

Synthesis and Characterization for Some New Organoselenium Compounds Depending on 8- Hydroxyquinoline

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Abstract

In the present research, New organoselenium compounds were prepared from the reacting between 7- (chloromethyl) quinoline-8-ol, selenium metal, and sodium cyanide (NaCN) in the presence of dimethylsulfoxide (DMSO) as a solvent. This reaction was carried out under a nitrogen atmosphere to give the compound 7- (selenocyanatomethyl) quinoline-8-ol (C1), then prepared the derivatives such as organyl selenium tribromide and diorganyl diselenide. All prepared compounds were characterized by using infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (¹H NMR), and mass spectroscopy. Such as explained below

Keywords: organoselenium, quinolone, ¹H NMR, selenocyanate and diselenide

Introduction

Selenium is an essential chemical element in active sites^{1,2}, including potassium selenocyanate (KSeCN). It is a reagent and is easy to deal with, and its properties are crystalline in shape that absorbs moisture and is sensitive to the presence of air. Selenocyanate has the advantage of being soluble in proton and polar non-protonal solvents such as DMF, DMSO, NMP and acetonitrile. Methods that use potassium selenocyanate (KSeCN) as a source of selenium in the preparation of organic KSeCN compounds and isocyanocyanates are very important as other functional groups. New carbon-selenium (C-Se) and the synthesis of many compounds of structural³, pharmacological and biological importance⁴ Researchers have discovered new direct methods for selenosine⁵, for example natural selenocyanation that is easily melted and catalyzed with solvents of activated alkenes⁶. Bromine-catalyzed selenocyanation⁷, iodine catalyst⁸ and organic copper catalyst⁹. In addition, organic selenium cells were discovered to be used as antioxidants¹⁰. Tests were conducted on organic selenium compounds and found that they act as anti-bacterial and histamine¹¹ In addition, it has been used as anti-tumor treatments such as breast tumors^{12,13}.

2-Experimental

2-a-Chemicals and Apparatus

Chemicals were used to prepare the compounds from Sigma-Aldrich, Fluka, and BDH without filtration. The melting point of the prepared compounds was measured using a Melting point

SMP31 device, the ^1H NMR spectra were using a Bruker AVANCE-DRX 300MHz device, and the mass spectra with a triple quad LC / MS 6410 agilent device. Using Bruker in the range (500-4000 cm^{-1}).

2-a-1- preparation of compounds:

7- (methyl selenocyanate) quinoline-8-ol

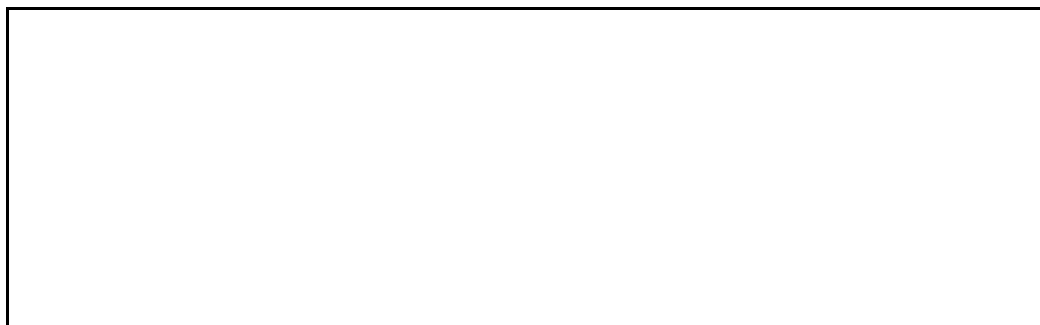
Add (0.0056 mole, 0.44 g) of selenium to (0.0055 mole, 0.27 g) of sodium cyanide, then dissolve them together in (15 ml) of freshly distilled dimethyl sulfoxide (DMSO), the mixture is stirred for one hour at a temperature of (100 °C) in the presence of Nitrogen (N_2) as an inert atmosphere. Then (15 ml) of (DMSO) is added to the hot mixture and then left to cool at laboratory temperature, changing its color to a pale yellow, adding to it (0.0056 mole, 0.95 g) of 7- (chloro methyl) quinolin-8-ol) in the presence of (N_2) for two hours and at a temperature of (100°C). The solution is filtered while it is hot, then it is cooled and poured into (300 ml) of cold distilled water. Yellow crystals are formed. We filter the solution and then wash it with ethanol. The result of the reaction was (66%), the resulting weight (0.99g) and the melting point (178-180 °C). As shown in Scheme (1).



