Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An Improved Transition-Metal-Free Synthesis of Aryl Alkynyl Sulfides *via* Substitution of a Halide at an *sp*-centre.

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Supplementary Information

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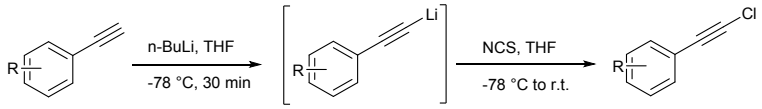
Experimental

General Experimental Methods

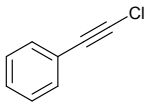
All reactions were carried out at atmospheric pressure, under argon, unless otherwise stated. Normal phase silica gel (BDH) was used for flash chromatography. Reactions were monitored by thin-layer chromatography (TLC) using plates precoated with silica gel 60 F254 on aluminum visualized by UV (254 nm) and chemical stain (potassium permanganate). Mass spectra were measured in EI and CI mode. Electron-spray ionization spectra were measured on a LC-TOF mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 or 600 MHz and 125 or 150 MHz, respectively, at ambient temperature. All chemical shifts were referenced to the residual proton impurity of the deuterated solvent. Coupling constants, *J*, are quoted in hertz to one decimal place. Infrared spectra were obtained on a FTIR Spectrometer operating in ATR mode. Melting points are uncorrected.

General procedure for the synthesis of chloroalkynes 1a-l



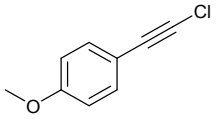
A flame-dried flask was charged with a stirring bar and the starting material acetylene (1.00 mmol, 1.0 equiv.), followed by anhydrous THF (2 mL) under argon and cooled to -78 °C. The solution was treated with *n*-butyllithium (1.6 M solution in hexanes, 0.75 mL, 1.20 mmol, 1.2 equiv.) over 5 min at -78 °C under argon. The resulting suspension was stirred at -78 °C for 30 min then a solution of recrystallised *N*-chlorosuccinimide (0.147 g, 1.10 mmol, 1.1 equiv.) in anhydrous THF (5 mL) was added in one portion. The reaction was allowed to warm to r.t. after 20 min and left to stir under an atmosphere of argon. Then the reaction mixture was quenched with saturated NH_4Cl (15 mL), diluted with Et_2O (30 mL) and washed with brine (20 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL) and the organic layers were combined, dried over Na_2SO_4 or $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography gave desired chloroalkyne product which was stored in the freezer.

(1a) (Chloroethynyl)benzene



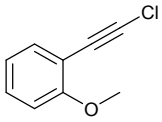
Column chromatography using PE gave colourless oil: 109 mg, 80%; IR ν_{max} (film)/cm^{-1} 3079, 2223, 1487, 751, 668; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.47−7.45 (m, 2 H), 7.35−7.32 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 132.0, 128.6, 128.4, 122.2, 69.4, 68.1; LRMS (EI) *m/z* (%) 138 (M^+, ^{37}Cl, 33%), 136 (M^+, ^{35}Cl, 100%), 101 (M^+, PhC≡C, 55%). HRMS (EI) calcd for C_7H_5Cl (M^+) 136.0074, found 136.0082. Data in agreement with literature.[1,2,3]

(1b) 1-(chloroethynyl)-4-methoxybenzene



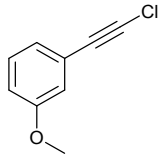
Column chromatography using 10% Et_2O/PE gave colourless oil, 90 mg, 54%; IR ν_{max} (film)/cm^{-1} 3082, 2225, 1604, 1506, 1290, 1245, 1171, 1031, 888, 828, 590, 529; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.39−7.37 (d, J = 10.3 Hz, 2 H), 6.84−6.82 (d, J = 10.3 Hz, 2 H), 3.80 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.8, 133.4, 114.2, 114.0, 69.3, 66.4, 55.3; LRMS (EI) *m/z* (%) 168 (M^+, ^{37}Cl, 33%), 166 (M^+, ^{35}Cl, 100%), 150 (45), 123 (65); HRMS (EI) calcd for C_9H_7ClO (M^+) 166.01854, found 166.018263. Data in agreement with literature.[2]

(1c) 1-(chloroethynyl)-2-methoxybenzene



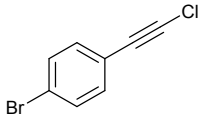
Column chromatography using 10% Et_2O/PE gave colourless oil, 79 mg, 47%; IR ν_{max} (film)/cm^{-1} 3067, 2227, 1595, 1490, 1461, 1432, 1258, 1116, 1023, 890, 748; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.42-7.40 (dd, J = 7.6, 1.7 Hz, 2 H), 7.32-7.29 (td, J = 8.3, 1.4 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 3.89 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 160.7, 134.1, 130.1, 120.6, 111.4, 110.7, 71.6, 66.0, 55.9; LRMS (EI) *m/z* (%) 168 (M^+, ^{37}Cl, 33%), 166 (M^+, ^{35}Cl, 100%), 131 (75), 123 (85); HRMS (EI) calcd for C_9H_7ClO (M^+) 166.01854, found 166.018331. Data in agreement with literature.[2]

(1d) 1-(chloroethynyl)-3-methoxybenzene



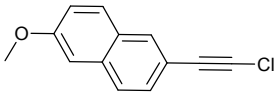
Column chromatography using 10% Et_2O/PE gave colourless oil, 97 mg, 58%; IR ν_{max} (film)/cm^{-1} 3081, 2223, 1573, 1487, 1419, 1284, 1159, 1039, 853, 785, 683; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.24-7.22 (t, J = 9.7 Hz, 1 H), 7.07-7.05 (dt, J = 9.1, 1.5 Hz, 1 H), 6.99 (s, 1 H), 6.92-6.89 (dd, J = 10.0, 3.2 Hz, 1 H), 3.80 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.4, 129.5, 124.6, 123.2, 116.9, 115.3, 69.4, 68.0, 55.3; LRMS (EI) *m/z* (%) 168 (M^+, ^{37}Cl, 15%), 166 (M^+, ^{35}Cl, 45%), 136 (40), 123 (100); HRMS (EI) calcd for C_9H_7ClO (M^+) 166.01854, found 166.018910.

(1e) 1-bromo-4-(chloroethynyl)benzene



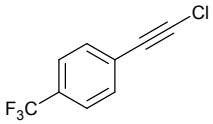
Column chromatography using PE gave white solid, 47 mg, 22%; IR ν_{max} (film)/cm^{-1} 2217, 1897,1581, 1481, 391, 1087, 1066, 1009, 828, 814, 511; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.45 (d, J = 8.5 Hz, 2 H), 7.30 (d, J = 8.5 Hz, 2 H; ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 133.5, 131.8, 123.0, 121.2, 69.5, 68.5; LRMS (EI) *m/z* (%) 217 (20), 215 (100), 213 (75), 134 (65); HRMS (EI) calcd for C_8H_4ClBr (M^+) 213.91849, found 213.918210. Data in agreement with literature.[2]

(1f) 2-(chloroethynyl)-6-methoxynaphthalene



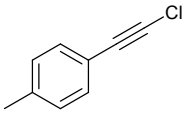
Column chromatography using 10% Et_2O/PE gave pale yellow oil, 156 mg, 72%; IR ν_{max} (film)/cm^{-1} 2956, 2224, 1620, 1597, 1479, 1268, 1163, 1029, 851, 737; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.89 (s, 1 H), 7.69-7.65 (m, 2 H), 7.45-7.43 (dd, J = 10.1, 1.9 Hz, 1 H), 7.17-7.14 (dd, J = 10.7, 3.1 Hz, 1 H), 7.09 (d, J = 2.9 Hz, 1 H), 3.92 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 158.5, 134.3, 132.0, 129.3, 129.1, 128.4, 126.9, 119.6, 117.1, 105.9, 69.9, 67.5, 55.4; LRMS (EI) *m/z* (%) 218 (M^+, ^{37}Cl, 33%), 216 (M^+, ^{35}Cl, 100%), 175 (33), 173 (100); HRMS (EI) calcd for $C_{13}H_9ClO$ (M^+) 216.03419, found 216.034287.

(1g) 1-(chloroethynyl)-4-(trifluoromethyl)benzene



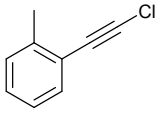
Column chromatography using 10% Et_2O/PE gave colourless oil, 90 mg, 44%; IR ν_{max} (film)/cm^{-1} 2224, 1617, 1320, 1127, 1065, 840, 732; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.60-7.54 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 132.4, 130.6 and 130.4 (q, J = 33.0 Hz), 126.1, 125.4 (q, J = 3.7 Hz), 124.8 and 123.0 (q, J = 272.1 Hz), 71.0, 68.3; LRMS (EI) *m/z* (%) 206 (M^+, ^{37}Cl, 33%), 204 (M^+, ^{35}Cl, 100%), 185 (20), 169 (35), 154 (20). HRMS (EI) calcd for $C_9H_4ClF_3$ (M^+) 203.99536, found 203.99520. Data in agreement with literature.[4]

(1h) 1-(chloroethynyl)-4-methylbenzene



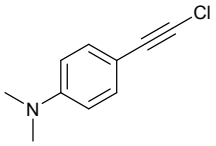
Column chromatography using PE gave colourless oil, 95 mg, 63%; IR ν_{max} (film)/cm^{-1} 3030, 2975, 2921, 2863, 2216, 1507, 1117, 887, 812, 519; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.35-7.33 (d, J = 7.6 Hz, 2 H), 7.13-7.11 (d, J = 7.6 Hz, 2 H), 2.35 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 138.9, 132.0, 129.2, 119.1, 69.6, 67.3, 21.6; LRMS (EI) *m/z* (%) 152 (M^+, ^{37}Cl, 8%), 150 (M^+, ^{35}Cl, 24%), 115 (28), 32 (30), 28 (100). HRMS (EI) calcd for C_9H_7Cl (M^+) 150.0231, found 150.0231. Data in agreement with literature.[2]

(1i) 1-(chloroethynyl)-2-methylbenzene



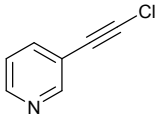
Column chromatography using PE gave a colourless oil, 84 mg, 56%; IR ν_{max} (film)/cm^{-1} 3065, 3023, 2950, 2921, 2216, 1483, 1454, 1111, 1042, 890, 753, 713, 651, 449; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.44-7.42 (d, J = 7.9 Hz, 1 H), 7.27-7.24 (t, J = 7.5 Hz, 1 H), 7.21 (d, J= 7.2 Hz, 1 H), 7.16-7.13 (t, J = 7.7Hz, 1H), 2.45 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 140.9, 132.4, 129.6, 128.6, 125.7, 122.0, 71.4, 68.5, 20.7; LRMS (EI) *m/z* (%) 152 (M^+, ^{37}Cl, 17%), 150 (M^+, ^{35}Cl, 51%), 115 (100), 28 (64). HRMS (EI) calcd for C_9H_7Cl (M^+) 150.0231, found 150.0231.

(1j) 4-(chloroethynyl)-*N*,*N*-dimethylaniline



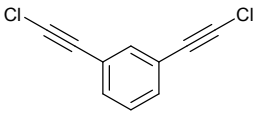
Column chromatography using 5% Et_2O/PE gave an orange oil, 100 mg, 56%; IR ν_{max} (film)/cm^{-1} 3280, 2890, 2857, 2806, 2092, 1602, 1515, 1441, 1356, 1224, 1184, 1121, 1062, 943, 812, 741, 572, 524; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.33-7.31 (d, J = 8.8 Hz, 2 H), 6.62-6.60 (d, J = 8.8 Hz, 2 H), 2.98 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 150.3, 133.1, 111.8, 108.8, 70.4, 65.2, 40.3; LRMS (EI) *m/z* (%) 181 (M^+, ^{37}Cl, 33%), 179 (M^+, ^{35}Cl, 100%), 162 (15), 110 (18), 96 (30). HRMS (EI) calcd for $C_{10}H_{10}ClN$ (M^+) 179.0496, found 179.0494. Data in agreement with literature.[2]

(1k) 3-(chloroethynyl)pyridine



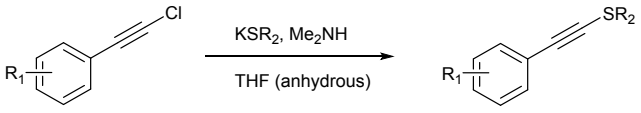
Column chromatography using 40% Et_2O/PE gave a colourless oil, 70 mg, 51%; IR ν_{max} (film)/cm^{-1} 3031, 2960, 2223, 1722, 1583, 1561, 1475, 1407, 1186, 1021, 890, 802, 753, 702, 620, 496; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.87 (d, J = 1.2 Hz, 1 H), 8.55-8.54 (dd, J = 1.9, 4.9 Hz, 1 H), 7.73-7.71 (dt, J = 1.9, 7.9 Hz, 1 H), 7.26-7.23 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 152.7, 148.9, 139.1, 123.1, 119.5, 71.8, 66.3; LRMS (EI) *m/z* (%) 139 (M^+, ^{37}Cl, 16%), 137 (M^+, ^{35}Cl, 48%), 32 (28), 28 (100). HRMS (EI) calcd for C_7H_4ClN (M^+) 137.0027, found 137.0026. Data in agreement with literature.[5]

(1l) 1,3-bis(chloroethynyl)benzene



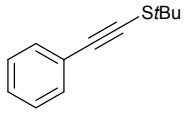
Variation from general procedure: 2.4 eq. of *n*-butyllithium and 2.2 eq. of *N*-chlorosuccinimide used. Column chromatography using PE gave a white solid, 132 mg, 68%; IR ν_{max} (film)/cm^{-1} 2987, 2901, 2213, 1594, 1572, 1472, 1259, 1054, 891, 857, 781, 678, 463; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.52-7.51 (t, J = 1.5 Hz, 1 H), 7.41-7.39 (dd, J = 7.9, 1.5 Hz, 2 H), 7.27-7.24 (t, J = 7.9 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 135.4, 132.1, 128.6, 122.6, 69.1, 68.4; LRMS (EI) *m/z* (%) 198 (M^+, ^{37}Cl+^{37}Cl, 11%), 196 (M^+, ^{35}Cl+^{37}Cl, 65%), 194 (M^+, ^{35}Cl+^{35}Cl, 100%), 159 (9). HRMS (EI) calcd for $C_{10}H_4Cl_2$ (M^+) 193.9685, found 193.9685.

General procedure for the synthesis of acetylenic sulfides 2a-p



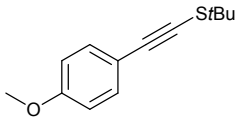
A flame-dried flask was charged with a stirring bar and 2-methylpropane-2-thiol (0.132 g, 1.46 mmol, 4.0 equiv.) (or the corresponding thiol for **2m-2p**), followed by anhydrous THF (2 mL) under argon and heated to 50 °C. Potassium hydride (59 mg, 1.46 mmol, 4.0 equiv., supplied as a 30% weight dispersion in mineral oil which was rinsed with PE and dried between filter paper immediately prior to use) was then added as a single portion and the mixture was stirred at 50 °C for 15 min. The mixture was allowed to cool, first to r.t. and then to -40 °C. Dimethylamine solution (2.0 M in THF, 0.37 mL, 0.73 mmol, 2.0 equiv.) was added *via* syringe, followed immediately after by alkynyl chloride **1a-l** (0.37 mmol, 1.0 equiv.) in anhydrous THF (1 mL). After 10 min, the solution was allowed to warm to r.t. and left to stir under an atmosphere of argon. The reaction mixture was then carefully quenched with water (20 mL), diluted with Et_2O (30 mL) and washed with brine (20 mL). The aqueous layer was extracted with Et_2O (30 mL) and the organic portions were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography to yield desired thioynol ether.

(2a) *Tert*-butyl(phenylethynyl)sulfane



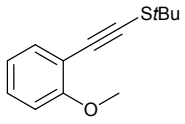
Column chromatography using PE gave a colourless oil: 54 mg, 77%; IR ν_{max} (film)/cm^{-1} 2961, 2921, 2895, 2162, 1595, 1489, 1454, 1364, 1161, 752, 689; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.45−7.43 (d, 2 H), 7.33−7.29 (m, 3 H), 1.49 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 131.4, 128.4, 128.0, 123.9, 96.2, 79.1, 48.6, 30.5; LRMS (CI) *m/z* (%) (M+H$^+$) 191 (50), 190 (60), 135 (PhC≡CSH, 100). HRMS (EI) calcd for $C_{12}H_{14}S$ (M$^+$) 190.0811, found 190.0780. Data in agreement with literature.[6]

(2b) *Tert*-butyl((4-methoxyphenyl)ethynyl)sulfane



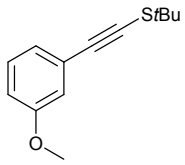
Column chromatography using PE gave an orange oil: 55 mg, 68%; IR ν_{max} (film)/cm^{-1} 2961, 2837, 1603, 1505, 1456, 1289, 1245, 1170, 829, 531; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.40-7.38 (d, *J* = 8.8 Hz, 2 H), 6.84-6.82 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 1.47 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.5, 133.3, 115.9, 113.7, 95.9, 55.4, 48.4, 31.7, 30.4; LRMS (EI) *m/z* (%) 220 (15), 164 (100), 149 (40); HRMS (EI) calcd for $C_{13}H_{16}SO$ (M$^+$) 220.09219, found 220.092557. Data in agreement with literature.[6]

(2c) *Tert*-butyl((2-methoxyphenyl)ethynyl)sulfane



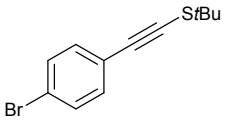
Column chromatography using 5% Et_2O/PE gave a pale yellow oil: 61 mg, 76%; IR ν_{max} (film)/cm^{-1} 2961, 2921, 2896, 2864, 2166, 1593, 1575, 1489, 1455, 1365, 1256, 1161, 1113, 1024, 749; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.39-7.37 (dd, J = 7.6, 1.7 Hz, 1 H), 7.27-7.24 (m, 1 H), 6.90-6.88(t, J = 7.5 Hz, 1 H), 6.87-6.85 (d, J = 8.2 Hz, 1 H), 3.87 (s, 3 H), 1.50 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.9, 132.9, 129.2, 120.4, 113.2, 110.6, 92.4, 83.1, 55.8, 48.7, 30.4; LRMS (EI) *m/z* (%) 220 (25), 164 (100), 149 (45), 131 (35); HRMS (EI) calcd for $C_{13}H_{16}SO$ (M^+) 220.09219, found 220.092011. Data in agreement with literature.[6]

(2d) *Tert*-butyl((3-methoxyphenyl)ethynyl)sulfane



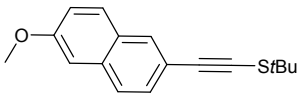
Column chromatography using PE gave a colourless oil: 77 mg, 96%; IR ν_{max} (film)/cm^{-1} 2960, 2159, 1573, 1456, 1365, 1315, 1283, 1195, 1040; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.22-7.20 (t, J = 7.9 Hz, 1 H), 7.04 (d, J = 7.5 Hz, 1 H), 6.96 (s, 1 H), 6.86-6.84 (dd, J – 8.3, 2.6 Hz, 1 H), 3.80 (s, 3 H), 1.49 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 159.3, 129.4, 124.8, 123.9, 116.1, 114.5, 96.1, 79.0, 55.3, 48.6, 30.4; LRMS (EI) *m/z* (%) 220 (10), 198 (10), 164 (100), 119 (18); HRMS (EI) calcd for $C_{13}H_{16}SO$ (M^+) 220.09219, found 220.092341. Data in agreement with literature.[6]

(2e) ((4-bromophenyl)ethynyl)(*tert*-butyl)sulfane



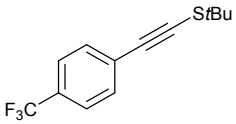
Column chromatography using PE gave a colourless oil: 75 mg, 76%; IR ν_{max} (film)/cm^{-1} 2962, 2922, 2861, 2163, 1584, 1482, 1456, 1393, 1365, 1240, 1162, 1069; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.44-7.42 (d, J = 8.5 Hz, 2 H), 7.29-7.27 (d, J = 8.5 Hz, 2 H), 1.48 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 132.7, 131.6, 122.8, 122.0, 95.2, 80.6, 48.7, 30.5; LRMS (EI) *m/z* (%) 268 (8), 214 (60), 85 (62), 83 (100); HRMS HRMS (EI) calcd for $C_{12}H_{13}BrS$ (M^+) 267.99213, found 267.992874. Data in agreement with literature.[6]

(2f) *Tert*-butyl((6-methoxynaphthalen-2-yl)ethynyl)sulfane



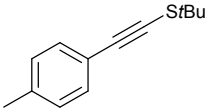
Column chromatography using PE gave a white solid: 92 mg, 94%; IR ν_{max} (film)/cm^{-1} 2960, 2156, 1627, 1599, 1480, 1338, 1364, 1267, 1234, 1195, 1160, 1119, 1030, 851, 804, 472; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.88 (s, 1 H), 7.69-7.65 (m, 2 H), 7.47-7.45 (dd, J = 8.4, 1.6 Hz, 1 H), 7.16-7.14 (dd, J = 9.0, 2.5 Hz, 1 H), 7.10 (d, J = 2.5 Hz, 1 H), 3.92 (s, 3 H), 1.49 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 158.3, 134.0, 131.1, 129.3, 129.1, 128.5, 126.8, 119.5, 118.7, 105.9, 96.7, 78.4, 55.4, 48.6, 30.5; LRMS (EI) *m/z* (%) 270 (30), 214 (100), 199 (22), 171 (20); HRMS (EI) calcd for $C_{17}H_{18}SO$ (M^+) 270.10784, found 270.107337.

(2g) *Tert*-butyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane



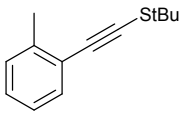
Column chromatography using PE gave a pale yellow oil: 72 mg, 76%; IR ν_{max} (film)/cm^{-1} 2964, 2926, 2860, 2161, 1613, 1366, 1320, 1161, 1122, 1064, 1016, 838; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.56-7.54 (d, J = 8.2 Hz, 2 H), 7.51-7.49 (d, J = 8.2 Hz, 2 H), 1.49 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 131.2, 129.5 and 129.3 (q, J = 32.8 Hz), 127.6, 125.3 (q, 3.5 Hz), 125.0 and 123.1 (q, J = 272.0 Hz), 95.2, 82.8, 49.0, 30.5; LRMS (EI) *m/z* (%) 258 (5), 236 (100), 202 (20), 57 (52); HRMS (EI) calcd for $C_{13}H_{13}F_3S$ (M^+) 258.0685, found 258.0675. Data in agreement with literature.[6]

(2h) *Tert*-butyl((4-tolylethynyl)sulfane



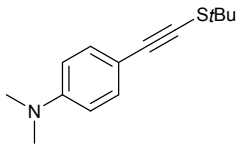
Column chromatography using PE gave a colourless oil: 70 mg, 93%; IR ν_{max} (film)/cm^{-1} 2962, 2921, 2895, 2862, 2163, 1507, 1454, 1364, 1161, 813, 757, 530; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.34-7.32 (d, J = 8.1 Hz, 2 H), 7.12-7.10 (d, J = 8.1 Hz, 2 H), 2.34 (s, 3 H), 1.47 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 138.2, 131.5, 129.1, 120.7, 96.2, 78.0, 48.5, 30.5, 21.6; LRMS (EI) *m/z* (%) 204 (20), 182 (28), 148 (100); HRMS (EI) calcd for $C_{13}H_{16}S$ (M^+) 204.0967, found 204.0962. Data in agreement with literature.[6]

(2i) *Tert*-butyl((2-tolylethynyl)sulfane



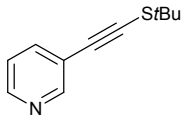
Column chromatography using PE gave a colourless oil: 69 mg, 92%; IR ν_{max} (film)/cm^{-1} 2962, 2922, 2897, 2861, 2158, 1482, 1455, 1364, 1161, 907, 753, 732; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.41-7.39 (d, J = 7.5 Hz, 1 H), 7.21-7.18 (m, 2 H), 7.15-7.11 (m, 1 H), 2.45 (s, 3 H), 1.50 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 139.9, 131.7, 129.5, 128.0, 125.8, 123.8, 95.2, 82.7, 48.4, 30.5, 21.1; LRMS (EI) *m/z* (%) 204 (70), 148 (100), 115 (29), 57 (35), 28 (28); HRMS (EI) calcd for $C_{13}H_{16}S$ (M^+) 204.0967, found 204.0963.

(2j) 4-((*tert*-butylthio)ethynyl)-*N*,*N*-dimethylaniline



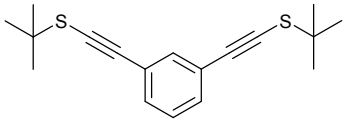
Column chromatography using 20% Et_2O/PE gave a colourless oil: 65 mg, 76%; IR ν_{max} (film)/cm^{-1} 2957, 2916, 2890, 2856, 2799, 2151, 1603, 1516, 1442, 1360, 1224, 1162, 907, 815, 733; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.36-7.34 (d, J = 8.8 Hz, 2 H), 6.63-6.61 (d, J = 8.8 Hz, 2 H), 2.98 (s, 6 H), 1.46 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 150.3, 133.4, 129.0, 111.8, 97.0, 48.1, 40.4, 31.8, 30.4; LRMS (EI) *m/z* (%) 233 (33), 213 (18), 177 (100); HRMS (EI) calcd for $C_{14}H_{19}NS$ (M^+) 233.1233, found 233.1234.

(2k) 3-((*tert*-butylthio)ethynyl)pyridine



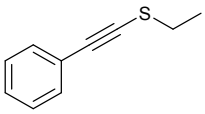
Column chromatography using 30% Et_2O/PE gave a colourless oil: 38 mg, 54%; IR ν_{max} (film)/cm^{-1} 2961, 2921, 2896, 2862, 2162, 1471, 1404, 1364, 1160, 1021, 907, 801, 729, 702; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.65 (s, 1 H), 8.49 (d, J = 3.4 Hz, 1 H), 7.70-7.68 (dt, J = 7.8, 2.1 Hz, 1 H), 7.24-7.22 (dd, J = 7.8, 4.8 Hz, 1 H), 1.49 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 152.1, 148.1, 138.2, 123.0, 121.0, 92.9, 83.5, 48.9, 30.5; LRMS (EI) *m/z* (%) 191 (10), 169 (100), 135 (47), 122 (15); HRMS (EI) calcd for $C_{11}H_{13}NS$ (M^+) 191.0763, found 191.0756.

(2l) 1,3-bis((*tert*-butylthio)ethynyl)benzene



Variation from general procedure: 8.0 eq. of thiol and potassium hydride used and 4.0 eq. of dimethylamine used. Column chromatography using PE gave a white solid: 65 mg, 59%; IR ν_{max} (film)/cm^{-1} 2957, 2918, 2897, 2860, 2154, 1586, 1470, 1453, 1363, 1158, 1066, 890, 791, 682, 569, 548, 473; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.48-7.47 (t, J = 1.5 Hz, 1 H), 7.34-7.32 (dd, J = 7.9, 1.5 Hz, 2 H), 7.25-7.22 (t, J = 7.9 Hz, 1 H), 1.48 (s, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 133.9, 130.6, 128.4, 124.1, 95.5, 80.1, 48.7, 30.5; LRMS (EI) *m/z* (%) 302 (20), 225 (15), 190 (100); HRMS (EI) calcd for $C_{18}H_{22}S_2$ (M^+) 302.1157, found 302.1159.

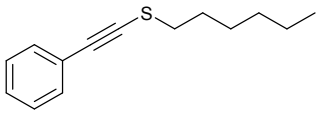
(2m) Ethyl(phenylethynyl)sulfane



Column chromatography using 10% Et_2O/PE gave a colourless oil: 38 mg, 64%; IR ν_{max} (film)/cm^{-1} 2965, 2926, 2869, 2165, 1595, 1486, 1442, 1375, 1263, 1069; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.43 (m, 2 H), 7.30 (m, 3 H), 2.85-2.81 (q, J = 7.3 Hz, 2 H), 1.48-1.45 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 131.5, 128.4, 128.1, 123.6, 93.5, 79.5, 30.4, 30.1, 14.9; LRMS (EI) *m/z* (%) 162 (10), 134 (20), 86 (47),

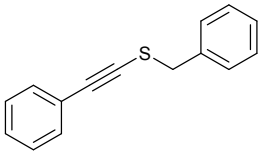
84 (100); HRMS (EI) calcd for $C_{10}H_{10}S$ (M^+) 162.0498, found 162.0498. Data in agreement with literature.[6]

(2n) Hexyl(phenylethynyl)sulfane



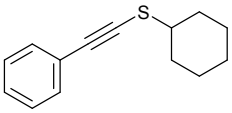
Column chromatography using PE gave a colourless oil: 55 mg, 69%; IR ν_{max} (film)/cm^{-1} 2956, 2927, 2857, 2168, 1595, 1486, 1463, 1441, 1378, 1258, 1067; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.42 (m, 2 H), 7.30 (m, 3 H), 2.81 (t, *J* = 7.3 Hz, 2 H), 1.83-1.78 (quint, *J* = 8.0 Hz, 2 H), 1.47-1.44 (m, 2 H), 1.35-1.32 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 131.5, 128.3, 128.0, 123.7, 92.9, 79.8, 35.9, 31.4, 29.3, 28.0, 22.6, 14.1; LRMS (EI) *m/z* (%) 218 (60), 134 (100); HRMS (EI) calcd for $C_{14}H_{18}S$ (M^+) 218.1124, found 218.1120. Data in agreement with literature.[6]

(2o) Benzyl(phenylethynyl)sulfane



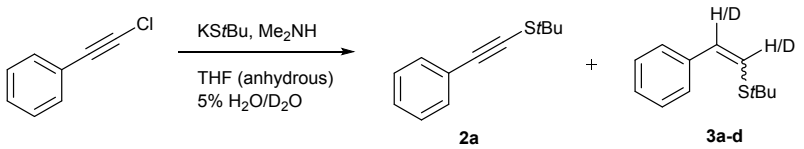
Column chromatography using PE gave a colourless oil: 53 mg, 65%; IR ν_{max} (film)/cm^{-1} 3058, 3025, 2922, 2165, 1595, 1491, 1451, 1214, 1068, 912, 750, 690, 467; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.41-7.23 (m, 10 H), 4.03 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 136.7, 131.4, 129.2, 128.7, 128.4, 128.1, 127.9, 123.4, 94.7, 79.2, 40.5; LRMS (EI) *m/z* (%) 224 (25), 191 (45), 91 (100); HRMS (EI) calcd for $C_{15}H_{12}S$ (M^+) 224.0654 found 224.0647. Data in agreement with literature.[6]

(2p) Cyclohexyl(phenylethynyl)sulfane



Column chromatography using PE gave a colourless oil: 77 mg, 97%; IR ν_{max} (film)/cm^{-1} 2930, 2902, 2852, 2161, 1485, 1446, 1261, 905, 729, 689, 648; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.43-7.41 (m, 2 H), 7.31-7.28 (m, 3 H), 3.03-2.98 (tt, *J* = 10.9, 3.7 Hz, 1 H), 2.14-2.09 (m, 2 H), 1.85-1.81 (dt, *J* = 13.5, 3.7 Hz, 2 H), 1.67-1.63 (m, 1 H), 1.60-1.53 (qd, *J* = 11.7, 3.4 Hz, 2 H), 1.41-1.33 (qt, *J* = 11.7, 3.4 Hz, 2 H), 1.30-1.26 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 131.5, 128.4, 128.0, 123.7, 94.5, 78.7, 47.8, 33.1, 26.2, 25.6; LRMS (EI) *m/z* (%) 216 (10), 134 (30), 89 (100), 83 (61), 62 (66); HRMS (EI) calcd for $C_{14}H_{16}S$ (M^+) 216.0967 found 216.0966. Data in agreement with literature.[6]

General procedure for the synthesis of addition products 3a-d



2a **3a-d**

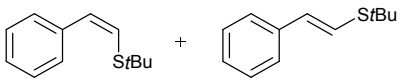
A flame-dried flask was charged with a stirring bar and 2-methylpropane-2-thiol (0.132 g, 1.46 mmol, 4.0 equiv.), followed by anhydrous THF (2 mL) under argon and heated to 50 °C. Potassium hydride (59 mg, 1.46 mmol, 4.0 equiv., supplied as a 30% weight dispersion in mineral oil which was rinsed with PE and dried between filter paper immediately prior to use) was then added as a single portion and the mixture was stirred at 50 °C for 15 min. The mixture was allowed to cool, first to r.t. and then to -40 °C. Dimethylamine solution (2.0 M in THF, 0.37 mL, 0.73 mmol, 2.0 equiv.) was added *via* syringe, followed immediately after by (chloroethynyl)benzene (**1a**) (0.37 mmol, 1.0 equiv.) in THF doped with H_2O or D_2O (1 mL). After 10 min, the solution was allowed to warm to r.t. and left to stir under an atmosphere of argon. The reaction mixture was then carefully quenched with water (20 mL), diluted with Et_2O (30 mL) and washed with brine (20 mL). The aqueous layer was extracted with Et_2O (30 mL) and the organic portions were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (PE) to yield desired thioynol ether (**2a**) and addition products (**3a-d)**.

Table of results

Dopant	Ratio of products (2a : 3)*	(*Z*):(*E*) ratio of minor product (3)**
H_2O	3 : 2	95 : 5
D_2O	3 : 1	95 : 5

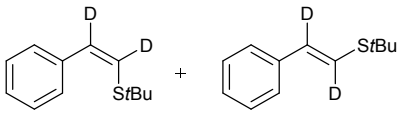
*Ratio of ynol ether, **2a** (major product) to enol ethers, **3** (minor products) calculated from ^{1}H NMR
Ratio of *Z* and *E* isomers of enol ethers (minor products); **3a:3b for H_2O and **3c:3d** for D_2O

(Z/E)-*tert*-butyl(styryl)sulfane (3a/b)



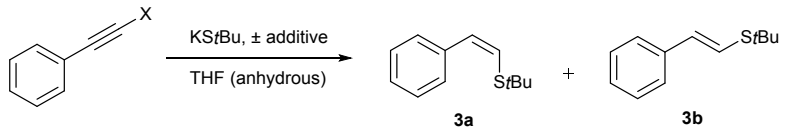
Inseparable isomers obtained as colourless oil (*Z*:*E* ratio of 95:5): 8 mg, 29%; IR ν_{max} (film)/cm^{-1} 2959, 2923, 2865, 1672, 1592, 1443, 1363, 1156, 845, 771, 734, 689, 526; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.51 (d, *J* = 7.8 Hz, 1 H, (*Z*) isomer), 7.36-7.33 (t, *J* = 18.7 Hz, 2 H, (*Z*) isomer), 7.36-7.19 (m, 4 H, (*E*) isomer), 7.22-7.18 (m, 1 H, (*E*) isomer and t, *J* = 18.1 Hz, 1 H, (*Z*) isomer), 6.89 (d, *J* = 15.7 Hz, 1 H, (*E*) isomer), 6.74 (d, *J* = 15.7 Hz, 1 H, (*E*) isomer), 6.50 (d, *J* = 11.2 Hz, 1 H, (*Z*) isomer), 6.46 (d, *J* = 11.2 Hz, 1 H, (*Z*) isomer), 1.43 (s, 9 H, (*Z*) isomer), 1.41 (s, 9 H, (*E*) isomer); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C (*Z*) isomer: 137.2, 128.8, 128.2, 126.6, 125.4, 123.5, 44.6, 30.8 and (*E*) isomer: 135.8, 132.1, 128.7, 126.1, 125.6, 122.2, 44.5, 31.1; LRMS (EI) *m/z* (%) 192 (20), 136 (100), 83 (45); HRMS (EI) calcd for $C_{12}H_{16}S$ (M^+) 192.0967, found 192.0968. Data in agreement with literature.[7]

(Z/E)-*tert*-butyl(styryl)sulfane-d_2 (3c/d)



Inseparable isomers obtained as colourless oil (*Z*:*E* ratio of 95:5): 7 mg, 39%; IR ν_{max} (film)/cm^{-1} 2962, 2924, 2897, 2862, 1717, 1597, 1490, 1457, 1443, 1365, 1156, 1115, 1055, 756, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.50 (d, J = 7.9 Hz, 1 H, (*Z*) isomer), 7.36-7.33 (t, J = 8.5 Hz, 2 H, (*Z*) isomer), 7.36-7.20 (m, 4 H, (*E*) isomer), 7.23-7.18 (m, 1 H, (*E*) isomer and t, J = 7.3 Hz, 1 H, (*Z*) isomer), 1.43 (s, 9 H, (*Z*) isomer), 1.41 (s, 9 H, (*E*) isomer); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C (*Z*) isomer: 137.2, 128.8, 128.2, 126.6, 125.3, 123.5, 44.6, 30.9 and (*E*) isomer: 135.2, 131.8, 128.7, 125.4, 124.4, 123.4, 31.4, 31.1; LRMS (CI) *m/z* (%) 194 (100), 138 (60), 124 (20); HRMS (EI) calcd for $C_{12}H_{16}S$ (M^+) 194.1093, found 194.1094.

General procedure for the treatment of bromo- and iodoalkynes with 2-methylpropane-2-thiol



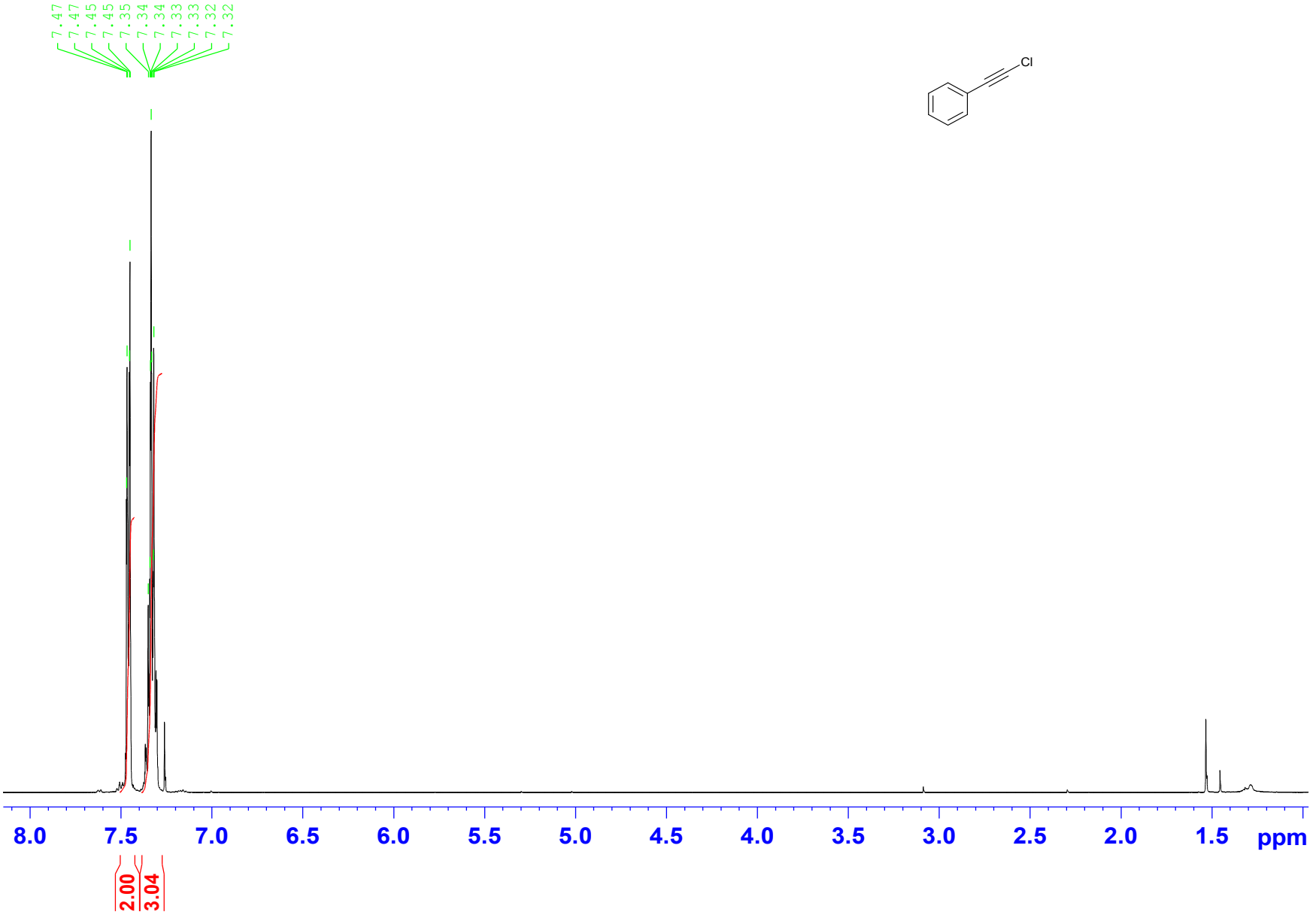
A flame-dried flask was charged with a stirring bar and 2-methylpropane-2-thiol (0.132 g, 1.46 mmol, 4.0 equiv.), followed by anhydrous THF (2 mL) under argon and heated to 50 °C. Potassium hydride (59 mg, 1.46 mmol, 4.0 equiv., supplied as a 30% weight dispersion in mineral oil which was rinsed with PE and dried between filter paper immediately prior to use) was then added as a single portion and the mixture was stirred at 50 °C for 15 min. The mixture was allowed to cool, first to r.t. and then to -40 °C. The additive (dimethylamine or *N,N*-dimethylethylenediamine) (0.73 mmol, 2.0 equiv.), if any, was added *via* syringe, followed immediately after by the alkynyl halide (0.37 mmol, 1.0 equiv.) in THF (1 mL). After 10 min, the solution was allowed to warm to r.t. and left to stir under an atmosphere of argon. The reaction mixture was then carefully quenched with water (20 mL), diluted with Et_2O (30 mL) and washed with brine (20 mL). The aqueous layer was extracted with Et_2O (30 mL) and the organic portions were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography using PE to yield the addition products as inseparable isomers.

