

Highly Efficient and Selective Synthesis of Conjugated Triynes and Higher Oligoynes of Biological and Materials Chemical Interest via Palladium-Catalyzed Alkynyl-Alkenyl Coupling

Estelle Métay, Qian Hu, and Ei-ichi Negishi.

Supporting Information

General. All experiments were conducted under argon atmosphere. THF was dried and distilled from sodium and benzophenone. ZnBr_2 was flame-dried under vacuum prior to use. Flash chromatographic purification was carried out on 230–400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatograph using a HP-5 capillary column (30 m \times 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or acetone- d_6 on a Varian Inova-300 or a Bruker ARX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. LRMS and HRMS data were obtained on Hewlett Packard 5995 GC-MS and Kratos MS-50 mass spectrometers, respectively. (*E*)- $\text{ICH}=\text{CHCl}$,¹ (*E*)- $\text{ICH}=\text{CHCH}_2\text{OTBS}$,² (*E*)- $\text{ICH}=\text{CHCH}_2\text{OH}$,³ (*E*)- $\text{BrCH}=\text{CHCO}_2\text{Et}$ ⁴ were prepared according to the literature. Prepared compounds were stored in the freezer at -20 °C for 1 month without observing any degradation.

Representative Procedure A: (*E*)-1-Chloro-4-phenyl-1-buten-3-yne (3a).⁵ To a solution of phenylacetylene (1.02 g, 10 mmol) in THF (15 mL) was added $n\text{BuLi}$ (2.5M in hexane, 0.8 mL, 10 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and treated with a solution of anhydrous ZnBr_2 (1.35 g, 6.0 mmol) in THF (10 mL). (*E*)-1-Iodo-2-chloroethylene (1.88 g, 10 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (231 mg, 200 μmol) in THF (5 mL) were added to the reaction mixture at 0 °C, which was then stirred at 23 °C. After 1 h GLC analysis indicated that the starting material had been completely consumed. The reaction mixture was quenched with aqueous NH_4Cl , extracted with ether, washed successively with saturated NaHCO_3 and brine, dried over MgSO_4 , filtered, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 1.49 g (92%) of the title compound: colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 6.33 (d, J = 13.4 Hz, 1H), 6.77 (d, J = 13.4 Hz, 1H), 7.45-7.5 (m, 3H), 7.6-7.65 (m,

¹ Negishi, E.; Okukado, N.; Lovich, S.; Luo, F. T. *J. Org. Chem.* **1984**, *49*, 2629.

² (a) Xu, C.; Negishi, E. *Tetrahedron Lett.* **1999**, *40*, 431. (b) Huang, Z.; Negishi, E. *Org. Lett.* **2006**, *8*, 3675.

³ Yin, N.; Wang, G.; Qian, M.; Negishi, E. *Angew. Chem. Int. Ed.* **2006**, *45*, 2916.

⁴ Wier, J. R.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 4926. Pattenden, G.; Walker B. J. *J. Chem. Soc.* **1969**, 531.

⁵ Negishi, E.; Hata, M.; Xu, C. *Org. Lett.* **2000**, *2*, 3687-3689.

2H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ 84.38, 91.94, 113.78, 122.54, 128.26 (2C), 128.49, 130.06, 131.41 (2C) ppm; IR (neat) 3069, 3023, 2253, 2201, 1581, 1488 cm^{-1} ; HRMS m/z calcd for $\text{C}_{10}\text{H}_7\text{Cl}$: 162.0236; found: 162.0234.

(*E*)-1-Chloro-4-trimethylsilyl-1-buten-3-yne (3b).⁶ The title compound was prepared according to Representative Procedure A: Yield 81%; colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 0.16 (s, 9H), 5.92 (d, J = 13.5 Hz, 1H), 6.55 (d, J = 13.5 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ -0.30 (3C), 97.64, 99.60, 113.89, 131.58 ppm.

(*E*)-1-Chloro-1-penten-3-yne (3c). The title compound was prepared according to Representative Procedure A: Yield 67%; colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 1.91 (d, J = 2.3 Hz, 3H), 5.87 (dq, J = 13.5 and 2.3 Hz, 1H), 6.41 (d, J = 13.5 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ 4.01, 74.84, 88.71, 114.17, 128.74 ppm; IR (neat) 3080, 3023, 2914, 2847, 2222 cm^{-1} ; HRMS m/z calcd for $\text{C}_5\text{H}_5\text{Cl}$: 100.0080; found: 100.0080.

Representative Procedure A' (*E*)-1-Chloro-6-phenyl-1-hexene-3,5-diyne (4a). To a solution of (*E*)-1-Chloro-4-phenyl-1-butene-3-yne (1.49 g, 9.2 mmol) in THF (27 mL) was added $n\text{BuLi}$ (2.5M in hexane, 7.4 mL, 18.4 mmol) at -78 °C. The reaction mixture was first stirred -78 °C for 30 min and then at -30 °C for 30 min and treated with anhydrous ZnBr_2 (1.24 g, 5.5 mmol) in THF (10 mL). (*E*)-Iodochloroethylene (1.74g, 9.2 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (213 mg, 0.18 mmol) in THF (10 mL) were added to the reaction at 0 °C which was then stirred at 0 °C. After 6 h GLC analysis indicated that the starting material had been completely consumed. The reaction mixture was quenched with aqueous NH_4Cl , extracted with ether, washed successively with saturated NaHCO_3 and brine, dried over MgSO_4 , filtered, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 1.33 g (78%) of the title compound: mp 41-42 °C; colorless solid; ^1H NMR (CDCl_3 , 300 MHz) δ 6.15 (d, J = 13.5 Hz, 1H), 6.80 (d, J = 13.5 Hz, 1H), 7.4-7.5 (m, 3H), 7.6-7.65 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ 73.49, 76.52 (2C), 82.56, 112.91, 121.36, 128.41 (2C), 129.39, 132.48 (2C), 133.77 ppm; IR (neat) 3069, 3049, 2304, 2217, 1576, 1488, 1439 cm^{-1} ; HRMS m/z calcd for $\text{C}_{12}\text{H}_7\text{Cl}$: 186.0236; found: 186.0235.

(1*E*,5*E*)-1-Chloro-1,5-heptadien-3-yne (3d). The title compound was prepared according to Representative Procedure A' from (*E*)-1,1-dibromo-1,3-pentadiene except that the reaction mixture was

⁶ Alami, M.; Gueugnot, S.; Domingues, E.; Linstumelle, G.; *Tetrahedron* **1995**, *51*, 1209.

stirred at -78 °C for 1 h after addition of ⁿBuLi: Yield 74%; colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 1.75 (dd, *J* = 6.9 and 1.8 Hz, 3H), 5.54 (d, *J* = 15.8 Hz, 1H), 5.98 (d, *J* = 13.5 Hz, 1H), 6.12 (dq, *J* = 15.8 and 6.9 Hz, 1H), 6.43 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 18.51, 82.73, 90.84, 110.34, 113.93, 128.97, 140.29 ppm; IR (neat) 3073, 3028, 2960, 2932, 2193 cm⁻¹; HRMS *m/z* calcd for C₇H₇Cl: 126.0236; found: 126.0235.

(1*E*,5*E*)-1-(2-Furyl)-6-chloro-1,5-hexadien-3-yne (3e). The title compound was prepared according to Representative Procedure A' from 1,1-dibromo-4-(2-furyl)-1,3-butadiene except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi: Yield 70%; colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 6.0-6.2 (m, 2H), 6.3-6.35 (m, 2H), 6.49 (d, *J* = 13.5 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 7.32 (s, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 87.64, 91.65, 105.41, 110.49, 111.81, 113.95, 128.63, 129.61, 143.11, 151.87 ppm; HRMS *m/z* calcd for C₁₀H₇ClO: 178.0185; found: 178.0187.

(*E*)-1-Chloro-6-trimethylsilyl-1-hexene-3,5-diyne (4b). The title compound was prepared according to Representative Procedure A': Yield 80%; colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.19 (s, 9H), 5.95 (d, *J* = 13.5 Hz, 1H), 6.67 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -0.54 (3C), 71.64, 76.72, 87.30, 91.94, 112.60, 134.41 ppm; IR (neat) 3073, 3024, 2961, 2900, 2202, 2102 cm⁻¹; HRMS *m/z* calcd for C₉H₁₁ClSi: 182.0319; found: 180.0320.

(*E*)-1-Chloro-1-heptene-3,5-diyne (4c). The title compound was prepared according to Representative Procedure A': Yield 73%; mp 39-40 °C; colorless solid; ¹H NMR (CDCl₃, 300 MHz) δ 2.03 (s, 3H), 6.98 (d, *J* = 13.5 Hz, 1H), 6.67 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ 4.48, 63.98, 69.11, 77.00, 81.49, 112.94, 133.13 ppm; IR (neat) 3074, 3028, 2910, 2839, 2232 cm⁻¹; HRMS *m/z* calcd for C₇H₅Cl: 124.0080; found: 124.0077.

(*E*)-2-Decene-4,6,8-triyn-1-ol (5e).⁷ The title compound was prepared according to Representative Procedure A' except after except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi, and that (*E*)-ICH=CHCH₂OZnBr was used instead of (*E*)-1-iodo-2-chloroethylene: Yield 69%; mp 127-128 °C; brown solid; ¹H NMR (acetone-*d*₆, 300 MHz) δ 2.1 (s, 3H), 4.25-4.3 (m, 3H), 5.90 (d, *J* = 14.6 Hz, 1H), 6.55-6.6 (m, 1H) ppm; ¹³C NMR (acetone-*d*₆, 75 MHz) δ 3.42, 58.73, 61.48, 64.20, 66.62, 73.83, 74.56, 78.94, 105.98, 149.97 ppm; IR (CCl₄) 3680-3650, 3006, 2962, 2917, 2849, 2225, 2201 cm⁻¹; HRMS *m/z* calcd for C₁₀H₈O: 144.0575; found: 144.0576.

⁷ Mahtabuddin, A.; Keeping, J. W.; Macrides, T. A.; Thaller, V. *J. Chem. Soc. Perkin Trans I* **1978**, 12, 1487.

(*E*)-1-(*tert*-Butyldimethylsilyloxy)-2-decene-4,6,8-triyn (5f). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi, and that (*E*)-ICH=CHCH₂OTBS was used instead of (*E*)-1-iodo-2-chloroethylene: Yield 71%; mp 50-51 °C; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 0.12 (s, 6H), 0.96 (s, 9H), 2.03 (s, 3H), 4.31 (dd, *J* = 3.5 and 1.7 Hz, 2H), 5.85 (dt, *J* = 15.8 and 1.7 Hz, 1H), 6.75 (dt, *J* = 15.7 and 3.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -5.56 (2C), 4.51, 18.21, 25.71 (3C), 59.03, 62.65, 64.90, 66.84, 74.02, 74.70, 77.87, 106.65, 147.66 ppm; IR (CCl₄) 2956, 2945, 2885, 2857, 2224, 2201, 2183 cm⁻¹; HRMS *m/z* calcd for C₁₆H₂₂OSi: 258.1440; found: 258.1439.

Ethyl (*E*)-2-Decene-4,6,8-triynoate (5g). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi, and that (*E*)-BrCH=CHCO₂Et was used instead of (*E*)-1-iodo-2-chloroethylene: Yield 68%; mp 64-65 °C; yellow solid; ¹H NMR (CDCl₃, 400 MHz) δ 1.23 (t, *J* = 7.1 Hz, 3H), 1.95 (s, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 4.69, 14.07, 58.06, 60.99, 64.6, 70.88, 71.55, 80.46, 82.75, 123.22, 134.03, 165.17 ppm; IR (CCl₄) 2983, 2939, 2915, 2873, 2225, 2178, 1717 cm⁻¹; HRMS *m/z* calcd for C₁₂H₁₀O₂: 186.0681; found: 186.0682.

(*E*)-1-Chloro-8-phenyl-1-octene-3,5,7-triyn (6a). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi: Yield 74%; mp 61-62°C; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 6.00 (d, *J* = 13.5 Hz, 1H), 6.74 (d, *J* = 13.5 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.55 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 65.94, 67.54, 73.55, 74.22, 77.00, 79.25, 112.32, 120.57, 128.40 (2C), 129.72, 132.89 (2C), 135.56 ppm; IR (neat) 3075, 2196, 2175, 1573, 1490 cm⁻¹; HRMS *m/z* calcd for C₁₄H₇Cl: 210.0236; found: 210.0236.

(*E*)-1-Chloro-8-trimethylsilyl-1-octene-3,5,7-triyn (6b). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi: Yield 76%; yellow oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.19 (s, 9H), 5.95 (d, *J* = 13.5 Hz, 1H), 6.73 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -0.62 (3C), 60.94, 67.79, 71.75, 76.83, 87.72, 89.83, 112.26, 135.95 ppm; IR (neat) 3072, 3023, 2962, 2899, 2167, 2079 cm⁻¹; HRMS *m/z* calcd for C₁₁H₁₁ClSi: 206.0319; found: 206.0321.

(*E*)-1-Chloro-1-nonene-3,5,7-triyn (6c). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of

ⁿBuLi: Yield 63%; mp 95-96 °C; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 1.97 (s, 3H), 6.93 (d, *J* = 13.5 Hz, 1H), 6.70 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 4.58, 58.33, 64.59, 68.30, 70.09, 76.89, 78.99, 112.29, 135.15 ppm; IR (CCl₄): 3074, 3024, 2915, 2842, 2226 cm⁻¹; HRMS *m/z* calcd for C₉H₅Cl: 148.0080; found: 148.0079.

(2*E*, 10*E*)-1-(*tert*-Butyldimethylsilyloxy)-2,10-diene-4,6,8-dodecatriyne (8). The title compound was prepared according to Representative Procedure A' except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi, and that (*E*)-ICH=CHCH₂OTBS was used instead of (*E*)-1-iodo-2-chloroethylene: Yield 71%; colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.81 (dd, *J* = 6.3 and 1.8 Hz, 3H), 4.24 (dd, *J* = 6.3 and 1.8 Hz, 2H), 5.52 (dd, *J* = 15.9 and 1.8 Hz, 1H), 5.81 (td, *J* = 15.3 and 2.1 Hz, 1H), 6.3-6.45 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -5.51 (2C), 18.21, 18.97, 25.74 (3C), 62.68, 65.49, 66.16, 72.87, 74.67, 76.92, 77.56, 106.73, 109.31, 145.53, 147.74 ppm; HRMS *m/z* calcd for C₁₈H₂₄OSi: 284.1596; found: 284.1598.

(1*E*,7*E*)-1-Chloro-1,7-nonadiene-3,5-diyne (9). The title compound was prepared according to Representative Procedure A', except that the reaction mixture was stirred at -78 °C for 1 h after addition of ⁿBuLi; Yield 68%; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 1.81 (dd, *J* = 6.9 and 1.8 Hz, 3H), 5.54 (d, *J* = 15.9 Hz, 1H), 5.99 (d, *J* = 13.5 Hz, 1H), 6.32 (dq, *J* = 15.9 and 6.9 Hz, 1H), 6.62 (d, *J* = 13.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 18.92, 71.81, 75.38, 76.68, 81.79, 109.55, 113.01, 133.25, 144.39 ppm; IR (neat): 3076, 3030, 2923, 2851, 2201 cm⁻¹; HRMS *m/z* calcd for C₉H₇Cl: 150.0236; found: 150.0239.

Representative Procedure B, 1-Phenyl-1,3-pentadiyne.¹ To a solution of (*E*)-1-Chloro-4-phenyl-1-butene-3-yne (324 mg, 2 mmol) in THF (20 mL) was added ⁿBuLi (2.5M in hexane, 1.6 mL, 4 mmol,) at -78 °C, the reaction was stirred at -78 °C for 1 h. Iodomethane (852 mg, 6 mmol) was then added to the reaction mixture which was warmed at 23 °C and kept at this temperature overnight. The reaction mixture was quenched with aqueous NH₄Cl, extracted with ether, washed successively with saturated NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 257 mg (92%) of the title compound: colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 1.82 (s, 3H), 7.3-7.35 (m, 3H), 7.45-7.5 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 4.43, 64.28, 74.02, 74.38, 80.28, 121.89, 128.23, 128.74, 132.38 ppm.

1,7-Diphenyl-2,4,6-heptatriyn-1-ol (5a).⁸ The title compound was prepared according to Representative Procedure B except that benzaldehyde (1.2 eq) was used instead of iodomethane: Yield 86%; red brown oil; ¹H NMR (CDCl₃, 300 MHz) δ 3.29, (bs, 1H), 5.52 (s, 1H), 7.3-7.6 (m, 10H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 64.20, 64.79, 65.83, 71.41, 74.11, 77.59, 79.05, 120.46, 126.61 (2C), 128.37 (2C), 128.68 (3C), 129.72, 132.89 (2C), 139.01 ppm; IR (neat) 3652-3090, 3064, 3033, 2976, 2874, 2191, 1600, 1491 cm⁻¹; HRMS m/z calcd for C₁₉H₁₂O: 256.0888; found: 256.0888.

1-(*tert*-Butyldimethylsilyl)-6-phenyl-1,3,5-hexatriyne (5b). The title compound was prepared according to representative Procedure B except that TBSCl (1.2 eq) was used instead of iodomethane: Yield 80%; colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.18 (s, 6H), 0.98 (s, 9H), 7.3-7.35 (m, 3H), 7.5-7.55 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -4.97 (2C), 16.79, 25.95 (3C), 61.18, 67.01, 74.29, 76.74, 87.85, 88.68, 120.75, 128.45 (2C), 129.73, 133.02 (2C) ppm; IR (neat) 2954, 2929, 2884, 2858, 2175, 2075, 1595, 1490 cm⁻¹; HRMS m/z calcd for C₁₈H₂₀Si: 264.1334; found: 264.1336.

1-Phenyl-1,3,5-heptatriyne (5c).⁹ The title compound was prepared according to Representative Procedure B: Yield 94%; mp 57-58 °C; colorless solid; ¹H NMR (CDCl₃, 300 MHz) δ 1.99 (s, 3H), 7.3-7.4 (m, 3H), 7.5-7.52 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 4.50, 58.89, 64.84, 67.43, 74.50, 75.15, 78.35, 120.89, 128.35 (2C), 129.42, 132.79 (2C) ppm; IR (CCl₄) 3064, 3038, 2217, 1491, 1439 cm⁻¹; HRMS m/z calcd for C₁₃H₈: 164.0626; found: 164.0625.

1-Trimethylsilyl-1,3,5-heptatriyne (5d).¹⁰ The title compound was prepared according to Representative Procedure B: Yield 81%; yellow oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.19 (s, 9H), 1.96 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -0.54 (3C), 4.51, 59.26, 62.51, 64.70, 76.56, 85.14, 88.31 ppm; IR (neat) 2900, 2842, 2218, 2169, 2082 cm⁻¹; HRMS m/z calcd for C₁₀H₁₂Si: 160.0708; found: 160.0707.

1-Phenyl-1,3,5,7-nonatetrayne (7a). The title compound was prepared according to Representative Procedure B: Yield 82%; mp 83-84 °C (decomposition); yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 2.07 (s, 3H), 7.35-7.45 (m, 3H), 7.55-7.6 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 4.70, 59.68, 60.18, 64.76, 64.96, 67.57, 74.47, 75.96, 77.87, 120.58, 128.49 (2C), 129.87, 133.18 (2C) ppm; IR (CCl₄) 3053, 3038, 2222, 1491, 1441 cm⁻¹; HRMS m/z calcd for C₁₅H₈: 188.0626; found: 188.0628.

⁸ Morisaki, Y.; Luu, T.; Tykwinski, R. R. *Org. Lett.* **2006**, *8*, 689.

⁹ Fiandanese, V.; Bottalico, D.; Marchese, G.; Punzi, A. *Tetrahedron* **2006**, *62*, 5126.

¹⁰ Mukai, C.; Miyakoshi, N.; Hanaoka, M. *J. Org. Chem.* **2001**, *66*, 5875.

1-Trimethylsilyl-8-phenyl-1,3,5,7-octatetrayne (7b). The title compound was prepared according to Representative Procedure B except that chlorotrimethylsilane (1.2 eq) was used instead of iodomethane: Yield 84%; colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 0.34 (s, 9H), 7.4-7.51 (m, 3H), 7.6-7.65 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ -0.46 (3C) 61.84, 62.15, 64.00, 67.12, 74.31, 76.86, 87.89, 88.76, 120.20, 128.49 (2C), 130.00, 133.18 (2C) ppm; IR (neat) 2961, 2899, 2195, 2132, 2059, 1491, 1442 cm^{-1} ; HRMS m/z calcd for $\text{C}_{17}\text{H}_{14}\text{Si}$: 246.0865; found: 246.0867.

(*E*)-1,1-Dibromo-1,3-pentadiene.¹¹ This experiment was carried out in the dark by covering the reaction flask with aluminum foil. To a solution of (*E*)-crotonaldehyde (0.41 mL, 5.0 mmol) and tetrabromomethane (3.32 g, 10 mmol) in CH_2Cl_2 (30 mL) was added PPh_3 (5.24 g, 20 mmol) in several portions at 0 °C over a period of 3 min, and the bright orange mixture was stirred for 10 min at 0 °C. The reaction mixture was diluted with pentane (200 mL), filtered through a layer of silica gel and concentrated. Purification by column chromatography (silica gel, pentane) afforded 960 mg (85%) of the title compound: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 1.75 (dd, J = 1.5 and 6.8 Hz, 3H), 5.85-5.95 (m, 1H), 6.0-6.1 (m, 1H), 6.86 (d, J = 10.0 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz, ppm) δ 18.51 88.15, 128.41, 133.99, 136.89 ppm.

(*E*)-1,1-Dibromo-4-(2-furyl)-1,3-butadiene. The title compound was prepared according to preceding Procedure: Yield 74%; ^1H NMR (CDCl_3 , 300 MHz) δ 6.35-6.4 (m, 2H), 6.43 (d, J = 15.5 Hz, 1H), 6.63 (dd, J = 10.5 and 15.5 Hz, 1H), 6.98 (d, J = 10.5 Hz, 1H), 7.39 (s, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ 91.28, 110.77, 111.95, 122.45, 123.40, 136.66, 143.08, 152.15 ppm; HRMS m/z calcd for $\text{C}_8\text{H}_6\text{Br}_2\text{O}$: 275.8785; found: 275.8786.

1,1-Dibromo-4-phenyl-1-buten-3-yne.¹² To a solution of phenylacetylene (3.06 g, 30 mmol) in dry THF (50 mL) was added $n\text{BuLi}$ (2.5 M in hexane, 12 mL, 30 mmol) at -78 °C. After 30 min, dry DMF (6.6 g, 90 mmol) was added at -78 °C, and the reaction mixture was warm to 23 °C. After 1 h of stirring, the mixture was poured into a vigorously stirred biphasic solution prepared from a 10% aqueous solution of KH_2PO_4 and ether cooled at 0 °C. The organic extract was washed with water, dried over MgSO_4 , filtered, and

¹¹ Bailly, L.; Waldmann, H. *Chem. Eur. J.* **2004**, *10*, 2759.

¹² Kuroda, H.; Hanaki, E.; Izawa, H.; Kano, M.; Itahashi, H. *Tetrahedron* **2004**, *60*, 1913. Uenishi, J.; Kawahama, R.; Yonemitsu, O. *J. Org. Chem.* **1996**, *61*, 5716.

concentrated. In another flask, a mixture of tetrabromomethane (16.6 g, 50 mmol) and PPh₃ (26.2 g, 100 mmol) in CH₂Cl₂ (150 mL) was stirred at 0 °C for 20 min. To this were added consecutively 2,6-lutidine (6.7 g, 62.5 mmol) and a solution of 3-phenylpropionaldehyde generated above (3.2 g) in CH₂Cl₂ at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and poured into pentane. After filtration through a layer of silica gel and concentration, purification by column chromatography (silica gel, pentane) afforded 6.86 g (79% from phenylacetylene) of the title compound: yellow oil; ¹H NMR (CDCl₃, 300 MHz) δ 6.79 (s, 1H), 7.3-7.4 (m, 3H), 7.5-7.55 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 86.17, 97.13, 101.81, 119.54, 122.31, 128.35, 128.95, 131.47 ppm.

1,1-Dibromo-4-(*p*-tolyl)-1-buten-3-yne: The title compound was prepared according to the preceding procedure from *p*-tolylacetylene: Yield 75%; mp 59-60 °C; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 2.32 (s, 3H), 6.71 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 21.56, 85.65, 97.47, 101.20, 119.28, 119.70, 129.16 (2C), 131.41 (2C), 139.24 ppm; IR (CCl₄) 3077, 3015, 2975, 2939, 2203, 1506, 1445 cm⁻¹; HRMS *m/z* calcd for C₁₁H₈Br₂: 297.8993; found: 297.8991.

(*Z*)-1-(*tert*-Butyldimethylsilyloxy)-4-bromo-7-phenyl-4-heptene-2,6-diyne: To a solution of 1-(*tert*-butyldimethylsilyloxy)-2-propyne (408 mg, 2.4 mmol) in THF (4 mL) was added ^{*n*}BuLi (2.5M in hexane, 0.96 mL, 2.4 mmol) at -78 °C for 30 min and treated with anhydrous ZnBr₂ (324 mg, 1.44 mmol) in THF (3 mL). The mixture thus obtained was stirred for 5 min at -78 °C, warmed to 0 °C over 25 min, and added via cannula to a mixture of 1,1-dibromo-4-phenyl-1-en-3-butyne (572 mg, 2 mmol) and Pd(DPEphos)Cl₂ (71.5 mg, 0.1 mmol) in THF (5 mL) at 0 °C. After 8 h GLC analysis indicated that the starting material had been completely consumed. The reaction mixture was quenched with aqueous NH₄Cl, extracted with ether, washed successively with saturated NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 532 mg (71%) of the title compound: colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 0.16 (s, 6H), 0.94 (s, 9H), 4.52 (s, 2H), 6.55 (s, 1H), 7.3-7.35 (m, 3H), 7.5-7.55 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ -5.16 (2C), 18.17, 25.73 (3C), 51.96, 83.31, 86.73, 94.53, 101.03, 110.35, 119.21, 122.49, 128.35 (2C), 129.01, 131.62 (2C) ppm; IR (neat) 2955, 2929, 2857, 2216, 2192 cm⁻¹; HRMS *m/z* calcd for C₁₉H₂₃BrOSi: 374.0702; found: 374.0703.

