Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Geometry-Dependent Divergence in Gold-Catalyzed Redox Cascade Cyclization of *o*-Alkynylaryl Ketoximes and Nitrones Leading to Isoindoles

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Table S1. Screening of Solvents in the Conversion of **(Z)-1e** into **3e**

entry[a]	solvent	conversion (%)[b]	yield (%)[b]
1	DMF	39	20
2	CH_3CN	49	22
3	CH_3NO_2	>95	70
4	$CHCl_3$	>95	65
5	MeOH	>95	58
6	$ClCH_2CH_2Cl$	>95	64
7	THF	83	53
8	toluene	93	65

[a]Conditions: Au(IMes)OTf (5 mol %) at 70 ^oC in solvents (sealed tube); after 4 h, the reaction was quenched with Et_3N. [b]Crude NMR yield.

Table S2. Screening of Ligands in the Conversion of **(Z)-1e** into **3e**

entry[a]	ligand	conversion (%)[a]	yield (%)[a]
1	PPh_3	74	53
2	P(*o*-toly)$_3$	28	13
3	$^tBu_2$P(*o*-biphenyl)	>95	62
4	$^tCy_2$ P(*o*-biphenyl)	>95	53
5	$P(C_6F_5)_3$	31	29
6	P^tBu_3	79	54
7	IPr	>95	69

[a]Conditions: Au(L)OTf (5 mol %) at 70 ^oC in CH_2Cl_2 (sealed tube) (reaction time: 0.5-1.5 h)

X-Ray Crystallography Data for 3e:

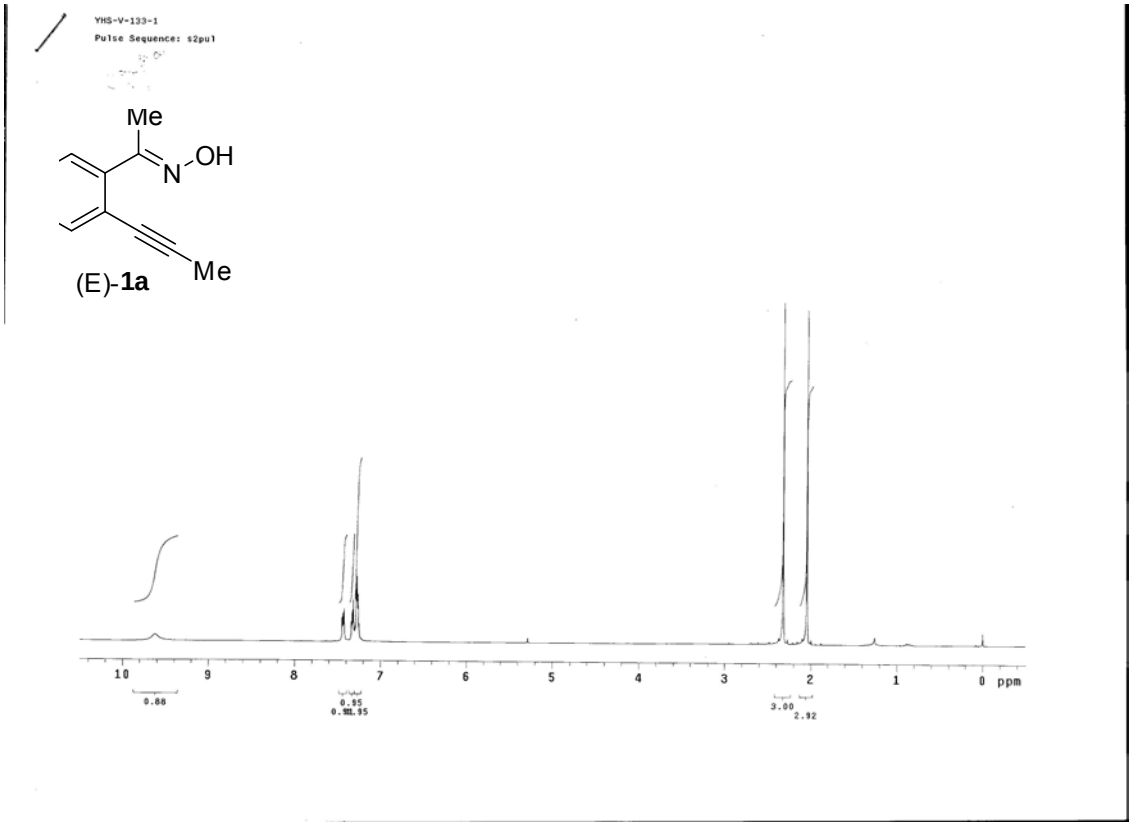
For each determination a suitable crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo_{Ka} (λ = 0.71073 Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. The frame data were processed to give structure factors using the program SAINT. [1] The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of direct and difference Fourier methods provided by the program package SHELXTL, [2] and refined using a full matrix least square against F^2 for all data. All non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. (Reference: [1] Bruker, *SMART, SAINT and XPREP: Area Detector Control and Integration Software Ver. 5.054*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2001. [2] Bruker, *SHELXTL*: *Structure Determination Programs, Ver. 6.12*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2000.)

Crystallographic data for compound **3e**: Triclinic, space group *P*-1, a = 12.3395(5) Å, b = 16.6385(9) Å, c = 16.9325(7) Å, α = 102.905(3) °, β = 101.820(2) °, γ = 111.464(2) ° V = 2992.1(2) Å^3, T = 146 K, Z = 8, $Mo_{K\alpha}$ radiation, graphite monochromator, scan width 0.3° in ω, 10 s irradiation time per measurement reflections, 12311 measurements, 24963 measured reflections, 12311 independent reflections, 766 parameters, GOF = 1.068, $R_1(I>2\sigma(I))$ = 0.0715, wR_2 = 0.1878.

Table S3. Selected bond lengths [Å] and angles [°] for **3e**.

O(1)-C(15)	1.236(3)
N(1)-C(1)	1.337(3)
N(1)-C(8)	1.381(3)
C(1)-C(2)	1.417(3)
C(1)-C(9)	1.467(3)
C(2)-C(3)	1.410(3)
C(2)-C(7)	1.434(3)
C(3)-C(4)	1.369(3)
C(4)-C(5)	1.413(3)
C(5)-C(6)	1.365(3)
C(6)-C(7)	1.417(3)
C(7)-C(8)	1.411(3)
C(8)-C(15)	1.440(3)
C(9)-C(10)	1.389(3)
C(9)-C(14)	1.402(3)
C(10)-C(11)	1.387(3)
C(11)-C(12)	1.383(4)
C(12)-C(13)	1.381(4)
C(13)-C(14)	1.386(3)
C(15)-C(16)	1.515(3)
C(16)-C(17)	1.518(3)
C(17)-C(18)	1.524(3)
C(18)-C(19)	1.524(3)
C(1)-N(1)-C(8)	112.26(18)
N(1)-C(1)-C(2)	107.47(18)
N(1)-C(1)-C(9)	123.65(19)
C(2)-C(1)-C(9)	128.8(2)
C(3)-C(2)-C(1)	131.9(2)
C(3)-C(2)-C(7)	121.21(19)
C(1)-C(2)-C(7)	106.85(19)
C(4)-C(3)-C(2)	118.5(2)
C(3)-C(4)-C(5)	120.8(2)
C(6)-C(5)-C(4)	121.9(2)

C(5)-C(6)-C(7)	119.3(2)
C(8)-C(7)-C(6)	134.8(2)
C(8)-C(7)-C(2)	106.96(18)
C(6)-C(7)-C(2)	118.24(19)
N(1)-C(8)-C(7)	106.45(18)
N(1)-C(8)-C(15)	119.66(19)
C(7)-C(8)-C(15)	133.9(2)
C(10)-C(9)-C(14)	118.8(2)
C(10)-C(9)-C(1)	121.1(2)
C(14)-C(9)-C(1)	120.1(2)
C(11)-C(10)-C(9)	120.4(2)
C(12)-C(11)-C(10)	120.6(2)
C(13)-C(12)-C(11)	119.6(2)
C(12)-C(13)-C(14)	120.4(3)
C(13)-C(14)-C(9)	120.3(2)
O(1)-C(15)-C(8)	121.8(2)
O(1)-C(15)-C(16)	121.2(2)
C(8)-C(15)-C(16)	117.06(19)
C(15)-C(16)-C(17)	115.31(18)
C(16)-C(17)-C(18)	111.35(18)
C(19)-C(18)-C(17)	113.7(2)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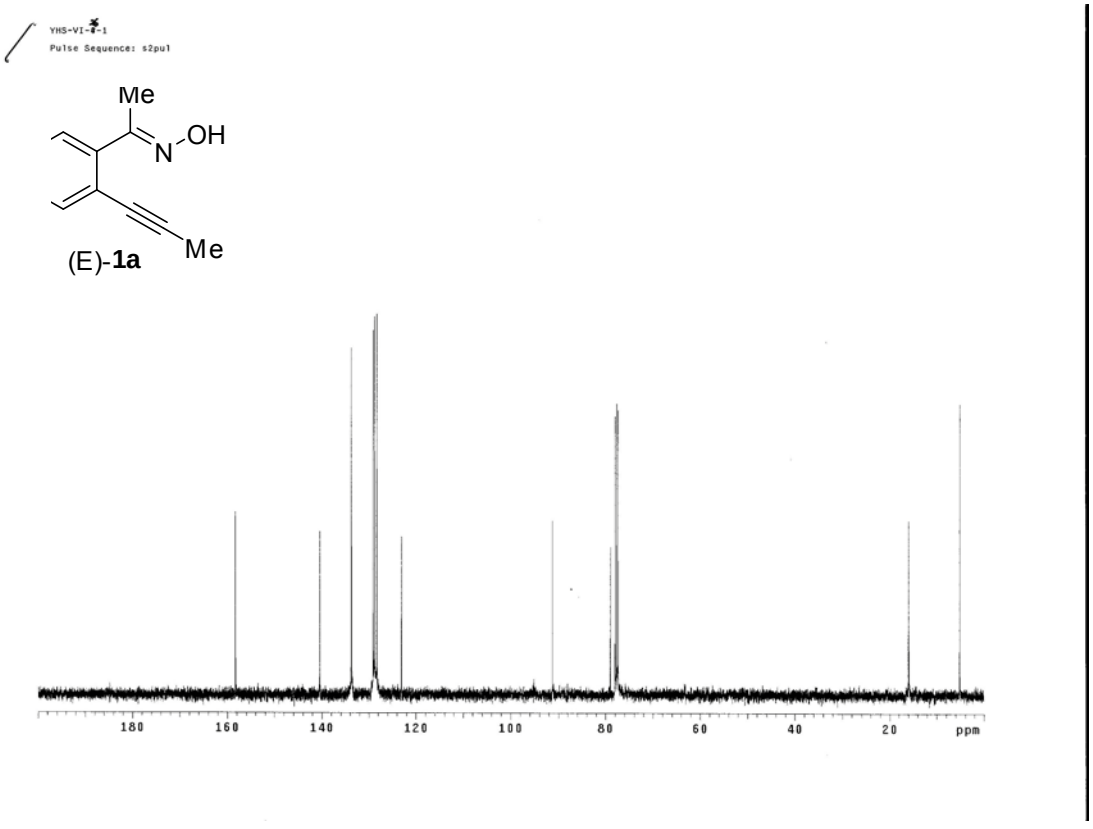
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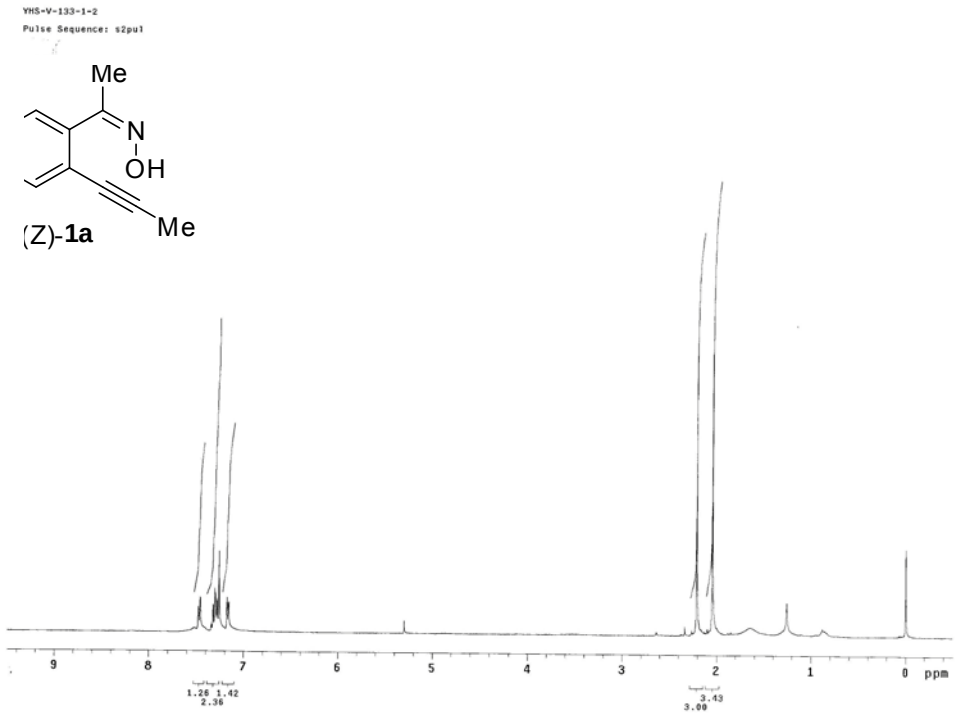

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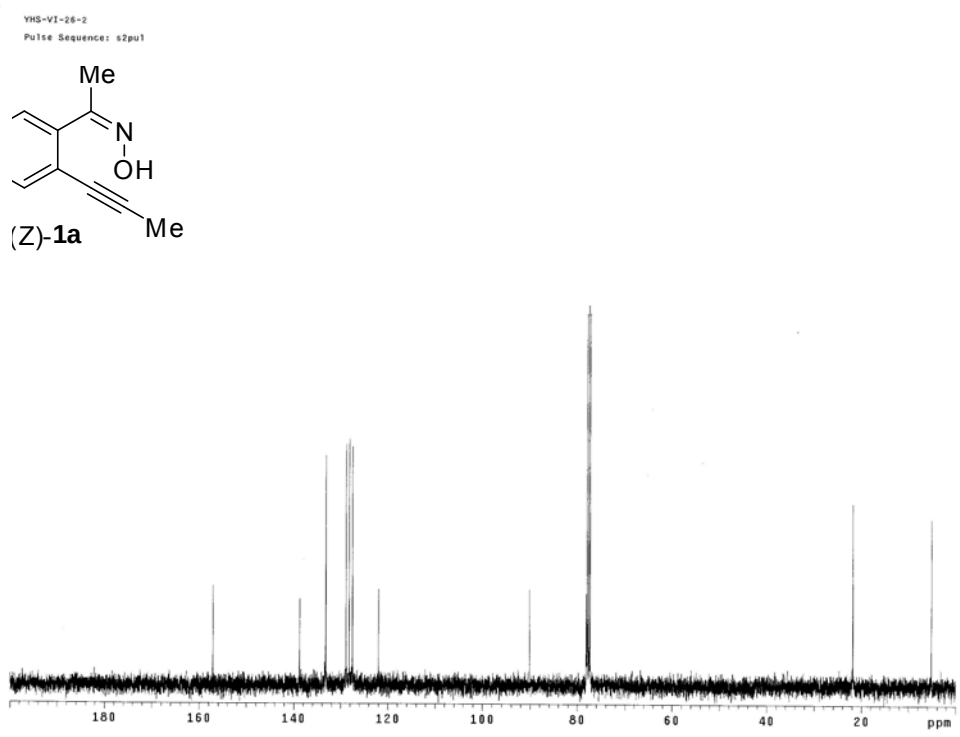

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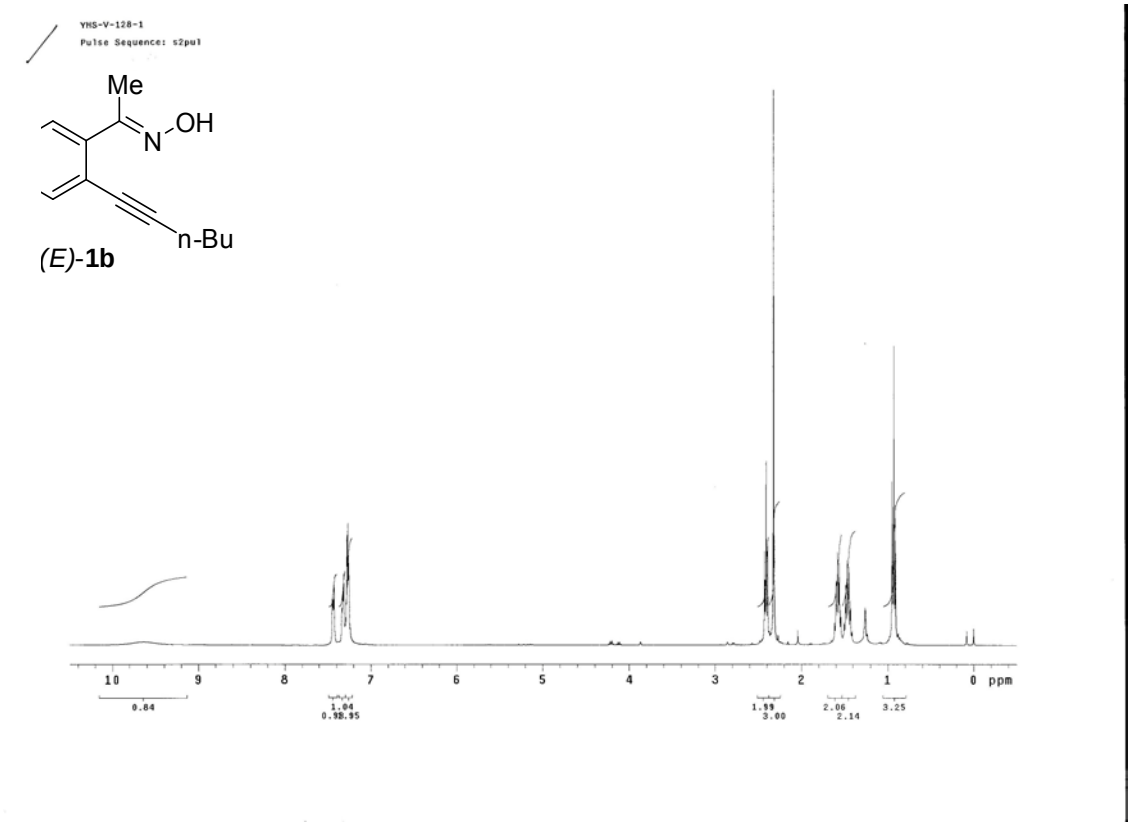
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9
8
7
6
5
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3
2
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0.98
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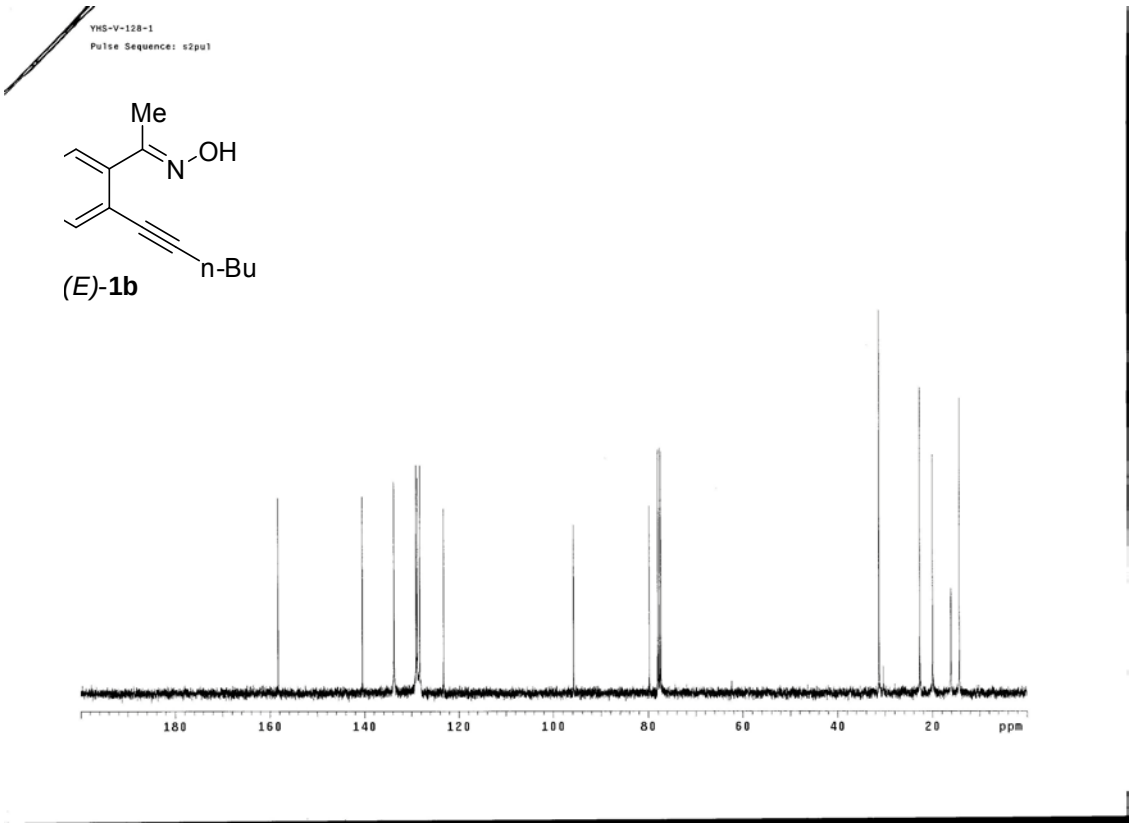
1.99
3.00
2.06
2.14
3.25

(E)-**1b**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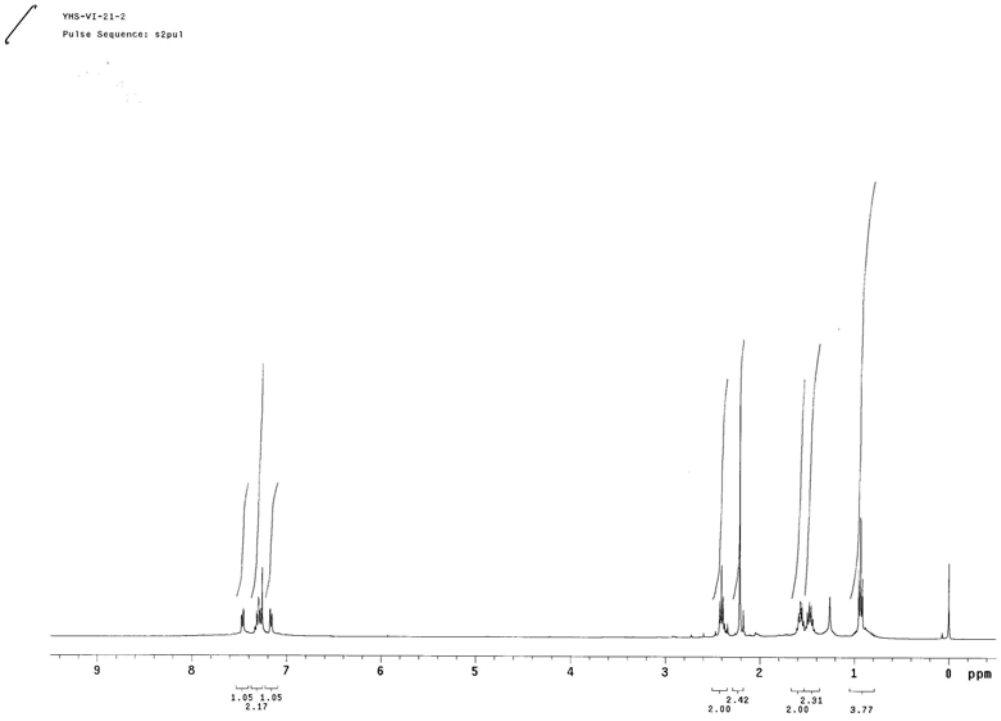
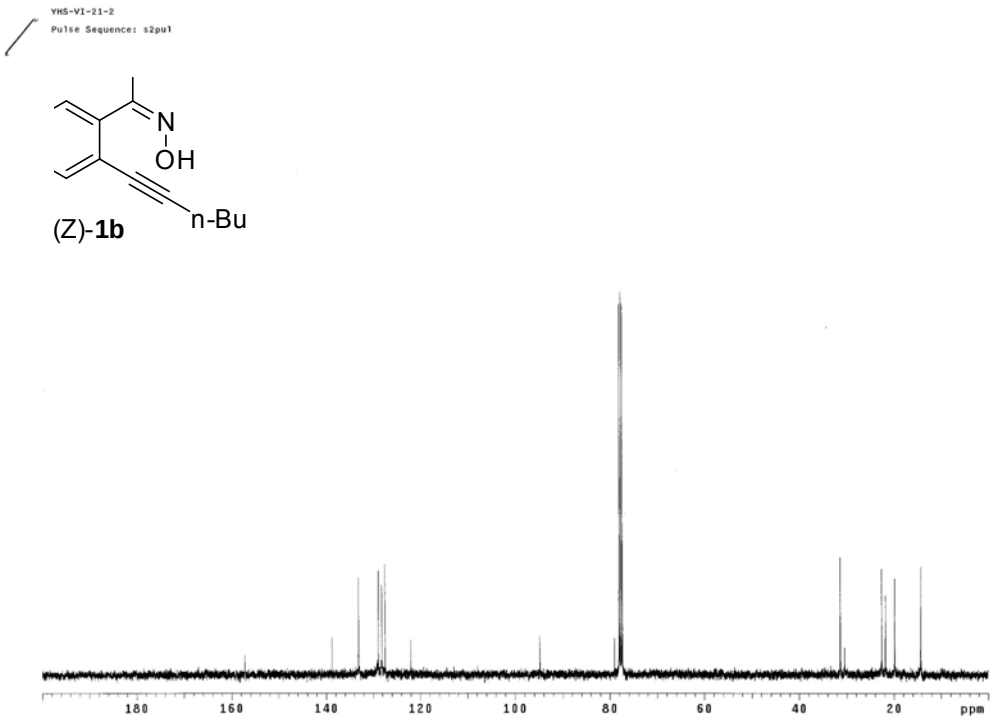
20
ppm

