Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Recyclable Electrochemical Allylation in $ZnCl_2$ Aqueous Medium: Synthesis and Reactivity of Wire Shaped Nano Zinc Architecture

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CONTENT

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 (400 MHz) and ^{13}C NMR (100 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 δ_H = 7.26 ppm and in ^{13}C NMR spectra δ_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 and HRMS spectra were taken using Waters LCT mass spectrometer. Elemental analyses were performed on Perkin Elmer Instruments 2400 Series II CHNS/O Analyzer and Vario EL, Elementar. 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.

Systronics Digital Dual Channel Power Supply (0-30 V, 0-2 amp variable) Type -615D has been used as external bias for construction of electrochemical cell 1B in **Fig. 1** (main manuscript).

Field emission scanning electron microscopy (FESEM) was used for size and shape of the Zn nano-wire with a supra 40, Carl Zeiss Pvt. Ltd. Instrument and an EDS machine (Oxford link and ISIS 300) attached to the instrument is used to obtain the elemental composition.

The chemical states of Zn nanowire was studied by X-ray photoelectron spectroscopy (XPS) using PHI 5000 Versa Probe II (ULVAC − PHI, INC, Japan)

system equipped with microfocused (100 μm, 25 W, 15 KV) monochromatic Al-Kα X-Ray source (hν = 1486.6 eV).

The phase of Zn nanowire was studied by X-ray diffraction (XRD) (Philips X-Pert MRD) at a grazing incidence mode using Cu Kα radiation (45 kV, 40 mA).

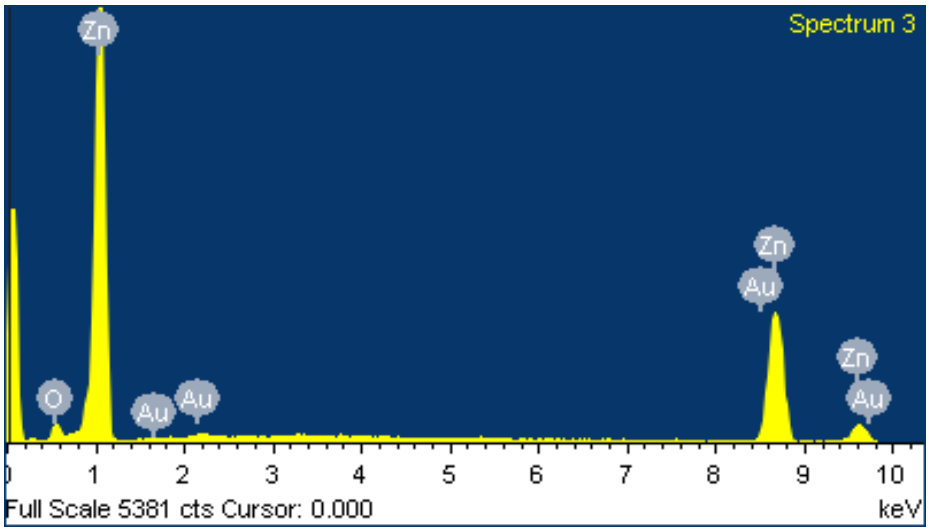
2. Synthesis of Starting Materials:

General procedure for the preparation of Sulfonimines:[1] A solution of the aldehyde (17 mmol) in toluene (70 mL) was placed in a round bottomed flask equipped with a Dean Stark assembly. p-Toluenesulfonamide (3.25 g, 19 mmol), amberlite H^+ resin IR-120 (2 g) and powdered molecular sieves (4 Å, 2 g) were added to the reaction flask and the mixture was stirred at 120 °C for 12 h, with azeotropic removal of water. After the reaction was complete (based upon the theoretical amount of water removal, and monitoring reaction by TLC), the mixture was allowed to cool at room temperature and filtered. The solvent was removed in vacuo and the resulting sulfonimines were further purified by crystallization from *n*-Hexane.

Synthesis of zinc coated ITO (F1) glass film: The Transparent Conducting Oxide (TCO) or Indium Tin Oxide (ITO) coated glass substrates were cleaned with liquid detergent and then inserted into concentrated chromic acid solution for about 20 minutes and washed thoroughly with cold distilled water to remove any adhering materials as impurities. These TCO glass substrates were then boiled in methanol and digested in a vapour of trichloroethelene. The properly cleaned TCO glass substrates and a Zn rod (99.9%purity) were dipped into a 0.02 M $ZnCl_2$ (99% purity) solution. The Zn rod and the TCO glass substrate were short-circuited externally through a copper wire. The Zn rod served as a self-decaying anode and the TCO glass substrate as the cathode (Fig. 1).The temperature was 70 degree centigrade and pH was maintained at 2.3 by changing concentration and adding required amount of HCl. The pH of the solution was kept at 2.3 which were found to be optimum for desired zinc film deposition. Time of deposition was ten minutes. The deposition was allowed till a typical type of effervescence of hydrogen gas evolved from the surface of the zinc coated ITO (F1).

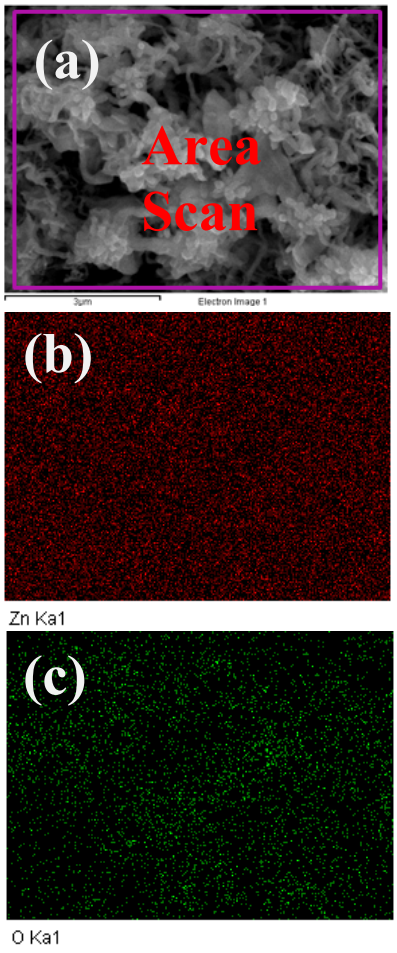
3. EDX and EDX mapping:

Fig. S1: EDX pattern and elemental composition of the deposited elemental Zinc film (F1)



Element	Weight%	Atomic%
O K	5.40	19.07
Zn K	93.00	80.46
Au M	1.61	0.46
Totals	100.00	100.00

EDX mapping **Fig. S2** The FESEM image along with scan area (a) of the as deposited Zn nanowire and the red color (b) represents the Zn and green color represents the presence of oxygen.



4. XRD Analysis:

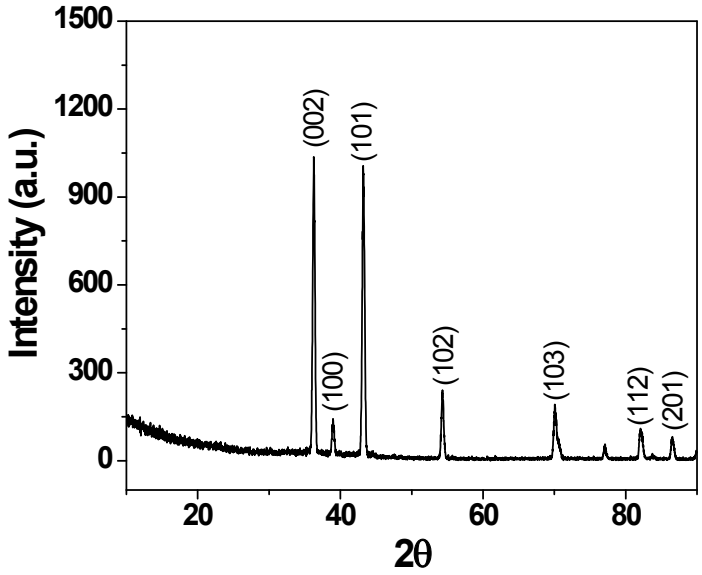


Fig. S3 XRD of the deposited elemental zinc film (F1)

5. Preparation of Rieke Zinc:[2] 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 non-electrochemical reaction conditions.

6. Spectral Characteristics /data for all compounds

1-(4-Chlorophenyl)but-3-en-1-ol (1a):[3]

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.42-2.51 (m, 2H), 4.67-4.73 (m, 1H), 5.09-5.2 (m, 2H), 5.67-5.88 (m, 1H), 7.2-7.34 (m, 1H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 43.81, 72.62, 118.76, 127.25, 128.54, 133.15, 134.01, 142.34; Anal. ($C_{10}H_{11}ClO$) calcd, C: 65.76, H: 6.07; found, C: 65.69, H:6.03.

1-Phenylbut-3-en-1-ol (1b):[4]

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.12 (s br, 1H), 2.48-2.56 (m, 2H), 4.74 (t, 1H, *J*=6.4 Hz), 5.12-5.21 (m, 2H), 5.72-5.92 (m, 1H), 7.23-7.38 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 43.85, 73.34, 118.41, 125.84, 127.57, 128.44, 134.48, 143.9; Anal. ($C_{10}H_{12}O$) calcd, C: 81.04, H: 8.16; found, C: 81.09, H: 8.20.

