NACIONALNI FORENZIČNI LABORATORIJ
NATIONAL FORENSIC LABORATORY
Vodovodna 95, 1000 LJUBLJANA, SLOVENIA
E: nfl@policija.si

EUROPEAN PROJECT RESPONSE 2
to challenges in forensic drugs analyses
Co-funded by the Internal Security Found of the European Union

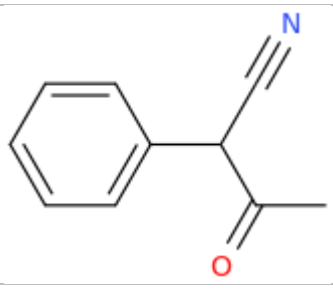
ANALYTICAL REPORT

APAAN (C10H9NO)

3-oxo-2-phenylbutanenitrile

Remark – other NPS detected: none

Sample ID:	2081-19
Sample description:	powder
Sample type:	seized /MB
Date of entry (DD/MM/YYYY) into NFL database:	13/08/2019
Report updates (if any) will be published here:	http://www.policija.si/apps/nfl_response_web/seznam.php

Substance identified - structure[1] (base form)	
Systematic name	3-oxo-2-phenylbutanenitrile
Other names	2-Phenylacetoacetonitrile; alpha-Acetylphenylacetonitrile; 1-Cyano-1-phenyl-2-propanone; alpha-Phenylacetoacetonitrile; alpha-Aceto-alpha-cyanotoluene; alpha-Acetylbenzeneacetonitrile; Phenylacetoacetonitrile; Benzeneacetonitrile, alpha-acetyl-; 2-Oxo-1-p
Formula (per base form)	C10H9NO
M_w (g/mol)	159,19
Salt form/anions detected	base
StdInChIKey (per base form)	KHNWFTMUBKJWRZ-UHFFFAOYSA-N
Other NPS detected	none
Additional info (purity..)	>90% purity of a sample based on 1H NMR spectrum

[1] Created by OPSIN free tool: http://opsin.ch.cam.ac.uk/ **DOI:** 10.1021/ci100384d

Report updates

date	comments (explanation)

Instrumental methods (if applied) in NFL

1. GC-MS (Agilent): GC-method is RT locked to tetracosane (9.258 min). Injection volume 1 ml and split mode (1:50). Injector temperature: 280 0C. Chromatographic separation: on column HP1-MS (100% dimethylpolysiloxane), length 30 m, internal diameter 0.25 mm, film thickens 0.25 µm. Carrier gas He: flow-rate 1.2 ml/min. GC oven program: 170 ^{0}C for 1 min, followed by heating up to 190 ^{0}C at rate 8 ^{0}C/min, then heating up to 293 0C at a rate of 18 ^{0}C/min, hold for 7.1 min, then heating at 50 ^{0}C/min up to 325 ^{0}C and finally 6.1 min isothermal. MSD source EI = 70 eV. GC-MS transfer line T= 235^{0}C, source and quadropole temperatures 280^{0}C and 180^{0}C, respectively. Scan range m/z scan range: from 50 (30 until 6 min.) to 550 (300 until 6 min) amu.

2. HPLC-TOF (Agilent): 6230B TOF with Agilent 1260 Infinity HPLC with binary pump, column: Zorbax Eclipse XDB-C18, 50 x 4.6 mm, 1.8 micron. Mobile phases (A) 0.1% formic acid and 1mM ammonium formate in water; (B) 0.1% formic acid in methanol (B). Gradient: starting at 5% B, changing to 40% B over 4 min, then to 70% over 2 min and in 5 min to 100%, hold 1 min and back to 5%, equilibration for 1.7 min. The flow rate: 1.0 ml/min; Injection volume 1 µl. MS parameters: 2GHz, Extended Dynamic range mode to a maximum of 1700 amu, acquisition rate 1.30 spectra/sec. Sample ionisation: by Agilent Jet Stream technology (Dual AJS ESI). Ion source: positive ion scan mode with mass scanning from 82 to 1000 amu. Other TOF parameters: drying gas (N2) and sheath temperature 325 °C; drying gas flow rate 6 l/min; sheath gas flow rate 8 l/min; nebulizer 25 psig; Vcap. 4000 V; nozzle 2000 V; skimmer 65 V; fragmentor 175 V and Octopole RF 750 V.

3.FTIR-ATR (Perkin Elmer): scan range 4000-400 cm-1; resolution 4cm-1

4. GC- (MS)-IR condensed phase (GC-MS (Agilent) & IR (Spectra analyses-Danny)
GC-method: Injection volume 1 ml and split mode (1:5). Injector temperature 280 ^{0}C. Chromatographic separation as above **(1).** Split MS : IR = 1: 9.
MSD source EI = 70 eV. GC-MS transfer line T= 235^{0}C, source and quadropole temperatures 280^{0}C and 180^{0}C, respectively. Scan range m/z scan range: from 50 (30 until 6 min.) to 550 (300) amu.
IR (condesed (solid) phase): IR scan range 4000 to 650, resolution 4 cm^{-1}.

