Electrophilic Alkynylation of Ketones using Hypervalent Iodine

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Contents

1. General Information

All known compounds were characterized by ^{1}H and ^{13}C NMR, melting point (for solids) and compared to literature values. All new compounds were characterized by ^{1}H and ^{13}C NMR, IR, high-resolution mass spectrometry (HRMS), and melting point (for solids).

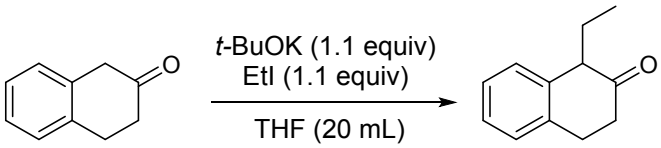
All commercially available reagents were used without further purification unless otherwise noted. All solvents used for reactions and chromatography were dried and purified by standard methods. TLC analysis were performed using silica gel 60F 254 precoated plates, with detection by UV-absorption (254 nm) and by spraying with *p*-anisaldehyde and phosphomolybdic acid solutions followed by charring at ~150 °C for visualization. Flash column chromatography was performed using silica gel 200-400 Mesh. Melting points were obtained in a Büchi Melting Point B-545 equipment and are uncorrected. ^{1}H and ^{13}C NMR experiments were recorded on Bruker or Varian spectrometers. IR spectra were recorded on a Perkin-Elmer 1750-FT apparatus. Gas chromatography analyses were performed in a Shimadzu QP5050A gas spectrometer. HRMS analyses were performed on a Bruker Daltonics Microtof Electrospray. All NMR analyses were recorded using $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts are reported in ppm downfield from TMS with reference to internal solvent. Preparation of reagent TMS-EBX **(2a)**,[1] TIPS-EBX **(2b)**,[1] Ochia´s reagent **(2c)**,[1] substrates **1c**,[2] **1e**[2] and **6a**[3] was performed as described in the literature.

[1] Gonzalez, D.F.; Brand, J.P.; Waser, J. *Chem. Eur. J.* **2010**, *16*, 9457.

[2] Ahmad, A.; Scarassati, P.; Jalalian, N.; Olofsson, B.; Silva, L. F., Jr. *Tetrahedron Lett.* **2013**, *54*, 5818.

[3] Ferraz, H. M. C.; Carneiro, V. M. T.; Silva, L. F., Jr. *Synthesis* **2009**, 385.

2. Preparation of 1-Ethyl-3,4-dihydronaphthalen-2(1*H*)-one (1d)[4]



1d

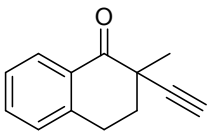
To a round bottom flask equipped with a magnetic stir bar was added 2-tetralone (0.73 g, 5.0 mmol) and anhydrous THF (0.25 M, 20 mL). To the solution was added *t*-BuOK (0.62 g, 5.5 mmol, 1.1 equiv). The flask was capped and the reaction stirred at rt under N_2. After 30 min, the reaction was cooled to 0 °C and EtI (0.50 mL, 5.5 mmol, 1.1 equiv) was added dropwised. After EtI addition, the ice bath was removed and the reaction was stirred at rt for 2 h (total consumption of 2-tetralone by GC). Subsequently, 20 mL of HCl (0.1 M) and CH_2Cl_2 (10 mL) were added and the contents of the flask were transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (Rf = 0.3, hexanes : EtOAc, 9 : 1) to afford **1d** as a light yellow oil in 80% (0.70 g, 4.0 mmol).

[4] Kirkiacharian, B. S.; Koutsourakis, P. G. *Synth. Commun.* **1993**, *23*, 737.

3. Alkynylation of Ketones and Aldehyde with TMS-EBX

3.1. General Procedure A (Monoalkynylation)

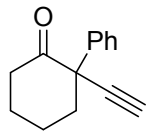
To a round bottom flask equipped with a magnetic stir bar was added the ketone (1.0 mmol) and THF (0.1 M, 10 mL). To the solution was added *t*-BuOK (0.14 g, 1.25 mmol, 1.25 equiv). The flask was capped and the reaction stirred at rt for 45 min. The reaction was then cooled to -78 °C and TMS-EBX (0.45 g, 1.3 mmol, 1.3 equiv) was added followed by addition of TBAF (1M in THF, 1.3 mL, 1.3 mmol, 1.3 equiv). The reaction was stirred at -78 °C until total consumption of ketone starting material or maximum conversion was achieved (as indicated by GC analysis). After the indicated time, silica gel was added to the mixture and the solvent removed under reduced pressure. The pure product was obtained after purification with flash column chromatography (hexanes : EtOAc).



3a

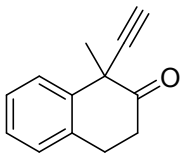
2-Ethynyl-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (3a).[5] The general procedure **A** was employed using 2-methyl-1-tetralone **1a** (0.16 g, 1.0 mmol), and the reaction was completed in 10 h. The desired pure product was obtained after column chromatography (R_f = 0.6, 15% EtOAc in hexanes) in 93% yield (0.17 g, 0.93 mmol) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5, 1H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 8.1 Hz, 1H), 3.40 (ddd, *J* = 27.0, 11.4, 4.5 Hz, 1H), 2.91 (dt, *J* = 4.2, 17.1 Hz, 1H), 2.29 (dt, *J* = 4.5, 13.2, 1H), 2.19 (s, 1H), 2.07 (ddd, *J* = 4.5, 11.4, 13.5 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 143.7, 133.5, 130.7, 128.7, 128.5, 126.7, 84.1, 71.4, 42.1, 36.4, 26.4, 23.7.

[5] Kende, A. S.; Fludzinski, P.; Hill, J. H.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 3551.



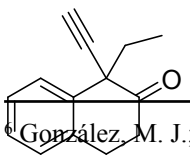
3b

2-Ethynyl-2-phenylcyclohexan-1-one (3b).[6] The general procedure **A** was employed using 2-phenylcyclohexan-1-one **1b** (0.17 g, 1.0 mmol), and the reaction was completed in 2 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 8:2) in 85% yield (0.17 g, 0.85 mmol) as a light yellow solid, mp 72 – 74 ºC. (lit.[5] light yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 5H), 3.09 (ddd, *J* = 13.7, 11.7, 5.9 Hz, 1H), 2.71 (s, 1H), 2.51 – 2.08 (m, 5H), 1.95 – 1.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 138.8, 128.3, 127.7, 127.5, 84.2, 76.7, 55.8, 40.9, 39.0, 27.7, 22.3.



3c

1-Ethynyl-1-methyl-3,4-dihydronaphthalen-2(1*H*)-one (3c). The general procedure **A** was employed using 1-methyl-2-tetralone **1c** (0.16 g, 1.0 mmol), and the reaction was completed in 3 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 9:1) in 60% yield (0.11 g, 0.60 mmol) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 1H), 7.35 – 7.18 (m, 3H), 3.36 (m, 1H), 3.15 – 2.59 (m, 3H), 2.40 (s, 1H), 1.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5, 138.5, 135.4, 128.1, 127.5, 127.3, 126.5, 83.9, 72.1, 47.7, 35.9, 27.9, 25.1. IR (neat) 3287, 2937, 1726, 1453, 760 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{12}NaO$ $(M+Na)^+$ 207.0780, found 207.0785.

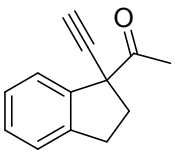


3d

1-Ethyl-1-ethynyl-3,4-dihydronaphthalen-2(1*H*)-one (3d). The general procedure **A** was employed using 1-ethyl-3,4-dihydronaphthalen-2(1*H*)-one

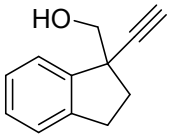
[6] González, M. J.; González, J.; Vicente, R. *Eur. J. Org. Chem.* **2012**, 6140

1d (0.17 g, 1.0 mmol), and the reaction was completed in 2 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 9:1) in 78% yield (0.15 g, 0.78 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.30 (m, 1H), 7.25 (td, *J* = 1.5, 7.5 Hz, 1H), 7.19 (m, 1H), 3.16 (m, 1H), 3.07 (m, 1H), 2.79 (m, 1H), 2.70 (m, 1H), 2.50 (s, 1H), 2.10 (m, 1H), 1.99 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 137.4, 134.8, 128.4, 128.3, 127.4, 127.1, 83.5, 73.4, 54.3, 36.7, 32.3, 27.9, 9.5. IR (neat) 3288, 2937, 1722, 1454, 756 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_8NaO$ $(M+Na)^+$ 221.0942, found 221.0934.



3e

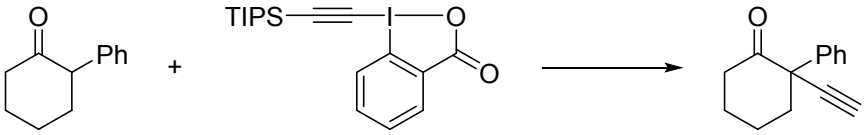
1-(1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)ethan-1-one (3e). The general procedure **A** was employed using 1-(2,3-dihydro-1*H*-inden-1-yl)ethan-1-one **1e** (0.16 g, 1.0 mmol), and the reaction was completed in 5 h. The desired pure product was obtained after column chromatography (R_f = 0.4, 5% EtOAc in hexanes) in 85% yield (0.16 g, 0.85 mmol) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 1H), 7.25 (m, 3H), 2.97 (m, 3H), 2.48 (s, 1H), 2.34 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 143.8, 141.9, 128.4, 126.9, 125.1, 124.5, 85.1, 72.5, 59.6, 37.5, 31.0, 25.4. IR (neat) 3290, 2948, 1715, 1354, 1168, 769, 648 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{13}O$ $(M+H)^+$ 185.0961, found 185.0969.



7a

(1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)methanol (7a). The general procedure **A** was employed using 2,3-dihydro-1*H*-indene-1-carbaldehyde **6a** (0.15 g, 1.0 mmol), and the reaction was completed in 2 h. After this time, $NaBH_4$ (0.19 g, 5.0 mmol, 5.0 equiv) was added and the mixture warmed up to rt. After 2 h the reaction was quenched with aqueous $NaHCO_3$ (sat.) (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (anhydrous $MgSO_4$), filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (Rf = 0.1, hexanes : EtOAc, 9:1) to afford **7a** as a light yellow oil in 50% (0.09 g, 0.5 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.24 – 7.23 (m, 3H), 3.69 – 3.57 (m, 2H), 3.00 – 2.94 (m, 2H), 2.50 – 2.30 (m, 3H), 1.94 (t, *J* = 6.9 Hz, 1H) . ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 143.2, 127.9, 126.8, 124.9, 124.0, 87.1, 70.9, 68.5, 49.7, 35.9, 30.1. IR (neat) 3545, 3291, 2943, 1477, 1457, 1072, 1049, 759, 648 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{12}NaO$ $(M+Na)^+$ 195.0780, found 195.0781.

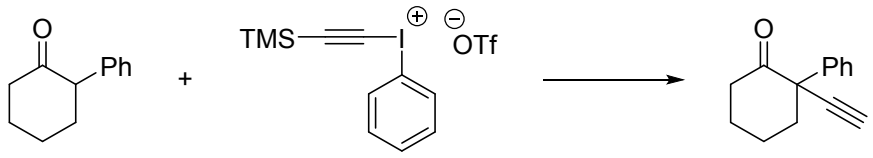
3.2 Alkynylation of 2-phenylcyclohexan-1-one (1b) with TIPS-EBX



1b TIPS-EBX **(2b)** **3b**

The general procedure **A** was employed using 2-phenylcyclohexan-1-one **1b** (0.17 g, 1.0 mmol), and TIPS-EBX (**2b**) (0.56 g, 1.3 mmol, 1.3 equiv) and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 8:2) in 80% yield (0.16 g, 0.80 mmol).

3.3 Alkynylation of 2-phenylcyclohexan-1-one (1b) with Ochiai´s reagent

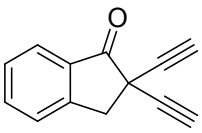


1b Ochiai´s reagent (**2c**) **3b**

The general procedure **A** was employed using 2-phenylcyclohexan-1-one **1b** (0.17 g, 1.0 mmol), and TIPS-EBX (**2b**) (0.59 g, 1.3 mmol, 1.3 equiv) and the reaction was completed in 12 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 8:2) in 67% yield (0.13 g, 0.67 mmol).

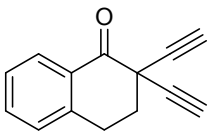
3.4 General Procedure B (Dialkynylation)

To a round bottom flask equipped with a magnetic stir bar was added the ketone (1.0 mmol) and THF (0.1 M, 10 mL). To the solution was added *t*-BuOK (0.28 g, 2.5 mmol, 2.5 equiv). The flask was capped and the reaction stirred at rt for 45 min. The reaction was then cooled to -78 °C and TMS-EBX (0.89 g, 2.6 mmol, 1.3 equiv) was added followed by addition of TBAF, 1M in THF (2.6 mL, 2.6 mmol, 2.6 equiv). The reaction was stirred at -78 °C until total consumption of ketone starting material or maximum conversion was achieved (as indicated by GC analysis). After the indicated time, silica gel was added to the mixture and the solvent removed under reduced pressure. The pure product was obtained after purification with flash column chromatography (hexanes : EtOAc).



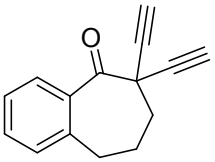
5a

2,2-Diethynyl-2,3-dihydro-1*H*-inden-1-one (5a). The general procedure **B** was employed using 1-indanone **4a** (0.13 g, 1.0 mmol), and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 8:2) in 69% yield (0.12 g, 0.69 mmol) as a orange solid, mp 106 – 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.70 (m, 1H), 7.50 – 7.45 (m, 2H), 3.72 (s, 2H), 2.36 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 150.6, 136.1, 132.6, 128.4, 126.5, 126.1, 80.9, 70.6, 44.1, 41.5. IR (neat) 3239, 2918, 1722, 1466, 729 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_8NaO$ $(M+Na)^+$ 203.0473, found 203.0467.



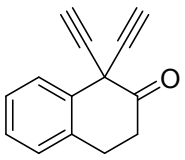
5b

2,2-Diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5b). The general procedure **B** was employed using 1-tetralone **4b** (0.15 g, 1.0 mmol), and the reaction was completed in 8 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 7:3) in 80% yield (0.16 g, 0.80 mmol) as a yellow solid, mp 71 – 73 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.52 (td, *J* = 1.0, 7.5 Hz, 1H), 7.35 (td, *J* = 0.6, 7.8 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 3.20 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 188.5, 143.0, 134.1, 129.6, 129.2, 128.7, 127.0, 79.6, 72.6, 42.5, 36.3, 25.8. IR (neat) 3252, 2931, 1698, 1455, 1223, 741, 666 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}NaO$ $(M+Na)^+$ 217.0624, found 217.0627.



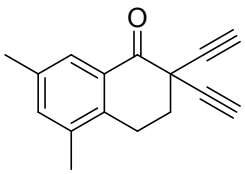
5c

6,6-Diethynyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (5c). The general procedure **B** was employed using 1-benzosuberone **4c** (0.16 g, 1.0 mmol), and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 9:1) in 81% yield (0.17 g, 0.81 mmol) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.32 (dd, *J* = 1.3, 7.5 Hz, 1H), 7.17 (m, 1H), 2.96 – 2.92 (m, 2H), 2.46 (s, 2H), 2.34 – 2.30 (m, 2H), 2.14 – 2.06 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 138.2, 137.8, 131.6, 128.9, 128.8, 126.5, 80.7, 73.1, 46.4, 38.5, 33.3, 23.4. IR (neat) 3288, 2942, 1703, 1449, 741, 659 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}NaO$ $(M+Na)^+$ 231.0786, found 231.0776.



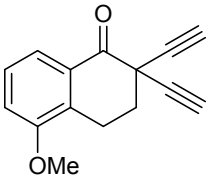
5d

1,1-Diethynyl-3,4-dihydronaphthalen-2(1*H*)-one (5d). The general procedure **B** was employed using 2-tetralone **4d** (0.15 g, 1.0 mmol), and the reaction was completed in 1 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 4:1) in 42% yield (0.08 g, 0.42 mmol) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 1H), 7.33 (m, 2H), 7.26 – 7.23 (m, 1H), 3.32 (t, *J* = 6.5 Hz, 2H), 2.83 (t, *J* = 6.5 Hz, 2H), 2.65 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 135.7, 134.0, 128.7, 128.3, 127.6, 127.3, 78.3, 74.5, 48.6, 34.4, 27.4. IR (neat) 3288, 2919, 1738, 1455, 1147, 759, 666 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{11}O$ $(M+H)^+$ 195.0804, found 195.0810.



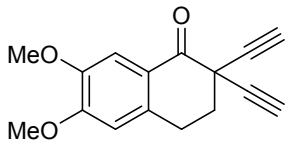
5e

2,2-Diethynyl-5,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (5e). The general procedure **B** was employed using 5,7-dimethyl-1-tetralone **4e** (0.18 g, 1.0 mmol), and the reaction was completed in 7 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 9:1) in 92% yield (0.20 g, 0.92 mmol) as a yellow solid, mp 111 – 113 °C . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.23 (s, 1H), 3.01 (t, *J* = 6.5 Hz, 2H), 2.52 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 2H), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 189.2, 138.4, 136.6, 136.2, 136.1, 129.5, 127.0, 79.8, 72.6, 42.1, 35.7, 22.9, 20.8, 19.2. IR (neat) 3268, 2922, 1688, 1478, 1226, 682 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}NaO$ $(M+Na)^+$ 245.0937, found 245.0940.



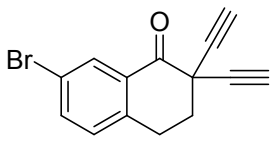
5f

2,2-Diethynyl-5-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (5f). The general procedure **B** was employed using 5-methoxy-1-tetralone **4f** (0.18 g, 1.0 mmol), and the reaction was completed in 9 h. The desired pure product was obtained after column chromatography (R_f = 0.4, 7% EtOAc in hexanes) in 60% yield (0.14 g, 0.60 mmol) as a yellow solid, mp 114 – 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 1.0, 8.0 Hz, 1H), 3.88 (s, 3H), 3.09 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 188.8, 156.4, 132.1, 130.5, 127.2, 120.6, 114.8, 79.6, 72.7, 55.7, 42.2, 35.6, 19.8. IR (neat) 3290, 2937, 1699, 1473, 1263, 748, 656 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}O_2$ $(M+H)^+$ 225.0910, found 225.0913.



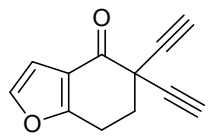
5g

2,2-Diethynyl-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (5g). The general procedure **B** was employed using 6,7-dimethoxy-1-tetralone **4g** (0.21 g, 1.0 mmol), and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 7:3) in 75% yield (0.19 g, 0.75 mmol) as a yellow solid, mp 166 – 168 °C . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (s, 1H), 6.66 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.12 (t, *J* = 6 Hz, 2H), 2.52 (t, *J* = 6 Hz, 2H), 2.42 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.4, 154.2, 148.3, 138.1, 122.5, 110.1, 110.0, 80.1, 72.2, 56.1, 56.0, 42.0, 36.7, 25.7. IR (neat) 3281, 2849, 1668, 1455, 1275, 649 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}NaO_3$ $(M+Na)^+$ 277.0835, found 277.0832.



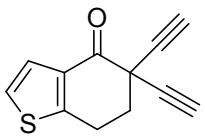
5h

7-bromo-2,2-diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5h). The general procedure **B** was employed using 7-bromo-3,4-dihydronaphthalen-1(2*H*)-one **4h** (0.07 g, 0.30 mmol), and the reaction was completed in 9 h. The desired pure product was obtained after column chromatography (R_f = 0.3, hexanes : EtOAc, 9:1) in 43% yield (0.03 g, 0.13 mmol) as a light yellow solid, mp 133 – 135 °C . ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 2.1, 8.1 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.4, 141.7, 136.9, 131.8, 131.1, 130.5, 121.0, 79.1, 73.1, 42.3, 36.0, 25.4. IR (neat) 3278, 2926, 1695, 1475, 1215, 666 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}BrO$ $(M+H)^+$ 272.9910, found 272.9904.



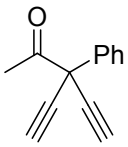
5i

5,5-Diethynyl-6,7-dihydrobenzofuran-4(5*H*)-one (5i). The general procedure **B** was employed using 6,7-dihydro-4(5*H*)-benzofuranone **4i** (0.16 g, 1.0 mmol), and the reaction was completed in 2 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 9:1) in 30% yield (0.06 g, 0.30 mmol) as a yellow solid, mp 127 – 129 °C . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.8 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 3.09 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 6.3 Hz, 2H), 2.42 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 165.5, 143.3, 118.1, 107.7, 79.4, 72.4, 42.2, 36.4, 21.1. IR (neat) 3239, 2850, 1698, 1431, 1213, 659 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_9O_2$ $(M+H)^+$ 185.0597, found 185.0602.



