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EUROPEAN PROJECT RESPONSE 2 to challenges in forensic drugs analyses

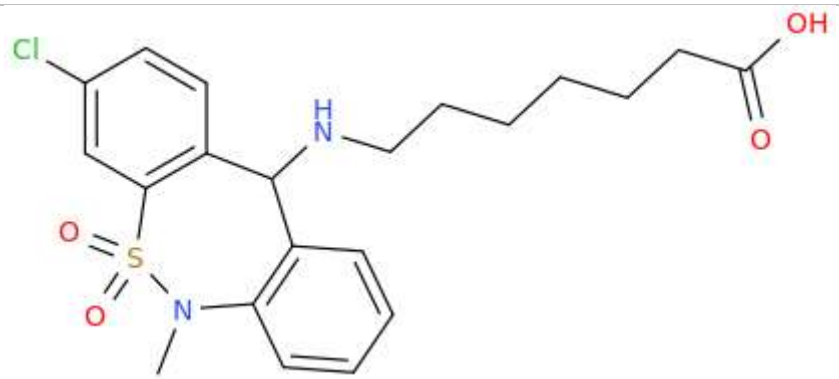
ANALYTICAL REPORT

Tianeptin (C21H25ClN2O4S)

7-({6-chloro-10-methyl-9,9-dioxo-9lambda6-thia-10-azatricyclo[9.4.0.03,8]pentadeca-1(11),3(8),4,6,12,14-hexaen-2-yl}amino)heptanoic acid

Remark – other NPS detected: none

Sample ID:	2149-19
Sample description:	powder - granulated
Sample type:	seized /KP
Date of entry (DD/MM/YYYY) into NFL database:	21/02/2020
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	7-({6-chloro-10-methyl-9,9-dioxo-9lambda6-thia-10-azatricyclo[9.4.0.03,8] pentadeca-1(11),3(8),4,6,12,14-hexaen-2-yl}amino)heptanoic acid
Other names	7-((3-chloro-6-methyl-5,5-dioxido-6,11-dihydrodibenzo[c,f][1,2]thiazepin-11-yl)amino)heptanoic acid, 7-[(3-chloro-6-methyl-5,5-dioxo-11H-benzo[c][2,1]benzothiazepin-11-yl)amino]heptanoic acid
Formula (per base form)	C21H25ClN2O4S
M_w (g/mol)	436,95
Salt form/anions detected	base
StdInChIKey (per base form)	JICJBGPOMZQUBB-UHFFFAOYSA-N
Other NPS detected	none
Additional info (purity..)	>96% pure 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 µl 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 µl 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}.

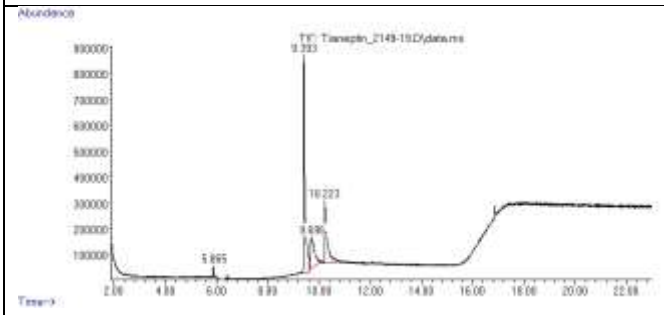
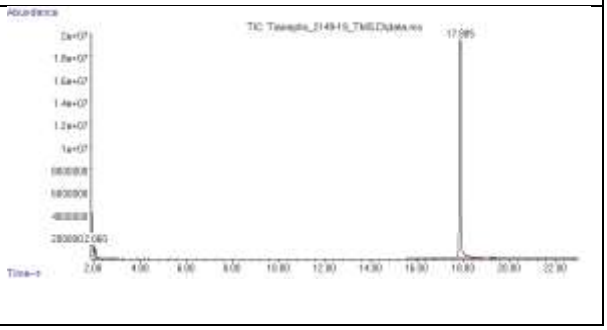
5. **IC** (anions) (Thermo Scientific, Dionex ICS 2100), Column: IonPac AS19, 2 x 250mm; Eluent: 10mM KOH from 0 to 10 min, 10-58 mM from 10 to 40min; Flow rate: 0.25 ml/min; Temperature: 30˚C; Suppressor: AERS 500 2mm, suppressor current 13mA; Inj. Volume: 25 µl