1-Phenylpent-4-en-2-ol (1c):[5,6]

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.81 (s br, 1H), 2.23-2.36 (m, 2H), 2.67-2.86 (m, 2H), 3.86-3.93 (m, 1H), 5.13-5.21 (m, 2H), 5.78-5.9 (m, 1H), 7.22-7.37 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 41.22, 43.34, 71.75, 118.13, 126.51, 128.57, 129.48, 134.75, 138.46; Anal. ($C_{11}H_{14}O$) calcd, C: 81.44, H: 8.70; found, C: 81.38, H: 8.67.

1-(4-Nitrophenyl)but-3-en-1-ol (1d):[7]

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.74 (s br, 1H), 2.27-2.62 (m, 2H), 4.82-4.89 (m, 1H), 5.12-5.21 (m, 2H), 5.68-5.88 (m, 1H), 7.52 (d, 2H, *J*= 8.6 Hz), 8.19 (d, 2H, *J*= 8.6 Hz); ^{13}C NMR (54.6 MHz, $CDCl_3$): 43.89, 72.21, 119.59, 123.63, 123.64, 126.60, 133.25, 151.19; Anal. ($C_{10}H_{11}NO_3$) calcd, C: 62.17, H: 5.74; found, C: 62.25, H: 5.78.

1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (1e):[8]

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (s, 3H), 0.99 (s, 3H), 4.39 (s, 1H), 5.02-5.18 (m, 2H), 5.8-5.95 (m, 1H), 7.19-7.31 (m, 4H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 20.95, 24.35, 42.27, 79.98, 114.24, 127.66, 129.13, 133.15, 139.25, 144.73; Anal. ($C_{12}H_{15}ClO$) calcd, C: 68.40, H: 7.18; found, C: 68.43, H: 7.19.

2,2-Dimethyl-1-phenylbut-3-en-1-ol (1f):[9]

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.97 (s, 3H), 1.02 (s, 3H), 4.43 (s, 1H), 5.04-5.18 (m, 2H), 5.85-6 (m, 1H), 7.26-7.32 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 21.12, 24.48, 42.28, 80.71, 113.83, 127.44, 127.51, 127.82, 140.84, 145.14; Anal. ($C_{12}H_{16}O$) calcd, C: 81.77, H: 9.15; found, C: 81.79, H: 9.19.

3,3-Dimethyl-1-phenylpent-4-en-2-ol (1g):[5,6]

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.12 (s, 6H), 1.58 (s br, 1H), 2.4-2.52 (m, 1H), 2.9 (dd, 1H, *J*=13.7 Hz, 1.7 Hz), 3.51 (dd, 1H, *J*=10.6 Hz, 1.9 Hz), 5.06-5.15 (m, 2H), 5.87-6.01 (m, 1H), 7.21-7.35 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 22.79, 38.38, 41.46, 79.34, 113.05, 126.26, 128.48, 129.3, 139.88, 145.26; ESI-MS: for $C_{13}H_{18}O$ [M], $[M-OH]^+$=173.1316; Anal ($C_{13}H_{18}O$) calcd, C: 82.06, H: 9.53; found, C: 81.98, H: 9.49.

4-Methyl-1-phenylpent-4-en-2-ol (1h):[5,6]

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.77 (s, 3H), 1.81 (s br, 1H), 2.19-2.25 (m, 2H), 2.77-2.80 (m, 2H), 3.93-4.02 (m, 1H), 4.83-4.9 (m, 2H), 7.23-7.32 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 22.46, 43.64, 45.54, 69.98, 113.39, 126.43, 128.48, 129.44, 138.6, 142.67; Anal ($C_{12}H_{16}O$) calcd, C: 81.77, H: 9.15; found, C: 81.68, H: 9.09.

3-Methyl-1-phenylpent-4-en-2-ol (1i):[10] (*syn*:*anti* 42:58)

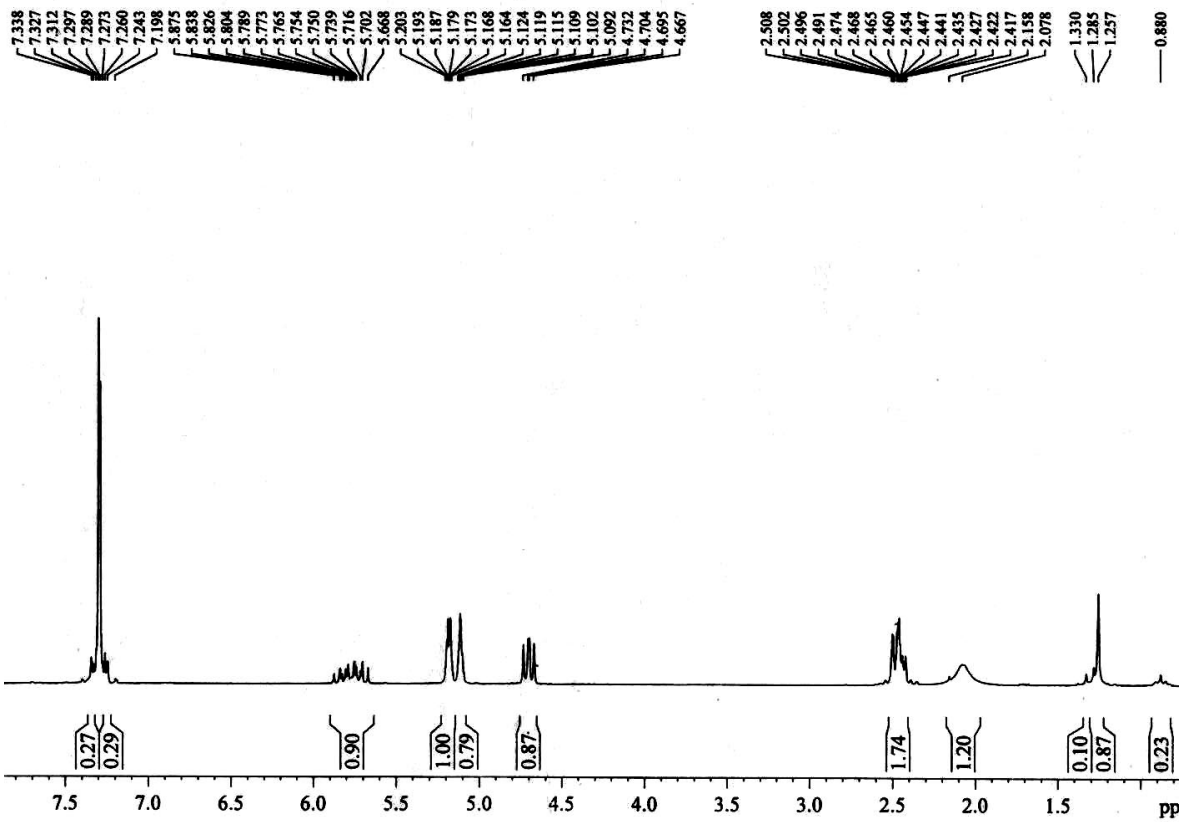
^{1}H NMR ($CDCl_3$): δ 1.01-1.04 (d, 3H, *J*= 6.8 Hz), 1.59 (br s, 1H), 2.17-2.29 (m, 1H), 2.45-2.59 (m, 1H), 2.71-2.83 (m, 1H), 3.54-3.65 (m, 1H), 4.99-5.08 (m, 2H), 5.69-5.86 (m, 1H), 7.08-7.26 (m, 5H); ^{13}C NMR ($CDCl_3$): δ [14.45, 16.20] (*anti*+*syn*), 40.73, [42.95, 43.10] (*anti*+*syn*), [75.52, 75.63] (*anti*+*syn*), [115.03, 115.86] (*anti*+*syn*), 126.57, 128.28, 129.18, 138.87, [139.79, 140.84] (*anti*+*syn*); EIMS m/z (rel abundance): 176 ($M^{\cdot+}$, <1), 159 [$(M-OH)^+$, 100], 131 (64), 121 (8) 117 (50), 103 (76), 91 (92), 77 (72), 55 (30), 65 (12).

4-Methyl-*N*-(1-phenylbut-3-enyl)benzenesulfonamide (2a):[11] ^{1}H NMR (200 MHz., $CDCl_3$): δ 2.32-2.49 (m, 5H), 4.36-4.39 (m, 1H), 4.9 (d, 1H, *J*= 6.3 Hz.), 5.02-5.1 (m, 2H), 5.44 (m, 1H), 7.05-7.21 (m, 7H), 7.55 (d, 2H, *J*= 8.3 Hz.); ^{13}C NMR (54.6 MHz.,$CDCl_3$): δ 21.43, 41.84, 57.59, 118.78, 126.64, 127.13, 127.21, 128.29, 129.27, 133.32, 137.66, 140.51, 142.94; HRMS (ESI) calcd for $C_{17}H_{20}NO_2S$ $[M+H]^+$= 302.1215, found 302.1225.

