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

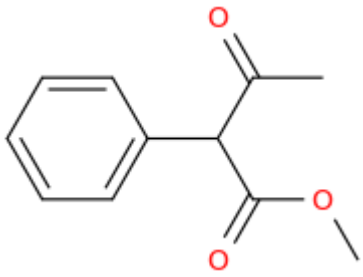
ANALYTICAL REPORT

MAPA (C11H12O3)

methyl 3-oxo-2-phenylbutanoate

Remark – other compounds detected: none

Sample ID:	2087-19
Sample description:	powder
Sample type:	seized /Customs, Slovenia
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	methyl 3-oxo-2-phenylbutanoate
Other names	Methyl alpha-acetylphenylacetate; Benzeneacetic acid, a-acetyl-, methyl ester
Formula (per base form)	C11H12O3
M_w (g/mol)	192,21
Salt form/anions detected	base
StdInChIKey (per base form)	CYSACHQWYQYLIG-UHFFFAOYSA-N
Other NPS detected	none
Additional info (purity..)	>98% 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 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

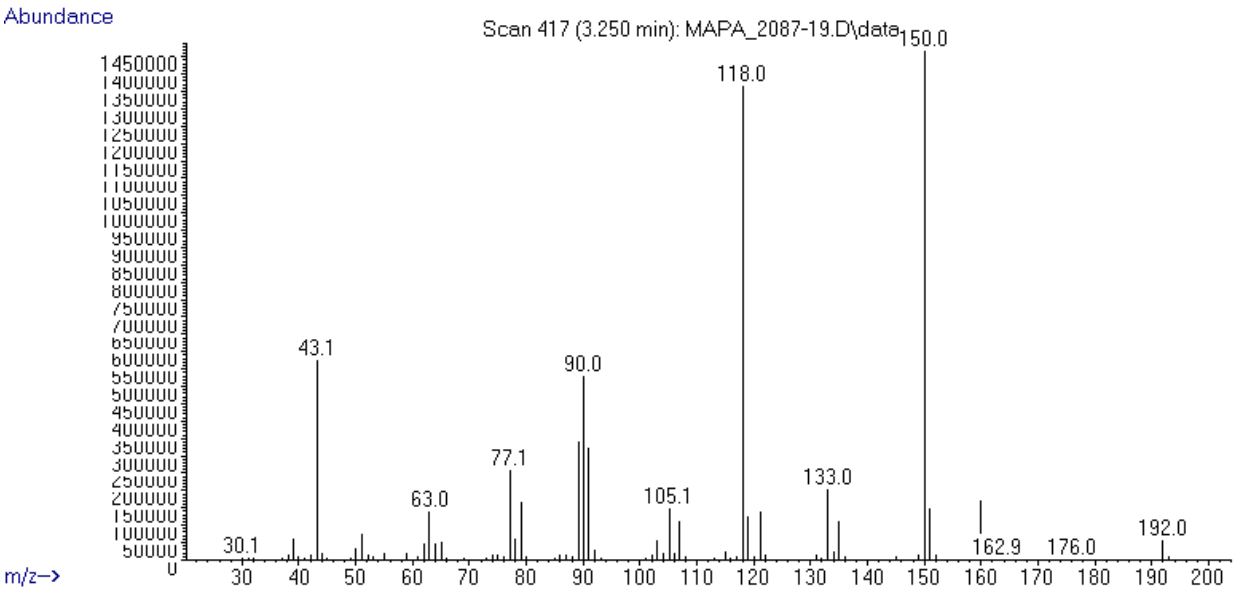
Supporting information

Solubility in	result/remark
CH_2Cl_2	soluble
MeOH	
H_2O	partially

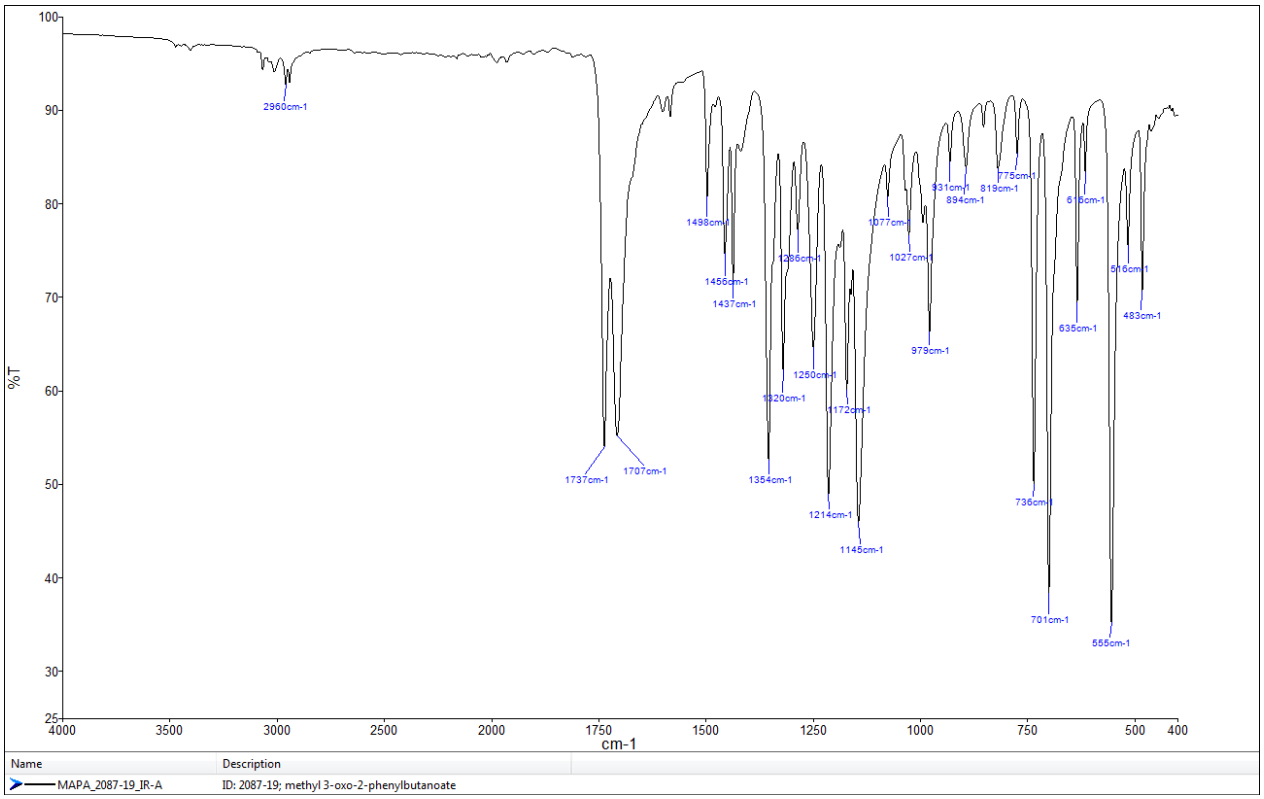
Analytical technique:	applied	remarks
GC-MS (EI ionization)	+	NFL GC-RT (min): 3,25 BP(1): 150; BP(2): 118,BP(3) :43,
HPLC-TOF	+	Exact mass (theoretical): 192,0786; measured value Δppm:0,56; formula:C11H12O3
FTIR-ATR	+	direct measurement (sample as received)
FTIR (solid phase) always as base form	+	
IC (anions)	+	
NMR (in FKKT)	+	
validation		
other		