7-Phenyl-2,4,6-heptatriyn-1-ol (10).¹³ To a solution of (*Z*)-1-(*tert*-butyldimethylsilyloxy)-4-bromo-7-phenyl-4-heptene-2,6-diyne (532 mg, 1.4 mmol) in methanol (5 mL) was added K₂CO₃ (580 mg, 4.2 mmol) at 23 °C. After 12 h, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (silica gel, ¼ ethyl acetate-hexane) afforded 204 mg (81%) of the title compound: colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ 2.12 (s, 1H), 4.39 (s, 2H), 7.3-7.4 (m, 3H), 7.5-7.55 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ 51.43, 63.38, 65.81, 70.71, 74.09, 77.28, 77.91, 120.61, 128.43, 129.74, 132.97 ppm.

Representative Procedure for the Convergent Synthesis: (*E*)-11-Phenyl-2-undecene-4,6,8,10-tetrayne (13). To a solution of (1*E*,5*E*)-1-chloro-1,5-heptadien-3-yne (278 mg, 2.2 mmol) in THF (6 mL) was added ⁿBuLi (2.5M in hexane, 1.76 mL, 4.4 mmol) at -78 °C for 1 h and treated with anhydrous ZnBr₂ (283 mg, 1.26 mmol) in THF (3 mL). The mixture thus obtained was stirred for 5 min at -78 °C and warmed to 0 °C over 25 min. 1,1-Dibromo-4-phenyl-1-buten-3-yne (572 mg, 2 mmol) and Pd(PPh₃)₄ (213 mg, 0.18 mmol) in THF (10 mL) and NEt₃ (0.28 mL, 2 mmol) were successively added to the reaction mixture at 0 °C. The reaction mixture was stirred at 23 °C for 12 h, quenched with aqueous NH₄Cl, extracted with ether, washed successively with saturated NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (silica gel, pentane) afforded 280 mg (66%) of the title compound: mp 82-83 °C; yellow solid; ¹H NMR (CDCl₃, 400 MHz) δ 1.85 (dd, *J* = 6.8 and 2.0 Hz, 3H), 5.46 (dd, *J* = 16.0 and 2.0 Hz, 1H), 6.45 (dq, *J* = 16.0 and 6.8 Hz, 1H), 7.3-7.4 (m, 5H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 19.16, 63.11, 63.98, 66.14, 67.31, 72.87, 74.43, 77.10, 77.37, 108.98, 120.47, 128.49 (2C), 129.89, 133.12 (2C), 147.06 ppm; IR (CCl₄): 2983, 2937, 2196, 1490, 1442 cm⁻¹; HRMS *m/z* calcd for C₁₇H₁₀: 214.0783; found: 214.0783.

1-Phenyl-8-(*p*-tolyl)-1,3,5,7-octatetrayne (14).⁸ The title compound was prepared according to the preceding procedure: Yield 68%; mp 93-94 °C; yellow solid; ¹H NMR (CDCl₃, 300 MHz) δ 2.33 (s, 3H), 7.05-7.1 (m, 2H), 7.3-7.4 (m, 5H), 7.45-7.5 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 21.67, 63.53, 63.92, 66.92, 67.29, 73.91, 74.45, 77.62, 78.15, 117.17, 120.40, 128.46 (2C), 129.300 (2C), 129.89, 133.09 (4C), 140.59 ppm.

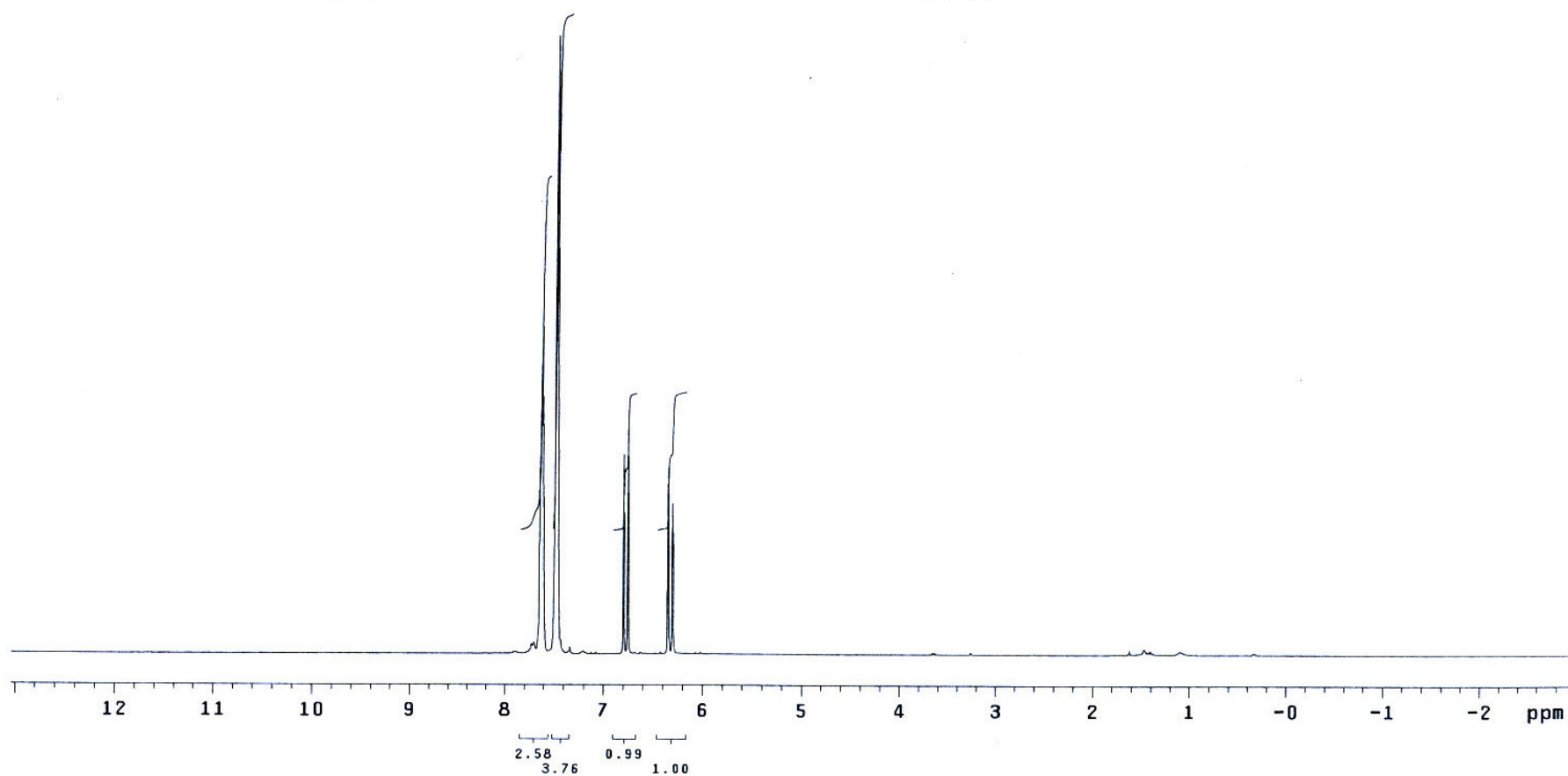
¹³ Luu, T.; Shi, W.; Lowary, T. L.; Tykwinski, R. R. *Synthesis*, **2005**, 3167.

1-Phenyl-1,3,5,7,9-undecapentayne (15a). The title compound was prepared according to the above-described the procedure for the synthesis of **13**: Yield 43%; decomposition at 75 °C; yellow solid; ^1H NMR (CDCl_3 , 400 MHz) δ 2.01 (s, 3H), 7.25-7.4 (m, 3H), 7.5-7.55 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 4.74, 59.73, 60.93 (2C), 63.91, 64.92 (2C), 67.42, 74.39, 76.51, 77.81, 120.28, 128.56 (2C), 130.11, 133.32 (2C) ppm; IR (CCl_4) 3070, 3040, 2212, 2188, 1495, 1441 cm^{-1} ; HRMS m/z calcd for C_{17}H_8 : 212.0626; found: 212.0627.

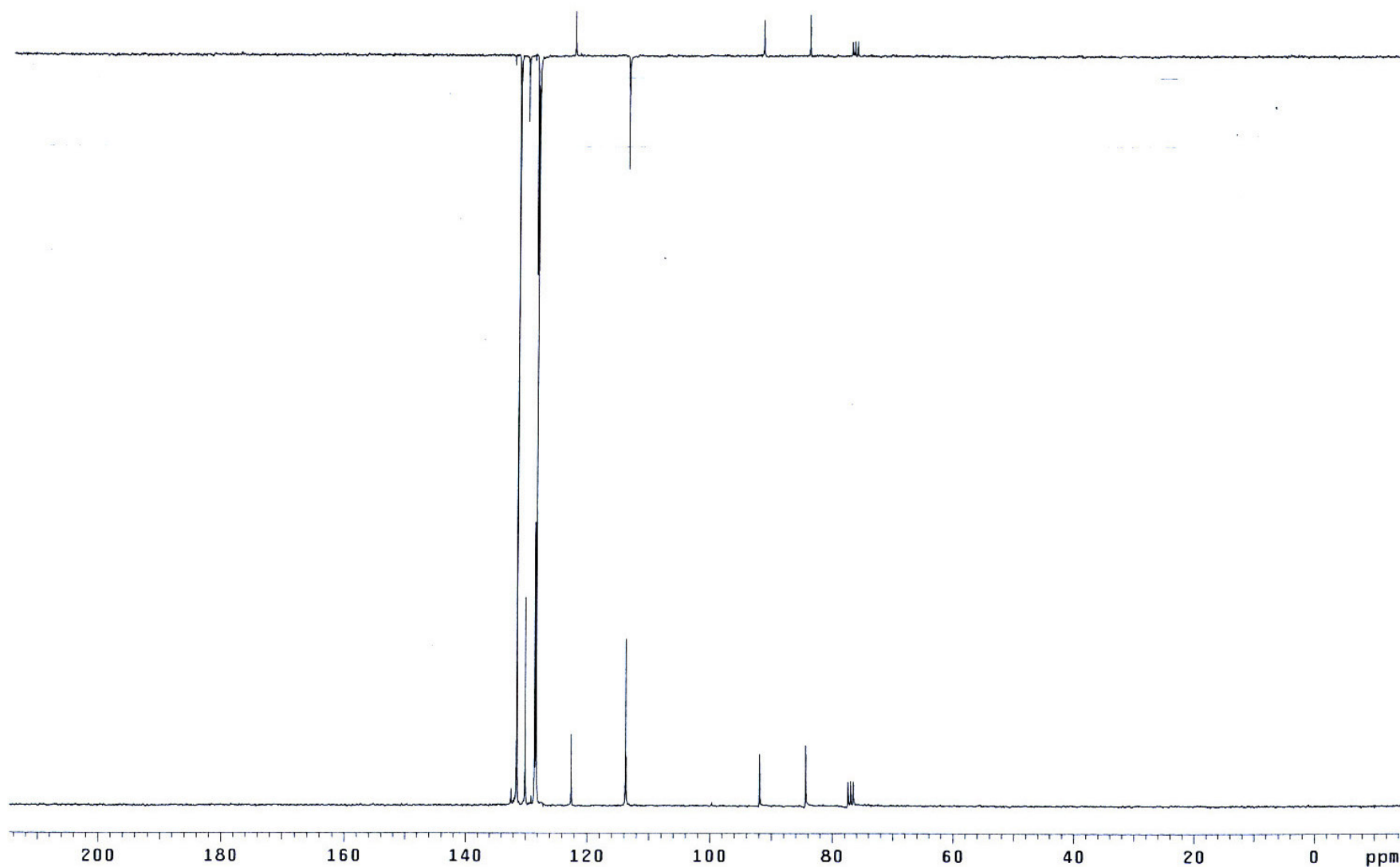
(E)-14-Phenyl-2-tridecene-4,6,8,10,12-pentayne (15b): The title compound was prepared according to the above-described the procedure for the synthesis of **13**: Yield 48%; decomposition started at 60 °C; yellow solid; ^1H NMR (CDCl_3 , 400 MHz) δ 1.85 (dd, J = 6.8 and 1.6 Hz, 3H) 5.56 (dd, J = 16.0 and 1.6 Hz, 1H), 6.50 (dq, J = 16.0 and 6.8 Hz, 1H), 7.2-7.4 (m, 3H), 7.5-7.55 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 19.24, 62.43, 63.09, 63.93, 64.60, 66.26, 67.32, 72.85, 74.39, 76.83, 77.24, 108.98, 120.28, 128.56 (2C), 130.13, 133.31 (2C), 147.71 ppm; IR (CCl_4): 2918, 2178, 1495, 1441 cm^{-1} ; HRMS m/z calcd for $\text{C}_{19}\text{H}_{10}$: 238.0783; found: 238.0780.

1-Phenyl-10-(p-tolyl)-1,3,5,7,9-decapentayne (15c). The title compound was prepared according to the above-described the procedure for the synthesis of **13**: Yield 55%; decomposition started at 110 °C; yellow solid; ^1H NMR (CDCl_3 , 400 MHz) δ 2.36 (s, 3H), 7.1-7.15 (m, 2H), 7.3-7.4 (m, 5H), 7.5-7.55 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.76, 62.65, 62.98, 64.31, 64.55, 67.01, 67.30, 73.88, 74.36, 77.87, 117.00, 120.23, 128.55 (2C), 129.38 (2C), 130.14, 133.30 (4C), 140.89 ppm; IR (CCl_4): 2918, 2842, 2174, 1441 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{12}$: 288.0939; found: 288.0939.

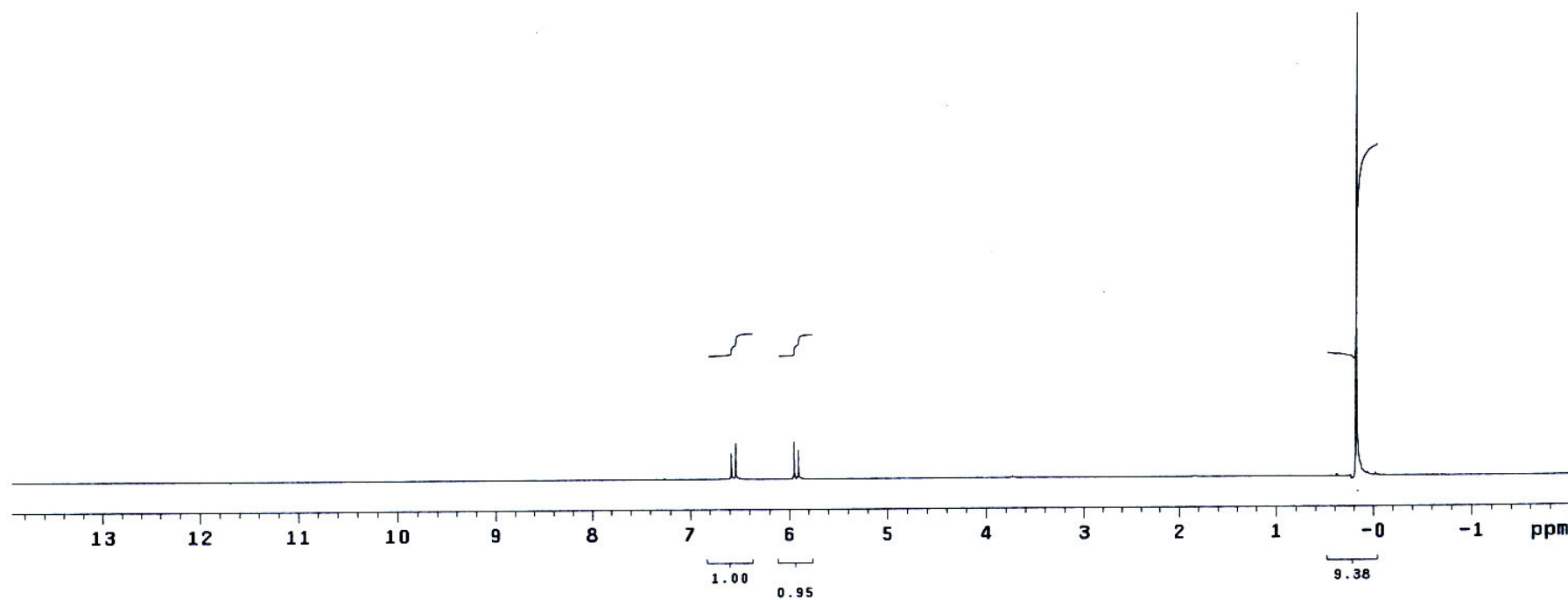
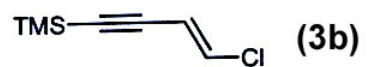
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3	2284.745	7.617	52.8
4	2281.230	7.605	25.2
5	2246.078	7.488	84.1
6	2243.735	7.480	100.0
7	2241.977	7.474	74.3
8	2239.634	7.466	65.4
9	2039.857	6.800	32.2
10	2038.100	6.795	22.8
11	2026.382	6.756	38.6
12	2024.625	6.750	29.1
13	1905.696	6.353	30.0
14	1903.353	6.345	25.9
15	1892.222	6.308	24.3
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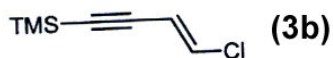


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4	9674.167	128.262	100.0
5	9242.209	122.535	12.9
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7	6934.202	91.935	9.3
8	6364.611	84.383	10.9

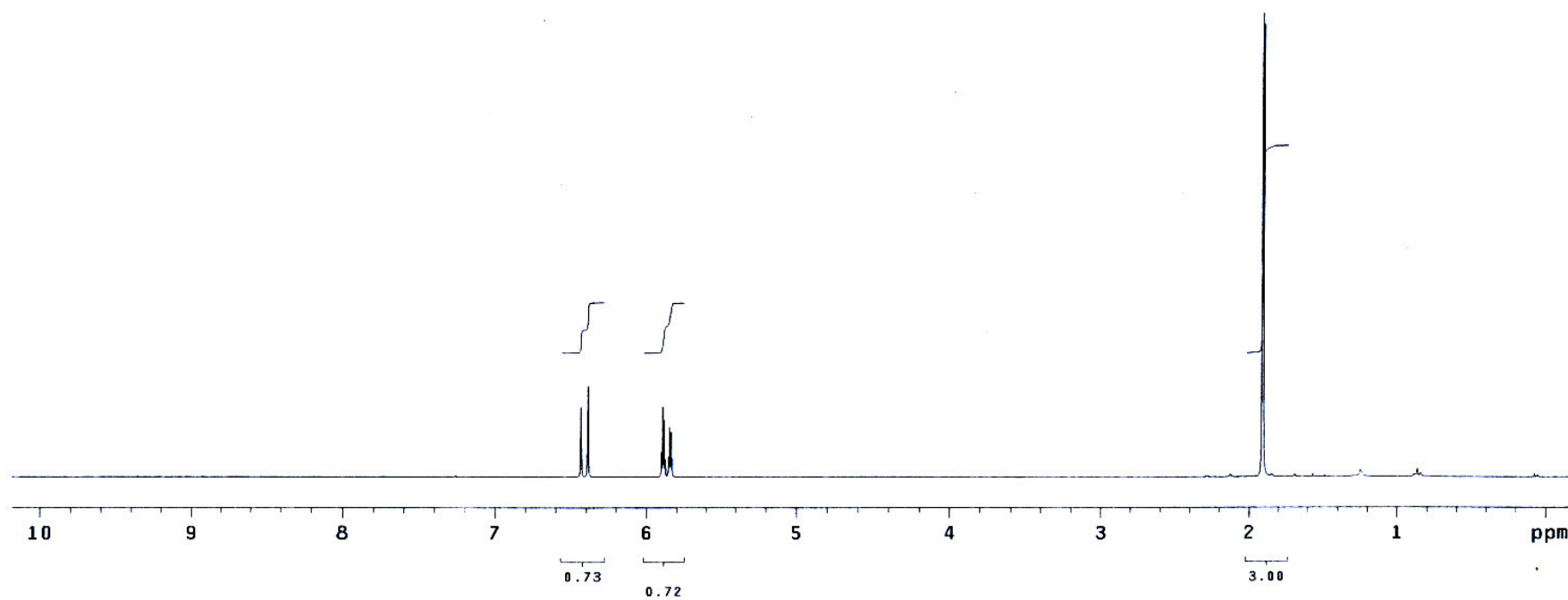
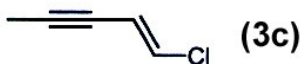


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6	54.488	0.182	75.0

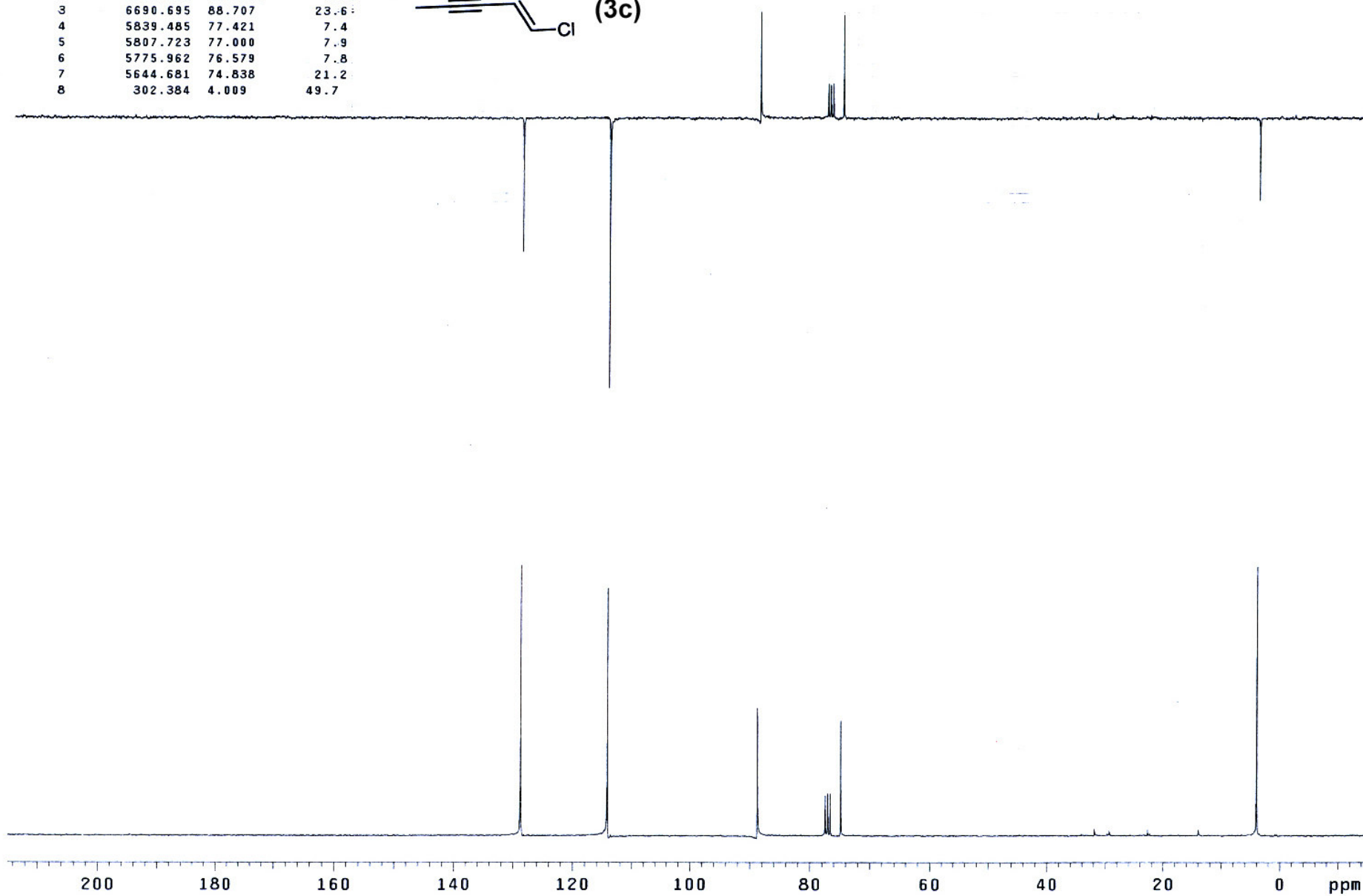
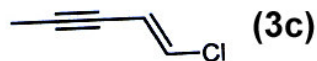




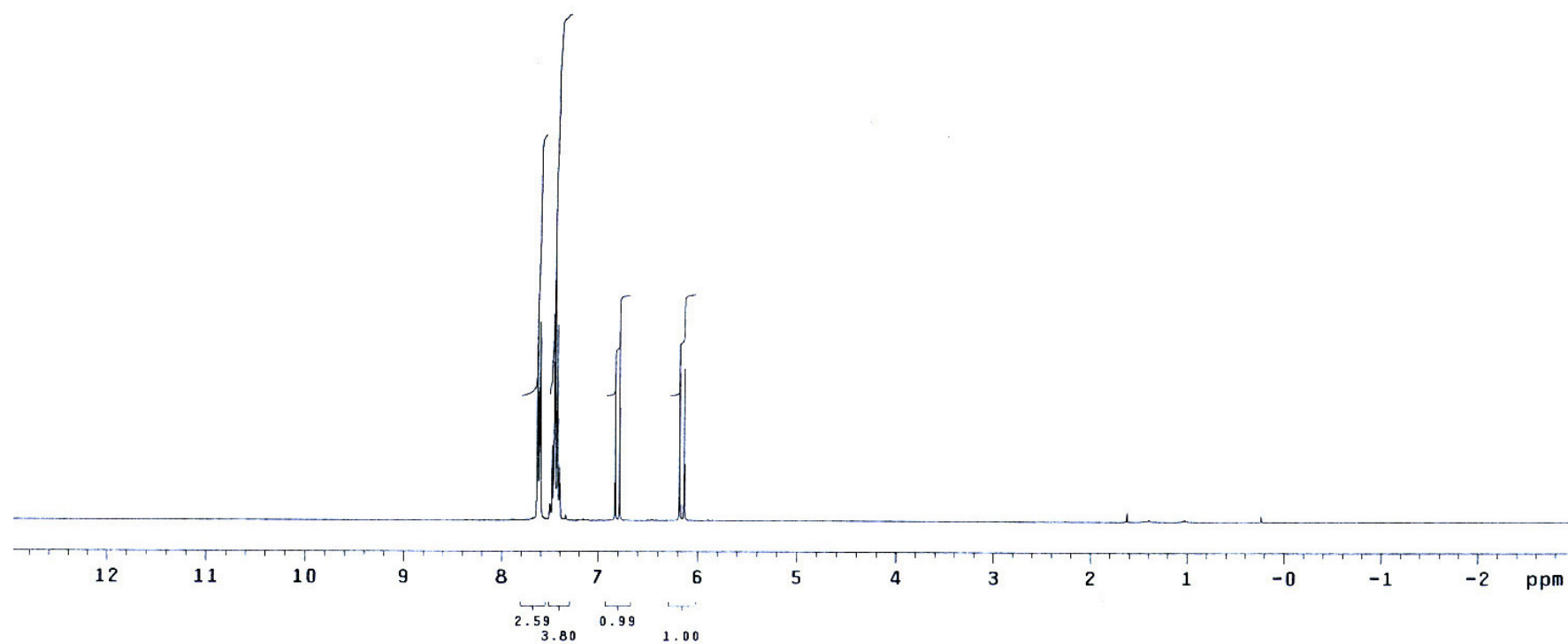
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4	1767.526	5.893	11.4
5	1765.182	5.885	9.3
6	1756.395	5.855	3.2
7	1754.051	5.848	8.1
8	1751.122	5.838	7.3
9	574.138	1.914	75.0
10	571.795	1.906	73.2