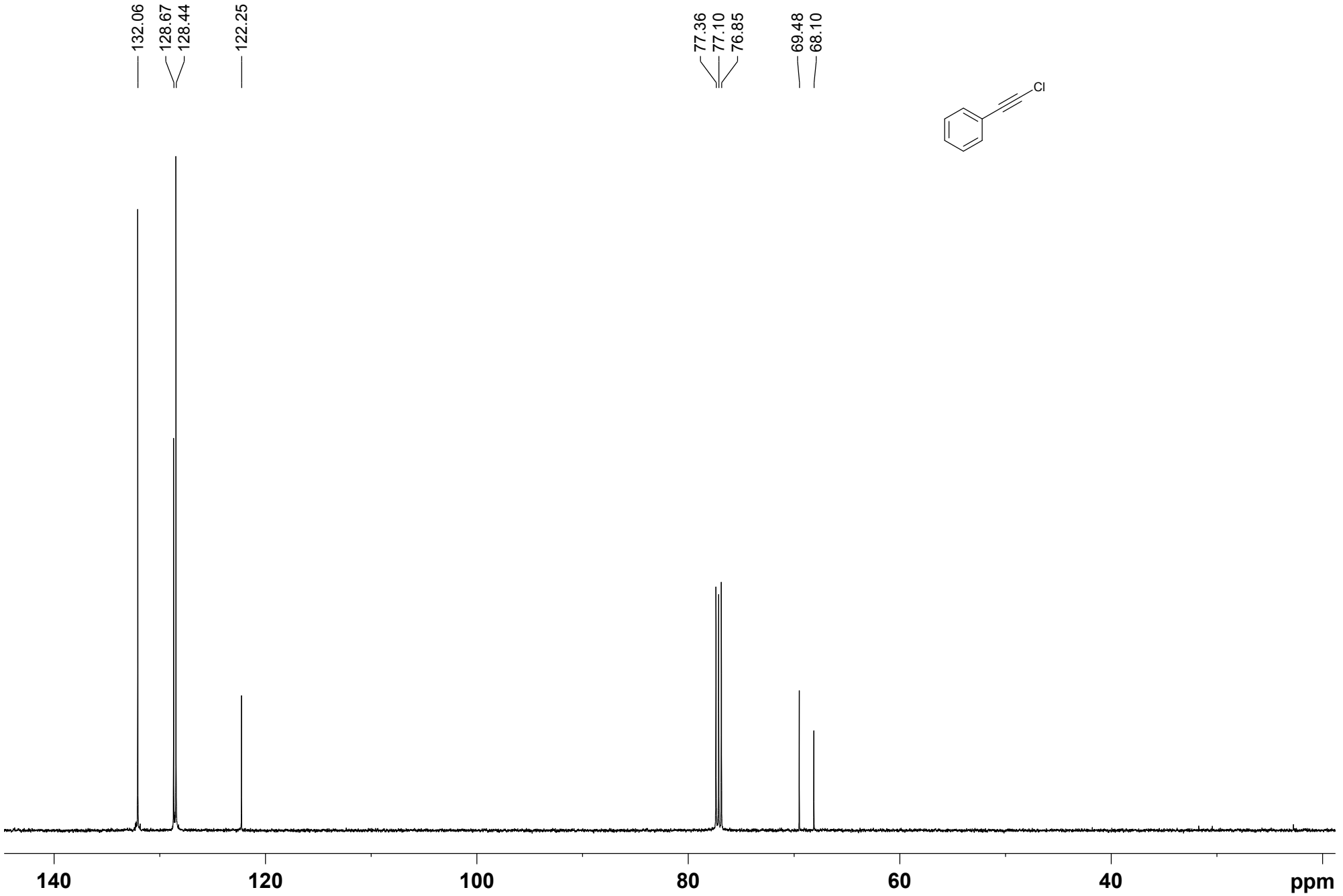
Table of results

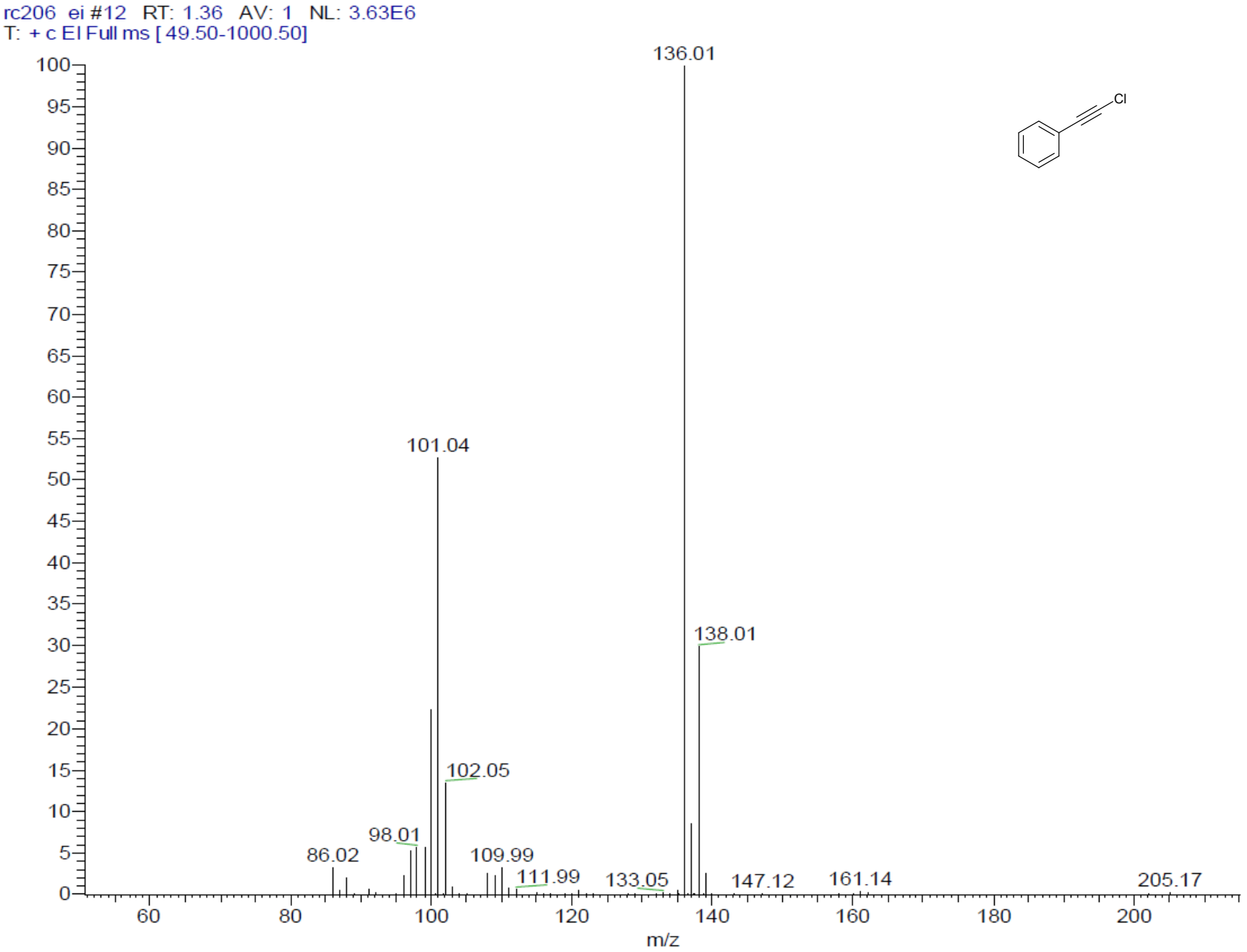
X	**Dimethylamine**		***N,N*-dimethylethylenediamine**		**No additive**	
	Yield (%)	(*Z*):(*E*)	Yield (%)	(*Z*):(*E*)	Yield (%)	(*Z*):(*E*)
Br	46	91:9	66	91:9	64	78:22
I	40	92:8	77	89:11	49	83:17

Spectra

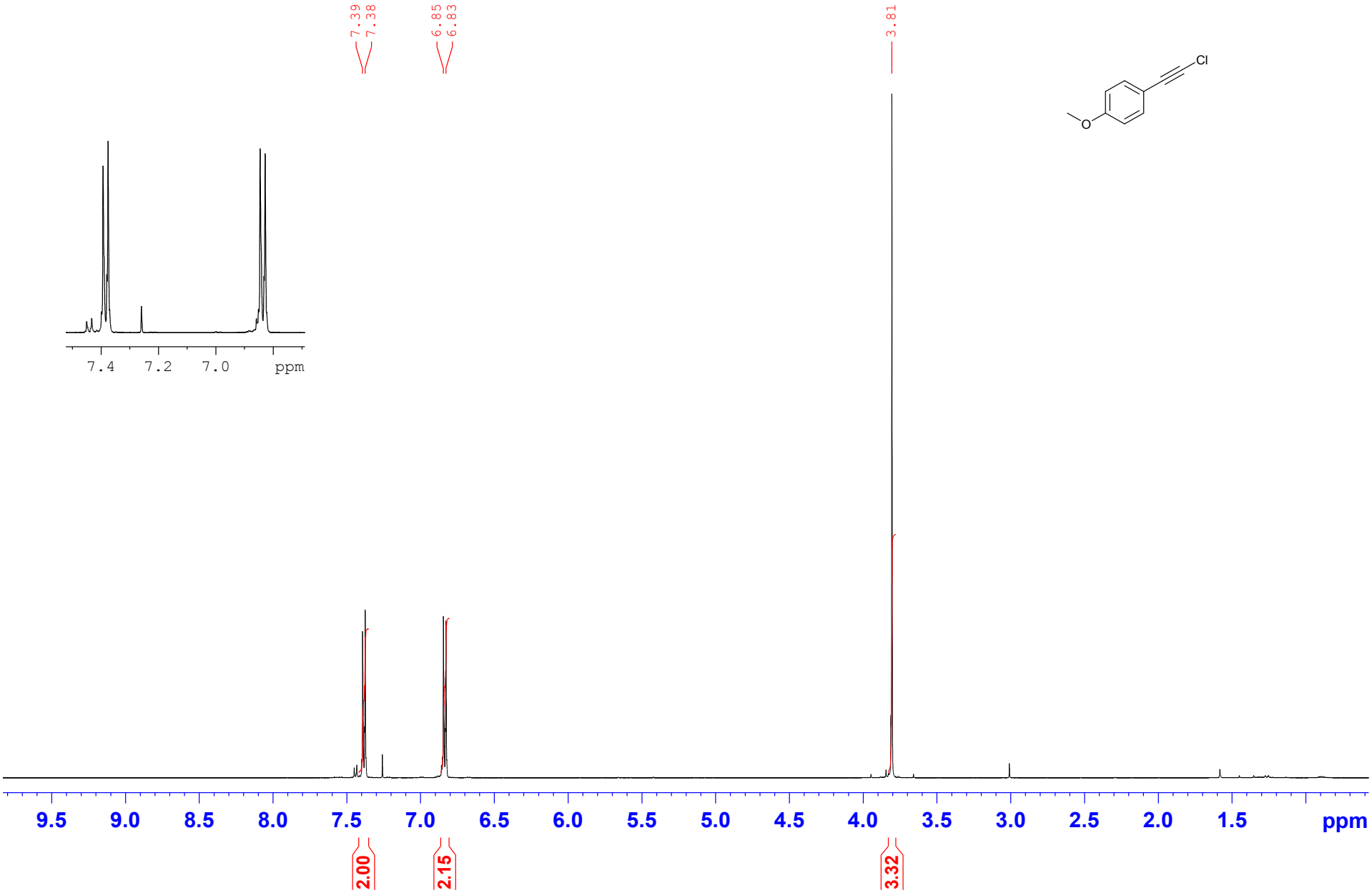
(Chloroethynyl)benzene (1a)

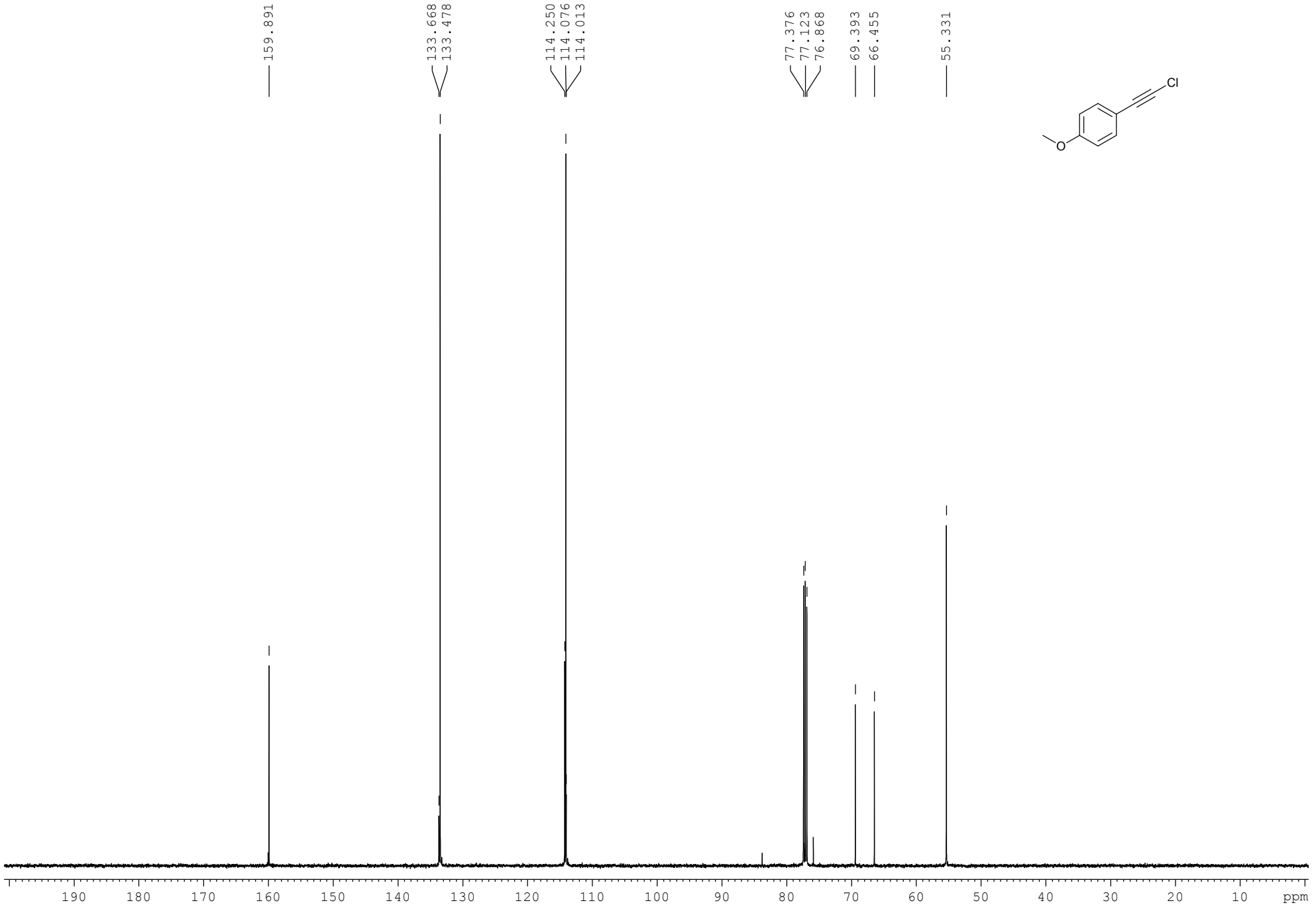



132.06
128.67
128.44
122.25
77.36
77.10
76.85
69.48
68.10
Cl
140
120
100
80
60
40
ppm

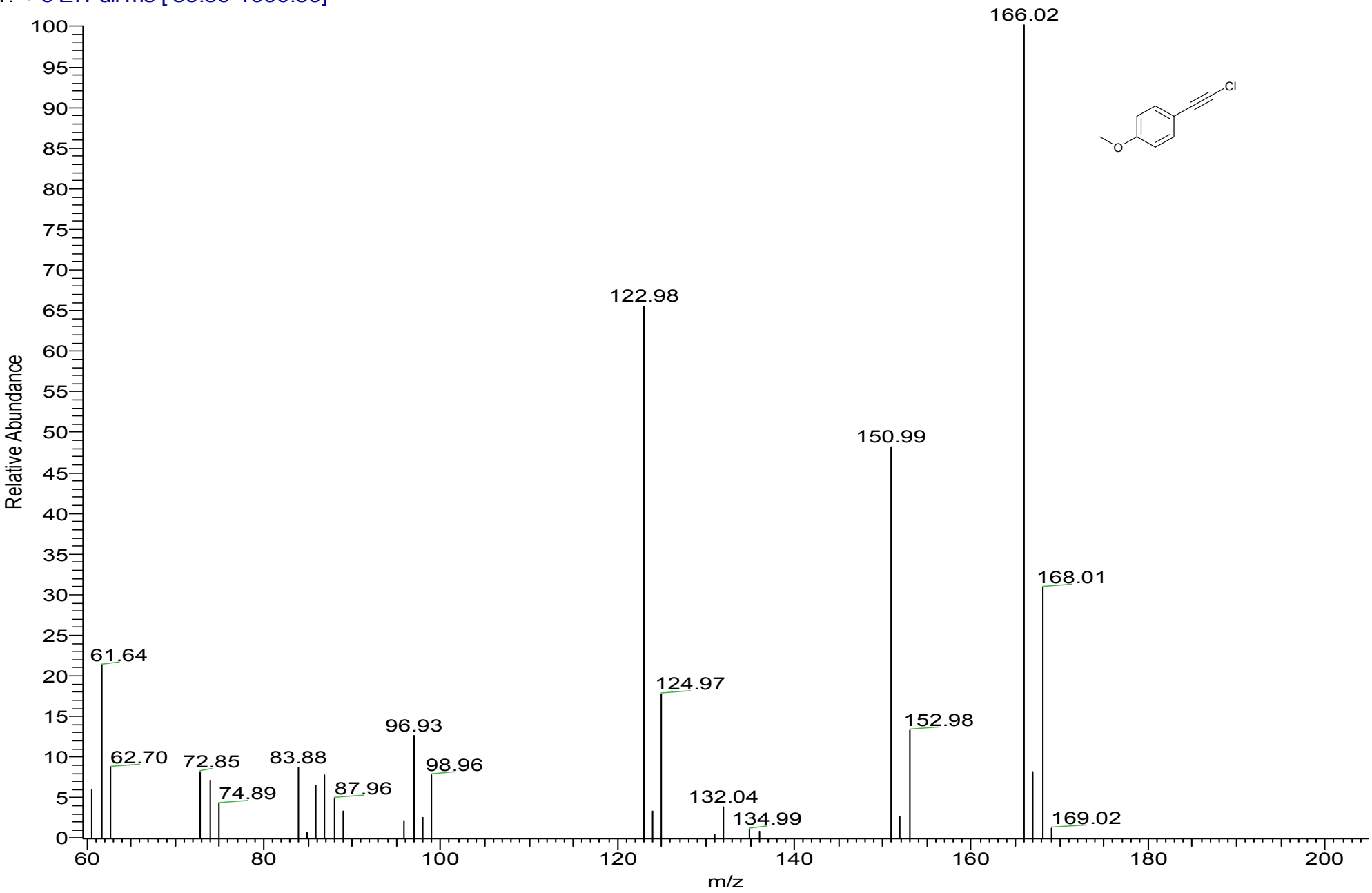

rc206 ei #12 RT: 1.36 AV: 1 NL: 3.63E6
T: + c EI Full ms [49.50-1000.50]
136.01
101.04
138.01
102.05
98.01
86.02
109.99
111.99
133.05
147.12
161.14
205.17
Cl
m/z

1-(chloroethynyl)-4-methoxybenzene (1b)

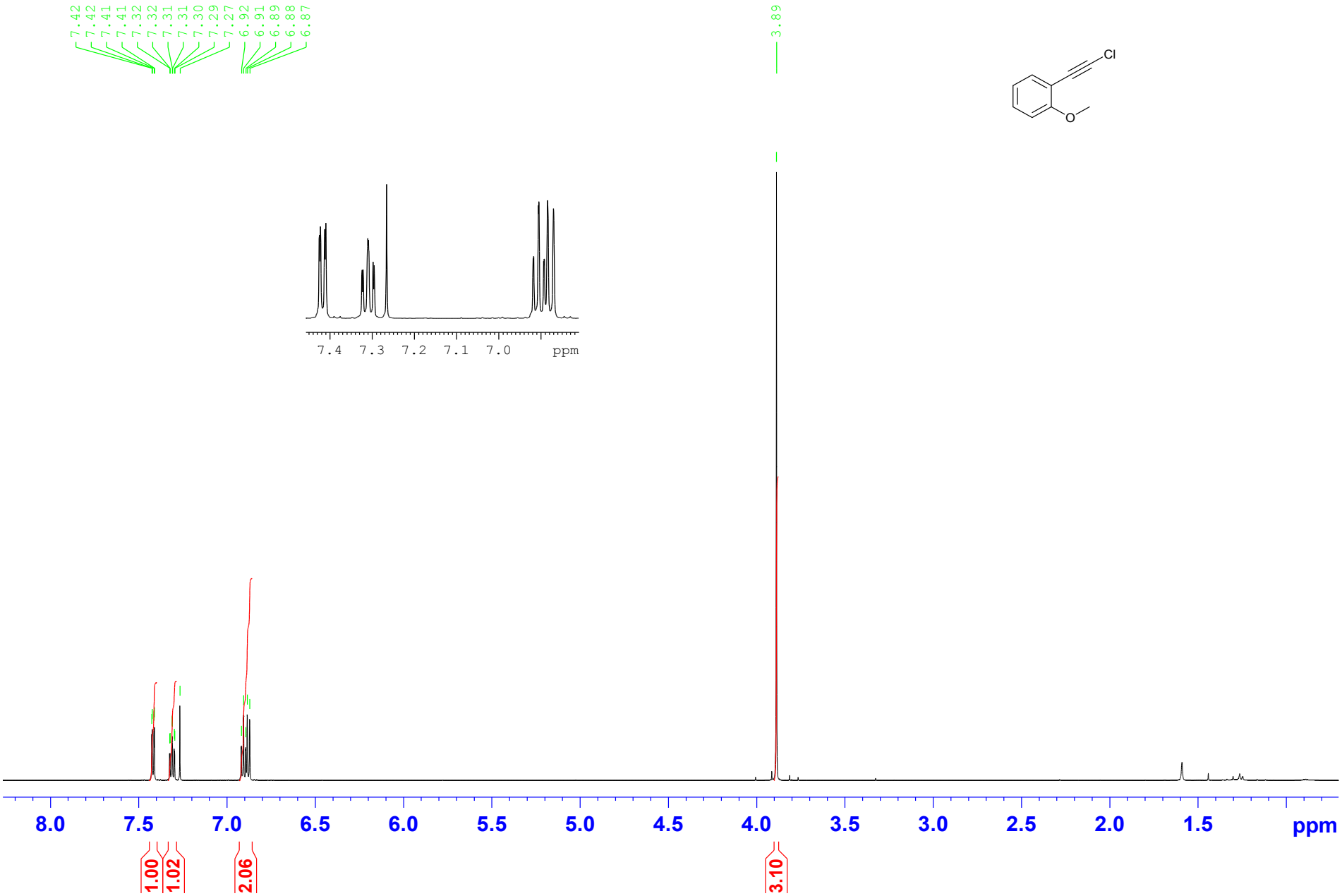


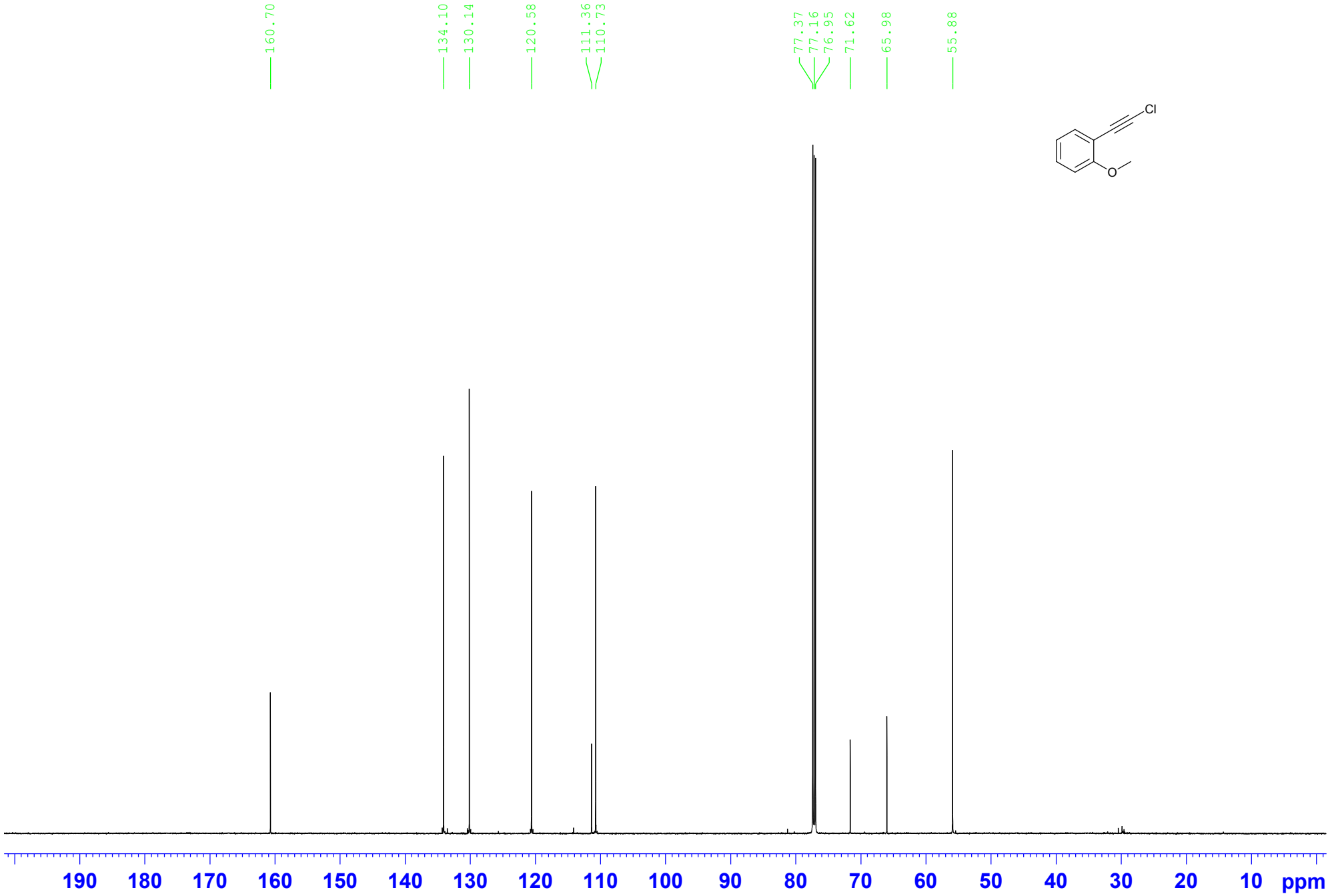

159.891
133.668
133.478
114.250
114.076
114.013
77.376
77.123
76.868
69.393
66.455
55.331
Cl
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc062_ei_140906094800 #1 RT: 0.20 AV: 1 NL: 6.42E4
T: + c EI Full ms [59.50-1000.50]

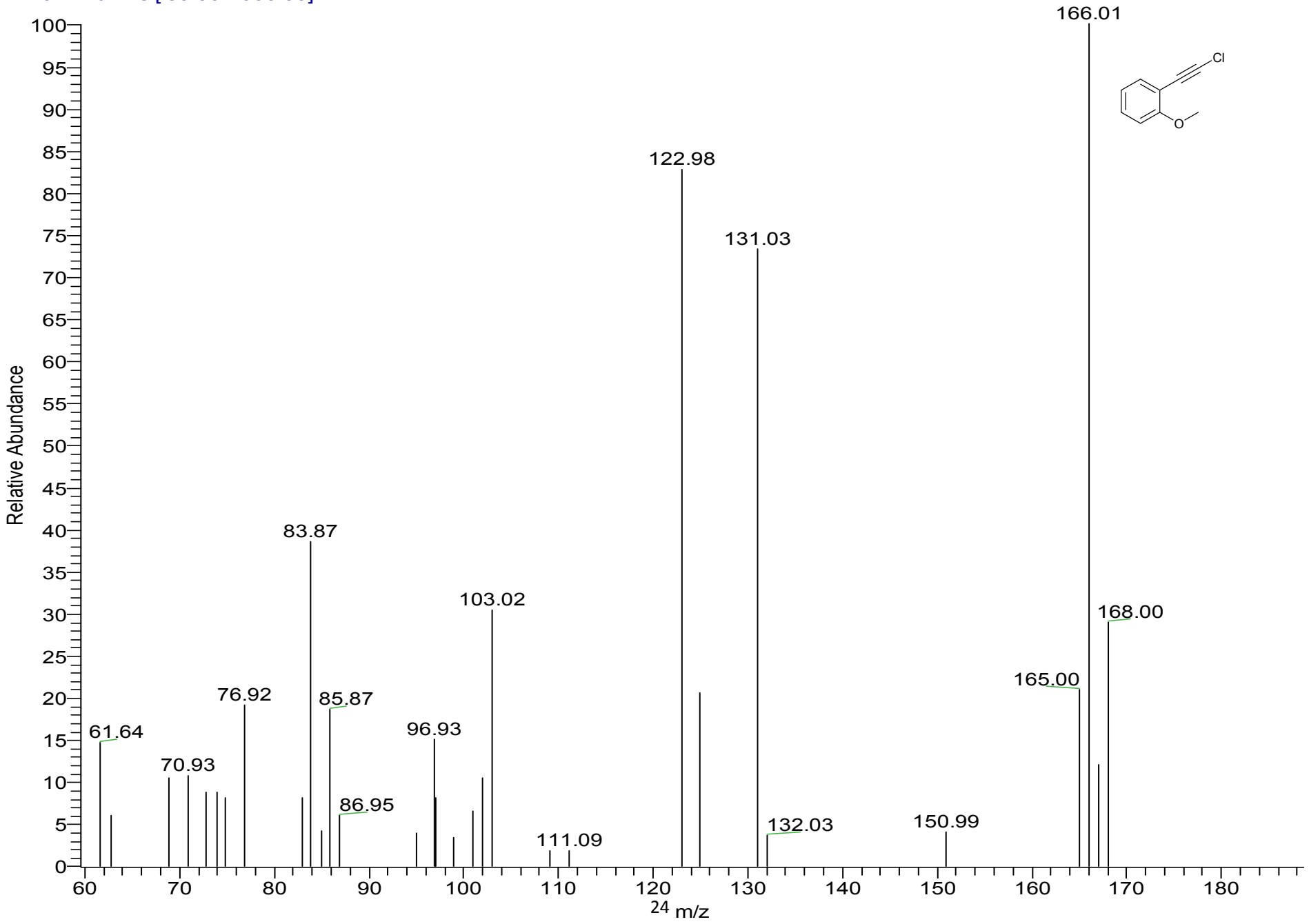


1-(chloroethynyl)-2-methoxybenzene (1c)

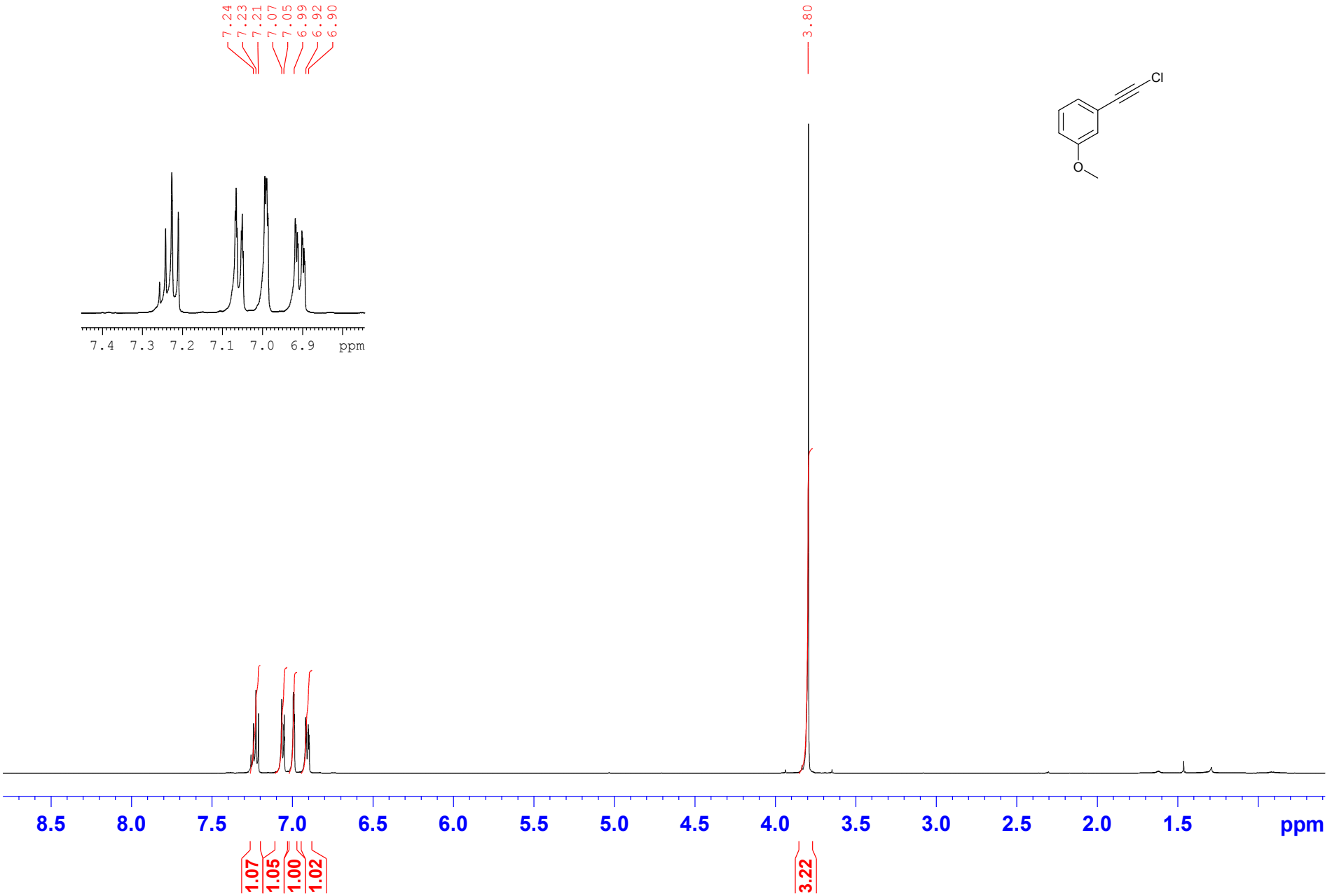


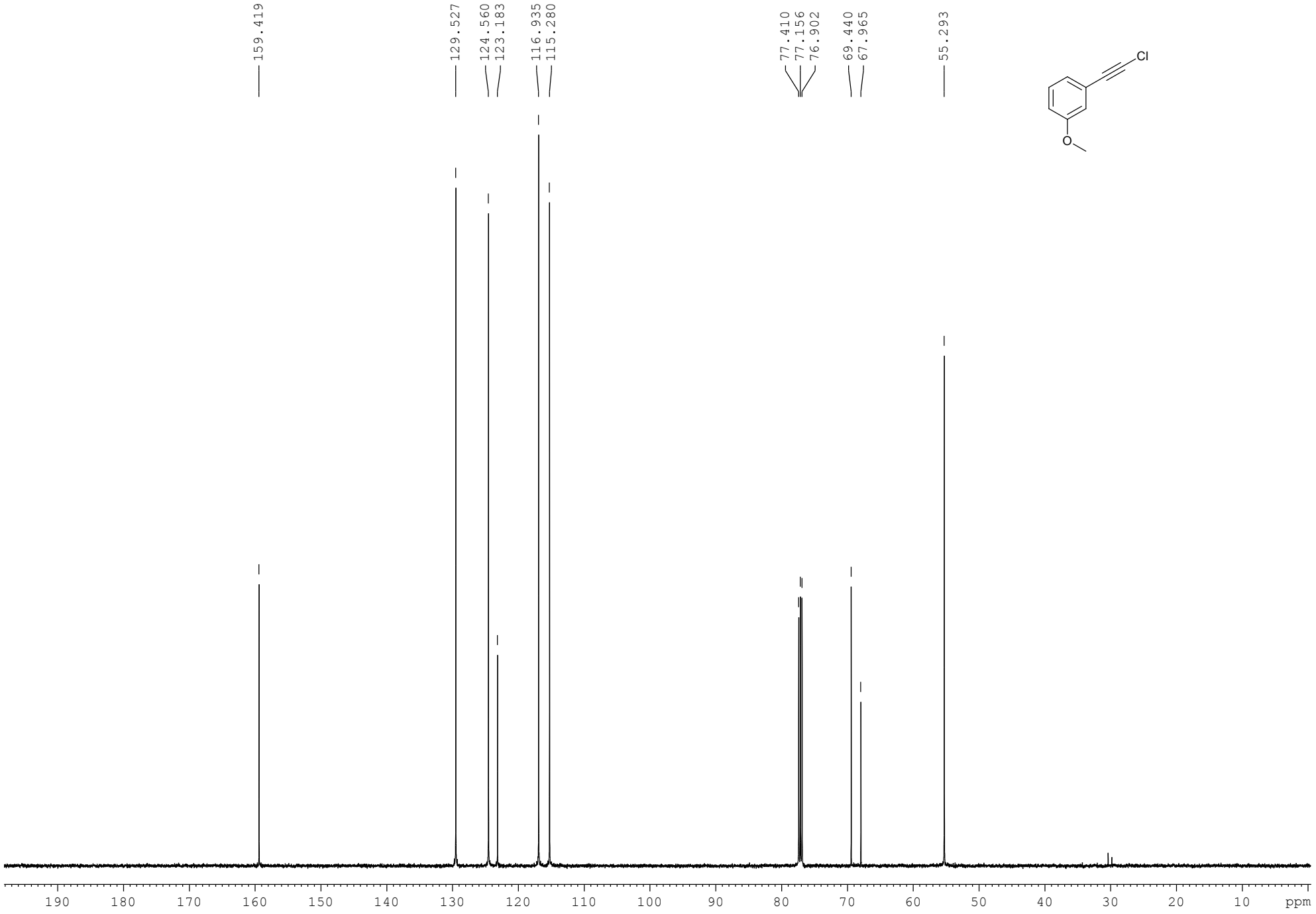

160.70
134.10
130.14
120.58
111.36
110.73
77.37
77.16
76.95
71.62
65.98
55.88
Cl
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc063_ei #2 RT: 0.30 AV: 1 NL: 1.68E4
T: + c EI Full ms [59.50-1000.50]

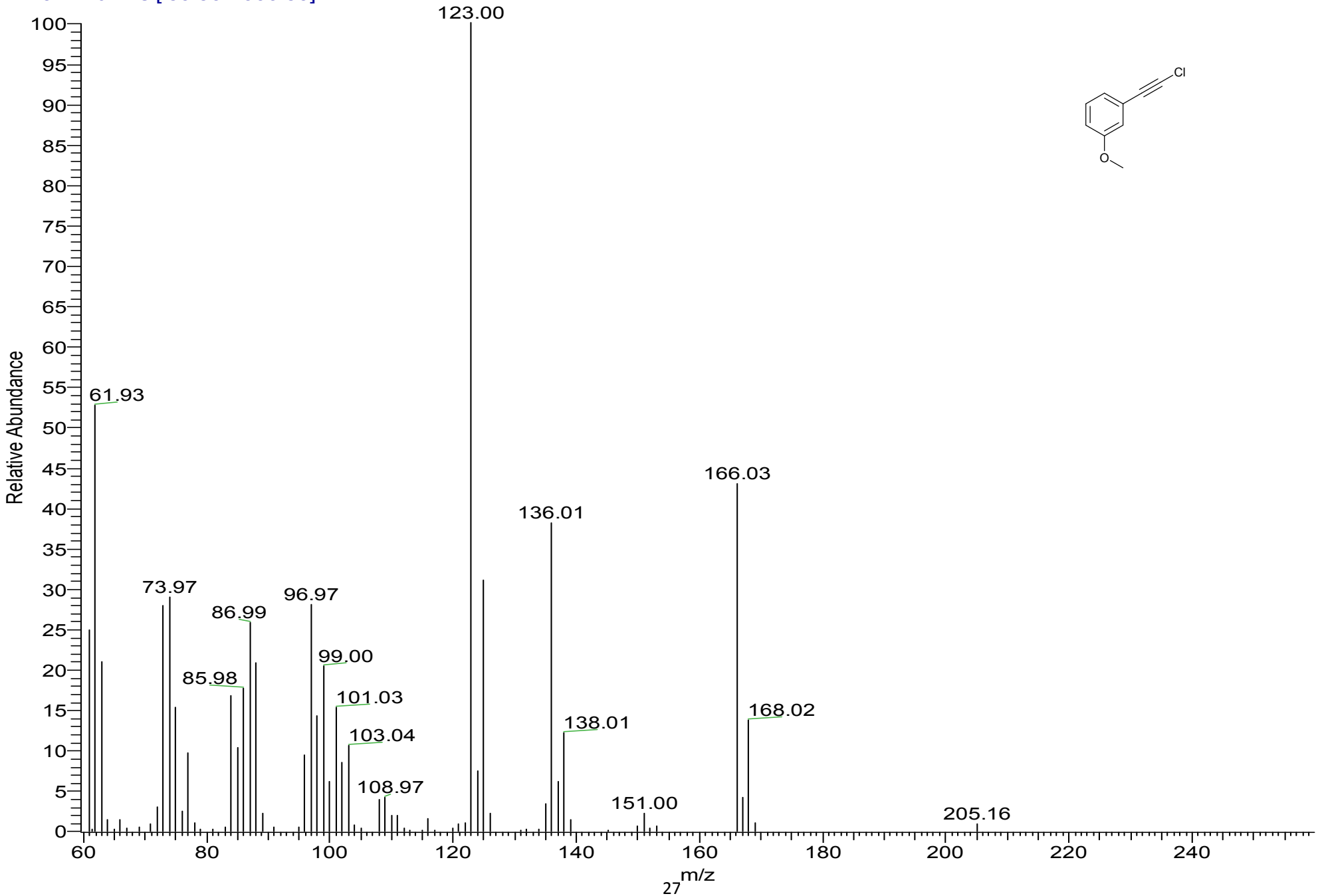


1-(chloroethynyl)-3-methoxybenzene (1d)

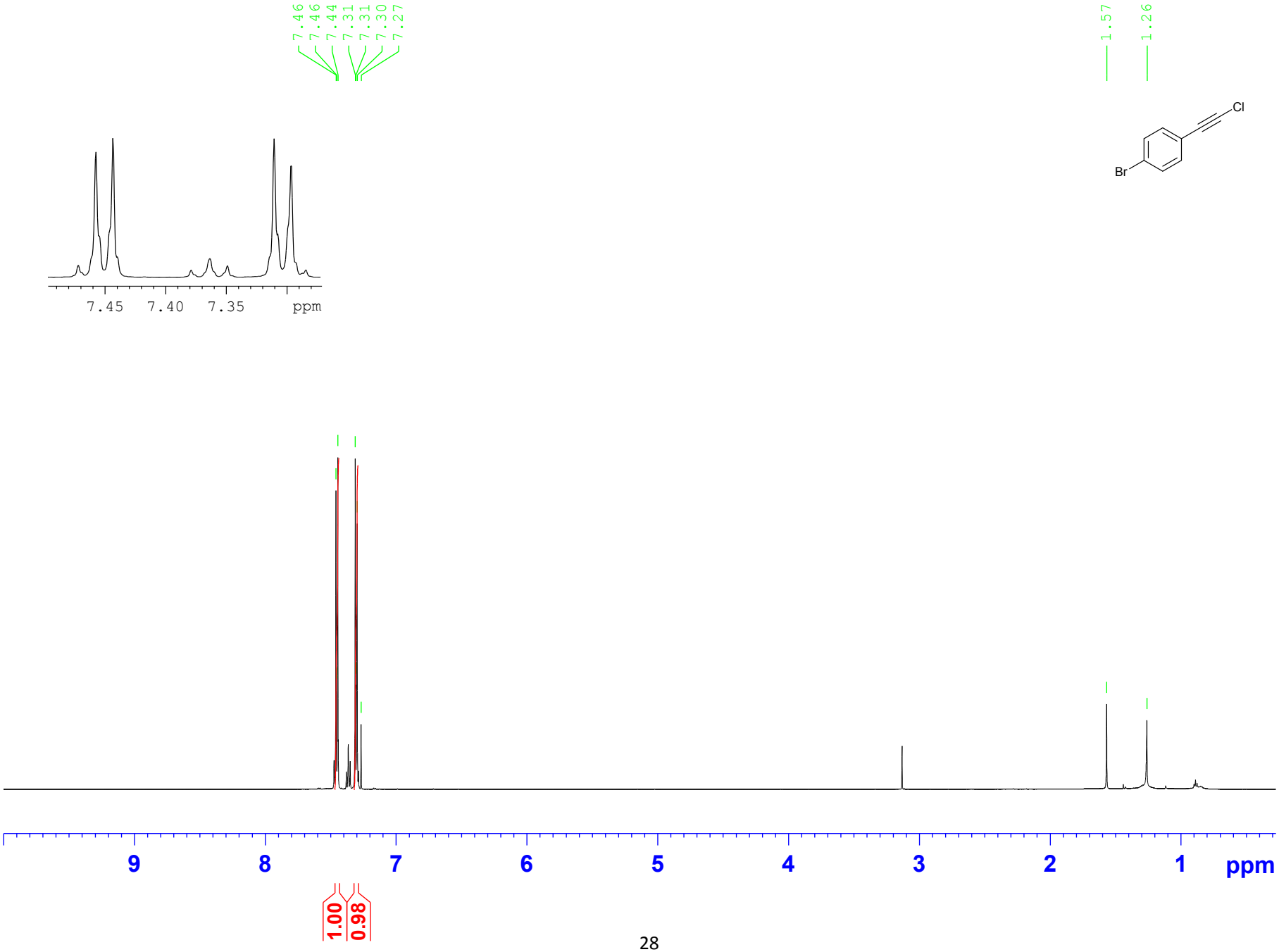


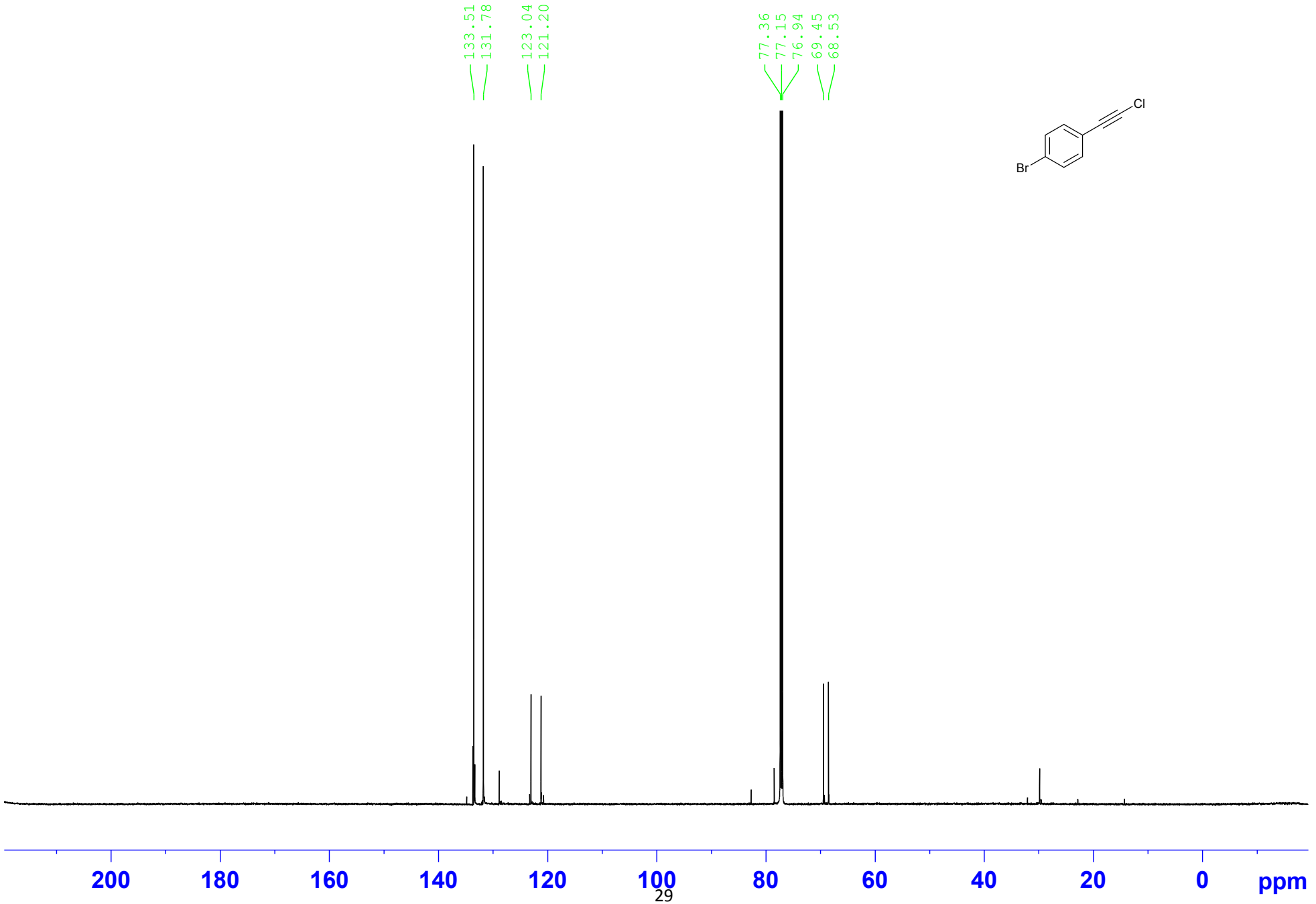

159.419
129.527
124.560
123.183
116.935
115.280
77.410
77.156
76.902
69.440
67.965
55.293
Cl
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

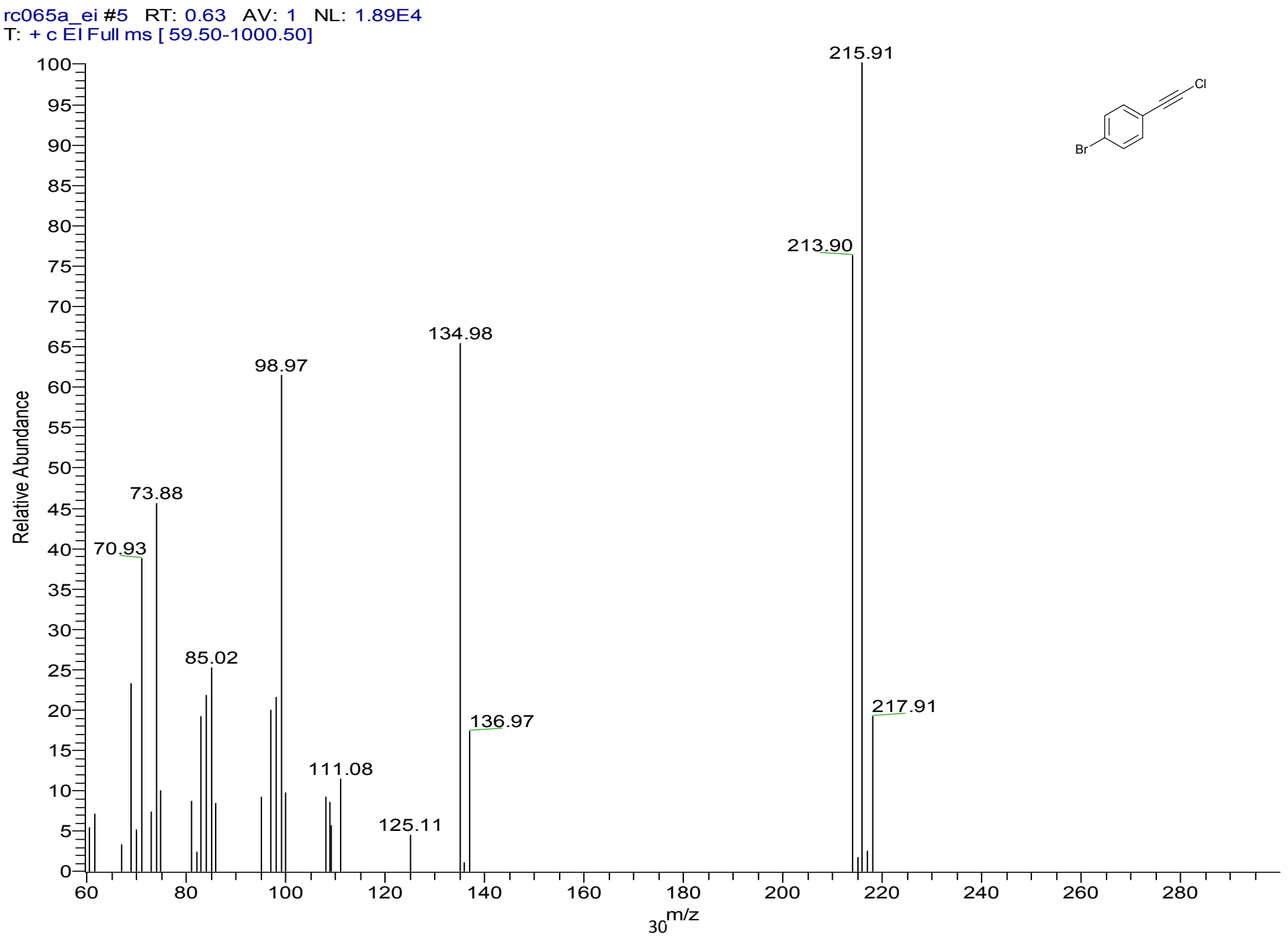
rc151_ei #1 RT: 0.12 AV: 1 NL: 4.35E5
T: + c EI Full ms [59.50-1000.50]



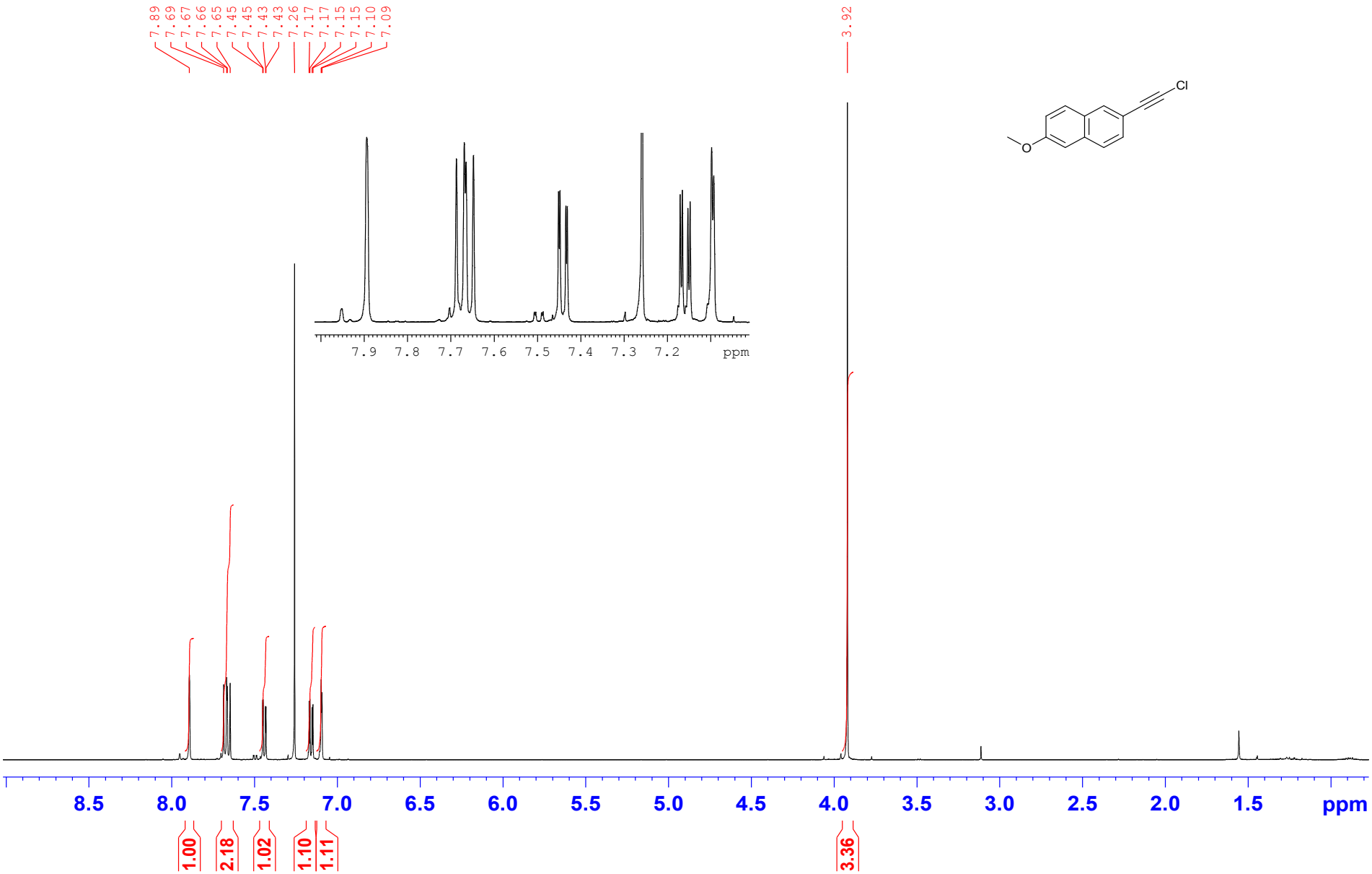
1-bromo-4-(chloroethynyl)benzene (1e)

