Palladium-Catalyzed Decarboxylative Cross-Coupling of Alkynyl Carboxylic Acids with Arylboronic Acids

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Supporting Information

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General methods

All reagents were obtained from commercial suppliers and used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with acidic solution of ceric molybdate or iodine.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditions.

High Resolution Mass (HRMS) spectra were obtained using Waters Q-Tof Permies Mass Spectrometer.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet).

Experimental procedure

General Procedure for the decarboxylative coupling of alkynyl carboxylic acids with arylboronic acids

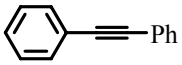
To a 5 mL round-bottomed flask were added arylboronic acid (0.2 mmol), alkynyl carboxylic acid (0.24 mmol), palladium acetate (0.01 mmol), silver oxide (0.3 mmol), and potassium acetate (0.3 mmol), 4 Å MS (0.1 g), dichloromethane (1 mL) sequentially, then it was stirred vigorously at room temperature for 12 hours. After reaction, the mixture was diluted with dichloromethane, and filtered through a short pad of celite. Removal of the solvent in vacuo and purification of the residue by column chromatography afforded the desired product.

General Procedure for the consecutive reaction

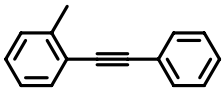
$Pd(OAc)_2(PPh_3)_2$ (0.008 mmol), CuI (0.016 mmol) were added to a 5 mL round-bottomed flask then subjected to vacuum and refilled with N_2 for three times. Phenyl iodide (0.4 mmol), propiolic acid (0.4 mmol), DMF (1 mL) and $^iPr_2NH$ (0.14 mL) were added in sequence. After stirring at room temperature for 5 hours, the resulting mixture was diluted with ethyl acetate,

washed with water, brine and dried over magnesium sulfate. The organic layer was concentrated in vacuo and transfered into a 5 mL round-bottomed flask followed by adding *p*-methoxyphenylboronic acid (0.3 mmol), silver oxide (0.4 mmol), potassium acetate (0.3 mmol) palladium acetate (0.015 mmol) and dichloromethane (1 mL). The resulting mixture was stirred vigorously at room temperature for 12 hours. After reaction, the mixture was diluted with dichloromethane, and filtered through a short pad of celite. Removal of the solvent in vacuo and purification of the residue by column chromatography afforded the desired product.

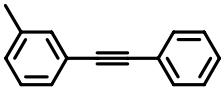
Spectroscopic data of products



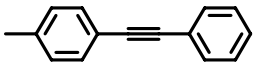
Diphenyl acetylene (Table 2, entry 1): White solid; Yield: 93%; FTIR (NaCl, neat): ν 2219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.40 (m, 6H), 7.56-7.59 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.4, 123.2, 128.2, 128.3, 131.6 ppm; HRMS (ESI, m/z): Calcd. for $C_{14}H_{10}Na$: 201.0680, found $[M+Na]^+$: 201.0677.



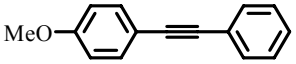
1-(2-*o*-Tolylethynyl)benzene (Table 2, entry 2): Colorless oil; Yield: 83%; FTIR (NaCl, neat): ν 2215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 7.14-7.19 (m, 1H), 7.23 (d, J = 3.80 Hz, 2H), 7.30-7.37 (m, 3H), 7.49-7.55 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 88.3, 93.3, 123.0, 123.5, 125.6, 128.2, 128.3, 128.3, 129.4, 131.5, 131.8, 140.2 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}Na$: 215.0837, found $[M+Na]^+$: 215.0843.



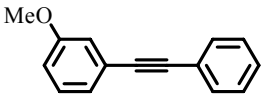
1-(2-*m*-Tolylethynyl)benzene (Table 2, entry 3): Colorless oil; Yield: 87%; FTIR (NaCl, neat): ν 2207 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.16 (d, J = 7.57 Hz, 1H), 7.25 (t, J = 7.62Hz, 1H), 7.34-7.38 (m, 5H), 7.53-7.55 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 89.0, 89.5, 123.0, 123.3, 128.2, 128.2, 128.3, 128.7, 129.1, 131.6, 132.2, 138.0 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}$: 193.1017, found $[M+H]^+$: 193.1014.



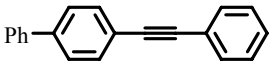
1-(2-*p*-Tolylethynyl)benzene (Table 2, entry 4): White solid; Yield: 91%; FTIR (NaCl, neat): ν 2217 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.16 (d, J = 7.90 Hz, 2H), 7.31-7.38 (m, 3H), 7.43 (d, J = 8.07 Hz, 2H), 7.50-7.54 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 88.7, 89.6, 120.2, 123.5, 128.1, 128.3, 129.1, 131.5, 131.6, 138.4 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}$: 193.1017, found $[M+H]^+$: 193.1015.



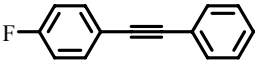
1-Methoxy-4-(phenylethynyl)benzene (Table 2, entry 5): Light yellow solid; Yield: 94%; FTIR (NaCl, neat): ν 2218 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.89 (d, J = 8.64 Hz, 2H), 7.32-7.37 (m, 3H), 7.47-7.54 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 88.0, 89.3, 114.0, 115.3, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}O$: 209.0966, found $[M+H]^+$: 209.0964.



1-Methoxy-3-(2-phenylethynyl)benzene (Table 2, entry 6): Light yellow soild; Yield: 89%; FTIR (NaCl, neat): ν 2209 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.91 (dd, J_1 = 2.15 Hz, J_2 = 8.00 Hz, 1H), 7.08 (s, 1H), 7.15 (d, J = 7.60 Hz, 1H), 7.27 (t, J = 7.87 Hz, 1H), 7.35-7.39 (m, 3H), 7.54-7.57 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 89.2, 89.3, 114.9, 116.3, 123.1, 124.1, 124.2, 128.3, 128.3, 129.4, 131.6, 159.3 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}ONa$: 231.0786, found $[M+Na]^+$: 231.0788.

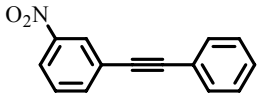


1-Phenyl-4-(2-phenylethynyl)benzene (Table 2, entry 7): White solid; Yield: 86%; FTIR (NaCl, neat): ν 2310 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.41 (m, 4H), 7.45-7.50 (m, *2*H), 7.57-7.64 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 89.3, 90.1, 122.2, 123.3, 127.0, 127.6, 128.3, 128.4, 128.8, 131.6, 132.0, 140.3, 140.9 ppm; HRMS (ESI, m/z): Calcd. for $C_{20}H_{15}$: 255.1174, found $[M+H]^+$: 255.1163.

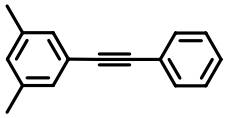


1-(2-(4-Fluorophenyl)ethynyl)benzene (Table 2, entry 8): White solid; Yield: 99%; FTIR (NaCl, neat): ν 2306 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, J = 8.62 Hz, 2H), 7.35-7.39 (m, 3H),

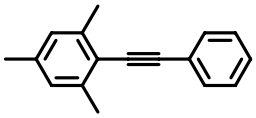
7.51-7.55 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.3, 89.0, 115.6 (d, J = 22.02 Hz), 119.3 (d, J = 3.61 Hz), 123.1, 128.3, 128.4, 131.5, 133.4 (d, J = 8.48 Hz), 162.5 (d, J = 249.68 Hz) ppm; HRMS (ESI, m/z): Calcd. for $C_{14}H_{10}F$: 197.0767, found $[M+H]^+$: 197.0751.



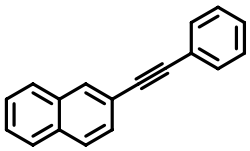
1-(2-(3-Nitrophenyl)ethynyl)benzene (Table 2, entry 10): Light yellow oil; Yield: 79%; FTIR (NaCl, neat): ν 2211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.40 (m, 3H), 7.50-7.57 (m, 3H), 7.82 (d, J = 7.72 Hz, 1H), 8.17 (d, J = 8.29 Hz, 1H), 8.36 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.8, 91.9, 122.1, 122.8, 125.1, 126.3, 128.4, 129.0, 129.3, 131.7, 137.1, 148.1 ppm; HRMS (ESI, m/z): Calcd. for $C_{14}H_9NO_2Na$: 246.0531, found $[M+Na]^+$: 246.0539.



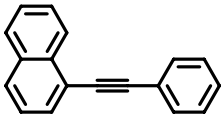
1,3-Dimethyl-5-(2-phenylethynyl)benzene (Table 2, entry 11): Colorless oil; Yield: 84%; FTIR (NaCl, neat): ν 2210 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 6H), 6.98 (s, 1H), 7.18 (s, 2H), 7.33-7.35 (m, 3H), 7.51-7.53 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 21.3, 87.3, 97.0, 120.0, 124.0, 127.6, 127.9, 128.3, 131.3, 137.8, 140.1 ppm; HRMS (ESI, m/z): Calcd. for $C_{16}H_{14}Na$: 229.0993, found $[M+Na]^+$: 229.1001.



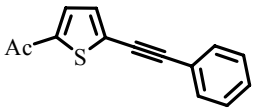
1-(2-Mesitylethynyl)benzene (Table 2, entry 12): White solid; Yield: 41%; FTIR (NaCl, neat): ν 2211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.49 (s, 6H), 6.91 (s, 2H), 7.33-7.39 (m, 3H), 7.55 (dd, J_1 = 1.52 Hz, J_2 = 7.88 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 21.3, 87.3, 97.0, 120.0, 124.0, 127.6, 127.9, 128.3, 131.3, 137.8, 140.1 ppm; HRMS (ESI, m/z): Calcd. for $C_{17}H_{16}Na$: 243.1150, found $[M+Na]^+$: 243.1150.



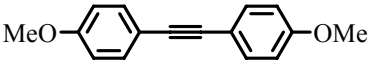
2-(2-Phenylethynyl)naphthalene (Table 2, entry 13): White solid; Yield: 92%; FTIR (NaCl, neat): ν 2252 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.42 (m, 3H), 7.50-7.54 (m, 2H), 7.61-7.63 (m, 3H), 7.82-7.86 (m, 3H), 8.09 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.7, 89.8, 120.6, 123.3, 126.5, 126.6, 127.8, 128.0, 128.3, 128.4, 128.4, 131.4, 131.6, 132.8, 133.0 ppm; HRMS (ESI, m/z): Calcd. for $C_{18}H_{13}$: 229.1017, found $[M+H]^+$: 229.1029.



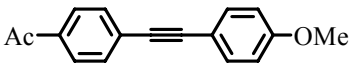
1-(2-Phenylethynyl)naphthalene (Table 2, entry 14): Colorless oil; Yield: 81%; FTIR (NaCl, neat): ν 2211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.43 (m, 3H), 7.47 (t, J = 7.85 Hz, 1H), 7.53-7.63 (m, 2H), 7.67 (d, J = 7.48 Hz, 2H), 7.78 (d, J = 7.16 Hz, 1H), 8.47 (d, J = 8.32 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 87.5, 94.3, 120.9, 123.4, 125.3, 126.2, 126.4, 126.8, 128.3, 128.4, 128.4, 128.7, 130.4, 131.7, 133.2, 133.3 ppm; HRMS (ESI, m/z): Calcd. for $C_{18}H_{13}$: 229.1017, found $[M+H]^+$: 229.1003.



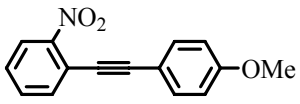
***N*-Benzyl-*N*-(1-phenylpentyl)hydroxylamine (Table 2, entry 15):** White solid; Yield: 76%; FTIR (NaCl, neat): ν 2201, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.56 (s, 3H), 7.24 (d, J = 3.92 Hz, 1H), 7.36-7.38 (m, 3H), 7.52-7.55 (m, 2H), 7.59 (d, J = 3.92 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.8, 82.1, 96.6, 122.1, 128.5, 129.1, 131.4, 131.6, 132.2, 132.4, 144.6, 190.1 ppm; HRMS (ESI, m/z): Calcd. for $C_{14}H_{11}OS$: 227.0531, found $[M+H]^+$: 227.0522.



1,2-Bis(4-methoxyphenyl)ethyne (Table 3, entry 1): White solid; Yield: 99%; FTIR (NaCl, neat): ν 2254 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 6H), 6.88 (d, J = 8.76 Hz, 4H), 7.46 (d, J = 8.75 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 87.9, 113.9, 115.7, 132.8, 159.3 ppm; HRMS (ESI, m/z): Calcd. for $C_{16}H_{14}O_2Na$: 261.0891, found $[M+Na]^+$: 261.0884.

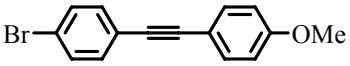


1-(4-(2-(4-Methoxylphenyl)ethynyl)phenyl)ethanone (Table 3, entry 2): White solid; Yield: 99%; FTIR (NaCl, neat): ν 2218, 1673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.60 (s, 3H), 3.83 (s, 3H), 6.89 (d, J = 8.76 Hz, 2H), 7.49 (d, J = 8.76 Hz, 2H), 7.58 (d, J = 8.32 Hz, 2H), 7.92 (d, J = 8.34 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 55.3, 87.5, 92.9, 114.1, 114.7, 128.2, 128.6, 131.4, 133.2, 135.8, 160.0, 197.3 ppm; HRMS (ESI, m/z): Calcd. for $C_{17}H_{15}O_2$: 251.1072, found $[M+H]^+$: 251.1072.

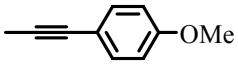


1-(2-(4-Methoxyphenyl)ethynyl)-2-nitrobenzene (Table 3, entry 3): Yellow solid; Yield: 72%; FTIR (NaCl, neat): ν 2213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.90 (d, J = 8.56 Hz,

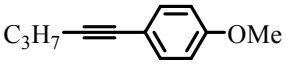
2H), 7.40-7.44 (m, 1H), 7.53-7.59 (m, 3H), 7.68 (d, J = 7.76 Hz, 1H), 8.06 (d, J = 8.25 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 83.9, 97.6, 114.1, 114.4, 119.2, 124.7, 128.0, 132.7, 133.6, 134.3, 149.3, 160.4 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}NO_3$: 254.0817, found $[M+H]^+$: 254.0809.



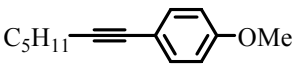
1-Bromo-4-(2-(4-methoxyphenyl)ethynyl)benzene (Table 3, entry 6): White solid; Yield: 89%; FTIR (NaCl, neat): ν 2217 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.88 (d, J = 8.64 Hz, 2H), 7.37 (d, J = 8.41 Hz, 2H), 7.46-7.48 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 87.0, 90.5, 114.0, 114.9, 122.0, 122.6, 131.5, 132.8, 133.0, 159.8 ppm; HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}OBr$: 287.0072, found $[M+H]^+$: 287.0087.



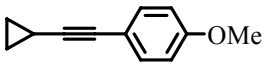
1-Methoxy-4-(prop-ynyl)benzene (Table 3, entry 7): Colorless oil; Yield: 50%; FTIR (NaCl, neat): ν 2311 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H), 3.79 (s, 3H), 6.81 (d, J = 8.68 Hz, 2H), 7.32 (d, J = 8.64 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.3, 55.2, 79.4, 84.1, 113.8, 116.2, 132.8, 159.0 ppm; HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}O$: 147.0810, found $[M+H]^+$: 147.0816.



1-Methoxy-4-(-pent-1-ynyl)benzene (Table 3, entry 8): Colorless oil; Yield: 89%; FTIR (NaCl, neat): ν 2234 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, J = 7.33 Hz, 3H), 1.58-1.67 (m, 2H), 2.37 (t, J = 7.04 Hz, 2H), 3.79 (s, 3H), 6.81 (d, J = 8.60 Hz, 2H), 7.34 (d, J = 8.64 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 21.4, 22.3, 55.2, 80.3, 88.6, 113.8, 116.2, 132.8, 158.9 ppm; HRMS (ESI, m/z): Calcd. for $C_{12}H_{15}O$: 175.1123, found $[M+H]^+$: 175.1113.

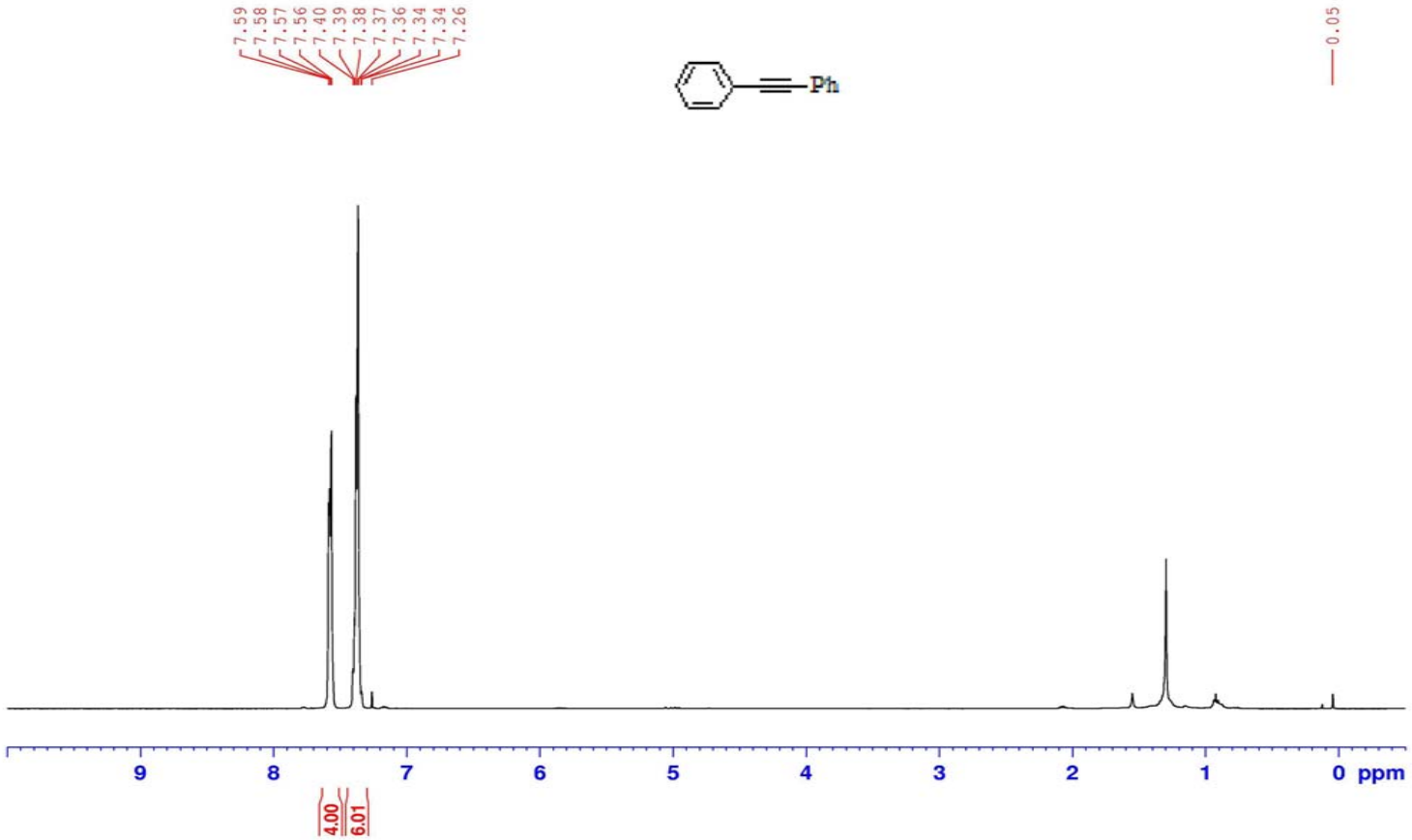


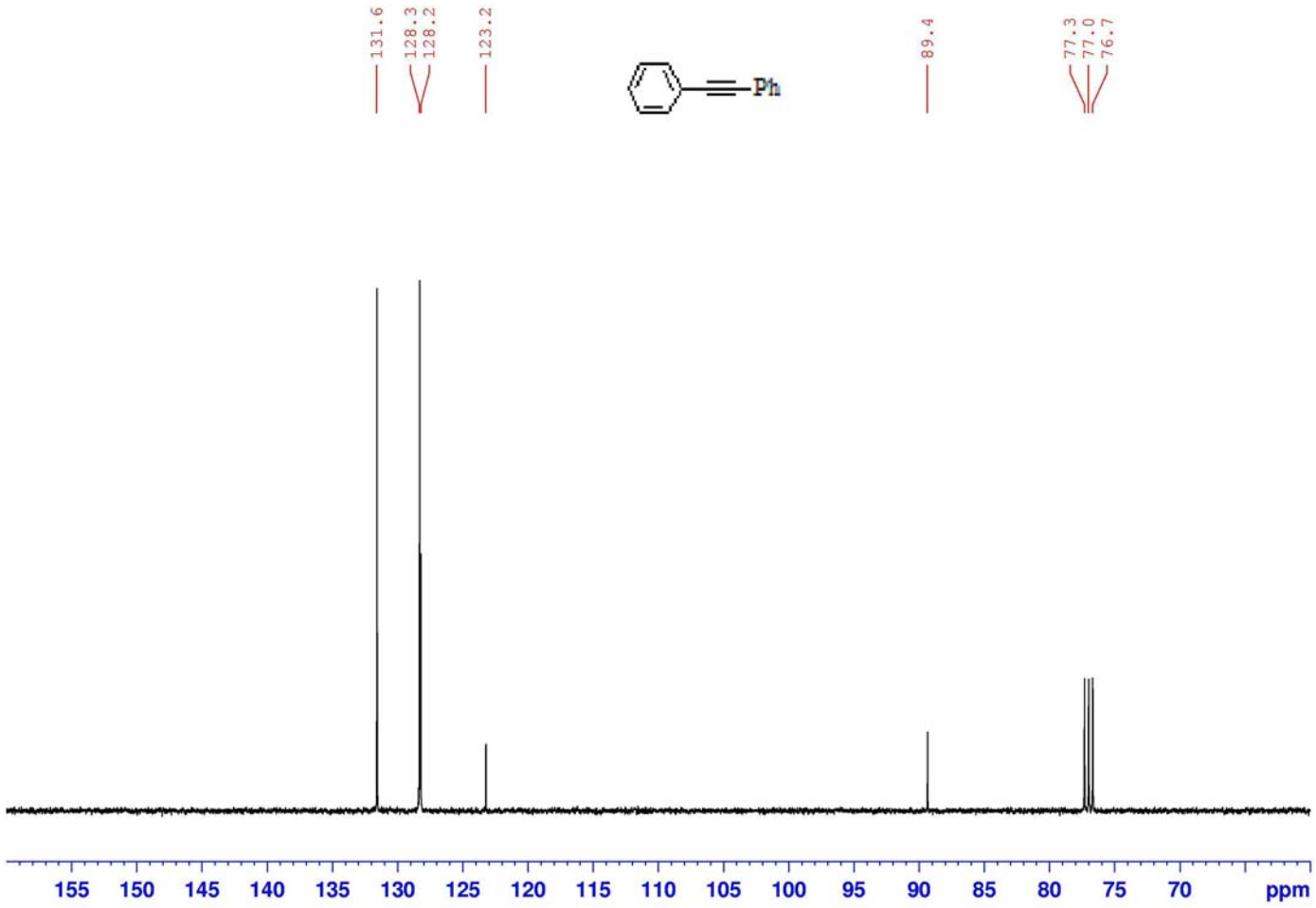
1-(Hept-1-ynyl)-4-methoxybenzene (Table 3, entry 9): Colorless oil; Yield: 94%; FTIR (NaCl, neat): ν 2233 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, J = 7.20 Hz, 3H), 1.33-1.47 (m, 4H), 1.56-1.64 (m, 2H), 2.38 (t, J = 7.13 Hz, 2H), 3.79 (s, 3H), 6.81 (d, J = 8.64 Hz, 2H), 7.33 (d, J = 8.64 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 19.4, 22.2, 28.6, 31.1, 55.2, 80.2, 88.8, 113.8, 116.2, 132.8, 158.9 ppm; HRMS (ESI, m/z): Calcd. for $C_{14}H_{19}O$: 203.1436, found $[M+H]^+$: 203.1431.



