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SUPPORTING INFORMATION

Allylation and Propargylation of Aldehydes mediated by *in situ* generated Zinc from the redox couple of Al and $ZnCl_2$ in 2N HCl

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1. General Comments:

The chemicals used were either commercial products (Aldrich, Lancaster, Fluka, Merck, SRL, Spectrochem) which were distilled or recrystallized whenever required, or were prepared according to literature procedures. All preparations and manipulations have been performed under an inert atmosphere of argon using standard vacuum lines and Schlenk techniques. All solvents used for the synthesis have been dried and distilled by standard methods and previously deoxygenated in the vacuum line. Pre-coated silica gel $60F_{254}$ (Merck) was used for thin layer chromatography and silica gel 60-120 and 100-200 mesh (SRL) was used for column chromatography.

^{1}H (200 MHz) and ^{13}C NMR (54.6 MHz) spectra were recorded on Brucker-AC 200 MHz spectrometer and ^{1}H (200&400 MHz) and ^{13}C NMR (50.4&100.6 MHz) spectra were recorded on Brucker-Avance II 400 MHz spectrometer at 300 K. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (for $CDCl_3$ in ^{1}H NMR spectra H = 7.26 ppm and in ^{13}C NMR spectra C = 77.0 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet). Coupling constants (*J*) are reported in Hz. ESI-MS spectra were taken using Waters LCT mass spectrometer. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

Chromatographic purification was done with either 60-120 or 100-200 mesh silica gel (SRL). For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (Merck) were used. Petroleum ether refers to the fraction boiling in the range 60-80^{0}C. Other solvents were dried and distilled prior to use.

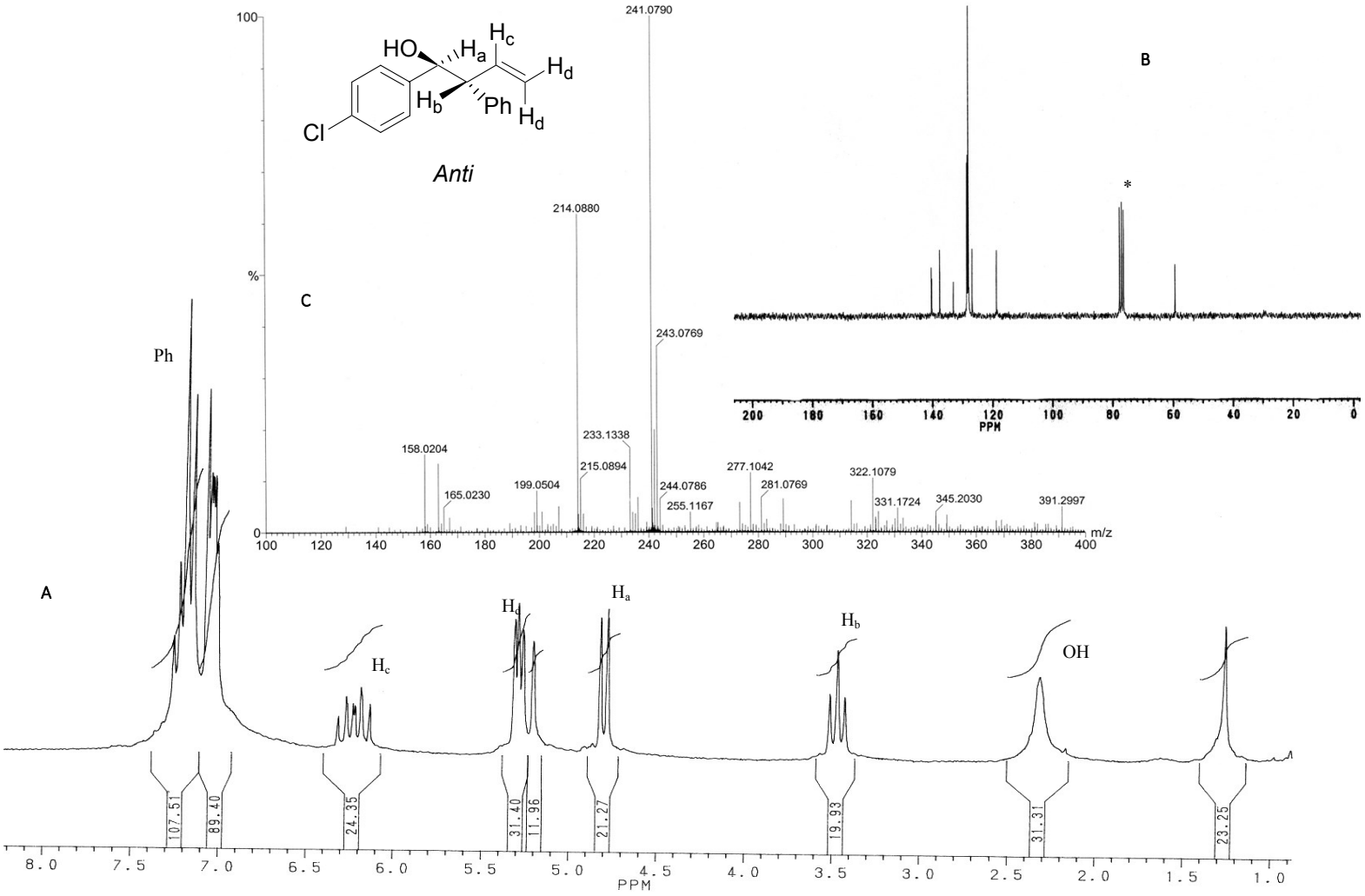
2. Synthesis of Starting Materials:

2.1. Preparation of Rieke Zinc: Two 10-mL Schlenk vessels, **A** and **B**, were dried by heating with a Bunsen burner under reduced pressure and cooled down to room temperature

under a stream of Ar. Schlenk vessel **A**, filled with Ar, was weighed and then reassembled to the Schlenk line. Under a stream of Ar, $ZnCl_2$ (273 mg, 2 mmol) was charged to the vessel. After three Ar/vacuum cycles, $ZnCl_2$ was wetted with a small amount of $SOCl_2$. The Schlenk vessel was heated by a Bunsen burner until the $ZnCl_2$ salt melted and a white fume was released, and the Schlenk flask was then cooled down under an Ar flow. Schlenk flask **A** was weighed again (to determine the exact amount of $ZnCl_2$) and a stirring bar was added. Dried $ZnCl_2$ (270 mg) was dissolved in freshly distilled THF (07 mL). Li pellets (28 mg, 4 mmol), naphthalene (526 mg, 4.1 mmol) and benzothiophene (9 μL, 0.08 mmol) were weighted in air and charged into Schlenk vessel **B** under an Ar stream. Dry THF (07 mL, the same amount as added to dissolve $ZnCl_2$) was added and the solution turned from colorless to dark green within less than 2 min. It was stirred further for 2 h to dissolve the Li pellets. The $ZnCl_2$ solution was transferred dropwise *via* cannula to the lithium naphthalenide solution over 10–15 min. The resulting black suspension was stirred for 1 more h to consume the remaining Li. The highly reactive zinc powder was allowed to settle down for a couple of hours. The supernatant was siphoned off *via* cannula leaving the Zn* powder. The thus prepared Rieke zinc was ready to use. The activated zinc was opened in air; residual THF was evaporated and used for stoichiometric comparative reactivity study under chemical redox reaction conditions.

6. Spectra of Products: ^{1}H & ^{13}C NMR spectra for all compounds**.**

^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of compound 1-(4-Chloro-phenyl)-2-phenyl-but-3-en-1-ol (3A)



^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of compound 4-Methyl-1-phenyl-hexa-1,5-dien-3-ol (3B).

