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A multicomponent, facile and catalyst-free microwave-assisted protocol for the synthesis of pyrazolo[3,4-*b*]-quinolines under green conditions

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Materials and instruments

All reagents and chemicals were of analytical grade, purchased from Sigma-Aldrich and used without further purification. MW-assisted reaction was carried out in a CEM-908010, 300-W bench mate model laboratory MW reactor at room temperature. The MW power was set to 100 W for the reaction at 80 °C with high stirring. Progress of the reaction was monitored by thin layer chromatography (TLC) coated with silica gel 60 F254. High-resolution mass data were obtained using a Bruker micro TOF-Q II ESI instrument operating at ambient temperature. A Bruker AMX 400 MHz NMR spectrometer was used to record the ^{1}H-NMR, ^{15}N-NMR, ^{13}C-NMR spectral values of the products in DMSO-d_6. TMS served as internal standard for reporting the chemical shifts in d (ppm).

Products characterization data:

4-(2,3-Dihydroxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4a): 94% Yield, White solid (282.56 mg); m.p. 119–121 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.89 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.89 (d, *J* = 5.12 Hz, 1H, CH), 2.05 (d, *J* = 16.36 Hz, 1H, CH), 2.22 (d, *J* = 16.24 Hz, 1H, CH), 2.63 (d, *J* = 5.28 Hz, 1H, CH), 5.25 (s, 1H, CH), 6.27 – 6.29 (m, 1H, CH), 6.50 (t, *J* = 3.28 2H, ArH), 7.37 – 7.39 (m, 1H, ArH), 7.52 (t, *J* = 1.72 Hz, 4H, ArH), 8.94 (s, 2H, OH), 9.59 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6):11.69, 26.60, 28.19, 28.64, 31.91, 40.74, 50.09, 104.43, 109.53, 112.66, 119.27, 119.33, 123.12, 126.77, 129.31, 134.78, 136.44, 138.13, 141.28, 145.48, 145.98, 153.13, 195.65; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.59 (s, 1H, NH); HRMS of $[C_{25}H_{25}N_3O_3 + Na]^+$ (m/z): 438.1734; Calcd.: 438.1794.

4-(2-(Trifluoromethyl)phenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo [3,4-b]quinolin-5(4H)-one (4b): 93% Yield, Light yellow solid (240.98 mg); m.p. 136–137 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.91 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.93 (d, *J* = 16.04 Hz, 1H, CH), 2.14 (d, *J* = 16.04 Hz, 1H, CH), 2.51 (d, *J* = 8.24 Hz, 2H, CH_2), 5.44 (s, 1H, CH), 7.27 – 7.39 (m, 4H, ArH), 7.40 – 7.53 (m, 5H, ArH), 9.44 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 12.24, 26.69, 28.66, 31.86, 32.08, 40.67, 50.38, 103.25, 109.67, 120.56, 123.38, 123.80, 126.05, 126.69, 127.00, 128.73, 129.32, 132.00, 132.23, 136.44, 137.92, 145.79, 151.55, 193.59; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.44 (s, 1H, NH); HRMS of $[C_{26}H_{24}F_3N_3O + Na]^+$ (m/z): 474.1776; Calcd.: 474.1769.

4-(2-Fluorophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4c): 94% Yield, Creamy solid (303.85 mg); m.p. 183–184 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.00 (s, 3H, CH_3), 107 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 2.04 (d, *J* = 16.08 Hz, 1H, CH), 2.22 (d, *J* = 16.08 Hz, 1H, CH), 2.57 (d, *J* = 7.8 Hz, 2H, CH_2), 5.31 (s, 1H, CH), 7.10 – 7.13 (m, 2H, ArH), 7.19 – 7.27 (m, 2H, ArH), 7.42 – 7.46 (m, 1H, ArH), 7.54 – 7.60 (m, 4H, ArH), 9.52 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 11.58, 26.58, 28.87, 31.92 ,38.84, 40.09, 50.29, 102.97, 108.14, 123.12, 124.15, 126.85, 129.35, 130.10, 136.35, 138.03, 145.80, 152.12, 193.82; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.52 (s, 1H, NH); HRMS of $[C_{25}H_{24}FN_3O + Na]^+$ (m/z): 424.1807; Calcd.: 424.1801.

4-o-Tolyl-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4d): 98% Yield, Creamy solid (323.98 mg); m.p. 200–201 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.90 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.70 (s, 1H, CH), 1.79 (s, 3H, CH_3), 1.93 (t, *J* = 16.24 Hz, 2H, CH_2), 2.14 (d, *J* = 16.12 Hz, 1H, CH), 2.59 (s, 3H, CH_3), 5.12 (s, 1H, CH), 6.94 – 6.97 (m, 1H, ArH), 7.02 (s, 3H, ArH), 7.36 – 7.40 (m, 1H, ArH), 7.51 (t, *J* = 2.44 Hz, 4H, ArH), 9.36 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 11.96, 19.35, 26.61, 28.81, 31.93, 40.64, 50.39, 104.64, 110.46, 120.48, 123.02, 125.21, 125.91, 126.73, 128.93, 129.16, 129.32, 134.02, 136.30, 138.14, 145.87, 151.20, 194.15; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.36 (s, 1H, NH); HRMS of $[C_{26}H_{27}N_3O+Na]^+$ (m/z): 420.2061; Calcd.: 420.2052.

4-(3,4,5-Trimethoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo [3,4-b]quinolin-5(4H)-one (4e): 94% Yield, White solid (226.72 mg); m.p. 197–198 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.01 (s, 3H, CH_3), 102 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.03 (d, *J* = 15.04 Hz, 1H, CH), 2.20 (d, *J* = 16.12 Hz, 1H, CH), 2.52 (d, *J* = 7.08 Hz, 2H, CH_2), 3.59 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.95 (s, 1H, CH), 6.49 (s, 2H, ArH), 7.33 – 7.39 (m, 2H, ArH), 7.50 (t, *J* = 3.64 Hz, 3H, ArH), 9.39 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 12.22, 13.84, 26.37, 27.68, 29.18, 31.86, 35.82, 40.64, 50.34, 55.64, 59.85, 104.16, 104.49, 105.29, 109.15, 120.64, 123.07, 126.01, 129.31, 135.40, 135.94, 138.09, 143.61, 145.91, 151.74, 152.43, 152.46, 163.54, 194.13; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.39 (s, 1H, NH); HRMS of $[C_{28}H_{31}N_3O_4+Na]^+$ (m/z): 496.2218; Calcd.: 496.2212.

4-(3-Hydroxy-4-methoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4f): 92% Yield, White solid (259.52 mg); m.p. 239–241 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.93 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.00 (d, *J* = 16.12 Hz, 2H, CH_2), 2.14 (d, *J* = 16.08 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 4.84 (s, 1H, CH), 6.57 – 6.61 (m, 2H, ArH), 6.73 (d, *J* = 8.12 Hz, 1H, ArH), 7.35 – 7.39 (m, 1H, ArH), 7.48 - 7.51 (m, 4H, ArH), 8.70 (s, 1H, OH), 9.34 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 11.96, 26.77, 28.85, 31.88, 34.81, 40.64, 50.47, 55.55, 104.43, 109.77, 111.62, 115.12, 118.08, 120.53, 122.96, 126.68, 129.31, 136.09, 138.18, 140.55, 145.50, 145.86, 150.87, 193.99; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.34 (s, 1H, NH); HRMS of $[C_{26}H_{27}N_3O_3+Na]^+$ (m/z): 452.1961; Calcd.: 452.1950.

4-(3-Methoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4g): 96% Yield, White solid (291.35 mg); m.p. 176–178 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.94 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.00 (d, *J* = 16.12 Hz, 1H, CH), 2.16 (d, *J* = 16.12 Hz, 1H, CH), 2.51 (d, *J* = 4.96 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 4.95 (s, 1H, CH), 6.65 – 6.67 (m, 1H, ArH), 6.74 – 6.79 (m, 2H, ArH), 7.13 (t, *J* = 7.84 Hz, 1H, ArH), 7.37 – 7.39 (m, 1H, ArH), 7.50 (t, *J* = 3.44 Hz, 4H, ArH), 9.38 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 12.01, 26.62, 27.70, 28.90, 31.90, 35.64, 50.37, 54.75, 104.07, 109.33, 110.41, 113.62, 119.86, 120.62, 123.05, 129.32, 136.09, 138.09, 145.93, 149.23, 151.47, 158.67, 158.92, 194.03; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.38 (s, 1H, NH); HRMS of $[C_{26}H_{27}N_3O_2+Na]^+$ (m/z): 436.2008; Calcd.: 436.2001.

4-(4-Ethylphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4h): 95% Yield, Light yellow solid (291.15 mg); m.p. 246–248 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.93 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.12 (t, *J* = 7.56 Hz, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.98 (d, *J* = 16.08 Hz, 1H, CH), 2.15 (d, *J* = 16.08 Hz, 2H, CH_2), 2.50 – 2.54 (m, 2H, CH_2), 4.94 (s, 1H, CH), 7.04 (d, *J* = 8.08, 2H, ArH), 7.10 (d, *J* = 8.08, 2H, ArH), 7.35 – 7.39 (m, 1H, ArH), 7.48 – 7.52 (m, 4H, ArH), 9.36 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 11.96, 26.75, 27.66, 28.84, 31.92, 35.22, 40.63, 50.40, 104.35, 109.60, 120.57, 123.00, 126.72, 127.17, 127.36, 129.15, 136.06, 138.14, 140.69, 145.02, 145.88, 151.29, 193.99; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.36 (s, 1H, NH); HRMS of $[C_{27}H_{29}N_3O+Na]^+$ (m/z): 434.2215; Calcd.: 434.2208.

4-(4-Methoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4i): 94% Yield, White solid (285.86 mg); m.p. 221–223 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.92 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.85 (s, 1H, CH), 1.87 (s, 3H, CH_3), 1.98 (d, *J* = 16.12 Hz, 1H, CH), 2.14 (d, *J* = 16.12 Hz, 1H, CH), 3.19 (s, 1H, CH), 3.68 (s, 3H, OCH_3), 4.93 (s, 1H, CH), 6.77 (d, *J* = 8.64 Hz, 2H, ArH), 7.10 (d, *J* = 8.64, 2H, ArH), 7.35 – 7.39 (m, 1H, ArH), 7.51 (t, *J* = 2.44, 4H, ArH), 9.34 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 11.91, 26.69, 27.67, 28.85, 31.89, 34.71, 47.73, 50.42, 54.85, 104.38, 109.77, 113.14, 120.56, 122.99, 126.69, 128.42, 128.88, 129.15, 129.30, 136.10, 138.16, 139.92, 145.91, 150.98, 157.08, 193.97; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.34 (s, 1H, NH).

1,4-Diphenyl-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4j): Yield 91%. White solid (32.60 mg); m.p. 190–192 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.00 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.02 (s, 3CH, CH_3) 2.18 (d, *J* = 6.64 Hz, 2H, CH_2), 2.36 (s, 2H, CH_2), 5.13 (s, 1H, CH), 6.53 (s, 1H, NH), 7.09 – 7.14 (m, 1H, ArH), 7.23 (t, *J* = 7.36, 2H, ArH), 7.28 (d, *J* = 7 Hz, 2H, ArH), 7.47 (s,5H, ArH), 9.36); ^{13}C NMR (100 MHz, DMSO-d_6): 12.12, 27.40, 28.22, 29.02, 32.61, 36.12, 42.51, 48.58, 50.84, 104.83, 112.21, 121.17, 122.90, 126.01, 126.07, 127.13, 127.55, 127.71, 127.94, 127.96, 128.11, 129.05, 129.97, 135.70, 137.76, 146.33, 147.58, 148.72, 195.38; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 6.53 (s, 1H, NH); HRMS of $[C_{25}H_{25}N_3O+Na]^+$ (m/z): 406.1901; Calcd.: 406.1895.

4-(Pyridin-3-yl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4k): Yield 94%. Brown solid (337.17 mg); m.p. 239–241 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.91 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.87 (s, 3CH, CH_3) 2.00 (d, *J* = 16.16 Hz, H, CH), 2.17 (d, *J* = 16.12 Hz, 1H, CH), 2.52(d, *J* = 10.16 Hz, 2H, CH_2), 5.04 (s, 1H, CH), 7.25 – 7.28 (m, 1H, ArH), 7.38 – 7.42 (m, 1H, ArH), 7.52 (d, *J* = 4.24 Hz, 4H, ArH), 7.56 – 7.58 (m, 1H, ArH), 8.31 (dd, *J* = 1.48, 3.2 Hz, 1H, ArH), 8.48 (d, *J* = 1.88 Hz, 1H, ArH), 9.52 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): 12.33, 27.20, 29.19, 32.45, 34.01, 41.07, 50.77, 103.64, 109.14, 121.09, 123.75, 123.79, 127.43, 129.70, 129.81, 135.46, 136.82, 138.53, 143.12, 146.38, 147.26, 149.39, 152.32, 194.48; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ = 9.52 (s, 1H, NH); HRMS of $[C_{24}H_{24}N_4O+Na]^+$ (m/z): 407.1859; Calcd.: 407.1848.

4-(3,4-Dihydroxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4l): 95% Yield, Pale red solid (285.57 mg); m.p. 216–217 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.99 (d, *J* = 16.12 Hz, 1H, CH), 2.16 (d, *J* = 16.08 Hz, 1H, CH), 2.49 (d, *J* = 3.48 Hz, 2H, CH_2), 4.81 (s, 1H, CH), 6.47 (d, *J* = 8.04 Hz, 1H, ArH), 6.57 (t, *J* = 6.52 Hz, 2H, ArH), 7.36 – 7.39 (m, 1H, ArH), 7.50 (t, *J* = 15.44, 4H, ArH), 8.53 (s, 1H, OH), 8.62 (s, 1H, OH), 9.30 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.47, 19.01, 27.27, 29.38, 32.37, 35.23, 41.16, 51.02, 56.51, 105.16, 110.49, 115.32, 115.68, 118.79, 123.42, 127.47, 129.82, 136.59, 138.71, 139.48, 143.48, 145.02, 146.47, 151.23, 194.55; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 9.30 (s, 1H, NH); HRMS of $[C_{25}H_{25}F_3N_3O_3+H]^+$ (m/z): 416.1319; Calcd.: 416.1331.

4-(3-Fluorophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4m): 93% Yield, White color solid (300.62 mg); m.p. 204–205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.10 (d, *J* = 8.92 Hz, 2H, CH_2), 2.28 (s, 2H, CH_2), 5.05 (s, 1H, CH), 6.72 – 6.76 (m, 1H, ArH), 6.85 (d, *J* = 10.08 Hz, 1H, ArH), 6.95 (s, 1H, NH), 7.02 (d, *J* = 7.56 Hz, 1H, 7.18 (s, 1H, ArH), 7.26 (d, *J* = 3.24 Hz, 1H, ArH), 7.32 (t, *J* = 2.44 Hz, 1H, ArH), 7.65 (d, *J* = 9.24 Hz, 1H, ArH) 7.77 (d, *J* = 7.68, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.08, 27.31, 29.00, 32.53, 36.01, 42.27, 50.67, 104.24, 111.40, 123.14, 124.48, 125.73, 125.76, 127.65, 129.86, 135.72, 137.69, 147.53, 149.78, 161.30, 161.75, 163.75, 164.19, 195.71; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 6.95 (s, 1H, NH). HRMS of $[C_{25}H_{24}FN_3O+Na]^+$ (m/z): 424.0843; Calcd.: 424.0836.

4-(4-Fluorophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4n): 94% Yield, Ash solid (303.85 mg); m.p. 221-223 ^{o}C; ^{1}H NMR (400 MHz, $CDCL_3$) δ = 0.91 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.09 (d, *J* = 7.24 Hz, 2H, CH_2), 2.28 (s, 2H, CH_2), 5.04 (s, 1H, CH), 6.60 (s, 1H, NH), 6.84 (d, *J* = 8.6 Hz, 2H, ArH), 7.18 (d, *J* = 10.32 Hz, 2H, ArH), 7.39 (s, 5H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): 12.14, 27.32, 28.99, 32.57, 35.48, 42.44, 50.82, 104.53, 111.98, 114.68, 114.89, 122.87, 124.44, 127.48, 129.36, 129.44, 129.93, 135.60, 137.95, 142.28, 142.31, 147.54, 148.82, 159.97, 162.39, 195.42; ^{15}N NMR (40.55 MHz, $CDCL_3$) δ = 6.60 (s, 1H, NH); HRMS of $[C_{25}H_{24}FN_3O+Na]^+$ (m/z): 424.1101; Calcd.: 424.1109.

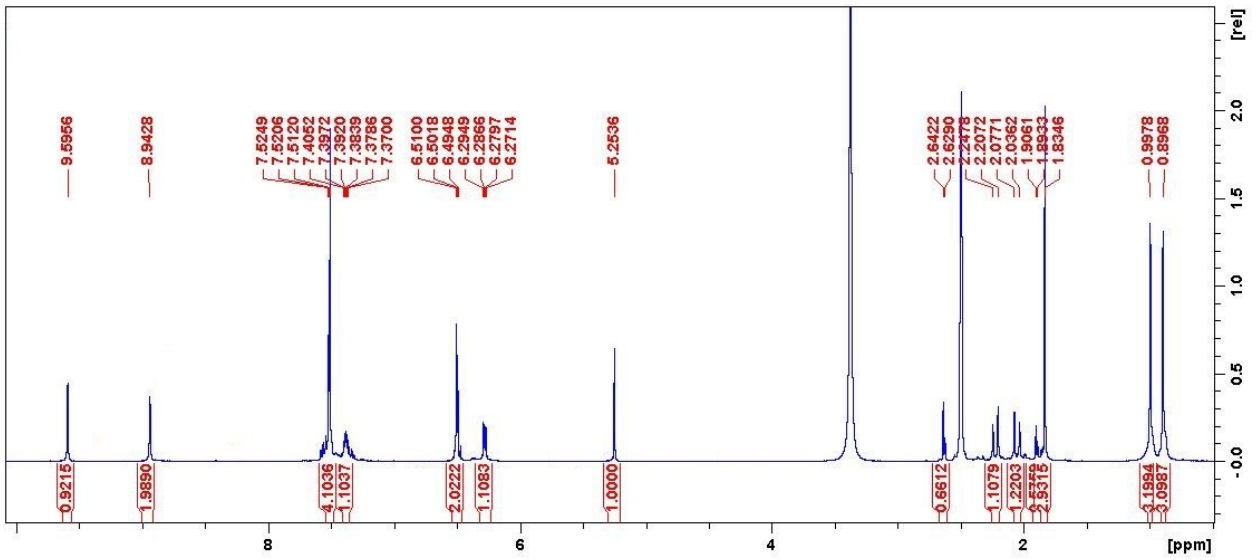
4-(4-Bromophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4o): 92% Yield, White solid (229.28 mg); m.p. 190-192 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.10 (d, *J* = 8.64 Hz, 2H, CH_2), 2.28 (s, 2H, CH_2), 5.04 (s, 1H, CH), 6.55 (s, 1H, NH), 7.14 (d, *J* = 3.92 Hz, 4H, ArH), 7.39 – 7.41 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.16, 27.34, 29.00, 32.59, 35.70, 42.47, 50.82, 104.26, 111.76, 122.87, 124.54, 127.52, 128.21, 129.39, 129.59, 129.95, 130.91, 131.62, 135.61, 137.90, 144.97, 147.51, 148.89, 195.34; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 6.55 (s, 1H, NH). HRMS of $[C_{25}H_{24}BrN_3O+Na]^+$ (m/z): 484.2441; Calcd.: 484.2445.

4-(4-Chlorophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b] quinolin-5(4H)-one (4p): 96% Yield, White solid (284.89 mg); m.p. 175–176 ^{o}C; ^{1}H NMR

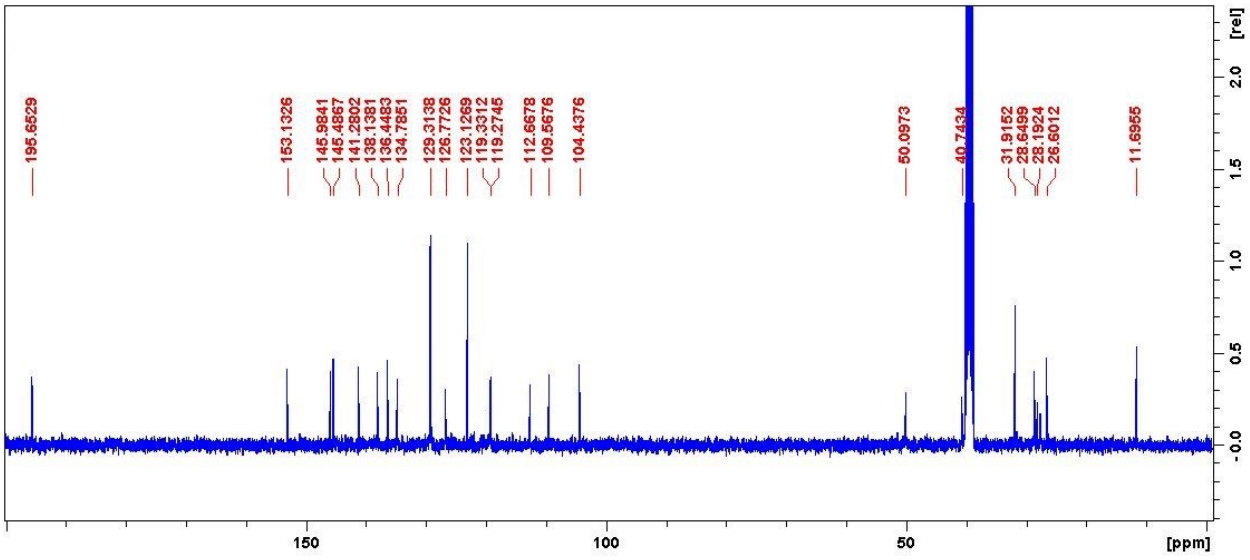
(400 MHz, $CDCl_3$) δ = 0.91 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.10 (d, *J* = 8.64 Hz, 2H, CH_2), 2.28 (s, 1H, CH_2), 5.04 (s, 1H, CH), 6.55 (s, 1H, NH), 7.14 (d, *J* = 3.92 Hz, 4H, ArH), 7.39 – 7.43 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.16, 27.34, 29.00, 32.59, 42.47, 50.82, 104.26, 111.76, 121.18, 122.87, 124.54, 127.52, 129.21, 129.39, 129.95, 130.91, 131.62, 135.65, 137.90, 144.97, 147.51, 148.89, 195.34; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 6.55 (s, 1H, NH). HRMS of $[C_{25}H_{24}ClN_3O + Na]^+$ (m/z): 440.0818; Calcd.: 440.0813.