5. **IC** (anions) (Thermo Scientific, Dionex ICS 2100), Column: IonPac AS19, 2 x 250mm; Eluent: 10mM KOH from 0 to 10 min, 10-58 mM from 10 to 40min; Flow rate: 0.25 ml/min; Temperature: 30˚C; Suppressor: AERS 500 2mm, suppressor current 13mA; Inj. Volume: 25 µl

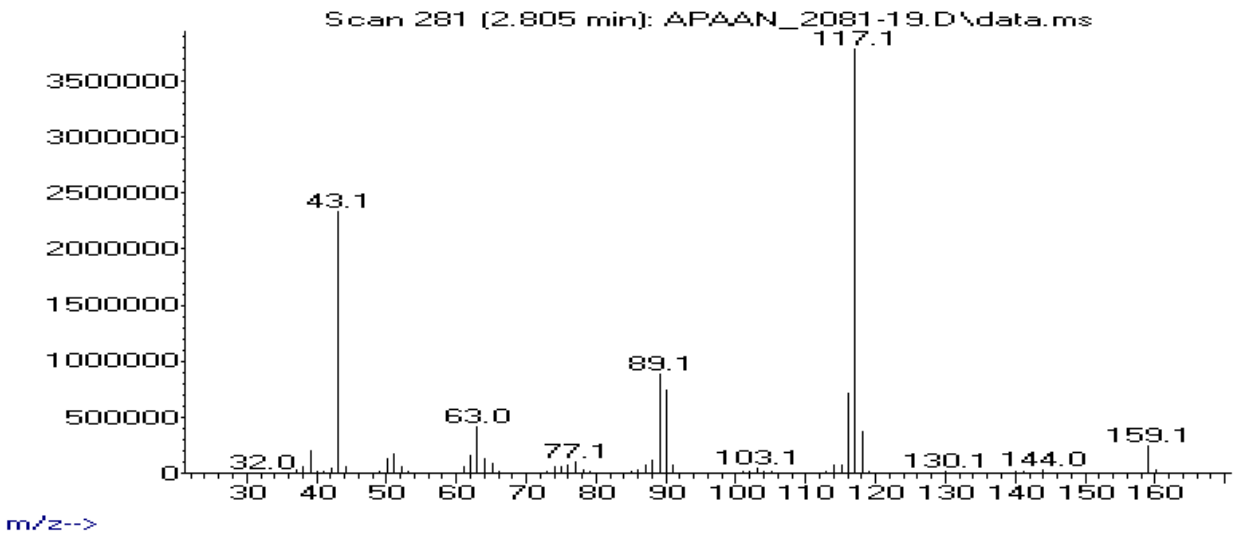
Supporting information

Solubility in	result/remark
CH_2Cl_2	soluble
MeOH	soluble
H_2O	

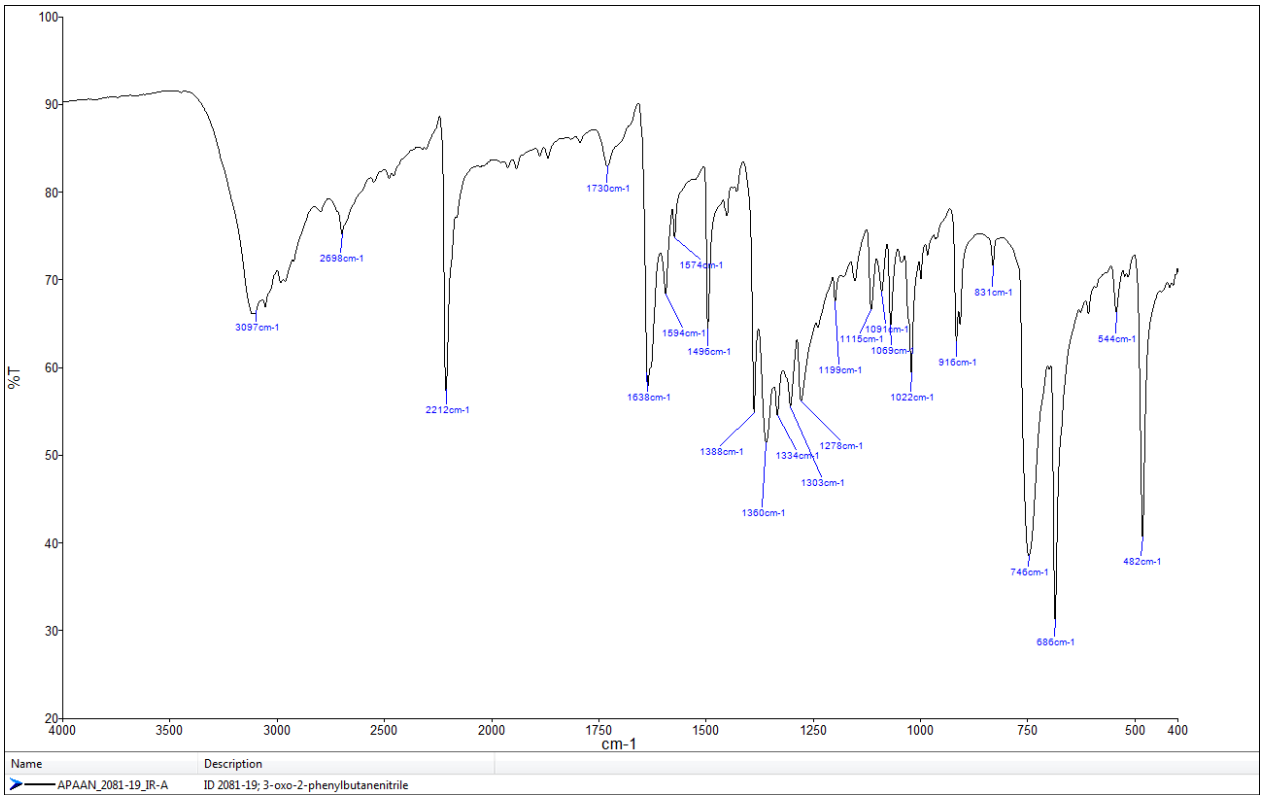
Analytical technique:	applied	remarks
GC-MS (EI ionization)	+	NFL GC-RT (min): 2,81 BP(1): 117; BP(2): 43,BP(3) :89,
HPLC-TOF	+	Exact mass (theoretical): 159,0684; measured value Δppm:-0,98; formula:C10H9NO
FTIR-ATR	+	direct measurement (sample as received)
FTIR (solid phase) always as base form	+	
IC (anions)	-	
NMR (in FKKT)	+	
validation		
other		