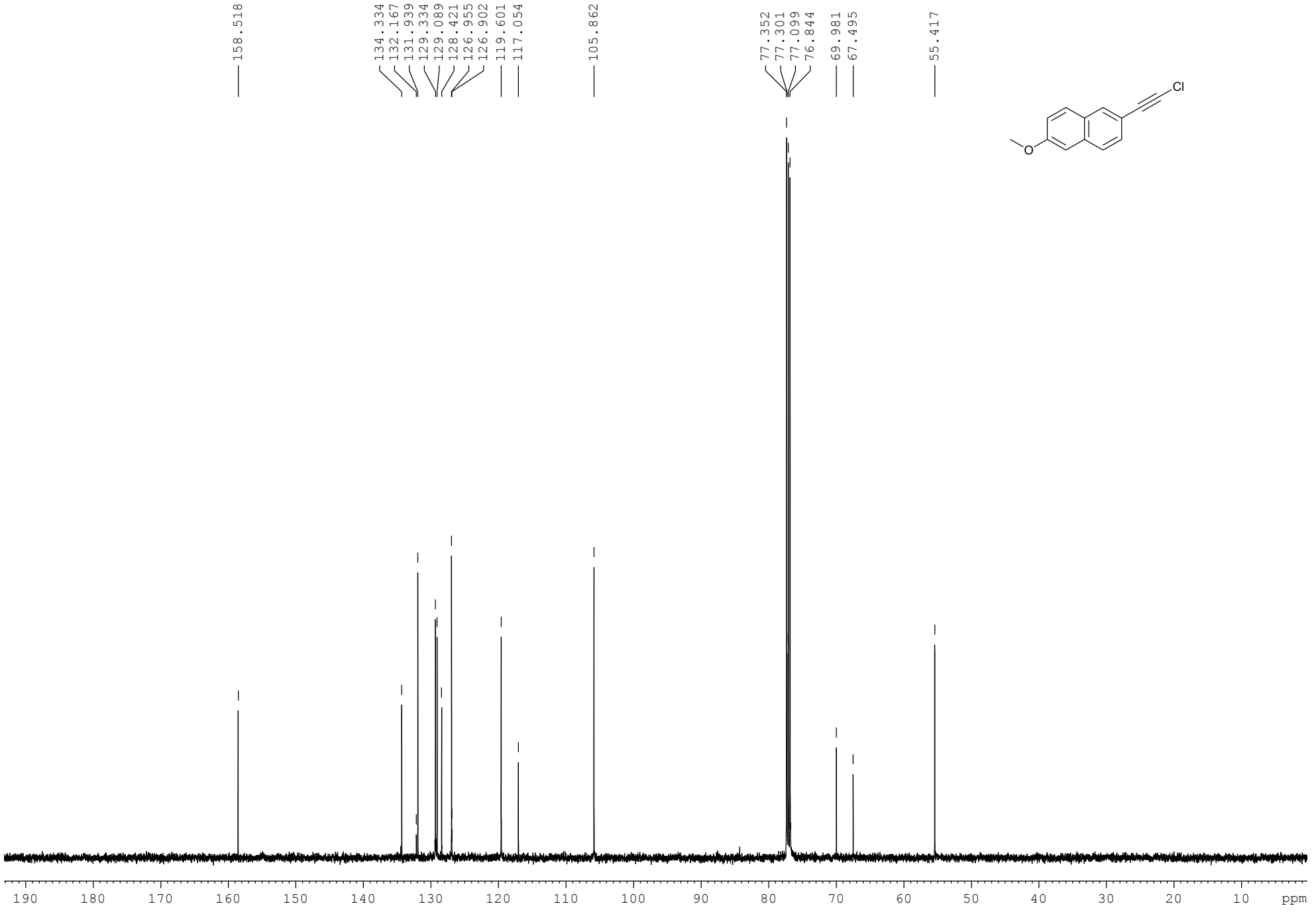


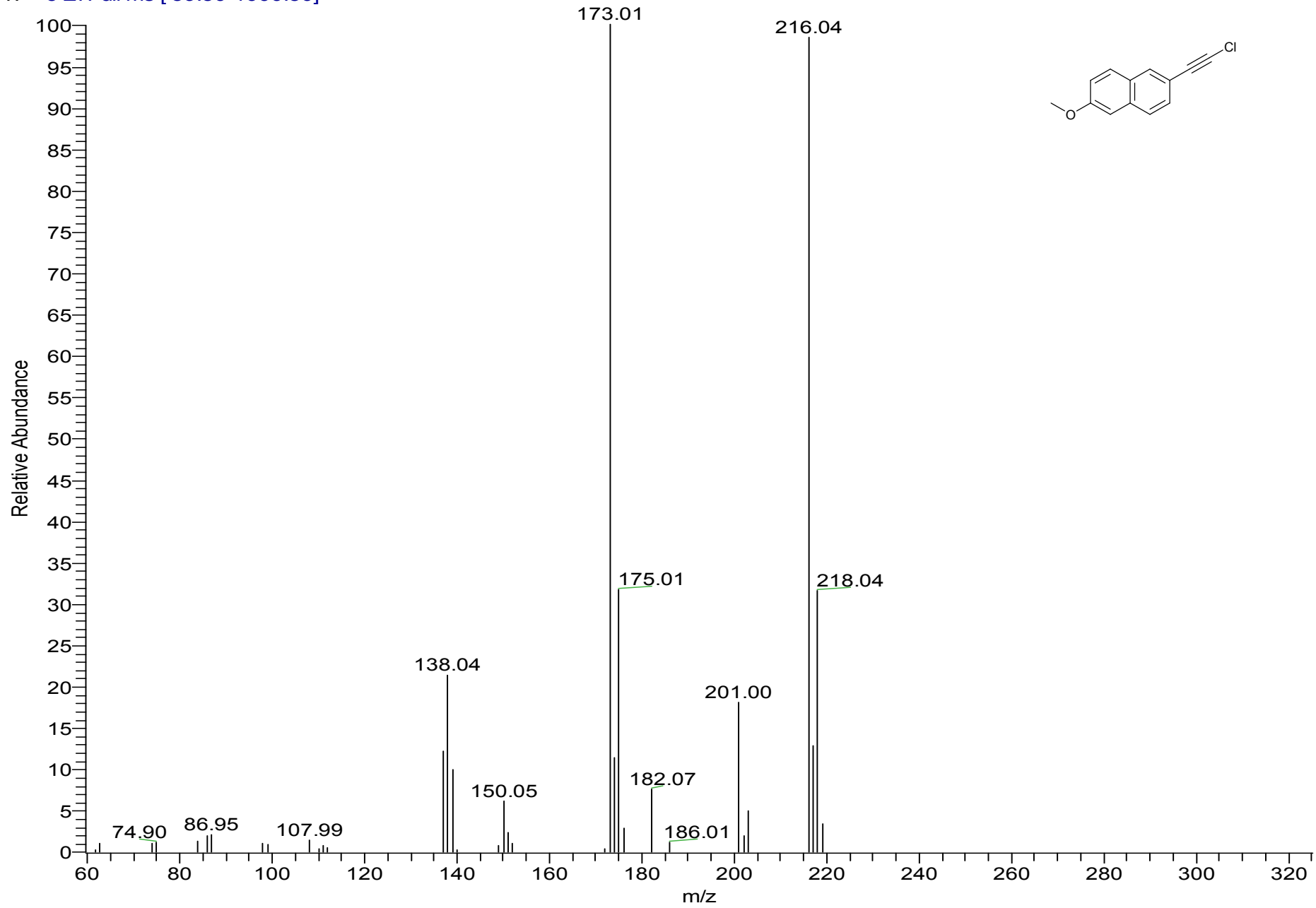

133.51
131.78
123.04
121.20
77.36
77.15
76.94
69.45
68.53
Cl
Br
200
180
160
140
120
100
80
60
40
20
0
ppm


rc065a_ei #5 RT: 0.63 AV: 1 NL: 1.89E4
T: + c EI Full ms [59.50-1000.50]
215.91
213.90
134.98
98.97
73.88
70.93
85.02
136.97
111.08
125.11
217.91
Cl
Br
Relative Abundance
m/z

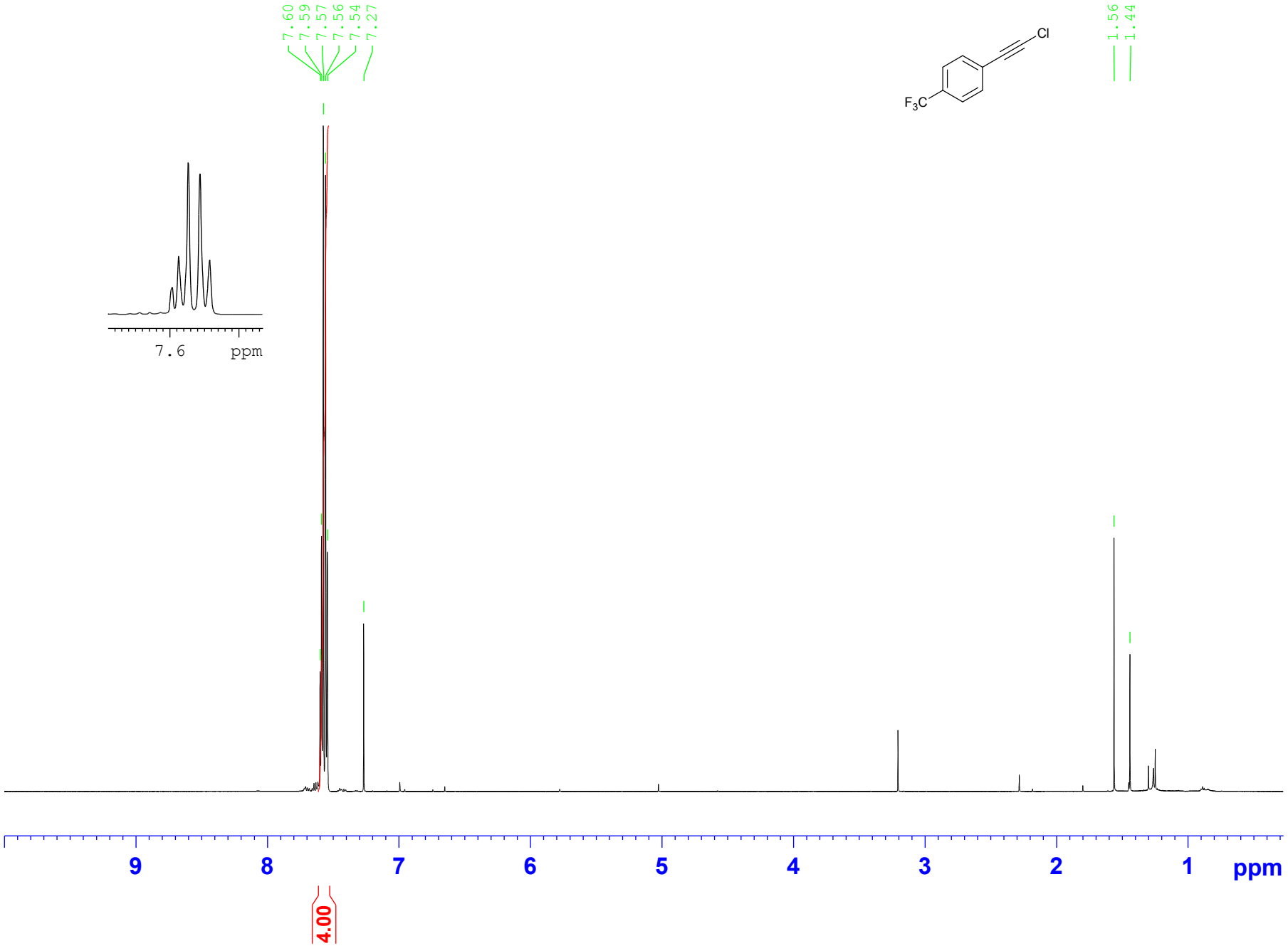
2-(chloroethynyl)-6-methoxynaphthalene (1f)

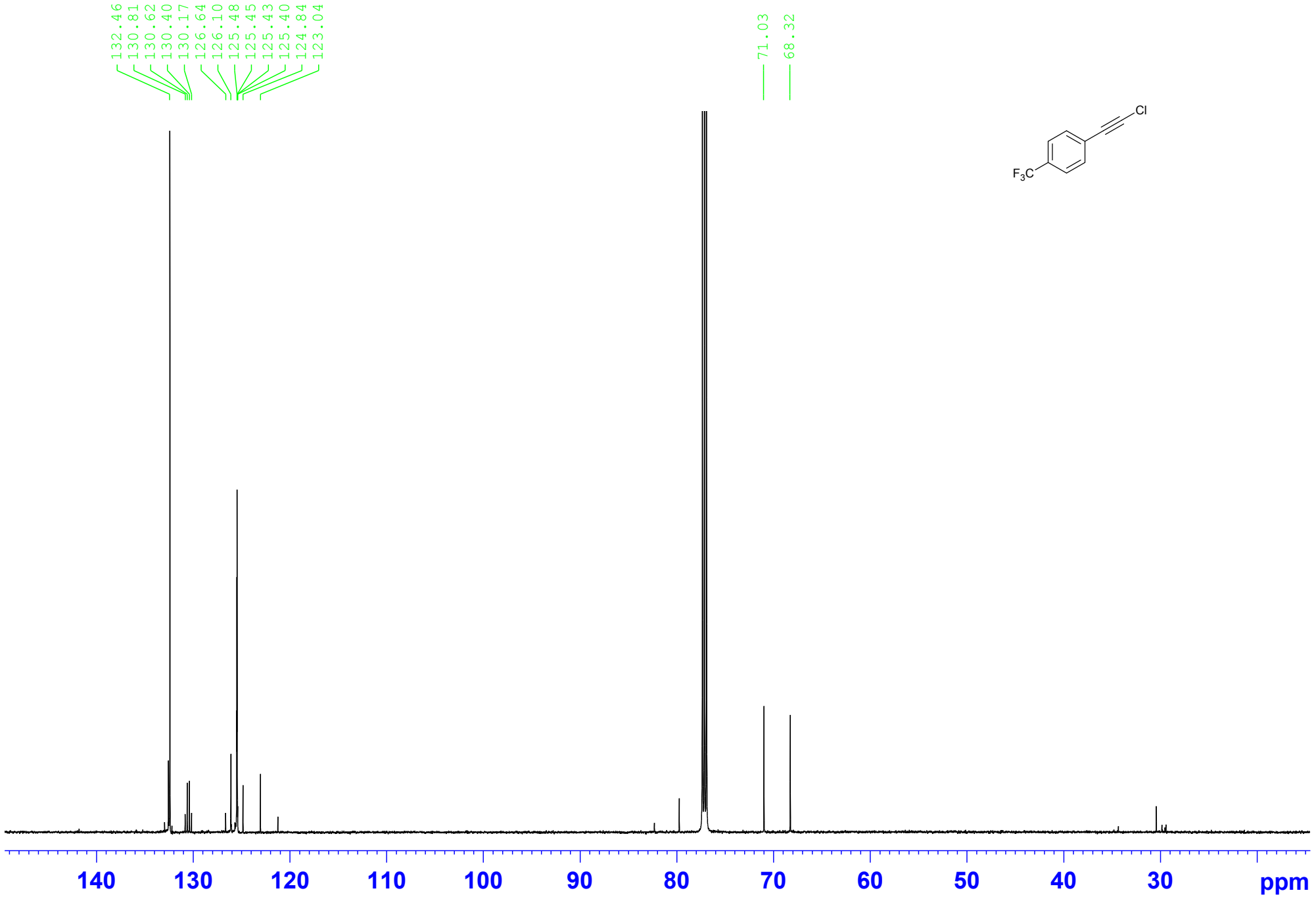


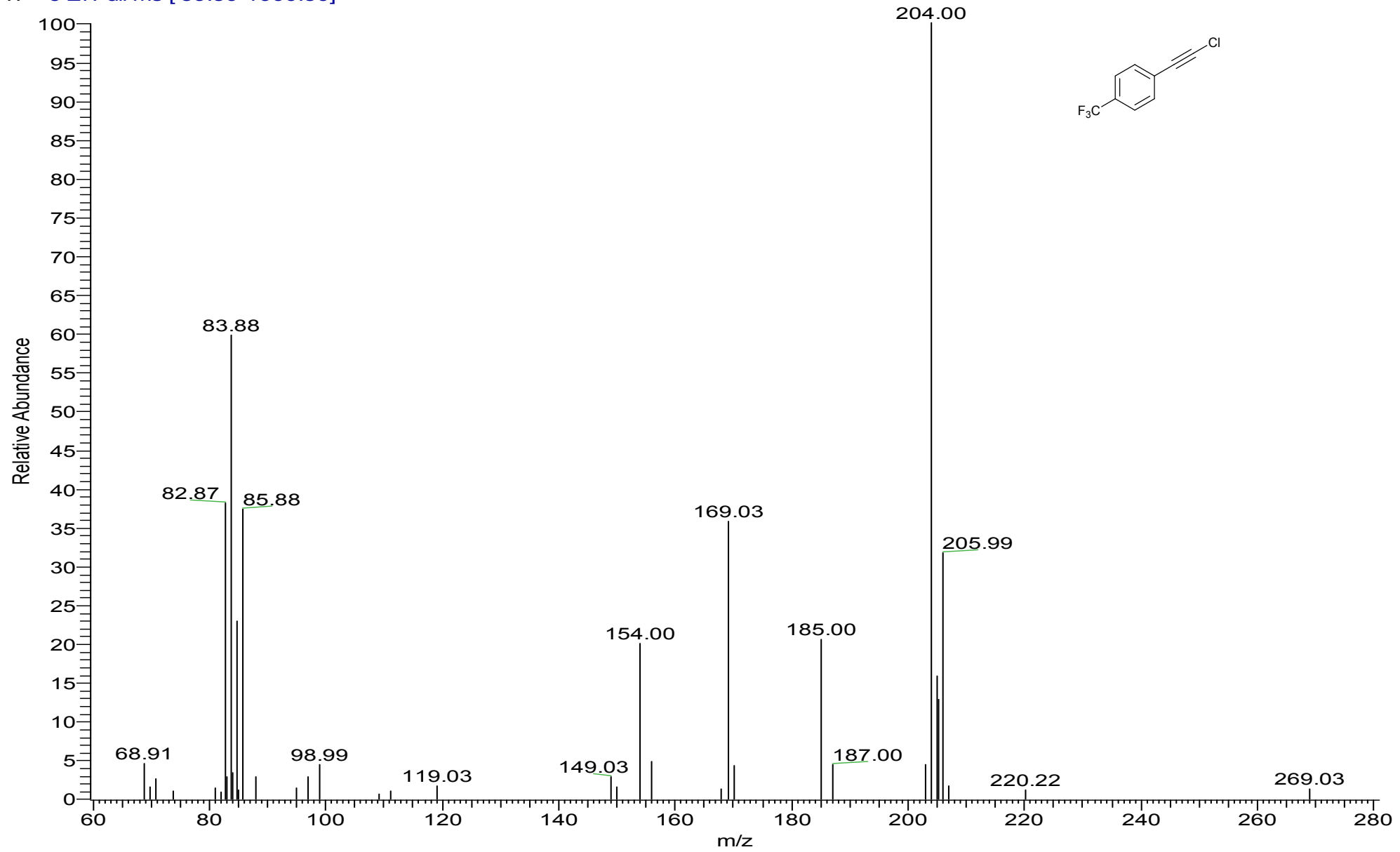

158.518
134.334
132.167
131.939
129.334
129.089
128.421
126.955
126.902
119.601
117.054
105.862
77.352
77.301
77.099
76.844
69.981
67.495
55.417
Cl
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc067_ei #1 RT: 0.21 AV: 1 NL: 1.23E5
T: + c EI Full ms [59.50-1000.50]
173.01
216.04
175.01
218.04
138.04
201.00
182.07
150.05
186.01
74.90
86.95
107.99
Relative Abundance
m/z
Cl
O

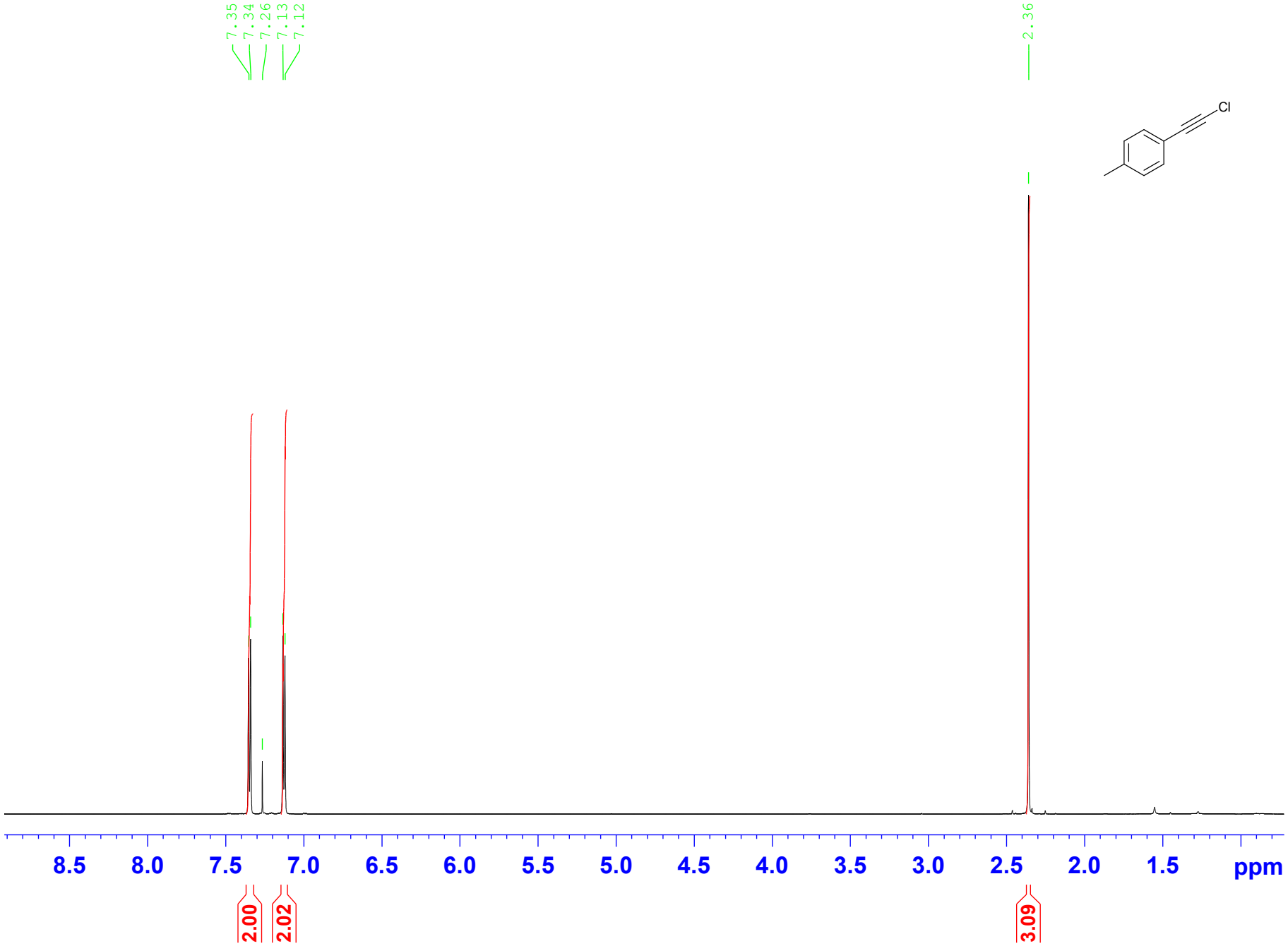
1-(chloroethynyl)-4-(trifluoromethyl)benzene (1g)

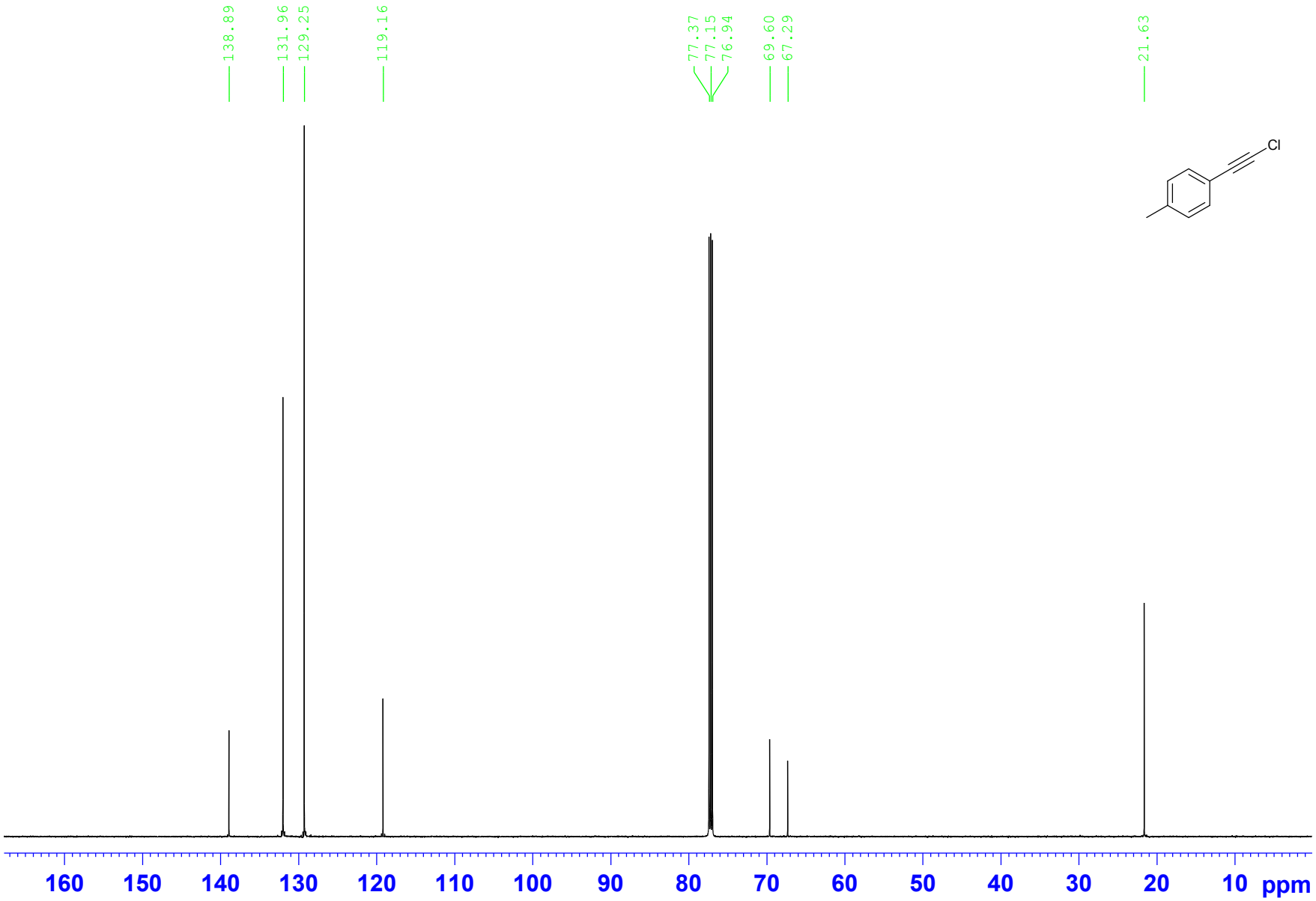


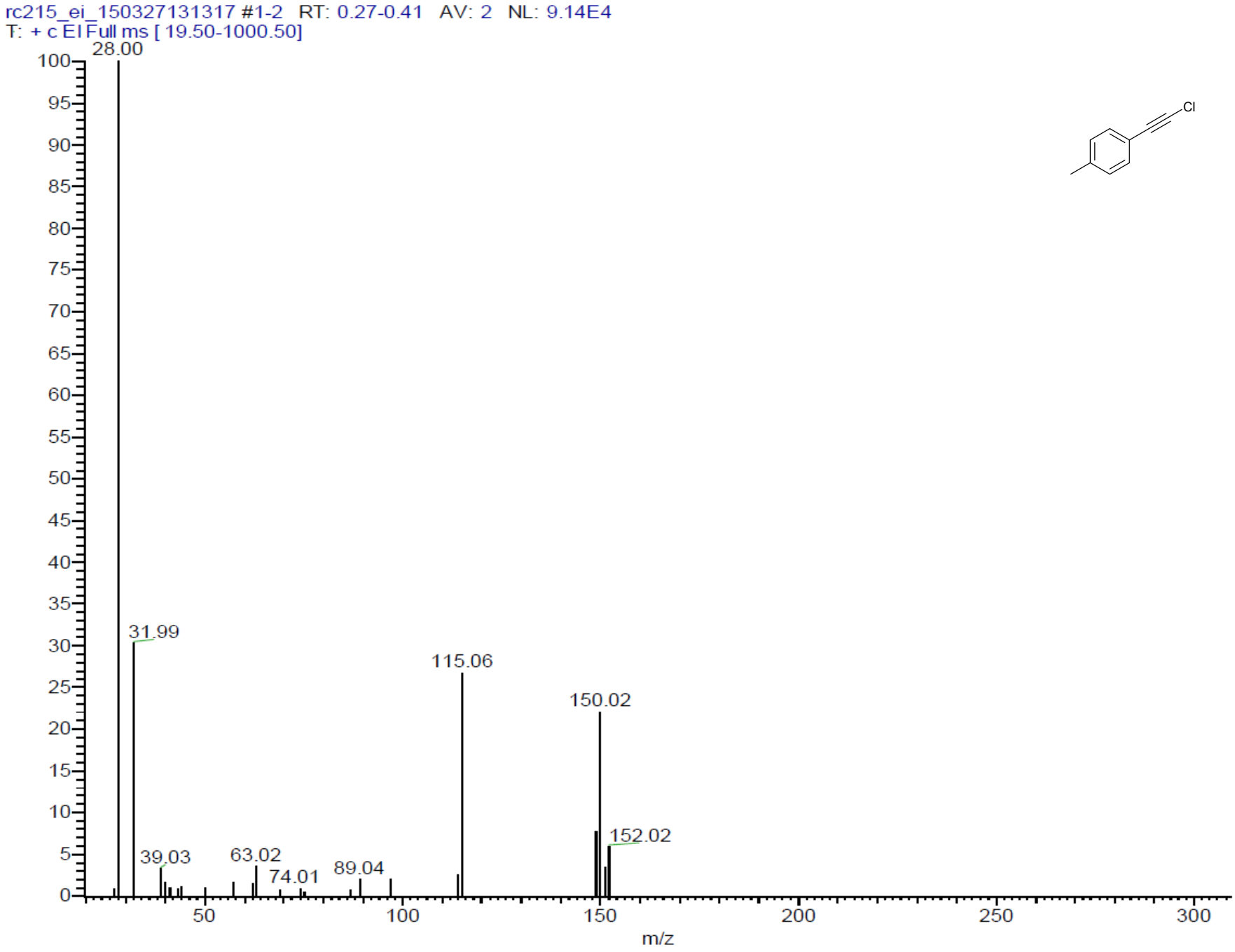

132.46
130.81
130.62
130.40
130.17
126.64
126.10
125.48
125.45
125.43
125.40
124.84
123.04
71.03
68.32
Cl
F3C
140
130
120
110
100
90
80
70
60
50
40
30
ppm


rc174_ei #2 RT: 0.25 AV: 1 NL: 4.30E4
T: + c EI Full ms [59.50-1000.50]
Relative Abundance
m/z
204.00
83.88
82.87
85.88
169.03
205.99
154.00
185.00
68.91
98.99
119.03
149.03
187.00
220.22
269.03
Cl
F3C

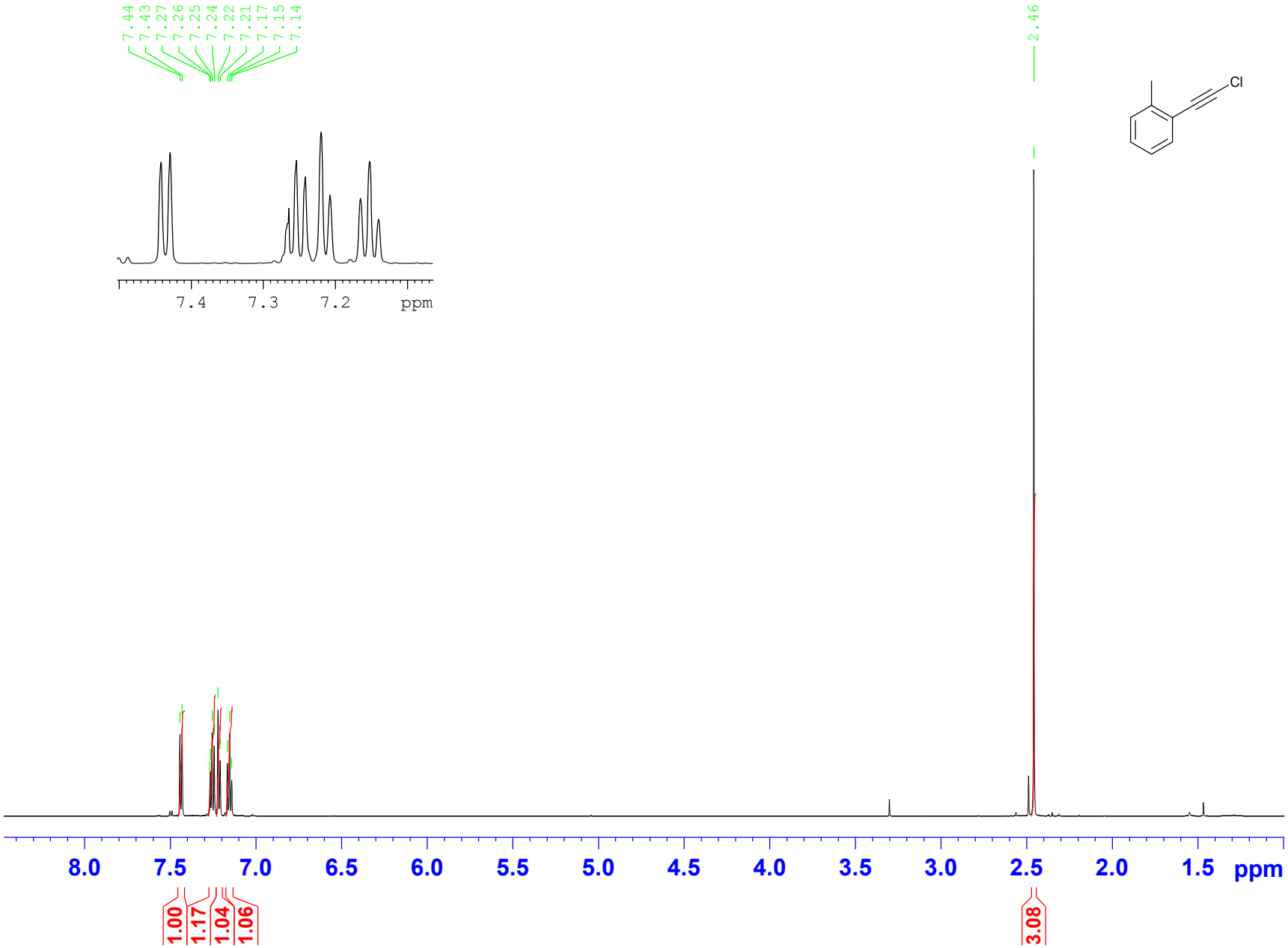
1-(chloroethynyl)-4-methylbenzene (1h)

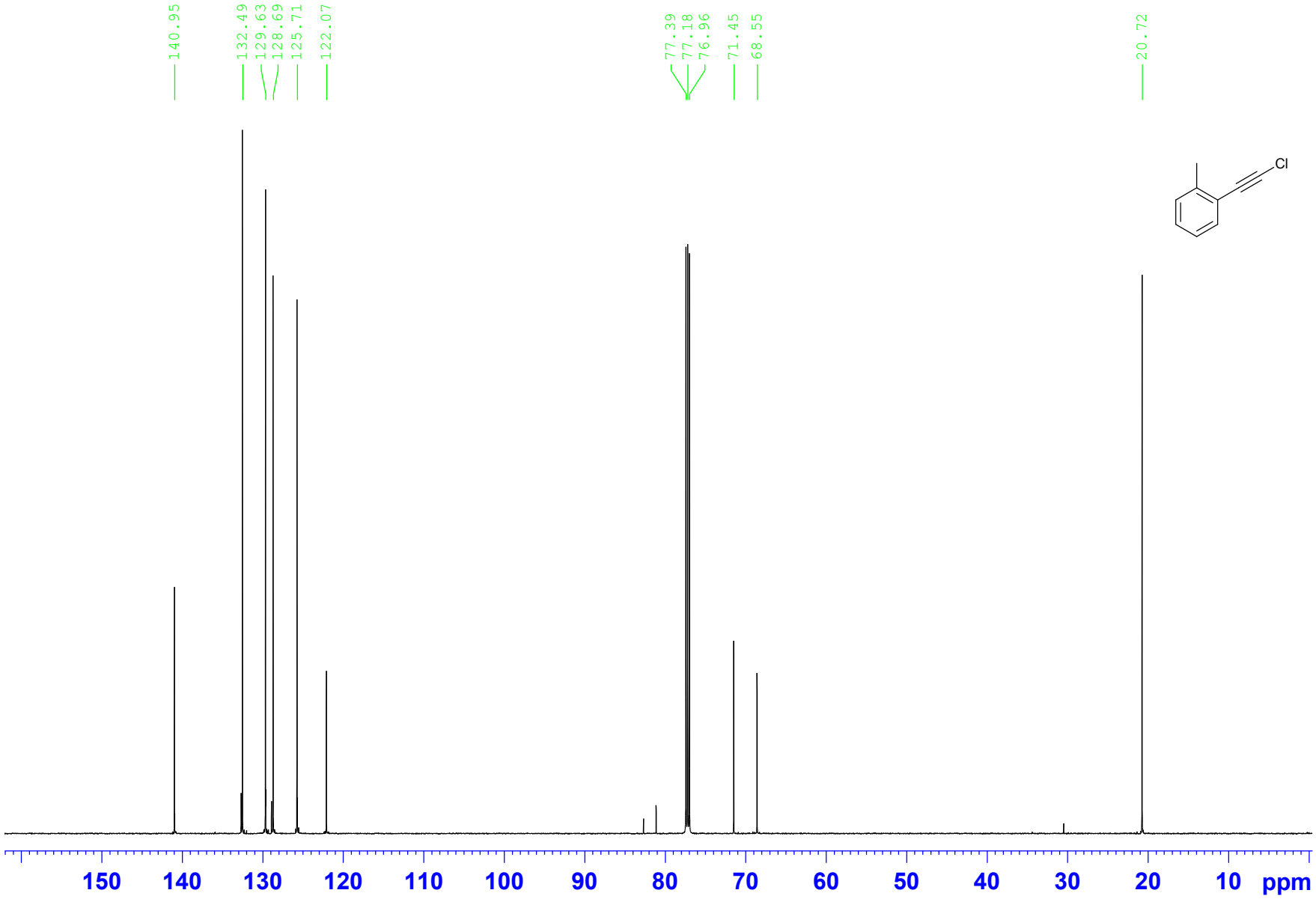


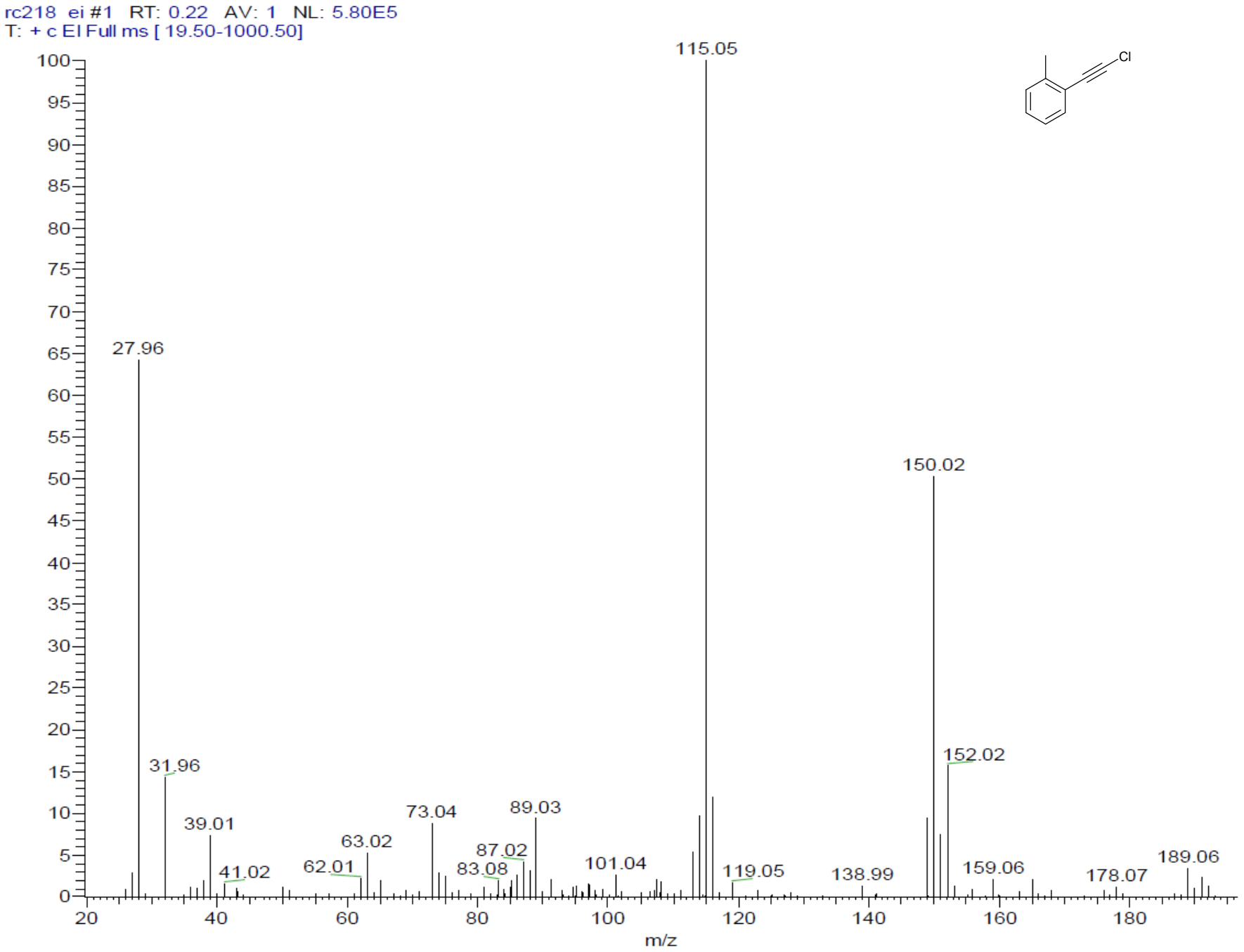

138.89
131.96
129.25
119.16
77.37
77.15
76.94
69.60
67.29
21.63
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc215_ei_150327131317 #1-2 RT: 0.27-0.41 AV: 2 NL: 9.14E4
T: + c EI Full ms [19.50-1000.50]
28.00
31.99
39.03
63.02
74.01
89.04
115.06
150.02
152.02
Cl
m/z

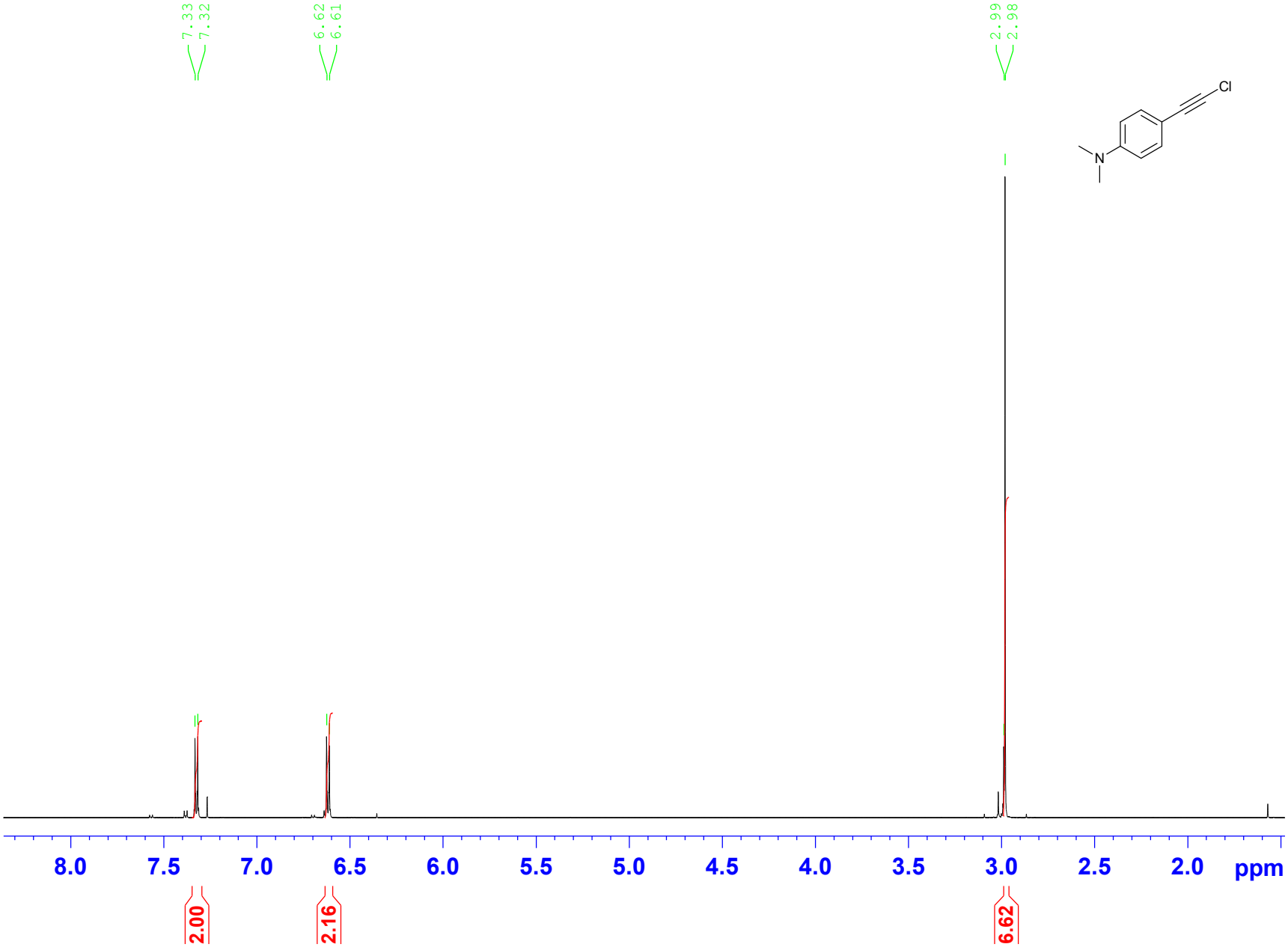
1-(chloroethynyl)-2-methylbenzene (1i)

