

Supporting Information

Dual Reactivity of a Photochemically-Generated Cyclic Enyne–Allene

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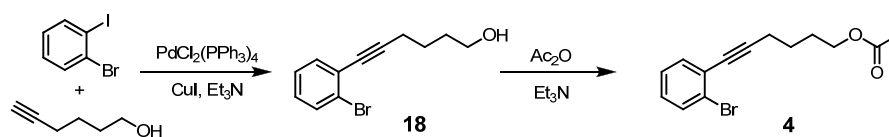
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General Procedures. All NMR spectra were recorded in CDCl₃ and referenced to TMS unless otherwise noted. Melting points are uncorrected. Purification of products by column chromatography was performed using 40-63 µm silica gel. Tetrahydrofuran was distilled from sodium/benzophenone ketyl; ether and hexanes were distilled from sodium. Other reagents were obtained from Aldrich or VWR and used as received unless otherwise noted. Transition metal compounds were purchased from Strem Chemicals.

Materials.

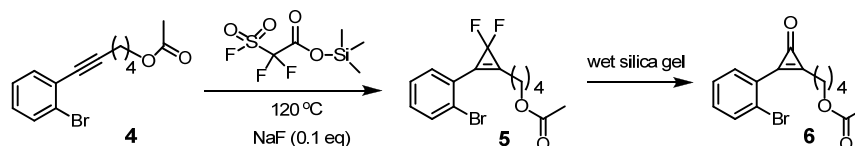


6-(2-Bromophenyl)hex-5-yn-1-ol¹ (18): PdCl₂(PPh₃)₂ (0.945 g, 2.149 mmol), CuI (0.819 g, 4.30 mmol), 5-hexyn-1-ol² (4.22 g, 43.0 mmol), and PPh₃ (0.564 g, 2.149 mmol) were added to a degassed solution of 2-bromoiodobenzene (12.77 g, 45.1 mmol) in THF (300 ml) and triethylamine (40 ml, 277 mmol) under Ar. The reaction vessel was sealed and heated at 55 °C for 2 days. The mixture was then filtered through small layer of silica gel, solvents were removed in vacuum, and residue purified by chromatography (EtOAc – hexanes 1: 3, R_f = 0.15) to give 10.2 g (40.3 mmol, 92%) of alcohol **19** as yellow oil. ¹H: 1.72-1.8 (m, 4H), 2.52 (t, 2H, *J* = 6.8 Hz), 3.72 (t, 2H, *J* = 6.0 Hz), 7.1-7.3 (m, 2H), 7.4 (d, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 8.0 Hz); ¹³C: 19.58, 25.09, 32.11, 62.66, 80.00, 95.26, 125.70, 126.22, 127.11, 128.93, 132.51, 133.52; FW calc. for C₁₂H₁₃BrO: 252.0150, EI-HRMS found: 252.0150.

6-(2-bromophenyl)hex-5-ynyl acetate (4). Acetic anhydride (3.63 g, 35.6 mmol) and pyridine (2.81 g, 35.6 mmol) were added to a solution of alcohol **18** (9 g, 35.6 mmol) in CH₂Cl₂ (20 ml). The reaction mixture was stirred for 3 hours at r.t., solvent was removed in vacuum, and residue was purified by chromatography (EtOAc – Hexanes 1: 9, R_f = 0.1) affording 9.45 g (32.1 mmol, 90%) of acetate **5** as yellow oil. ¹H: 1.65-1.75 (m, 2H), 1.8-1.9 (m, 2H), 2.05 (s, 3H), 2.52 (t, 2H, *J* = 7.2 Hz), 4.13 (t, 2H, *J* = 6.0 Hz), 7.05-7.12 (m, 1H), 7.2-7.28 (m, 1H), 7.41 (d, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 8.0 Hz); ¹³C: 19.46, 21.23, 25.26, 28.00, 64.25, 80.10, 94.80, 125.68, 126.06, 127.14, 129.02, 132.51, 133.51, 171.42; FW calc. for C₁₄H₁₅BrO₂: 294.0255, EI-HRMS found: 294.0258.

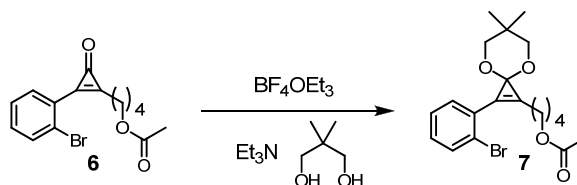
¹ D. L. Boger and J. Zhou *J. Org. Chem.*, 1993, **58**, 3018.

² 5-Hexyn-1-ol was purified by flash chromatography (EtOAc/Hexanes 6:1) before the reaction.

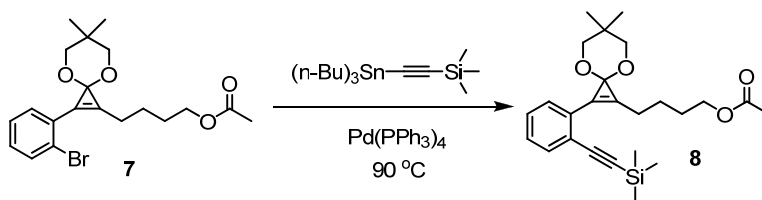


3-(4-Acetoxybutyl)-2-(2-bromophenyl)cyclopropenone (6). A solution of trimethylsilyl fluoro-sulfonyl difluoroacetate (TFDA, 6.3 ml, 32.0 mmol) was added via syringe pump over 15 minutes under argon flow to a pre-heated (120 °C) solution of acetylene **4** (3.14 g, 10.64 mmol) and sodium fluoride (0.050 g, 1.191 mmol) in diglyme (6 mL). The reaction mixture was kept at this temperature for 20 min, cooled, and transferred into silica gel column. Flash chromatography with EtOAc – hexanes (1:10, R_f = 0.3) provided 3.3 g, (9.57 mmol, 90%) of 3-(4-acetoxybutyl)-2-(2-bromophenyl)-1,1-difluorocyclopropene (**5**) as yellow oil. ^1H : 1.75-1.85 (m, 4H), 2.05 (s, 3H), 2.8-2.88 (m, 2H), 4.1-4.18 (m, 2H), 7.3 (t, 1H, J = 8.0 Hz), 7.39 (t, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 7.2 Hz), 7.66 (d, 1H, J = 7.6 Hz); ^{13}C : 20.81, 23.69, 28.1, 58.82, 99.9, 102.61, 105.3, 123.46, 124.78, 125.96, 127.66, 128.63, 128.73, 128.84, 131.98, 132.45, 133.38, 170.89, 170.92.

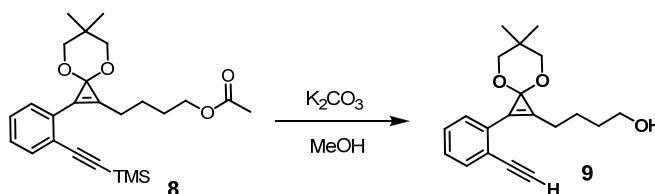
Crude difluorocyclopropene (**5**) was transferred into wet silica gel column, washed with 200 mL of an AcOH – hexanes mixture (1: 99) and left overnight in the column. Elution with gradient EtOAc – hexanes mixture (1:9 → 1:1) produced, after solvents removal, 2.92 g (9.04 mmol, 85%, 2 steps) of cyclopropenone **6** as viscous yellow oil. ^1H : 1.8-1.9 (m, 4H), 2.04 (s, 3H), 2.96 (t, 2H, J = 7.2 Hz), 4.11 (t, 2H, J = 6.4 Hz), 7.36-7.48 (m, 2H), 7.15 (dd, 1H, J = 8.0 Hz, 1.2 Hz), 7.8 (dd, 1H, J = 7.6 Hz, 1.6 Hz); ^{13}C : 20.97, 23.26, 27.51, 28.27, 63.65, 123.95, 125.61, 127.9, 133.65, 133.68, 134.07, 153.38, 156.87, 157.21, 171.13; FW calc. for $\text{C}_{15}\text{H}_{16}\text{BrO}_3$ ($\text{M}+\text{H}$): 323.0283, ESI-HRMS found: 323.0276.



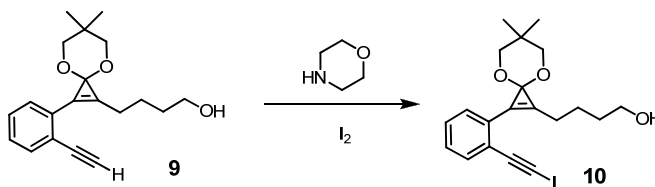
4-[2-(2-bromophenyl)-6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-en-1-yl]butyl acetate (7). Et_3N (3.59 g, 27.3 mmol) was added to solution of cyclopropenone **6** (5.87 g, 18.17 mmol) in CH_2Cl_2 (30 mL) under vigorous stirring at r.t. After 30 min, a solution of neopentylglycol (3.78 g, 36.3 mmol) and triethylamine (3.68 g, 36.3 mmol) in CH_2Cl_2 (10 mL) was added dropwise. In 1 hour the reaction mixture was washed with saturated solution of NaHCO_3 (2x100 mL), dried with Na_2SO_4 , and solvents removed in vacuum. The crude product was purified by chromatography (ether – hexanes 1:10, 1% of Et_3N , R_f = 0.1) to give 5.95 g (14.53 mmol, 80%) of acetal **7** as a yellow solid. M.p. 52 °C; ^1H : 0.96 (s, 3H), 1.22 (s, 3H), 1.65-1.75 (m, 4H), 2.04 (s, 3H), 2.91 (t, 2H, J = 7.2 Hz), 3.65-3.8 (m, 4H), 4.12 (t, 2H, J = 6.0 Hz), 7.16-7.22 (m, 1H), 7.32-7.37 (m, 1H), 7.6-7.64 (m, 2H); ^{13}C : 21.20, 22.11, 22.35, 22.70, 25.09, 25.99, 28.57, 30.54, 64.29, 78.27, 83.39, 123.03, 124.42, 127.61, 128.46, 130.57, 132.24, 133.44, 171.39; FW calc. for $\text{C}_{20}\text{H}_{25}\text{BrO}_4+\text{H}$: 409.1014, ESI-HRMS found: 409.1012.



4-(6,6-dimethyl-2-(2-((trimethylsilyl)ethynyl)phenyl)-4,8-dioxaspiro[2.5]oct-1-en-1-yl)butyl acetate (8). Pd(PPh₃)₄ (0.555 g, 0.480 mmol) was added to a degassed solution of bromide **7** (6.55 g, 16.00 mmol) in toluene (100 mL) and heated to 90 °C under vigorous stirring for 10 min. A solution of trimethyl((tributylstannyl)ethynyl)silane (7.75 g, 20.00 mmol) in toluene (5 mL) was added to the reaction mixture and heated at 90 °C in a sealed vessel for 3 h. Solvent was removed in vacuum and residue was purified by chromatography (ether – hexanes 1:10, 1% of Et₃N) to yield 4.89 g of **8** (11.46 mmol, 71.6 %), as yellowish crystals. M.p. 64-65 °C; ¹H: 0.25 (s, 9H), 1.02 (s, 3H), 1.16 (s, 3H), 1.75-1.85 (m, 4H), 2.04 (s, 3H), 2.91 (t, 2H, *J* = 6.8 Hz), 3.73 (m, 4H), 4.11 (t, 2H, *J* = 6.0 Hz), 7.24-7.37 (m, 2H), 7.54-7.58 (m, 2H); ¹³C: 0.19, 21.18, 22.50, 22.67, 25.00, 26.32, 28.59, 30.54, 64.45, 78.35, 83.90, 98.53, 105.37, 122.96, 124.58, 128.89, 129.73, 130.69, 130.85, 134.49, 171.36; FW calc. for C₂₅H₃₄O₄Si+H: 427.2305, ESI-HRMS found: 427.2299.

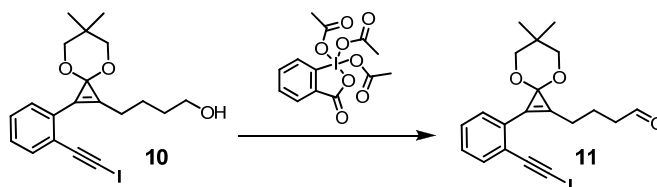


4-(2-(2-ethynylphenyl)-6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-en-1-yl)butan-1-ol (9). Potassium carbonate (0.5 g, 3.62 mmol, 0.3 eq.) was added to a solution of acetate **8** (4.89 g, 11.46 mmol) in MeOH (50 mL), the mixture was stirred for 2 h. at r.t., diluted with 40 mL of water, and extracted with ether (2x75 mL). Combined organic layers were evaporated in vacuum and the residue was purified by chromatography (ether – hexanes 1:5, 1% of Et₃N) to give 3.01 g (9.6 mmol, 84%) of alcohol **9** as yellow oil. ¹H: 1.02 (s, 3H), 1.15 (s, 3H), 1.65-1.74 (m, 2H), 1.75-1.85 (m, 2H), 1.85-1.9 (broad OH), 2.80-2.90 (m, 2H), 3.36 (s, 1H), 3.68-3.80 (m, 6H), 7.25-7.33 (m, 1H), 7.36-7.42 (m, 1H), 7.55-7.61 (m, 1H); ¹³C: 22.49, 22.64, 24.51, 26.31, 30.59, 31.14, 32.65, 62.45, 78.36, 81.57, 83.63, 83.86, 121.97, 124.30, 128.96, 129.18, 130.60, 130.66, 131.64, 134.00; FW calc. for C₂₀H₂₅O₃+H: 313.1804, ESI-HRMS found: 313.1801.

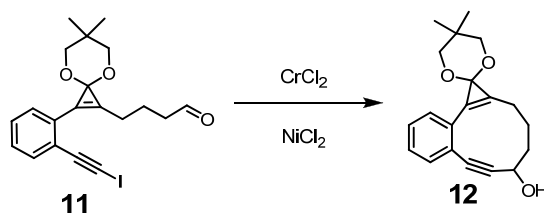


4-(2-(2-(iodoethynyl)phenyl)-6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-en-1-yl)butan-1-ol (10). A solution of morpholine (0.742 mL, 8.58 mmol) and iodine (1.089 g, 4.29 mmol) in benzene (20

mL) was vigorously stirred at 45 °C for 15 min to form orange suspension. A solution of acetylene **9** (0.670 g, 2.145 mmol) in benzene (3 mL) was added to the reaction mixture. In 30 min the reaction mixture was diluted with 40 mL of ether, filtered, and solvents were removed in vacuum. The residue was purified by chromatography (ether – hexanes 1:4, 1% Et₃N, R_f = 0.1) to give 0.675 g (1.540 mmol, 72 %) of **10** as yellow oil. ¹H: 1.04 (s, 3H), 1.15 (s, 3H), 1.70-1.90 (m, 5H), 2.85 (t, 2H, *J* = 6.8 Hz), 3.67-3.79 (m, 6H), 7.26-7.30 (m, 1H), 7.34-7.39 (m, 1H), 7.50-7.58 (m, 2H); ¹³C: 22.51, 22.7, 24.57, 26.25, 32.75, 62.5, 78.39, 83.83, 93.67, 123.2, 124.08, 128.86, 129.17, 130.29, 130.56, 131.84, 134.41; FW calc. for C₂₀H₂₃IO₃+H: 439.0770, ESI-HRMS found: 439.0768.