4-(3,4-Dimethoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4q): 96% Yield, Red solid (256.05 mg). m.p. 235–237 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 0.94 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.11 (d, *J* = 17.92 Hz, 2H, CH_2), 2.33 (d, *J* = 19.08 Hz, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 5.02 (s, 1H, CH), 6.67 – 6.71 (m, 3H, ArH), 6.81 (s, 1H, NH), 7.40 – 7.46 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.06, 14.42, 20.59, 29.15, 32.54, 35.52, 42.41, 50.82, 55.79, 104.91, 111.00, 111.74, 119.96, 121.17, 123.01, 127.71, 129.05, 129.97, 135.93, 139.24, 139.28, 147.28, 148.55, 195.61; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 6.81 (s, 1H, NH). HRMS of $[C_{27}H_{29}N_3O_3 + H]^+$ (m/z): 443.3232; Calcd.: 443.3230.

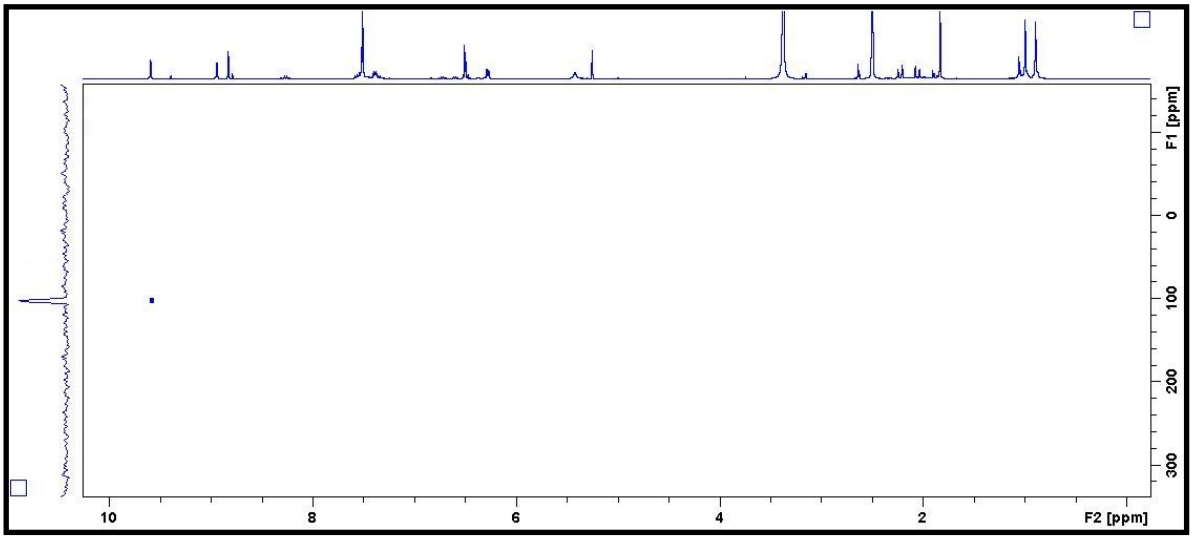
4-(Thiophen-2-yl)-3,7,7-trimethyl-1-phenyl-7,8-dihydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4r): Yield 94%. Yellow solid (326.17 mg); m.p. 218–219 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.05 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.21 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 5.50 (s, 1H, CH), 6.87 (d, *J* = 5.24 Hz, 2H, ArH), 7.07 (t, *J* = 10 Hz, 2H), 7.34 (s, 1H, NH), 7.47 (d, *J* = 3.42 Hz, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.12, 27.30, 29.17, 30.58, 32.51, 42.23, 50.75, 104.13, 111.58, 121.21, 123.00, 123.54, 123.63, 126.42, 127.58, 129.90, 135.80, 137.73, 147.45, 149.22, 151.11, 195.45; ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = 7.34 (s, 1H, NH).



^{1}H NMR spectra of compound **4a**



^{13}C NMR spectra of compound **4a**



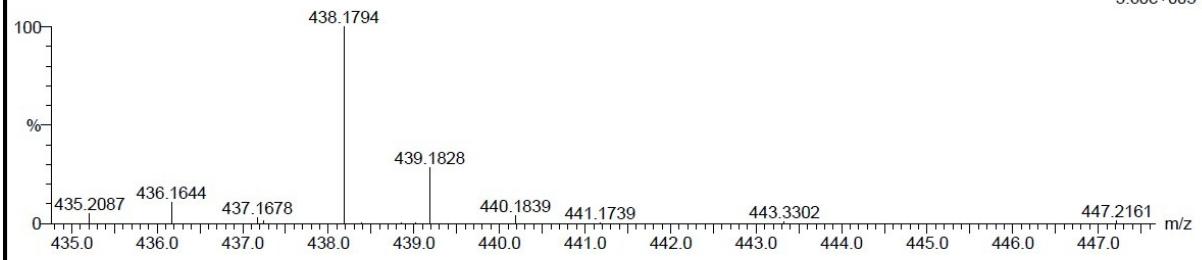
^{15}N NMR spectra of compound **4a**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

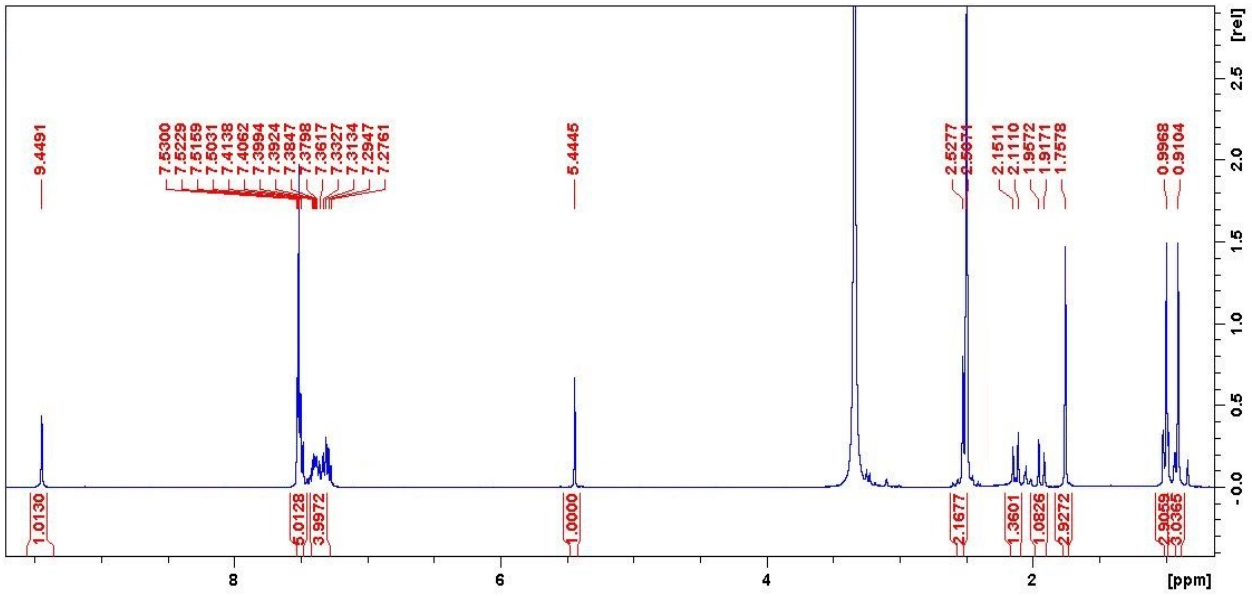
Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 25-30 N: 0-5 O: 1-5 Na: 1-1
FP-17 23 (0.742) Cm (1:61)
TOF MS ES+

3.60e+005

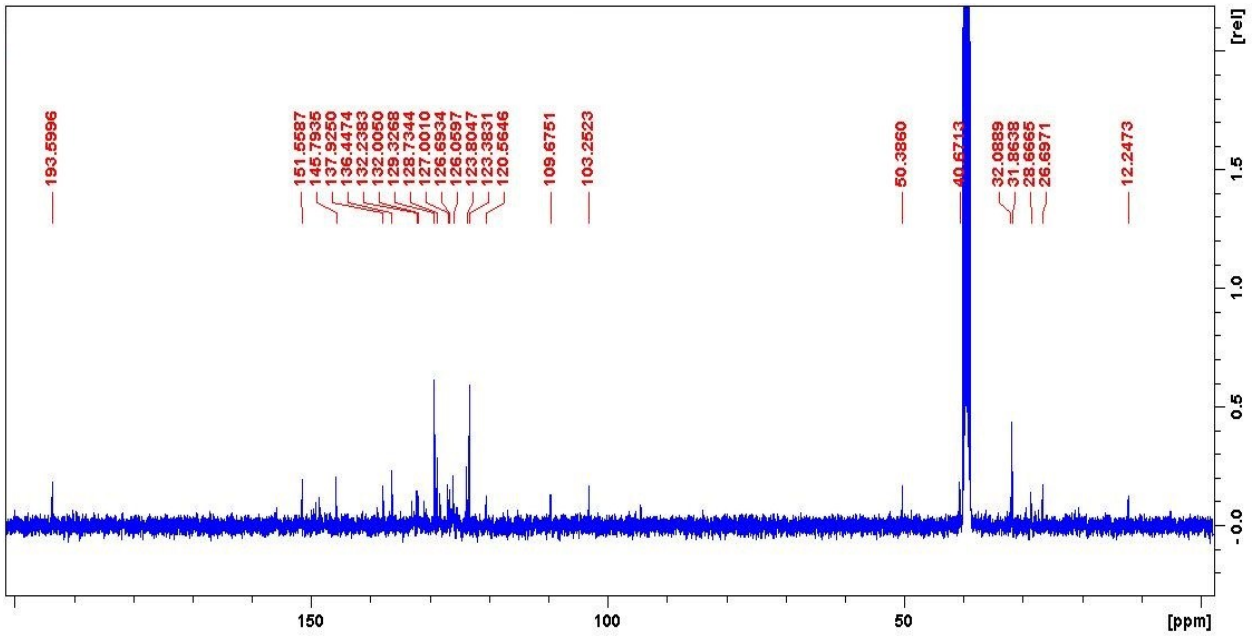


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
438.1794	438.1794	0.0	0.0	14.5	63.8	0.0	C25 H25 N3 O3 Na

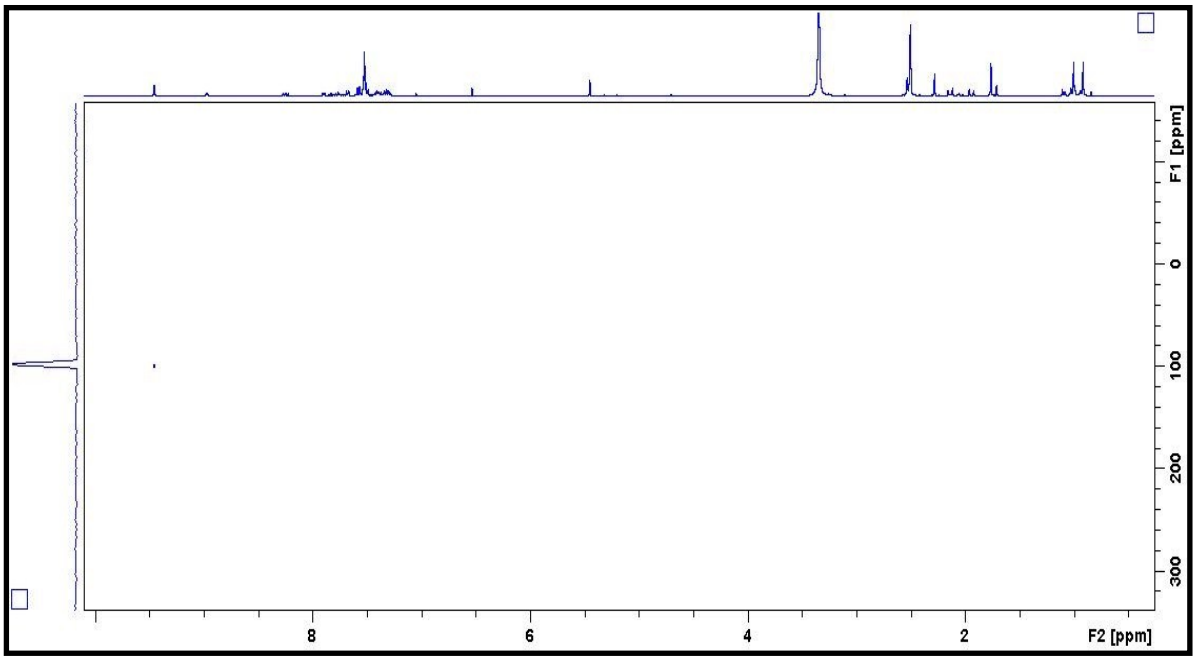
HRMS spectra of compound **4a**



^{1}H NMR spectra of compound **4b**



^{13}C NMR spectra of compound 4b



^{15}N NMR spectra of compound **4b**

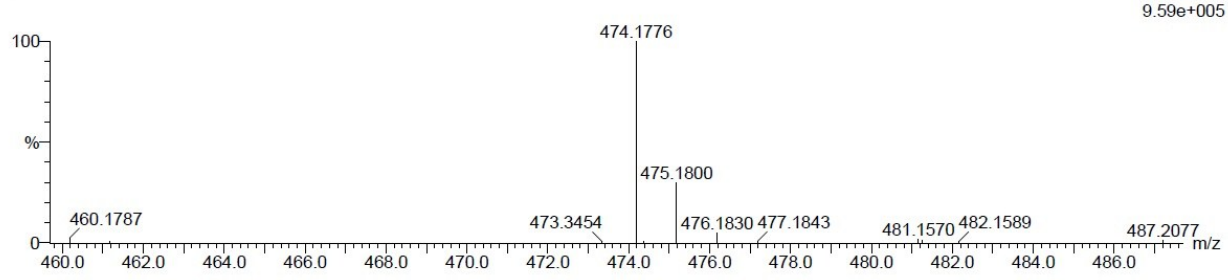
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
82 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 1-5 Na: 1-1 F: 1-5

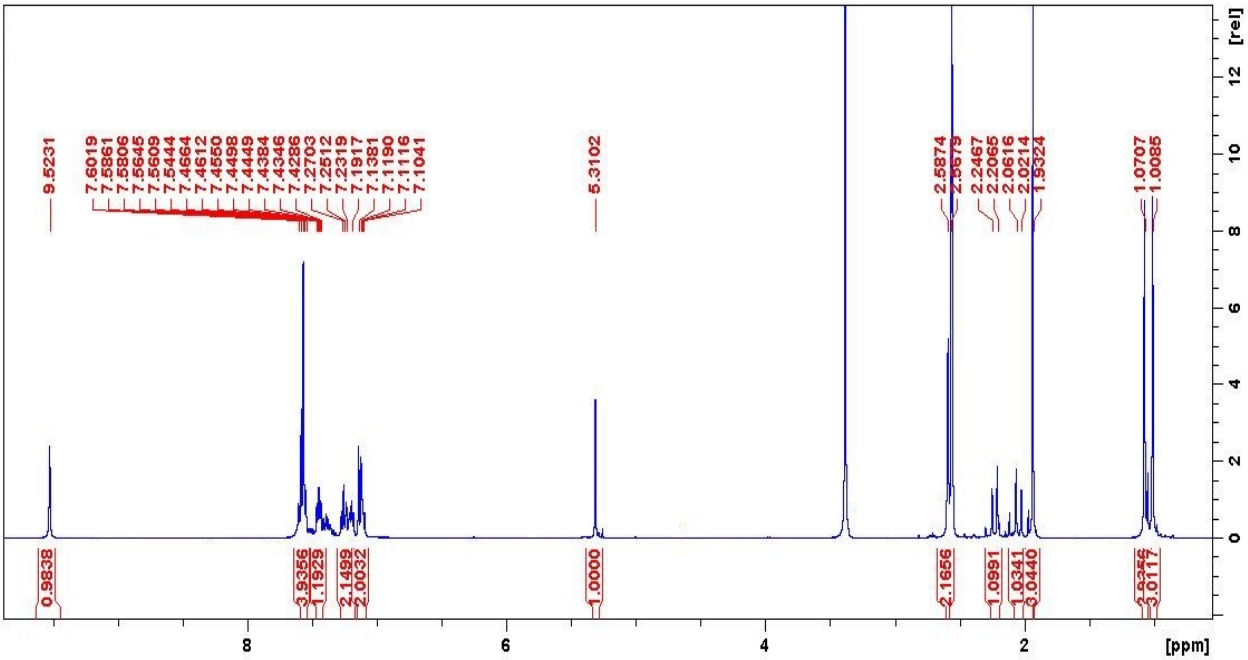
FP-13 22 (0.709) Cm (1:61)
TOF MS ES+

9.59e+005

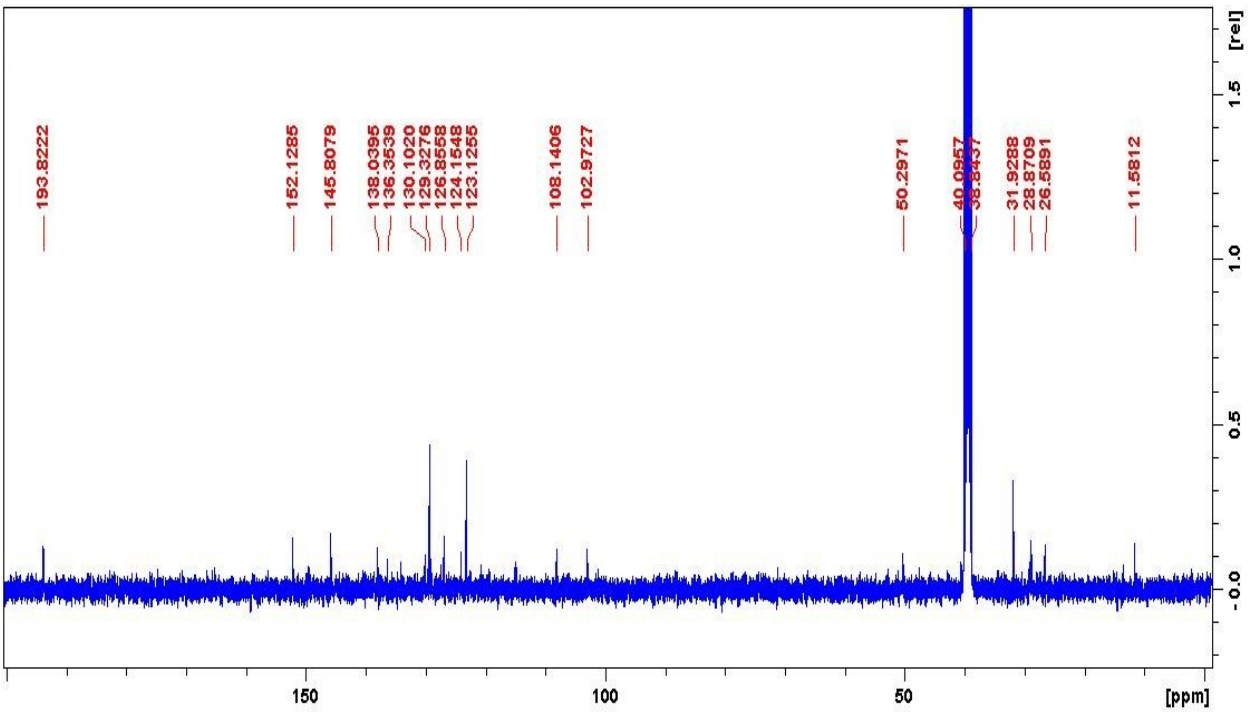


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
474.1776	474.1769	0.7	1.5	14.5	33.4	0.0	C26 H24 N3 O Na F3

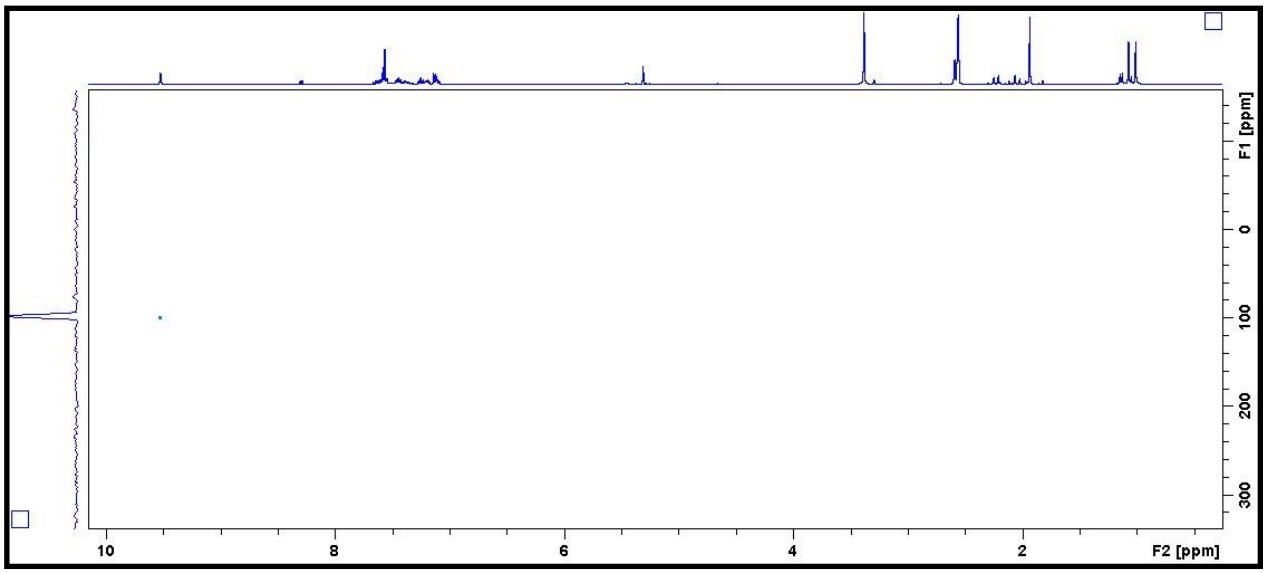
HRMS spectra of compound **4b**



^{1}H NMR spectra of compound **4c**



^{13}C NMR spectra of compound **4c**

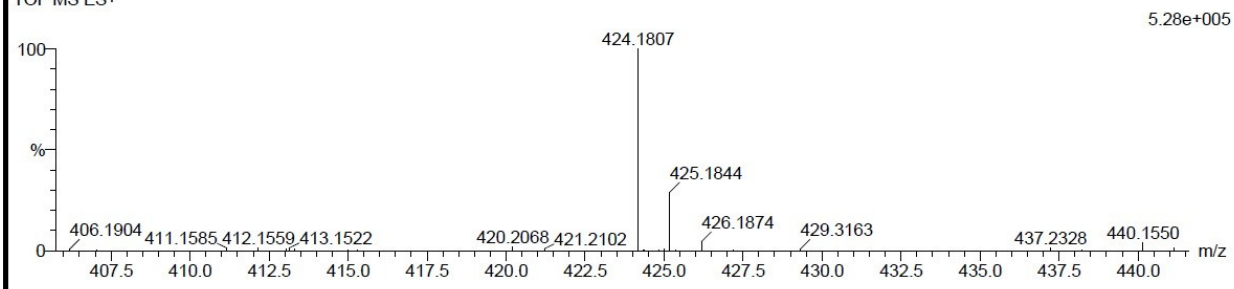


^{15}N NMR spectra of compound **4c**

Elemental Composition Report **Page 1**

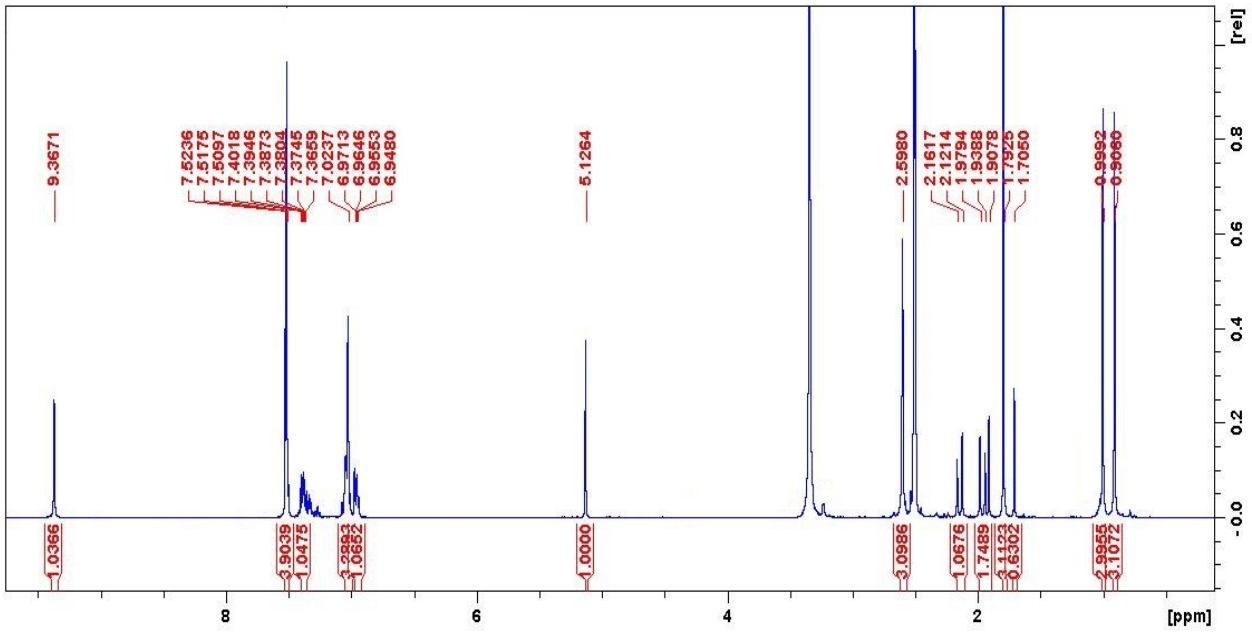
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
122 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 1-5 F: 1-5 Na: 1-1
FP-14 7 (0.202) Cm (1:61)
TOF MS ES+