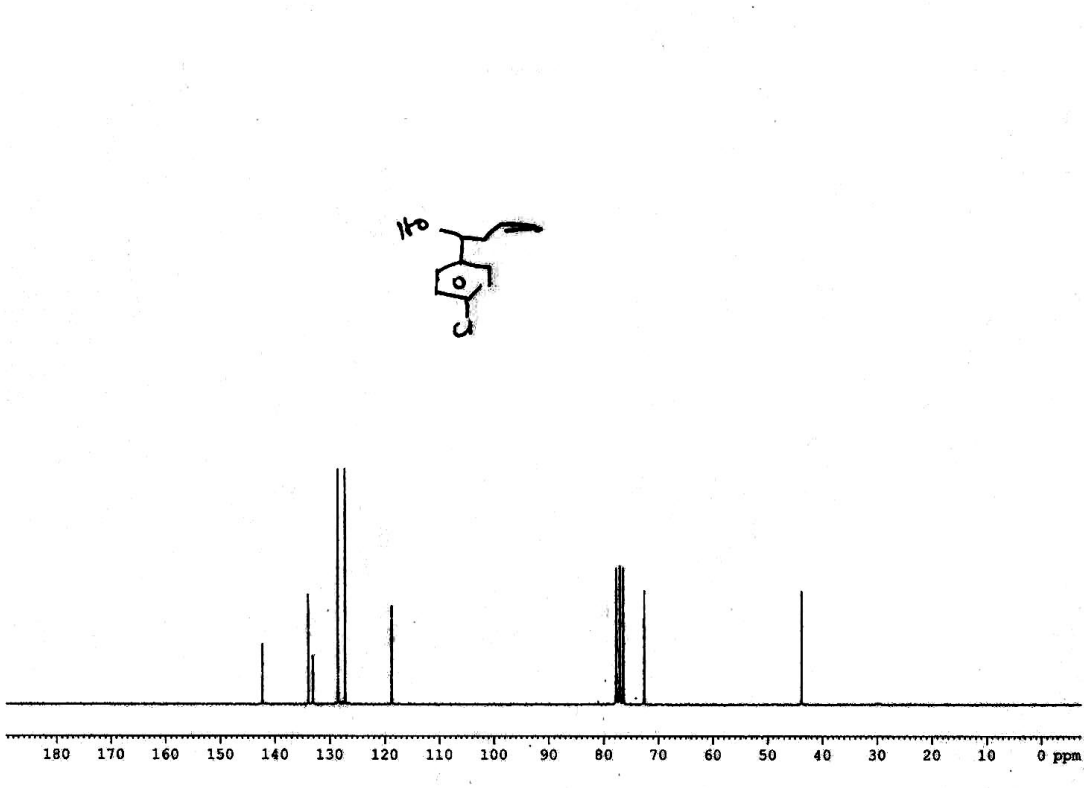
***N*-[1-(4-Chlorophenyl)but-3-enyl]-4-methylbenzenesulfonamide (2b):**[12] ^{1}H NMR (400 MHz., $CDCl_3$): δ 2.27-2.39 (m, 5H), 4.23-4.28 (m, 1H), 4.93-4.98 (m, 2H), 5.35-5.46 (m, 2H), 6.93 (d, 2H, *J*= 8.4 Hz.), 7.02-7.07 (m, 4H), 7.46 (d, 2H, *J*= 8 Hz.); ^{13}C NMR (100 MHz.; $CDCl_3$): δ 21.49, 41.71, 56.71, 119.53, 127.09, 128.09, 128.43, 129.38, 132.74, 133.11, 137.28, 138.91, 143.37; HRMS (ESI) calcd for $C_{17}H_{19}ClNO_2S$ $[M+H]^+$= 336.0825, found 336.0842.

7. ^{1}H & ^{13}C NMR spectra for all compounds:

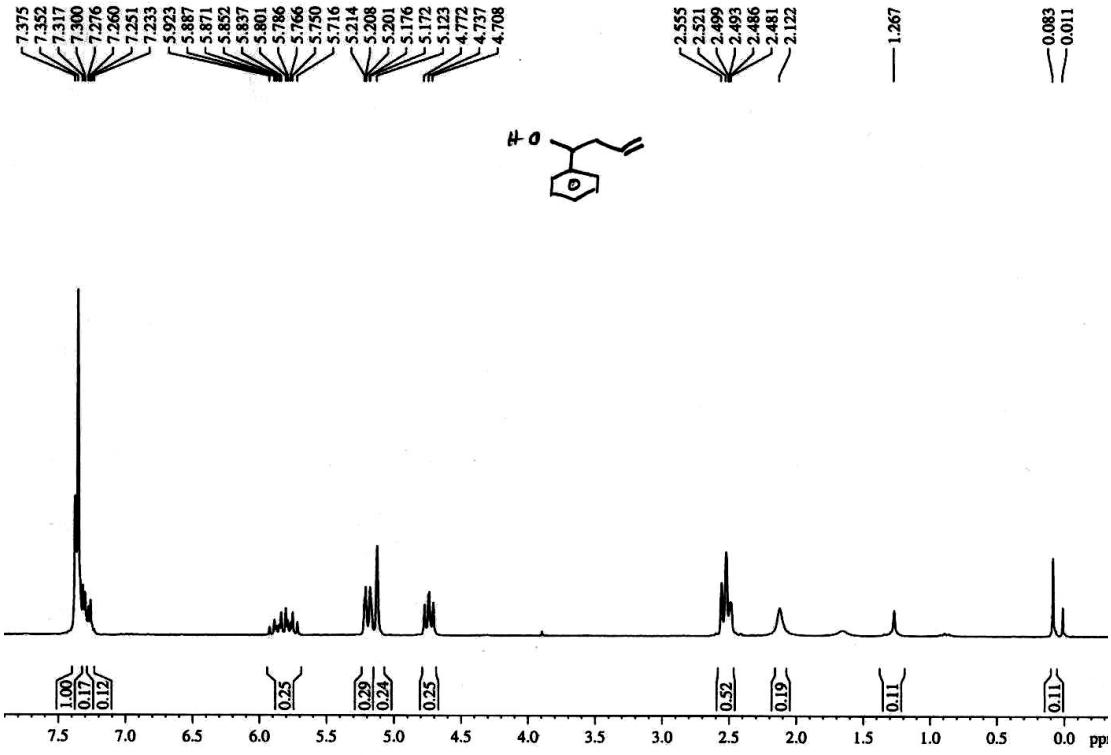
^{1}H NMR spectrum of 1-(4-Chlorophenyl)but-3-en-1-ol (1a):



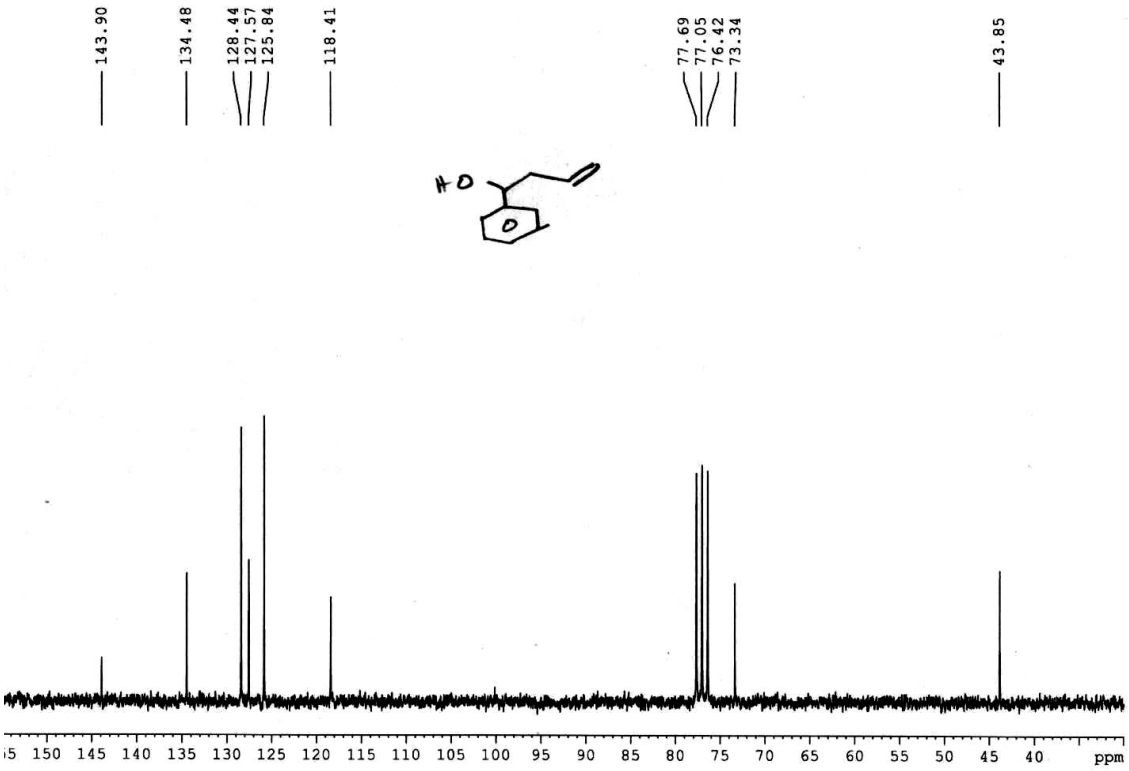
^{13}C-NMR spectrum of 1-(4-Chlorophenyl)but-3-en-1-ol (1a):