(E)-**1b**





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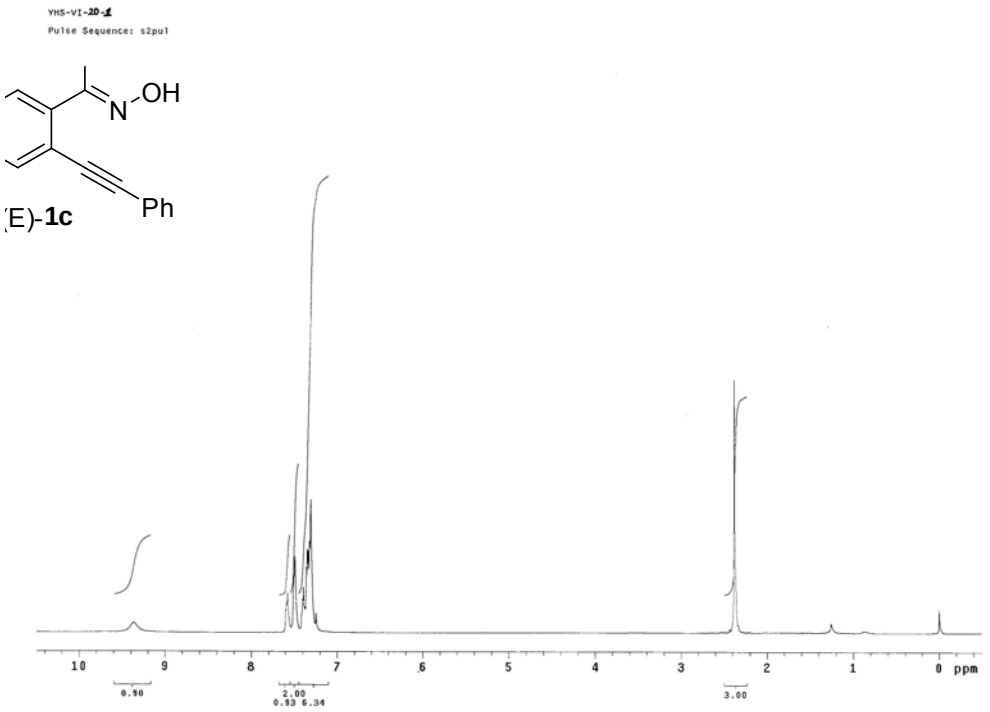
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8
7
6
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1
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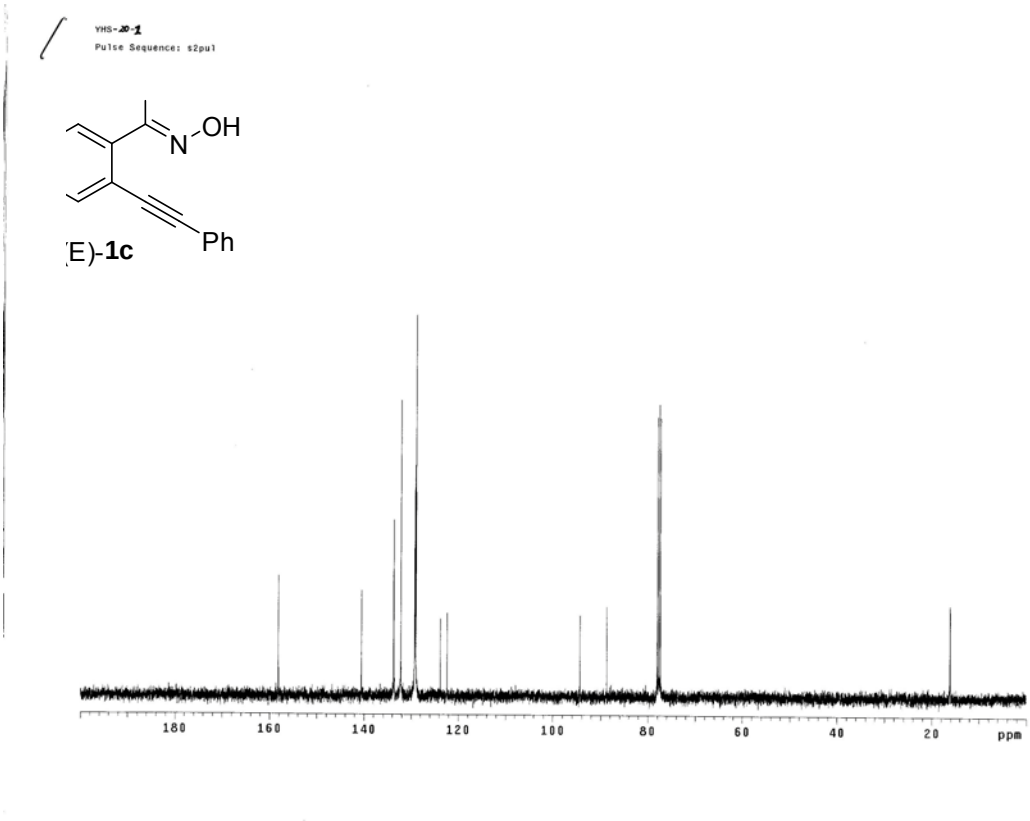
0.90
2.00
0.93 6.34
3.00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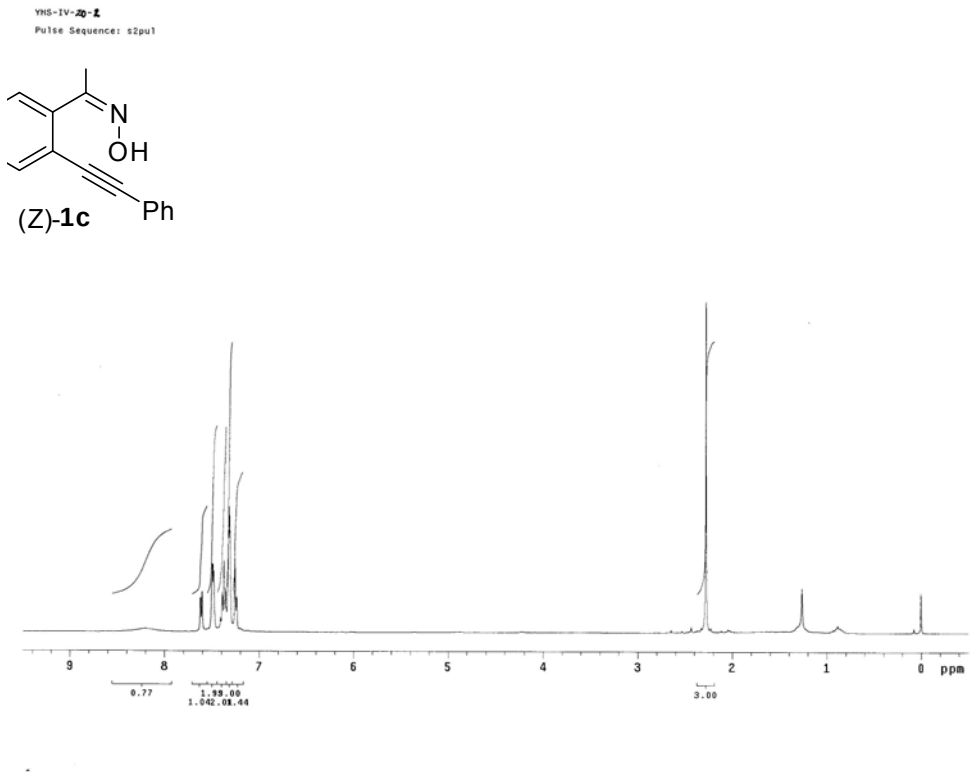
ppm



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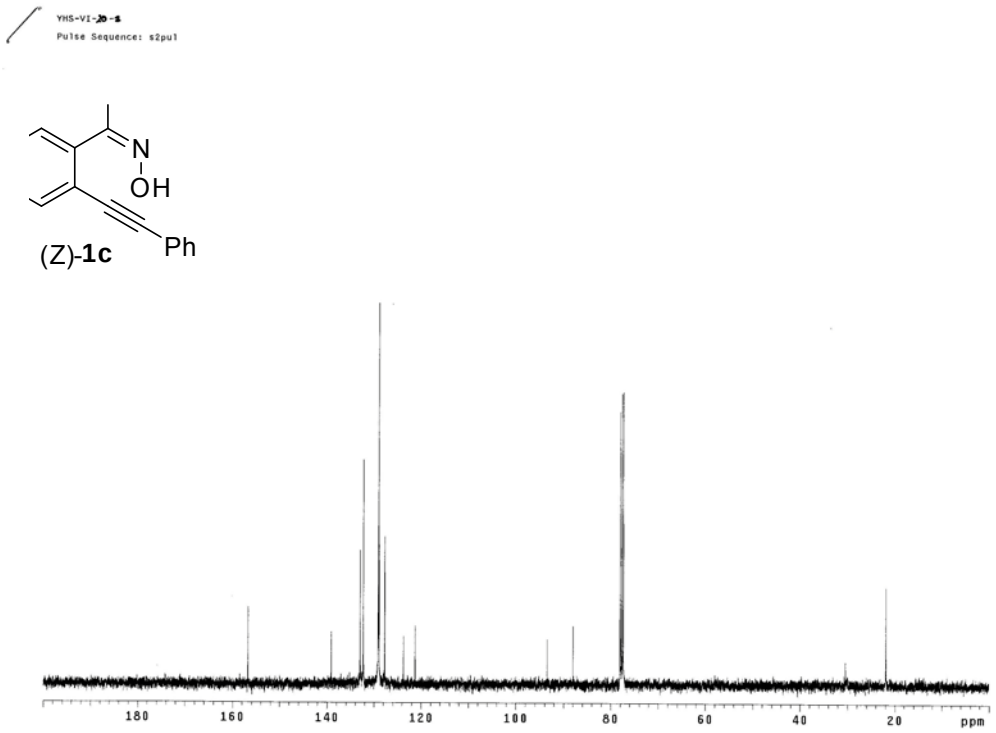

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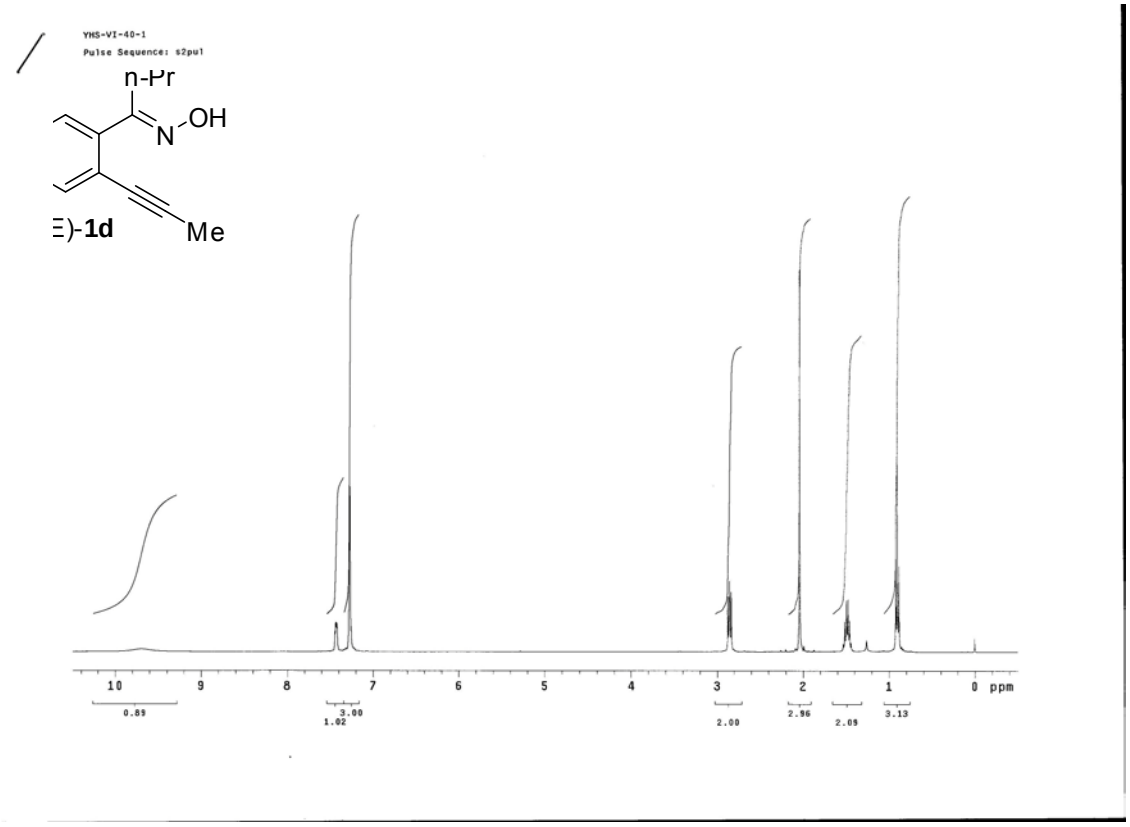
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OH
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Ξ)-1d
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9
8
7
6
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3
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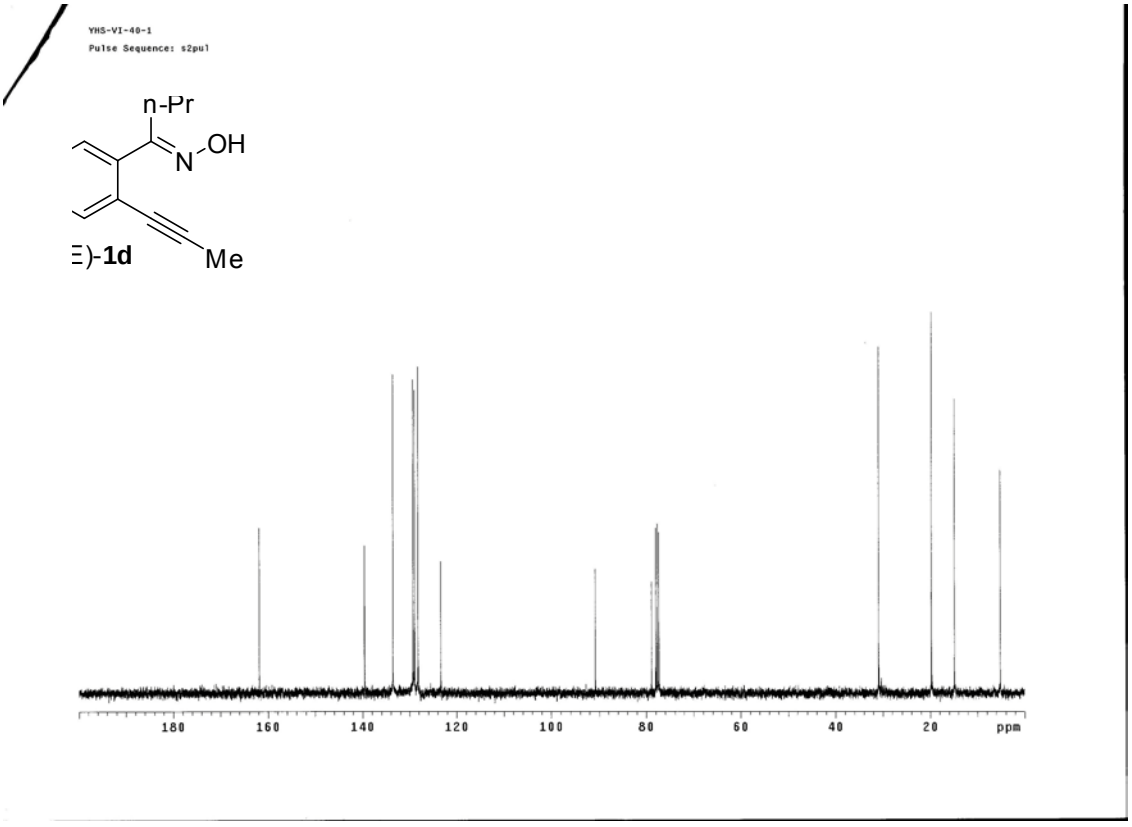
3.00
1.02
2.00
2.96
2.09
3.13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Ξ)-1d
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140
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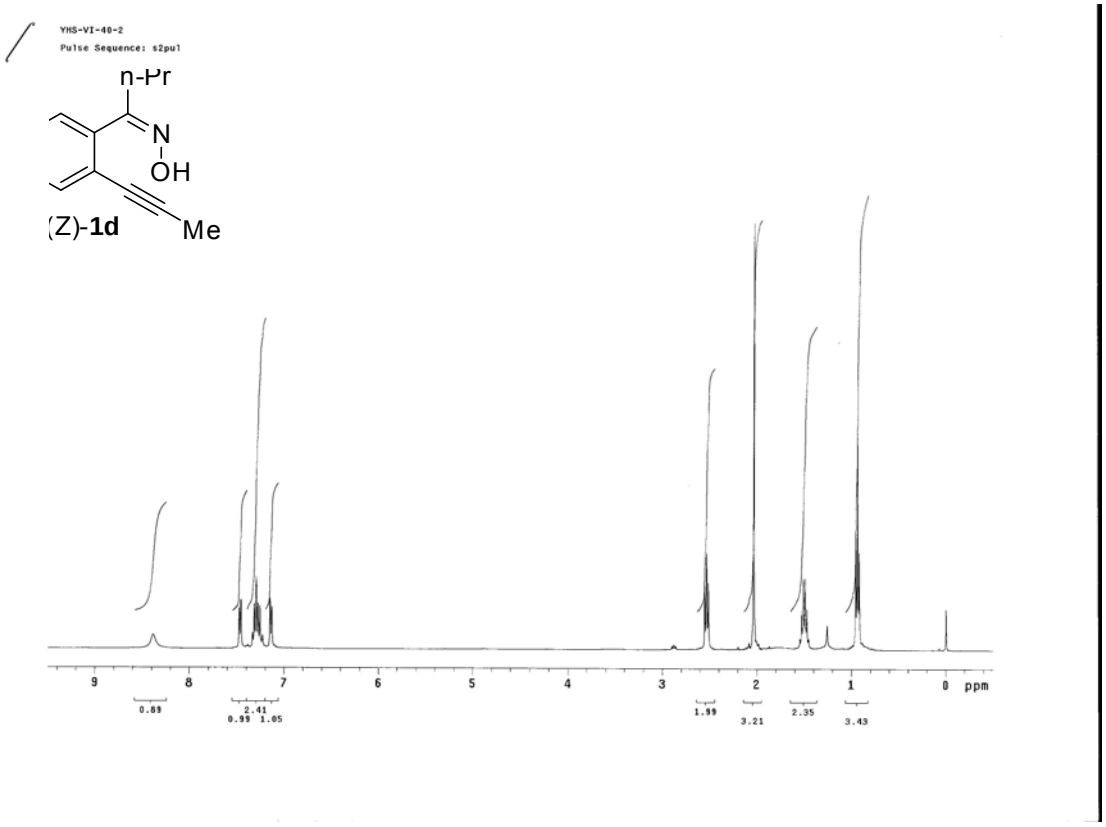
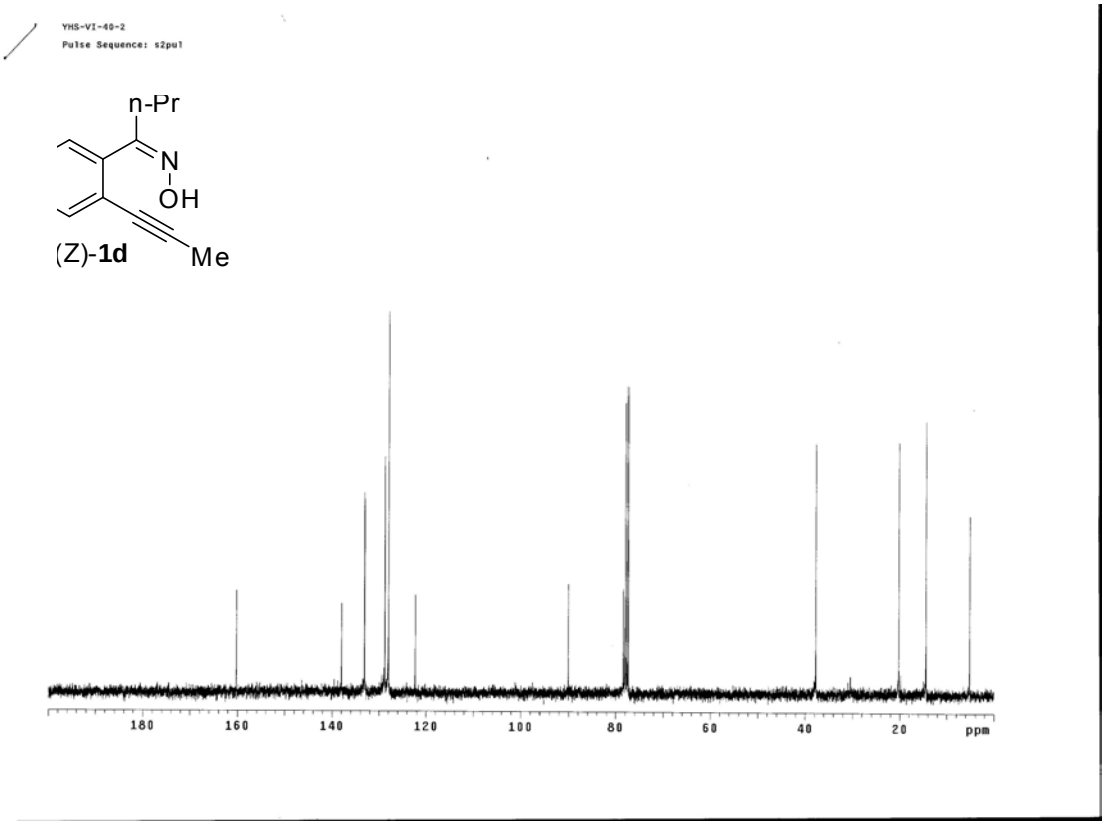
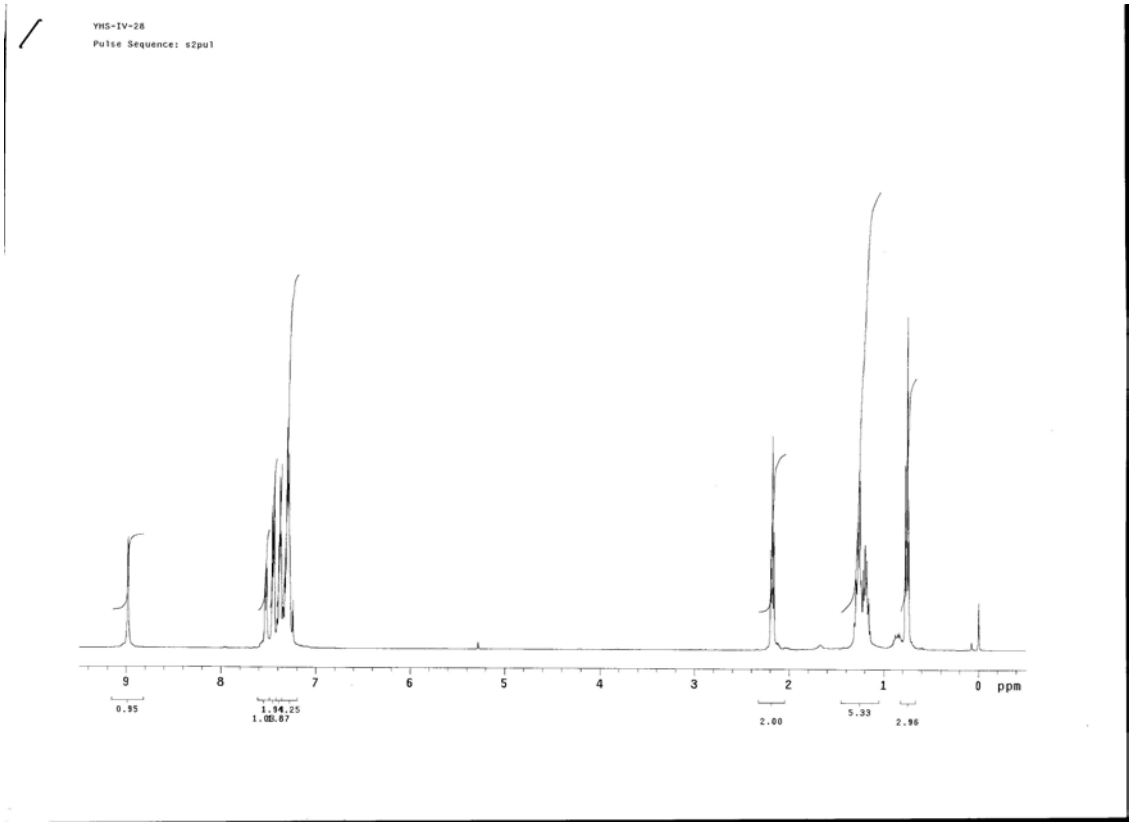
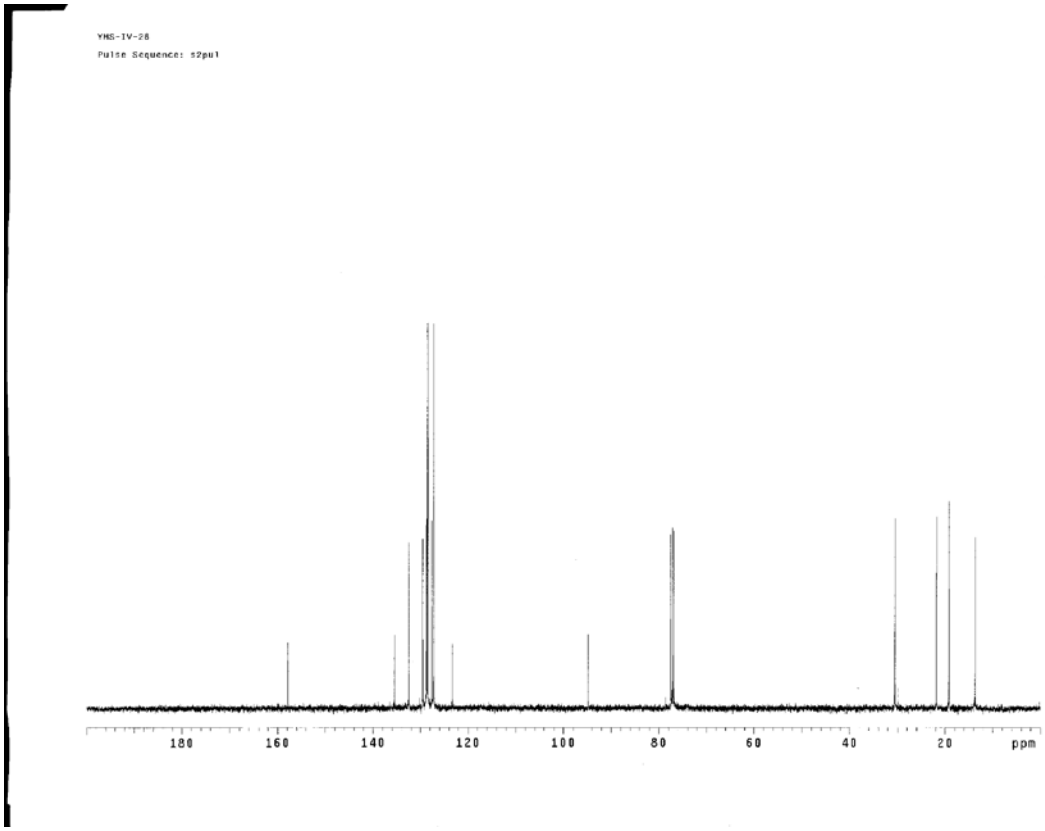
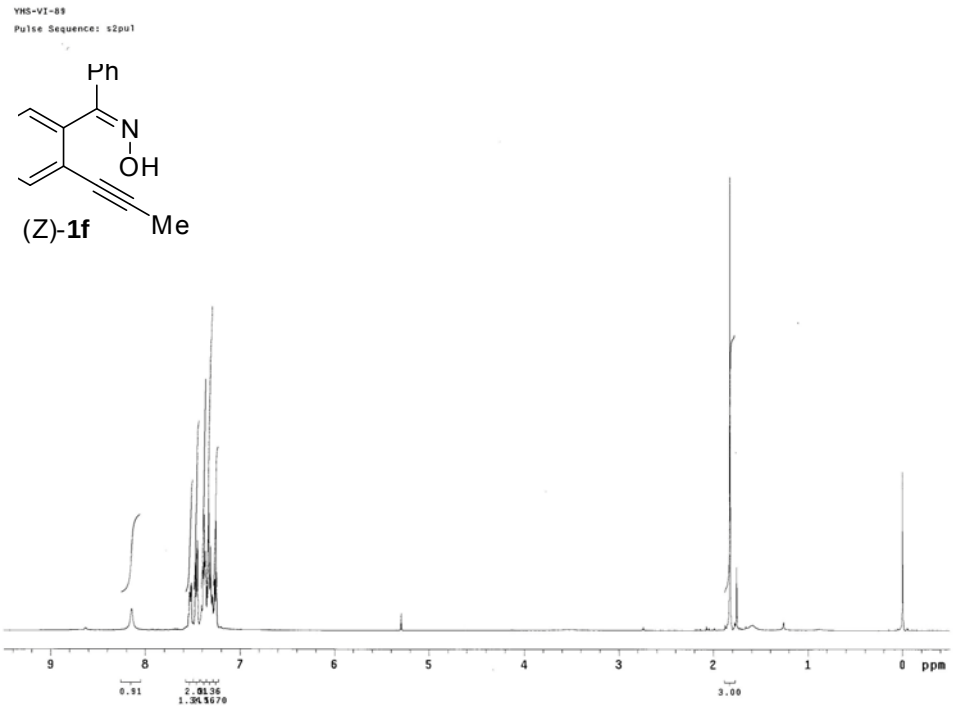
100
80
60
40
20
ppm