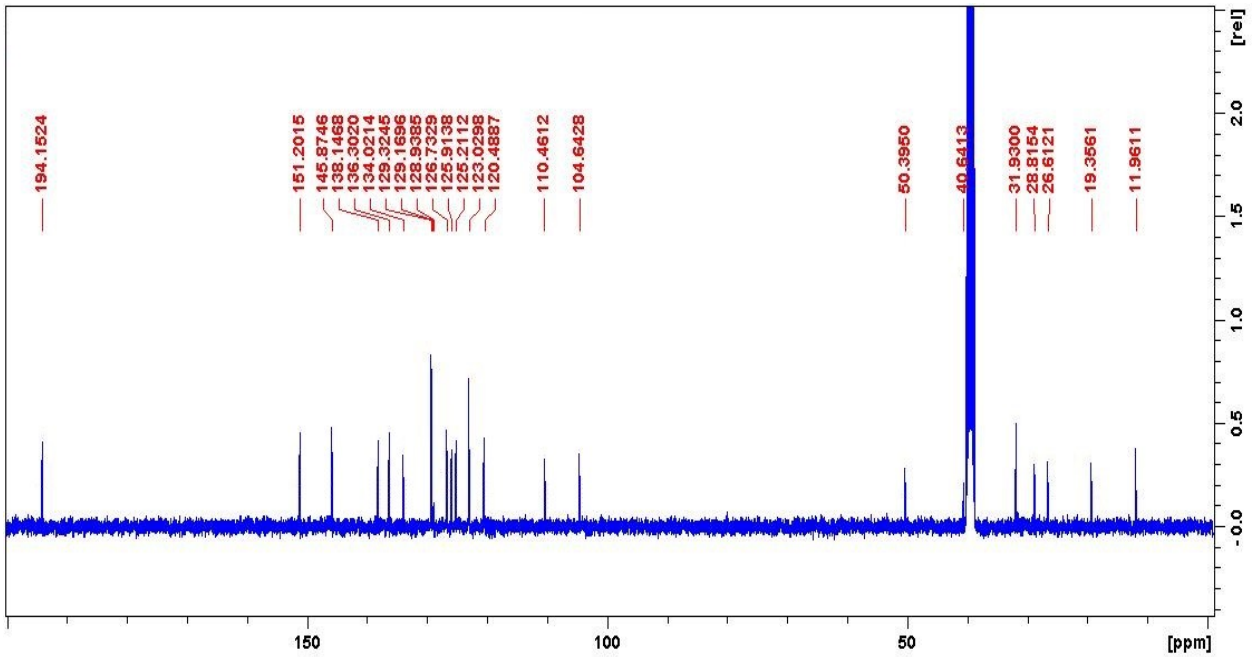


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
424.1807	424.1801	0.6	1.4	14.5	90.6	0.0	C25 H24 N3 O F Na

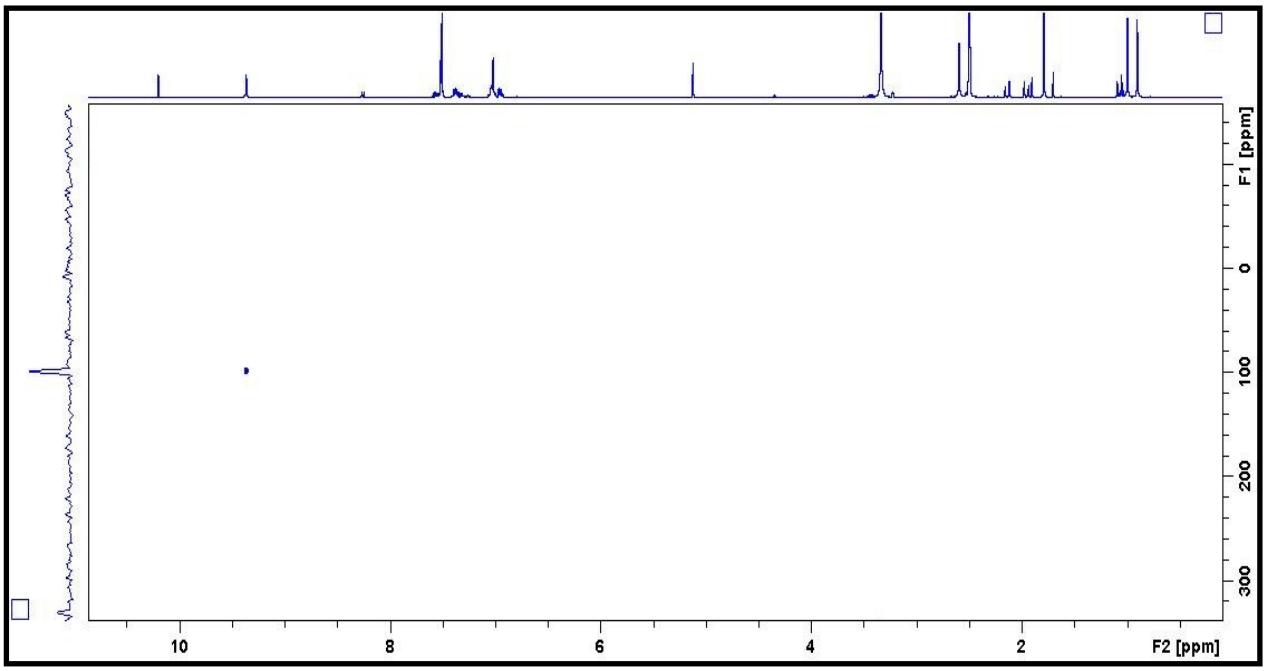
HRMS spectra of compound **4c**



^{1}H NMR spectra of compound **4d**



^{13}C NMR spectra of compound 4d

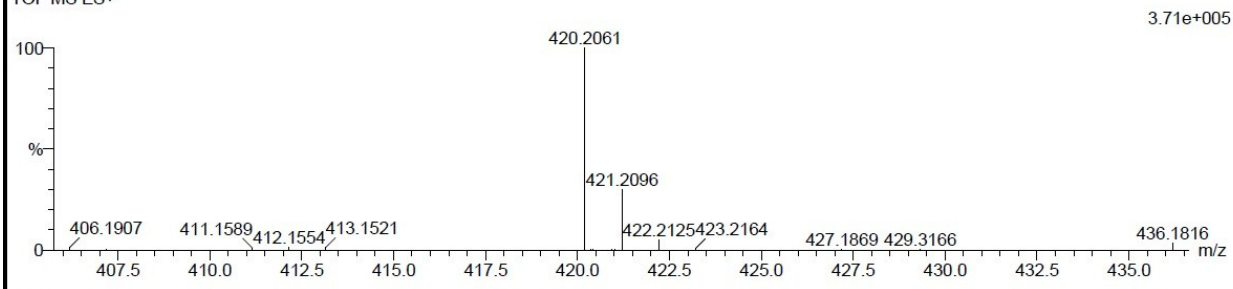


^{15}N NMR spectra of compound **4d**

Elemental Composition Report **Page 1**

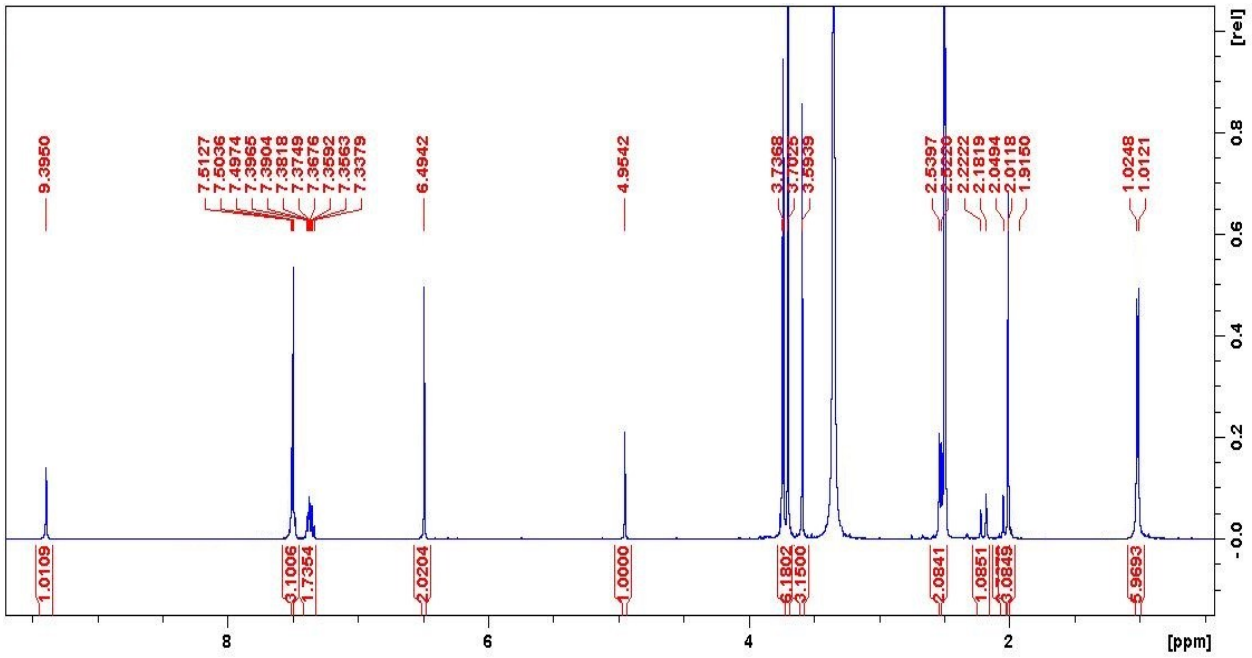
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
18 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 25-30 N: 0-5 O: 0-5 Na: 1-1
FP-12 2 (0.034) Cm (1:61)
TOF MS ES+

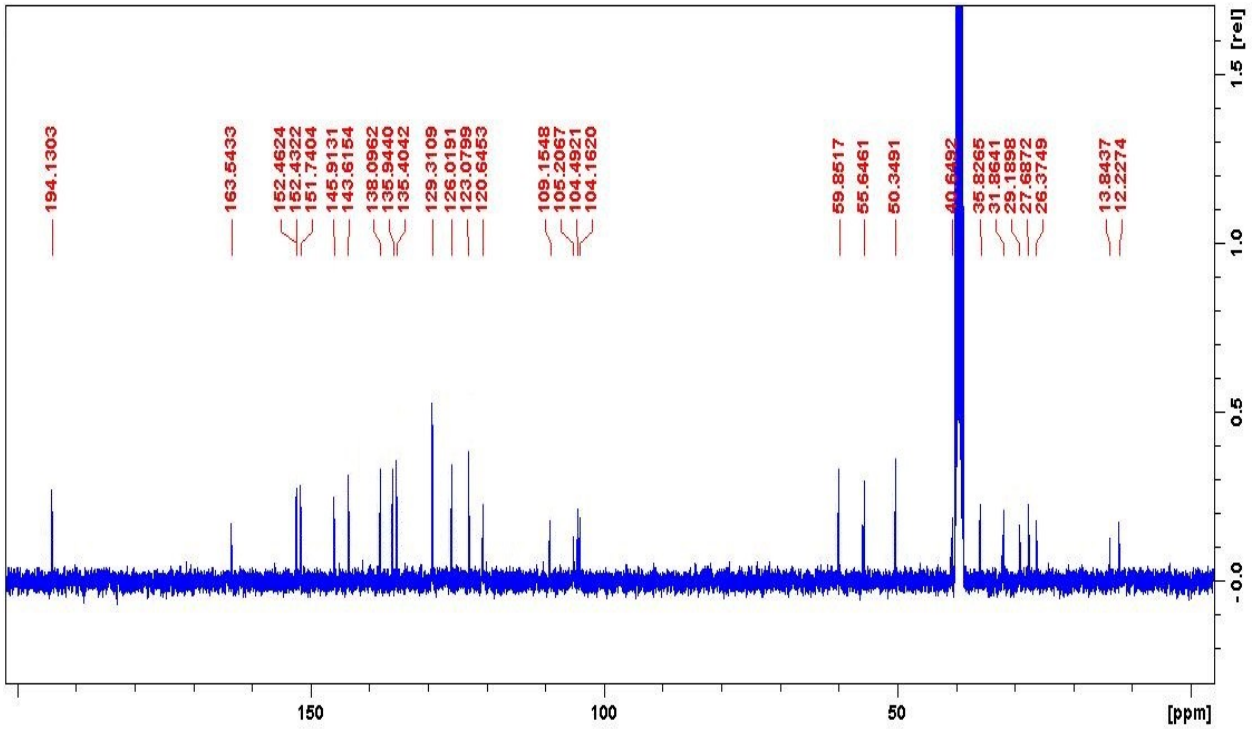


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
420.2061	420.2052	0.9	2.1	14.5	70.5	0.0	C26 H27 N3 O Na

HRMS spectra of compound **4d**



^{1}H NMR spectra of compound **4e**

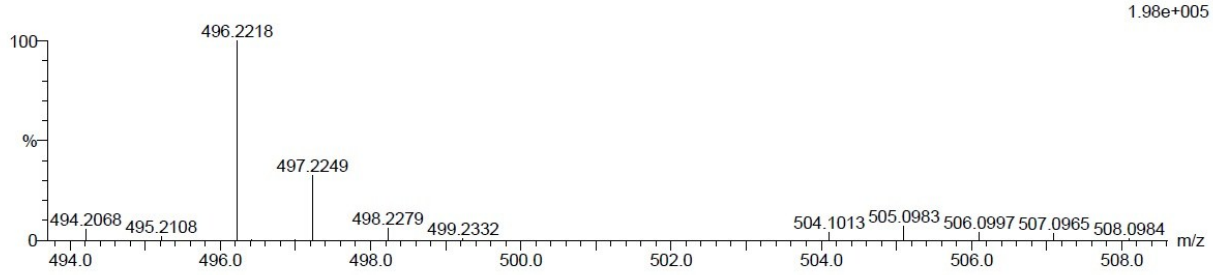


^{13}C NMR spectra of compound 4e

Elemental Composition Report **Page 1**

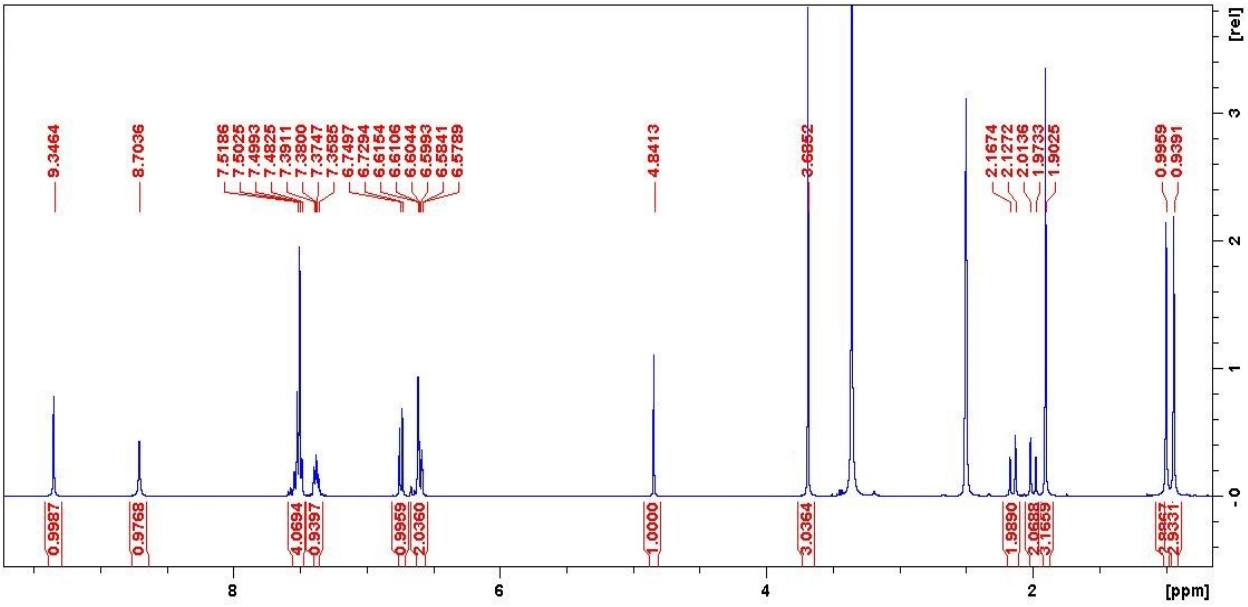
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 30-35 N: 0-5 O: 1-5 Na: 1-1
FP-18 17 (0.540) Cm (1:61)
TOF MS ES+

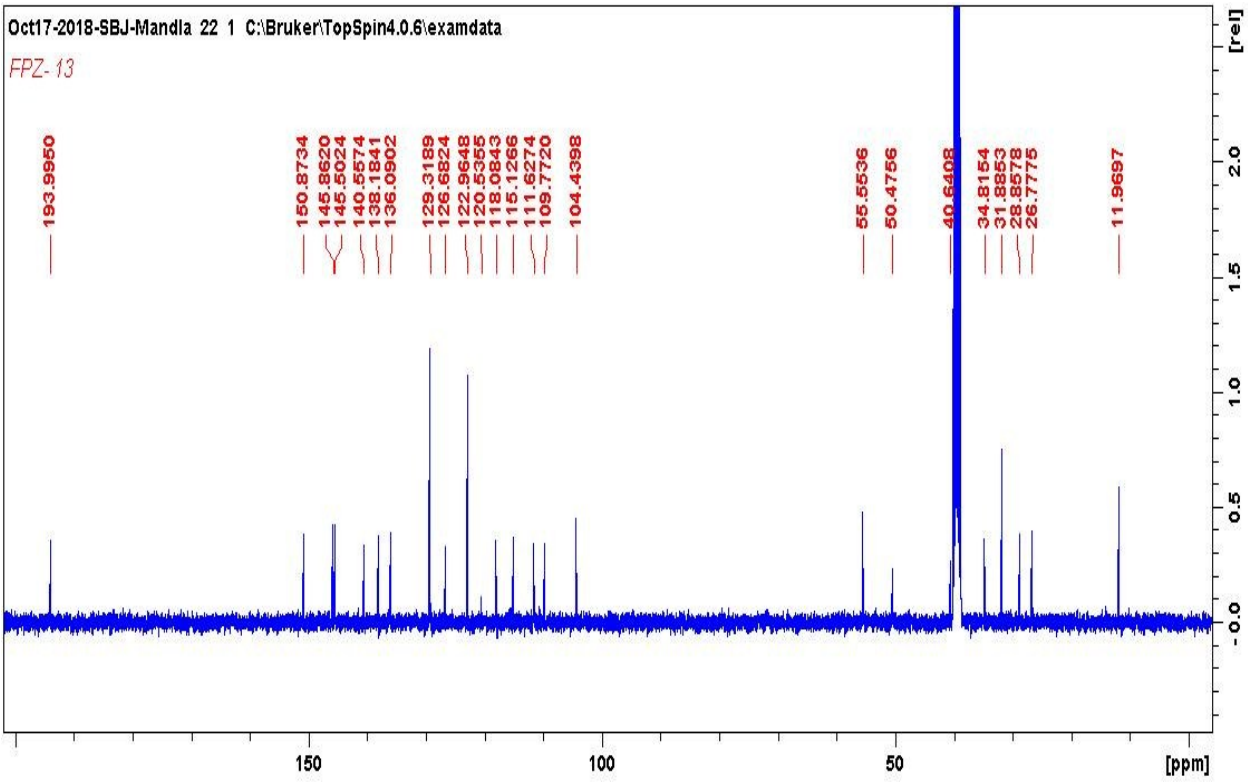


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
496.2218	496.2212	0.6	1.2	14.5	38.0	0.0	C28 H31 N3 O4 Na