1-(2-Cyclopropylethynyl)-4-methoxybenzene (Table 3, entry 10): Colorless oil; Yield: 87%; FTIR (NaCl, neat): ν 2233 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.77-0.85 (m, 4H), 1.40-1.46 (m, 1H), 3.78 (s, 3H), 6.80 (d, J = 8.36 Hz, 2H), 7.31 (d, J = 8.41 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.5, 133.0, 131.1, 129.0, 128.3, 128.0, 127.1, 76.6, 61.8, 29.5, 20.6, 18.6 ppm; HRMS (ESI, m/z): Calcd. for $C_{12}H_{12}O$: 195.0786, found $[M+H]^+$: 195.0780.

^{1}H and ^{13}C NMR Spectra of Products

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128.2
123.2
Ph
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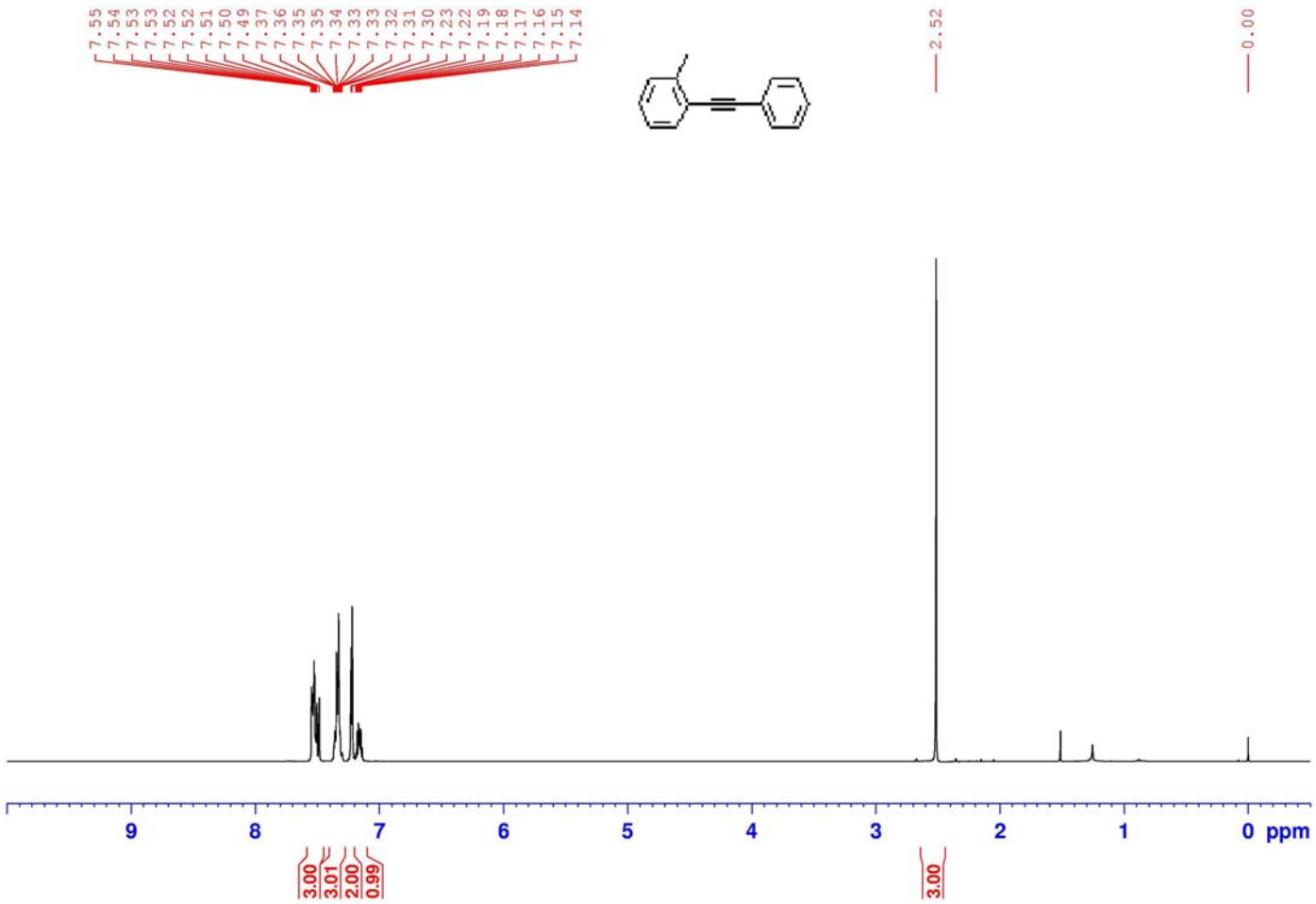
77.3
77.0
76.7
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 ppm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7.50
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7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.23
7.22
7.19
7.18
7.17
7.16
7.15
7.14
2.52
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7
6
5
4
3
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2.00
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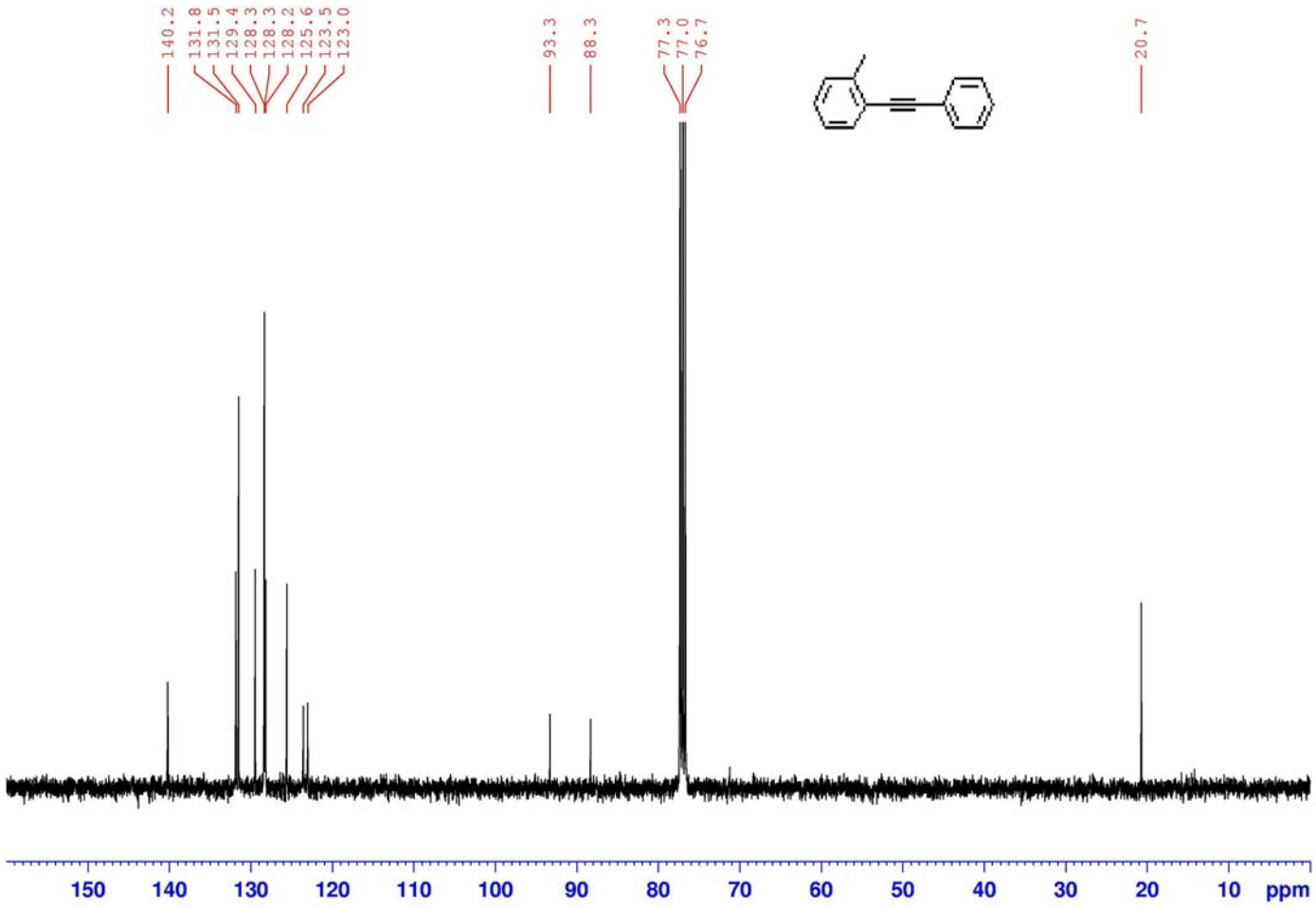
3.00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125.6
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77.3
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150
140
130
120
110
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70
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30
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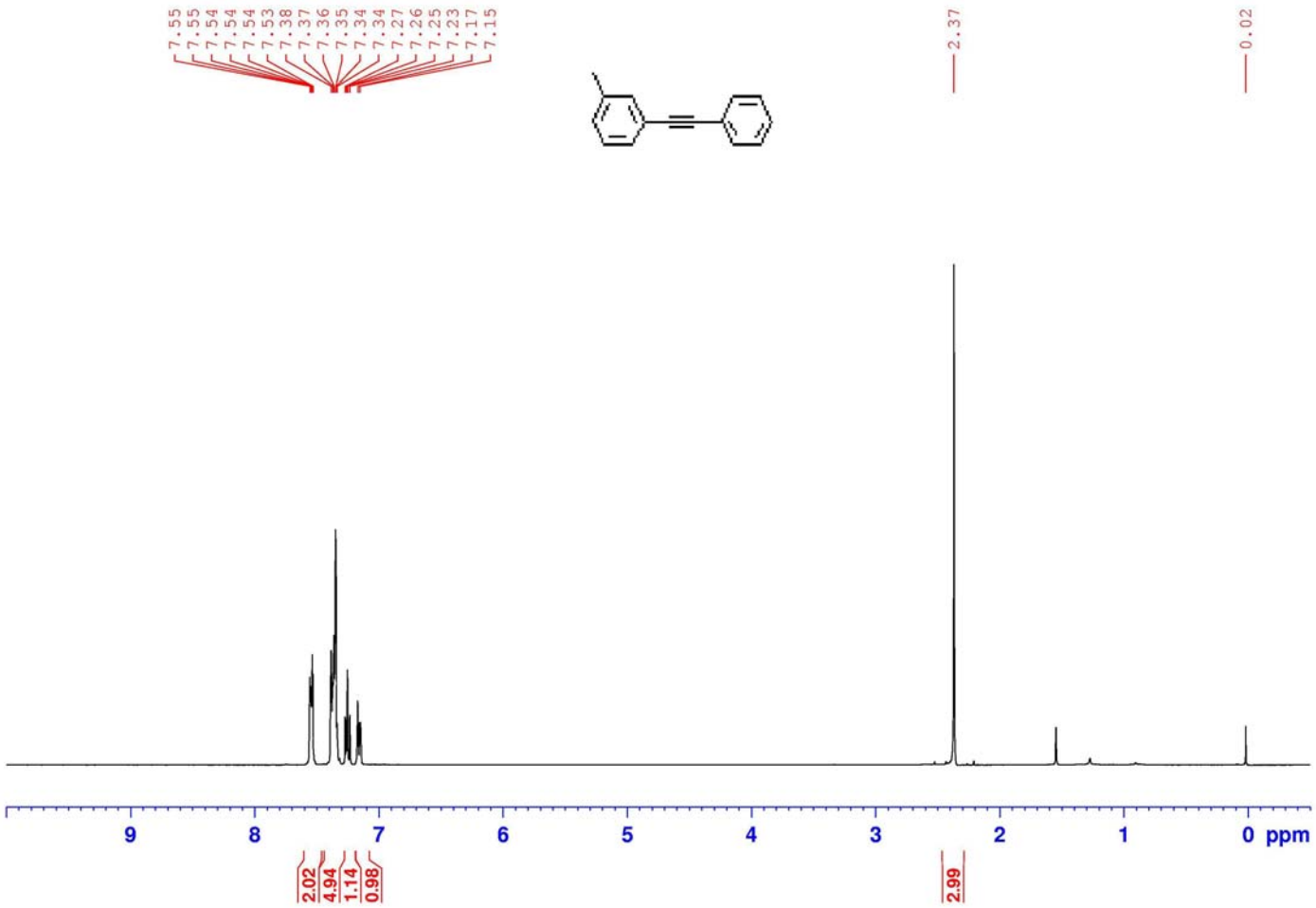
10
ppm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7.34
7.34
7.27
7.26
7.25
7.23
7.17
7.15
2.37
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9
8
7
6
5
4
3