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7
6
5
4
3
2
1
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ppm
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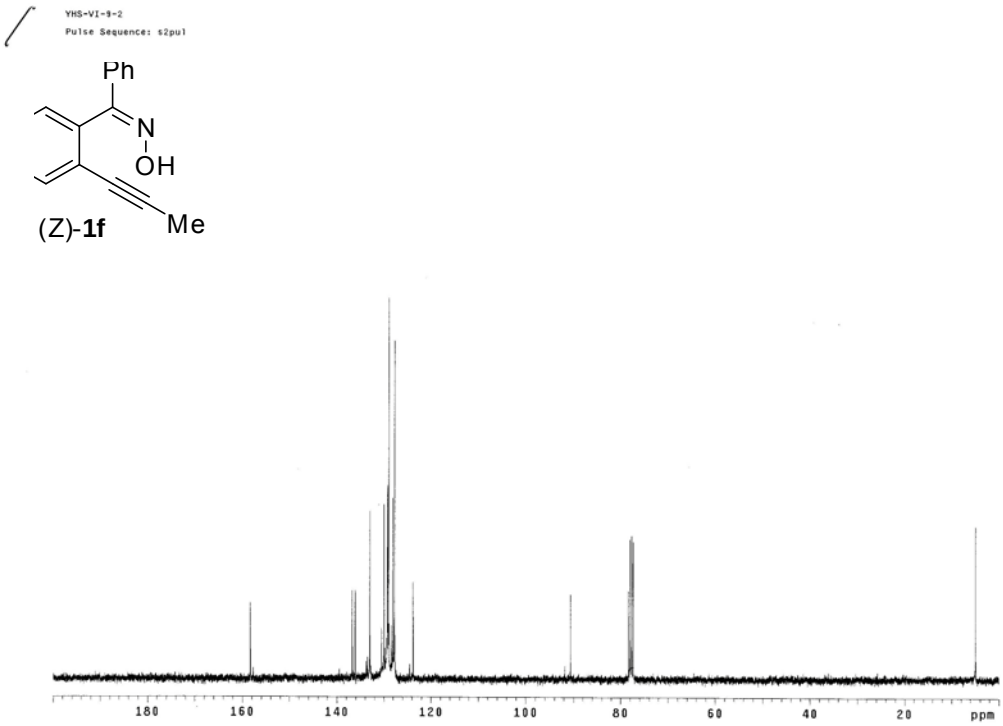
3.00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60
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20
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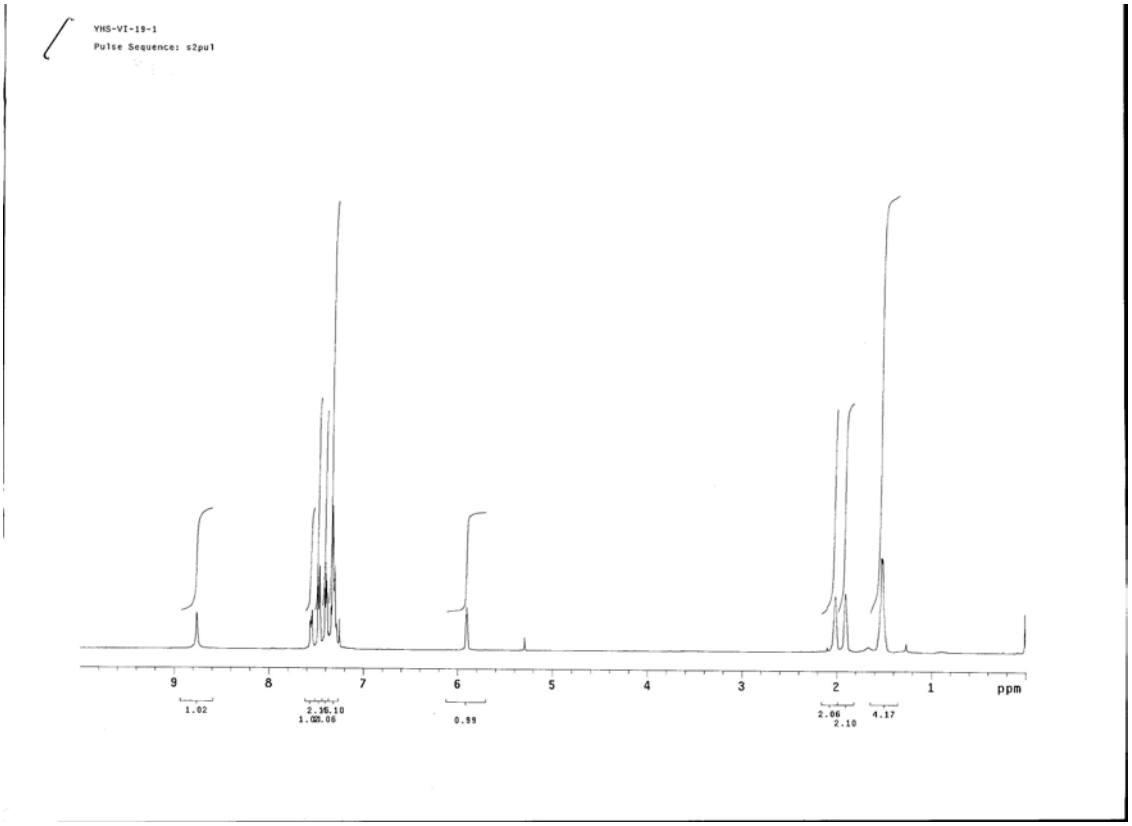
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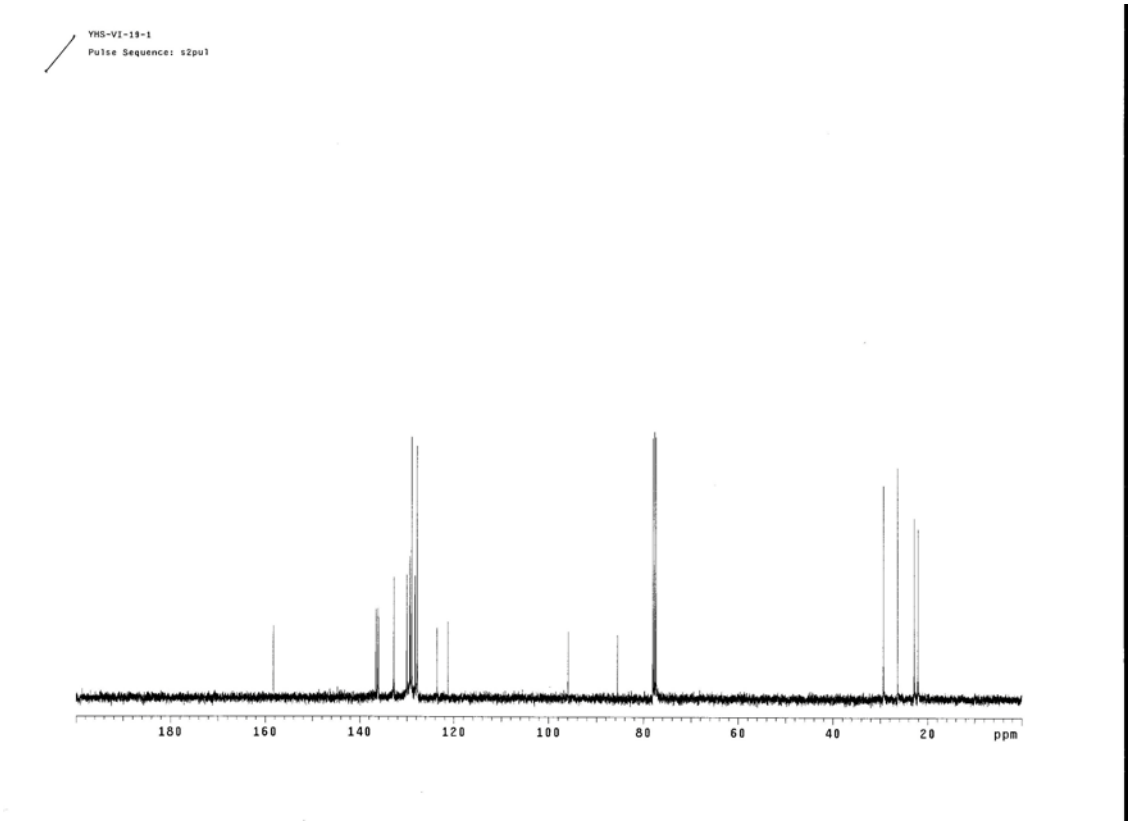
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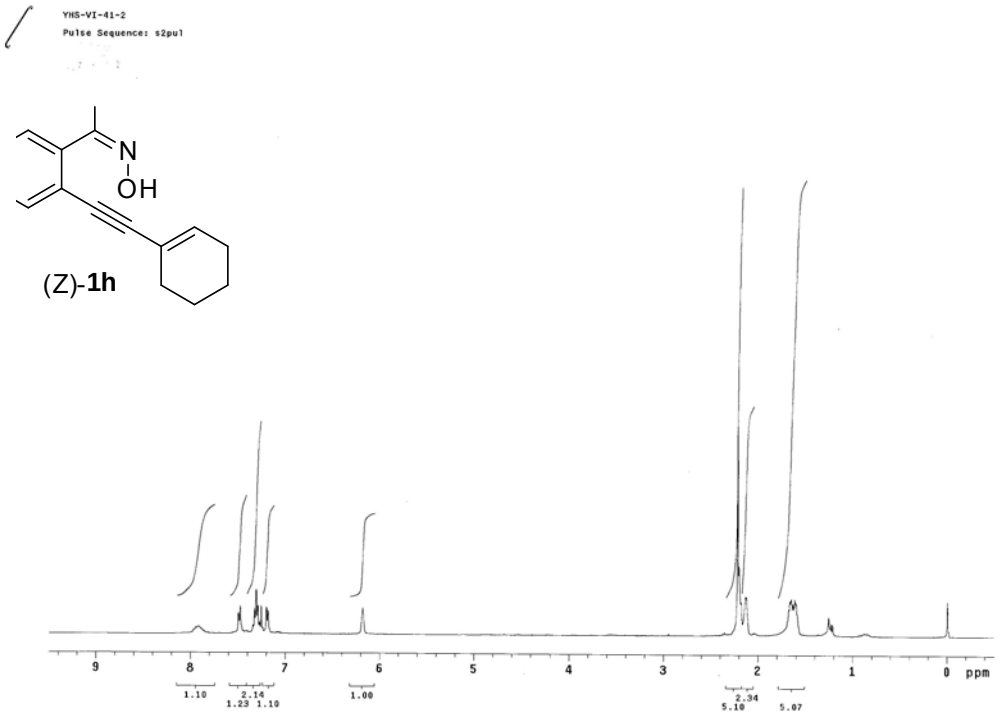

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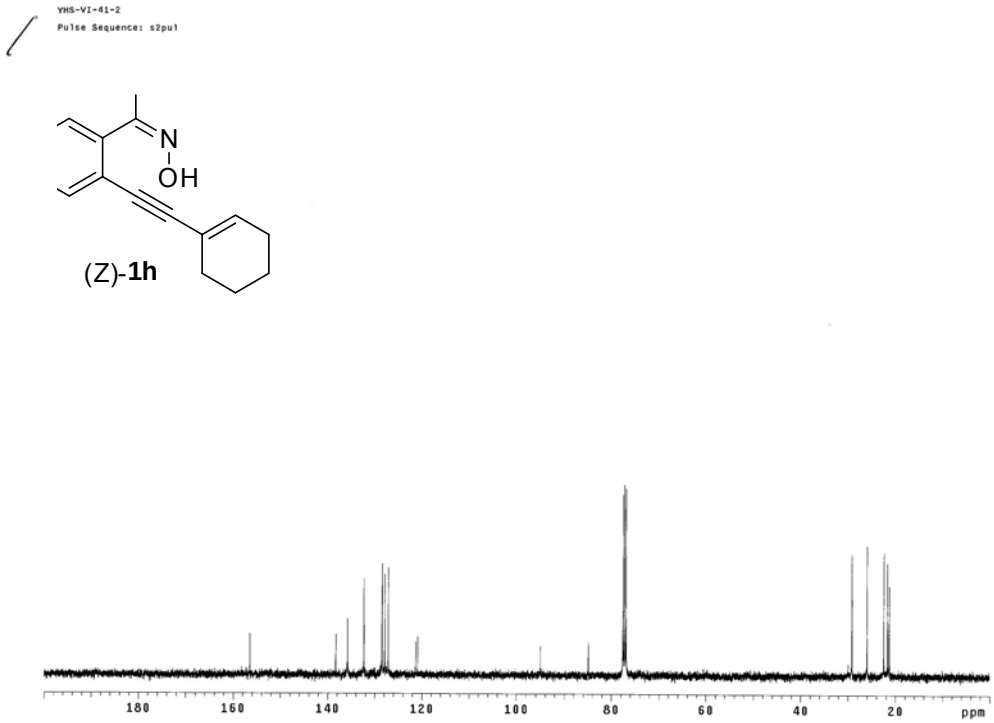

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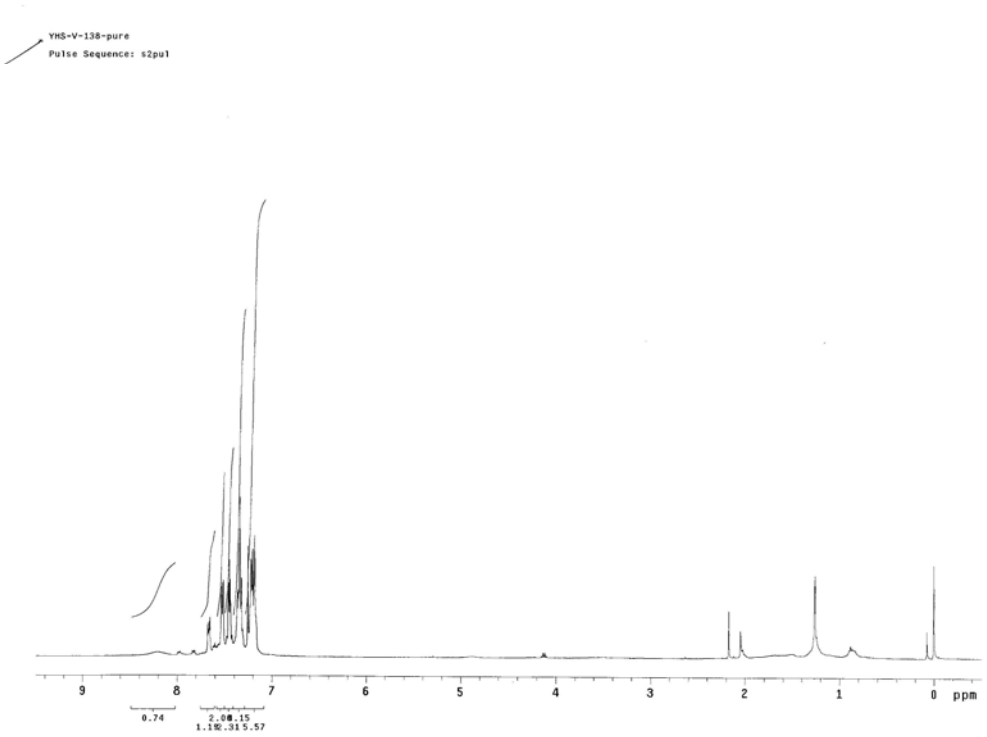
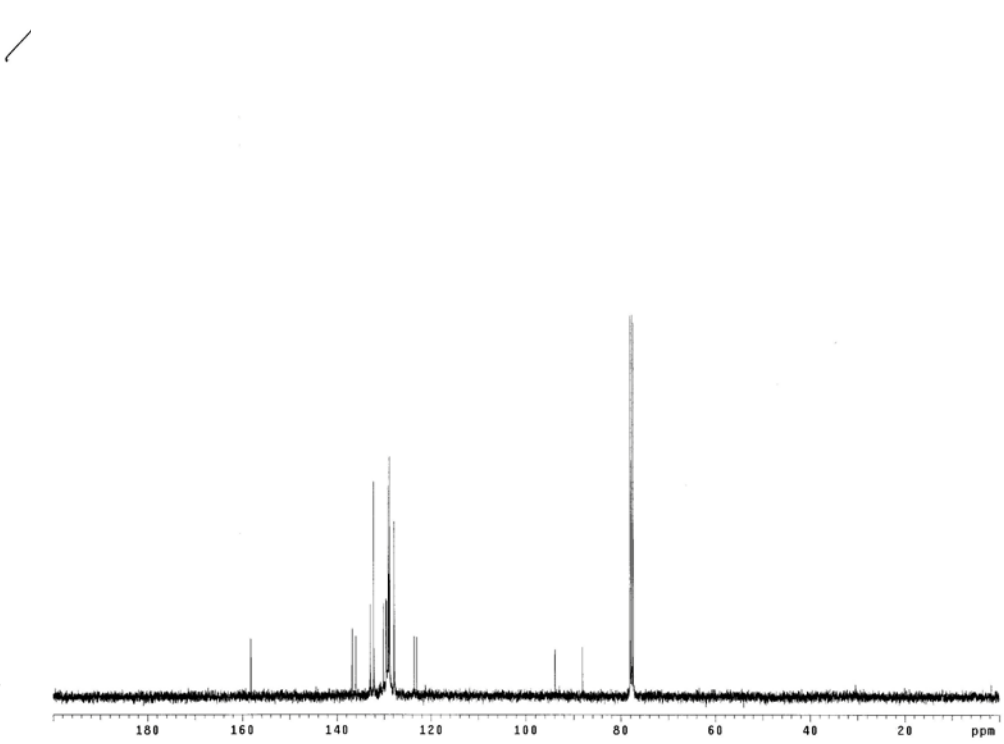
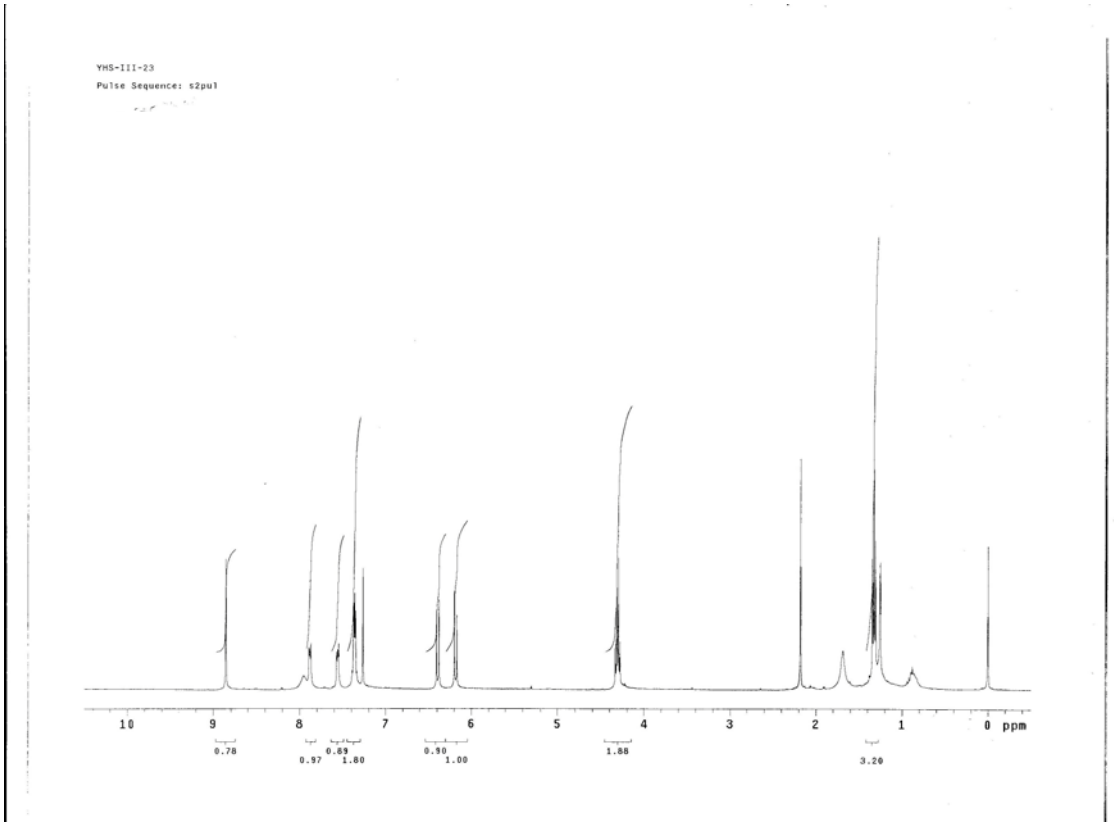
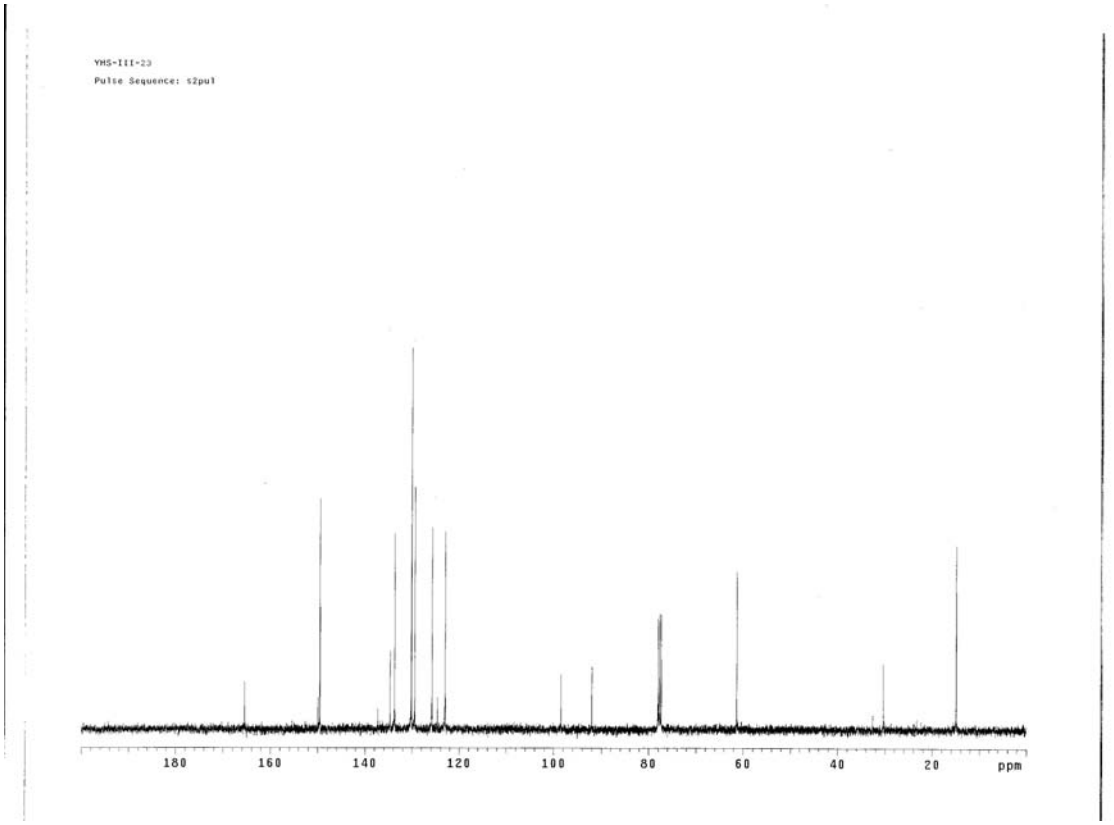
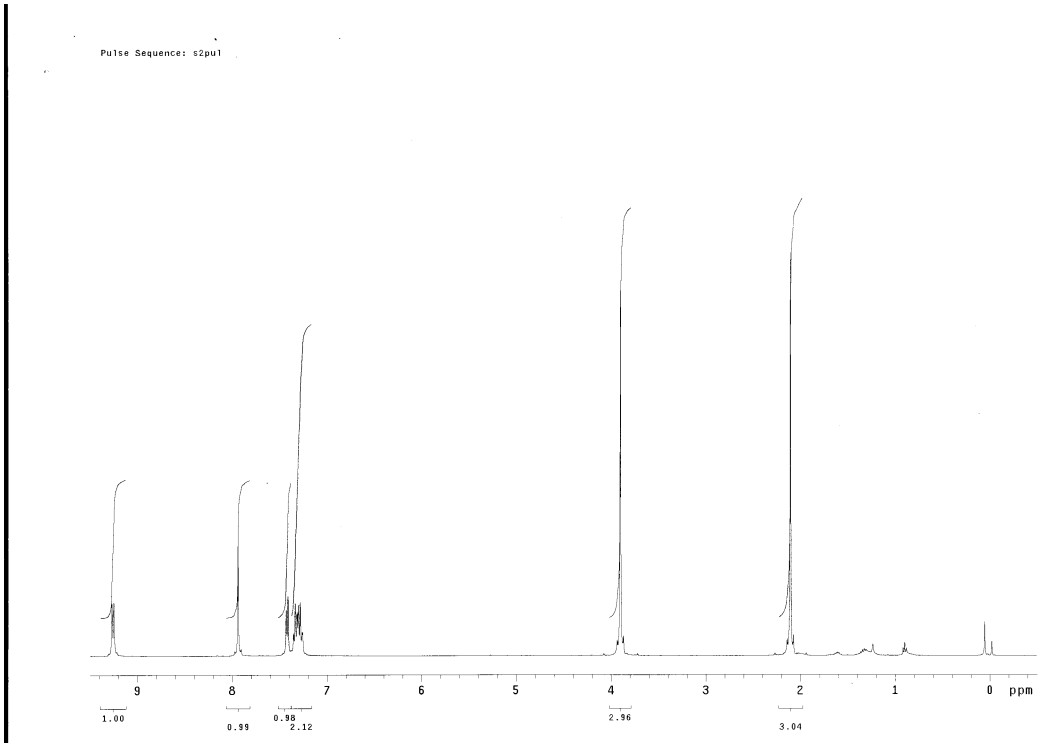
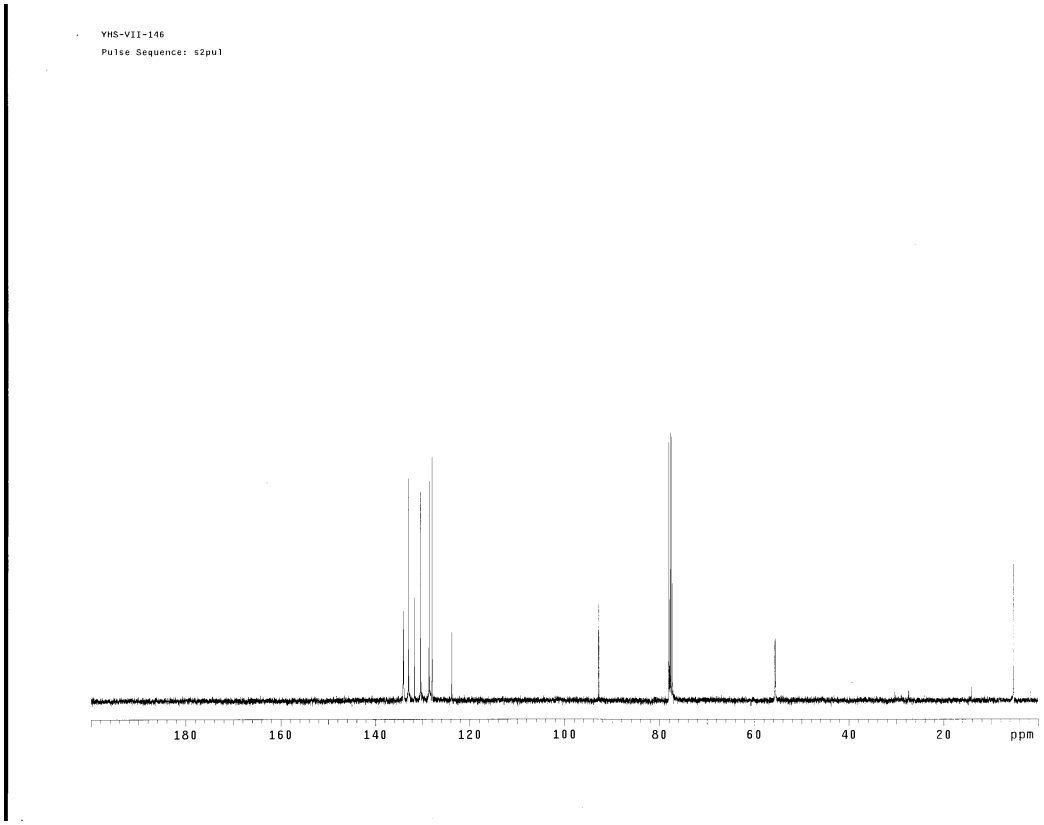