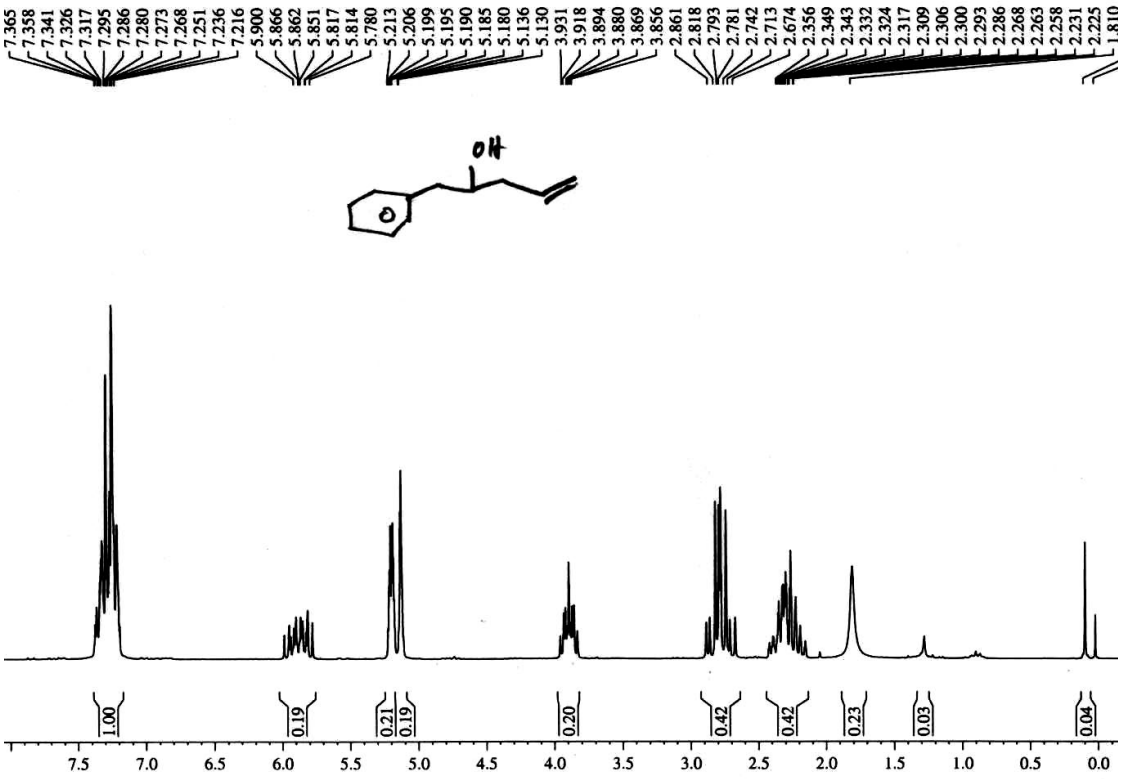
^{1}H NMR spectrum of 1-Phenylbut-3-en-1-ol (1b):



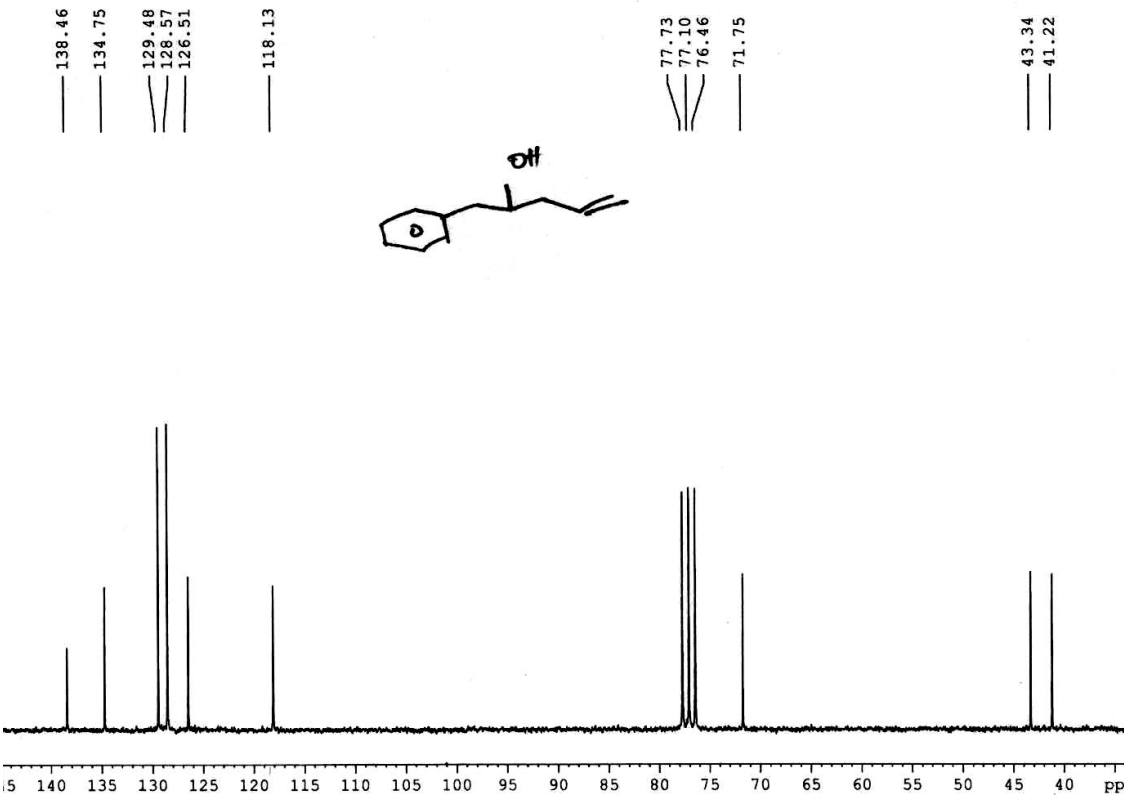
^{13}C-NMR spectrum of 1-Phenylbut-3-en-1-ol (1b):



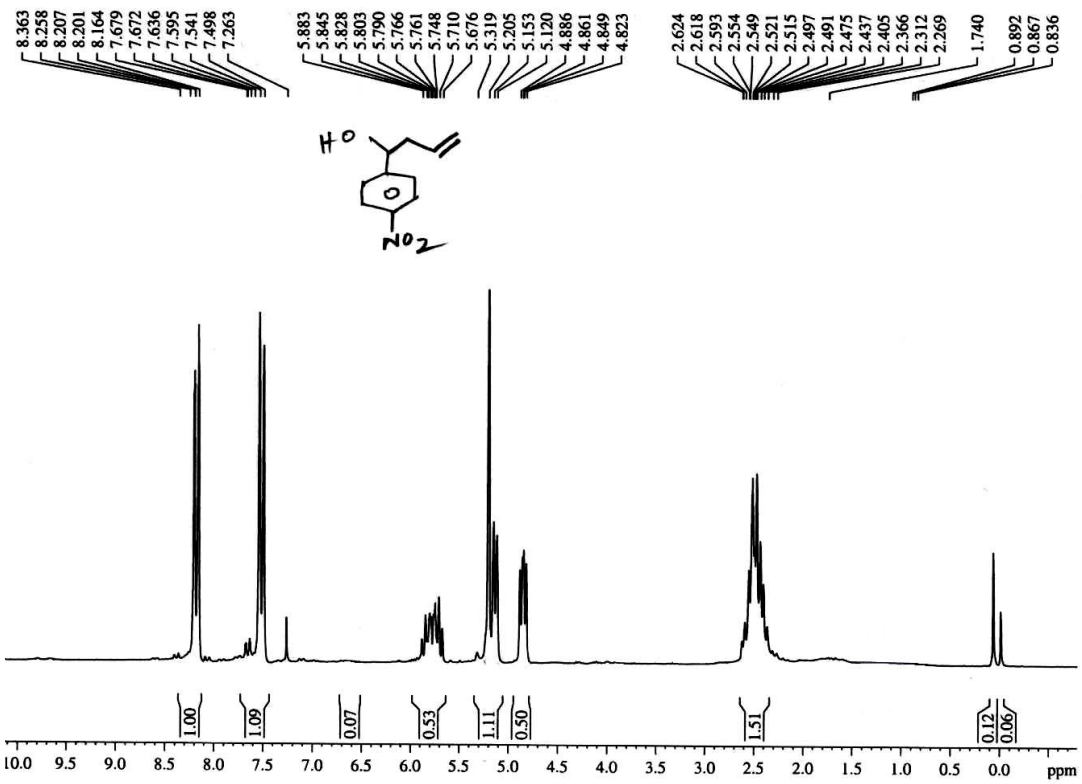
^{1}H NMR spectrum of 1-Phenylpent-4-en-2-ol (1c):



