Supporting Information

Organocatalytic Allylic Alkylation of Alkyne-Substituted MBH Carbonates: Access to Quaternary Carbon-Containing 1,4-Enynes

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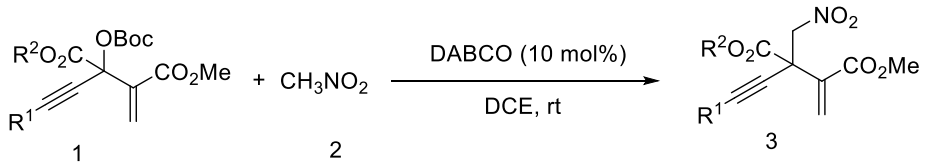
1. General Information

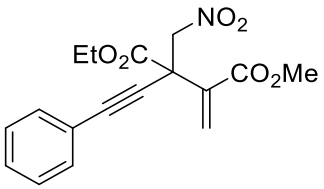
All reactions were carried out in glassware with magnetic stirring. Unless otherwise noted, solvents were either purchased from commercial suppliers or purified by standard procedures. Purification of the reaction products was carried out by flash column chromatography at reduced pressure. Thin layer chromatography was performed using silica gel plates and visualized with ultraviolet light. ^{1}H NMR spectra was recorded on JEOL 400MHz spectrometer and the chemical shifts were reported in ppm (δ) relative to internal standard TMS (0 ppm). ^{13}C NMR spectra are recorded at 100 MHz and referenced to the central $CDCl_3$ resonance (77.0 ppm). The results of mass spectrometry under ESI light source were recorded by Thermo Scientific Q Exactive instrument. MBH carbonates[1] were synthesized according to literature and the spectral data are consistent with those reported.

2. General Procedure for the Synthesis of 1,4-Enyne Product



1 2 3

To the solution of MBH carbonate **1** (0.2 mmol) in DCE (1 mL), nitromethane **2** (0.6 mmol) and DABCO (0.02 mmol) were successively added under stirring. The reaction was stirred at room temperature and monitored by thin layer chromatography. Upon the completion of the reaction, the solvent was evaporated and the residue was purified by flash column chromatography to give 1,4-enyne product **3**.



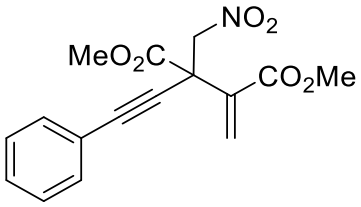
1-ethyl 4-methyl 3-methylene-2-(nitromethyl)-2-(phenylethynyl)succinate (**3a**).

White solid, 51.2 mg, 77% yield; mp 65-66 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 6.4 Hz, 2H), 7.35 (dd, J = 8.9, 7.1 Hz, 3H), 6.66 (s, 1H), 6.50 (s, 1H), 5.26 (d, J = 11.4 Hz, 1H), 5.16 (d, J = 11.0 Hz, 1H), 4.29 (dd, J = 6.9, 5.5 Hz, 2H), 3.83 (s, 3H), 1.26-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

166.83, 165.27, 134.97, 132.10, 131.94, 129.24, 128.35, 121.30, 89.89, 81.83, 79.58, 63.12, 52.52, 50.53, 13.75 ppm;

ESI-HRMS calcd for $C_{17}H_{17}NO_6$ $[M+H]^+$: 332.1128, found 332.1129.



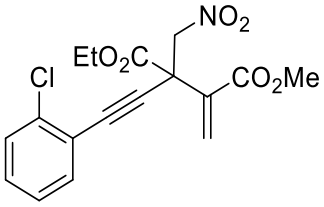
dimethyl 3-methylene-2-(nitromethyl)-2-(phenylethynyl)succinate (**3b**).

White solid, 46.9 mg, 74% yield; mp 113-114 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 6.9 Hz, 2H), 7.35 (t, J = 8.5 Hz, 3H), 6.67 (s, 1H), 6.52 (s, 1H), 5.25 (d, J = 11.0 Hz, 1H), 5.16 (d, J = 11.4 Hz, 1H), 3.83 (d, J = 6.6 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.41, 165.23, 134.88, 132.17, 131.95, 129.28, 128.34, 121.16, 90.06, 81.53, 79.53, 53.99, 52.60, 50.33 ppm

ESI-HRMS calcd for $C_{16}H_{15}NO_6$ $[M+H]^+$: 318.0972, found 318.0973.



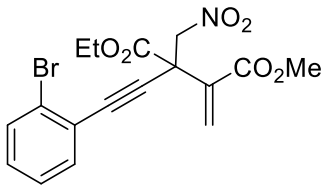
1-ethyl 4-methyl 2-((2-chlorophenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3c**).

White solid, 57.0 mg, 78% yield; mp 72-74 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J = 7.5, 1.6 Hz, 1H), 7.40-7.42 (m, 1H), 7.27 (dd, J = 27.4, 1.4 Hz, 2H), 6.68 (s, 1H), 6.63 (s, 1H), 5.28 (d, J = 11.4 Hz, 1H), 5.18 (d, J = 11.4 Hz, 1H), 4.29 (dd, J = 6.9, 1.4 Hz, 2H), 3.84 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.60, 165.21, 136.34, 134.61, 133.68, 132.46, 130.25, 129.30, 126.49, 121.38, 86.97, 86.31, 79.30, 63.19, 52.54, 50.70, 13.76 ppm;

ESI-HRMS calcd for $C_{17}H_{17}ClNO_6$ $[M+H]^+$: 366.0739, found 366.0742.



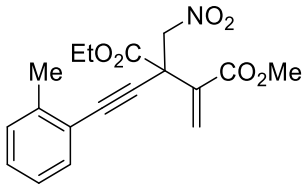
1-ethyl 4-methyl 2-((2-bromophenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3d**).

White solid, 51.0 mg, 64% yield; mp 70-71 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, J = 8.0, 1.1 Hz, 1H), 7.51 (dd, J = 7.8, 1.8 Hz, 1H), 7.22-7.29 (m, 2H), 6.68 (s, 1H), 6.65 (s, 1H), 5.28 (d, J = 11.4 Hz, 1H), 5.18 (d, J = 11.4 Hz, 1H), 4.29 (dd, J = 7.1, 2.1 Hz, 2H), 3.84 (s, 3H), 1.28 (t, J = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.56, 165.22, 134.58, 133.85, 132.55, 132.46, 130.39, 127.06, 125.70, 123.59, 87.96, 86.31, 79.27, 63.20, 52.54, 50.70, 13.81 ppm;

ESI-HRMS calcd for $C_{17}H_{17}BrNO_6$ $[M+H]^+$: 410.0234, found 410.0237.



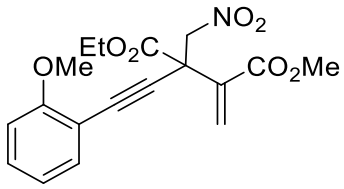
1-ethyl 4-methyl 3-methylene-2-(nitromethyl)-2-(o-tolylethynyl)succinate (**3e**).

White solid, 55.2 mg, 80% yield; mp 52-53 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.3 Hz, 1H), 7.25-7.27 (m, 1H), 7.21 (d, J = 6.9 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.66 (s, 1H), 6.52 (s, 1H), 5.28 (d, J = 11.4 Hz, 1H), 5.17 (d, J = 11.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 2.43 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.93, 165.27, 140.72, 135.07, 132.31, 132.09, 129.53, 129.22, 125.57, 121.11, 88.68, 85.61, 79.58, 63.08, 52.53, 50.74, 20.58, 13.78 ppm;

ESI-HRMS calcd for $C_{18}H_{20}NO_6$ $[M+H]^+$: 346.1285, found 346.1286.



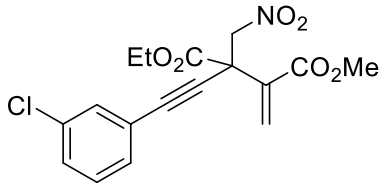
1-ethyl 4-methyl 2-((2-methoxyphenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3f**).

White solid, 54.5 mg, 75% yield; mp 124-125 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 6.9 Hz, 1H), 7.28-7.31 (m, 1H), 6.84-6.90 (m, 2H), 6.67 (d, J = 10.1 Hz, 2H), 5.20 (dd, J = 35.0, 11.2 Hz, 2H), 4.24-4.28 (m, 2H), 3.82 (d, J = 9.6 Hz, 6H), 1.25 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.08, 165.50, 160.75, 135.07, 133.61, 132.66, 130.74, 120.39, 110.78, 86.55, 85.76, 79.60, 63.11, 55.78, 52.58, 50.87, 13.86 ppm;

ESI-HRMS calcd for $C_{18}H_{20}NO_7$ $[M+H]^+$: 362.1234, found 362.1237.



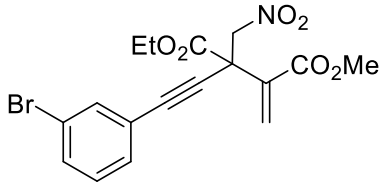
1-ethyl 4-methyl 2-((3-chlorophenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3g**).

White solid, 44.9 mg, 61% yield; mp 64-66 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, J = 1.6 Hz, 1H), 7.34-7.38 (m, 2H), 7.27 (t, J = 7.8 Hz, 1H), 6.66 (s, 1H), 6.46 (s, 1H), 5.26 (d, J = 11.0 Hz, 1H), 5.15 (d, J = 11.4 Hz, 1H), 4.29 (t, J = 7.3 Hz, 2H), 3.83 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.54, 165.12, 134.72, 134.20, 132.04, 131.71, 130.10, 129.63, 129.55, 122.89, 88.32, 83.07, 79.41, 63.23, 52.55, 50.46, 13.73 ppm;

ESI-HRMS calcd for $C_{17}H_{17}ClNO_6$ $[M+H]^+$: 366.0739, found 366.0740.



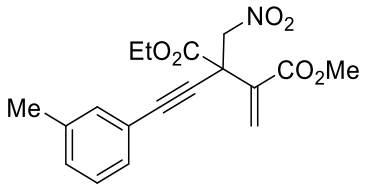
1-ethyl 4-methyl 2-((3-bromophenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3h**).

White solid, 32.9 mg, 40% yield; mp 44-45 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (t, J = 1.6 Hz, 1H), 7.50-7.52 (m, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.65 (s, 1H), 6.45 (s, 1H), 5.26 (d, J = 11.4 Hz, 1H), 5.14 (d, J = 11.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.56, 165.14, 134.72, 134.57, 132.46, 132.08, 130.56, 129.83, 123.20, 122.14, 88.20, 83.19, 79.42, 63.26, 52.58, 50.47, 13.76 ppm;

ESI-HRMS calcd for $C_{17}H_{17}BrNO_6$ $[M+H]^+$: 410.0234, found 410.0235.



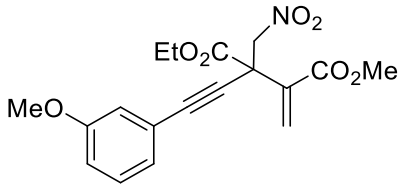
1-ethyl 4-methyl 3-methylene-2-(nitromethyl)-2-(m-tolylethynyl)succinate (**3i**).

White solid, 49.4 mg, 72% yield; mp 74-75 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.30 (m, 2H), 7.19-7.24 (m, 2H), 6.65 (s, 1H), 6.50 (s, 1H), 5.26 (d, J = 11.0 Hz, 1H), 5.15 (d, J = 11.0 Hz, 1H), 4.28 (dd, J = 7.1, 6.2 Hz, 2H), 3.83 (s, 3H), 2.34 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.85, 165.27, 138.11, 134.97, 132.46, 132.12, 130.11, 128.99, 128.23, 121.06, 90.09, 81.38, 79.58, 63.10, 52.51, 50.50, 21.13, 13.75 ppm.

ESI-HRMS calcd for $C_{18}H_{20}NO_6$ $[M+H]^+$: 346.1285, found 346.1288.



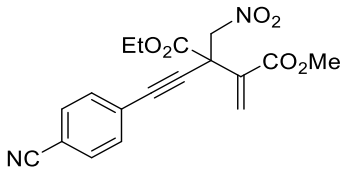
1-ethyl 4-methyl 2-((3-methoxyphenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3j**).

White solid, 47.7 mg, 59% yield; mp 86-87 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.27 (m, 1H), 7.07-7.09 (m, 1H), 6.99 (q, J = 1.4 Hz, 1H), 6.92 (dt, J = 7.3, 1.3 Hz, 1H), 6.66 (s, 1H), 6.50 (s, 1H), 5.26 (d, J = 11.0 Hz, 1H), 5.16 (d, J = 11.4 Hz, 1H), 4.30 (q, J = 6.9 Hz, 2H), 3.82 (d, J = 9.6 Hz, 6H), 1.28 (t, J = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.77, 165.22, 159.24, 134.90, 132.10, 129.44, 124.43, 122.20, 116.62, 115.82, 89.76, 81.58, 79.52, 63.12, 55.29, 52.51, 50.48, 13.73 ppm;

ESI-HRMS calcd for $C_{18}H_{20}NO_7$ $[M+H]^+$: 362.1234, found 362.1235.



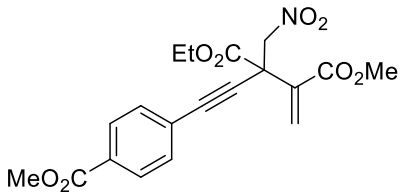
1-ethyl 4-methyl 2-((4-cyanophenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3k**).

White solid, 40.0 mg, 56% yield; mp 119-120 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J = 6.6, 2.1 Hz, 2H), 7.57-7.59 (m, 2H), 6.66 (s, 1H), 6.42 (s, 1H), 5.27 (d, J = 11.4 Hz, 1H), 5.15 (d, J = 11.4 Hz, 1H), 4.28-4.33 (m, 2H), 3.84 (s, 3H), 1.28 (q, J = 6.9 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.30, 165.01, 134.52, 132.51, 132.06, 132.00, 126.03, 118.12, 112.71, 87.91, 86.16, 79.31, 63.39, 52.65, 50.54, 13.74 ppm;

ESI-HRMS calcd for $C_{18}H_{17}N_2O_6$ $[M+H]^+$: 357.1081, found 357.1081.



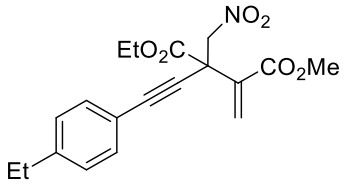
1-ethyl 4-methyl 2-((4-(methoxycarbonyl)phenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3l**).

White solid, 38.9 mg, 50% yield; mp 81-82 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 6.67 (s, 1H), 6.47 (s, 1H), 5.27 (d, J = 11.4 Hz, 1H), 5.17 (d, J = 11.4 Hz, 1H), 4.28-4.33 (m, 2H), 3.93 (s, 3H), 3.84 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.50, 166.25, 165.10, 134.66, 132.09, 131.89, 130.44, 129.46, 125.79, 88.89, 84.63, 79.39, 63.27, 52.58, 52.31, 50.53, 13.74 ppm;

ESI-HRMS calcd for $C_{19}H_{20}NO_8$ $[M+H]^+$: 390.1183, found 390.1184.



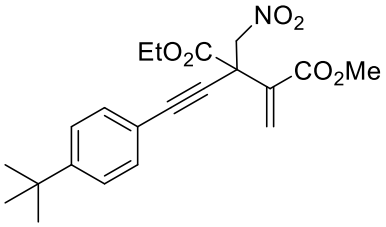
1-ethyl 4-methyl 2-((4-ethylphenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3m**).

white solid, 43.2 mg, 60% yield; mp 54-55 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.41 (m, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.65 (s, 1H), 6.50 (s, 1H), 5.25 (d, J = 11.4 Hz, 1H), 5.15 (d, J = 11.4 Hz, 1H), 4.25-4.32 (m, 2H), 3.83 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 1.25 (td, J = 14.5, 7.0 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.91, 165.30, 145.80, 135.01, 132.14, 131.93, 127.91, 118.44, 90.13, 81.09, 79.62, 63.08, 52.51, 50.53, 28.84, 15.36, 13.76 ppm

ESI-HRMS calcd for $C_{19}H_{22}NO_6$ $[M+H]^+$: 360.1441, found 360.1441.



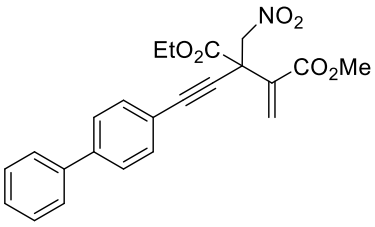
1-ethyl 4-methyl 2-((4-(tert-butyl)phenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3n**).

White solid, 49.9 mg, 64% yield;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.42 (m, 2H), 7.33-7.35 (m, 2H), 6.64 (s, 1H), 6.49 (s, 1H), 5.24 (d, J = 11.0 Hz, 1H), 5.14 (d, J = 11.0 Hz, 1H), 4.27 (dd, J = 7.3, 5.0 Hz, 2H), 3.82 (s, 3H), 1.25-1.29 (m, 12H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.89, 165.28, 152.61, 134.99, 132.11, 131.67, 125.34, 118.23, 90.05, 81.13, 79.61, 63.06, 52.50, 50.51, 34.82, 31.07, 13.75 ppm;

ESI-HRMS calcd for $C_{21}H_{26}NO_6$ $[M+H]^+$: 388.1755, found 388.1754



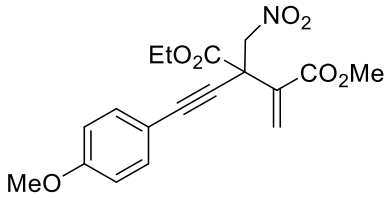
1-ethyl 4-methyl 2-([1,1'-biphenyl]-4-ylethynyl)-3-methylene-2-(nitromethyl)succinate (**3o**).

White solid, 46.0 mg, 56% yield;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.60 (m, 6H), 7.43-7.47 (m, 2H), 7.37-7.39 (m, 1H), 6.67 (s, 1H), 6.52 (s, 1H), 5.28 (d, J = 11.0 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 4.30 (dd, J = 7.1, 6.2 Hz, 2H), 3.84 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.91, 165.36, 142.10, 140.15, 135.04, 132.47, 132.25, 128.98, 127.92, 127.14, 120.20, 89.89, 82.49, 79.69, 63.26, 52.65, 50.69, 13.88 ppm;

ESI-HRMS calcd for $C_{23}H_{22}NO_6$ $[M+H]^+$: 408.1442, found 408.1442.



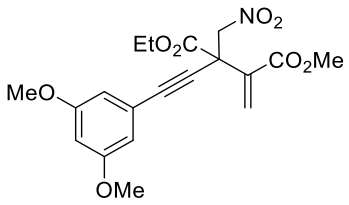
1-ethyl 4-methyl 2-((4-methoxyphenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3p**).

White solid, 53.3 mg, 74% yield; mp 72-73 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.43 (m, 2H), 6.84-6.87 (m, 2H), 6.65 (s, 1H), 6.50 (s, 1H), 5.25 (d, J = 11.0 Hz, 1H), 5.15 (d, J = 11.0 Hz, 1H), 4.26-4.31 (m, 2H), 3.82 (d, J = 4.6 Hz, 6H), 1.28 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.95, 165.30, 160.24, 135.09, 133.44, 132.09, 113.93, 113.30, 89.98, 80.41, 79.66, 63.04, 55.29, 52.48, 50.54, 13.74 ppm;

ESI-HRMS calcd for $C_{18}H_{20}NO_7$ $[M+H]^+$: 362.1234, found 362.1237.



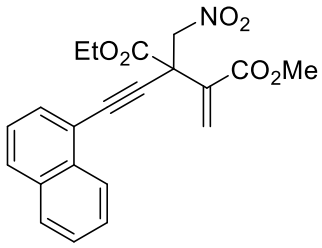
1-ethyl 4-methyl 2-((3,5-dimethoxyphenyl)ethynyl)-3-methylene-2-(nitromethyl)succinate (**3q**).

White solid, 67.1 mg, 86% yield; mp 76-78 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (s, 1H), 6.64 (d, J = 2.3 Hz, 2H), 6.50 (t, J = 2.7 Hz, 2H), 5.27 (d, J = 11.4 Hz, 1H), 5.17 (d, J = 11.4 Hz, 1H), 4.31 (t, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.76, 165.22, 160.48, 134.87, 132.14, 122.50, 109.64, 102.56, 89.82, 81.30, 79.49, 63.15, 55.44, 52.53, 50.47, 13.75 ppm;

ESI-HRMS calcd for $C_{19}H_{22}NO_8$ $[M+H]^+$: 392.1340, found 392.1340.



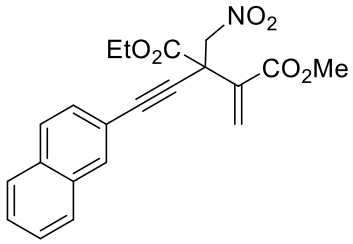
1-ethyl 4-methyl 3-methylene-2-(naphthalen-1-ylethynyl)-2-(nitromethyl)succinate (**3r**).

White solid, 34.0 mg, 45% yield; mp 79-80 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.2 Hz, 1H), 7.86 (t, J = 7.1 Hz, 2H), 7.71-7.73 (m, 1H), 7.51-7.61 (m, 2H), 7.43 (dd, J = 8.2, 7.3 Hz, 1H), 6.69 (s, 1H), 6.60 (s, 1H), 5.34 (d, J = 11.0 Hz, 1H), 5.26 (d, J = 11.0 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.90, 165.26, 135.02, 133.25, 132.99, 132.28, 131.29, 129.75, 128.32, 127.20, 126.57, 125.76, 125.03, 118.86, 87.95, 86.55, 79.59, 63.19, 52.57, 50.90, 13.83 ppm;

ESI-HRMS calcd for $C_{21}H_{20}NO_6$ $[M+H]^+$: 382.1285, found 382.1286.



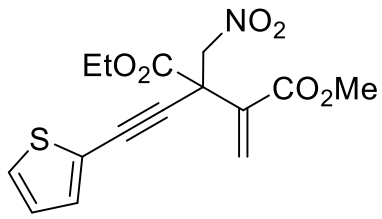
1-ethyl 4-methyl 3-methylene-2-(naphthalen-2-ylethynyl)-2-(nitromethyl)succinate (**3s**).

White solid, 16.5 mg, 22% yield; mp 79-80 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.79-7.84 (m, 3H), 7.49-7.52 (m, 3H), 6.69 (s, 1H), 6.56 (s, 1H), 5.30 (d, J = 11.0 Hz, 1H), 5.21 (d, J = 11.4 Hz, 1H), 4.29-4.33 (m, 2H), 3.85 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.84, 165.28, 134.96, 133.15, 132.69, 132.25, 132.22, 128.16, 128.10, 127.83, 127.78, 127.14, 126.73, 118.49, 90.26, 82.00, 79.63, 77.20, 63.19, 52.56, 50.62, 13.80 ppm;

ESI-HRMS calcd for $C_{21}H_{20}NO_6$ $[M+H]^+$: 382.1285, found 382.1286.



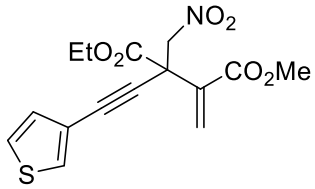
1-ethyl 4-methyl 3-methylene-2-(nitromethyl)-2-(thiophen-2-ylethynyl)succinate (**3t**).

White solid, 58.6 mg, 85% yield; mp 44-45 ºC;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (q, J = 4.6 Hz, 2H), 7.00 (dd, J = 5.0, 3.7 Hz, 1H), 6.66 (s, 1H), 6.46 (s, 1H), 5.26 (d, J = 11.0 Hz, 1H), 5.15 (d, J = 11.4 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 3.84 (s, 3H), 1.29 (t, J = 7.1 Hz, 4H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.54, 165.15, 134.69, 133.40, 132.17, 128.28, 127.03, 120.93, 85.55, 83.17, 79.32, 63.20, 52.54, 50.73, 13.73 ppm;

ESI-HRMS calcd for $C_{15}H_{16}NO_6S$ $[M+H]^+$: 338.0693, found 338.0693.



1-ethyl 4-methyl 3-methylene-2-(nitromethyl)-2-(thiophen-3-ylethynyl)succinate (**3u**).

White solid, 31.7 mg, 47% yield; mp 48-49 ºC;

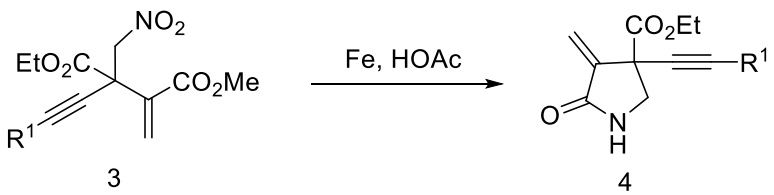
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (q, J = 1.4 Hz, 1H), 7.29 (q, J = 2.6 Hz, 1H), 7.14 (dd, J = 5.0, 1.4 Hz, 1H), 6.65 (s, 1H), 6.48 (s, 1H), 5.25 (d, J = 11.0 Hz, 1H), 5.14 (d, J = 11.0 Hz, 1H), 4.28 (dd, J = 9.6, 6.9 Hz, 2H), 3.83 (s, 3H), 1.28 (t, J = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.77, 165.23, 134.89, 132.13, 130.34, 129.82, 125.60, 120.29, 85.12, 81.45, 79.51, 63.14, 52.54, 50.55, 13.75 ppm;

ESI-NRMS calcd for $C_{15}H_{16}NO_6S$ $[M+H]^+$: 338.0693, found 338.0694.

3. Synthetic Elaboration of the Product

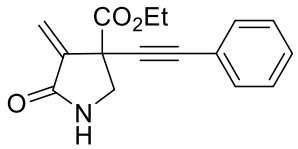
Synthesis of product **4**



3 4

To the solution of 1,4-enyne compound **3** (0.2 mmol) in acetic acid (1.0 mL), iron

powder (0.04 mmol) was added under stirring. The reaction mixture was stirred at 90 °C for several hours and monitored by TLC analysis. Upon the completion of the reaction, 2-pyrrolidinone **4** was obtained by flash column chromatography.



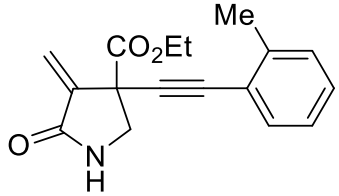
ethyl 4-methylene-5-oxo-3-(phenylethynyl)pyrrolidine-3-carboxylate (**4a**)

White solid, 17.8 mg, 33% yield; m.p. 123-125 °C;

^{1}H HMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.43-7.45 (m, 2H), 7.32-7.34 (m, 3H), 6.30 (s, 1H), 6.01 (s, 1H), 4.25-4.30 (m, 3H), 3.72 (d, J = 9.6 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H);

^{13}C HMR (100 MHz, $CDCl_3$): δ 168.76, 168.15, 140.82, 131.77, 128.68, 128.29, 122.07, 120.82, 86.49, 83.75, 62.91, 50.05, 47.72, 13.88 ppm;

ESI-HRMS calcd for $C_{16}H_{15}NO_3$ $[M+H]^+$: 270.1125, found 270.1128.



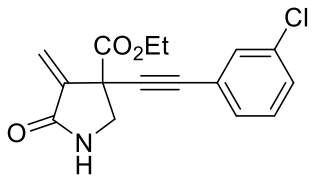
ethyl 4-methylene-5-oxo-3-(o-tolylethynyl)pyrrolidine-3-carboxylate(**4e**)

yellow oil, 47.0 mg, 82% yield;

^{1}H HMR (400 MHz, $CDCl_3$): δ 7.39-7.42 (m, 2H), 7.20-7.27 (m, 2H), 7.15 (t, J = 7.3 Hz, 1H), 6.32 (s, 1H), 6.02 (s, 1H), 4.25-4.31 (m, 3H), 3.73 (d, J = 9.6 Hz, 1H), 2.43 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H)

^{13}C HMR (100 MHz, $CDCl_3$): δ168.96, 168.21, 141.08, 140.68, 132.00, 129.55, 128.80, 125.64, 121.93, 120.94, 90.48, 82.97, 63.03, 50.18, 48.01, 20.71, 14.01

ESI-HRMS calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$: 284.1281, found 284.1280.



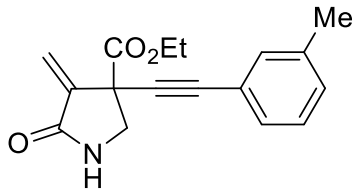
ethyl 3-((3-chlorophenyl)ethynyl)-4-methylene-5-oxopyrrolidine-3-carboxylate (**4g**)

White solid, 57.0 mg, 93% yield; mp 87-99 °C;

^{1}H HMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.30-7.23 (m, 3H), 6.27 (s, 1H), 5.96 (s, 1H), 4.28-4.22 (m, 3H), 3.68 (d, J = 10.1 Hz, 1H), 1.29 (t, J = 7.3 Hz, 3H)

^{13}C HMR (100 MHz, $CDCl_3$): δ168.52, 168.11, 140.67, 134.09, 131.64, 129.90, 129.53, 128.98, 123.73, 120.83, 87.76, 82.34, 63.01, 50.00, 47.58, 13.88

ESI-HRMS calcd for $C_{16}H_{15}ClNO_3$ $[M+H]^+$: 304.0735, found 304.0732.



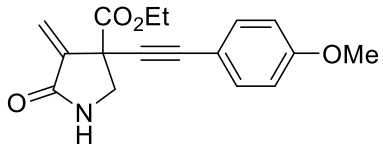
ethyl 4-methylene-5-oxo-3-(m-tolylethynyl)pyrrolidine-3-carboxylate(**4i**)

White solid, 47.0 mg, 82% yield; m.p. 88-90 °C;

^{1}H HMR (400 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.19-7.27 (m, 3H), 7.16 (s, 1H), 6.30 (s, 1H), 6.00 (d, J = 0.9 Hz, 1H), 4.24-4.29 (m, 3H), 3.71 (d, J = 9.6 Hz, 1H), 2.33 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H)

^{13}C HMR (100 MHz, $CDCl_3$): δ168.79, 168.14, 140.84, 137.99, 132.33, 129.55, 128.80, 128.17, 121.84, 120.79, 86.08, 83.91, 62.88, 50.05, 47.73, 21.14, 13.87

ESI-HRMS calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$: 284.1281, found 284.1286.



ethyl 3-((4-methoxyphenyl)ethynyl)-4-methylene-5-oxopyrrolidine-3-carboxylate (**4p**)

yellow oil, 37.0 mg, 62% yield;

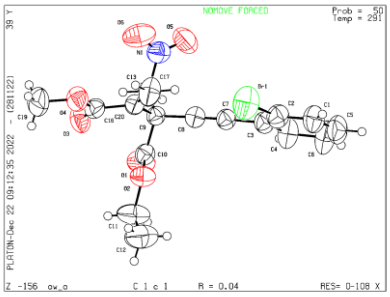
^{1}H HMR (400 MHz, $CDCl_3$): δ7.41-7.34 (2H), 6.87-6.80 (2H), 6.67-6.60 (1H), 6.33-6.29 (1H), 6.03-5.98 (1H), 4.33-4.18 (4H), 3.84-3.78 (3H), 3.73-3.65 (1H), 1.35-1.27 (3H)

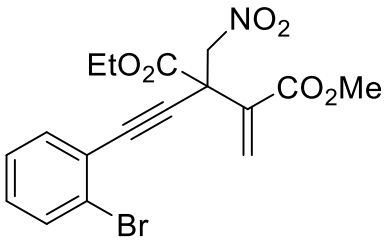
^{13}C HMR (100 MHz, $CDCl_3$): δ175.92, 168.93, 168.78, 159.73, 140.94, 133.13, 120.98, 113.97, 113.78, 84.93, 83.60, 62.78, 60.33, 55.15, 50.43, 47.54, 20.90, 14.05, 13.77

ESI-HRMS calcd for $C_{17}H_{18}NO_4$ $[M+H]^+$: 300.1230, found 300.1238.

