Identification and characterization of a novel cathinone derivative 1-(2,3dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-ethanone seized by customs in Jersey

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Abstract A suspicious white powder labeled “idanyl-biphenyl-amninone”, which was seized by customs at the “channel island” of Jersey, UK, was brought to our laboratory to identify and characterize its structure. For the elucidation process it required the use of several complementary analytical techniques, such as gas chromatography-mass spectrometry, liquid chromatography coupled to high-resolution mass spectrometry, nuclear magnetic resonance spectroscopy, and X-ray crystallography. The unknown compound was finally identified as 1-(2,3dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-ethanone, a novel cathinone derivative. To the best of our knowledge this compound has not been registered in the CAS or IUPAC database. However it has recently been marketed on the internet as “indapyrophenidone” and we therefore propose this as common name of the compound. The results of this study may serve forensic and clinical laboratories to identify its related compounds with similar backbone structure by using the information reported in this article by applying the advanced analytical techniques. It may also lead to timely and adequate responses by legislators and law enforcement in the near future.

Keywords New psychoactive substances • Novel cathinone derivative • 1-(2,3dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-ethanone • indapyrophenidone • High-resolution mass spectrometry • Nuclear magnetic resonance spectroscopy • X-ray crystallography

Introduction

The increase in the number, type and availability of new psychoactive substances (NPSs) with possible health and social risks is of alarming concern [1]. NPSs often have only minor modifications to the backbone structure of existing substances and many of them are designed and intended as legal replacement of conventional illicit drugs like cocaine, cannabis, and amphetamines. They produce similar effects. Although there is usually little or no information on their acute and particularly chronic harm, several intoxications and deaths have been reported [1, 2].

In 2014, 101 NPSs were detected for the first time in the European Union (EU), and they were mostly synthetic cannabinoids, stimulants, hallucinogens and opioids. Thirty-one of these substances were synthetic cathinones, the largest class of new drugs identified in Europe in 2014. In 2013, over 10,000 seizures of synthetic cathinones were reported to the EU Early Warning System. The cathinones are misused in similar ways to other stimulants such as amphetamine and MDMA [3, 4]. Since the mid-2000s, many ring-substituted cathinone derivatives have been sold on the recreational market usually as highly pure white or brown powders, but little is known of their detailed pharmacology [5]. With the communication facilities nowadays available, these new drugs may spread rapidly worldwide [1]. However, there is little knowledge on these new substances and they normally get missed in routine drug analysis [6], putting users at risk when abusing them. In addition, users often take new substances unknowingly, as branded products change their ingredients over time or vendors mislabel products to be able to sell out their stock. For analytical chemists and clinical toxicologists it becomes more and more difficult to keep their analytical screening methodologies up to date, due to the rapid introduction of new substances. Moreover, the detection and identification of NPSs is time consuming, complex and expensive. Nevertheless, it is an essential and first step to assess the risks, and ultimately to control potentially dangerous new drugs [7].

A good analytical strategy is needed for detecting and identifying NPSs. The absence of reference standards and the limited availability of NPSs, both in terms of sample amount and/or purity, makes this task increasingly challenging. For these reasons, the combination of spectroscopic and mass spectrometric techniques is required for a true confirmation of the identity [8]. For example, the use of orthogonal 1D and 2D NMR and mass spectrometric techniques represents a versatile approach that could

reach the sensitivity and structural detail required when unknown substances are to be detected or identified [9–11].

In this paper, we described the structure elucidation strategy, at our laboratory, for an unknown white powder labeled “idanyl-biphenyl-amninone”, seized by customs at the “channel island” of Jersey. Although Jersey is a self-governing parliamentary democracy, the United Kingdom (UK) is constitutionally responsible and therefore the unknown substance falls within its jurisdiction. Analysis of the unknown sample has been undertaken by combination of different spectroscopic techniques *i.e.* gas chromatography–mass spectrometry (GC–MS), liquid chromatography–quadrupole time-of-flight-mass spectrometry (LC–QTOF-MS), nulcear magnetic resonance (NMR) and finally X-ray crystallography. The aim of the present work was to identify and characterize the unknown substance and to provide analytical information regarding GC–MS, LC–QTOF-MS and NMR spectra. This information is important for forensic and clinical laboratories and allows tracking of possible further spreading of this NPS or potential derivatives worldwide.

