Electronic Supplementary Material (ESI) for RSC Advances.

Pentakis(trifluoromethyl)phenol from Nitrobenzene

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Electronic Supplementary Information

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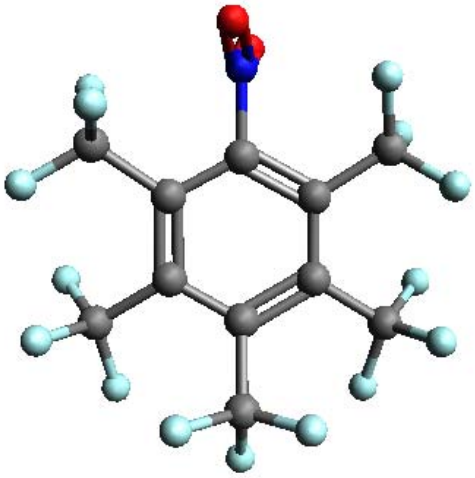
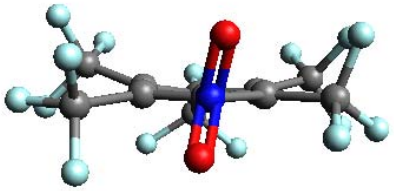
Contents

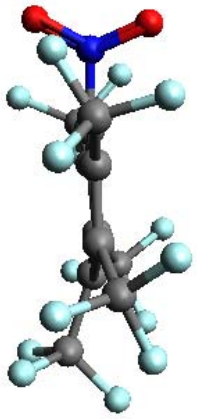
Computational Data of Pentakis(trifluoromethyl)nitrobenzene–2

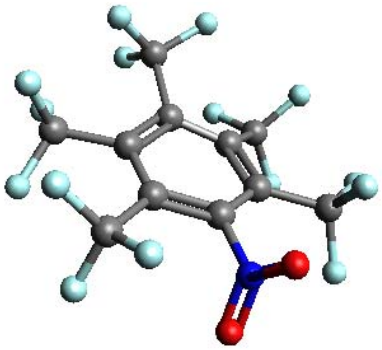


Brutoformula: $C_{11}F_{15}NO_2$
Basis set: def-TVZP
Kinetic energy = 2115.686577
Potential energy = -4238.510719

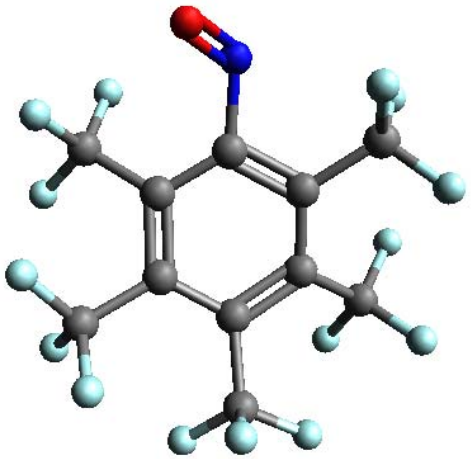
atom	x	y	z
C	-5.44246985	3.19459864	-0.15634628
C	-7.58208381	1.62803020	-0.07918411
C	-7.20400179	-1.01573645	0.00188869
C	-4.71964588	-1.99960632	-0.09776062
C	-2.61735913	-0.36867996	0.20722304
C	-2.95547975	2.26483454	-0.01597404
C	-10.24694317	2.83996129	-0.22170829
C	-9.45410408	-2.83133000	0.52475246
C	-4.26009266	-4.75974918	-1.01248677
C	-0.07049371	-1.46926360	1.17239044
C	-0.77642304	4.19085908	-0.37540158
F	-10.18448173	5.02963165	-1.55278238
F	-11.16702417	3.36707659	2.09730210
F	-11.90266511	1.33801360	-1.45144193
F	-11.05820297	-1.74562734	2.20509398
F	-10.76931545	-3.48049232	-1.55370225
F	-8.63675506	-4.97866309	1.64882746
F	-6.13222293	-5.41379510	-2.64317517
F	-4.11139540	-6.55393159	0.77483778
F	-2.08536228	-4.81739725	-2.38236341
F	-0.40386619	-3.79328274	2.18244753
F	1.74771519	-1.64349370	-0.59724657
F	0.76551921	-0.00308879	3.10974935
F	1.55912195	3.22570969	-0.19458388
F	-0.96357138	5.18026919	-2.73463470
F	-0.96002994	6.10343863	1.32197371
N	-5.83188681	6.03409644	-0.10019745
O	-6.41174948	6.87058006	1.98787629
O	-5.54519538	7.21620292	-2.06543010



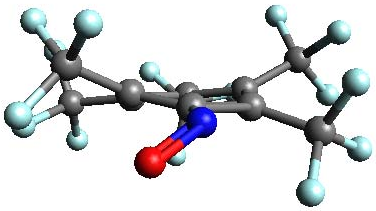


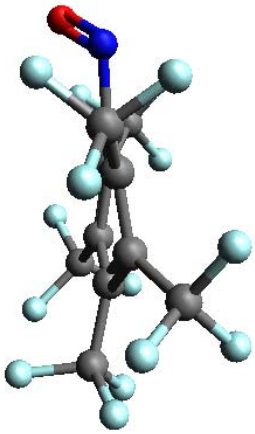


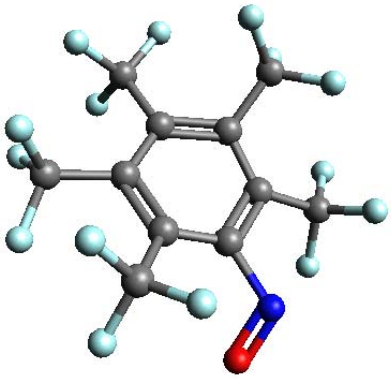
Computational Data of Pentakis(trifluoromethyl)nitrosobenzene–3



Brutoformula: $C_{11}F_{15}NO$
Basis set: def-TVZP
Kinetic energy = 2040.674074
Potential energy = -4088.243238







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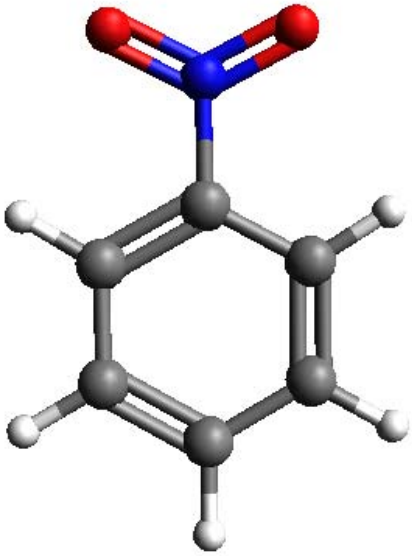
C	-2.63709878	-0.42620273	-0.18564271
C	-3.00119029	2.21236258	0.06715524
C	-10.09909792	2.74950831	-1.22755908
C	-9.45277770	-2.41693483	- 1.42854520
C	-4.48293009	-4.92835806	-0.58486514
C	0.10460456	-1.43601425	-0.48384883
C	-0.97307721	4.03877440	1.12569980
F	-9.69466673	4.28574544	-3.25810071
F	-11.22318729	4.12603855	0.59276828
F	-11.73456903	0.95364481	-2.02671589
F	-11.03635286	-0.71164872	2.51826394
F	-10.84268174	-3.88770559	-0.10891270
F	-8.54972088	-3.83576716	3.36726017
F	-6.58991929	-6.27689574	-0.12583394
F	-2.62197649	-5.95182883	0.83381359
F	-3.95200173	-5.29604416	-3.07199999
F	0.26792837	-3.30774715	-2.20966278
F	1.65614481	0.41274178	-1.34094712
F	1.03813978	-2.30408150	1.72863387
F	0.57156010	2.81758539	2.76239134
F	0.44969444	5.19350743	-0.63546019
F	-2.14793654	5.86833547	2.51055404
N	-5.99416066	6.00151870	-0.74420529
O	-4.43845493	7.11240877	-1.97135894

Computational Data of Nitrobenzene



Brutoformula: $C_6H_5NO_2$
Basis set: def-TVZP
Kinetic energy = 435.147237
Potential energy = -872.091368

atom	x	y	z
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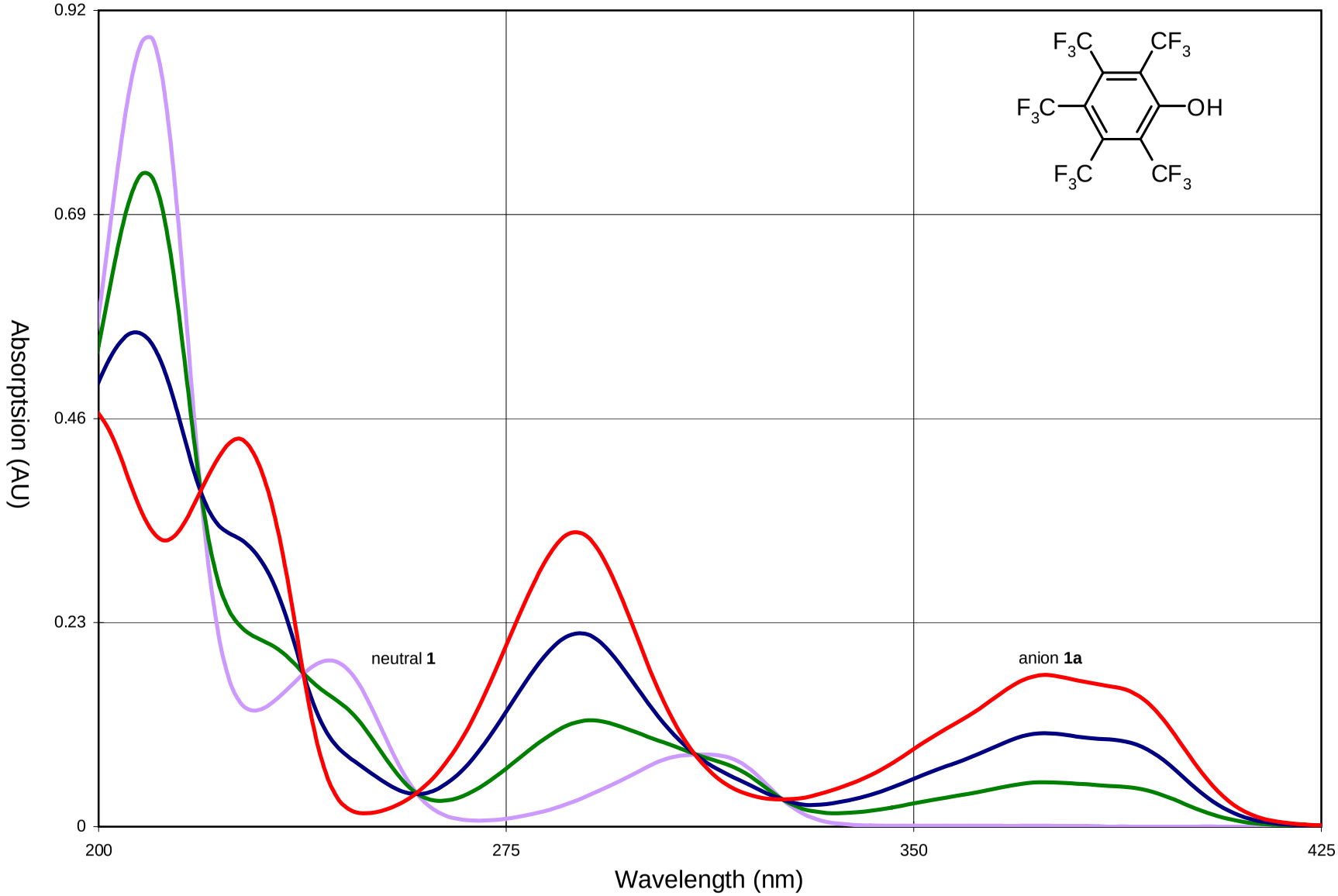
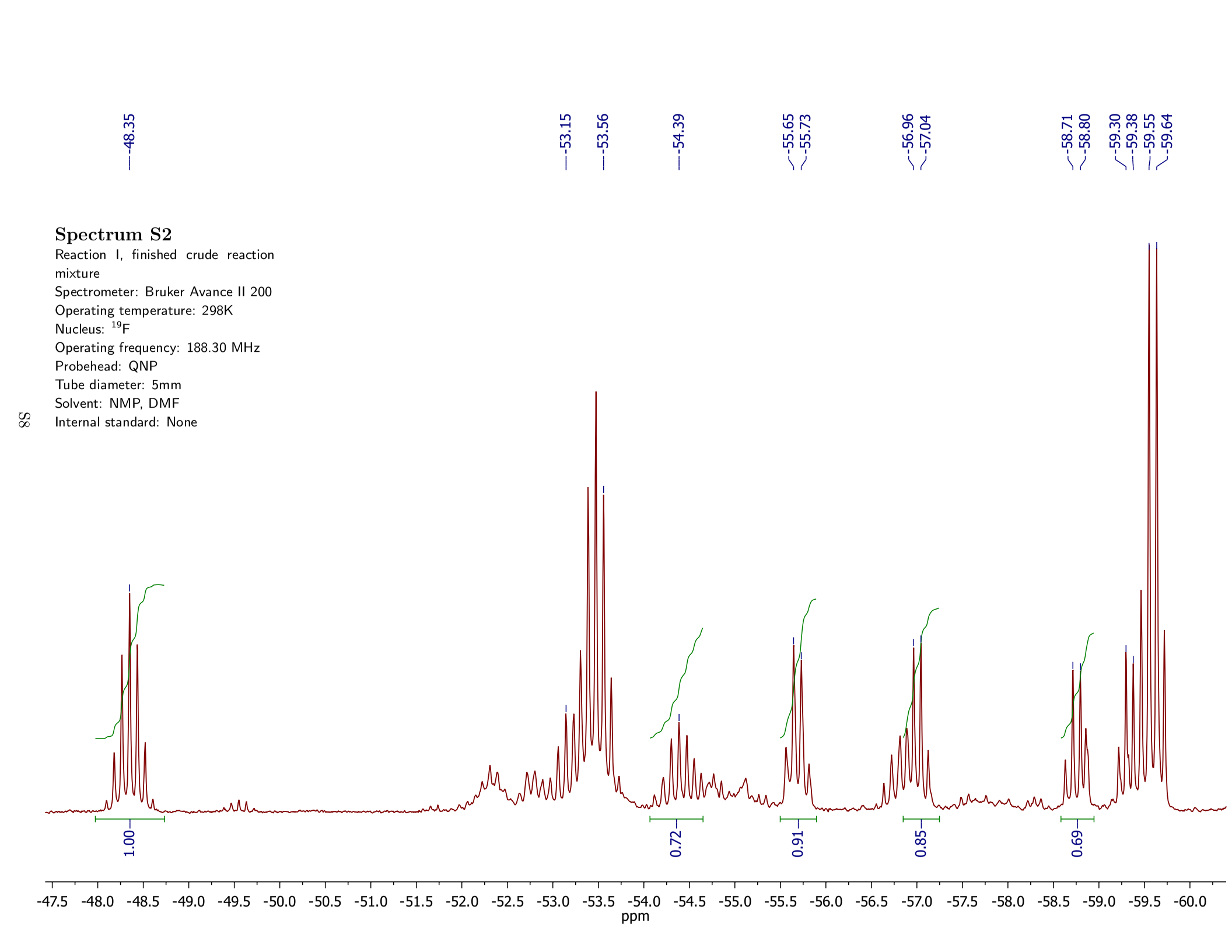
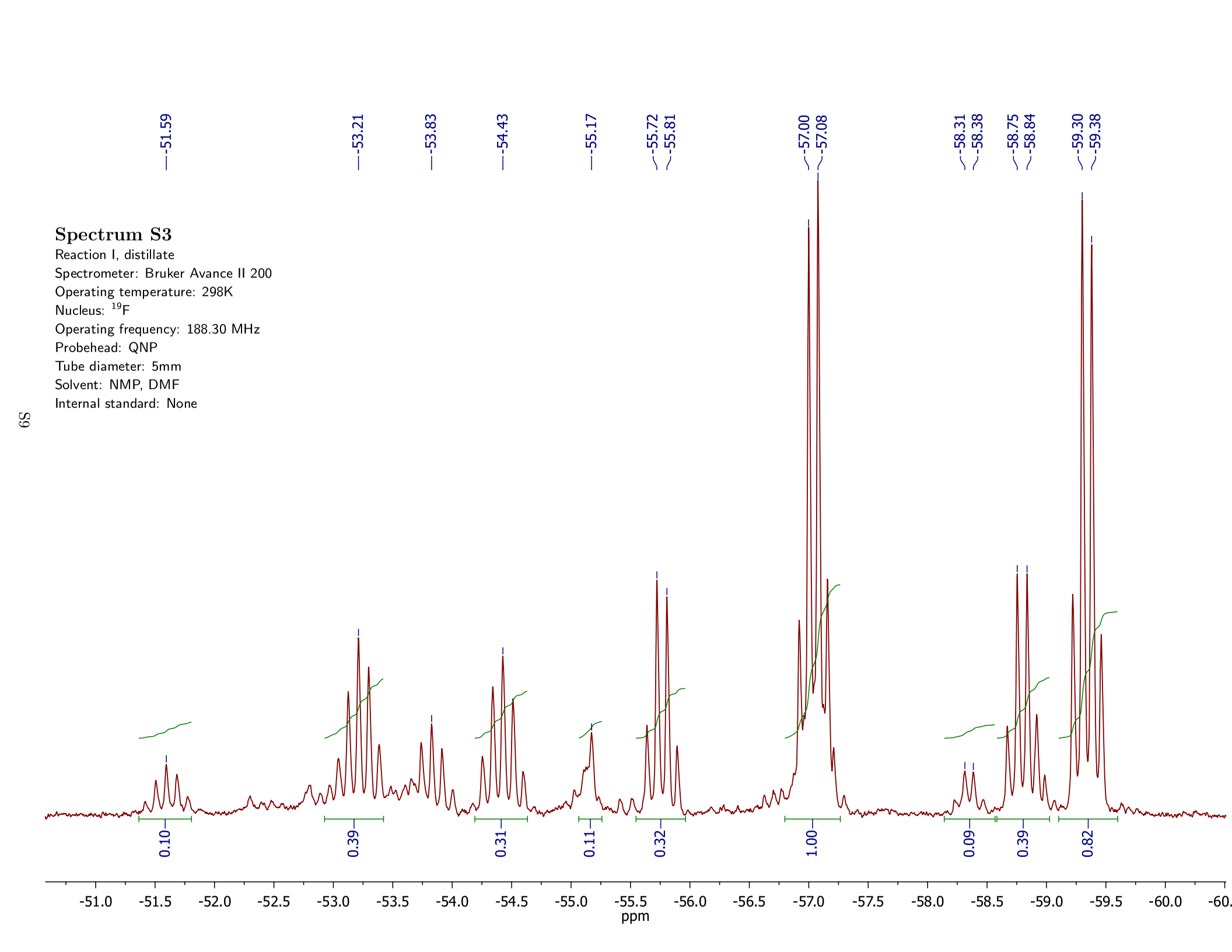
C	-7.36434812	-0.79437288	0.13677610
C	-4.97788122	-1.92077186	-0.04060586
C	-2.79988039	-0.42336425	-0.14764845
C	-2.99293873	2.20617495	-0.07862633
N	-5.61523893	6.09448186	0.17677865
O	-7.76191276	7.00541369	0.33886251
O	-3.64023321	7.34156870	0.07587790
H	-0.94191596	-1.30511717	-0.28502367
H	-1.33602725	3.42367257	-0.15925707
H	-4.81410173	-3.97542657	-0.09575971
H	-9.05903883	-1.96422774	0.22098971
H	-9.41689141	2.76805155	0.34436079