4. X-ray Crystallographic Analysis

X-ray Crystallographic Data of **3d** (CCDC 2232307)





Bond precision:	C-C = 0.0113 A		Wavelength=0.71013
Cell:	a=9.220(3)	b=27.479(9)	c=8.339(3)
	alpha=90	beta=118.518(1)	gamma=90
Temperature:	291 K		

	Calculated	Reported
Volume	1856.3(11)	1856.5(10)
Space group	C c	C c
Hall group	C -2 γ c	C -2 γ c
Moiety formula	C18 H16 Br O6	?
Sum formula	C18 H16 Br O6	C18 H16 Br O6
Mr	408.21	408.22
Dx,g cm-3	1.329	1.329
Z	4	4
Mu (mm-1)	2.244	2.243
F000	828.0	828.0
F000'	827.29	
h,k,lmax	11,35,10	11,35,10
Nref	4259[2138]	3197
Tmin,Tmax	0.754,0.799	0.054,0.095
Tmin'	0.739	

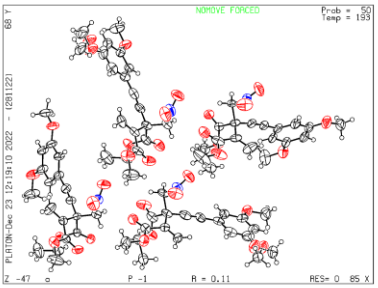
Correction method= # Reported T Limits: Tmin=0.054 Tmax=0.095
AbsCorr = MULTI-SCAN

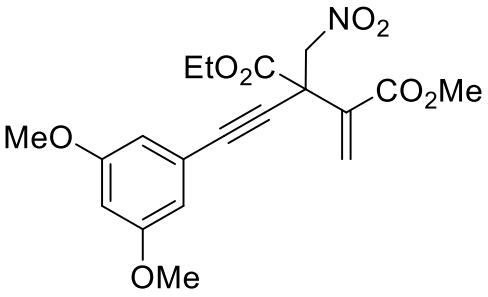
Data completeness= 1.50/0.75 Theta(max)= 27.510

R(reflections)= 0.0431(2255) wR2(reflections)= 0.1521(3197)

S = 0.915 Npar= 228

X-ray Crystallographic Data of **3q** (CCDC 2232796)





Bond precision:	C-C = 0.0103 A		Wavelength=0.71073
Cell:	a=9.065(2)	b=14.720(3)	c=31.665(9)
	alpha=102.672(11)	beta=97.280(12)	gamma=94.451(7)
Temperature:	291 K		

	Calculated	Reported
Volume	4064.8(17)	4064.9(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H21 N O8	C19 H21 N O8
Sum formula	C19 H21 N O8	C19 H21 N O8
Mr	391.37	391.37
Dx,g cm-3	1.279	1.279
Z	8	8
Mu (mm-1)	0.101	0.101
F000	1648.0	1648.0
F000'	1649.02	
h,k,lmax	11,19,41	11,19,40
Nref	18855	18223
Tmin,Tmax	0.987,0.990	0.489,0.746
Tmin'	0.987	

Correction method= # Reported T Limits: Tmin=0.489 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.966 Theta(max)= 27.599

R(reflections)= 0.1110(8959) wR2(reflections)= 0.3516(18223)

S = 1.049 Npar= 1066

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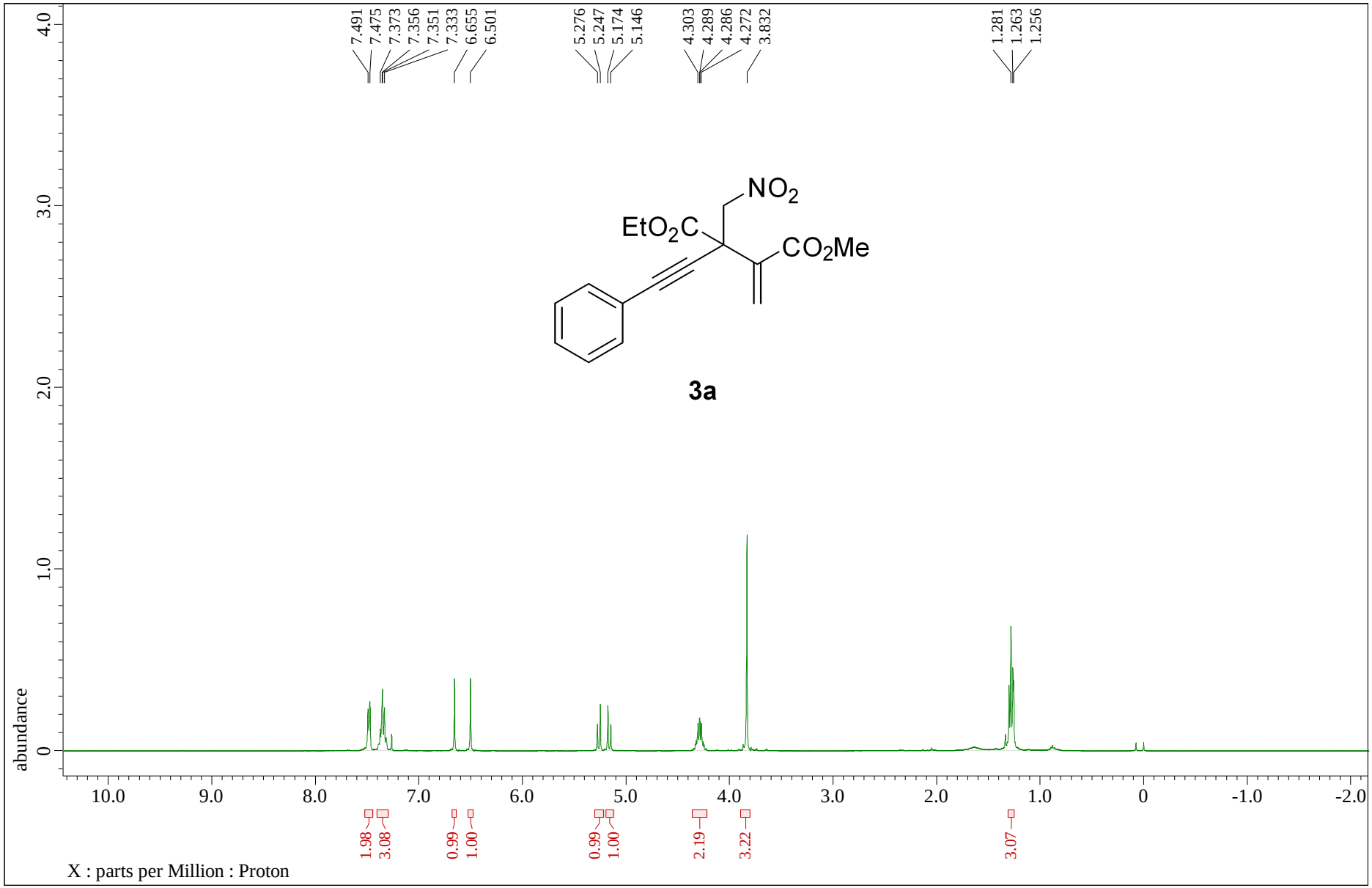
5. Reference

1. Z.-H. Yang, P. Chen, Z.-C. Chen, Z. Chen, W. Du, Y.-C. Chen, *Angew. Chem., Int. Ed.* **2021**, 60, 13913-13917.

6. Copies of NMR spectra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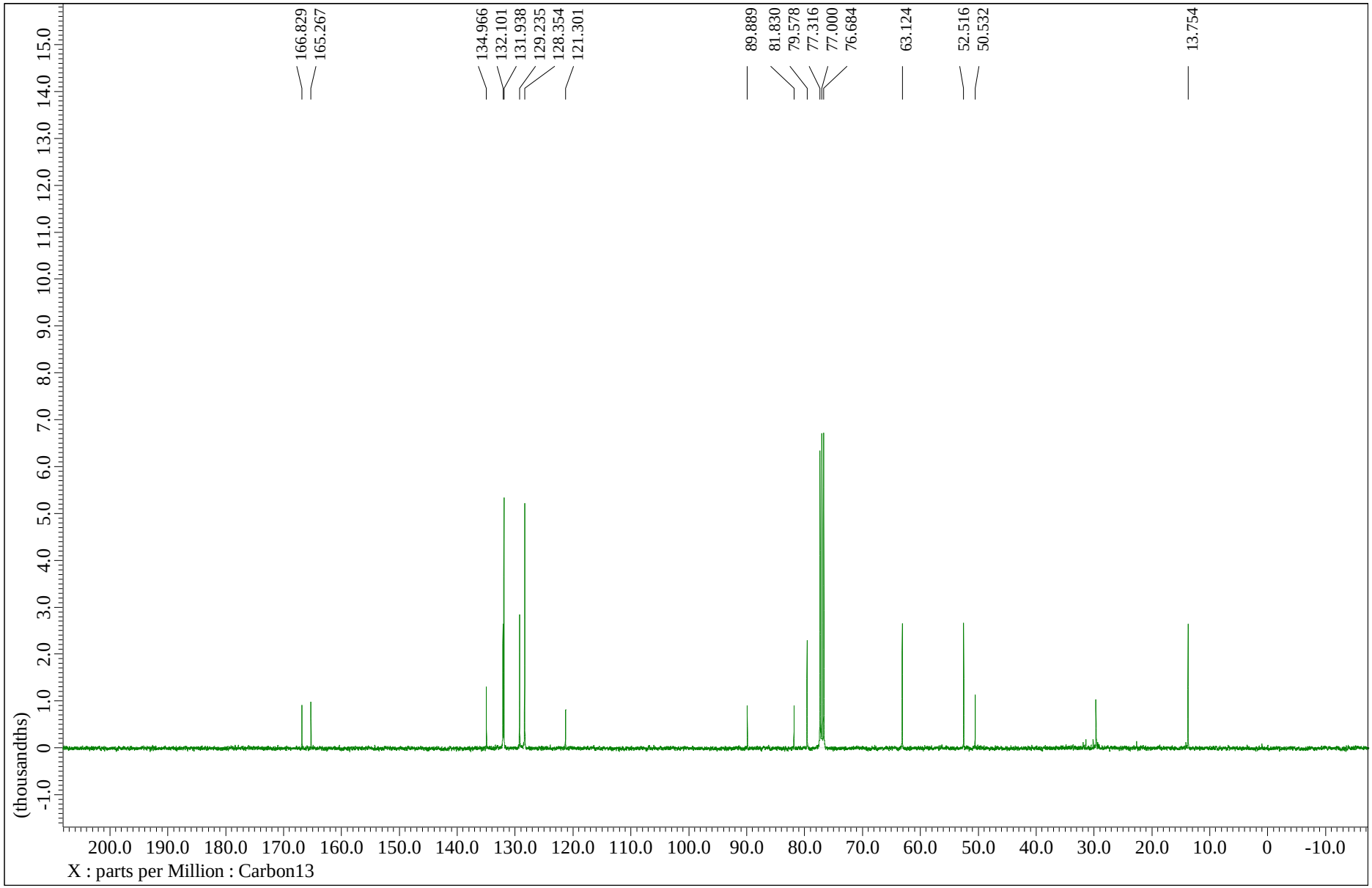
7.475
7.373
7.356
7.351
7.333
6.655
6.501
5.276
5.247
5.174
5.146
4.303
4.289
4.286
4.272
3.832
1.281
1.263
1.256
NO2
EtO2C
CO2Me
3a
abundance
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
1.98
3.08
0.99
1.00
0.99
1.00
2.19
3.22
3.07
X : parts per Million : Proton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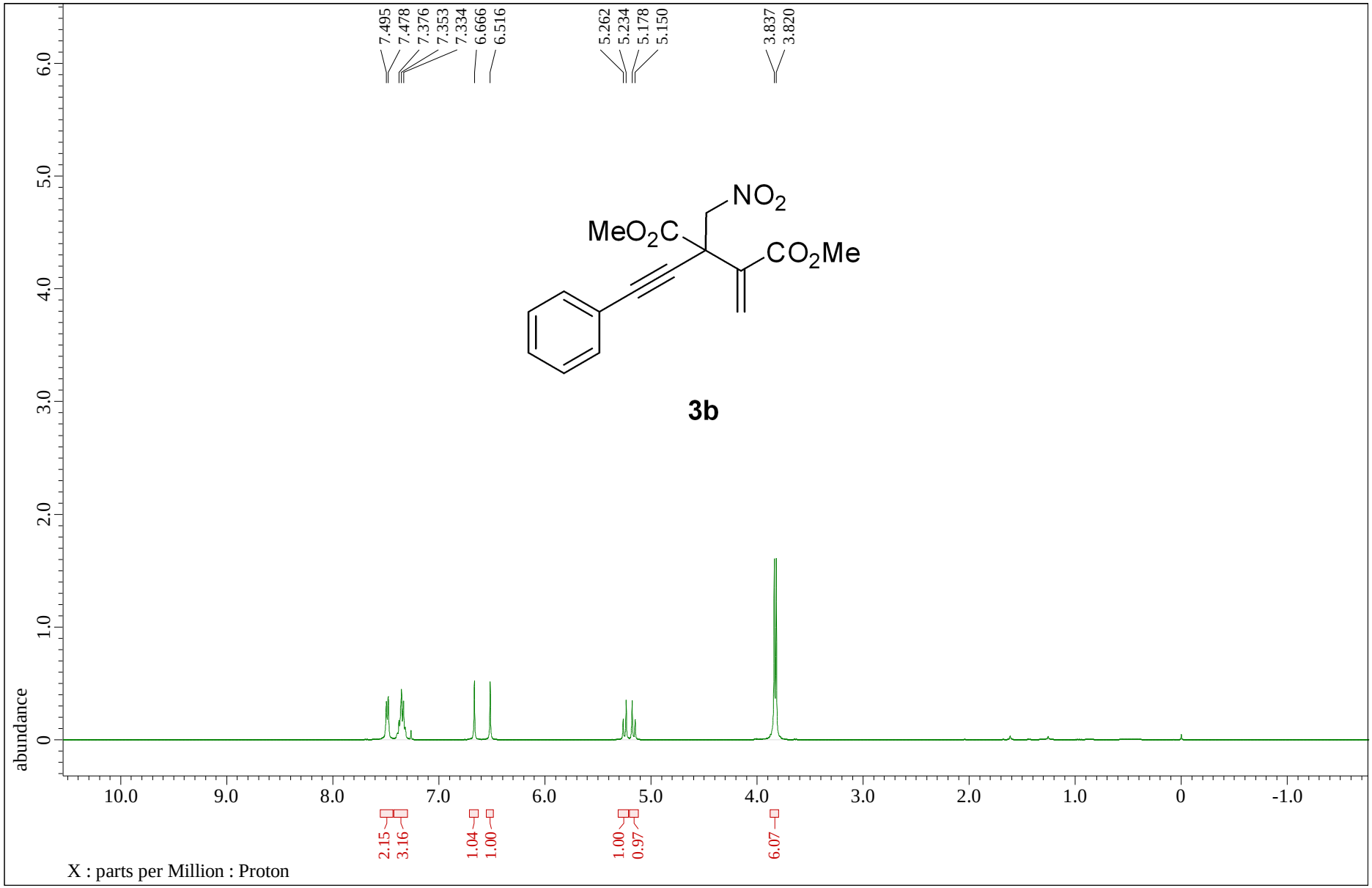
165.267
134.966
132.101
131.938
129.235
128.354
121.301
89.889
81.830
79.578
77.316
77.000
76.684
63.124
52.516
50.532
13.754
(thousandths)
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
X : parts per Million : Carbon13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7.353
7.334
6.666
6.516
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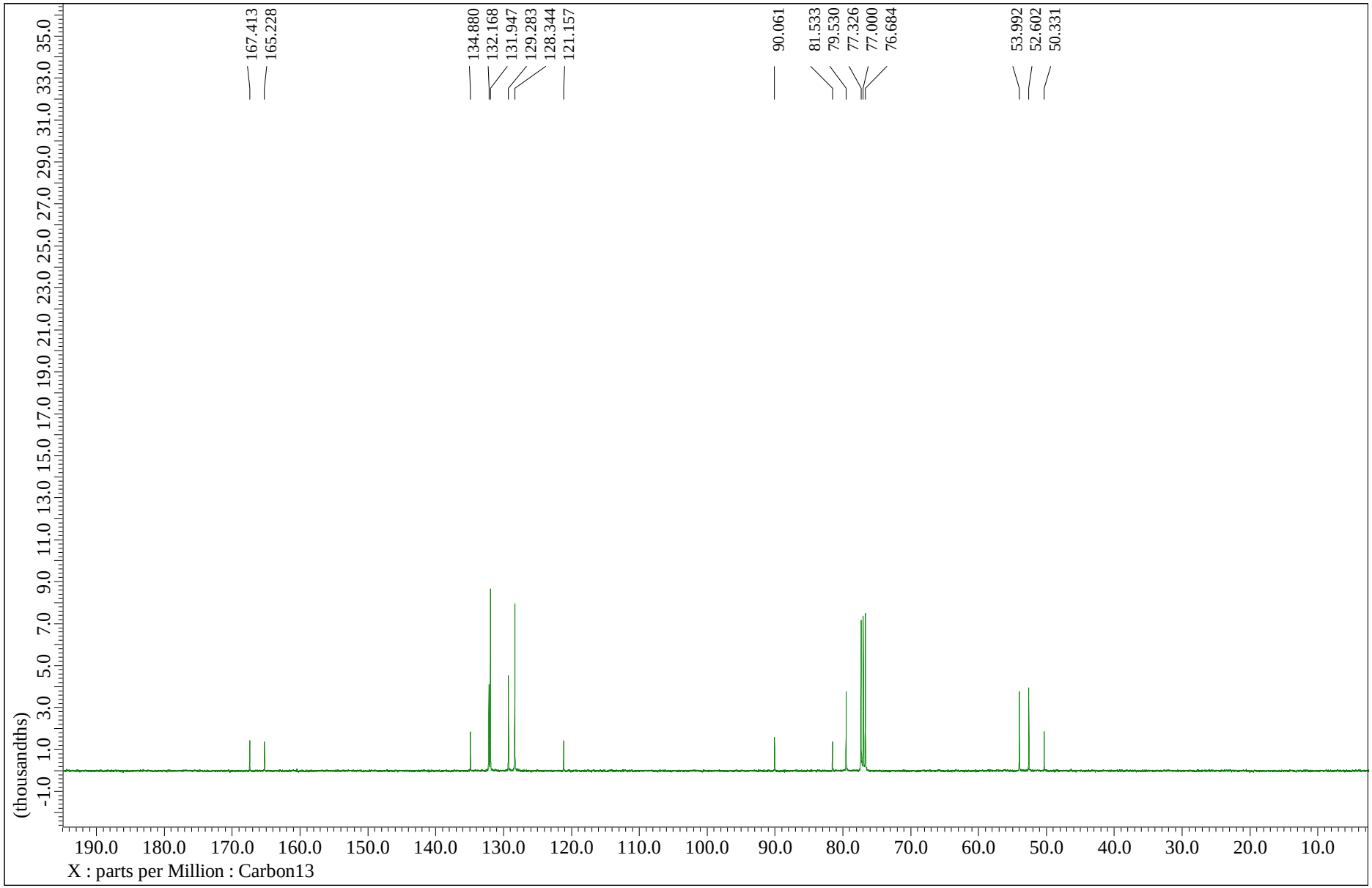
5.234
5.178
5.150
3.837
3.820
NO2
MeO2C
CO2Me
3b
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
2.15
3.16
1.04
1.00
1.00
0.97
6.07
X : parts per Million : Proton


167.413
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134.880
132.168
131.947
129.283
128.344
121.157
90.061
81.533
79.530
77.326
77.000
76.684
53.992
52.602
50.331
(thousandths)
35.0
33.0
31.0
29.0
27.0
25.0
23.0
21.0
19.0
17.0
15.0
13.0
11.0
9.0
7.0
5.0
3.0
1.0
-1.0
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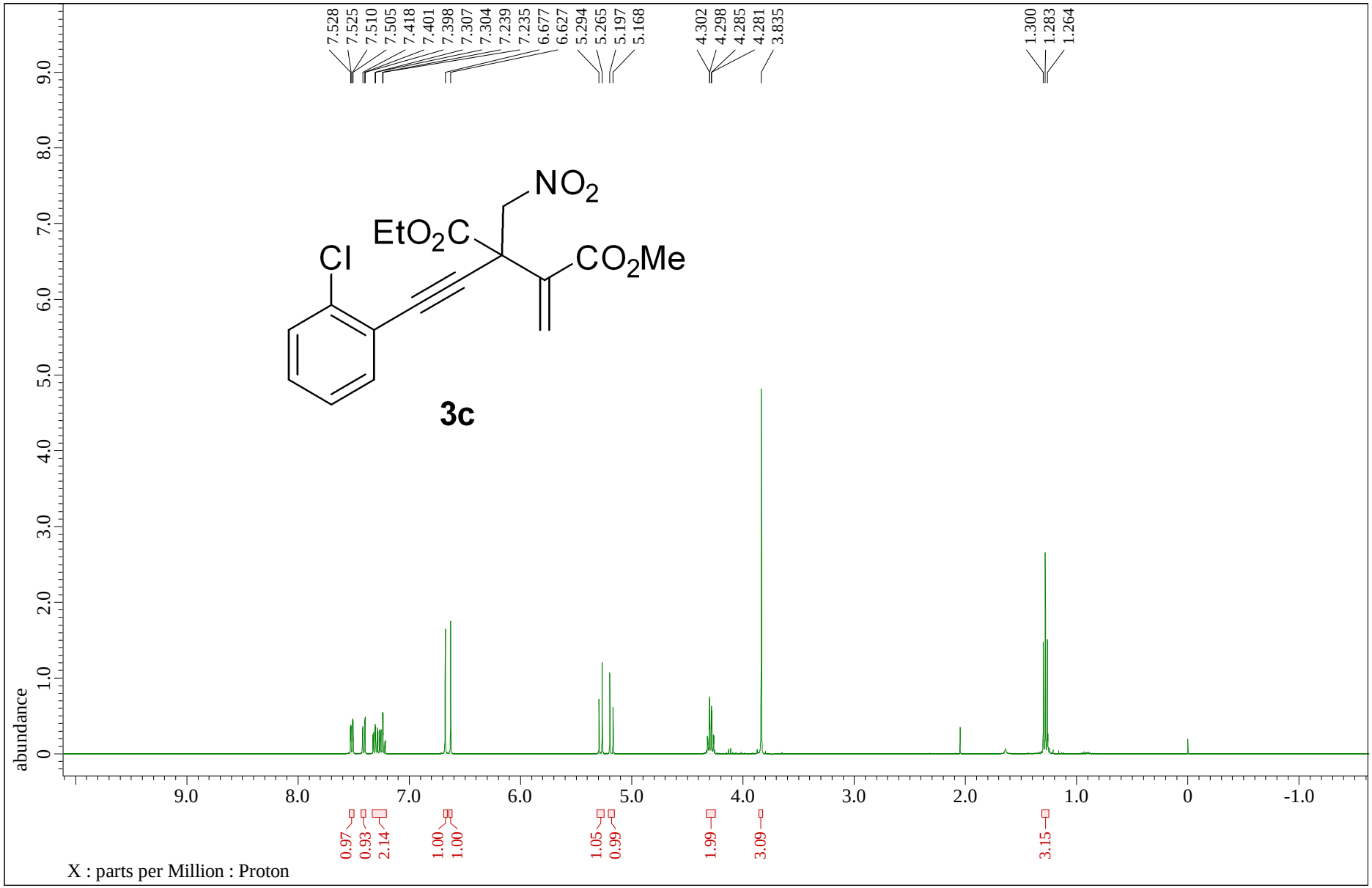
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
X : parts per Million : Carbon13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7.525
7.510
7.505
7.418
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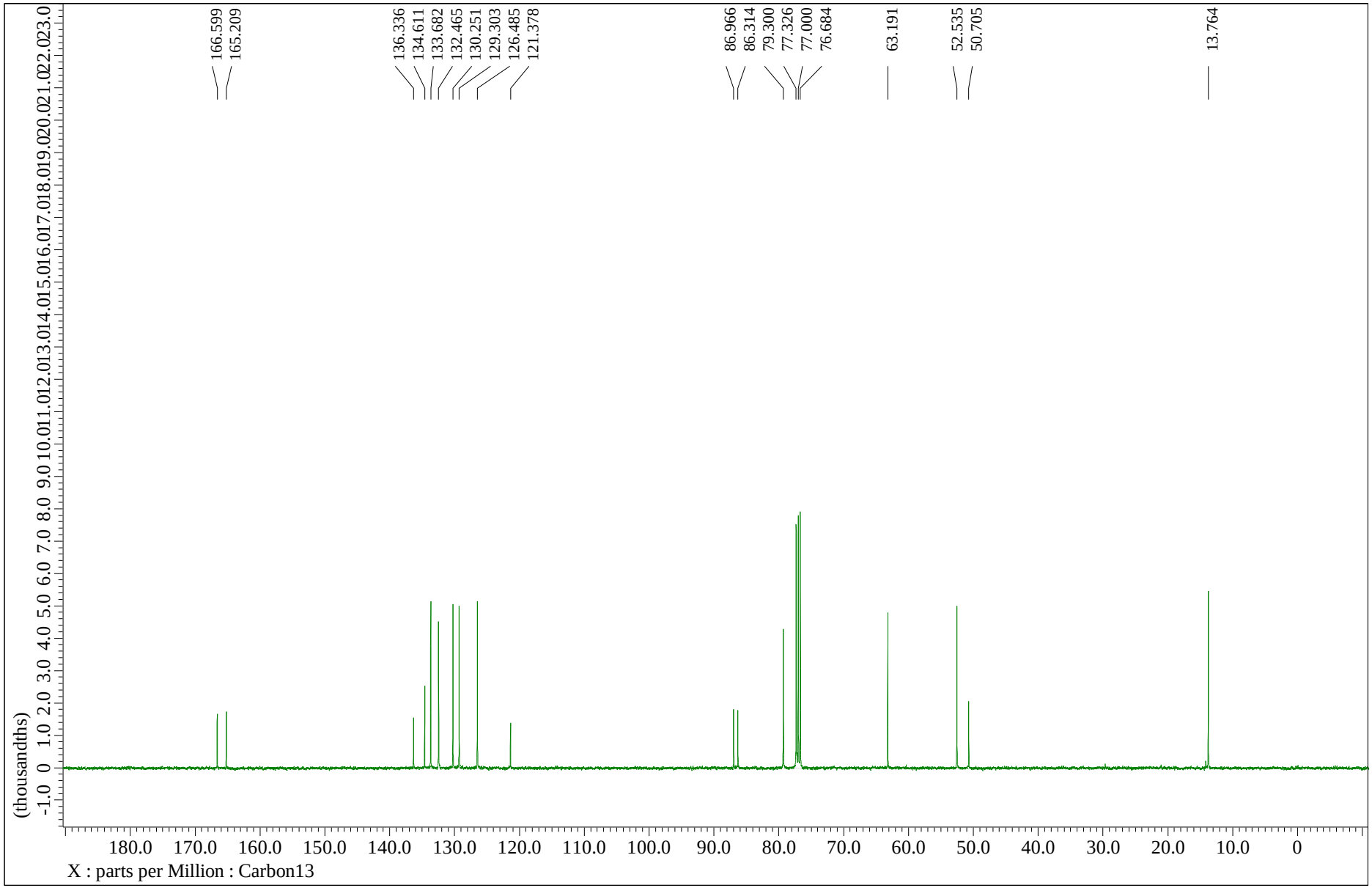
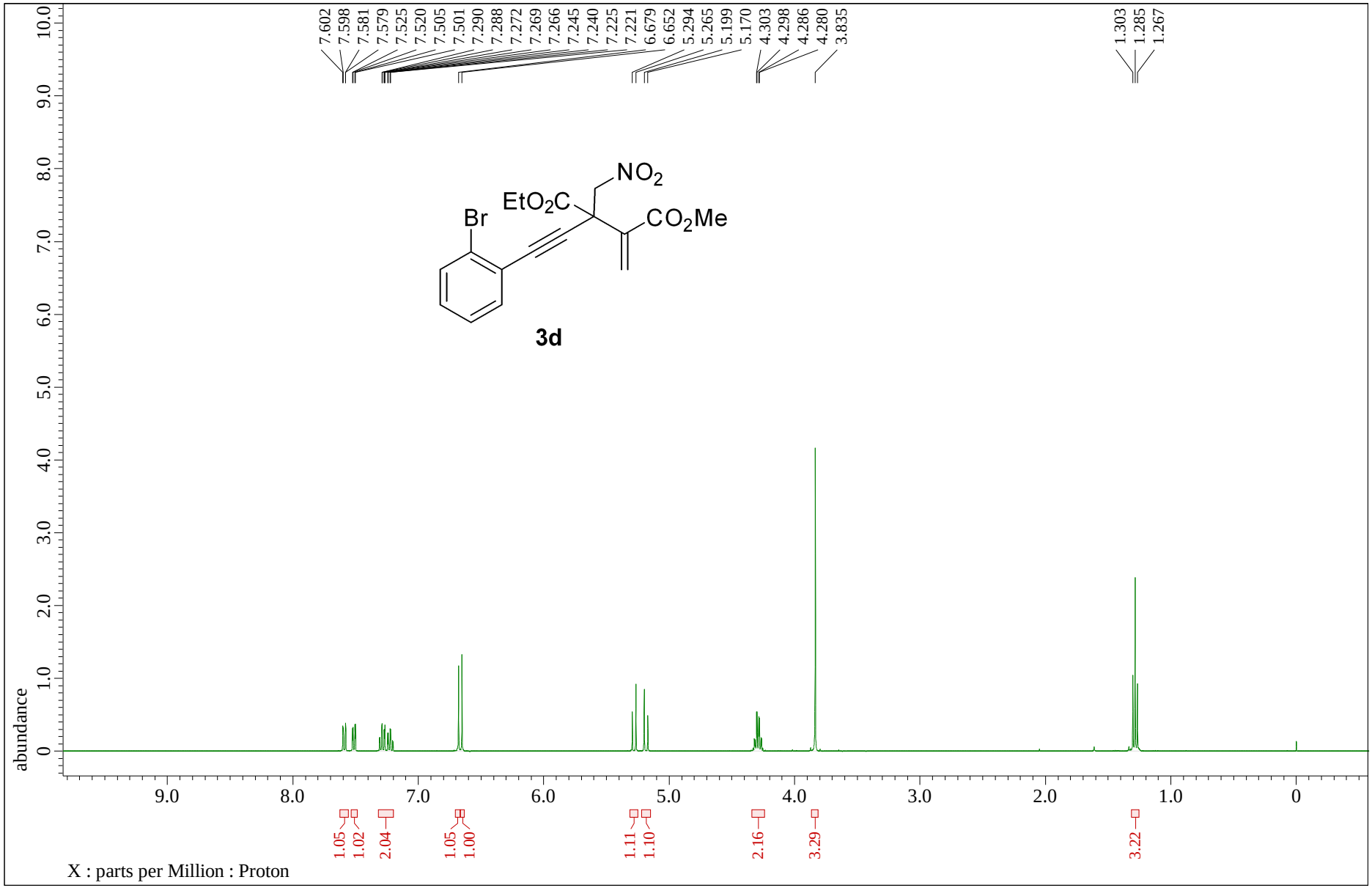
7.304
7.239
7.235
6.677
6.627
5.294
5.265
5.197
5.168
4.302
4.298
4.285
4.281
3.835
1.300
1.283
1.264
NO2
EtO2C
Cl
CO2Me
3c
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
0.97
0.93
2.14
1.00
1.00
1.05
0.99
1.99
3.09
3.15
X : parts per Million : Proton