Scheme (1) Preparation of the compound 7- (selenocyanato methyl) quinolin-8-ol

7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol

(0.002 mole, 0.5 g) of 7- (selenocyanato methyl) quinolin-8-ol is dissolved in (50 ml) of ethanol and then carefully added to it (5 ml) of bromine dissolved in (15 ml) of ethanol with continued stirring, consisting of Crystals leave the solution to stagnate, then filter and wash the sediment with ethanol and dry the result of the reaction (26%) of yellow crystals, the resulting weight (0.25 g) and the melting point (213-215°C)



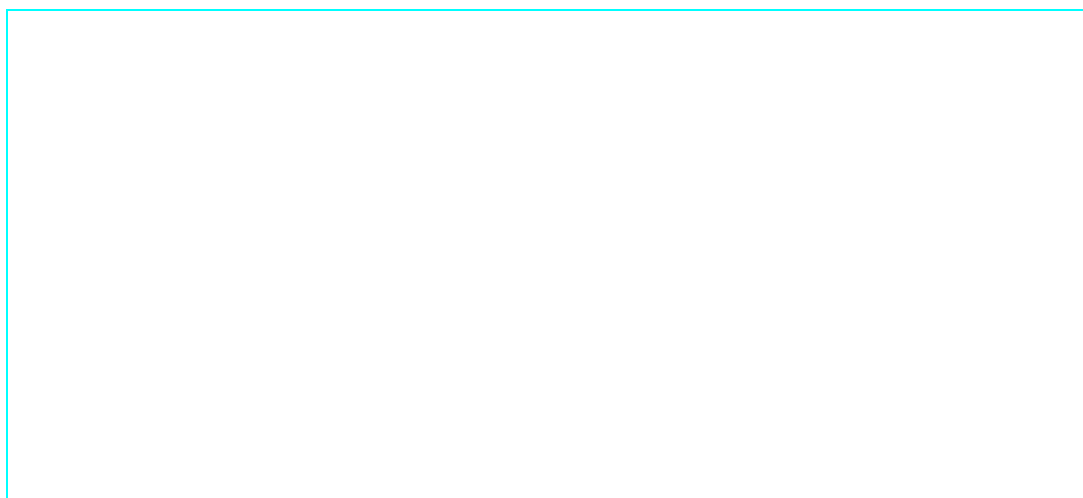
Scheme (2) Prepare 7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol

Table (1) the molecular weights and some physical properties of the prepared compounds

Comp ound	Chemical formula	Molecular weight	color	Melting point	yield
C1	C ₁₁ H ₈ N ₂ OSe	263.16	Pale yellow	173-175D	66%
C2	C ₁₀ H ₈ Br ₃ NOSe	476.85	Orange-yellow	213-215D	26%

3- Results and discussion

An organometallic compound derived from selenium is 7- (selenocyanato methyl) quinolin-8-ol was prepared by reacting the mineral selenium and sodium cyanide with 7- (chloro methyl) quinolin-8-ol derived from 8-hydroxyquinolin and the reaction was carried out under nitrogen as an inert gas. A second selenium compound, 7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol was synthesized from the addition of bromine dissolved in ethanol to 7- (selenocyanato methyl) quinolin-8-ol also dissolved in Ethanol. The prepared compounds were characterized by infrared, ¹H NMR, MASS spectroscopy. measured .



Scheme (3) preparation of the 7- (selenocyanato methyl) quinolin-8-ol compound and 7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol

4- Characterization of prepared compounds

The prepared compounds were characterized based on results from infrared (FT-IR) spectrum, nuclear magnetic resonance (^1H NMR) spectrum and mass spectroscopy (MASS)

4-a- spectrum of C1 7- (selenocyanato methyl) quinolin-8-ol

In the infrared spectrum, we notice a group of diagnostic beams, which is the appearance of a clear beam at (2062 cm^{-1}) belonging to the $\text{C}\equiv\text{N}$ group as well as the appearance of a beam at ($3059\text{-}3037\text{ cm}^{-1}$) belonging to the aromatic CH group, while the aliphatic CH group appears at a beam at (2919 cm^{-1}), Another bundle within the range (3359 cm^{-1}) indicates phenolic OH while the $\text{C}=\text{N}$ group shows a very clear bundle at (1647 cm^{-1}), and the $\text{CH}=\text{CH}$ beam that indicates the aromatic ring appears at (1549 cm^{-1}). Table No. (2) shows the infrared absorption beams and Fig. No. (1) shows the infrared spectrum of the compound.

