Supporting Information

Copper(I) Iodide Catalyzed Synthesis of Primary Propargylic Alcohols from Terminal Alkyne

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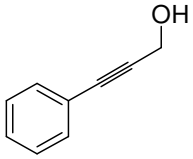
Methods and Materials

General: All reactions carried out in a vial and heated in oil bath. Thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates and the purification of the crude product by column chromatography using 100-200 mesh silica gels (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV-400 Ultra Shield (400 MHz) NMR spectrometers using tetramethylsilane as an internal standard in $CDCl_3$ or d^6 DMSO. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with and FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 mm film thickness.

Materials. All materials were commercially available and purchased from Aldrich, Merck, and other commercial suppliers and were used without further purification.

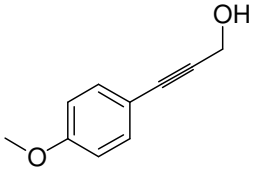
General Experimental procedure: To a stirred solution of terminal alkyne (1eq), para formaldehyde (2 equiv), triethyl amine (1equiv) in DMSO, CuI (0.05 equiv) and KOH (1 equiv) was added. This reaction mixture was heated to 100^0 C for 4-9 hours (monitored by TLC) in an open mouth vessel. After completion of reaction, it was cooled to room temperature and was diluted with ethyl acetate. Organic layer was washed with water, brine, dried over Na_2SO_4 and was concentrated under reduced pressure. The crude was purified by column chromatography on silica gel, 100-200 mesh (eluted with 5-30% ethyl acetate-hexane) to get respective analytically pure product.

^{1}H NMR, ^{13}CNMR and GCMS spectral data of all products:



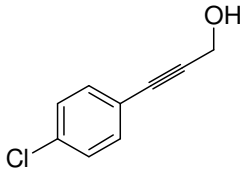
3-phenylprop-2-yn-1-ol (3a):[2]

^{1}H NMR (400MHz, $CDCl_3$): δ 7.46-7.41(m, 2H), 7.31-7.28(m, 3H), 4.49 (d, *J* = 5.4 Hz, 2H), 1.69-1.66 (m, 1H). ^{13}C- NMR (100 MHz, $CDCl_3$): δ 131.61, 128.39, 122.51, 87.27, 85.50, 51.43. GCMS: m/z = 132



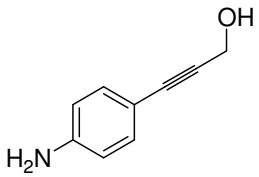
3-(4-methoxyphenyl)prop-2-yn-1-ol (3b):[3]

^{1} NMR (400MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.5 Hz, 2H), 6.83 (d, , *J* = 8.6 Hz, 2H), 4.47-4.46 (d, *J* = 4.8 Hz, 2H), 3.80 (s, 3H), 1.62 (bs, 1H). ^{13}C- NMR(100 MHz,$CDCl_3$): δ 159.82, 133.28, 114.73, 114.05, 86.01, 85.69, 55.38, 51.74. GCMS: m/z = 162.



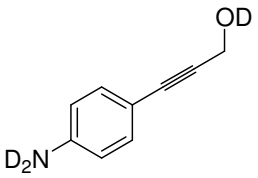
3-(4-chlorophenyl)prop-2-yn-1ol (3c):

^{1}H NMR (400MHz,$CDCl_3$): δ 7.35 (d, *J* = 8.4, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.47 (s, 2H), 1.66 (bS, 1H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 134.69, 133.03, 128.80, 121.12, 88.27, 84.71, 51.67. Anal. Calcd. For (%) C_9H_7ClO C, 64.88; H, 4.23. Found C, 64.85; H, 4.30. GCMS: m/z = 166.



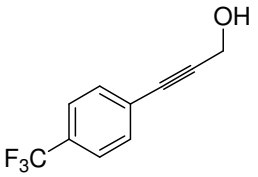
3-(4-aminophenyl)prop-2-yn-1ol (3e):

^{1}H NMR(400 MHz,$CDCl_3$): δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.45 (s, 2H), 3.79 (bS, 2H), 1.6 (bs, 1H). ^{13}C-NMR (100MHz, DMSO-d_6): δ 149.52, 132.61, 114.02, 108.99, 86.97, 85.50, 50.01. Anal. Calcd. For (%) C_9H_9NO. C, 73.45; H, 6.16; N, 9.52. Found C, 73.54; H, 6.25; N, 9.55. GCMS: m/z = 147.



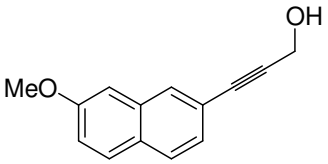
D_2O exchange of 3-(4-aminophenyl) prop-2-yn-1ol:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.59-6.57(d, *J* = 8.4 Hz,2H), 4.44 (s, 2H).



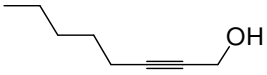
3-(4-(trifluoromethyl) phenyl) prop-2-yn-1-ol (3f):[3]

^{1}H NMR (400MHz, DMSO-d_6): δ 7.54 (m, 4H), 4.51 (d, *J* = 6.2 Hz, 2H), 1.68 (t, *J* = 6.2 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 131.8, 130.2 ($^2J_{C\text{-}F}$ = 33 Hz), 126.3, 125.2 ($^3J_{C\text{-}F}$ = 4 Hz), 123.8 ($^1J_{C\text{-}F}$ = 271 Hz), 89.6, 84.2, 51.3. GCMS: m/z = 200.



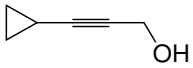
3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-ol (3g):

^{1}H NMR (400MHz, DMSO-d_6): δ 7.95 (s, 1H), 7.76 (m, 2H), 7.42 (d, *J* = 9.2 Hz, 1H), 7.33 (s, 1H), 7.19 (dd, *J* = 6.4 Hz, 2.4 Hz, 1H), 5.32 (t, *J* = 6 Hz, 1H), 4.33 (d, *J* = 6 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.35, 134.20, 131.48, 129.31, 128.93, 126.80, 119.42, 117.36, 105.74, 86.77, 86.20, 55.33, 51.75. Anal. Calcd. For (%)$C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found C, 78.84; H, 5.18. GCMS: m/z = 212.



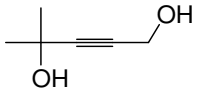
Oct-2-yn-1-ol (3i):[2]

^{1}H NMR (400MHz, DMSO-d_6): δ 5.00 (t, *J* = 4.1 Hz, 1H), 4.02-4.00 (m, 2H), 2.19-2.14 (m, 2H), 1.44-1.39 (m, 2H), 1.34-1.23 (m,4H), 0.88-0.84 (m,J=8Hz,3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.76, 78.40, 51.51, 31.15, 28.41, 22.32, 18.82, 14.07. GCMS: m/z = 126.



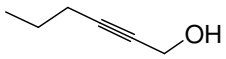
3-cyclopropylprop-2-yn-1-ol (3j):

^{1}H NMR (400MHz,DMSO-d_6): δ 4.99 (t, *J* = 3.9 Hz, 2H), 3.98 (dd, *J* = 4 Hz, 2 Hz, 2H), 1.32-1.25 (m, 1H), 0.78-0.70 (m, 2H), 0.57-0.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.26, 73.71, 50.83, 8.03. Anal. Calcd. For (%) C_6H_8O: C, 74.97; H, 8.39 Found C, 75.18; H, 8.52. GCMS: m/z = 96.



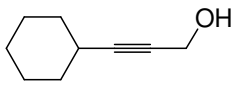
4-methylpent-2-yne-1, 4-diol (3k):

^{1}H MNR (400MHz, DMSO-d_6): δ 5.23 (s, 1H), 5.09 (t, *J* = 5.9 Hz, 1H), 4.05 (d, J = 5.9 Hz,2H), 1.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 90.36, 80.40, 65.13, 50.55, 31.30. Anal. Calcd. For (%) $C_6H_{10}O_2$: C, 63.14; H, 8.83 Found C, 63.19; H, 8.91. GCMS: m/z =114.



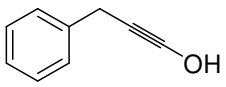
Hex-2-yn-1-ol (3l):[2]

^{1}H NMR (400MHz, DMSO-d_6): δ 5.01 (t, *J* = 5.8 Hz, 1H), 4.03-4.01 (m, 2H), 2.17-2.11 (m, 2H), 1.49-1.40 (m, 2H), 0.92(t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.33, 78.39, 51.28, 23.96, 20.64, 13.40. GCMS: m/z = 98.



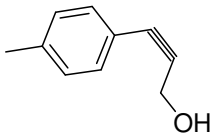
3-cyclohexylprop-2-yn-1-ol (3m):

^{1}H NMR (400MHz, DMSO-d_6): δ 5.01 (t, *J* = 5.8 Hz, 2H), 4.03-4.01(m, 2H), 2.38 (bs, 1H), 1.74-1.71 (m, 2H), 1.63-1.62 (m, 2H), 1.48 (bs, 1H), 1.34-1.24 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 90.72, 78.32, 51.47, 32.73, 29.20, 25.93, 25.02. Anal. Calcd. For (%) $C_9H_{14}O$: C, 78.21; H, 10.21. Found C, 78.35; H, 10.33. GCMS: m/z = 138.



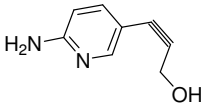
4-phenylbut-2-yn-1-ol (3n):

^{1}H NMR (400MHz, DMSO-d_6): δ 7.41-7.28 (m, 5H), 4.97-4.92 (m, 1H), 4.88-4.85 (m, 1H), 3.46 (t, *J* = 5.2 Hz, 2H). Anal. Calcd. For (%) C_9H_8O: C, 81.79; H, 6.10. Found C, 81.87; H, 6.30. GCMS: m/z = 146.



3-*p*-tolylprop-2-yn-1-ol (3o)

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.30 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 5.29 (t, *J* = 6 Hz, 1H), 4.27 (d, *J* = 6 Hz, 2H), 2.30 (s, 3H). Anal. Calcd. For (%) $C_{10}H_{10}O$: C, 82.16; H, 6.89; Found C, 82.36; H, 6.95;. GCMS: m/z = 146.

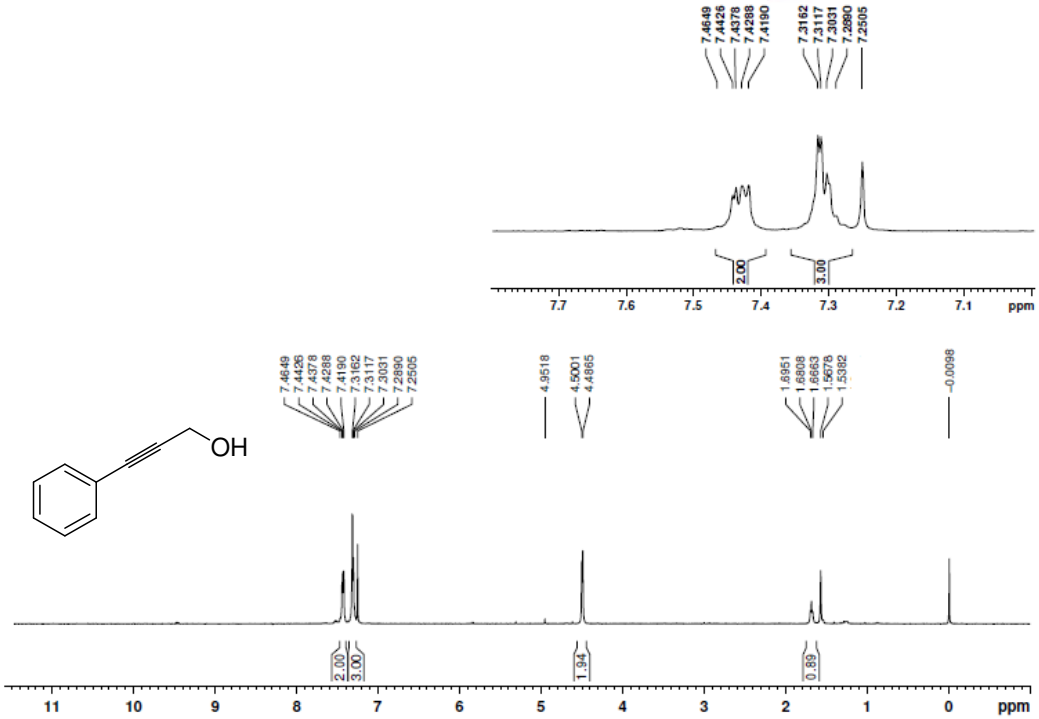


3-(6-aminopyridin-3-yl)prop-2-yn-1-ol(3p)

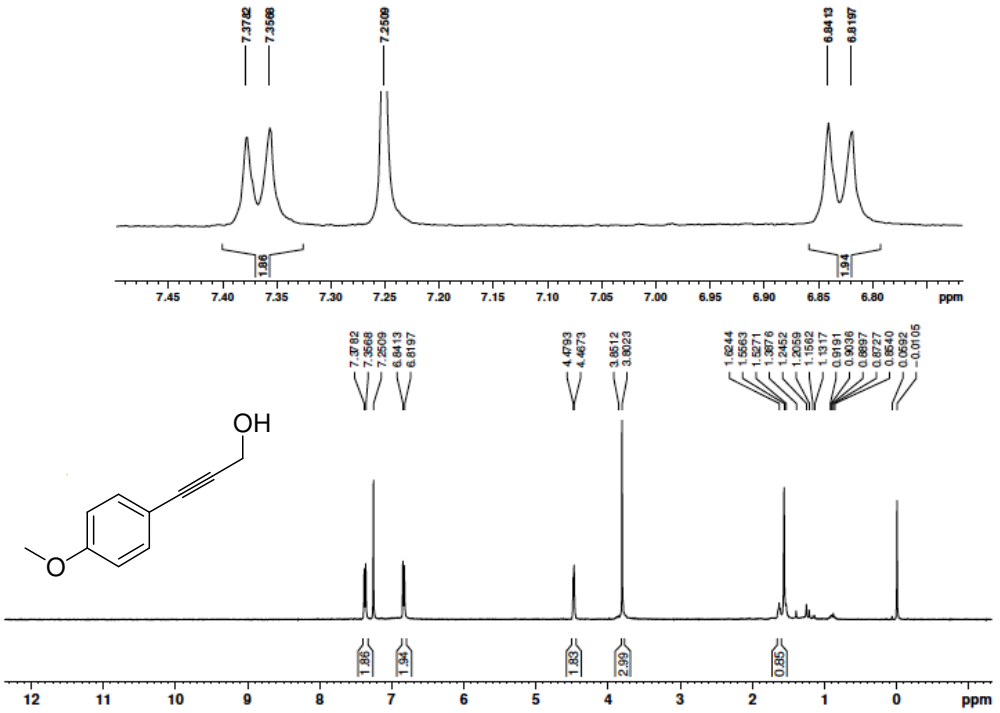
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (s, 1H), 7.41 (d, *J* = 8 Hz, 2H), 6.54 (d, *J* = 8 Hz, 2H), 5.24 (t, *J* = 6 Hz, 1H), 4.86 (s, 1H), 4.25(d, *J* = 6 Hz, 2H),. Anal. Calcd. For (%) $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91; Found C, 64.55; H, 5.21; N, 18.65. LCMS: m/z = 149.2

^{1}H NMR, ^{13}CNMR spectra and GCMS spectra of all products: ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6, in these spectra there is some unwanted peak of solvent impurity[1].