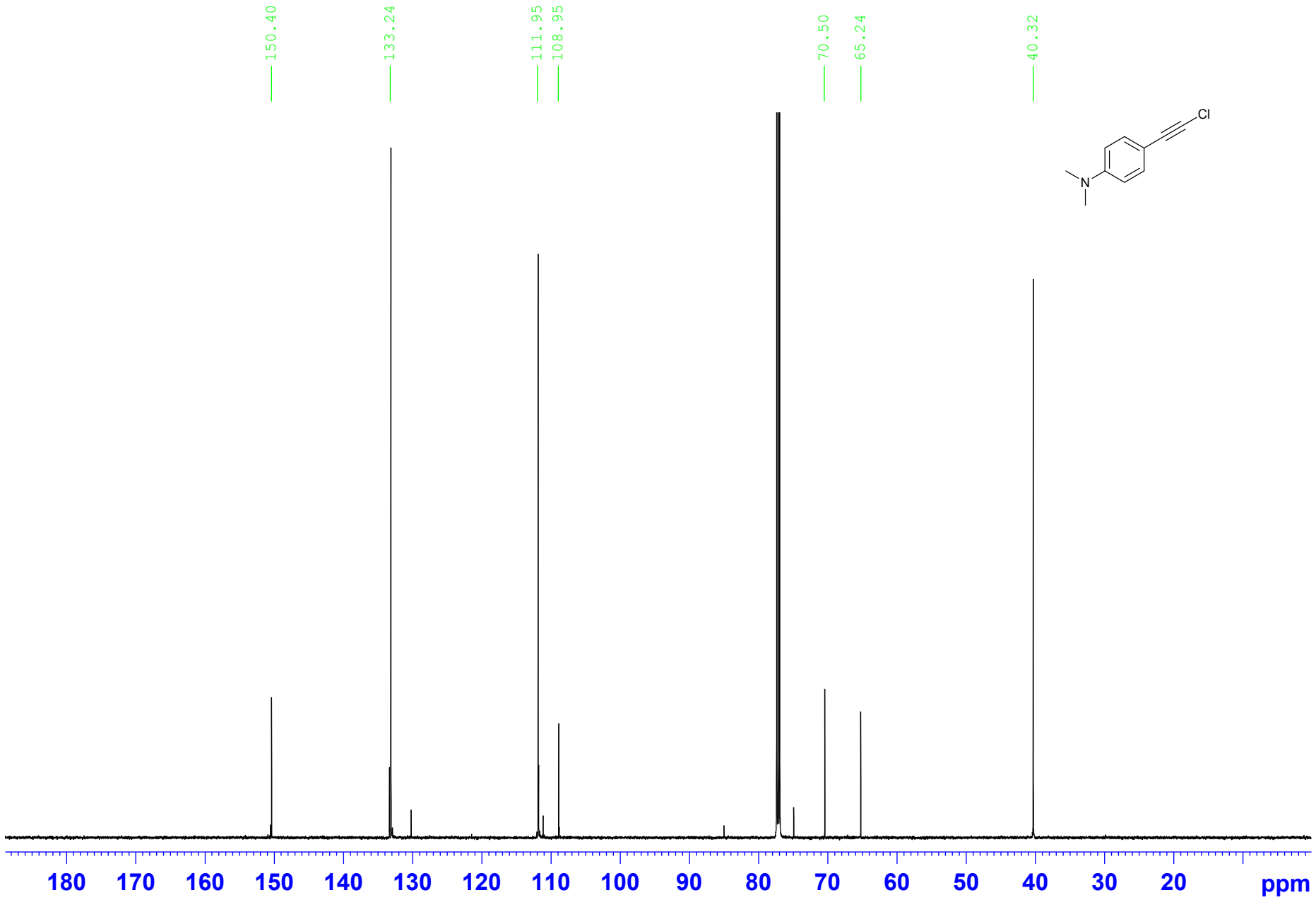


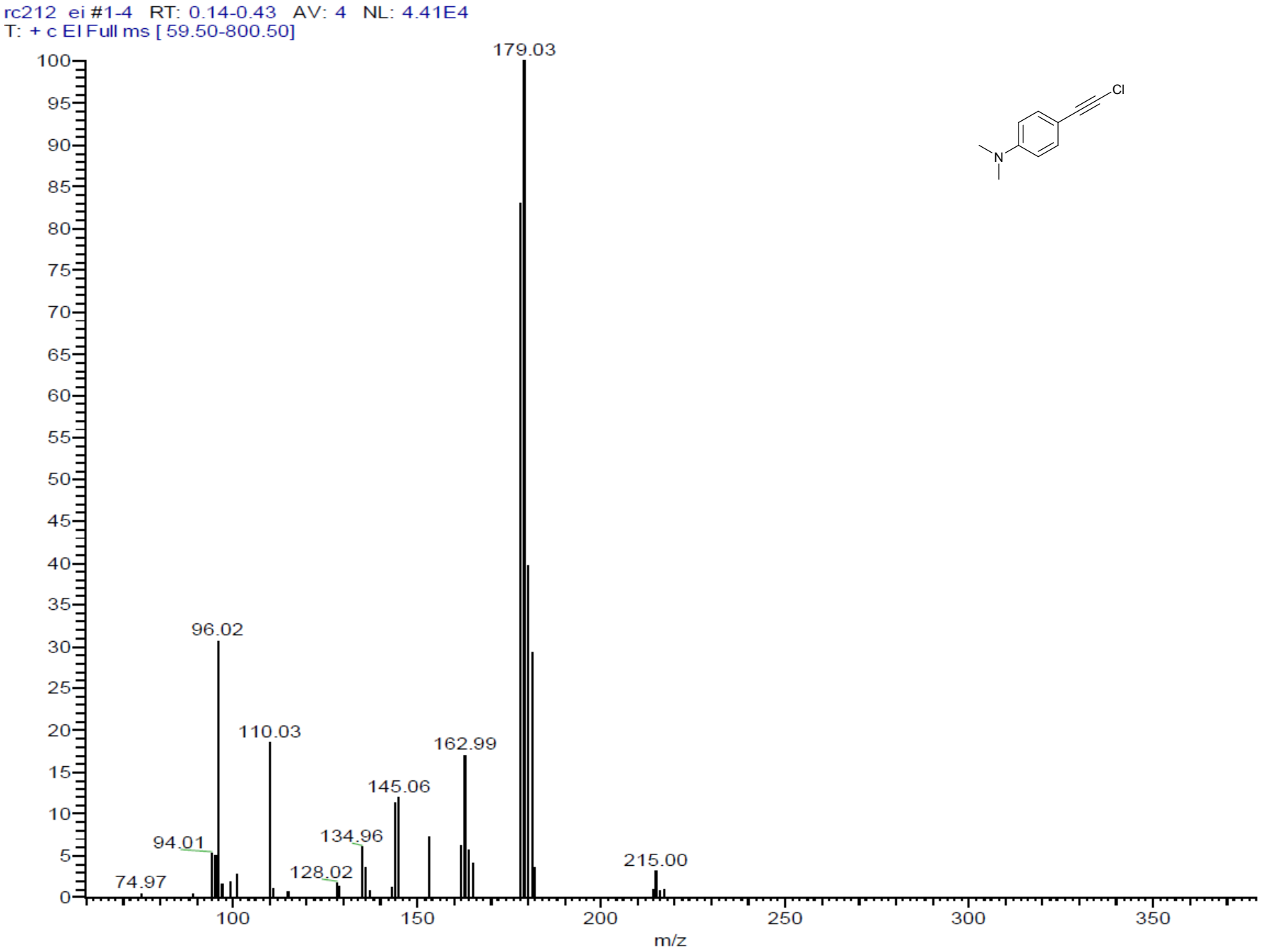

140.95
132.49
129.63
128.69
125.71
122.07
77.39
77.18
76.96
71.45
68.55
20.72
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc218 ei #1 RT: 0.22 AV: 1 NL: 5.80E5
T: + c EI Full ms [19.50-1000.50]
115.05
27.96
150.02
31.96
152.02
39.01
73.04
89.03
63.02
87.02
41.02
62.01
83.08
101.04
119.05
138.99
159.06
178.07
189.06
Cl
m/z

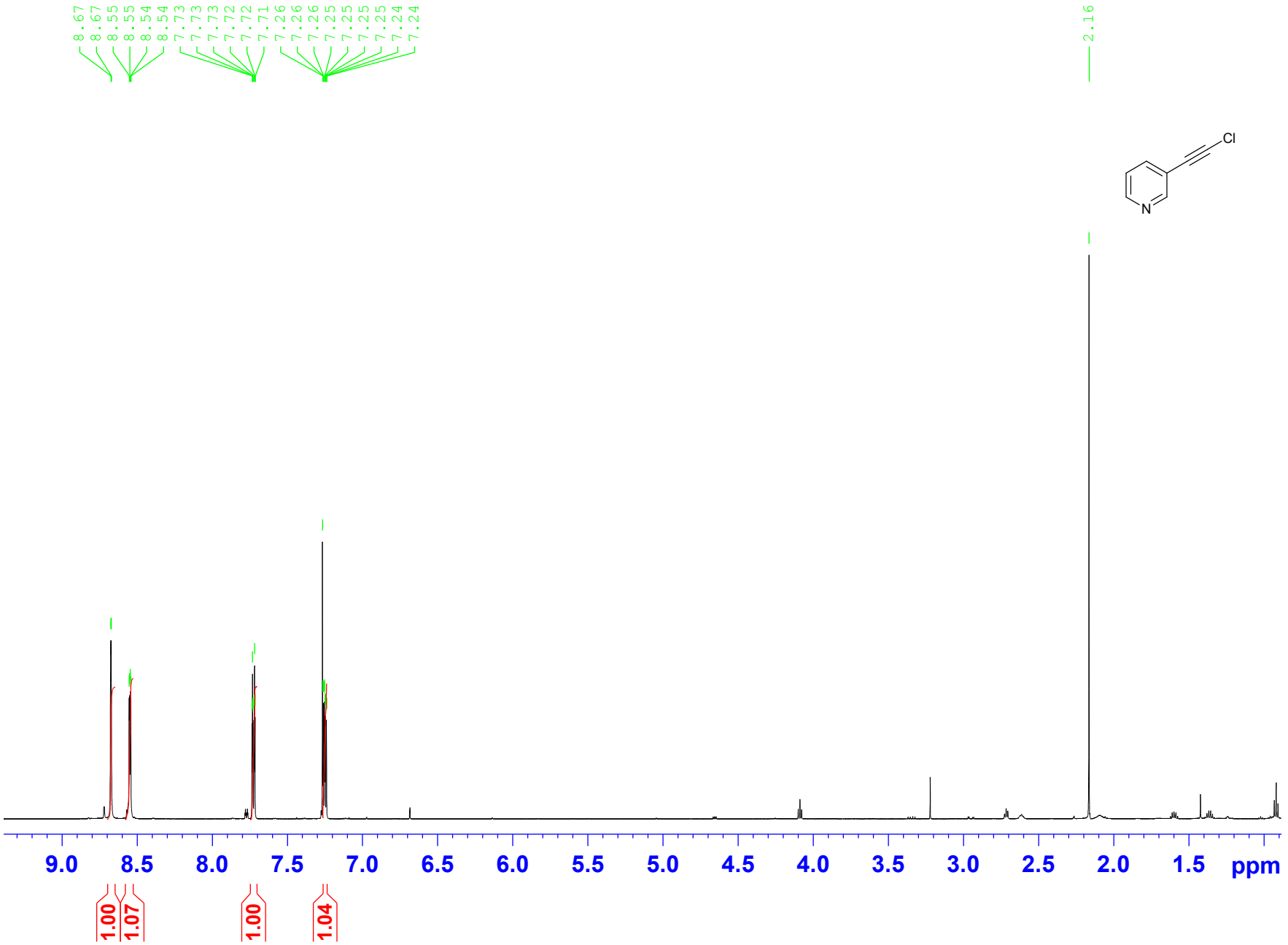
4-(chloroethynyl)-*N*,*N*-dimethylaniline (1j)

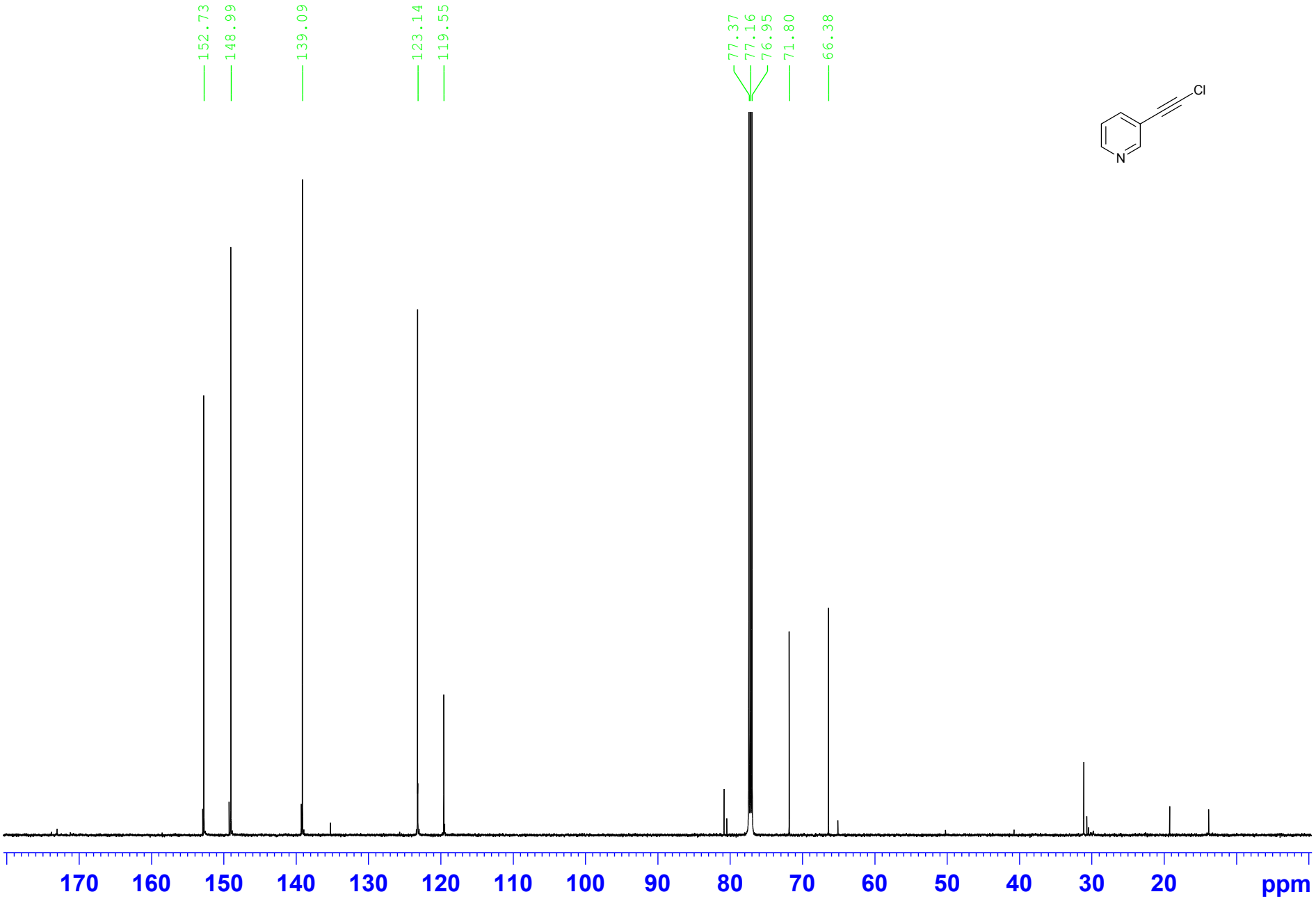


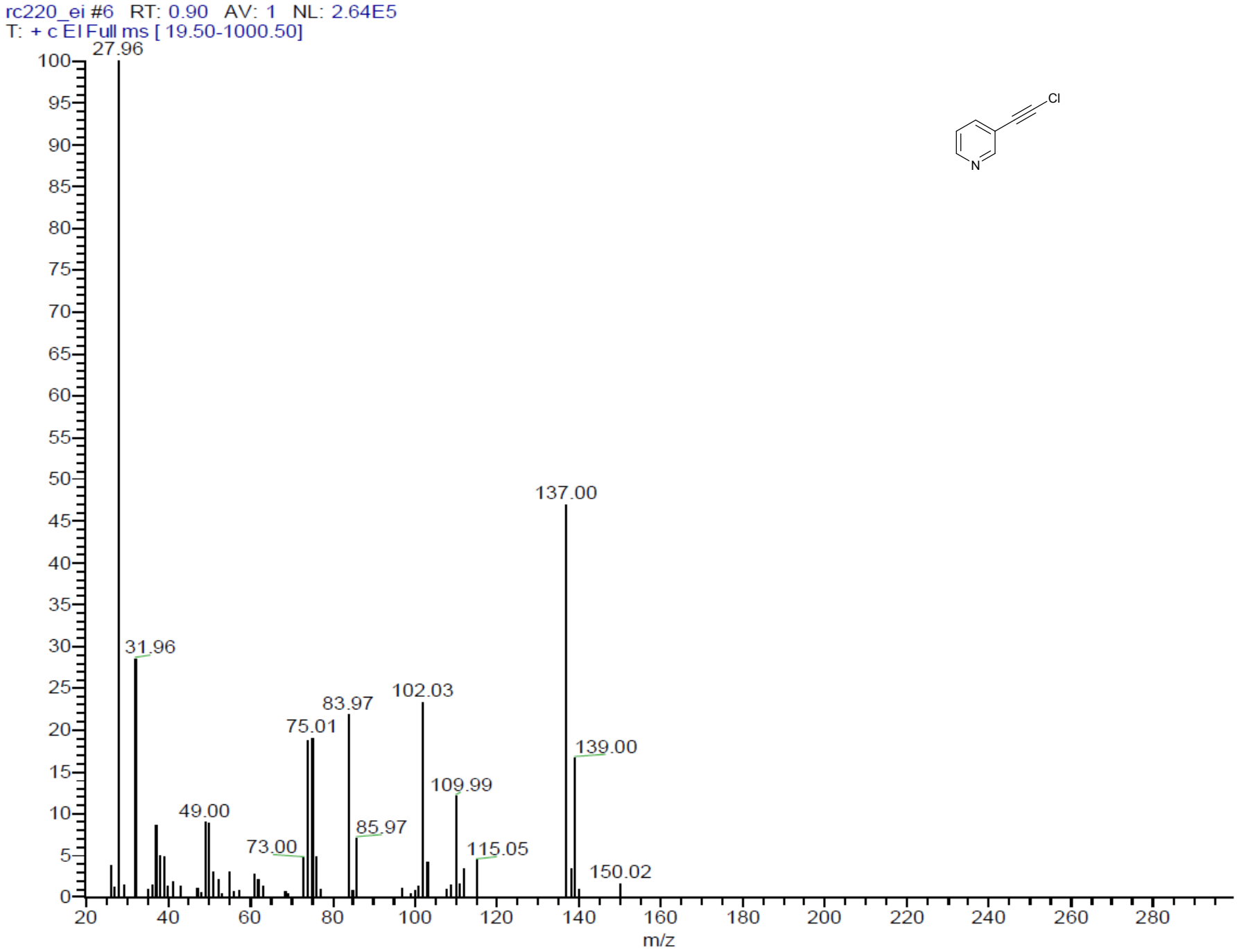

150.40
133.24
111.95
108.95
70.50
65.24
40.32
Cl
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


rc212 ei #1-4 RT: 0.14-0.43 AV: 4 NL: 4.41E4
T: + c EI Full ms [59.50-800.50]
179.03
96.02
110.03
162.99
145.06
134.96
94.01
128.02
74.97
215.00
Cl
N
m/z

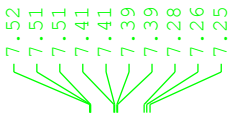
3-(chloroethynyl)pyridine (1k)

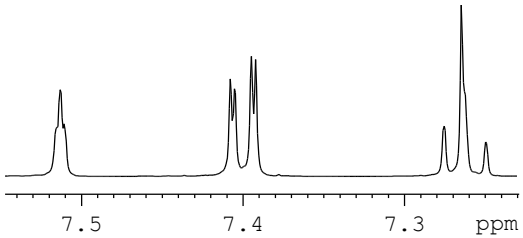


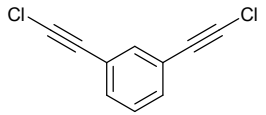

152.73
148.99
139.09
123.14
119.55
77.37
77.16
76.95
71.80
66.38
Cl
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

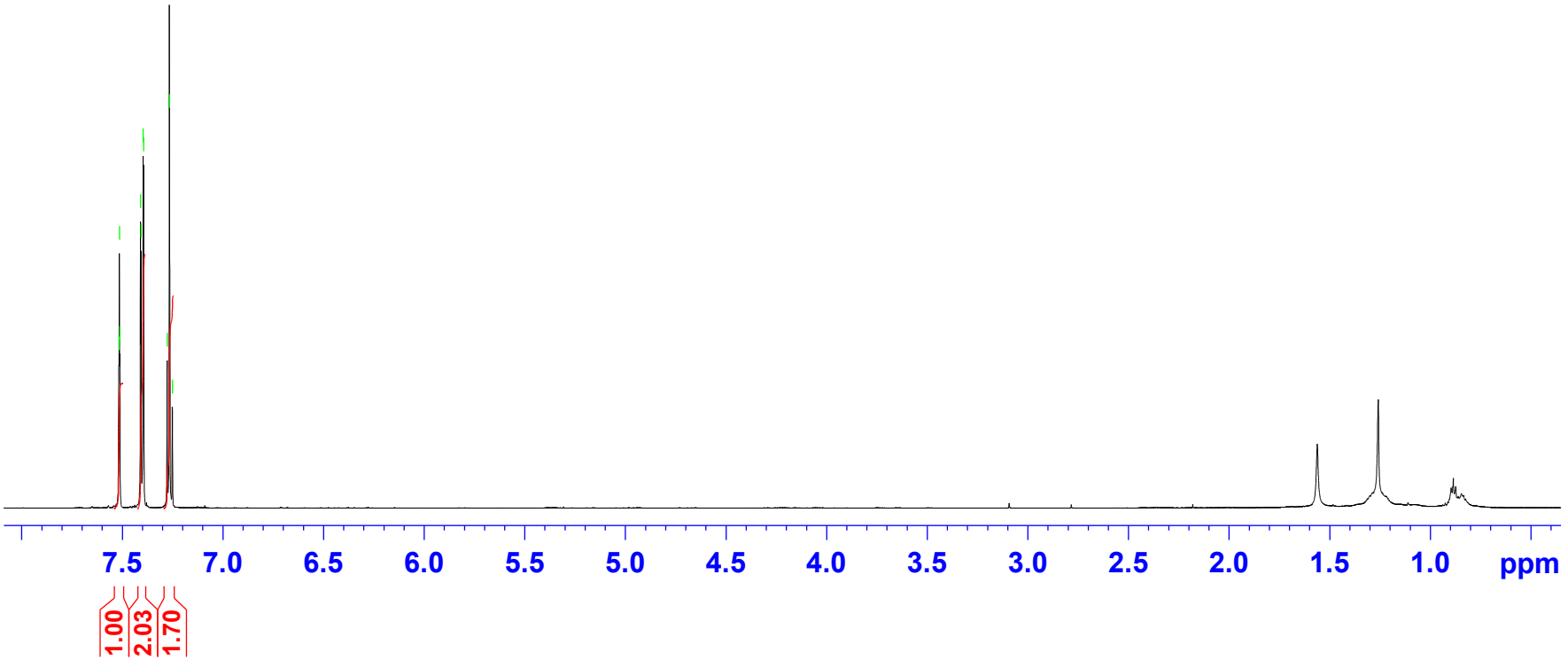

rc220_ei #6 RT: 0.90 AV: 1 NL: 2.64E5
T: + c EI Full ms [19.50-1000.50]
27.96
31.96
49.00
73.00
75.01
83.97
85.97
102.03
109.99
115.05
137.00
139.00
150.02
Cl
N
m/z

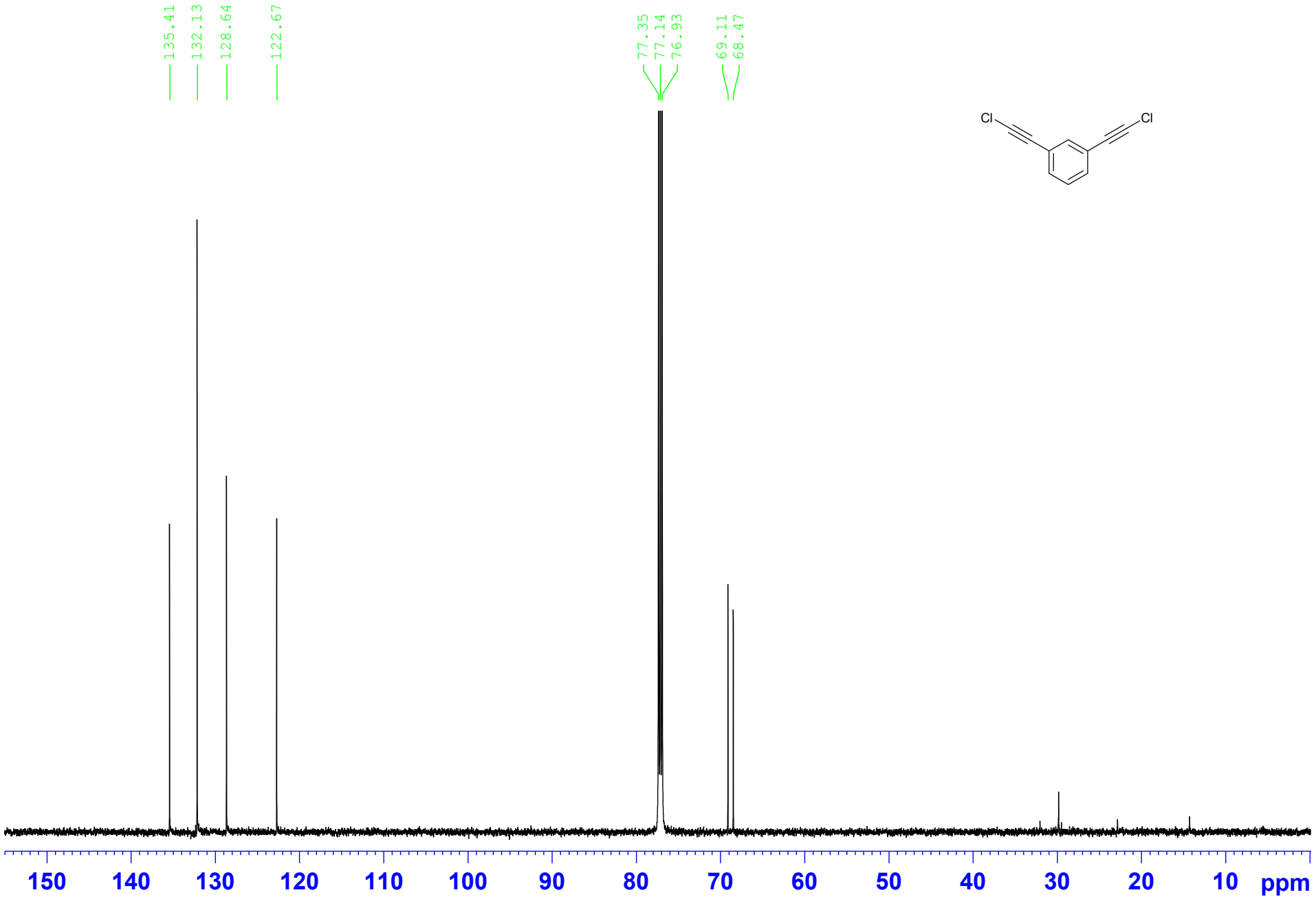
1,3-bis(chloroethynyl)benzene (1l)

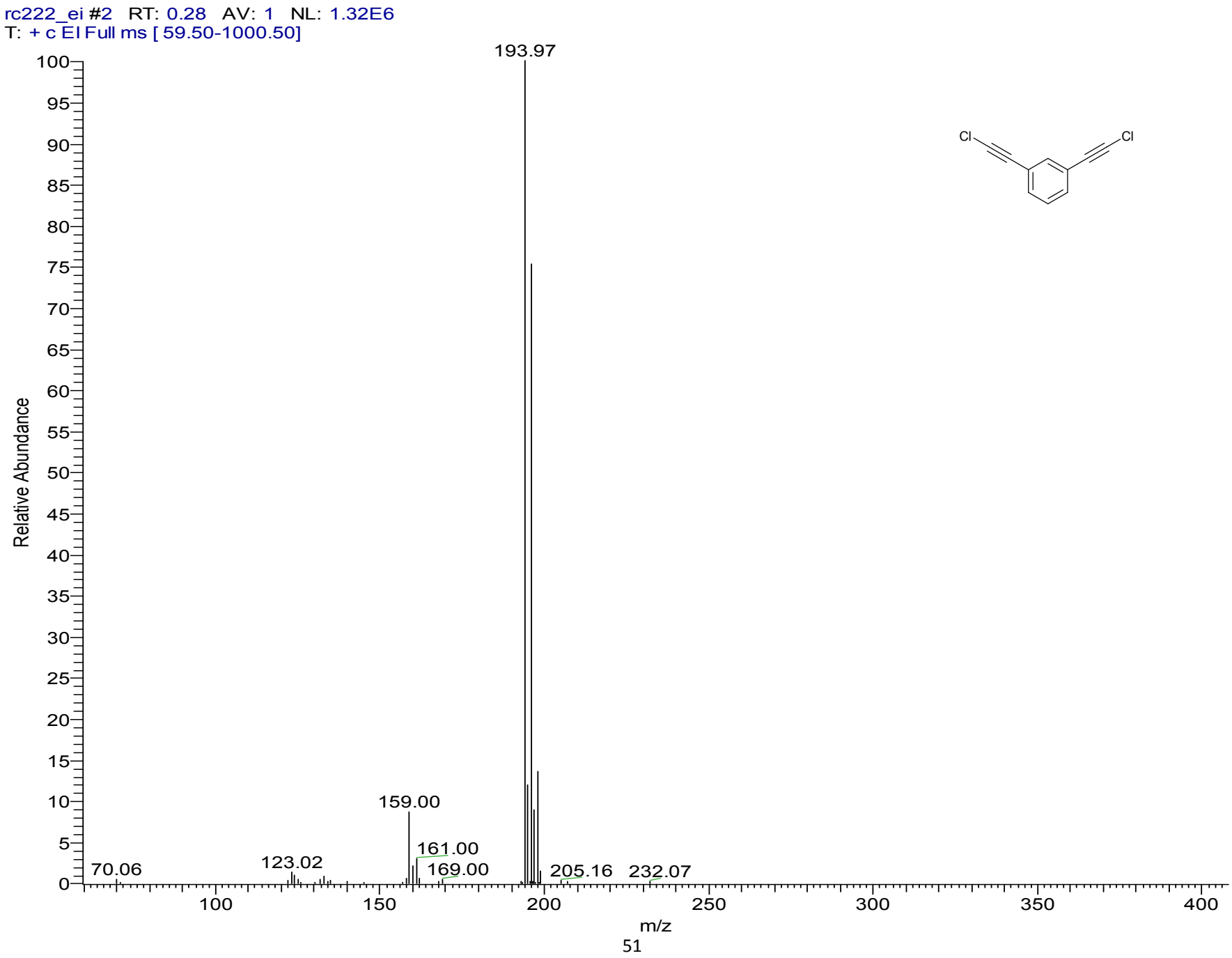




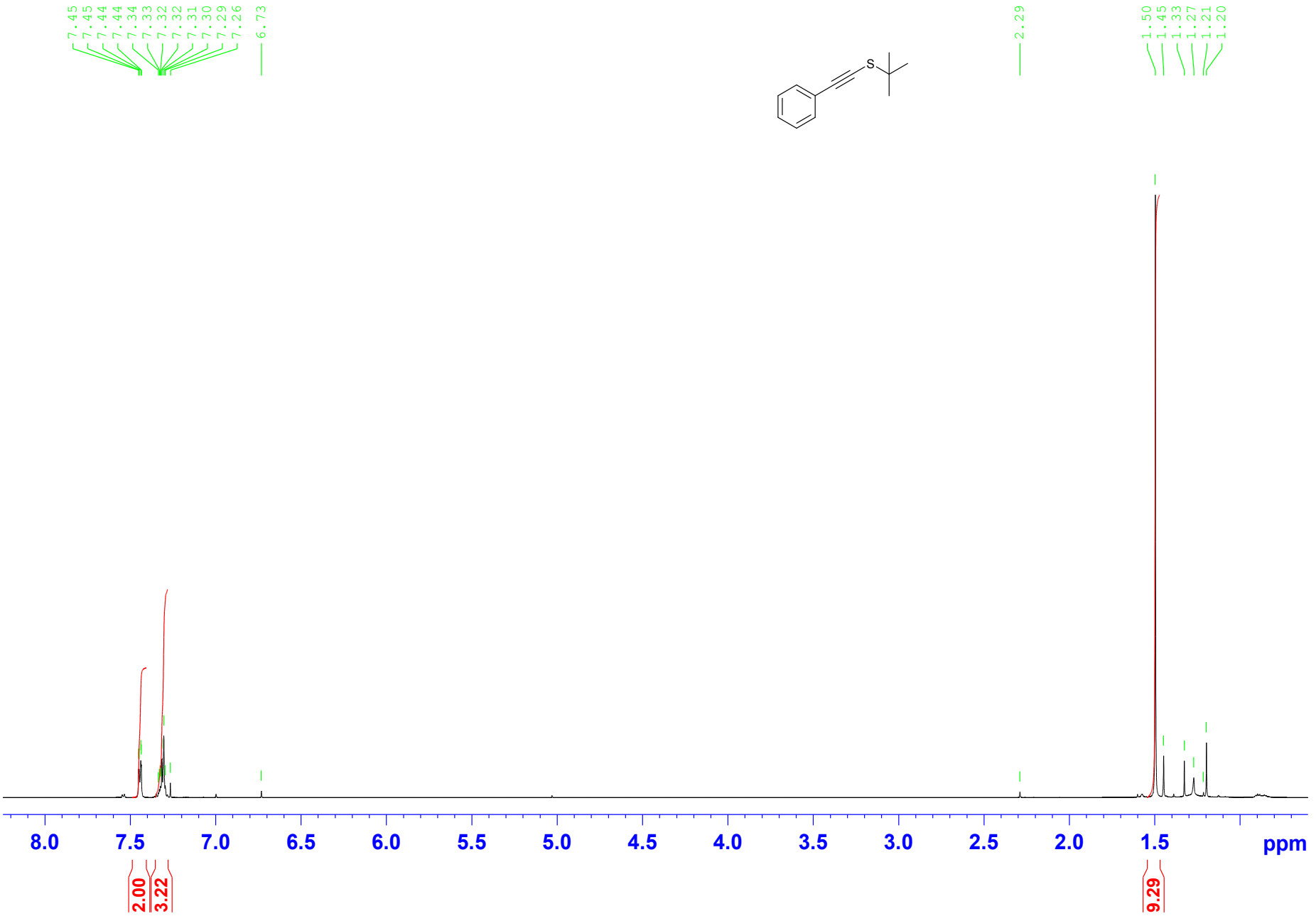


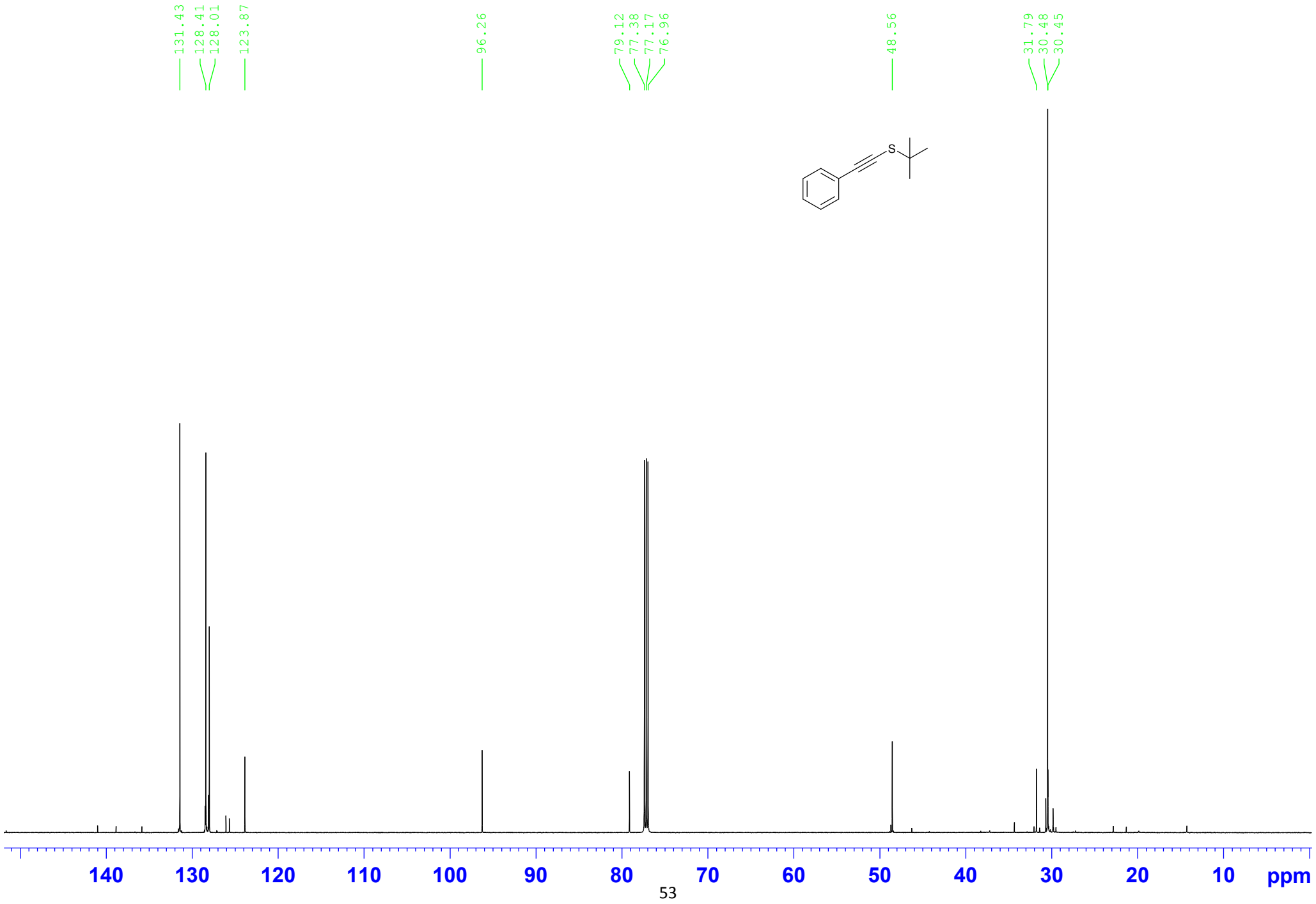



135.41
132.13
128.64
122.67
77.35
77.14
76.93
69.11
68.47
Cl
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

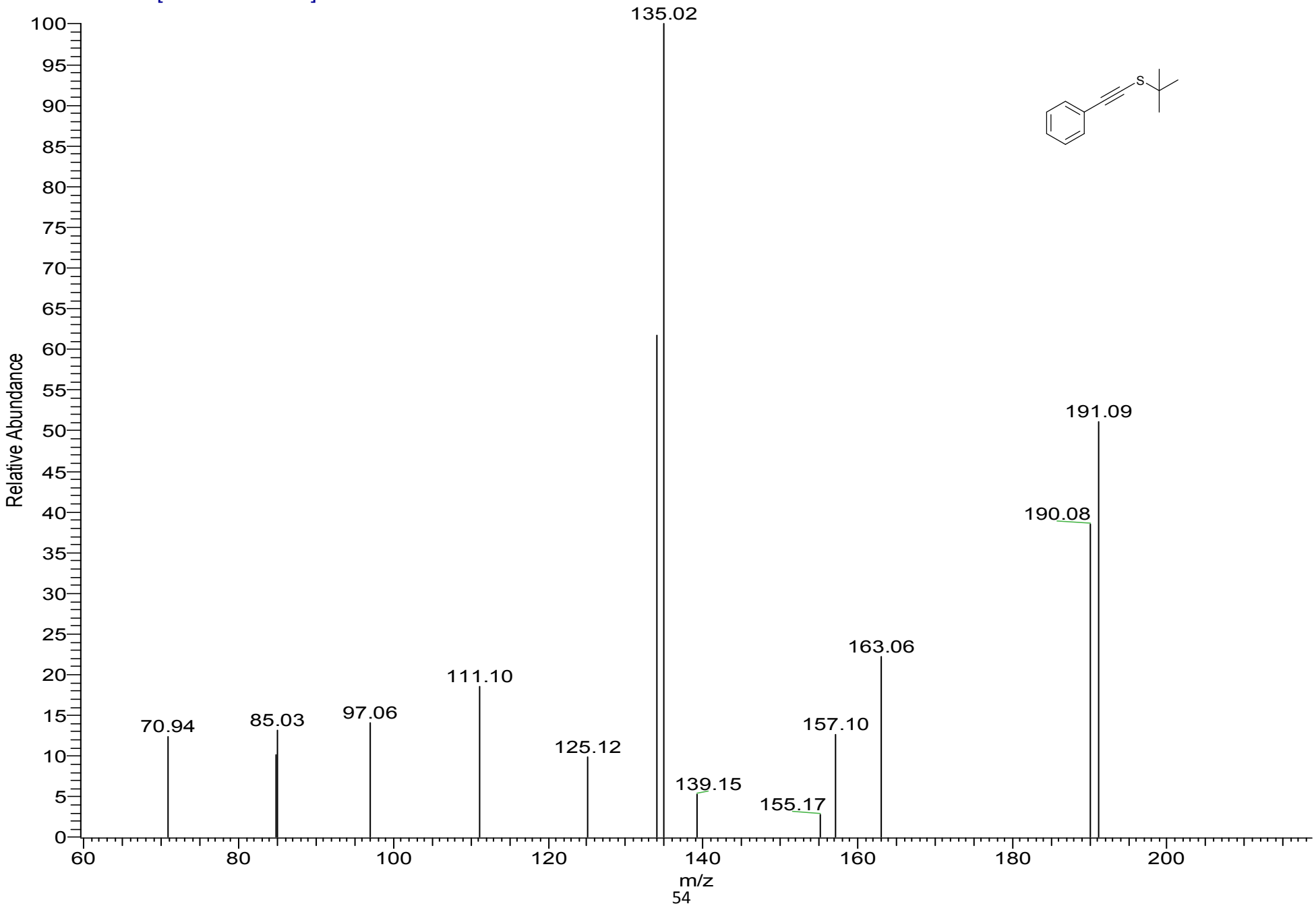

rc222_ei #2 RT: 0.28 AV: 1 NL: 1.32E6
T: + c EI Full ms [59.50-1000.50]
193.97
159.00
161.00
169.00
123.02
70.06
205.16
232.07
Cl
Cl
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
100
150
200
250
300
350
400

***Tert*-butyl(phenylethynyl)sulfane (2a)**

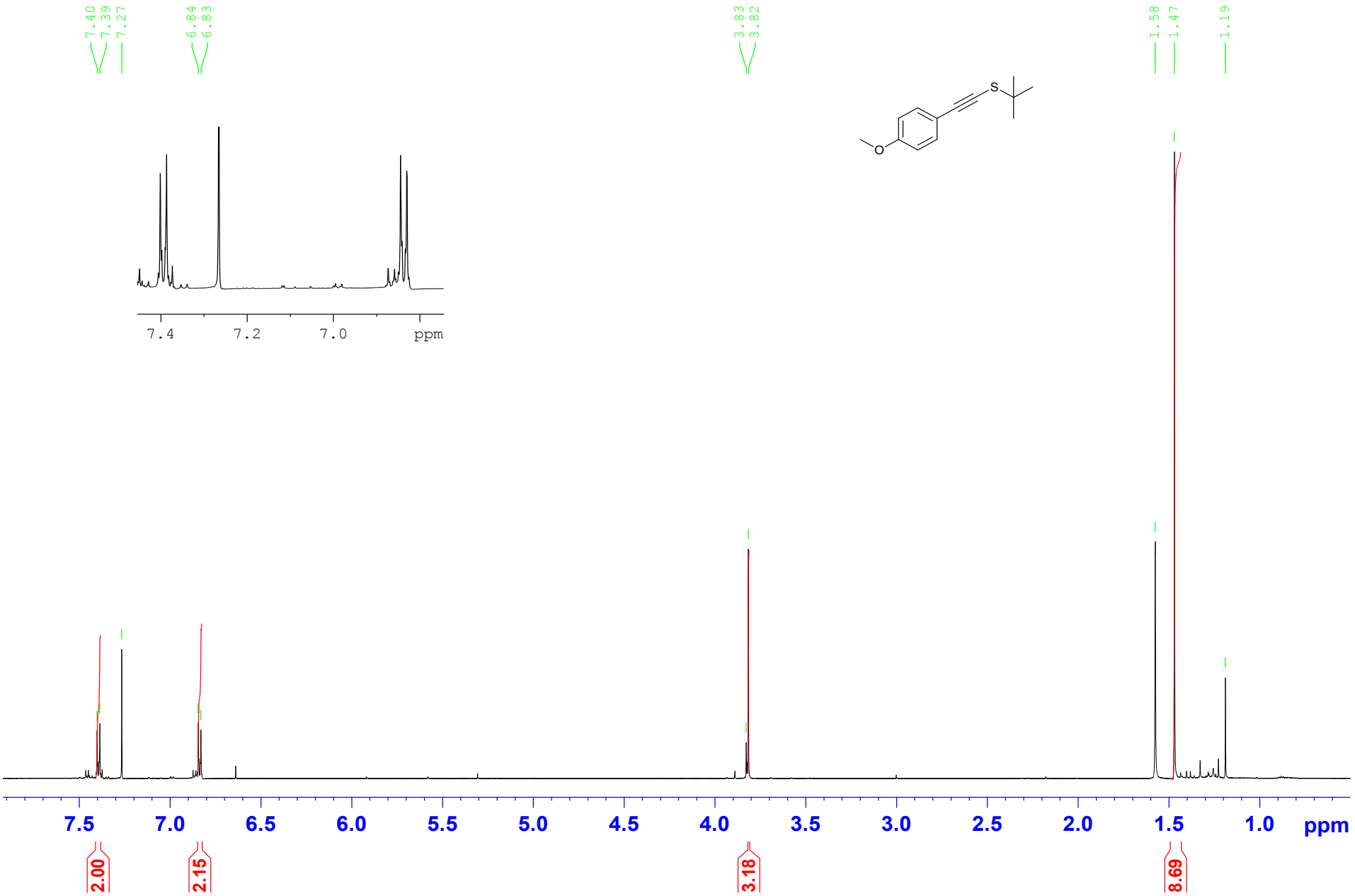


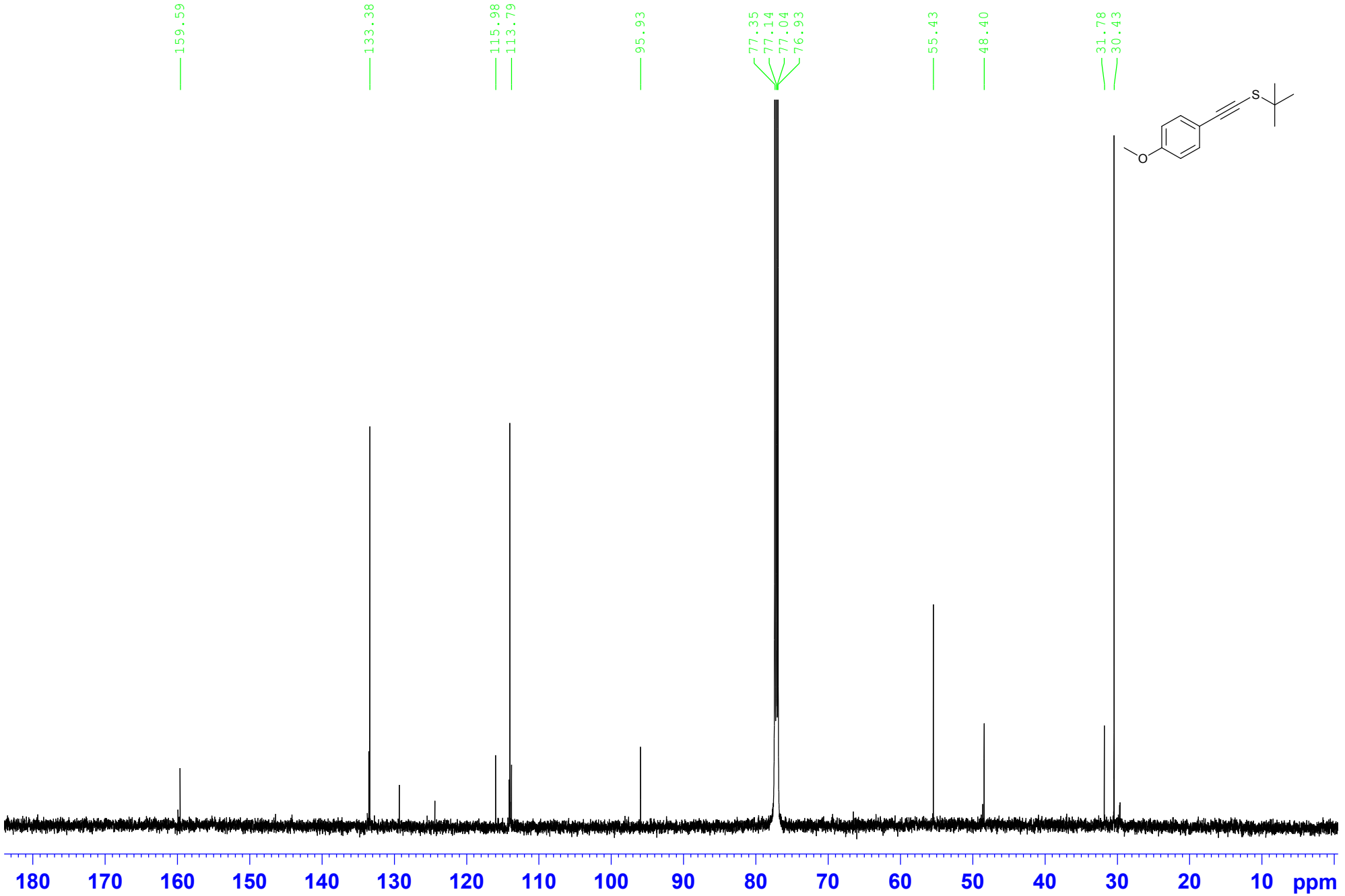

131.43
128.41
128.01
123.87
96.26
79.12
77.38
77.17
76.96
48.56
31.79
30.48
30.45
S
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc157_ci #2 RT: 0.23 AV: 1 NL: 1.04E4
T: + c CI Full ms [59.50-1000.50]

