Supporting Information

Iron-Catalyzed Ring-Opening Azidation and Allylation of *O*-Heterocycles

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Contents

1. General information: All reactions were performed in oven-dried glassware under argon. Anhydrous CH_2Cl_2 as solvent was purchased from commercial sources and used without further purification.Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX 400, AL 400 or ECA 500 spectrometer at room temperature in $CDCl_3$ as a solvent and internal standard (^{1}H NMR: δ = 7.27; ^{13}C NMR: δ = 77.0) with tetramethylsilane as an internal standard, or CD_3OD as a solvent and internal standard (^{1}H NMR: δ = 3.31; ^{13}C NMR: δ = 49.0). IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimazu hybrid IT-TOF mass spectrometer. FAB mass spectra was taken on a JEOL JMS-SX102A instrument. Substrate **1a, 1b, 1c, 1d, 1i** and **1j** were prepared according to the procedure depicted in

references1, 2 and 3. Substrate **1e** was prepared according to the procedure depicted in reference 4. Substrate **1f** was prepared according to the procedure depicted in references 5 and 6. Substrate **1g** and **1h** were prepared according to the procedure depicted in reference7.Substrate **1k** was purchased from Aldrich. Substrate **1l** was prepared according to the procedure depicted in references 8 and 9. Substrate **1m** was prepared according to the procedure depicted in references 10 and 11. Substrate **1n** was purchased from TCI. Substrate **1o** was prepared according to the procedure depicted in references 12 and 13.

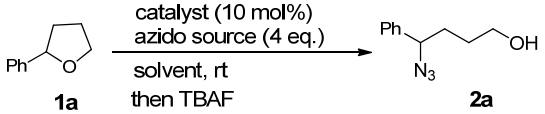
2. General procedure

Typical procedure for the azidation: To a solution of the 2-aryltetrahydrofuran (0.25 mmol) in dry CH_2Cl_2 (0.2 M) was added $TMSN_3$ (0.50 mmol) and $FeCl_3$ (0.0125 mmol) in order and the reaction mixture was stirred at room temperature under argon. After the adequate reaction time, the reaction mixture was quenched with *n*-Bu_4NF (0.60 mmol) and water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel-columun chromatography using hexane/EtOAc (2/1) as an eluent.

Typical procedure for the allylation: To a solution of the 2-aryltetrahydrofuran (0.25 mmol) in dry CH_2Cl_2 (0.2 M) was added allylsilane (0.50 mmol) and $FeCl_3$ (0.0125 mmol) in order and the reaction mixture was stirred at room temperature under argon. After the adequate reaction time, the reaction mixture was quenched with *n*-Bu_4NF (0.60 mmol) and water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel-columun chromatography using hexane/EtOAc (3/1) as an eluent.

3. Optimization of reaction conditions in azidative ring-opening of 2-phenylteterahydrofuran (1a)

Table. Lewis acid-catalyzed azidative ring-opening of 2-phenylteterahydrofuran (**1a**)



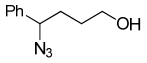
1a **2a**

entry	catalyst	azido source	solvent	time	yield (%)
1	$HAuCl_4•3H_2O$	$TMSN_3$	CH_2Cl_2	5 min.	81
2	$AuCl_3$	$TMSN_3$	CH_2Cl_2	5 min.	79

3	$(Ph_3P)AuCl$ / $AgSbF_6$	$TMSN_3$	CH_2Cl_2	1 h	38
4	AgOTf	$TMSN_3$	CH_2Cl_2	24 h	NR
5	$BF_3•Et_2O$	$TMSN_3$	CH_2Cl_2	24 h	trace
6	TMSOTf	$TMSN_3$	CH_2Cl_2	24 h	trace
7	$ZnCl_2$	$TMSN_3$	CH_2Cl_2	24 h	68
8	$FeCl_2•4H_2O$	$TMSN_3$	CH_2Cl_2	24 h	53
9	TFA	$TMSN_3$	CH_2Cl_2	24 h	trace
10	$FeCl_3$	$TMSN_3$	CH_2Cl_2	5 min.	87
11	$FeBr_3$	$TMSN_3$	CH_2Cl_2	5 min.	88
12[a]	$FeCl_3$	$TMSN_3$	CH_2Cl_2	15 min.	85
13	$FeCl_3$	NaN_3	CH_2Cl_2	24 h	NR
14	$FeCl_3$	DPPA	CH_2Cl_2	24 h	NR
15	$FeCl_3$	$TMSN_3$	$CHCl_3$	6 h	60
16	$FeCl_3$	$TMSN_3$	toluene	6 h	67
17	$FeCl_3$	$TMSN_3$	1,4-dioxane	6 h	trace
18	$FeCl_3$	$TMSN_3$	THF	6 h	trace

[a] 5 mol% of $FeCl_3$ and 1. 5 eq. of $TMSN_3$ were used.

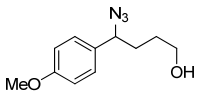
4. Spectroscopic data of products



2a

4-Azido-4-phenylbutan-1-ol (2a):

Colorless oil; IR (ATR) cm^{-1}: 3331, 2945, 2091, 1493, 1453, 1243; ^1H NMR (400 MHz, CD_3OD): δ7.40—6.30 (5H, m), 4.89 (1H, s), 4.53 (1H,t, J = 7.0 Hz), 3.55 (2H,t, J = 6.5 Hz,),1.92—1.84 (1H, m), 1.83—1.76 (1H, m), 1.65—1.56 (1H, m), 1.52—1.43 (1H, m); ^{13}C NMR (100 MHz, CD_3OD): δ141.1, 129.7, 129.2, 128.0, 67.35, 62.36, 33.6, 30.2; FAB-HRMS m/z: 192.1133 ($[M]^+$); Calcd for $C_{10}H_{14}N_3O$: 192.1136.

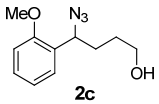


2b

4-Azido-4-(4-methoxyphenyl)butan-1-ol (2b):

Colorless oil; IR (ATR) cm^{-1}: 3347, 2936, 2091, 1610, 1512, 1245; ^1H NMR (500 MHz, $CDCl_3$): δ7.23 (2H, d, J = 9.0 Hz), 6.90 (2H, d, J = 9.0 Hz), 4.41 (1H, t, J = 7.0 Hz), 3.81 (3H, s), 3.64 (2H, t, J = 6.0 Hz), 1.93—1.86 (1H, m), 1.85—1.77 (1H, m), 1.67—1.60 (1H, m), 1.56—1.49 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ159.5, 131.6, 128.2,

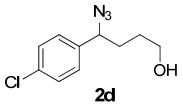
114.2, 65.8, 62.4, 55.3, 32.5, 29.5; ESI-HRMS m/z: 221.1132 ($[M]^+$); Calcd for $C_{11}H_{15}N_3O_2$: 221.1159.



2c

4-Azido-4-(2-methoxyphenyl)butan-1-ol (2c):

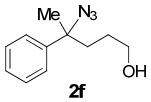
Colorless oil; IR (ATR) cm^{-1}: 3333, 2939, 2839, 2090, 1600, 1587, 1491, 1462; ^1H NMR (400 MHz, $CDCl_3$): δ7.33—7.24 (2H, m), 6.98 (1H, t, *J* = 7.2 Hz), 6.90 (1H, d, *J* = 8.0 Hz), 4.96 (1H, t, *J* = 6.8 Hz), 3.83 (3H, s), 3.64 (2H, t, *J* = 6.4 Hz), 1.90—1.80 (2H,m), 1.73—1.63 (1H, m), 1.62—1.53 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ156.6, 129.1, 127.8, 127.1, 120.8, 110.7, 62.4, 59.5, 55.4, 31.1, 29.4; ESI-HRMS m/z: 244.1052 ($[M+Na]^+$); Calcd for $C_{11}H_{15}N_3O_2Na$: 244.1056.



2d

4-Azido-4-(4-chlorophenyl)butan-1-ol (2d):

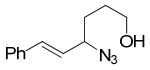
Colorless oil; IR (ATR) cm^{-1}: 3322, 2945, 2876, 2090, 1595, 1491, 1448, 1410, 1330; ^1H NMR (400 MHz, $CDCl_3$): δ7.36 (2H, d, *J* = 8.4 Hz),7.25 (2H, d, *J* = 8.4 Hz), 4.48 (1H, t, *J* = 7.0 Hz),3.66 (2H, t, *J* = 6.0 Hz),3.81 (3H, s), 1.91—1.86 (1H, m), 1.85—1.79 (2H, m), 1.68—1.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ138.1, 134.0, 129.0, 128.2, 65.4, 62.2, 32.6, 29.1; ESI-HRMS m/z: 248.0582 ($[M+Na]^+$); Calcd for $C_{10}H_{12}N_3OClNa$:248.0561.



2f

4-Azido-4-phenylpentan-1-ol (2f):

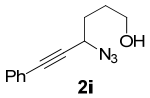
Colorless oil; IR (ATR) cm^{-1}: 3332, 3060, 2948, 2875, 2101, 1600, 1494, 1445, 1380; ^1H NMR (400MHz; $CDCl_3$): δ 7.41—7.34 (4H, m), 7.32—7.26 (1H, m), 3.58 (2H, t, *J* = 6.4 Hz), 1.98—1.86 (2H, m), 1.70 (3H, s), 1.57 (1H, s, br), 1.55—1.35 (2H, m);^{13}C NMR (125 MHz; $CDCl_3$):δ 143.4, 128.6, 127.4, 125.7, 66.8,62.7, 38.7, 27.7, 25.8; ESI-HRMS m/z: 205.1212 ($[M]^+$); Calcd for $C_{11}H_{15}N_3O$: 205.1210.



2g

***cis*-4-Azido-6-phenyl-5-hexen-1-ol (2g):**

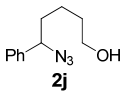
Colorless oil; IR (ATR) cm^{-1}: 3360, 2927, 2096, 1493, 1449, 1236; ^1H NMR (400 MHz, $CDCl_3$): δ7.42—7.39 (2H, m), 7.36—7.31 (2H, m), 7.30—7.27 (1H, m), 6.63 (1H, d, *J* = 16.0 Hz),6.12 (1H, dd, *J* = 16.0, 8.0 Hz),4.09—4.03 (1H, m),3.69 (2H, t, *J* = 6.0 Hz), 1.77—1.62 (4H, m), 1.36 (1H,brs); ^{13}C NMR (100 MHz, $CDCl_3$): δ136.0, 133.7, 128.8, 128.4, 127.0, 126.8, 64.9, 62.6, 31.4, 29.2; ESI-HRMS m/z: 217.1213 ($[M]^+$); Calcd for $C_{12}H_{15}N_3O$: 217.1210.



2i

4-Azido-6-phenyl-5-hexyne-1-ol (2i):

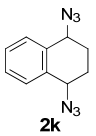
Colorless oil; IR (ATR) cm^{-1}:3320, 2935, 2872, 2100, 1598, 1490, 1443, 1331; ^1H NMR (400MHz; $CDCl_3$): δ 7.49—7.44 (2H, m), 7.40—7.30 (3H, m), 4.39 (1H, t, *J* = 6.4 Hz), 3.73 (2H, t, *J* = 6.0 Hz), 1.93—1.83 (2H, m), 1.82—1.76 (2H, m); ^{13}C NMR (125 MHz; $CDCl_3$):δ 131.9, 128.8,128.3, 121.9, 87.3, 84.2, 62.1, 53.4, 31.9, 28.7; ESI-HRMS m/z: 216.1120 ($[M+H]^+$); Calcd for $C_{12}H_{14}N_3O$: 216.1131.



2j

5-Azido-5-phenylpentan-1-ol (2j):

Colorless oil; IR (ATR) cm^{-1}:3325, 3030, 2936, 2863, 2091, 1602, 1493, 1453; ^1H NMR (400MHz; $CDCl_3$): δ 7.41—7.29 (5H, m), 4.42 (1H, t, *J* = 7.2 Hz), 3.63 (2H, t, *J* = 6.4 Hz), 1.89—1.76 (2H, m), 1.62—1.55 (3H, m), 1.49—1.46 (1H, m), 1.38—1.34 (1H, m), 1.33(1H, s, br); ^{13}C NMR (125 MHz; $CDCl_3$):δ139.7, 128.8, 128.2, 126.8, 66.3, 62.6, 36.0, 32.2, 22.5; ESI-HRMS m/z: 205.1221 ($[M]^+$); Calcd for $C_{11}H_{15}N_3O$: 205.1210.

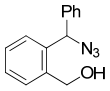


2k

1,4-Diazido-tetraline(2k)

Sseparable diastereomers: First one; Colorless oil; IR (ATR) cm^{-1}: 2936, 2085, 1489, 1450, 1335, 1296; ^1H NMR (400MHz; $CDCl_3$): δ 7.42—7.39 (2H, m), 7.37—7.33 (2H,

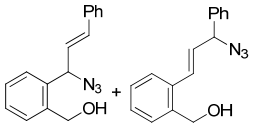
m), 4.64—4.63 (2H, m), 2.27—2.23 (2H, m), 2.00—1.94 (2H, m); ^{13}C NMR (125 MHz; $CDCl_3$): δ 133.6, 129.7, 129.0, 58.4, 24.7; ESI-HRMS m/z: 215.1027 ($[M+H]^+$); Calcd for $C_{10}H_{11}N_6$: 215.1040. Second one; Colorless oil; IR (ATR) cm^{-1}: 2951, 2094, 1490, 1452, 1350, 1325, 1241; ^{1}H NMR (400MHz; $CDCl_3$): δ 7.43—7.37 (4H, m), 4.55—4.52 (2H, m), 2.19—2.08 (4H, m); ^{13}C NMR (125 MHz; $CDCl_3$):δ 134.4, 128.9, 128.8, 58.9, 26.0; ESI-HRMS m/z: 215.1048 ($[M+H]^+$); Calcd for $C_{10}H_{11}N_6$: 215.1040.



2l

1-(Azidophenylmethyl)-2-(hydroxymethyl)benzene (2l):

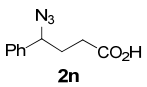
Brown oil; IR (ATR) cm^{-1}: 3346, 3064, 3029, 2888, 2096, 1493, 1453, 1238;^{1}H NMR (400MHz; $CDCl_3$): δ7.47—7.45 (2H, m), 7.41—7.29 (7H, m), 6.12 (1H, s), 4.63 (1H, d, *J* = 13.2 Hz), 4.62 (1H, d, *J* = 13.2 Hz), 1.68 (1H, brs); ^{13}C NMR (125 MHz; $CDCl_3$): 140.0, 138.1, 137.5, 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 127.4, 65.0, 63.0; ESI-HRMS m/z: 239.1048 ($[M]^+$); Calcd for $C_{14}H_{13}N_3O$: 239.1053.



