Imposed hydrophobic interactions by NaCl: Accountable attribute for the synthesis of spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole] derivatives *via* 1,3-dipolar cycloaddition reaction in aqueous medium

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General

All the chemicals used were of research grade (purchased from Sigma Aldrich and Acros) and used without further purification. The melting points of all compounds were determined on a Toshniwal apparatus in capillary and uncorrected. IR spectra were recorded on a Shimadzu FT IR- 8400S spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as an internal standard on a Bruker spectrophotometer at 400 and 75 MHz respectively. Chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectrum of representative compound was recorded on Shimadzu GC-MS-QP-2010 spectrometer and Waters-Xeevo G_2S Q-Tof. X-ray intensity data were collected on Bruker Kappa Apex II diffractometer.

General procedure for the synthesis of spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole] 4

An equimolar appropriate mixture of acenaphthenequinone **1** (1 mmol), 1,3-thiazoles-4-carboxylic acid **2** (1 mmol) and Knoevenagel adduct **3a-n** (1 mmol) and 10 mol% sodium chloride in 20 ml water were mixed and stirred at 80 °C for the appropriate time (25–35 min). The progress of the reaction was monitored by TLC. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature, the water was decanted off, and the solid precipitates were crystallized (if required) to furnish pure

spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole] derivatives. All the synthesized compounds were well characterized by ^{1}H NMR, ^{13}C NMR, Mass and single crystal X-ray analysis

Spectral data of synthesized compounds:

Ethyl 6′-cyano-7′-phenyl-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4a)

Mp: 190-192 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1756 (C=O), 1738 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 1.30 (t, *J* = 8 Hz, 3H, CH_3), 3.19-3.31 (m, 1H, CH_2), 3.34-3.48 (m, 2H, OCH_2), 3.55-3.58 (m, 1H, CH) 3.96 (d, *J* = 10.8 Hz, 2H, *N*–CH_2), 4.49 (d, *J* = 10.4 Hz, 1H, CH), 4.84 (t, *J* = 7.2 Hz, 1H, CH), 7.51-8.52 (m, 11H, ArH); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 11.87, 35.85, 53.32, 53.97, 62.33, 63.24, 70.97, 79.10 (spiro C), 114.48, 122.23, 126.29, 127.03, 127.93, 128.26, 128.46, 128.55, 130.05, 130.16, 130.27, 132.64, 133.56, 141.66, 163.05 (C=O), 199.31 (C=O); MS m/z: 455 $[M+H]^+$ for $C_{27}H_{22}N_2O_3S$.

Ethyl 6′-cyano-7′-(4-methylphenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4b)

Mp: 206-208 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2242 (C≡N), 1758 (C=O), 1732 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 1.19 (s, 3H, CH_3), 1.36 (t, *J* = 7.2 Hz, 3H, CH_3), 2.05-2.55 (m, 2H, CH_2), 3.19-3.40 (m, 1H, CH), 3.51 (d, *J* = 8.8 Hz, 1H, CH), 3.65-3.68 (m, 2H, OCH_2), 3.95 (d, *J* = 9.2 Hz, 1H, *N*–CH_2), 4.34-4.39 (m, 1H, CH), 7.27-8.43 (m, 10H, ArH); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 11.88, 12.46, 20.28, 36.56, 51.07, 55.53, 62.24, 66.37, 71.42, 76.68, 78.14 (spiro C), 115.74, 122.32, 126.61, 128.36, 128.53, 128.74, 128.84, 128.96, 129.11, 129.94, 130.15, 131.26, 132.85, 134.23, 141.47, 162.99 (C=O), 202.93 (C=O); MS m/z: 469 $[M+H]^+$ for $C_{28}H_{24}N_2O_3S$.

Ethyl 6′-cyano-7′-(4-fluorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4c)

Mp: 202-204 °C; IR (KBr, ν_{max}, cm^{-1}): 2248 (C≡N), 1760 (C=O), 1730 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.20 (t, *J* = 8 Hz, 3H, CH_3), 3.21-3.34 (m, 3H, CH_2), 3.38-3.54 (m, 2H, OCH_2), 3.96 (d, *J* = 10.8 Hz, 1H, *N*–CH_2), 4.54 (d, *J* = 10.0 Hz, 2H, CH), 4.84 (d, *J* = 7.6 Hz, 1H, CH), 7.39-8.54 (m, 10H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 17.09, 40.87, 57.58, 57.75, 58.03, 59.10, 59.25, 67.63, 68.37, 68.92, 76.21 (spiro C), 84.18, 119.59, 120.44, 127.52, 131.38, 131.57, 132.31, 133.17, 133.81, 134.94, 135.21, 137.38, 146.94, 166.17, 168.88 (C=O), 204.55 (C=O); MS m/z: 473 $[M+H]^+$ for $C_{27}H_{21}FN_2O_3S$.

Ethyl 6′-cyano-7′-(2,4-dichlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4d)

Mp: 209-211 °C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1750 (C=O), 1735 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.28 (t, *J* = 7.2 Hz, 3H, CH_3), 3.09-3.21 (m, 2H, CH_2), 3.28-3.45 (m, 2H, OCH_2), 3.54-3.61 (m. 1H, CH_2), 3.84 (d, *J* = 10.4 Hz, 1H, *N*–CH_2), 4.24 (d, *J* = 9.2 Hz, 2H, CH), 4.71 (t, *J* = 8.0 Hz, 1H, CH), 7.54-8.26 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d6) δ: 12.91, 21.16, 38.54, 45.20, 52.37, 58.52, 59.76, 70.98, 78.43 (spiro C), 114.25, 121.51, 126.58, 126.94, 127.11, 128.33, 128.46, 129.08, 129.49, 130.81, 131.14, 132.53, 133.20, 133.64, 137.39, 141.28, 169.64 (C=O), 199.69 (C=O); MS m/z: 523 $[M+H]^+$ for $C_{27}H_{20}Cl_2N_2O_3S$.

Ethyl 6′-cyano-7′-(4-nitrophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4e)

Mp: 214-216 °C; IR (KBr, ν_{max}, cm^{-1}): 2248 (C≡N), 1755 (C=O), 1725 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.34 (t, *J* = 6.4 Hz, 3H, CH_3), 3.11-3.34 (m, 3H, CH_2), 3.38-3.49 (m, 2H, OCH_2), 3.96 (d, *J* = 10.8 Hz, 1H, *N*–CH_2), 4.71 (d, *J* = 10.4 Hz, 2H, CH), 4.91 (t, *J* = 9.6 Hz, 1H, CH), 7.91-8.53 (m, 10H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 11.78, 33.28, 35.58, 52.60, 53.81, 54.54, 62.56, 63.81, 70.75, 73.93, 78.85 (spiro C), 114.15, 121.95, 122.32, 122.87, 123.08, 126.45, 127.87, 128.54, 129.78, 130.70, 131.71, 132.32, 133.33, 139.51, 141.15, 164.47 (C=O), 198.99 (C=O); MS m/z: 500 $[M]^+$ for $C_{27}H_{21}N_3O_5S$.

Ethyl 6′-cyano-7′-(4-chlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4f)

Mp: 203-205 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2246 (C≡N), 1760 (C=O), 1735 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.24 (t, *J* = 7.2 Hz, 3H, CH_3), 3.14-3.23 (m, 1H, CH_2), 3.28-3.37 (m, 2H, OCH_2), 3.48-3.55 (m, 1H, CH) 3.84 (d, *J* = 10.4 Hz, 2H, *N*–CH_2), 4.22 (d, *J* = 10.4 Hz, 1H, CH), 4.48 (t, *J* = 7.2 Hz, 1H, CH), 7.09-8.15 (m, 10H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 10.80, 34.05, 53.12, 53.45, 61.40, 62.84, 70.20, 78.48 (spiro C), 113.38, 122.30, 125.87, 126.40, 127.07, 128.02, 128.32, 128.48, 129.52, 130.04, 130.20, 132.12, 133.33, 141.21, 164.09 (C=O), 199.14 (C=O); MS m/z: 489 $[M+H]^+$ for $C_{27}H_{21}ClN_2O_3S$.

Ethyl 6′-cyano-7′-(3,4-dichlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4g)

Mp: 217-219 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2248 (C≡N), 1755 (C=O), 1738 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.21 (t, *J* = 7.6 Hz, 3H, CH_3), 3.02-3.11 (m, 2H, CH_2), 3.19-3.30 (m, 2H, OCH_2), 3.42-3.58 (m. 1H, CH_2), 3.74 (d, *J* = 10.4 Hz, 1H, *N*–CH_2), 4.18 (d, *J* = 9.2 Hz, 2H, CH), 4.62 (t, *J* = 8.4 Hz, 1H, CH), 7.23-8.09 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d6) δ: 15.04, 28.60, 36.05, 45.30, 51.82, 58.08, 59.46, 69.33, 78.94 (spiro C), 114.39, 121.28, 126.14, 126.81, 127.46, 128.07, 128.55, 129.69, 130.52, 130.90, 131.12, 132.30, 132.27, 133.45, 137.62, 142.40, 169.82 (C=O), 198.24 (C=O); MS m/z: 523 $[M+H]^+$ for $C_{27}H_{20}Cl_2N_2O_3S$.

Ethyl 6′-cyano-7′-(4-bromophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4h)

Mp: 195-201 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2242 (C≡N), 1728 (C=O), 1715 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.32 (t, *J* = 7.2 Hz, 3H, CH_3), 2.99-3.15 (m, 2H, OCH_2), 3.21-3.34 (m, 1H, CH_2), 3.42 (d, *J* = 10.4 Hz, 2H, *N*–CH_2), 4.09 (d, *J* = 10.4 Hz, 2H, CH), 4.55 (d, *J* = 8.4 Hz, 1H, CH), 7.35-8.54 (m, 10H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 12.50, 35.24, 52.35, 56.08, 57.20, 58.38, 60.12, 66.42, 68.20, 68.66, 78.52 (spiro C), 115.09, 118.45, 125. 93, 126.40, 129.87, 130.26, 132.02, 132.62, 133.44, 134.58, 135.80, 137.20, 141.28, 146.57, 168.32 (C=O), 200.56 (C=O); MS m/z: 535 $[M+2]^+$ for $C_{27}H_{21}BrN_2O_3S$.

Ethyl 6′-cyano-7′-(thiophene)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4i)

Mp: 200-202 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2250 (C≡N), 1768 (C=O), 1730 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.30 (t, *J* = 8.0 Hz, 3H, CH_3), 3.11-3.18 (m, 1H, CH_2), 3.30-3.36 (m, 2H, OCH_2), 3.45-3.50 (m, 1H, CH) 3.78 (d, *J* = 10.0 Hz, 2H, *N*–CH_2), 4.15 (d, *J* = 10.8 Hz, 1H, CH), 4.52 (t, *J* = 8.0 Hz, 1H, CH), 6.95-8.03 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.50, 32.24, 45.67, 52.45, 60.42, 63.84, 72.30, 79.35 (spiro C), 114.47, 122.80, 123.40 125.90, 126.05, 126.23, 127.07, 128.09, 128.52, 128.95, 129.04, 130.63, 132.40, 133.64, 145.20, 166.60 (C=O), 198.20 (C=O); MS m/z: 461 $[M+H]^+$ for $C_{25}H_{20}N_2O_3S_2$.

Ethyl 6′-cyano-7′-(3,4-dimethoxyphenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate (4j)

Mp: : 185-190^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1745 (C=O), 1732 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.26 (t, *J* = 7.6 Hz, 3H, CH_3), 2.95-3.07 (m, 2H, CH_2), 3.14-3.23 (m, 2H, OCH_2), 3.29-3.42 (m. 1H, CH_2), 3.51 (s, 6H, OCH_3), 3.62 (d, *J* = 10.4 Hz, 1H, *N*–CH_2), 4.09 (d, *J* = 9.2 Hz, 2H, CH), 4.45 (t, *J* = 8.4 Hz, 1H, CH), 7.02-7.98 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d6) δ: 14.50, 27.34, 36.10, 45.39, 51.74, 56.30, 58.09, 59.60, 68.44, 79.20 (spiro C), 114.09, 121.50, 126.34, 126.87, 127.90, 128.06, 128.67, 129.04, 130.15, 130.70, 131.40, 132.50, 132.94, 133.60, 137.46, 141.25, 170.13 (C=O), 199.35 (C=O); MS m/z: 515 $[M+H]^+$ for $C_{29}H_{26}N_2O_5S$.

6′-cyano-7′-(phenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4k)

Mp: 200-202 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2238 (C≡N), 1730 (C=O), 1680 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.99-3.02 (m, 1H, CH_2), 3.20-3.25 (m, 1H, CH_2), 3.28-3.34 (m, 1H, CH_2), 3.77 (d, *J* = 10.0 Hz, 1H, CH), 4.45 (d, *J* = 10.4 Hz, 1H, CH), 4.67-4.72 (m, 1H, CH), 7.12-8.33 (m, 11H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 35.75, 53.04, 53.26, 64.94, 70.79, 79.24 (spiro C), 116.30, 122.16, 126.44, 127.80, 128.10, 128.20, 128.25, 129.74, 129.99, 130.34, 130.85, 132.33, 134.58, 141.74, 163.24 (C=O), 199.82 (C=O); MS m/z: 426 $[M+H]^+$ for $C_{25}H_{19}N_3O_2S$.

6′-cyano-7′-(4-methylphenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4l)

Mp: 204-206 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1732 (C=O), 1685 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.15 (s, 3H, CH_3), 2.95-3.04 (m, 1H, CH_2), 3.16-3.28 (m, 1H, CH_2), 3.32-3.40 (m, 1H, CH_2), 3.73 (d, *J* = 9.2 Hz, 1H, CH_2), 4.38 (d, *J* = 10.4 Hz, 1H, CH), 4.62-4.69 (m, 1H, CH), 7.02-8.21 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 19.54, 34.10, 52.71, 53.18, 64.22, 70.52, 78.63 (spiro C), 114.69, 121.94, 125.78, 127.03, 127.56, 127.97, 128.30, 129.74, 130.13, 130.62, 130.91, 132.05, 134.13, 141.20, 162.73 (C=O), 198.60 (C=O); MS m/z: 440 $[M+H]^+$ for $C_{26}H_{21}N_3O_2S$.

6′-cyano-7′-(4-fluorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4m)

Mp: 198-200 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2245 (C≡N), 1728 (C=O), 1690 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.99-3.03 (m, 1H, CH_2), 3.19-3.24 (m, 1H, CH_2), 3.28-3.36 (m, 1H, CH_2), 3.77 (d, *J* = 10.0 Hz, 1H, CH), 4.47 (d, *J* = 10.0 Hz, 1H, CH), 4.67-4.70 (m, 1H, CH), 7.17-8.33 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 30.59, 35.57, 52.50, 53.06, 64.77, 70.67, 79.08 (spiro C), 114.87, 115.08, 116.16, 122.17, 126.39, 127.69, 128.13, 129.91, 130.22, 130.60, 130.63, 130.74, 131.74, 131.82, 132.29, 141.68, 160.65, 163.06 (C=O), 199.73 (C=O); MS m/z: 444 $[M+H]^+$ for $C_{25}H_{18}FN_3O_2S$.

6′-cyano-7′-(2,4-dichlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4n)

Mp: 158-160 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2238 (C≡N), 1730 (C=O), 1710 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.91-2.97 (m, 1H, CH_2), 3.07-3.24 (m, 1H, CH_2), 3.27-3.35 (m, 1H, CH_2), 3.55 (d, *J* = 10.4 Hz, 1H, CH_2), 3.97 (d, *J* = 10.4 Hz, 1H, CH), 4.45-4.52 (m, 1H, CH), 7.02-8.19 (m, 9H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 30.11, 34.70, 51.94, 52.82, 64.16, 69.95, 79.40 (spiro C), 114.19, 115.66, 115.93, 121.64, 126.18, 127.37, 127.70, 128.52, 129.24, 129.76, 130.18, 130.37, 131.25, 131.64, 132.09, 133.76, 141.12, 163.40 (C=O), 198.32 (C=O); MS m/z: 494 $[M]^+$ for $C_{25}H_{17}Cl_2N_3O_2S$.

6′-cyano-7′-(4-nitrophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4o)

Mp: 172-174 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2242 (C≡N), 1735 (C=O), 1688 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.00-3.07 (m, 1H, CH_2), 3.17-3.24 (m, 1H, CH_2), 3.30-3.38 (m, 1H, CH_2), 3.62 (d, *J* = 9.2 Hz, 1H, CH_2), 4.34 (d, *J* = 10.8 Hz, 1H, CH), 4.61-4.74 (m, 1H, CH), 7.06-8.10 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 29.14, 34.52, 52.19, 52.90, 64.24, 70.38, 78.31 (spiro C), 114.30, 115.62, 116.21, 121.95, 125.77, 127.16, 127.64, 128.45, 129.20, 130.18, 130.31, 130.73, 131.24, 131.83, 132.58, 145.06, 163.79 (C=O), 197.62 (C=O); MS m/z: 470 $[M]^+$ for $C_{25}H_{18}N_4O_4S$.

6′-cyano-7′-(4-chlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4p)

Mp: 219-221 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2255 (C≡N), 1745 (C=O), 1678 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.72-2.89 (m, 1H, CH_2), 3.04-3.12 (m, 1H, CH_2), 3.16-3.28 (m, 1H, CH_2), 3.66 (d, *J* = 10.4 Hz, 1H, CH), 4.19 (d, *J* = 10.8 Hz, 1H, CH), 4.46-4.58 (m, 1H, CH), 7.03-8.17 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 34.67, 52.87, 53.01, 64.24, 70.18, 78.52 (spiro C), 115.16, 122.30, 126.80, 127.44, 127.92, 128.15, 128.30, 129.50, 129.64, 130.18, 130.45, 131.58, 134.38, 142.82, 164.60 (C=O), 200.05 (C=O); MS m/z: 460 $[M+H]^+$ for $C_{25}H_{18}ClN_3O_2S$.

6′-cyano-7′-(3,4-dichlorophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4q)

Mp: 215-217 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2232 (C≡N), 1734 (C=O), 1705 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.84-2.95 (m, 1H, CH_2), 3.01-3.18 (m, 1H, CH_2), 3.21-3.32 (m, 1H, CH_2), 3.62 (d, *J* = 10.8 Hz, 1H, CH_2), 3.88 (d, *J* = 9.6 Hz, 1H, CH), 4.23-4.36 (m, 1H, CH), 6.92-8.05 (m, 9H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 28.70, 35.25, 51.17, 52.76, 64.12, 70.32, 79.30 (spiro C), 114.70, 115.20, 115.84, 122.76, 127.39, 127.68, 128.05, 128.60, 129.40, 129.82, 130.64, 130.85, 130.98, 131.20, 132.14, 132.60, 142.27, 163.55 (C=O), 198.68 (C=O); MS m/z: 494 $[M]^+$ for $C_{25}H_{17}Cl_2N_3O_2S$.