Supporting information

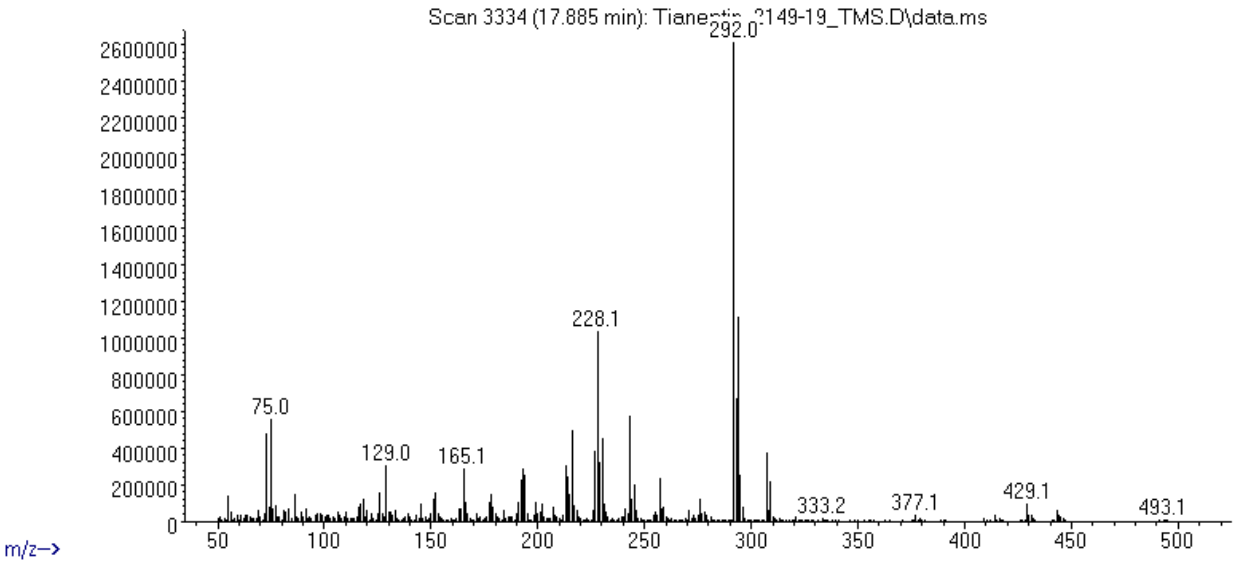
Solubility in	result/remark
CH_2Cl_2	soluble
MeOH	soluble
H_2O	soluble

Analytical technique:	applied	remarks
GC-MS (EI ionization)	+	NFL GC-RT (min): 17,89 BP(1): 292; BP(2): 294,BP(3) :228, **DATA for TMS derivative, nonderivatized compound decomposes**
HPLC-TOF	+	Exact mass (theoretical): 436,1224; measured value Δppm:-0,01; formula:C21H25ClN2O4S
FTIR-ATR	+	direct measurement (sample as received)
FTIR (solid phase) always as base form	-	
IC (anions)	+	
NMR (in FKKT)	+	
validation		
other		