Material and methods

Sample for analysis

A white powder containing an unknown substance was obtained by customs of the island of Jersey (off the coast of Normandy, France) in 2014.

Chemicals and reagents

For GC–MS analysis, methanol, methyl-*tert*-butyl ether, quinoline and tripelennamine were purchased from Sigma-Aldrich (Madrid, Spain). For liquid chromatography–high resolution mass spectrometry (LC–HRMS) analysis, HPLC-grade water was obtained by purifying demineralised water in a Milli-Q plus system from Millipore (Bedford, MA, USA). HPLC-grade methanol (MeOH), formic acid (HCOOH) and sodium hydroxide (NaOH > 99%) were acquired from Scharlau (Barcelona, Spain). Leucine enkephalin was acquired also from Sigma-Aldrich. For NMR analysis, deuterated chloroform ($CDCl_3$) was purchased from Sigma-Aldrich, and for X-ray diffraction, diethyl ether and acetonitrile were acquired from Scharlau.

Sample treatment

Approximately 1 mg of powder was dissolved in 1 mL of methanol in 1.5 mL polypropylene tubes. The methanolic solutions were vortexed for 1 min and subsequently centrifuged at 8000 rpm (6030 *g*) for 5 min. For GC analysis, an aliquot of 10 µL of the supernatant was diluted with 1 mL of methyl-*tert*-butyl ether, containing 10 µg/mL quinoline and tripelennamine. For LC analysis, an aliquot of 100 µL of the supernatant was ten-fold diluted with water. For NMR analysis 10 mg of powder were dissolved in $CDCl_3$, and suitable single crystals for X-ray diffraction analysis were obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile sample solution to obtain colorless needle-shaped single-crystals.

Instrumentation

GC–MS analyses with electron ionization (EI) were done using an Agilent 7890A GC with 5975C VL MSD (Agilent, Santa Clara, CA, USA) equipped with a split-splitless injector and an HP5-MS column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness) and running on Agilent ChemStation. A 1-µL aliquot of the diluted sample was injected for GC–MS analysis using 5:1 split ratio. The column was held at 80°C for 4 min and then ramped up at 40°C/min to 290°C and held to a total run time of 40 min. A mass range of *m/z* 40 to 400 was scanned.

For LC–QTOF-MS analysis, we used a Waters Acquity UPLC system (Waters, Milford, MA, USA) interfaced to a hybrid quadrupole-orthogonal acceleration-TOF mass spectrometer (XEVO G2 QTOF, Waters Micromass, Manchester, UK), using a Z-Spray electrospray ionization (ESI) interface operating in positive ionization mode. The chromatographic separation was performed using an Acquity UPLC BEH C18 column (1.7 µm particle size, column 100 × 2.1 mm; Waters) at a flow rate of 300 µL/min. The mobile phases used were A = H_2O and B = MeOH, both with 0.01% formic acid. MS data were acquired over therange *m/z* 50–1000. A capillary voltage of 0.7 kV was used. A cone voltage of 20 V was used. For further details, see our previous report [12].

High-field ^{1}H and $^{13}C\{^{1}H\}$ NMR analyses were recorded with Varian NMR System 500 MHz spectrometer at 303 K using $CDCl_3$ (Varian, Palo Alto, CA, USA). The residual solvent signals [$CHCl_3$ (^{1}H: δ = 7.26) and $CDCl_3$ (^{13}C: δ = 77.16)] were

used as the internal references. Full characterization of the described compound was performed using gradient-enhanced two dimensional experiments: total correlated spectroscopy (TOCSY) and phase-sensitive hetero-nuclear single quantum coherence (HSQC) recorded under routine conditions using the Varian vnmrj2.2c software

X-ray crystallography diffraction data were collected by using an Agilent Supernova diffractometer equipped with an Atlas CCD detector using CuK_{α} radiation (λ = 1.54184 Å) at 293 K [13]. Data collection and integration was performed with the program SHELXS-2013 (Yale University, New Haven, CT, USA), using the OLEX software package (Olex AS, Trondheim, Norway).