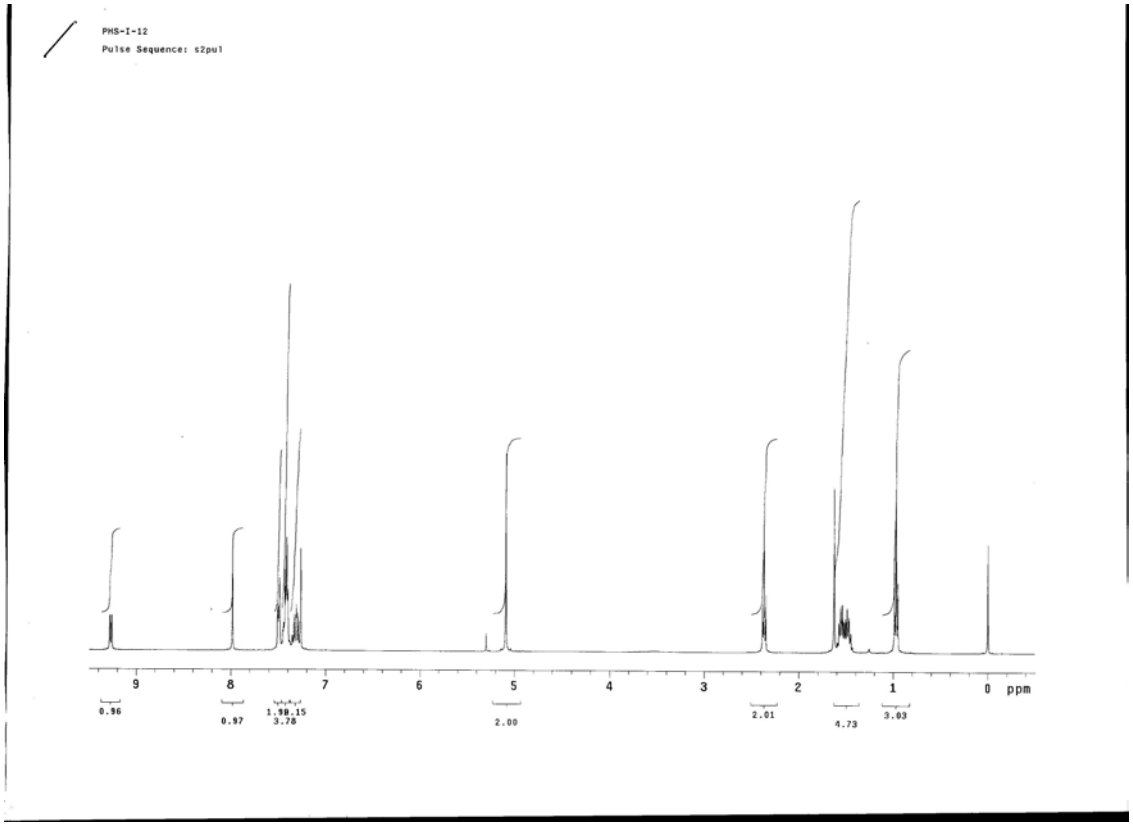


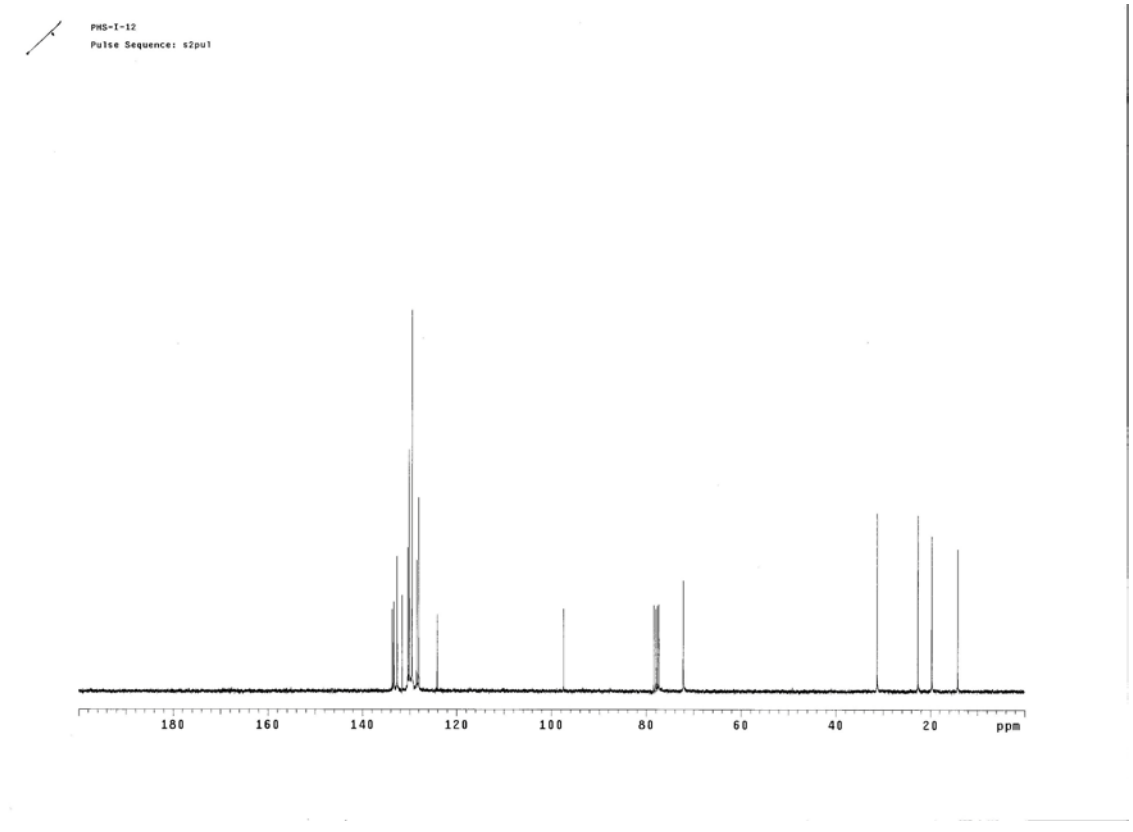


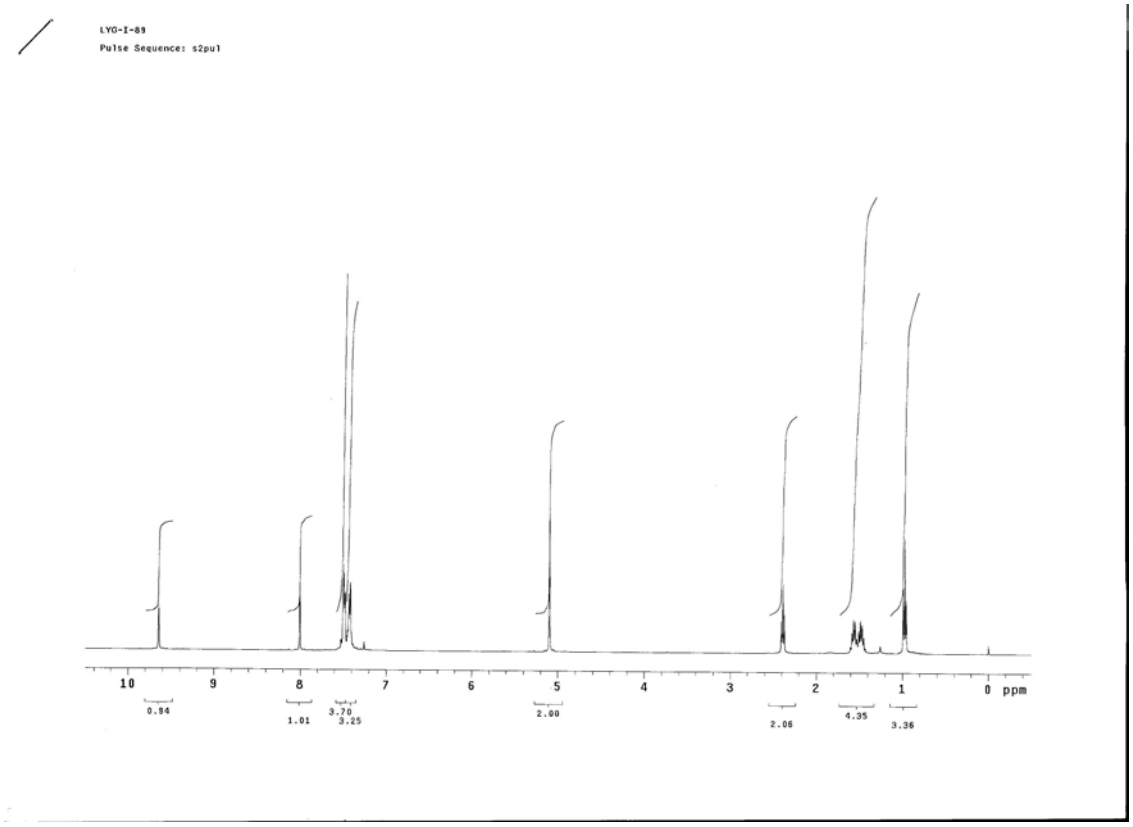


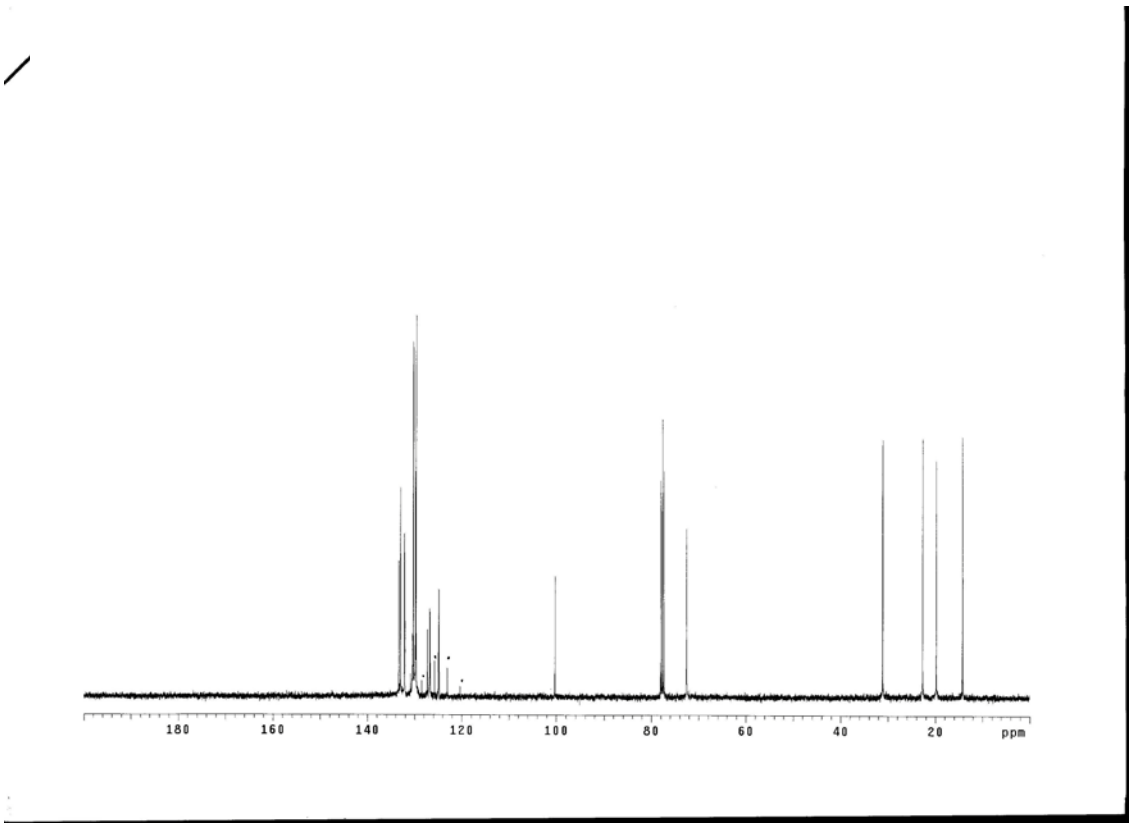


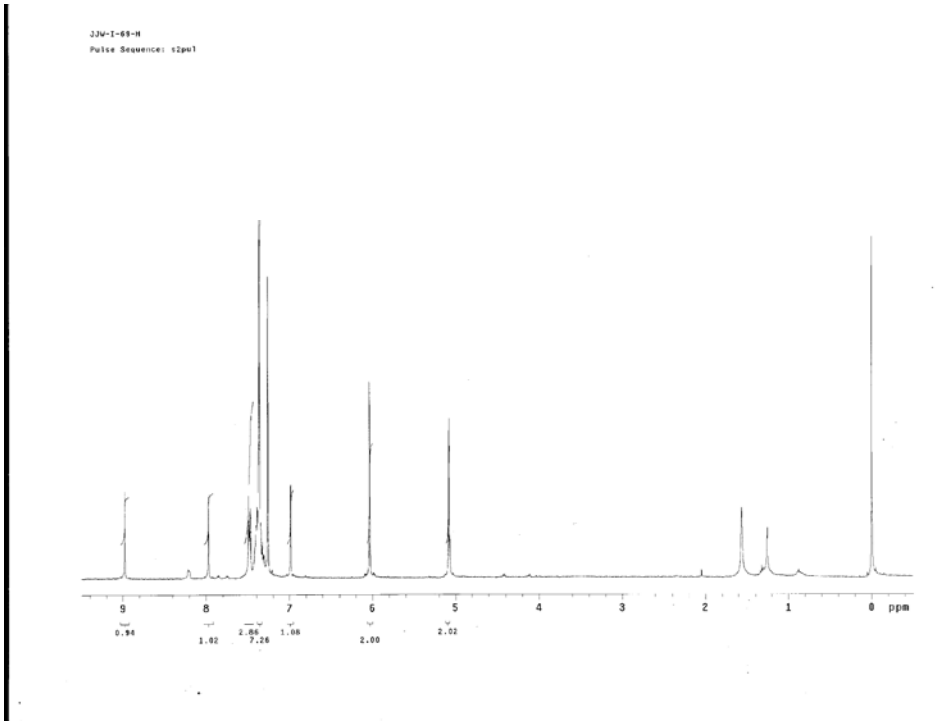


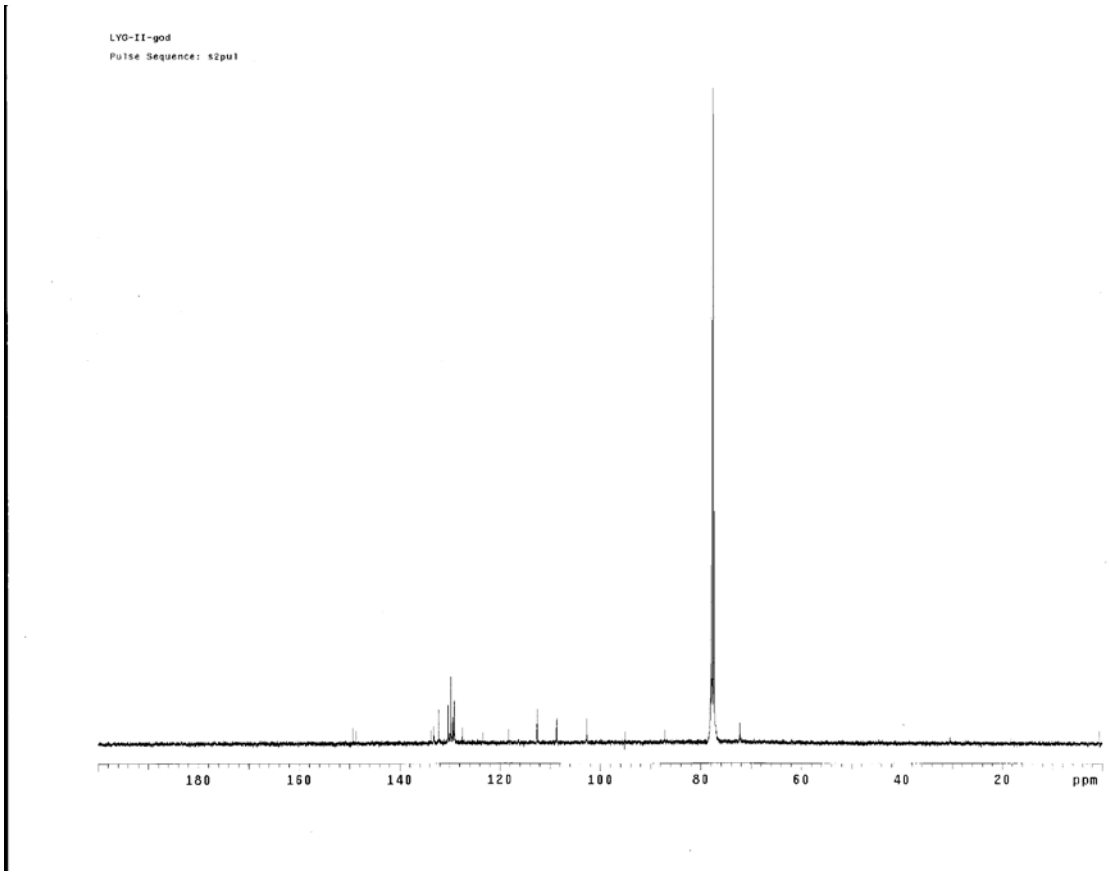


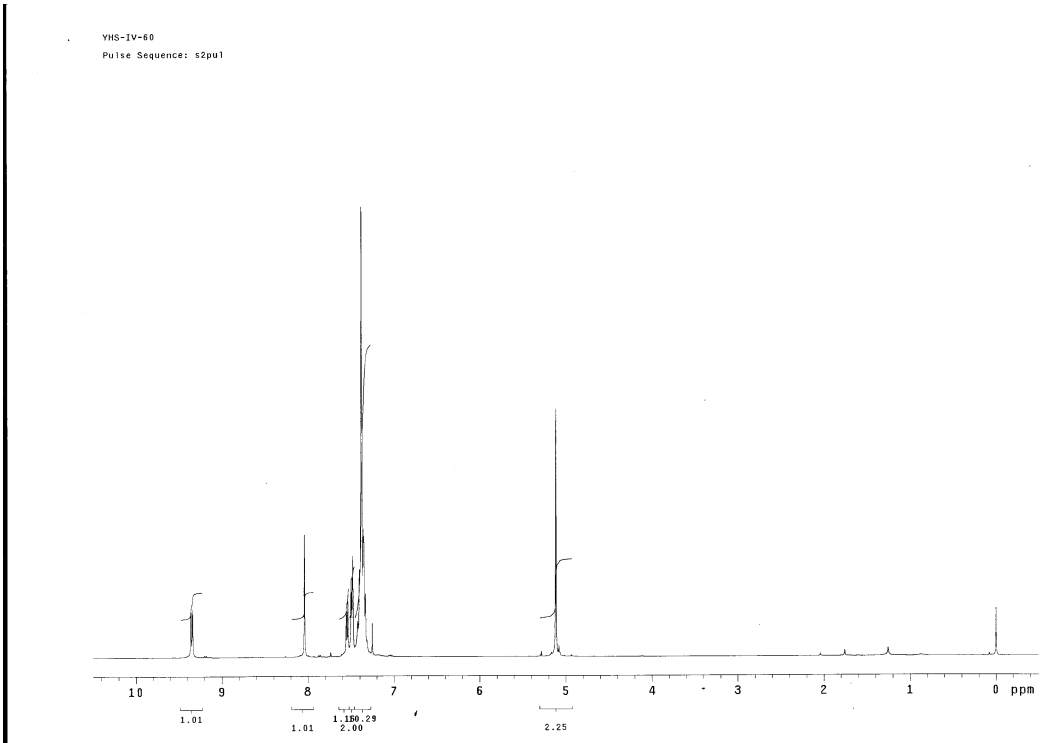


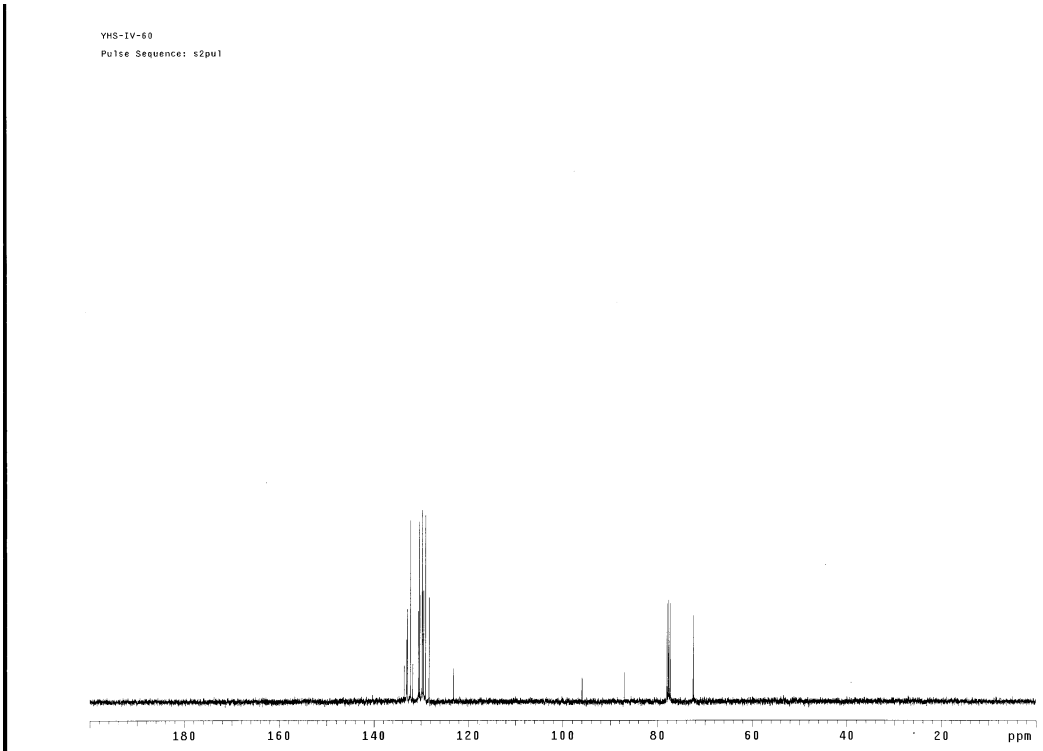


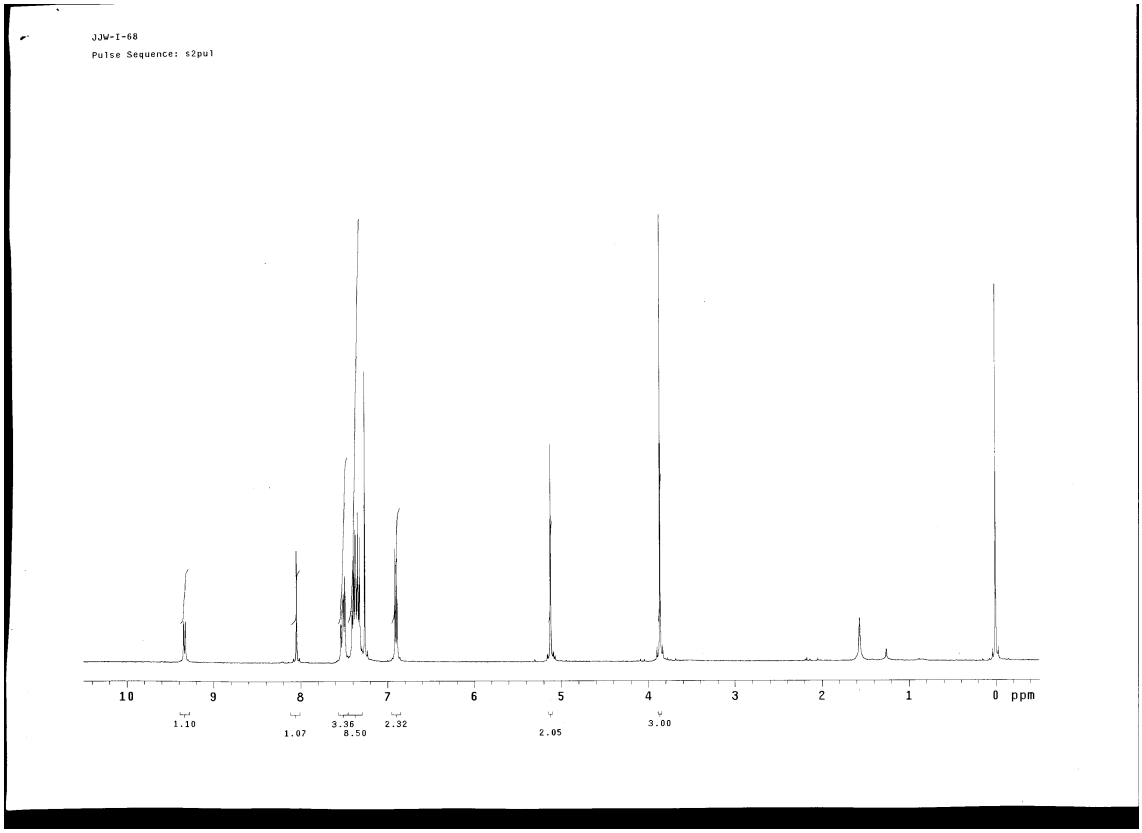


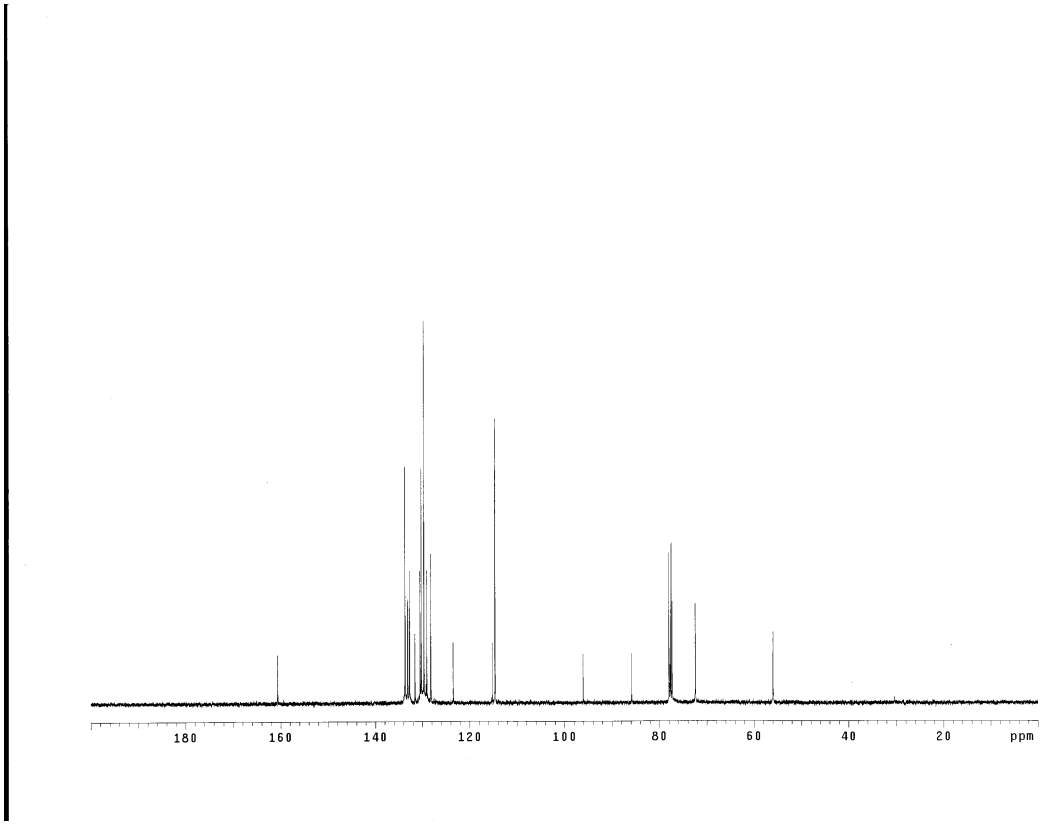


