Supplementary Material (ESI) for Chemical Communication

An Expedient Approach to Pyrrolo[3,2-*c*]quinolines via Regioselective Formation of Pyrrole Nucleus Over Indoles

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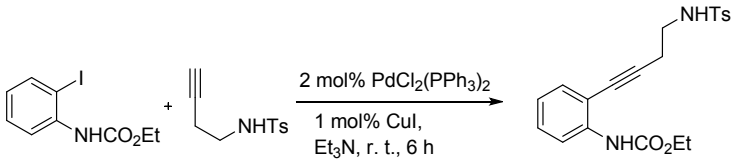
General Techniques:

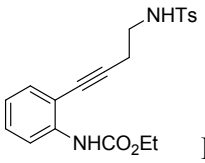
All reactions were carried out in oven dried glassware under an atmosphere of nitrogen. Chemicals were purchased from Aldrich and used as it is unless mentioned otherwise. All the solvents used for the reaction were dried before use. The product purification by column chromatography was accomplished using silica gel 60-120 mesh. The technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded in fourier transform mode. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-Avance (300 MHz); Inova (400 MHz) and Avance (500 MHz) spectrophotometer using $CDCl_3$ and TMS as the internal standard. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting point is uncorrected.

Experimental Procedure:

2-(4-aminobut-1-yn-1-yl) protected aniline were prepared according to the literature procedure.[1]

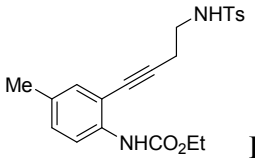


General procedure for the synthesis of Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate 1a–e: To a stirred solution of ethyl 2-iodophenylcarbamate (1.0 mmol) and $Pd(PPh_3)_2Cl_2$ (2 mol %) in Et_3N was added *N*-(but-3-ynyl)-4-methylbenzenesulfonamide and CuI (1 mol %) successively under N_2 atmosphere. The reaction mixture was stirred at room temperature until the starting material consumed. The reaction mixture was filtered and solvent was removed from filtrate. The crude product obtained was purified by column chromatography using hexane-ethyl acetate mixture (80:20).

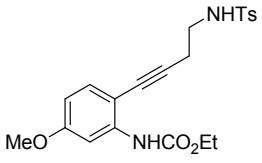


Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1a): The product was obtained as a yellow solid, mp: 87–90°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.33–7.27 (m, 4H), 7.24 (s, 1H), 6.96 (dt, *J* = 7.6 and 1.1 Hz, 1H), 4.86 (t, *J* = 5.9 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.24 (q, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.3, 143.7, 139.1, 136.9, 131.8, 129.7, 129.4, 127.0,

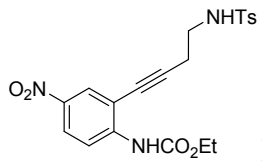
122.4, 117.8, 92.8, 78.0, 61.4, 41.9, 21.5, 21.1, 14.5; HRMS (ESI) $[M+Na]^+$ Calcd for $C_{20}H_{23}O_4N_2SNa$: 409.1192, found 409.1186.



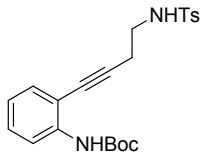
Ethyl-4-methyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1b): The product was obtained as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 3H), 7.20–7.08 (m, 2H), 4.82 (t, *J* = 6.7 Hz, 1H), 4.33 (q, *J* = 6.7 Hz, 2H), 3.23 (q, *J* = 6.7 Hz, 2H), 2.67 (t, *J* = 6.7 Hz, 2H), 2.4 (s, 3H), 2.2 (s, 3H), 1.37–1.30 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.2, 143.0, 136.8, 136.3, 131.9, 131.6, 129.6, 129.4, 126.7, 117.7, 111.4, 92.5, 77.5, 61.0, 41.7, 21.1, 20.8, 20.1, 14.2; HRMS (ESI) $[M+H]^+$ Calcd for $C_{21}H_{25}O_4N_2S$: 401.1529, found 401.1525.



Ethyl-5-methoxy-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1c): The product was obtained as a brown solid, mp: 70-74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 3H), 7.31–7.26 (m, 3H), 7.20 (d, *J* = 8.54 Hz, 1H), 6.52 (dd, *J* = 8.5 and 2.4 Hz, 1H), 5.08 (t, *J* = 5.9 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.8 (s, 3H), 3.21 (q, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 153.2, 143.5, 140.4, 136.9, 132.7, 129.7, 126.9, 109.1, 103.3, 102.8, 91.5, 77.7, 61.4, 55.3, 41.9, 21.5, 21.1, 14.48; HRMS (ESI) $(M)^+$ Calcd for $C_{21}H_{25}O_5N_2S$: 417.1478, found 417.1473.



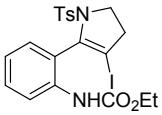
Ethyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)-4 nitrophenylcarbamate(1d): The product was obtained as a brown solid, mp: 122-124°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.1 Hz, 1H), 8.17–8.09 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 3H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.48 (s, 1H), 4.72 (t, *J* = 6.1 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.36 (q, *J* = 6.4 Hz, 2H), 3.24 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 144.5, 143.8, 141.9, 136.8, 129.8, 129.6, 127.5, 127.0, 124.9, 117.0, 95.5, 75.9, 62.2, 41.6, 21.4, 21.3, 14.4; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{20}H_{21}O_6N_3SNa$: 454.1043, found 454.1058



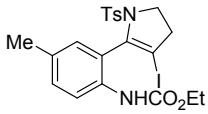
***tert*-Butyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1e):** The product was obtained as a brown solid, mp: 82–84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7,77 (d, *J* = 8.2 Hz, 2H), 7.31–7.27 (m, 4H), 7.11 (brs, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 4.85 (bs, 1H), 3.26–3.19 (m, 2H), 2.69 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.3, 143.5, 139.3, 136.8, 131.8, 129.6, 129.2, 126.9, 121.9, 117.5, 110.9, 92.6, 80.8, 77.9, 41.8, 28.2, 21.4, 21.0; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{22}H_{27}O_4N_2SNa$: 437.1496, found 437.1497.

General procedure for iodocyclization of ethyl 2-(4-(4-methylphenyl sulfonamido)but-1-ynyl)phenylcarbamate 5a–e: To a solution of ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate **1a–e** (1.0 mmol) and K_2CO_3 (3.0 equiv.) in dry acetonitrile (2 mL) under N_2 atmosphere at 0ºC was added solution of

iodine (3.0 equiv) in acetonitrile (0.6 mL) dropwise and the resulting mixture was allowed to stir at room temperature for required time and was then diluted with EtOAc and washed with saturated solution of $Na_2S_2O_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (3X 5mL). The organic solution were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography using hexane-ethyl acetate mixture (70:30).

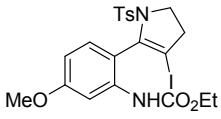


Ethyl-2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5a): The product was obtained as a pale yellow solid, mp: 128-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.12 Hz, 2H), 7.37 (t, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.13–6.97 (m, 3H), 4.27–4.05 (m, 4H), 2.89–2.63(m, 2H), 2.42 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 150.4, 144.4, 141.7, 136.7, 133.9, 131.1, 130.3, 129.5, 127.9, 122.3, 120.2, 82.0, 61.2, 50.2, 39.3, 21.6, 14.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{20}H_{22}O_4N_2IS$: 513.0339, found 513.0334.

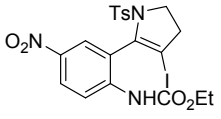


Ethyl-2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-methylphenylcarbamate (5b): The product was obtained as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.40(d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.13 (dd, *J* = 8.3 and 1.9 Hz, 1H), 6.93 (s, 1H), 6.70 (d, *J* = 1.9 Hz, 1H), 4.24 (m, 3H), 4.10–4.03 (m, 1H), 2.92–2.84 (m, 1H), 2.76–2.68 (m, 1H), 2.41(s, 3H), 2.20 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 150.5, 144.4, 141.8, 135.8, 134.1, 131.3, 130.9,

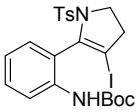
129.4, 129.3, 127.9, 127.0, 64.2, 50.0, 39.2, 29.6, 21.5, 20.5, 14.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{21}H_{24}O_4N_2IS$: 527.0496, found 527.0488.



Ethyl-2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-5-methoxyphenylcarbamate (5c): The product was obtained as a brown solid, mp: 154–155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s,1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.56 (dd, *J* = 8.5 and 2.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.15–4.10 (m, 2H), 3.84 (s, 3H), 2.83–2.75 (m, 1H), 2.72–2.63 (m, 1H), 2.43 (s, 3H), 1.34 (t, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 161.1, 153.3, 144.4, 141.5, 138.1, 133.8, 132.1, 129.5, 129.4, 127.9, 112.8, 109.0, 81.6, 61.2, 55.2, 50.2, 39.1, 21.5, 14.5; HRMS (ESI) $(M+H)^+$ Calcd for $C_{21}H_{24}O_5N_2IS$: 543.0445, found 543.0436.

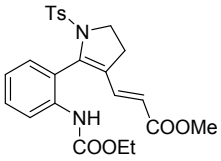


Ethyl-2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-nitrophenylcarbamate (5d): The product was obtained as a yellow solid, mp: 168–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 9.2 Hz, 1H), 8.22 (dd, *J* = 9.2 and 2.6 Hz, 1H), 7.85 (d, *J* = 2.6 Hz, 1H), 7.55–7.41 (m, 3H), 7.29–7.25 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.23–4.05 (m, 2H), 2.97–2.83 (m, 1H), 2.81–2.65 (m, 1H), 2.43 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.8, 151.3, 145.3, 142.8, 139.7, 133.4, 129.9, 127.8, 126.8, 125.7, 119.1, 84.4, 62.1, 50.2, 39.4, 21.6, 14.4; HRMS (ESI) $(M+H)^+$ Calcd for $C_{20}H_{21}O_6N_3IS$: 558.0190, found 558.0205.



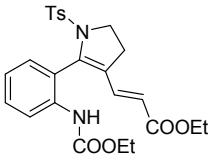
***t*ert-Butyl-2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5e):** The product was obtained as a yellow solid, mp: 94–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.07–6.89 (m, 3H), 4.18–4.06 (m, 2H), 2.88–2.60 (m, 2H), 2.41 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.6, 144.3, 141.8, 137.1, 133.8, 131.0, 130.2, 129.4, 127.9, 122.0, 121.0, 120.3, 82.1, 80.4, 50.1, 39.3, 28.3, 21.6; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{22}H_{25}O_4N_2INaS$: 563.0471, found 563.0469.

Typical procedure for Heck coupling of substituted iodo compound 3a–h: To a solution of ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate in DMF was added $Pd(PPh_3)_2Cl_2$ (5 mol %), alkene (2.0 equiv) and Et_3N (3.0 equiv). The reaction mixture was stirred at 80ºC for 2–4 h. Then the reaction mixture was allowed to room temperature and diluted with EtOAc and washed with water and brine solution. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane-ethyl acetate mixture (80:20).

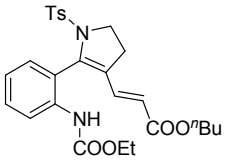


(*E*)-Methyl-3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3a): The product was obtained as a colourless needles (DCM/Ether), mp: 140–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.49–7.37 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.12–6.96 (m, 3H), 6.88 (dd, *J* = 7.5 and 1.3 Hz, 1H), 5.63 (d, *J* = 15.6 Hz, 1H), 4.26–4.07 (m, 4H), 3.65 (s, 3H), 2.72–2.61 (m, 2H),

2.42 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 153.3, 144.6, 143.4, 137.3, 137.2, 134.0, 131.1, 130.8, 129.5, 127.7, 124.5, 122.6, 118.3, 61.2, 51.4, 49.5, 30.8, 21.5, 14.4; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{24}H_{26}O_6N_2NaS$: 493.1403, found 493.1404.

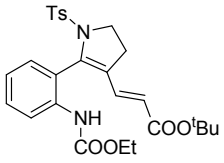


(*E*)-Ethyl-3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3b): The product was obtained as a brown needles, mp: 125–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (brs, 1H), 7.47–7.39 (m, 3H), 7.22 (d, J = 7.9 Hz, 2H), 7.10–7.00 (m, 3H), 6.90 (dd, J = 7.6 and 1.5 Hz, 1H), 5.63 (d, J = 15.5 Hz, 1H), 4.23–4.08 (m, 6H), 2.71–2.57 (m, 2H), 2.42 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 153.4, 144.6, 143.3, 137.4, 137.0, 134.1, 131.1, 130.8, 129.6, 127.8, 124.6, 122.6, 118.9, 61.2, 60.3, 49.5, 27.9, 21.6, 14.5, 14.1; HRMS (ESI) $(M+H)^+$ Calcd for $C_{25}H_{28}O_6N_2S$: 485.1742, found 485.1740.

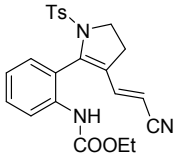


(*E*)-Butyl-3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3c): The product was obtained as a white solid, mp: 126–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 1H), 7.49–7.39 (m, 3H), 7.22 (d, J = 8.1 Hz, 2H), 7.11–6.99 (m, 3H), 6.89 (dd, J = 7.5 and 1.3 Hz, 1H), 5.63 (d, J = 15.4 Hz, 1H), 4.26–4.10 (m, 4H), 4.06 (t, J = 6.6 Hz, 2H), 2.72– 2.58 (m, 2H), 2.42 (s, 3H), 1.38–1.23 (m, 7H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.6,

153.4, 144.6, 143.4, 137.4, 137.1, 134.1, 131.1, 130.9, 129.6, 127.8, 124.7, 122.6, 118.9, 64.2, 61.3, 49.5, 30.6, 27.9, 21.6, 19.0, 14.5, 13.6; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{27}H_{32}O_6N_2NaS$: 535.1873, found 535.1862.

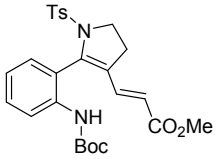


(*E*)-*tert*-Butyl-3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3d): The product was obtained as a yellow needles, mp: 136–140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (brs, 1H), 7.45–7.40 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.07 (dt, *J* = 7.4 and 1.0 Hz, 2H), 6.97 (d, *J* = 15.5 Hz, 1H), 6.91 (dd, *J* = 7.6 and 1.5 Hz, 1H), 5.57 (d, *J* = 15.5 Hz, 1H), 4.24–4.07 (m, 4H), 2.70–2.53 (m, 2H), 2.42 (s, 3H), 1.40 (s, 9H), 1.31(t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 165.9, 153.4, 146.3, 145.5, 144.6, 137.3, 136.2, 133.9, 131.1, 130.7, 129.6, 127.8, 127.0, 125.0, 122.5, 120.9, 80.4, 61.2, 49.5, 28.0, 21.6, 14.5; HRMS (ESI) $(M+H)^+$ Calcd for $C_{27}H_{33}N_2O_6S$: 513.20538, found 513.20531.

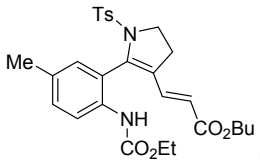


(*E*)-Ethyl-2-(3-(2-cyanovinyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (3e): The product was obtained as a yellow needles, mp: 127–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 5.01 (d, *J* = 16.1Hz, 1H), 4.27–4.17 (m, 3H), 4.15–4.06 (m, 1H), 2.75–2.58 (m, 2H), 2.41 (s. 3H), 1.31(t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 144.8, 144.4, 142.9, 137.3, 133.9, 131.1, 130.9, 129.8, 129.6,

127.7, 127.6, 123.1, 122.8, 118.2, 94.9, 61.3, 49.4, 26.9, 21.5, 14.4; HRMS (ESI) $(M+H)^+$ Calcd for $C_{23}H_{24}O_4N_3S$: 438.1482, found 438.1481.

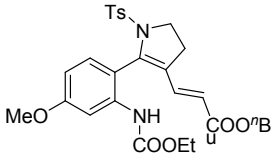


(*E*)-Methyl-3-(2-(2-(*tert*-butoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3f): The product was obtained as a yellow needles, mp: 160–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (brs, 1H), 7,45–7.39 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.07–7.01 (m, 2H), 6.88–6.81 (m, 2H), 5.63 (d, *J* = 15.7 Hz, 1H), 4.24–4.08 (m, 2H), 3.65 (s, 3H), 2.73–2.58 (m, 2H), 2.41 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.9, 152.6, 144.5, 143.7, 137.7, 137.4, 134.1, 131.1, 130.7, 129.5, 127.8, 124.5, 122.3, 120.7, 119.6, 118.2, 80.6, 51.4, 49.4, 28.2, 21.5; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{26}H_{30}O_6N_2NaS$: 521.1716, found 521.1710.



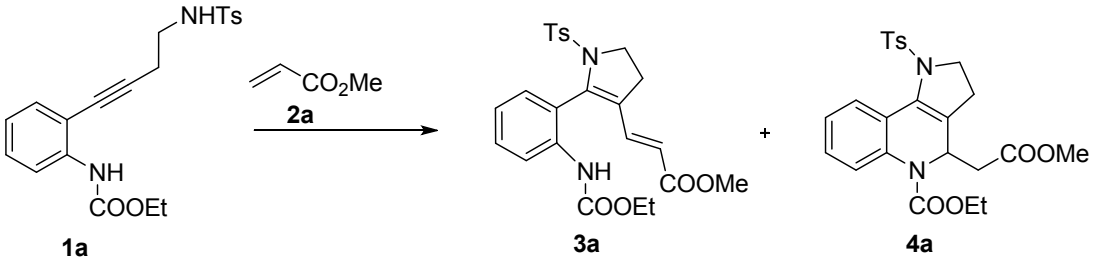
(*E*)-Butyl-3-(2-(2-(ethoxycarbonylamino)-5-methylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3g): The product was obtained as a brown needles, mp: 110-112°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.24–7.18 (m, 3H), 7.02 (d, *J* = 15.5 Hz, 1H), 6.87 (brs, 1H), 6.58 (d, *J* = 1.5 Hz, 1H), 5.62 (d, *J* = 15.5 Hz, 1H), 4.25–4.15 (m, 2H), 4.14–4.09 (m, 2H), 4.09–4.01 (m, 2H), 2.75–2.58 (m, 2H), 2.41 (s, 3H), 2.26 (s, 3H), 1.60–1.53 (m, 2H), 1.34–1.29 (m,5H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.6, 159.1, 150.1, 143.5, 137.1, 134.8, 134.4, 131.5, 131.4, 129.8, 129.4, 128.2, 127.8, 126.9, 118.5, 64.1,

61.1, 49.5, 31.5, 22.6, 21.5, 19.0, 14.5, 13.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{28}H_{35}O_6N_2S$: 527.2210, found 527.2209.



(*E*)-Butyl-3-(2-(2-(ethoxycarbonylamino)-4-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3h): The product was obtained as a brown needles, mp: 105–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.69 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09–7.00 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.61 (dd, *J* = 8.3 and 2.4 Hz, 1H), 5.61 (d, *J* = 15.5 Hz, 1H), 4.25–4.15 (m, 2H), 4.12–4.09 (m, 4H), 3.87 (s, 3H), 2.66–2.56 (m, 2H), 2.41(s, 3H), 1.63–1.54 (m, 2H), 1.41–1.36 (m, 2H), 1.33–1.30 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.7, 161.6, 153.2, 144.5, 143.5, 138.8, 137.3, 134.1, 132.1, 129.5, 129.3, 128.1, 127.8, 124.4, 118.5, 109.1, 64.1, 61.2, 55.3, 49.5, 30.61, 27.8, 21.5, 19.0, 14.5, 13.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{28}H_{35}O_7N_2S$: 543.2159, found 543.2158.

Table SI1 Optimization of reaction conditions[a)]



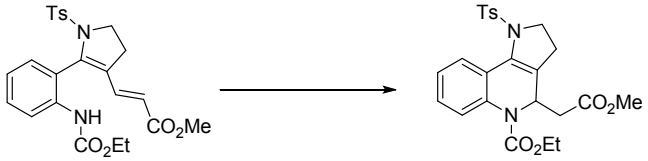
1a **3a** **4a**

Entry	Catalyst (mol %)	Oxidant	solvent	*T* (°C)/ Time (h)	yield(%)[b] **3a**	**4a**
1	$Pd(OAc)_2$/5	$Cu(OAc)_2$	MeCN	50/4	17	00
2	$Pd(OAc)_2$/10	$Cu(OAc)_2$	MeCN	75/10	23	00
3	$PdCl_2$/ 10	$Cu(OAc)_2$	MeCN	75/18	41	05
4	$Pd(PPh_3)_2Cl_2$/10	$Cu(OAc_2$	MeCN	75/18	30	00

5	$Pd(PPh_3)_4$/10	$Cu(OAc)_2$	MeCN	75/18	30	00
6	$PdCl_2$/ 10	$CuCl_2$	MeCN	75/18	44	07
7	$PdCl_2$/ 10	Ag_2O	MeCN	75/18	26	00
8	$PdCl_2$/ 10	$(C_6H_5CO)_2O_2$	MeCN	75/18	21	00
9	$PdCl_2$/ 10	$CuCl_2$	MeCN	75/18	35	06[c]
10	$PdCl_2$/ 10	$CuCl_2$	MeCN	75/18	33	08[d]
11	$PdCl_2$/ 10	$CuCl_2$	THF	75/18	25	00
12	$PdCl_2$/ 10	$CuCl_2$	EtOH	75/18	27	00
13	$PdCl_2$/ 10	$CuCl_2$	H_2O	100/18	00	00
14	$PdCl_2$/ 10	$CuCl_2$	Toluene	110/18	15	00
15	$PdCl_2$/ 10	$CuCl_2$	DMSO	120/18	48	10
16	**$PdCl_2$/ 10**	**$CuCl_2$**	**DMF**	**120/18**	**58**	**12**
17	$PdCl_2$/ 20	$CuCl_2$	DMF	140/24	58	12
18	$PdCl_2$/ 10	$CuCl_2$	DMF	120/18	53	10[e]
19	$PdCl_2$/ 10	$CuCl_2$	DMF	120/18	58	12[f]
20	$PdCl_2$/ 10	$CuCl_2$	DMF	120/18	11	00[g]

[a)]Reaction was performed using 0.5 mmol of **1a**, acrylate **2a** (1.0 mmol), 2.0 equiv of oxidant, 2.0 equiv of NaOAc, 2.0 equiv TBAF in 2.0 mL of solvent. [b] Isolated yields. [c]Using KOH, [d]Using NaOH, [g]Reaction without TBAF.

Table SI2. Optimization of Michael addition



3a **4a**

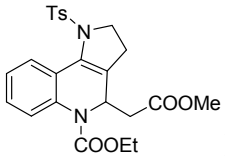
entry	catalyst (mol %)	solvent	oxidant	base	temp (°C)/ time (h)	yield (%)[b]
1	$Pd(OAc)_2$/ 10	THF	$Cu(OAc)_2$	CsOAc	70/12	00
2	$Pd(OAc)_2$/ 10	THF	$Cu(OAc)_2$	KOAc	70/12	07
3	$Pd(OAc)_2$/ 10	DMF	$Cu(OAc)_2$	KOAc	100/12	25
4	$Pd(OAc)_2$/ 10	DMF	$Cu(OAc)_2$	NaOAc	120/12	82
5	$Pd(OAc)_2$/ 10	DMSO	$Cu(OAc)_2$	NaOAc	120/12	79
6	$Pd(OAc)_2$/ 10	NMP	$Cu(OAc)_2$	NaOAc	120/12	76
7	$Pd(OAc)_2$/ 10	NMP	$Cu(OAc)_2$	KOH	120/12	80

8	$Pd(OAc)_2$/ 10	NMP	$Cu(OAc)_2$	KOH	120/18	80
9	$Pd(OAc)_2$/ 10	NMP	Ag_2O	KOH	120/12	73
10	$Pd(OAc)_2$/ 10	NMP	$CuCl_2$	KOH	120/12	76
11	$PdCl_2$/ 10	NMP	$Cu(OAc)_2$	KOH	120/12	82
12	**-**	**NMP**	**-**	**KOH**	**120/12**	**82**
13	-	NMP	-	KOH	120/18	82
14	-	NMP	-	KOH	120/6	82
15	-	NMP	-	NaOH	120/6	75
16	-	DMF	-	KOH	120/6	80
17	-	DMSO	-	KOH	120/6	74

[a]Reactions were performed using 0.5 mmol of **3a**, 2.0 equiv. of Base, in 2.0 mL solvent, catalyst, temperature and time. [b] Isolated yield

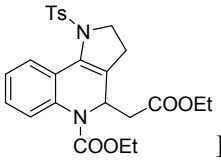
Typical procedure for Michael addition (Pyrrolo-quinoline derivatives) (4a–i):

Pyrrolo quinoline derivatives were prepared by Heck product of ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate **5a**–**h**. To a solution Heck product **3a**–**h** (0.5 mmol) in NMP (2 mL) was added KOH (2.0 equiv) and stirred to 120ºC for 4–6 h, then diluted with EtOAc and washed with water and brine solution. The organic layer was concentrated under reduced pressure. The product was purified by column chromatography on silica gel hexane-ethyl acetate mixture (80:20).

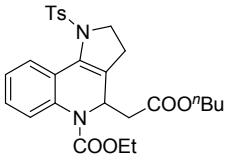


Ethyl-4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline 5(4*H*)-carboxylate (4a): The product was obtained as a white needles, mp: 133–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7 and 1.3 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 3H), 7.34–7.29 (m, 1H), 7.24–7.13 (m, 3H), 5.23 (t, *J* = 6.4 Hz, 1H), 4.40–4.24

(m, 2H), 4.19–4.06 (m, 1H), 3.89–3.75 (m, 1H), 3.5 (s, 3H), 2.4 (s, 3H), 2.32 (d, *J* = 6.9 Hz, 2H), 2.19–2.04 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 153.8, 144.1, 136.4, 133.2, 132.4, 129.2, 128.0, 127.9, 125.5, 124.7, 124.4, 122.9, 62.3, 52.0, 51.7, 50.3, 36.3, 29.6, 21.6, 14.5; HRMS (ESI) $(M+H)^+$ Calcd for $C_{24}H_{27}O_6N_2S$: 471.1584, found 471.1586.

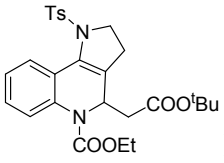


Ethyl-4-(2-ethoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4b): The product was obtained as a yellow needles, mp: 125–127 °C; ^{1}H NMR (300, $CDCl_3$) δ 7.77 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 3H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.25–7.14 (m, 3H), 5.24 (t, *J* = 6.7 Hz, 1H), 4.36 (m, 2H), 4.12 (q, *J* = 6.7 Hz, 2H), 4.05–3.95 (m, 1H), 3.89–3.74 (m, 1H), 2.40 (s, 3H), 2.30 (d, *J* = 6.7 Hz, 2H), 1.19 (t, *J* = 6.7 Hz, 3H), 1.35 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 165.1, 144.1, 136.3, 133.2, 132.4, 129.4, 128.0, 127.9, 125.6, 125.5, 124.7, 123.1, 62.3, 60.7, 51.9, 50.3, 36.6, 29.7, 21.6, 14.5, 14.0; HRMS (ESI) $(M+H)^+$ Calcd for $C_{25}H_{28}O_6N_2S$: 485.1740, found 485.1739.

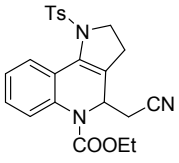


Ethyl-4-(2-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4c): The product was obtained as a brown needles, mp: 126–128 °C; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.77 (dd, *J* = 7.7 and 1.5 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.32–7.27 (m,2H), 7.23 (dt, *J* = 7.6 and 1.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.24 (brs, 1H), 4.33–4.24 (m ,2H), 4.09–4.02 (m, 1H), 3.99–3.90 (m, 2H), 3.86–3.77 (m, 1H), 2.40 (s, 3H), 2.31 (dd, *J* = 7.3 and 1.5 Hz, 2H), 4.14–2.03 (m, 2H), 1.57–1.48

(m, 4H), 1.35 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 144.1, 136.3, 133.3, 132.4, 129.2, 128.0, 127.9, 127.1, 125.6, 124.7, 123.0, 119.9, 64.7, 62.3, 52.0, 50.3, 36.5, 30.4, 29.6, 21.6, 19.0, 14.5, 13.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{27}H_{33}O_6N_2S$: 513.2053, found 513.2054.

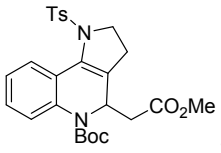


Ethyl-4-(2-*tert*-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4d): The product was obtained as a yellow needles, mp: 120–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.74 (m, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.32–7.27 (m, 1H), 7.23 (dt, J = 7.6 and 1.2 Hz, 1H), 7.16 (d, J = 7.9 Hz, 2H), 5.21 (brs, 1H), 4.41–4.33 (m, 1H), 4.30–4.21 (m, 2H), 4.16–4.08 (m, 1H), 3.85–3.76 (m, 1H), 2.40 (s, 3H), 2.36–2.32 (m, 1H), 2.21(d, J = 7.0 Hz, 2H), 2.15–2.07 (m, 1H), 1.38–1.34 (m, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.1, 153.9, 144.1, 136.1, 133.3, 132.4, 129.6, 129.2, 128.6, 127.9, 126.3, 125.5, 124.7, 123.1, 81.0, 62.2, 52.0, 50.4, 37.9, 29.6, 27.8, 21.6, 14.5; HRMS (ESI) $(M+Na)^+$ Calcd for $C_{27}H_{33}O_6N_2NaS$: 535.1873, found 535.1878.

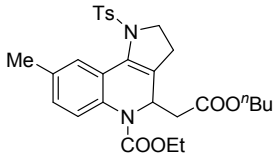


Ethyl-4-(cyanomethyl)-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4e): The product was obtained as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.3Hz, 2H), 7.38–7.22 (m, 3H), 7.16 (d, J = 7.5 Hz, 2H), 5.19 (t, J = 6.7 Hz, 1H), 4.43–4.28 (m, 2H), 4.21–4.06 (m, 2H), 3.95–3.80 (m, 1H), 2,44–2.34 (m, 5H), 2.33–2.21(m, 1H), 1.38 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75.5

MHz, $CDCl_3$) δ 151.9, 144.3, 137.5, 132.5, 132.4, 129.3, 128.6, 127.8, 127.0, 126.1, 125.4, 125.1, 122.4, 116.2, 62.9, 52.0, 49.4, 29.6, 21.6, 20.0, 14.5; HRMS (ESI) $(M+H)^+$ Calcd for $C_{23}H_{24}O_4N_3S$: 438.1482, found 438.1486.

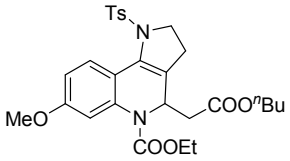


***tert*-Butyl-4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4f):** The product was obtained as a yellow needles, mp: 135–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7Hz, 1H), 7.48 (d, J = 8.2Hz, 2H), 7.30–7.27 (m, 2H), 7.22–7.17 (m, 3H), 5.20 (brs, 1H), 4.29 (dd, J = 11.9 Hz, J = 4.27 Hz, 1H), 3.86–3.77 (m, 1H), 3.56 (s, 3H), 2.39 (s, 3H), 2.30 (m, 2H), 1.55 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.4, 152.6, 144.1, 136.4, 133.6, 132.4, 130.2, 129.2, 127.9, 127.8, 125.5, 125.4, 124.2, 122.7, 81.6, 52.0, 51.7, 50.1, 36.5, 29.6, 28.3, 21.6; HRMS (ESI) $(M)^+$ Calcd for $C_{26}H_{30}O_6N_2NaS$: 521.1716, found 521.1723.



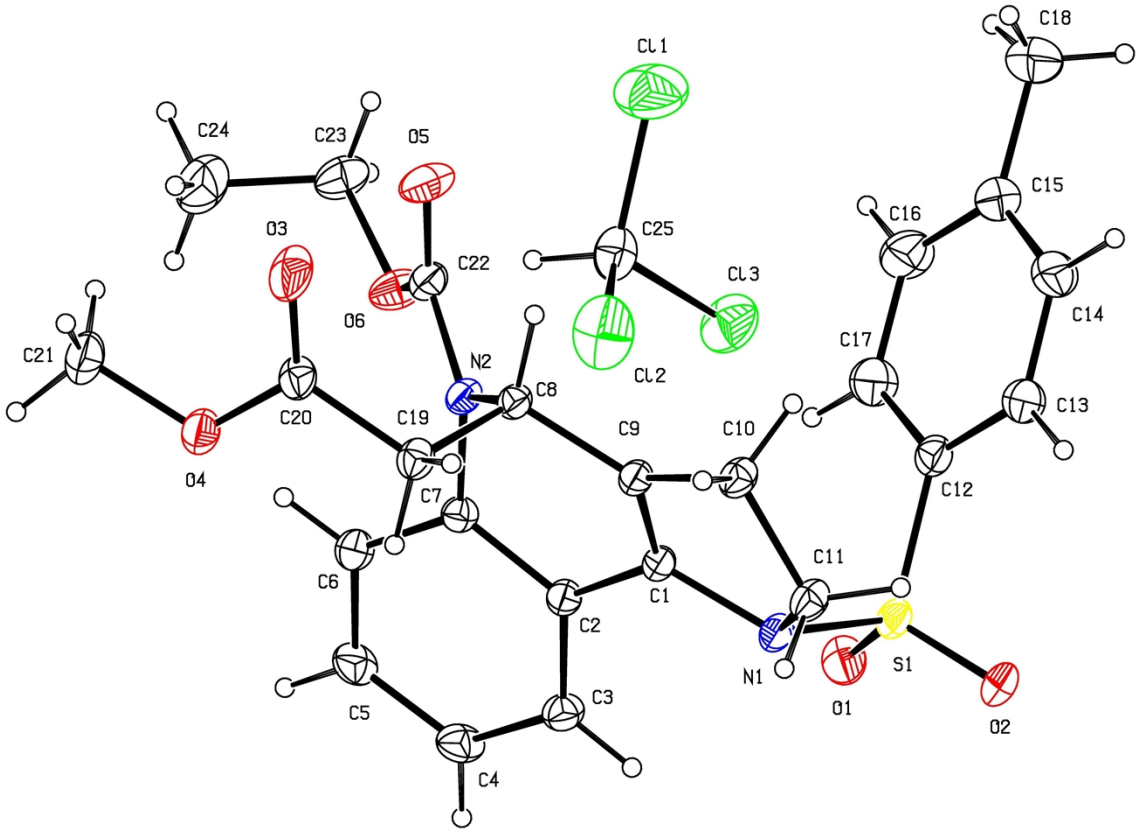
Ethyl-4-(2-butoxy-2-oxoethyl)-8-methyl-1-tosyl-2,3 dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4g): The product was obtained as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 1H), 7.24–7.08 (m, 3H), 5.26–5.78 (m, 1H), 4.36–4.22 (m, 2H), 4.19–4.05 (m, 2H), 4.00–3.91 (m, 2H), 3.86–3.73 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.33–2.25 (m, 2H), 2.12–2.01 (m, 1H), 1.58–1.48 (m, 2H), 1.38–1.31 (m, 5H), 0.9 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.1, 157.3, 144.2, 136.3, 134.3, 131.4, 129.4, 129.2, 128.8,

127.9, 126.1, 125.8, 125.4, 122.8, 64.7, 42.3, 51.9, 50.2, 36.4, 30.4, 29.6, 21.6, 21.0, 18.9, 14.5, 13.6; HRMS (ESI) $(M+H)^+$ Calcd for $C_{28}H_{35}O_6N_2S$: 527.2210, found 527.2203.