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2.02
4.94
1.14
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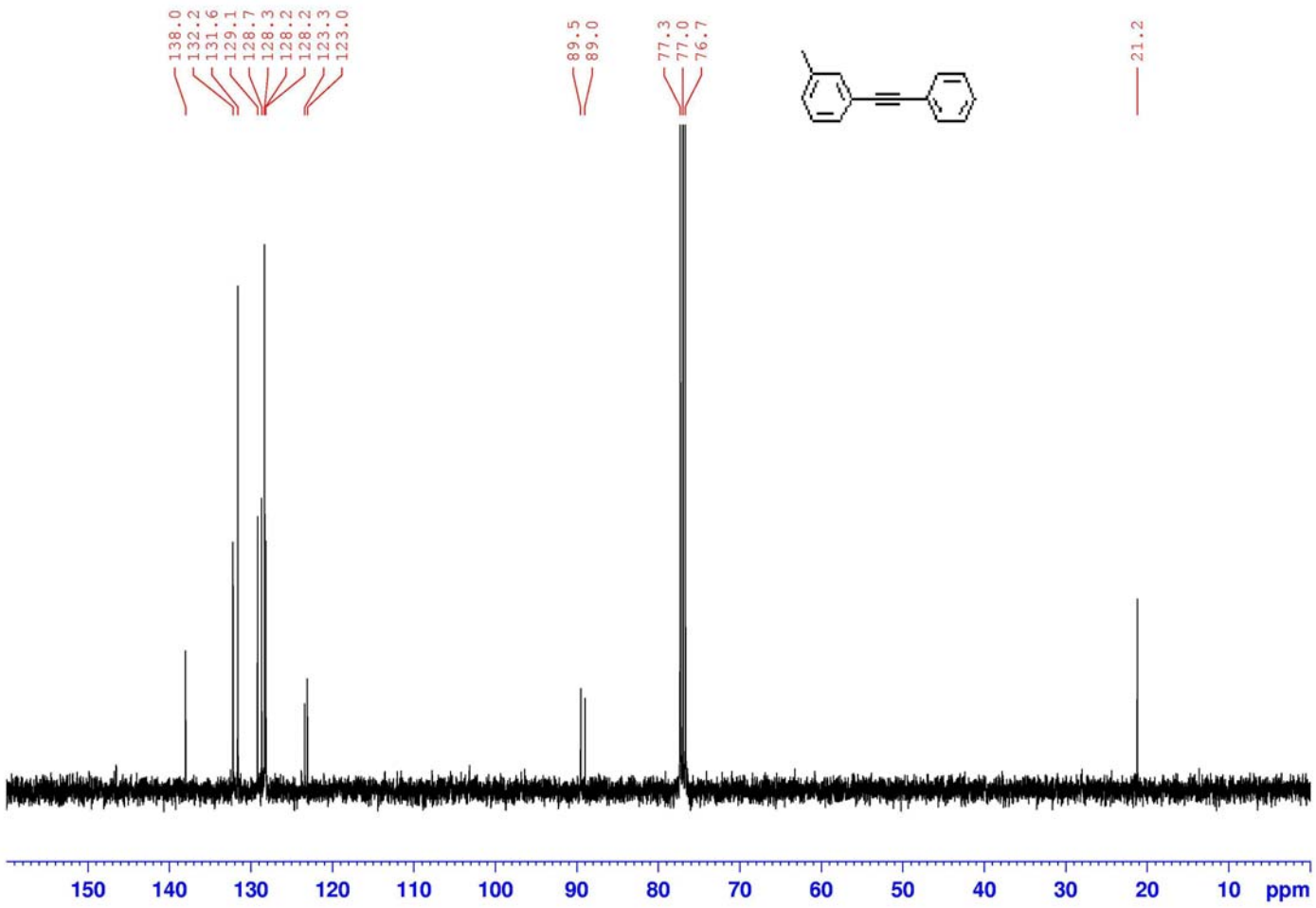
2.99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128.2
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77.3
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70
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30
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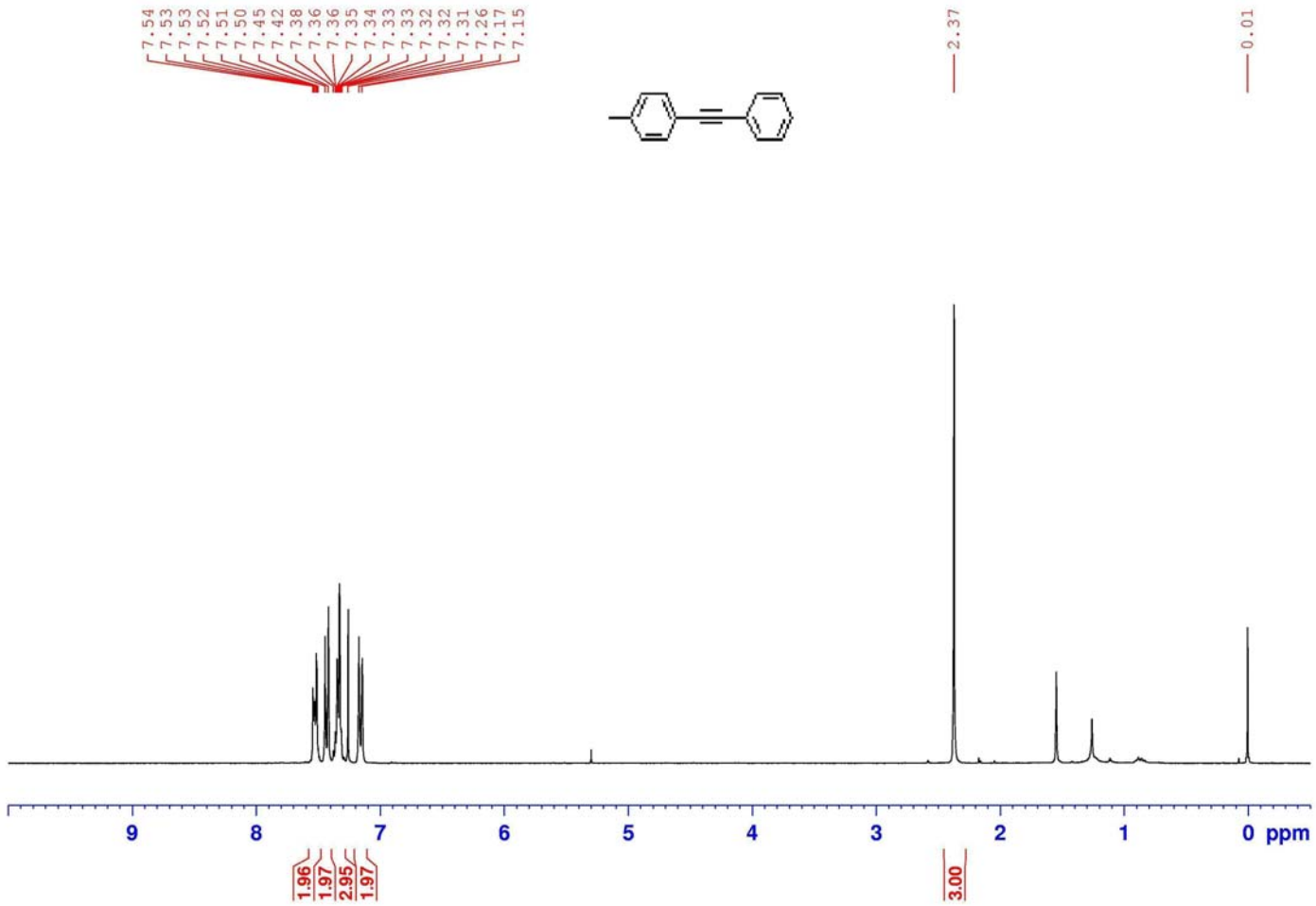
10
ppm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7.32
7.31
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7.17
7.15
2.37
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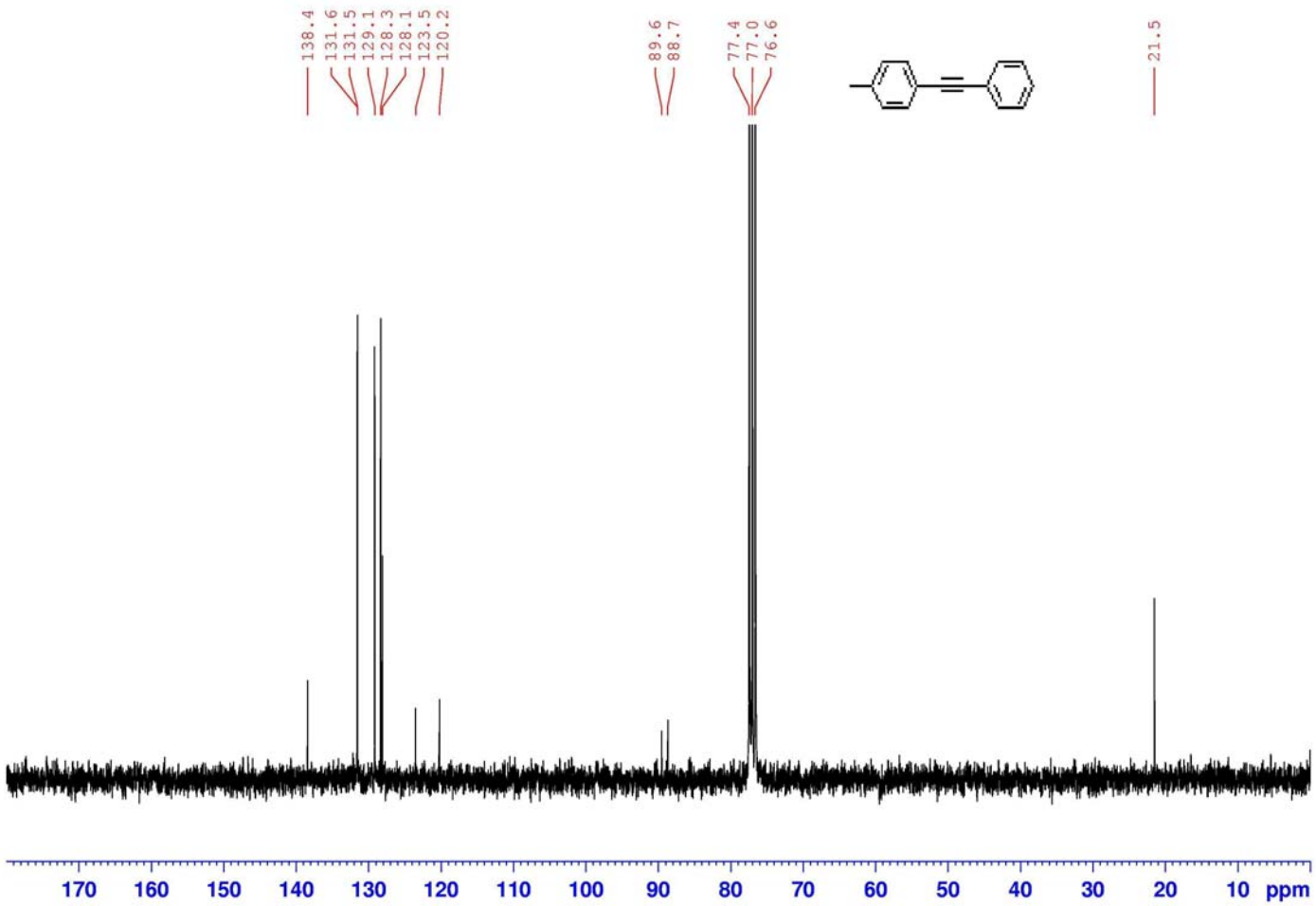
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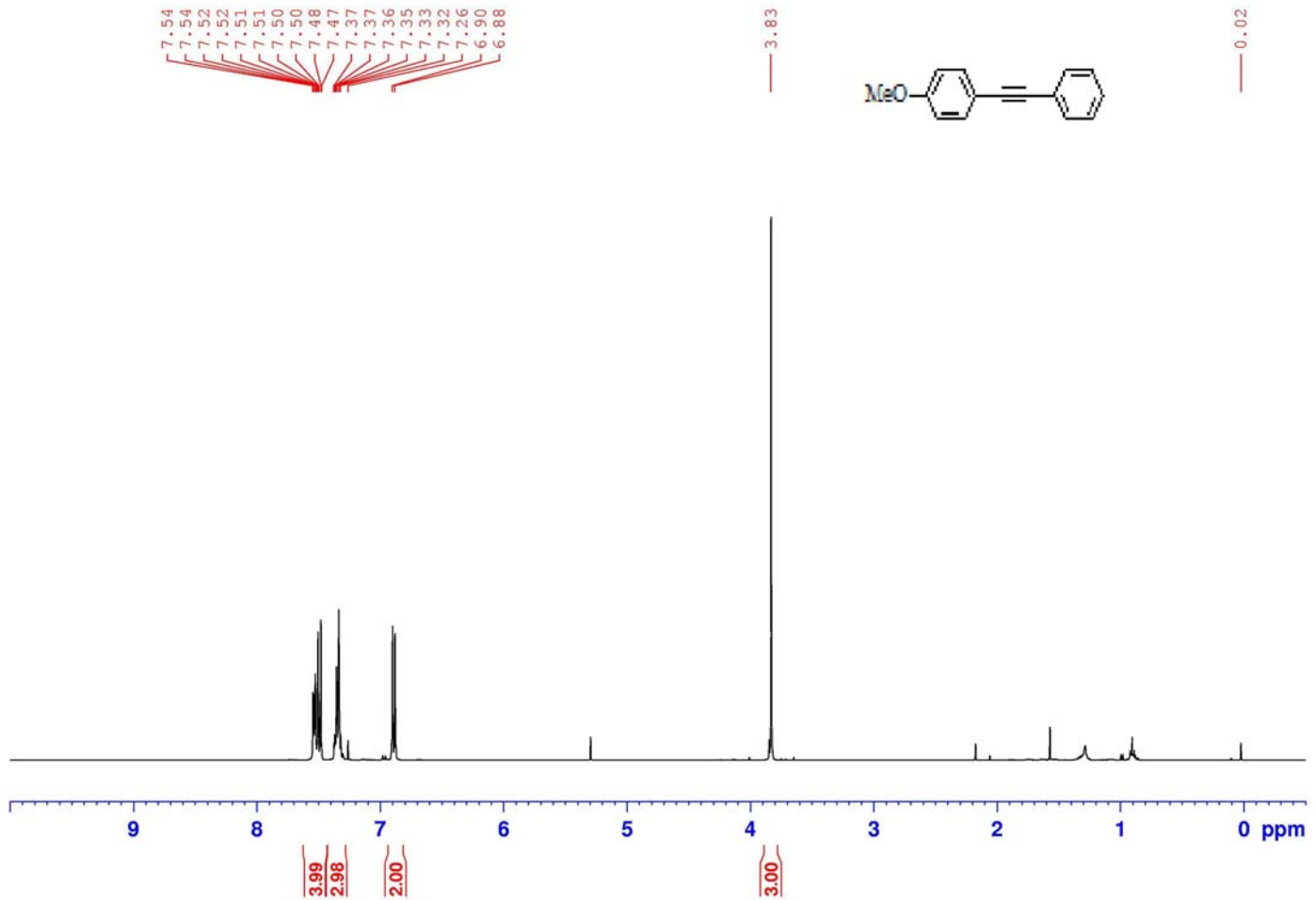
ppm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7.50
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7.33
7.32
7.26
6.90
6.88
3.83
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8
7
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4
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2
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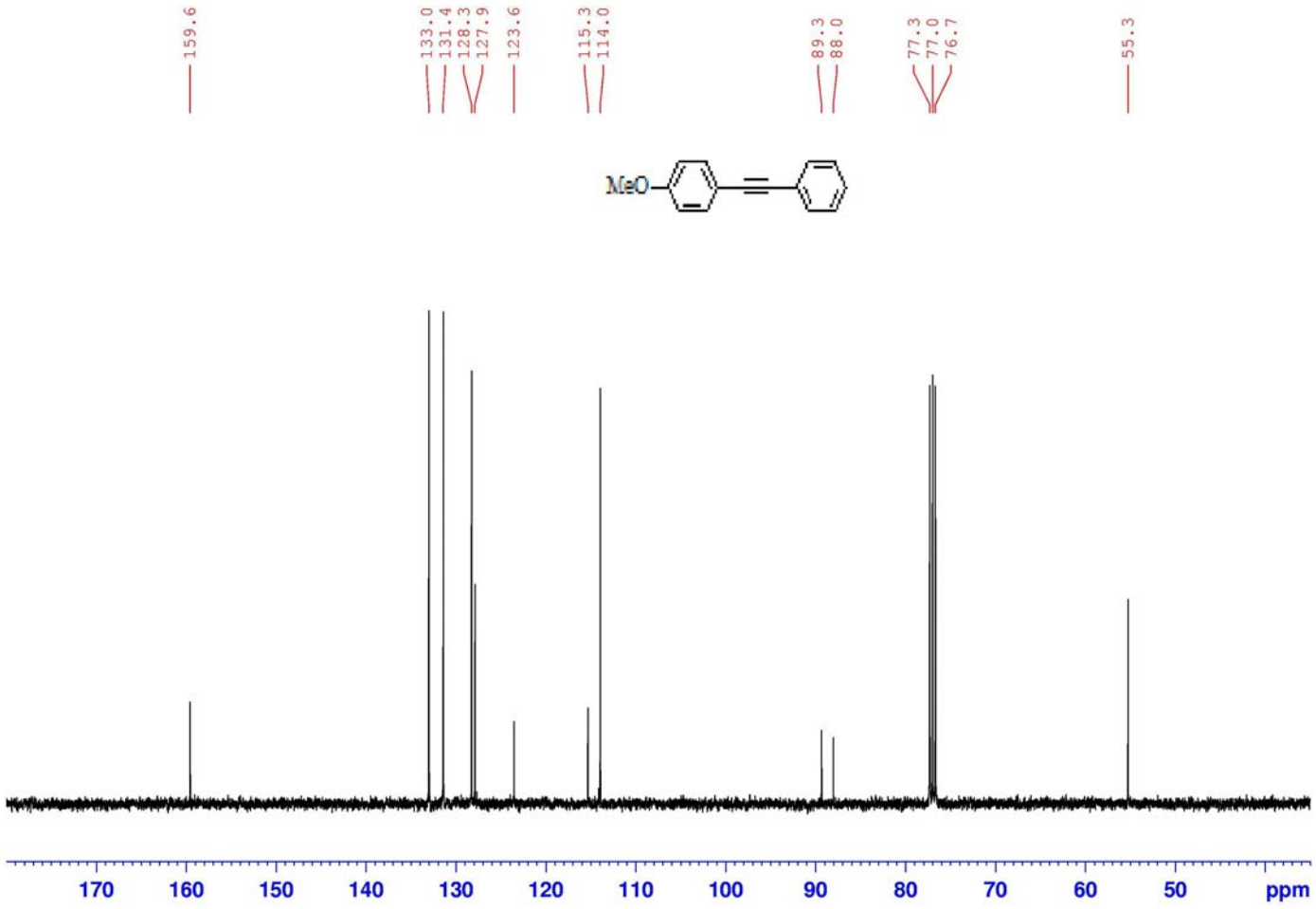
2.00
3.00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114.0
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77.3
77.0
76.7
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MeO
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160
150
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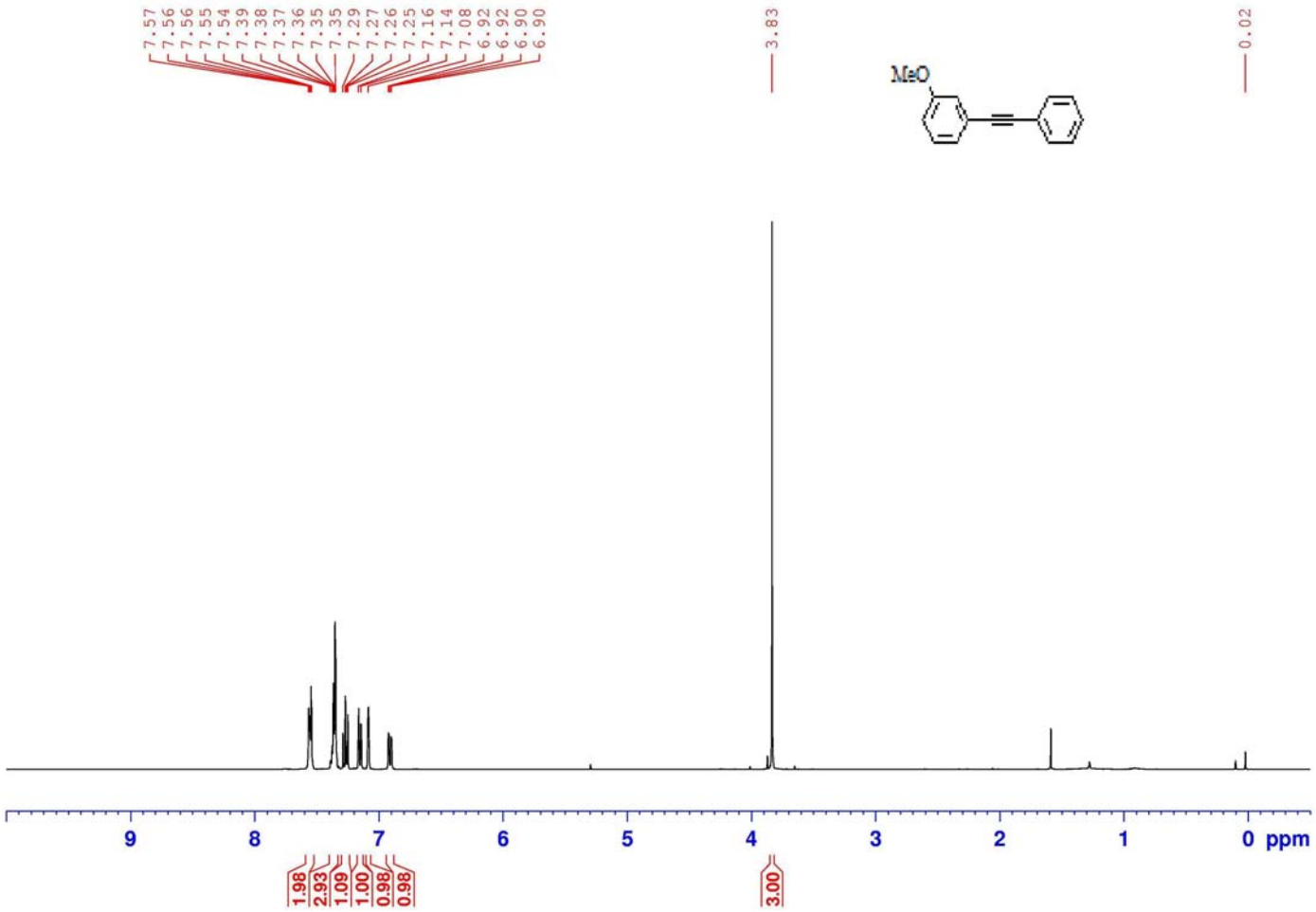
120
110
100
90
80
70
60
50
ppm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7.26
7.25
7.16
7.14
7.08
6.92
6.90
6.90
3.83
0.02
MeO
9
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1.09
