

## Supporting information

### Phenyl Trimethyl Ammonium Tribromide Mediated Robust One-pot Synthesis of Spiro-oxacycles – An Economic Way Out – Stereoselective Synthesis of Oxaspirohexacyclodieneones

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## 1. Materials & Methods-

All reactions were performed under nitrogen atmosphere using oven dried glass wires. All solvents are used in dried condition. THF was first dried over potassium carbonate then by metallic sodium with benzophenone. Diethyl ether also dried over metallic sodium with benzophenone. Anhydrous sodium sulphate was used for drying reaction mixture after aqueous workup.

TLC was performed with .25mm coated commercial silica gel plates (DC-kiesel gel 60 F<sub>254</sub>) and stain by Iodine, vanillin solution. Chromatographic separation was done by using (200-400mesh) silica gel. NMR chemical shift value are reported in ( $\delta$ ppm) .TMS taken as internal standard for <sup>1</sup>H the residual signal for CDCl<sub>3</sub> taken as 7.28 ppm & for <sup>13</sup>C 77.00ppm. <sup>1</sup>H spectral data reported as  $\delta$  (multiplicity, Coupling constant, integration). Multiplicity reported as follows, s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet, dd = doublet of a doublet, td = triplate of a doublet. HRMS (High resolution Mass Spectra) was measured in a Q-TOF I (quadrupolehexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface on micro mass spectrometer. IR spectra were recorded using thin film deposit on NaCl & absorption frequency reported in cm<sup>-1</sup>.

### List of Abbreviations:

THF= Tetrahydrofuran,

EtOAc= Ethyl acetate

TLC= Thin layer chromatography

DCM = Dichloro methane

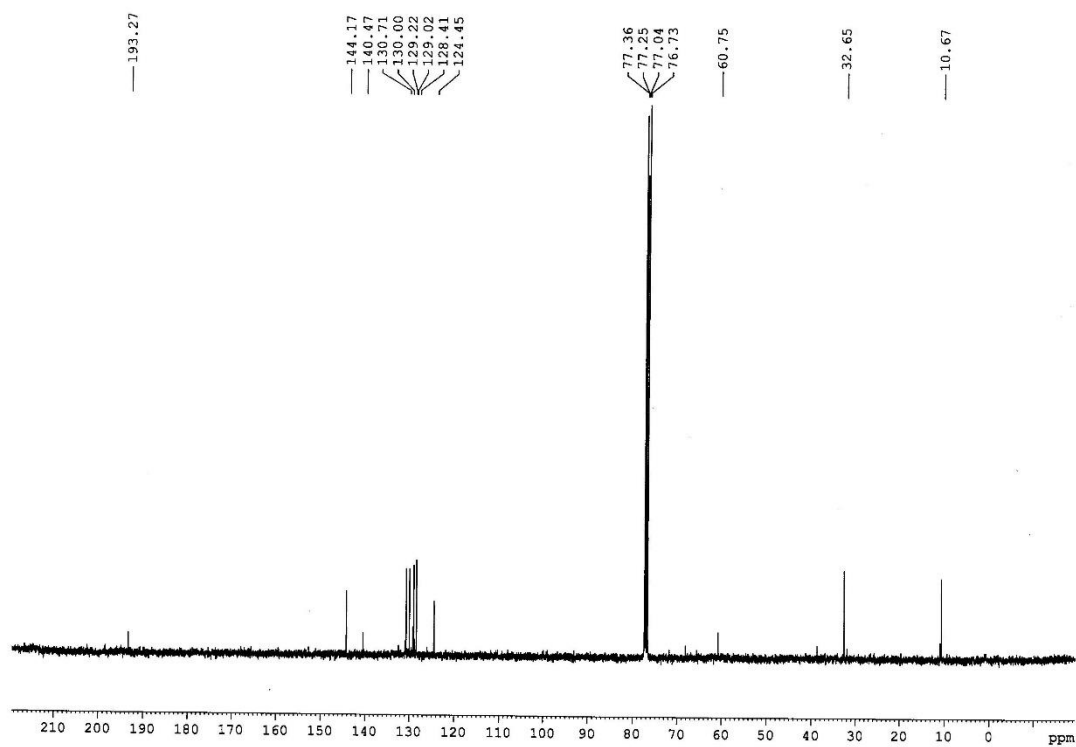
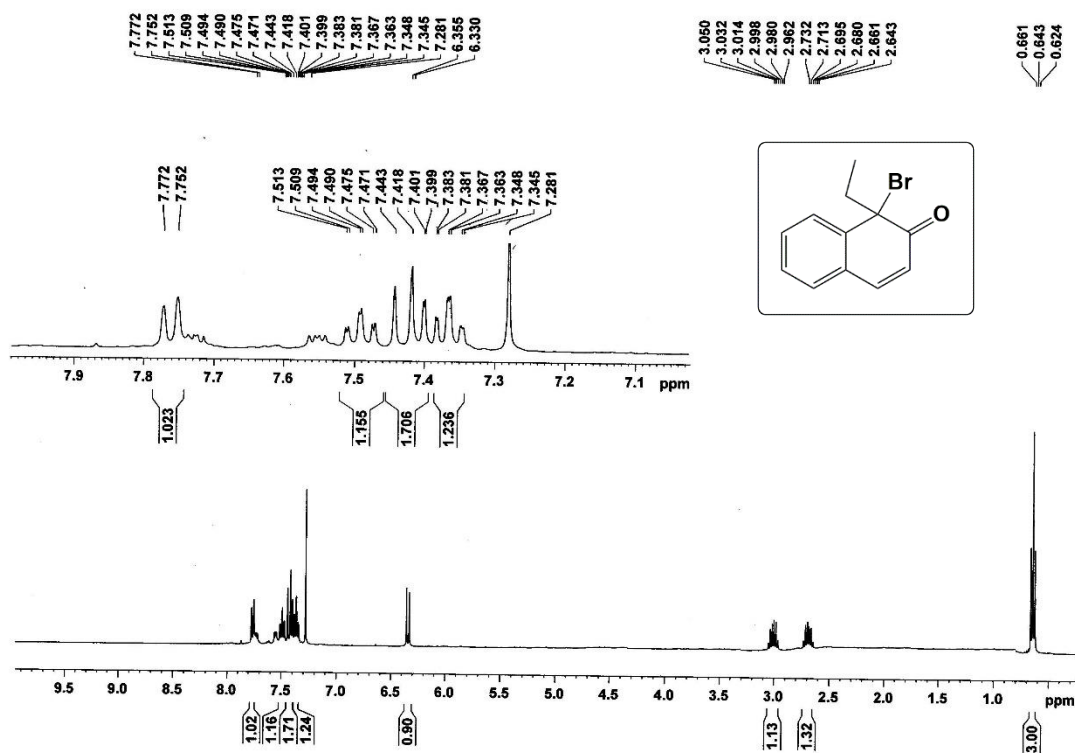
DIBAL- Diisobutyl aluminium hydride

MeI-Methyl Iodide

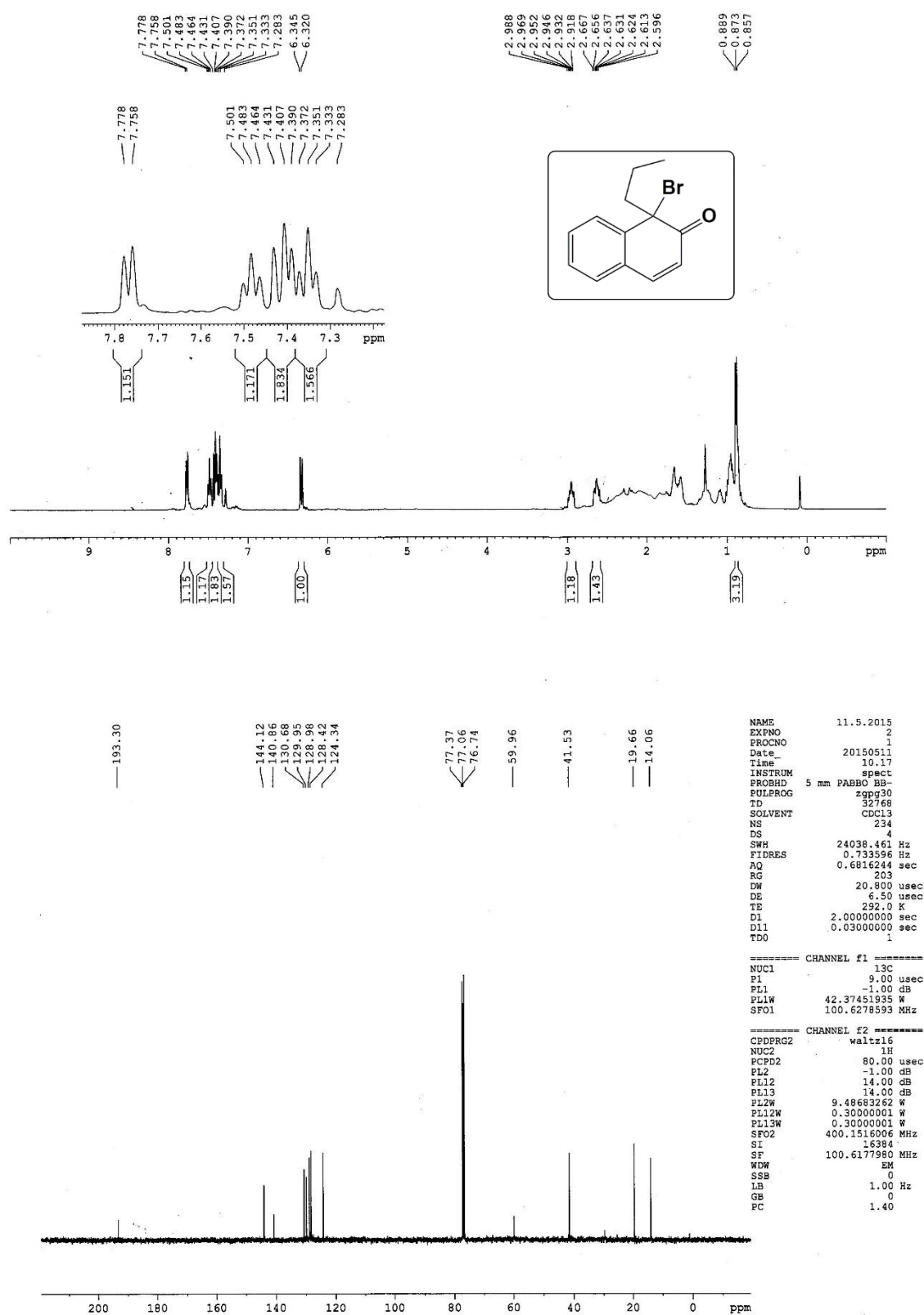
BnBr-Benzyl Bromide

LiAlH- lithium Aluminium Hydride

# 1-bromo-1-ethylnaphthalen-2(1H)-one (2a)

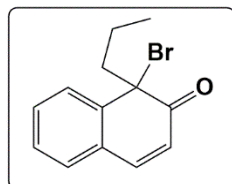


# 1-bromo-1-propylnaphthalen-2(1H)-one (2b)

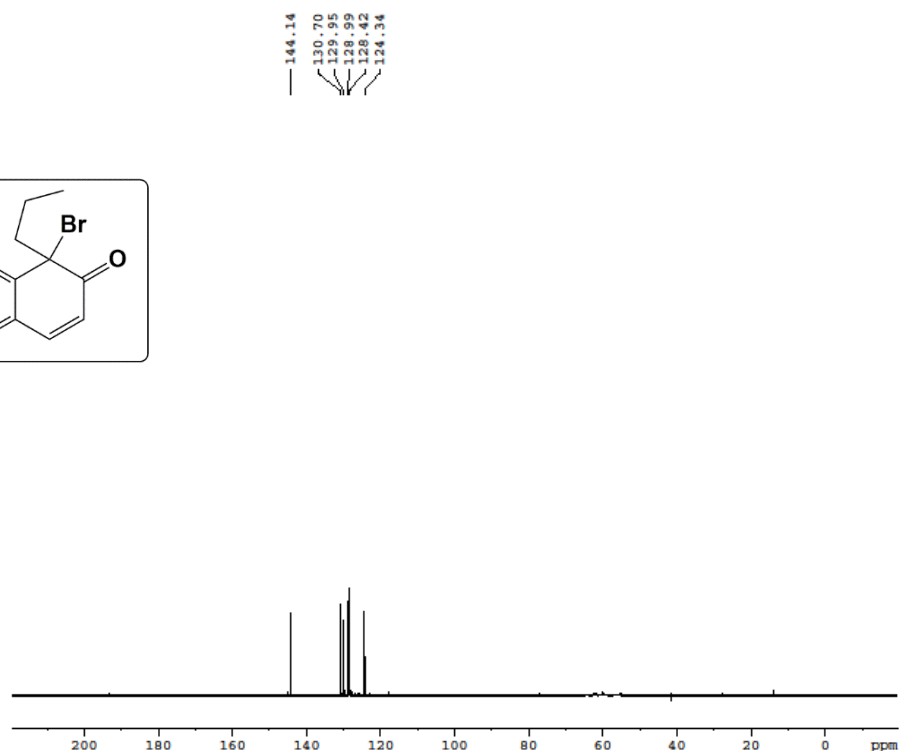




# DEPT-90 & DEPT-135 of 1-bromo-1-propylnaphthalen-2(1H)-one (2b)



DEPT-90 of DS-Bpr-PTAB



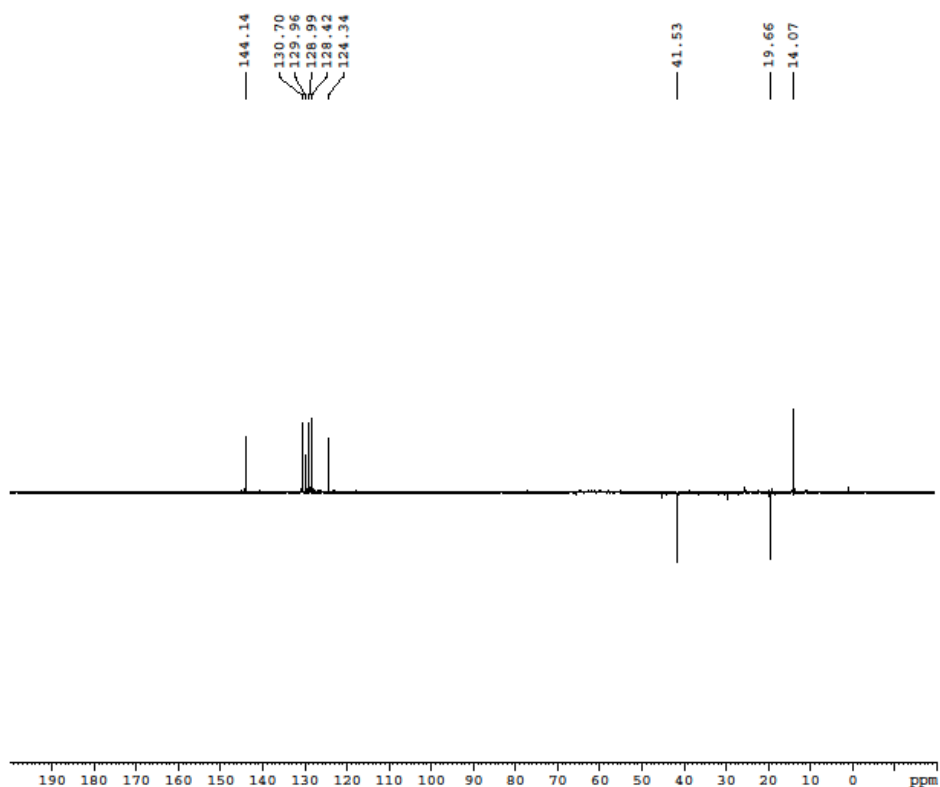
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DEPT-135 of DS-BPr-PTAB



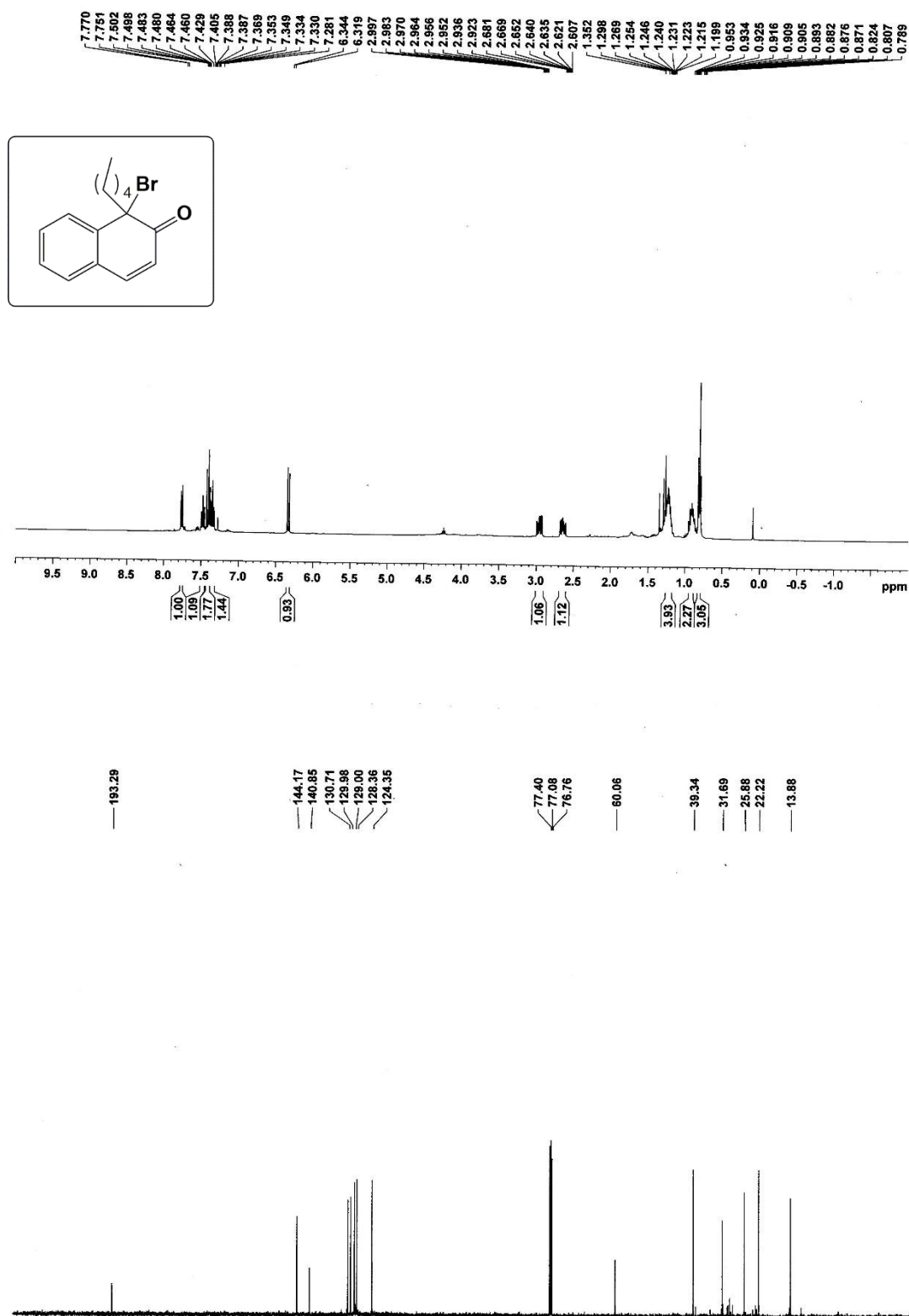
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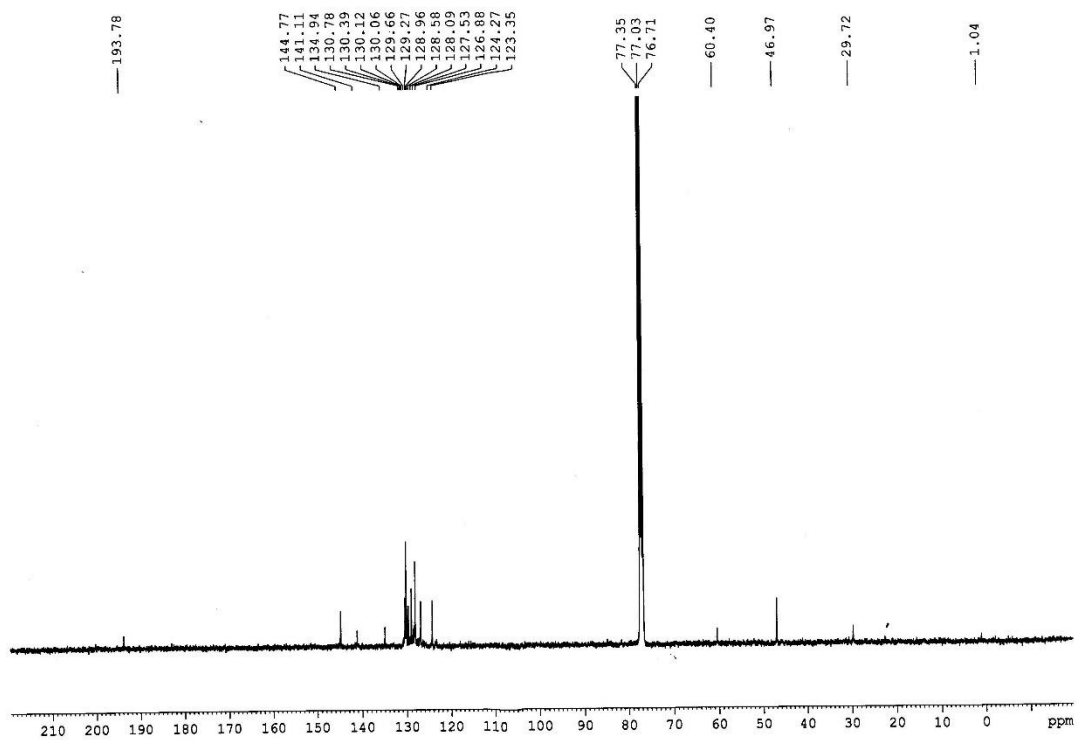
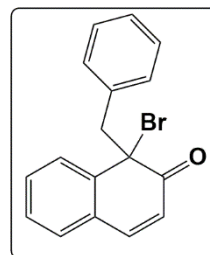
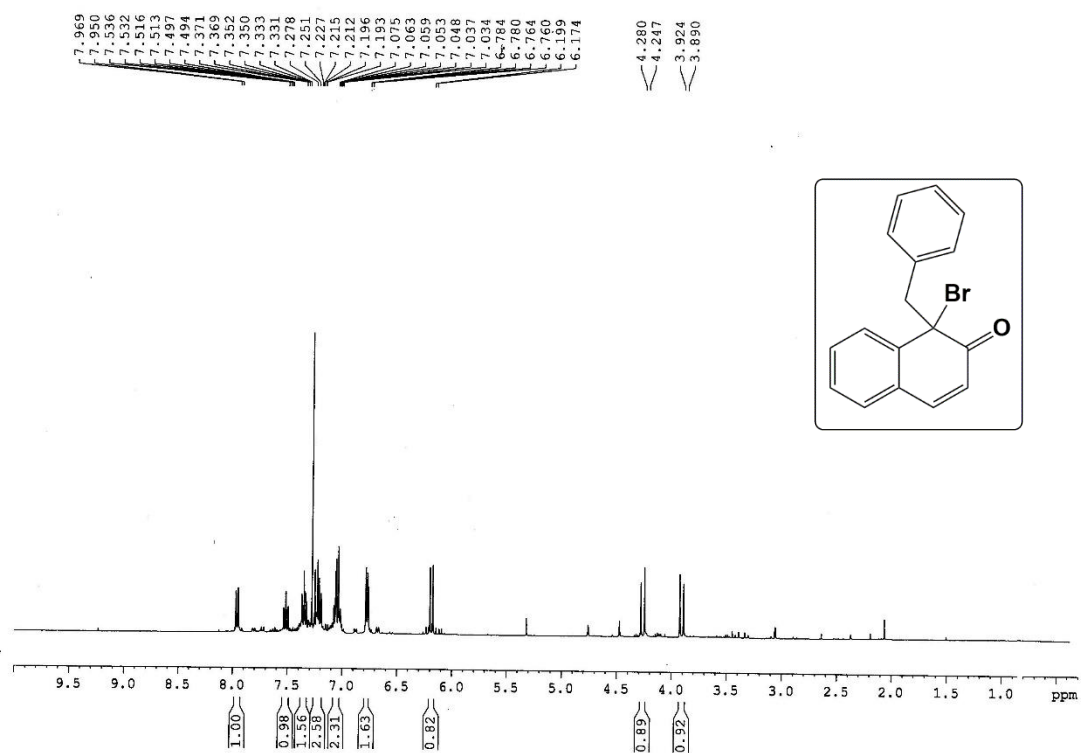
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SFO1       100.6278593 MHz

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PCPD2      80.00 usec
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PL12       14.00 dB
PL2W       9.48683262 W
PL12W      0.30000001 W
SFO2       400.1516006 MHz
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PC         1.40
    
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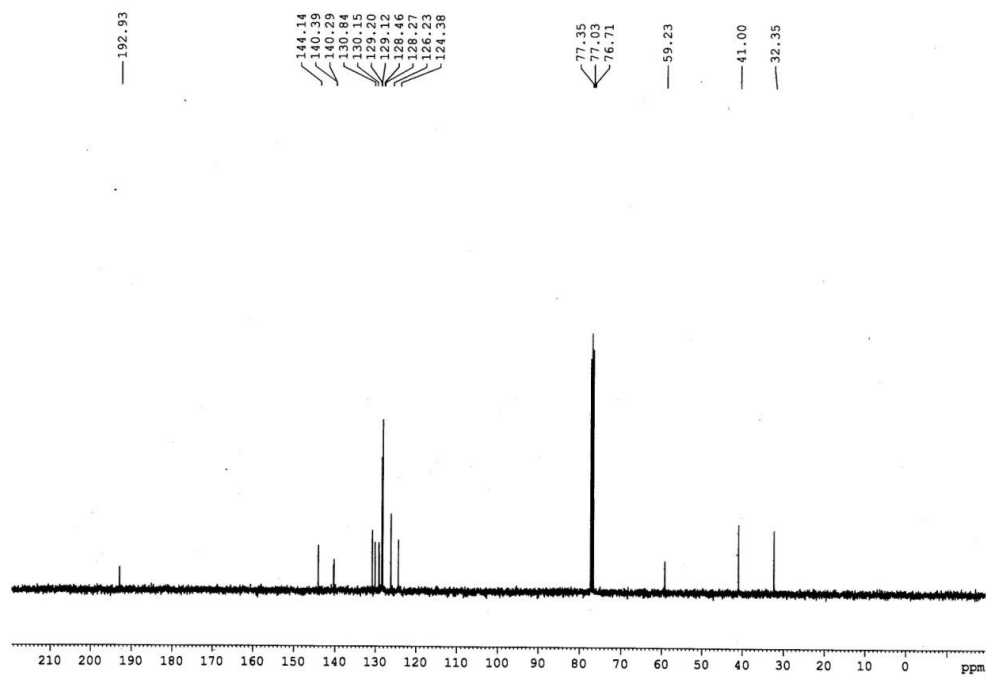
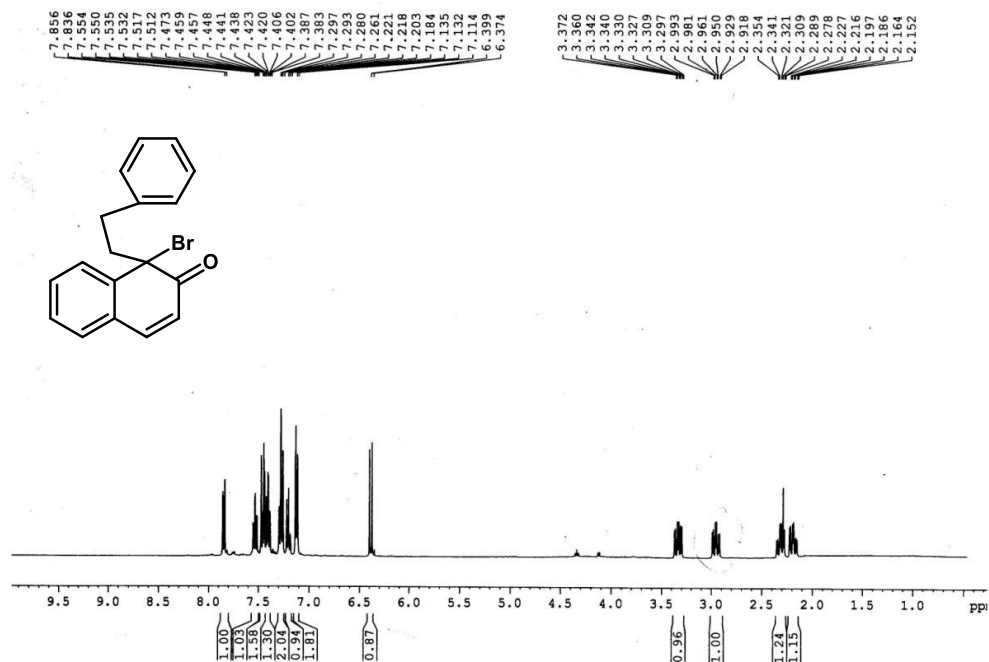
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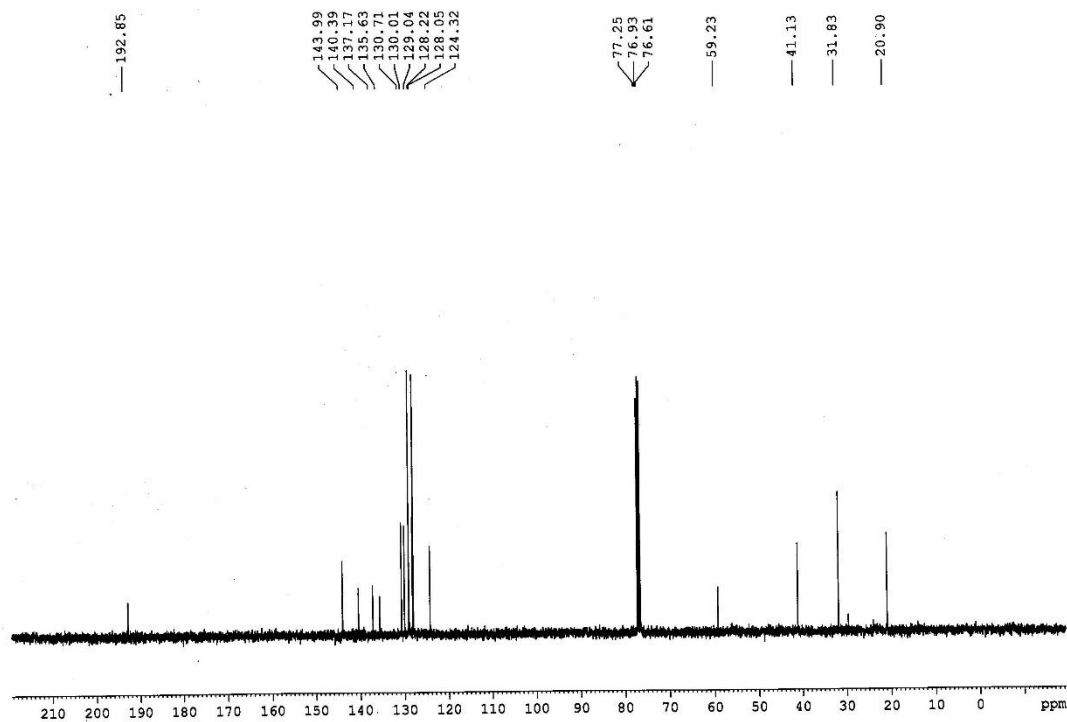
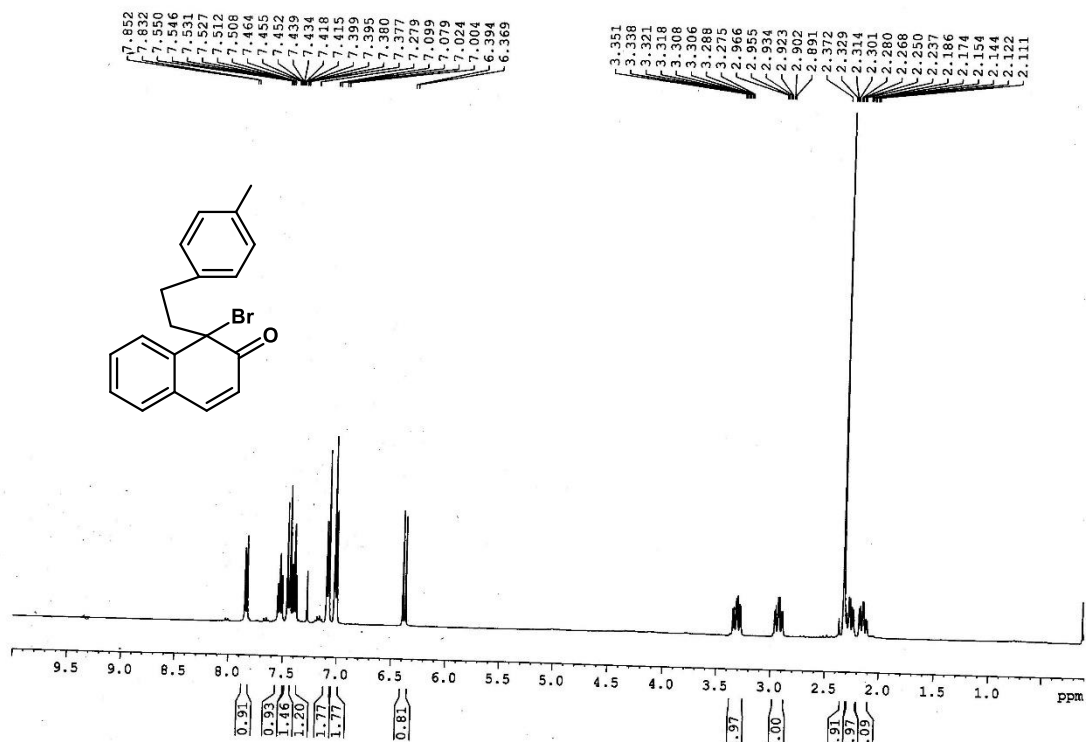
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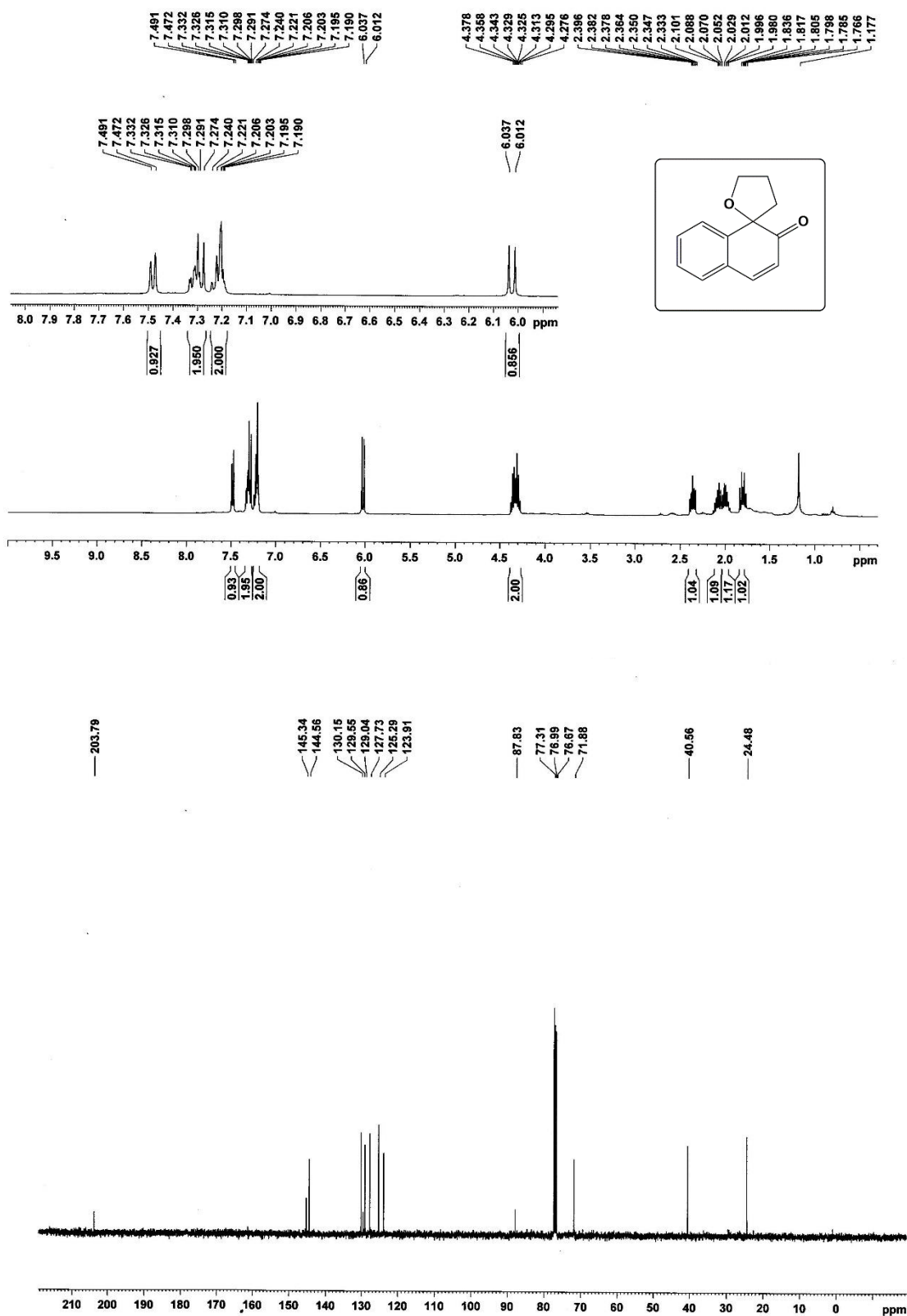
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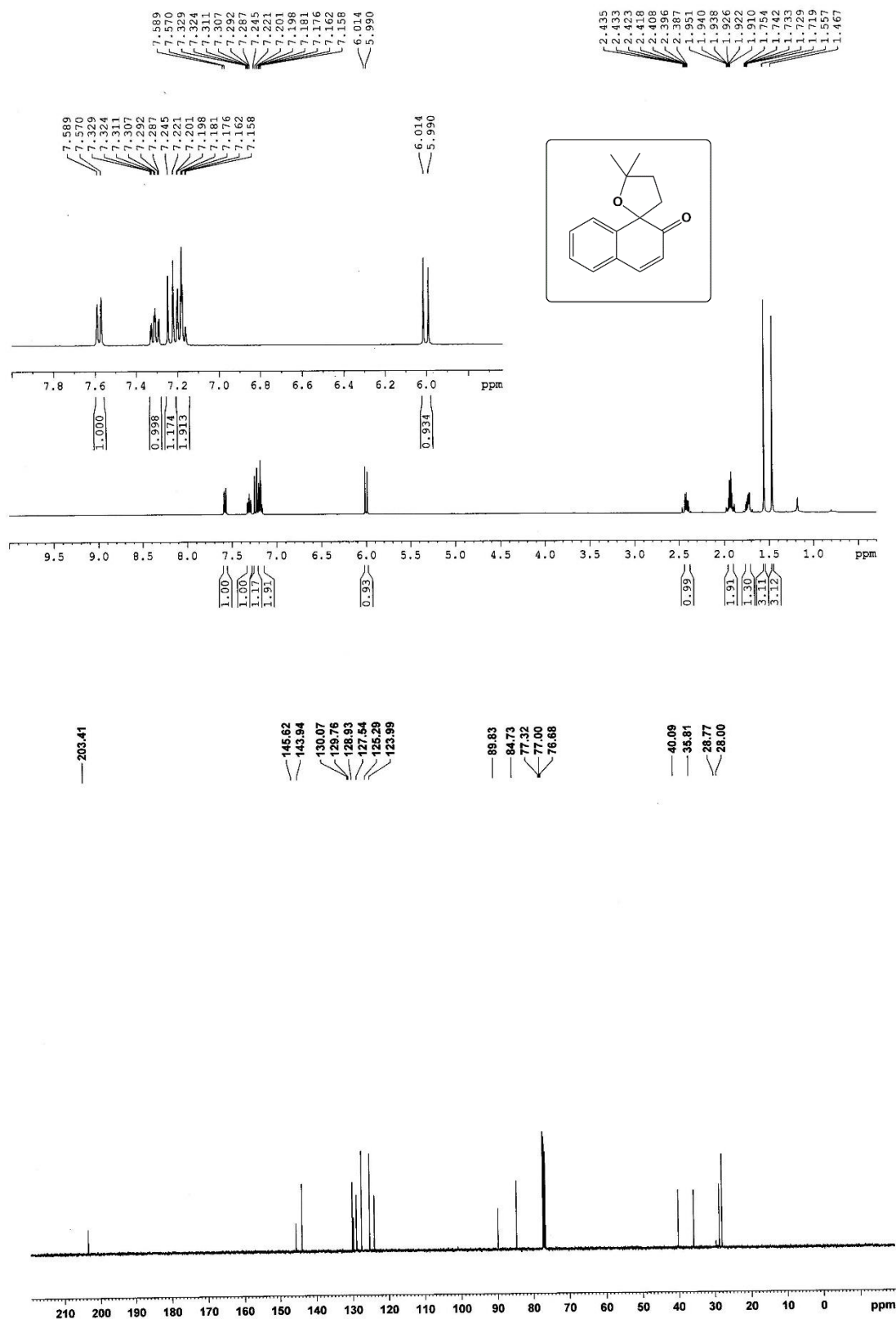
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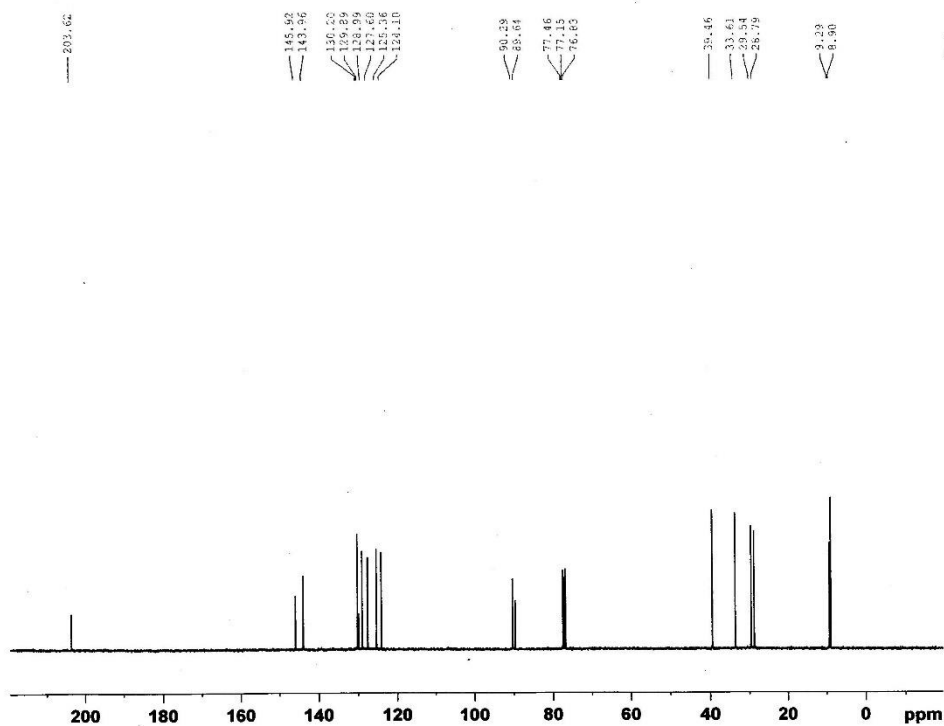
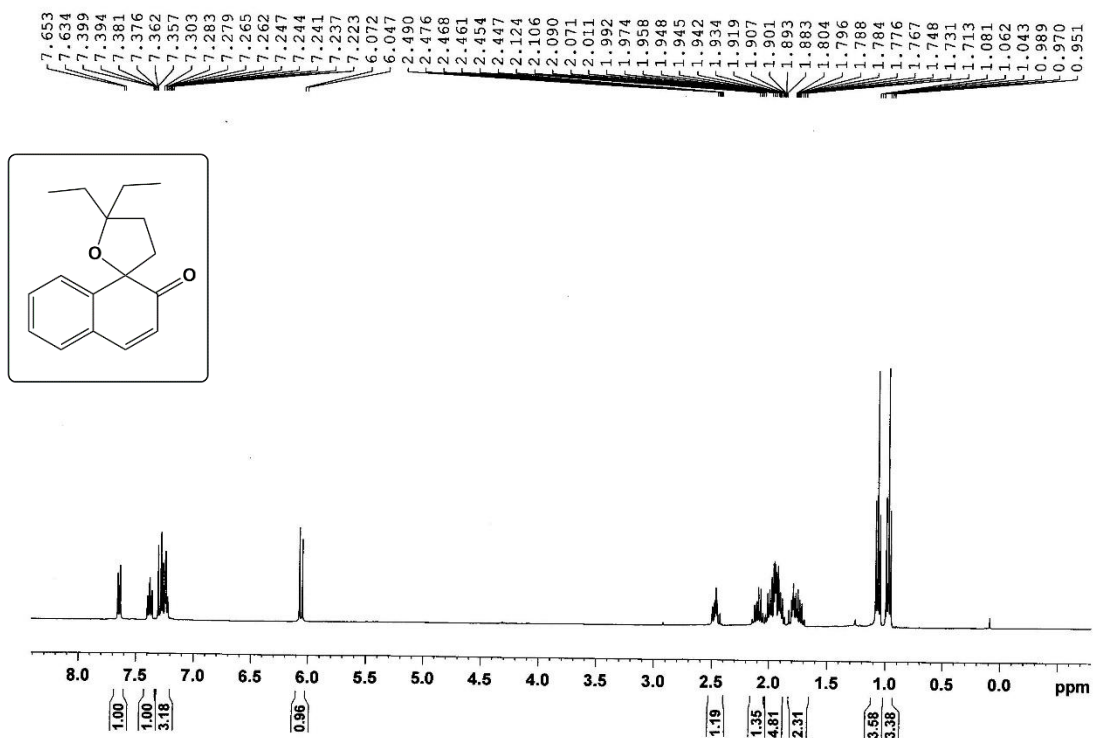
4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (4a)