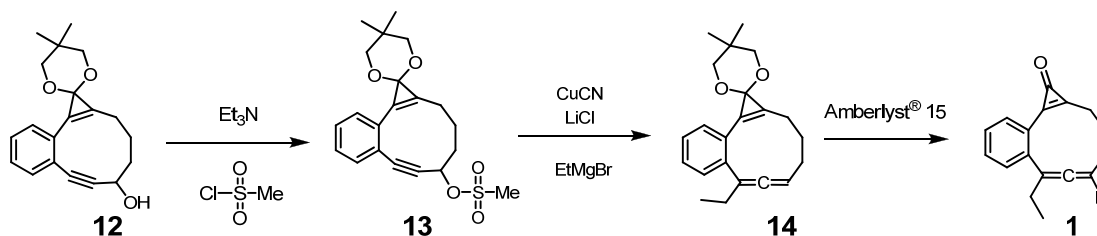


4-(2-(2-(iodoethynyl)phenyl)-6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-en-1-yl)butanal (11). Dess-Martin periodinane (0.755 g, 1.780 mmol) was added to a solution of alcohol **10** (0.65 g, 1.483 mmol) in CH₂Cl₂ (50 mL) under vigorous stirring at r.t. In 2 h the reaction mixture was diluted with ether (40 mL), stirred for 15 min, and solvents removed in vacuum. Chromatographic purification of the residue (ether – hexanes 1:20, 1% of Et₃N) gave 0.469 g (1.075 mmol, 72.5 %) of aldehyde **11** as yellow oil. ¹H: 1.03 (s, 3H), 1.16 (s, 3H), 2.03-2.09 (m, 2H), 2.65 (t, 2H, *J* = 7.2 Hz), 2.88 (t, 2H, *J* = 7.2 Hz), 3.68-3.78 (m, 4H), 7.26-7.32 (m, 1H), 7.35-7.40 (m, 1H), 7.50-7.58 (m, 2H), 9.83 (s, 1H); ¹³C: 20.98, 22.51, 22.71, 25.78, 30.57, 43.6, 46.41, 78.39, 83.64, 93.71, 123.23, 124.96, 129.01, 129.24, 130.16, 130.63, 130.95, 134.46, 202.22; FW calc. for C₂₀H₂₃IO₃+H: 437.0614, ESI-HRMS found: 437.0615.



6,7-didehydro-3,4,5-trihydro-5',5'-dimethyl-spiro[benzo[a]cyclopropa[c]cyclodecene-1(2H),2'-[1,3]dioxan]-5-ol (12). A solution of aldehyde **11** (0.215 g, 0.493 mmol) in THF (20 mL) was added dropwise over 5 min to a degassed solution CrCl₂ (0.2 g, 1.627 mmol) and NiCl₂ (6.39 mg, 0.049 mmol) in anhydrous THF (250 mL) at r.t. The reaction mixture was stirred for 2 h, diluted with hexanes (200 mL), and filtered through small layer of silica gel to give the 145 mg (0.467 mmol, 95%) of **12** as yellow oil. ¹H: 1.06 (s, 3H), 1.12 (s, 3H), 1.80-1.90 (m, 1H), 2.0-2.20 (m, 1H), 2.32 (s, OH), 2.53 (dd, 2H, *J* = 7.2 Hz), 2.82-2.92 (m, 1H), 2.98-3.06 (m, 1H), 3.68-3.80 (m, 4H), 4.58 (broad signal, 1H), 7.25-7.31 (m, 1H), 7.33-7.39 (m, 1H), 7.4 (d, 1H, *J* = 7.6 Hz), 7.5 (d, 1H, *J* = 7.6 Hz); ¹³C: 11.44, 21.71, 22.34, 22.38, 25.01, 30.46, 36.78, 46.15,

62.26, 78.33, 78.39, 85.16, 86.08, 97.21, 122.3, 126.56, 128.53, 128.58, 129.06, 130.15, 131.62, 132.00; FW calc. for C₂₀H₂₂O₃+H: 311.1647, ESI-HRMS found: 311.1646.



7-Ethyl-6-dehydro-2,3,4-trihydro-1H-benzo[a]cyclo-propa[c]cyclodecen-1-one (1). Methanesulfonyl chloride (0.102 mL, 1.321 mmol) was added to a solution of alcohol **12** (0.41 g, 1.321 mmol) and triethylamine (1.91 mL, 1.321 mmol) in CH₂Cl₂ (4 mL) at 0 °C. The reaction mixture was stirred for 1 h and quenched with biphosphate buffer (1 mL, pH = 8). Organic layer was washed with biphosphate buffer (2x2 mL, pH = 8), separated, and dried over sodium sulfate. Solvent was evaporated to give 0.462 g (90%, 1.189 mmol) of crude mesylate **13** as yellowish oil.

A solution of EtMgBr (2.379 mL, 1M in THF) was added an ice-cold suspension of CuCN (0.213 g, 2.379 mmol) and LiCl (0.202 g, 4.76 mmol) in dry THF (5 mL). Reaction mixture was stirred for 25 min, cooled down to -78 °C, and a solution of crude mesylate **13** (0.37 g, 1.650 mmol) in dry THF (2 mL) was added dropwise. After 2 hours at -78 °C, the reaction was quenched by addition of biphosphate buffer (3 mL, pH = 8). The reaction mixture was extracted with ether (3x15 mL), washed with brine (1x20 mL), dried over sodium sulfate, and concentrated under reduced pressure to give 0.32 g (0.992 mmol, 83%) of crude acetal **14**.

Amberlyst[®] 15 (5 mg) was added to a solution of crude acetal **14** (0.115 g, 0.357 mmol) in aqueous acetone (ca. 5% H₂O, 5 mL), stirred for 2 h at r.t., and sodium sulfate (100 mg) was added. Solids were removed by filtration, solvents removed in vacuum, and residue purified by chromatography (EtOAc – hexanes 1:1 → AcOEt) to give 63 mg (0.266 mmol, 75%) of cyclopropenone **1** as yellowish oil. ¹H: 1.16 (t, 3H, *J* = 7.6 Hz), 1.85-1.95 (m, 1H), 2.1-2.25 (m, 2H), 2.25-2.37 (m, 1H), 2.4-2.45 (m, 1H), 2.47-2.65 (m, 1H), 2.81-2.85 (m, 1H), 3.0-3.1 (m, H), 5.44-5.48 (m, 1H allenic hydrogen), 7.35 (t, 1H, *J* = 7.2 Hz), 7.45-7.52 (m, 2H), 7.87 (d, 1H, *J* = 7.2 Hz); ¹³C: 12.49, 20.88, 25.09, 26.46, 26.66, 93.73, 106.5, 122.55, 126.69, 127.07, 132.08, 135.03, 139.04, 153.67, 154.91, 160.27, 203.57; FTIR (cm⁻¹ in CCl₄) 2950 [aromatic], 1955 [C=C=C], 1840 (C=O), 1720, 1620; FW calc. for C₁₇H₁₆O: 236.1201, EI-HRMS found: 236.1208.

Photolytic experiments. Analytical photolyses were performed by the irradiation of ca. 10⁻⁵ M solutions of cyclopropenone **1** in a 1 cm quartz cell using a RMR-600 Rayonet[™] photochemical reactor equipped with carousel and 300 nm florescent lamps. Determination of a quantum yield was performed using a ferrioxalate chemical actinometer.³

³ S. L. Murov, I. Carmichael, and G.L. Hug *in*: Handbook of Photochemistry, Marcel Dekker: New York, 1993, p.299.

Preparative photolysis of cyclopropenone 1 in 2-propanol. A degassed solution of cyclopropenone **1** (20 mg, 0.085 mmol) in *i*-PrOH (150 mL) was placed in a quartz vessel and irradiated for 15 min in mini-Rayonet® photoreactor equipped with 8 300 nm x 4W lamps. The reaction mixture was left in the dark for 5 h at r.t., solvent was removed in vacuum, and residue separated by TLC (1 mm silica gel on glass plate, 5% of EtOAc in hexanes) to afford 4 mg of 9-ethyl-1-isopropoxy-1,2,3,4-tetrahydroanthracene (**17**) (0.015 mmol, 17.3%) and 0.5 mg of 10-ethyl-1,2-dihydroanthracene (2.77 μ mol, 3.3%).

9-ethyl-1-isopropoxy-1,2,3,4-tetrahydroanthracene (17). ^1H : 1.24 (d, 3H, $J = 6.4$ Hz), 1.28 (d, 3H, $J = 6.0$ Hz), 1.34 (t, 3H, $J = 7.6$ Hz), 1.55-1.6 (m, 1H), 1.68-1.77 (m, 1H), 2.05-2.18 (m, 1H), 2.4-2.48 (m, 1H), 2.86-2.96 (m, 1H), 3.1-3.18 (m, 1H), 3.2-3.32 (m, 2H), 3.9 (tt, 1H, $J = 6.0$ Hz, 12.0 Hz), 5-5.04 (m, 1H), 7.36-7.45 (m, 2H), 7.47 (s, 1H), 7.68-7.74 (m, 1H), 8.02-8.08 (m, 1H); ^{13}C : 16.14, 17.00, 20.85, 21.96, 24.23, 27.25, 30.25, 67.86, 69.09, 124.49, 124.96, 125.53, 126.18, 128.05, 130.84, 133.00, 133.78, 136.11, 139.89; FW calc. for $\text{C}_{19}\text{H}_{24}\text{O}$: 268.1827, EI-HRMS found: 268.1833

10-ethyl-1,2-dihydroanthracene: FW calc. for $\text{C}_{16}\text{H}_{16}$: 208.1252, EI-HRMS found: 208.1251;

Preparative photolysis of cyclopropenone 1 in the presence of 1,4-cyclohexadiene. A degassed solution of cyclopropenone **1** (10 mg, 0.042 mmol) in 1M solution of 1,4-cyclohexadiene in toluene (50 mL) was placed in a quartz vessel and irradiated for 3 min in mini-Rayonet® photoreactor equipped with 8 300 nm x 4W lamps was irradiated for 3 min. The reaction mixture was left in the dark overnight at r.t., solvent was removed in vacuum, and residue separated by TLC (1 mm silica gel on glass plate, 5% of EtOAc in hexanes) to give 2 mg (23%) of 9-ethyl-1,2,3,4-tetrahydroanthracene (**3**) containing minor impurities (<10%) of 10-ethyl-1,2-dihydroanthracene. The latter was identified by GC-MS-HRMS analysis.

9-ethyl-1,2,3,4-tetrahydroanthracene (3):⁴ ^1H : 1.33 (t, 3H, $J = 7.5$ Hz), 1.8-1.87 (m, 2H), 1.88-1.95 (m, 2H), 2.9-3.0 (m, 4H), 3.08 (q, 2H, $J = 7.6$), 7.36-7.42 (m, 2H), 7.46 (s, 1H), 7.68-7.72 (m, 1H), 8.02-8.07 (m, 1H); FW calc. for $\text{C}_{16}\text{H}_{18}$: 210.1409, EI-HRMS found: 210.1406.

Kinetics. Rate measurements were performed using Carry-300 Bio UV-Vis spectrometer equipped with a thermostatable cell holder. The temperature was controlled with 0.1 $^{\circ}\text{C}$ accuracy. Reactions were monitored by following the growth of the characteristic 232 nm absorbance of 9-ethyl-1-isopropoxy-1,2,3,4-tetrahydroanthracene (**17**, in 2-propanol) or 9-ethyl-1,2,3,4-tetrahydroanthracene (**3**, in THF with 0.05 M of 1,4-cyclohexadiene). Observed first-order rate constants were calculated by least-squares fitting of a single exponential function.

⁴ J. Colonge and L. Bonnard *Bull. Soc. Chim. Fr.* 1958, 742.

DNA cleavage experiments. In a typical experiment aqueous solutions of cyclopropanone **1** (10 μ L) was added to a solution of plasmid DNA (10 ng/ μ L) in TE buffer (pH 8.0, 27 μ L) and irradiated in a Rayonet photoreactor equipped with 6x4W 350 nm lamps for 10 min. After irradiation solution was incubated in the dark for 16 h at 25 $^{\circ}$ C. Control samples were incubated with cyclopropanone solution in the dark. Incubated samples and the standard marker solution (1.0-8.0 kb) were mixed with a glycerol based loading buffer (7 μ L) containing xylene cyanol loading dye and loaded onto a 1% agarose gel containing 0.5 μ g/mL of ethidium bromide. Gel was developed at 80 V (400 mA) for 2 h and photographed on the UV transilluminator. The relative intensities of fluorescent bands on the developed gel were calculated using Alpha Ease FC software package by Alpha Innotech, Inc.