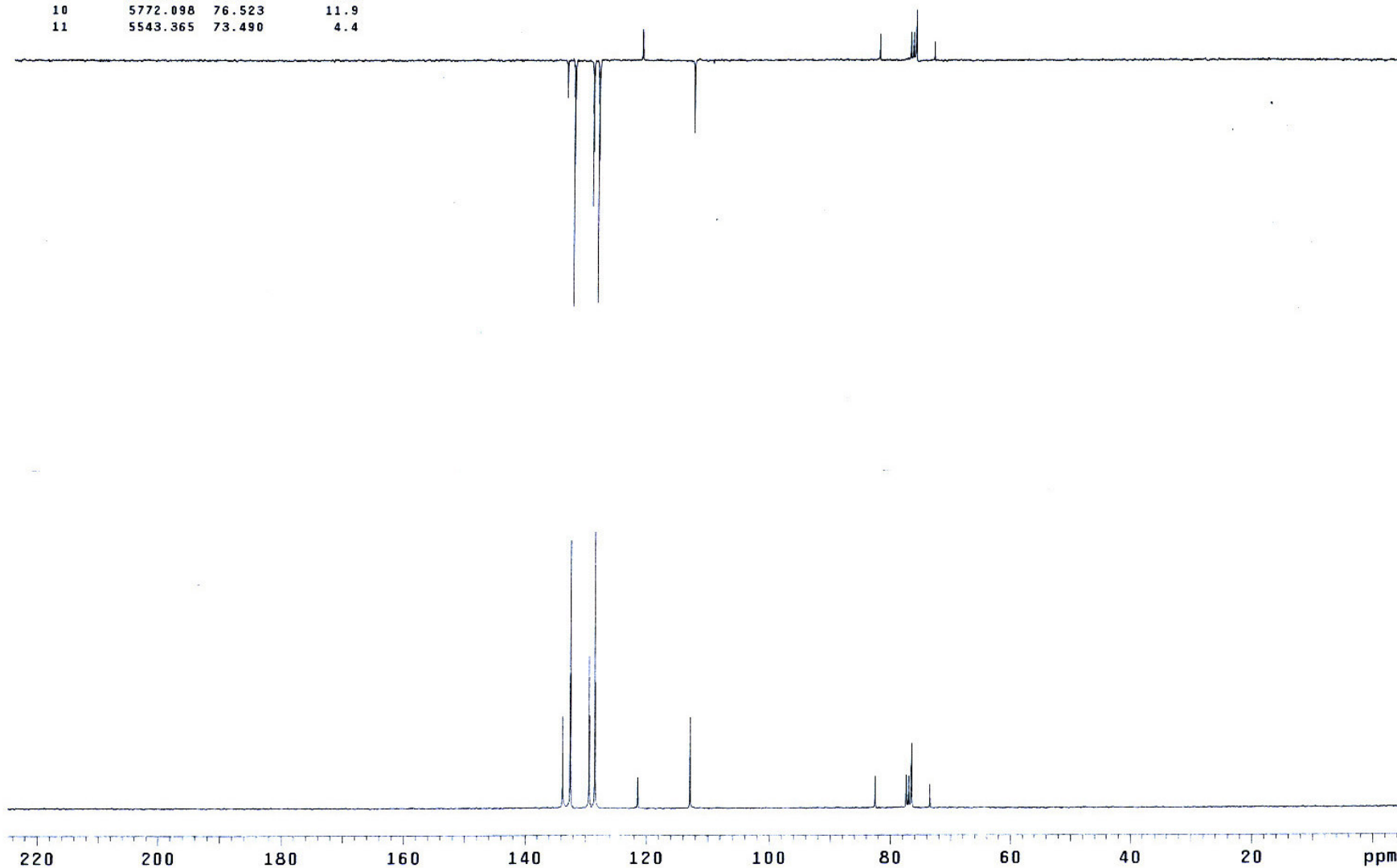
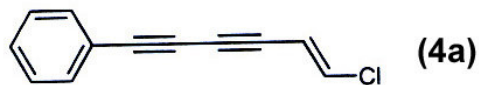
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4	5839.485	77.421	7.4
5	5807.723	77.000	7.9
6	5775.962	76.579	7.8
7	5644.681	74.838	21.2
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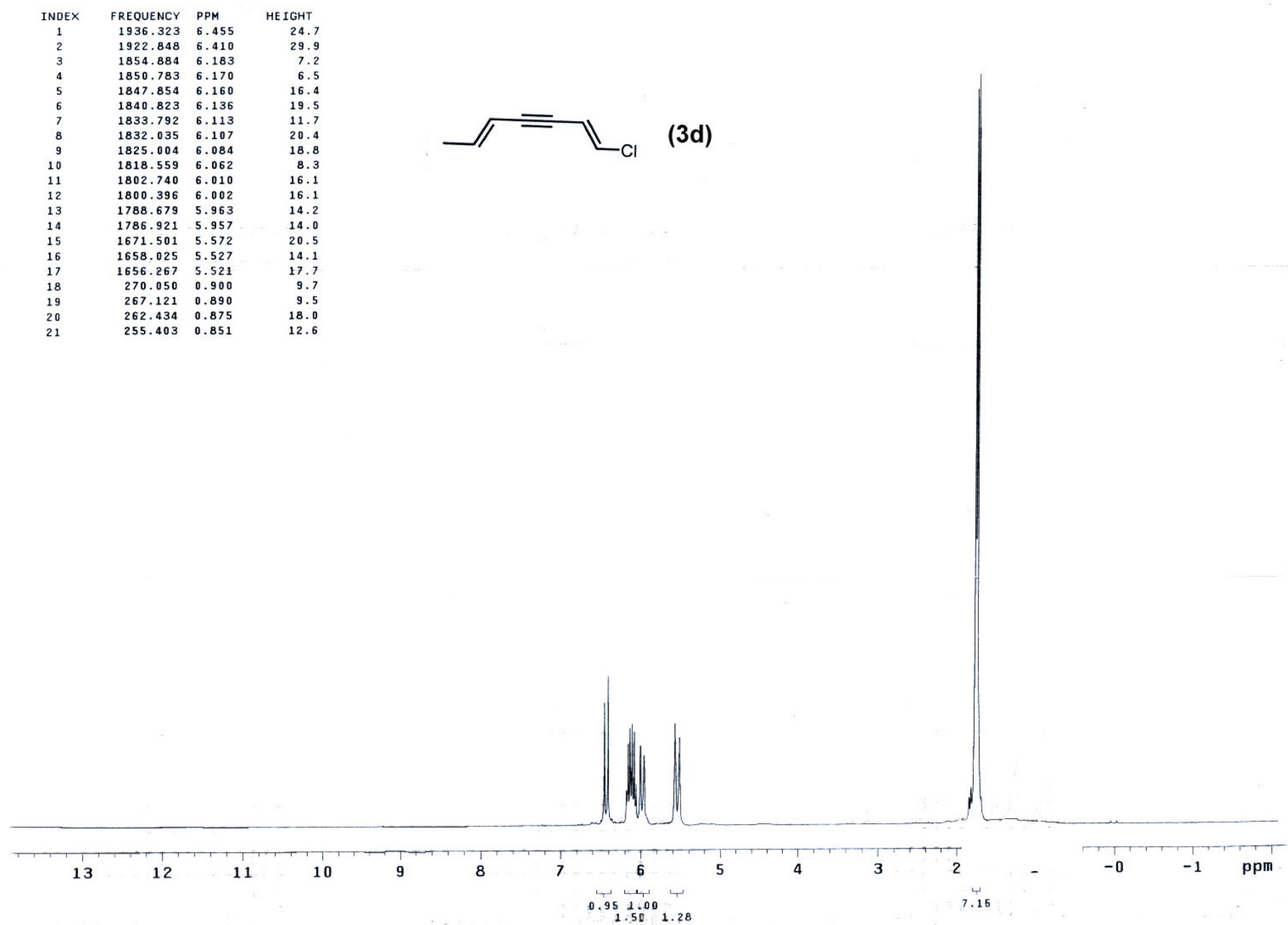


INDEX	FREQUENCY	PPM	HEIGHT
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2	2288.845	7.631	27.3
3	2282.987	7.611	31.8
4	2281.229	7.605	31.4
5	2239.048	7.464	15.7
6	2237.290	7.459	28.9
7	2235.532	7.453	45.0
8	2228.502	7.429	31.4
9	2048.059	6.828	25.8
10	2034.584	6.783	30.7
11	1854.140	6.181	28.4
12	1840.080	6.134	24.3

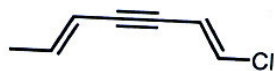


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4	9685.972	128.410	50.0
5	9154.380	121.363	5.7
6	8516.893	112.911	16.6
7	6227.446	82.559	5.8
8	5841.988	77.449	6.0
9	5810.220	77.028	5.8
10	5772.098	76.523	11.9
11	5543.365	73.490	4.4

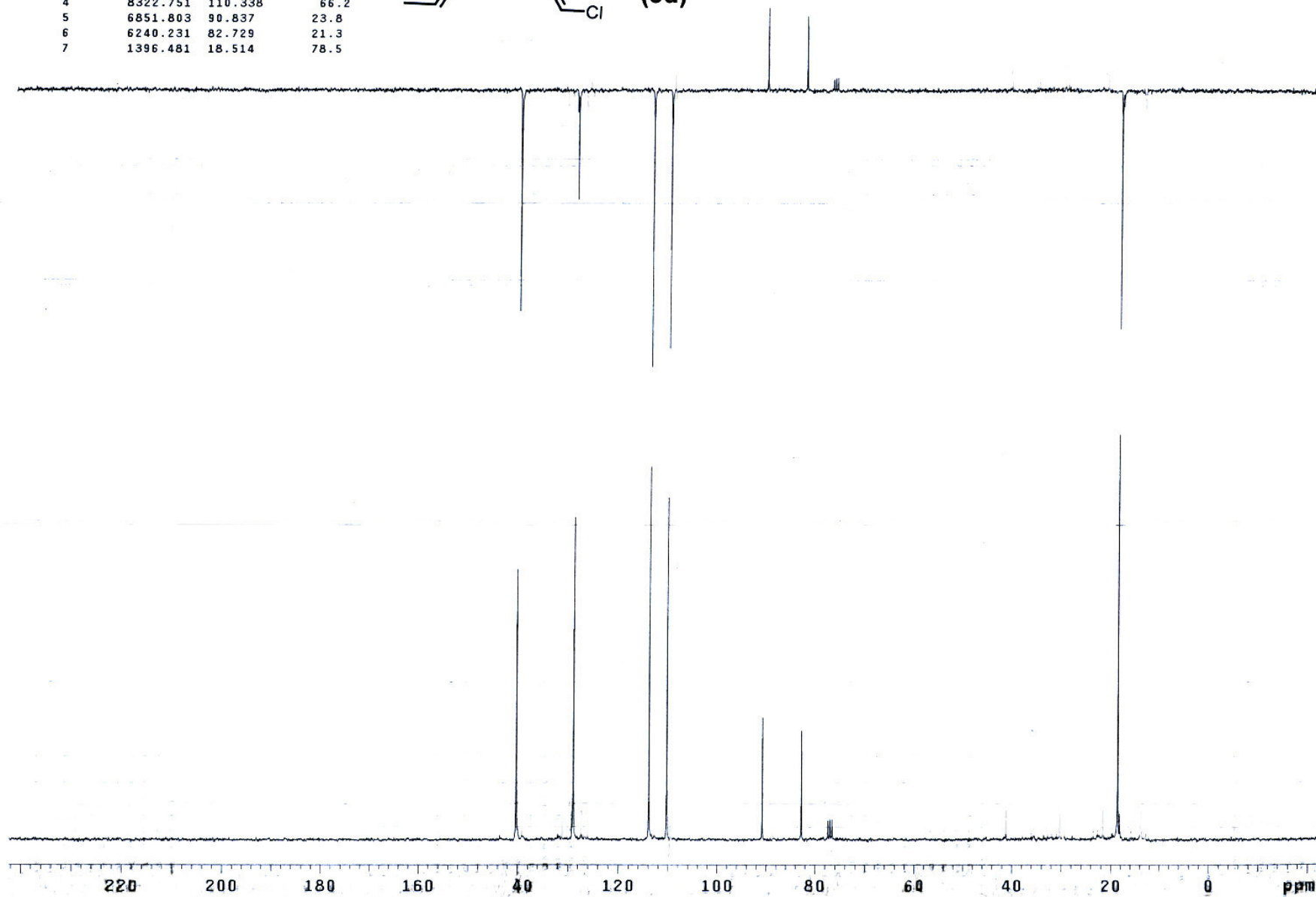




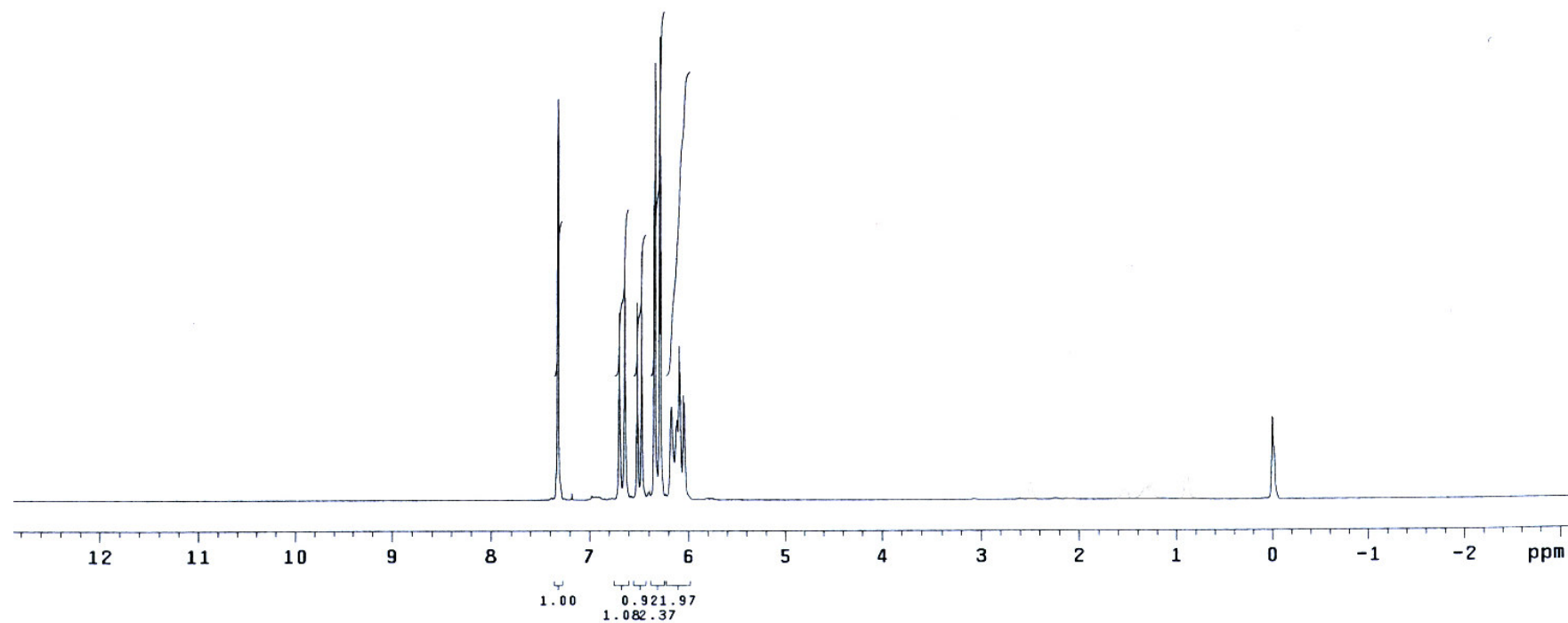
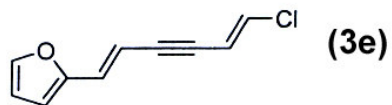
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4	8322.751	110.338	66.2
5	6851.803	90.837	23.8
6	6240.231	82.729	21.3
7	1396.481	18.514	78.5

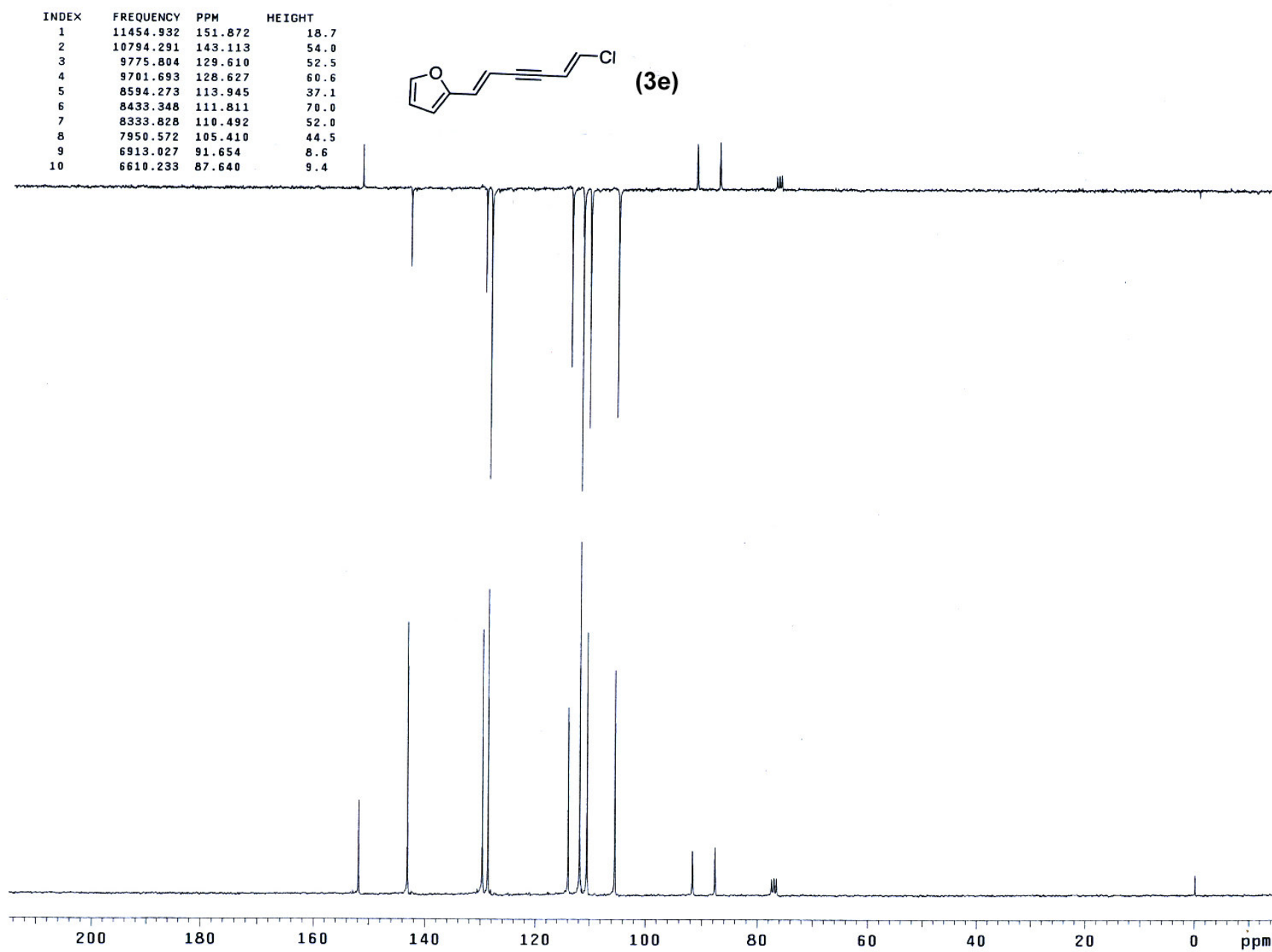


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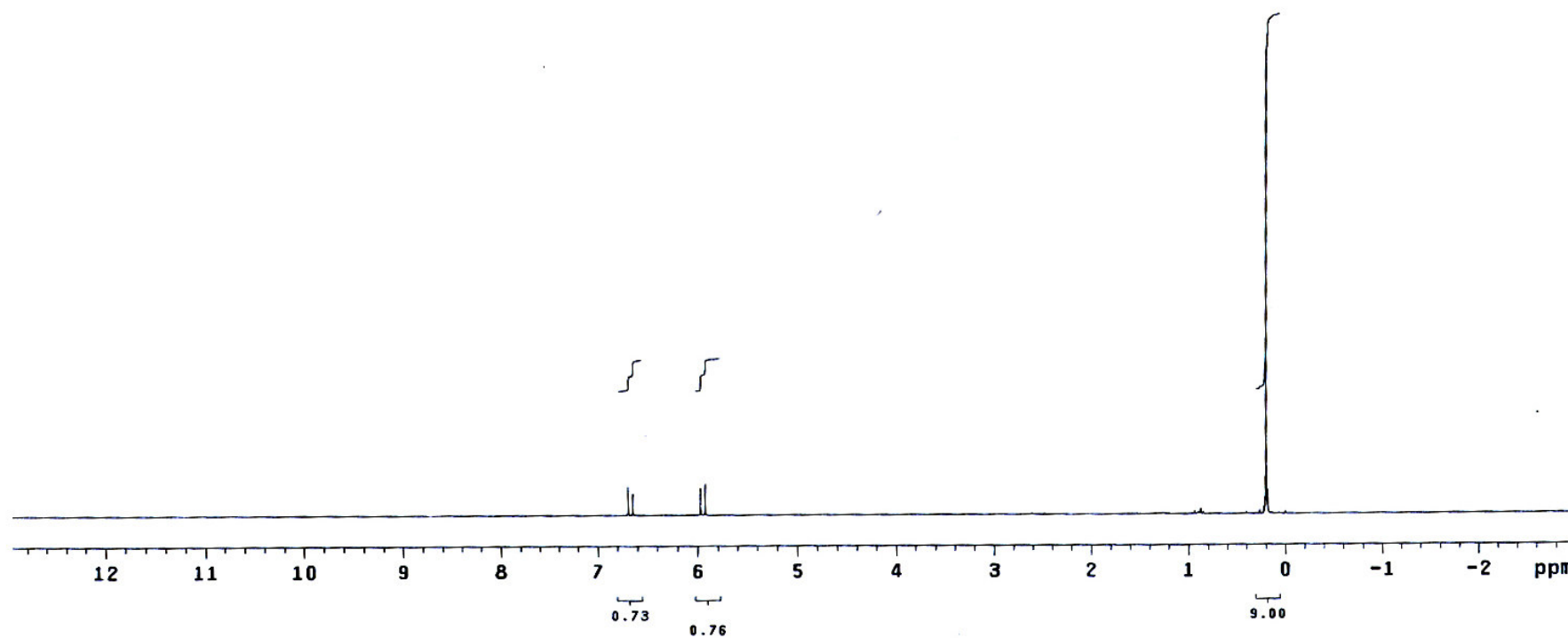
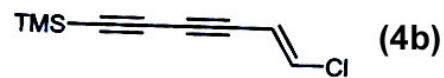