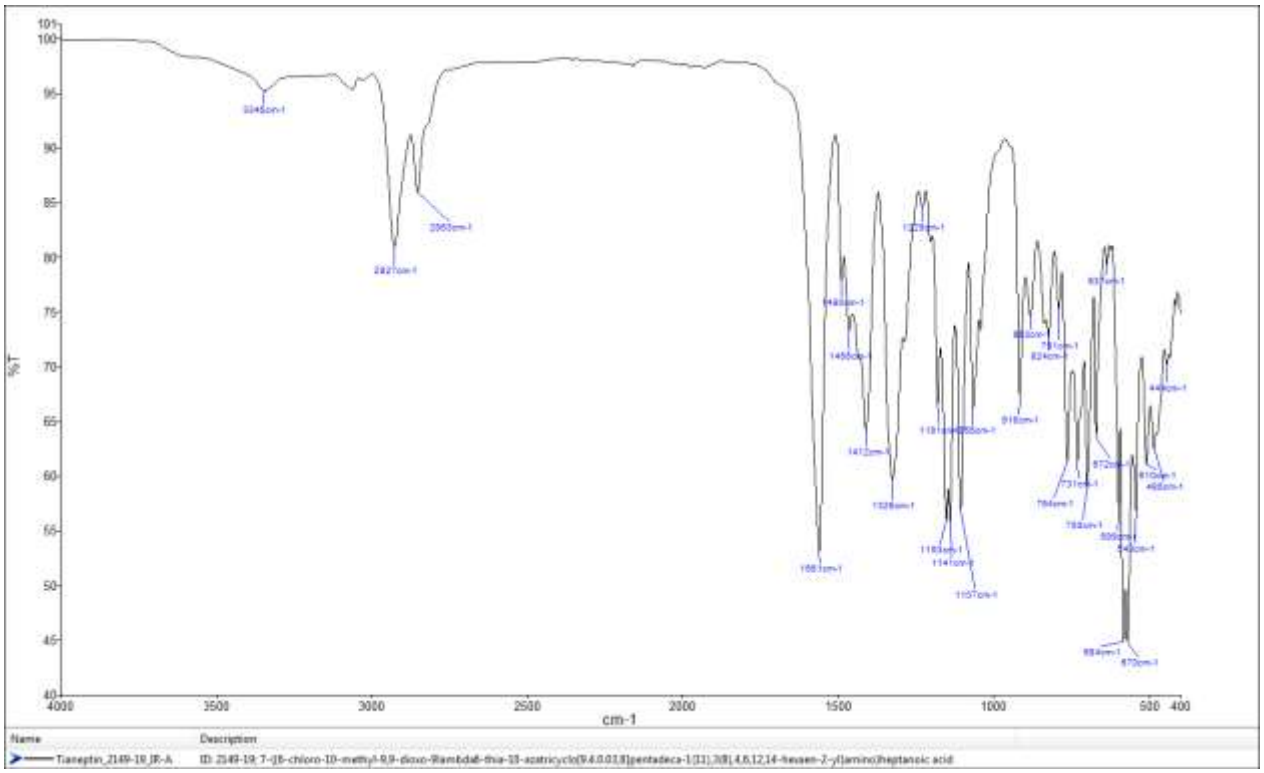
ANALYTICAL RESULTS

GC chromatogram of non derivatized sample	GC chromatogram of TMS-derivative
	

MS (EI) TMS-derivative



FTIR-ATR - direct measurement (sample as received)



TOF REPORT

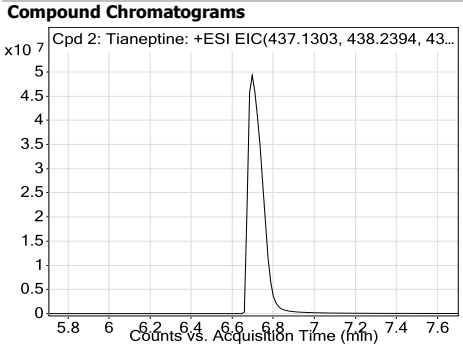
Data File	233-4893-2019_6.d	**Sample Name**	vz-6
Sample Type	Sample	**Position**	P1-D1
Instrument Name	6230B TOF LC-MS	**User Name**	TG
Acq Method	general-19_10_2019-XDB-C18-ESI+.m	**Acquired Time**	1/14/2020 1:13:12 PM
IRM Calibration Status	Success	**DA Method**	a-Drugs_NFL.m
Comment	MeOH		

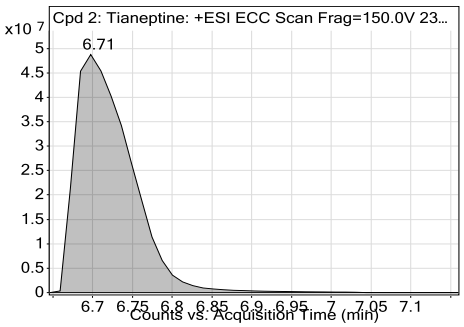
Compound Table

Label	Compound Name	MFG Formula	Obs. RT	Obs. Mass
Cpd 2: Tianeptine	Tianeptine	C21 H25 Cl N2 O4 S	6.71	436.1224

