Copper-catalyzed tandem reaction in ionic liquid: an efficient reusable catalyst and solvent media for the synthesis of fused poly hetero cyclic compounds

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Supporting Information

General Experimental Procedures: All the reactions were carried out in sealed tube. Commercially available starting materials and other chemicals are purchased from Sigma-Aldrich chemicals, SD-Fine chemicals (India). 4-pentynoic acid and 5-hexynoic acid purchased from Sigma-Aldrich chemicals and used in reactions without further purification. Ionic liquid ([bmim]OTf) was prepared and purified as per reported method.[±] Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence lamp. Silica gel (particle size 100-200 mesh) purchased from Merck, was used for chromatography. ^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument. Spectra were reported relative to Me_4Si (δ 0.0 ppm) or $CHCl_3$ residual peak (δ 7.26 ppm). ^{13}C 100 MHz NMR were reported relative to $CDCl_3$ (δ 77.16 ppm). All the products were characterized by their NMR, GC/MS LCMS ESI and HRMS spectra. The first-order peak patterns are indicated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet). Complex non-first-order signals are indicated as m (multiplet). FTIR spectra were recorded on a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm-^{1}). GCMS recorded on instrument Perkin Elmer mass spectrometer.

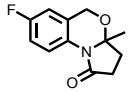
Experimental

General procedure for 3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one

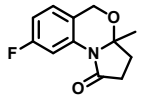
A sealed tube was charged with1.25 mmol (123 mg) of 4-pentynoic acid, 0.5 mL of [bmim]OTf and $Cu(OAc)_2.H_2O$ (5mol%,5 mg). After stirring the above solution for 15min at room temperature, *o*-amino benzyl alcohol 0.5mmol (62 mg) was added to the reaction vial and sealed. The reaction mixture was stirred in an oil bath maintained at 100 °C until the

completion of reaction. After the completion of reaction, 5mL of water and ethyl acetate were added to the reaction mixture and combined layers were filtered through celite bed and washed with minimum amount of ethyl acetate. The organic layers were separated and concentrated under reduced pressure and the deposit was purified by column chromatography with hexane and ethyl acetate as eluent in a ratio of 4:1 to afford compound **4a** with 92% (94.2 mg) yield. Colourless solid, m.p. 68-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J=8.24 Hz, 1H), 7.30 (t, J=7.6Hz,1 H), 7.13(t J=7.44, 1H), 7.05(d, J=7.56, 1H), 5.03 (d, J=15.6Hz, 1H), 4.88 (d, J=15.6Hz, 1H), 2.69-2.54 (m,2H),2.29-2.08 (m,2H), 1.51(s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ171.5, 133.0, 127.7,1124.2, 124.2, 123.2, 120.7,90.1,62.9, 33.1,30.3,21.4. LC MS (m/z): [M + H^+] calcd for $C_{12}H_{13}NO_2$: 203.8; found: 204.9

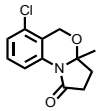
3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f] **4a.** Colourless solid,m.p. 68-72˚C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J=8.24Hz, 1H), 7.30 (t, J=7.6Hz,1H), 7.13(t, J=7.44 Hz, 1H), 7.05(d, J=7.56 Hz, 1H), 5.03 (d, J=15.6Hz, 1H), 4.88 (d, J=15.6Hz, 1H), 2.69-2.54 (m,2H),2.29-2.08 (m,2H), 1.51(s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ171.5, 133.0, 127.7,1124.2, 124.2, 123.2, 120.7,90.1,62.9, 33.1,30.3,21.4. LC MS (m/z): [M + H^+] calcd for $C_{12}H_{13}NO_2$: 203.8;found: 204.9.



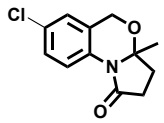
7-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f] **4b**.Colourless solid, m.p. 96-100 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29(m, 1H), 7.02 (m, 1H), 6.79, (m, 1H), 5.01 (d, J=15.9 Hz, 2H), 4.86, (d, J=15.9Hz, 1H),2.69-2.59(m, 2H),2.31-2.16(m,2H),1.50(s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ171.4, 160.5(d, J=250 Hz), 129.1, 126.6(d, J=7Hz), 122.6(d, J=8Hz) 114.8(d, J=22 Hz),111.0 (d, J=23 Hz) 90.8, 62.8, 33.03, 28.1, 21.3.GCMS: Calculated for $C_{12}H_{12}FNO_2$: 221.0, found: 221.4.



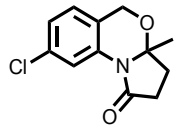
8-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[6d] **4c**.Colourless solid,m.p. 78-81˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14(m, 1H), 7.02 (m, 1H), 6.84, (m, 1H), 5.0 (d,J=15.3Hz, 1H), 4.86, (d,J=15.3Hz, 1H),2.69-2.54(m, 2H),2.30-2.11(m,2H),1.50 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ171.4, 163.1(d, J=243 Hz), 134.1(d, J=12Hz), 125.5(d, J=9Hz), 118.5, 111.5(d, J=22Hz), 107.8(d, J=27Hz), 90.0, 62.6, 33.1, 30.3, 21.3. ESI-MS [M + H^+]: Calculated for $C_{12}H_{12}FNO_2$: 221.0, found: 221.1.



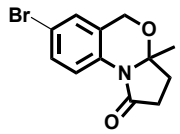
6-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[6d] **4d.** Colourless solid,m.p. 105-110˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.2 Hz, 1H), 7.30(t, J=8.0Hz, 1H), 7.17 (d,J=7.9Hz, 1H), 4.96 (d,J=16.5Hz, 1H), 4.88 (d, J=16.8Hz, 1H), 2.70-2.56 (m, 2H) ,2.30-2.14(m, 2H), 1.51 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 134.5, 130.6, 128.2, 124.8, 121.4, 119.0, 89.9, 62.0, 32.9, 30.4, 21.3. LCMS Calculated for $C_{12}H_{12}ClNO_2$: 237.6, found, 237.9.



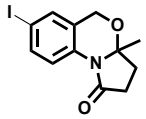
7-chloro-3a-methyl-2,3,3a,4-tetrahydro-1H-benzo[b]pyrrolo[1,2-d][1,4]oxazin-1-one[5f] **4e.** Colourless solid,m.p. 80-85˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J=8.8 Hz, 1H), 7.24 (m, 1H), 7.05 (m, 1H), 5.0 (d, J= 15.8Hz, 1H), 4.80(d, J=15.8 Hz, 1H), 2.58-2.64 (m,2H), 2.29-2.13 (m, 2H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 131.6, 129.5, 127.9, 124.9, 124.2, 122.0, 90.2, 62.6, 30.1, 30.3, 21.3.LCMS Calculated for $C_{12}H_{12}ClNO_2$: 237.6, found: 237.8.



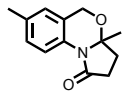
8-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f] **4f**.Colourless solid, m.p. 127-130 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.10 (d, J=8.2 Hz, 1H), 6.99 (d,J=8.2 Hz, 1H), 4.99 (d, J=15.7 Hz, 1H), 4.85(d,J=15.7 Hz, 1H), 2.64-2.59(m, 2H), 2.29-2.12(m, 2H), 1.49(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4,133.9, 133.3, 125.4, 124.4, 121.3, 120.5, 90.0, 62.6, 30.1, 30.3, 21.3.LCMS Calculated for $C_{12}H_{12}ClNO_2$: 237.6, found: 237.9.



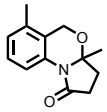
7-bromo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f] **4g.** Colourless solid, m.p. 116-120 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J=8.8Hz,1H), 7.41 (m, 1H), 7.21 (m, 1H), 5.0 (d, J=15.8 Hz,1H), 4.8 (d,J=15.8 Hz, 1H), 2.64-2.58 (m, 2H), 2.30-2.15(m, 2H), 1.50 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 132.1, 130.8, 127.2, 125.2, 122.3, 117.2, 90.1, 62.4, 30.1, 30.3, 21.3. LCMS Calculated for $C_{12}H_{12}BrNO_2$: 281.0, found: 281.8.



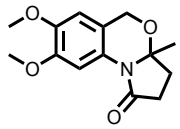
7-iodo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f]**4h.**Colorless liquid,[1]H NMR (400 MHz, $CDCl_3$): δ 8.30 (m, 1H), 7.39 (m, 1H), 7.13 (m, 1H), 5.04(dd, 1H), 4.88(dd, J=15.6 Hz, 1H), 2.64-2.57 (m, 2H),2.29-2.12(m, 2H), 1.51-1.49(d, J=8.1Hz, 3H);[13]C NMR (100 MHz, $CDCl_3$): δ 171.4(d, J=7.5Hz), 136.5,132.9(d, J=9.6Hz), 127.6, 124.1 (d, J=3.9Hz),122.3, 120.5, 90.0 (d, J=5.9Hz), 62.9, 33.0, 30.2, 21.2. ESI-MS (m/z): [M + H^+]; Calculated for $C_{12}H_{12}INO_2$: 328.9, found: 329.9.



3a,7-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one[5f]**4i.** Colourless solid, m.p.89-94 °C; [1]H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J=8.36,1H), 7.10 (d,J=7.76 Hz, 1H), 6.85(s, 1H), 4.99-4.79(dd, 2H), 2.67-2.52 (m, 2H), 2.30(s ,3H),2.28-2.11(m, 2H),1.49(s, 3H);[13]C NMR (100 MHz, $CDCl_3$): δ171.2, 133.8, 130.5, 128.3, 124.5, 123.0, 120.5, 90.1, 62.9, 33.1, 30.3, 21.3, 21.0. LCMS Calculated for $C_{13}H_{15}NO_2$: 217.1, found: 217.9.

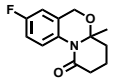


3a,6-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4j**.Semisolid,[1]H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=8.28Hz,1H), 7.22 (t,J=7.48 HZ, 1H), 6.95(d,J=7.48Hz, 1H), 4.84(d,J=7Hz, 2H), 2.67-2.54 (m, 2H), 2.28-2.18(m ,2H),2.16(s, 3H),1.49(s, 3H);[13]C NMR (100 MHz, $CDCl_3$): δ171.6, 133.5, 132.9, 127.4, 125.9, 121.8, 118.5, 89.7, 62.1, 33.0, 30.3, 21.3, 18.1. ESI-MS (m/z): [M + H^+]; Calculated for $C_{13}H_{15}NO_2$: 217.1, found: 217.8. HRMS: [M + H^+]; Calculated for $C_{13}H_{16}NO_2$:218.1176, found: 218.1176.

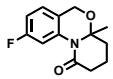


7,8-dimethoxy-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4k**.semisolid;[1]H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 6.51 (s, 1H), 4.96(d,J=15.2Hz, 1H), 4.80(d,J=15.2Hz, 1H), 3.90 (s, 3H),3.83 (s,3H) 2.63-2.55(m ,2H),2.27-2.13(m, 2H),1.49(s, 3H);[13]C NMR (100 MHz, $CDCl_3$): δ171.1, 148.3, 146.1, 126.5, 114.9, 106.8, 104.4, 90.1, 62.8, 56.2, 56.2, 33.1, 30.4.ESI-MS (m/z): [M + H^+]; Calculated for $C_{14}H_{17}NO_4$: 263.1, Found: 264.2. HRMS: [M + H^+]; Calculated for $C_{14}H_{118}NO_4$: 264.12303, Found: 264.12403.

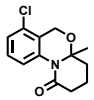
4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f]**4l.**Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J=8.2 Hz, 1H), 7.25 (m, 1H), 7.14(d, J=7.56Hz, 1H), 7.01(d, J=7.0Hz, 1H), 4.91(s, 2H), 2.69-2.49 (m,2H),2.15-1.91 (m,3H), 1.83-1.72(m, 1H), 1.47(s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ169.7, 134.7, 127.4, 126.6, 126.4, 125.0, 123.9, 86.7, 62.8, 37.1, 34.3, 23.8, 16.9. ESI-MS(m/z): [M + H^+]; Calculated for $C_{13}H_{15}NO_2$: 217.3,found: 218.1.



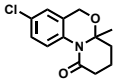
8-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f]**4m.**Colourless solid,m.p.76-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (m, 1H), 6.96 (m, 1H), 6.72(m, 1H), 4.87(s, 2H), 2.71-2.48 (m,2H),2.15-1.91 (m,3H), 1.81-1.73(m, 1H),1.45(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 158.5(d, J=243Hz), 130.6 (d, J=3Hz), 129.3 (d, J=7Hz), 128.4(d, J=8Hz), 113.9(d, J=22Hz), 110.3(d, J=23Hz), 86.7, 62.6, 37.0, 34.2, 23.7, 16.8.GCMS: Calculated for $C_{13}H_{14}FNO_2$: 235.1,found: 235.1.



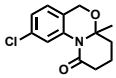
9-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[6d]**4n.**Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.62 (m, 1H), 6.97-6.93 (m, 1H), 6.87-6.82(m, 1H), 4.87(s, 2H), 2.68-2.50 (m,2H),2.15-1.90 (m,3H), 1.86-1.73(m, 1H), 1.42(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 159.8(d, J=240Hz), 135.7 (d, J=10Hz), 124.8 (d, J=10Hz), 122.8(d, J=10Hz), 113.2(d, J=30Hz), 112.3(d, J=30Hz), 86.8, 62.3, 37.0, 34.3, 23.5, 16.8. ESI-MS (m/z): [M + H^+]; Calculated for $C_{13}H_{14}FNO_2$: 235.1,found: 236.2.



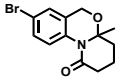
7-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[6d]**4o**. Colourless solid,m.p.116-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22(d, J=8.08Hz,1H), 7.21 (m, 2H), 4.88(dd, J=16.52Hz,2H), 2.68-2.49 (m, 2H), 2.15-1.91 (m, 3H),1.82-1.72(m, 1H), 1.47 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 136.2, 130.1, 127.2, 125.5, 125.1, 124.9, 86.5, 61.7, 37.1, 34.4, 23.3, 16.7. ESI-MS (m/z): [M + H^+]:[M + 2]: Calculated for $C_{13}H_{14}ClNO_2$: 251.0, found: 252.2, 254.2. HRMS (m/z): [M + H^+]: Calculated for $C_{13}H_{15}ClNO_2$: 252.07953, found: 252.07858.



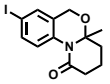
8-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f] **4p**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76(d,J=8.8Hz,1H), 7.20 (m, 1H), 7.0(m,1H), 4.86(s, 2H), 2.71-2.49 (m, 2H), 2.16-1.90 (m, 3H),1.81-1.73 (m, 1H), 1.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 133.2, 130.3, 129.0, 127.8, 126.8, 123.8, 86.8, 62.3, 37.0, 34.2, 23.5, 16.9. ESI-MS (m/z): [M + H^+], [M + 2]: Calculated for $C_{13}H_{14}ClNO_2$: 251.7,found : 252.2, 254.2.



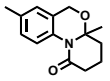
9-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f] **4q**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87(d, J=2.04Hz,1H), 7.11 (dd,J=6.2Hz 1H), 6.94(d,J=8.32Hz,1H), 4.87(s, 2H), 2.68-2.46 (m, 2H), 2.11-1.91 (m, 3H),1.80-1.70 (m, 1H), 1.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 135.6, 132.1, 126.3, 125.6, 125.3, 124.9, 86.8, 62.4, 36.9, 34.3, 23.6, 16.7.ESI-MS (m/z): [M + H^+], [M + 2]: Calculated for $C_{13}H_{14}ClNO_2$: 251.7,found: 252.2, 254.1.



8-bromo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f] **4r**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71(d, J=8.8Hz,1H), 7.35 (d,J=8.8Hz, 1H), 7.15(s,1H), 4.86(s, 2H), 2.66-2.48 (m, 2H), 2.15-1.94 (m, 3H),1.81-1.73(m, 1H), 1.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 133.8, 129.7, 129.3, 128.1, 126.8,118.1,86.8, 62.2, 36.9, 34.3, 23.6, 16.9. ESI-MS (m/z): [M + H^+], [M + 2]: Calculated for $C_{13}H_{14}BrNO_2$: 295.0,found: 296.1, 298.0.

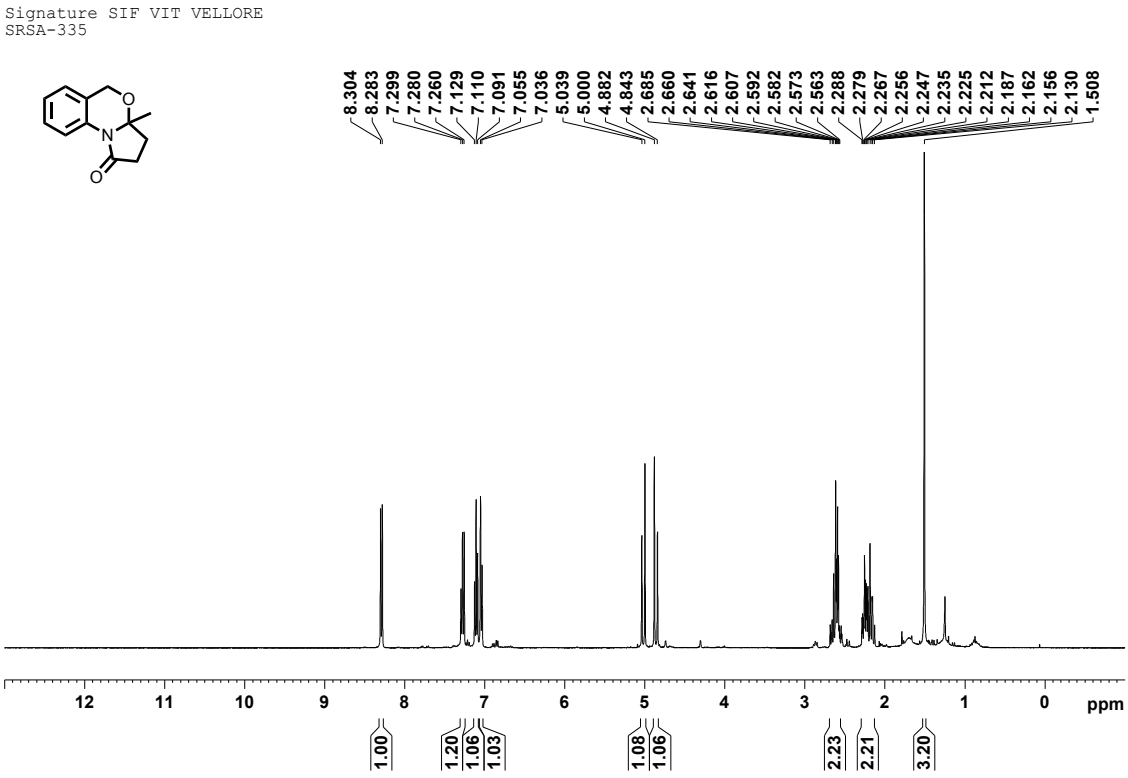


8-iodo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f] **4s**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59(m, 2H), 7.35 (s, 1H), 4.85(s, 2H), 2.66-2.48 (m, 2H), 2.12-1.92 (m, 3H),1.81-1.72 (m, 1H), 1.47 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 135.6, 134.6, 132.8, 129.6, 129.3,118.1,89.1, 86.8,61.9 37.0, 34.3, 23.6, 16.8. ESI-MS (m/z): [M + H^+]: Calculated for $C_{13}H_{14}INO_2$: 343.0,found: 344.1



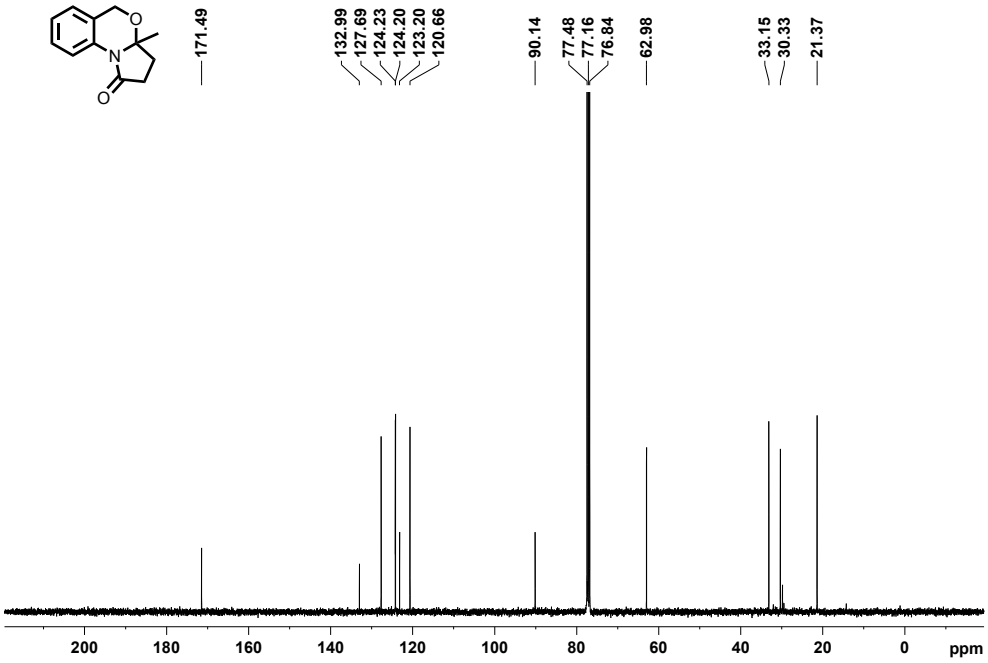
4a,8-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one[5f] **4t**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67(d, J=8.4Hz,1H), 7.05 (d,J=8.3Hz, 1H), 6.80(s,1H), 4.86(s, 2H), 2.66-2.48 (m, 2H), 2.30 (s, 3H),2.14-1.90(m, 3H),1.81-1.71(m, 1H), 1.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 134.7, 132.1, 127.4, 127.0, 126.1, 124.2, 86.7, 62.8, 37.1, 34.3, 23.7,21.1,16.9. ESI-MS (m/z): [M + H^+]: Calculated for $C_{14}H_{17}NO_2$: 231.1,found 232.3.

4a,7-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4u**.Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59(d, J=8.24Hz,1H), 7.17 (t,J=7.8Hz, 1H), 6.95(d, J=7.44 Hz,1H), 4.81(d,J=3.24 Hz,2H), 2.67-2.48 (m, 2H), 2.14 (s, 3H),2.12-1.91(m, 3H),1.82-1.72(m, 1H), 1.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 134.5, 133.0, 126.9, 126.2, 125.6, 124.2, 86.1, 61.8, 37.2, 34.4, 23.5,17.8,16.8. ESI-MS (m/z): [M + H^+]:Calculated for $C_{14}H_{17}NO_2$: 231.1,found: 232.3.HRMS: [M + H^+]:Calculated for $C_{14}H_{18}NO_2$: 232.13394,found: 232.13321.



^{1}HNMR spectrum of 3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4a**

SRSN-36



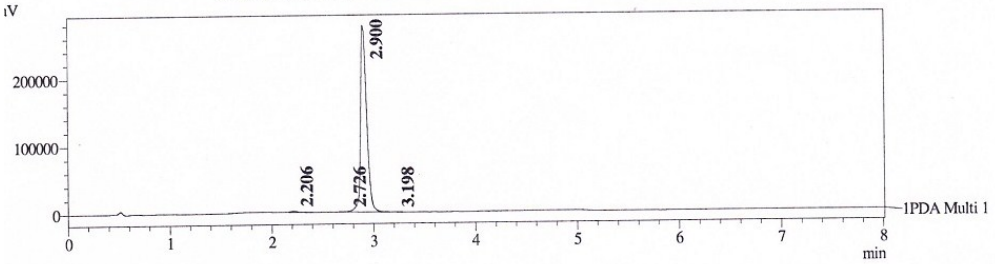
^{13}C NMR spectrum of 3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4a**

Sample Information

Sample Name :SEV-MA1413-58
Date Acquired : 4/25/2014 7:14:48 PM
Data File : 250414M 32.lcd
Method File : Test Method - LCMS.lcm
Tuning File : D:\Shimadzu MS Data\Tuning Files\ESI 060314---4.lct
Vial :17
Column : X-Select CSH C18 (50x3.0mm,3.5um)
M.P : A-0.05% Aq TFA , B:ACN
T%B :0.01/10,0.5/10,4/90,8/90
Flow : 0.8ml/min(Gradient)

Chromatogram

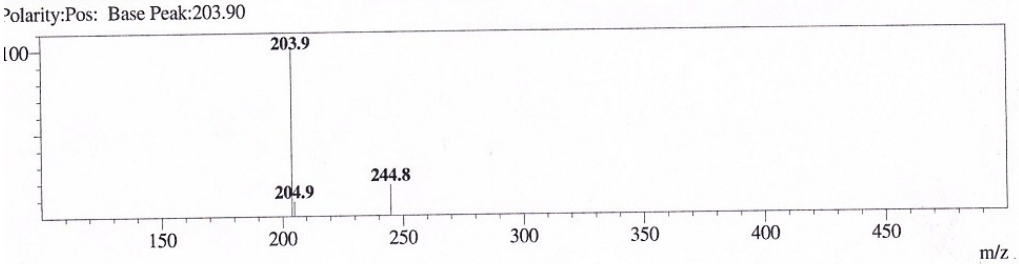
SEV-MA1413-58 D:\Shimadzu MS Data\2014 Data\APRIL-2014\LCMS\250414M 32.lcd



1 PDA Multi 1 / 245nm 4nm

MS Spectrum

Ret Time:2.900-2.967
Polarity:Pos: Base Peak:203.90

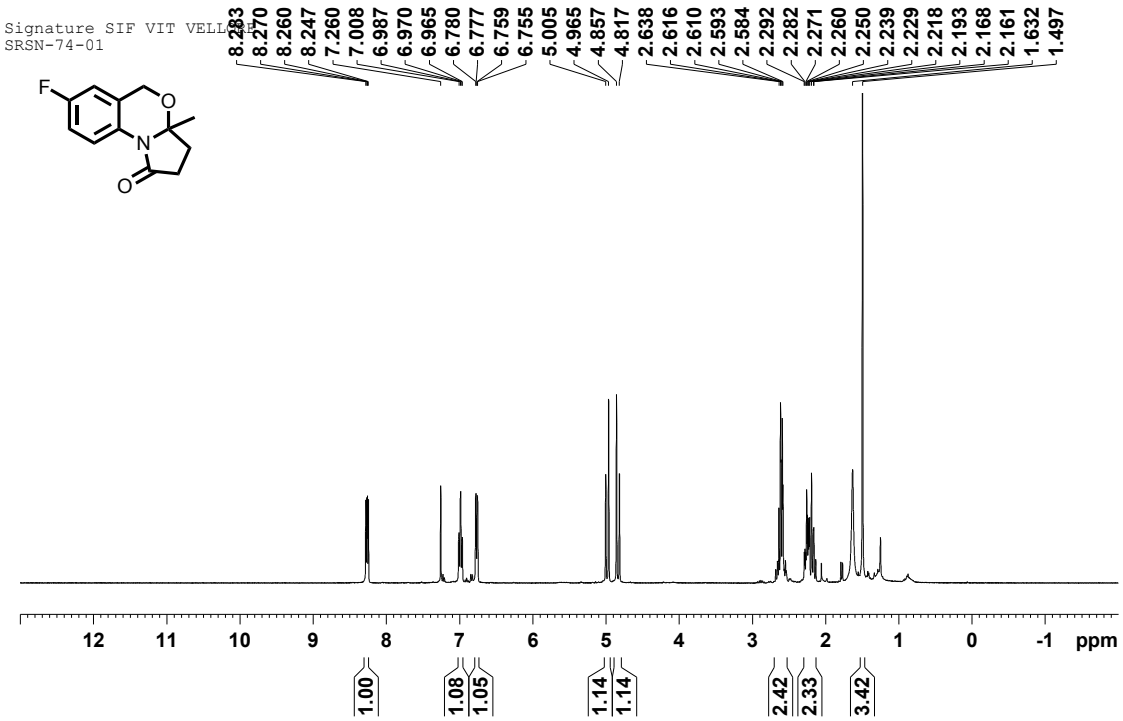


PeakTable

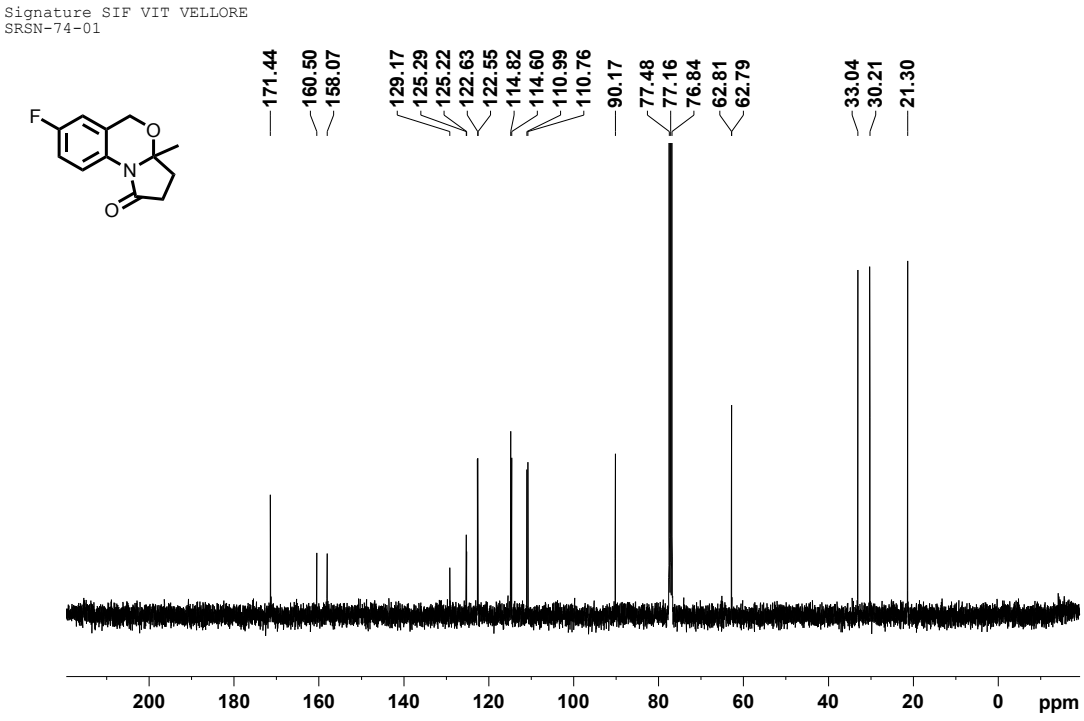
PDA Ch1 245nm 4nm

Peak#	Ret. Time	Area	Area %
1	2.206	6922	0.602
2	2.726	3012	0.262
3	2.900	1138936	99.067
4	3.198	790	0.069
Total		1149660	100.000