166.599
165.209
136.336
134.611
133.682
132.465
130.251
129.303
126.485
121.378
86.966
86.314
79.300
77.326
77.000
76.684
63.191
52.535
50.705
13.764
(thousandths)
-1.0 0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13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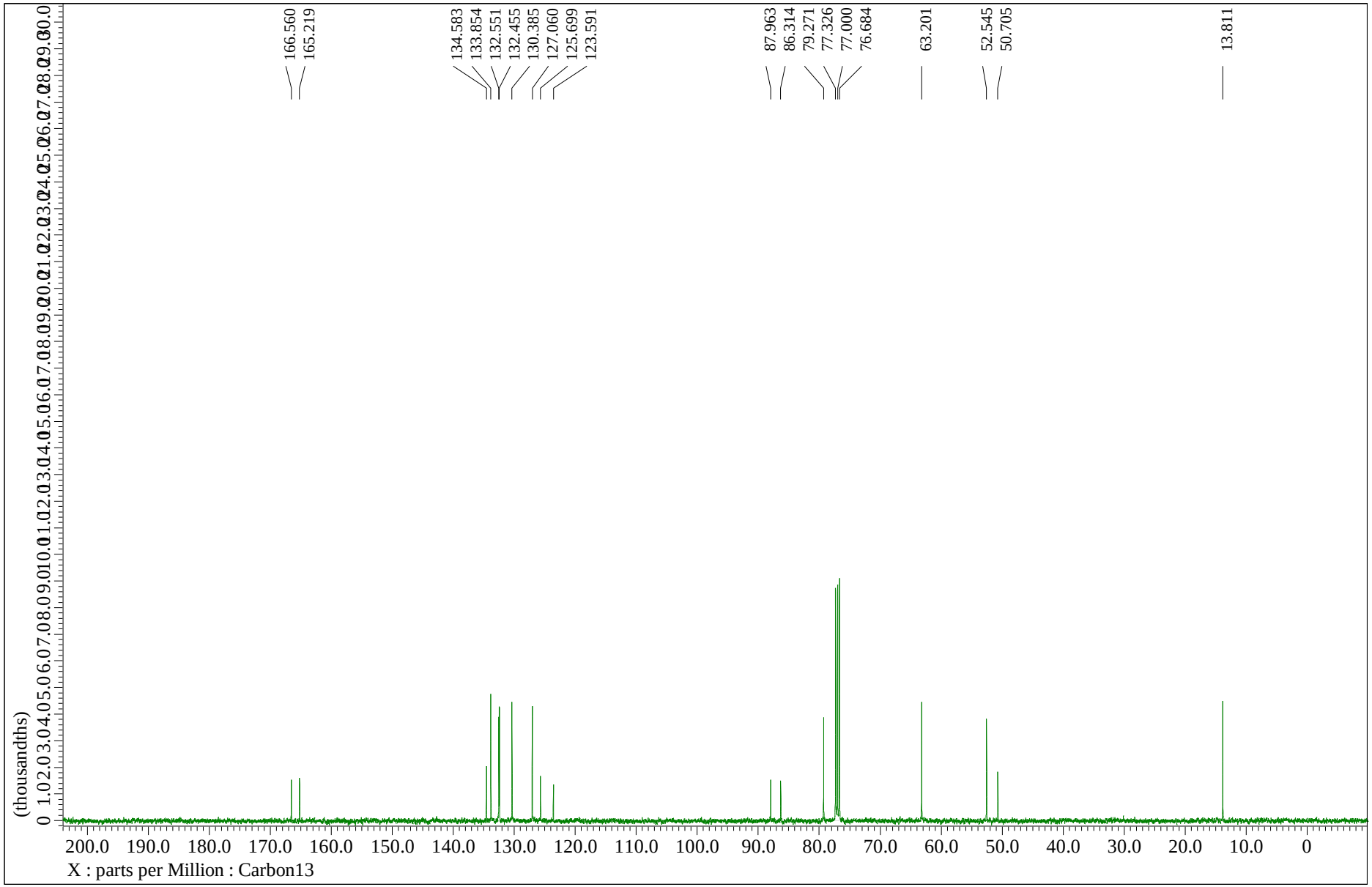
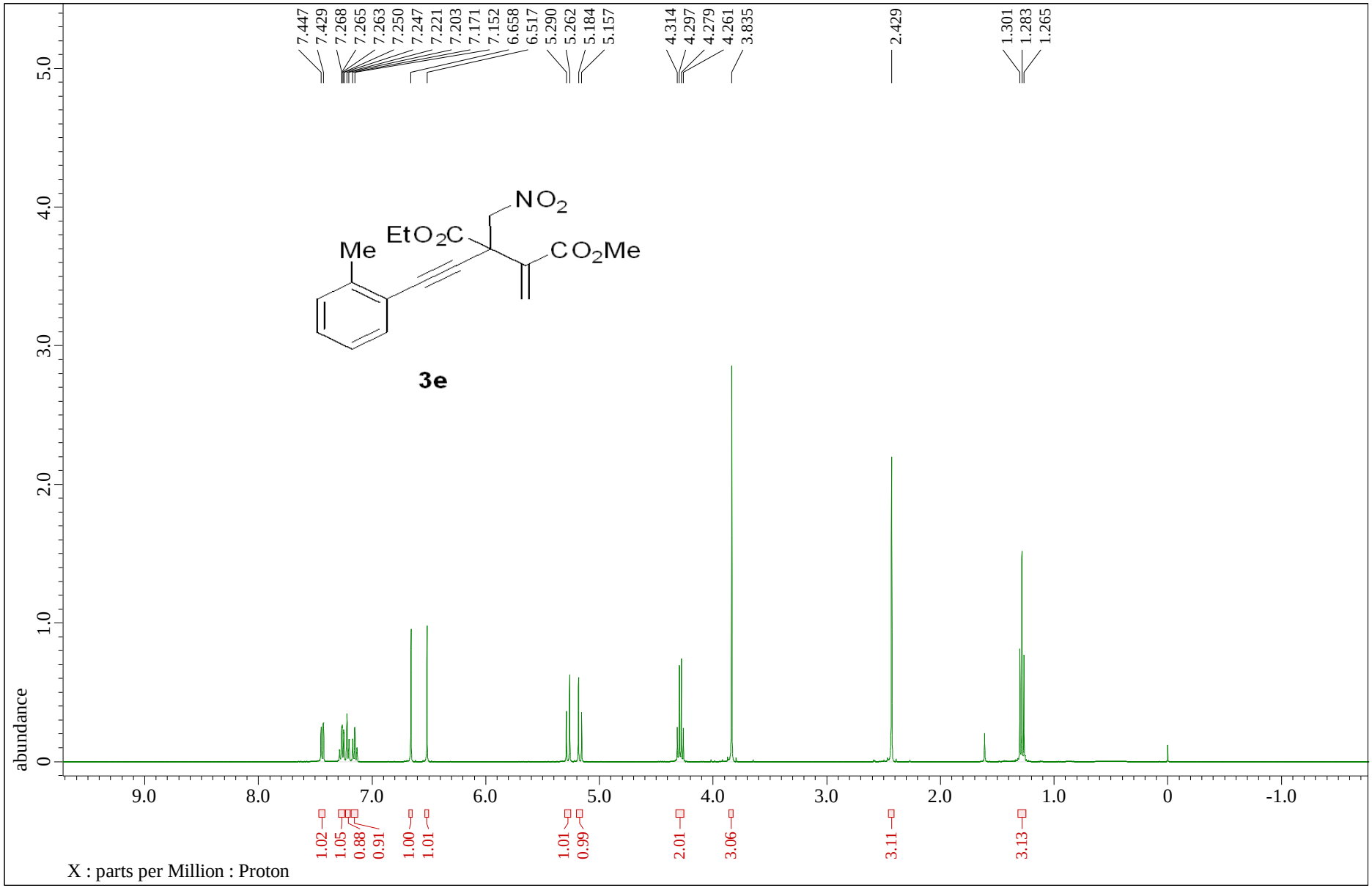
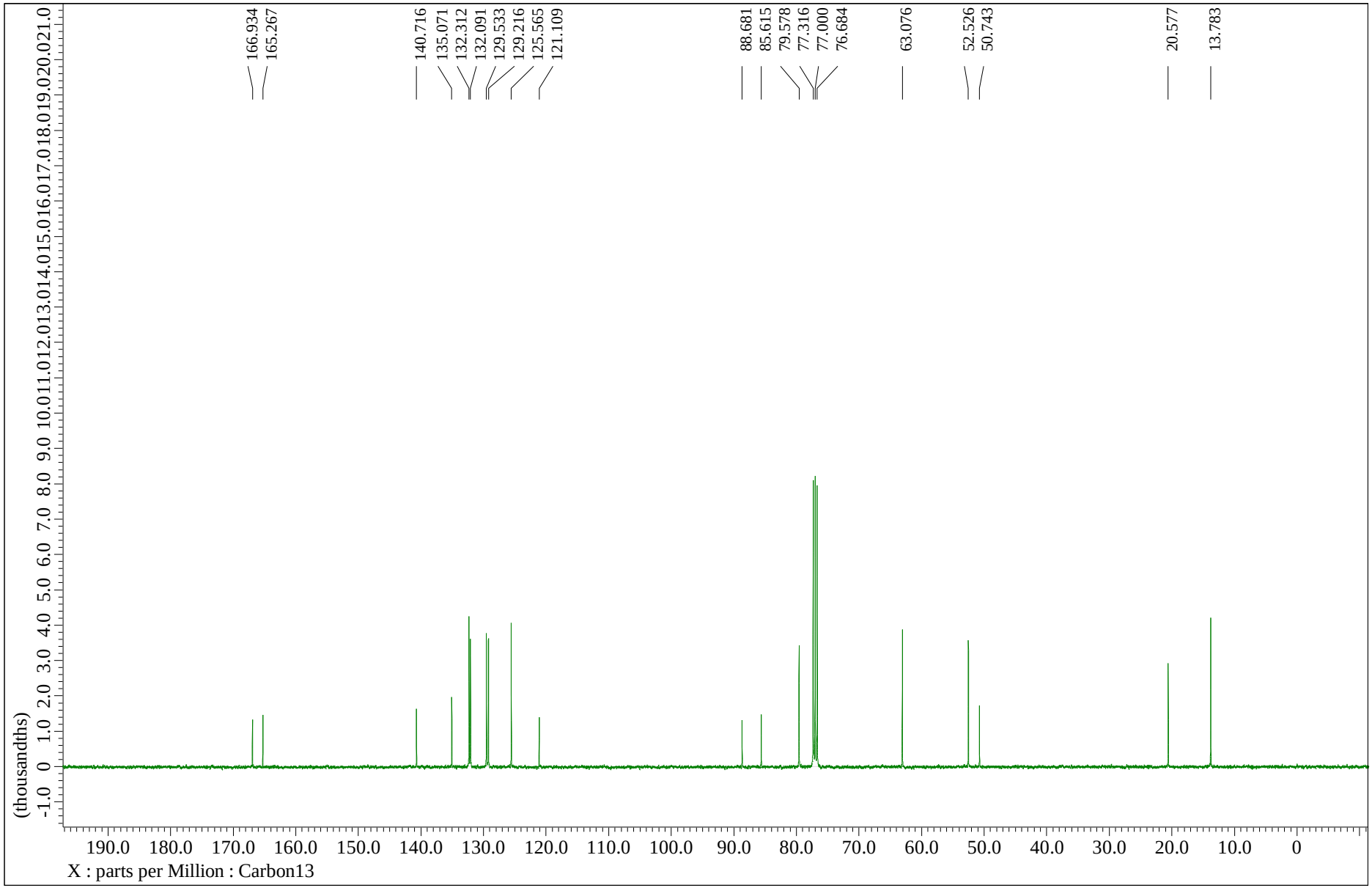
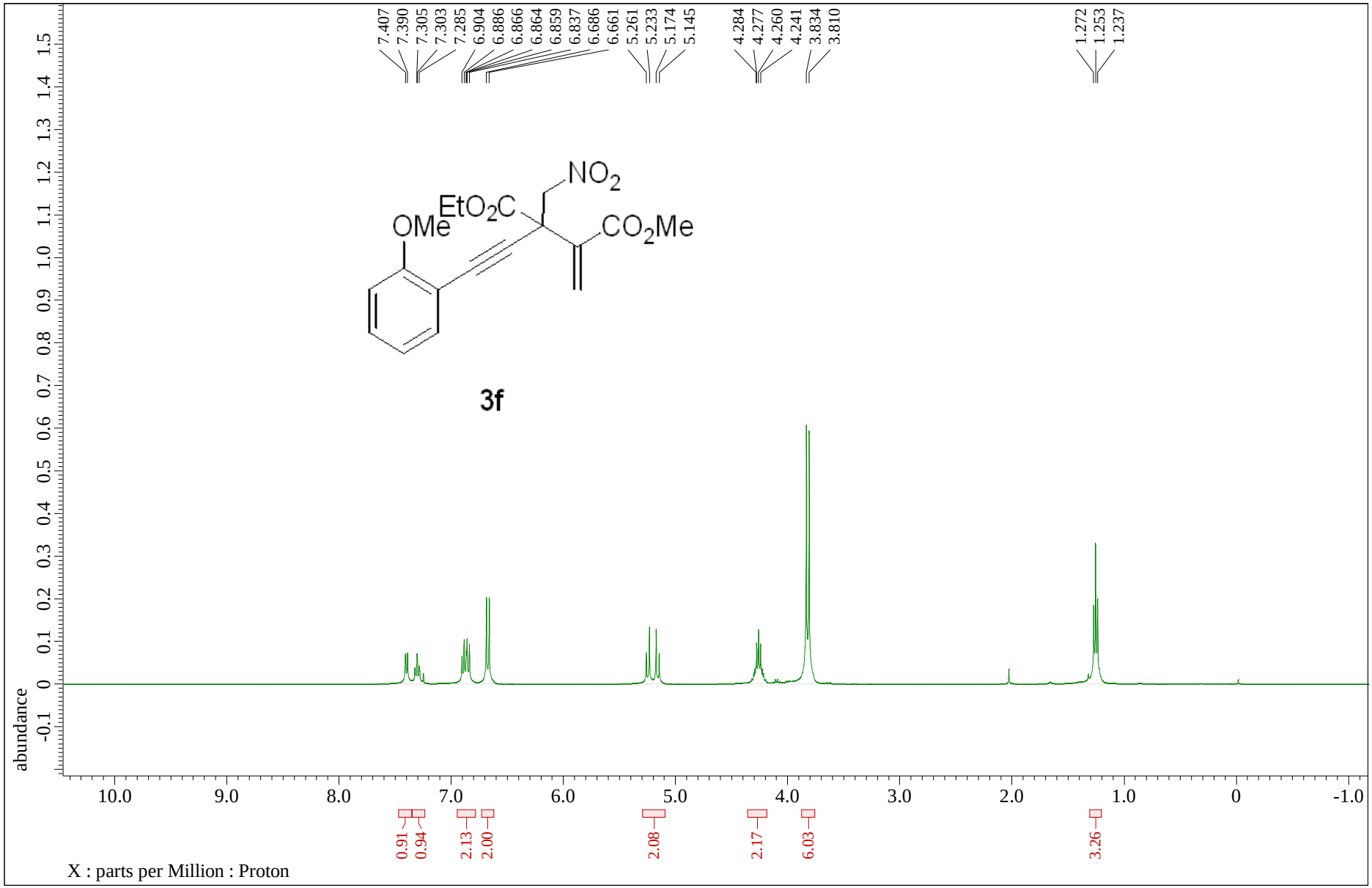
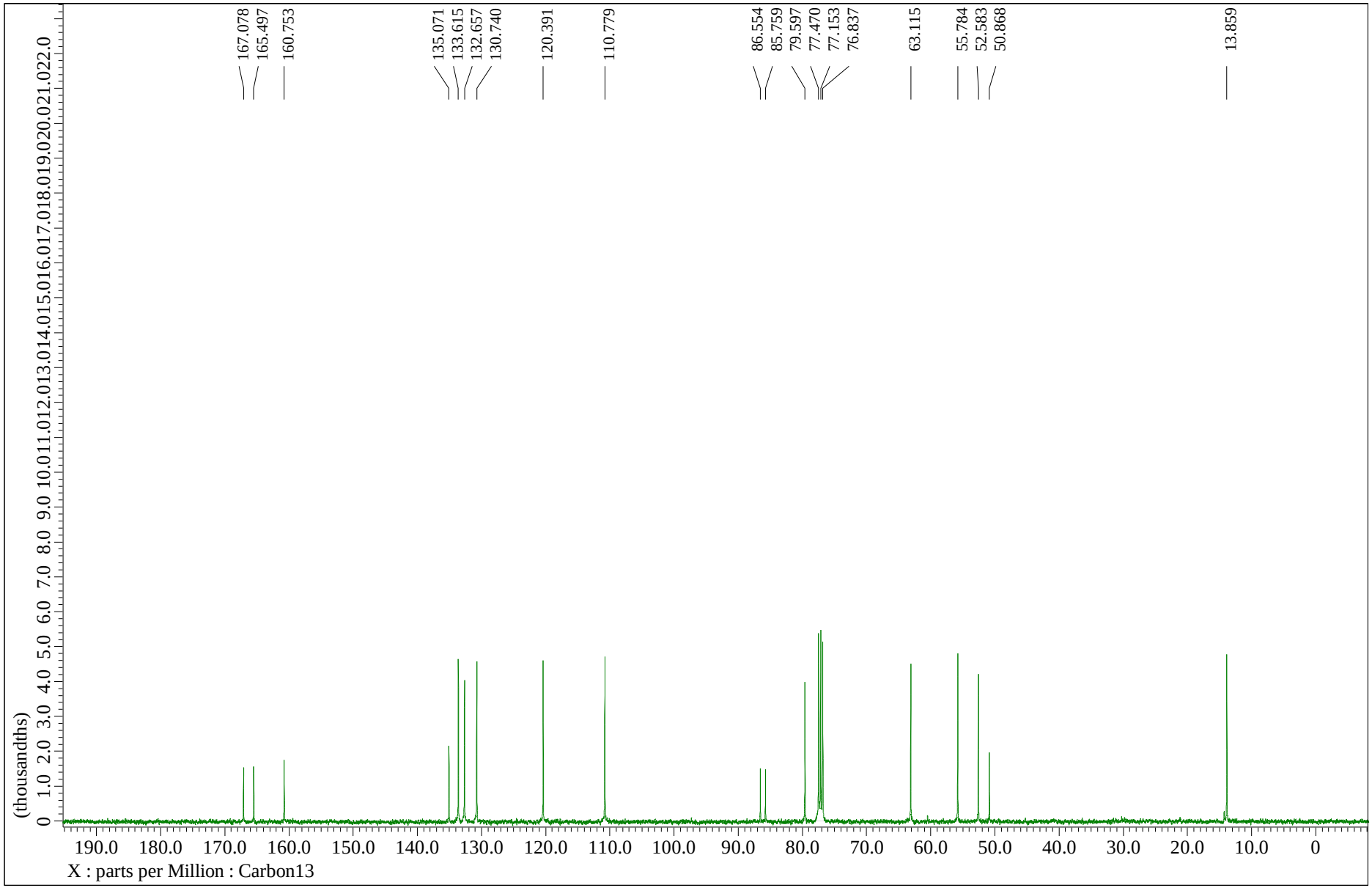
7.598
7.581
7.579
7.525
7.520
7.505
7.501
7.290
7.288
7.272
7.269
7.266
7.245
7.240
7.225
7.221
6.679
6.652
5.294
5.265
5.199
5.170
4.303
4.298
4.286
4.280
3.835
1.303
1.285
1.267
NO2
EtO2C
Br
CO2Me
3d
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.05
1.02
2.04
1.05
1.00
1.11
1.10
2.16
3.29
3.22
X : parts per Million : Proton

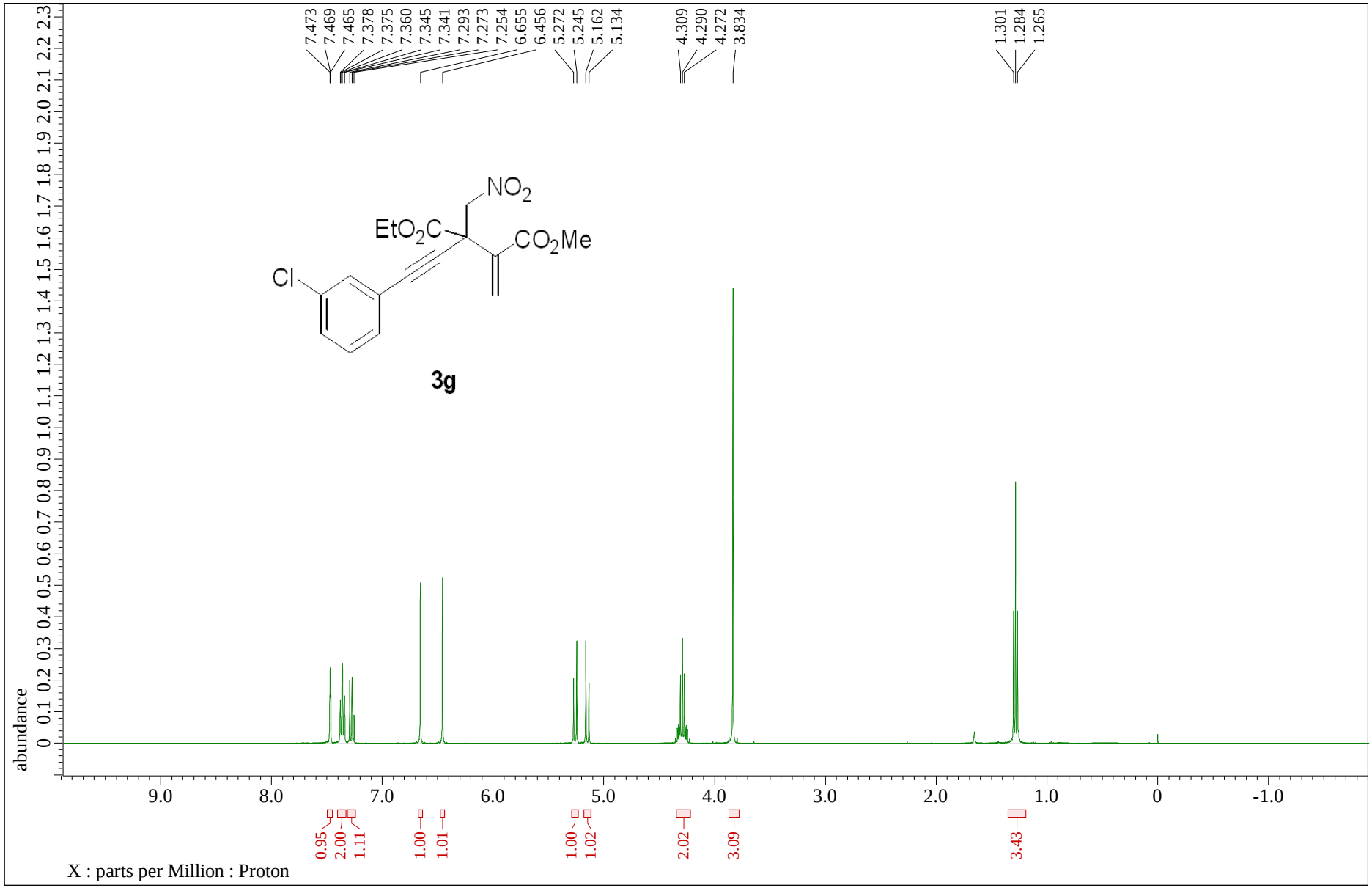

166.560
165.219
134.583
133.854
132.551
132.455
130.385
127.060
125.699
123.591
87.963
86.314
79.271
77.326
77.000
76.684
63.201
52.545
50.705
13.811
(thousandths)
X : parts per Million : Carbon13

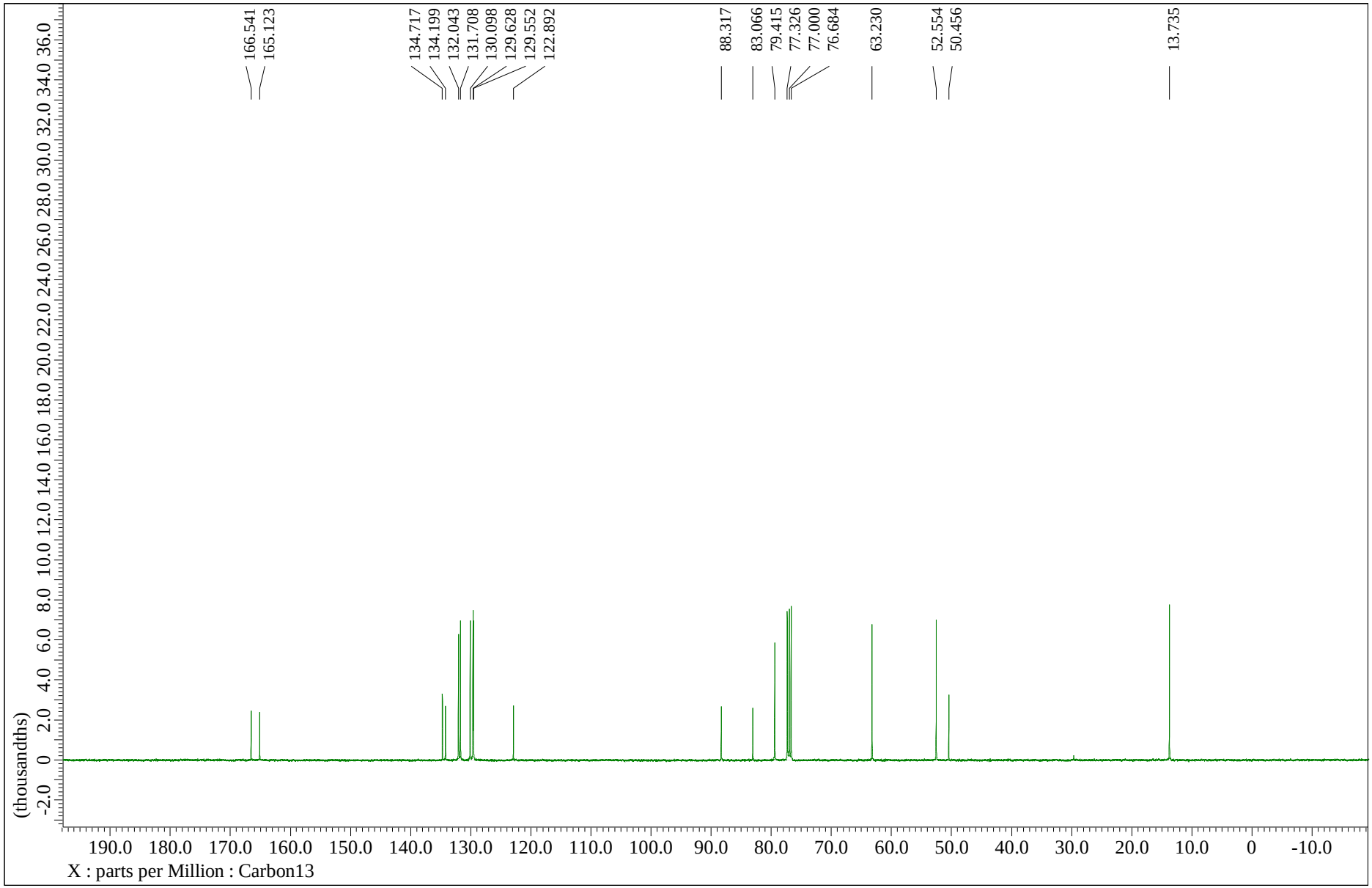

7.447
7.429
7.268
7.265
7.263
7.250
7.247
7.221
7.203
7.171
7.152
6.658
6.517
5.290
5.262
5.184
5.157
4.314
4.297
4.279
4.261
3.835
2.429
1.301
1.283
1.265
NO2
EtO2C
Me
CO2Me
3e
abundance
X : parts per Million : Proton
1.02
1.05
0.88
0.91
1.00
1.01
1.01
0.99
2.01
3.06
3.11
3.13

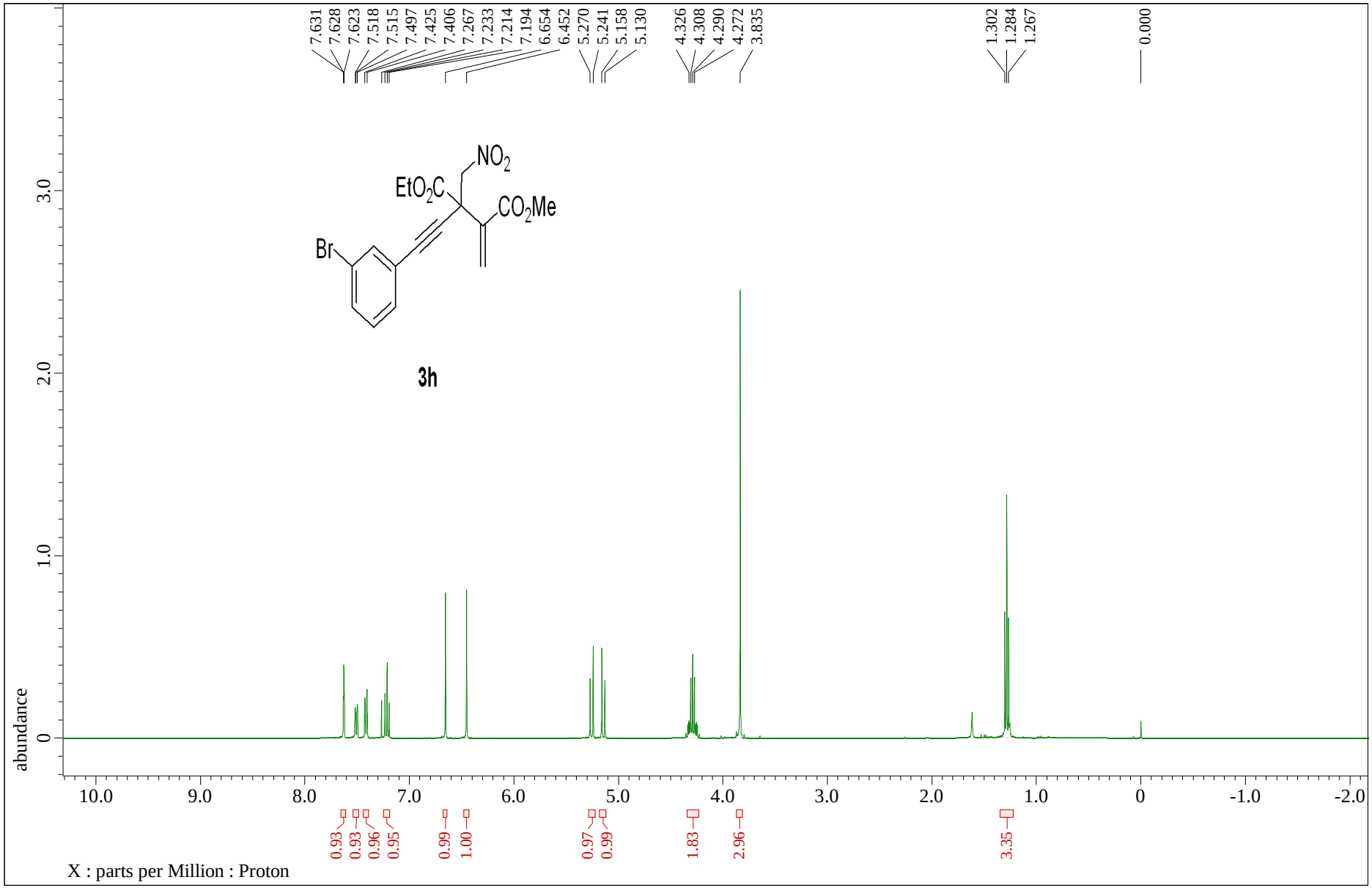

166.934
165.267
140.716
135.071
132.312
132.091
129.533
129.216
125.565
121.109
88.681
85.615
79.578
77.316
77.000
76.684
63.076
52.526
50.743
20.577
13.783
(thousandths)
X : parts per Million : Carbon13