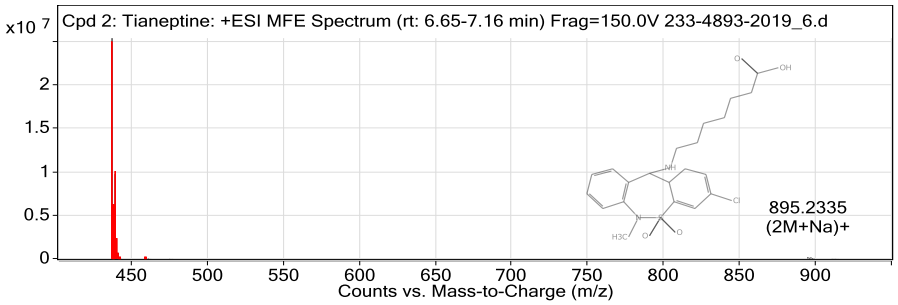
Name	*Obs. m/z*	Obs. RT	Obs. Mass	DB RT	DB Formula	DB Mass	DB Mass Error (ppm)
Tianeptine	437.1302	6.71	436.1224	6.72	C21 H25 Cl N2 O4 S	436.1224	-0.01

Compound Chromatograms

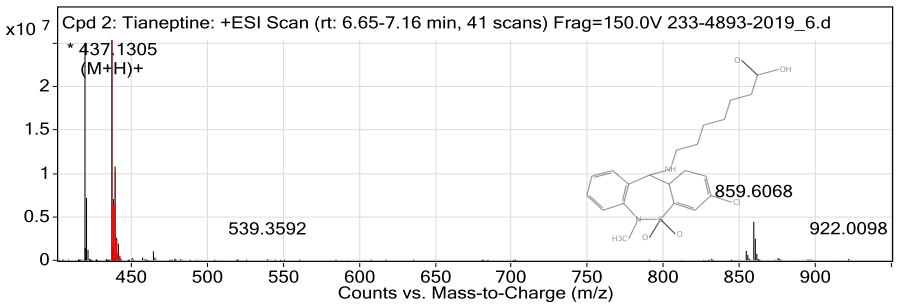




MFE MS Zoomed Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

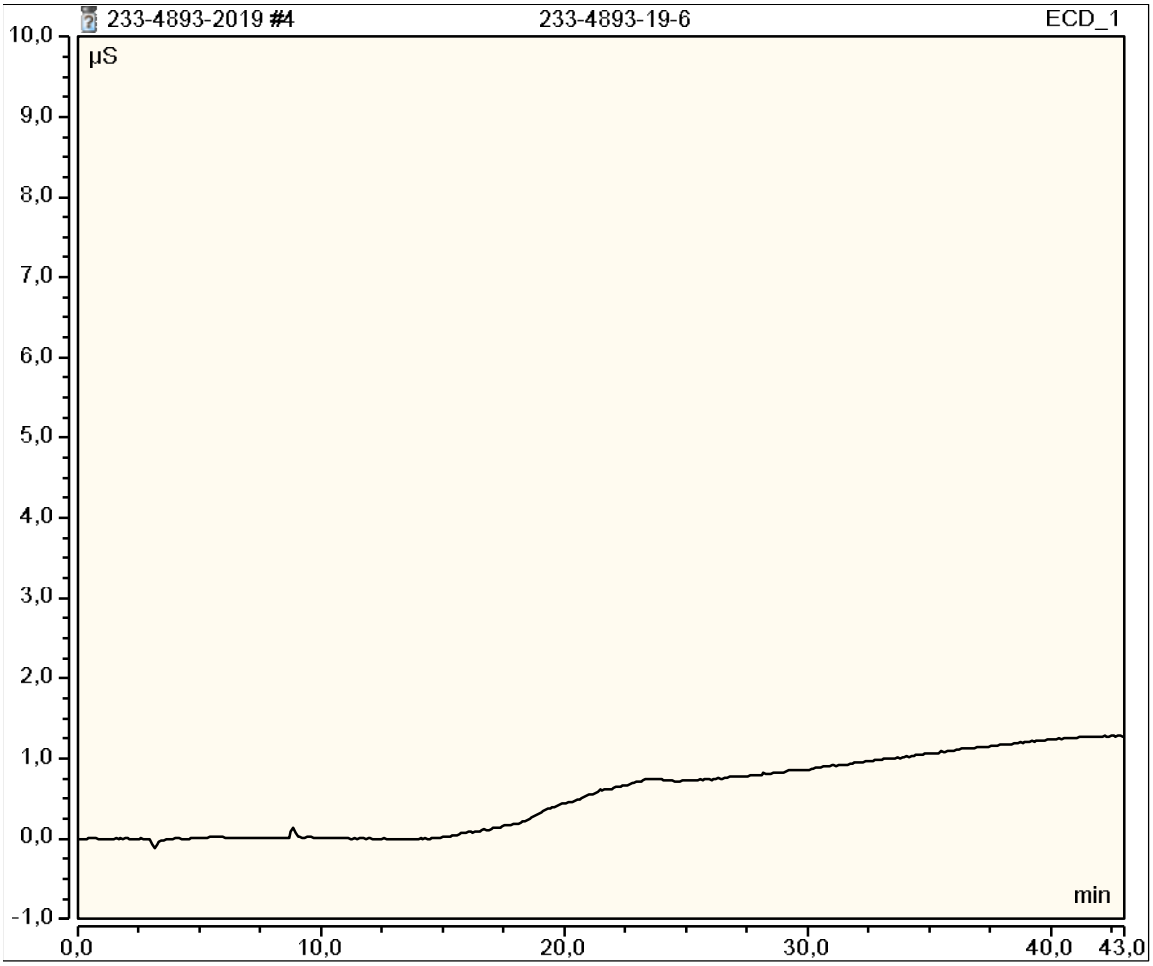
Obs. m/z	Charge	Abund	Formula	Ion/Isotope
437.1302	1	25396304	C21 H25 Cl N2 O4 S	(M+H)+
438.1328	1	6239494.94	C21 H25 Cl N2 O4 S	(M+H)+
439.1274	1	9724880.21	C21 H25 Cl N2 O4 S	(M+H)+
440.1302	1	2262884.93	C21 H25 Cl N2 O4 S	(M+H)+
441.1288	1	653016.28	C21 H25 Cl N2 O4 S	(M+H)+
442.1291	1	96601.77	C21 H25 Cl N2 O4 S	(M+H)+
459.1115	1	88400.08	C21 H25 Cl N2 O4 S	(M+Na)+
895.2335	1	157430.75		(2M+Na)+
896.2363	1	75733.5		(2M+Na)+
897.2319	1	133836.68		(2M+Na)+

--- End Of Report ---

Peak Integration Report

Sample Name:	**233-4893-19-6**	*Inj. Vol.:*	**25,00**
Injection Type:	**Unknown**	*Dilution Factor:*	**1,0000**
Program:	**ANIONI**	*Operator:*	**kemija**
Inj. Date / Time:	**15-jan-2020 / 10:45**	*Run Time:*	**43,00**

No.	Time min	Peak Name	Peak Type	Area µS*min	Height µS	Amount n.a.
		TOTAL:		0,00	0,00	0,0