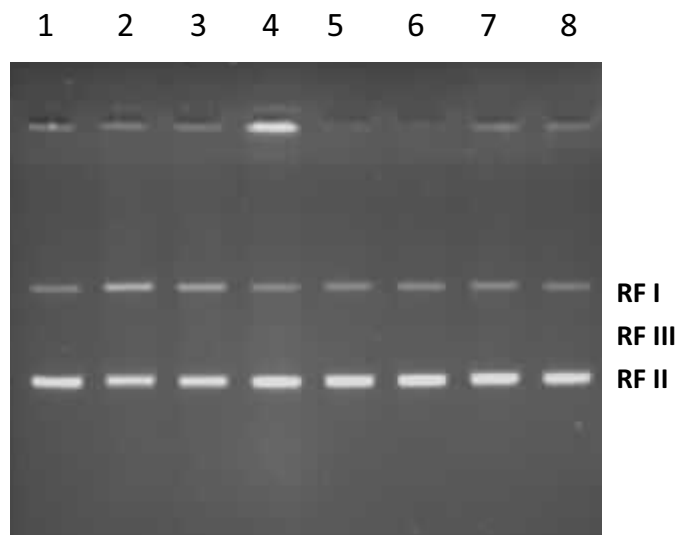
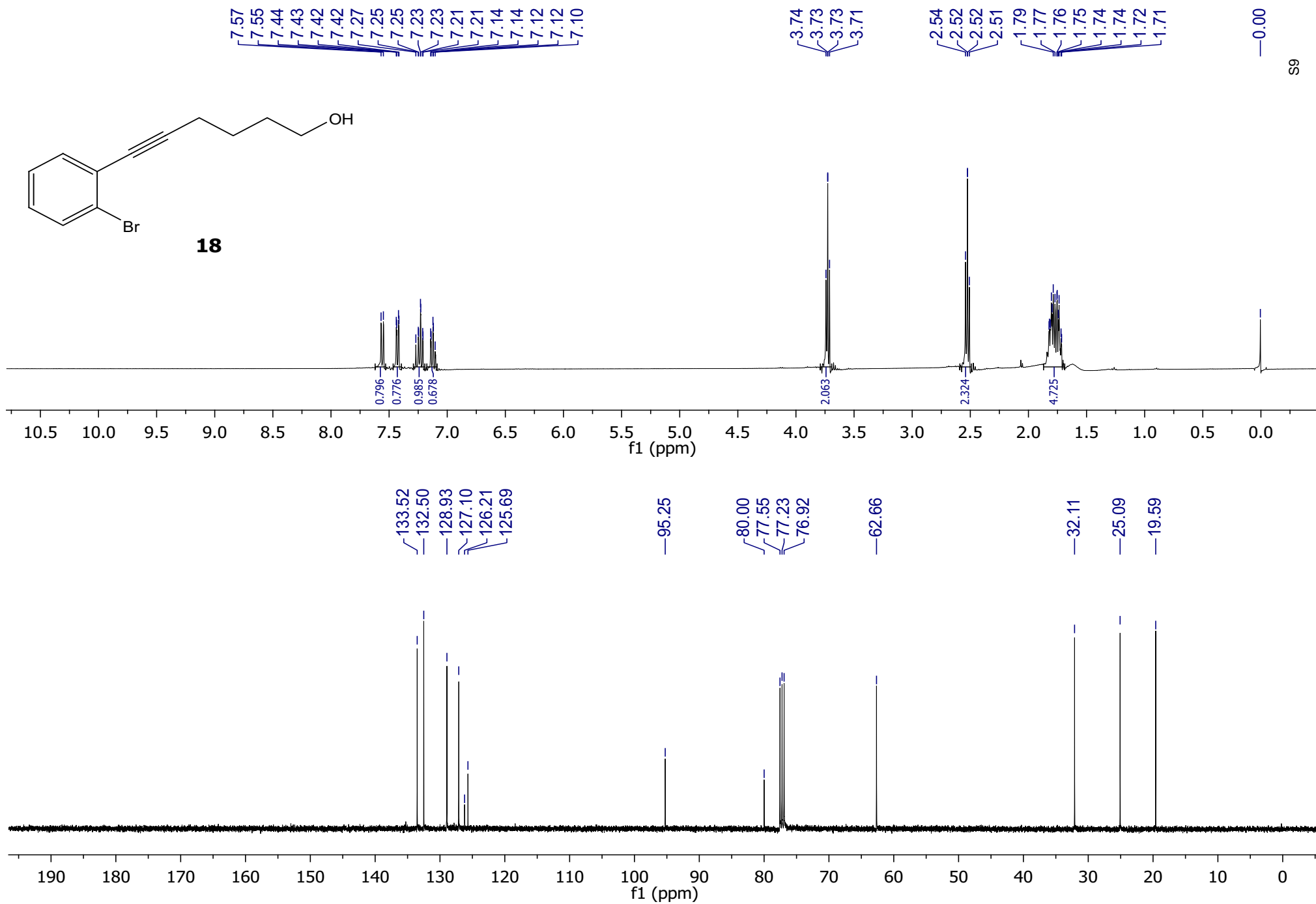
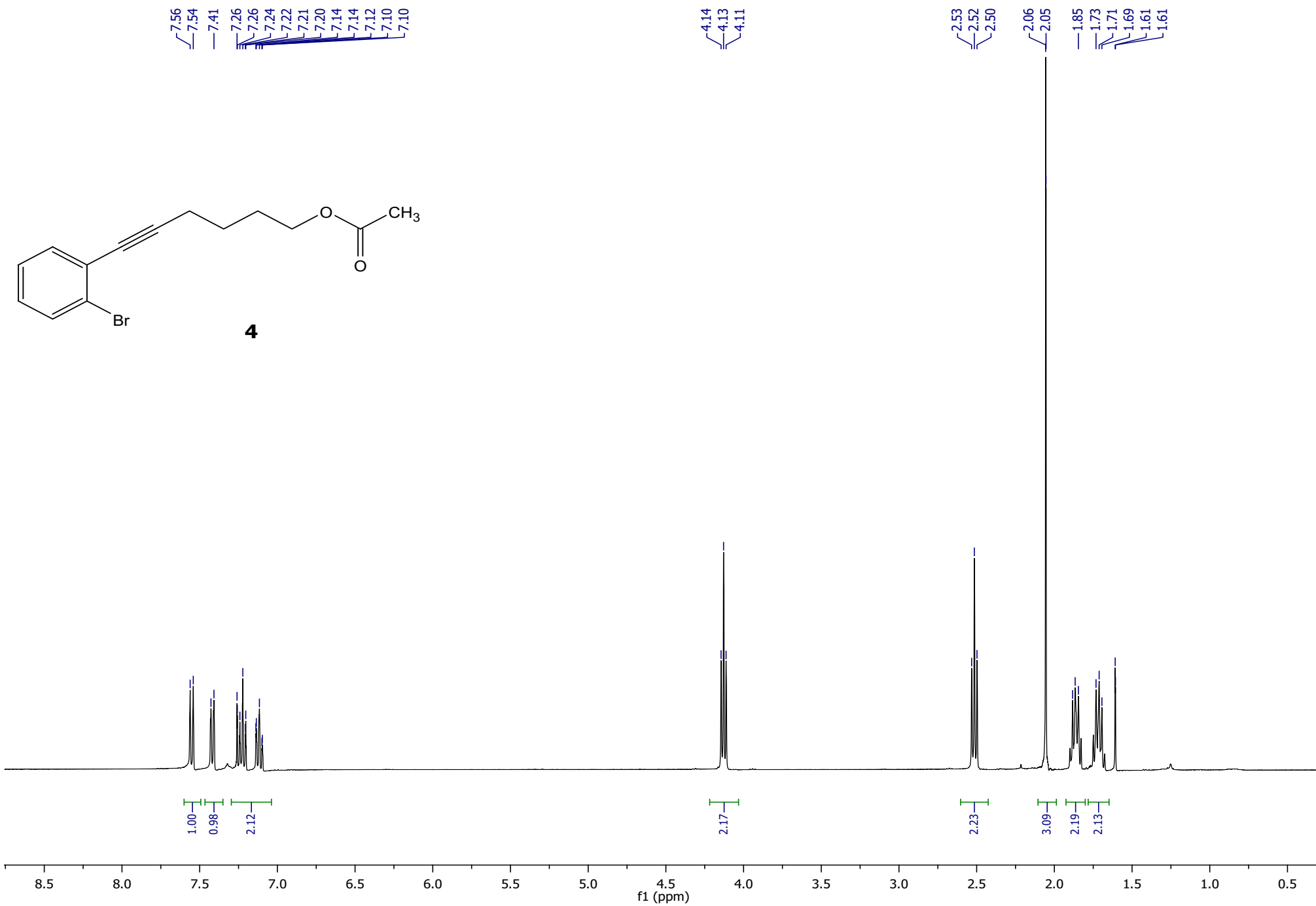
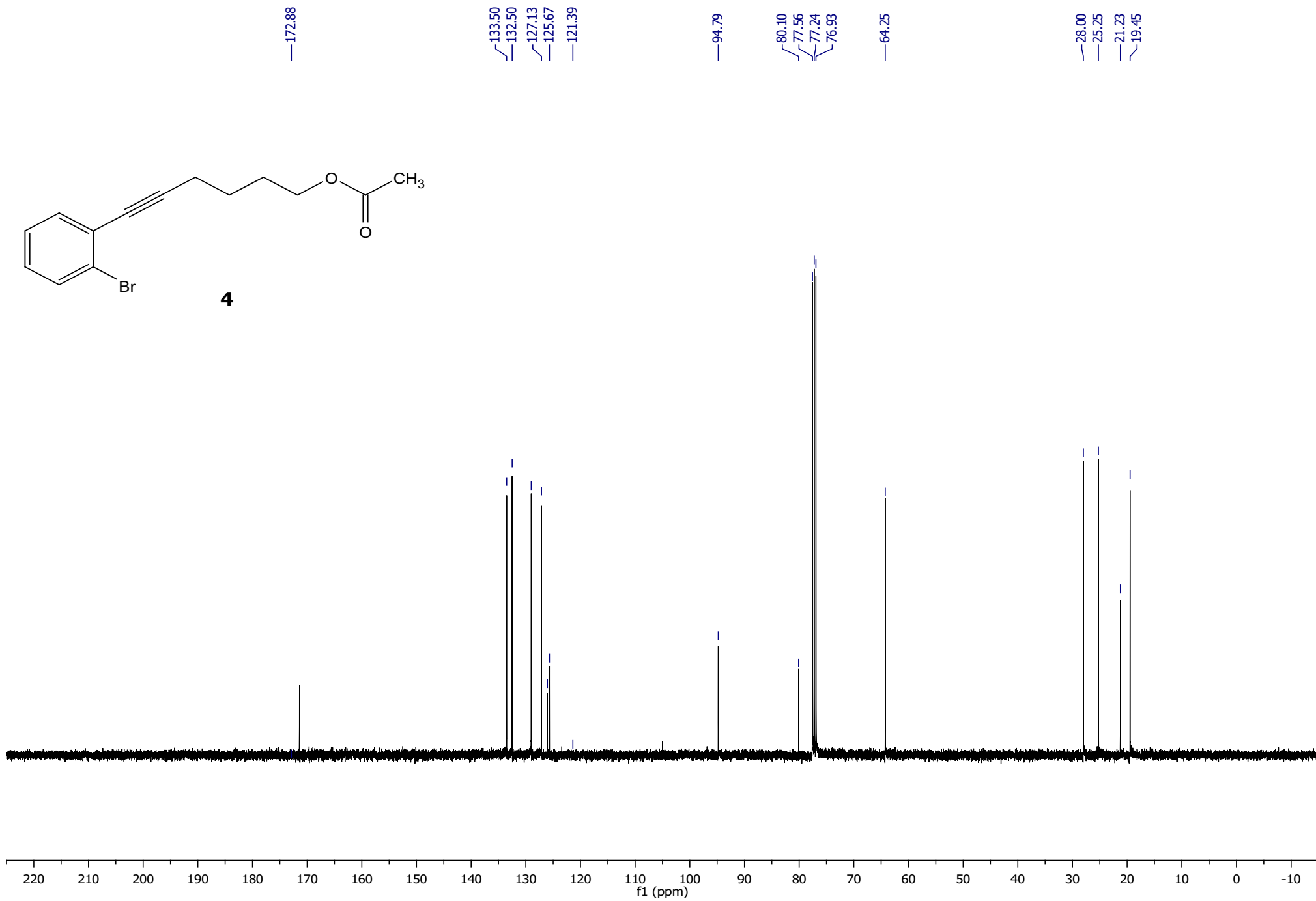
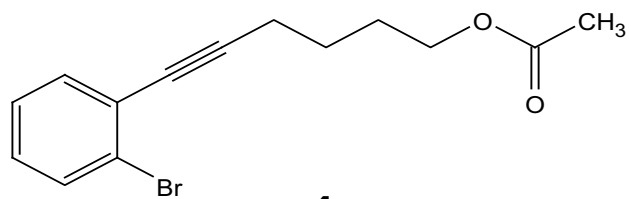
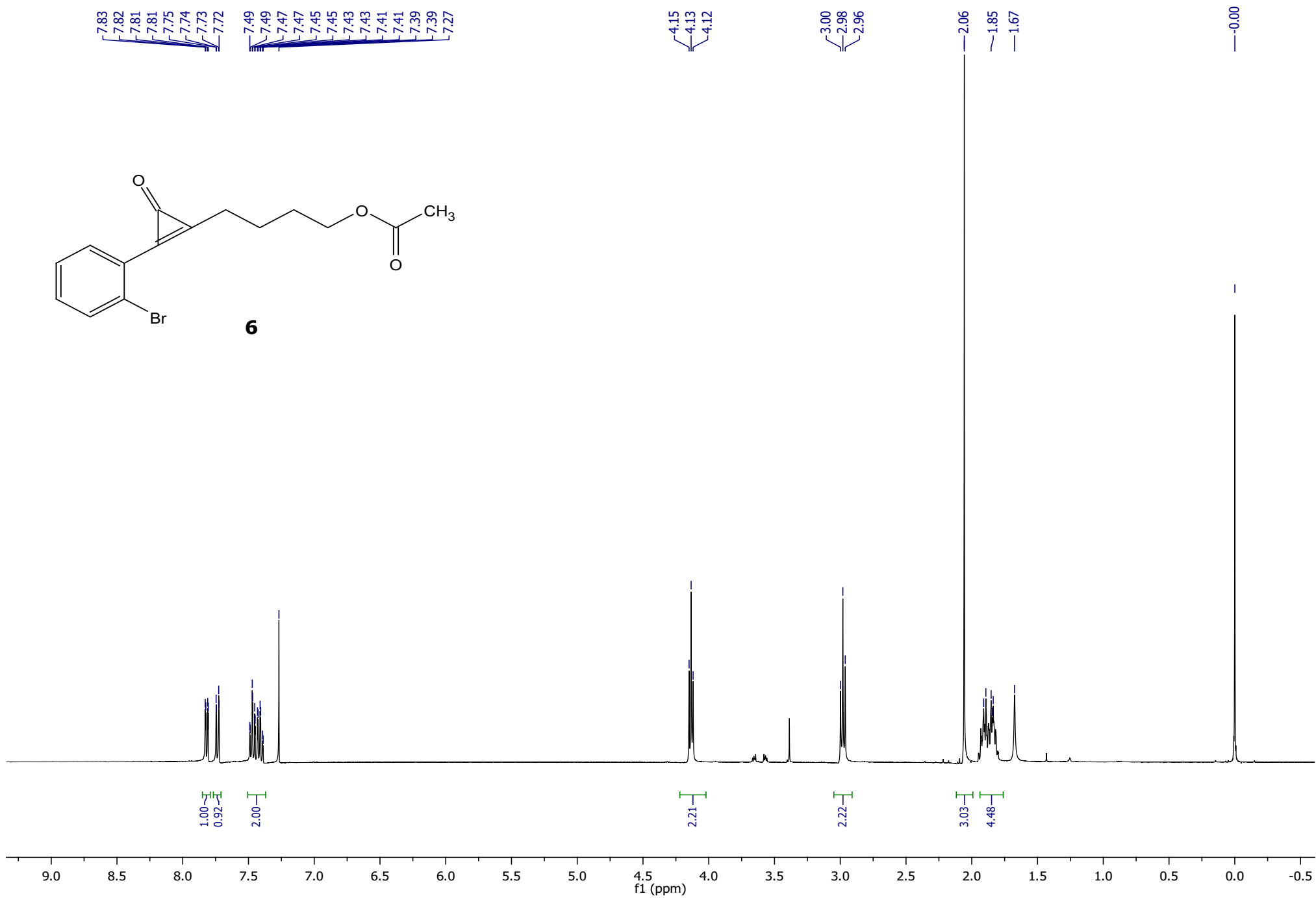
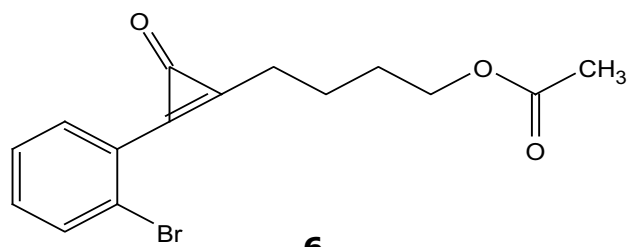


