Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A benzimidazolium-based organic trication: a selective fluorescent sensor for detecting cysteine in water

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X-ray structure determination: The X-ray diffraction data for KPK 102 were collected on a Bruker X8 APEX II KAPPA CCD diffractometer at 293 K using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The crystals were positioned at 40 mm from the CCD and the diffraction spots were measured using a counting time of 10 s. Data reduction and multi-scan absorption were carried out using the APEX II program suite (Bruker, 2007). The structures were solved by direct methods with the SIR97 program[1] and refined using full-matrix least squares with SHELXL-97.[2] Anisotropic thermal parameters were used for all non-H-atoms. The hydrogen atoms of C–H groups were with isotropic parameters equivalent to 1.2 times those of the atom to which they were attached. All other calculations were performed using the programs WinGX[3] and PARST.[4] The molecular diagrams were drawn with DIAMOND.[5] Final R-values together with selected refinement details are given in Table 1.

Structure description: Compound **1** crystallizes in monoclinic crystal system with $P2_1/c$ space group. The asymmetric unit is consisting of one cationic moiety ($C_{11}H_{13}Br_2N_2$), bromide as counter ion and one water molecule of crystallization. ORTEP diagram along with atom numbering scheme is shown in Figure S1. In the crystal lattice the molecules are interacting with each other by two type of hydrogen bonding interactions (O-H…Br and C-H…O). The bromide ion and water molecule of crystallization are forming a chain running in between the cationic moieties. The C-H…O hydrogen bonds held together these cationic moieties and chain of bromide ion and water molecules. This arrangement of molecules in the crystal lattice down a-axis is shown in Figure S4.

Measurement of fluorescence quantum yields:[6] The fluorescence quantum yield (QY) of **R1** was determined relative to a reference compound of known QY. 2-Aminopyridine was chosen as reference compound because it has emission profile between 320-480 nm similar to probe **R1**. The same excitation wavelength, gain and slit bandwidths were applied for the both samples. The QY was calculated from following equation:

$$QY = QY_{ref}\frac{\eta^2}{\eta^2_{ref}}\frac{I}{A}\frac{A_{ref}}{I_{ref}}$$

Where QY_{ref} is the quantum yield of the reference compound, η is the refractive index, I is the integrated fluorescence intensity and A is the absorbance at the excitation wavelength.

Table S1. Crystal data and refinement parameters of compound **1**.

Compound	Compound **1**
Empirical Formula	$C_{11}H_{15}Br_3N_2O$
M_w	430.98
Temperature [K]	293(2) K
Crystal System	Monoclinic
Space group	$P2_1/c$
a / [Å]	10.2281(8)
b / [Å]	8.6541(7)
c / [Å]	16.8320(14)
β / [º]	94.512(4)°
V [Å^3]	1485.3(2)
Z	4
D_c [Mg m^{-3}]	1.927
µ / [mm^{-1}]	8.135
Reflections collected	46209
Data / restraints / parameters	2918 / 0 / 156
Unique reflections, [R_{int}]	2918 [0.0420]
GOF = S_{all}	1.032
R_1, wR_2 [I>2σI]	0.0315, 0.0748
R_1, wR_2 (all data)	0.0379, 0.0774
Δρmax/Δρmin [Å^3]	1.012/ -0.653

Table S2. Selected bond lengths and angles (Å,°) for compound **1**.

Bond lengths (Å)					
Br(2)-C(9)	1.941(3)	N(1)-C(7)	1.396(4)	N(2)-C(2)	1.393(4)
Br(3)-C(11)	1.936(4)	N(1)-C(8)	1.463(4)	N(2)-C(10)	1.464(4)
N(1)-C(1)	1.328(4)	N(2)-C(1)	1.323(4)	C(2)-C(3)	1.386(4)
Bond angles (°)					
C(1)-N(1)-C(7)	108.2(3)	C(1)-N(2)-C(2)	108.5(3)	N(2)-C(1)-N(1)	110.4(3)
C(1)-N(1)-C(8)	126.0(3)	C(1)-N(2)-C(10)	125.5(3)	C(3)-C(2)-C(7)	121.7(3)
C(7)-N(1)-C(8)	125.8(3)	C(2)-N(2)-C(10)	126.0(3)	C(3)-C(2)-N(2)	131.8(3)
C(7)-C(2)-N(2)	106.4(3)	C(8)-C(9)-Br(2)	112.5(2)	C(10)-C(11)-Br(3)	112.5(3)

Table S3. Hydrogen bonding parameters (Å, °) of compound **1**.