6′-cyano-7′-(4-bromophenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4r)

Mp: 208-211 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1715 (C=O), 1678 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.75-2.90 (m, 1H, CH_2), 3.05-3.14 (m, 1H, CH_2), 3.18-3.34 (m, 1H, CH_2), 3.59 (d, *J* = 10.4 Hz, 1H, CH), 4.13 (d, *J* = 10.8 Hz, 1H, CH), 4.36-4.48 (m, 1H, CH), 6.93-8.07 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 34.57, 52.82, 53.11, 64.34, 70.28, 78.92 (spiro C), 114.16, 122.30, 126.80, 127.44, 127.92, 128.15, 128.30, 129.52, 129.60, 130.18, 130.25, 131.48, 134.40, 141.72, 163.60 (C=O), 199.05 (C=O); MS m/z: 503 $[M]^+$ for $C_{25}H_{18}BrN_3O_2S$.

6′-cyano-7′-(thiophene)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4s)

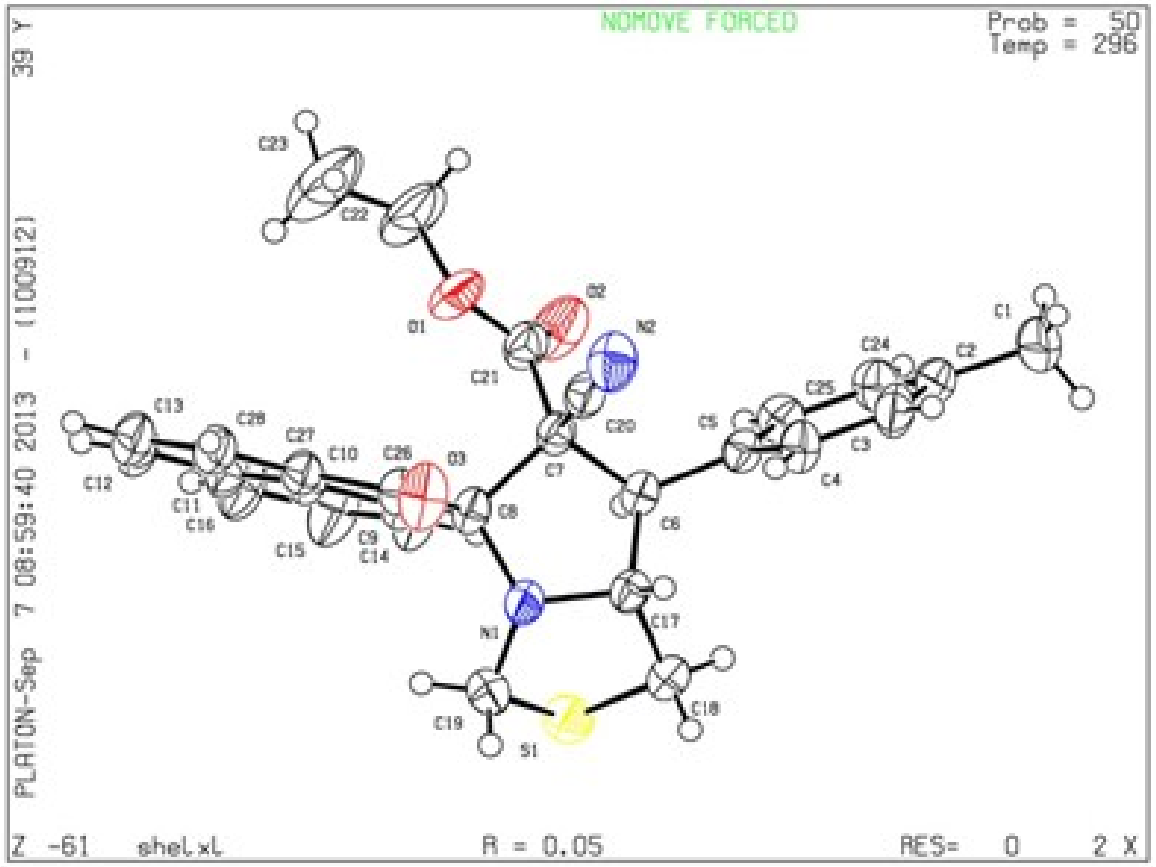
Mp: 218-220 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2252 (C≡N), 1738 (C=O), 1685 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.61-2.68 (m, 1H, CH_2), 2.98-3.07 (m, 1H, CH_2), 3.14-3.22 (m, 1H, CH_2), 3.55 (d, *J* = 10.8 Hz, 1H, CH), 4.11 (d, *J* = 10.4 Hz, 1H, CH), 4.37-4.49 (m, 1H, CH), 6.97-8.05 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 35.24, 51.07, 53.28, 63.50, 69.76, 77.34 (spiro C), 114.20, 123.40, 126.55, 126.49, 127.80, 128.26, 128.45, 129.38, 129.72, 130.40, 130.68, 131.50, 132.64, 135.30, 141.27, 164.08 (C=O), 199.28 (C=O); MS m/z: 432 $[M+H]^+$ for $C_{23}H_{17}N_3O_2S_2$.

6′-cyano-7′-(4-ethylphenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (4t)

Mp: 193-200 ^{o}C; IR (KBr, ν_{max}, cm^{-1}): 2236 (C≡N), 1732 (C=O), 1688 (C=O); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 1.25 (t, *J* = 8.0, 3H, CH_3), 2.64-2.72 (m, 2H, CH_2), 2.90-2.98 (m, 1H, CH_2), 3.08-3.15 (m, 1H, CH_2), 3.23-3.30 (m, 1H, CH_2), 3.74 (d, *J* = 10.4 Hz, 1H, CH), 4.41 (d, *J* = 10.0 Hz, 1H, CH), 4.57-4.65 (m, 1H, CH), 7.12-8.24 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 14.50, 28.65, 30.40, 36.57, 48.27, 53.06, 64.70, 79.20 (spiro C), 115.87, 121.08, 122.17, 125.48, 126.39, 127.54, 128.04, 128.89, 129.20, 130.02, 130.40, 131.63, 131.80, 132.46, 132.75, 133.29, 137.50, 142.68, 164.50 (C=O), 199.10 (C=O); MS m/z: 454 $[M+H]^+$ for $C_{27}H_{23}N_3O_2S$.

6′-cyano-7′-(4-propylphenyl)-2-oxo-3′,6′,7′,7*a*′-tetrahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxamide (**4u**)

Mp: 235-241°C; IR (KBr, ν_{max}, cm^{-1}): 2240 (C≡N), 1736 (C=O), 1692 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J* = 7.6, 3H, CH_3) 1.52-1.64 (m, 2H, CH_2), 2.40 (t, *J* = 7.2, 2H, CH_2), 2.70-2.75 (m, 2H, CH_2), 2.86-2.93 (m, 1H, CH_2), 3.10-3.21 (m, 1H, CH_2), 3.28-3.35 (m, 1H, CH_2), 3.66 (d, *J* = 10.0 Hz, 1H, CH), 4.38 (d, *J* = 10.8 Hz, 1H, CH), 4.53-4.60 (m, 1H, CH), 6.98-7.84 (m, 10H, ArH & 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.25, 23.46, 31.23, 34.67, 36.74, 49.20, 52.46, 64.40, 78.40 (spiro C), 114.80, 120.13, 122.30, 125.36, 126.49, 127.38, 128.42, 128.70, 129.07, 129.40, 130.72, 131.50, 131.87, 132.54, 132.80, 133.04, 137.20, 141.78, 165.08 (C=O), 200.05 (C=O); MS m/z: 468 $[M+H]^+$ for $C_{28}H_{25}N_3O_2S$.