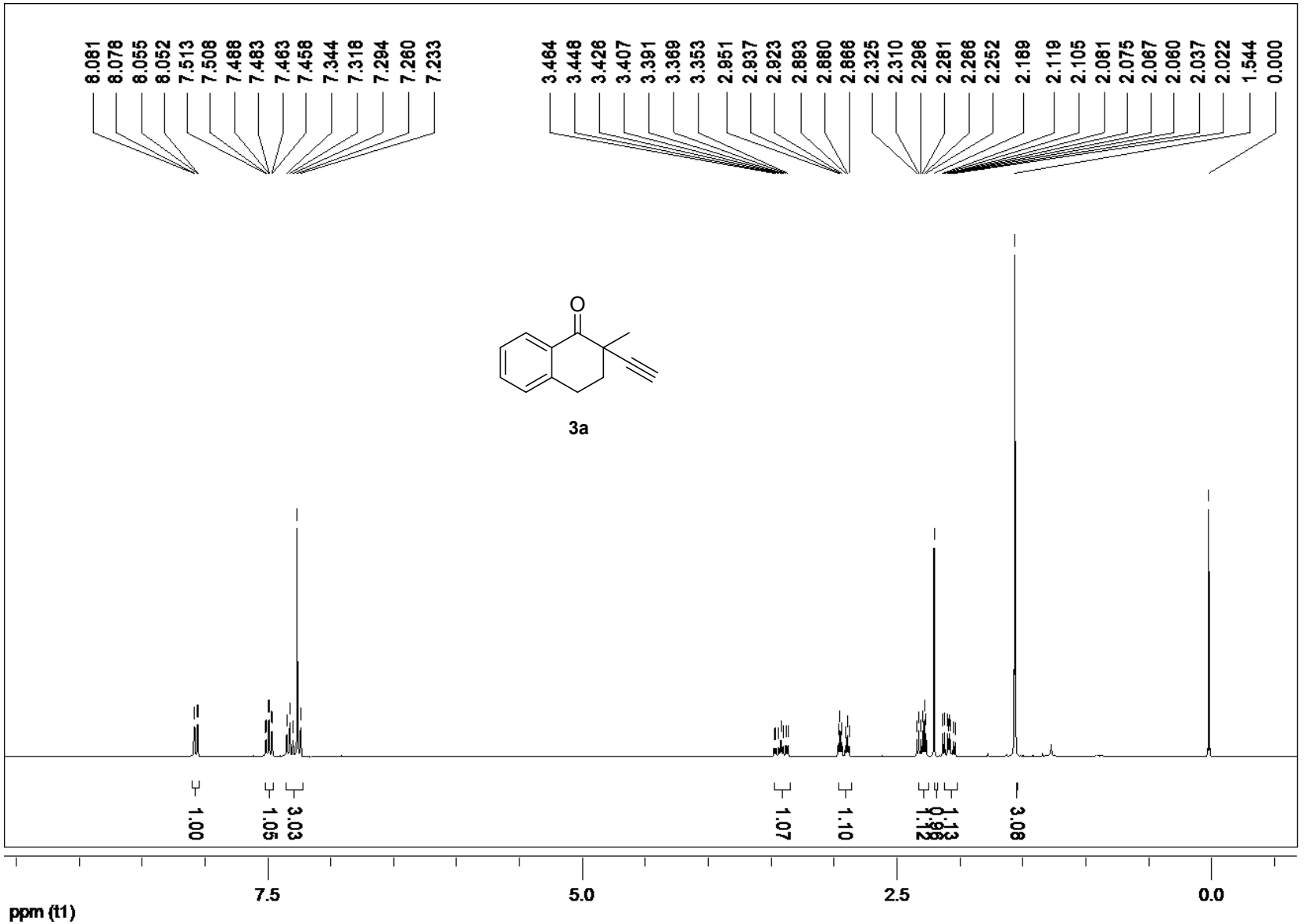
5j

5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(5*H*)-one (5j). The general procedure B was employed using 6,7-dihydro-4(5*H*)-benzothiophenone **4j** (0.15 g, 1.0 mmol), and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.4, hexanes : EtOAc, 8:2) in 74% yield (0.15 g, 0.74 mmol) as a light yellow solid, mp 128 – 130 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6 Hz, 1H), 7.13 (d, *J* = 6 Hz, 1H), 3.25 (t, *J* = 6 Hz, 2H), 2.60 (t, *J* = 6 Hz, 2H), 2.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1, 154.9, 133.5, 126.1, 124.0, 79.5, 72.5, 42.0, 38.1, 22.7. IR (neat) 3228, 2106, 1663, 1519, 1403, 1267, 902 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_8OS$ $(M+H)^+$ 201.0296, found 201.0363.

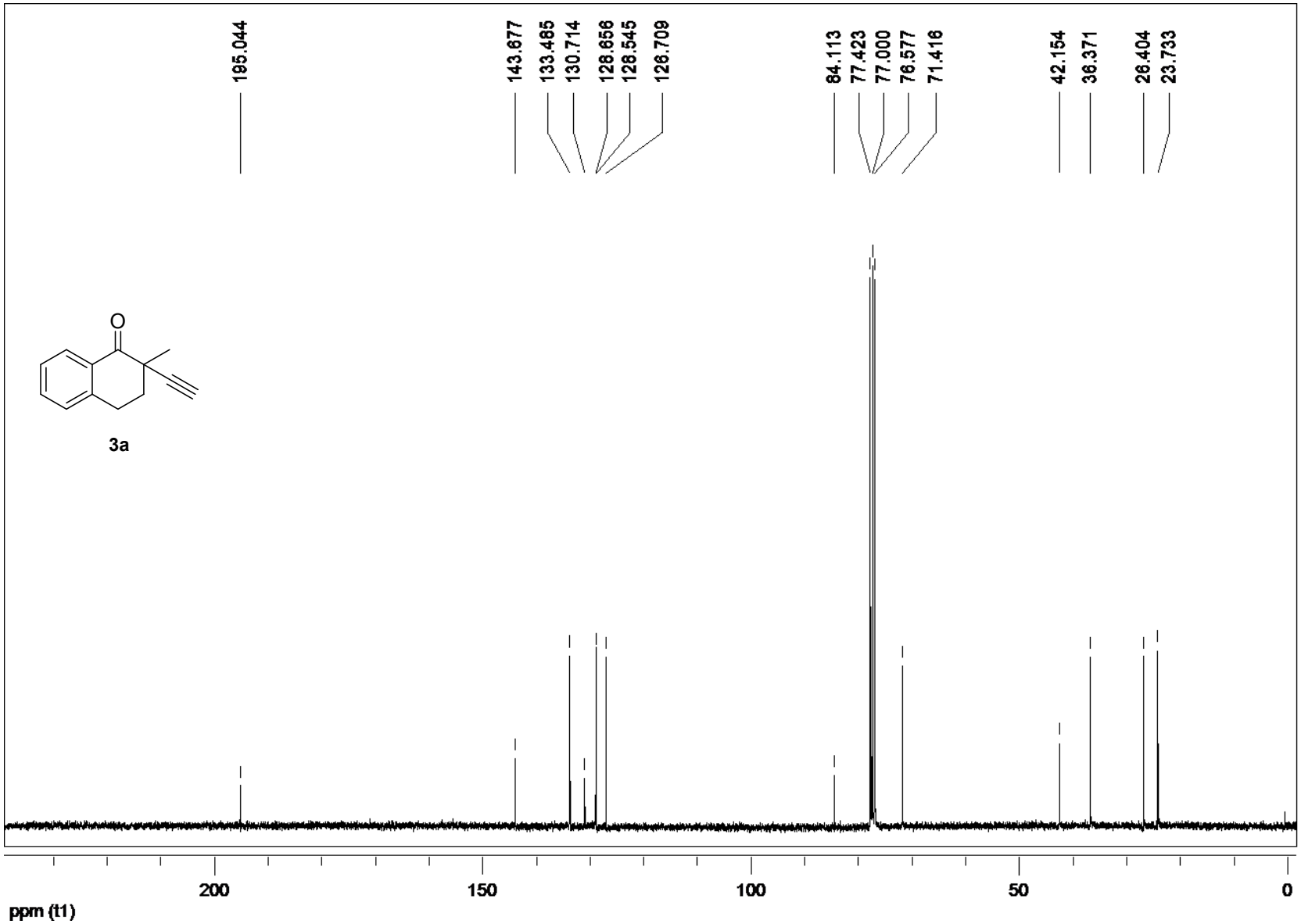


5k

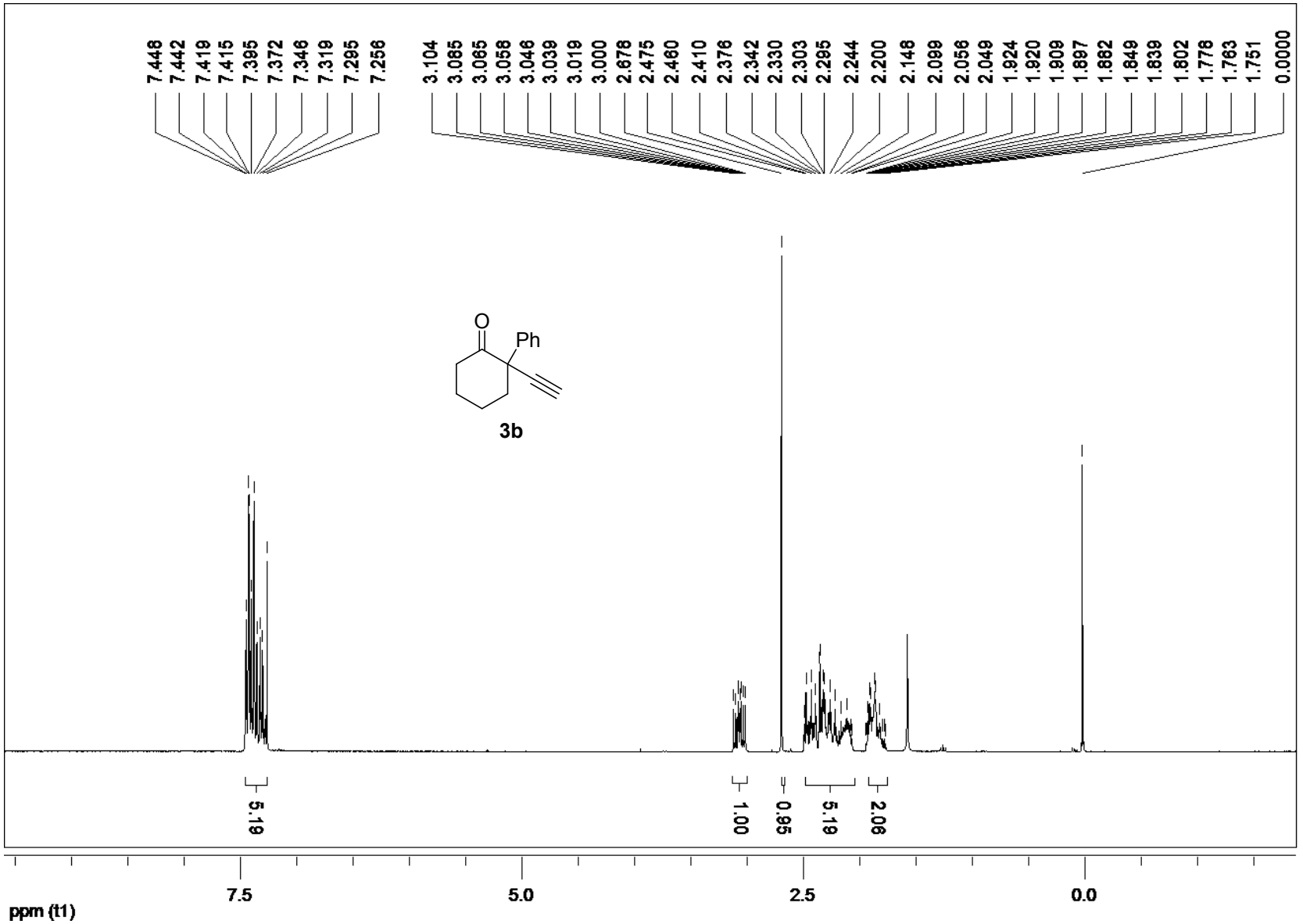
3-ethynyl-3-phenylpent-4-yn-2-one (5k). The general procedure B was employed using 1-phenylpropan-2-one **4k** (0.14 g, 1.0 mmol), and the reaction was completed in 4 h. The desired pure product was obtained after column chromatography (R_f = 0.5, hexanes : EtOAc, 8:2) in 74% yield (0.13 g, 0.74 mmol) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.44 – 7.33 (m, 3H), 2.73 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 135.5, 128.9, 128.6, 126.9, 80.0, 75.1, 53.5, 24.4. IR (neat) 3290, 2121, 1734, 1489, 1449, 1356, 698 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{10}O$ $(M+Na)^+$ 205.0624, found 205.0628.



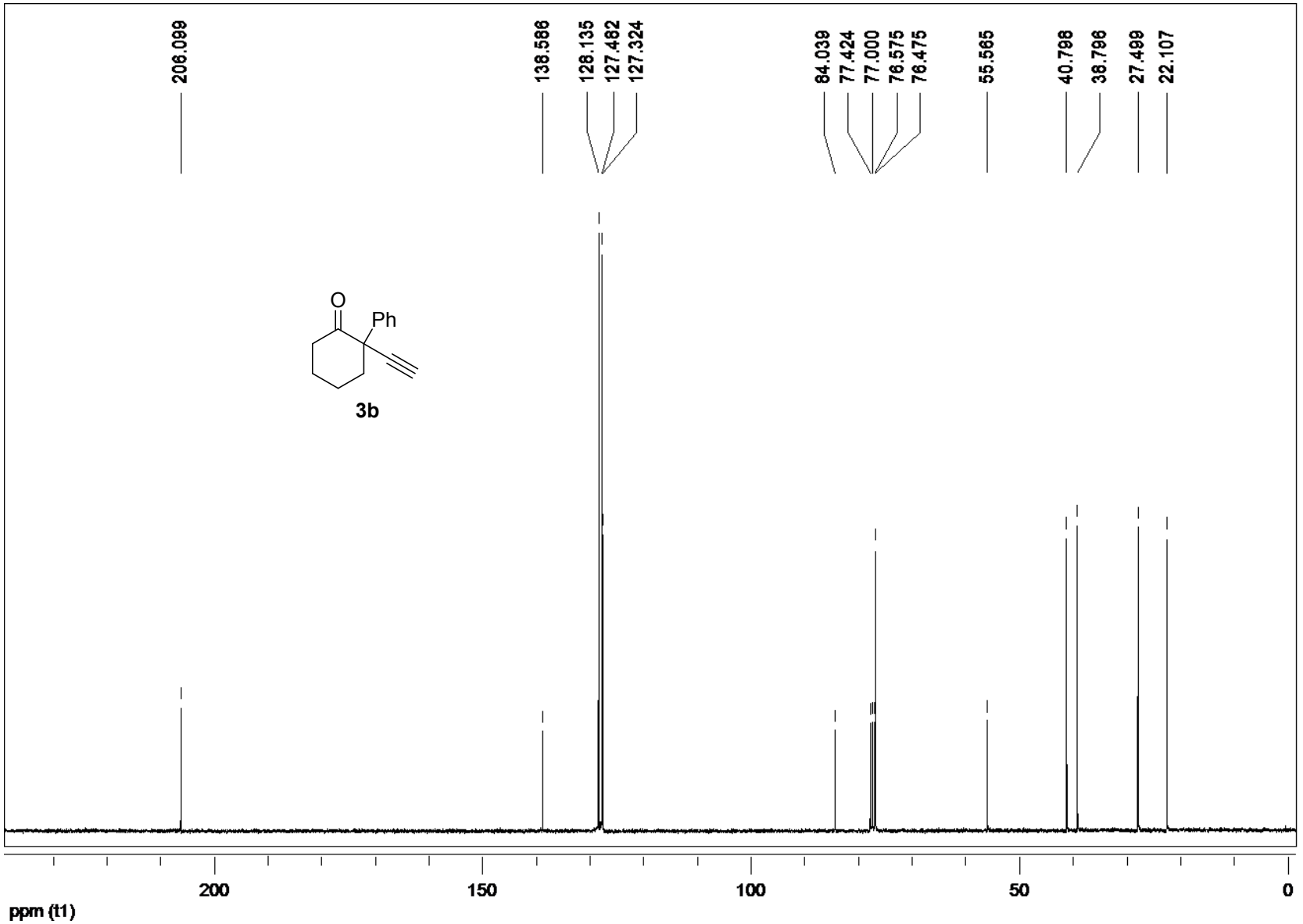
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 2-Ethynyl-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (3a)



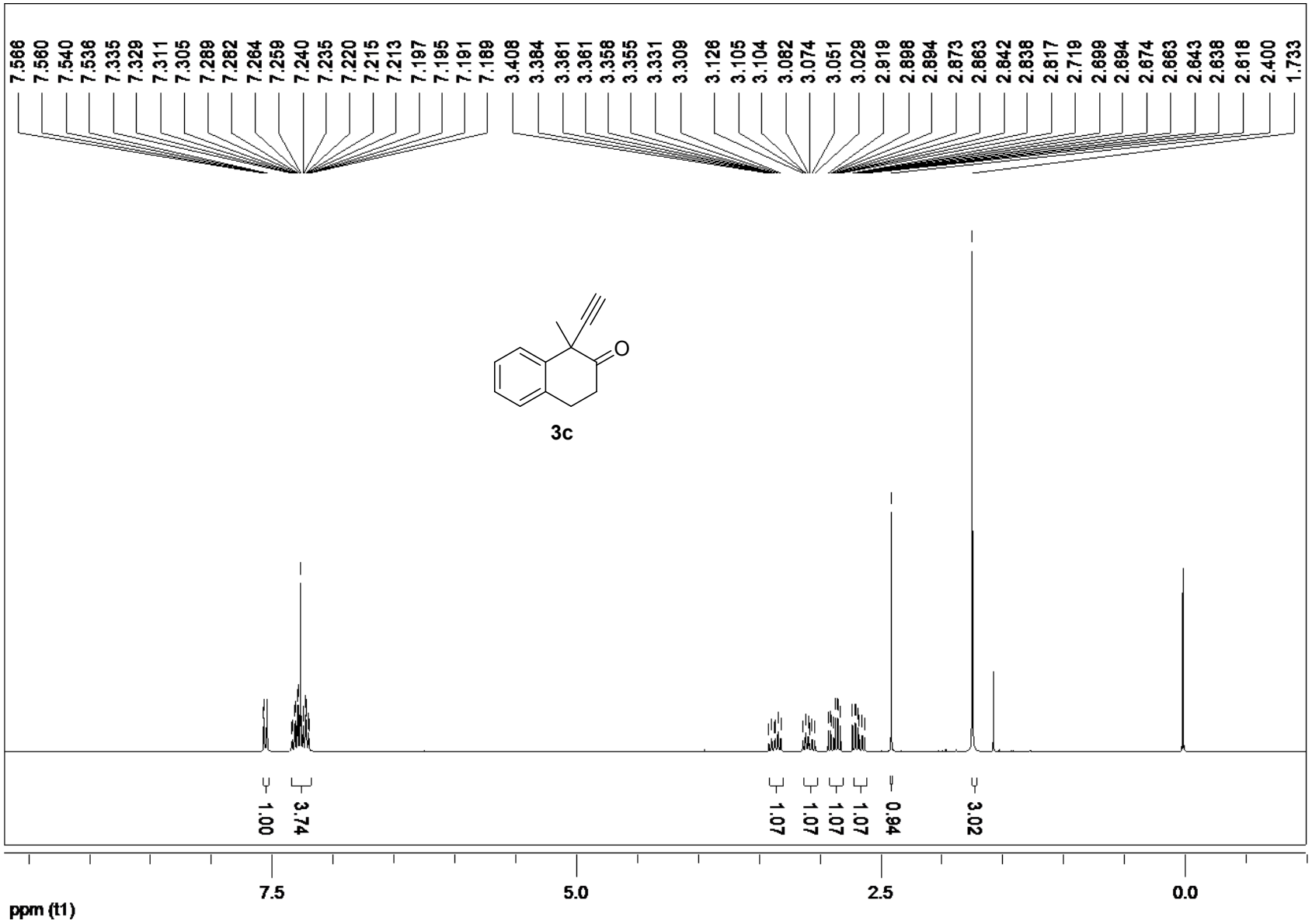
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 2-Ethynyl-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (3a)