D-H···A	D···A/ Å	H···A/ Å	D-H···A/°
O1-H1W...Br1^{i}	3.310(3)	2.459(0)	172.4(2)
O1-H2W...Br1^{ii}	3.332(3)	2.519(0)	172.4(2)
C8-H8A...O1	3.341(5)	2.487(3)	146.8(2)
C10-H10A...O1^{iii}	3.317(5)	2.606(3)	130.3(2)

Equivalent positions: (i) -x+1,+y-1/2,-z+1/2, (ii) x+1,+y,+z, (iii) x,-y-1/2,+z+1/2

Table S4. Change in bond length of C-H bonds upon interaction of **R1** with Cys and binding energy.

Bond*	Bond length (nm)		
	Probe **R1**	Probe **R1** + Cys	Probe **R1** + Hcys
CH1	1.083 Å	1.140 Å	1.083 Å
CH2	1.025 Å	1.091 Å	1.025 Å
CH3	1.024 Å	1.092 Å	1.024 Å
Binding energy	-270.15684 eV	-273.11555 eV	-270.17956 eV

*C-H bonds are shown in Figure S6.

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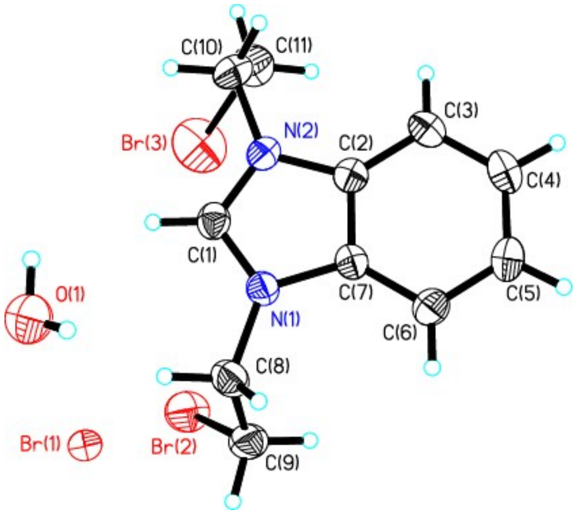

Figure S1. ORTEP diagram of compound **1** with 40% probability thermal ellipsoids and the atom-numbering scheme.

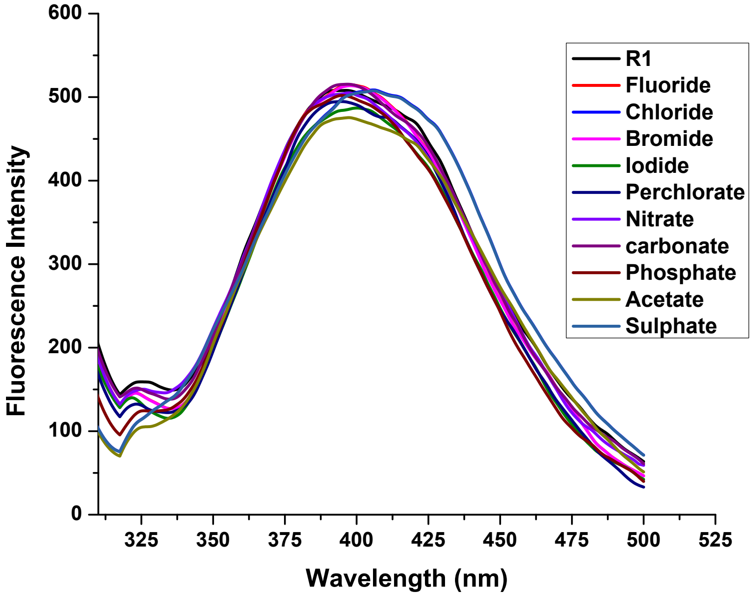

Figure S2. Changes in emission profile of **R1** (10 μM) upon addition different analytes (1.0 equiv) excited at λ_{ex} = 290 nm.