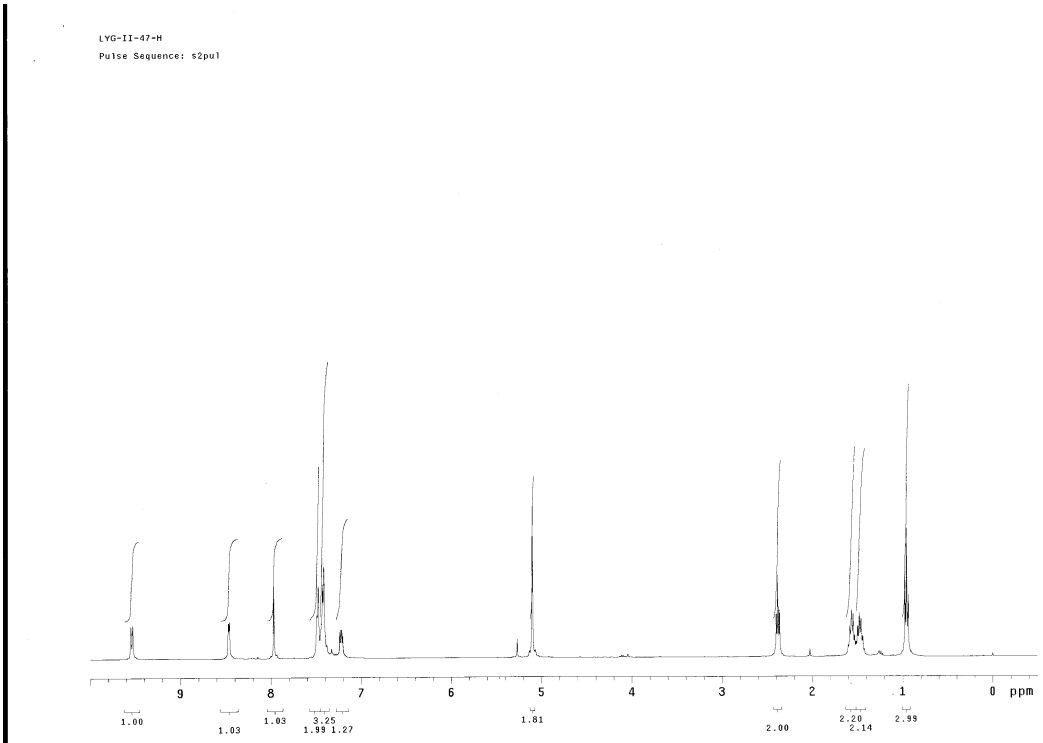


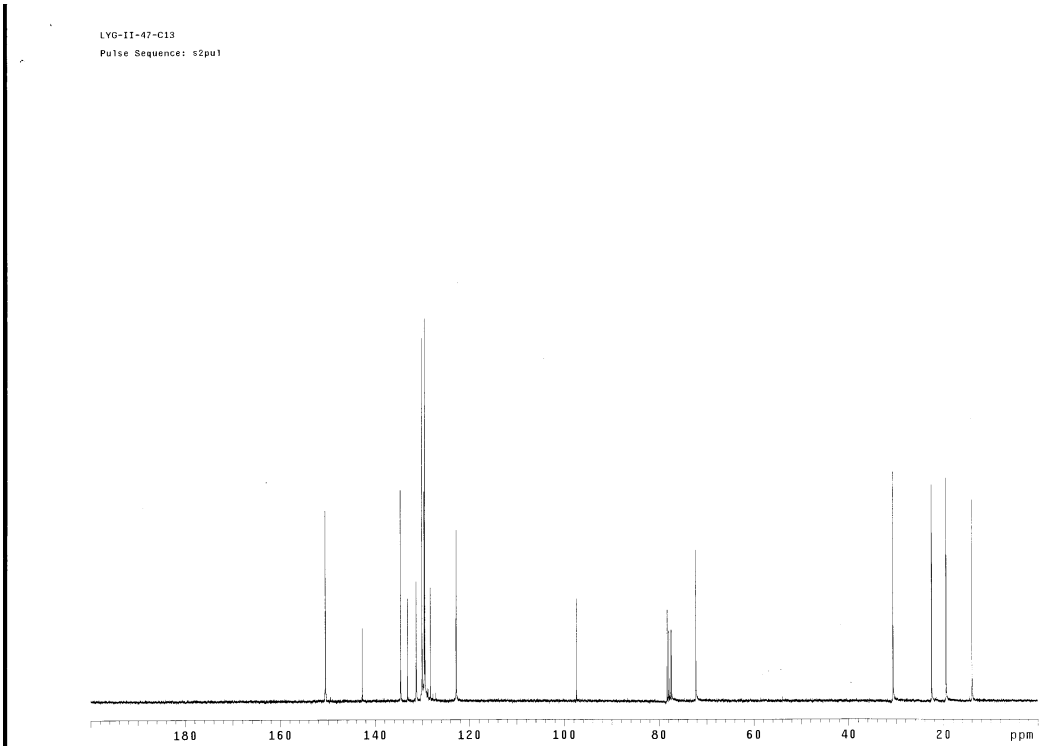


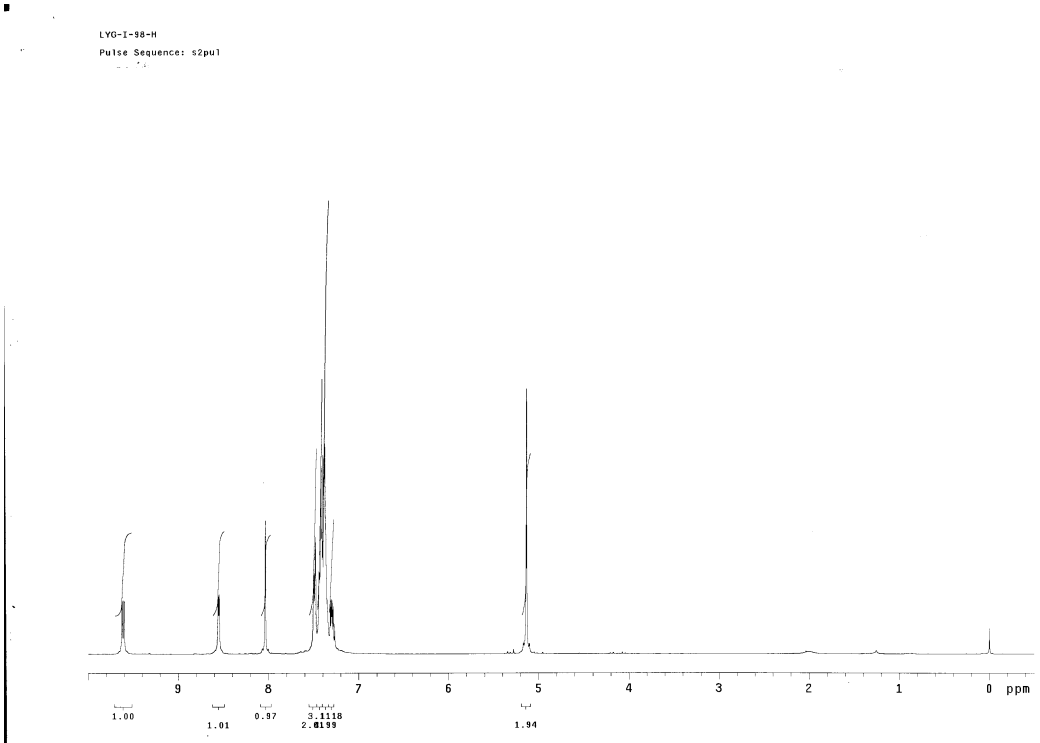


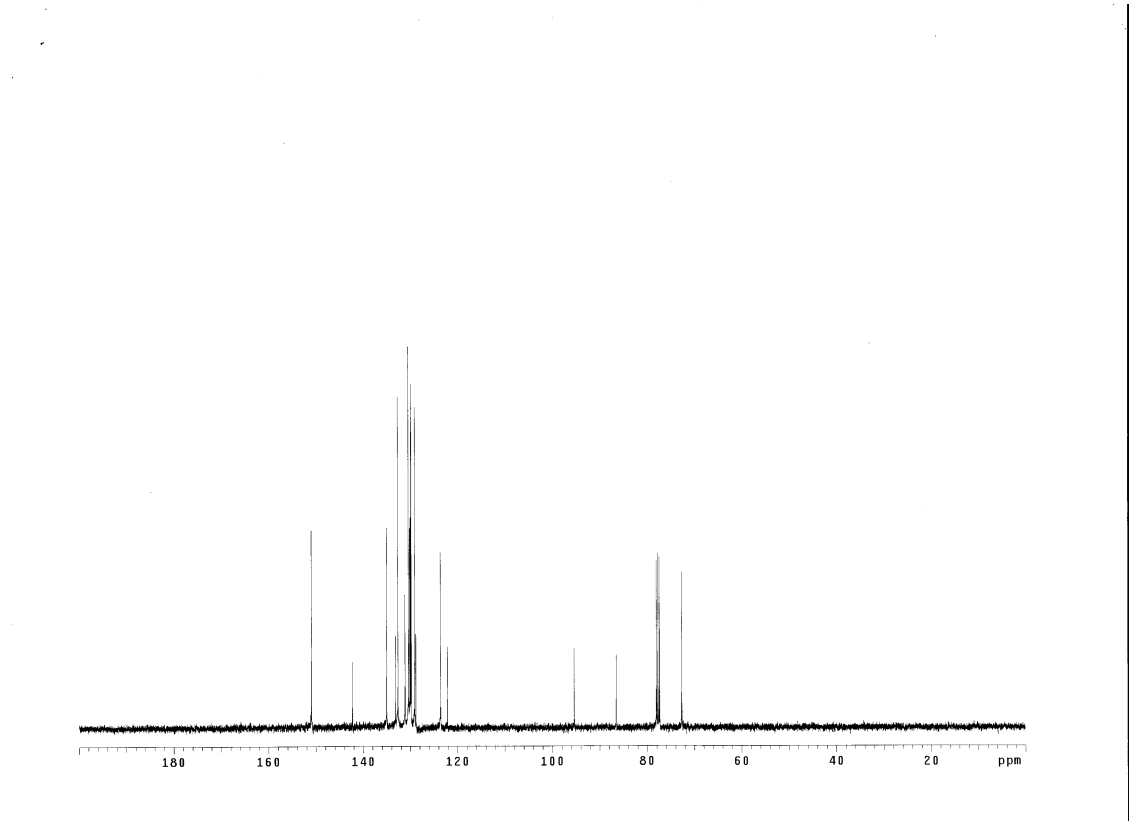


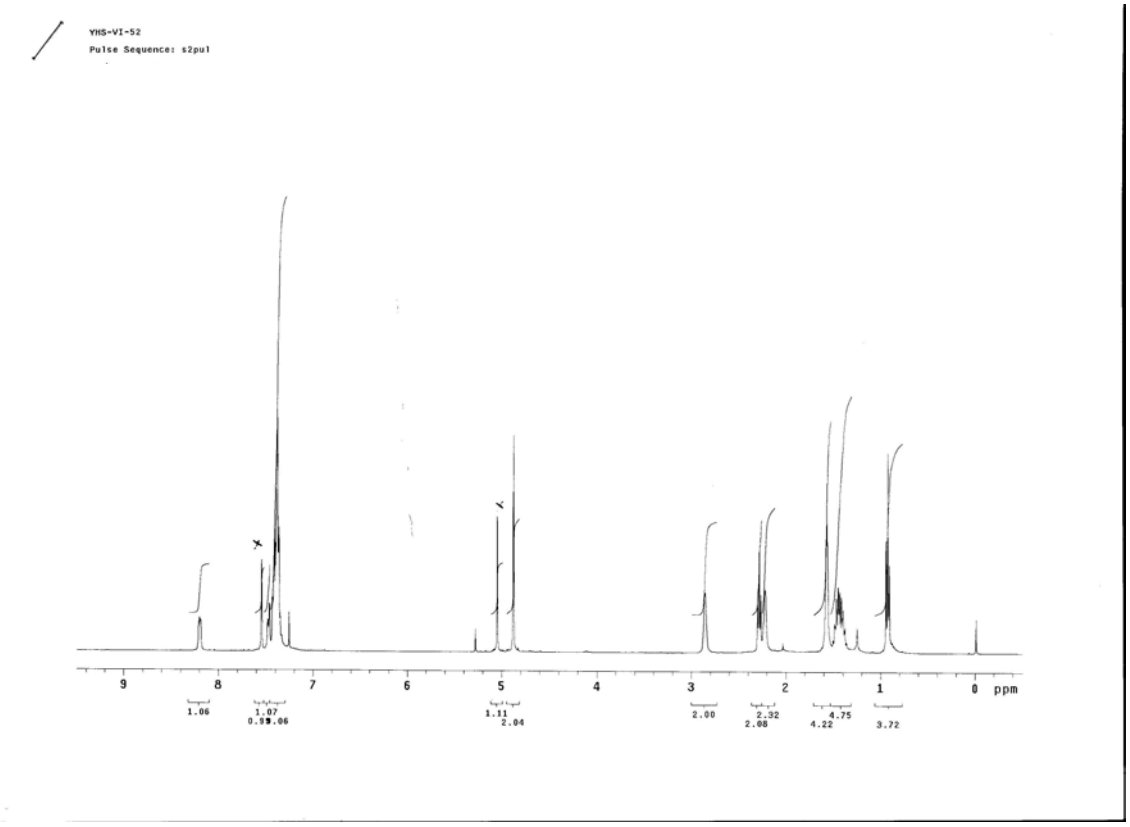


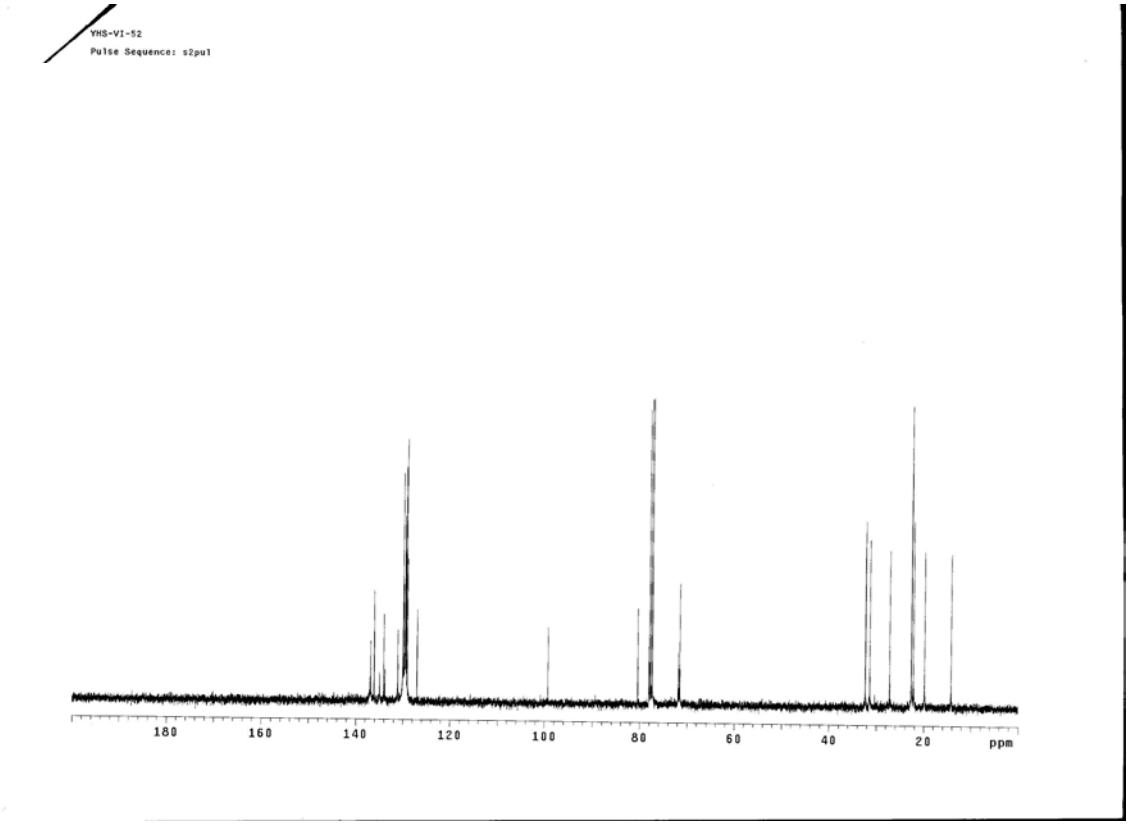


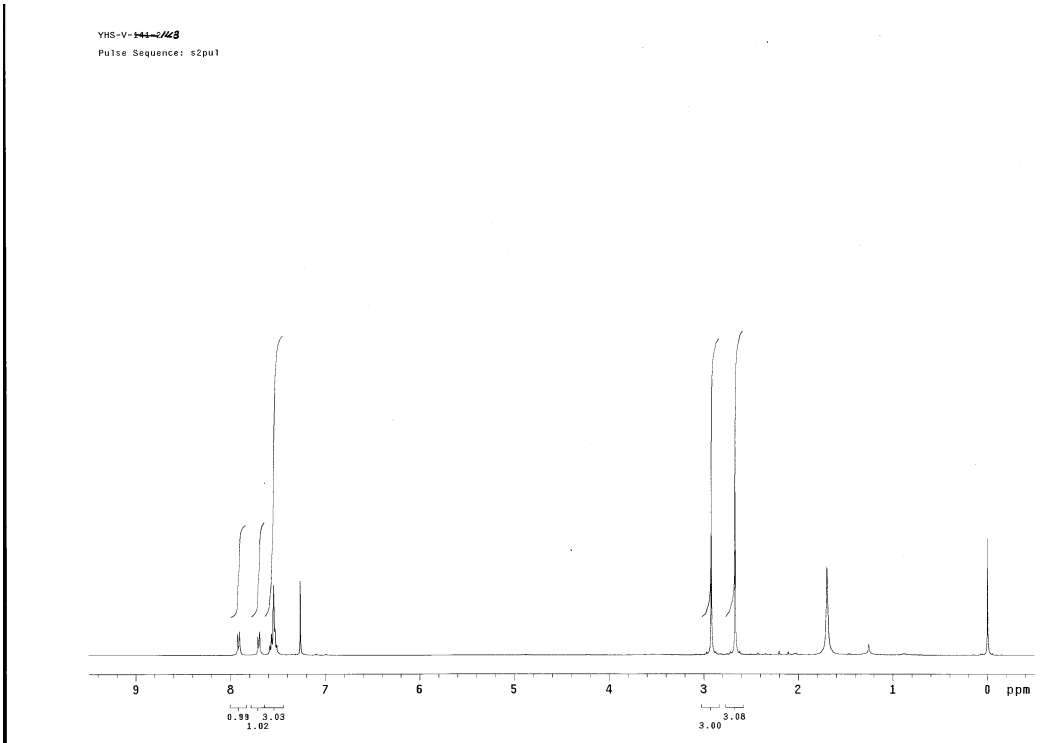


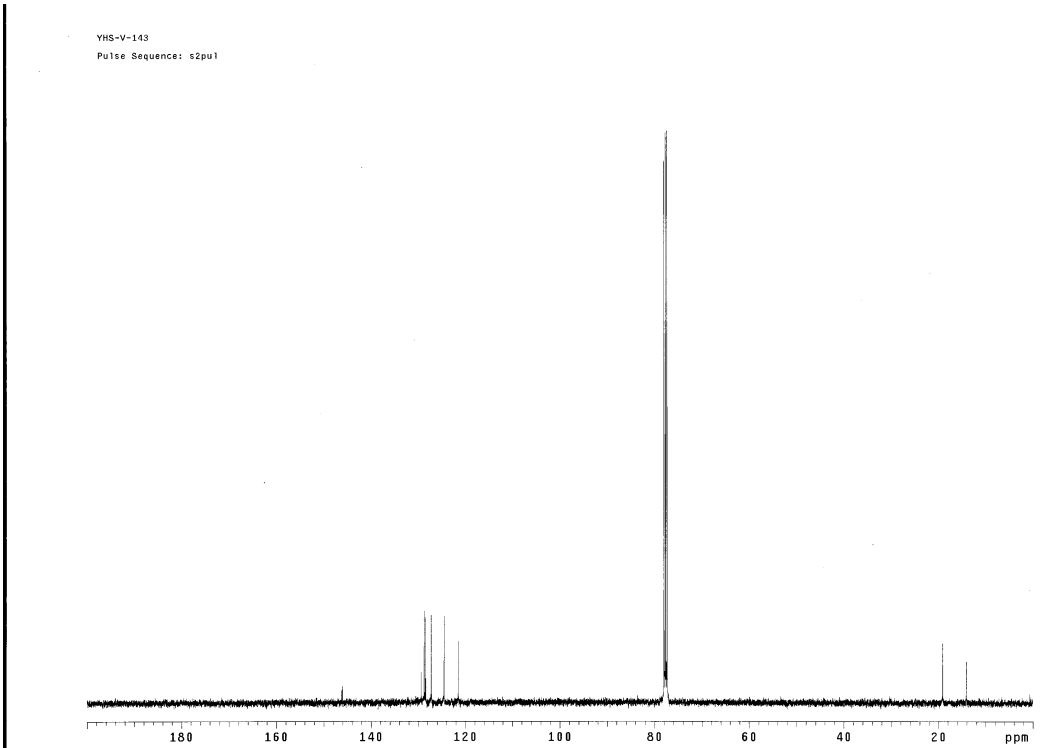


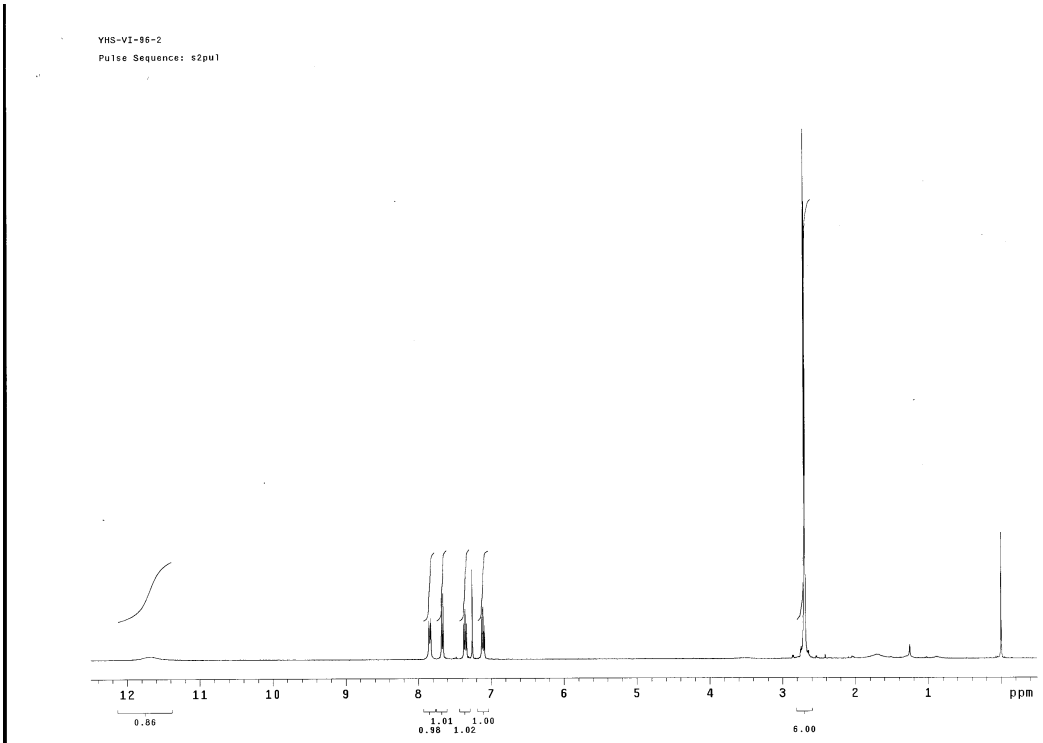


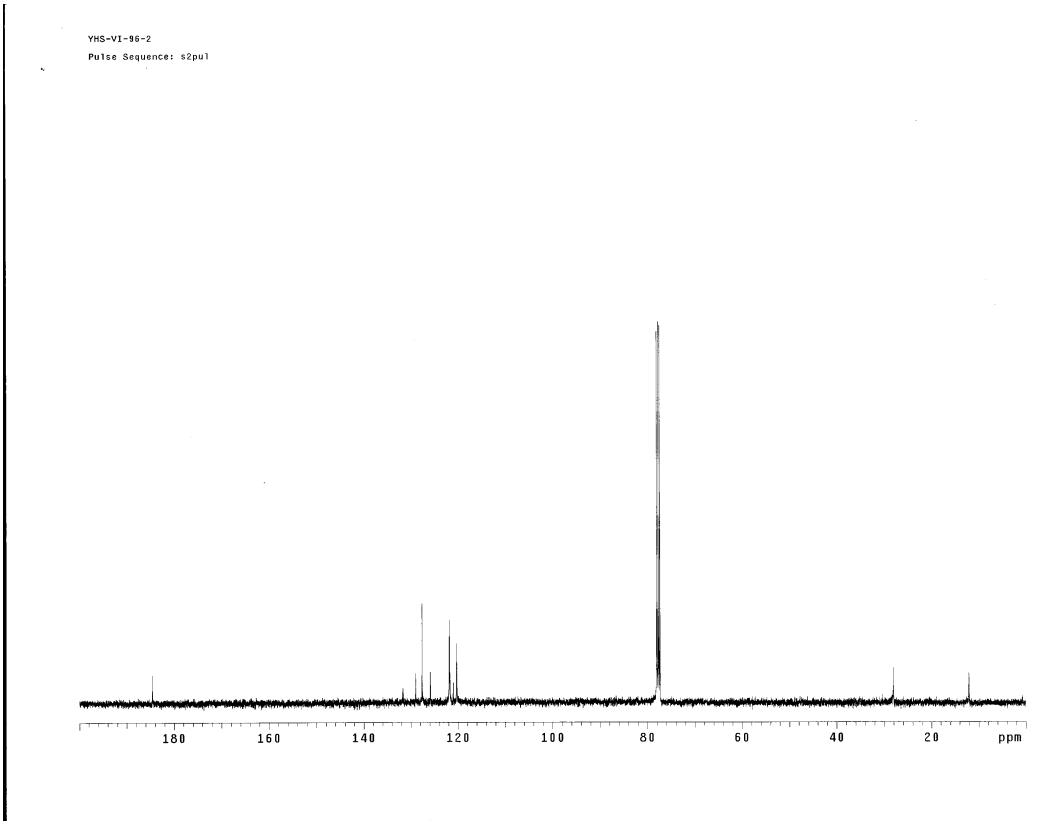


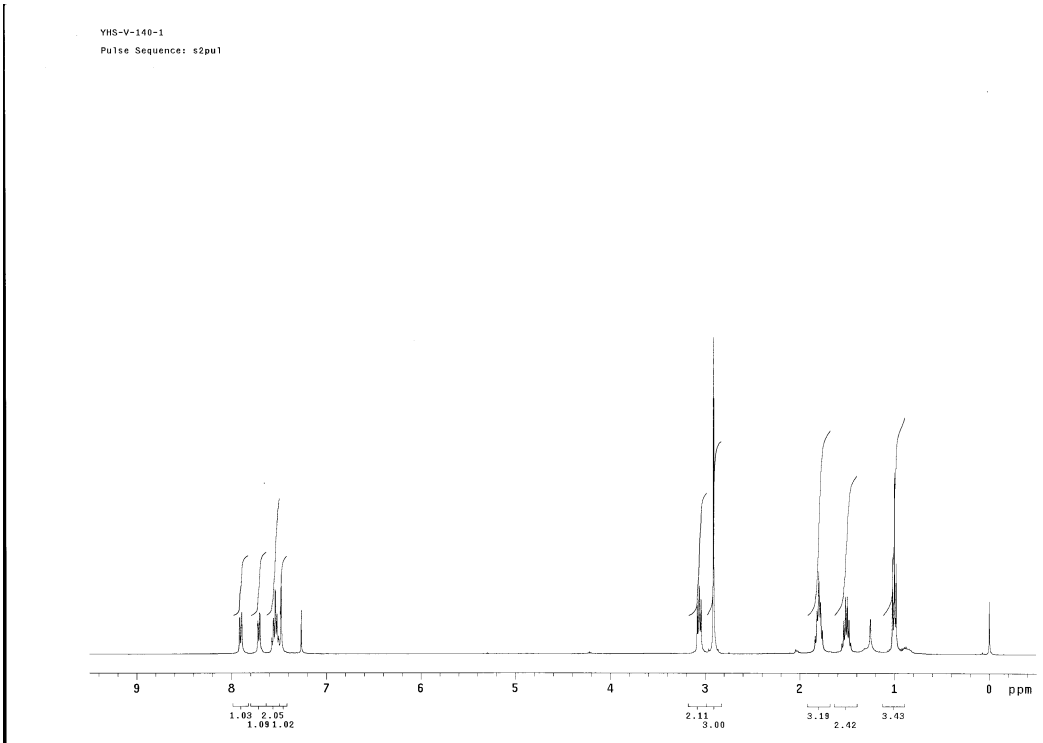