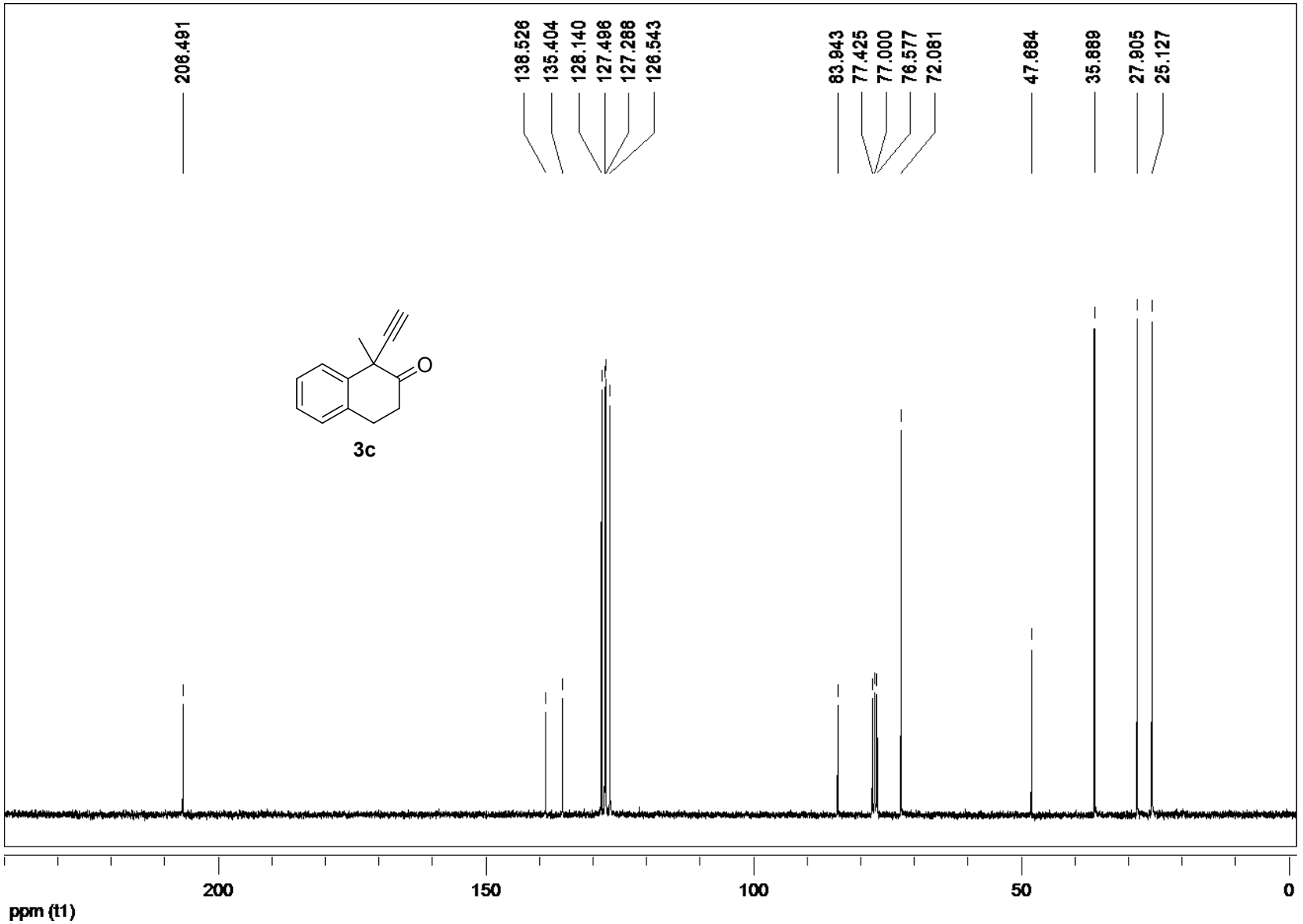
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 2-Ethynyl-2-phenylcyclohexan-1-one (3b)



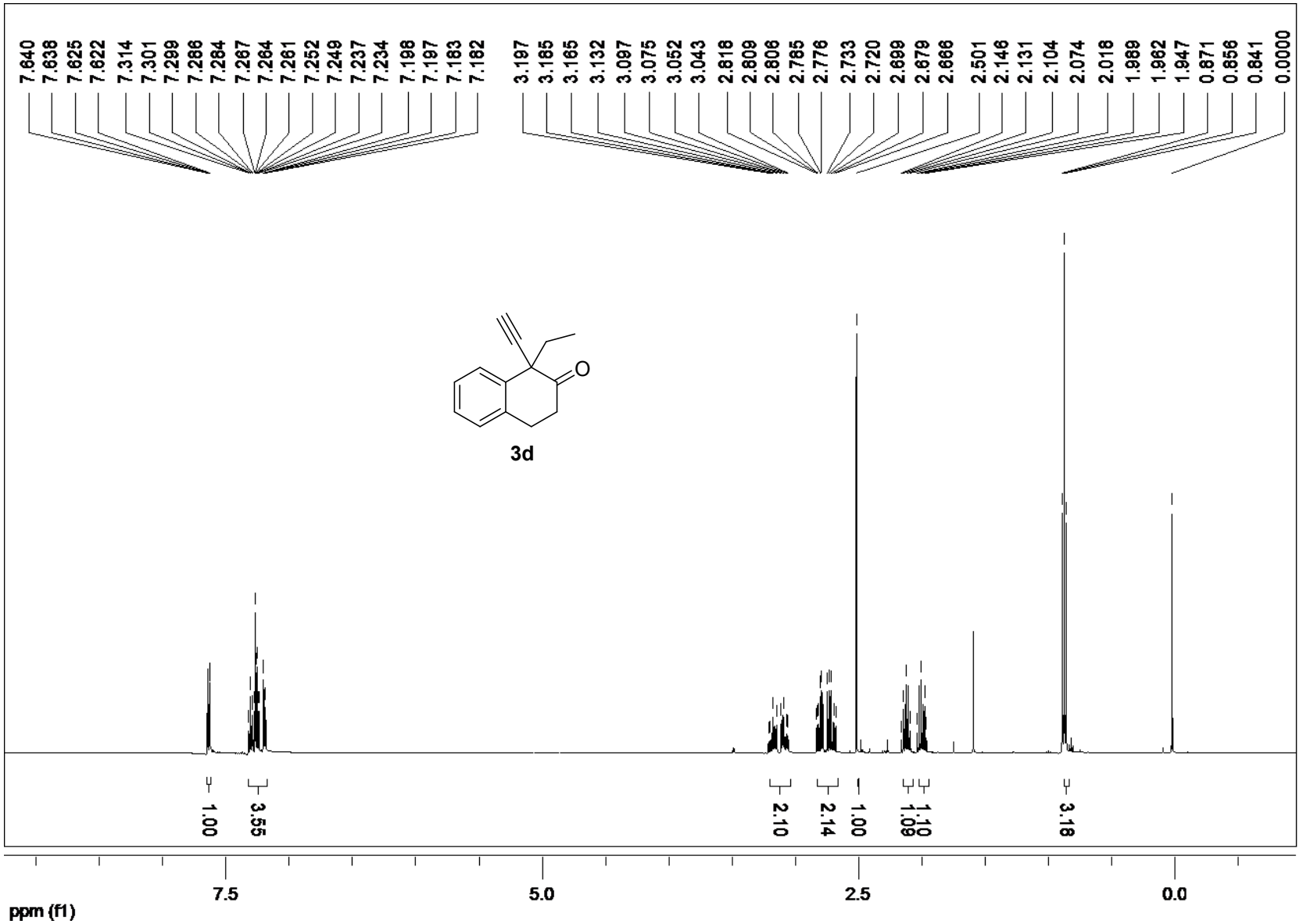
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 2-Ethynyl-2-phenylcyclohexan-1-one (3b)



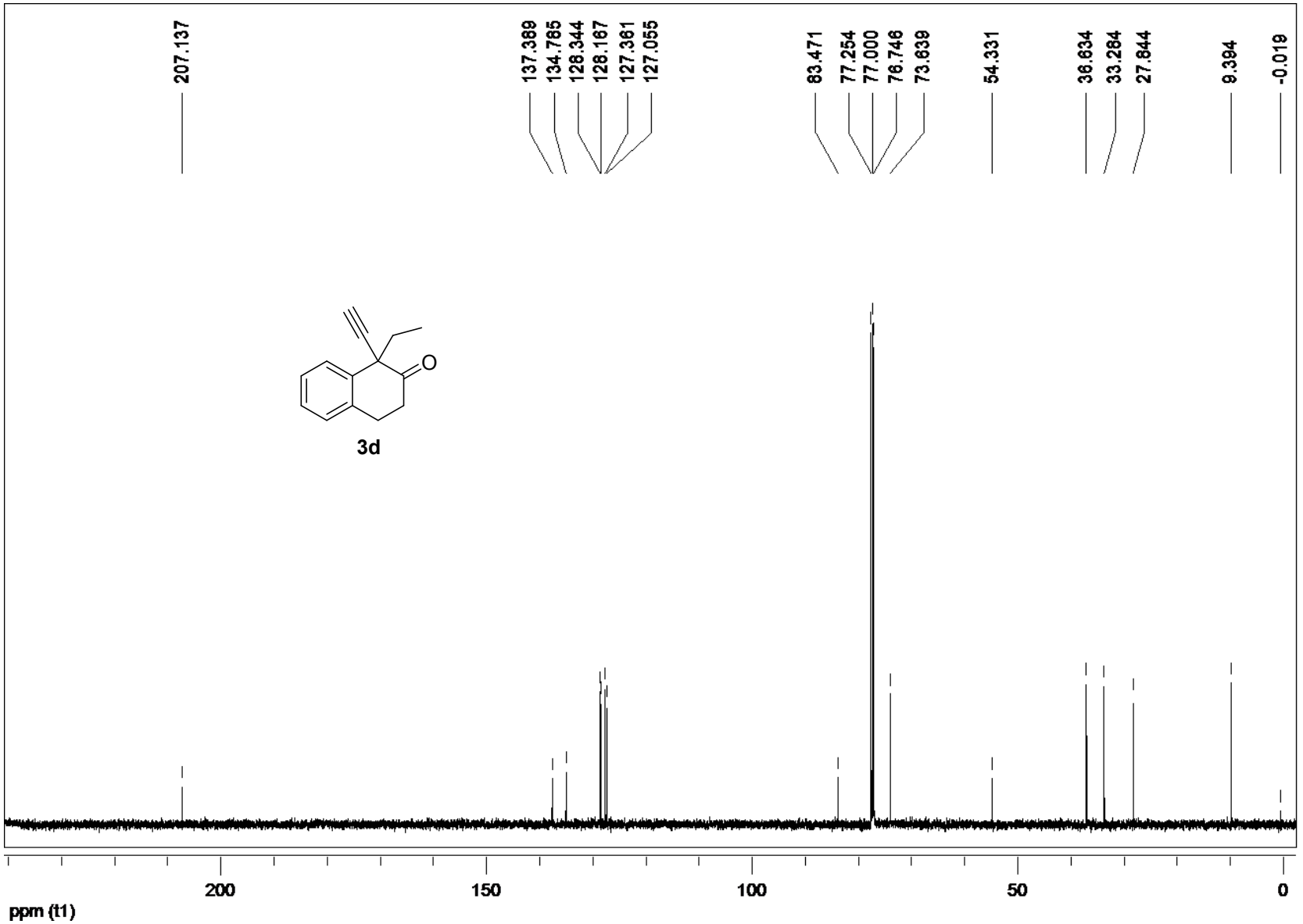
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 1-Ethynyl-1-methyl-3,4-dihydronaphthalen-2(1*H*)-one (3c)



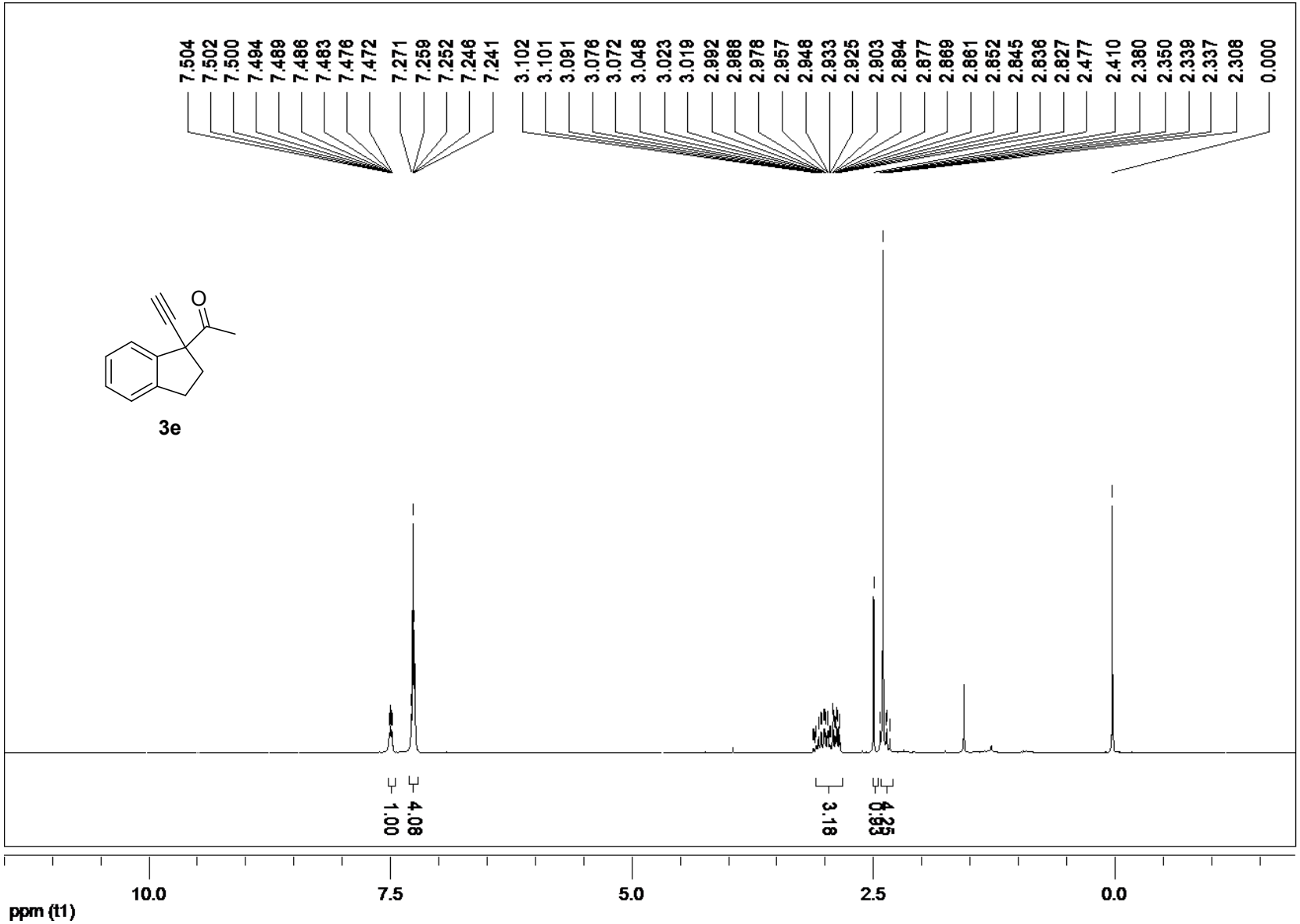
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 1-Ethynyl-1-methyl-3,4-dihydronaphthalen-2(1*H*)-one (3c)



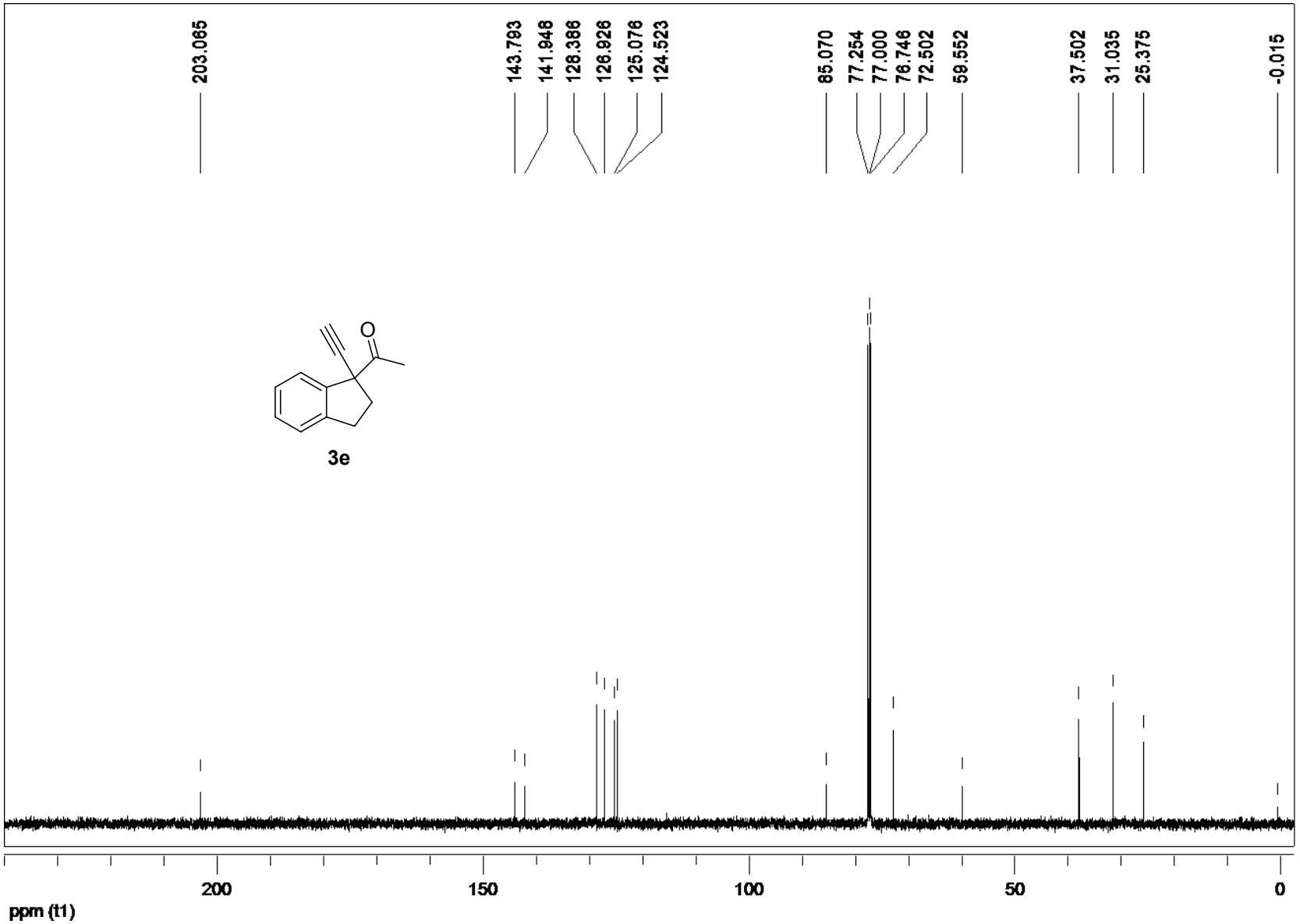
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-Ethyl-1-ethynyl-3,4-dihydronaphthalen-2(1*H*)-one (3d)



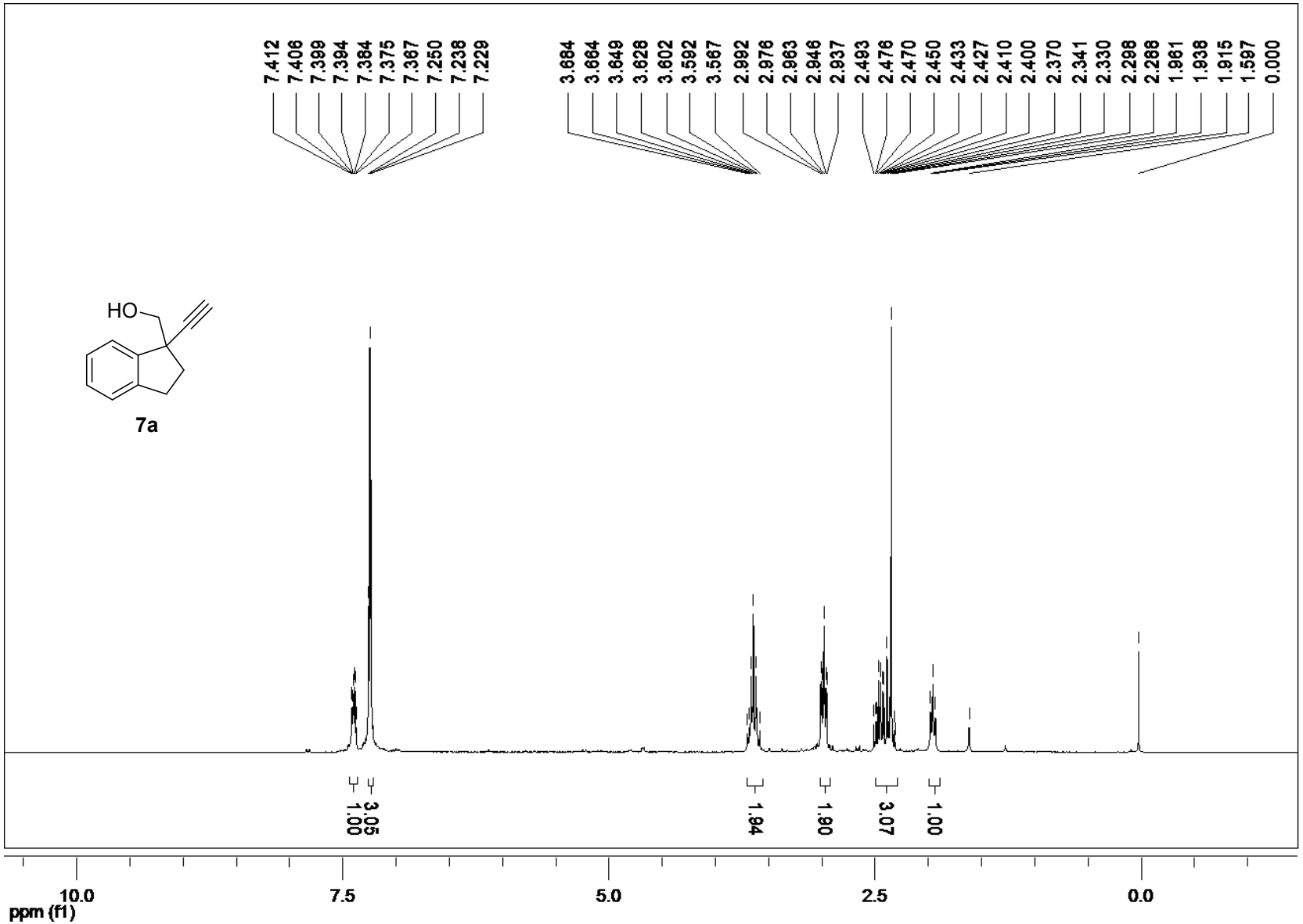
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-Ethyl-1-ethynyl-3,4-dihydronaphthalen-2(1*H*)-one (3d)