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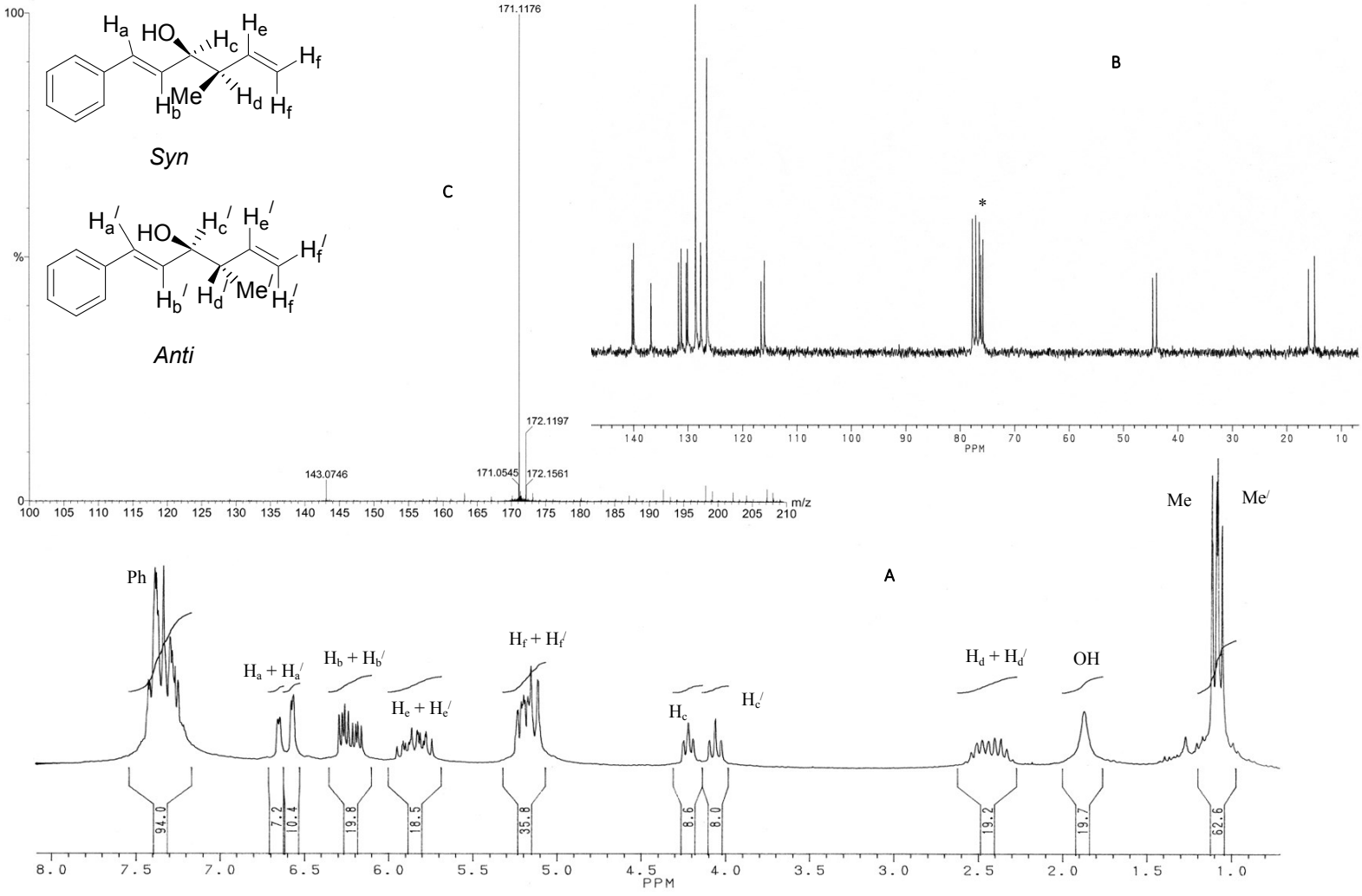
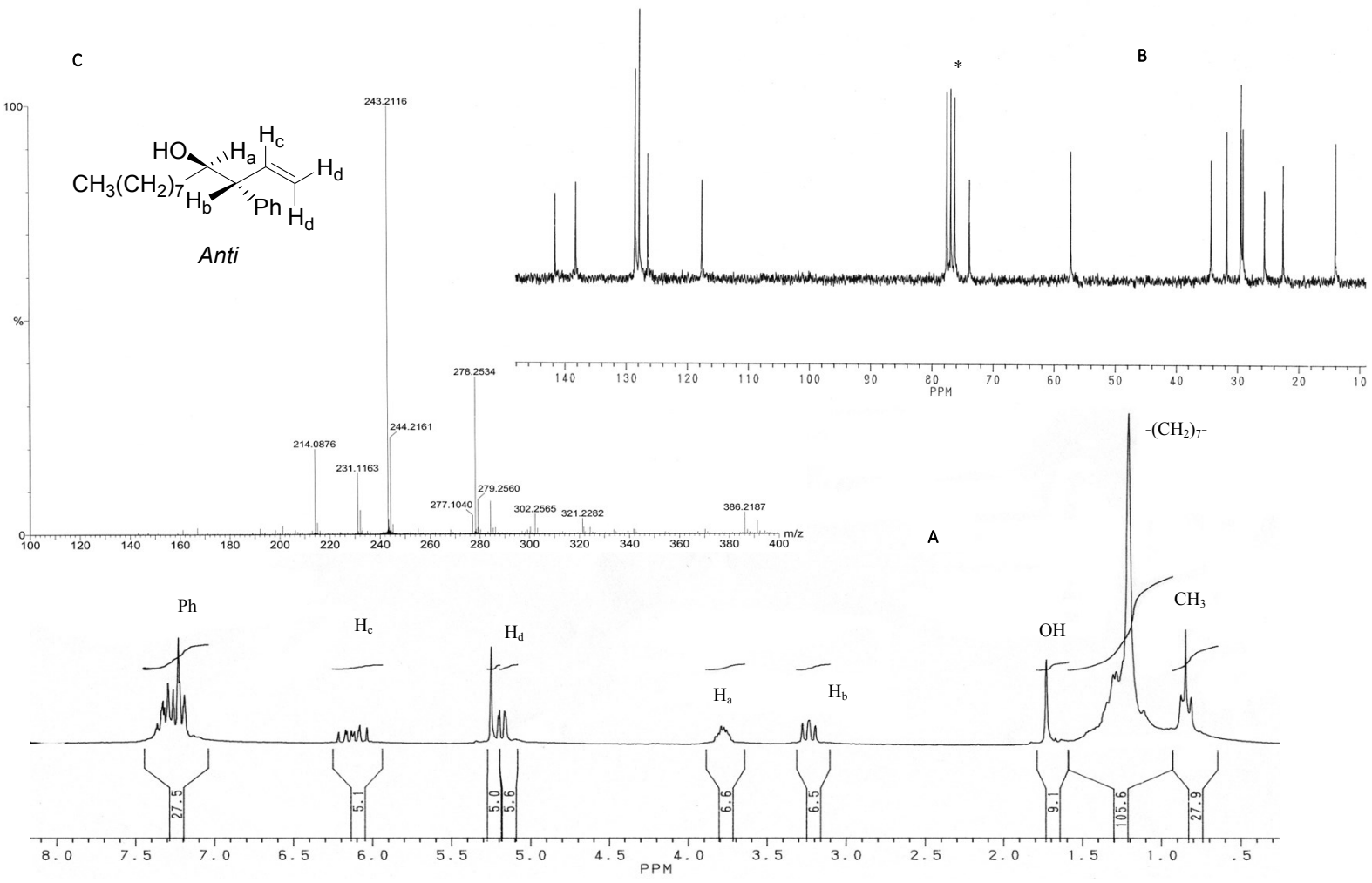
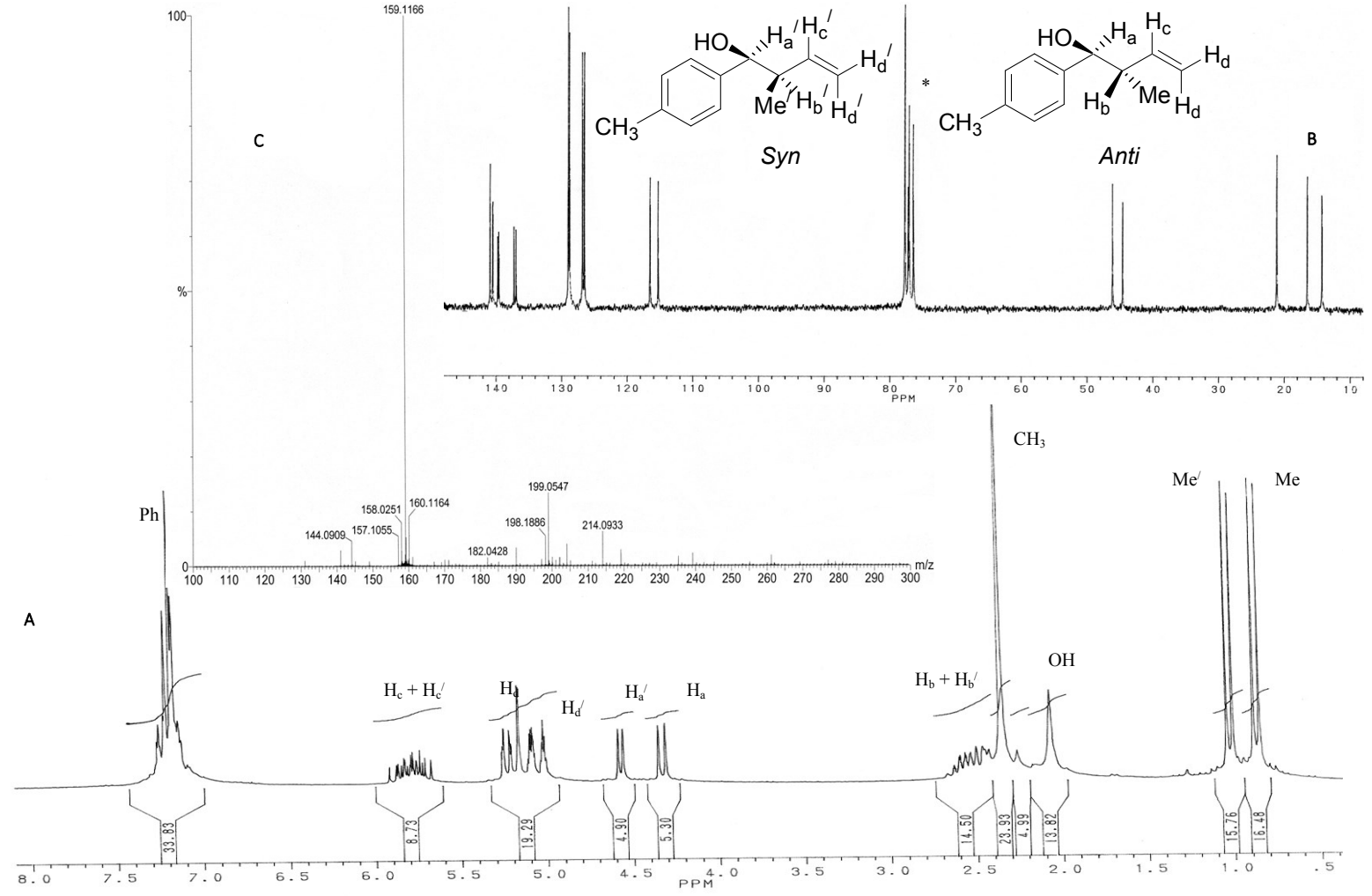


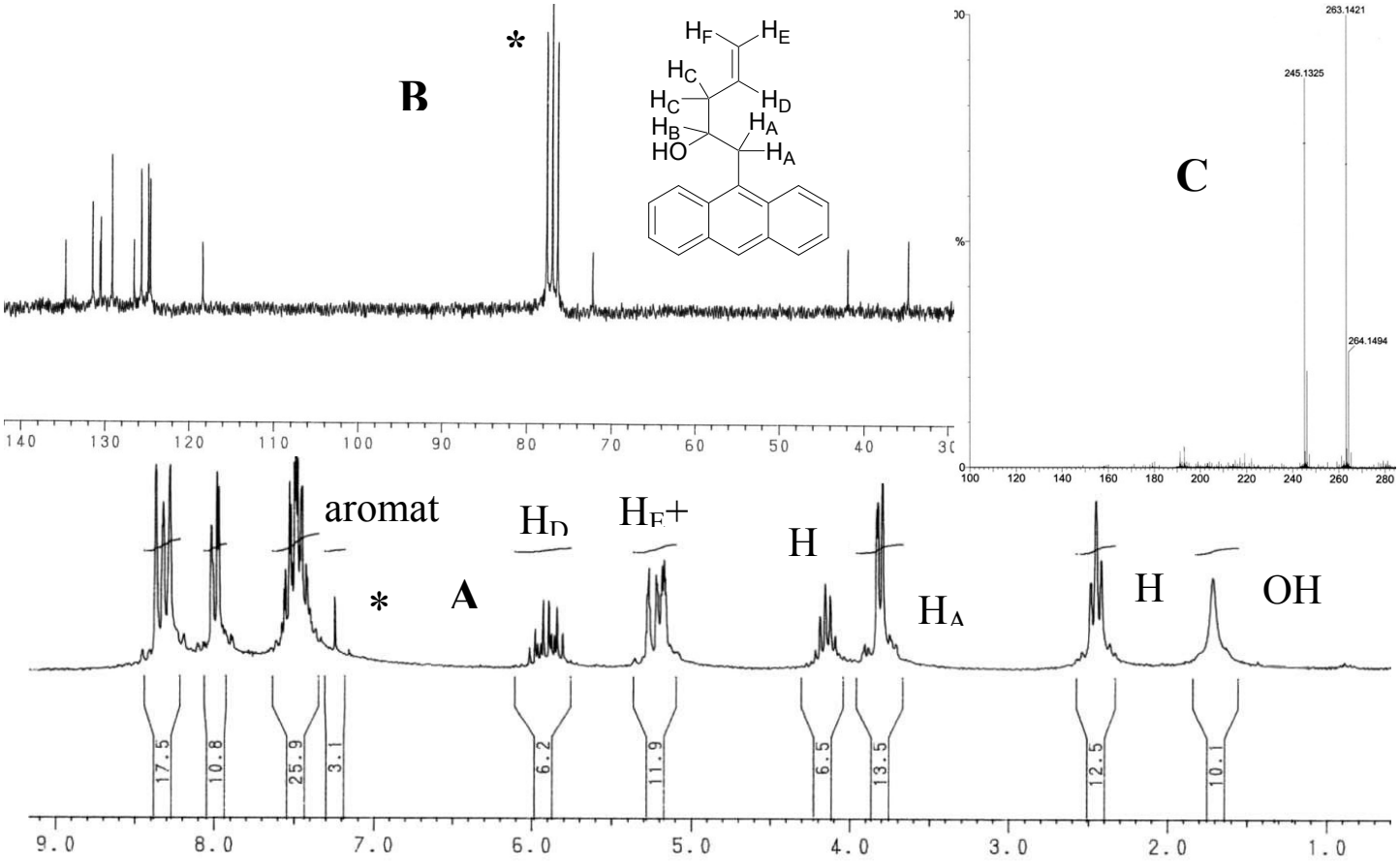
^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of compound 3-Phenyl-dodec-1-en-4-ol (3C).