Results and discussion

Gas chromatography – mass spectrometry

First of all, we measured the total ion current chromatogram (TIC) of this sample by GC–MS. The TIC showed a single sharp peak, illustrating that the dubious powder consisted of a single compound with high purity (probably more than 95 %). GC–MS analysis is often used to identify drugs of abuse, as mass spectra searching can be used for GC–EI-MS using commercial or free standardized libraries (e.g. NIST, Cayman Spectral Library, SWGDrug GC-MS library). However, searching the obtained spectrum of the suspected compound in several forensic databases did not return any result. Nevertheless, some structural information was gained from the GC–MS measurements (Fig. 1), and together with the labeled name (“indanyl-biphenyl-amninone”) of the powder, which might give some indications, the interpretation GC–MS mass spectrum was done with great care.

The GC–MS spectrum and the label suggested the presence of an indanyl group, possible next to a carbonyl and next to a nitrogen (indanyl-CO-NH-, *m/z* 160.1). A further loss of a CH group of this main ion, may result in an ion at *m/z* 146. In addition, the presence of a phenyl- ring, linked by a carbon atom (C_6H_5-CH_2-, *m/z* 91.1) *i.e.* a tropylium ion, can be assumed. Information on some functional groups, e.g. indanyl and a benzene group, was useful. However, for structure elucidation, additional analyses were necessary.

Liquid chromatography – quadrupole time of flight mass spectrometry

LC–HRMS can provide the elemental composition based on the accurate-mass full-acquisition data provided. The low fragmentation commonly ocurring in the soft ionization employed (*i.e.* ESI) favours the presence of the (de)protonated molecule in the mass spectra. The use of the hybrid QTOF analyzer makes it possible to perform additional tandem mass spectrometry analysis, obtaining the accurate-mass product ion mass spectra to be used in the elucidation process [14]. Information on the structure may be also obtained by applying strategies on the basis of mass-defect filtering or common fragmentation pathways [15, 16]. This, for example, helps to identify compounds, such as derivatives that share a common moiety.

Fig. 2 shows the TIC, the corresponding accurate-mass spectrum and product ion mass spectra of the unknown substance generated by UHPLC–QTOF-MS. The retention time was 8.88 min (Fig. 2a) and the molecular formula was $C_{21}H_{23}NO$. The latter could be calculated with high confidence (mass error 0.6 ppm) from the accurate mass, *m/z* 306.1860, obtained for the protonated molecule $[M+H]^+$ (Fig. 2b bottom). The elemental composition of the product ions was also estimated and the structures of most of them could be tentatively elucidated and explained by an initial neutral loss of a pyrrolidine C_4H_9N fragment, and subsequent loss of CO (Fig. 2b middle). At higher collision energy, two losses of CH_3 radical and C_2H_4 were observed from fragment $C_{16}H_{15}^+$ with *m/z* 207.1174 (Fig. 2b top) that may intuitively come from the propylene group of the indanyl moiety. The unknown compound was tentatively identified as 1-(2,3-dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-ethanone. Although it seemed feasible to explain the fragment $C_{16}H_{15}^+$ from subsequent neutral losses of C_4H_9N and CO, some doubts were generated due to the major rearrangement needed to form this product ion (Fig. S1). Therefore, NMR analysis was performed to make the final elucidation of the structure of this compound.

Nuclear magnetic resonance

NMR is a powerful structure elucidation technique [17], and was used in the present work for further structure elucidation. The ^1H NMR spectrum (500 MHz, $CDCl_3$) of the unknown compound displayed partial signal overlapping both in the aliphatic and in the aromatic region (Fig. S2). The TOCSY and phase-sensitive HSQC spectra were particularly useful to unambiguously assign proton and carbon resonances. Figure 3

