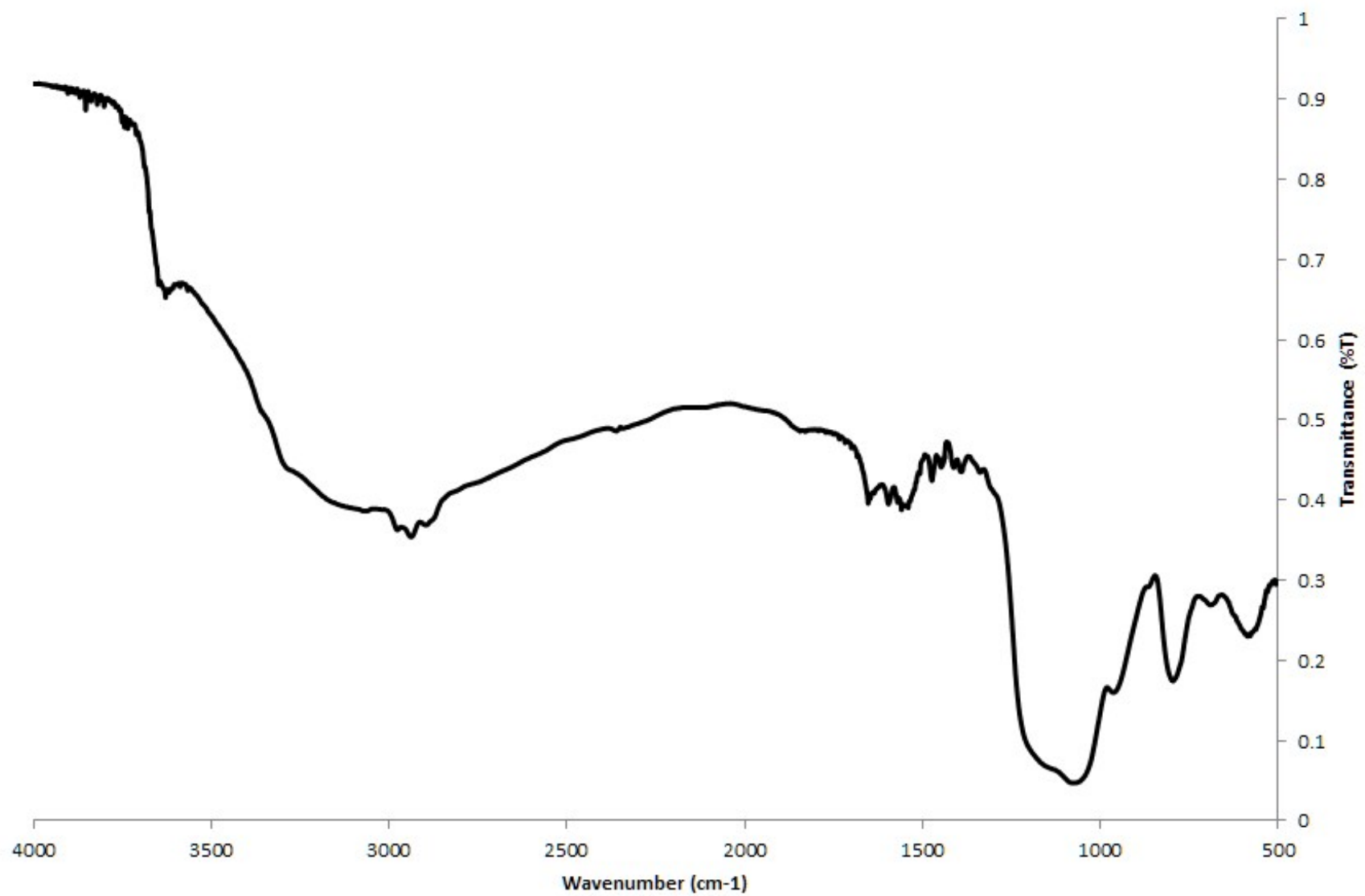
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21b.