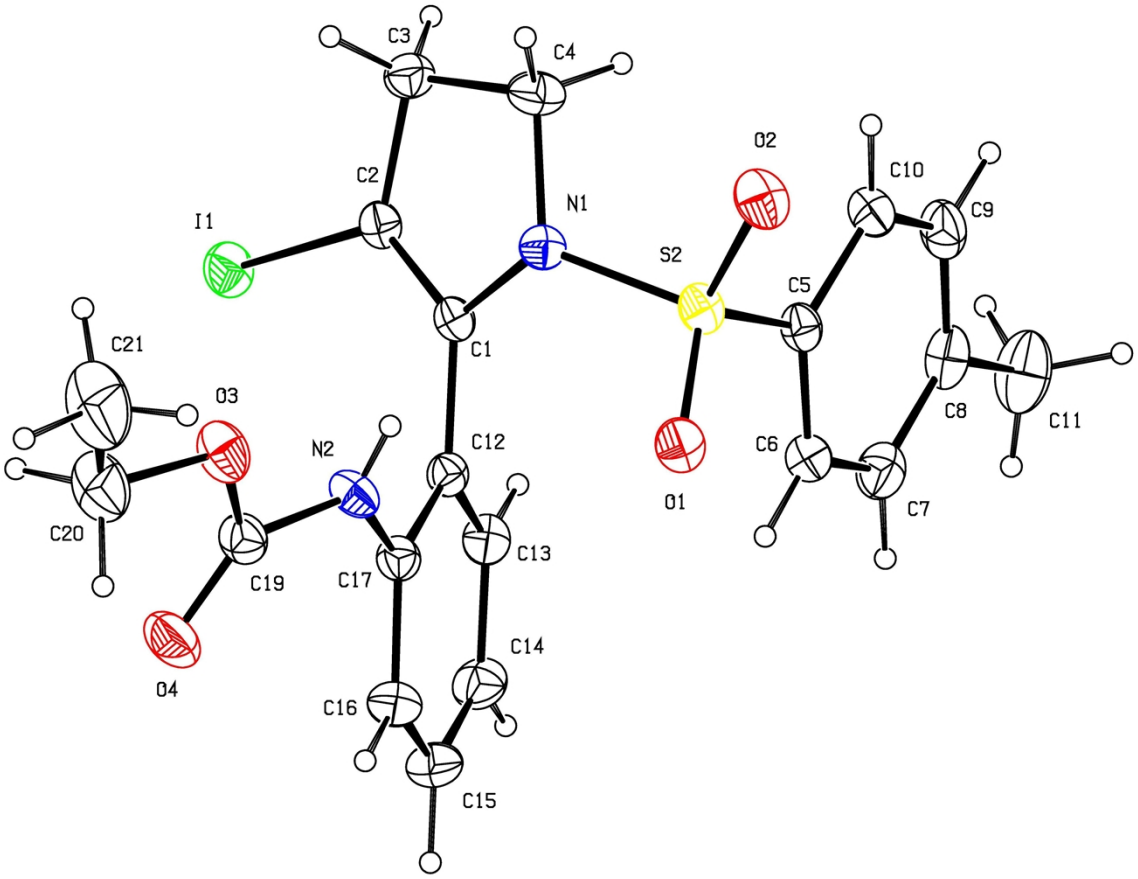


Ethyl-4-(2-butoxy-2-oxoethyl)-7-methoxy-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4h): The product was obtained as a yellow needles, mp: 110–112 °C; This compound is unstable in solid and solution form. The yellow color solid was gradually decomposing by addition of solvent (THF, $CDCl_3$, CH_3CN, CH_2Cl_2, DMSO) to green color. HRMS (ESI) $(M+H)^+$ Calcd for $C_{28}H_{35}O_7N_2S$: 543.2159, found 543.2158.

X-Ray Crystallographic Studies



ORTEP structure of compound **4a.**



ORTEP structure of compound **5a.**

X-ray data of compounds **4a** and **5a** was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[3] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined from the setting angles of 7435 reflections for **4a** and 6143 reflections for **5a.**

Integration and scaling of intensity data were accomplished using SAINT program.[3] The structures were solved by Direct Methods using SHELXS97[4] and refinement was carried

out by full-matrix least-squares technique using SHELXL97.[4] Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atom attached to nitrogen atom of AT23 was located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal data for **5a**: $C_{20}H_{21}IN_2O_4S$, M = 512.35, colorless needle, 0.12 × 0.08 × 0.06 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 8.0734(5), b = 17.0233(10), c = 15.3571(9) Å, β = 96.854(1)°, V = 2095.5(2) $Å^3$, Z = 4, D_c = 1.624 g/cm^3, F_{000} = 1024, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 50.0º, 19693 reflections collected, 3691 unique (R_{int} = 0.0207). Final *GooF* = 1.047, *R1* = 0.0341, *wR2* = 0.0830, *R* indices based on 3452 reflections with I>2σ(I) (refinement on F^2), 259 parameters, 0 restraints, μ = 1.656 mm^{-1}. **CCDC 970675** contains supplementary Crystallographic data for the structure.

Crystal data for **4a**: $C_{25}H_{27}Cl_3N_2O_6S$, M = 589.90, colorless block, 0.15 × 0.13 × 0.07 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 17.5098(18), b = 8.4729(9), c = 18.956(2) Å, β = 94.435(2)°, V = 2803.9(5) $Å^3$, Z = 4, D_c = 1.397 g/cm^3, F_{000} = 1224, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 50.0º, 25991 reflections collected, 4925 unique (R_{int} = 0.0223). Final *GooF* = 1.037, *R1* = 0.0448, *wR2* = 0.1200, *R* indices based on 4315 reflections with I>2σ(I) (refinement on F^2), 337 parameters, 0 restraints, μ = 0.443 mm^{-1}. **CCDC 970676** contains supplementary Crystallographic data for the structure.

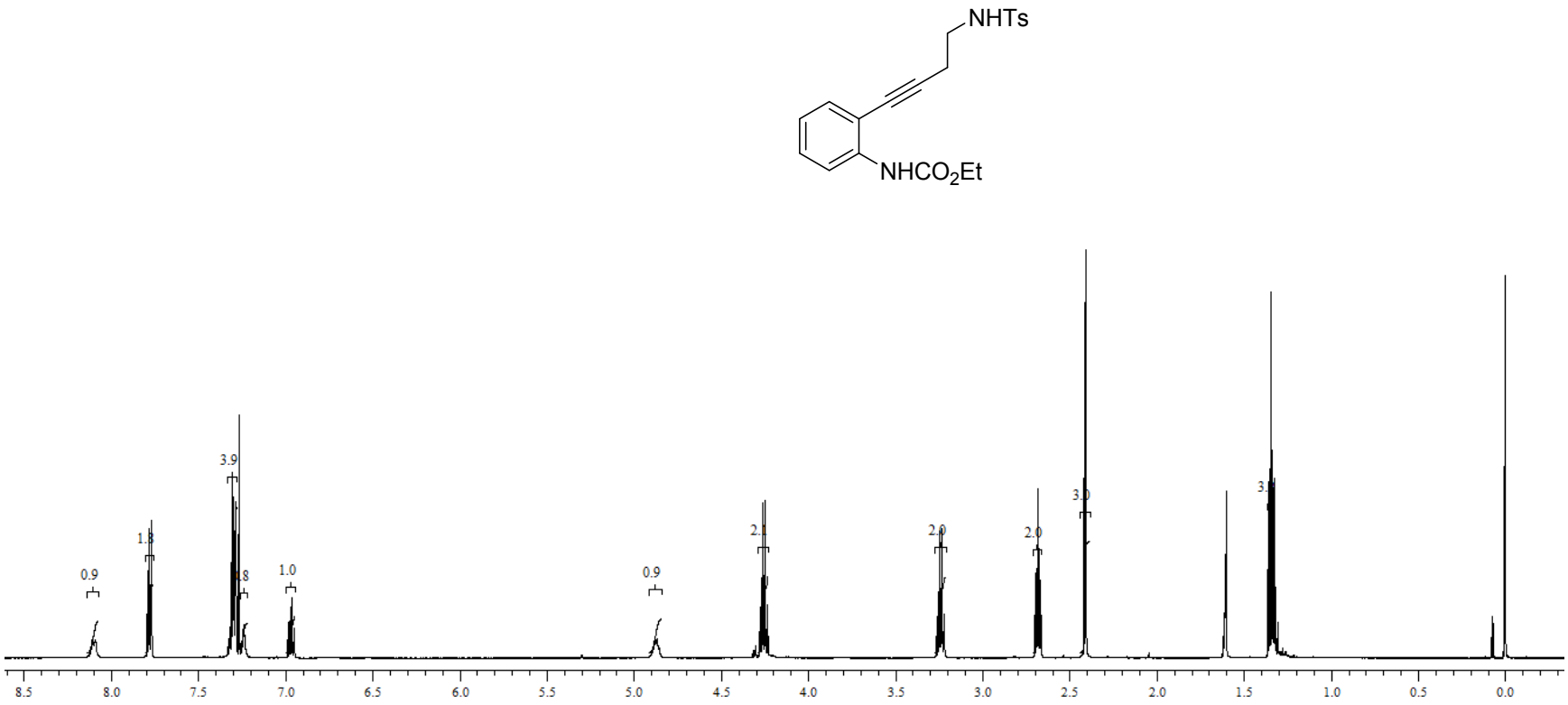
These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

References:

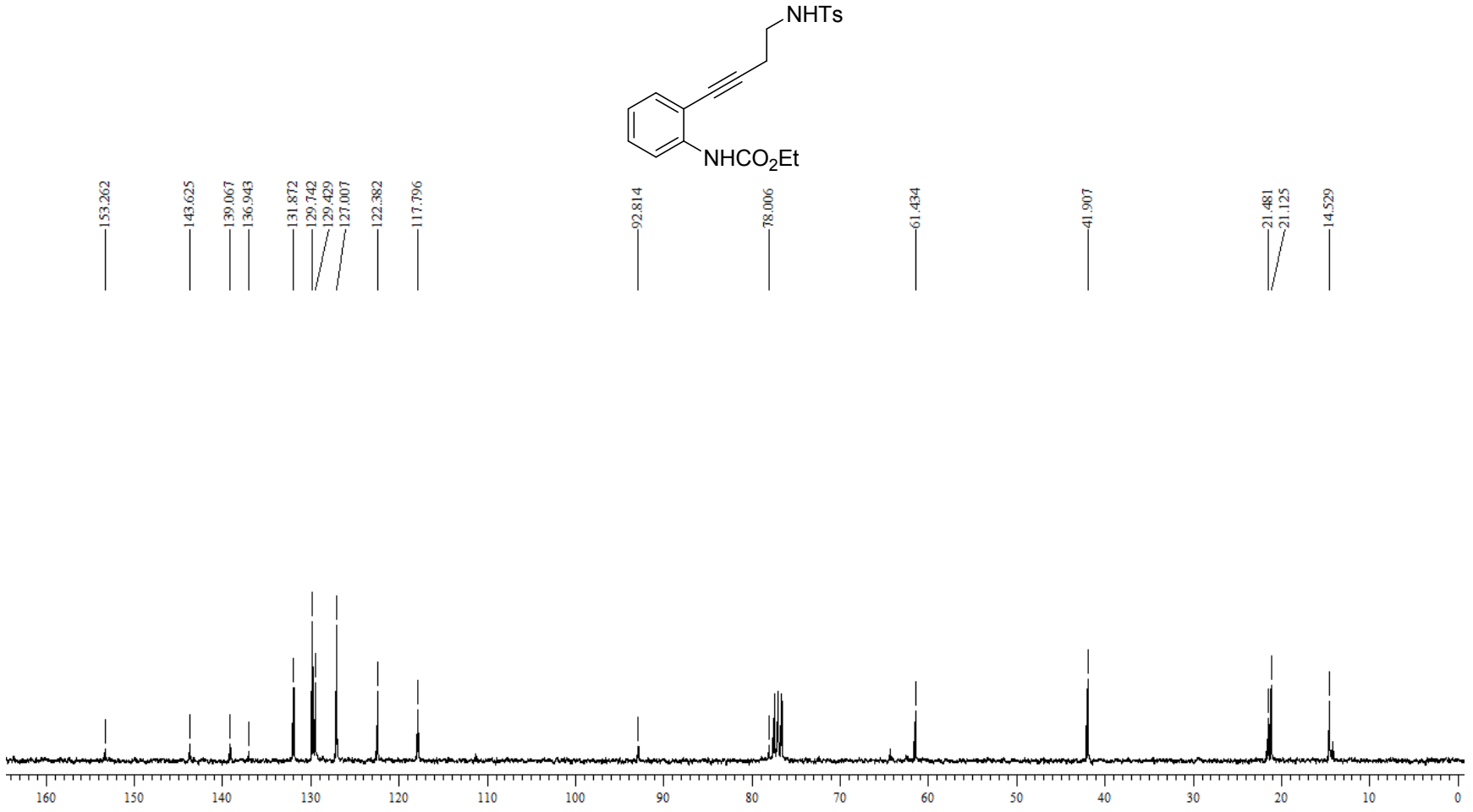
1. (a) Likhar, P. R.; Subhas, M. S.; Roy, S.; Kantam, M. L.; Sridhar, B.; Seth, R. K. Biswas, S. *Org. Bio. Chem* **2009**, *7*, 85. (b) Likhar, P. R.; Racharlawar, S. S.; Karkhelikar, M. V., Subhas, M. S. *Synthesis* **2011***,* 2407. (c) Subba Reddy, B. V.; Swain, M.; Reddy, S.M.; Yadav, J. S.; Sridhar, B. *J. Org. Chem*. **2012**, *77*, 11355.
2. Verma, A. K.; Jha, R. R.; Chaudhary, R.; Tiwari, R. K.; Danodia, A. K. *Adv. Synth. Catal.* **2013**, *355*, 421.
3. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
4. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

^{1}H NMR, ^{13} C NMR and HRMS Spectra

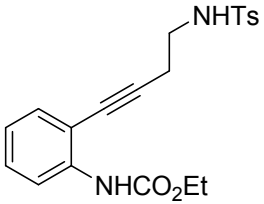
^{1}H NMR of **Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1a)**

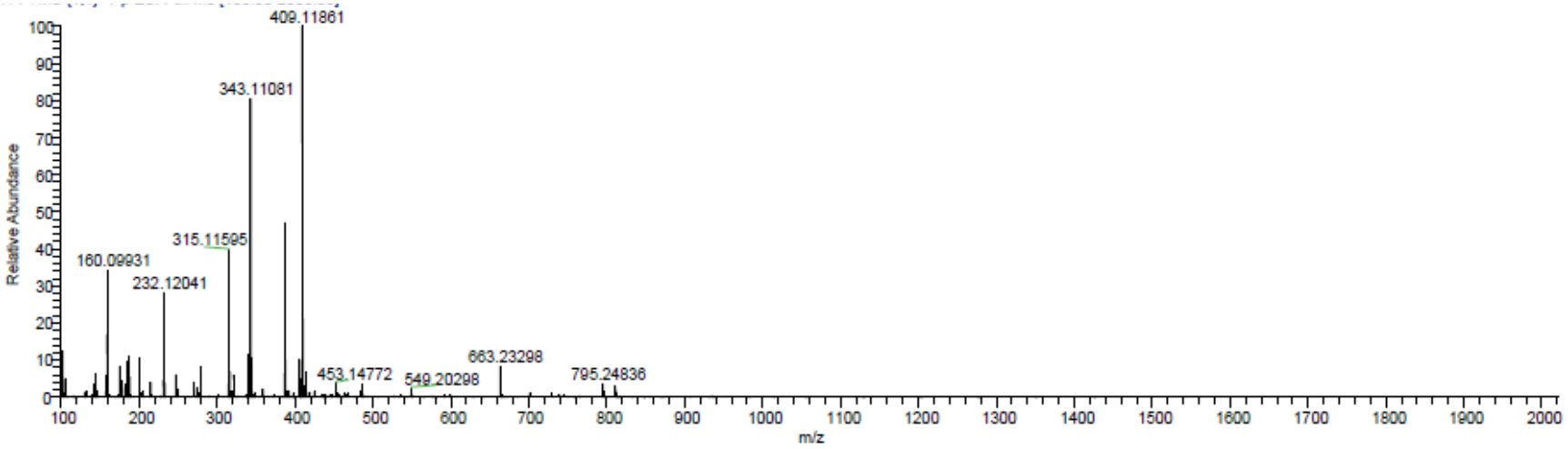


^{13}C NMR of **Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1a)**

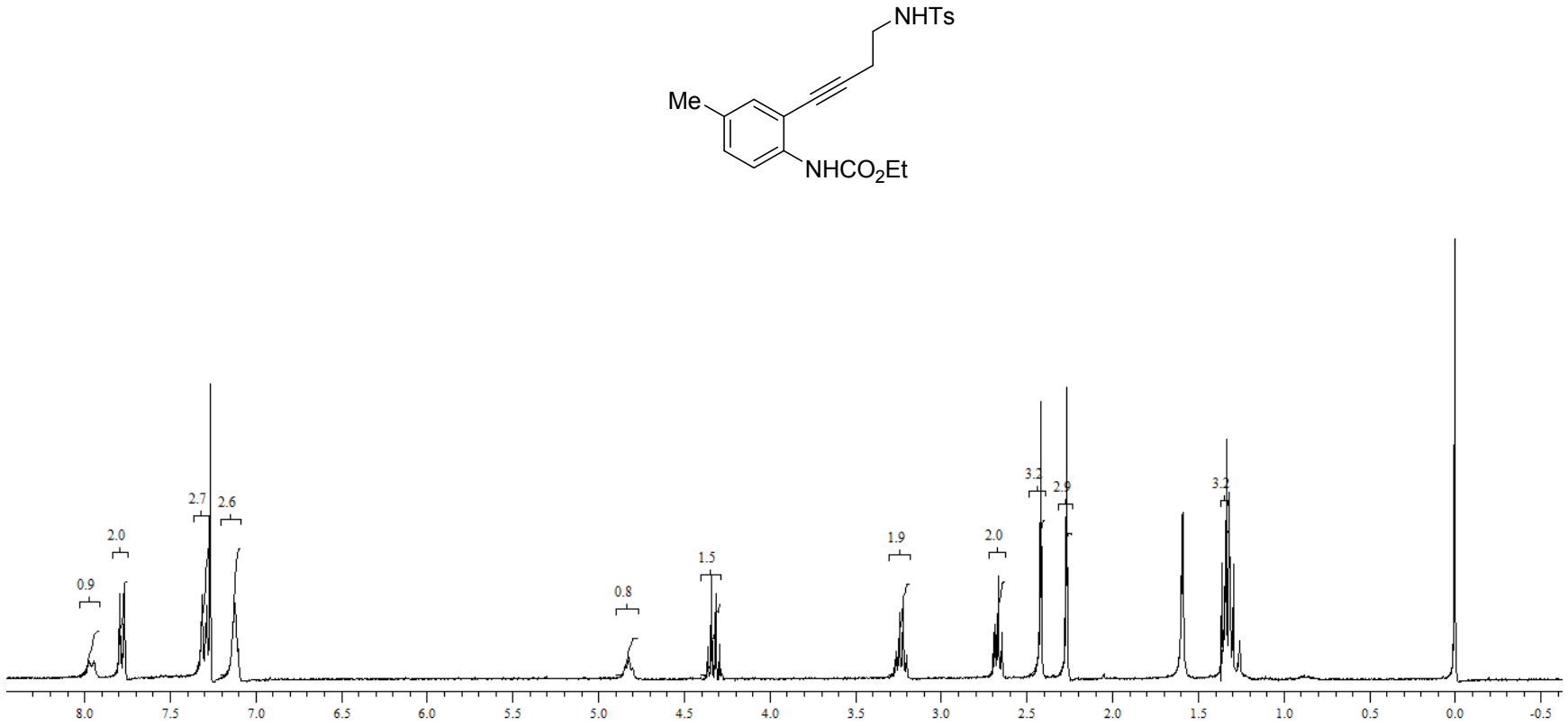


HRMS of Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1a)

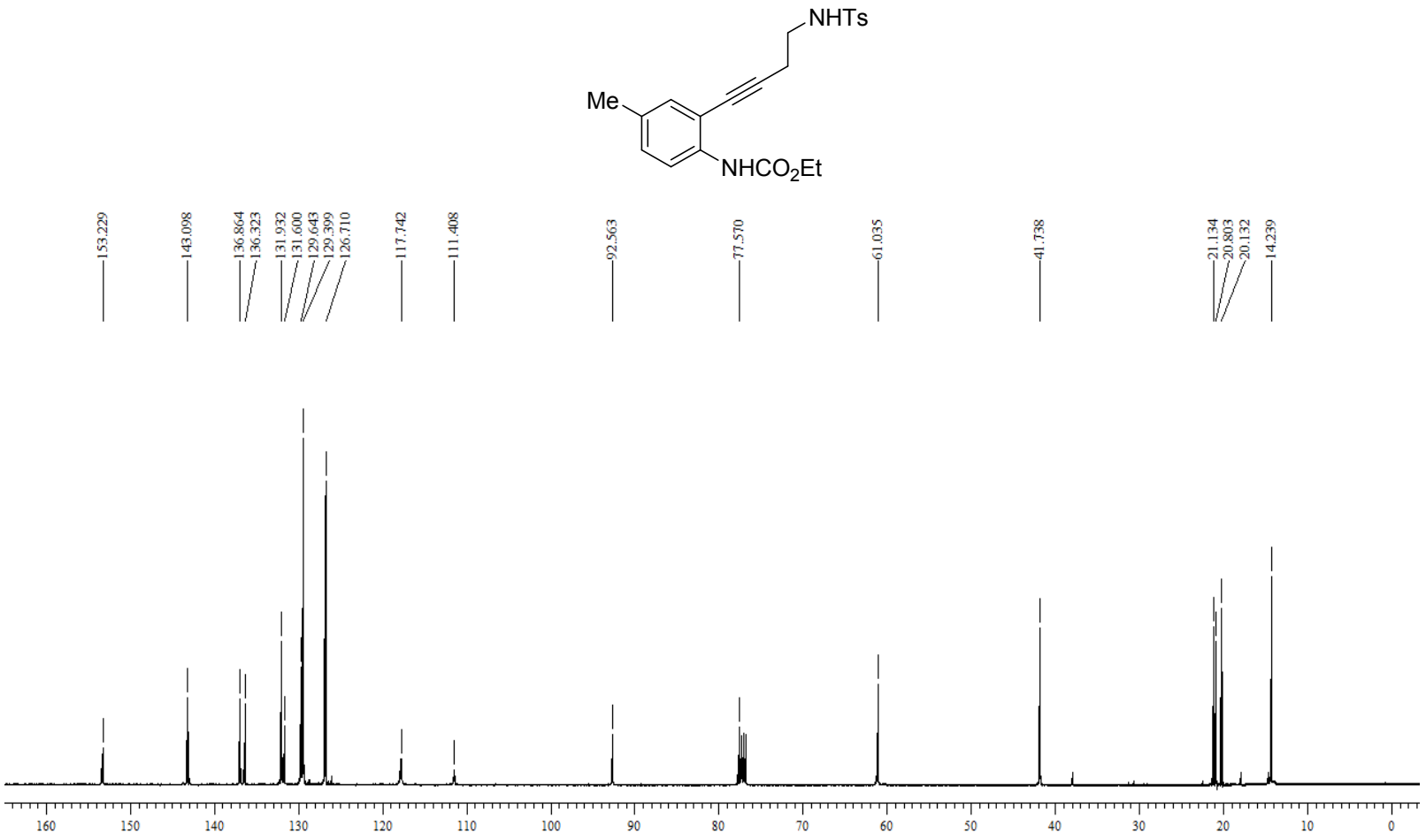




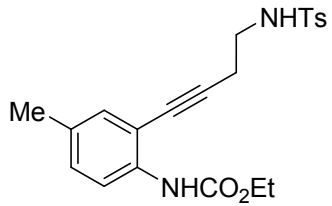
^{1}H NMR of Ethyl 4-methyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1b)

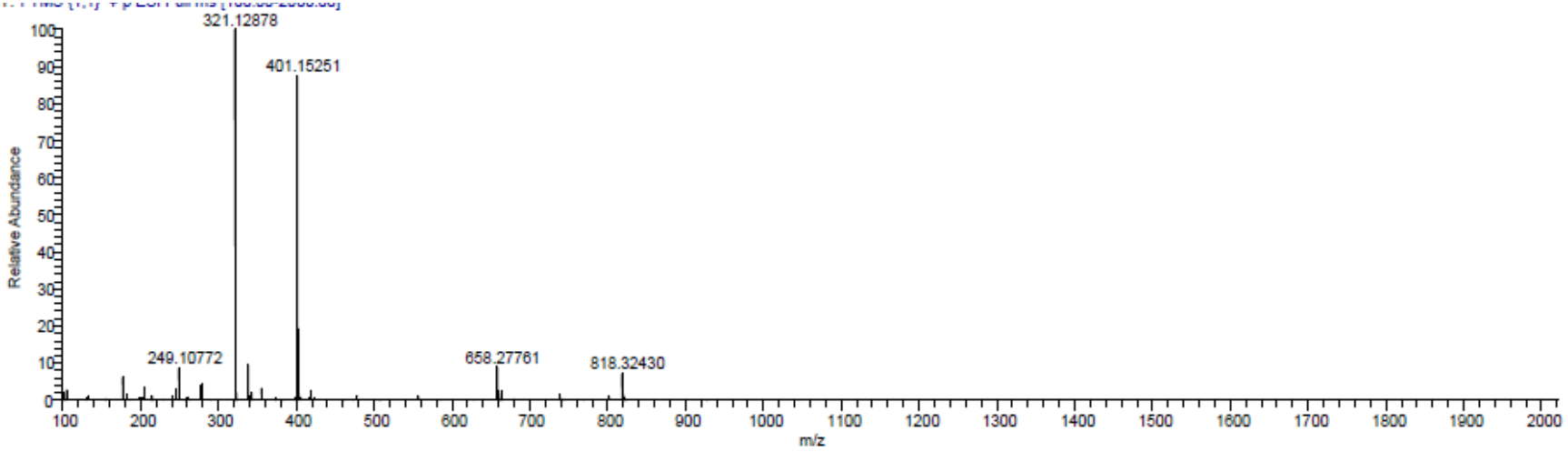


^{13}C NMR of **Ethyl 4-methyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1b)**

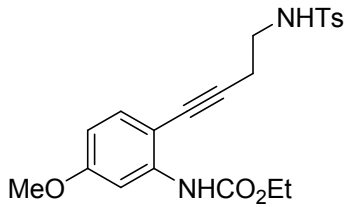


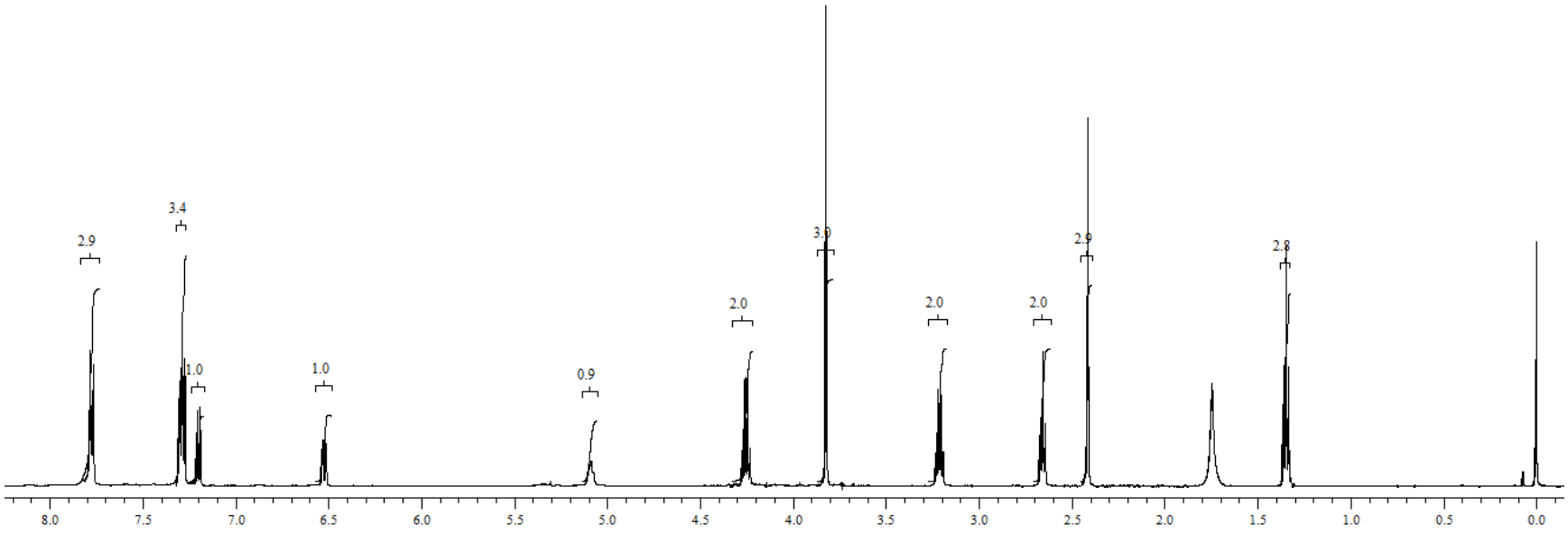
HRMS of **Ethyl 4-methyl-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1b)**



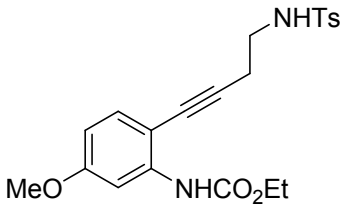


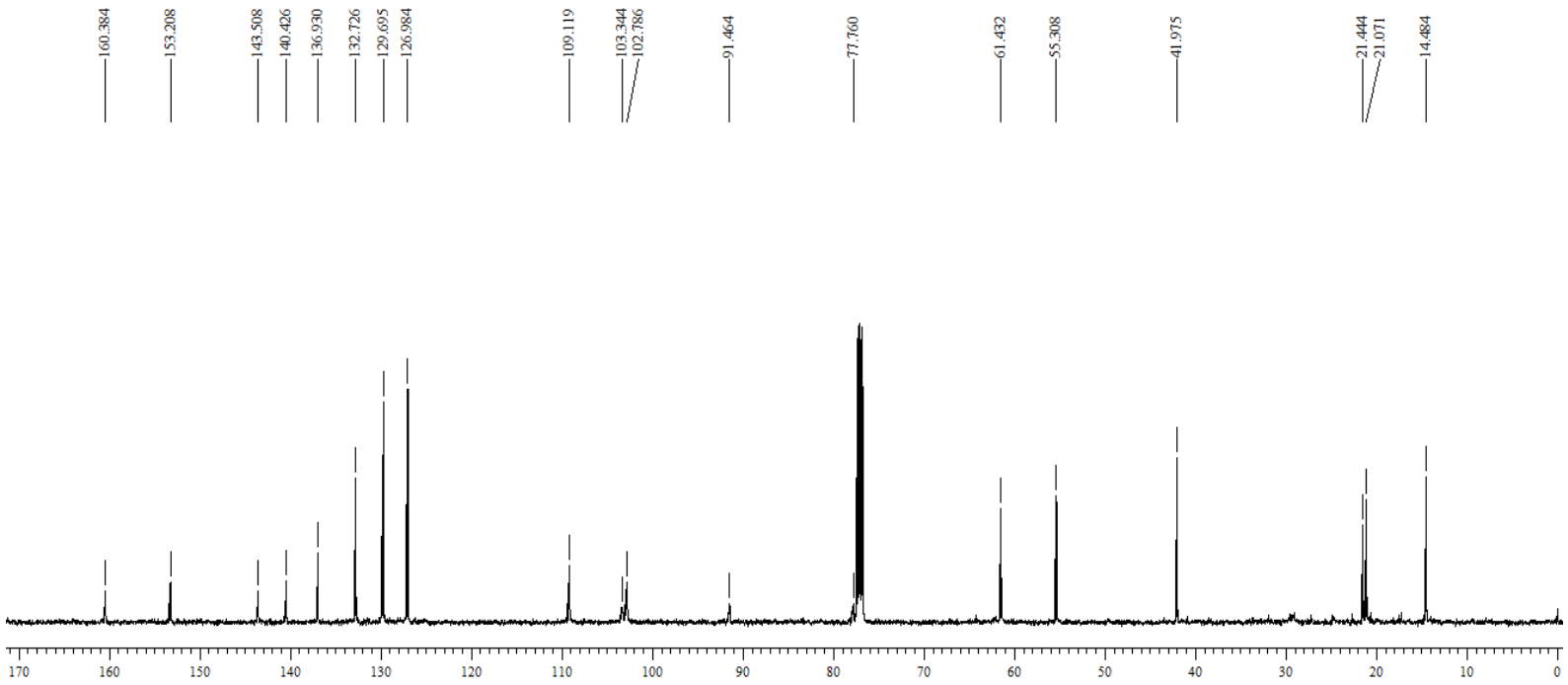
^{1}H NMR of **Ethyl 5-methoxy-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1c)**



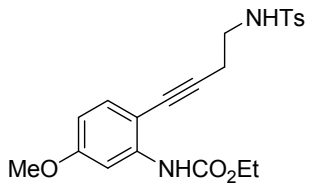


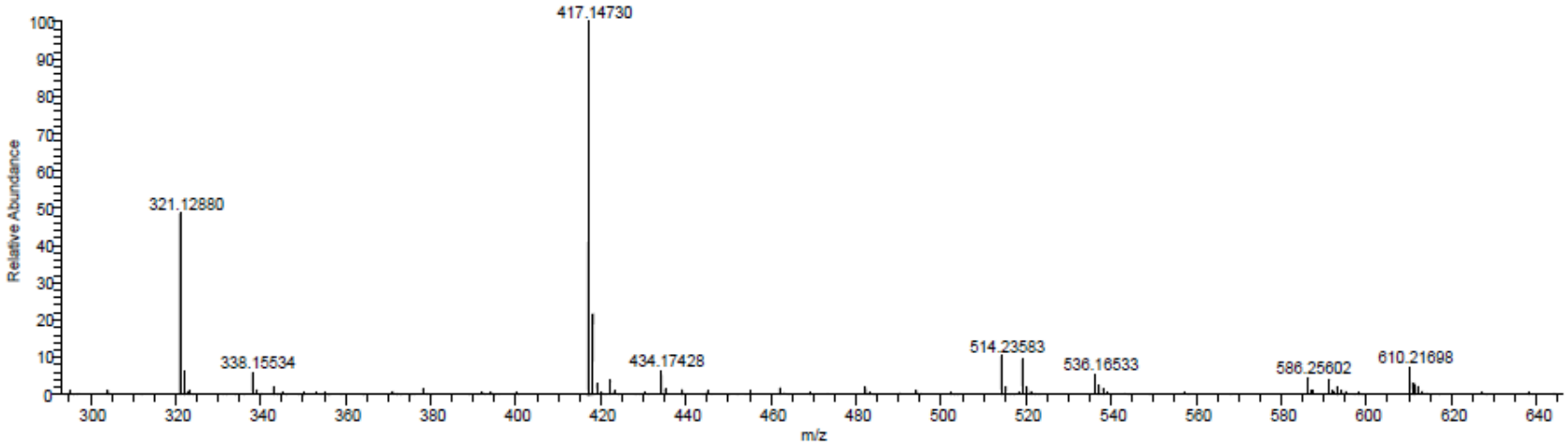
^{13}C NMR of **Ethyl 5-methoxy-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1c)**