ANALYTICAL RESULTS

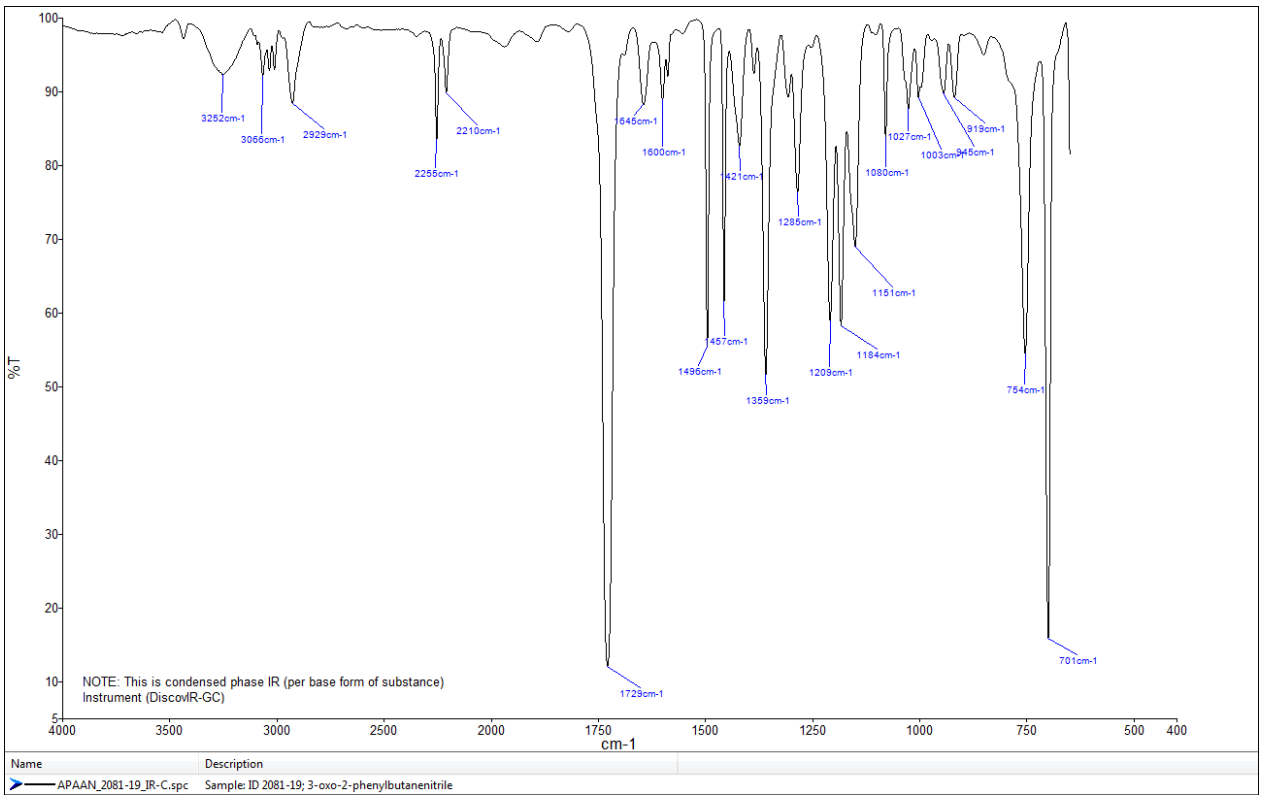
MS (EI)