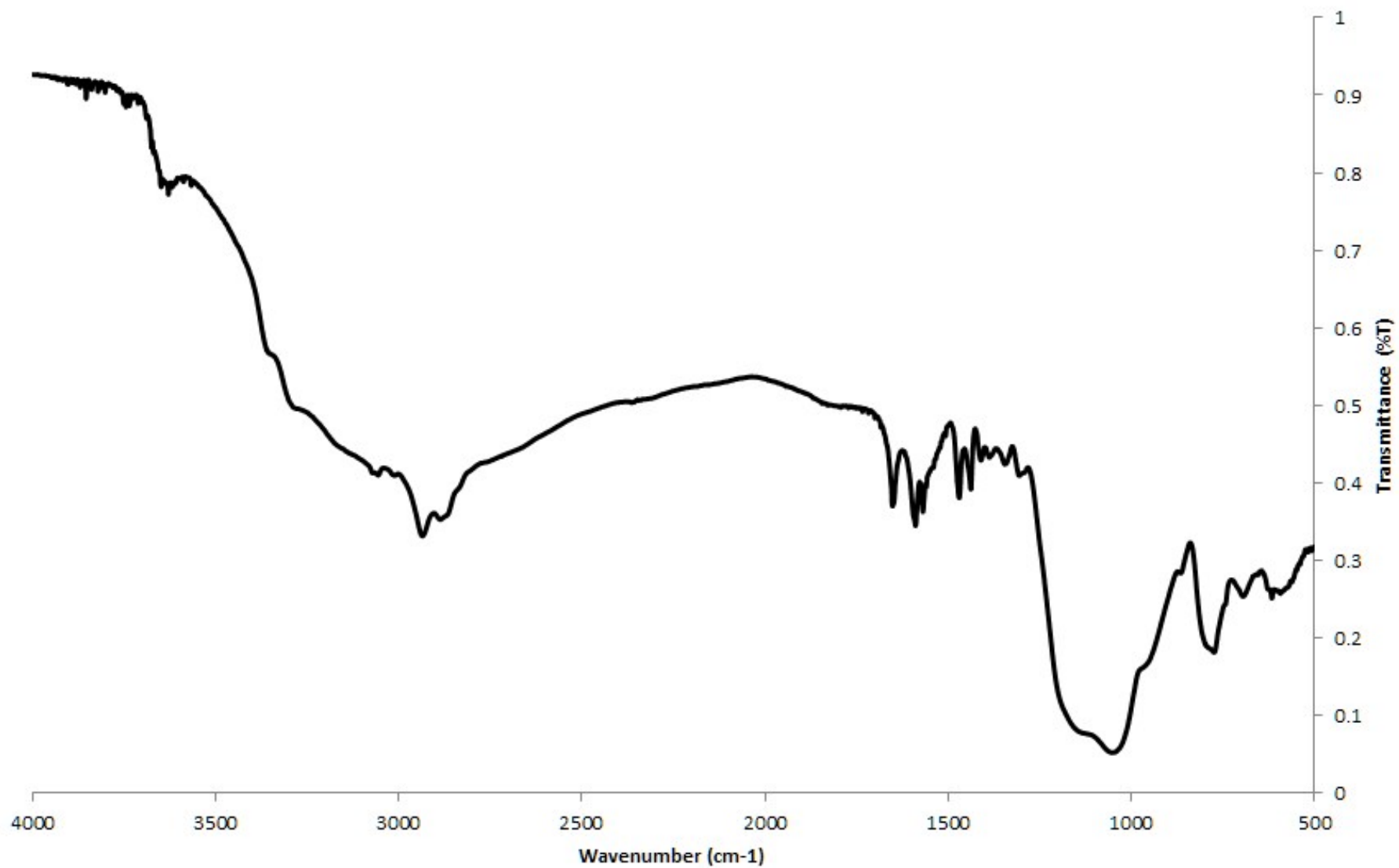
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21c.