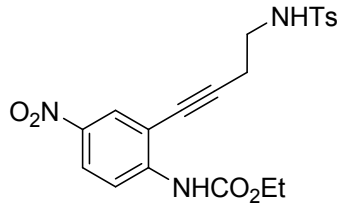


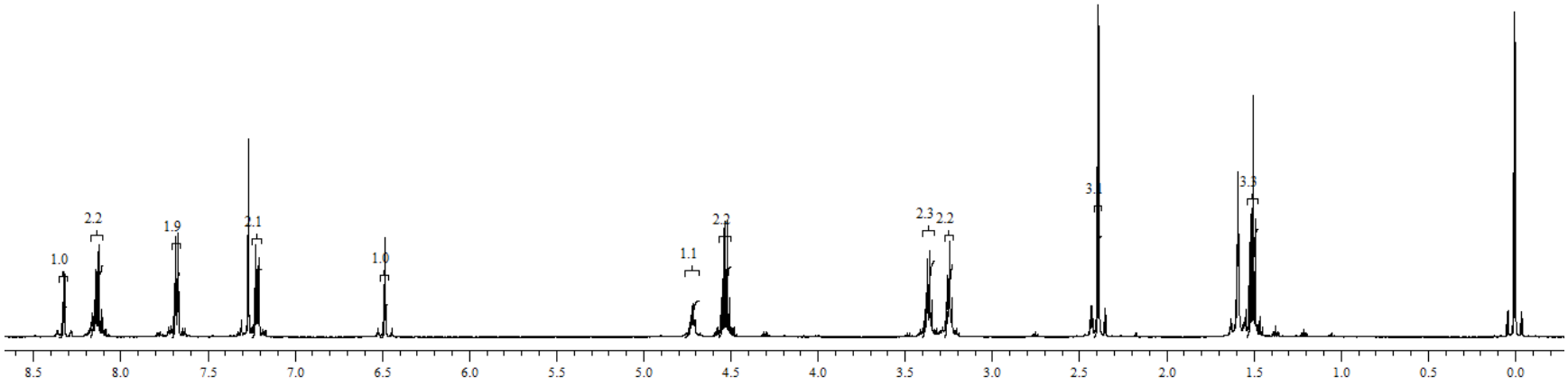
HRMS of **Ethyl 5-methoxy-2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1c)**



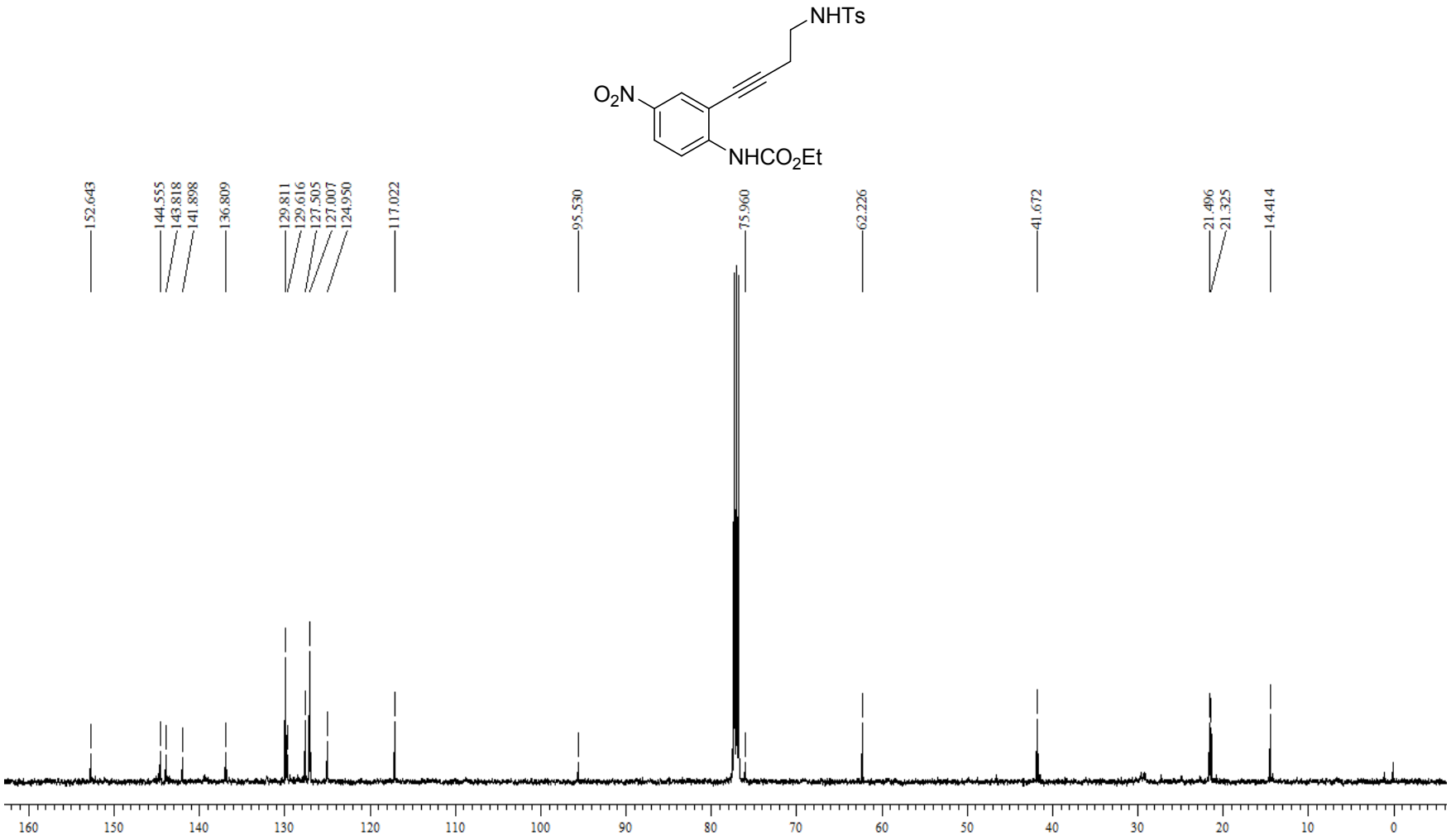


^{1}H NMR of **Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)-4-nitrophenylcarbamate (1d)**

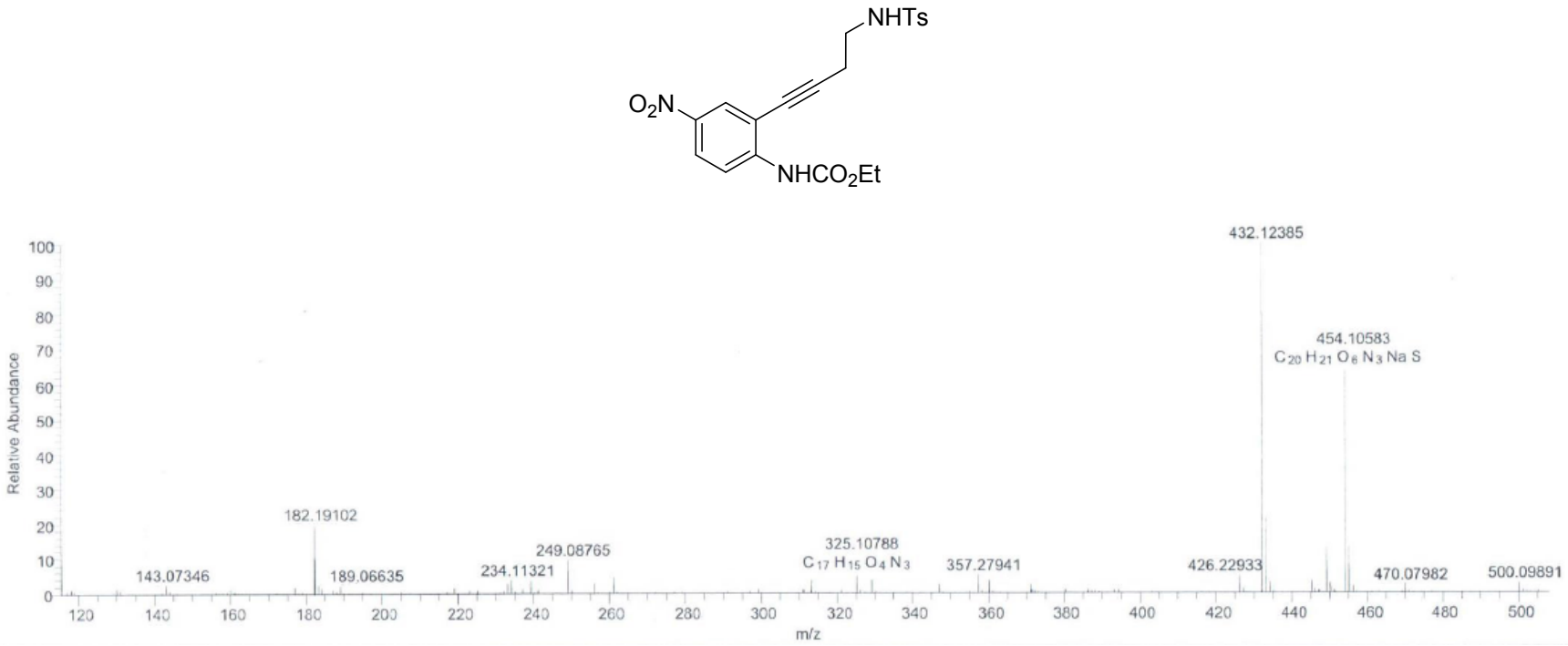




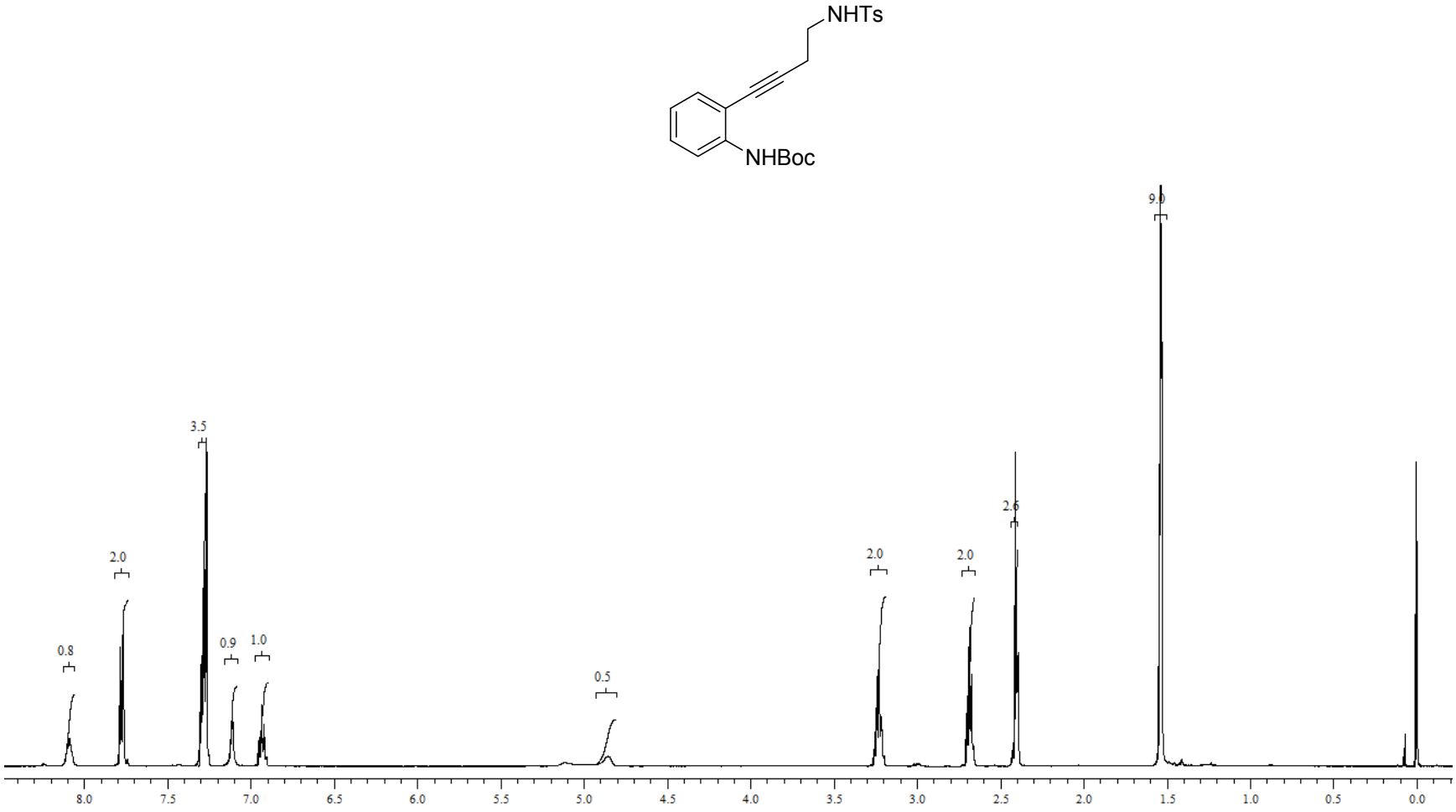
^{13}C NMR of **Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)-4-nitrophenylcarbamate (1d)**



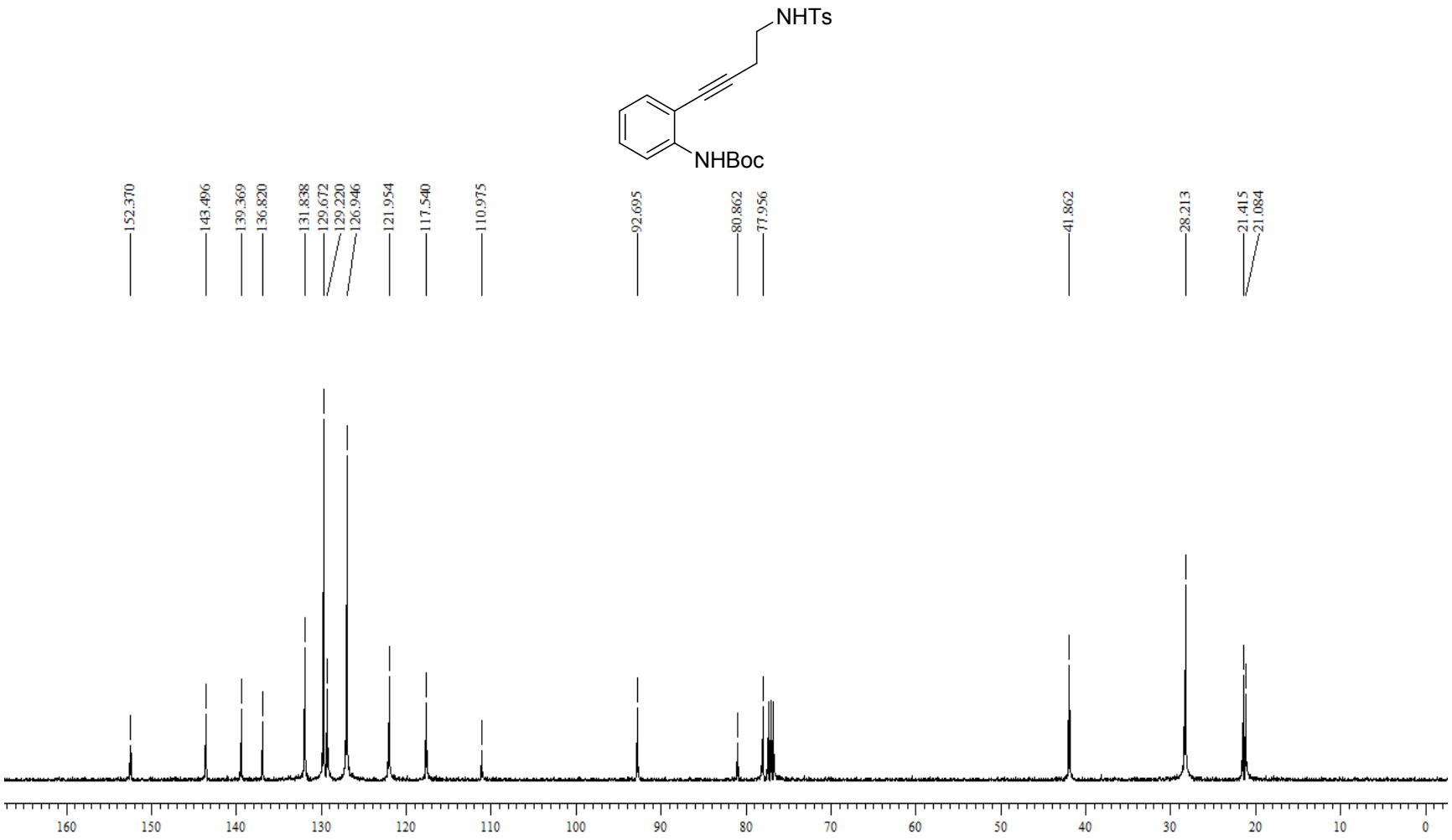
HRMS of **Ethyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)-4-nitrophenylcarbamate (1d)**



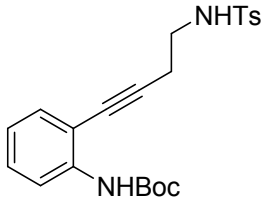
^{1}H NMR of ***t*ert-Butyl 2-(4-(4-methylphenylsulfonamido) but-1-ynyl) phenylcarbamate (1e)**

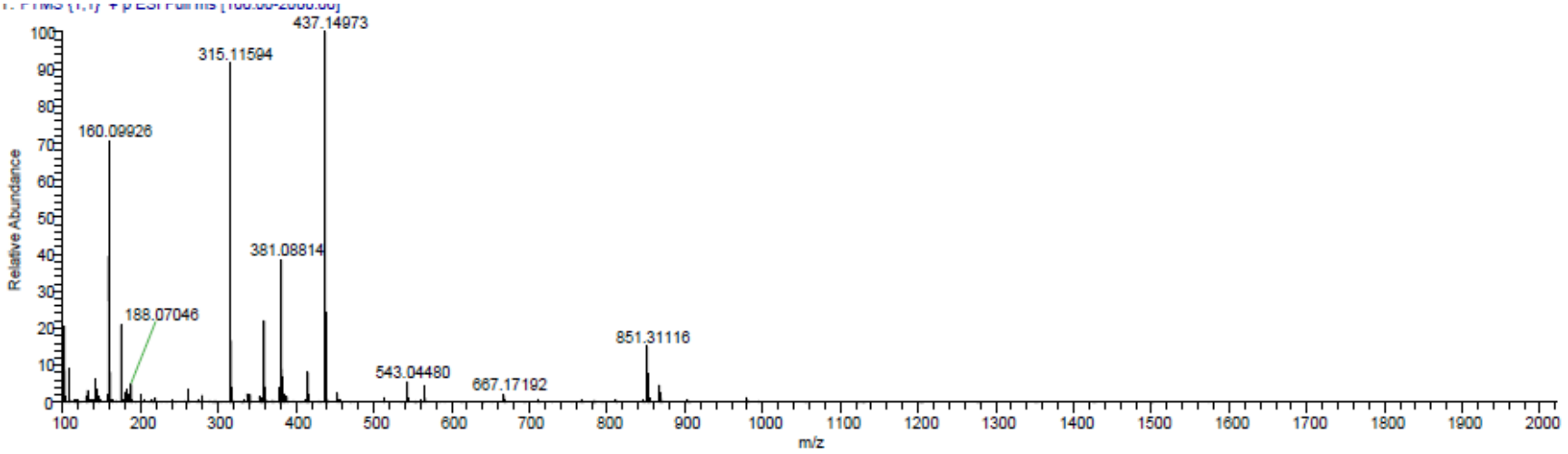


^{13}C NMR of ***t*ert-Butyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1e)**

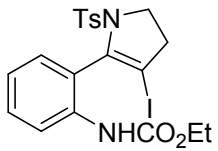


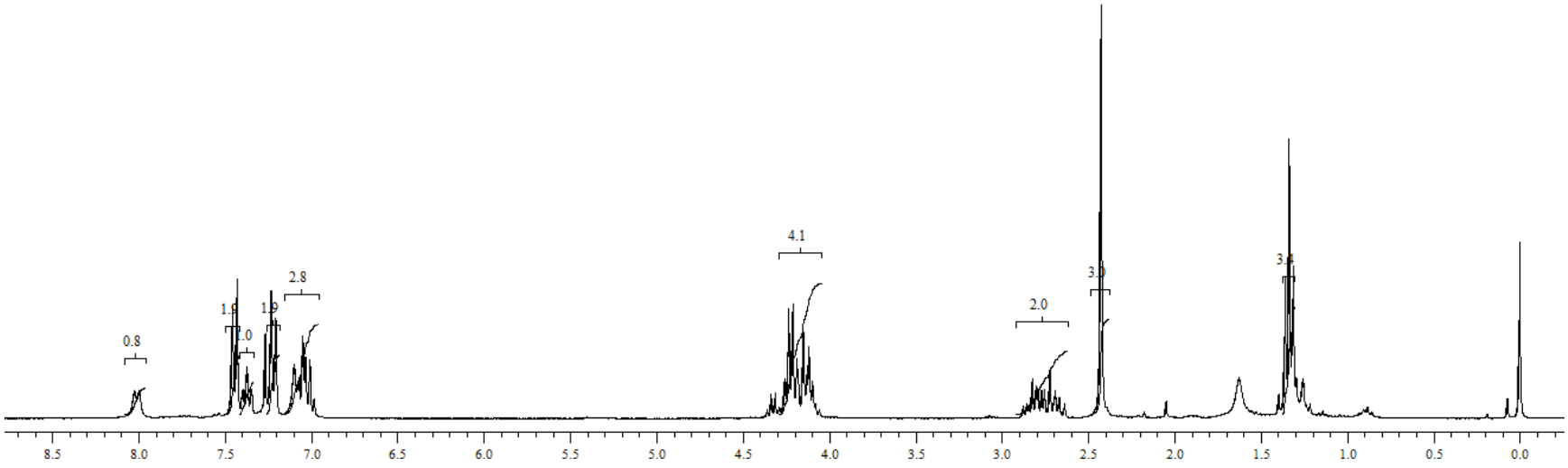
HRMS of ***t*ert-Butyl 2-(4-(4-methylphenylsulfonamido)but-1-ynyl)phenylcarbamate (1e)**



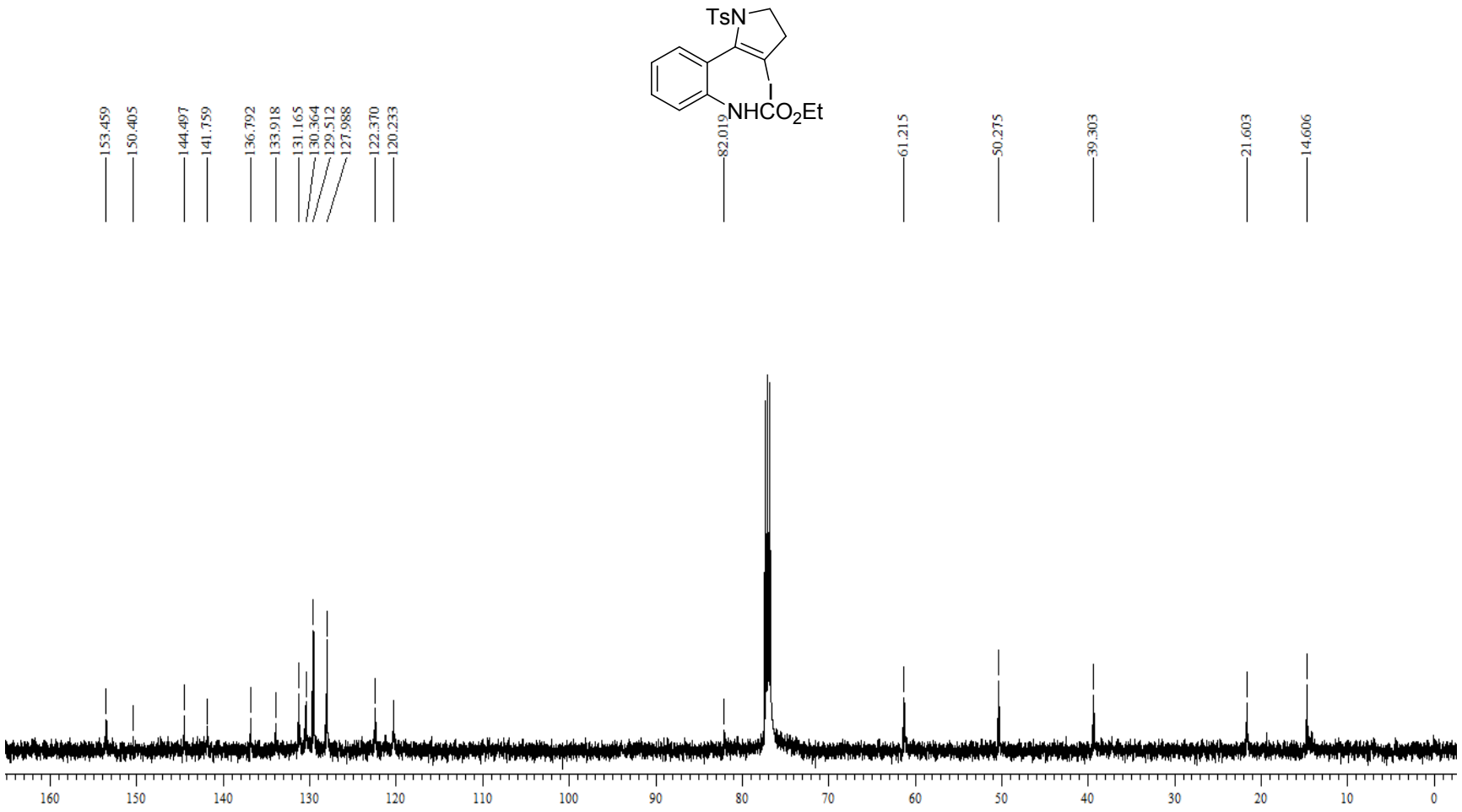


^{1}H NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5a)**

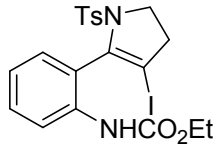


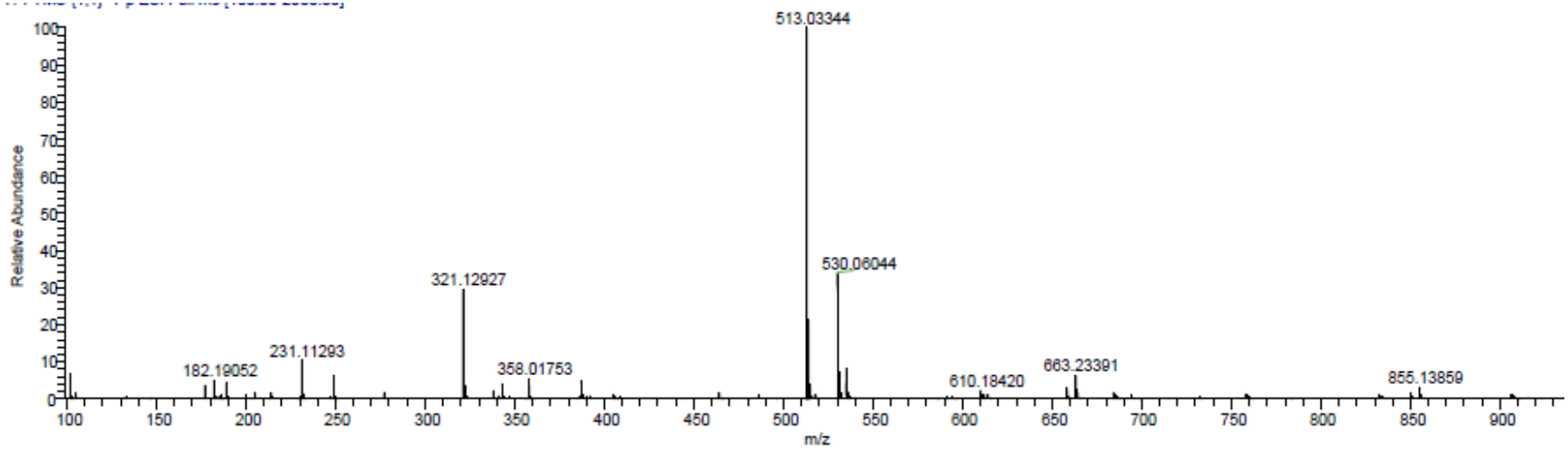


^{13}C NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5a)**

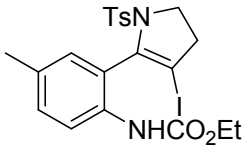


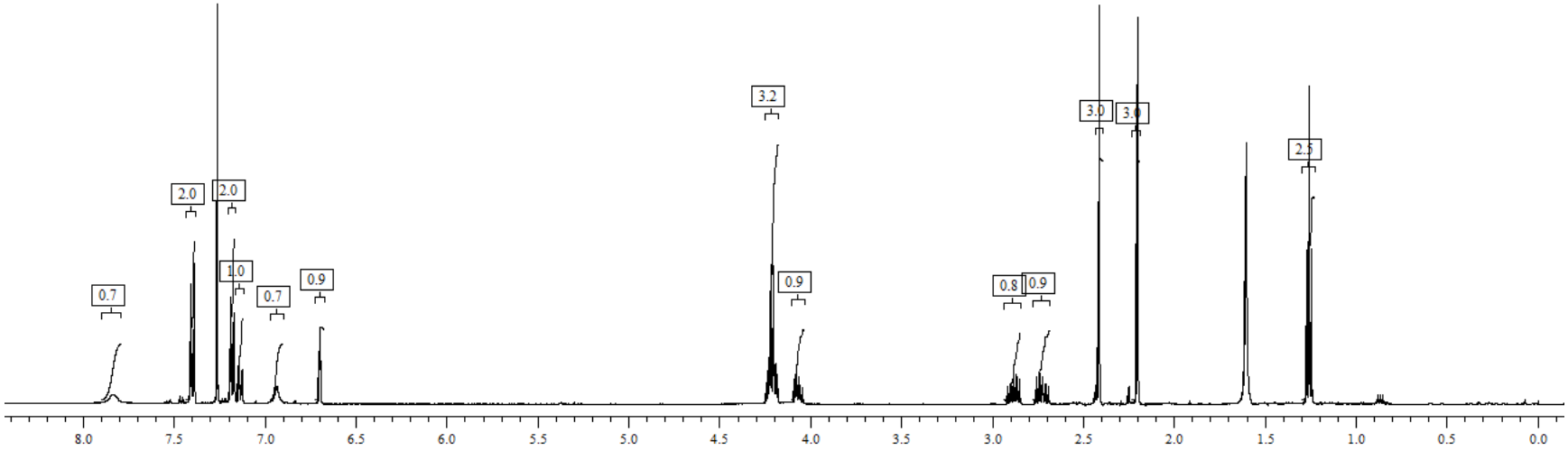
HRMS of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5a)**



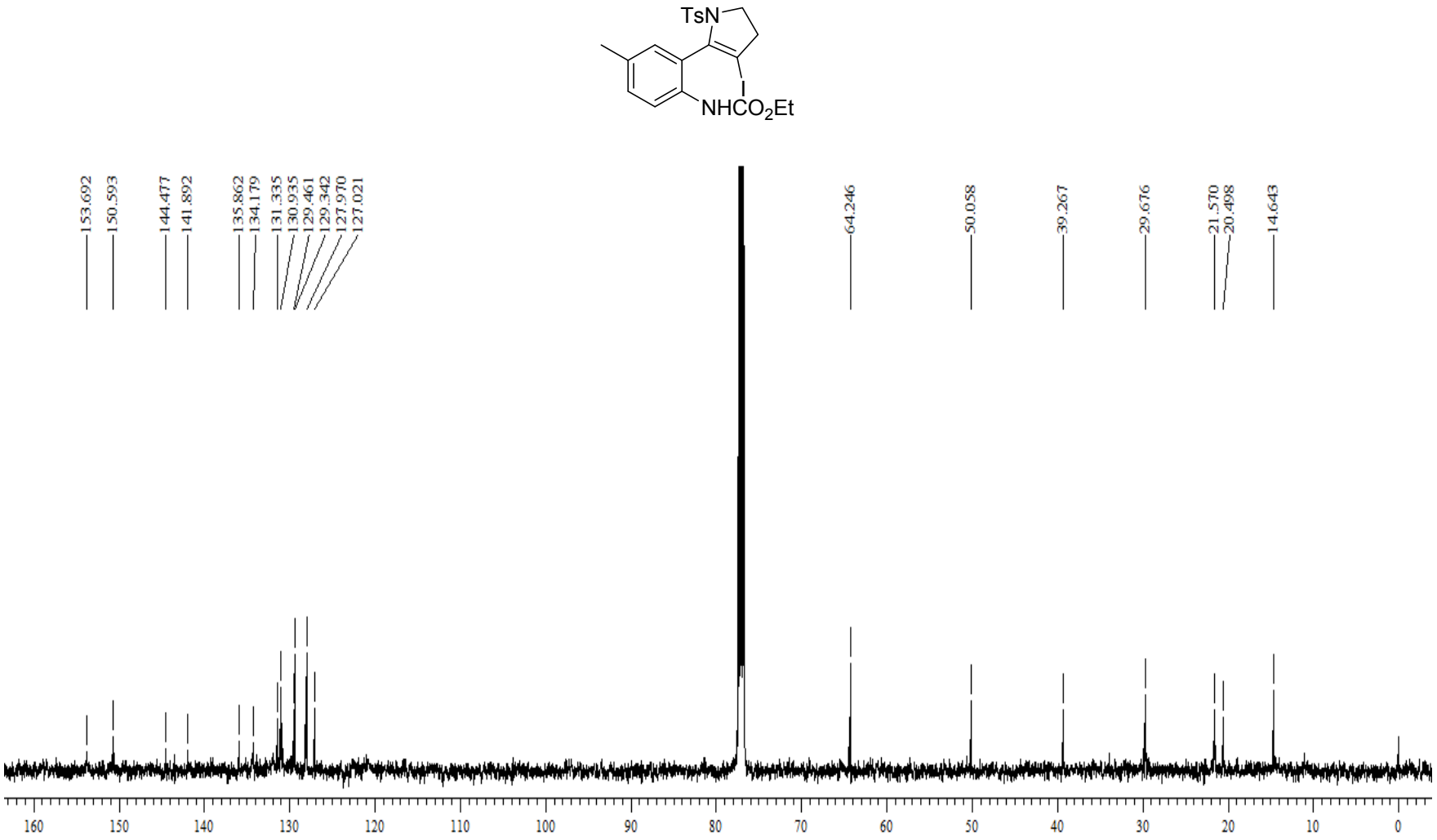


^{1}H NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-methylphenylcarbamate (5b)**