5,5-dimethyl-4,5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (4b)



5,5-diethyl-4,5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (4c)



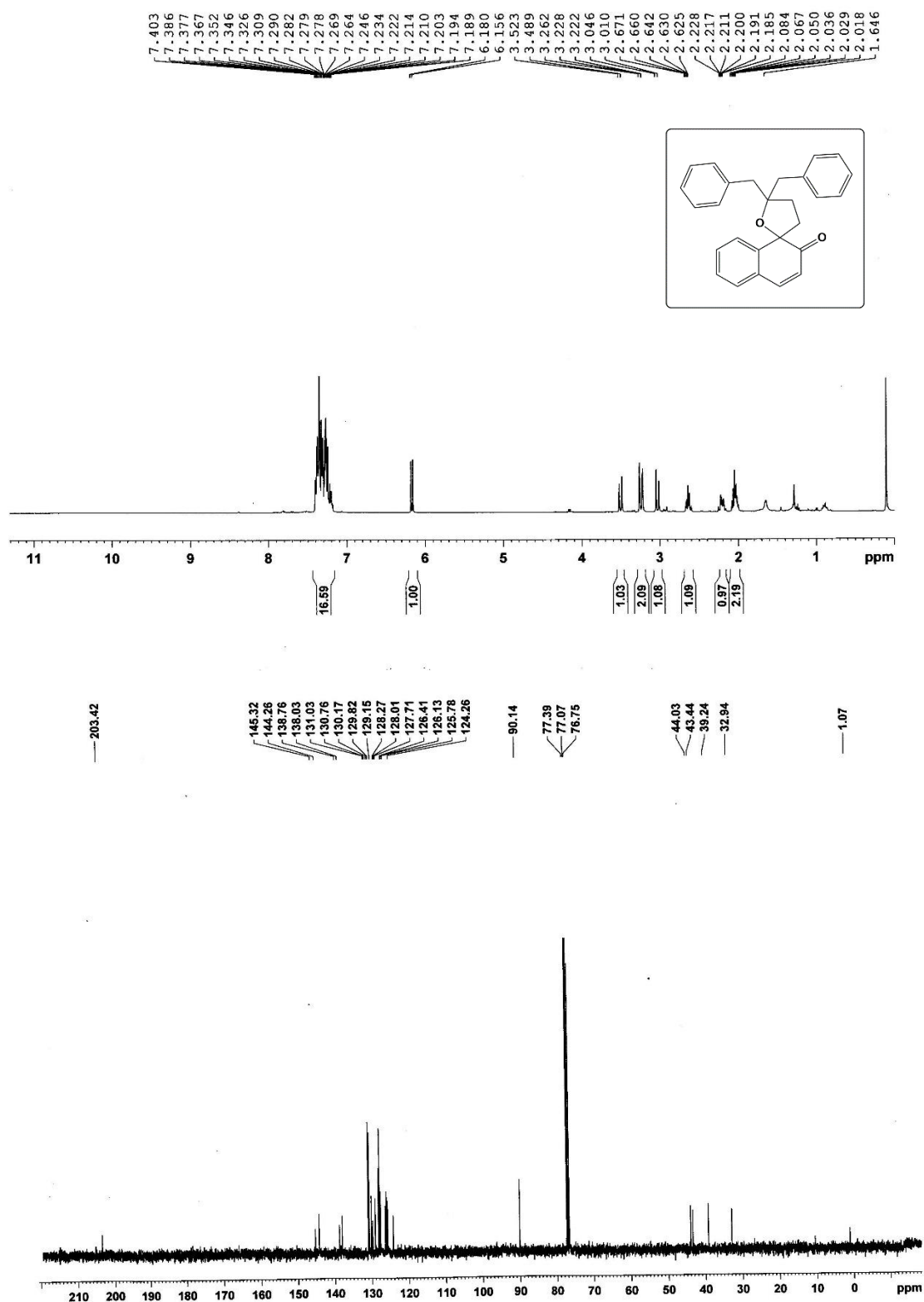
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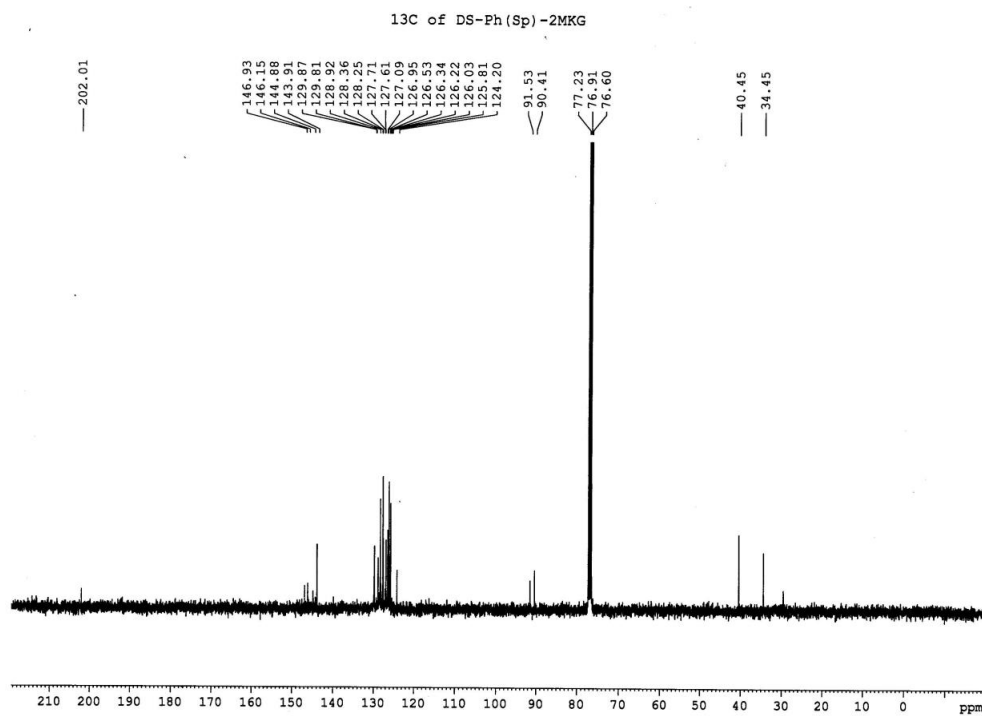
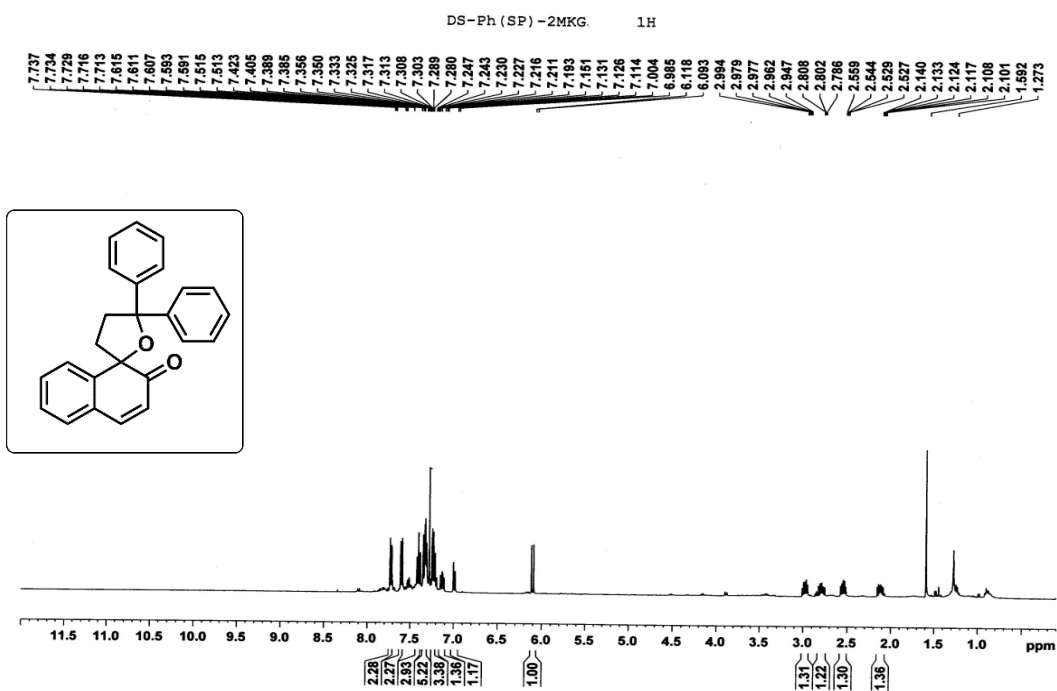
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PL12 14.00 dB  
PL13 14.00 dB  
PL2W 9.48683262 W  
PL12W 0.30000001 W  
PL13W 0.30000001 W  
SFO2 400.1516006 MHz  
SI 16384  
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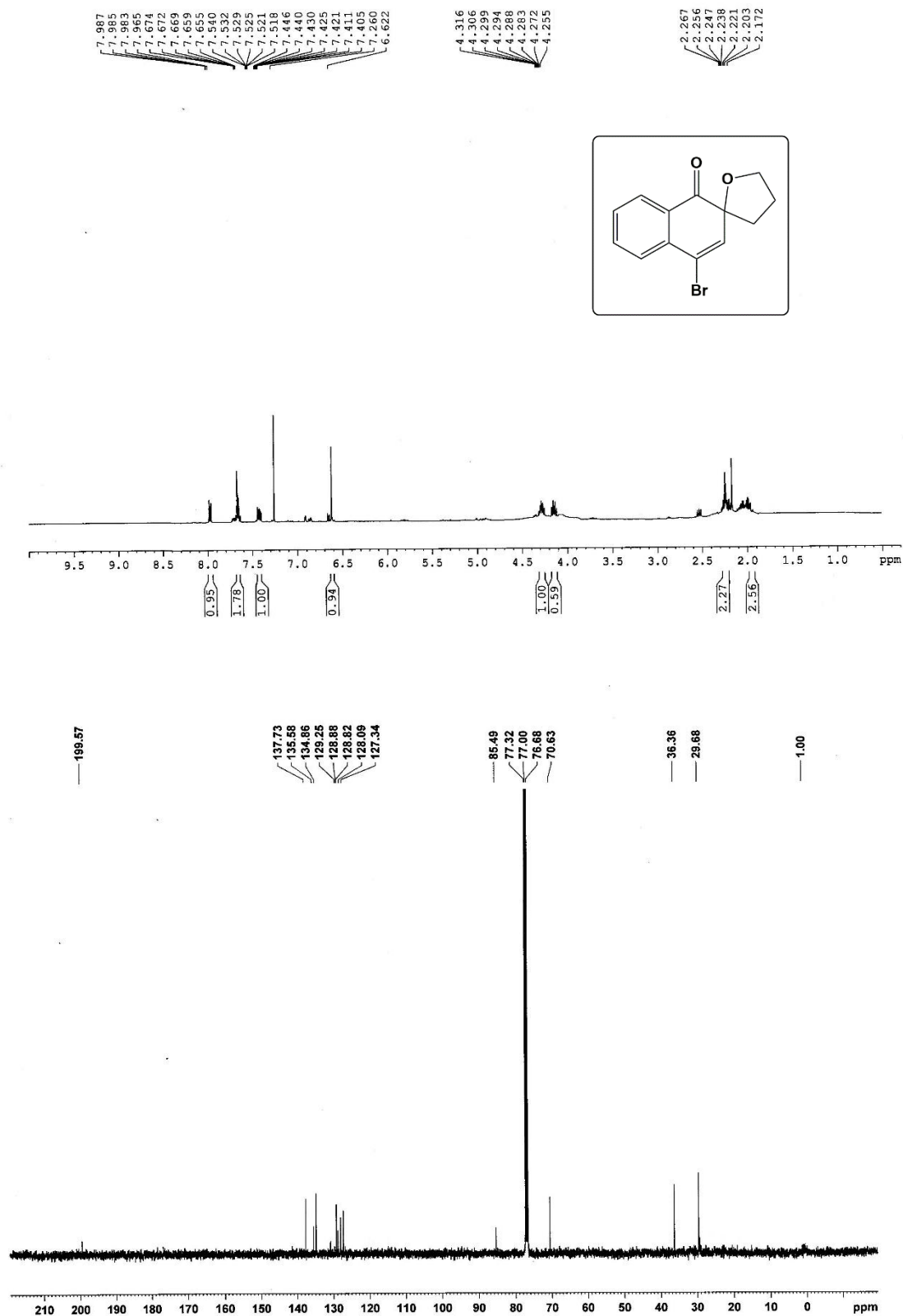
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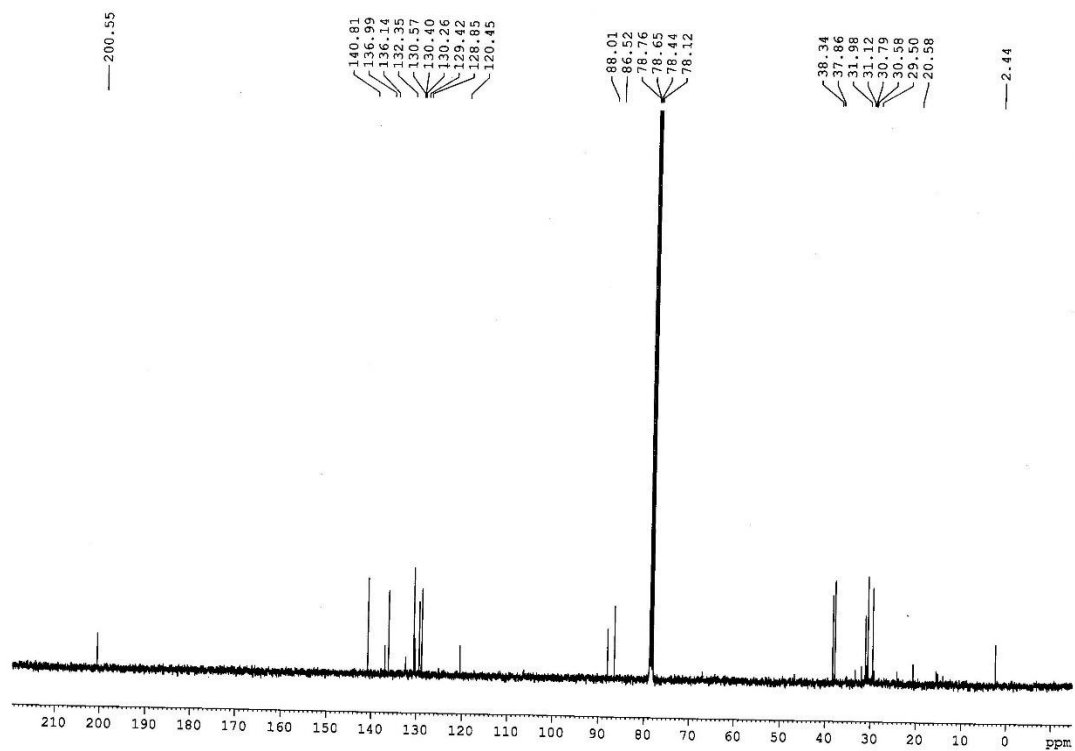
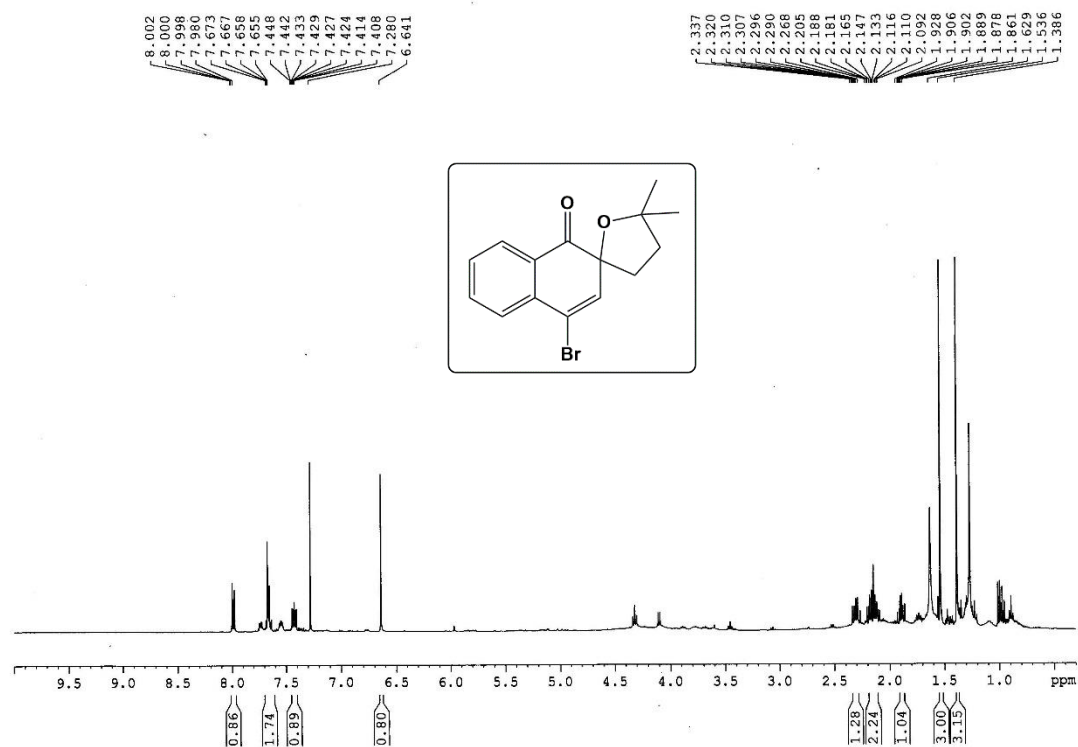
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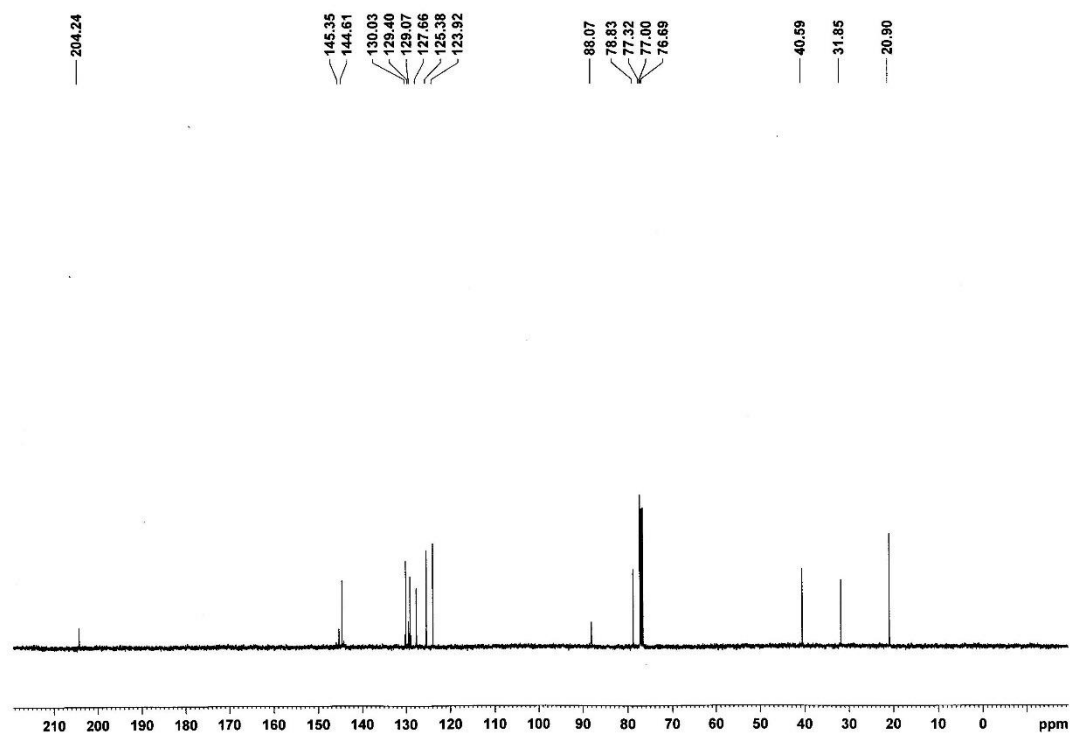
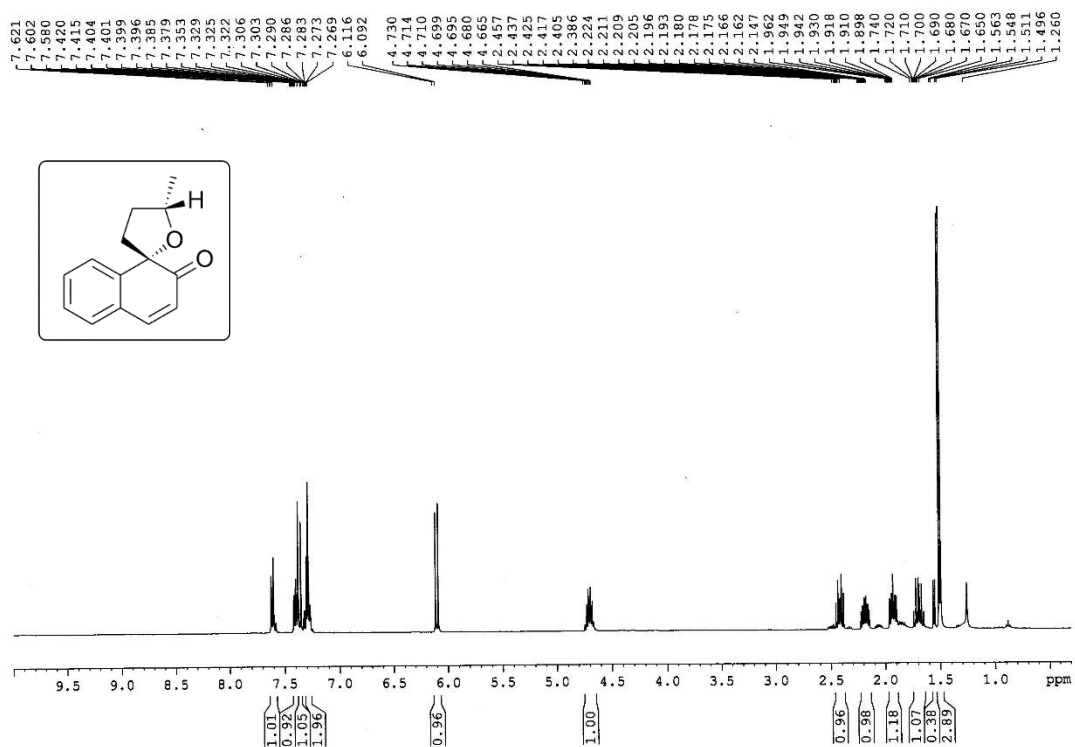
4'-bromo-4,5-dihydro-1'H, 3H-spiro[furan-2, 2'-naphthalen]-1'-one (4f)



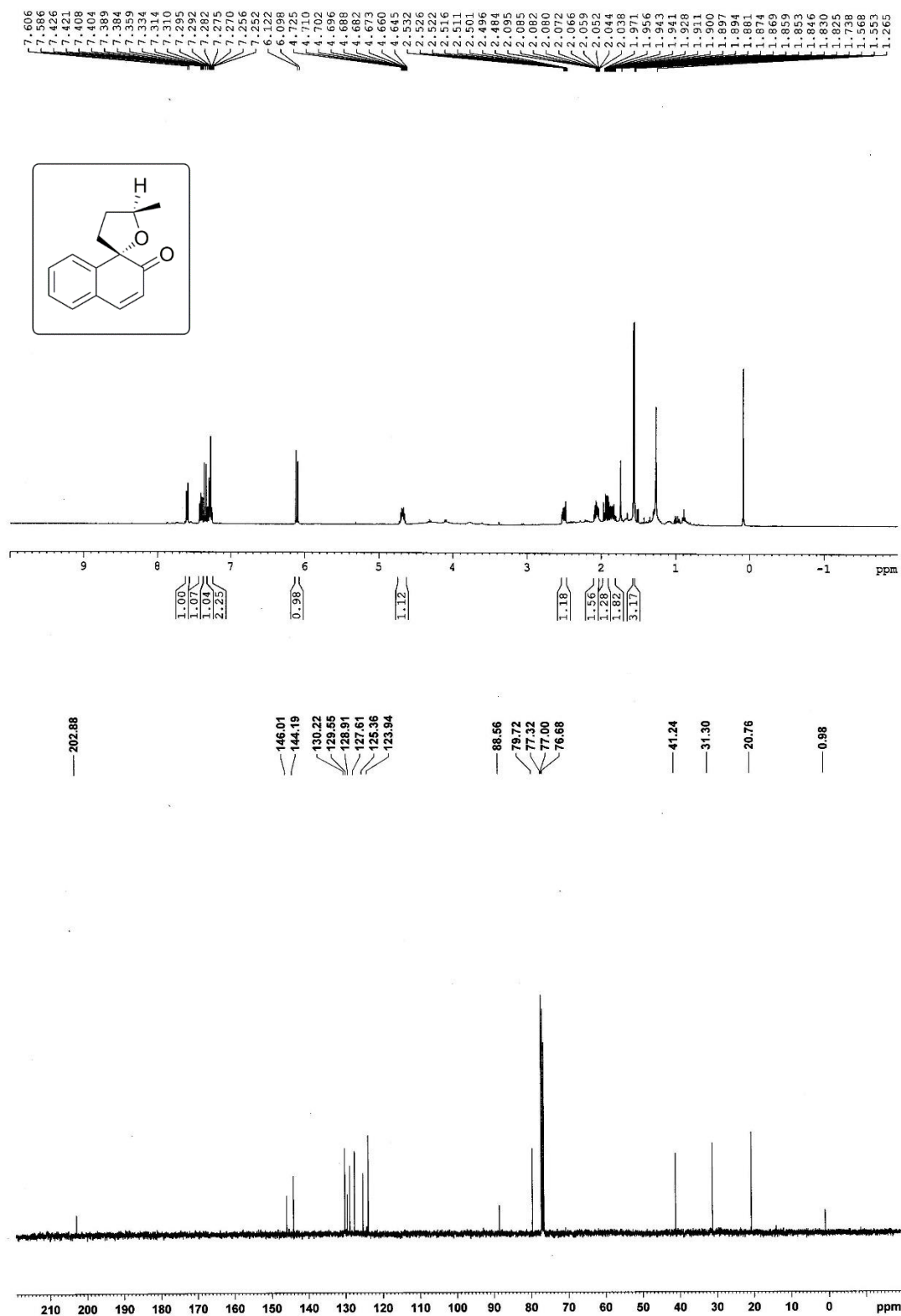
4'-bromo-5,5-dimethyl-4,5-dihydro-1'H, 3H-spiro[furan-2, 2'-naphthalen]-1'-one (4g)



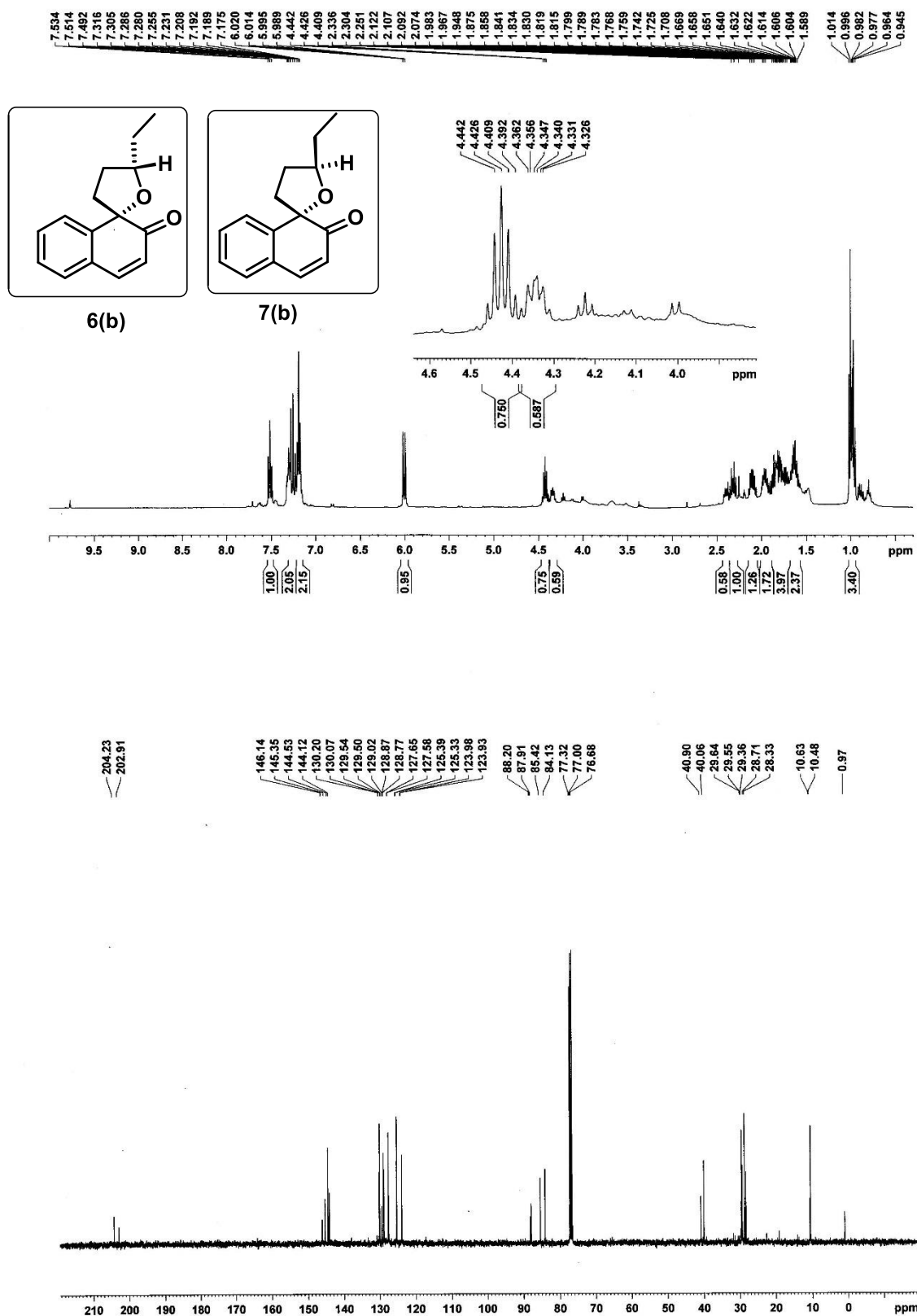
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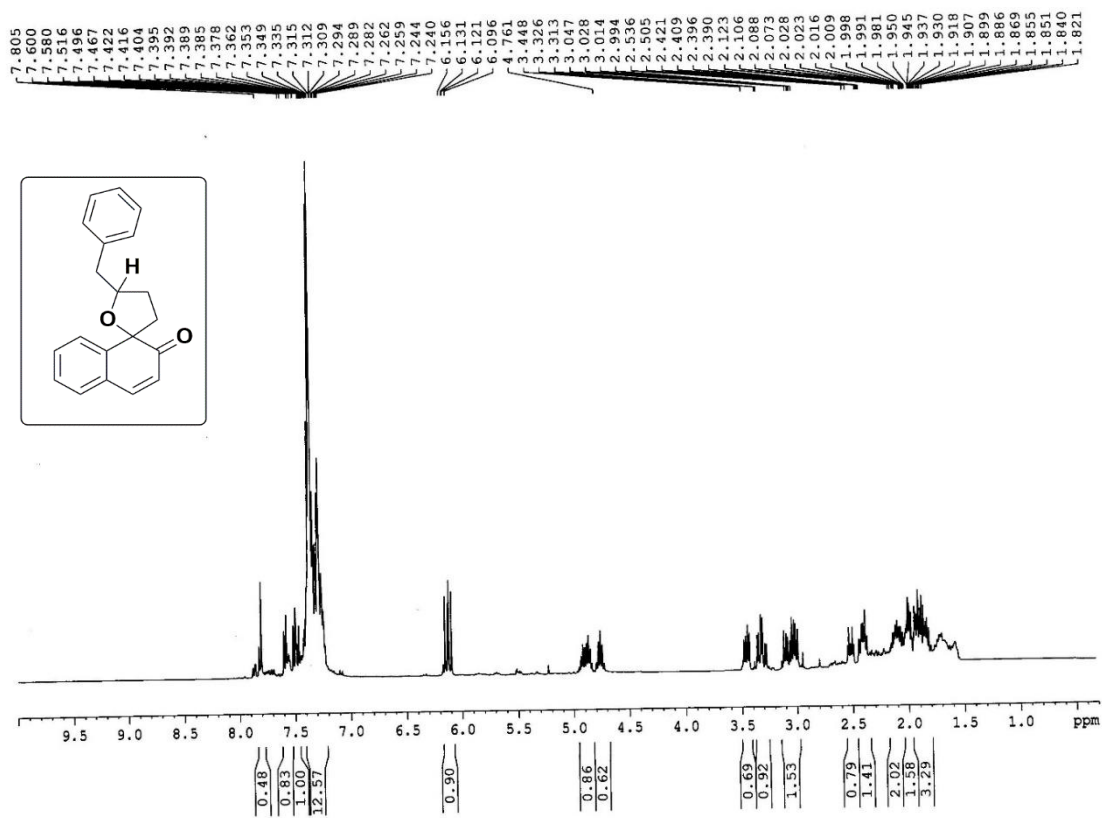
(1'S, 5R)/(1'R,5S)--5-methyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (7a)