FTIR-ATR - direct measurement (sample as received)



IR (solid phase – after chromatographic separation)



TOF REPORT

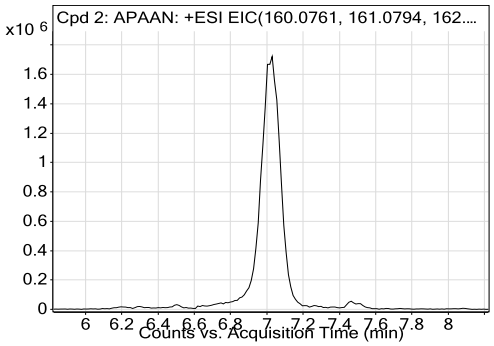
Data File	APAAN-2081_19.d	**Sample Name**	ID_2081-19
Sample Type	Sample	**Position**	P1-F7
Instrument Name	6230B TOF LC-MS	**User Name**	
Acq Method	general-8_1_2019-XDB-C18-ESI+.m	**Acquired Time**	7/15/2019 1:08:33 PM
IRM Calibration Status	Success	**DA Method**	a-Drugs_NFL.m
Comment			

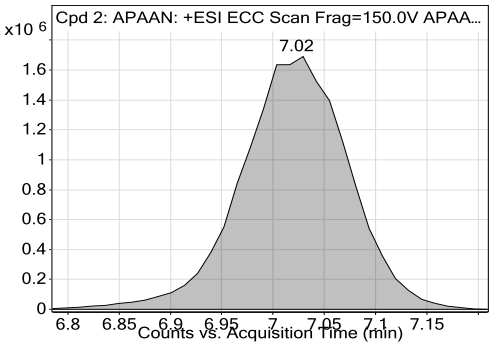
Compound Table

Label	Compound Name	MFG Formula	Obs. RT	Obs. Mass
Cpd 2: APAAN	APAAN	C10 H9 N O	7.02	159.0686

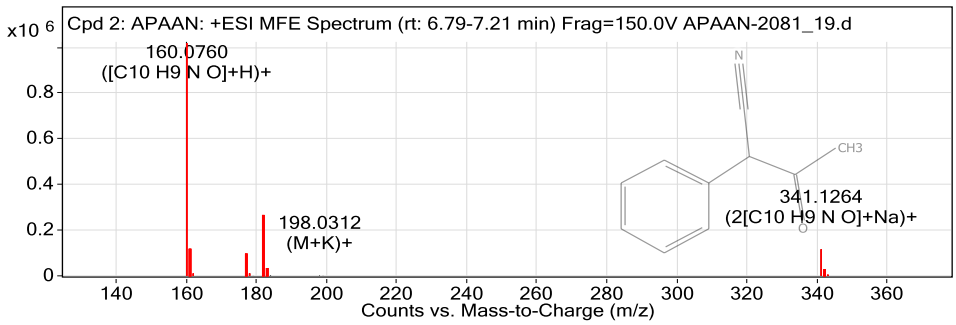
Name	*Obs. m/z*	Obs. RT	Obs. Mass	DB RT	DB Formula	DB Mass	DB Mass Error (ppm)
APAAN	160.076	7.02	159.0686	7.02	C10 H9 N O	159.0684	-0.98

Compound Chromatograms

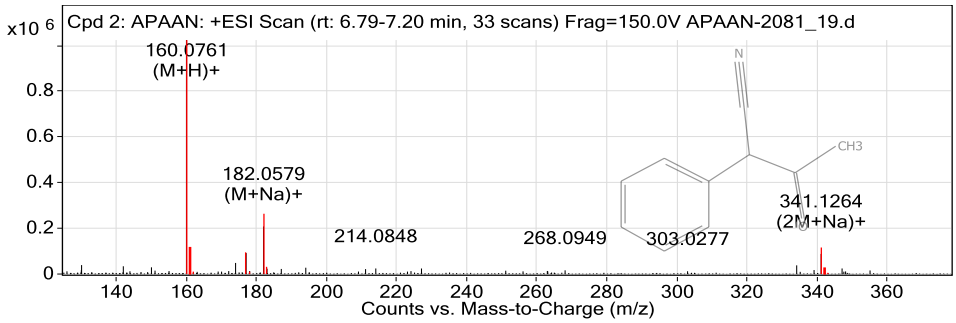




MFE MS Zoomed Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Charge	Abund	Formula	Ion/Isotope
160.076	1	1024034.75	C10 H9 N O	(M+H)+
161.079	1	110470.3	C10 H9 N O	(M+H)+
162.0818	1	7741.59	C10 H9 N O	(M+H)+
177.1024	1	94946.79	C10 H9 N O	(M+NH4)+
178.1057	1	11600.08	C10 H9 N O	(M+NH4)+
182.0578	1	263935.31	C10 H9 N O	(M+Na)+
183.061	1	30569.37	C10 H9 N O	(M+Na)+
341.1264	1	115982.2	C10 H9 N O	(2M+Na)+
342.1293	1	25767.38	C10 H9 N O	(2M+Na)+
343.1346	1	3651.57	C10 H9 N O	(2M+Na)+