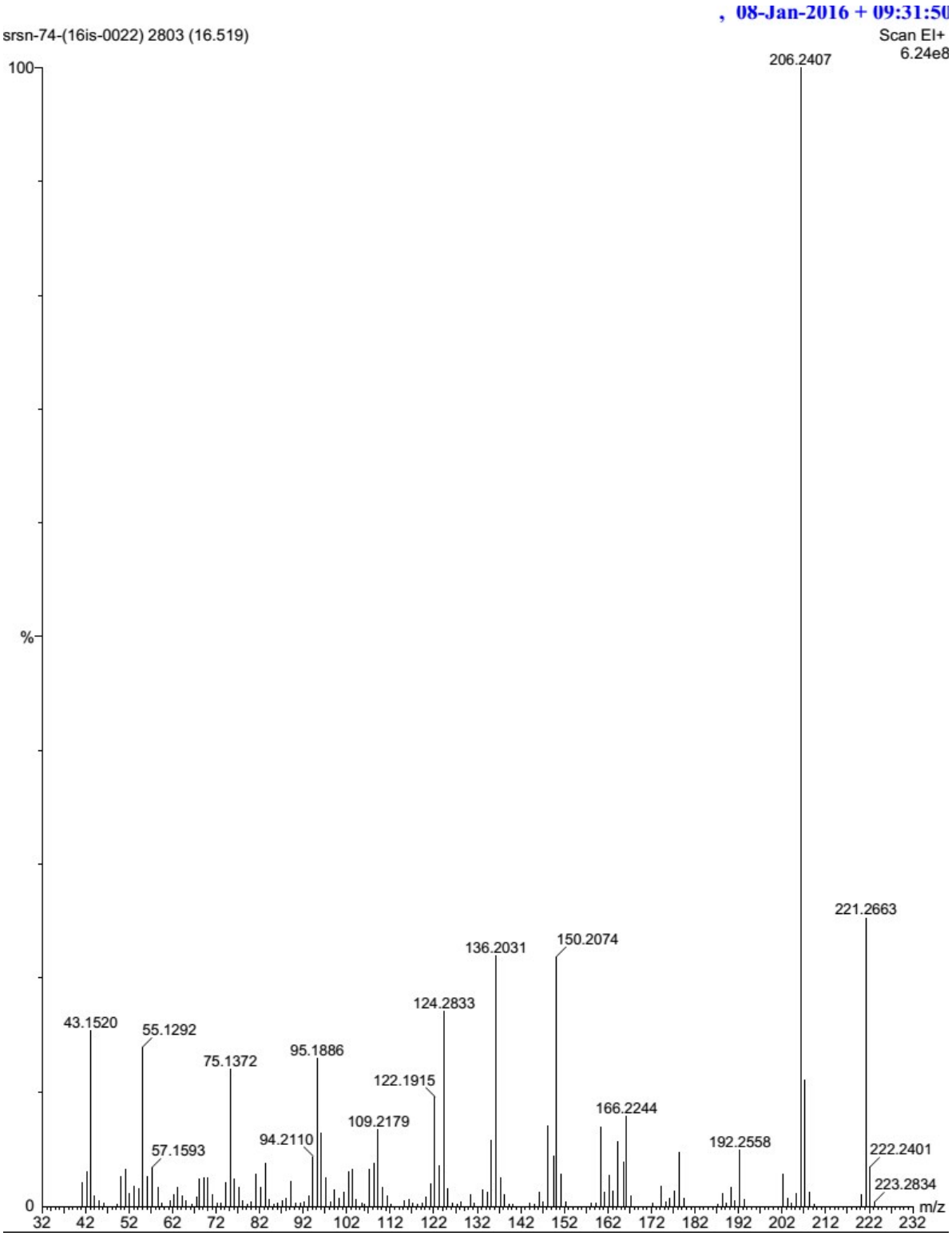
LCMS of 3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4a**



^{1}HNMR spectrum of 7-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4b**

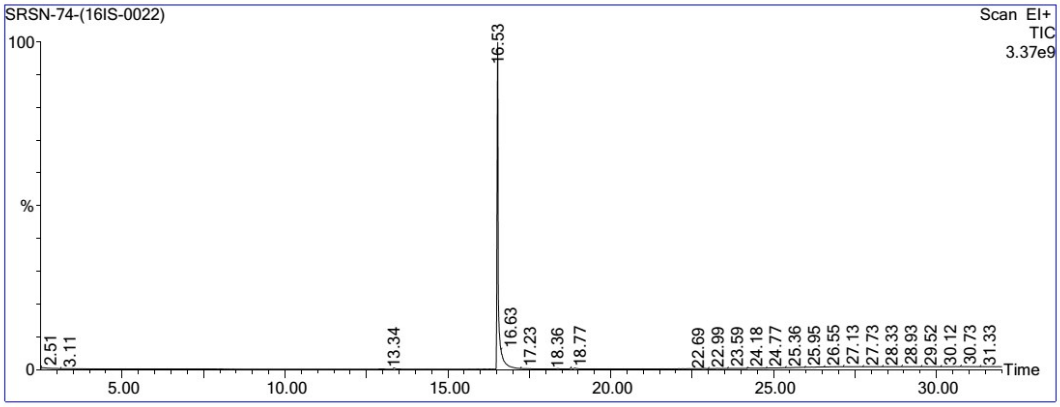


^{13}C NMR spectrum of 7-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4b**


, 08-Jan-2016 + 09:31:50
srsn-74-(16is-0022) 2803 (16.519)
Scan EI+
6.24e8
100
%
0
206.2407
221.2663
150.2074
136.2031
124.2833
43.1520
55.1292
95.1886
75.1372
122.1915
166.2244
109.2179
94.2110
57.1593
192.2558
222.2401
223.2834
m/z
32 42 52 62 72 82 92 102 112 122 132 142 152 162 172 182 192 202 212 222 232

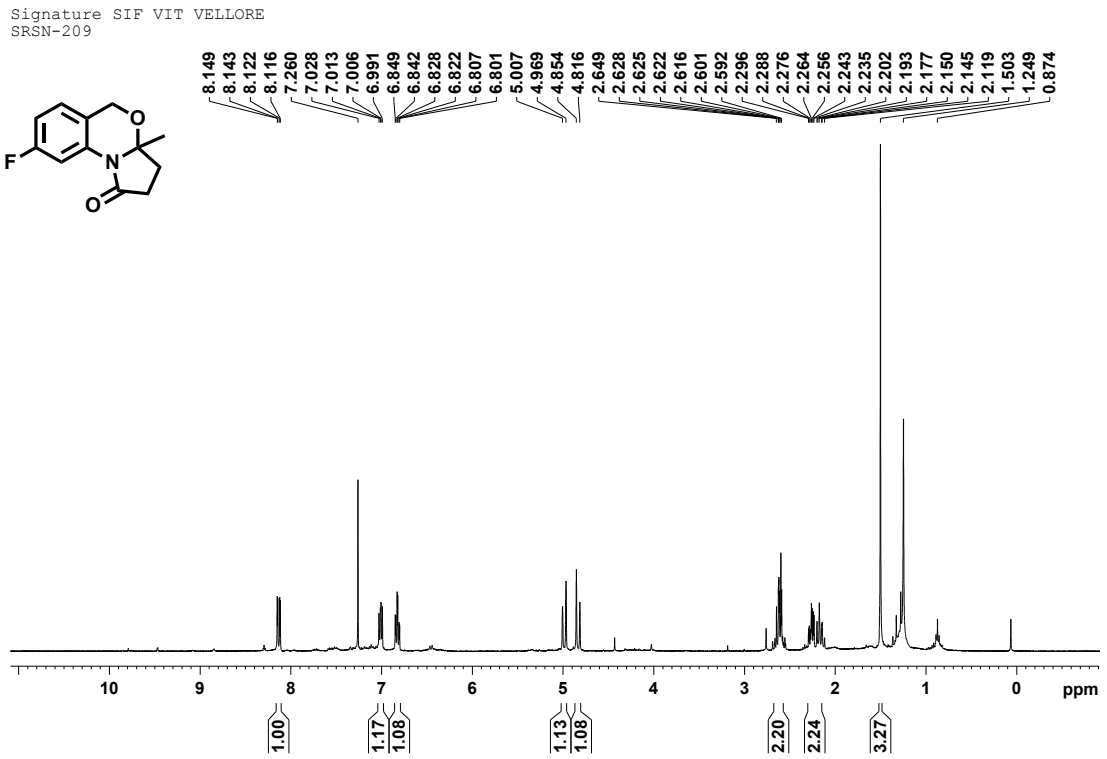
Qualitative Report

File: C:\TurboMass\2016.PRO\Data\SRSN-74-(16IS-0022).raw
Acquired: 08-Jan-16 09:31:50 AM Printed: 24-Jan-16 01:07 PM
Description:
GC/MS Method: GC: METHOD-1.mth MS: METHOD-1.EXP Page 1 of 1
Sample ID: SRSN-74-(16IS-0022) Vial Number: 60

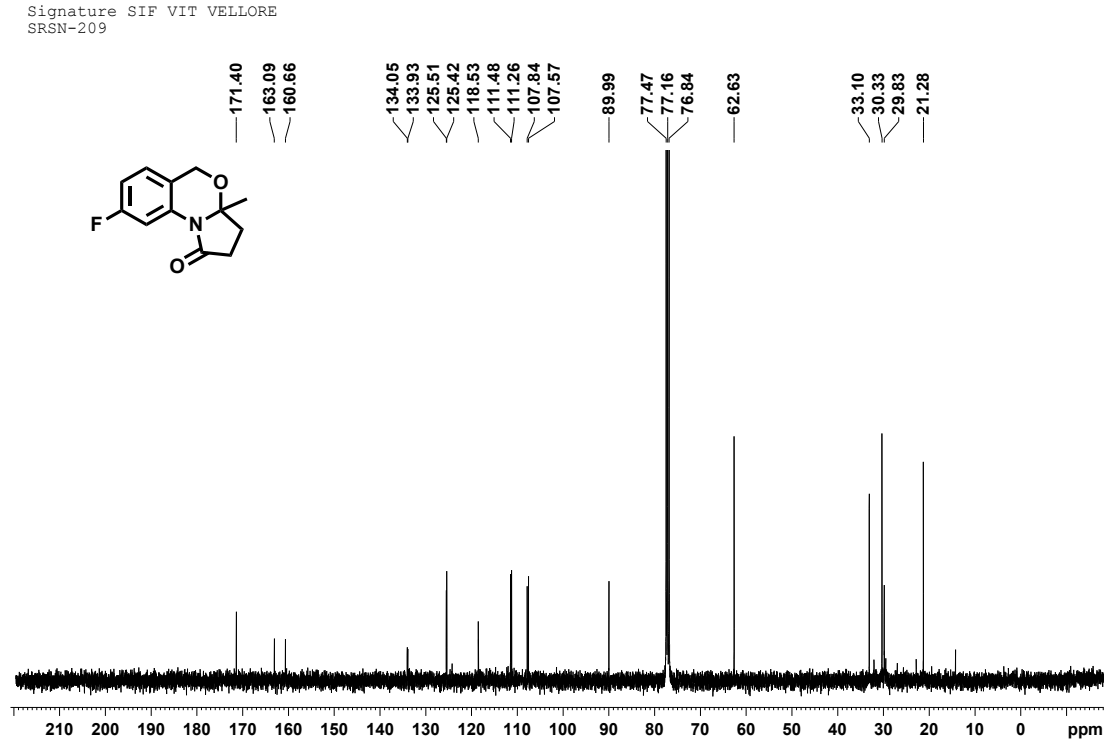


#	RT	Scan	Height	Area	Area %	Norm %
1	13.338	2167	13,470,882	879,466.8	0.620	0.63
2	16.529	2805	3,325,406,208	139,439,728.0	98.235	100.00
3	18.770	3253	8,297,768	381,329.2	0.269	0.27
4	18.890	3277	8,438,605	661,103.1	0.466	0.47
5	22.812	4061	3,638,243	348,149.4	0.245	0.25
6	24.232	4345	5,605,049	235,905.5	0.166	0.17

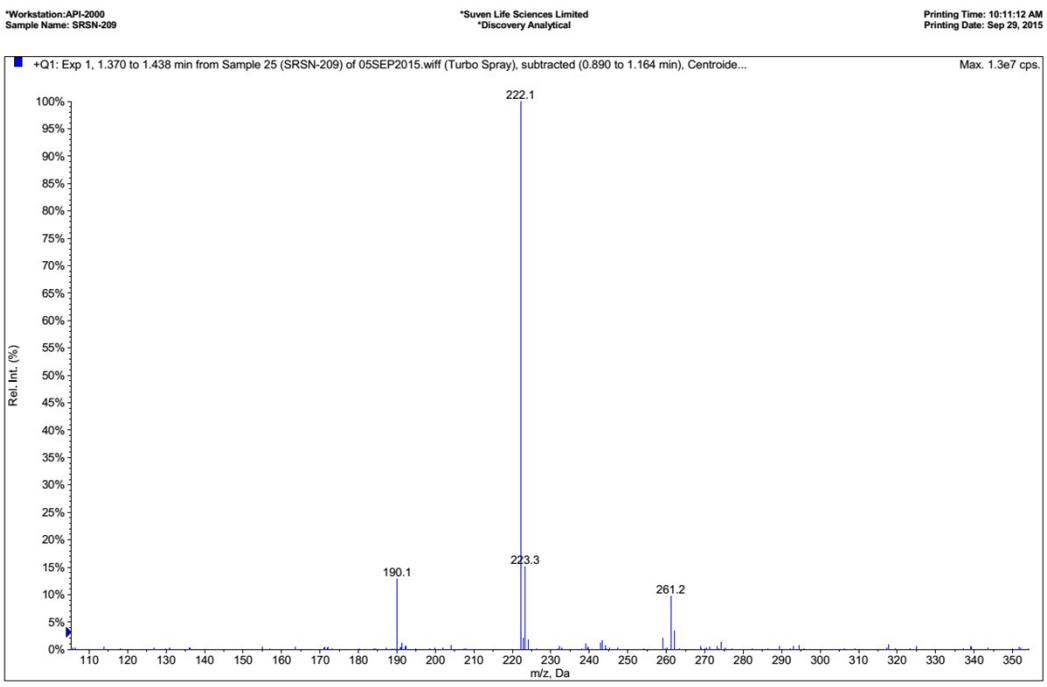
GCMS of 7-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4b**



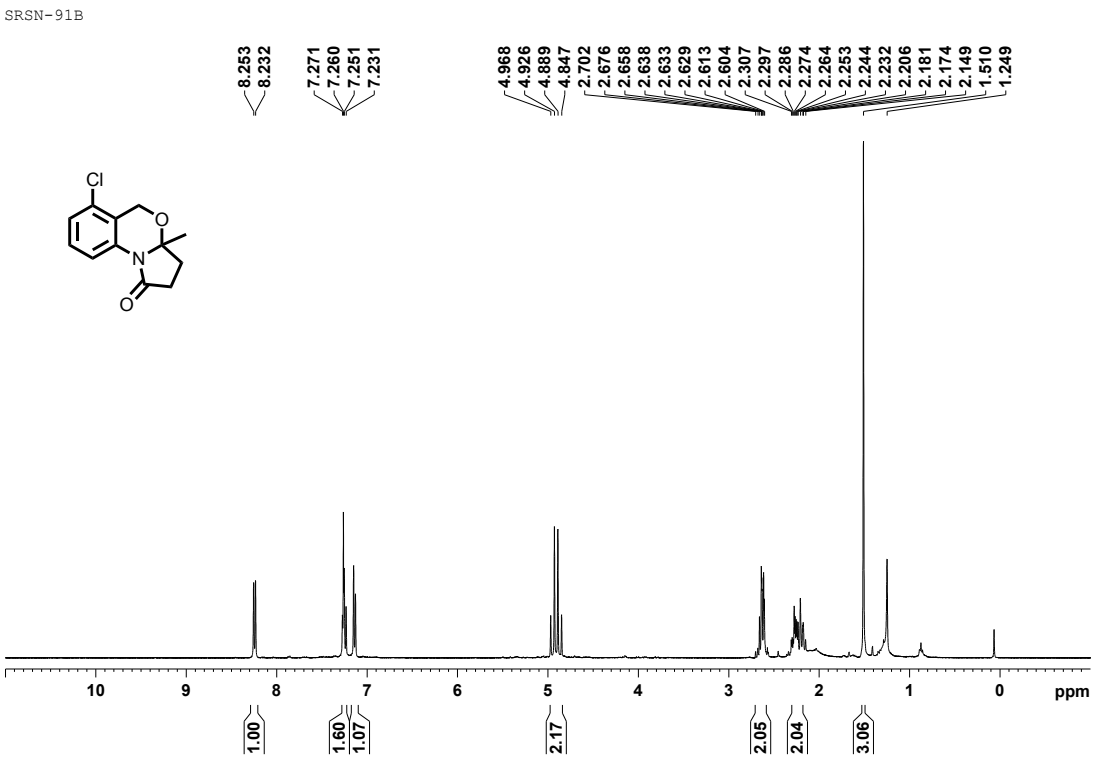
^{1}HNMR spectrum of8-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4c**



^{13}C NMR NMR spectrum of8-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4c**

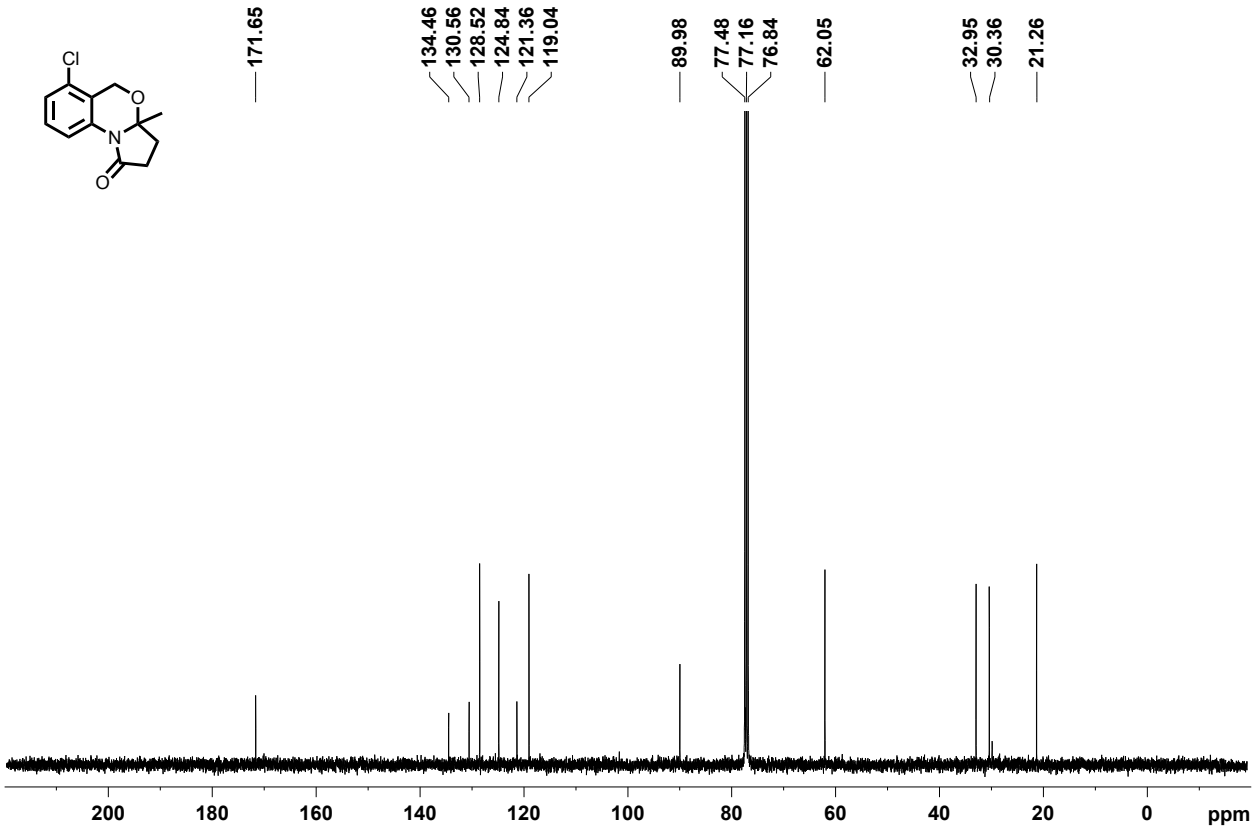


ESI-MS of8-fluoro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4c**



[1]HNMR spectrum of 6-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4d**

SRSN-91B



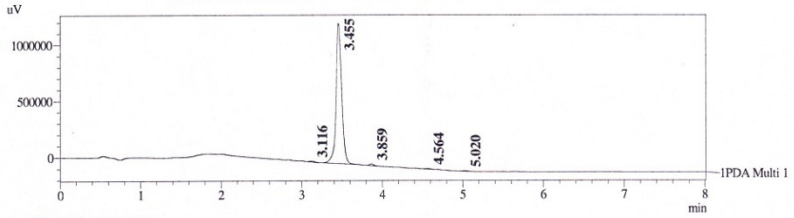
^{13}C NMR spectrum of 6-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4d**

Sample Information

Sample Name :SEV-MA~~1417-11 R~~ 1413-532-S.
Date Acquired : 4/21/2014 5:42:23 PM
Data File : 210414M 41.lcd
Method File : Test Method - LCMS.lcm
Tuning File : D:\Shimadzu MS Data\Tuning Files\ESI 060314---4.lct
Vial :32
Column : X-Select CSH C18 (50x3.0mm,3.5um)
M.P : A-0.05% Aq TFA , B:ACN
T%B :0.01/10,0.5/10,4/90,8/90
Flow : 0.8ml/min(Gradient)

Chromatogram

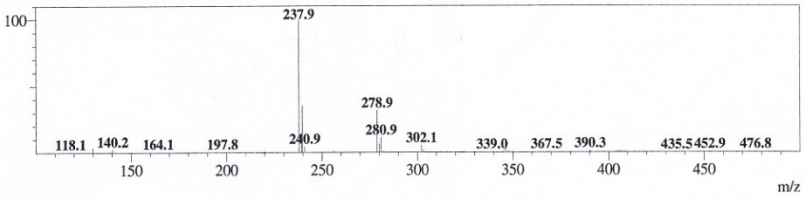
SEV-MA1417-11 R D:\Shimadzu MS Data\2014 Data\APRIL-2014\LCMS\210414M 41.lcd



1 PDA Multi 1 / 215nm 4nm

MS Spectrum

Ret Time:3.433-3.500
Polarity:Pos: Base Peak:237.90



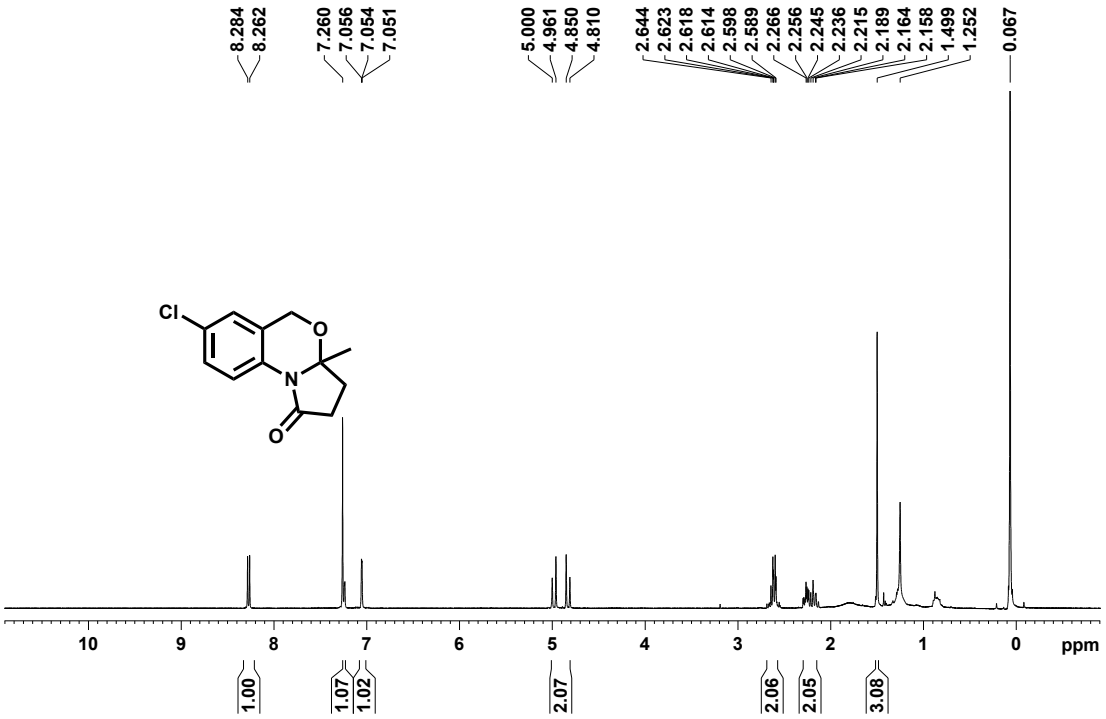
PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.116	25324	0.410
2	3.455	6068254	98.305
3	3.859	41599	0.674
4	4.564	21355	0.346
5	5.020	16321	0.264
Total		6172854	100.000

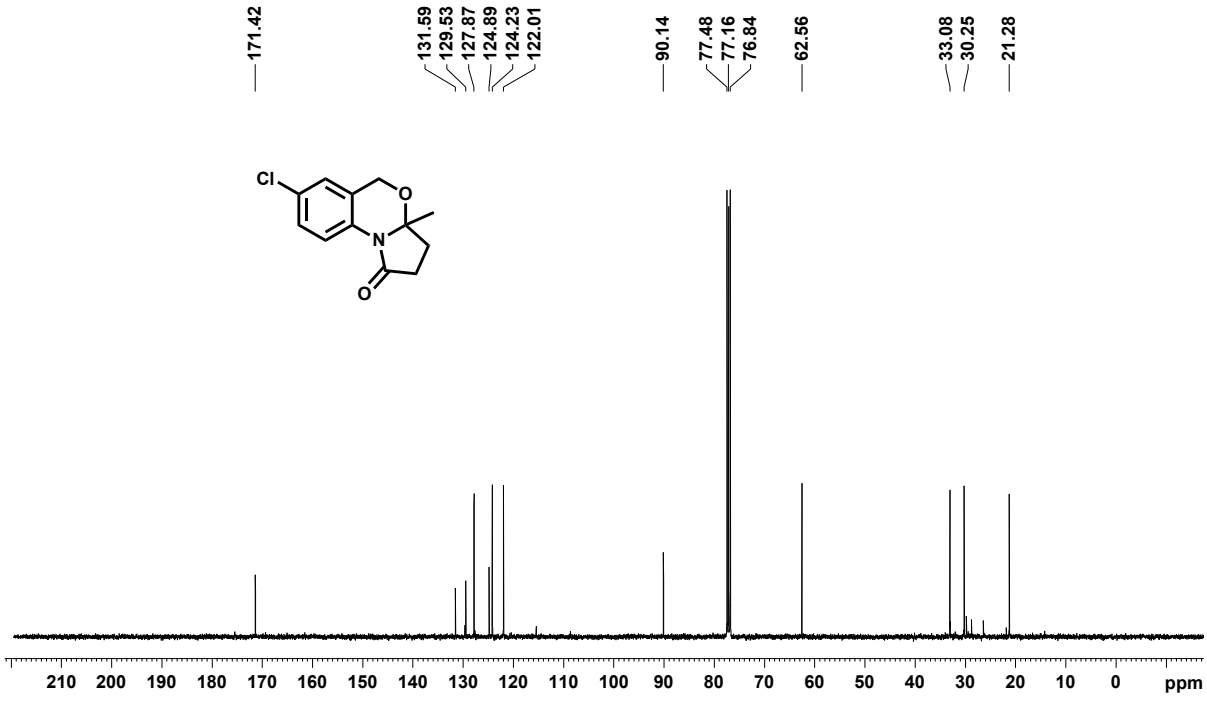
LCMS of 6-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4d**