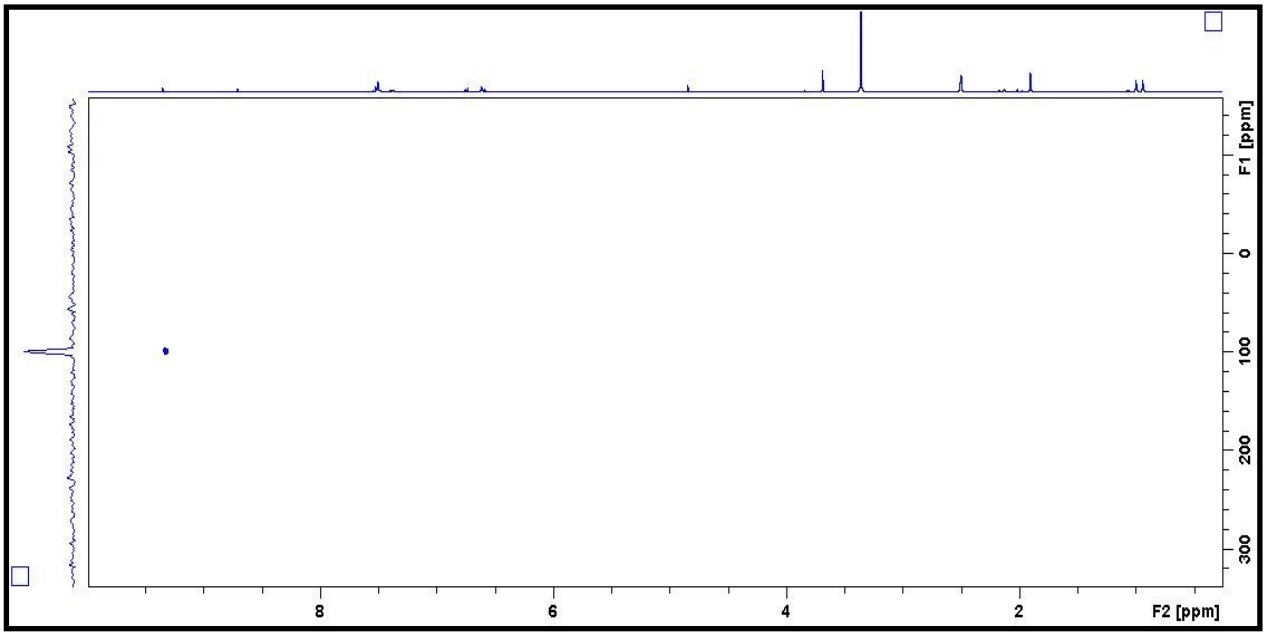
HRMS spectra of compound **4e**



^{1}H NMR spectra of compound **4f**



^{13}C NMR spectra of compound 4f

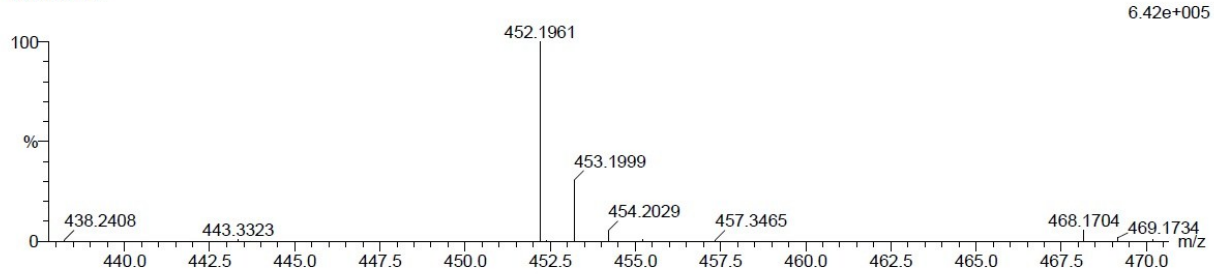


^{15}N NMR spectra of compound **4f**

Elemental Composition Report **Page 1**

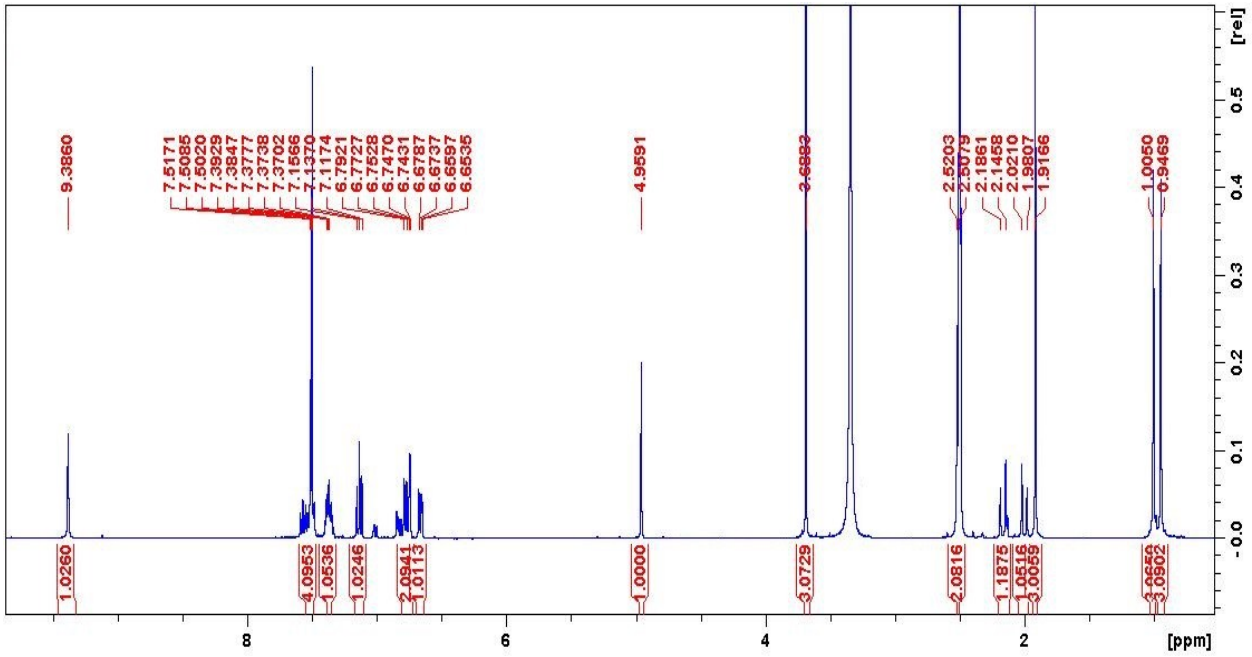
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 25-30 N: 0-5 O: 1-5 Na: 1-1
FP-15 22 (0.708) Cm (1:61)
TOF MS ES+

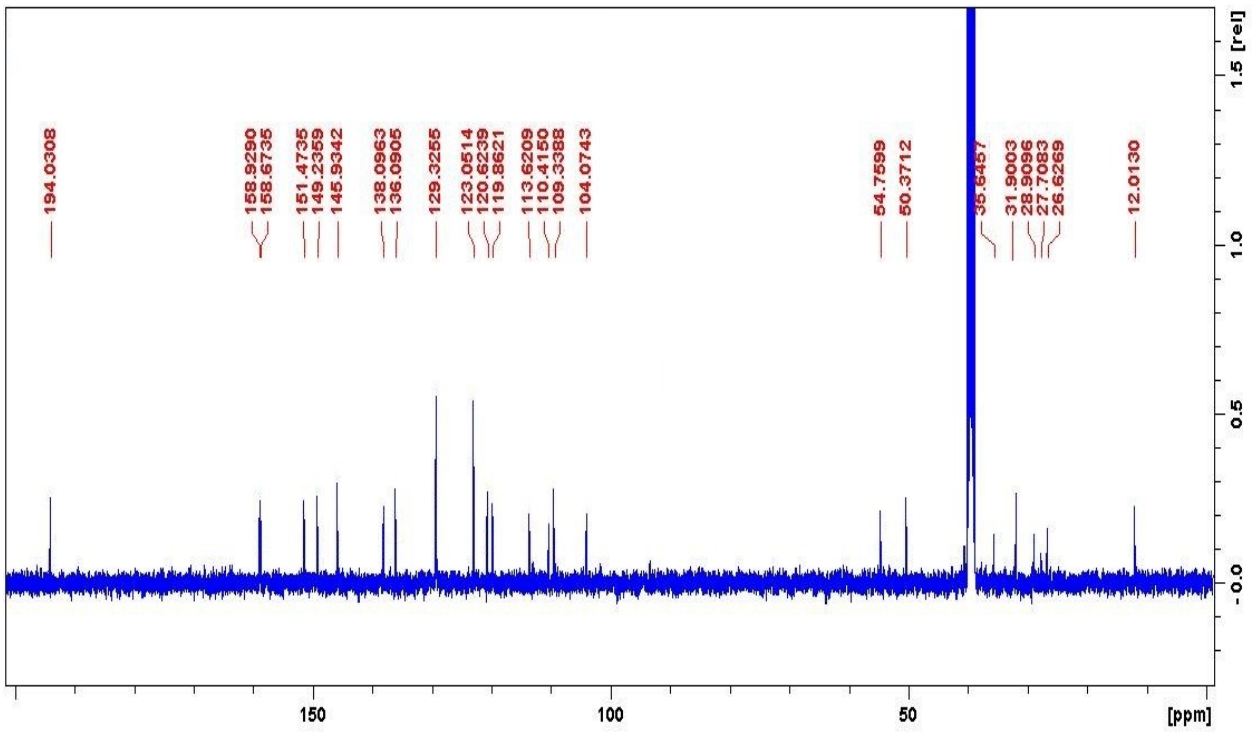


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
452.1961	452.1950	1.1	2.4	14.5	29.1	0.0	C26 H27 N3 O3 Na

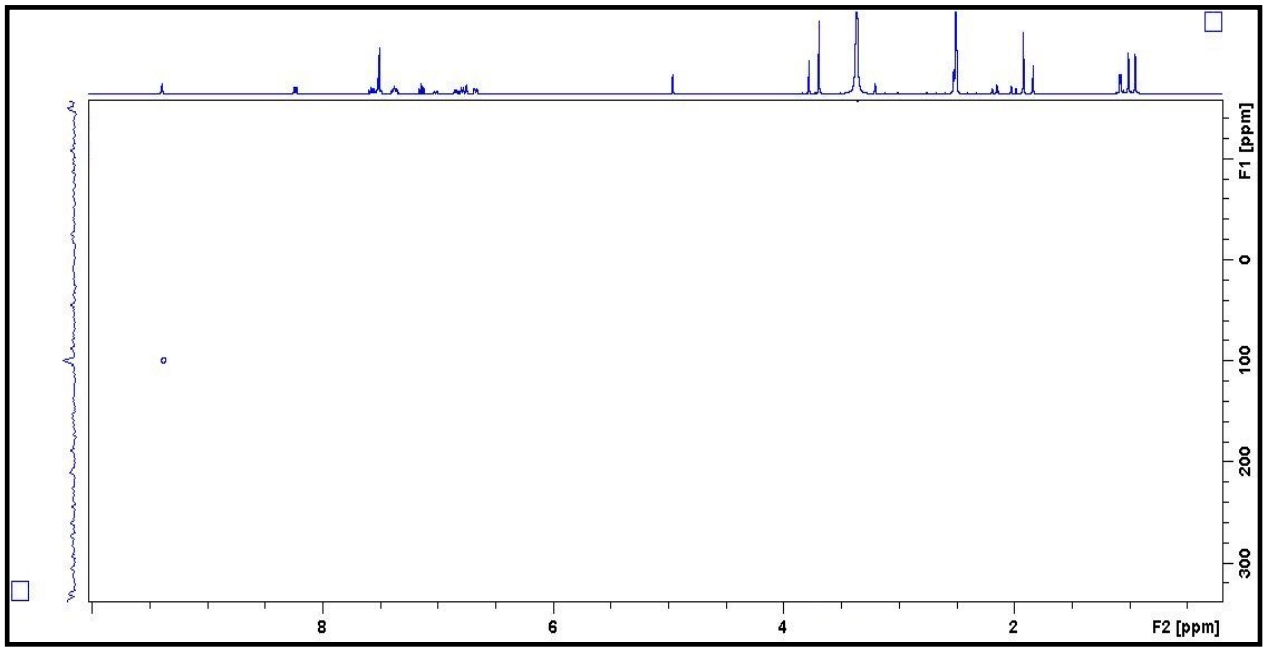
HRMS spectra of compound **4f**



^{1}H NMR spectra of compound **4g**



^{13}C NMR spectra of compound 4g

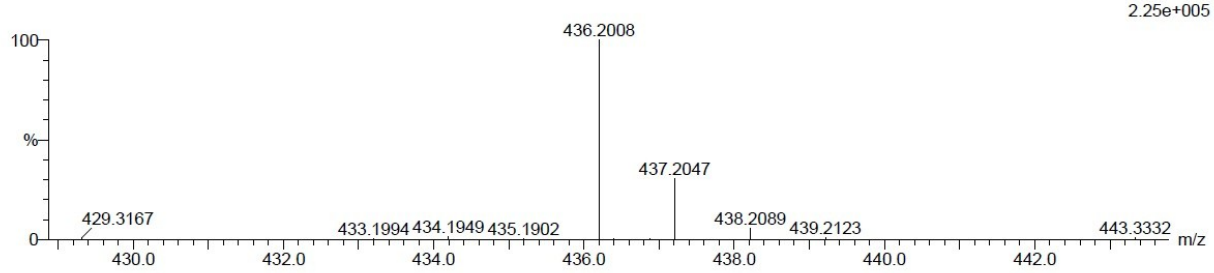


^{15}N NMR spectra of compound **4g**

Elemental Composition Report **Page 1**

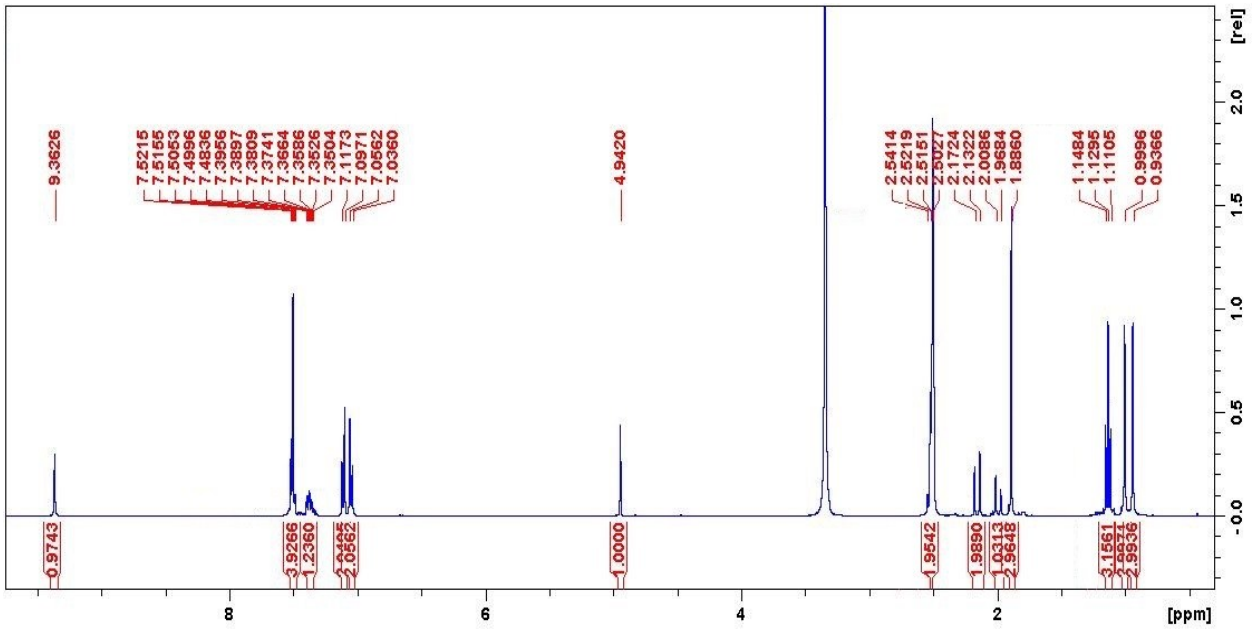
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 25-30 N: 0-5 O: 1-5 Na: 1-1
FP-20 34 (1.113) Cm (1:61)
TOF MS ES+

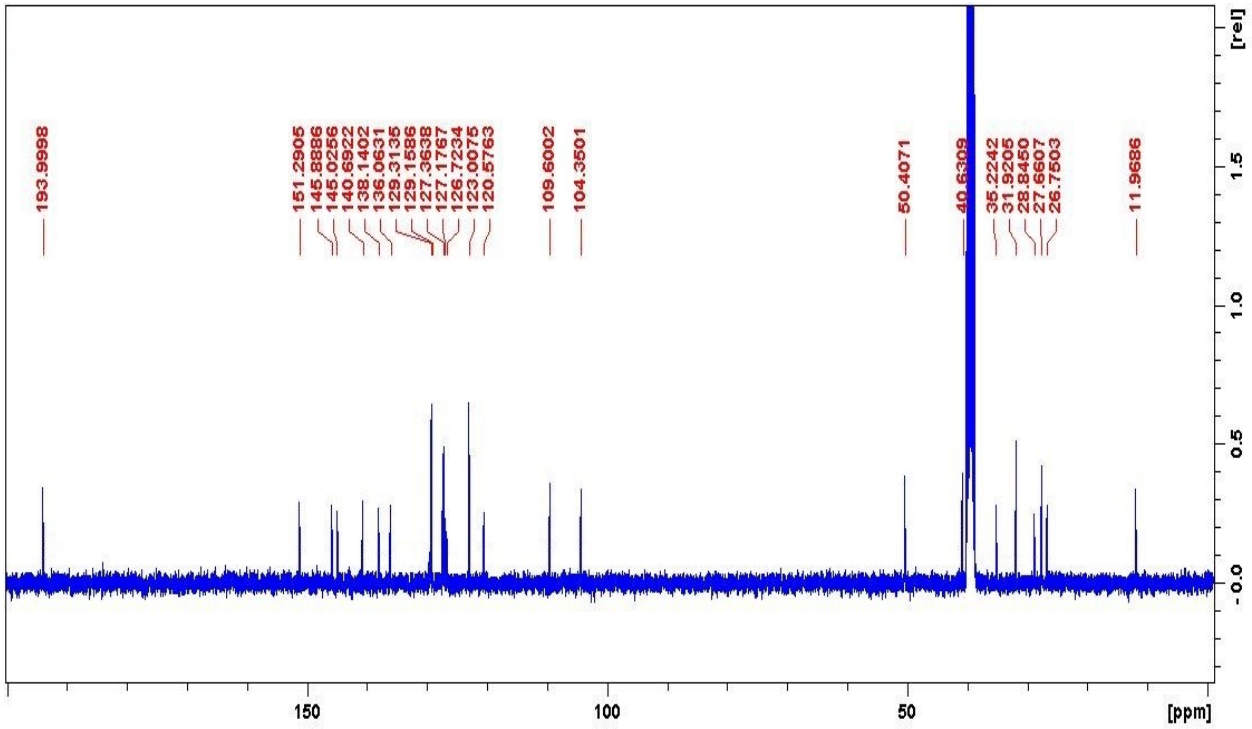


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
436.2008	436.2001	0.7	1.6	14.5	47.4	0.0	C26 H27 N3 O2 Na

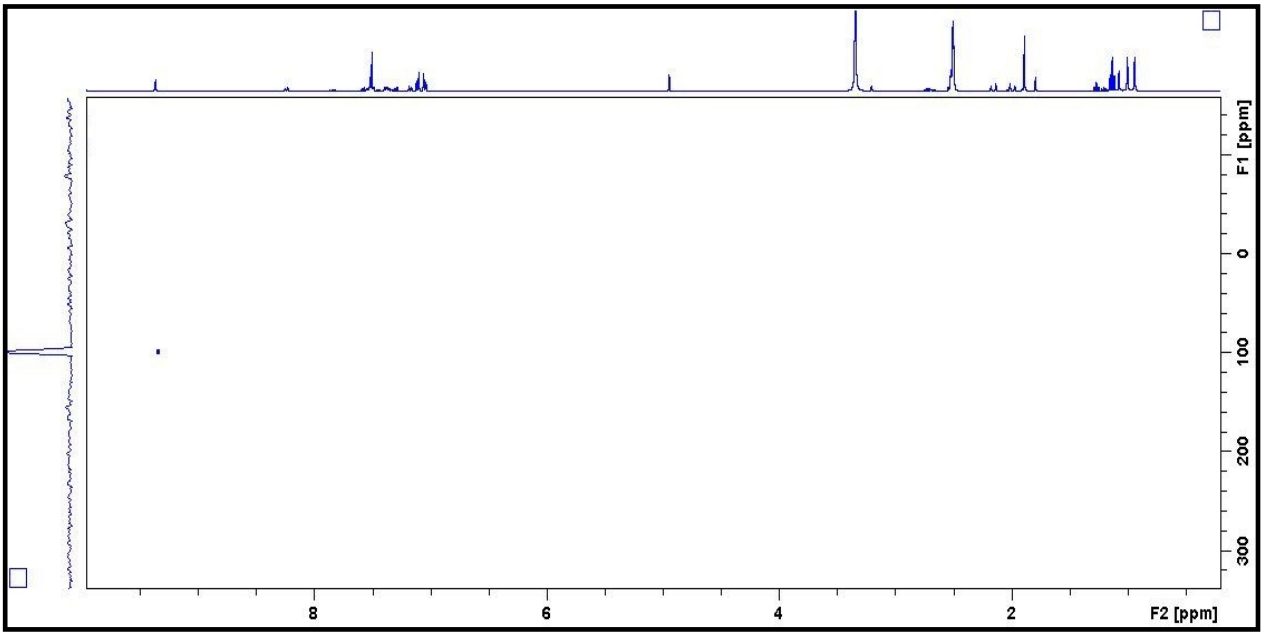
HRMS spectra of compound **4g**



^{1}H NMR spectra of compound **4h**



^{13}C NMR spectra of compound 4h

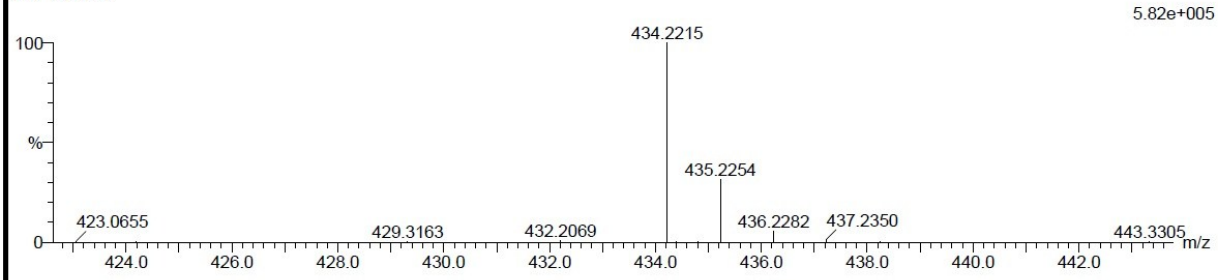


^{15}N NMR spectra of compound **4h**

Elemental Composition Report **Page 1**

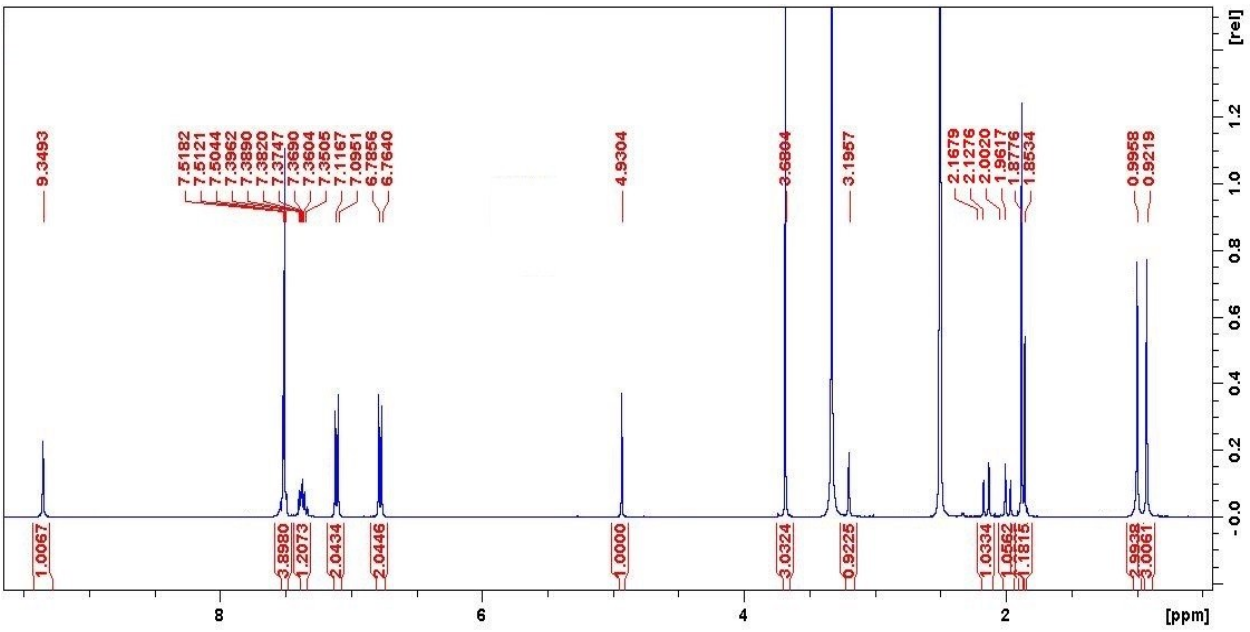
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 25-30 N: 0-5 O: 1-5 Na: 1-1
FP-16 49 (1.619) Cm (1:61)
TOF MS ES+