2ma **2mb**

Mixture of 1-(1-Azido-3-phenyl-2-propen-1-yl)-2-(hydroxymethyl)benzene (2ma) and 1-(3-Azido-3-phenyl-1-propen-1-yl)-2-(hydroxymethyl)benzene (2mb):

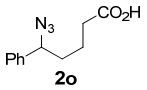
Mixture of regioisomers; Colorless oil; IR (ATR) cm^{-1}: 3333, 3062, 3029, 2886, 2096, 1601, 1492, 1452; ^{1}H NMR (400MHz; $CDCl_3$): δ 7.50—7.47 (1H, m), 7.41—7.24 (8H, m), 7.07(0.6H, d, *J* = 15.6 Hz), 6.71(0.4H, d, *J* = 15.6 Hz), 6.31(0.4H, dd, *J* = 15.6 Hz, *J* = 6.8 Hz), 6.22(0.6H, dd, *J* = 15.6 Hz, *J* = 7.2 Hz), 5.62(0.4H, d, *J* = 6.8 Hz), 5.24(0.6H, d, *J* = 7.2 Hz), 4.78(0.8H, s), 4.77(1.2H, s), 1.91(0.4H, s, br),1.70(0.6H, s, br); ^{13}C NMR (125 MHz; $CDCl_3$):δ 138.4, 138.0, 137.8, 137.0, 135.8, 135.1, 132.9, 129.9, 129.4, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.0, 126.7, 126.5, 126.4, 67.2, 63.6, 63.4, 63.2;ESI-HRMS m/z: 265.1223 ($[M]^+$); Calcd for $C_{16}H_{15}N_3O$: 265.1210.



2n

4-Azido-4-phenylbutanoic acid (2n):

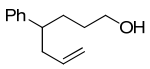
Colorless oil;^{1}H NMR (400MHz; $CDCl_3$): δ7.42—7.31 (5H, m), 4.56 (1H, t, *J* = 7.0 Hz), 2.45 (2H, t, *J* = 7.2 Hz), 2.15—2.04 (2H, m); ^{1}H NMR data was identical with that in the reference 14.



2o

5-Azido-5-phenylpentanoic acid (2o):

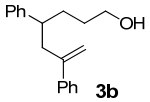
Colorless oil;^{1}H NMR (400MHz; $CDCl_3$): δ7.41—7.29 (5H, m), 4.43 (1H, t, *J* = 6.8 Hz), 2.38 (2H, t, *J* = 7.0 Hz), 1.92—1.57 (4H, m); ^{1}H NMR data was identical with that in the reference 14.



3a

4-Phenyl-6-heptene-1-ol (3a):

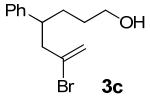
Colorless oil; IR (ATR) cm^{-1}: 3347, 3077, 3027, 2931, 2249, 1639, 1602, 1493, 1451;^{1}H NMR (400MHz; $CDCl_3$): δ 7.30—7.25 (2H, m), 7.20—7.14 (3H, m), 5.70—5.61 (1H, m), 4.49—4.91 (2H, m), 3.55 (2H, t, *J* = 6.6 Hz), 2.63—2.59 (1H, m), 2.37 (2H, t, *J* = 7.0 Hz), 1.81—1.74 (1H, m), 1.64—1.55 (1H, m), 1.48—1.34 (2H, m), 1.32(1H, s, br); ^{13}C NMR (125 MHz; $CDCl_3$):δ 144.9, 136.9, 128.3, 127.6, 126.1, 115.9, 62.9, 45.7, 41.4, 31.9, 30.7;ESI-HRMS m/z: 190.1346 ($[M]^+$); Calcd for $C_{13}H_{18}O$: 190.1352.



3b

4,6-Diphenyl-6-heptene-1-ol (3b):

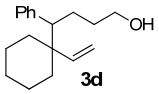
Colorless oil; IR (ATR) cm^{-1}: 3353, 3027, 2929, 2249, 1627, 1600, 1493, 1451;^{1}H NMR (400MHz; $CDCl_3$): δ 7.33—7.26 (7H, m), 7.19—7.15 (1H, m), 7.08—7.06 (2H, m), 5.16 (1H, d, *J* = 1.4 Hz), 4.89 (1H, d, *J* = 1.4 Hz), 3.49 (2H, t, *J* = 6.6 Hz), 2.86—2.75 (2H, m), 2.66—2.61 (1H, m), 1.83—1.74 (1H, m), 1.65—1.55 (1H, m), 1.38—1.30 (2H, m), 1.15 (1H, brs); ^{13}C NMR (125 MHz; $CDCl_3$): 146.7, 144.9, 141.0, 128.3, 128.2, 127.6, 127.3, 126.4, 126.1, 114.4, 62.9, 43.7, 43.4, 31.7, 30.7; HRMS (EI): ESI-HRMS m/z: 266.1651 ($[M]^+$); Calcd for $C_{19}H_{22}O$: 266.1665.



3c

6-Bromo-4-phenyl-6-heptene-1-ol (3c):

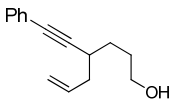
Colorless oil; IR (ATR) cm^{-1}: 3348, 3061, 3027, 2929, 2858, 1629, 1601, 1493, 1452, 1428;^{1}H NMR (400MHz; $CDCl_3$): δ 7.31—7.27 (2H, m), 7.22—7.16 (3H, m), 5.38 (1H, dd, *J* = 1.6, 0.8 Hz), 5.30 (1H, d, *J* = 1.6 Hz), 3.59 (2H, t, *J* = 7.0 Hz), 3.02—2.95 (1H, m), 2.73—2.63 (2H, m), 1.83—1.75 (1H, m), 1.68—1.58 (1H, m), 1.52—1.37 (2H, m), 1.18(1H, s, br); ^{13}C NMR (125 MHz; $CDCl_3$):143.5, 132.6, 128.4, 127.7, 126.5, 118.3, 62.8, 48.8, 43.7, 31.3, 30.6;HRMS (EI): ESI-HRMS m/z: 269.0539 ($[M+H]^+$); Calcd for $C_{13}H_{18}OBr$: 269.0536.



3d

1-Ethenyl-(4-hydroxy-1-pnehyl-1-butyl)cyclohexane (3d):

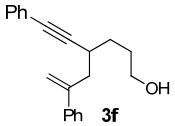
Colorless oil; IR (ATR) cm^{-1}:3352, 3080, 3026, 2930, 2854, 2249, 1632, 1601, 1492, 1450, 1410; ^{1}H NMR (400MHz; $CDCl_3$): δ7.41—7.28 (5H, m), 5.73 (1H, dd, *J* = 18.0,11.2 Hz), 5.42 (1H, dd, *J* = 11.2, 1.6 Hz), 5.07 (1H, dd, *J* = 18.0,1.6 Hz), 3.67 (2H, t, *J* = 7.0 Hz), 2.55 (1H, dd, *J* = 12.4,3.2 Hz), 2.08—1.99 (2H, m), 1.81—1.71 (1H, m), 1.69—1.55 (4H, m), 1.48—1.26 (7H, m); ^{13}C NMR (125 MHz; $CDCl_3$):δ 143.1, 141.8, 129.8, 127.5, 126.0, 115.5, 63.1, 56.7, 43.1, 35.1, 34.5, 31.5, 29.7, 26.5, 25.1, 22.3; HRMS (EI): ESI-HRMS m/z: 281.1852 ($[M+Na]^+$); Calcd for $C_{18}H_{26}ONa$: 281.1876.



3e

4-Phenylethynyl-6-heptene-1-ol (3e):

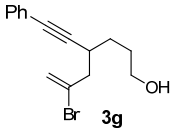
Colorless oil; IR (ATR) cm^{-1}: 3343, 3077, 2933, 2863, 2230, 1640, 1597, 1572, 1489, 1441; ^{1}H NMR (400MHz; $CDCl_3$): δ7.40—7.38 (2H, m), 7.29—7.26 (3H, m), 5.98—5.91 (1H, m), 5.16—5.07 (2H, m), 3.71 (2H, t, *J* = 6.4 Hz), 2.68—2.64 (1H, m), 2.33 (2H, t, *J* = 6.8 Hz), 1.89—1.83 (1H, m), 1.76—1.52 (3H, m), 1.39 (1H, brs); ^{13}C NMR (125 MHz; $CDCl_3$): δ 135.9, 131.6, 128.2, 127.6, 123.8, 116.7, 92.5, 82.4, 62.8, 39.5, 32.0, 30.7, 30.6; HRMS (EI): ESI-HRMS m/z: 215.1444 ($[M+H]^+$); Calcd for $C_{15}H_{19}O$: 215.1430.



3f

6-Phenyl-4-phenylethynyl-6-heptene-1-ol (3f):

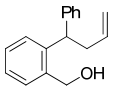
Colorless oil; IR (ATR) cm^{-1}: 3388, 3081, 2927, 2249, 1627, 1598, 1491, 1444; ^1H NMR (400MHz; $CDCl_3$): δ 7.44—7.41 (2H, m), 7.36—7.24 (8H, m), 5.36 (1H, d, *J* = 1.2 Hz), 5.20 (1H, d, *J* = 1.2 Hz), 3.66 (2H, t, *J* = 6.4 Hz), 2.87—2.75 (1H, m), 2.71—2.68 (2H, m), 1.87—1.84 (1H, m), 1.73—1.65 (2H, m), 1.56—1.53 (1H, m); ^{13}C NMR (125 MHz; $CDCl_3$): δ 146.1, 140.8, 131.6, 128.4, 128.1, 127.6, 127.5, 126.4, 123.9, 114.9, 92.6, 82.6, 62.8, 41.4, 30.9, 30.6, 30.5; HRMS (EI): ESI-HRMS m/z: 291.1735 ($[M+H]^+$); Calcd for $C_{21}H_{23}O$: 291.1743.



3g

6-Bromo-4-phenylethynyl-6-heptene-1-ol (3g):

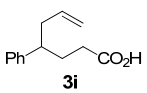
Colorless oil; IR (ATR) cm^{-1}: 3345, 2926, 2859, 1722, 1630, 1598, 1490, 1442, 1346; ^1H NMR (400MHz; $CDCl_3$):δ7.40—7.37 (2H, m), 7.29—7.27 (3H, m), 5.72 (1H, m), 5.53 (1H, d, *J* = 1.6 Hz), 3.73 (2H, t, *J* = 6.2 Hz), 3.02—3.00 (1H, m), 2.75—2.69 (1H, m), 2.63—2.58 (1H, m), 1.91—1.88 (1H, m), 1.81—1.68 (2H, m), 1.59—1.54 (1H, m);^{13}C NMR (125 MHz; $CDCl_3$): δ 131.6, 131.3, 128.2, 127.8, 123.5, 118.9, 91.1, 83.0, 62.6, 47.0, 30.8, 30.4, 30.2;HRMS (EI): ESI-HRMS m/z: 315.0351 ($[M+Na]^+$); Calcd for $C_{15}H_{17}OBrNa$: 315.0355.



3h

1-(1-Phenyl-3-butene-1-yl)-2-(hydroxymethyl)benzene (3h):

Colorless oil;IR (ATR) cm^{-1}: 3027, 2944, 2250, 1600, 1487, 1450; ^1H NMR (400MHz; $CDCl_3$): δ7.40—7.13 (9H, m), 5.78—5.67 (1H, m), 5.04 (2H, m), 4.65 (2H, m,), 4.37 (1H, t, *J* = 7.8 Hz), 2.80 (2H, t, *J* = 7.4 Hz), 1.56 (1H, s, br);^{13}C NMR (125 MHz; $CDCl_3$): δ144.2, 142.0, 138.4, 136.7, 128.7, 128.4, 128.3, 128.0, 127.4, 126.5, 126.2, 116.6, 63.2, 45.8, 40.5;HRMS (EI):ESI-HRMS m/z: 239.1429 ($[M+H]^+$); Calcd for $C_{17}H_{19}O$: 239.1430.



3i

4-Phenyl-6-heptenolic acid (3i):

Colorless oil; IR (ATR) cm^{-1}: 3400, 3062, 3028, 2924, 1703, 1640, 1602, 1494, 1452, 1413, 1291; ^1H NMR (400MHz; $CDCl_3$):δ7.34—7.25 (2H, m), 7.20—7.18 (1H, m),

7.15—7.13(2H, m), 5.71—5.61(1H, m), 5.01—4.93(2H, m), 2.68—2.60(1H, m), 2.38 (2H, t, *J* = 6.8 Hz), 2.18 (2H, t, *J* = 7.8 Hz), 2.11—2.03(1H, m), 1.89—1.79(1H, m); ^{13}C NMR (125 MHz; $CDCl_3$): δ; 180.1, 143.7, 136.4, 128.5, 127.6, 126.4, 116.3, 45.1, 41.1, 32.0, 30.5;HRMS (EI): ESI-HRMS m/z: 204.1167 ($[M]^+$); Calcd for $C_{13}H_{16}O_2$: 204.1145.

5. References

1) W. Li; Y.Lam, *J. Comb. Chem.* **2005**, *7,* 721-725.

2)D. S. Brown; M. Bruno; R. J. Davenport; S.V. Ley, *Tetrahedron* **1989**, *13*, 4293-4308.

3) S. V. Ley; B. Lygo; F. Sternfeld; A. Wonnacott, *Tetrahedron* **1986**, *15,*4333-4342.

4) T. Maegawa; A. Akashi; H. Sajiki, *Synlett* **2006**, *9,* 1440-1442.

5)A. Takemura; J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128,* 6042-6043.

6) X. Franck; B. Figadére; A. Cavé, *Tetrahedron Lett.* **1997**, *8,* 1413-1414.

7) Z.-Q. Liu; L. Sun; J.-G. Wang; J. Han; Y.-K.Zhao; B. Zhou, *Org. Lett.* **2009**, *6,* 1437-1439.

8) M. Yoshioka; H. Osawa; S. Fukuzawa, *Bull. Chem. Soc. Jpn.* **1982**, *55,* 877-879.

9) N. Meyer, D. Seebach, *Angew. Chem. Int. Ed.* **1978**, *7,* 521-522.

10) S. G. Newman, C. S. Bryan, D. Perez; M. Lautens, *Synthesis* **2011**, *2,* 342-346.

11) T. Delacroix, L. Bérillon, G. Cahiez, P. Knochel, *J. Org. Chem.* **2000**, *65,* 8108-8110.

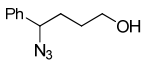
12) P. Kazmierczak; L. Skulski; L. Kraszkiewicz, *Molecules* **2001**, *6,* 881-891.

13) T. Dohi; N. Takenaga; A. Goto; A. Maruyama; Y. Kita, *Org. Lett.* **2007**, *16,* 3129-3132.

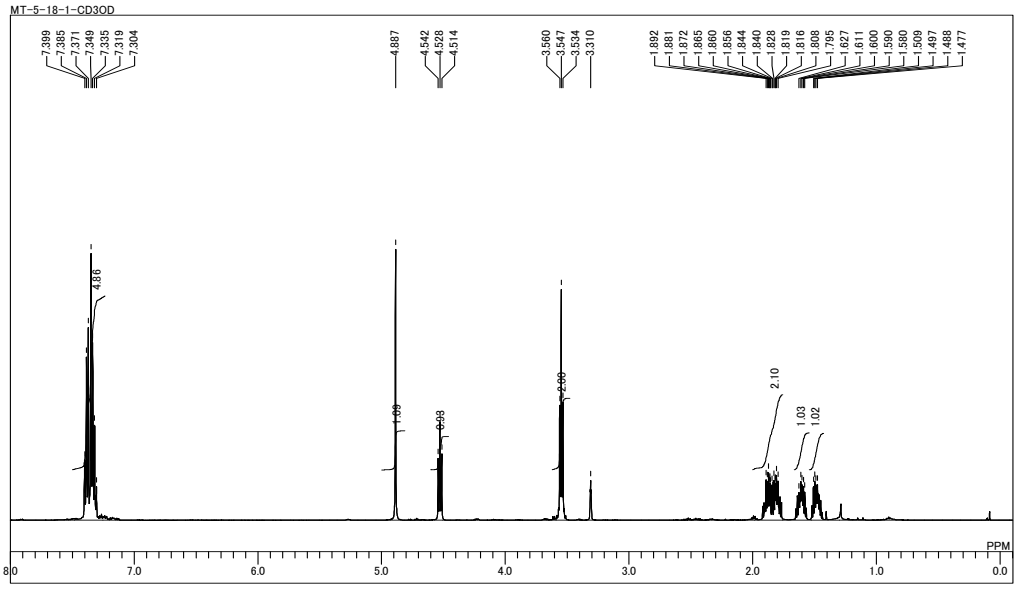
14) L. Benati; R. Leardini; M. Minozzi; D. Nanni; P. Spagnolo; S. Strazzari; G. Zanardi, *Org. Lett.* **2002**, *18,* 3079-3081.