5-ethyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6b & 7b)

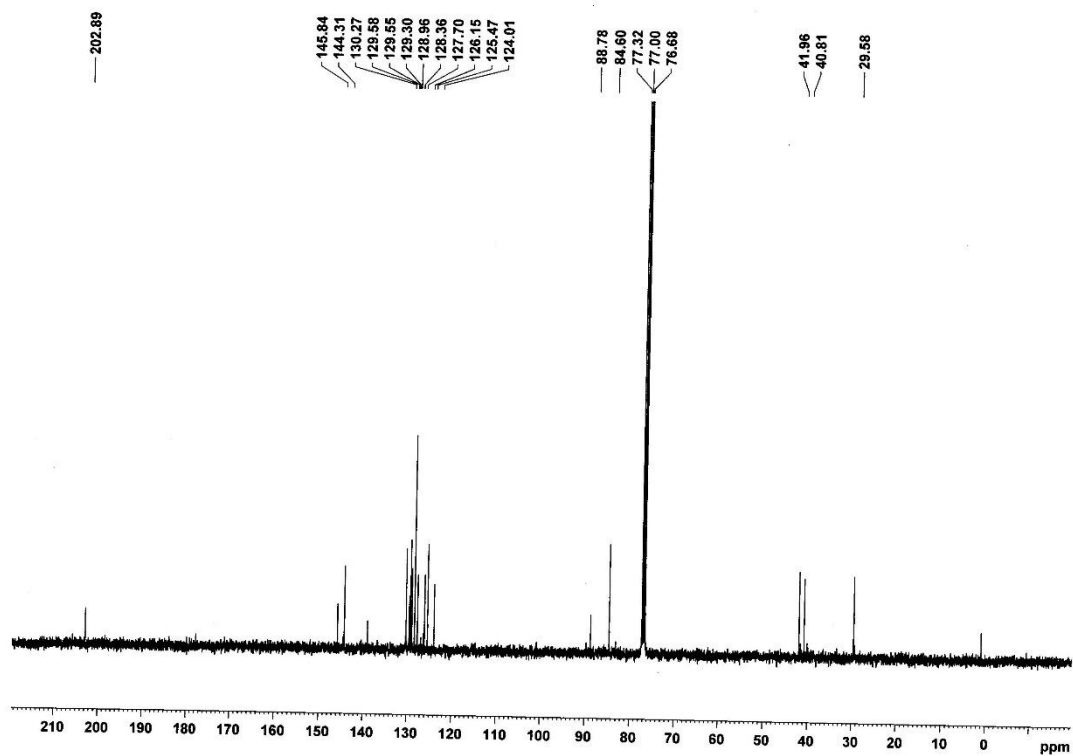
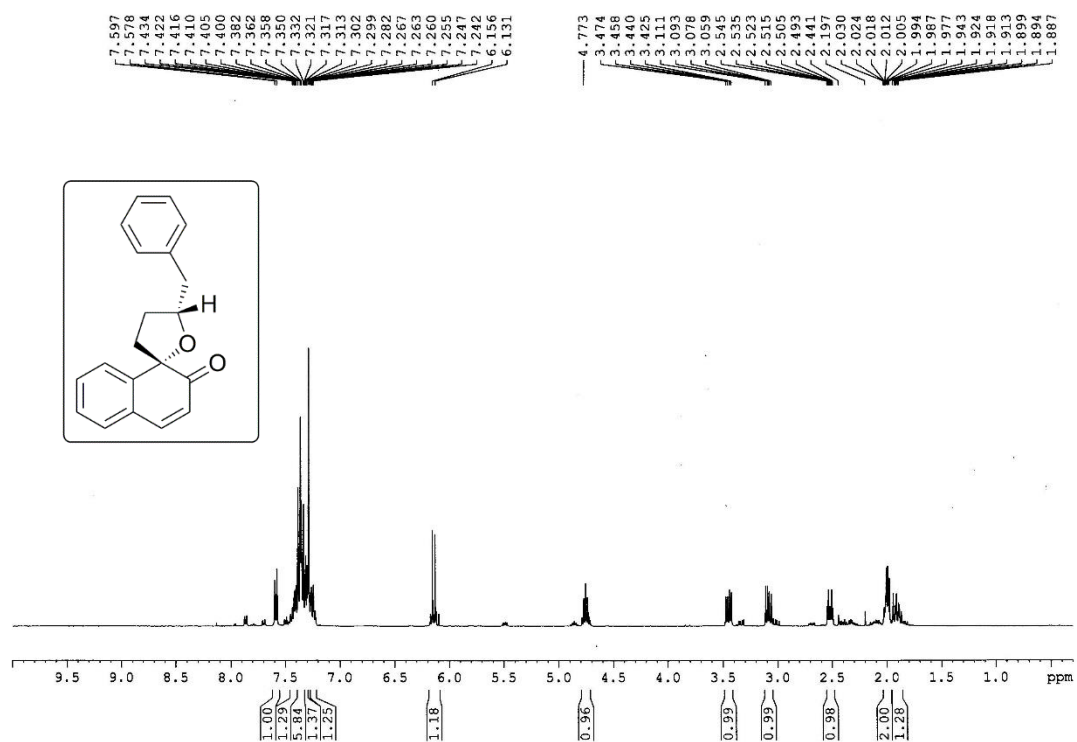


Mixture NMR of 5-benzyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one

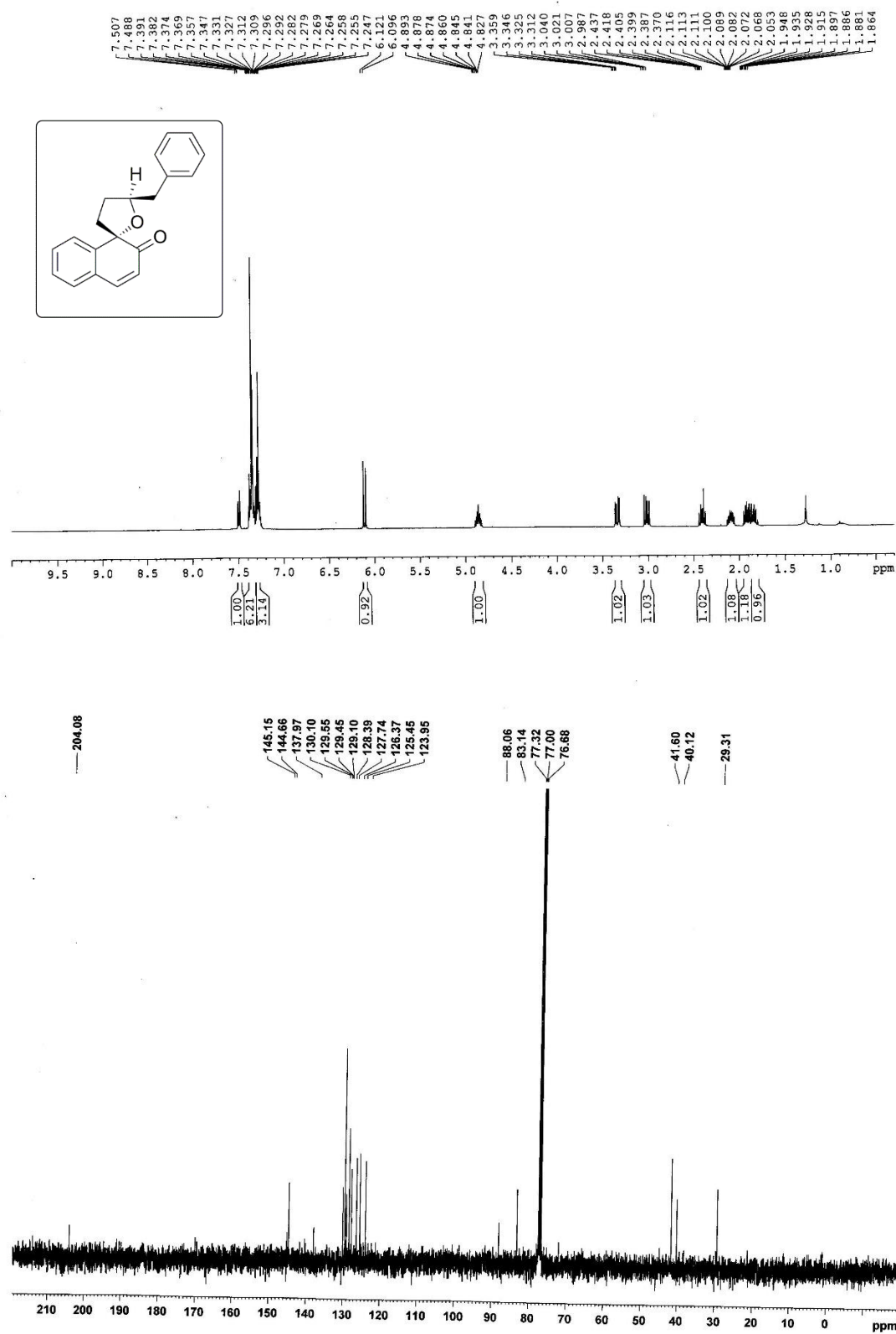




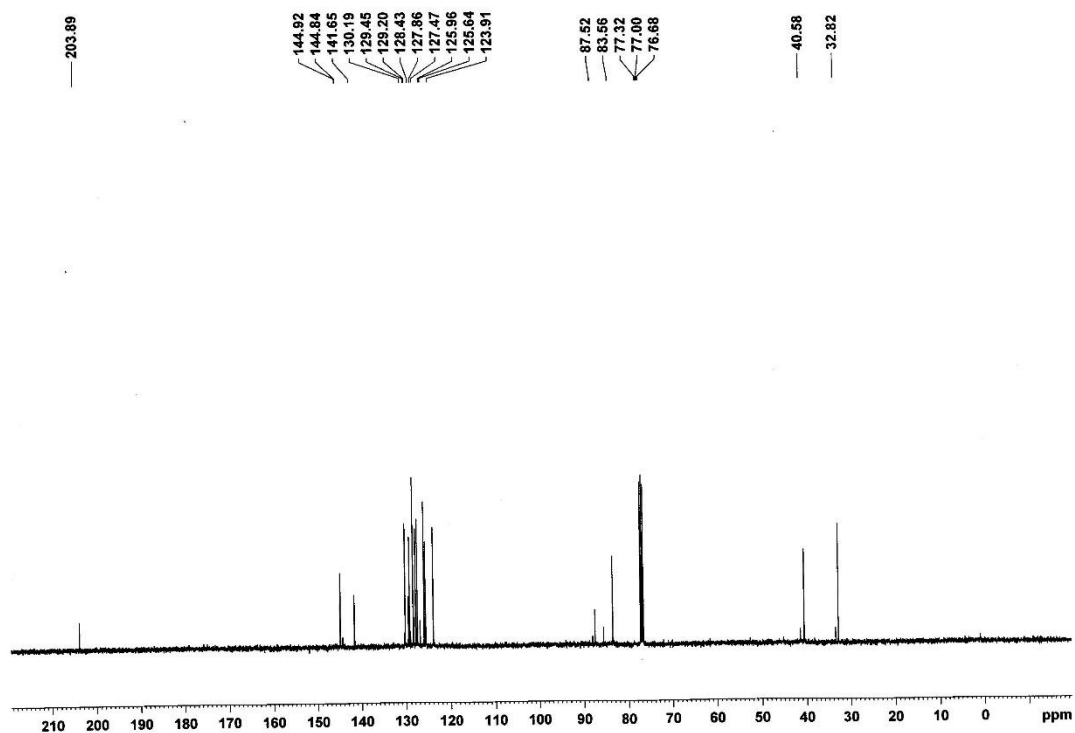
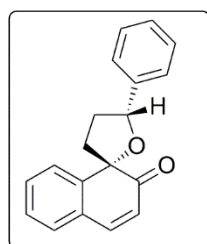
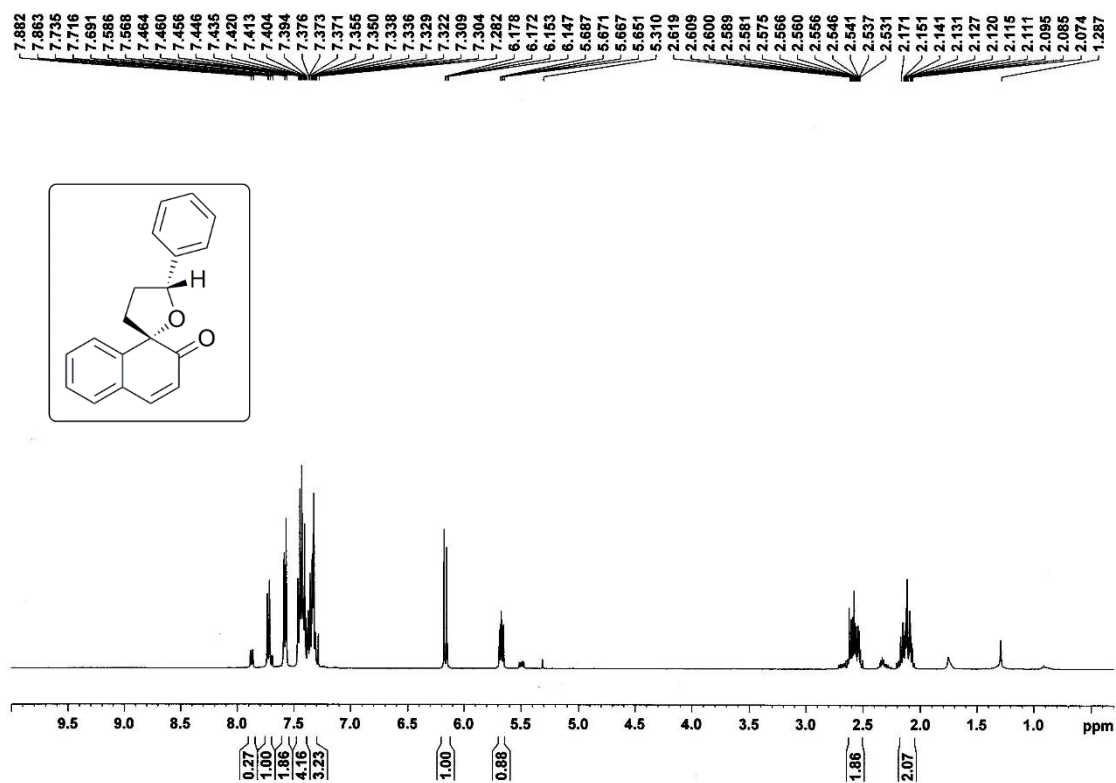
**(1'S, 5R)/(1'R, 5S)-5-benzyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6c)**



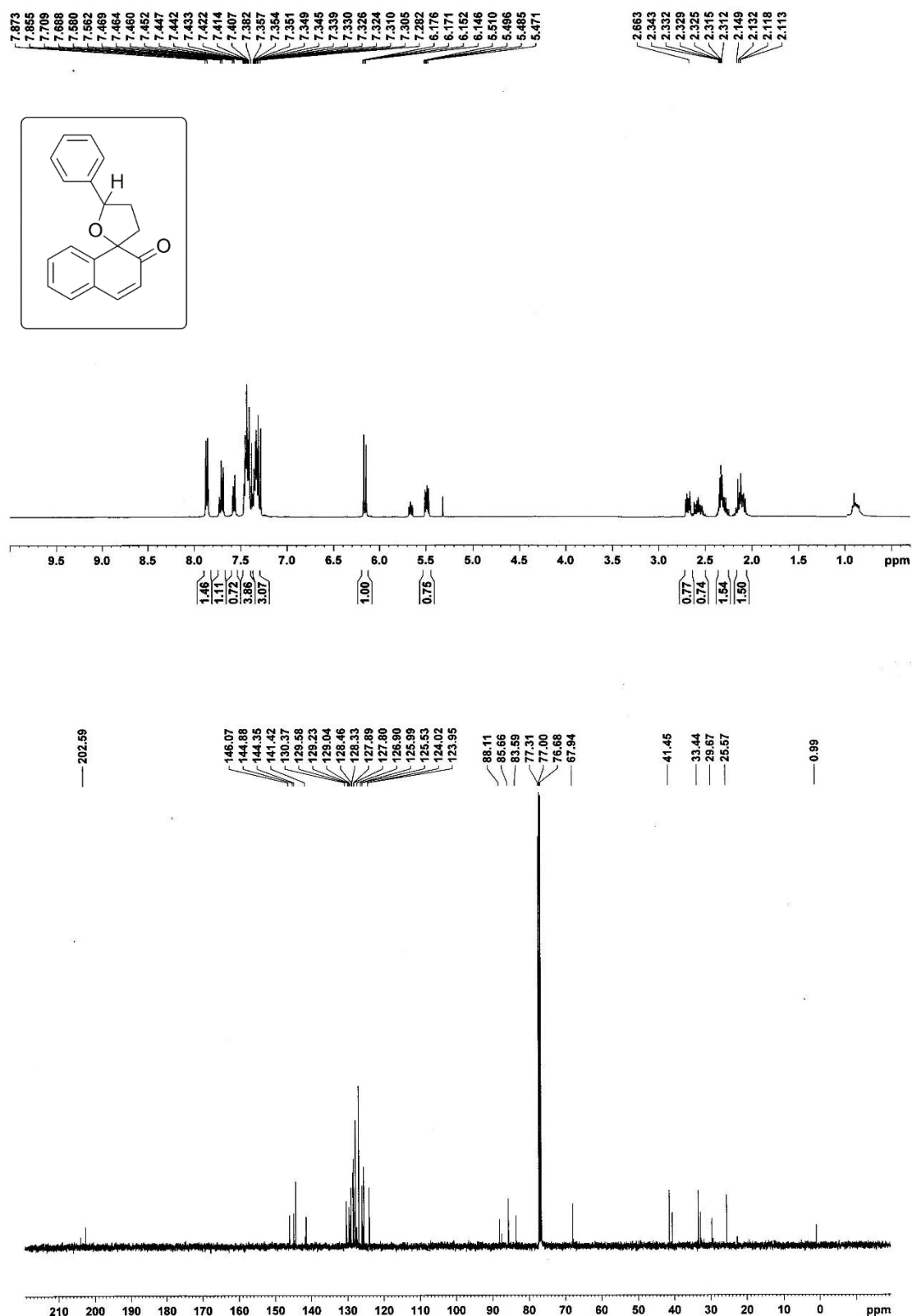
(1'S, 5S)/ (1'R, 5R)-5-benzyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (7c)



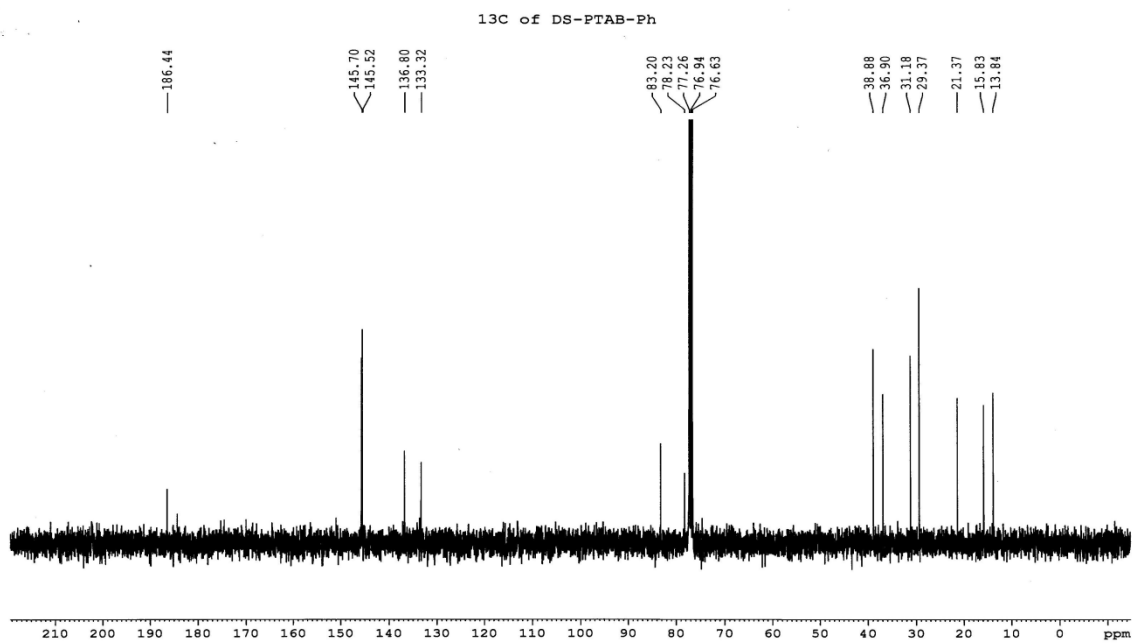
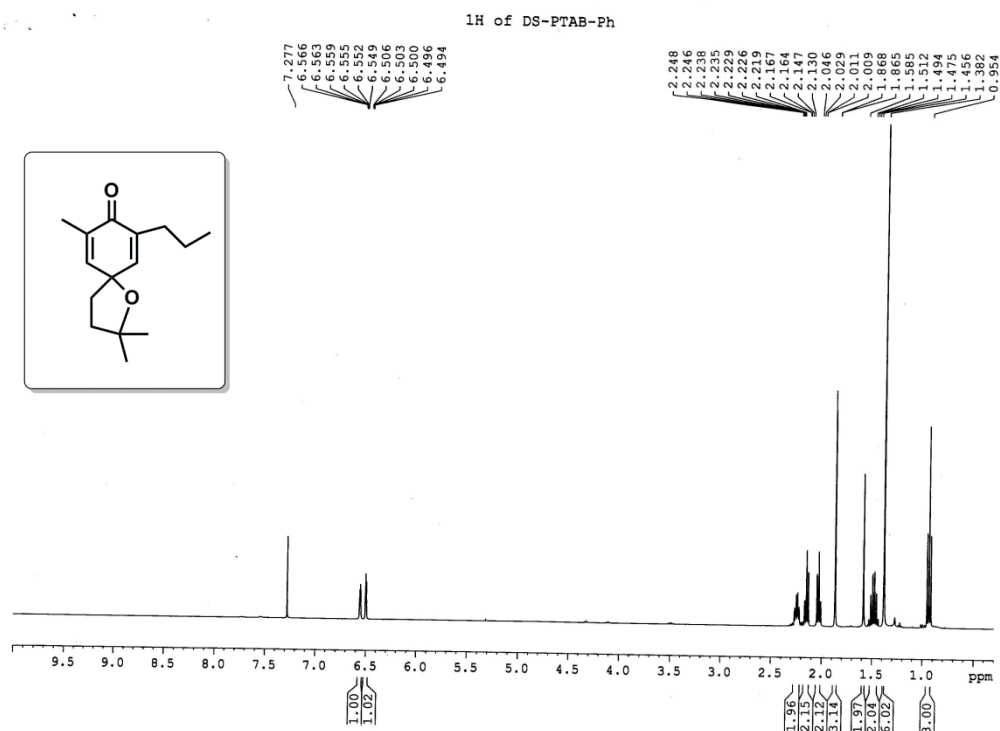
(1'S,5R)/ (1'R,5S)-5-phenyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6d)



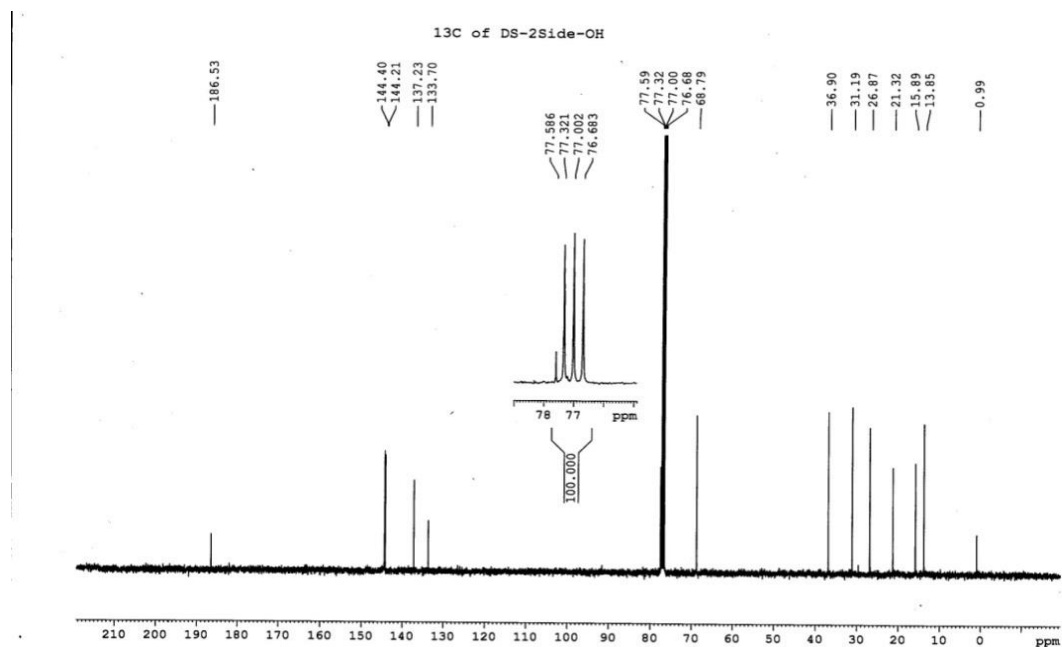
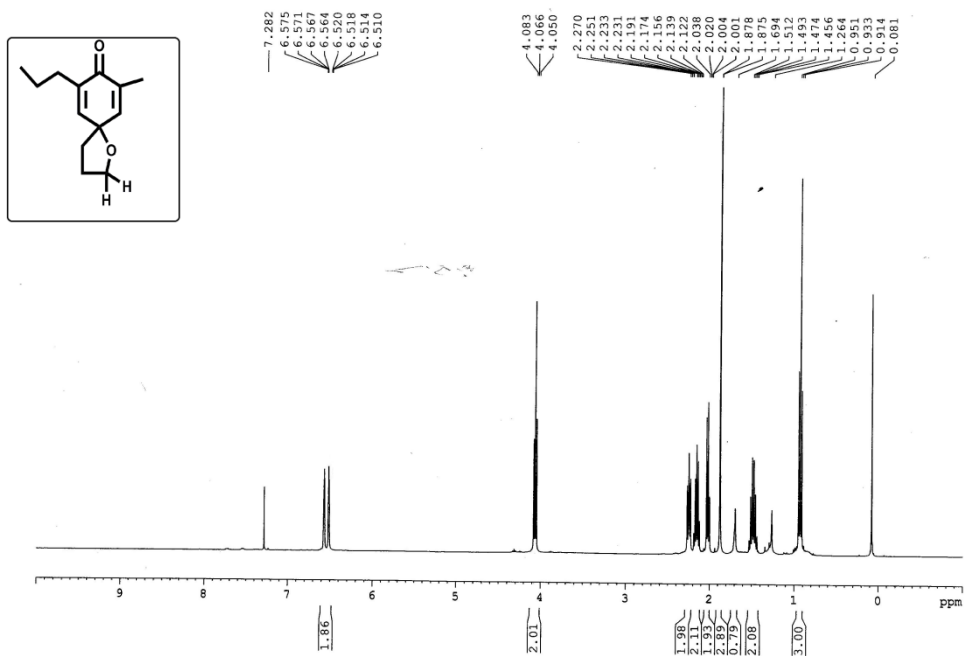
Mixture NMR of 5-phenyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6d& 7d)



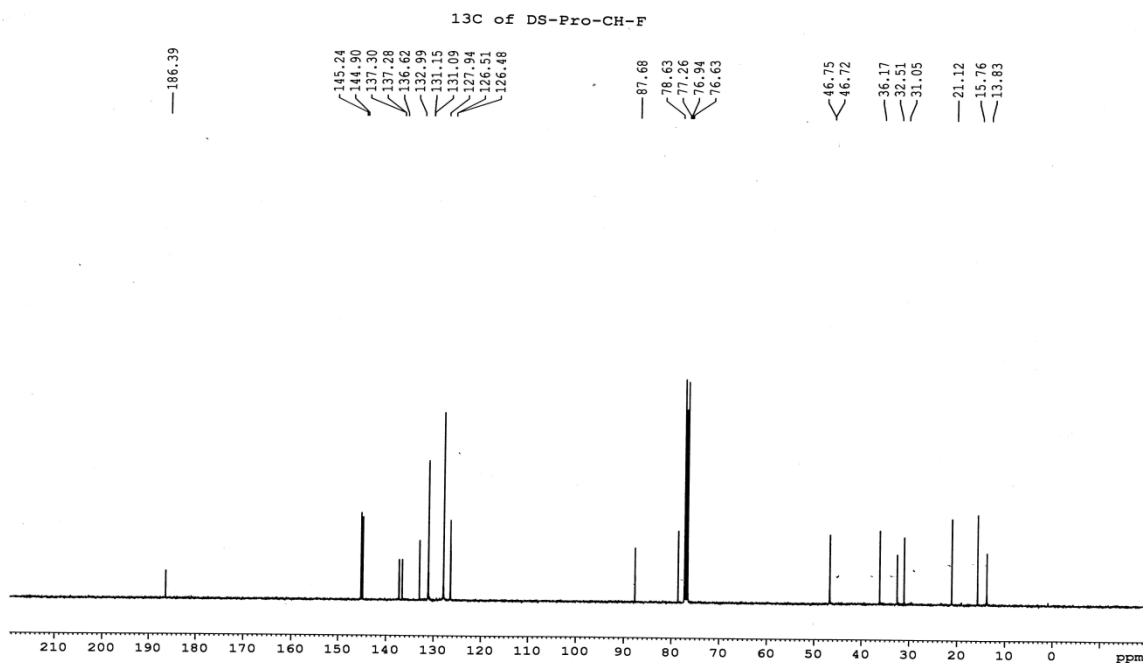
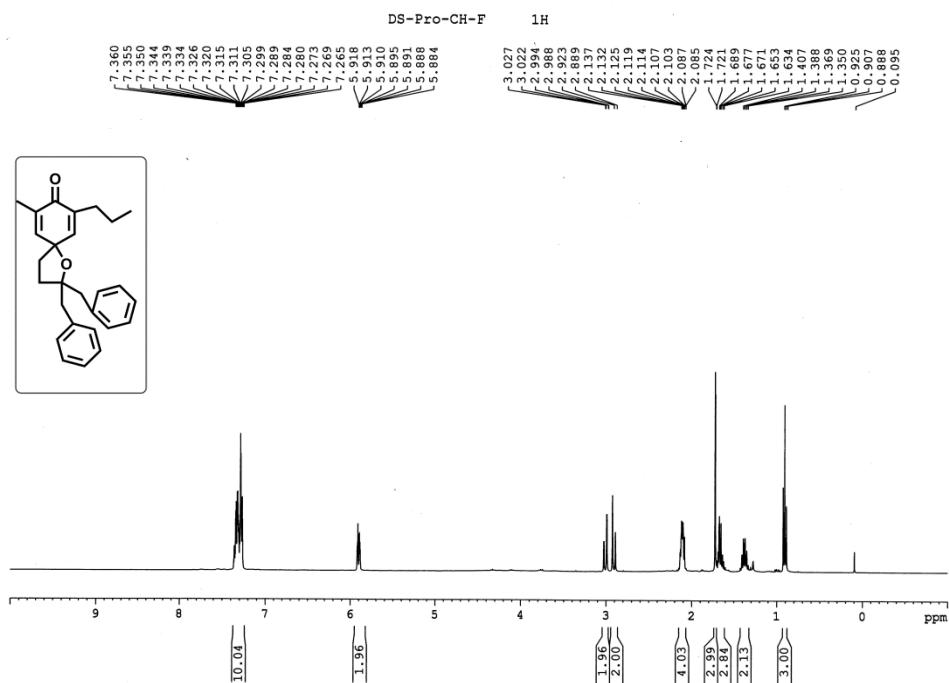
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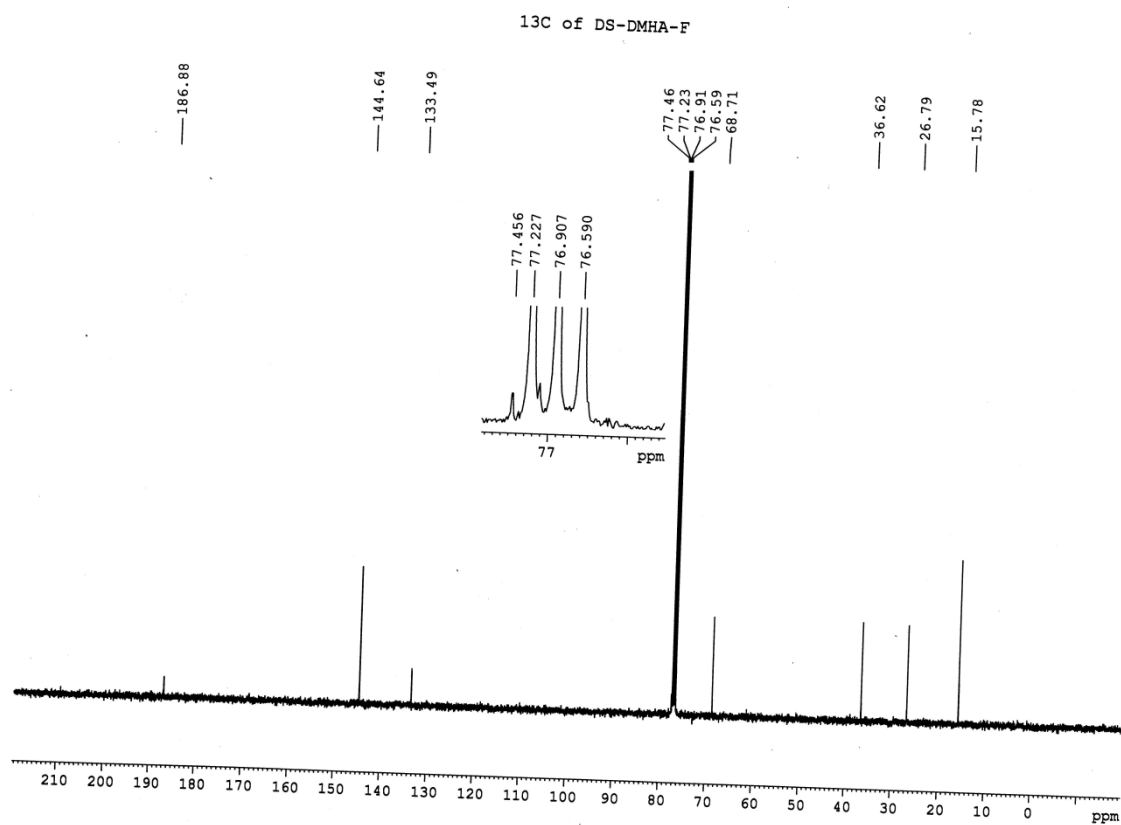
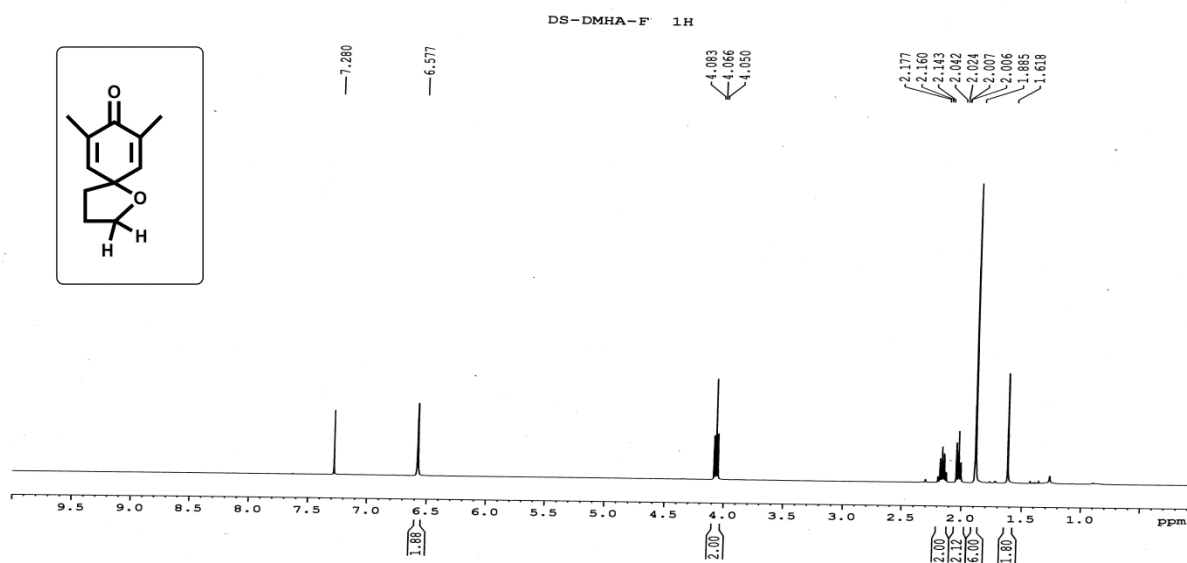
7-methyl-9-propyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (9b)