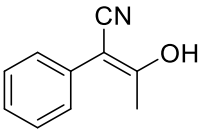
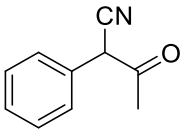
--- End Of Report ---

Večna pot 113
P. O. Box 537
SI-1001 Ljubljana
Slovenia
Phone: +386 1 479 8558
janez.kosmrlj@fkkt.uni-lj.si

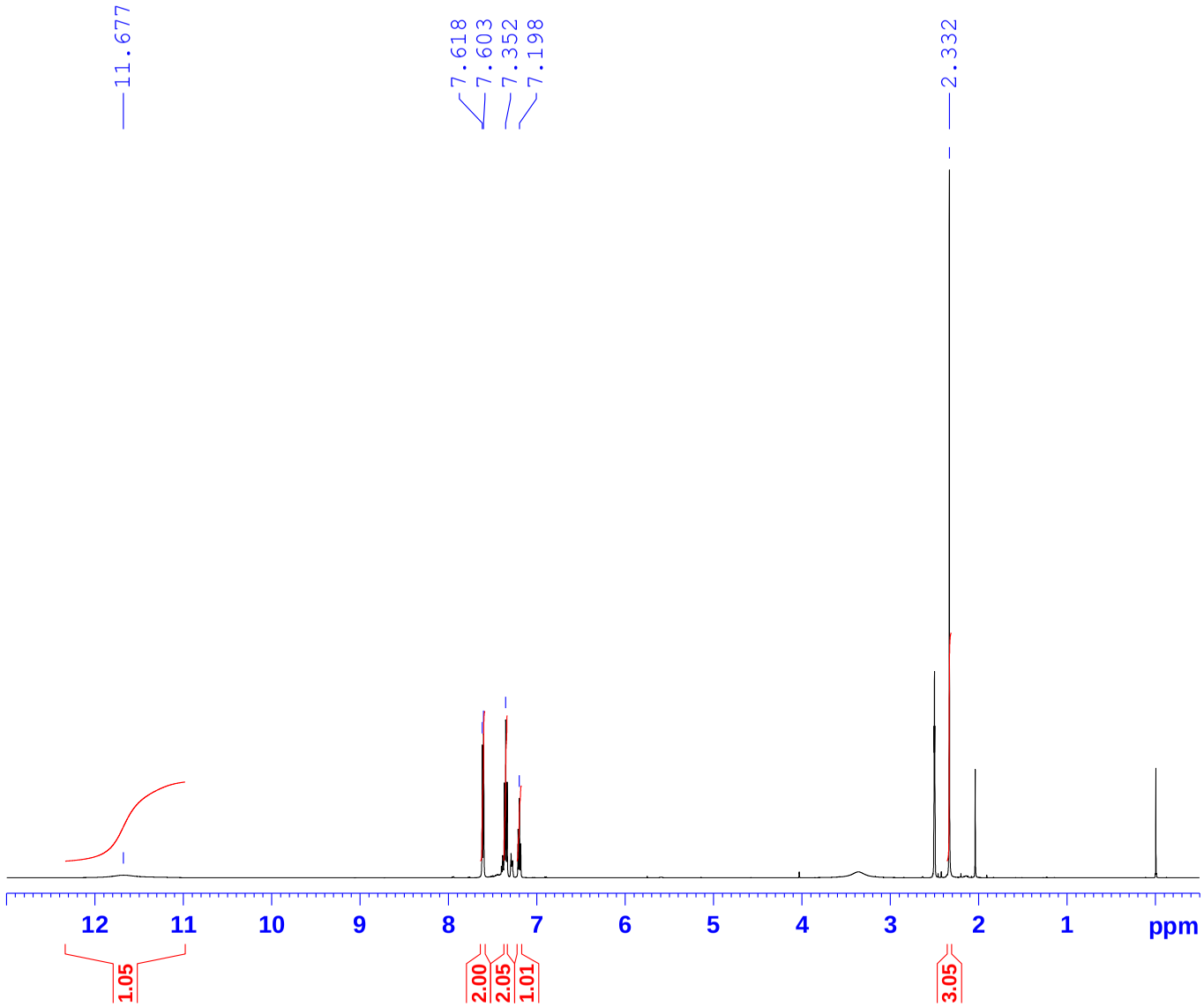
University
of Ljubljana

Faculty *of Chemistry*
and Chemical Technology

R E P O R T

Contract No.	C1714-19-460155 (Republic of Slovenia, Ministry of the Interior, POLICE)
Sample ID:	**2081-19**
Received date:	July 30, 2019
Our notebook code:	NFL-2081-19
NMR sample preparation:	18.2 mg dissolved in 0.7 mL DMSO-d_6
NMR experiments:	^{1}H, ^{13}C, ^{1}H–^{1}H *gs*-COSY, ^{1}H–^{13}C *gs*-HSQC, ^{1}H–^{13}C *gs*-HMBC, ^{1}H–^{15}N *gs*-HMBC
Proposed structure with formula, exact mass, molecular weight:	**Enol** (in DMSO-d_6)  Chemical Formula: $C_{10}H_9NO$ Exact Mass: 159.0684 Molecular Weight: 159.1880 **Keto** (in $CDCl_3$)  Chemical Formula: $C_{10}H_9NO$ Exact Mass: 159,0684 Molecular Weight: 159,1880
Chemical name:	3-hydroxy-2-phenylbut-2-enenitrile (**enol tautomer**), 3-oxo-2-phenylbutanenitrile (**keto tautomer**)