6. ^{1}H and ^{13}C NMR spectra of products

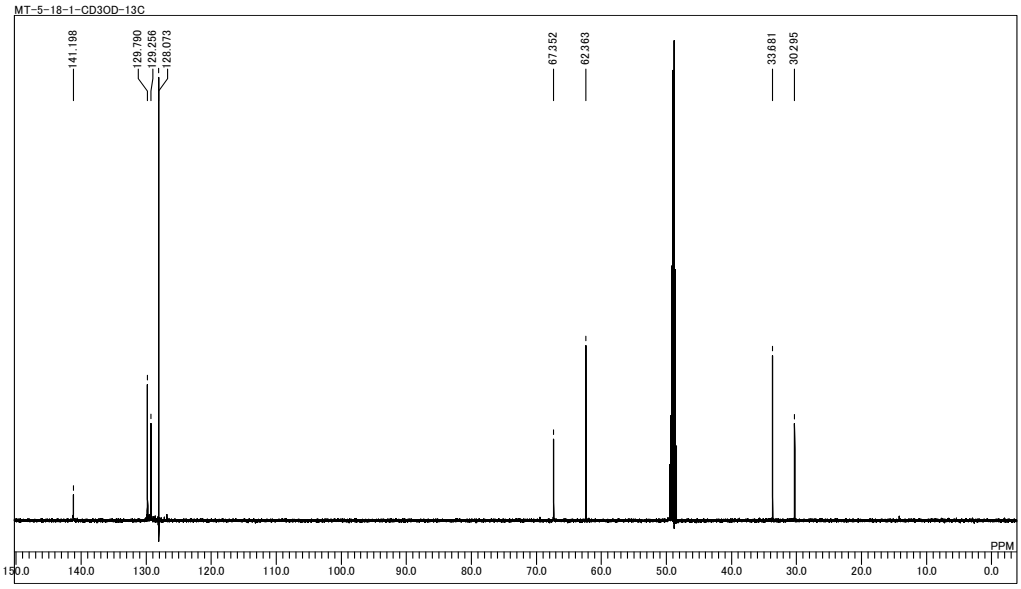
^{1}H NMR of 4-azido-4-phenylbutan-1-ol (**2a**)



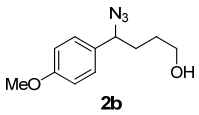
2a



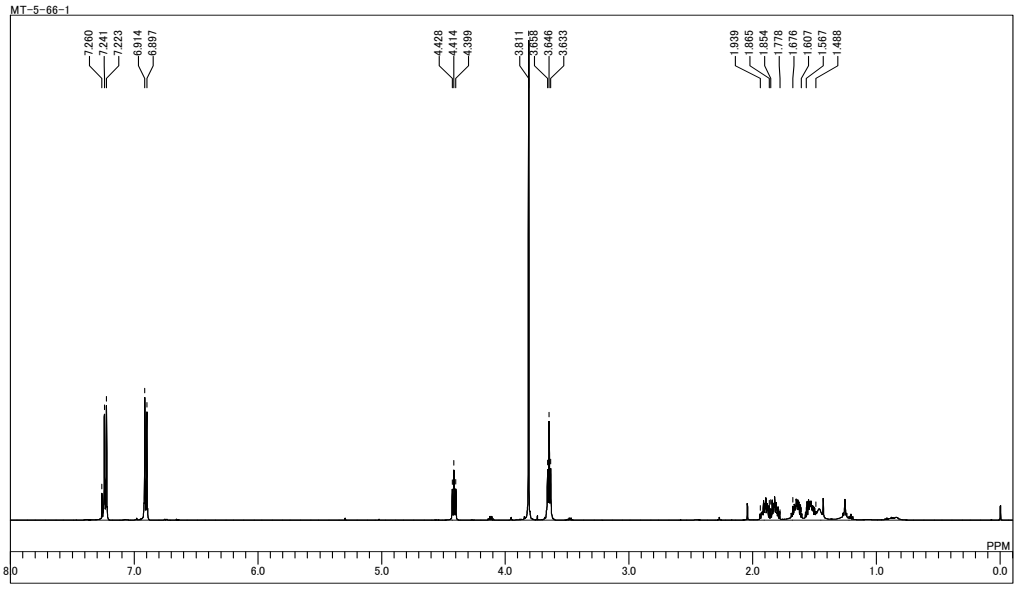
^{13}C NMR of 4-azido-4-phenylbutan-1-ol (**2a**)



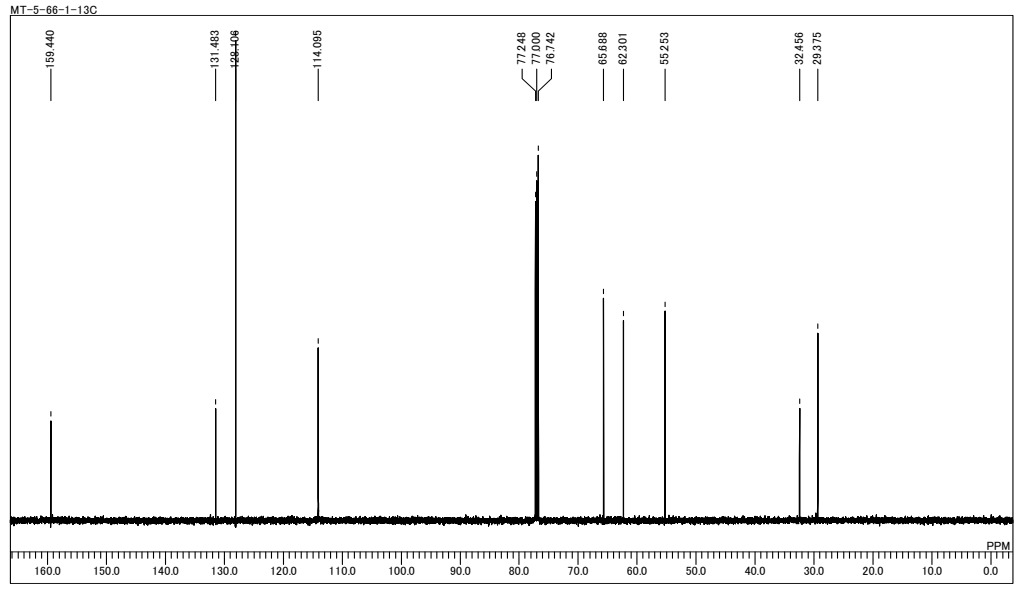
^{1}H NMR of 4-azido-4-(4-methoxyphenyl)butan-1-ol (**2b**)



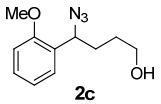
2b



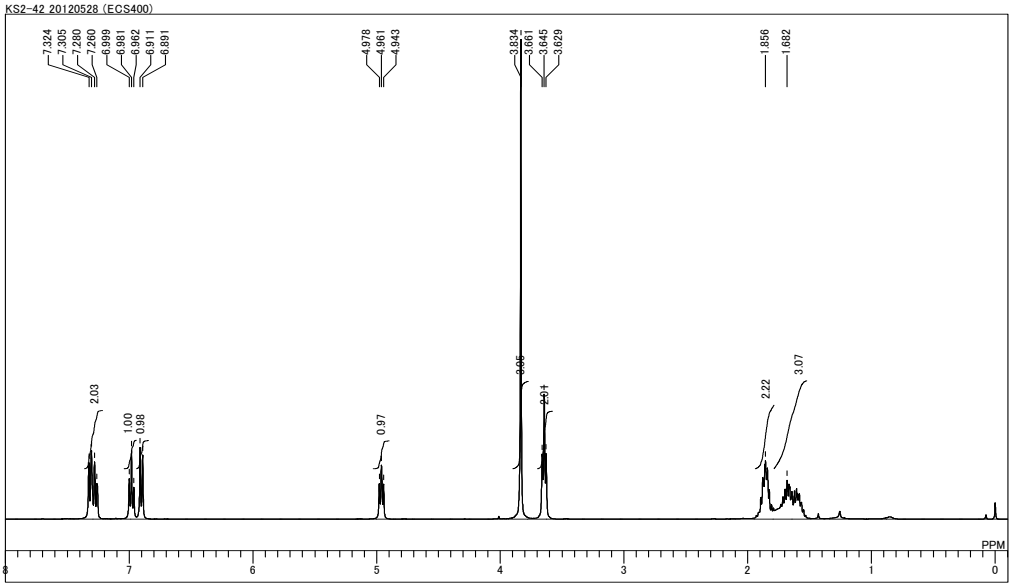
^{13}C NMR of 4-azido-4-(4-methoxyphenyl)butan-1-ol (**2b**)



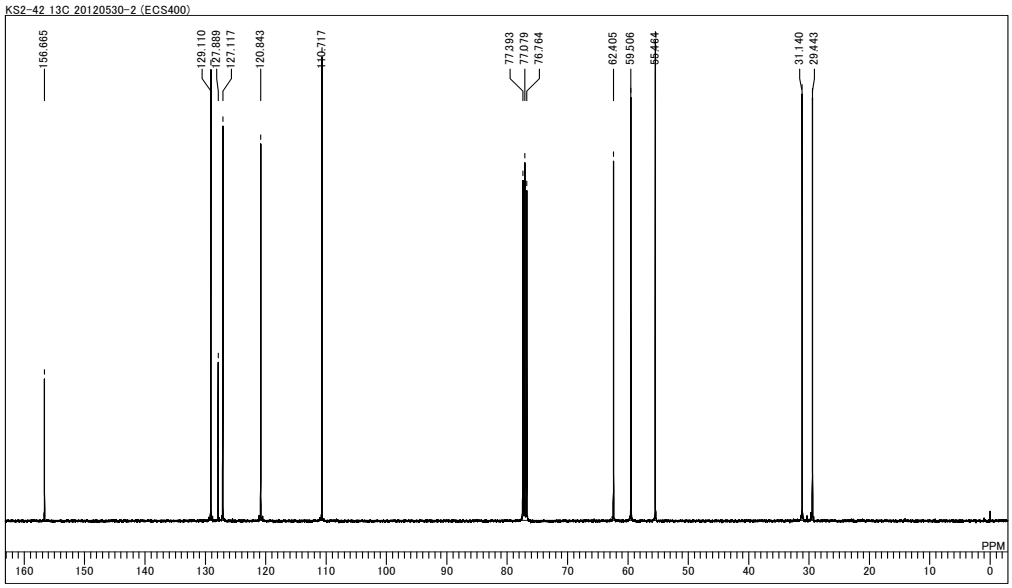
^{1}H NMR of 4-azido-4-(2-methoxyphenyl)butan-1-ol (**2c**)



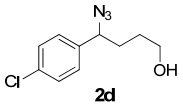
2c



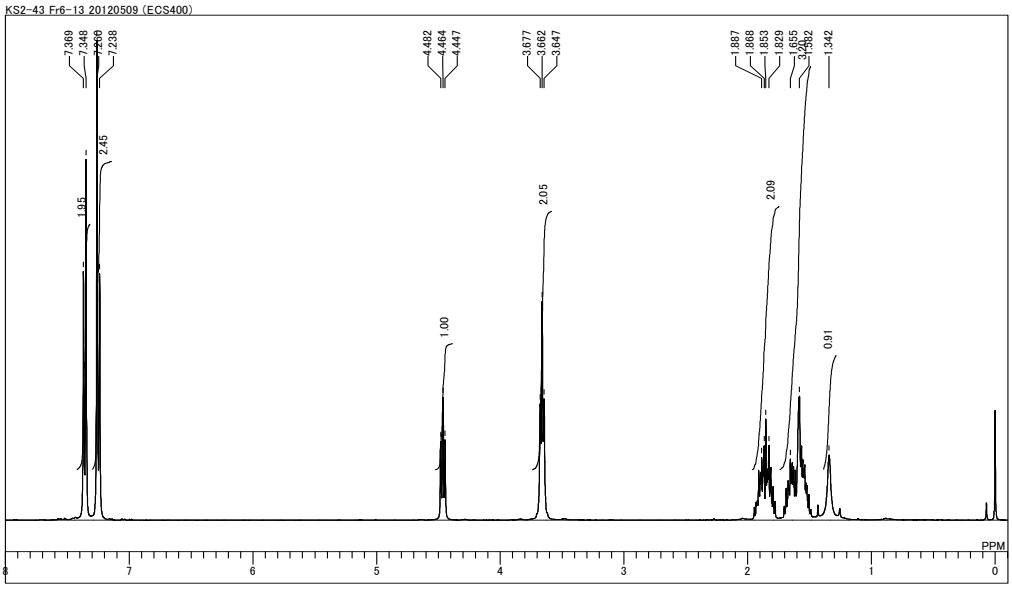
^{13}C NMR of 4-azido-4-(2-methoxyphenyl)butan-1-ol (**2c**)



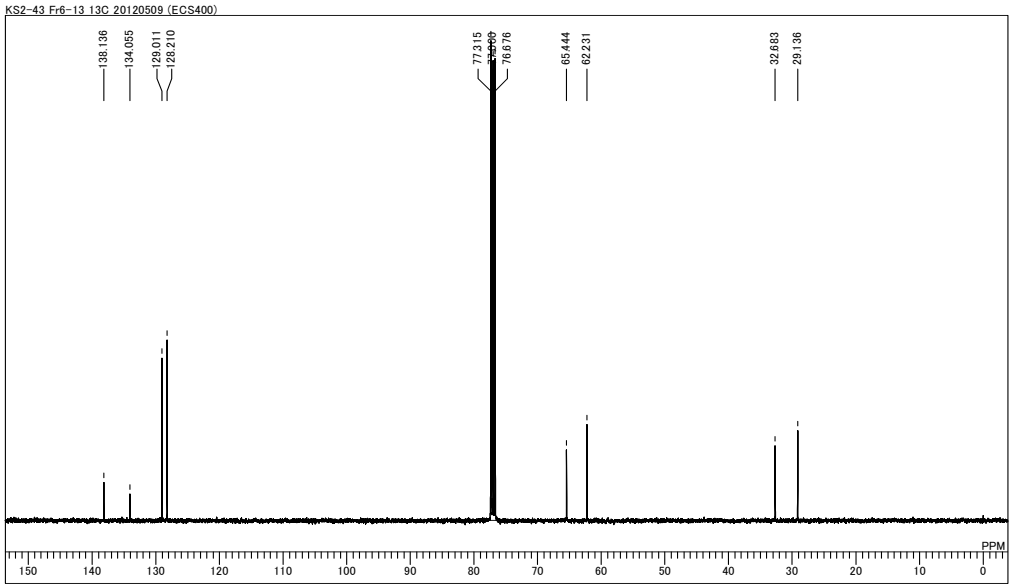
^{1}H NMR of 4-azido-4-(4-chlorophenyl)butan-1-ol (**2d**)