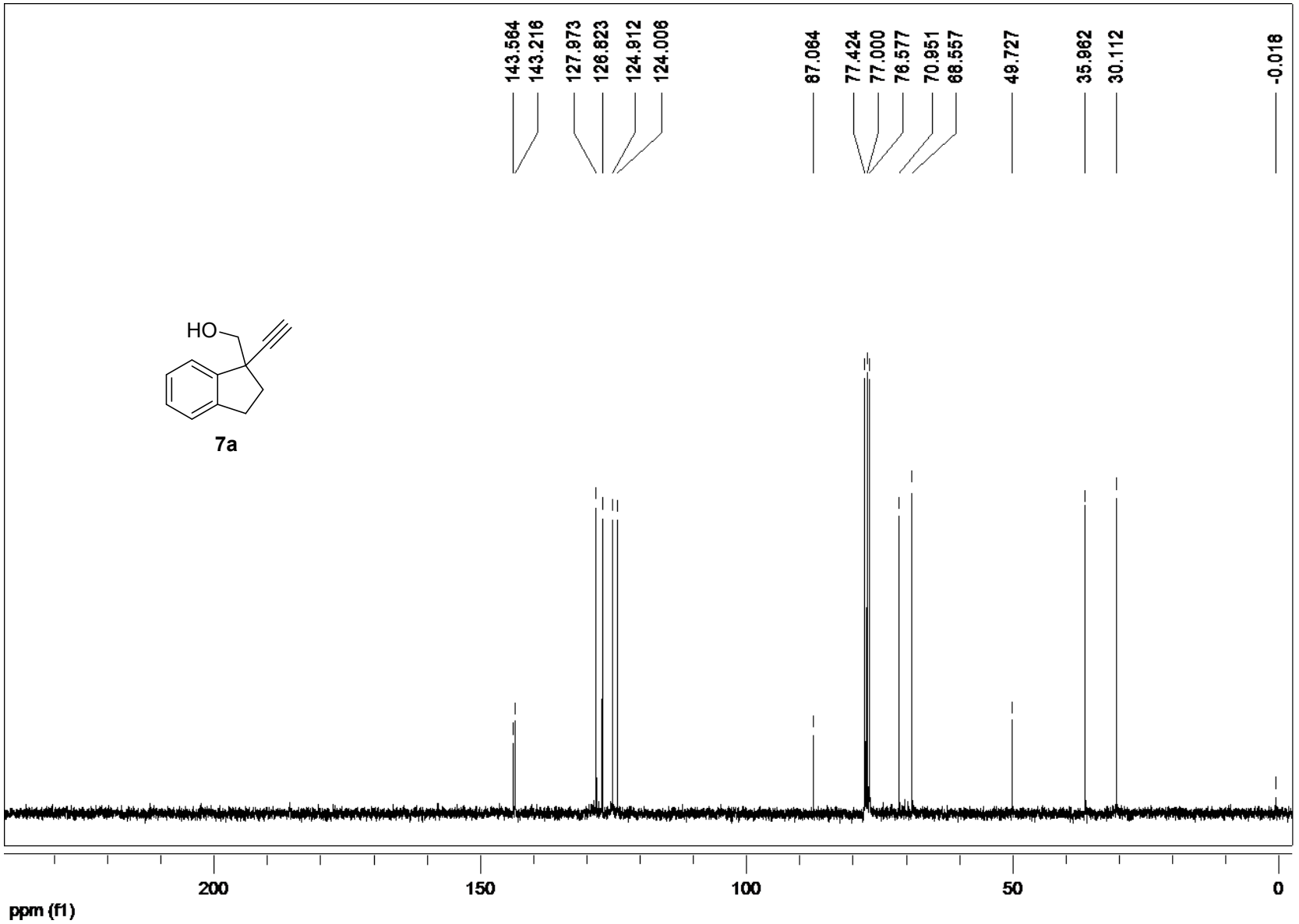
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 1-(1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)ethan-1-one (3e)



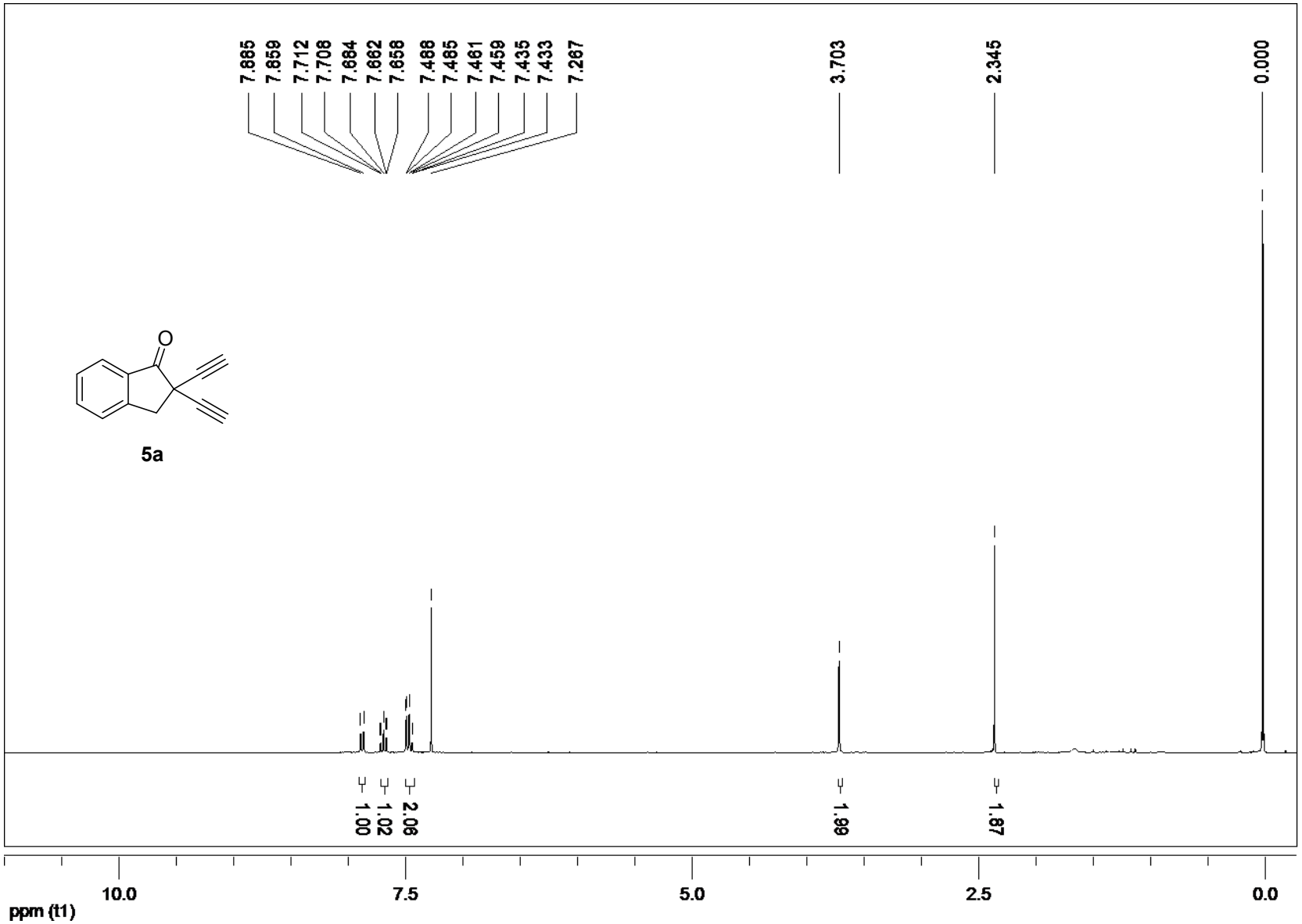
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)ethan-1-one (3e)



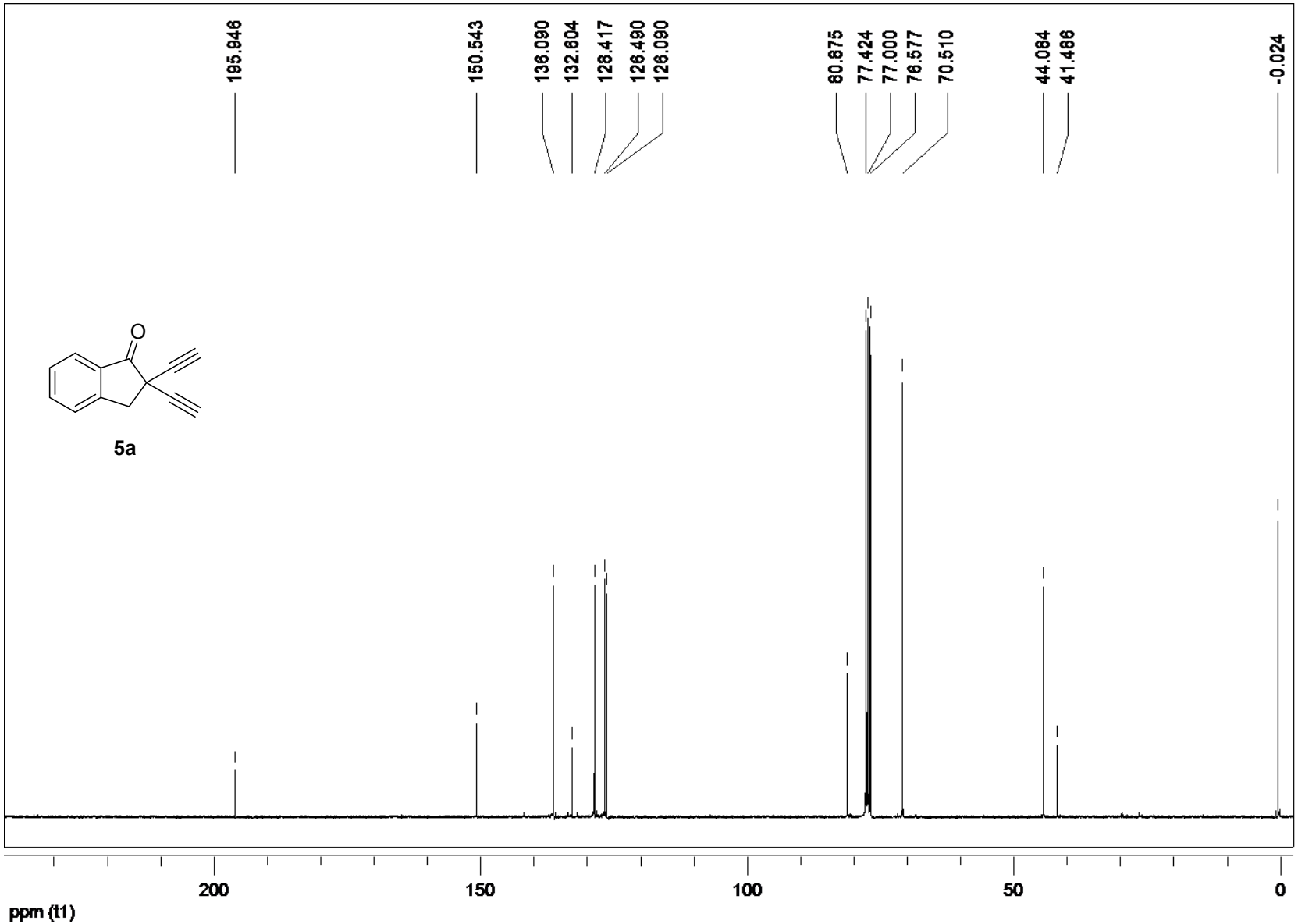
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of (1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)methanol (7a)



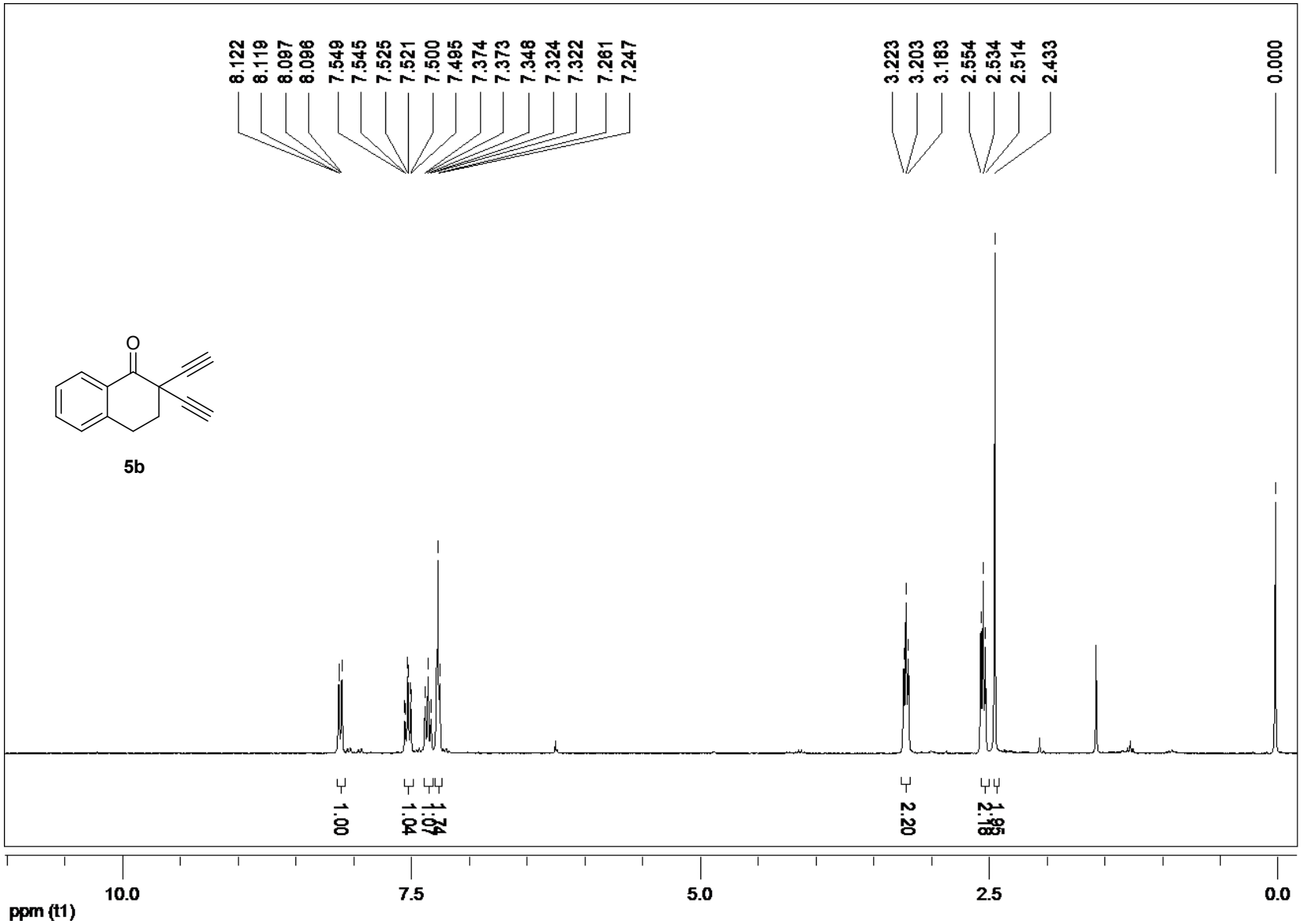
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of (1-Ethynyl-2,3-dihydro-1*H*-inden-1-yl)methanol (7a)



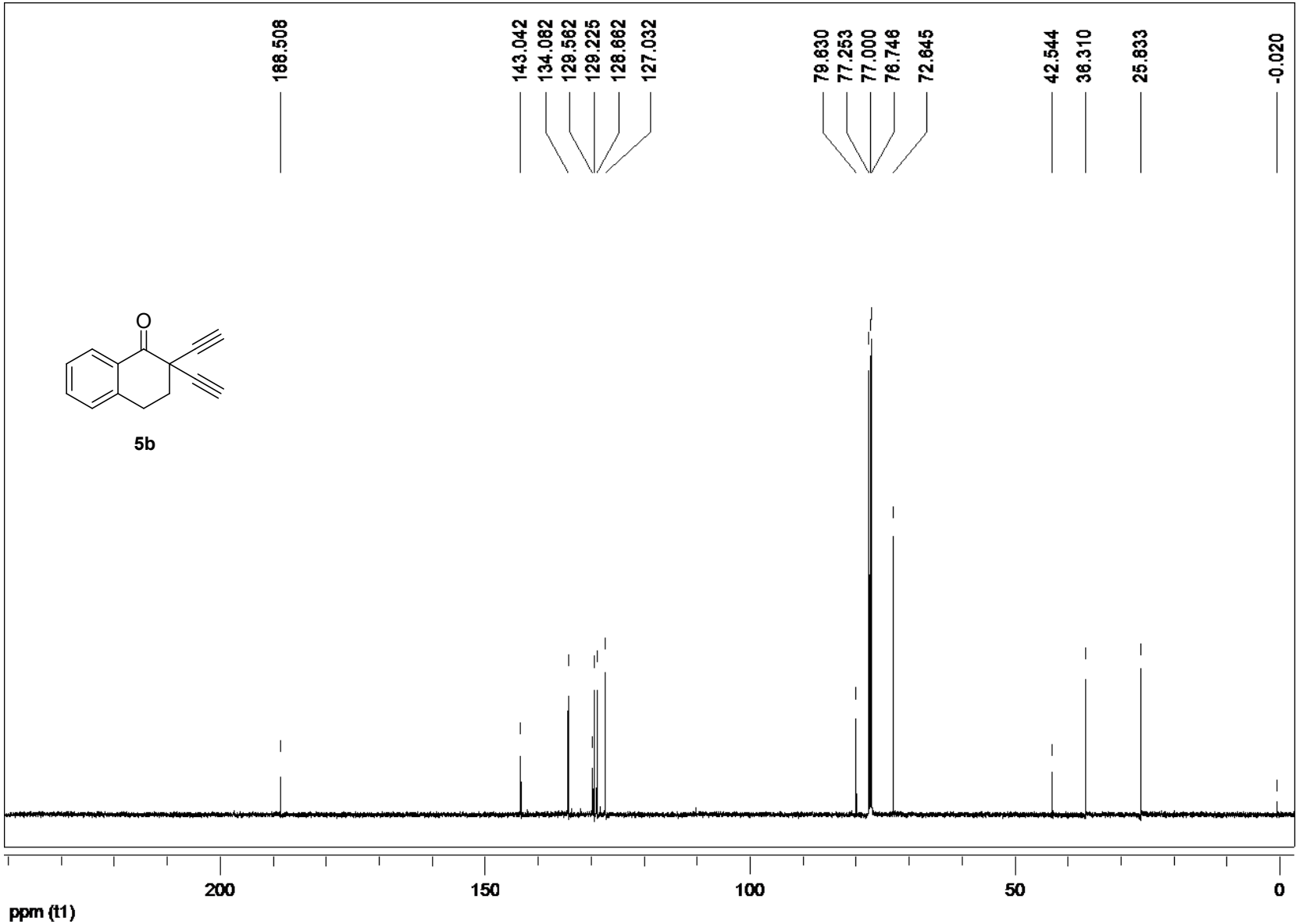
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-2,3-dihydro-1*H*-inden-1-one (5a)