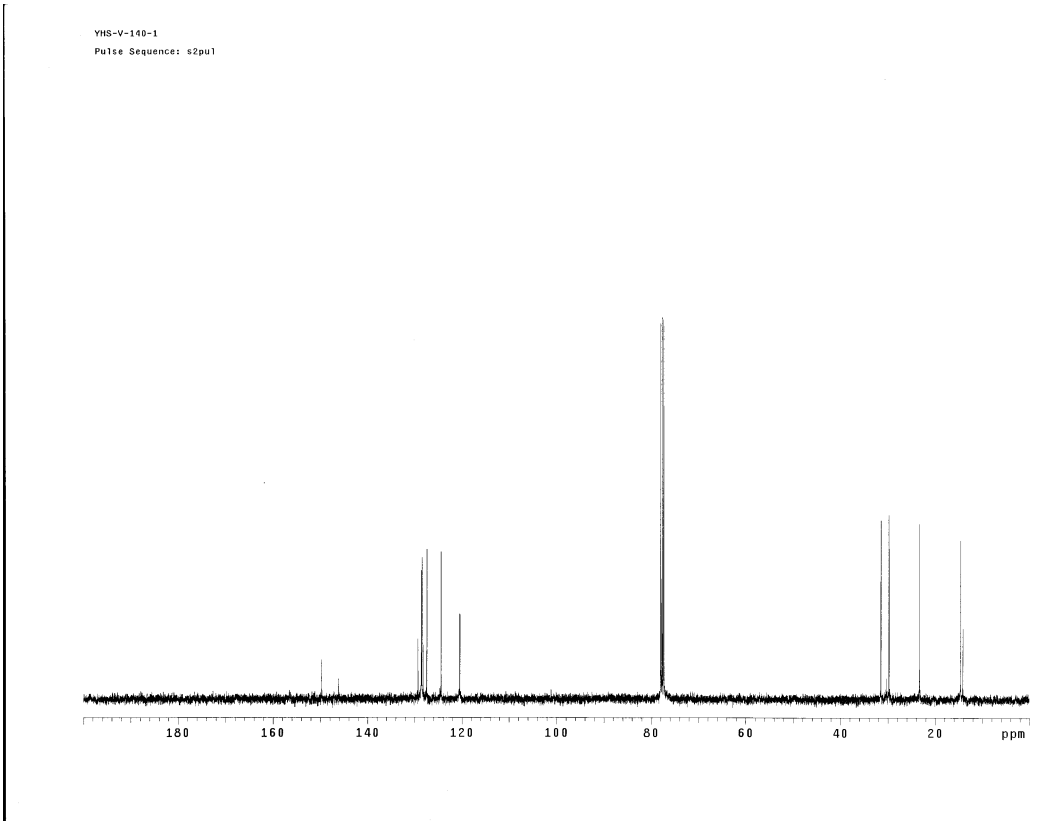


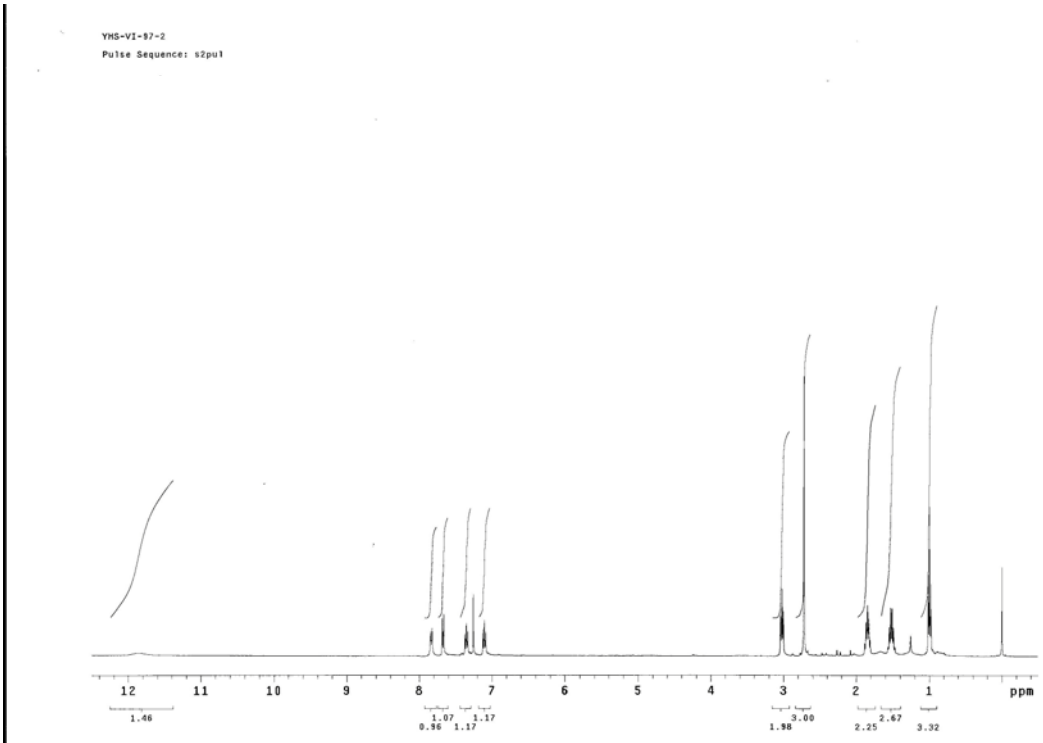


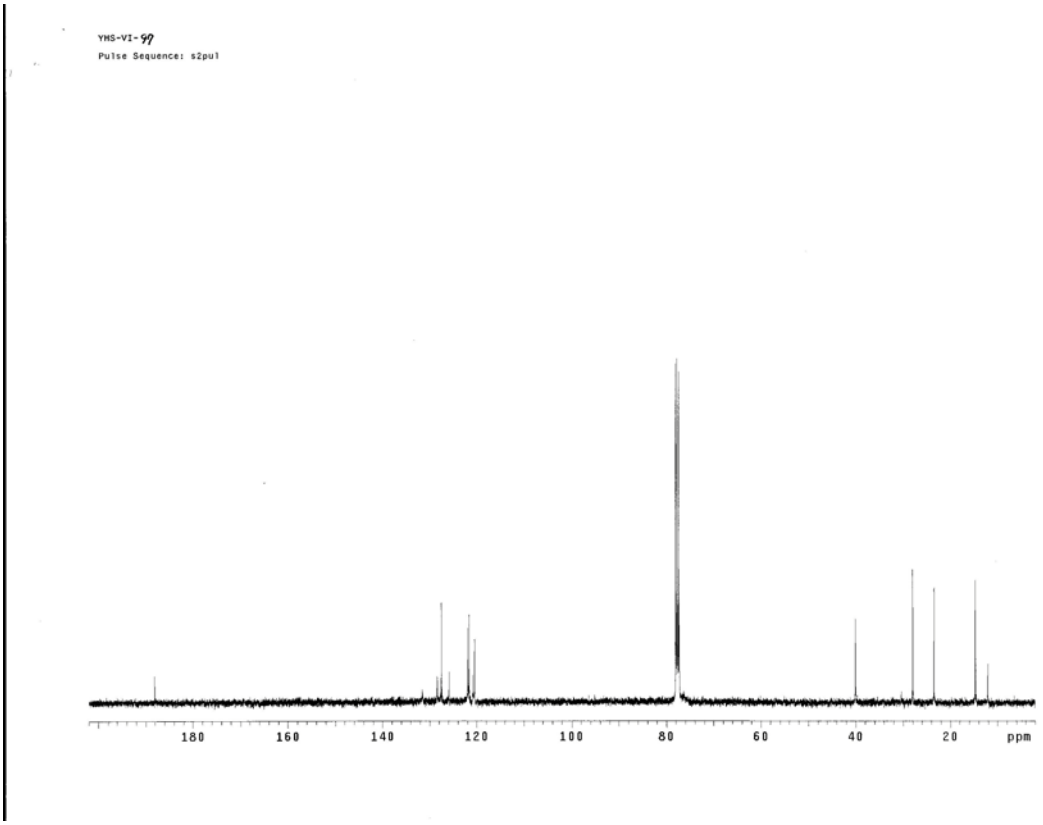


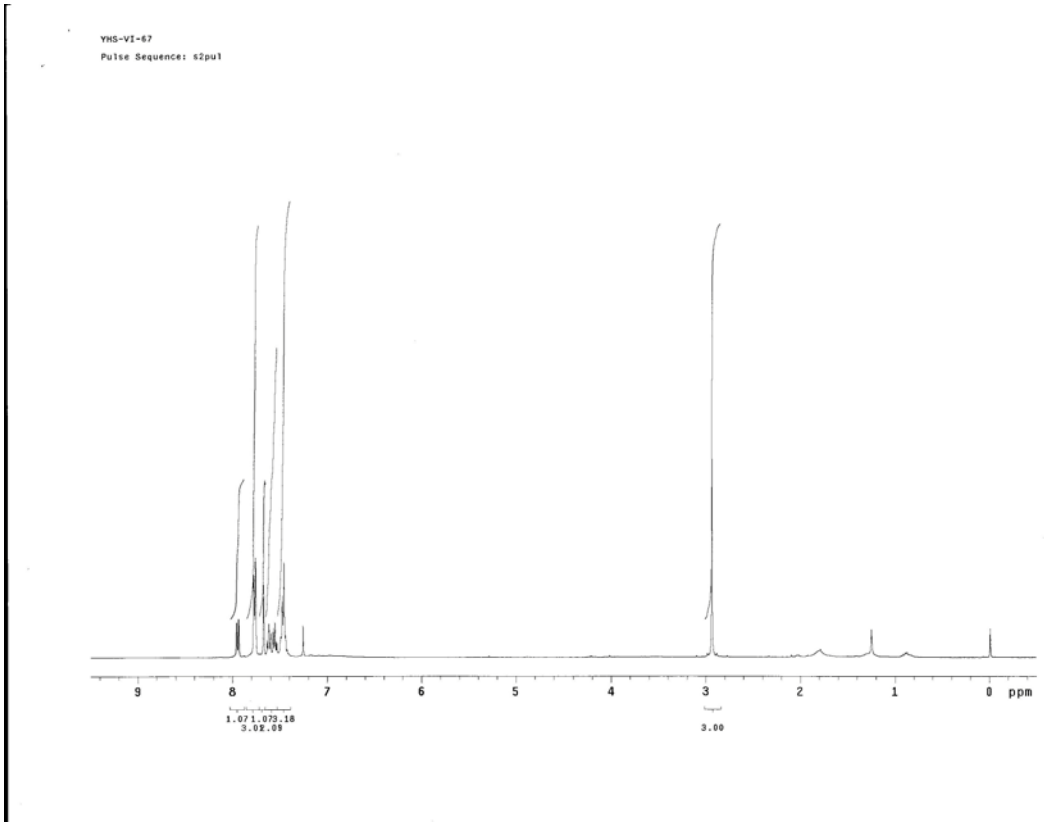


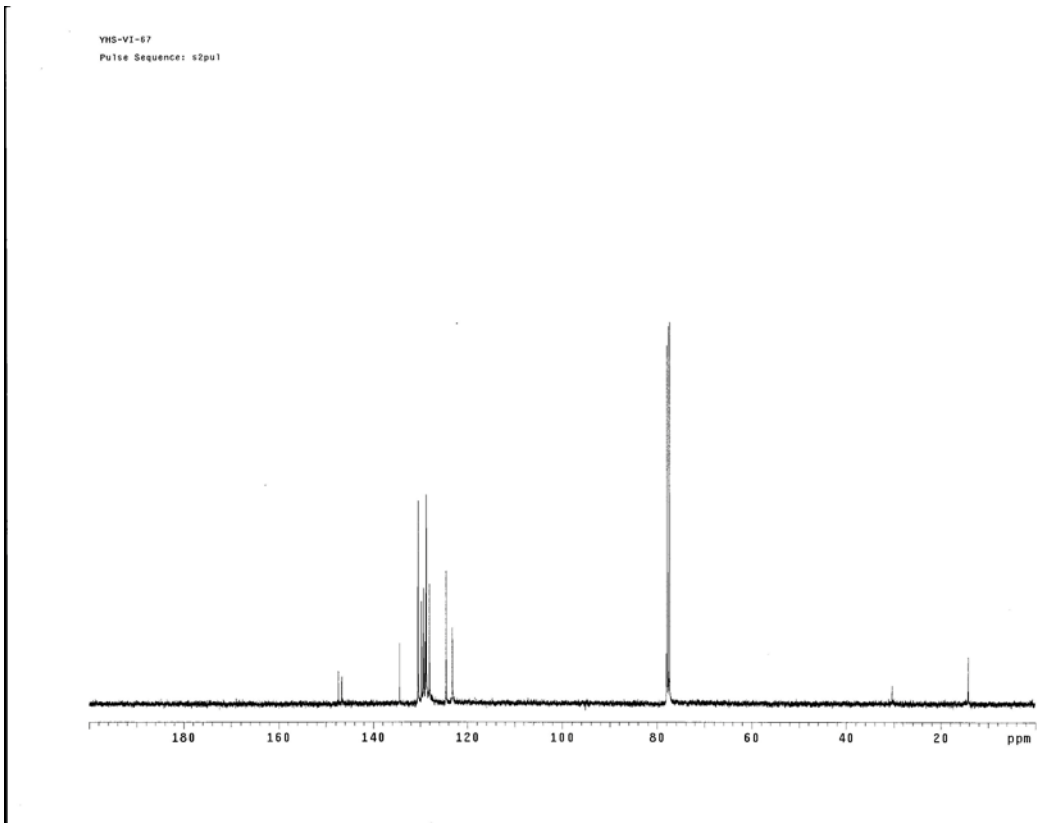


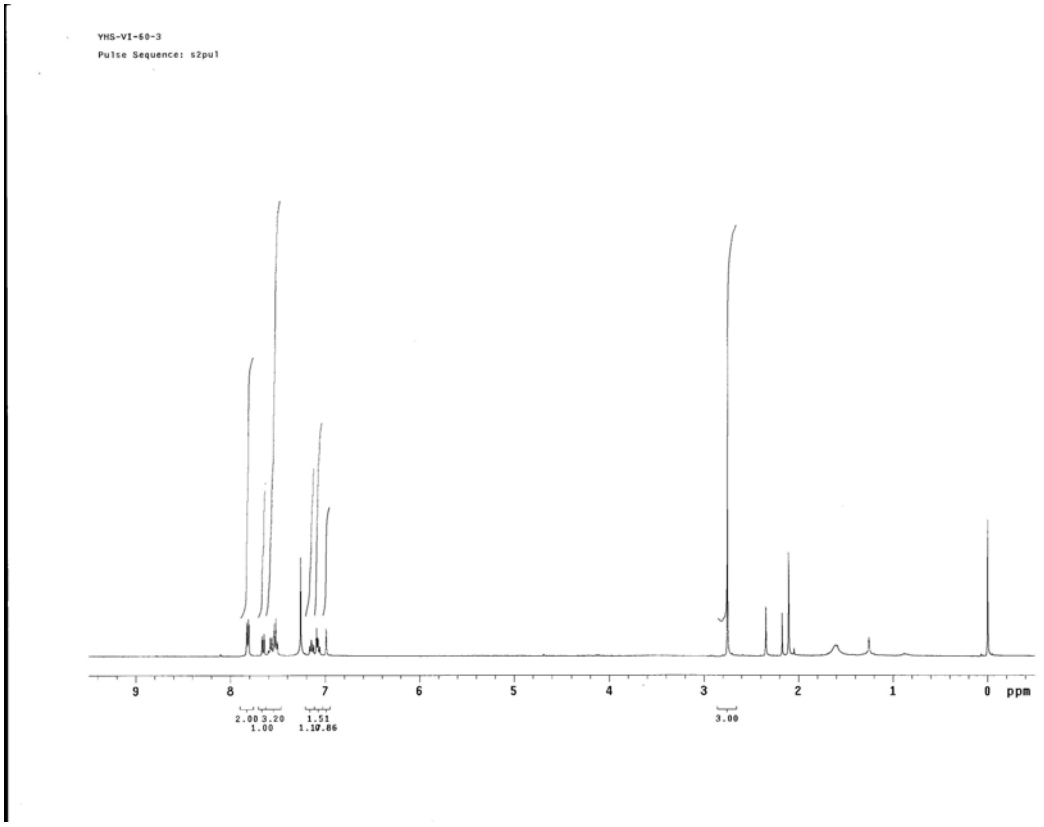


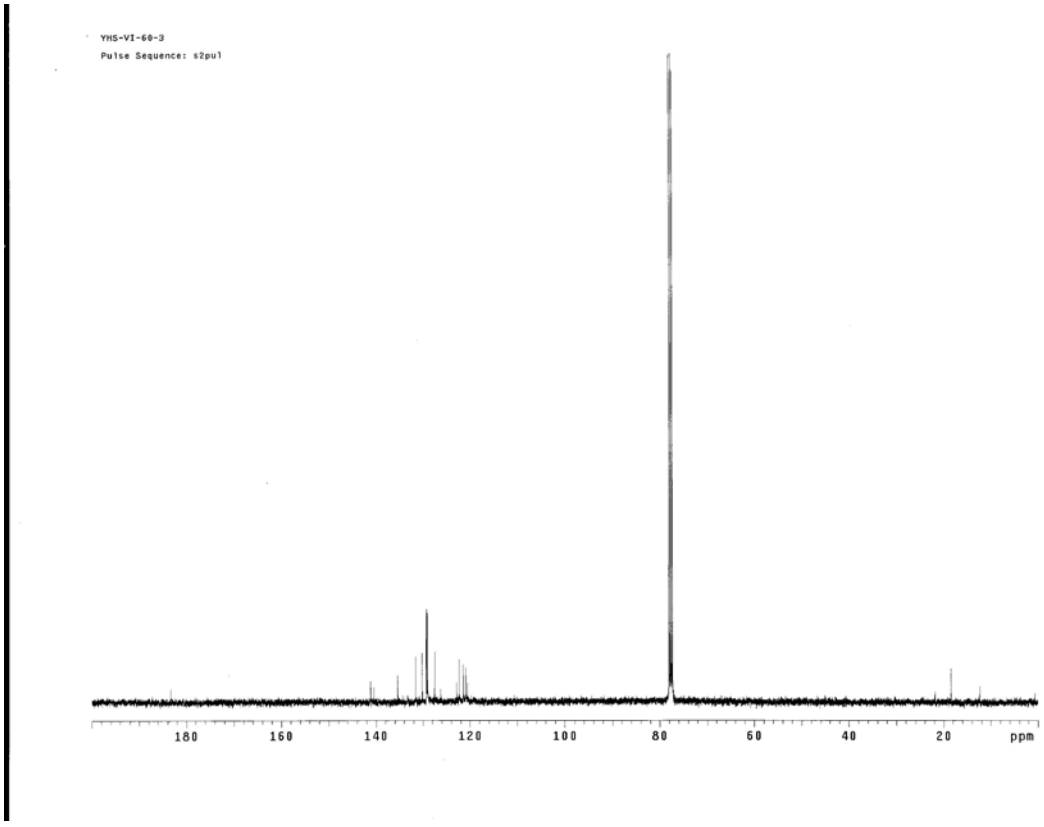

YHS-VI-97-2
Pulse Sequence: s2pul
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.46
1.07
0.96
1.17
1.17
3.00
1.98
2.67
2.25
3.32