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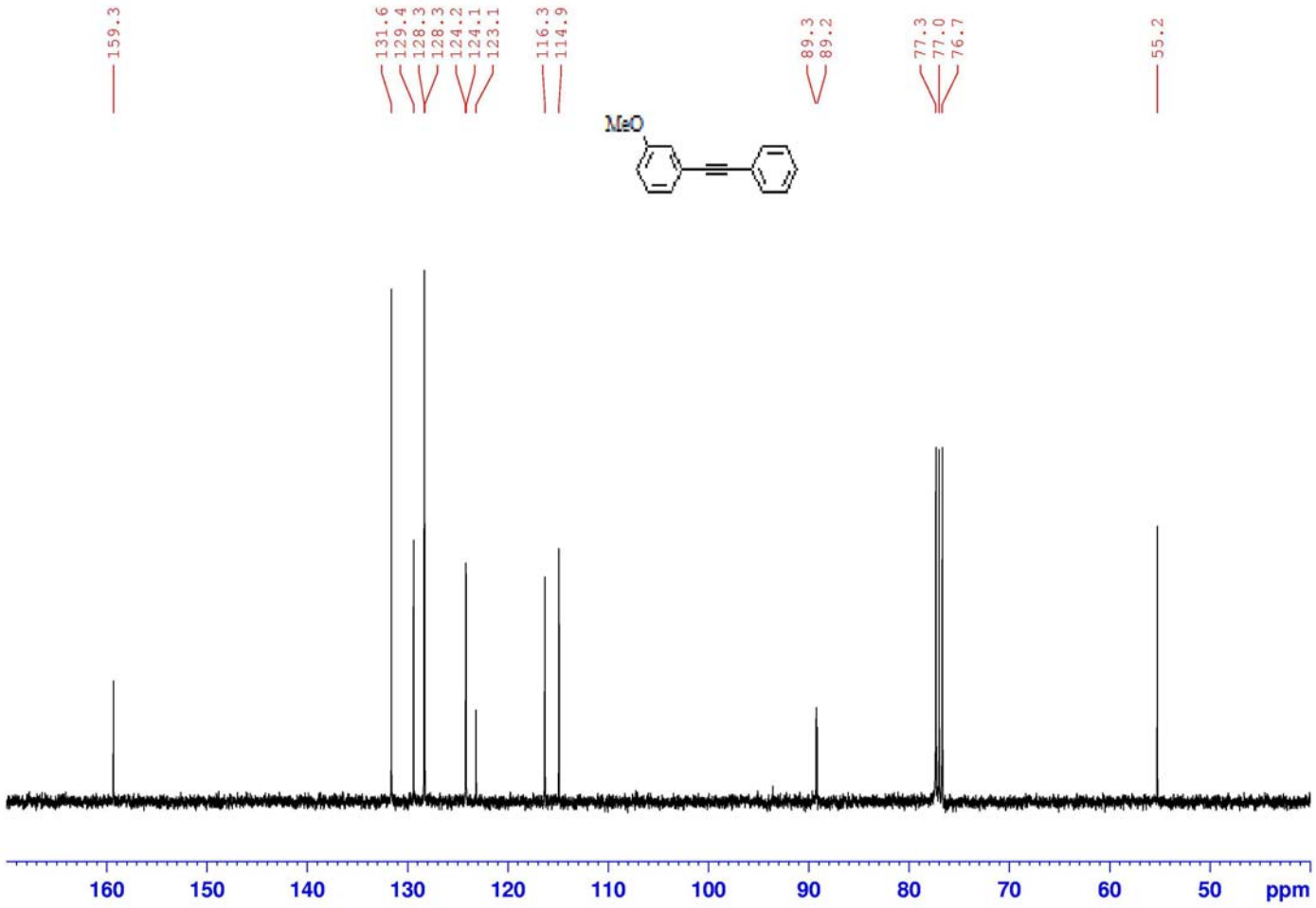
3.00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123.1
116.3
114.9
89.3
89.2
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55.2
MeO
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120
110
100
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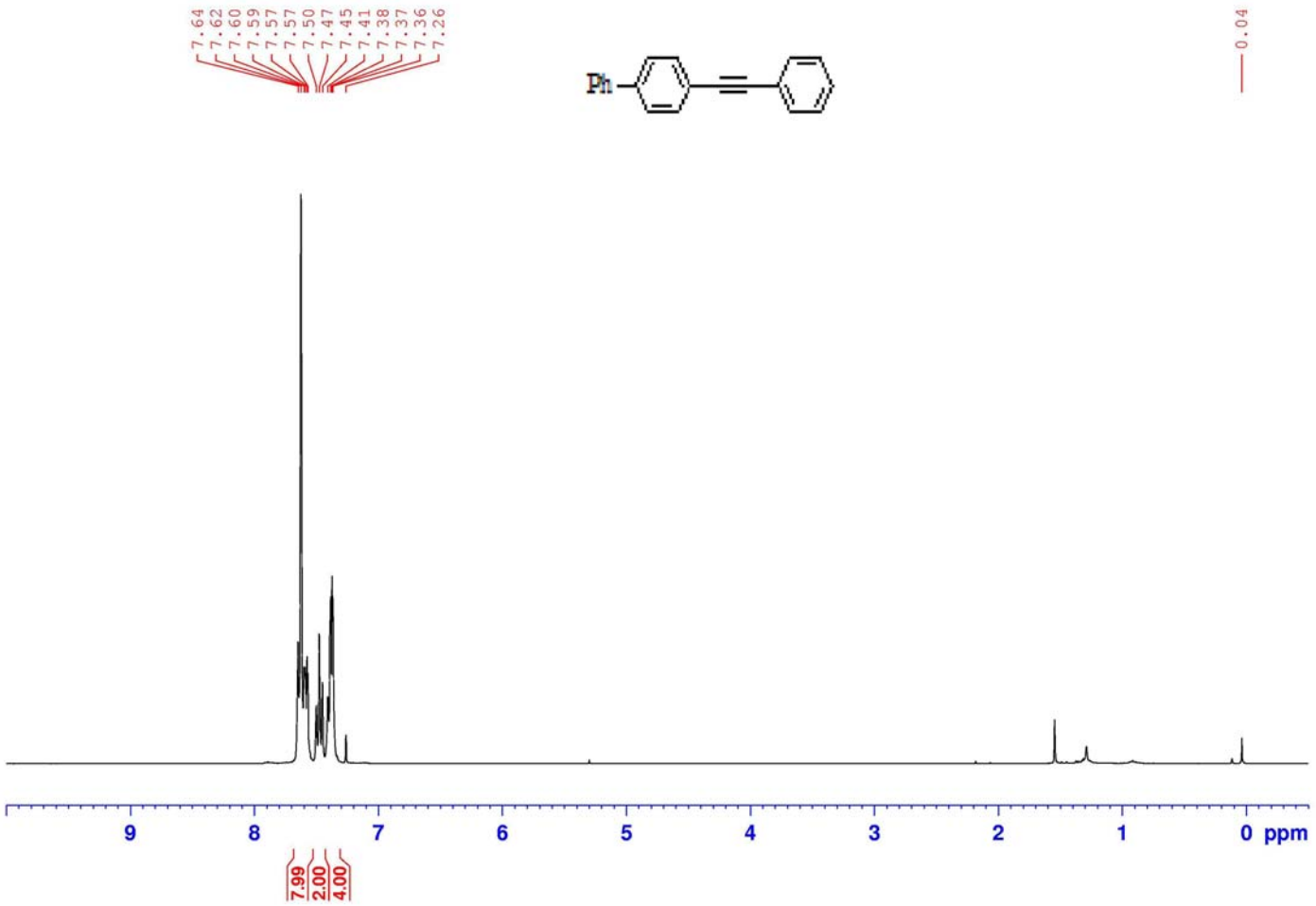
50
ppm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7.36
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8
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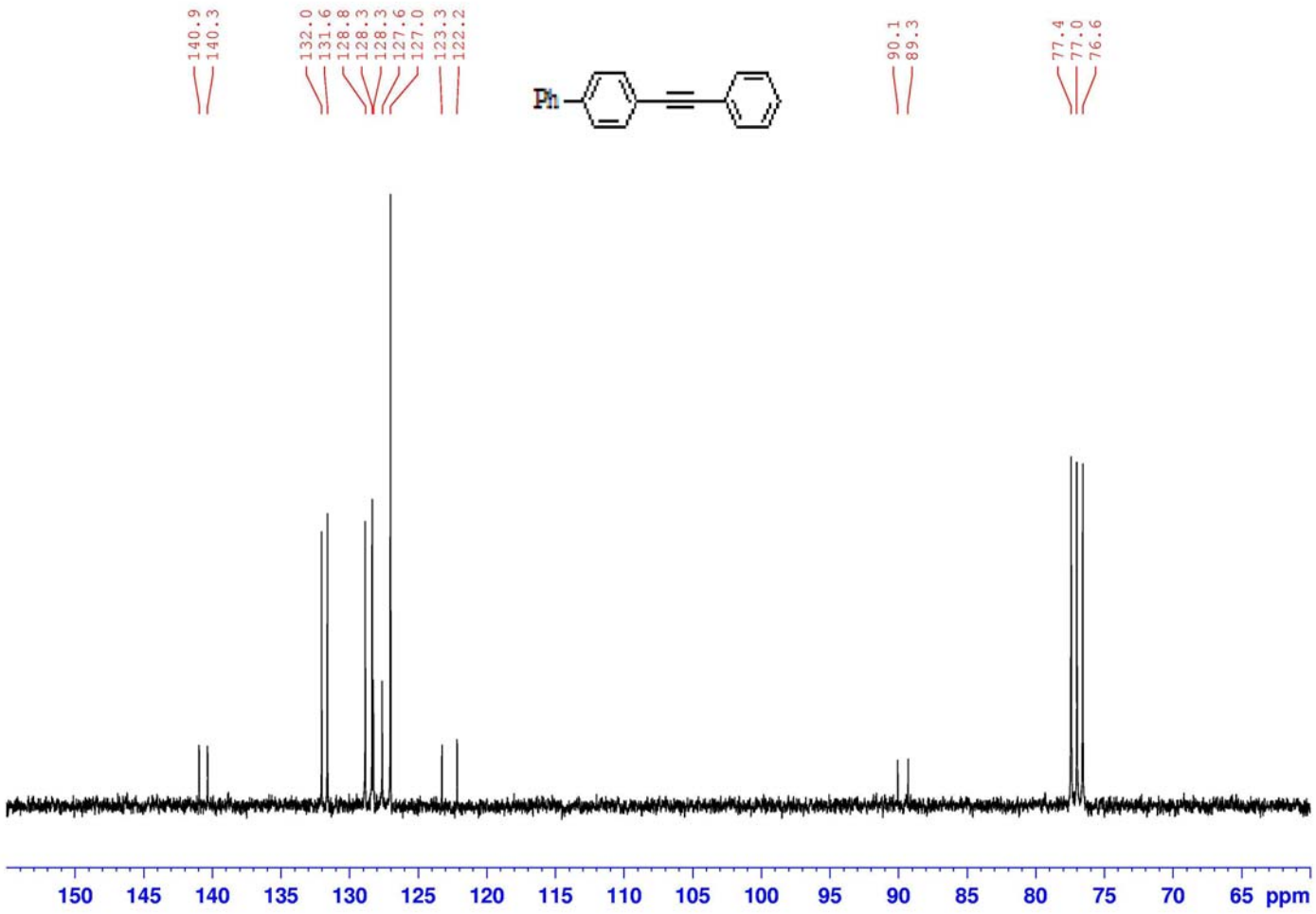
4.00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127.6
127.0
123.3
122.2
Ph
90.1
89.3
77.4
77.0
76.6
150
145
140
135
130
125
120
115
110
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100
95
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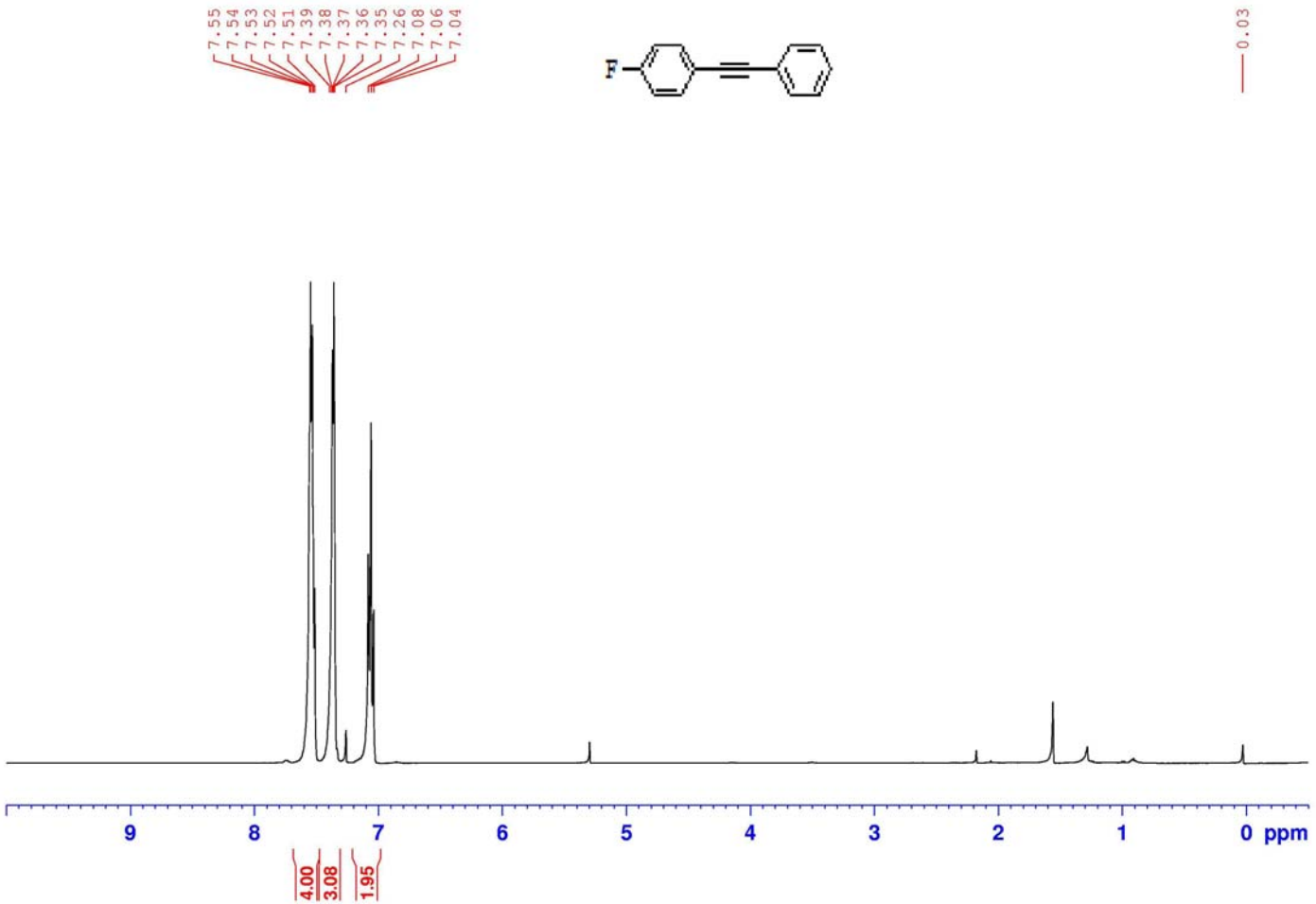
85
80
75
70
65 ppm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7.37
7.36
7.35
7.26
7.08
7.06
7.04
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9
8
7
6
5
4
3
2
1
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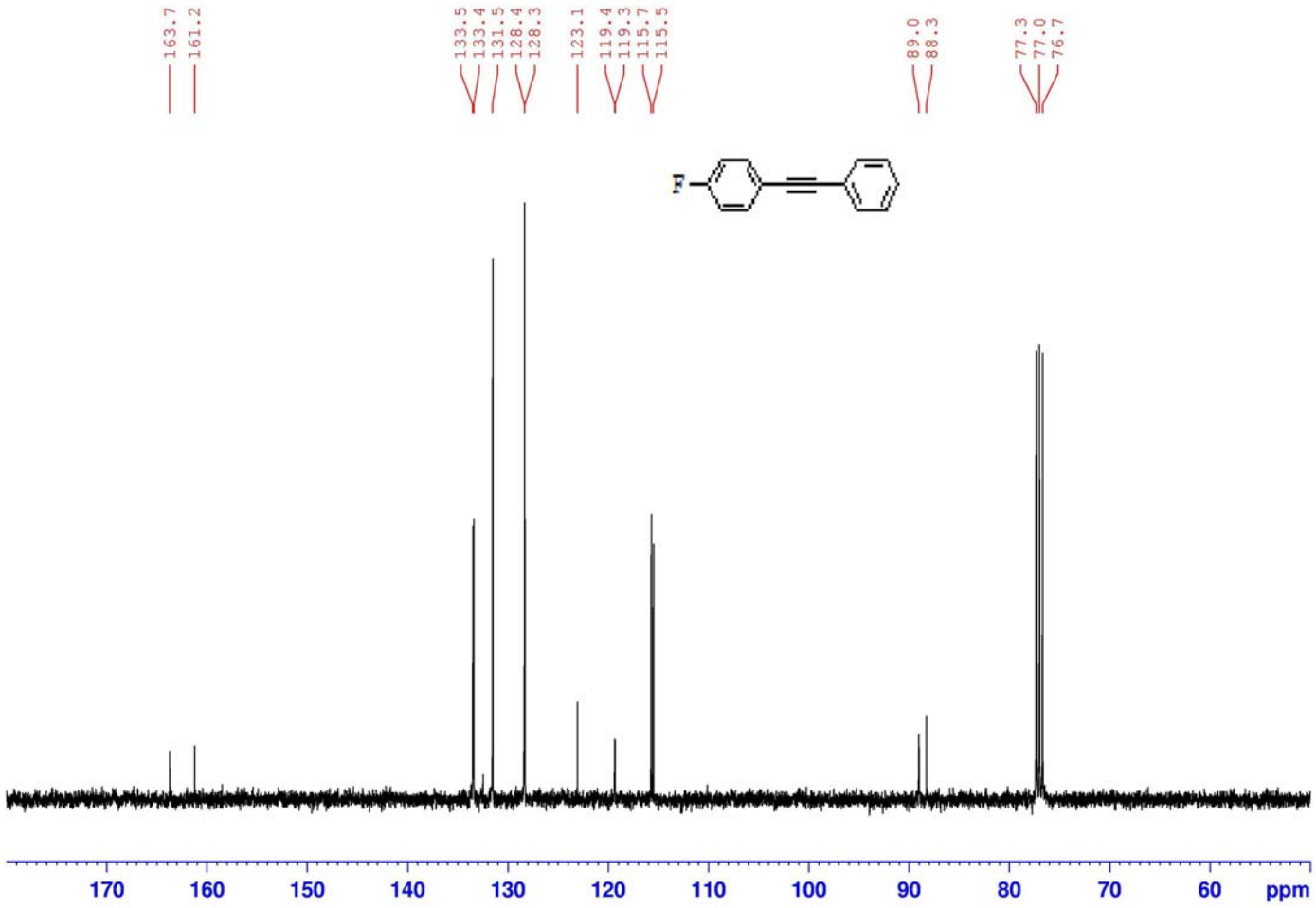
4.00
3.08
1.95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115.5
89.0
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F
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160
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120
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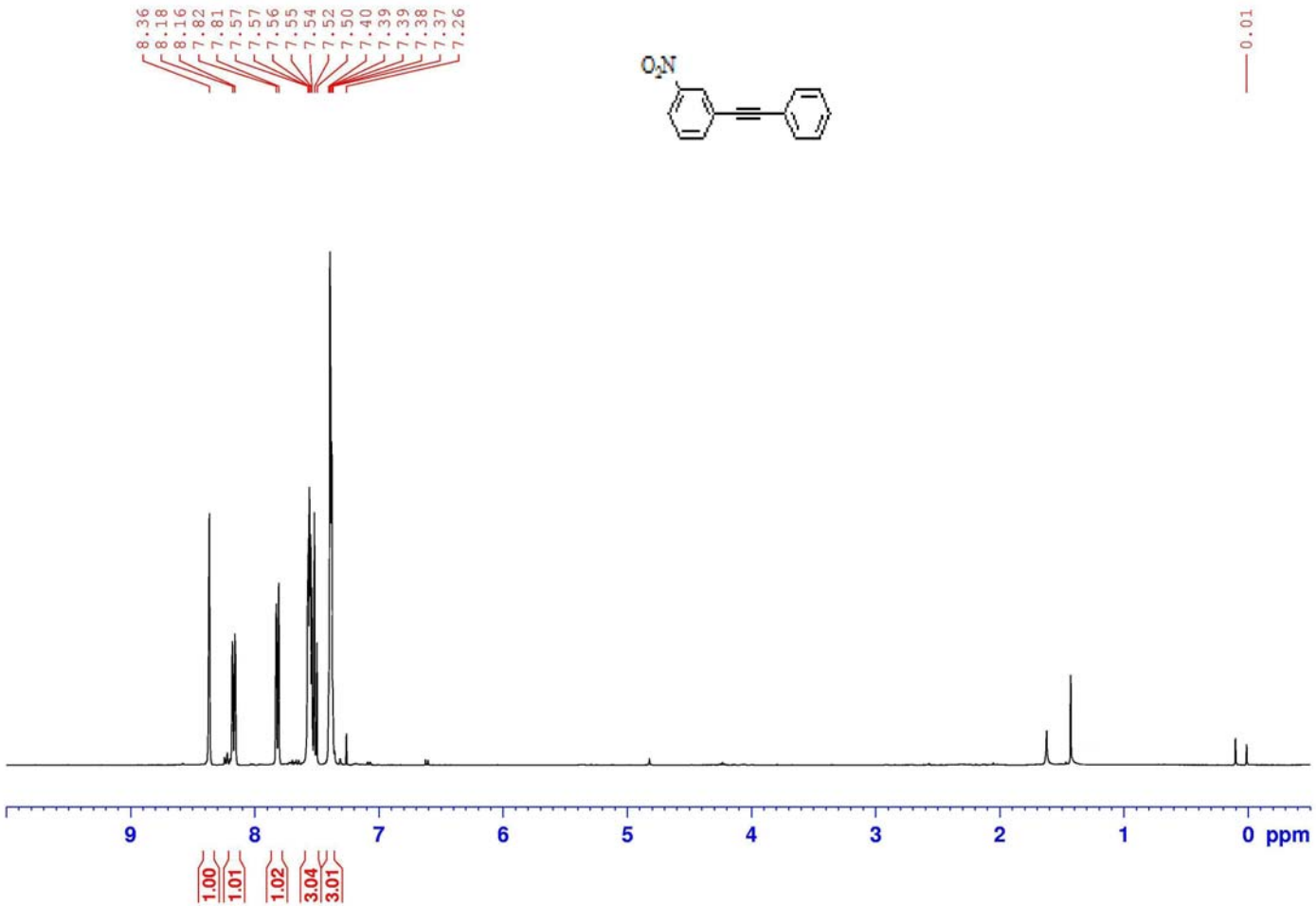
60
ppm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7.40
7.39
7.39
7.38
7.37
7.26
0.01
O2N
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8
7
6
5
4
3
2
1
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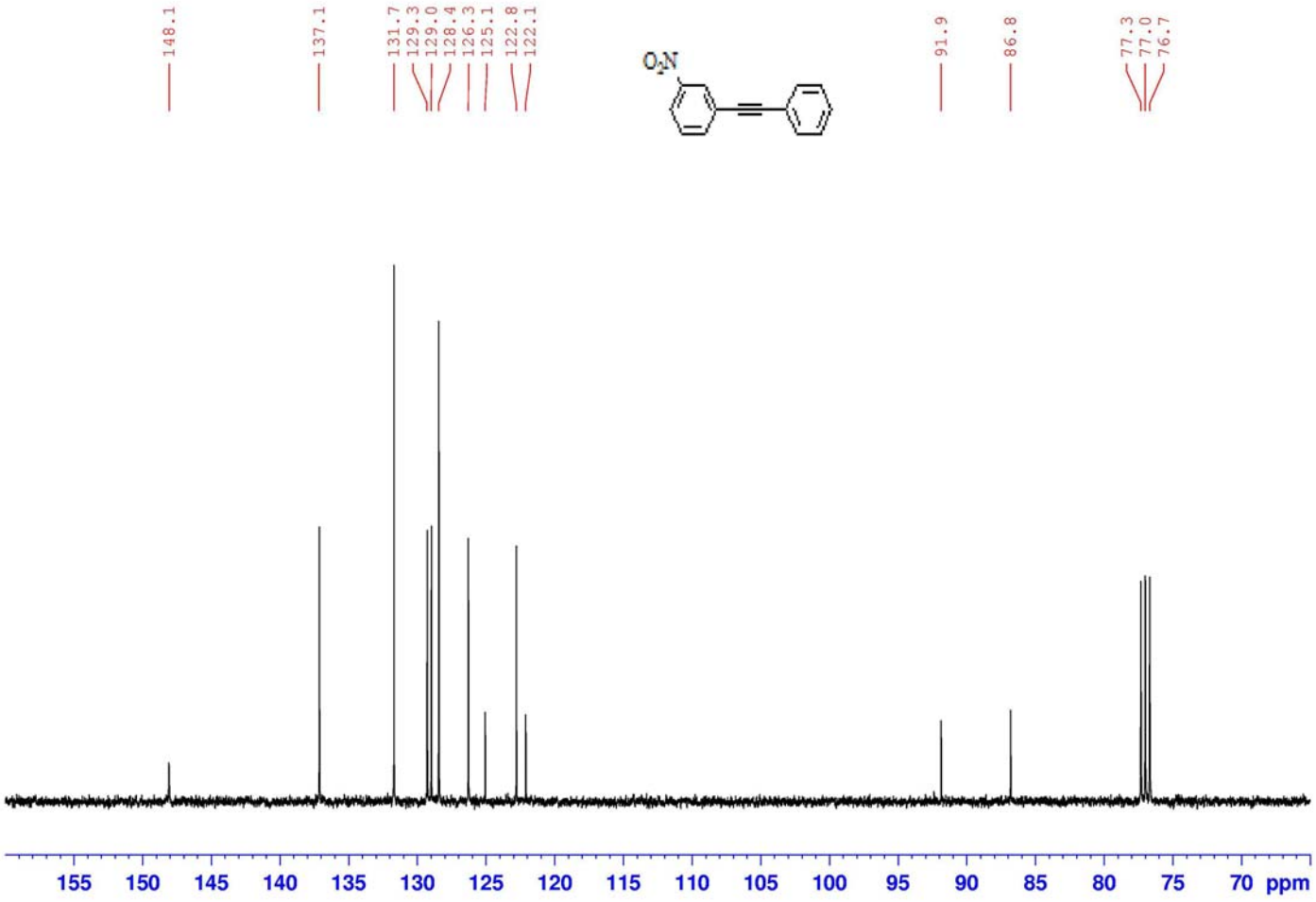