SRSN-90-F2

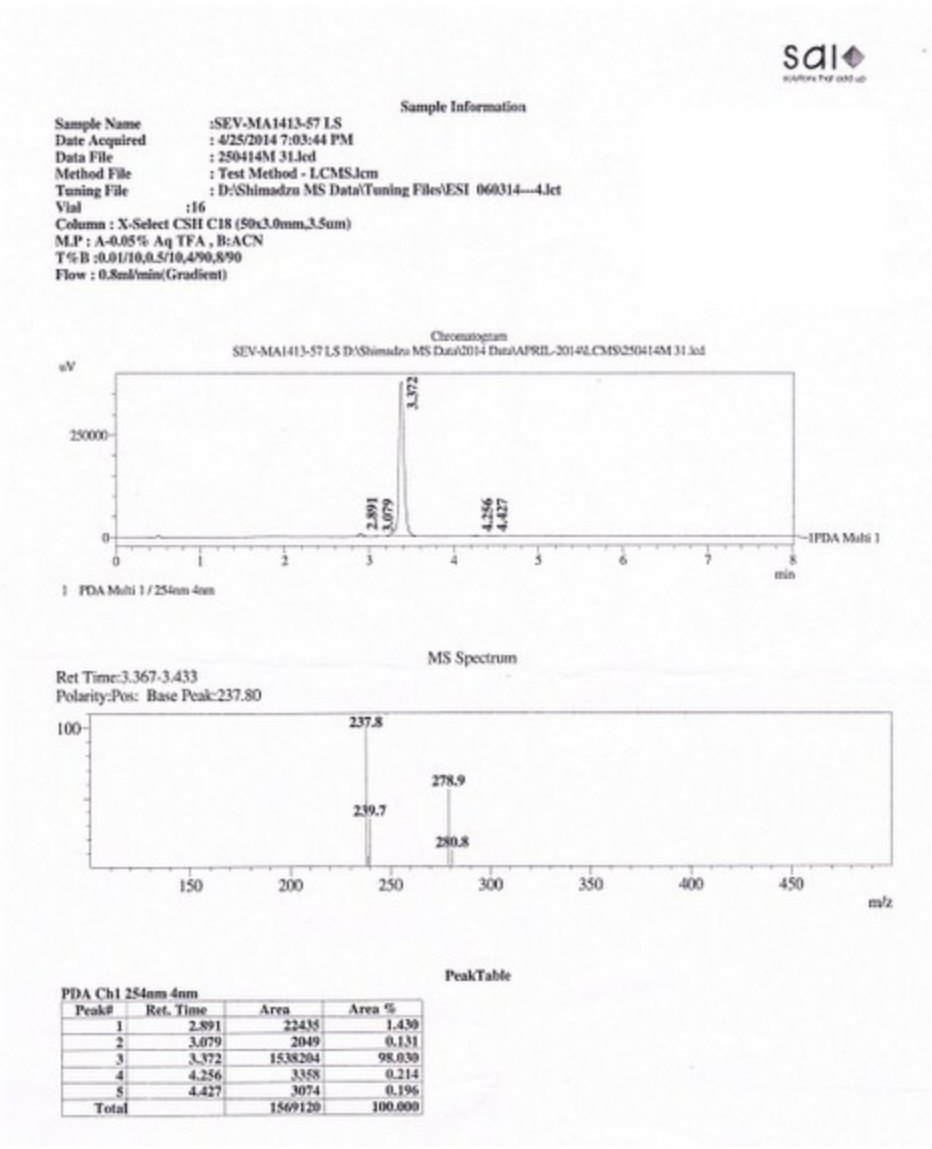


^{1}HNMR spectrum of 7-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4e**

Signature SIF VIT VELLORE
SRSN-90-01

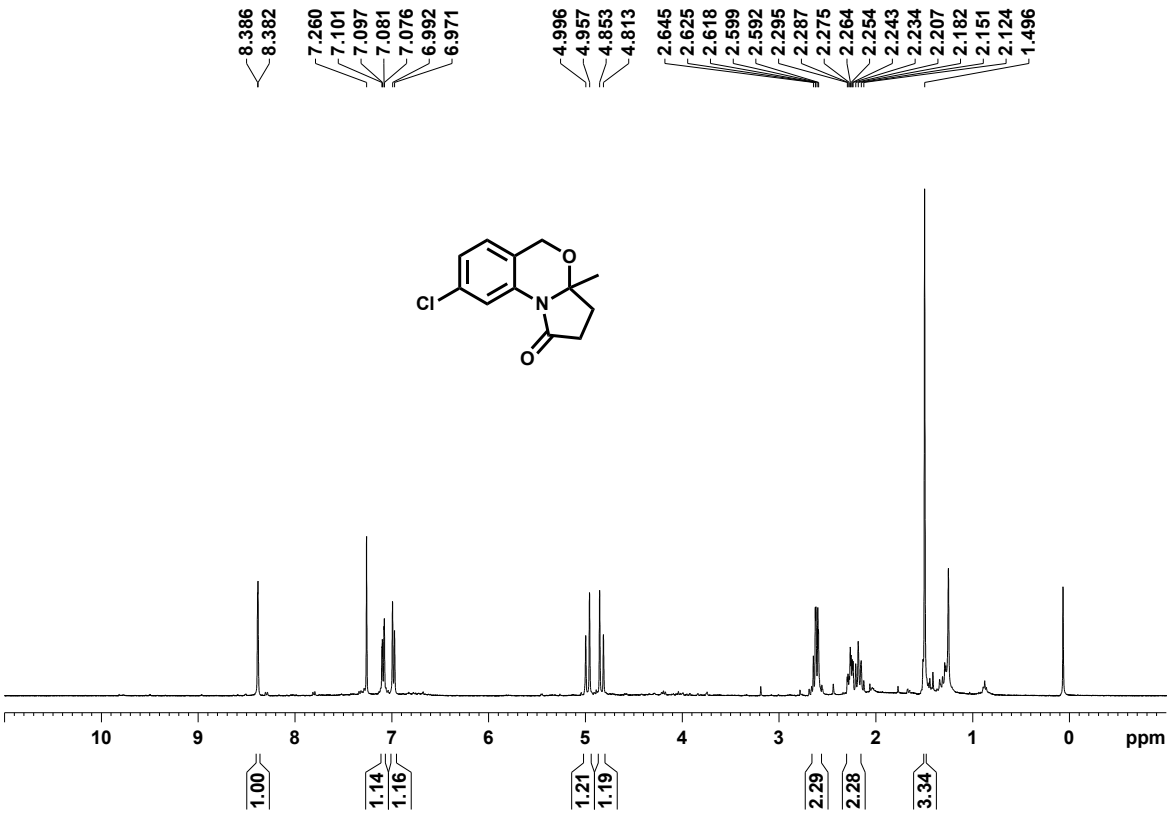


^{13}C NMR spectrum of 7-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4e**

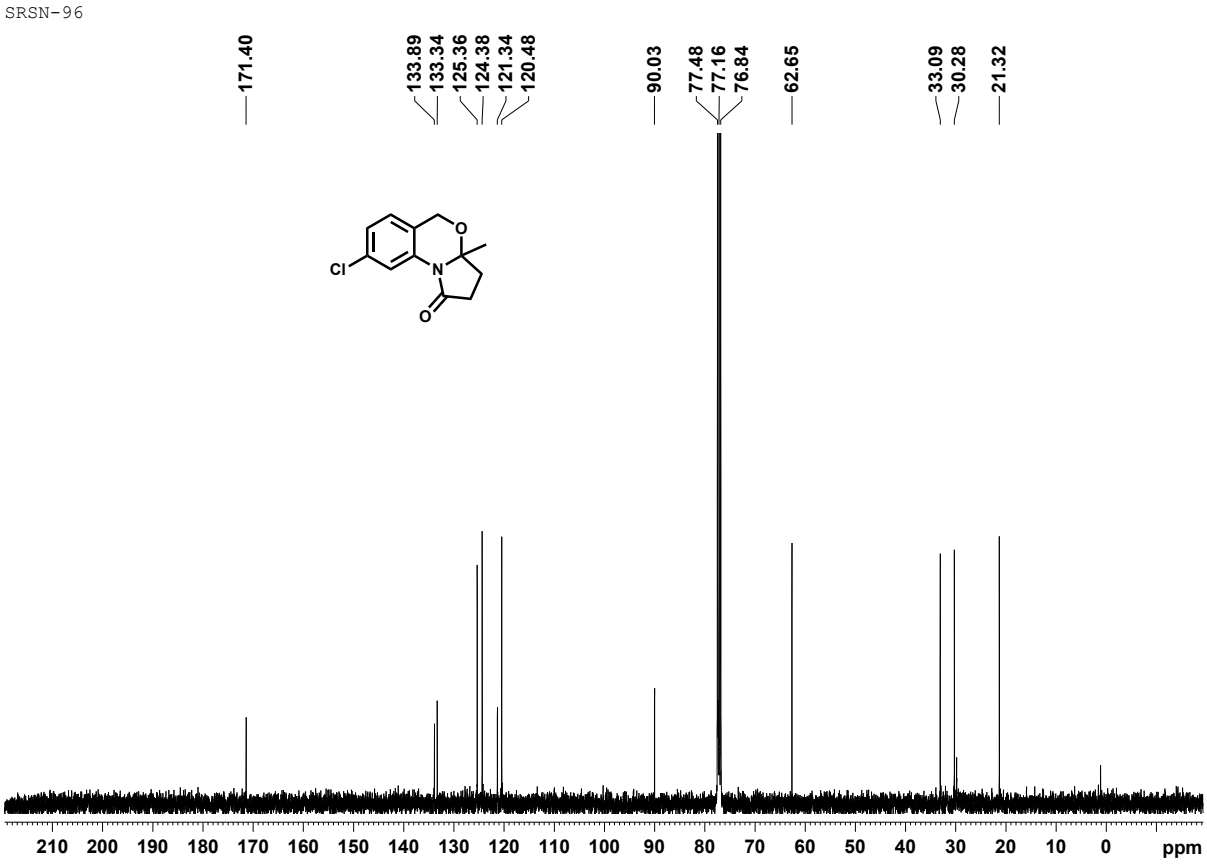


LCMSof 7-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4e**

SRSN-96



^{1}HNMR spectrum of 8-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4f**



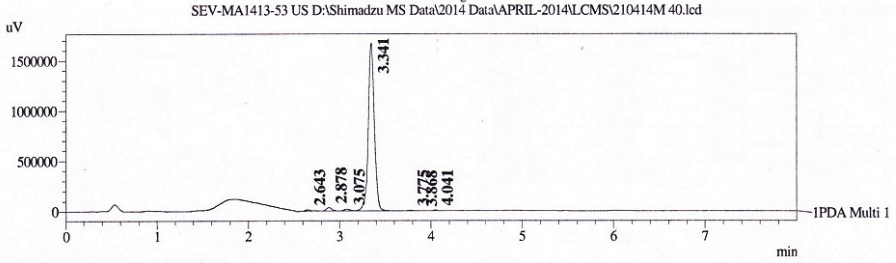
^{13}C NMR spectrum of 8-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4f**

sai
solutions that add up

Sample Information

Sample Name :SEV-MA1413-53 US
Date Acquired : 4/21/2014 5:31:17 PM
Data File : 210414M 40.lcd
Method File : Test Method - LCMS.lcm
Tuning File : D:\Shimadzu MS Data\Tuning Files\ESI 060314---4.lct
Vial :31
Column : X-Select CSH C18 (50x3.0mm,3.5um)
M.P : A-0.05% Aq TFA , B:ACN
T%B :0.01/10,0.5/10,4/90,8/90
Flow : 0.8ml/min(Gradient)

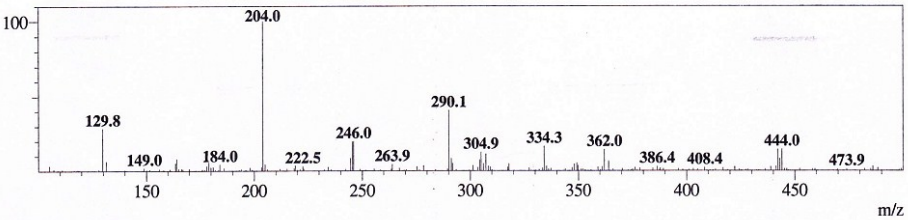
Chromatogram
SEV-MA1413-53 US D:\Shimadzu MS Data\2014 Data\APRIL-2014\LCMS\210414M 40.lcd



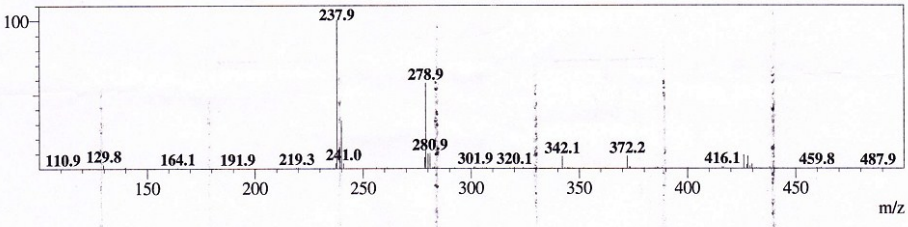
1 PDA Multi 1 / 200nm - 400nm 4nm

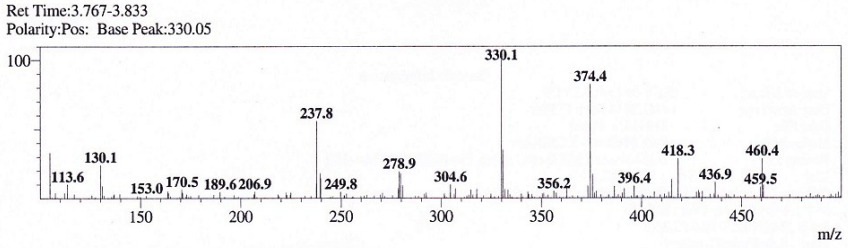
MS Spectrum

Ret Time:2.850-2.933
Polarity:Pos: Base Peak:203.95



Ret Time:3.317-3.433
Polarity:Pos: Base Peak:237.90





PeakTable

PDA Ch1 200nm - 400nm 4nm

Peak#	Ret. Time	Area	Area %
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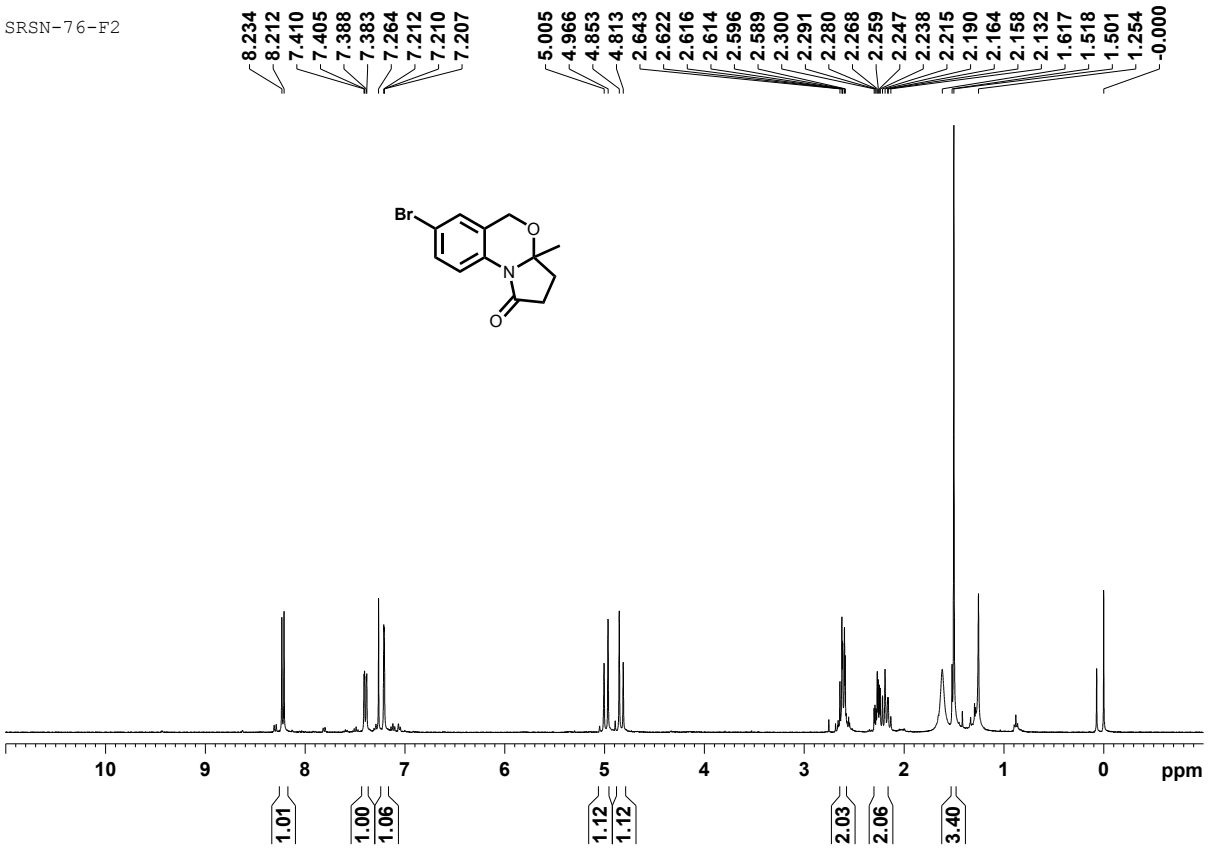
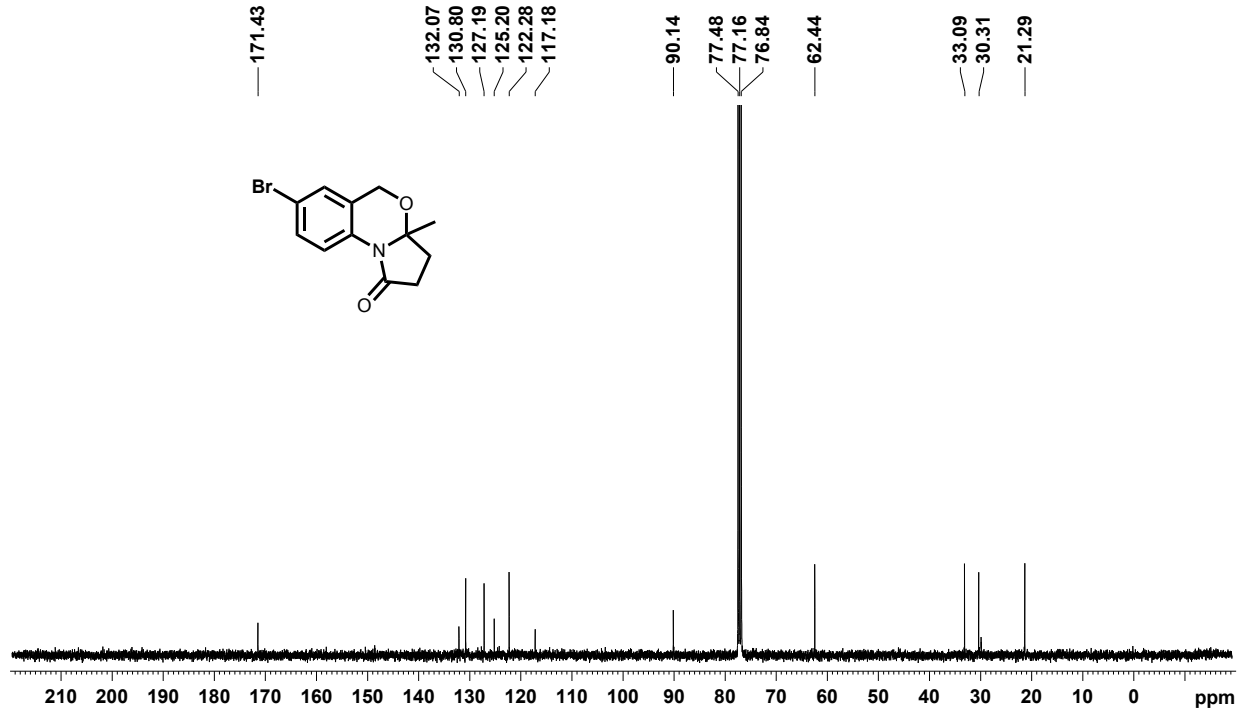
2	2.878	134734	1.691
3	3.075	73191	0.919
4	3.341	7687359	96.477
5	3.775	13639	0.171
6	3.868	3349	0.042
7	4.041	18397	0.231
Total		7968060	100.000

LCMSof8-chloro-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4f**



^{1}HNMR spectrum 7-bromo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4g**

SRSN-76-F2



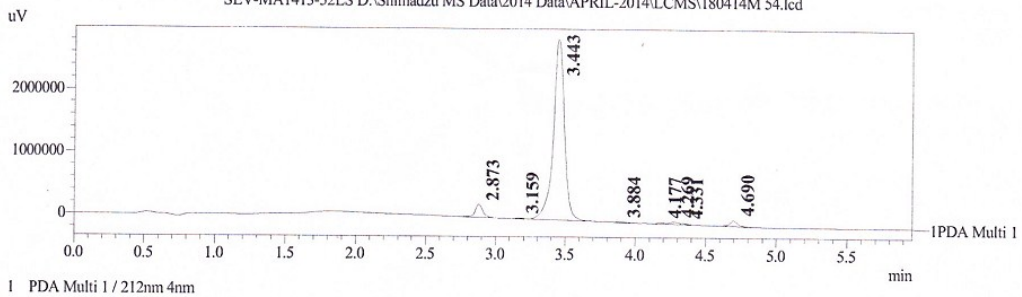
^{13}C NMR spectrum of 7-bromo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4g**

sai
solutions that add up

Sample Information

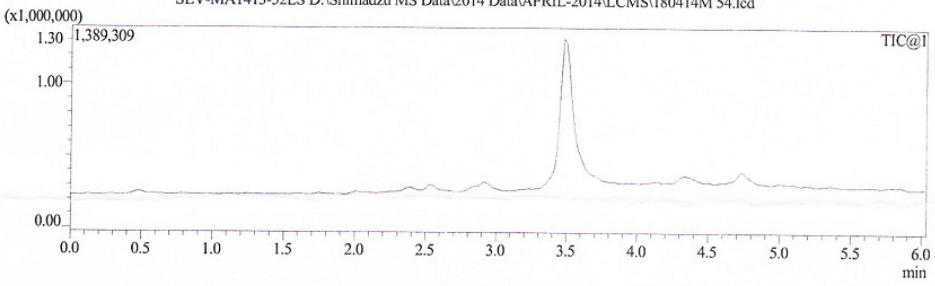
Sample Name :SEV-MA1413-52LS
Date Acquired : 4/18/2014 8:28:23 PM
Data File : 180414M 54.lcd
Method File : Test Method - LCMS.lcm
Tuning File : D:\Shimadzu MS Data\Tuning Files\ESI 060314---4.lct
Vial :28
Column : X-Select CSH C18 (50x3.0mm,3.5um)
M.P : A-0.05% Aq TFA , B:ACN
T%B :0.01/10,0.5/10,4/90,8/90
Flow : 0.8ml/min(Gradient)

Chromatogram
SEV-MA1413-52LS D:\Shimadzu MS Data\2014 Data\APRIL-2014\LCMS\180414M 54.lcd



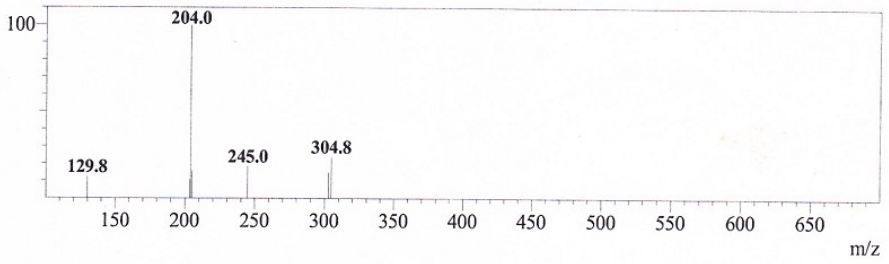
1 PDA Multi 1 / 212nm 4nm

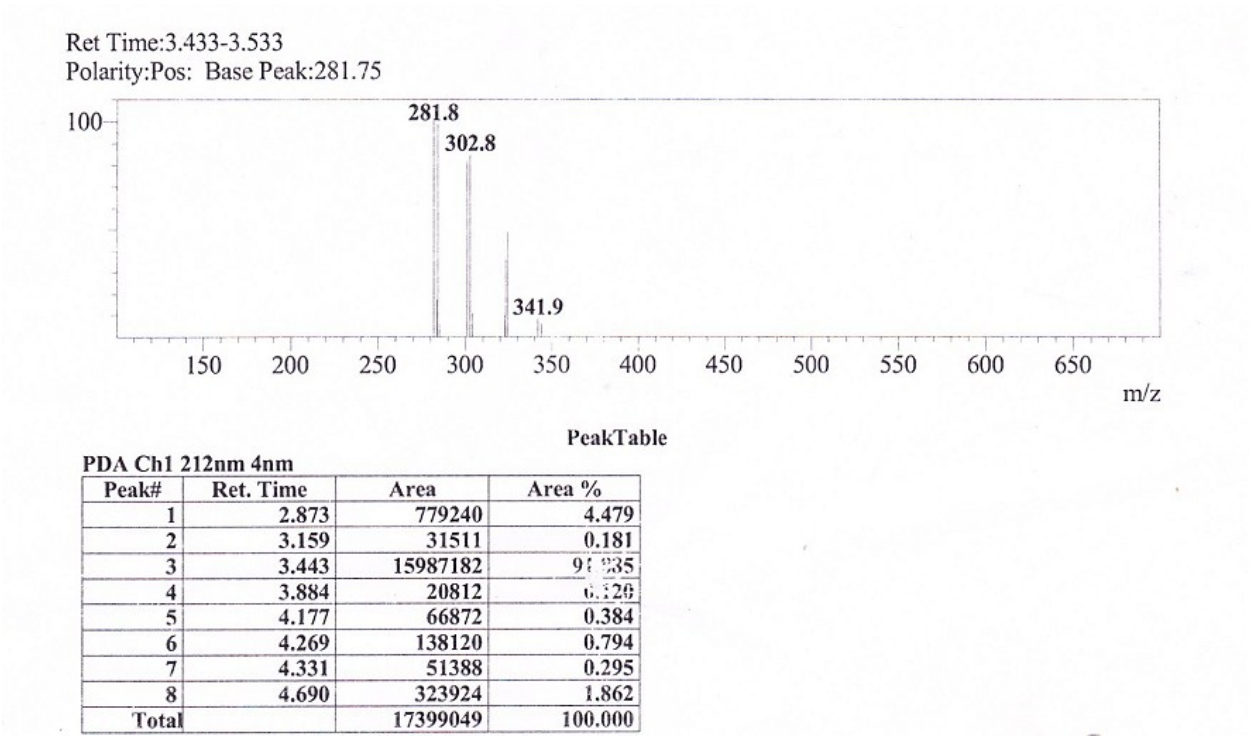
MS Chromatogram
SEV-MA1413-52LS D:\Shimadzu MS Data\2014 Data\APRIL-2014\LCMS\180414M 54.lcd



MS Spectrum

Ret Time:2.850-2.950
Polarity:Pos: Base Peak:203.95





PeakTable

PDA Ch1 212nm 4nm

Peak#	Ret. Time	Area	Area %
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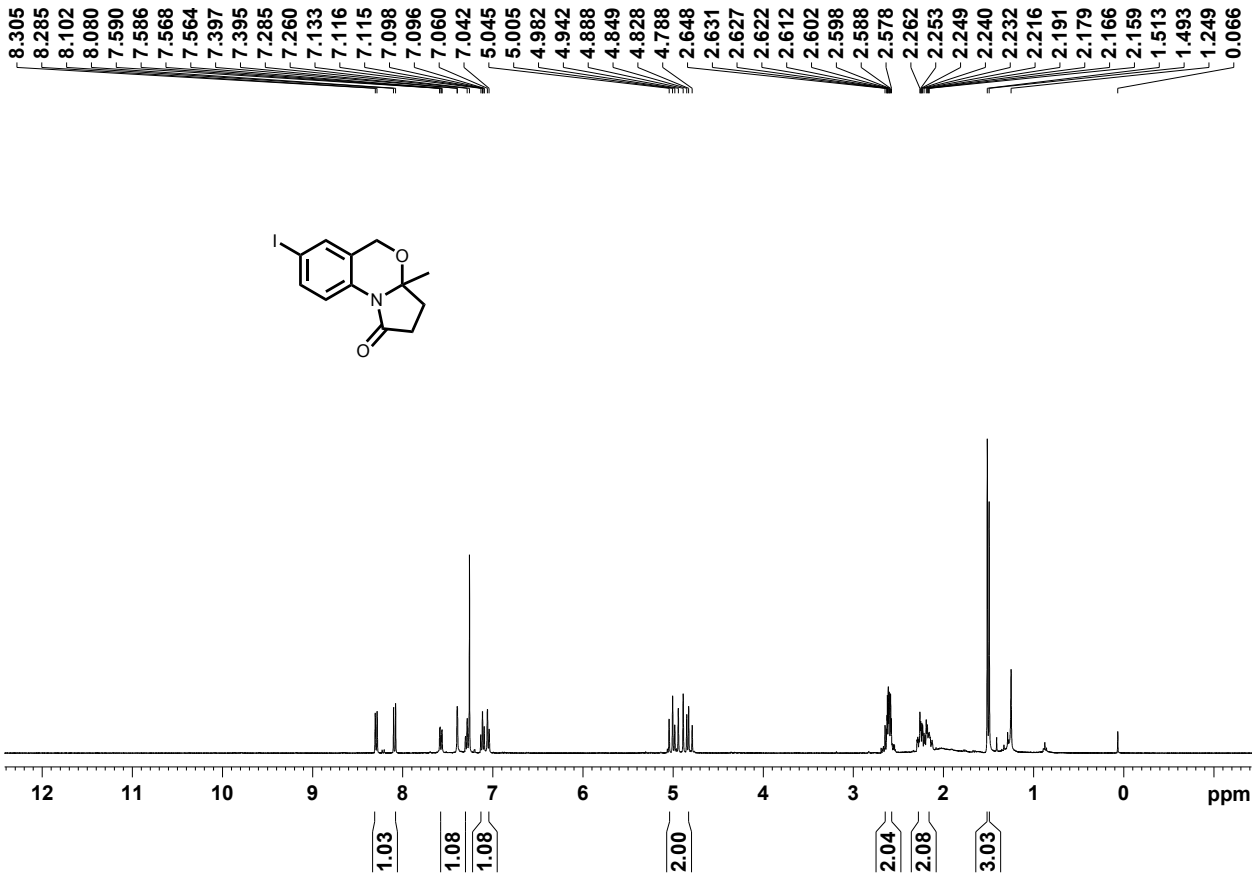
3	3.443	15987182	91.935
4	3.884	20812	0.120
5	4.177	66872	0.384
6	4.269	138120	0.794
7	4.331	51388	0.295
8	4.690	323924	1.862
Total		17399049	100.000