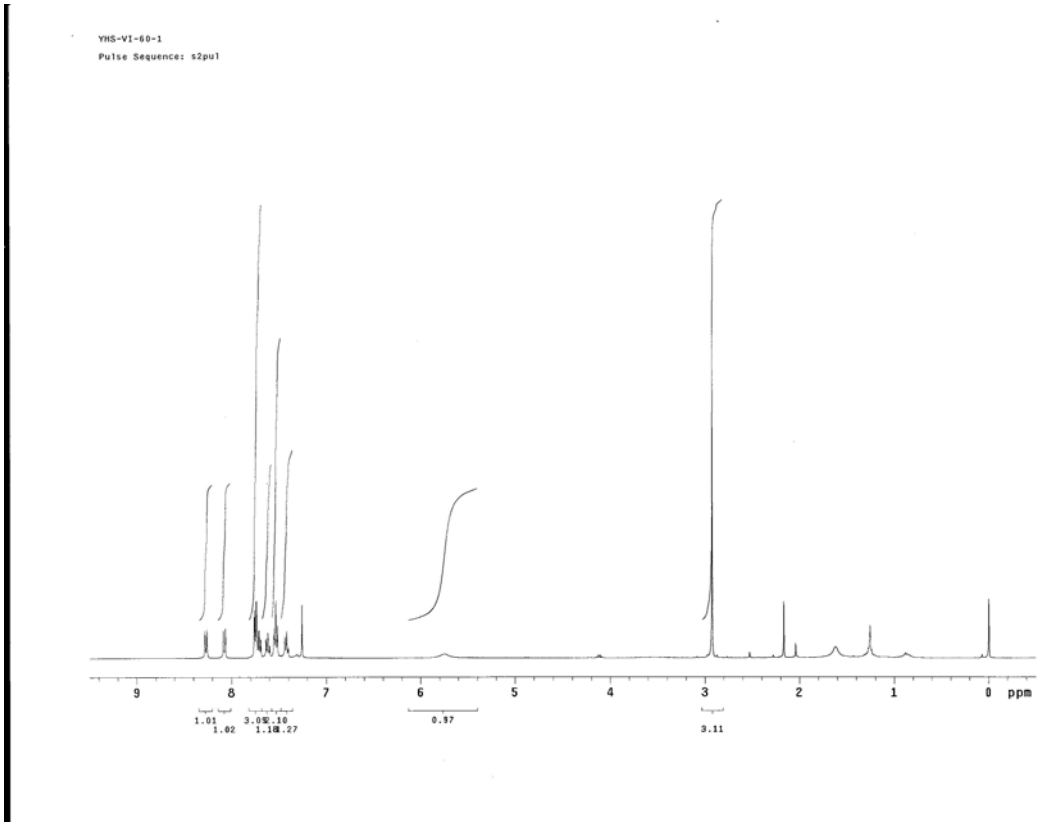

YHS-VI-97
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
ppm

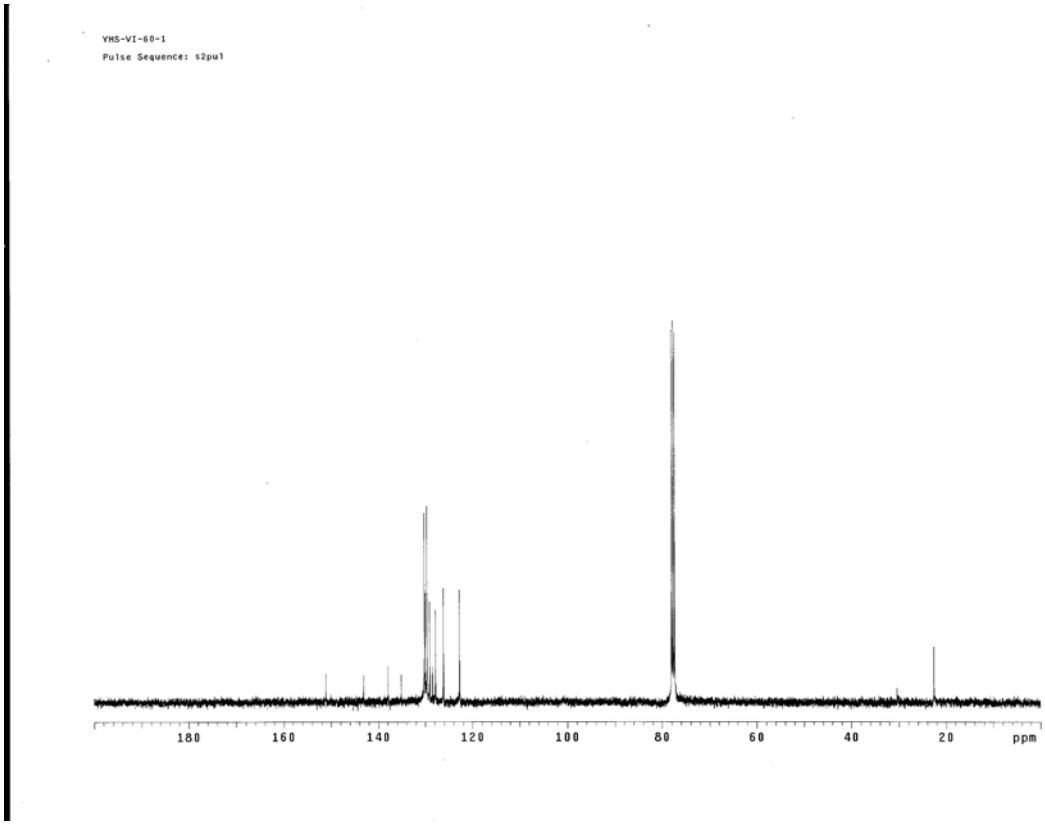


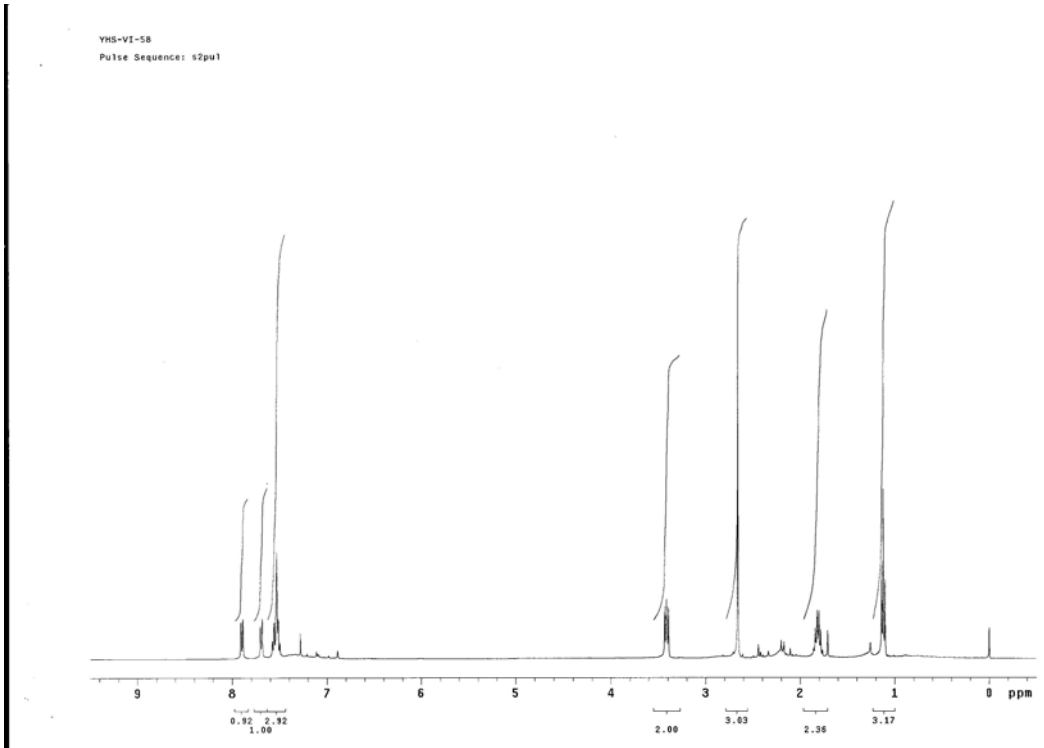


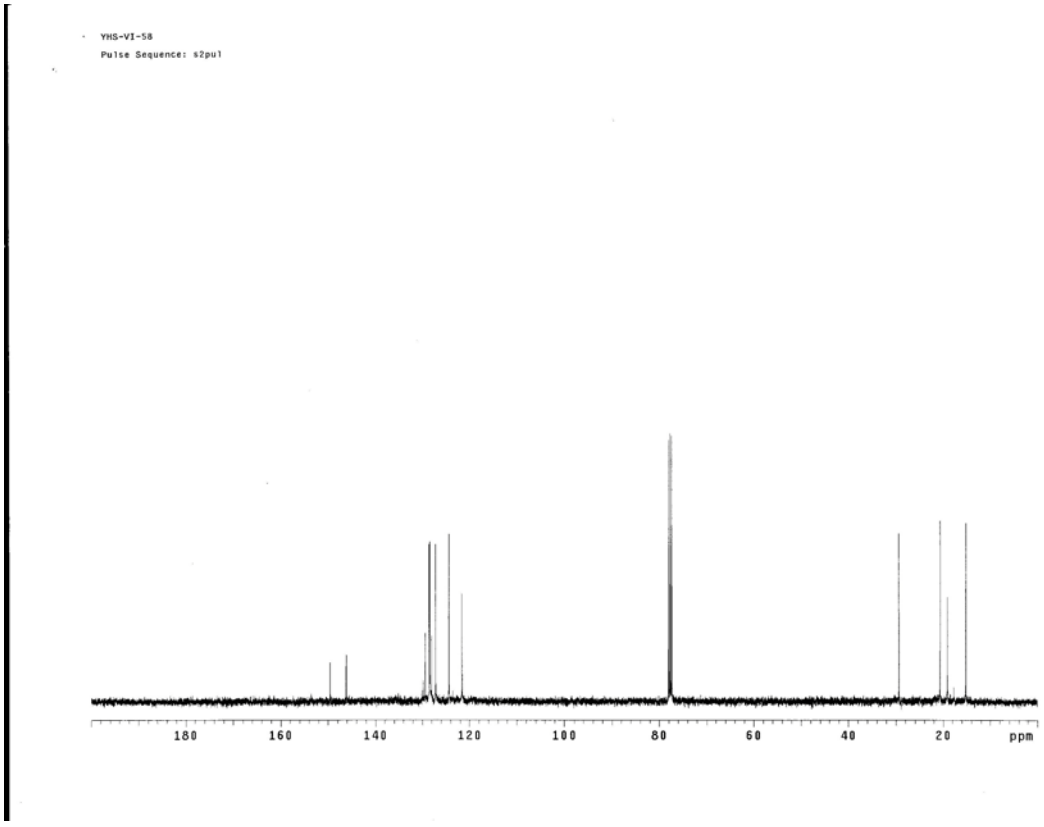


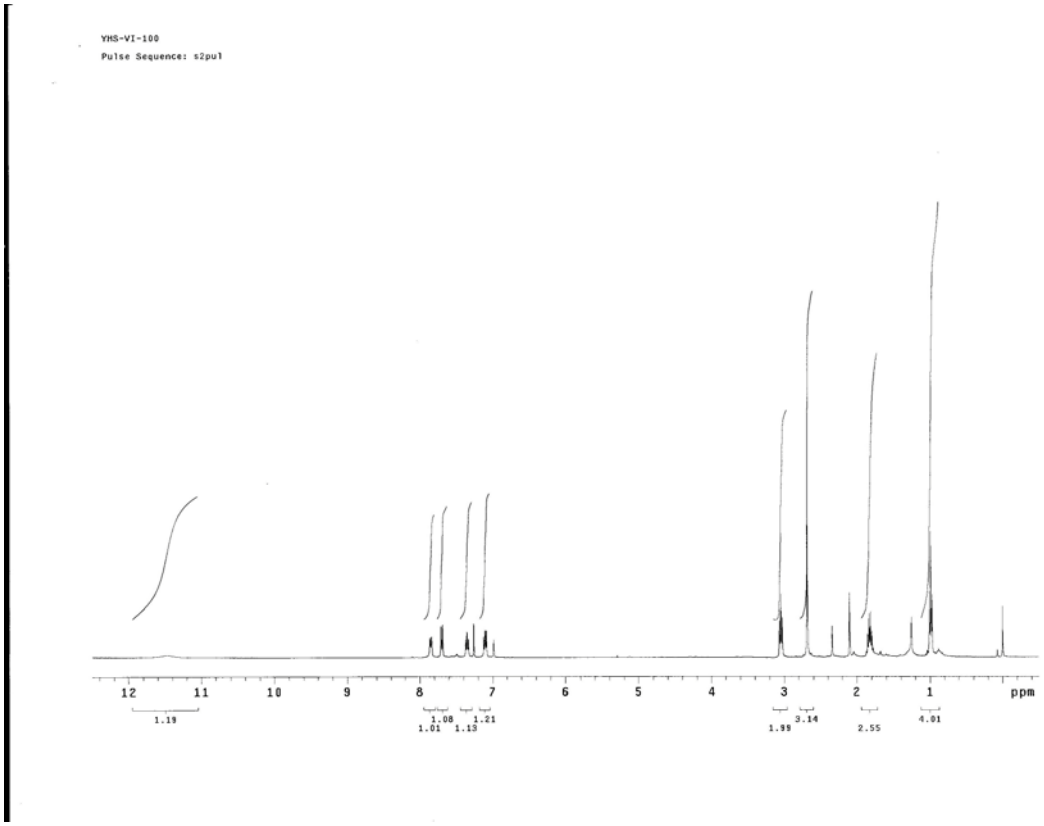


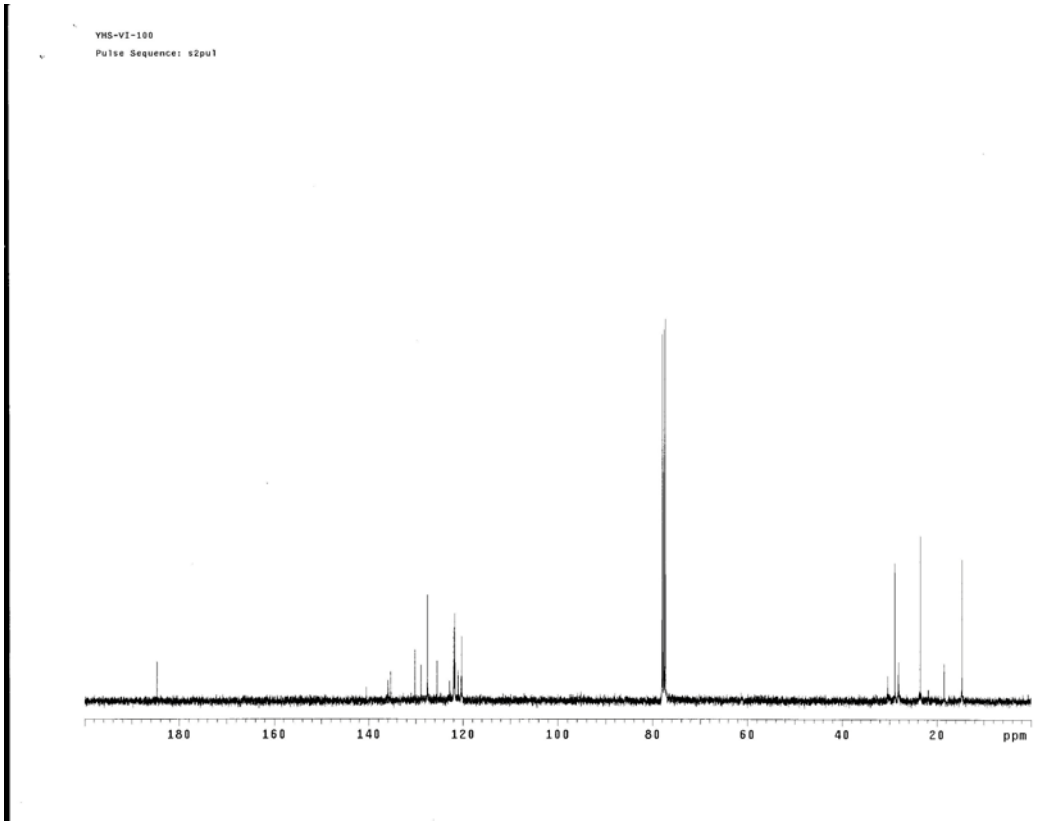


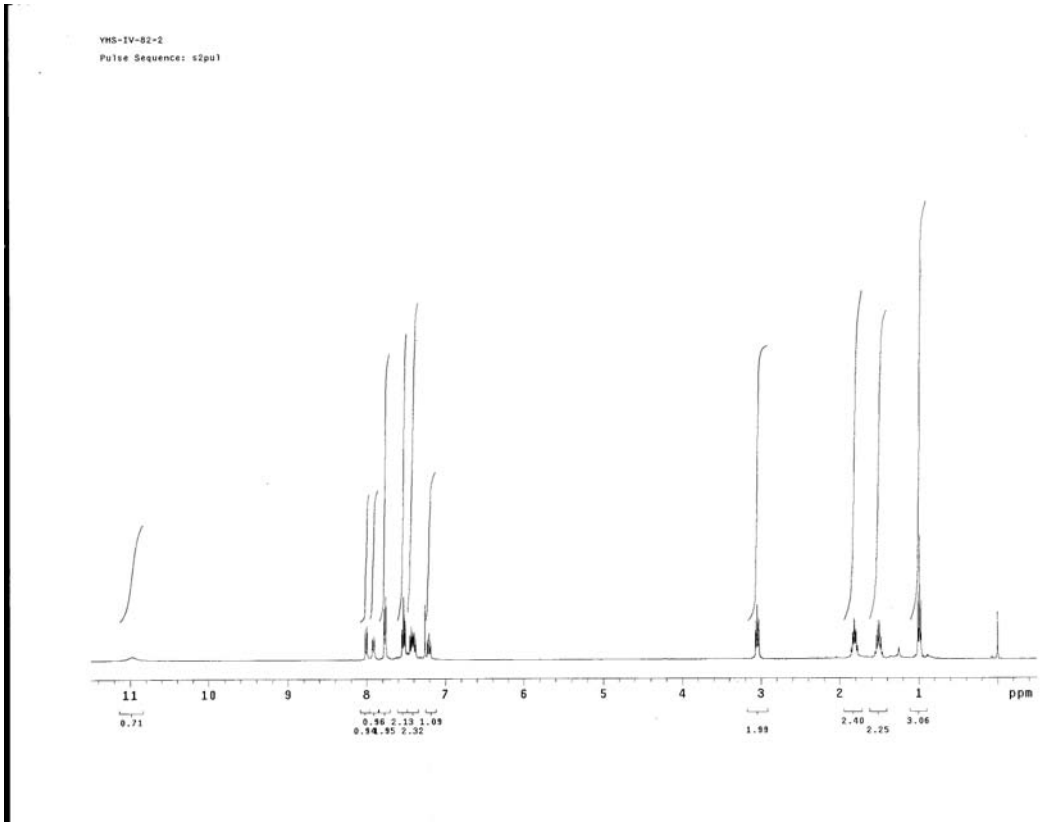


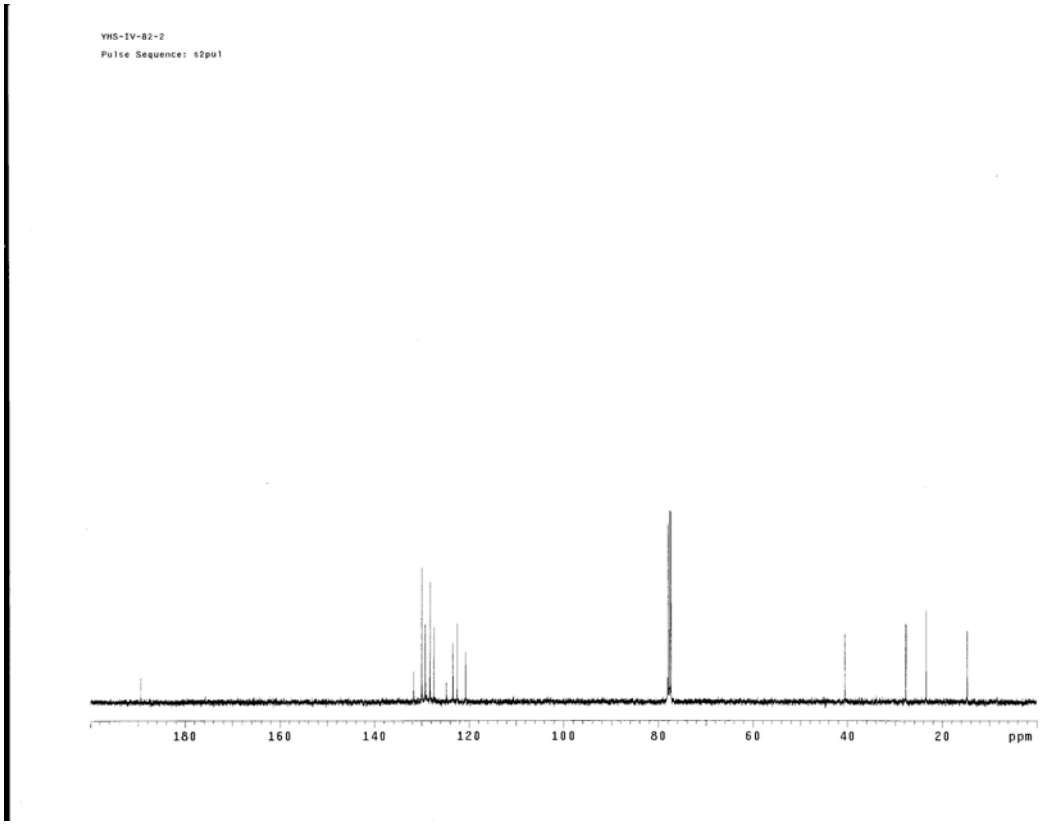

YHS-VI-58
Pulse Sequence: s2pul
9
8
7
6
5
4
3
2
1
0 ppm
0.92
2.92
1.00
2.00
3.03
2.36
3.17

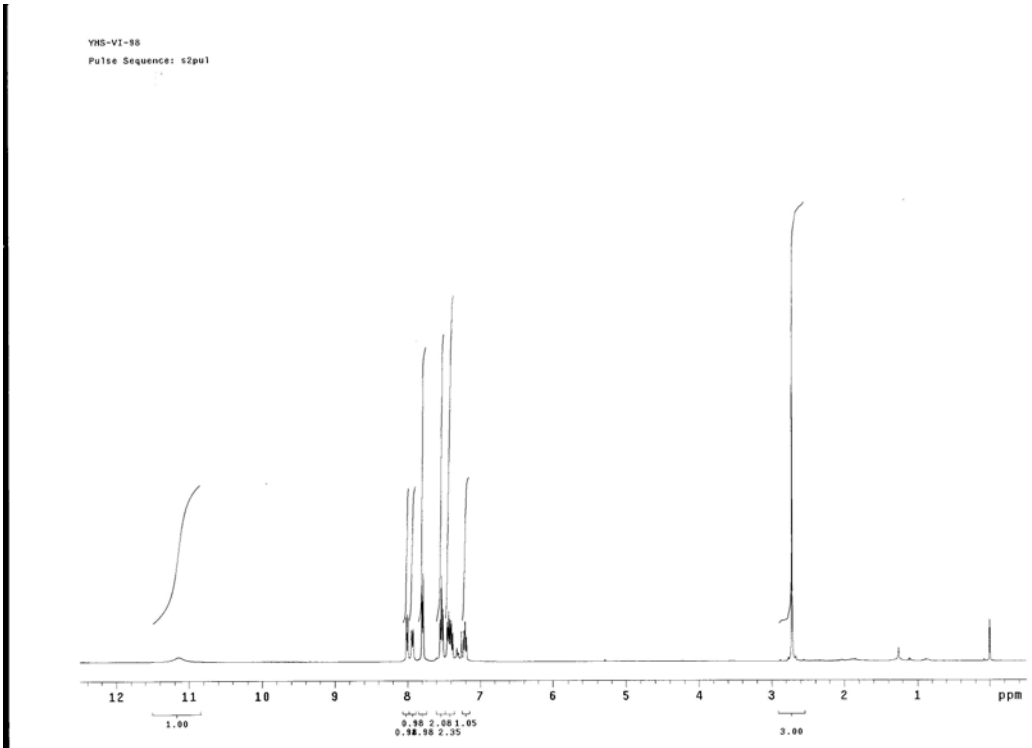

YHS-VI-58
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
ppm

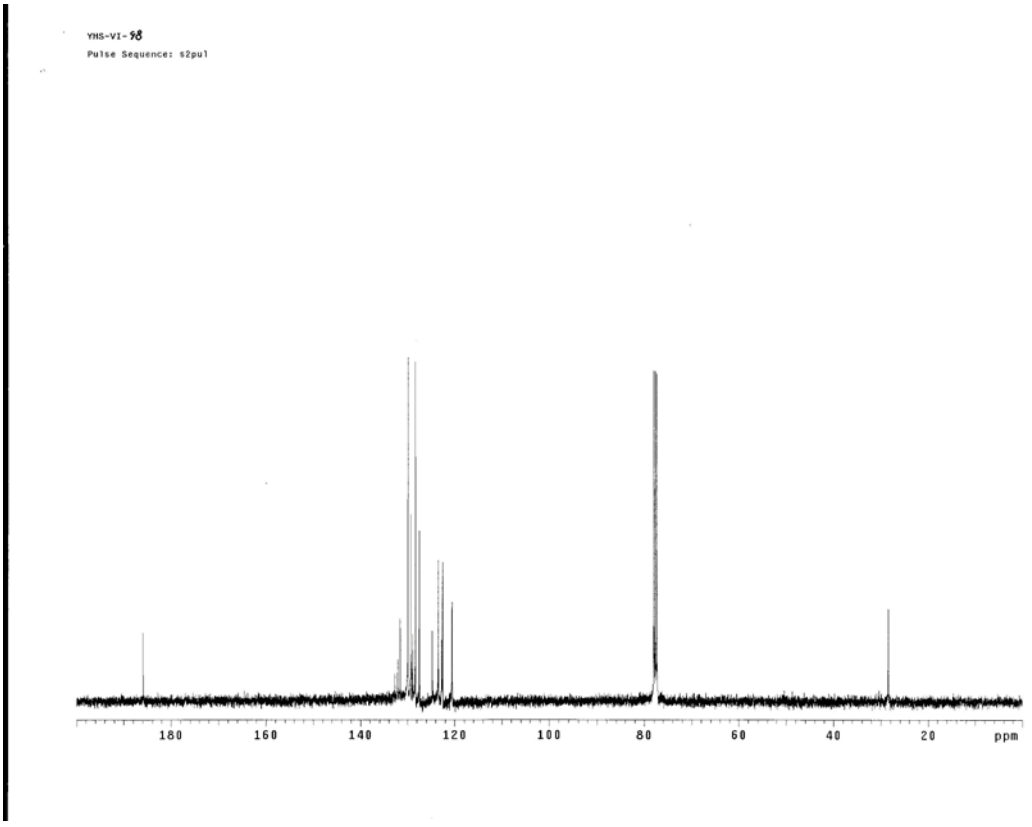


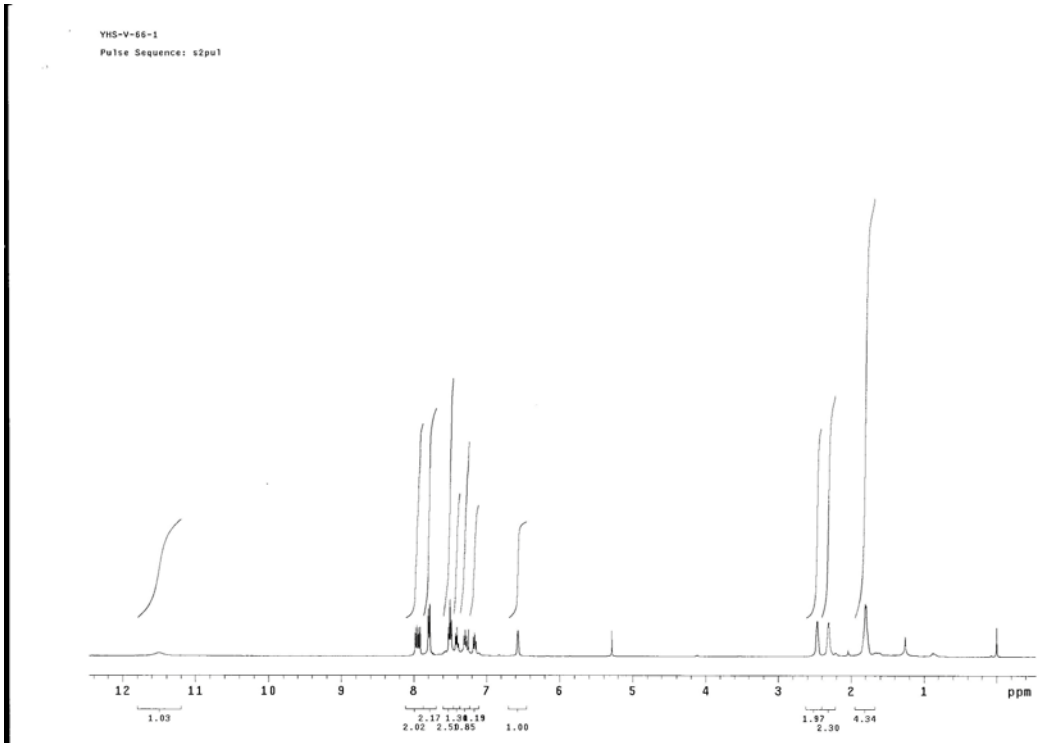


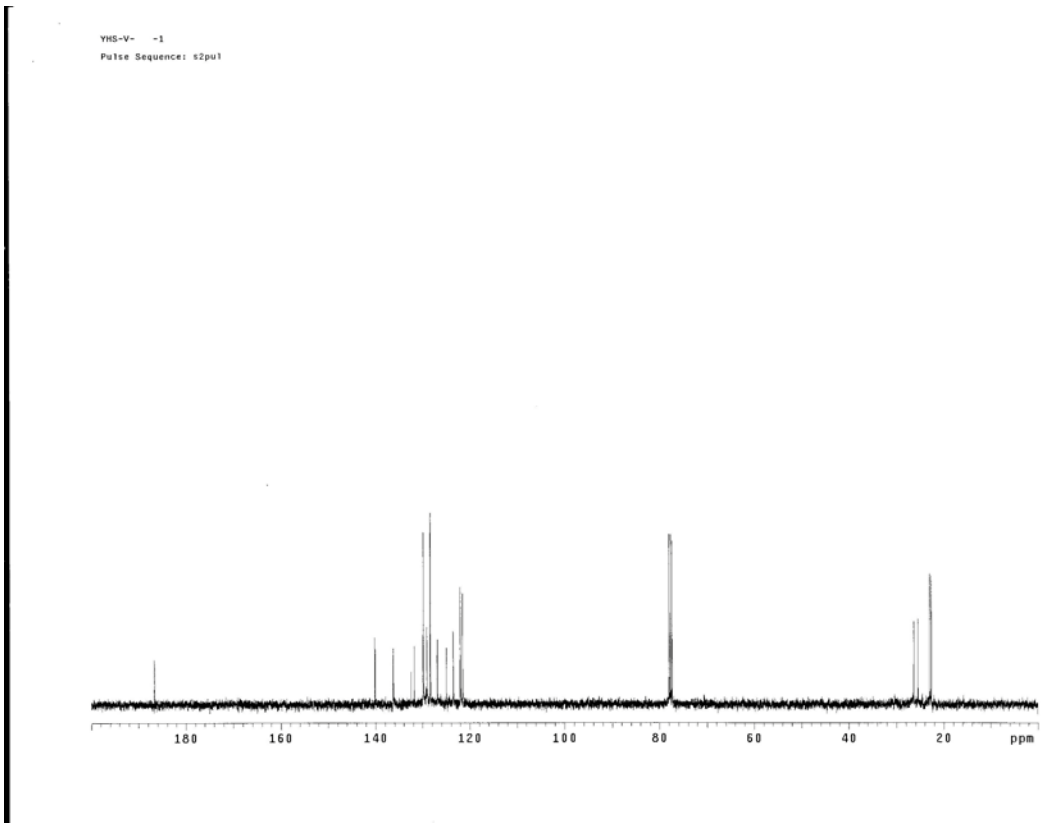

YHS-IV-82-2
Pulse Sequence: s2pul
11
10
9
8
7
6
5
4
3
2
1
ppm
0.71
0.96 2.13 1.09
0.94 1.95 2.32
1.99
2.40
2.25
3.06