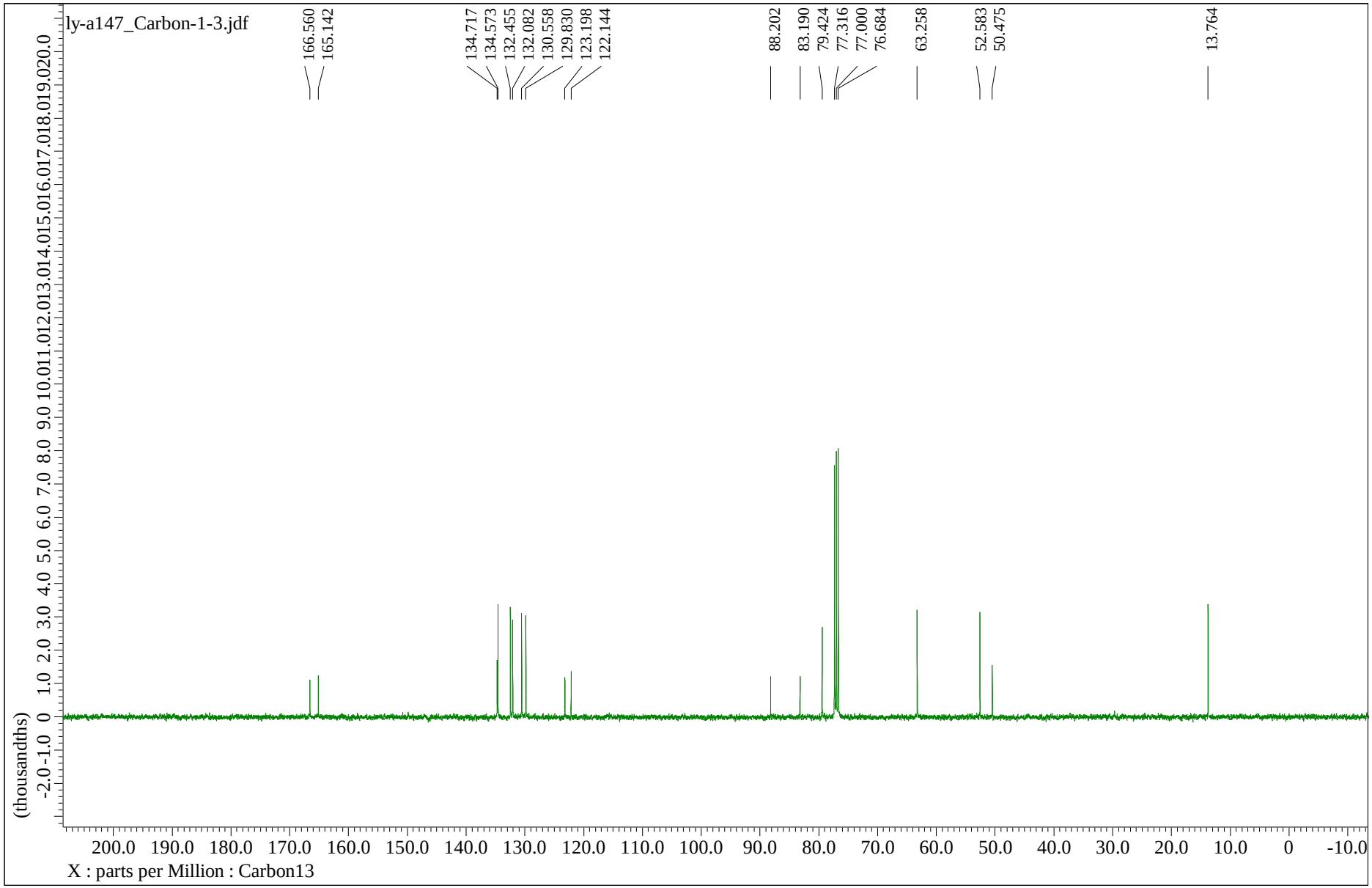

7.407
7.390
7.305
7.303
7.285
6.904
6.886
6.866
6.864
6.859
6.837
6.686
6.661
5.261
5.233
5.174
5.145
4.284
4.277
4.260
4.241
3.834
3.810
1.272
1.253
1.237
NO2
EtO2C
OMe
CO2Me
3f
abundance
X : parts per Million : Proton
0.91
0.94
2.13
2.00
2.08
2.17
6.03
3.26

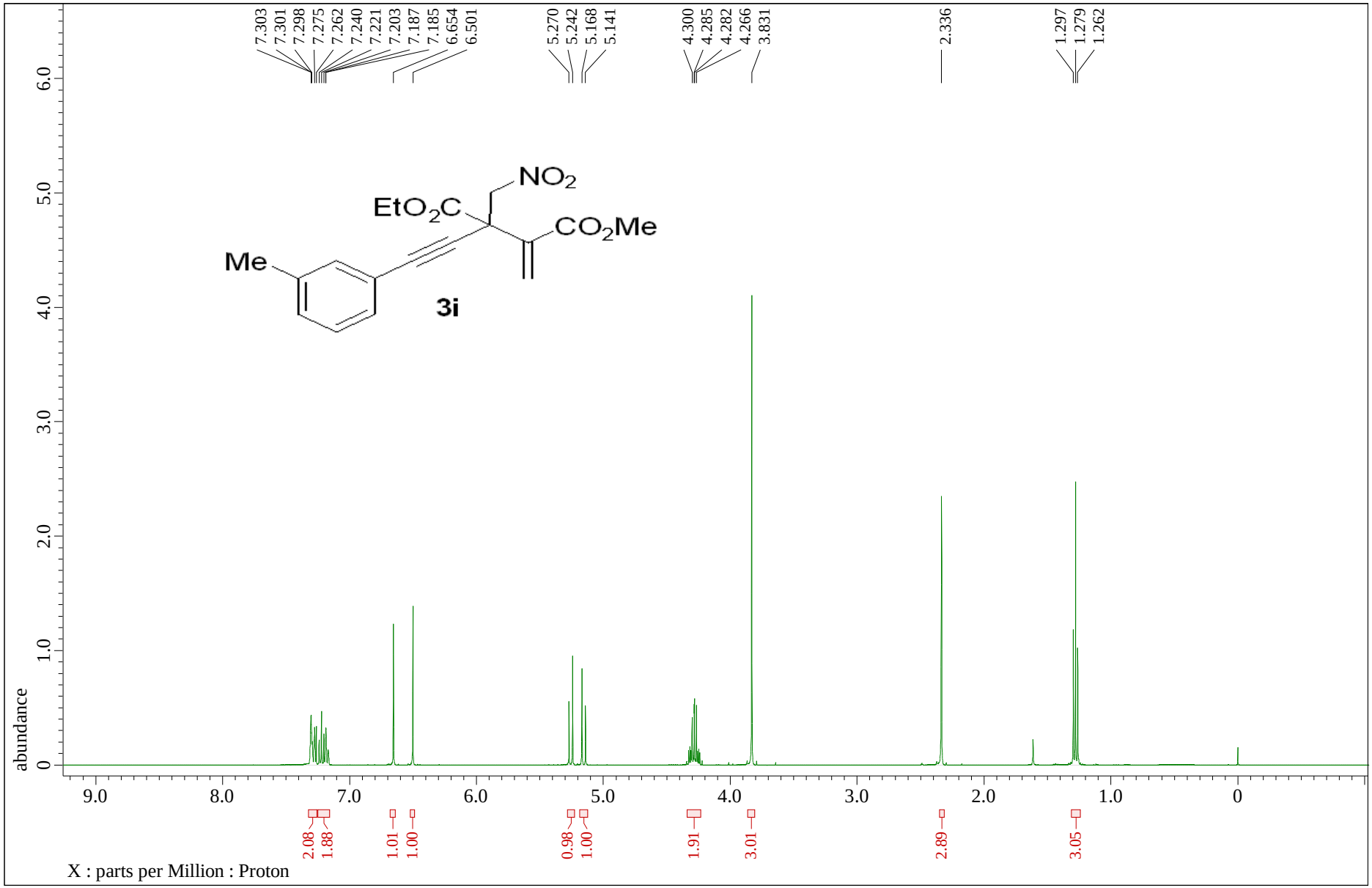

167.078
165.497
160.753
135.071
133.615
132.657
130.740
120.391
110.779
86.554
85.759
79.597
77.470
77.153
76.837
63.115
55.784
52.583
50.868
13.859
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

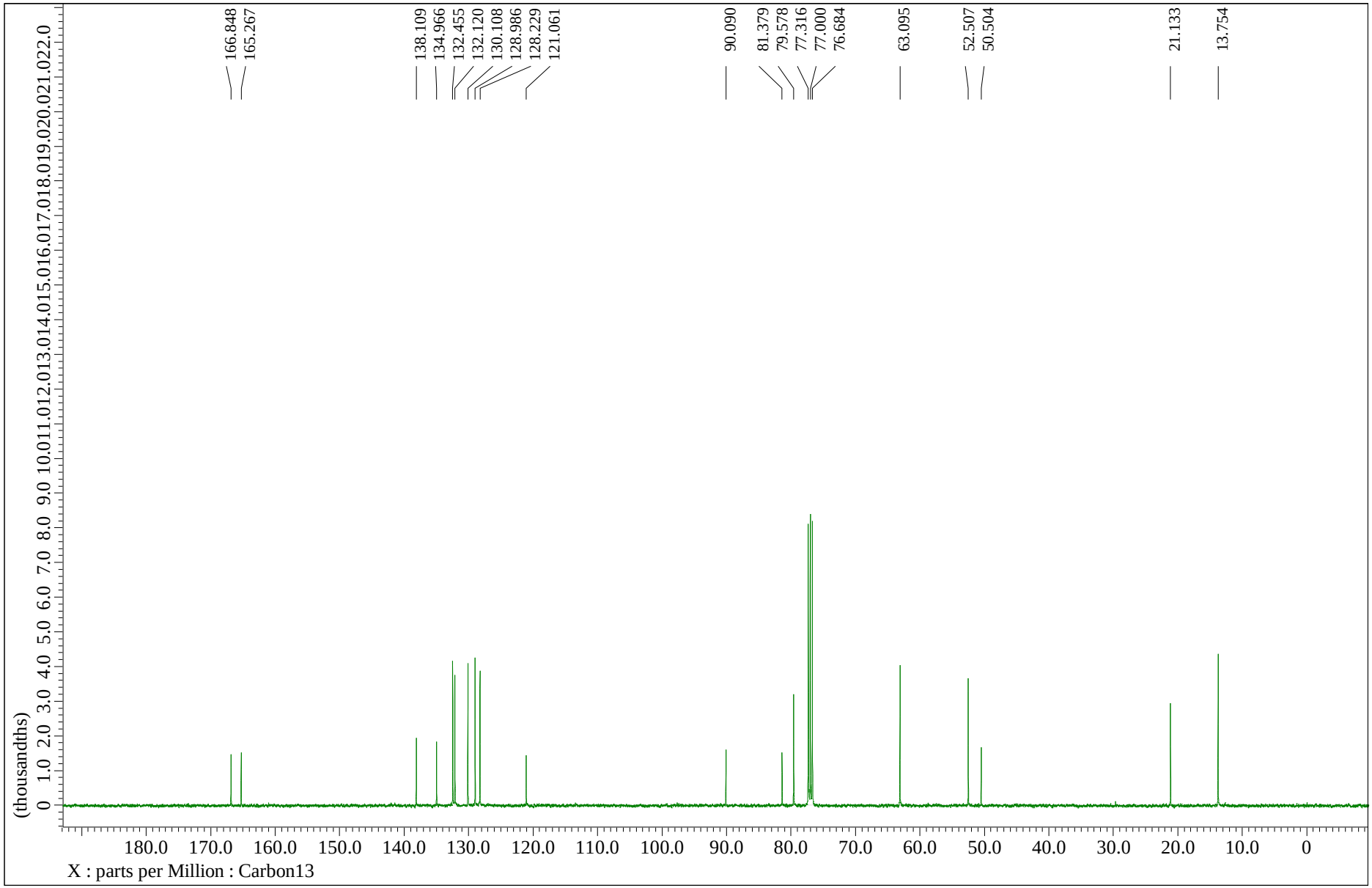

7.473
7.469
7.465
7.378
7.375
7.360
7.345
7.341
7.293
7.273
7.254
6.655
6.456
5.272
5.245
5.162
5.134
4.309
4.290
4.272
3.834
1.301
1.284
1.265
NO2
EtO2C
CO2Me
Cl
3g
abundance
X : parts per Million : Proton
0.95
2.00
1.11
1.00
1.01
1.00
1.02
2.02
3.09
3.43

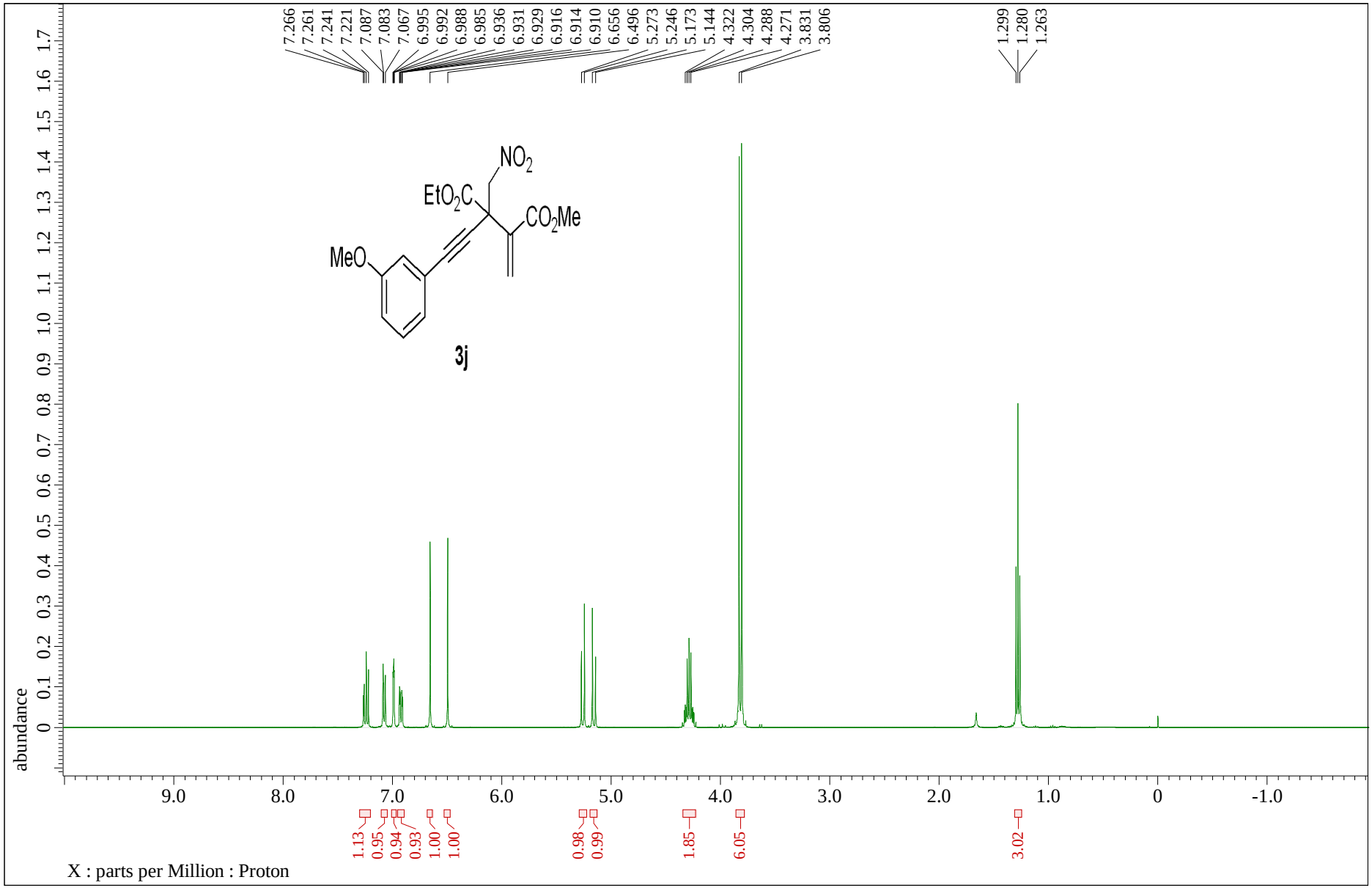

166.541
165.123
134.717
134.199
132.043
131.708
130.098
129.628
129.552
122.892
88.317
83.066
79.415
77.326
77.000
76.684
63.230
52.554
50.456
13.735
(thousandths)
-2.0 0 2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 18.0 20.0 22.0 24.0 26.0 28.0 30.0 32.0 34.0 36.0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : Carbon13

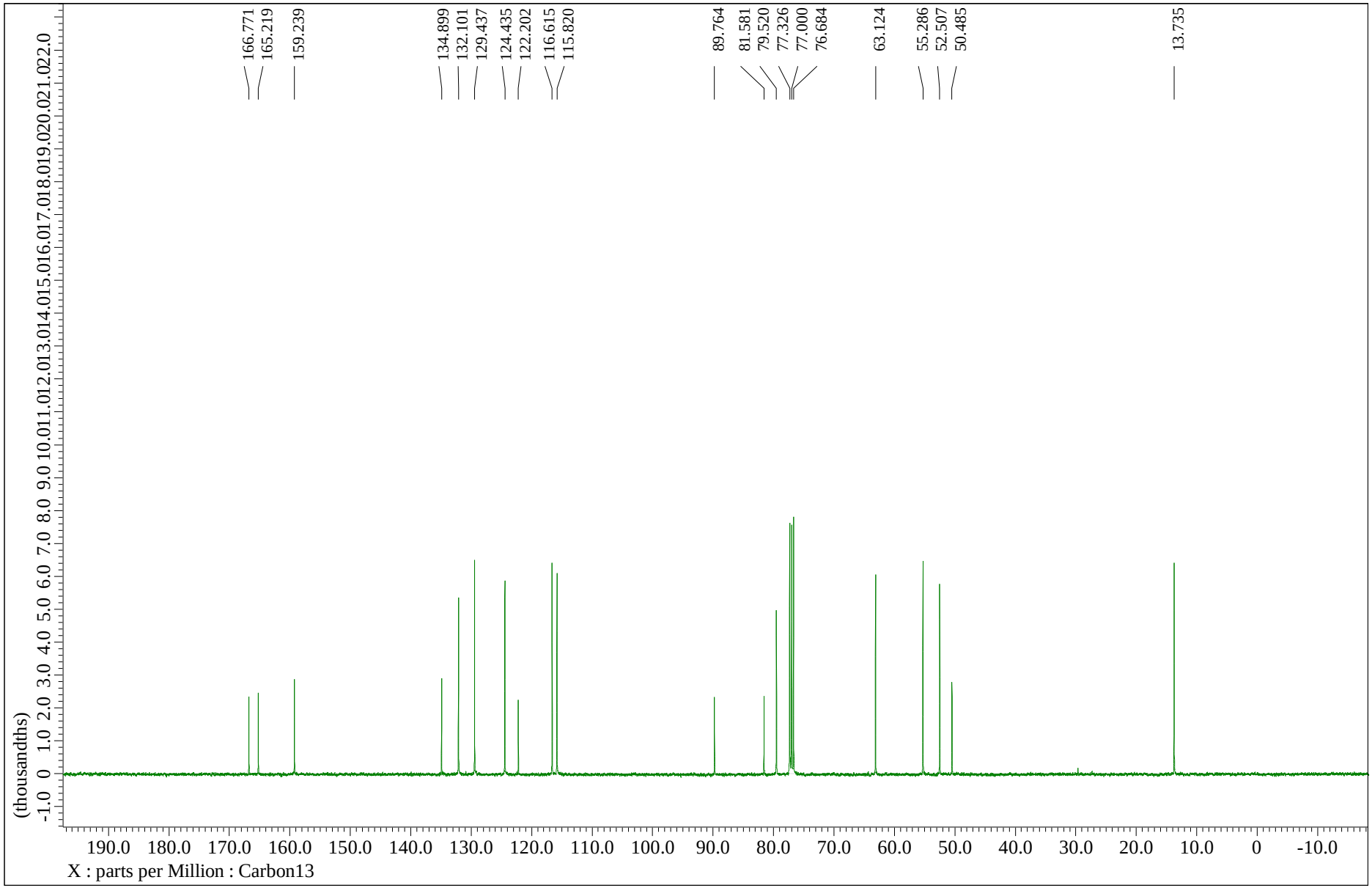

7.631
7.628
7.623
7.518
7.515
7.497
7.425
7.406
7.267
7.233
7.214
7.194
6.654
6.452
5.270
5.241
5.158
5.130
4.326
4.308
4.290
4.272
3.835
1.302
1.284
1.267
0.000
NO2
EtO2C
CO2Me
Br
3h
abundance
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
0.93
0.93
0.96
0.95
0.99
1.00
0.97
0.99
1.83
2.96
3.35
X : parts per Million : Proton

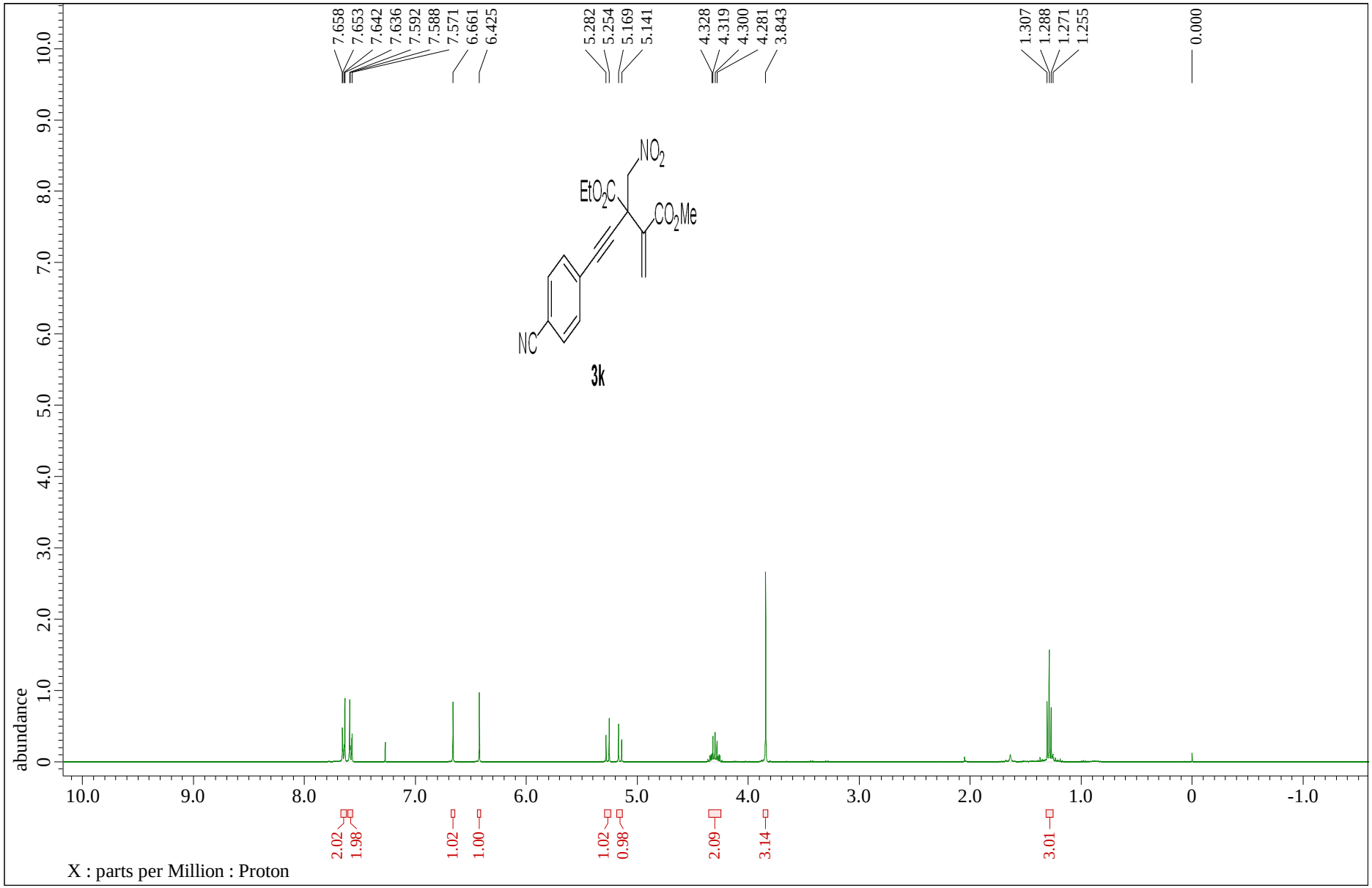

ly-a147_Carbon-1-3.jdf
166.560
165.142
134.717
134.573
132.455
132.082
130.558
129.830
123.198
122.144
88.202
83.190
79.424
77.316
77.000
76.684
63.258
52.583
50.475
13.764
(thousandths)
X : parts per Million : Carbon13

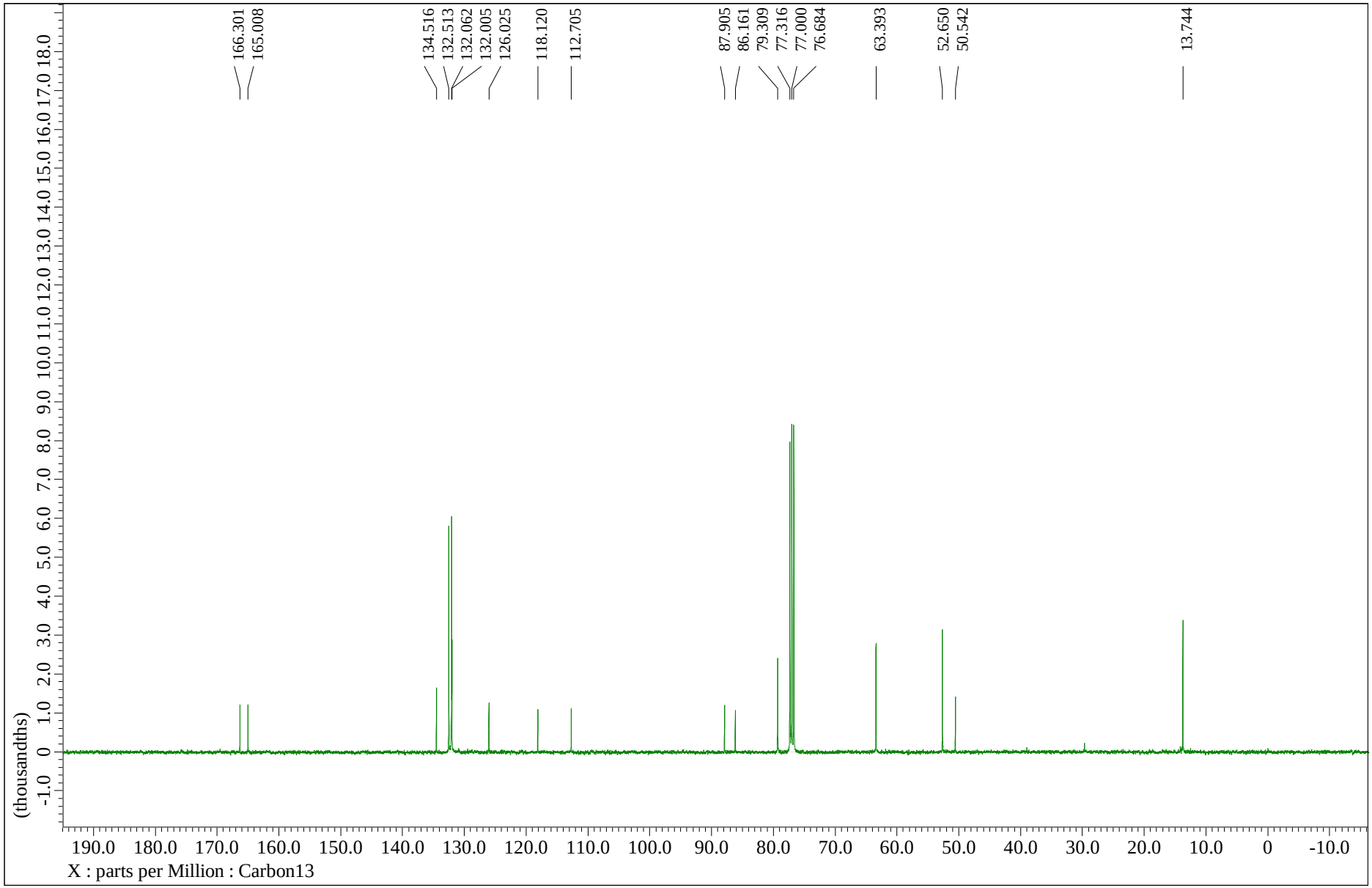

7.303
7.301
7.298
7.275
7.262
7.240
7.221
7.203
7.187
7.185
6.654
6.501
5.270
5.242
5.168
5.141
4.300
4.285
4.282
4.266
3.831
2.336
1.297
1.279
1.262
NO2
EtO2C
CO2Me
Me
3i
abundance
X : parts per Million : Proton
2.08
1.88
1.01
1.00
0.98
1.00
1.91
3.01
2.89
3.05