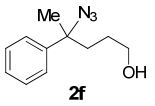
2d



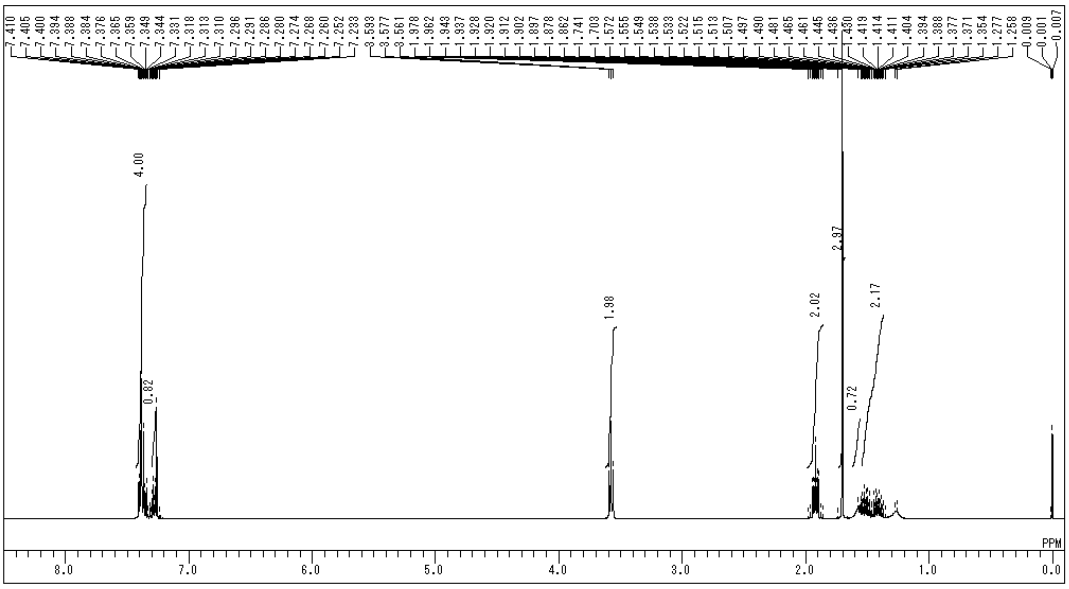
^{13}C NMR of 4-azido-4-(4-chlorophenyl)butan-1-ol (**2d**)



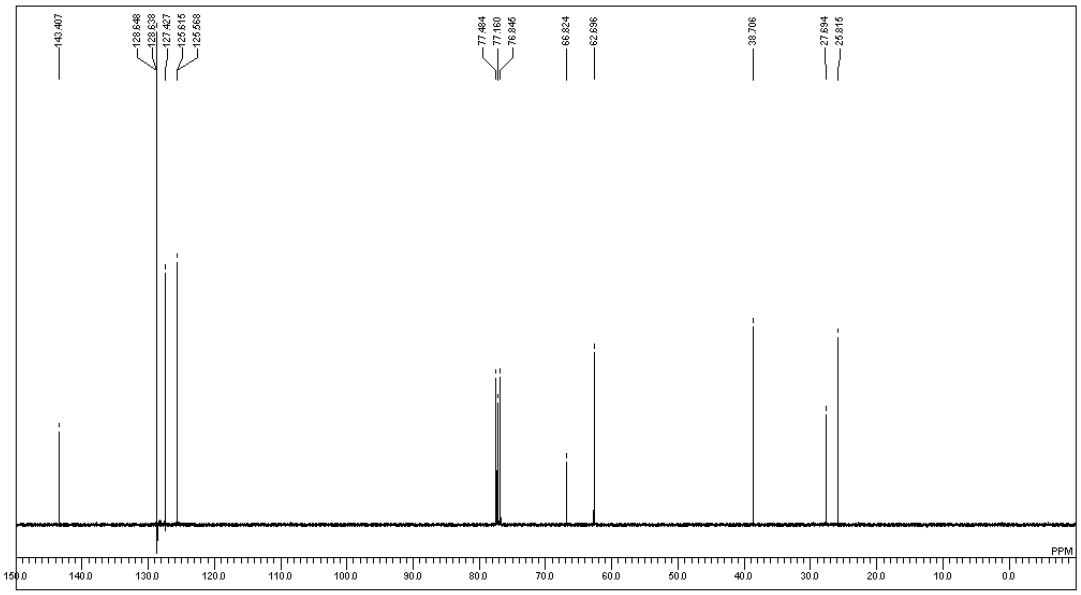
^{1}H NMR of 4-azido-4-phenylpentan-1-ol (**2f**)



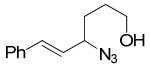
2f



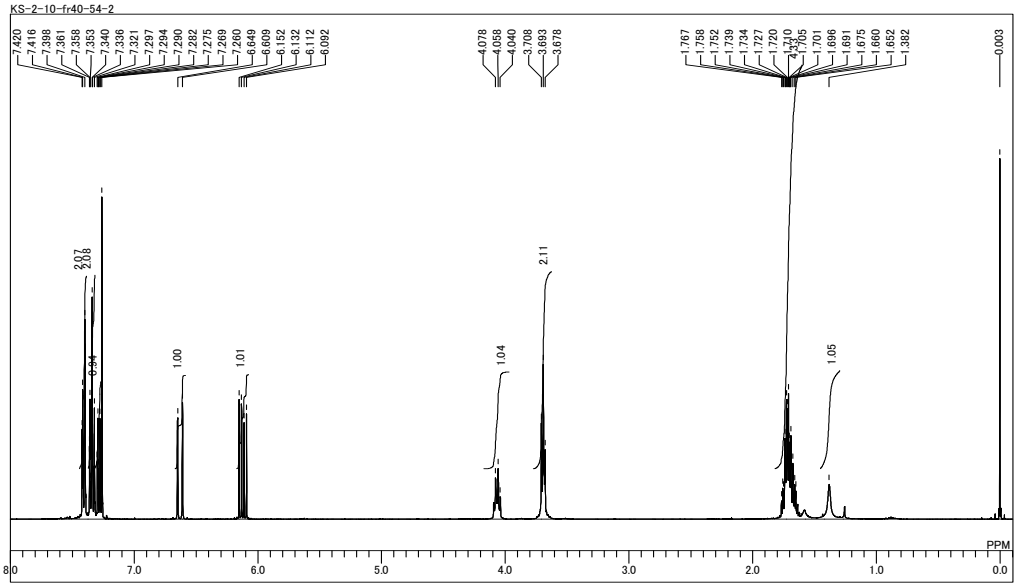
^{13}C NMR of 4-azido-4-phenylpentan-1-ol (**2f**)



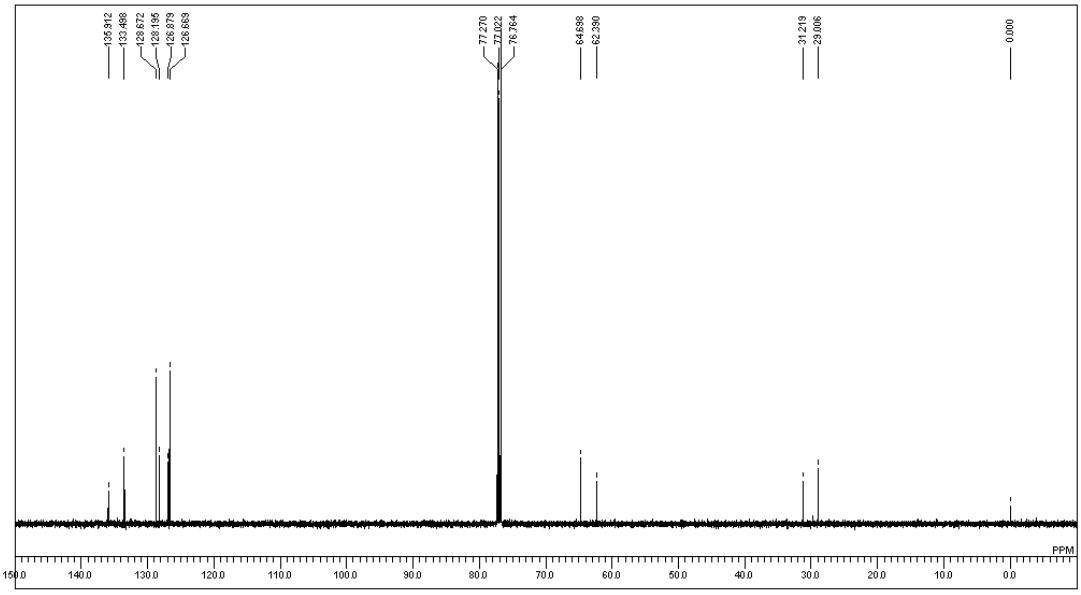
^{1}H NMR of *cis*-4-azido-6-phenyl-5-hexen-1-ol (**2g**)



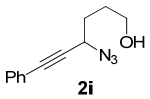
2g



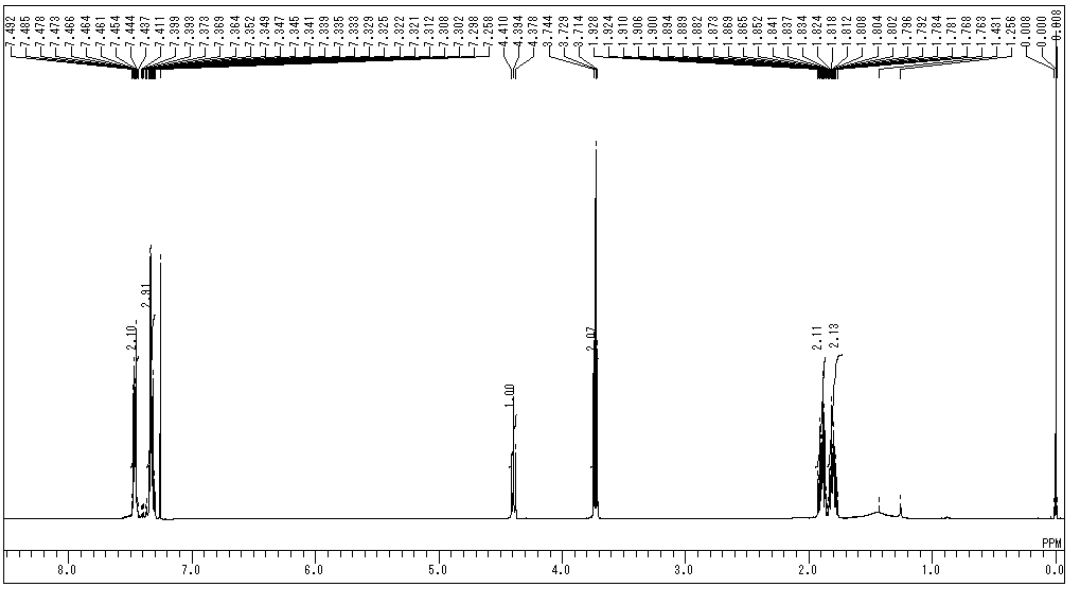
^{13}C NMR of *cis*-4-azido-6-phenyl-5-hexen-1-ol (**2g**)



^{1}H NMR of 4-Azido-6-phenyl-5-hexyne-1-ol (**2i**)



2i



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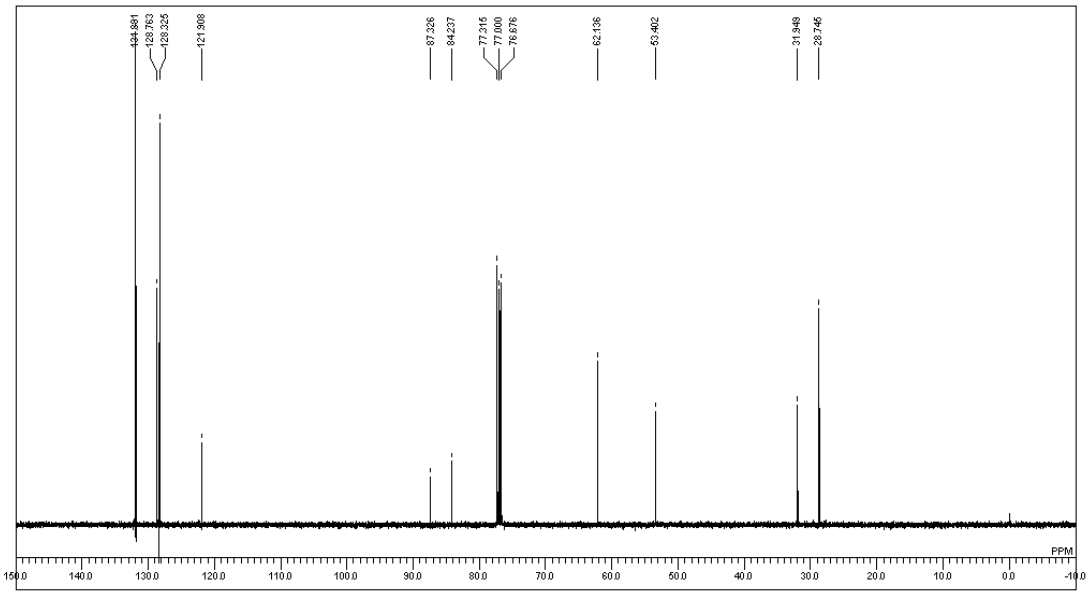
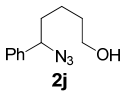
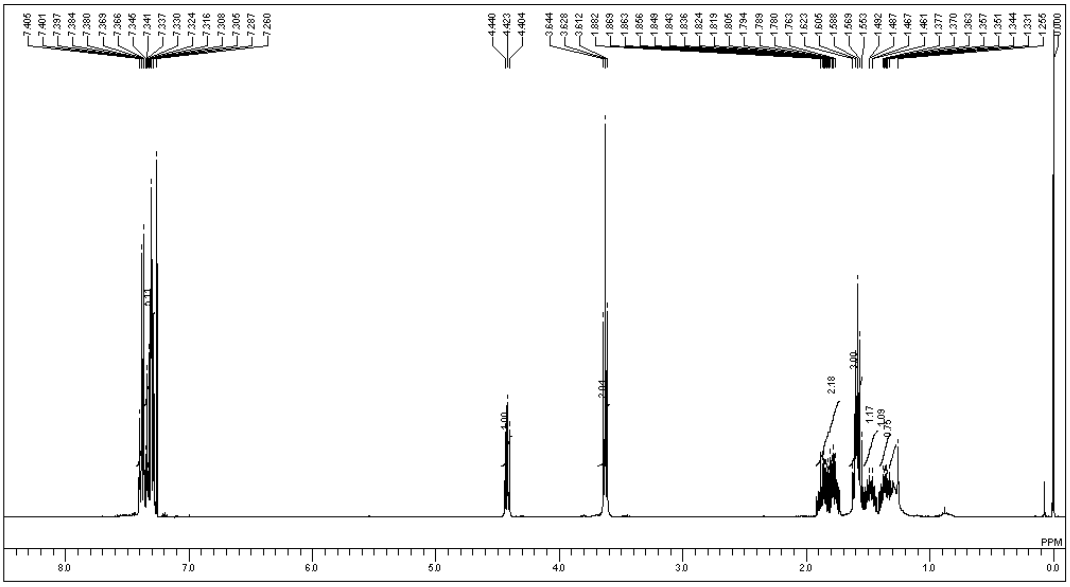