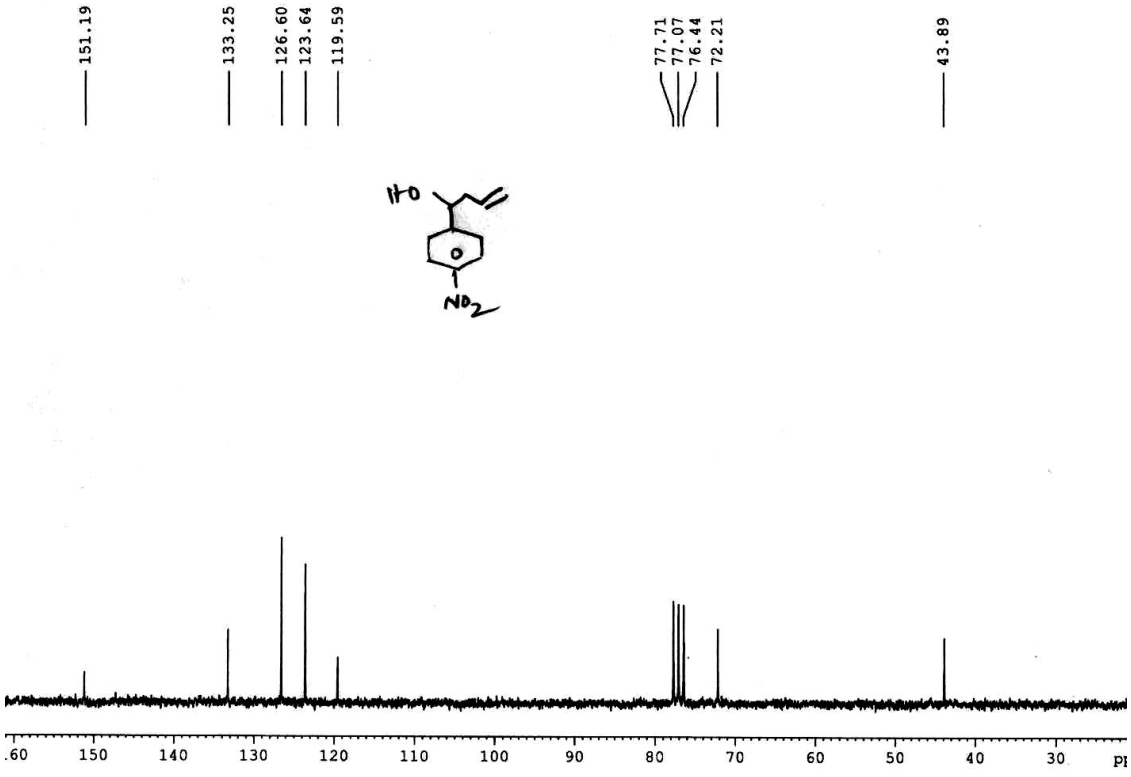
^{13}C-NMR spectrum of 1-Phenylpent-4-en-2-ol (1c):



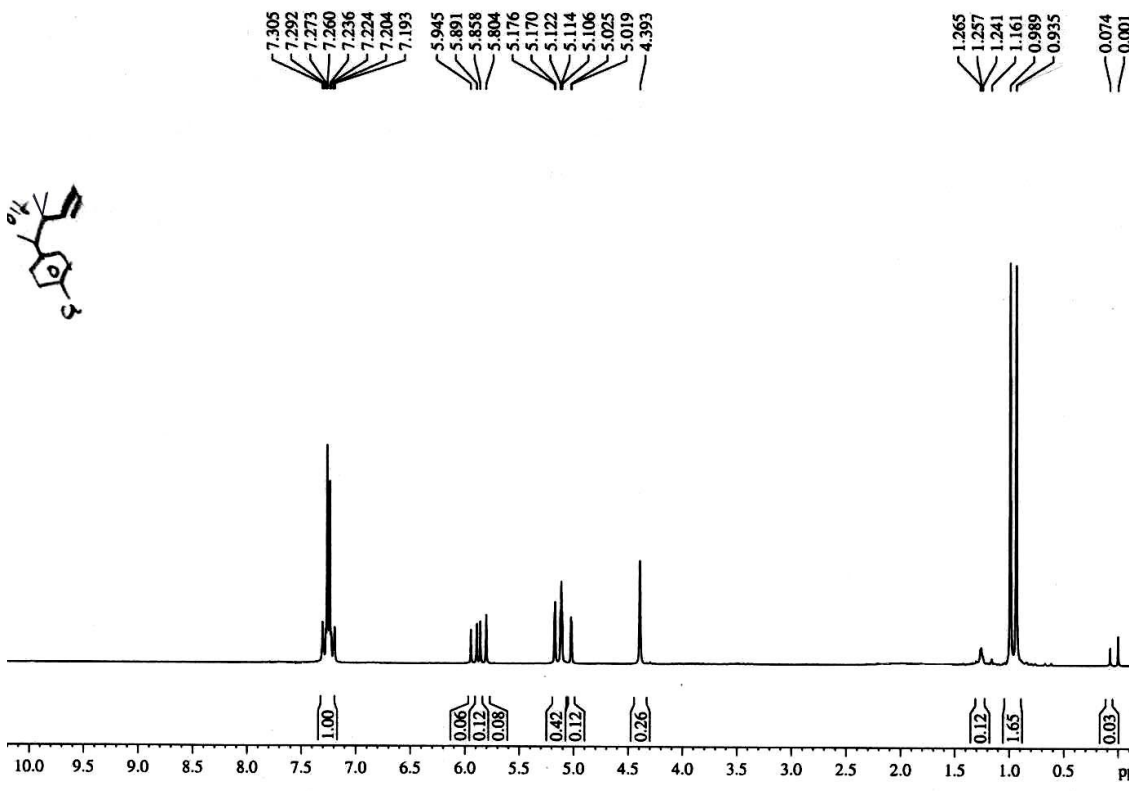
^{1}H NMR spectrum of 1-(4-Nitrophenyl)but-3-en-1-ol (1d):



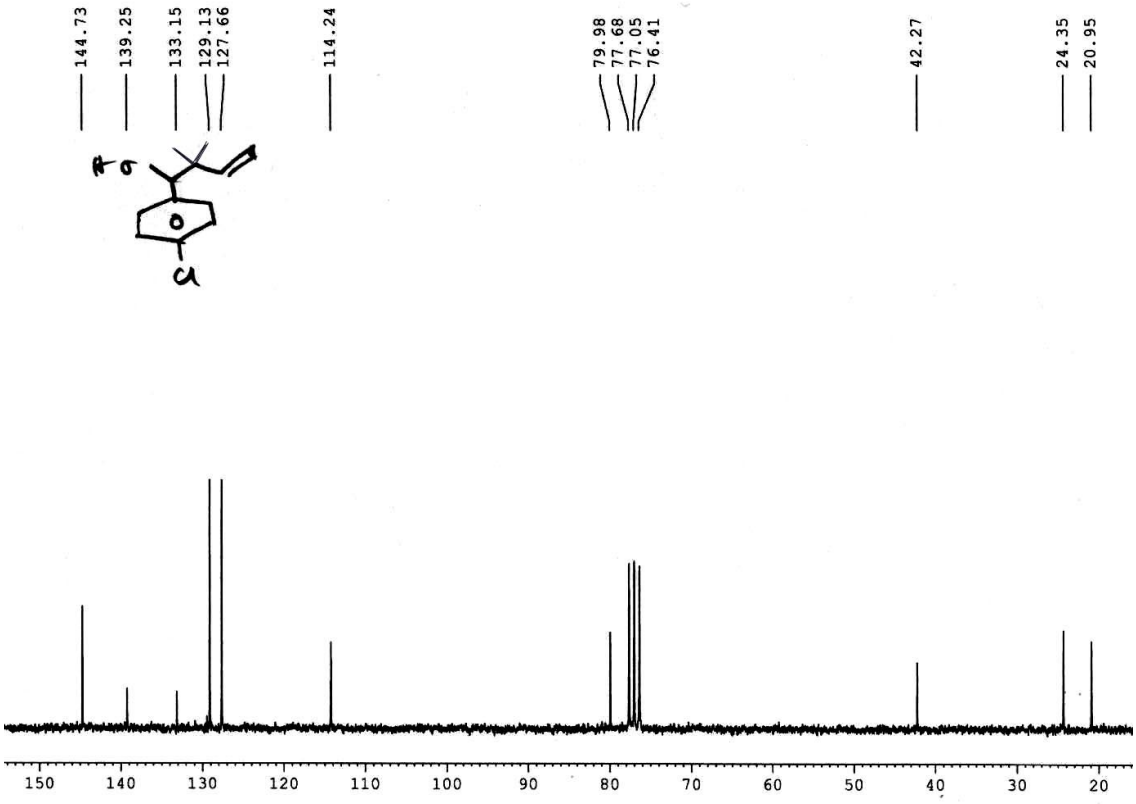
^{13}C-NMR spectrum of 1-(4-Nitrophenyl)but-3-en-1-ol (1d):



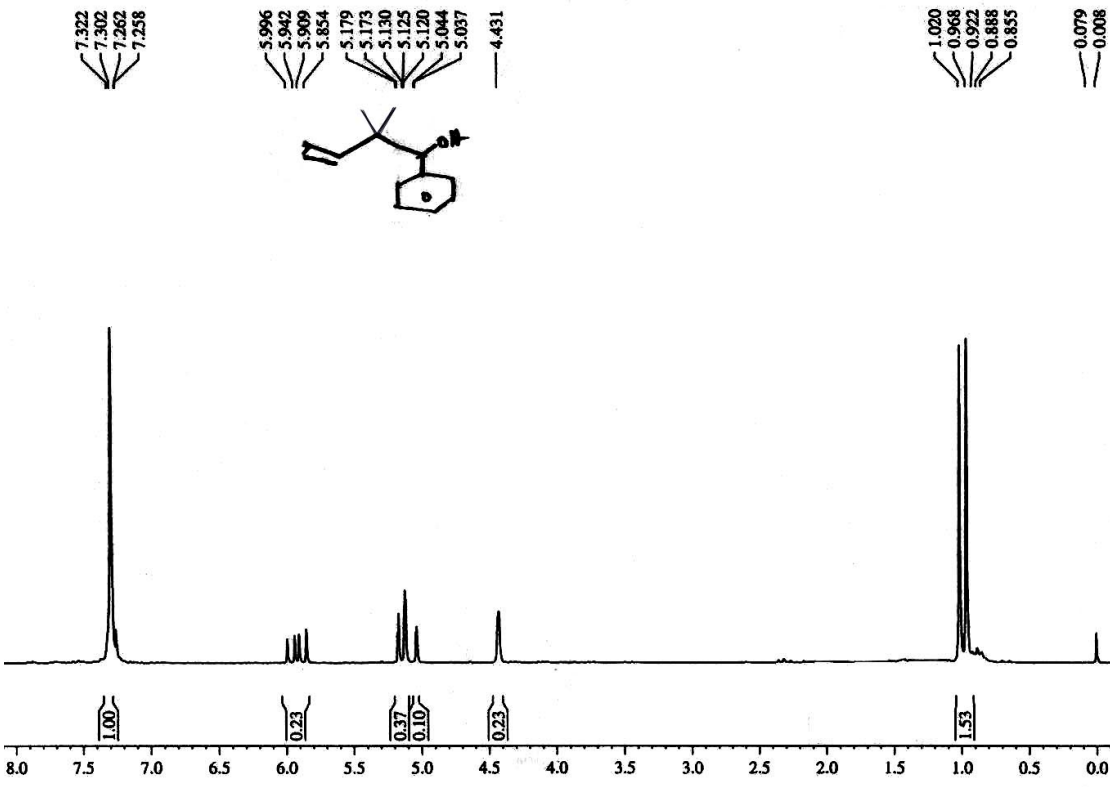
^{1}H NMR spectrum of 1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (1e):