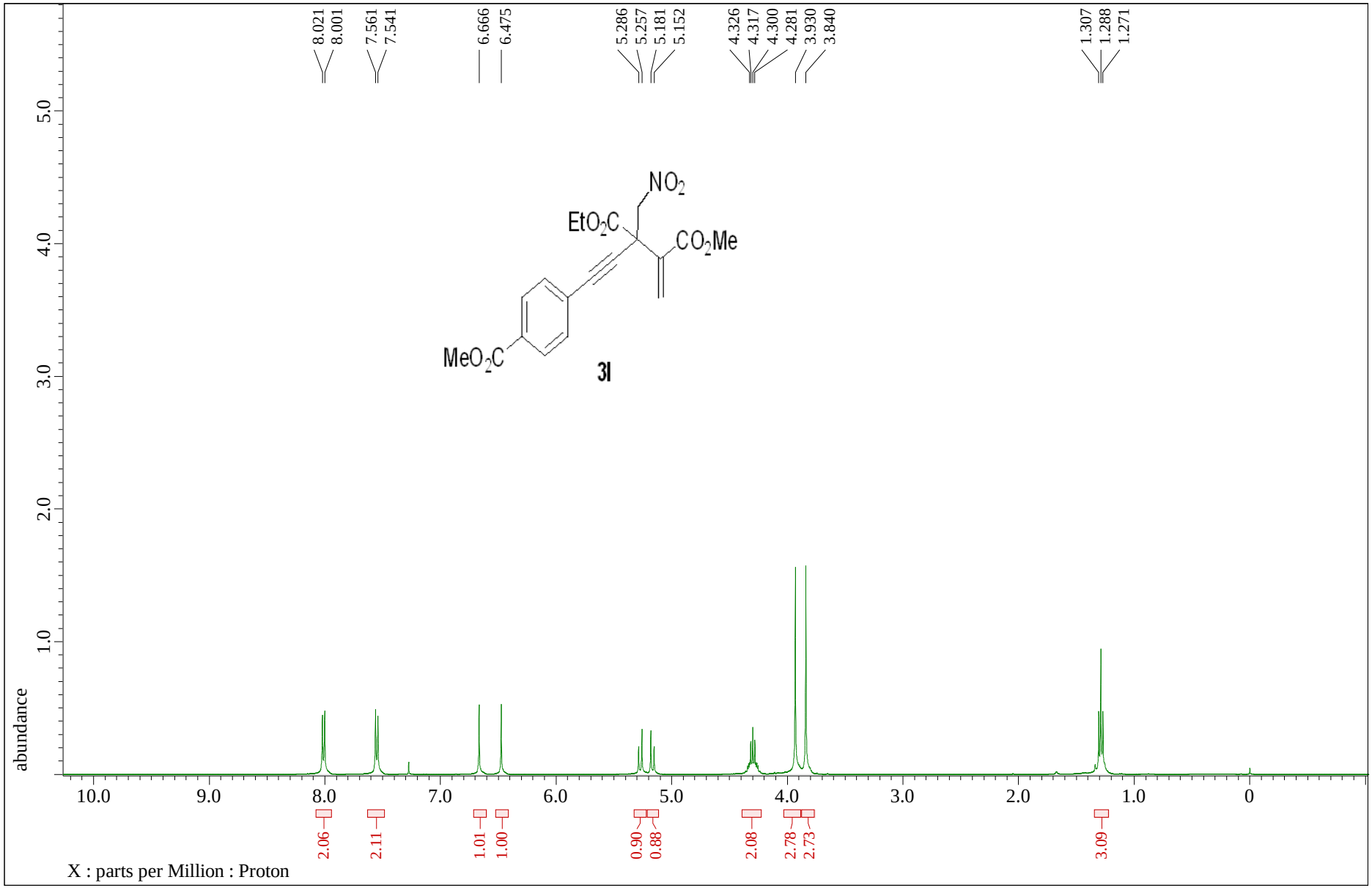

166.848
165.267
138.109
134.966
132.455
132.120
130.108
128.986
128.229
121.061
90.090
81.379
79.578
77.316
77.000
76.684
63.095
52.507
50.504
21.133
13.754
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : Carbon13

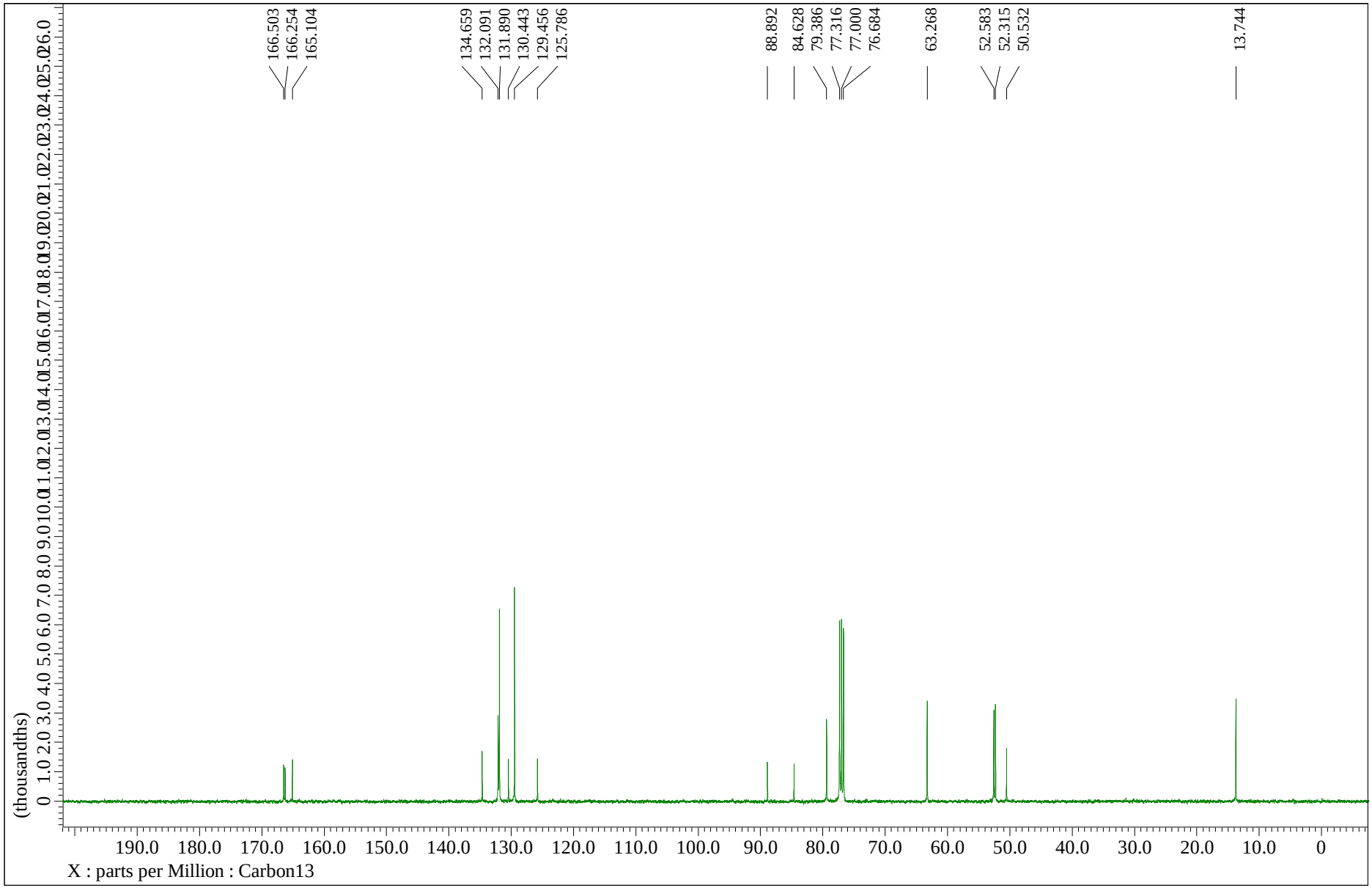

7.266
7.261
7.241
7.221
7.087
7.083
7.067
6.995
6.992
6.988
6.985
6.936
6.931
6.929
6.916
6.914
6.910
6.656
6.496
5.273
5.246
5.173
5.144
4.322
4.304
4.288
4.271
3.831
3.806
1.299
1.280
1.263
NO2
EtO2C
CO2Me
MeO
3j
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.13
0.95
0.94
0.93
1.00
1.00
0.98
0.99
1.85
6.05
3.02
X : parts per Million : Proton

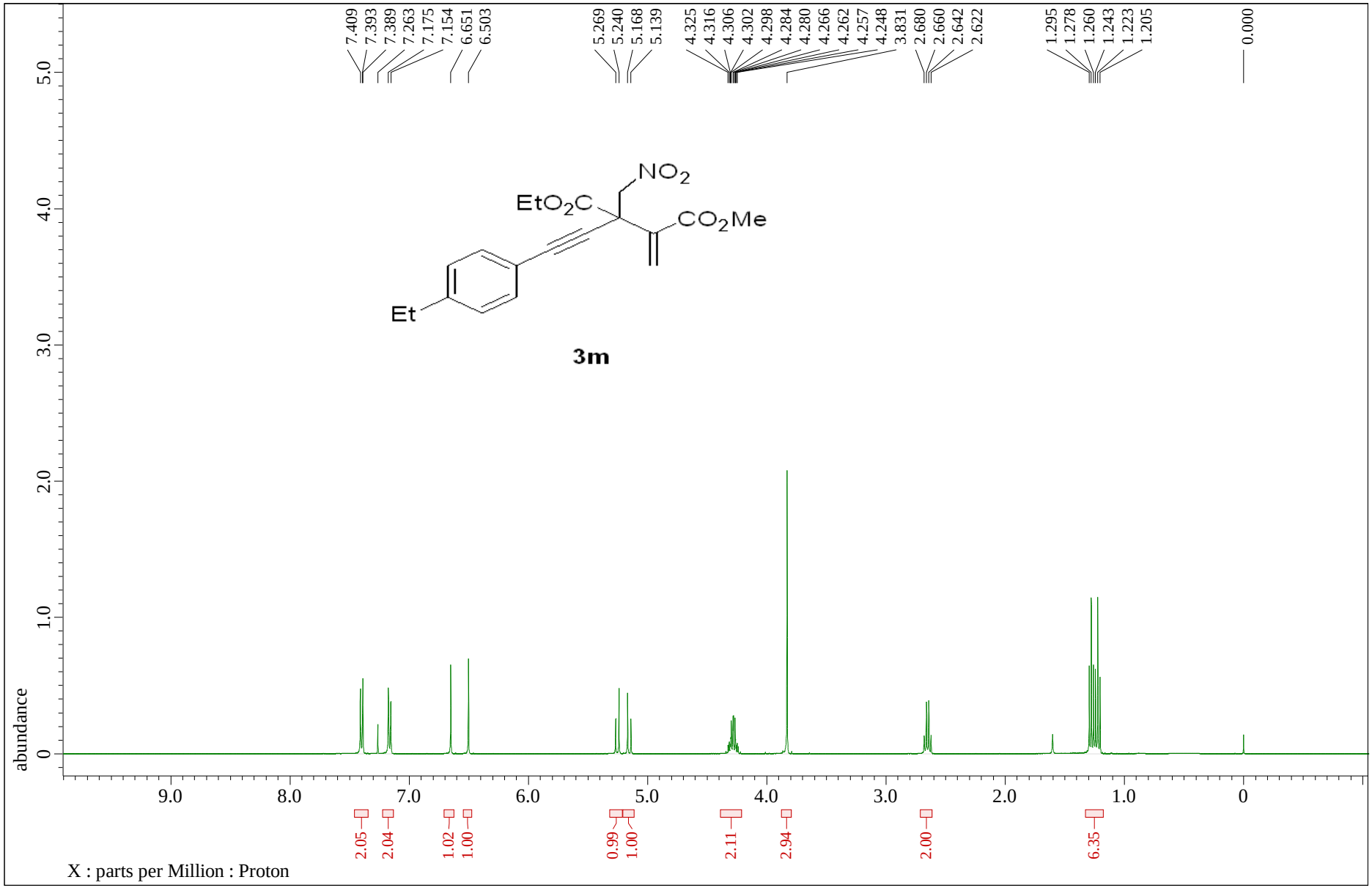

166.771
165.219
159.239
134.899
132.101
129.437
124.435
122.202
116.615
115.820
89.764
81.581
79.520
77.326
77.000
76.684
63.124
55.286
52.507
50.485
13.735
(thousandths)
X : parts per Million : Carbon13

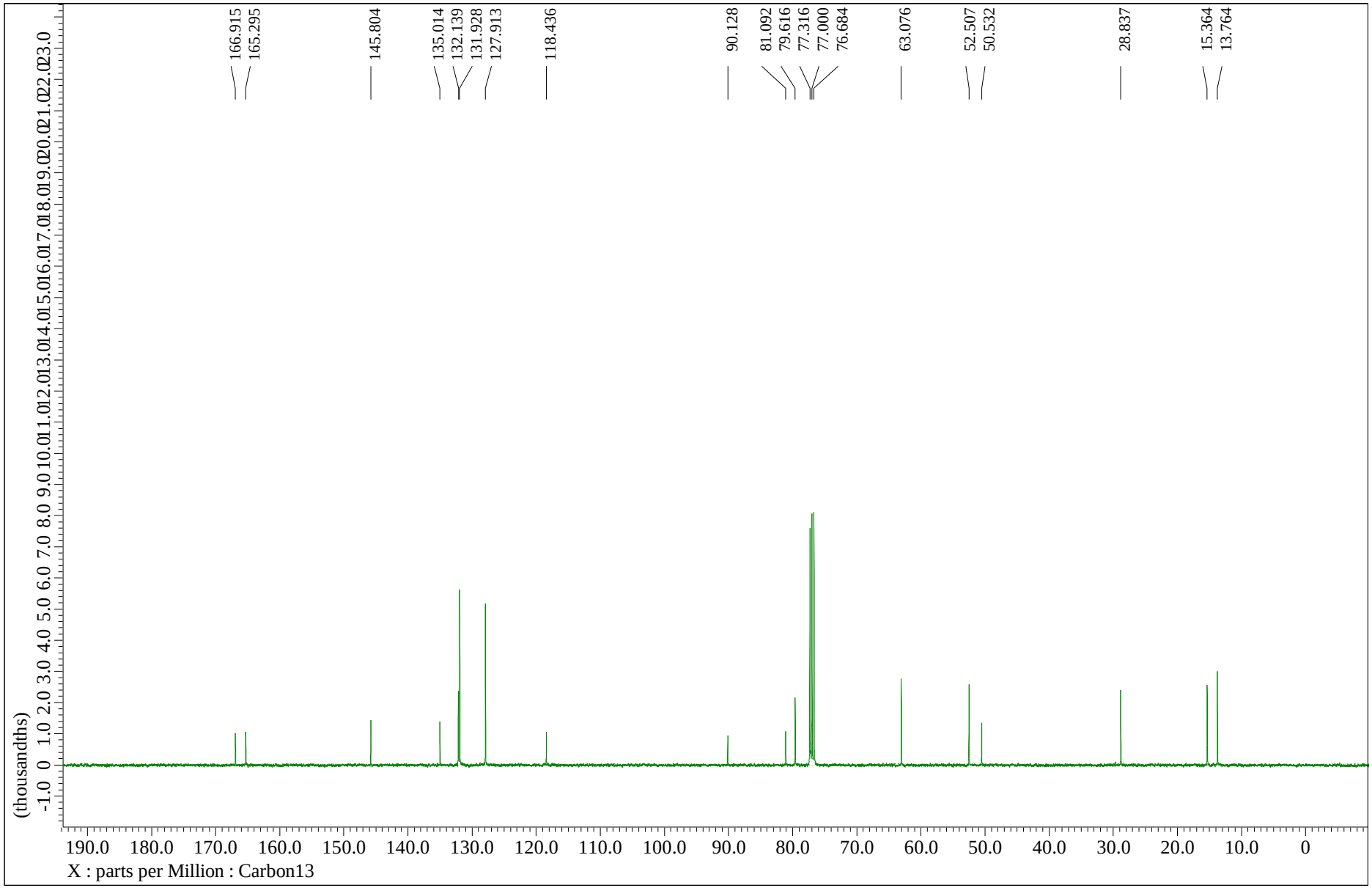

7.658
7.653
7.642
7.636
7.592
7.588
7.571
6.661
6.425
5.282
5.254
5.169
5.141
4.328
4.319
4.300
4.281
3.843
1.307
1.288
1.271
1.255
0.000
NO2
EtO2C
CO2Me
NC
3k
abundance
X : parts per Million : Proton
2.02
1.98
1.02
1.00
1.02
0.98
2.09
3.14
3.01

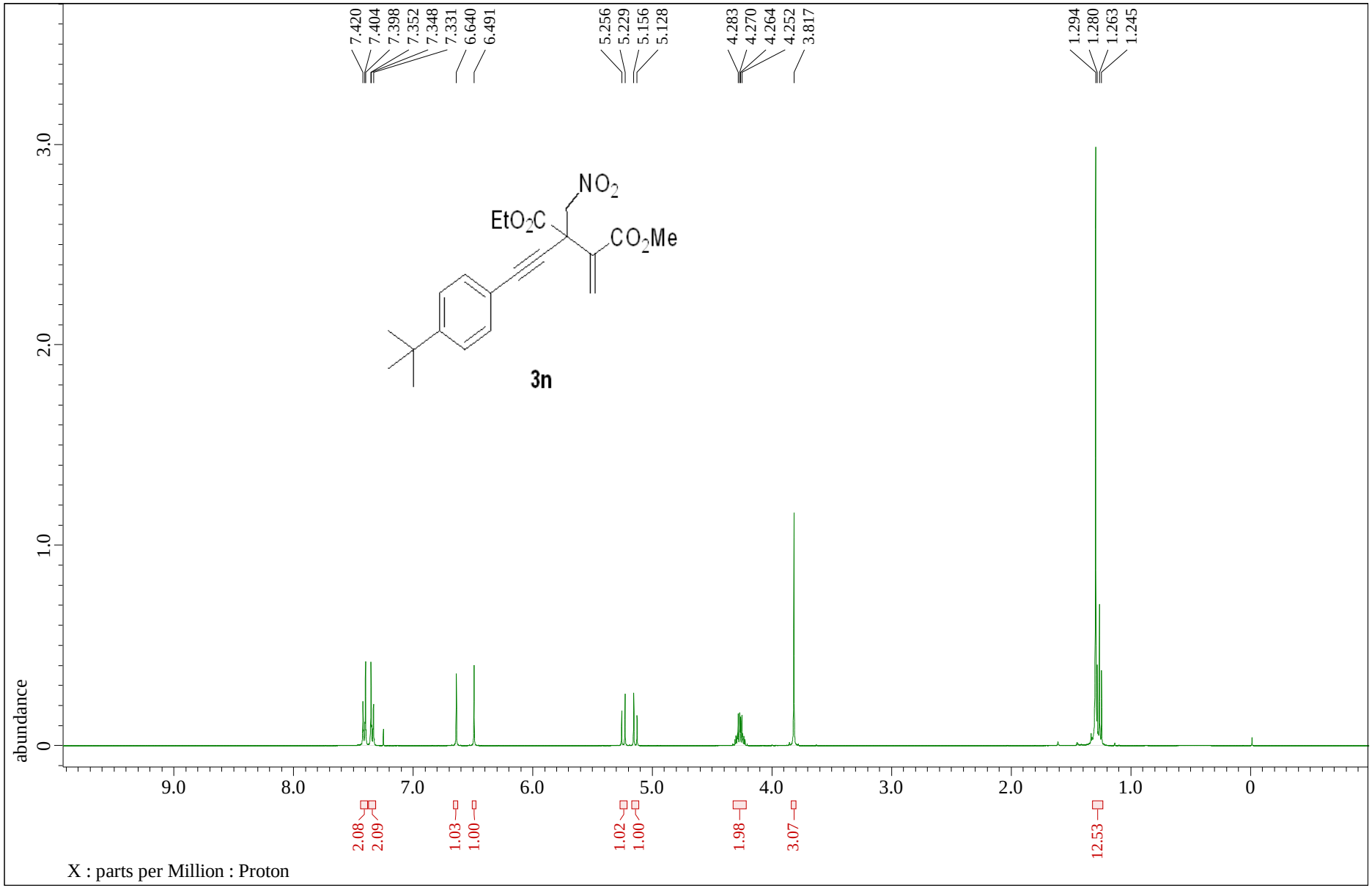

166.301
165.008
134.516
132.513
132.062
132.005
126.025
118.120
112.705
87.905
86.161
79.309
77.316
77.000
76.684
63.393
52.650
50.542
13.744
(thousandths)
X : parts per Million : Carbon13

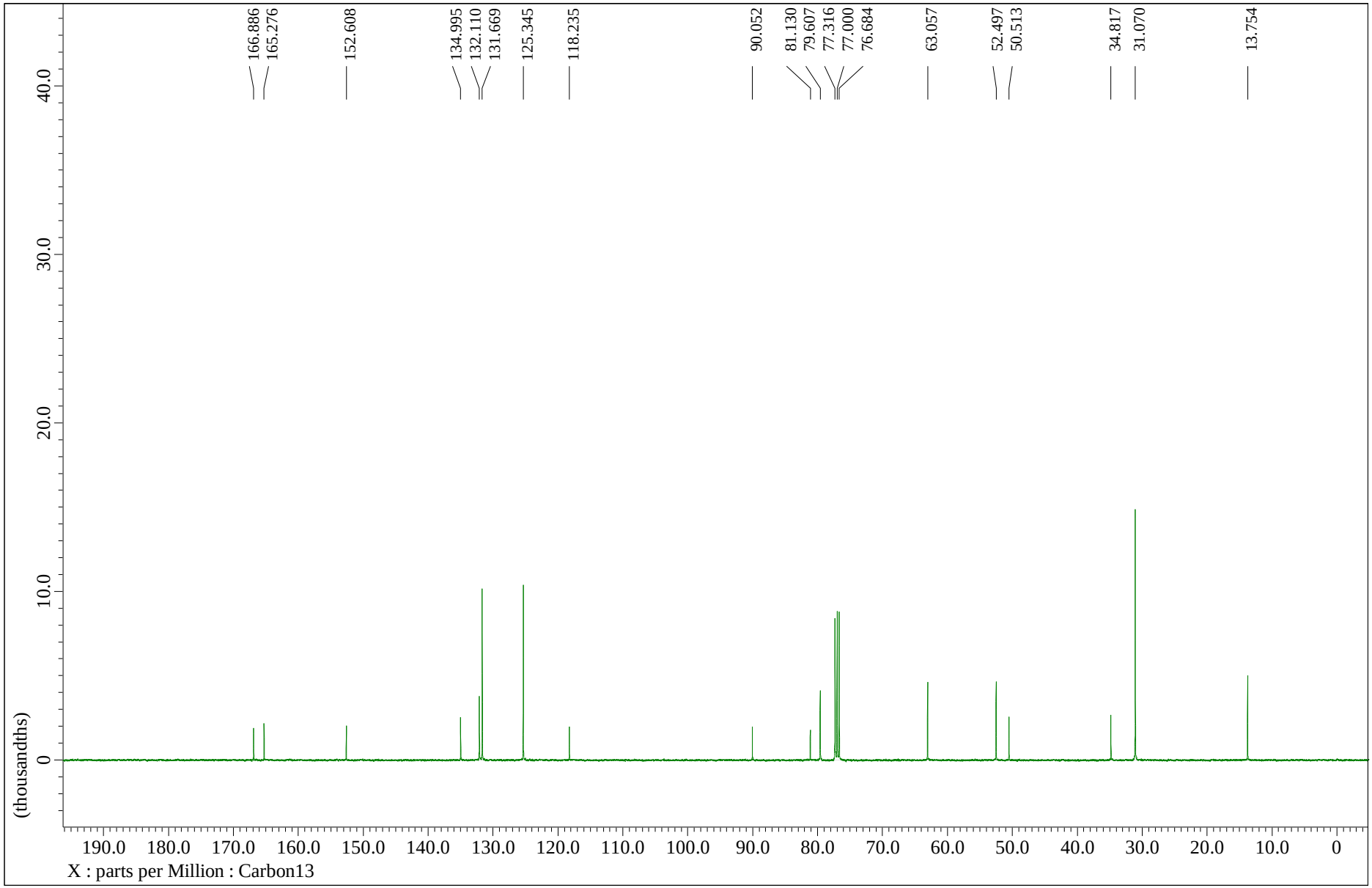

8.021
8.001
7.561
7.541
6.666
6.475
5.286
5.257
5.181
5.152
4.326
4.317
4.300
4.281
3.930
3.840
1.307
1.288
1.271
NO2
EtO2C
CO2Me
MeO2C
3l
abundance
5.0
4.0
3.0
2.0
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.06
2.11
1.01
1.00
0.90
0.88
2.08
2.78
2.73
3.09
X : parts per Million : Proton

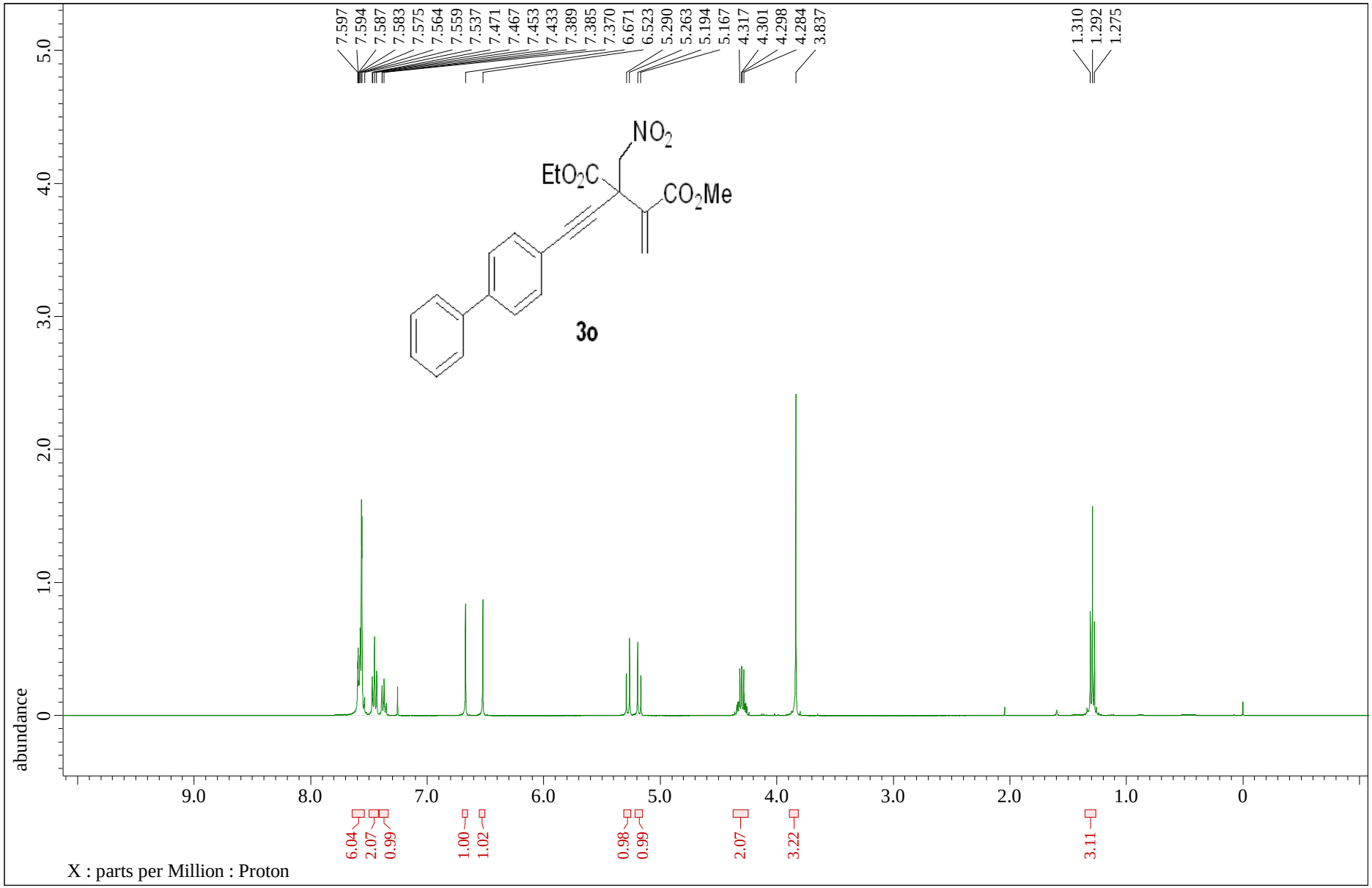

166.503
166.254
165.104
134.659
132.091
131.890
130.443
129.456
125.786
88.892
84.628
79.386
77.316
77.000
76.684
63.268
52.583
52.315
50.532
13.744
(thousandths)
X : parts per Million : Carbon13

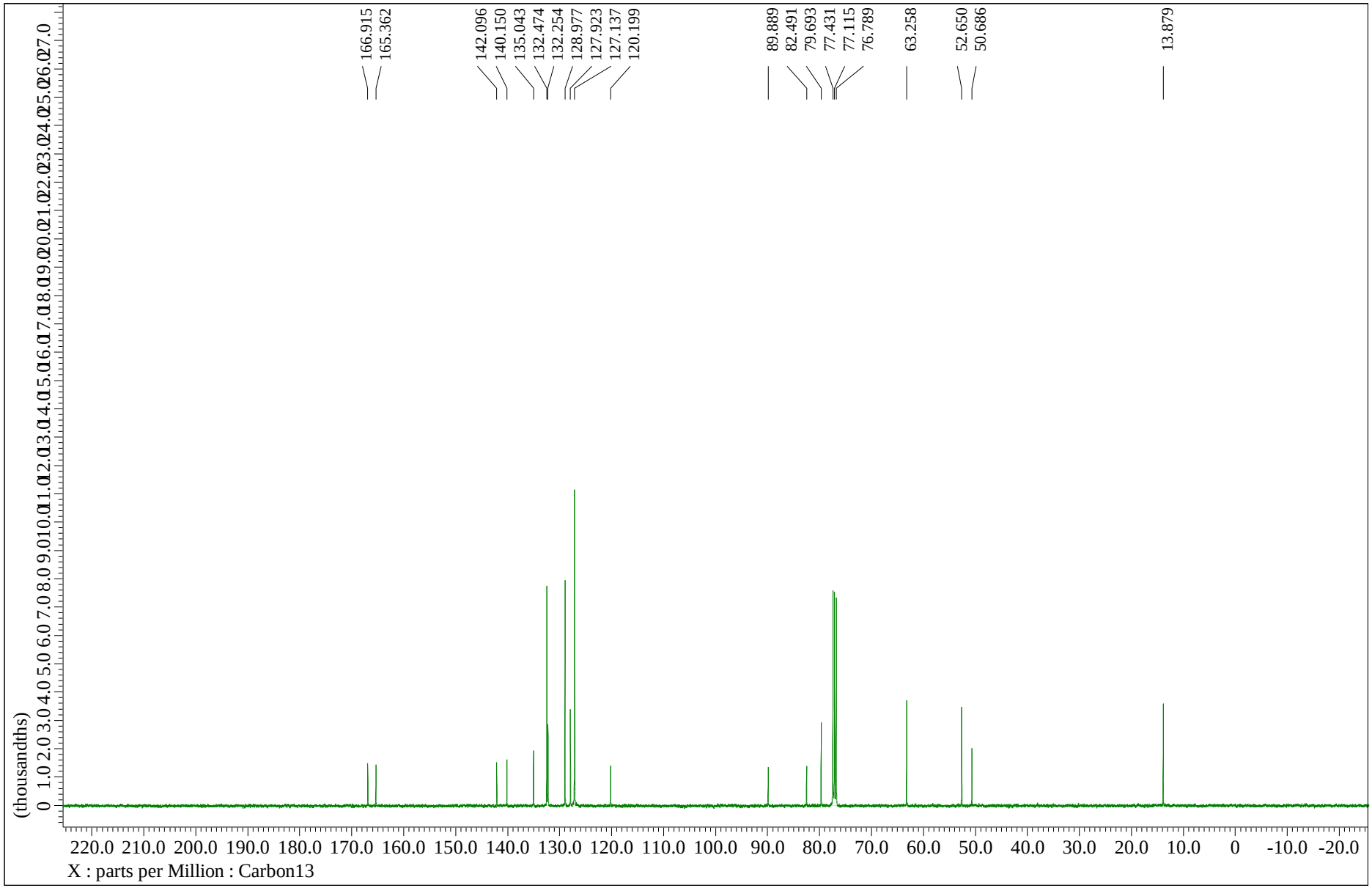

7.409
7.393
7.389
7.263
7.175
7.154
6.651
6.503
5.269
5.240
5.168
5.139
4.325
4.316
4.306
4.302
4.298
4.284
4.280
4.266
4.262
4.257
4.248
3.831
2.680
2.660
2.642
2.622
1.295
1.278
1.260
1.243
1.223
1.205
0.000
NO2
EtO2C
CO2Me
Et
3m
abundance
X : parts per Million : Proton
2.05
2.04
1.02
1.00
0.99
1.00
2.11
2.94
2.00
6.35