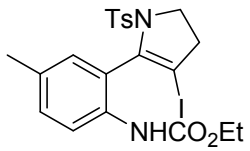


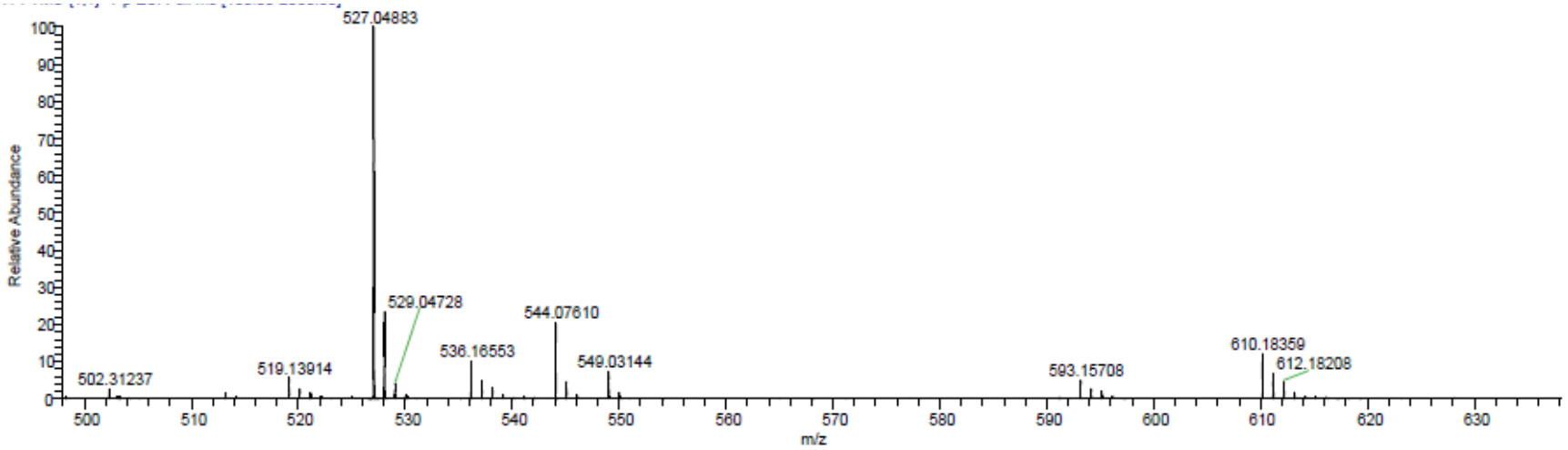


^{13}C NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-methylphenylcarbamate (5b)**

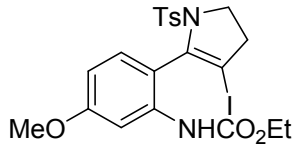


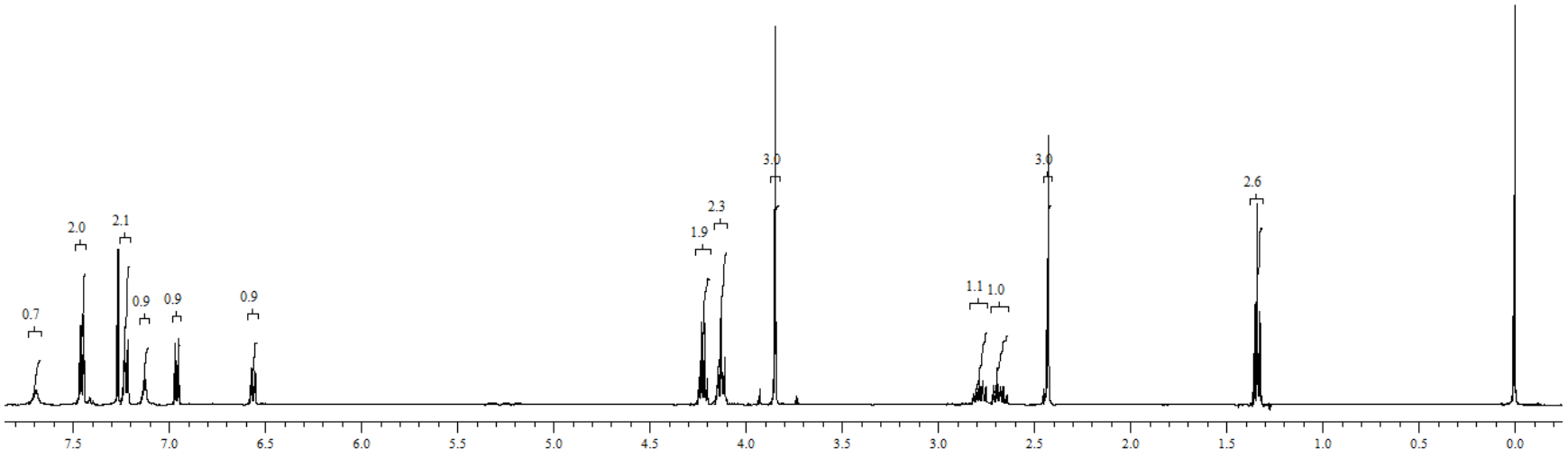
HRMS of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-methylphenylcarbamate (5b)**



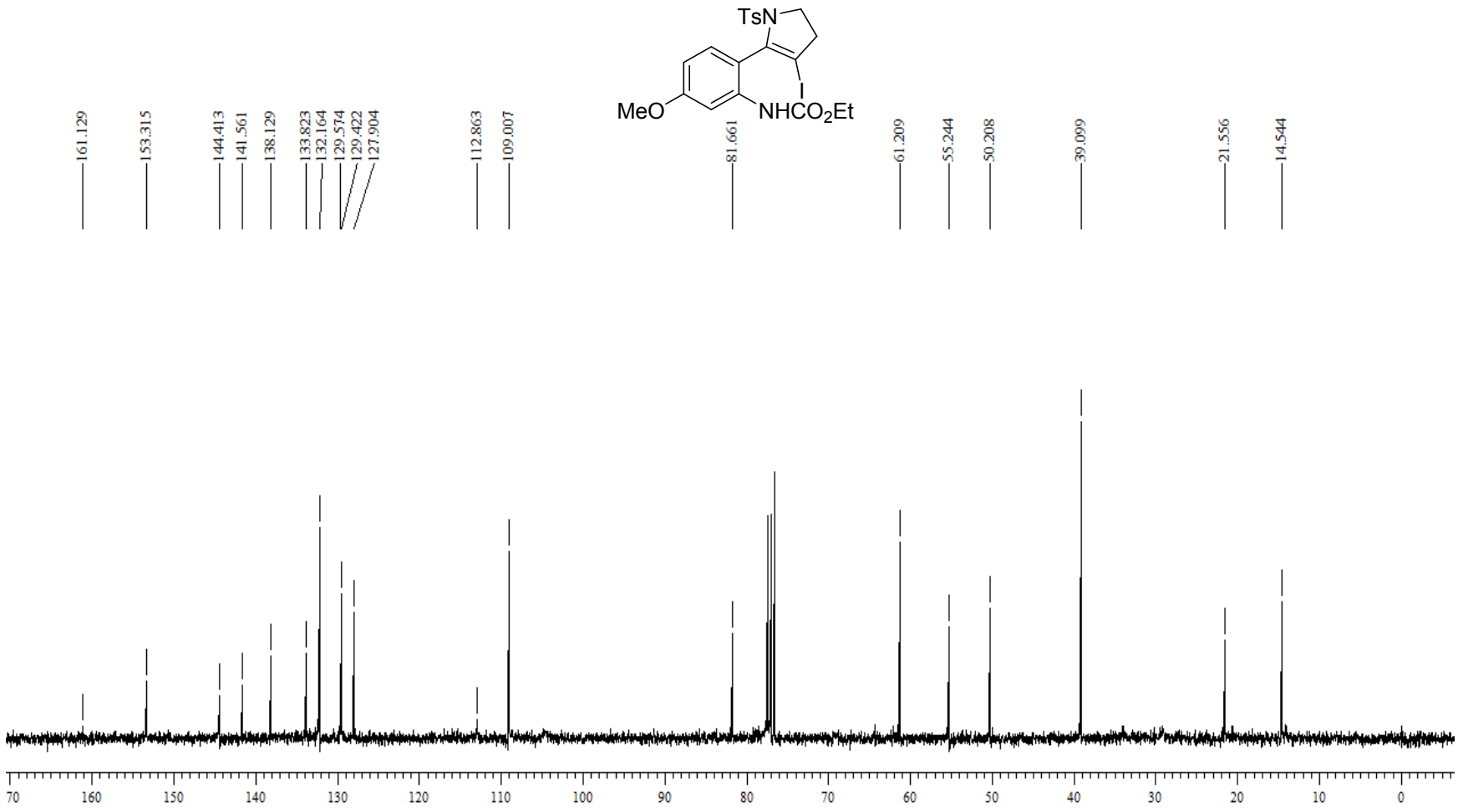


^{1}H NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-5-methoxyphenylcarbamate (5c)**

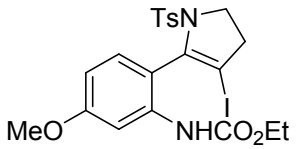


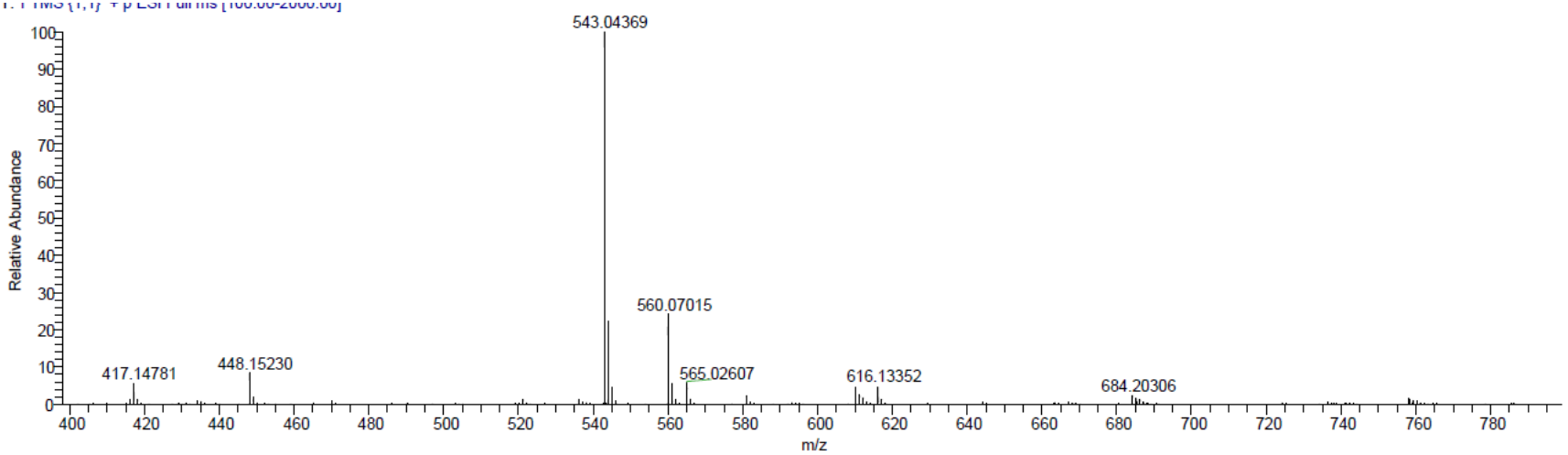


^{13}C NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-5-methoxyphenylcarbamate (5c)**

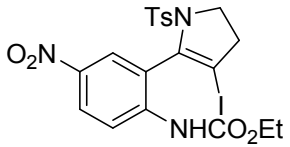


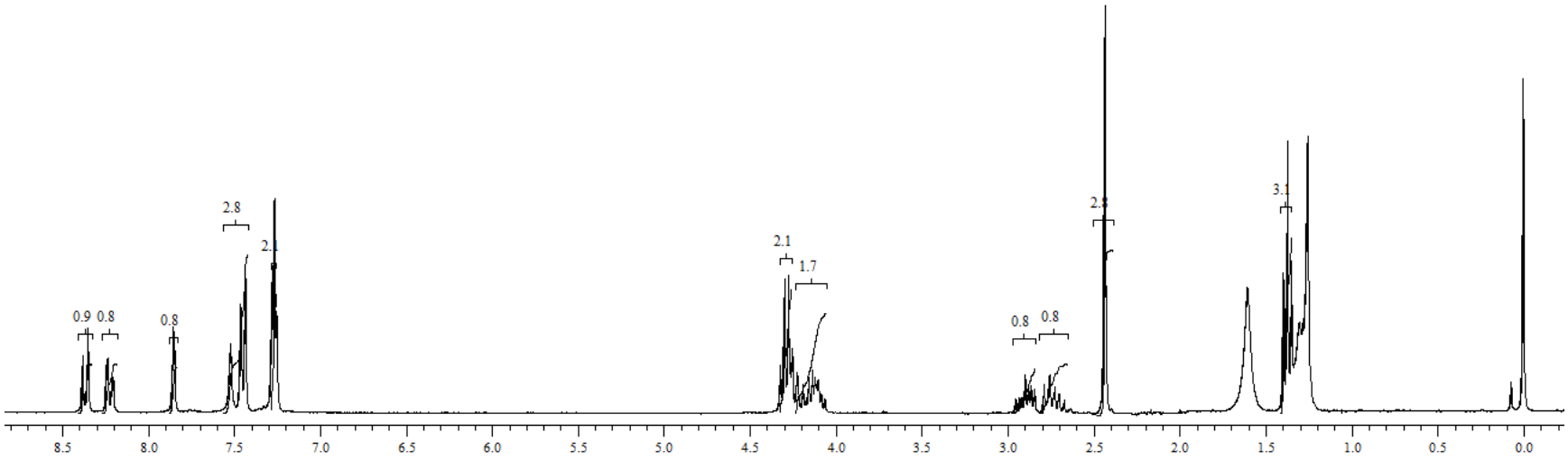
HRMS of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-5-methoxyphenylcarbamate (5c)**



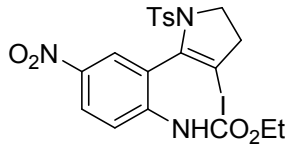


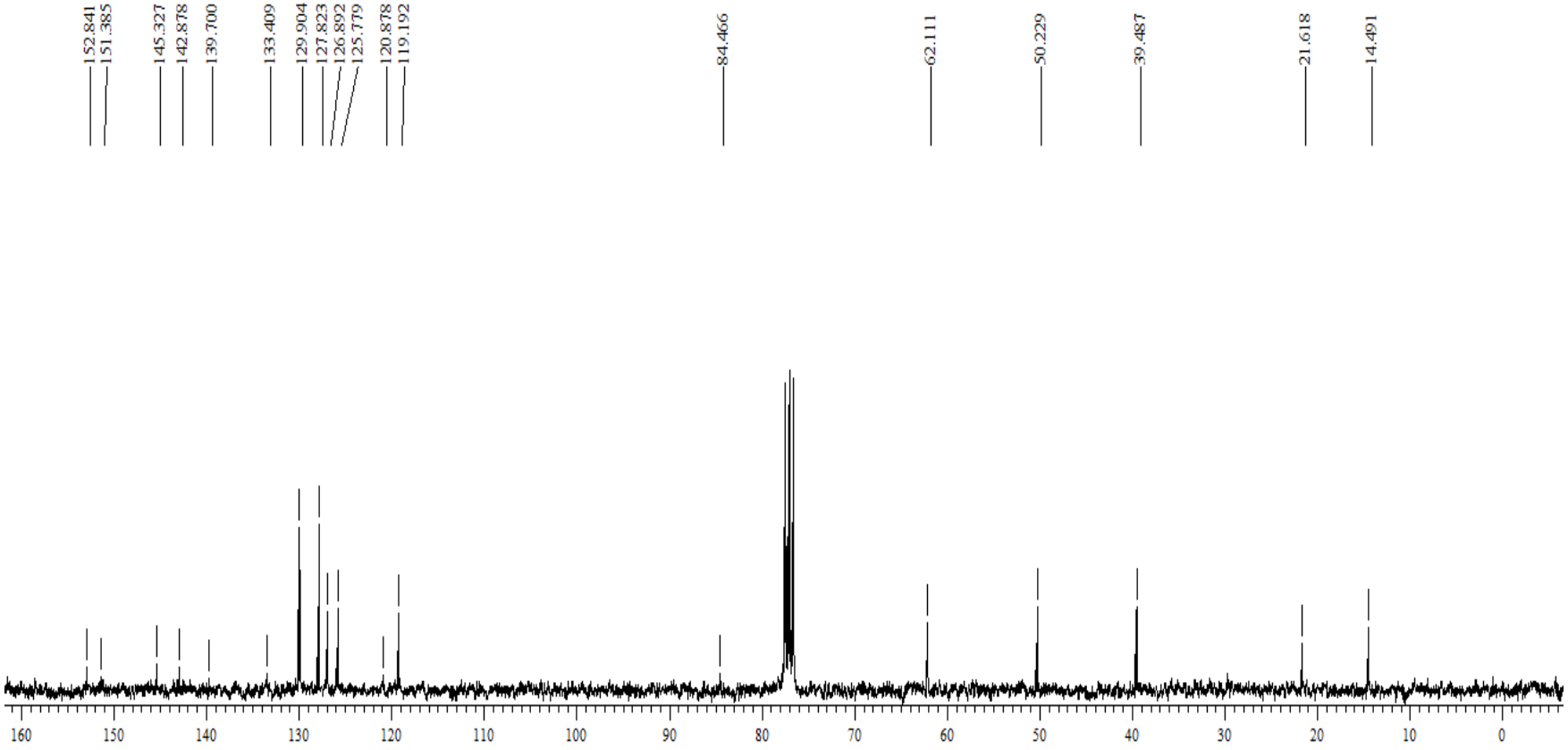
^{1}H NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-nitrophenylcarbamate (5d)**



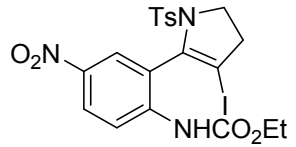


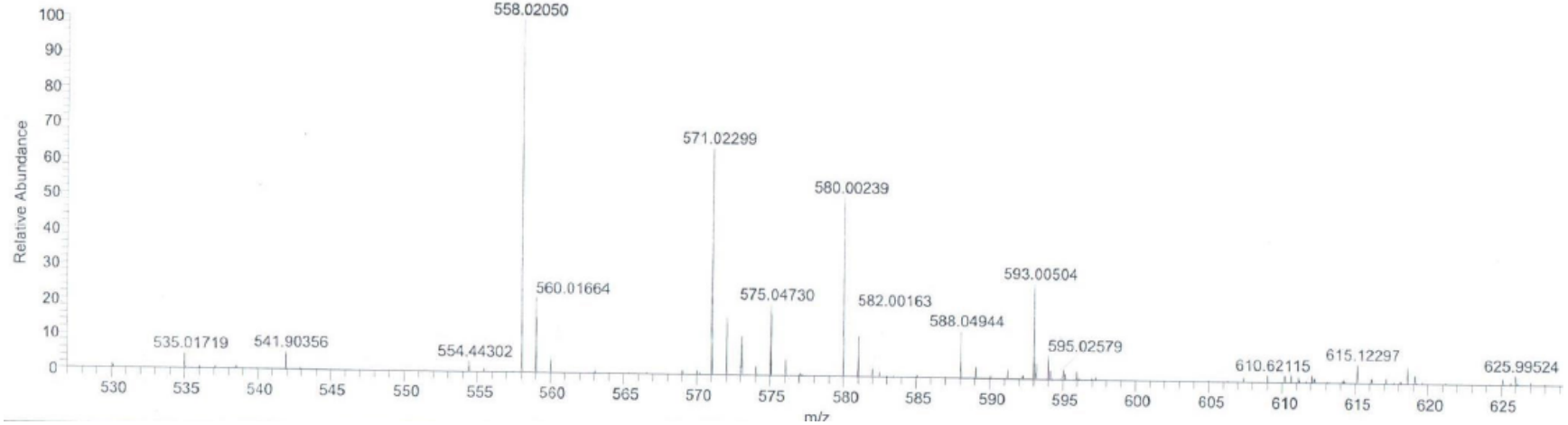
^{13}C NMR of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-nitrophenylcarbamate (5d)**



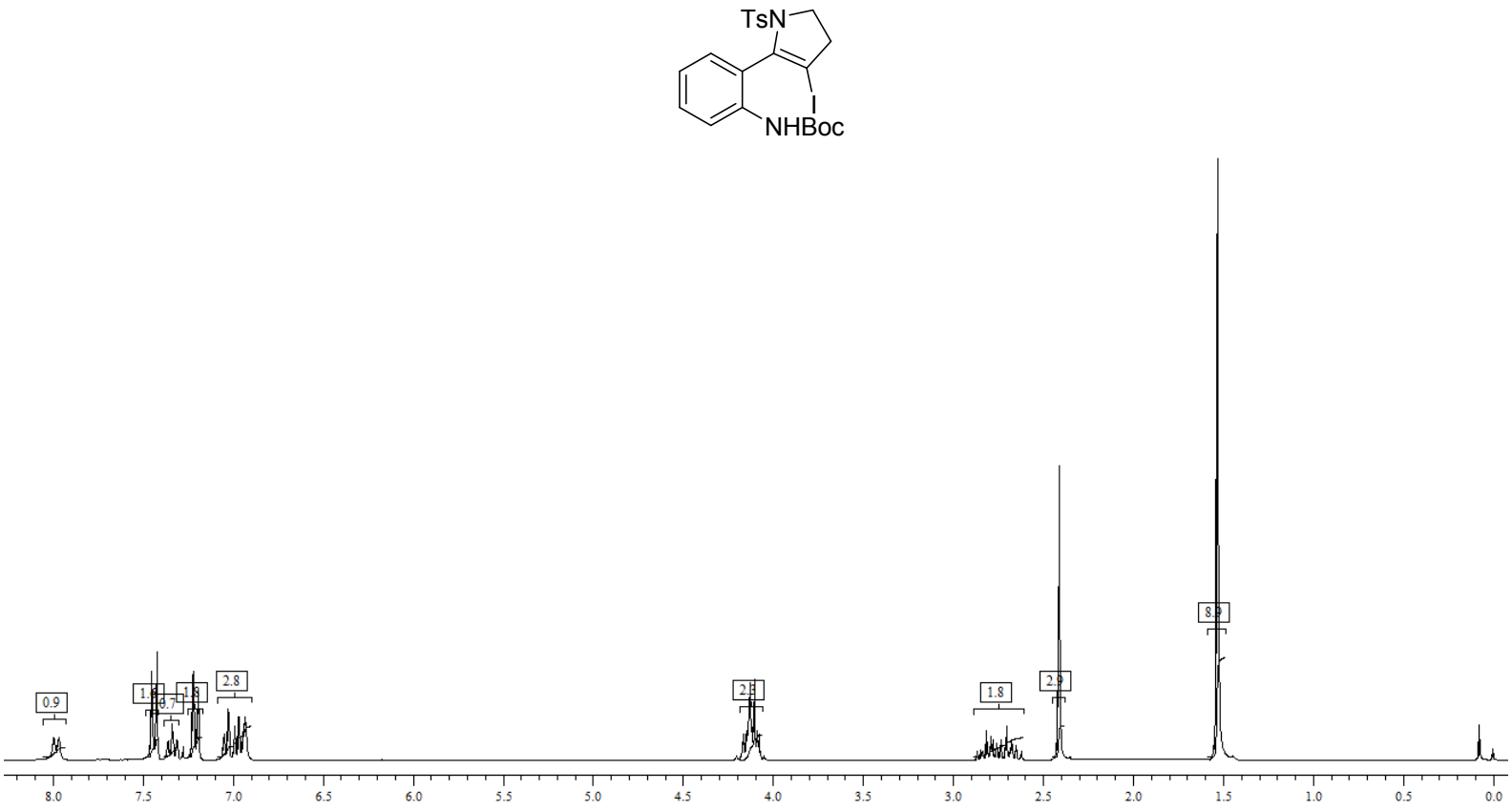


HRMS of **Ethyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)-4-nitrophenylcarbamate (5d)**

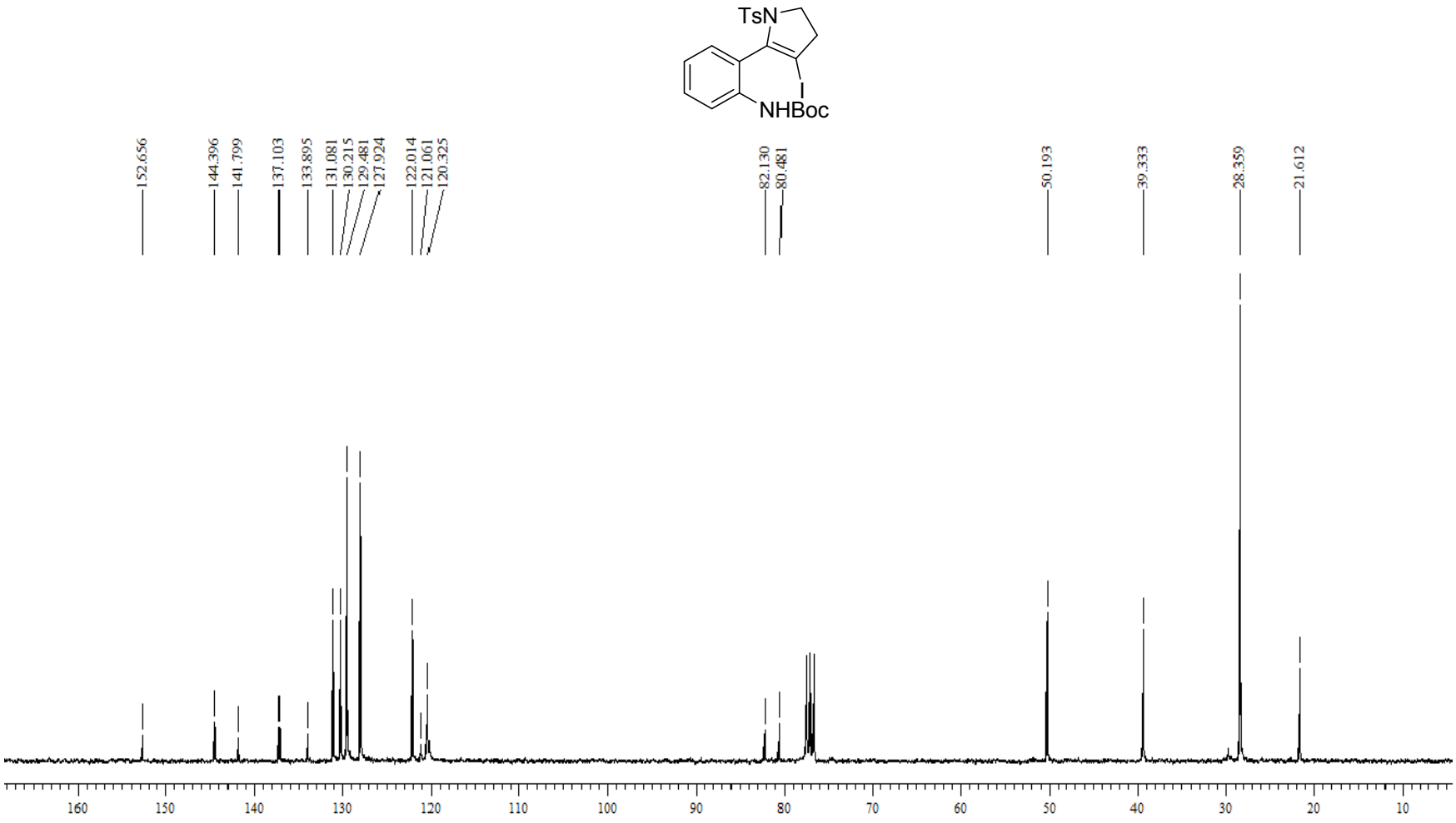




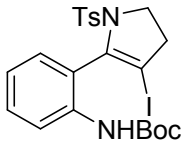
^{1}H NMR of ***t*ert-Butyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5e)**

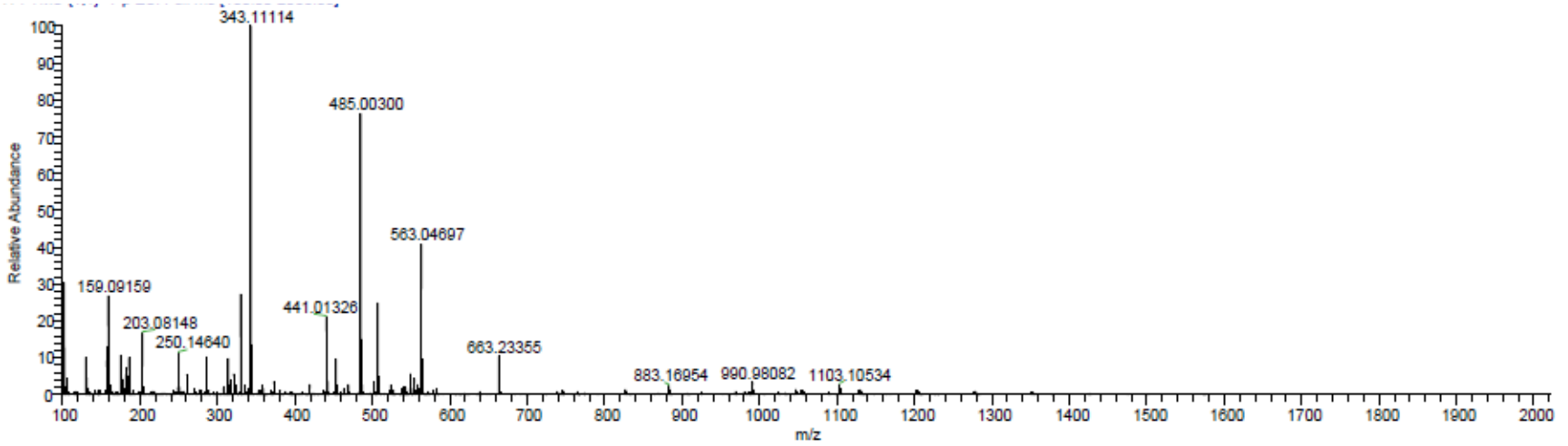


^{13}C NMR of ***t*ert-Butyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5e)**

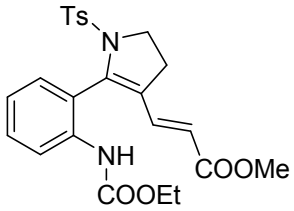


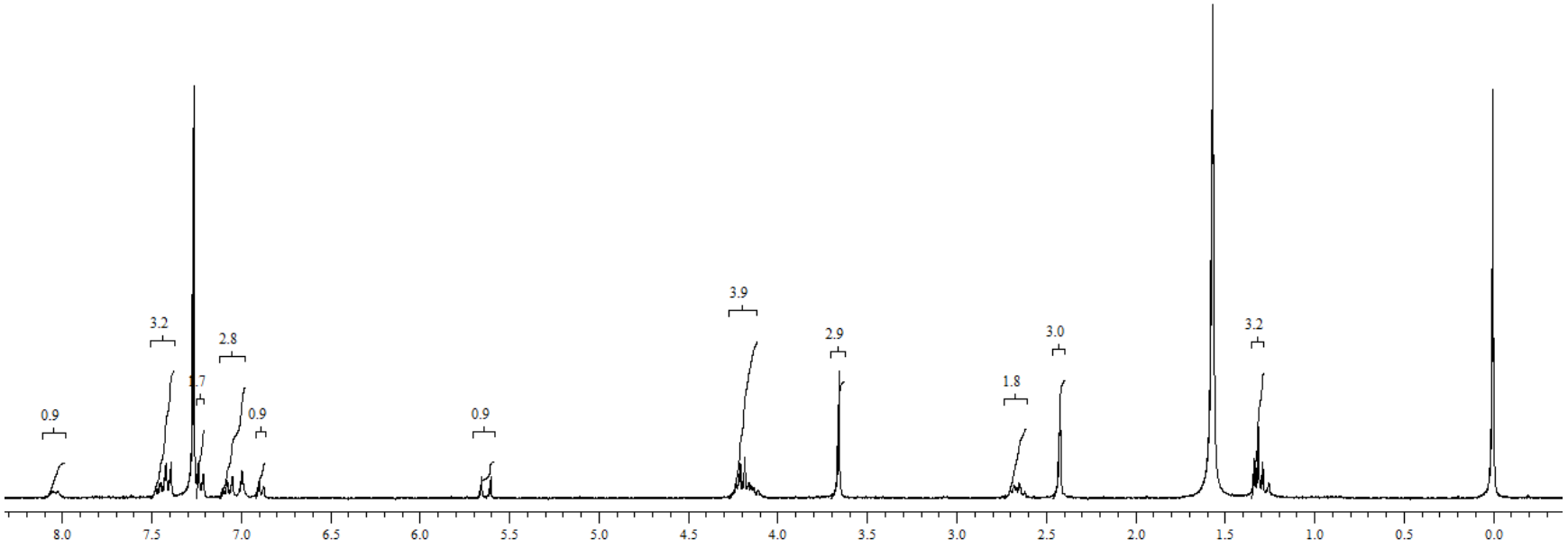
HRMS of ***t*ert-Butyl 2-(3-iodo-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (5e)**



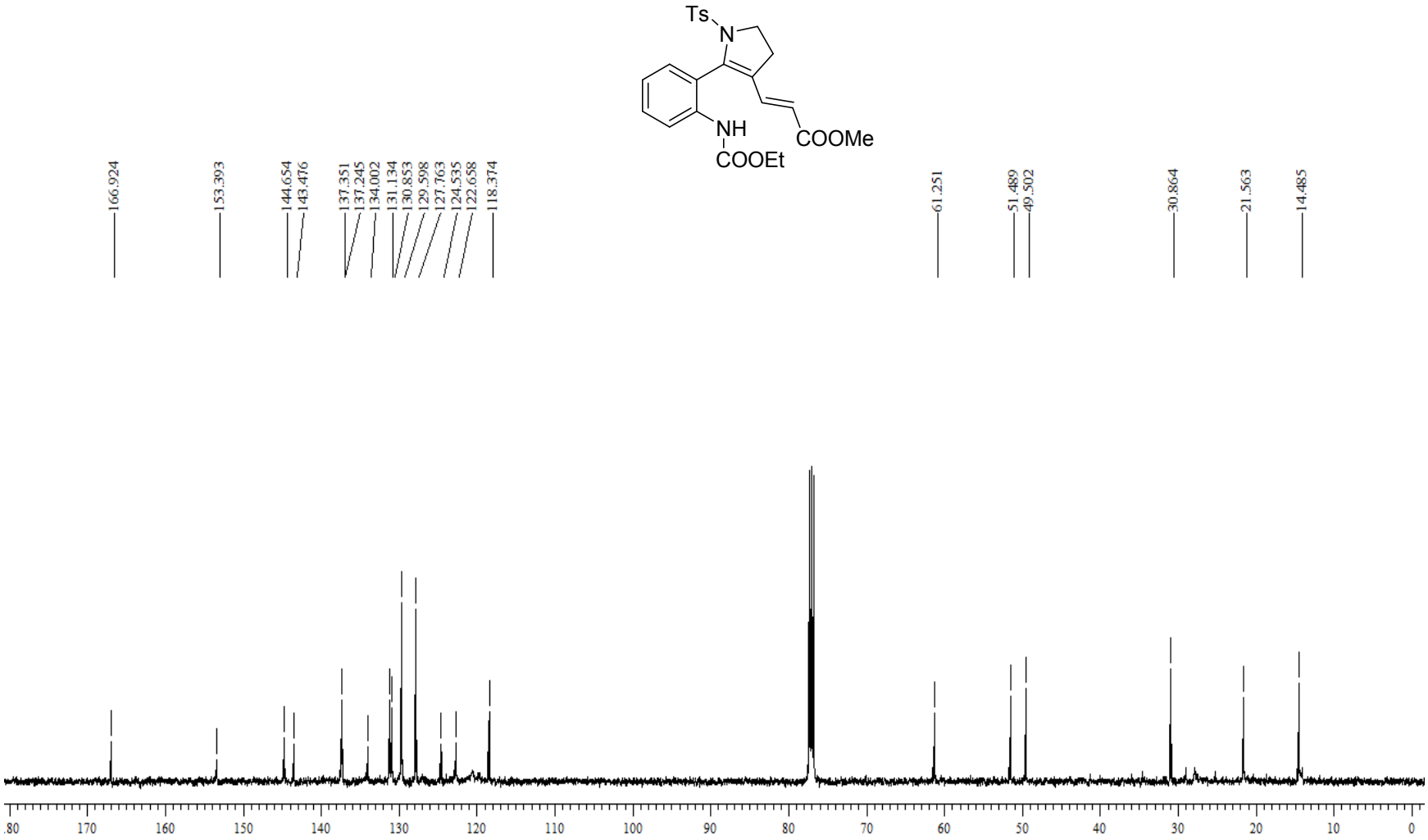


^{1}H NMR of **(*E*)-Methyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3a)**