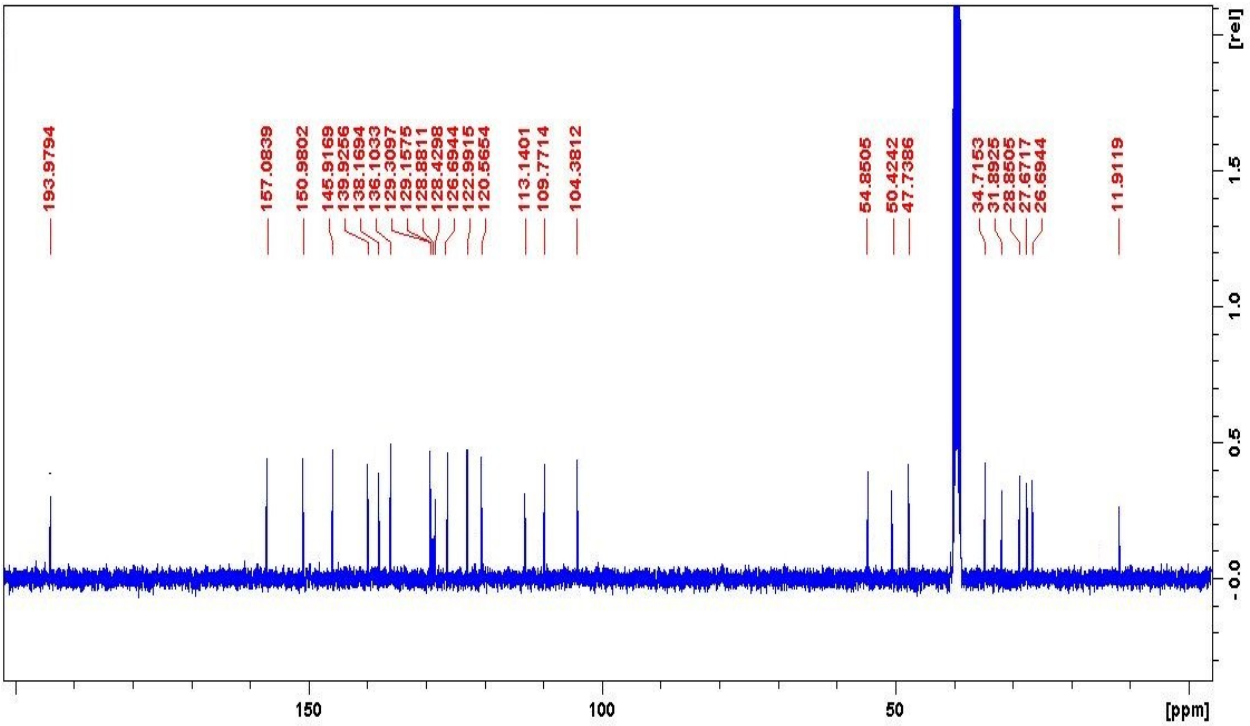


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
434.2215	434.2208	0.7	1.6	14.5	47.0	0.0	C27 H29 N3 O Na

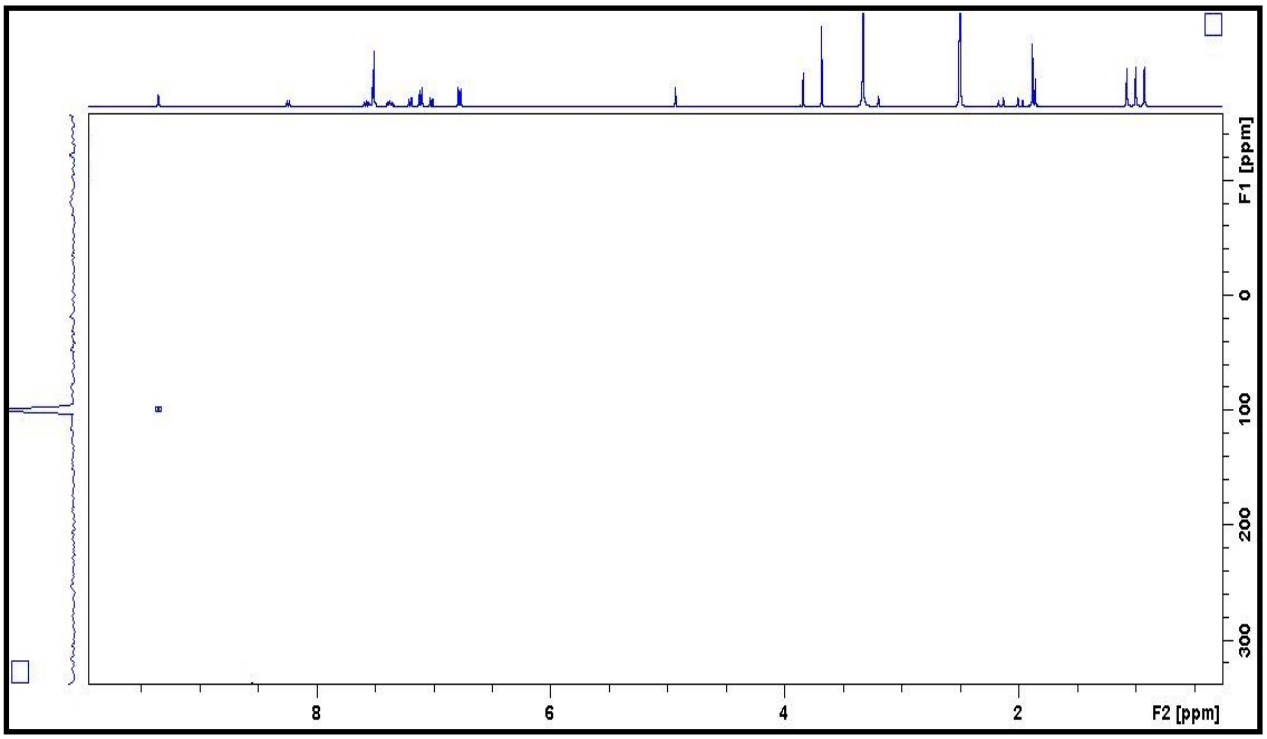
HRMS spectra of compound **4h**



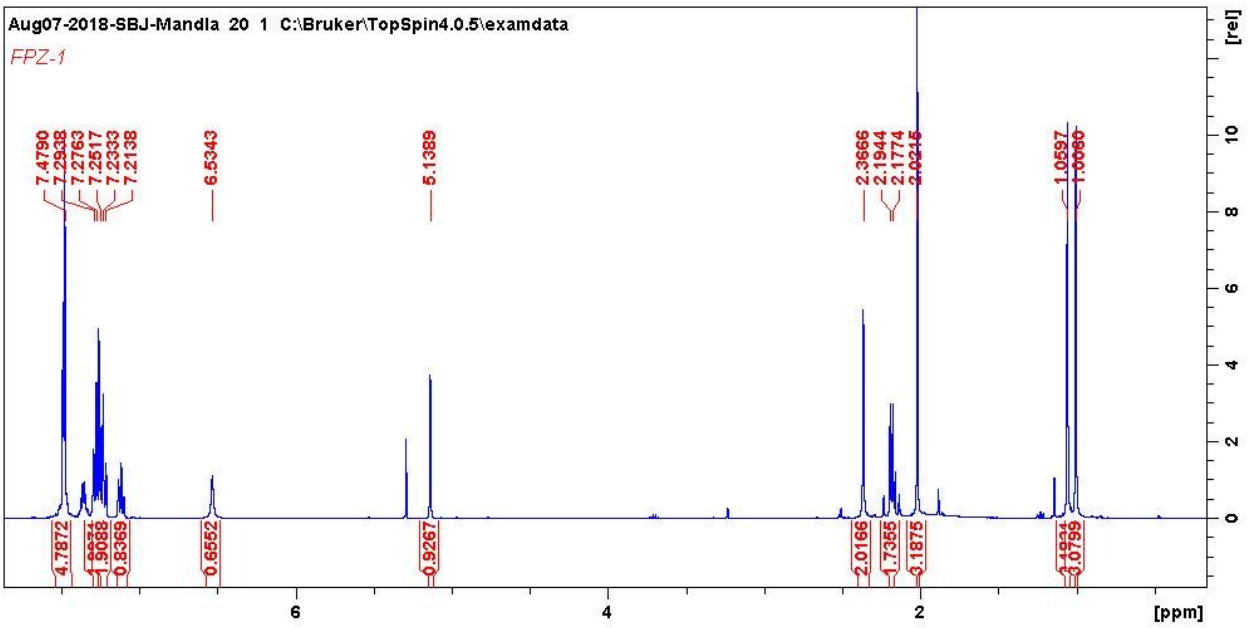
^{1}H NMR spectra of compound **4i**



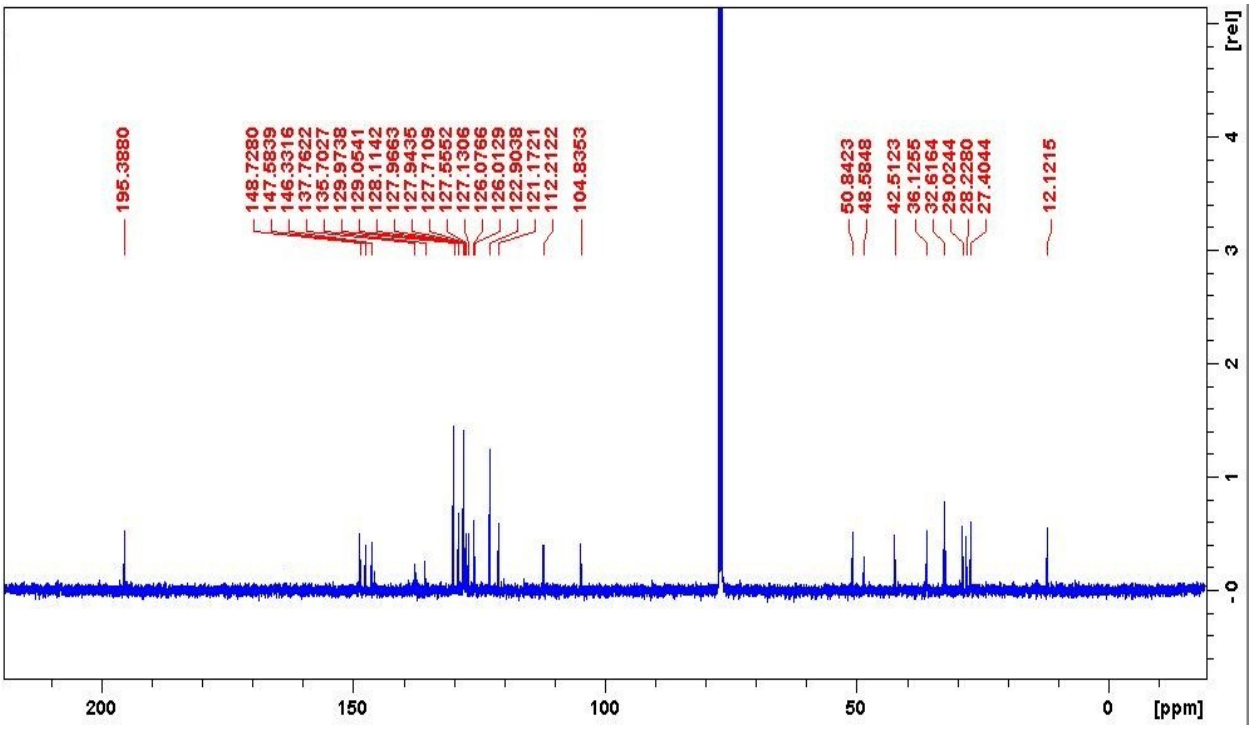
^{13}C NMR spectra of compound 4i



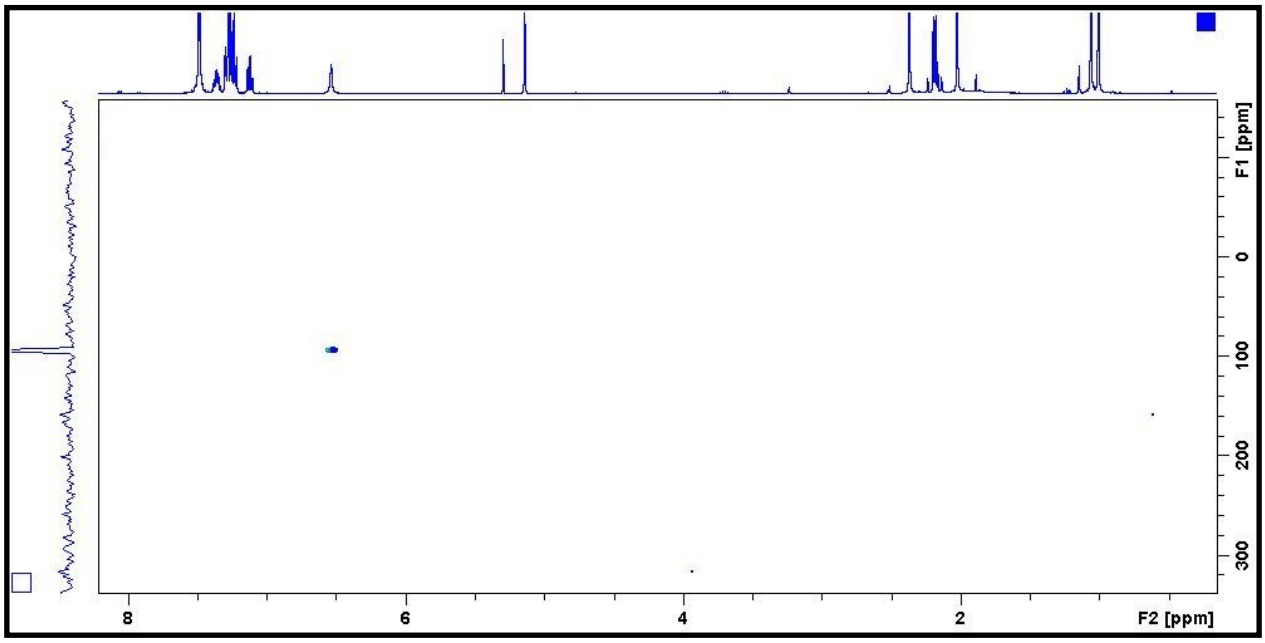
^{15}N NMR spectra of compound **4i**



^{1}H NMR spectra of compound 4**j**



^{13}C NMR spectra of compound 4j



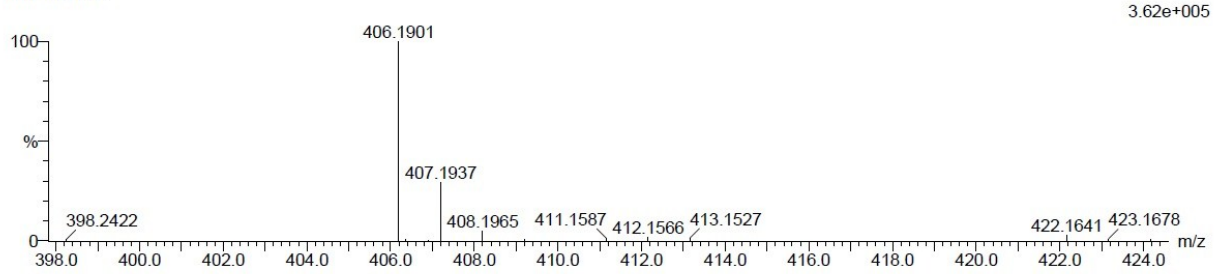
^{15}N NMR spectra of compound 4**j**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

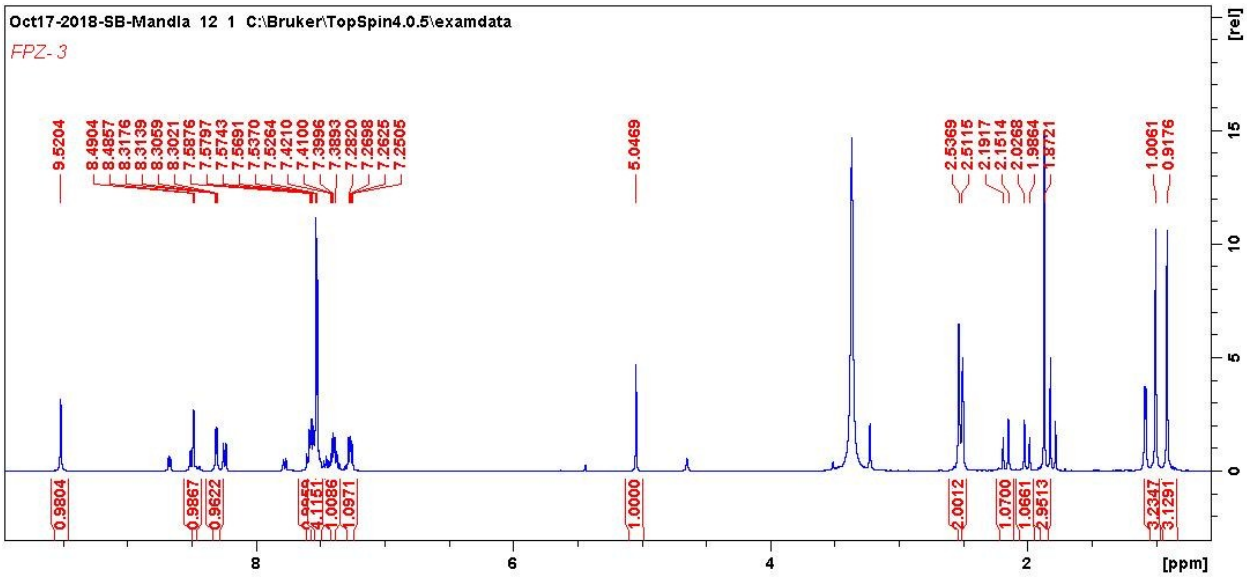
Monoisotopic Mass, Even Electron Ions
71 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 20-25 H: 20-25 N: 0-5 O: 0-5 Na: 0-1 Br: 0-1

FP-11 59 (1.956) Cm (1:61)
TOF MS ES+

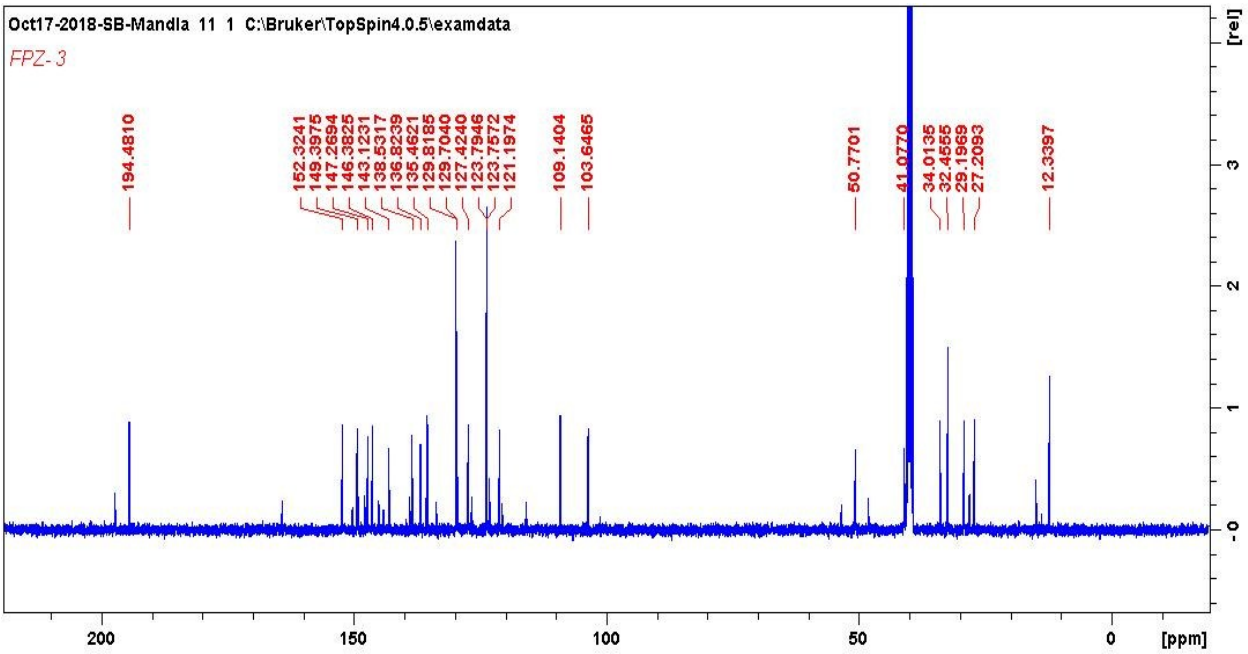


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
406.1901	406.1895	0.6	1.5	14.5	41.4	0.0	C25 H25 N3 O Na