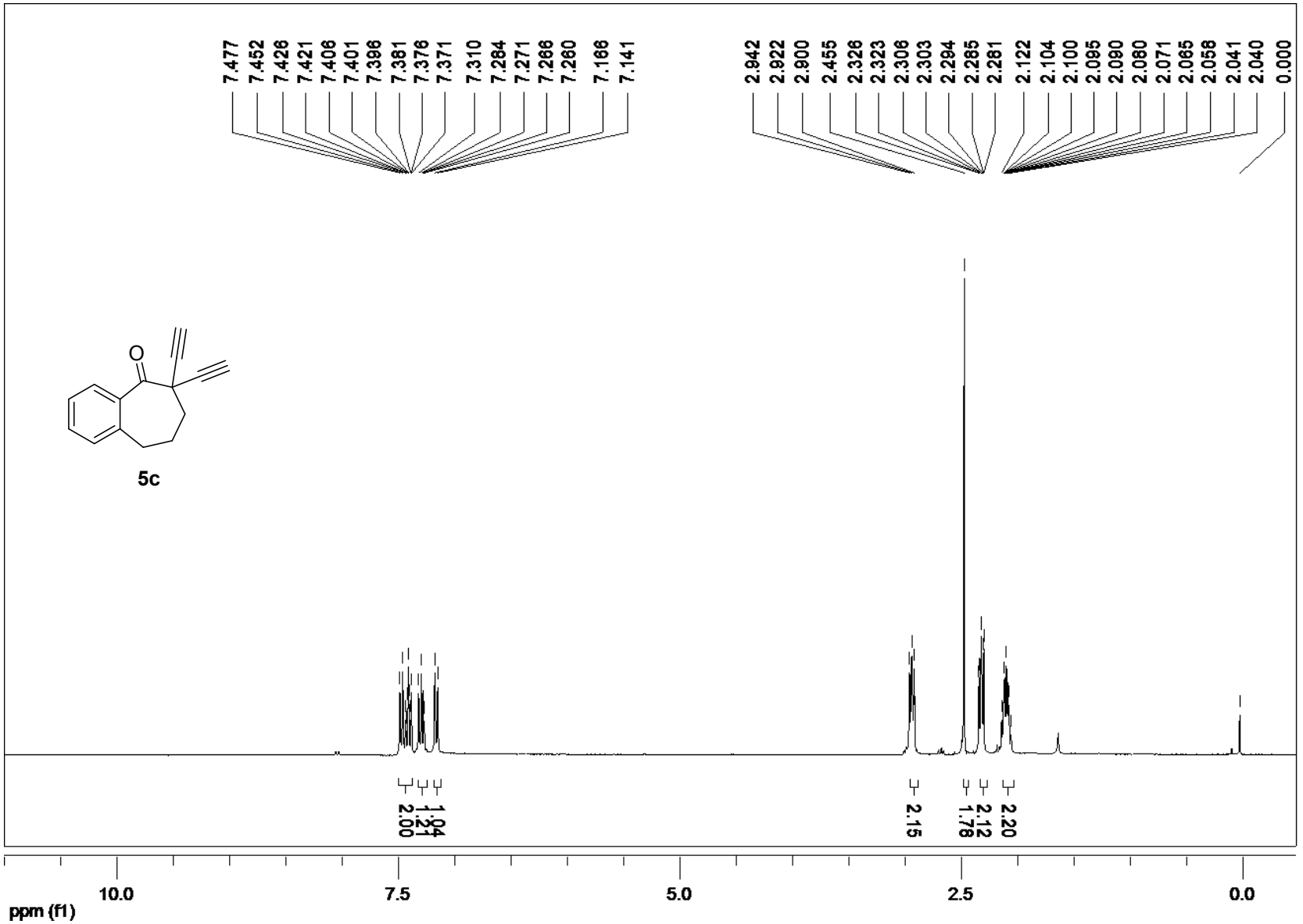
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-2,3-dihydro-1*H*-inden-1-one (5a)



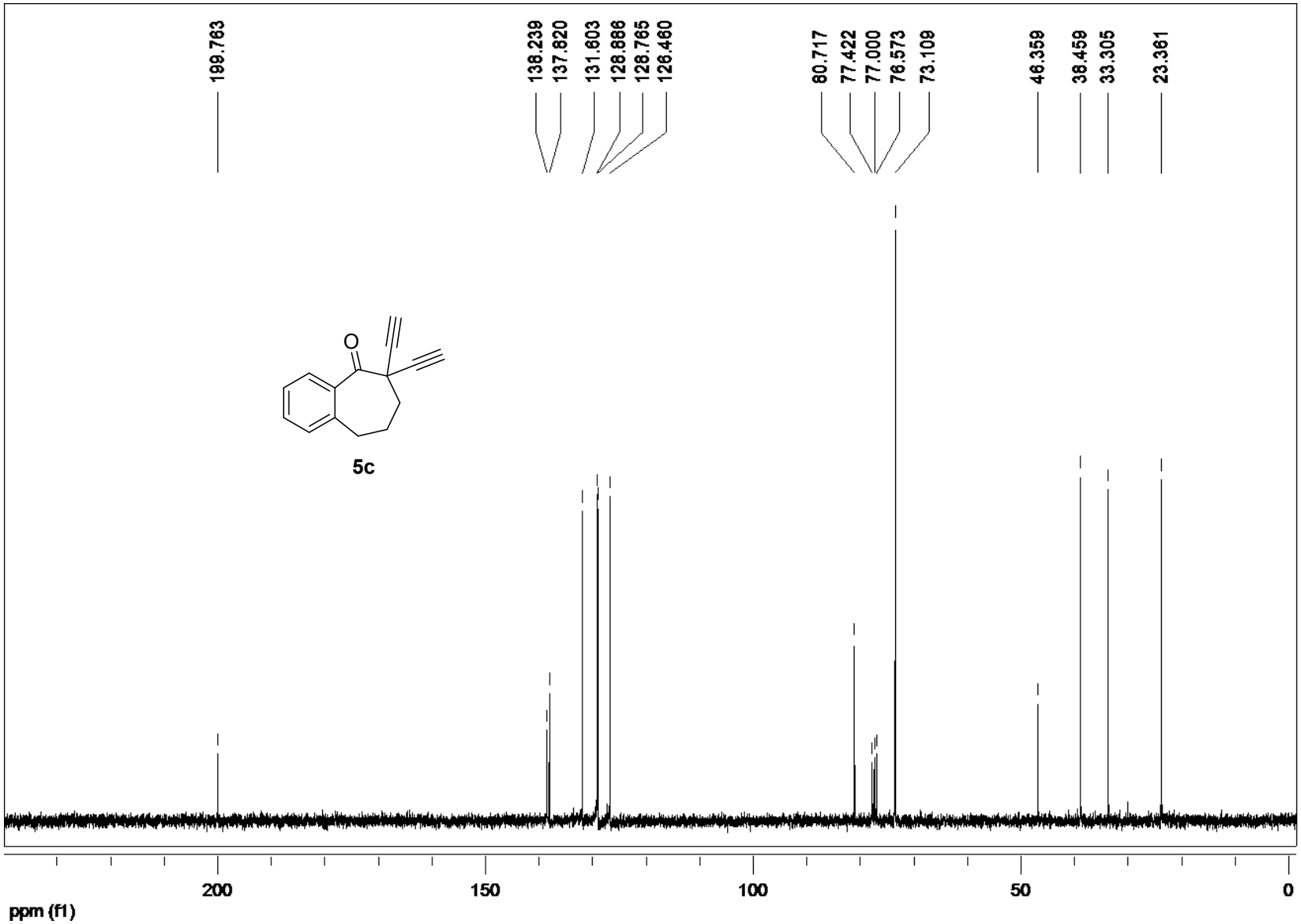
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5b)



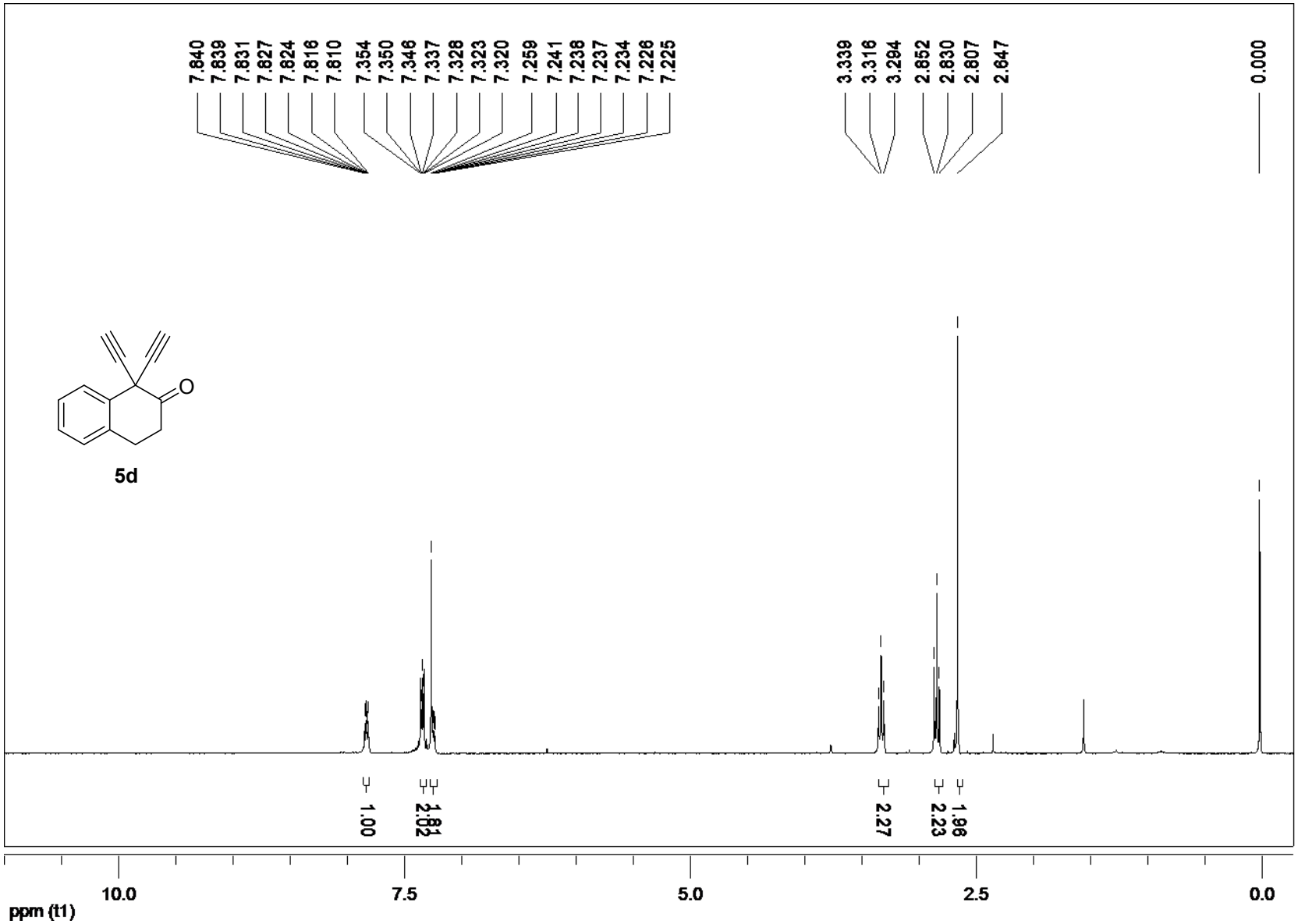
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5b)



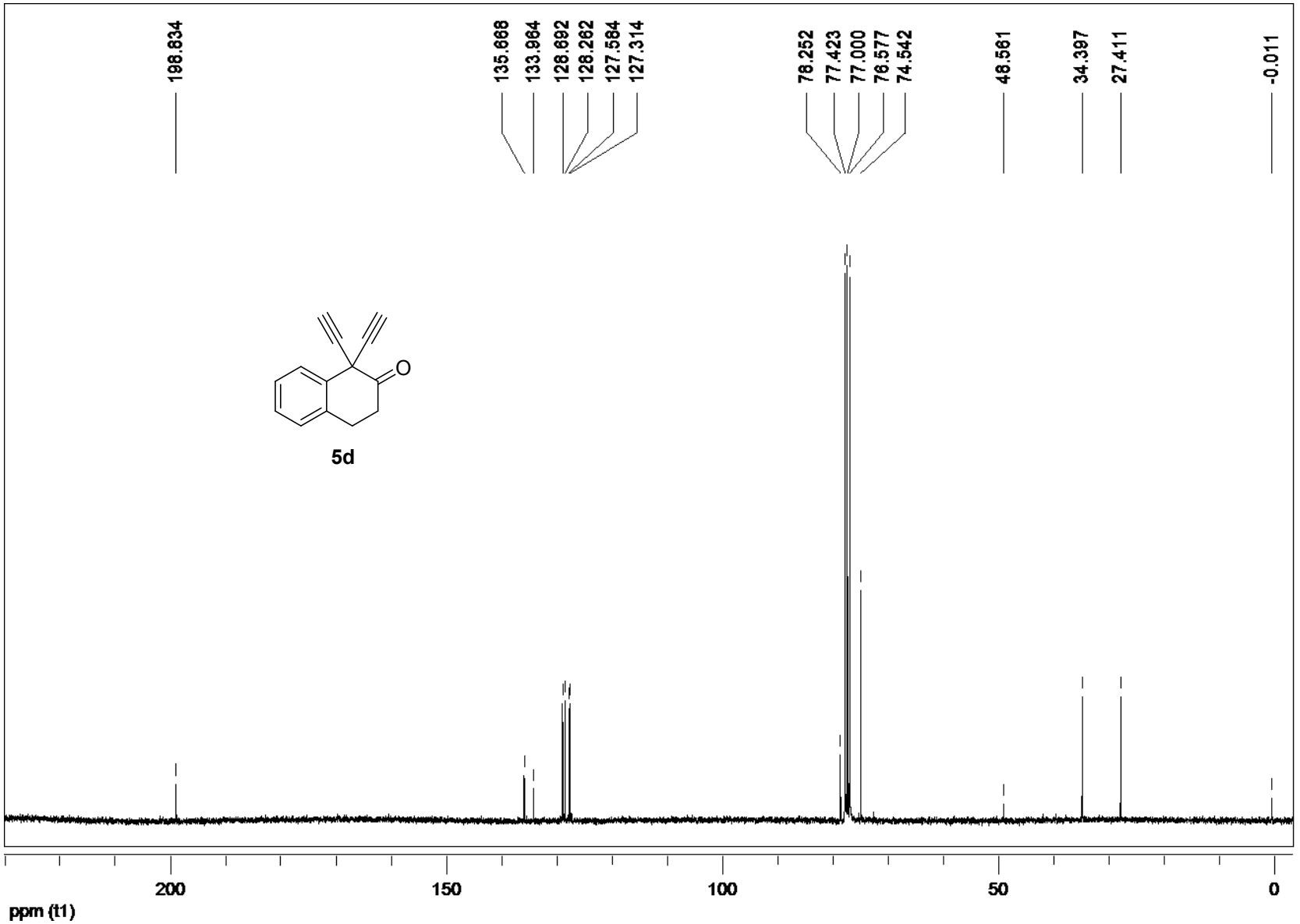
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 6,6-Diethynyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (5c)



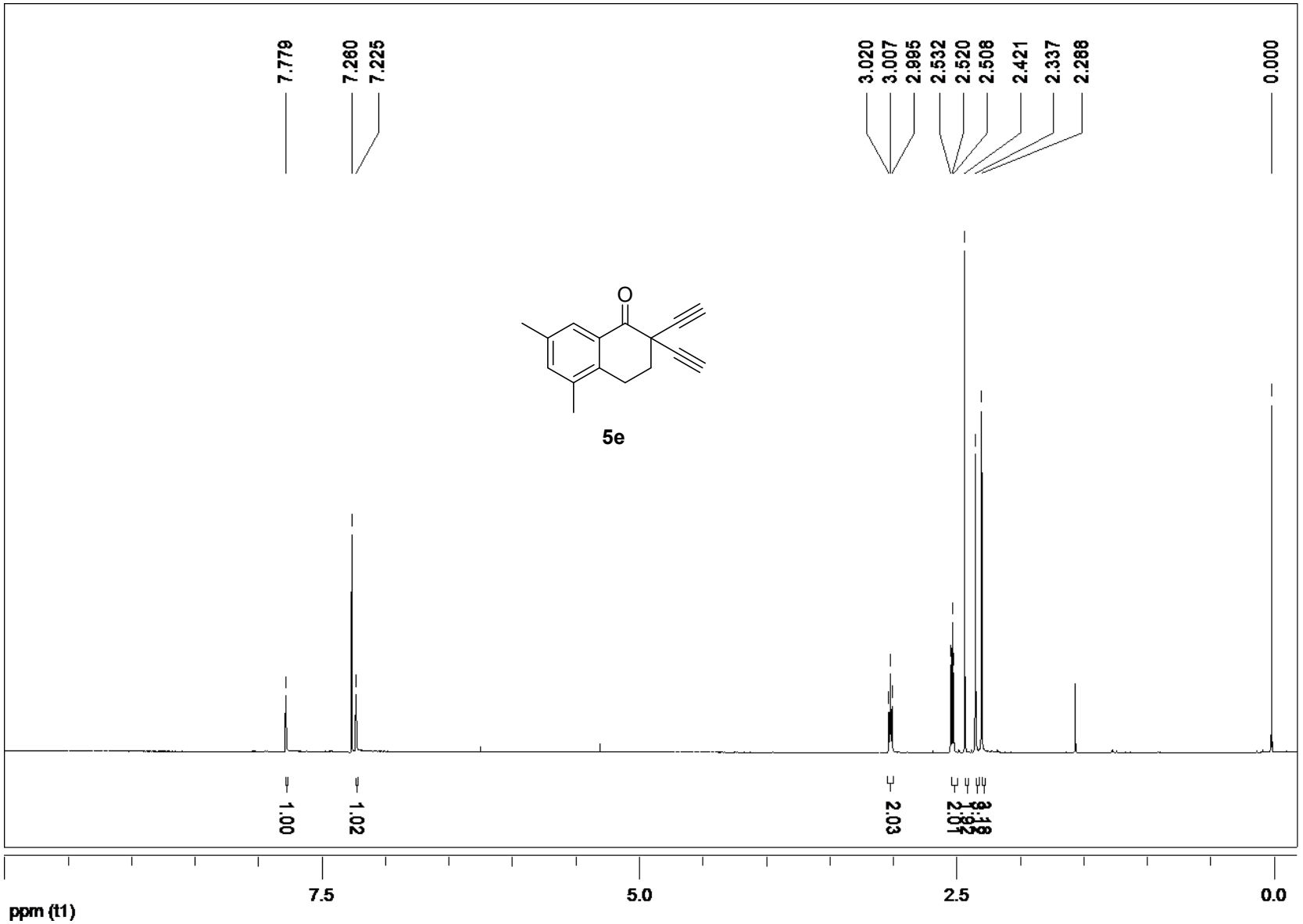
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 6,6-Diethynyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (5c)



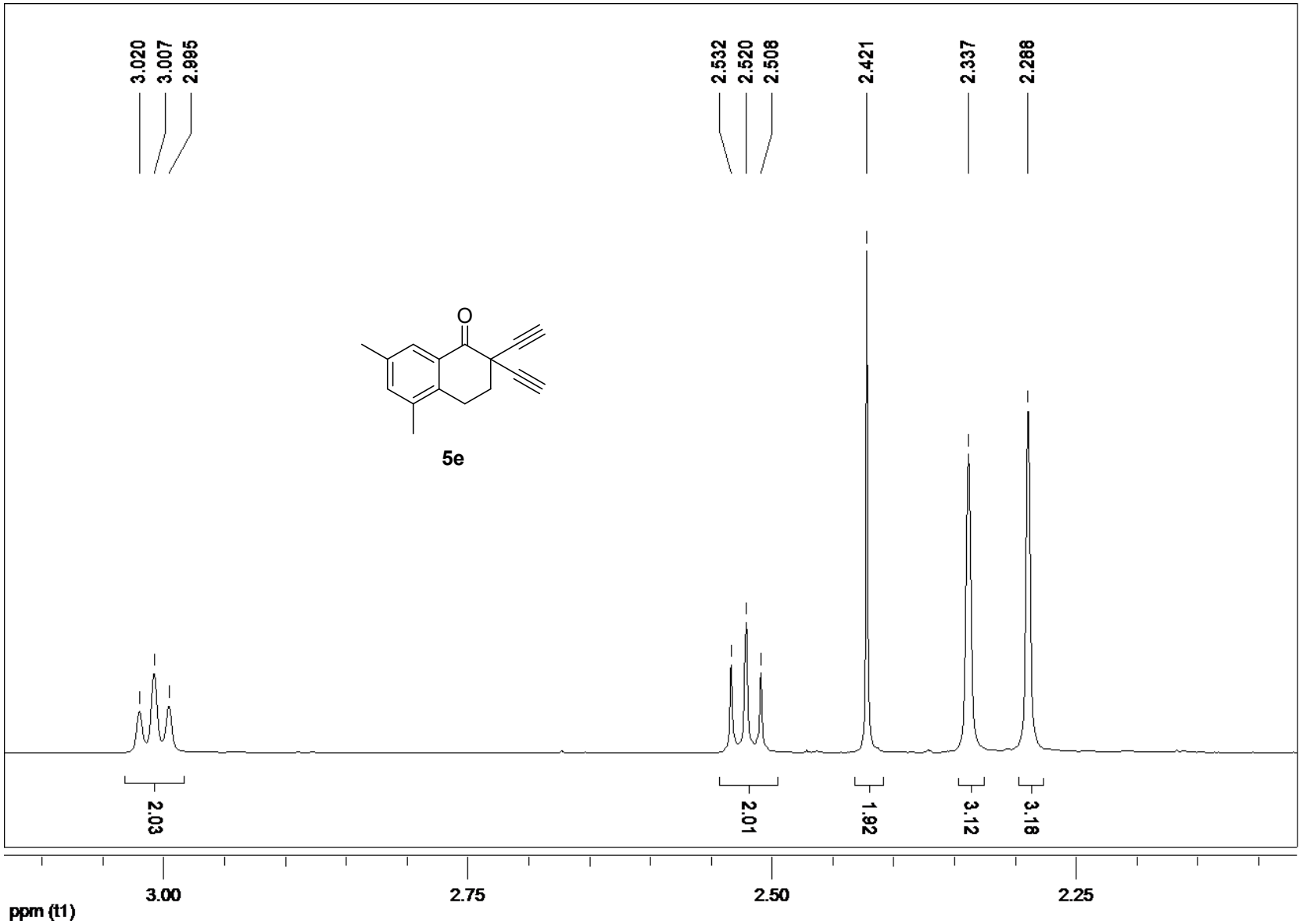
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 1,1-Diethynyl-3,4-dihydronaphthalen-2(1*H*)-one (5d)