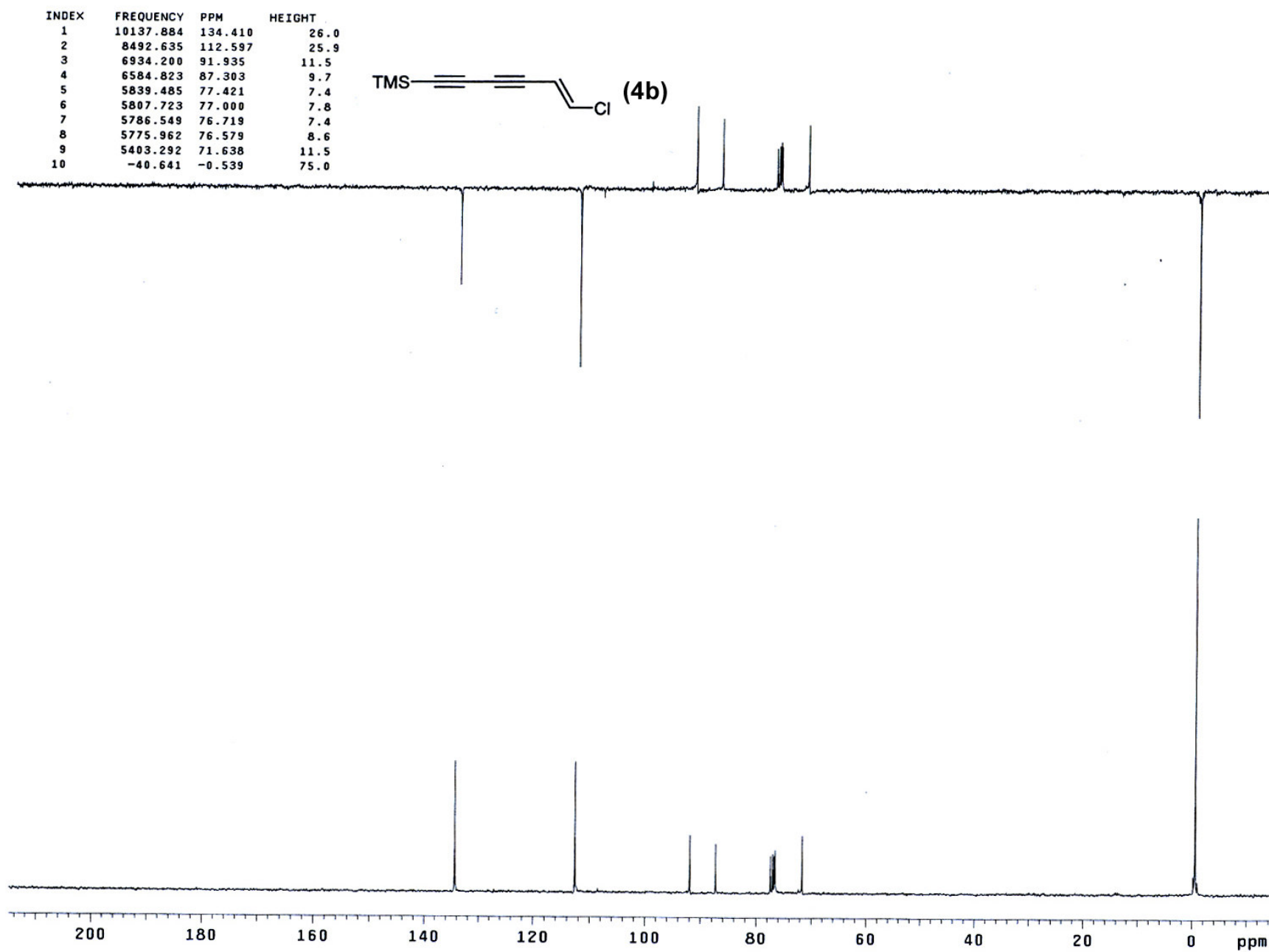
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5	1955.586	6.519	31.9
6	1942.111	6.475	40.2
7	1905.788	6.353	47.5
8	1904.030	6.348	51.5
9	1902.273	6.342	70.9
10	1900.515	6.336	67.7
11	1887.626	6.293	75.0
12	1884.111	6.281	55.6
13	1851.889	6.174	15.1
14	1835.485	6.119	13.0
15	1828.455	6.096	24.9
16	1826.112	6.088	20.6
17	1814.980	6.051	16.9
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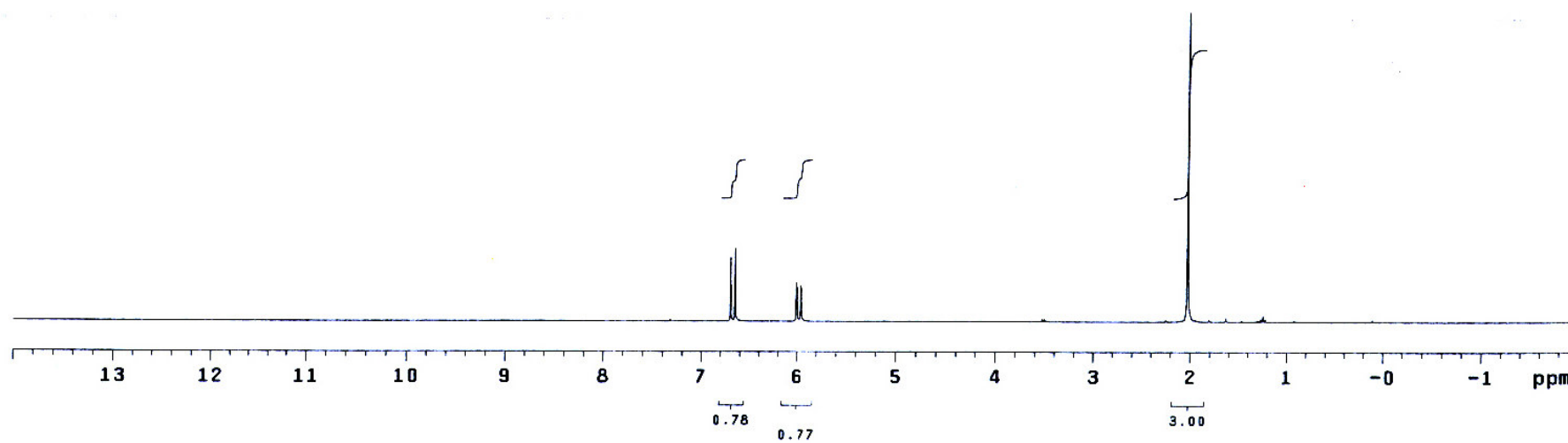
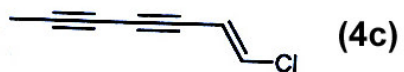


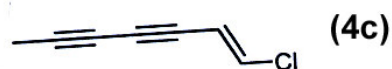
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5	59.841	0.199	75.0
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7	54.569	0.182	4.0



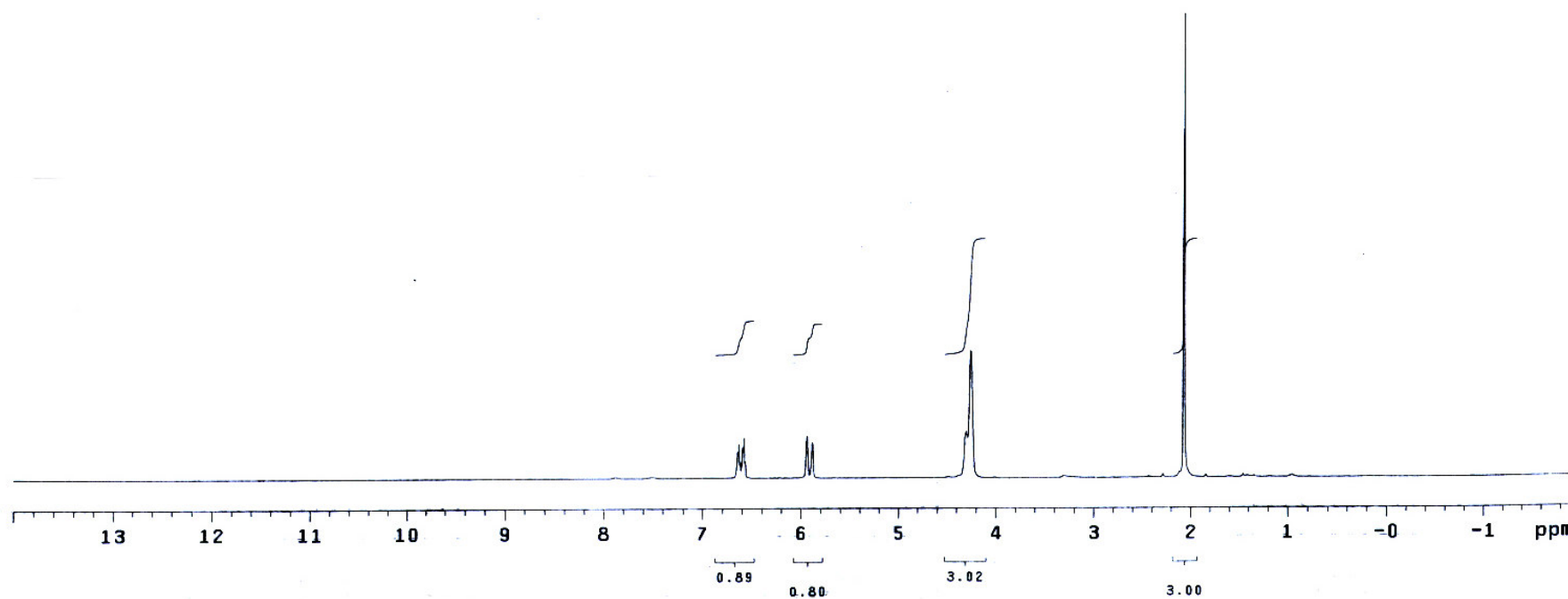


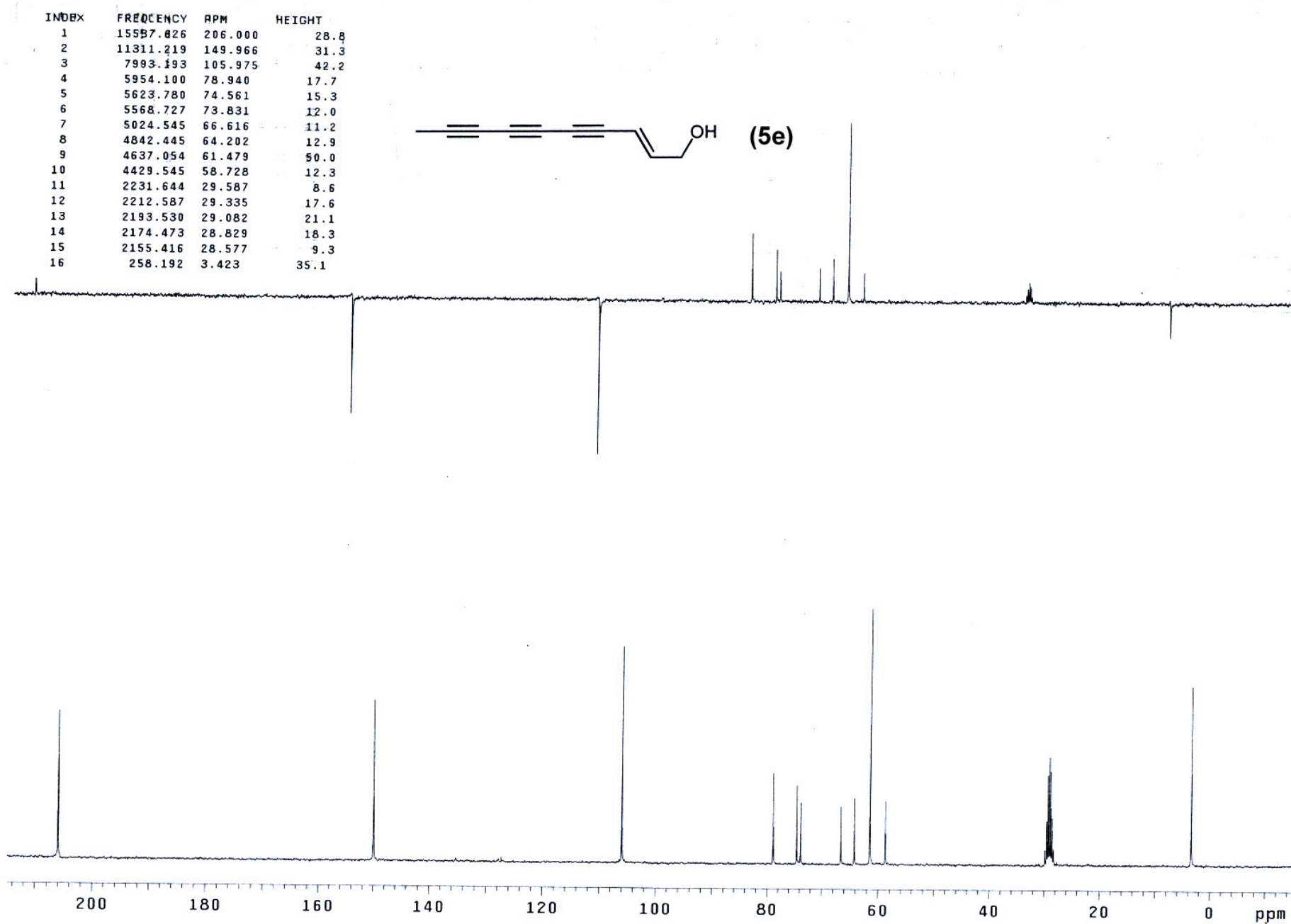
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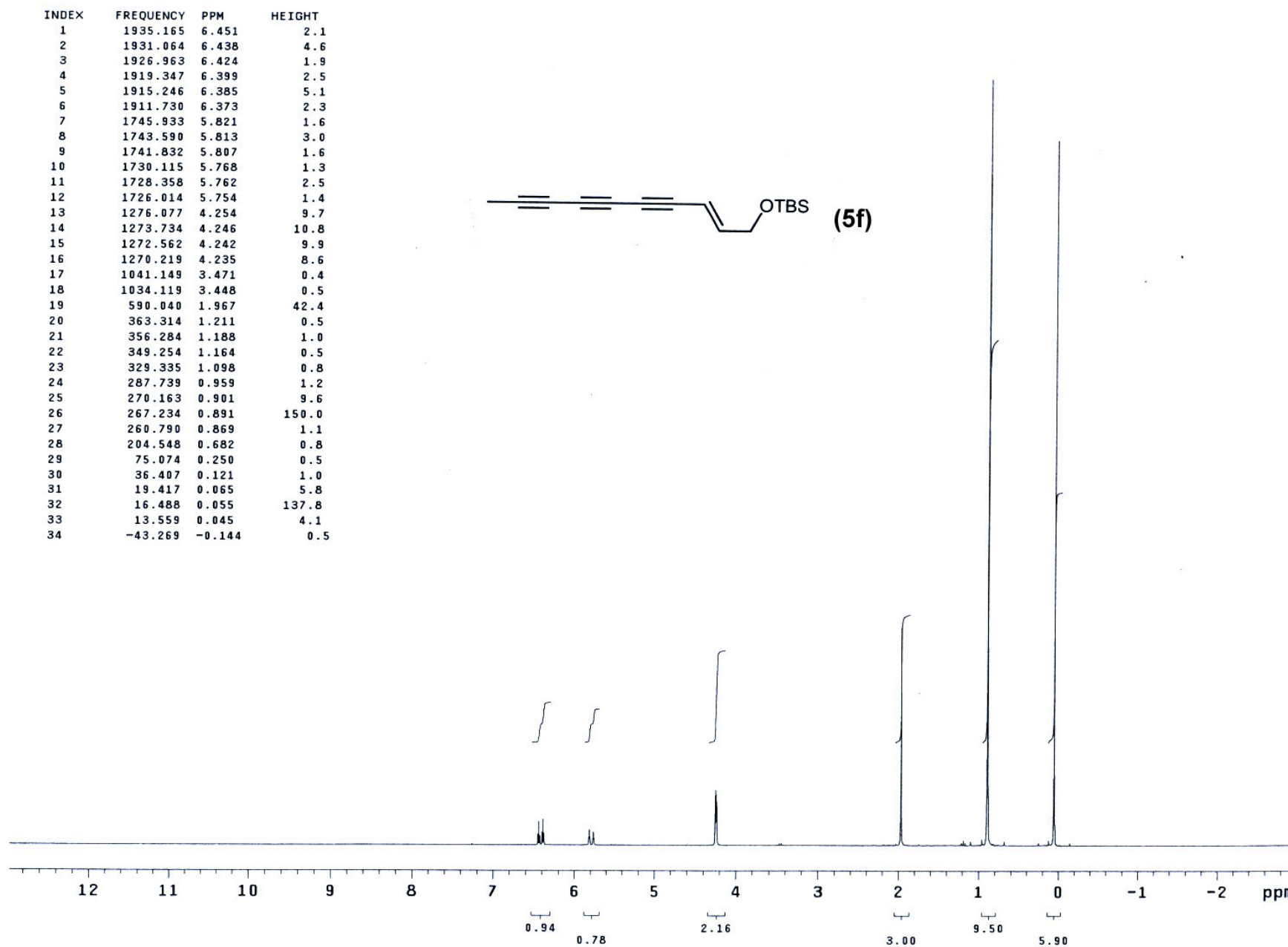


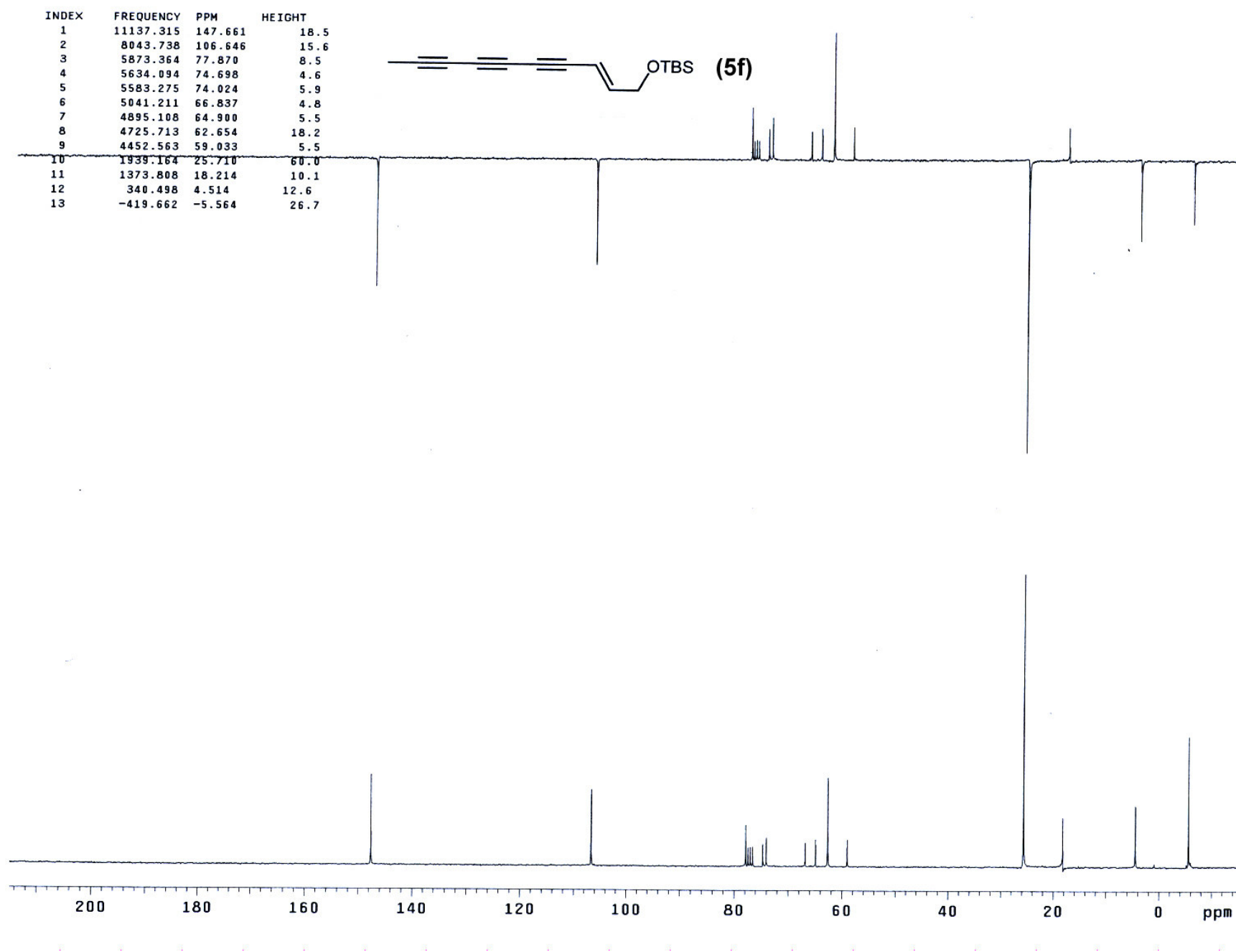


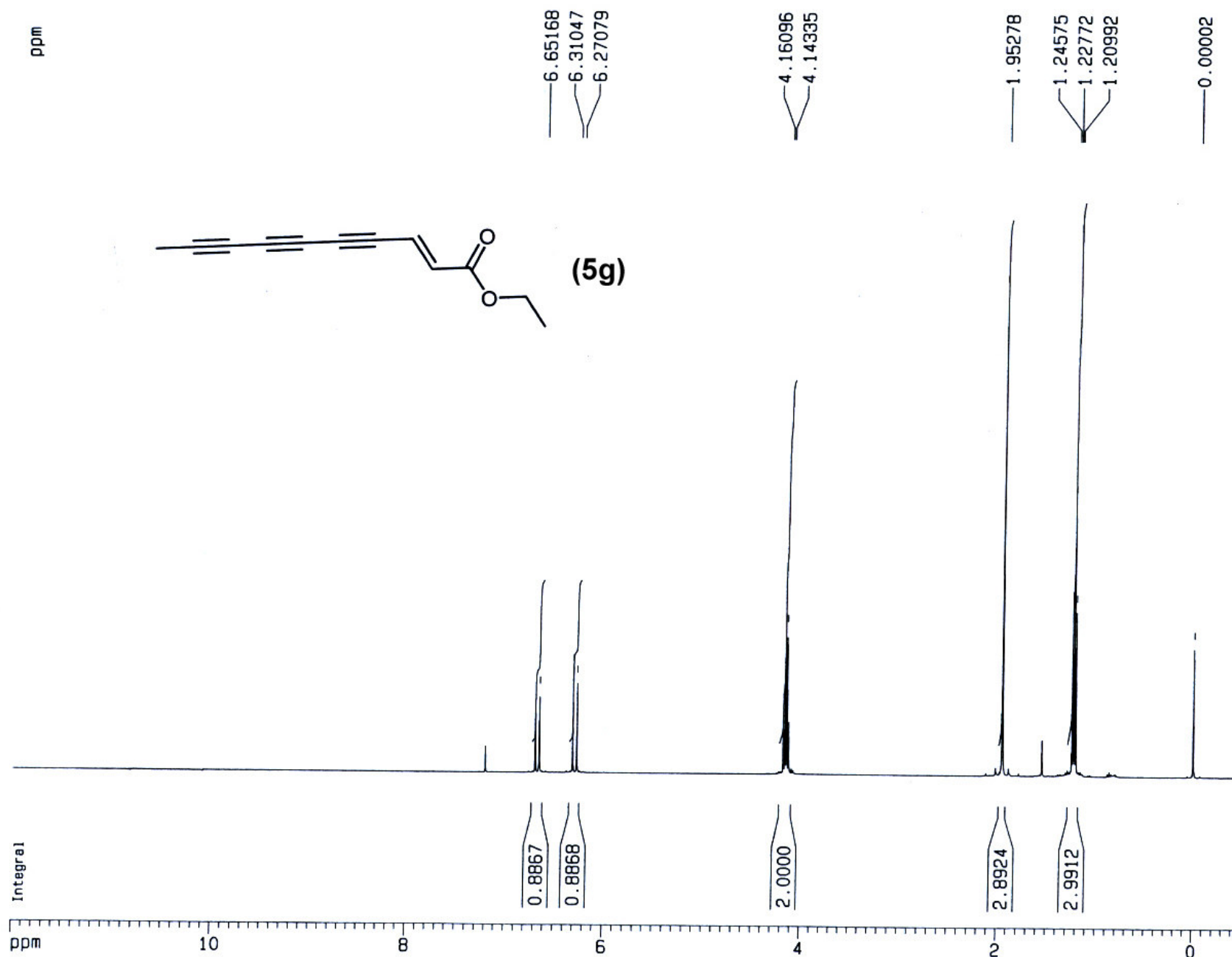
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6	1765.301	5.885	5.7
7	1764.129	5.881	5.8
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10	619.299	2.064	75.0

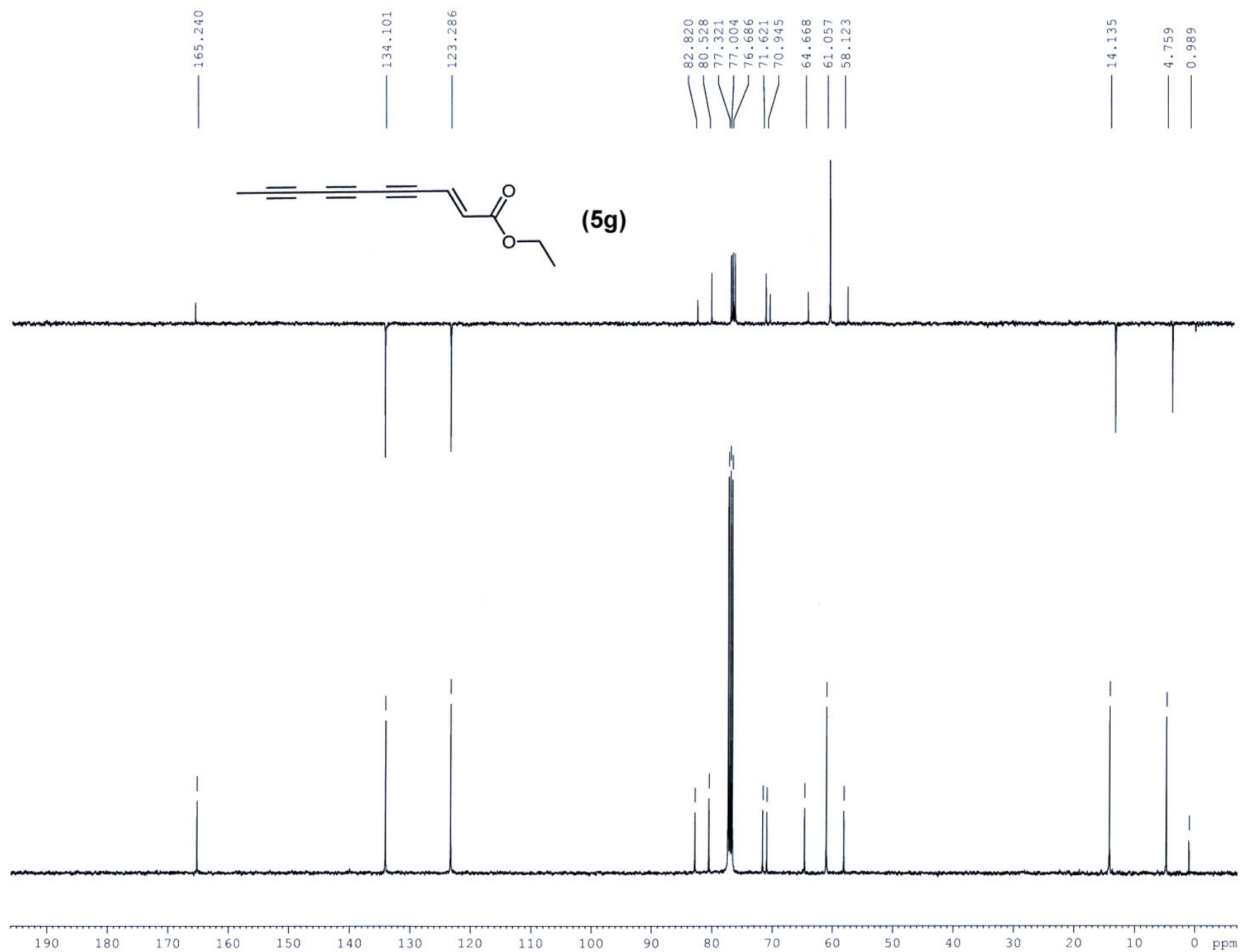




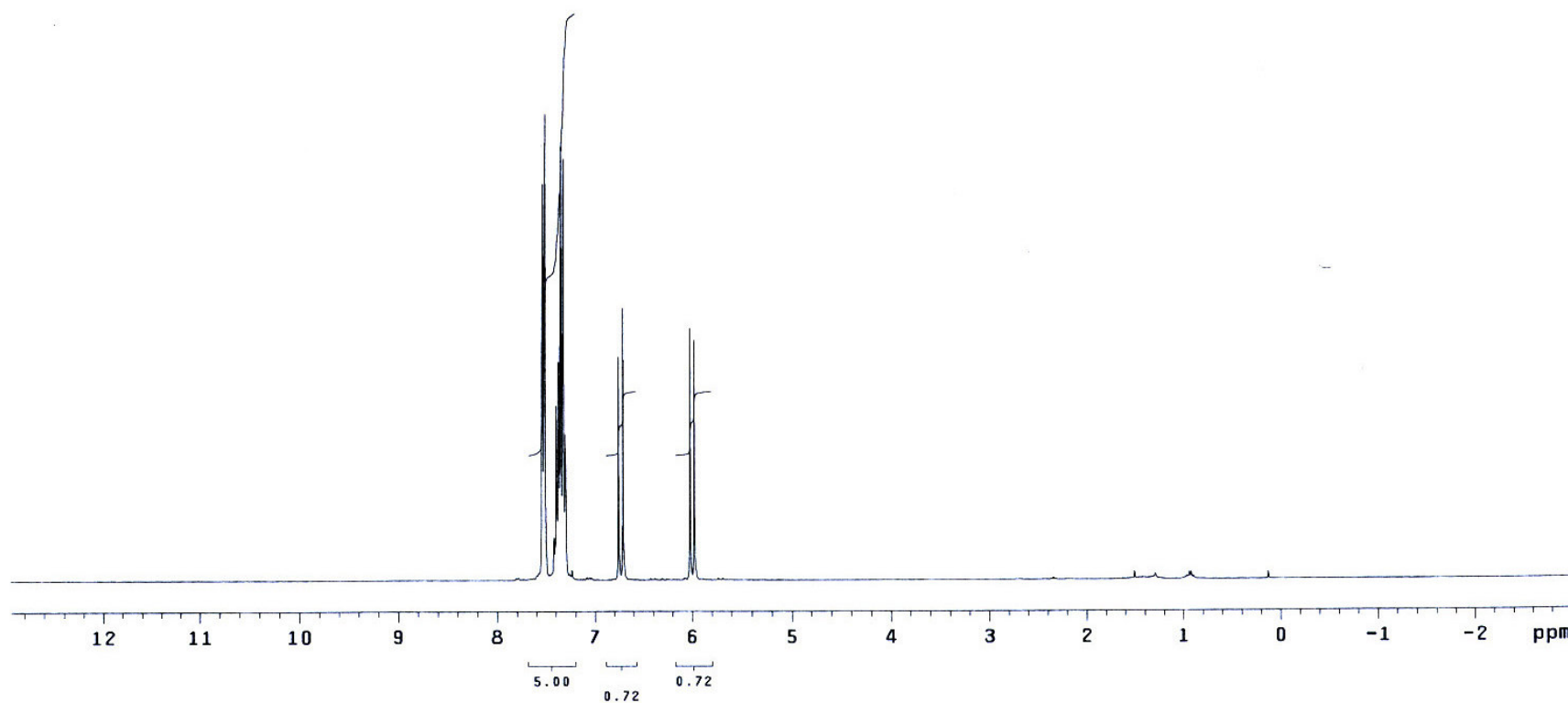
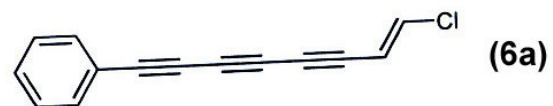