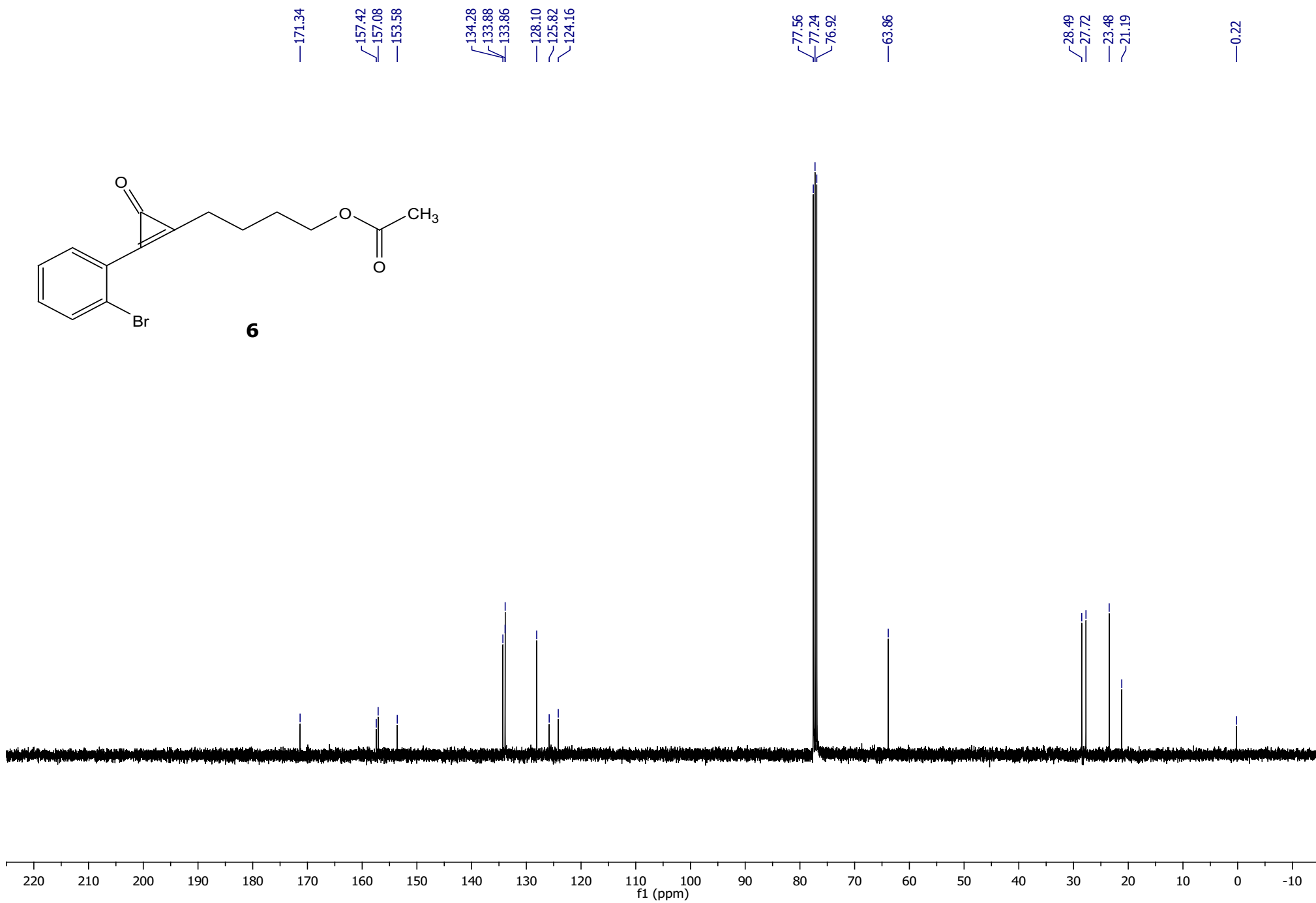
Figure S1. Light-induced cleavage of ϕ X174 plasmid DNA by the photogenerated enyne-allene **2**. Lanes 1-4: Cyclopropanone **1** (0.1, 0.5, 1, and 5 mM) is irradiated in the presence of DNA; lane 5: DNA irradiated without **1**; lanes 6-8: DNA incubated in the dark with cyclopropanone **1** (0.1, 0.5, and 1 mM).