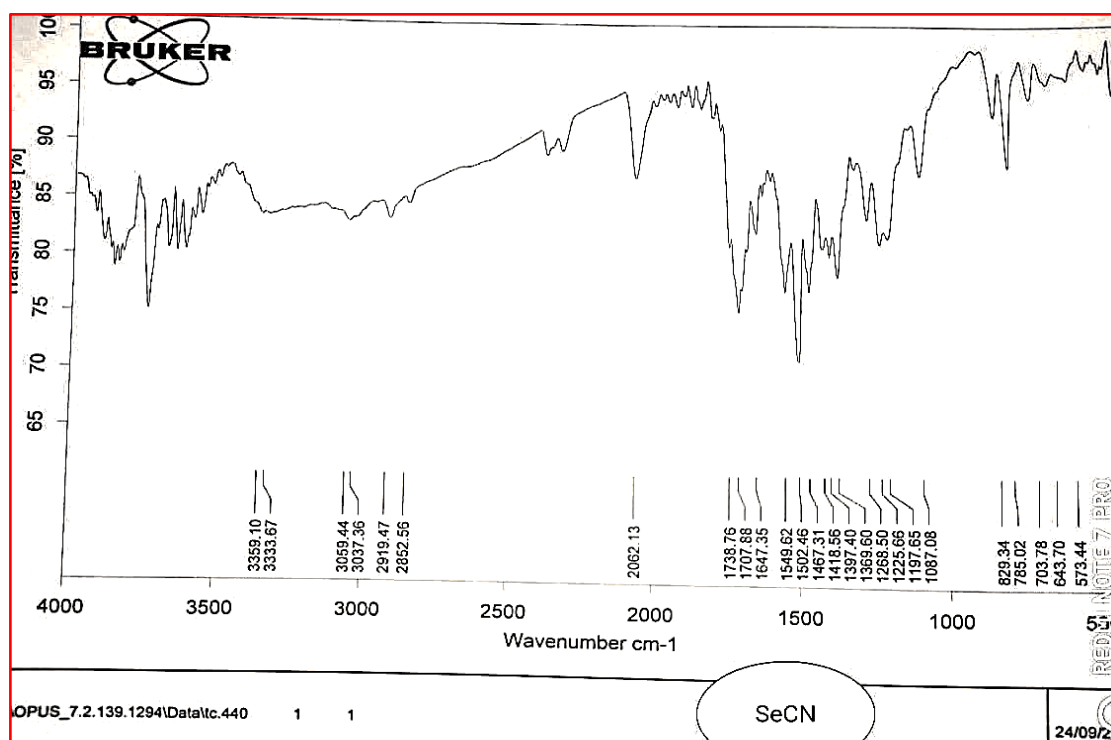


Figure (1) the spectrum of C1

4-b- spectrum of

7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol

The infrared spectrum showed a clear band at (3353 cm^{-1}) belonging to the aromatic OH group, while the CH aromatic group showed a beak at (3008 cm^{-1}), and the aliphatic C - H bond showed bands at (2925 cm^{-1}), Another bundle within the range (3353 cm^{-1}) indicates phenolic OH And a beak at (1618 cm^{-1}) refer to $\text{C} = \text{N}$ bond within the ring, and the bond ($\text{CH} = \text{CH}$) appearance at (1588 cm^{-1}). Table No. (2) shows the infrared absorption beaks, and Fig. (2) shows the infrared

spectrum of the compound.