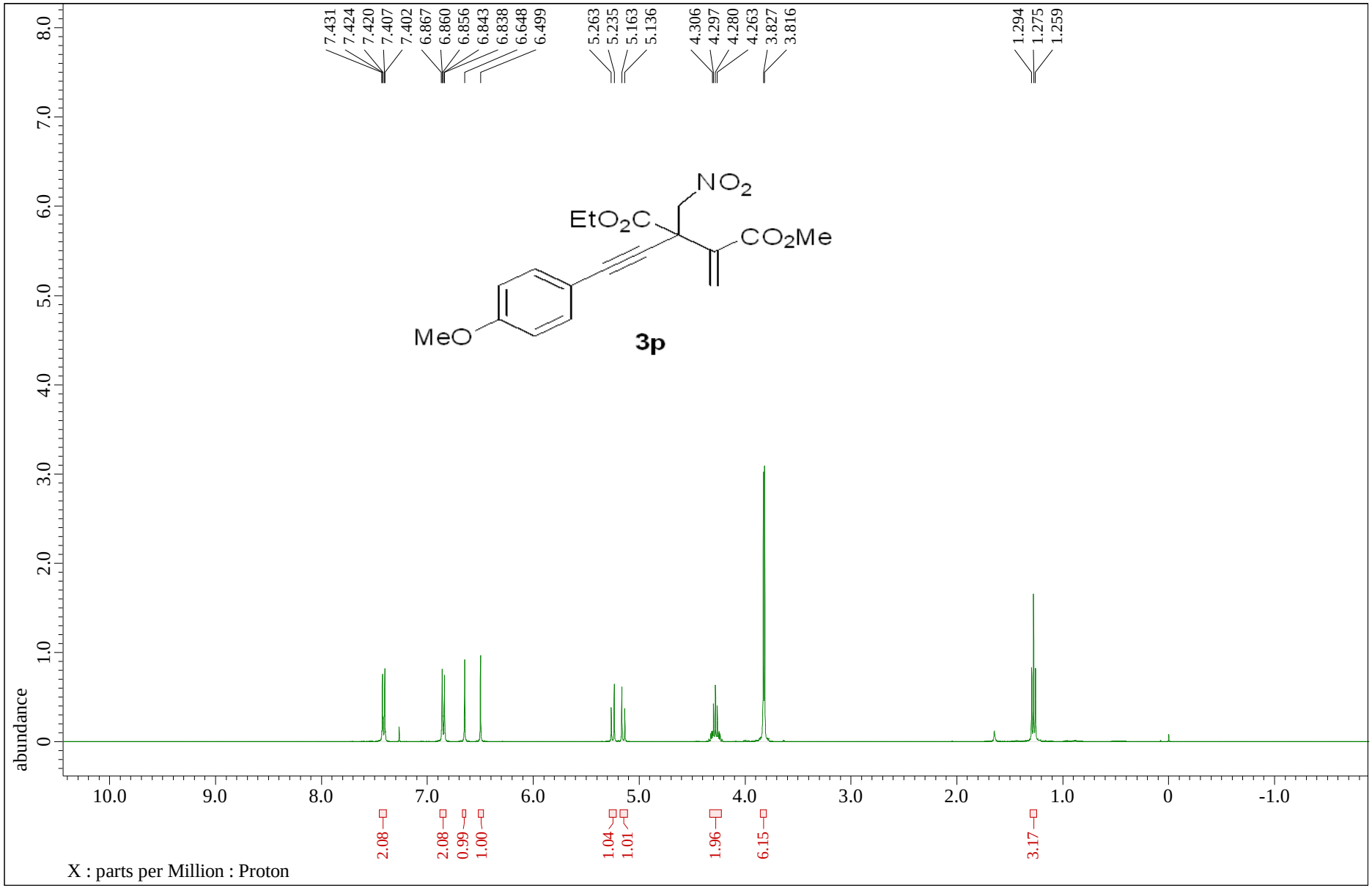

166.915
165.295
145.804
135.014
132.139
131.928
127.913
118.436
90.128
81.092
79.616
77.316
77.000
76.684
63.076
52.507
50.532
28.837
15.364
13.764
(thousandths)
X : parts per Million : Carbon13

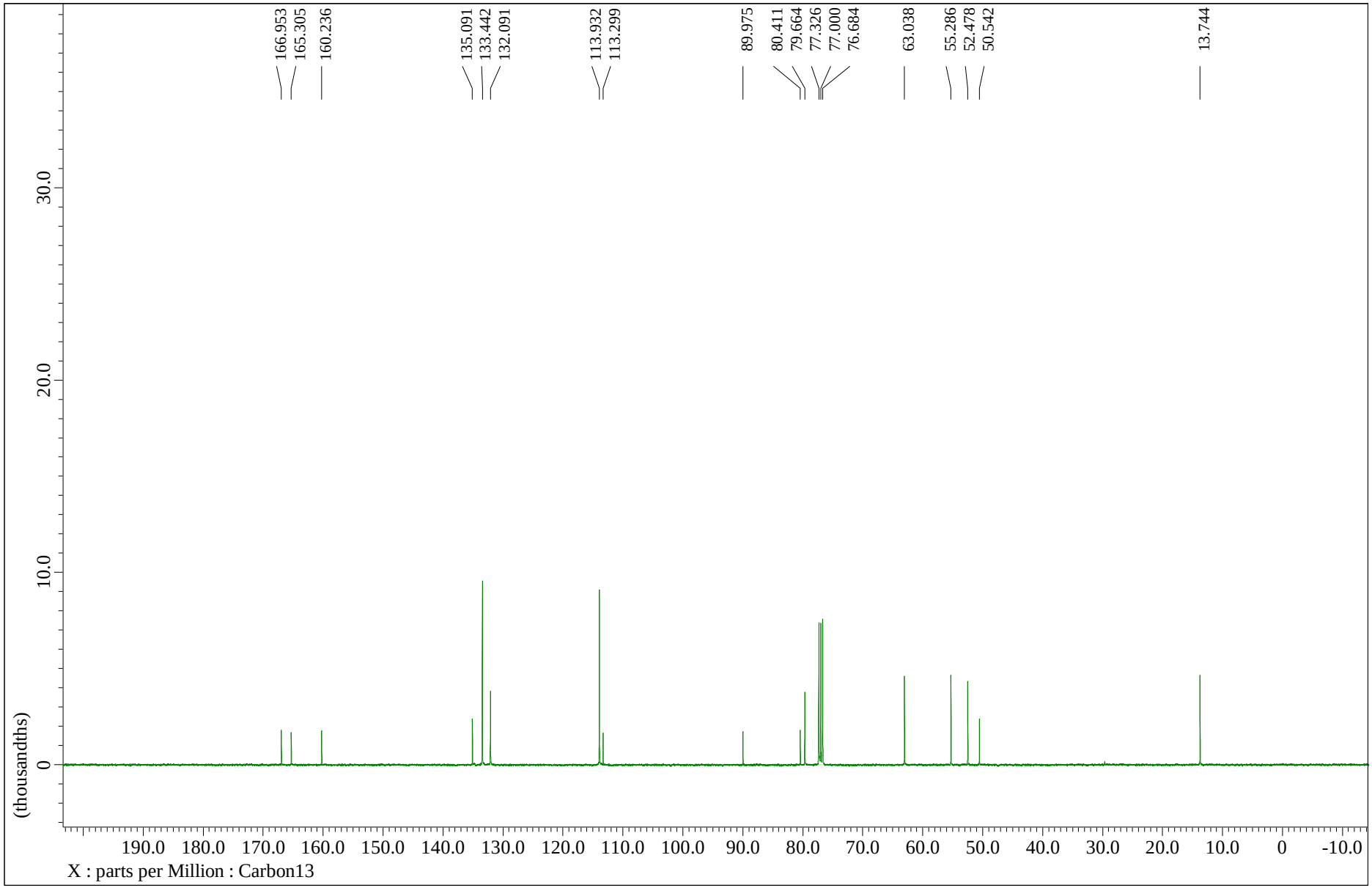

7.420
7.404
7.398
7.352
7.348
7.331
6.640
6.491
5.256
5.229
5.156
5.128
4.283
4.270
4.264
4.252
3.817
1.294
1.280
1.263
1.245
NO2
EtO2C
CO2Me
3n
abundance
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.08
2.09
1.03
1.00
1.02
1.00
1.98
3.07
12.53
X : parts per Million : Proton

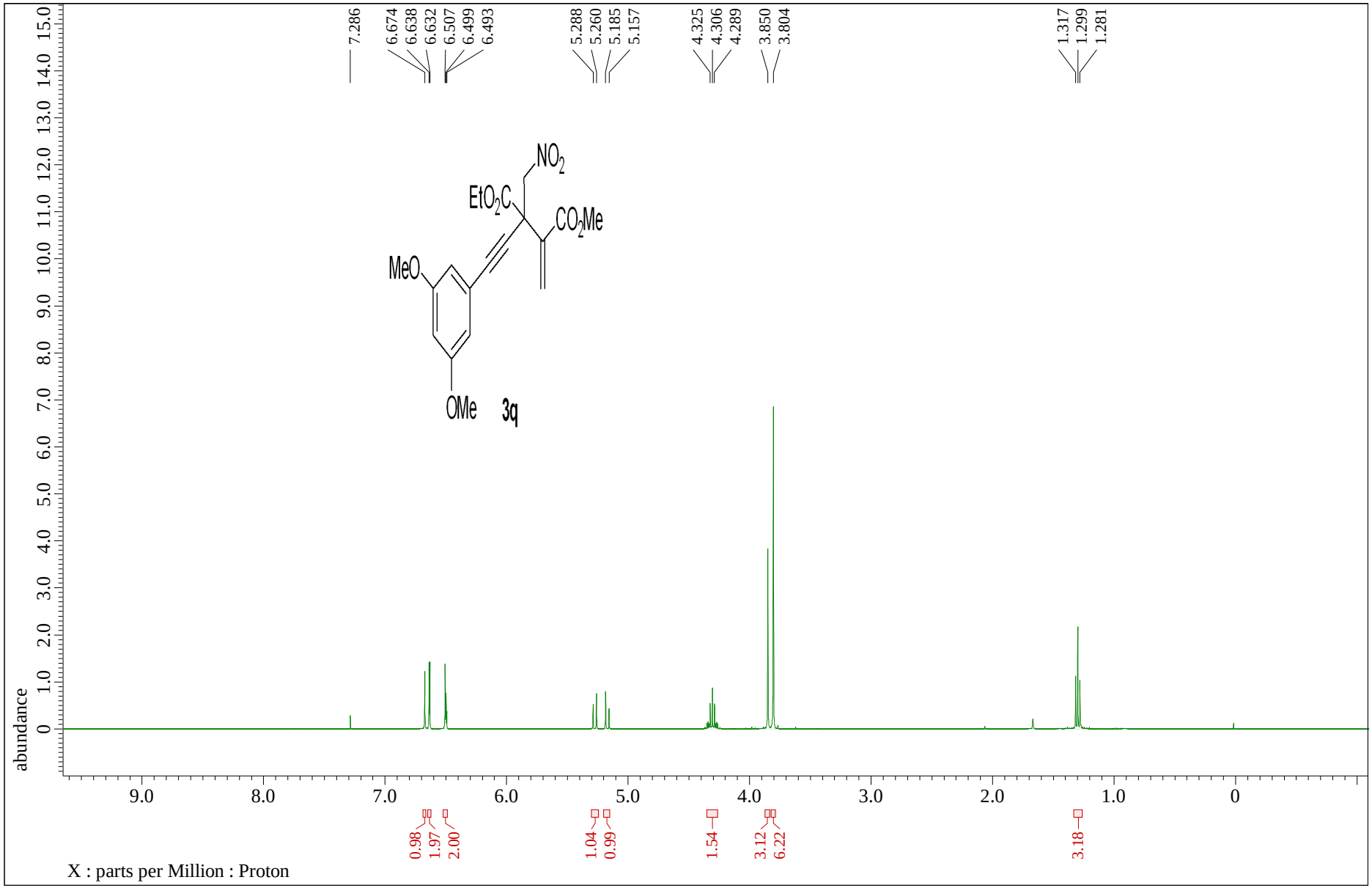

166.886
165.276
152.608
134.995
132.110
131.669
125.345
118.235
90.052
81.130
79.607
77.316
77.000
76.684
63.057
52.497
50.513
34.817
31.070
13.754
40.0
30.0
20.0
10.0
0
(thousandths)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13

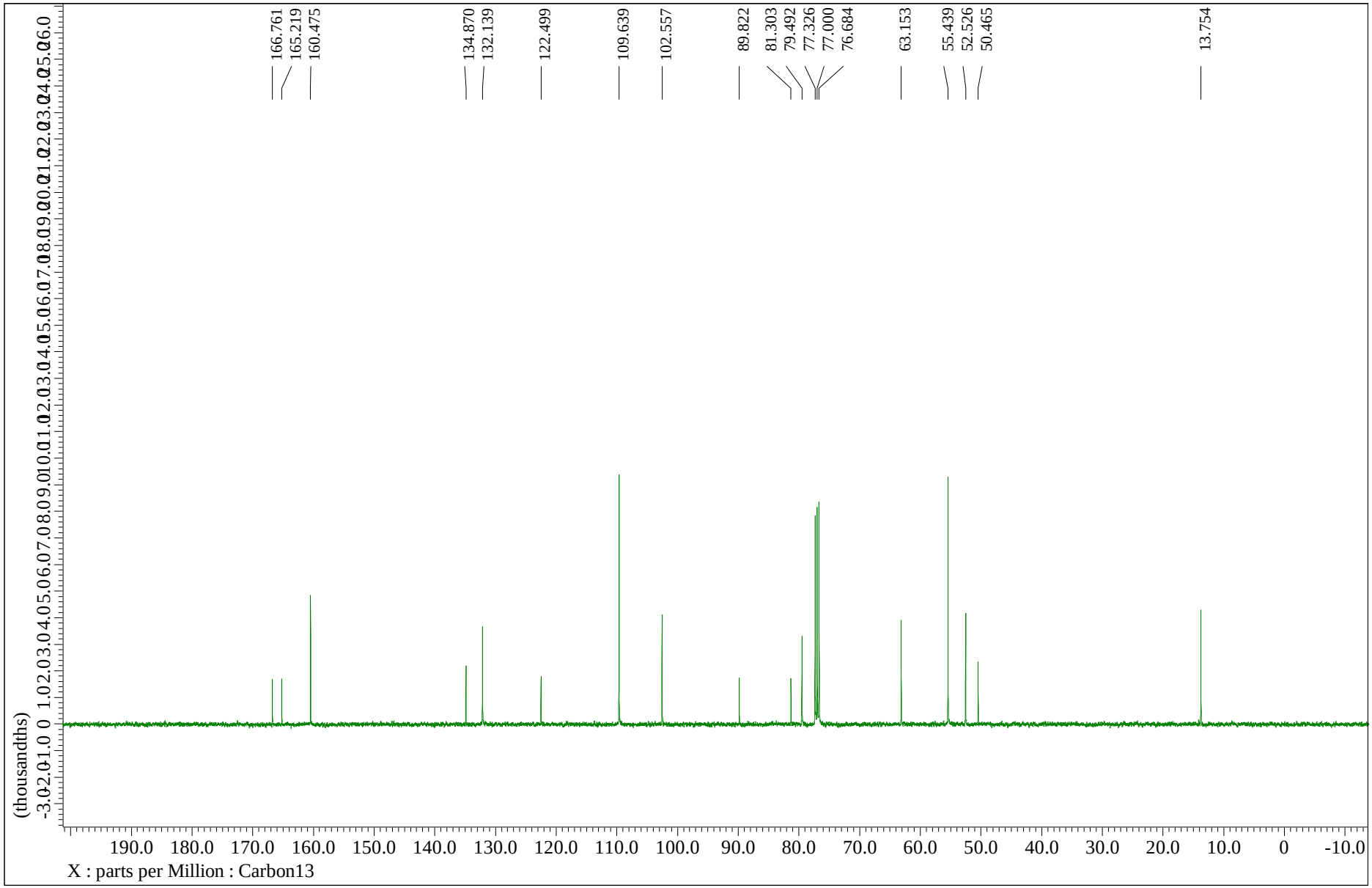

7.597
7.594
7.587
7.583
7.575
7.564
7.559
7.537
7.471
7.467
7.453
7.433
7.389
7.385
7.370
6.671
6.523
5.290
5.263
5.194
5.167
4.317
4.301
4.298
4.284
3.837
1.310
1.292
1.275
NO2
EtO2C
CO2Me
3o
abundance
X : parts per Million : Proton
6.04
2.07
0.99
1.00
1.02
0.98
0.99
2.07
3.22
3.11

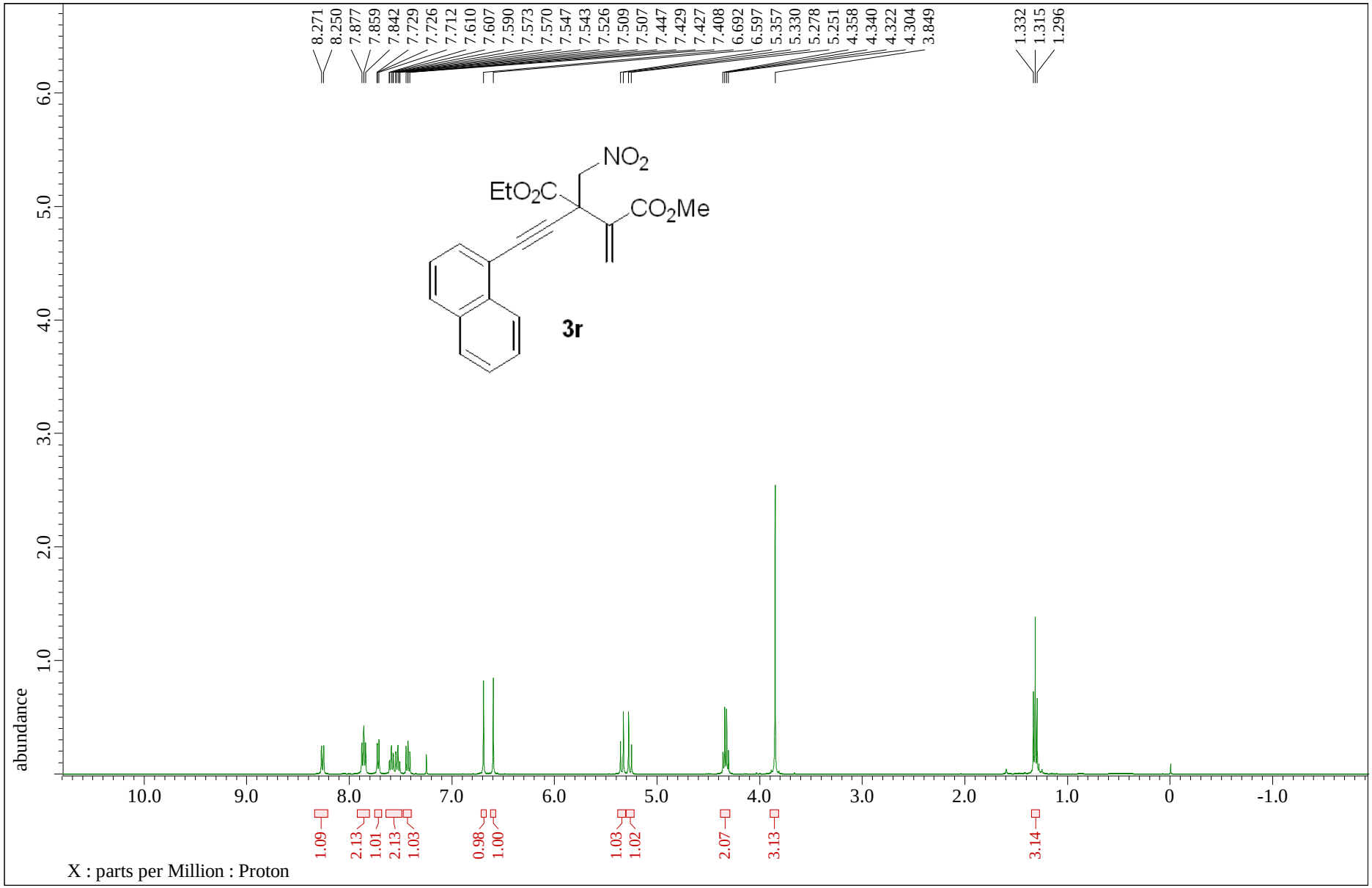

166.915
165.362
142.096
140.150
135.043
132.474
132.254
128.977
127.923
127.137
120.199
89.889
82.491
79.693
77.431
77.115
76.789
63.258
52.650
50.686
13.879
(thousandths)
X : parts per Million : Carbon13

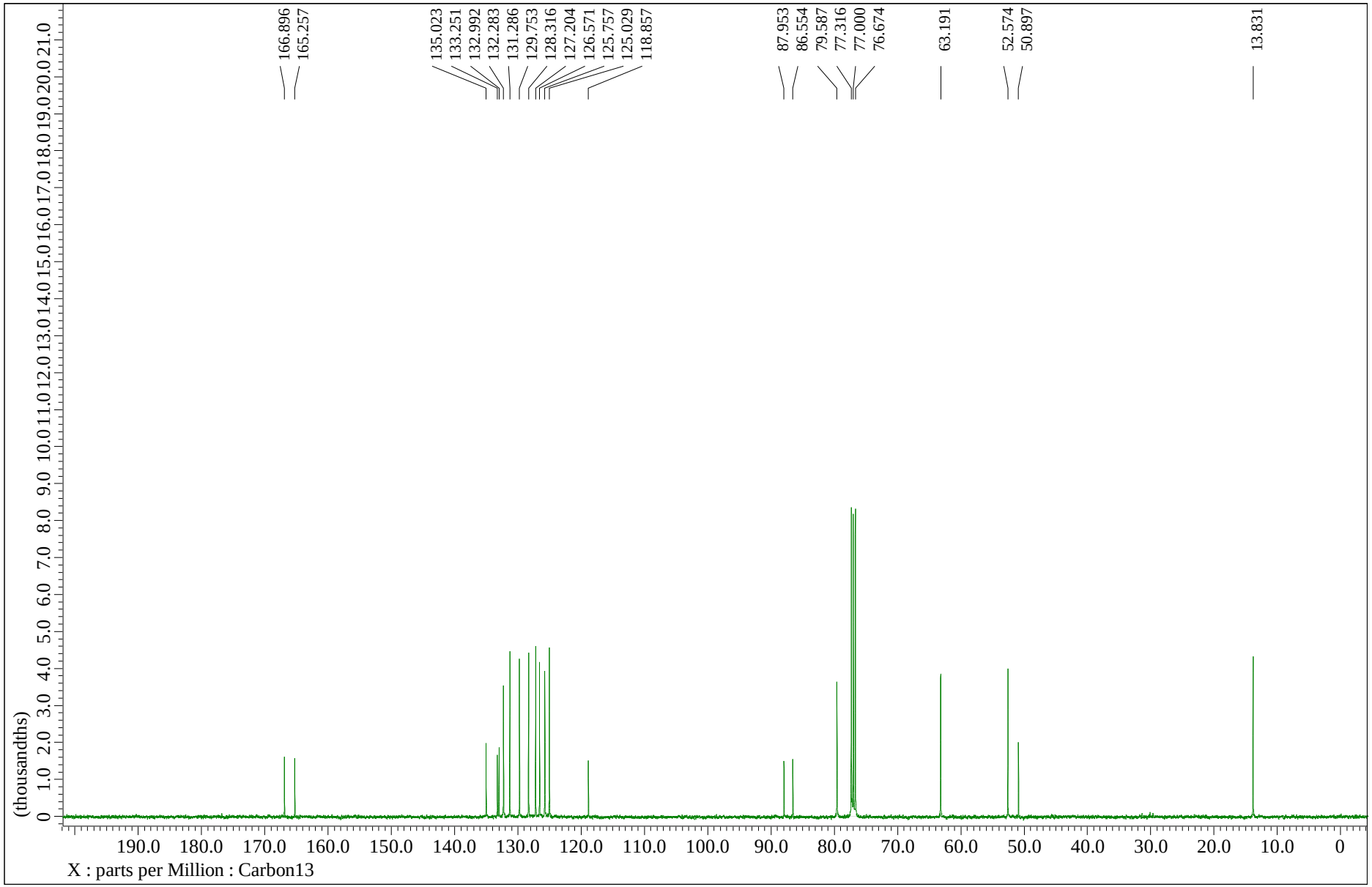

7.431
7.424
7.420
7.407
7.402
6.867
6.860
6.856
6.843
6.838
6.648
6.499
5.263
5.235
5.163
5.136
4.306
4.297
4.280
4.263
3.827
3.816
1.294
1.275
1.259
NO2
EtO2C
CO2Me
MeO
3p
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
2.08
2.08
0.99
1.00
1.04
1.01
1.96
6.15
3.17
X : parts per Million : Proton


166.953
165.305
160.236
135.091
133.442
132.091
113.932
113.299
89.975
80.411
79.664
77.326
77.000
76.684
63.038
55.286
52.478
50.542
13.744
30.0
20.0
10.0
0
(thousandths)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
X : parts per Million : Carbon13


7.286
6.674
6.638
6.632
6.507
6.499
6.493
5.288
5.260
5.185
5.157
4.325
4.306
4.289
3.850
3.804
1.317
1.299
1.281
NO2
EtO2C
CO2Me
MeO
OMe
3q
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.98
1.97
2.00
1.04
0.99
1.54
3.12
6.22
3.18
X : parts per Million : Proton


166.761
165.219
160.475
134.870
132.139
122.499
109.639
102.557
89.822
81.303
79.492
77.326
77.000
76.684
63.153
55.439
52.526
50.465
13.754
(thousandths)
X : parts per Million : Carbon13