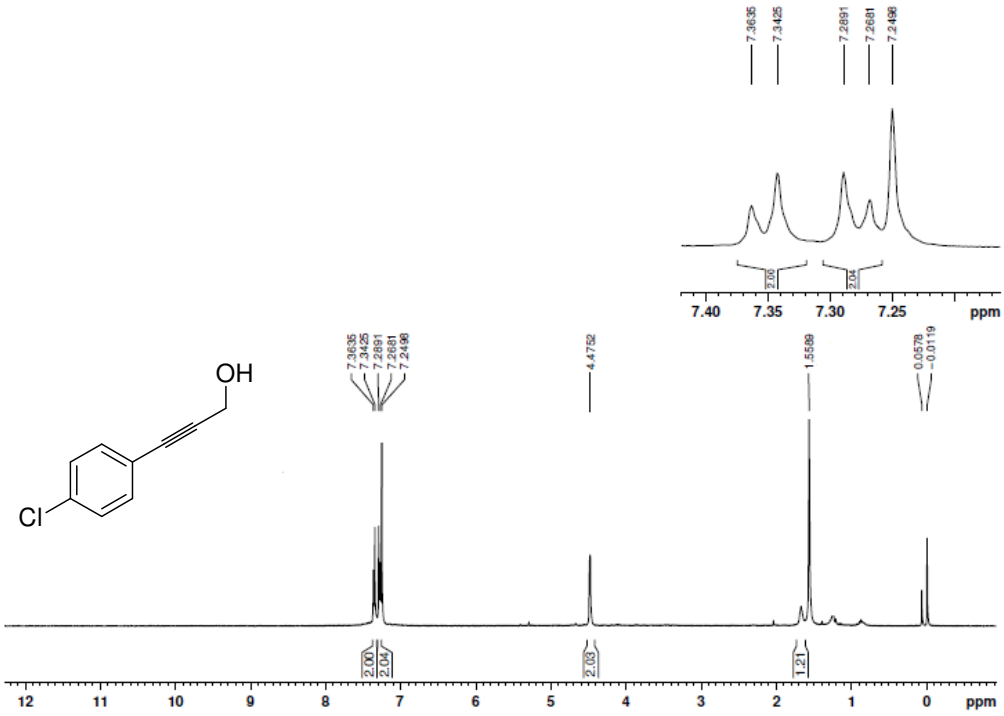
1H NMR of 3-phenylprop-2-yn-1-ol in CDCl3 , 400 MHz (3a)



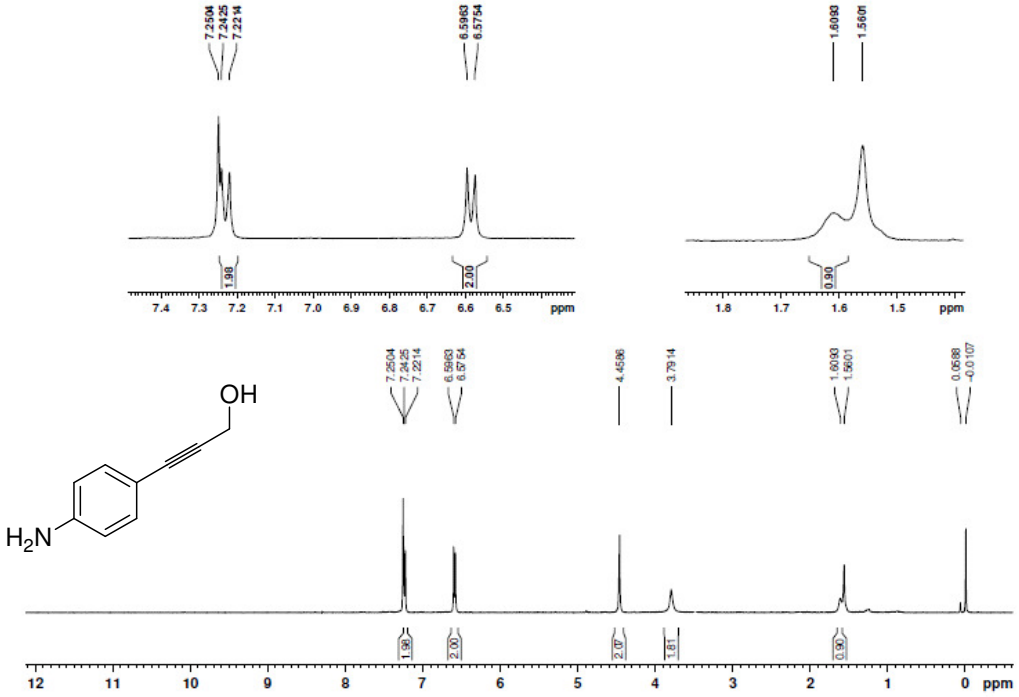
1H NMR of 3-(4-methoxyphenyl)prop-2-yn-1-ol in CDCl3 , 400 MHz (3b)



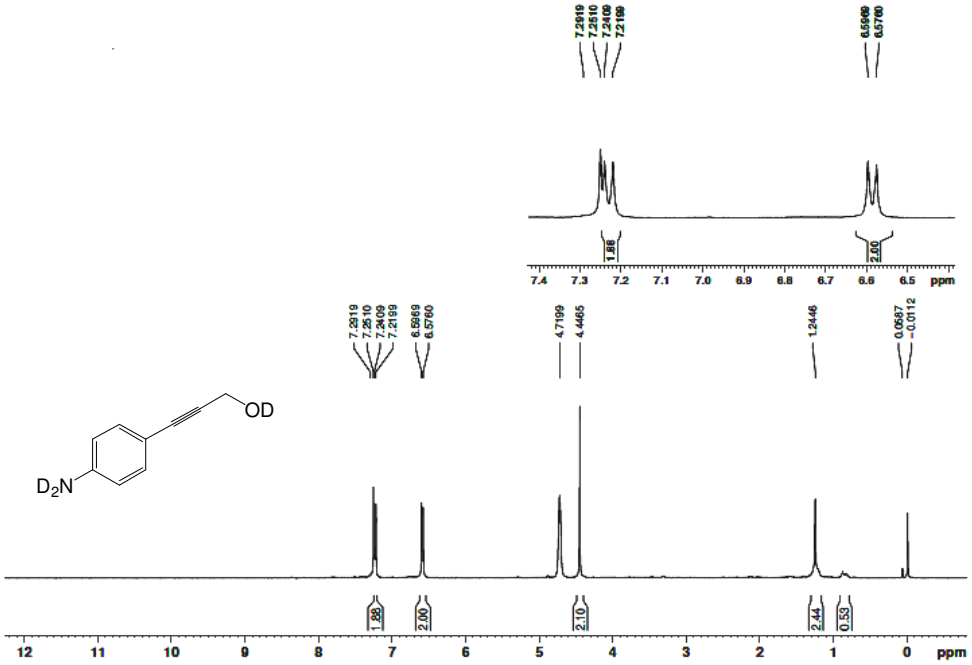
1H NMR of 3-(4-chlorophenyl)prop-2-yn-1-ol in CDCl3 , 400 MHz (3c)



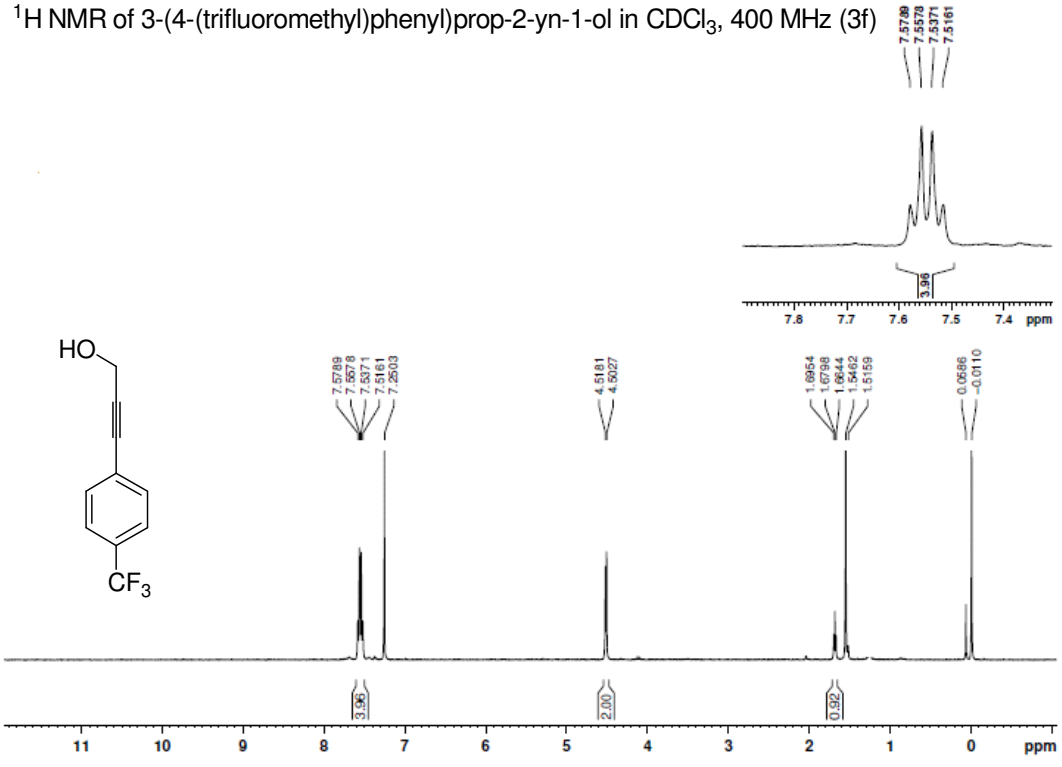
^{1}H NMR of 3-(4-aminophenyl)prop-2-yn-1-ol in $CDCl_3$, 400 MHz (3e)



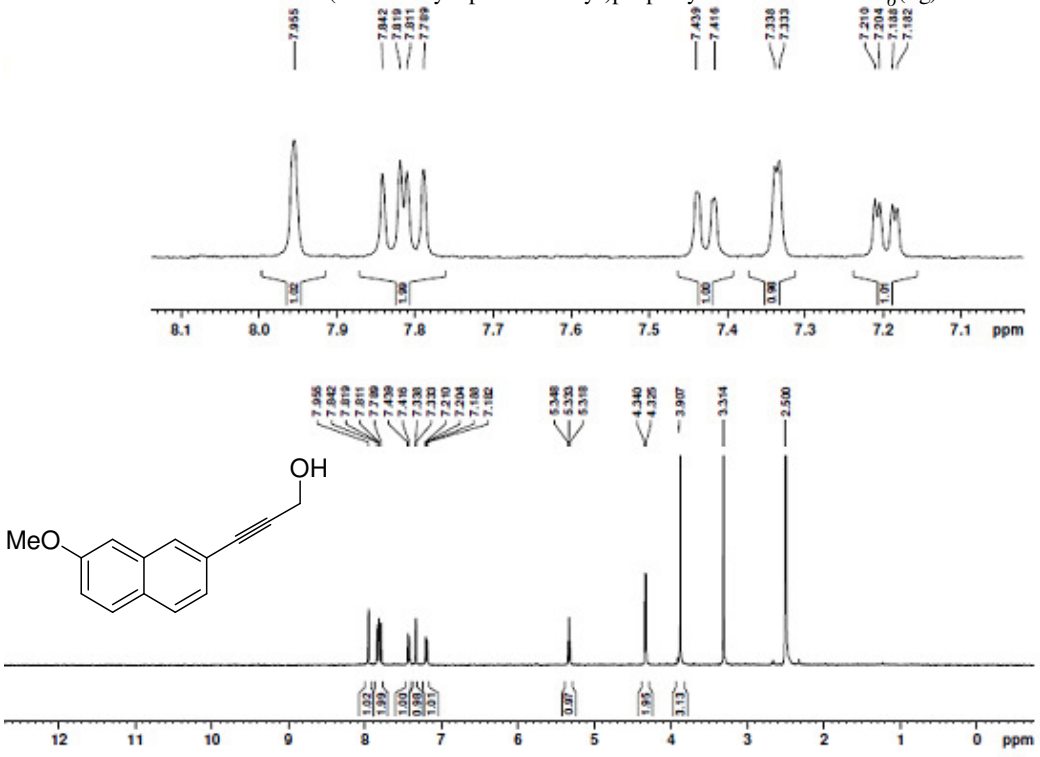
^{1}H NMR of D_2O exchange of 3-(4-aminophenyl)prop-2-yn-1-ol in $CDCl_3$, 400 MHz



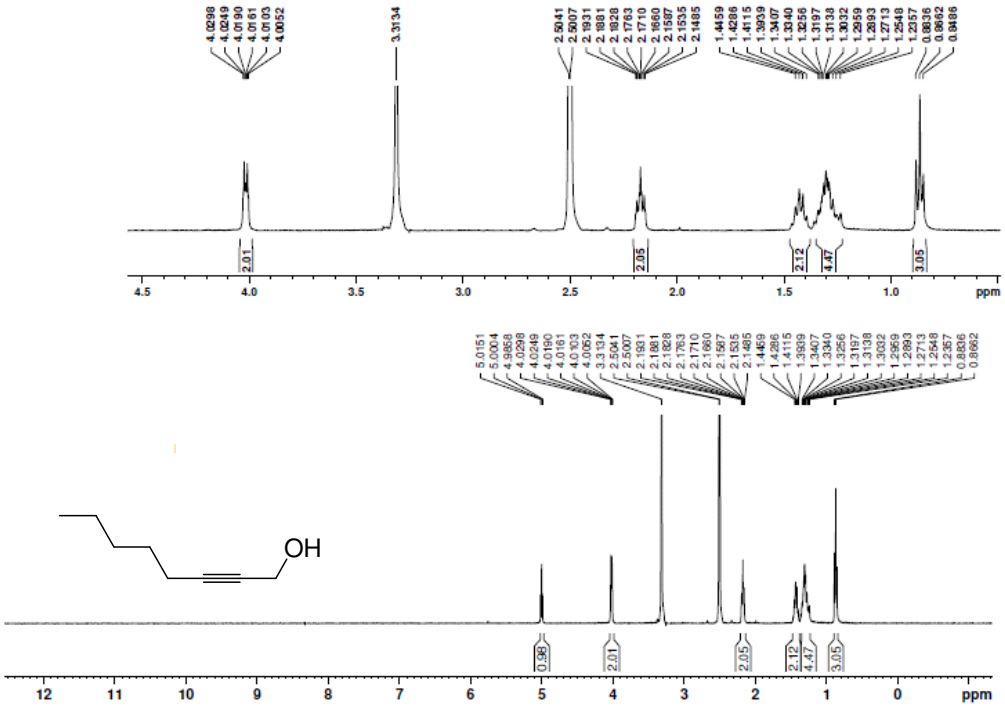
^{1}H NMR of 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol in $CDCl_3$, 400 MHz (3f)