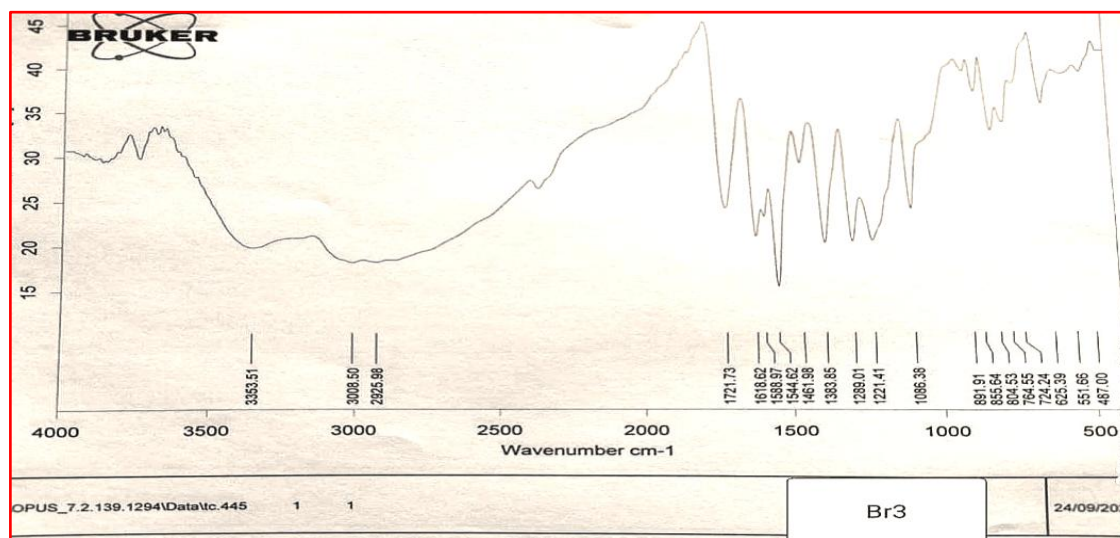


Figure (2) the spectrum of C2

Table (2) shows the IR beams of the prepared compounds

No	OH Phenolic cm ⁻¹	C-H Aromatic cm ⁻¹	C-H Aliphatic cm ⁻¹	C≡N cm ⁻¹	C=N cm ⁻¹	CH = CH cm ⁻¹
C1	3359	3059-3037	2919	2062	1647	1549
C2	3353	3008	2925	–	1618	1588

5- nuclear magnetic resonancespectra¹HNMR

One of the important techniques in characterizing the structure is ¹HNMR nuclear magnetic resonance spectroscopy, by inferring the location of the protons within the compound.

5-a- spectrum of 7- (selenocyanato methyl) quinolin-8-ol

The ¹HNMR spectrum showed a single beam at (4.7ppm) returning to the CH₂ group adjacent to the selenium atom. The protons of the aromatic region appeared as multiple beam within a displacement of (7.02-8.89ppm) with the complement of 5 protons. A single beam appears at (9.98ppm) and with a single proton integral, it belongs to the phenolic OH group. The packages can be seen in Table (3) and Figure (3) .

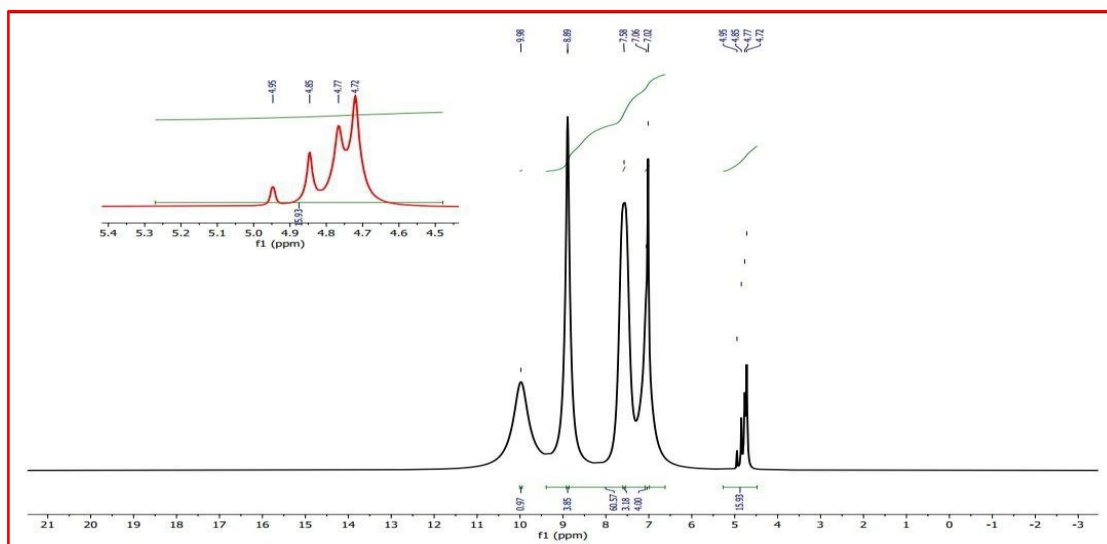


Figure (3) H^1 -NMR spectrum of C1

7- (selenocyanato methyl) quinolin-8-ol

5-b- spectrum of

7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol

The $1H$ NMR spectrum showed a single signal at (4.57ppm) and the integration of two protons back to the CH_2 group adjacent to the selenium atom (Se). 10.09ppm) by integrating one proton back to the phenolic OH group. The beams can be seen in Table (3) and Fig. (4).