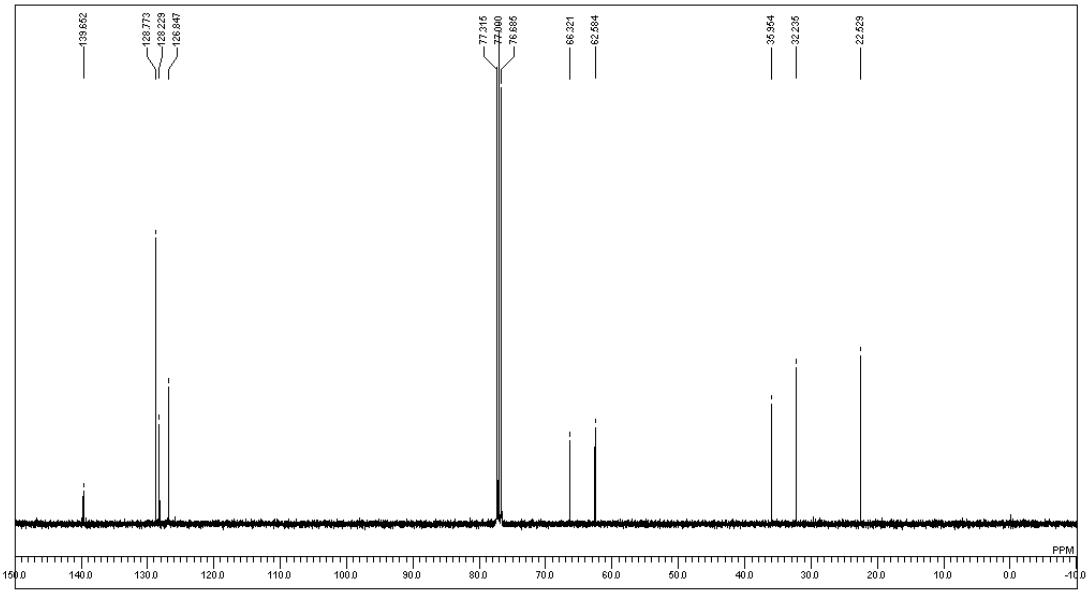
^{1}H NMR of 5-azido-5-phenylpentan-1-ol (**2j**)



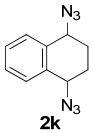
2j



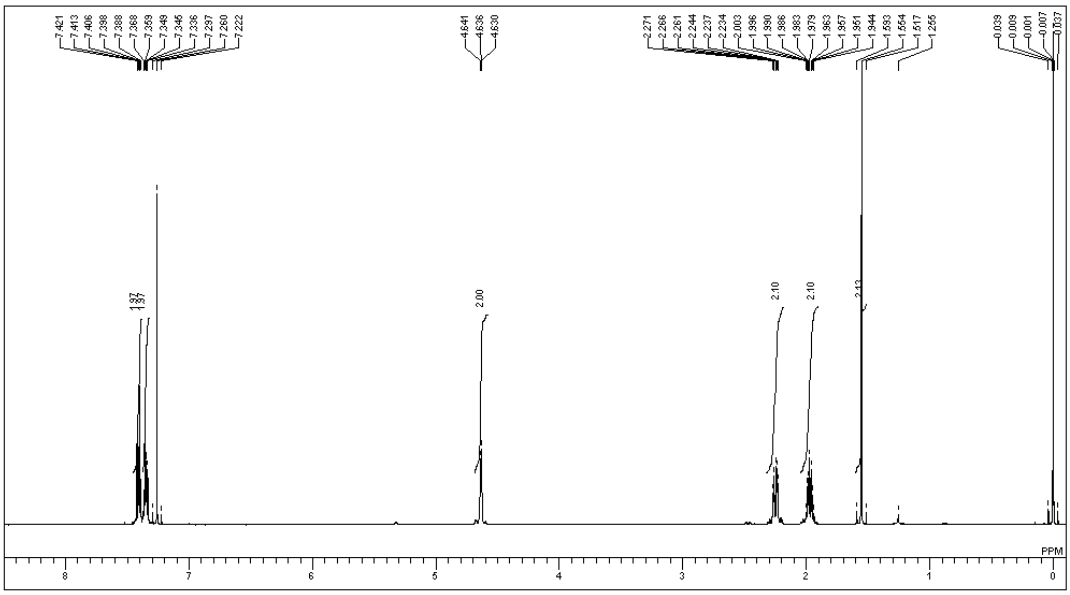
^{13}C NMR of 5-azido-5-phenylpentan-1-ol (**2j**)



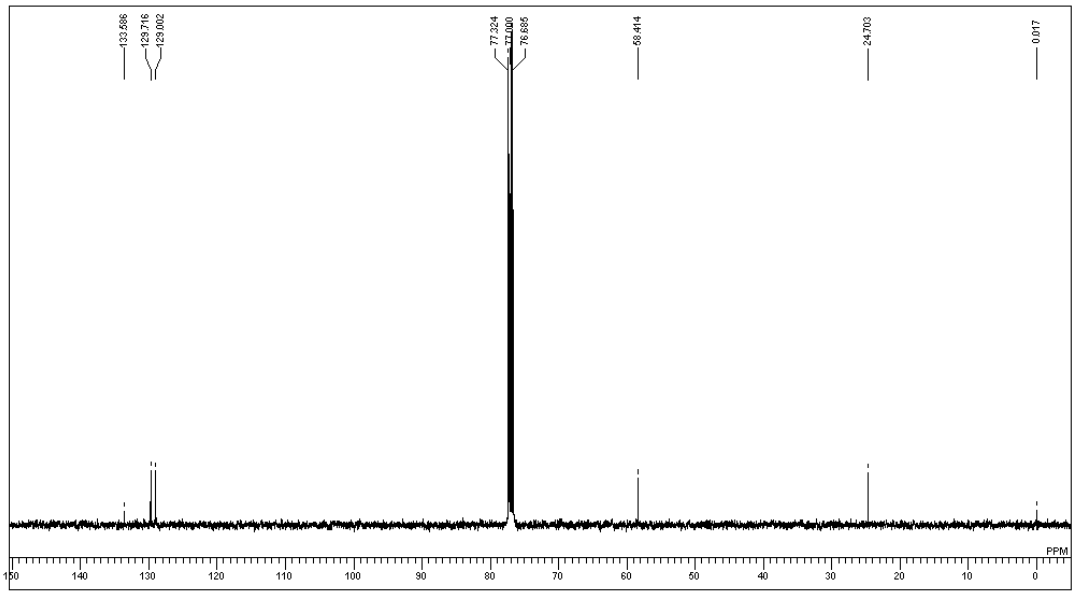
^{1}H NMR of 1,4-diazido-tetraline (**2k**, First one)



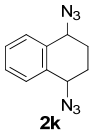
2k



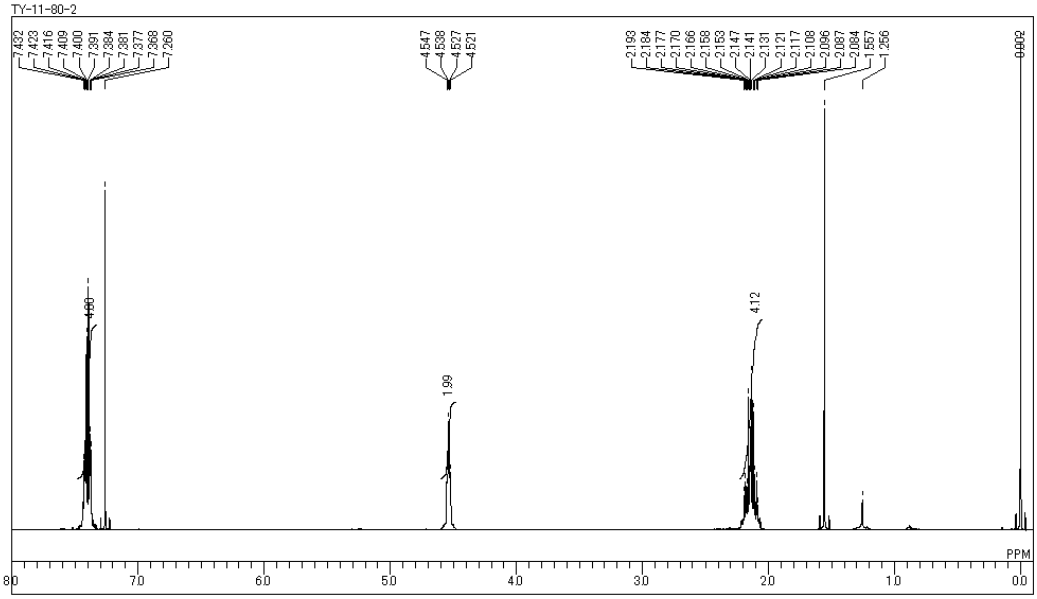
^{13}C NMR of 1,4-diazido-tetraline (**2k**, First one)



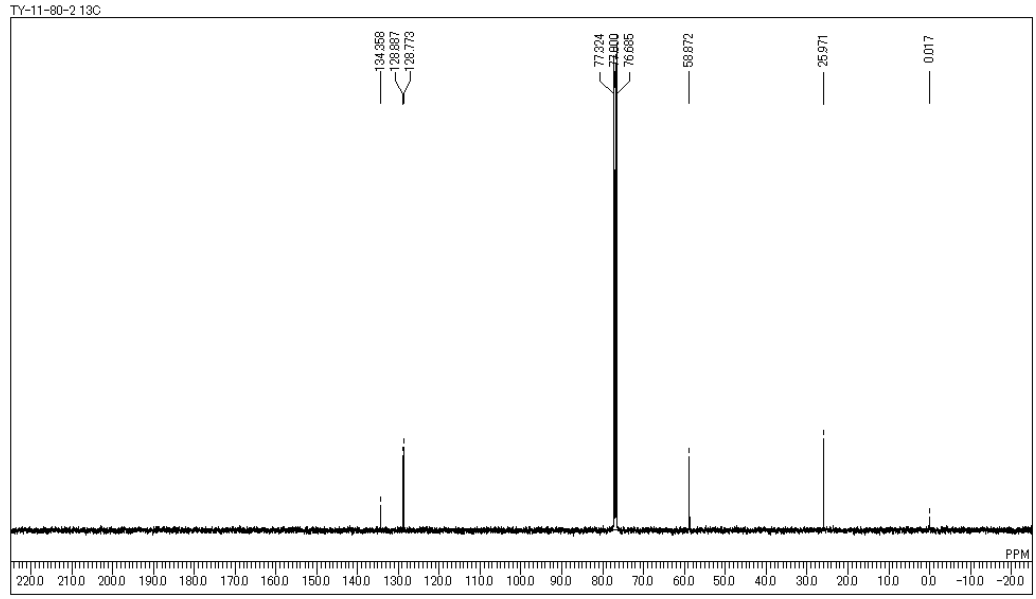
^{1}H NMR of 1,4-diazido-tetraline (**2k**, Second one)



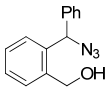
2k



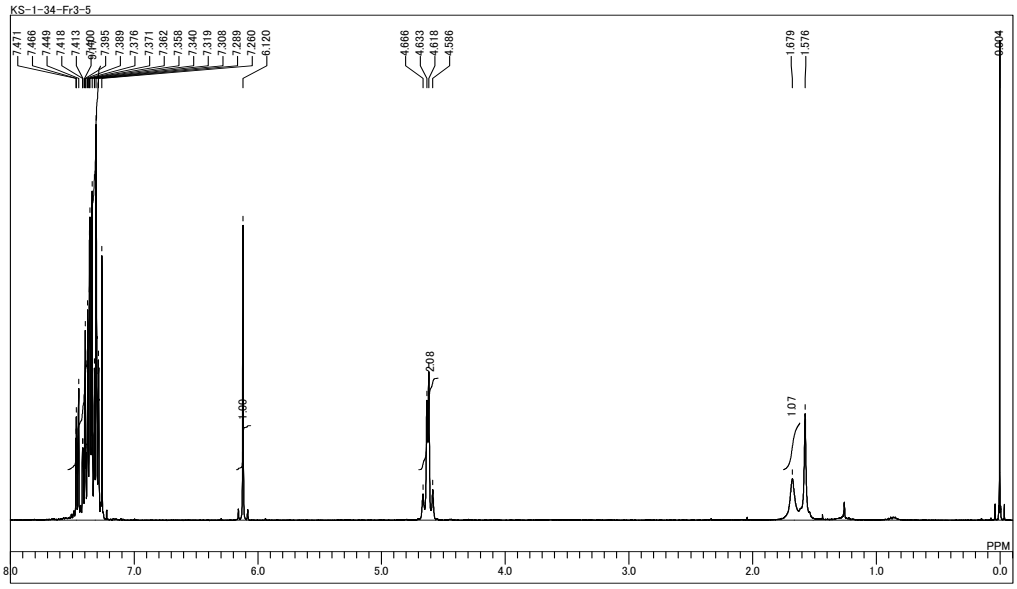
^{13}C NMR of 1,4-diazido-tetraline (**2k**, Second one)



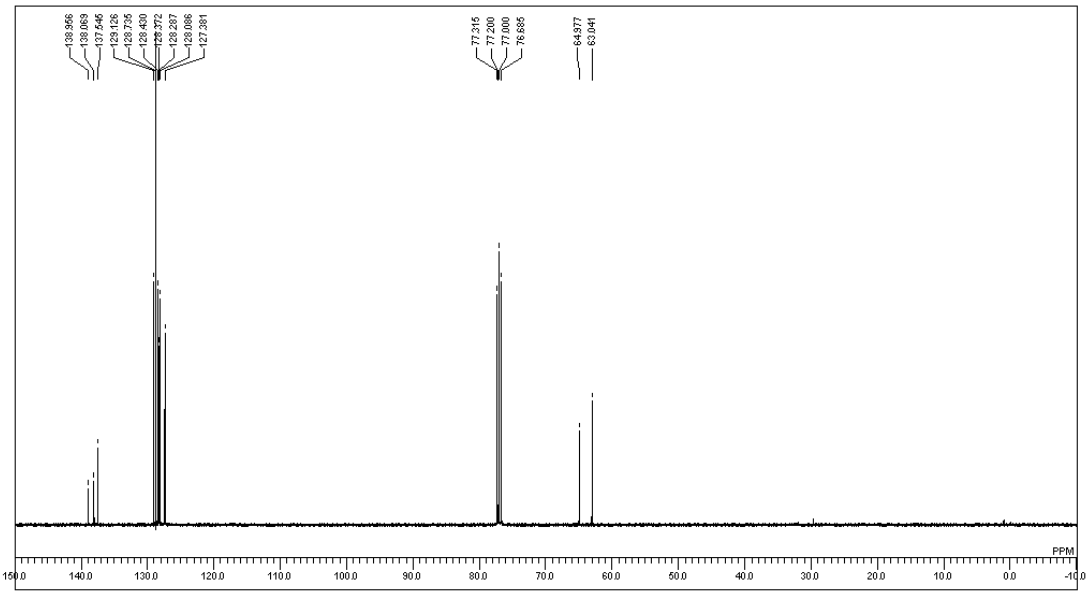
^{1}H NMR of 1-(azidophenylmethyl)-2-(hydroxymethyl)benzene (**2l**)