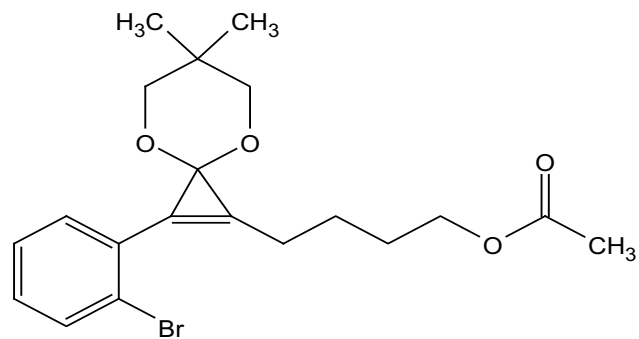




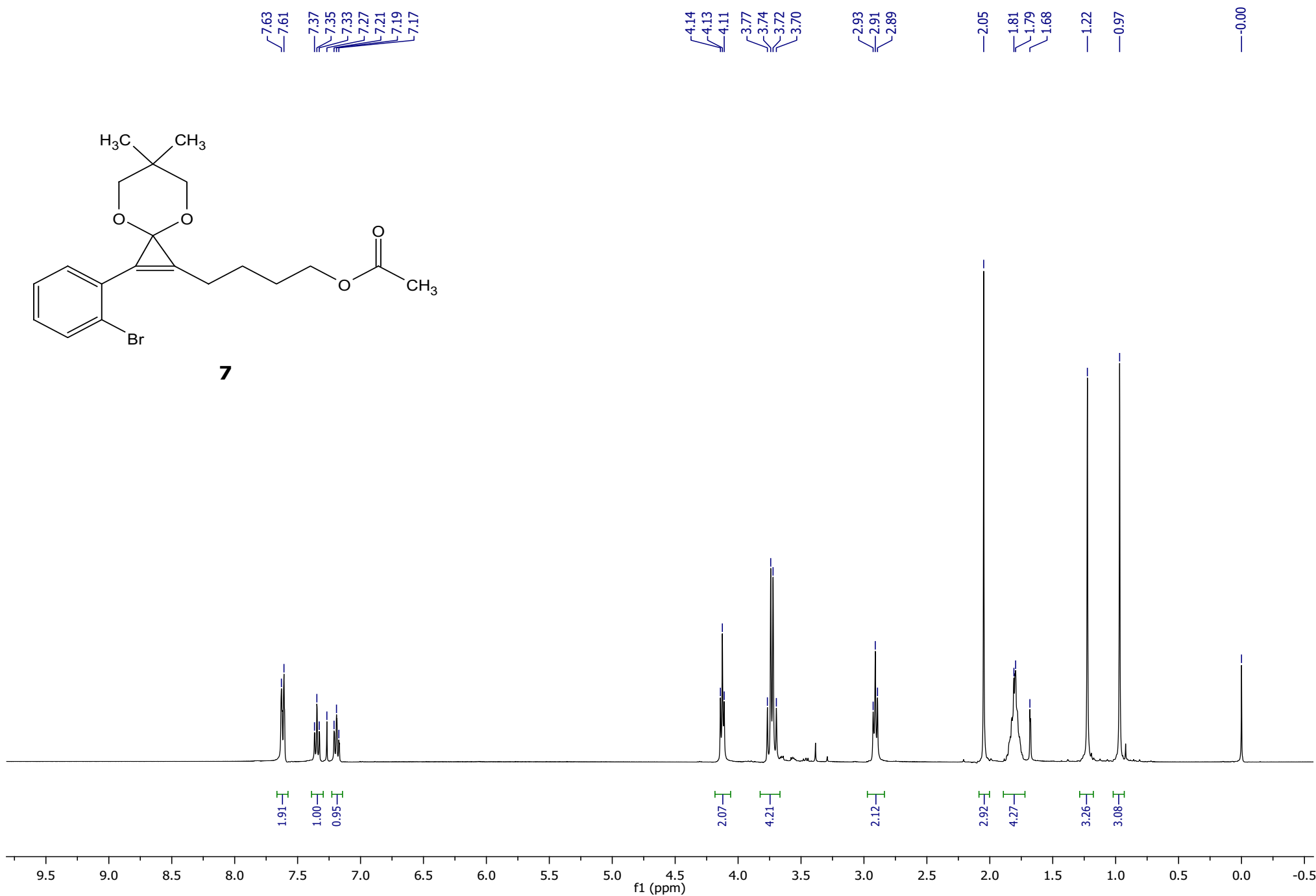


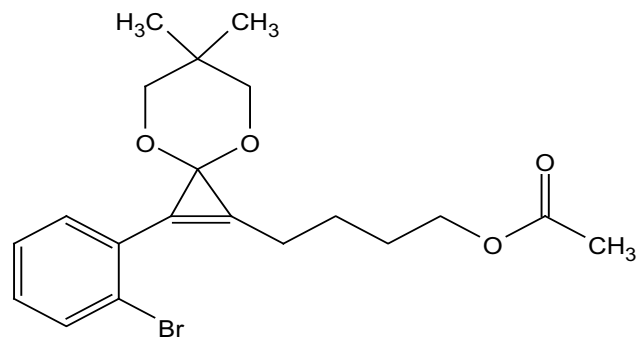




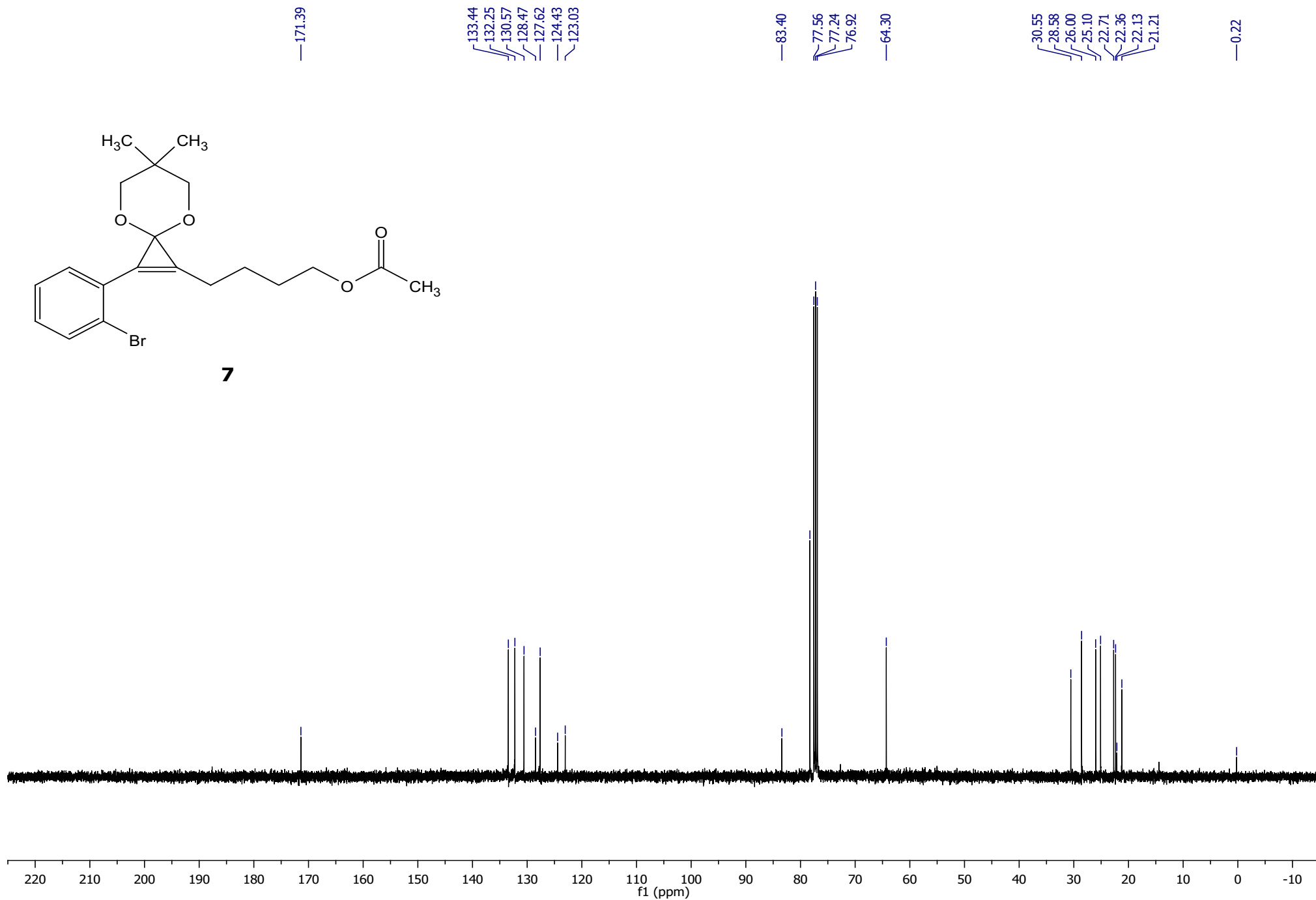


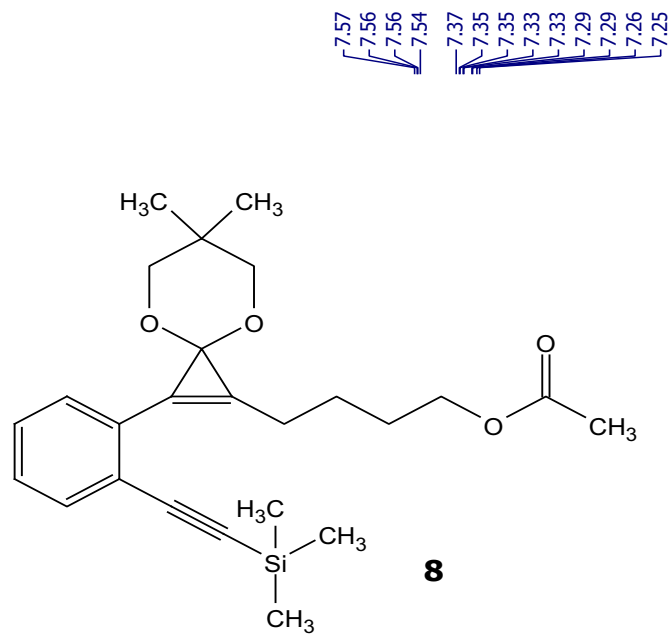
7





7

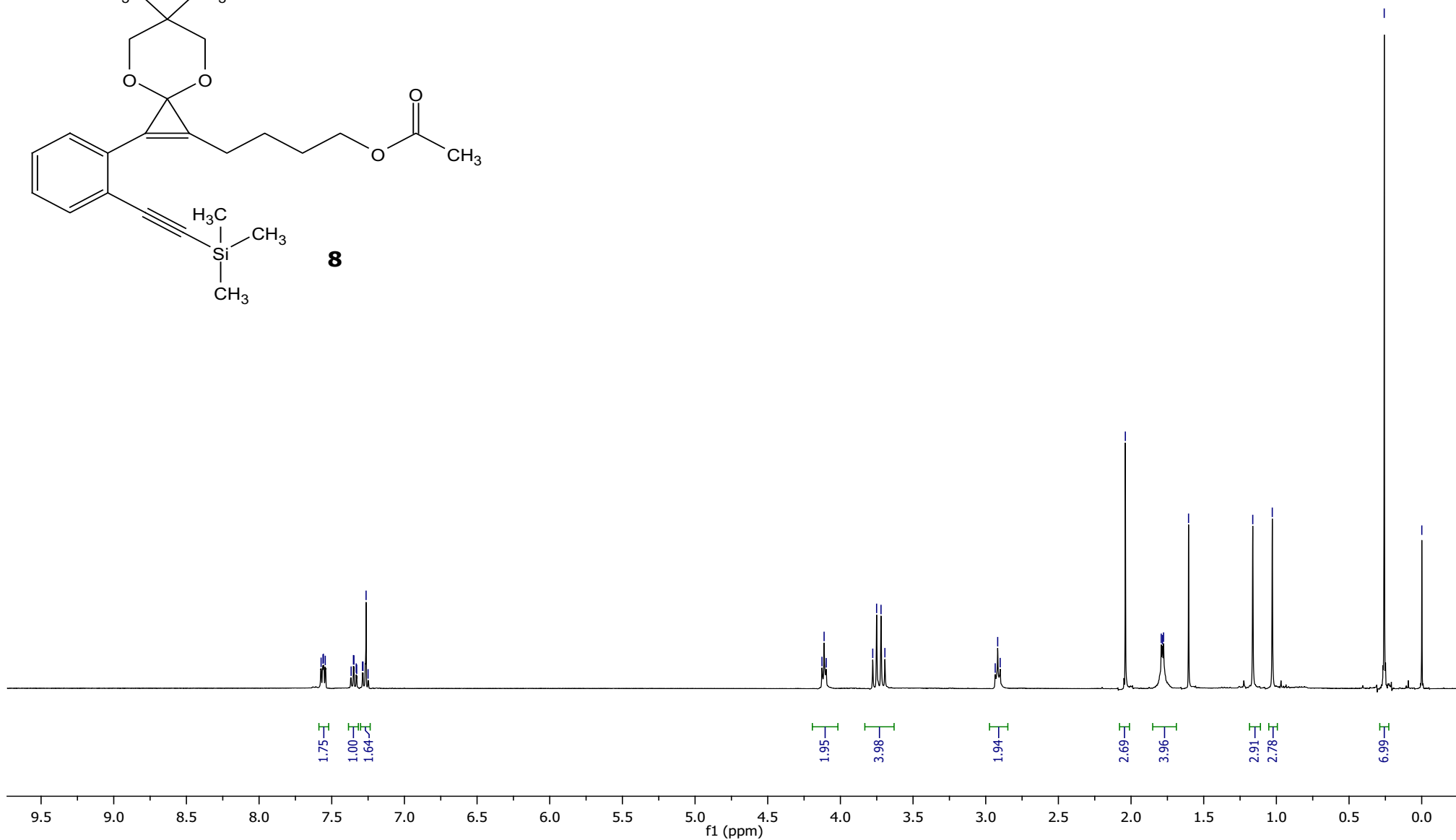


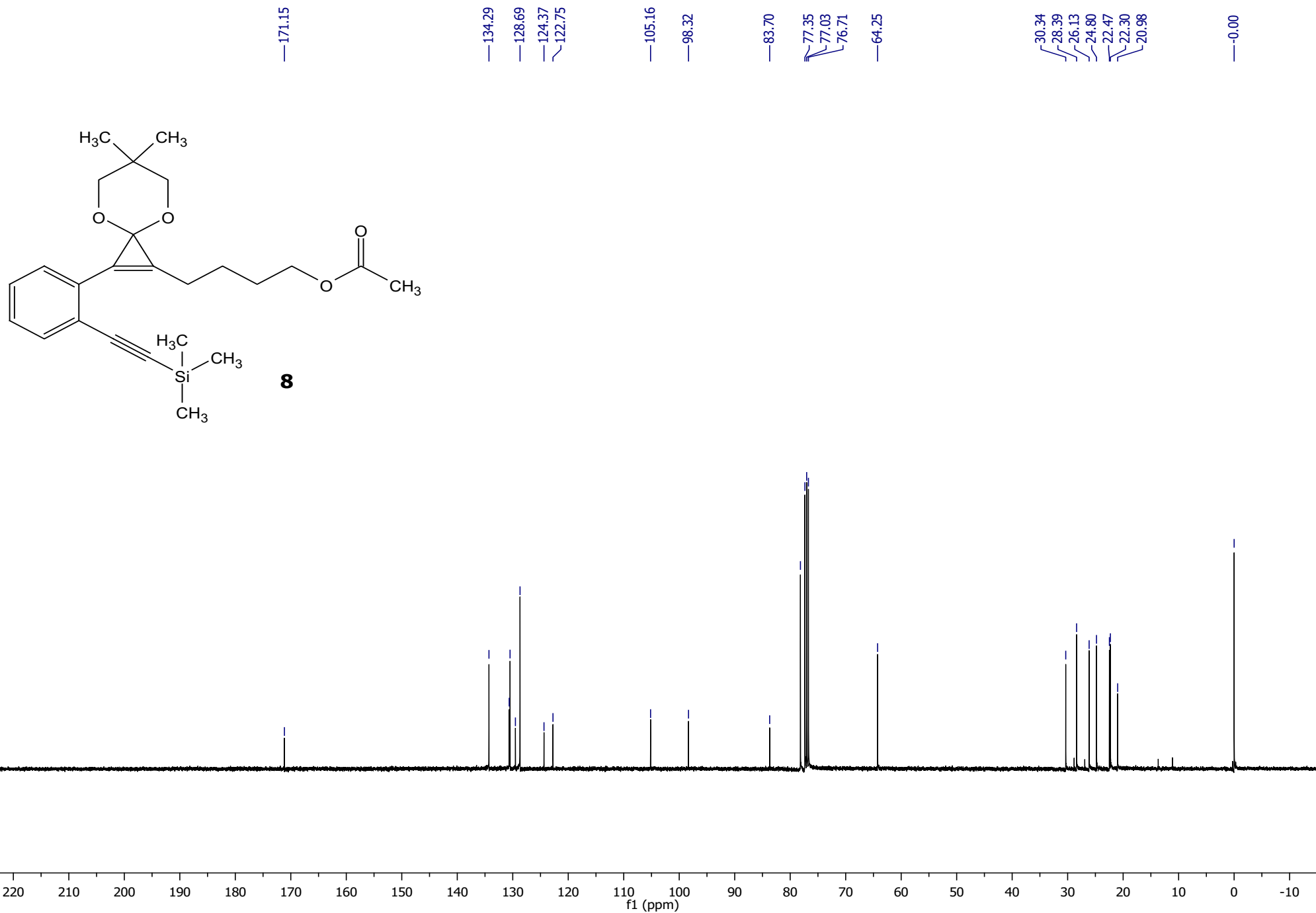


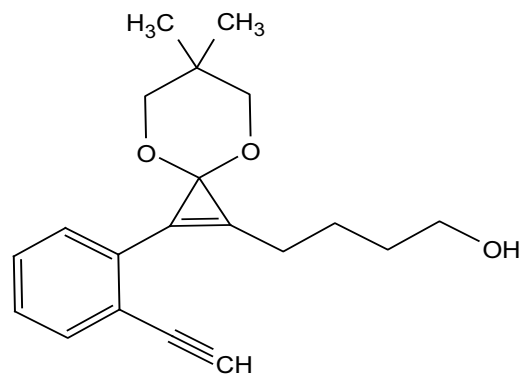
7.57
7.56
7.56
7.54
7.37
7.35
7.35
7.33
7.33
7.29
7.29
7.26
7.25

4.13
4.11
4.10
3.78
3.75
3.72
3.69
2.93
2.92
2.90

2.04
1.78
1.60
1.16
1.03
0.26
0.00







9

7.59
7.58
7.56
7.41
7.39
7.38
7.37
7.36
7.31
7.31
7.29
7.29
7.27
7.27

3.79
3.76
3.74
3.71
3.67
3.36
2.90
2.89
2.87
2.55
2.53
2.52
2.50

1.16
1.03

0.00

1.66
0.96
1.06

6.12

0.79

1.94

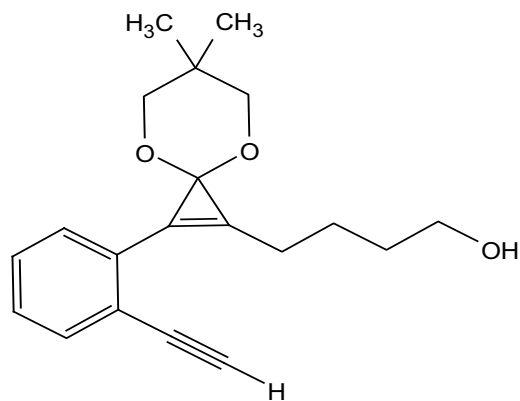
0.90

5.75

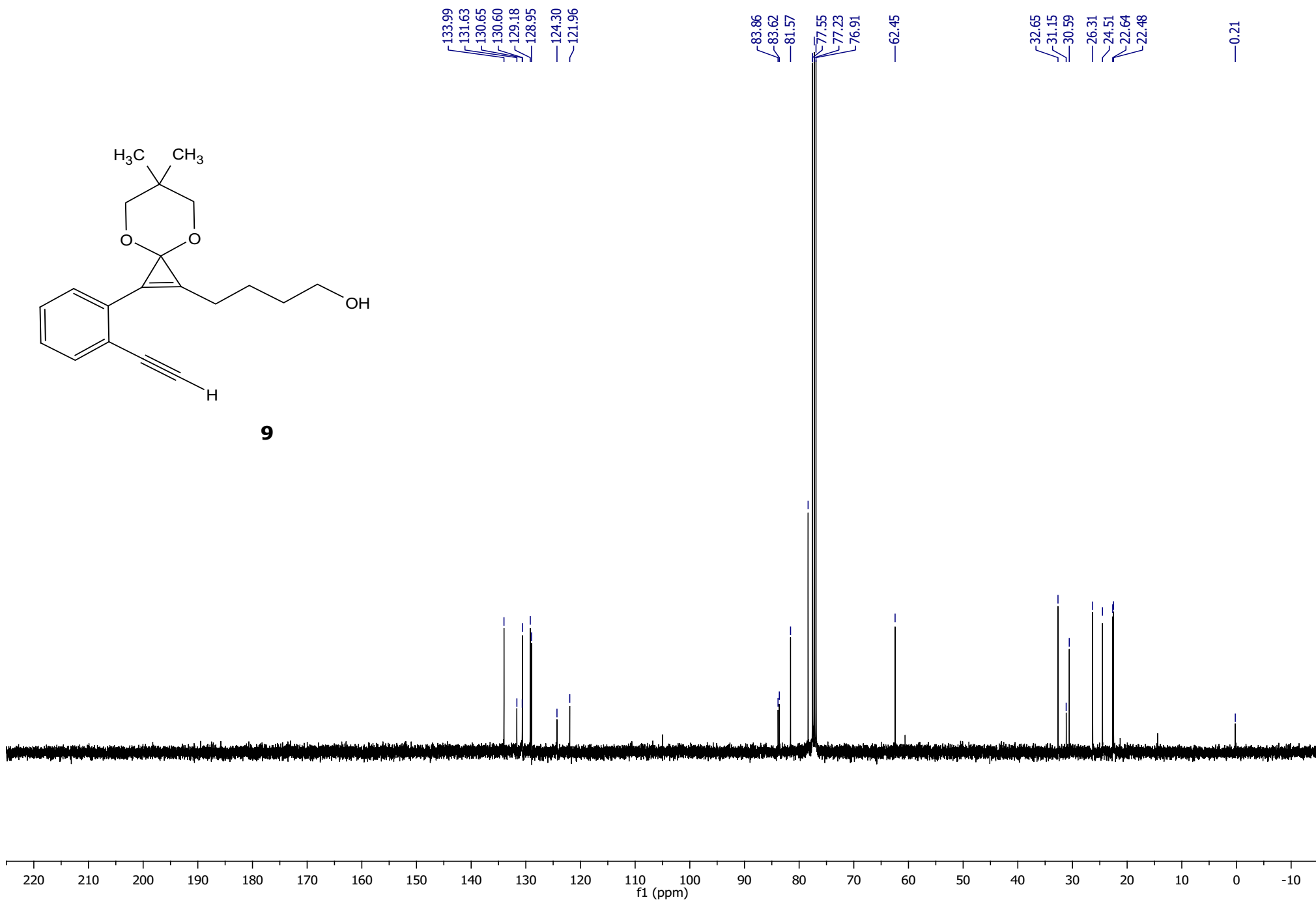
2.87
3.21

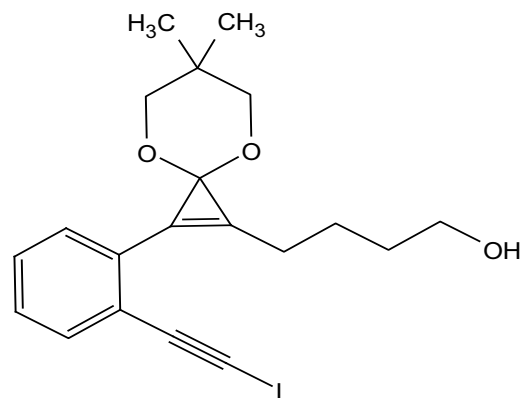
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)