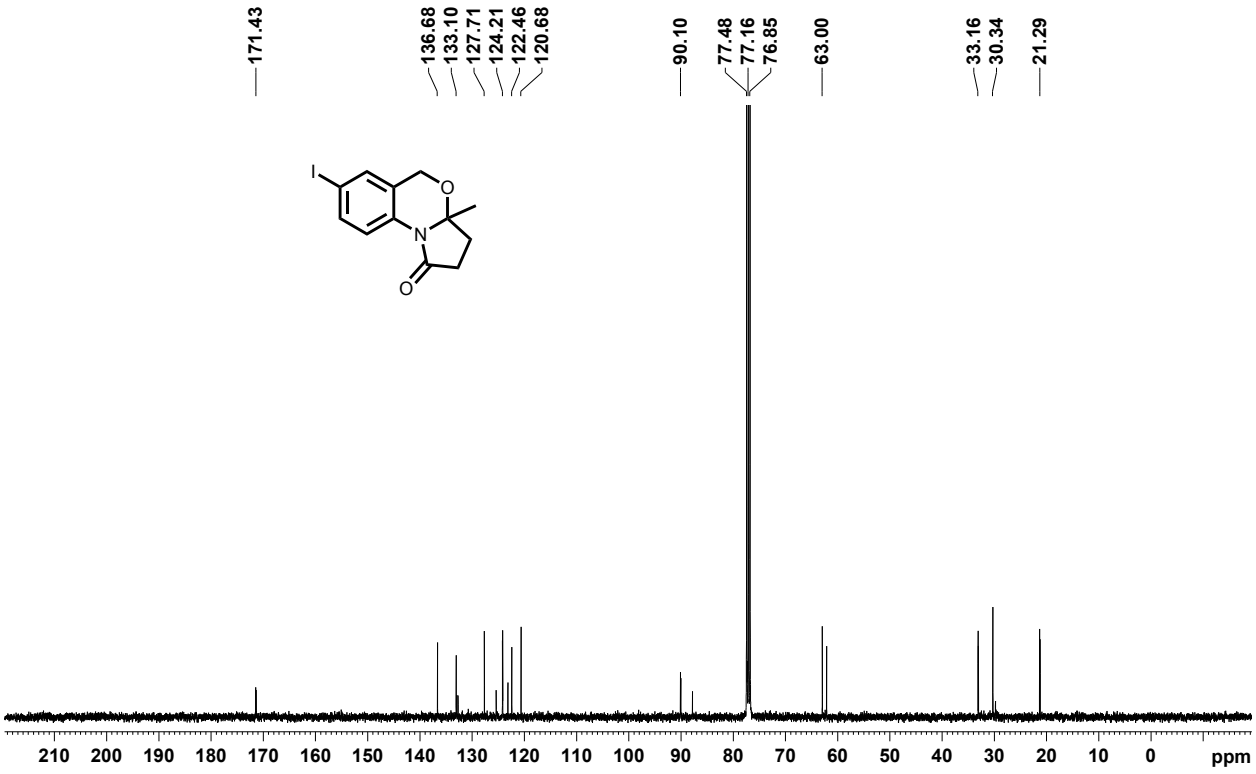
LCMS of7-bromo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4g**

SRSN-92A

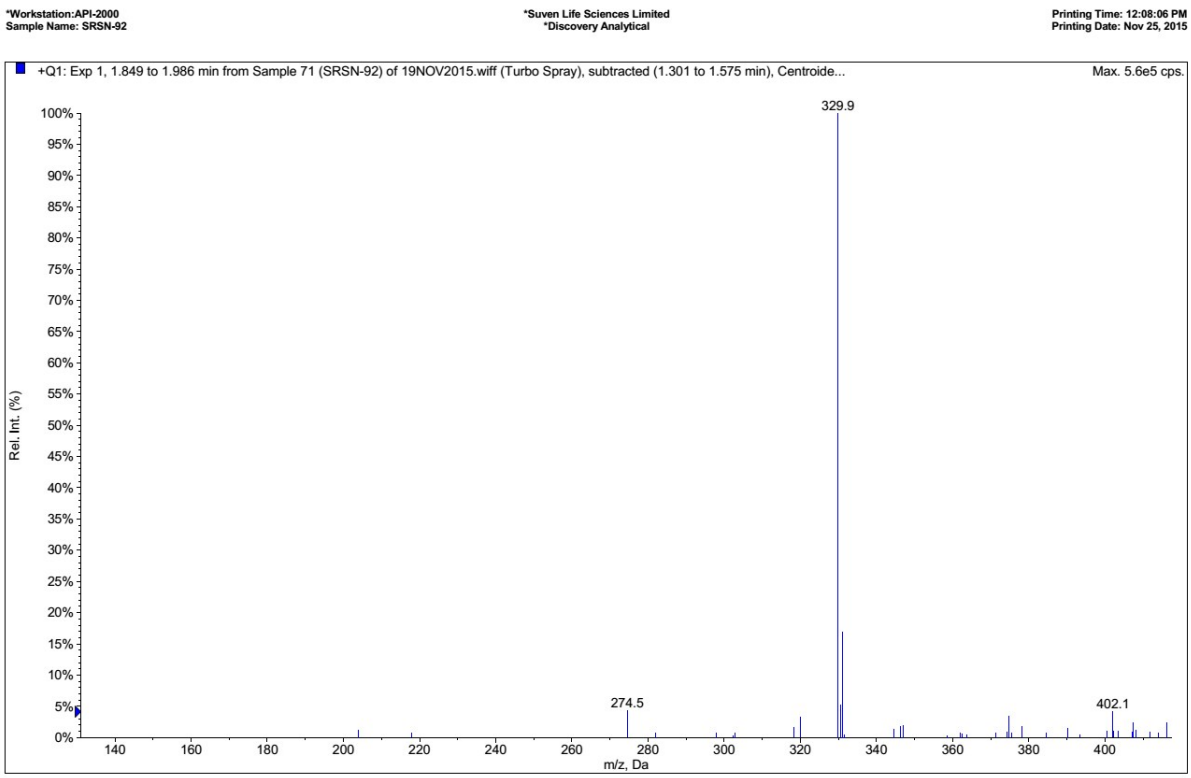


^{1}HNMR spectrum of 7-iodo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4h**

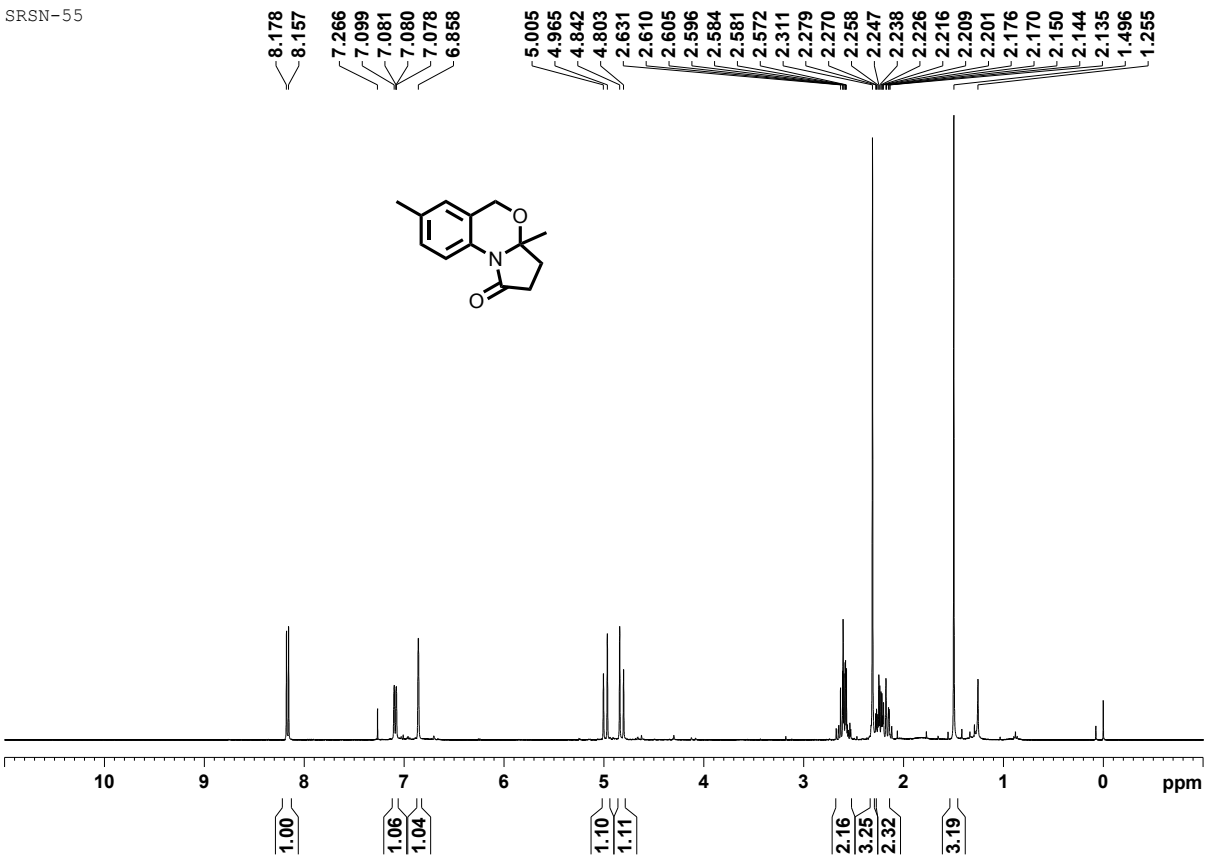
SRSN-92A



^{13}C NMR spectrum of 7-iodo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4h**

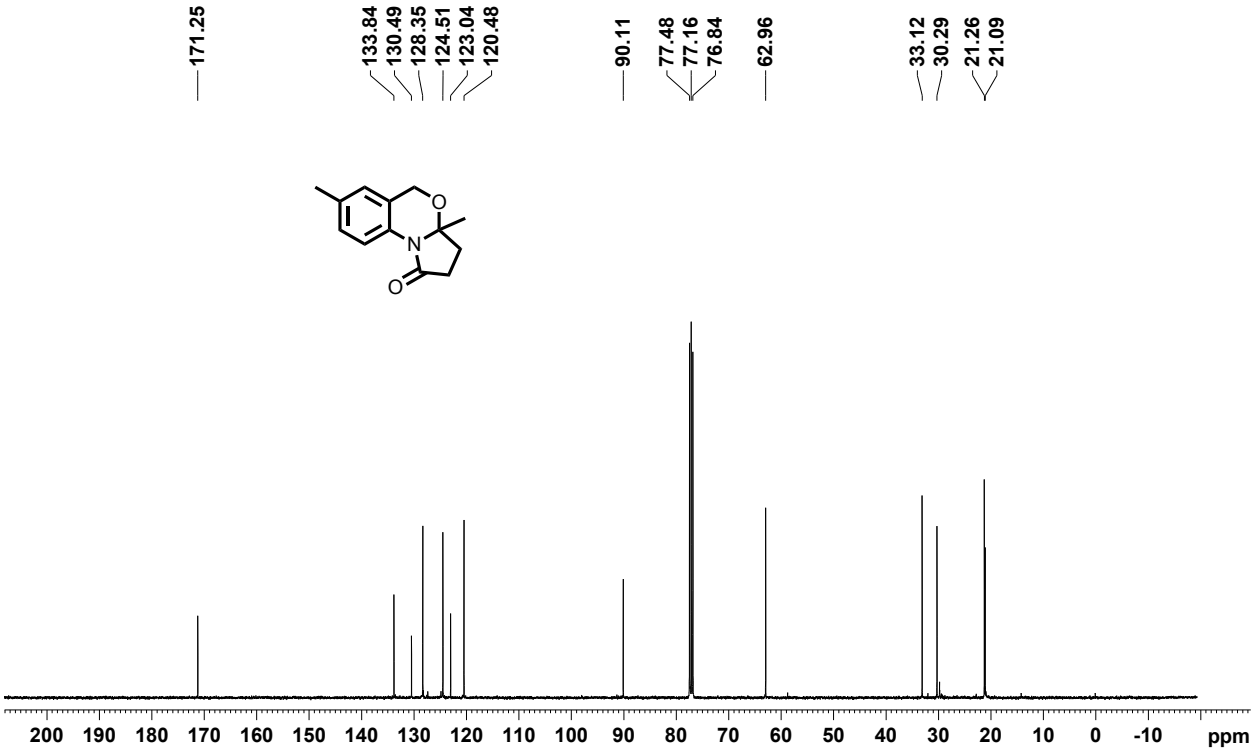


ESI-MSof 7-iodo-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4h**



^{1}HNMR spectrum of 3a,7-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4i**

SRSN-55



^{13}C NMR spectrum of 3a,7-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4i**

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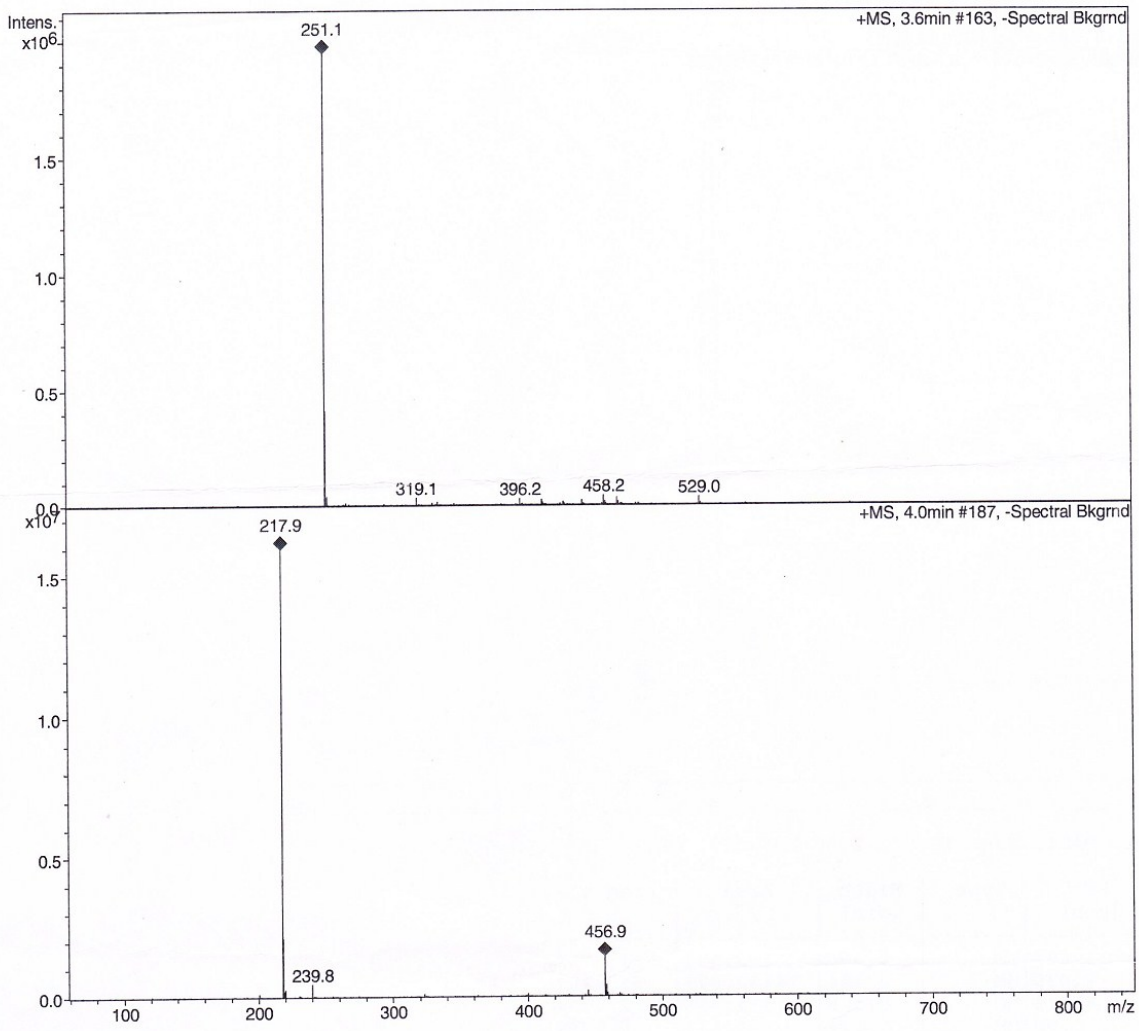
solutions that add up

Sample Name SEV-MA1413-56US **Data file :** APR-24000017.D **Acq. Date :** 4/24/2014 12:28:48 PM

Method LCMS-II.M **Analyst :** ksn

Instrument Agilent 6310 Ion Trap



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ample Name: SEV-MA1413-56US

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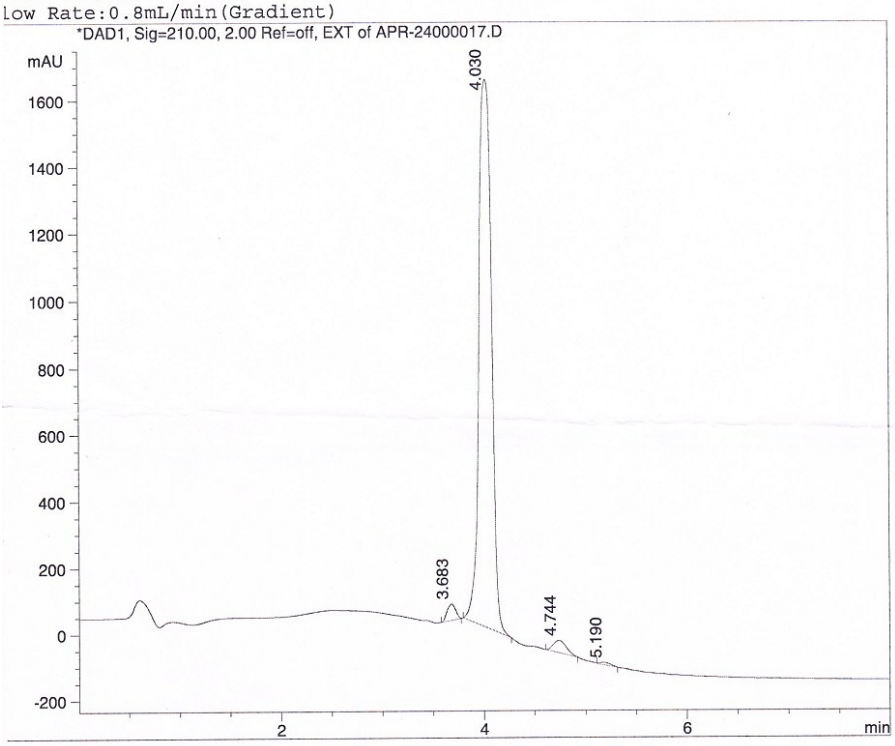
njection Date : 4/24/2014
ample Name : SEV-MA1413-56US
eq Operator : YR

Seq Line : 7
Location : Vial 9
Inj. No. : 1
Inj. Vol. : 4 µl

eq. Method : D:\methods\LCMS-I.m
nalysis Method : D:\methods\LCMS-I.m
ast Changed : 4/24/2014 11:36:58 AM
(modified after loading)
olumn:X Select CSH C-18(50X3mm,3.5um)
obile Phase:A:0.05% Aq TFA, B- ACN
/B%:0.01/10,0.5/10,4/90,8/90
low Rate:0.8mL/min(Gradient)



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2	4.030	MM	0.144	14152.677	95.410
3	4.744	MM	0.148	331.716	2.236
4	5.190	MM	0.121	56.111	0.378

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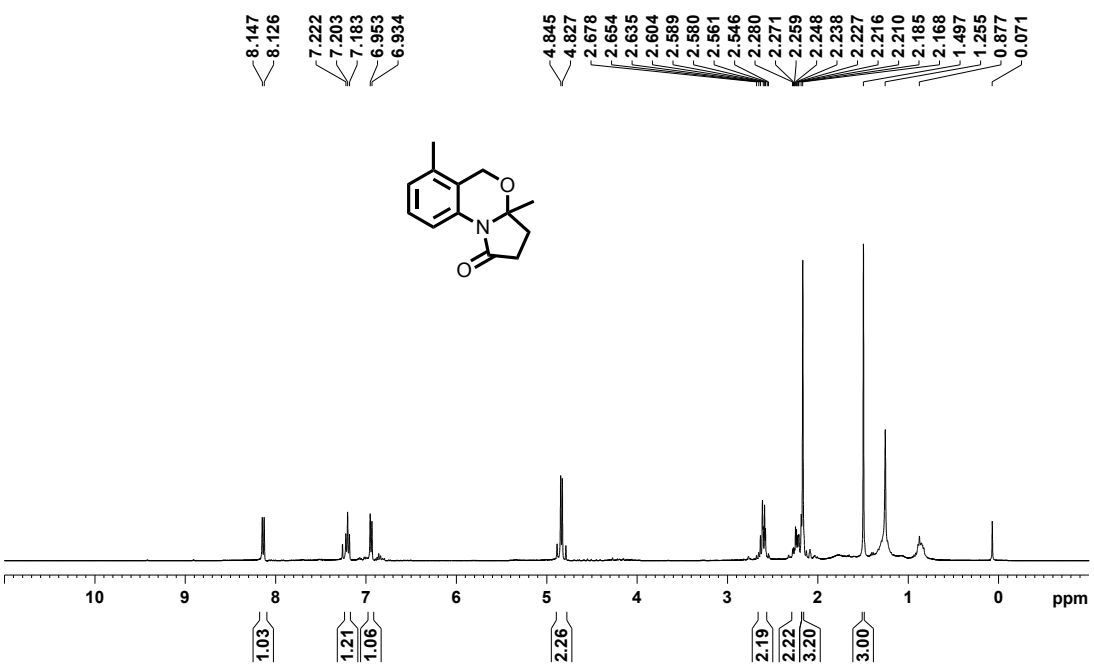
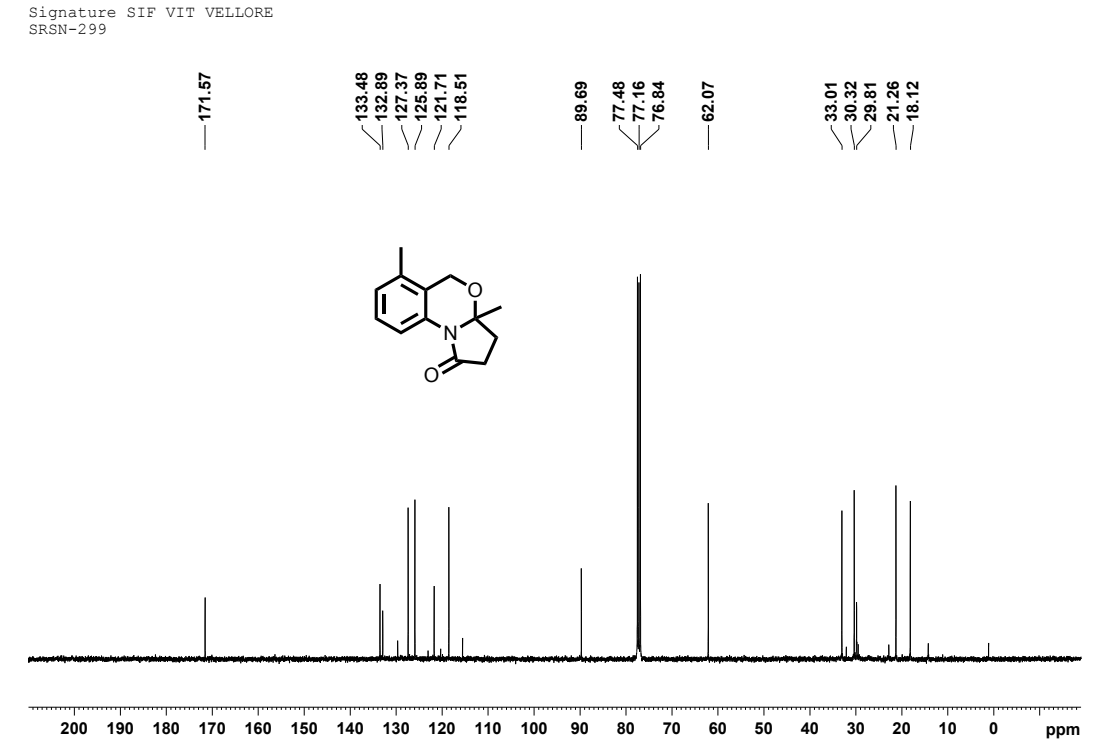
*** End of Report ***

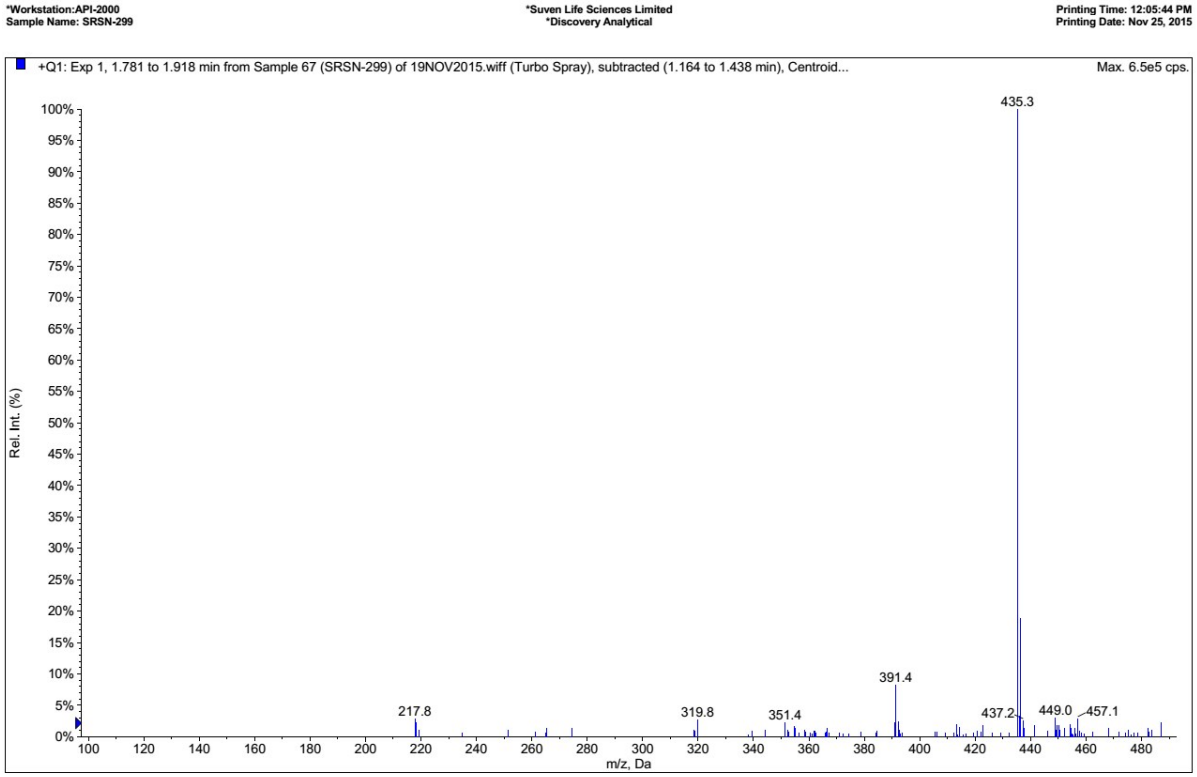
LCMS of 3a,7-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4i**