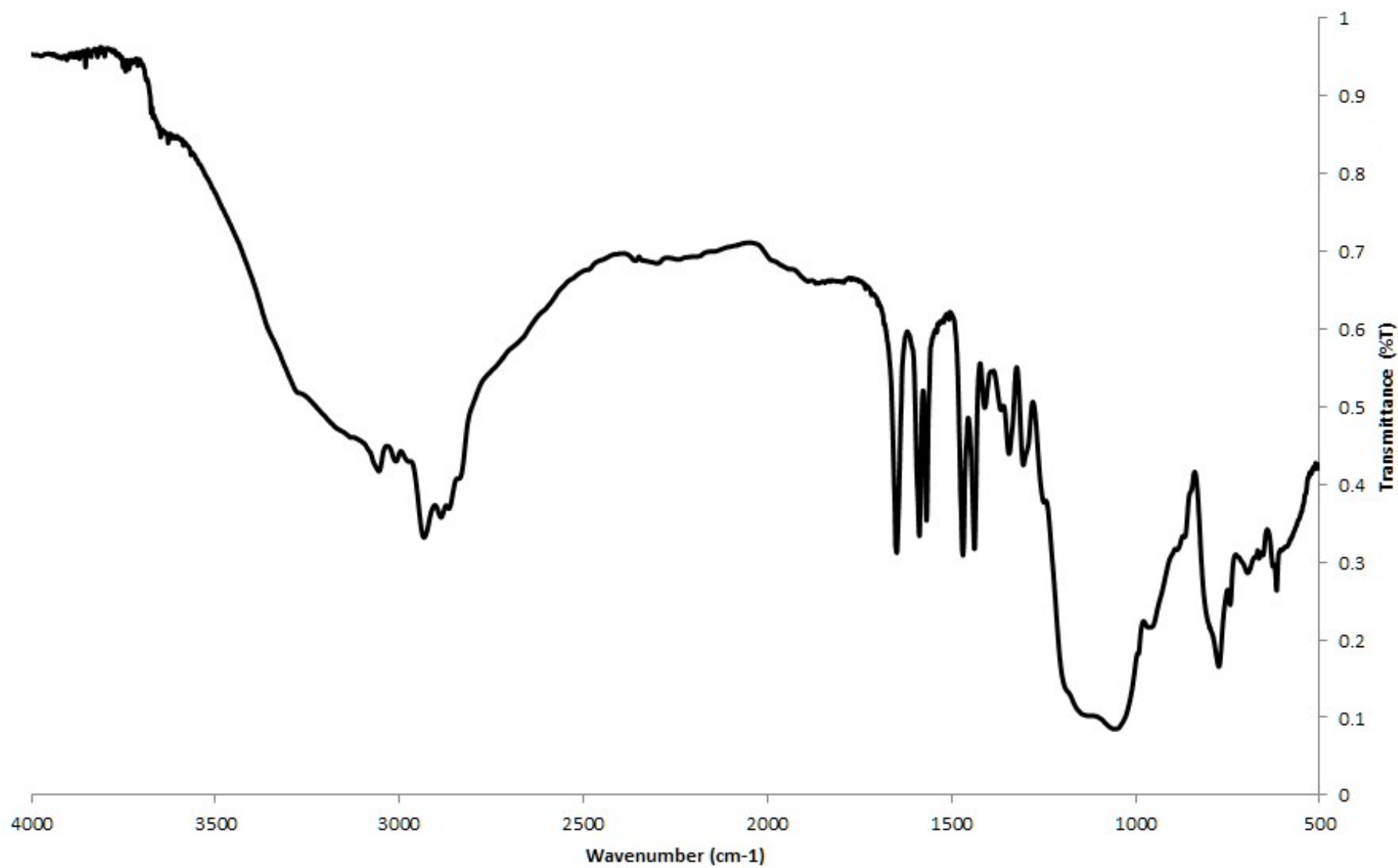
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22a.