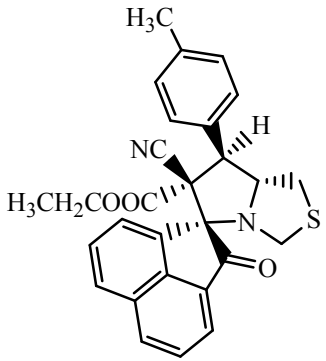


Figure 1: ORTEP diagram of **4b**

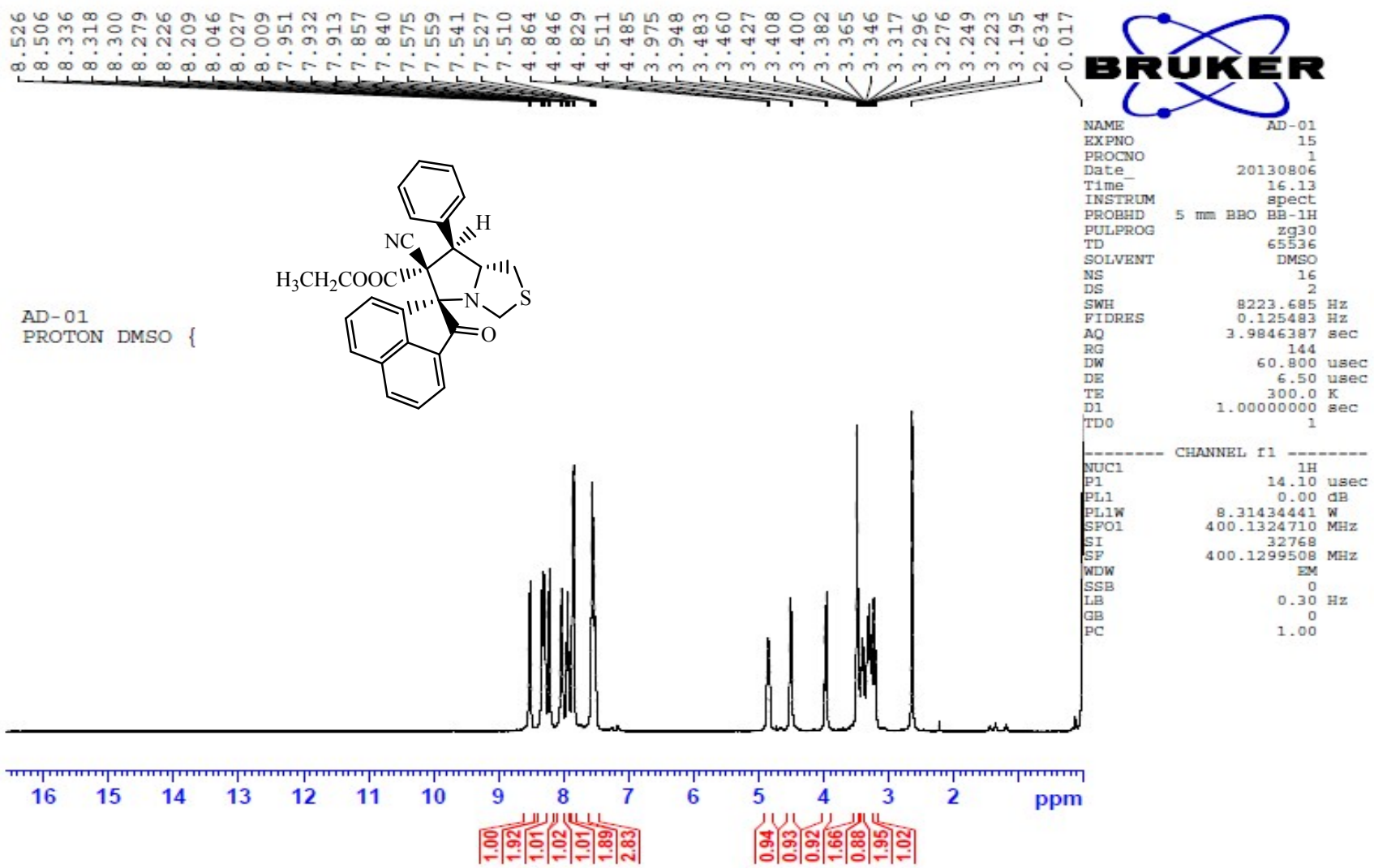


Figure 2: ^{1}H NMR spectrum of **4a**

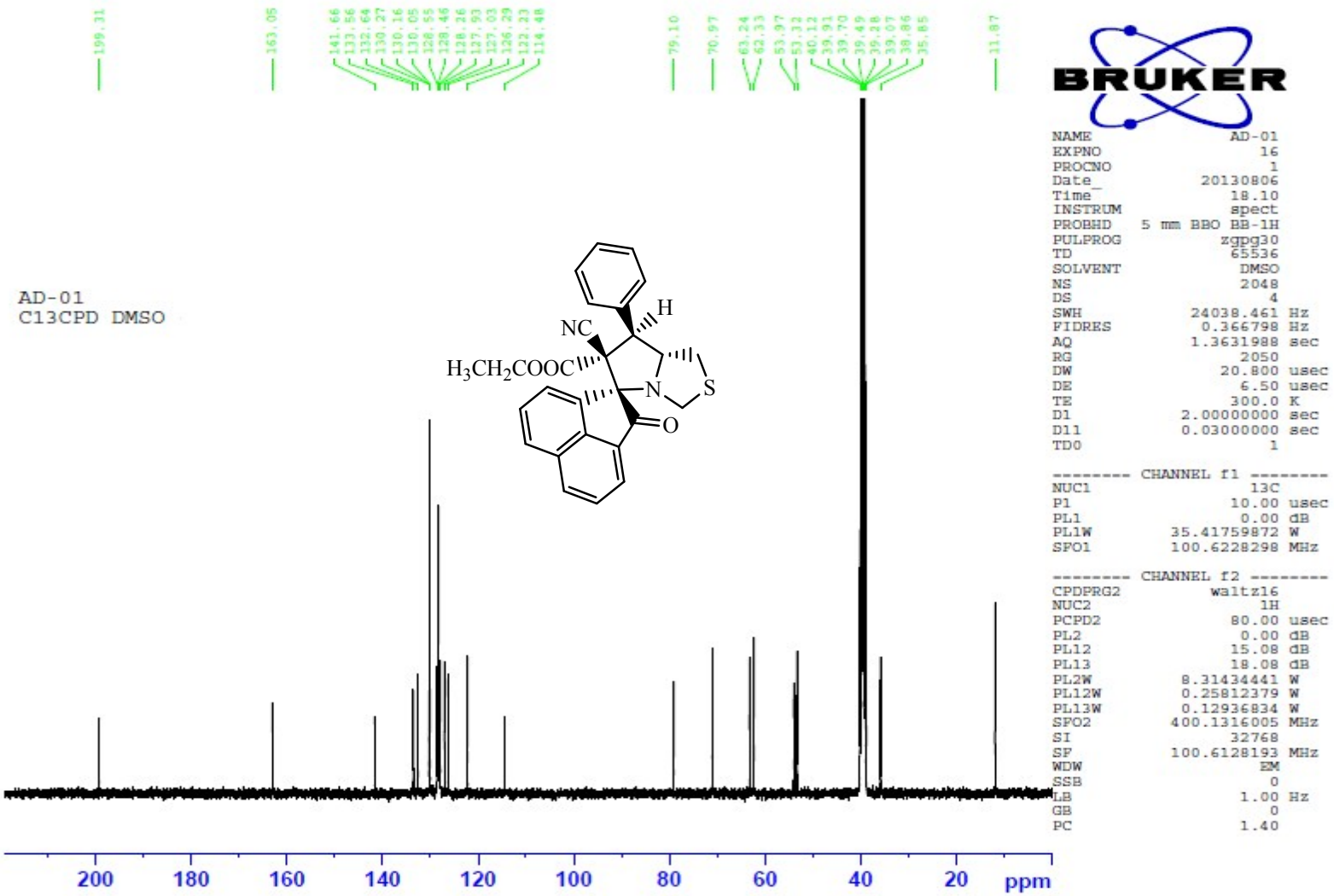


Figure 3: ^{13}C NMR spectrum of **4a**

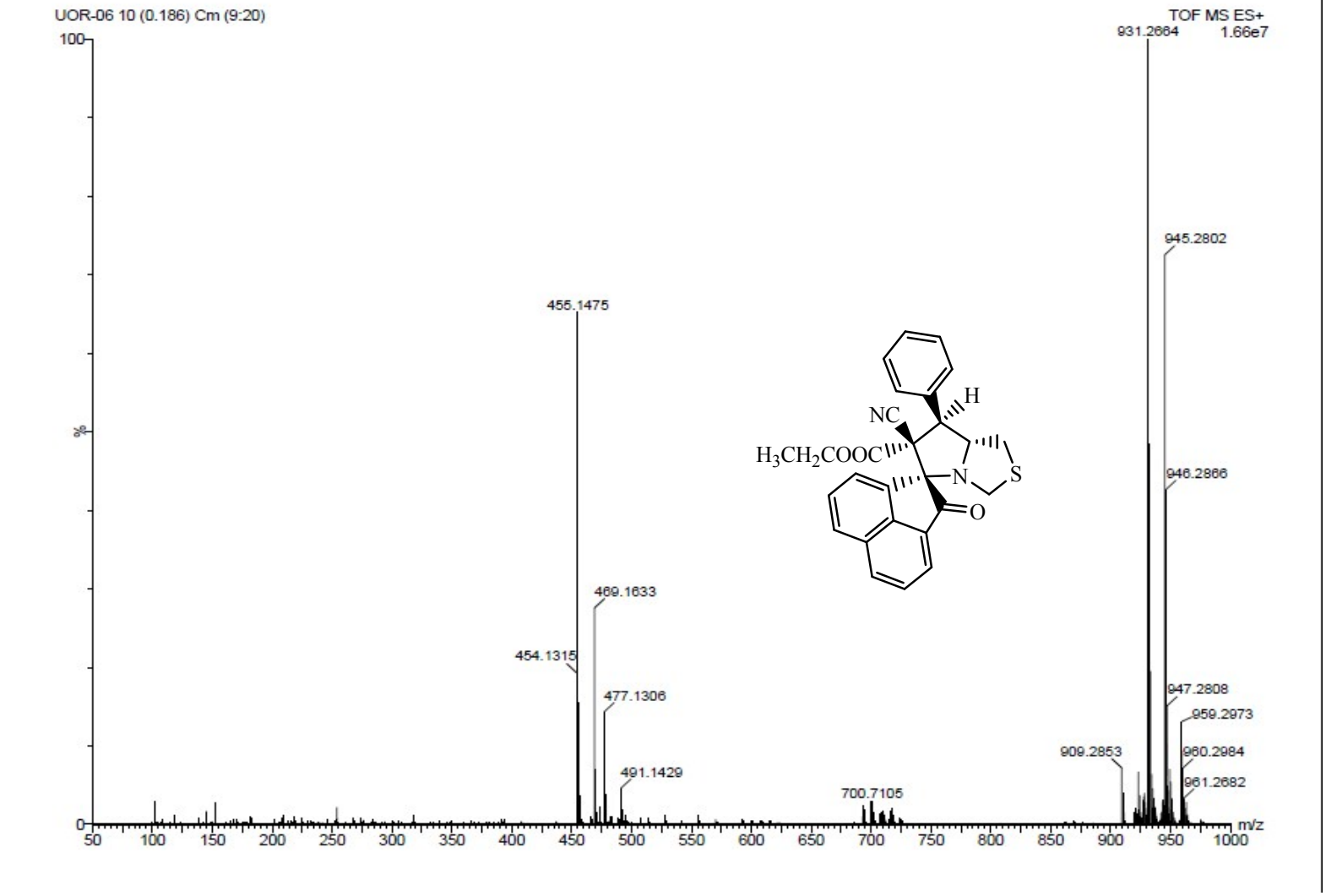


Figure 4: Mass Spectrum of **4a**

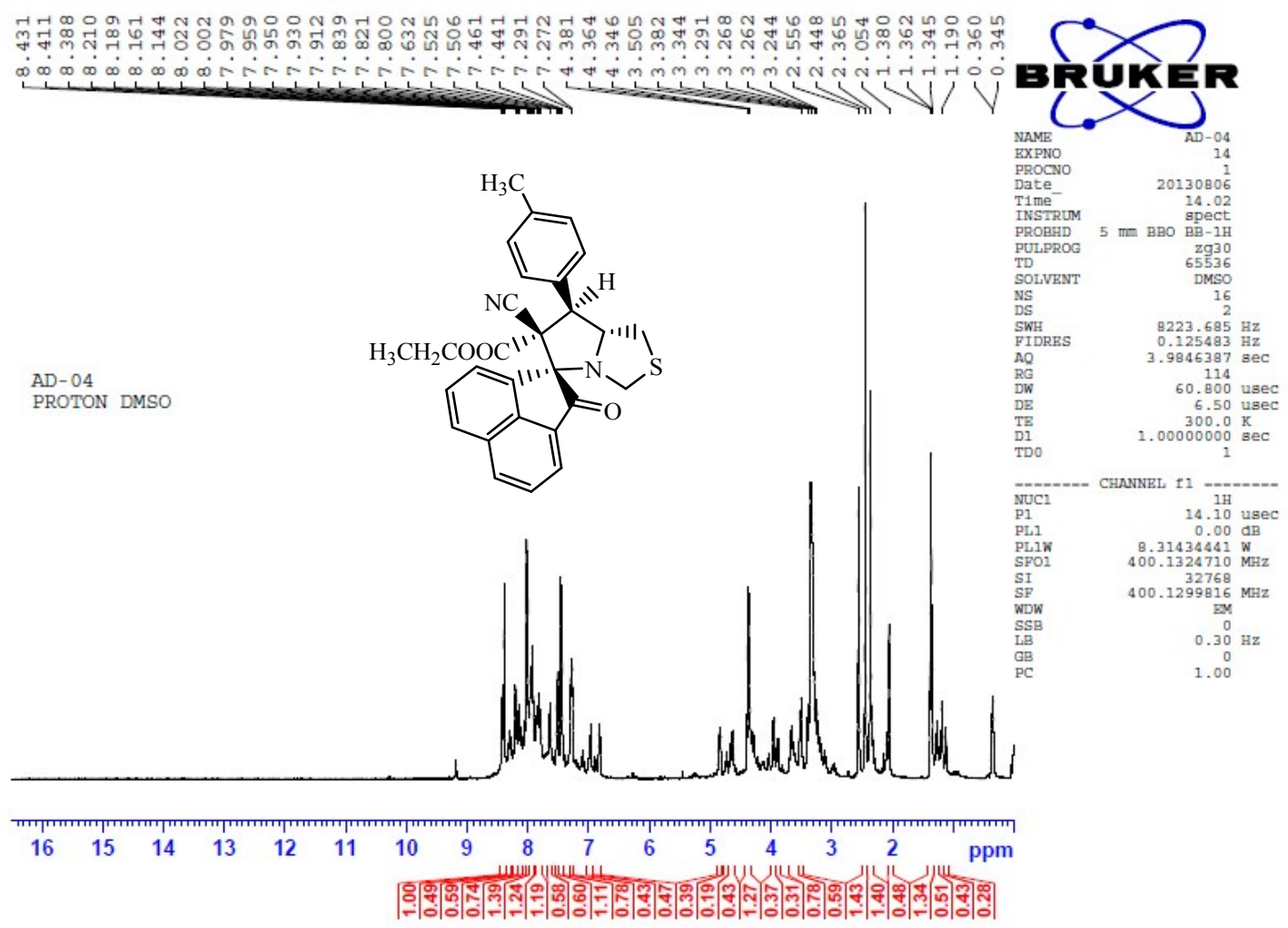


Figure 5: ^{1}H NMR spectrum of **4b**

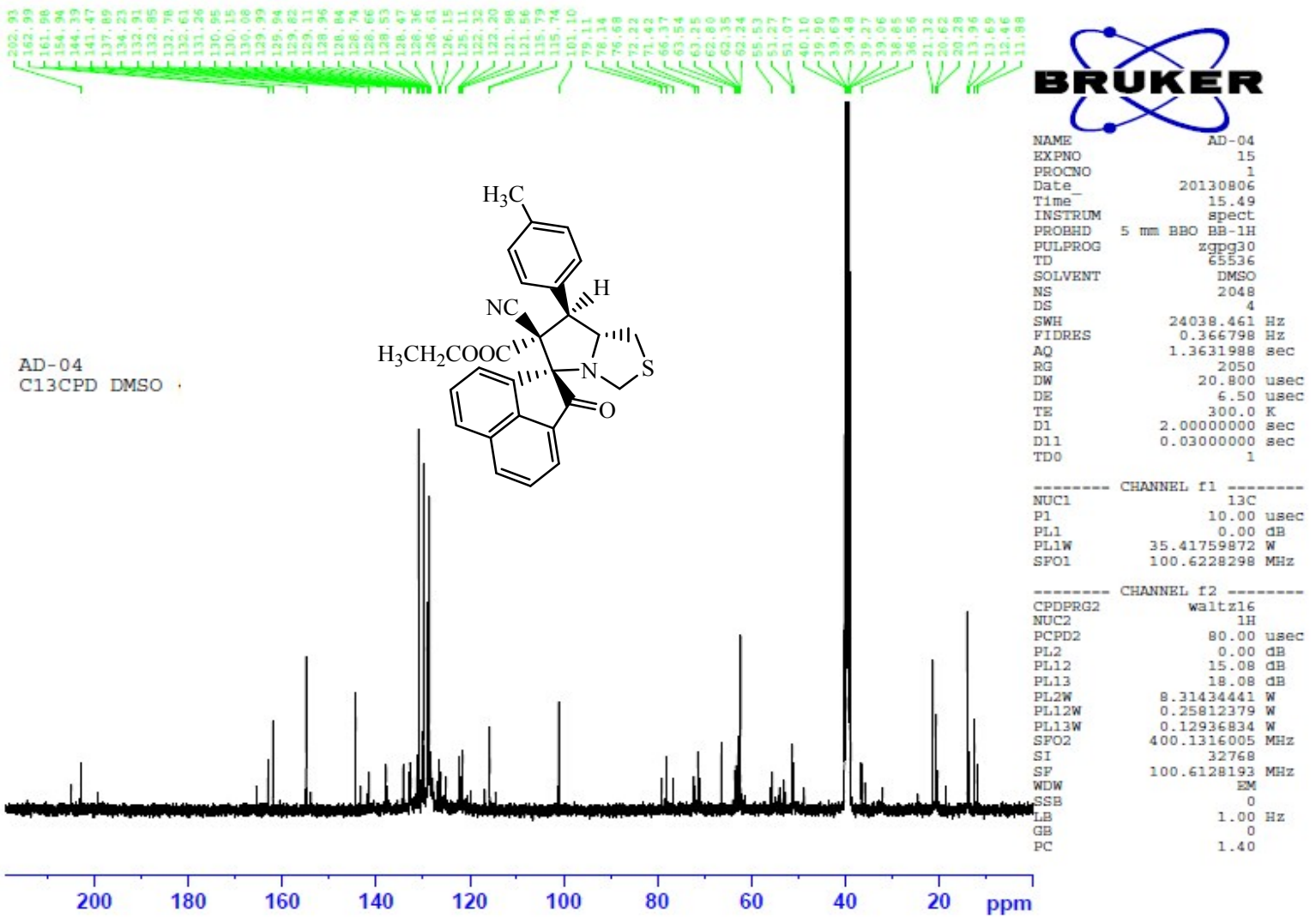