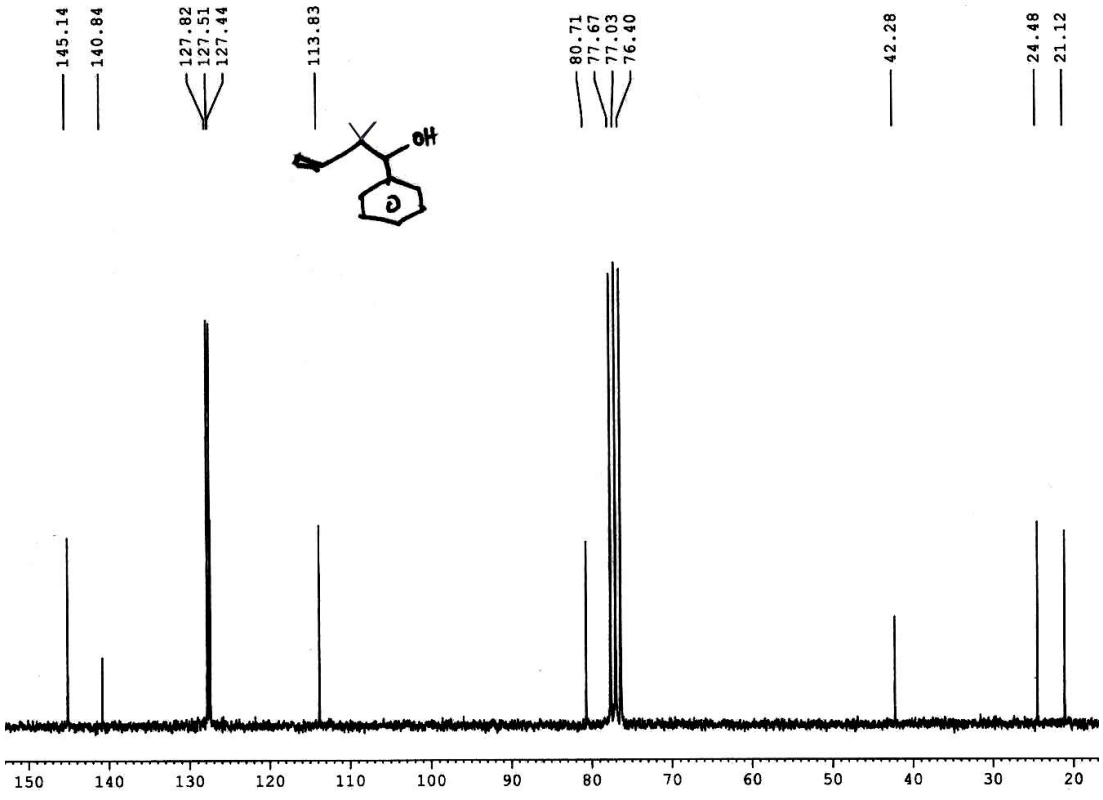
^{13}C-NMR spectrum of 1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (1e):



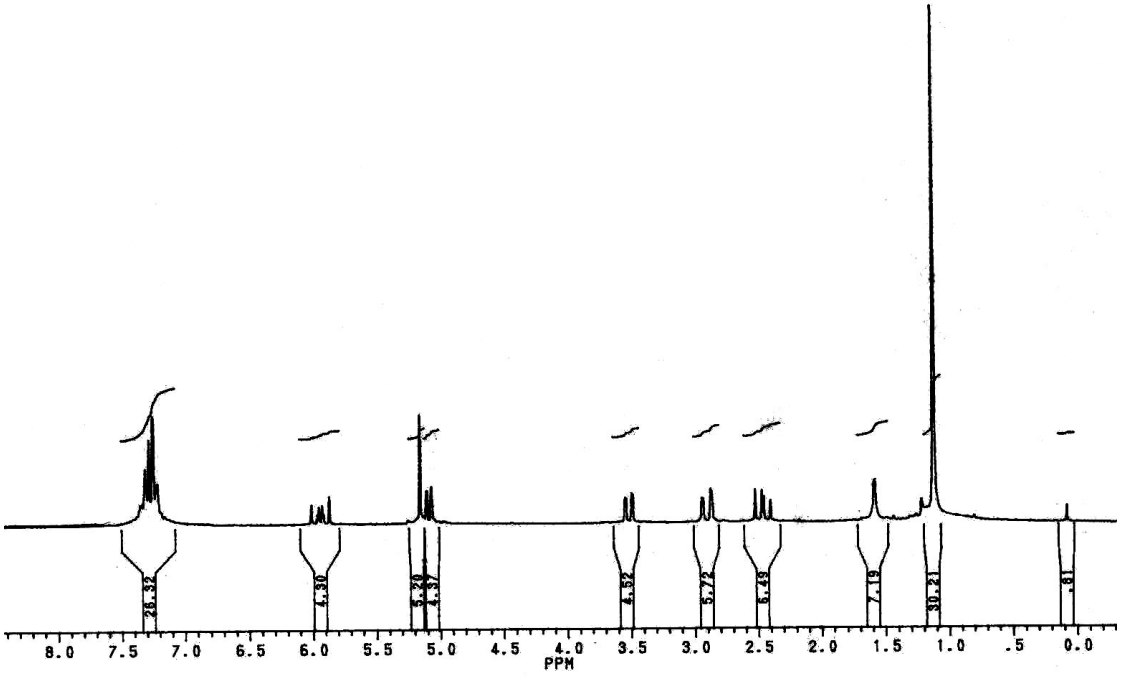
^{1}H NMR spectrum of 2,2-Dimethyl-1-phenylbut-3-en-1-ol (1f):



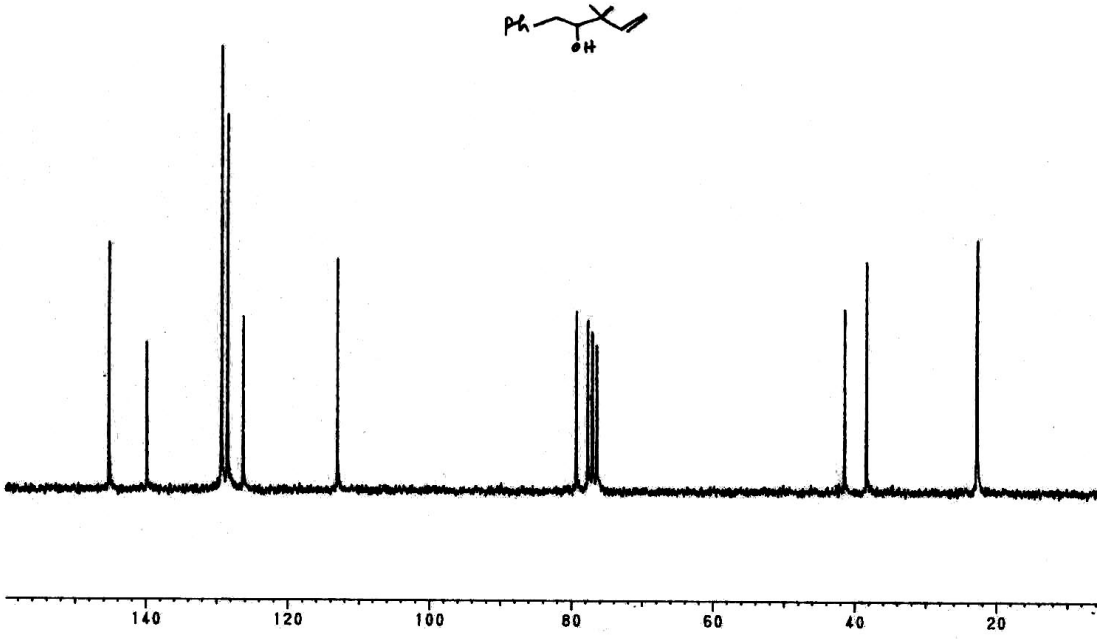
^{13}C-NMR spectrum of 2,2-Dimethyl-1-phenylbut-3-en-1-ol (1f):