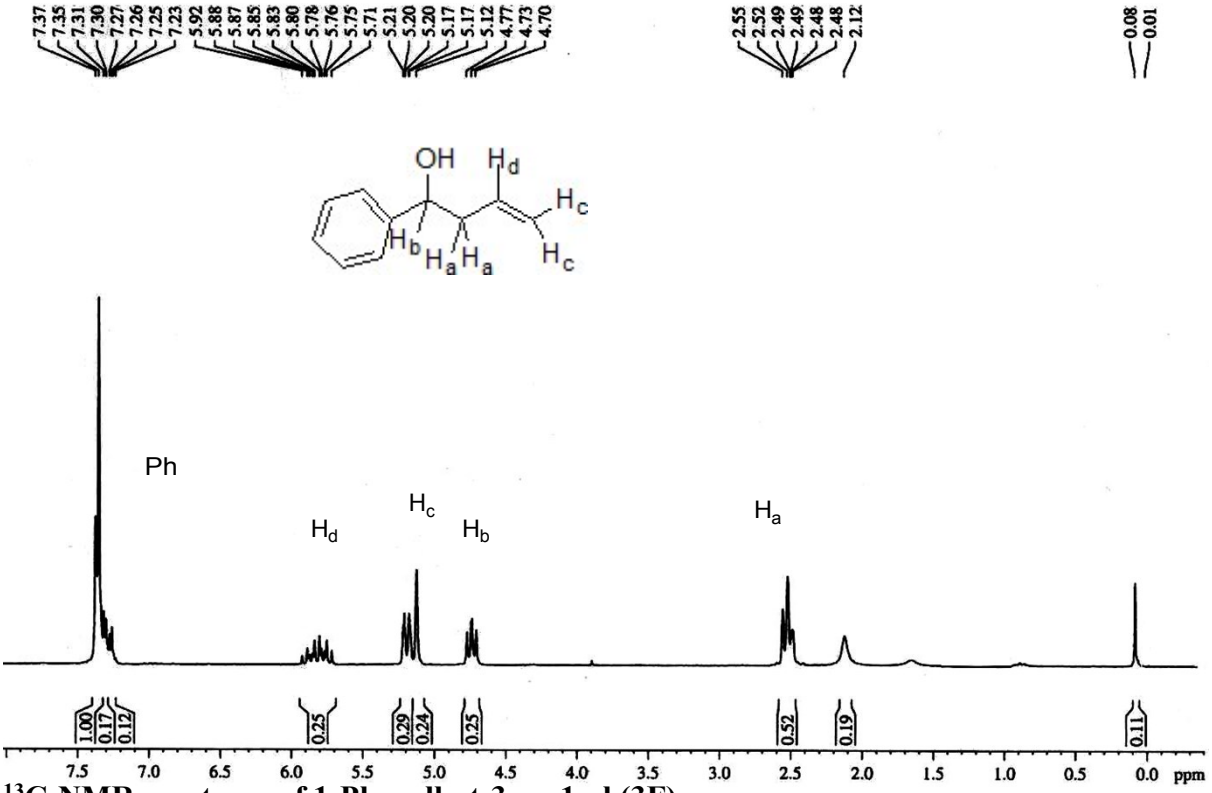
^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of compound 2-Methyl-1-p-tolyl-but-3-en-1-ol (3D).



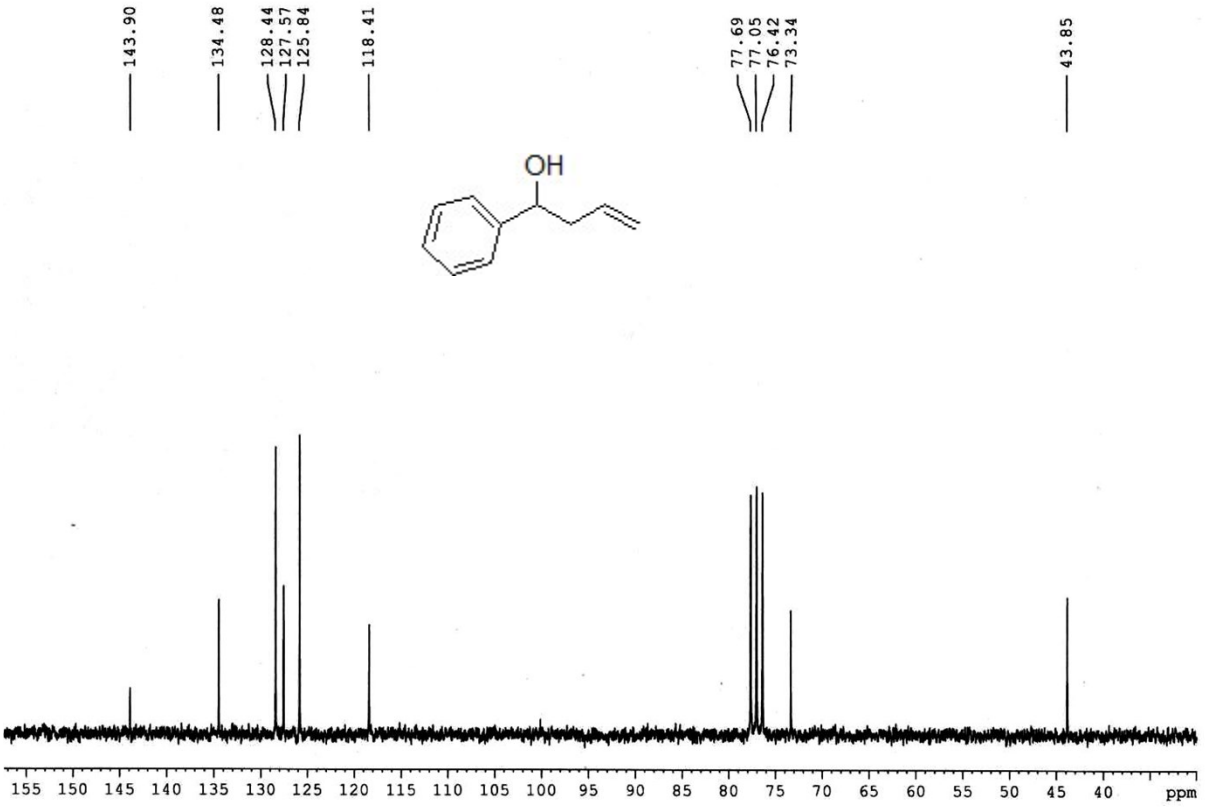
^{1}H NMR (A), ^{13}C NMR (B) and ESI-MS (C) spectra of compound 1-Anthrylpent-4-en-2-ol (3E).



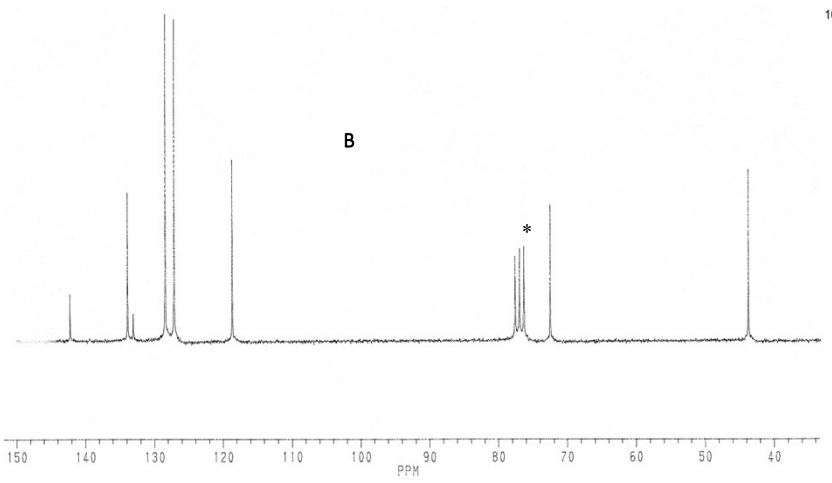
^{1}H NMR spectrum of 1-Phenylbut-3-en-1-ol (3F):