9





7.57
7.57
7.56
7.52
7.52
7.50
7.50
7.38
7.36
7.36
7.34
7.34
7.30
7.30
7.28
7.28
7.27
7.26

3.78
3.76
3.74
3.72
3.70
3.69

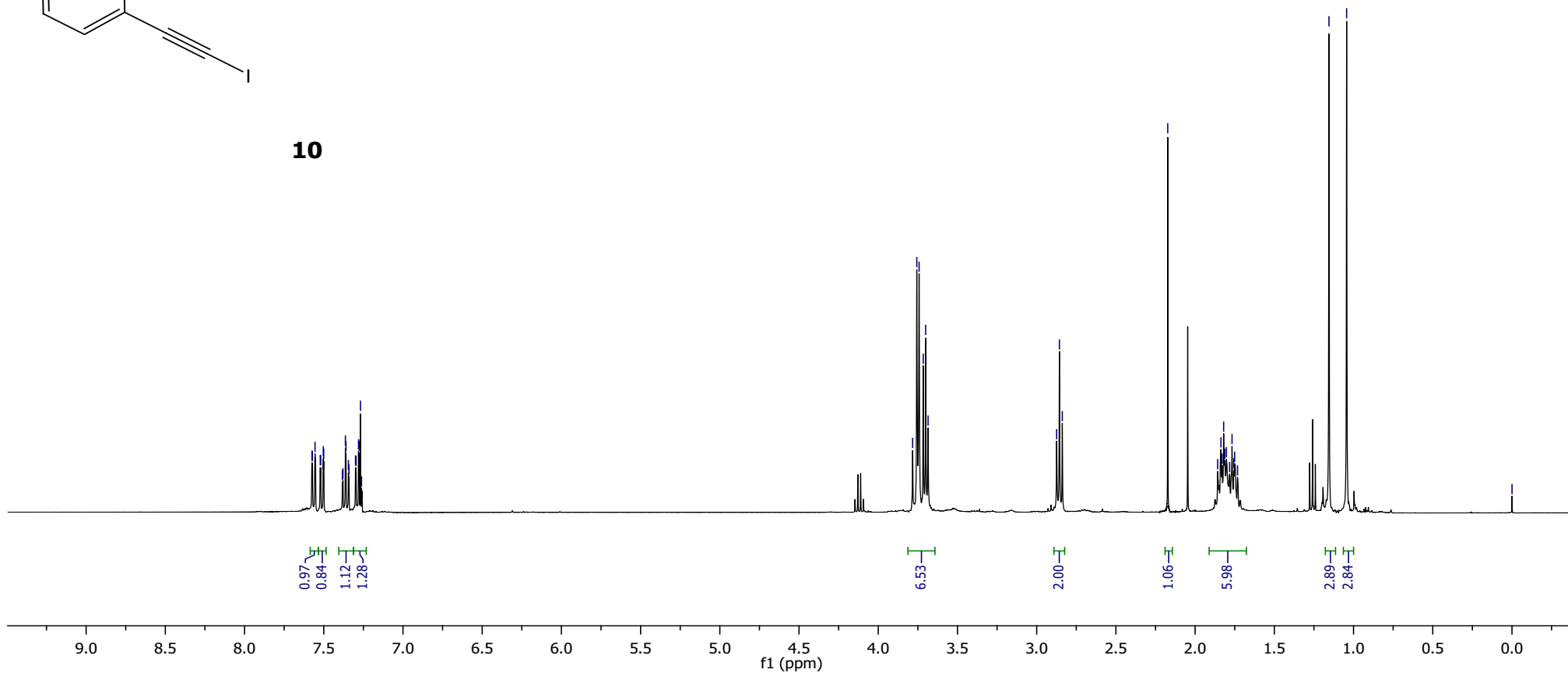
2.87
2.86
2.84

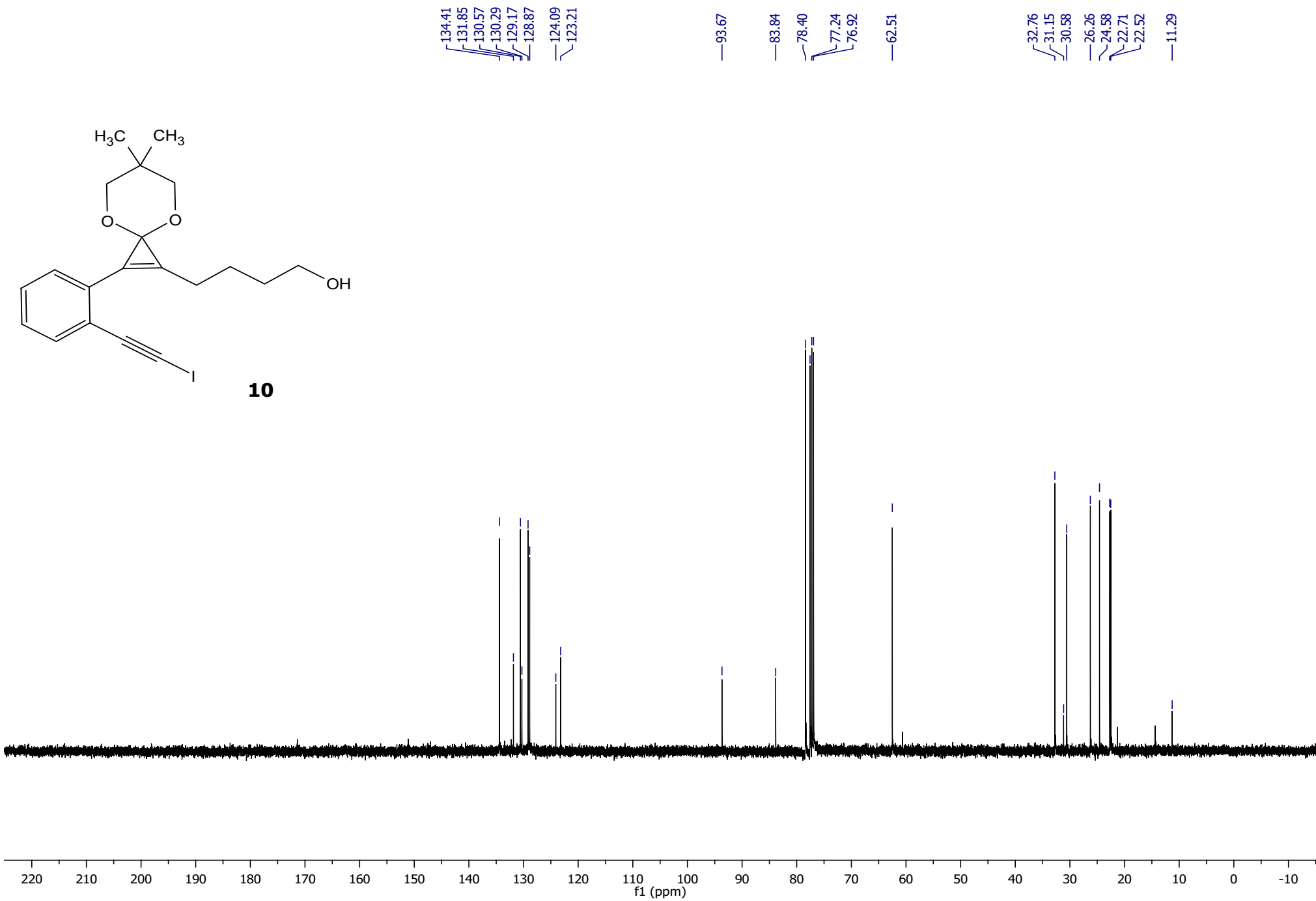
2.17

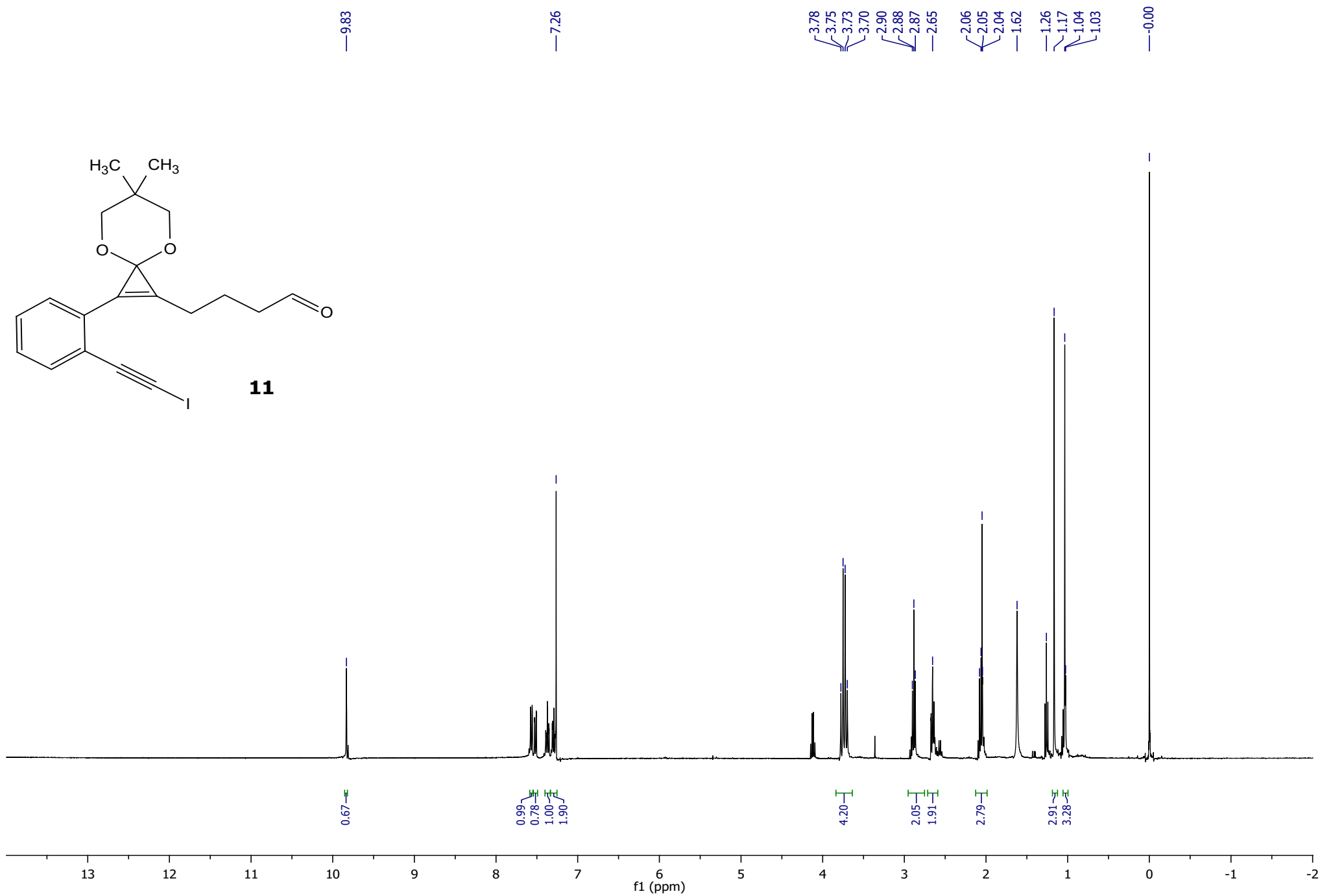
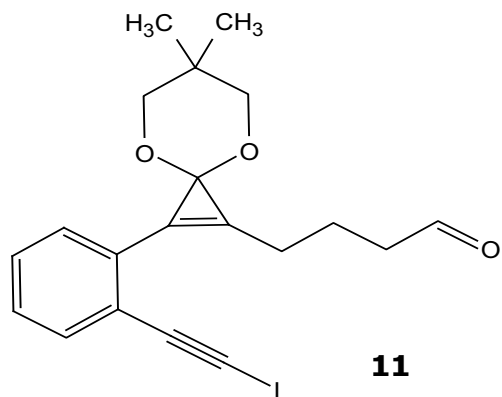
1.83
1.81
1.78
1.76
1.73