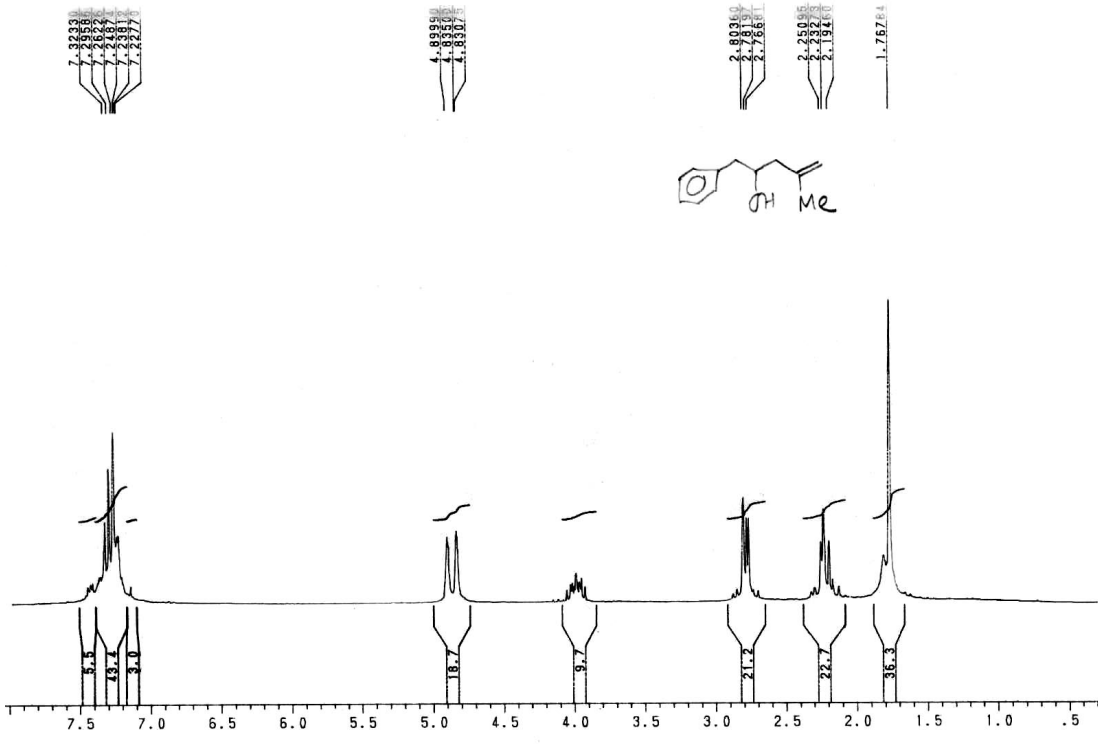
^{1}H NMR spectrum of 3,3-Dimethyl-1-phenylpent-4-en-2-ol (1g):



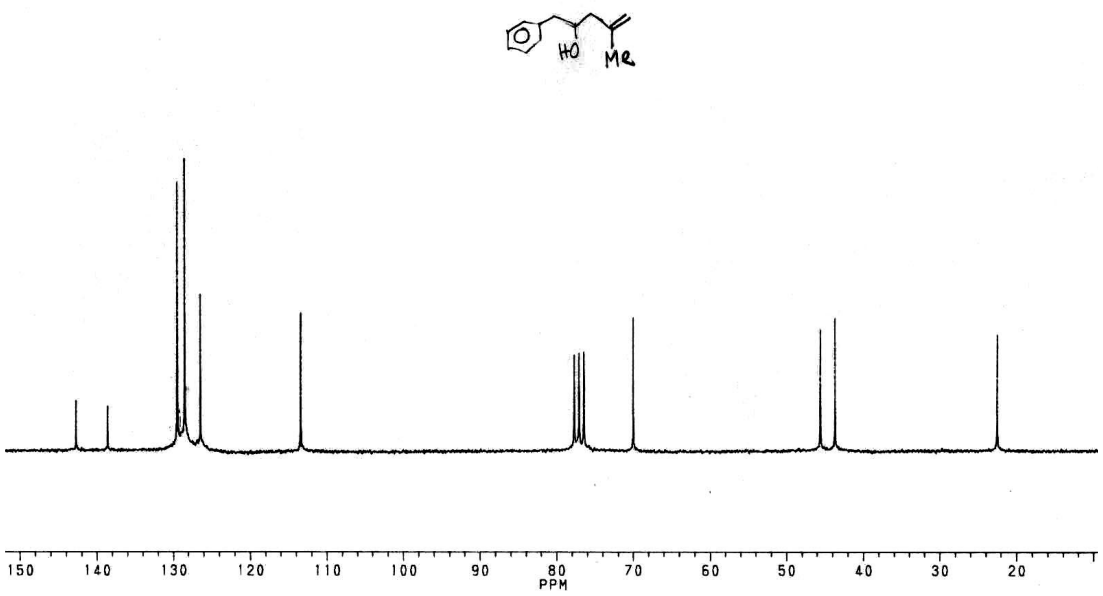
^{13}C-NMR spectrum of 3,3-Dimethyl-1-phenylpent-4-en-2-ol (1g):



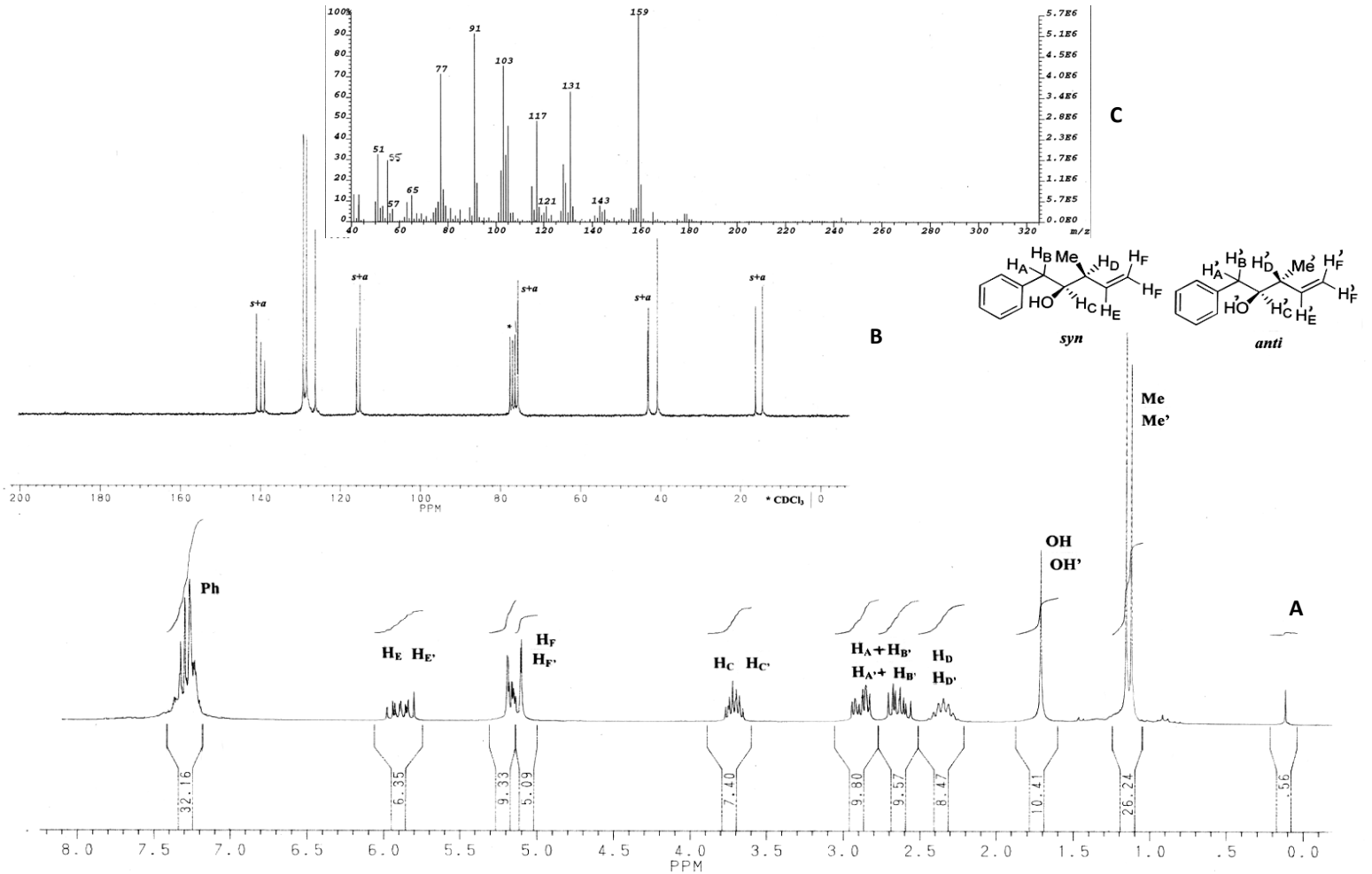
^{1}H NMR spectrum of 4-Methyl-1-phenylpent-4-en-2-ol (1h):