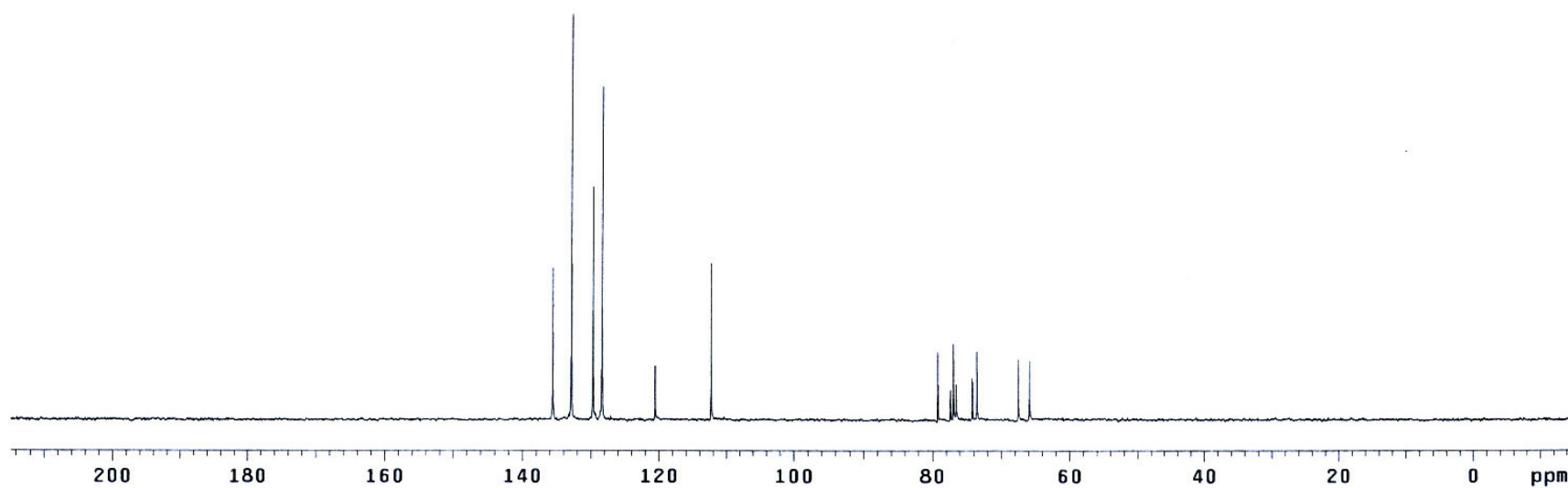
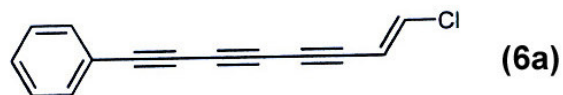




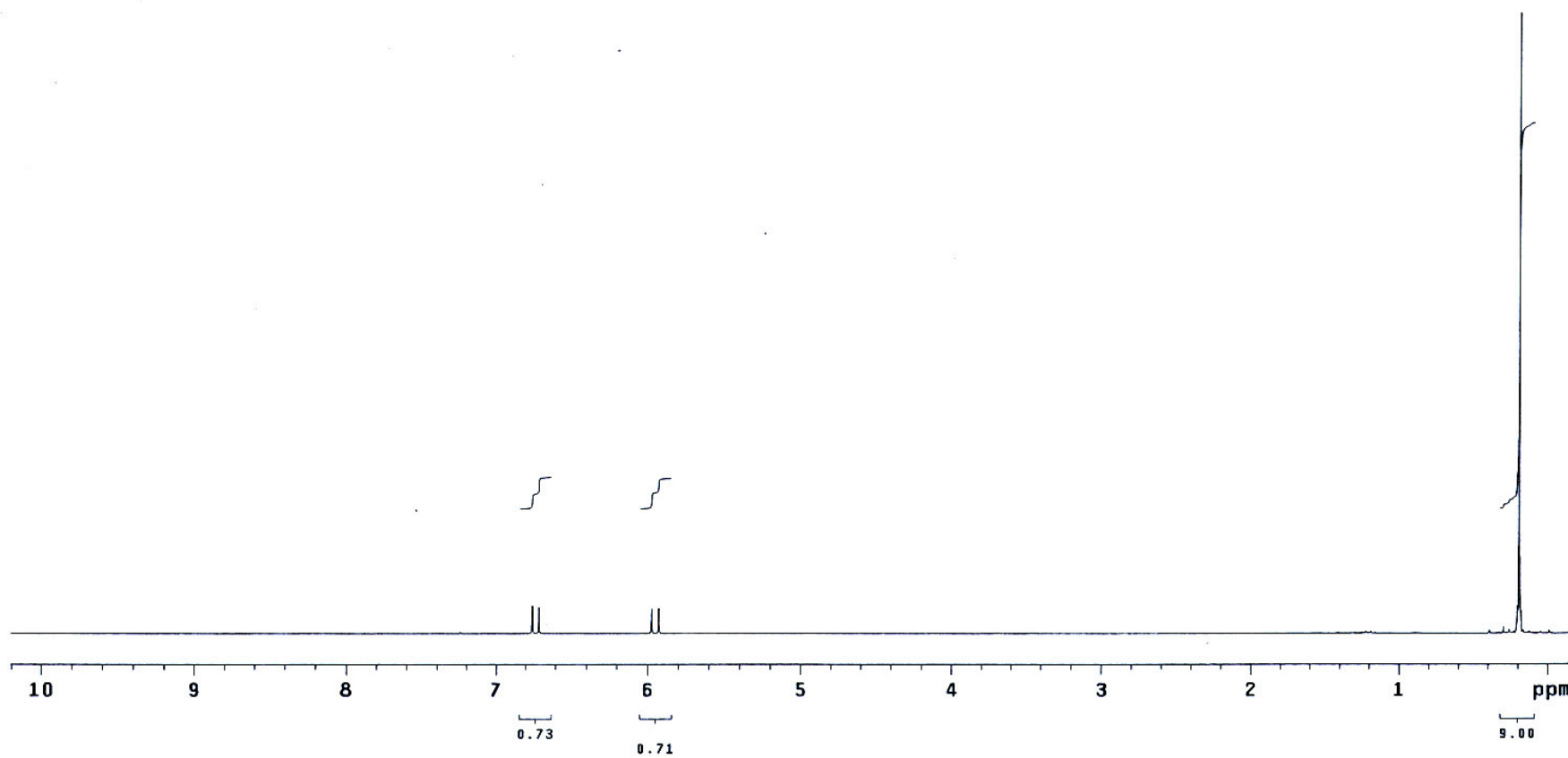
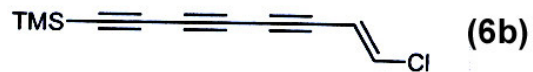
INDEX	FREQUENCY	PPM	HEIGHT
1	2261.932	7.541	63.6
2	2254.901	7.517	70.2
3	2253.730	7.513	75.0
4	2218.578	7.396	28.0
5	2212.134	7.375	35.0
6	2205.690	7.353	69.7
7	2198.073	7.328	67.6
8	2191.629	7.306	23.4
9	2027.589	6.760	35.8
10	2014.115	6.715	43.6
11	1806.722	6.023	40.4
12	1793.247	5.978	38.5

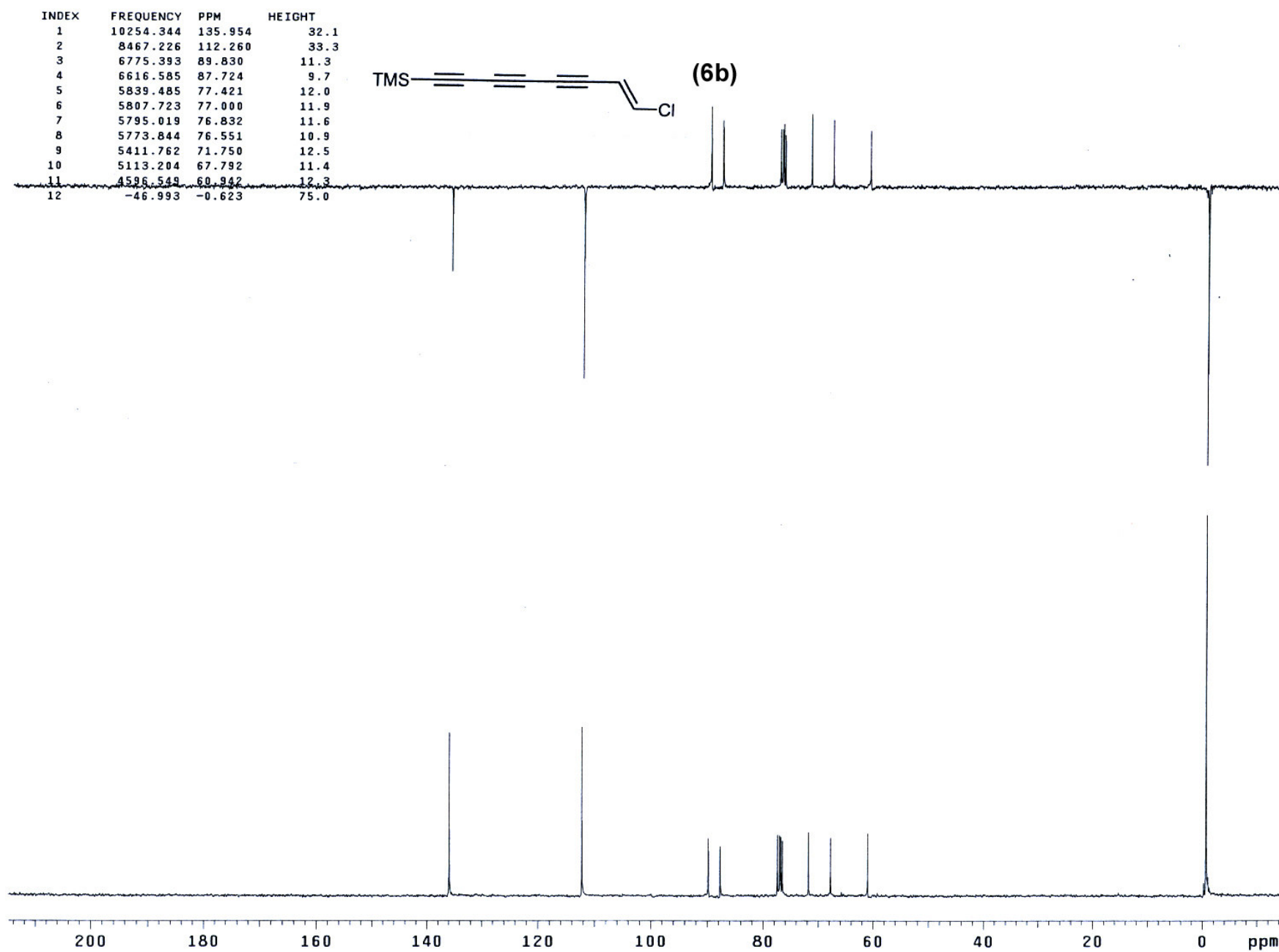


INDEX	FREQUENCY	PPM	HEIGHT
1	10224.700	135.561	24.3
2	10023.544	132.894	65.0
3	9784.273	129.722	37.3
4	9684.754	128.402	53.4
5	9093.988	120.570	8.6
6	8471.461	112.316	25.0
7	5977.119	79.246	10.8
8	5837.368	77.393	4.8
9	5807.724	77.000	12.2
10	5773.845	76.551	5.7
11	5598.098	74.221	6.7
12	5547.279	73.547	11.0
13	5094.147	67.539	9.7
14	4973.453	65.939	9.5

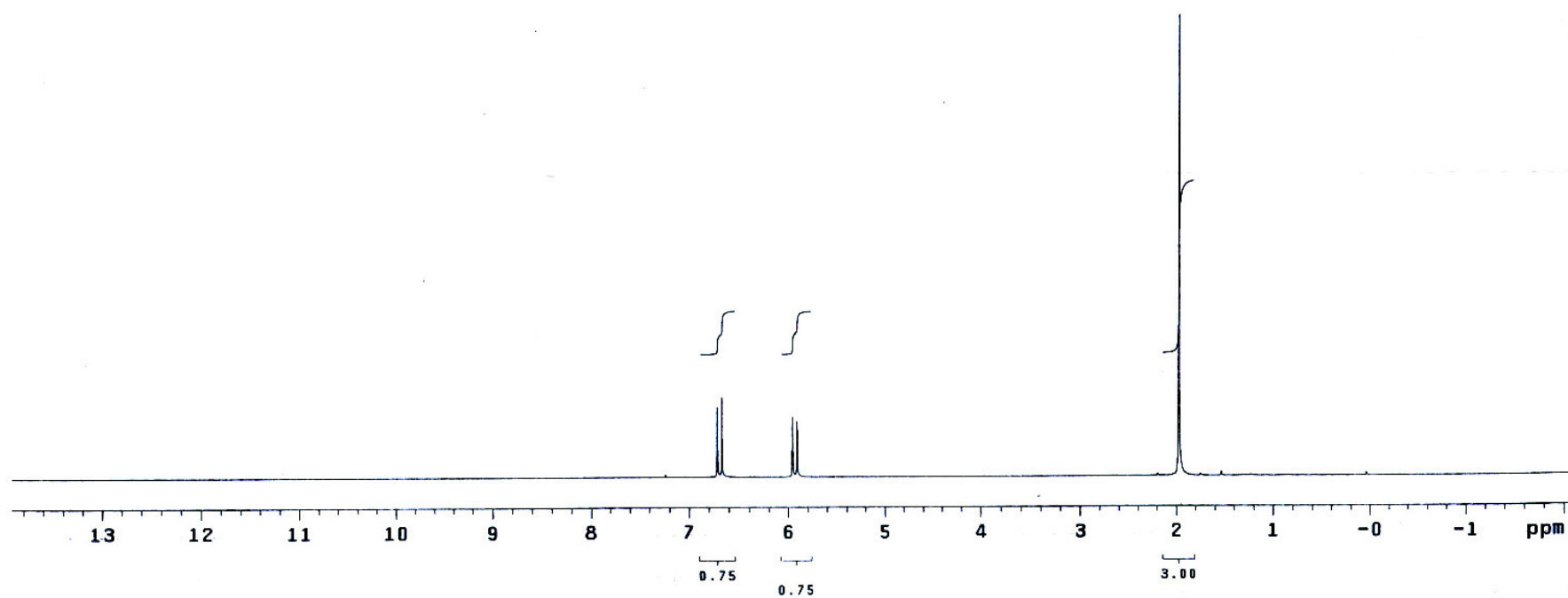
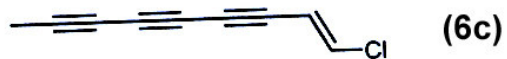


INDEX	FREQUENCY	PPM	HEIGHT
1	2026.418	6.756	4.5
2	2012.943	6.711	4.3
3	1791.490	5.972	3.9
4	1778.015	5.928	4.0
5	60.873	0.203	4.3
6	57.357	0.191	100.0
7	53.842	0.179	3.7

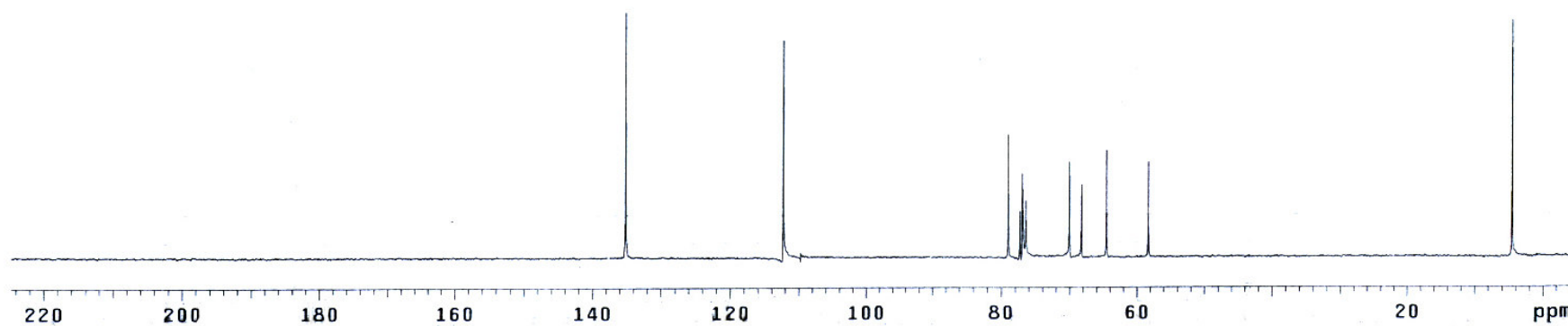
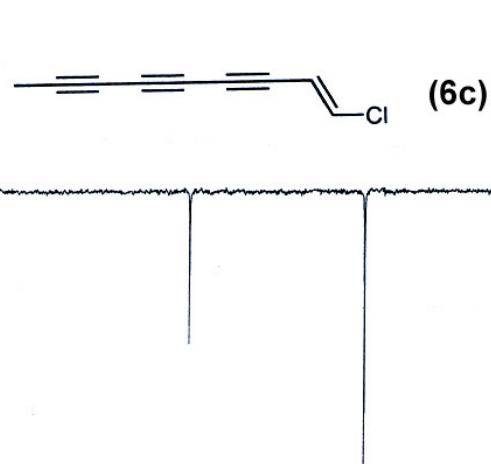


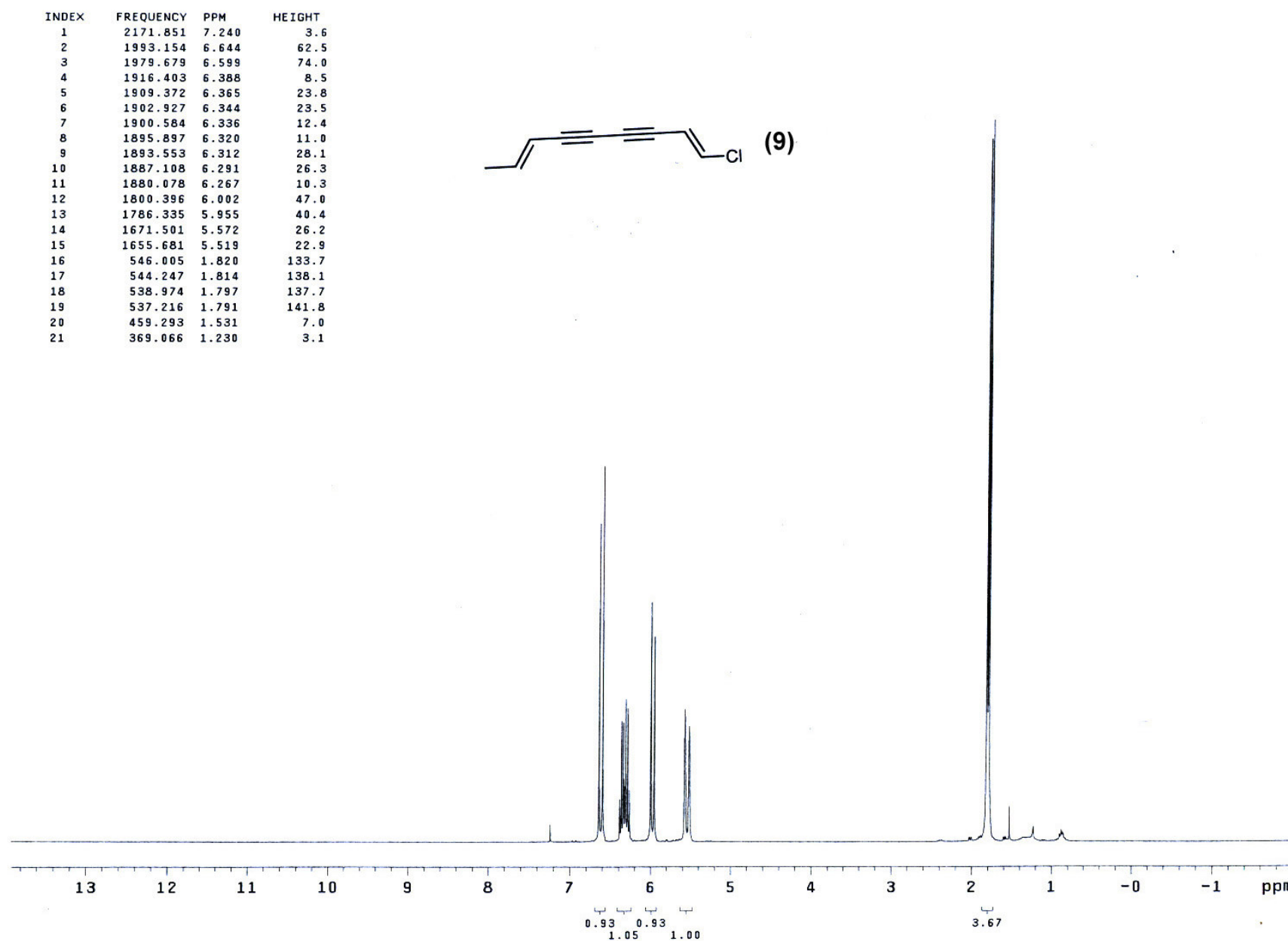


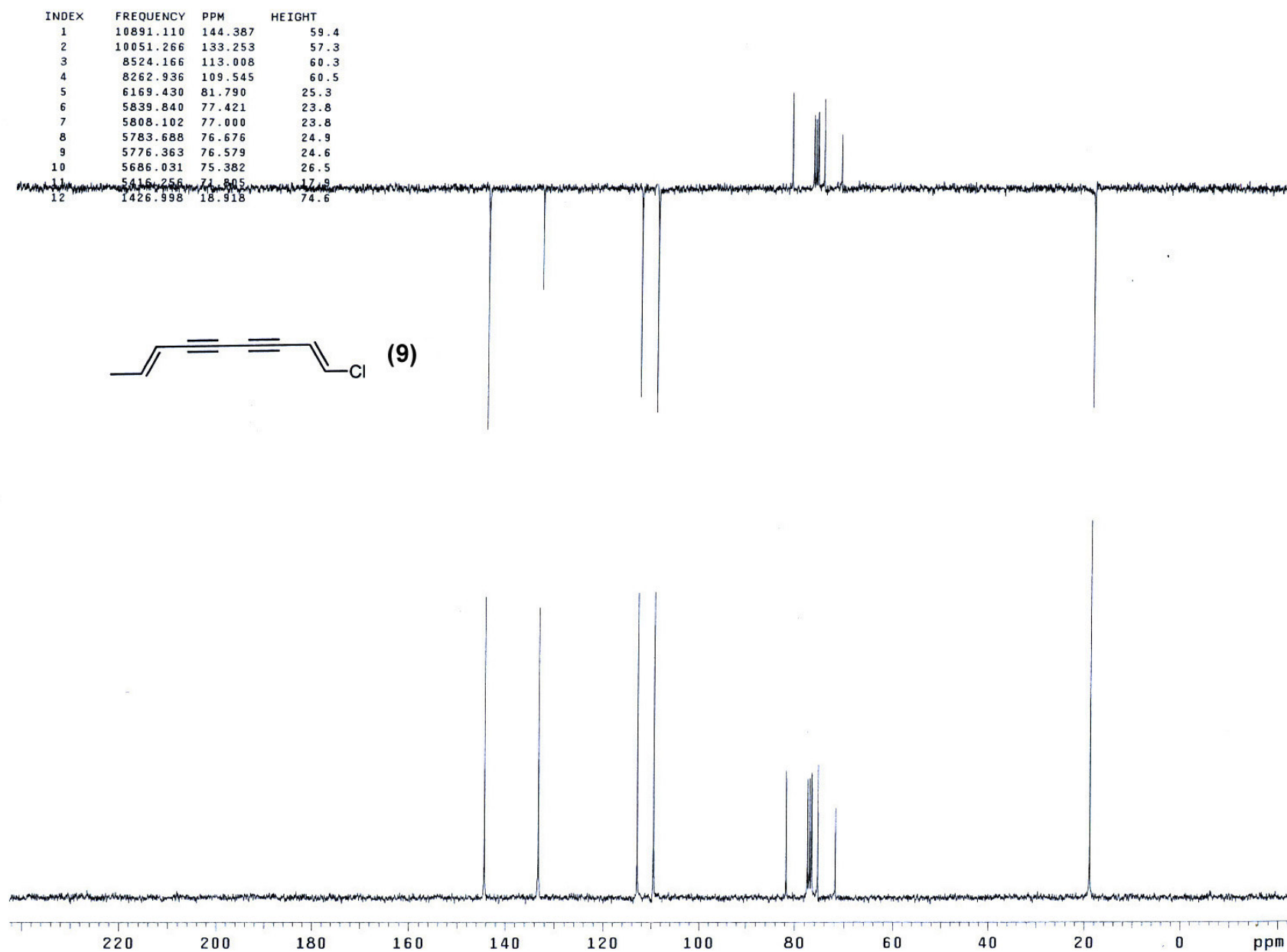
INDEX	FREQUENCY	PPM	HEIGHT
1	2016.636	6.723	11.4
2	2002.574	6.676	13.1
3	1787.553	5.959	9.8
4	1774.077	5.914	9.1
5	592.336	1.975	75.0