Figure 6: ^{13}C NMR spectrum of **4b**

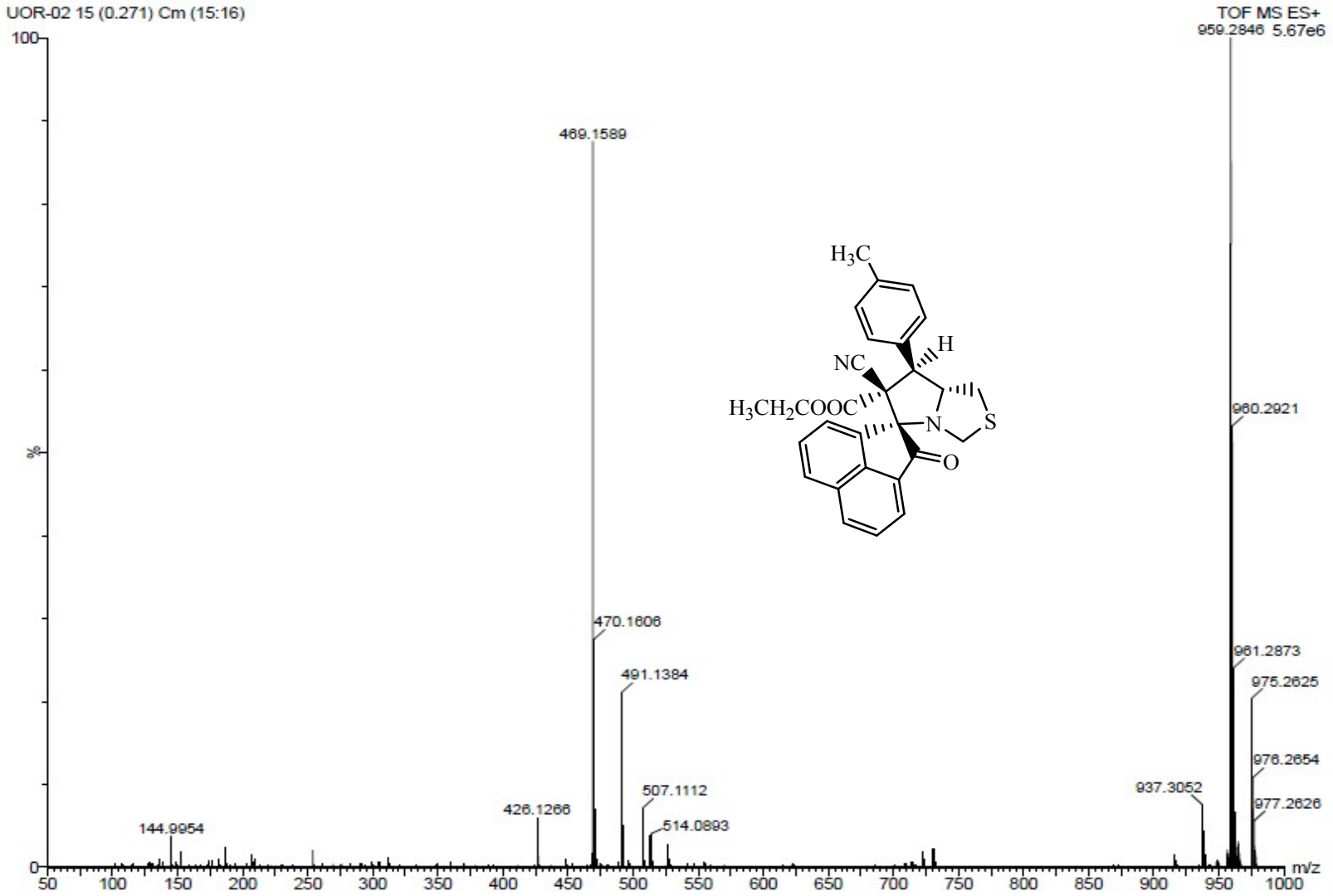


Figure 7: Mass spectrum of **4b**

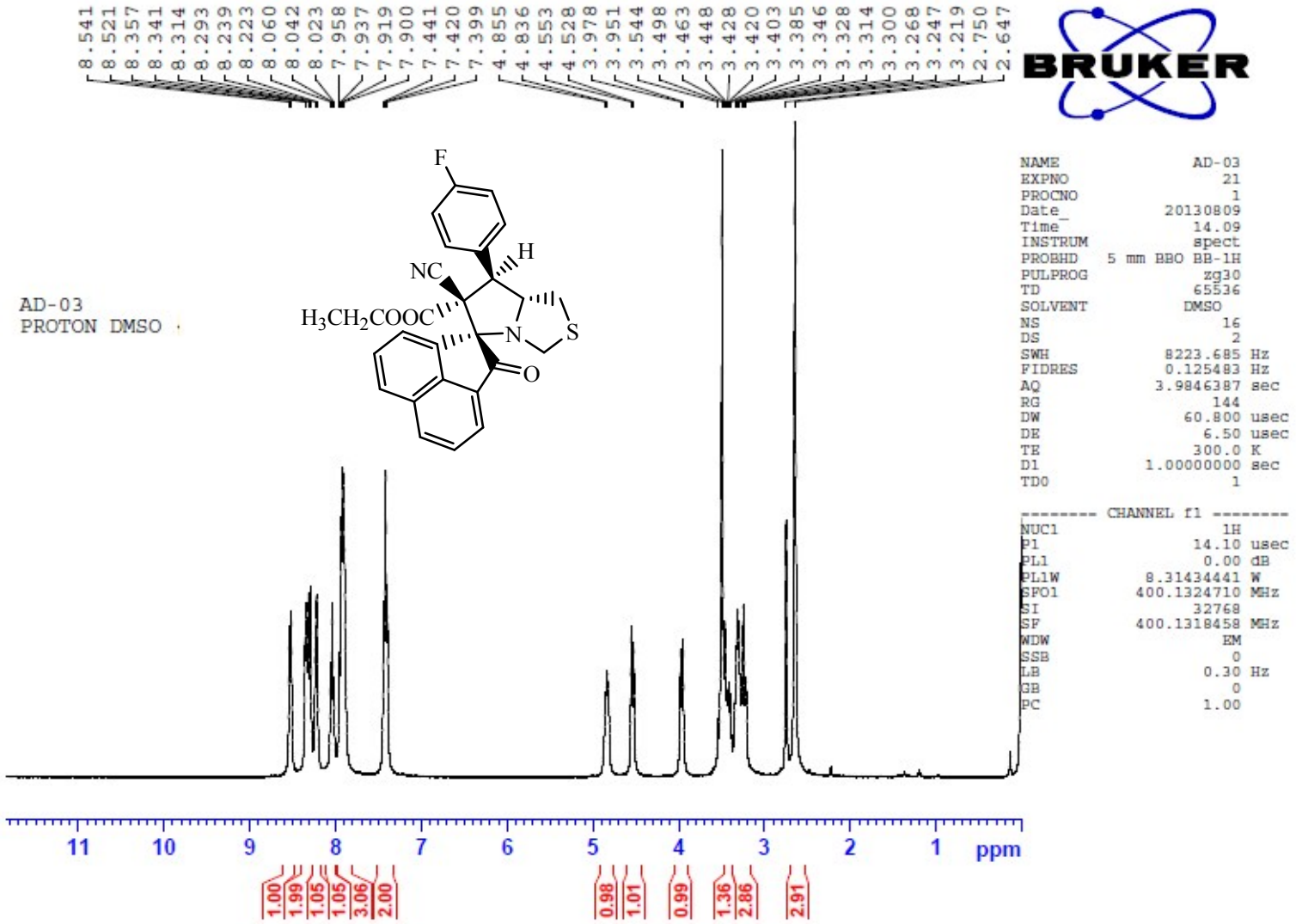


Figure 8: ^{1}H NMR spectrum of **4c**

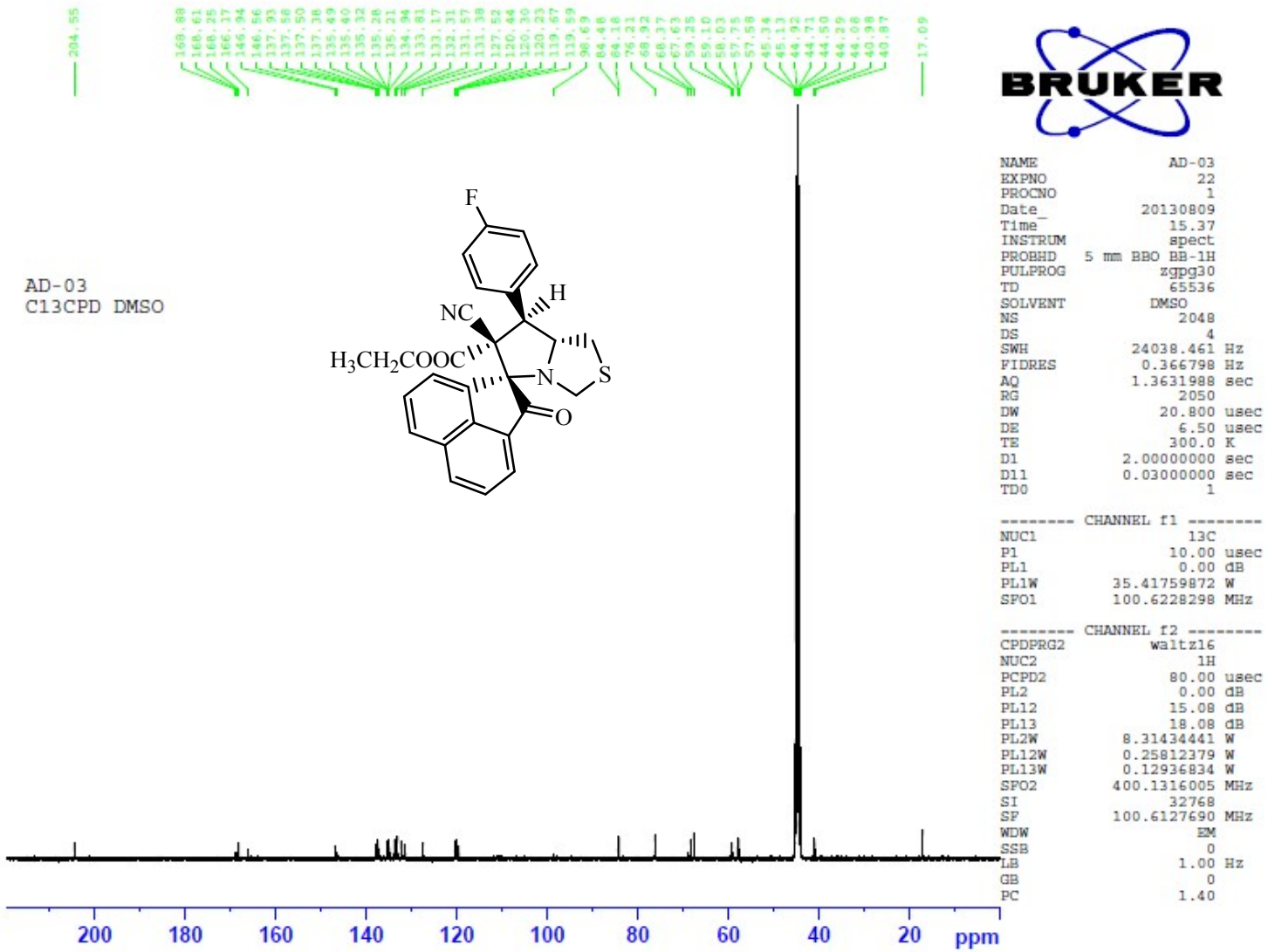


Figure 9: ^{13}C NMR spectrum of **4c**

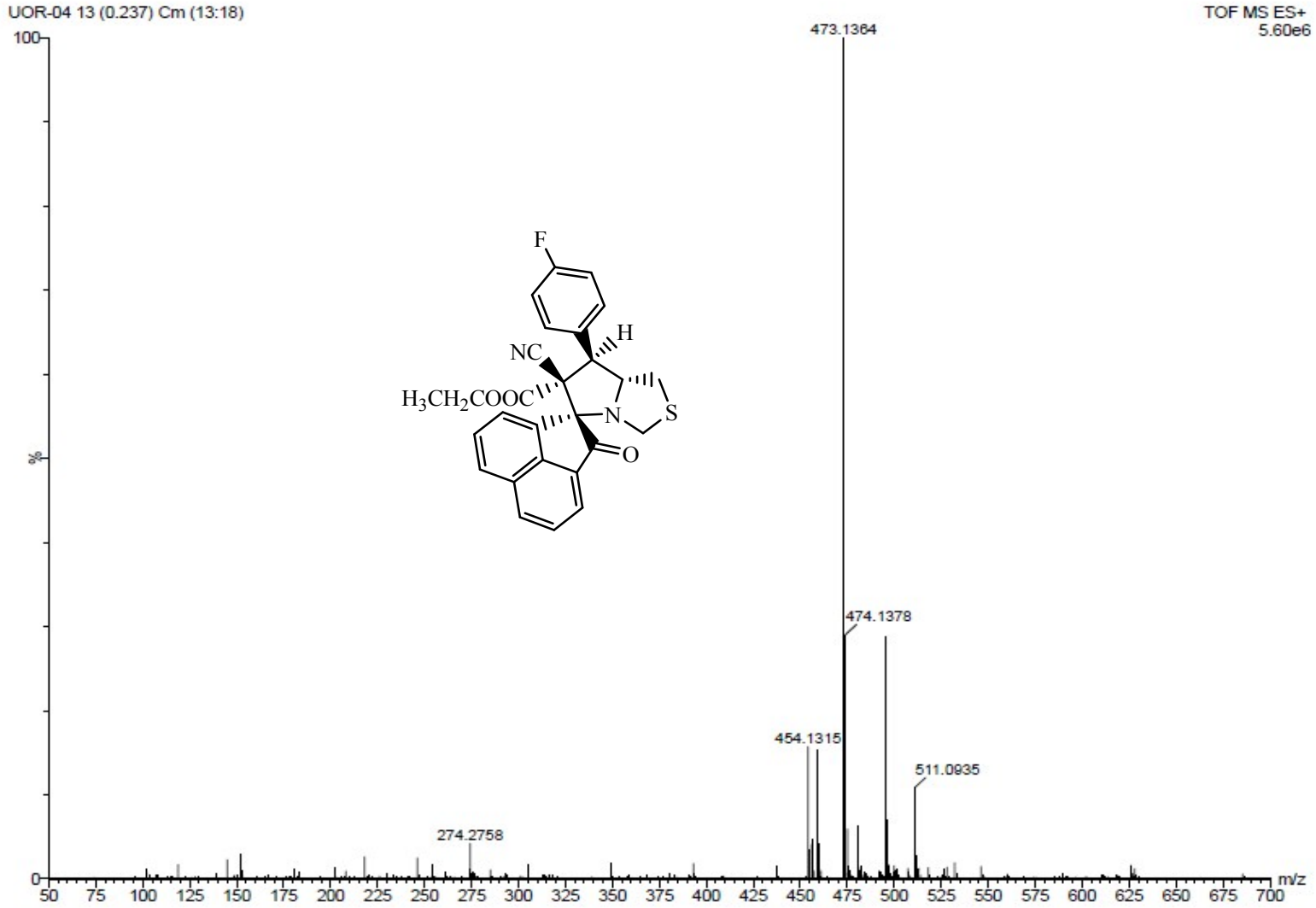


Figure 10: Mass spectrum of **4c**

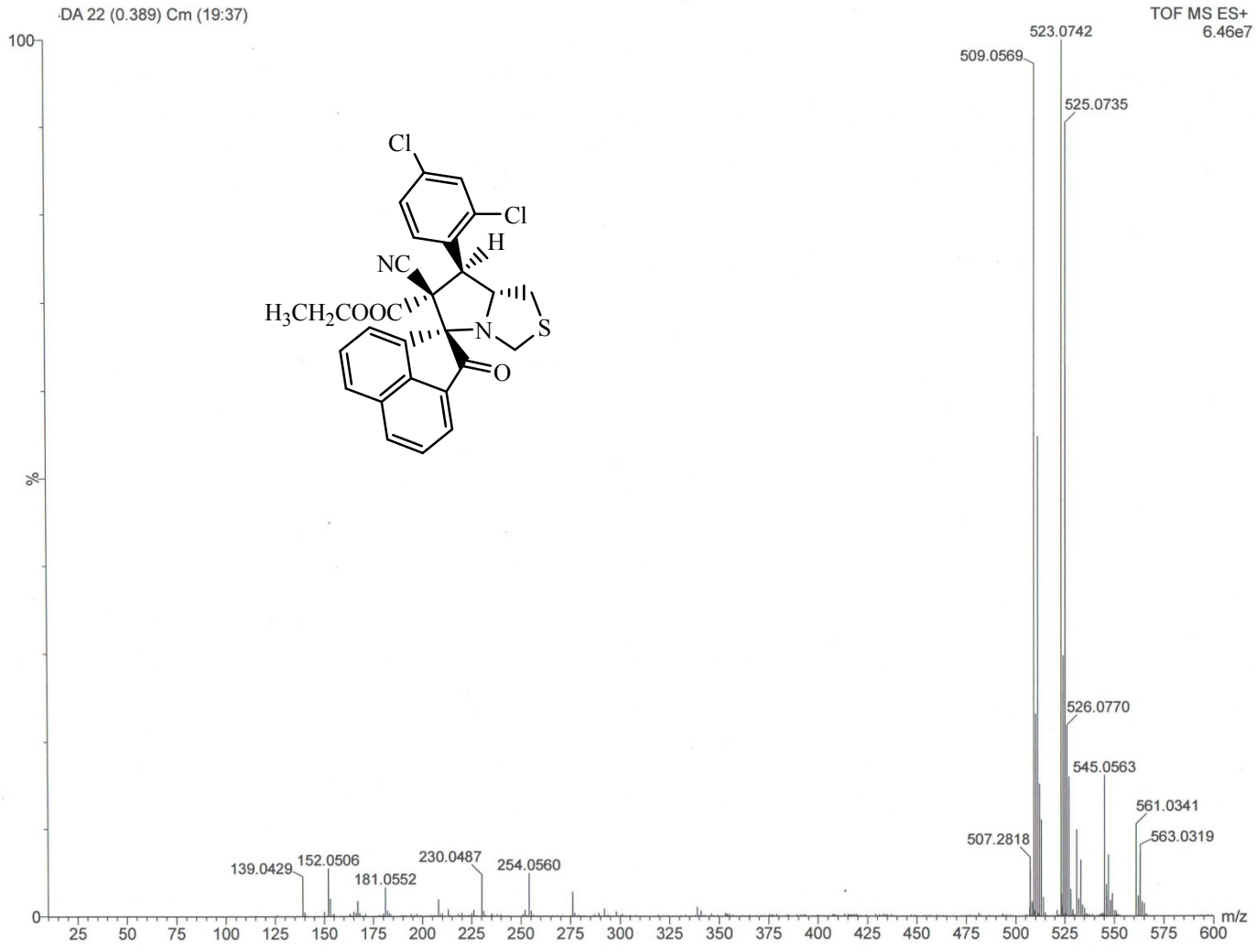


Figure 11: Mass spectrum of **4d**