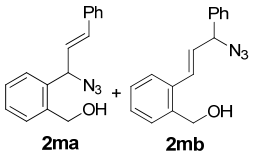
2l

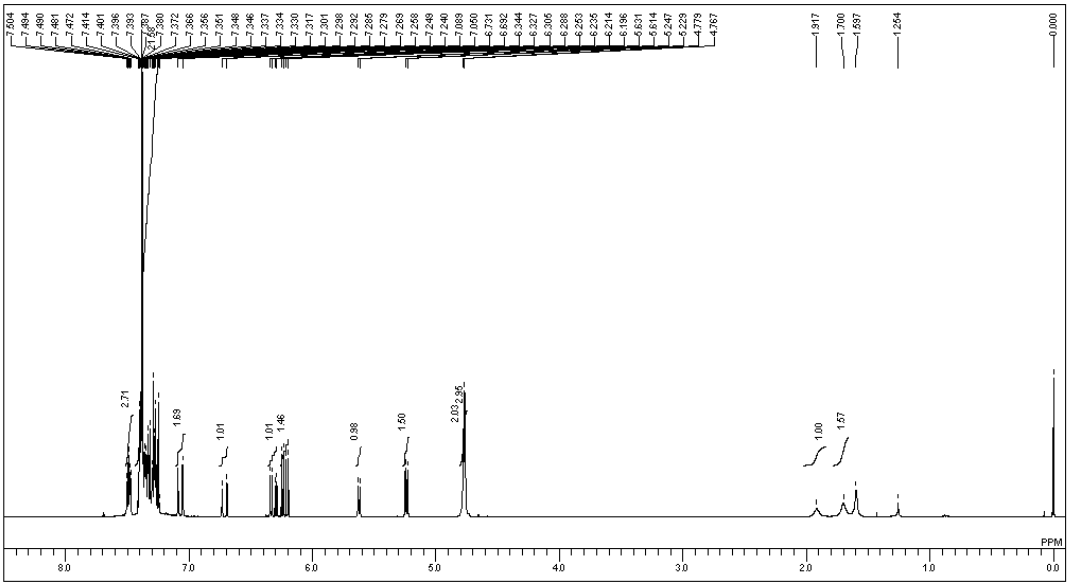


^{13}C NMR of 1-(azidophenylmethyl)-2-(hydroxymethyl)benzene (**2l**)

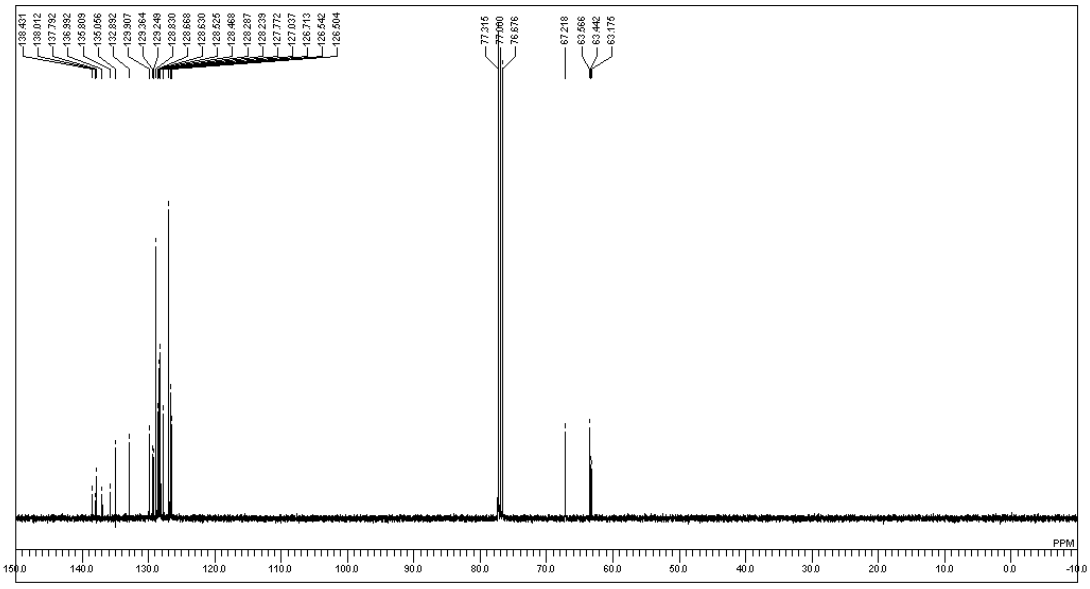


^{1}H NMR ofmixture of 1-(1-azido-3-phenyl-2-propen-1-yl)-2-(hydroxymethyl)benzene (**2ma**) and 1-(3-Azido-3-phenyl-1-propen-1-yl)-2-(hydroxymethyl)benzene (**2mb**)

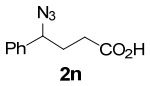




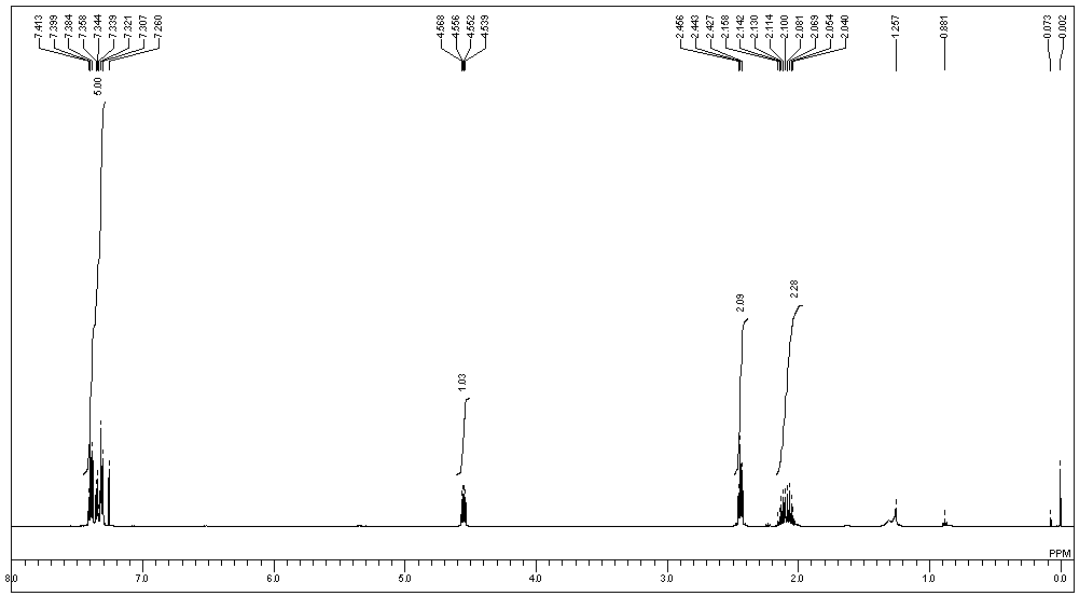
^{13}C NMR ofmixture of 1-(1-azido-3-phenyl-2-propen-1-yl)-2-(hydroxymethyl)benzene (**2ma**) and 1-(3-Azido-3-phenyl-1-propen-1-yl)-2-(hydroxymethyl)benzene (**2mb**)



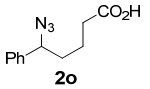
^{1}H NMR of 4-Azido-4-phenylbutanoic acid (**2n**)



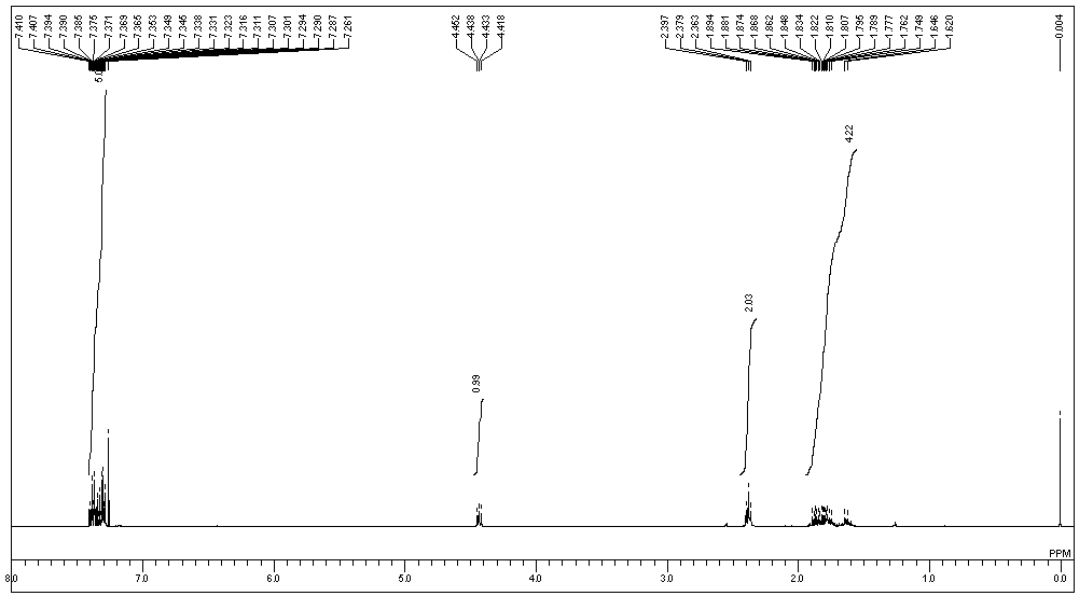
2n



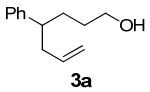
^{1}H NMR of 5-Azido-5-phenylbutanoic acid (**2o**)



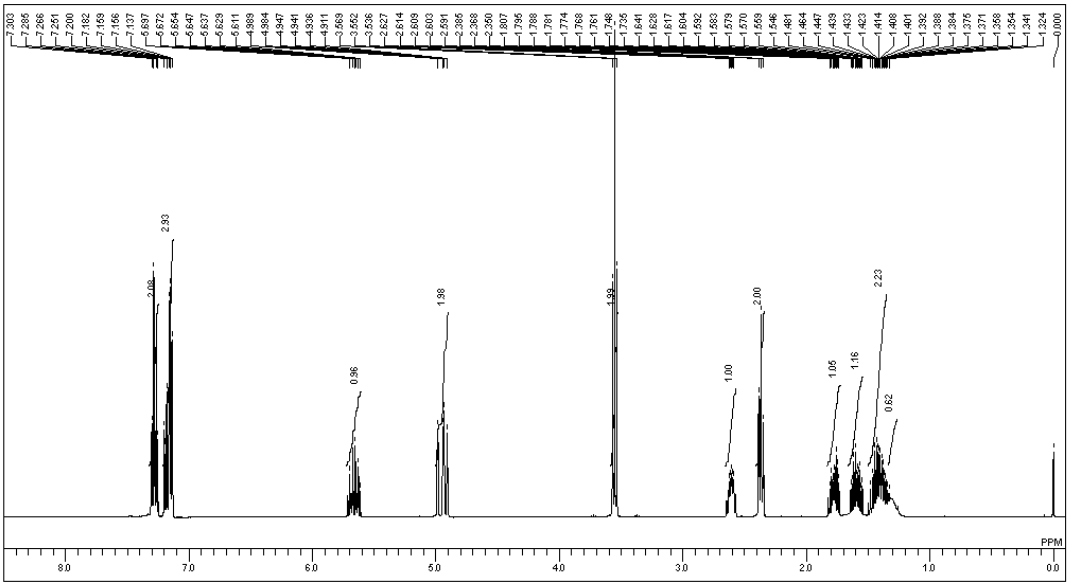
2o



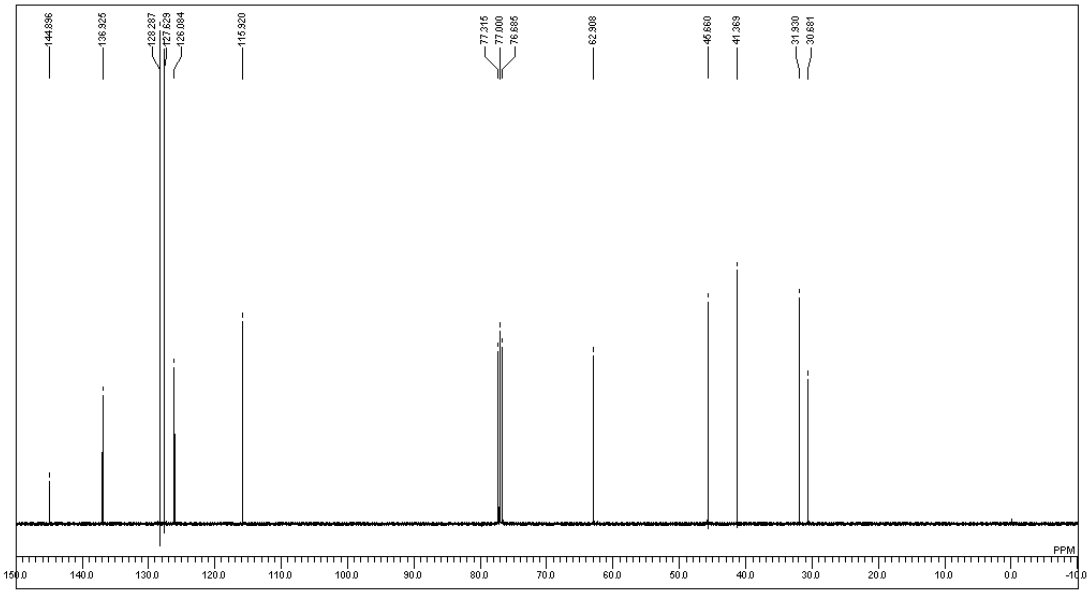
^{1}H NMR of 4-phenyl-6-heptene-1-ol (**3a**)



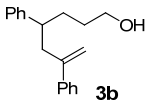
3a



^{13}C NMR of 4-phenyl-6-heptene-1-ol (**3a**)



^{1}H NMR of 4,6-diphenyl-6-heptene-1-ol (**3b**)



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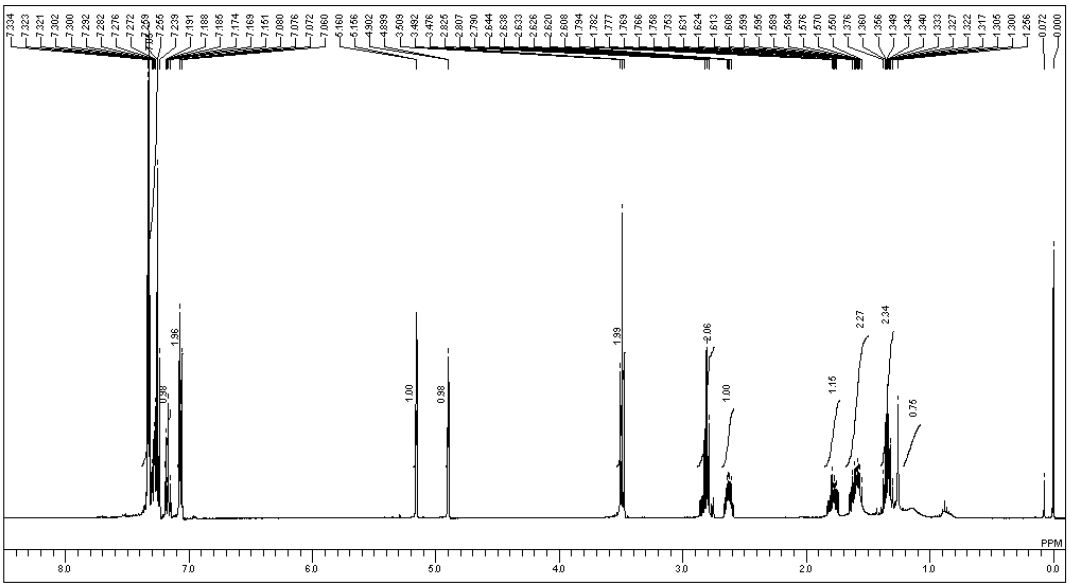
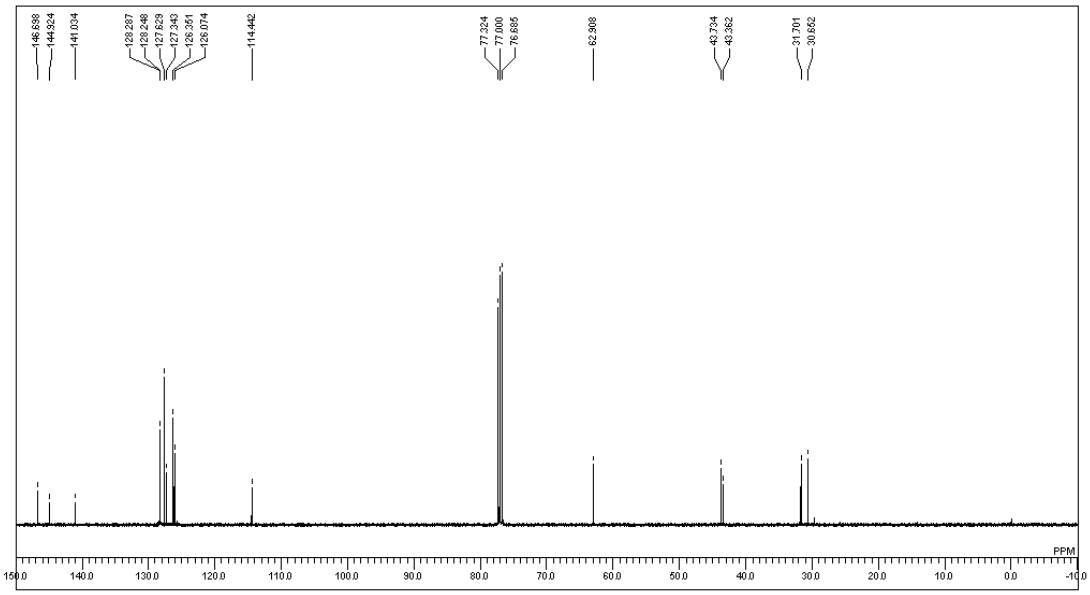
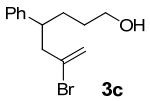