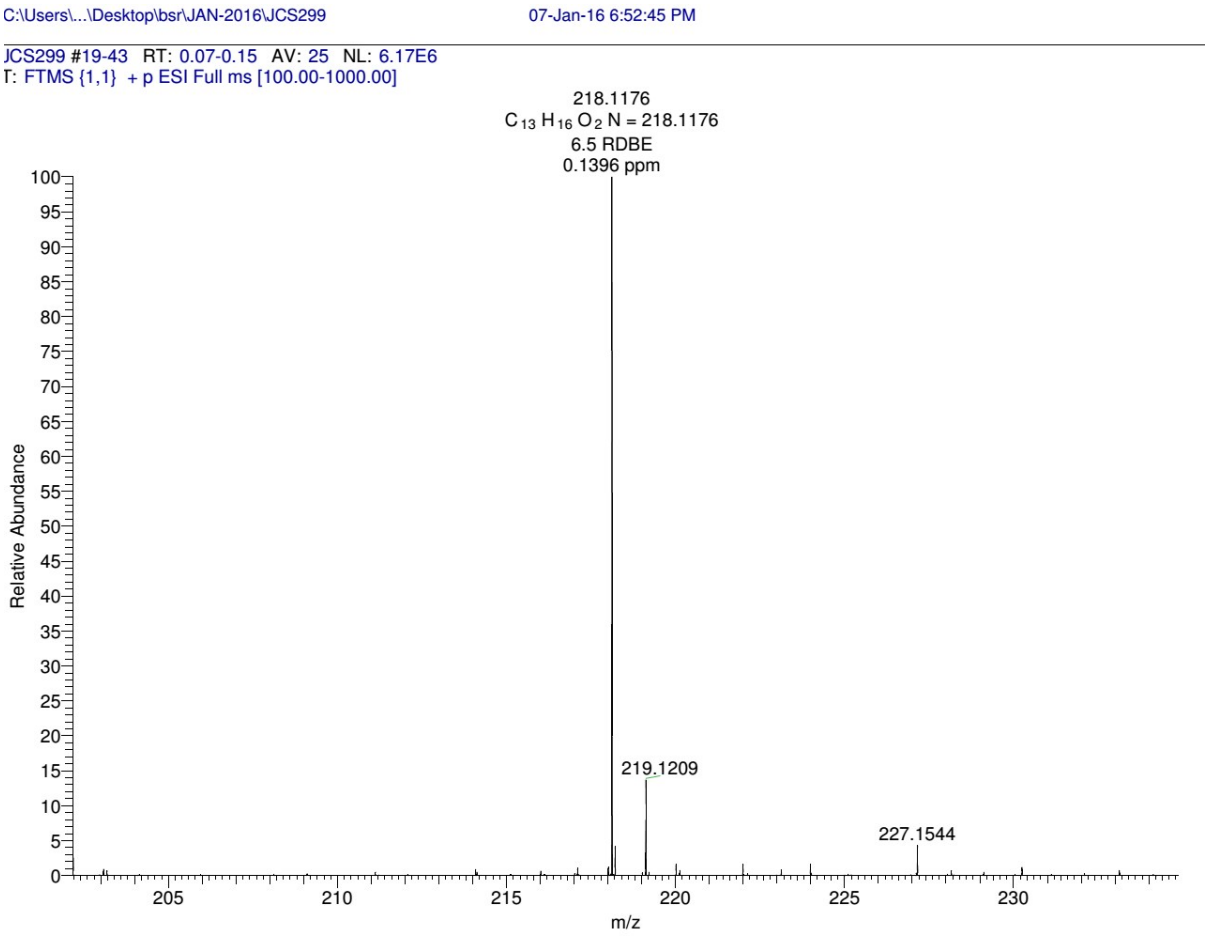
^{1}HNMR spectrum of 3a,6-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one-**4j**



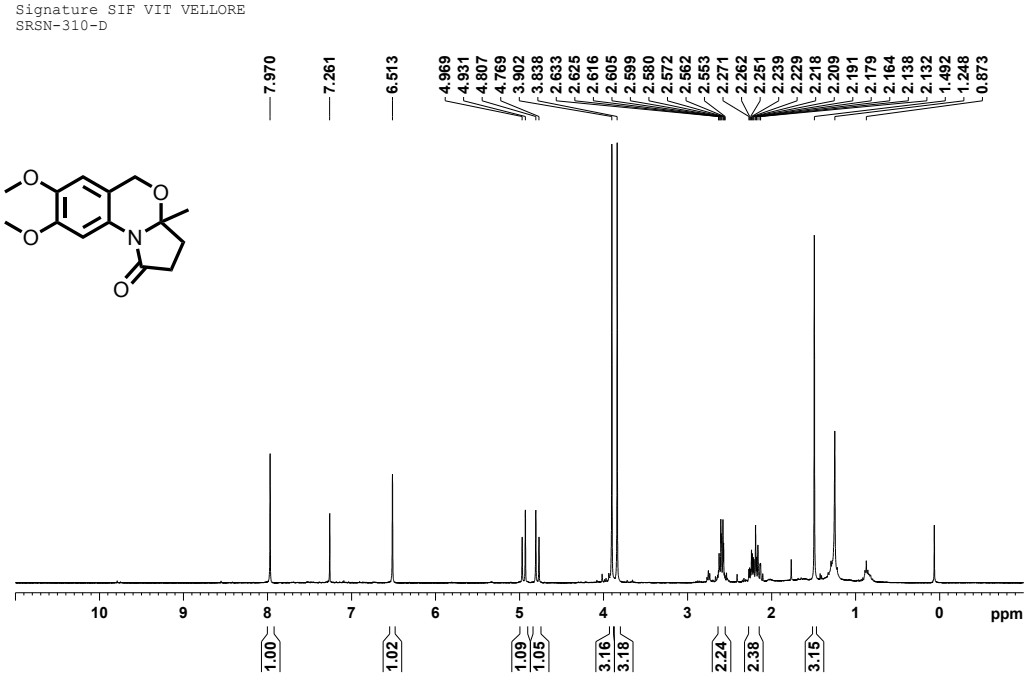
^{13}C NMR spectrum of 3a,6-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4j**



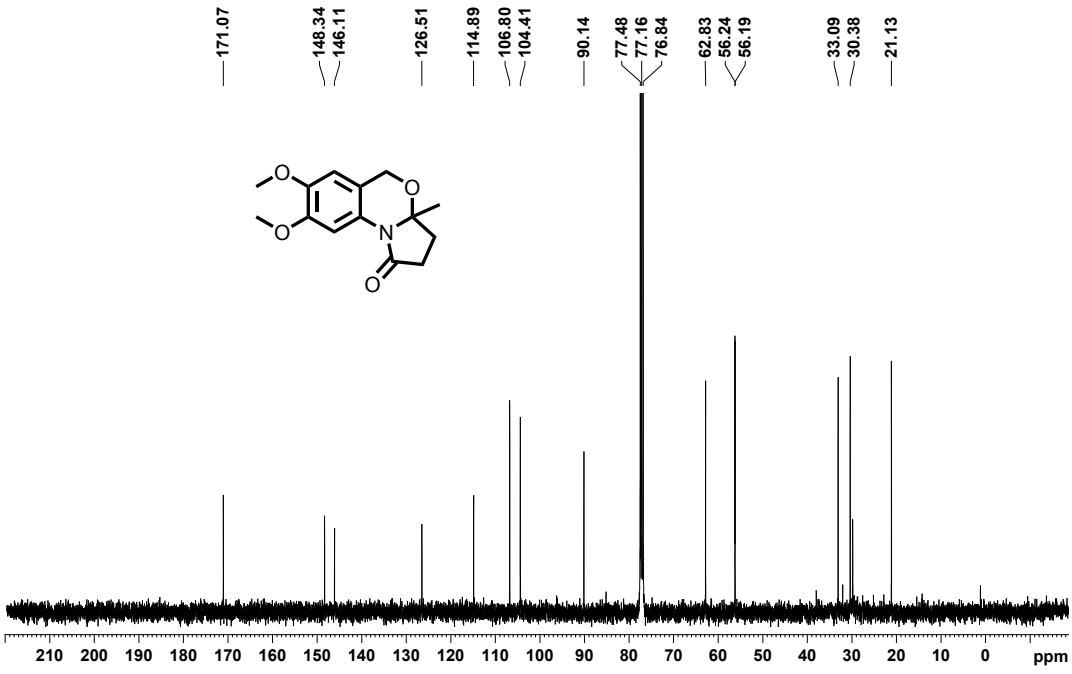
ESI-MSof 73a,6-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4j**



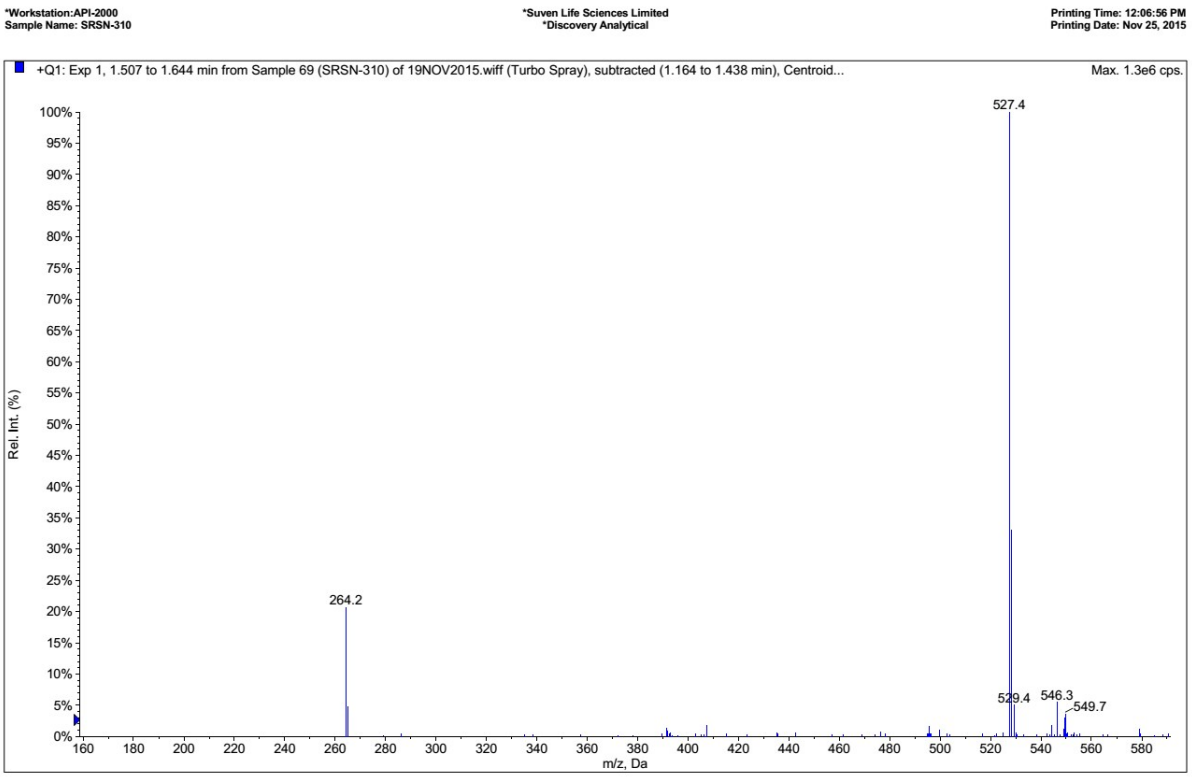
HRMS of 73a,6-dimethyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4j**



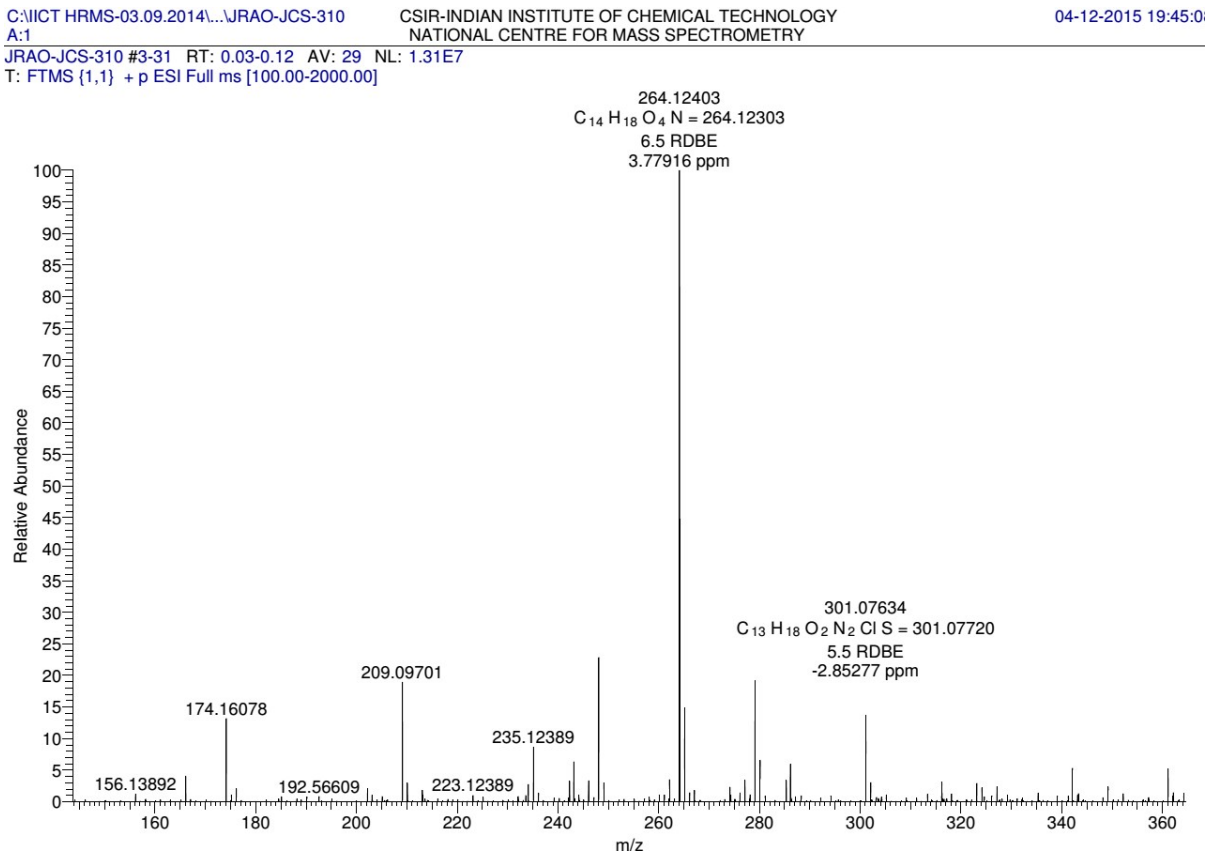
[1]HNMR spectrum of 7,8-dimethoxy-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4k**



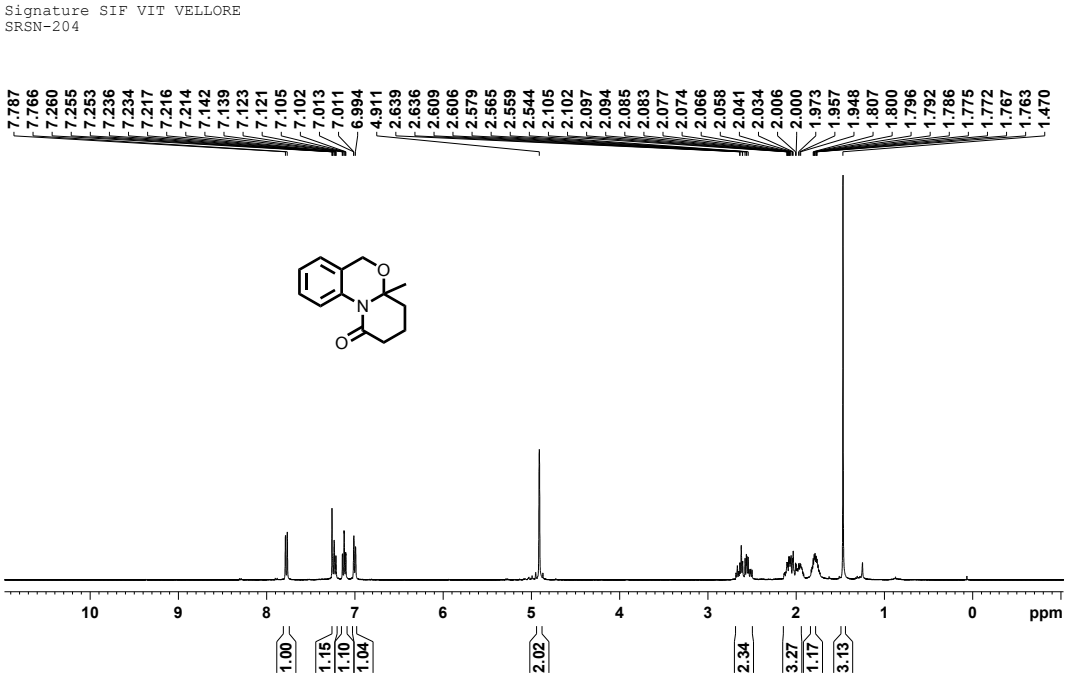
[13]C NMR spectrum of 7,8-dimethoxy-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one**4k**



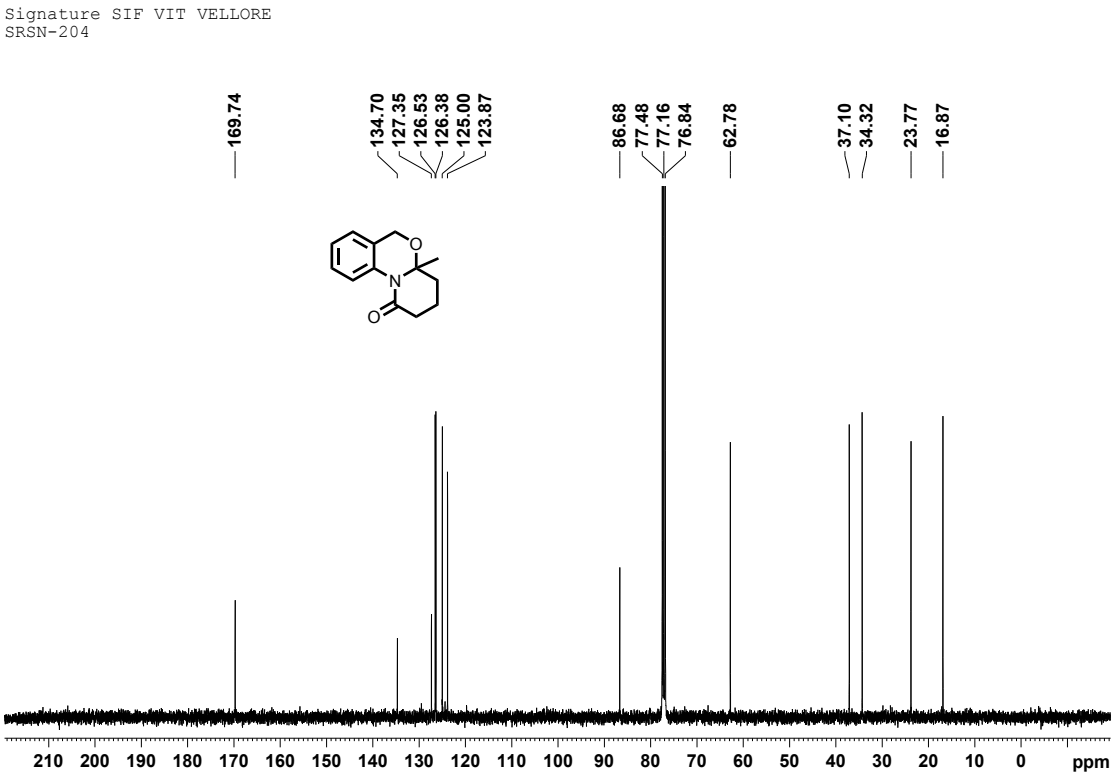
ESI-MS of 7,8-dimethoxy-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4k**



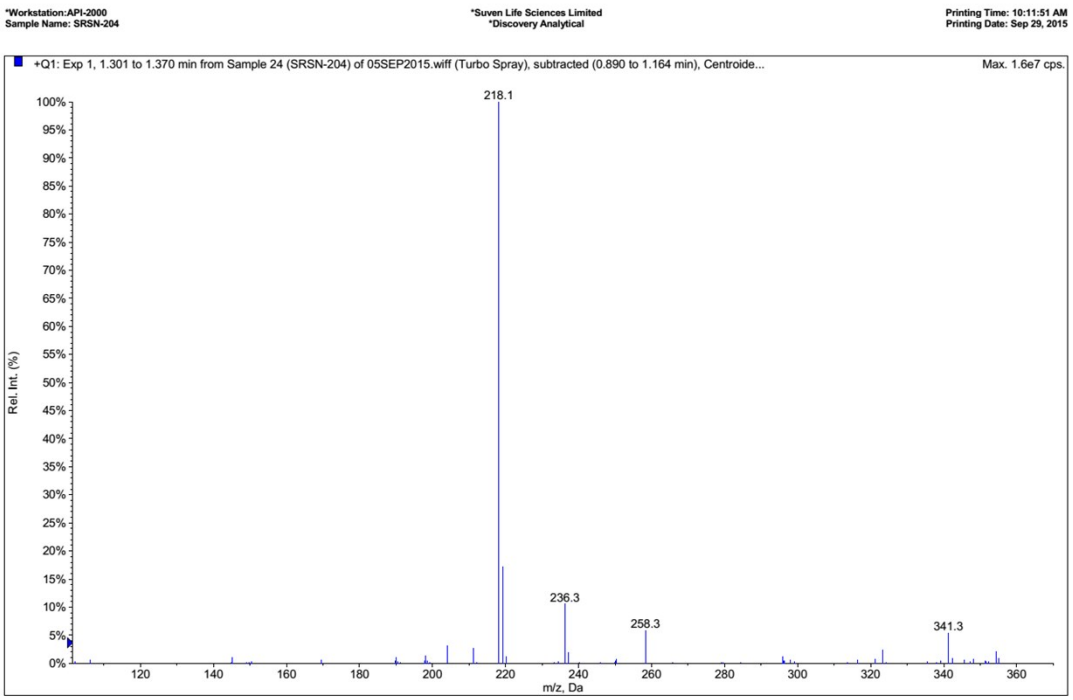
HRMS of 7,8-dimethoxy-3a-methyl-2,3,3a,5-tetrahydro-1H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1-one **4k**



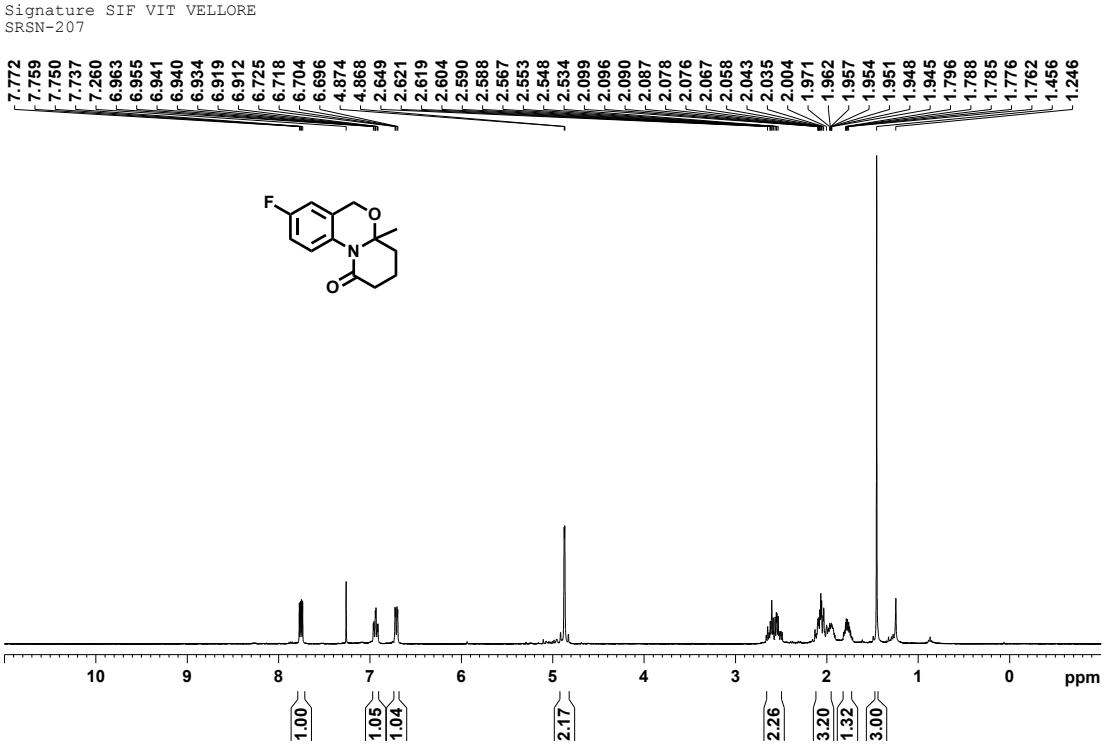
[1]HNMR spectrum of 4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4l**



[13]C NMR spectrum of 4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4l**

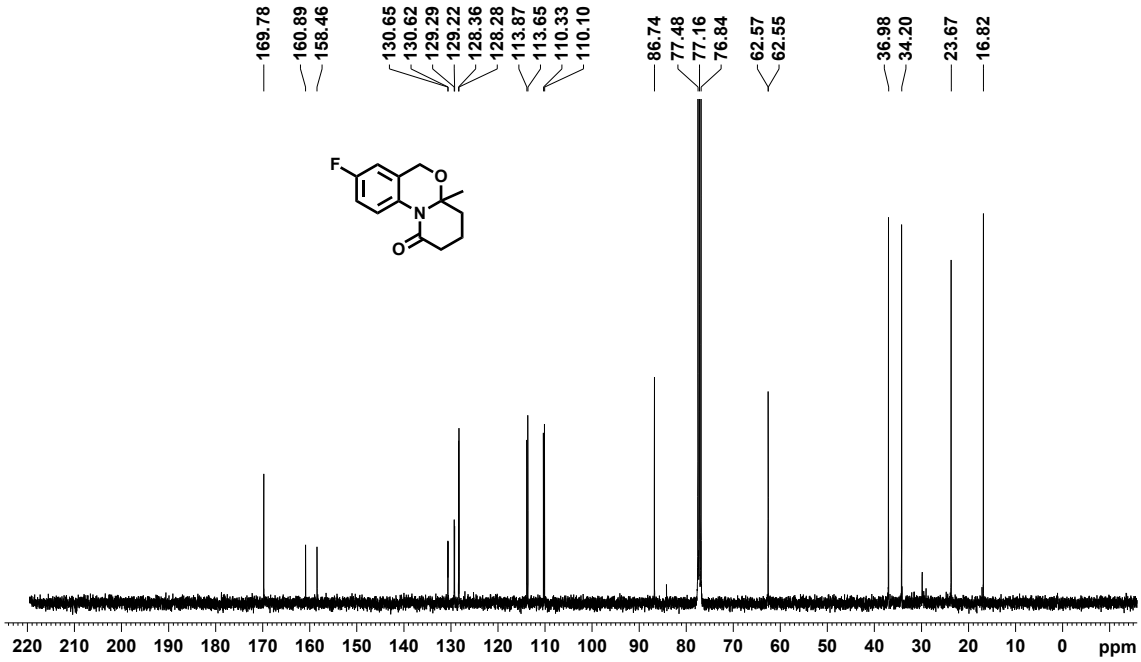


ESI-MSof 4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4l**

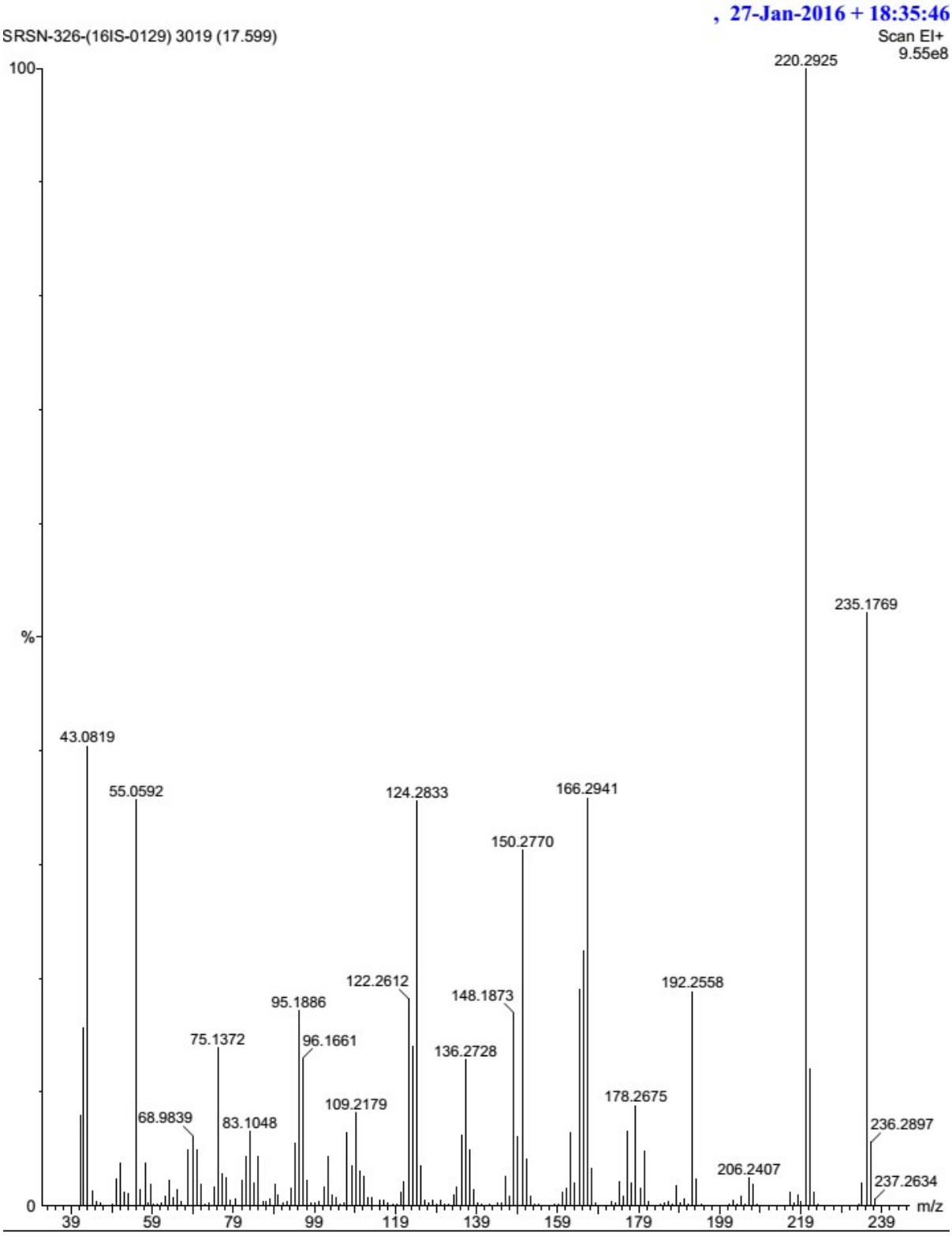


[1]HNMR spectrum of 8-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one4**m**