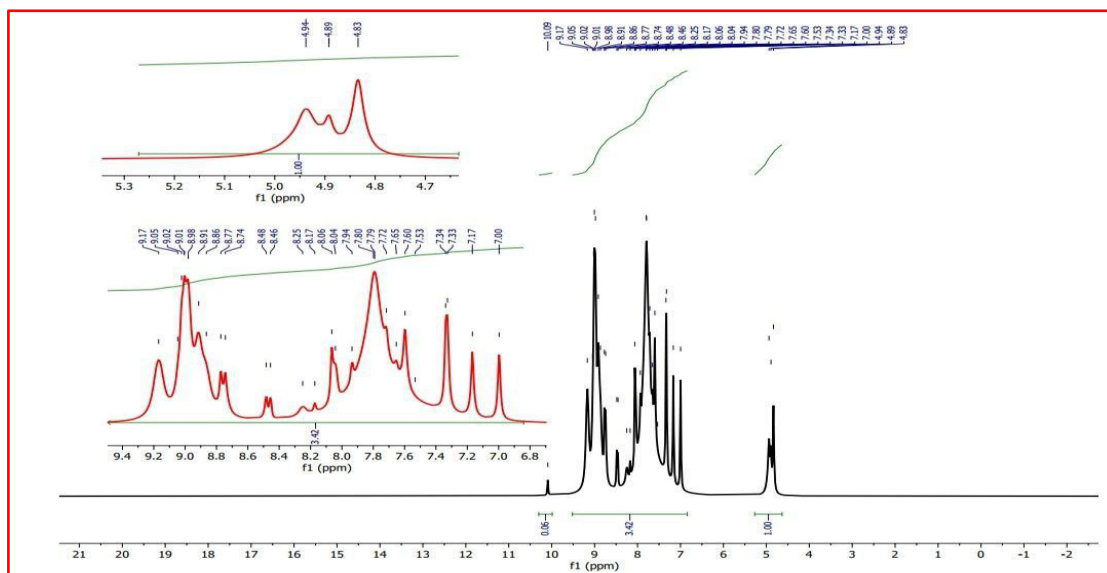


Figure (4) H^1 -NMR spectrum of C2

7-((di(λ^2 -bromaneylidene)bromo- λ^6 -selanyl)methyl)quinolin-8-ol

Table (3) ^1H NMR spectra for the prepared compounds

Compound	The name and formula of the compound	^1H NMR spectrum beams
C1		4.7 (s,2H) aliphatic proton , 7.02-8.89 (m,5H) aromatic proton , 9.98 (s,1H) OH phenol
C2		4.57 (s, 2H) aliphatic proton , 7.00-9.17(m,5H)aromatic proton ,10.09(s,1H)OH phenol

6- spectra of mass

The mass spectrum gives clear guide about the formula of the proposed compounds by observing the value of the molecular ion (parent ion), which indicates the total molecular weight of the compound, in addition to observing the base beam with a high peak, which indicates the high stability of the fragmented molecule, and the presence of other beams gives us an idea of the structural formula. The probability of forming ions depends on the fractionation rules.

6-a- spectrum of 7- (selenocyanato methyl) quinolin-8-ol

The mass spectrum of the compound above showed the parent ion beam at (268 m / z), which indicates the molecular weight of the resulting compound, and the spectrum showed the base beam with high relative abundance at (199 m / z) belonging to the group ($\text{C}_8 \text{H}_{11}\text{NSe}$) and a good abundant beam at (158m / z) refers to the group ($\text{C}_{10} \text{H}_9\text{NO}$), and the spectrum showed other beams that can be observed through Table No (4). The mechanism of cracking the compound can be explained through Scheme (4), and the shape of the spectrum can be seen in Fig(5)