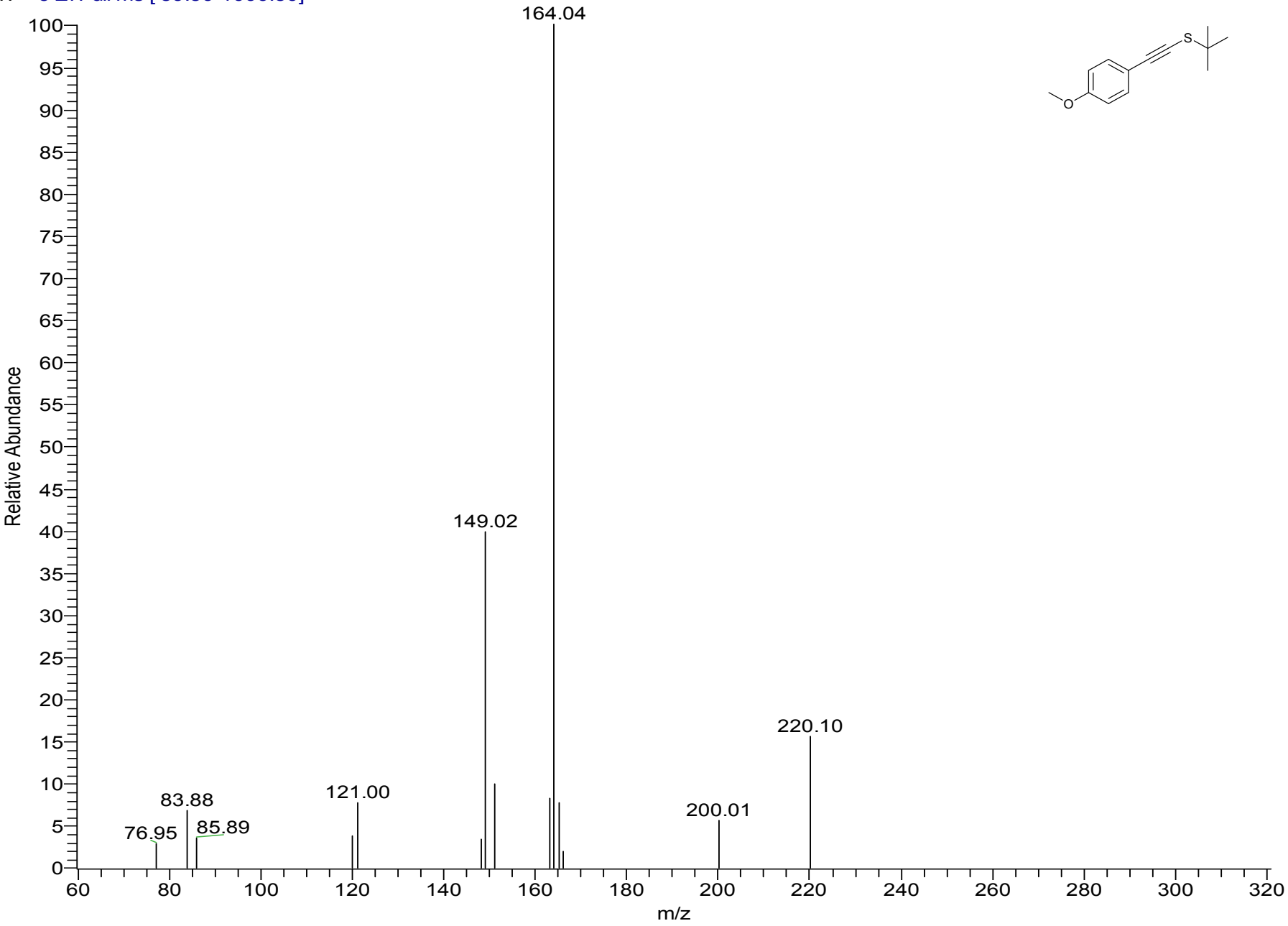


***Tert*-butyl((4-methoxyphenyl)ethynyl)sulfane (2b)**

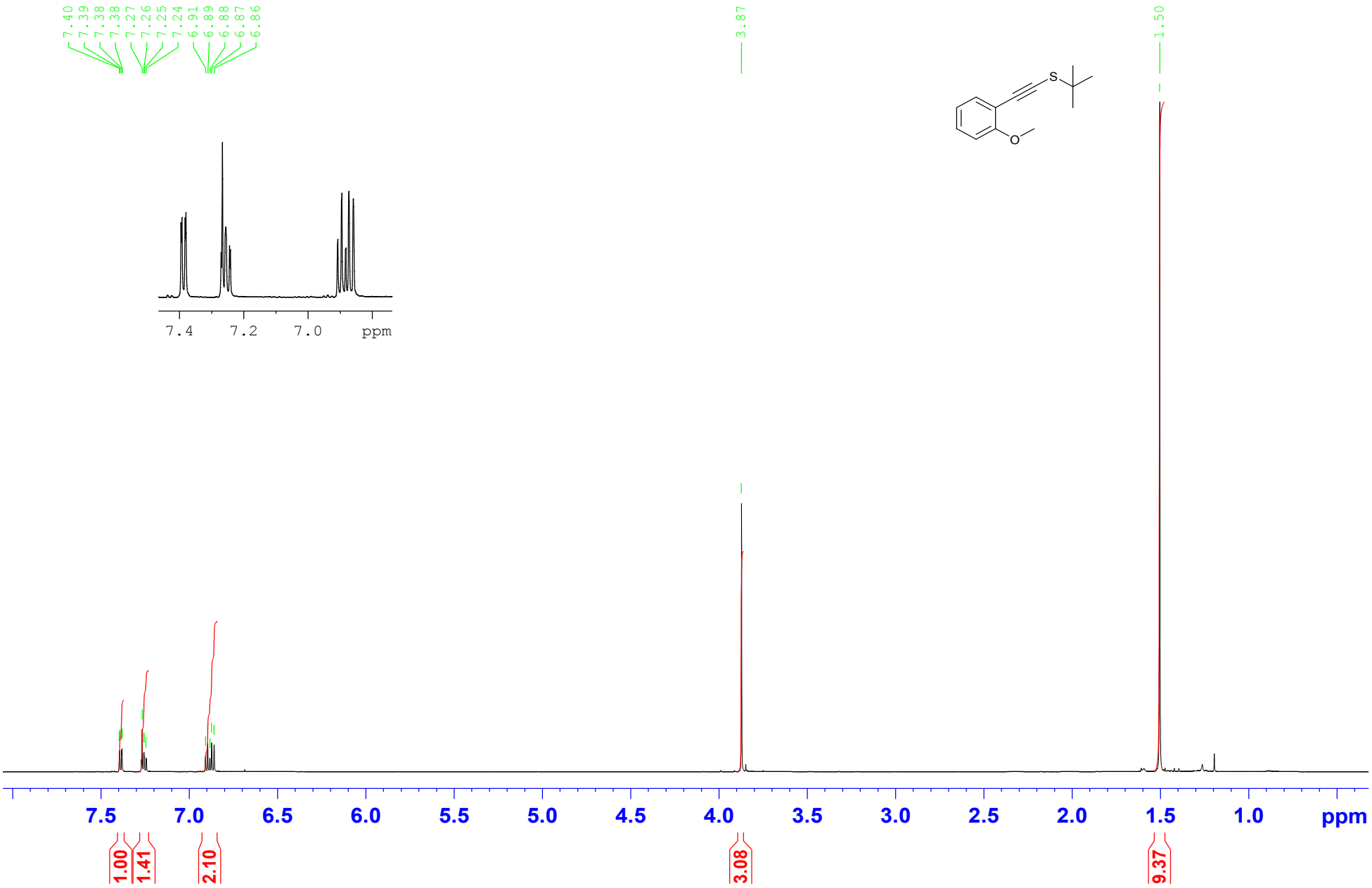


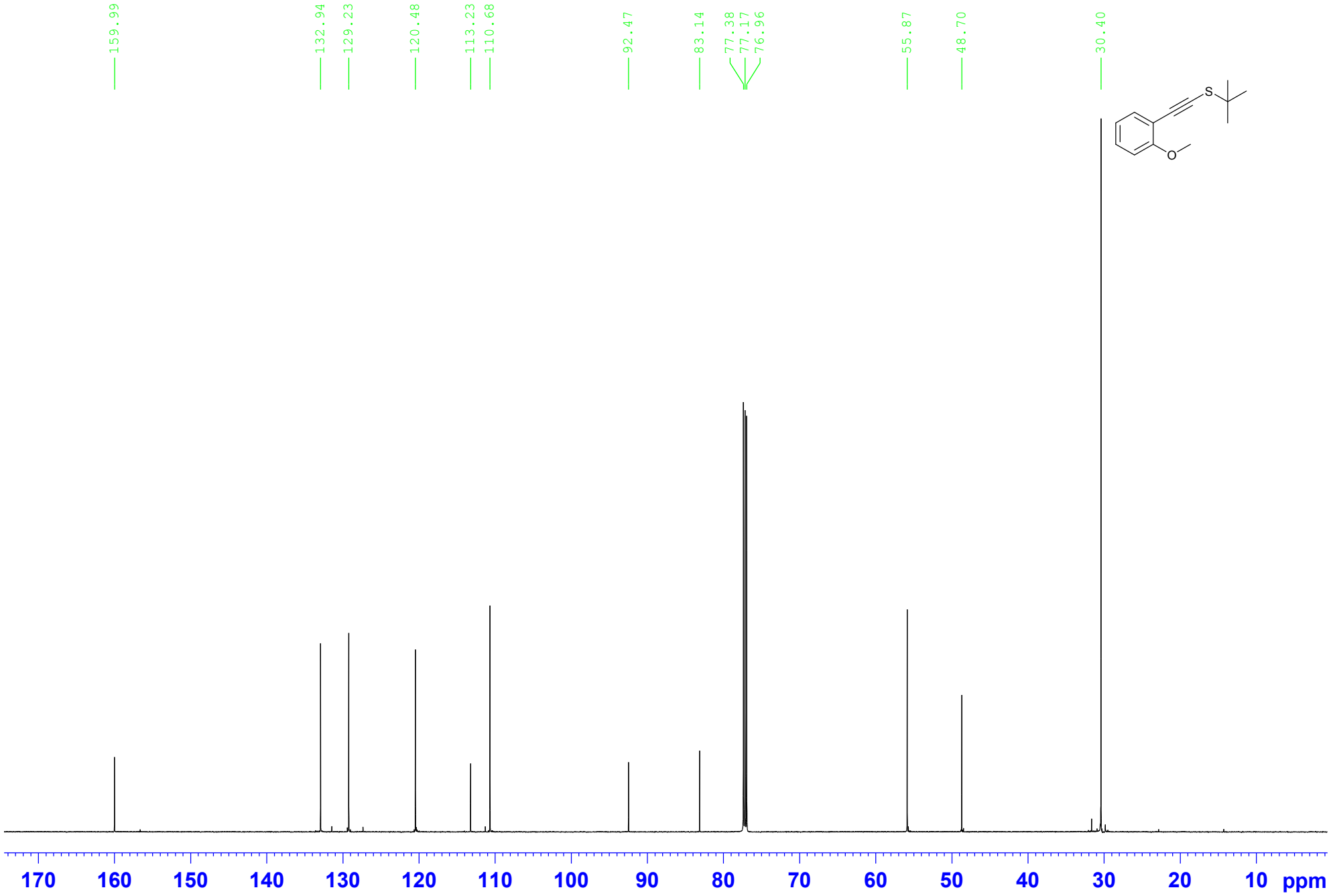

159.59
133.38
115.98
113.79
95.93
77.35
77.14
77.04
76.93
55.43
48.40
31.78
30.43
S
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc166c_ei_140913125921 #1 RT: 0.12 AV: 1 NL: 3.02E4
T: + c EI Full ms [59.50-1000.50]

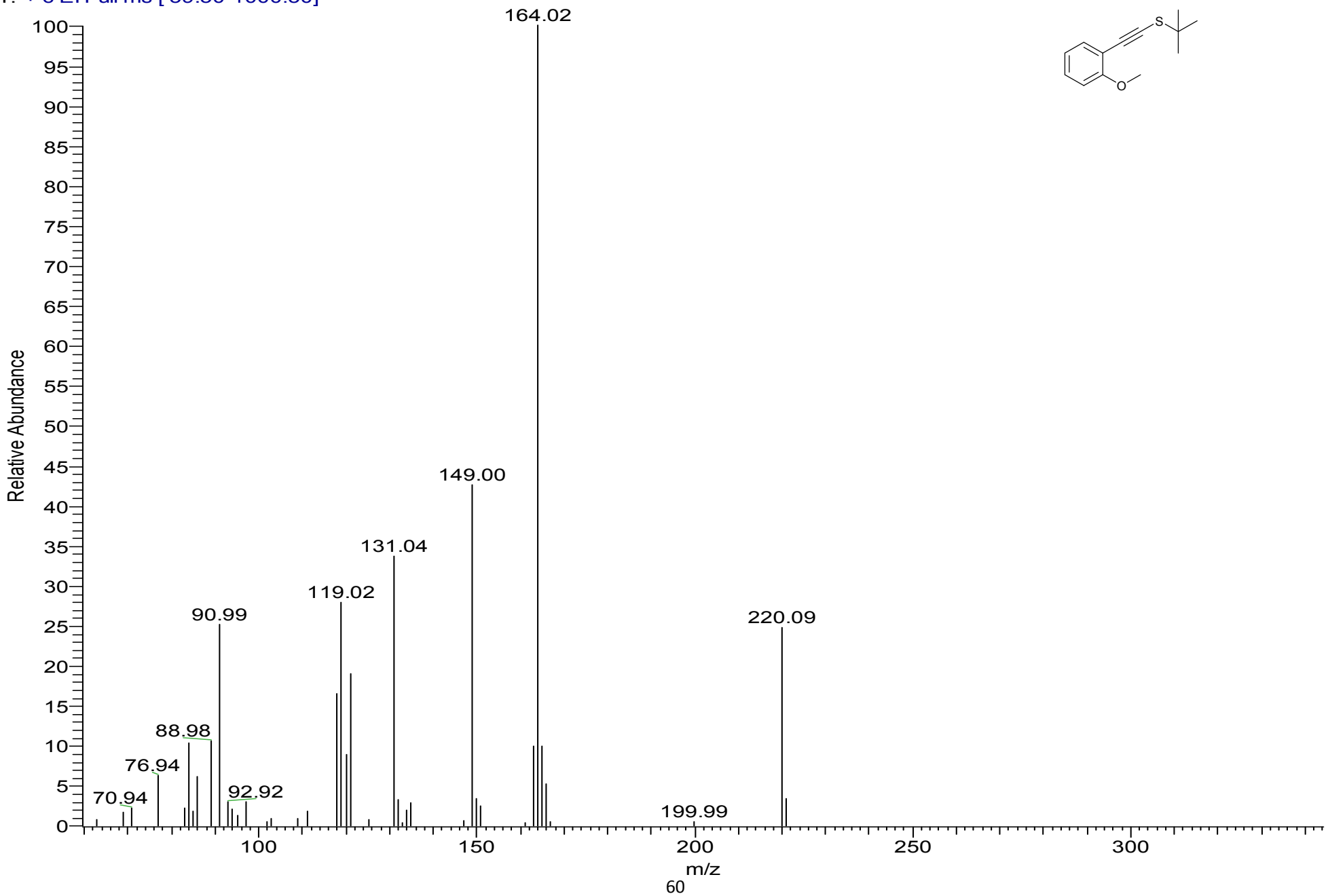


***Tert*-butyl((2-methoxyphenyl)ethynyl)sulfane (2c)**

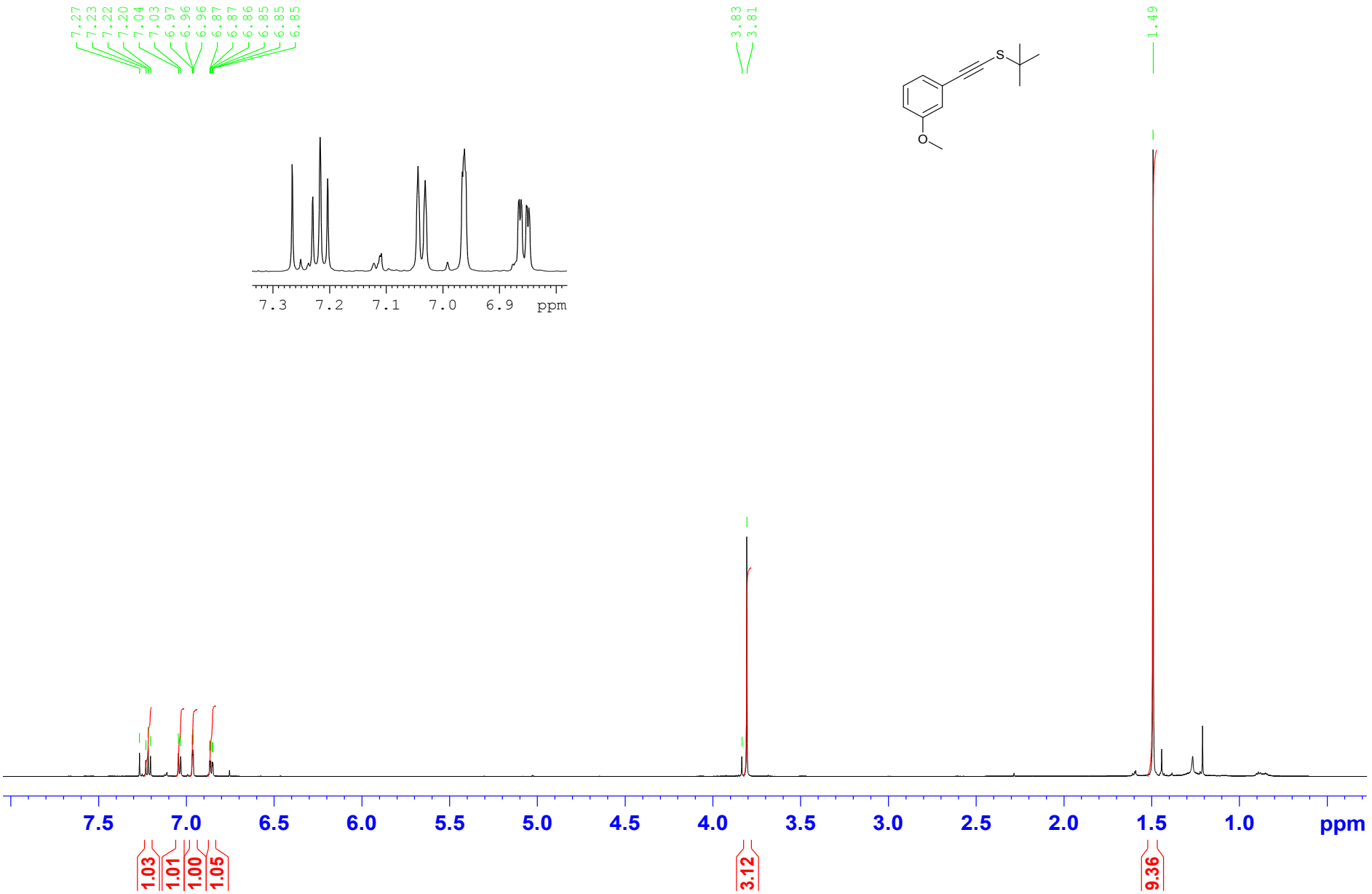


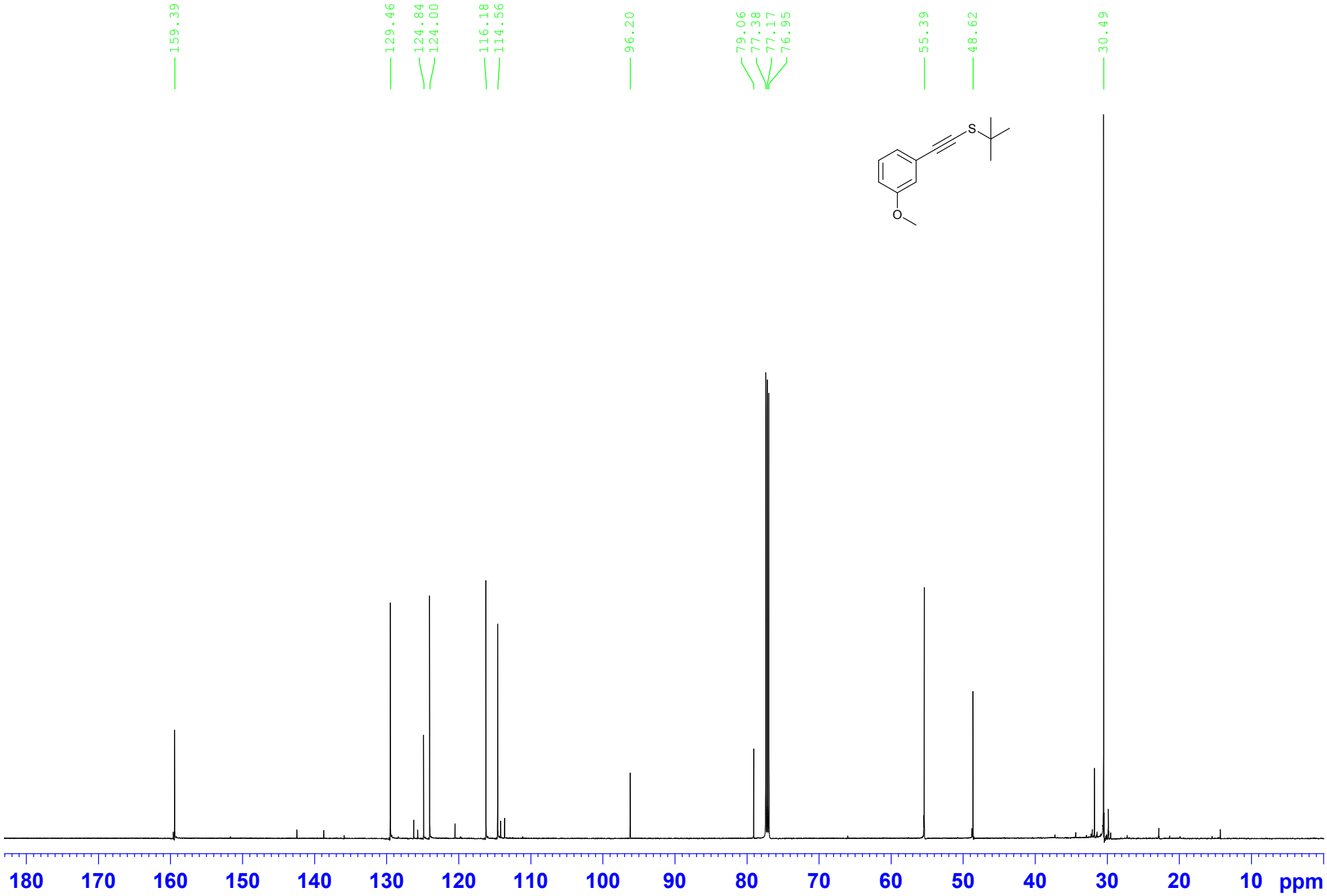

159.99
132.94
129.23
120.48
113.23
110.68
92.47
83.14
77.38
77.17
76.96
55.87
48.70
30.40
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc161b_ei #3 RT: 0.37 AV: 1 NL: 6.50E4
T: + c EI Full ms [59.50-1000.50]

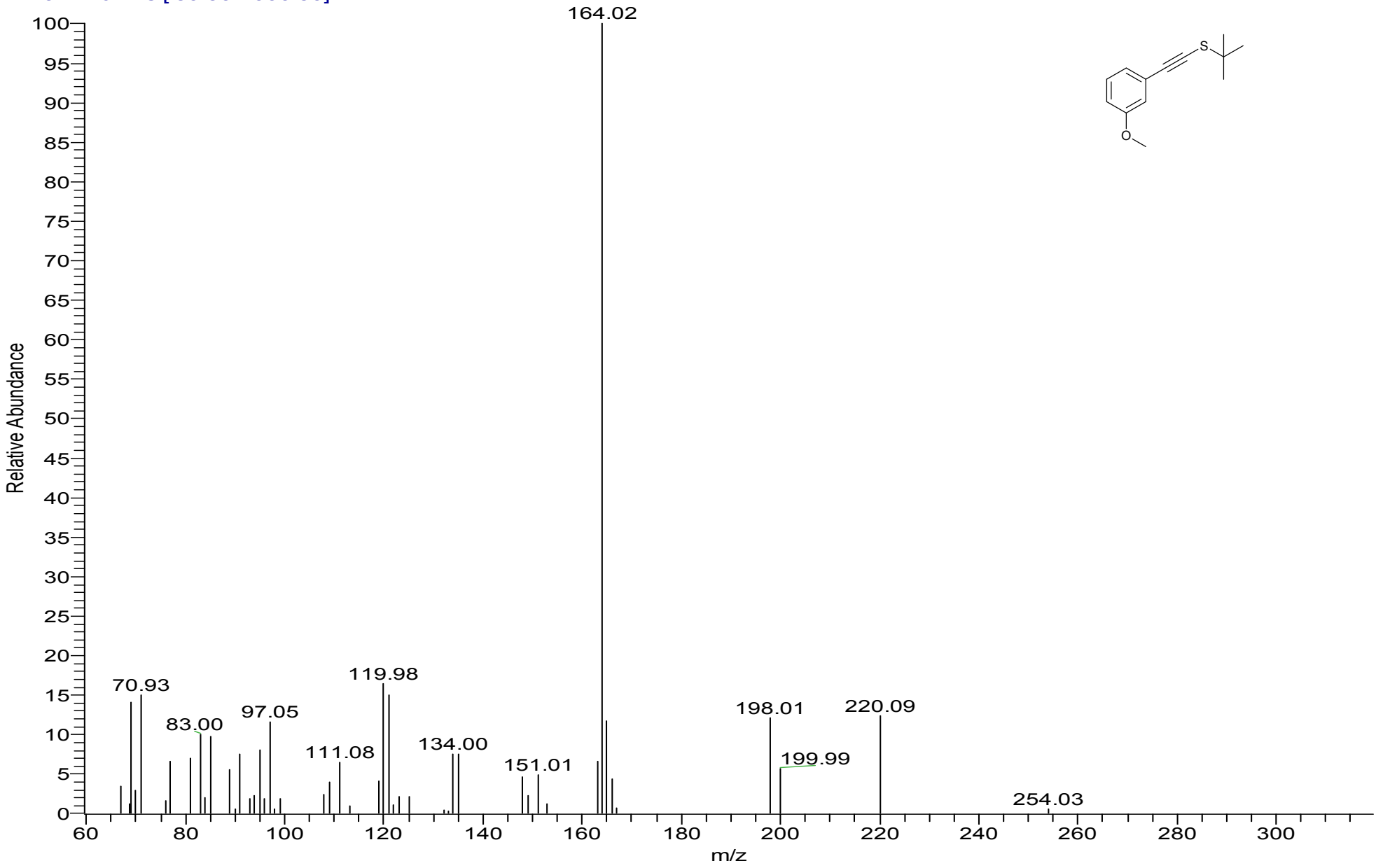


***Tert*-butyl((3-methoxyphenyl)ethynyl)sulfane (2d)**

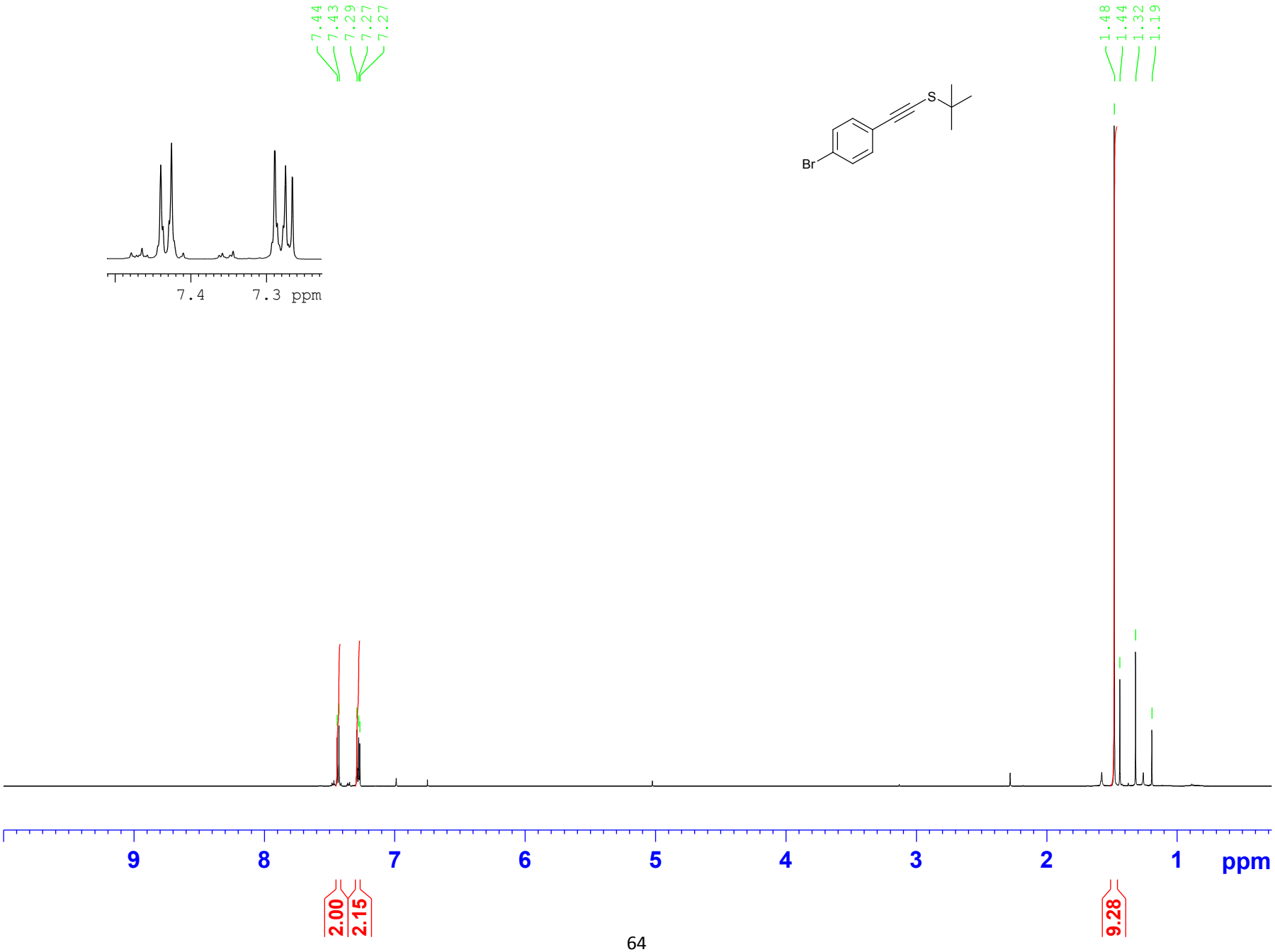


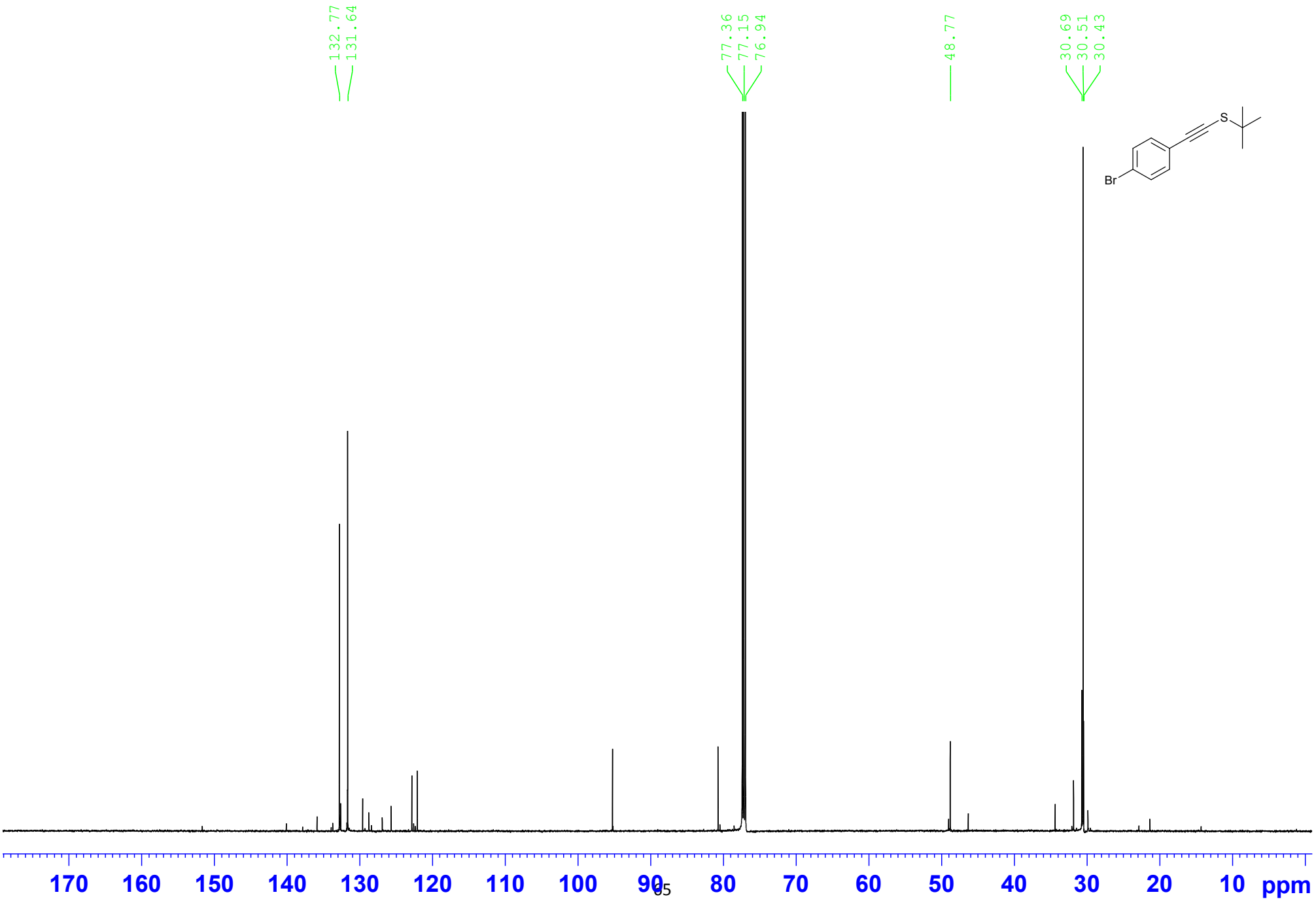

159.39
129.46
124.84
124.00
116.18
114.56
96.20
79.06
77.38
77.17
76.95
55.39
48.62
30.49
S
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

rc162_ei #2 RT: 0.25 AV: 1 NL: 5.32E4
T: + c EI Full ms [59.50-1000.50]

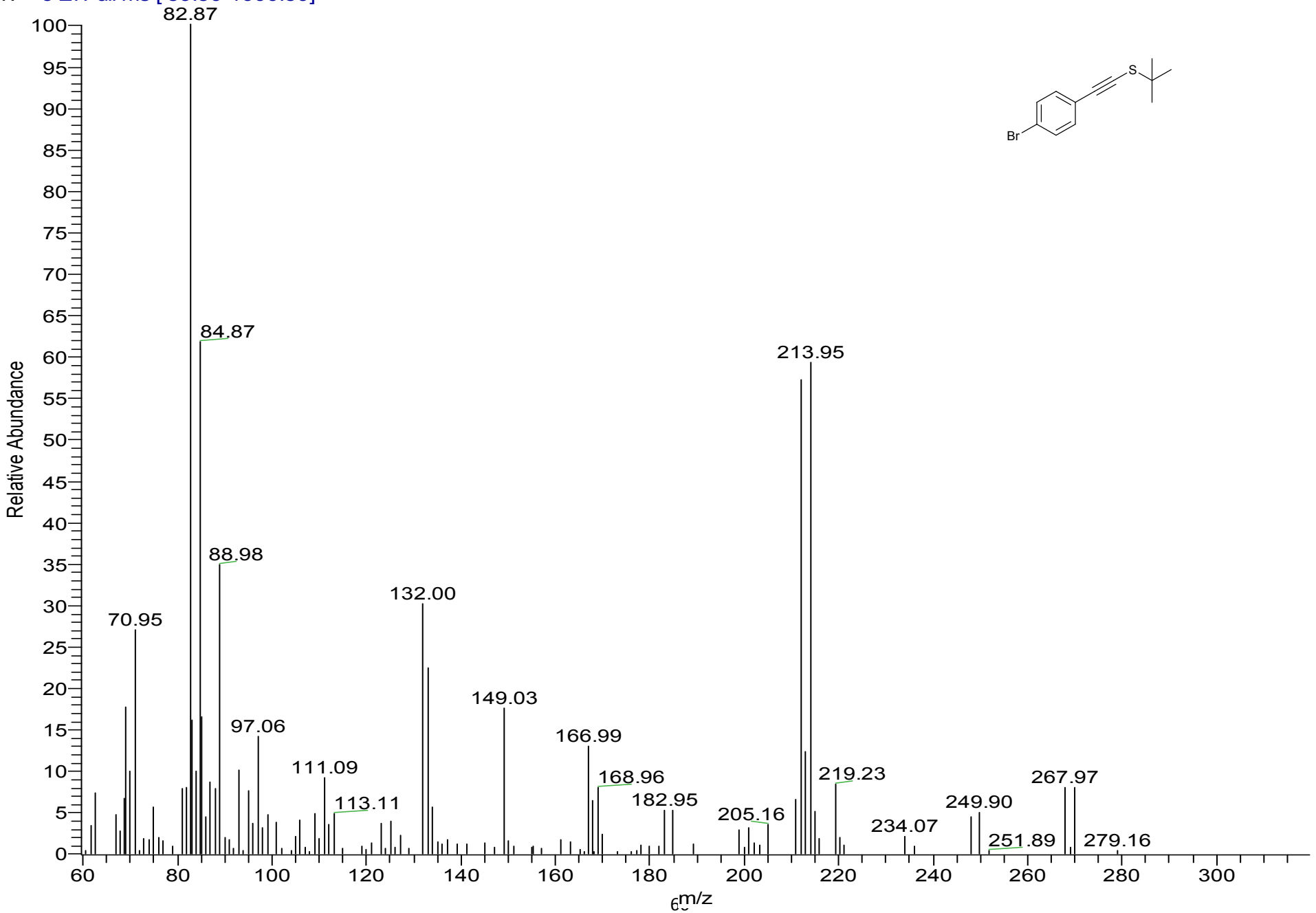


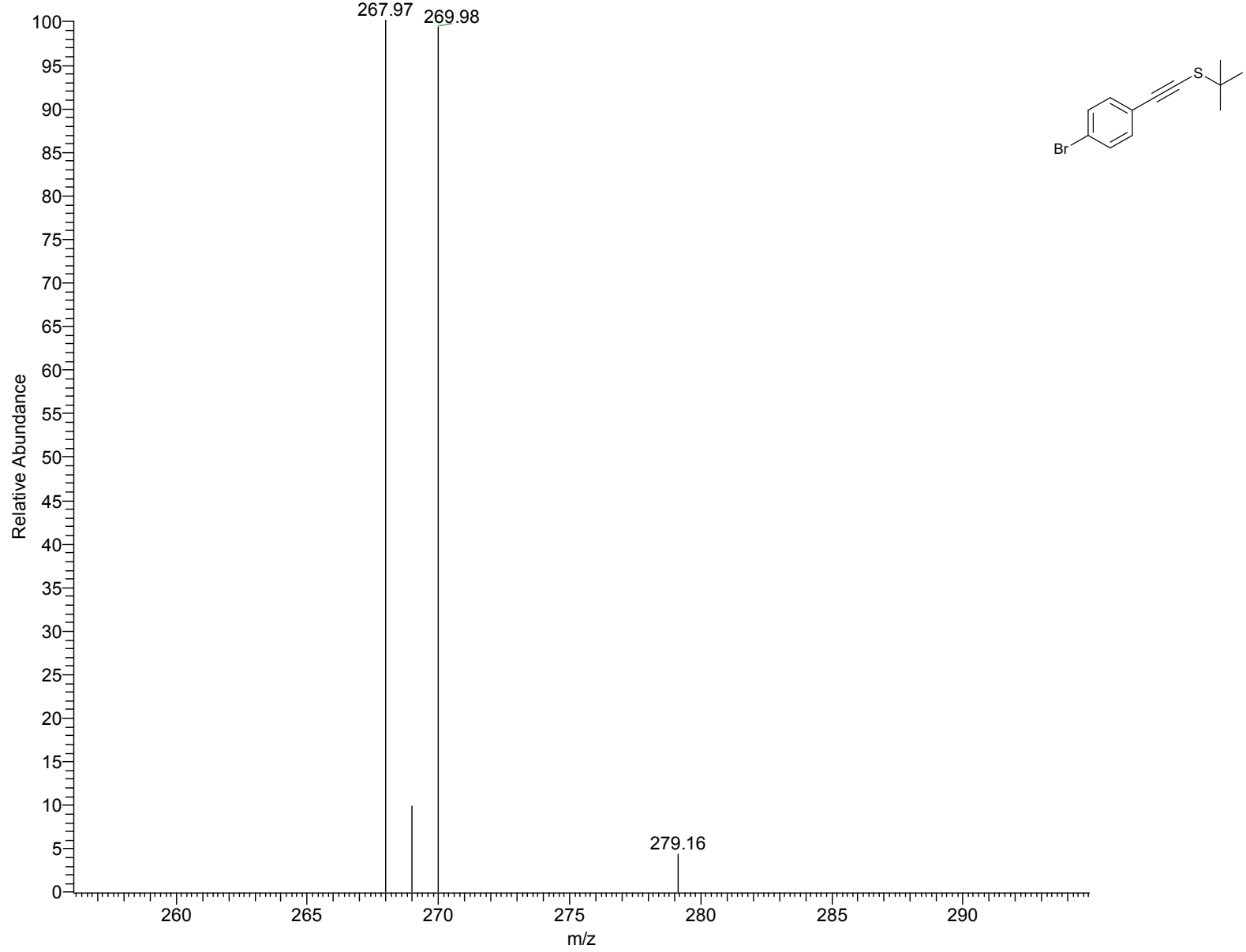
((4-bromophenyl)ethynyl)(*tert*-butyl)sulfane (2e)



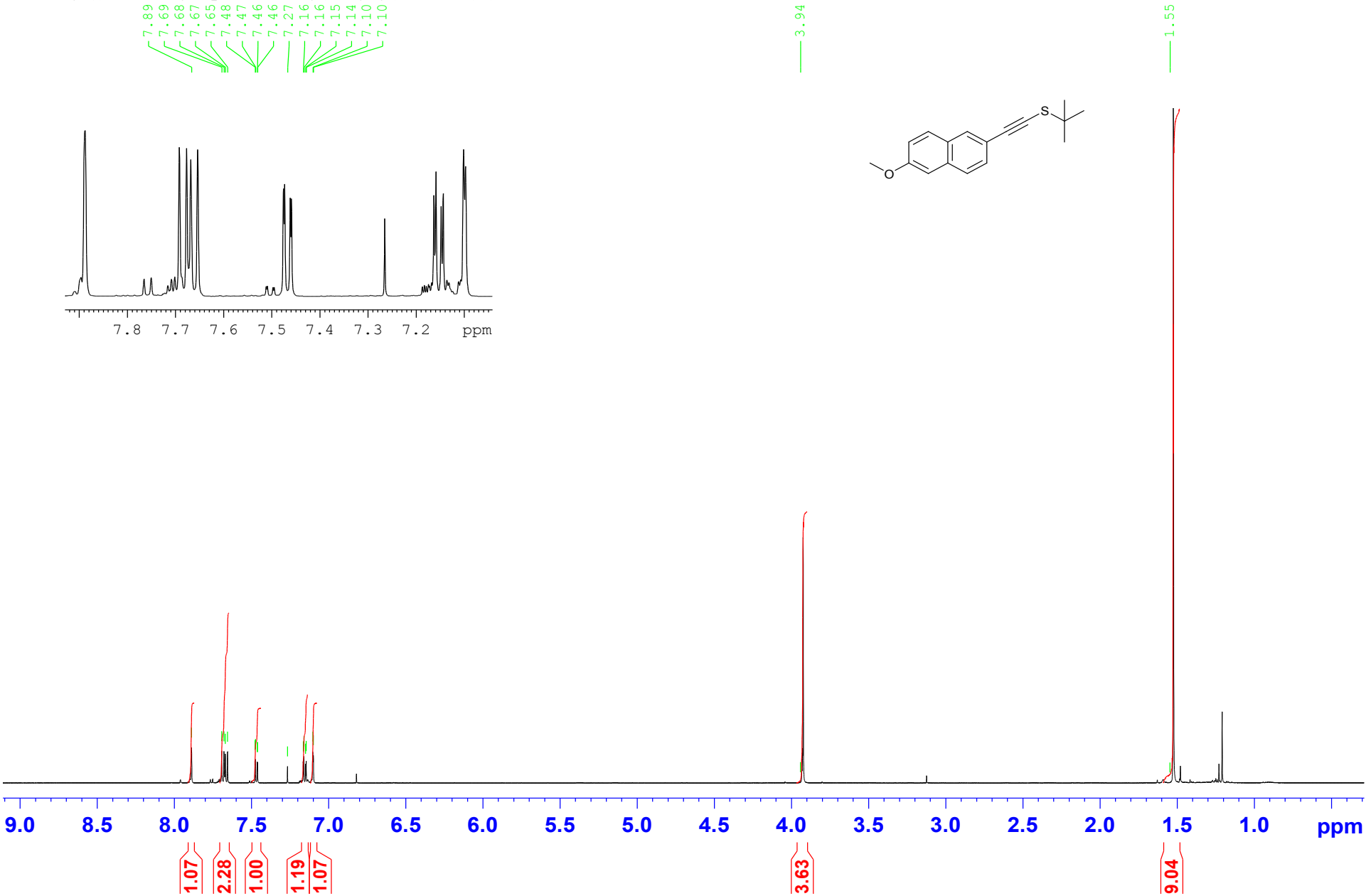

132.77
131.64
77.36
77.15
76.94
48.77
30.69
30.51
30.43
S
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