ANALYTICAL RESULTS

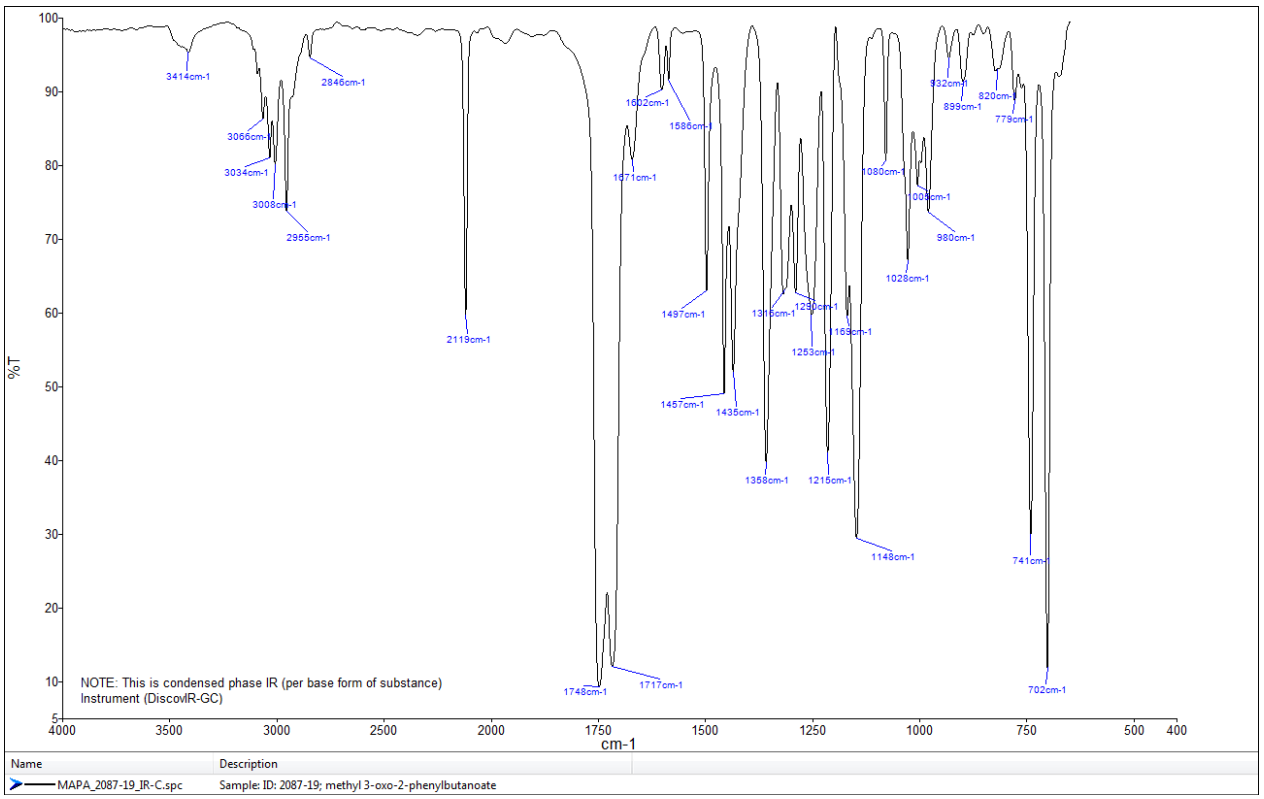
MS (EI)



FTIR-ATR - direct measurement (sample as received)



IR (solid phase – after chromatographic separation)



TOF REPORT

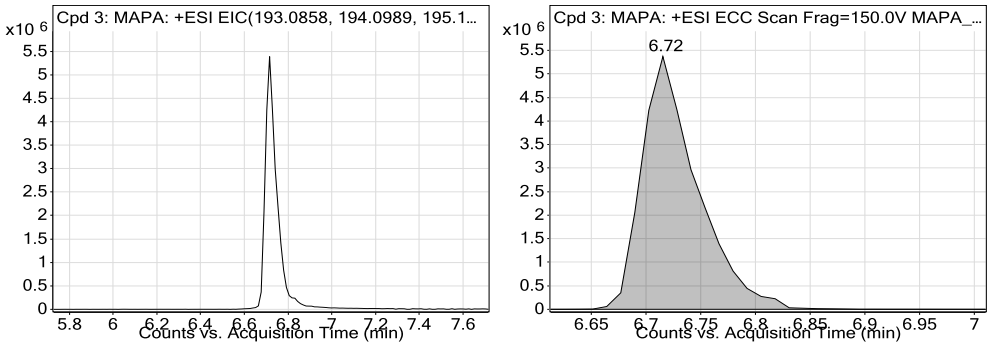
Data File	MAPA_2087-19.d	**Sample Name**	extract in MeOH
Sample Type	Sample	**Position**	P1-D2
Instrument Name	6230B TOF LC-MS	**User Name**	
Acq Method	general-8_1_2019-XDB-C18-ESI+.m	**Acquired Time**	4/18/2019 1:15:06 PM
IRM Calibration Status	Success	**DA Method**	a-Drugs_NFL.m
Comment			