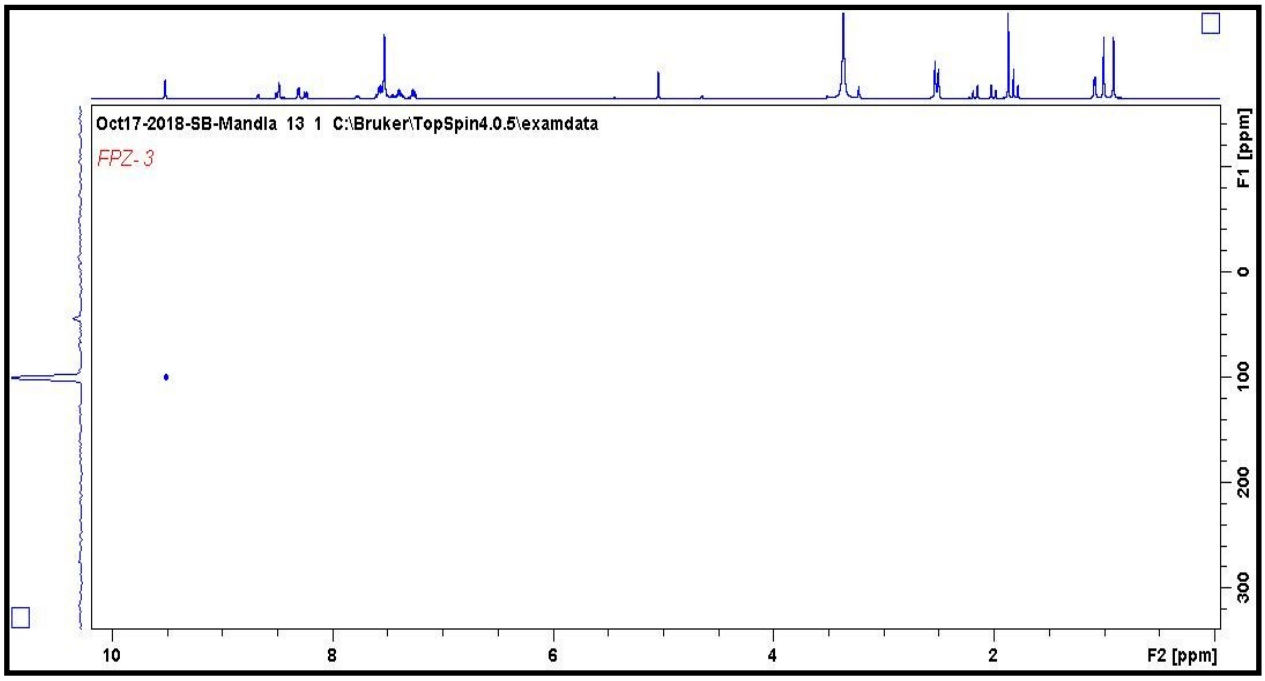
HRMS spectra of compound **4j**



^{1}H NMR spectra of compound 4**k**



^{13}C NMR spectra of compound 4k

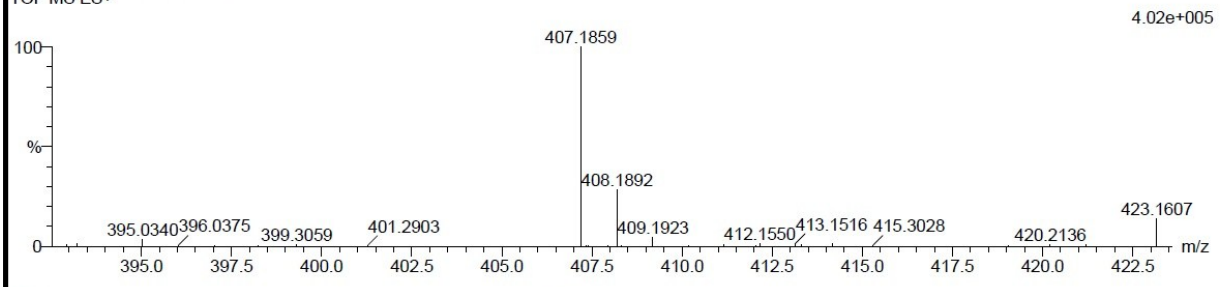


^{15}N NMR spectra of compound 4**k**

Elemental Composition Report **Page 1**

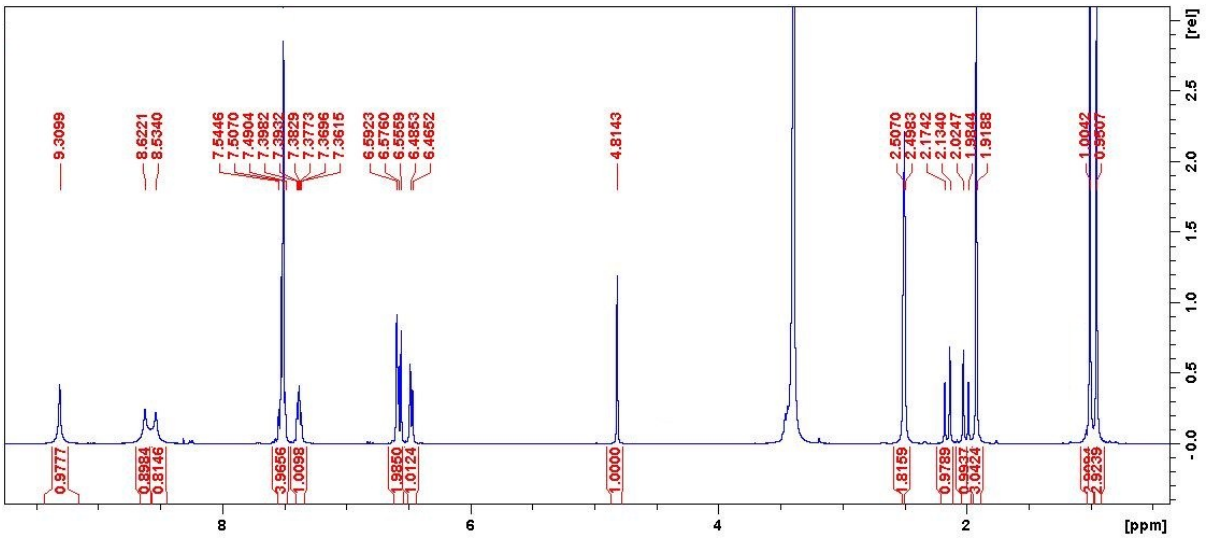
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 20-25 H: 20-25 N: 0-5 O: 0-5 Na: 1-1
FP-21 26 (0.843) Cm (1:61)
TOF MS ES+

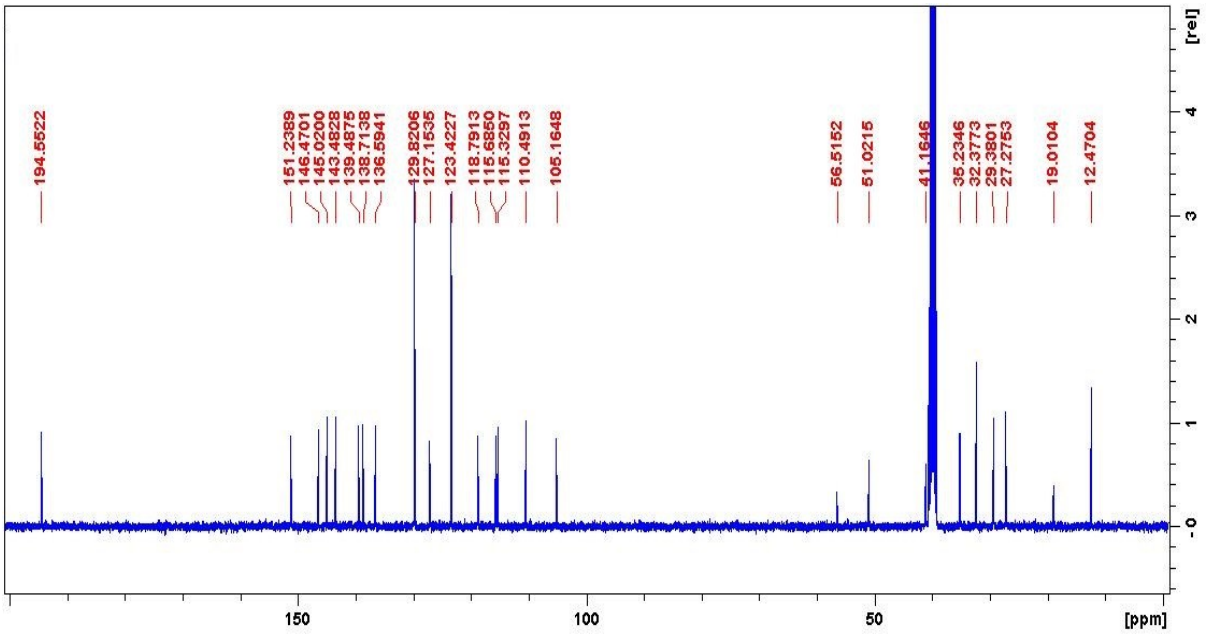


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
407.1859	407.1848	1.1	2.7	14.5	72.6	0.0	C24 H24 N4 O Na

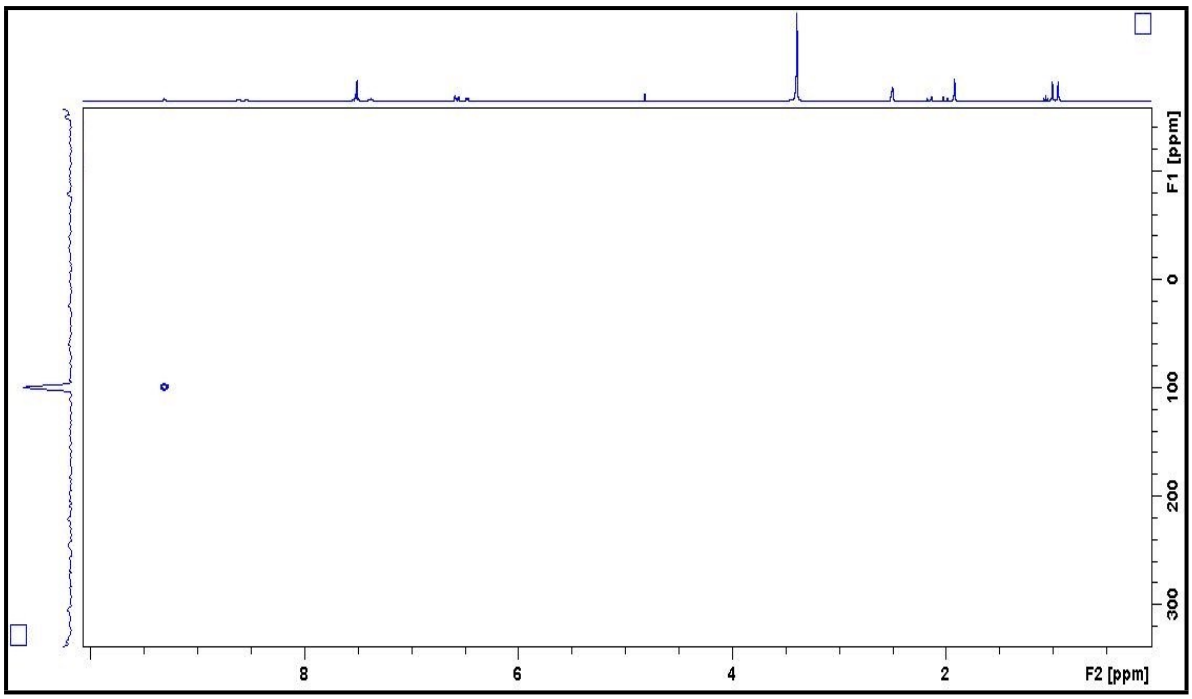
HRMS spectra of compound **4k**



^{1}H NMR spectra of compound 4l



^{13}C NMR spectra of compound 4l



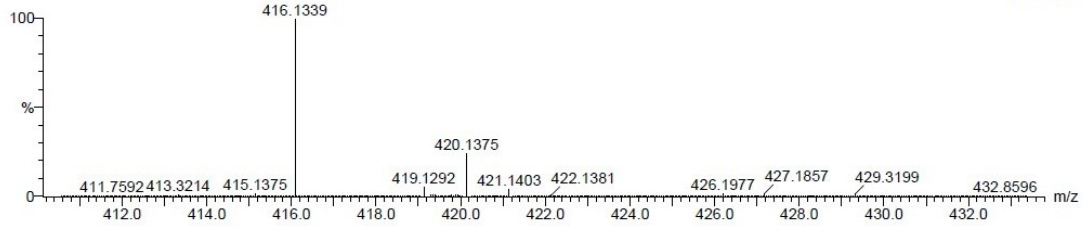
^{15}N NMR spectra of compound 4l

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

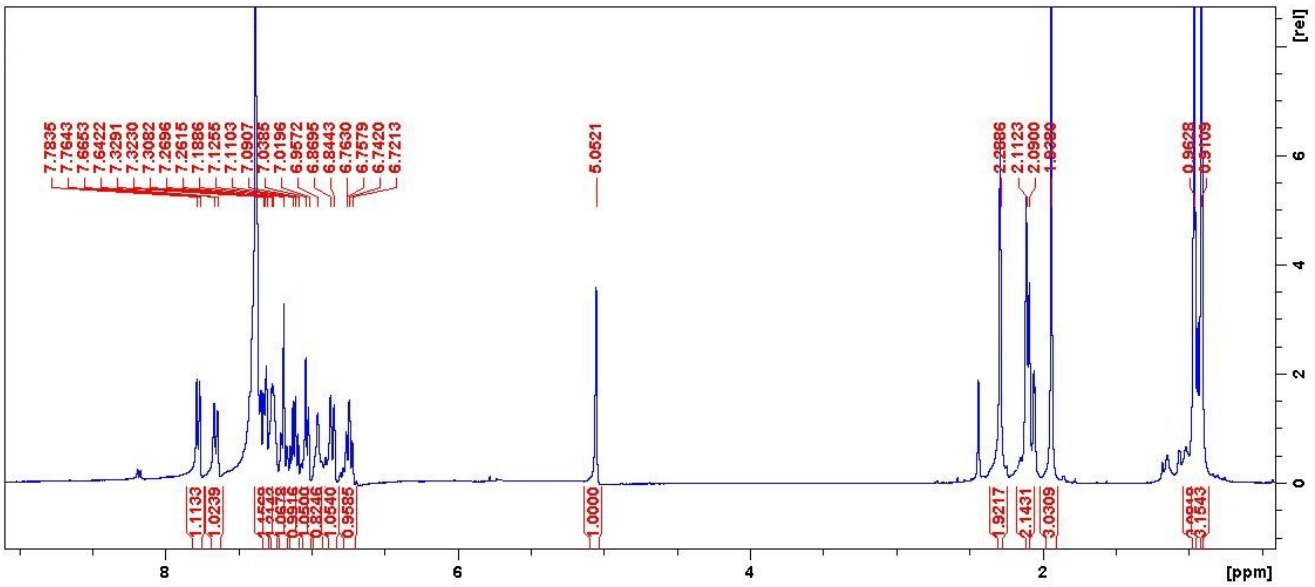
Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 20-25 H: 25-30 N: 0-5 O: 0-5
R1 13 (0.422) Cm (1:58)
TOF MS ES+

7.31e+004

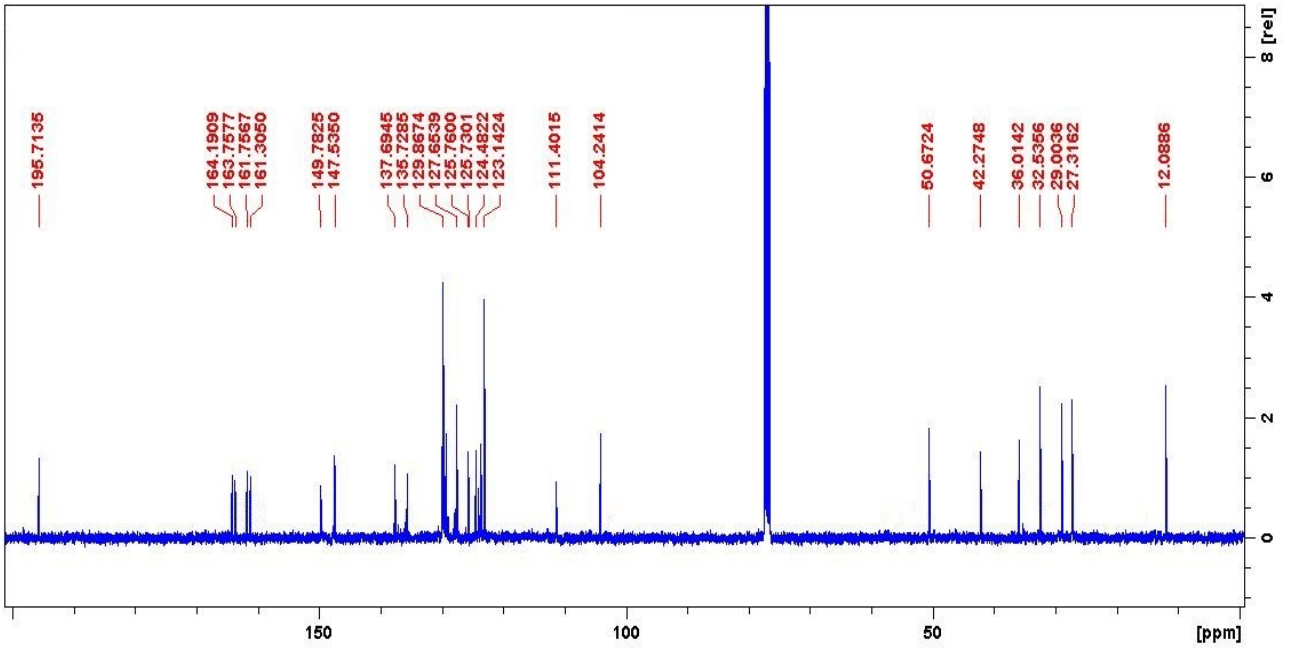


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
416.1339	416.1331	0.8	1.9	12.5	495.7	0.0	C25 H26 N3 O3

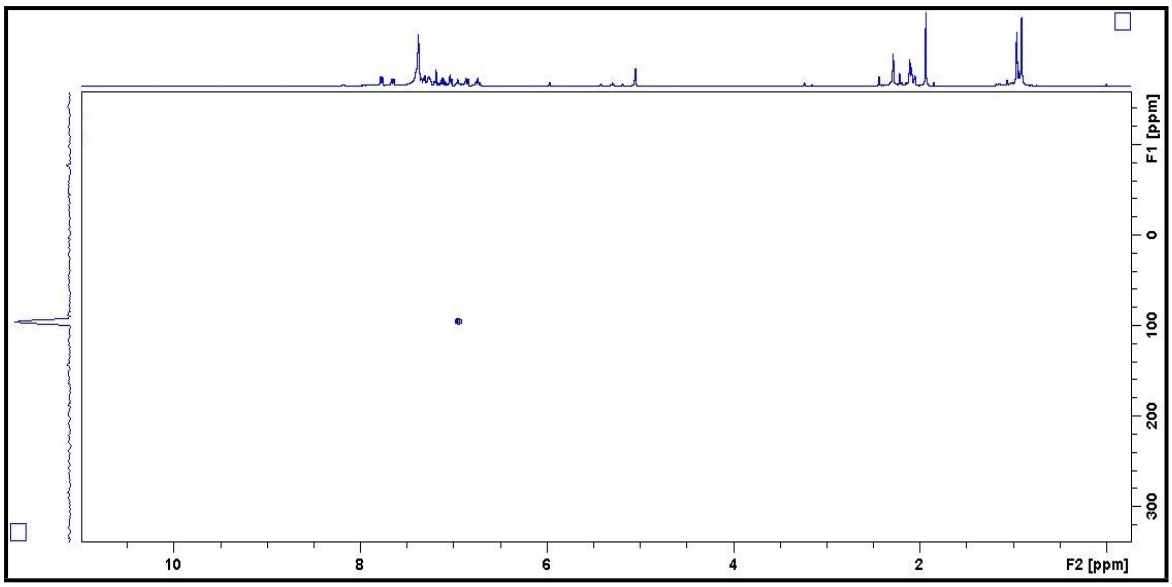
HRMS spectra of compound **4l**



^{1}H NMR spectra of compound 4m



^{13}C NMR spectra of compound 4m



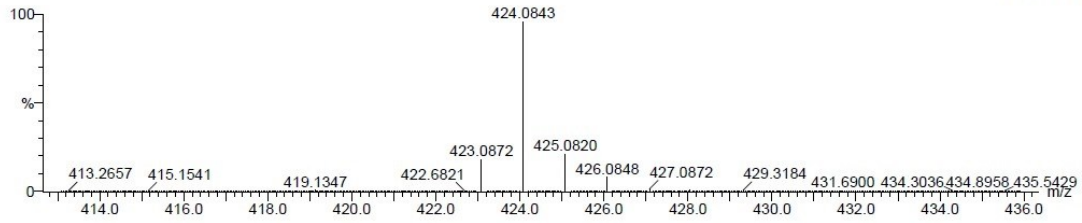
^{15}N NMR spectra of compound 4m

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

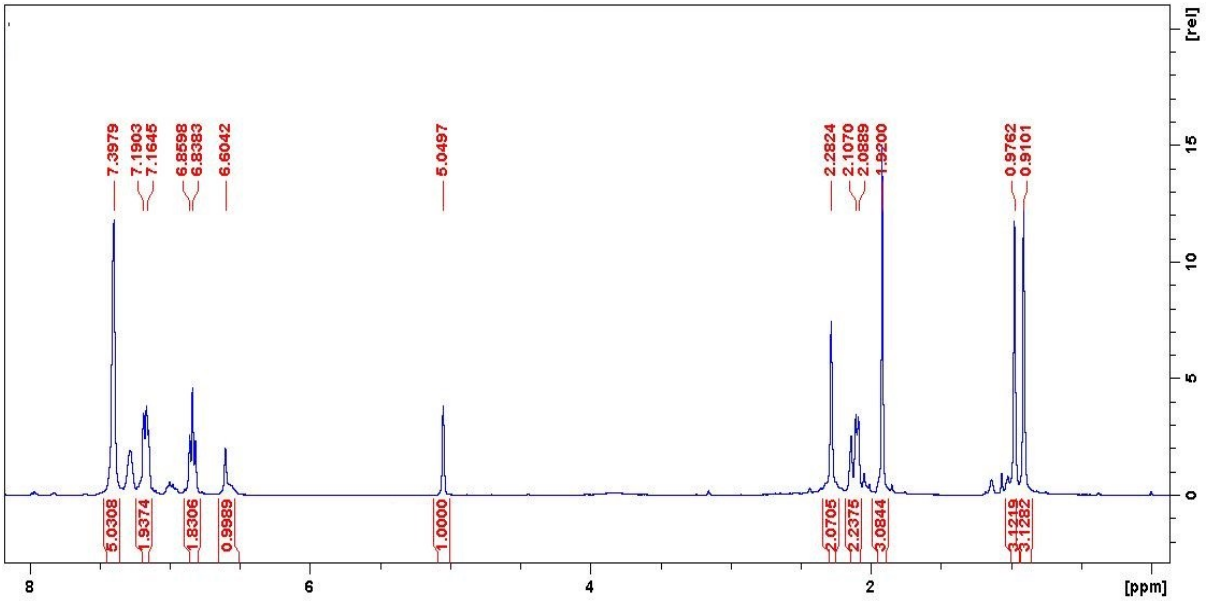
Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 1-5 F: 1-5 Na: 1-1
R1 2 (0.035) Cm (1:58)
TOF MS ES+