Table No. (4) the most important peaks of C1 fission

7- (selenocyanato methyl) quinolin-8-ol

7-(selenocyanato methyl)quinolin-8-ol			
Molecular formula	m/z	Molecular formula	m/z
$\text{C}_{11}\text{H}_8\text{N}_2\text{OSe}$	263	$[\text{C}_9\text{H}_7\text{NO}]^+$	145

$[\text{C}_{10}\text{H}_8\text{NOSe}]^+$	237	$[\text{C}_7\text{H}_7\text{N}]^+$	105
$[\text{C}_{10}\text{H}_9\text{NO}]^+$	159	$[\text{C}_8\text{H}_{11}\text{NSe}]^+$	200.14

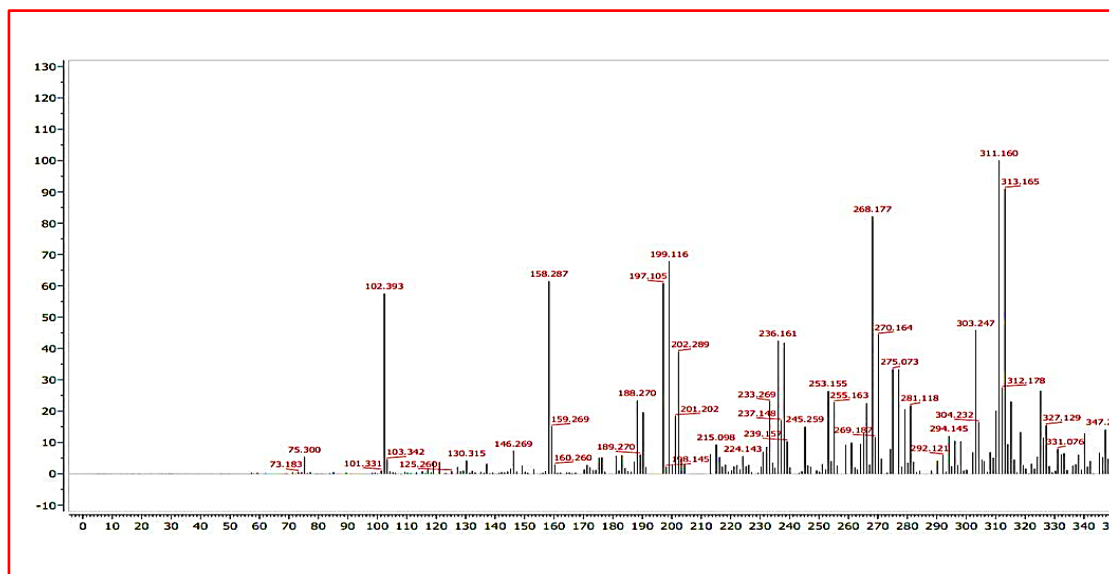
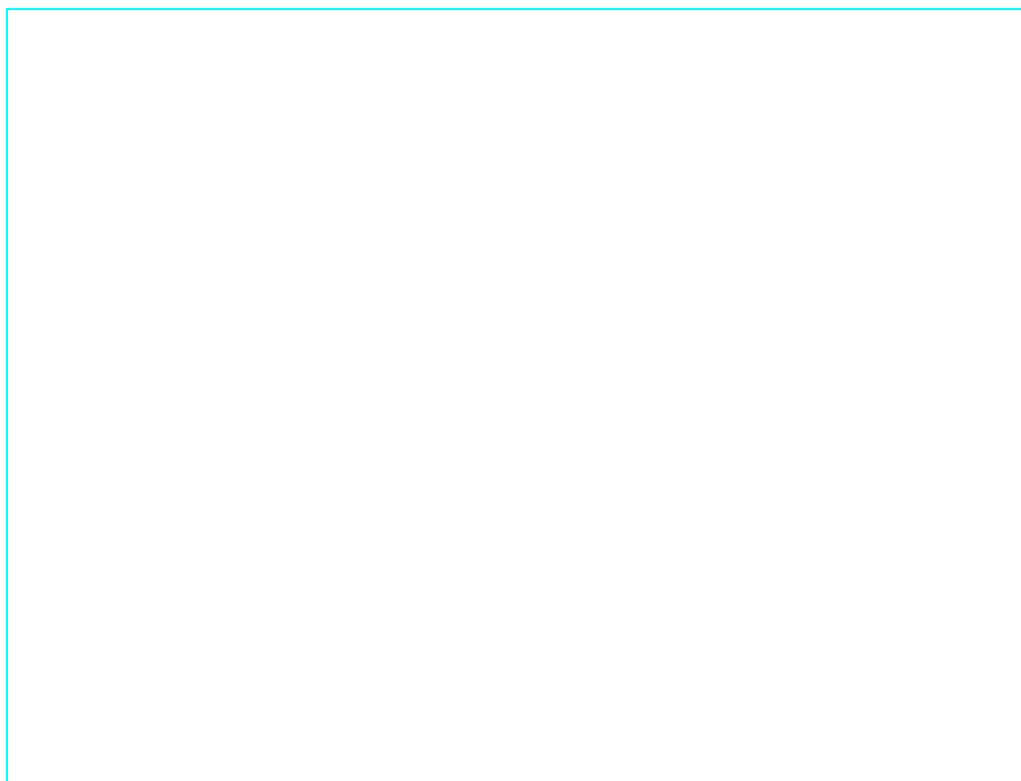