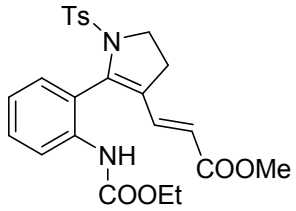


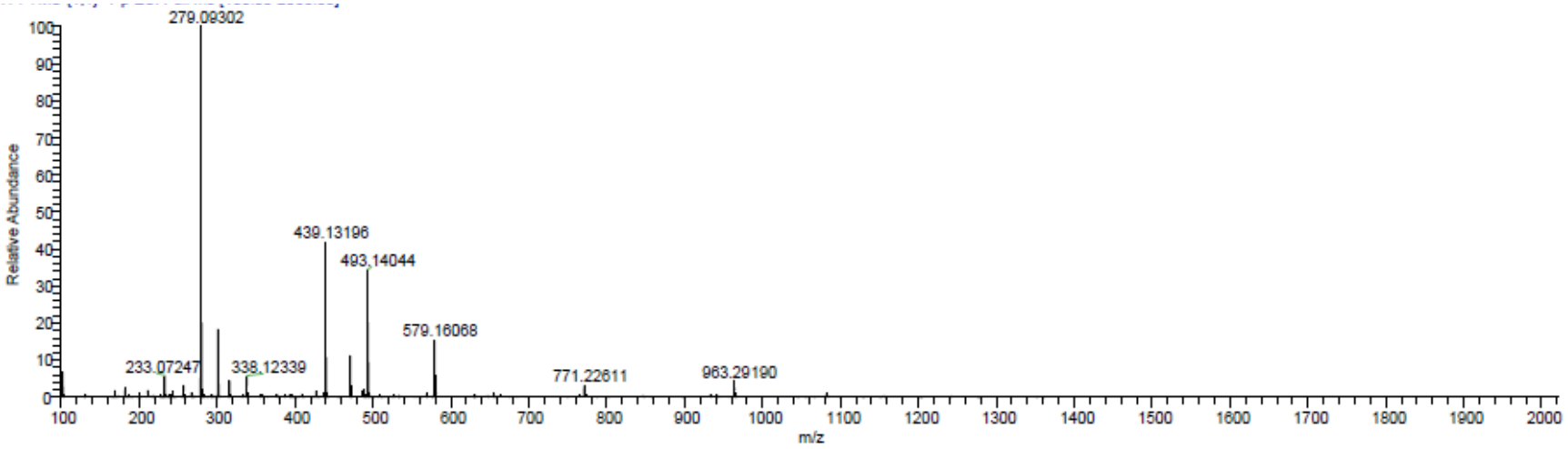


^{13}C NMR of **(*E*)-Methyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3a)**

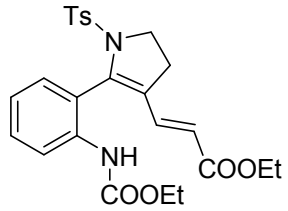


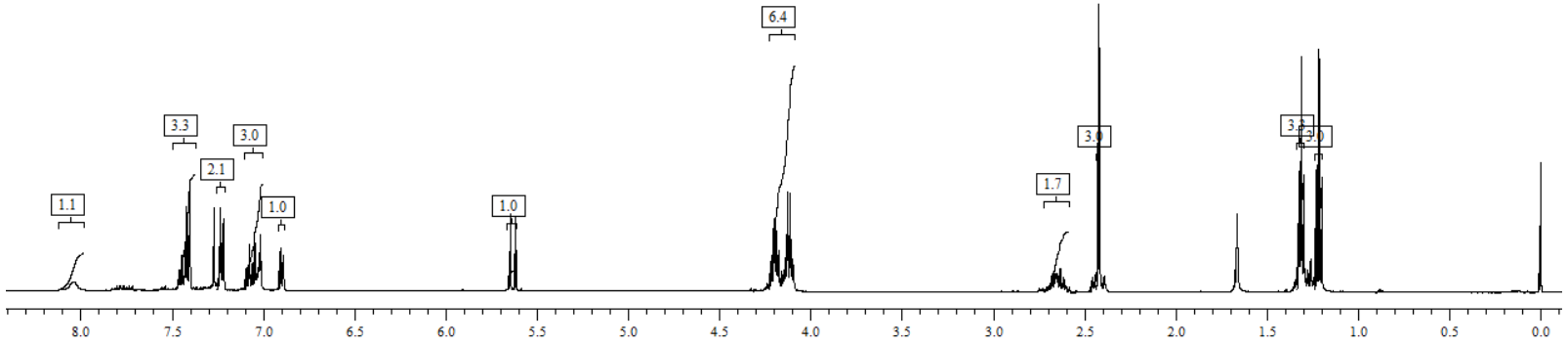
HRMS of (***E***)**-Methyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3a)



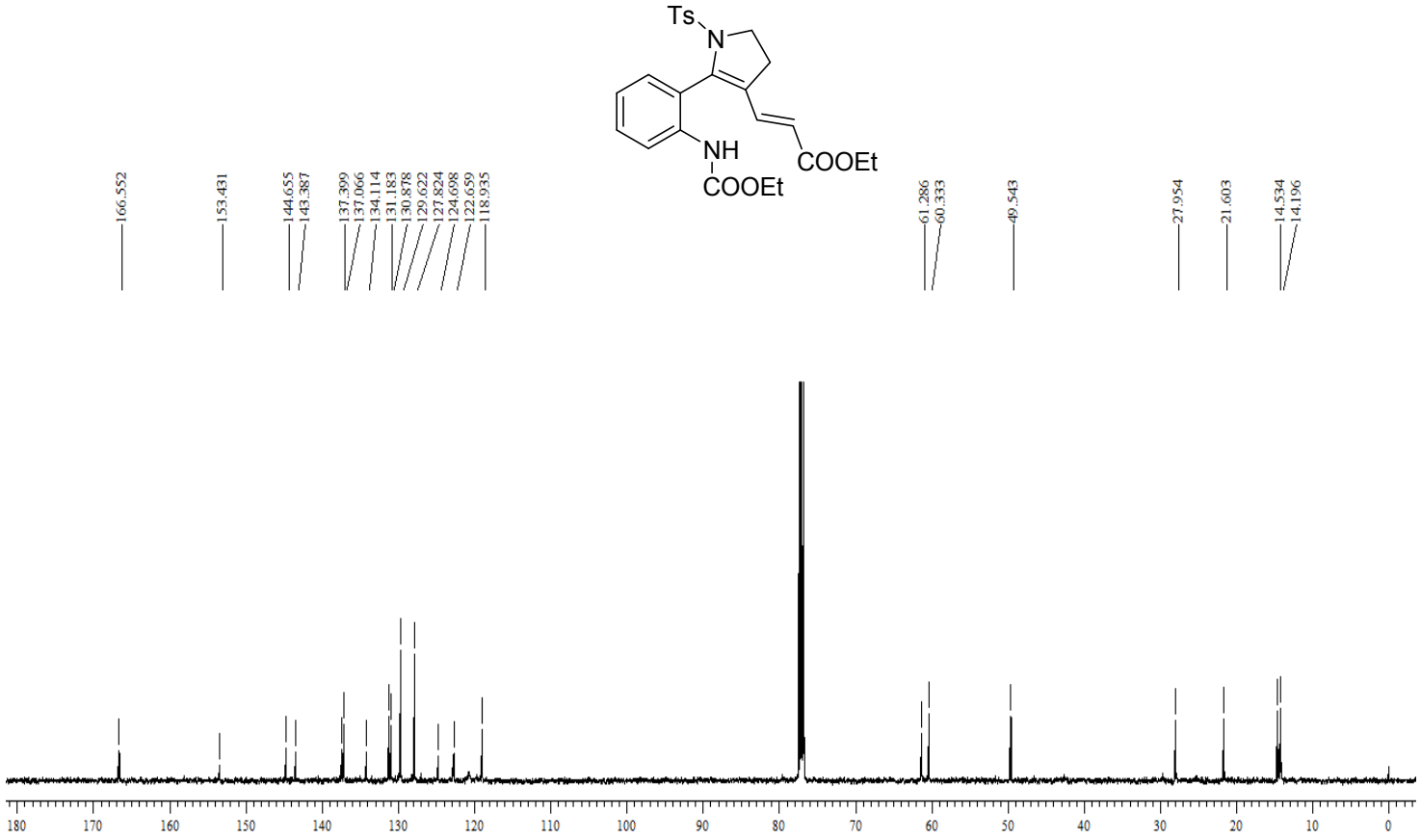


^{1}H NMR of **(*E*)-Ethyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3b)**

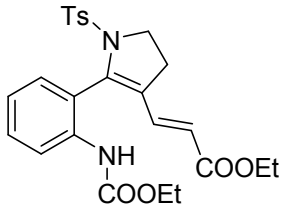


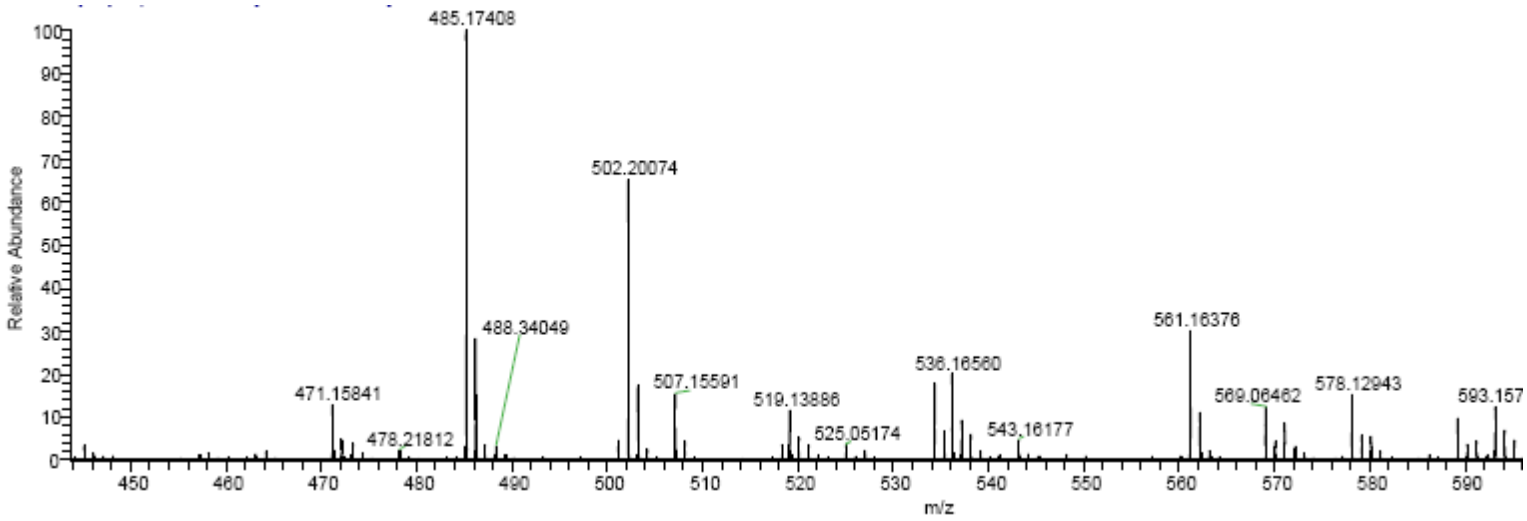


^{13}C NMR of **(*E*)-ethyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3b)**

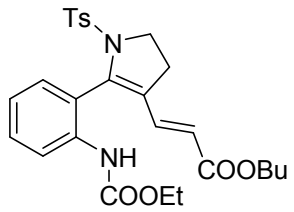


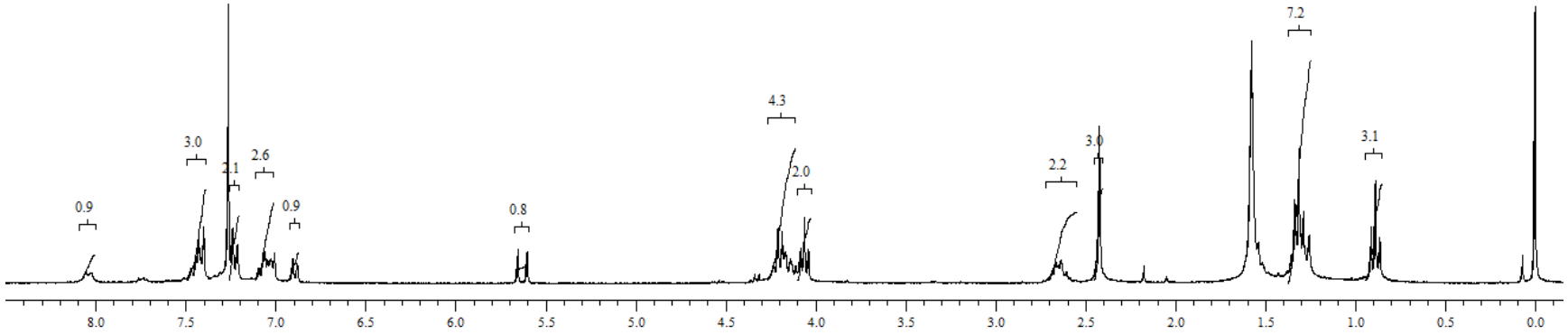
HRMS of **(*E*)-Ethyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3b)**



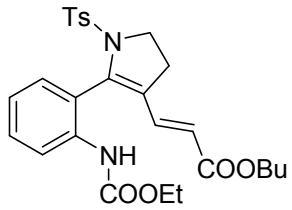


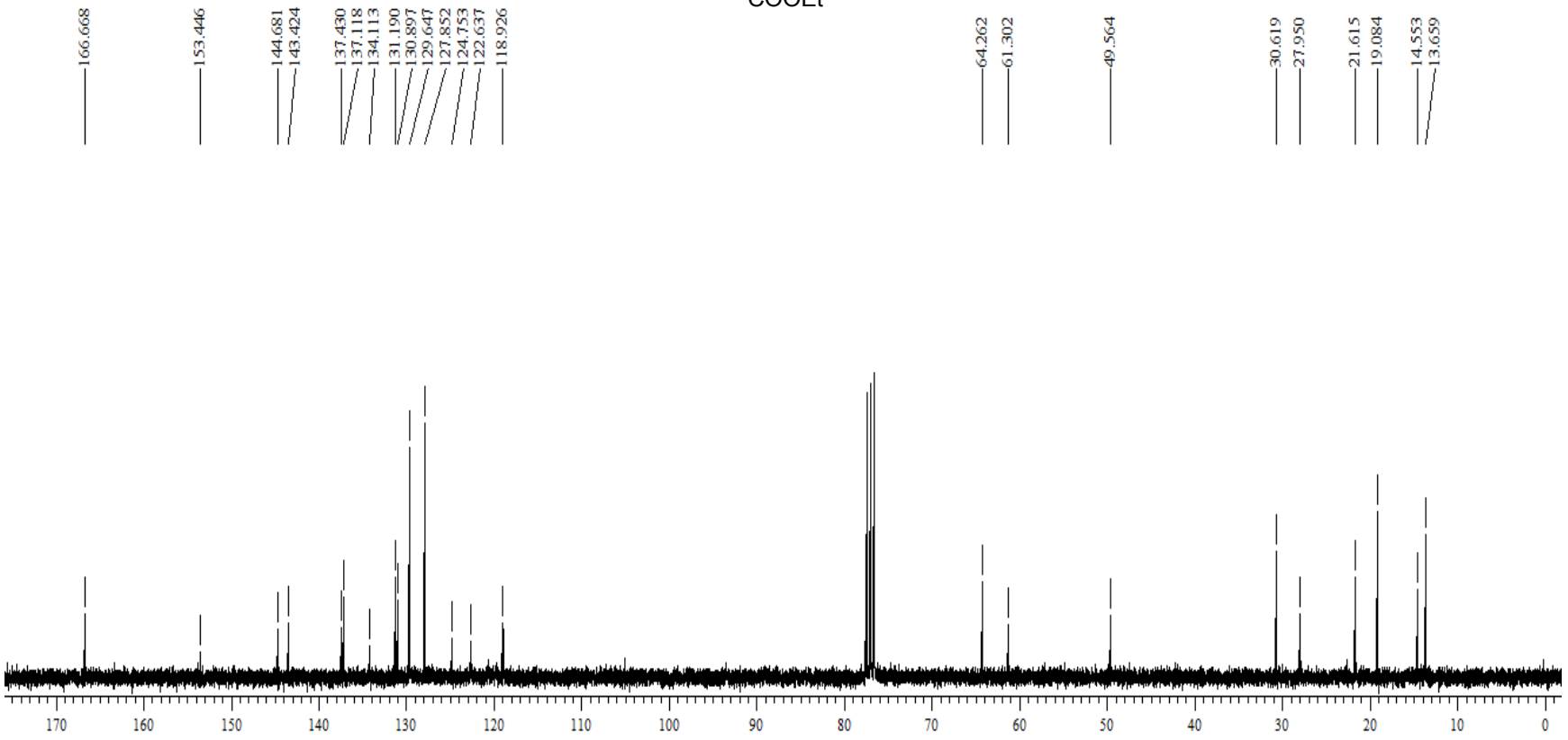
^{1}H NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3c)**



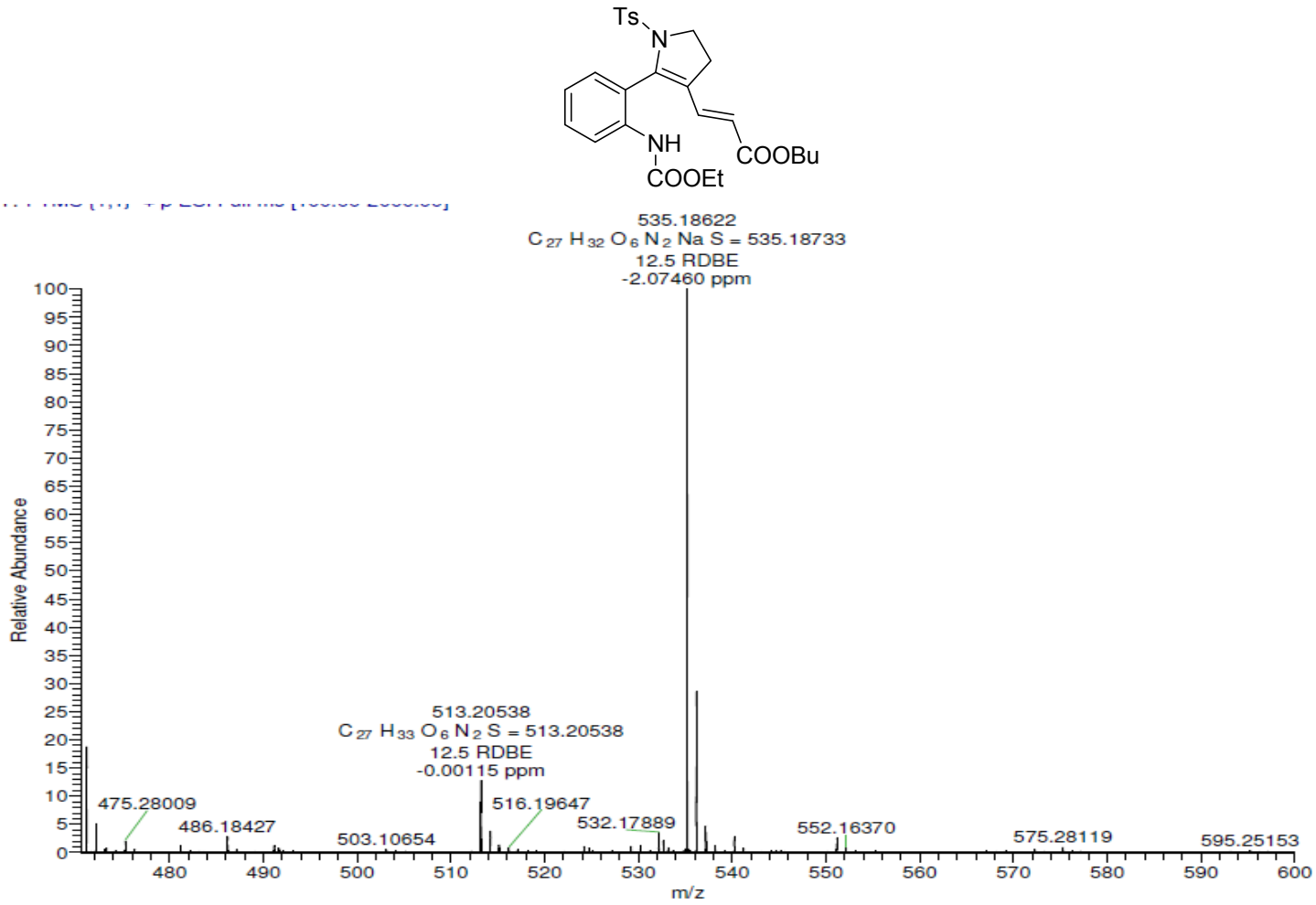


^{13}C NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3c)**

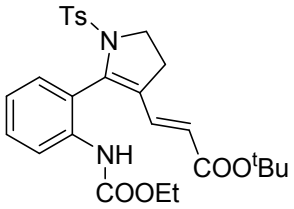


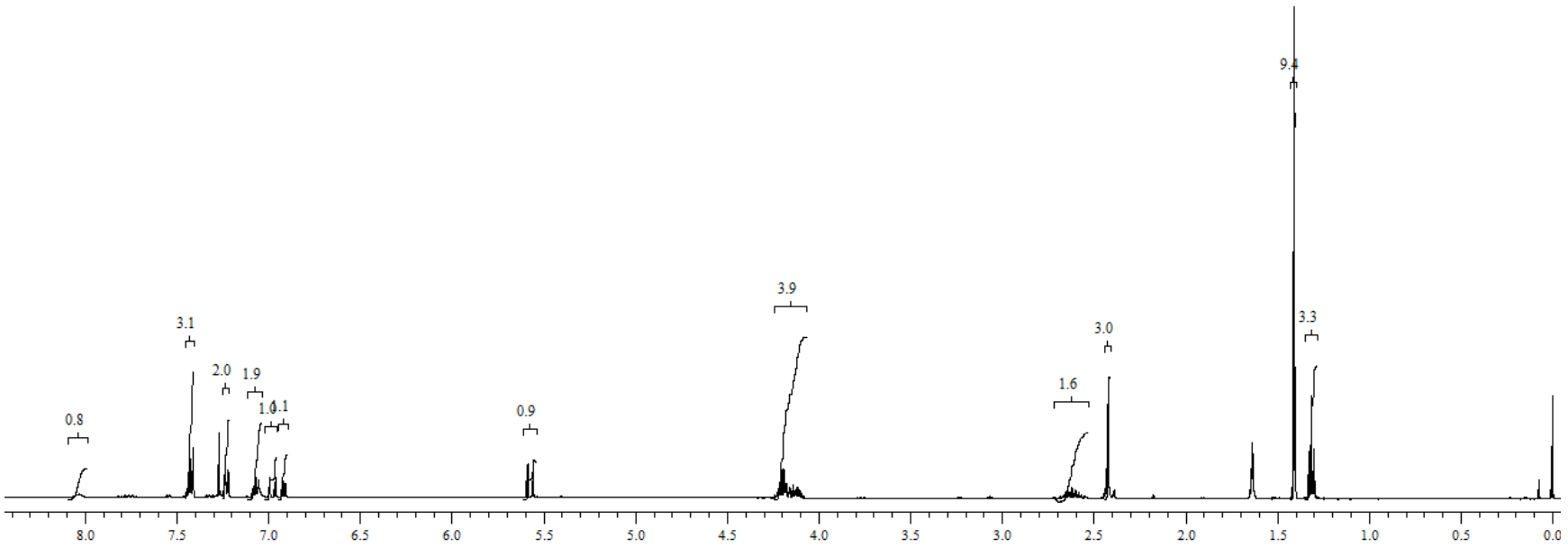


HRMS of **(*E*)-butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1H-pyrrol-3-yl)acrylate (3c)**

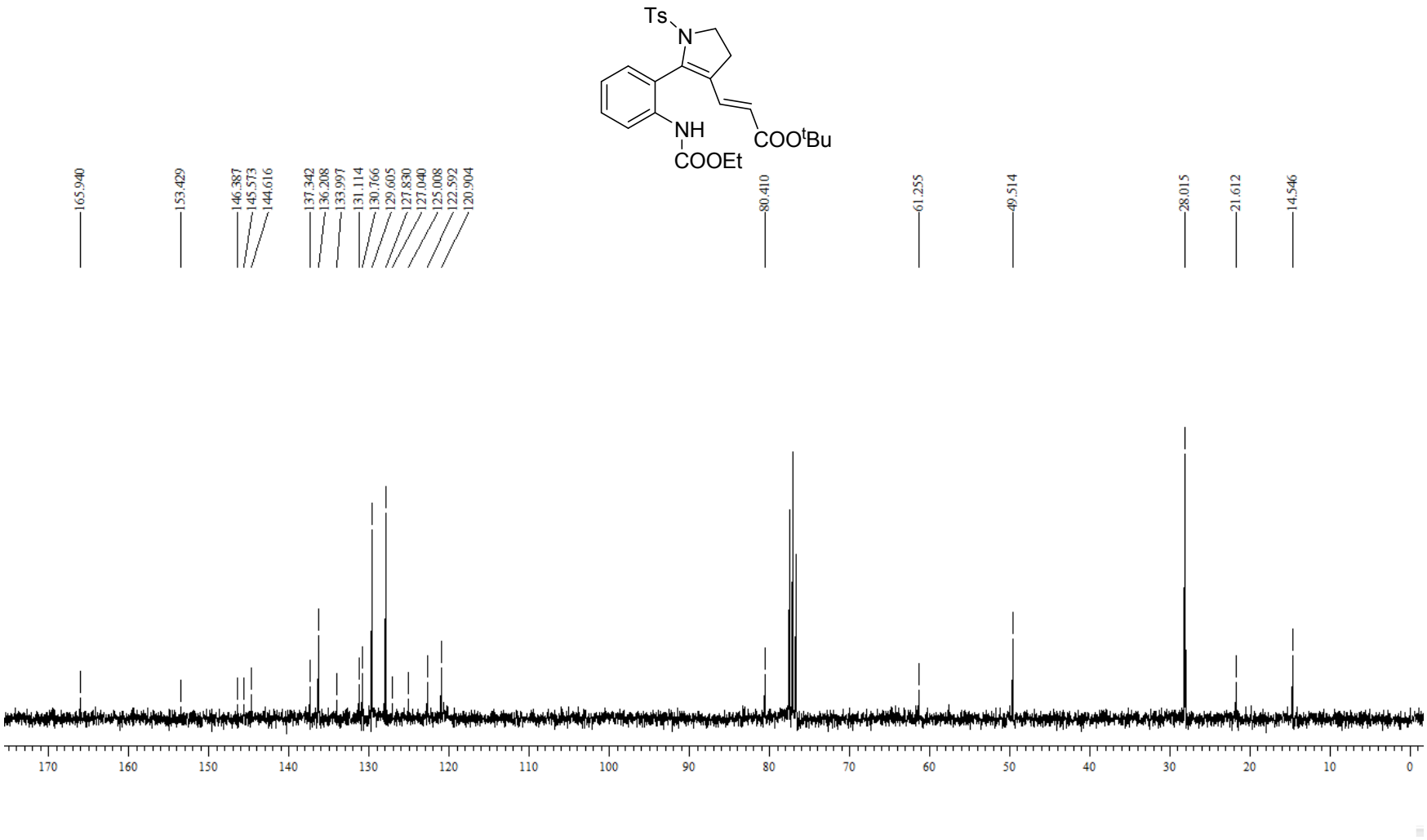


^{1}H NMR of **(*E*)-*tert*-Butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3d)**

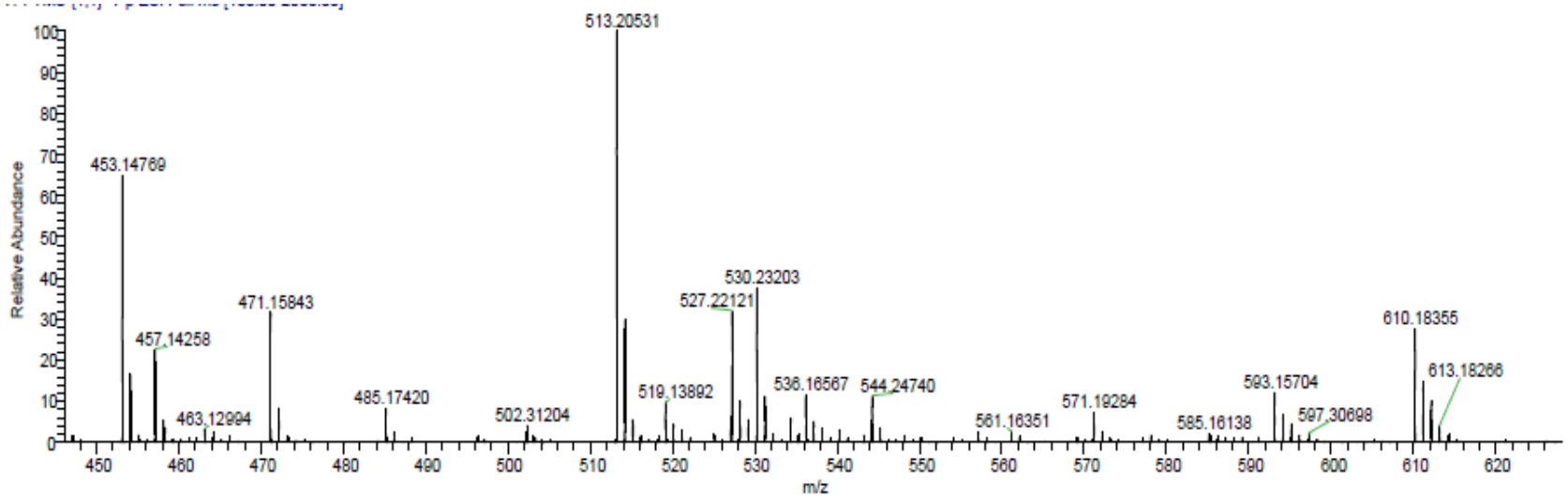




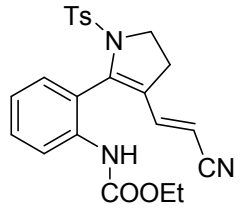
^{13}C NMR of **(*E*)-*tert*-Butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3d)**

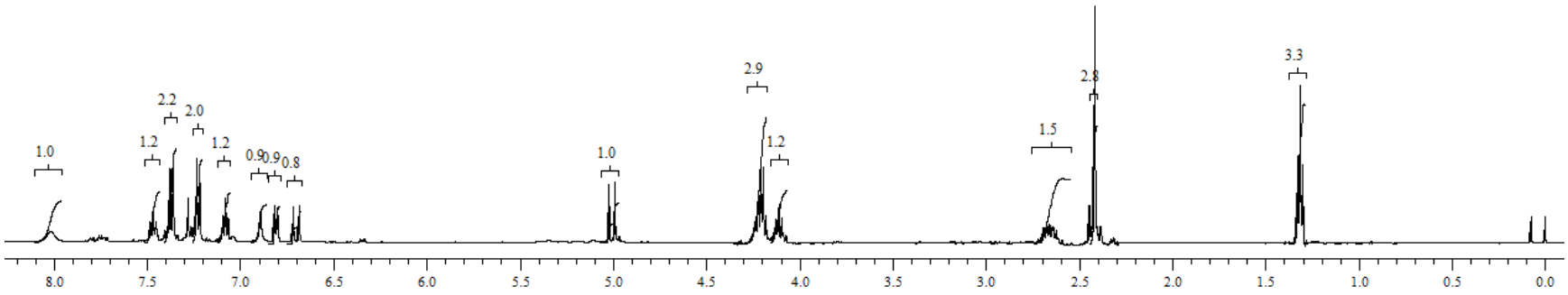


HRMS of **(*E*)-*tert*-Butyl 3-(2-(2-(ethoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3d)**

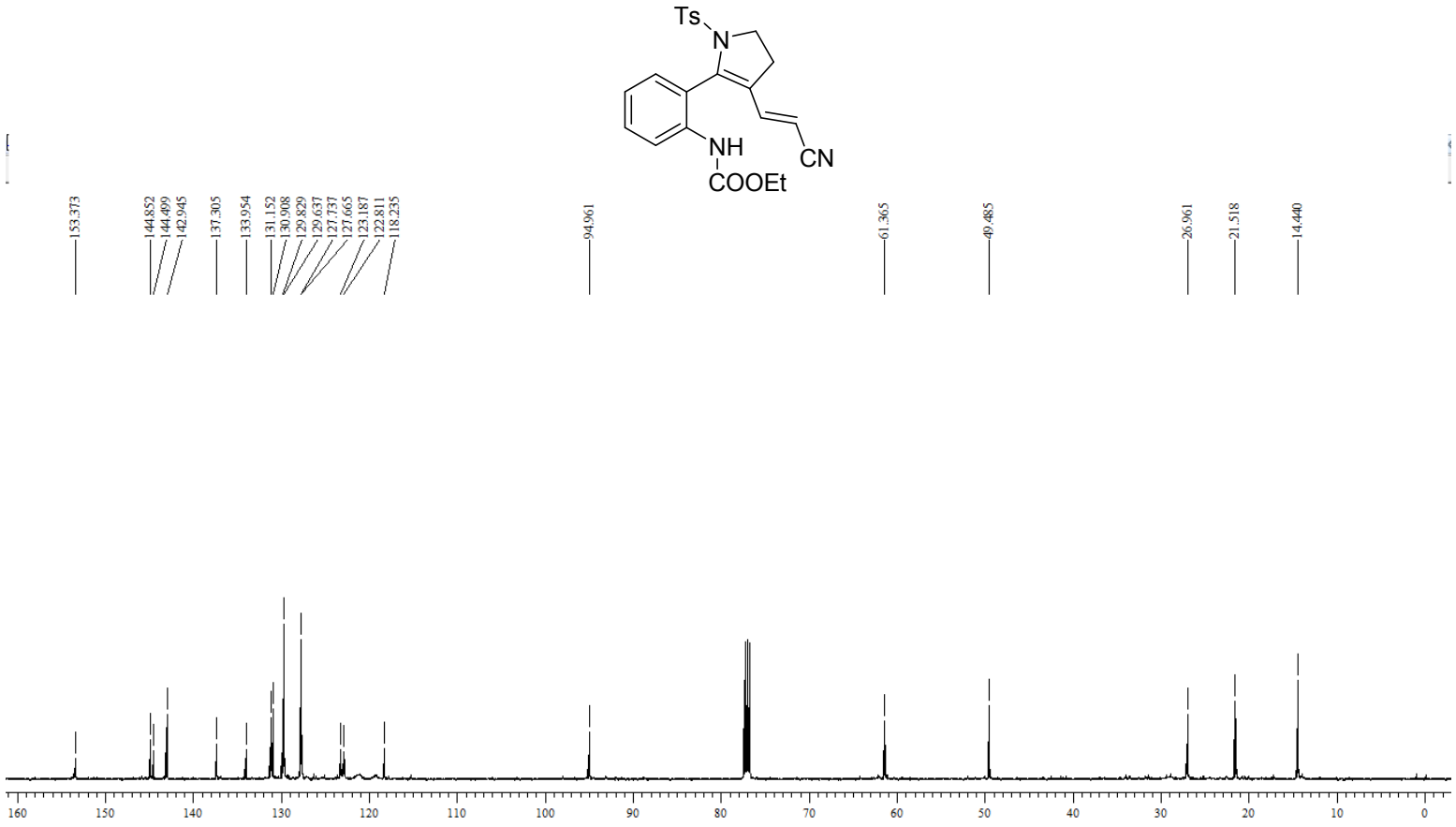


^{1}H NMR of (***E***)**-Ethyl 2-(3-(2-cyanovinyl)-1-tosyl-4,5-dihydro-1H-pyrrol-2-yl)phenylcarbamate (3e)