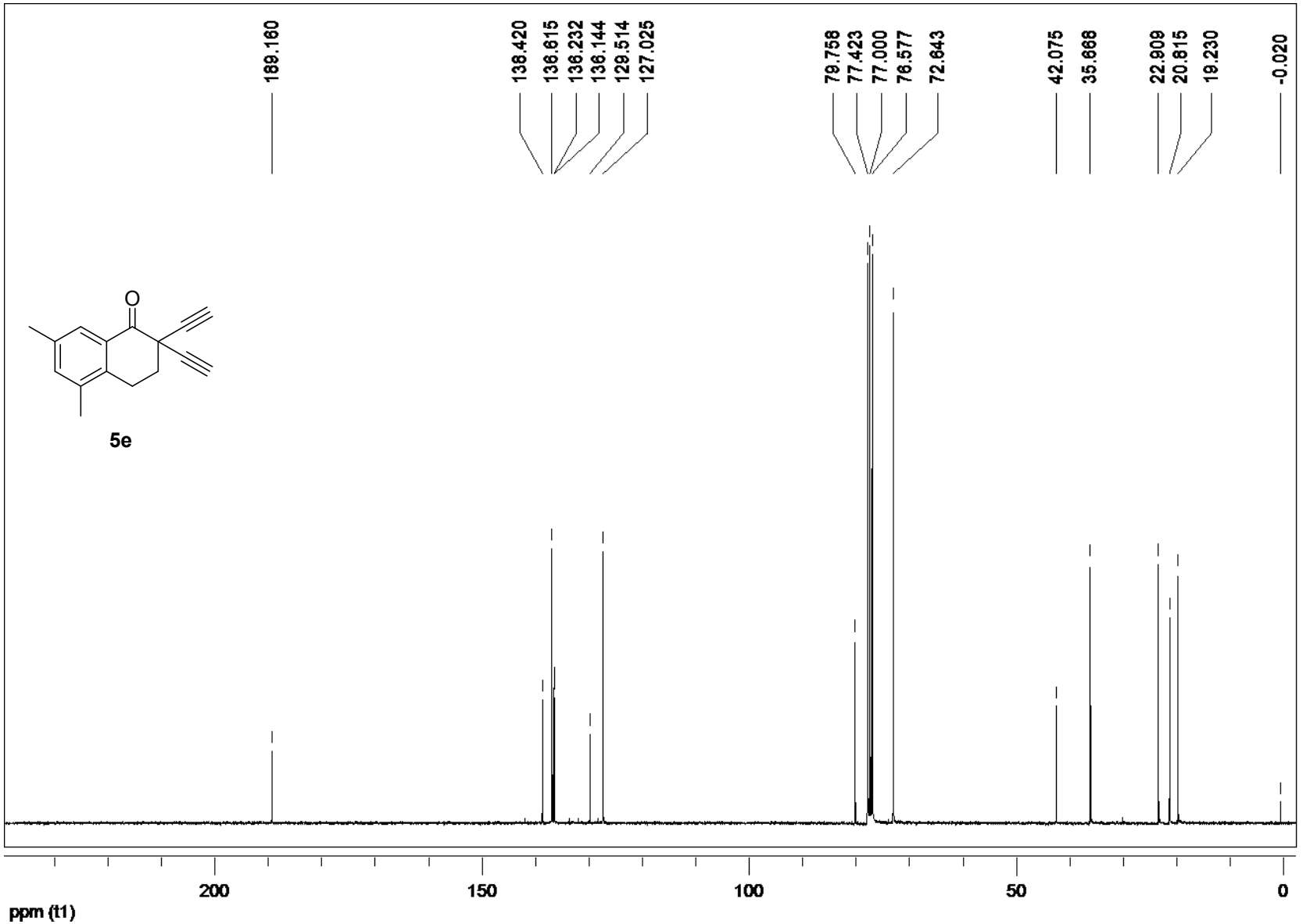
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 1,1-Diethynyl-3,4-dihydronaphthalen-2(1*H*)-one (5d)



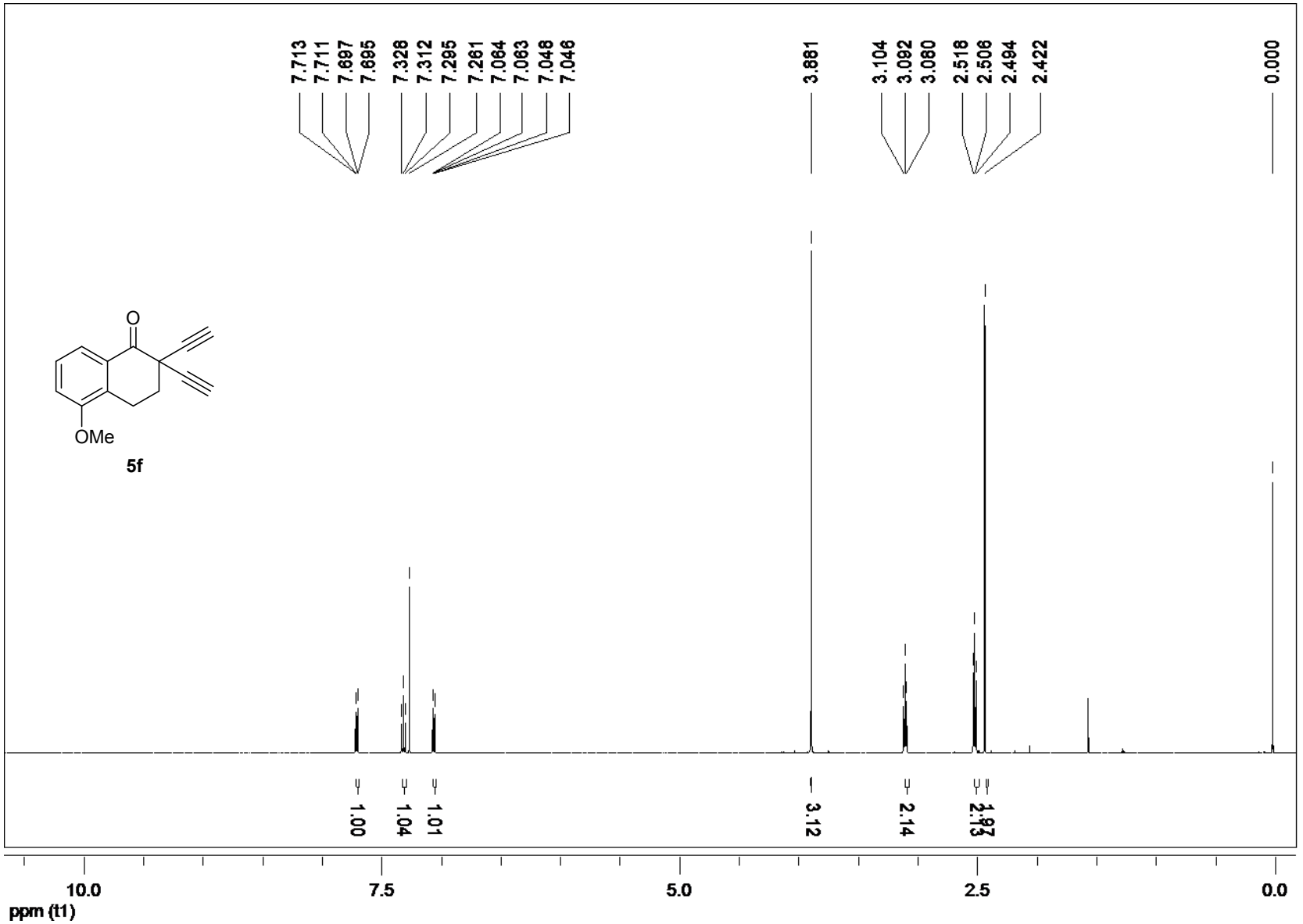
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-5,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (5e)



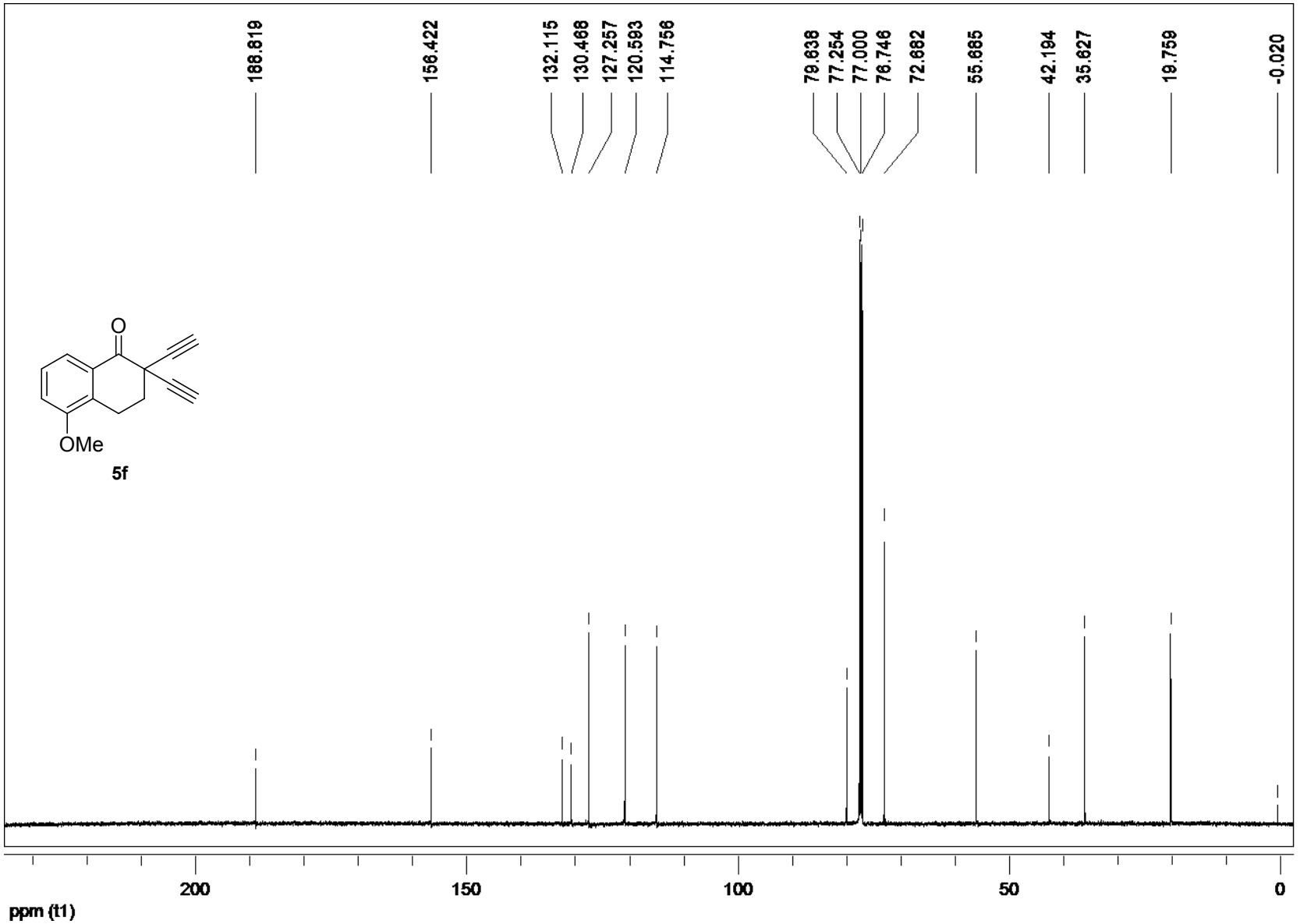
^{1}H NMR (500 MHz, $CDCl_3$) Expansion of spectrum of 2,2-Diethynyl-5,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (5e)



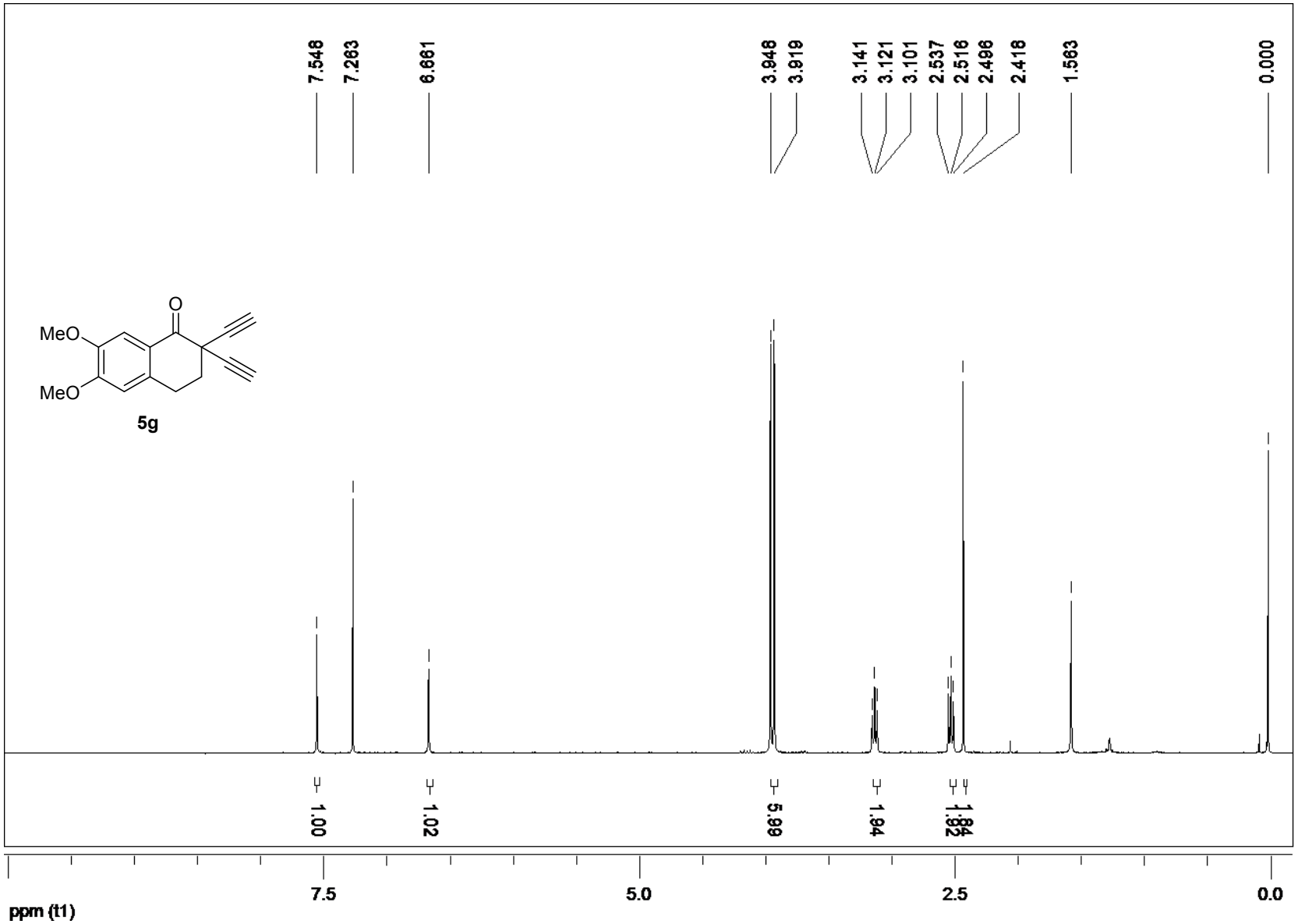
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-5,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (5e)



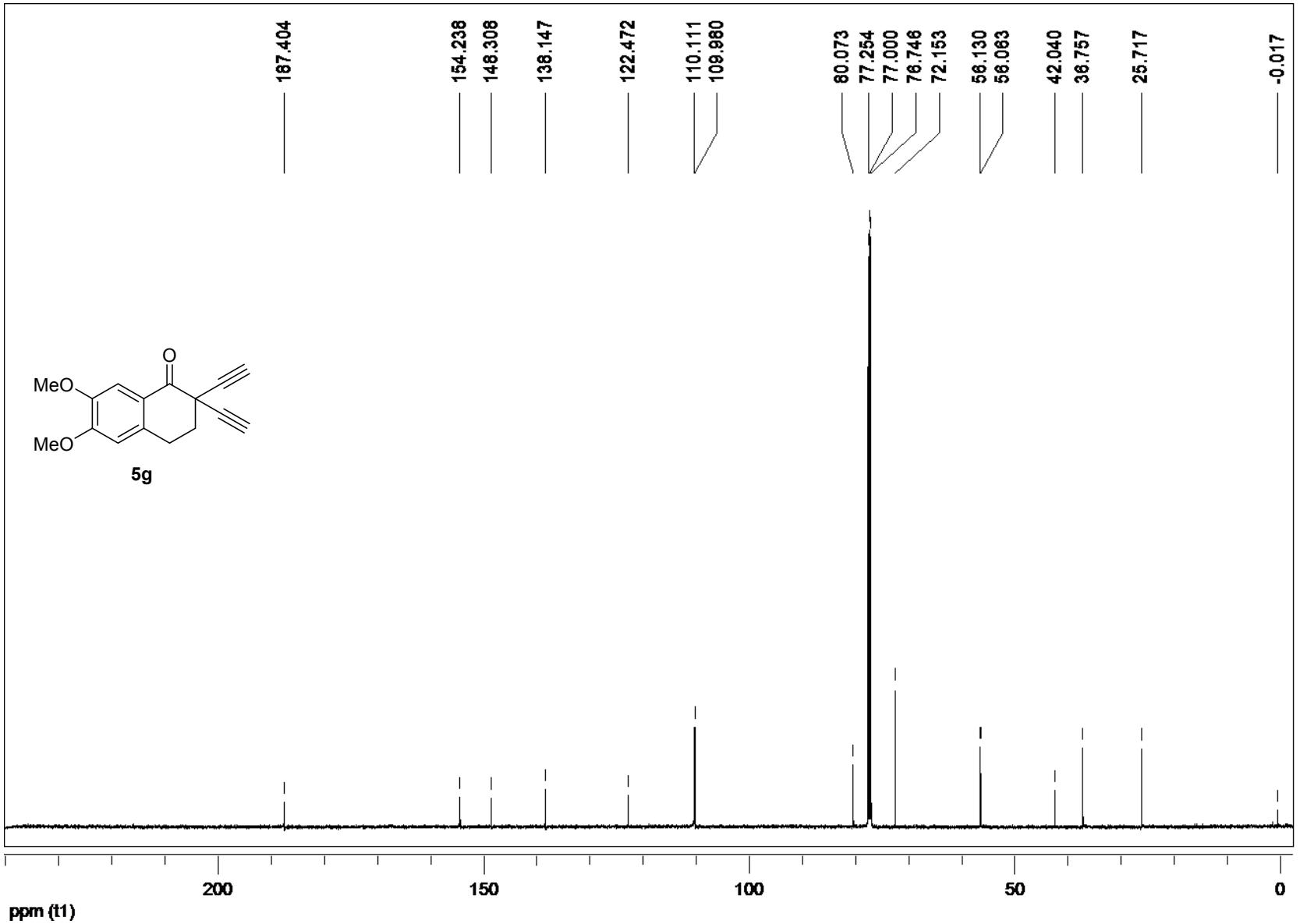
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-5-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (5f)