^{13}C NMR of 4,6-diphenyl-6-heptene-1-ol (**3b**)



^{1}H NMR of 6-bromo-4-phenyl-6-heptene-1-ol (**3c**)



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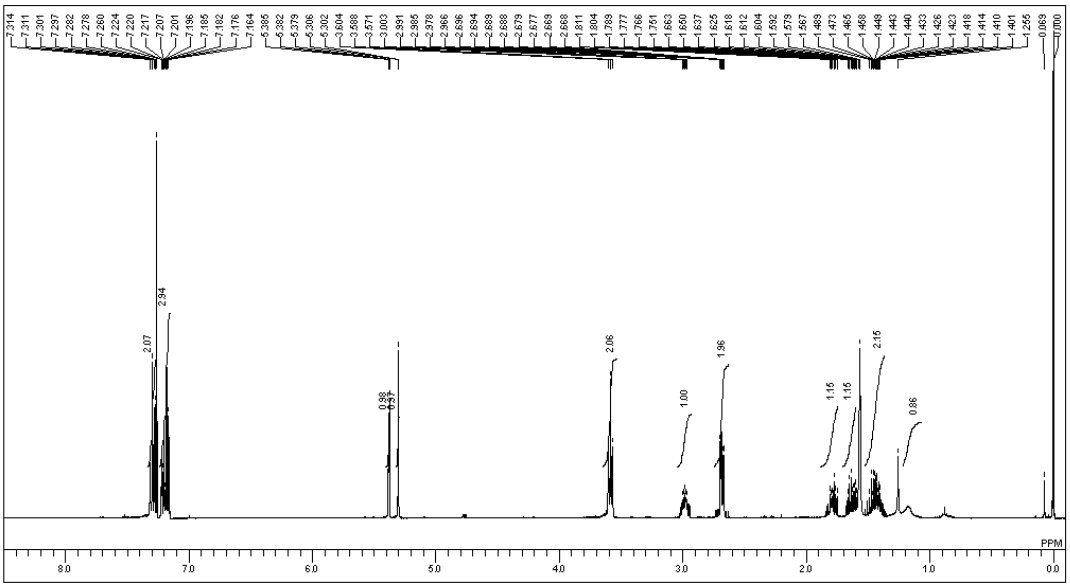
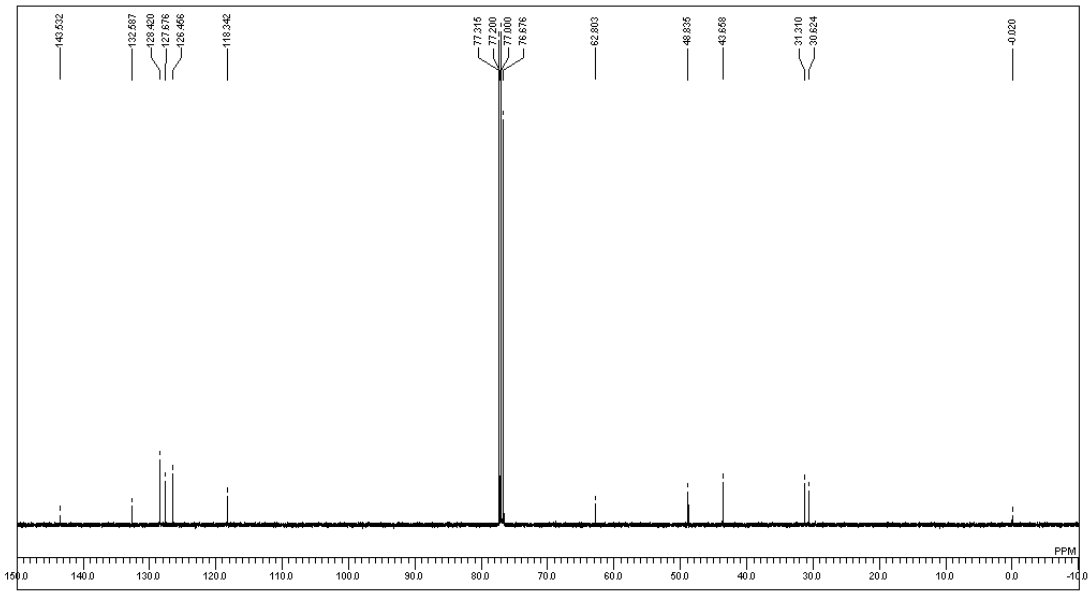
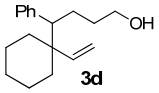
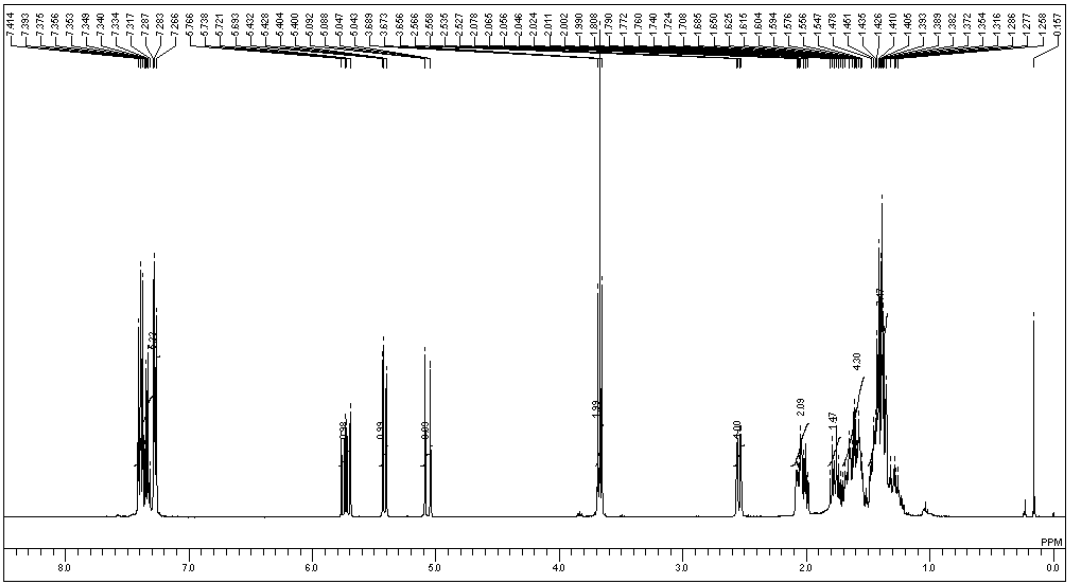


^{13}C NMR of 6-bromo-4-phenyl-6-heptene-1-ol (**3c**)

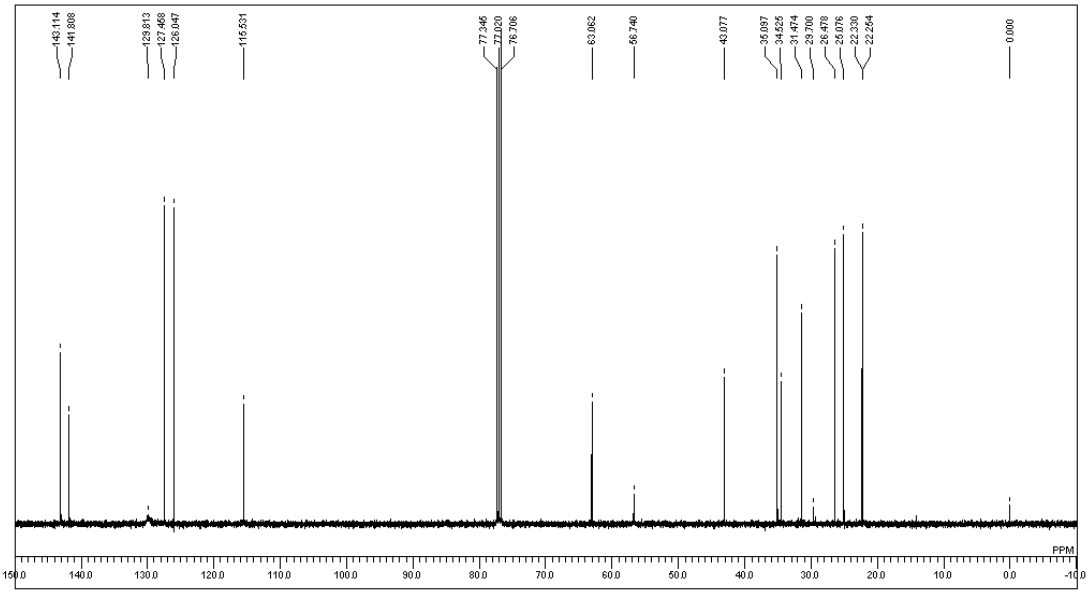


^{1}H NMR of 1-ethenyl-(4-hydroxy-1-pnehyl-1-butyl)cyclohexane (**3d**)

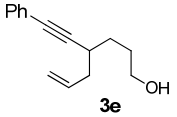




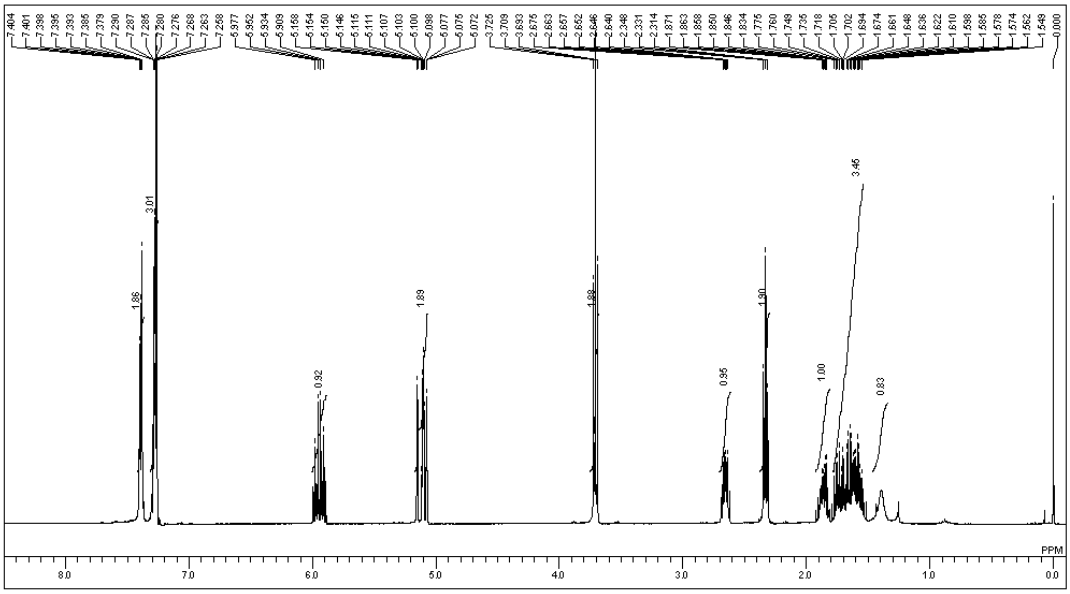
^{13}C NMR of 1-ethenyl-(4-hydroxy-1-pnehyl-1-butyl)cyclohexane (**3d**)



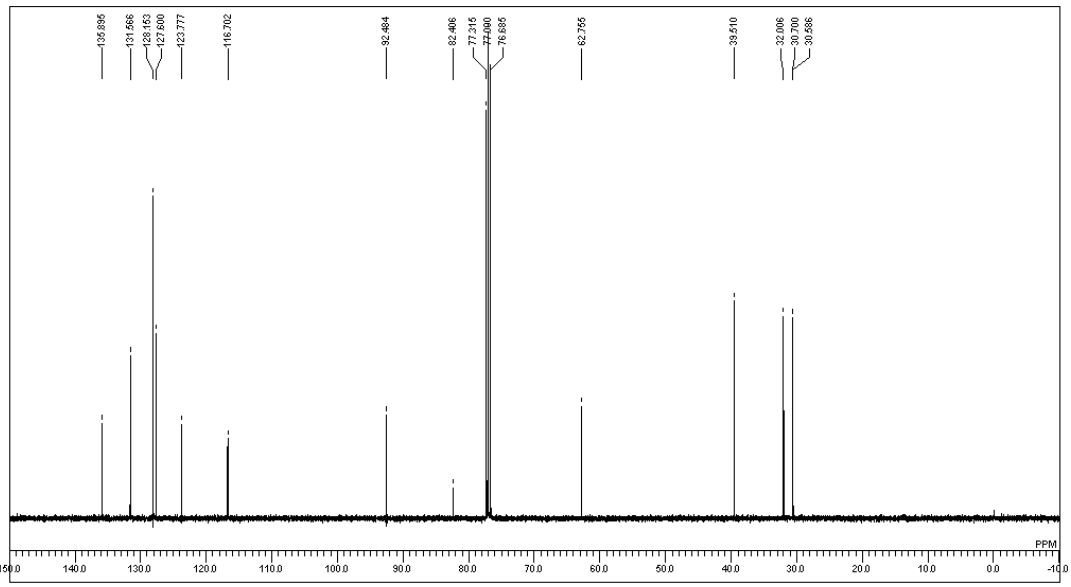
^{1}H NMR of 4-phenylethynyl-6-heptene-1-ol (**3e**)



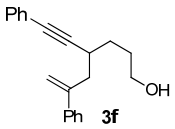
3e



^{13}C NMR of 4-phenylethynyl-6-heptene-1-ol (**3e**)



^{1}H NMR of 6-phenyl-4-phenylethynyl-6-heptene-1-ol (**3f**)