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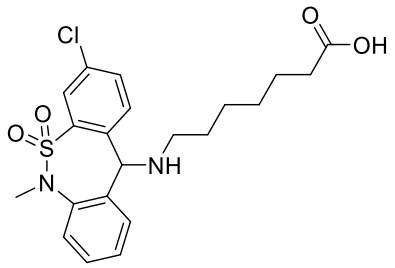
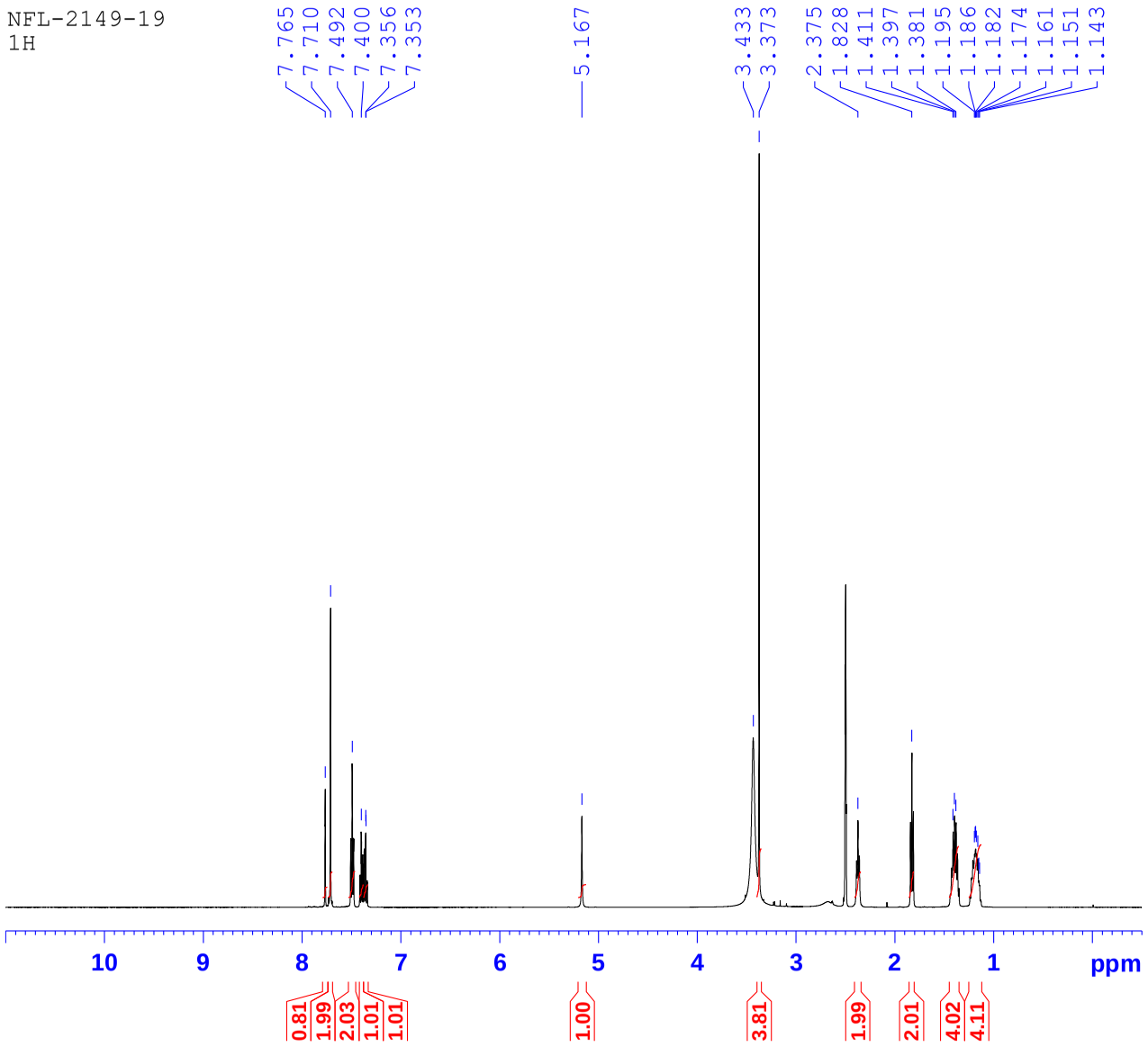
Faculty *of Chemistry*
and Chemical Technology

R E P O R T

Contract No.	C1714-19-460155 (Republic of Slovenia, Ministry of the Interior, POLICE)
Sample ID:	**2149-19**
Received date:	January 23, 2020
Our notebook code:	NFL-2149-19
NMR sample preparation:	20.9 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:	 Chemical Formula: $C_{21}H_{25}ClN_2O_4S$ Exact Mass: 436.1224 Molecular Weight: 436.9510
Chemical name:	7-((3-chloro-6-methyl-5,5-dioxido-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepin-11-yl)amino)heptanoic acid
Comments:	- Structure elucidation based on 1D and 2D NMR spectra and HRMS. - >96% purity of a sample based on ^{1}H NMR spectrum.
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:	February 17, 2020