**2,2-dibenzyl-7-methyl-9-propyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (9c)**

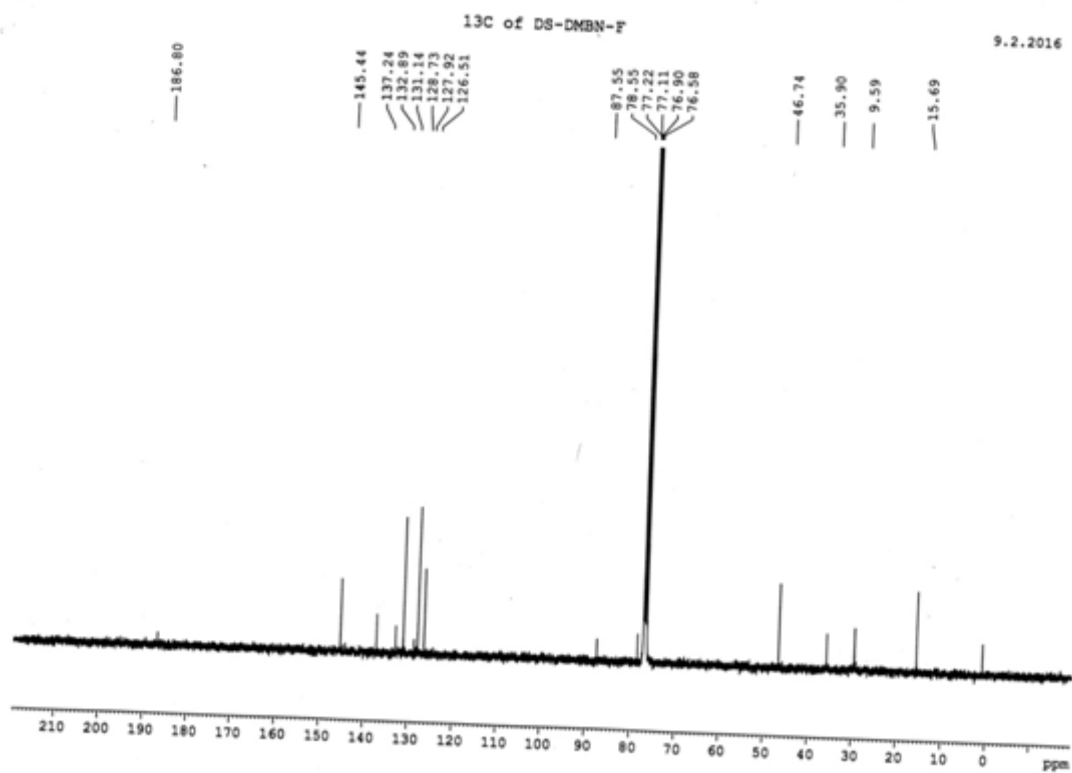
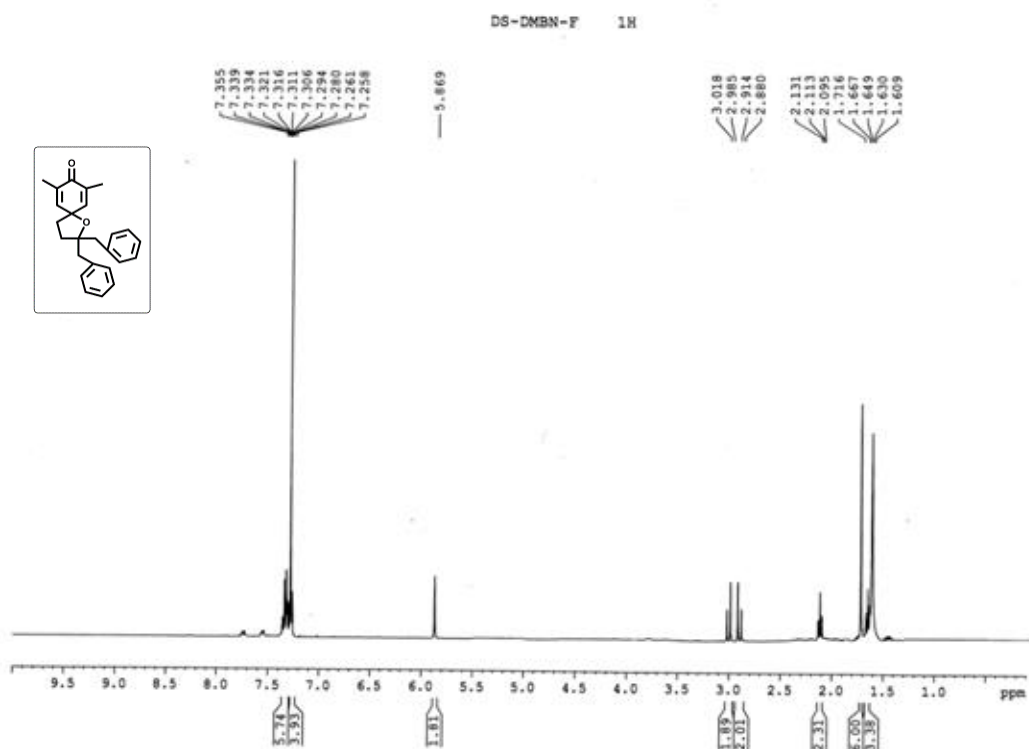


7,9-dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (9d)

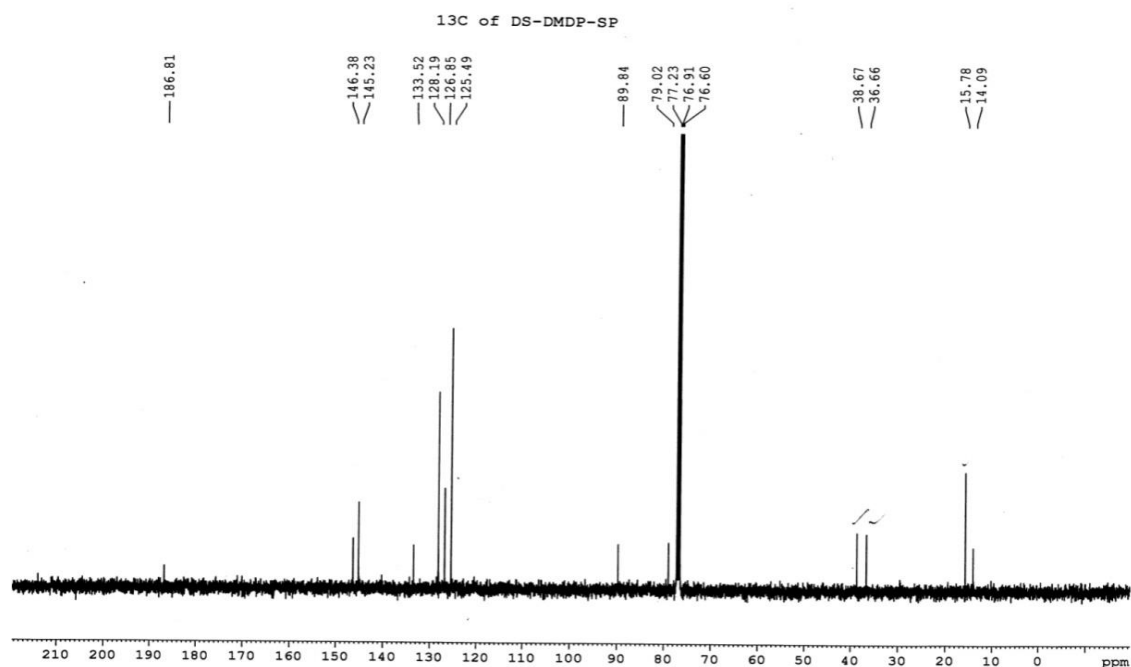
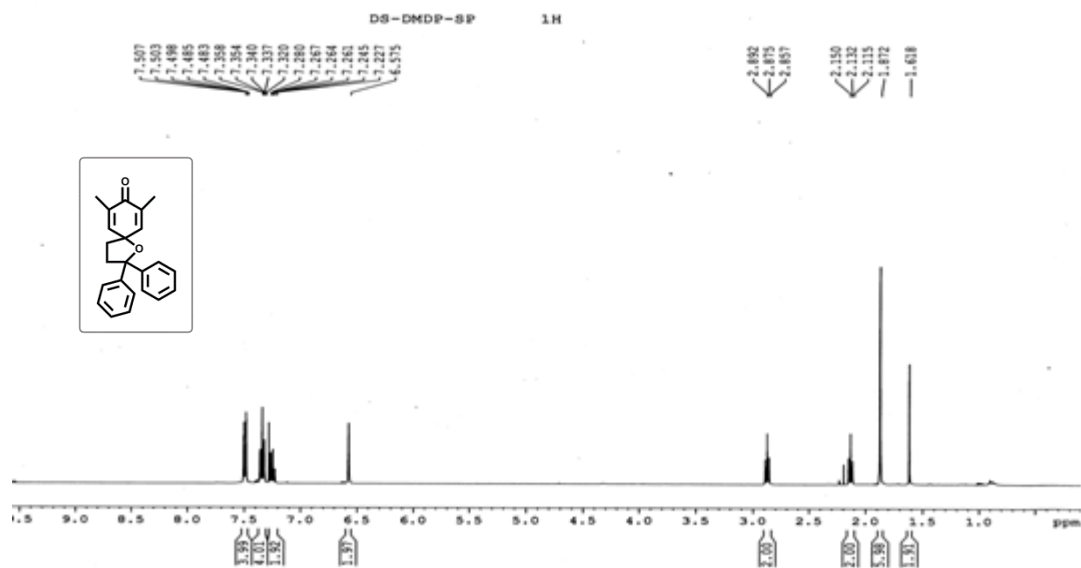




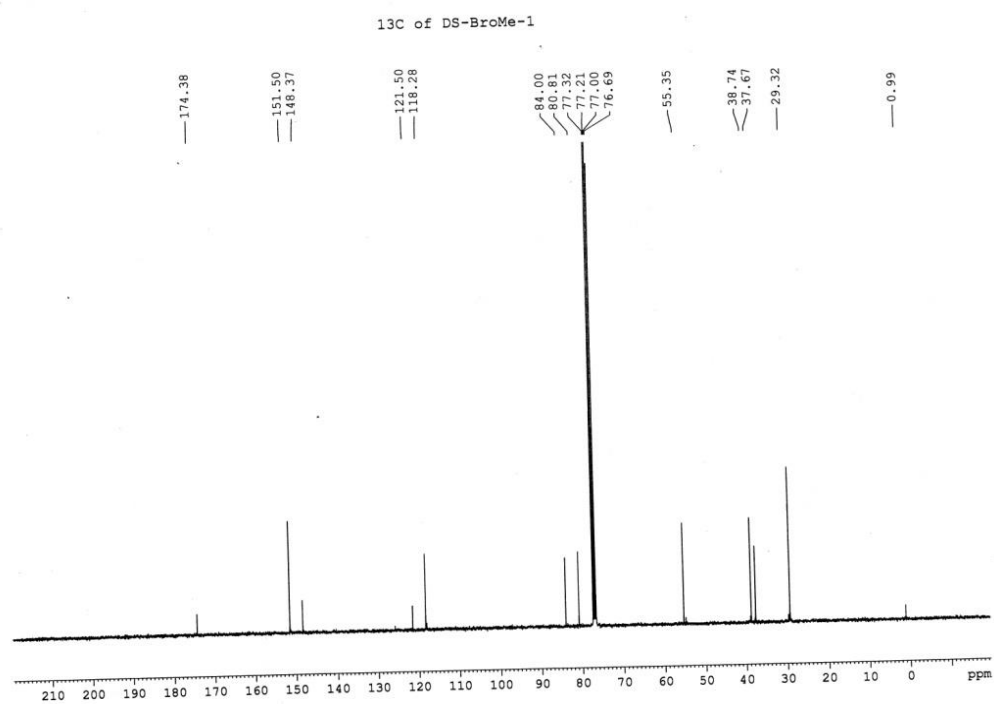
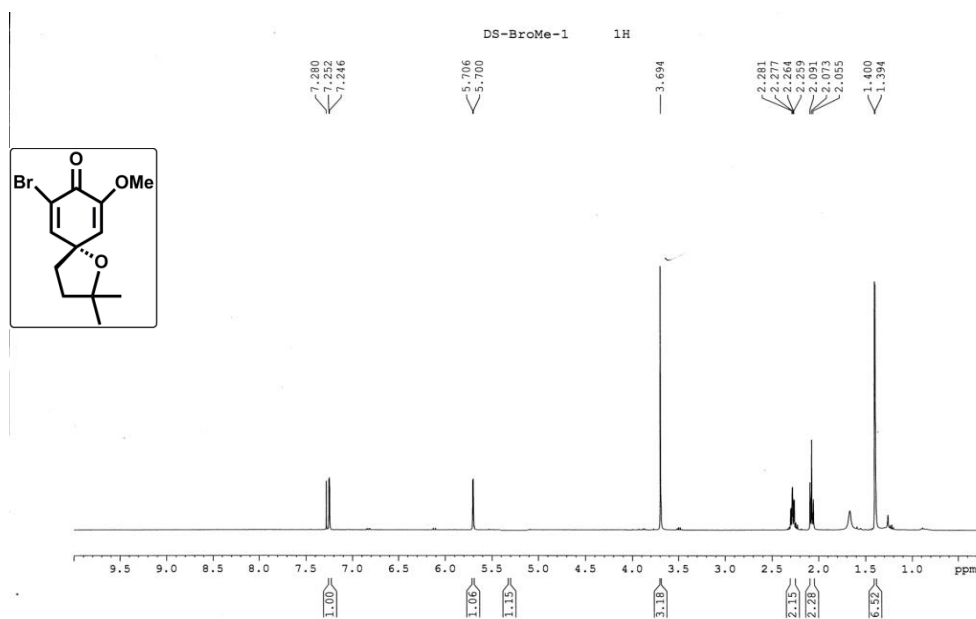
2,2-dibenzyl-7,9-dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (9e)



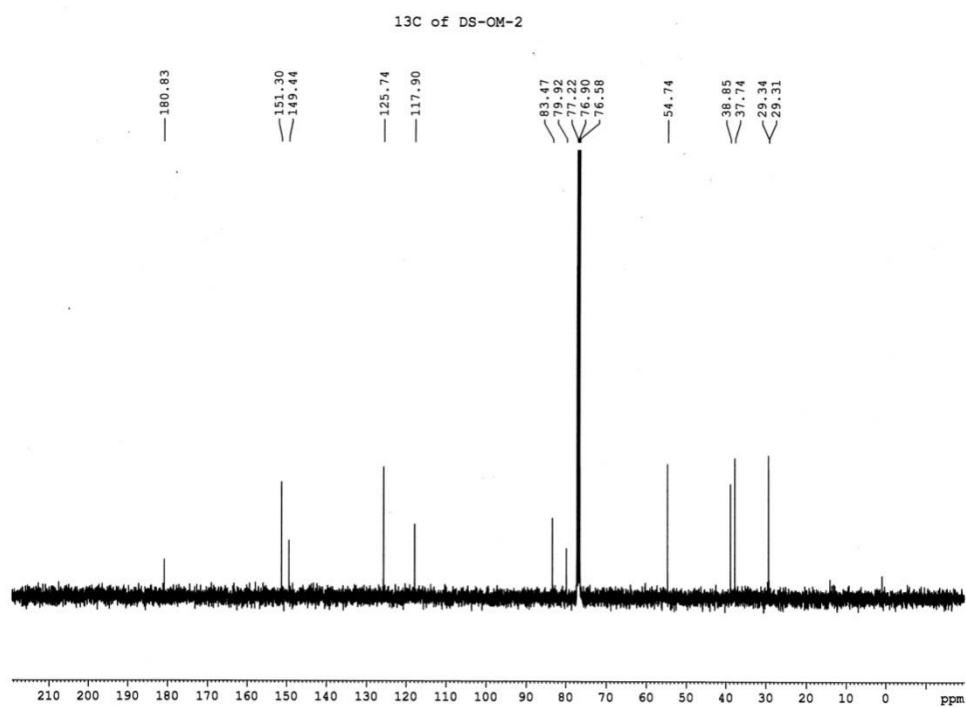
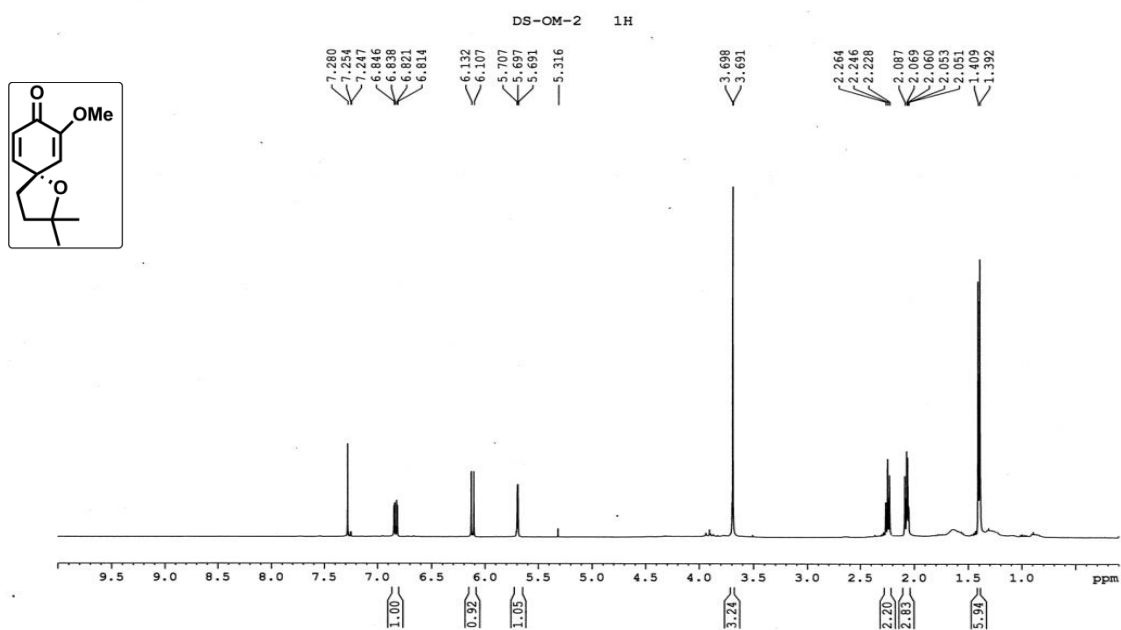
7,9-dimethyl-2,2-diphenyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (9f)



**7-bromo-9-methoxy-2,2-dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (12a)**



7-methoxy-2,2-dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one(11a)



DS-V(Ben) -F 1H

Chemical structure of DS-V(Ben) is shown in the inset:

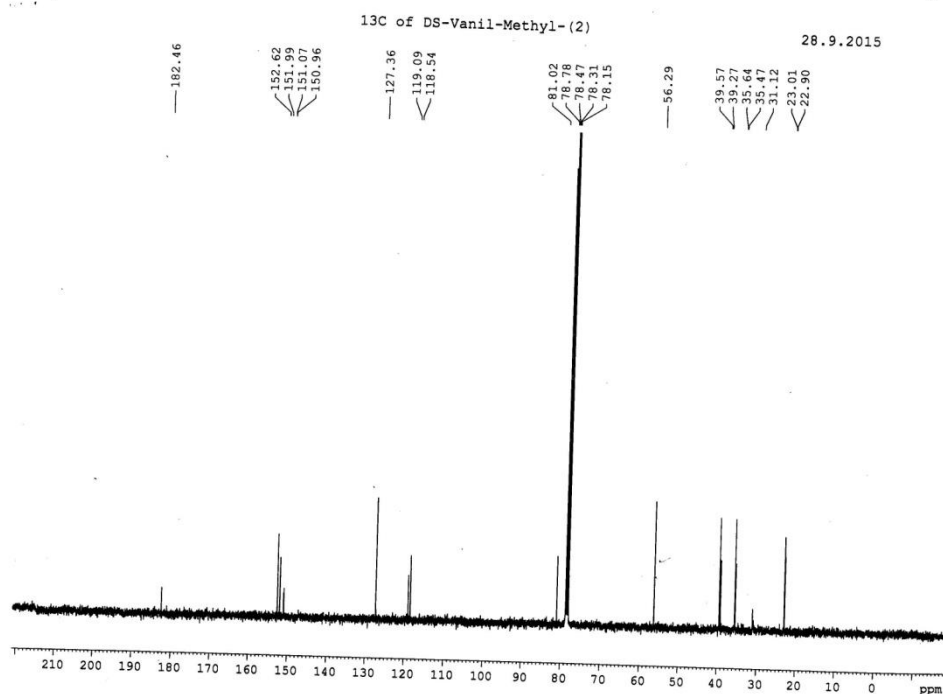
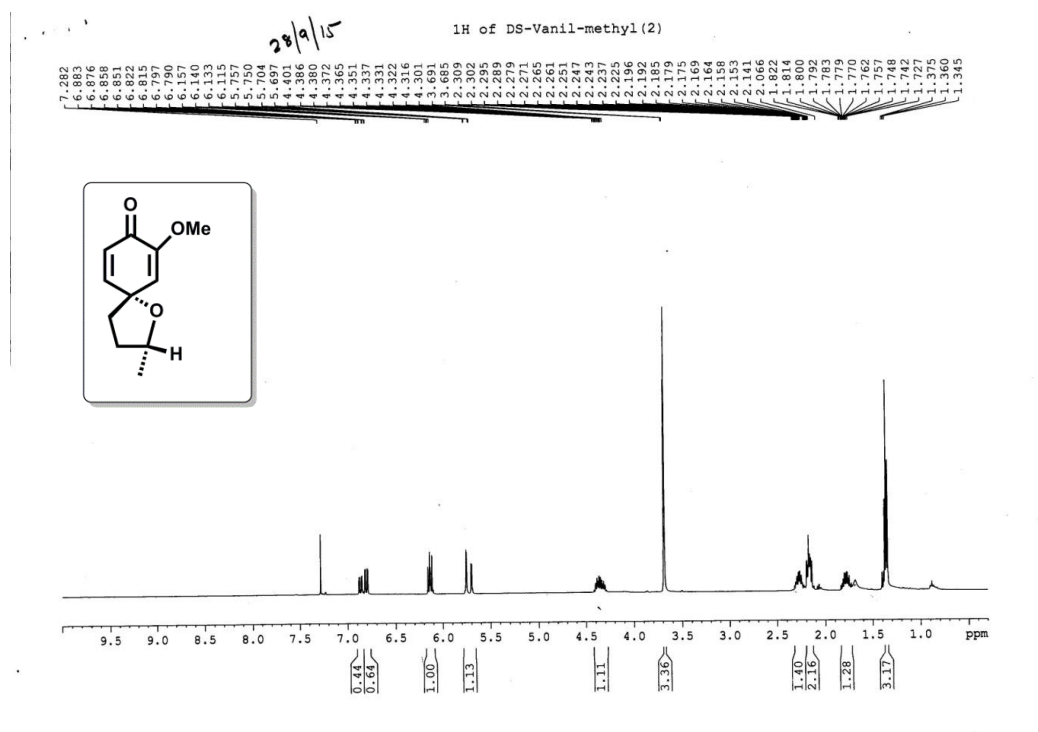
COC1=CC=C(C(=O)C1)C2CCc3ccccc3C2

1H NMR spectrum (CDCl<sub>3</sub>) data:

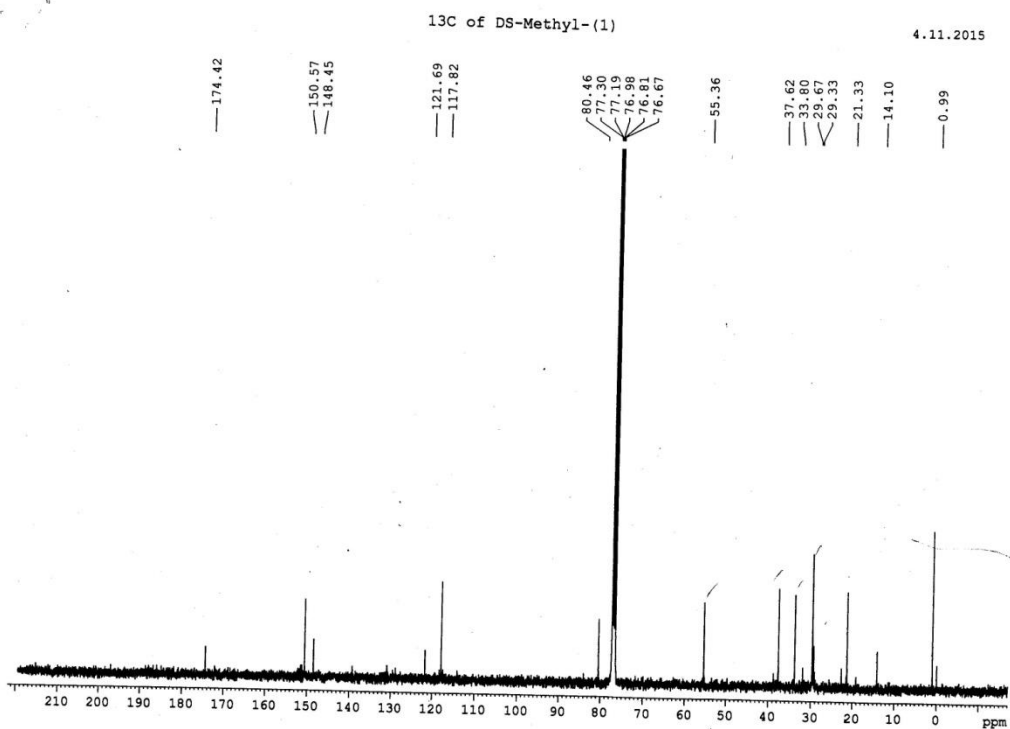
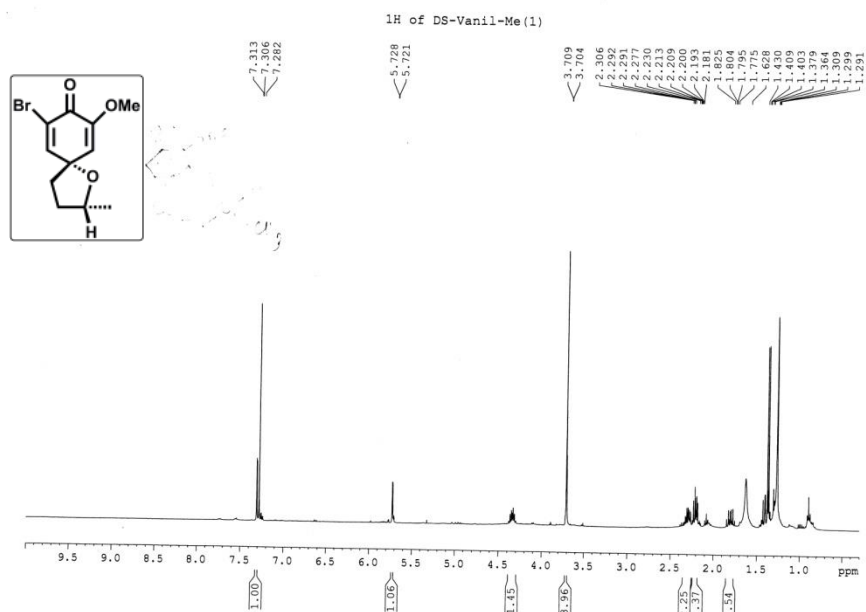
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| 5.116, 5.109  | 1.00        |
| 3.828, 3.468, 3.044, 3.034, 3.010, 3.000, 2.986, 2.982, 2.903, 2.898, 2.869, 2.175, 2.157, 2.139, 1.826, 1.811, 1.794, 1.776, 1.682, 1.664, 1.650, 1.645, 1.632 | 2.99        |
| 2.07  | 2.86        |
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| 0.092   | 0.96        |



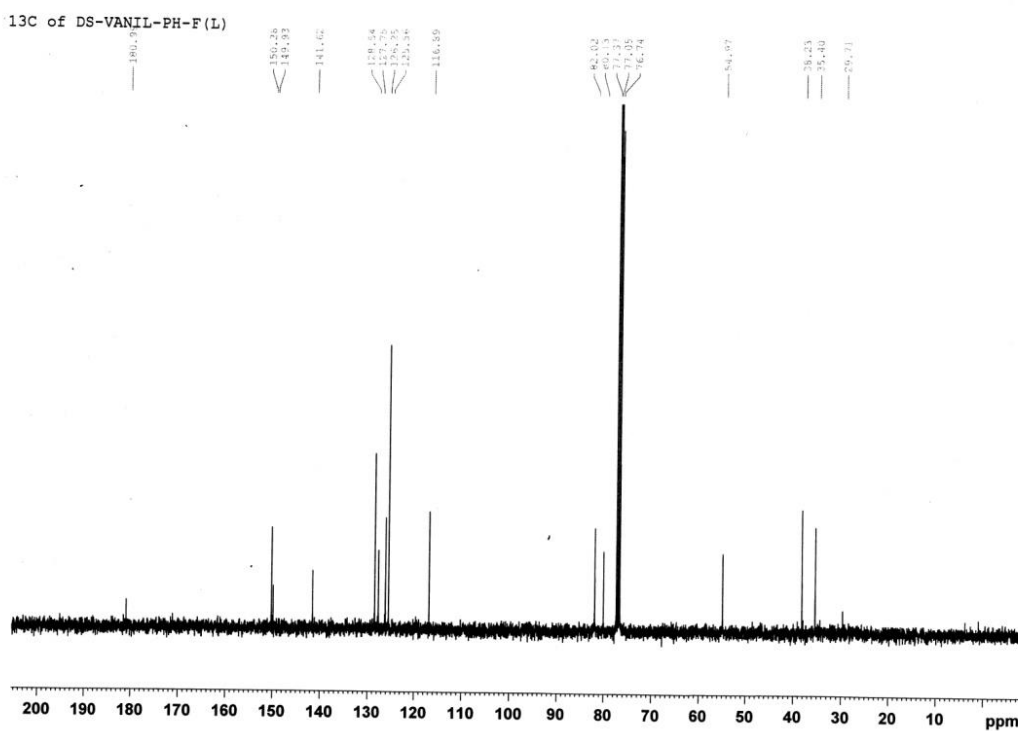
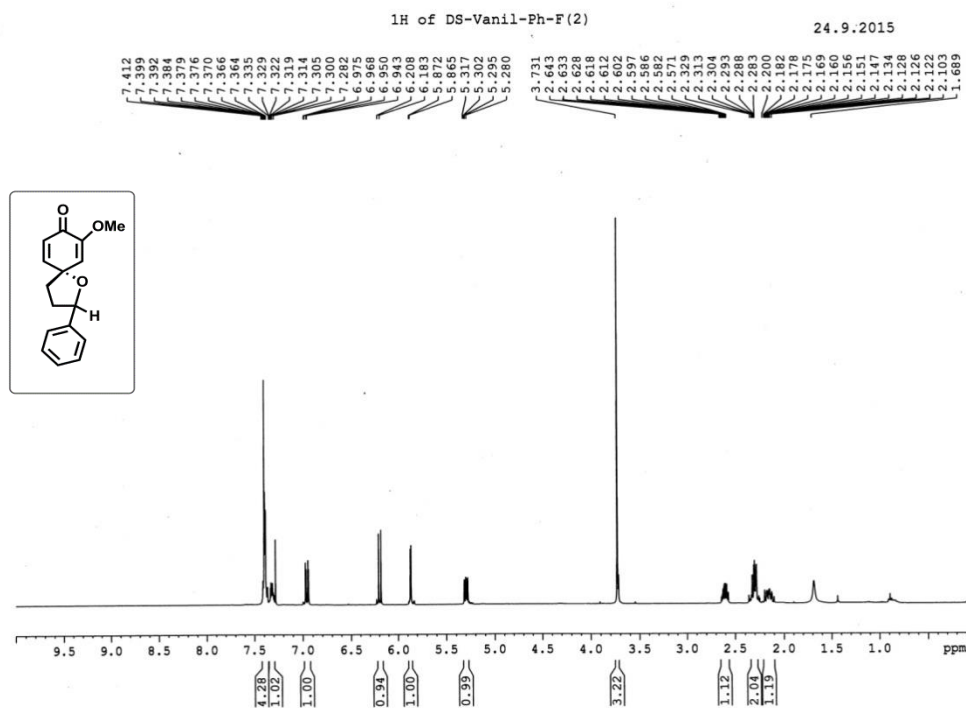
(2R,5R)/(2S,5S)-7-methoxy-2-methyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (14a)



(2R, 5S) / (2S,5R)-7-bromo-9-methoxy-2-methyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (15a)

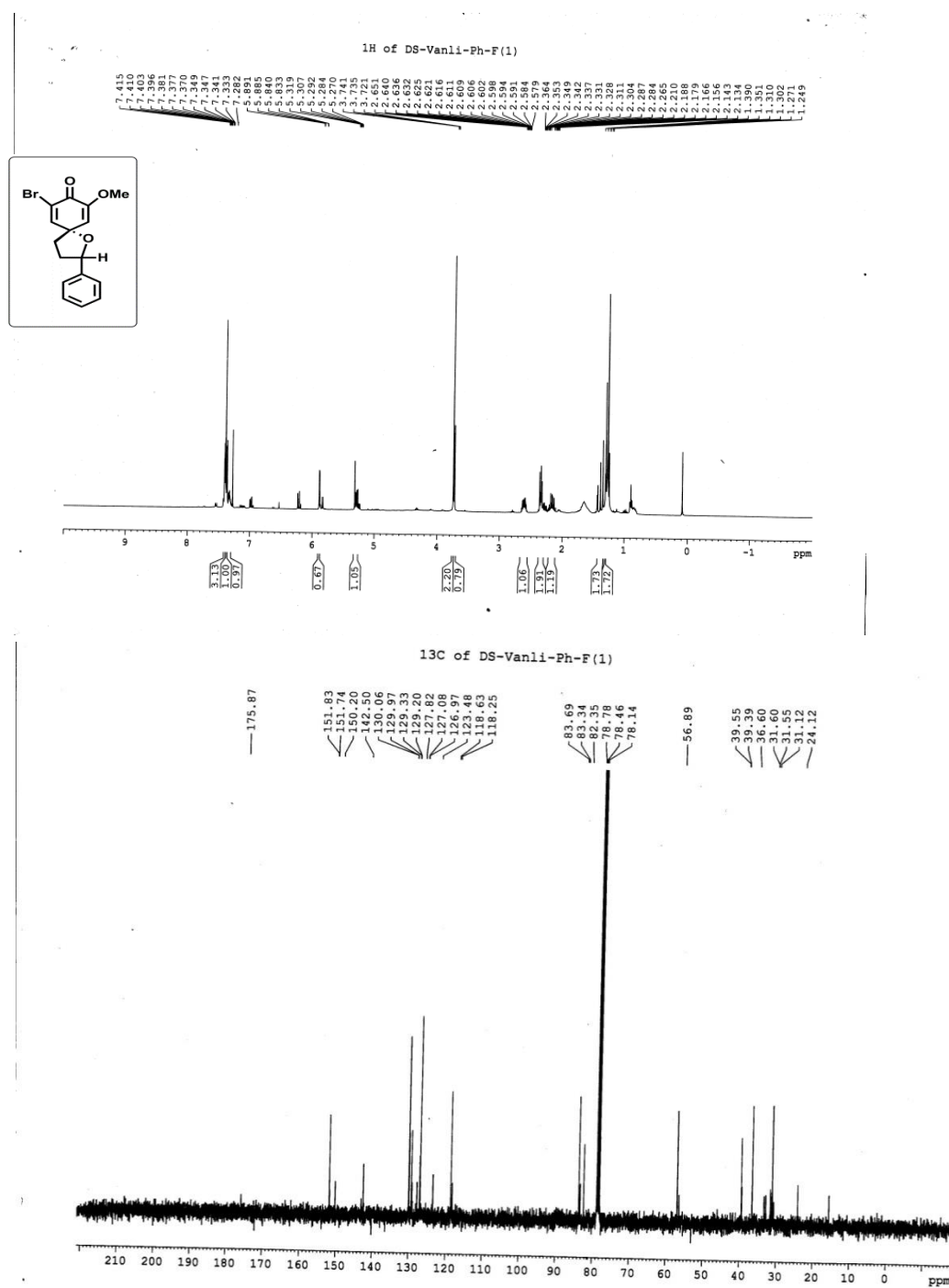


(2S, 5R)/ (2R,5S)-7-methoxy-2-phenyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (14b)

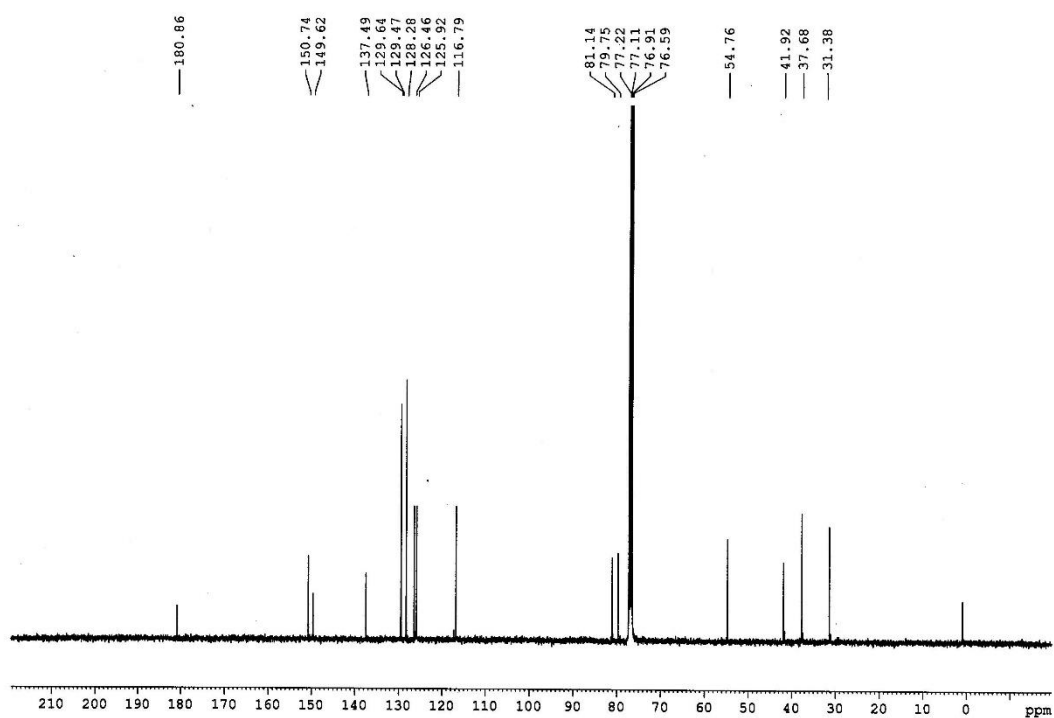
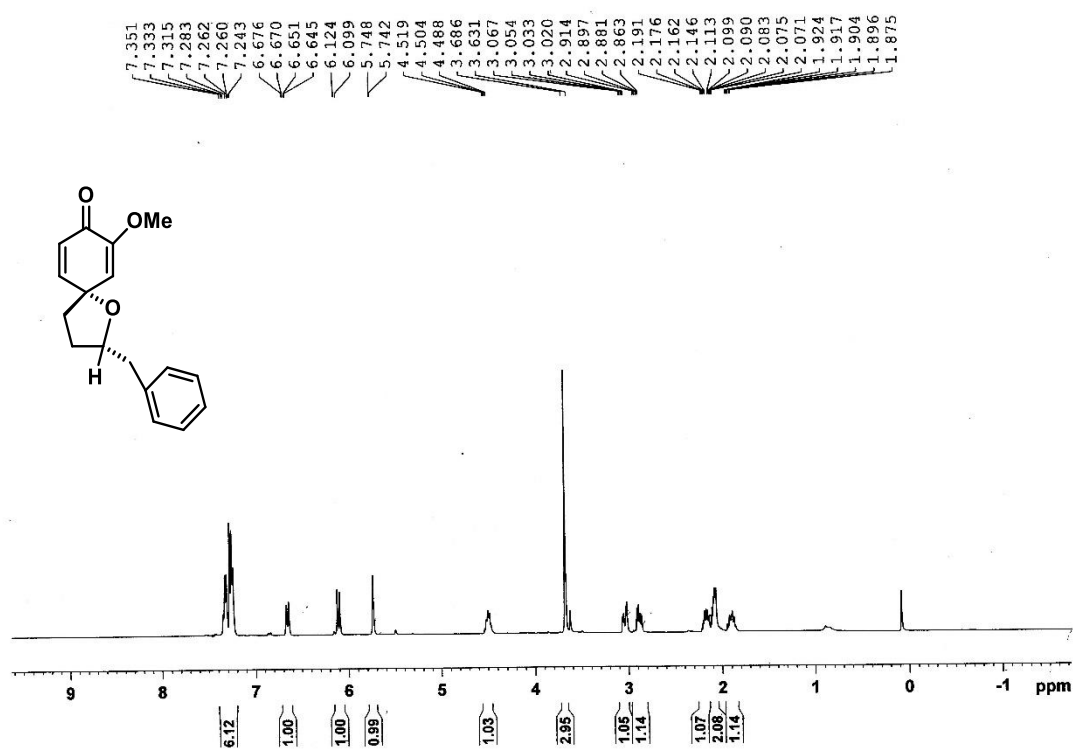