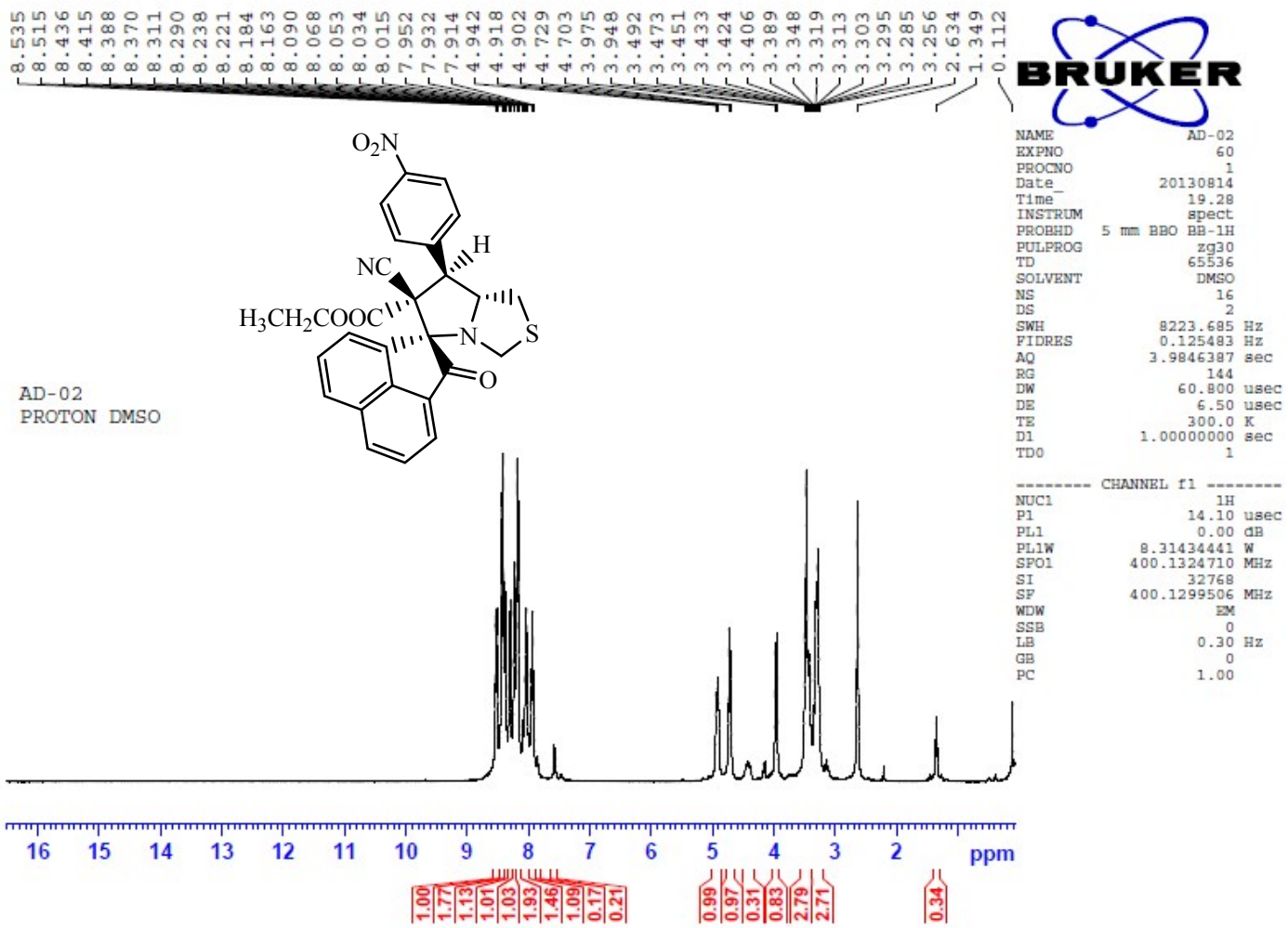


Figure 12: ^{1}H NMR spectrum of **4e**

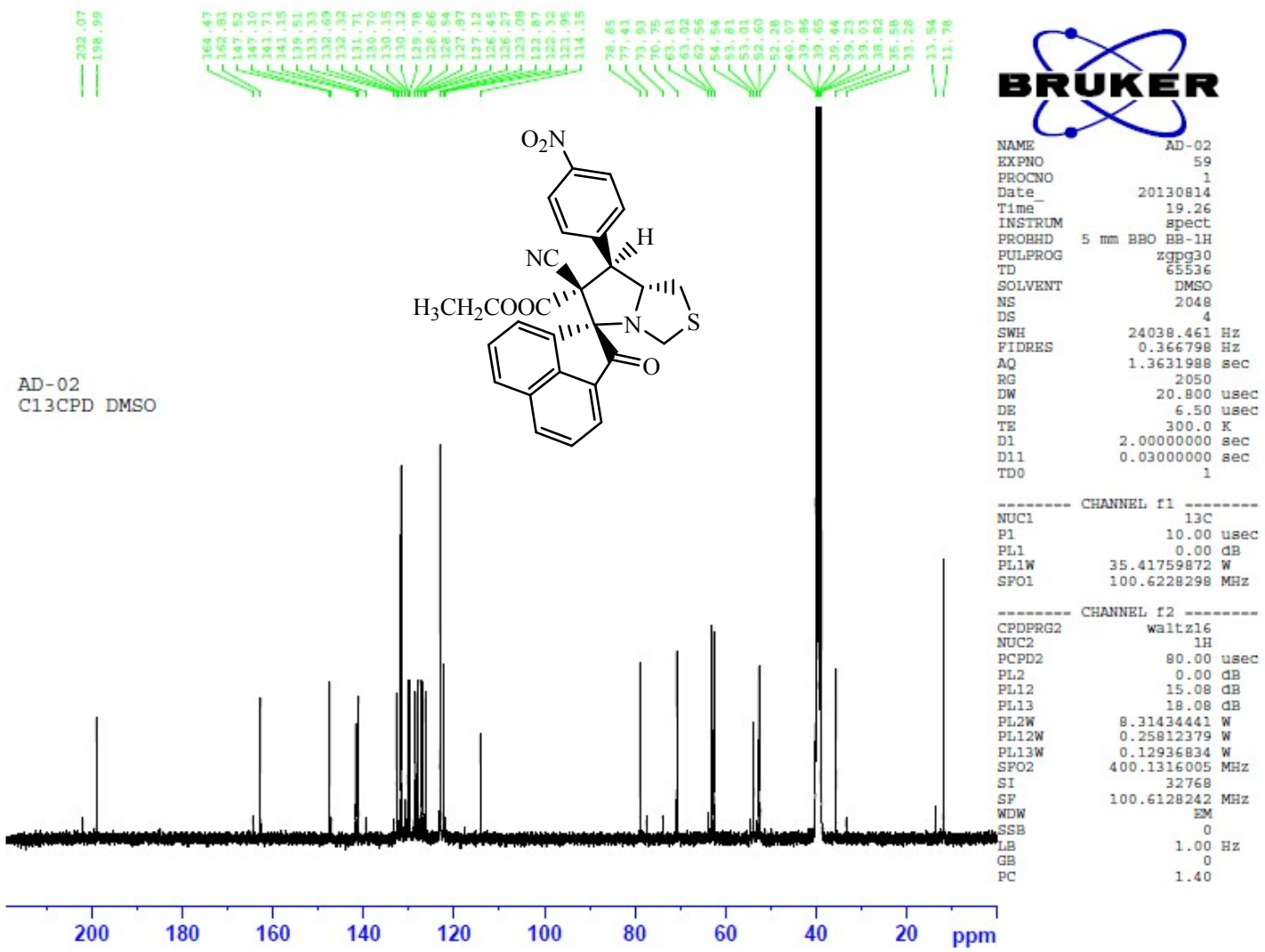


Figure 13: ^{13}C NMR spectrum of **4e**

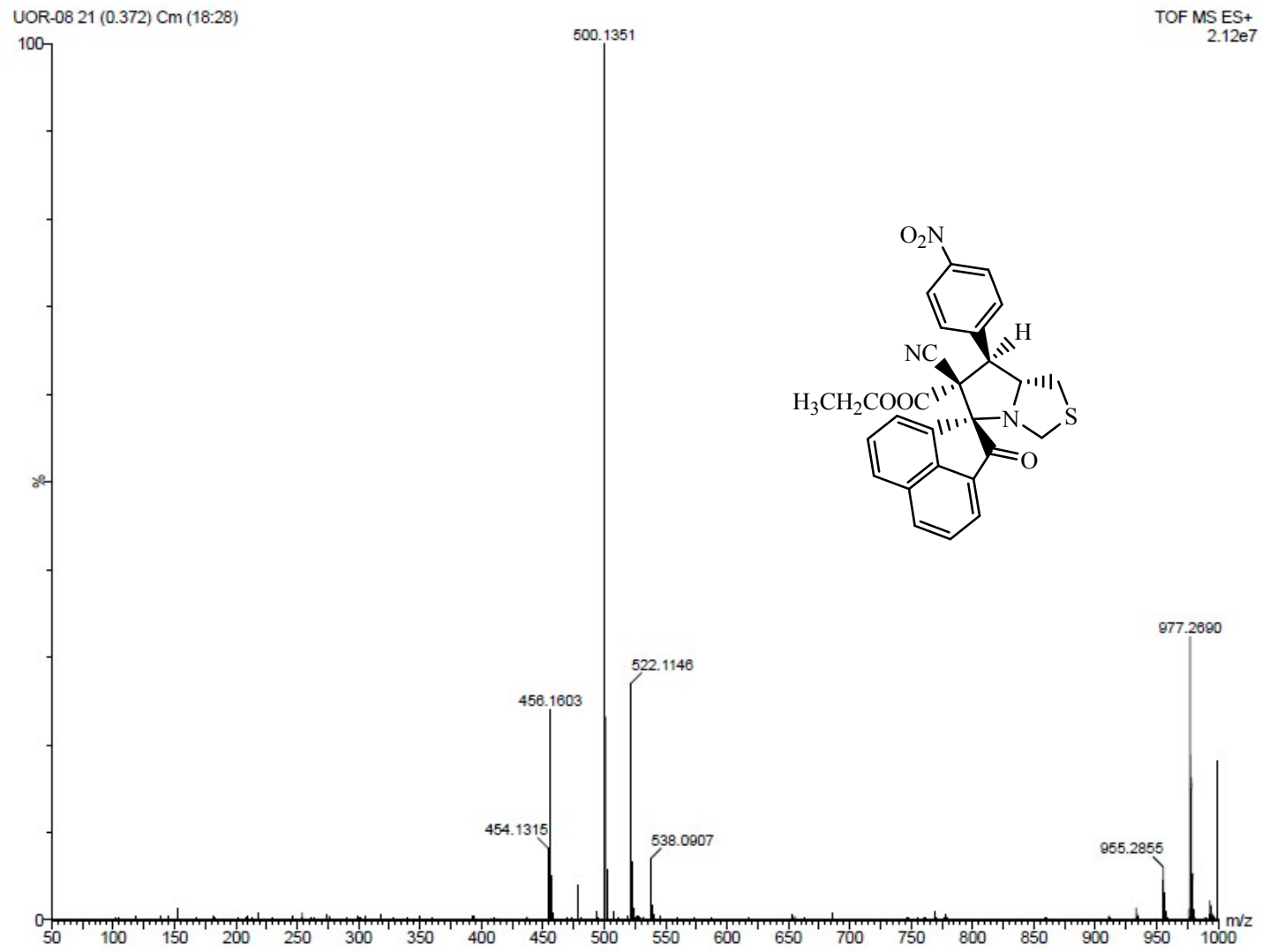


Figure 14: Mass spectrum of **4e**

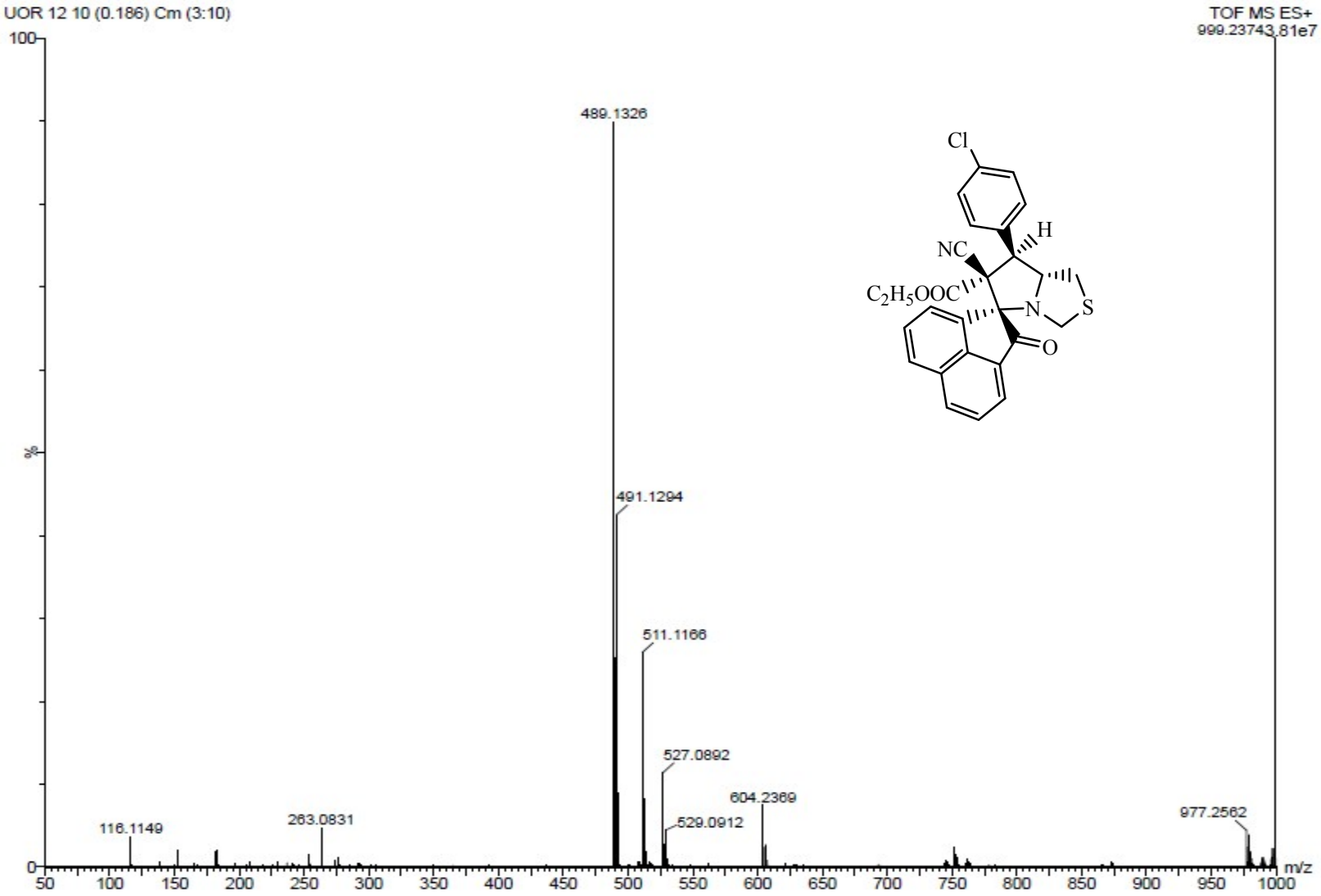


Figure 15: Mass spectrum of **4f**

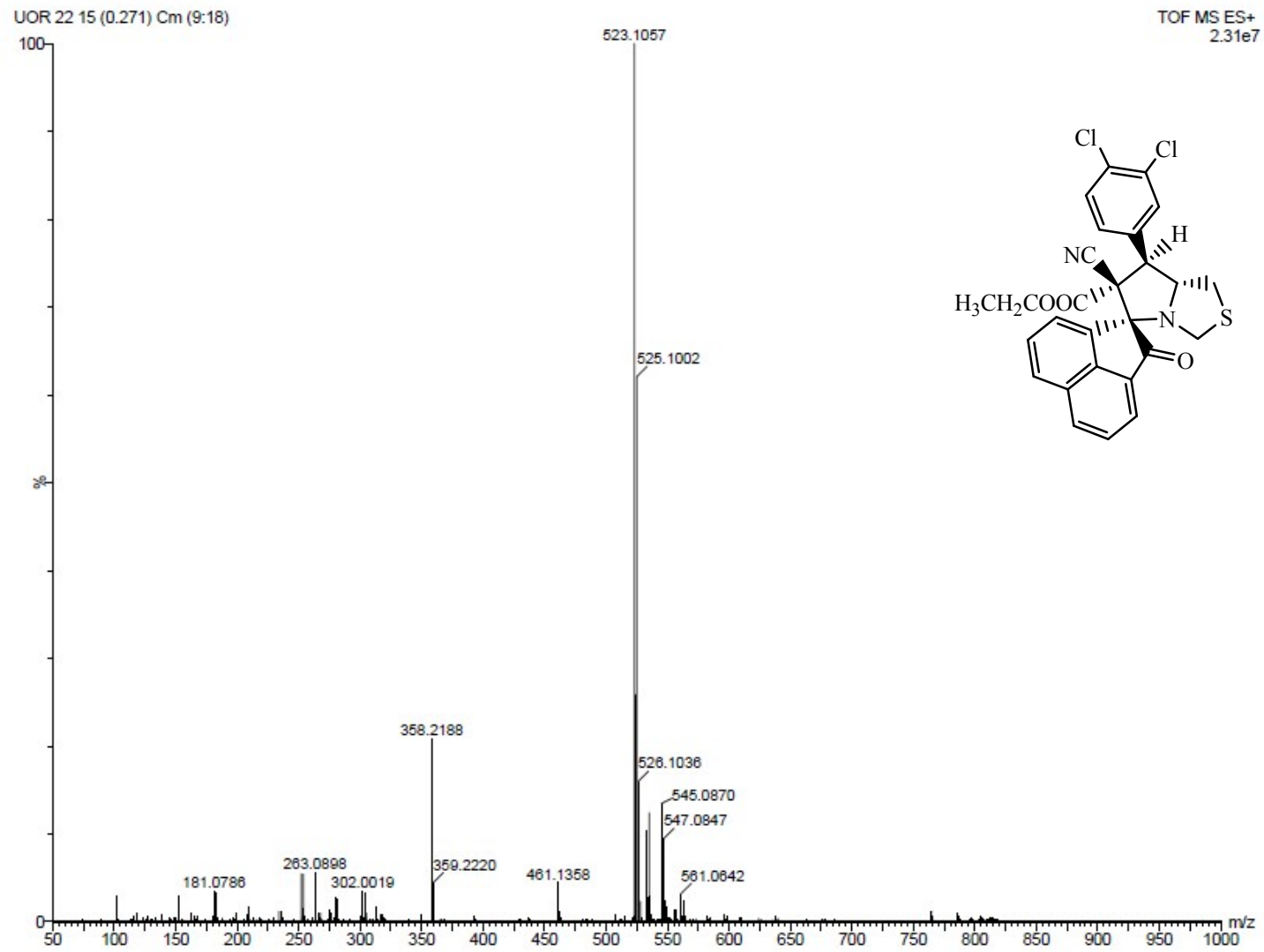


Figure 16: Mass spectrum of **4g**

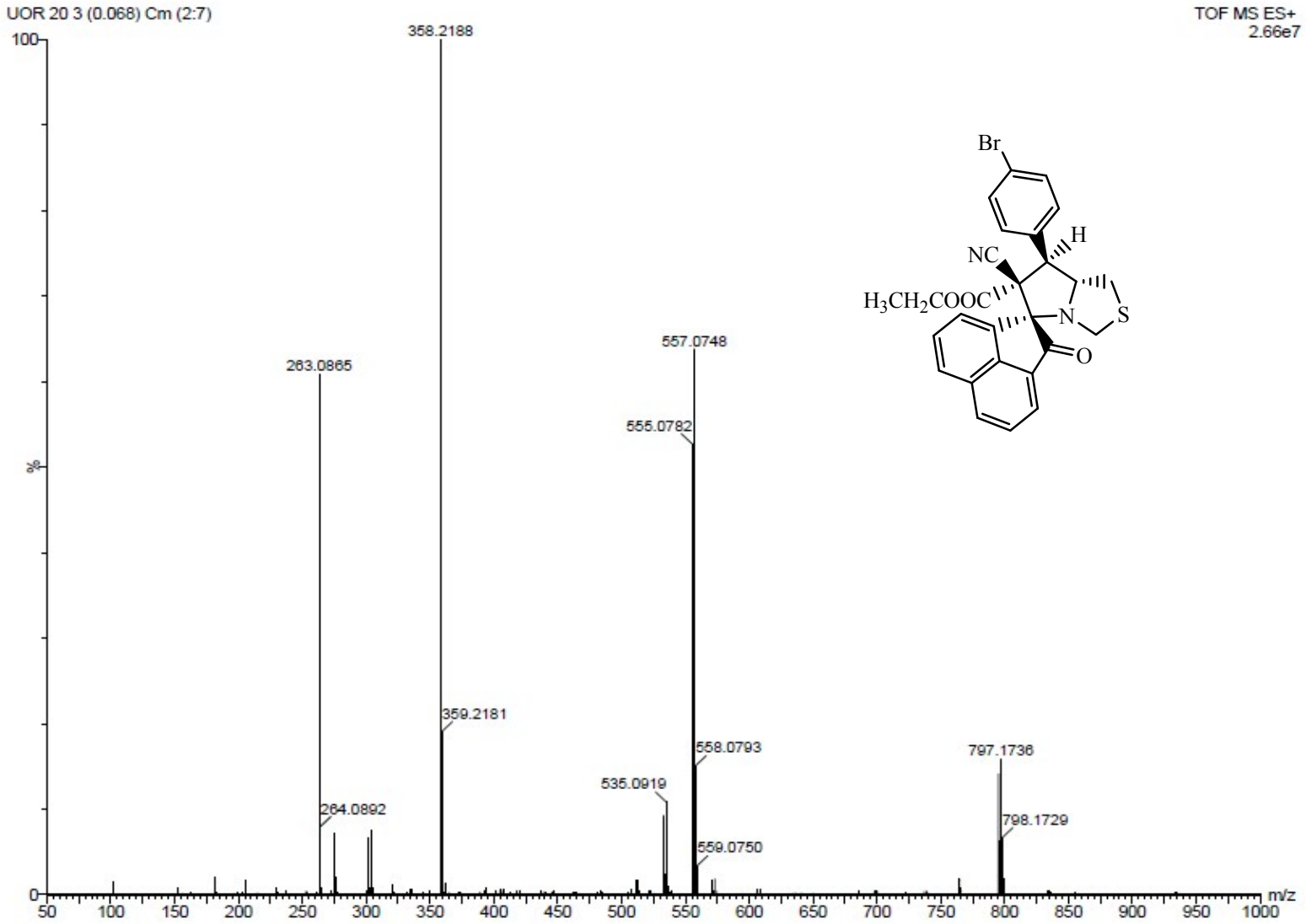


Figure 17: Mass spectrum of **4h**