Compound Table

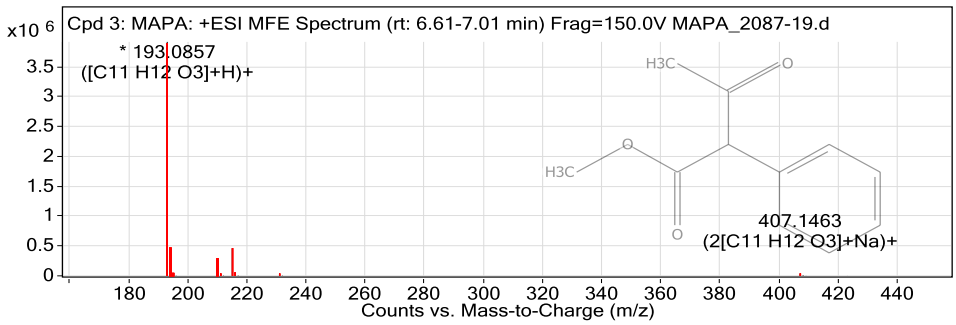
Label	Compound Name	MFG Formula	Obs. RT	Obs. Mass
Cpd 3: MAPA	MAPA	C11 H12 O3	6.72	192.0785

Name	*Obs. m/z*	Obs. RT	Obs. Mass	DB RT	DB Formula	DB Mass	DB Mass Error (ppm)
MAPA	193.0857	6.72	192.0785	6.72	C11 H12 O3	192.0786	0.56

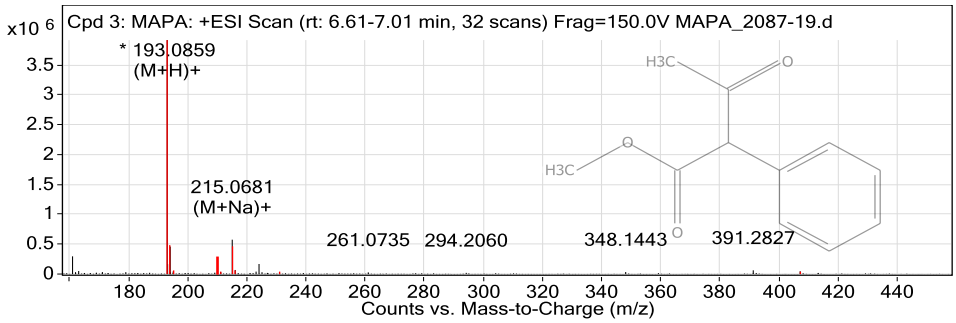
Compound Chromatograms



MFE MS Zoomed Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Charge	Abund	Formula	Ion/Isotope
193.0857	1	3914086	C11 H12 O3	(M+H)+
194.0893	1	465408.33	C11 H12 O3	(M+H)+
195.092	1	42448.45	C11 H12 O3	(M+H)+
210.1123	1	283580.91	C11 H12 O3	(M+NH4)+
211.1157	1	35314.92	C11 H12 O3	(M+NH4)+
215.0679	1	462412.16	C11 H12 O3	(M+Na)+
216.0712	1	54112.2	C11 H12 O3	(M+Na)+
231.0416	1	30670.49	C11 H12 O3	(M+K)+
407.1463	1	38507.9	C11 H12 O3	(2M+Na)+
408.1496	1	9849.2	C11 H12 O3	(2M+Na)+