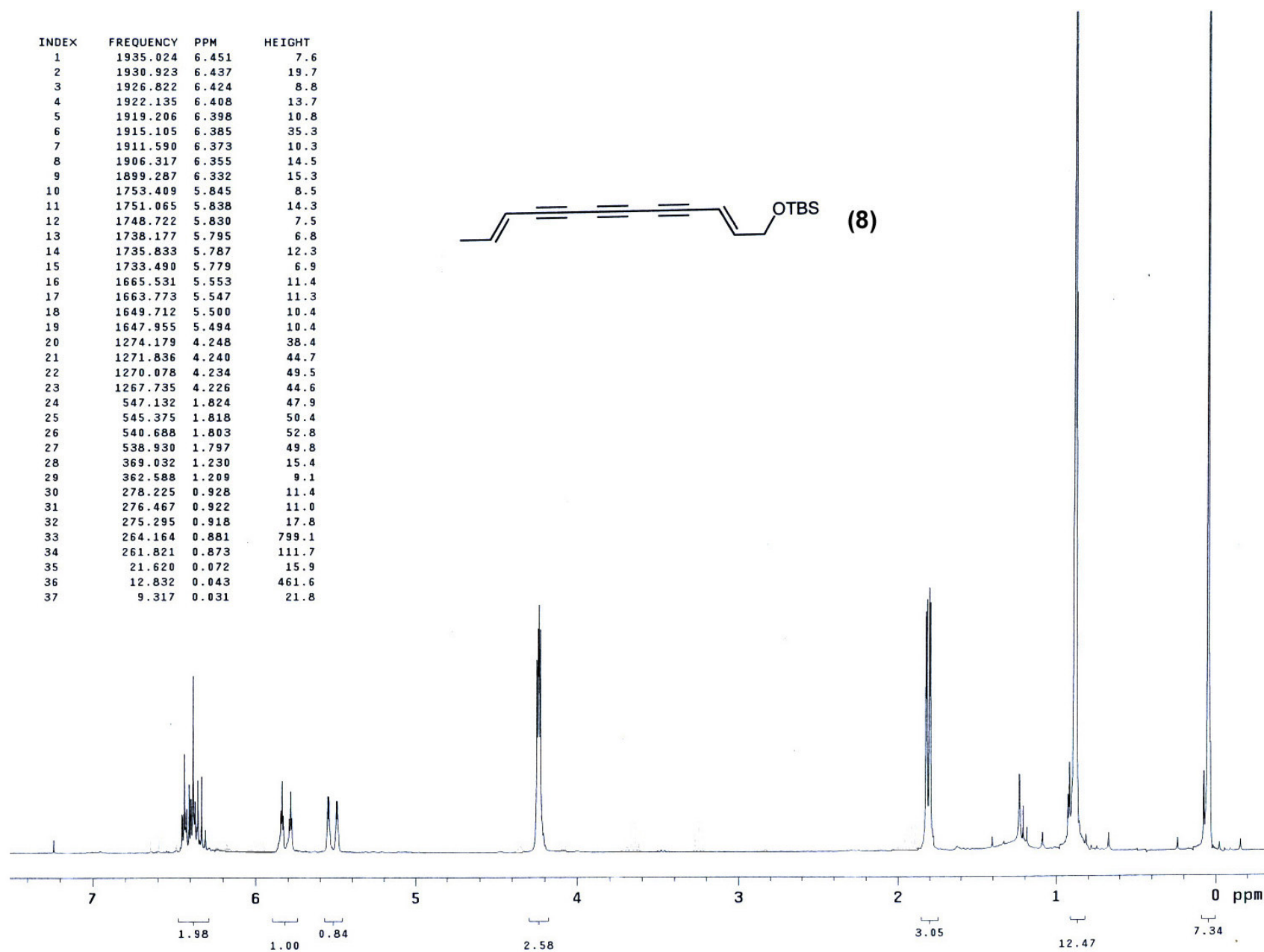


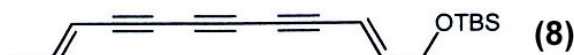
INDEX	FREQUENCY	PPM	HEIGHT
1	10194.268	135.149	40.0
2	8470.300	112.294	35.4
3	5958.473	78.994	20.1
4	5831.399	77.309	7.5
5	5808.103	77.000	13.8
6	5799.631	76.888	11.1
7	5767.862	76.467	9.4
8	5287.100	70.093	15.6
9	5151.554	68.296	11.9
10	4871.992	64.590	17.5
11	4399.701	58.328	15.6
12	337.573	4.475	38.5



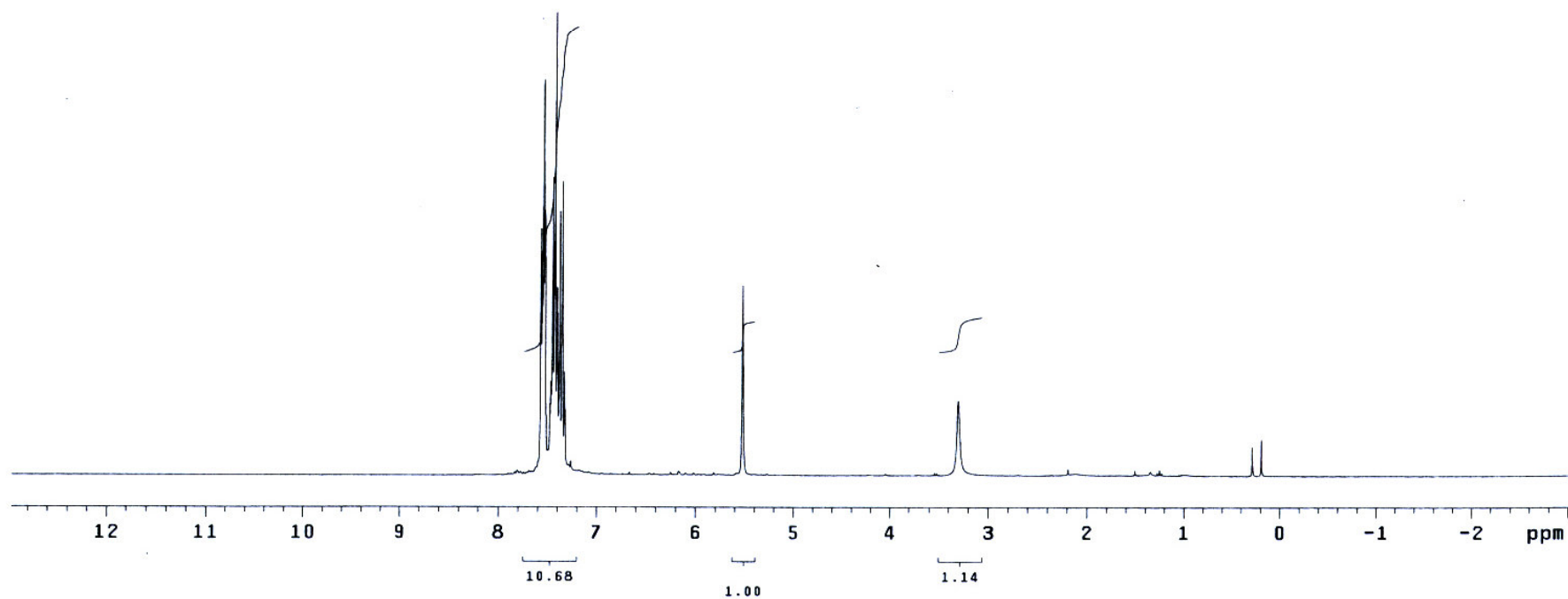


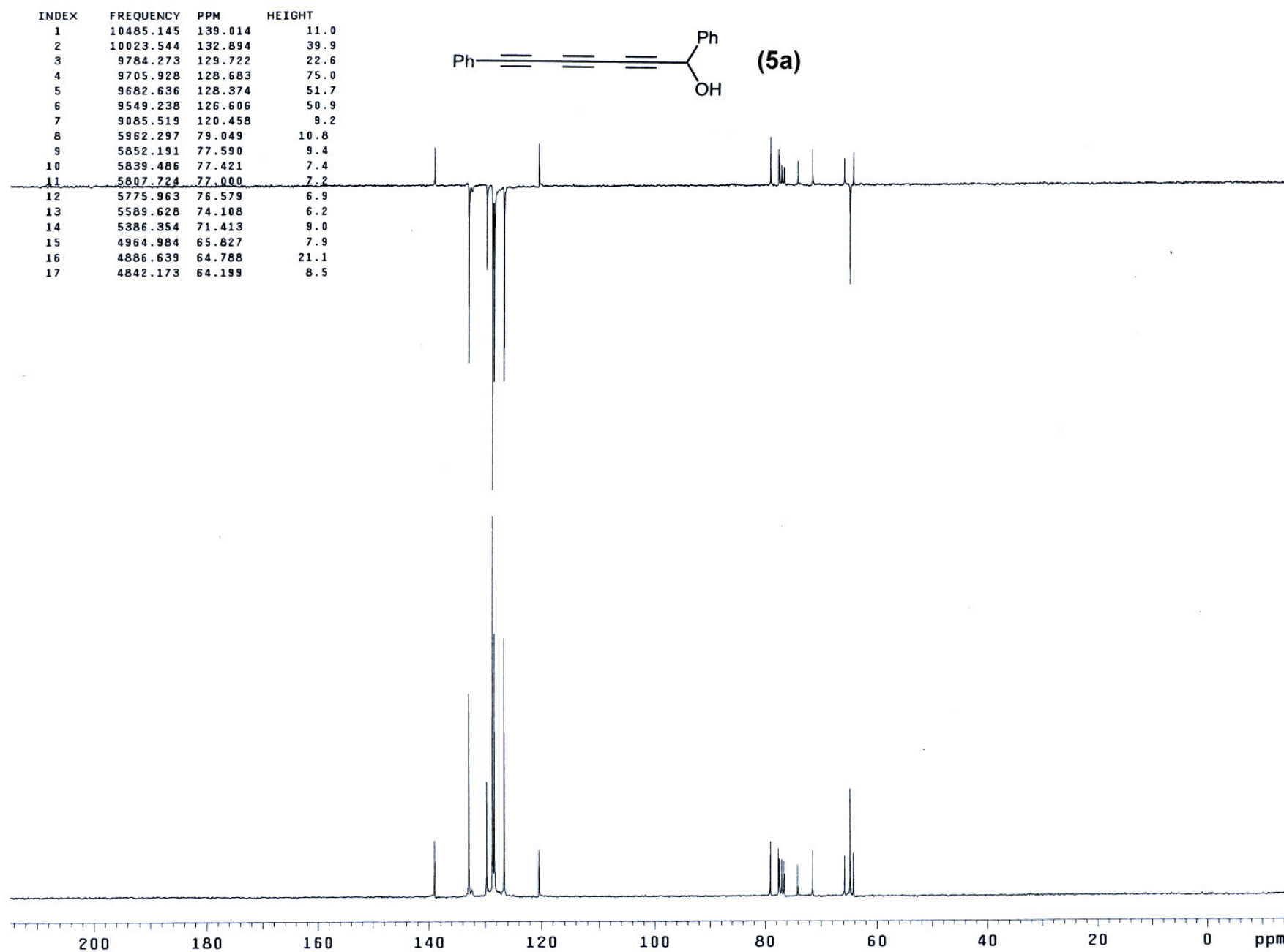




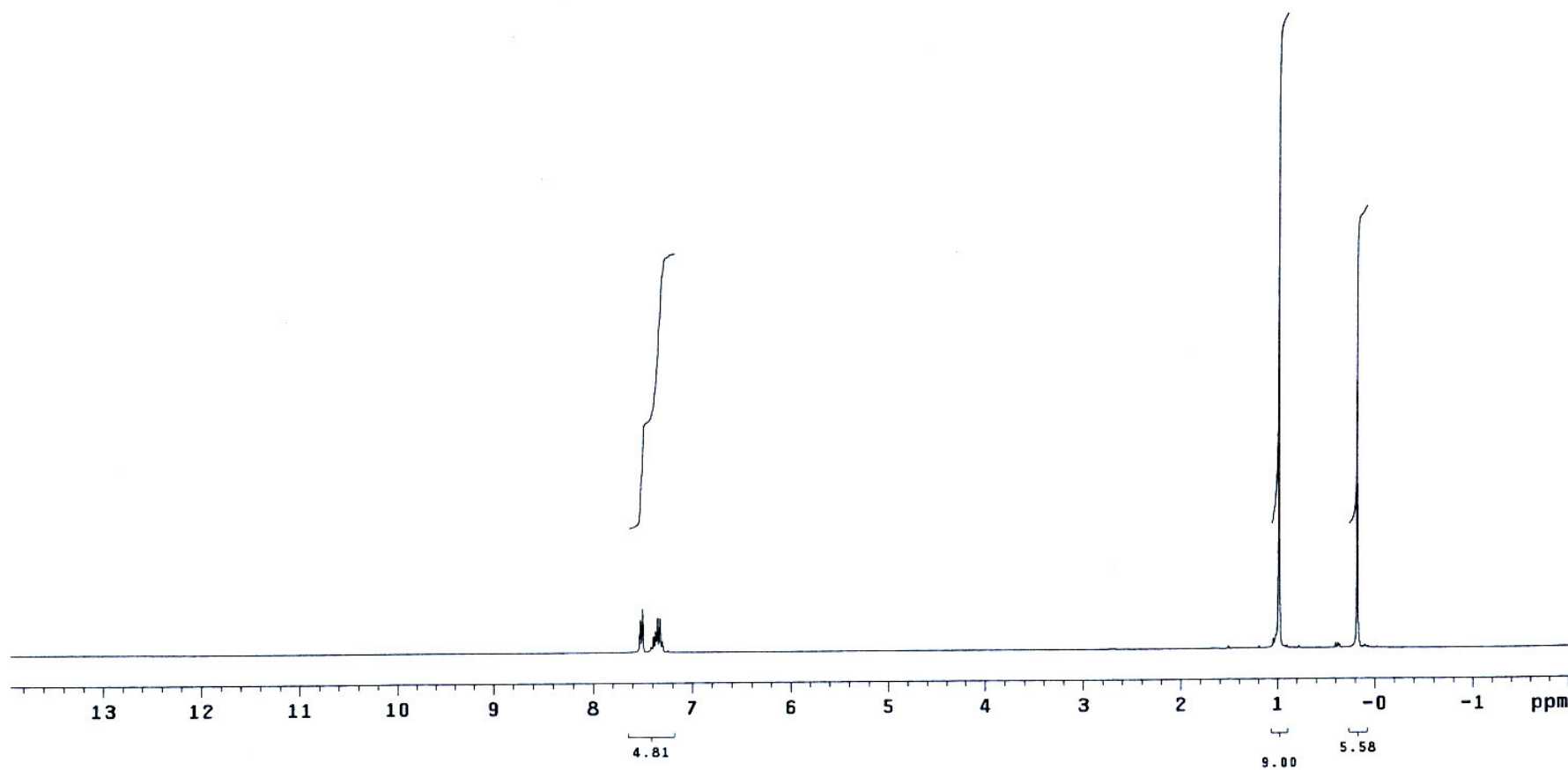
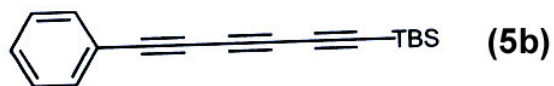


INDEX	FREQUENCY	PPM	HEIGHT
1	2269.688	7.567	39.8
2	2262.658	7.543	64.0
3	2257.971	7.528	42.8
4	2242.153	7.475	11.7
5	2239.810	7.467	15.3
6	2237.466	7.459	13.5
7	2233.951	7.447	48.1
8	2226.921	7.424	75.0
9	2220.476	7.403	30.4
10	2212.274	7.375	42.7
11	2204.658	7.350	47.5
12	2197.628	7.326	16.8
13	1656.298	5.522	30.8
14	989.594	3.299	12.2

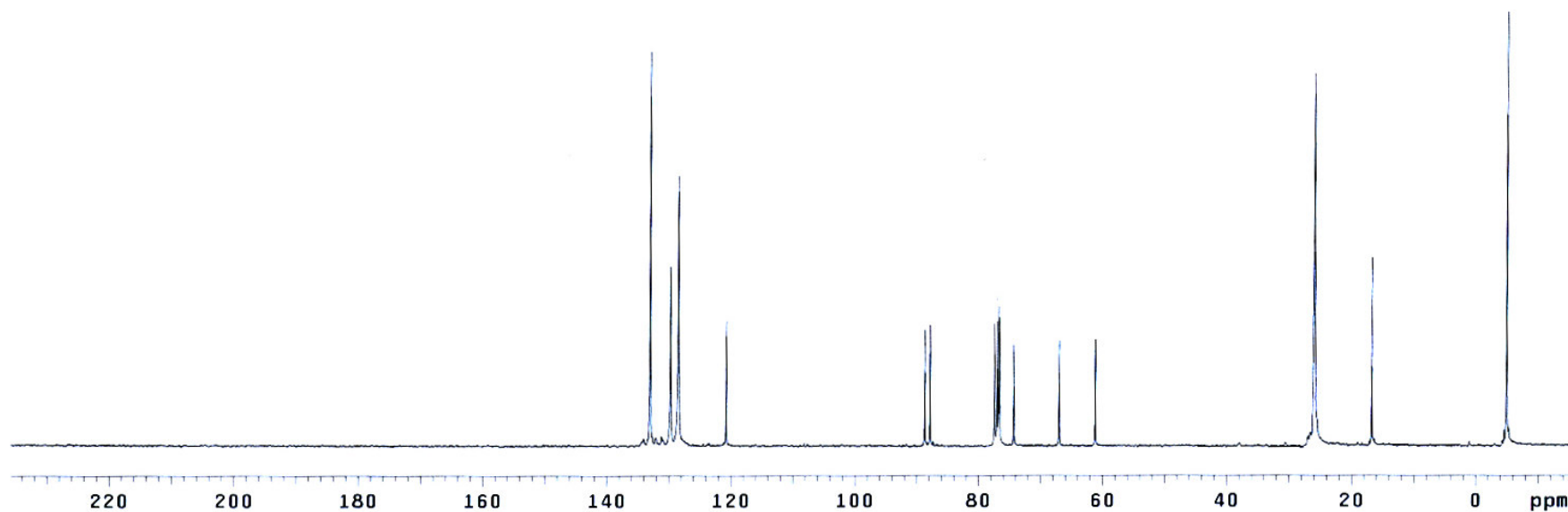
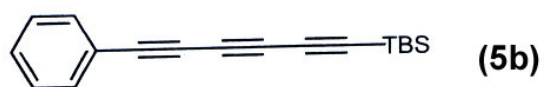




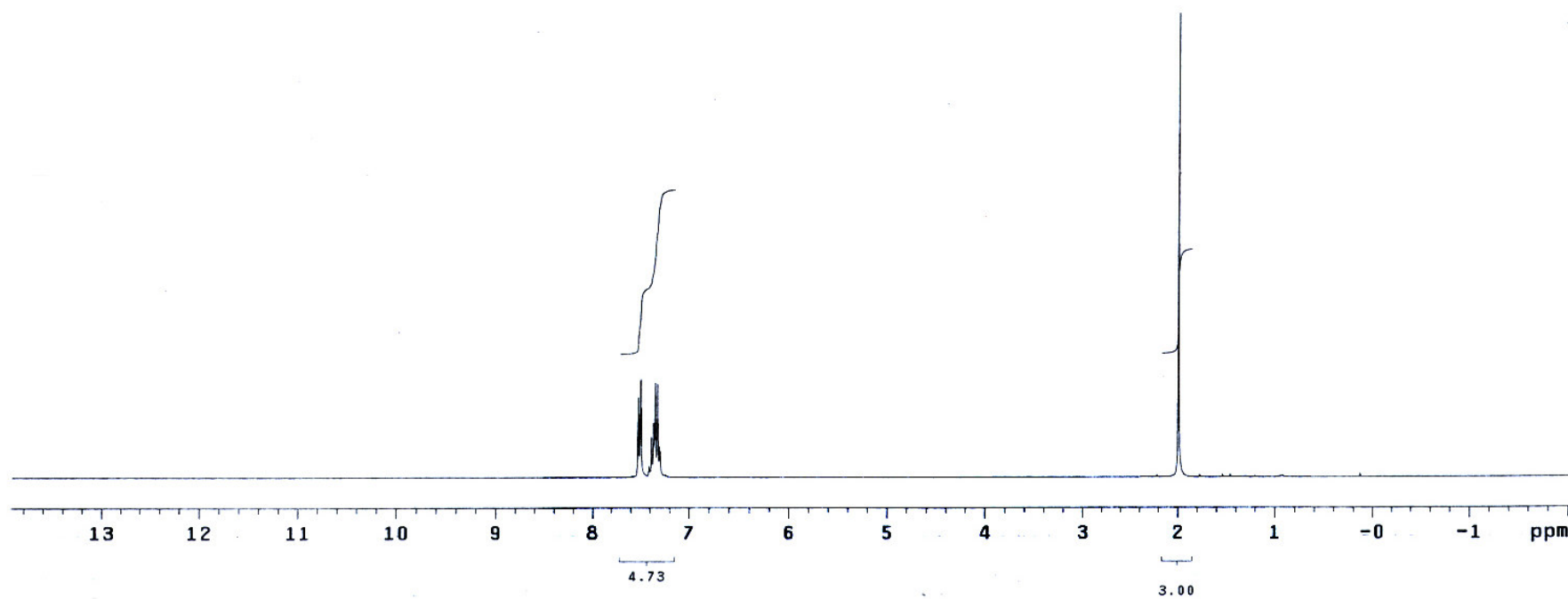
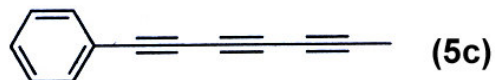
INDEX	FREQUENCY	PPM	HEIGHT
1	2258.608	7.529	5.3
2	2257.437	7.525	5.2
3	2250.992	7.504	7.2
4	2204.706	7.350	5.6
5	2198.848	7.330	5.6
6	2197.676	7.326	5.4
7	296.461	0.988	61.2
8	295.289	0.984	75.0
9	54.488	0.182	42.7
10	53.316	0.178	52.6

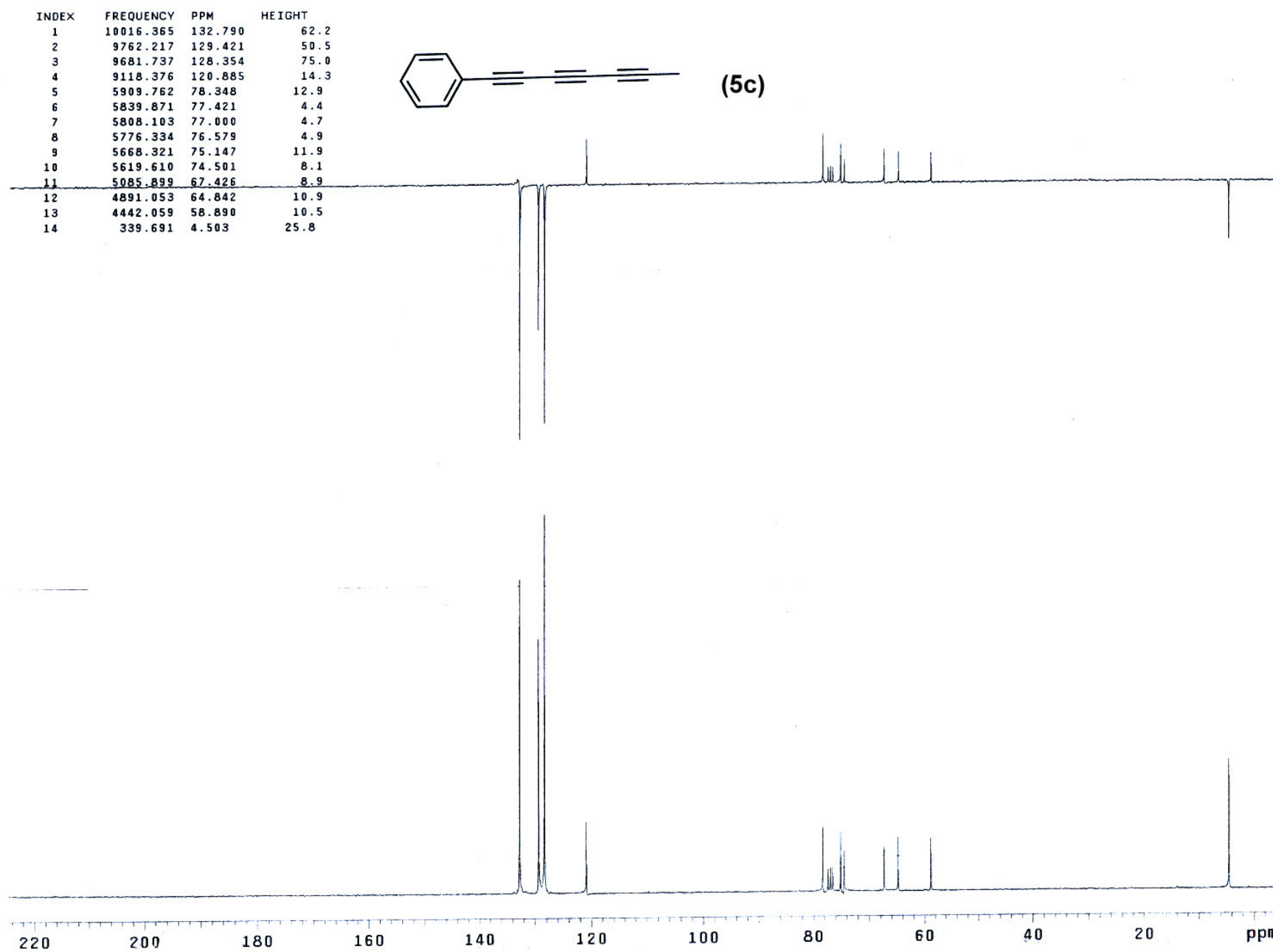


INDEX	FREQUENCY	PPM	HEIGHT
1	10033.456	133.017	63.6
2	9785.315	129.727	28.9
3	9689.074	128.451	43.5
4	9108.145	120.750	20.2
5	6689.350	88.683	18.7
6	6626.735	87.853	19.6
7	5839.409	77.415	19.8
8	5808.102	77.000	20.1
9	5788.390	76.739	22.5
10	5775.635	76.570	20.7
11	5604.023	74.294	16.4
12	5054.402	67.008	17.0
13	4614.938	61.182	17.2
14	1963.075	26.025	56.4
15	1957.278	25.948	59.9
16	1266.193	16.786	30.4
17	-374.552	-4.966	70.0