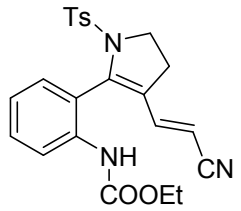


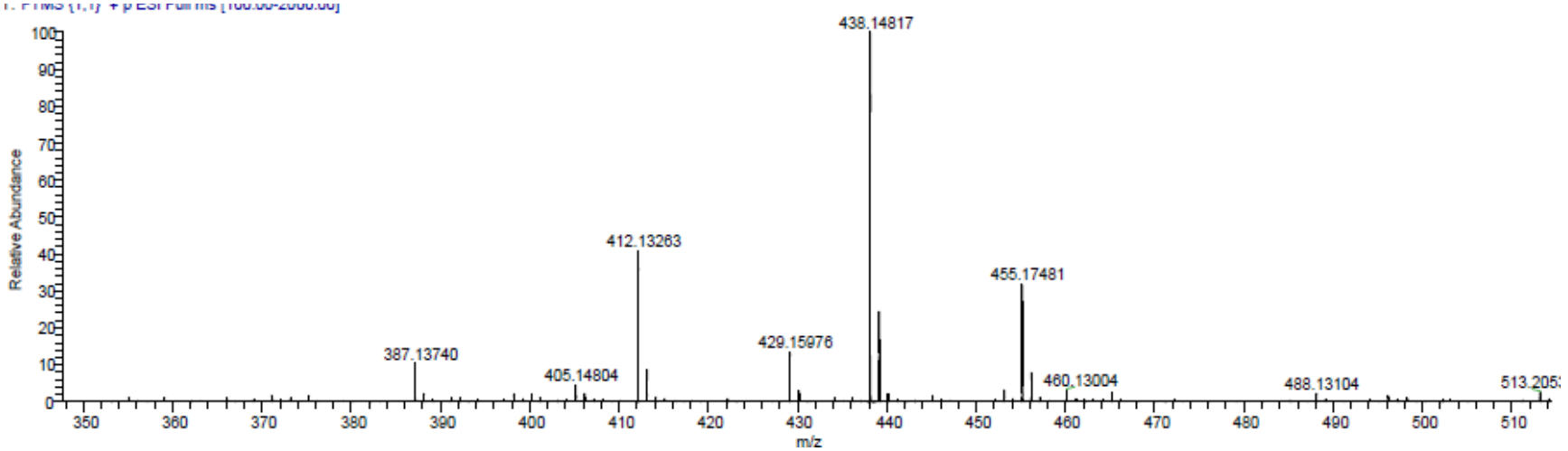


^{13}C NMR of **(*E*)-ethyl 2-(3-(2-cyanovinyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (3e)**

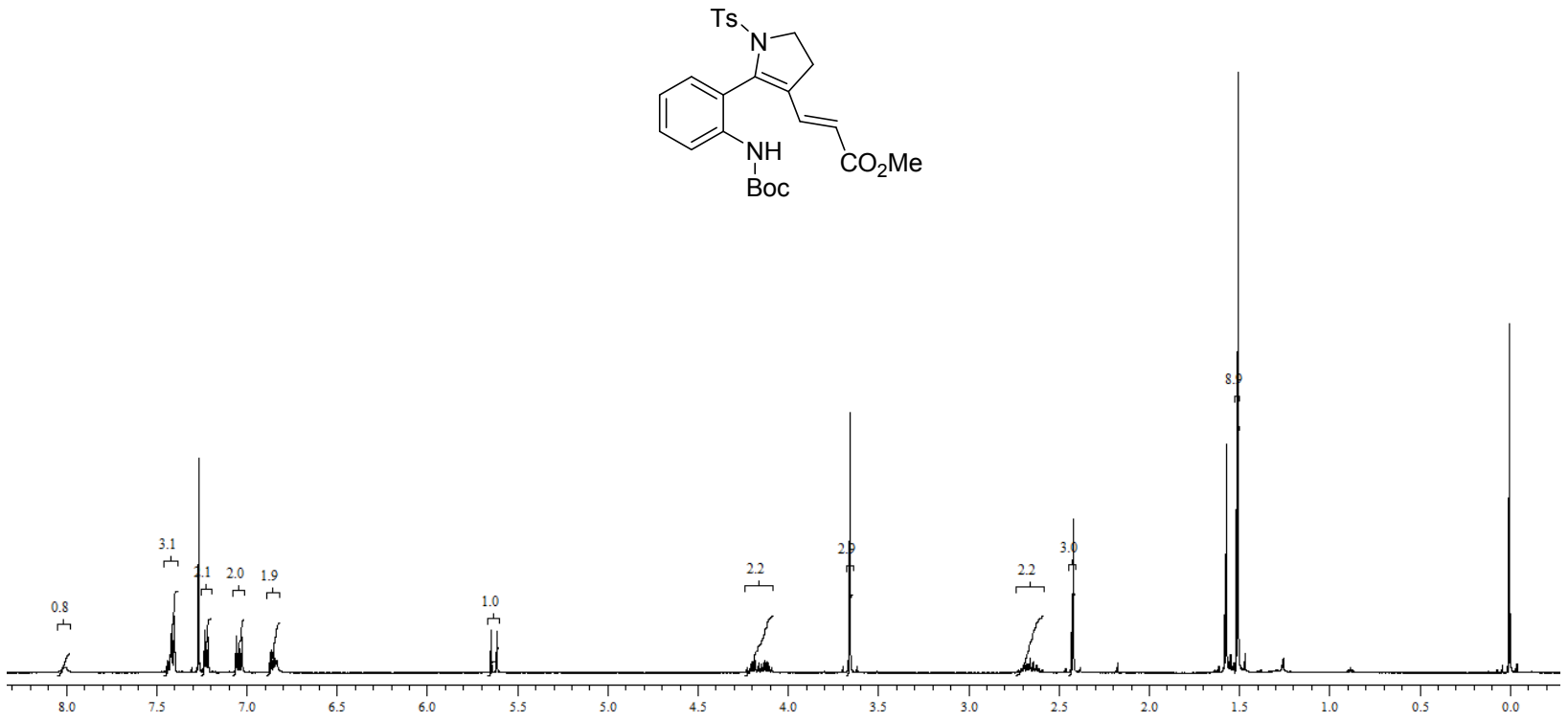


HRMS of **(*E*)-Ethyl 2-(3-(2-cyanovinyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)phenylcarbamate (3e)**

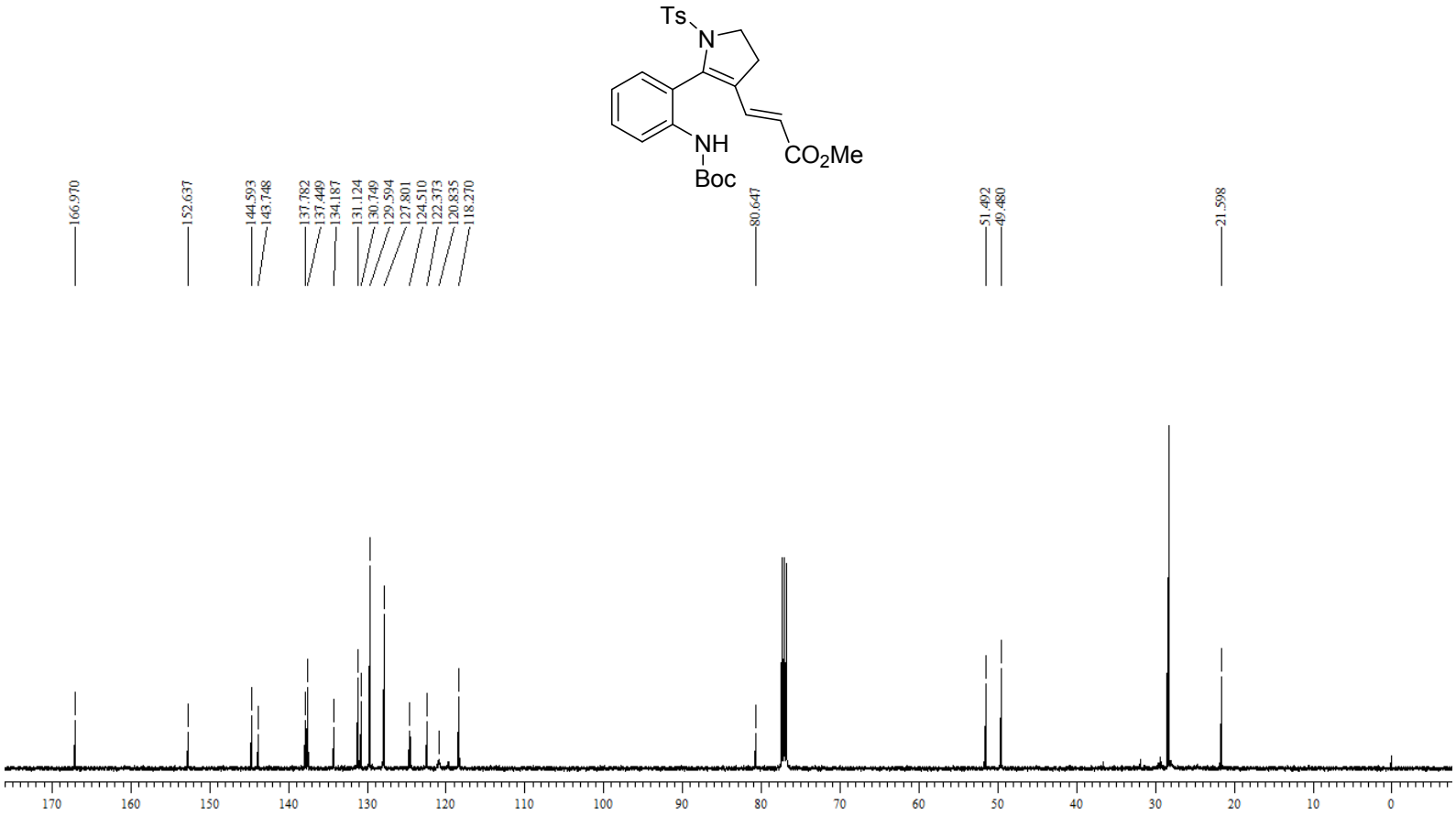




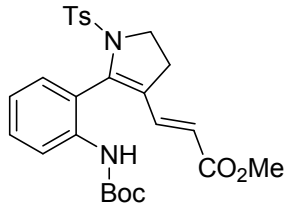
^{1}H NMR of **(*E*)-Methyl 3-(2-(2-(tert-butoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3f)**

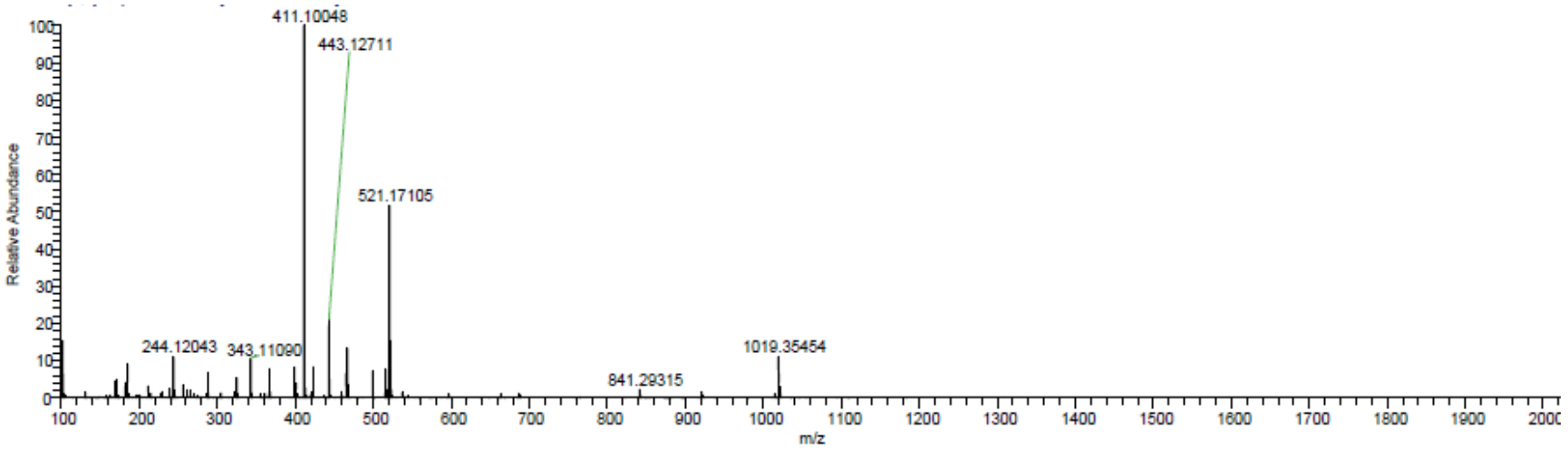


^{13}C NMR of **(*E*)-Methyl 3-(2-(2-(tert-butoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3f)**

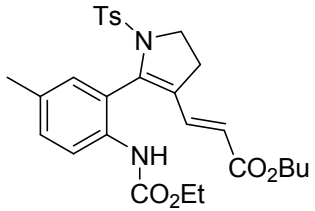


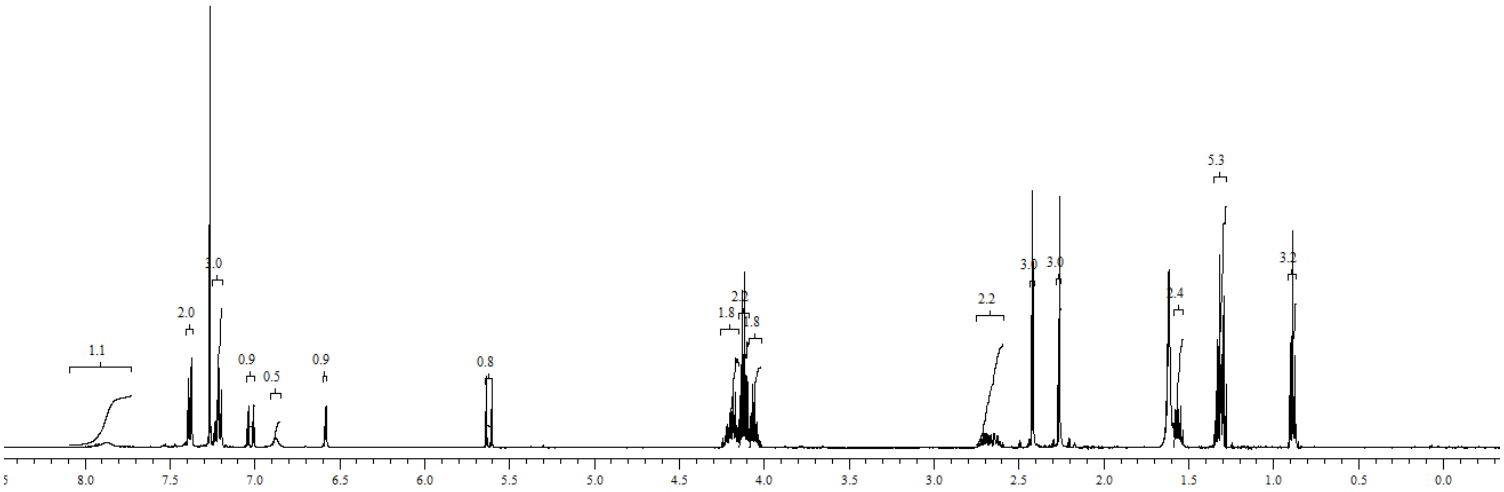
HRMS of **(*E*)-Methyl 3-(2-(2-(tert-butoxycarbonylamino)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3f)**



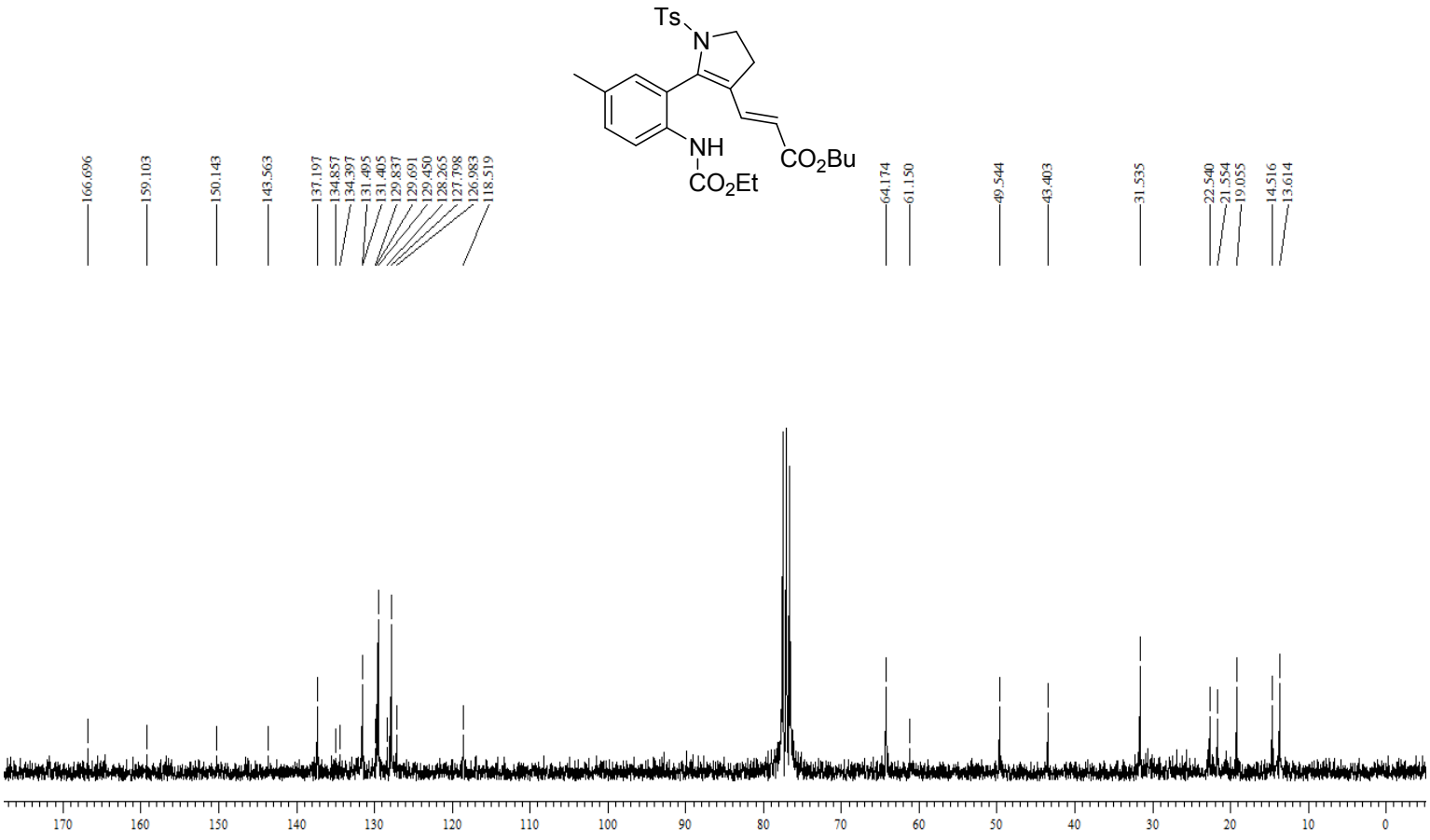


^{1}H NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)-5-methylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3g)**

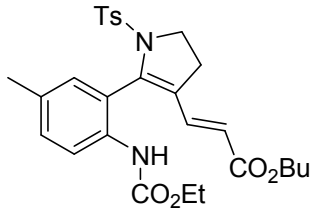


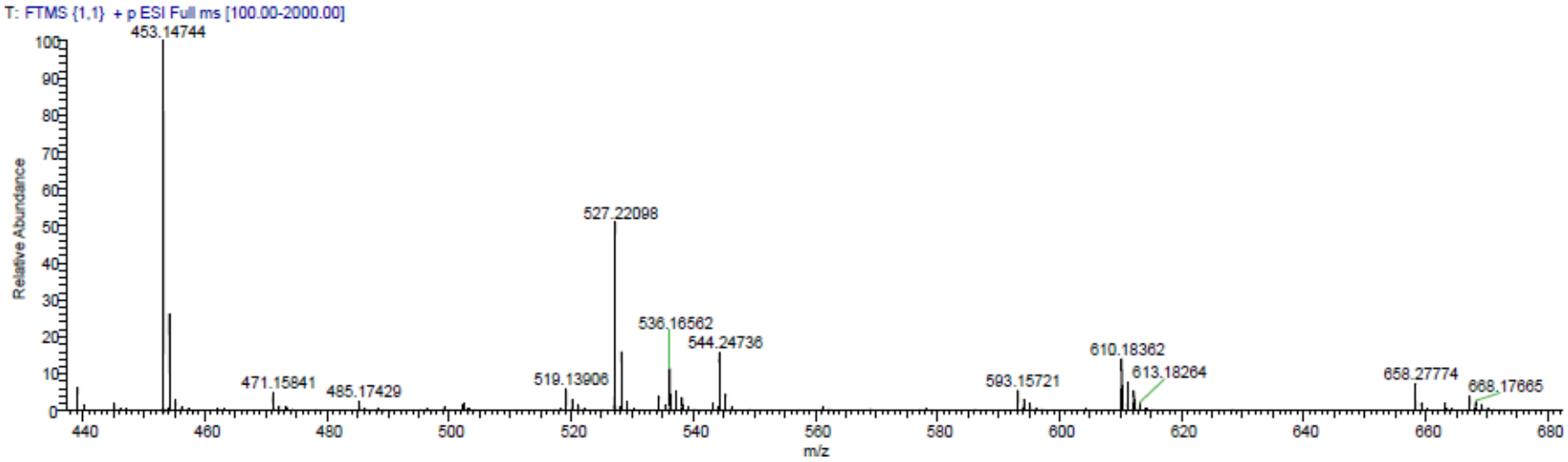


^{13}C NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)-5-methylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3g)**

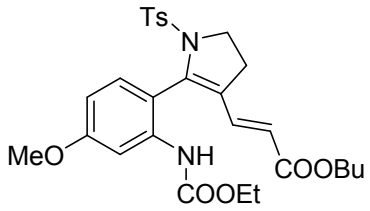


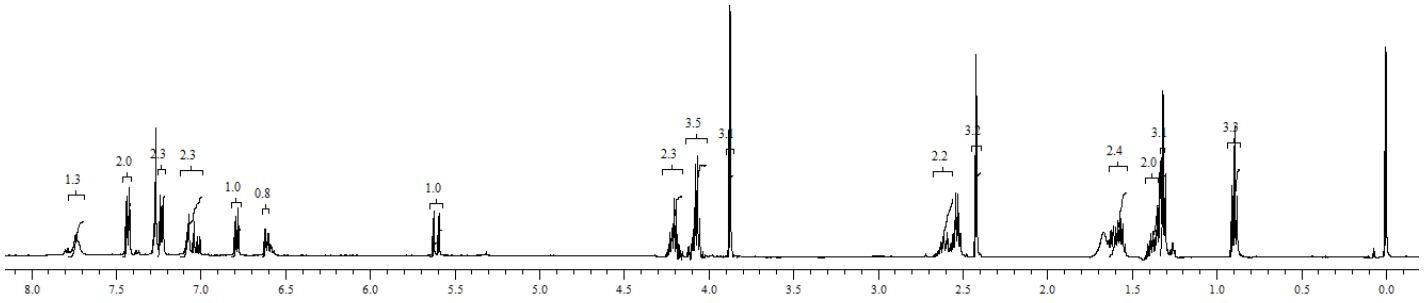
HRMS of (***E***)**-butyl 3-(2-(2-(ethoxycarbonylamino)-5-methylphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3g)



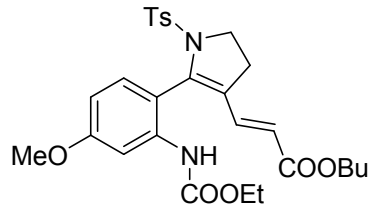


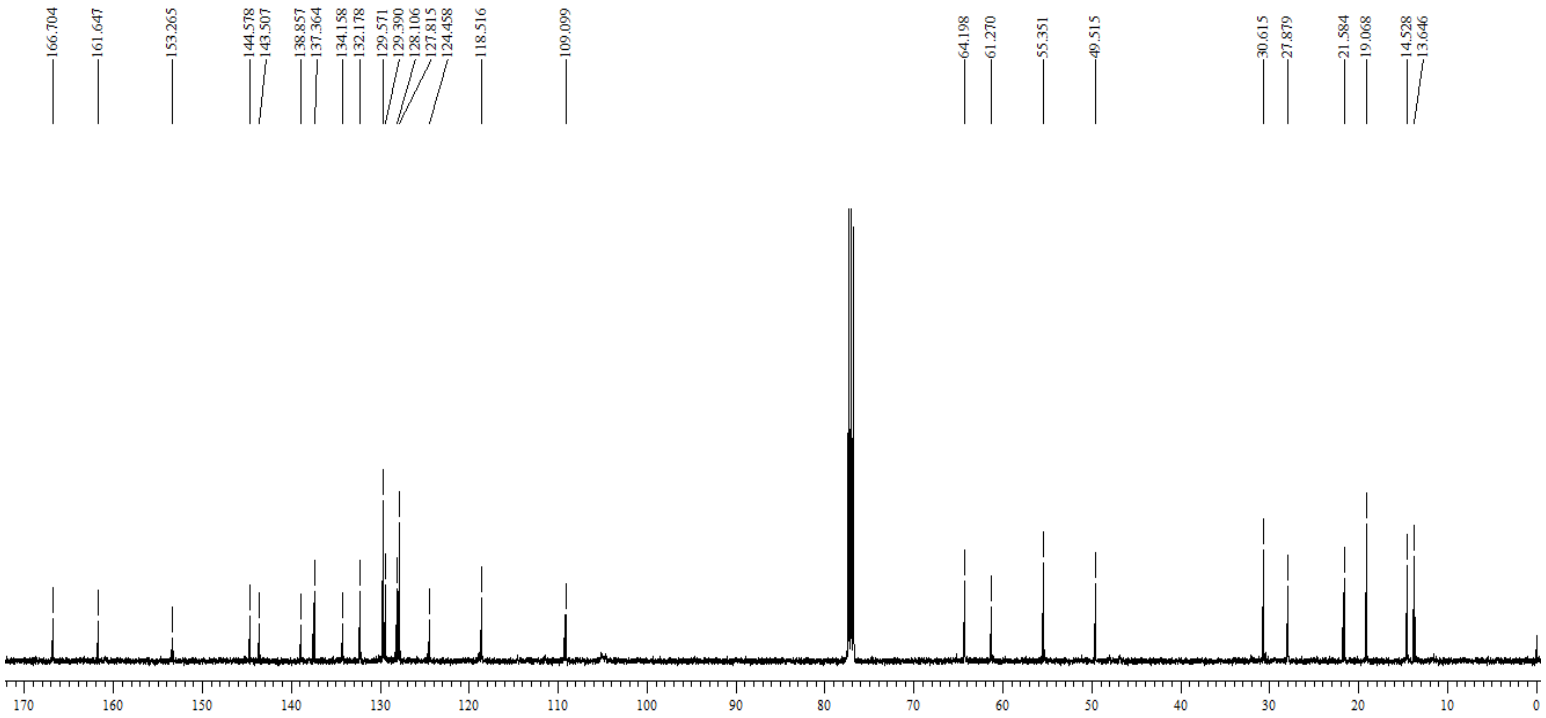
^{1}H NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)-4-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3h)**



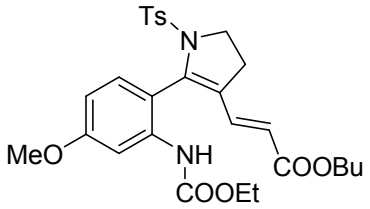


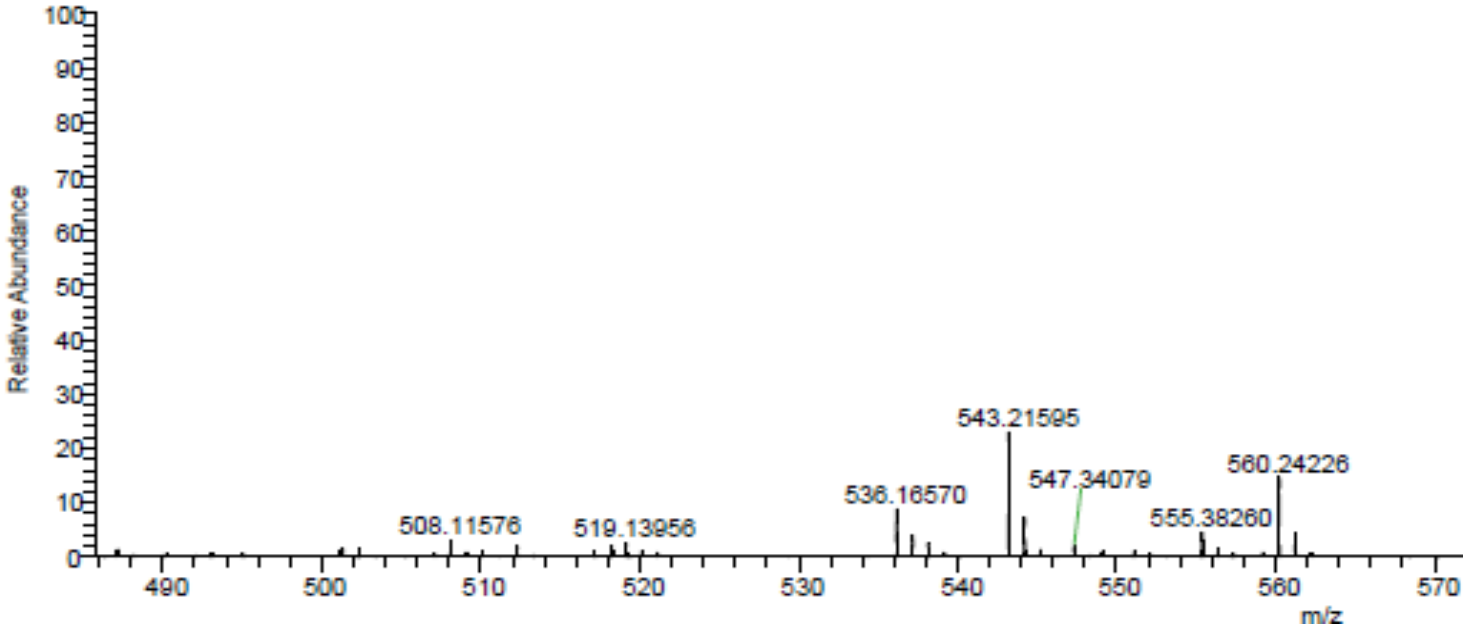
^{13}C NMR of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)-4-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3h)**



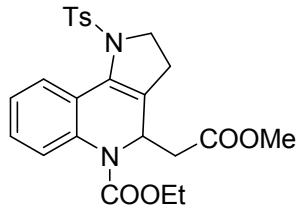


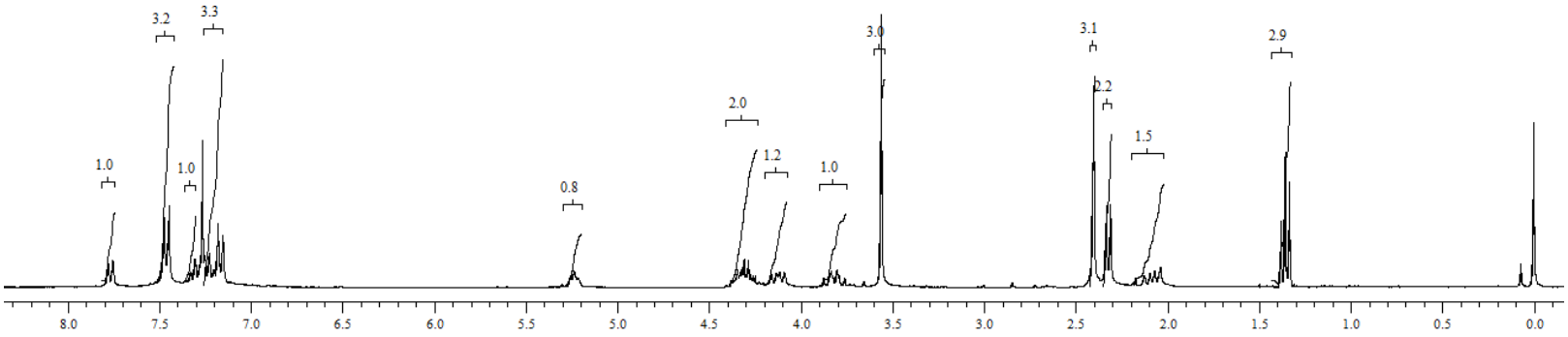
HRMS of **(*E*)-Butyl 3-(2-(2-(ethoxycarbonylamino)-4-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (3h)**