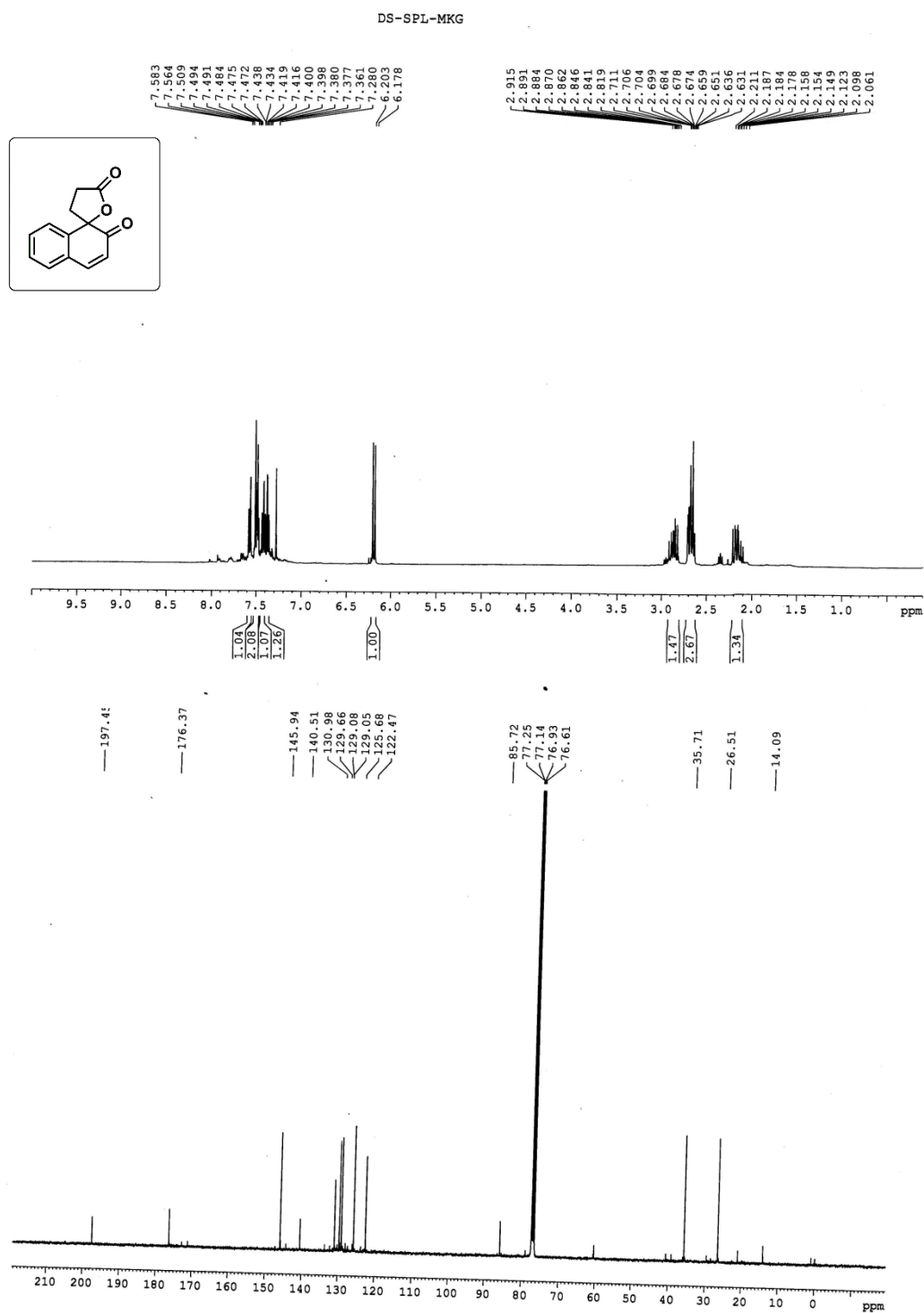
(2S, 5S)/ (2R, 5R)-7-bromo-9-methoxy-2-phenyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (15b)



**(2S, 5R/ (2R, 5S))-2-benzyl-7-methoxy-1-oxaspiro [4.5]deca-6,9-dien-8-one (14c)**

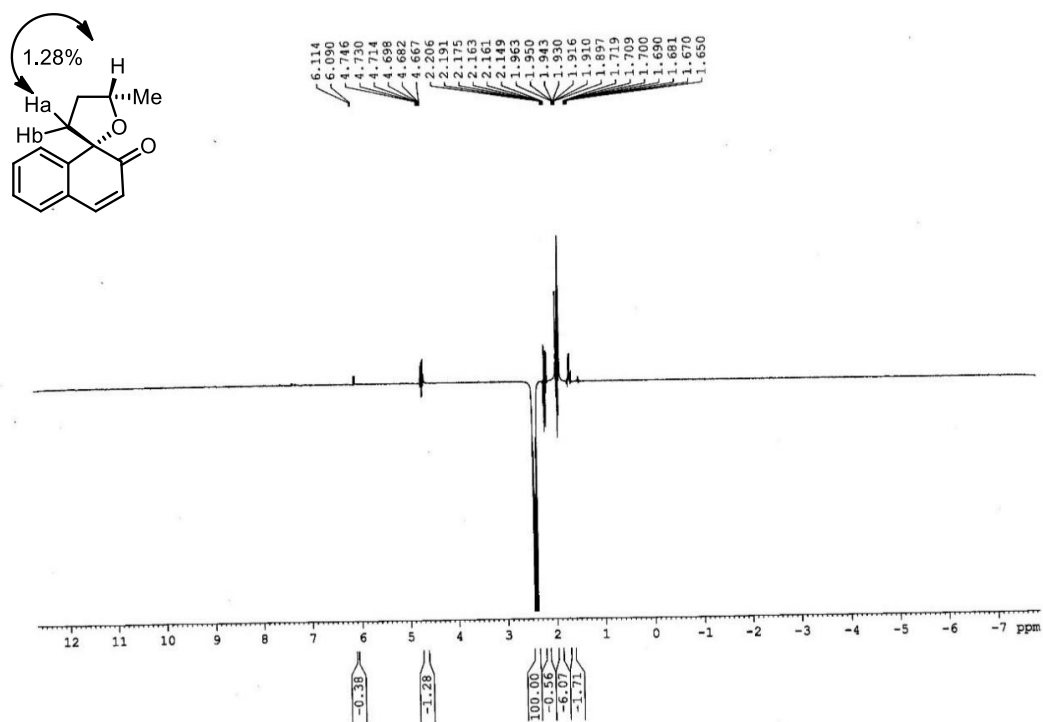
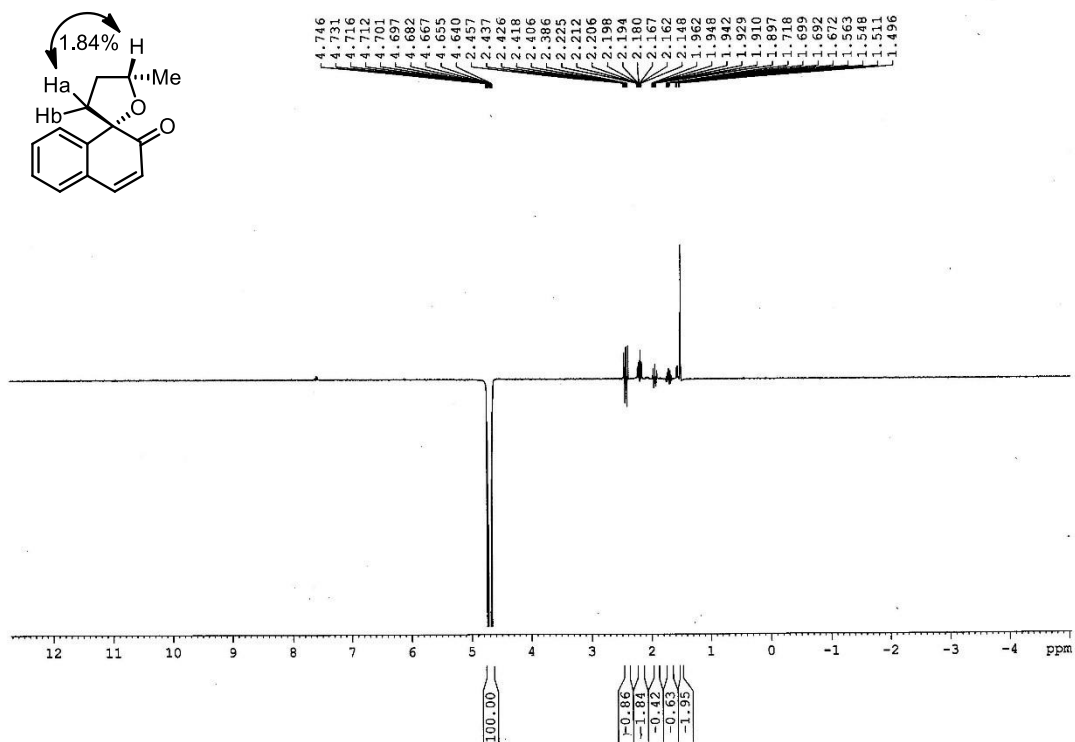


2'H,3H-spiro[furan-2,1'-naphthalene]-2',5(4H)-dione from naphthol ester (17)

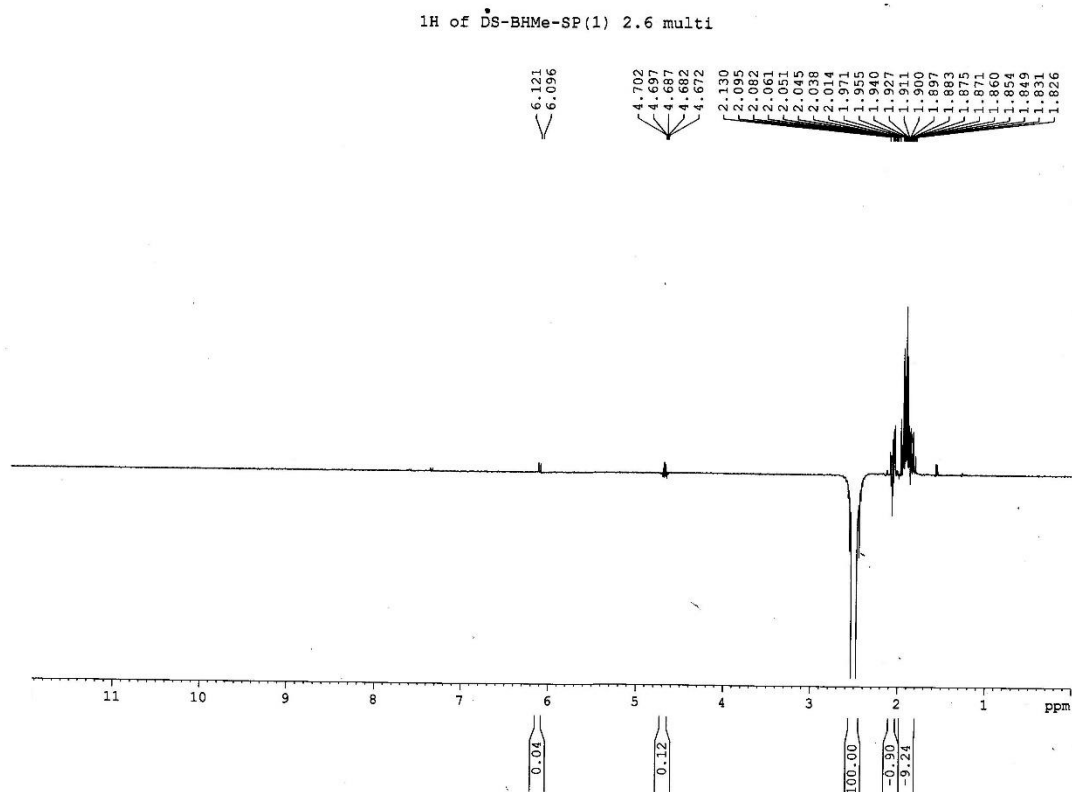
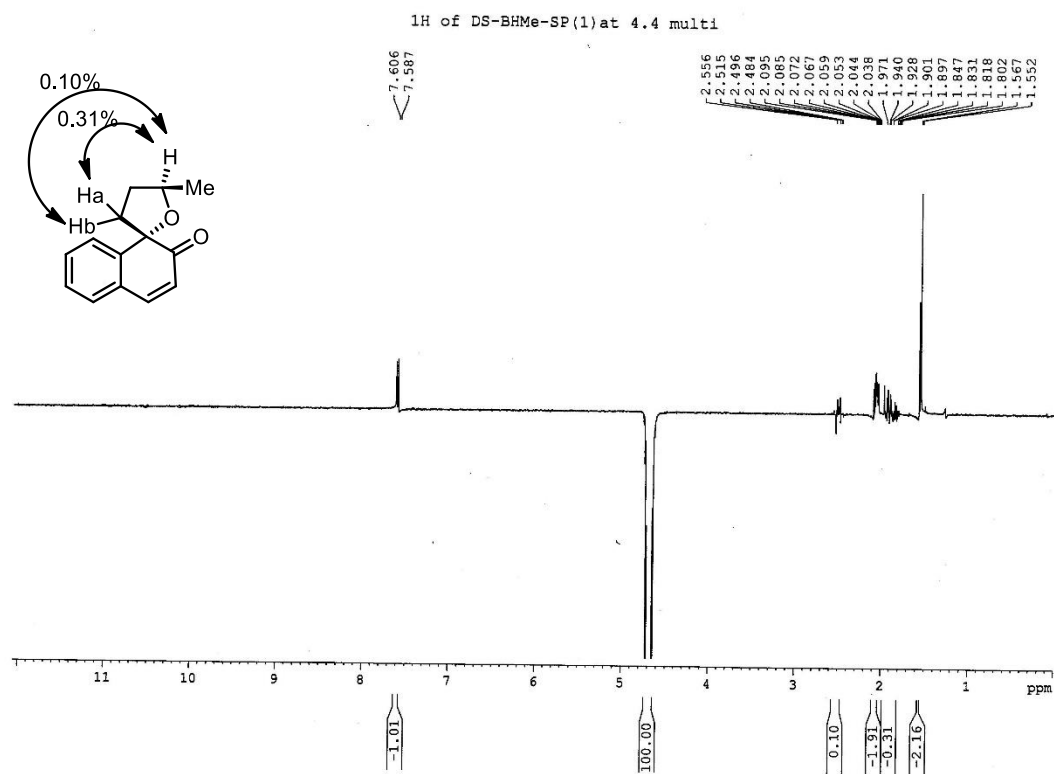


# NOE Experimental spectra

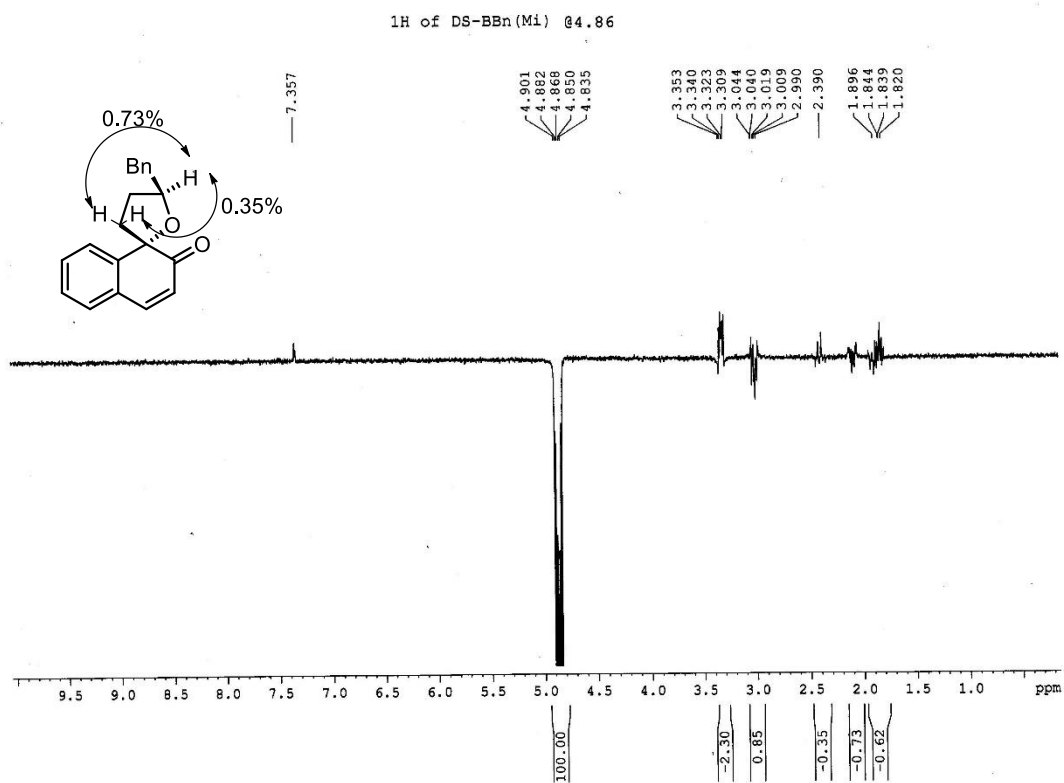
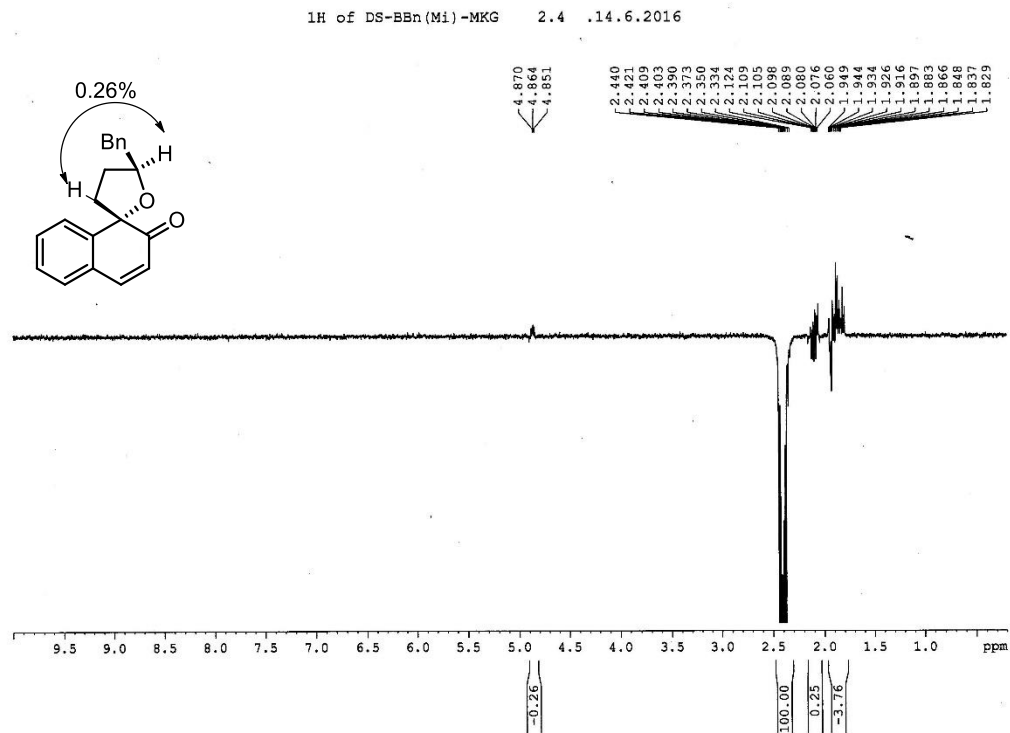
## NOE of (1'S,5S)-5-methyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6a)



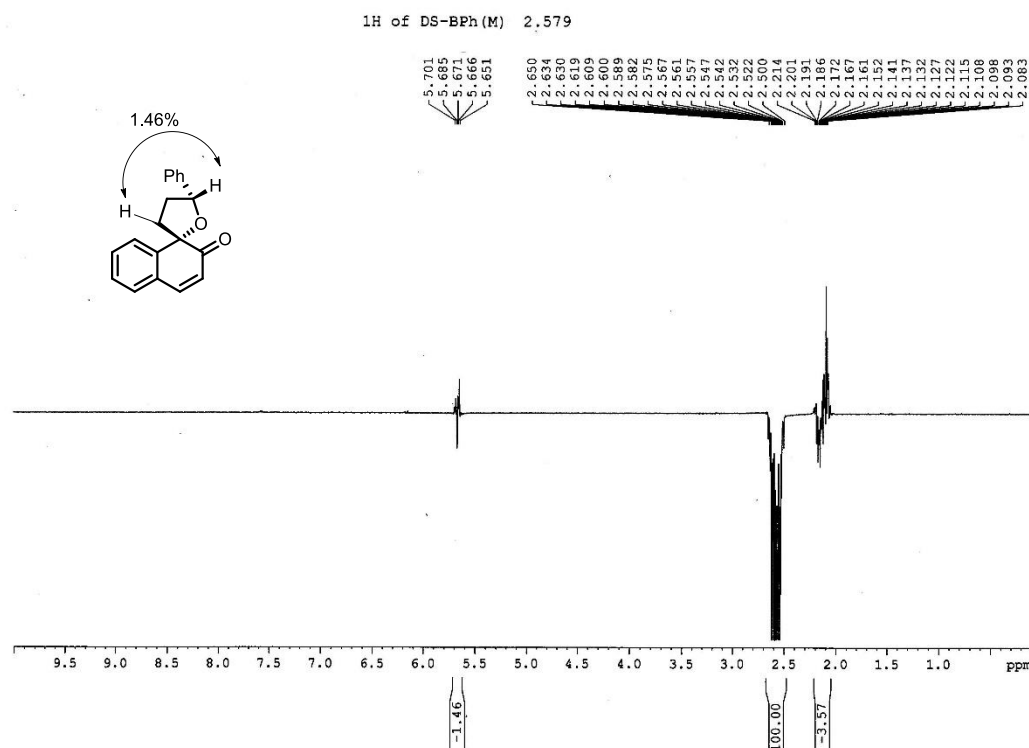
# NOE of (1*S*,5*R*)-5-methyl-4,5-dihydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalen]-2'-one (7a)



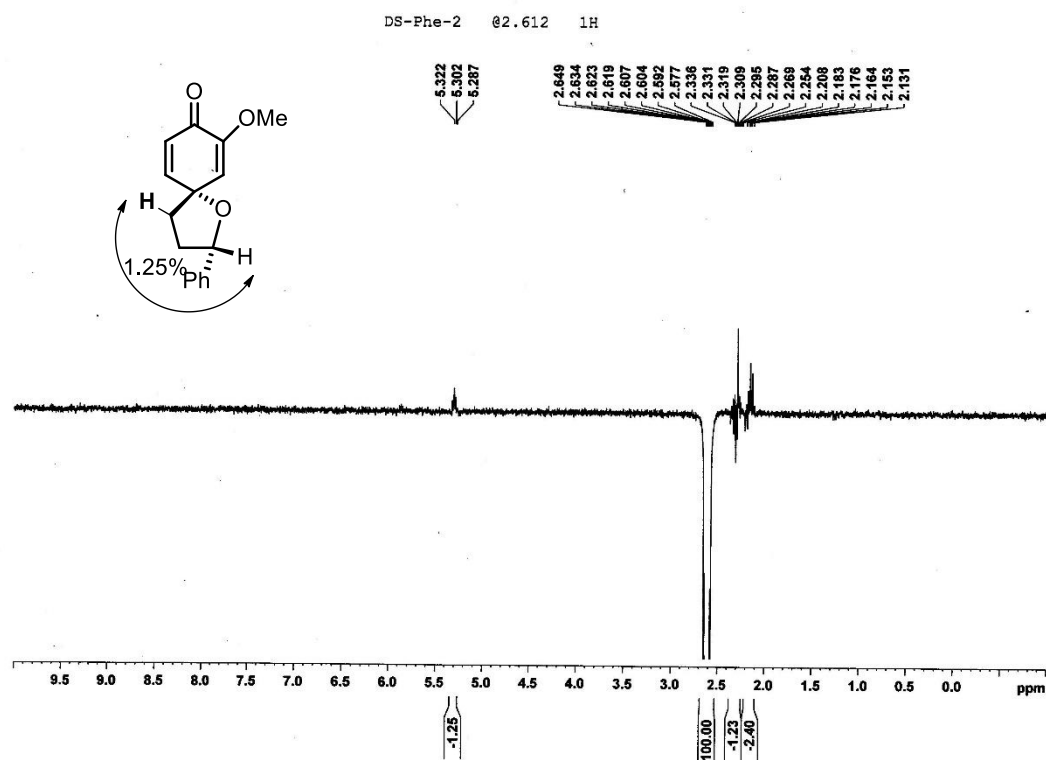
# NOE of (1'S,5S)-5-benzyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (7c)



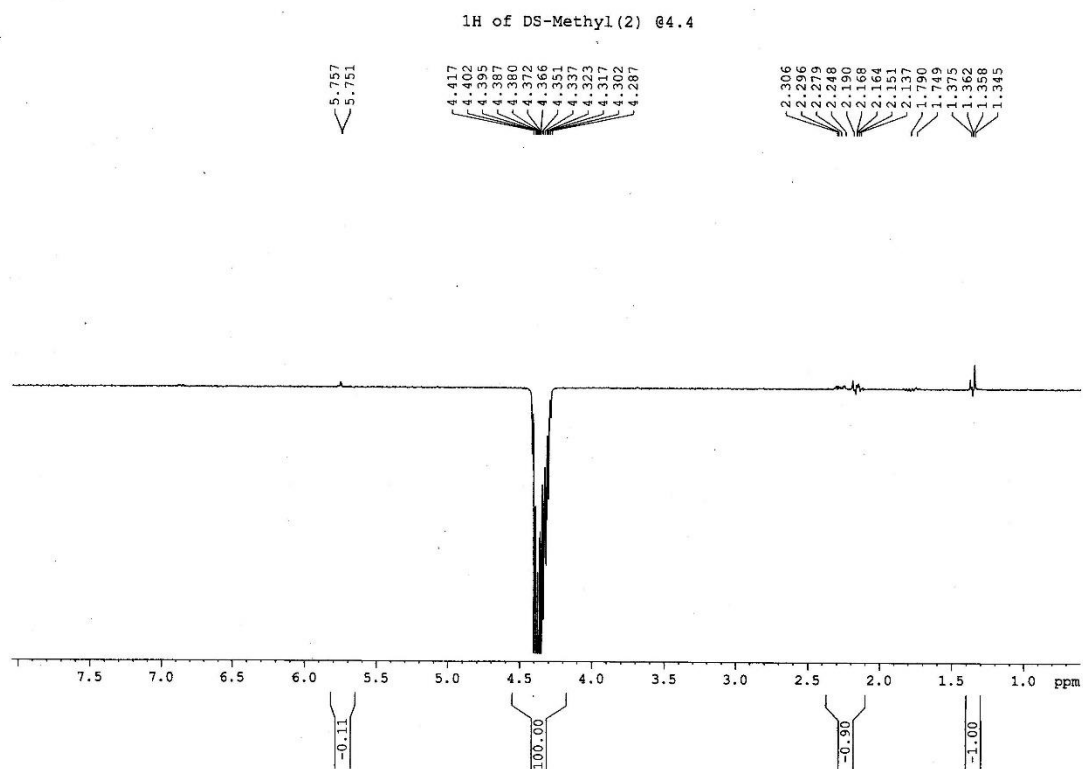
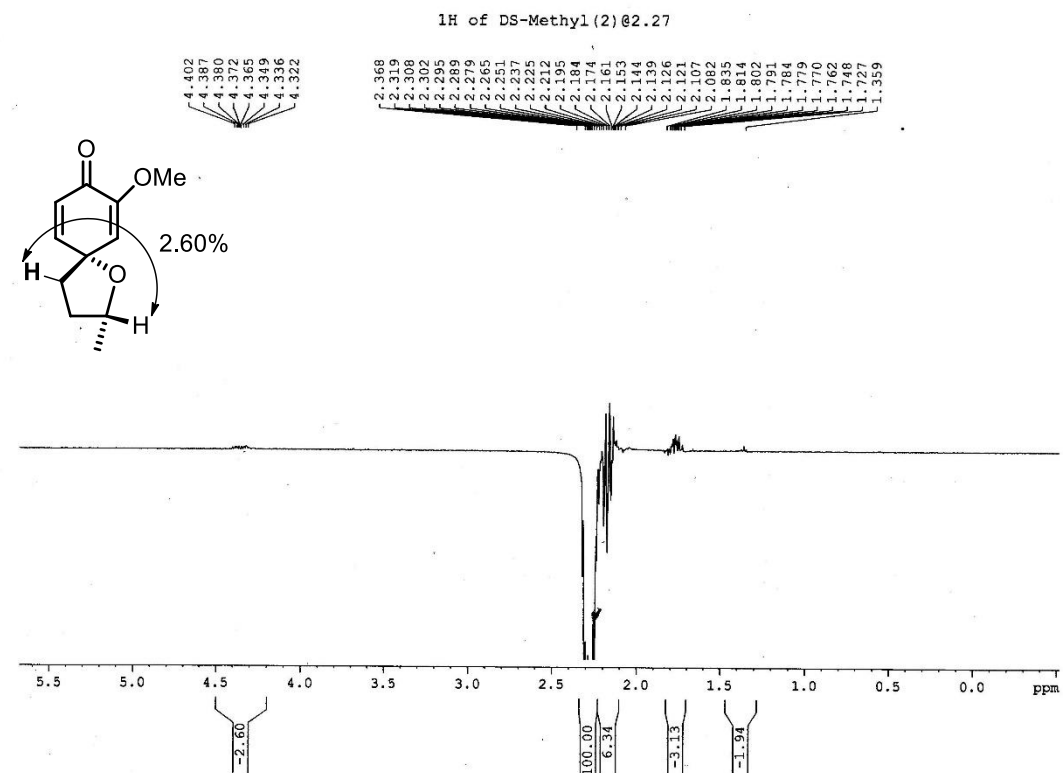
# NOE of (1'S,5R)-5-phenyl-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one (6d)



# NOE of (5R)-7-methoxy-2-phenyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (14b)

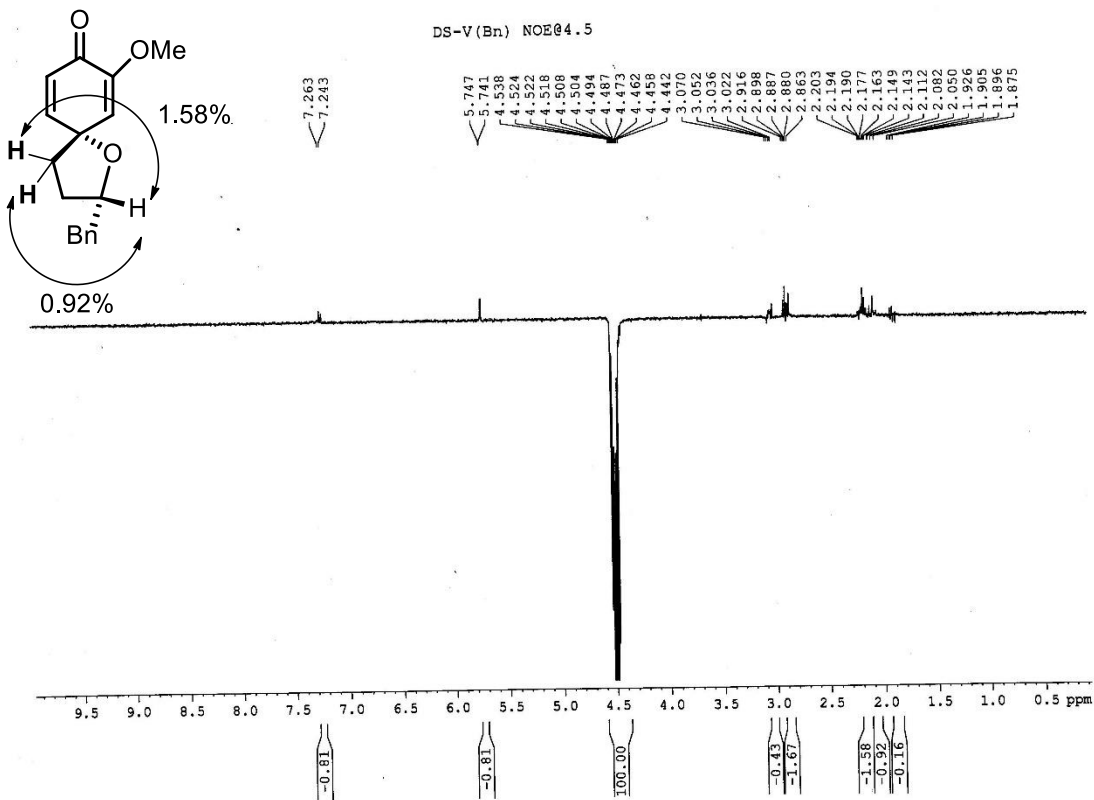
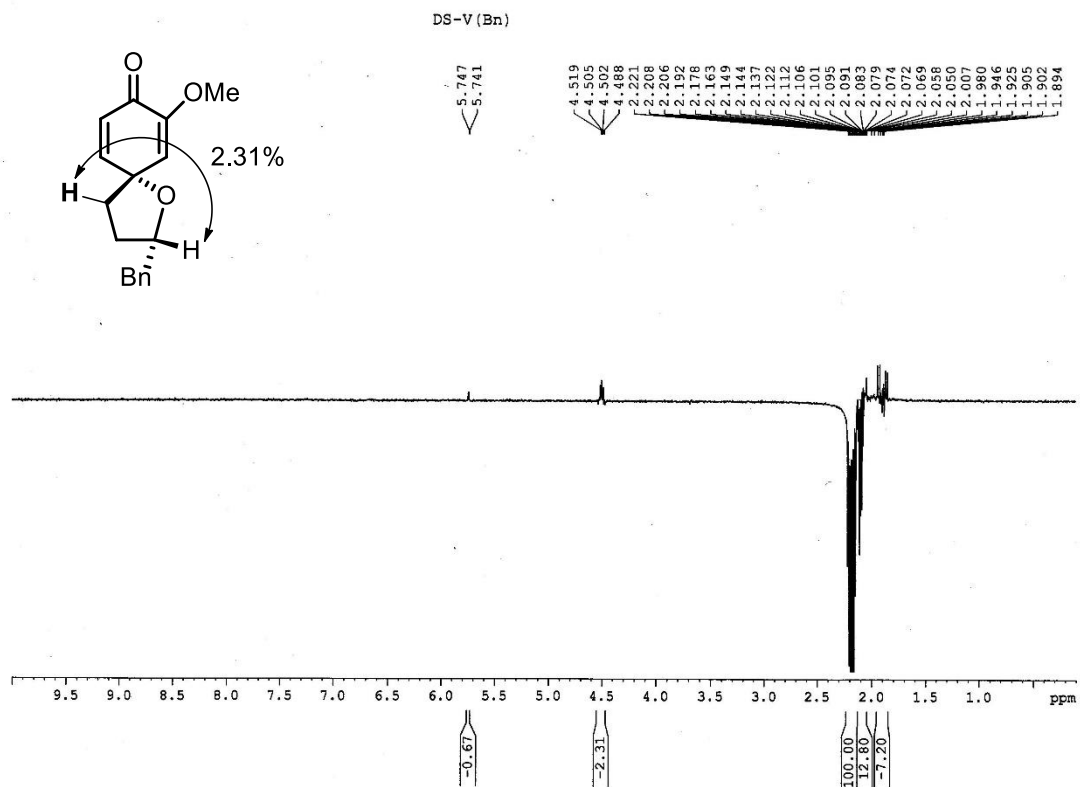


# NOE of (2R,5R)-7-methoxy-2-methyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (14a)

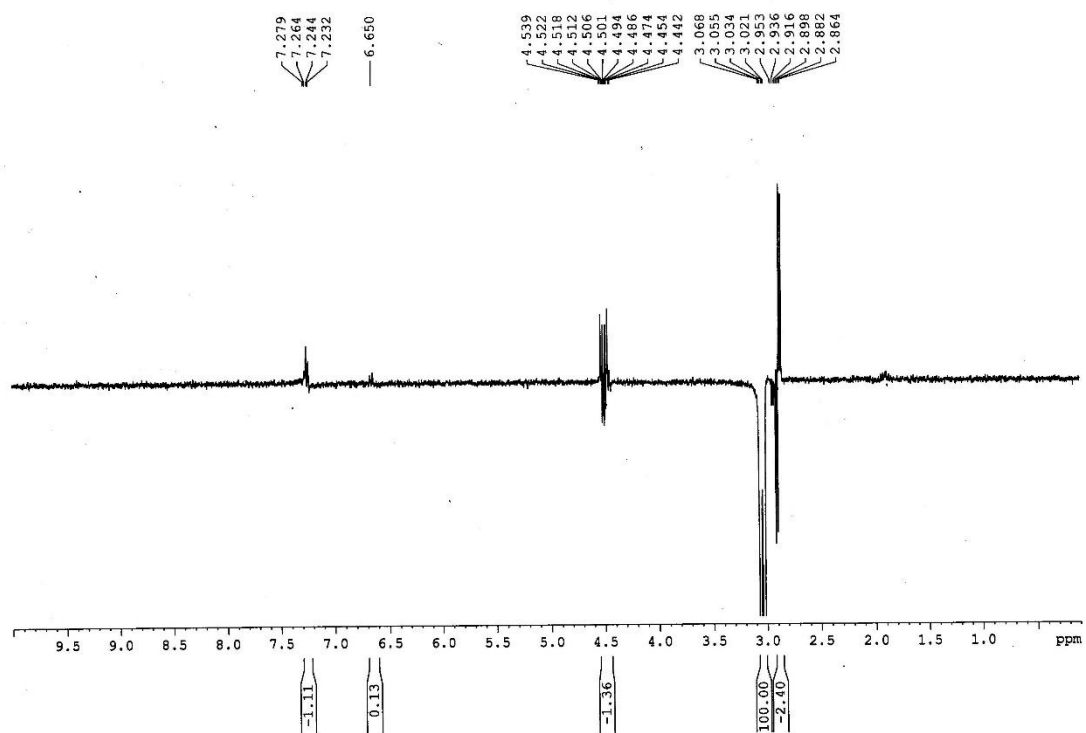




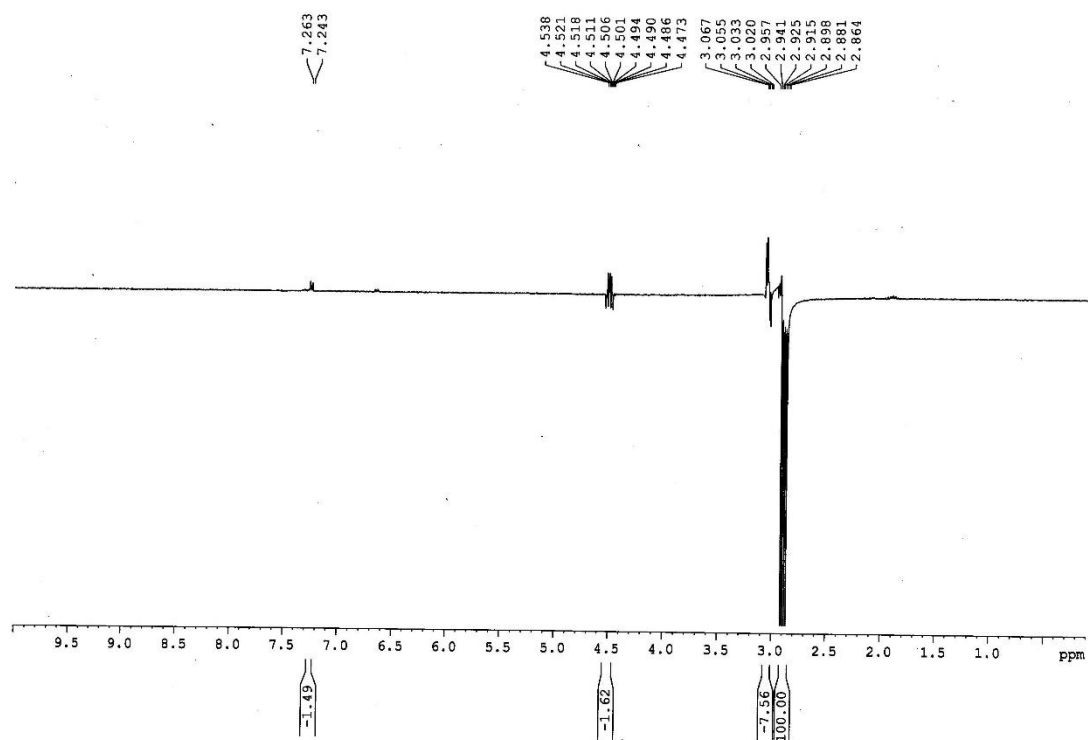
# NOE of (5R)-2-benzyl-7-methoxy-1-oxaspiro [4.5]deca-6,9-dien-8-one (14c)