Comments:	- Structure elucidation based on 1D and 2D NMR spectra and HRMS. - >90% purity of a sample, based on ^{1}H NMR spectrum. - For the purpose of keto-enol tautomerisms examination, 14.2 mg of the sample was dissolved in 0.7 mL $CDCl_3$, and ^{1}H and ^{13}C NMR spectra were recorded (Supporting information, Expno 100 and 200). - The comparison of measured ^{1}H and ^{13}C NMR spectra shows solely presence of **enol**-form in DMSO-d_6 and **keto**-form in $CDCl_3$. - In the case of **enol**-form, *E–Z* configuration was not determined.
Supporting information:	Copies of ^{1}H and ^{13}C NMR spectra, ^{1}H and ^{13}C FIDs.
Principal investigator:	Prof. Dr. Janez Košmrlj
Date of report:	August 12, 2019

NFL-2081-19
1H

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Current Data Parameters
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EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190731
Time              16.59
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                 90.5
DW               50.000 usec
DE                6.50 usec
TE                297.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                 8.70 usec
PLW1        26.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300045 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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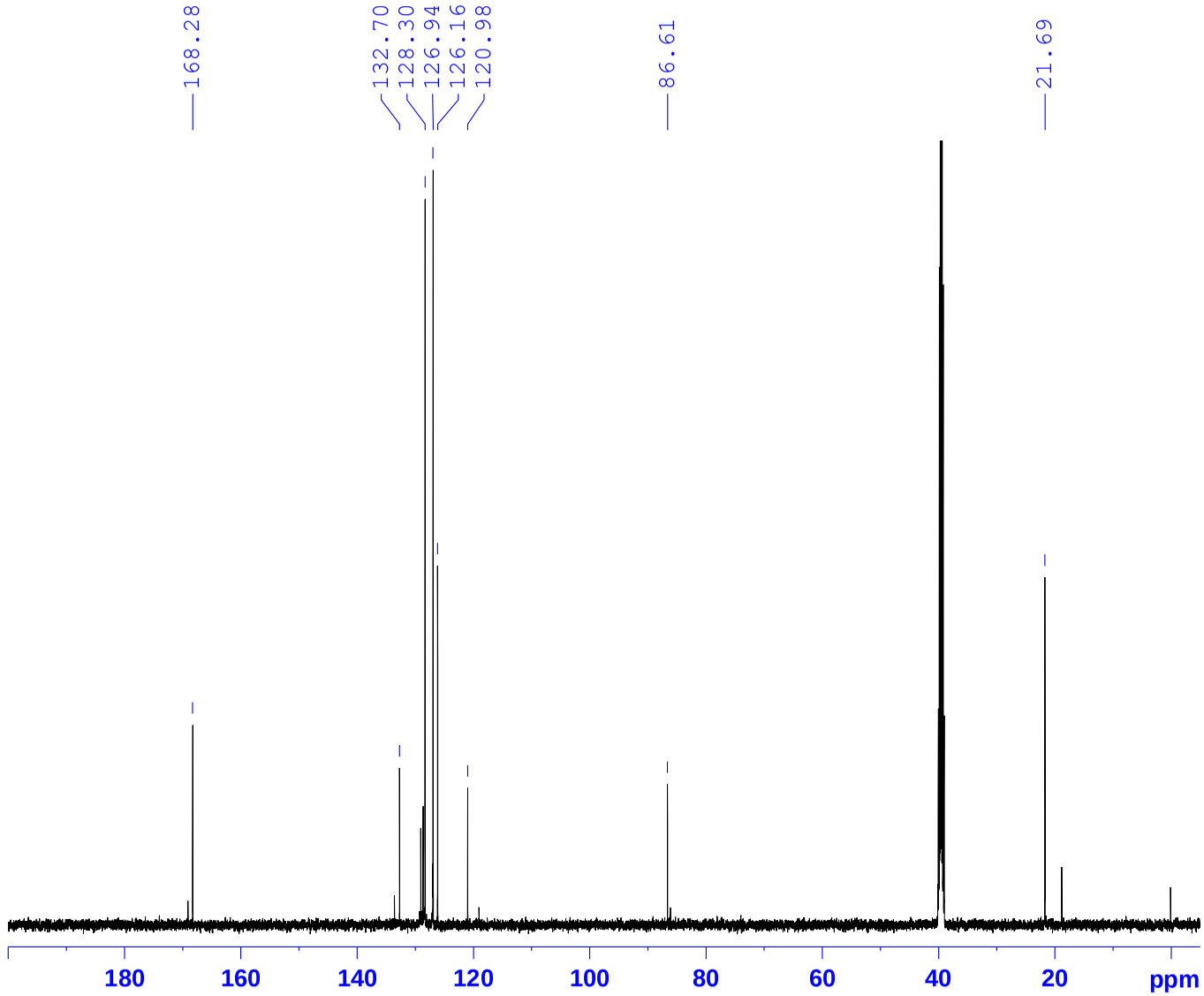
NFL-2081-19
13C