Signature SIF VIT VELLORE
SRSN-207



^{13}C NMR spectrum of 8-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4m**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Scan EI+
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Qualitative Report

File: C:\TurboMass\2016.PRO\Data\SRSN-326-(16IS-0129).raw
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Printed: 28-Jan-16 04:07 PM
Description:
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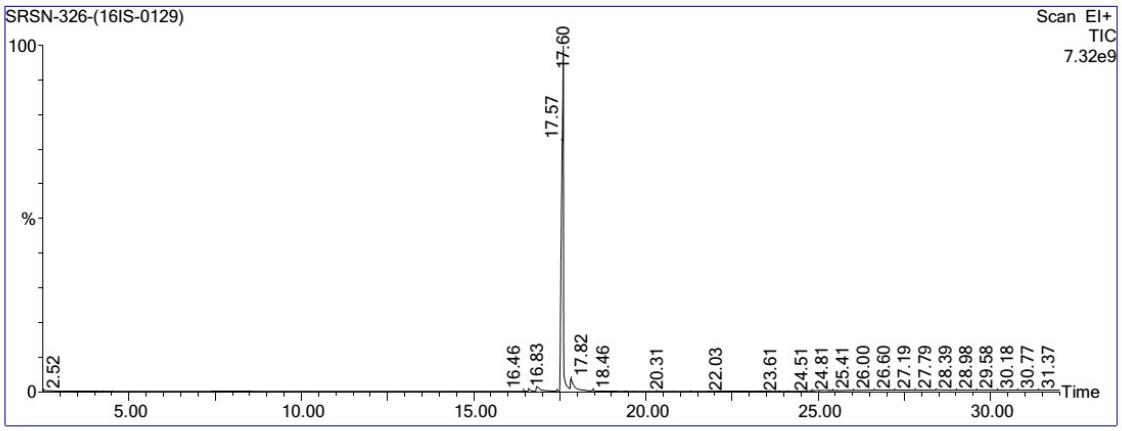
Page 1 of 1
Sample ID: SRSN-326-(16IS-0129)
Vial Number: 7



#	RT	Scan	Height	Area	Area %	Norm %
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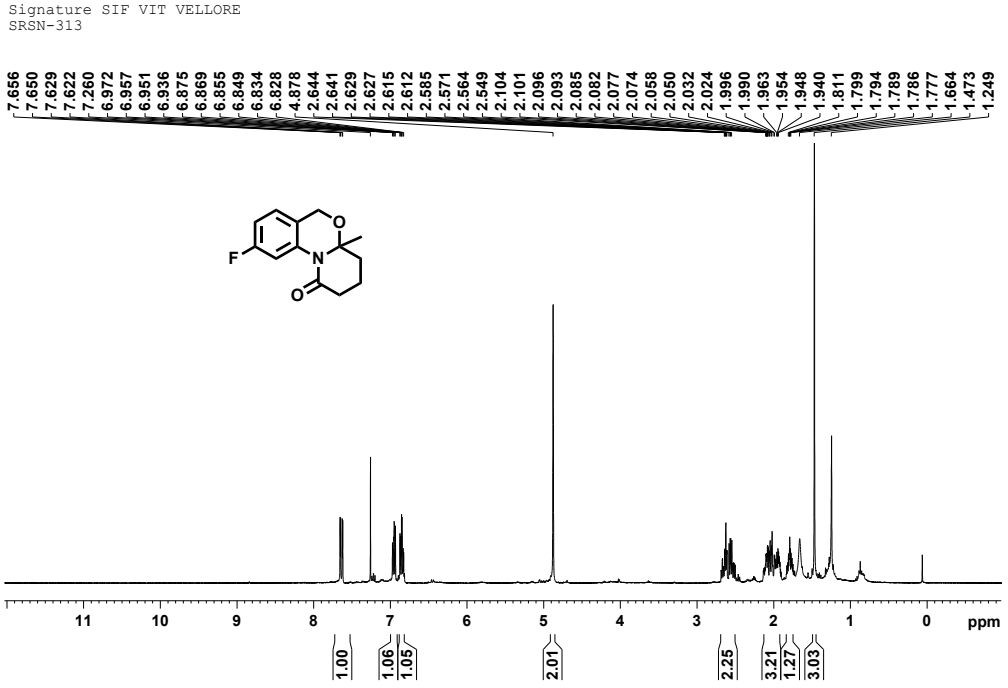
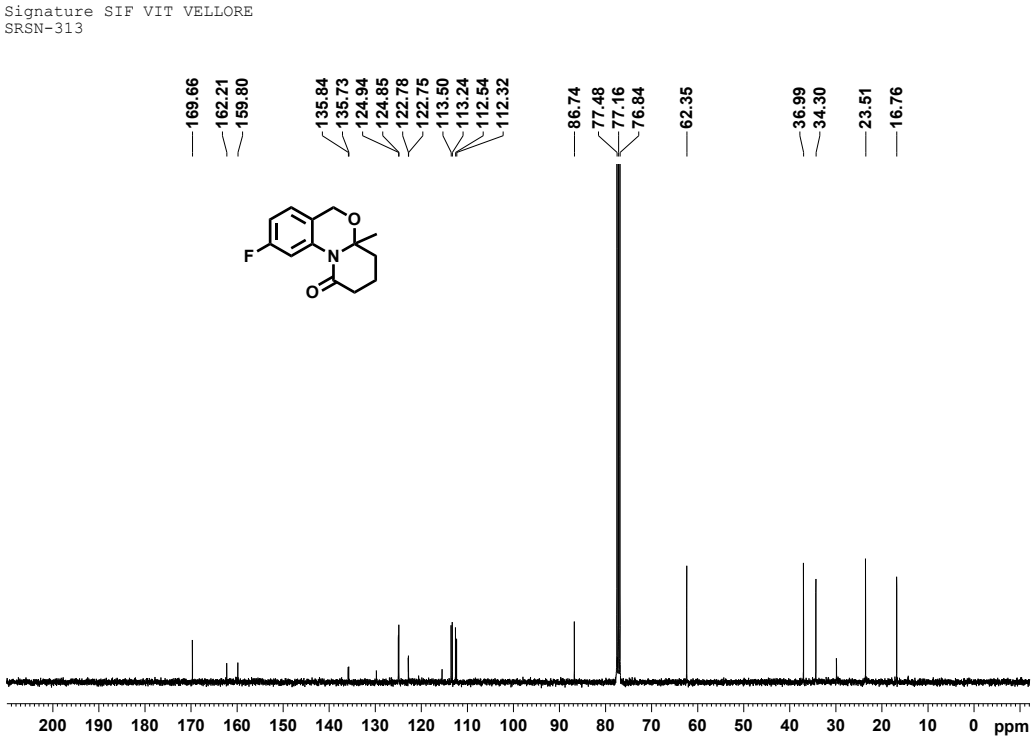
2	17.825	3064	222,234,896	17,438,058.0	3.633	3.77

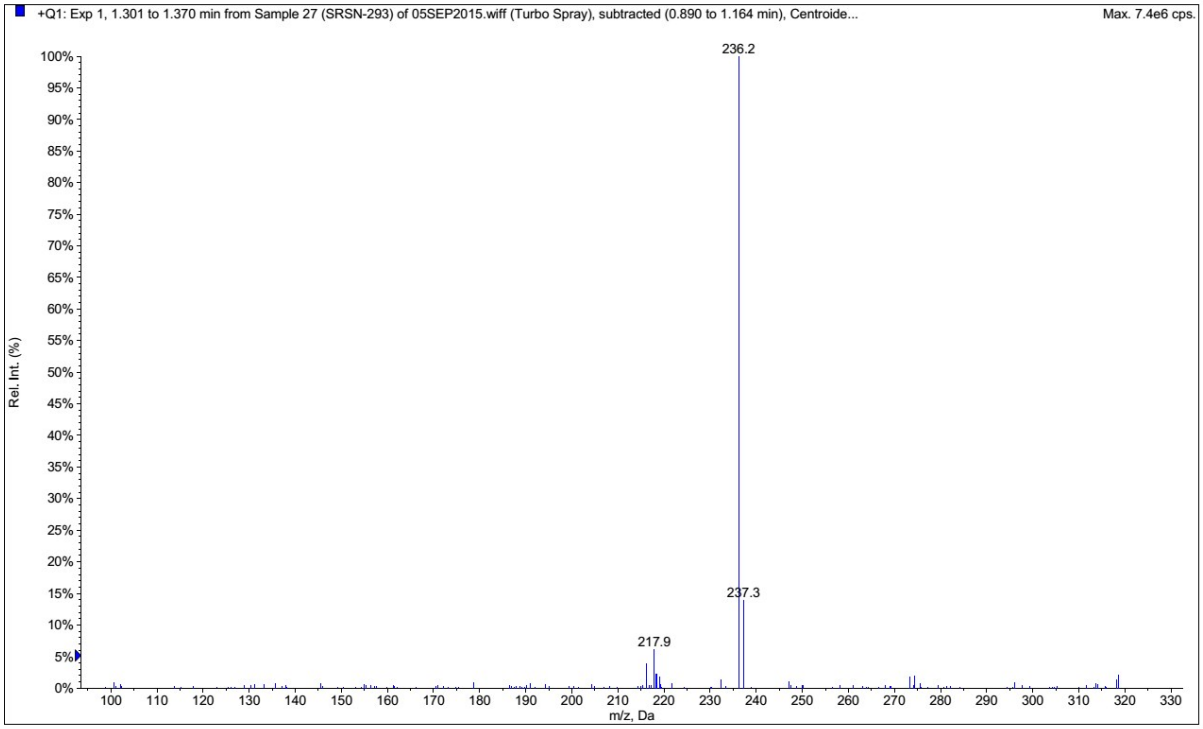
GCMS of 8-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4m**



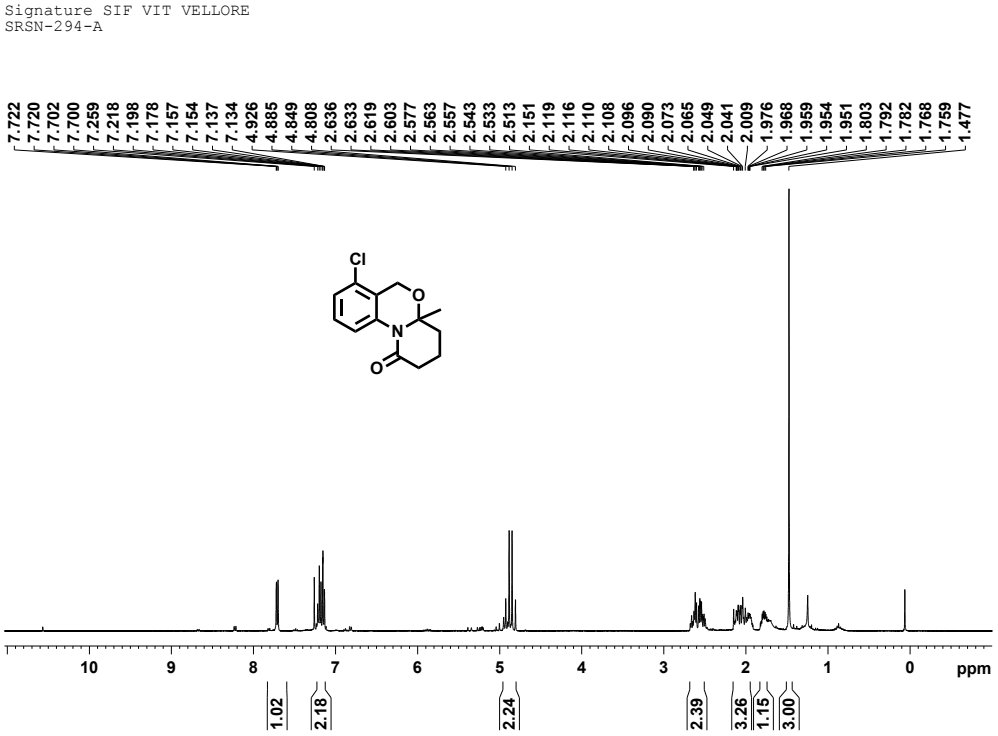
^{1}HNMR spectrum of 9-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4n**



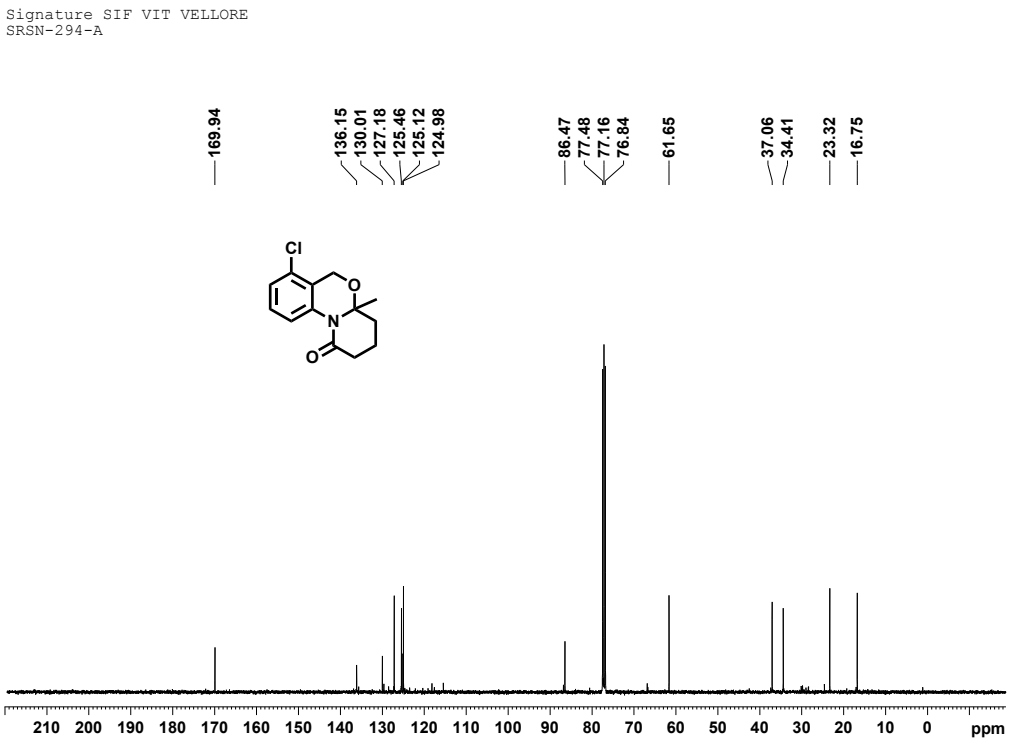
^{13}C NMR spectrum of 9-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4n**



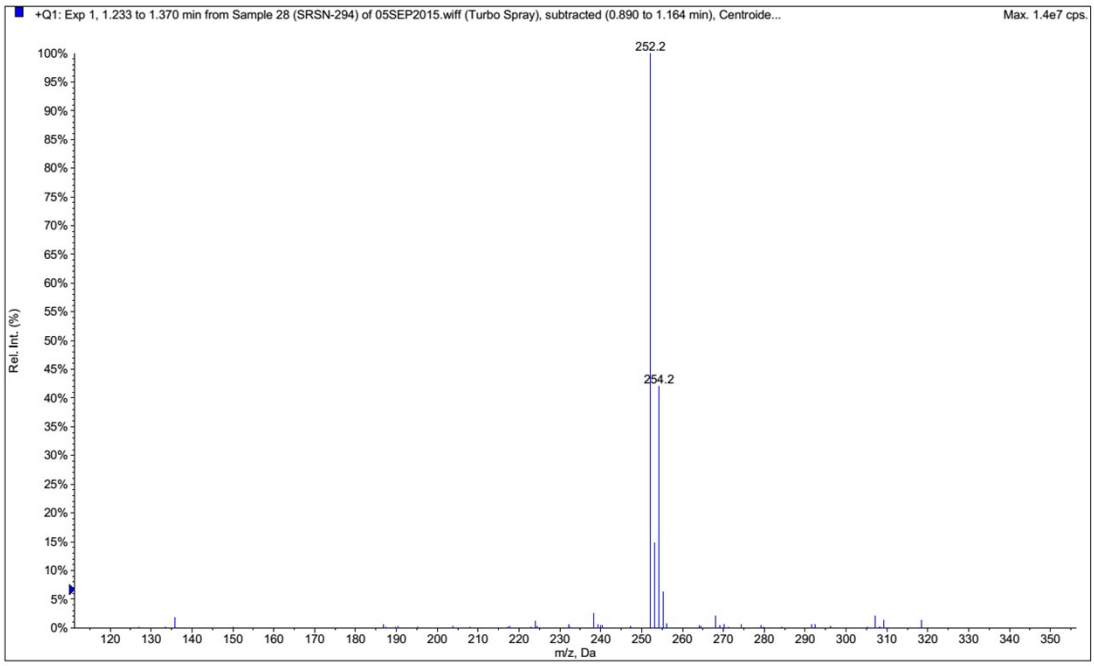
ESI-MS of 9-fluoro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4n**



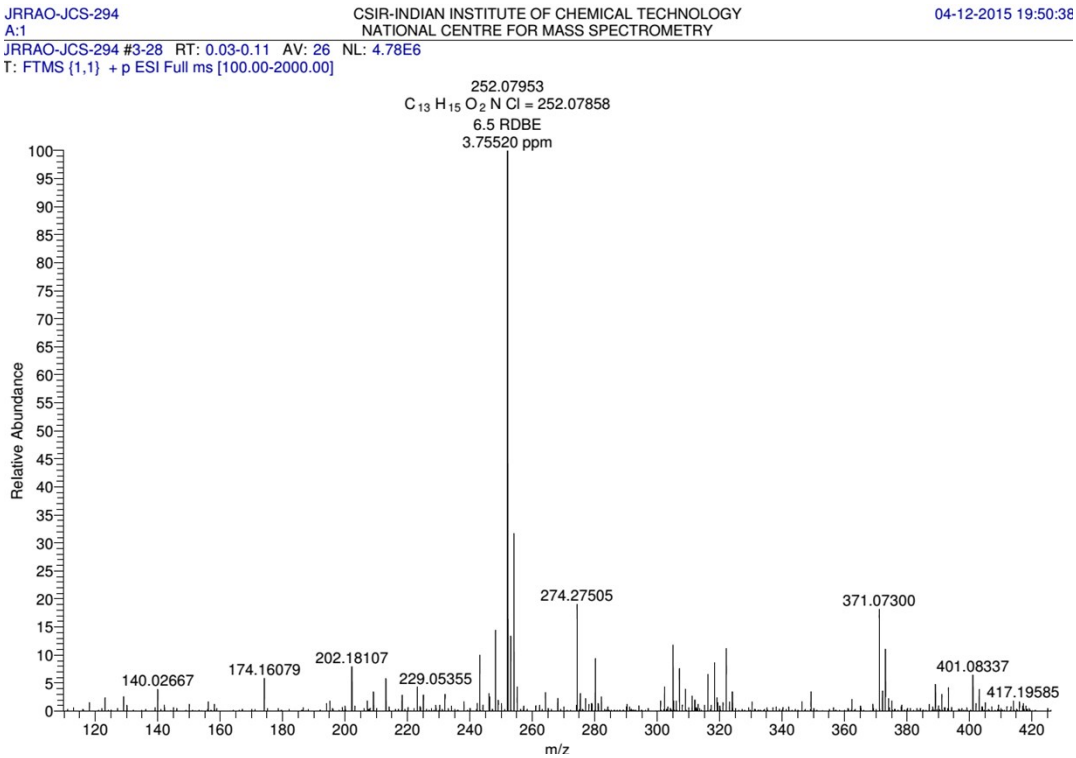
^{1}HNMR spectrum of 7-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4o**



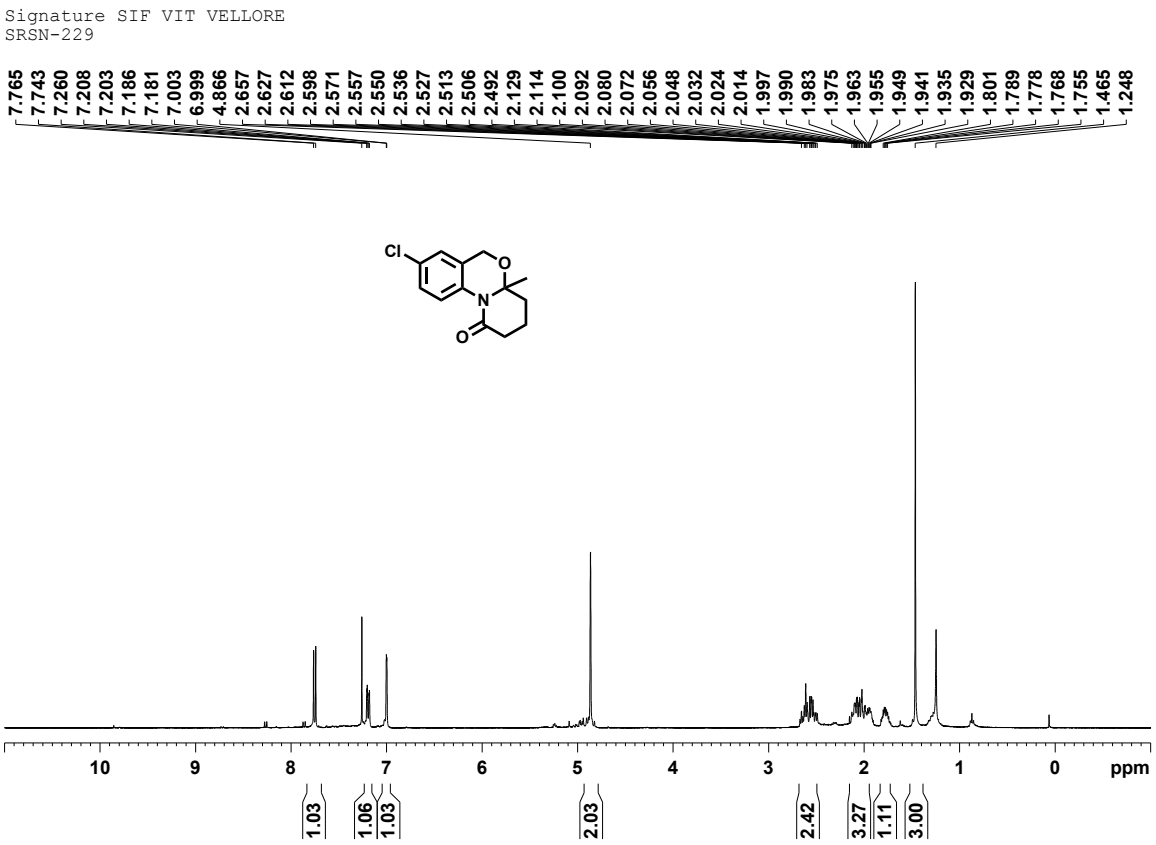
^{13}CNMR spectrum of 7-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4o**



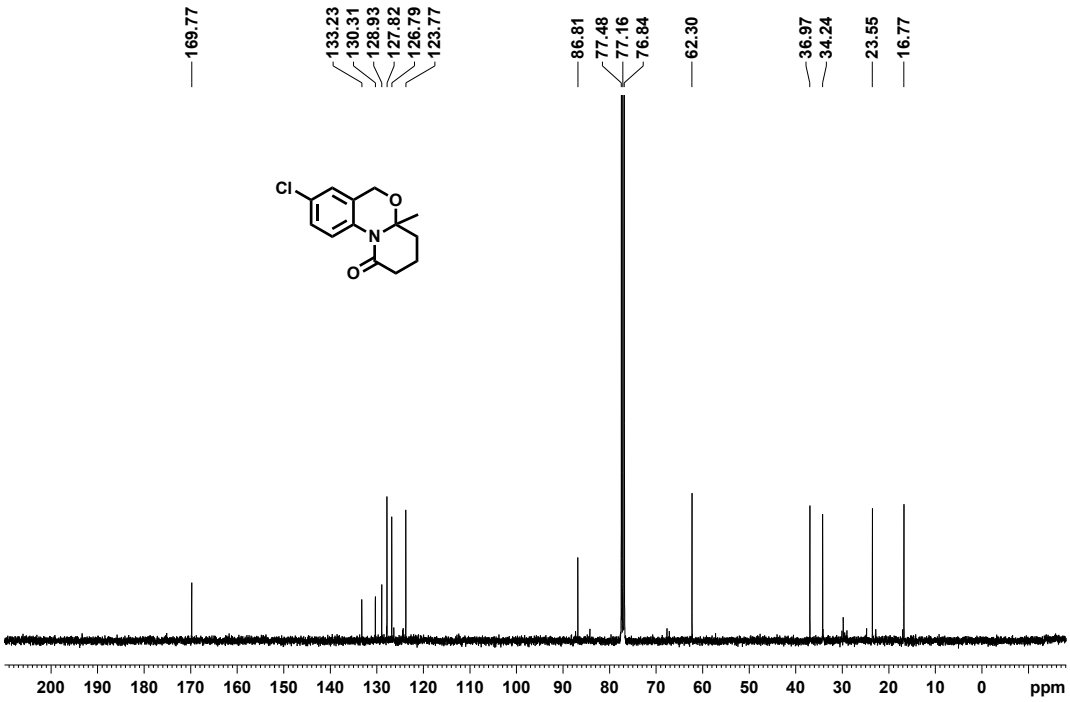
ESI-MSof 7-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4o**



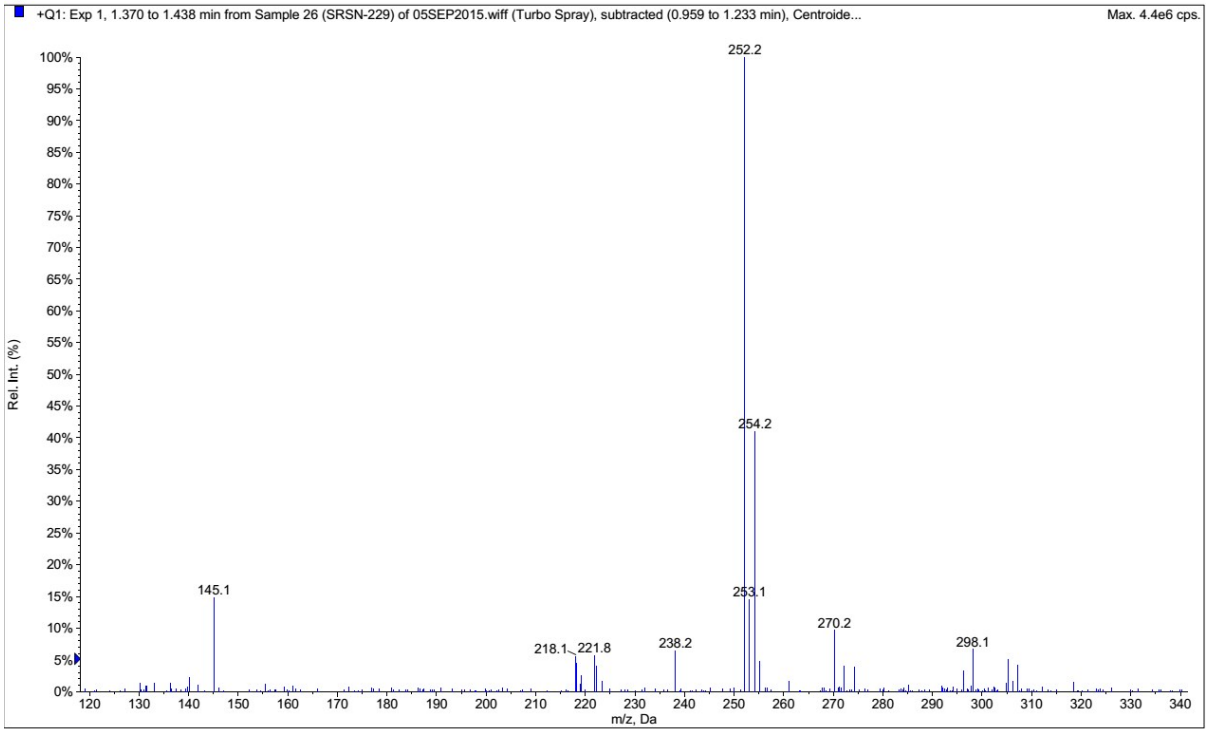
HRMS of 7-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4o**