illustrates the TOCSY spectrum recorded in $CDCl_3$, from which it can be inferred the presence of 4 spin systems and two isolated resonances. The pyrrolidine group (depicted in red in the online version) displayed two pairs of diastereotopic protons (manifested as 4 equally populated broad resonances) in the δ = 3.2–3.8 ppm range, accompanied by a group of signals in the δ = 2.0–2.3 ppm range from the methylene groups at the 2 and 3 pyrrolidine position. These signals were broad most likely due to the conformational exchange in the intermediate NMR time scale regime of the 5-membered pyrrolidine ring. Two resonances at δ = 2.0 and 2.8 ppm (marked in blue in the online version) with a 1:2 relative area were attributed to the propylene group from the indanyl moiety. Two additional equally populated resonances at δ = 7.2, 7.7 ppm were also detected from the trisubstituted phenyl ring group of the indanyl moiety (marked in pink in the online version). The single-substituted phenyl ring produced a set of signals at δ = 7.3 and 7.8 ppm (depicted in green in the online version). Two isolated resonances, one at δ = 6.6 ppm assigned to the CH neighbouring group to the carbonyl and the other overlapped with the single-substituted phenyl resonances, were also observed. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum was consistent with the proposed structure (Fig. S3) and the phase-sensitive HSQC connectivities (Fig. S4) allowed the assignments of proton and carbon resonances to the structure of the sample. Two single carbon resonances (δ = 23.9 and 52.7 ppm) for the methylene groups of the pyrrolidine at the 2 and 3 positions were observed. The propylene group of the indanyl moiety displayed three carbon resonances at δ = 25.2, 32.4 and 33.1 ppm, whereas the central quaternary carbon atoms of this fragment appeared in the usual δ =145–152 ppm range. The single-substituted phenyl group showed carbon resonances at the expected chemical shifts in the δ = 120 to 130 ppm range, but most of them were partially overlapped with those from the CH groups of the indanyl framework (Fig. S3 and S4). The resonances for the isolated CH group neighbouring to the CO group and the CO group were observed at δ = 71.0 and 192.1, respectively.

X-ray crystallography

X-ray crystallography was the ultimate confirmation step to establish the structure of the unknown substance. Diffraction data were collected by using an Agilent Supernova diffractometer equipped with an Atlas CCD detector. No instrument or crystal instabilities were observed during data collection. The structures were solved by charge-

flipping methods by using Superflip and refined by the full-matrix method on the basis of F^2 with the program SHELXL-2013, using the OLEX software package [18–20]. Absorption corrections based on the multiscan method were applied [21]. Details regarding the data collection and the refinement parameters used are listed in Table 1.All non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were included at their idealized positions and refined as riders with isotropic displacement parameters assigned as 1.2 times the U_{eq} value of the corresponding bonding partner.

Suitable crystals for X-ray studies of the $C_{21}H_{24}ClNO$ chloride protonated salt were grown by slow vapor diffusion of diethyl ether into a sample solution in acetonitrile. The structure of $C_{21}H_{23}NO$ was refined in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with cell dimensions: a = 7.1019(2), b = 16.0703(5), c = 16.1084(5) Å and α = β = γ = 90° (Table 1). Figures 4 shows the ORTEP representation of the structure with the atom numbering scheme and selected average bond lengths. Chlorine atom of the counter anion was found disordered between two positions and occupation factors of the chlorine atoms were expressed in terms of a "free variable", so that, their sum was constrained to 1. The flack parameter equal to 0.42 indicates that this substance has crystallized with an excess of one enantiomer over the other due to the non-centrosymmetric character of the space group. The structural figure was drawn (Fig. 4) using Diamond (a visual crystal-structure-information software system) [22] and unambiguously confirmed 1-(2,3-dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-ethanone to be the unknown compound. To the best of our knowledge this compound has not been registered in the CAS or IUPAC database. However it has recently been sold on the internet under the product name "indapyrophenidone".

Finally, all data regarding X-ray crystallography and structure refinement were checked and deposited in the Cambridge Crystallographic Data Centre. CCDC 1426092 contains the supplementary crystallographic data for this compound and can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

The identification and characterization of the unknown compound, identified as a novel cathinone derivative 1-(2,3-dihydro-1*H*-inden-5-yl)-2-phenyl-2-(pyrrolidin-1-yl)-

ethanone, ($C_{21}H_{23}NO$) was an analytical challenge that required the complementary use of several advanced analytical techniques, including GC–MS, LC–HRMS, NMR and X-ray crystallography. It was the first step required, which will allow controlling the possible consumption of this compound. Although the toxicity and pharmacological actions in human are unknown, it is expected that this compound exerts its psychoactive actions in humans that are similar to those of other cathinone derivatives. The strategy applied in this work can be used to identify other NPSs that continuously are appearing in the market. The analytical data obtained in this paper may contribute to the discovery of other potential cathinone derivatives. The presented information on the novel cathinone derivative will serve analytical chemists in forensic and clinical laboratories, toxicologists and other healthcare professionals.