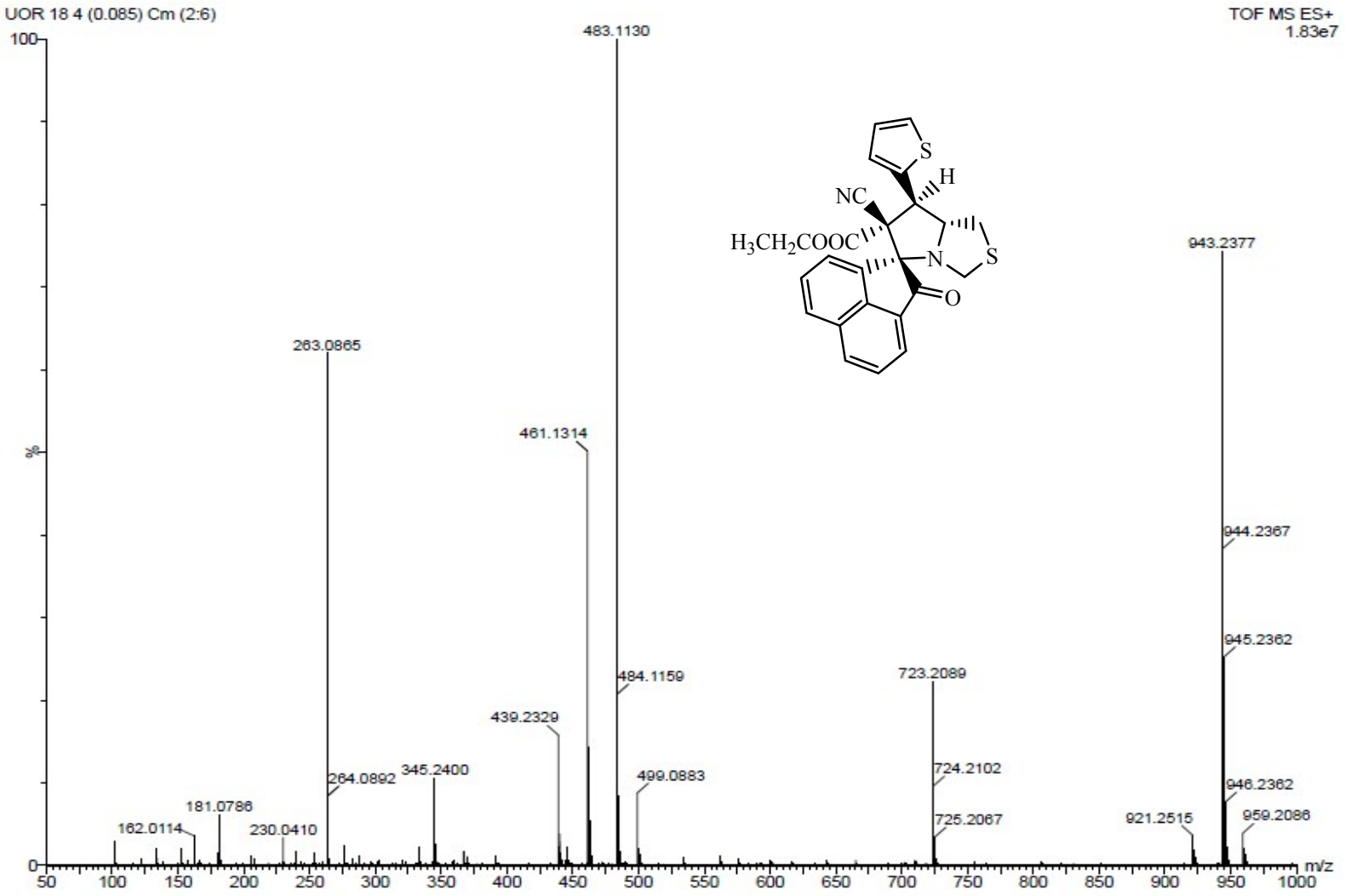


Figure 18: Mass spectrum of **4i**

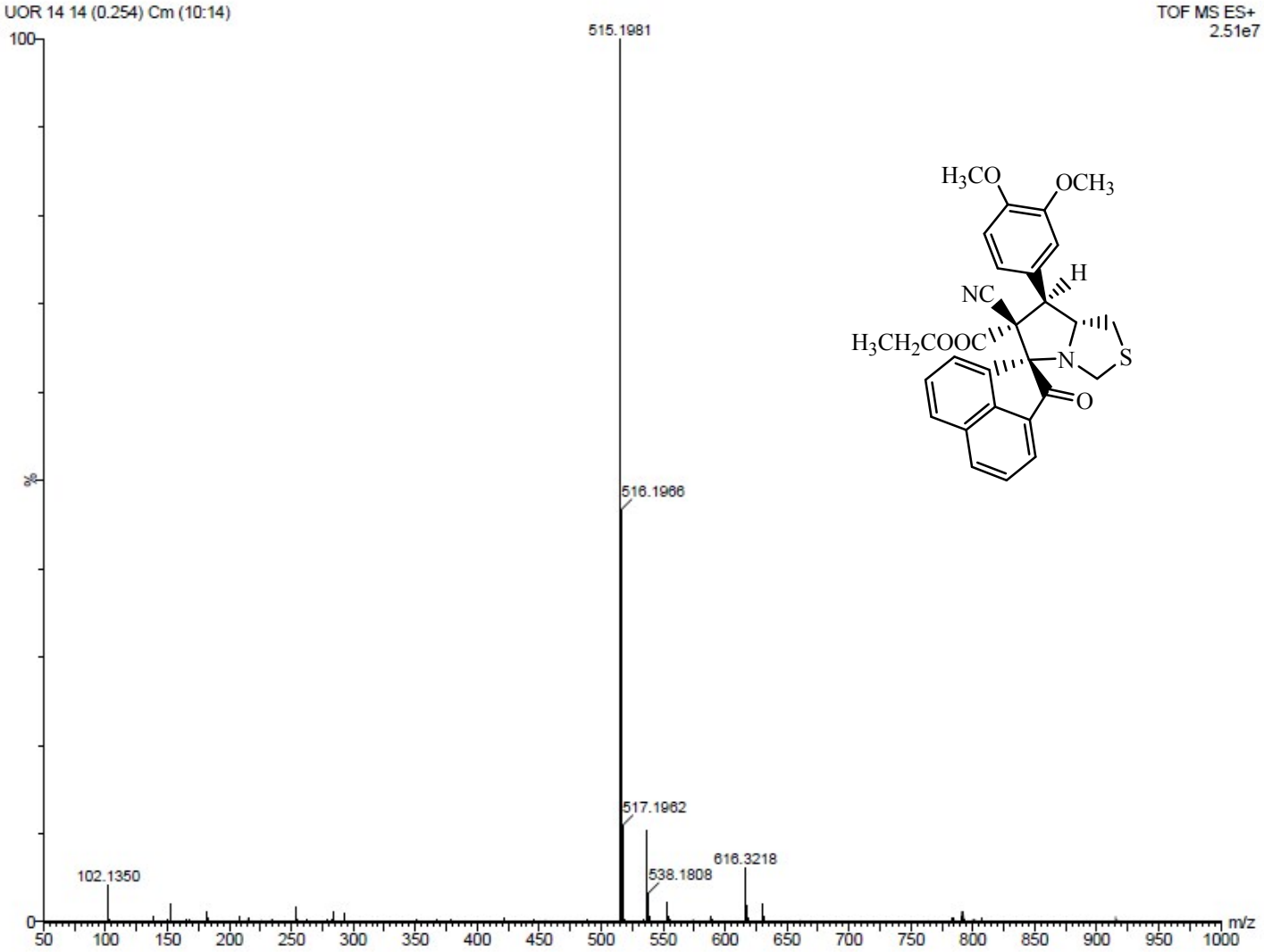


Figure 19: Mass spectrum of **4j**

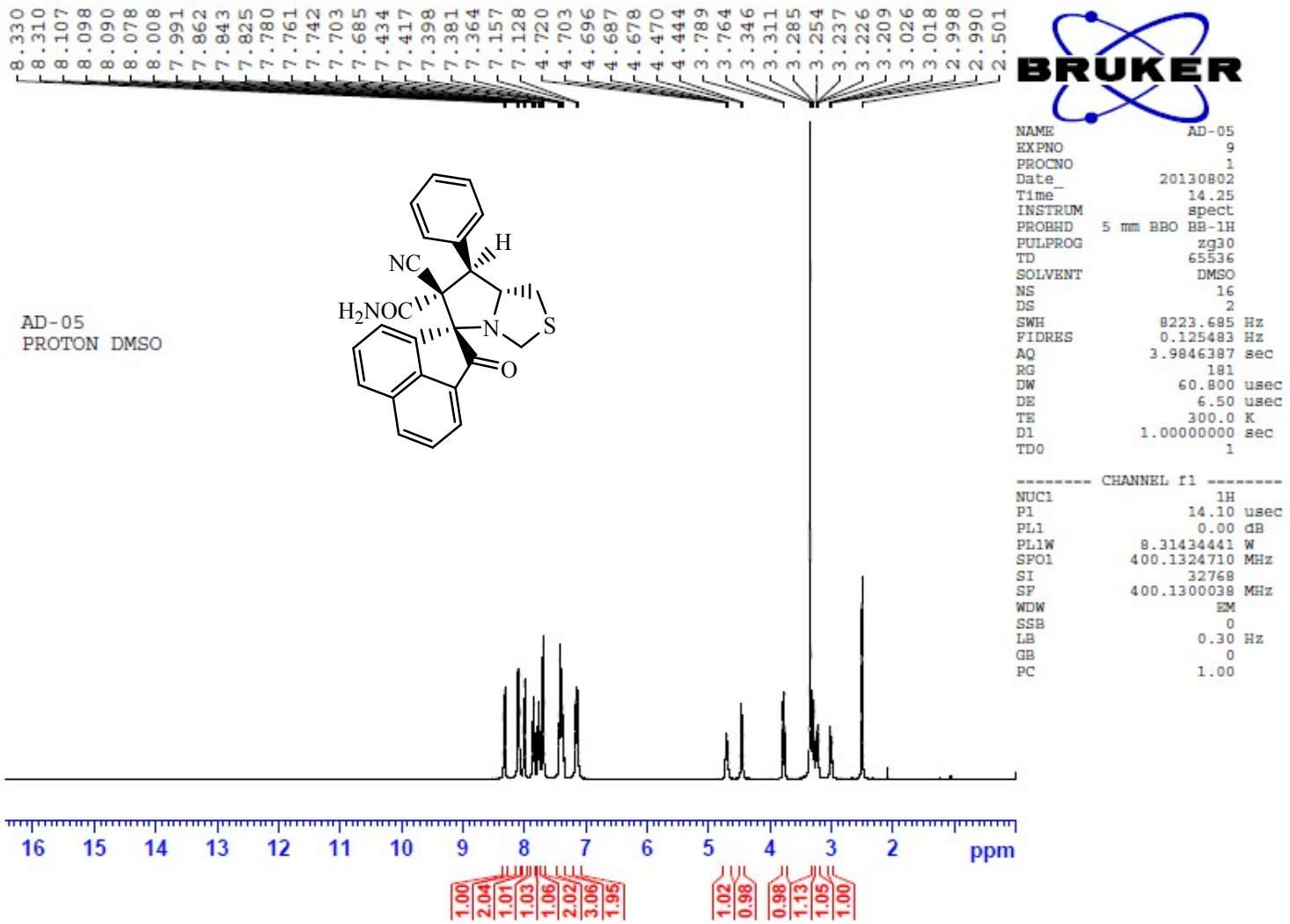


Figure 20: ^{1}H NMR spectrum of **4k**

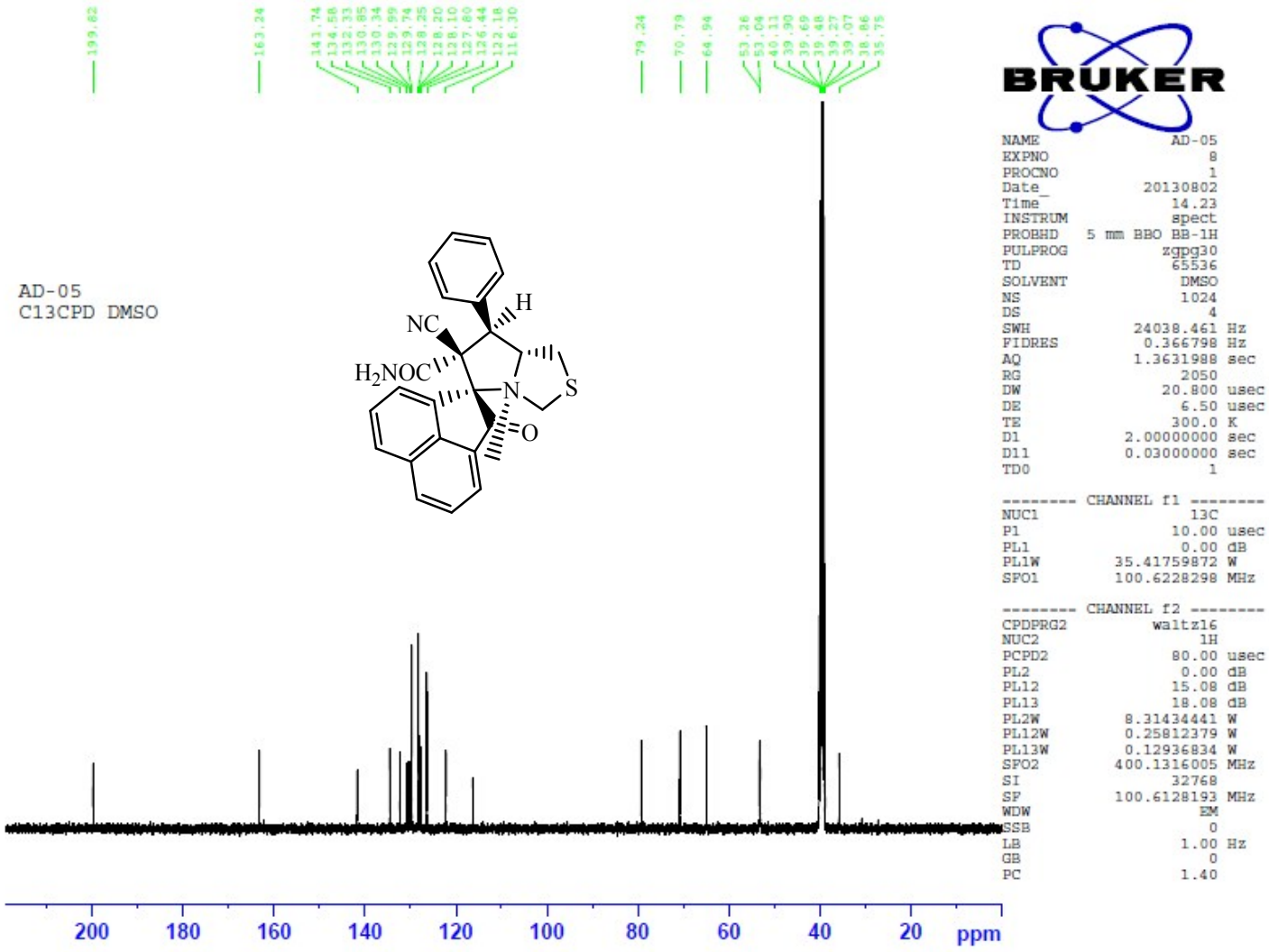


Figure 21: ^{13}C NMR spectrum of **4k**

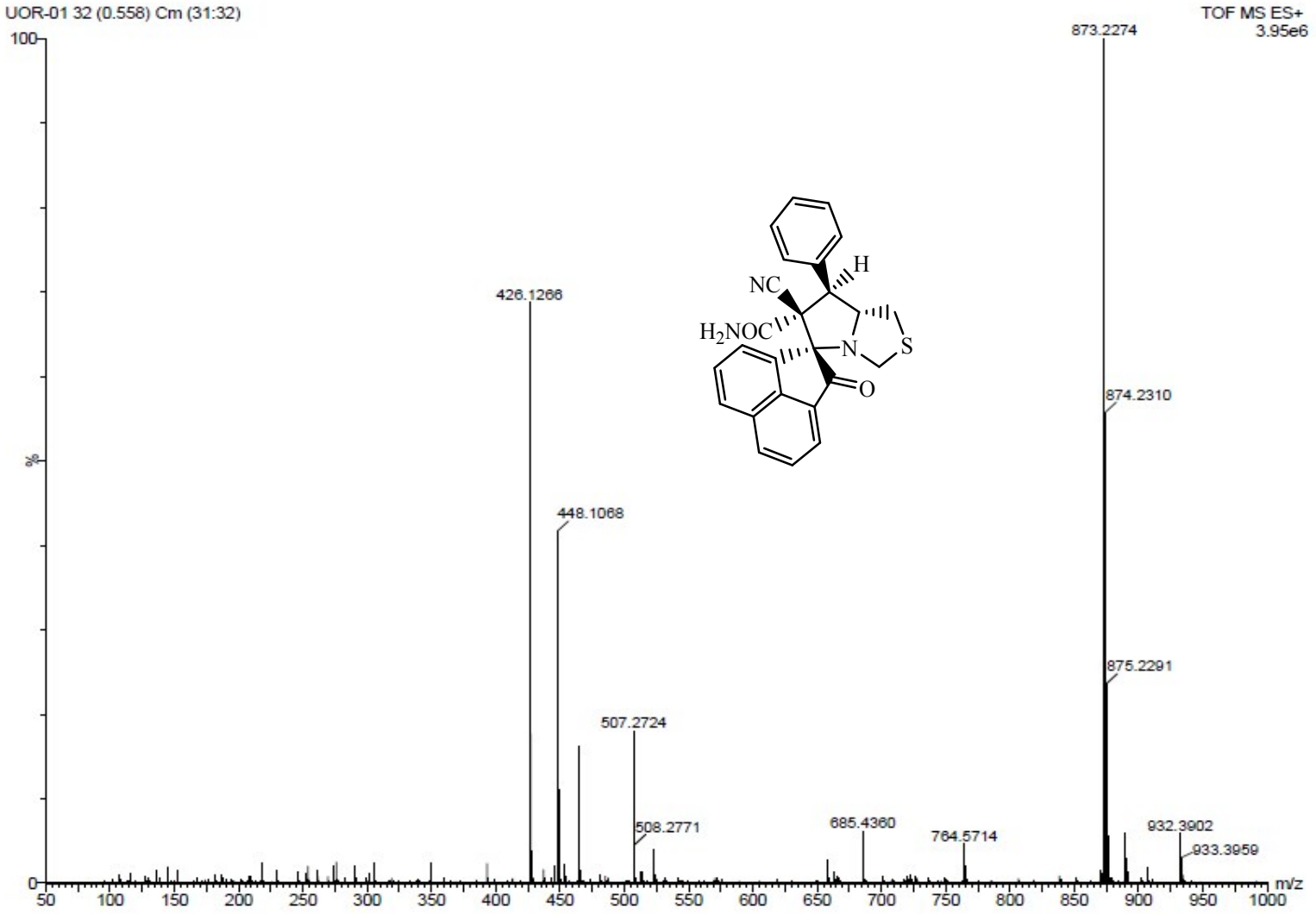


Figure 22: Mass spectrum of **4k**

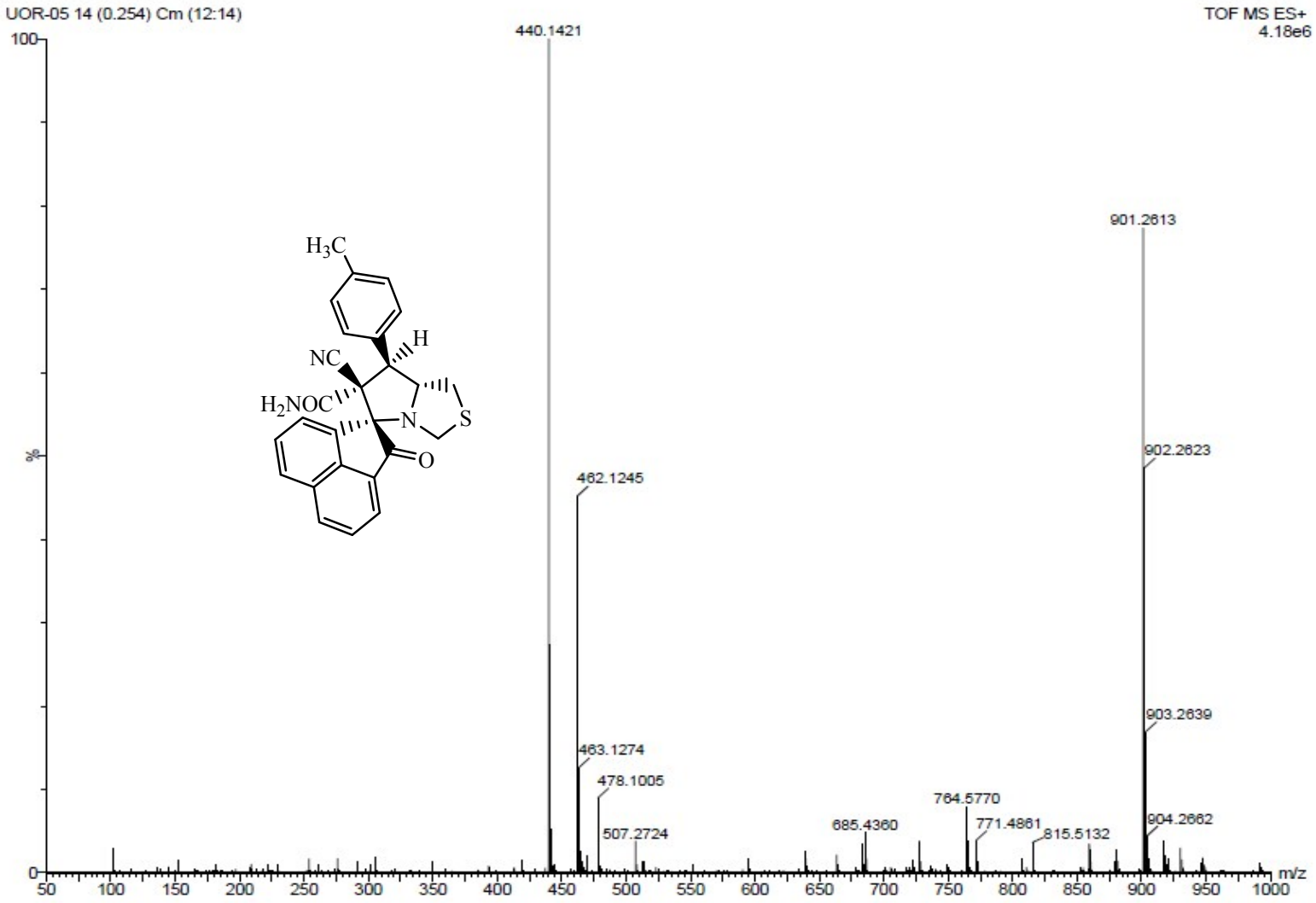