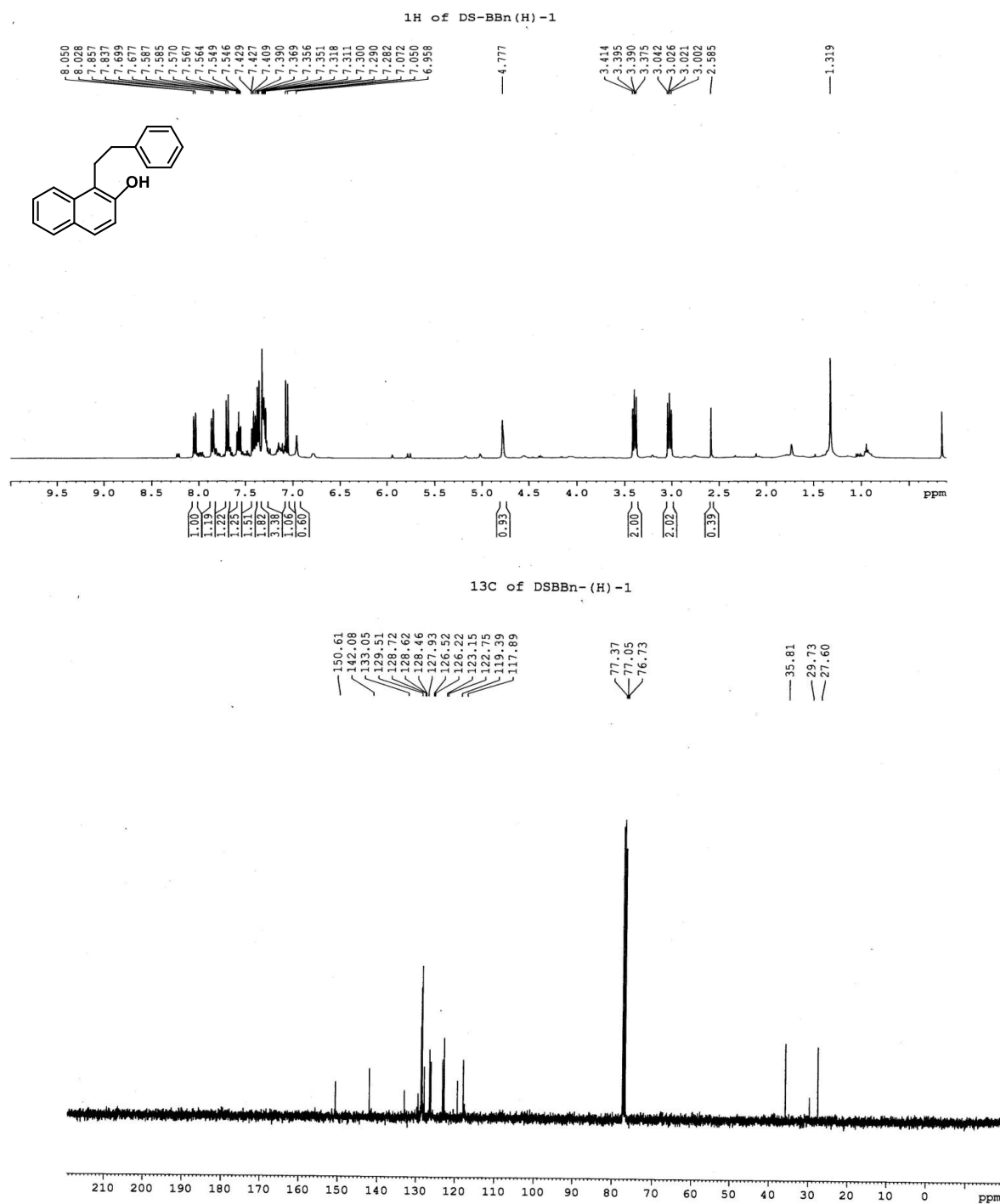
DS-V(Bn)-MKG @3.04 14.6.2016 1H



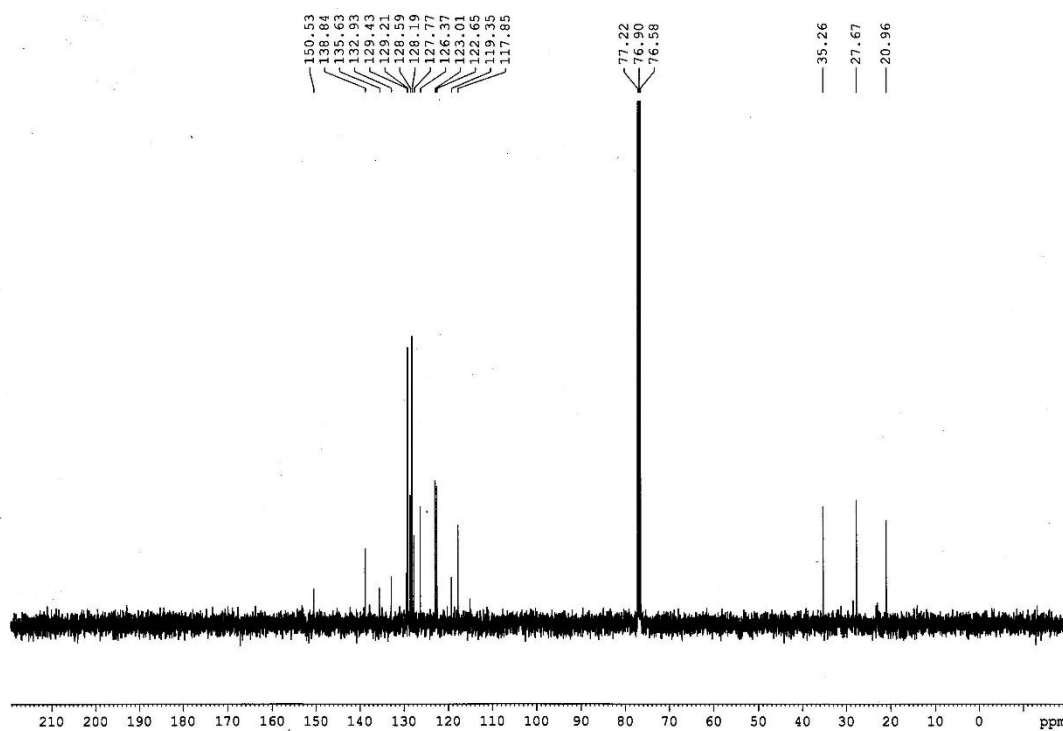
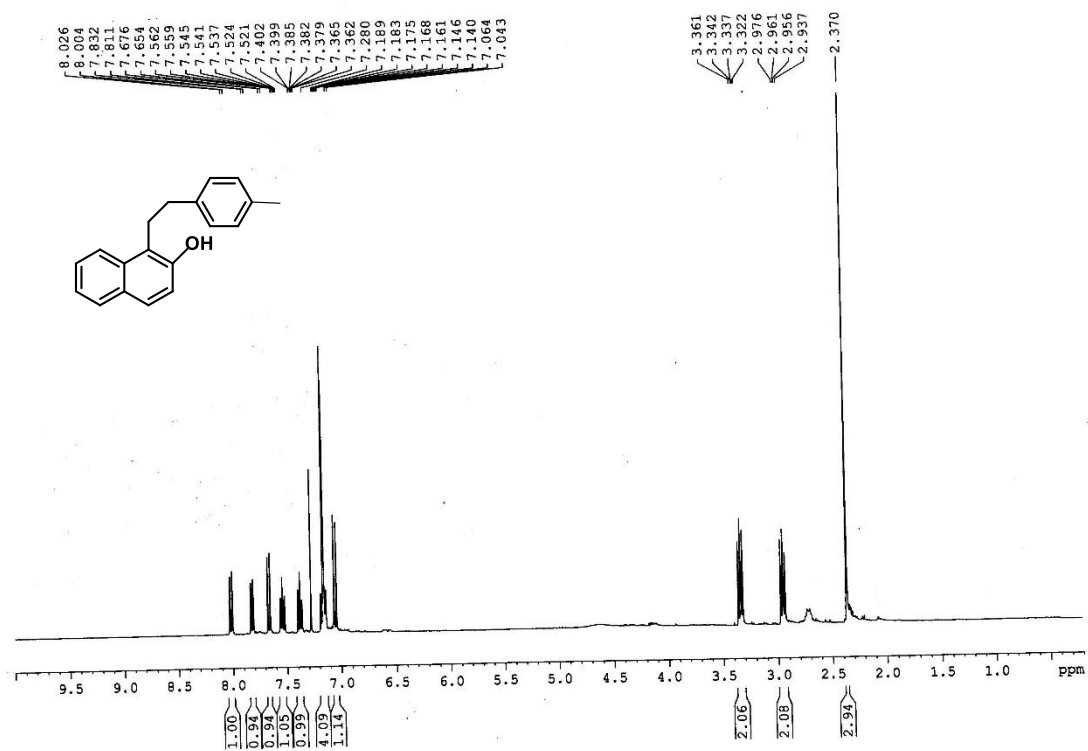
DS-V(Bn) @2.88



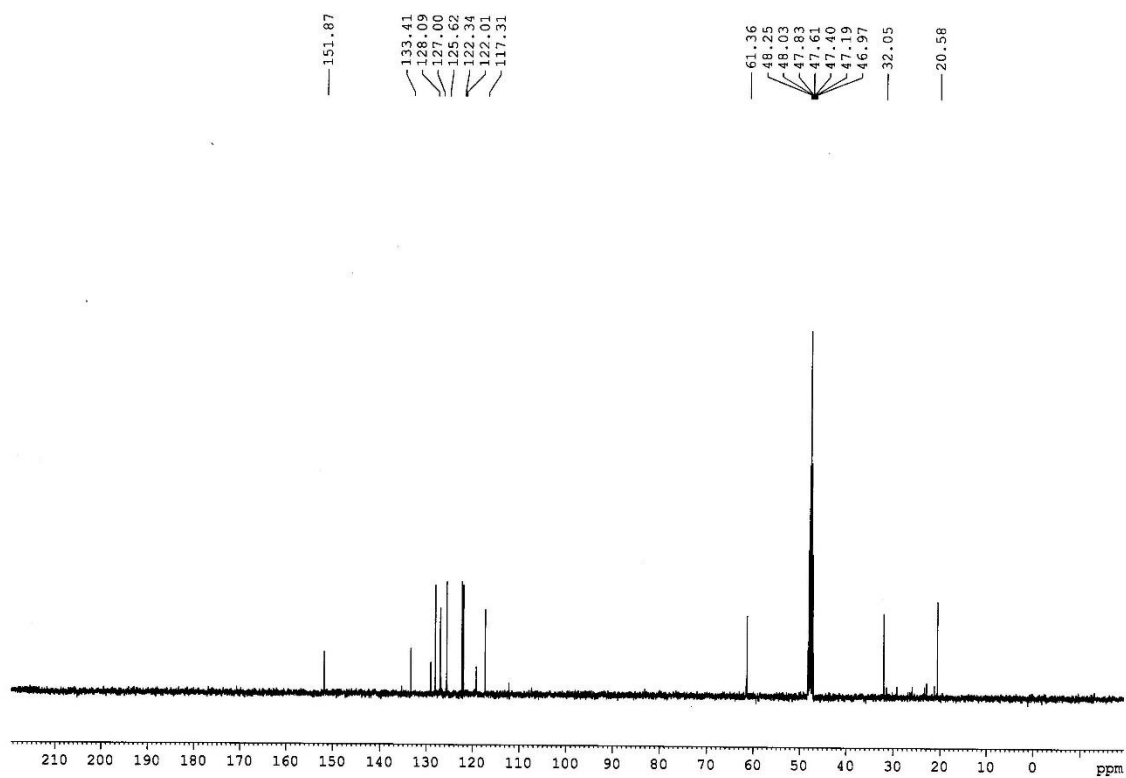
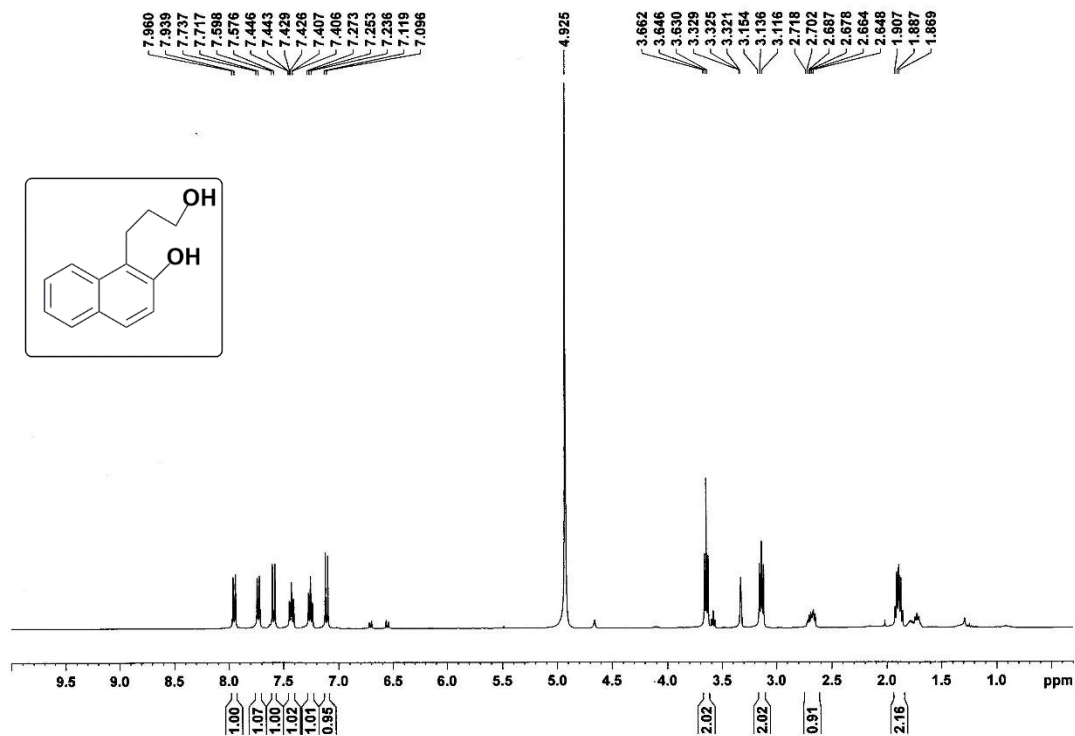
# 1-phenethylnaphthalen-2-ol (1e)



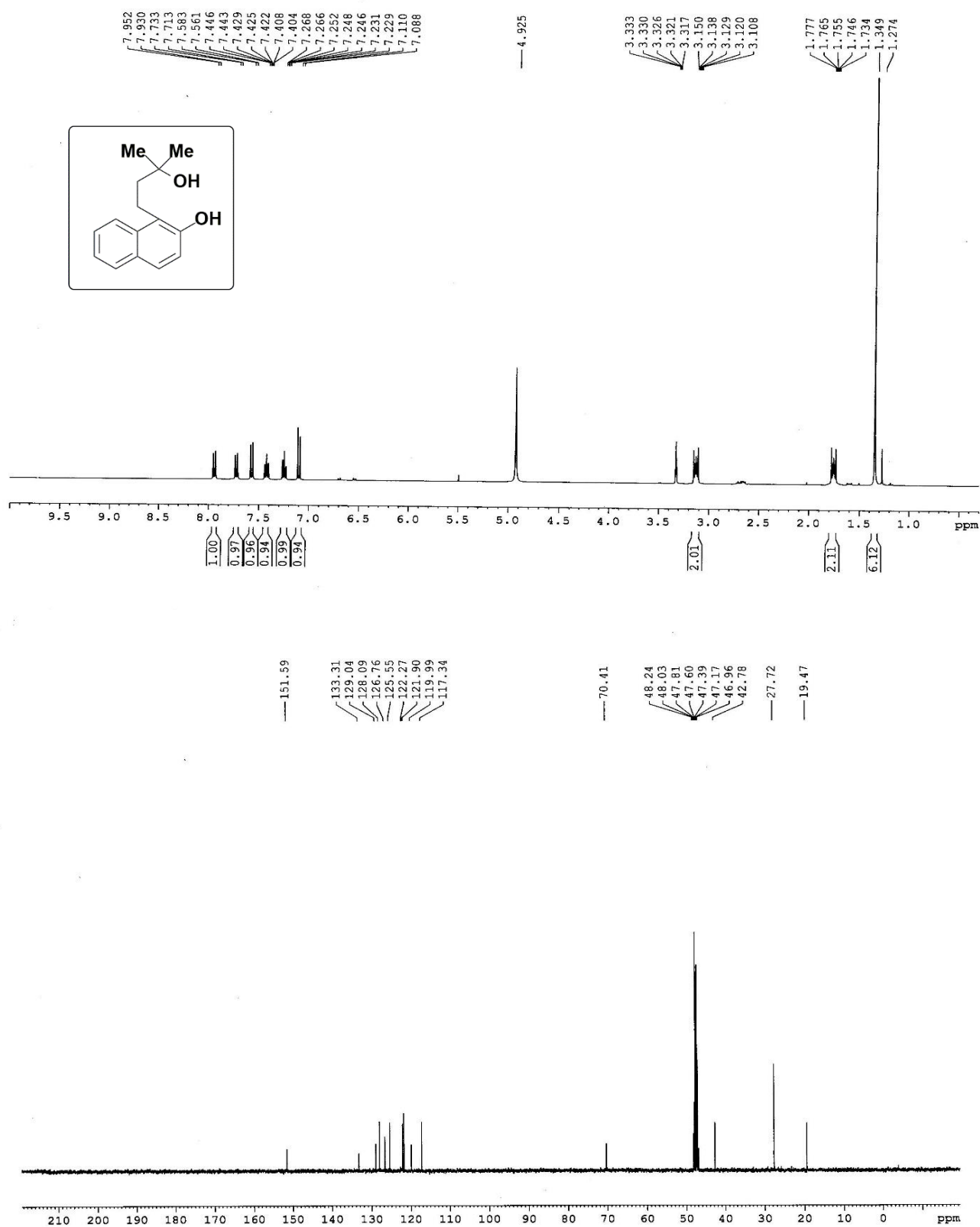
1-(4-methylphenethyl) naphthalene-2-ol (1f)



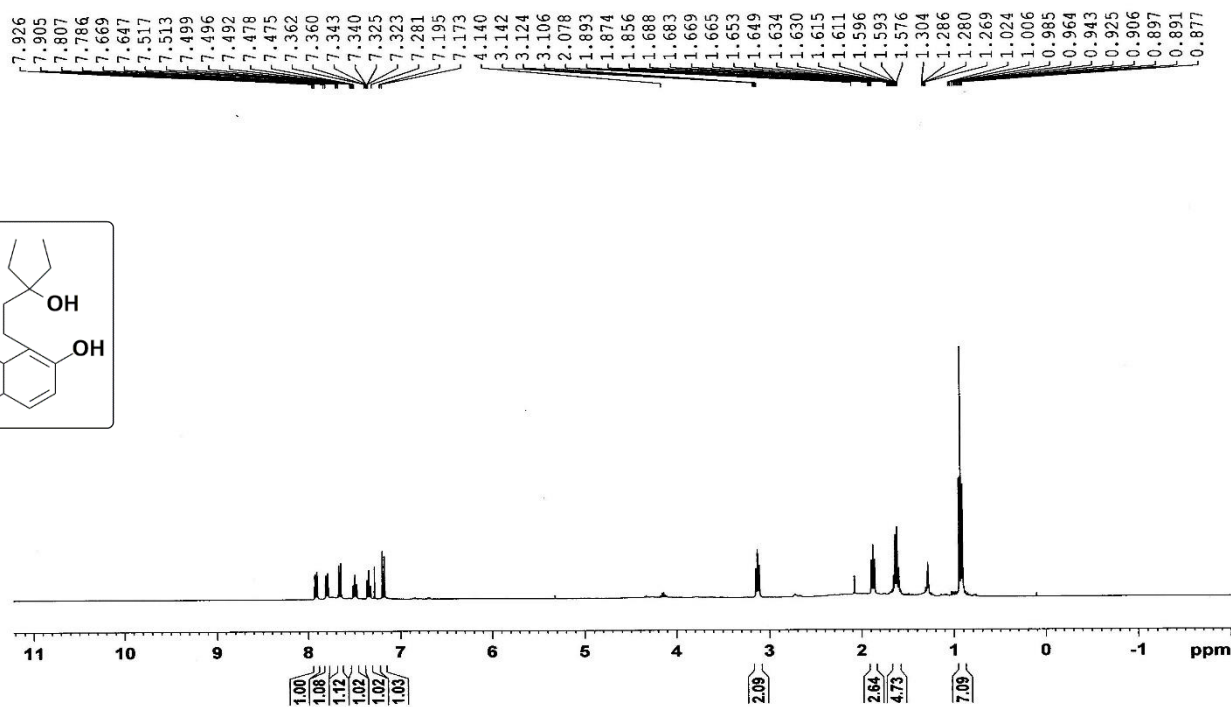
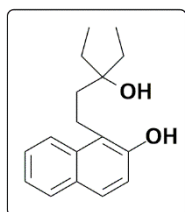
1-(3-hydroxypropyl) naphthalene-2-ol (3a)



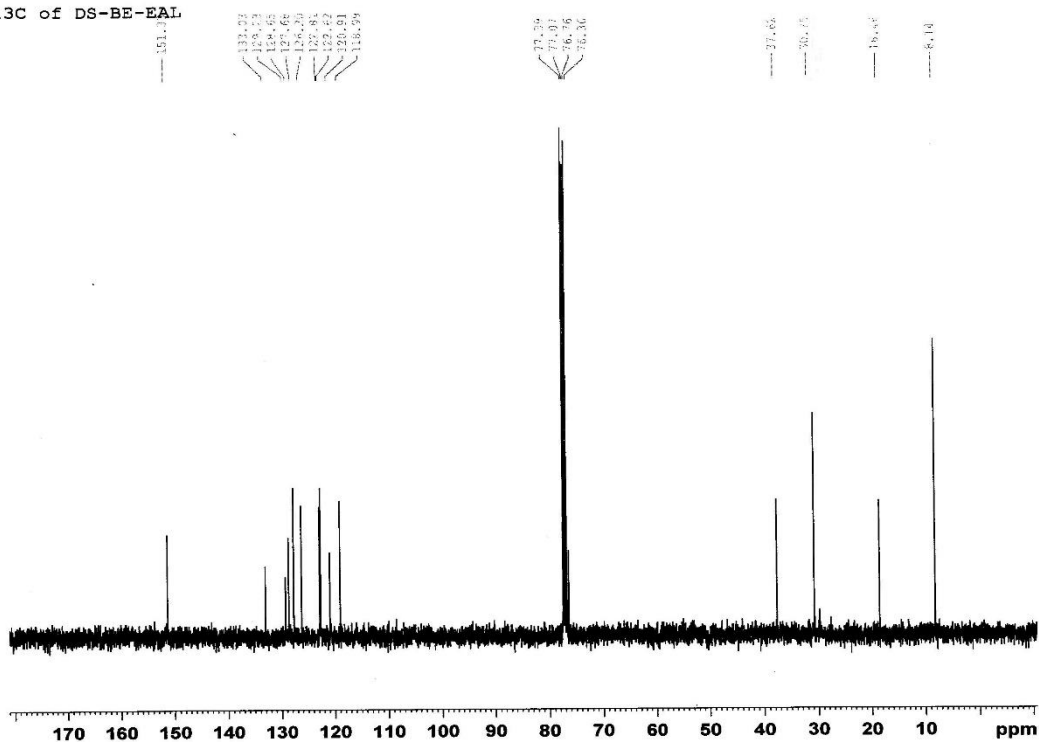
1-(3-hydroxy-3-methylbutyl) naphthalene-2-ol (3b)



# 1-(3-hydroxy-(3-ethyl-3hydroxypentyl) naphthalene-2-ol (3c)



13C of DS-BE-EAL



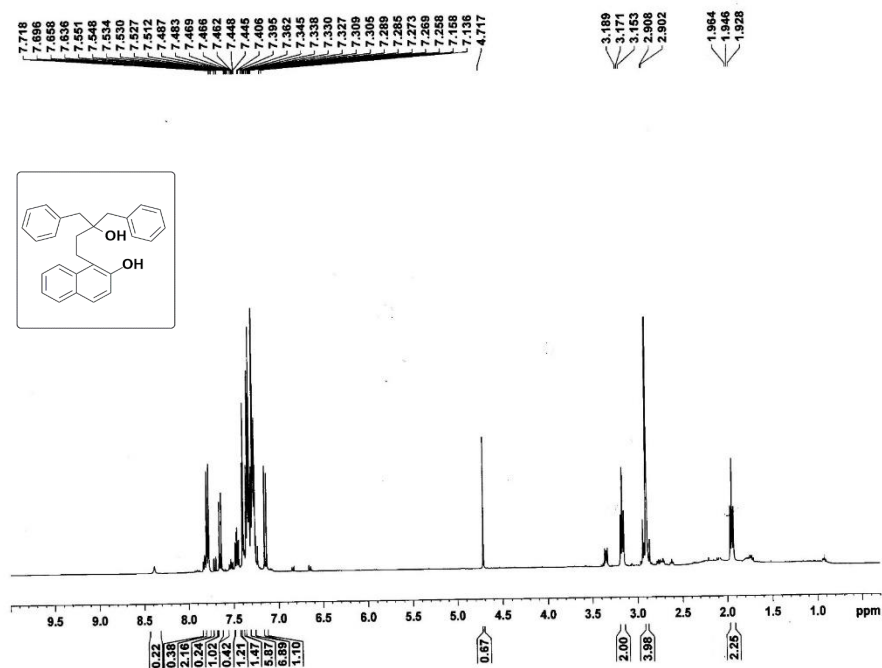
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NAME      08.06.2015
EXPNO     26
PROCNO    1
Date_     20150730
Time      6.25
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         71
DS         4
SWH        24038.465 Hz
FIDRES     0.733596 Hz
AQ         0.6810244 sec
RG         203
DN         20.800 usec
DE         6.50 usec
TE         298.3 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

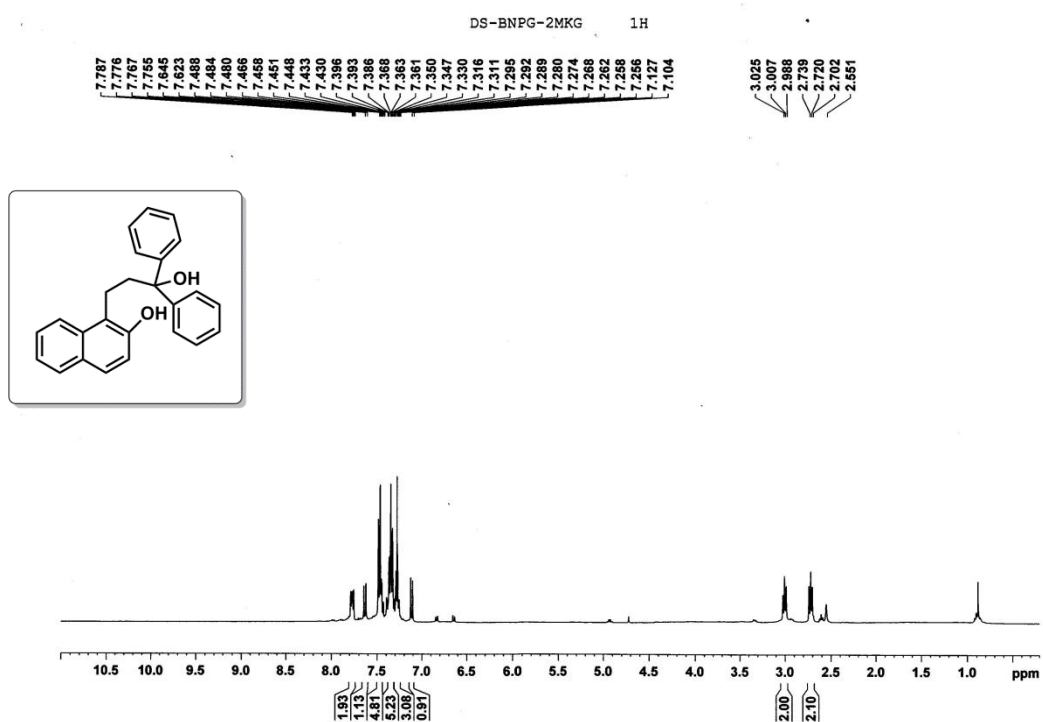
===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -1.00 dB
PL1W       42.37451935 W
SFO1       100.6278585 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -1.00 dB
PL12       14.00 dB
PL13       14.00 dB
PL1W       9.4868322 W
PL12W      0.30000001 W
PL13W      0.30000001 W
SFO2       400.1514606 MHz
SI         16384
SF         100.6177980 MHz
MDM        EM
SSB        0
SB         1.00 Hz
GB         0
PC         1.40
    