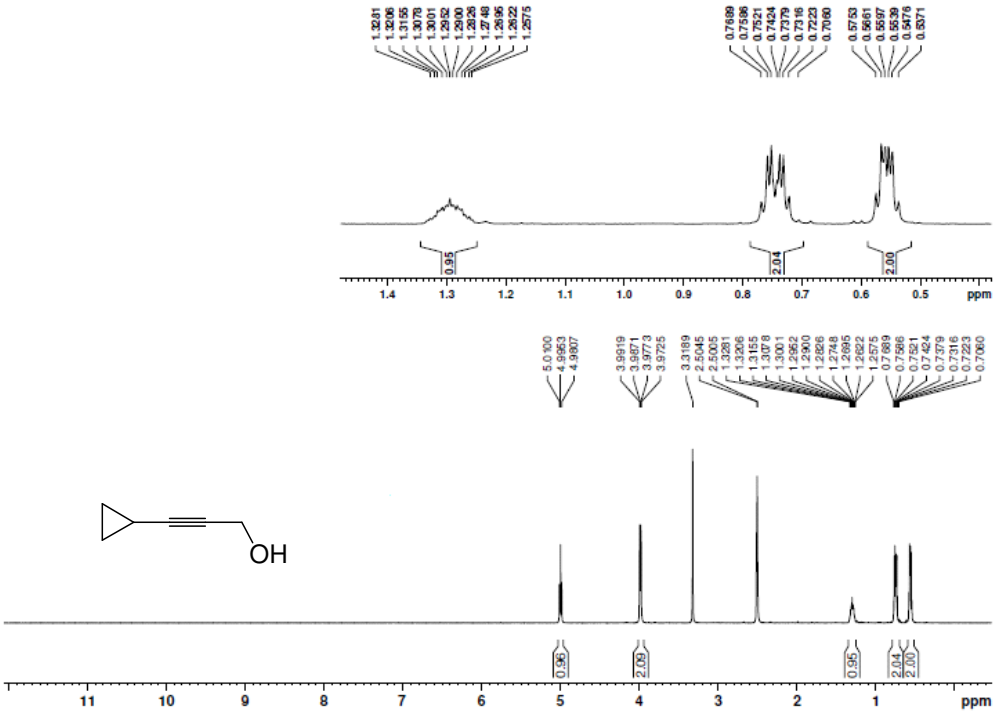
^{1}H NMR of 3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-ol in DMSO-d_6(3g)



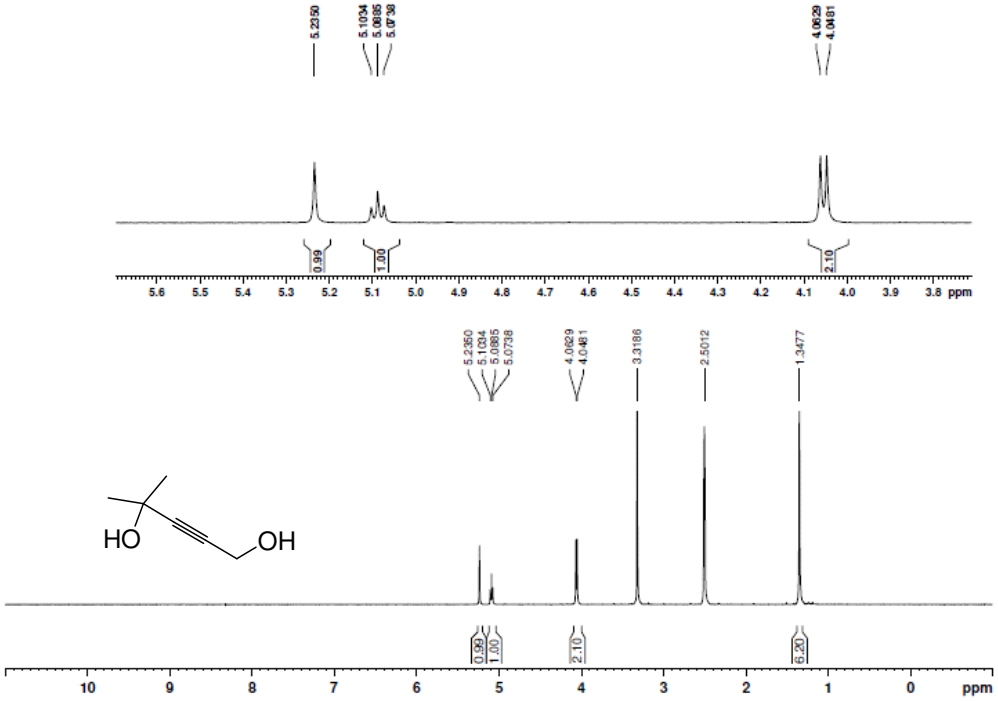
^{1}H NMR of oct-2-yn-1-ol in DMSO-d_6, 400 MHz (3i)



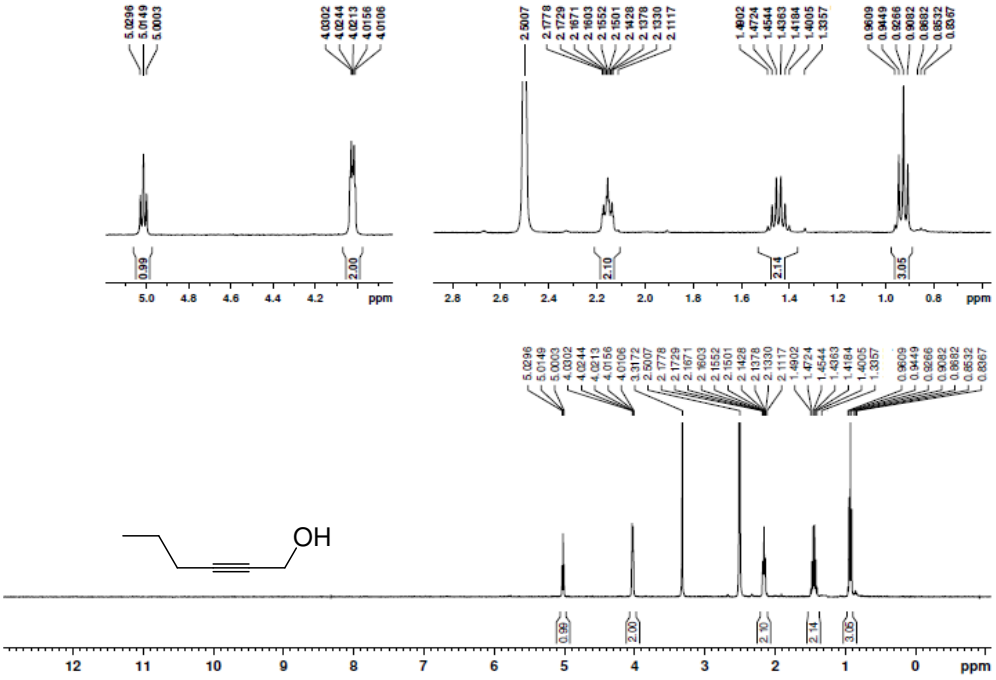
^{1}H NMR of 3-cyclohexylprop-2-yn-1-ol in DMSO-d_6, 400 MHz (3j)



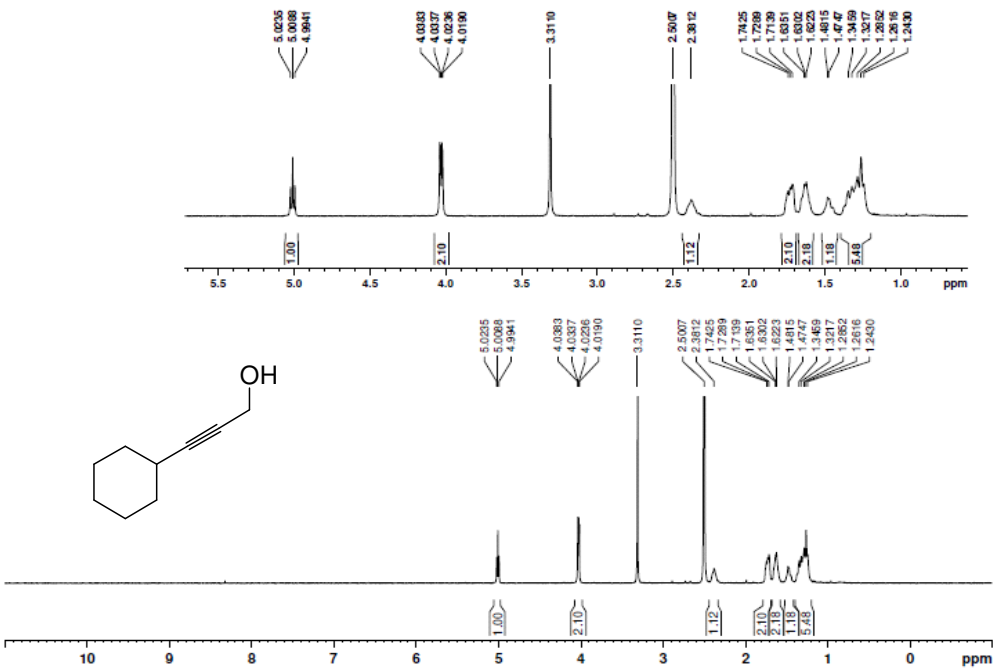
^{1}H NMR of 4-methylpent-2-yne-1,4-diol in DMSO-d_6, 400 MHz (3k)



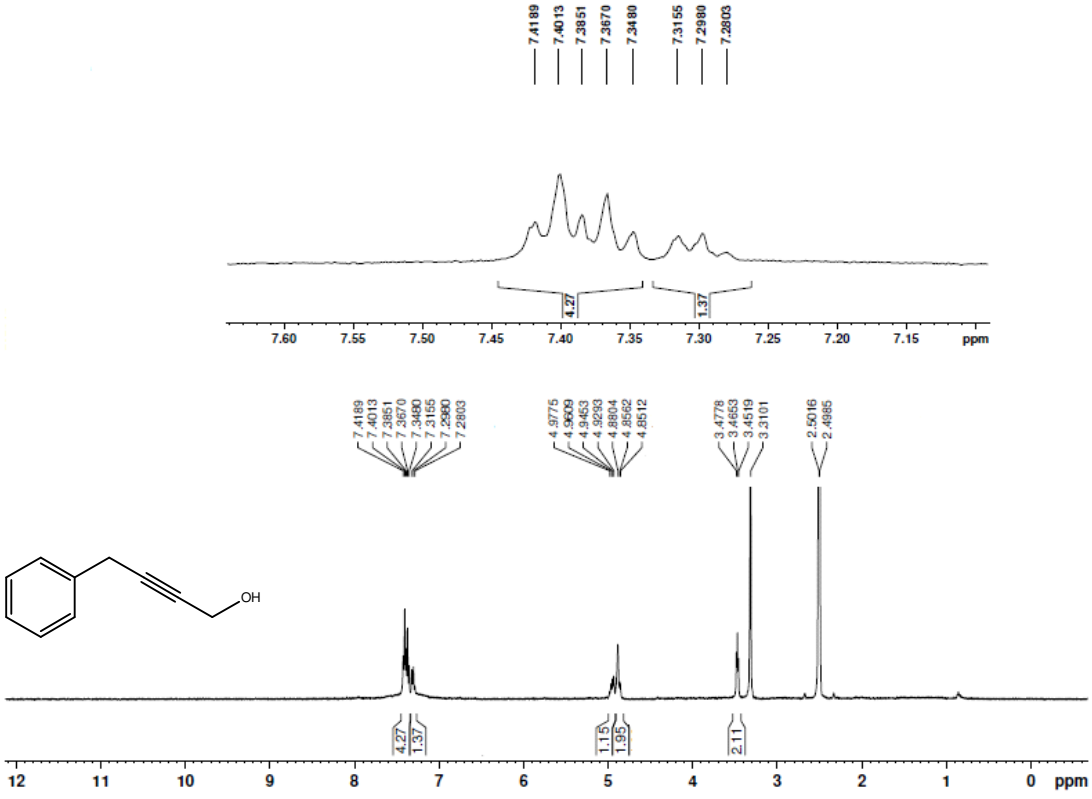
^{1}H NMR of Hex-2-yn-1-ol in DMSO-d_6, 400 MHz (3l)



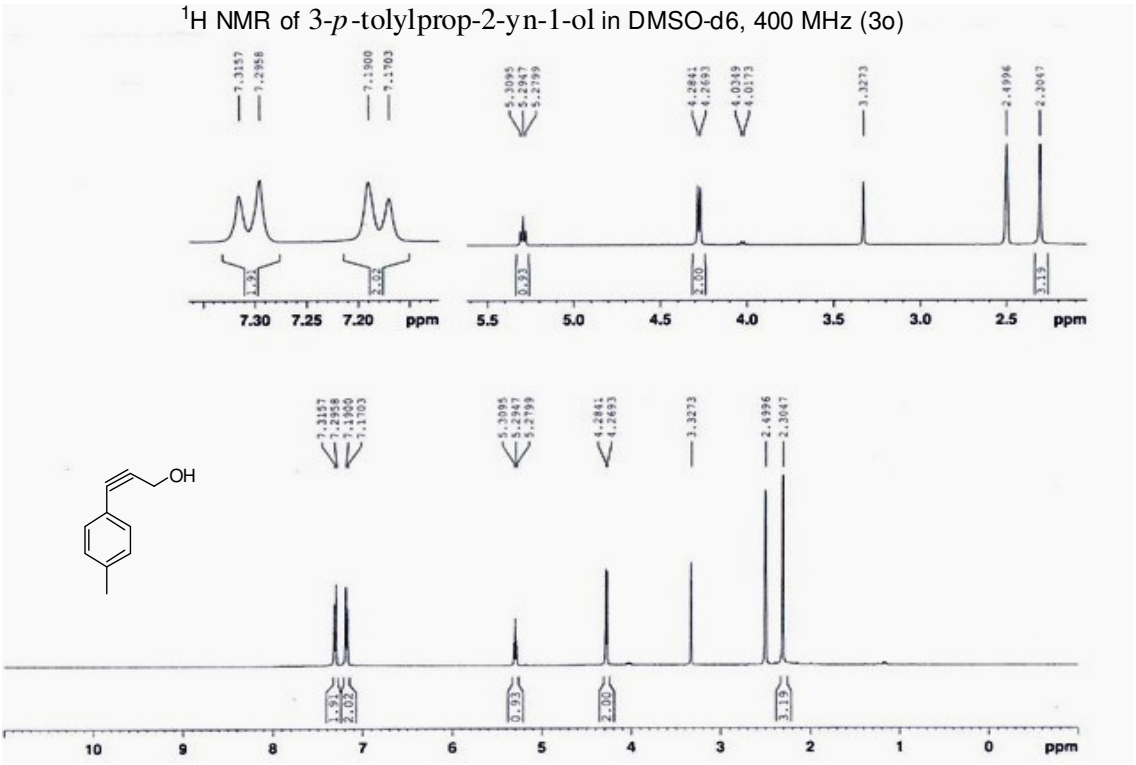
^{1}H NMR of 3-cyclohexylprop-2-yn-1-ol in DMSO-d_6, 400 MHz (3m)