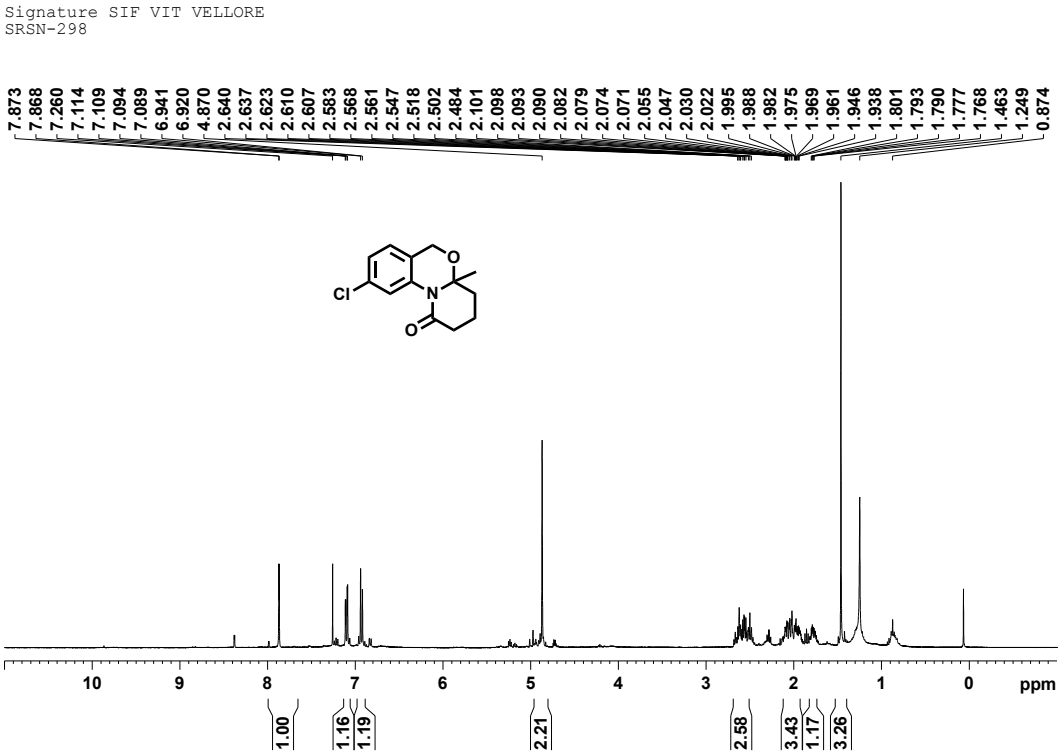
[1]HNMR spectrum of 8-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4p**



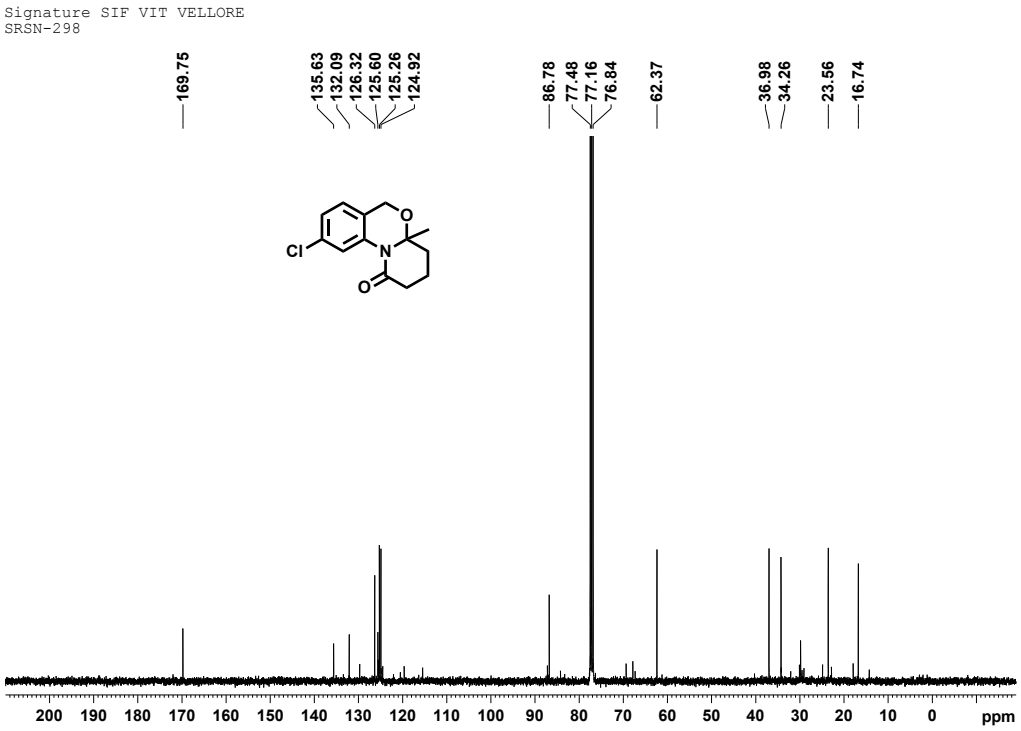
^{13}C NMR spectrum of8-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4p**



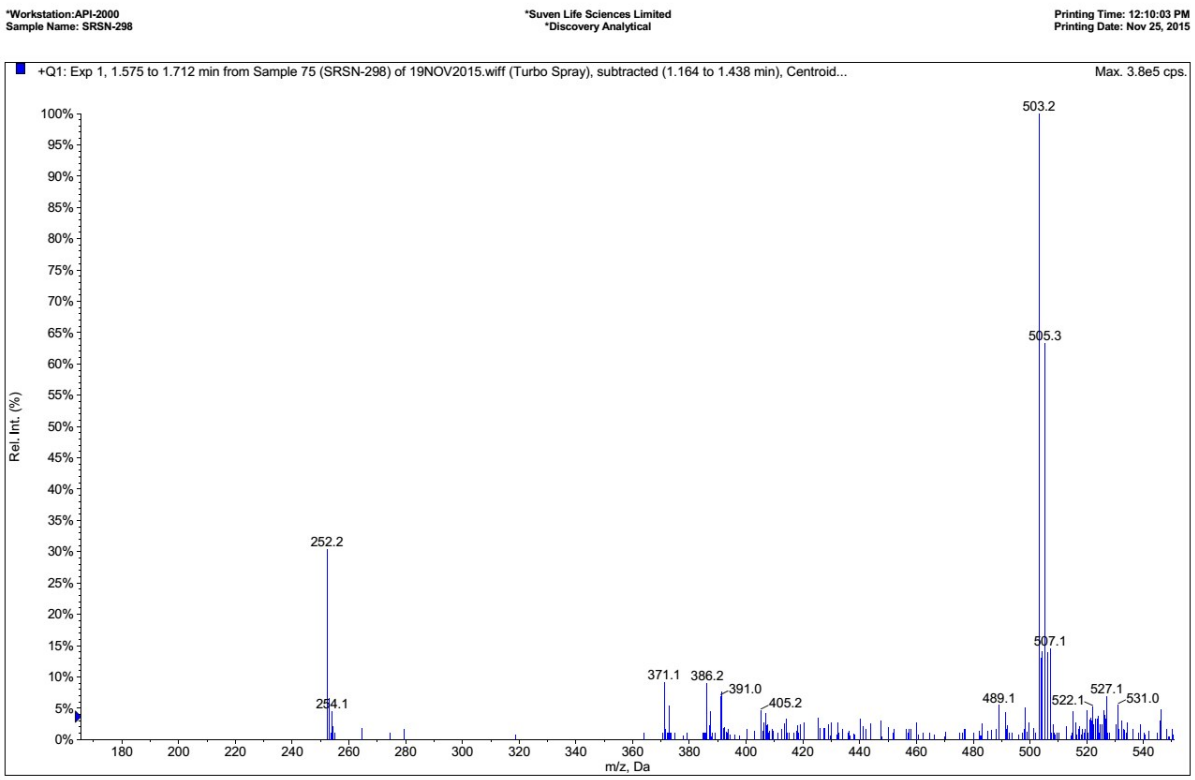
ESI-MS of 8-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4p**



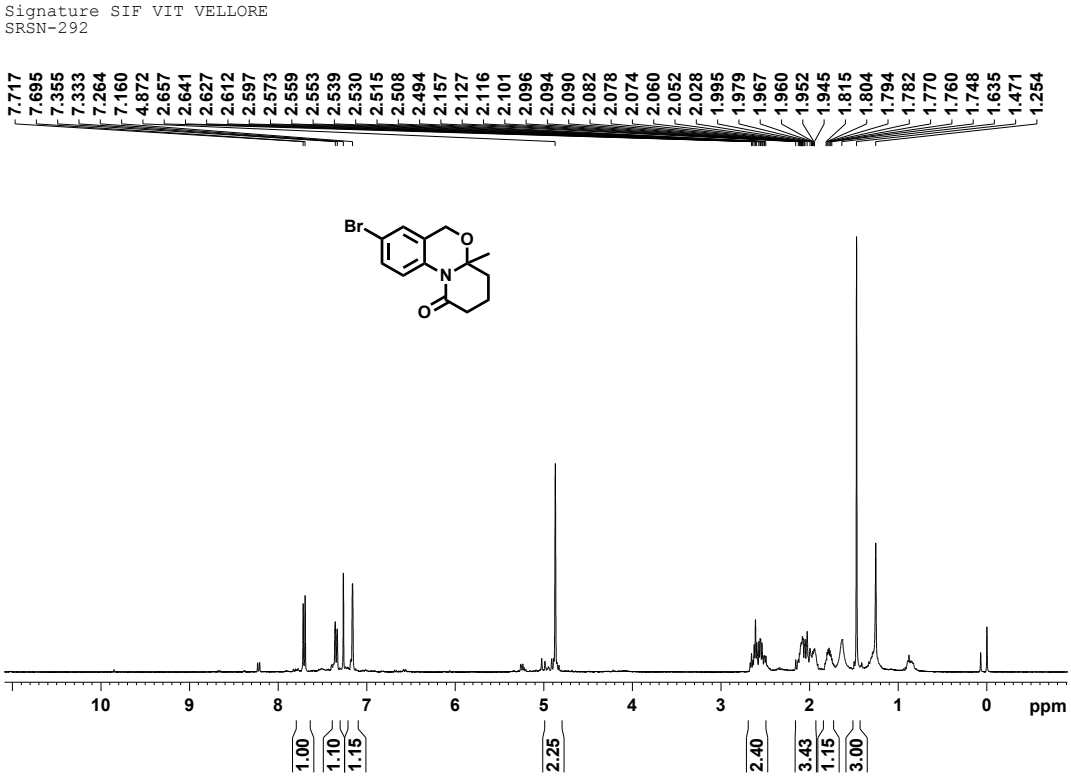
^{1}HNMR spectrum of 9-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4q**



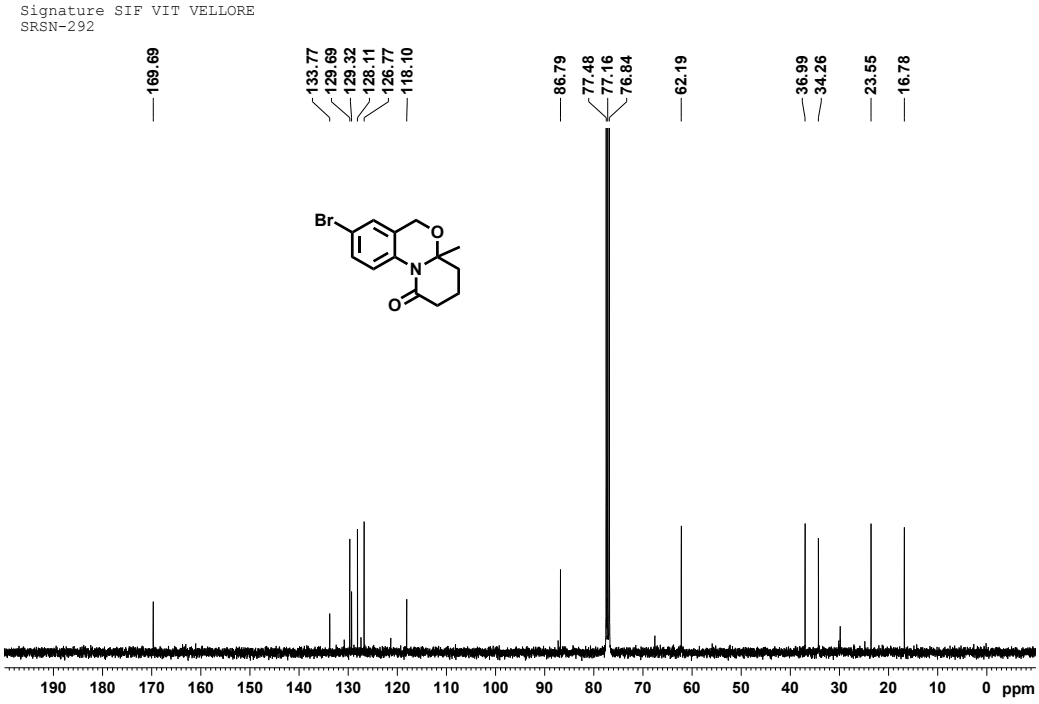
^{13}C spectrum of 9-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4q**



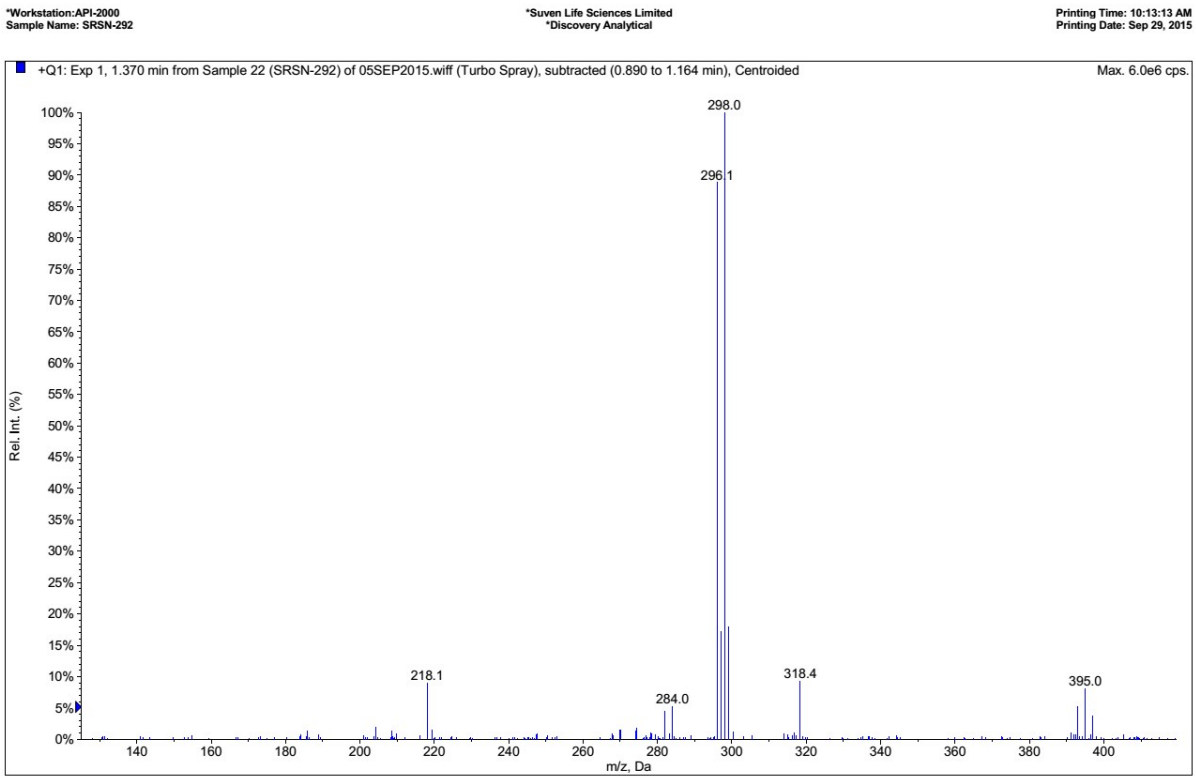
ESI-MS of9-chloro-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4q**



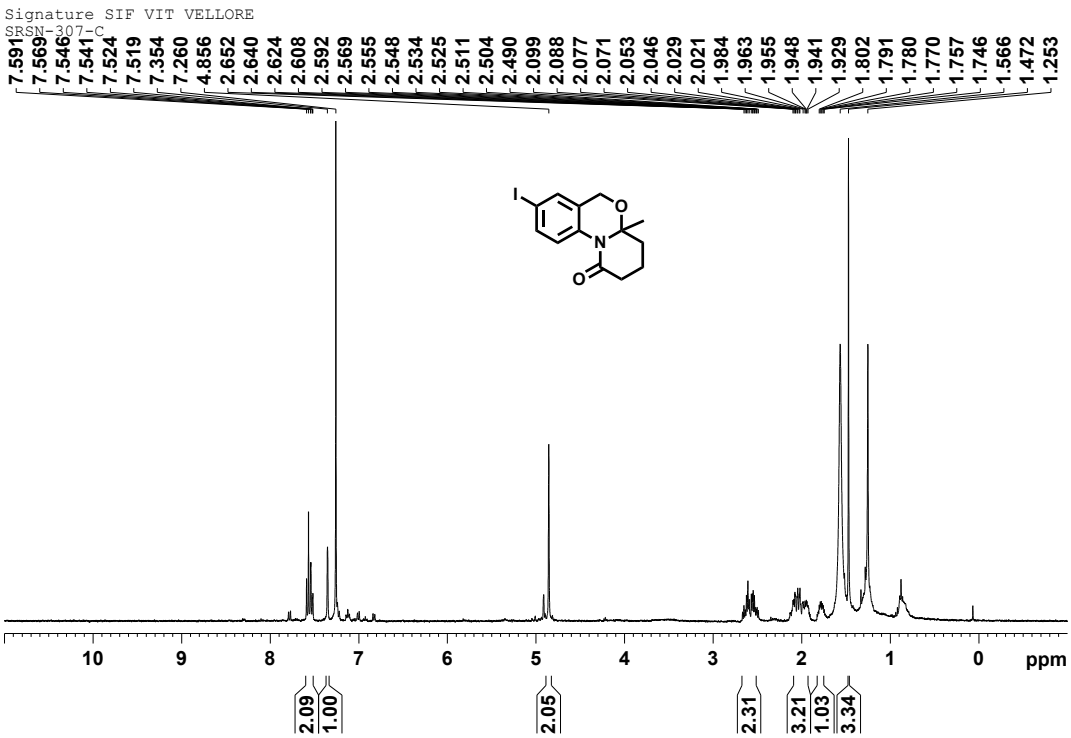
^{1}HNMR spectrum of 8-bromo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4r**



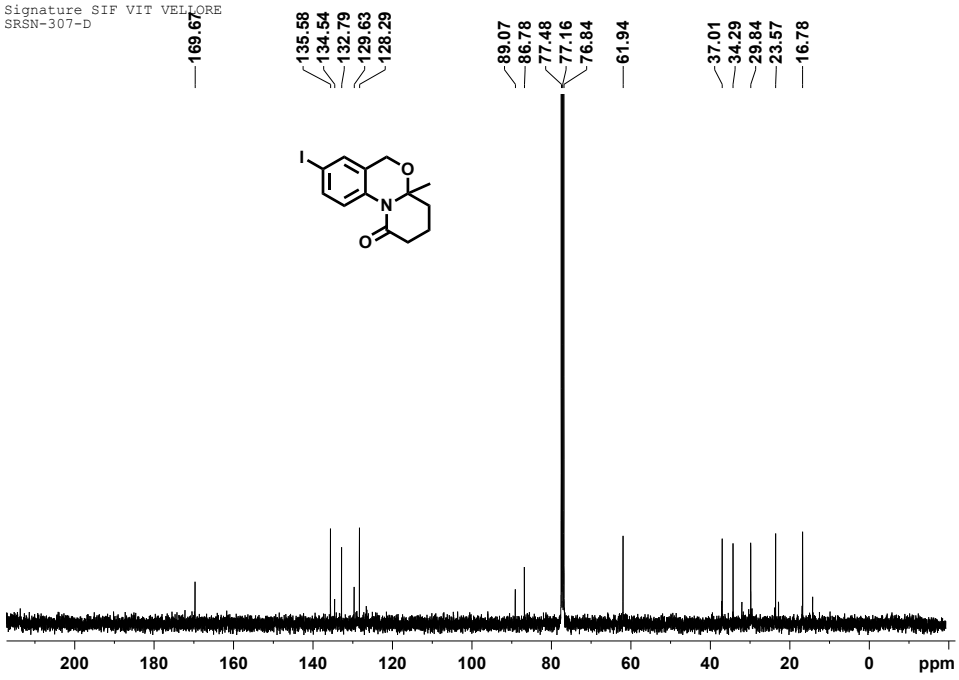
^{13}C NMR spectrum of 8-bromo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4r**



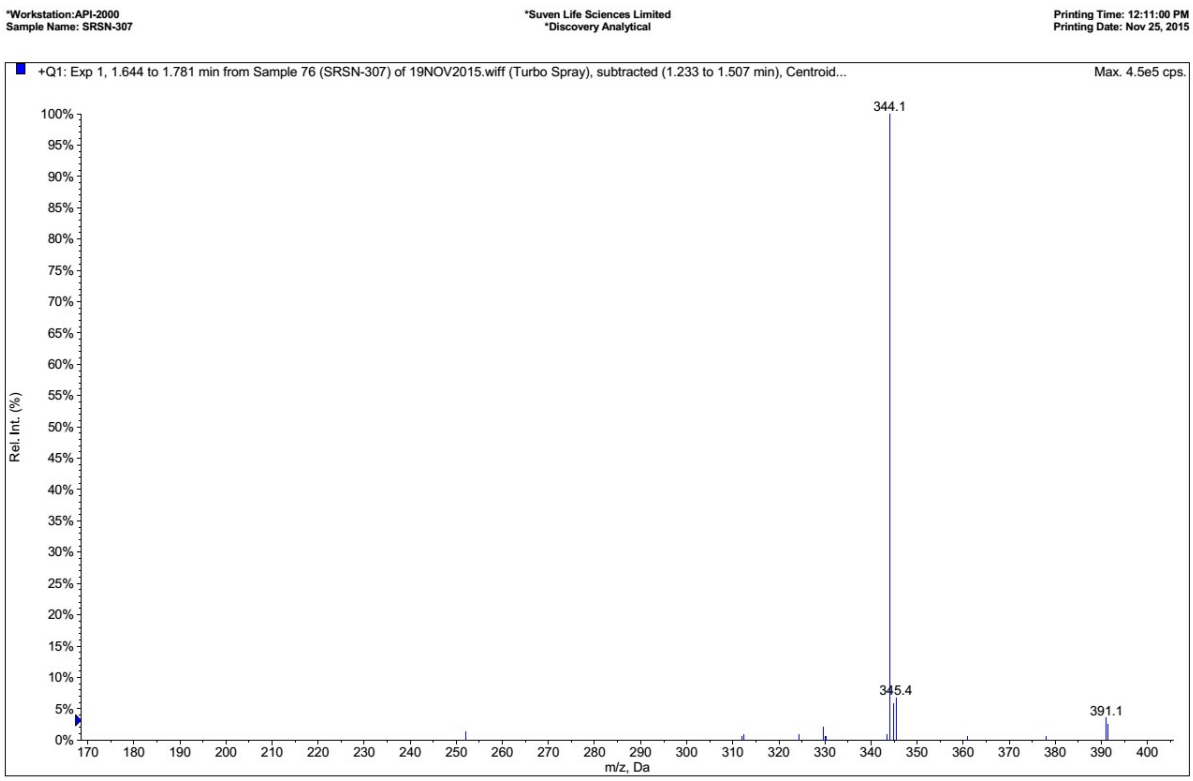
ESI-MS of 8-bromo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4r**



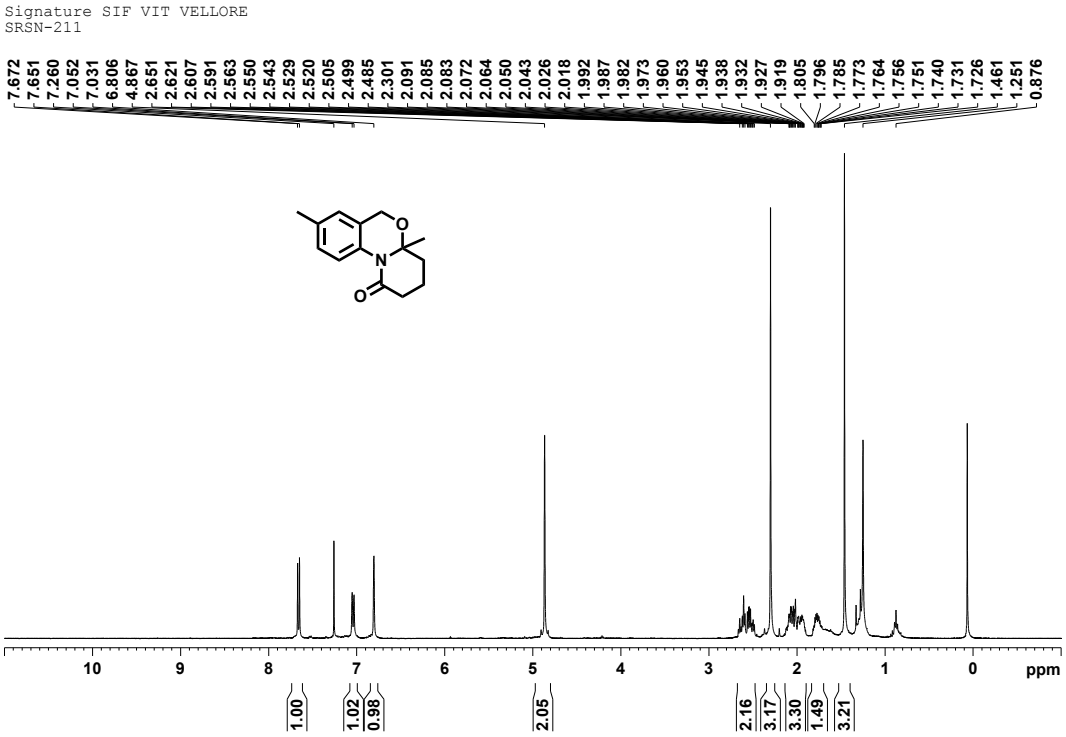
[1] H NMR spectrum 8-iodo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one 4s



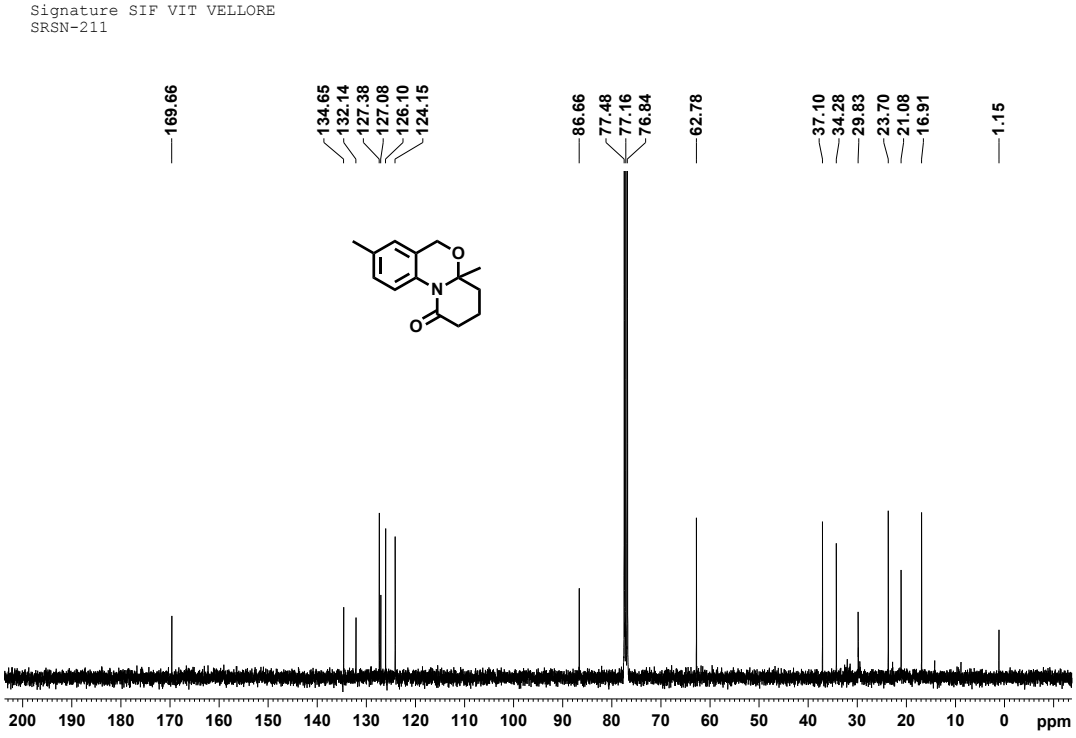
[13]C NMR spectrum 8-iodo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one 4s



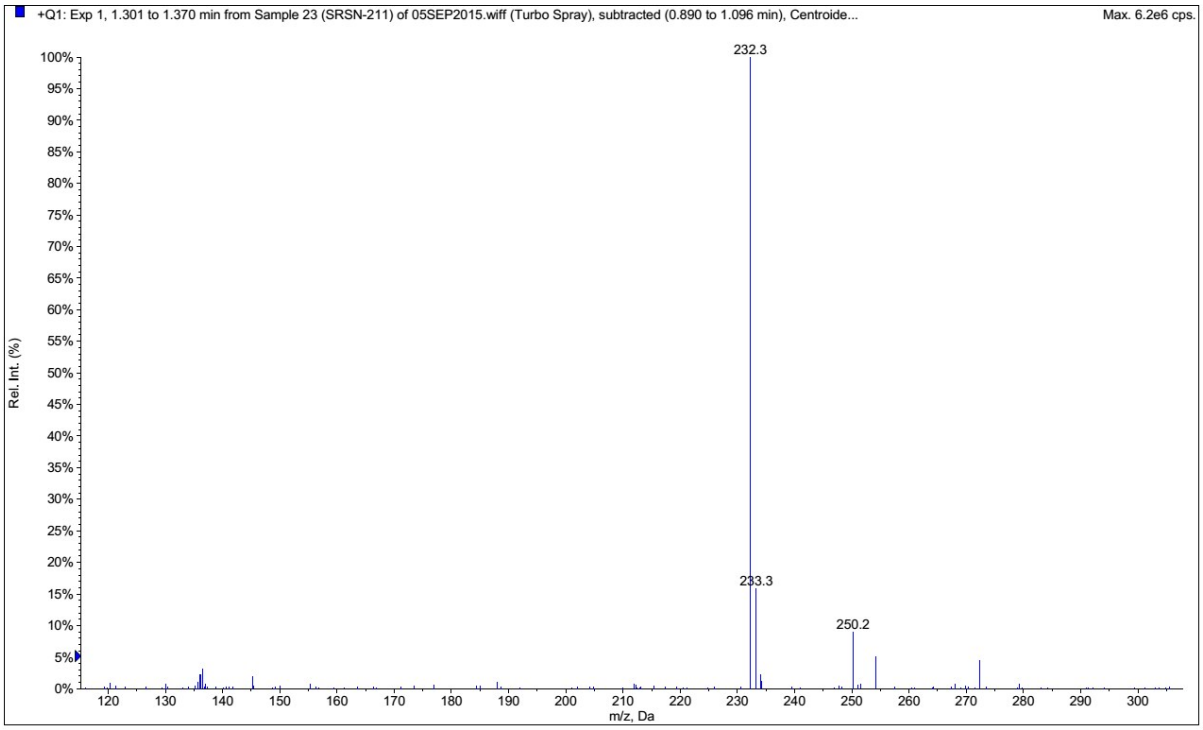
ESI-MS of 8-iodo-4a-methyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one 4s