1.53e+005

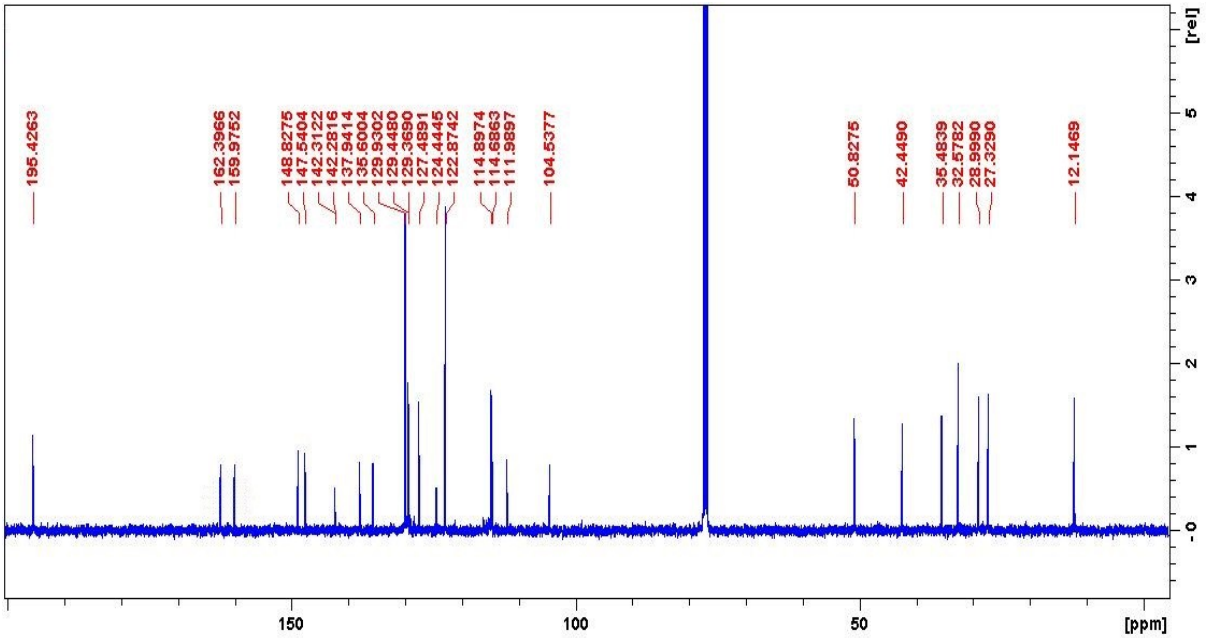


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
424.0843	424.0836	0.7	1.7	12.5	549.6	0.0	C25 H24 N3 O F Na

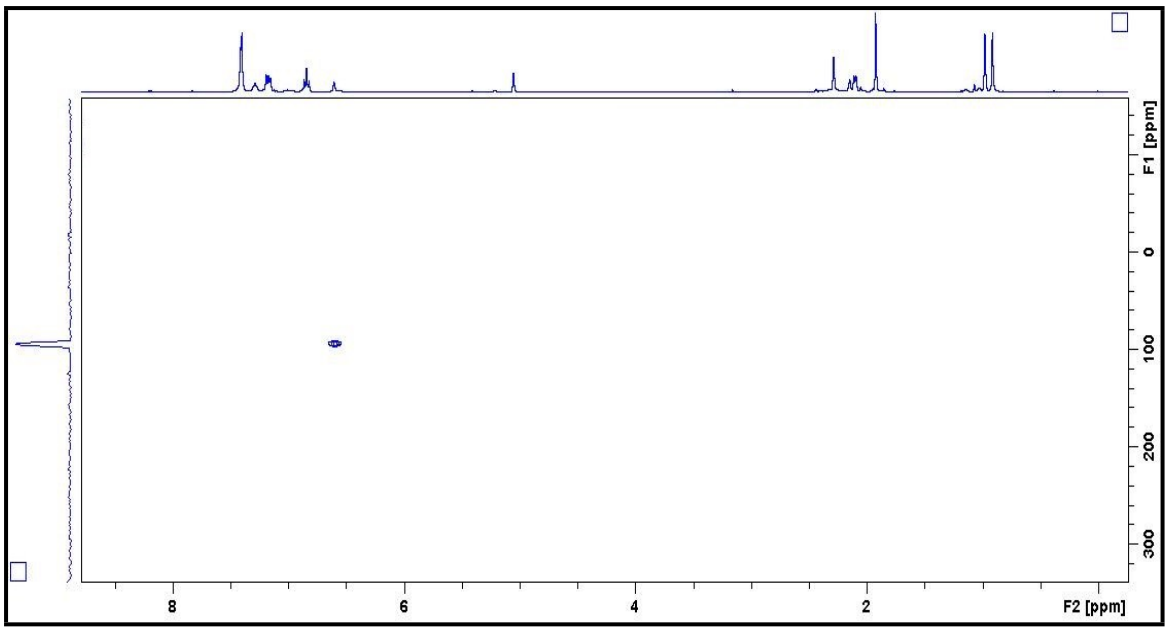
HRMS spectra of compound **4m**



^{1}H NMR spectra of compound 4n



^{13}C NMR spectra of compound 4n

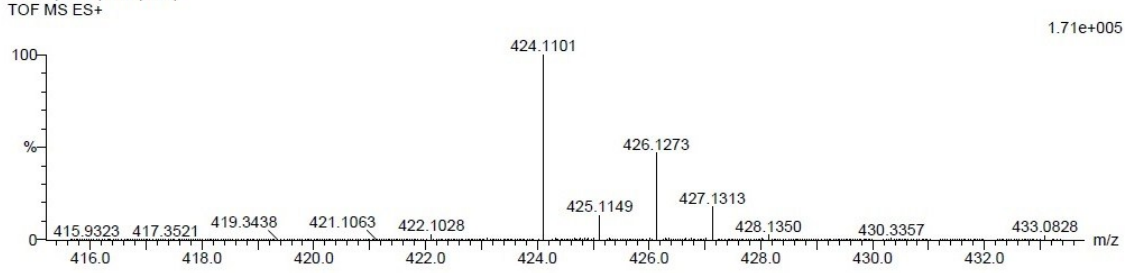


^{15}N NMR spectra of compound 4n

Elemental Composition Report Page 1

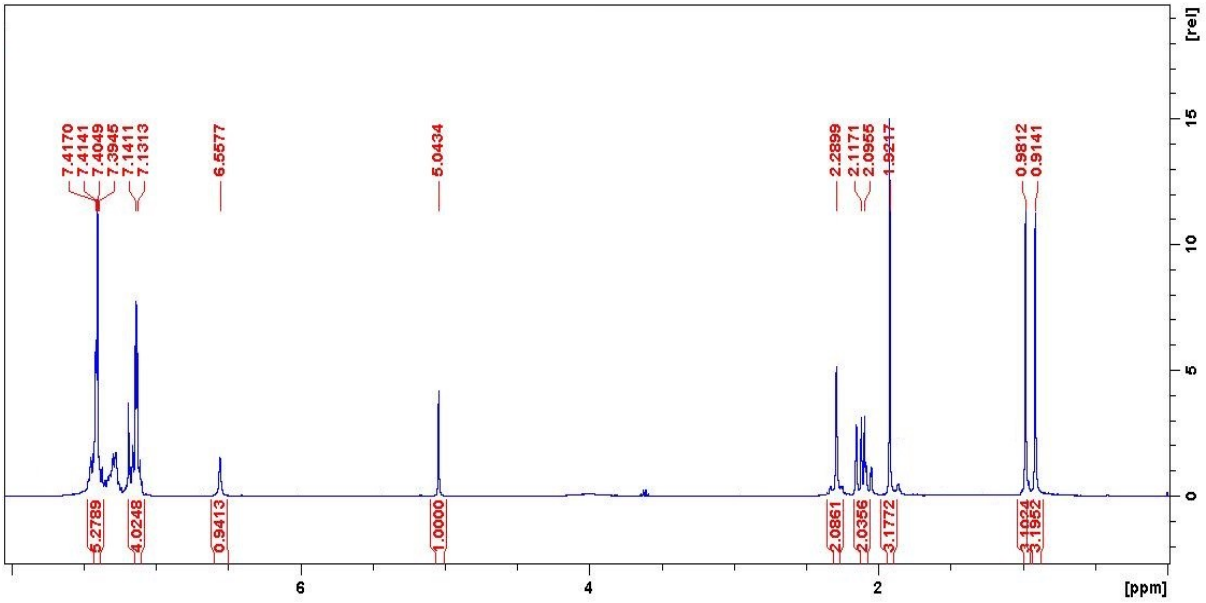
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
18 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 1-5 F: 1-5 Na: 1-1
F9 5 (1.484) Cm (1:61)
TOF MS ES+

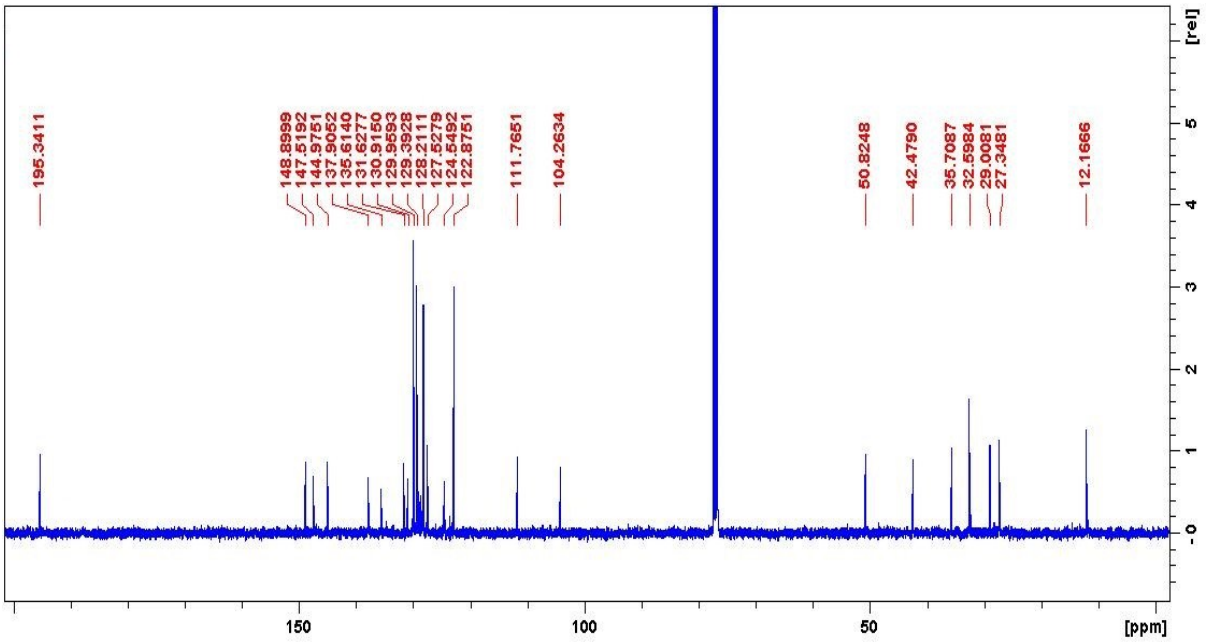


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
424.1101	424.1109	-0.8	-1.9	15.5	620.1	0.0	C25 H24 N3 O F Na

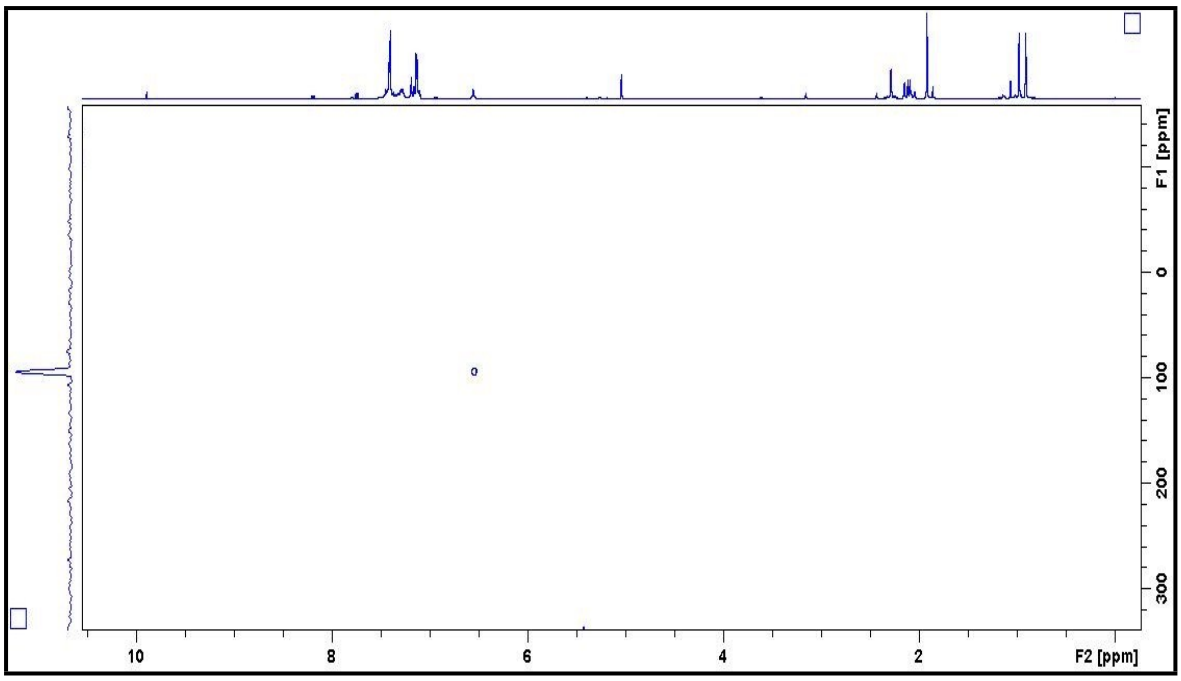
HRMS spectra of compound **4n**



^{1}H NMR spectra of compound 4o



^{13}C NMR spectra of compound 4o



^{15}N NMR spectra of compound 4o

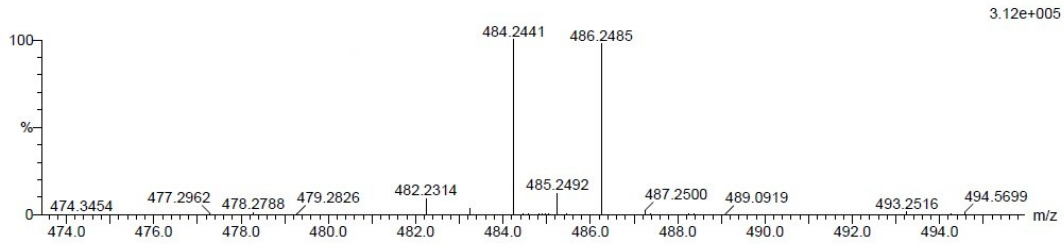
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
432 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 0-5 Br: 0-1 Na: 1-1

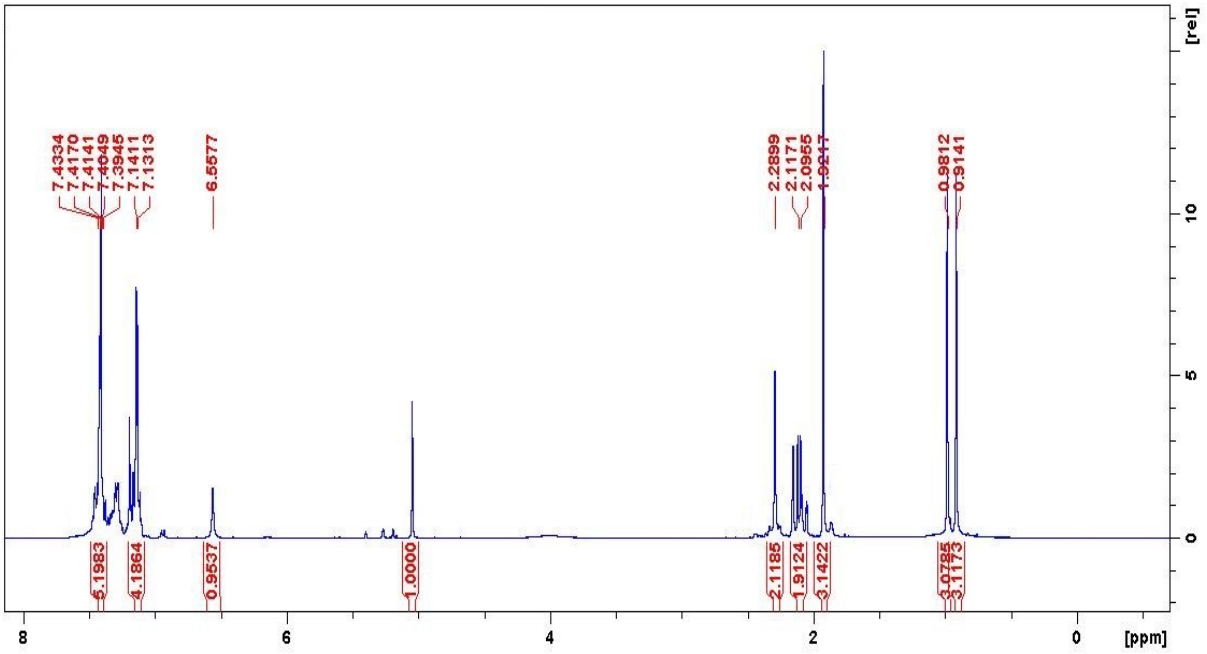
F2 4 (0.100) Cm (1:61)
TOF MS ES+

3.12e+005

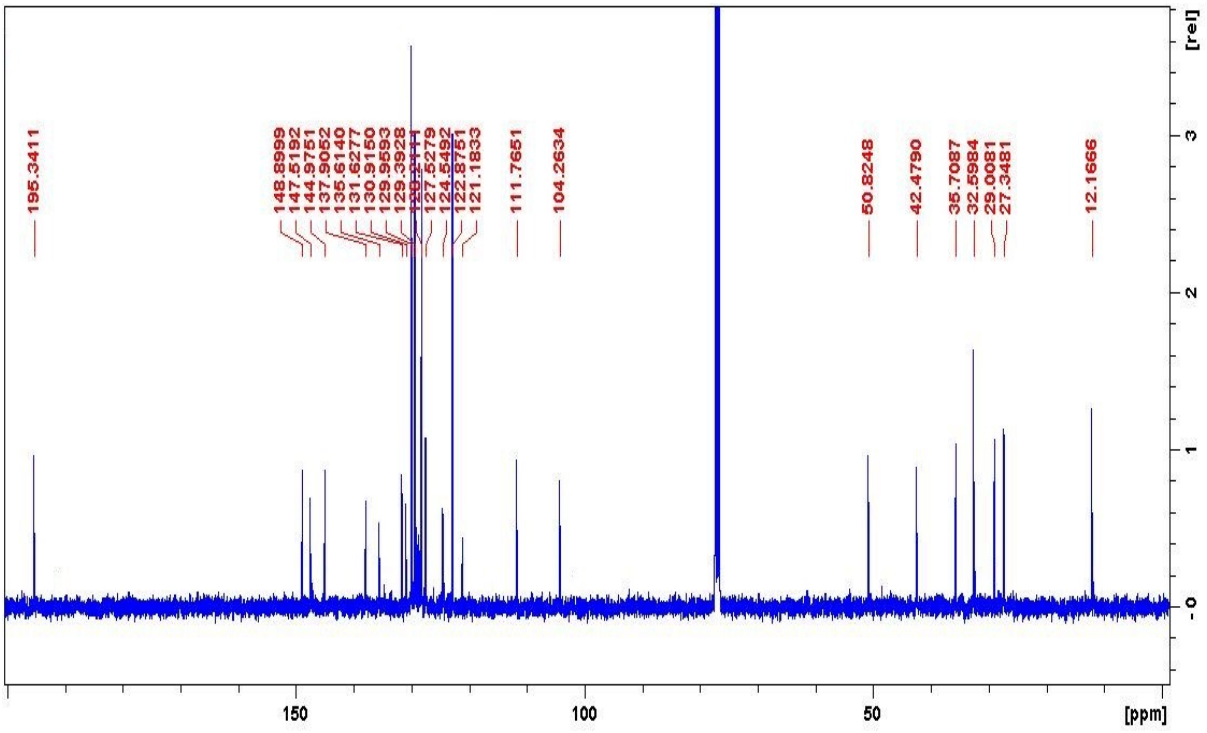


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
484.2441	484.2445	-0.4	-0.8	7.5	600.7	0.0	C25 H24 N3 O Br Na