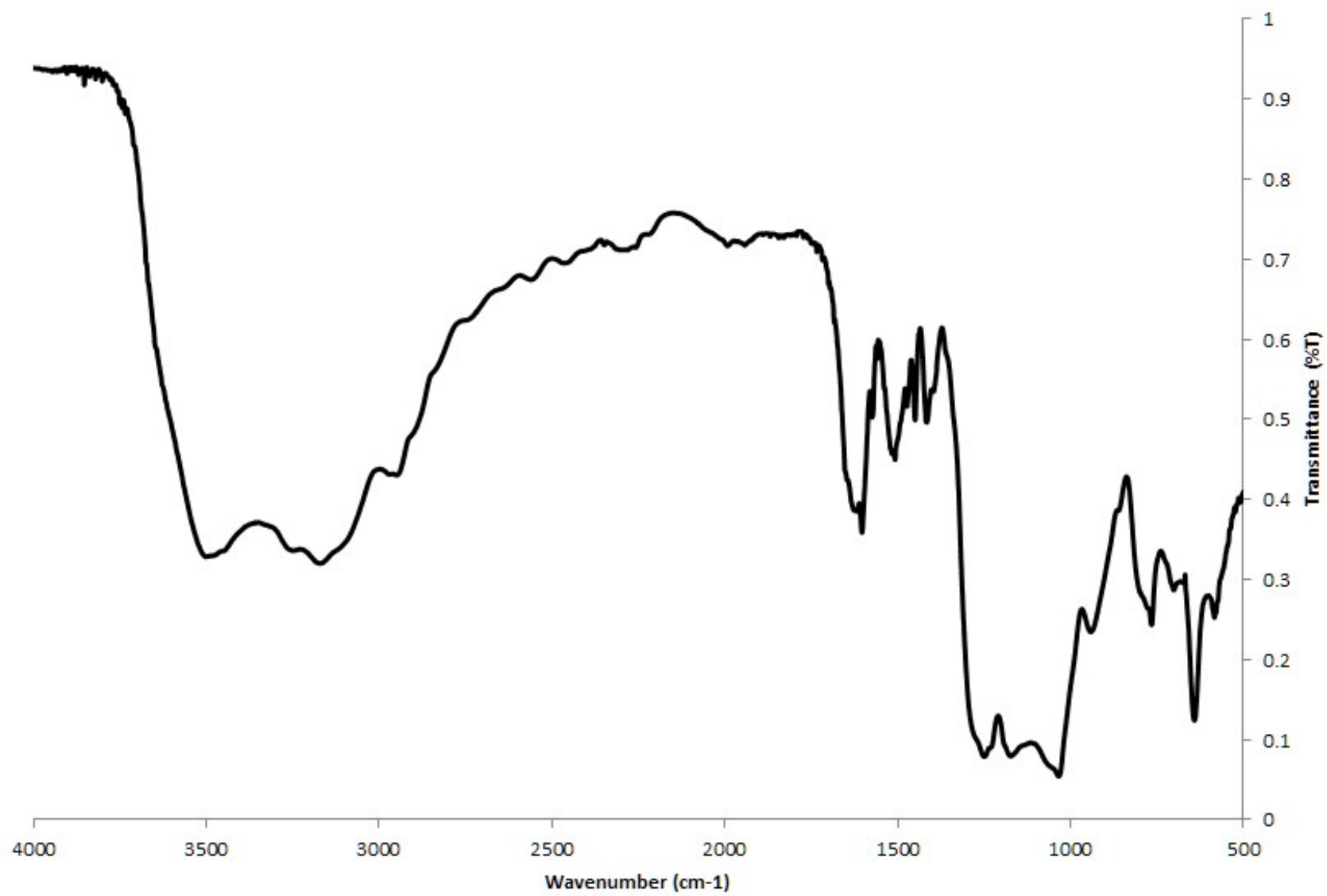
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22b.



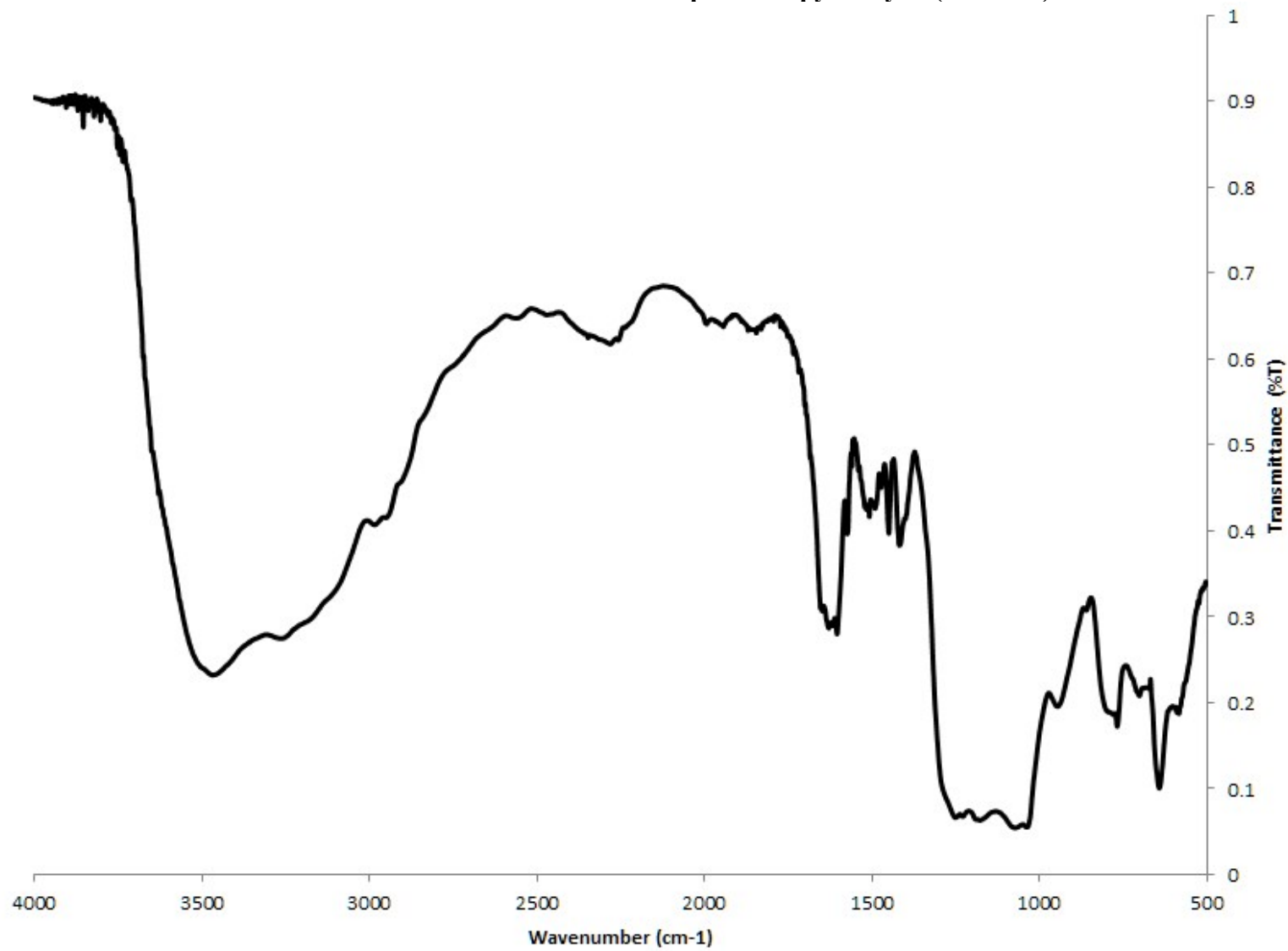
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22c.



Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23a.



Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23b.



Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23c.