```

**1-(3-benzyl-3-hydroxy-4-phenylbutyl) naphthalene-2-ol (3d)**

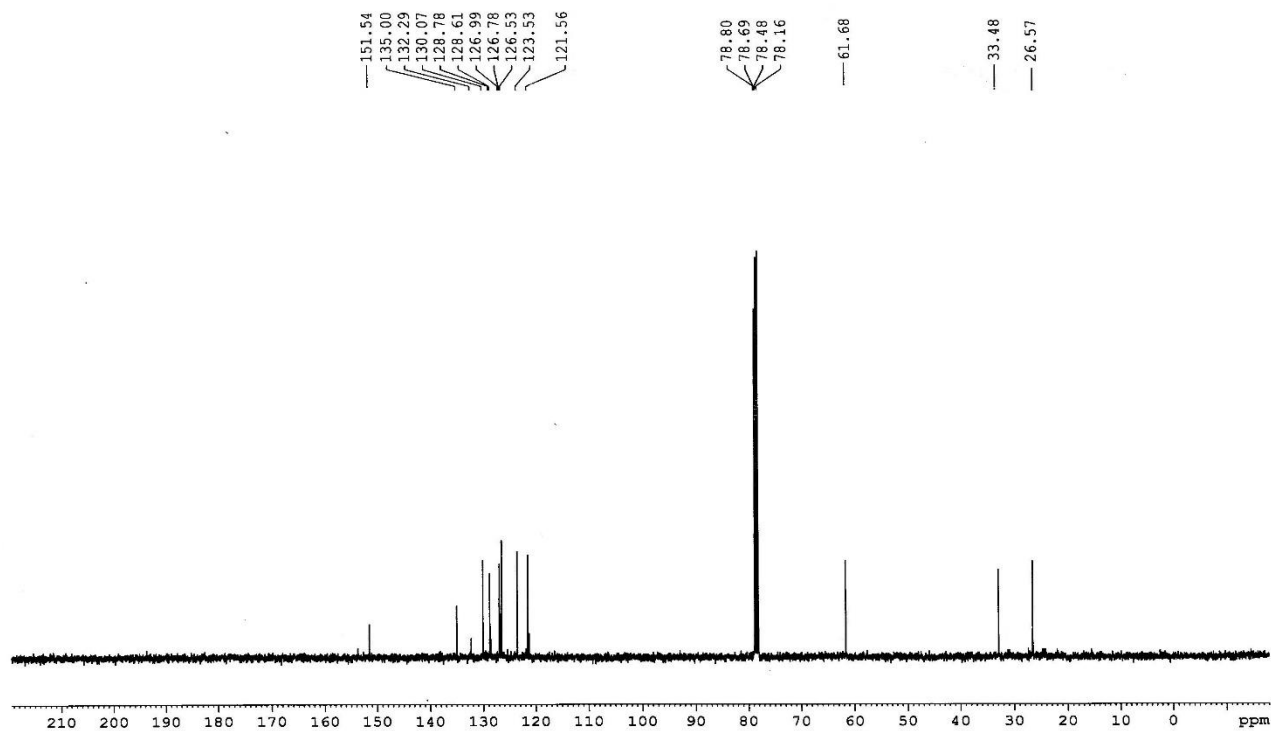
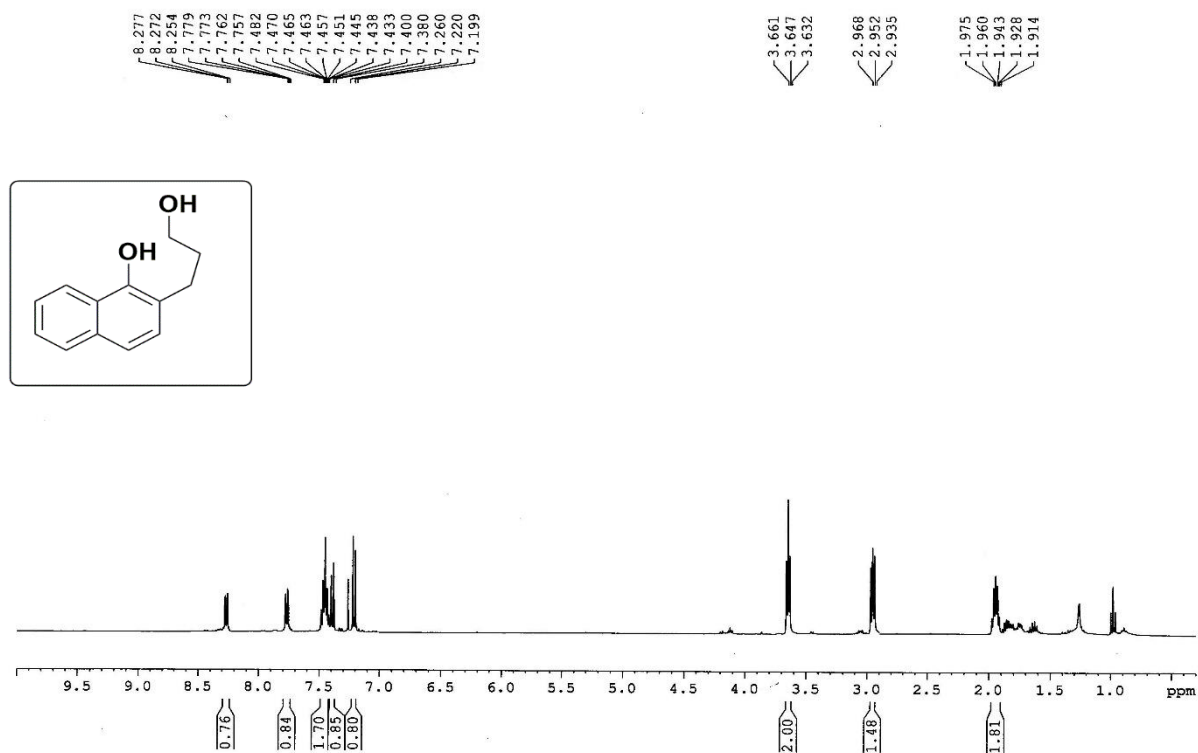


**1-(3-hydroxy-3,3-diphenylpropyl)naphthalen-2-ol (3e)**

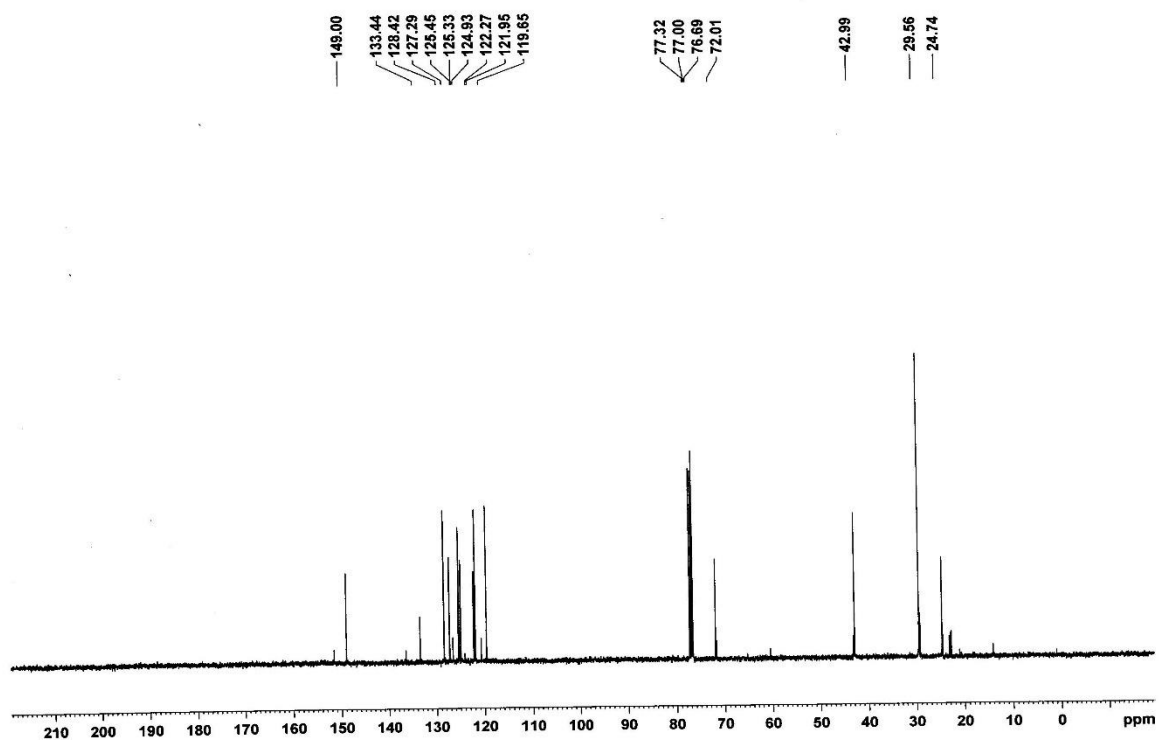
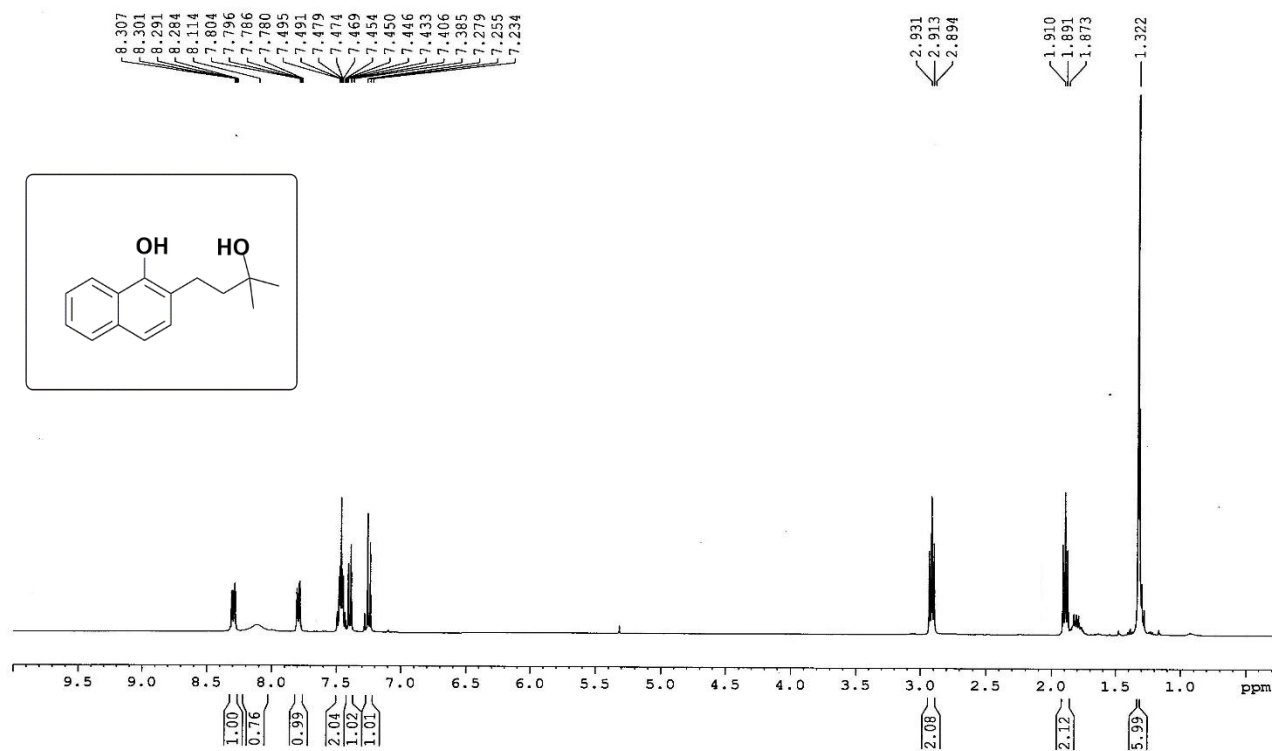




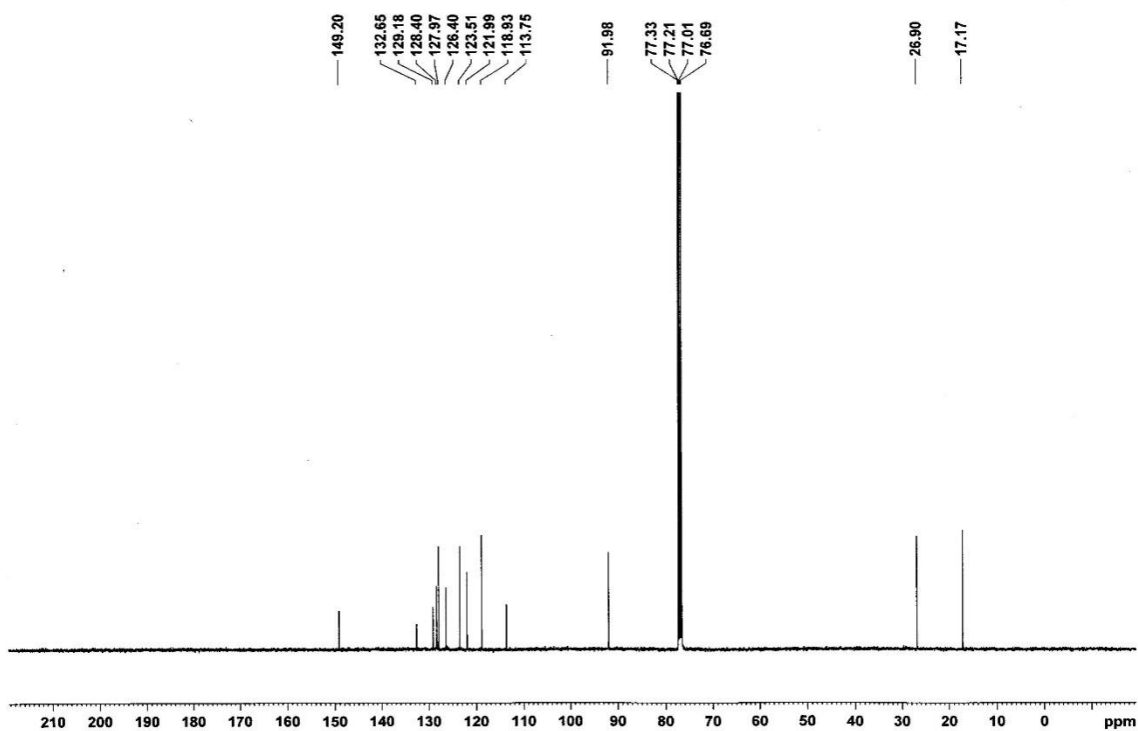
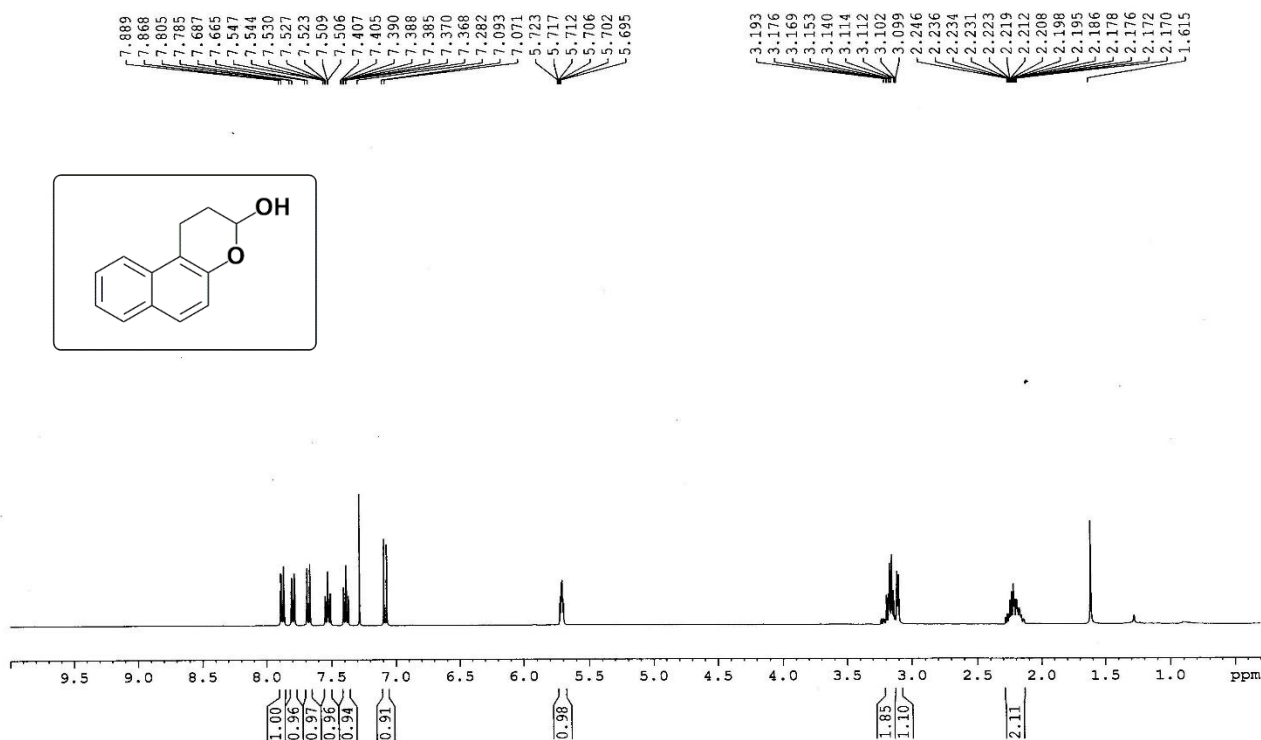
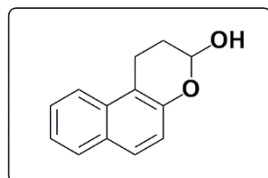
# 2-(3-hydroxypropyl) naphthalene-1-ol (3f)



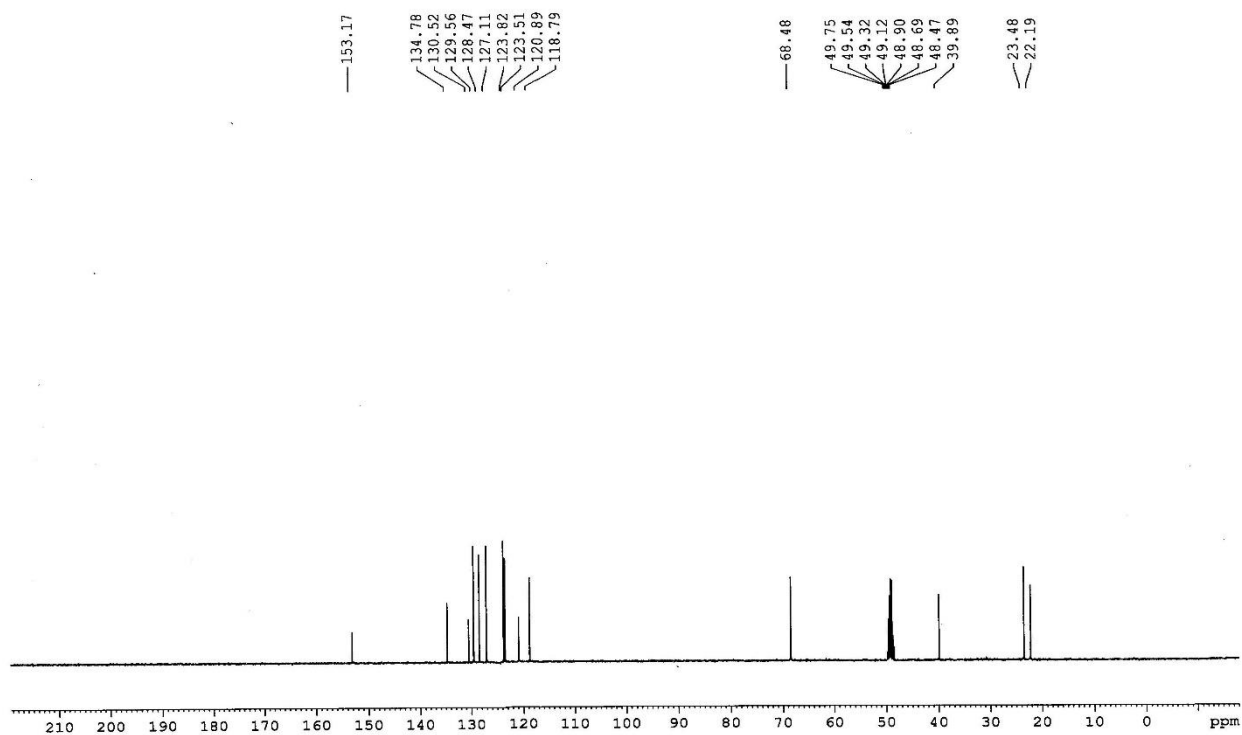
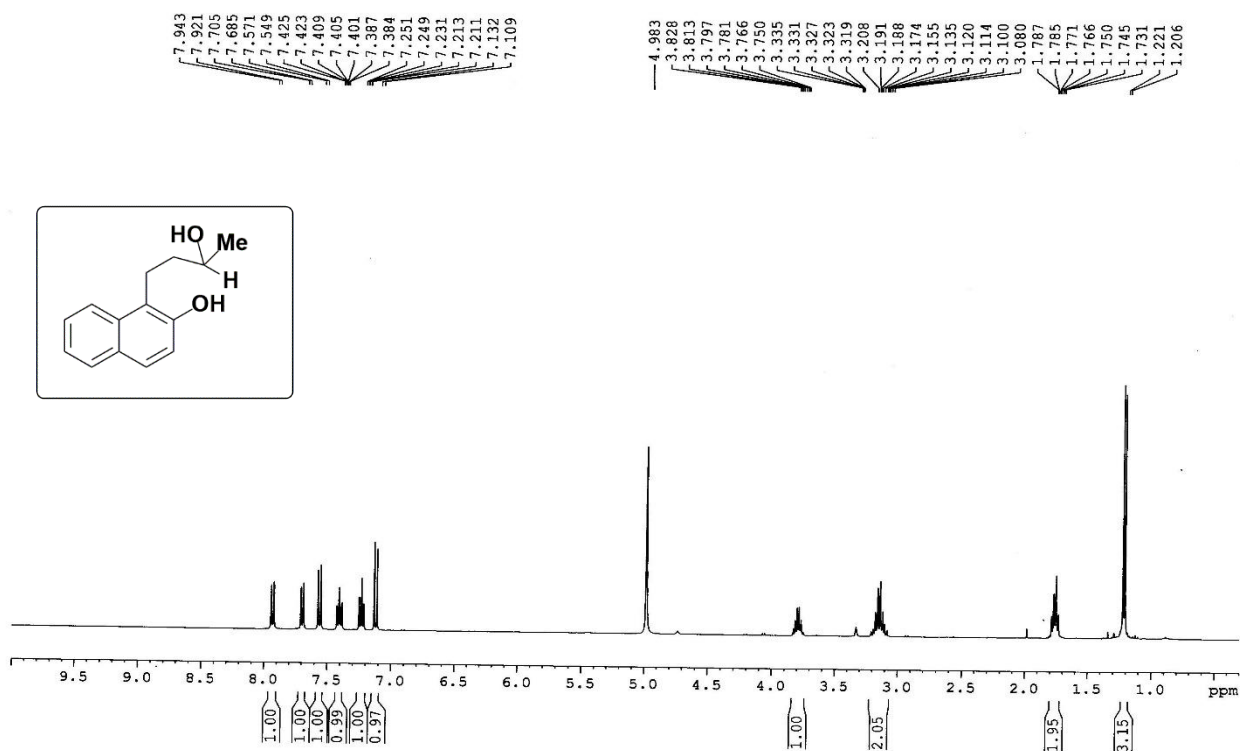
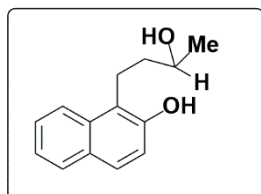
2-(3-hydroxy-3-methylbutyl) naphthalene-1-ol (3g)



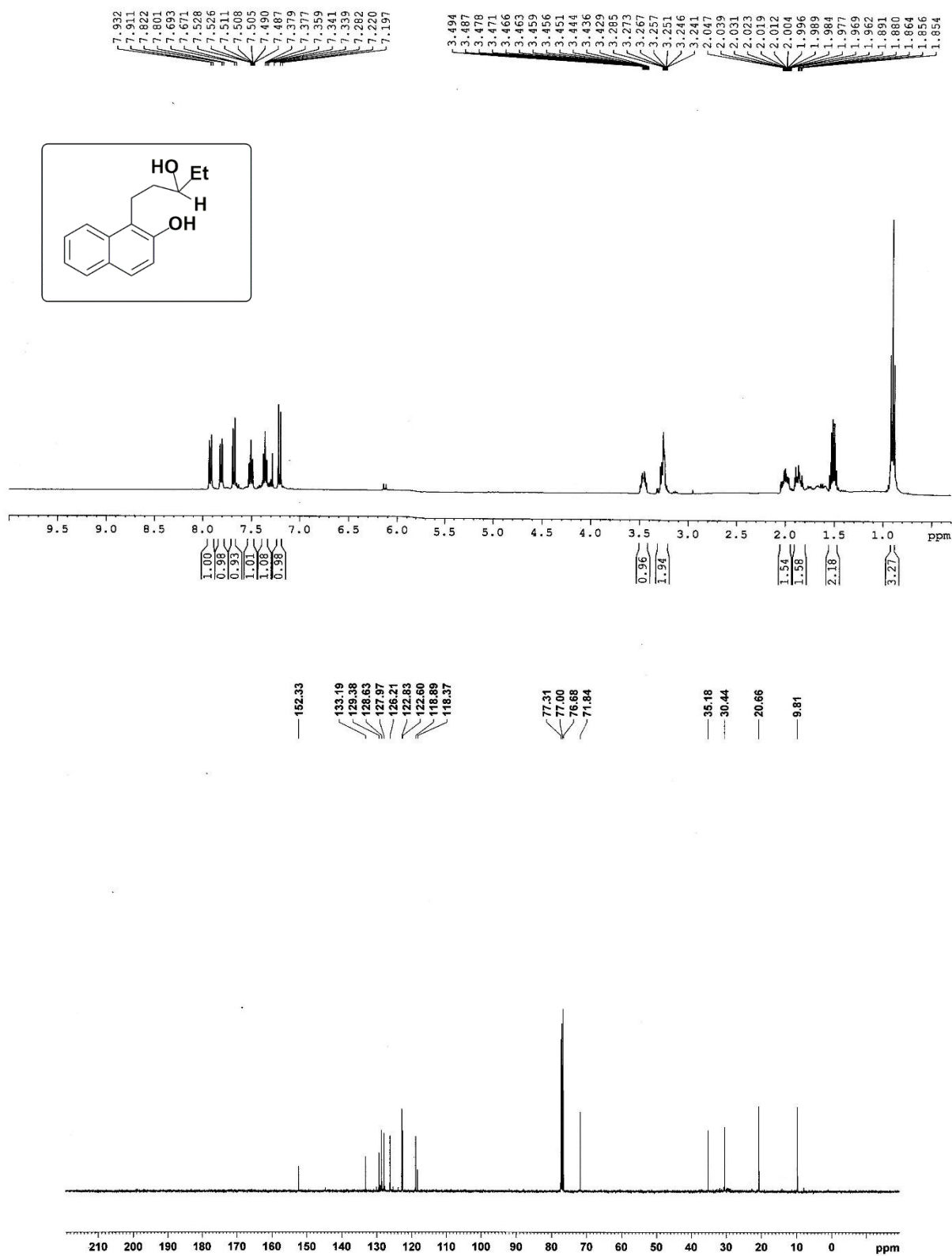
2,3-dihydro-1H-benzo(f)chromen-3-ol (1p)



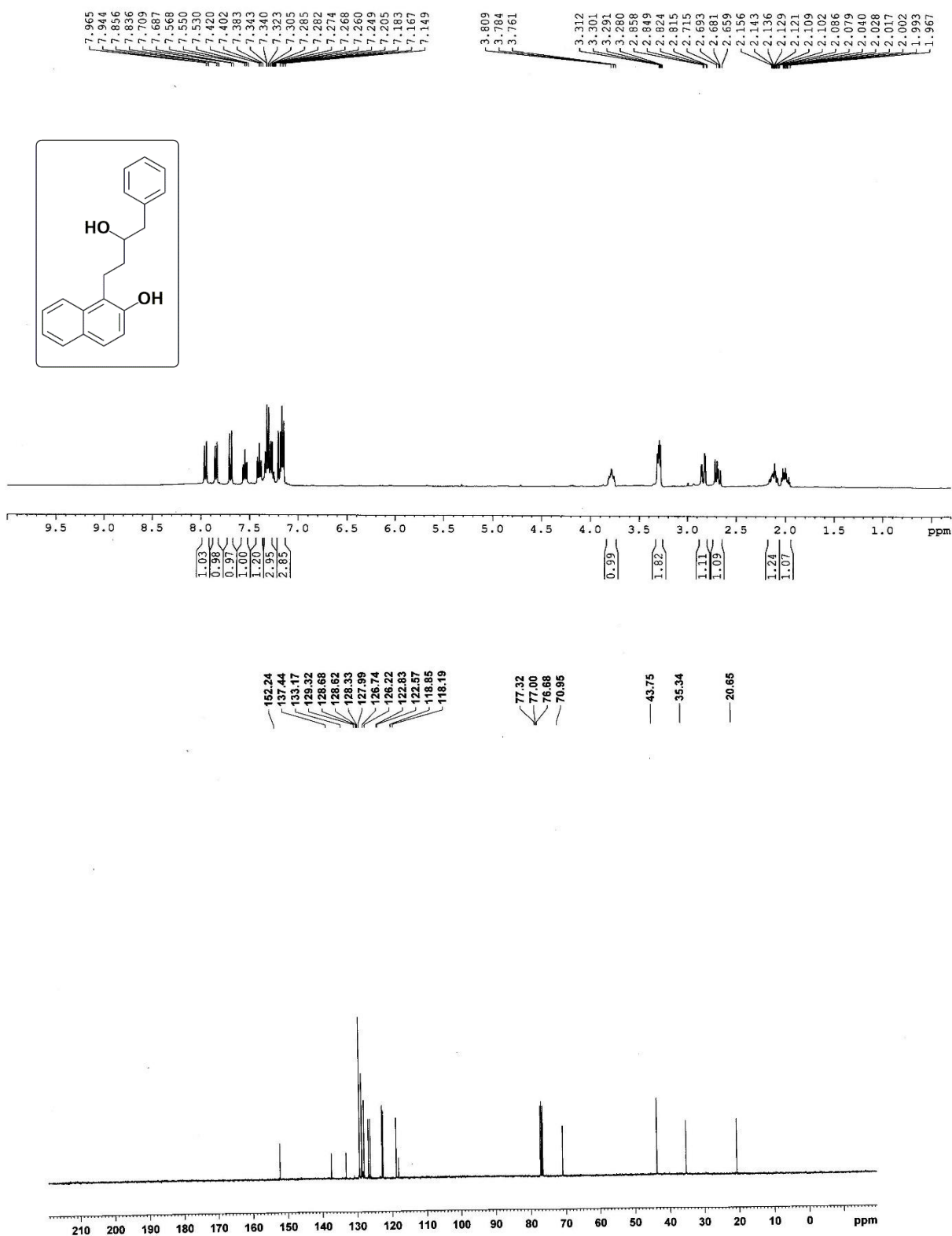
1-(3-hydroxybutyl) naphthalene-2-ol (5a)



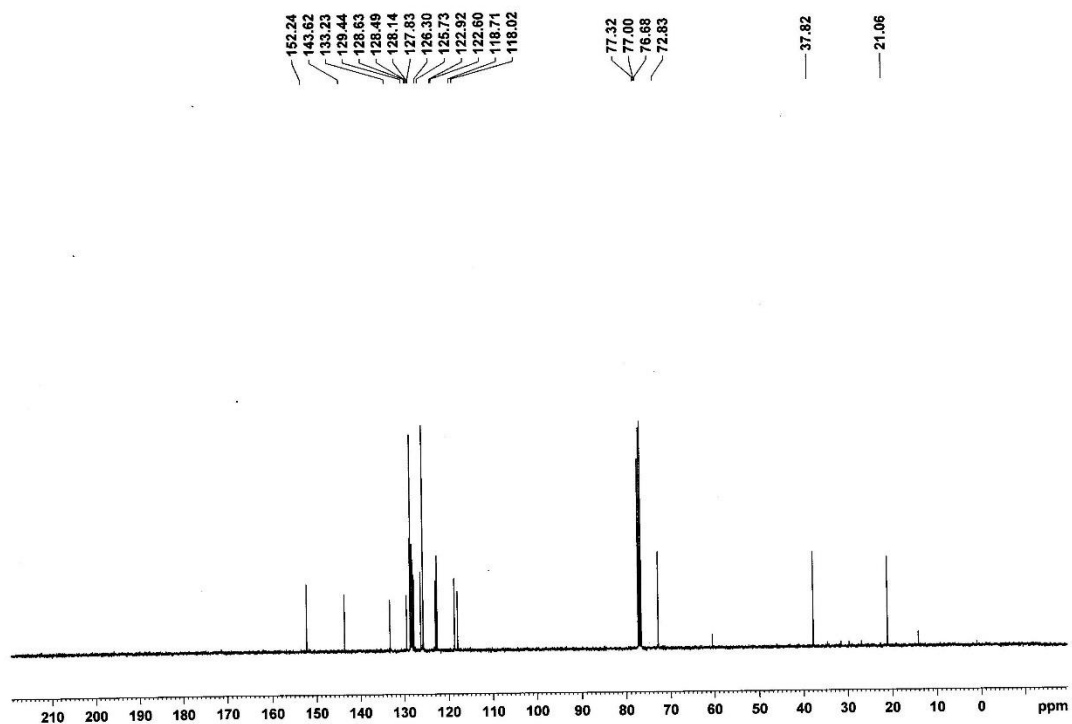
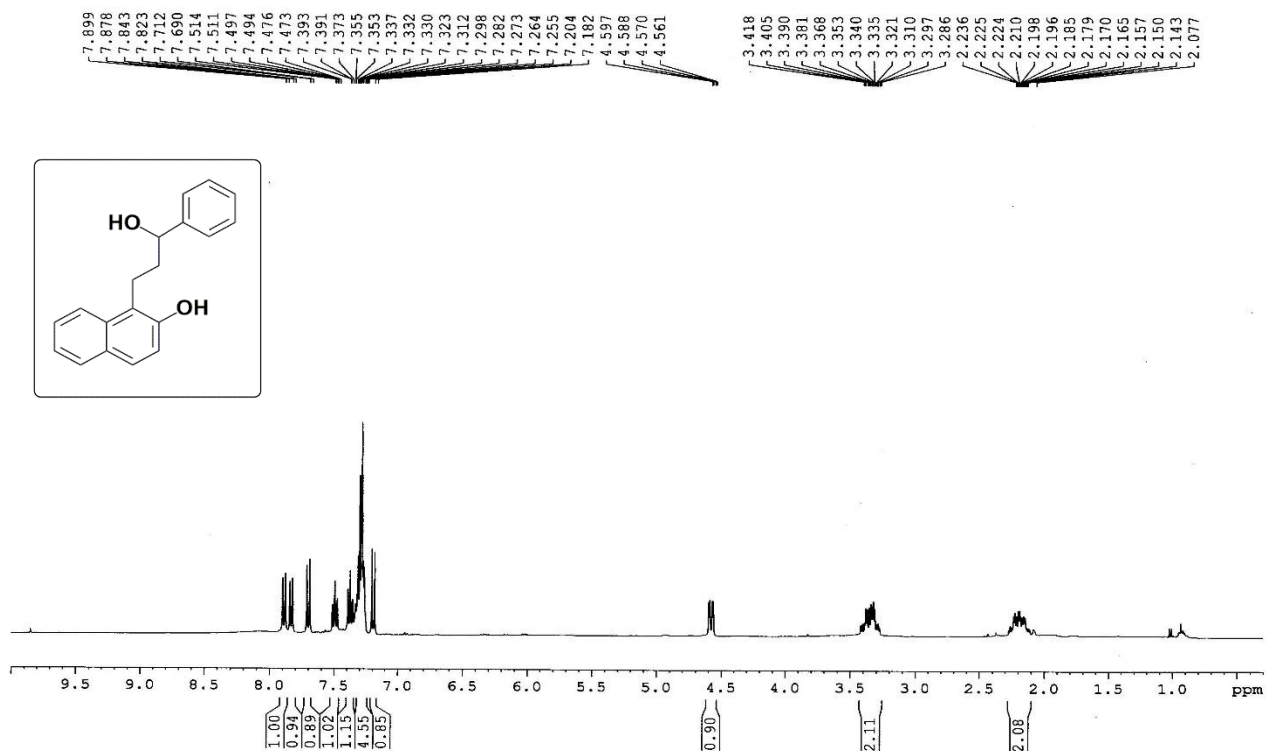
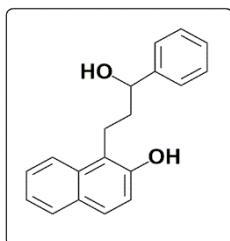
1-(3-hydroxypentyl) naphthalene-2-ol (5b)



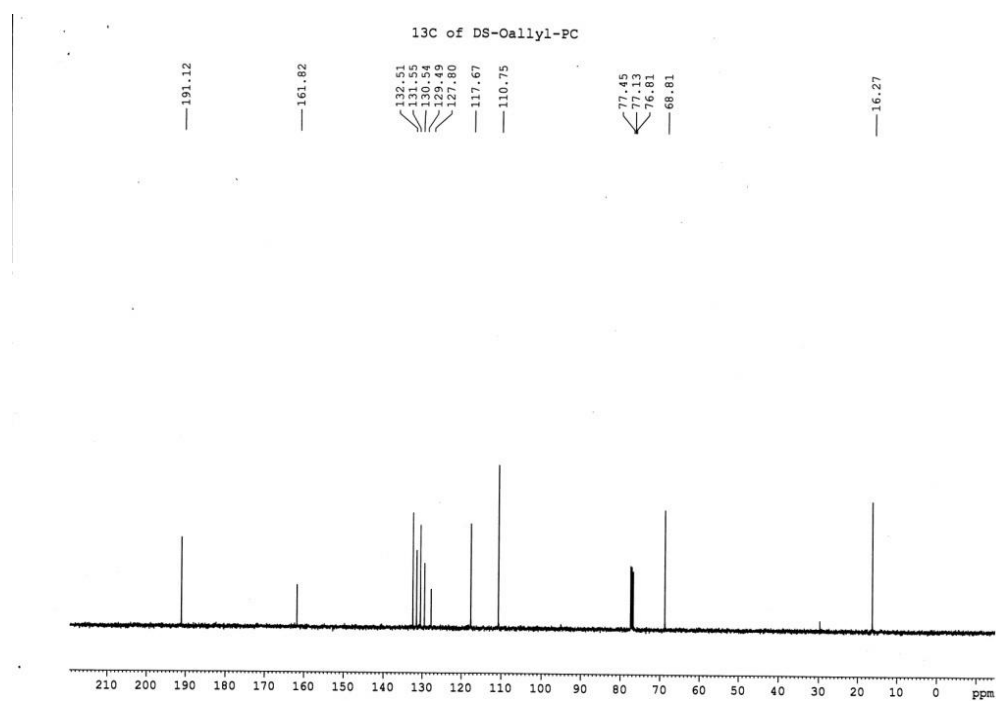
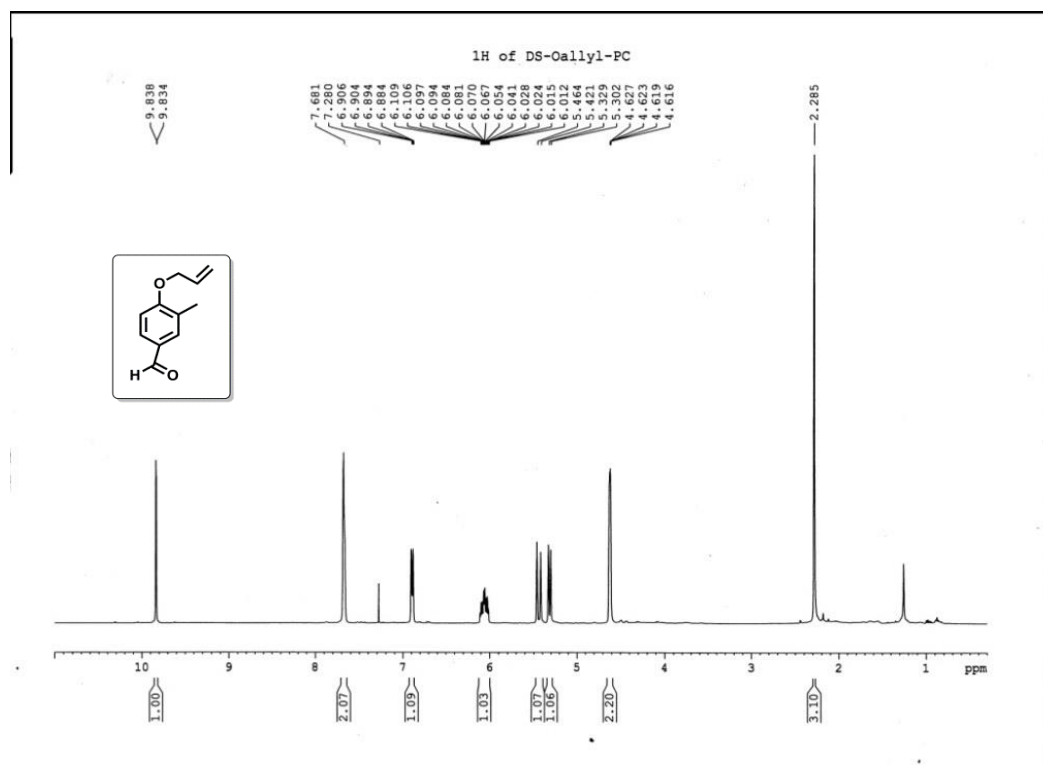
1-(3-hydroxy-4-phenylbutyl)naphthalene-2-ol (5c)



1-(3-hydroxy-3-phenylpropyl) naphthalene-2-ol (5d)

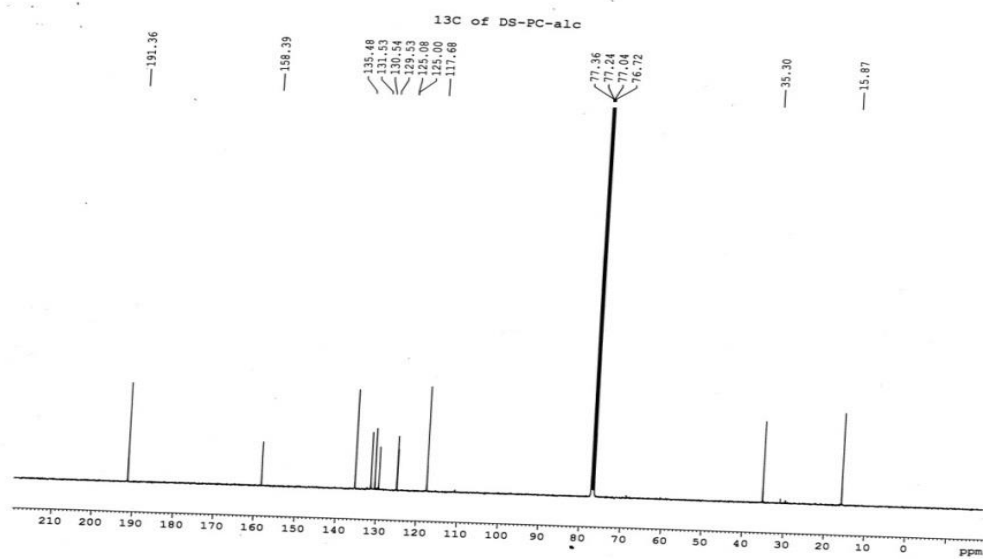
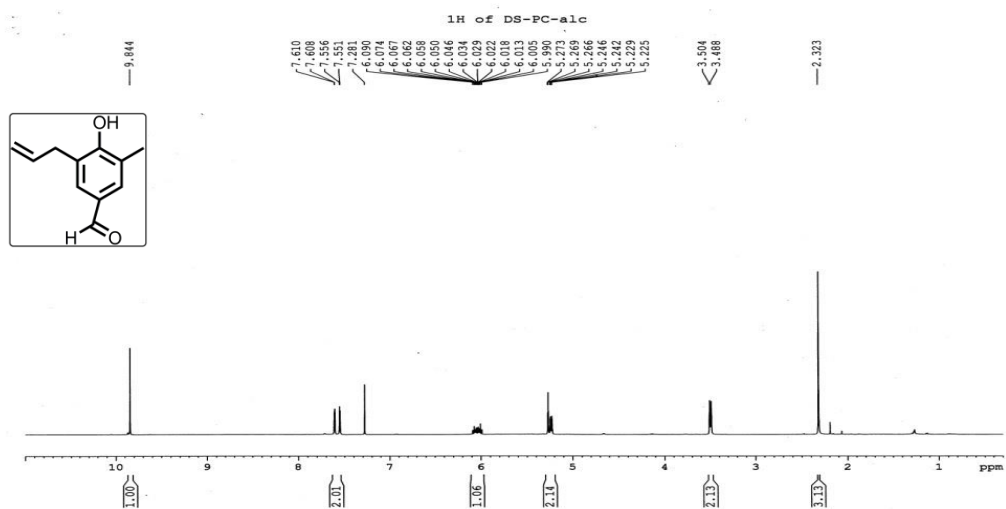


# 4-(allyloxy)-3-methylbenzaldehyde (iii)

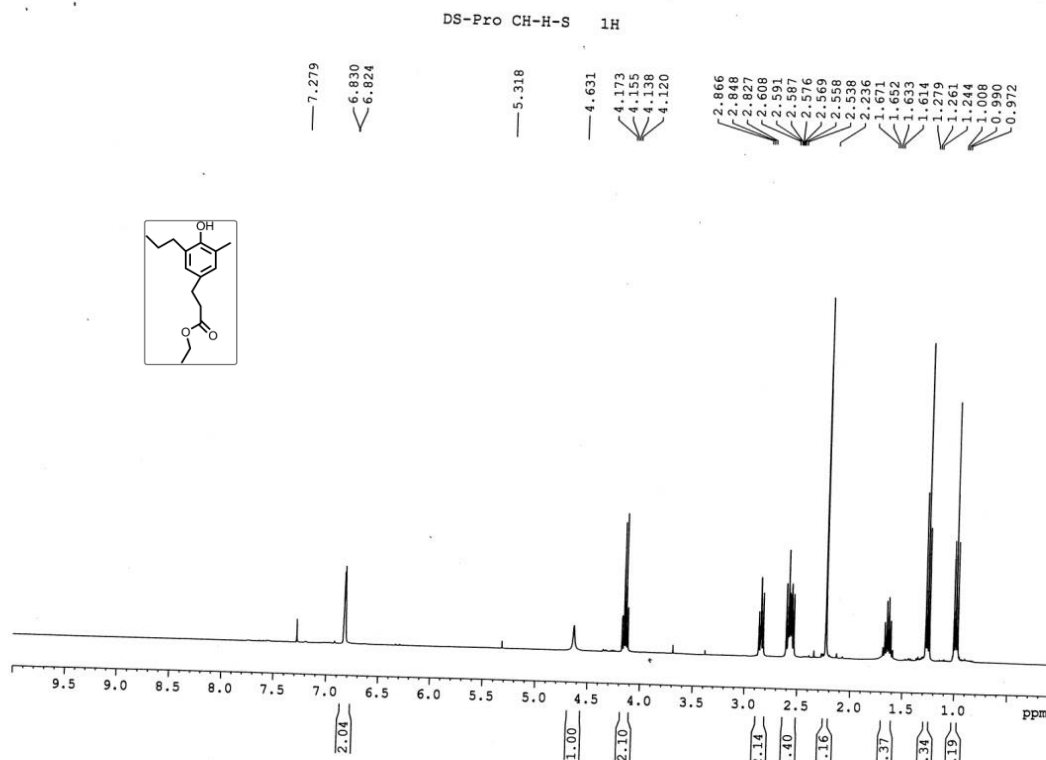




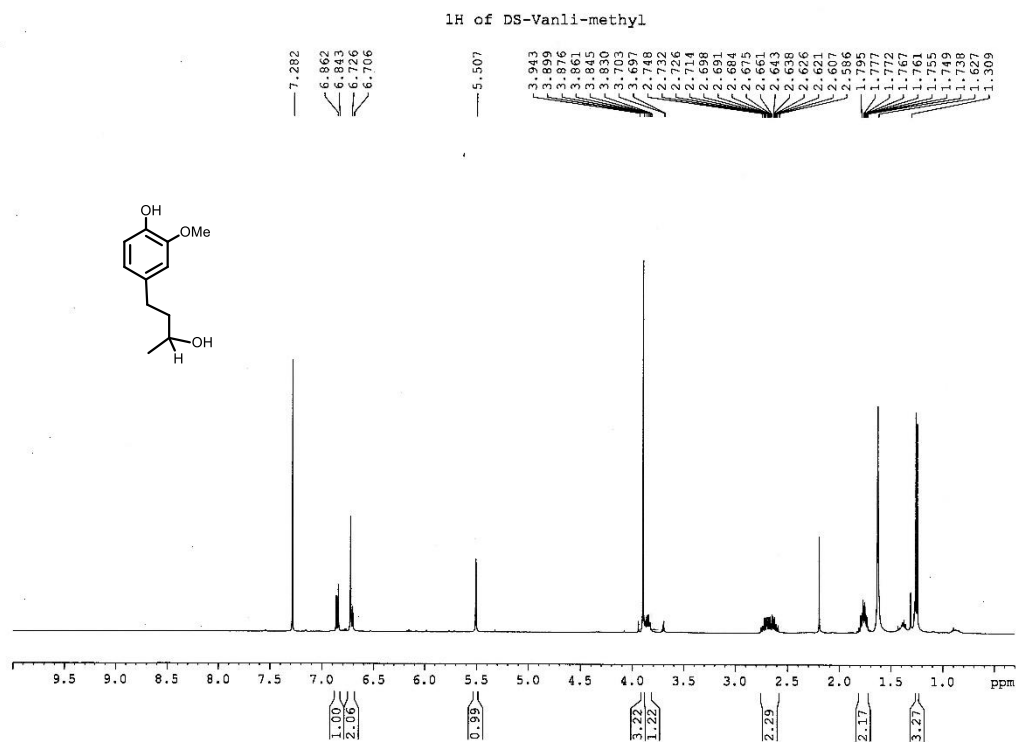
### 3-allyl-4-hydroxy-5-methylbenzaldehyde (iv)



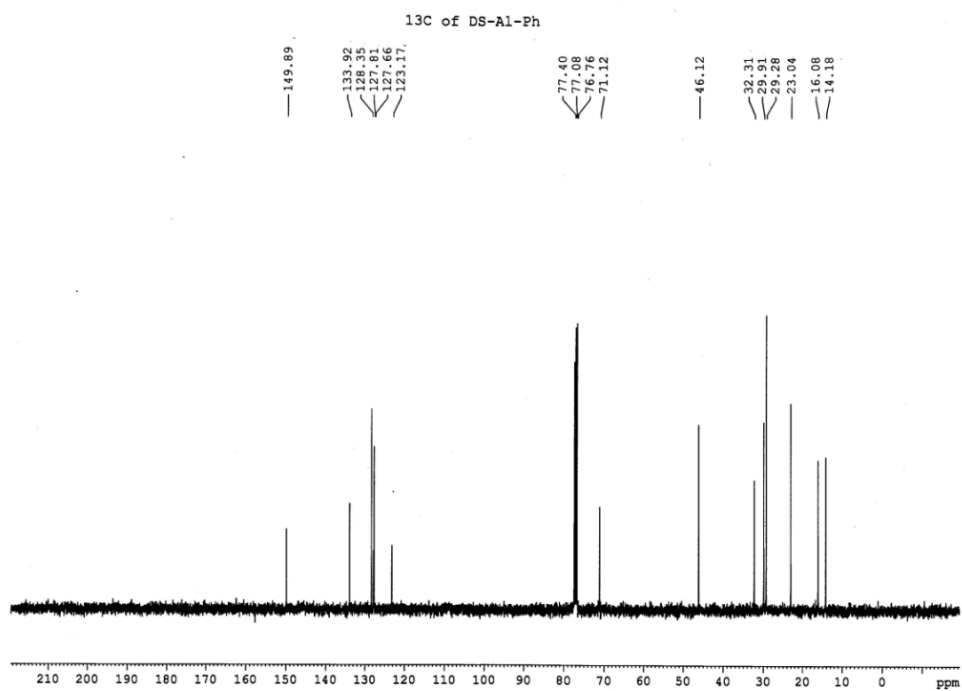