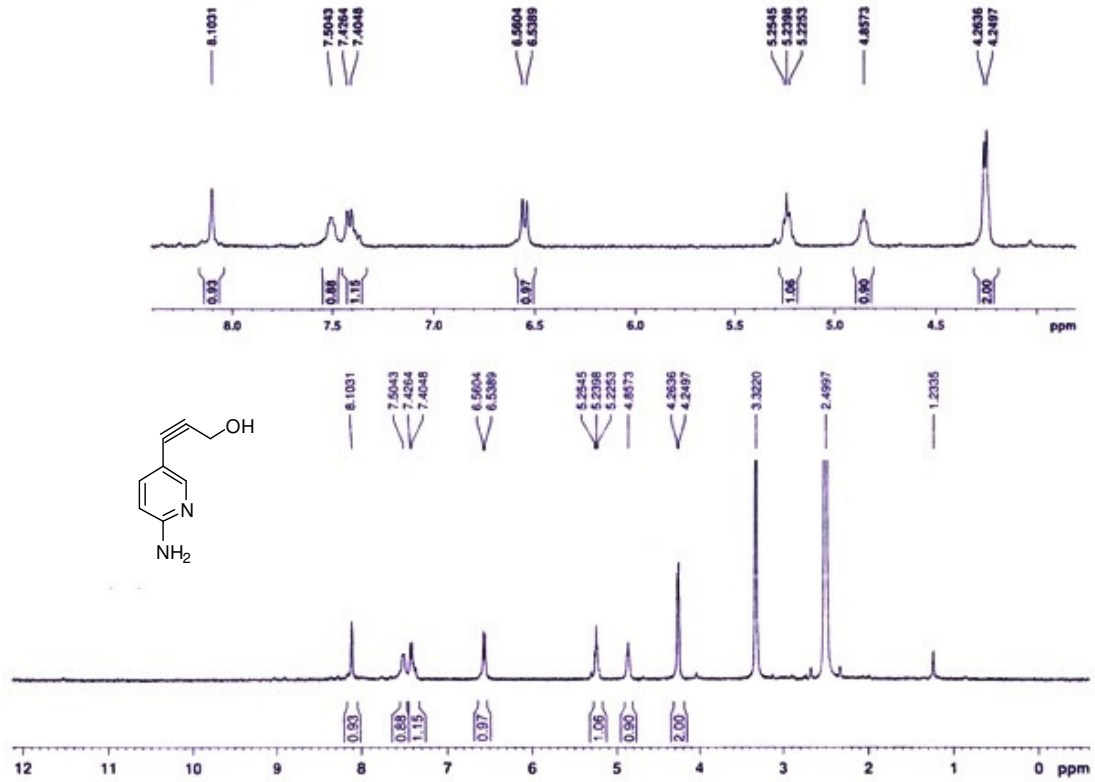
^{1}H NMR of 4-phenylbut-2-yn-1-ol in DMSO-d_6, 400 MHz (3n)



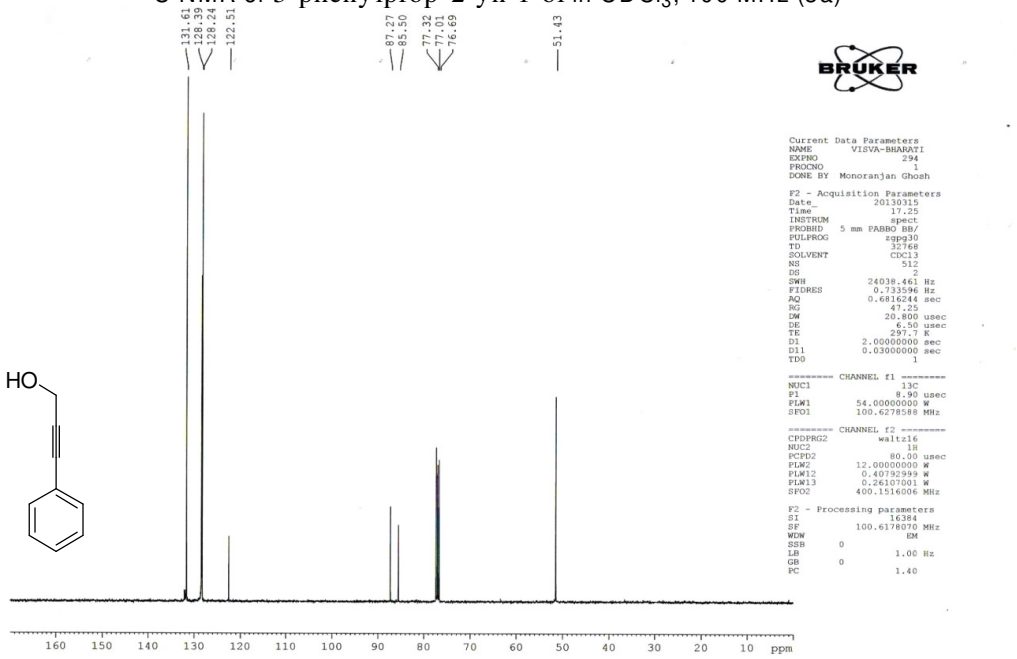
^{1}H NMR of 3-*p*-tolylprop-2-yn-1-ol in DMSO-d6, 400 MHz (3o)



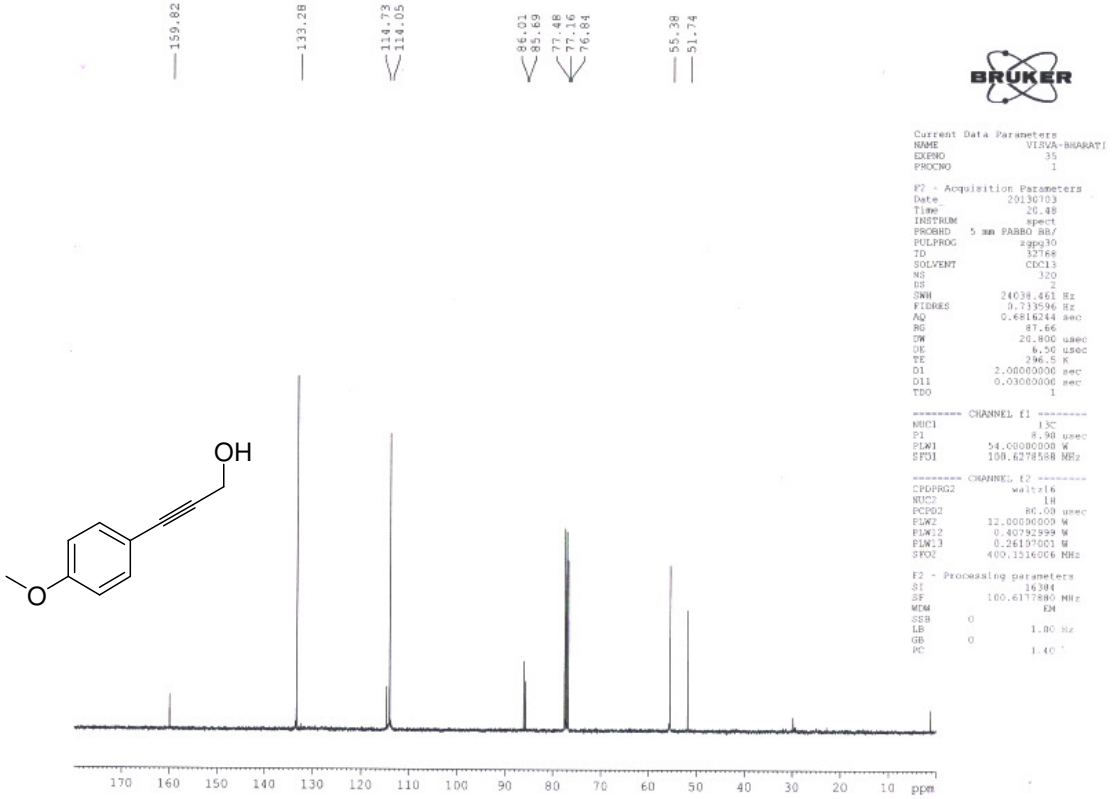
^{1}H NMR of 3-(6-aminopyridin-3-yl)prop-2-yn-1-ol in d^{6}DMSO, 400MHz(3p)



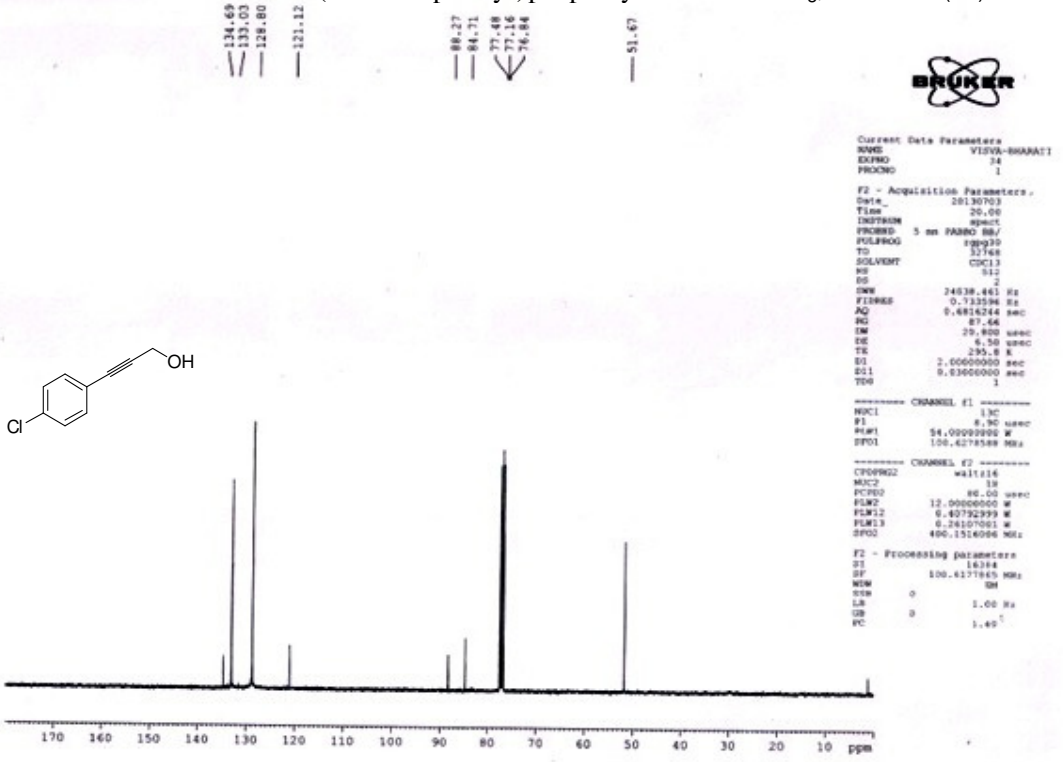
^{13}C NMR of 3-phenylprop-2-yn-1-ol in $CDCl_3$, 100 MHz (3a)



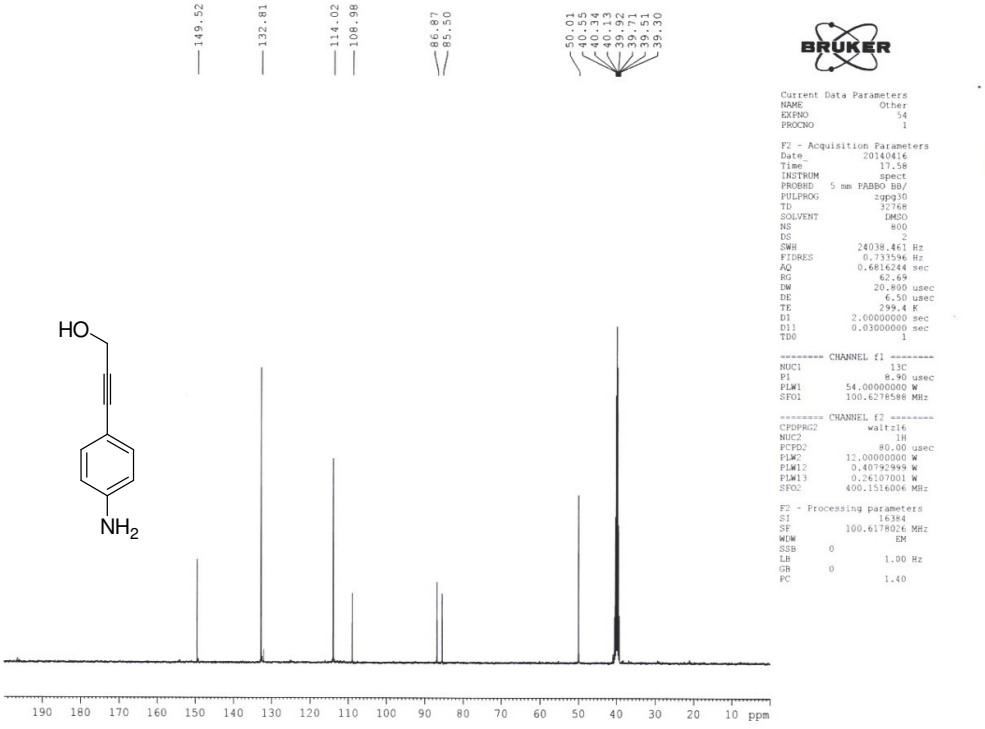
^{13}C NMR of 3-(4-methoxyphenyl)prop-2-yn-1-ol in $CDCl_3$, 400 MHz (3b)