Figure (5) the mass spectrum of the compound C1



Scheme (4) suggested a mechanical fashioning of the mass spectrum of C1 [7-(selenocyanato methyl)quinolin-8-ol]

6-b- spectrum of**7 - ((di (λ^2 -bromaneylidene) bromo- λ^6 -selanyl) methyl) quinolin-8-ol**

The mass spectrum of the compound above showed the parent ion beam at (478m / z), which indicates the molecular weight of the resulting compound. The spectrum also showed the base beam with high relative abundance at (413 m / z) belonging to the group (C₇H₁₁Br₃ Se) in addition to a good abundant beam at (C₇H₁₁Br₂Se). (381 m / z) refers to a group (C₁₀ H₈Br₂NSe) and the spectrum showed another beam at (460 m / z) belonging to the group (C₁₀H₈Br₃NSe). The spectrum showed other bands that can be observed through Table (5). As for the mechanism of breaking the compound, it can be observed from Diagram (5) and the spectrum shape can be seen from Fig(6).

Table (5) of the most important peaks of C2 fashioning

7-((di(λ^2 -bromaneylidene)bromo- λ^6 -selanyl)methyl)quinolin-8-ol

<i>7-((di(λ^2-bromaneylidene)bromo-λ^6-selanyl)methyl)quinolin-8-ol</i>			
Molecular formula	m/z	Molecular formula	m/z
C ₁₀ H ₈ Br ₃ NSe	476.85	[C ₁₀ H ₈ Br ₃ NSe] ⁺	460.85
[C ₁₀ H ₈ Br ₂ NSe] ⁺	396.95	[C ₉ H ₁₃ Br ₃ Se] ⁺	439.88
[C ₁₀ H ₈ Br ₂ NSe] ⁺	380.95	[C ₇ H ₁₁ Br ₃ Se] ⁺	413.84
[C ₁₀ H ₈ NSe] ⁺	221		