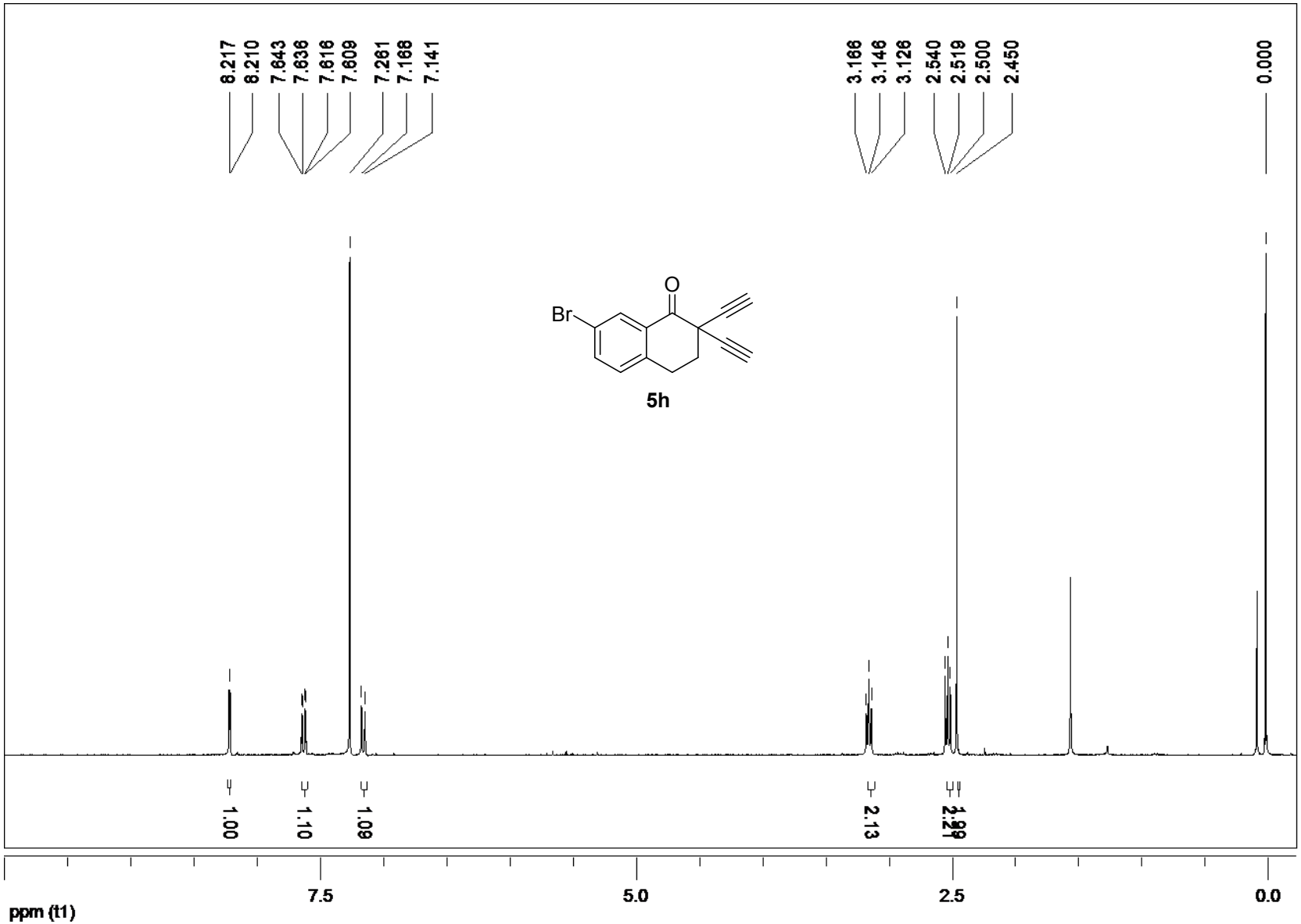
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-5-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (5f)



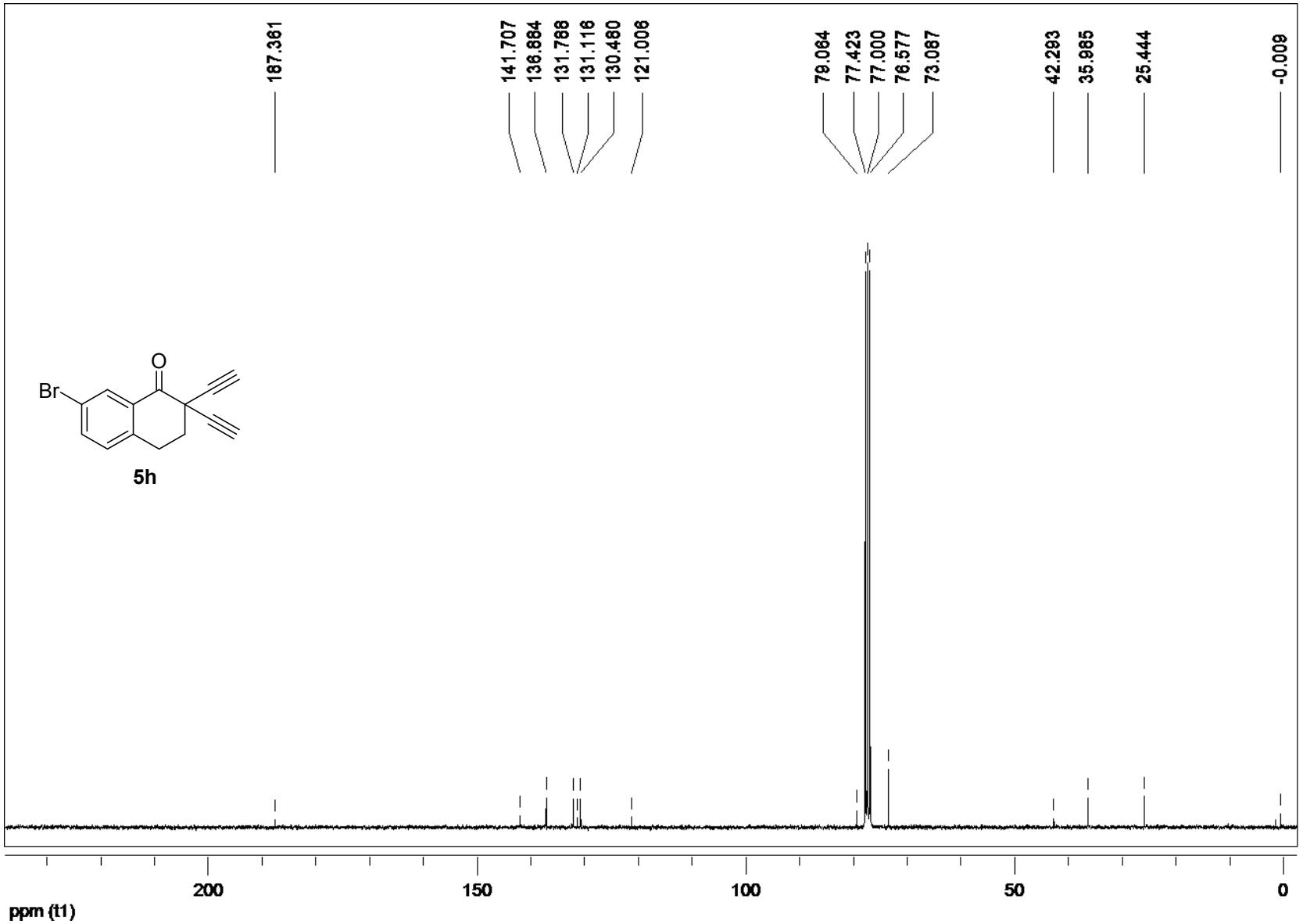
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (5g)



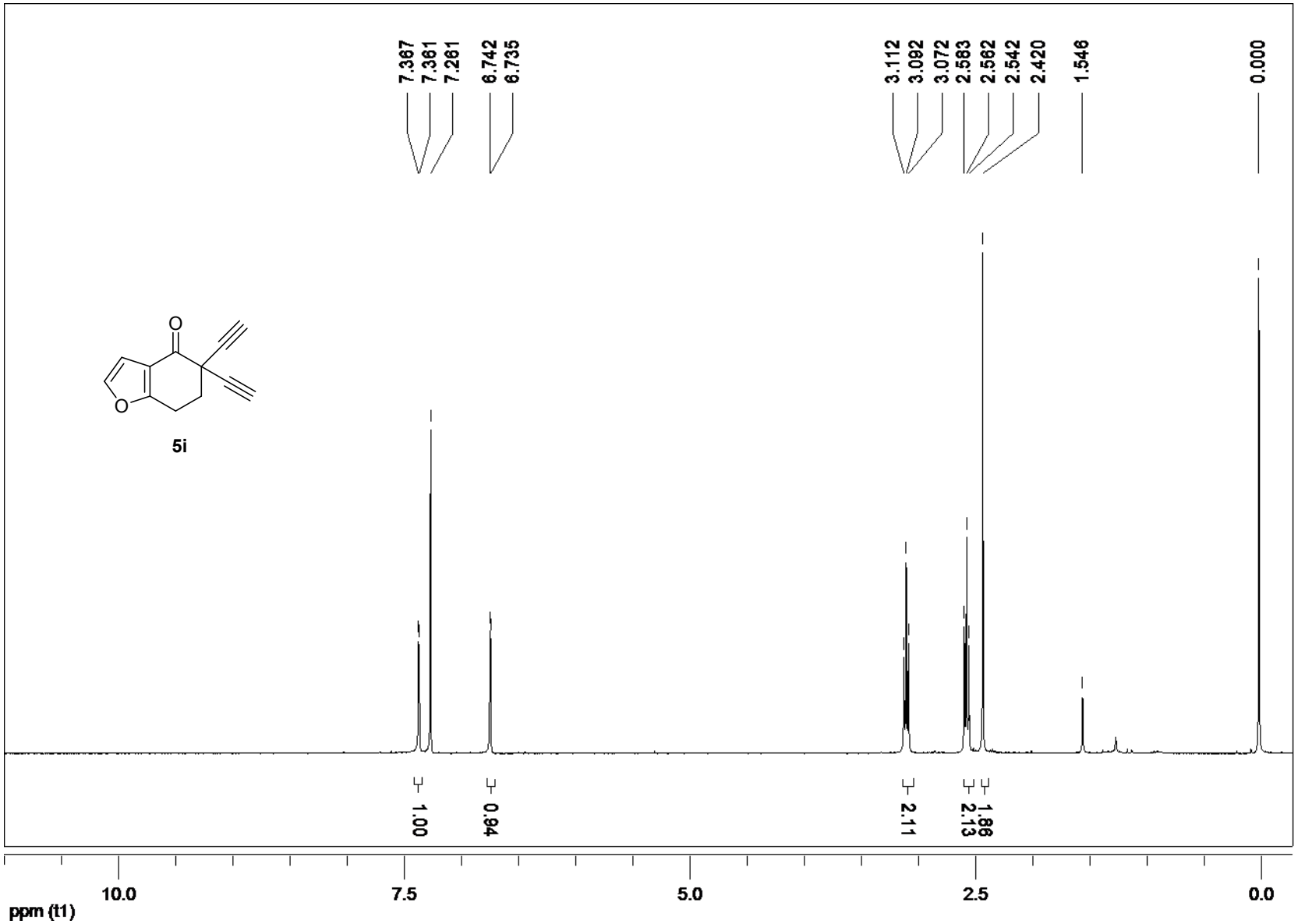
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2,2-Diethynyl-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (5g)



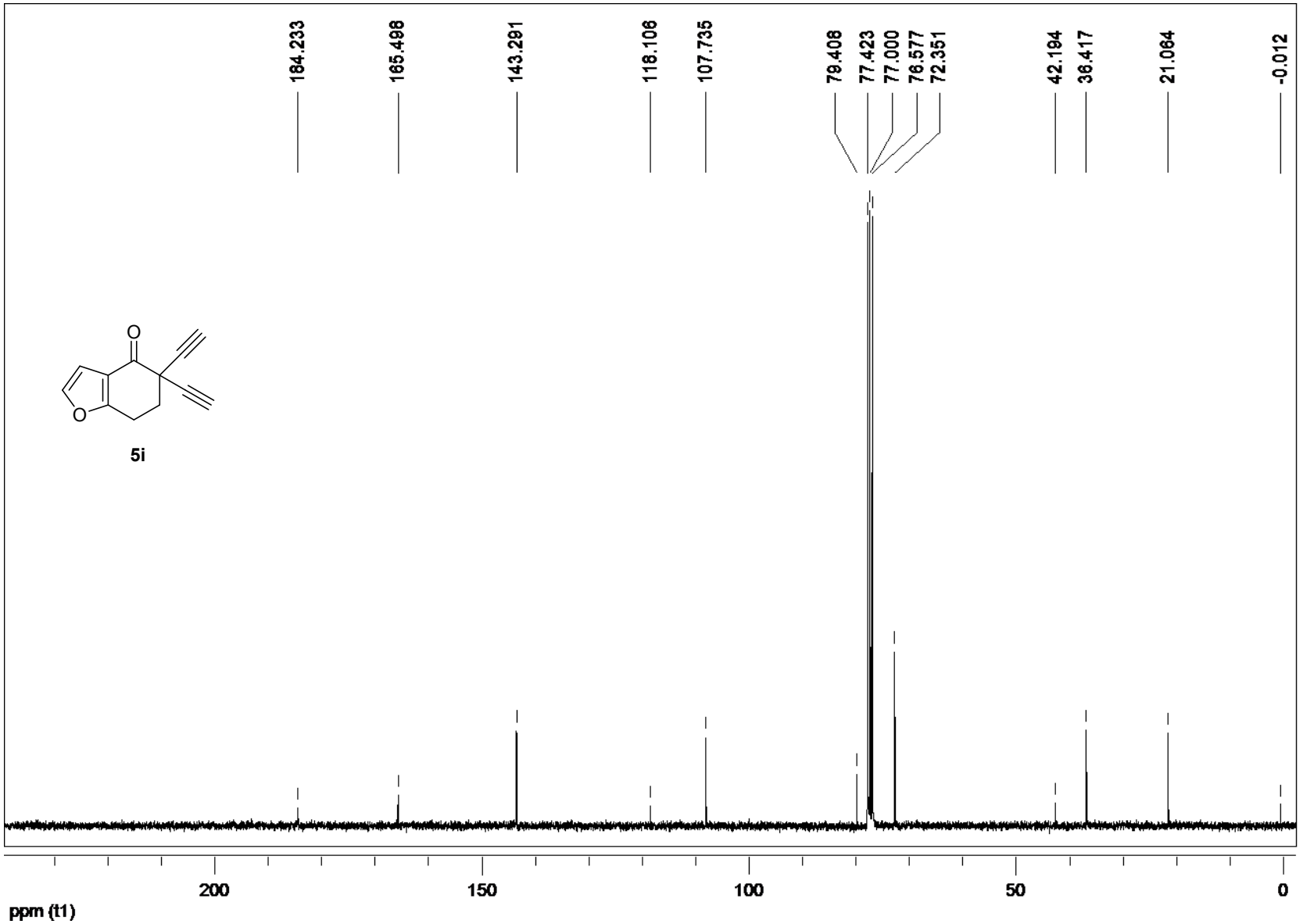
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 7-Bromo-2,2-diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5h)



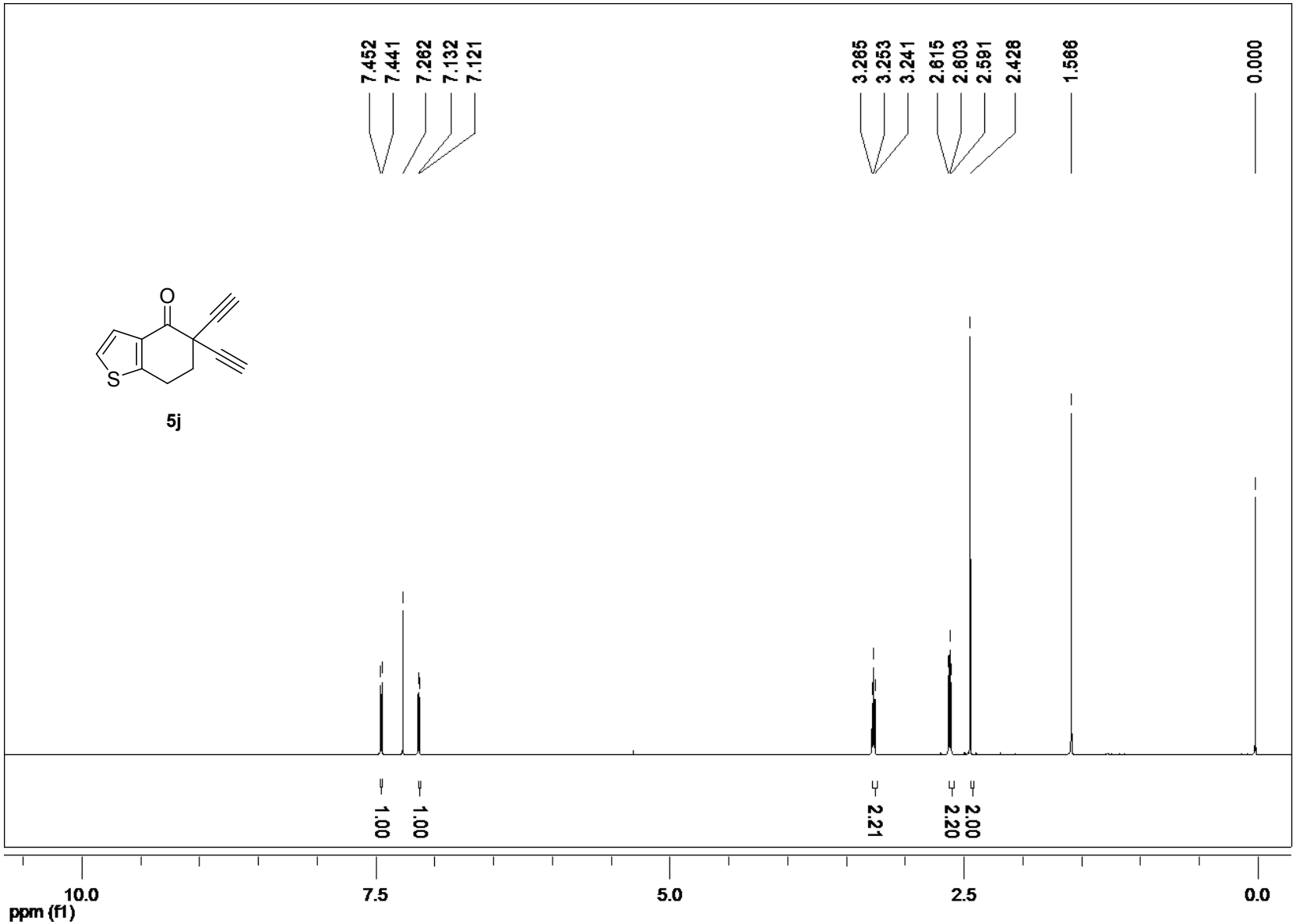
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 7-Bromo-2,2-diethynyl-3,4-dihydronaphthalen-1(2*H*)-one (5h)



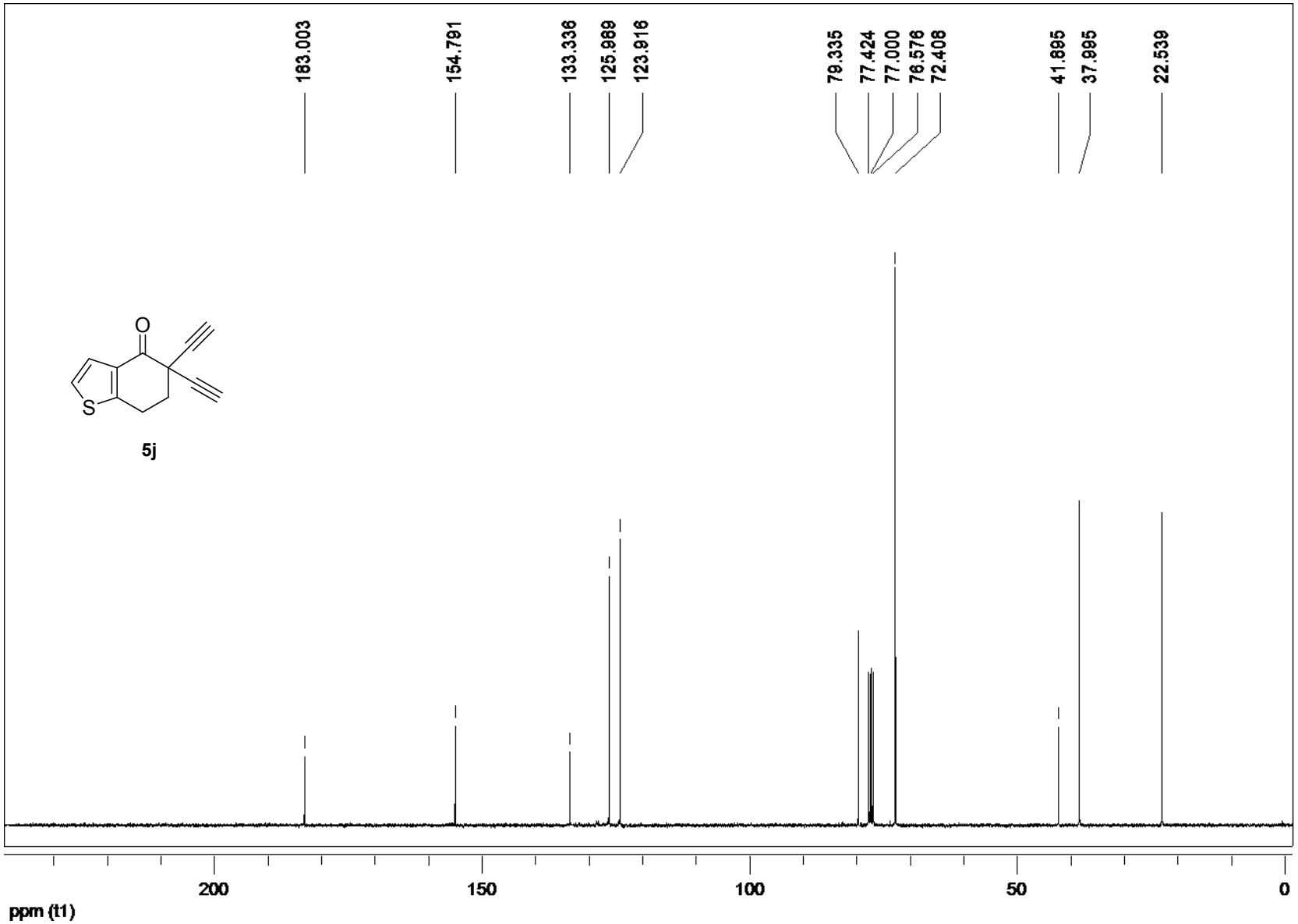
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzofuran-4(5*H*)-one (5i)