1.00
1.01
1.02
3.04
3.01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125.1
122.8
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O2N
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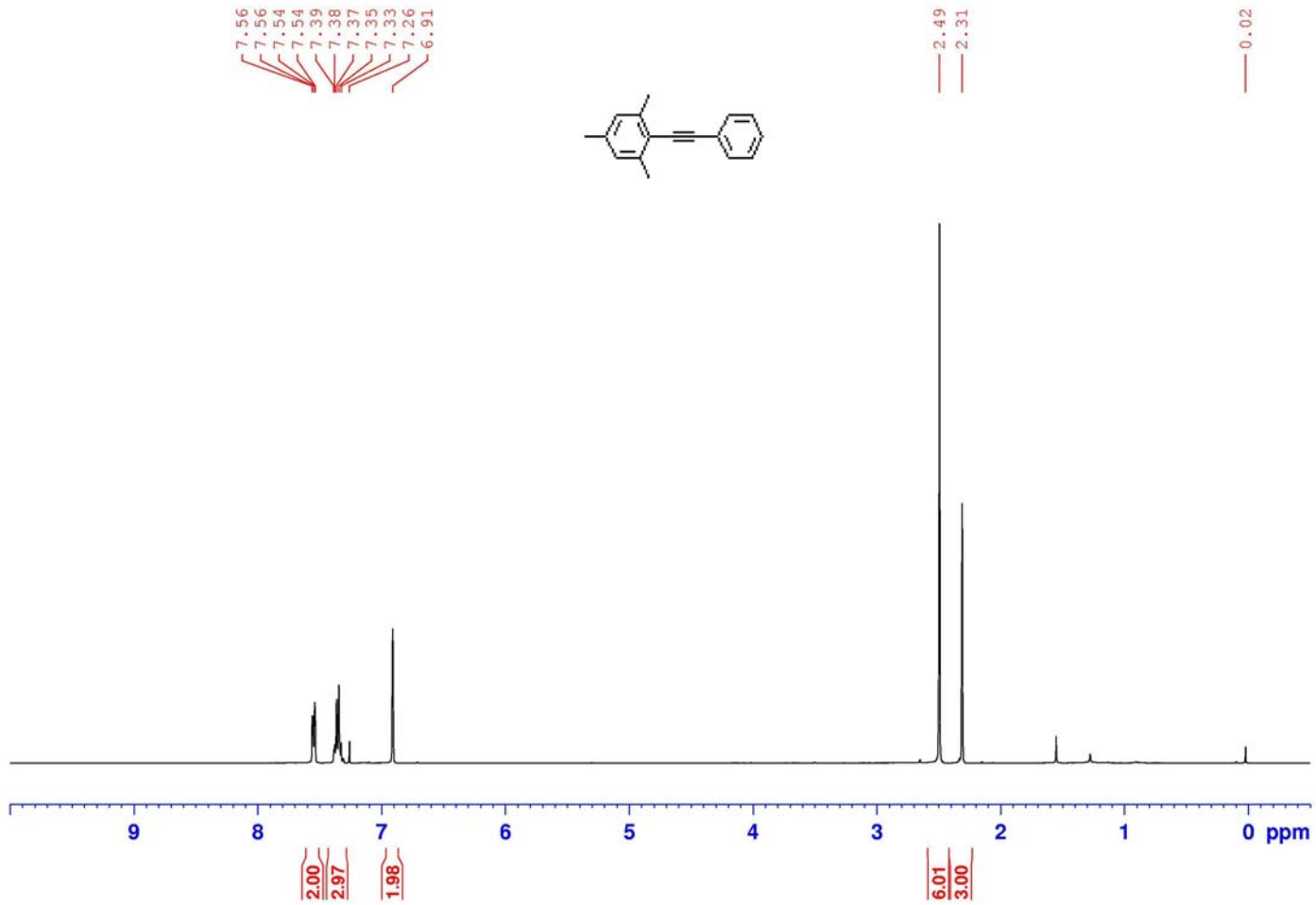
86.8
77.3
77.0
76.7
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 ppm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2.31
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9
8
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6
5
4
3
2
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0 ppm
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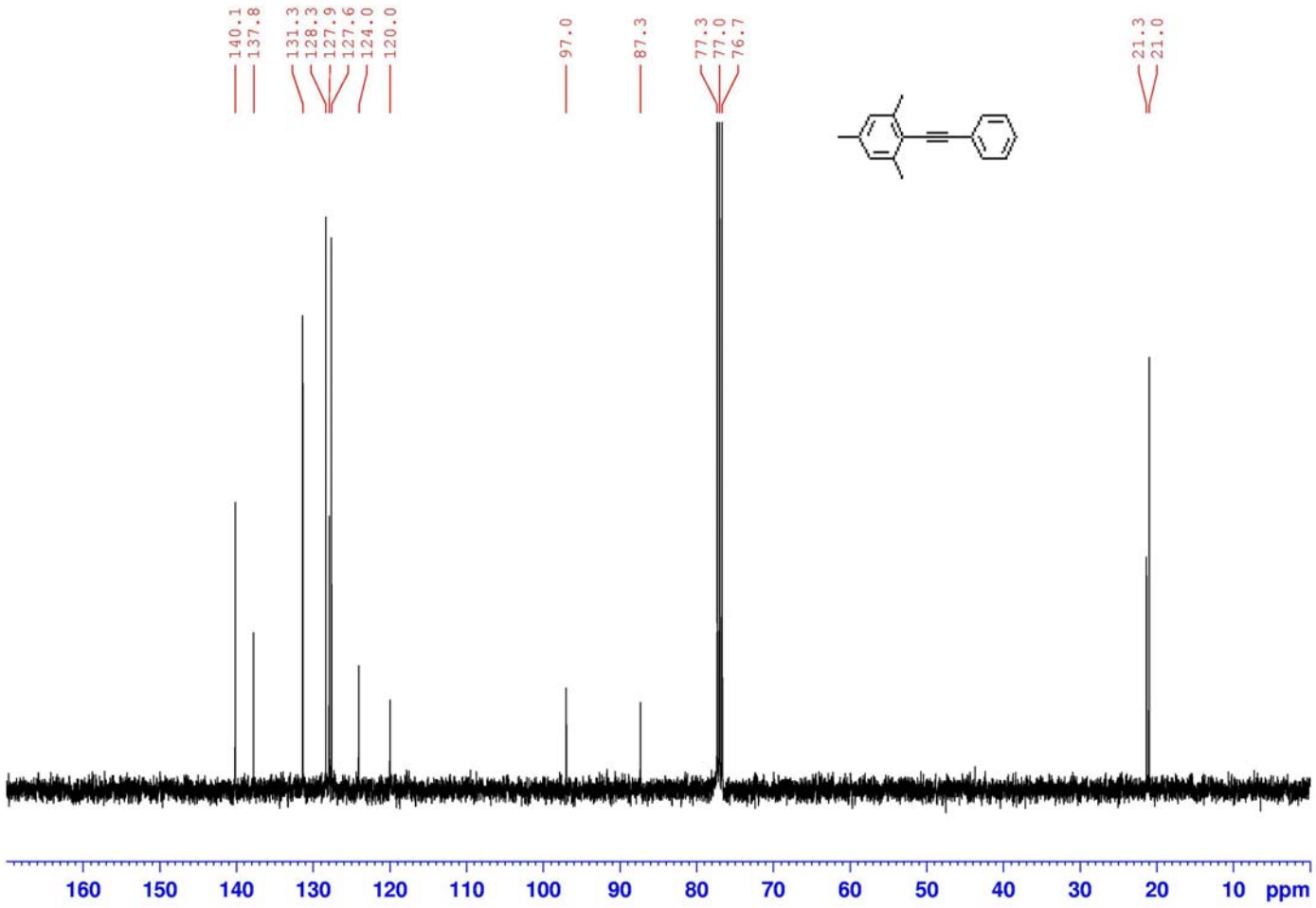
3.00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70
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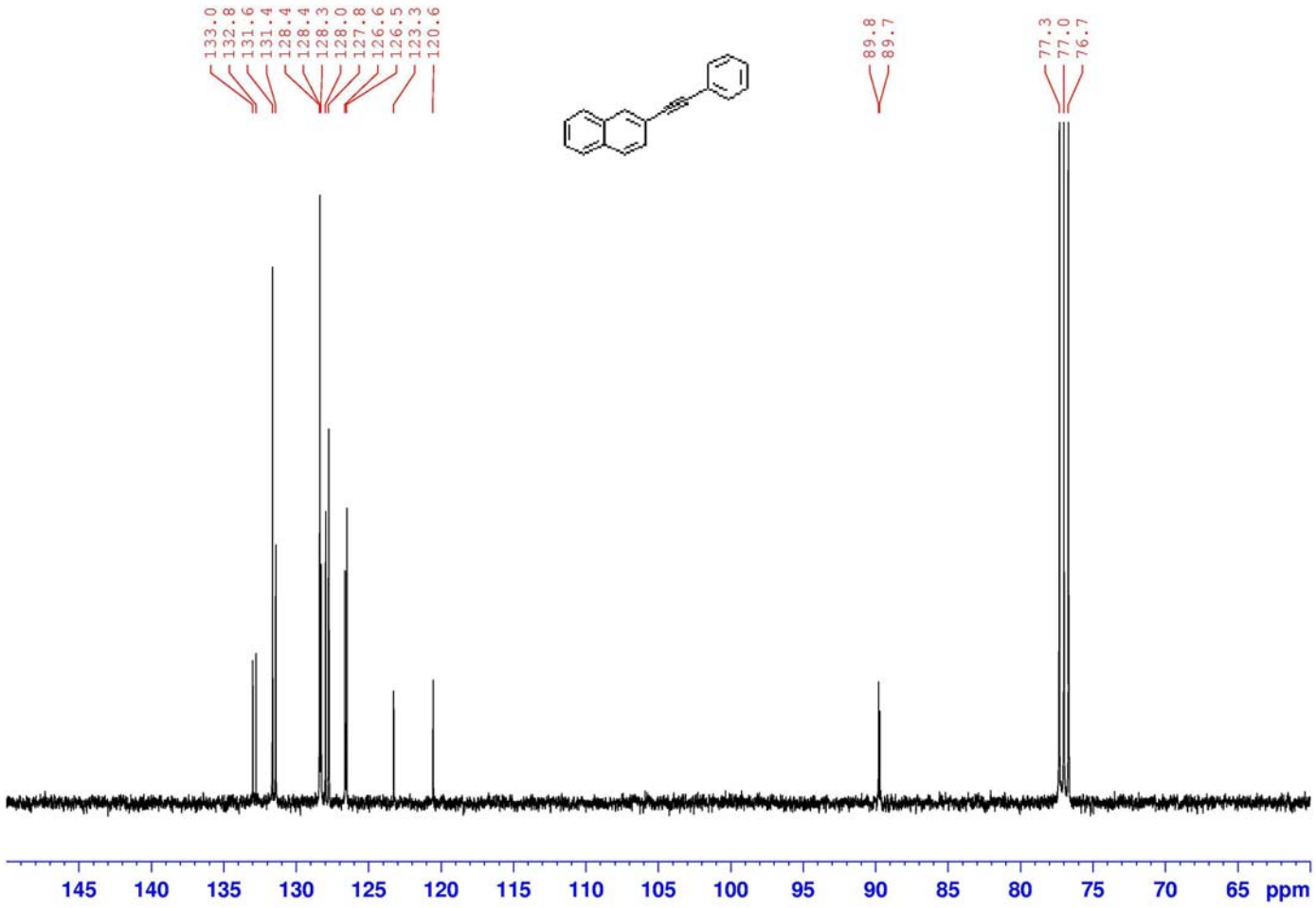
ppm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120.6
89.8
89.7
77.3
77.0
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135
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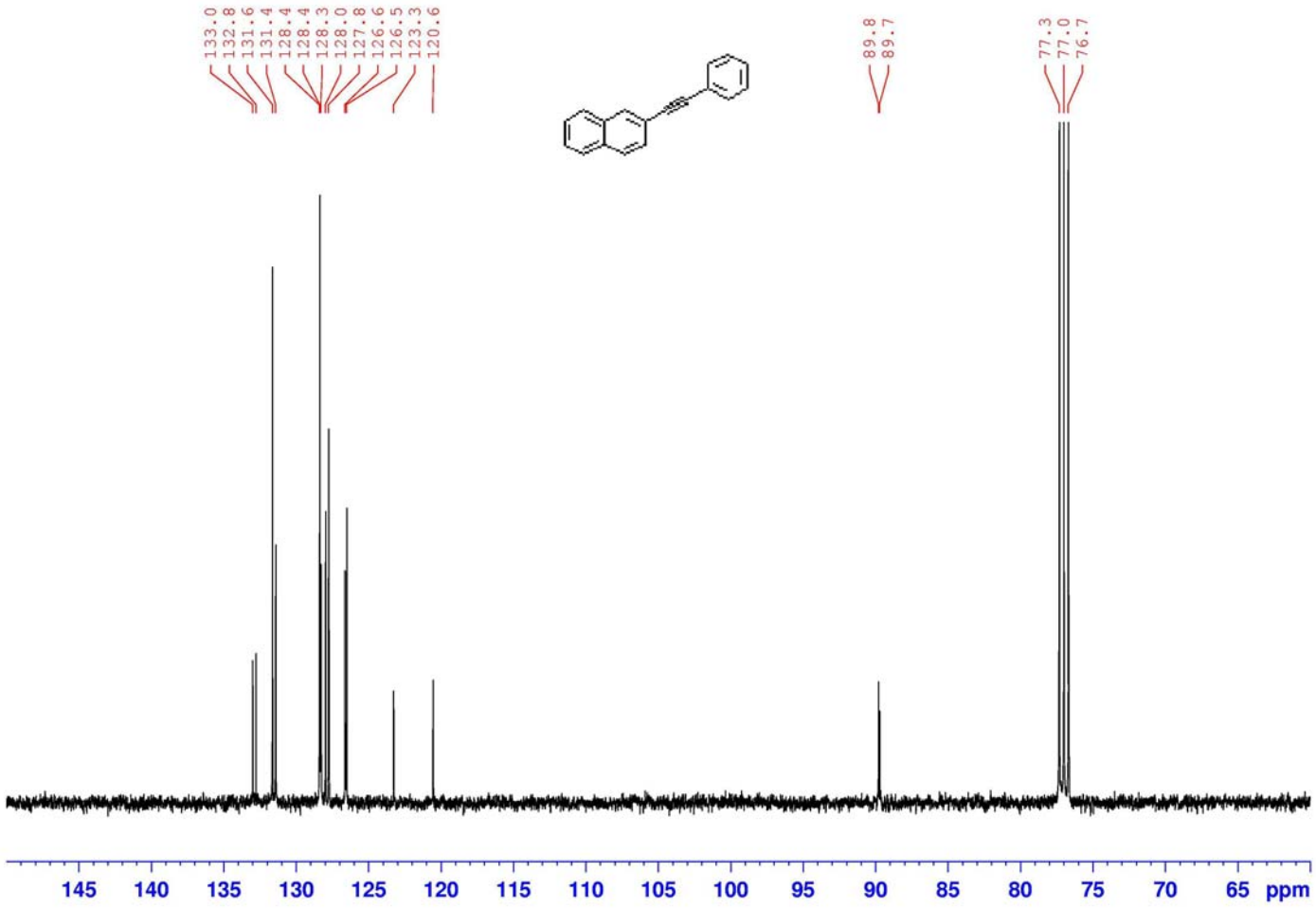
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89.8
89.7
77.3
77.0
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135
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95
90
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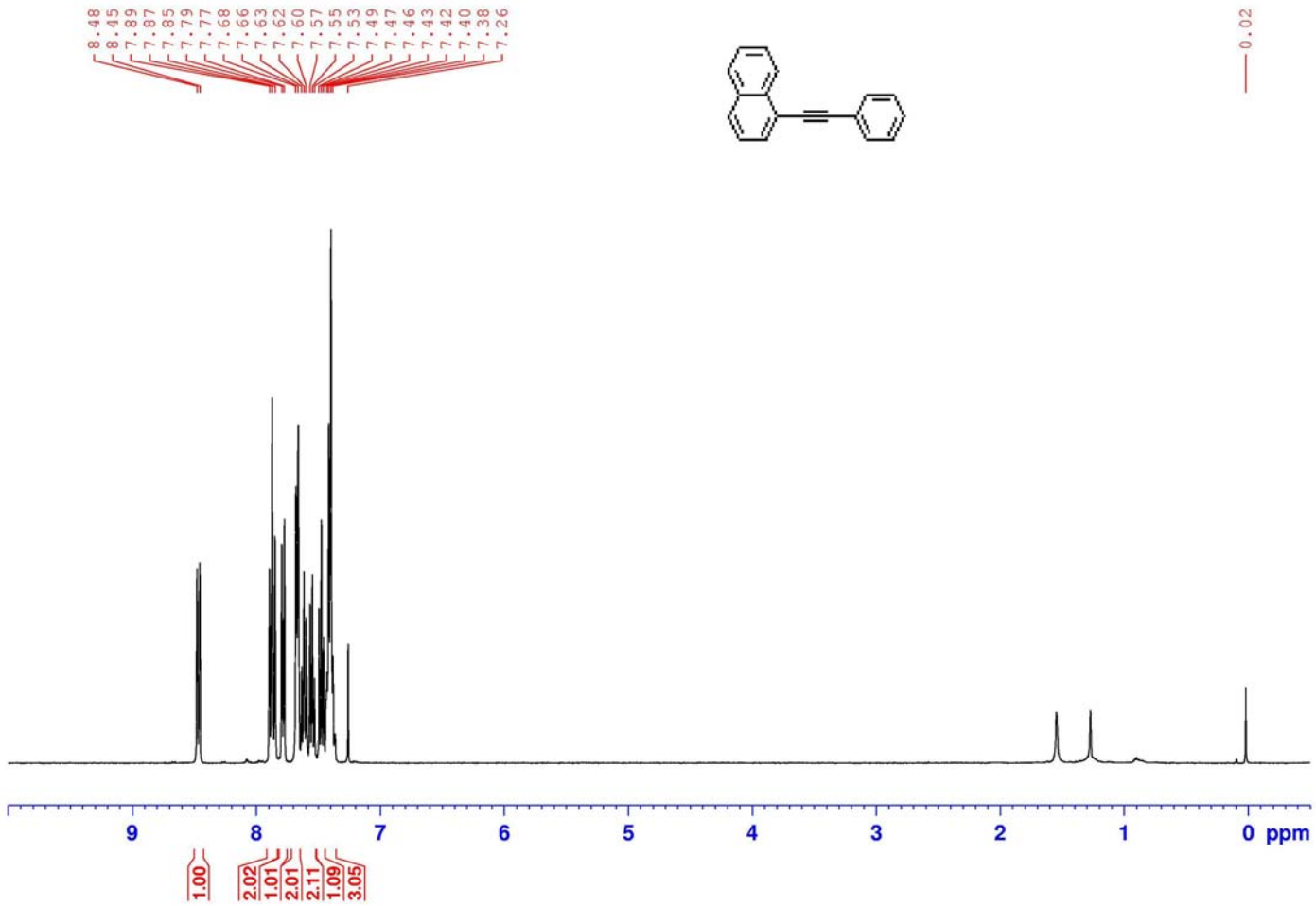
80
75
70
65
ppm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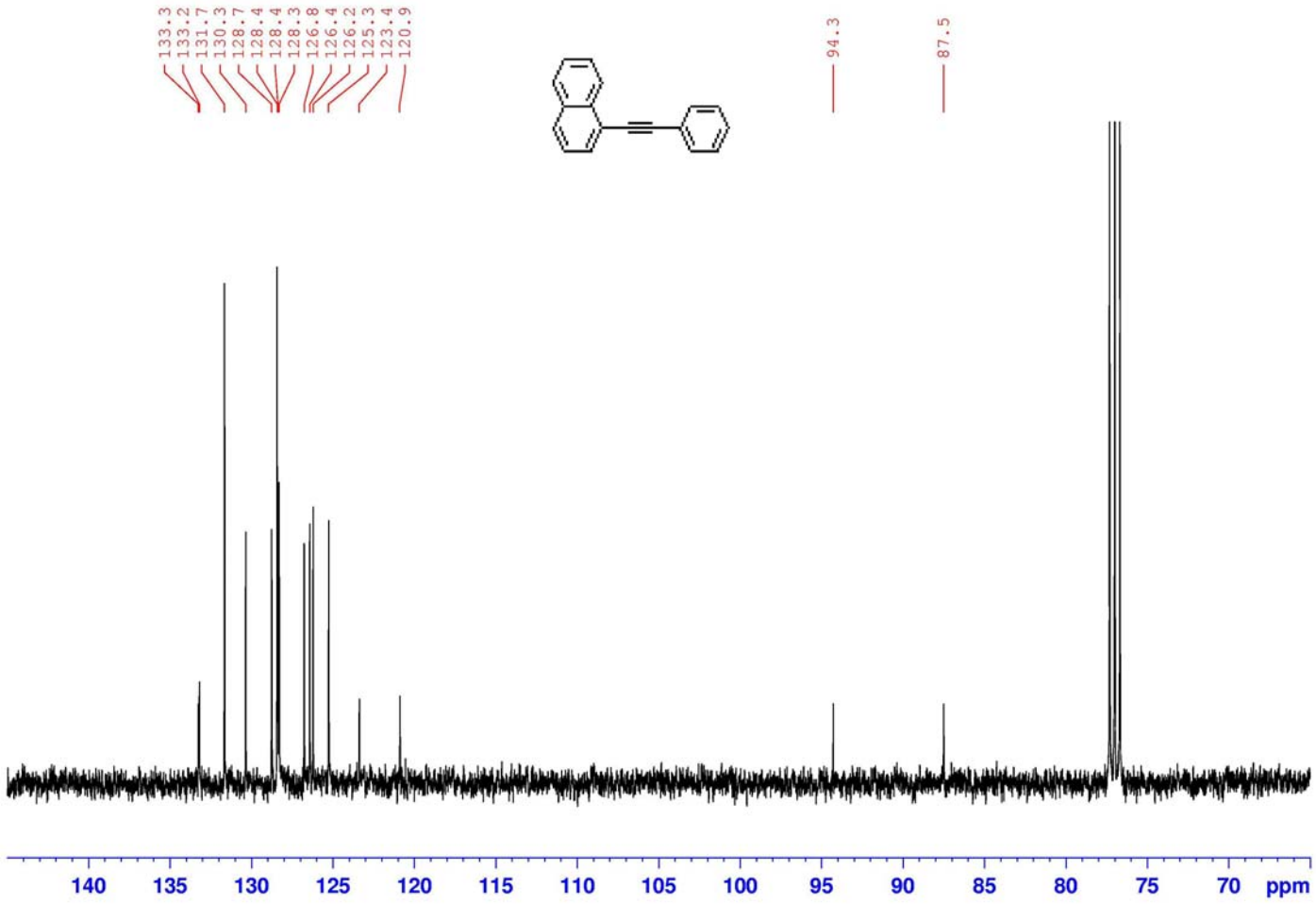
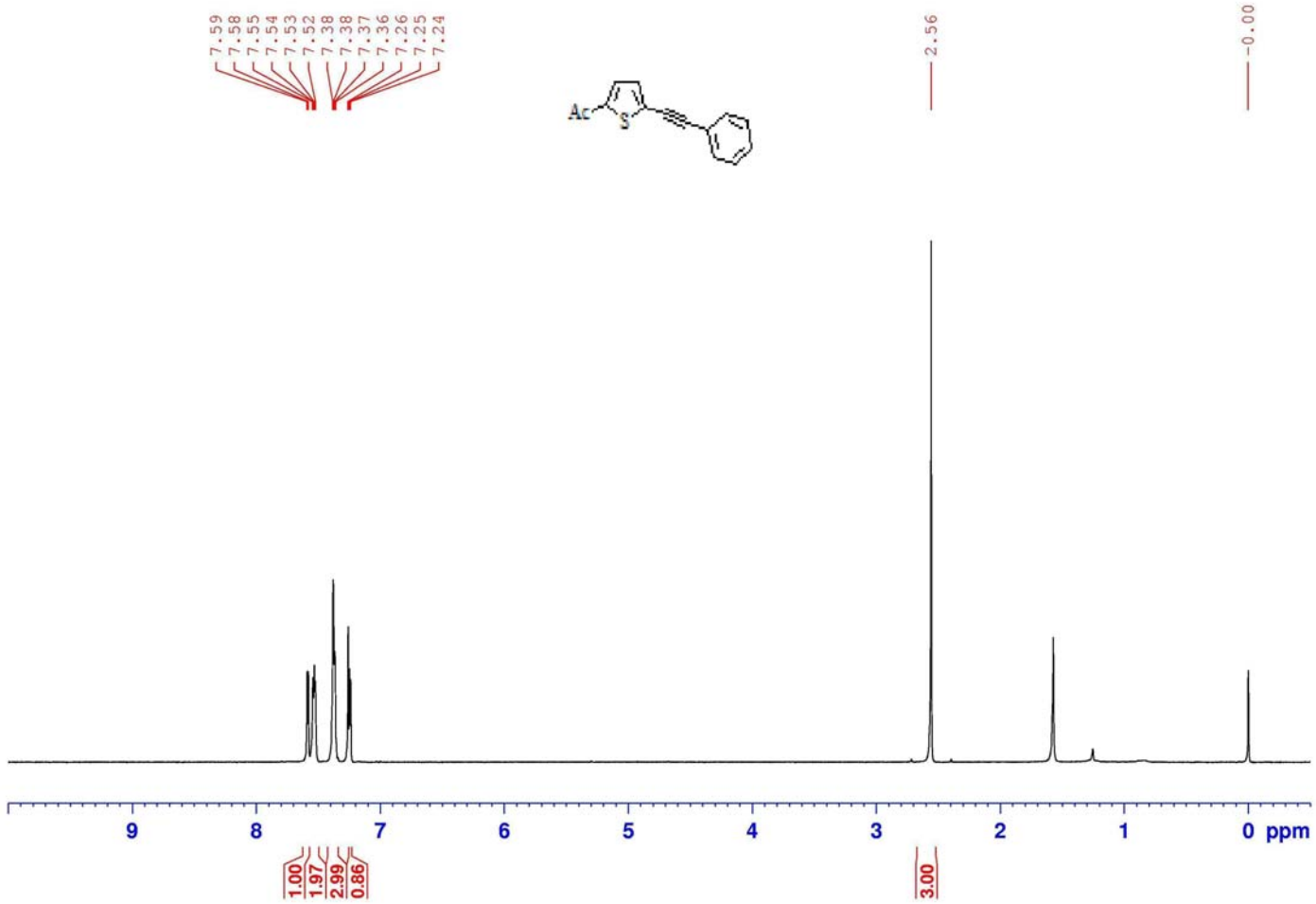
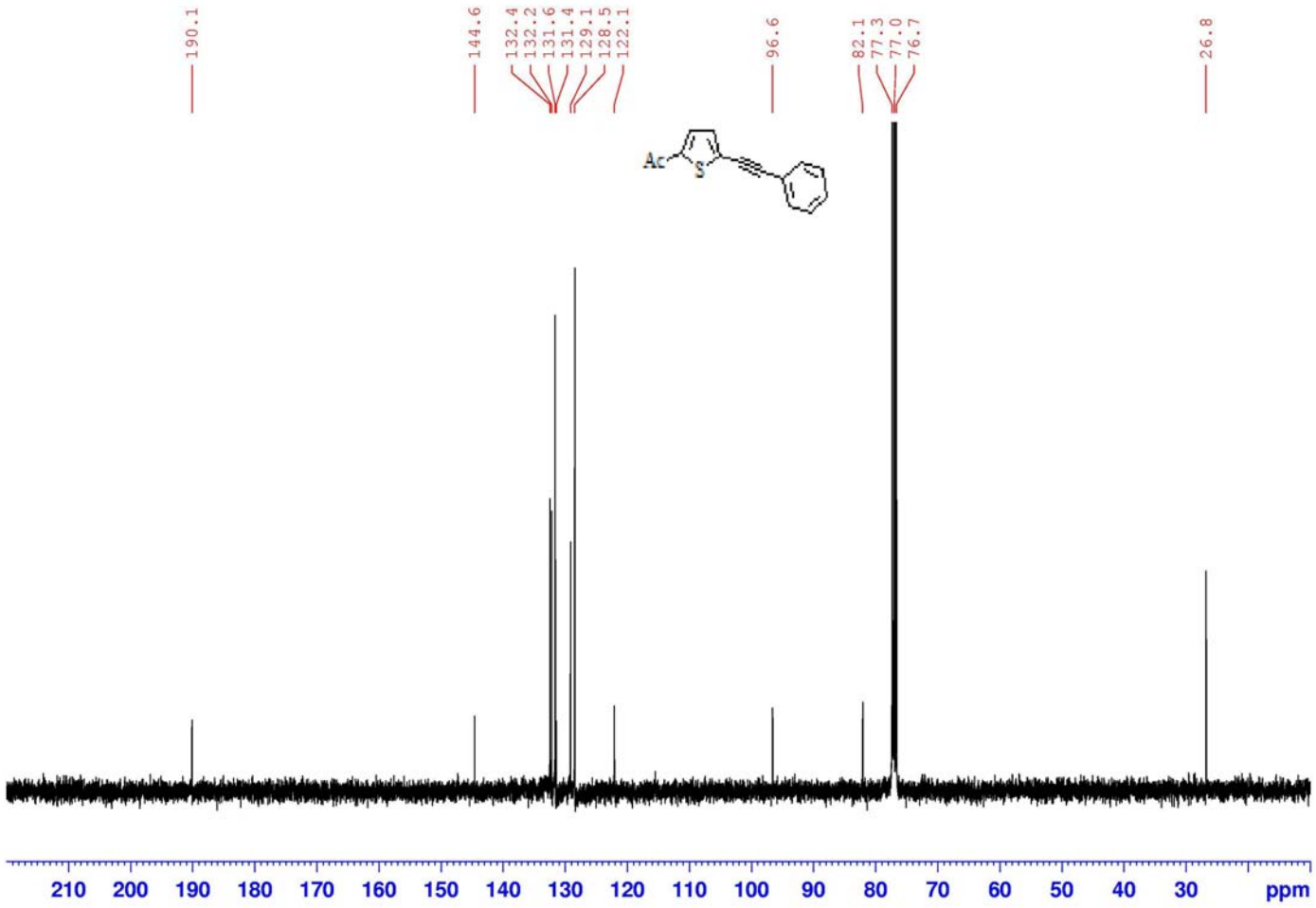
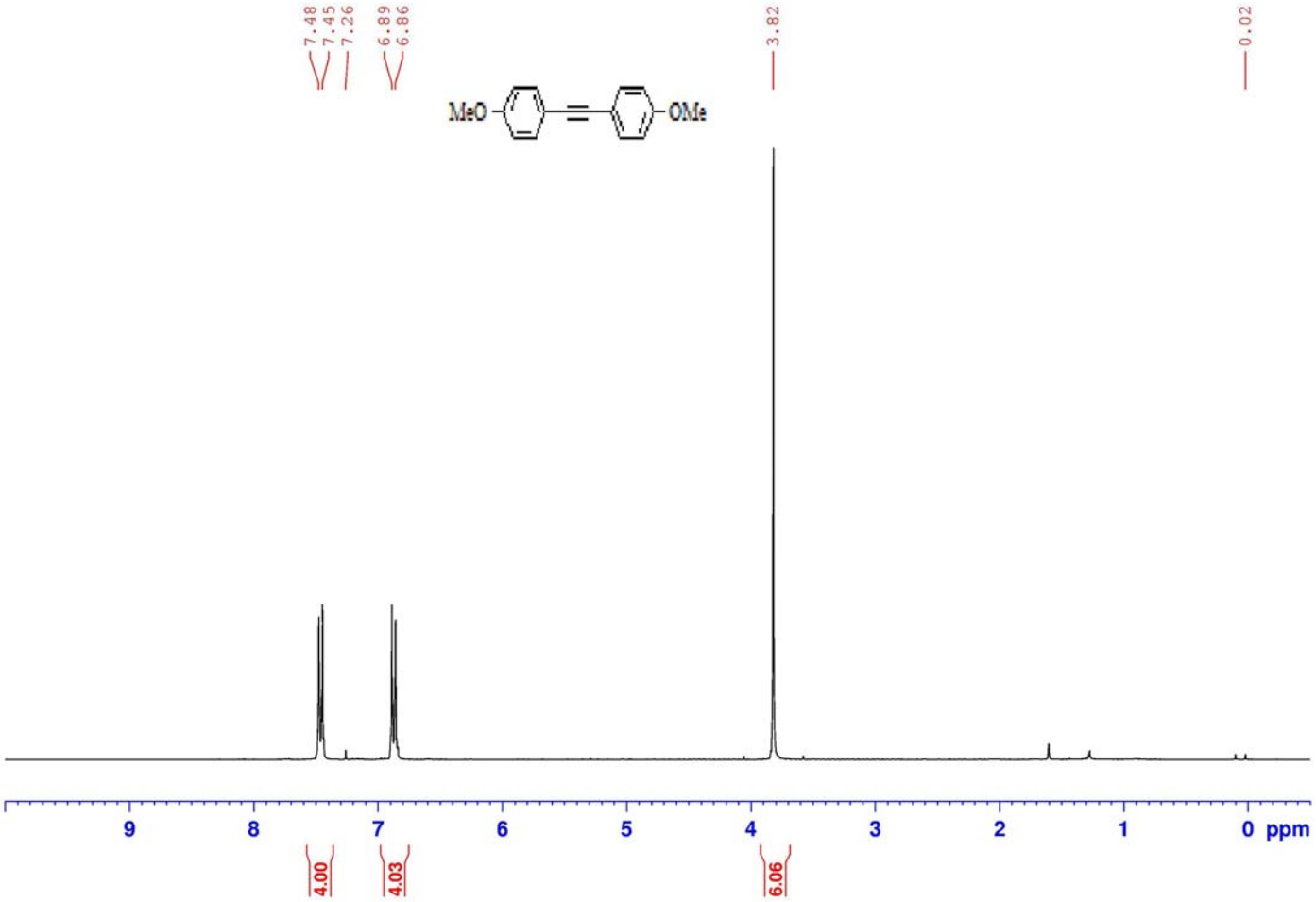
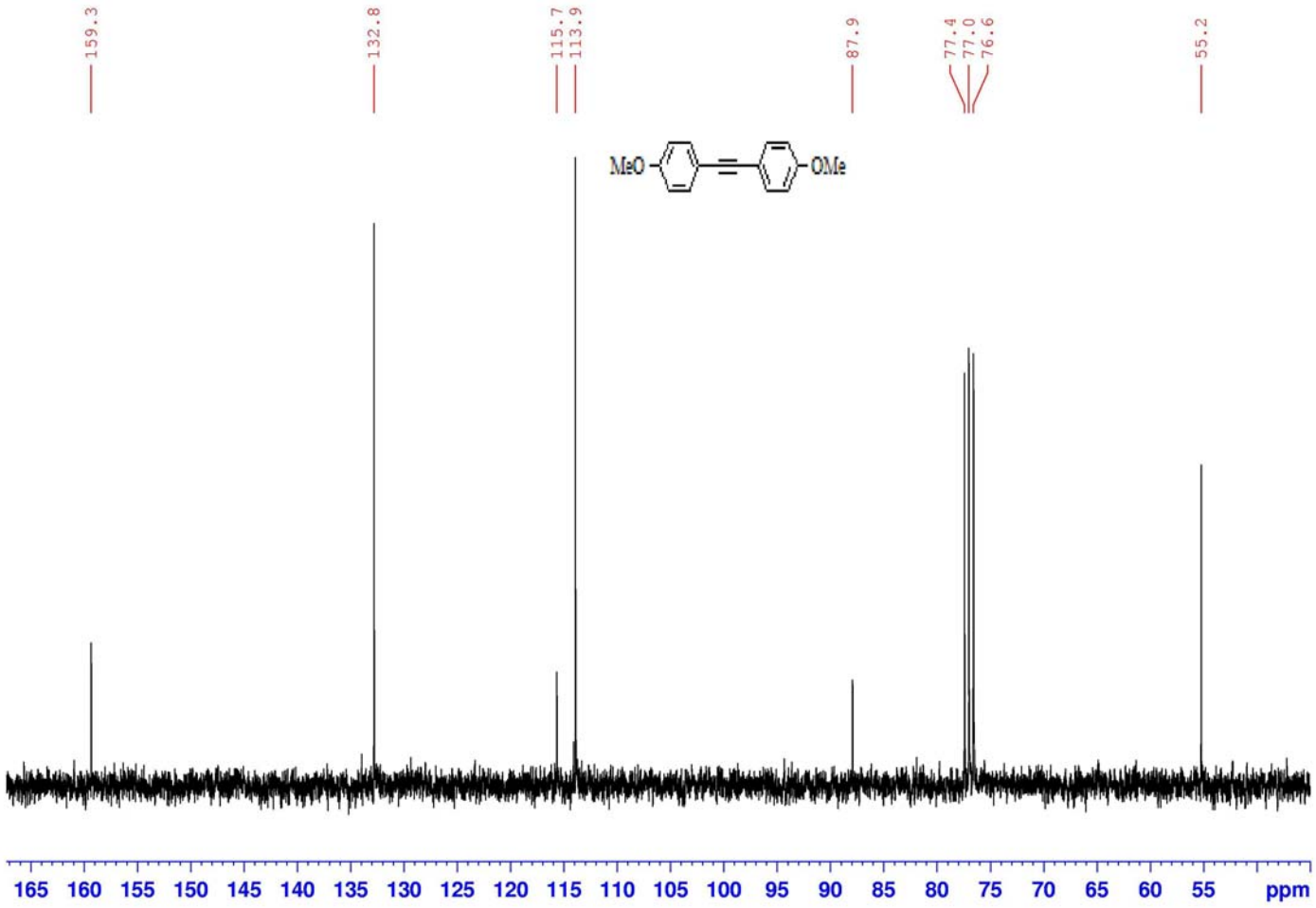
7.57
7.55
7.53
7.49
7.47
7.46
7.43
7.42
7.40
7.38
7.26
0.02
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.02
1.01
2.01
2.11
1.09
3.05