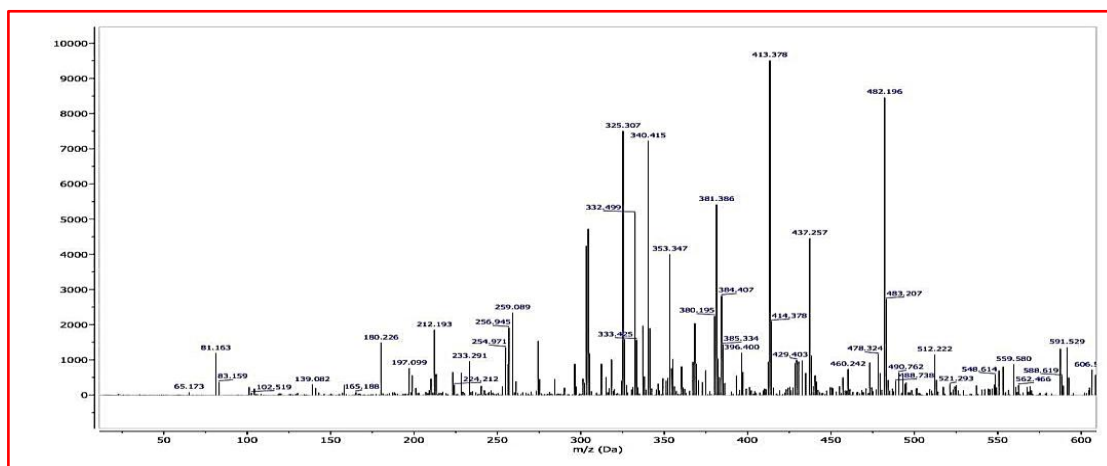
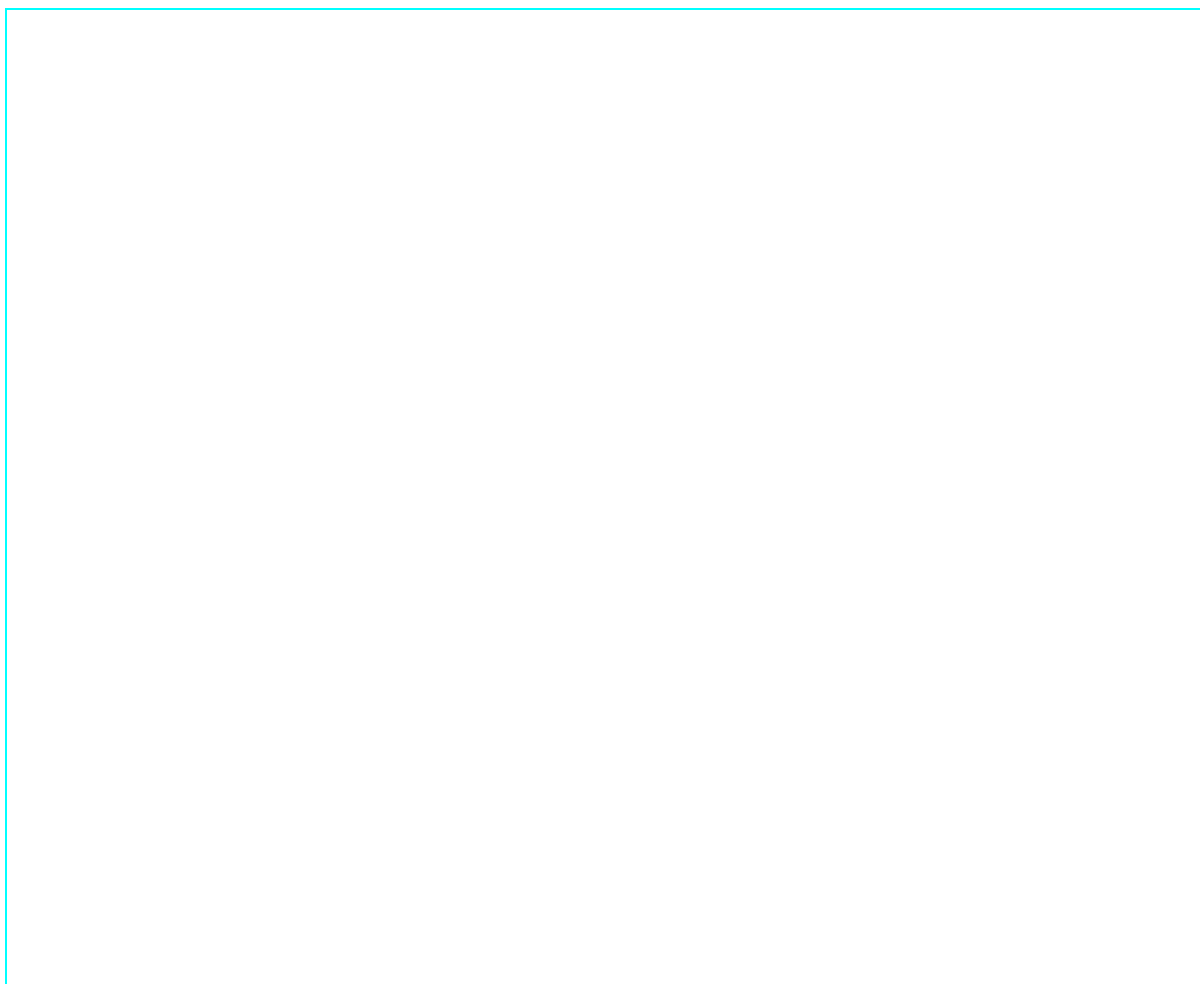
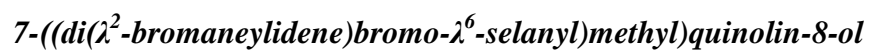


Figure (6), the mass spectrum of C2



Scheme (5) suggested a mechanical splitting of the mass spectrum of C2 [7-((di(λ^2 -bromanylidene)bromo- λ^6 -selanyl)methyl)quinolin-8-ol]

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