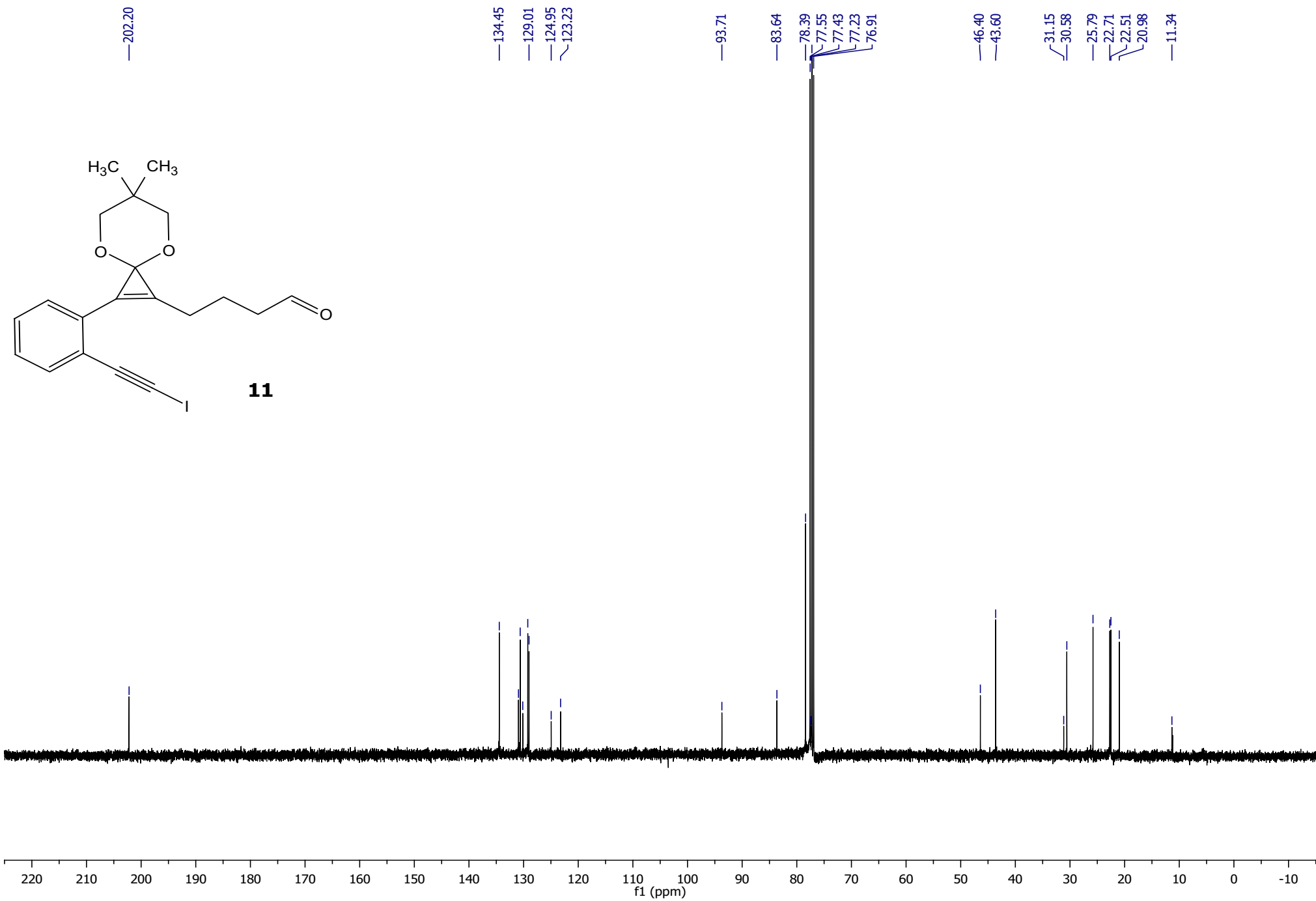
1.16
1.04

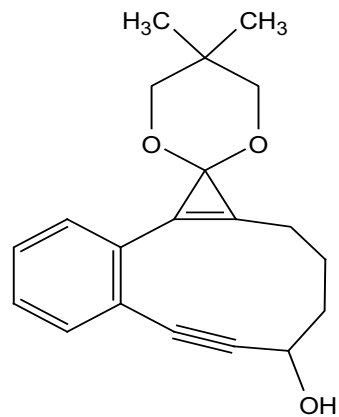
-0.00



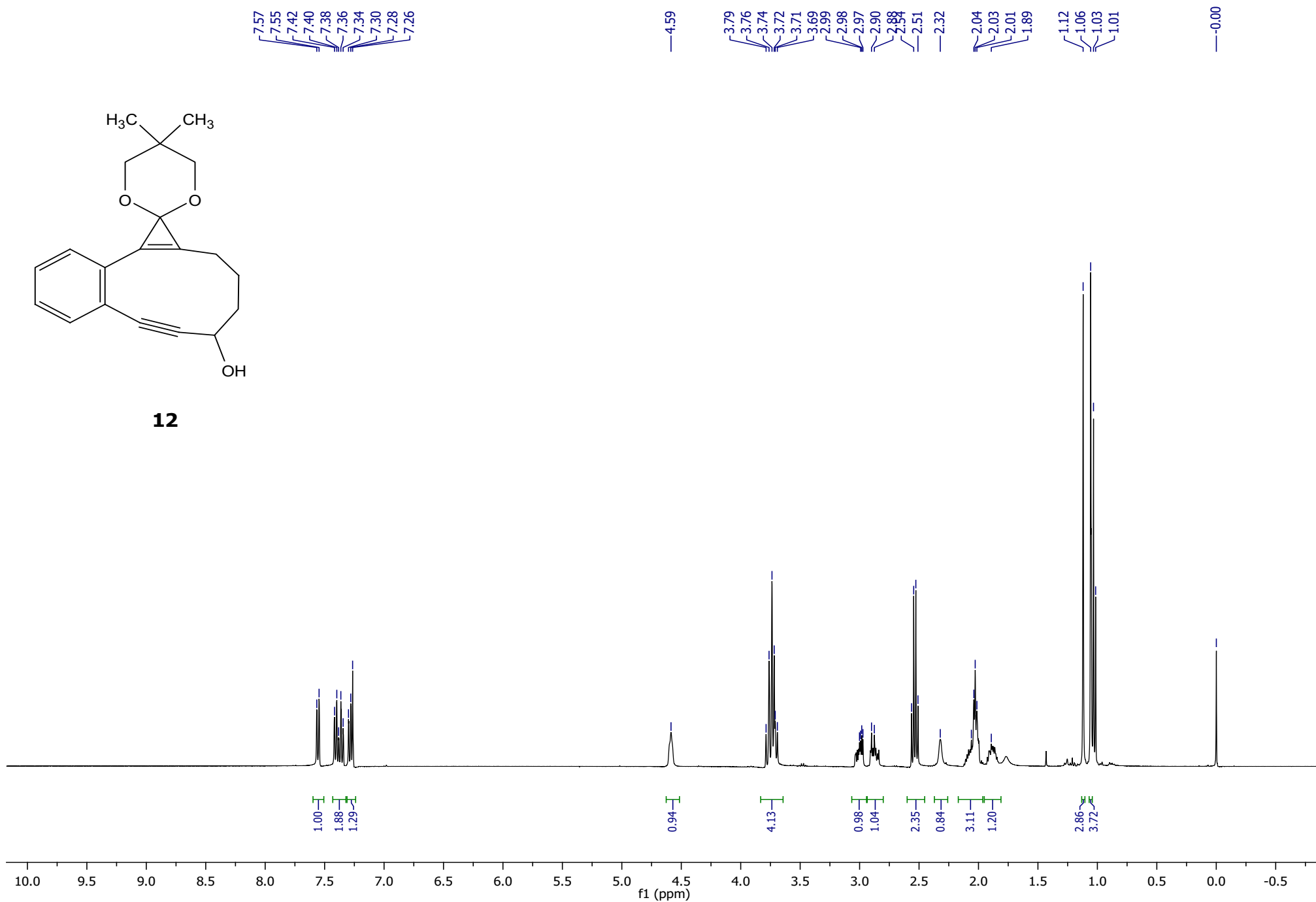


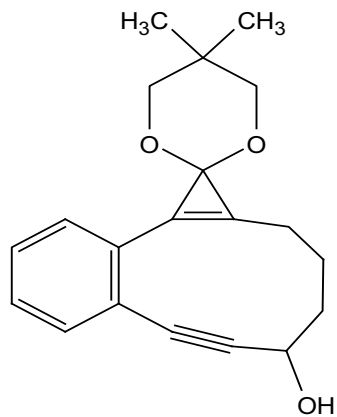




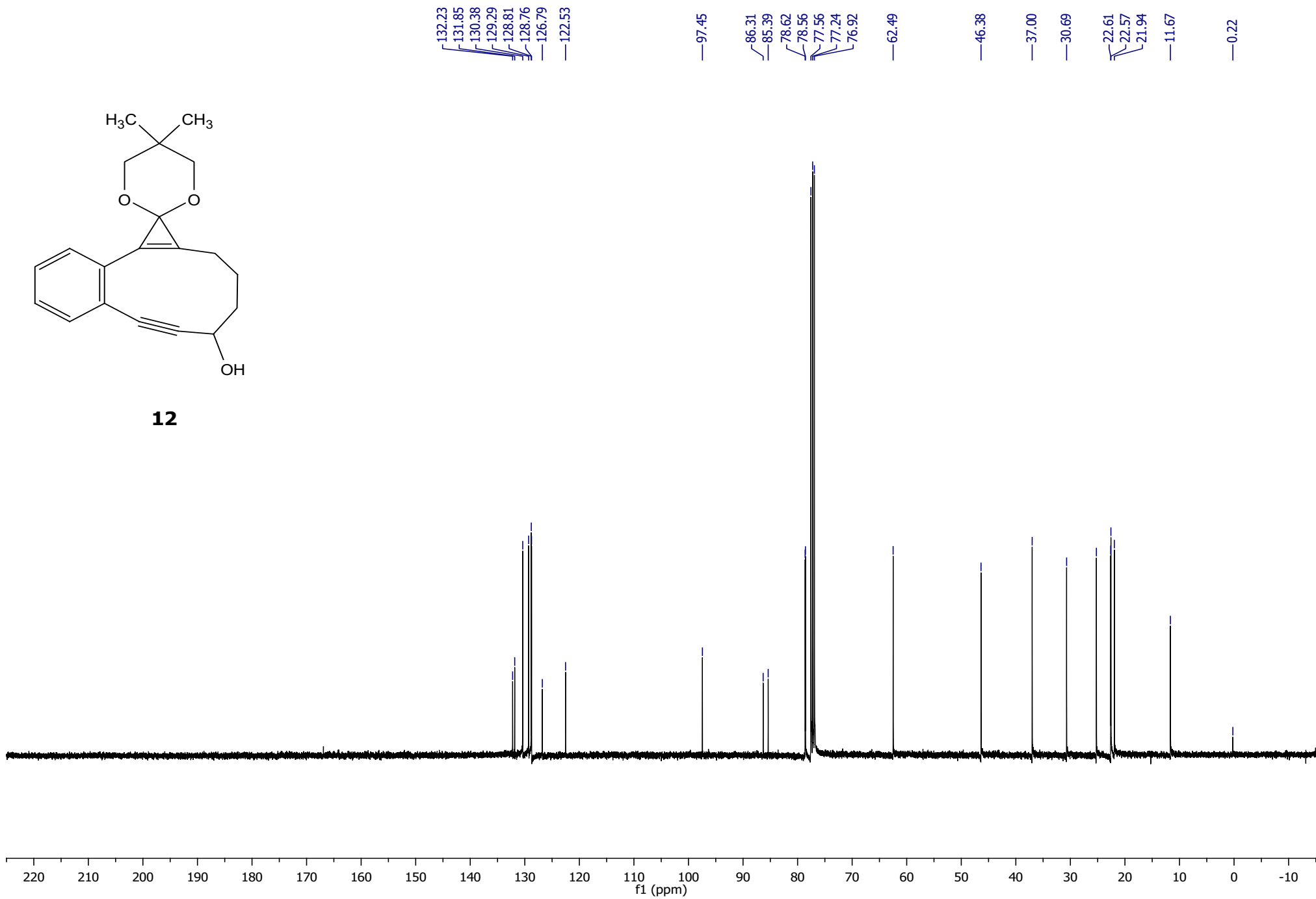


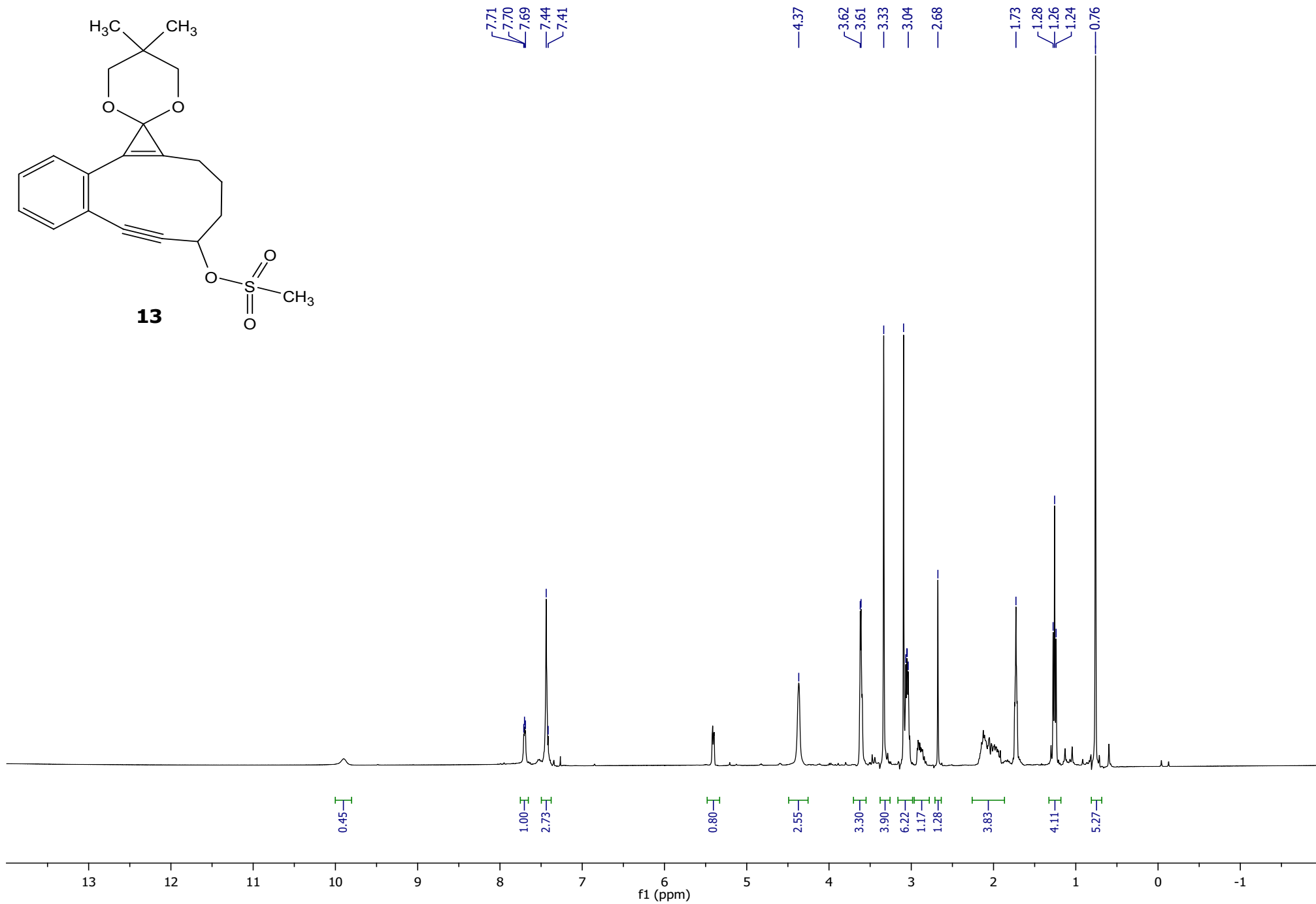
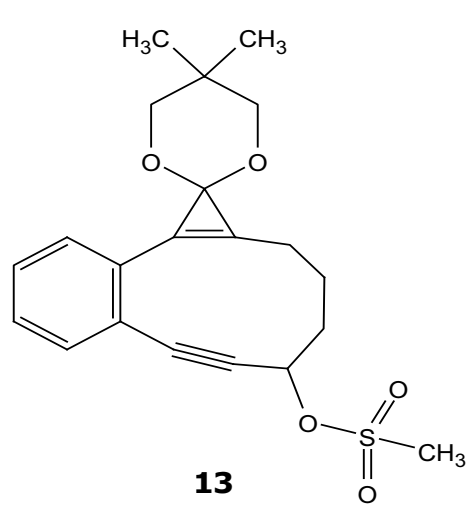
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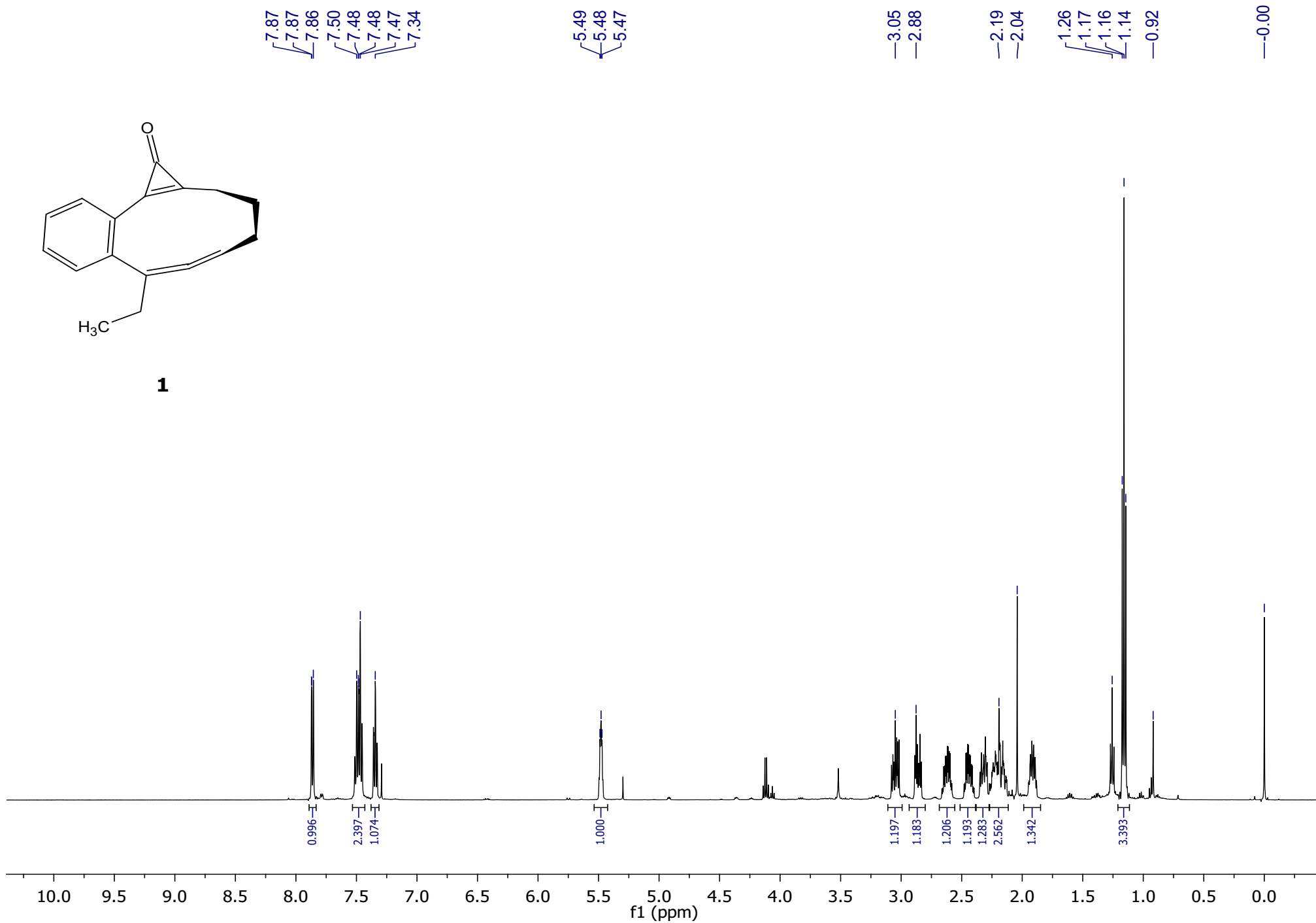
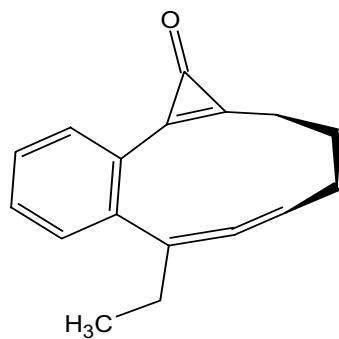