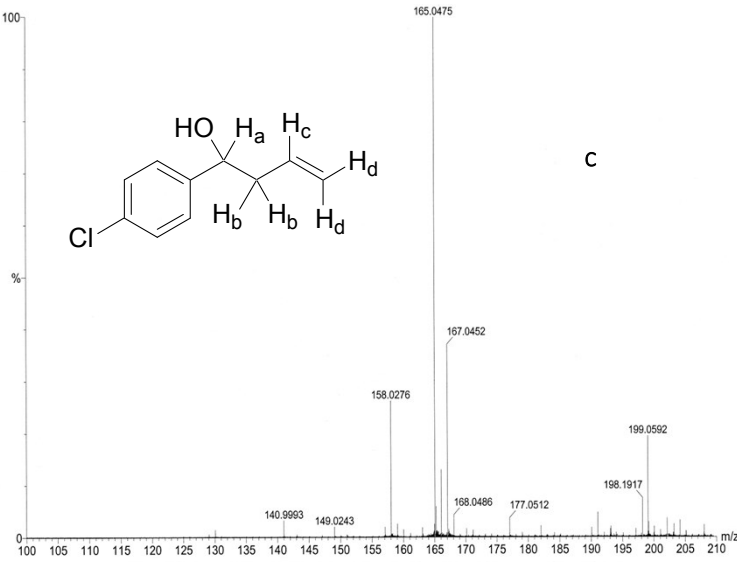


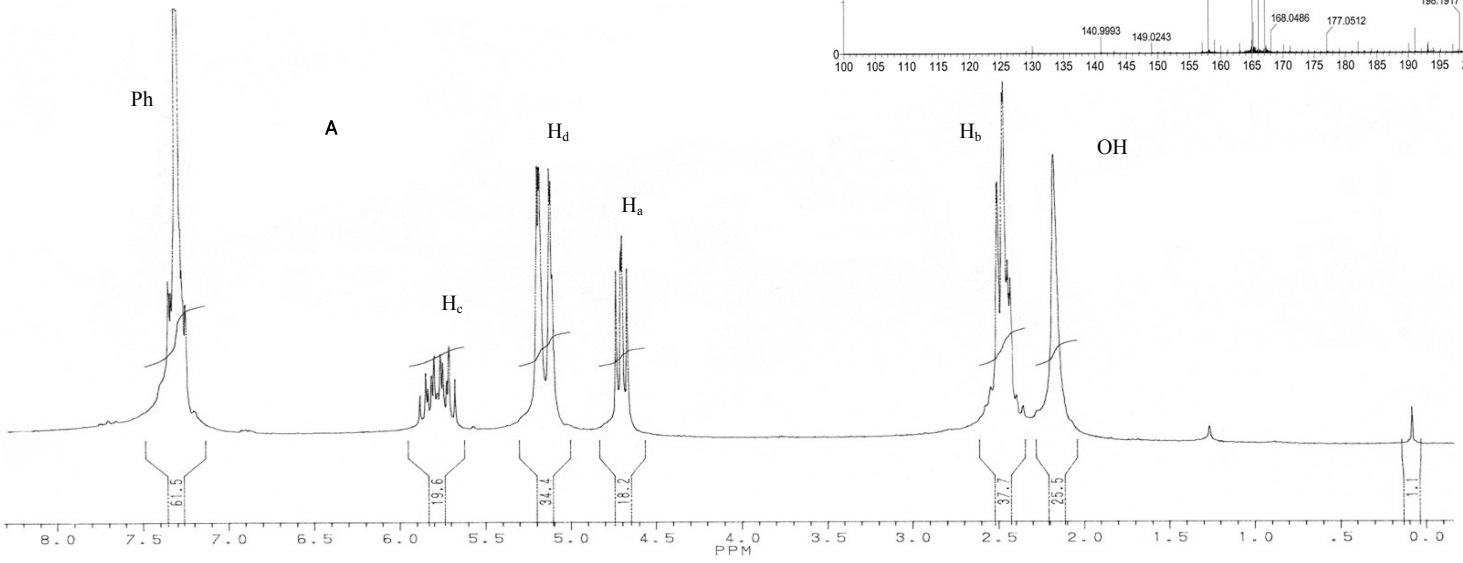
^{13}C-NMR spectrum of 1-Phenylbut-3-en-1-ol (3F):



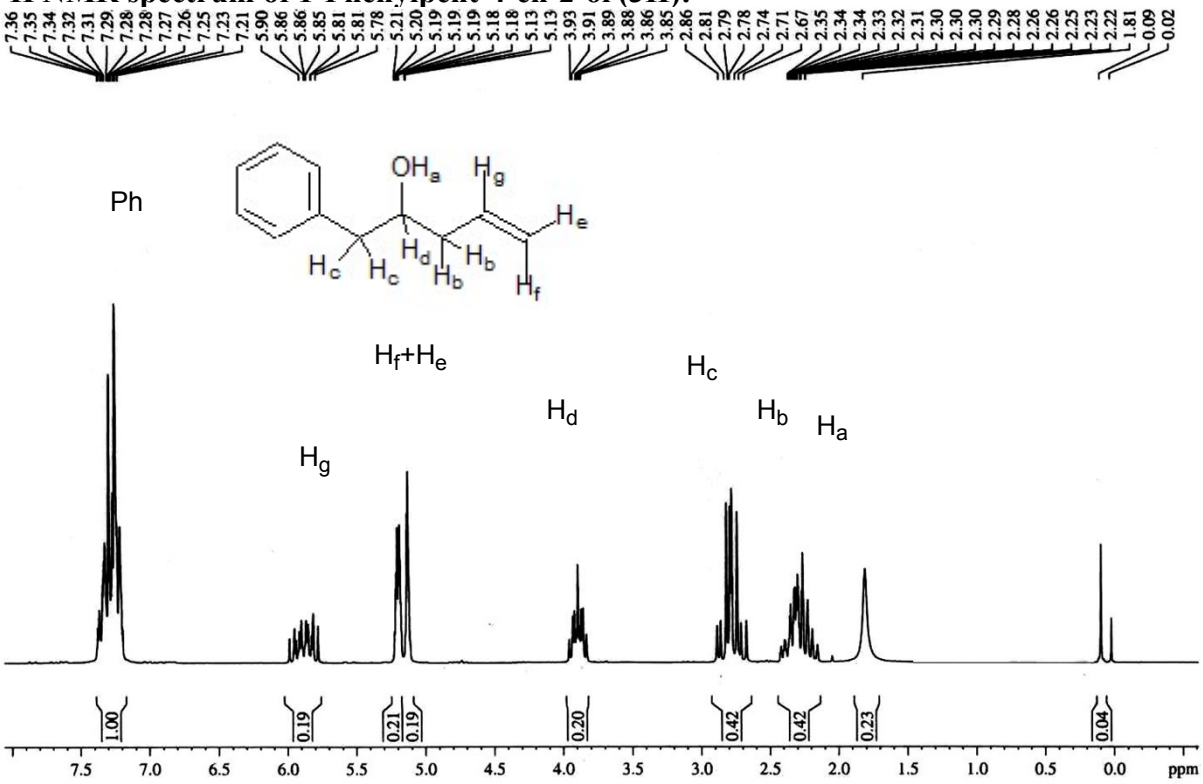
^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of 1-(4-Chloro-phenyl)-but-3-en-1-ol (3G)



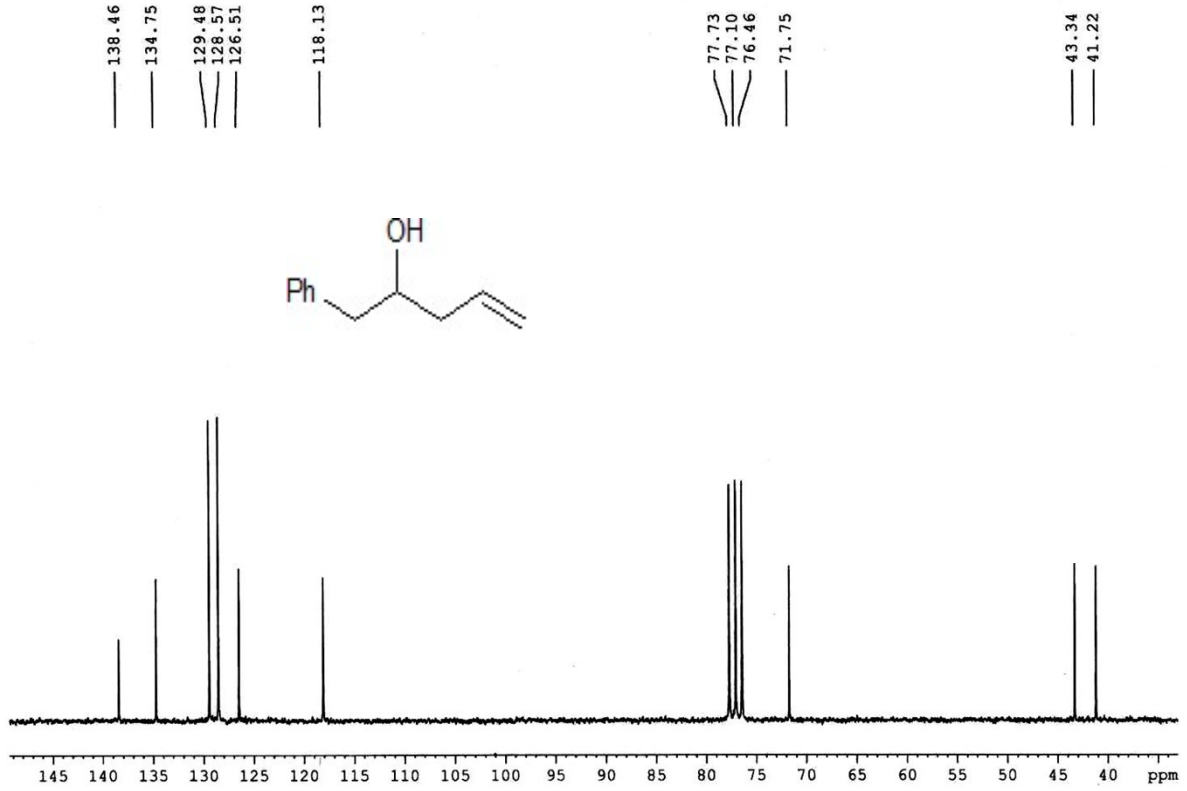




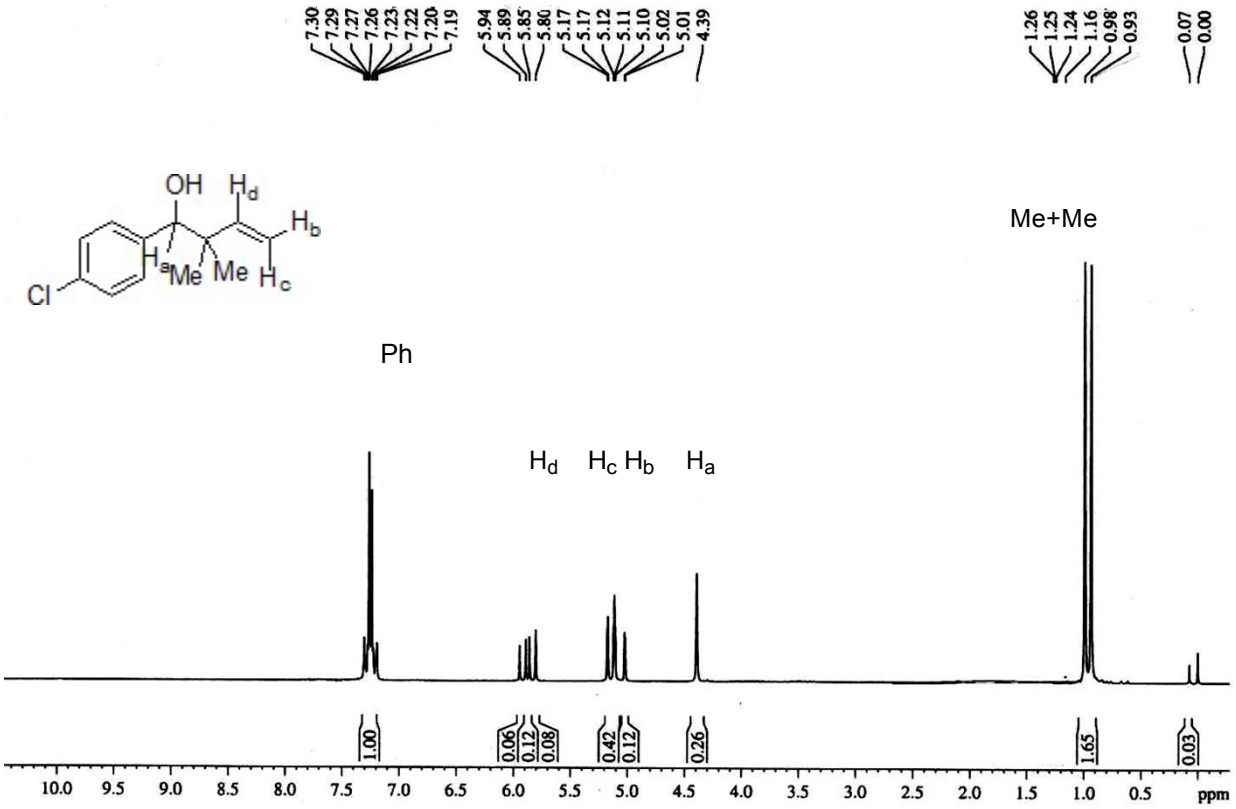
^{1}H NMR spectrum of 1-Phenylpent-4-en-2-ol (3H):