Figure 23: Mass spectrum of **4l**

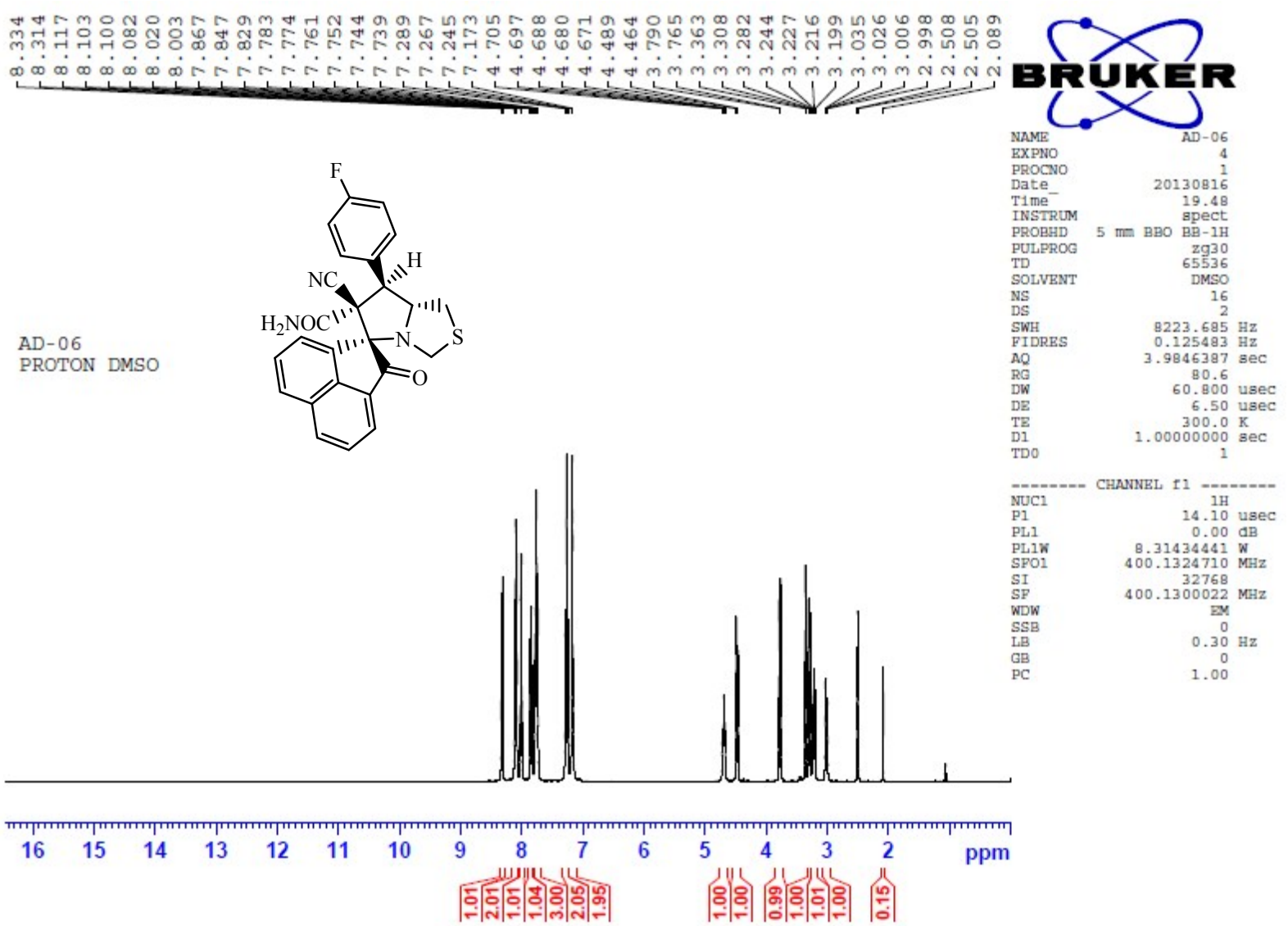


Figure 24: ^{1}H NMR spectrum of **4m**

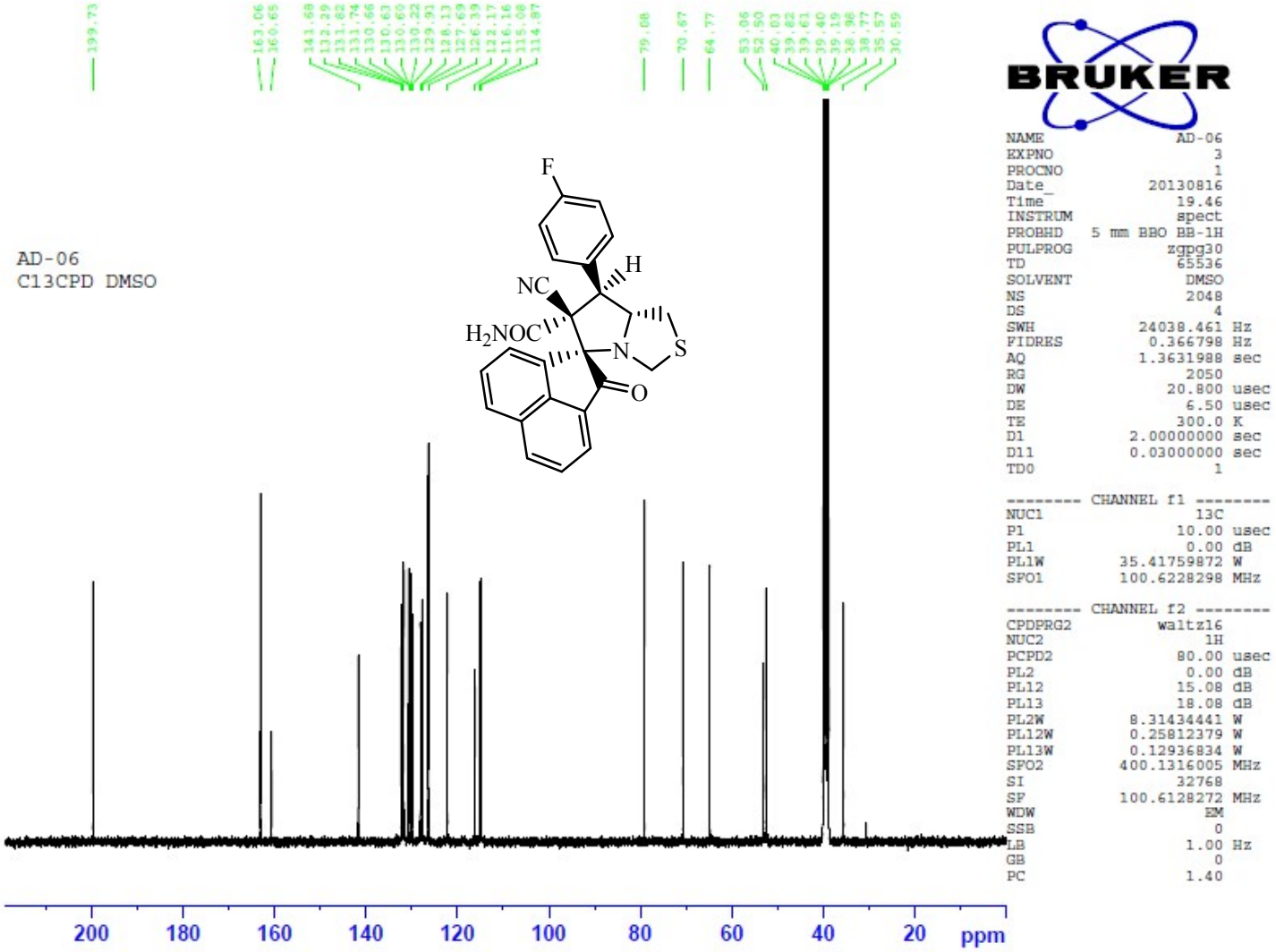


Figure 25: ^{13}C NMR spectrum of **4m**

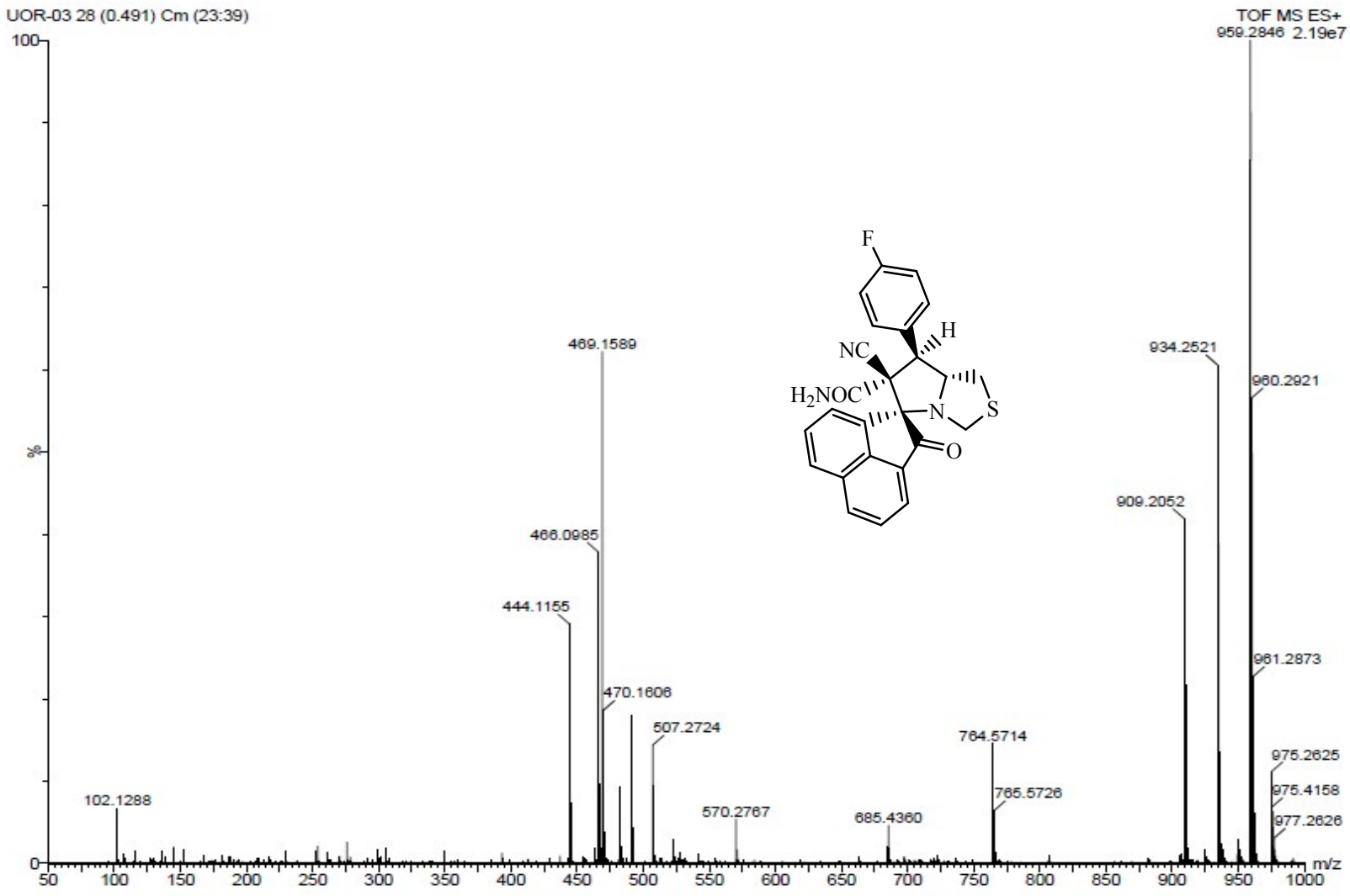


Figure 26: Mass spectrum of **4m**

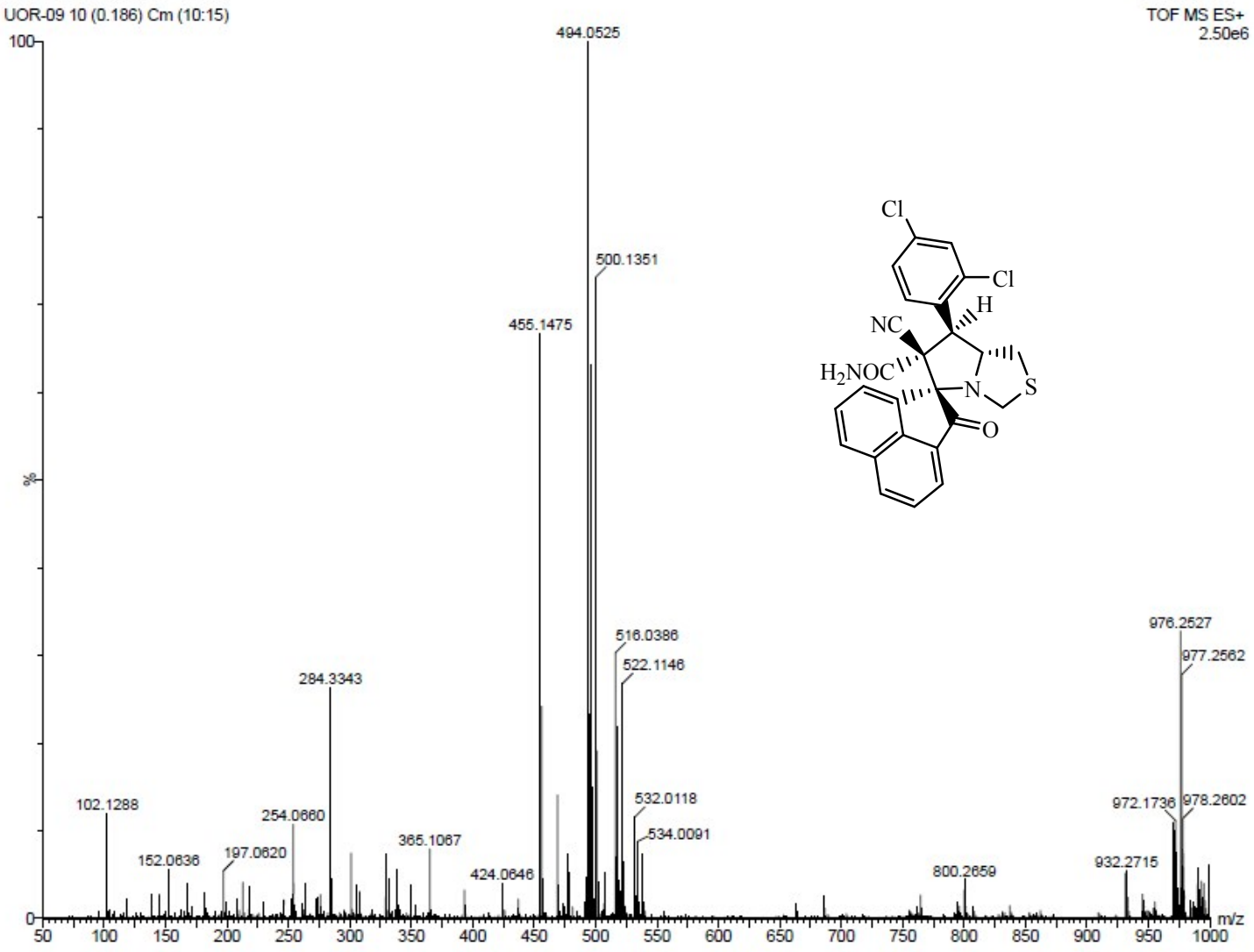


Figure 27: Mass spectra of **4n**

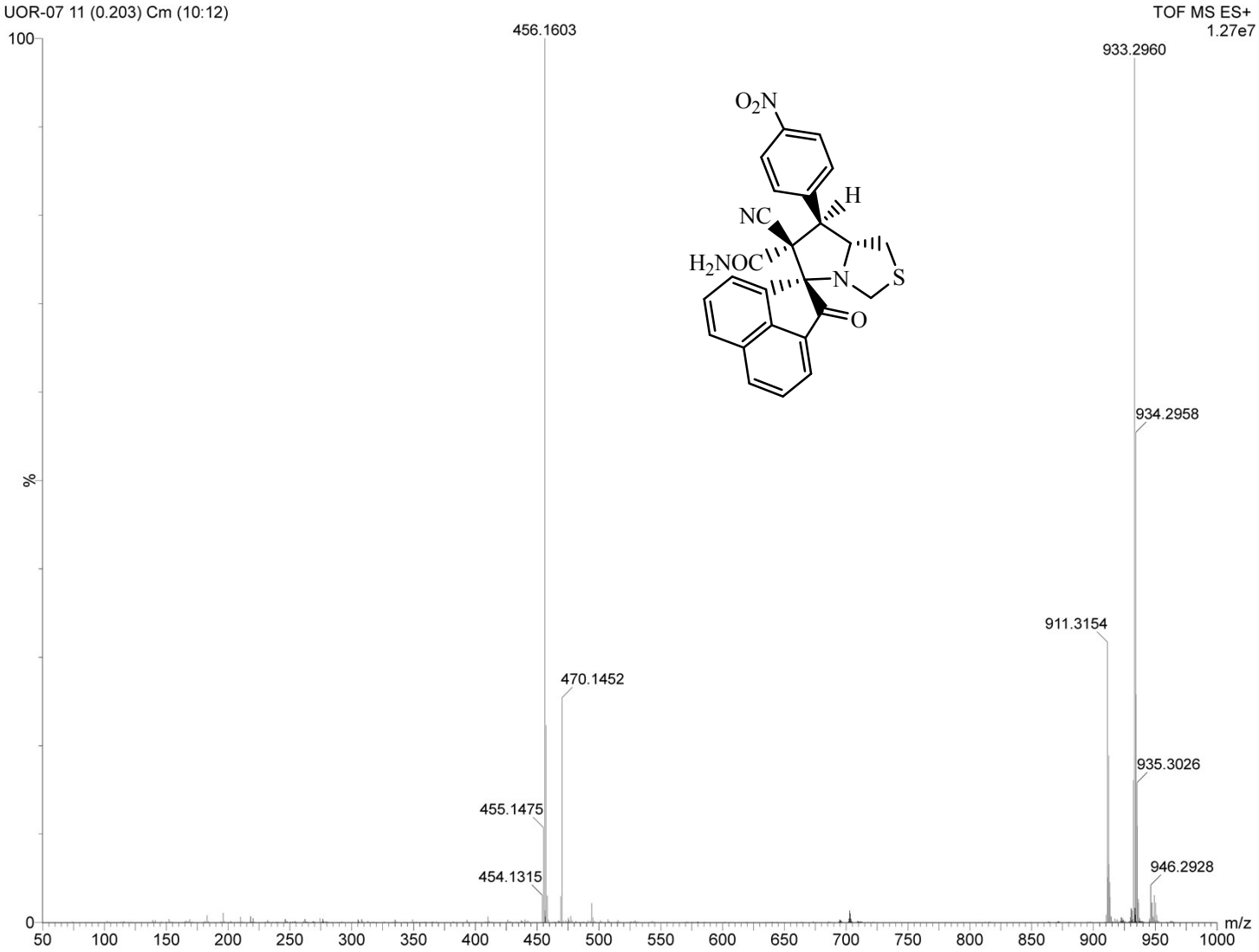


Figure 28: Mass spectra of **4o**