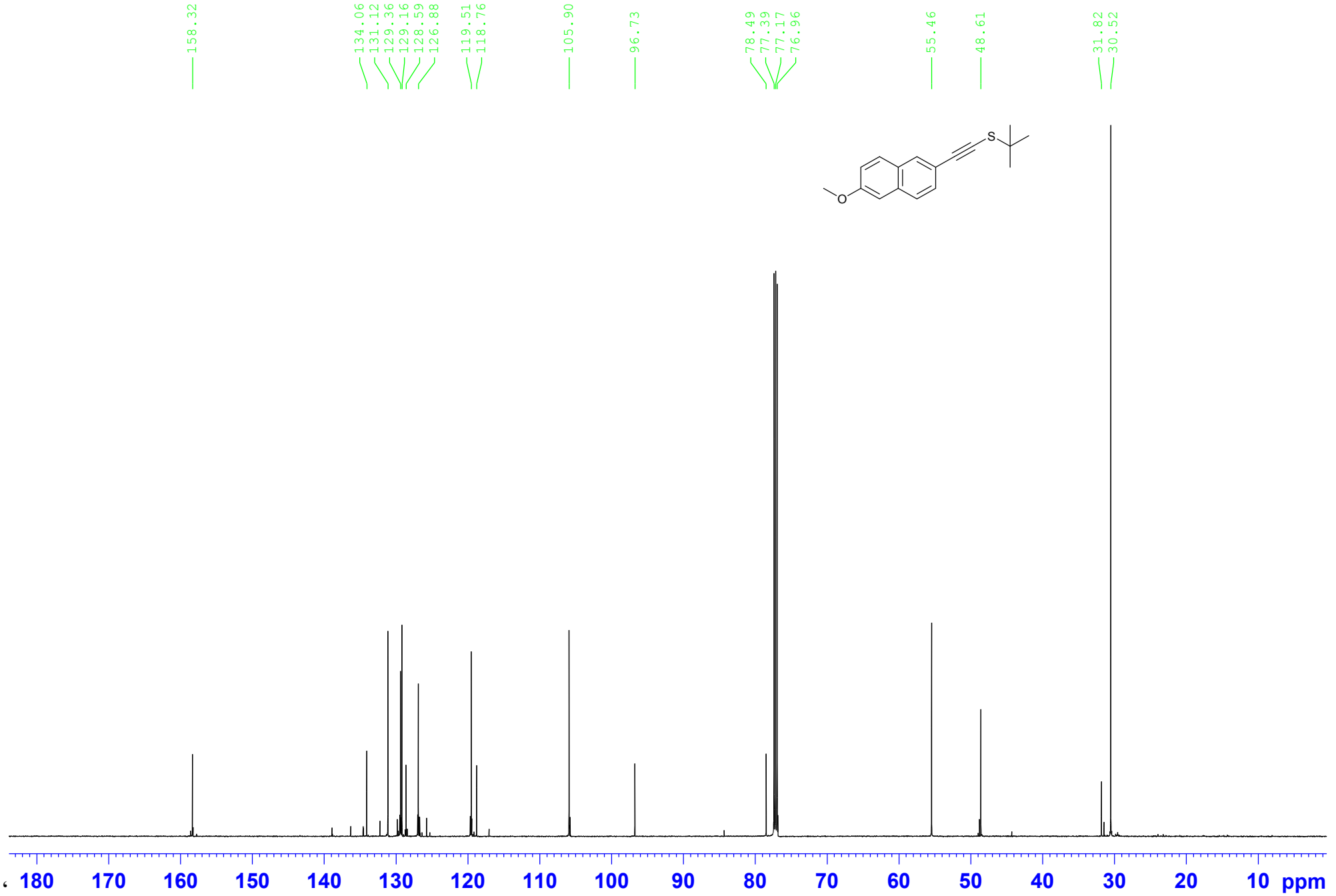
rc169_ei #4 RT: 0.47 AV: 1 NL: 9.81E4
T: + c EI Full ms [59.50-1000.50]



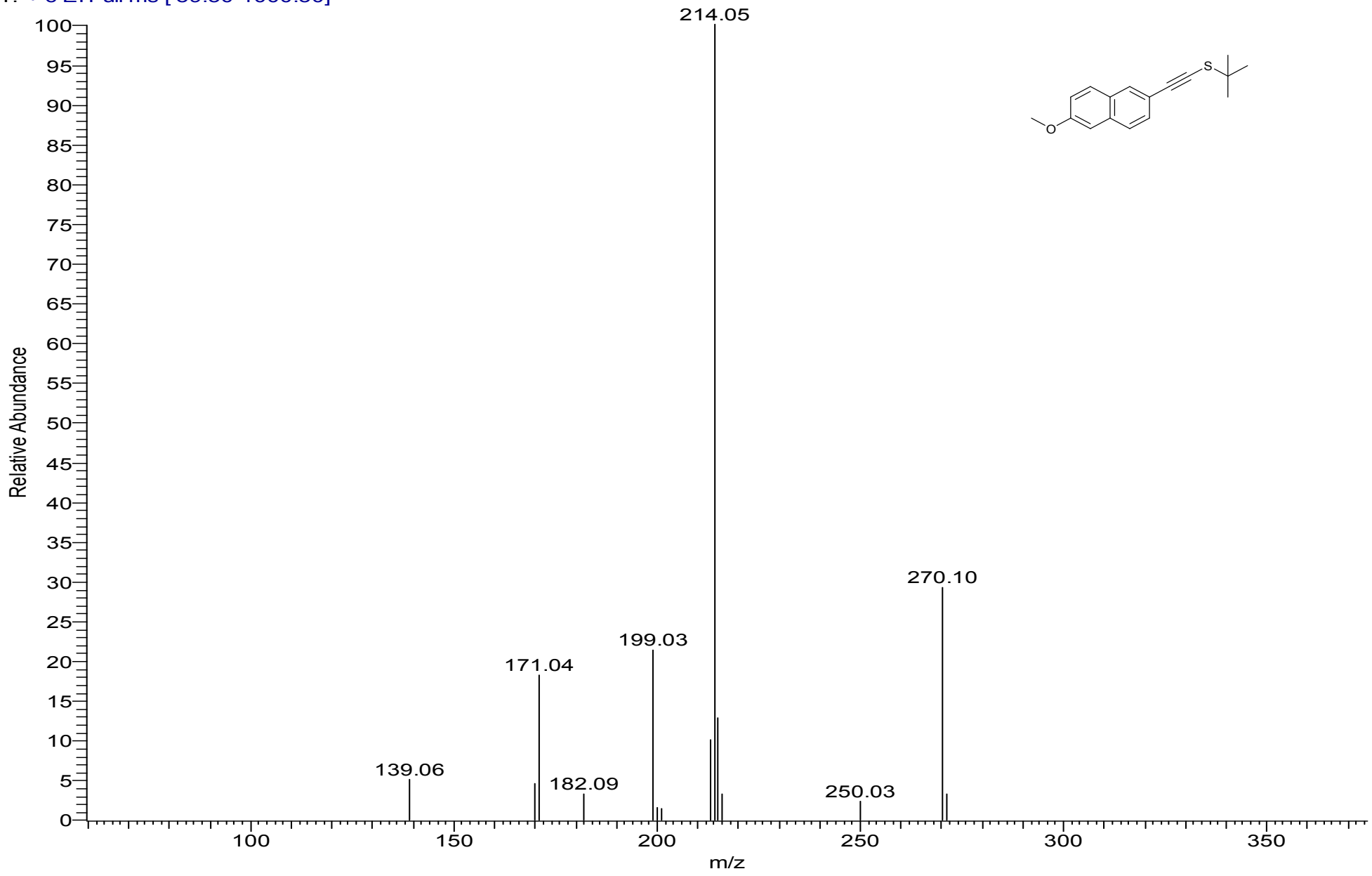

rc169_ei #4 RT: 0.47 AV: 1 NL: 7.85E3
T: + c EI Full ms [59.50-1000.50]
267.97
269.98
279.16
Relative Abundance
m/z
Br
S

***Tert*-butyl((6-methoxynaphthalen-2-yl)ethynyl)sulfane (2f)**

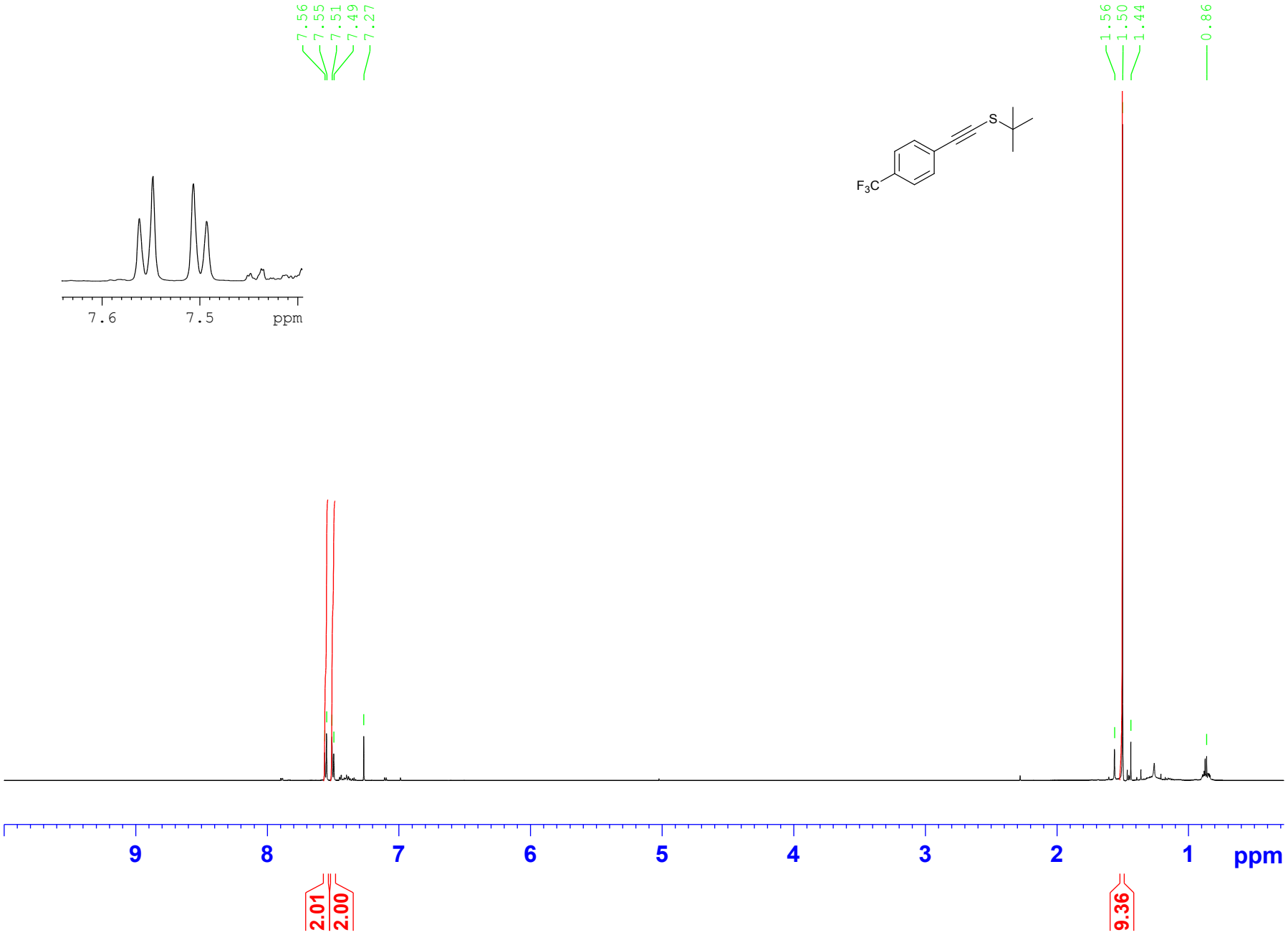


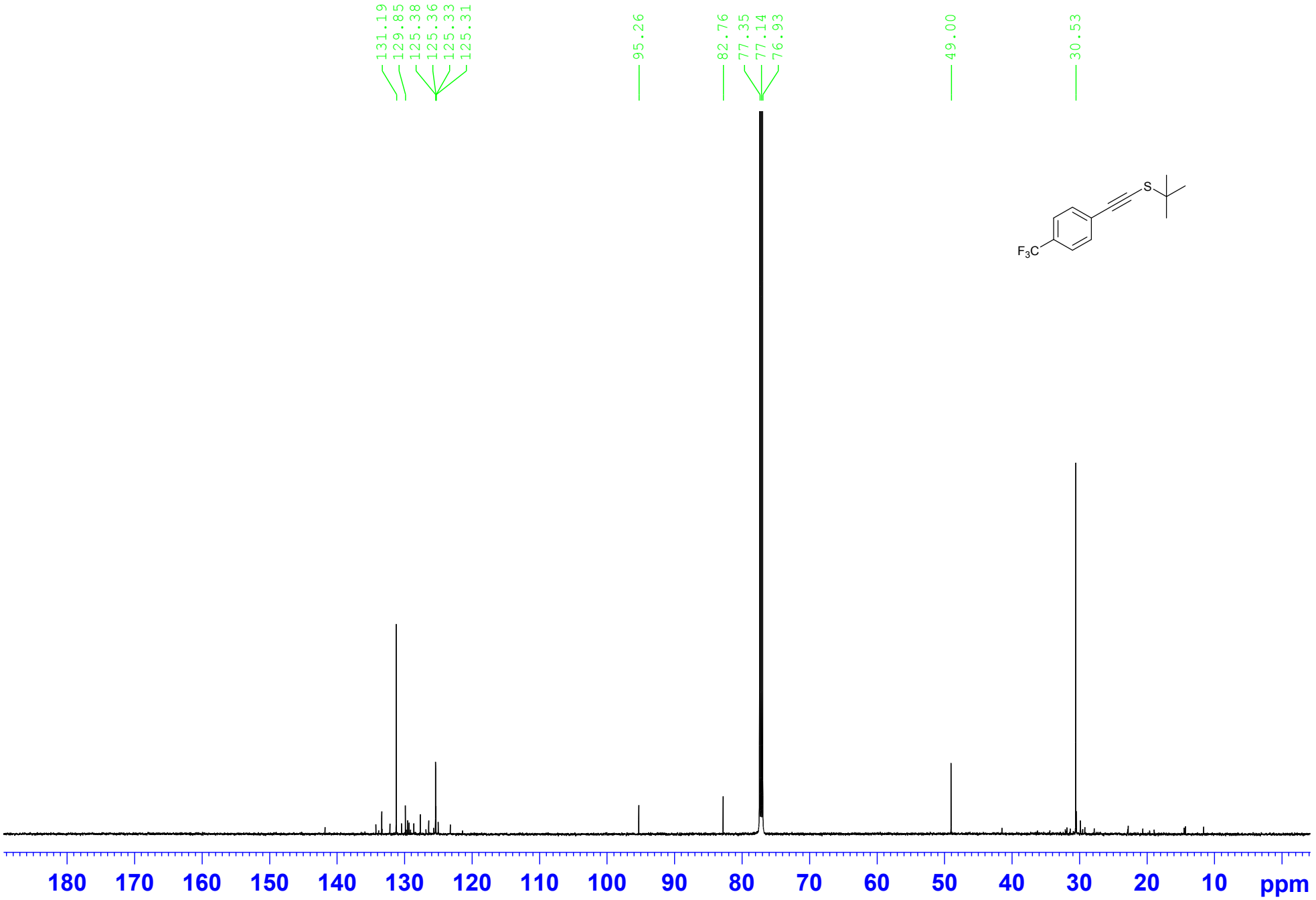

158.32
134.06
131.12
129.36
129.16
128.59
126.88
119.51
118.76
105.90
96.73
78.49
77.39
77.17
76.96
55.46
48.61
31.82
30.52
S
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

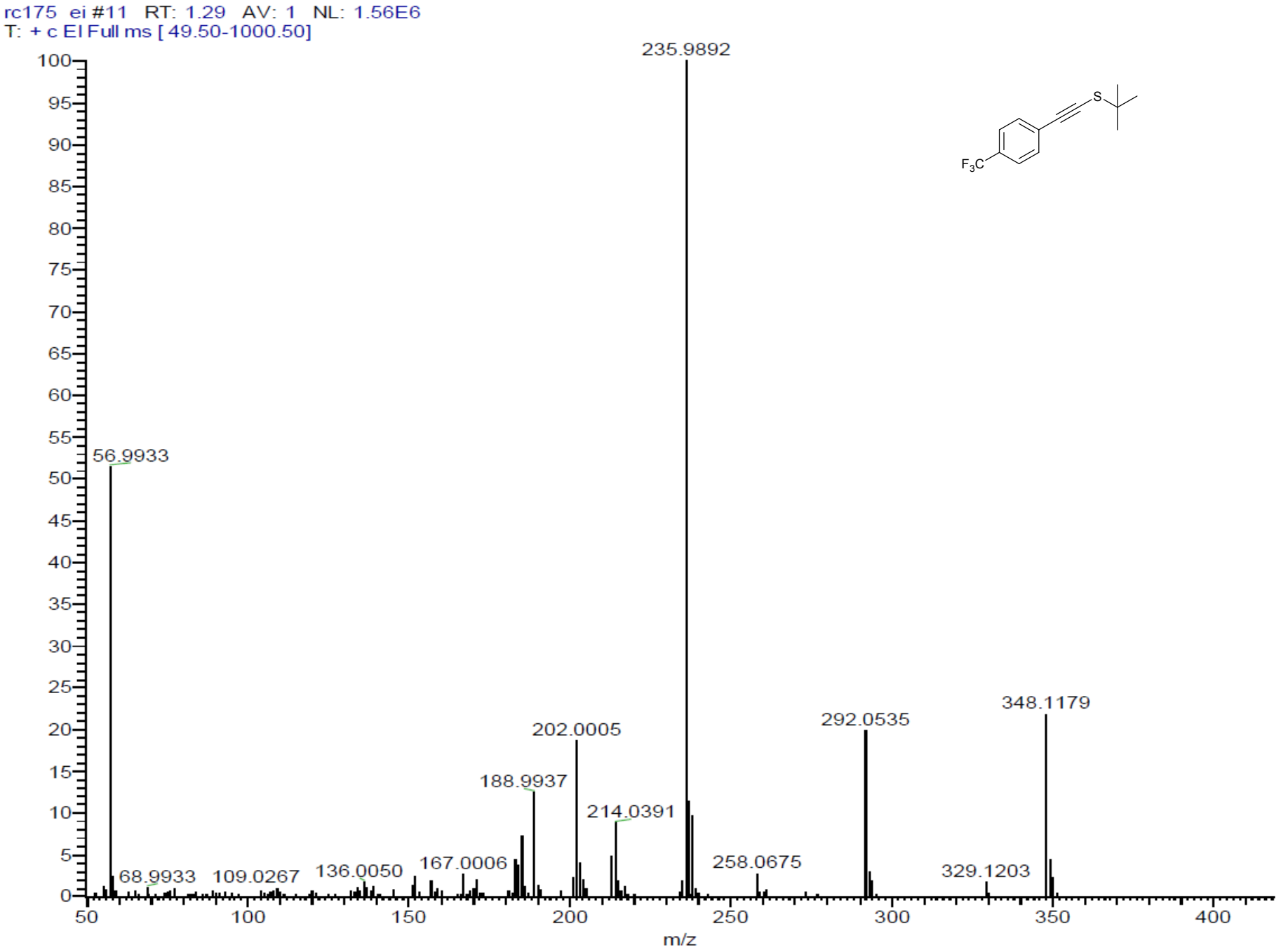
rc167b_ei #1 RT: 0.21 AV: 1 NL: 4.64E4
T: + c EI Full ms [59.50-1000.50]



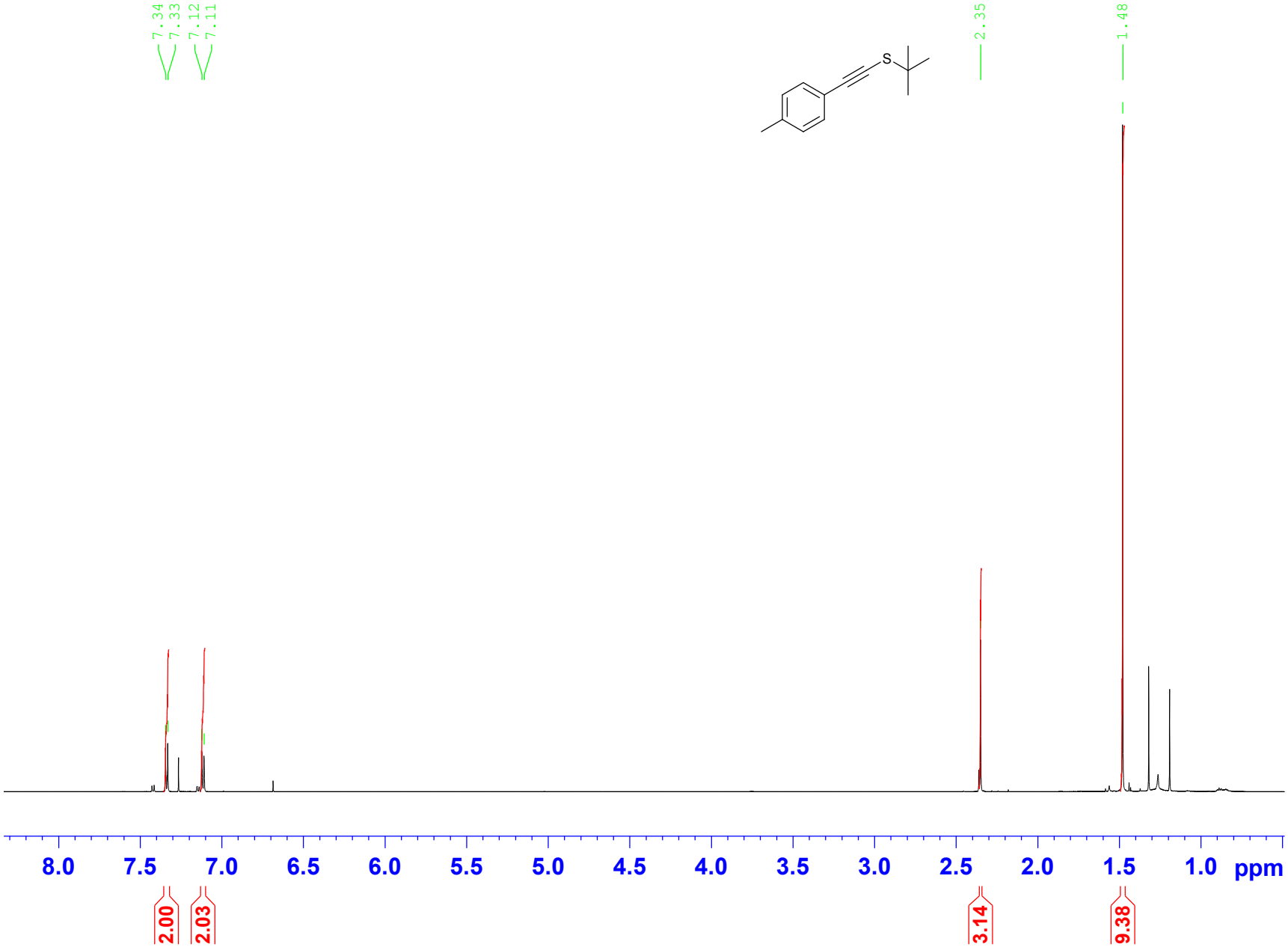
***Tert*-butyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane (2g)**

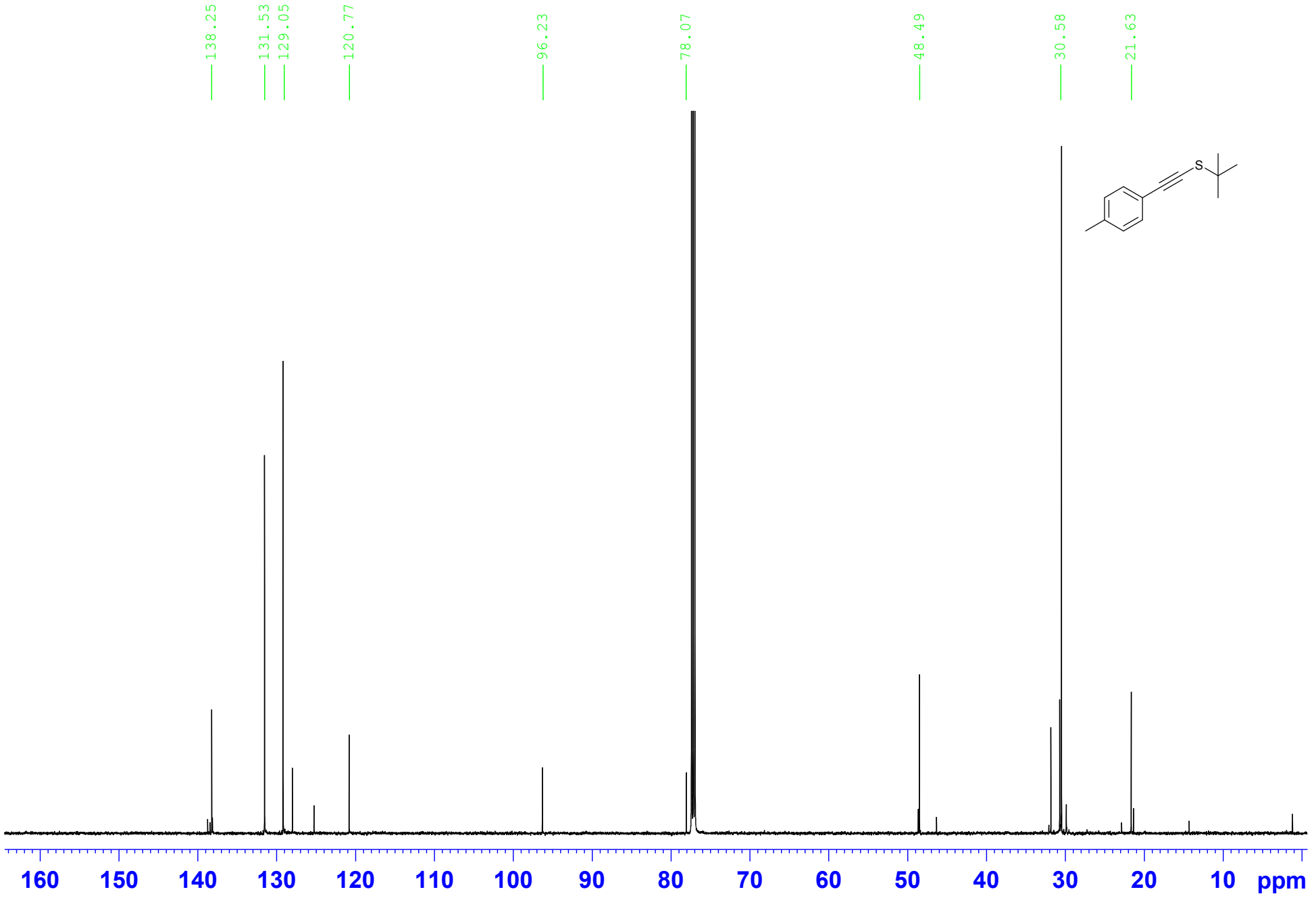


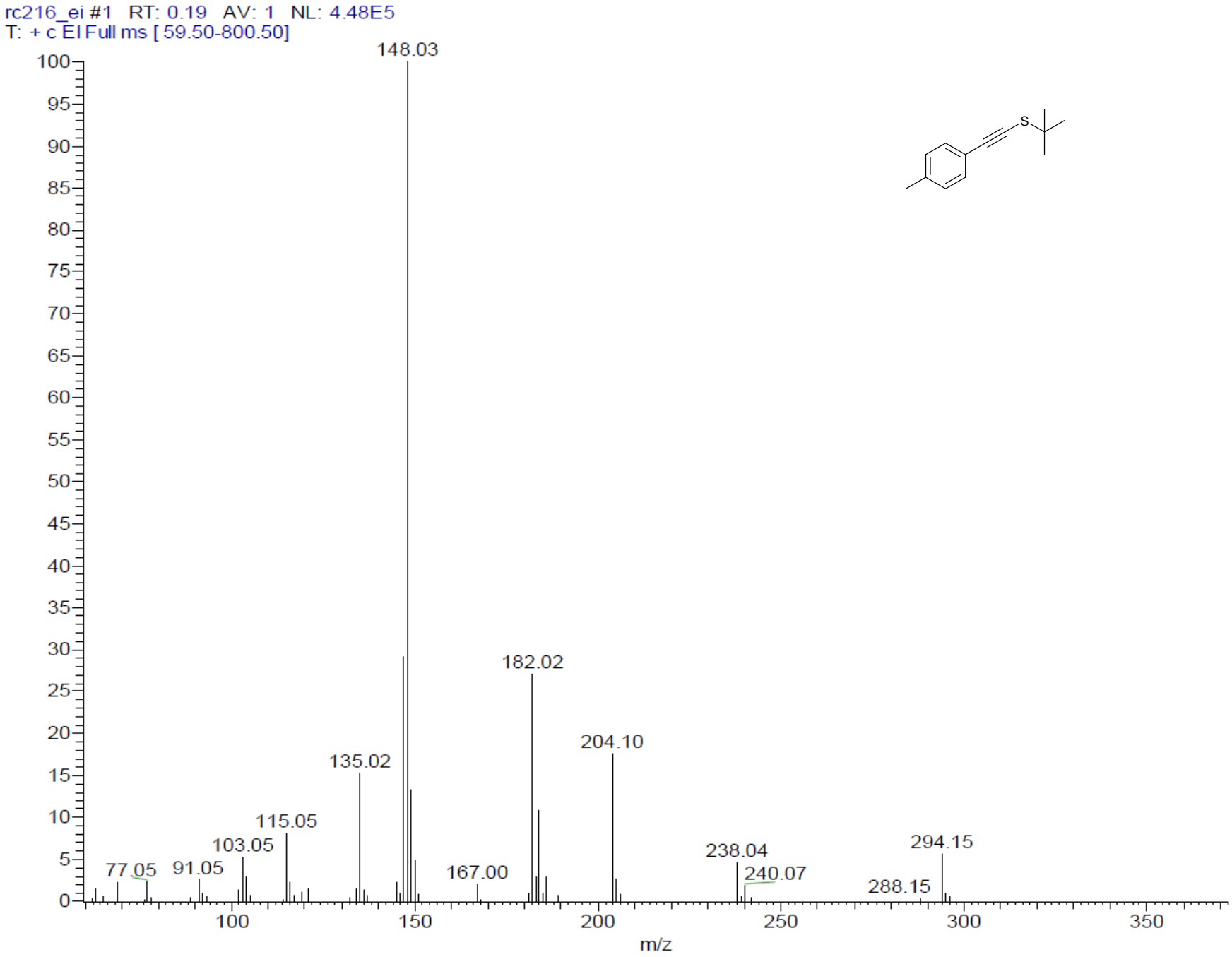

131.19
129.85
125.38
125.36
125.33
125.31
95.26
82.76
77.35
77.14
76.93
49.00
30.53
S
F3C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc175 ei #11 RT: 1.29 AV: 1 NL: 1.56E6
T: + c EI Full ms [49.50-1000.50]
235.9892
56.9933
68.9933
109.0267
136.0050
167.0006
188.9937
202.0005
214.0391
258.0675
292.0535
329.1203
348.1179
F3C
S
m/z

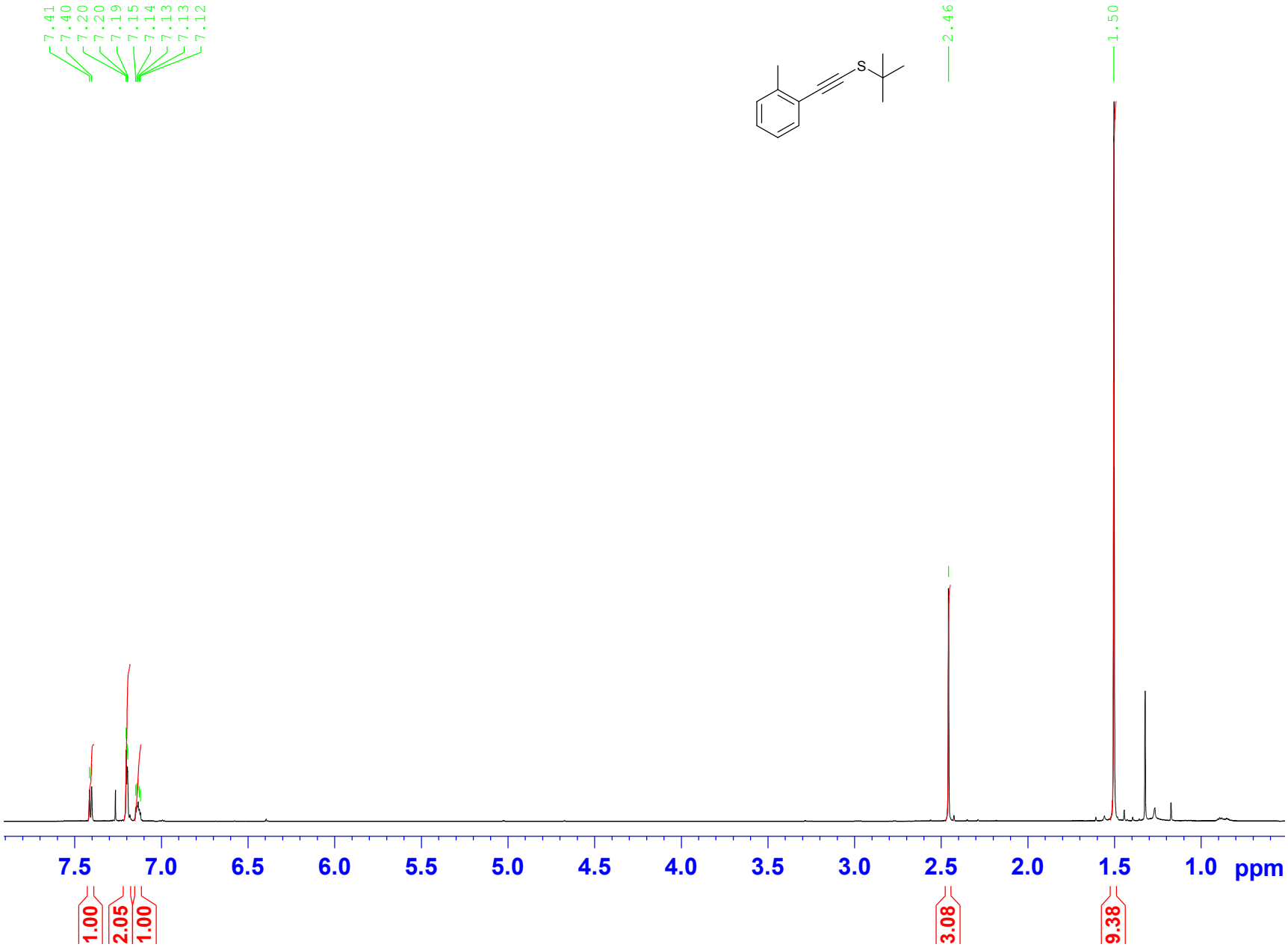
***Tert*-butyl((4-tolylethynyl)sulfane (2h)**

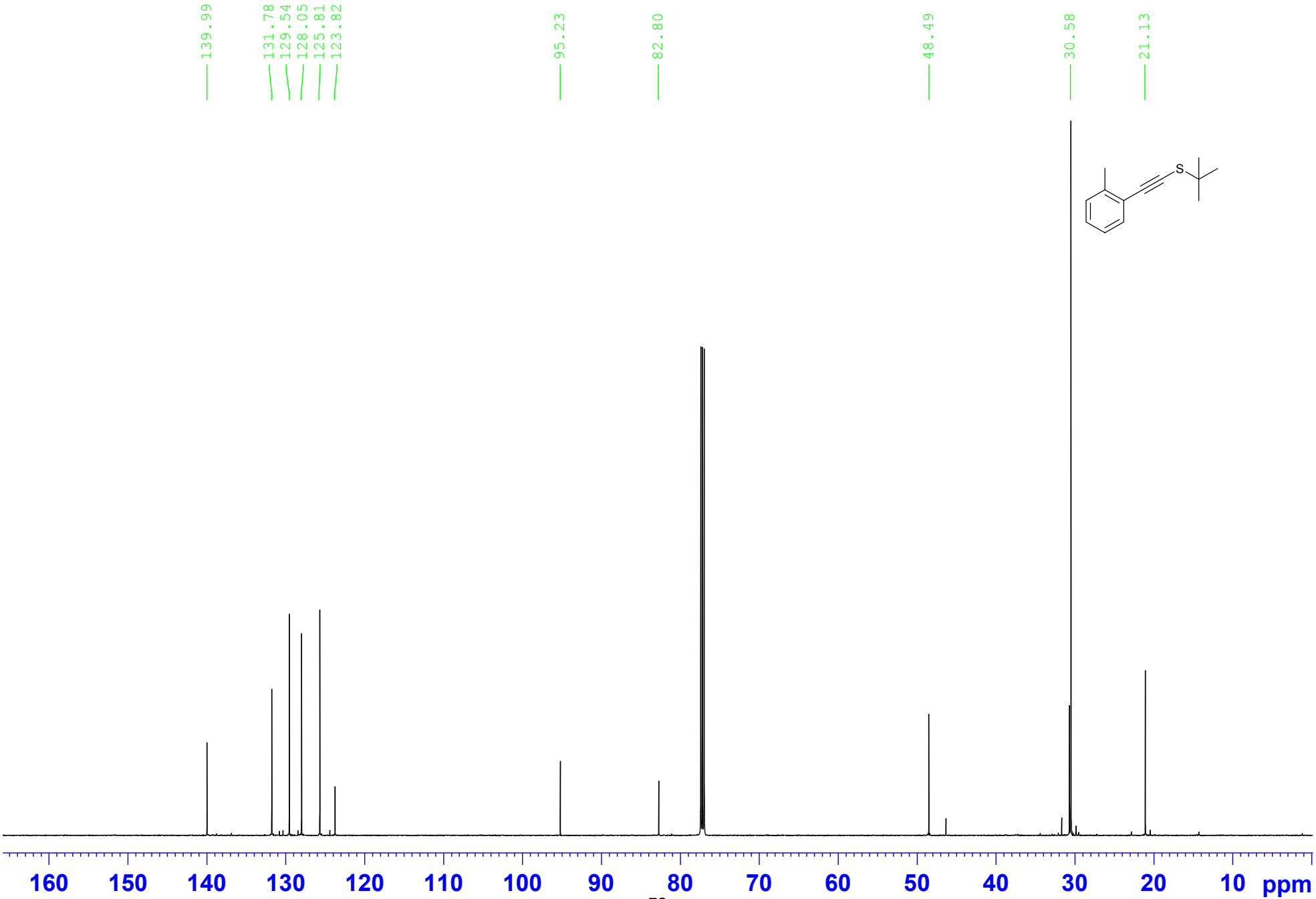


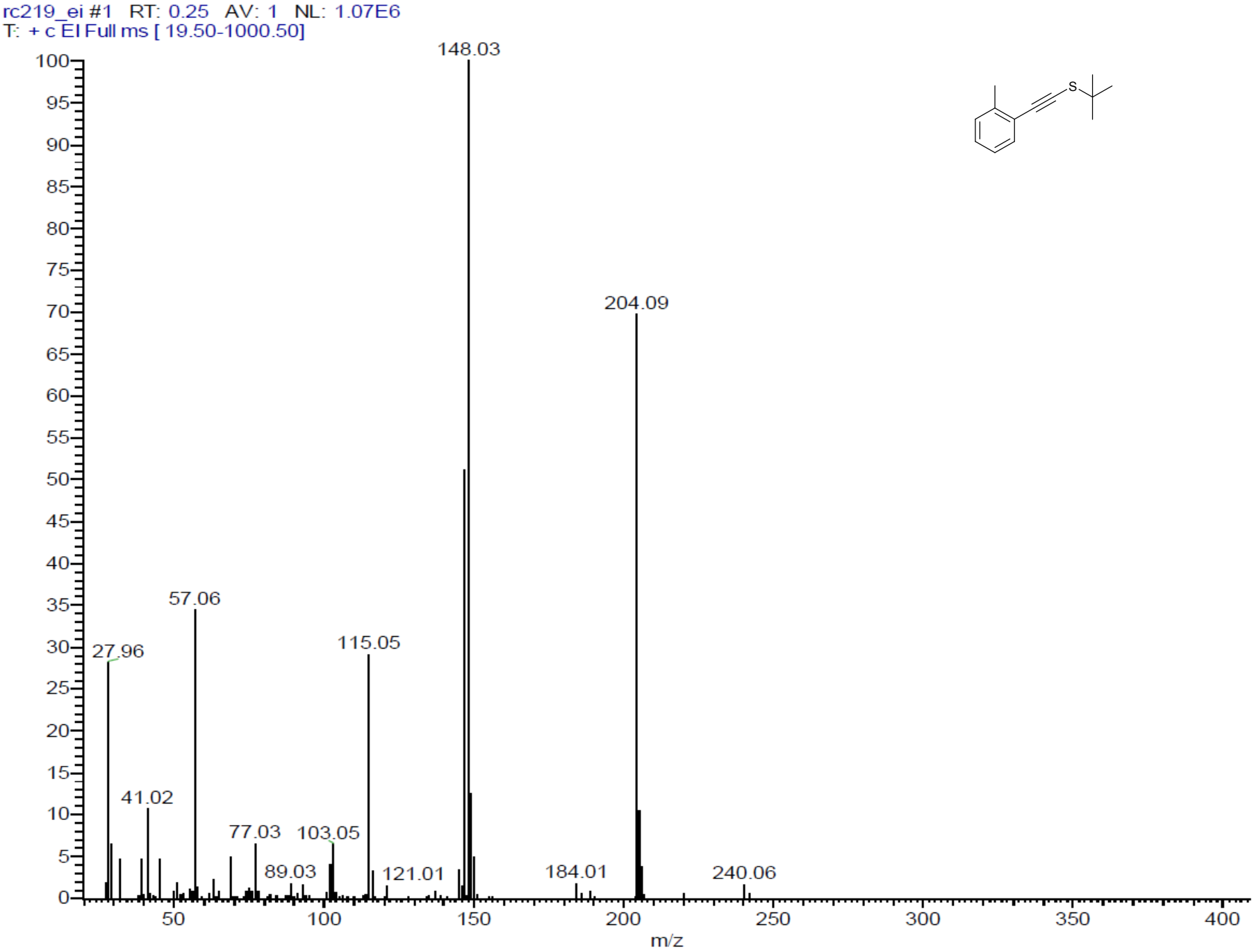

138.25
131.53
129.05
120.77
96.23
78.07
48.49
30.58
21.63
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc216_ei #1 RT: 0.19 AV: 1 NL: 4.48E5
T: + c EI Full ms [59.50-800.50]
148.03
182.02
204.10
135.02
115.05
103.05
77.05
91.05
167.00
238.04
240.07
294.15
288.15
S
m/z

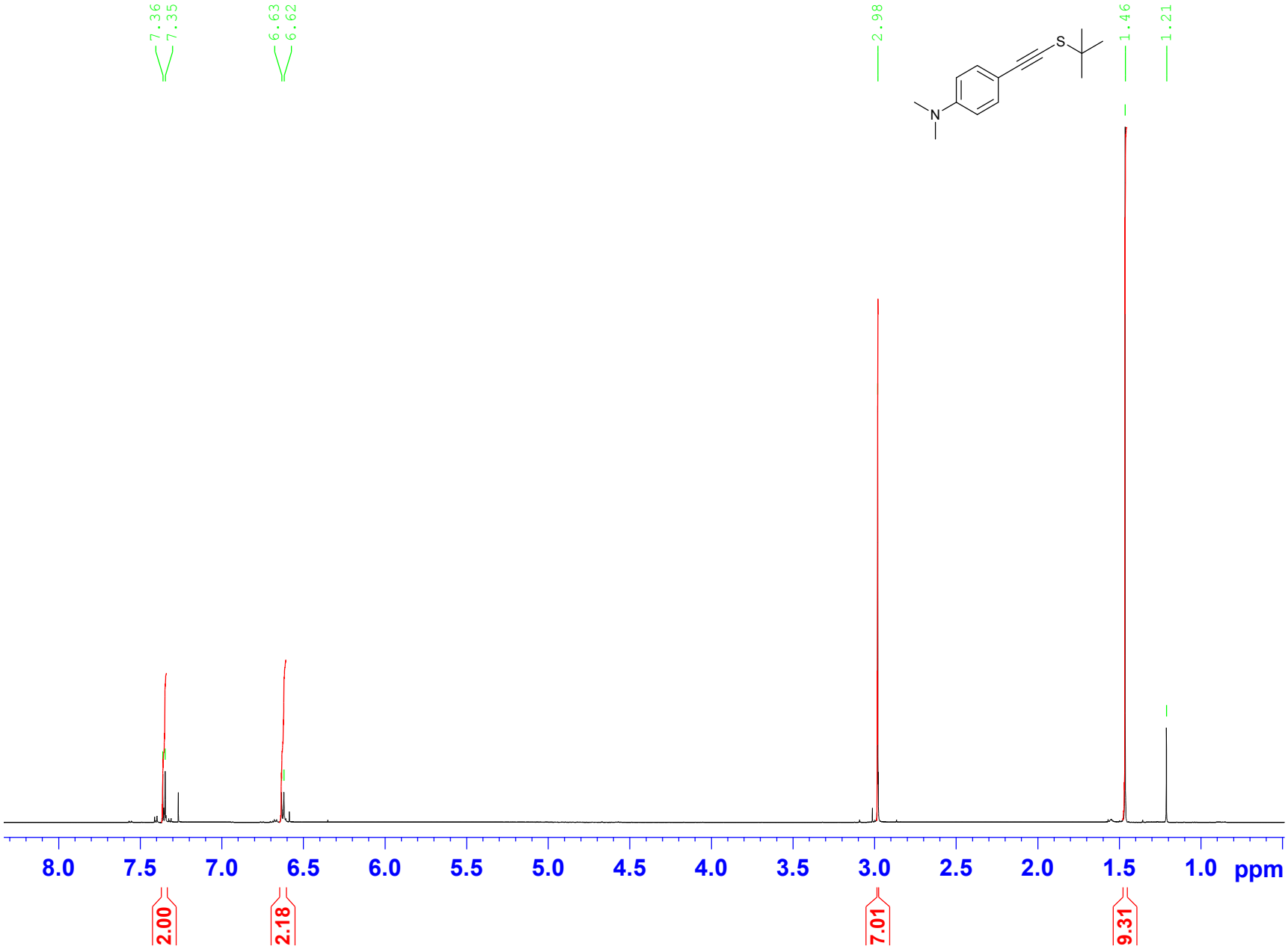
***Tert*-butyl((2-tolylethynyl)sulfane (2i)**

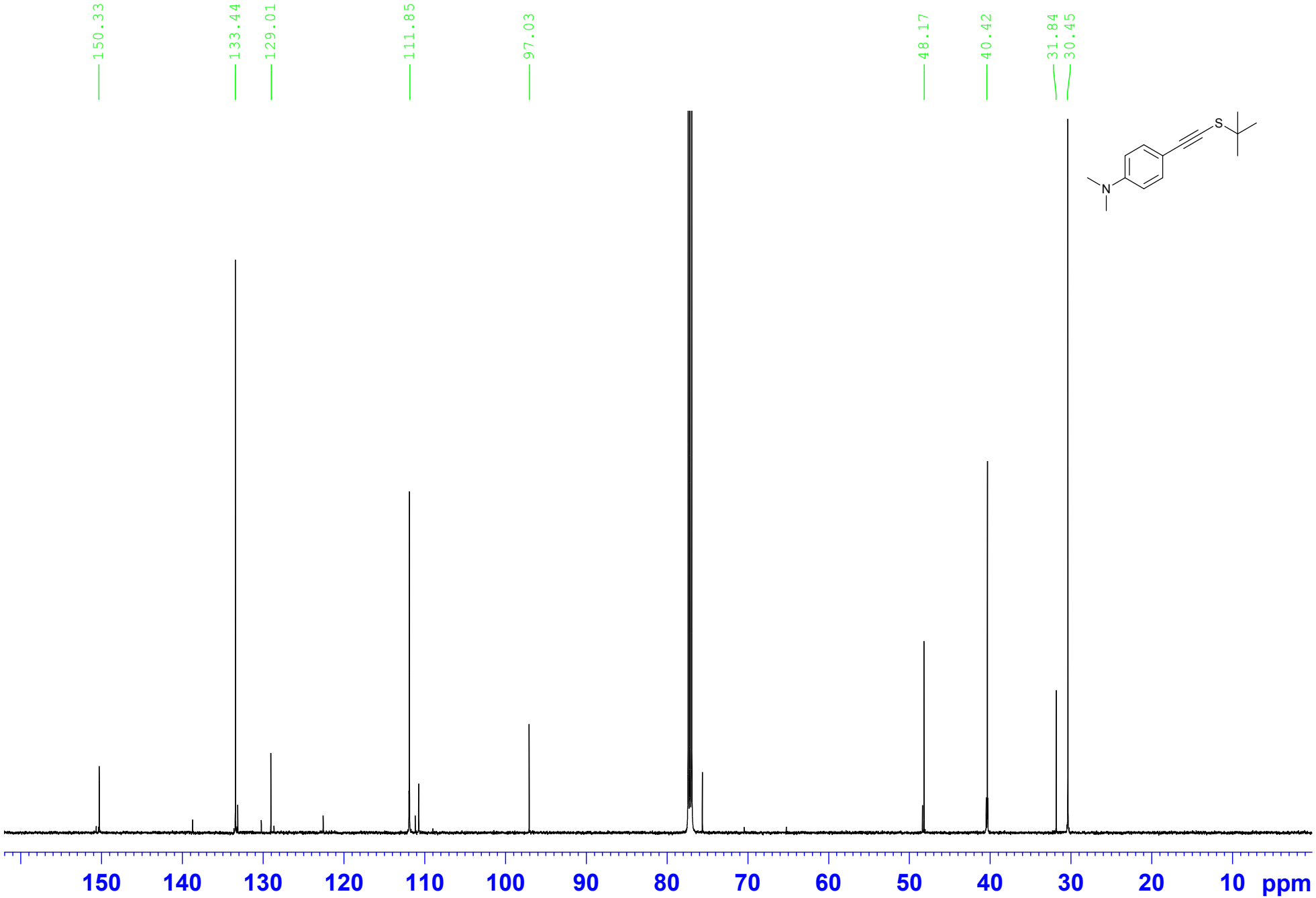


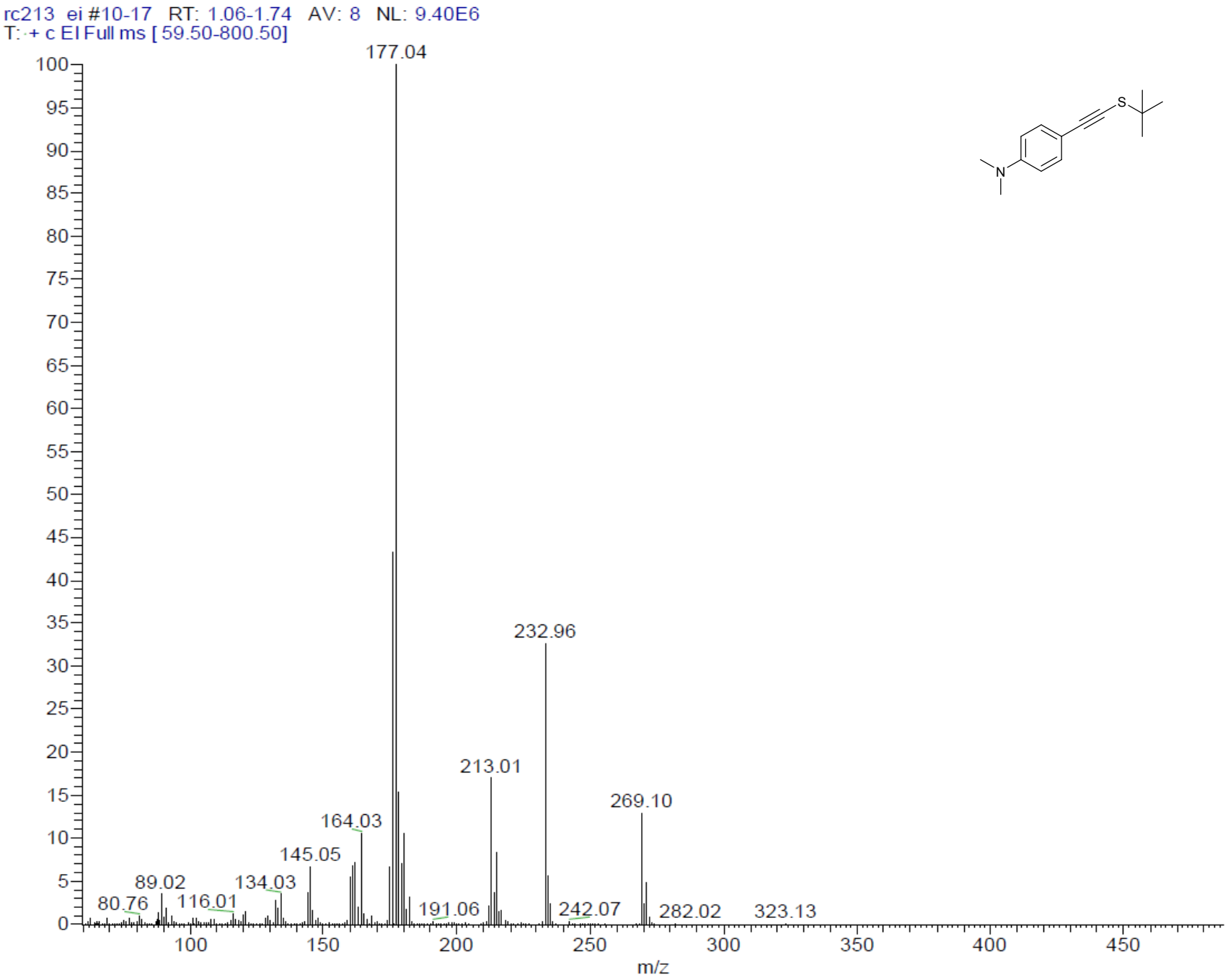

139.99
131.78
129.54
128.05
125.81
123.82
95.23
82.80
48.49
30.58
21.13
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc219_ei #1 RT: 0.25 AV: 1 NL: 1.07E6
T: + c EI Full ms [19.50-1000.50]
148.03
204.09
57.06
27.96
115.05
41.02
77.03
103.05
89.03
121.01
184.01
240.06
S
m/z

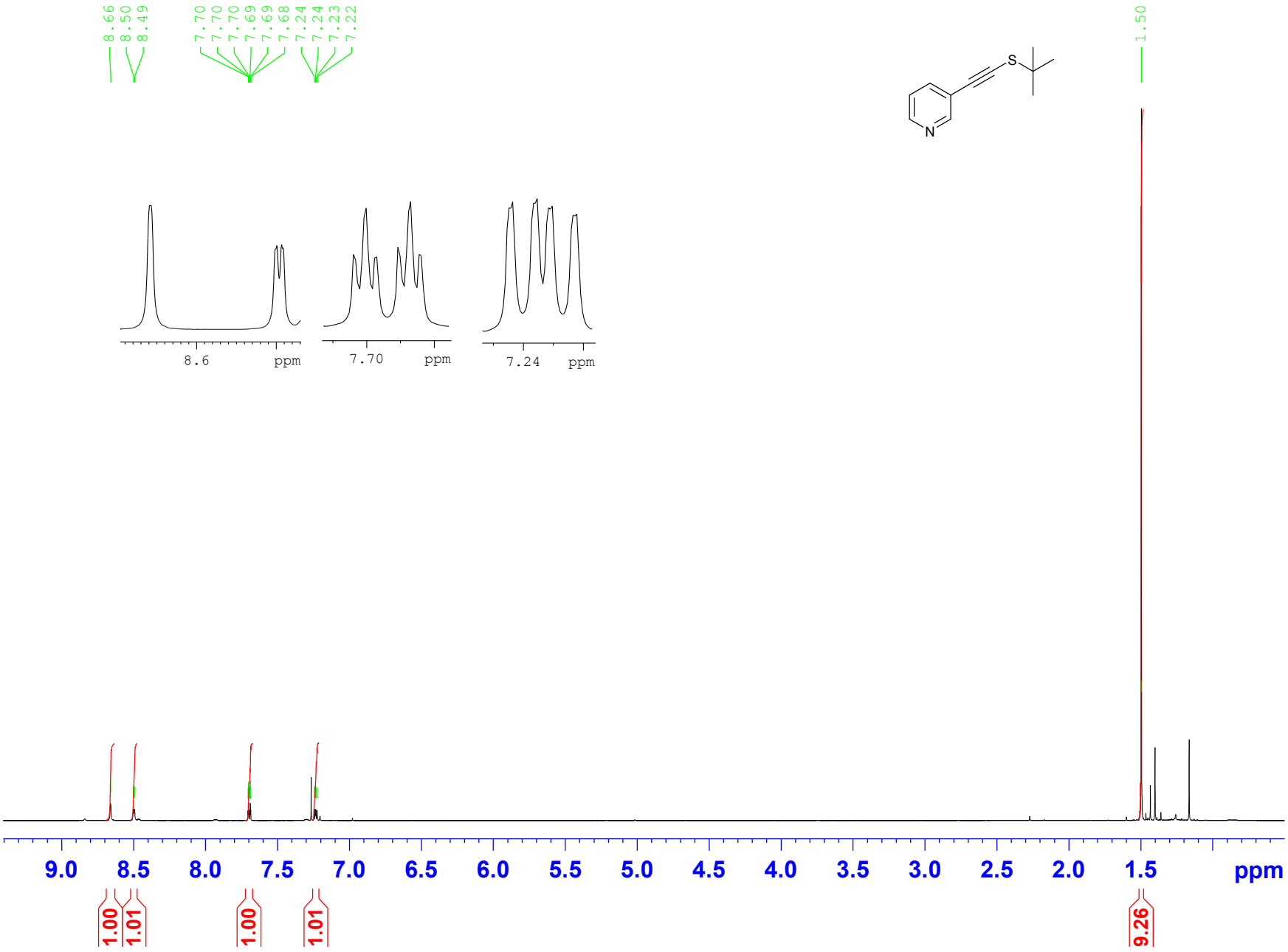
4-((*tert*-butylthio)ethynyl)-*N*,*N*-dimethylaniline (2j)

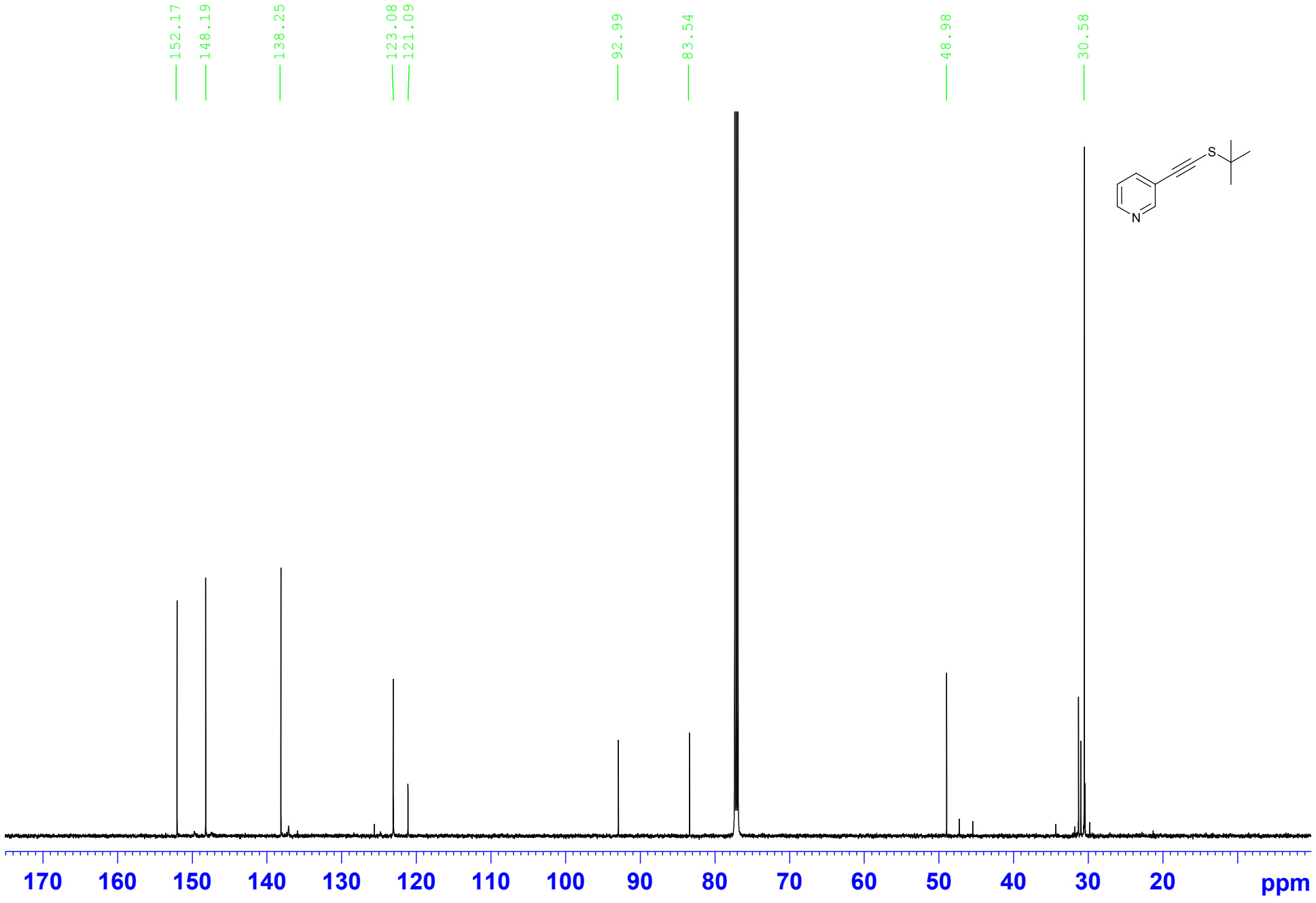


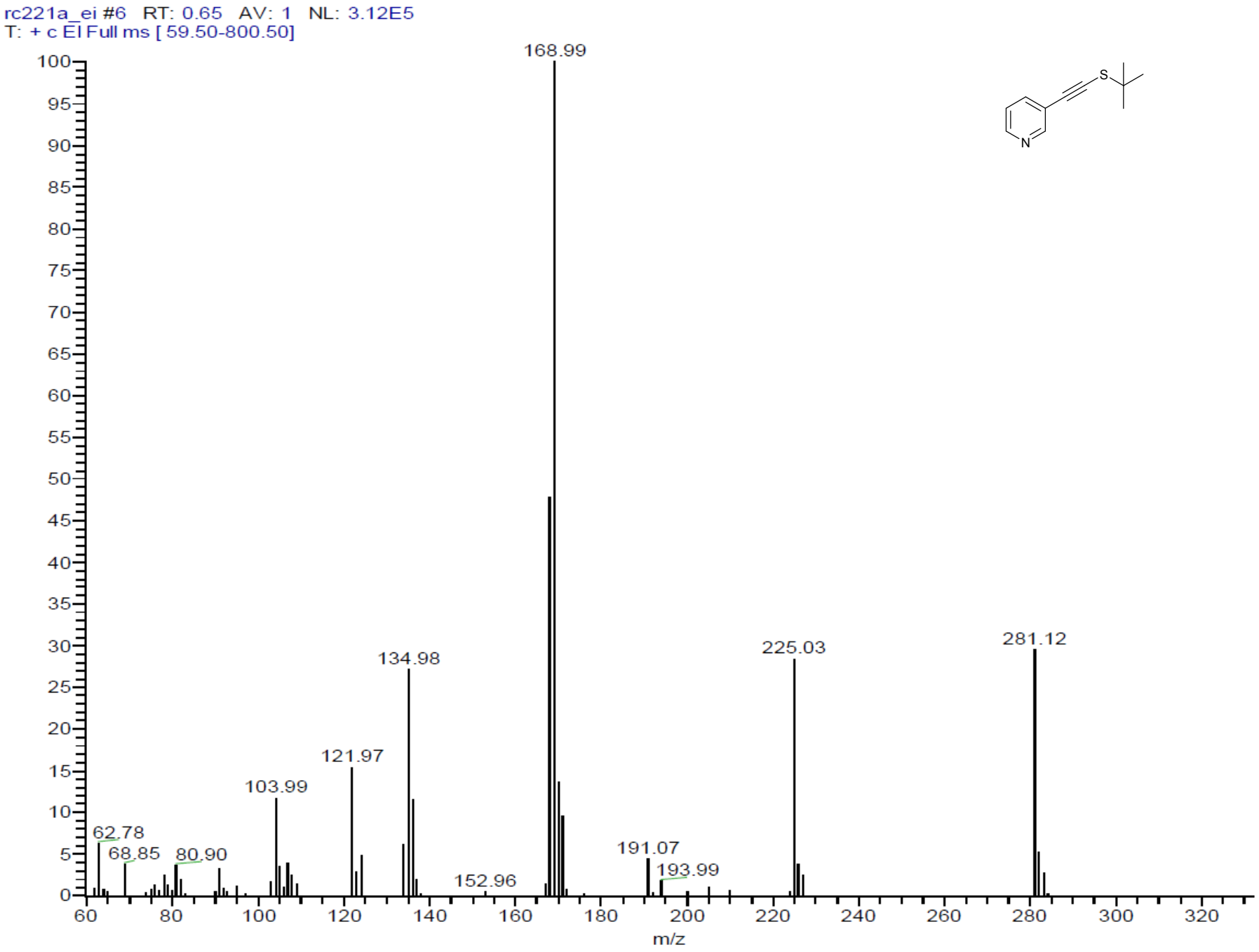

150.33
133.44
129.01
111.85
97.03
48.17
40.42
31.84
30.45
S
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc213 ei #10-17 RT: 1.06-1.74 AV: 8 NL: 9.40E6
T: + c EI Full ms [59.50-800.50]
177.04
232.96
213.01
269.10
164.03
145.05
89.02
134.03
80.76
116.01
191.06
242.07
282.02
323.13
m/z
S
N

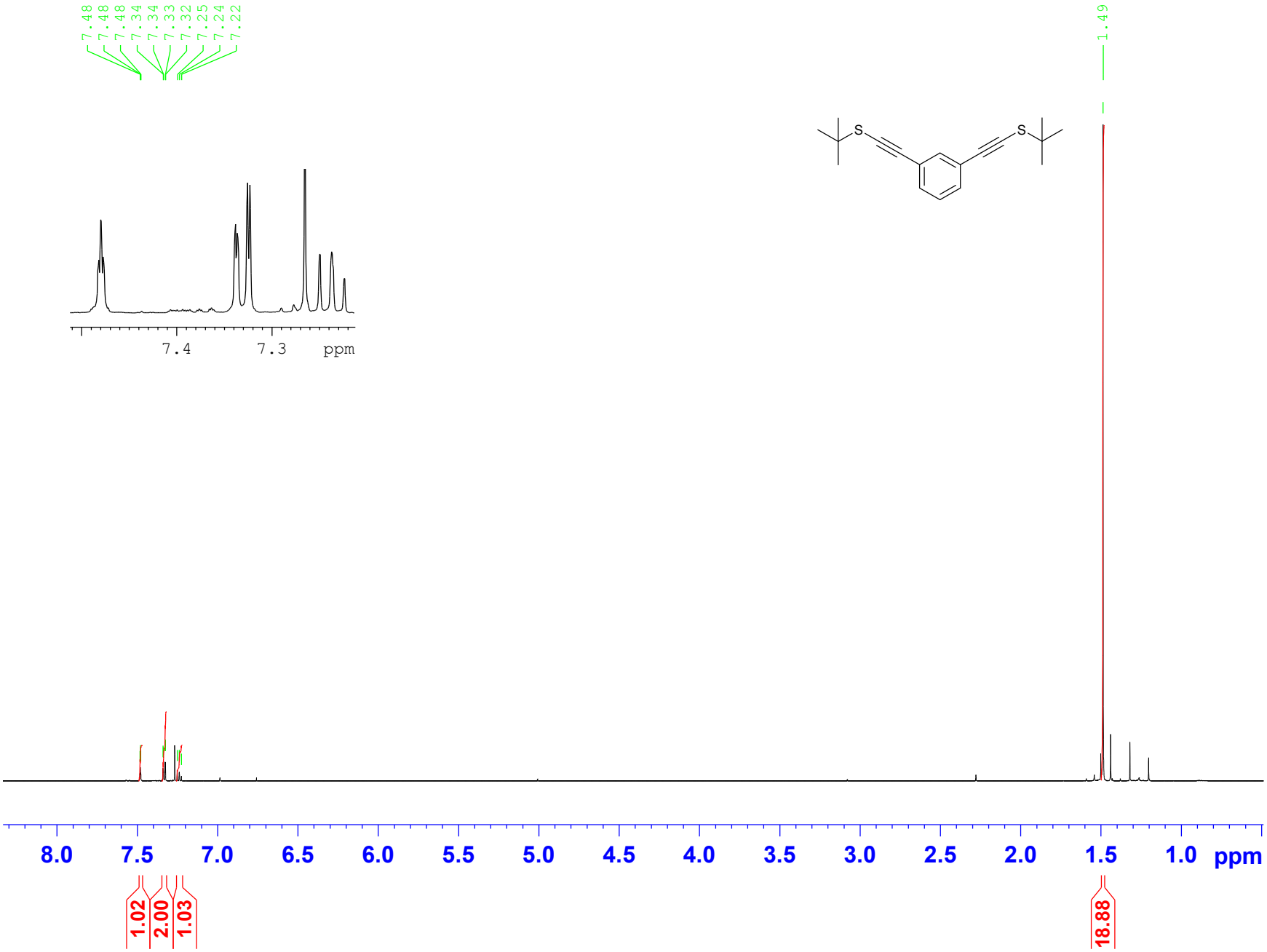
3-((*tert*-butylthio)ethynyl)pyridine (2k)

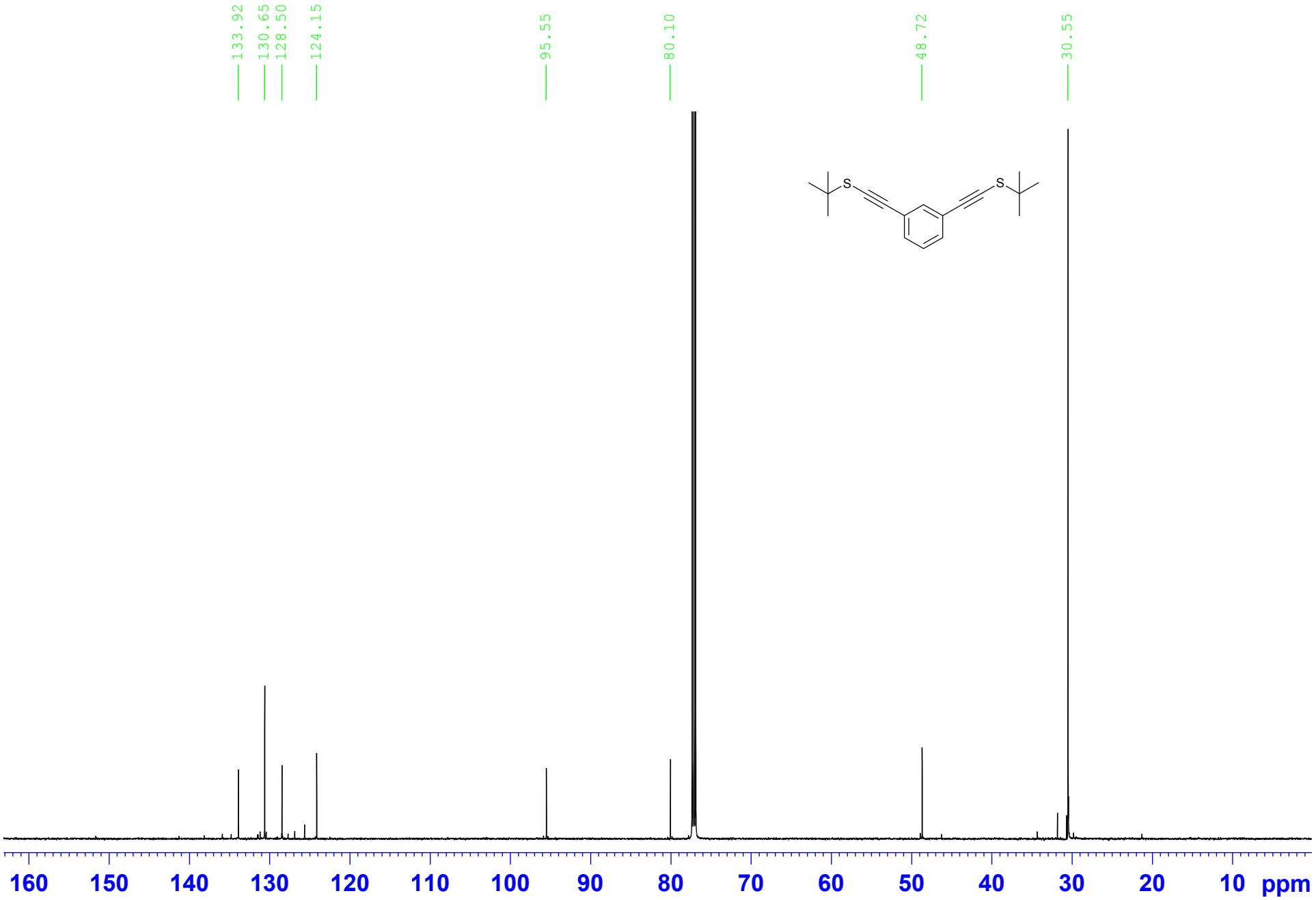


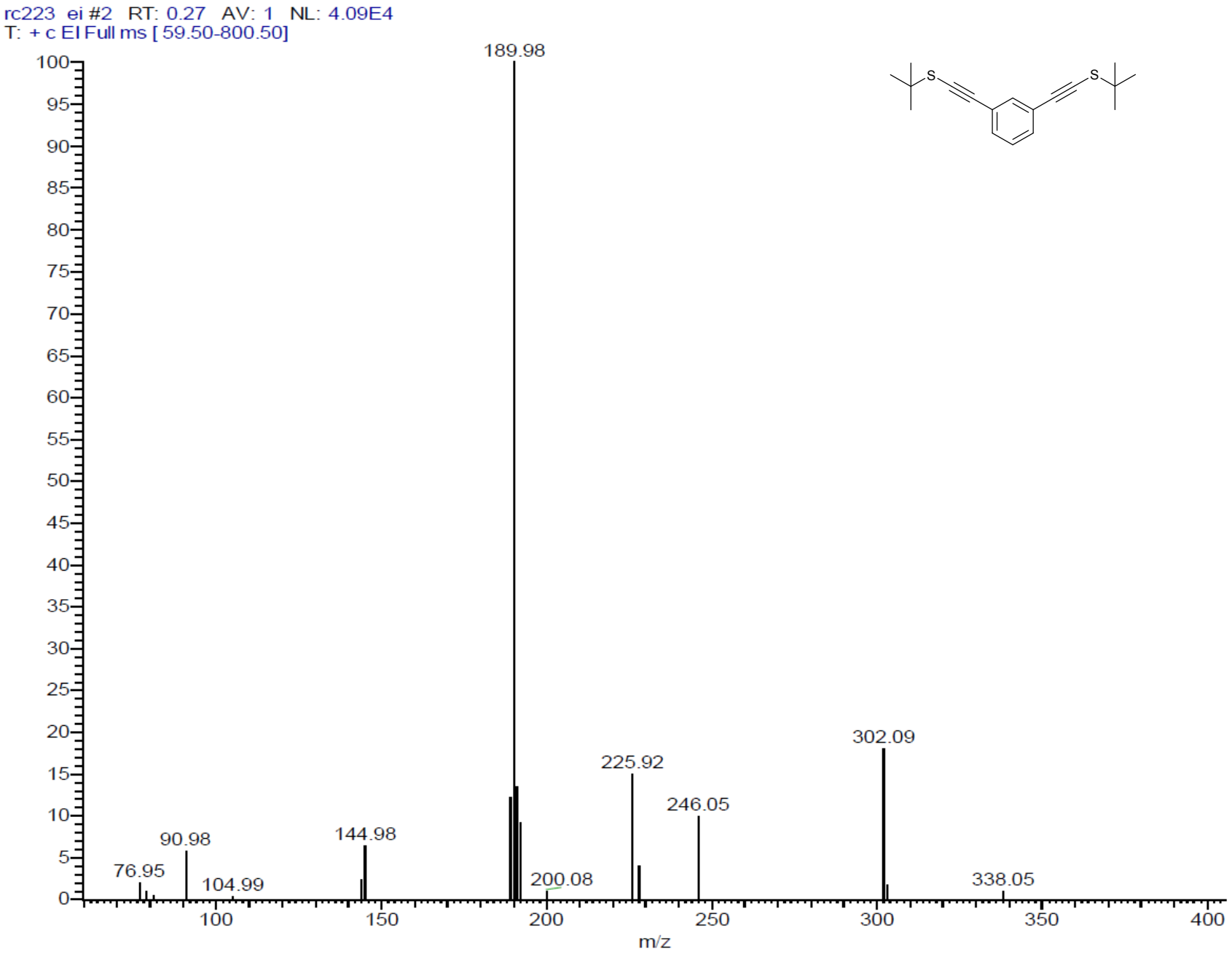

152.17
148.19
138.25
123.08
121.09
92.99
83.54
48.98
30.58
S
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


rc221a_ei #6 RT: 0.65 AV: 1 NL: 3.12E5
T: + c EI Full ms [59.50-800.50]
168.99
134.98
225.03
281.12
121.97
103.99
62.78
68.85
80.90
152.96
191.07
193.99
S
N
m/z

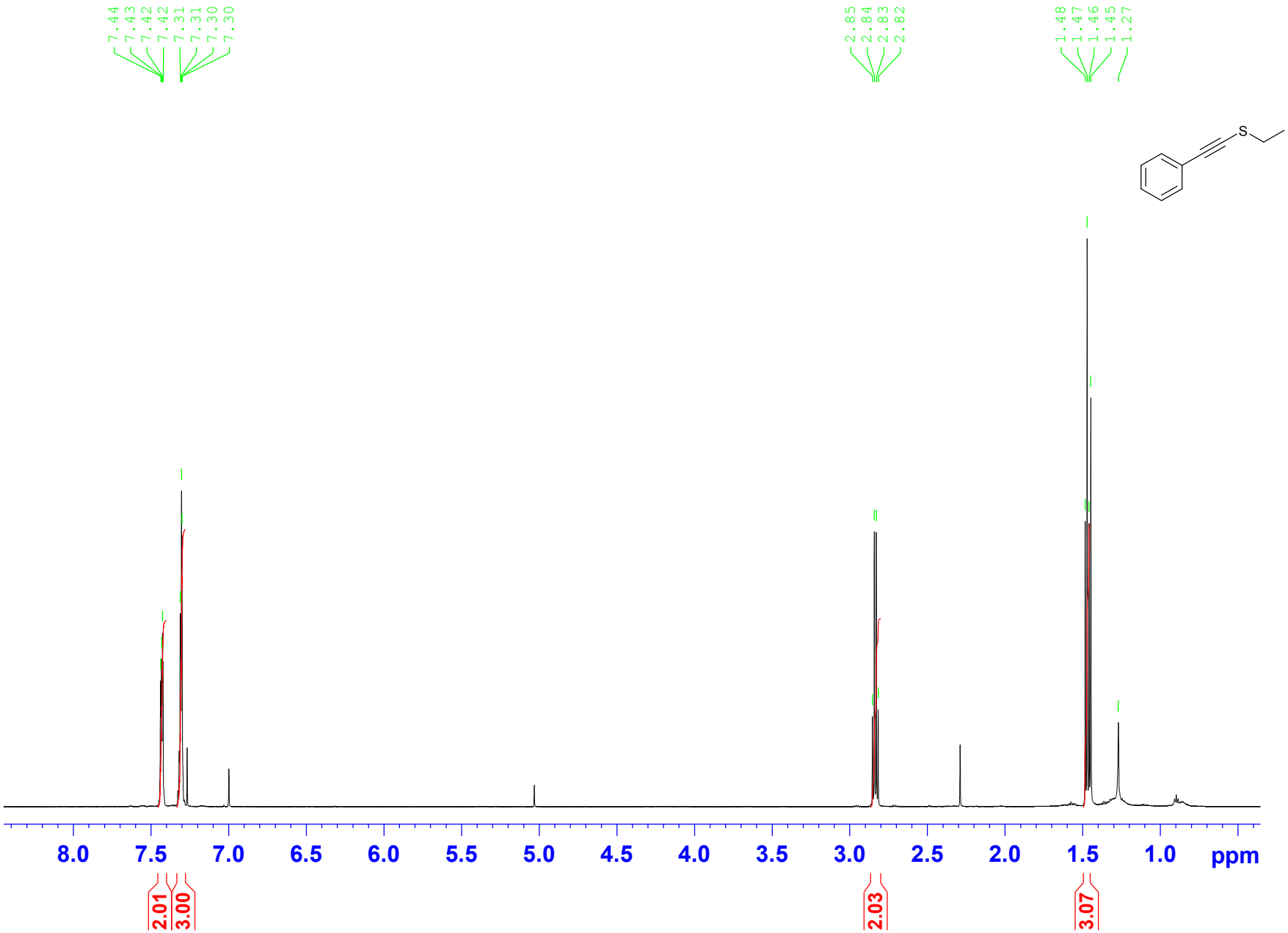
1,3-bis((*tert*-butylthio)ethynyl)benzene (2l)

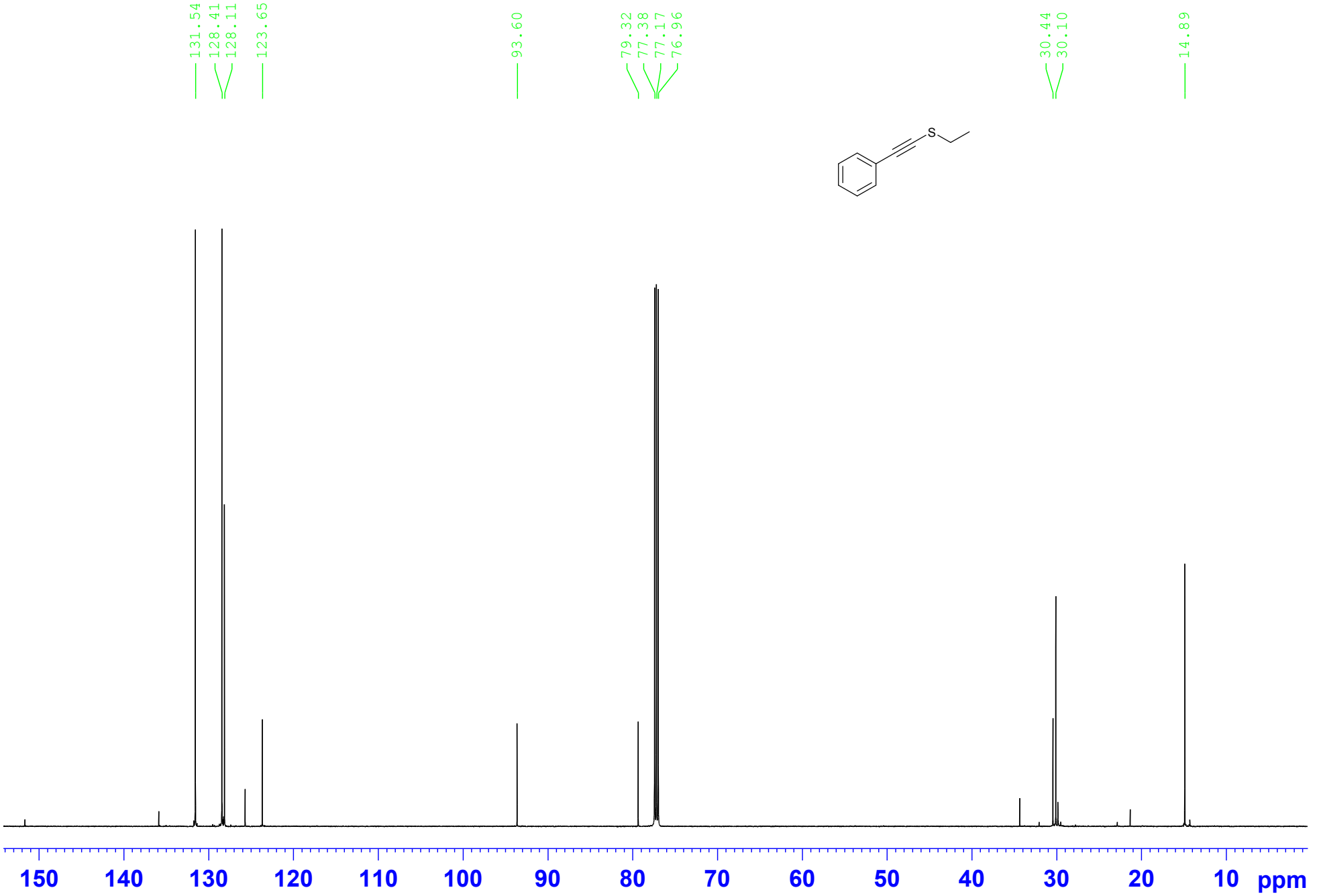


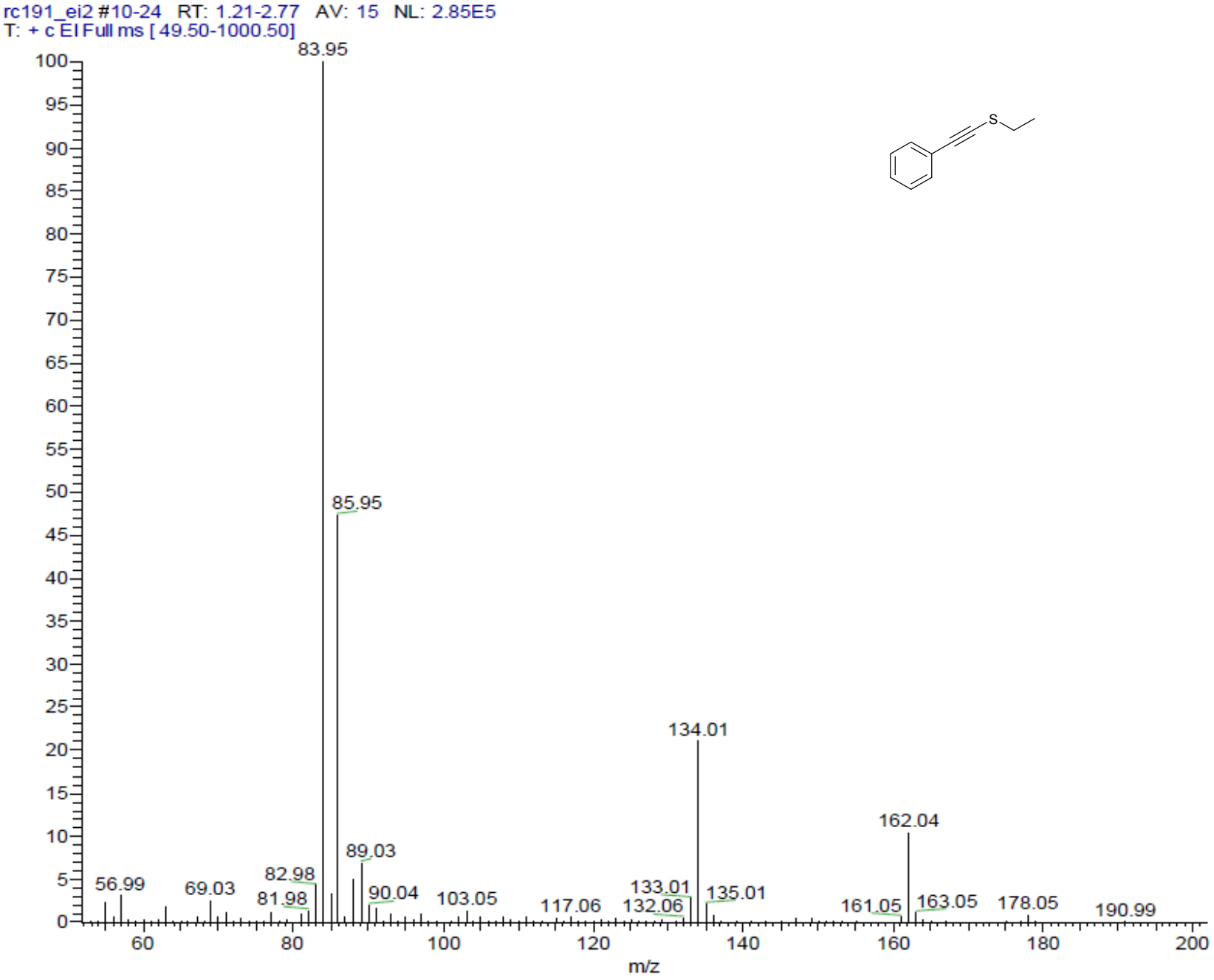

133.92
130.65
128.50
124.15
95.55
80.10
48.72
30.55
S
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc223 ei #2 RT: 0.27 AV: 1 NL: 4.09E4
T: + c EI Full ms [59.50-800.50]
189.98
302.09
225.92
246.05
90.98
144.98
76.95
104.99
200.08
338.05
m/z

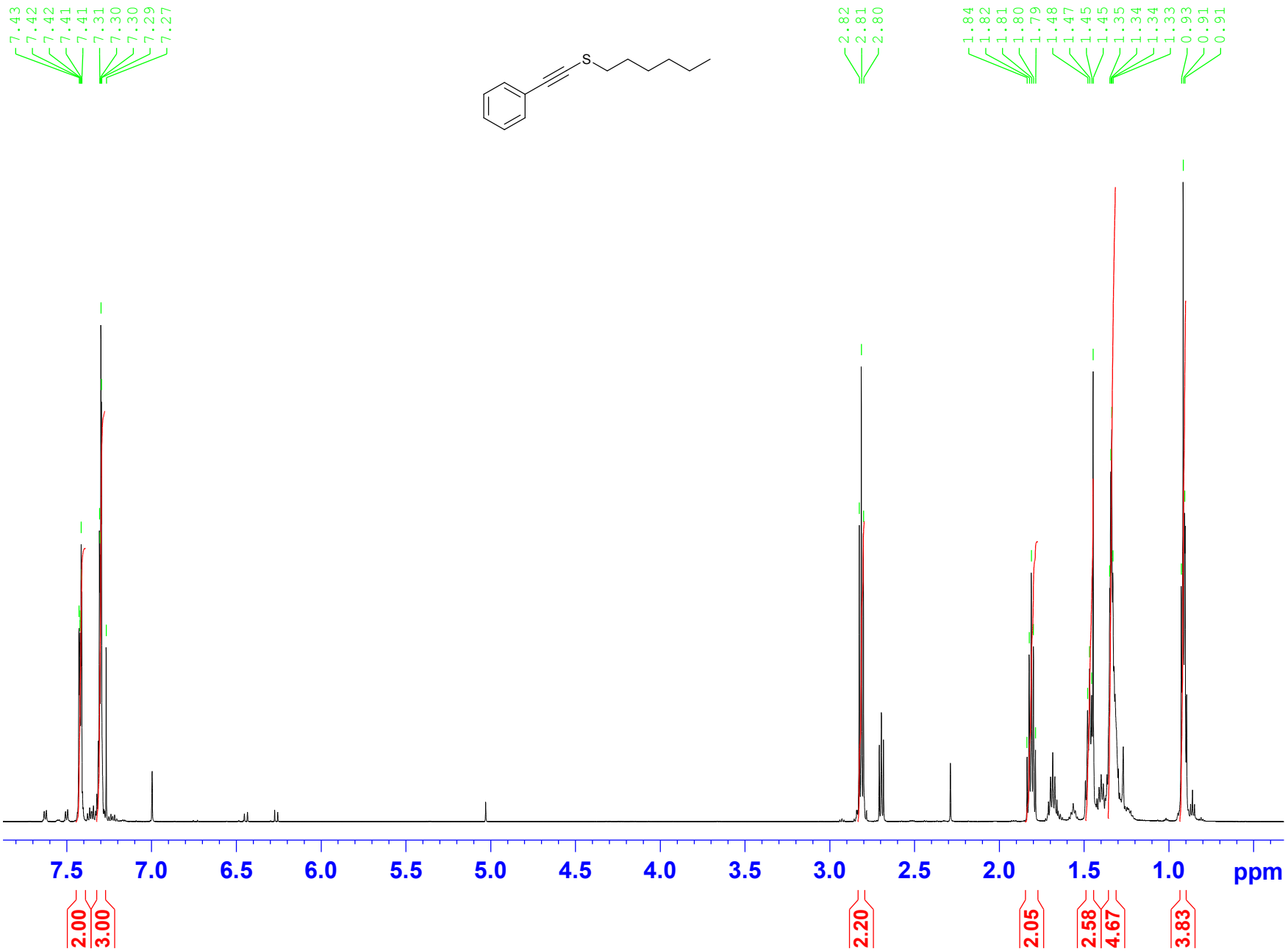
Ethyl(phenylethynyl)sulfane (2m)

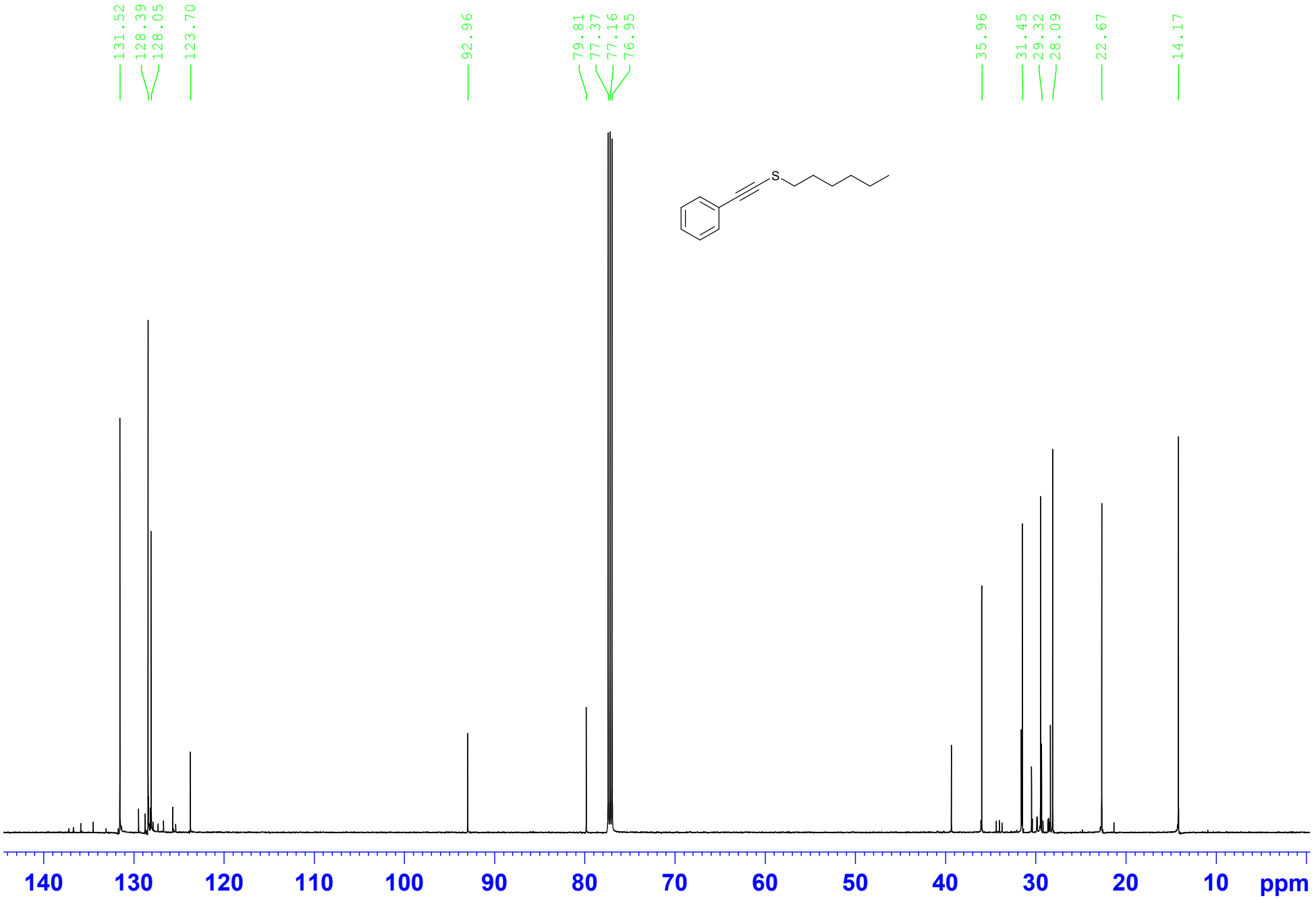


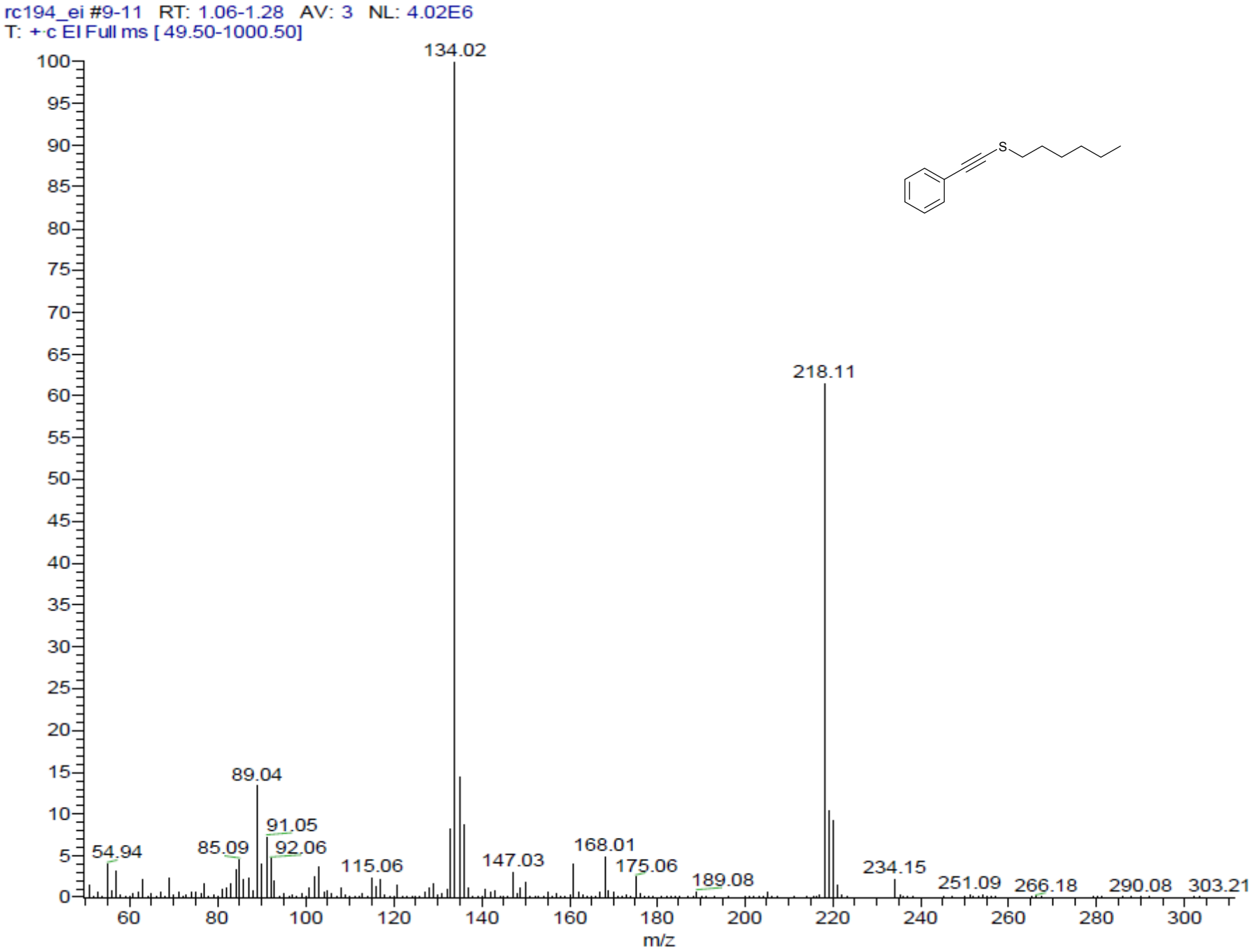

131.54
128.41
128.11
123.65
93.60
79.32
77.38
77.17
76.96
30.44
30.10
14.89
S
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc191_ei2 #10-24 RT: 1.21-2.77 AV: 15 NL: 2.85E5
T: + c EI Full ms [49.50-1000.50]
83.95
85.95
134.01
162.04
89.03
82.98
56.99
69.03
81.98
90.04
103.05
117.06
133.01
132.06
135.01
161.05
163.05
178.05
190.99
S
m/z

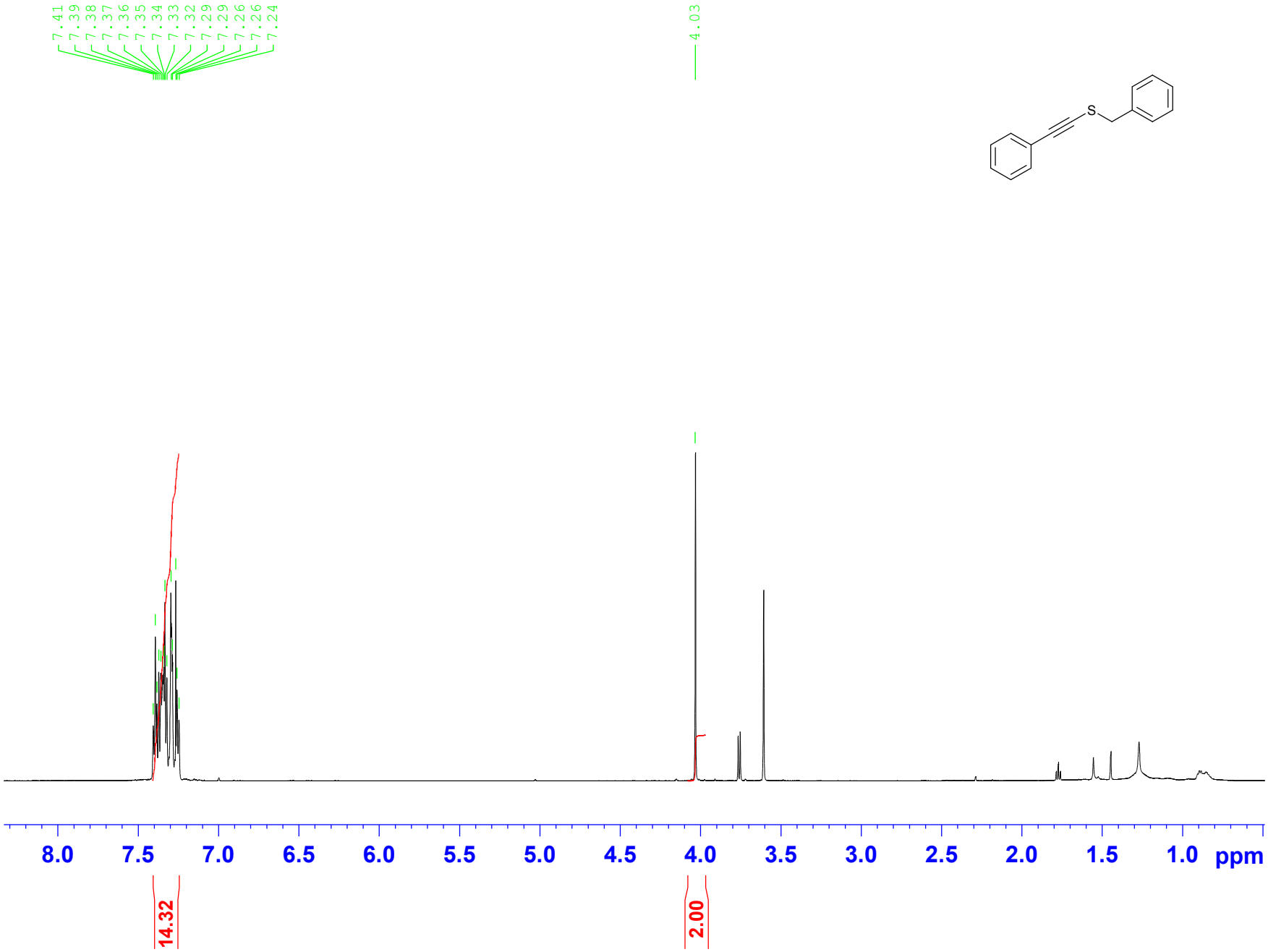
Hexyl(phenylethynyl)sulfane (2n)

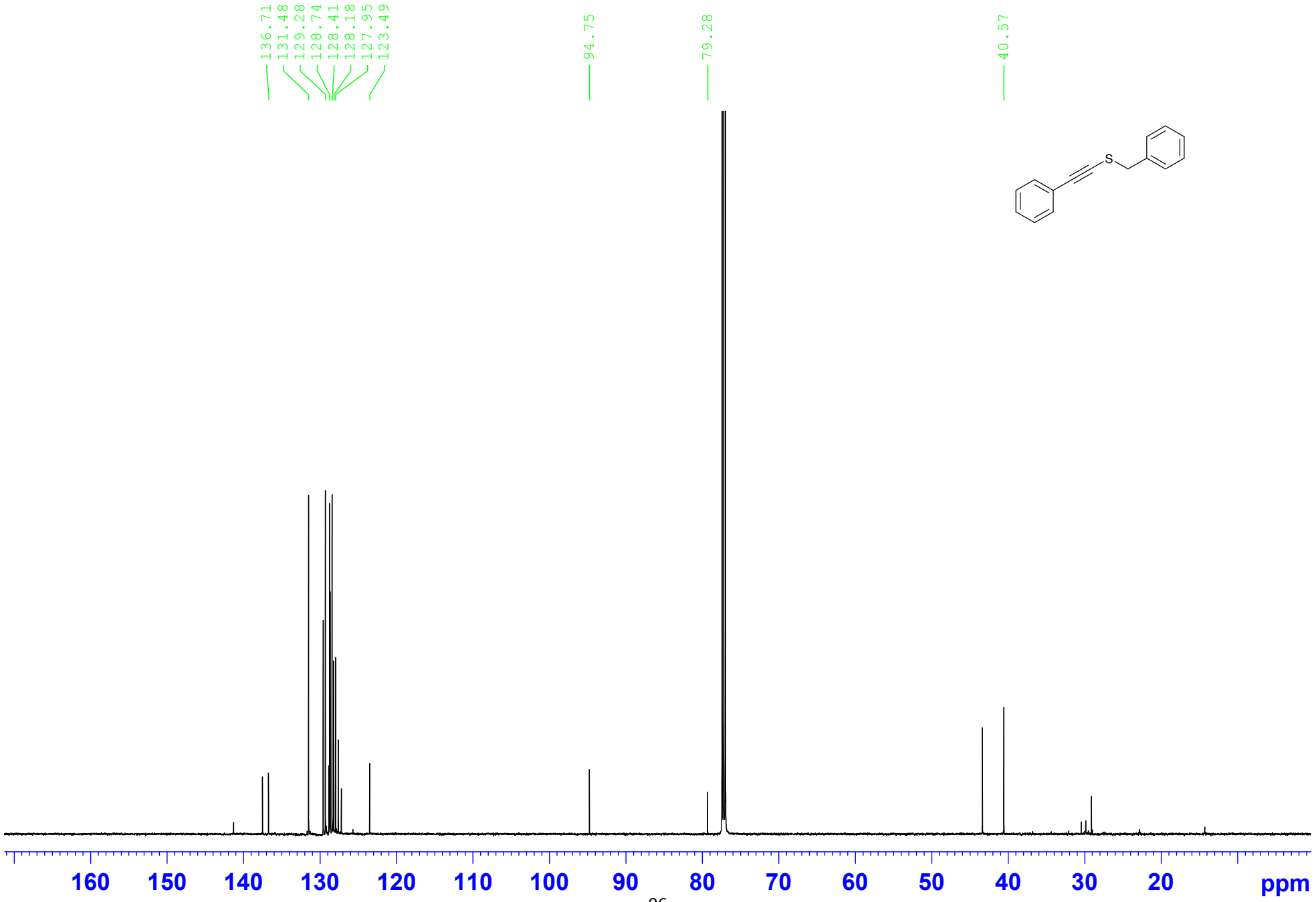


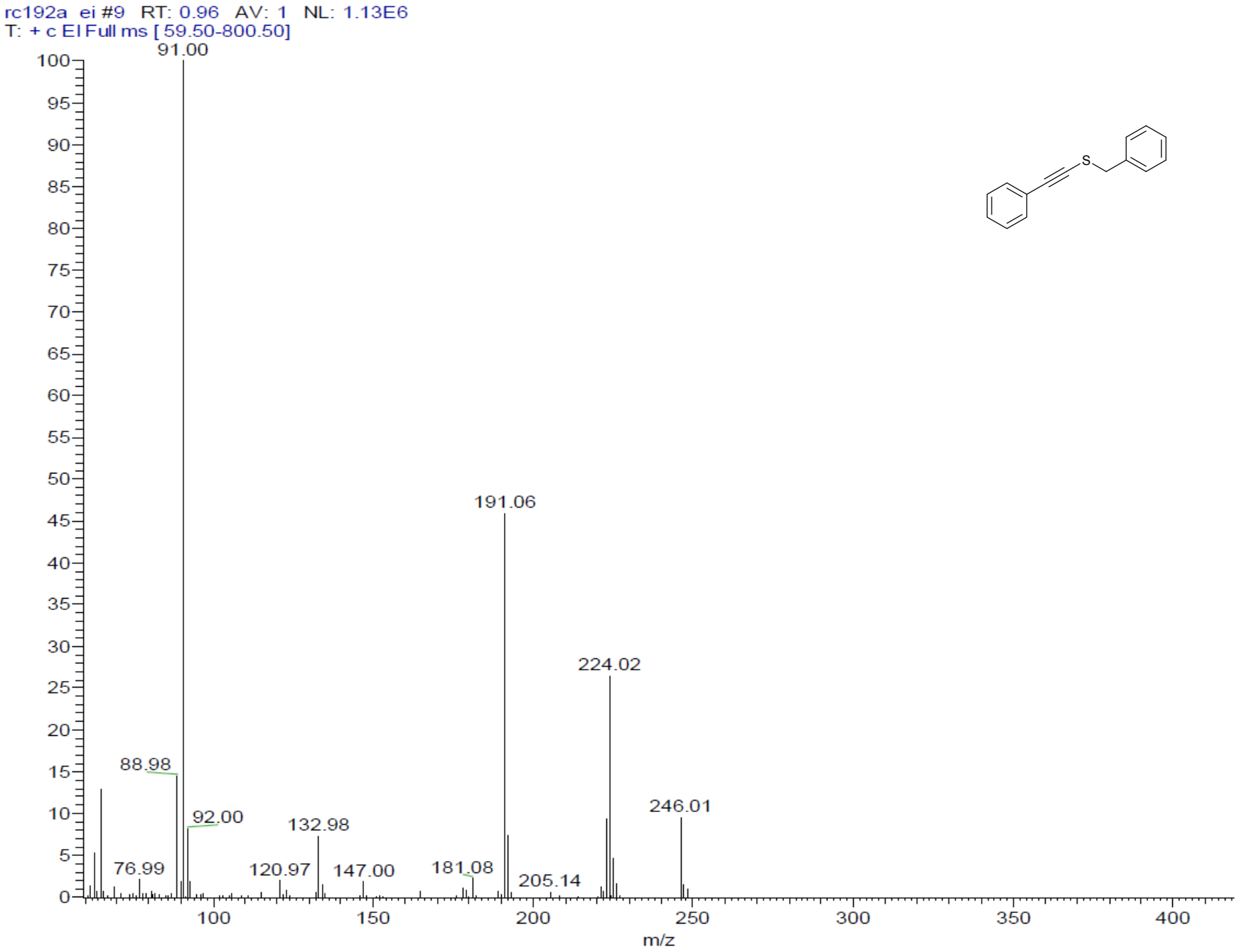

131.52
128.39
128.05
123.70
92.96
79.81
77.37
77.16
76.95
35.96
31.45
29.32
28.09
22.67
14.17
S
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc194_ei #9-11 RT: 1.06-1.28 AV: 3 NL: 4.02E6
T: +c EI Full ms [49.50-1000.50]
134.02
218.11
89.04
91.05
92.06
54.94
85.09
115.06
147.03
168.01
175.06
189.08
234.15
251.09
266.18
290.08
303.21
S
m/z

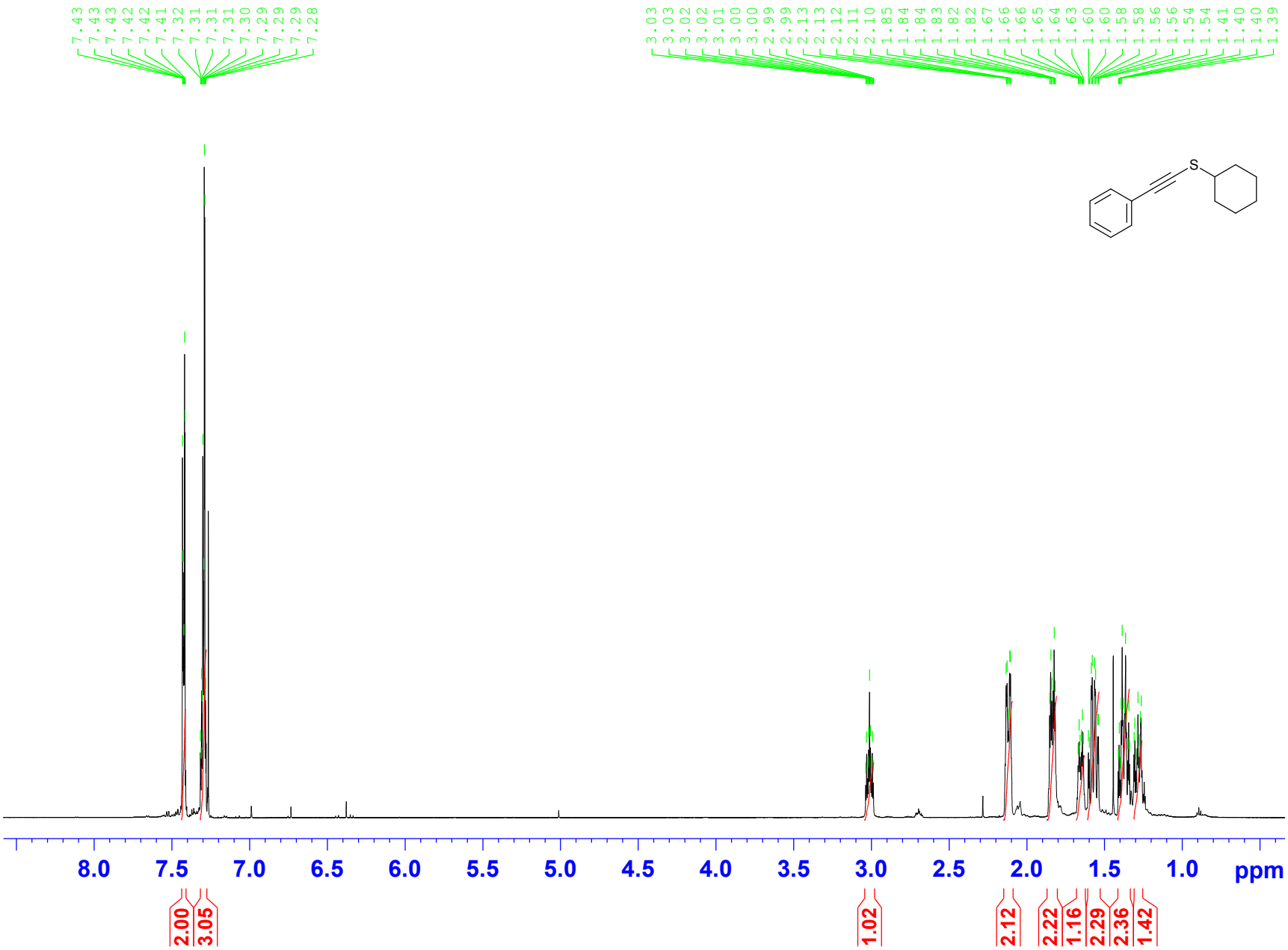
Benzyl(phenylethynyl)sulfane (2o)

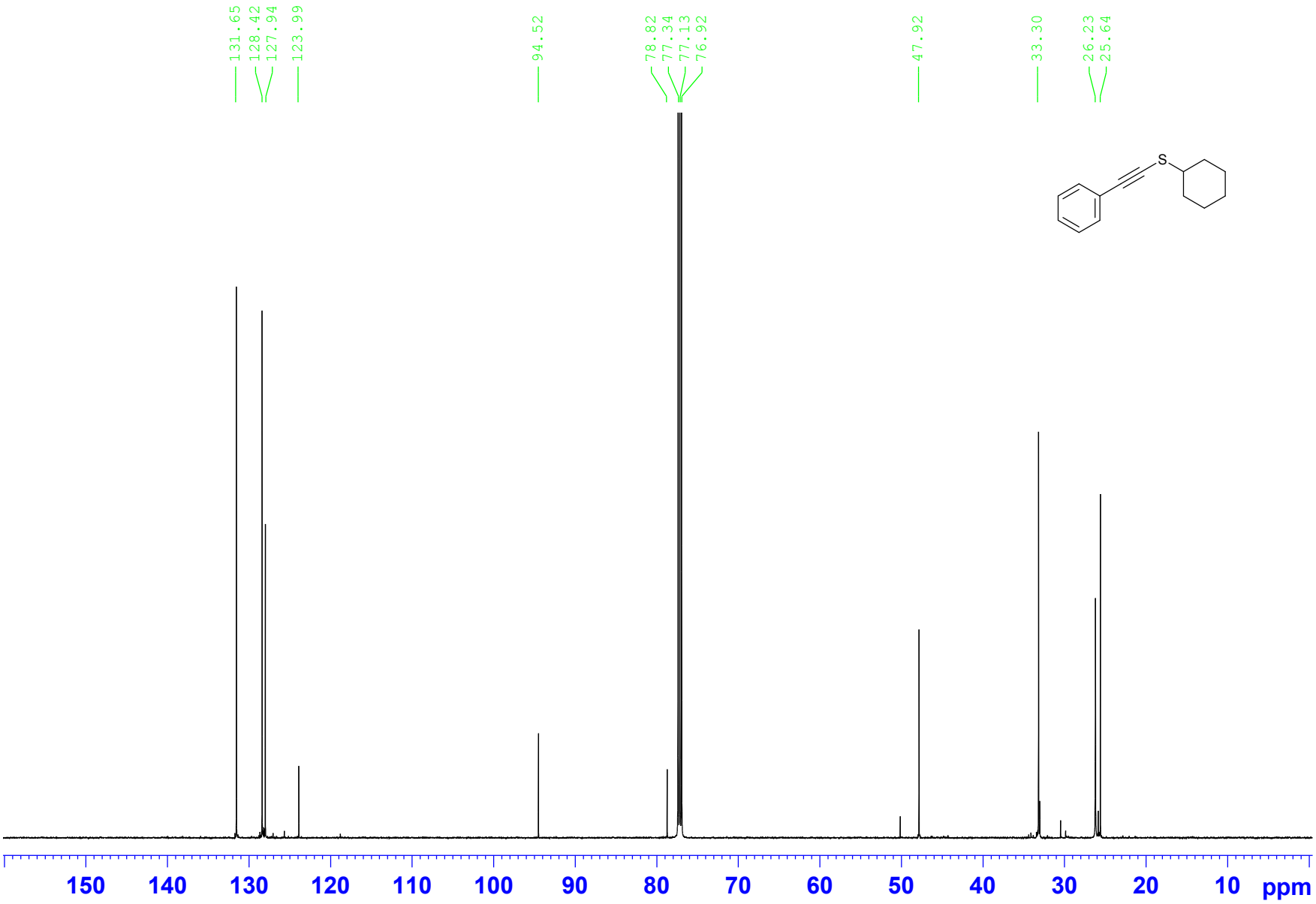


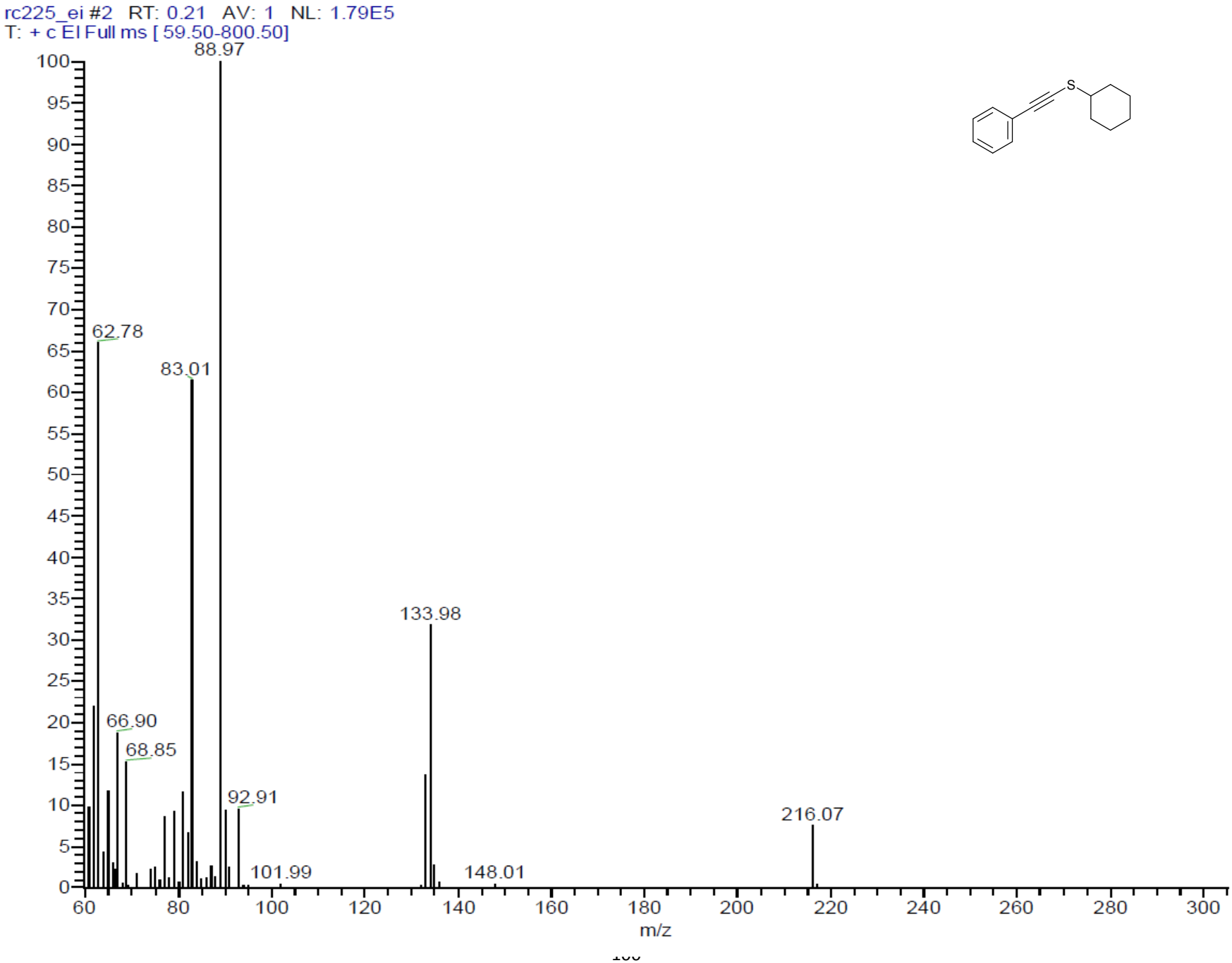

136.71
131.48
129.28
128.74
128.41
128.18
127.95
123.49
94.75
79.28
40.57
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


rc192a ei #9 RT: 0.96 AV: 1 NL: 1.13E6
T: + c EI Full ms [59.50-800.50]
91.00
191.06
224.02
246.01
88.98
92.00
132.98
76.99
120.97
147.00
181.08
205.14
S
m/z

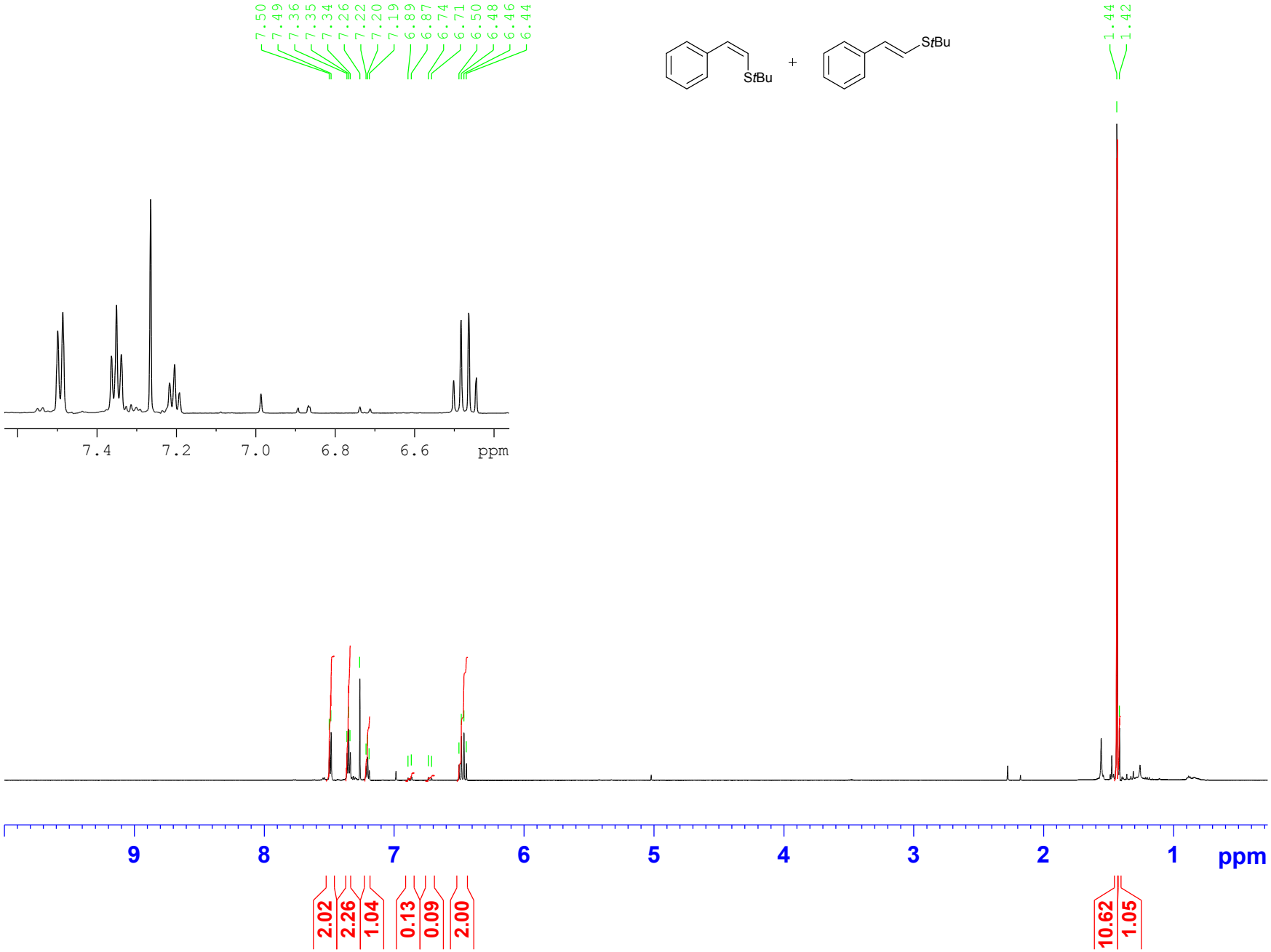
Cyclohexyl(phenylethynyl)sulfane (2p)

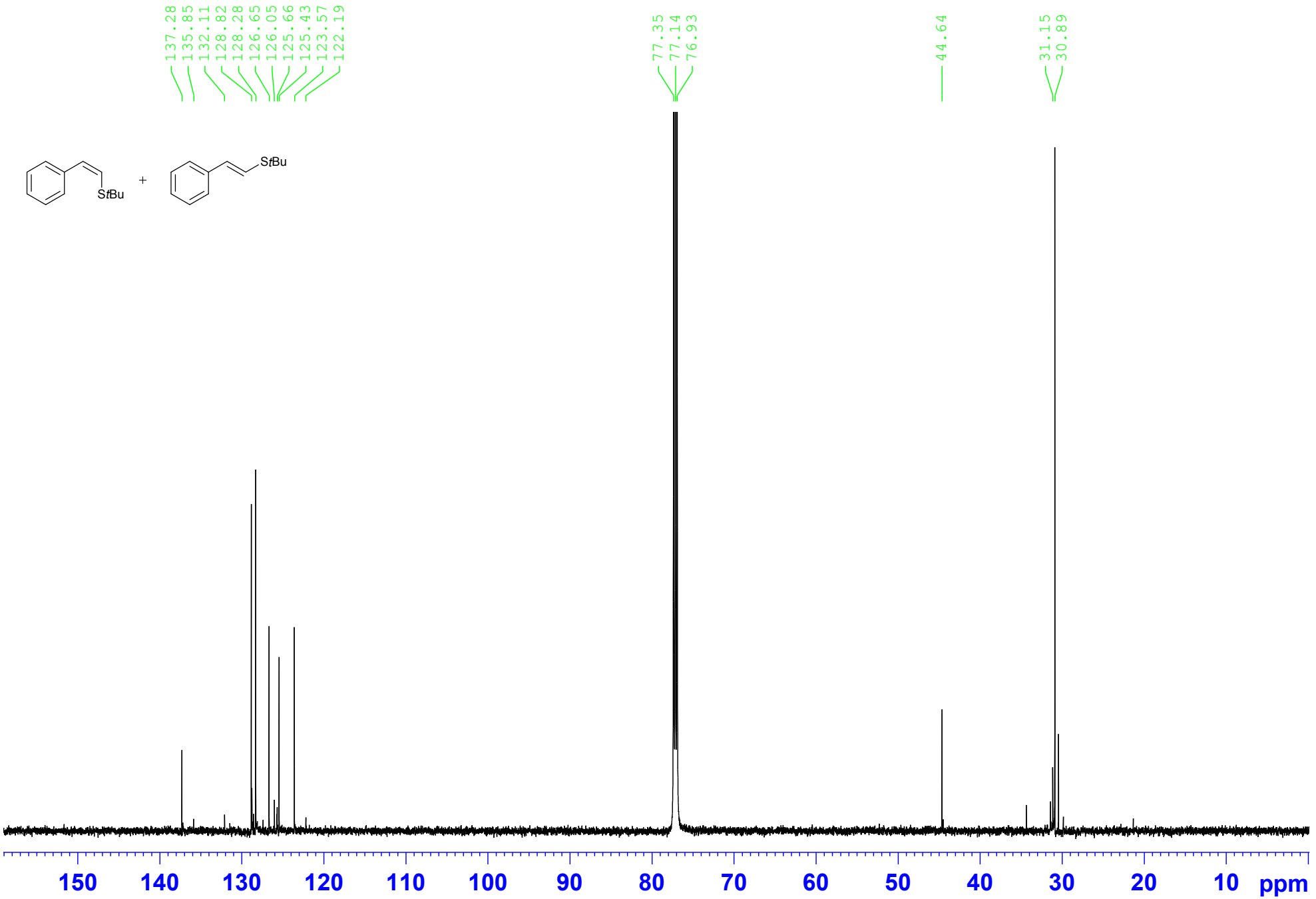


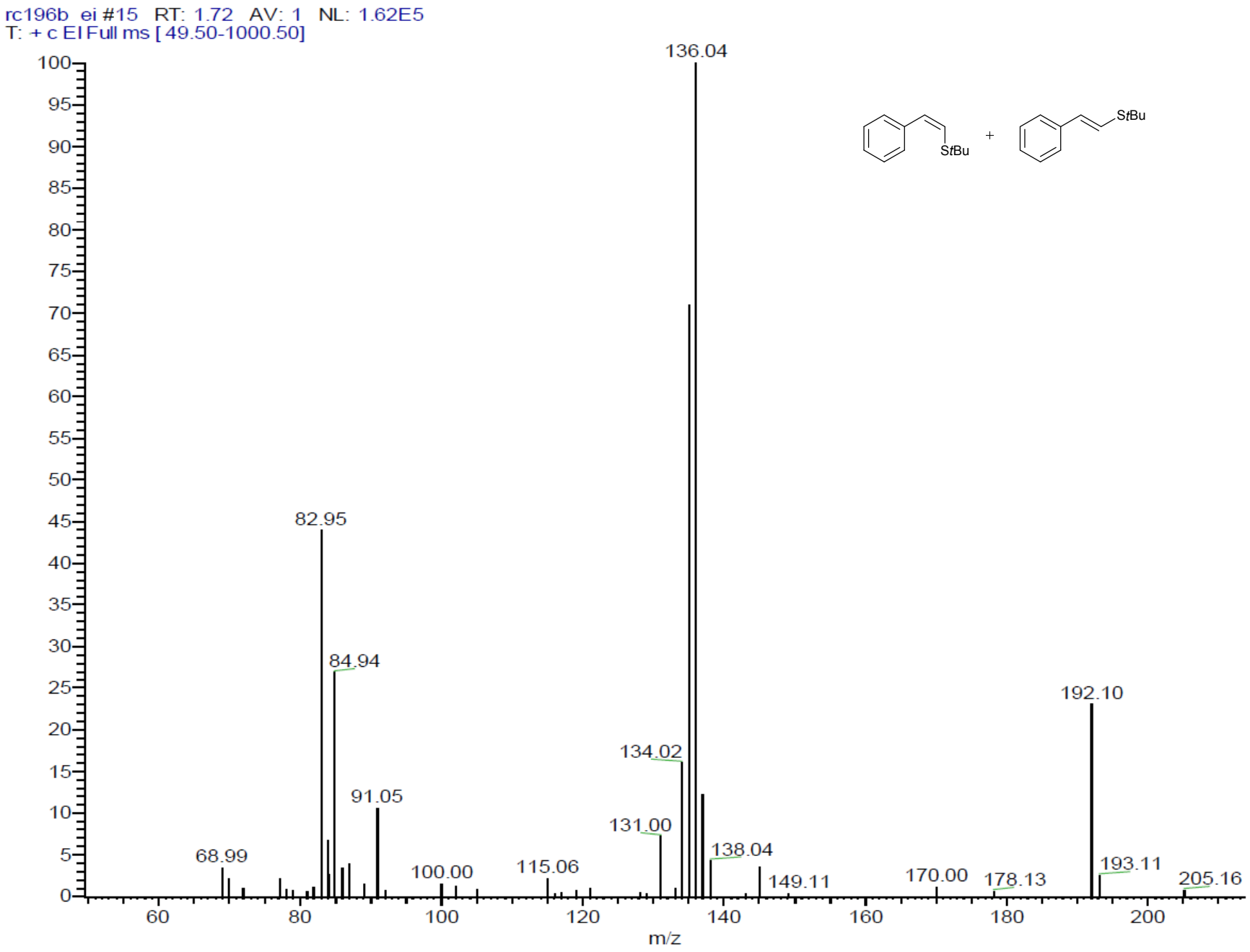

131.65
128.42
127.94
123.99
94.52
78.82
77.34
77.13
76.92
47.92
33.30
26.23
25.64
S
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc225_ei #2 RT: 0.21 AV: 1 NL: 1.79E5
T: + c EI Full ms [59.50-800.50]
88.97
62.78
83.01
133.98
66.90
68.85
92.91
216.07
101.99
148.01
S
m/z

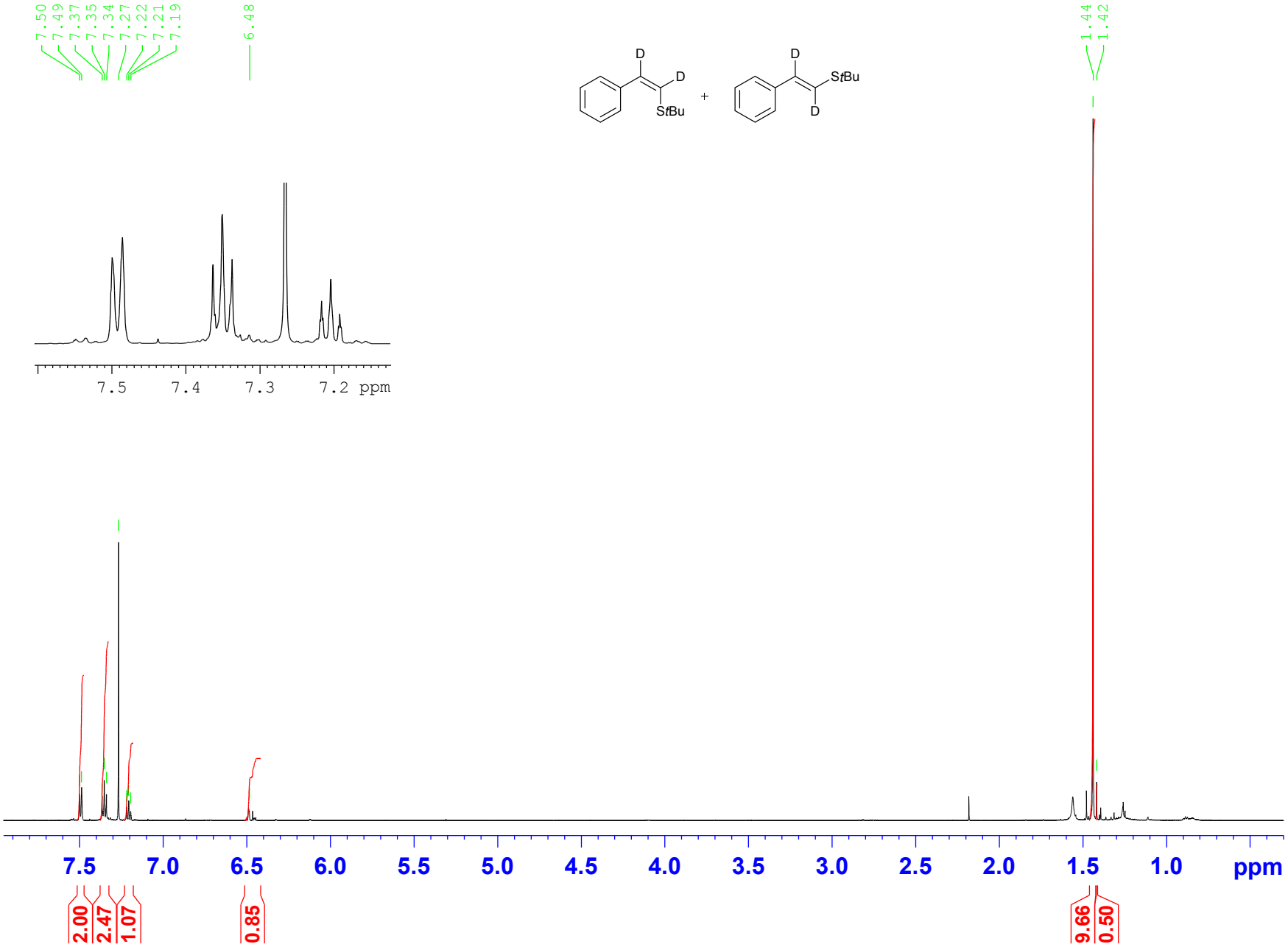
(Z/E)-*tert*-butyl(styryl)sulfane (3a/b)

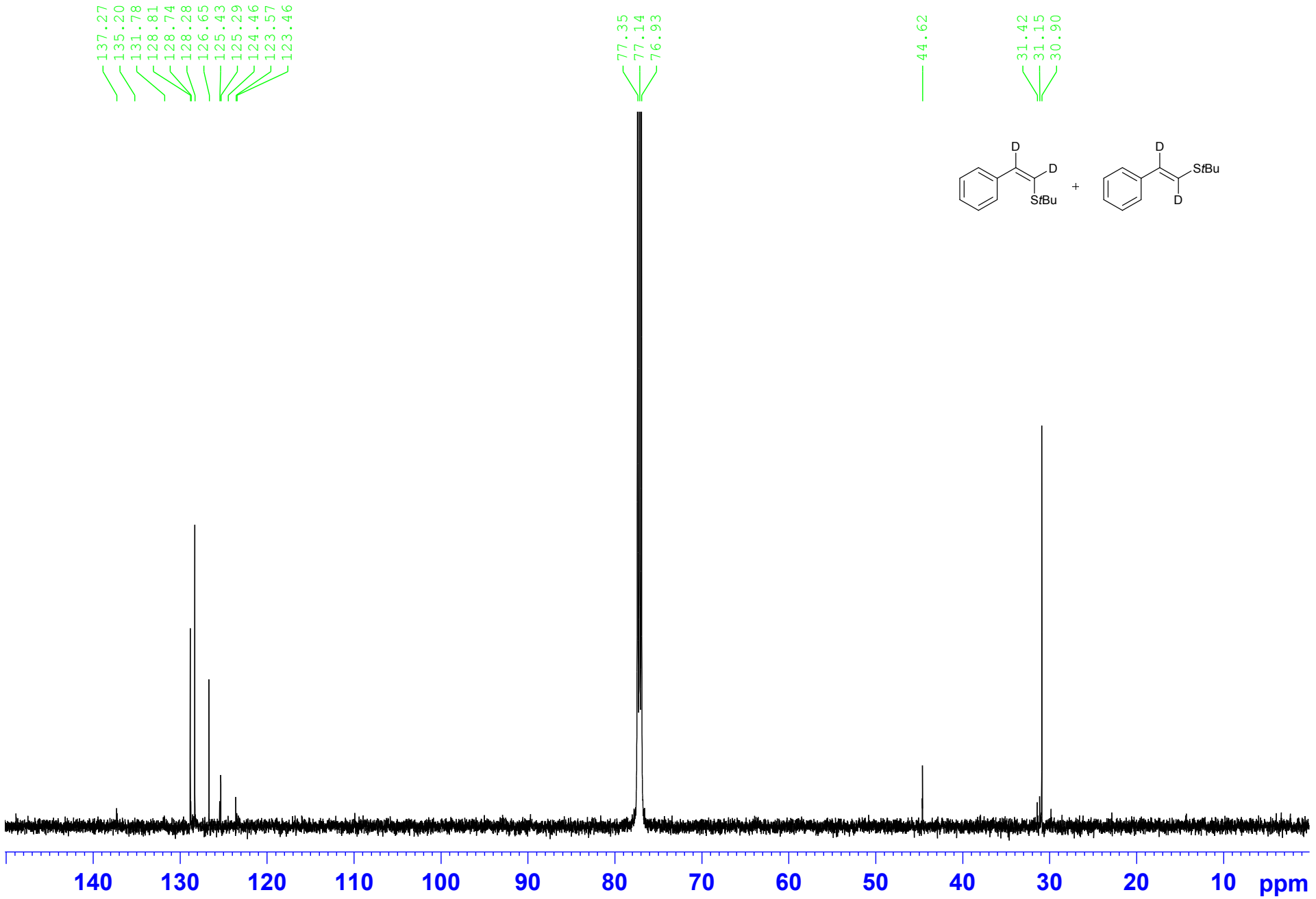


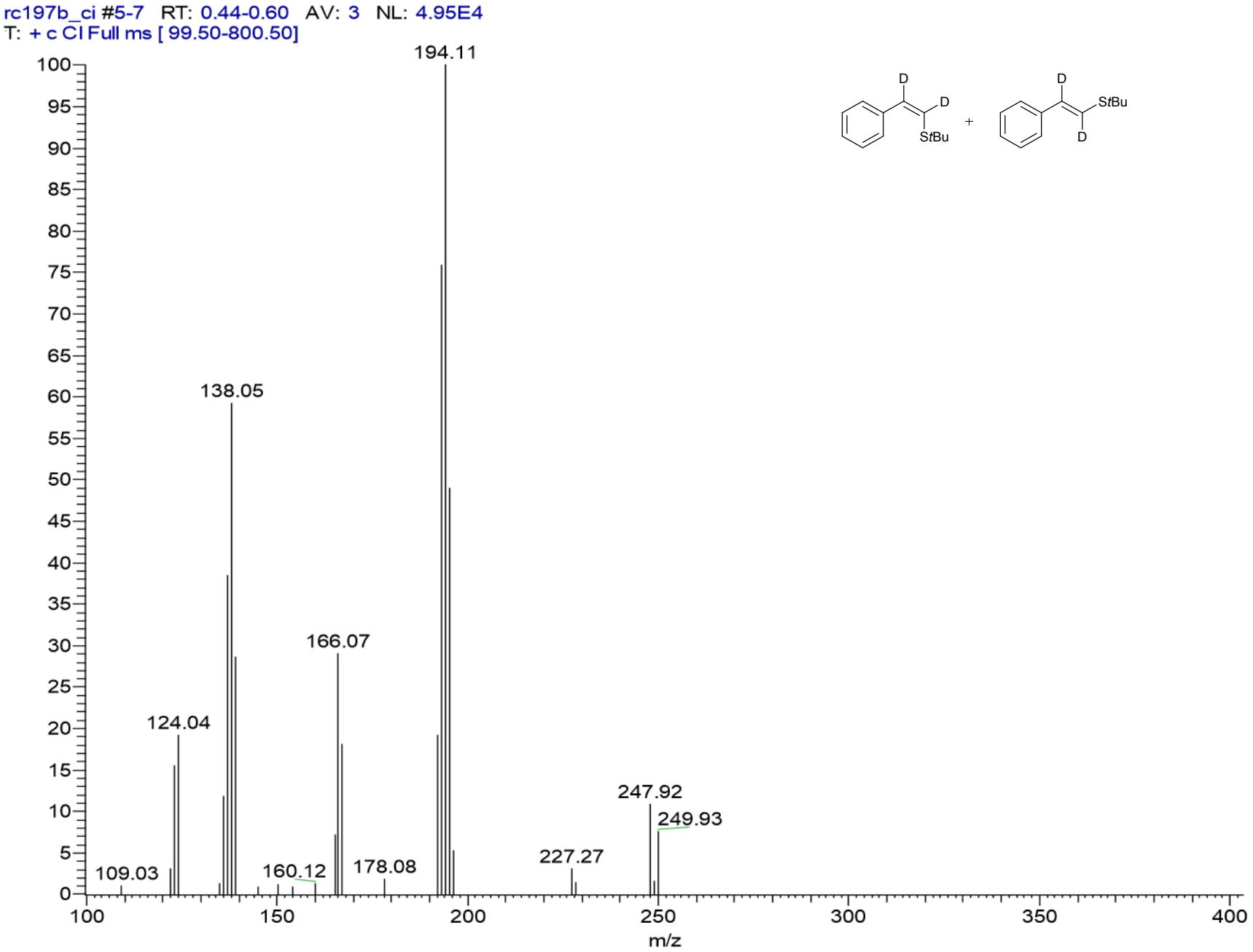

137.28
135.85
132.11
128.82
128.28
126.65
126.05
125.66
125.43
123.57
122.19
77.35
77.14
76.93
44.64
31.15
30.89
StBu
+
StBu
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc196b ei #15 RT: 1.72 AV: 1 NL: 1.62E5
T: + c EI Full ms [49.50-1000.50]
136.04
82.95
84.94
192.10
134.02
91.05
131.00
138.04
68.99
100.00
115.06
149.11
170.00
178.13
193.11
205.16
StBu
StBu
m/z

(Z/E)-*tert*-butyl(styryl)sulfane-d^2 (3c/d)




137.27
135.20
131.78
128.81
128.74
128.28
126.65
125.43
125.29
124.46
123.57
123.46
77.35
77.14
76.93
44.62
31.42
31.15
30.90
D
D
StBu
+
D
StBu
D
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


rc197b_ci #5-7 RT: 0.44-0.60 AV: 3 NL: 4.95E4
T: + c CI Full ms [99.50-800.50]
194.11
138.05
166.07
124.04
247.92
249.93
227.27
109.03
160.12
178.08
m/z
D
D
StBu
D
StBu
D

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