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EXPNO                  2
PROCNO                 1

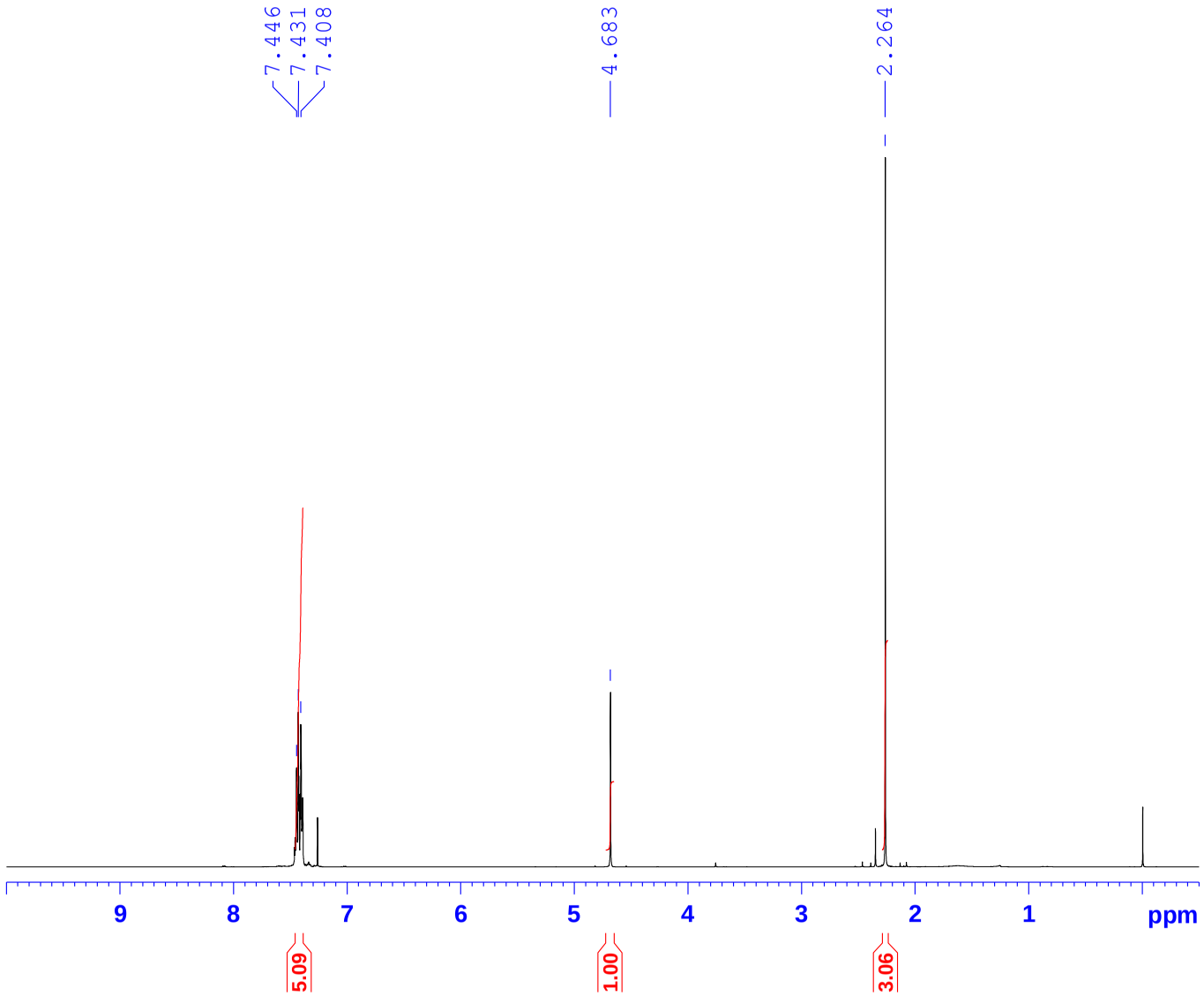
F2 - Acquisition Parameters
Date_           20190731
Time               17.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                   314
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                297.9 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                  13C
P1                   8.70 usec
PLW1       122.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2               80.00 usec
PLW2         26.00000000 W
PLW12         0.30046001 W
PLW13         0.15113001 W