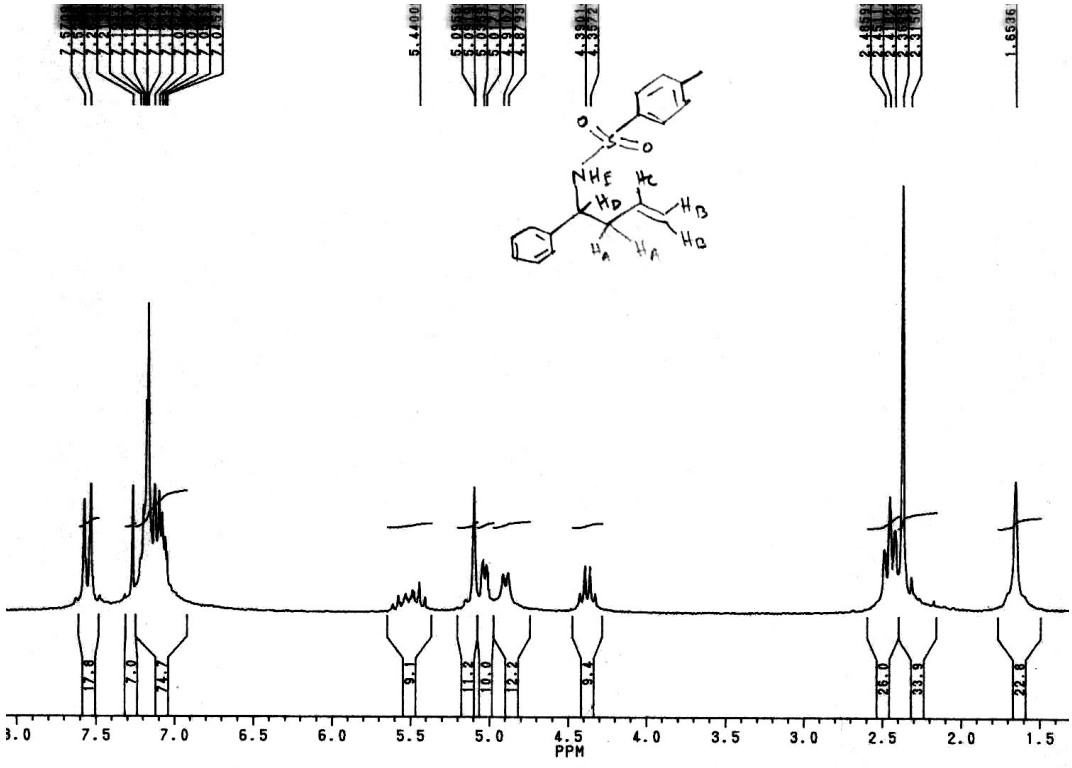
^{13}C-NMR spectrum of 4-Methyl-1-phenylpent-4-en-2-ol (1h):



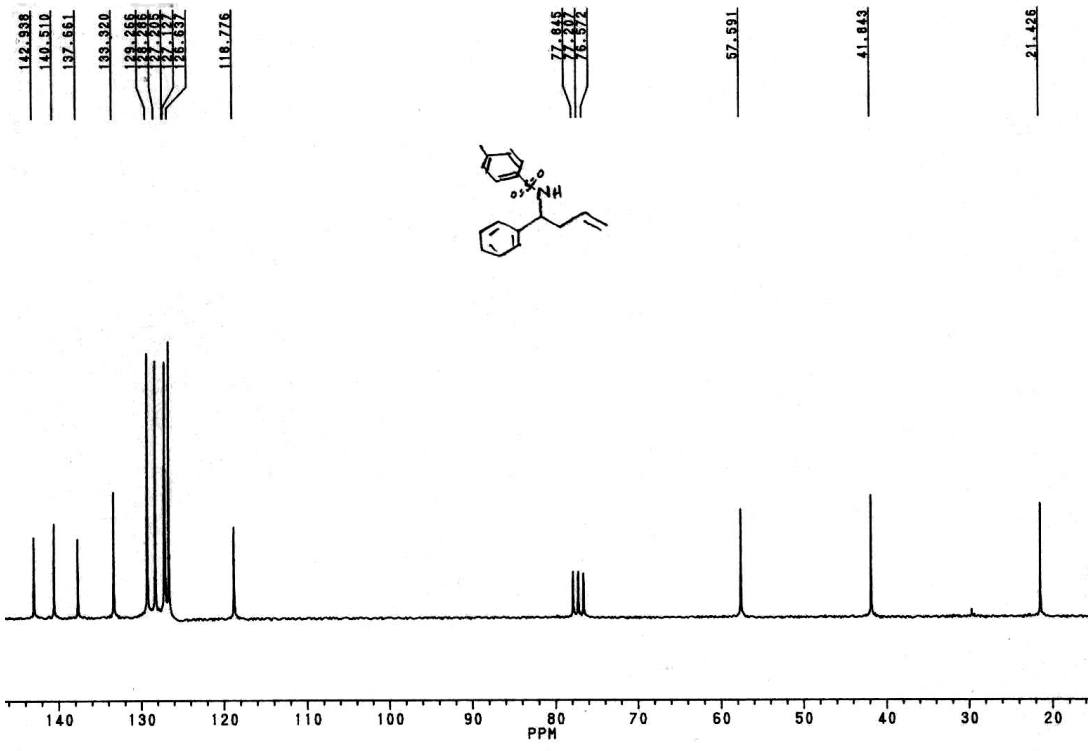
^{1}H-NMR (A), ^{13}C-NMR (B) & EIMS (C) spectra of 3-Methyl-1-phenylpent-4-en-2-ol (1i)



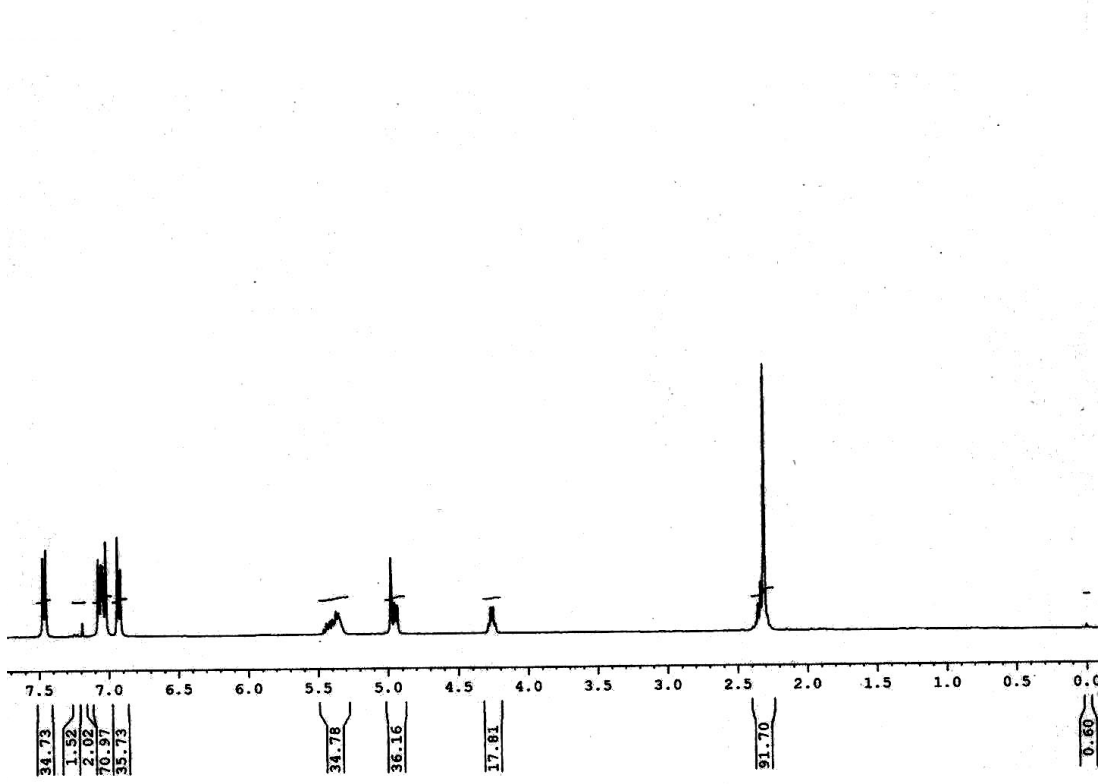
^{1}H NMR spectrum of 4-Methyl-*N*-(1-phenylbut-3-enyl)benzenesulfonamide (2a):



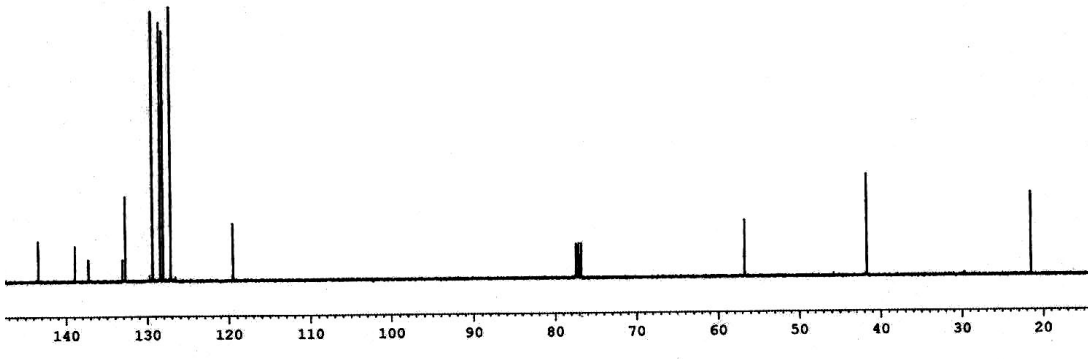
^{13}C-NMR spectrum of 4-Methyl-*N*-(1-phenylbut-3-enyl)benzenesulfonamide (2a):



^{1}H NMR spectrum of *N*-[1-(4-Chlorophenyl)but-3-enyl]-4-methylbenzenesulfonamide (2b):



^{13}C NMR spectrum of *N*-[1-(4-Chlorophenyl)but-3-enyl]-4-methylbenzenesulfonamide (2b):



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