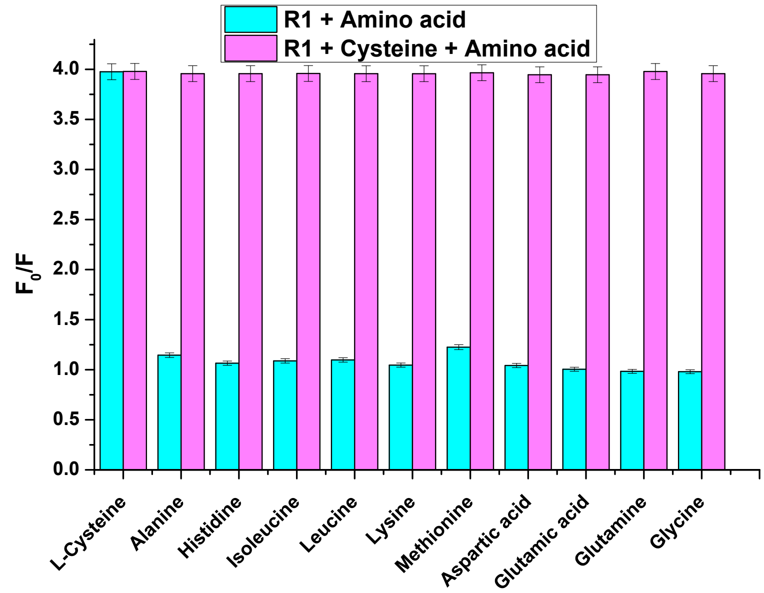

Figure S3. Comparison of fluorescent intensity (F$_o$/F) of **R1** (10 μM) at 390 nm in the presence of Cys (4.0 equiv) and other analytes (4.0 equiv) in a HEPES buffer (pH = 7.4) solution with excitation at 290 nm.

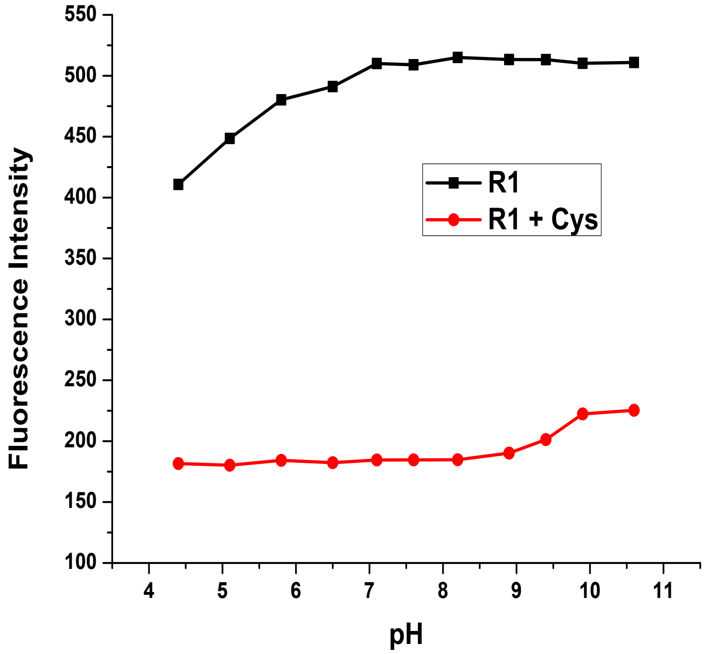

Figure S4. Fluorescence intensity of **R1** at 390 nm in the absence and presence of cysteine at different pHs.