Spectrum S1

UV-Vis spectra of pentakis(trifluoromethyl)phenol **1** titrated with a base triethylamine to obtain phenolate **1a** in acetonitrile.

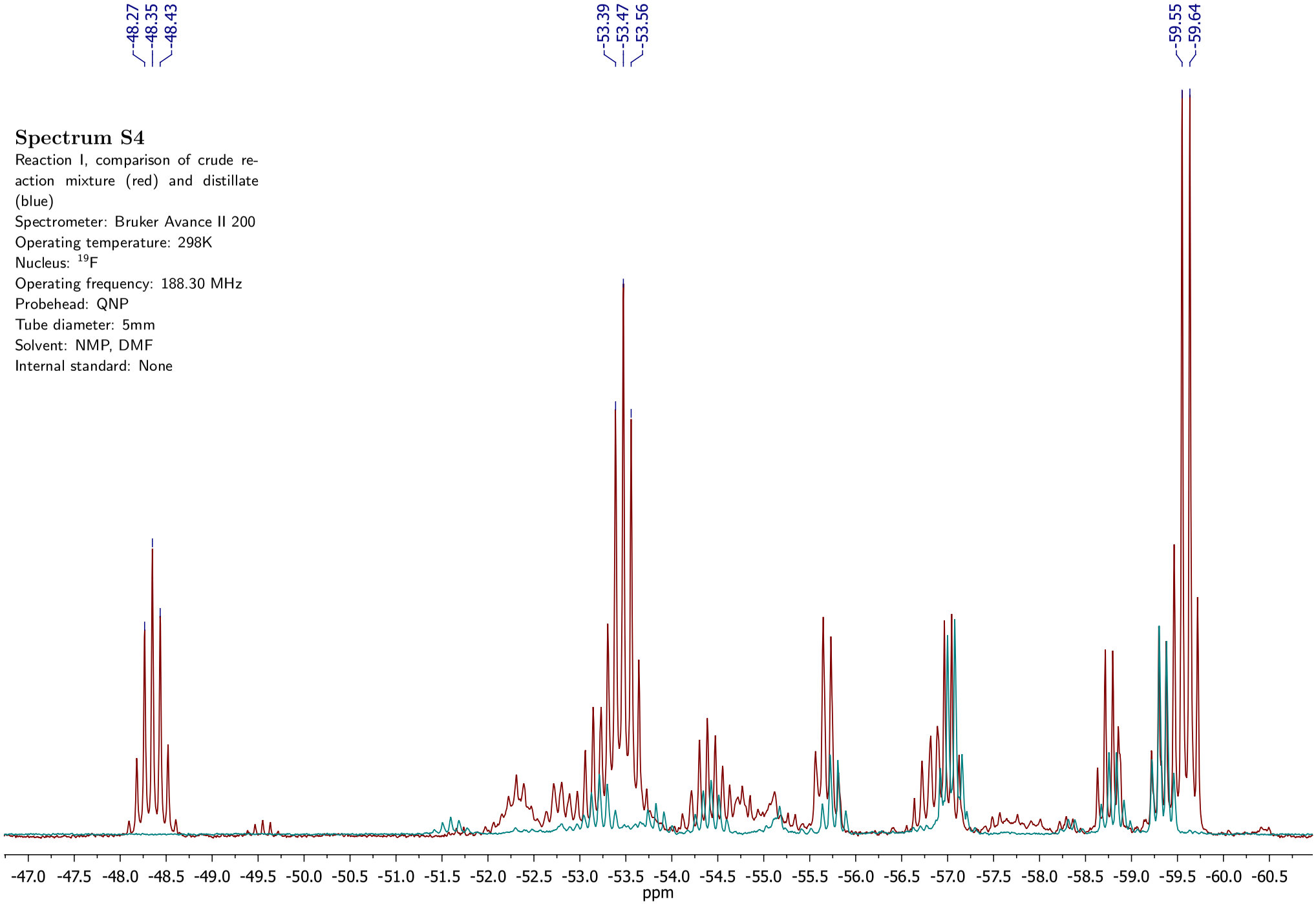


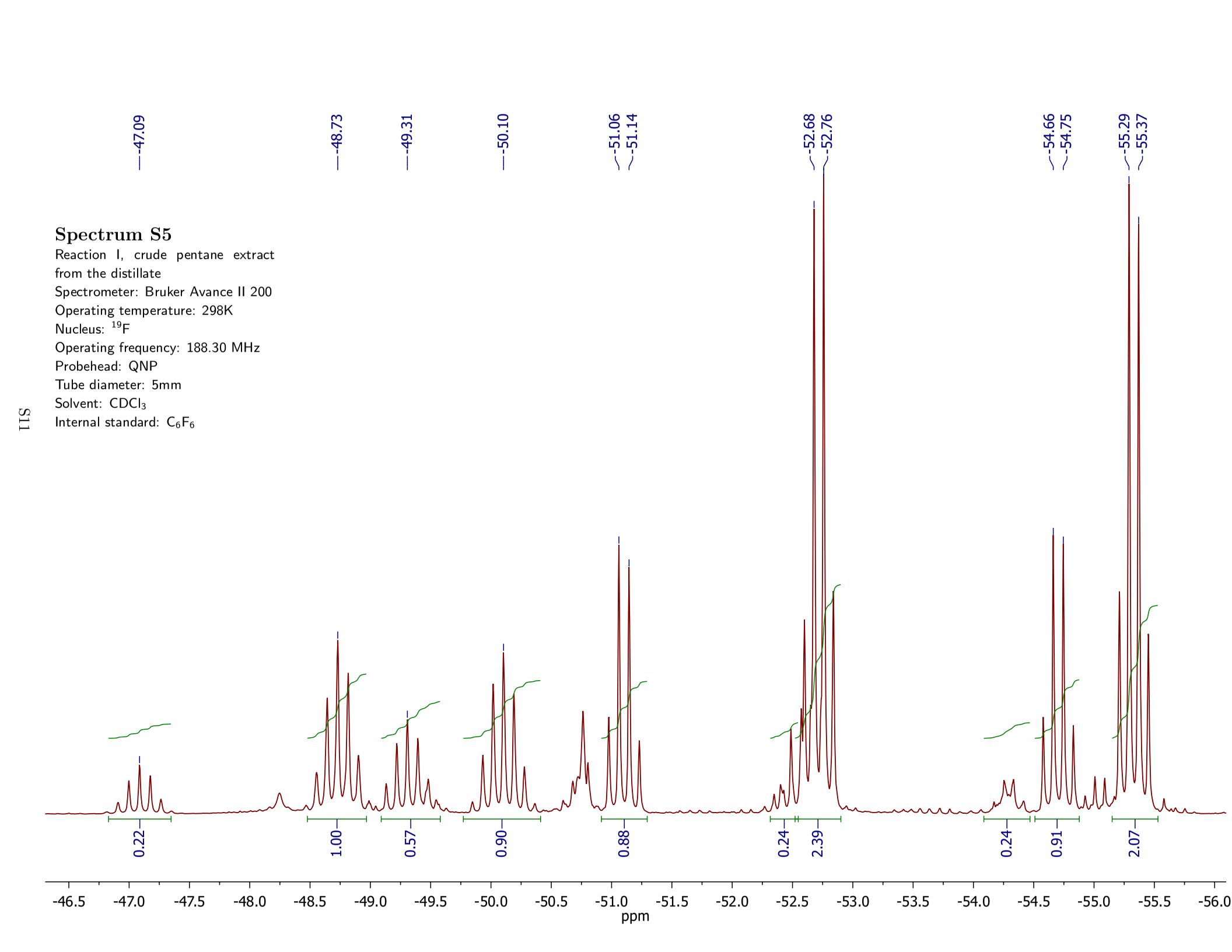

-48.35
-53.15
-53.56
-54.39
-55.65
-55.73
-56.96
-57.04
-58.71
-58.80
-59.30
-59.38
-59.55
-59.64
Spectrum S2
Reaction I, finished crude reaction mixture
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: 19F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None
8S
1.00
0.72
0.91
0.85
0.69
-47.5 -48.0 -48.5 -49.0 -49.5 -50.0 -50.5 -51.0 -51.5 -52.0 -52.5 -53.0 -53.5 -54.0 -54.5 -55.0 -55.5 -56.0 -56.5 -57.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0
ppm


-51.59
-53.21
-53.83
-54.43
-55.17
-55.72
-55.81
-57.00
-57.08
-58.31
-58.38
-58.75
-58.84
-59.30
-59.38
Spectrum S3
Reaction I, distillate
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: 19F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None
6S
0.10
0.39
0.31
0.11
0.32
1.00
0.09
0.39
0.82
-51.0
-51.5
-52.0
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
ppm