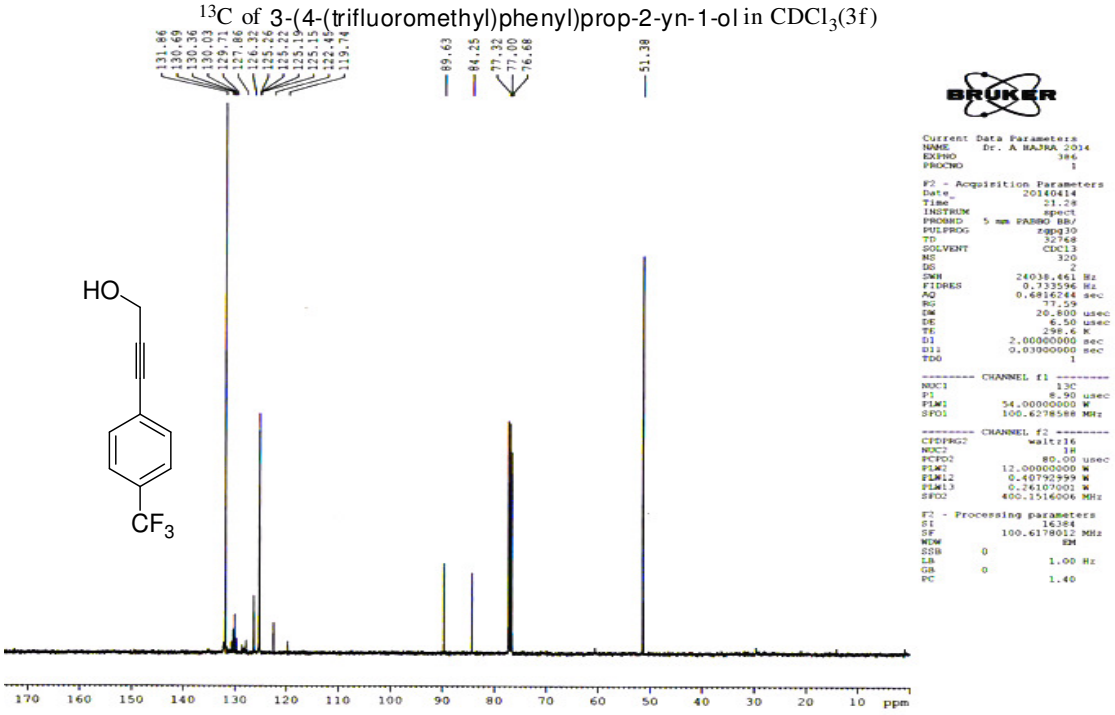
^{13}C NMR of 3-(4-chlorophenyl)prop-2-yn-1-ol in $CDCl_3$, 100 MHz (3c)



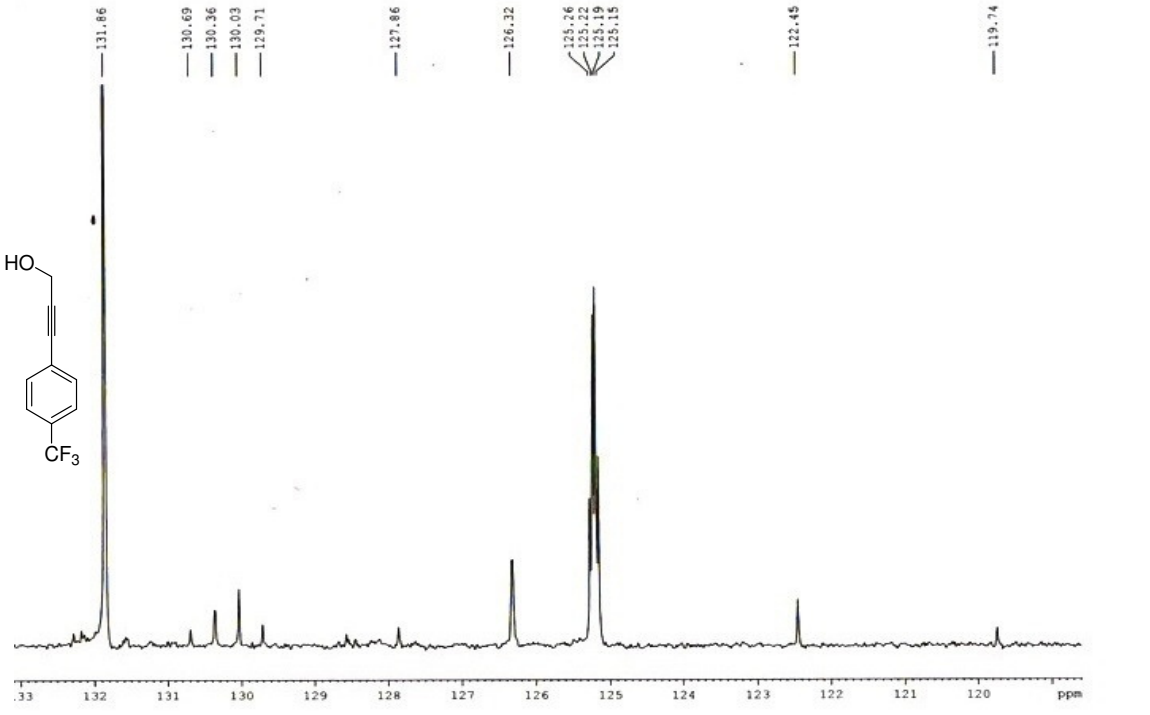
^{13}C NMR of 3-(4-aminophenyl)prop-2-yn-1-ol in DMSO-d_6, 100 MHz (3e)



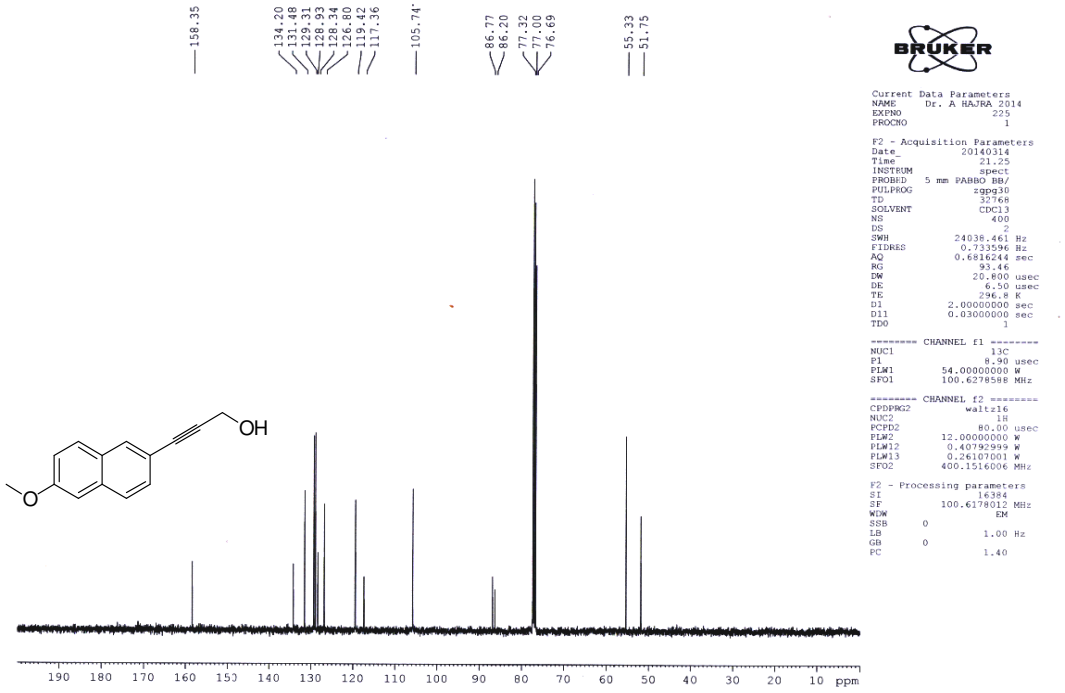
^{13}C of 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol in $CDCl_3$(3f)



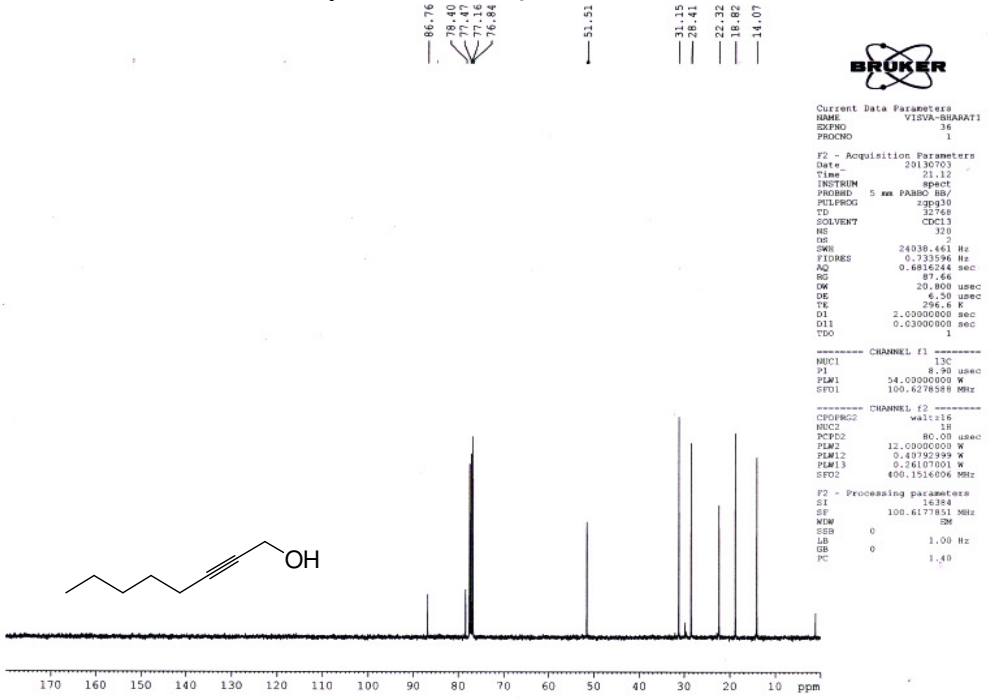
^{13}C (expansion)of 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol in $CDCl_3$(3f)



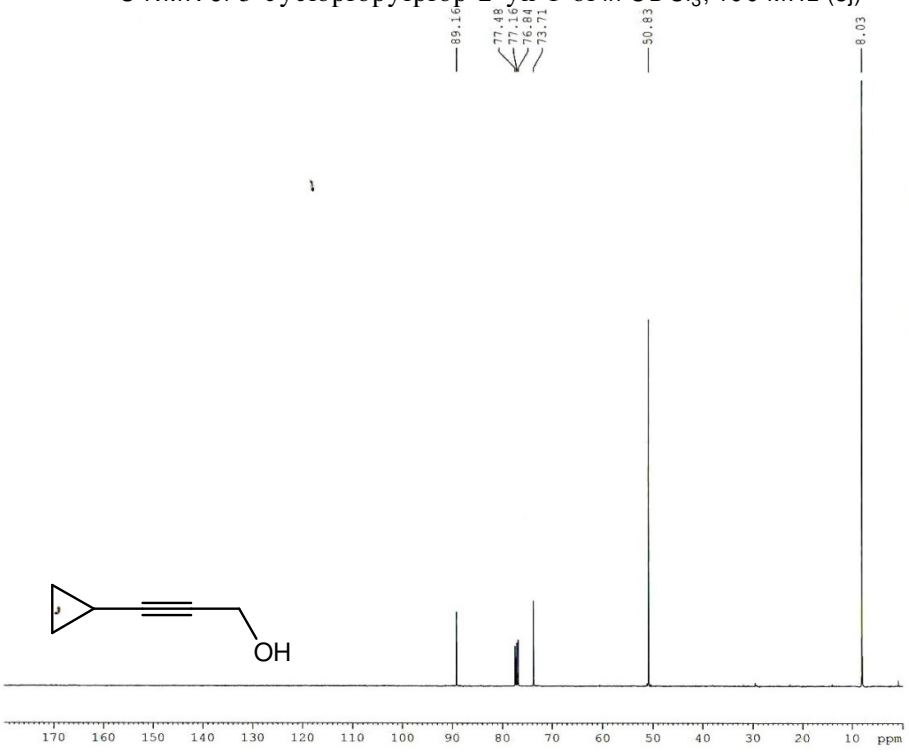
^{13}C of 3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-ol in $CDCl_3$(3g)



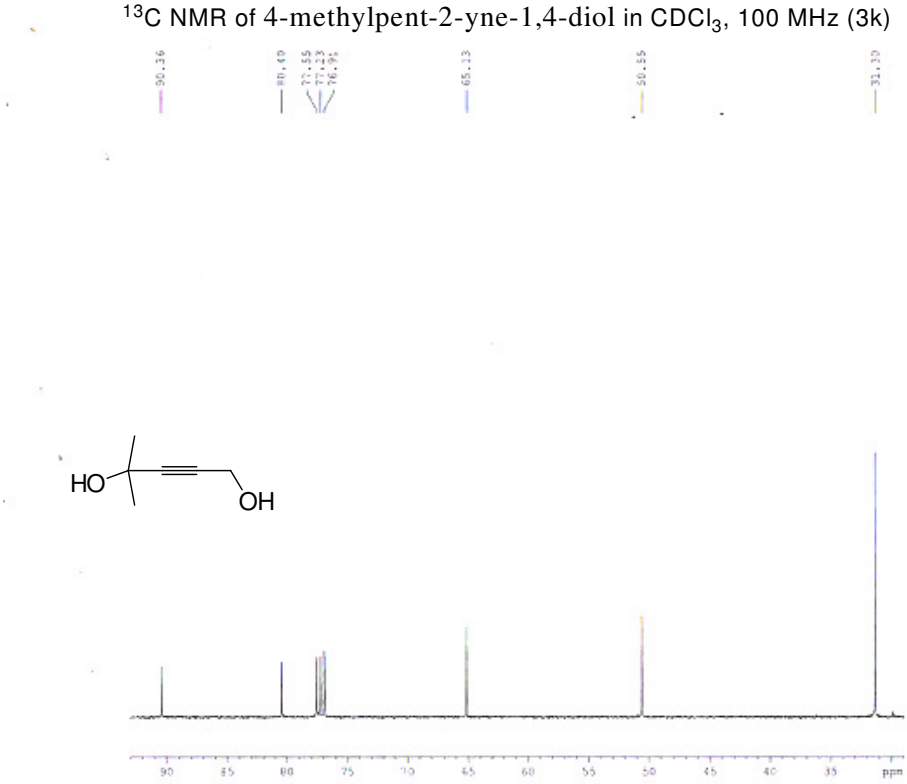
^{13}C NMR of oct-2-yn-1-ol in $CDCl_3$, 100 MHz (3i)