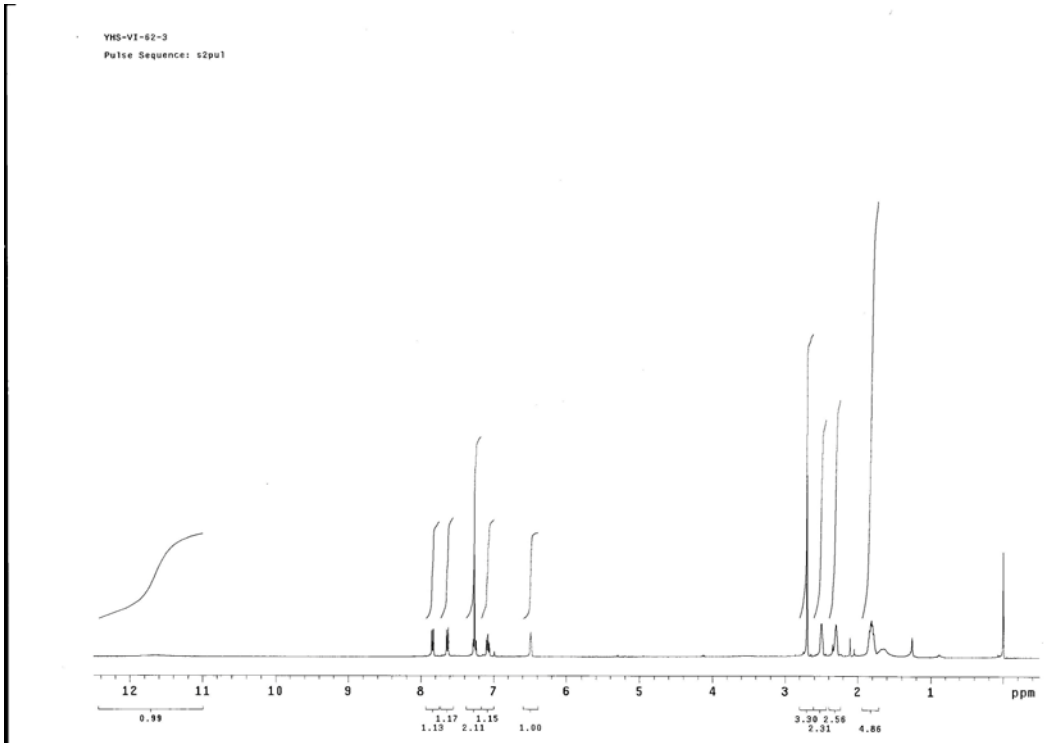

YHS-IV-82-2
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
ppm

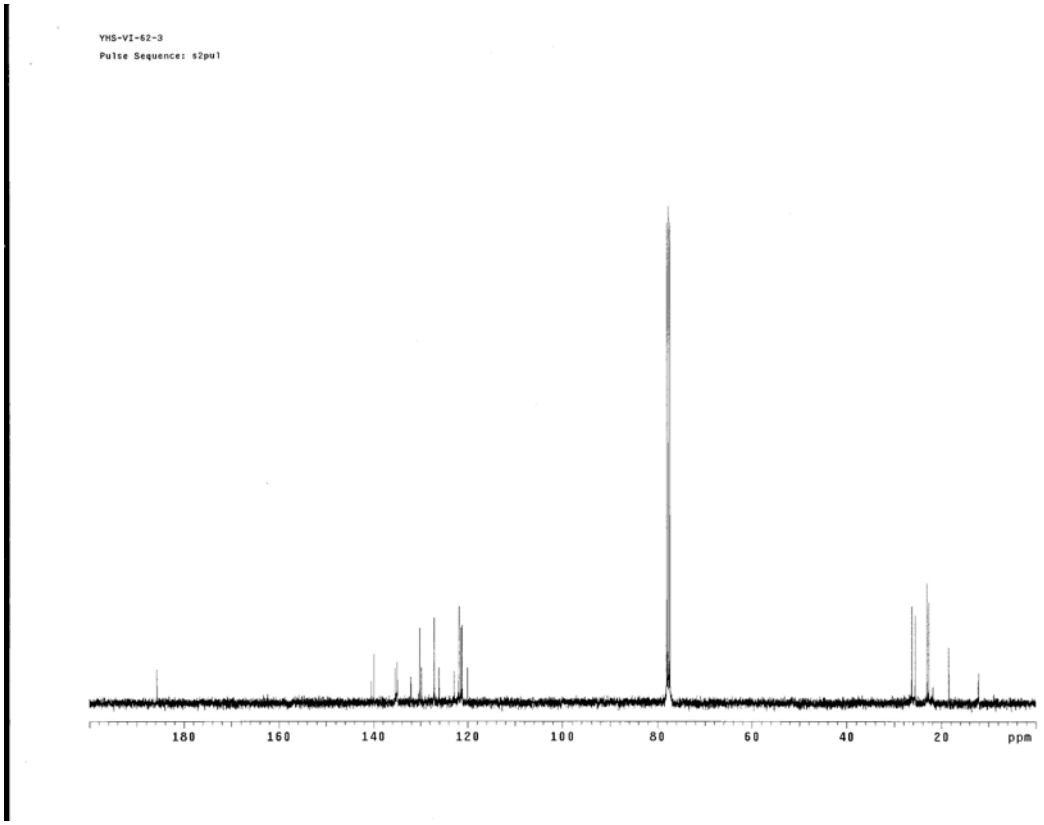


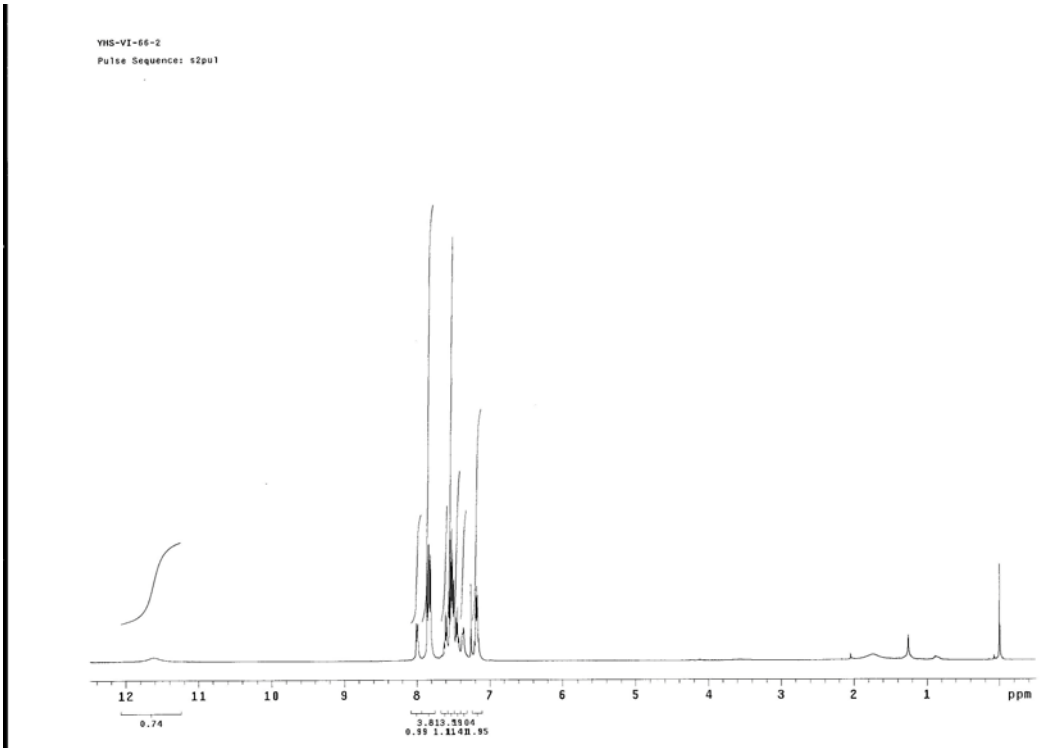


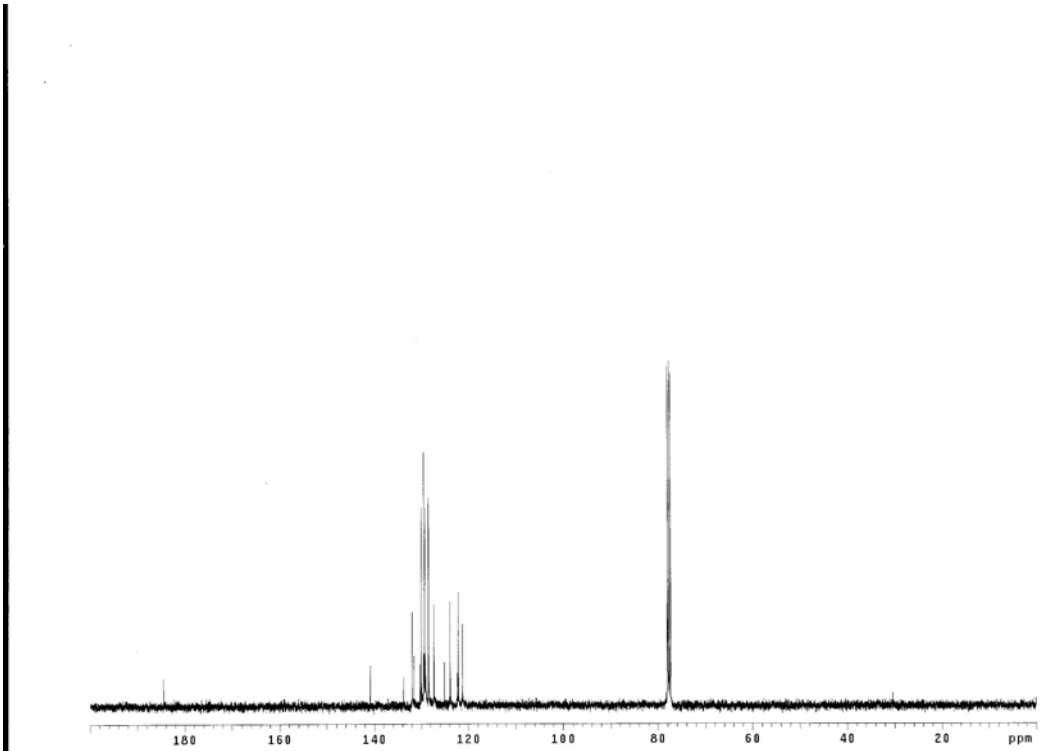

YHS-V-66-1
Pulse Sequence: s2pul
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
2.02
2.17
1.34
2.50
1.19
0.85
1.00
1.97
2.30
4.34

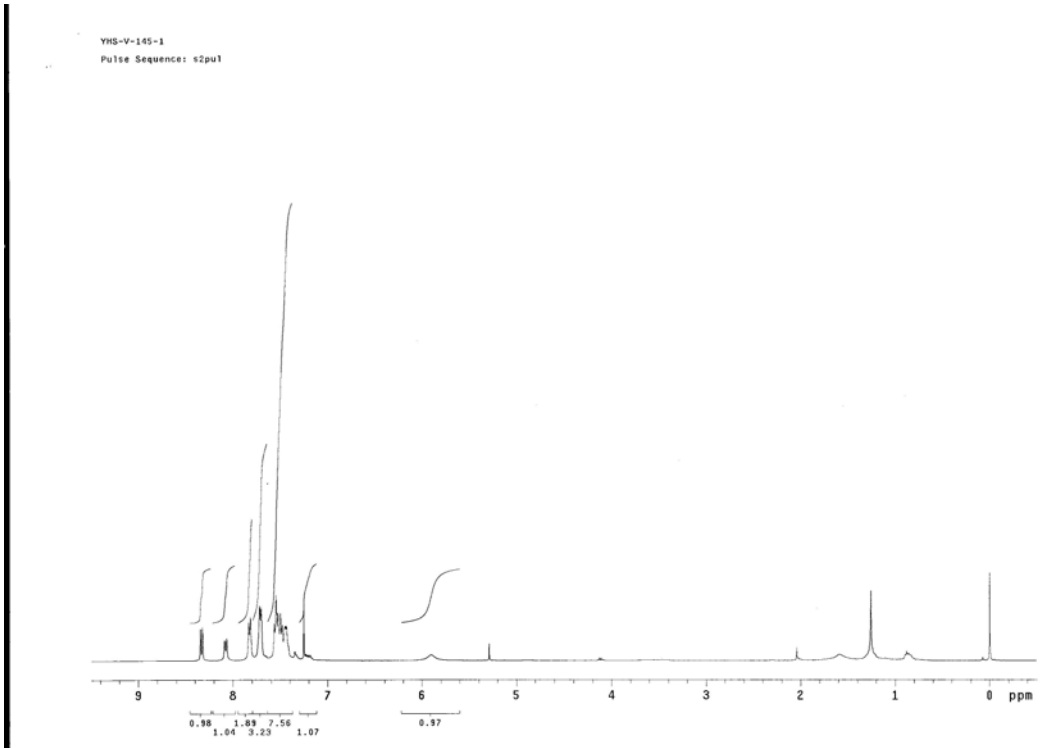

YHS-V- -1
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
ppm

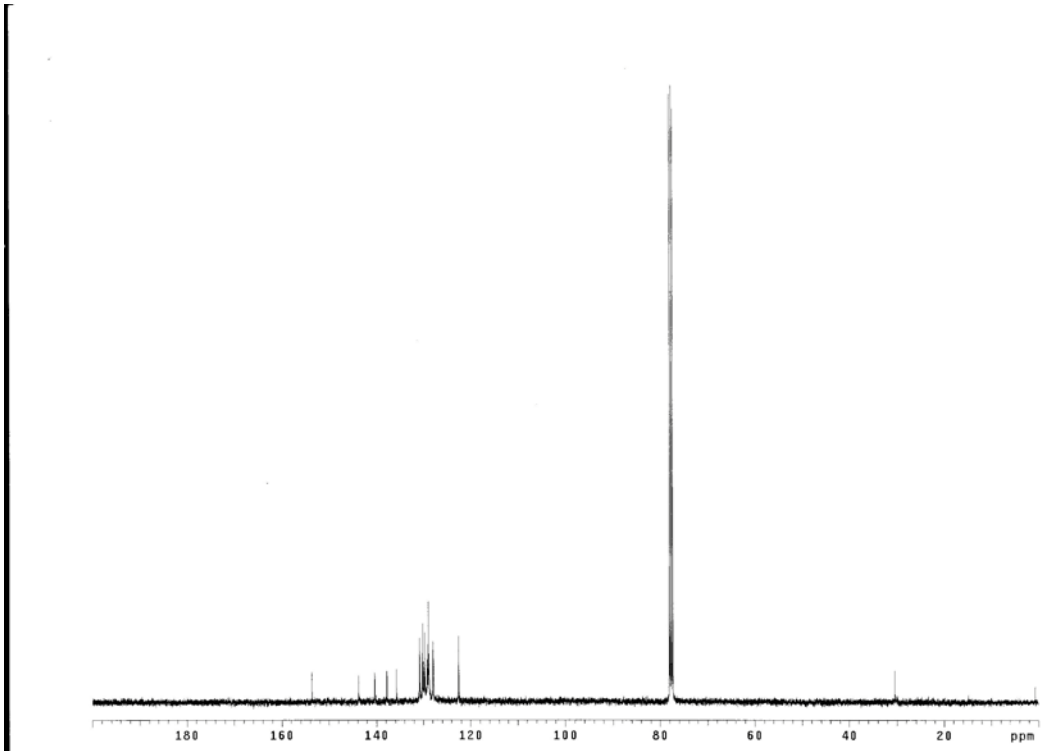


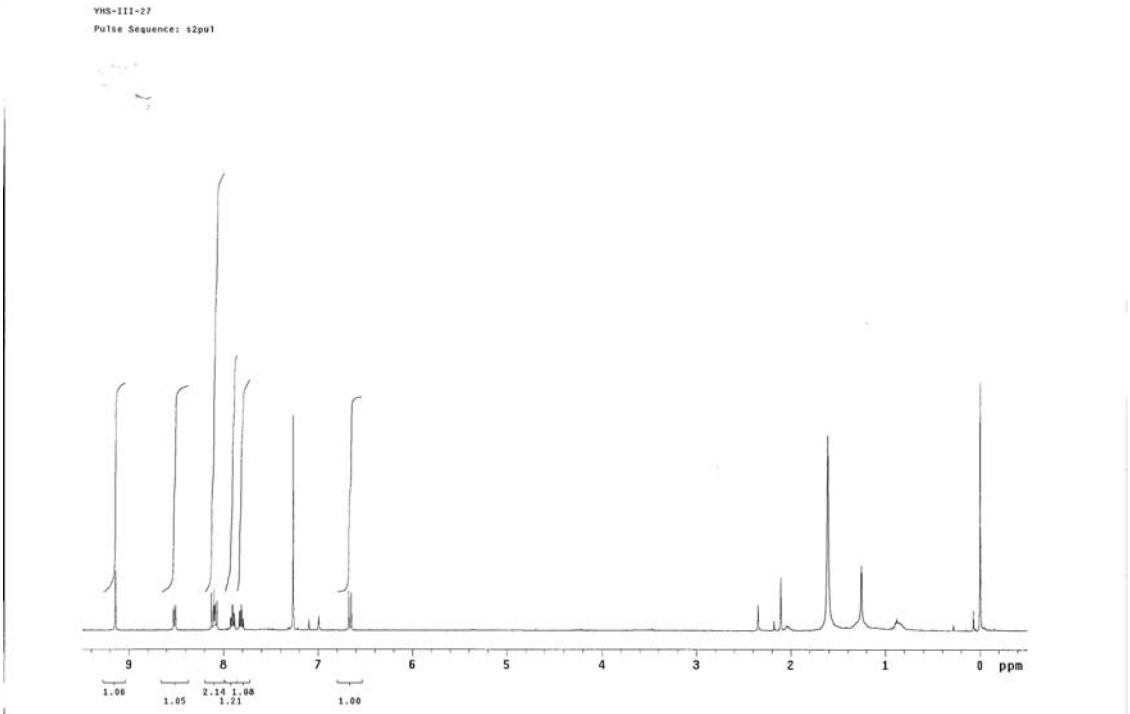


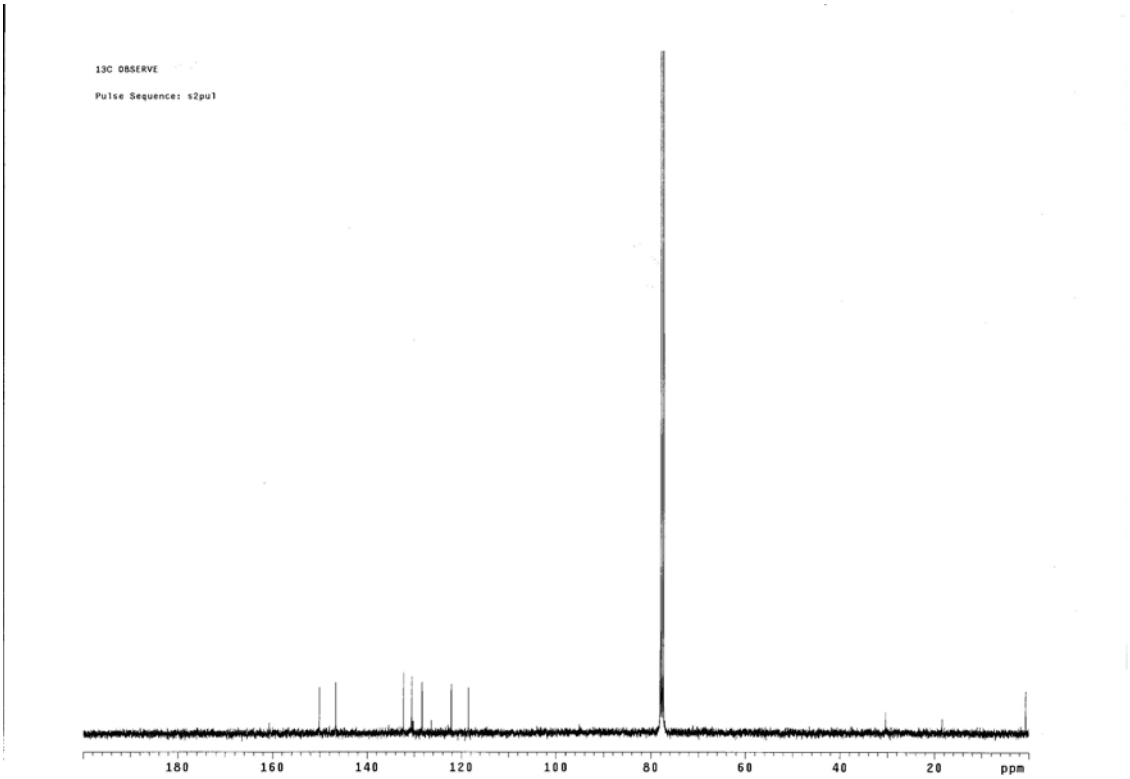

YHS-VI-66-2
Pulse Sequence: s2pul
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.74
3.813.3804
0.99 1.1141.95

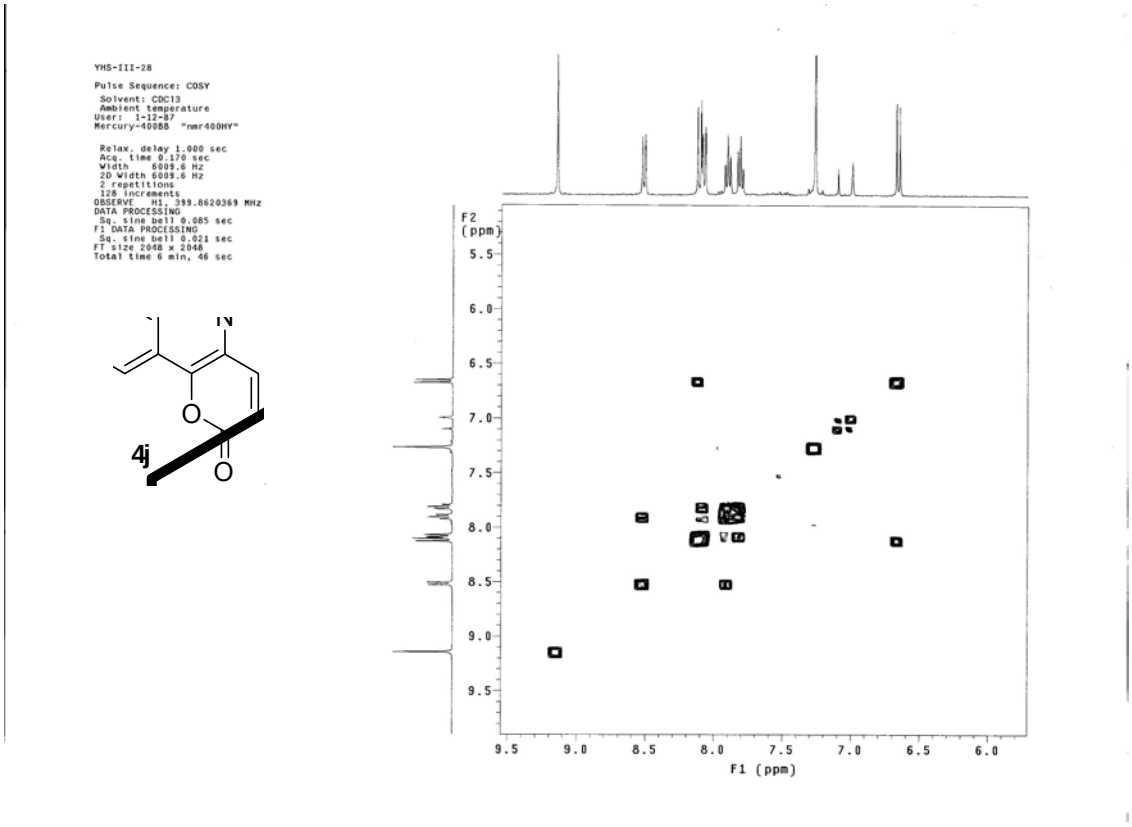

180
160
140
120
100
80
60
40
20
ppm










YHS-III-28
Pulse Sequence: COSY
Solvent: CDCl3
Ambient temperature
User: 1=12=87
Mercury-400BB "nmr400HY"
Relax. delay 1.000 sec
Acq. time 0.170 sec
Width 6009.6 Hz
2D Width 6009.6 Hz
2 repetitions
128 increments
OBSERVE H1, 399.8620369 MHz
DATA PROCESSING
Sq. sine bell 0.085 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
FT size 2048 x 2048
Total time 6 min, 46 sec
N
O
4j
O
F2 (ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
F1 (ppm)