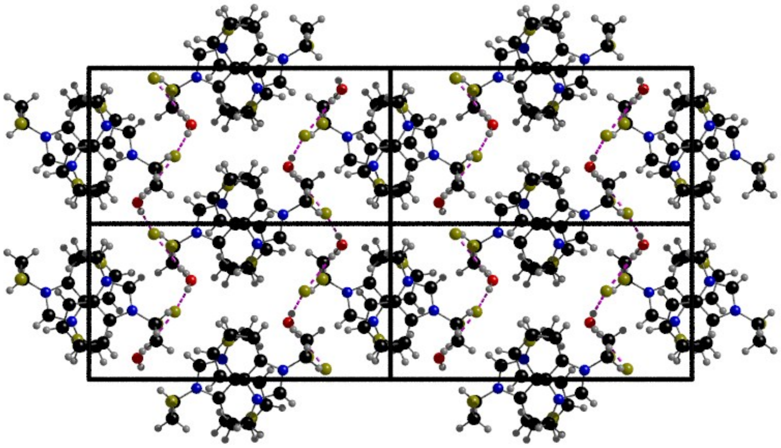

Figure S5. Packing diagram of compound **1** down a–axis.

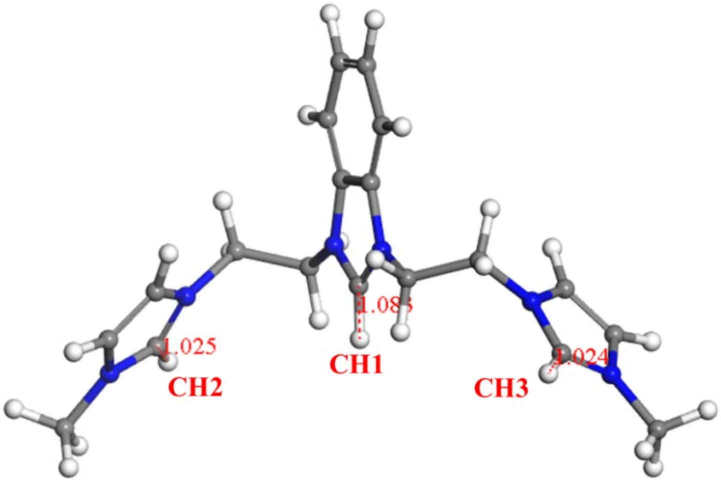

Figure S6. Optimized structure of probe **R1**, showing C-H bond length of imidazolium and benzimidazolium rings.