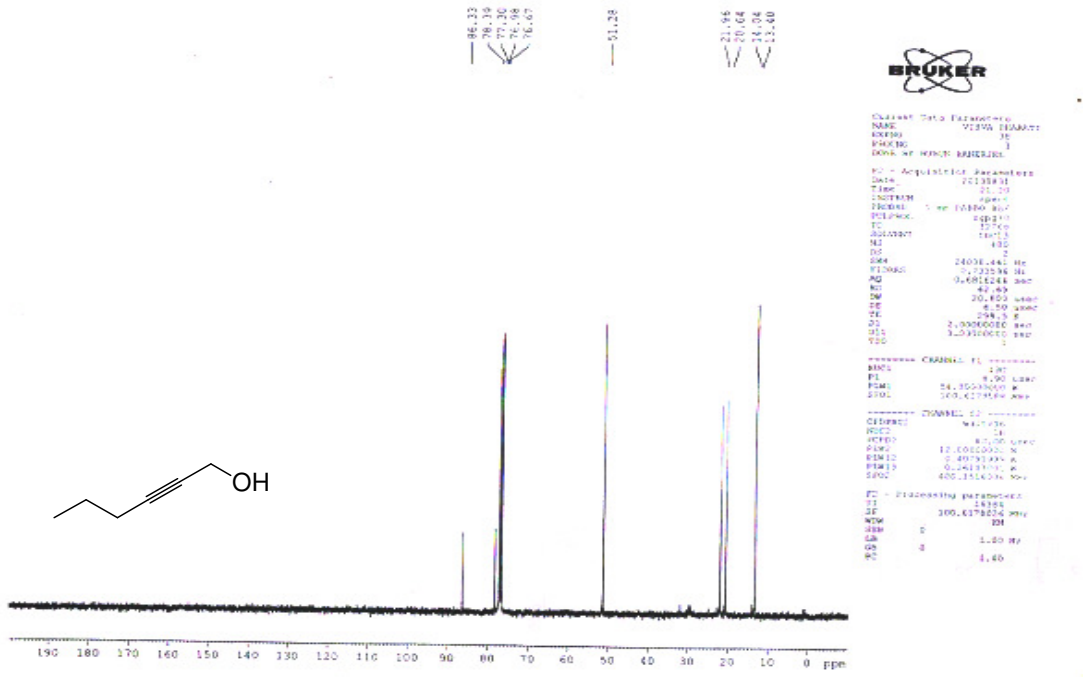
^{13}C NMR of 3-cyclopropylprop-2-yn-1-ol in $CDCl_3$, 100 MHz (3j)



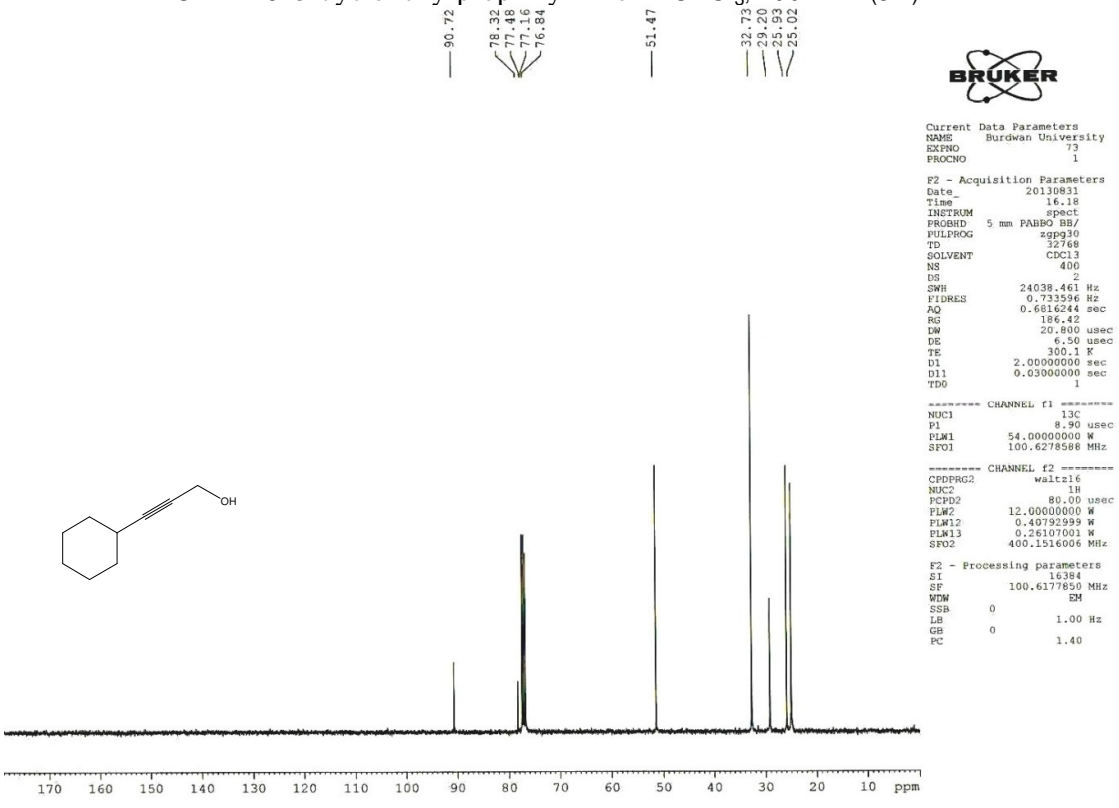
^{13}C NMR of 4-methylpent-2-yne-1,4-diol in $CDCl_3$, 100 MHz (3k)



^{13}C NMR of hex-2-yn-1-ol in $CDCl_3$, 100 MHz (3l)



^{13}C NMR of 3-cyclohexylprop-2-yn-1-ol in $CDCl_3$, 100 MHz (3m)



Current Data Parameters
NAME Burdwan University
EXPNO 73
PROCNO 1

F2 - Acquisition Parameters
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Time 16.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 400
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W
SFO1 100.6278588 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.00000000 W
PLW12 0.40792999 W
PLW13 0.26107001 W
SFO2 400.1516006 MHz

F2 - Processing parameters
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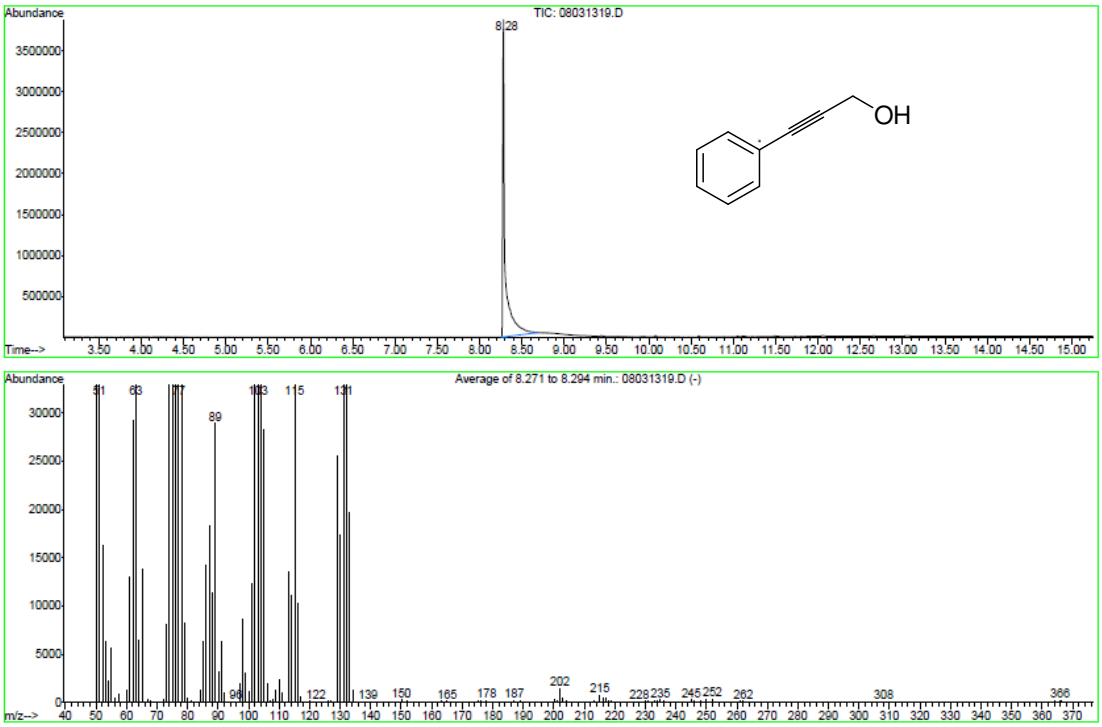
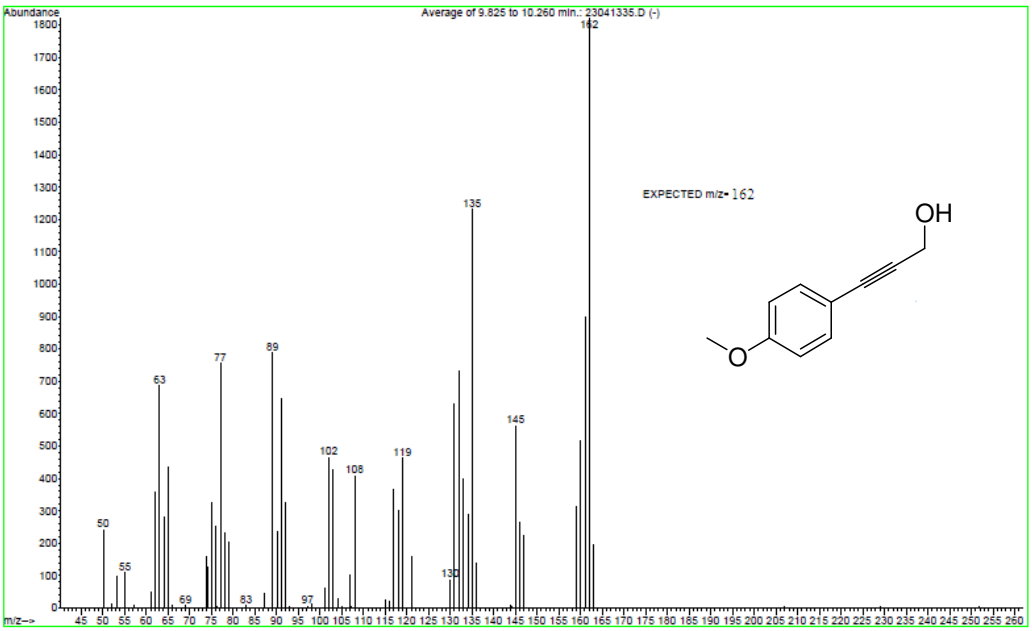
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

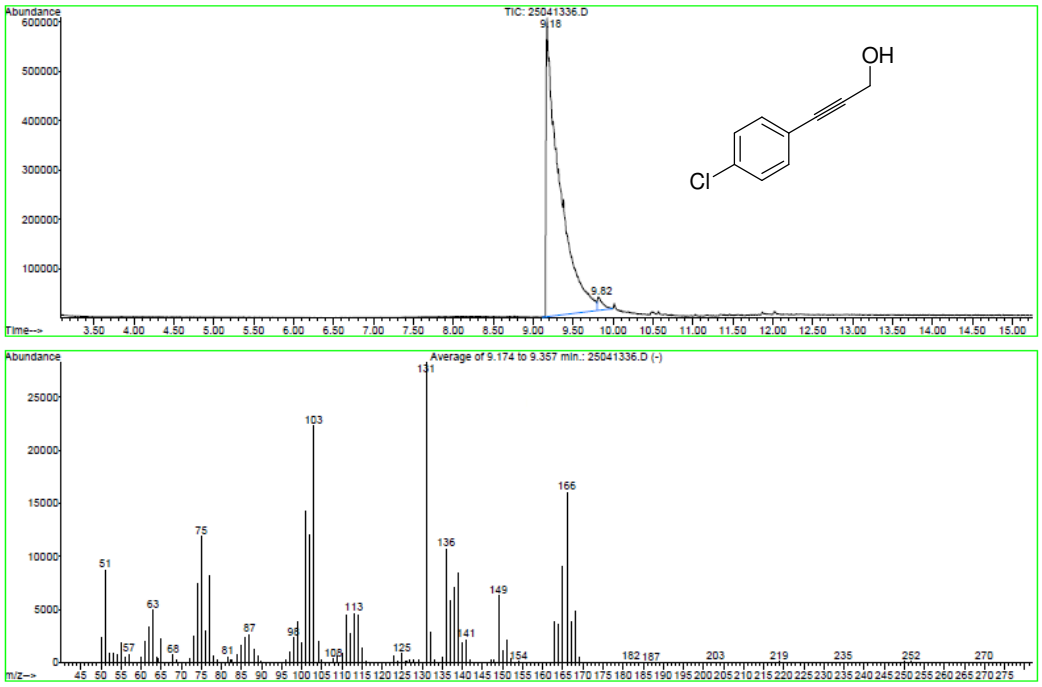
GCMS of 3-phenylprop-2-yn-1-ol (3a)



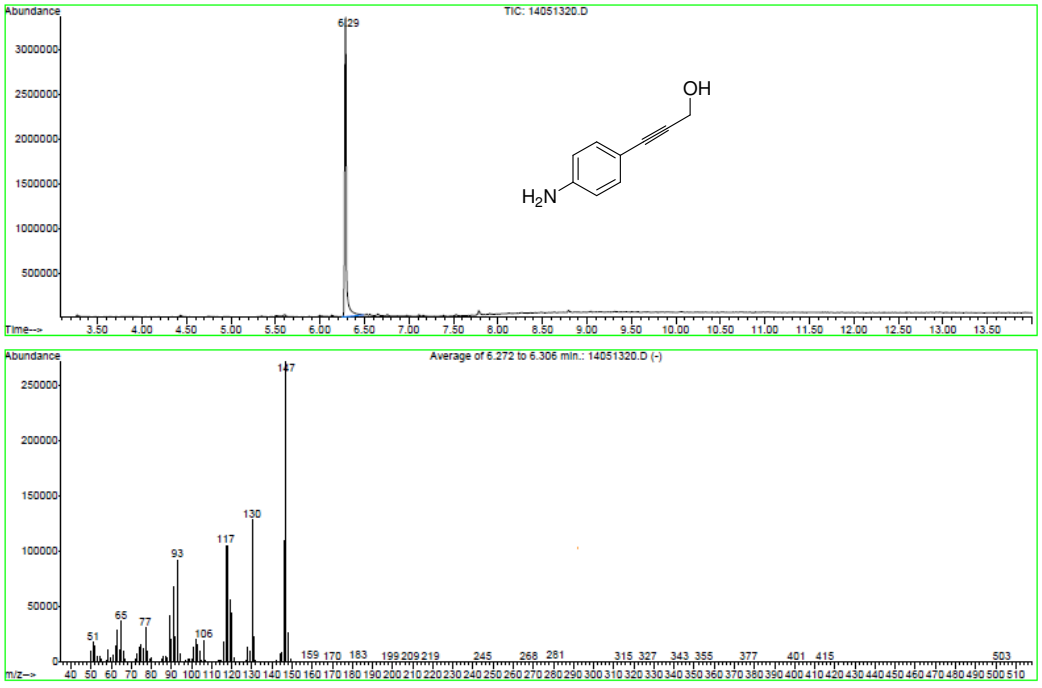
GCMS of 3-(4-methoxyphenyl)prop-2-yn-1-ol (3b)