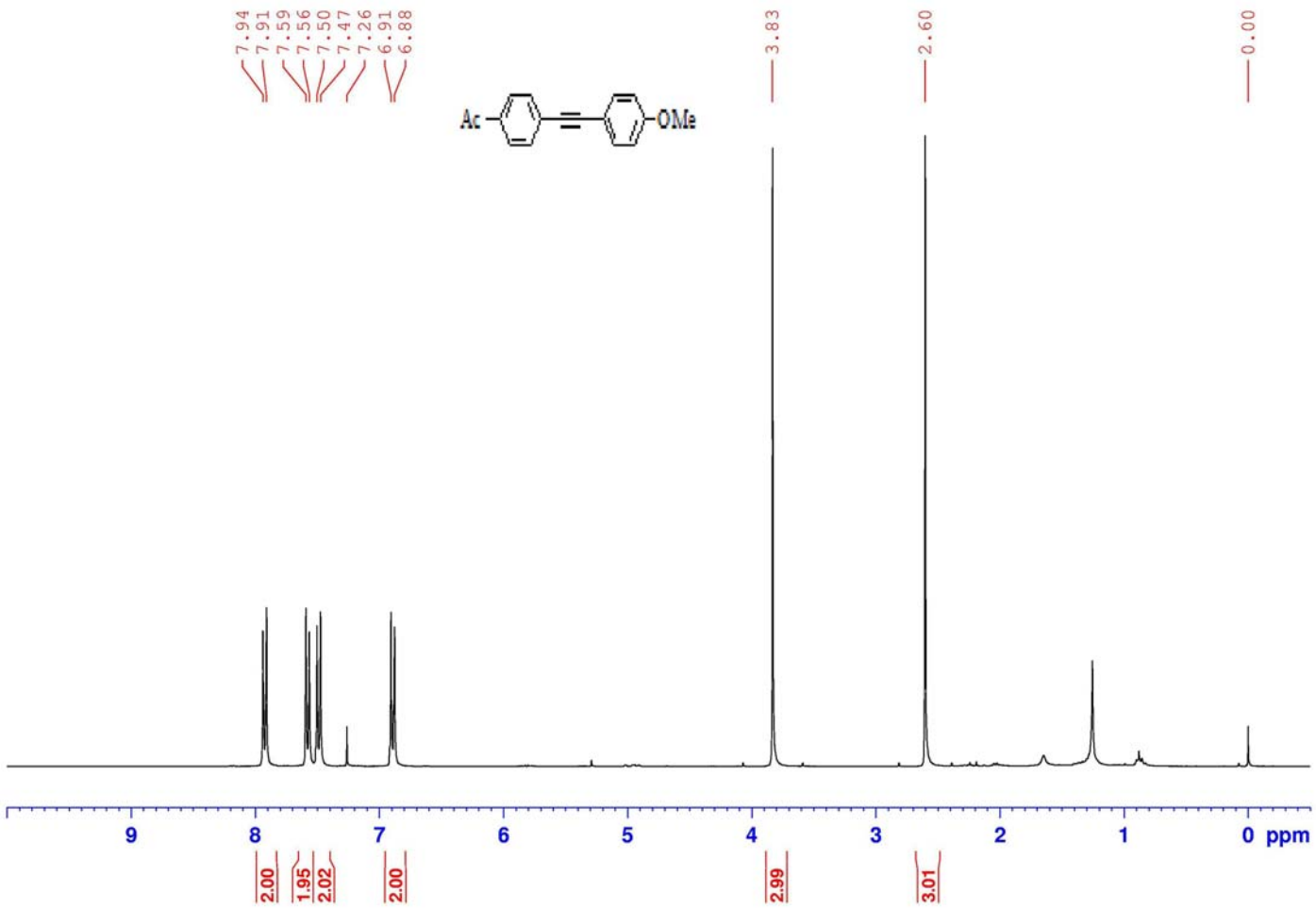

133.3
133.2
131.7
130.3
128.7
128.4
128.4
128.3
126.8
126.4
126.2
125.3
123.4
120.9
94.3
87.5
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
ppm

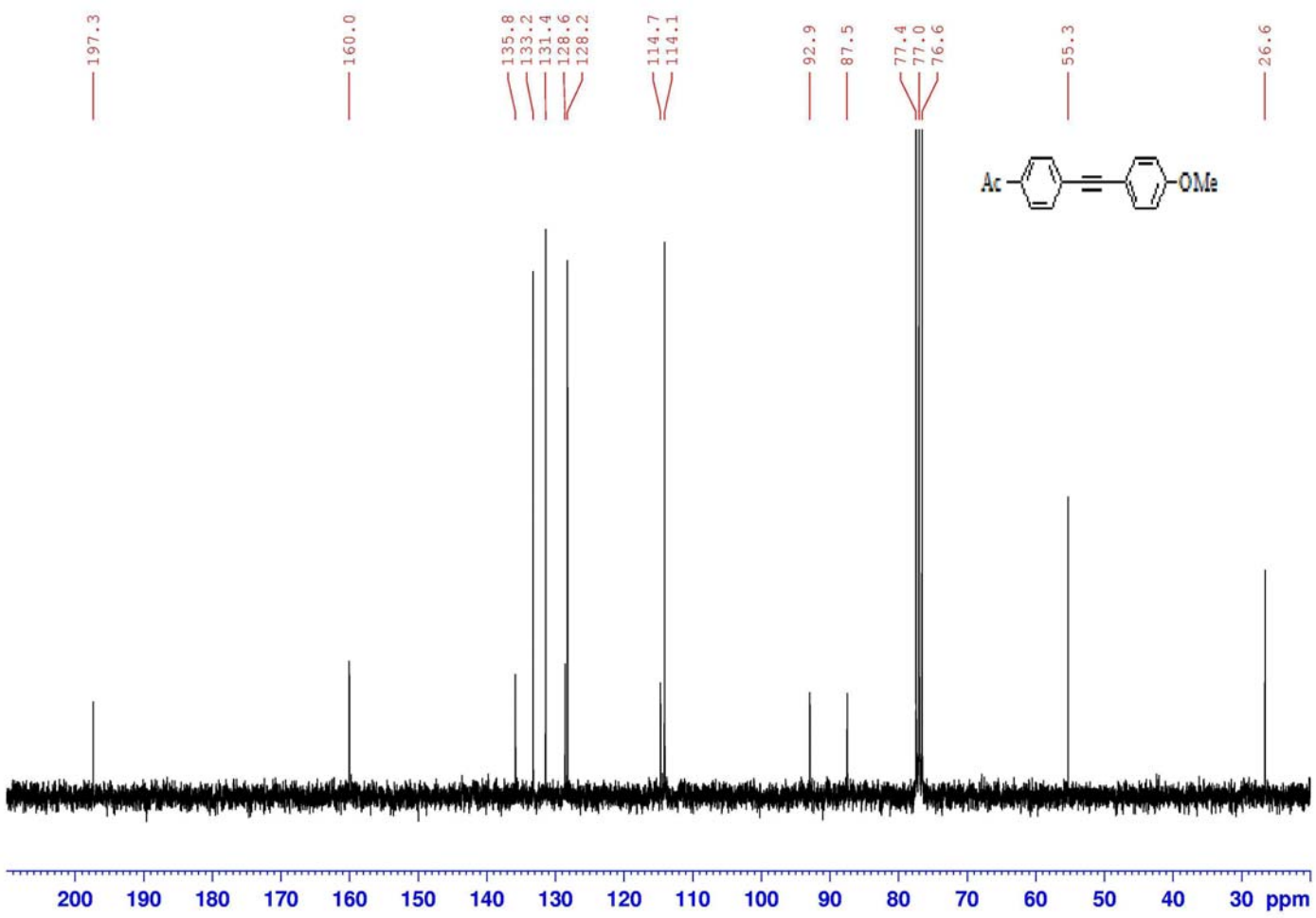

7.59
7.58
7.55
7.54
7.53
7.52
7.38
7.38
7.37
7.36
7.26
7.25
7.24
Ac
S
2.56
-0.00
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.97
2.99
0.86
3.00

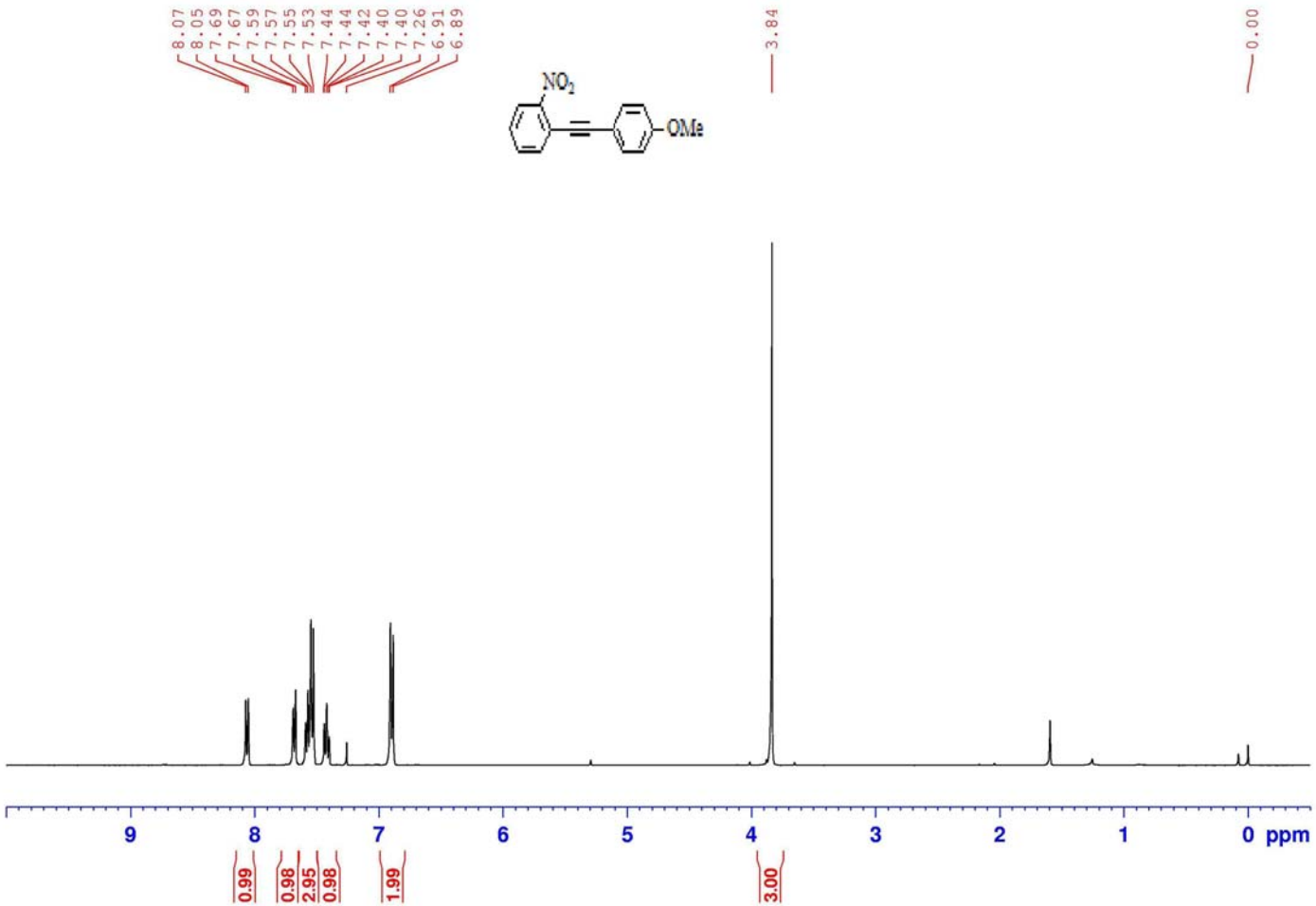

190.1
144.6
132.4
132.2
131.6
131.4
129.1
128.5
122.1
96.6
82.1
77.3
77.0
76.7
26.8
Ac
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