--- End Of Report ---

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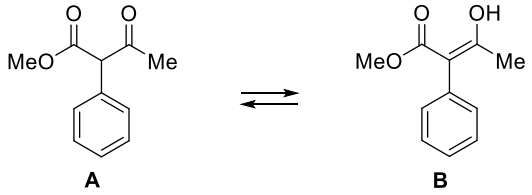
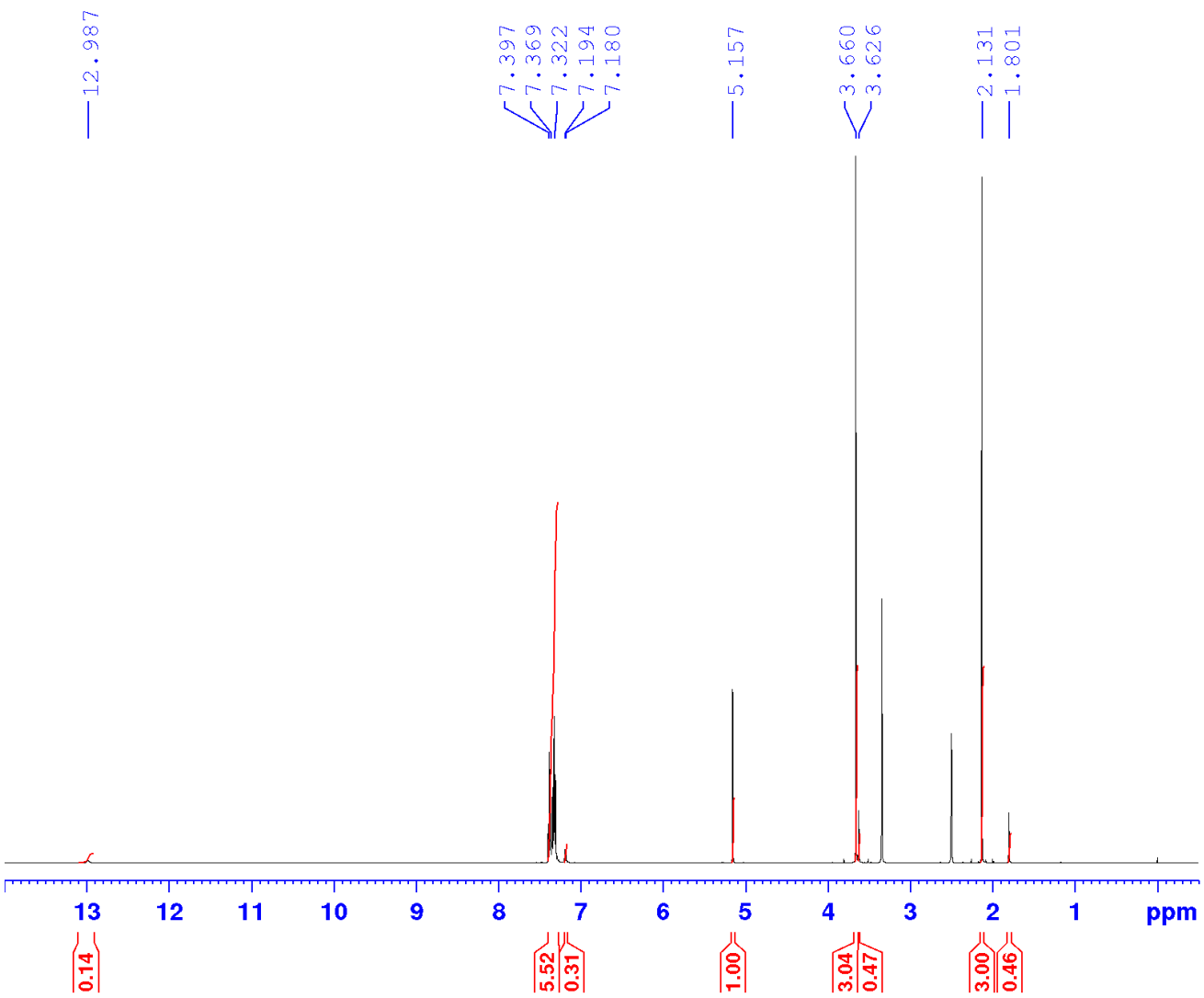
University
of Ljubljana

Faculty *of Chemistry*
and Chemical Technology

R E P O R T

Contract No.	C1714-17-460078 (Republic of Slovenia, Ministry of the Interior, POLICE)
Sample ID:	**carina-306_2019**
Received date:	April 29, 2019
Our notebook code:	NFL-carina-306_2019
NMR sample preparation:	21.6 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
Proposed structure with formula, exact mass, molecular weight:	 **A** **B** Chemical Formula: $C_{11}H_{12}O_3$ Exact Mass: 192,0786 Molecular Weight: 192,2140
Chemical name:	methyl 3-oxo-2-phenylbutanoate (**A**)
Comments:	- Structure elucidation based on 1D and 2D NMR spectra and HRMS. - The sample consists of herein identified compounds **A** (>98% purity), which is presumably partly in enol tautomer **B** (molar ratio **A** : **B** = 1 : 0.16) 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:	May 8, 2019

NFL-carina-306_2019
1H

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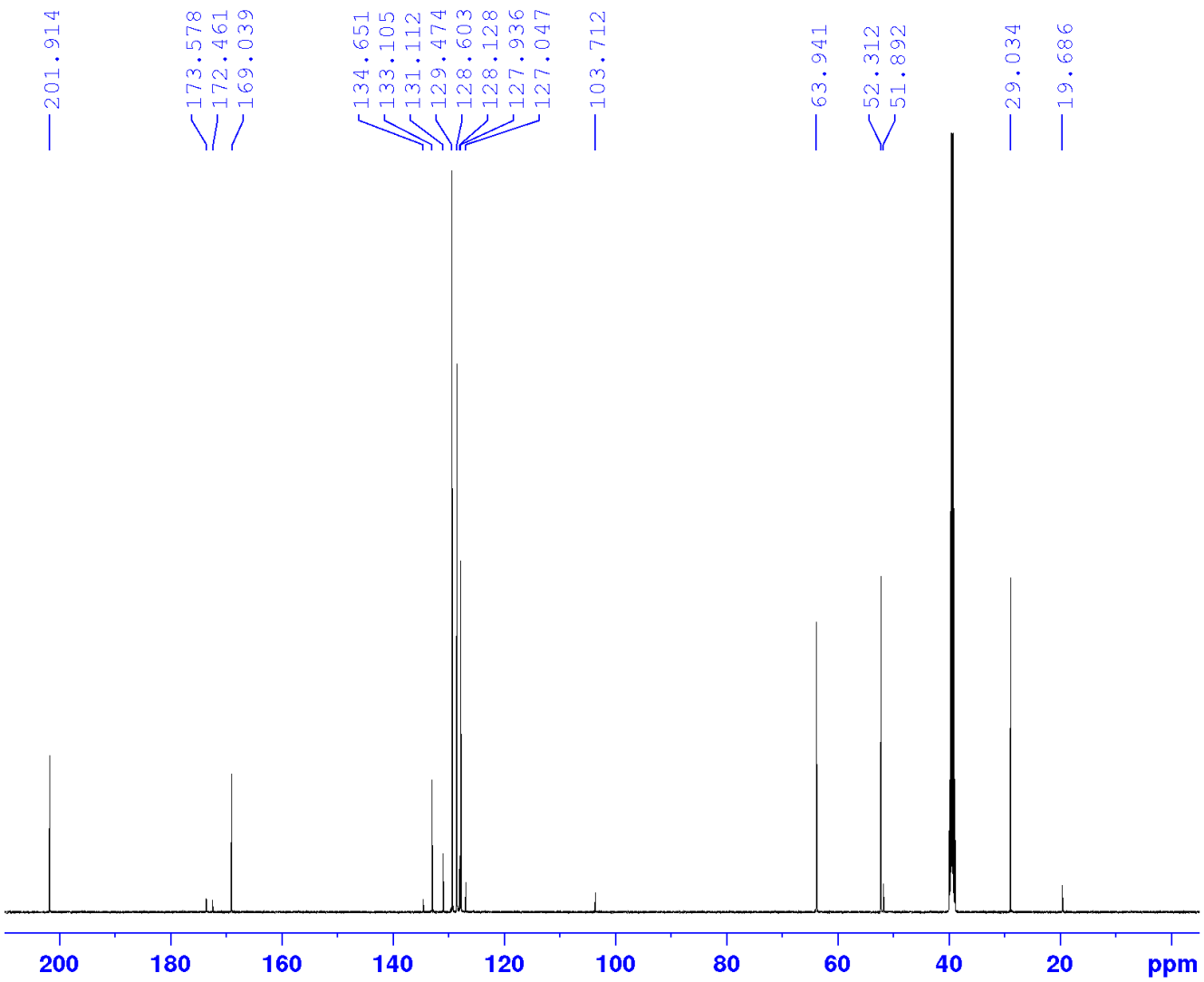
Current Data Parameters
NAME      NFL-carina-306_2019
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190501
Time                4.01
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                  71.8
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           500.1300043 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

NFL-carina-306_2019
13C

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EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_            20190501
Time                 6.31
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT               DMSO
NS                    4096
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            125.7578456 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```