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Compliance with ethical standards

Conflict of interest There are no financial or other relations that could lead to a conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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Table 1 Crystallographic data for the unknown compound

Parameter	Data
Empirical formula	$C_{21}H_{24}ClNO$
Formula weight	341.86
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a, Å	7.1019(2)
b, Å	16.0703(5)
c, Å	16.1084(5)
α≡	90
β≡	90
γ ≡	90
Volume, $Å^3$	1838.45(10)
Z	4
D_{calc} (Mg m^{-3})	1.235
Absorption coeffient (mm^{-1})	1.876
F(000)	728.0
Crystal size (mm^3)	0.19 x 0.16 x 0.12
Theta range for data collection (º)	3.89 to 66.95
Index ranges	$-8 \le h \le 6$,
	$-17 \le k \le 18$,
	$-18 \le l \le 19$
Reflections collected	8720
Independent reflections	3130 [R_{int} = 0.0561]
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3130/0/227
Goodness-of-fit on F^2	1.110
Final R indices [I>2σ(I)]	R_1 = 0.0969, wR_2 = 0.2675
R indices (all data)	R_1 = 0.1030, wR_2 = 0.2747
Largest difference in peak and hole ($e \cdot A^{-3}$)	1.07 and –0.38
Flack parameter	0.42(7)

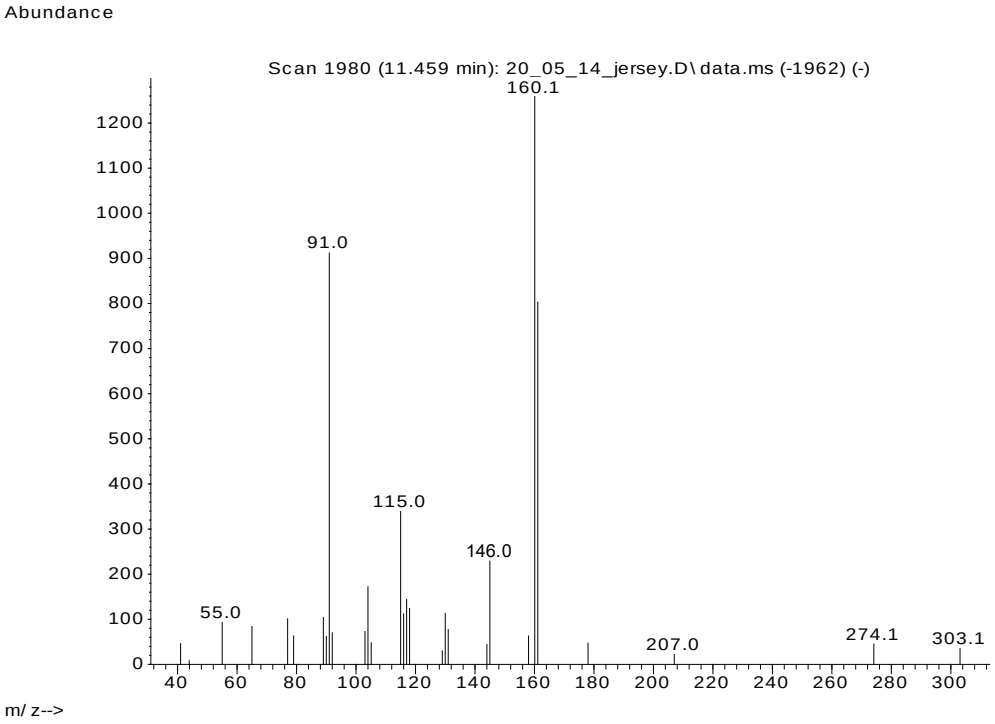
Figure captions

Fig. 1 Electron ionization mass spectrum of the unknown compound obtained by gas chromatography – mass spectrometry

Fig. 2 Detection of the unknown compound by UHPLC– quadrupole time-of-flight-mass spectrometry **a** total ion current chromatogram **b** full accurate-mass spectra applying collision energy of 4 eV (bottom), and tandem accurate-mass spectra applying collision energy of 20 and 30 eV (middle and top, respectively)

Fig. 3 Total correlated spectroscopy (TOCSY) nuclear magnetic resonance spectrum of the unknown compound recorded in $CDCl_3$ together with the proposed structure and proton signal assignments based on the chemical shift, signal intensities, multiplicity and connectivities derived from ^{1}H TOCSY and phase-sensitive hetero-nuclear single quantum coherence experiments