F2 - Processing parameters
SI                 32768
SF          125.7578477 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

NFL-2081-19
1H

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EXPNO                100
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190809
Time                9.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ             3.2767999 sec
RG                   114
DW                50.000 usec
DE                 6.50 usec
TE                296.0 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                1H
P1                 8.70 usec
PLW1        26.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300126 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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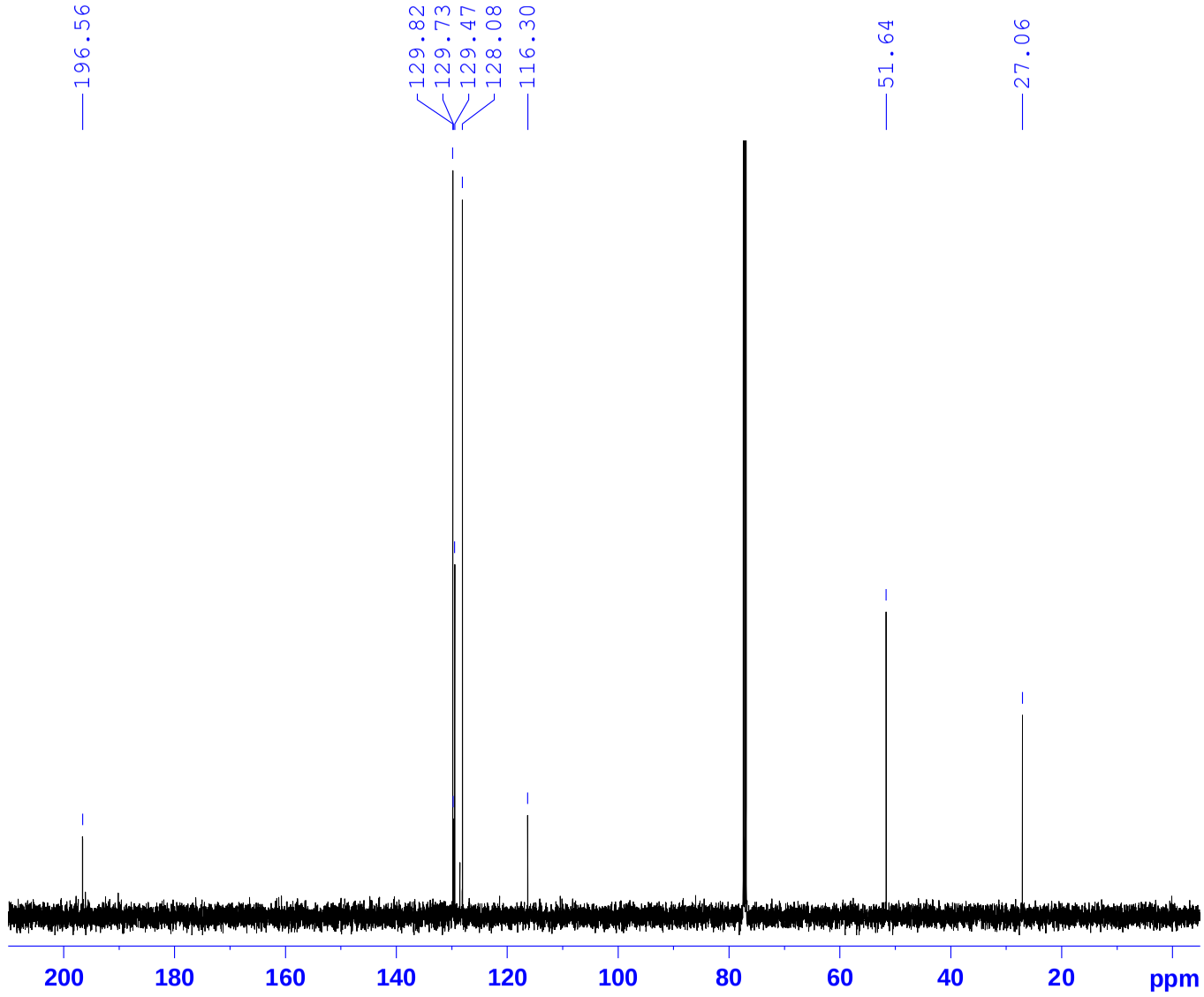
NFL-2081-19
13C

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Current Data Parameters
NAME         NFL-2081-19
EXPNO                200
PROCNO                 1

F2 - Acquisition Parameters
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Time                9.17
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   69
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                 2050
DW               16.800 usec
DE                6.50 usec
TE               296.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                 13C
P1                  8.70 usec
PLW1       122.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         26.00000000 W
PLW12         0.30046001 W
PLW13         0.15113001 W

F2 - Processing parameters
SI                  32768
SF          125.7577753 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```