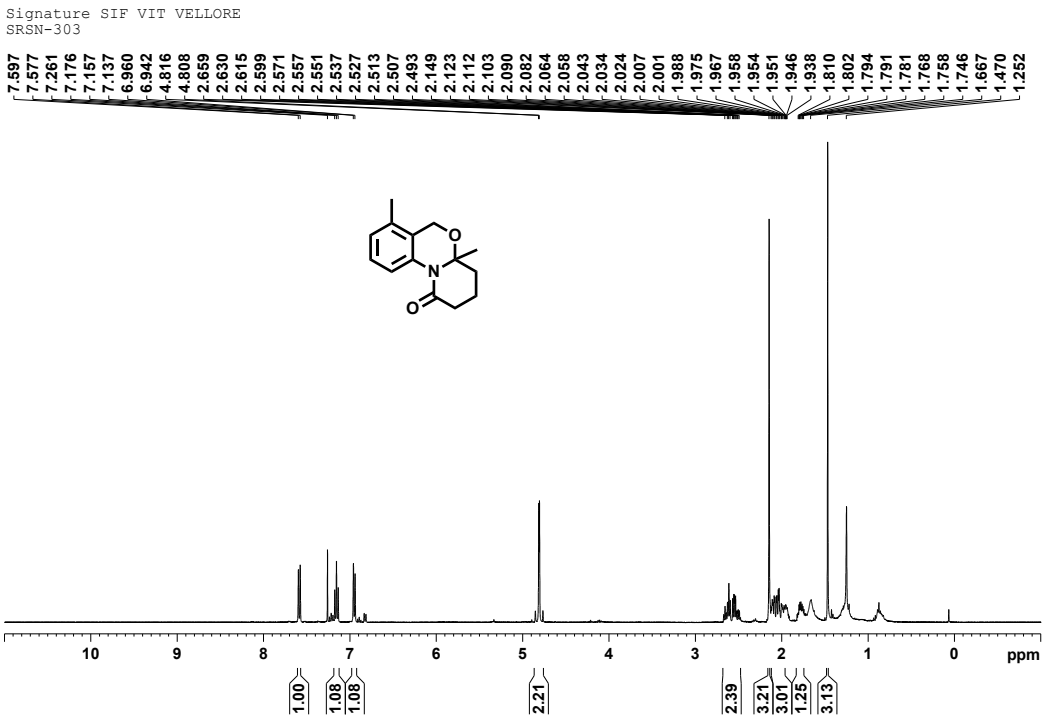
^{1}HNMR spectrum of 4a,8-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4t**



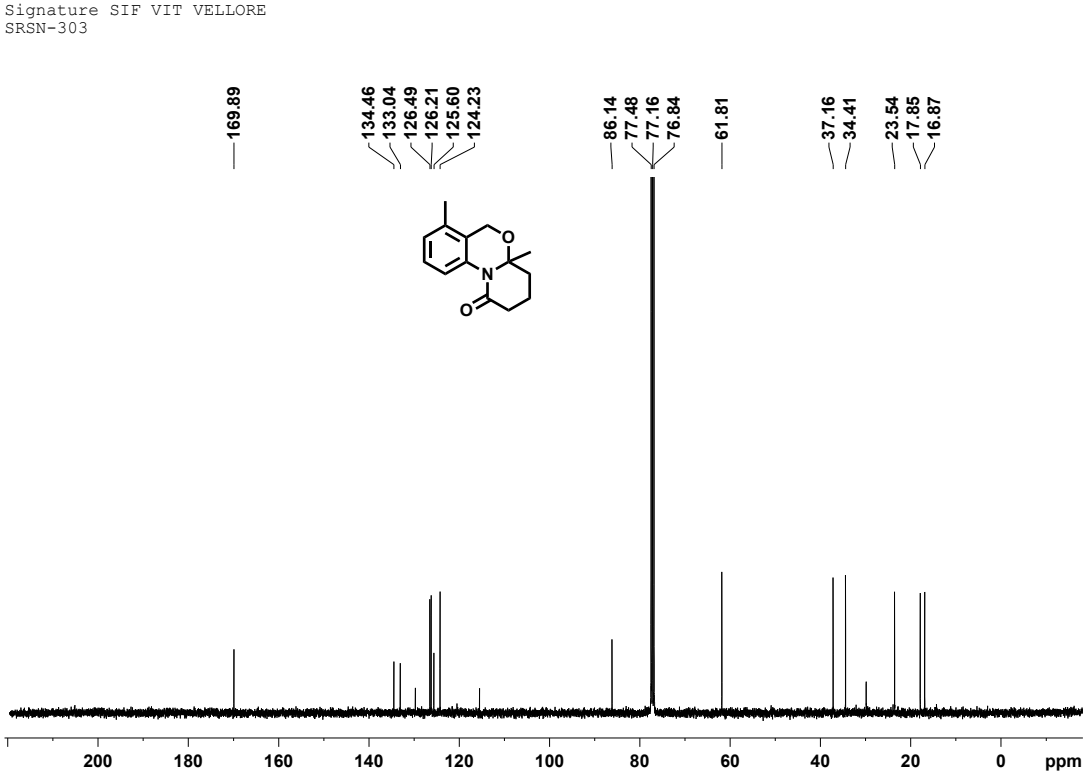
^{13}C NMR spectrum of 4a,8-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4t**



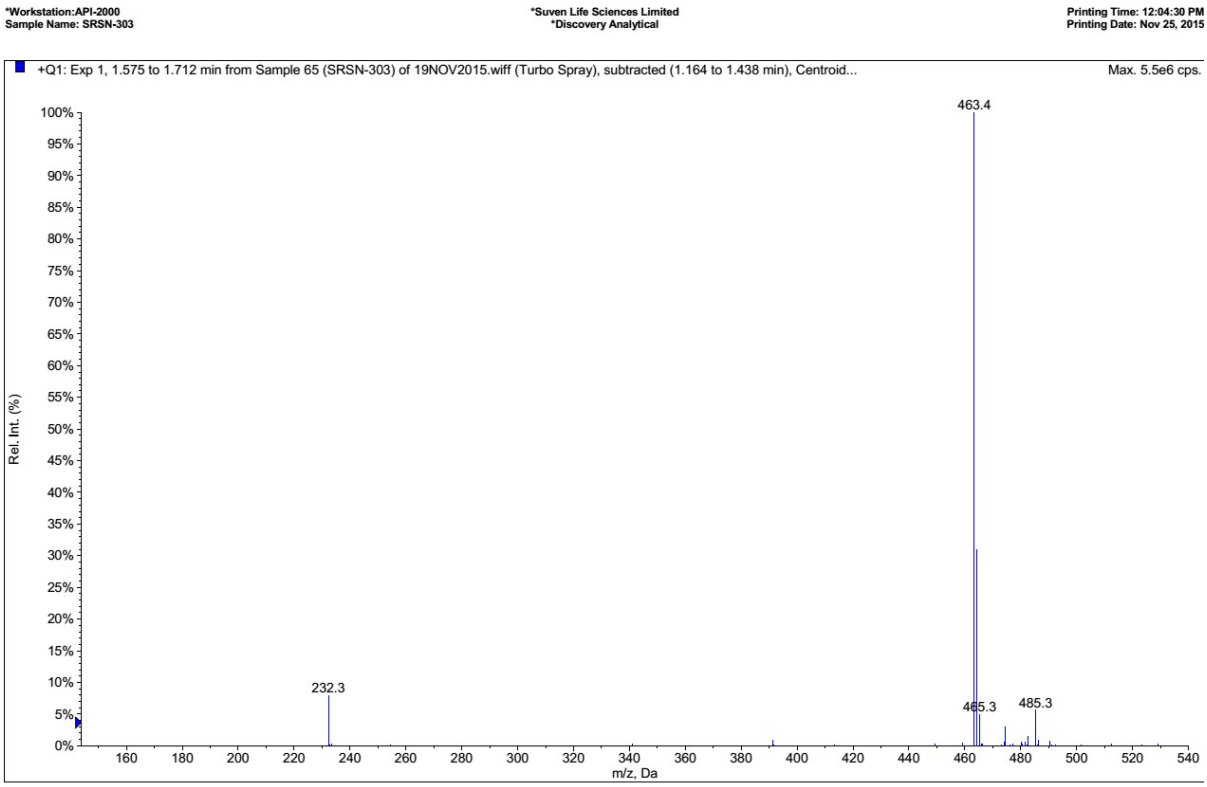
ESI-MS of 4a,8-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4t**



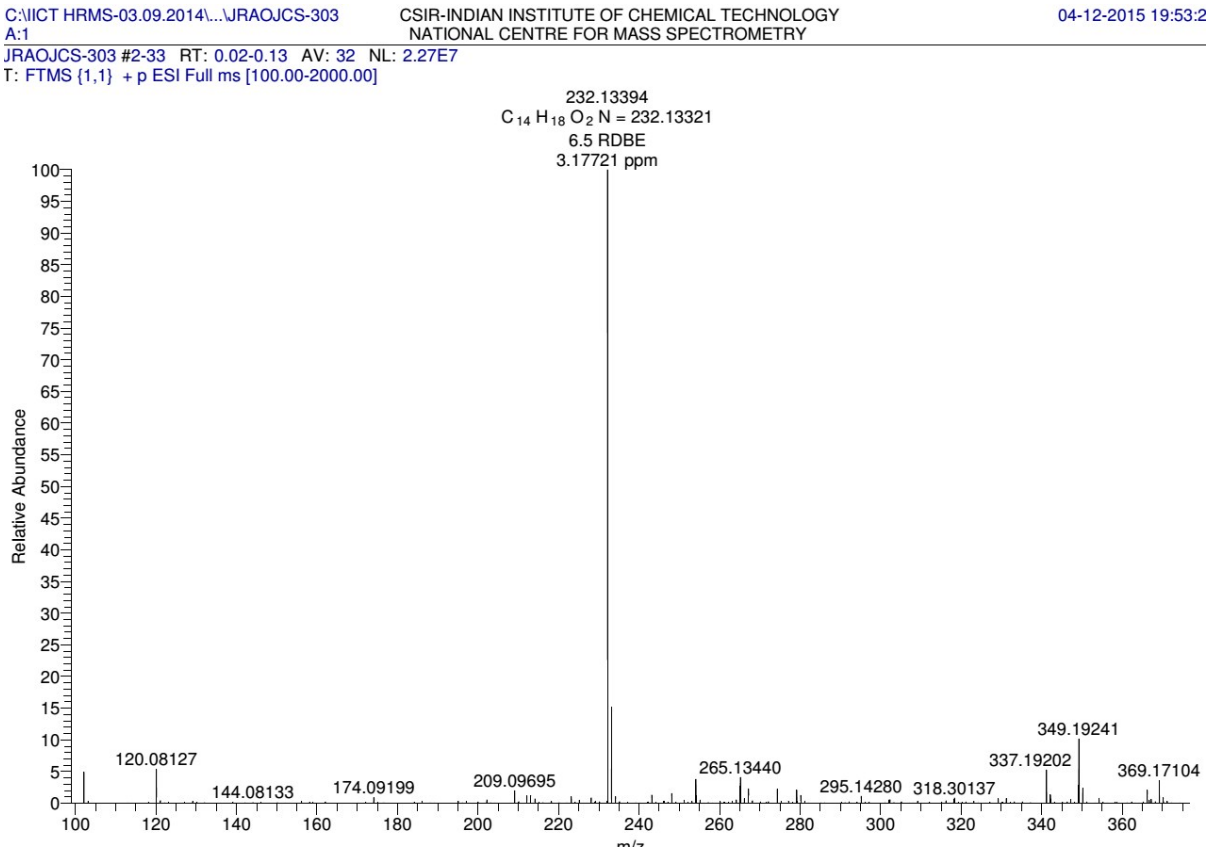
^{1}HNMR spectrum of 4a,7-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4u**



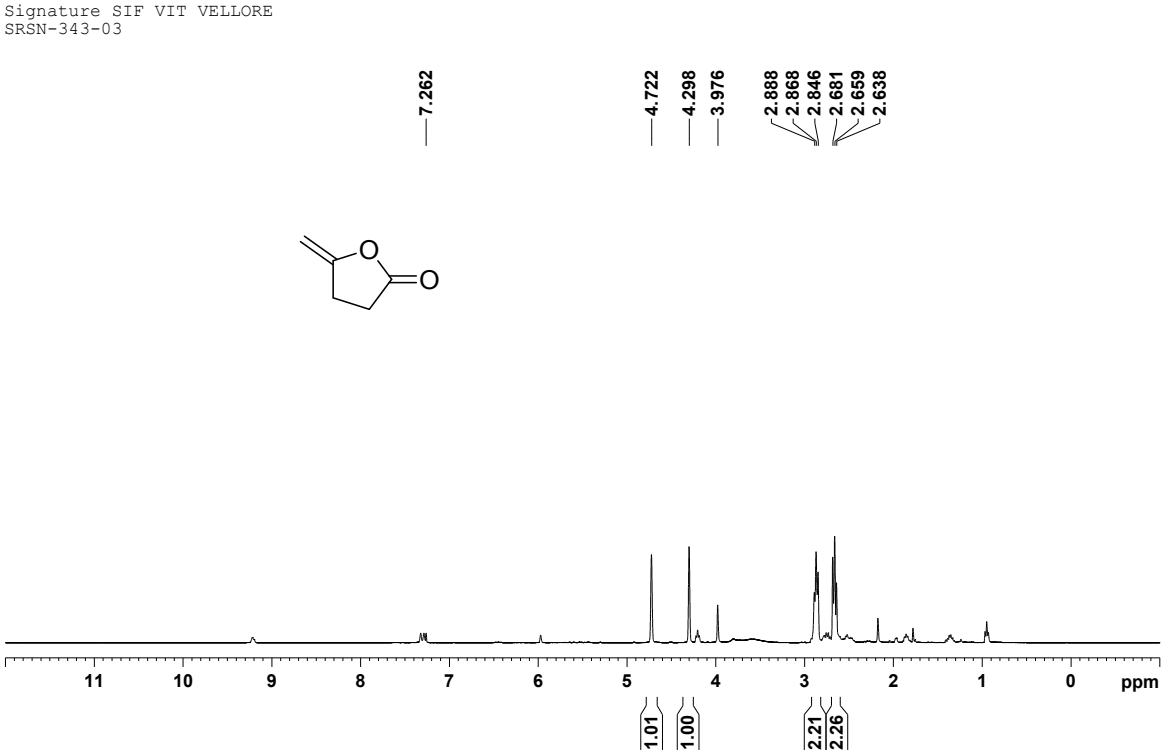
^{13}C NMR spectrum 4a,7-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4u**



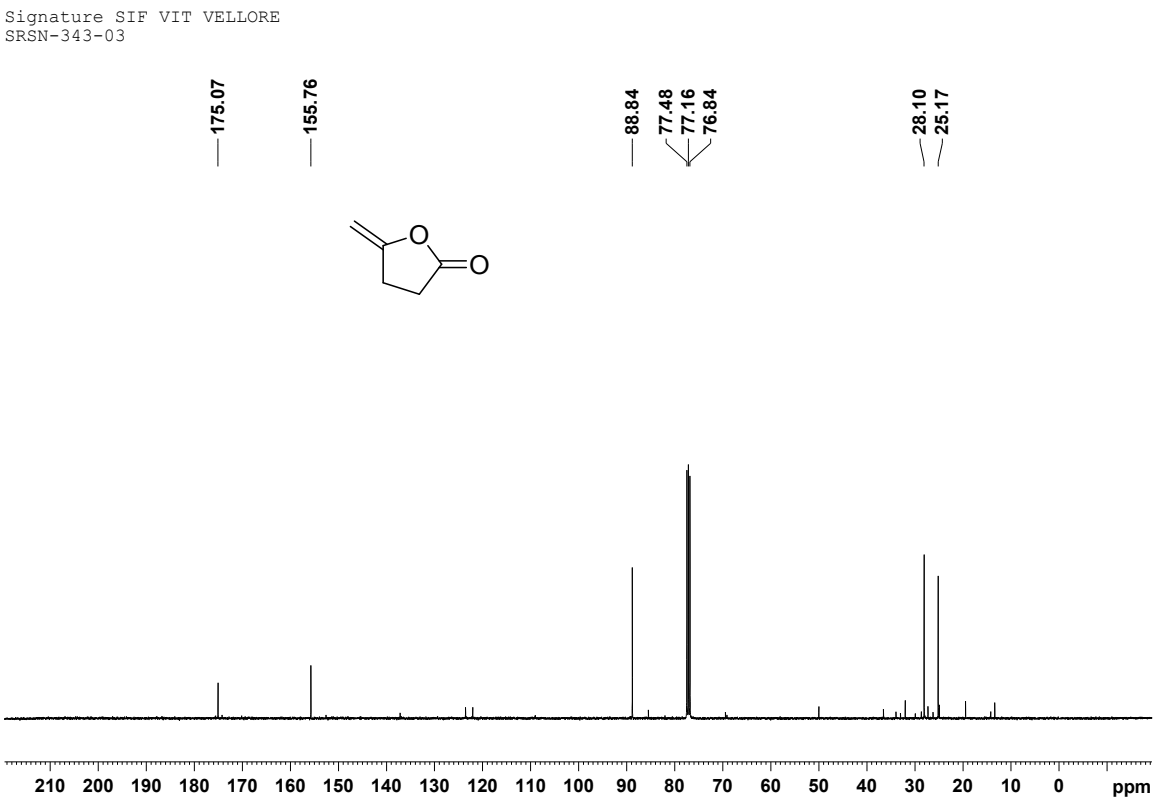
ESI-MS of 4a,7-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one**4u**



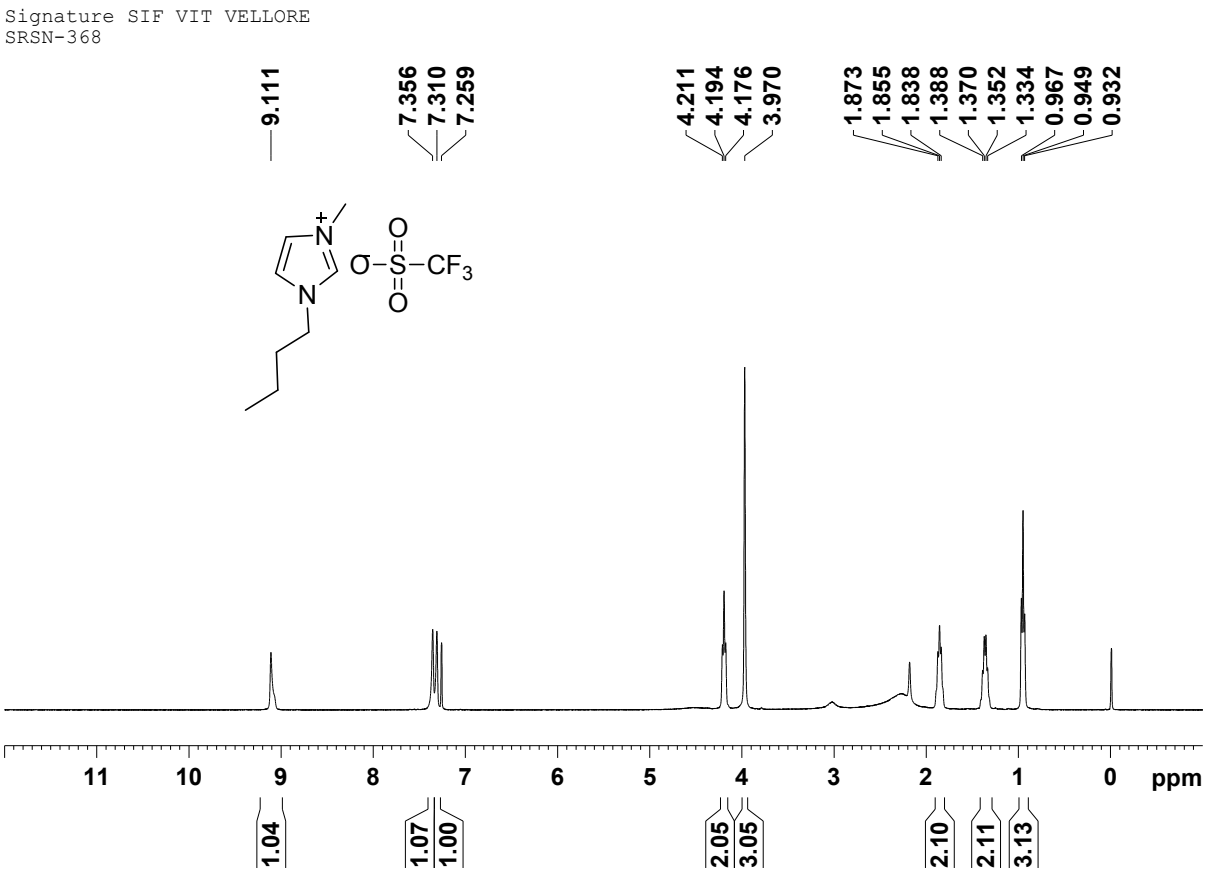
HRMS of 4a,7-dimethyl-2,3,4,4a-tetrahydrobenzo[d]pyrido[2,1-b][1,3]oxazin-1(6H)-one **4u**



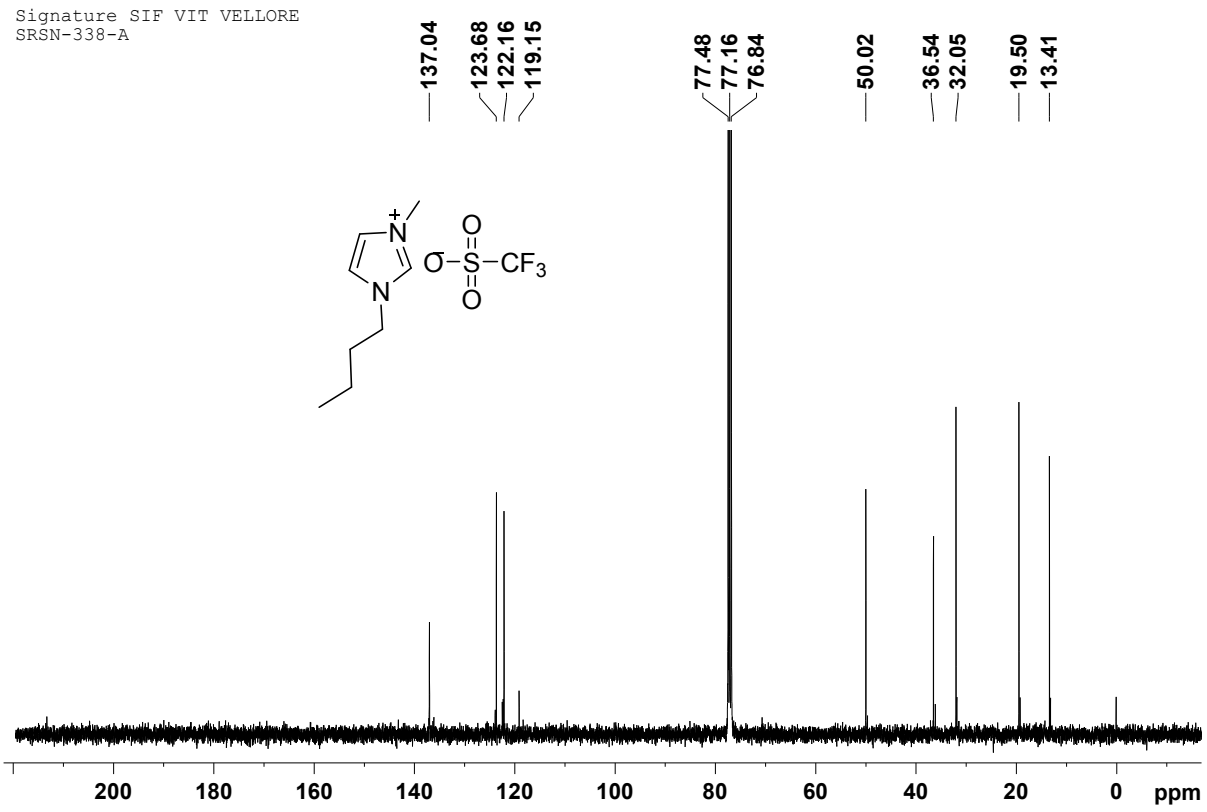
^{1}HNMR spectrum of 5-methylenedihydrofuran-2(3H)-one **II**



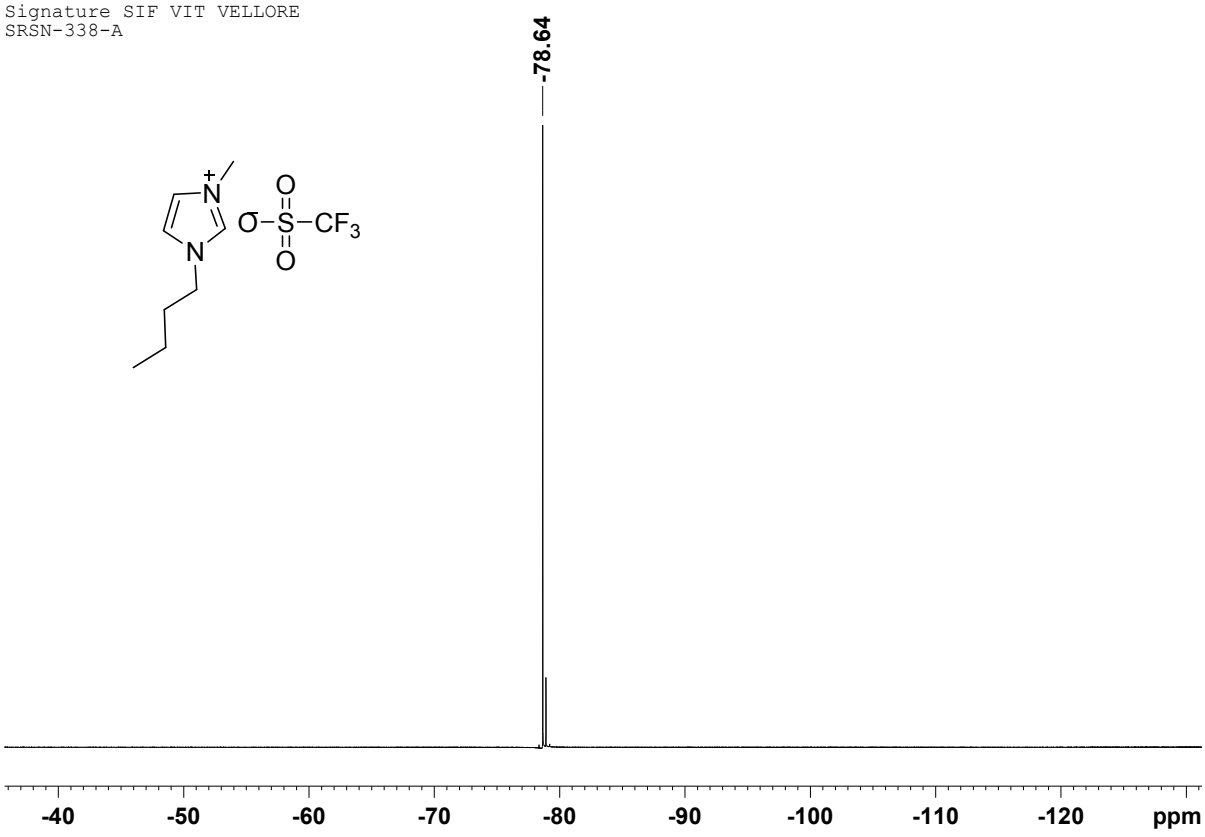
^{13}C NMR spectrum 5-methylenedihydrofuran-2(3H)-one **II**



^{1}HNMR spectrum of [bmim]OTf



^{13}C NMR spectrum of [bmim]OTf



^{19}F-NMR spectrum of [bmim]OTf

1-Butyl-3-methylimidazolium trifluoromethanesulfonate[±]

Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 7.35 (s, 1H), 7.31 (s, 1H), 4.21 (t, J= 7 Hz, 2H), 3.96(s , 3H), 1.87-1.83 (m,2H), 1.38-1.33 (m, 2H), 0.96 (s, J= 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 123.7, 122.2, 119.2, 50.0, 36.5, 32.0, 19.5, 13.4. ^{19}F-NMR (376.5 MHz, $CDCl_3$)): δ -78.6.

References

[±]P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.