References

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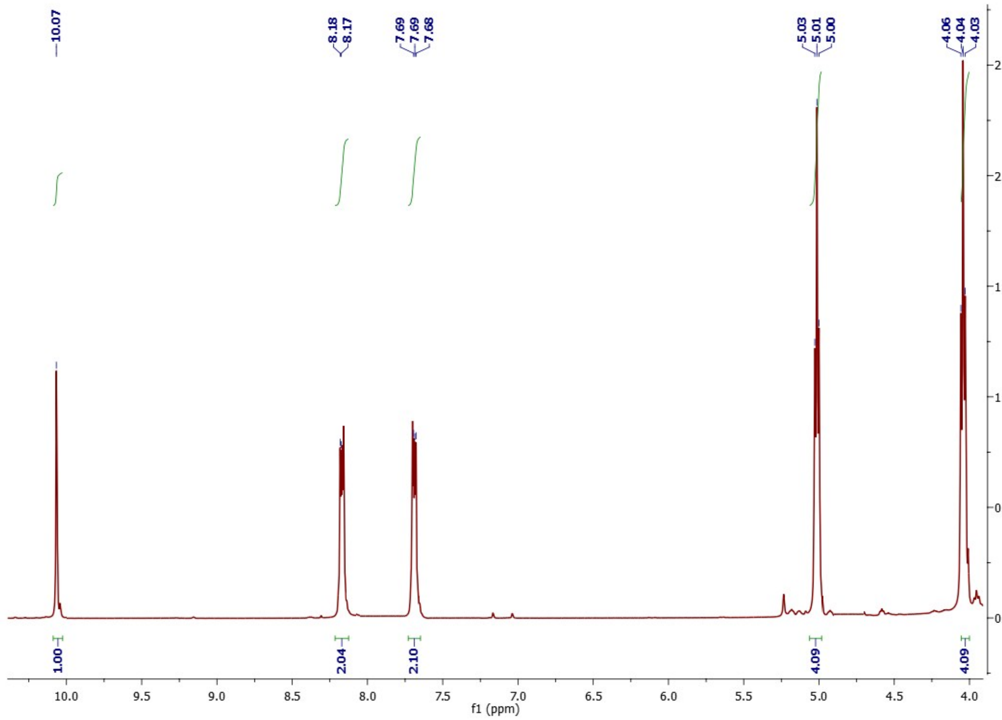
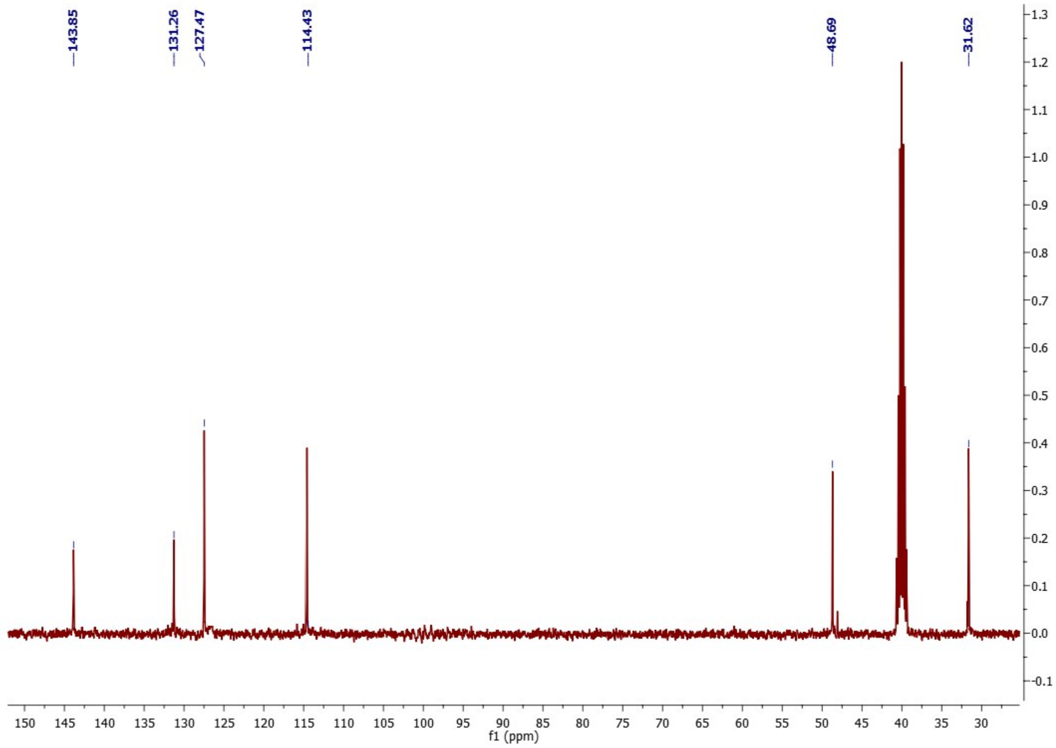
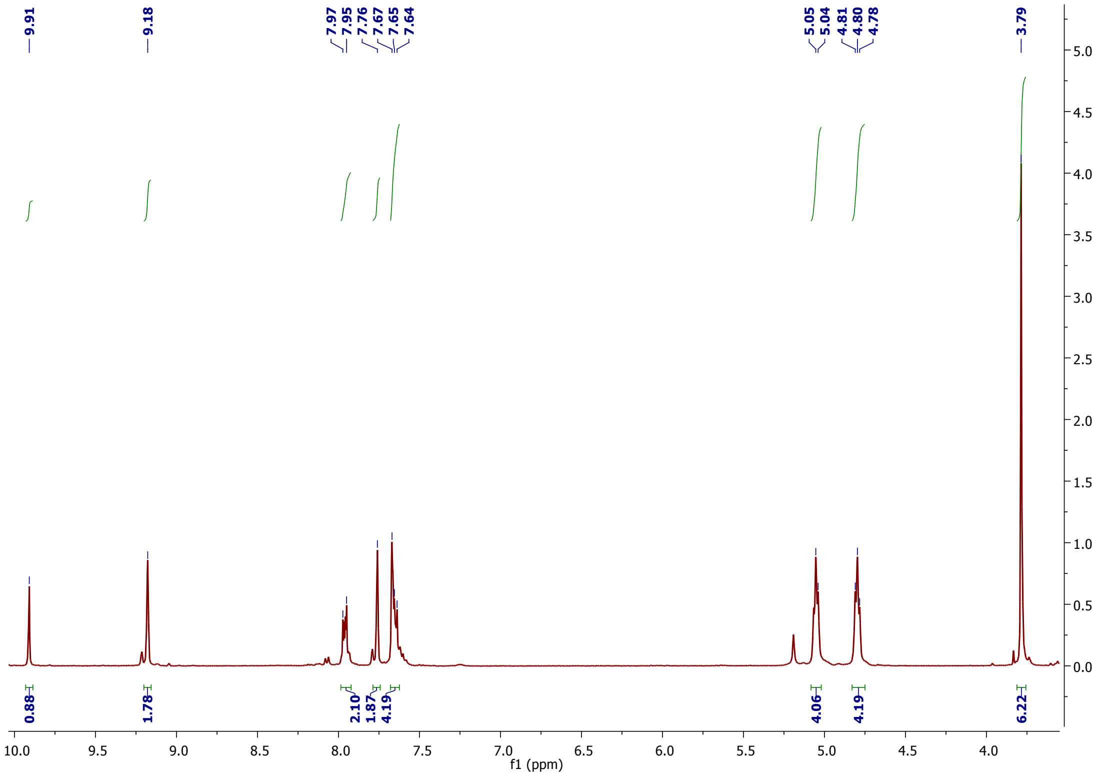