Fig. 4 Oak ridge thermal ellipsoid plot **(**ORTEP) X-ray crystallography presentation (ellipsoids at the 50 % probability level) of the unknown compound with atom numbering scheme. Selected bond lengths [Å]: N1–C1 1.519(9); N1–C5 1.479(9); C5–C6 1.530(10); C5–C12 1.548(11); C12–O1 1.194(12); C12–C13 1.493(12). Hydrogen atoms have been omitted for clarity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Scan 1980 (11.459 min): 20_05_14_jersey.D\data.ms (-1962) (-)
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91.0
115.0
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274.1
303.1
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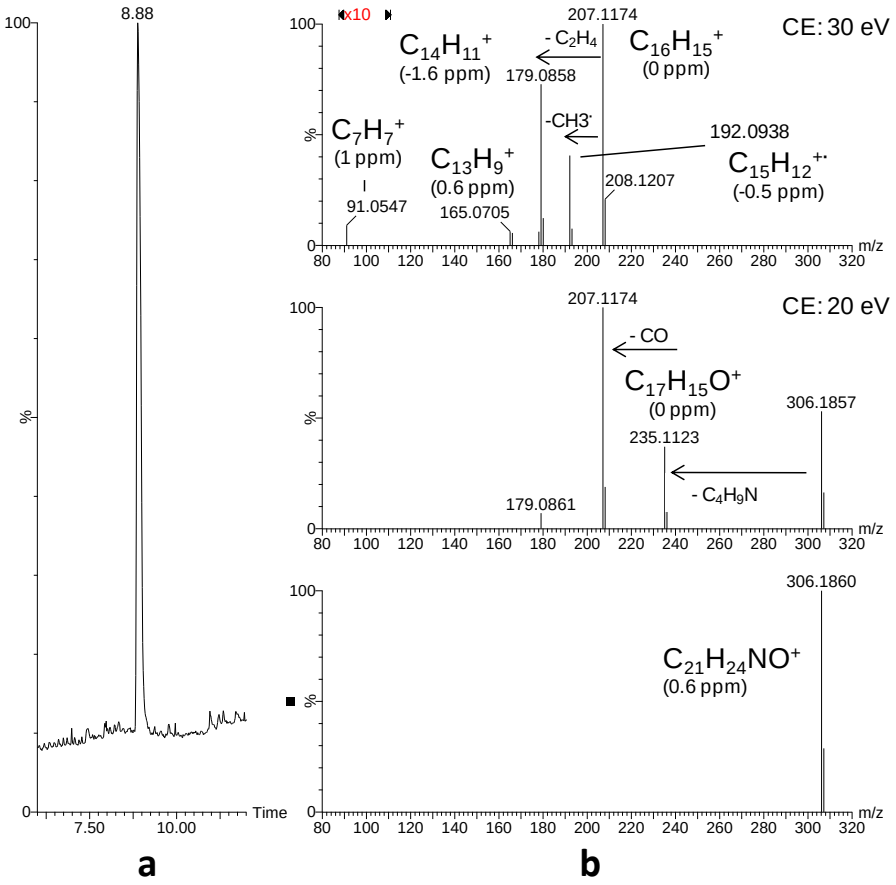
Figure 1