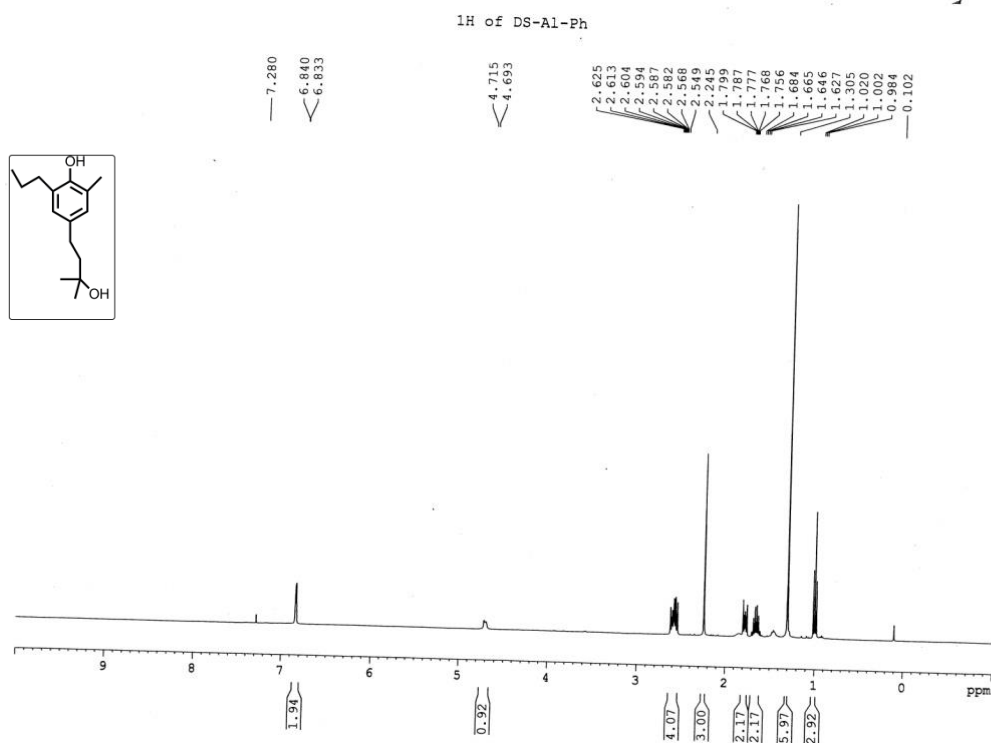
**(E)-ethyl 3-(4-hydroxy-3-methyl-5-propylphenyl)acrylate (vi)**



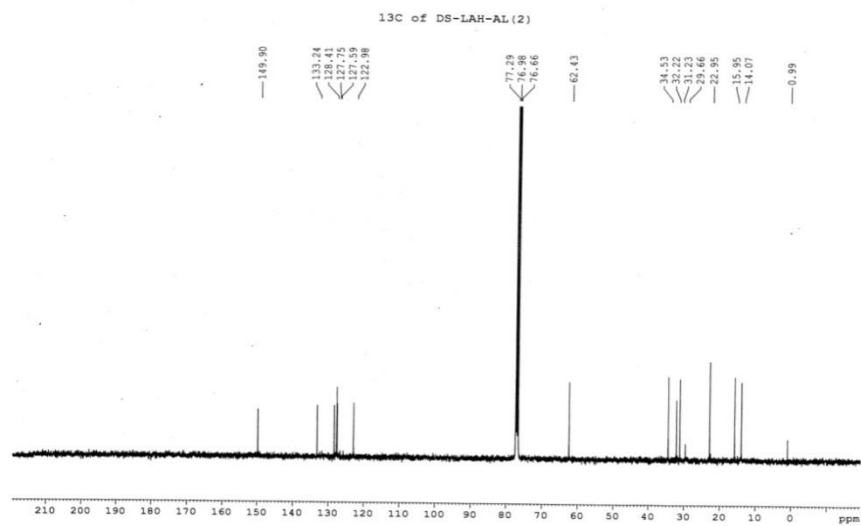
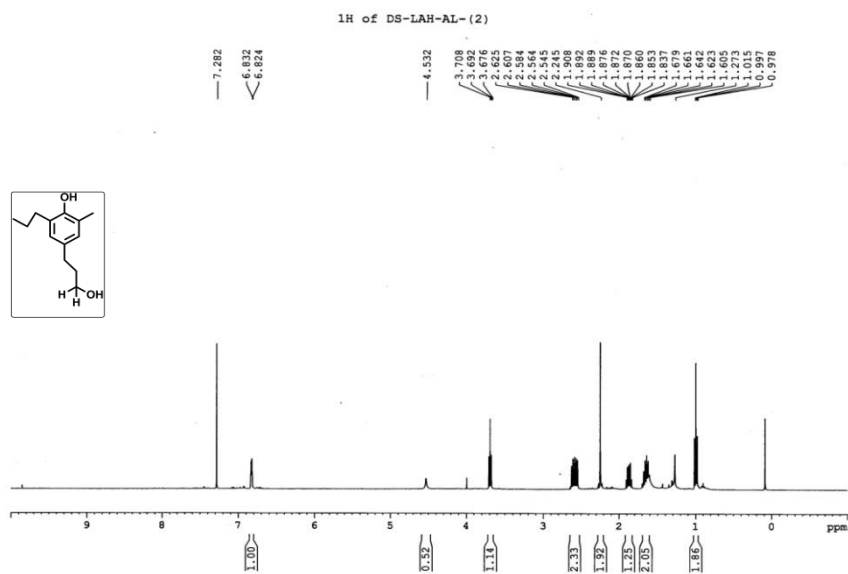
**4-(3-hydroxybutyl)-2-methoxyphenol (13a)**



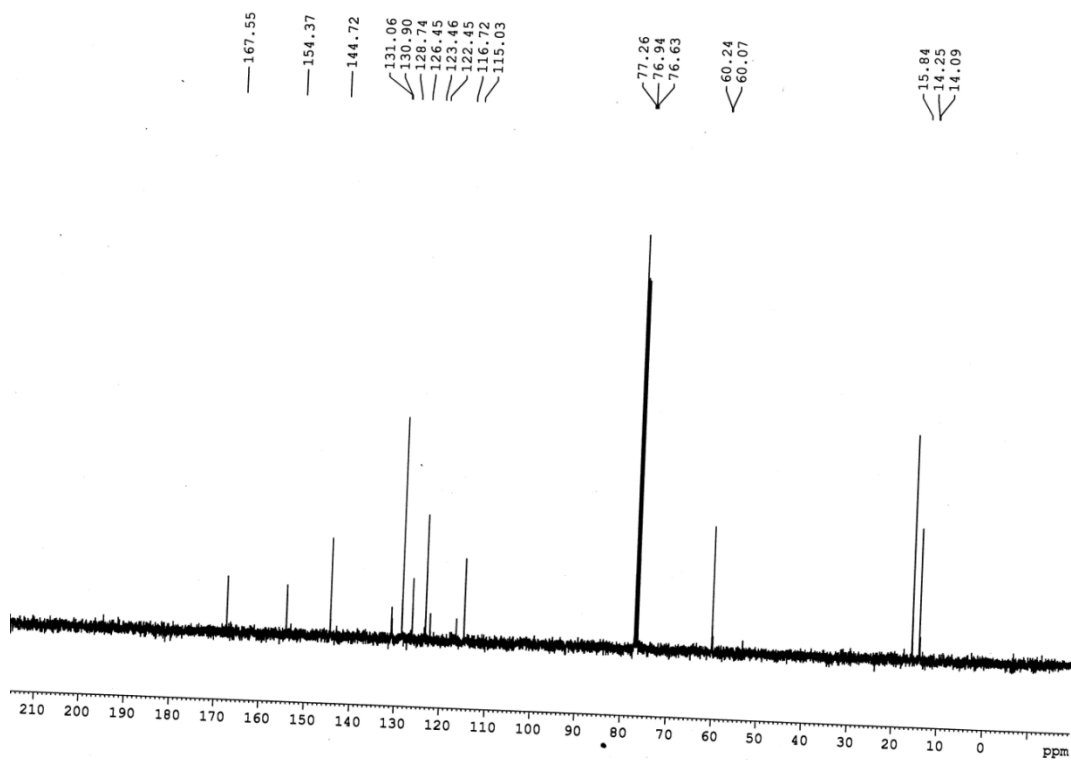
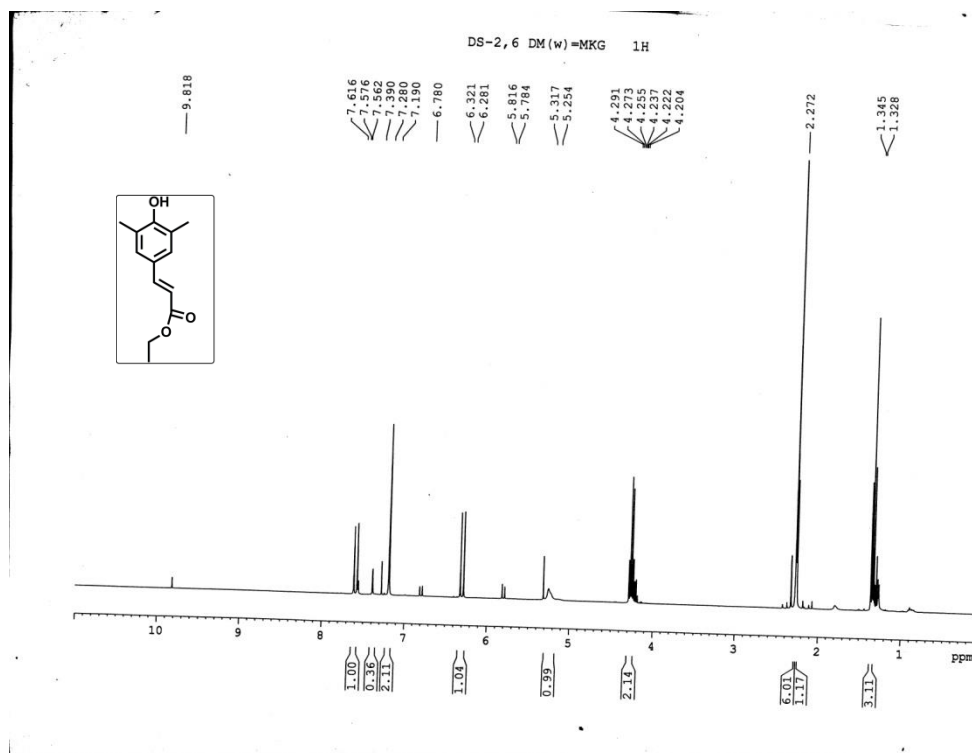
4-(3-hydroxy-3-methylbutyl)-2-methyl-6-propylphenol (8a)



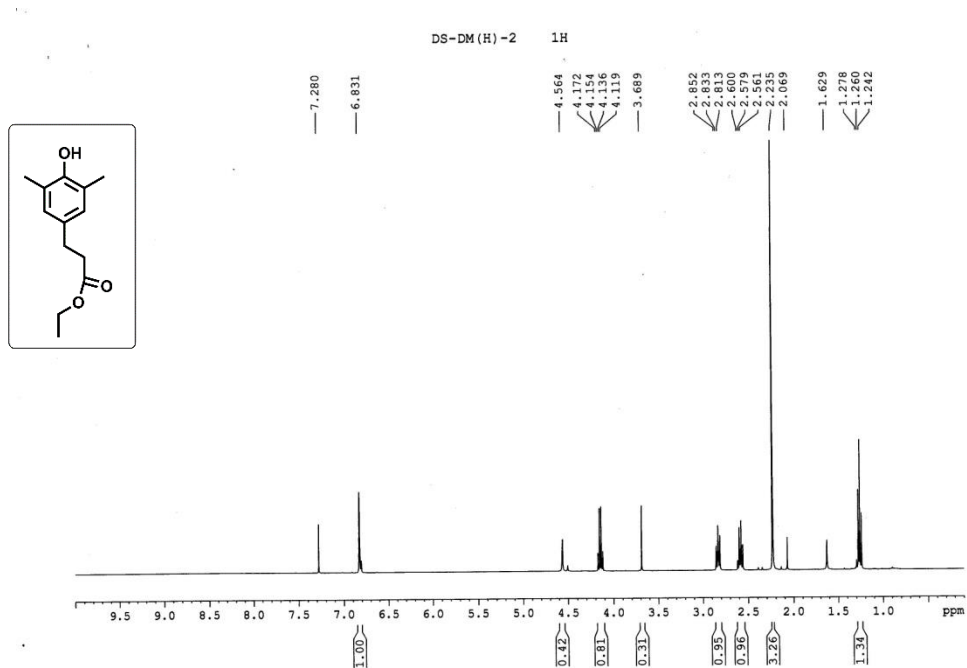
# 4-(3-hydroxypropyl)-2-methyl-6-propylphenol (8b)



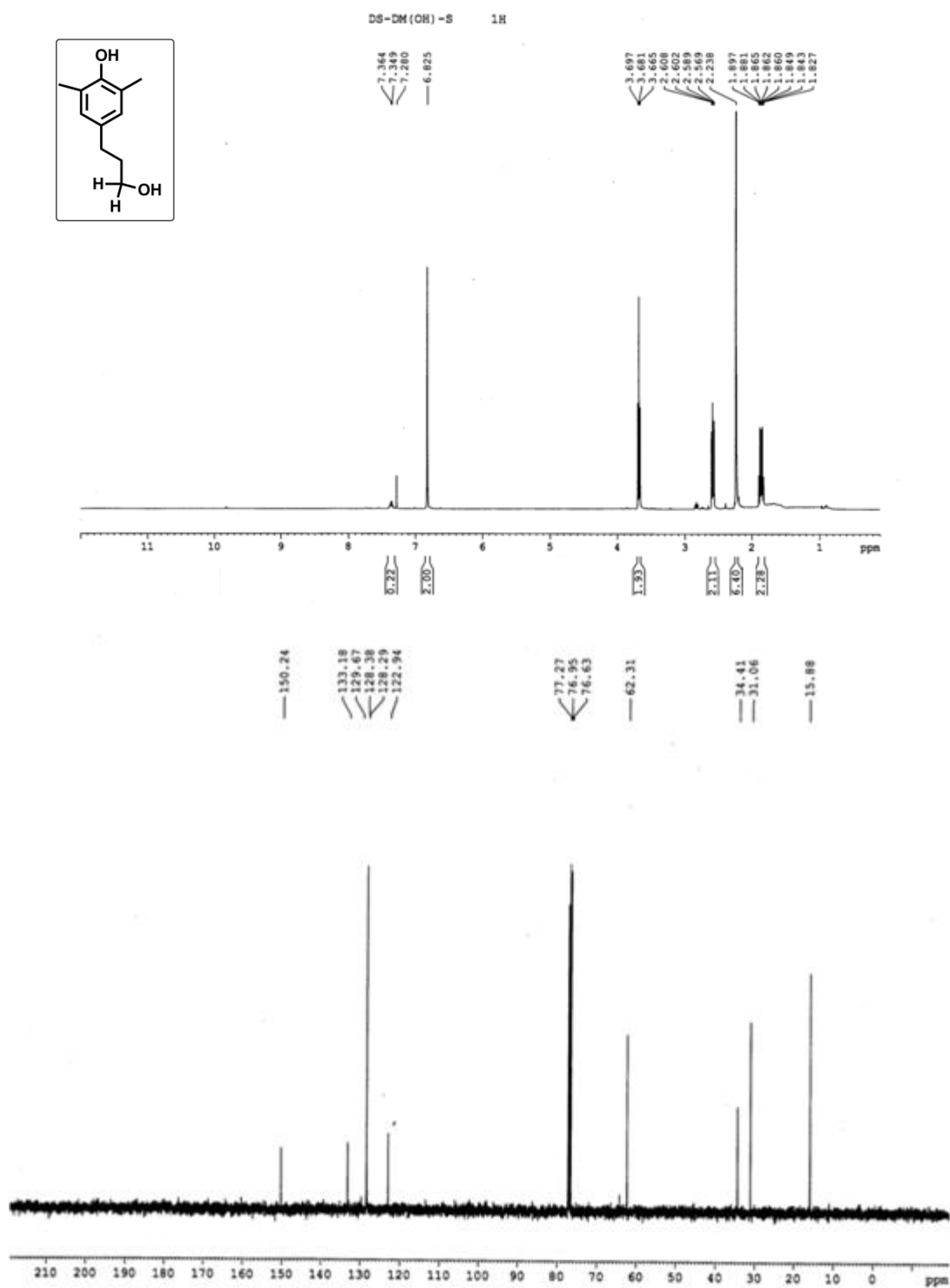
(E)-ethyl 3-(4-hydroxy-3,5-dimethylphenyl)acrylate (ix)



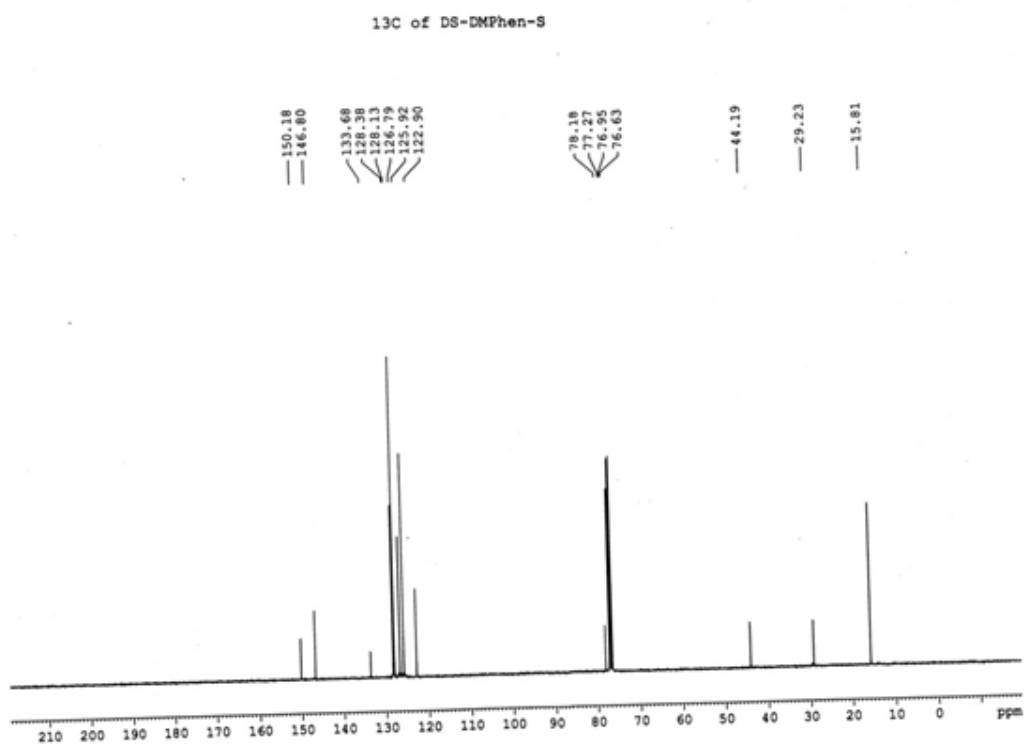
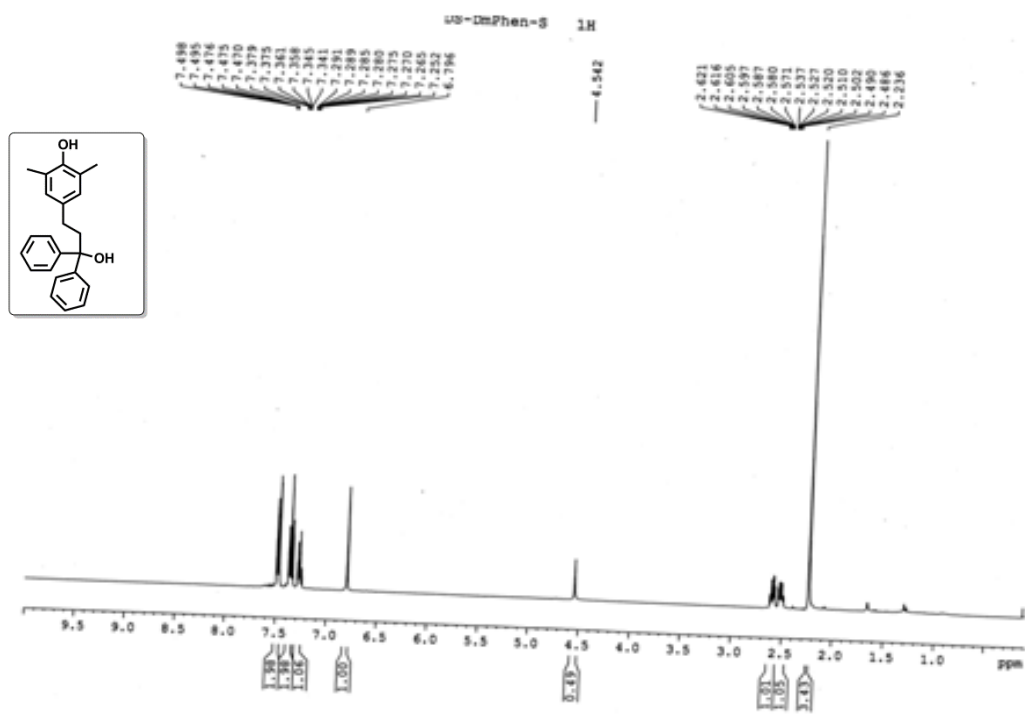
# Ethyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate (x)



4-(3-hydroxypropyl)-2, 6-dimethylphenol 8(d)

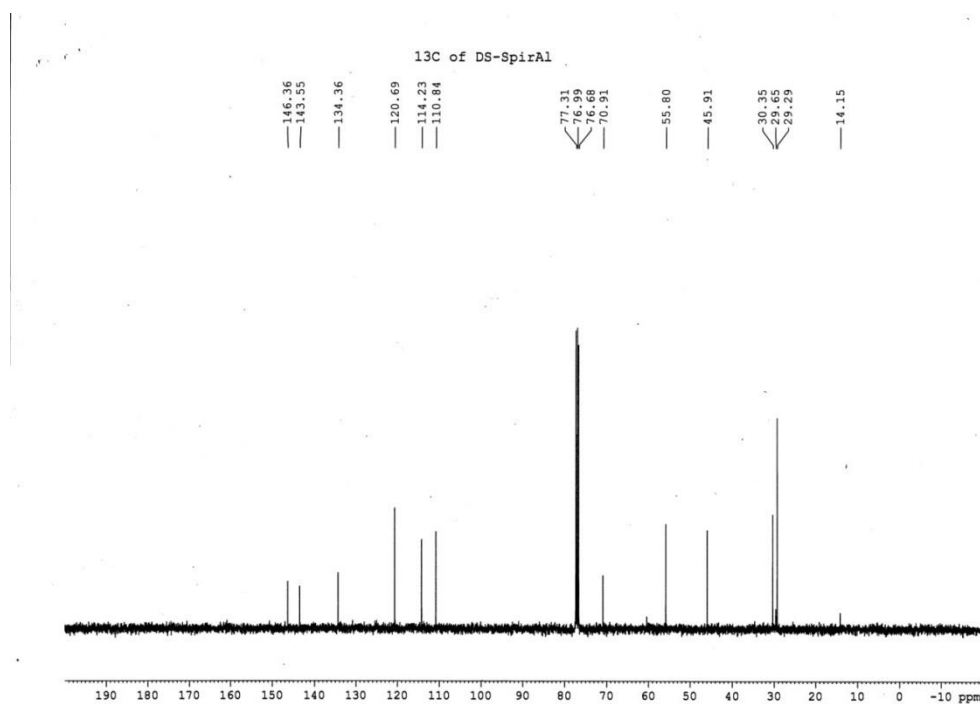
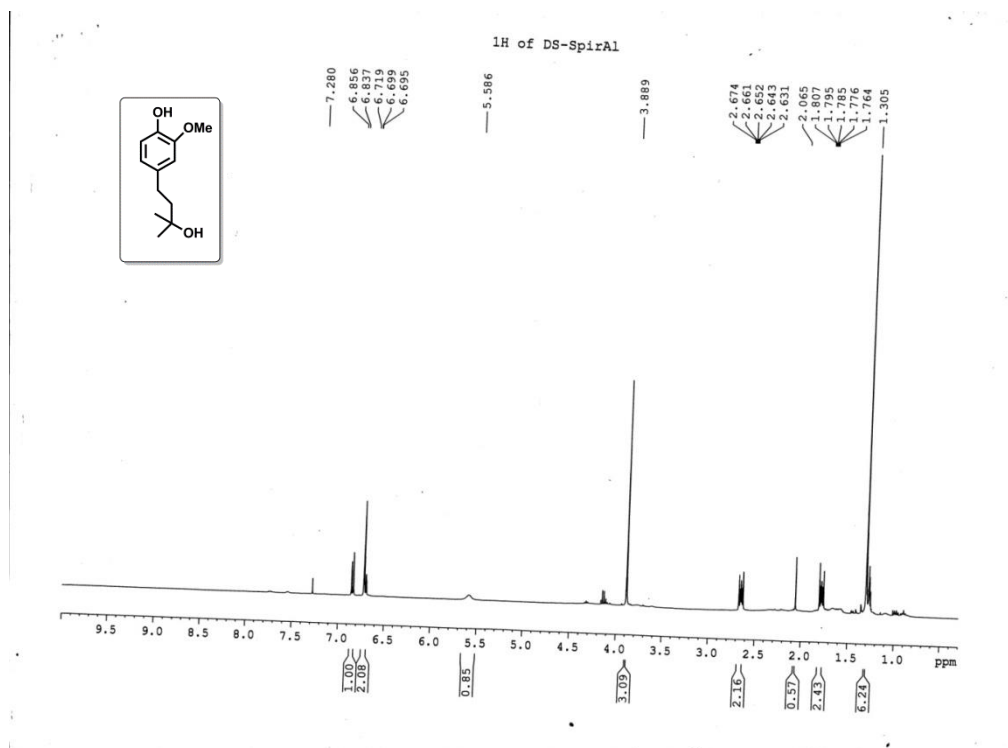


4-(3-hydroxy-3,3-diphenylpropyl)-2,6-dimethylphenol (8f)

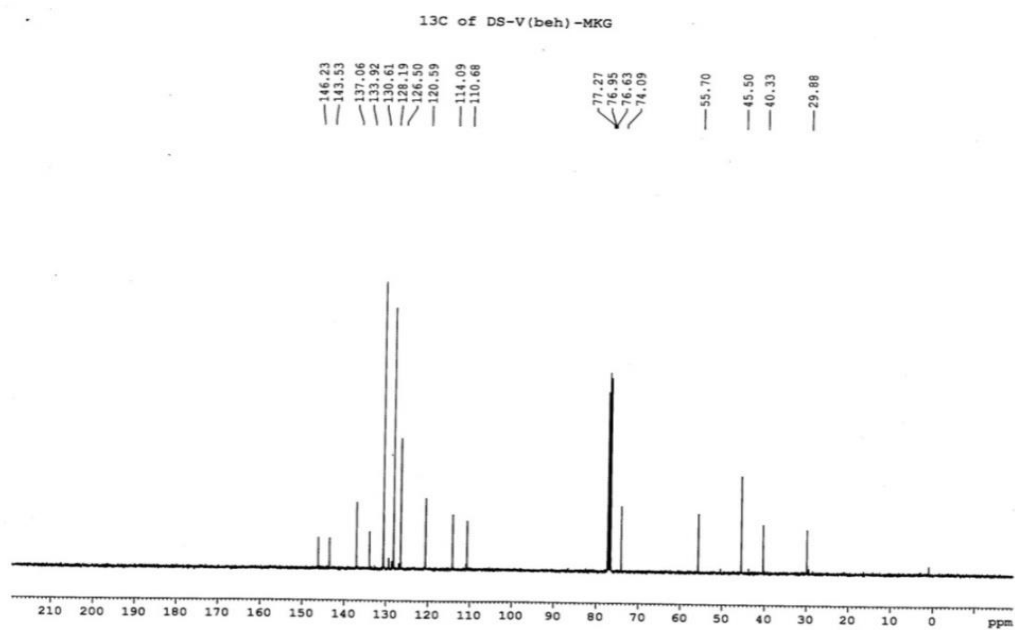
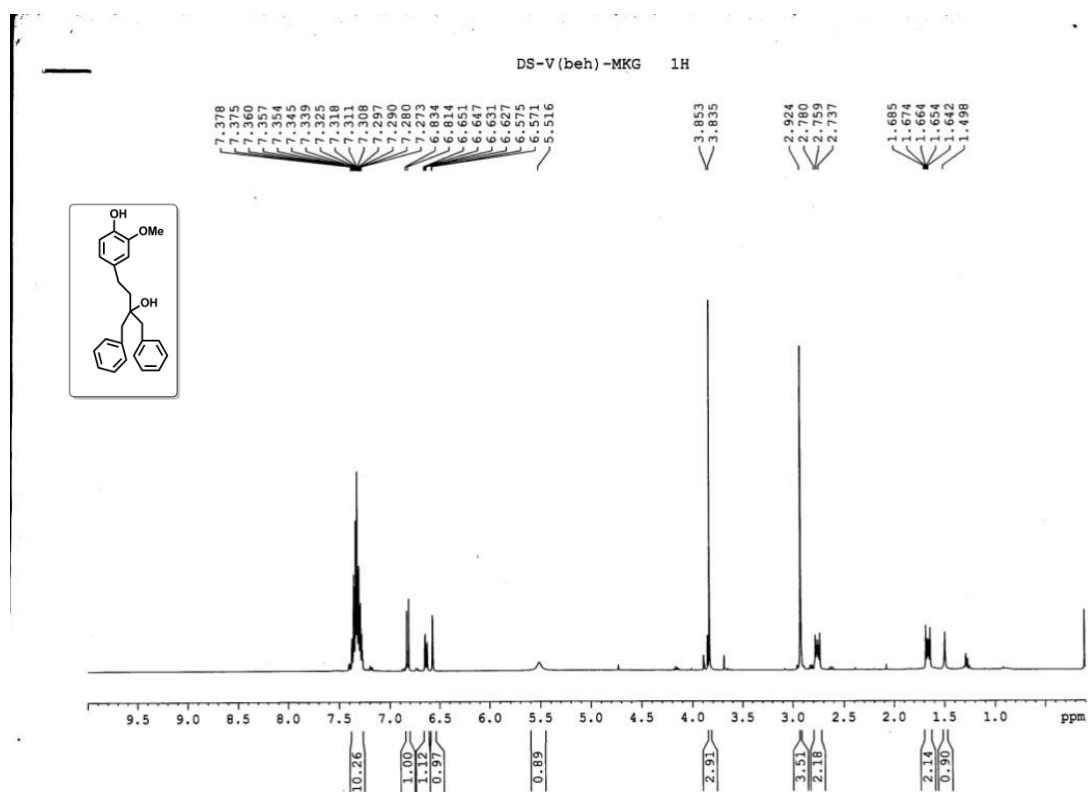




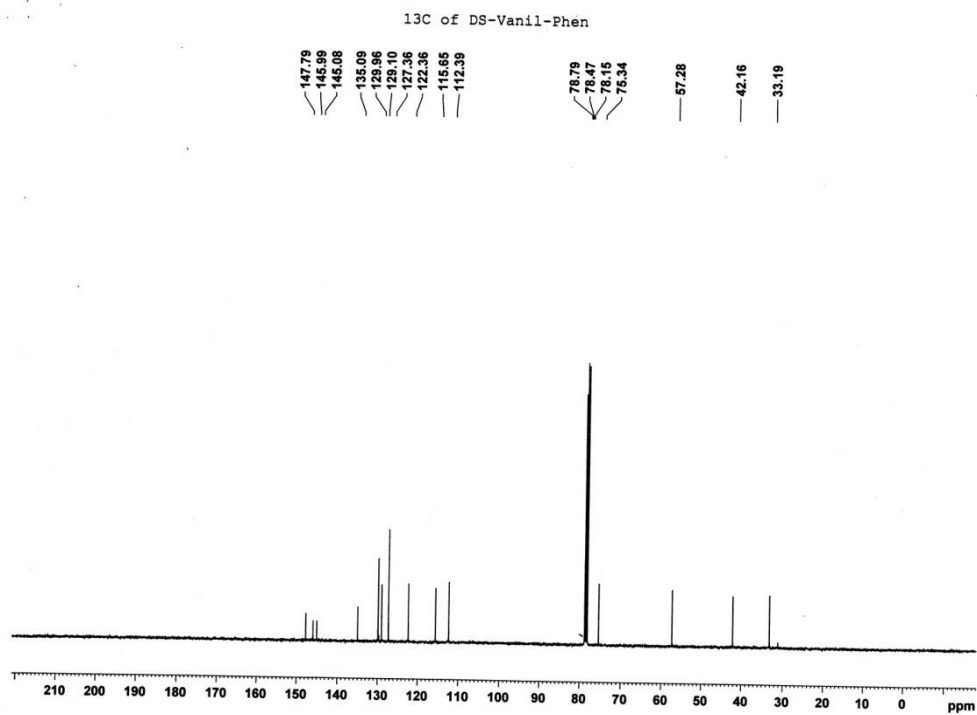
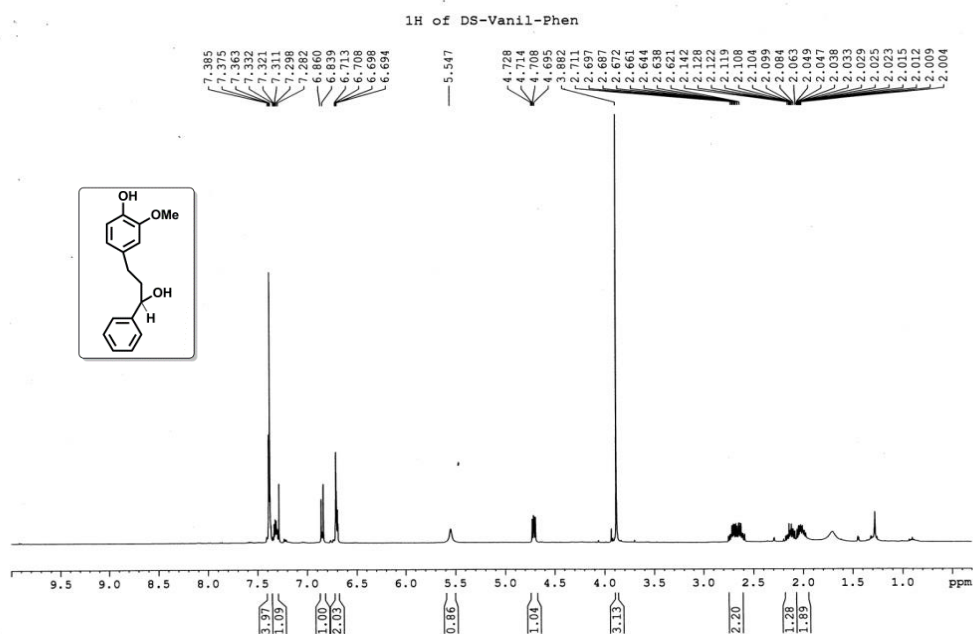
# 4-(3-hydroxy-3-methylbutyl)-2-methoxyphenol (10a)



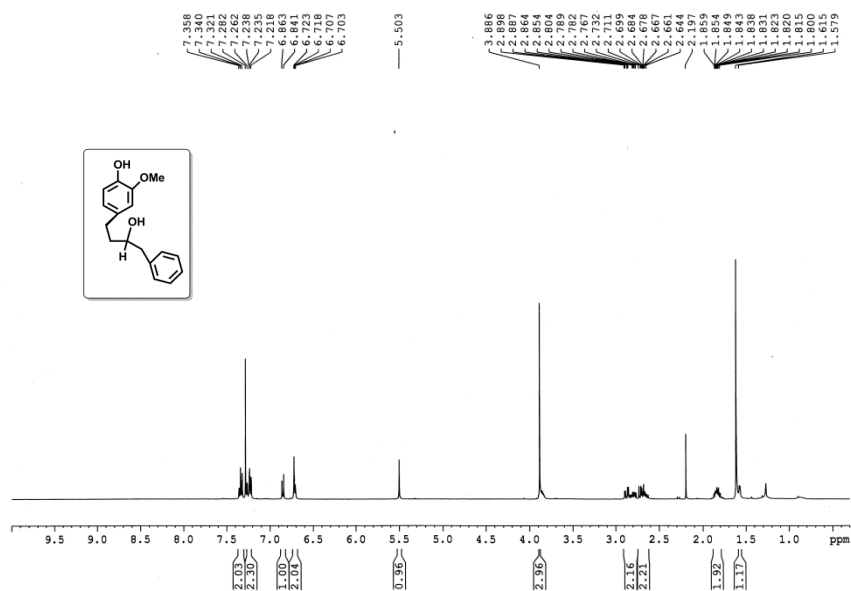
# 4-(3-hydroxy-3,3-diphenylpropyl)-2-methoxyphenol (10b)



# 4-(3-hydroxy-3-phenylpropyl)-2-methoxyphenol (13b)



4-(3-hydroxy-4-phenylbutyl)-2-methoxyphenol 13(c)



<sup>13</sup>C of DS-VANIL-BENZYL