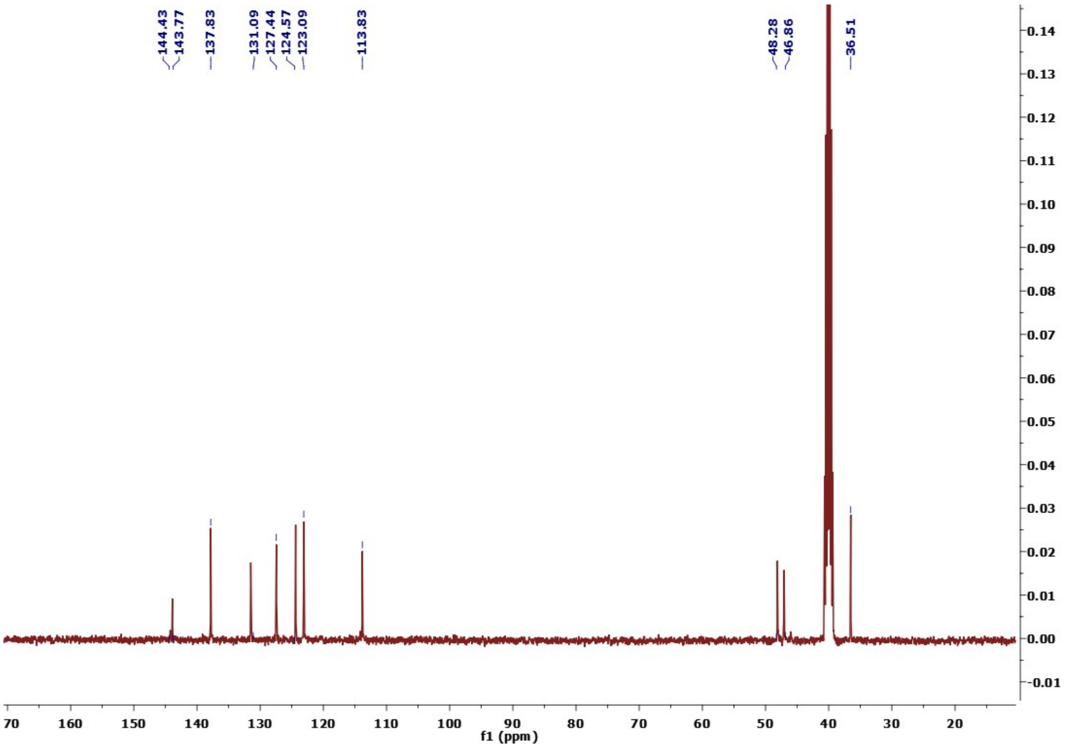
^{1}H NMR of compound **1**.