8.271
8.250
7.877
7.859
7.842
7.729
7.726
7.712
7.610
7.607
7.590
7.573
7.570
7.547
7.543
7.526
7.509
7.507
7.447
7.429
7.427
7.408
6.692
6.597
5.357
5.330
5.278
5.251
4.358
4.340
4.322
4.304
3.849
1.332
1.315
1.296
NO2
EtO2C
CO2Me
3r
abundance
X : parts per Million : Proton
1.09
2.13
1.01
2.13
1.03
0.98
1.00
1.03
1.02
2.07
3.13
3.14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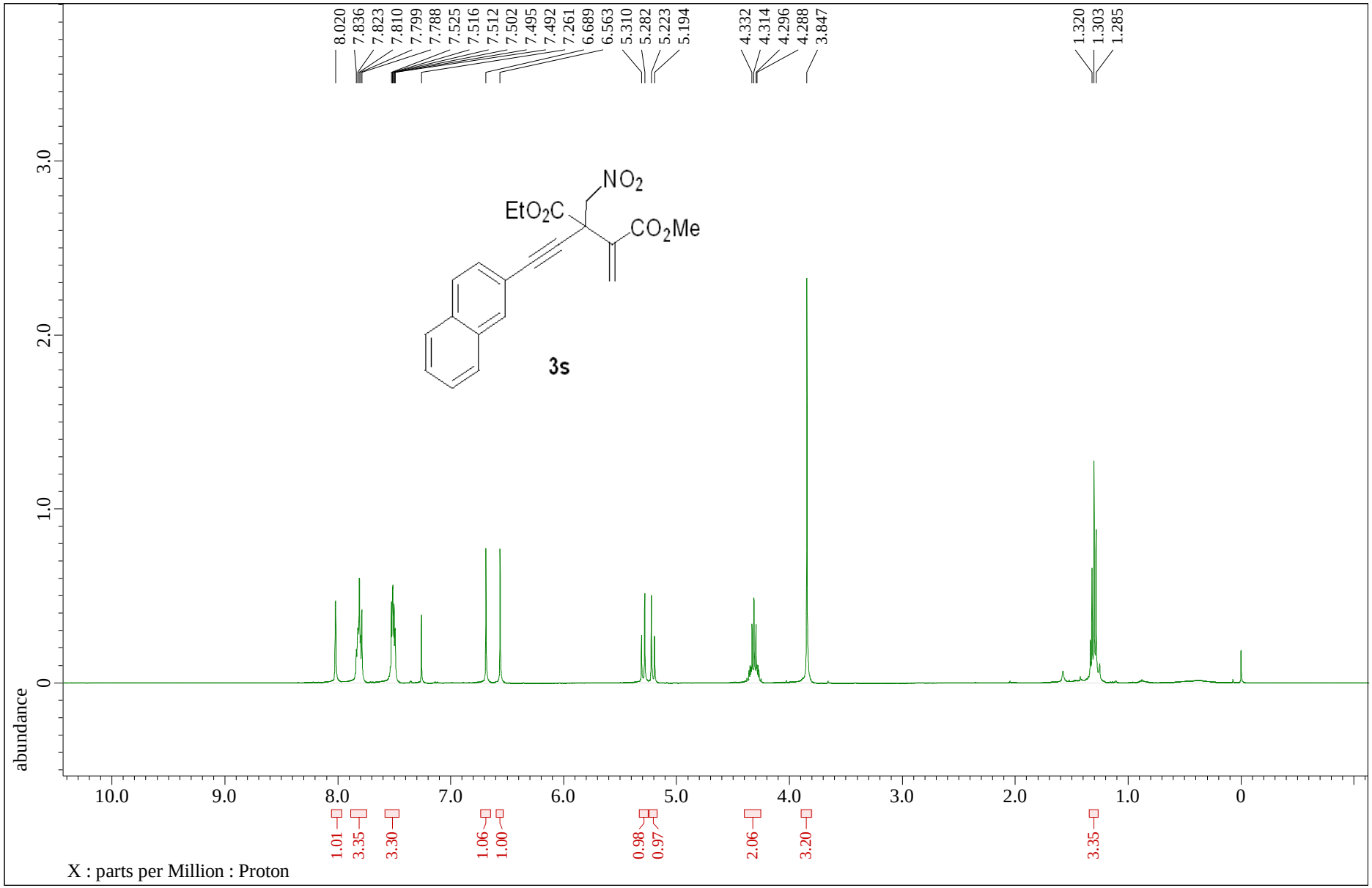
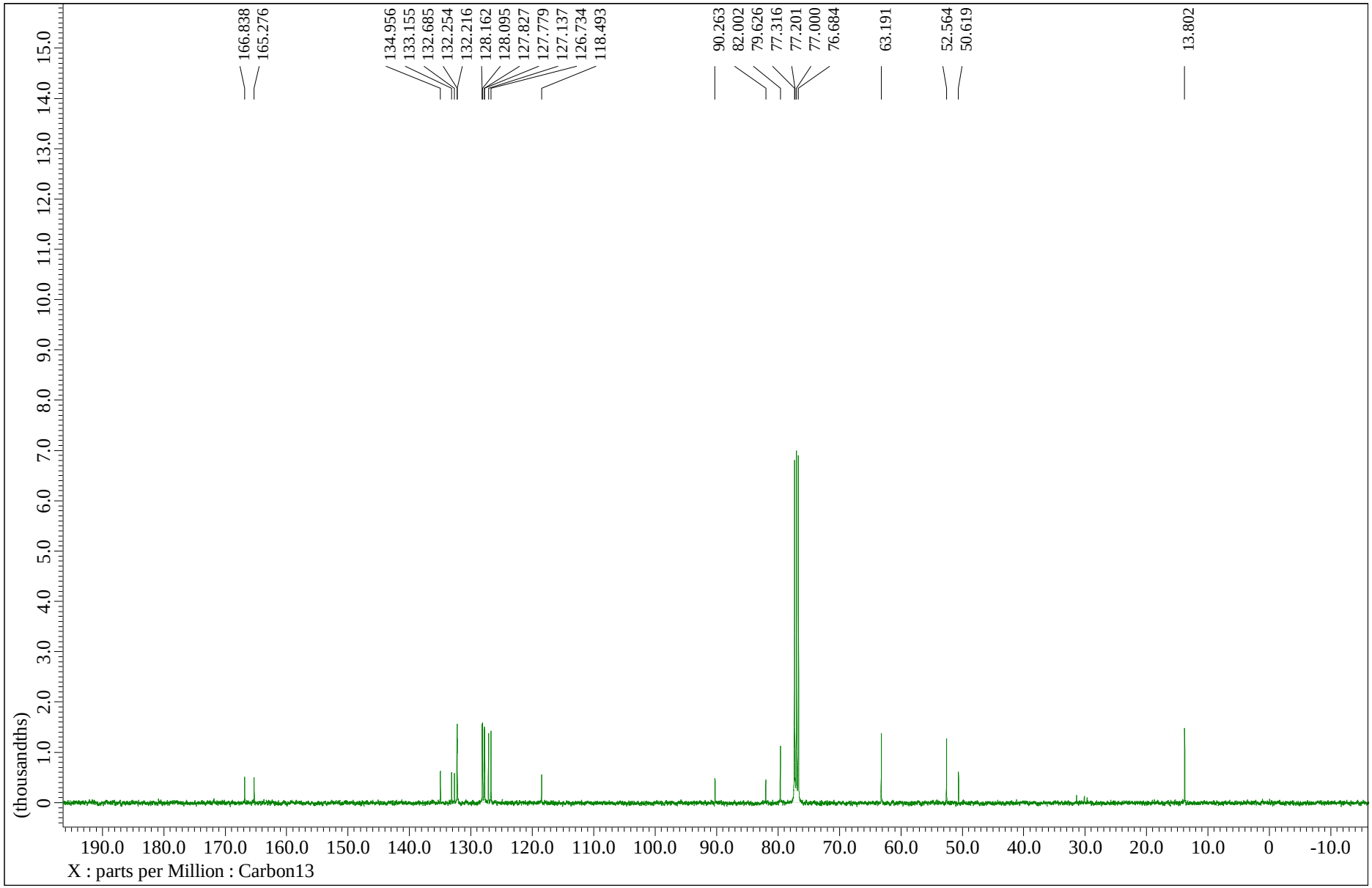
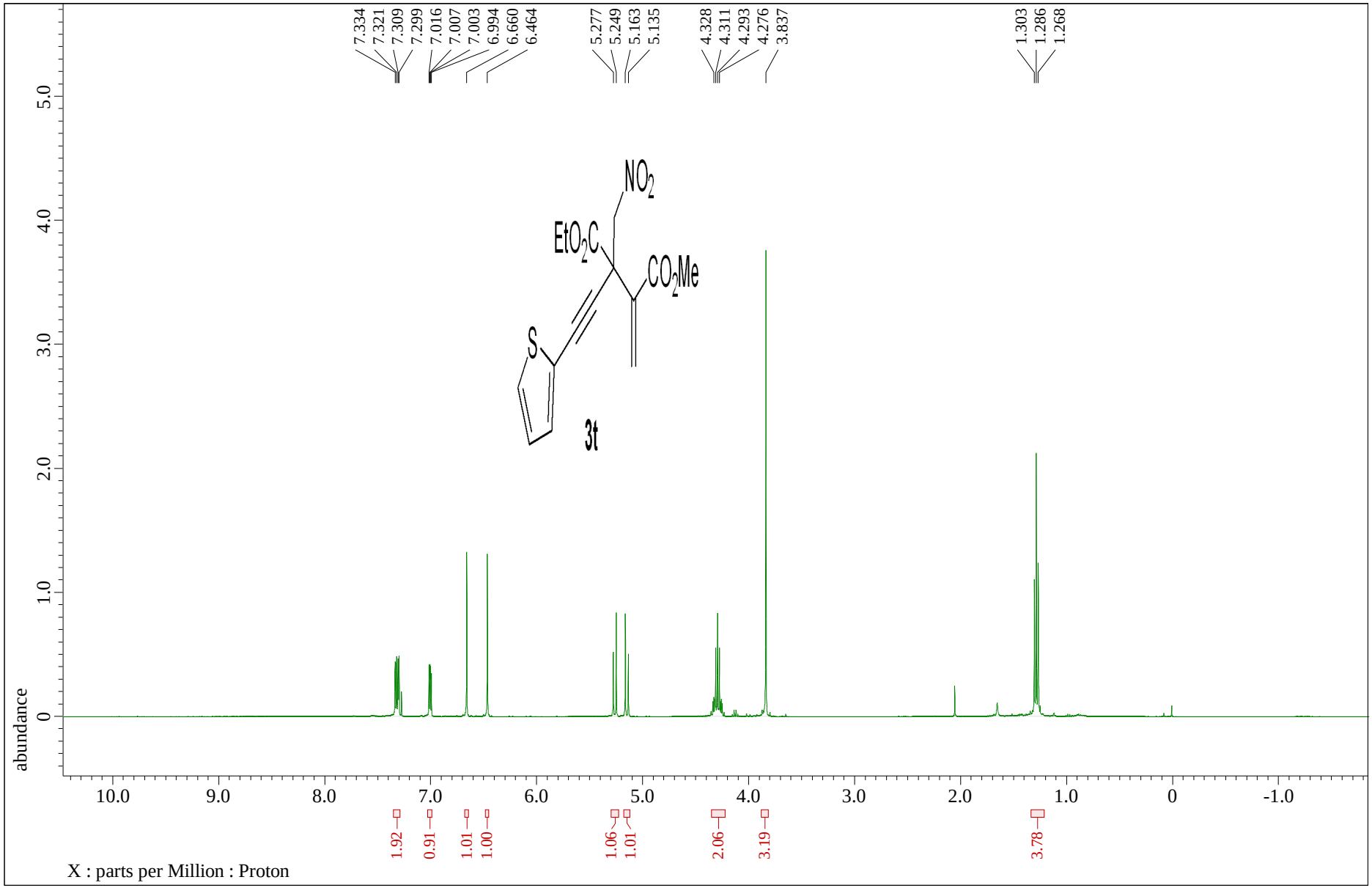
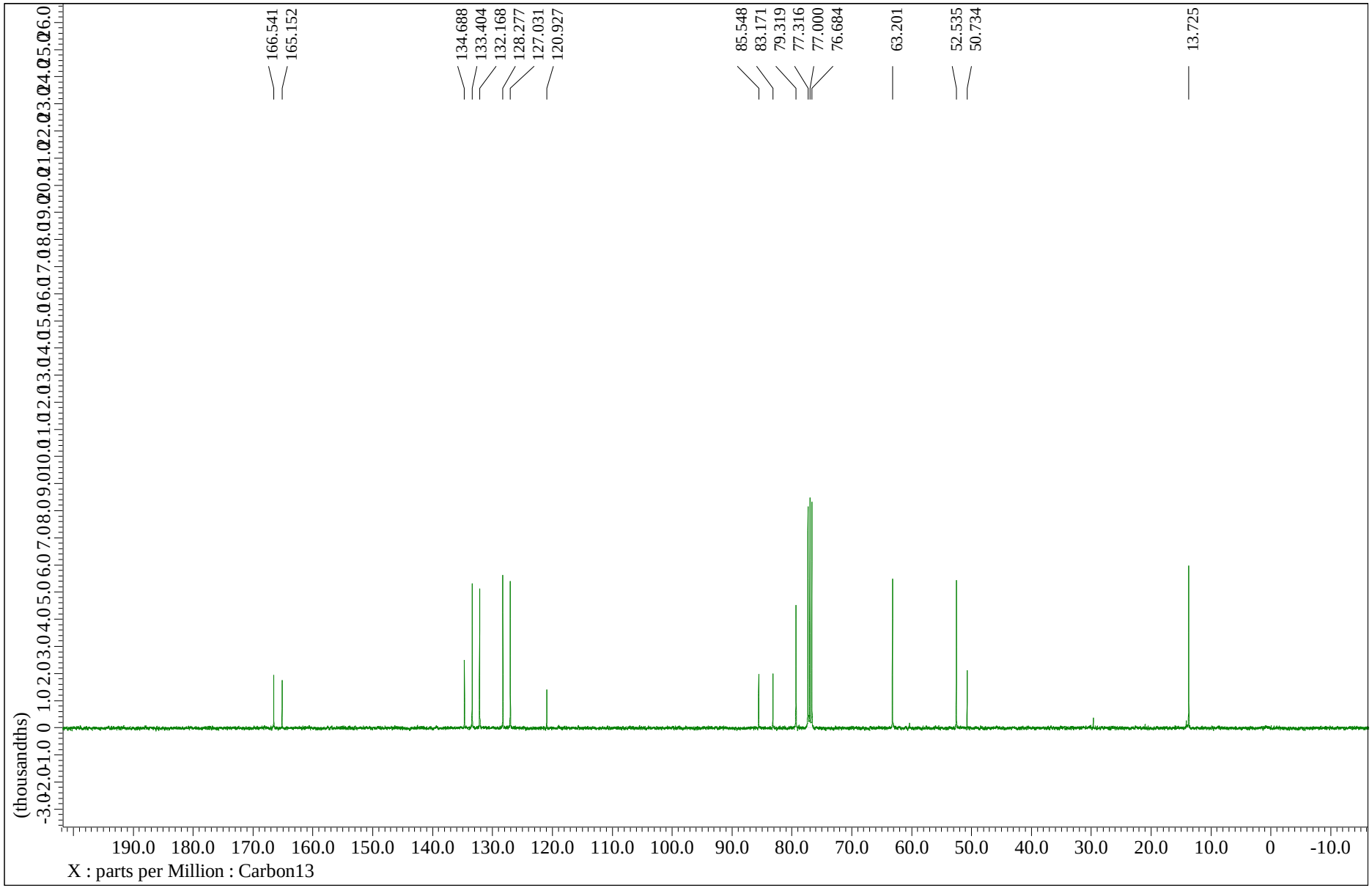
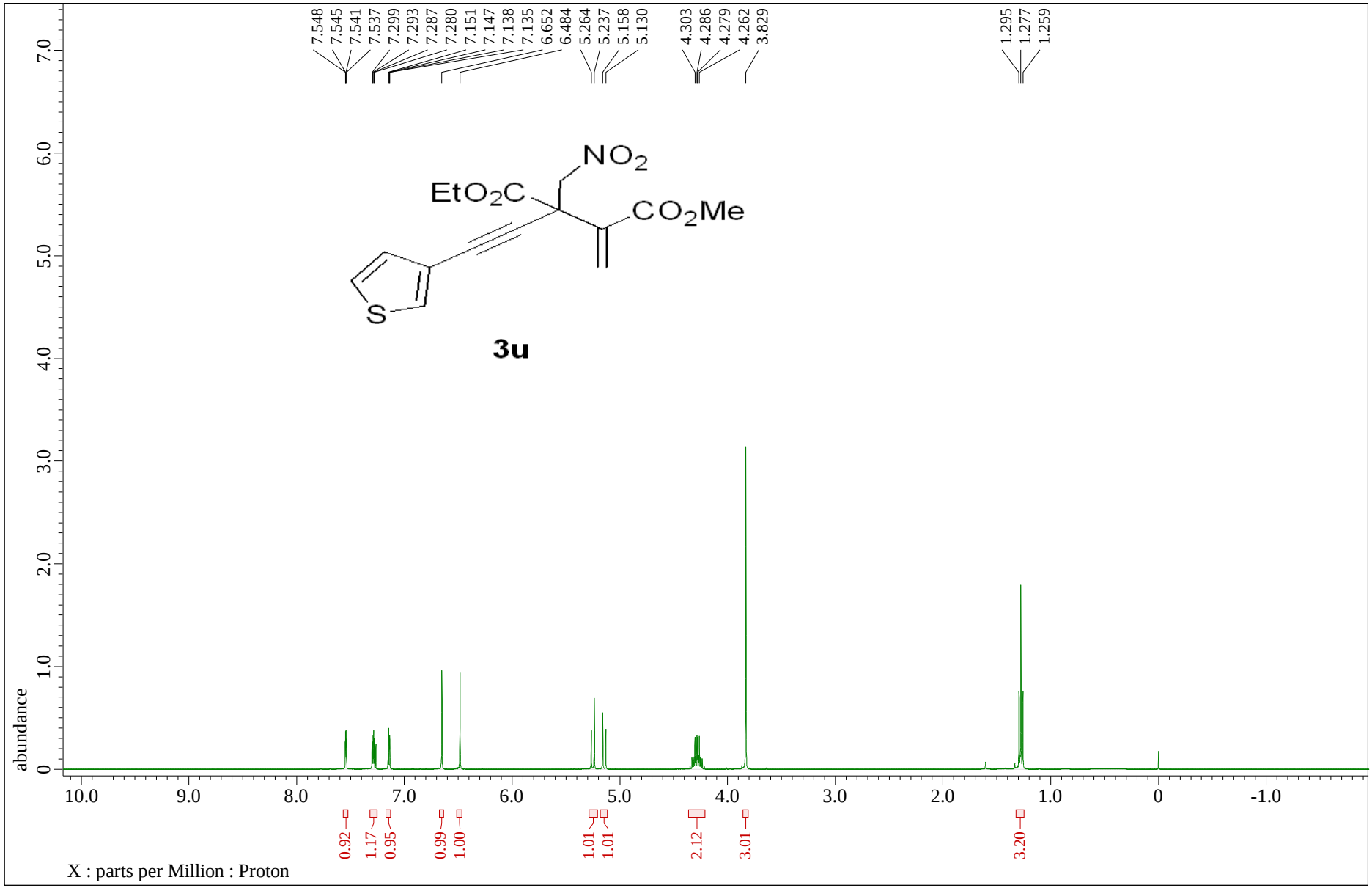
165.257
135.023
133.251
132.992
132.283
131.286
129.753
128.316
127.204
126.571
125.757
125.029
118.857
87.953
86.554
79.587
77.316
77.000
76.674
63.191
52.574
50.897
13.831
(thousandths)
X : parts per Million : Carbon13

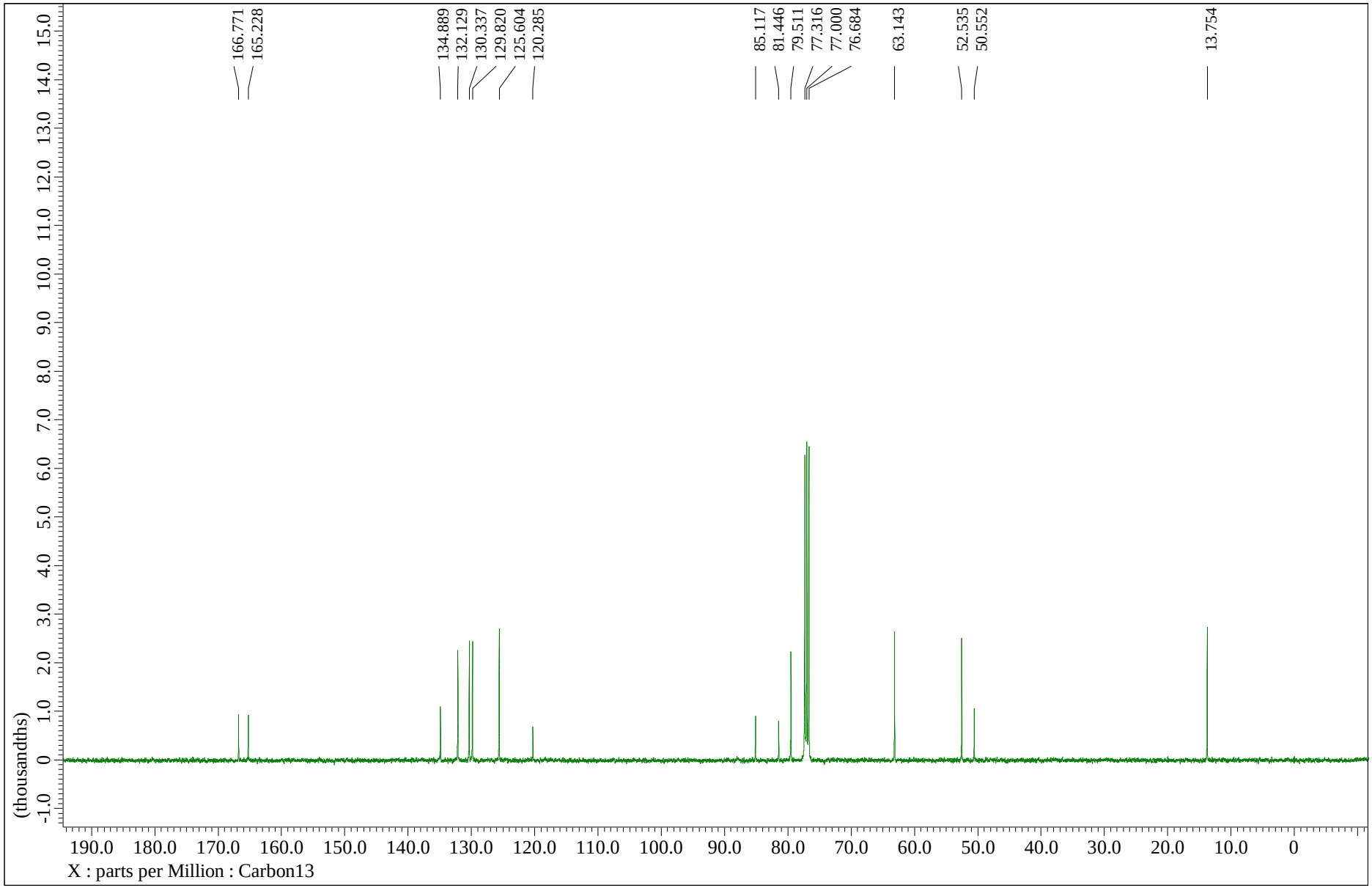

8.020
7.836
7.823
7.810
7.799
7.788
7.525
7.516
7.512
7.502
7.495
7.492
7.261
6.689
6.563
5.310
5.282
5.223
5.194
4.332
4.314
4.296
4.288
3.847
1.320
1.303
1.285
NO2
EtO2C
CO2Me
3s
abundance
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.01
3.35
3.30
1.06
1.00
0.98
0.97
2.06
3.20
3.35
X : parts per Million : Proton

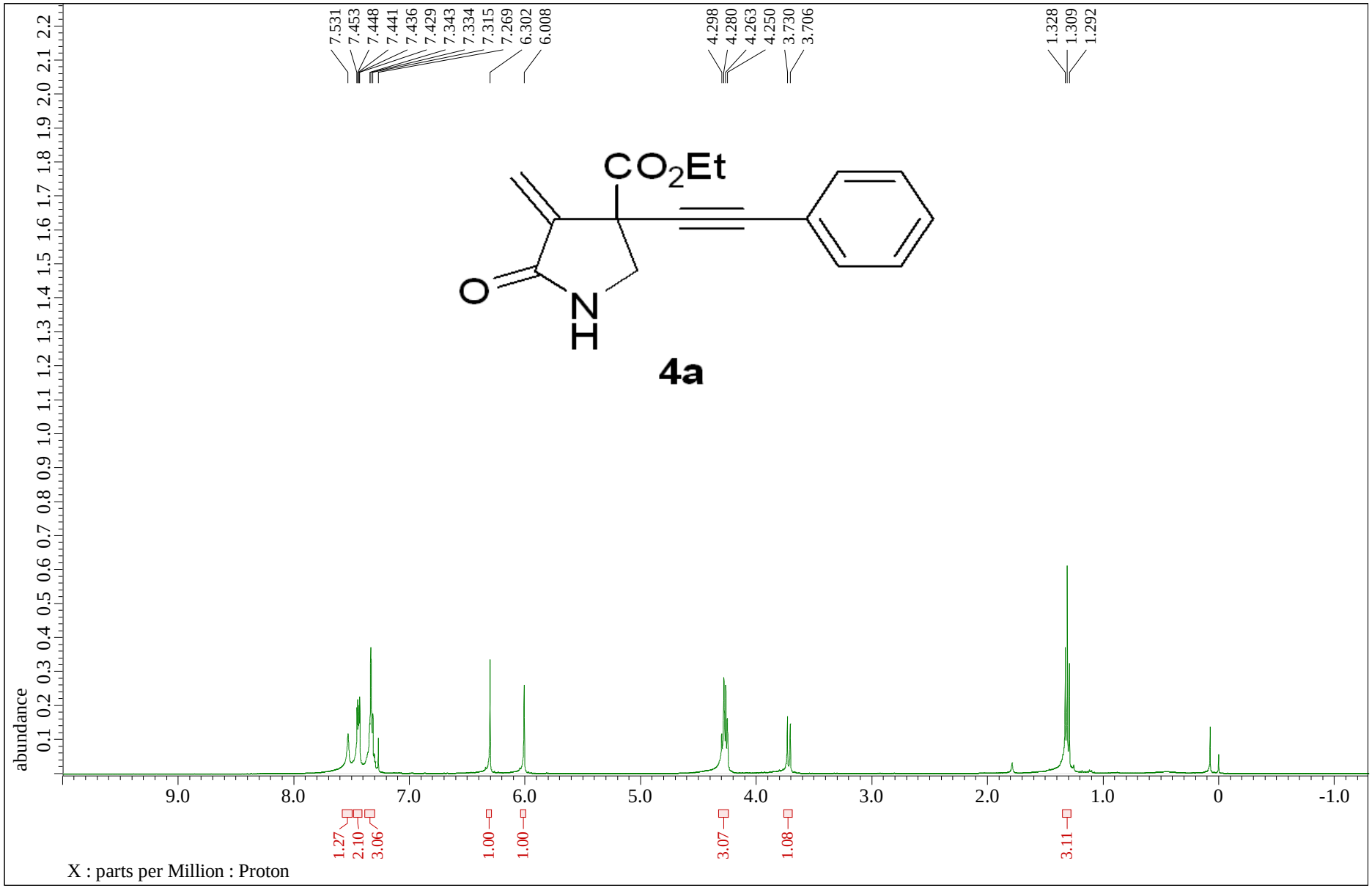

166.838
165.276
134.956
133.155
132.685
132.254
132.216
128.162
128.095
127.827
127.779
127.137
126.734
118.493
90.263
82.002
79.626
77.316
77.201
77.000
76.684
63.191
52.564
50.619
13.802
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
X : parts per Million : Carbon13

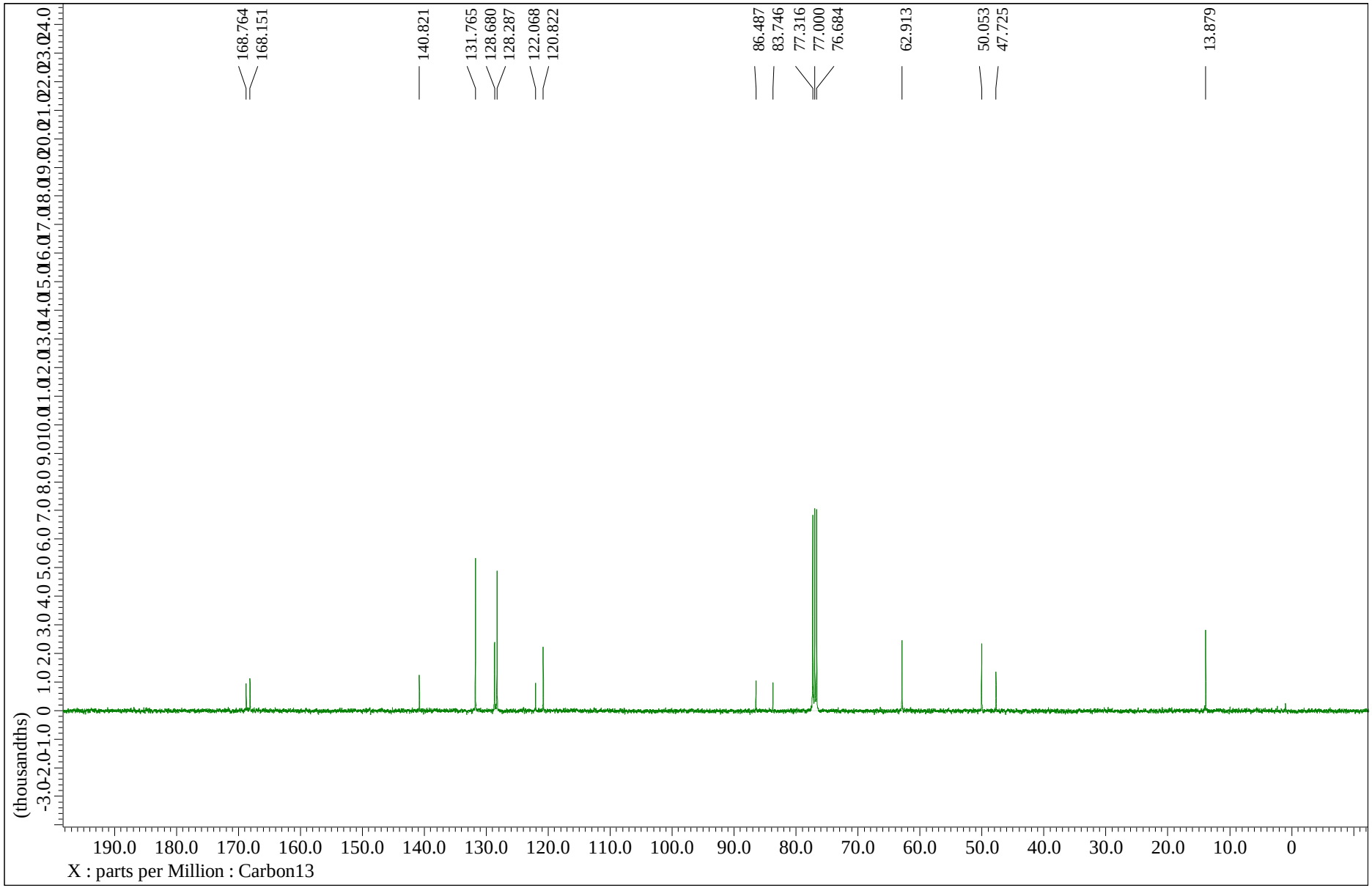

7.334
7.321
7.309
7.299
7.016
7.007
7.003
6.994
6.660
6.464
5.277
5.249
5.163
5.135
4.328
4.311
4.293
4.276
3.837
1.303
1.286
1.268
NO2
EtO2C
CO2Me
S
3t
abundance
X : parts per Million : Proton
1.92
0.91
1.01
1.00
1.06
1.01
2.06
3.19
3.78

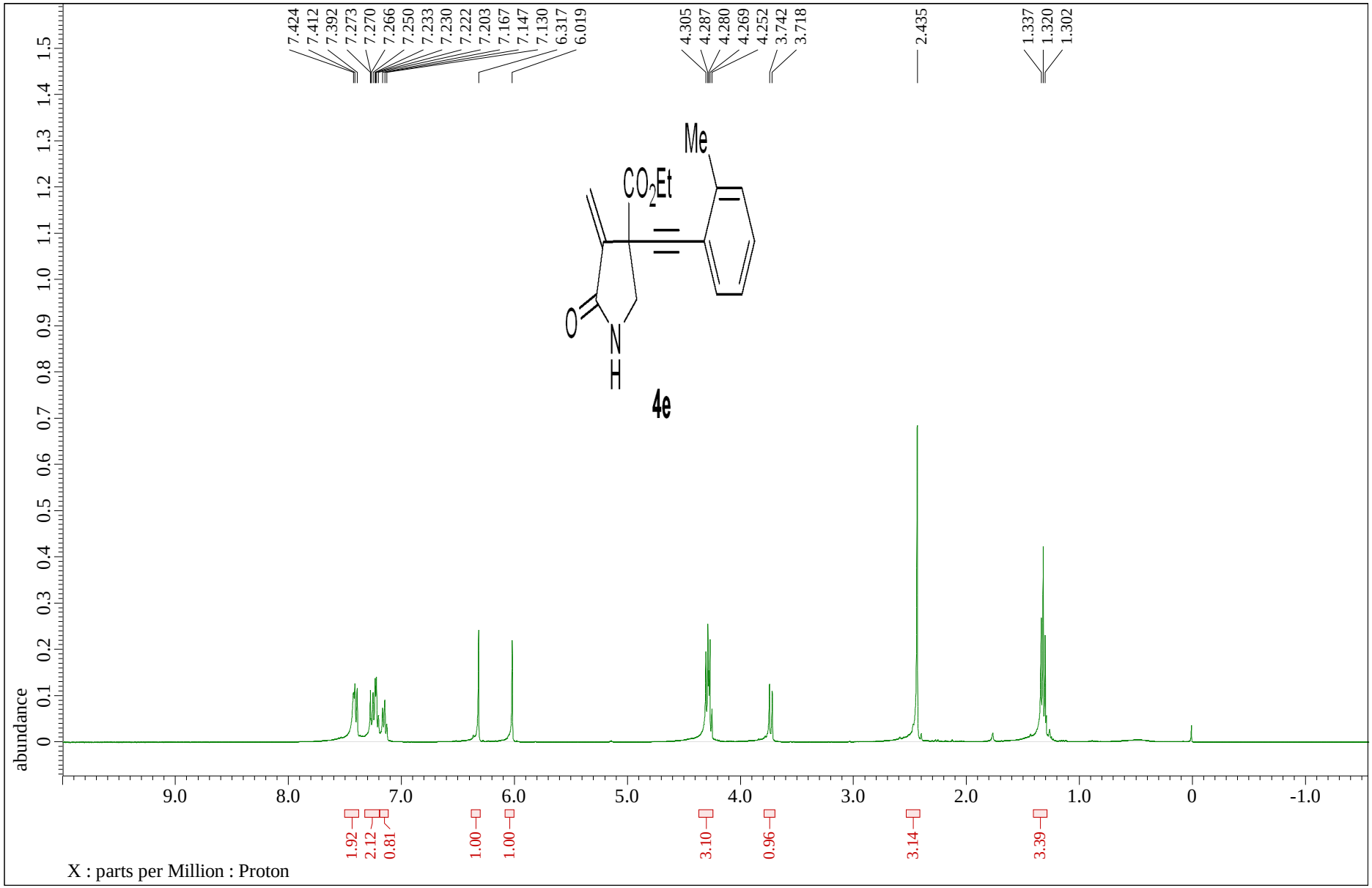

166.541
165.152
134.688
133.404
132.168
128.277
127.031
120.927
85.548
83.171
79.319
77.316
77.000
76.684
63.201
52.535
50.734
13.725
(thousandths)
X : parts per Million : Carbon13