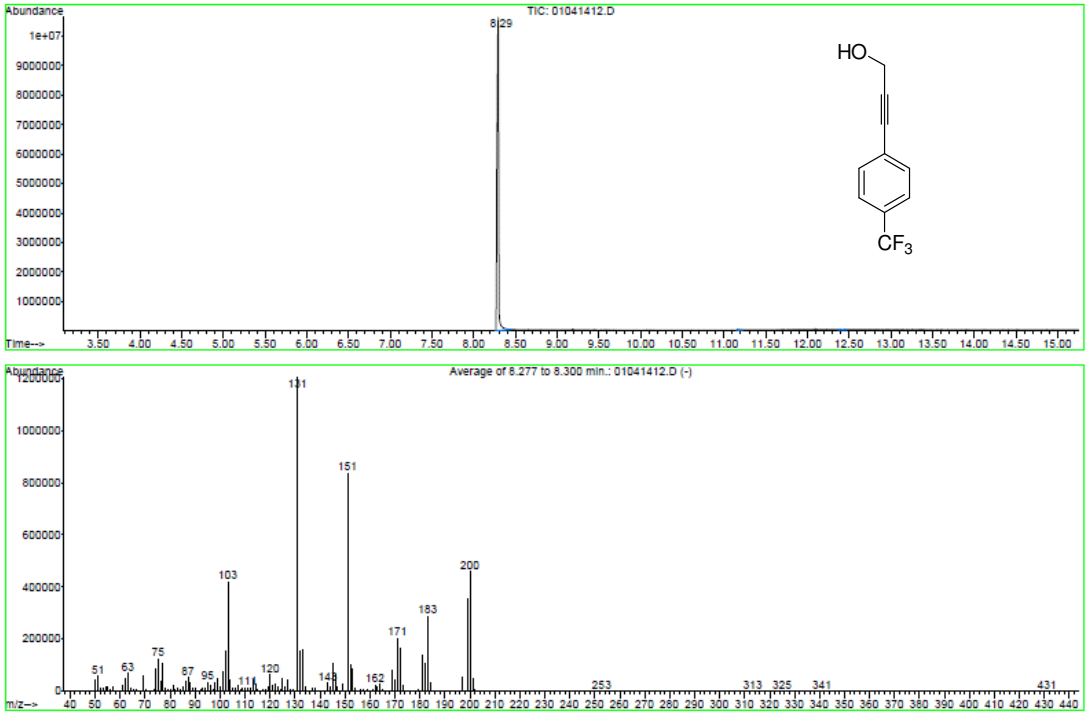
GCMS of 3-(4-chlorophenyl)prop-2-yn-1-ol (3c)



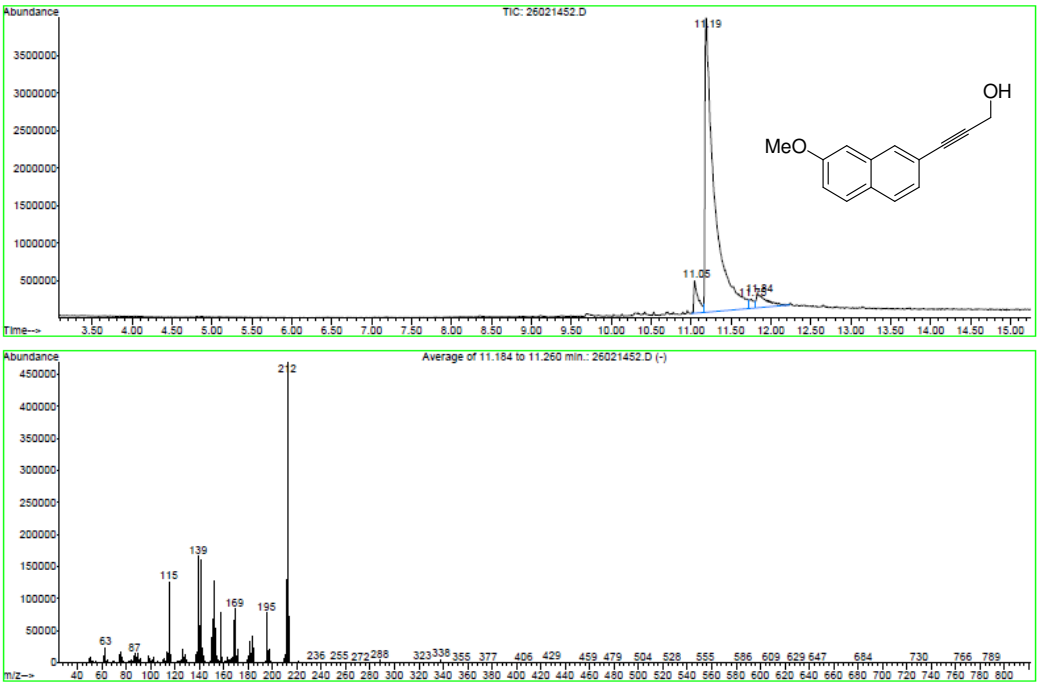
GCMS of 3-(4-aminophenyl)prop-2-yn-1-ol (3e)

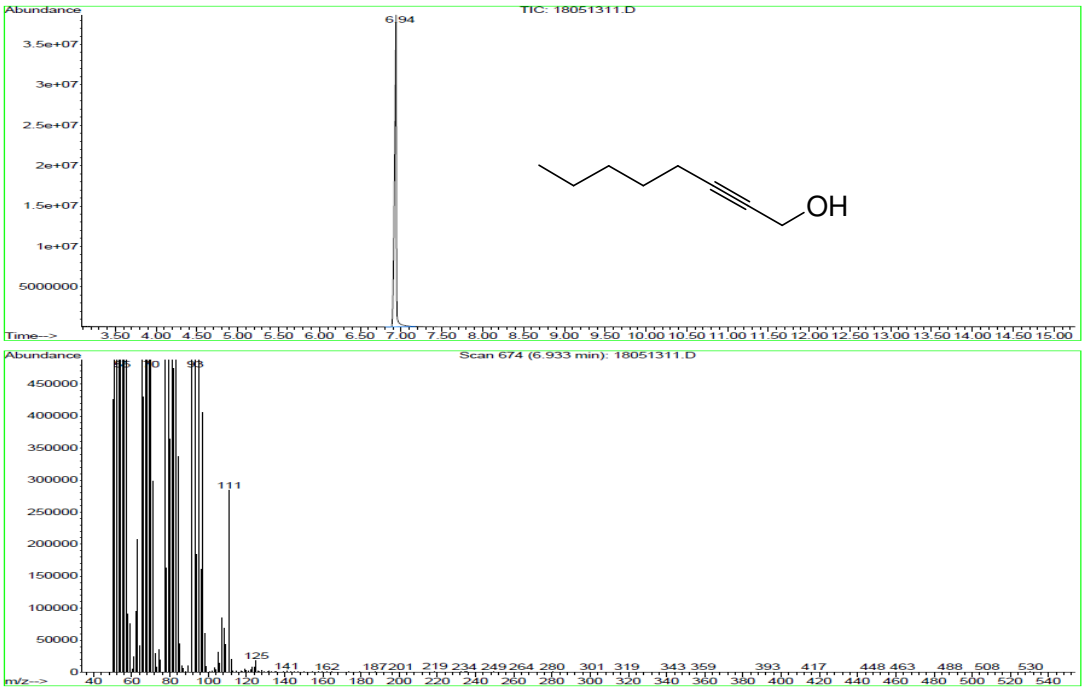


GCMS of 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol(3f)

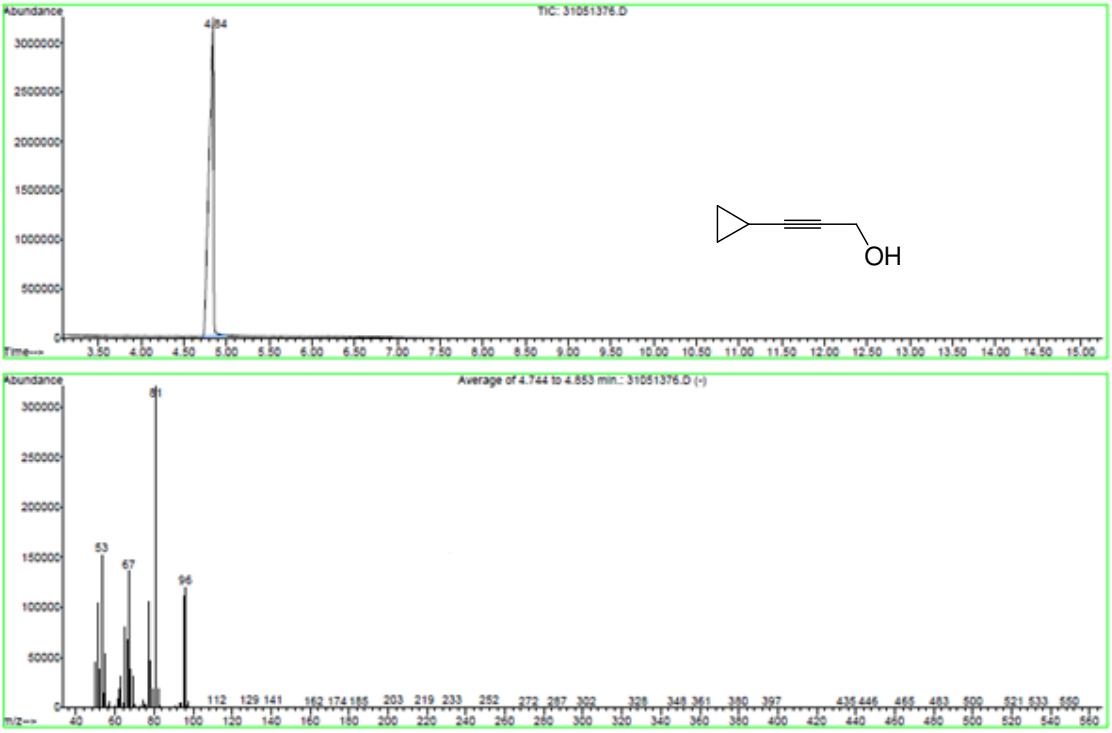


GCMS of 3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-ol (3g)

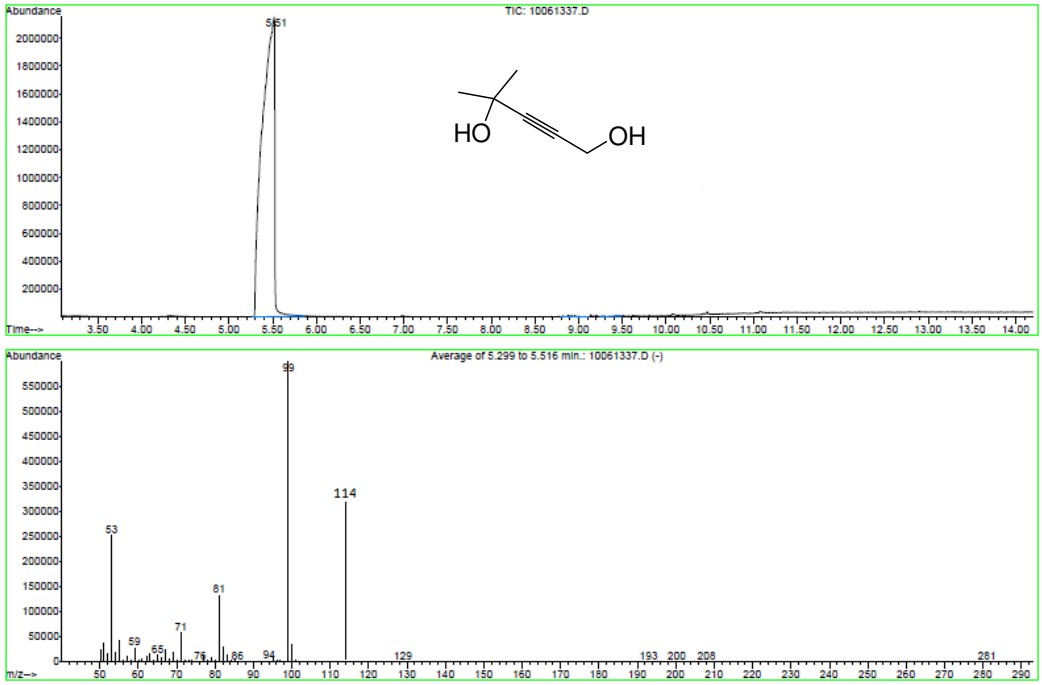




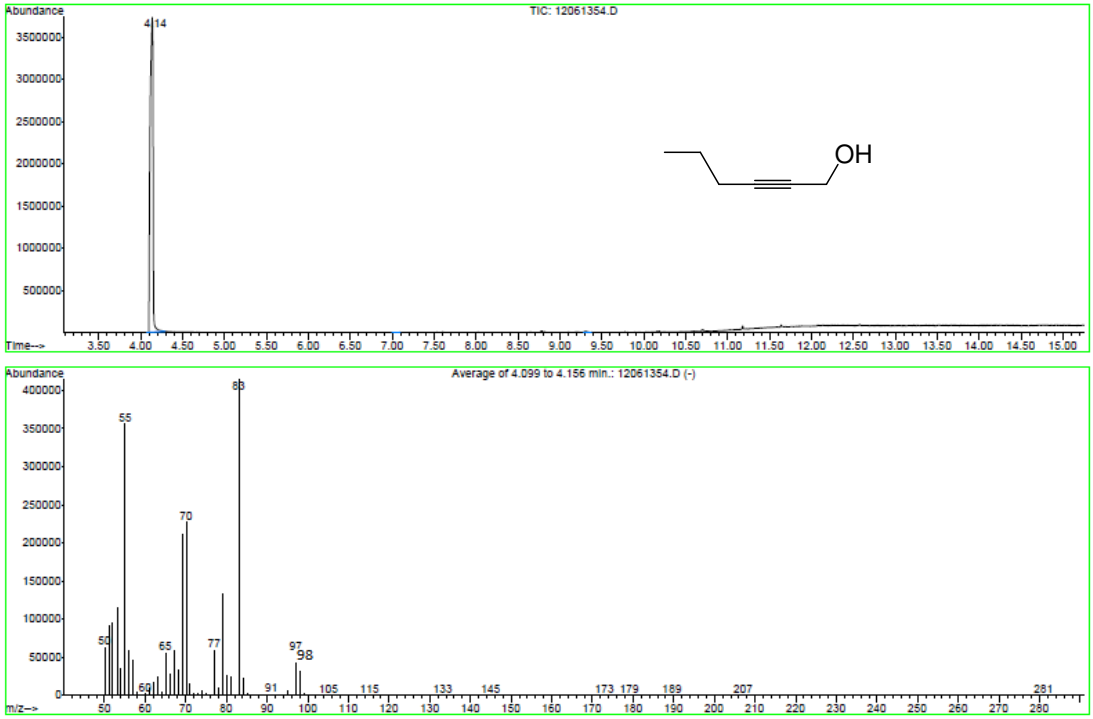
GCMS of 3-Cyclopropylprop-2-yn-1-ol (3j)