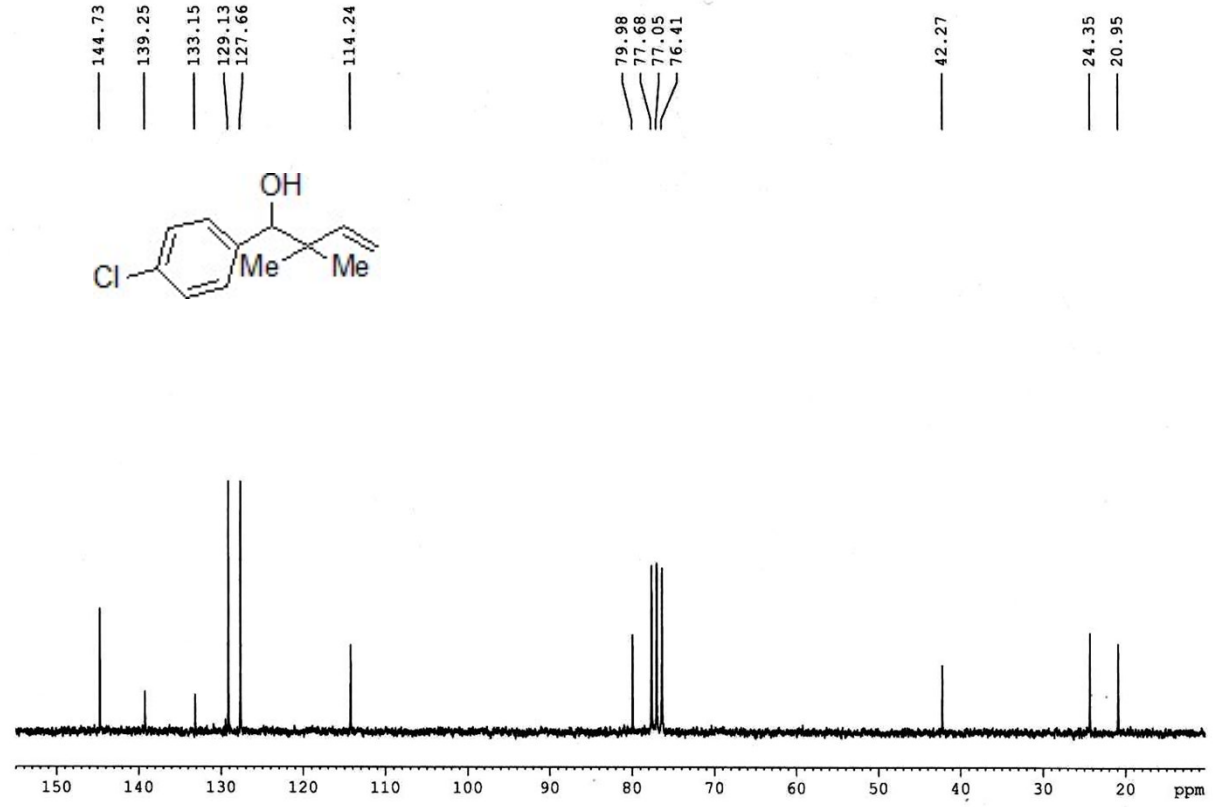
^{13}C-NMR spectrum of 1-Phenylpent-4-en-2-ol (3H):



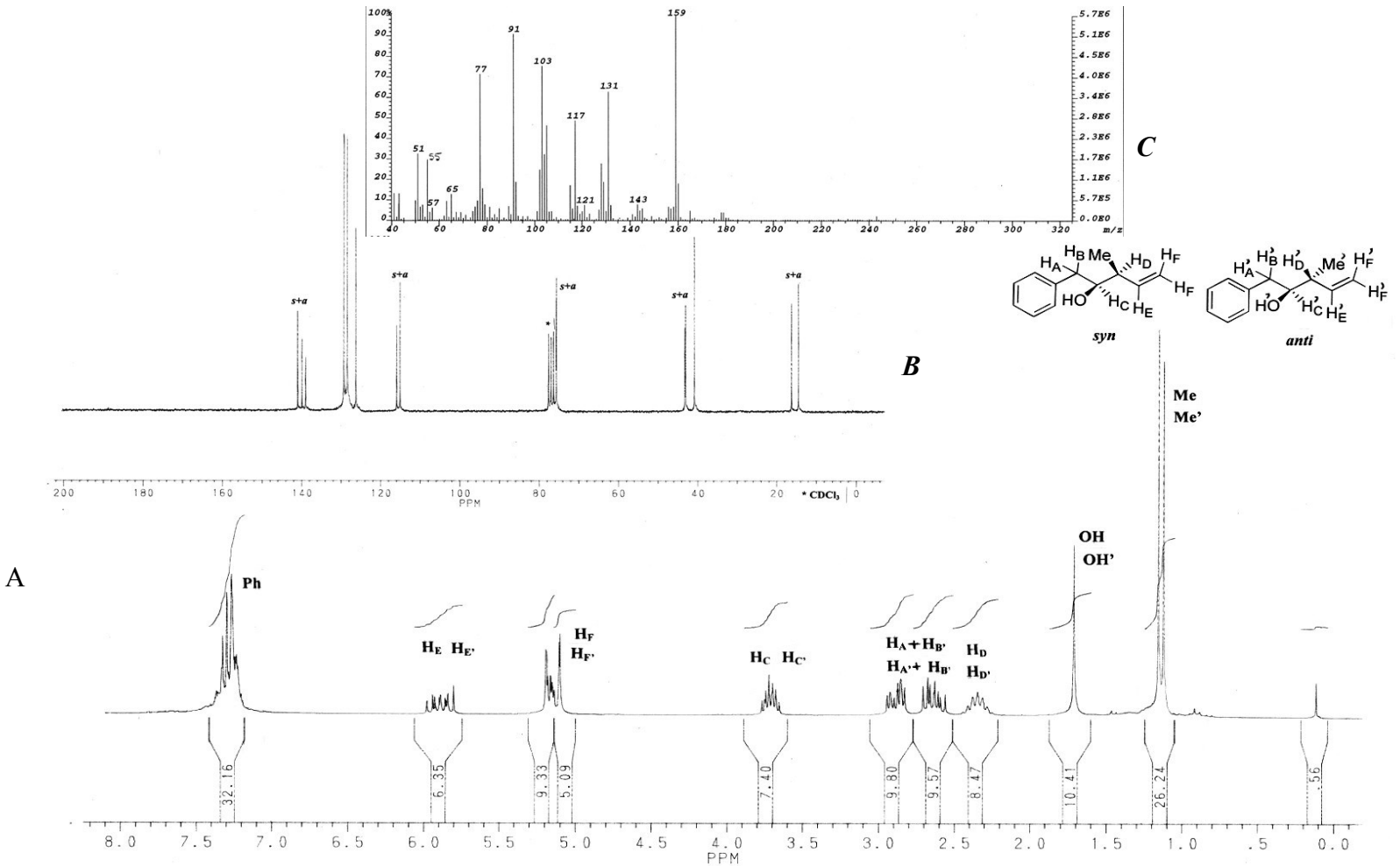
^{1}H NMR spectrum of 1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (3I):



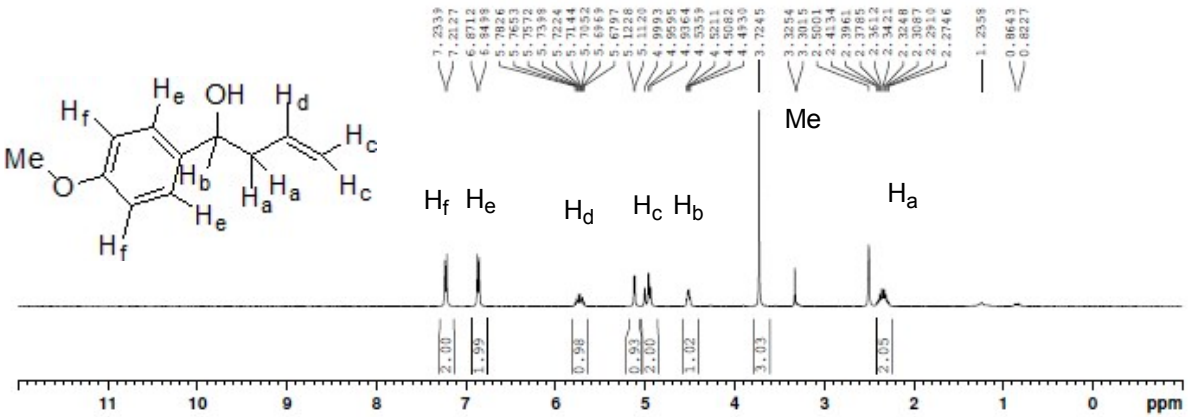
^{13}C-NMR spectrum of 1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (3I):

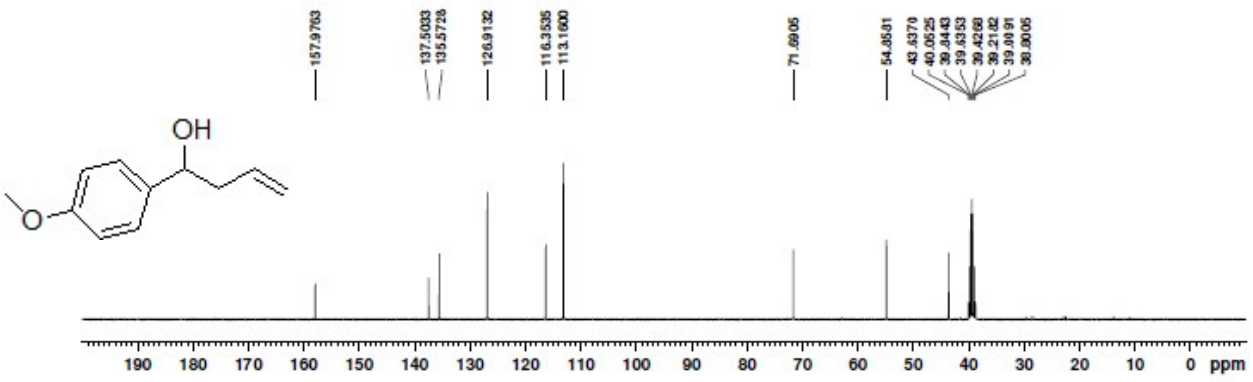


^{1}H-NMR (*A*), ^{13}C-NMR (*B*) & EIMS (*C*) spectra of 3-Methyl-1-phenylpent-4-en-2-ol (3J)