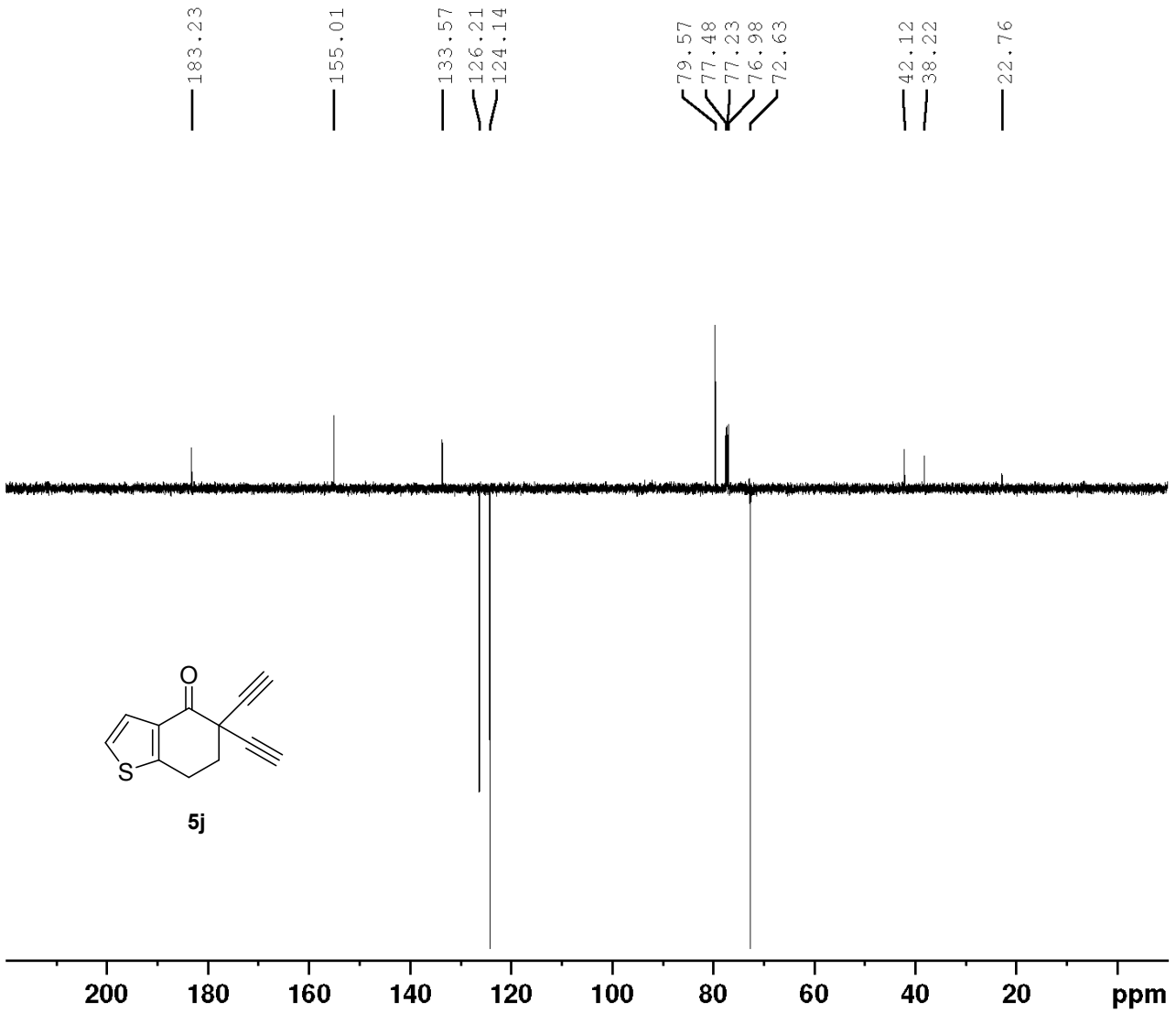
^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzofuran-4(5*H*)-one (5i)



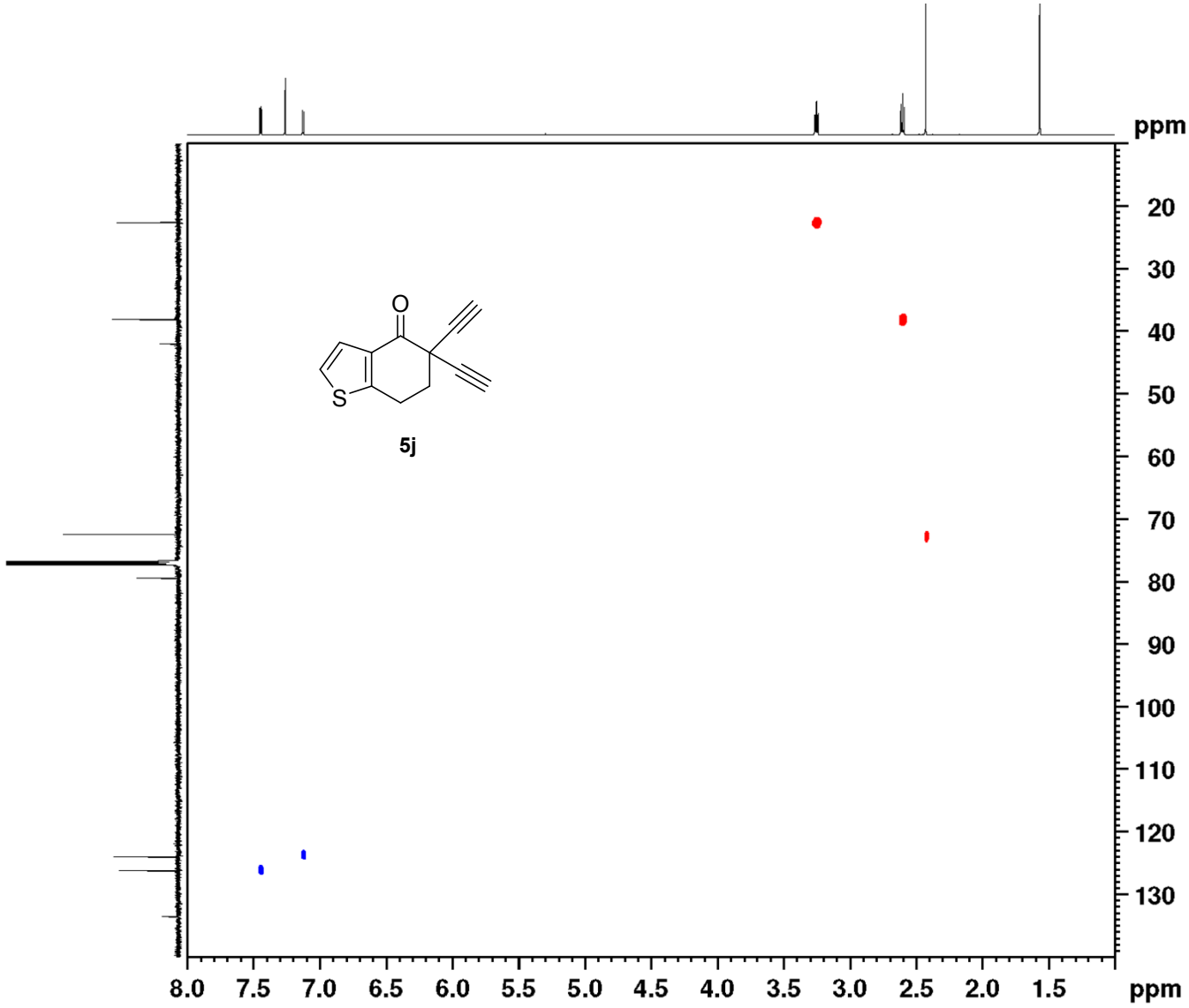
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(5*H*)-one (5j)



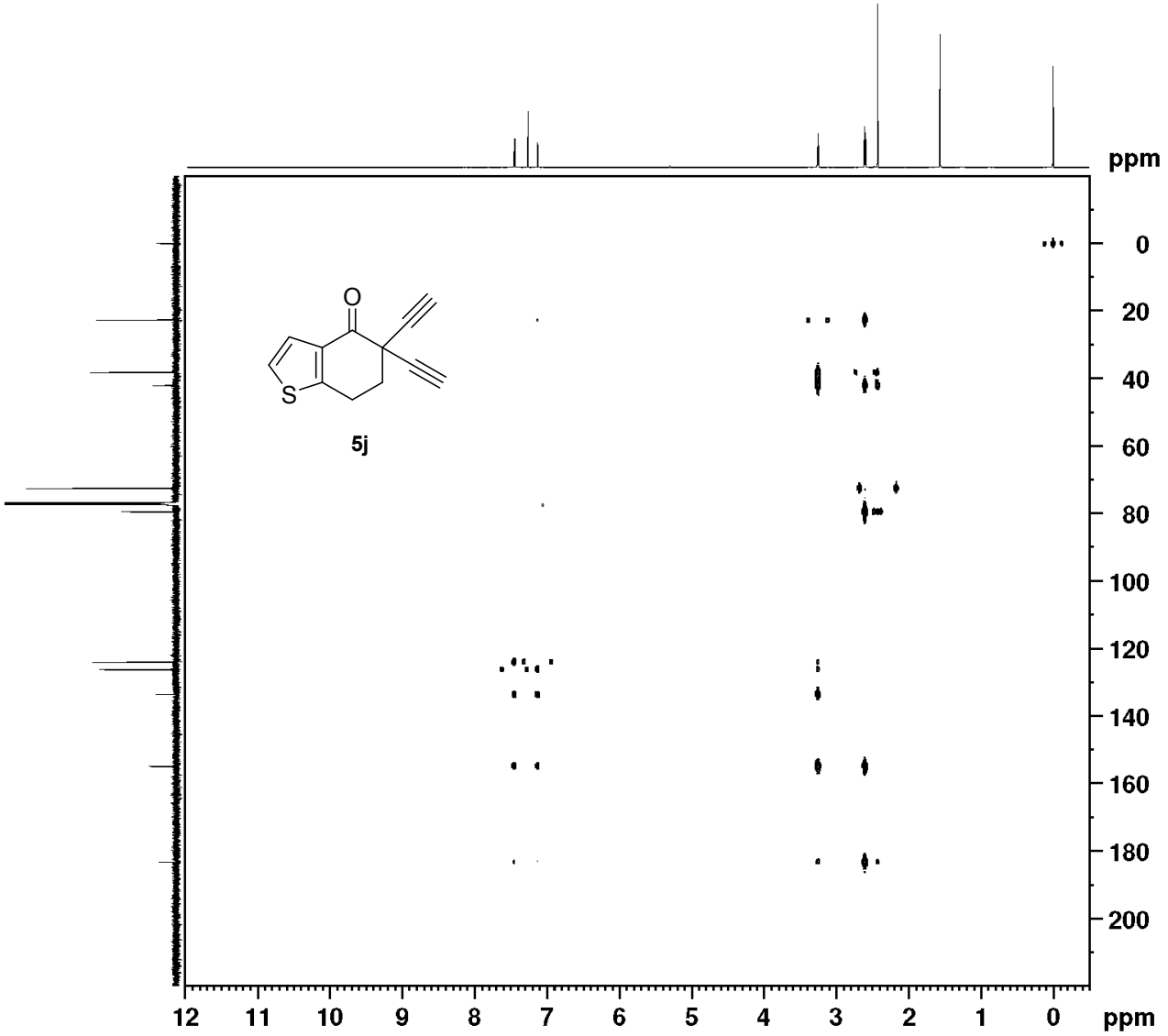
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(5*H*)-one (5j)



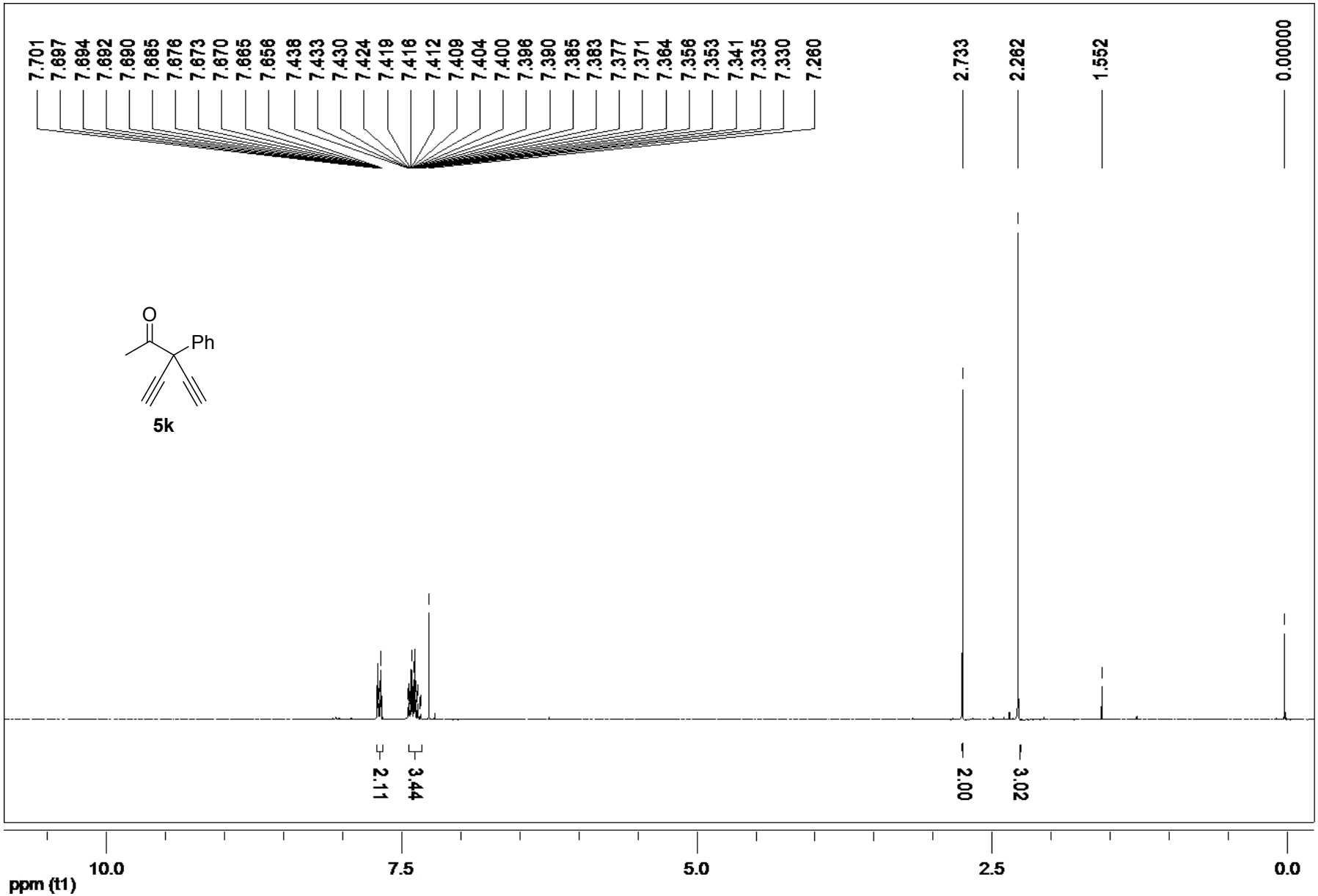
^{13}C-APT - NMR (255 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(*5H*)-one (5j)



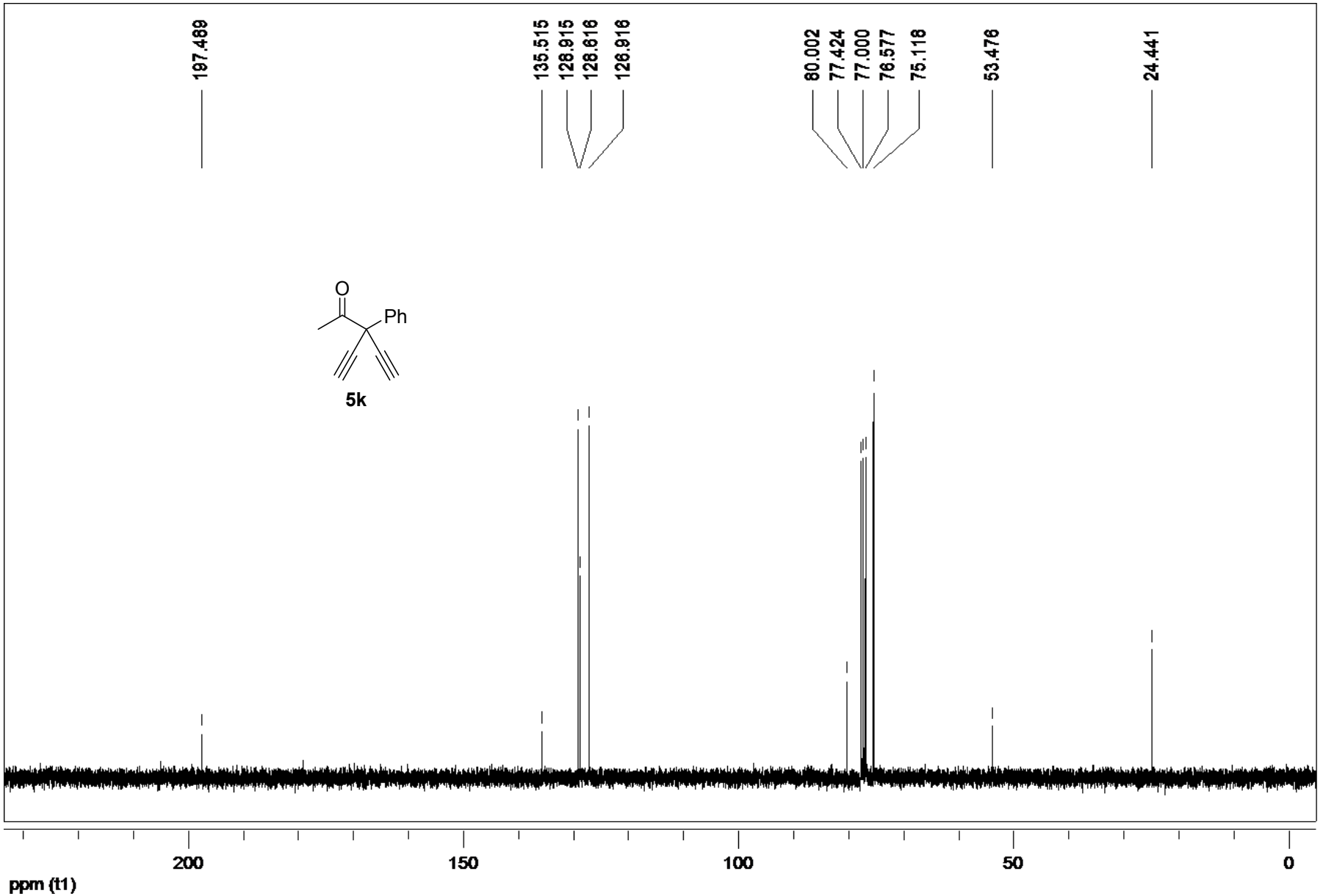
HSQC - NMR (500 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(5*H*)-one (5j)



HMBC - NMR (500 MHz, $CDCl_3$) Spectrum of 5,5-Diethynyl-6,7-dihydrobenzo[b]thiophen-4(5*H*)-one (5j)



^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3-ethynyl-3-phenylpent-4-yn-2-one (5k)



^{13}C NMR (75 MHz, $CDCl_3$) Spectrum of 3-ethynyl-3-phenylpent-4-yn-2-one (5k)