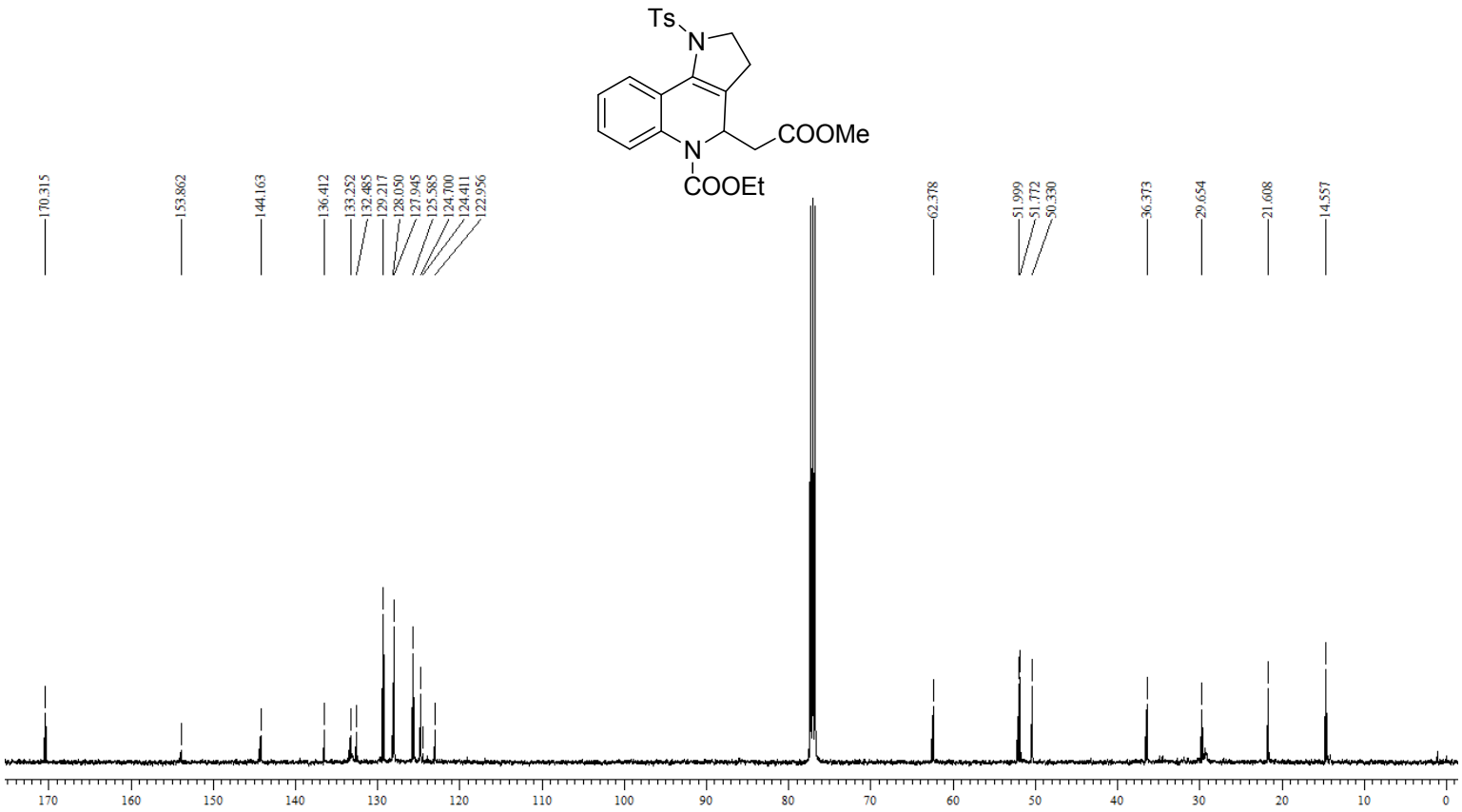


^{1}H NMR of **Ethyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4a)**

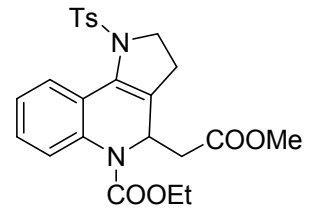


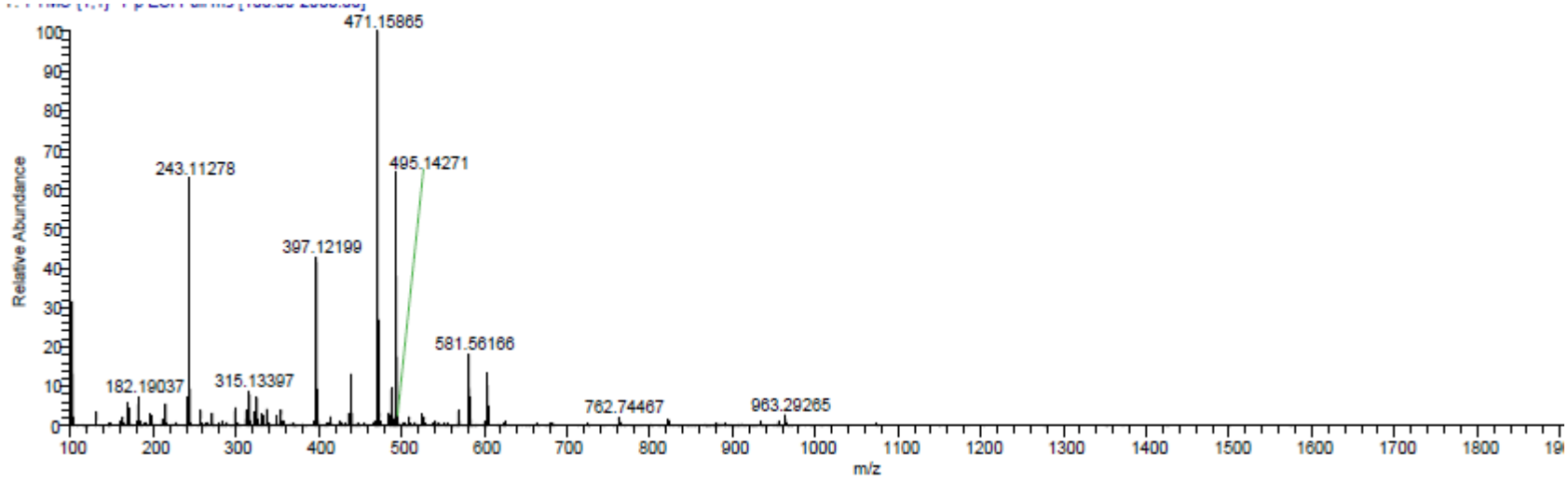


^{13}C NMR of **Ethyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4a)**

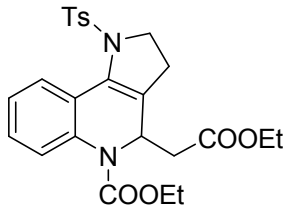


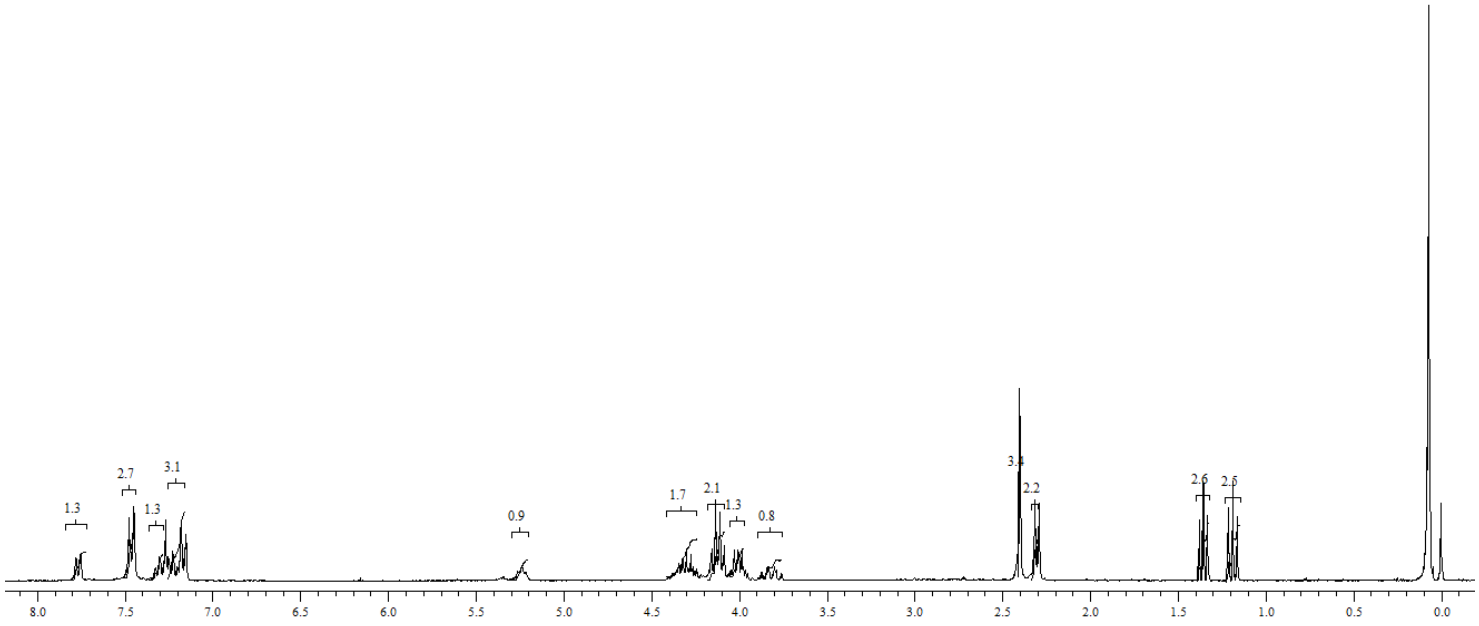
HRMS of **Ethyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4a)**



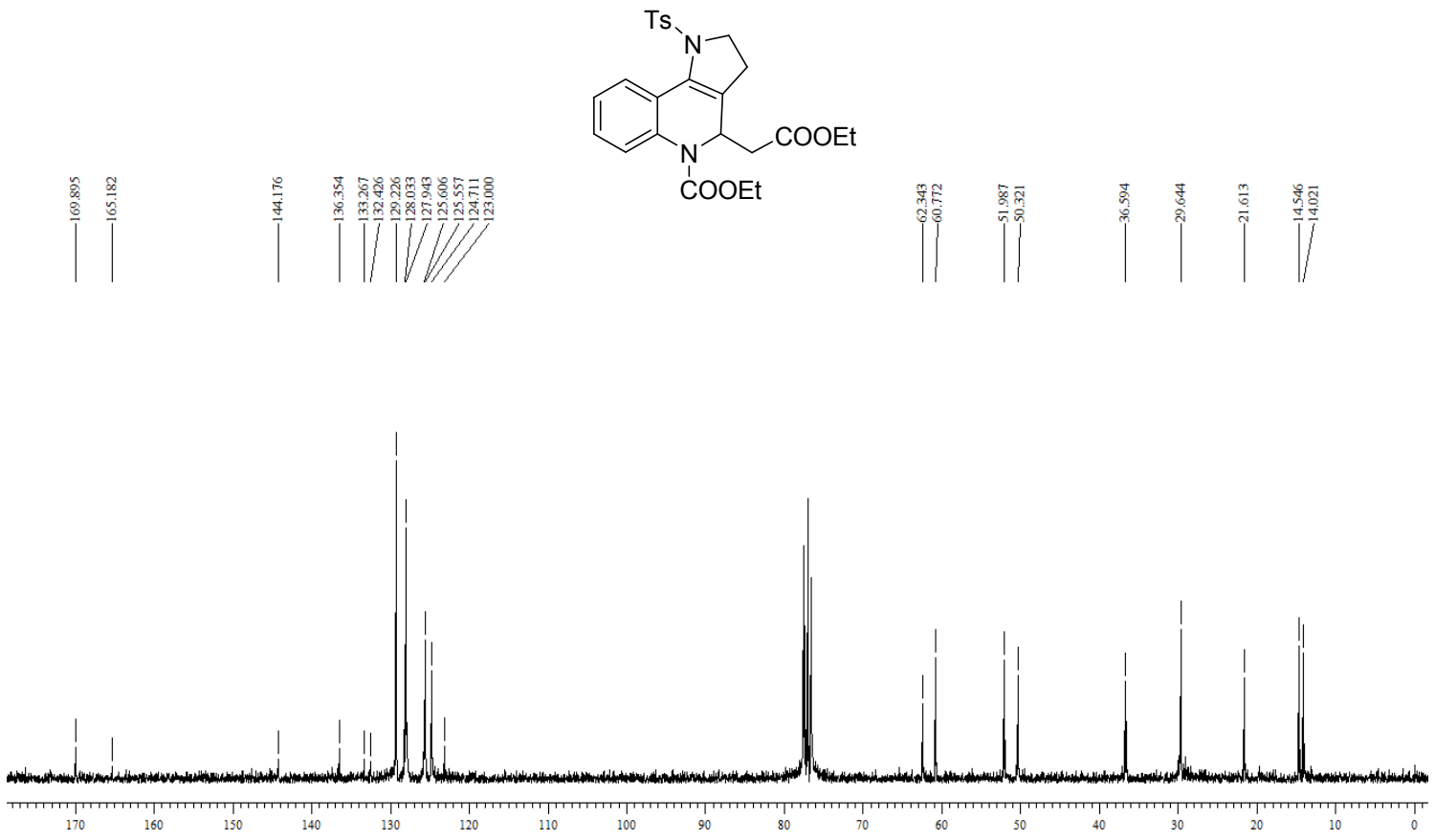


^{1}H NMR of **Ethyl 4-(2-ethoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4b)**

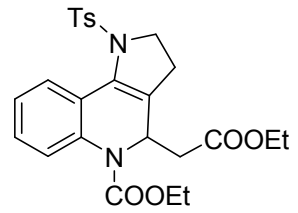


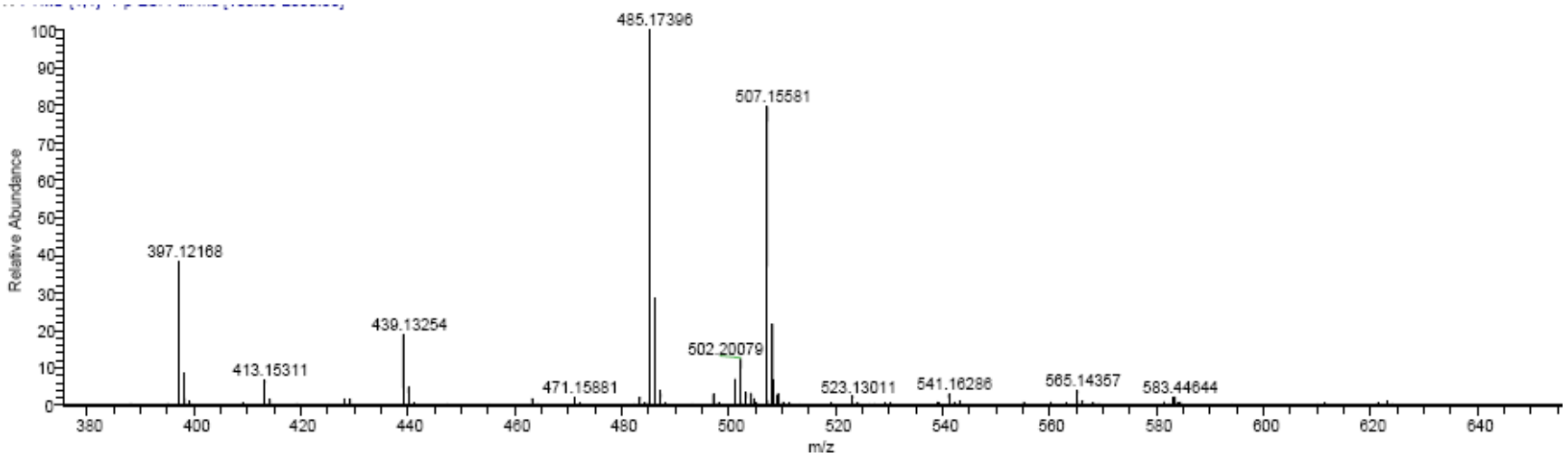


^{13}C NMR of **Ethyl 4-(2-ethoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4b)**

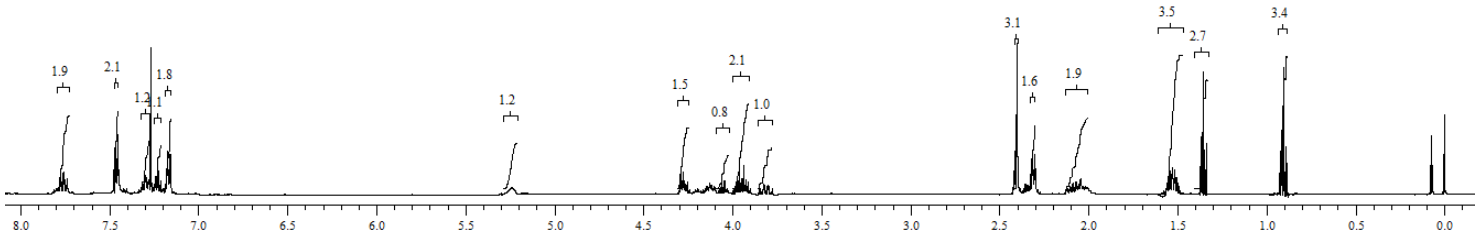


HRMS of **Ethyl 4-(2-ethoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4b)**

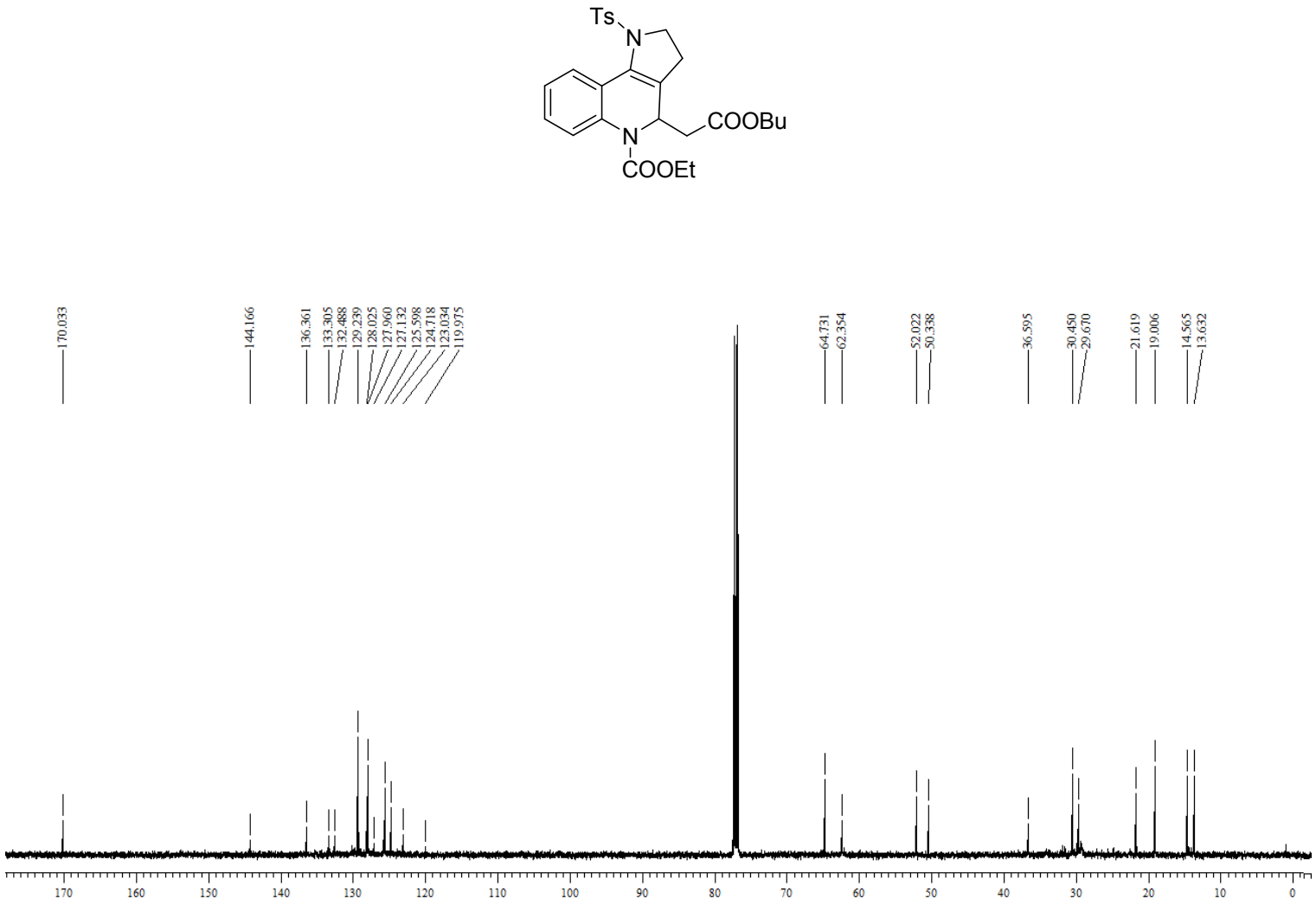




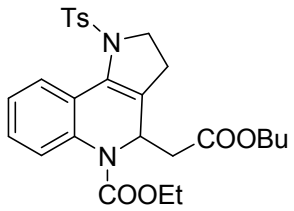
^{1}H NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4c)**

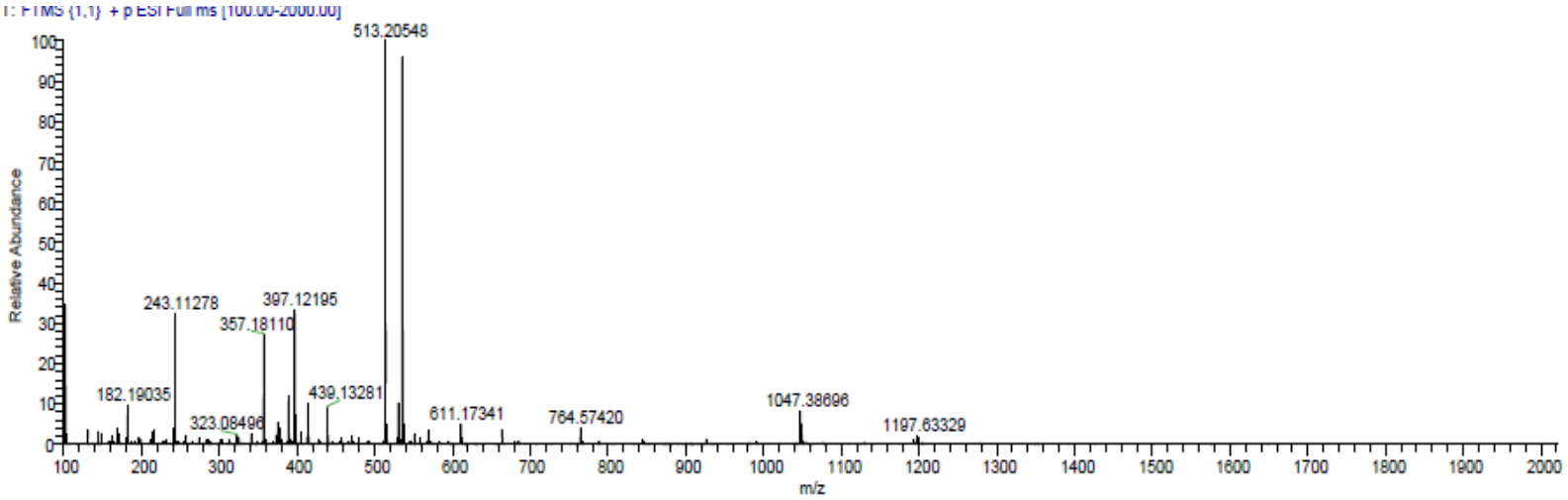


^{13}C NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4c)**

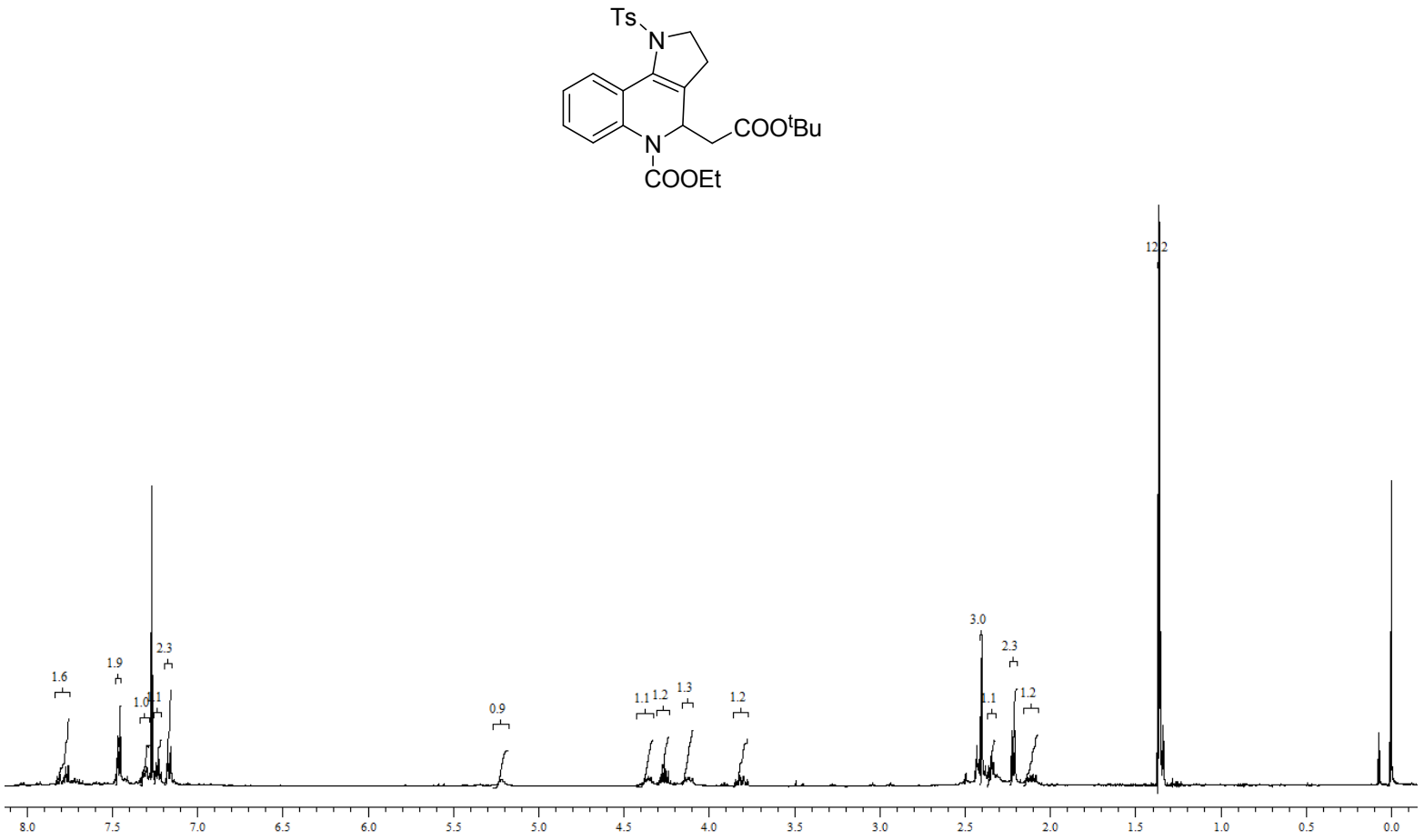


HRMS of **Ethyl 4-(2-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4c)**

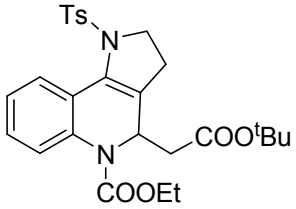


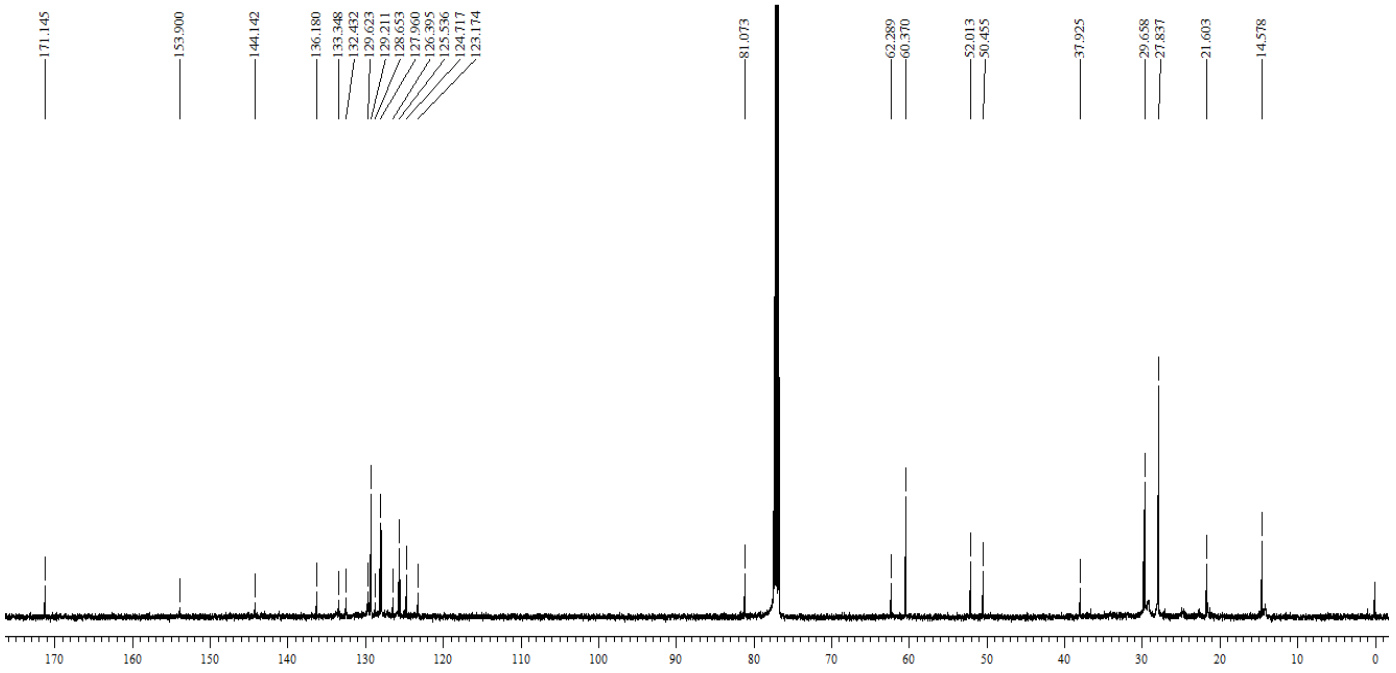


^{1}H NMR of **Ethyl 4-(2-*tert*-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4d)**

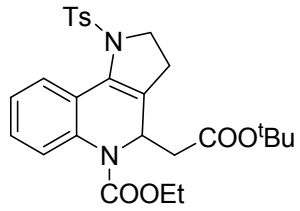


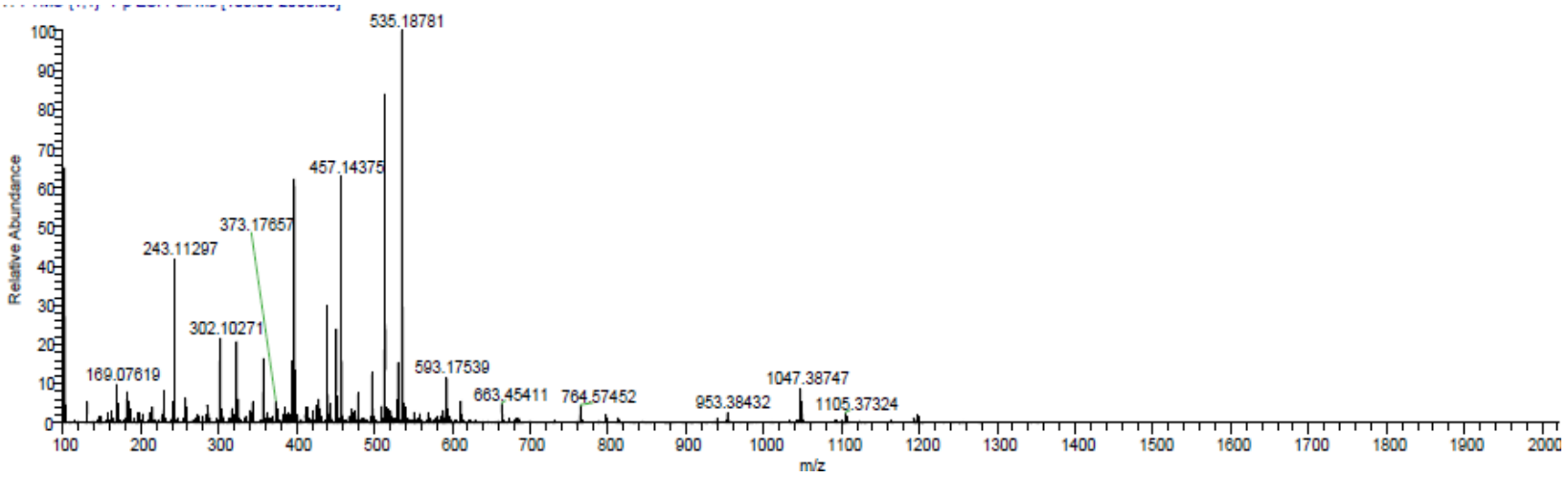
^{13}C NMR of **Ethyl 4-(2-*tert*-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4d)**



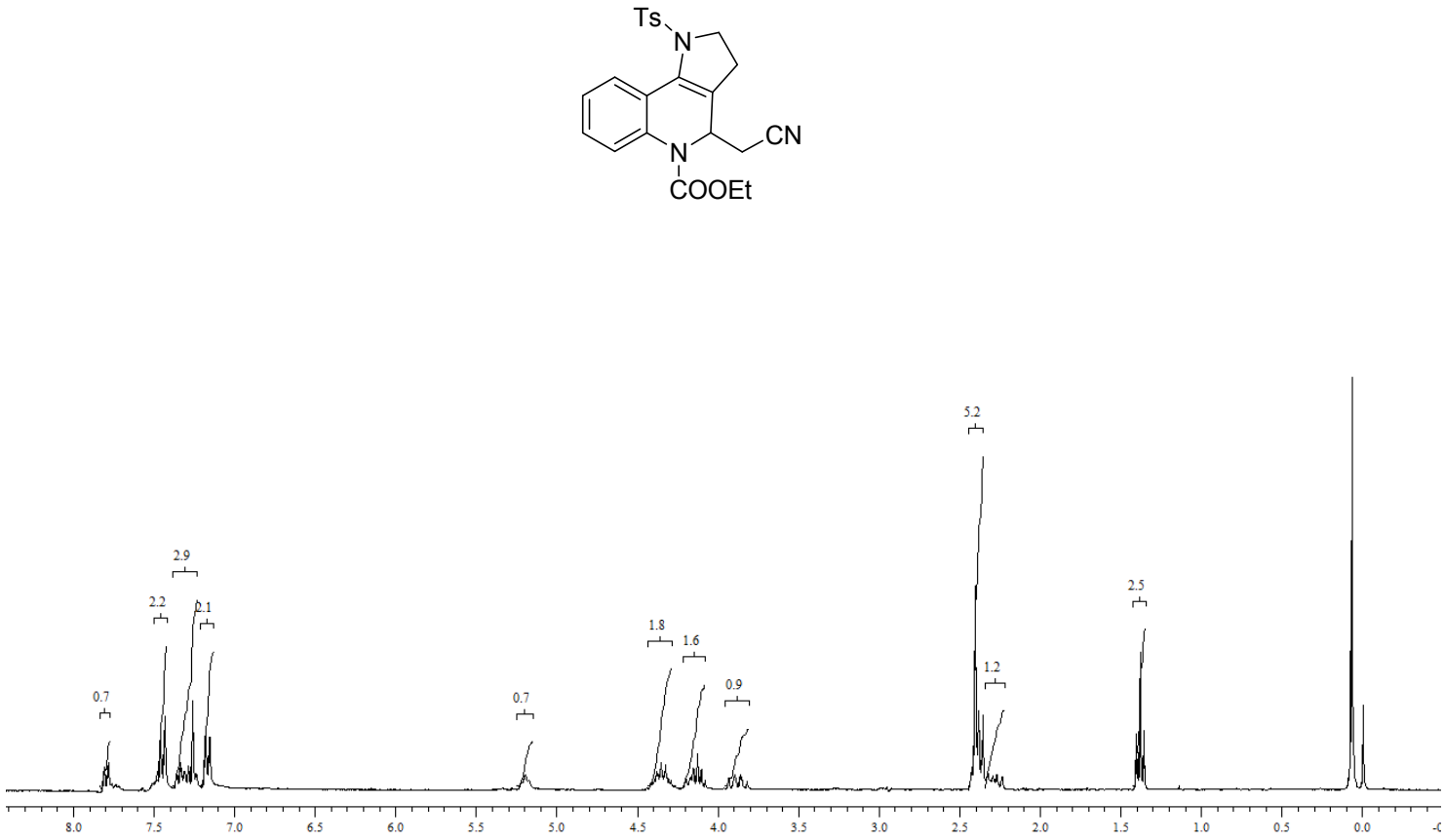


HRMS of **Ethyl 4-(2-*tert*-butoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4d)**