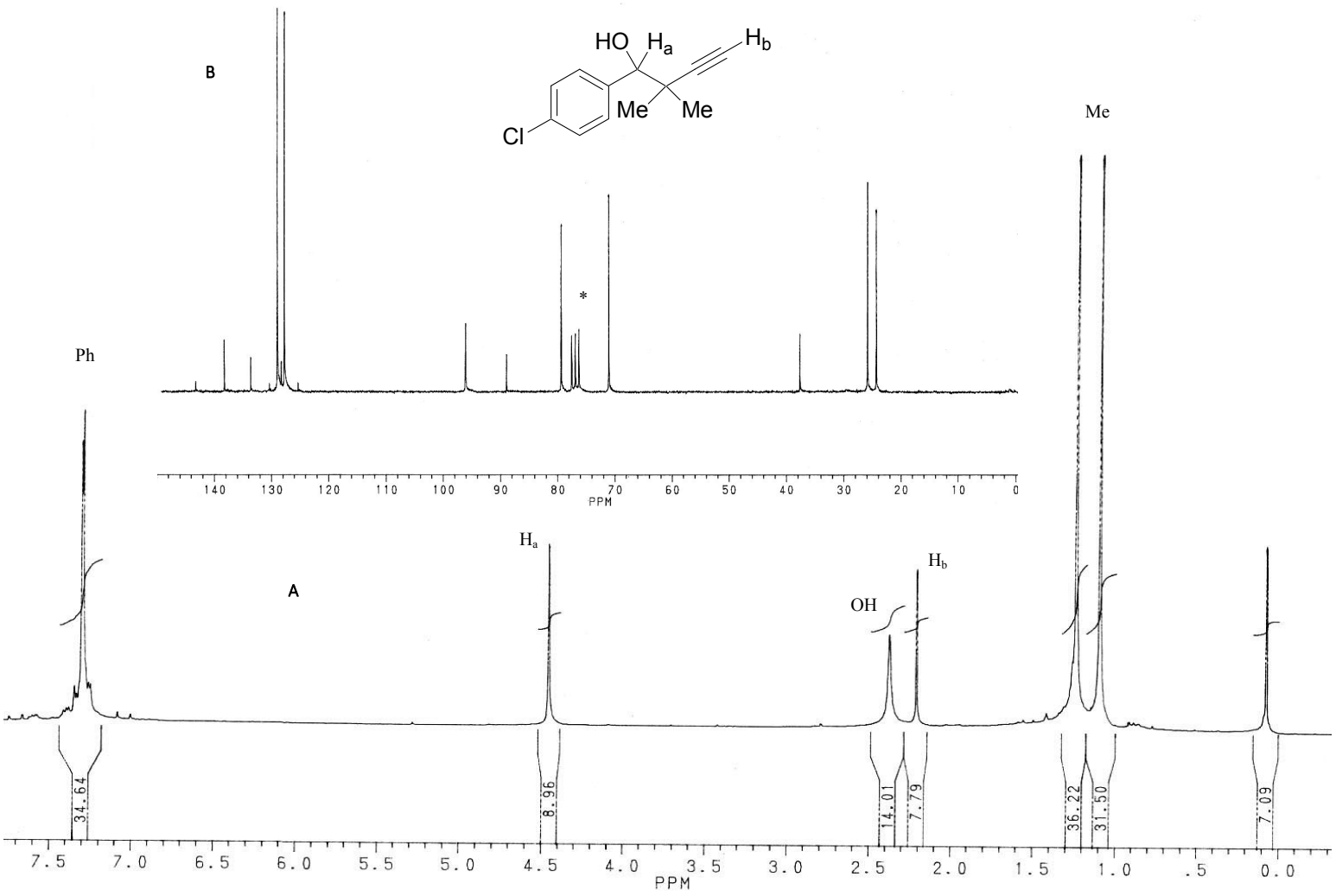


^{1}H-NMR and ^{13}C-NMR 1-(4-Methoxy-phenyl)-but-3-en-1-ol (3K)

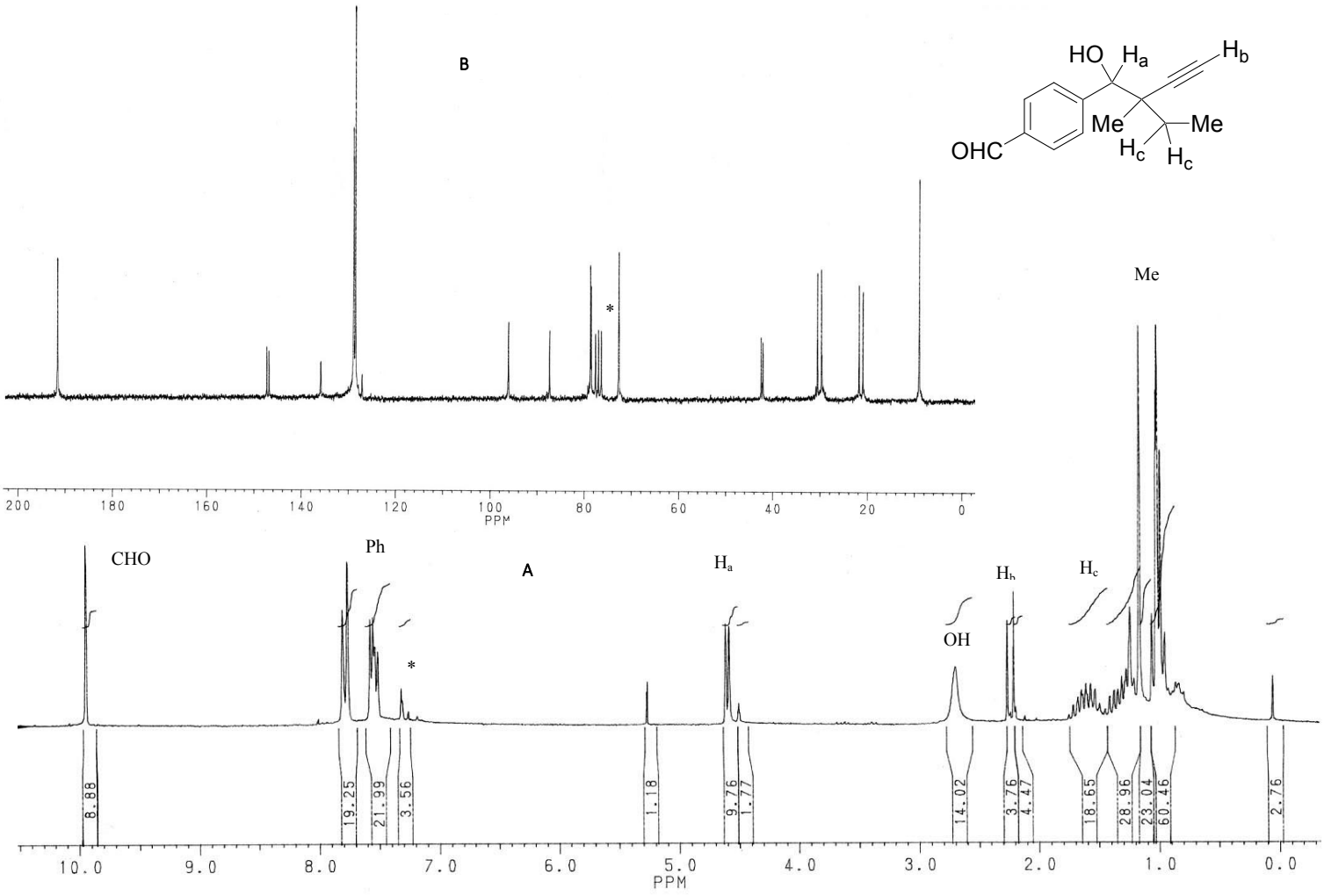




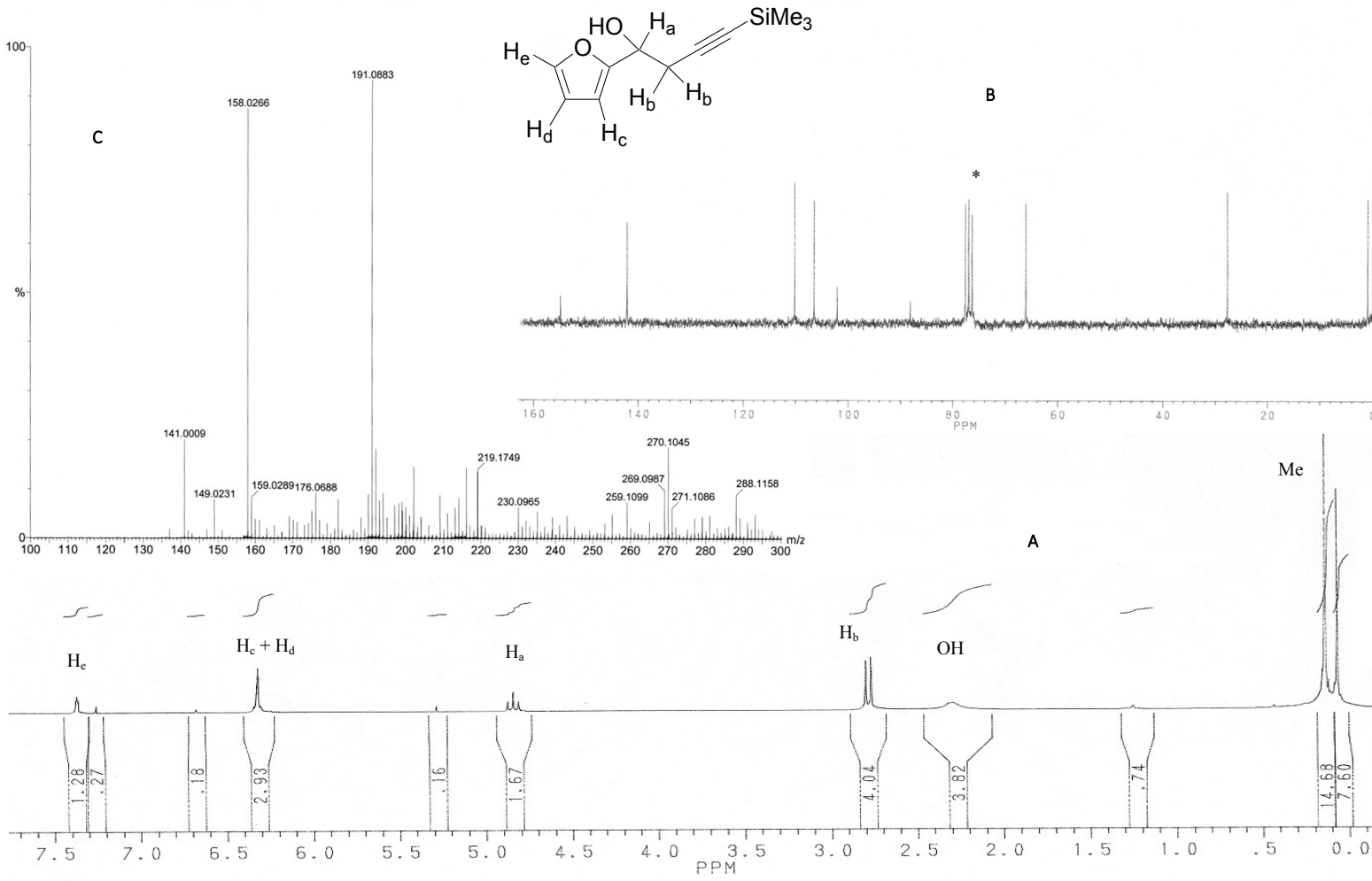
^{1}H (A) and ^{13}C (B) spectra of compound **1-(4-Chloro-phenyl)-2,2-dimethyl-3-butyn-1-ol (5A)**.