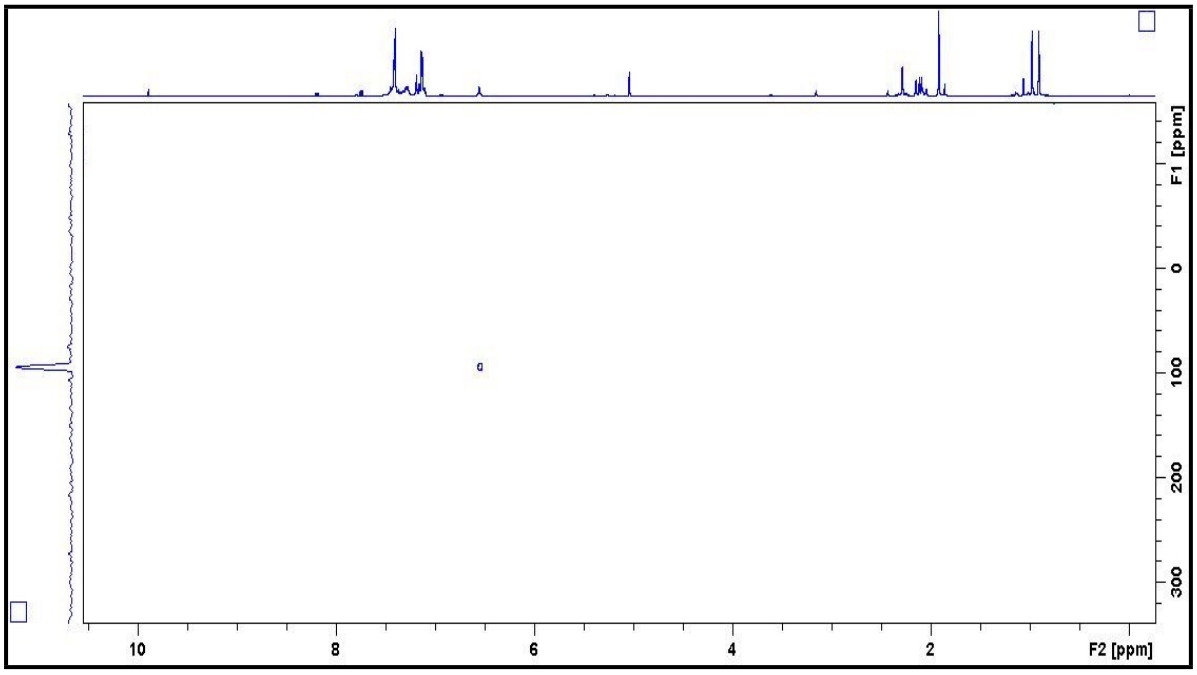
HRMS spectra of compound **4o**



^{1}H NMR spectra of compound 4p



^{13}C NMR spectra of compound 4p



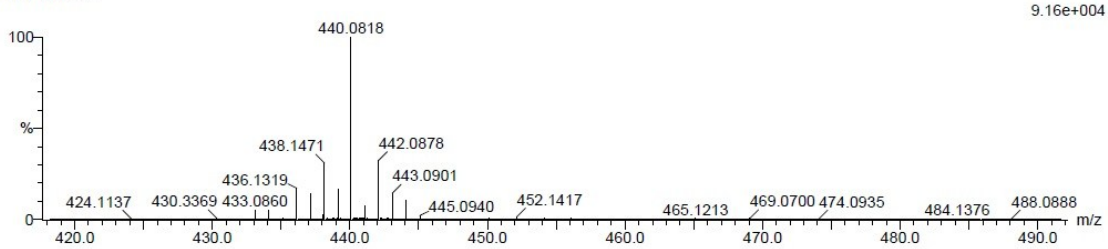
^{15}N NMR spectra of compound 4p

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

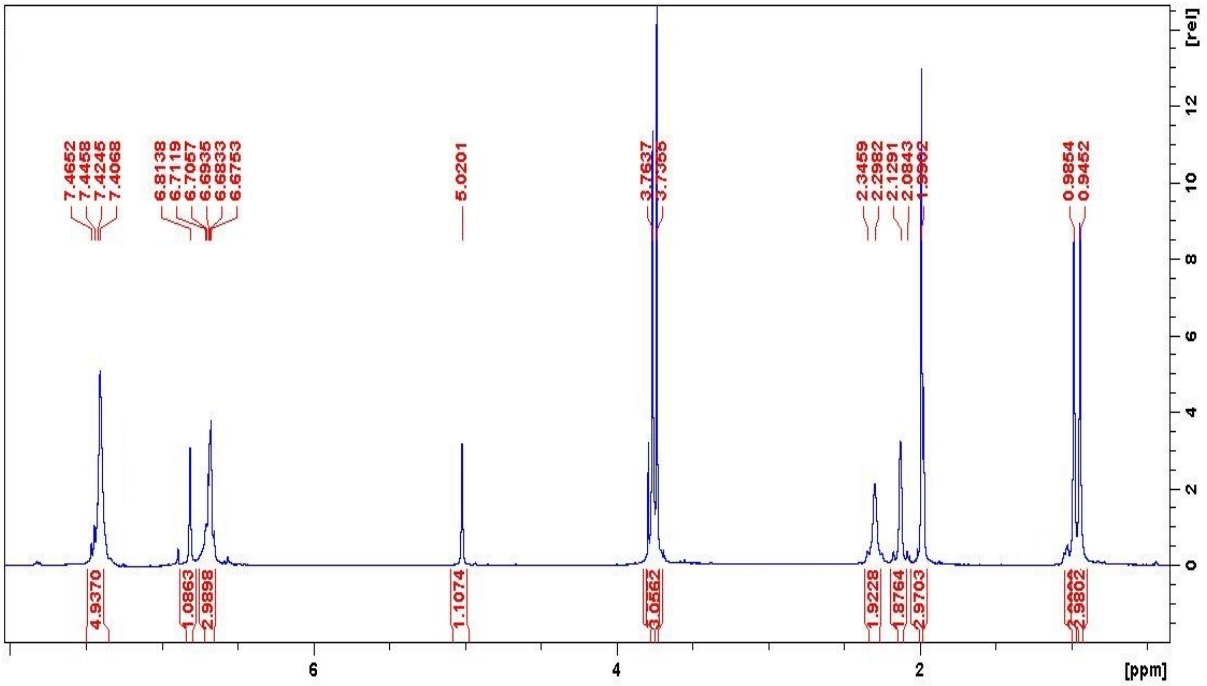
Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 25-30 H: 20-25 N: 0-5 O: 0-5 Cl: 0-1 Na: 1-1
F2 2 (0.034) Cm (1:61)
TOF MS ES+

9.16e+004

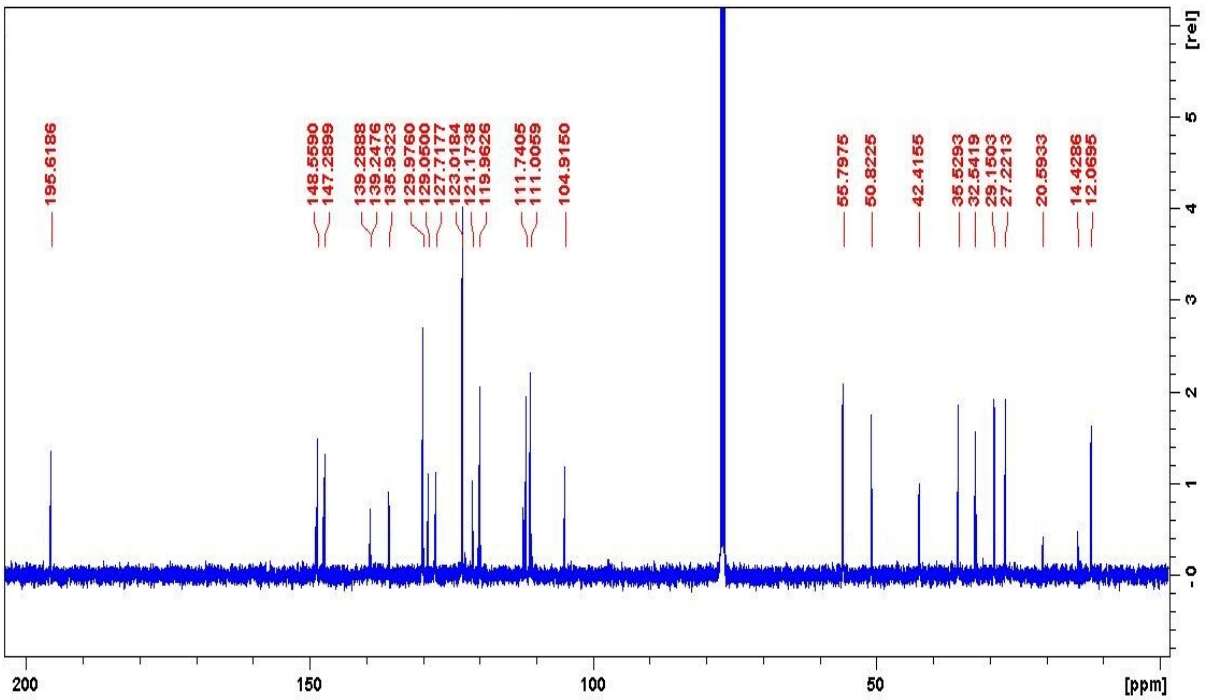


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
440.0818	440.0813	0.5	1.1	15.5	569.5	0.0	C25 H24 N3 O Cl Na

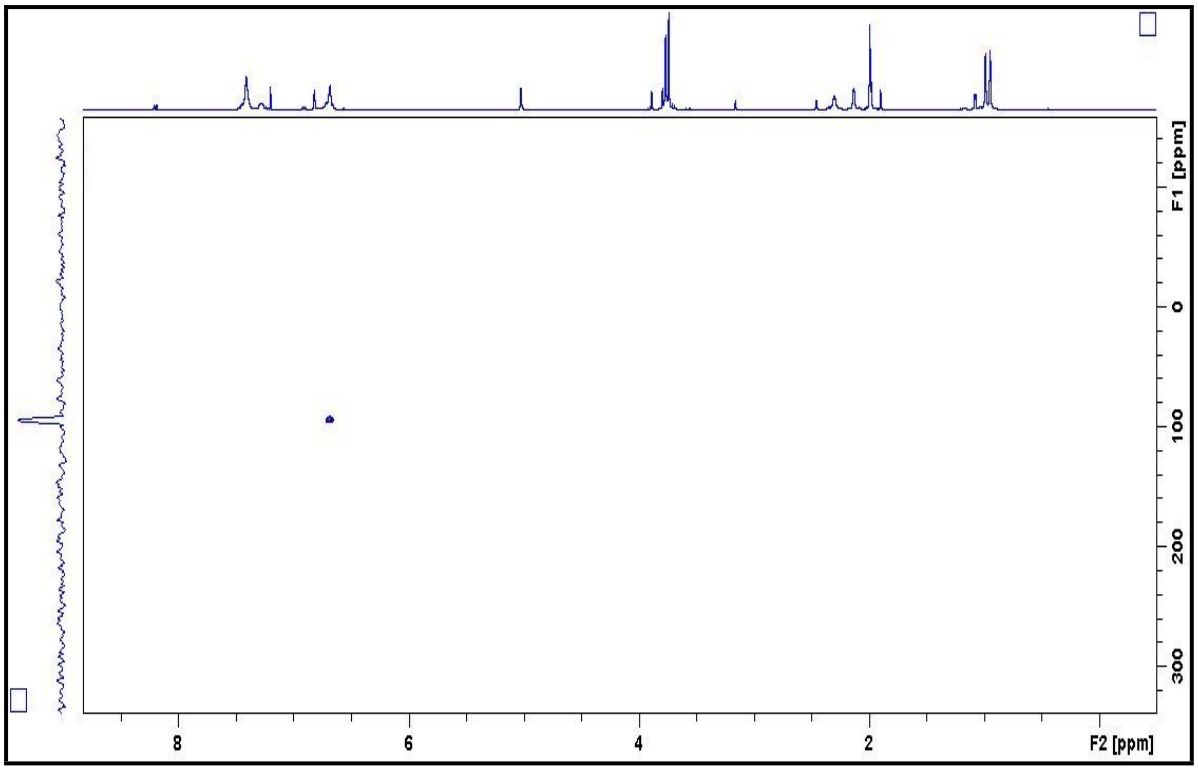
HRMS spectra of compound **4p**



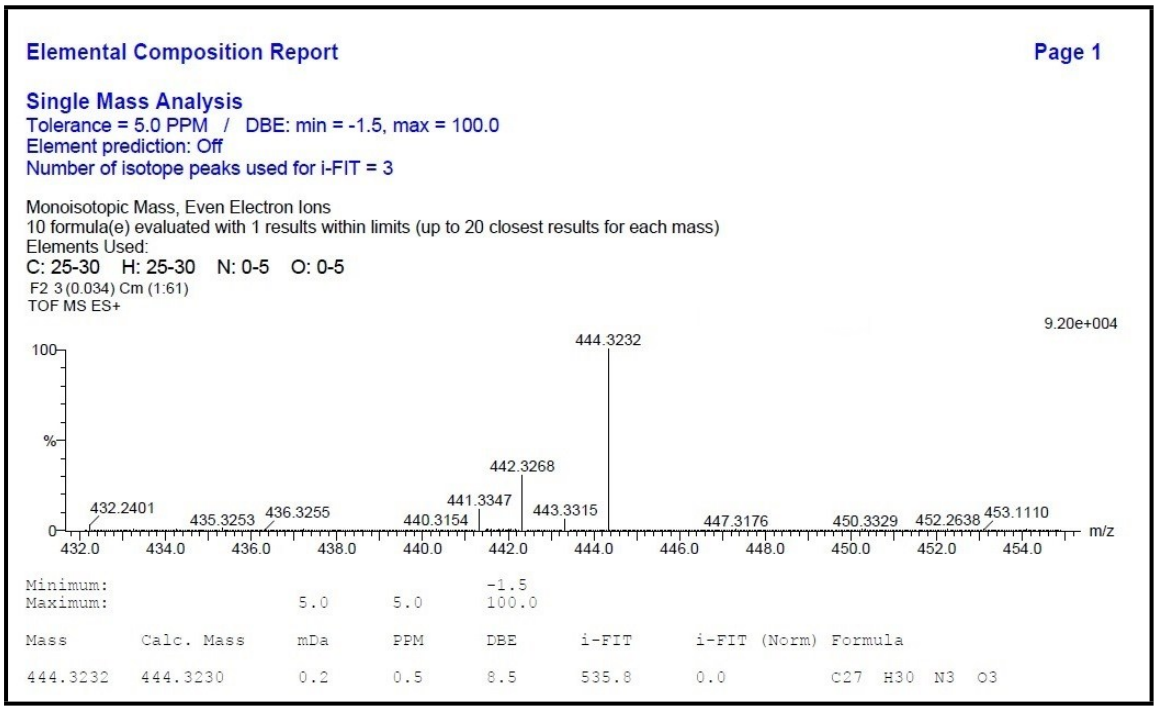
^{1}H NMR spectra of compound 4q



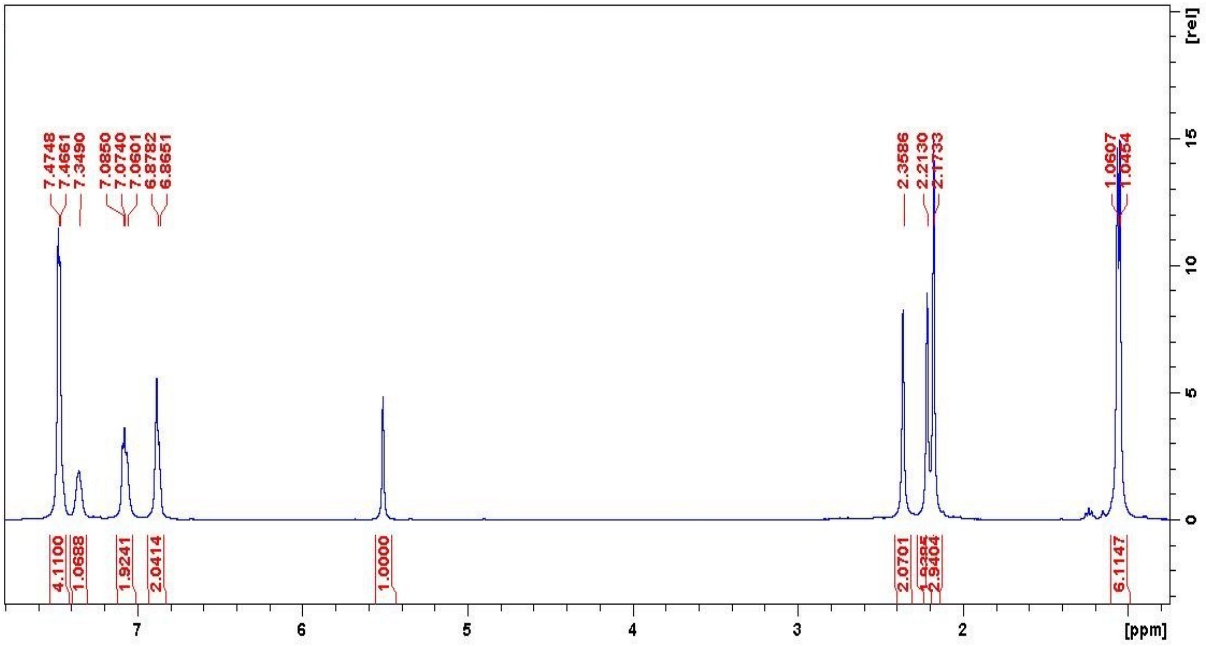
^{13}C NMR spectra of compound 4q



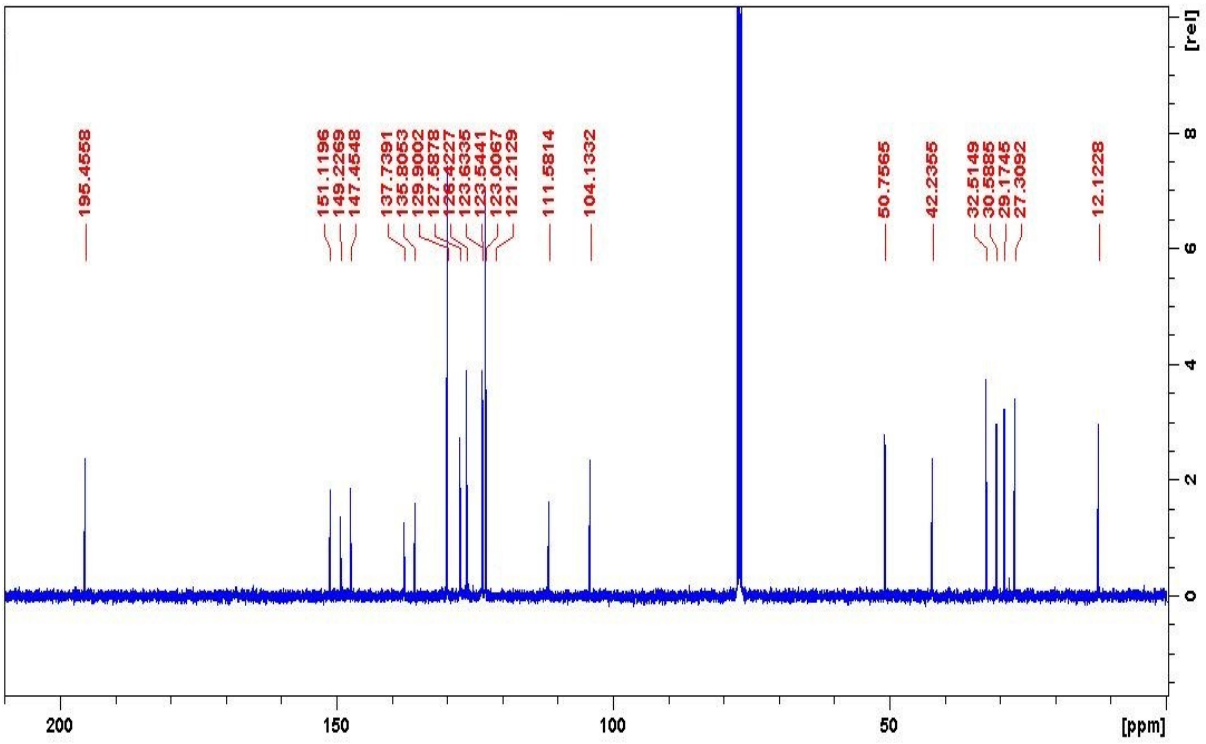
^{15}N NMR spectra of compound 4q



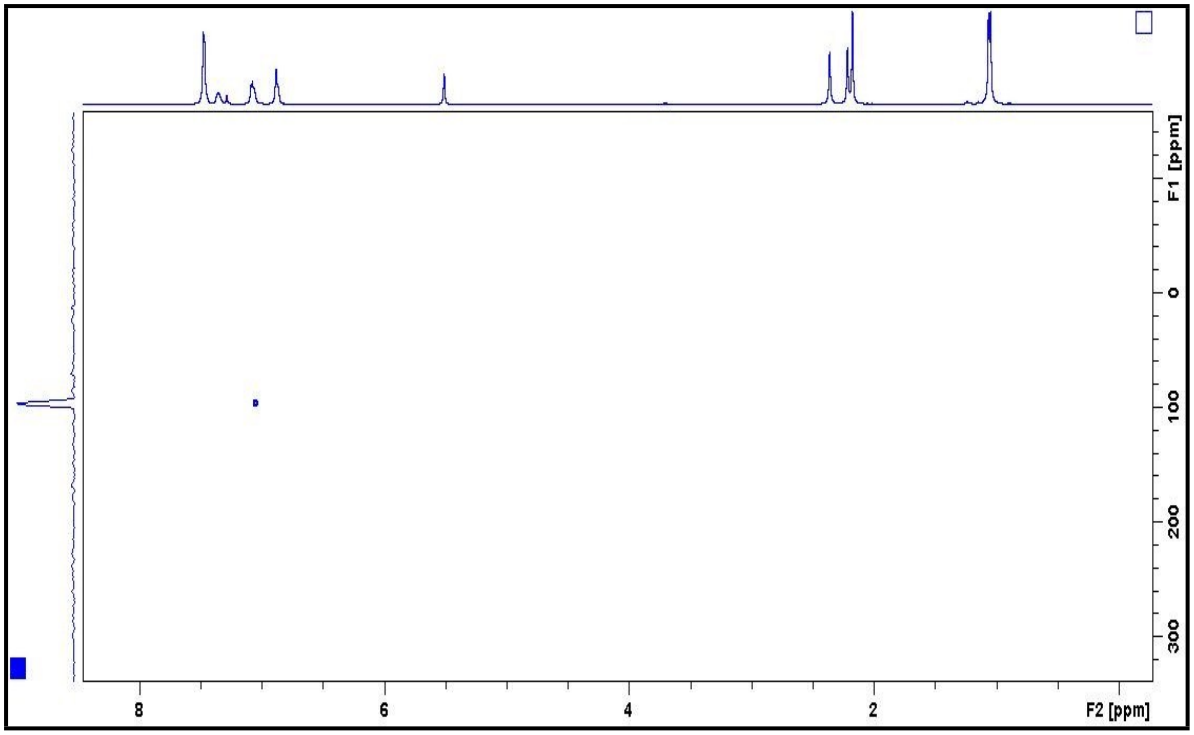
HRMS spectra of compound **4q**



^{1}H NMR spectra of compound 4r



^{13}C NMR spectra of compound 4r



^{15}N NMR spectra of compound 4r