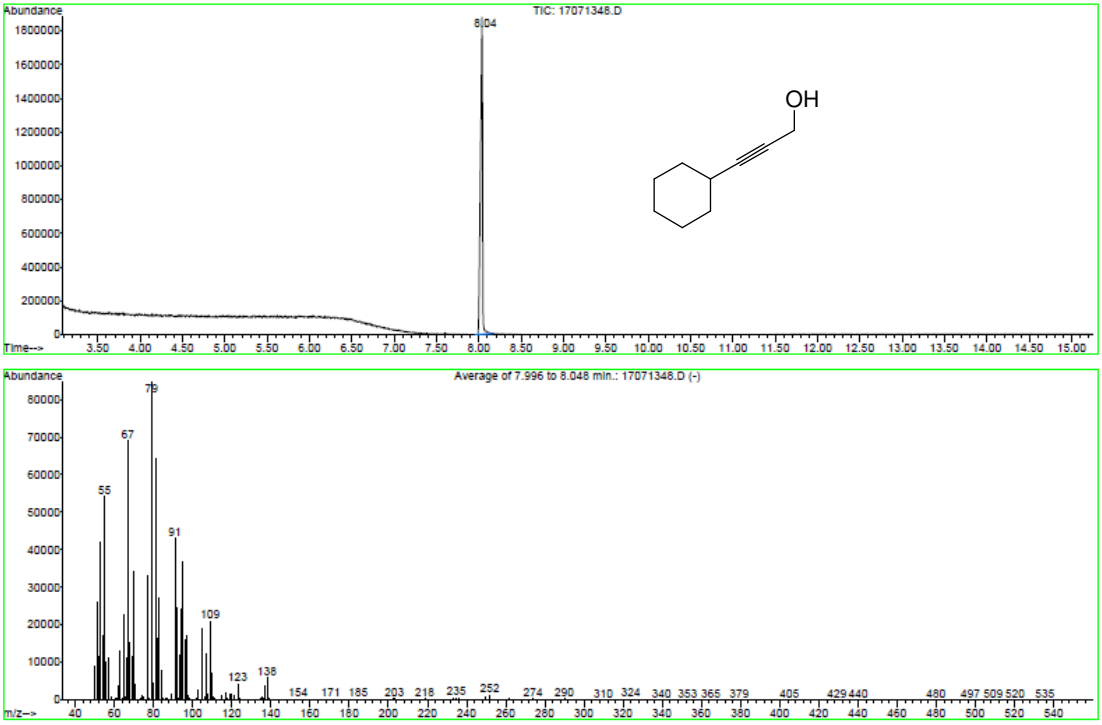
GCMS of 4-methylpent-2-yne-1,4-diol (3k)



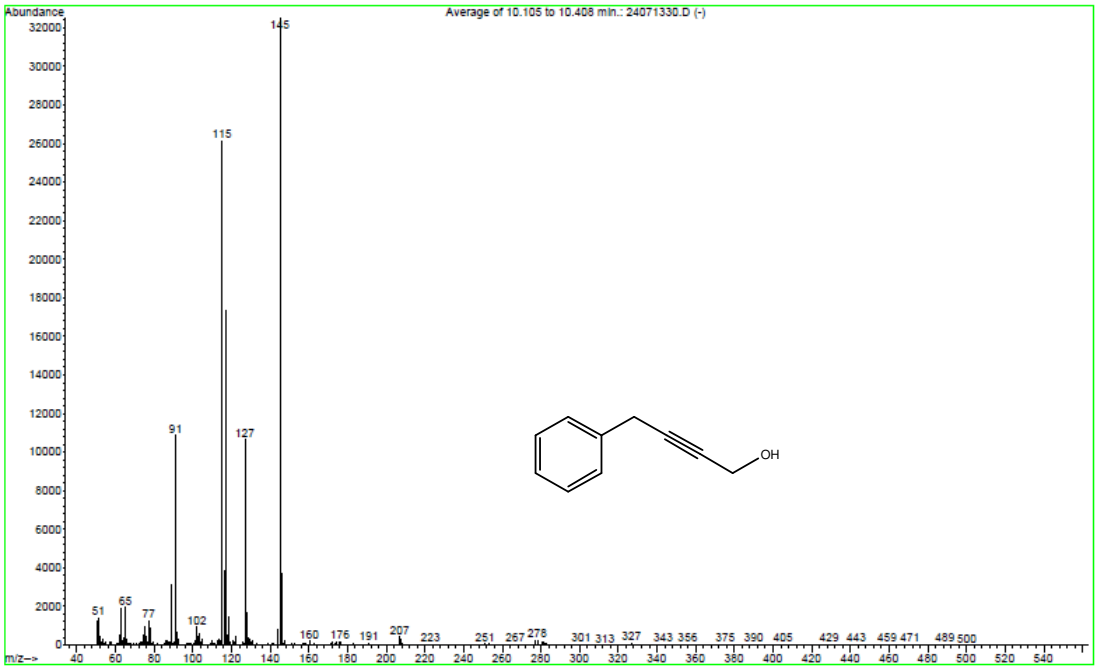
GCMS of Hex-2-yn-1-ol(3l)



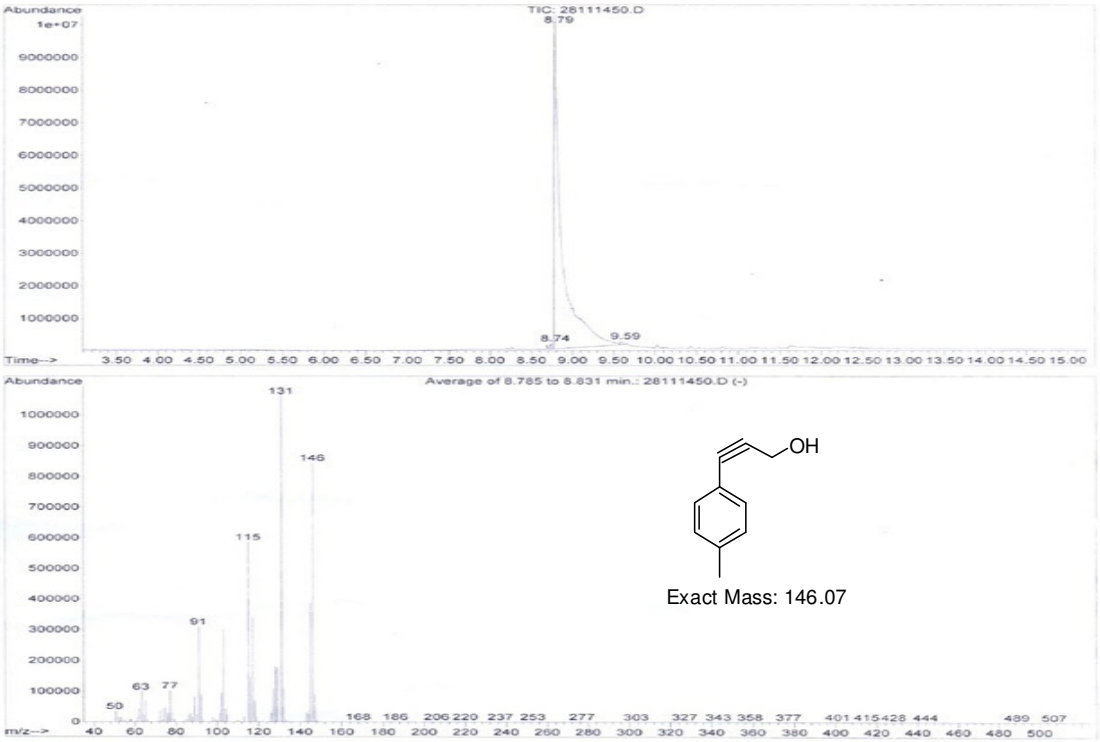
GCMS of 3-cyclohexylprop-2-yn-1-ol (3m)



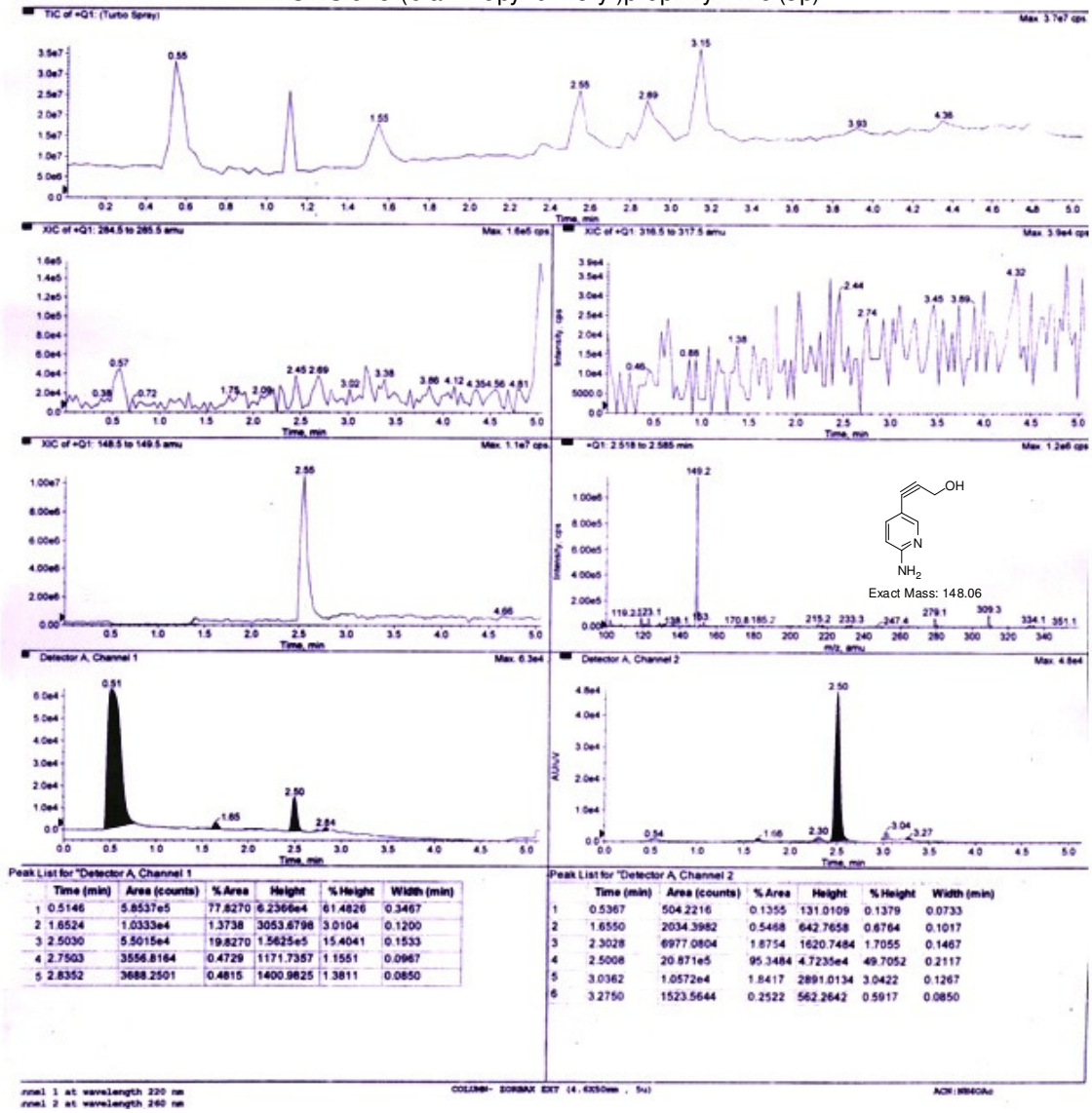
GCMS of 4-phenylbut-2-yn-1-ol (3n)



GCMS of 3-*p*-tolylprop-2-yn-1-ol (3o)



LCMS of 3-(6-aminopyridin-3-yl)prop-2-yn-1-ol(3p)



Peak List for "Detector A, Channel 1

	Time (min)	Area (counts)	% Area	Height	% Height	Width (min)
1	0.5146	5.8537e5	77.8270	6.2366e4	61.4826	0.3467
2	1.6524	1.0333e4	1.3738	3053.6798	3.0104	0.1200
3	2.5030	5.5015e4	19.8270	1.5625e5	15.4041	0.1533
4	2.7503	3556.8164	0.4729	1171.7357	1.1551	0.0967
5	2.8352	3688.2501	0.4815	1400.9825	1.3811	0.0850

Peak List for "Detector A, Channel 2

	Time (min)	Area (counts)	% Area	Height	% Height	Width (min)
1	0.5367	504.2216	0.1355	131.0109	0.1379	0.0733
2	1.6550	2034.3982	0.5468	642.7658	0.6764	0.1017
3	2.3028	6977.0804	1.8754	1620.7484	1.7055	0.1467
4	2.5008	20.871e5	95.3484	4.7235e4	49.7052	0.2117
5	3.0362	1.0572e4	1.8417	2891.0134	3.0422	0.1267
6	3.2750	1523.5644	0.2522	562.2642	0.5917	0.0850

References

1. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997,** *62,* 7512.

2. (a) Zwierzak A.; Tomassy, B. *Synth. Commun*. **1996**, *26*, 3593. (b) Poleschner, H.; Heydenreich, M. *Magn. Reson. Chem*. **1995**, *33*, 917.

3. Franks, M. A.; Schrader, E. A.; Pietsch, E. C.; Pennella, D. R.; Tortib, S. V.; Welker, M. E. *Bioorg. Med. Chem.* **2005**, *13*, 2221.