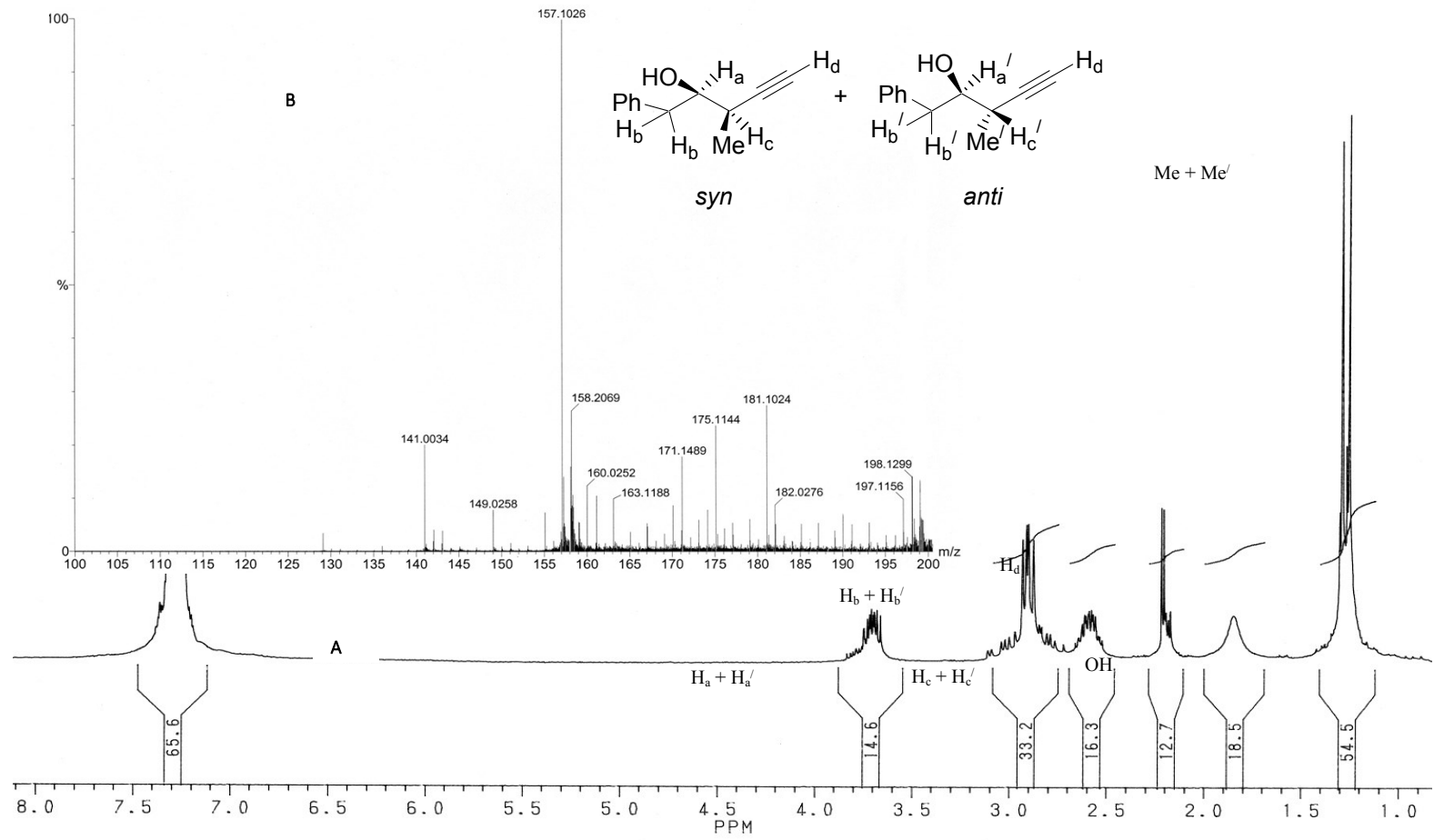
^{1}H (A) and ^{13}C spectra (B) of compound **1-(4-Formyl-phenyl)-2-ethyl-2-methyl-3-butyn-1-ol (5B)**.



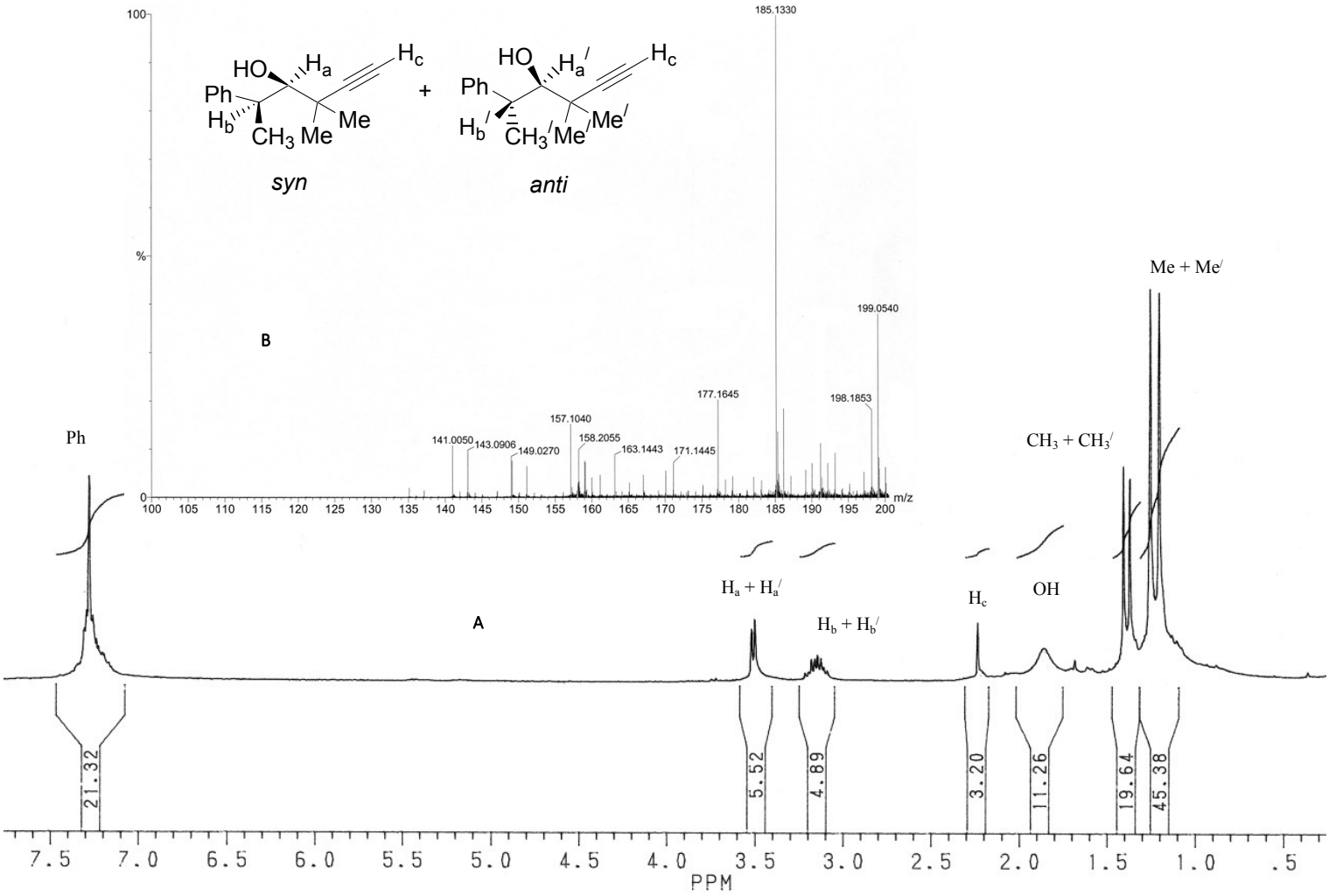
^{1}H (A), ^{13}C (B) and ESI-MS(+) (C) spectra of compound **1-Furan-2-yl-4-trimethylsilanyl-but-3-yn-1-ol (5C)**.



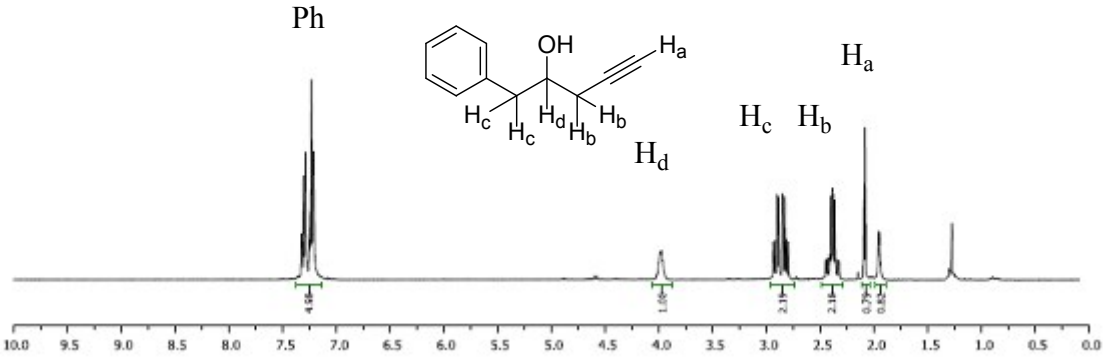
^{1}H (A) and ESI-MS(+) (B) spectra of compound **3-Methyl-1-phenyl-pent-4-yn-2-ol (5D)**.