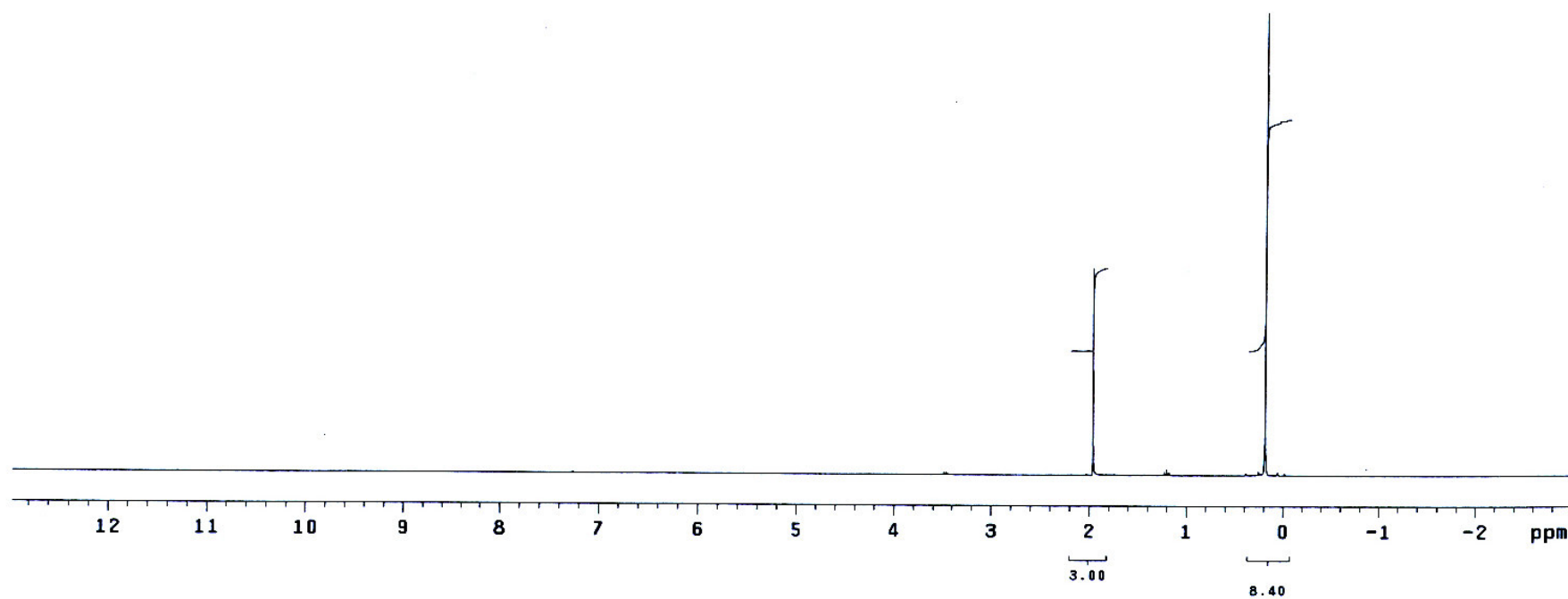
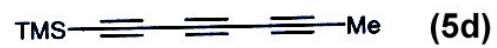


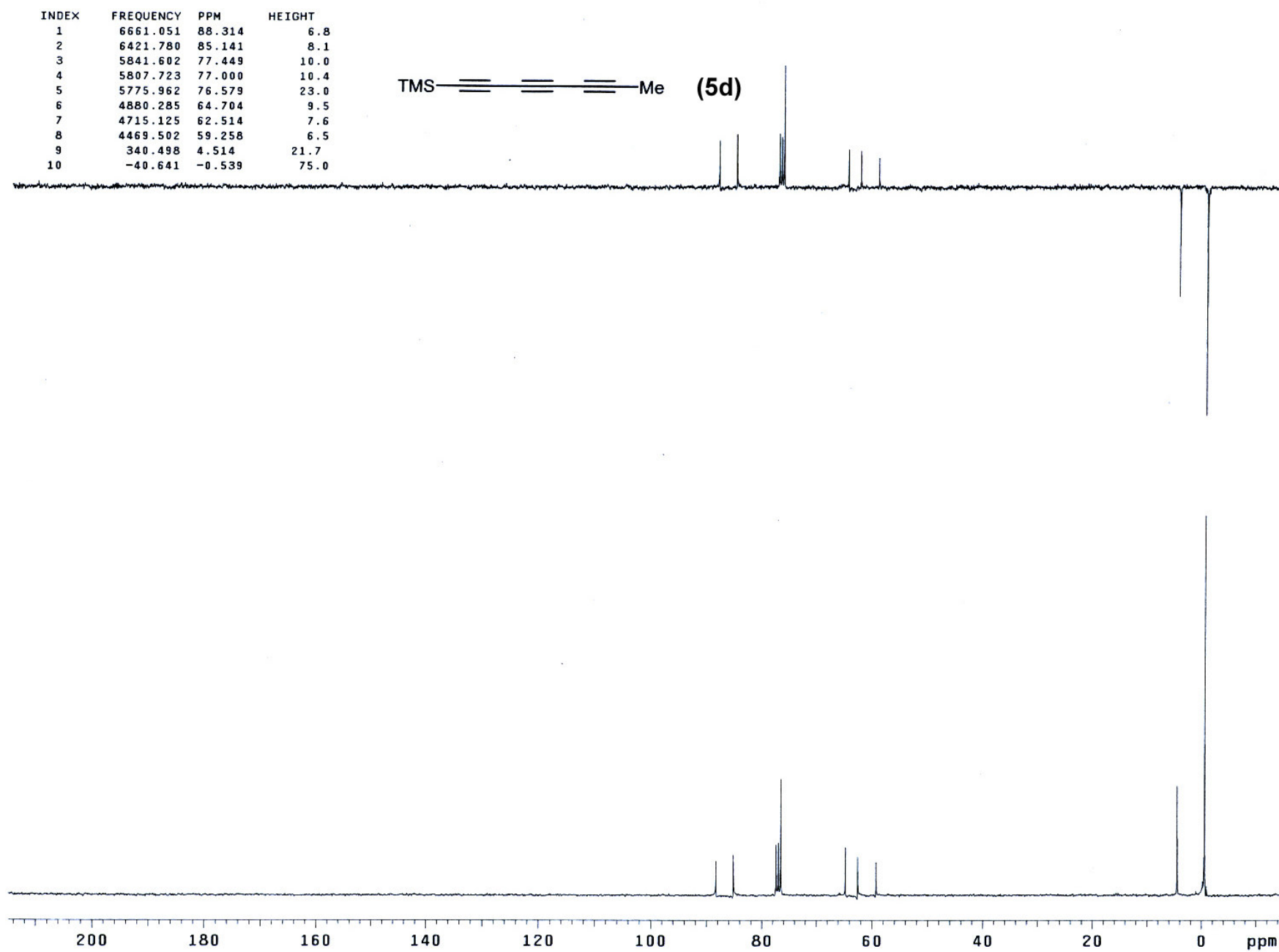
INDEX	FREQUENCY	PPM	HEIGHT
1	2257.437	7.525	9.0
2	2256.265	7.521	13.0
3	2254.507	7.516	7.6
4	2249.820	7.500	15.7
5	2248.063	7.494	15.9
6	2214.667	7.383	6.6
7	2209.394	7.365	5.6
8	2208.222	7.361	8.9
9	2205.879	7.353	6.8
10	2203.535	7.346	15.4
11	2196.504	7.322	15.2
12	2189.474	7.299	5.0
13	598.195	1.994	75.0



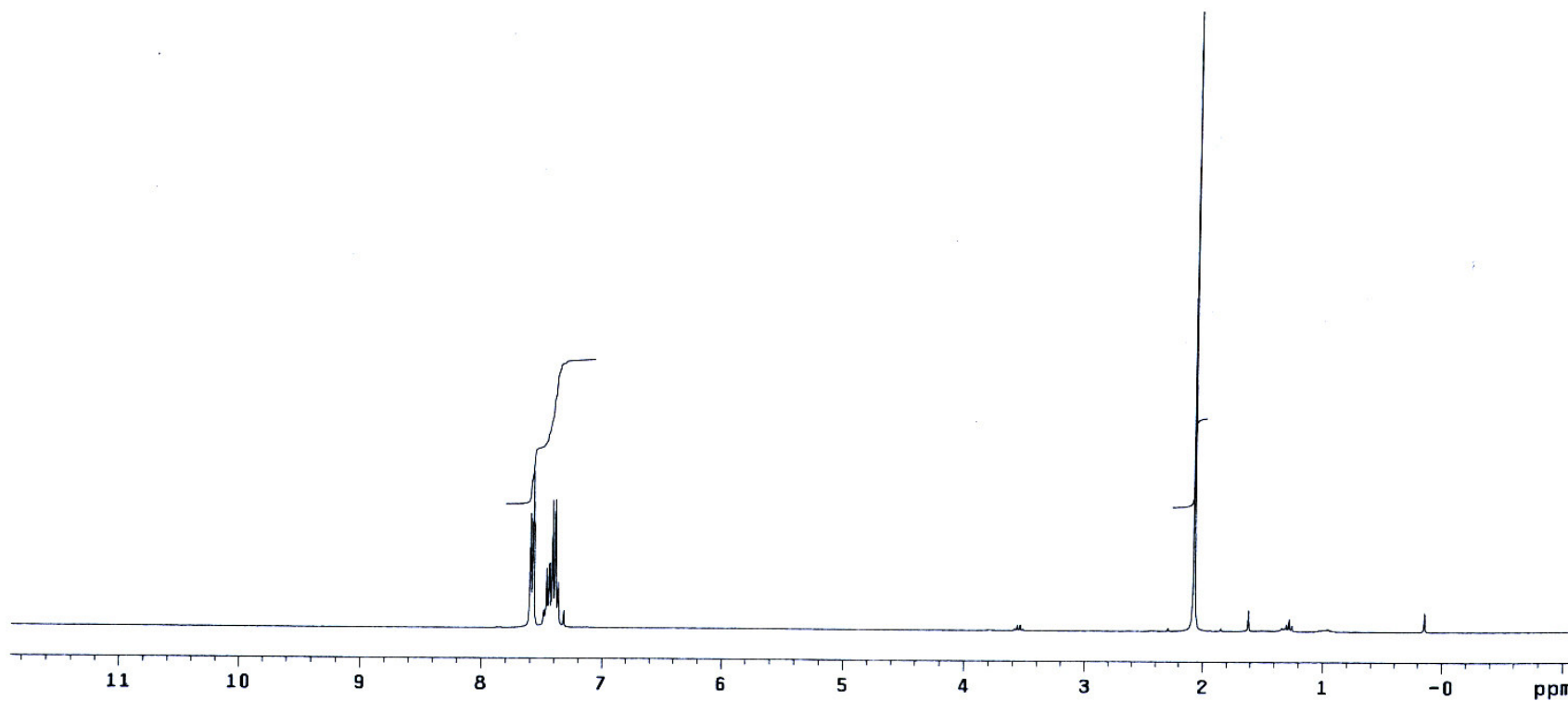
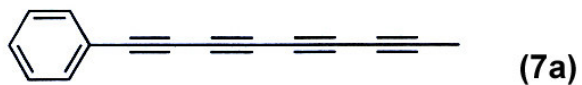


INDEX	FREQUENCY	PPM	HEIGHT
1	588.869	1.963	33.3
2	56.326	0.188	75.0

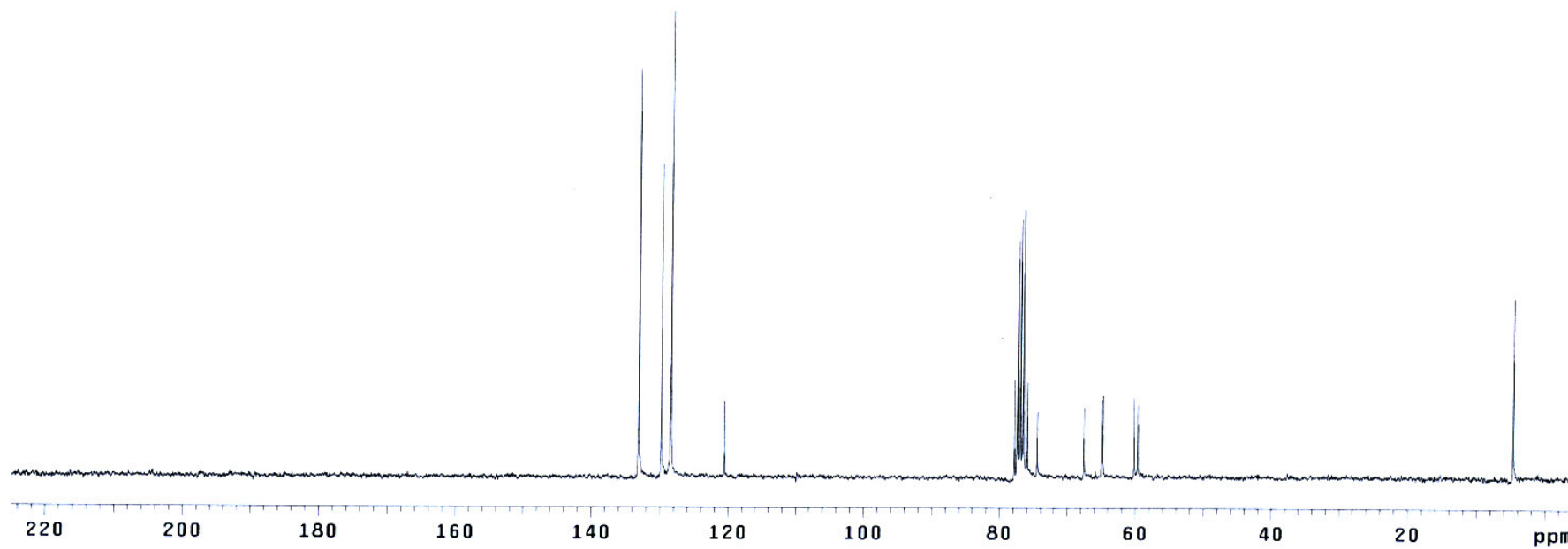
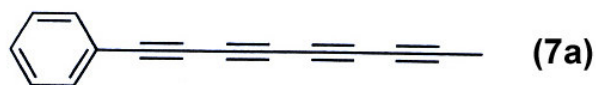


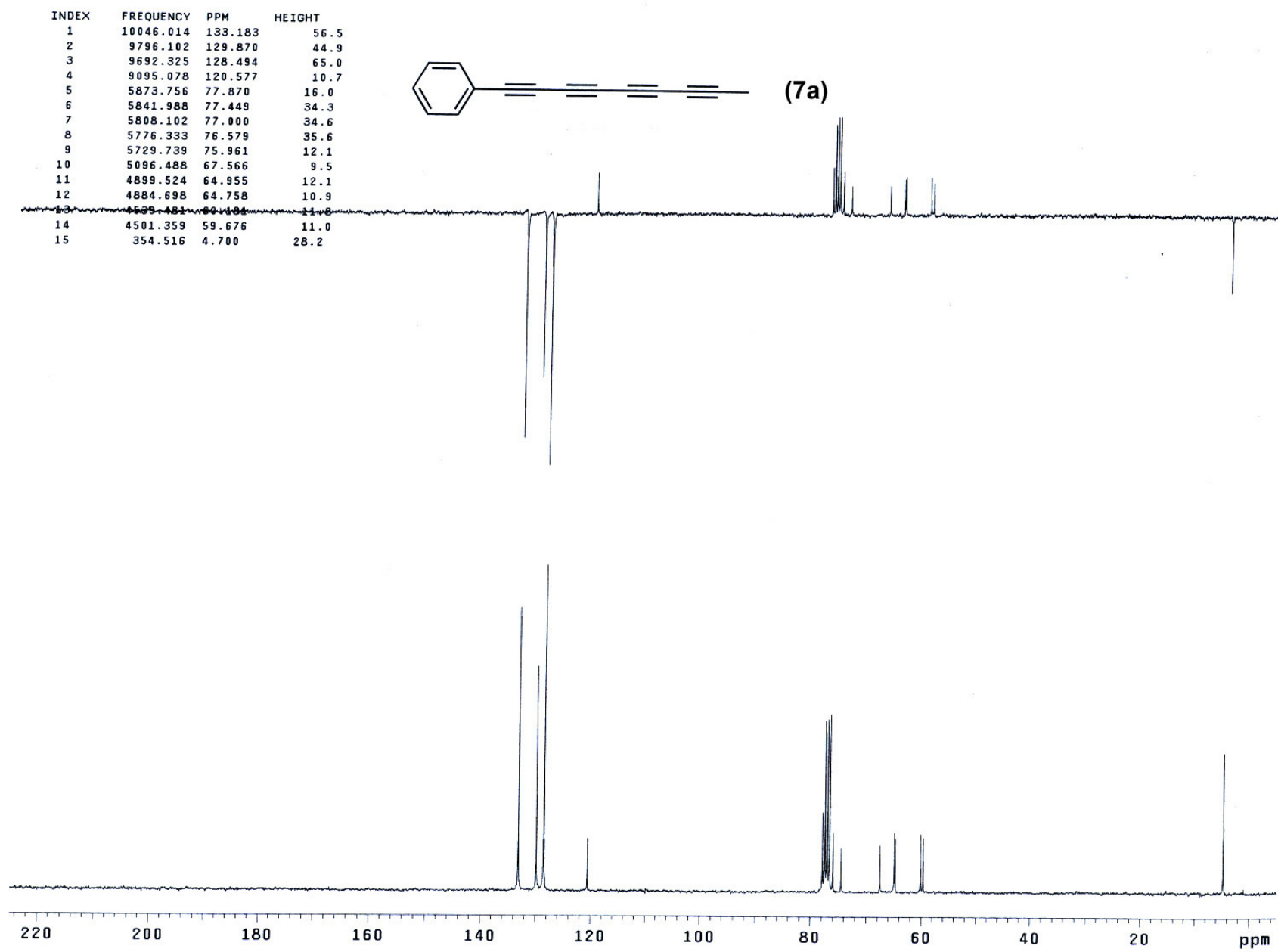


INDEX	FREQUENCY	PPM	HEIGHT
1	2279.117	7.598	18.5
2	2272.086	7.574	25.3
3	2238.690	7.463	9.7
4	2236.347	7.455	3.8
5	2232.832	7.443	10.3
6	2231.660	7.439	10.5
7	2224.629	7.416	20.7
8	2218.184	7.394	18.9
9	2217.013	7.391	20.7
10	2209.982	7.367	7.5
11	620.461	2.068	100.0

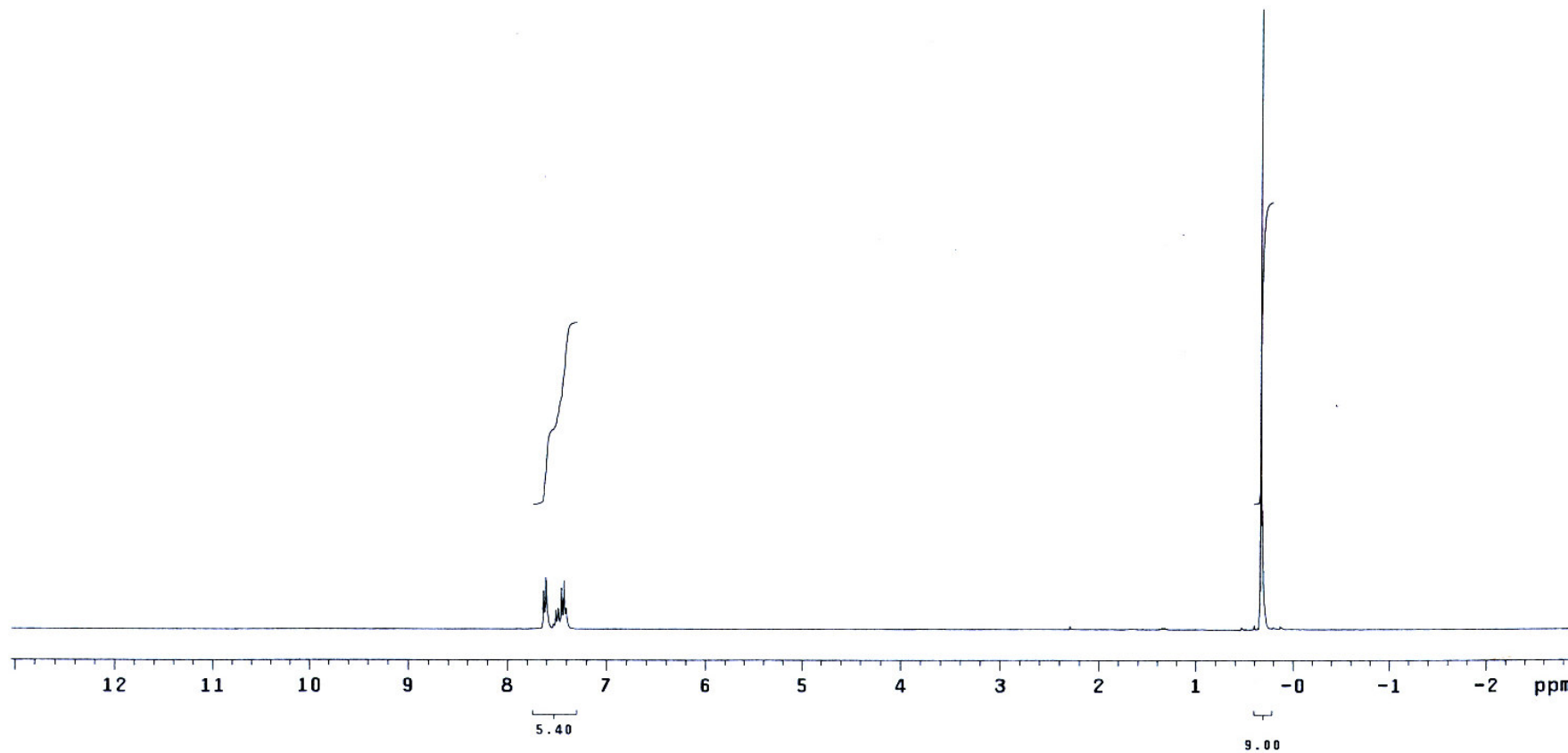
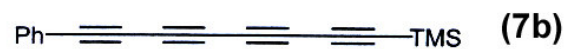