Spectrum S4

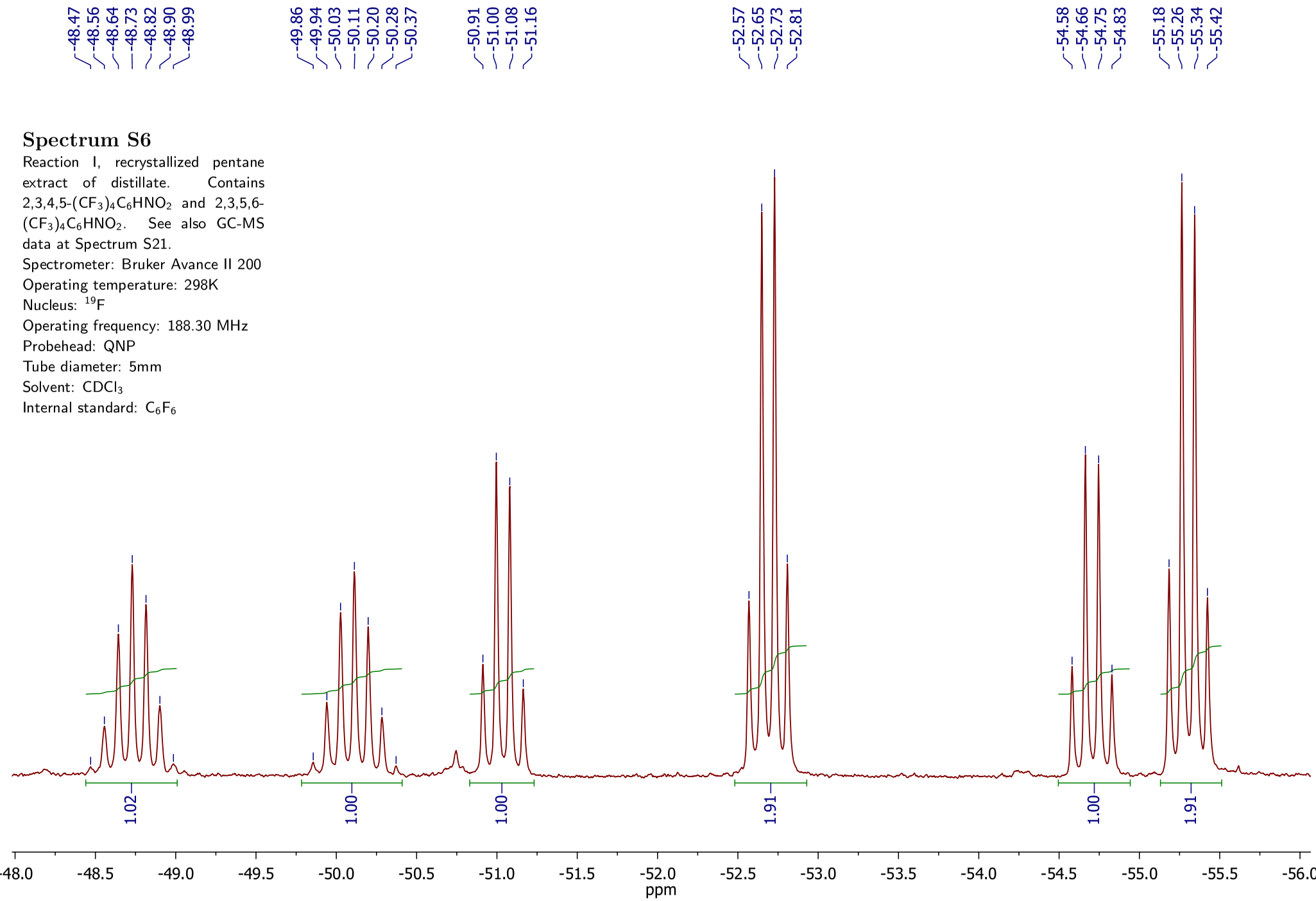
Reaction I, comparison of crude reaction mixture (red) and distillate (blue)
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None




-47.09
-48.73
-49.31
-50.10
-51.06
-51.14
-52.68
-52.76
-54.66
-54.75
-55.29
-55.37
Spectrum S5
Reaction I, crude pentane extract from the distillate
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: 19F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: CDCl3
Internal standard: C6F6
0.22
1.00
0.57
0.90
0.88
0.24
2.39
0.24
0.91
2.07
-46.5
-47.0
-47.5
-48.0
-48.5
-49.0
-49.5
-50.0
-50.5
-51.0
-51.5
-52.0
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
ppm

Spectrum S6

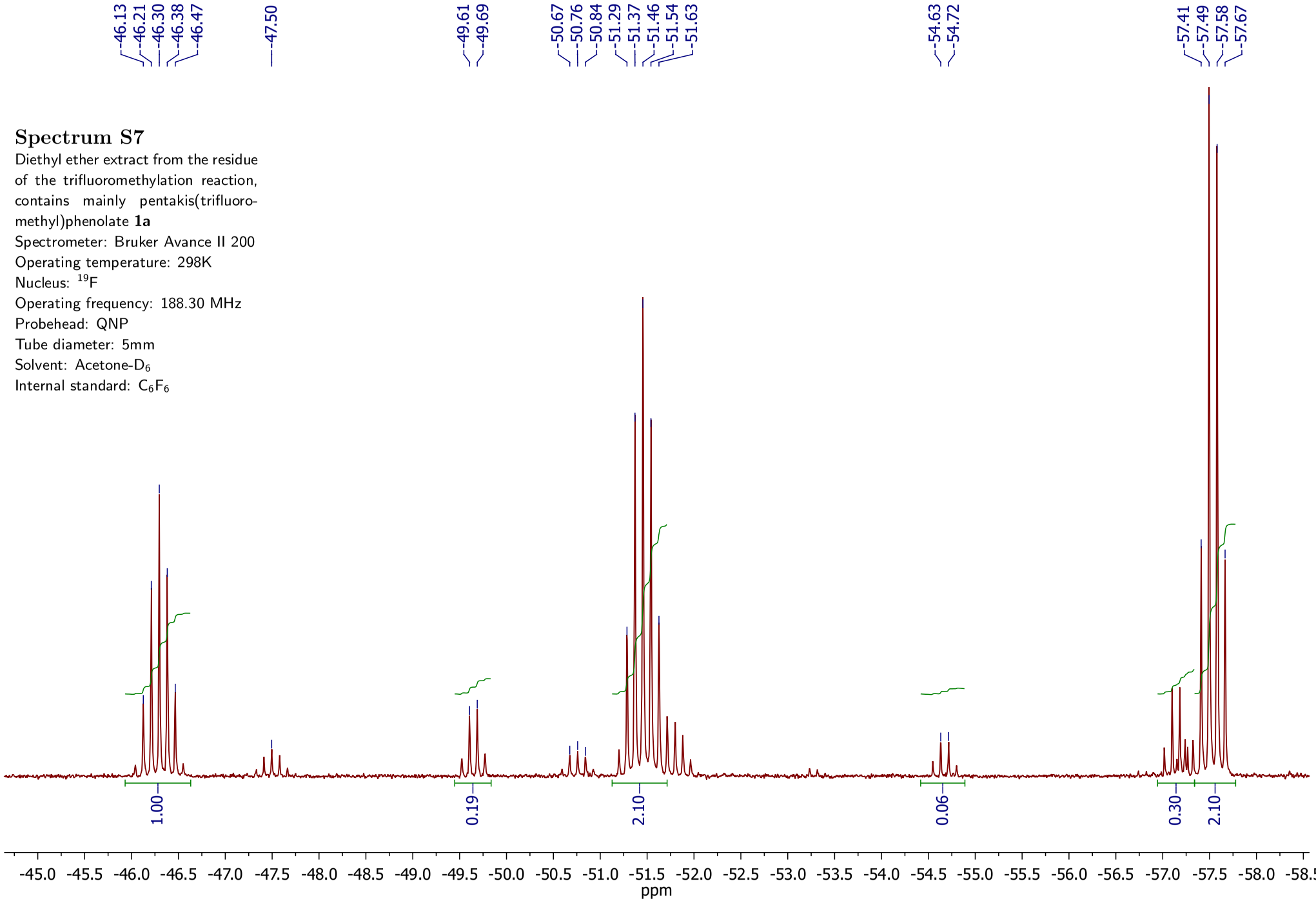
Reaction I, recrystallized pentane extract of distillate. Contains 2,3,4,5-$(CF_3)_4C_6HNO_2$ and 2,3,5,6-$(CF_3)_4C_6HNO_2$. See also GC-MS data at Spectrum S21.
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: $CDCl_3$
Internal standard: C_6F_6



Spectrum S7

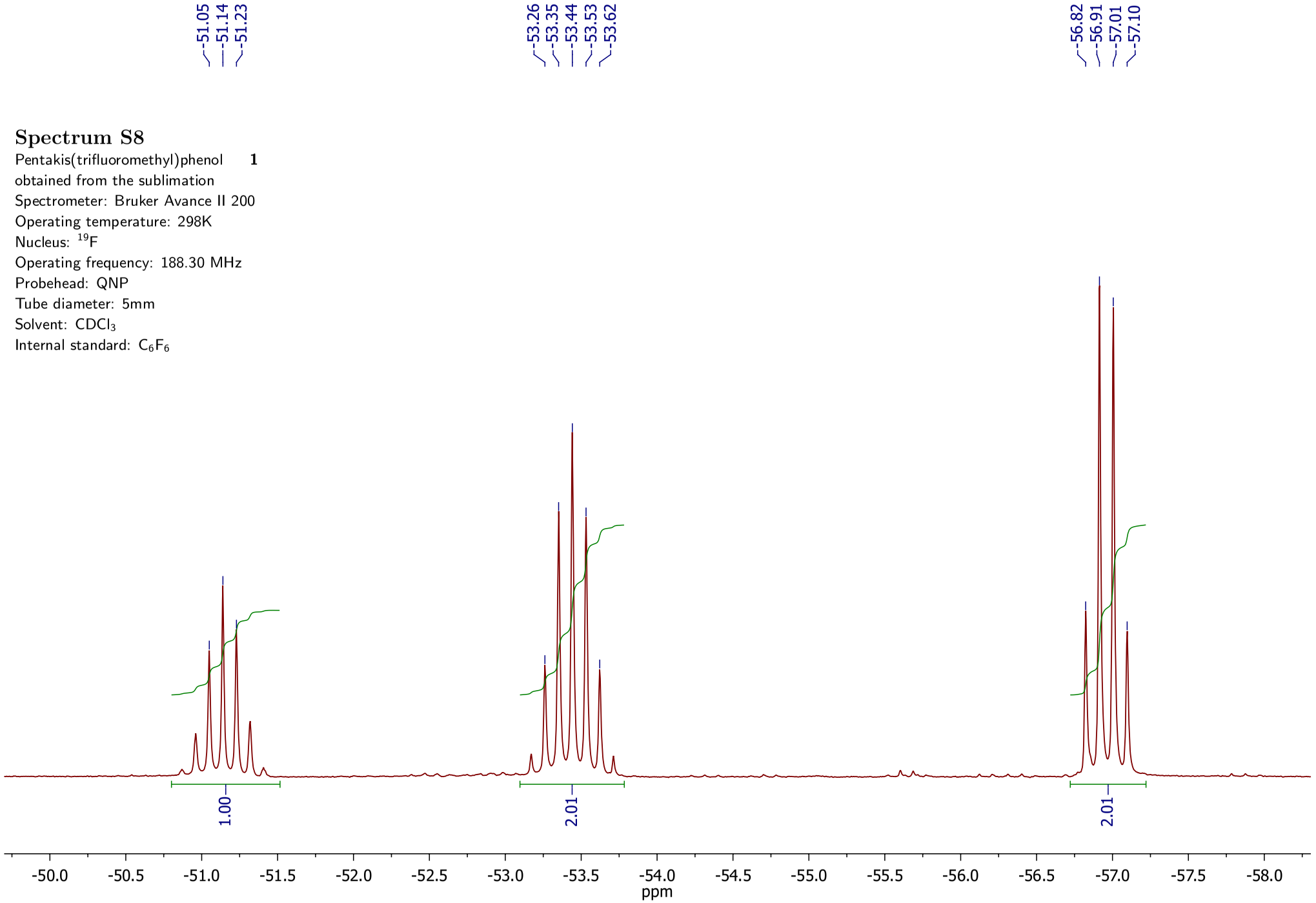
Diethyl ether extract from the residue of the trifluoromethylation reaction, contains mainly pentakis(trifluoromethyl)phenolate **1a**

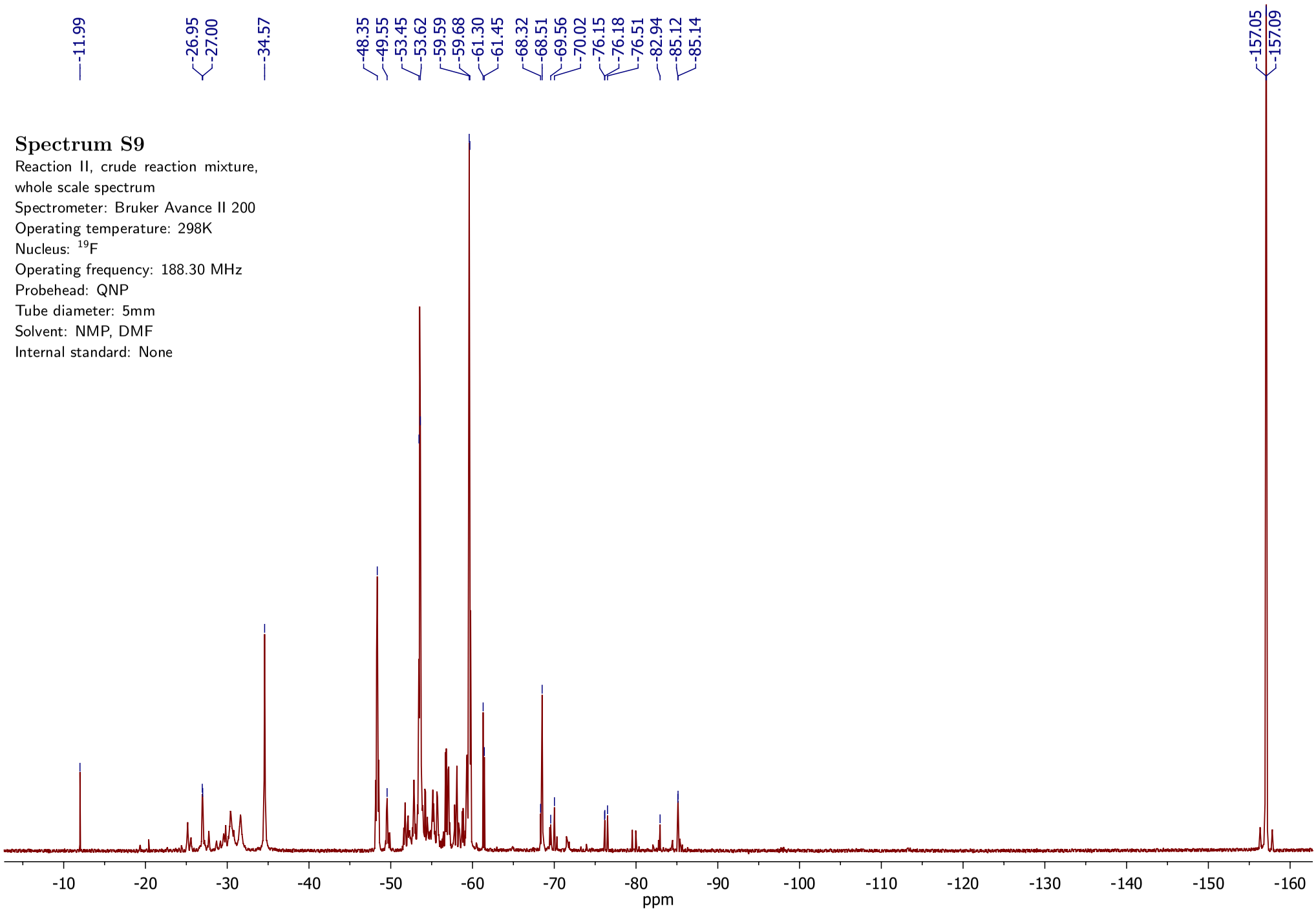
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: Acetone-D_6
Internal standard: C_6F_6



Spectrum S8

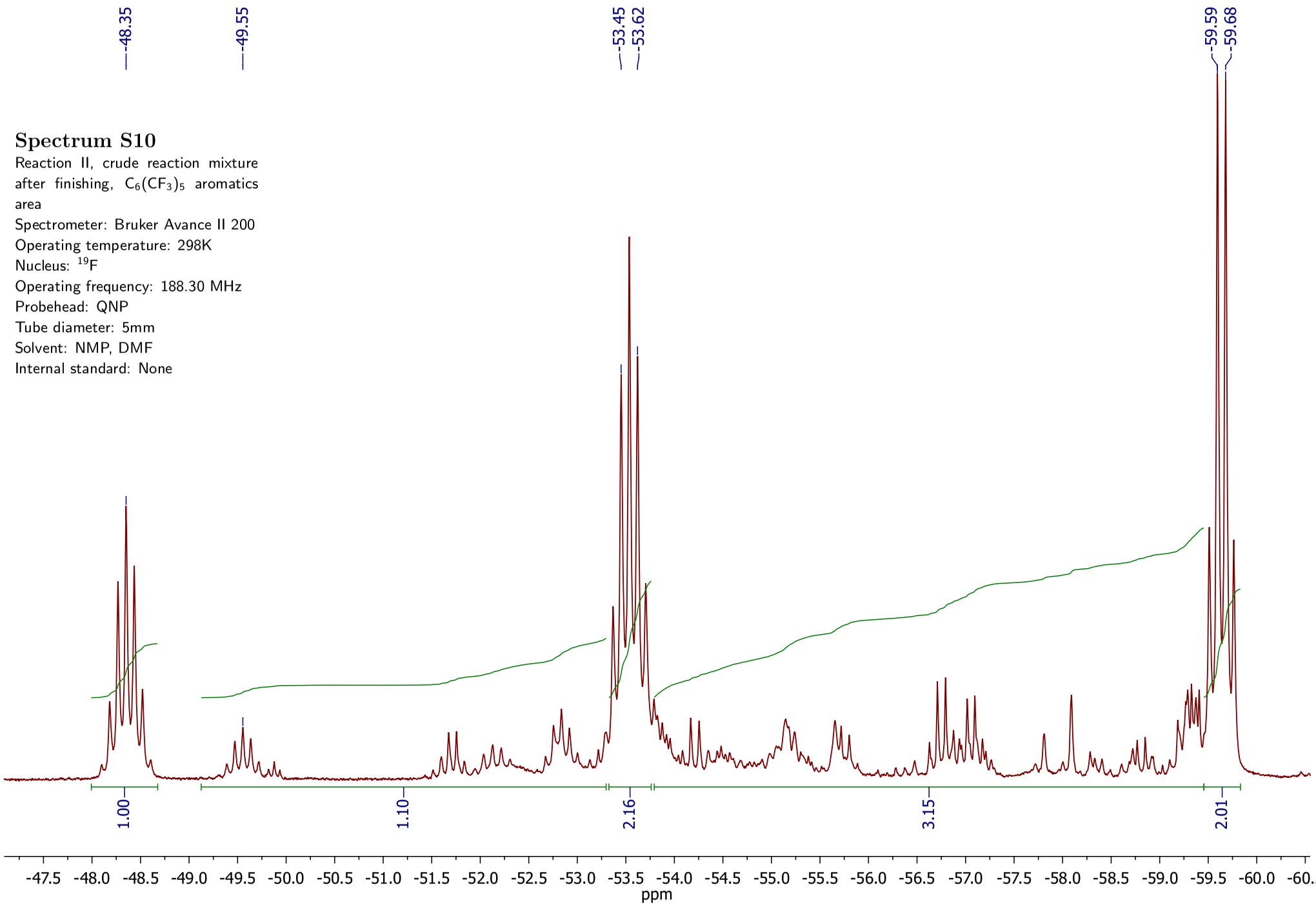
Pentakis(trifluoromethyl)phenol **1**
obtained from the sublimation
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: $CDCl_3$
Internal standard: C_6F_6





Spectrum S9

Reaction II, crude reaction mixture, whole scale spectrum
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None



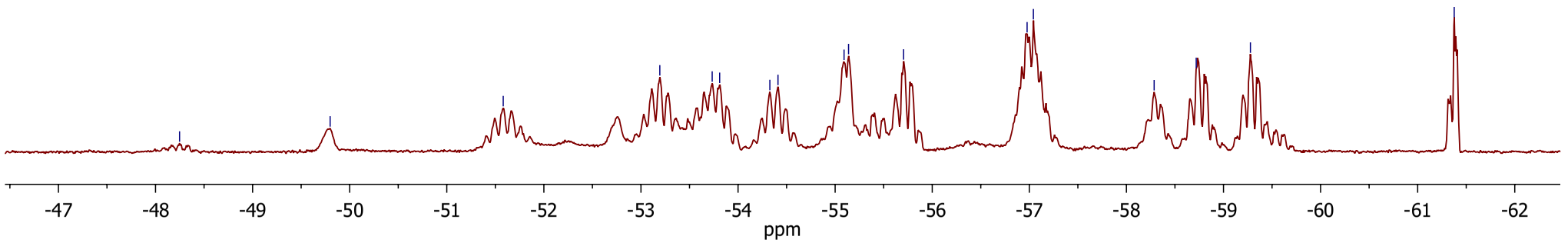
Spectrum S10

Reaction II, crude reaction mixture after finishing, $C_6(CF_3)_5$ aromatics area

Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None

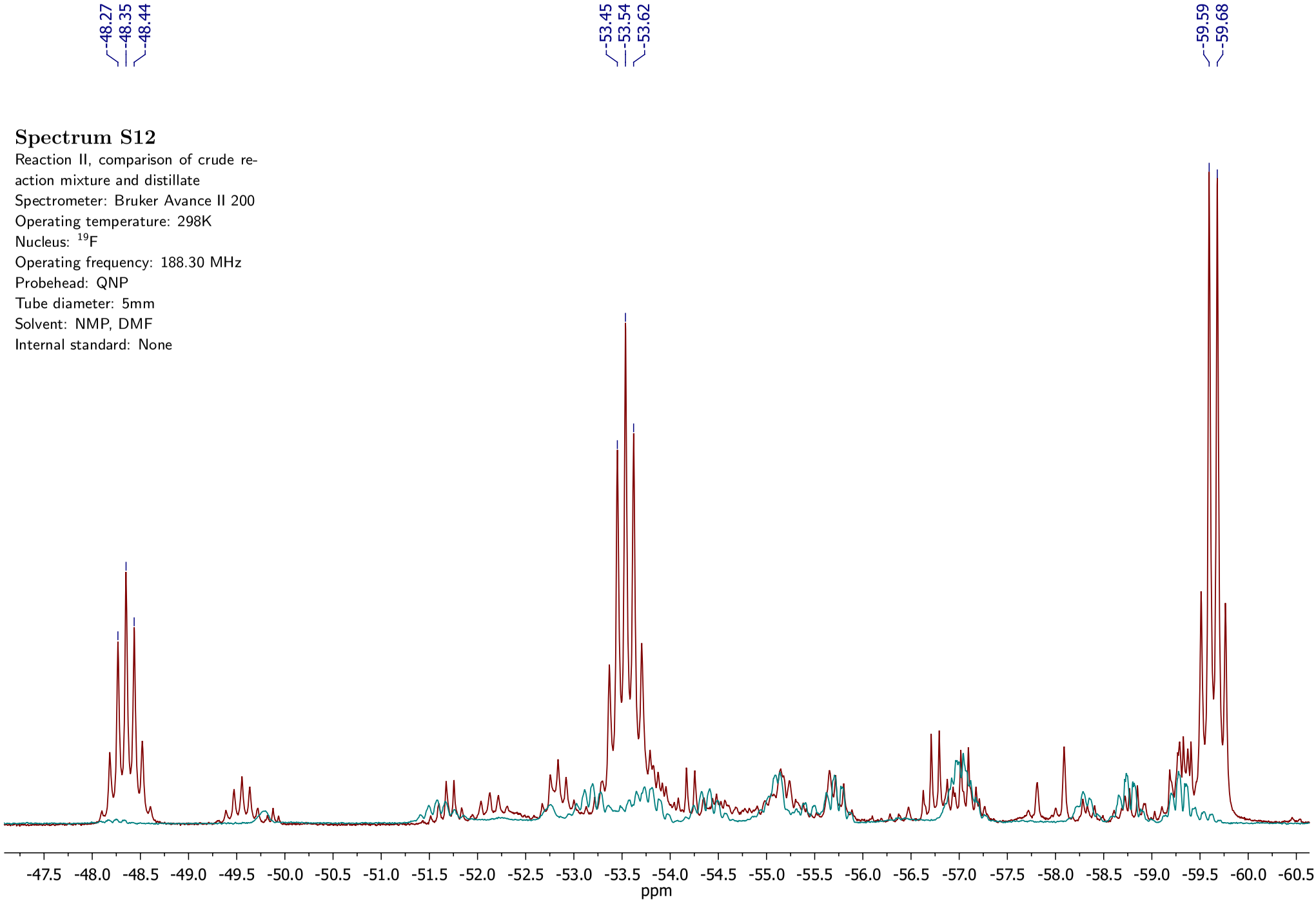
Spectrum S11

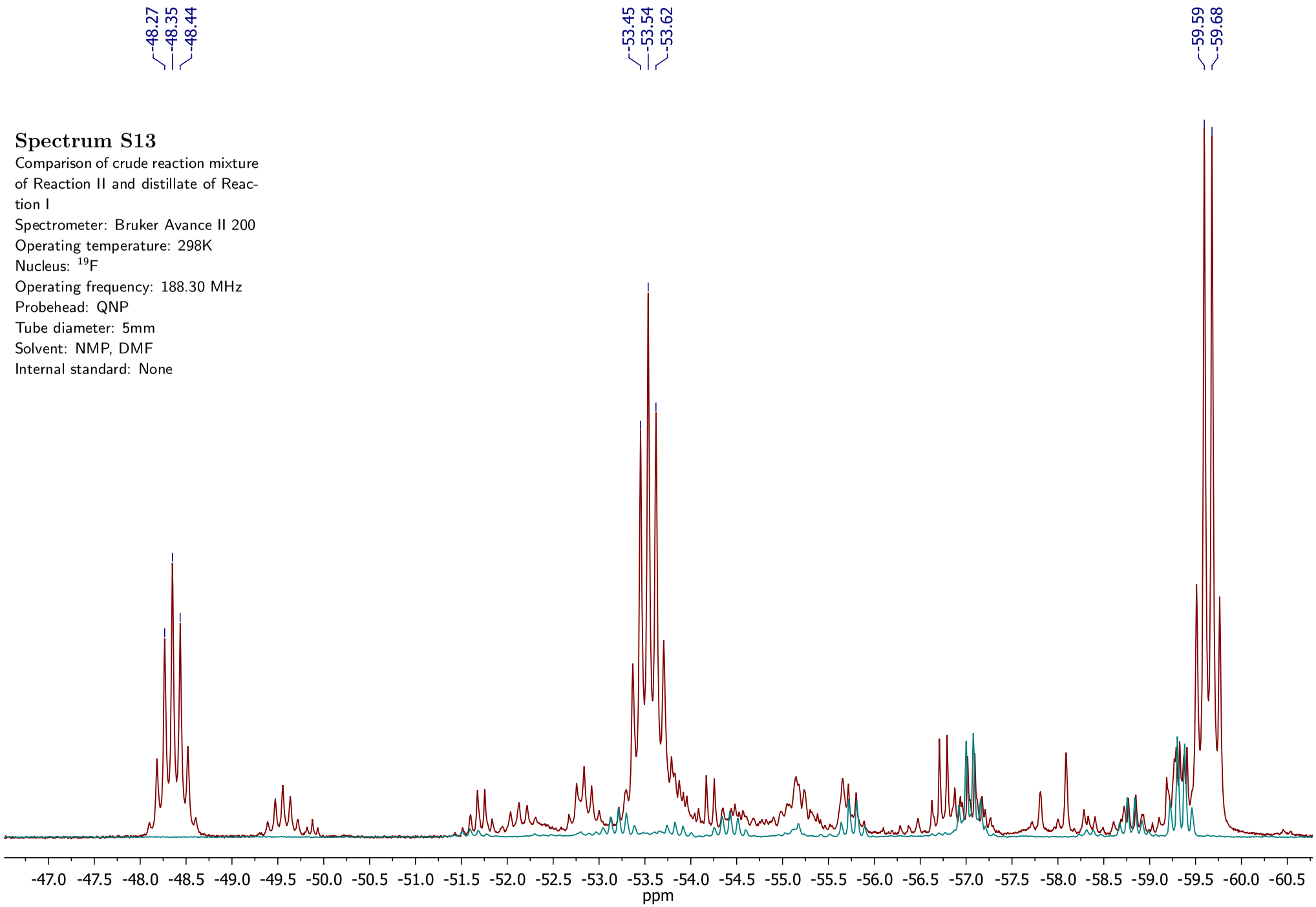
Reaction II, distillate
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None



Spectrum S12

Reaction II, comparison of crude reaction mixture and distillate
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None





Spectrum S13

Comparison of crude reaction mixture of Reaction II and distillate of Reaction I

Spectrometer: Bruker Avance II 200

Operating temperature: 298K

Nucleus: ^{19}F

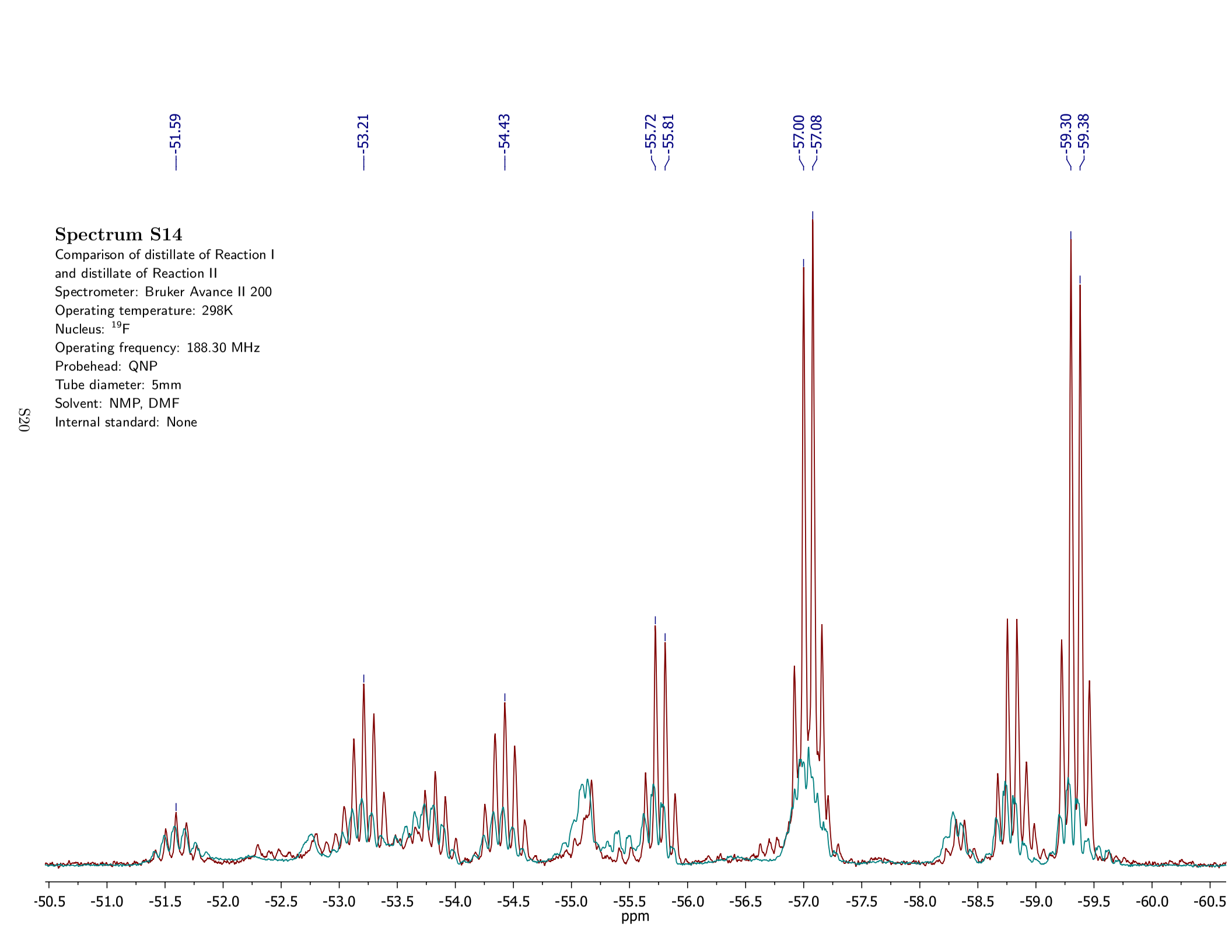
Operating frequency: 188.30 MHz

Probehead: QNP

Tube diameter: 5mm

Solvent: NMP, DMF

Internal standard: None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-53.21
-54.43
-55.72
-55.81
-57.00
-57.08
-59.30
-59.38
Spectrum S14
Comparison of distillate of Reaction I
and distillate of Reaction II
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: 19F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: NMP, DMF
Internal standard: None
S20
-50.5
-51.0
-51.5
-52.0
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
-56.5
-57.0
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-58.0
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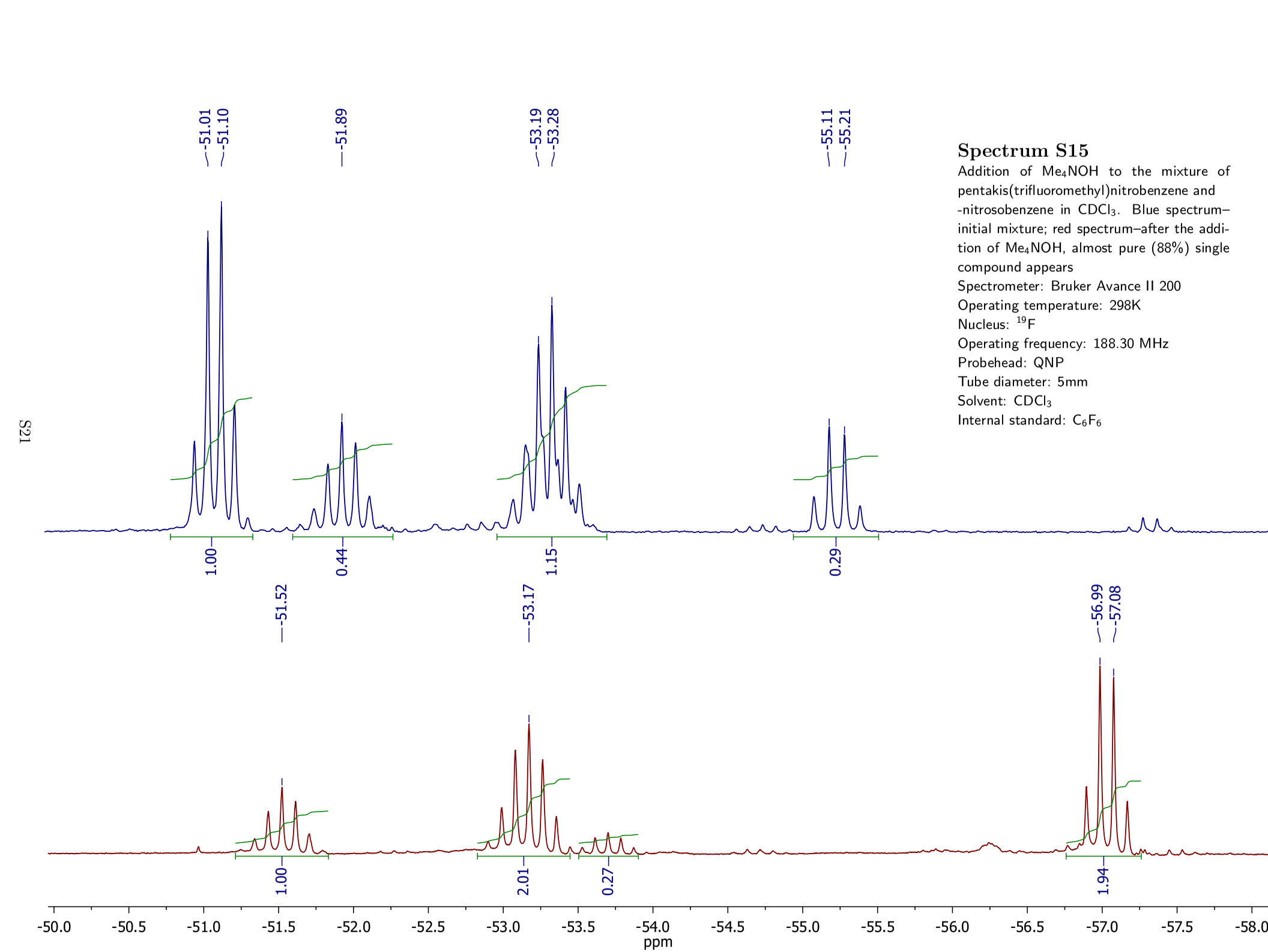
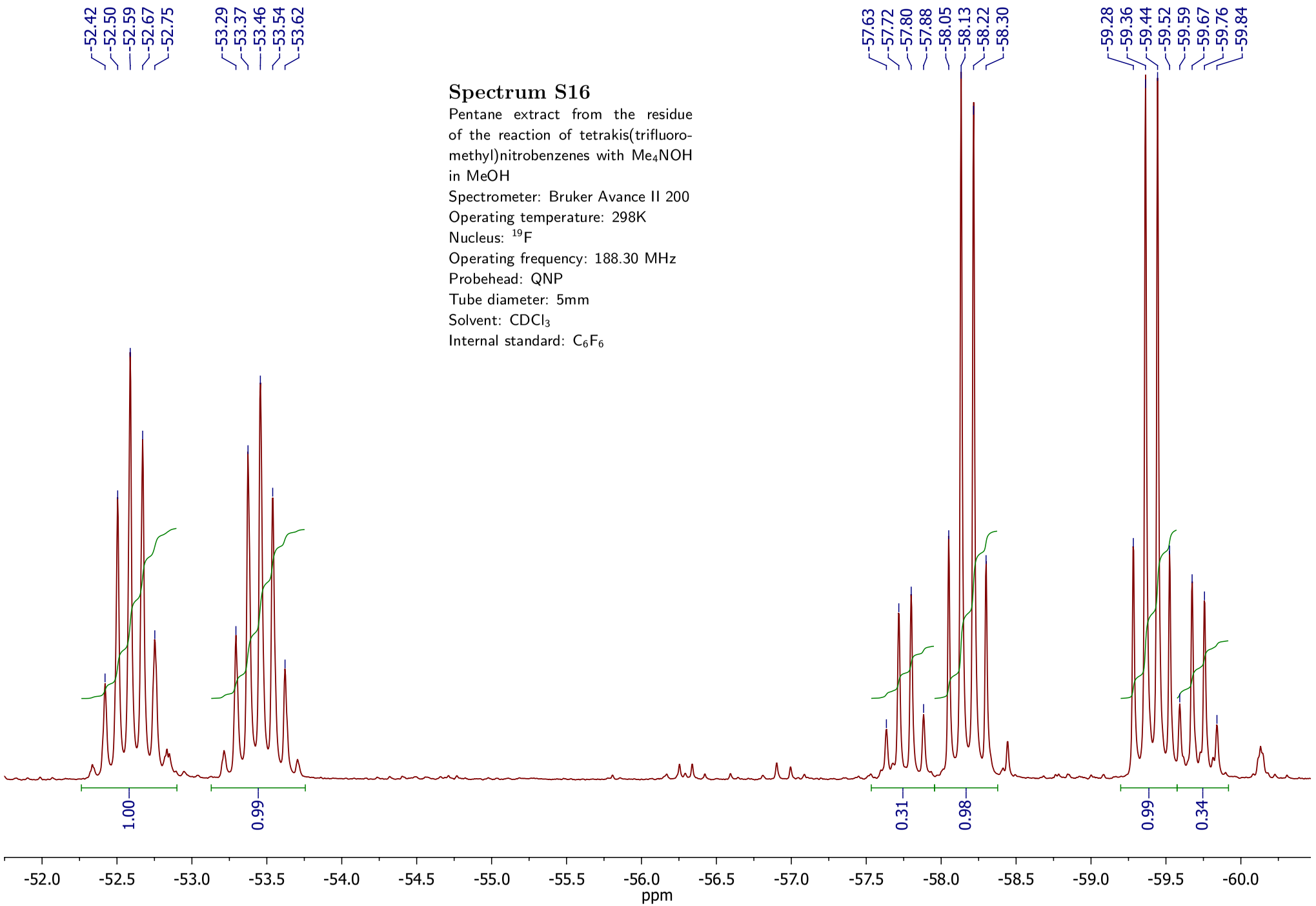
-59.0
-59.5
-60.0
-60.5
ppm



Spectrum S15

Addition of Me_4NOH to the mixture of pentakis(trifluoromethyl)nitrobenzene and -nitrosobenzene in $CDCl_3$. Blue spectrum–initial mixture; red spectrum–after the addition of Me_4NOH, almost pure (88%) single compound appears

Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: ^{19}F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: $CDCl_3$
Internal standard: C_6F_6



Spectrum S16

Pentane extract from the residue of the reaction of tetrakis(trifluoromethyl)nitrobenzenes with Me_4NOH in MeOH

Spectrometer: Bruker Avance II 200

Operating temperature: 298K

Nucleus: ^{19}F

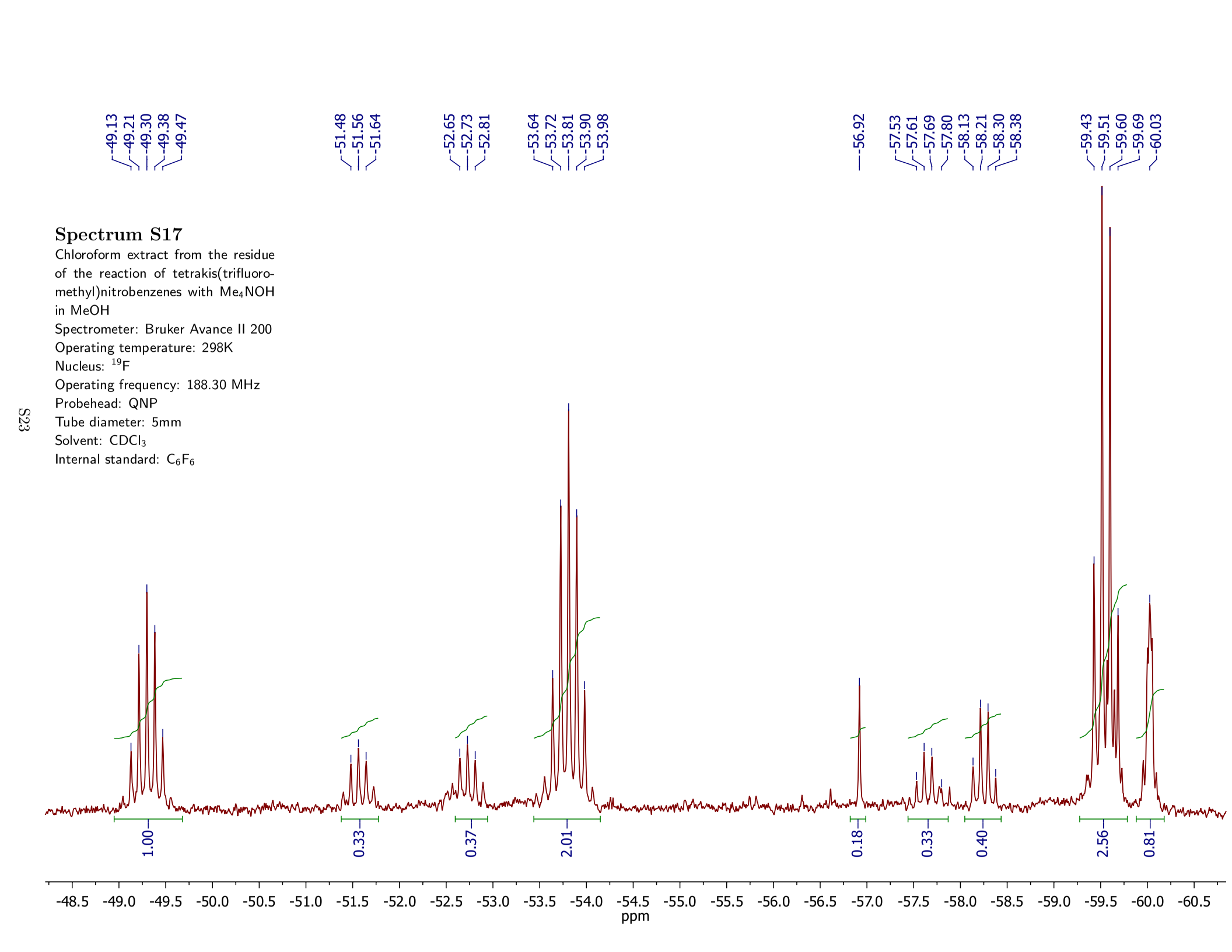
Operating frequency: 188.30 MHz

Probehead: QNP

Tube diameter: 5mm

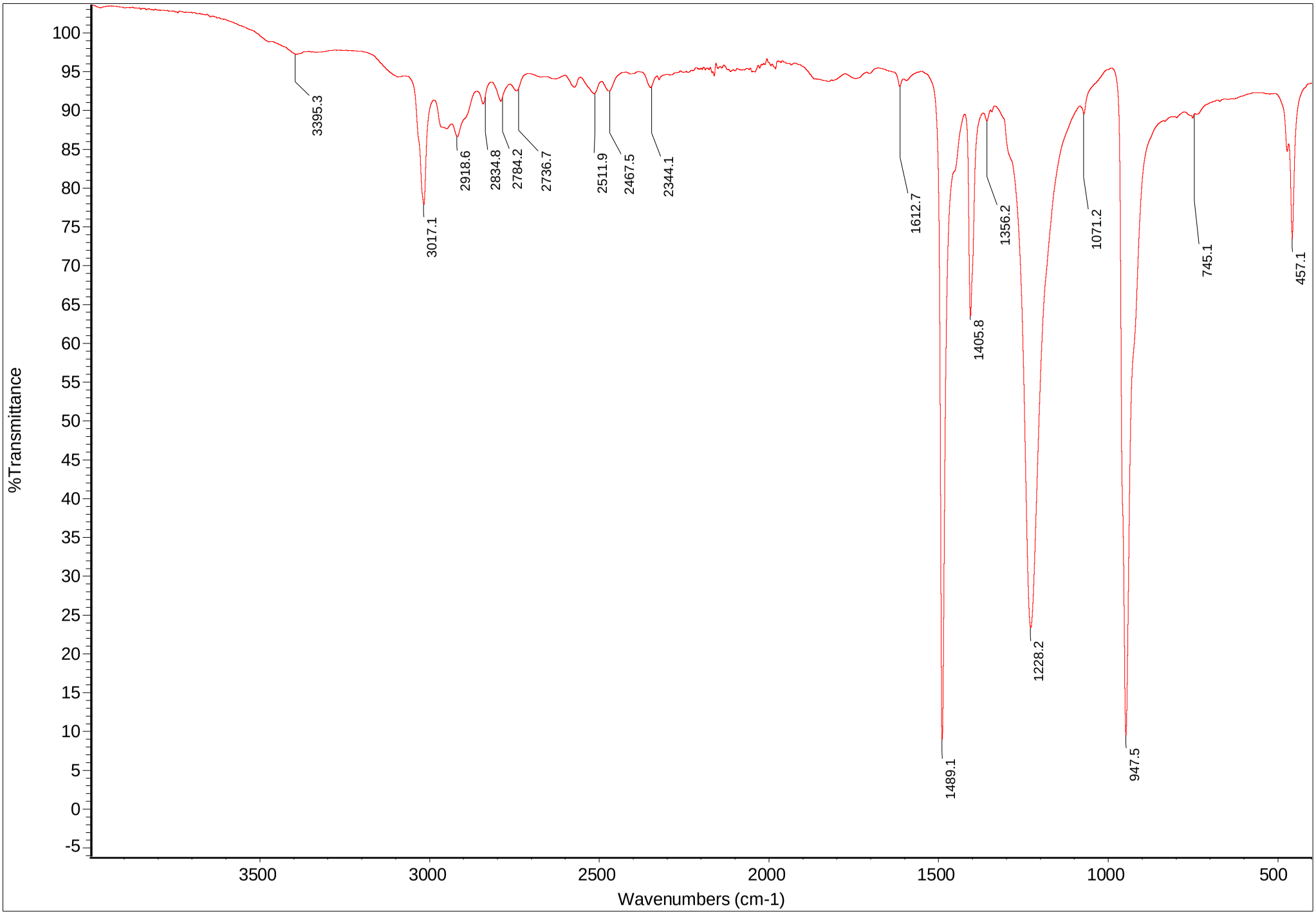
Solvent: $CDCl_3$

Internal standard: C_6F_6


-49.13
-49.21
-49.30
-49.38
-49.47
-51.48
-51.56
-51.64
-52.65
-52.73
-52.81
-53.64
-53.72
-53.81
-53.90
-53.98
-56.92
-57.53
-57.61
-57.69
-57.80
-58.13
-58.21
-58.30
-58.38
-59.43
-59.51
-59.60
-59.69
-60.03
Spectrum S17
Chloroform extract from the residue of the reaction of tetrakis(trifluoromethyl)nitrobenzenes with Me4NOH in MeOH
Spectrometer: Bruker Avance II 200
Operating temperature: 298K
Nucleus: 19F
Operating frequency: 188.30 MHz
Probehead: QNP
Tube diameter: 5mm
Solvent: CDCl3
Internal standard: C6F6
1.00
0.33
0.37
2.01
0.18
0.33
0.40
2.56
0.81
-48.5 -49.0 -49.5 -50.0 -50.5 -51.0 -51.5 -52.0 -52.5 -53.0 -53.5 -54.0 -54.5 -55.0 -55.5 -56.0 -56.5 -57.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5
ppm

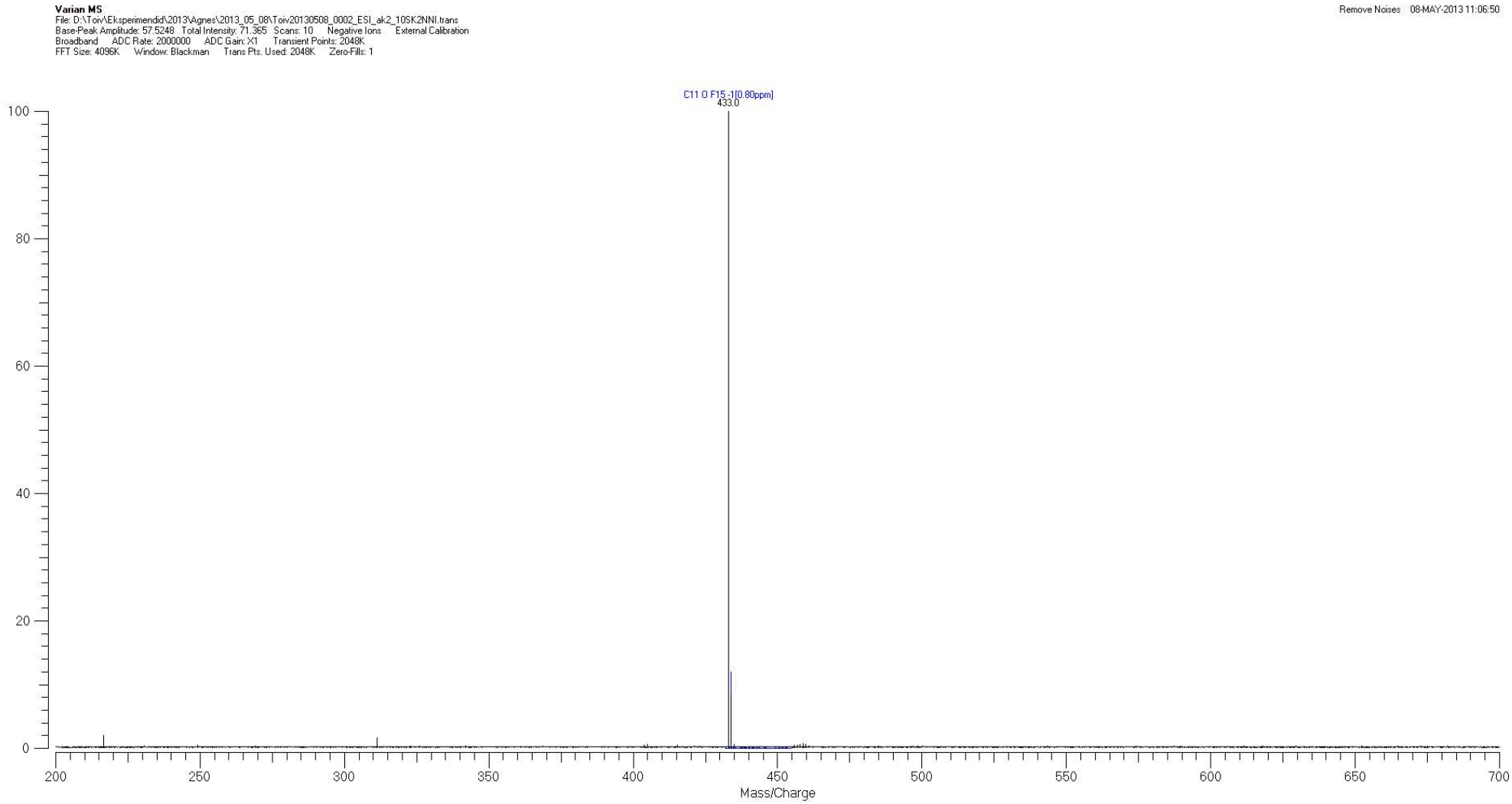
Spectrum S18

IR-ATR spectrum of $Me_4N\ NO_3$ obtained after the reaction of tetrakis(trifluoromethyl)nitrosobenzenes with Me_4NOH in MeOH; Solid that is obtained after removal of MeOH and extraction with pentane and chloroform.



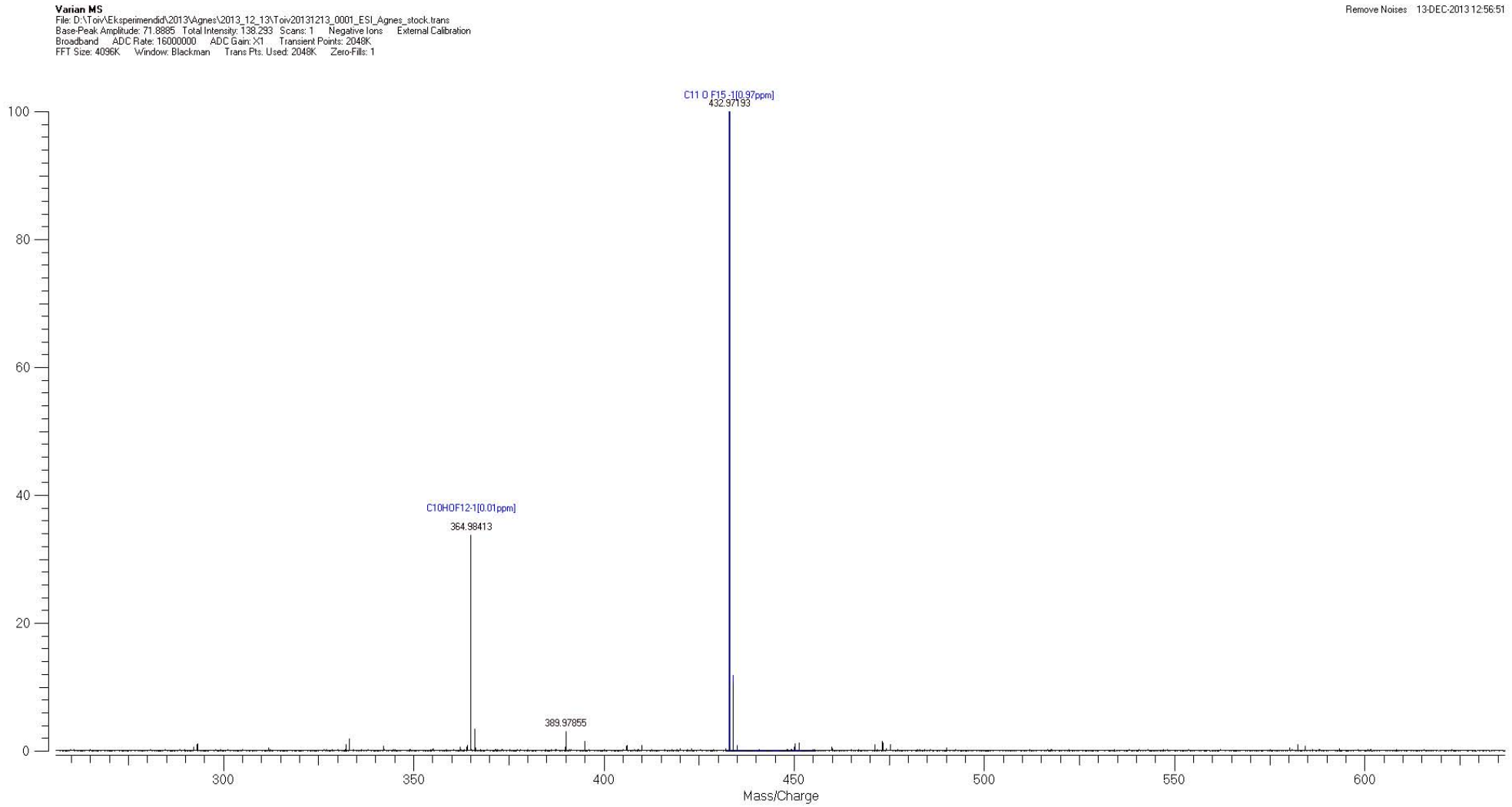
Spectrum S19

ESI-HRMS spectrum at negative mode of the crystal obtained from the NMR tube after the reaction of the mixture of pentakis(trifluoromethyl)nitrobenzene **2** and -nitrosobenzene **3** with Me_4NOH in $CDCl_3$. According to the results it is pure tetramethylammonium pentakis(trifluoromethyl)phenolate **1a**.



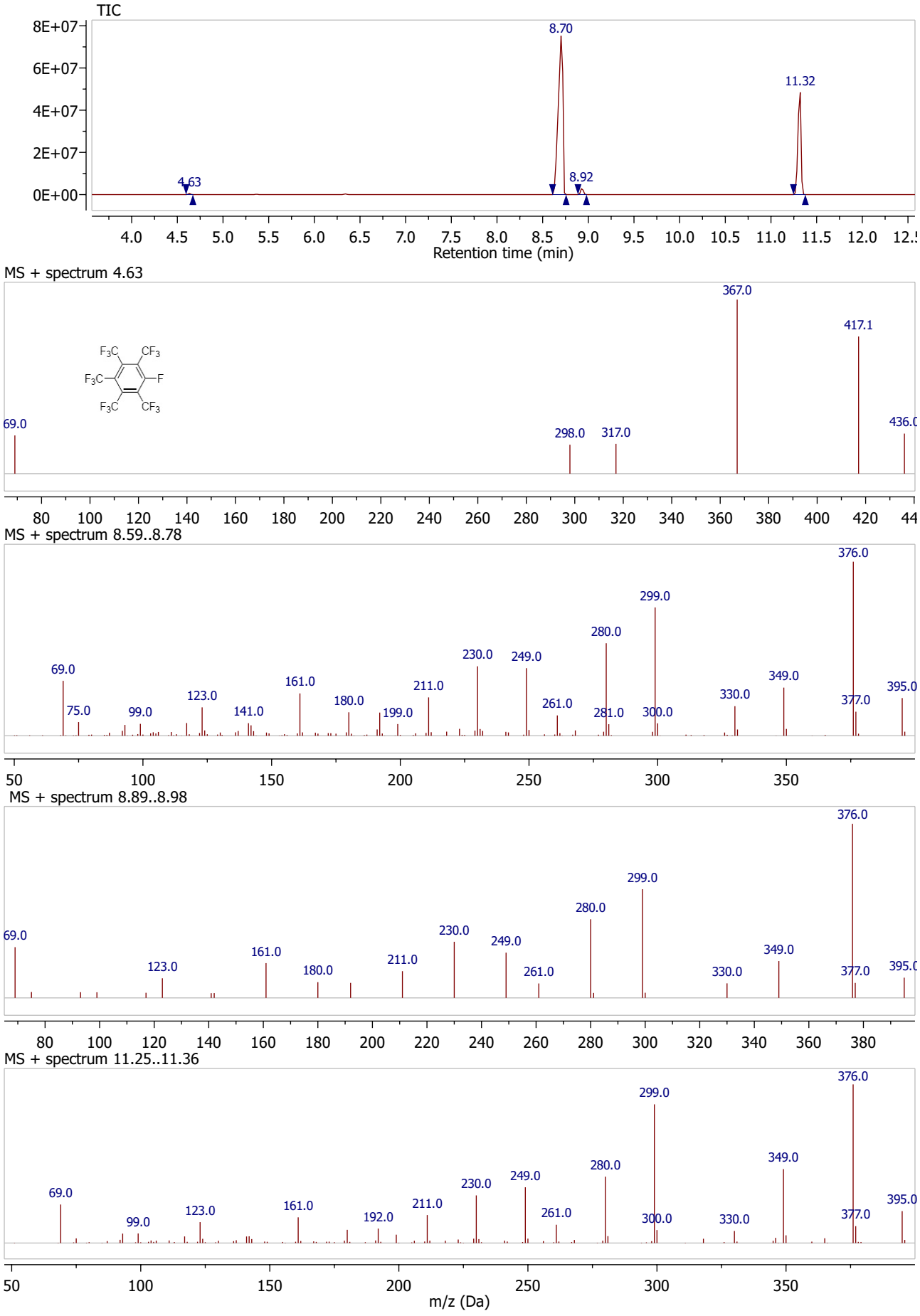
Spectrum S20

ESI-HRMS spectum of the chloroform extract obtained after reaction of two isomers of tetrakis(trifluoromethyl)nitrobenzenes with Me_4NOH in MeOH. Results show that these two peaks belong to the tetrakis(trifluoromethyl)phenolate and pentakis(trifluoromethyl)phenolate **1a**.



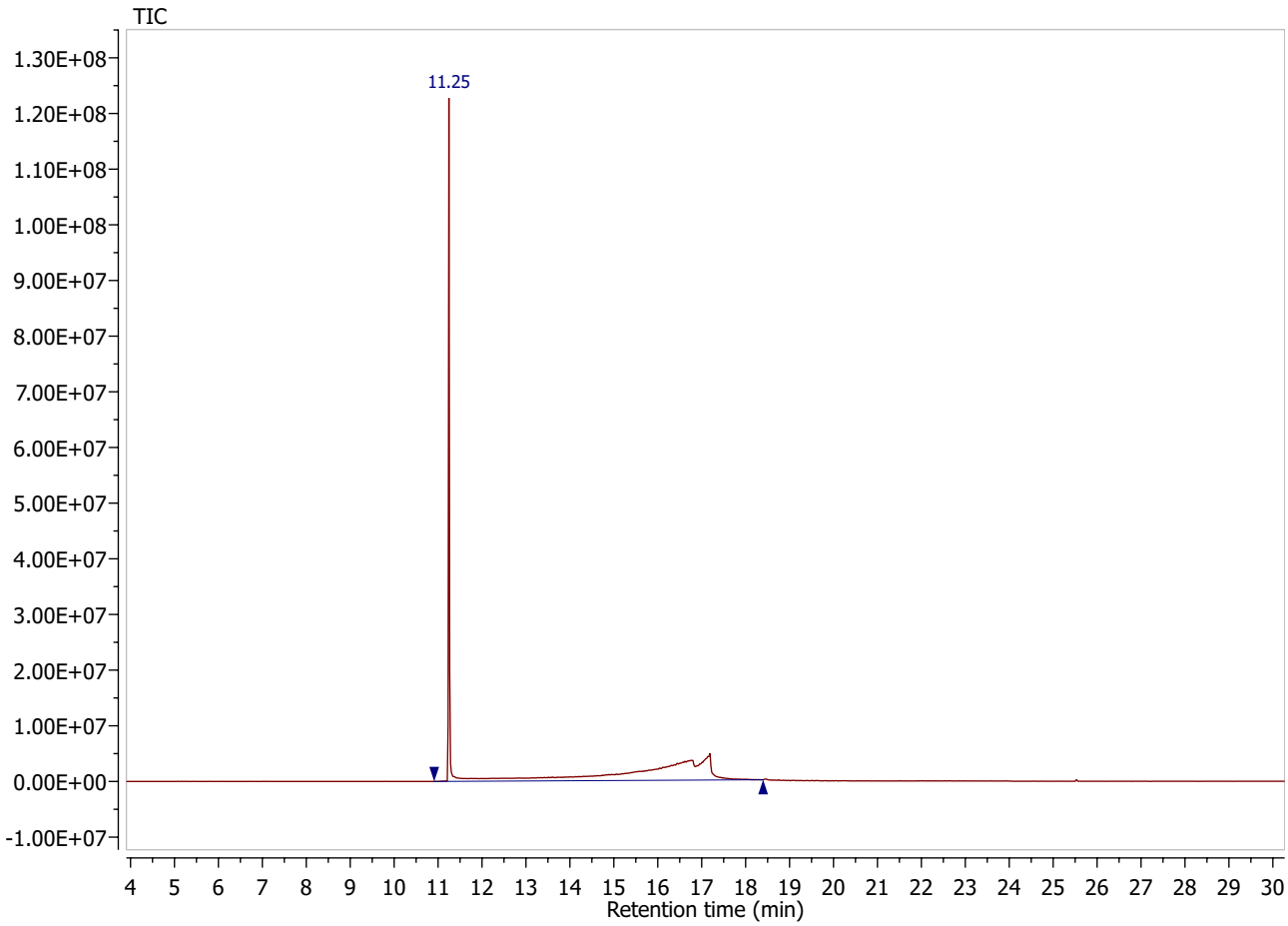
Spectrum S21

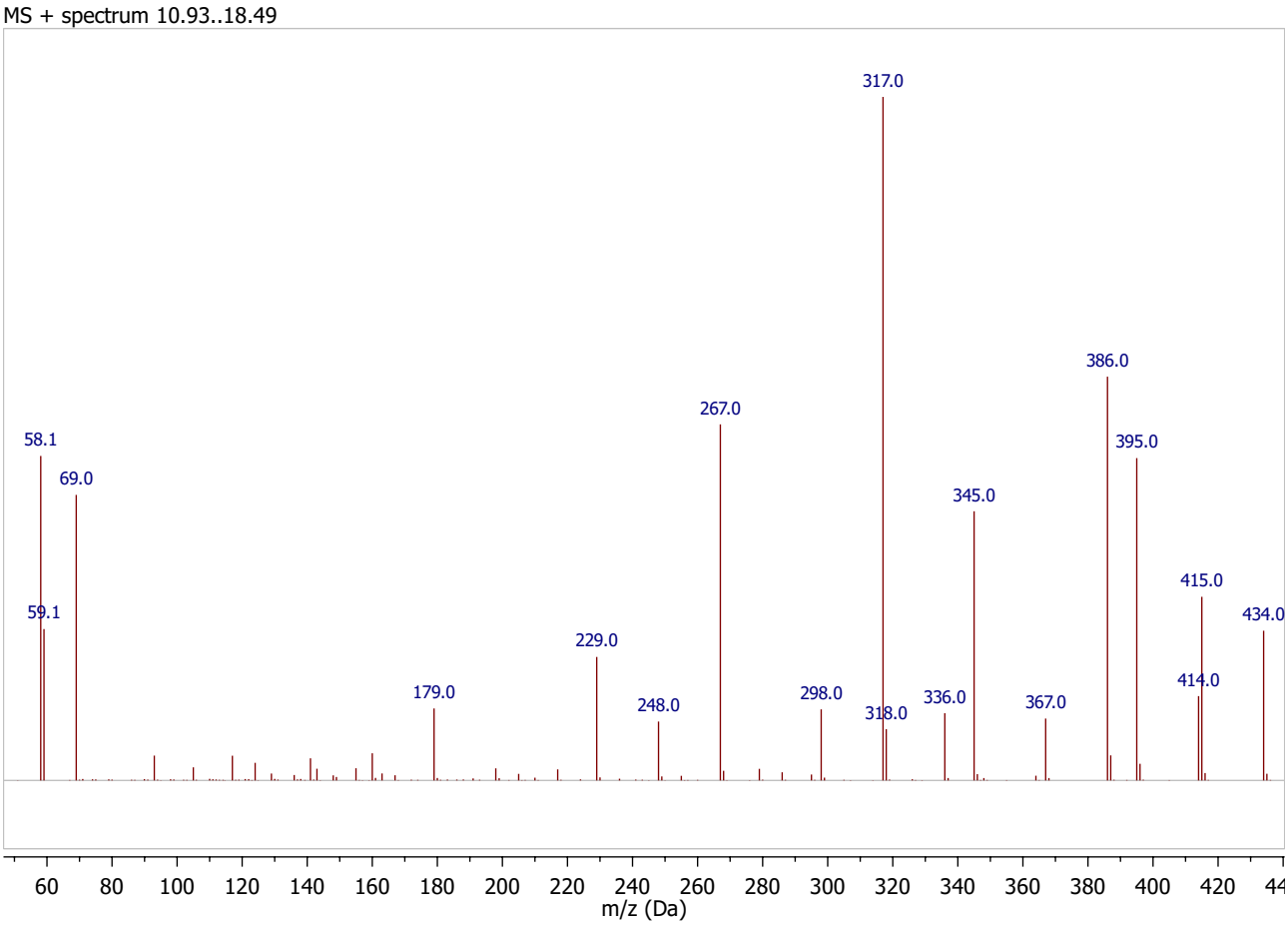
GC-MS spectra of the recrystallized product obtained from the pentane extraction from the distillate of Reaction I. Three peaks in GC with the molecular ion 395 belong to the three different isomers of tetrakis(trifluoromethyl)nitrobenzene.



Spectrum S22

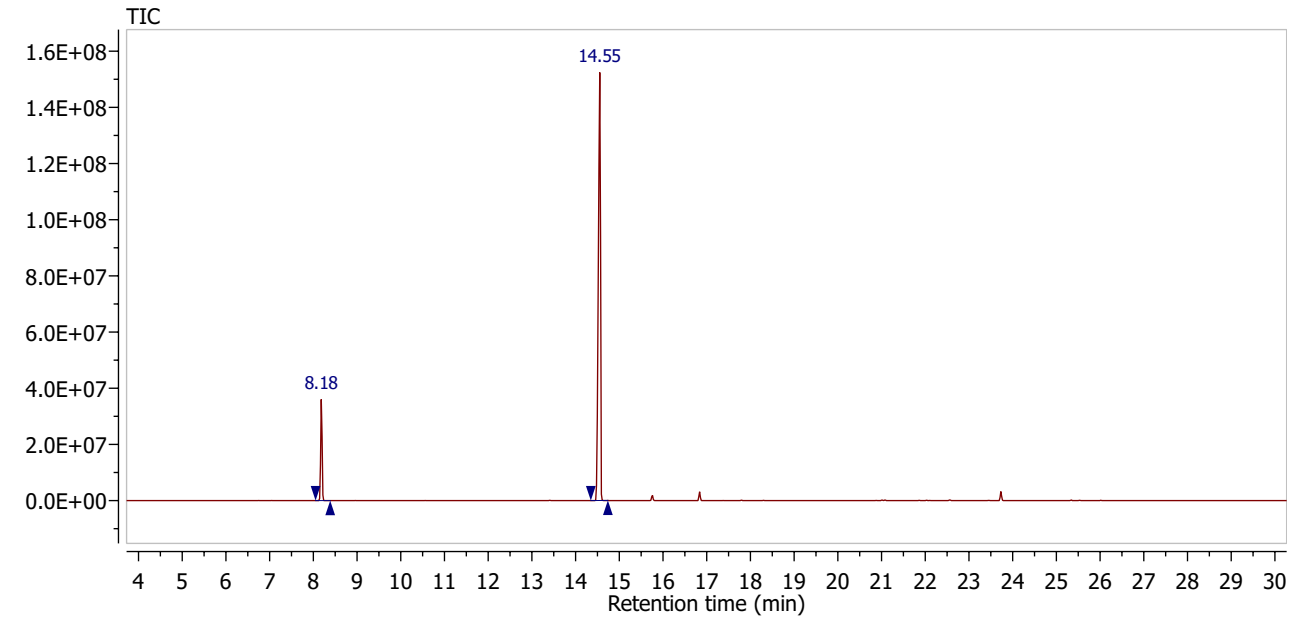
GC-MS spectra of pentakis(trifluoromethyl)phenol **1**.