NFL-2149-19
1H



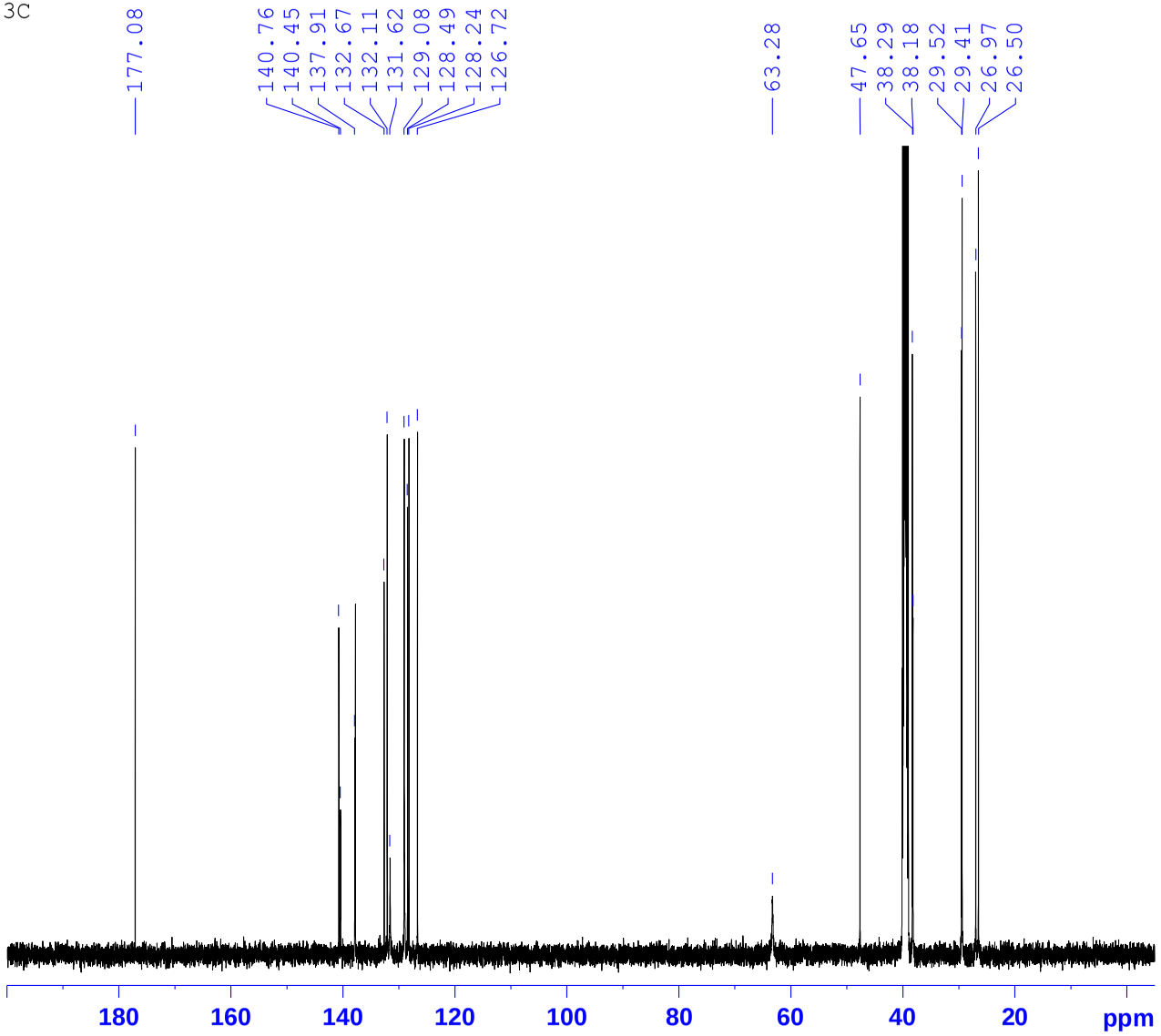

```
Current Data Parameters
NAME         NFL-2149-19
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200126
Time               17.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    32
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                296.0 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           500.1300038 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

NFL-2149-19
13C




```
Current Data Parameters
NAME         NFL-2149-19
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200126
Time              19.23
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT             DMSO
NS                 3072
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          125.7578450 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```