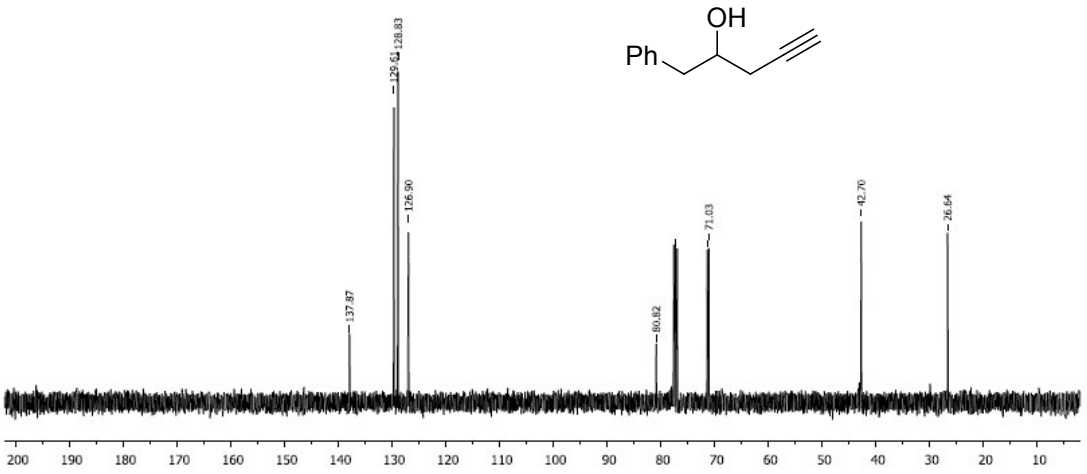
^{1}H (A) and ESI-MS(+) (B) spectra of compound **4,4-Dimethyl-2-phenyl-hex-5-yn-3-ol (5E)**.



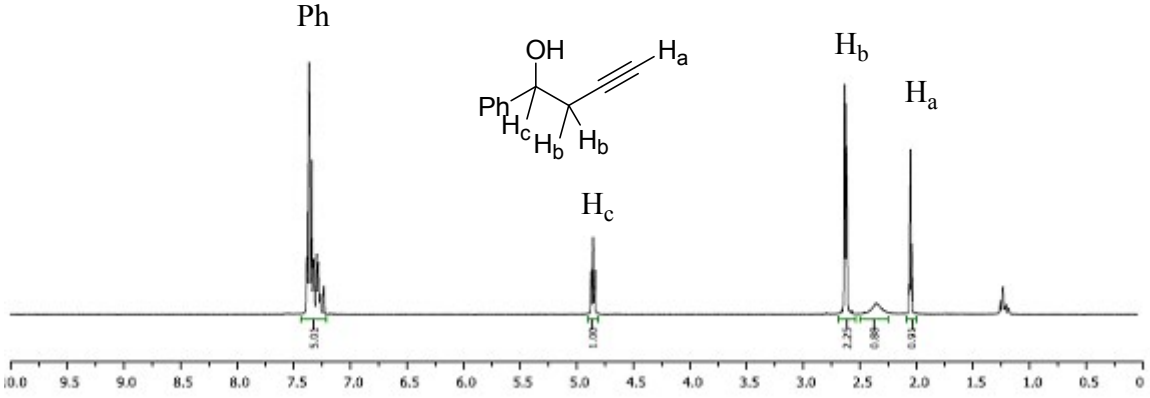
^{1}H NMR spectrum of 1-Phenyl-pent-4-yn-2-ol (5F)



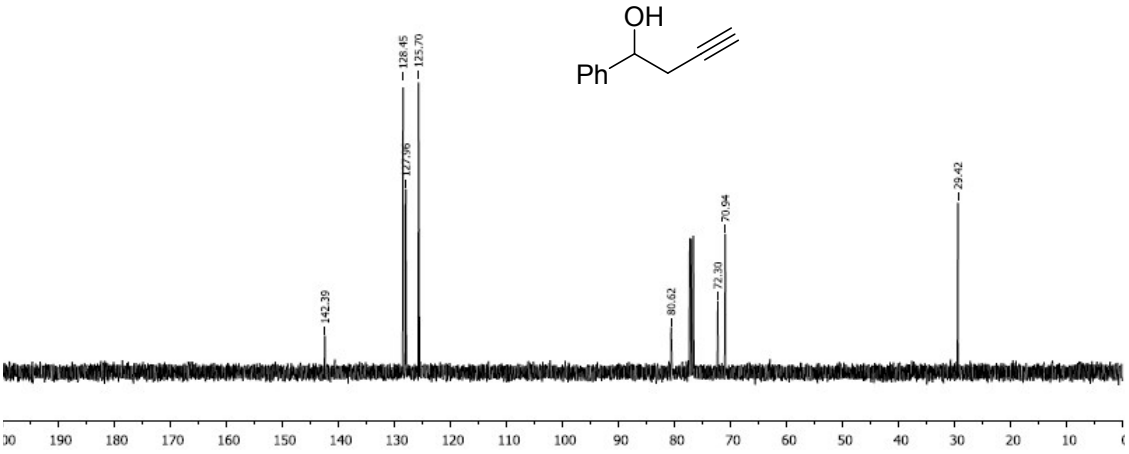
^{13}C NMR spectrum of 1-Phenyl-pent-4-yn-2-ol (5F)



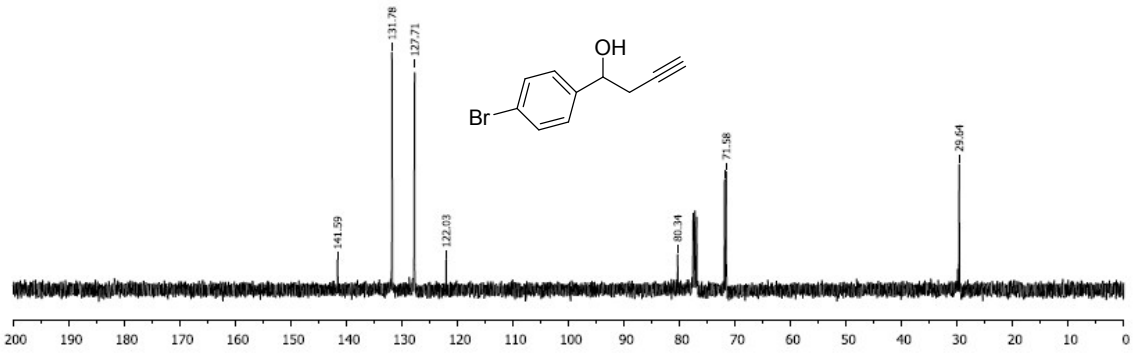
^{1}H NMR spectra of 1-Phenyl-but-3-yn-1-ol (5G)



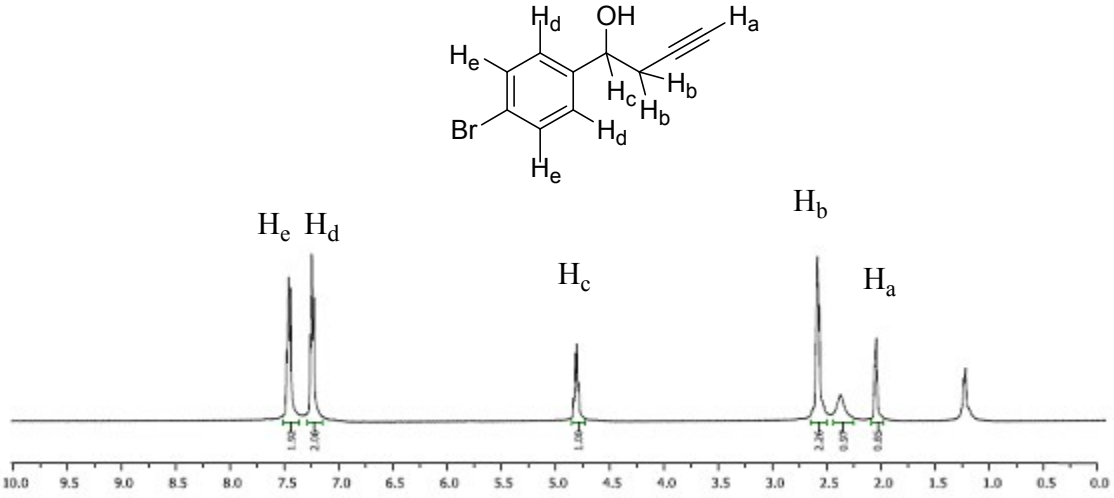
^{13}C NMR spectra of 1-Phenyl-but-3-yn-1-ol (5G)



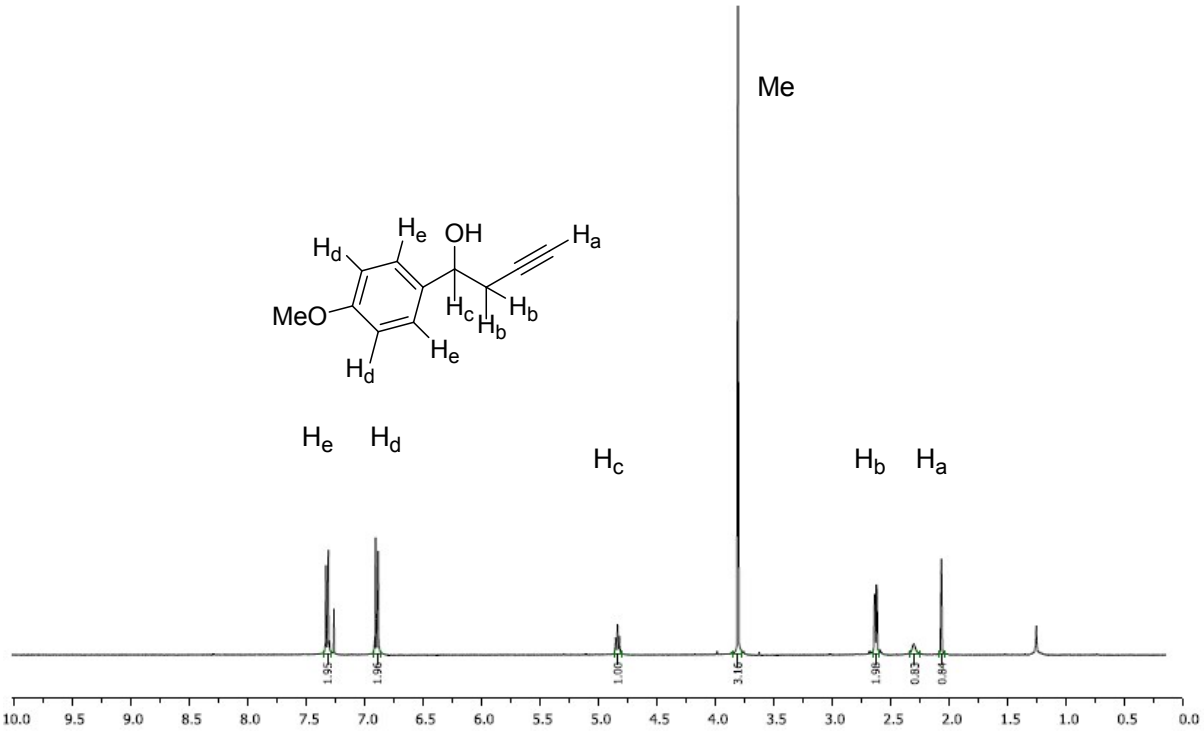
^{13}C NMR spectrum of 1-(4-Bromo-phenyl)-but-3-yn-1-ol (5H)



^{1}H NMR spectrum of 1-(4-Bromo-phenyl)-but-3-yn-1-ol (5H)



[1]H NMR spectrum of 1-(4-Methoxy-phenyl)-but-3-yn-1-ol (5I)



[13]C NMR spectrum of 1-(4-Methoxy-phenyl)-but-3-yn-1-ol (5I)