8.88
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207.1174
CE: 30 eV
C14H11+
(-1.6 ppm)
- C2H4
179.0858
C16H15+
(0 ppm)
C7H7+
(1 ppm)
-CH3·
192.0938
C13H9+
(0.6 ppm)
C15H12+·
(-0.5 ppm)
208.1207
91.0547
165.0705
m/z
207.1174
CE: 20 eV
- CO
C17H15O+
(0 ppm)
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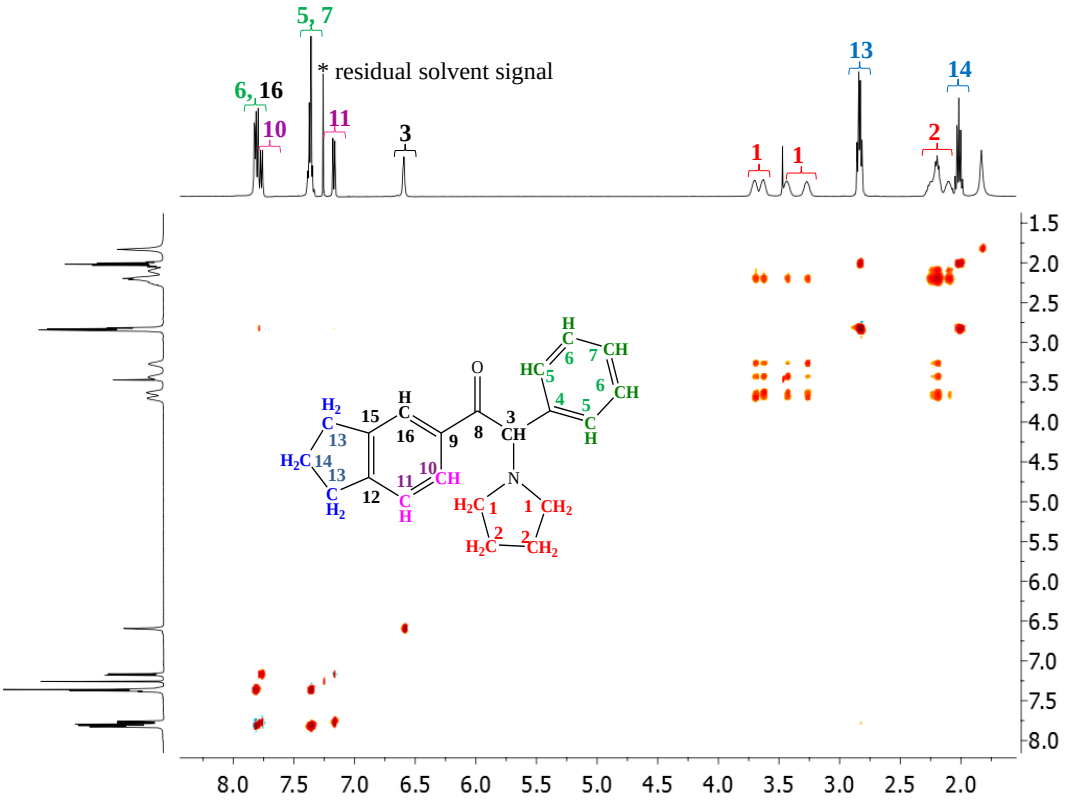
235.1123
- C4H9N
179.0861
306.1860
C21H24NO+
(0.6 ppm)
b

Figure 2


5, 7
* residual solvent signal
6, 16
10
11
3
1
1
13
14
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1.5
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8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0

Figure 3

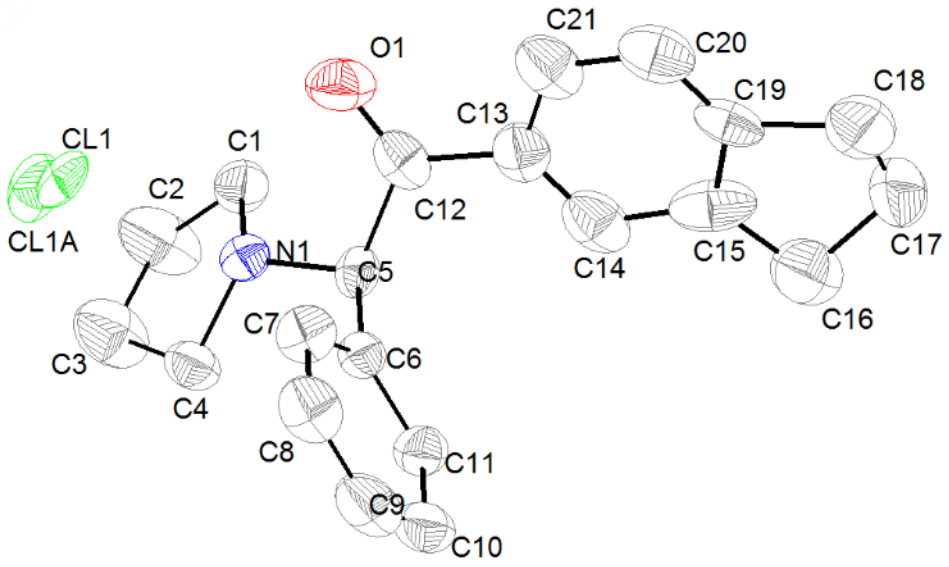
C21
O1
C20
C19
C18
C13
CL1
C1
C2
C12
CL1A
N1
C5
C14
C15
C17
C7
C16
C6
C3
C4
C8
C11
C9
C10

Figure 4