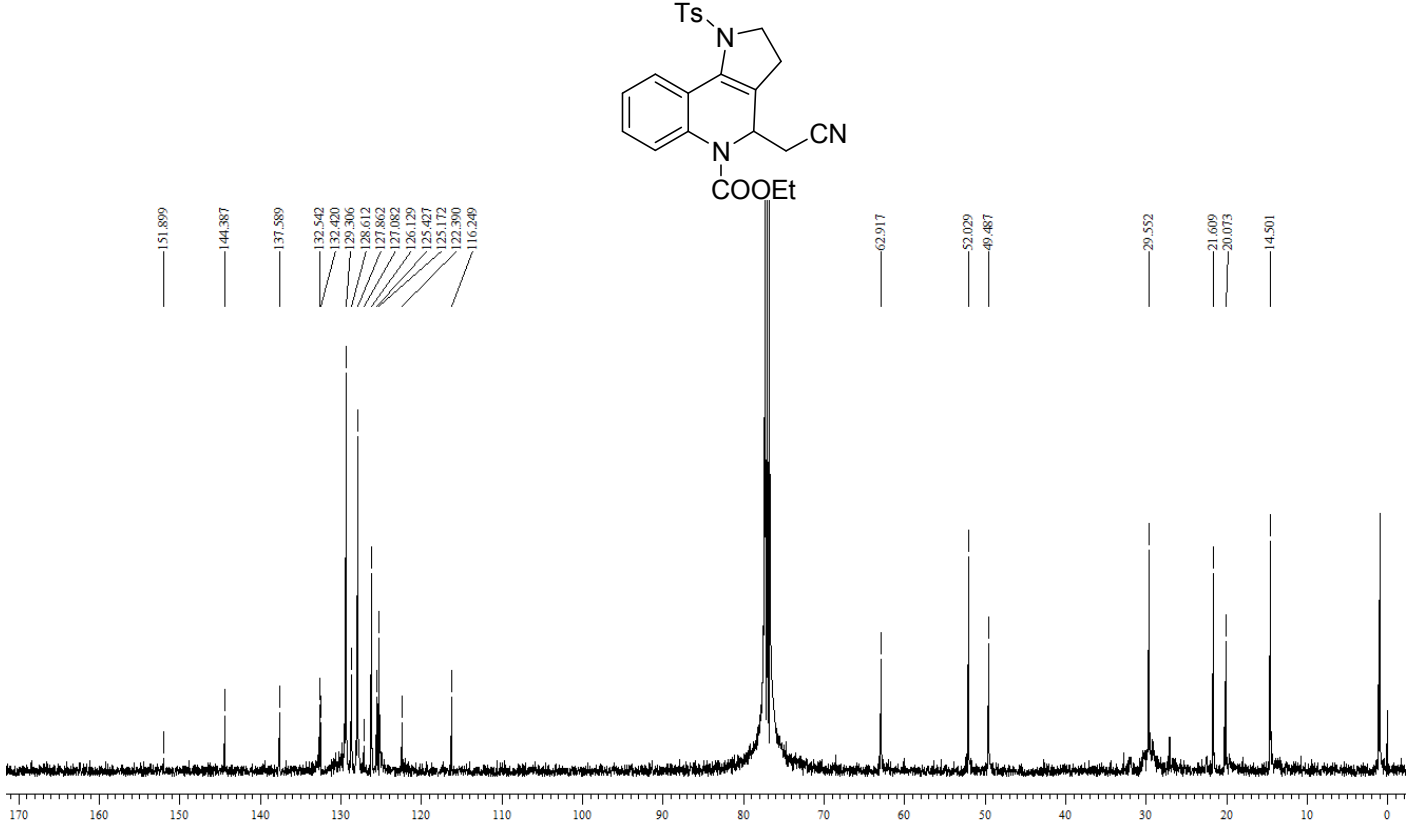




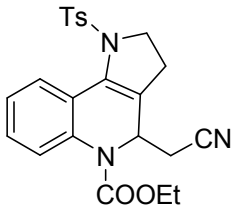
^{1}H NMR of **Ethyl 4-(cyanomethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4e)**

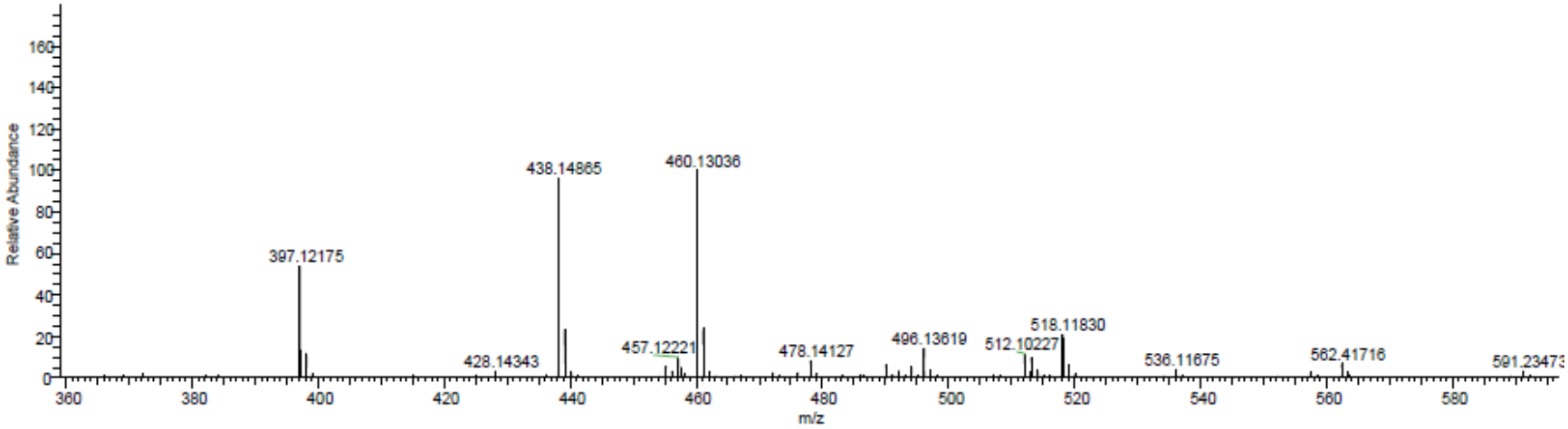


^{13}C NMR of **Ethyl 4-(cyanomethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4e)**

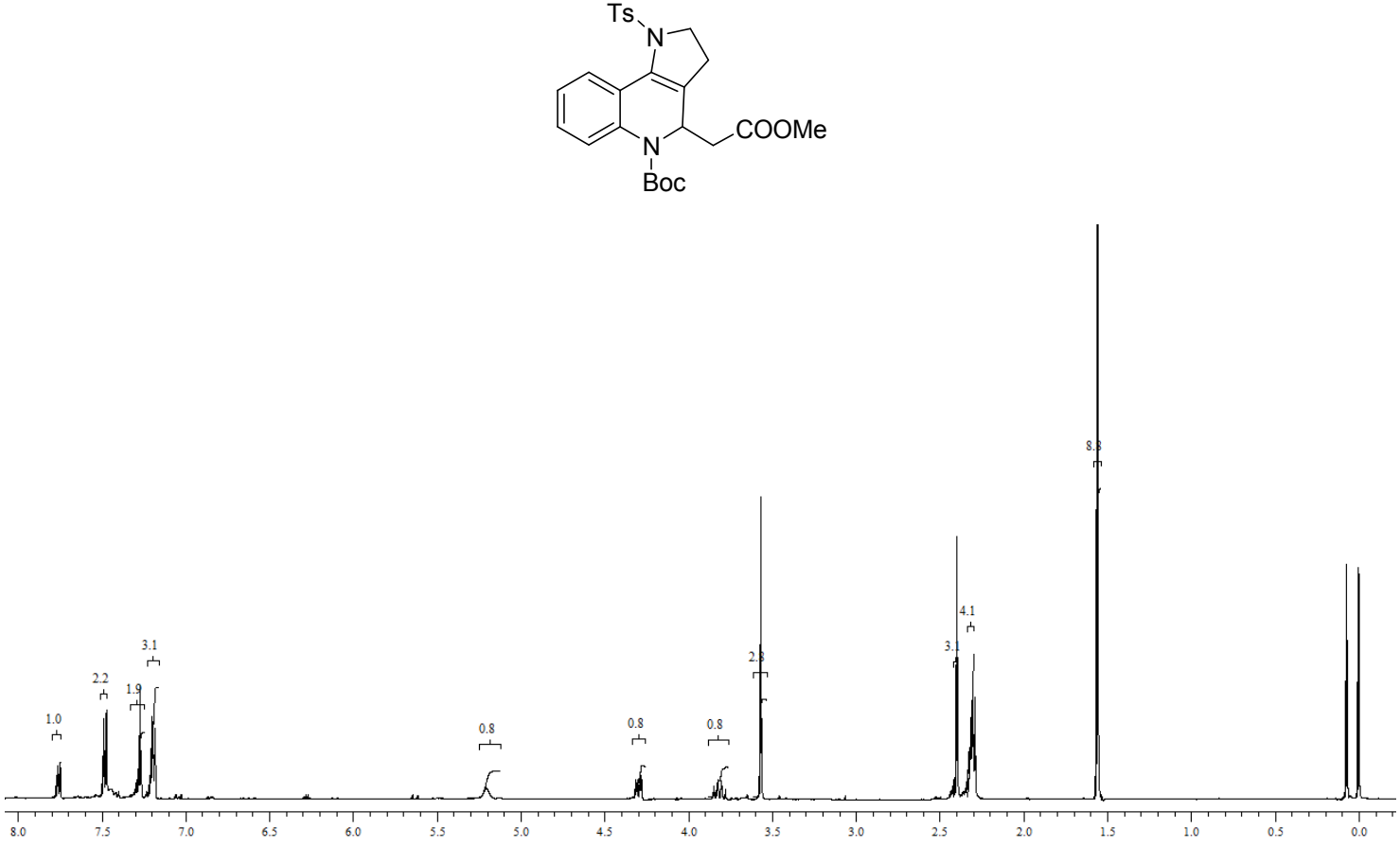


HRMS of **Ethyl 4-(cyanomethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4e)**

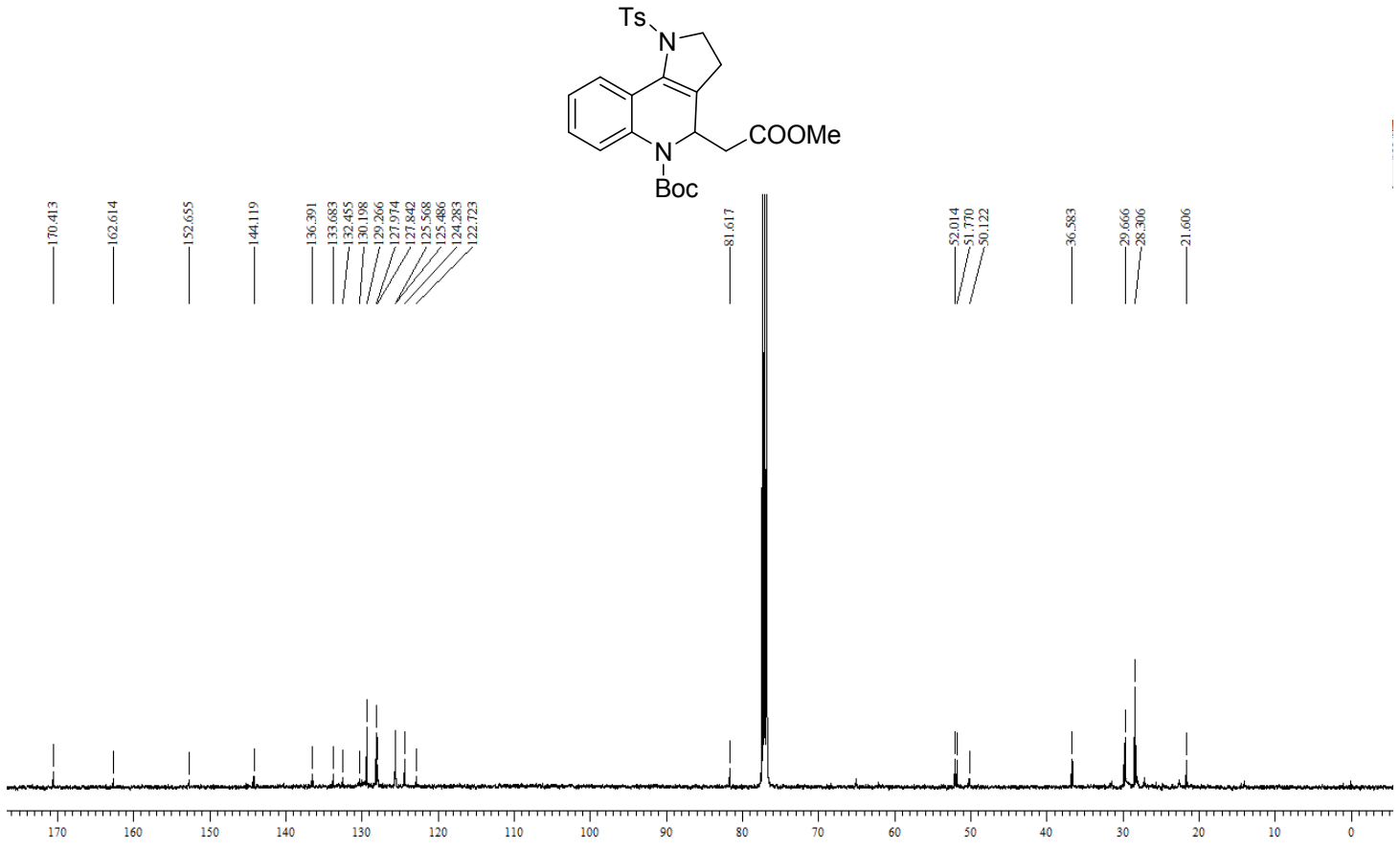




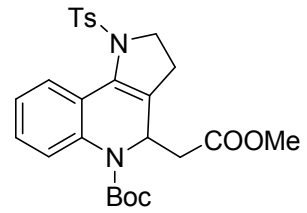
^{1}H NMR of ***tert*-Butyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4f)**

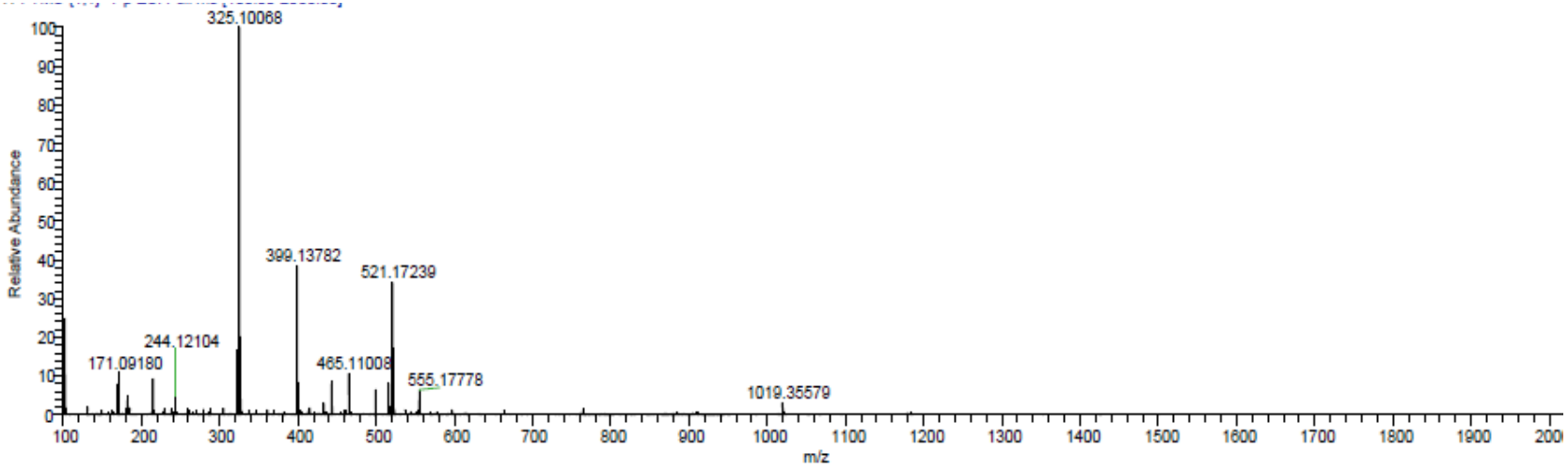


^{13}C NMR of ***tert*-Butyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4f)**

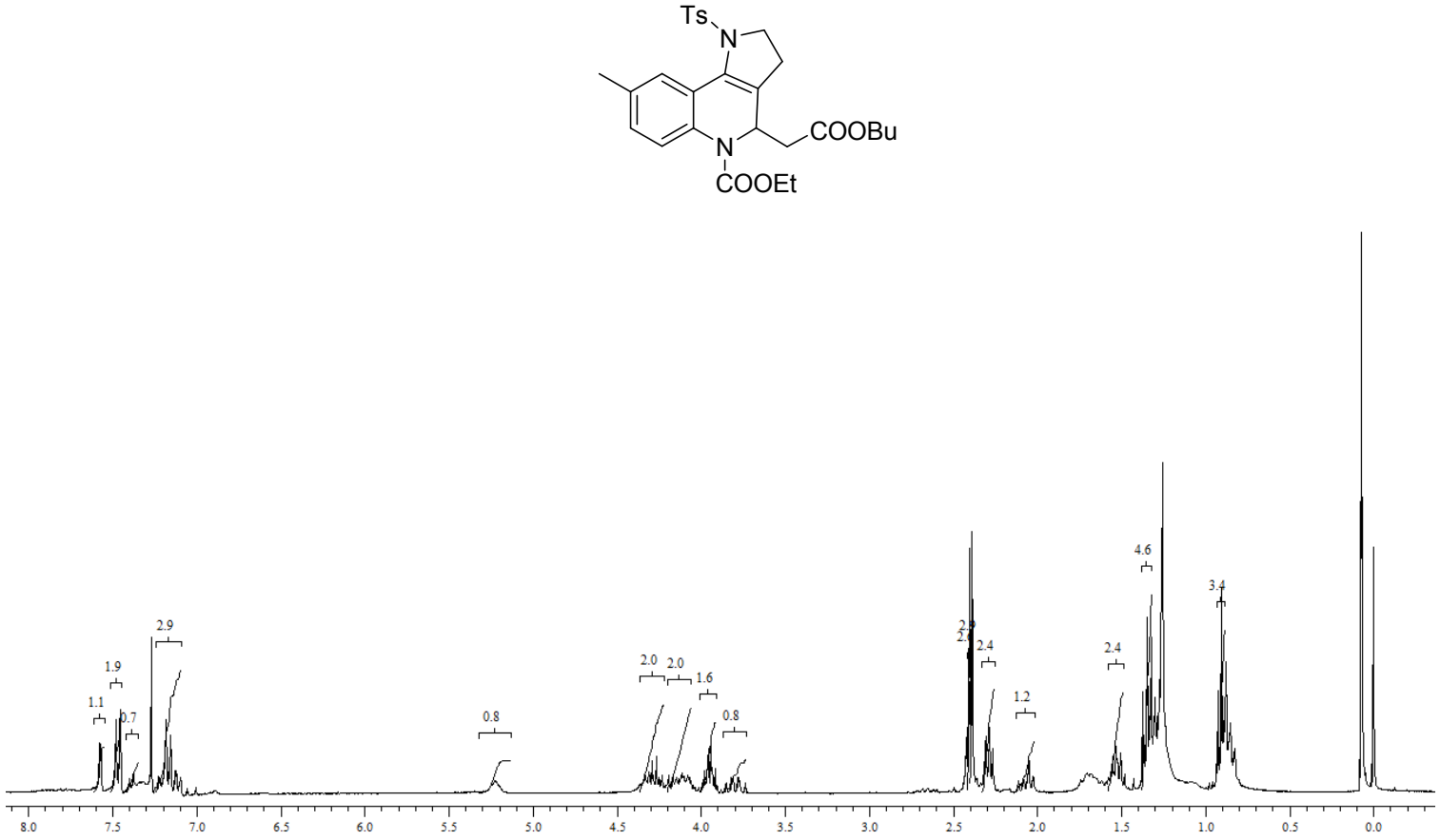


HRMS of ***tert*-butyl 4-(2-methoxy-2-oxoethyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4f)**

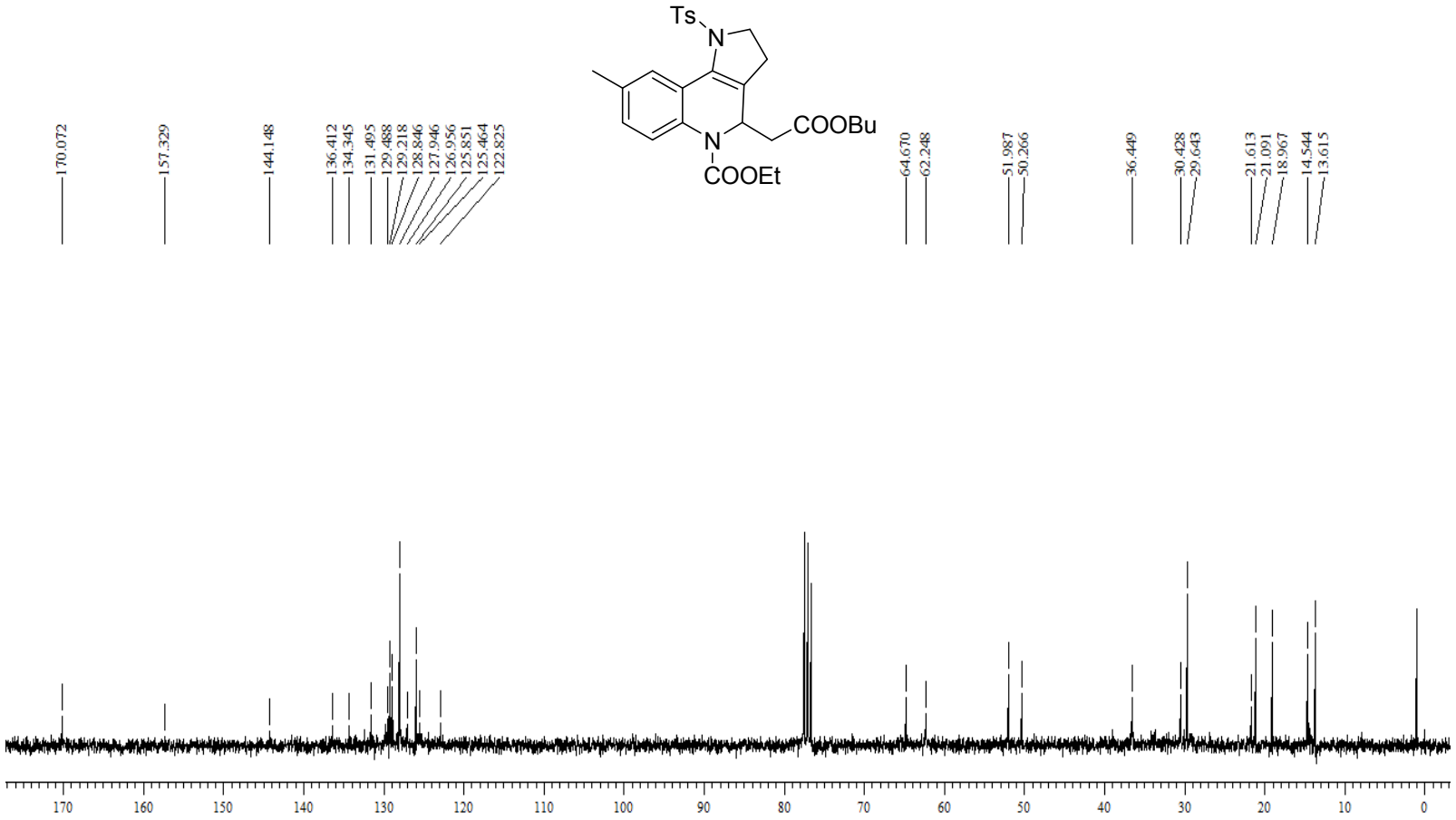




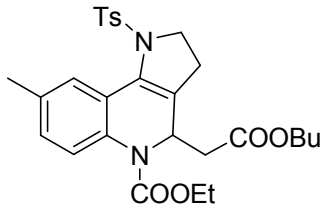
^{1}H NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-8-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4g)**

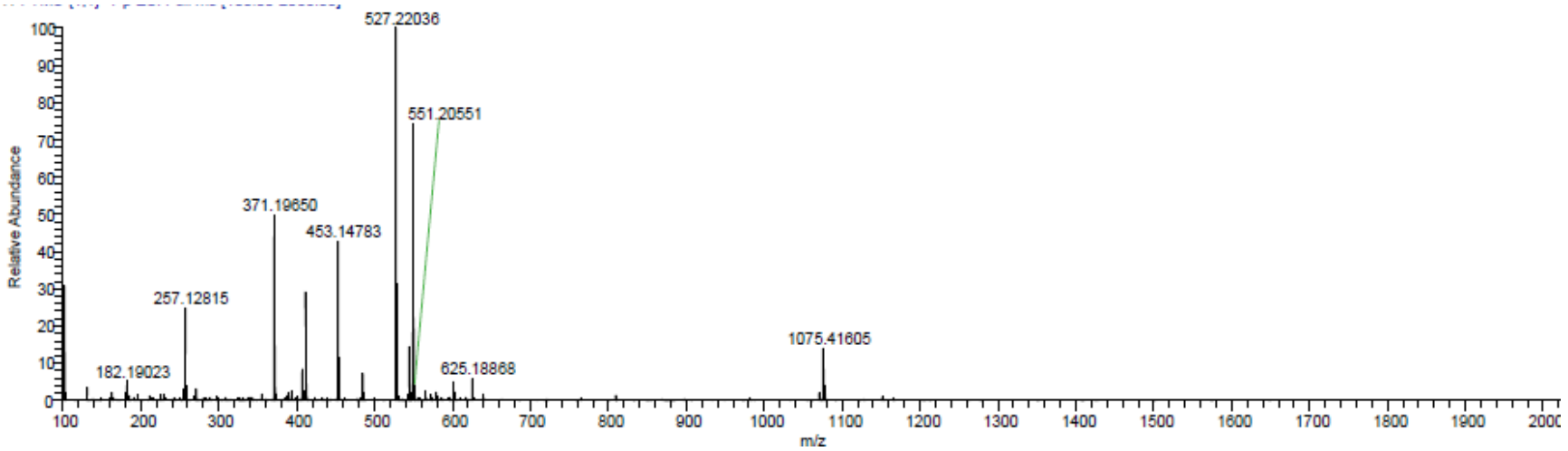


^{13}C NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-8-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4g)**

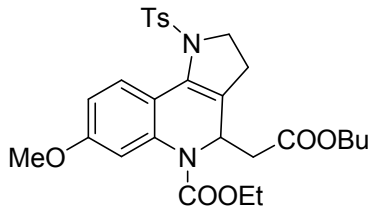


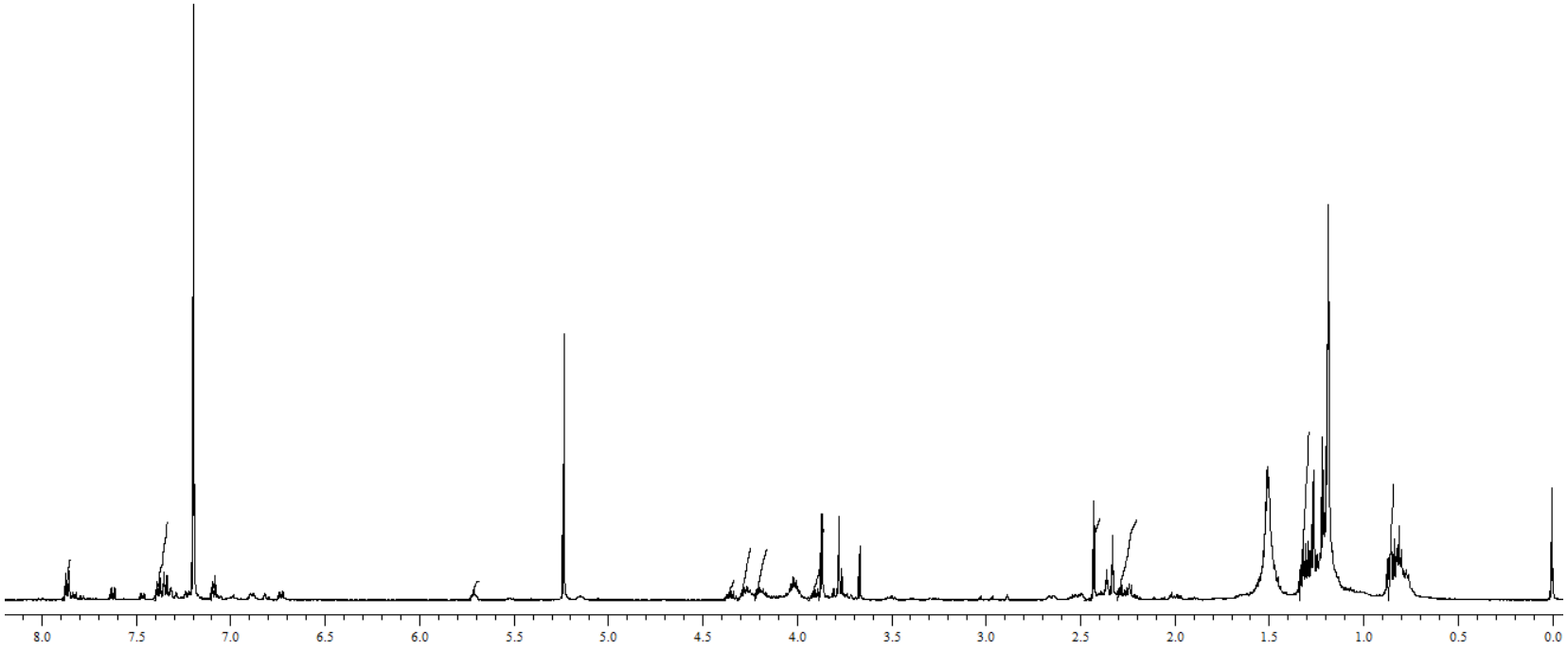
HRMS of **Ethyl 4-(2-butoxy-2-oxoethyl)-8-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4H)-carboxylate (4g)**



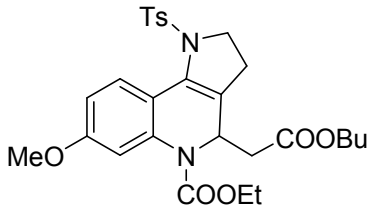


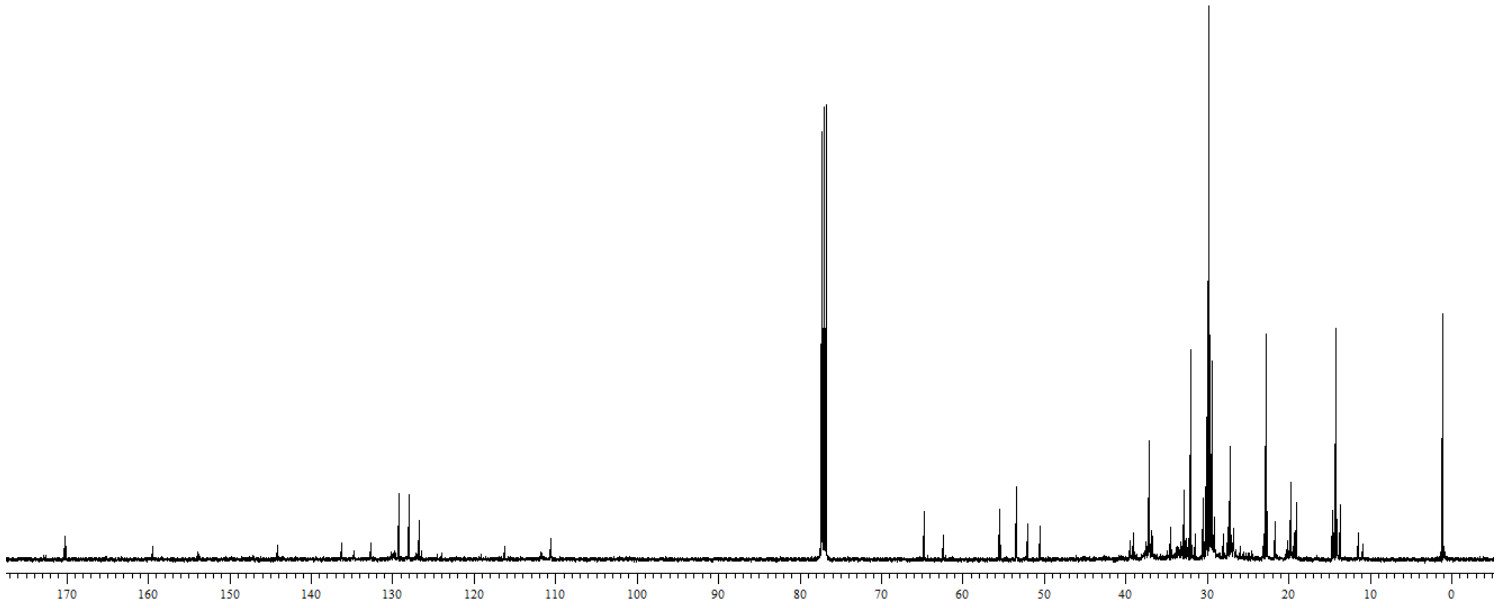
^{1}H NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-7-methoxy-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4h)**





^{13}C NMR of **Ethyl 4-(2-butoxy-2-oxoethyl)-7-methoxy-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4h)**





HRMS of **Ethyl 4-(2-butoxy-2-oxoethyl)-7-methoxy-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*c*]quinoline-5(4*H*)-carboxylate (4h)**