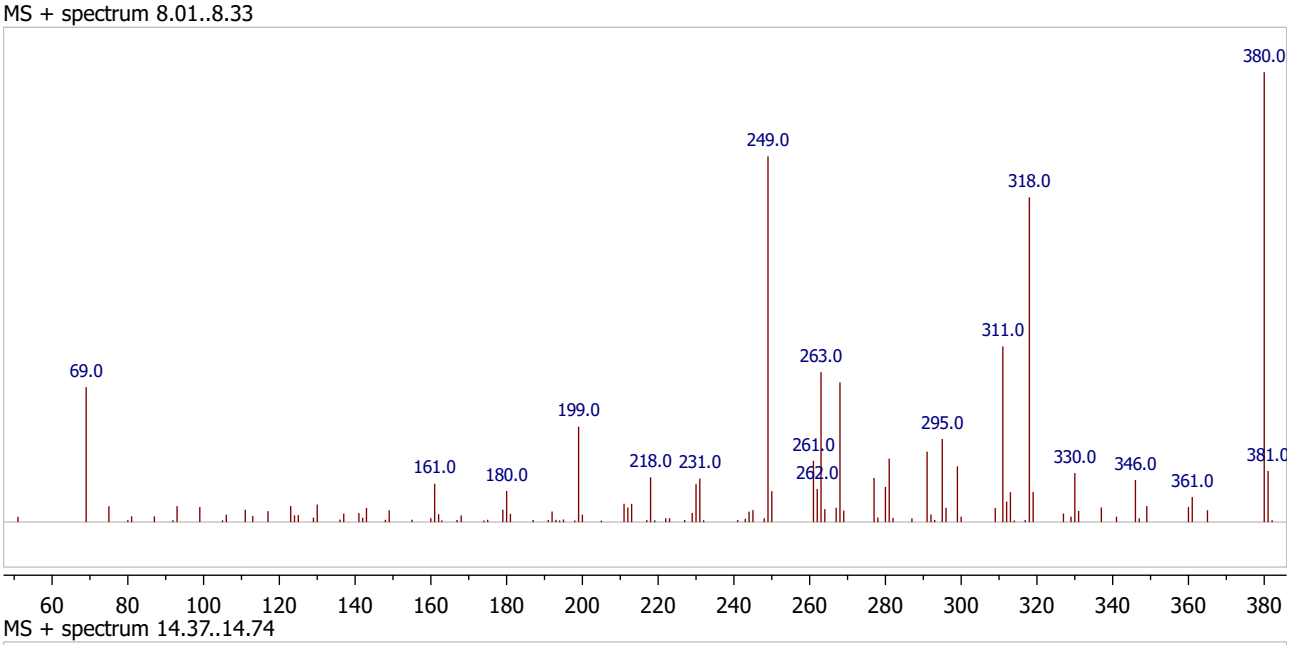


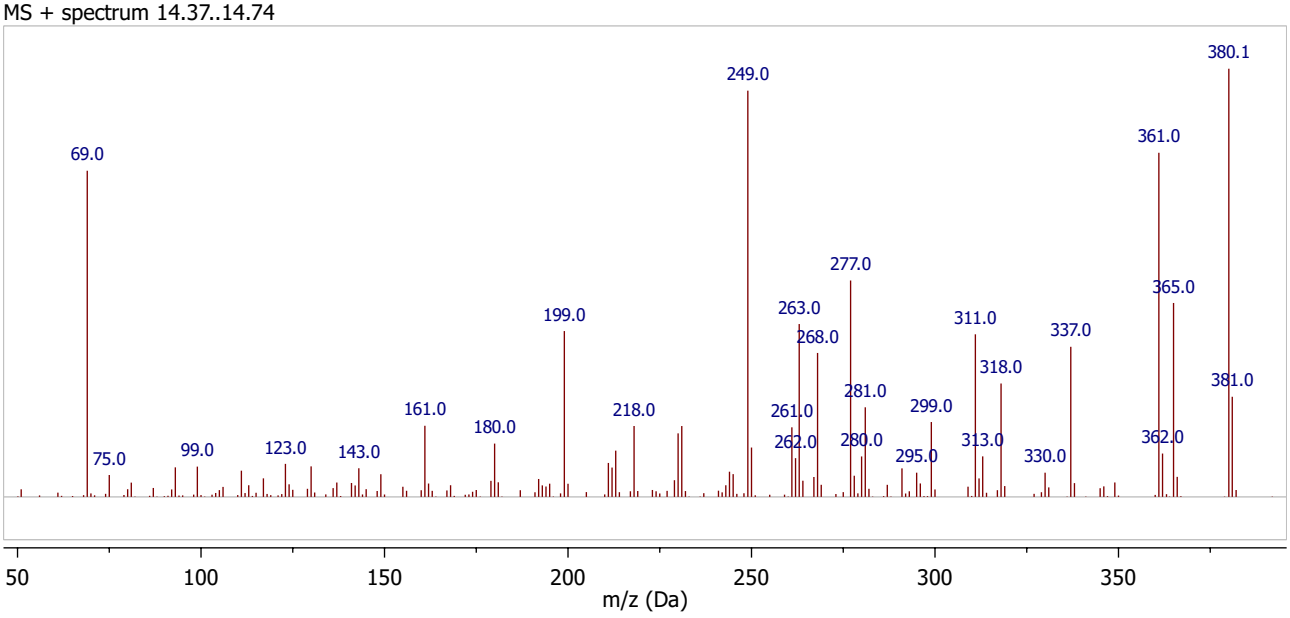


Spectrum S23

GC-MS spectra of the pentane extract from the reaction mixture with tetrakis(trifluoromethyl)nitrobenzenes and Me_4NOH in MeOH. Two major peaks correspont to the two different isomers of tetrakis(trifluoromethyl)methoxybenzenes.





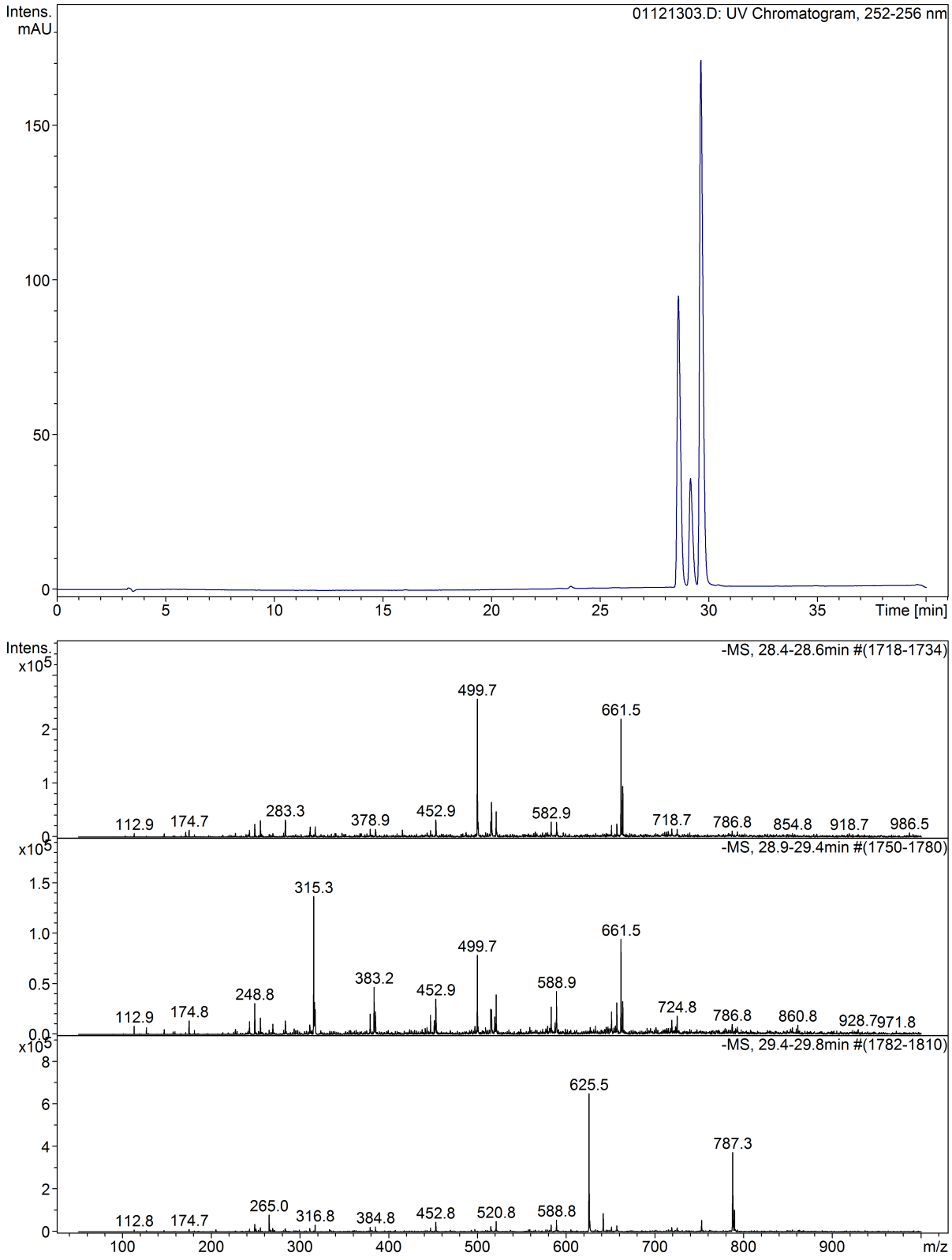


Spectrum S24

HPLC-ESI-MS-UV-vis spectra of the crude product obtained from periodination of nitrobenzene. Contains 31% and 12% of two isomers tetraiodonitrobenzenes and 57% of pentaiodonitrobenzene. ESI spectrum in negative mode is obtained from the complex of the analytes and Cl anion.

Display Report - All Windows All Analyses

Operator: operaator **Instrument:** LC-MSD-Trap-XCT **Print Date:** 18.12.2013 21:16:06

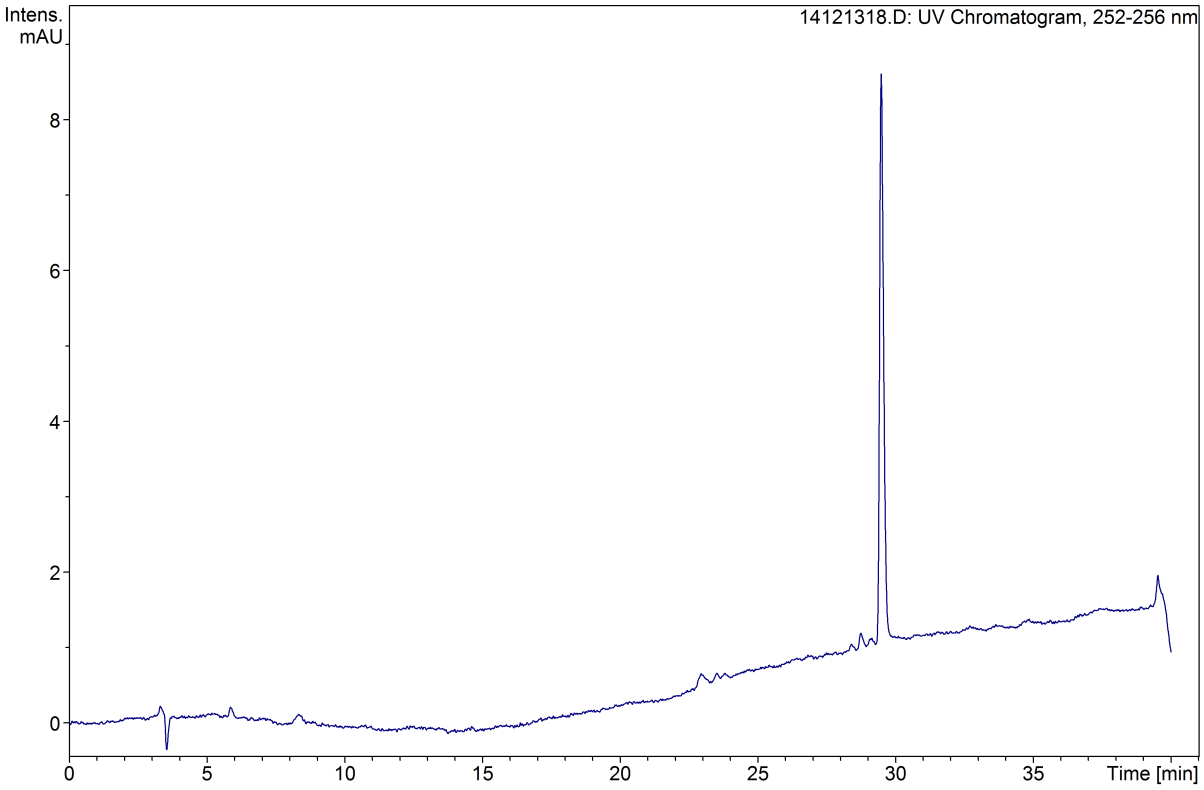


Spectrum S25

The HPLC-ESI-MS-UV-vis spectra of the measurements of the product that is obtained when the mixture of pentaiodo- and tetraiodonitrobenzene is recrystallized two times from the mixture of benzene and ethanol. ESI-MS spectrum in negative mode is obtained from the complex of the analyte and Cl anion. Includes mainly pentaiodonitrobenzene.

Display Report - All Windows All Analyses

Operator: operaator **Instrument:** LC-MSD-Trap-XCT **Print Date:** 25.12.2013 17:20:02



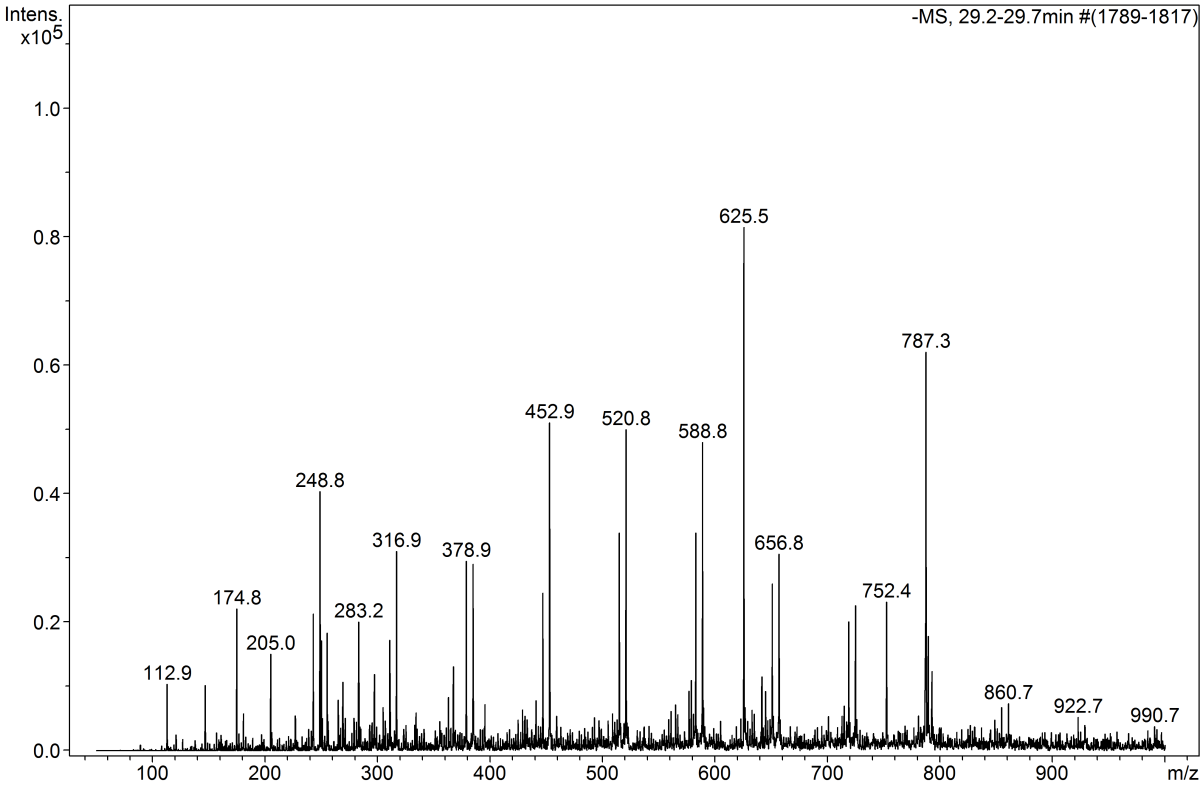


Figure S26

Photograph of liquid nitrogen trap after the distilaation of NMP and DMF from the trifluoromethylation reaction. Blue compound, that turns gasues when warming up correspond to N_2O_3.