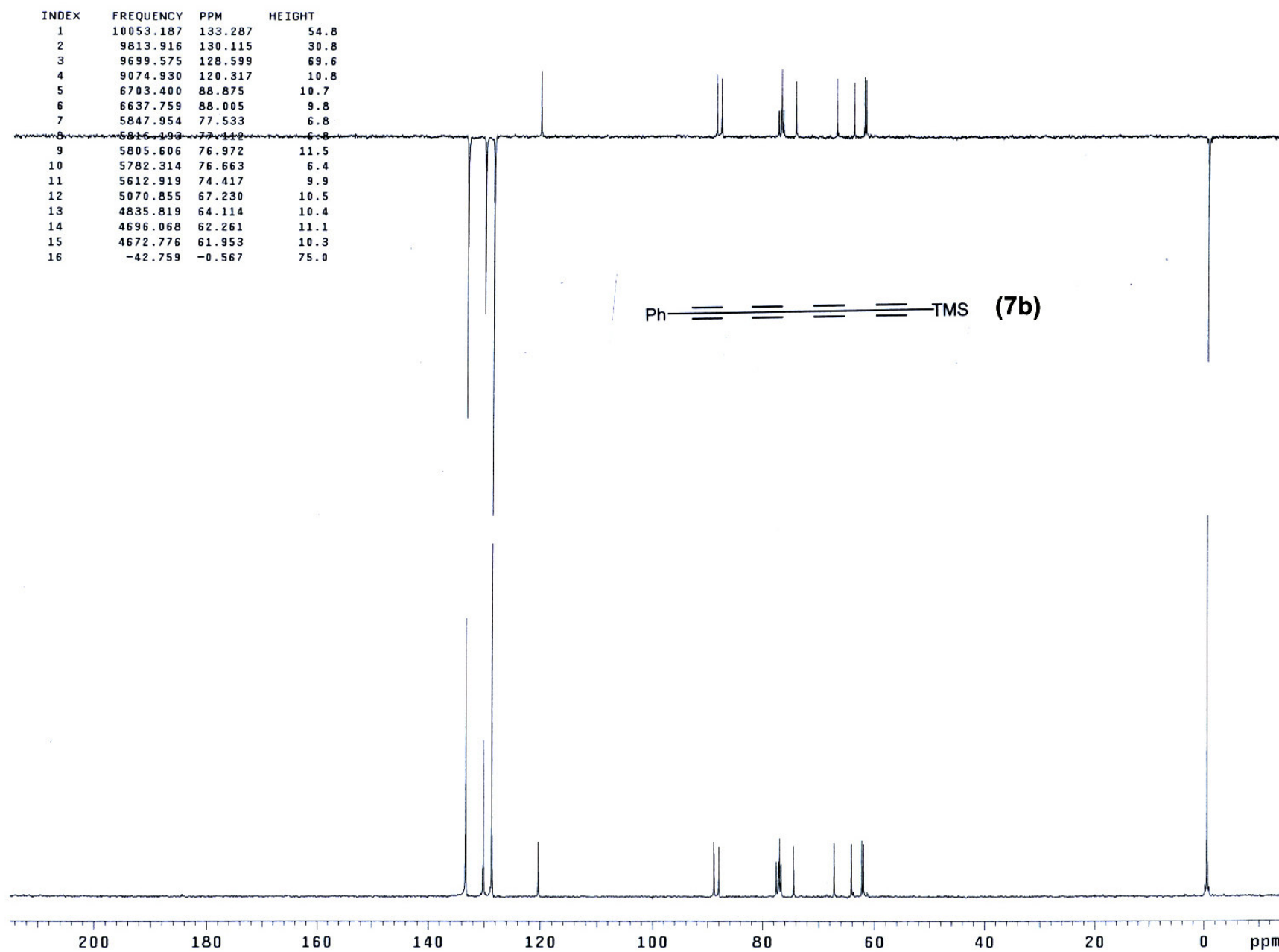
INDEX	FREQUENCY	PPM	HEIGHT
1	10043.896	133.155	65.5
2	9796.102	129.870	50.2
3	9692.325	128.494	75.0
4	9092.960	120.549	12.3
5	5873.756	77.870	15.8
6	5839.870	77.421	38.0
7	5808.102	77.000	41.5
8	5776.333	76.579	43.1
9	5729.739	75.961	15.6
10	5617.491	74.473	10.7
11	5096.488	67.566	11.3
12	4899.524	64.955	12.6
13	4884.698	64.758	13.4
14	4539.481	60.181	13.0
15	4501.359	59.676	11.9
16	354.516	4.700	29.1



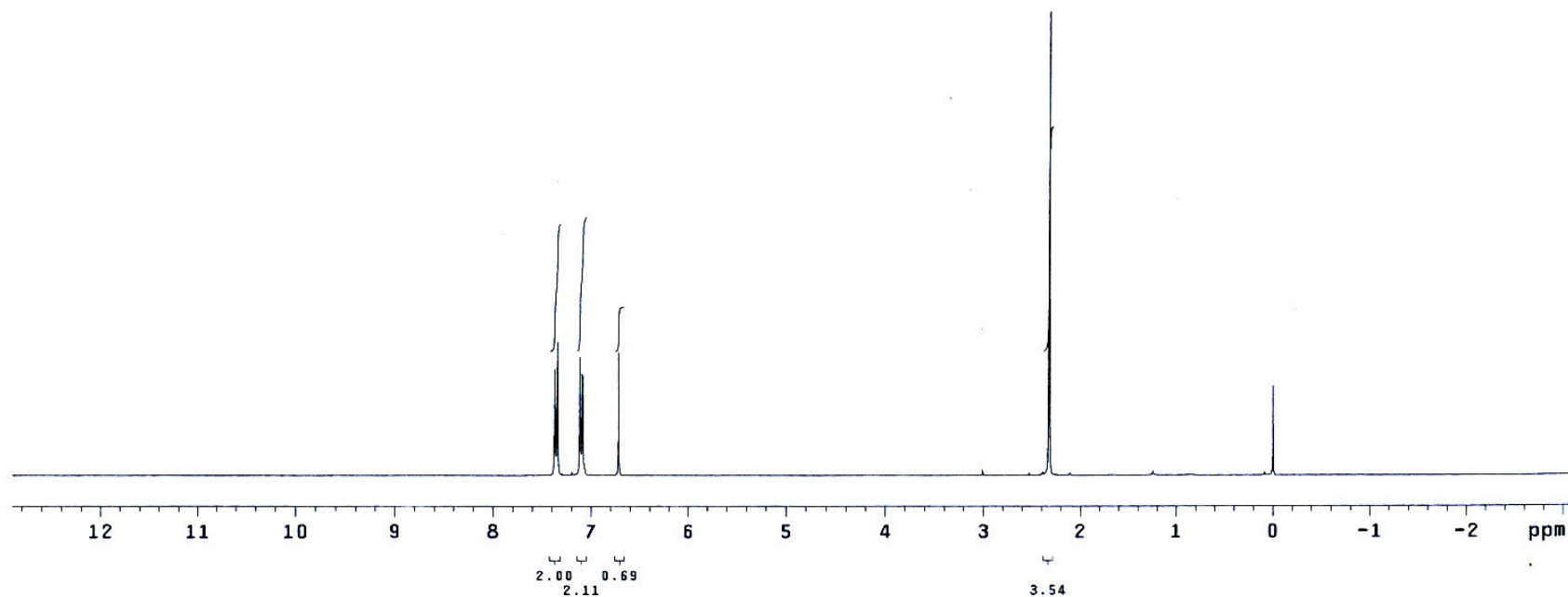
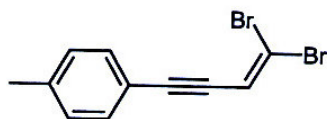


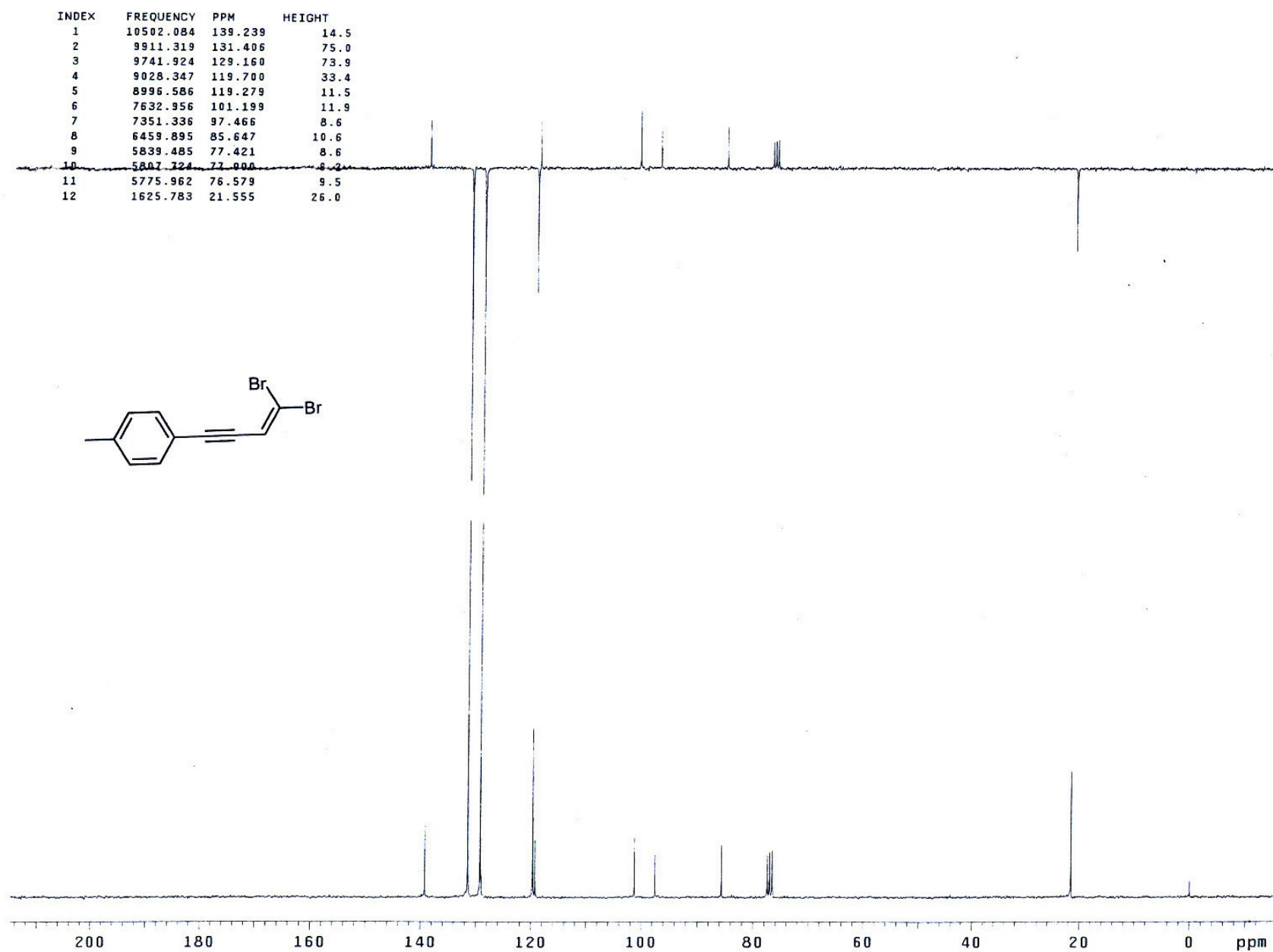
INDEX	FREQUENCY	PPM	HEIGHT
1	2289.431	7.632	6.2
2	2287.674	7.627	4.5
3	2284.744	7.617	3.5
4	2282.401	7.609	8.3
5	2280.643	7.603	7.7
6	2251.936	7.507	3.1
7	2246.078	7.488	2.5
8	2244.906	7.484	3.3
9	2243.148	7.478	2.6
10	2235.532	7.453	6.6
11	2229.674	7.433	4.9
12	2227.916	7.427	7.8
13	2222.644	7.410	2.7
14	2220.886	7.404	3.3
15	2219.714	7.400	2.8
16	104.190	0.347	3.3
17	100.675	0.336	100.0
18	95.988	0.320	19.1



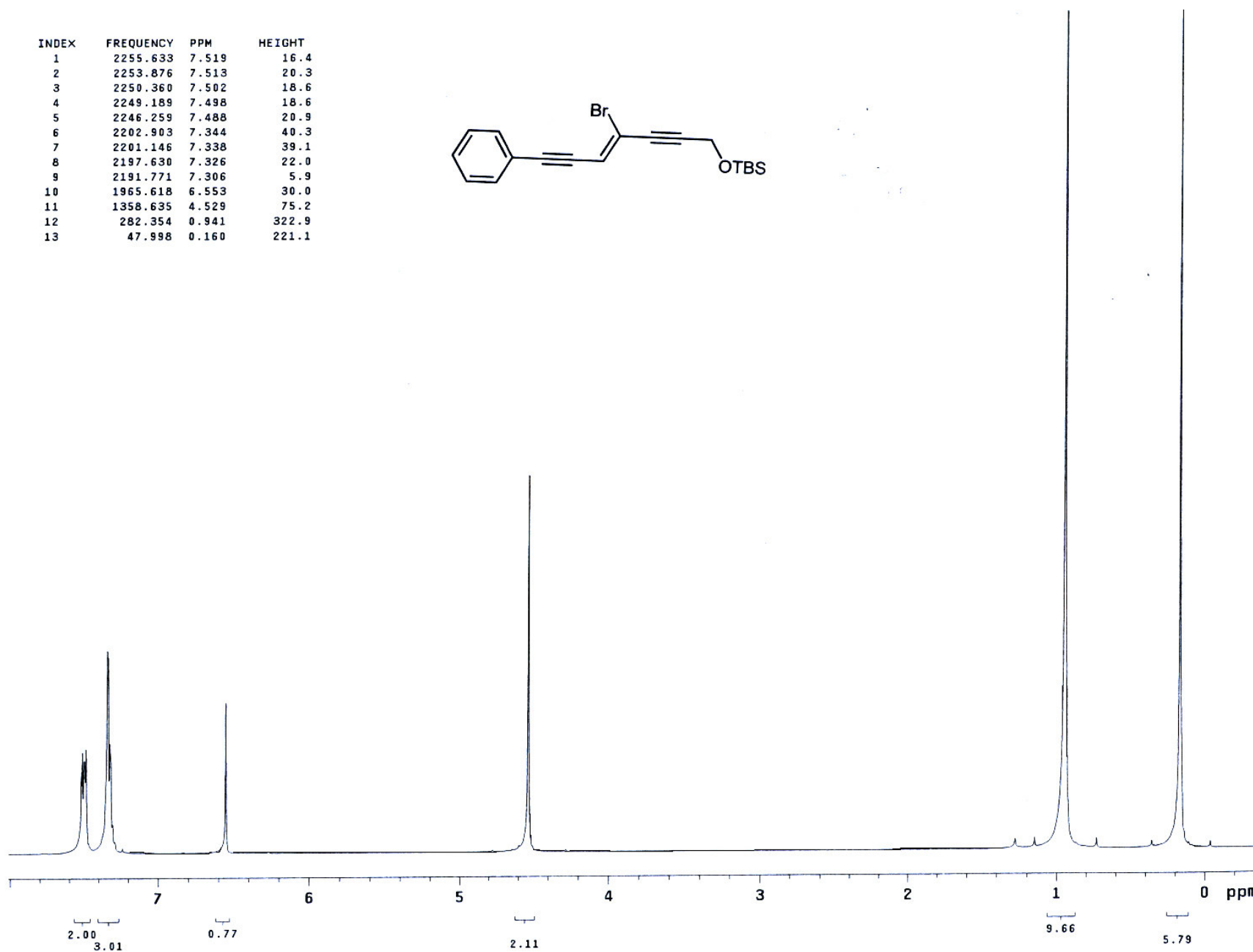
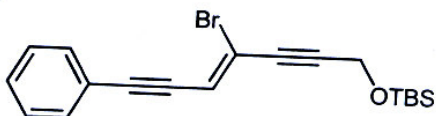


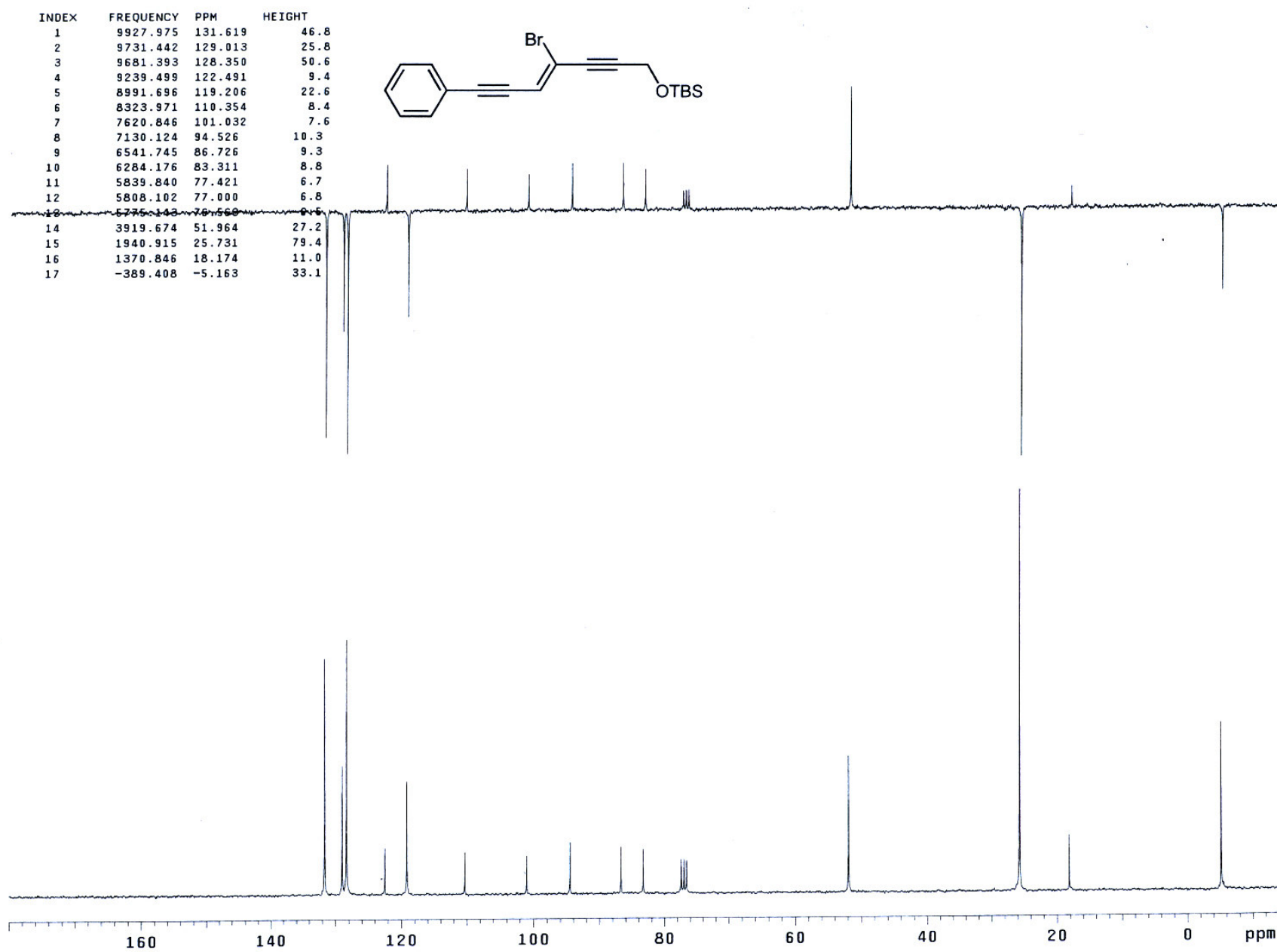
INDEX	FREQUENCY	PPM	HEIGHT
1	2211.019	7.371	17.2
2	2202.817	7.344	21.5
3	2134.272	7.115	19.1
4	2126.655	7.090	16.4
5	2015.929	6.721	19.9
6	695.410	2.318	75.0
7	0.000	0.000	14.4
8	-1.172	-0.004	8.0

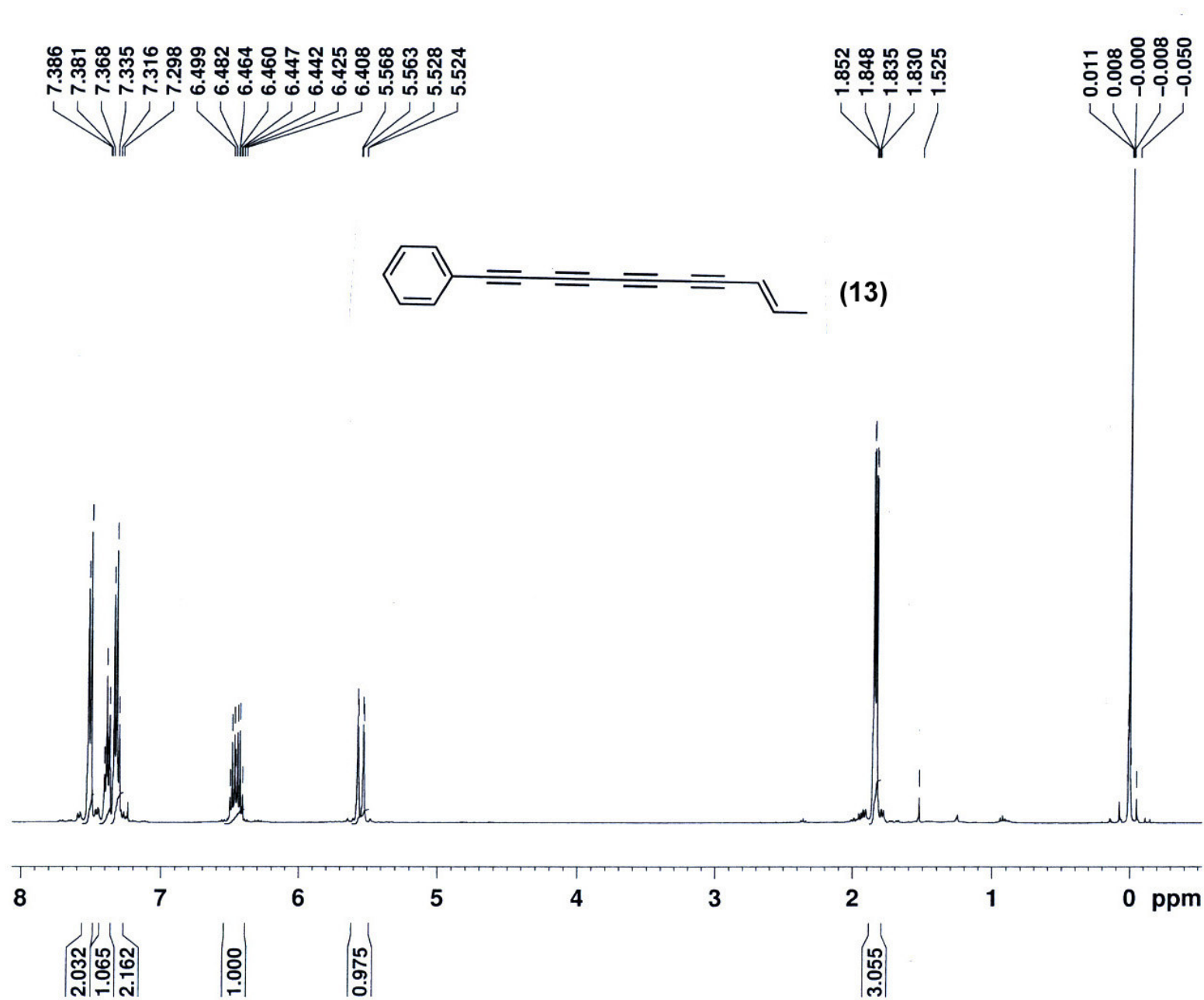


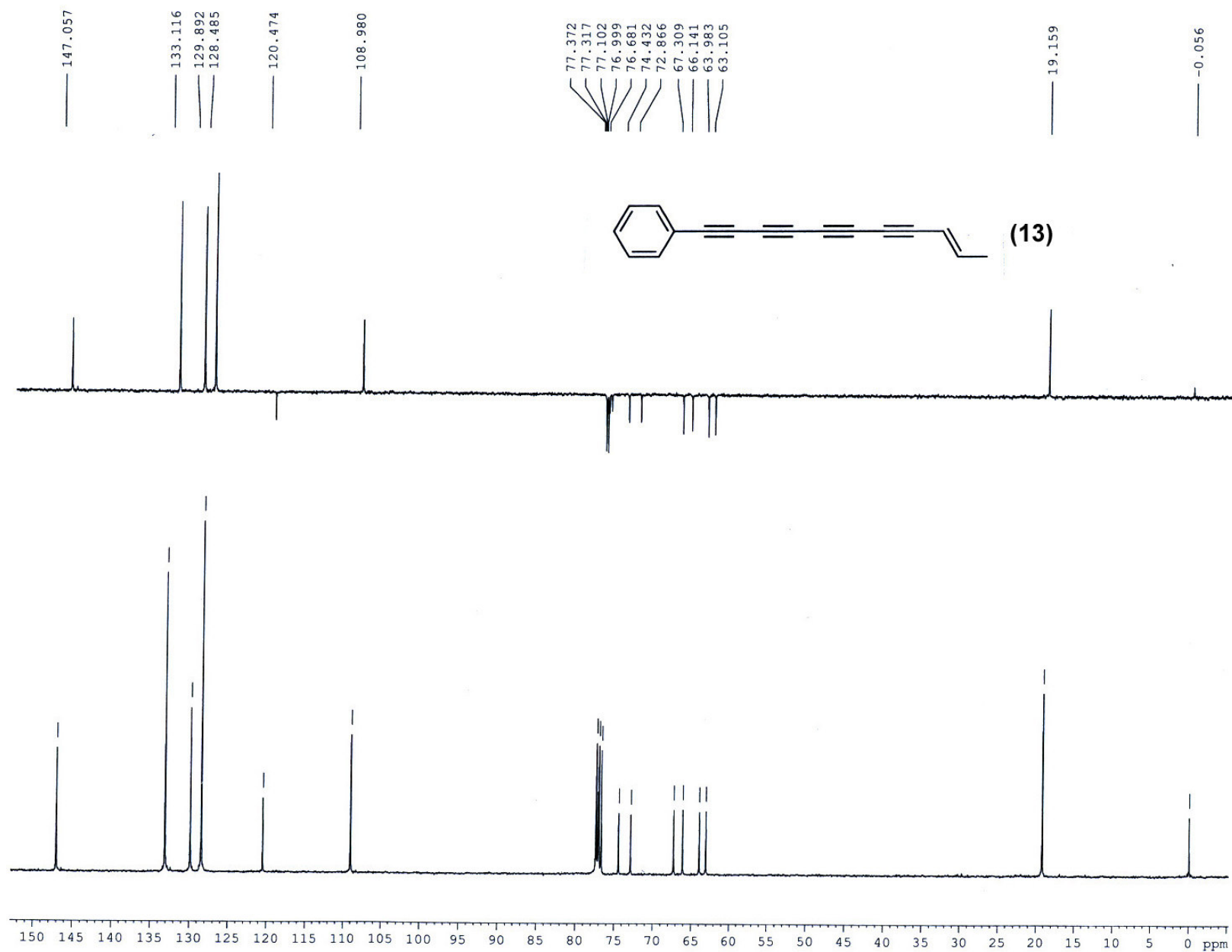


INDEX	FREQUENCY	PPM	HEIGHT
1	2255.633	7.519	16.4
2	2253.876	7.513	20.3
3	2250.360	7.502	18.6
4	2249.189	7.498	18.6
5	2246.259	7.488	20.9
6	2202.903	7.344	40.3
7	2201.146	7.338	39.1
8	2197.630	7.326	22.0
9	2191.771	7.306	5.9
10	1965.618	6.553	30.0
11	1358.635	4.529	75.2
12	282.354	0.941	322.9
13	47.998	0.160	221.1









INDEX	FREQUENCY	PPM	HEIGHT
1	2249.685	7.500	25.3
2	2242.655	7.477	32.0
3	2241.483	7.473	27.6
4	2219.221	7.398	29.7
5	2211.604	7.373	41.1
6	2194.615	7.316	28.2
7	2186.999	7.291	30.7
8	2133.686	7.113	33.5
9	2125.484	7.086	28.3
10	699.511	2.332	100.0
11	0.000	0.000	20.5