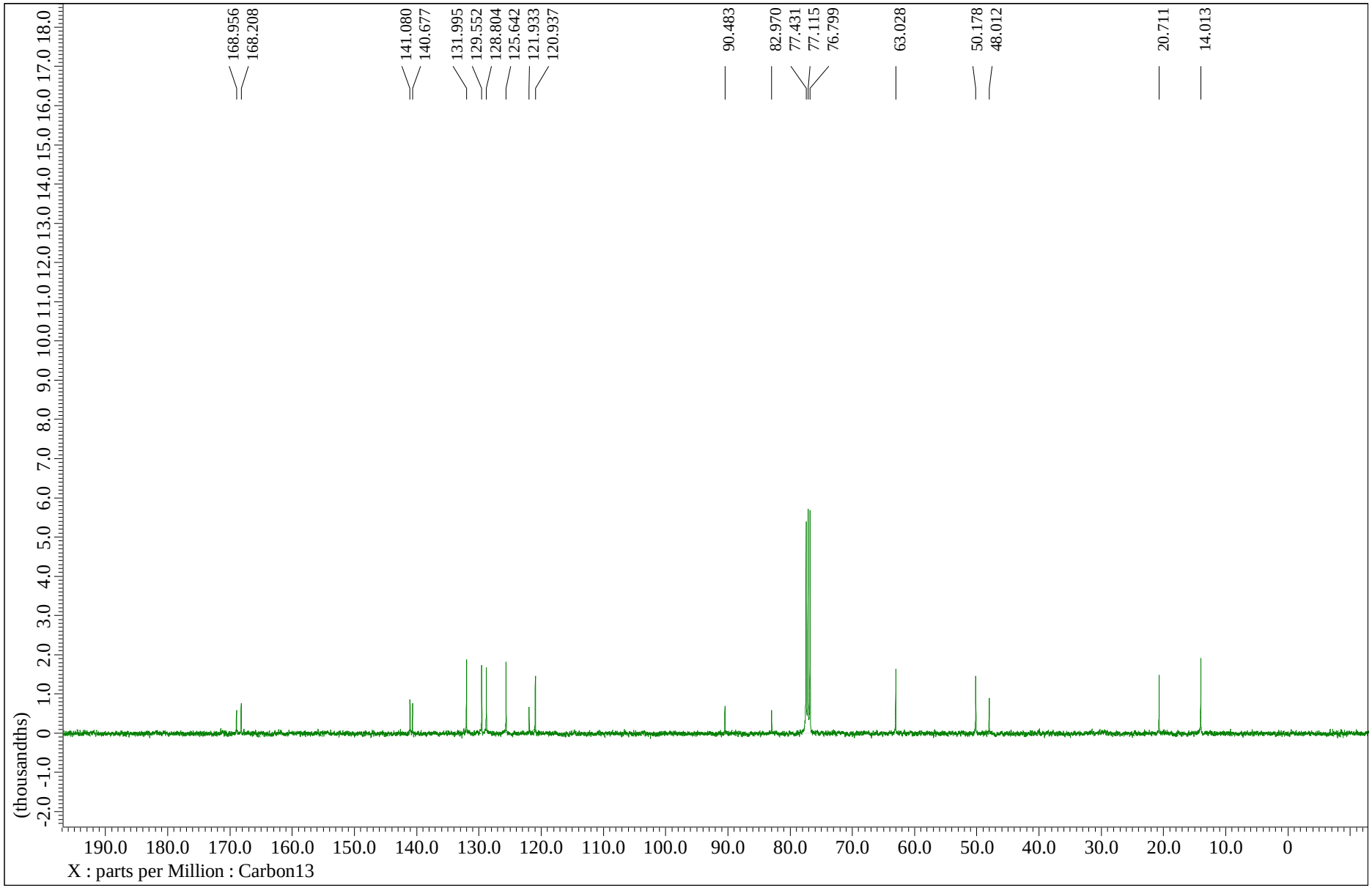

7.548
7.545
7.541
7.537
7.299
7.293
7.287
7.280
7.151
7.147
7.138
7.135
6.652
6.484
5.264
5.237
5.158
5.130
4.303
4.286
4.279
4.262
3.829
1.295
1.277
1.259
NO2
EtO2C
CO2Me
S
3u
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
0.92
1.17
0.95
0.99
1.00
1.01
1.01
2.12
3.01
3.20
X : parts per Million : Proton

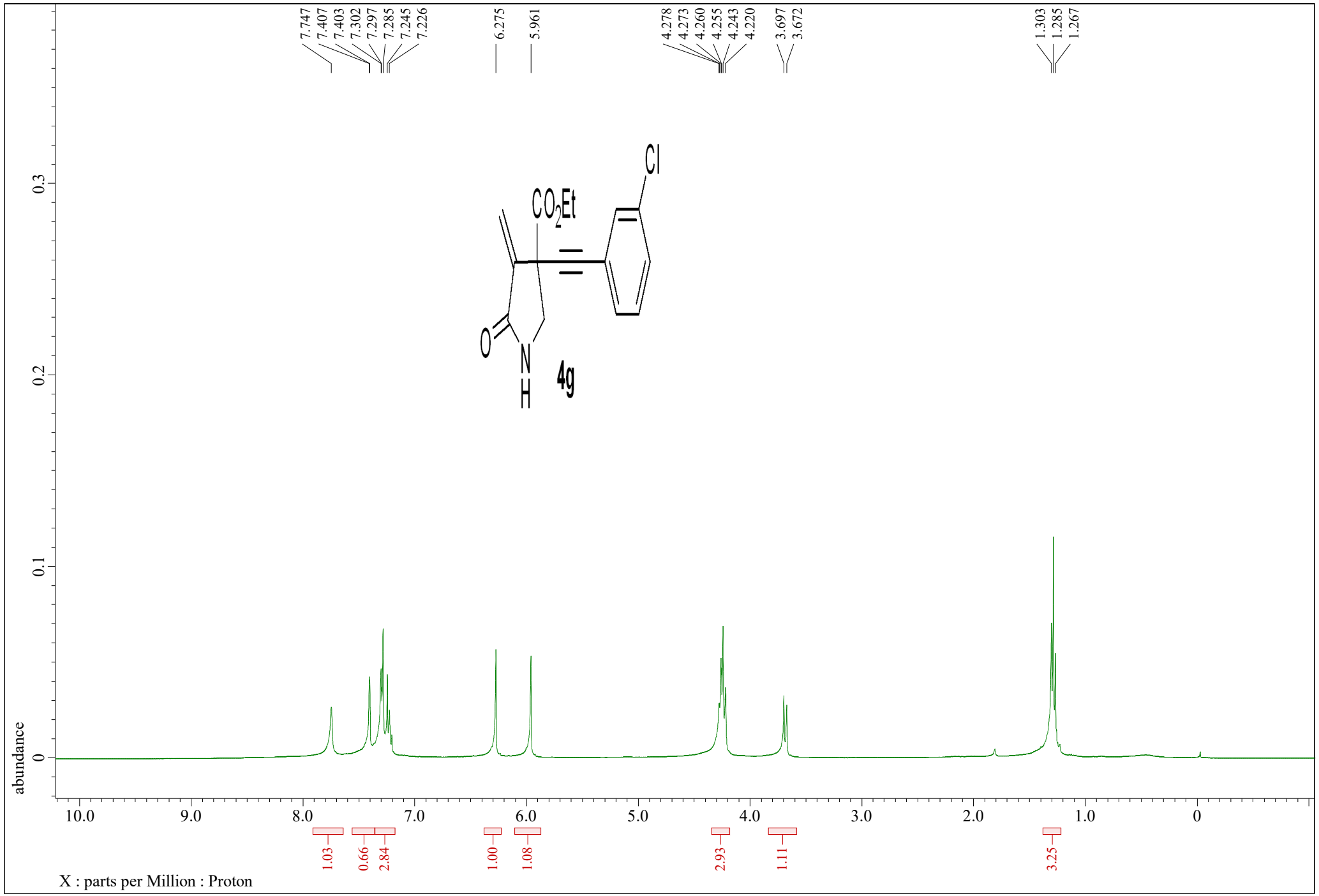

166.771
165.228
134.889
132.129
130.337
129.820
125.604
120.285
85.117
81.446
79.511
77.316
77.000
76.684
63.143
52.535
50.552
13.754
(thousandths)
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13

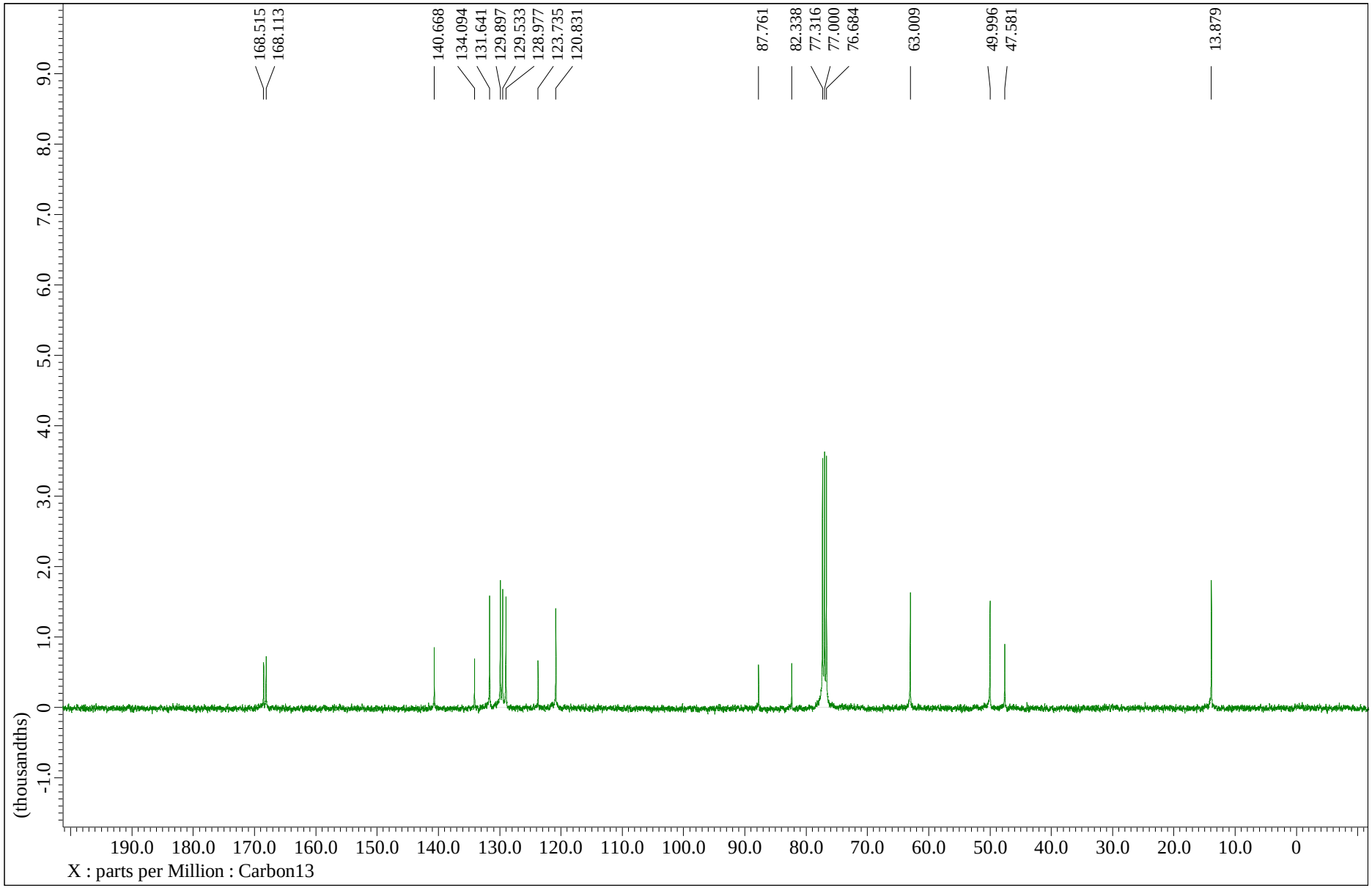

7.531
7.453
7.448
7.441
7.436
7.429
7.343
7.334
7.315
7.269
6.302
6.008
4.298
4.280
4.263
4.250
3.730
3.706
1.328
1.309
1.292
CO2Et
O
N
H
4a
abundance
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
1.27
2.10
3.06
1.00
1.00
3.07
1.08
3.11
X : parts per Million : Proton

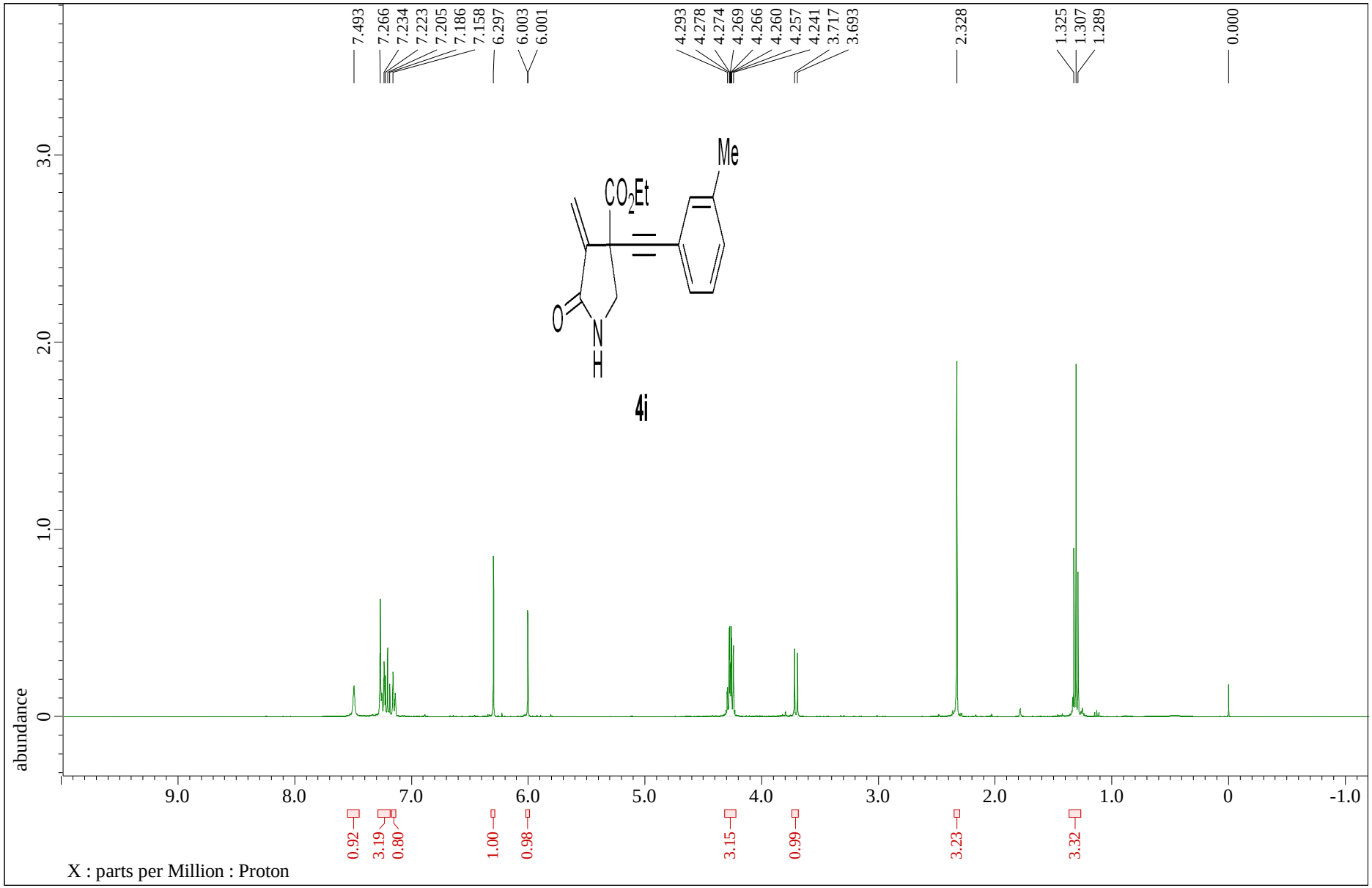

168.764
168.151
140.821
131.765
128.680
128.287
122.068
120.822
86.487
83.746
77.316
77.000
76.684
62.913
50.053
47.725
13.879
(thousandths)
X : parts per Million : Carbon13

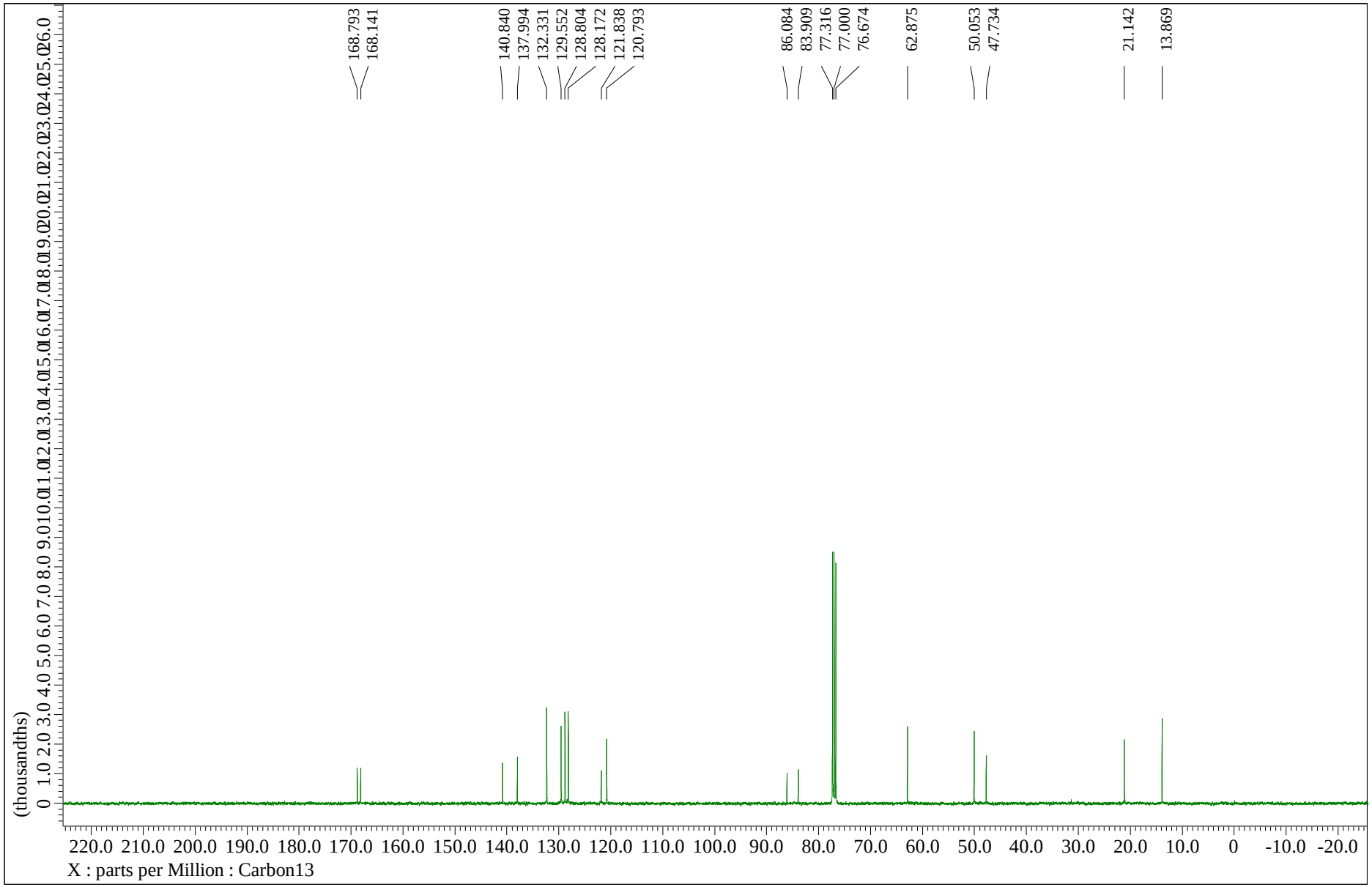

7.424
7.412
7.392
7.273
7.270
7.266
7.250
7.233
7.230
7.222
7.203
7.167
7.147
7.130
6.317
6.019
4.305
4.287
4.280
4.269
4.252
3.742
3.718
2.435
1.337
1.320
1.302
Me
CO2Et
O
N
H
4e
abundance
X : parts per Million : Proton
1.92
2.12
0.81
1.00
1.00
3.10
0.96
3.14
3.39

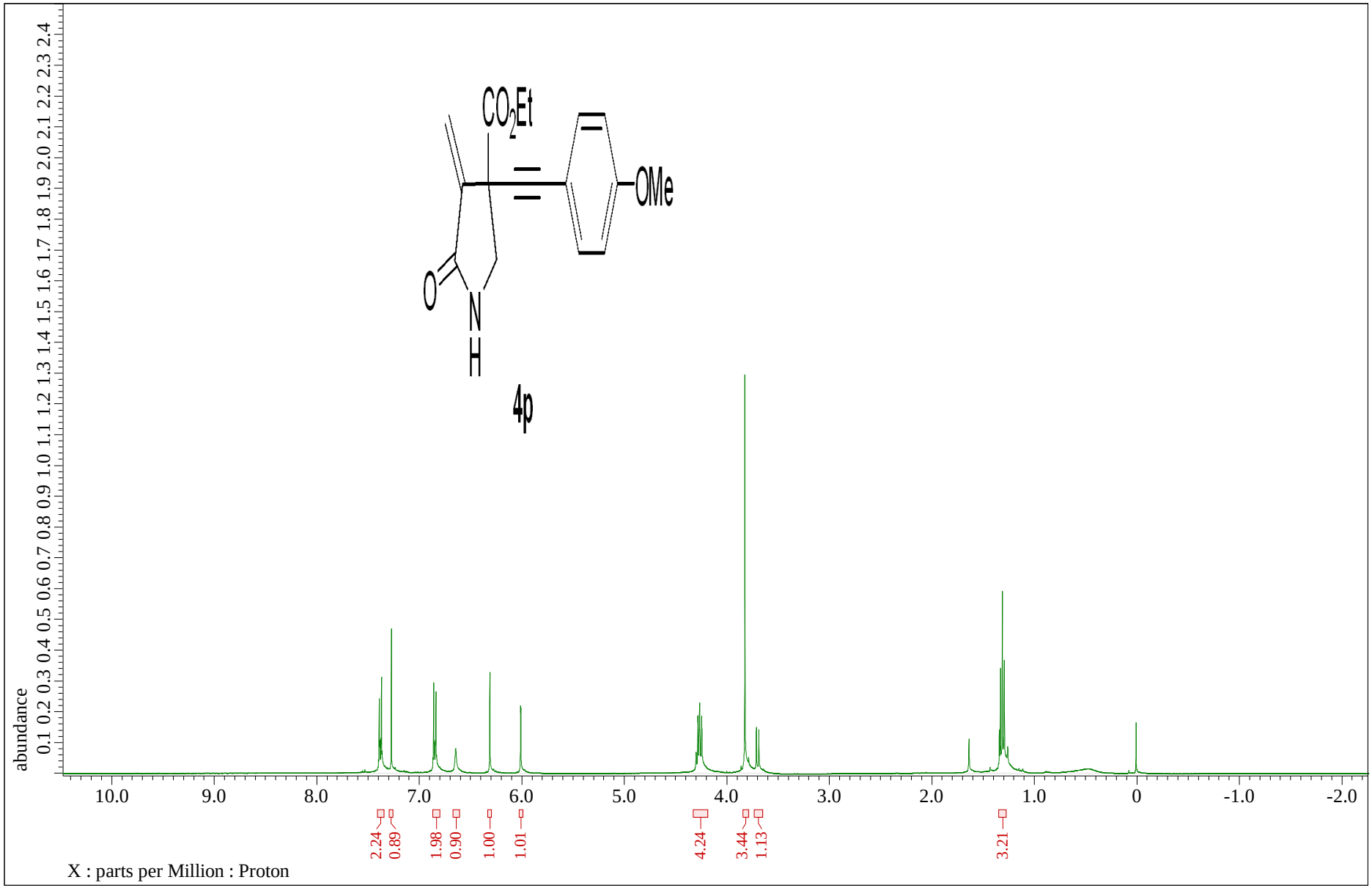

168.956
168.208
141.080
140.677
131.995
129.552
128.804
125.642
121.933
120.937
90.483
82.970
77.431
77.115
76.799
63.028
50.178
48.012
20.711
14.013
(thousandths)
X : parts per Million : Carbon13

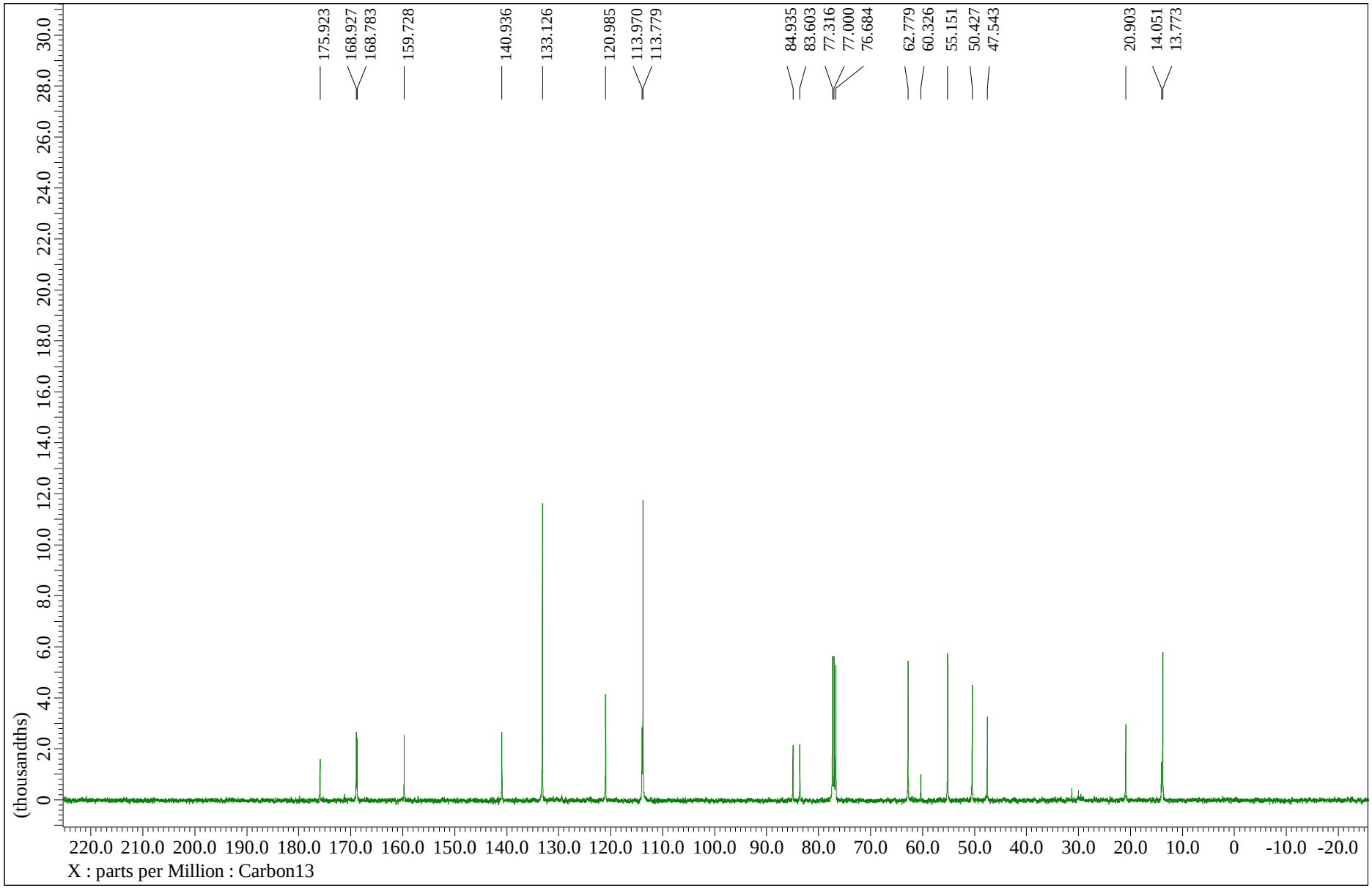

7.747
7.407
7.403
7.302
7.297
7.285
7.245
7.226
6.275
5.961
4.278
4.273
4.260
4.255
4.243
4.220
3.697
3.672
1.303
1.285
1.267
Cl
CO2Et
O
N
H
4g
abundance
0.3
0.2
0.1
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.03
0.66
2.84
1.00
1.08
2.93
1.11
3.25
X : parts per Million : Proton


168.515
168.113
140.668
134.094
131.641
129.897
129.533
128.977
123.735
120.831
87.761
82.338
77.316
77.000
76.684
63.009
49.996
47.581
13.879
(thousandths)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : Carbon13


7.493
7.266
7.234
7.223
7.205
7.186
7.158
6.297
6.003
6.001
4.293
4.278
4.274
4.269
4.266
4.260
4.257
4.241
3.717
3.693
2.328
1.325
1.307
1.289
0.000
Me
CO2Et
O
N
H
4i
abundance
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
0.92
3.19
0.80
1.00
0.98
3.15
0.99
3.23
3.32
X : parts per Million : Proton


168.793
168.141
140.840
137.994
132.331
129.552
128.804
128.172
121.838
120.793
86.084
83.909
77.316
77.000
76.674
62.875
50.053
47.734
21.142
13.869
(thousandths)
X : parts per Million : Carbon13


CO2Et
OMe
O
N
H
4p
abundance
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
2.24 0.89 1.98 0.90 1.00 1.01 4.24 3.44 1.13 3.21
X : parts per Million : Proton


175.923
168.927
168.783
159.728
140.936
133.126
120.985
113.970
113.779
84.935
83.603
77.316
77.000
76.684
62.779
60.326
55.151
50.427
47.543
20.903
14.051
13.773
(thousandths)
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
28.0
30.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13