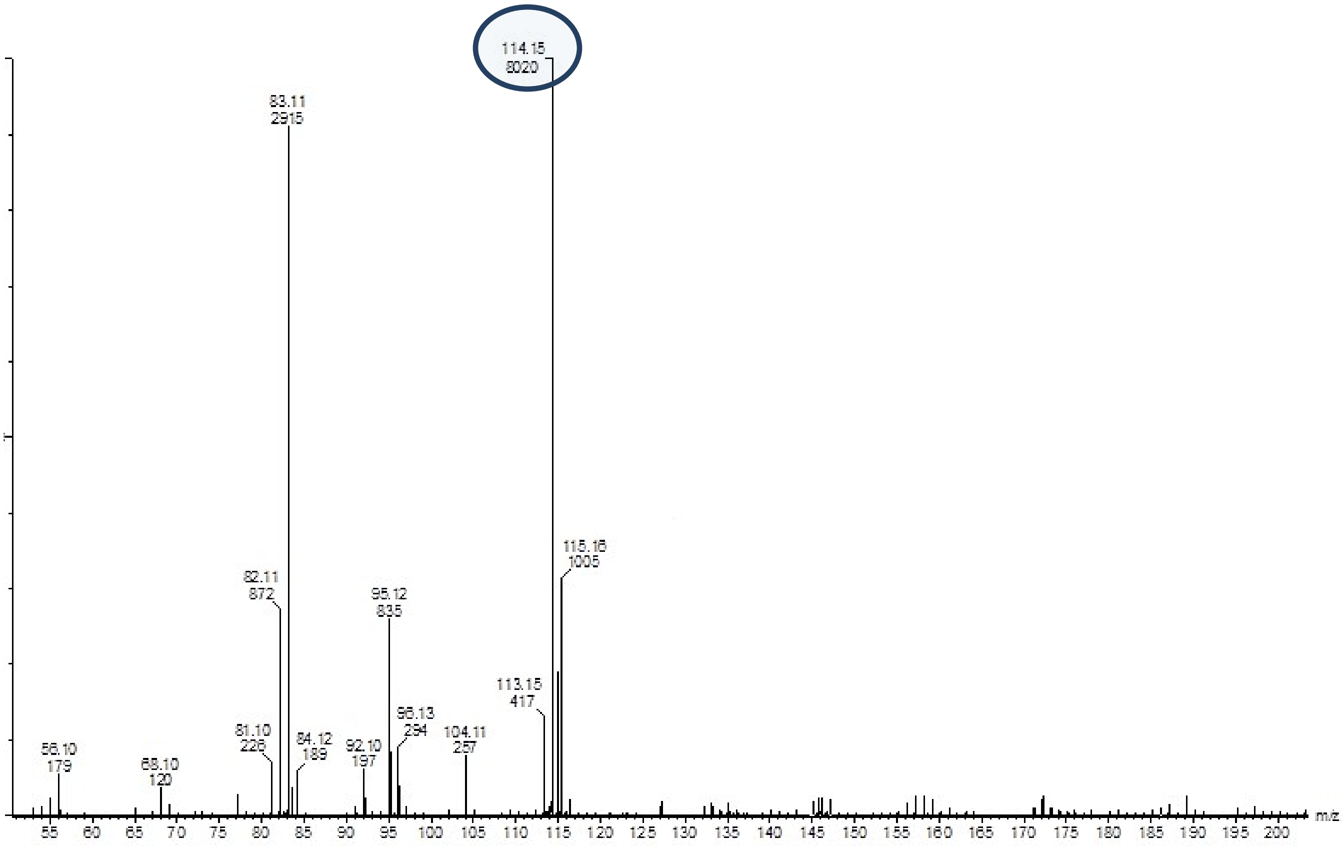
^{13}C NMR spectra of compound **1**.



^{1}H NMR spectra of probe **R1**.



^{13}C NMR spectra of probe **R1**.



Mass spectra of probe **R1**.