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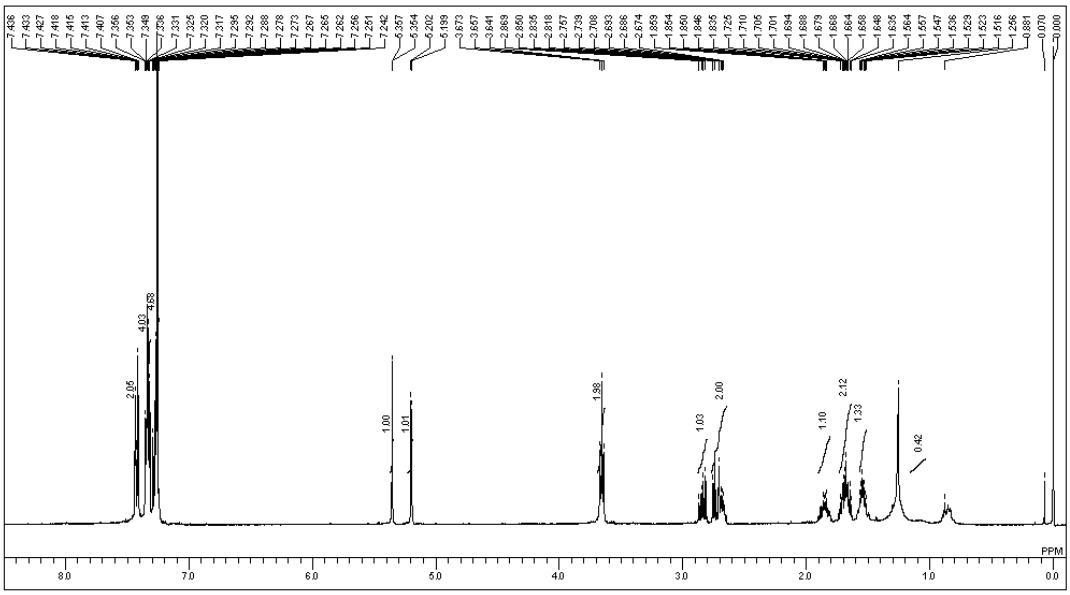
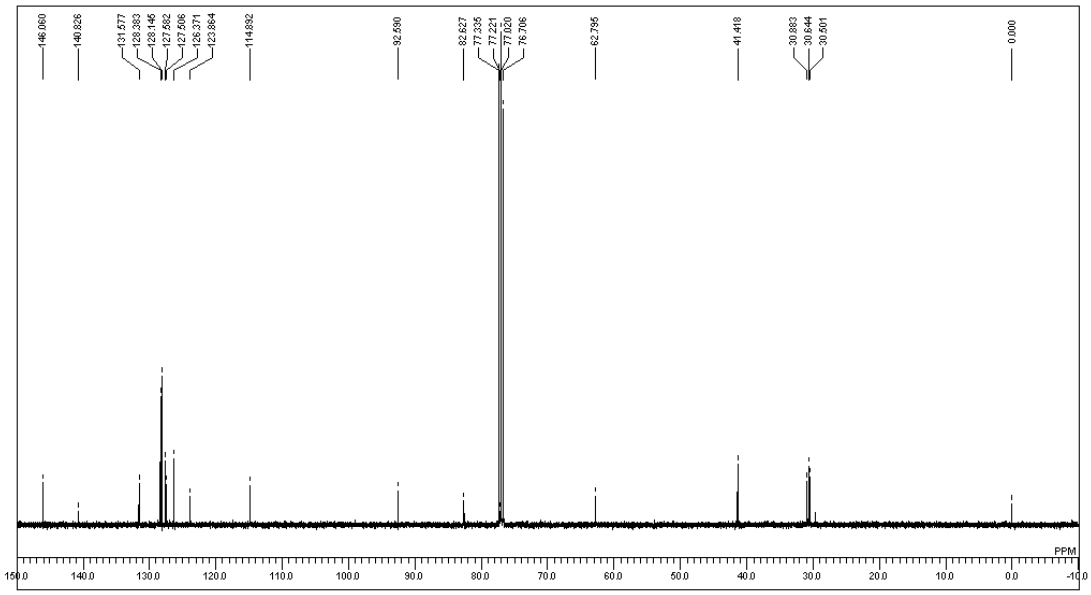
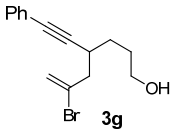
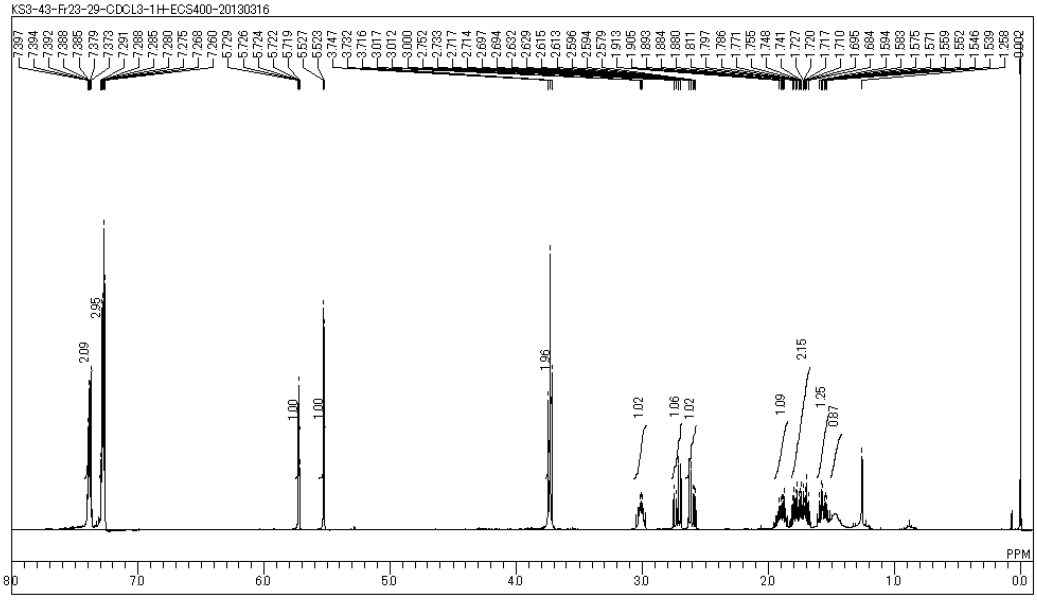


^{13}C NMR of 6-phenyl-4-phenylethynyl-6-heptene-1-ol (**3f**)

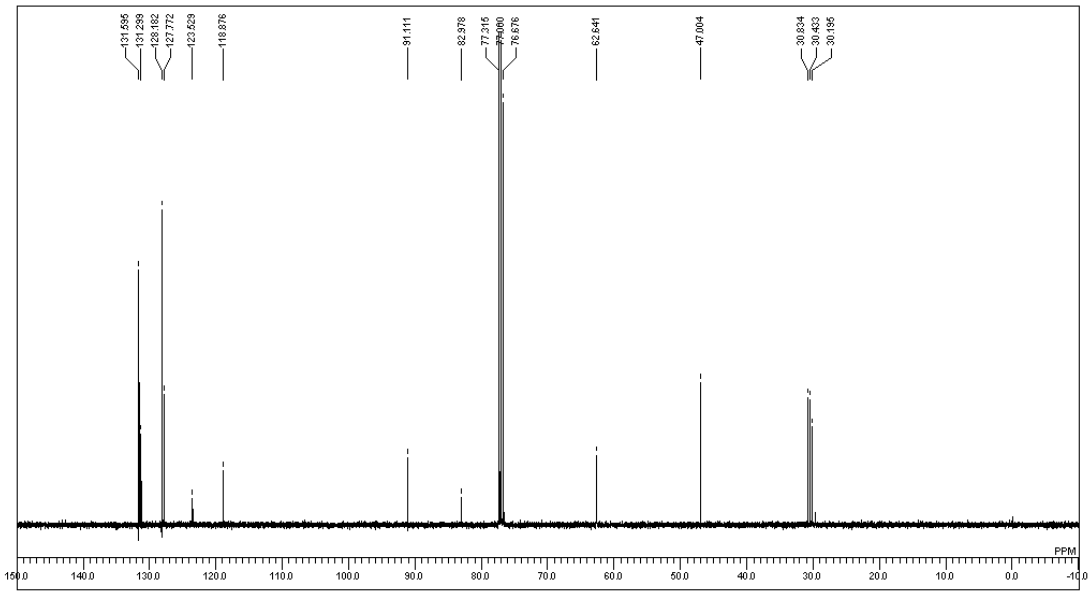


^{1}H NMR of 6-bromo-4-phenylethynyl-6-heptene-1-ol (**3g**)

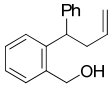




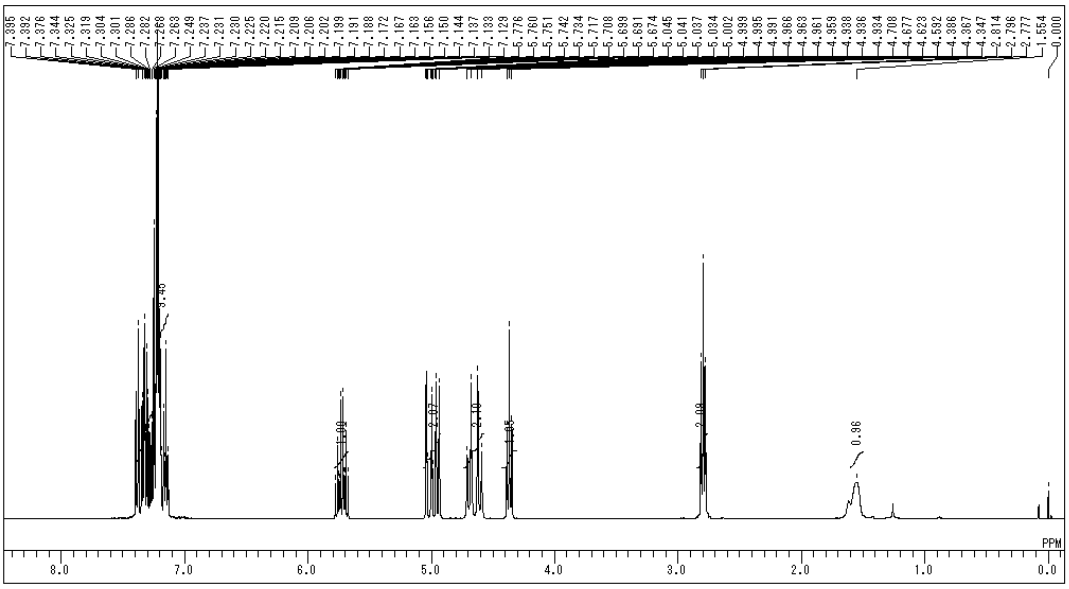
^{13}C NMR of 6-bromo-4-phenylethynyl-6-heptene-1-ol (**3g**)



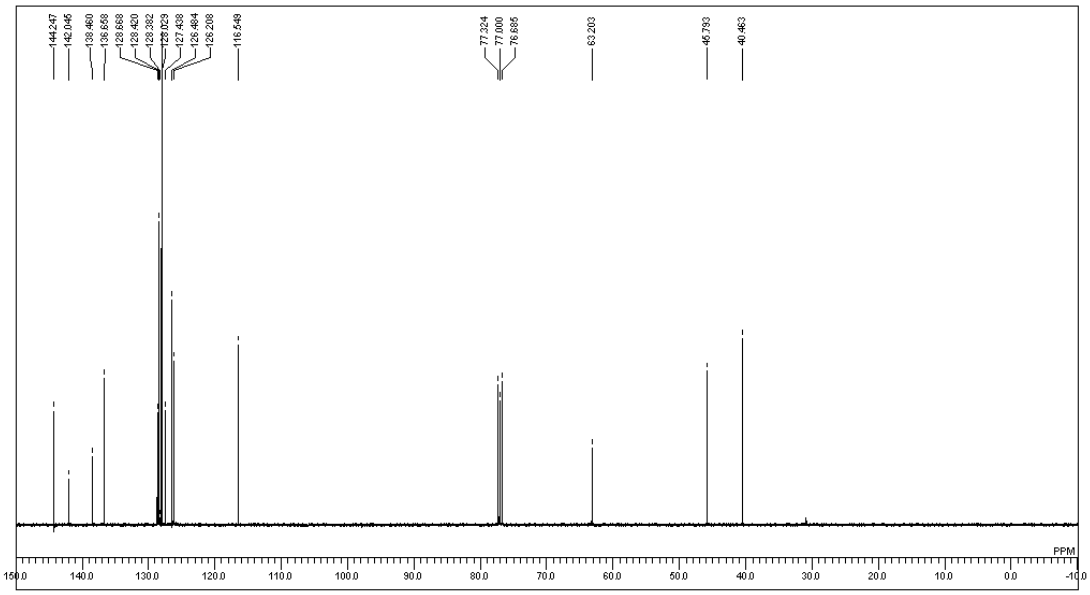
^{1}H NMR of 1-(1-phenyl-3-butene-1-yl)-2-(hydroxymethyl)benzene (**3h**)



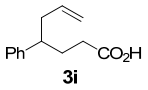
3h



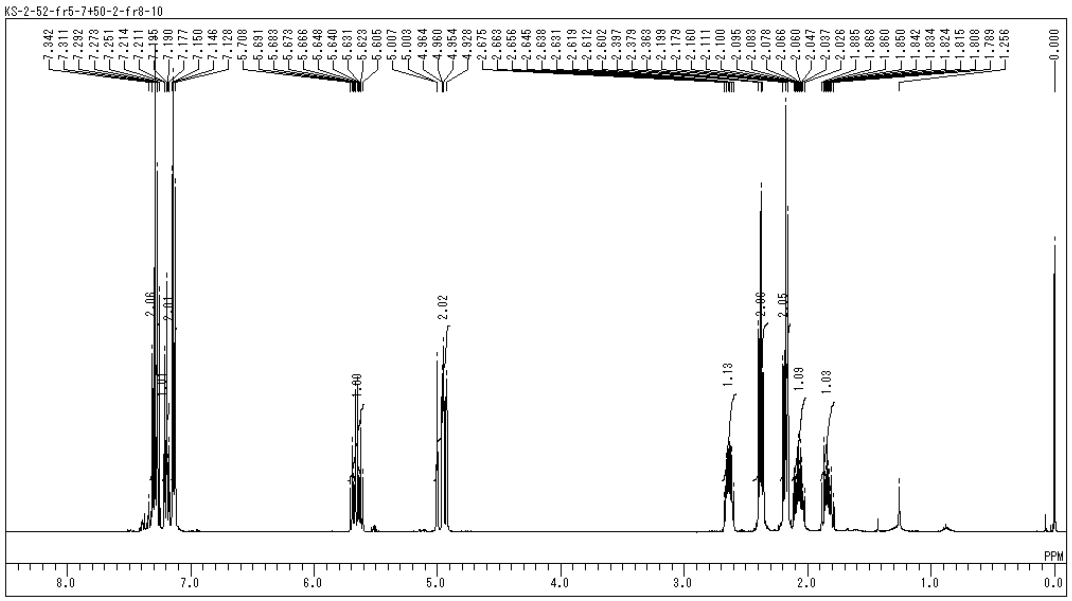
^{13}C NMR of 1-(1-phenyl-3-butene-1-yl)-2-(hydroxymethyl)benzene (**3h**)



^{1}H NMR of 4-phenyl-6-heptenolic acid (**3i)**



3i



^{13}C NMR of 4-phenyl-6-heptenolic acid (**3i)**