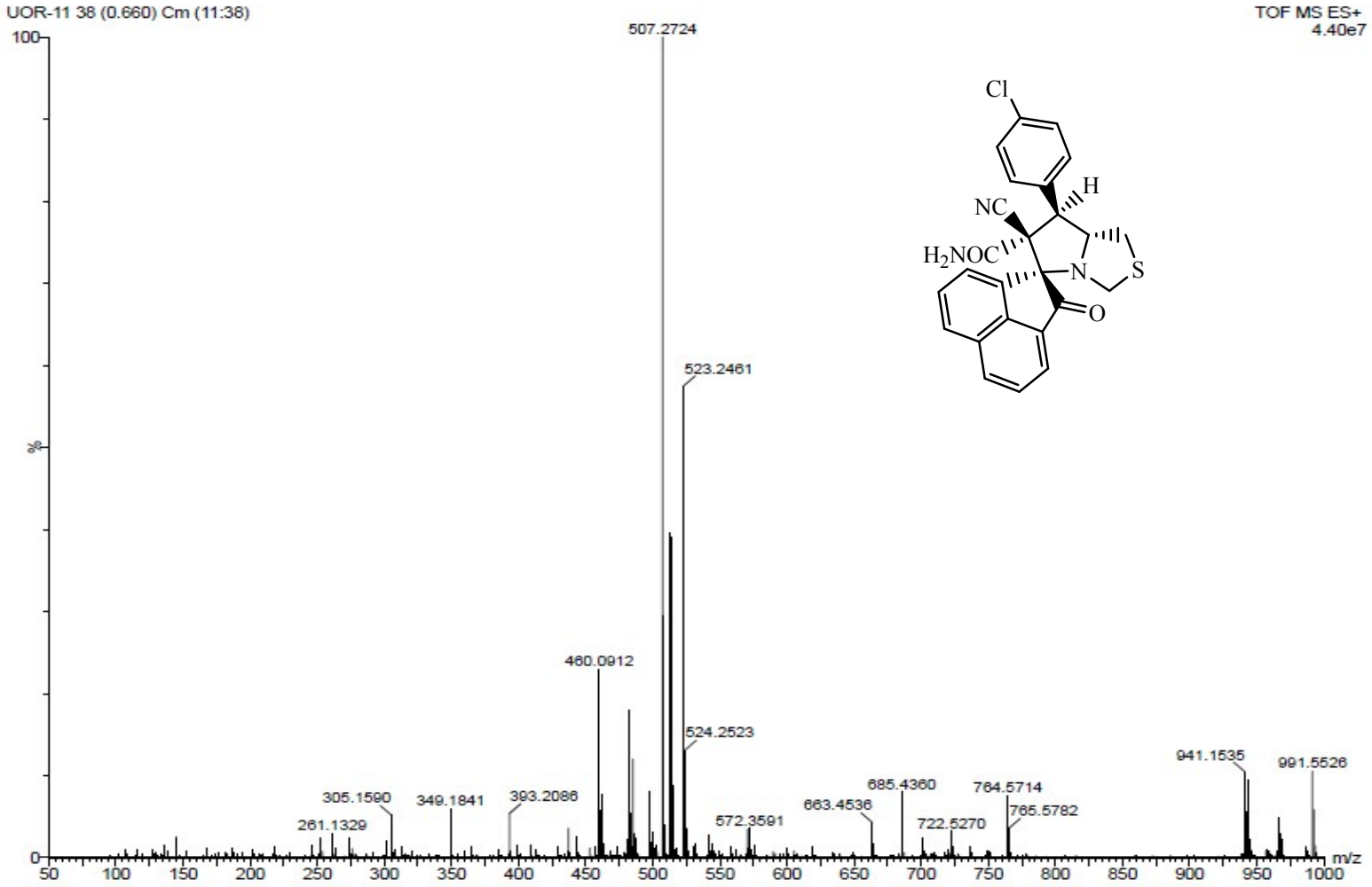


Figure 29: Mass spectra of **4p**

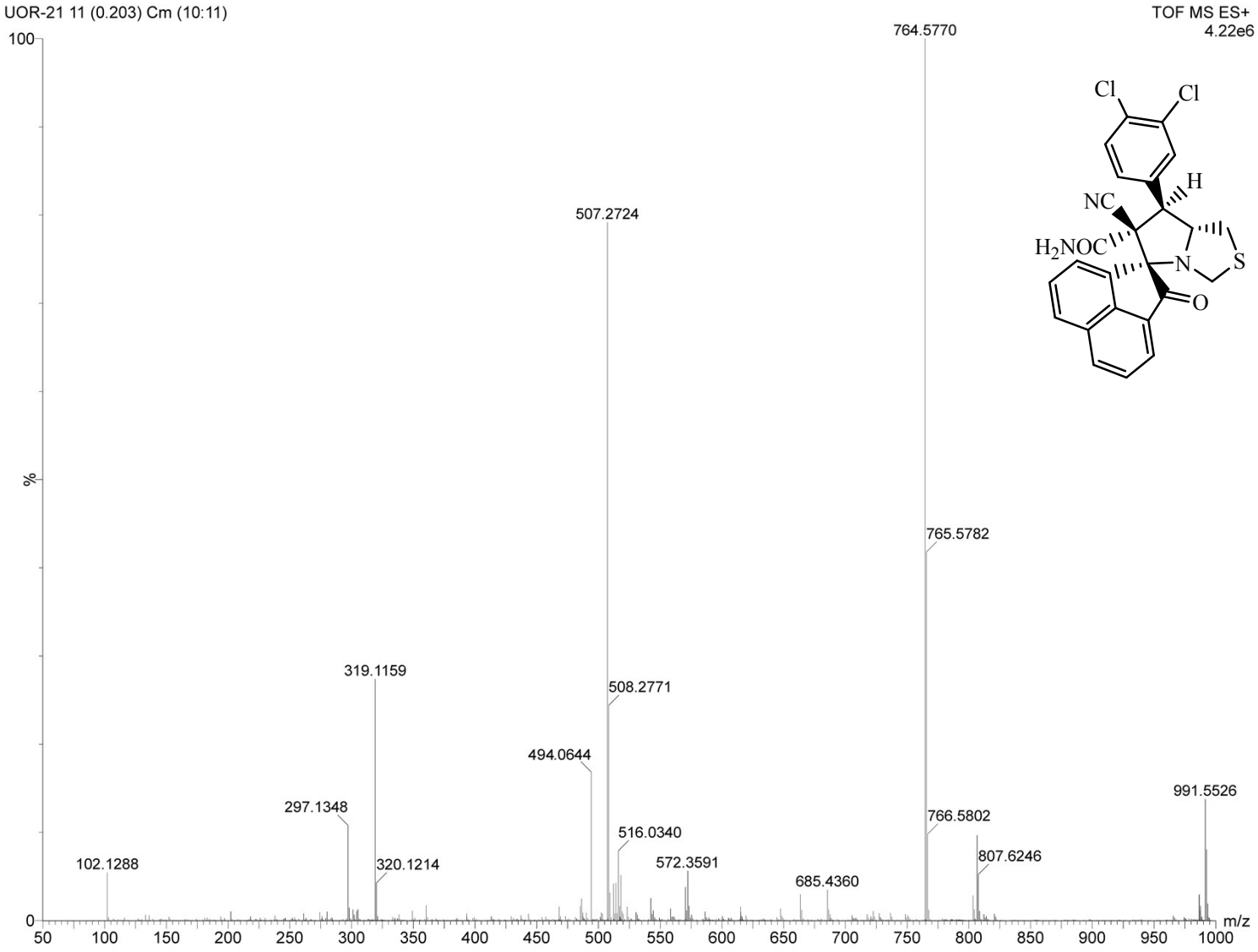


Figure 30: Mass spectra of **4q**

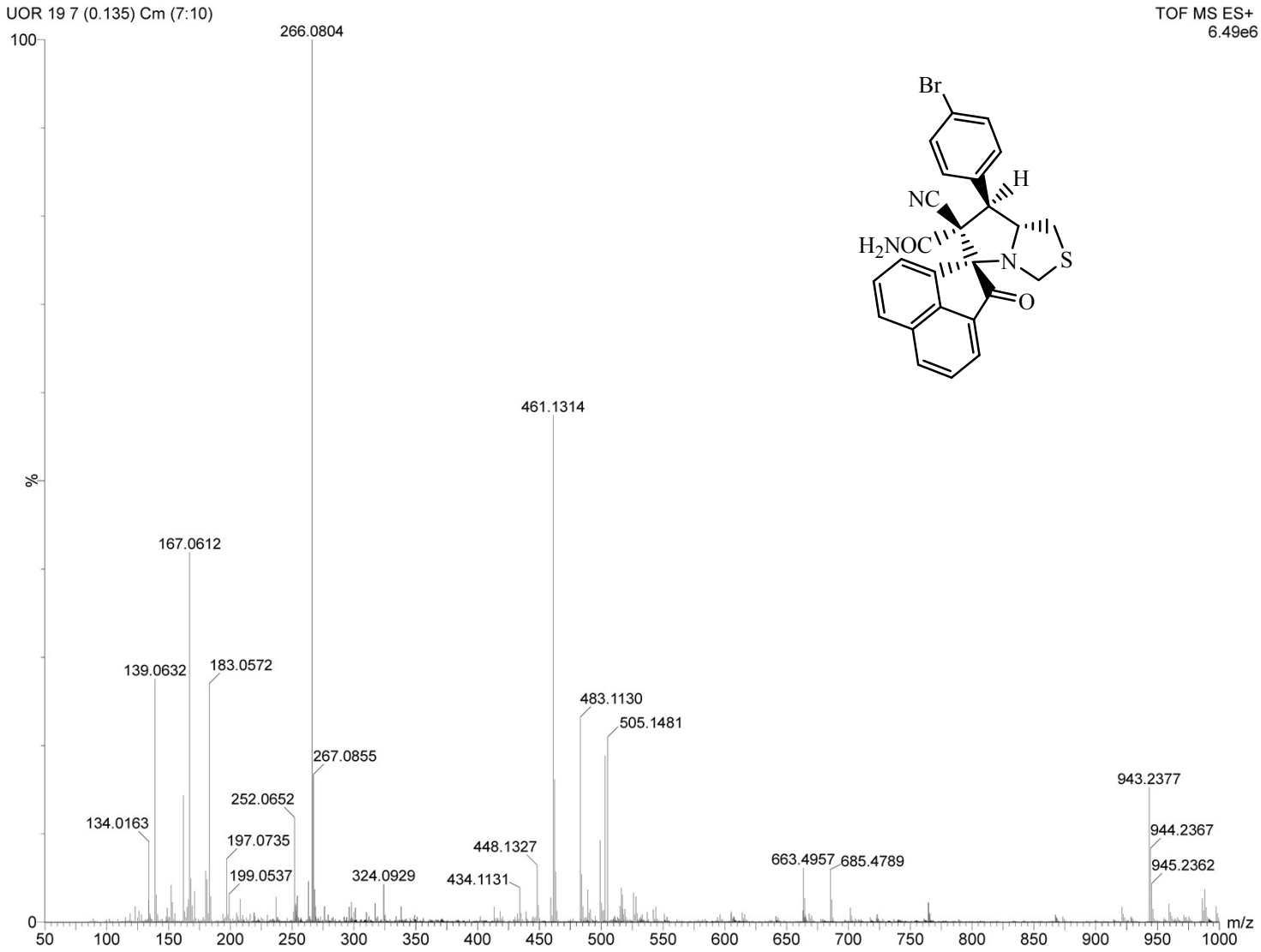


Figure 31: Mass spectra of **4r**

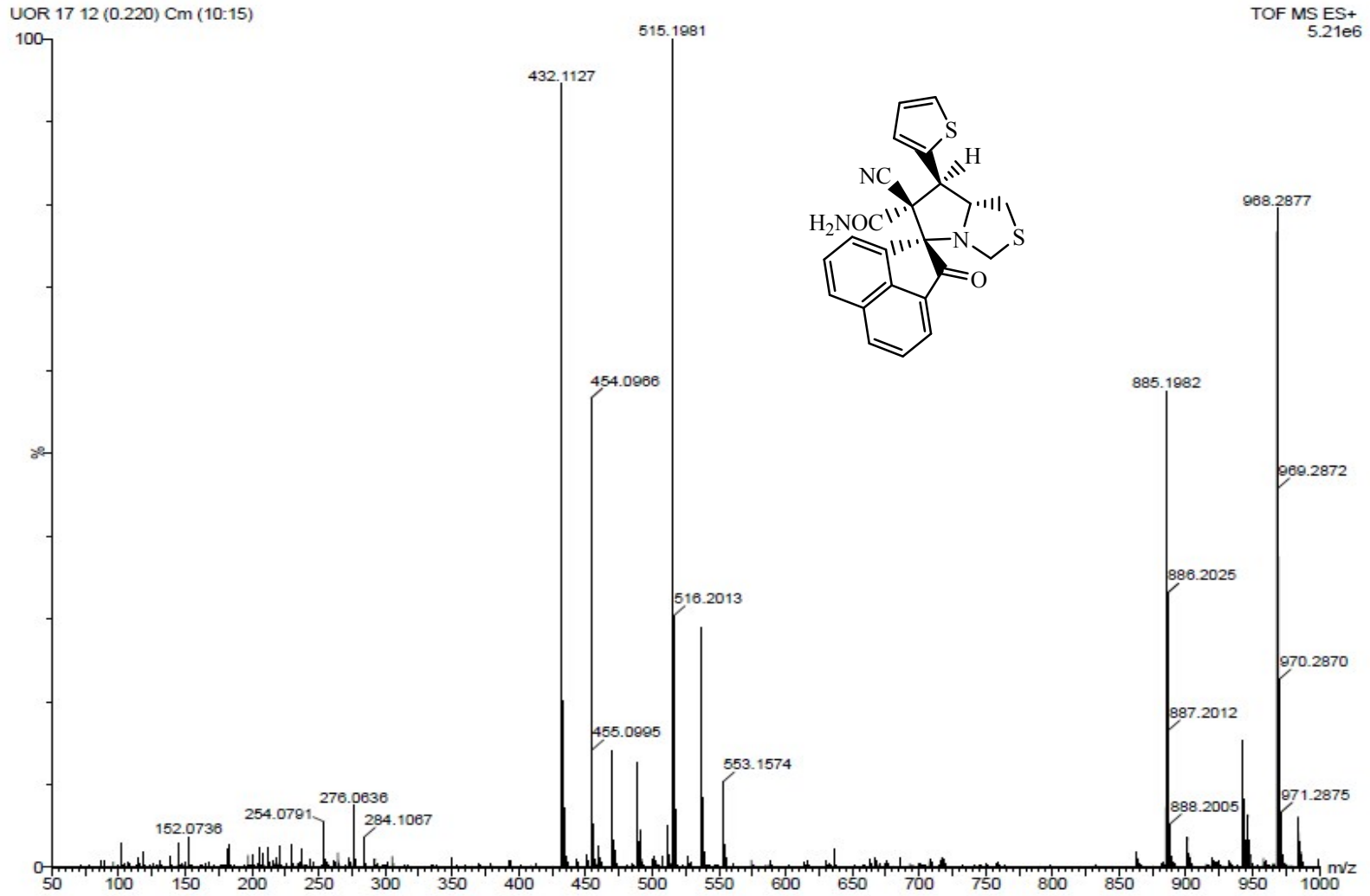


Figure 32: Mass spectra of **4s**

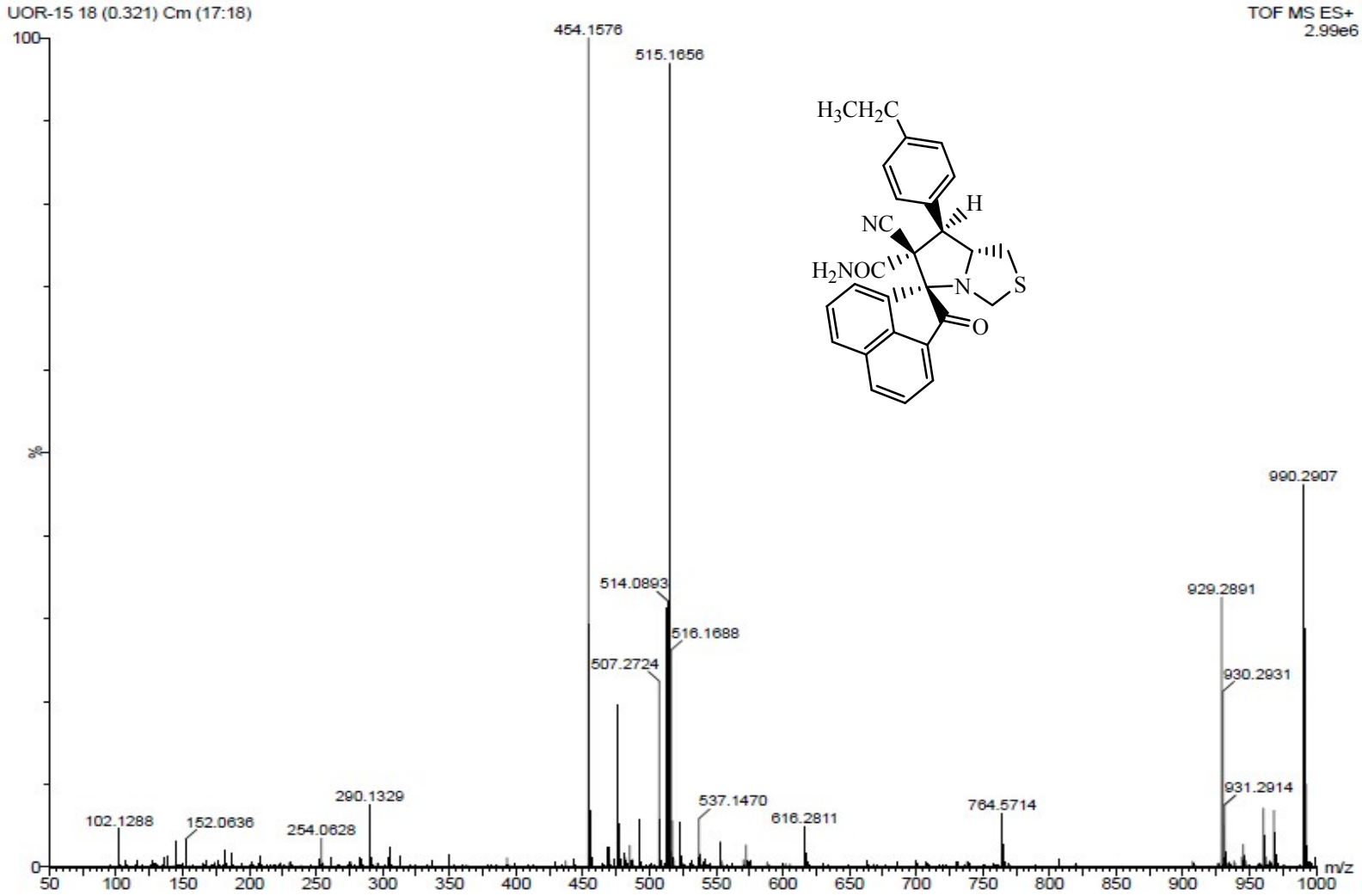


Figure 33: Mass spectra of **4t**

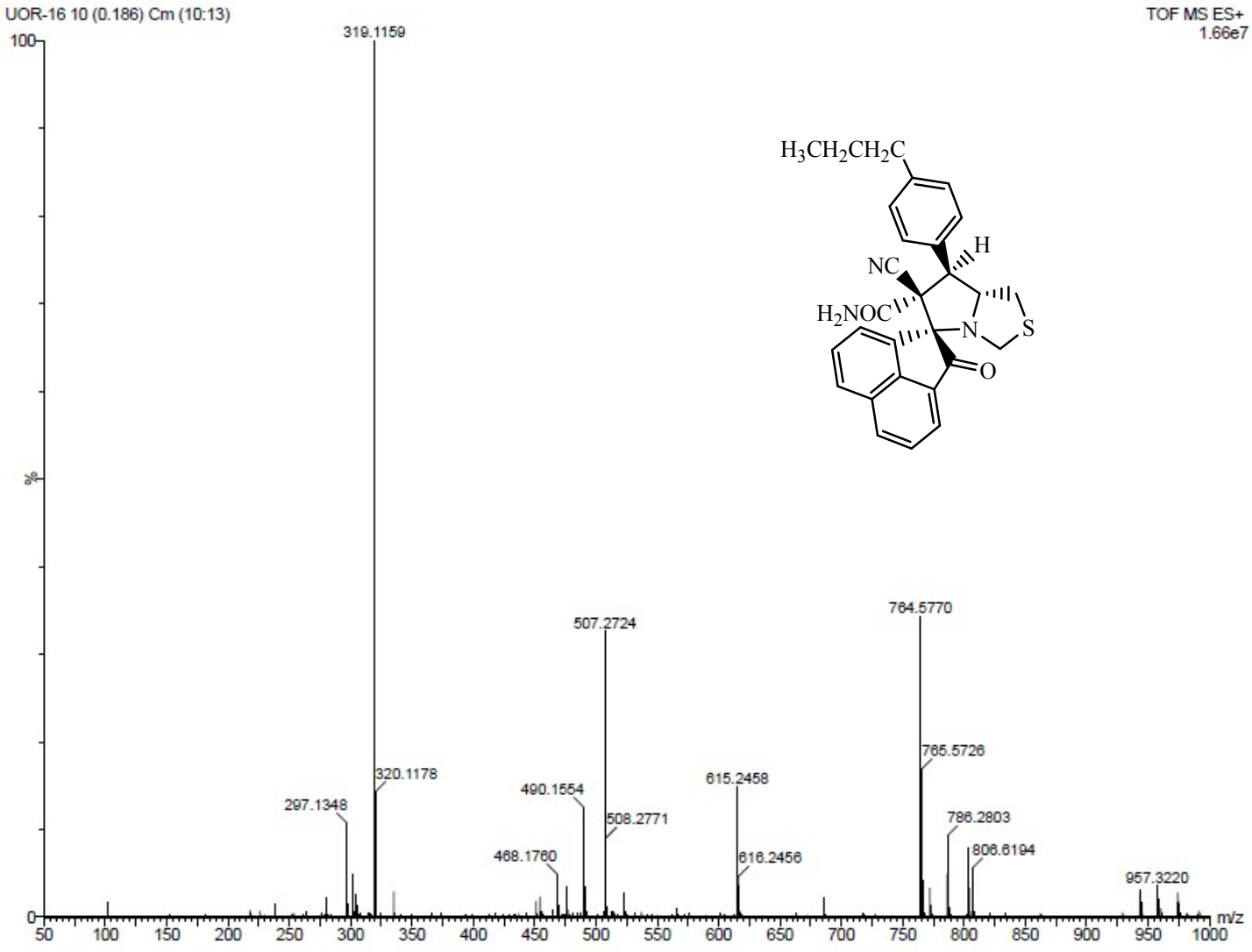


Figure 34: Mass spectra of **4u**