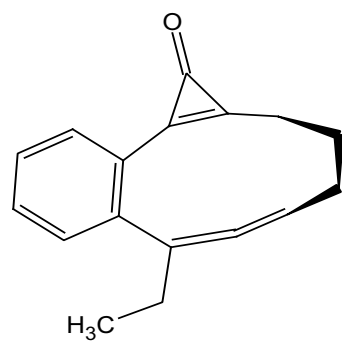


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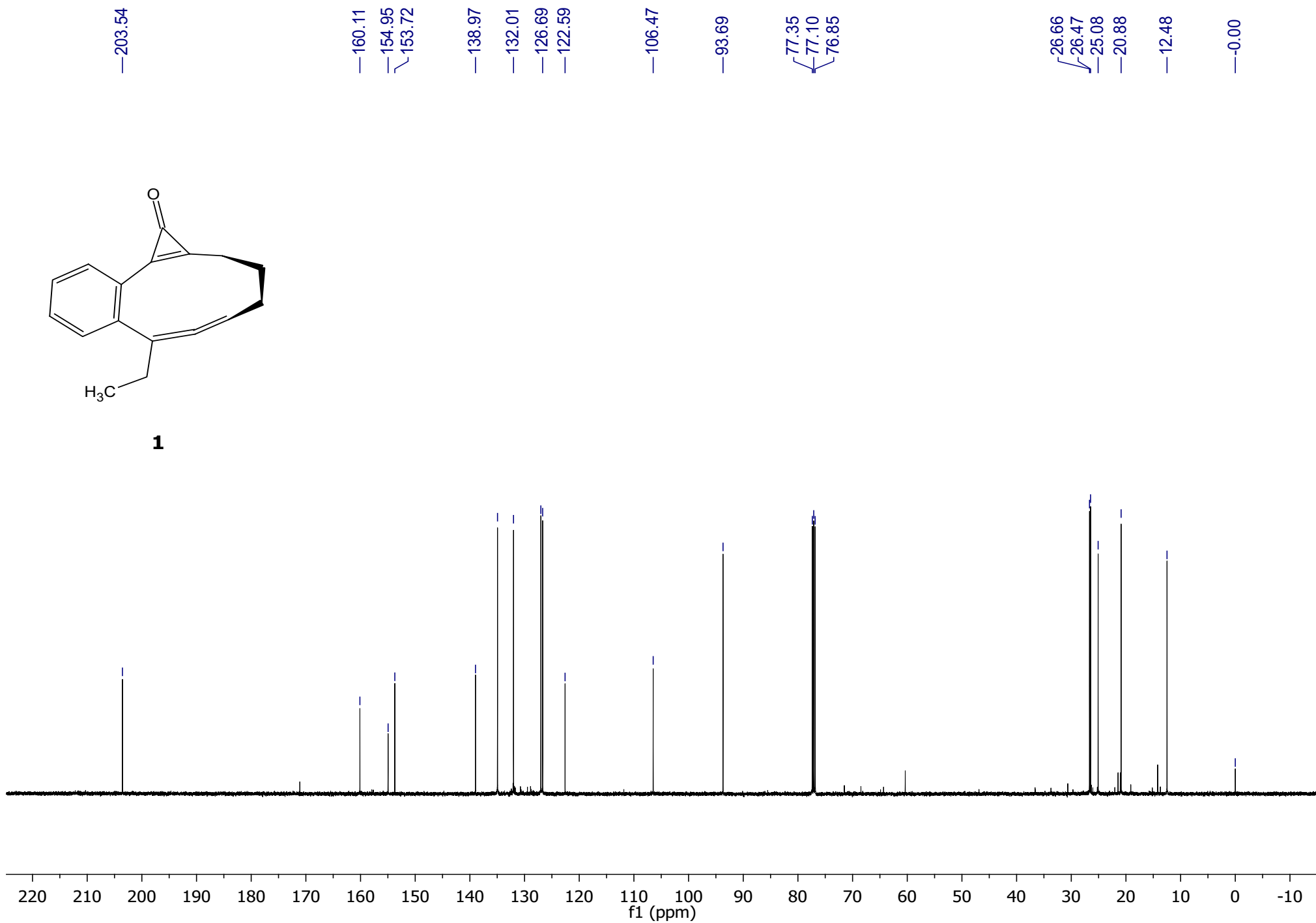


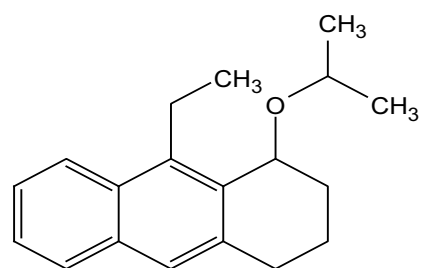




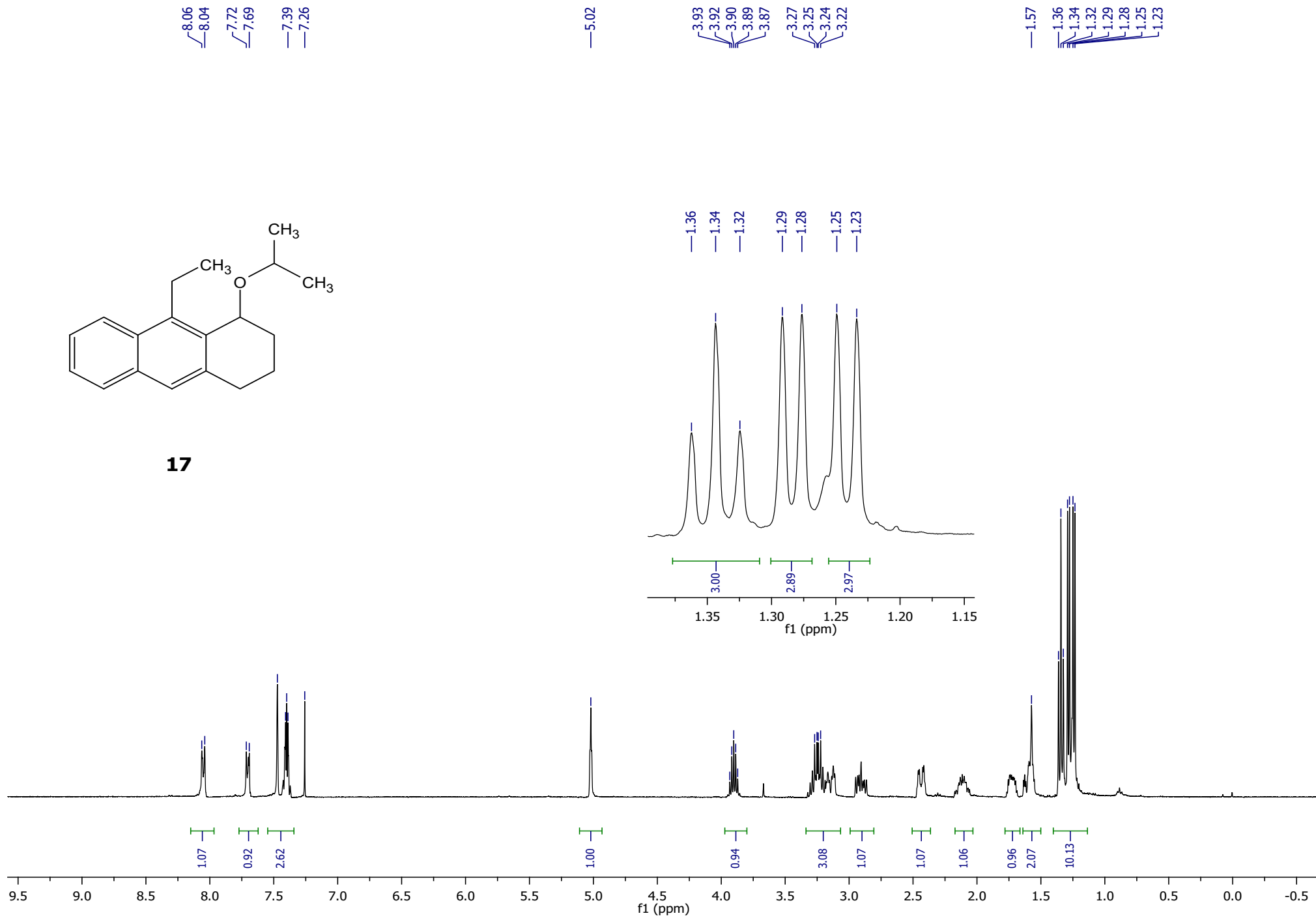


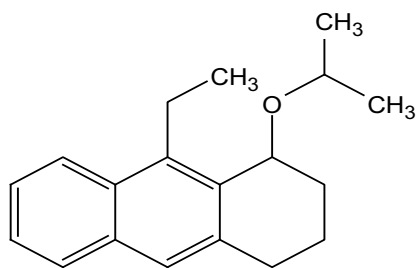
1





17





17

139.89
136.11
133.00
130.84
128.05
126.18
125.54
124.95
124.49

77.56
77.24
76.92

69.10
67.86

30.26
27.26
24.24
20.86
17.01
16.15