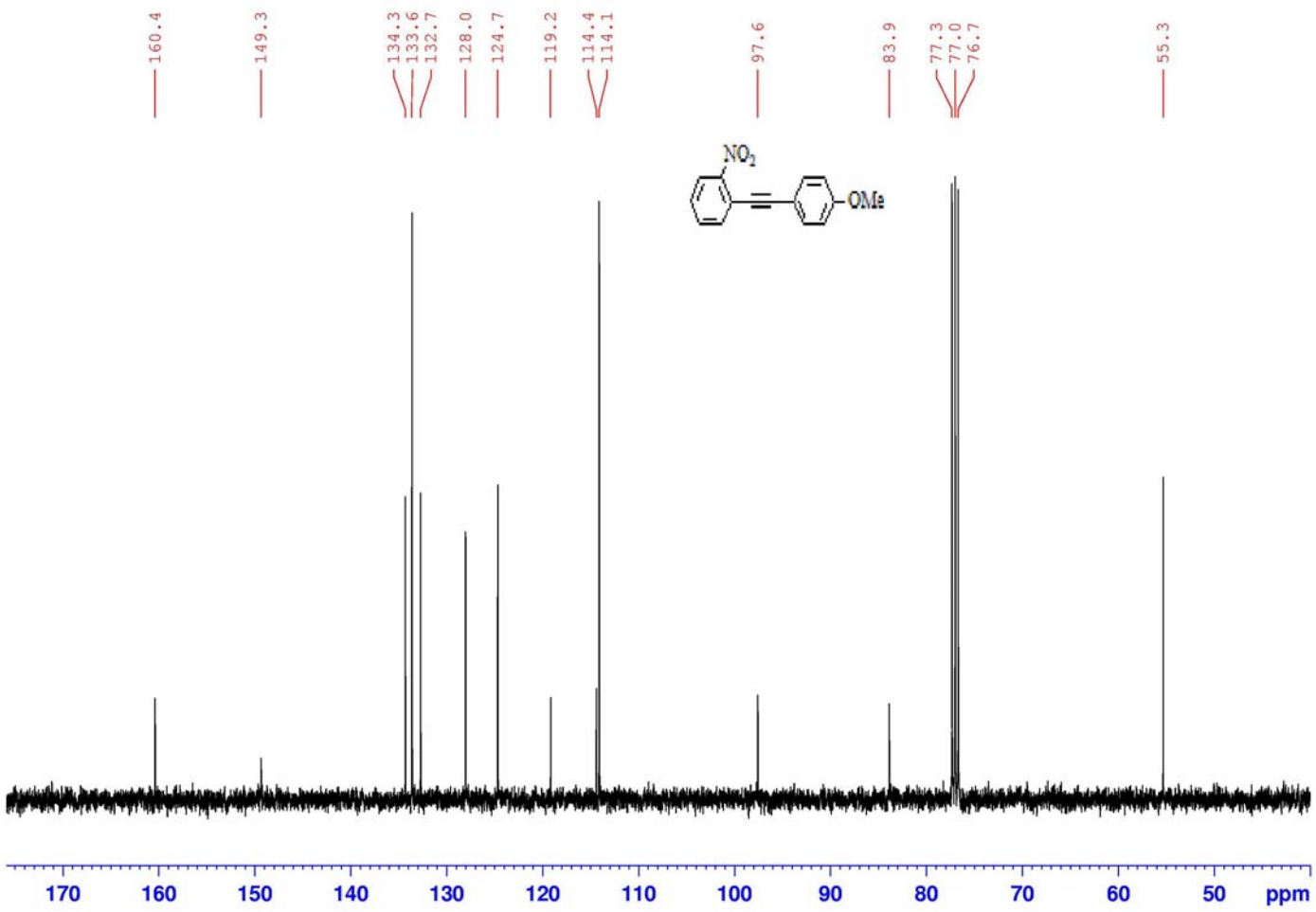

7.48
7.45
7.26
6.89
6.86
3.82
0.02
MeO
OMe
9
8
7
6
5
4
3
2
1
0 ppm
4.00
4.03
6.06

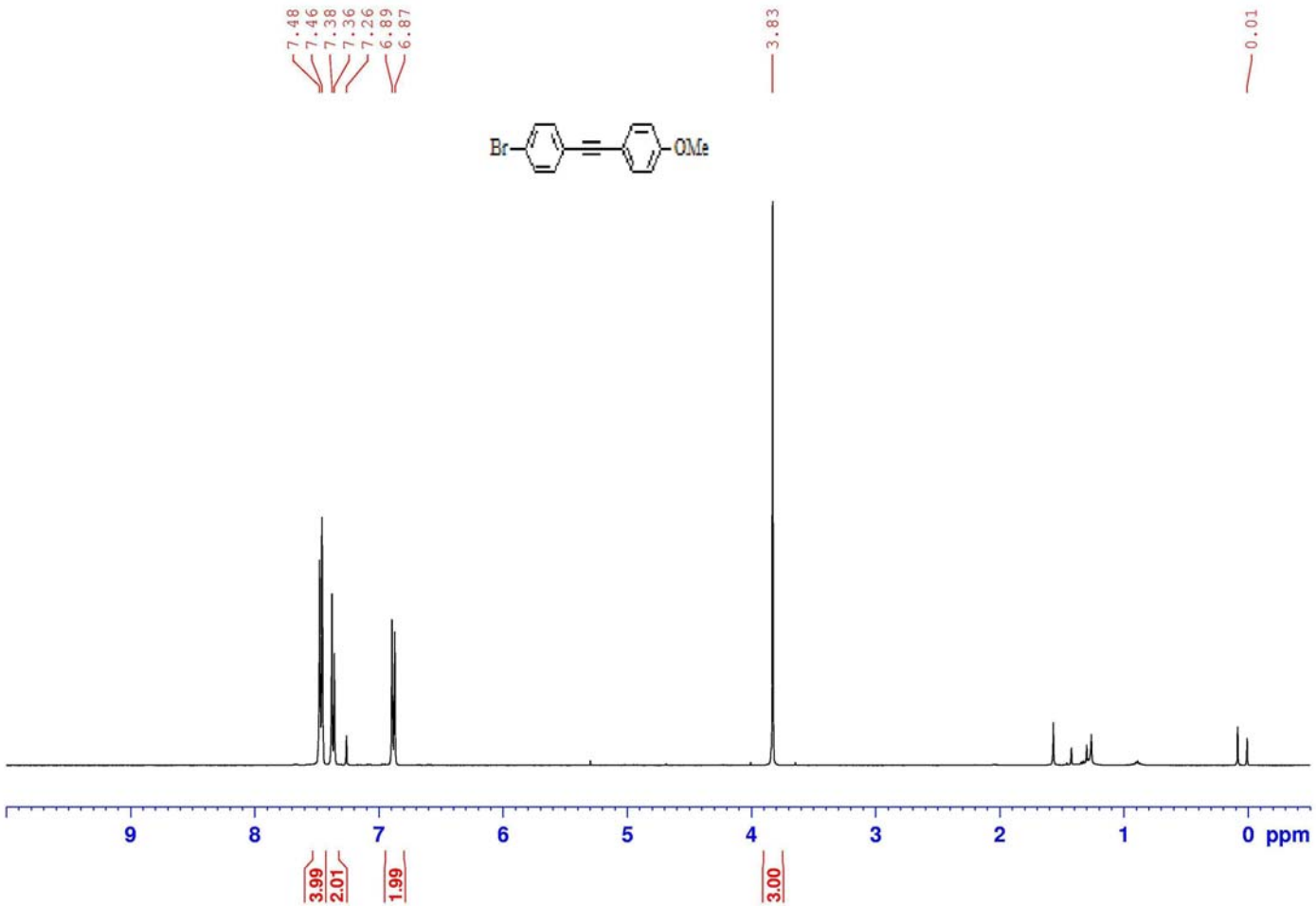

159.3
132.8
115.7
113.9
87.9
77.4
77.0
76.6
55.2
MeO
OMe
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 ppm

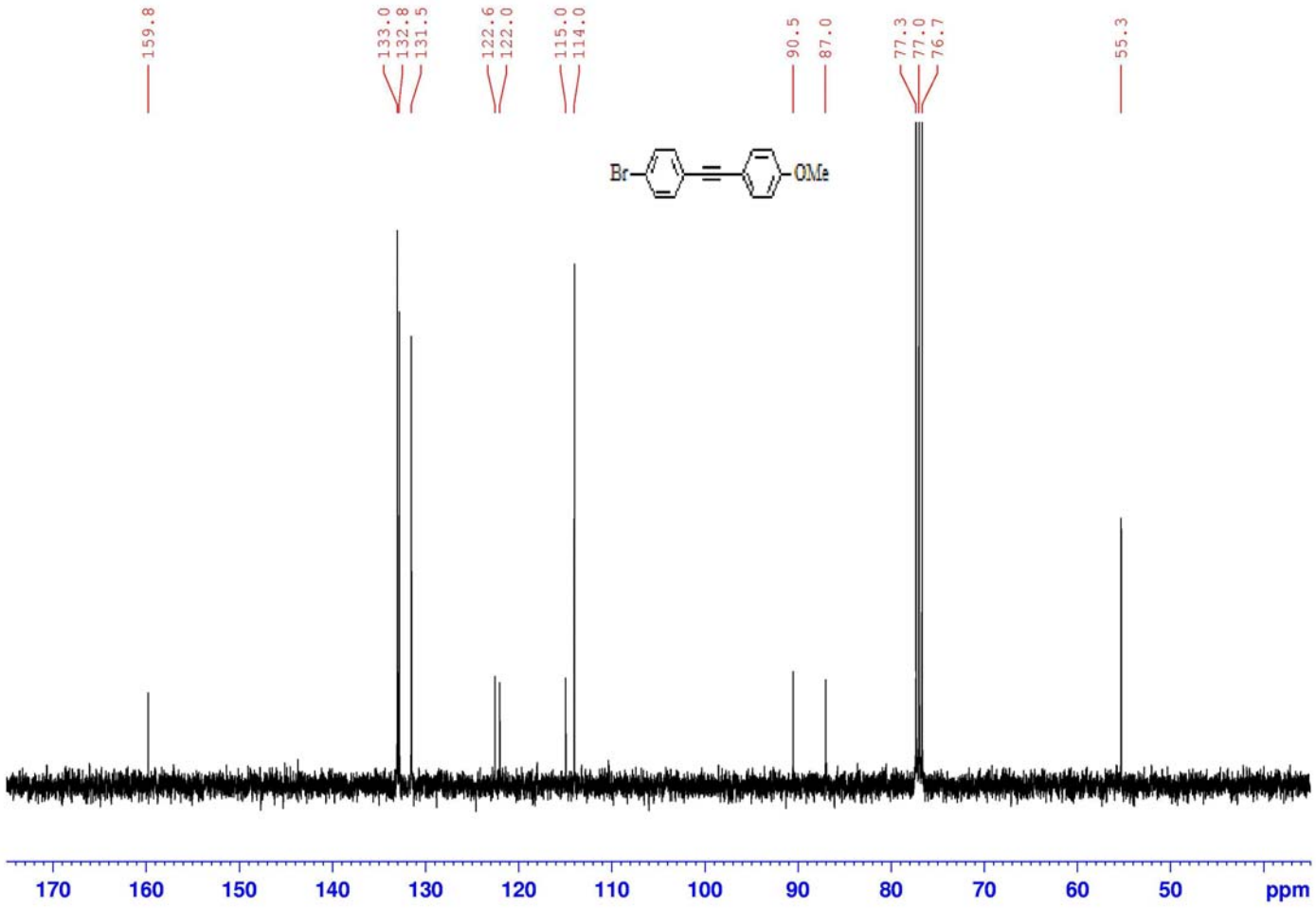

7.94
7.91
7.59
7.56
7.50
7.47
7.26
6.91
6.88
3.83
2.60
0.00
Ac
OMe
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.95
2.02
2.00
2.99
3.01

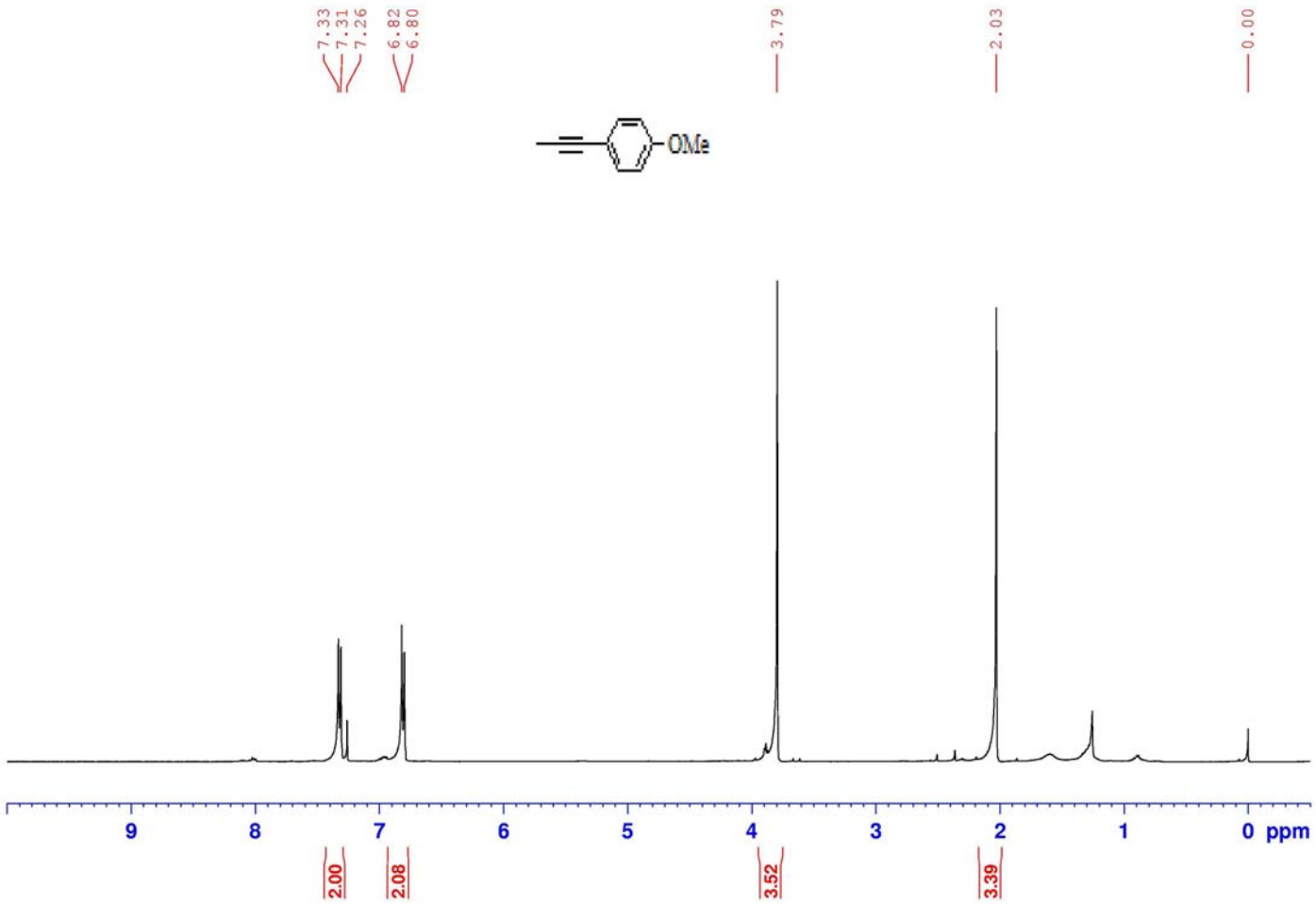

197.3
160.0
135.8
133.2
131.4
128.6
128.2
114.7
114.1
92.9
87.5
77.4
77.0
76.6
55.3
26.6
Ac
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

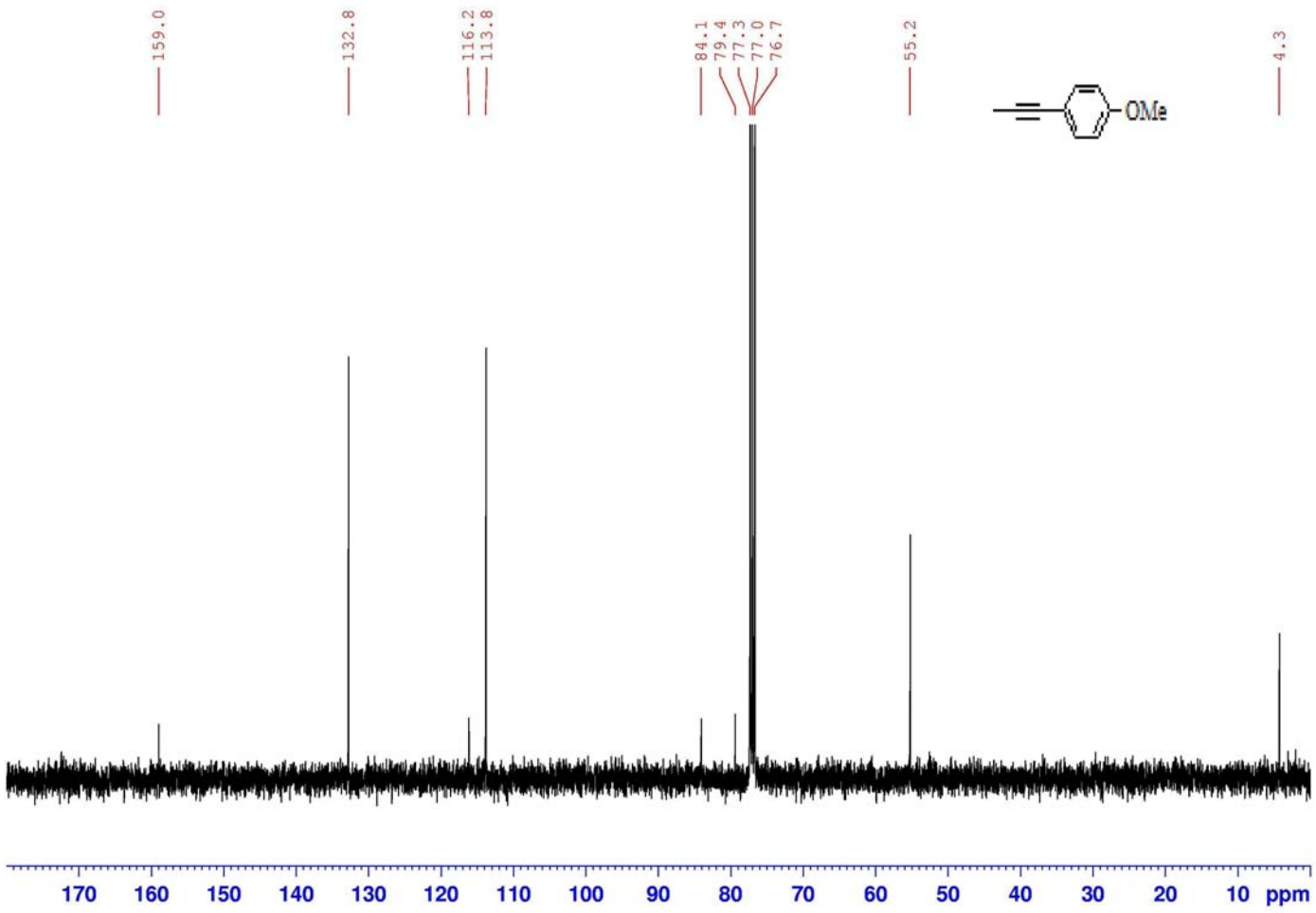

8.07
8.05
7.69
7.67
7.59
7.57
7.55
7.53
7.44
7.44
7.42
7.40
7.40
7.26
6.91
6.89
3.84
0.00
NO2
OMe
9
8
7
6
5
4
3
2
1
0 ppm
0.99
0.98
2.95
0.98
1.99
3.00

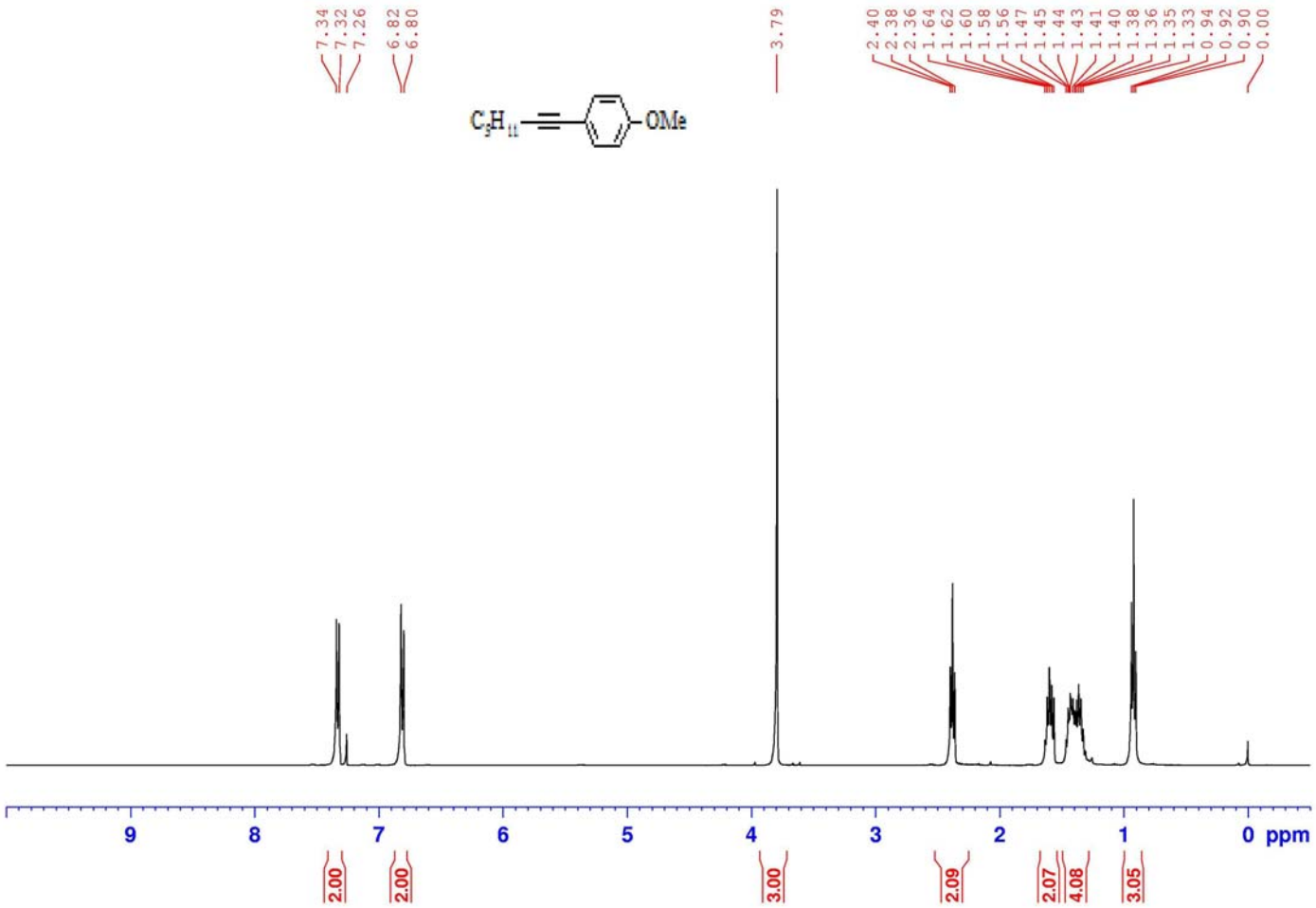

160.4
149.3
134.3
133.6
132.7
128.0
124.7
119.2
114.4
114.1
97.6
83.9
77.3
77.0
76.7
55.3
NO2
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm

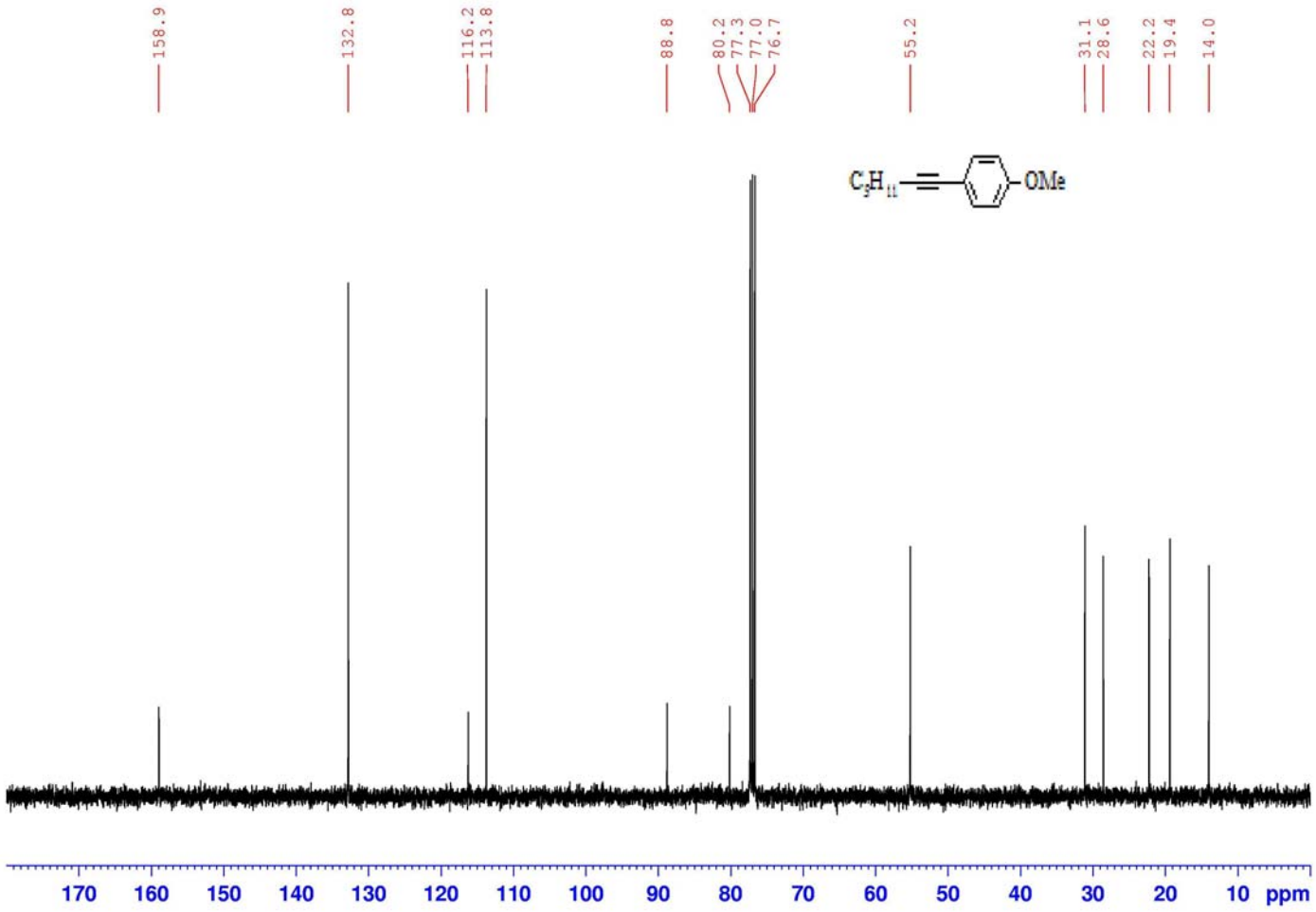

7.48
7.46
7.38
7.36
7.26
6.89
6.87
3.83
0.01
Br
OMe
9
8
7
6
5
4
3
2
1
0 ppm
3.99
2.01
1.99
3.00

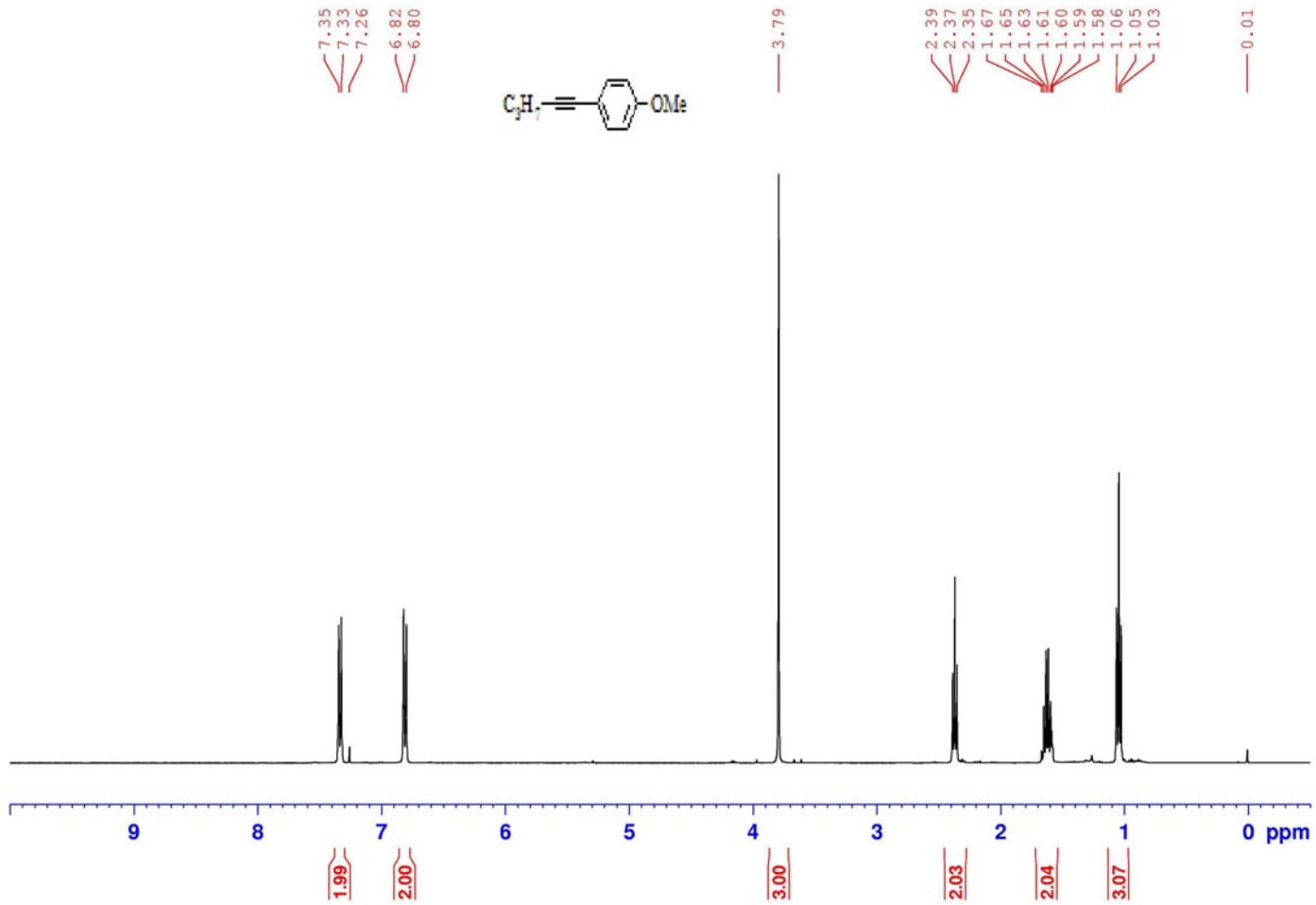

159.8
133.0
132.8
131.5
122.6
122.0
115.0
114.0
90.5
87.0
77.3
77.0
76.7
55.3
Br
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm

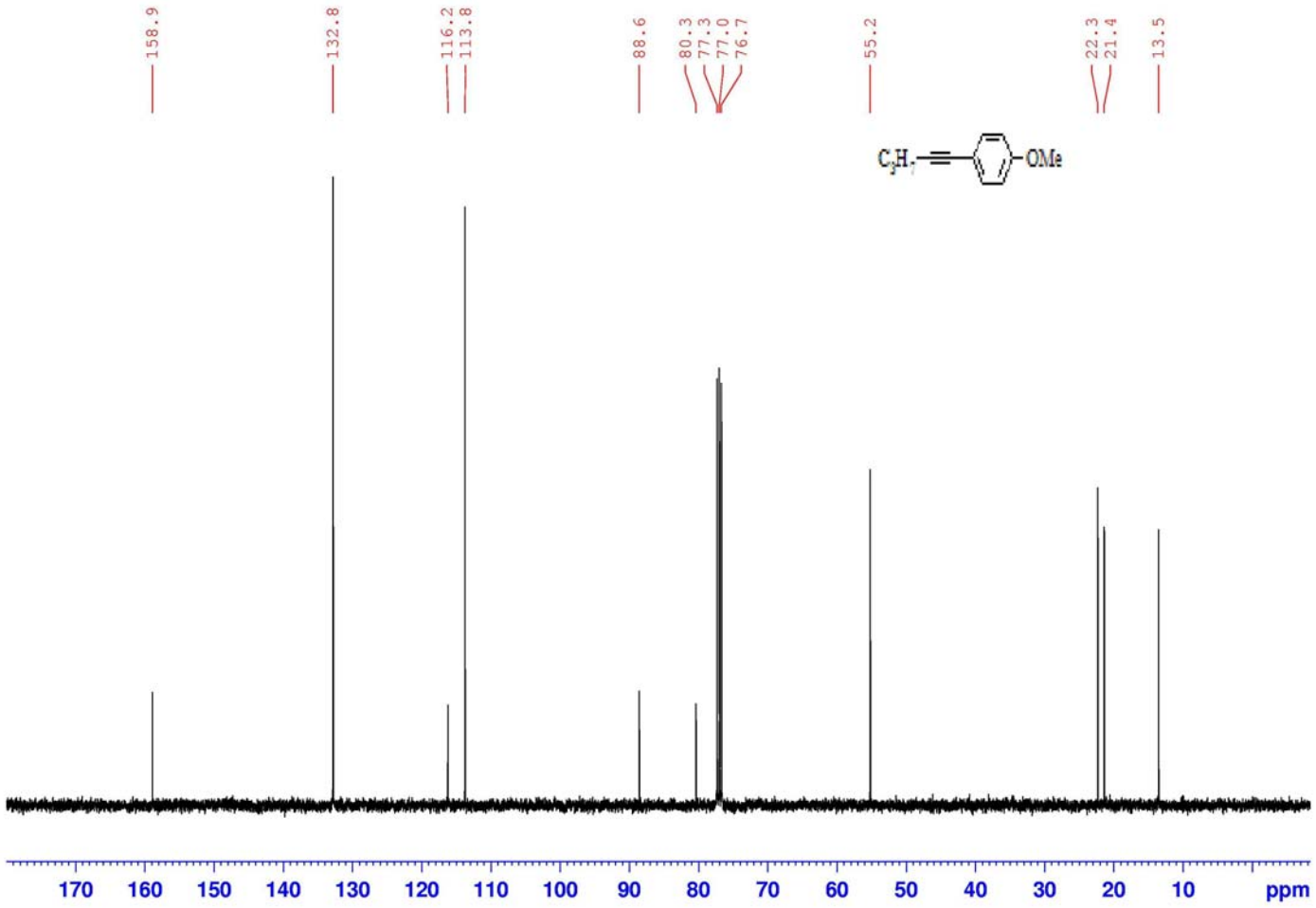

7.33
7.31
7.26
6.82
6.80
3.79
2.03
0.00
OMe
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.08
3.52
3.39

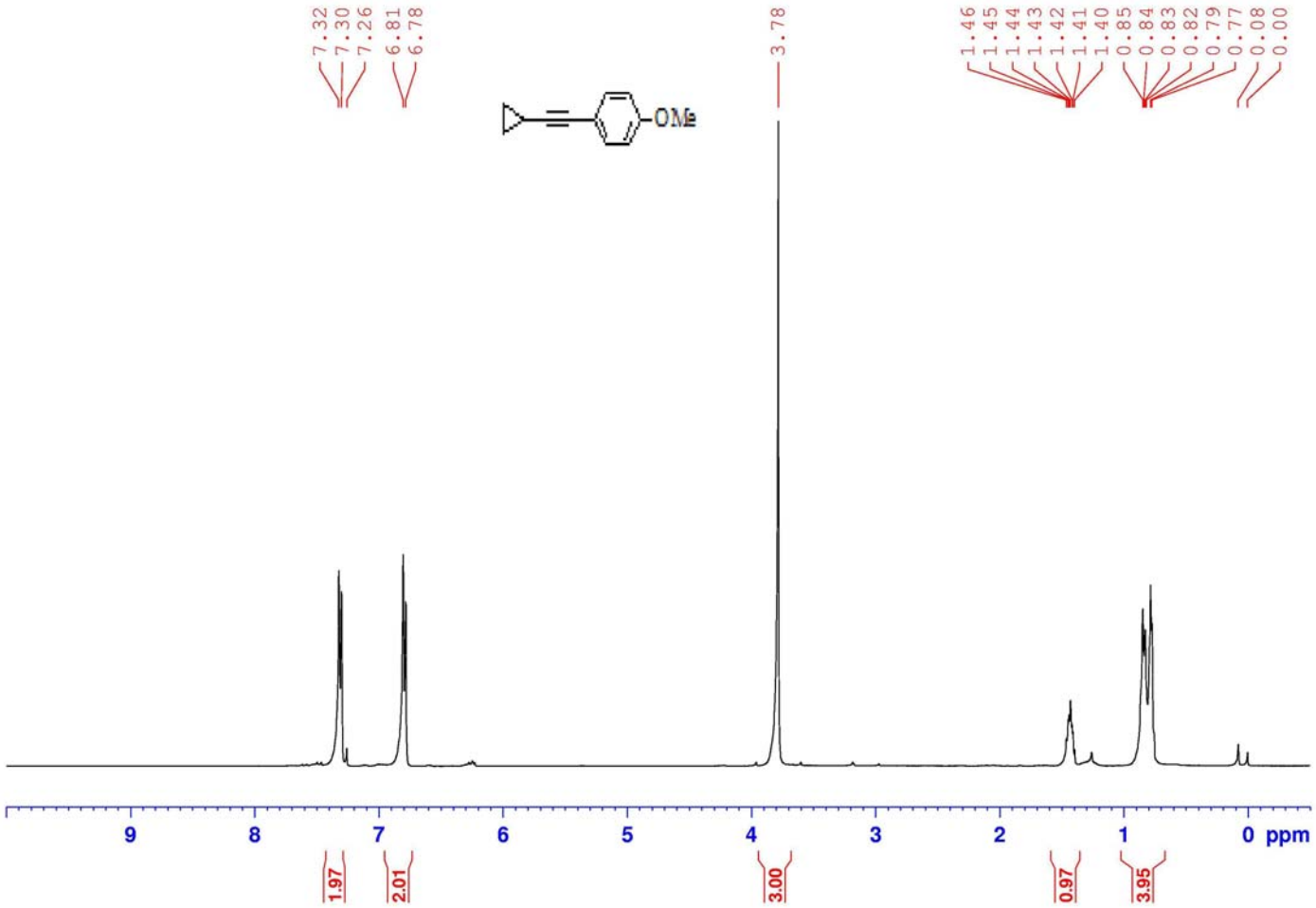

159.0
132.8
116.2
113.8
84.1
79.4
77.3
77.0
76.7
55.2
4.3
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

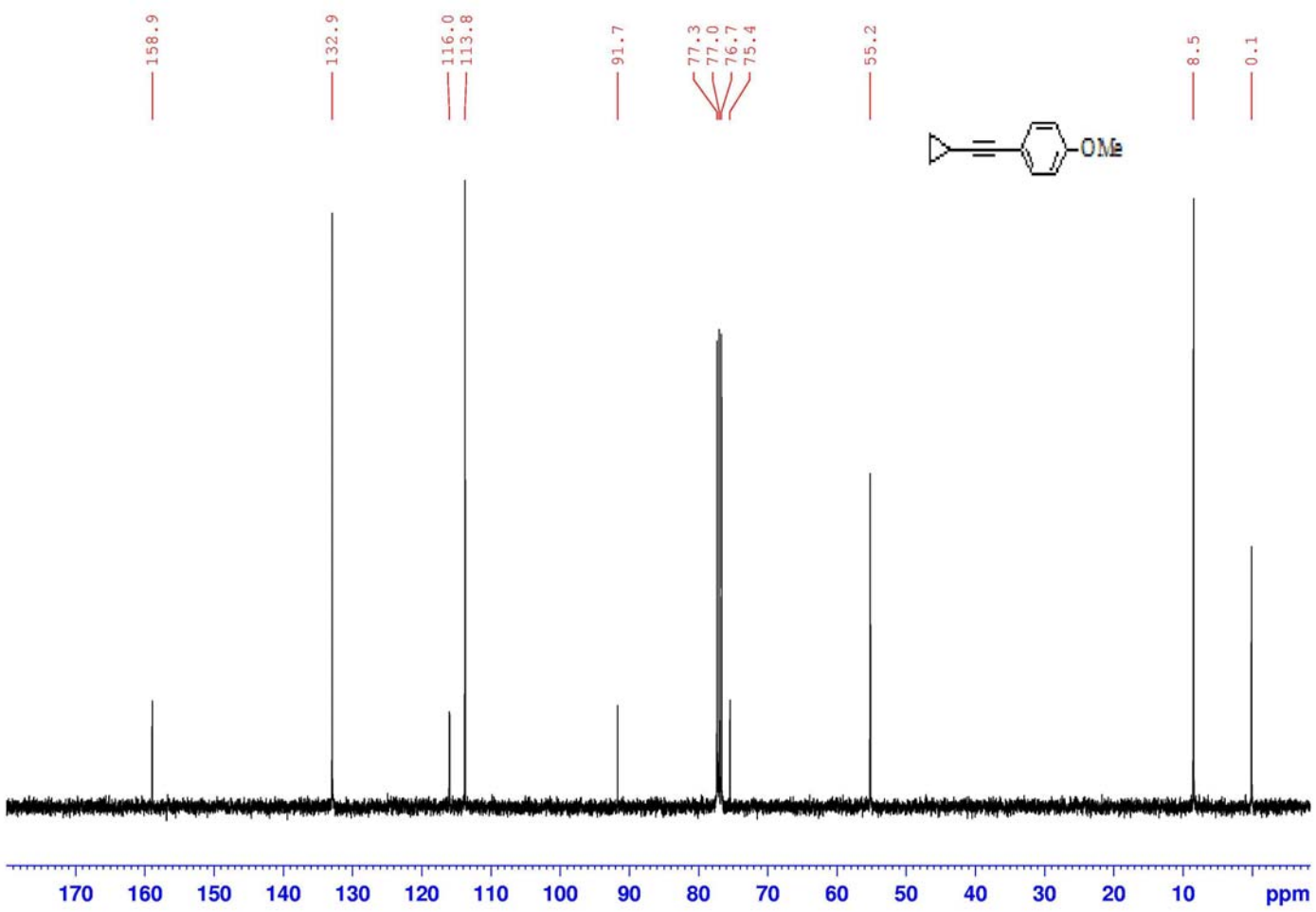

7.34
7.32
7.26
6.82
6.80
3.79
2.40
2.38
2.36
1.64
1.62
1.60
1.58
1.56
1.47
1.45
1.44
1.43
1.41
1.40
1.38
1.36
1.35
1.33
0.94
0.92
0.90
0.00
C5H11
OMe
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.00
3.00
2.09
2.07
4.08
3.05


158.9
132.8
116.2
113.8
88.8
80.2
77.3
77.0
76.7
55.2
31.1
28.6
22.2
19.4
14.0
C5H11
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.35
7.33
7.26
6.82
6.80
3.79
2.39
2.37
2.35
1.67
1.65
1.63
1.61
1.60
1.59
1.58
1.06
1.05
1.03
0.01
C5H11
OMe
9
8
7
6
5
4
3
2
1
0 ppm
1.99
2.00
3.00
2.03
2.04
3.07


158.9
132.8
116.2
113.8
88.6
80.3
77.3
77.0
76.7
55.2
22.3
21.4
13.5
C3H7
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.32
7.30
7.26
6.81
6.78
3.78
1.46
1.45
1.44
1.43
1.42
1.41
1.40
0.85
0.84
0.83
0.82
0.79
0.77
0.08
0.00
OMe
9
8
7
6
5
4
3
2
1
0 ppm
1.97
2.01
3.00
0.97
3.95


158.9
132.9
116.0
113.8
91.7
77.3
77.0
76.7
75.4
55.2
8.5
0.1
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm