Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Au(I)-Catalyzed Intramolecular Oxidative Cyclopropanation of 1,6-Enynes Derived from Propiolamides with Diphenyl Sulfoxide

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Contents

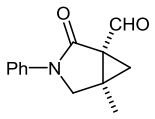
1. General Information

All commercially available reagents used without further purification. All solvents were purified according to the literature unless otherwise specified.[1] TLC (Thin-layer chromatography) analysis was carried out on Merck silica gel 60 F254 TLC plate and was visualized with UV lamp and potassium permanganate solution. Flash column chromatography was performed on Kieselgel 60 (230-400 mesh). ^{1}H, ^{13}C NMR and COSY spectra were recorded on a Varian (Mercury, 400 MHz) spectrometer with TMS as an internal standard. High resolution mass spectra (HRMS) were obtained from Korea Basic Science Institute (KBSI) at Seoul, Korea.

2. Representative Procedure

A mixture of Au(SPhos)Cl (6.4 mg, 0.01 mmol) and $AgNTf_2$ (3.9 mg, 0.01 mmol) was dissolved in 1,2-dichloroethane and was stirred for 10 min at room temperature. To this mixture was added 1,6-enyne **4a** (39.9 mg, 0.20 mmol) and diphenyl sulfoxide (80.9 mg, 0.40 mmol). The resulting mixture was heated at 60 ^{o}C for 2 h. After completion of reaction (TLC), solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (EtOAc:Hex = 1:6) to provide cyclohexane carboxaldehyde **5a** (24.0 mg, 56 %) along with a small amount of enyne metathesis product **6a** (2.9 mg, 7 %). For substrates **4c, 4g-4i**, the corresponding products **5c, 5g-i** co-eluted with the residual $Ph_2S{=}O$. In these cases, the products were treated with $NaBH_4$ (2 equiv.) in MeOH before chromatographic purification.

3. Characterization Data

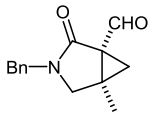


5a

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (s, H), 7.55 (d, *H* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, H), 3.81 (s, 2H), 2.04 (d, *J* = 3.9 Hz, H), 1.56 (d, *J* = 3.9 Hz, H), 1.52

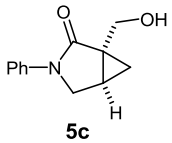
[1] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals;* Elsevier: Oxford, 2009.

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 171.6, 138.7, 129.2, 125.0, 119.8, 54.6, 43.6, 34.9, 30.0, 15.3; HRMS(EI+) Calcd for $C_{13}H_{14}NO_2$ [M+1] 216.1025, found 216.1025.



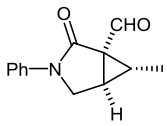
5b

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, H), 7.40-7.25 (m, 3H), 7.20 (d, *J* = 6.6 Hz, 2H), 4.52 (d, *J* = 14.8 Hz, H), 4.30 (d, *J* = 14.4 Hz, H), 3.26 (d, *J* = 10.2 Hz, H), 3.17 (10.1 Hz, H); 1.93 (d, *J* = 3.5 Hz, H), 1.36 (s, 3H), 1.34 (d, *J* = 3.9 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 172.2, 136.2, 128.9, 128.4, 127.9, 52.9, 46.4, 42.6, 35.9, 29.9, 15.3; HRMS(EI+) Calcd for $C_{14}H_{16}NO_2$ [M+1] 230.1181, found 230.1182.



5c

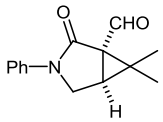
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, H), 4.05 (dd, *J* = 5.9, 10.2 Hz, H), 3.97 (d of ABq, *J* = 12.1 Hz, H), 3.85 (d of ABq, *J* = 12.1 Hz, H), 3.69 (d, *J* = 10.2 Hz, H), 2.81 (br s, H), 2.09-2.03 (m, H), 1.25-1.22 (m, H), 0.95 (t, *J* = 4.3 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 139.2, 129.1, 124.6, 119.7, 62.4, 49.7, 33.6, 17.2, 16.3; HRMS(EI+) Calcd for $C_{12}H_{14}NO_2$ [M+1] 204.1025, found 204.1025.



5d

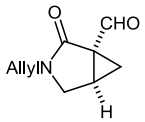
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, H), 3.99 (dd, *J* = 5.9, 9.8 Hz, H), 3.76 (d, *J* = 9.7 Hz, H), 2.51 (t, *J* = 5.5 Hz, H), 1.97 (app quintet, *J* = 6.1 Hz, H), 1.30 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 196.8, 170.9, 138.8, 129.1, 125.0, 120.0, 49.0, 44.7, 36.1, 28.6, 11.1; HRMS(EI+) Calcd for $C_{13}H_{14}NO_2$ [M+1] 216.1025, found 216.1023.



5e

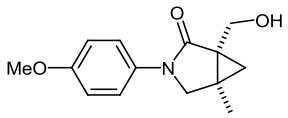
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, H), 4.02 (dd, *J* = 6.6, 10.9 Hz, H), 3.65 (d, *J* = 10.5 Hz, H), 2.55 (t, *J* = 6.3 Hz, H), 1.32 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 169.6, 138.3, 129.2, 125.2, 120.0, 50.3, 46.3, 39.3, 32.7, 20.3, 16.0; HRMS(EI+) Calcd for $C_{14}H_{16}NO_2$ [M+1] 230.1181, found 230.1182. The Alder-ene type product **7e** are known. [2]



5f

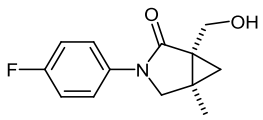
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.22 (s, H), 5.68 (dt, *J* = 17.2, 10.6, 6.2 Hz, H), 5.20 (d, *J* = 17.2 Hz, H), 5.19 (d, *J* = 10.5 Hz, H), 3.89 (dd, *J* = 14.8, 5.8 Hz, H), 3.81 (dd, *J* = 15.2, 6.2 Hz, H), 3.50 (dd, *J* = 10.5, 5.8 Hz, H), 3.28 (d, *J* = 10.6 Hz, H), 2.58 (dt, *J* = 7.8, 5.4 Hz, H), 1.95 (dd, *J* = 8.2, 3.9 Hz, H), 1.31 (dd, *J* = 4.2, 5.0 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 171.4, 132.7, 119.3, 47.8, 45.6, 39.7, 26.5, 26.1; HRMS(EI+) Calcd for $C_9H_{12}NO_2$ [M+1] 166.0868, found 166.0869.

[2] Koo, J.; Park, H. –S.; Shin, S. *Tetrahedron Lett.* **2012**, doi: tetlet.2012.11.067.



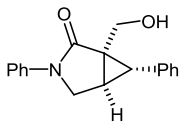
5g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 4.01 (dd, *J* = 6.3, 12.1 Hz, H), 3.82-3.78 (m, H), 3.79 (s, 3H), 3.73 (d of ABq, *J* = 9.7 Hz, H), 3.70 (d of ABq, *J* = 10.1 Hz, H), 2.85 (br s, H), 1.41 (s, 3H), 1.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 156.5, 132.1, 121.6, 114.1, 60.2, 55.6, 55.4, 36.3, 23.0, 22.9, 16.1; HRMS(EI+) Calcd for $C_{14}H_{18}NO_3$ [M+1] 248.1287, found 248.1286.



5h

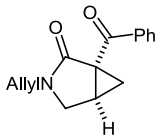
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H), 7.03 (t, *J* = 9.0 Hz, 2H), 4.03 (dd, *J* = 5.9, 12.1 Hz, H), 3.78 (dd, *J* = 4.3, 12.1 Hz, H), 3.74 (s, 2H), 2.78 (br s, H), 1.45 (s, 3H), 1.05-1.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 159.2 (d, *J* = 242 Hz), 135.0, 121.4 (d, *J* = 7.4 Hz), 115.5 (d, *J* = 22 Hz), 60.0, 55.3, 36.5, 29.7, 23.0, 16.0; HRMS(EI+) Calcd for $C_{13}H_{15}FNO_2$ [M+1] 236.1087, found 236.1085.



5i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.41-7.30 (m, 4H), 7.30-7.26 (m, 3H), 7.16 (t, *J* = 7.0 Hz, H), 4.18 (dd, *J* = 5.9, 9.8 Hz, H), 3.87 (d, *J* = 10.1 Hz, H), 3.84 (d, *J*

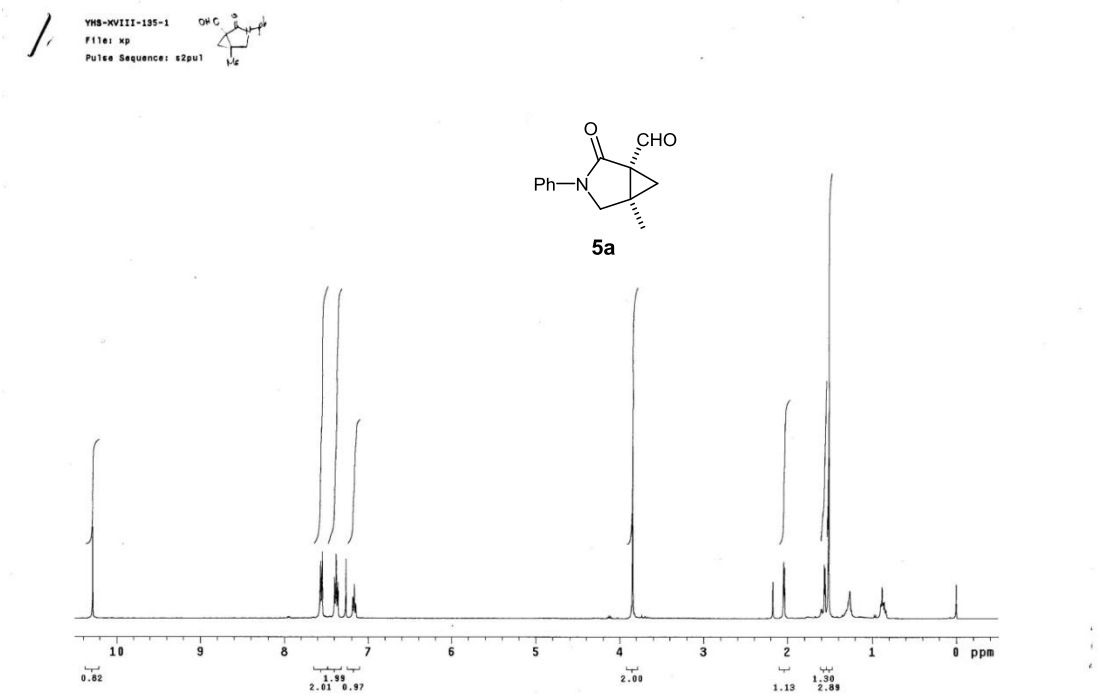
= 5.8 Hz, H), 3.63 (d, *J* = 12.1 Hz, H), 2.92 (s br, H), 2.59 (dd, *J* = 4.3, 5.5 Hz, H), 2.51 (d, *J* = 3.9 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 139.1, 134.4, 129.1, 128.8, 128.7, 127.4, 124.8, 119.8, 58.6, 49.9, 39.8, 33.9, 19.9; HRMS(EI+) Calcd for $C_{18}H_{18}NO_2$ [M+1] 280.1338, found 280.1338.

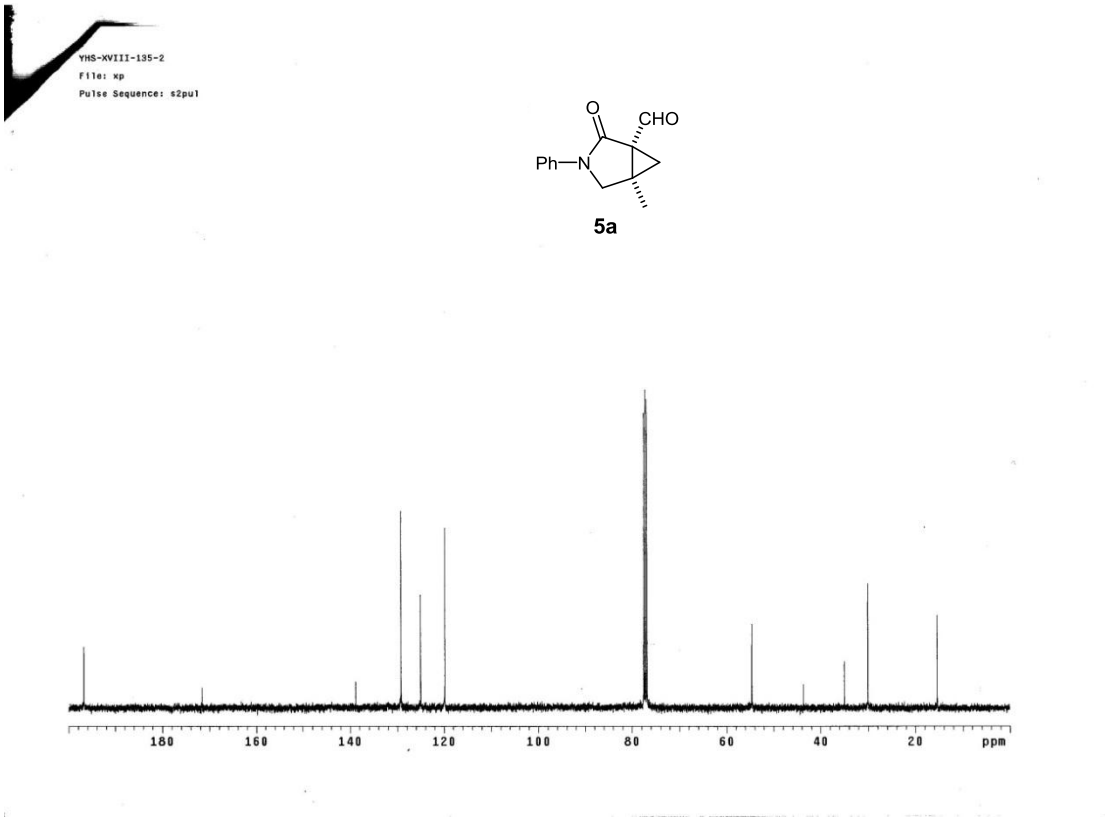


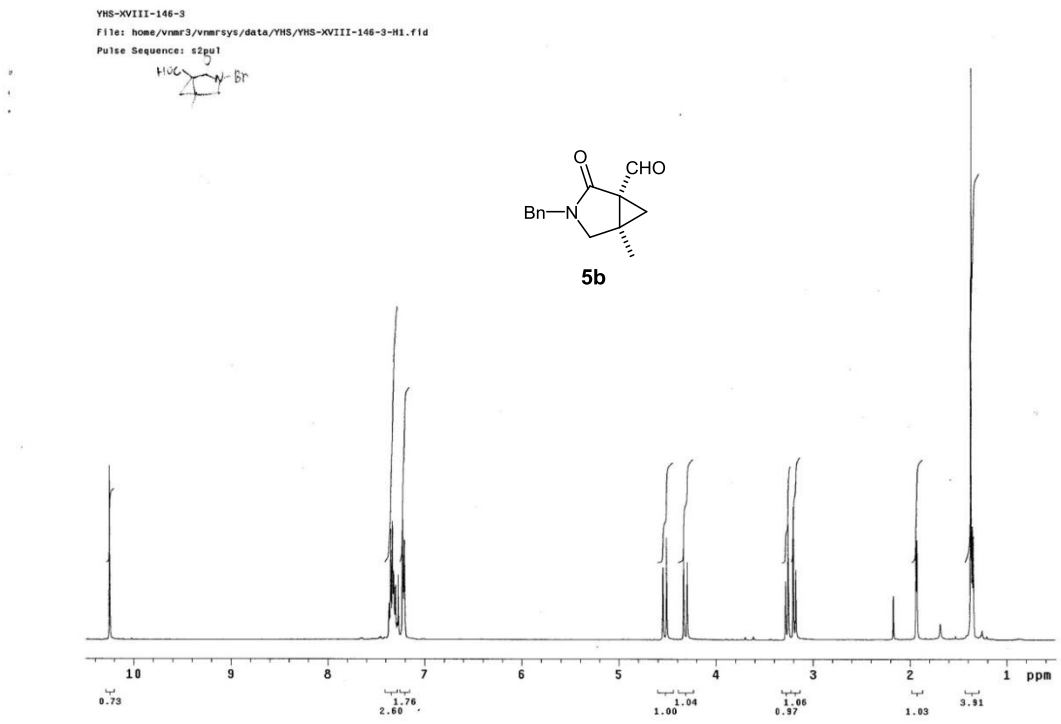
5j

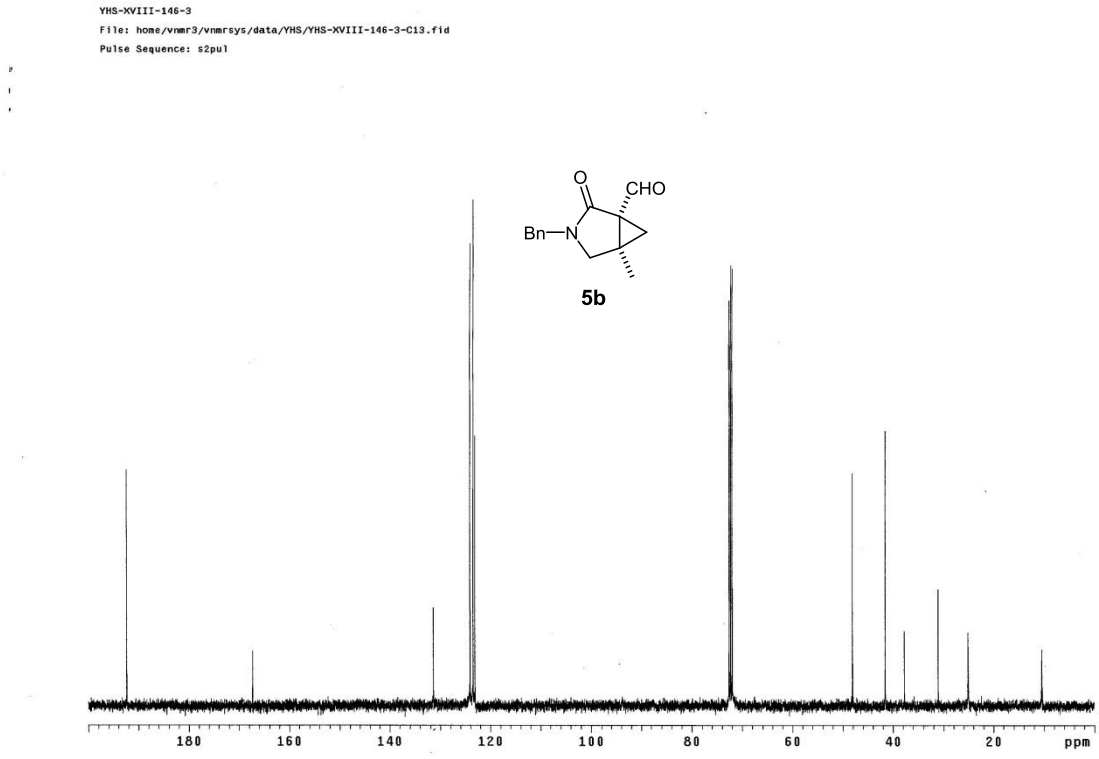
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.72 (tdd, *J* = 6.2, 10.6, 16.8 Hz, H), 3.92-3.80 (m, 2H), 3.74 (dd, *J* = 5.9, 10.9 Hz, H), 3.38 (d, *J* = 10.5 Hz, H), 2.44 (td, *J* = 5.4, 7.9 Hz, H), 2.01 (dd, *J* = 4.7, 7.8 Hz, H), 1.15 (t, *J* = 4.7 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 171.3, 136.7, 133.3, 132.4, 129.2, 128.4, 118.8, 47.4, 45.3, 38.8, 22.3, 19.4; HRMS(EI+) Calcd for $C_{15}H_{16}NO_2$ [M+1] 242.1181, found 242.1180.

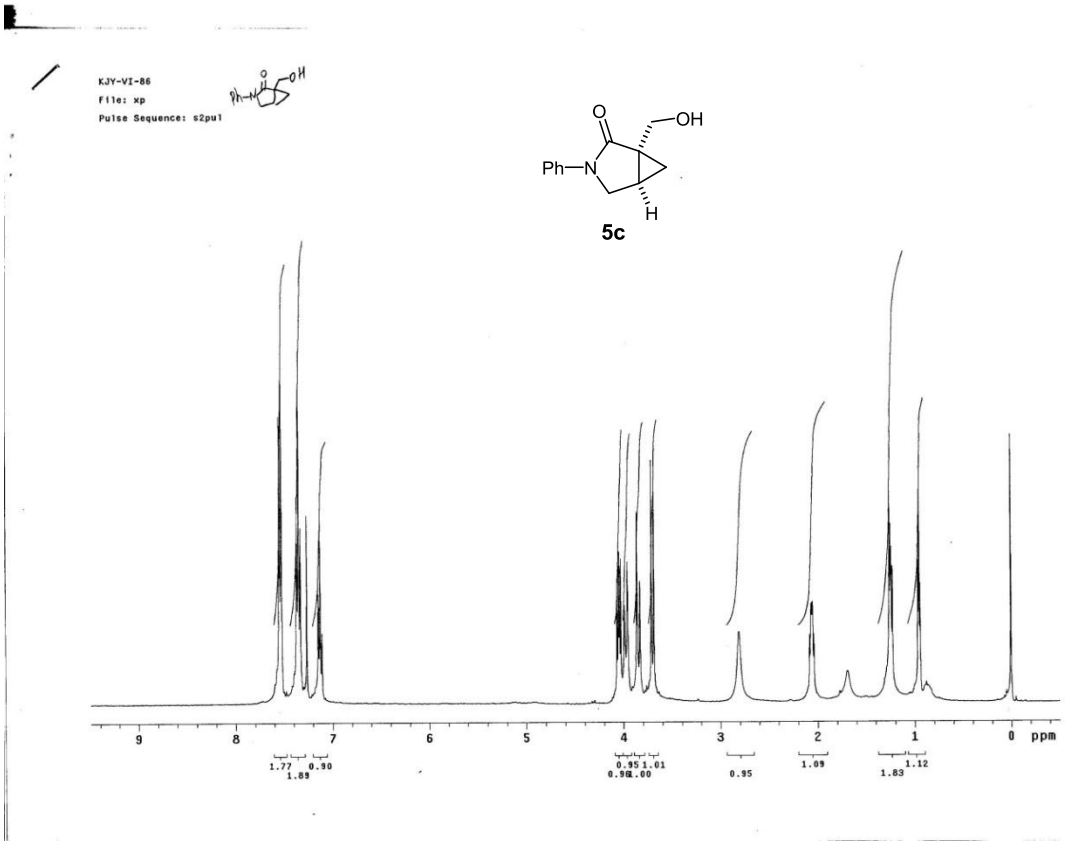
4. Scanned spectra

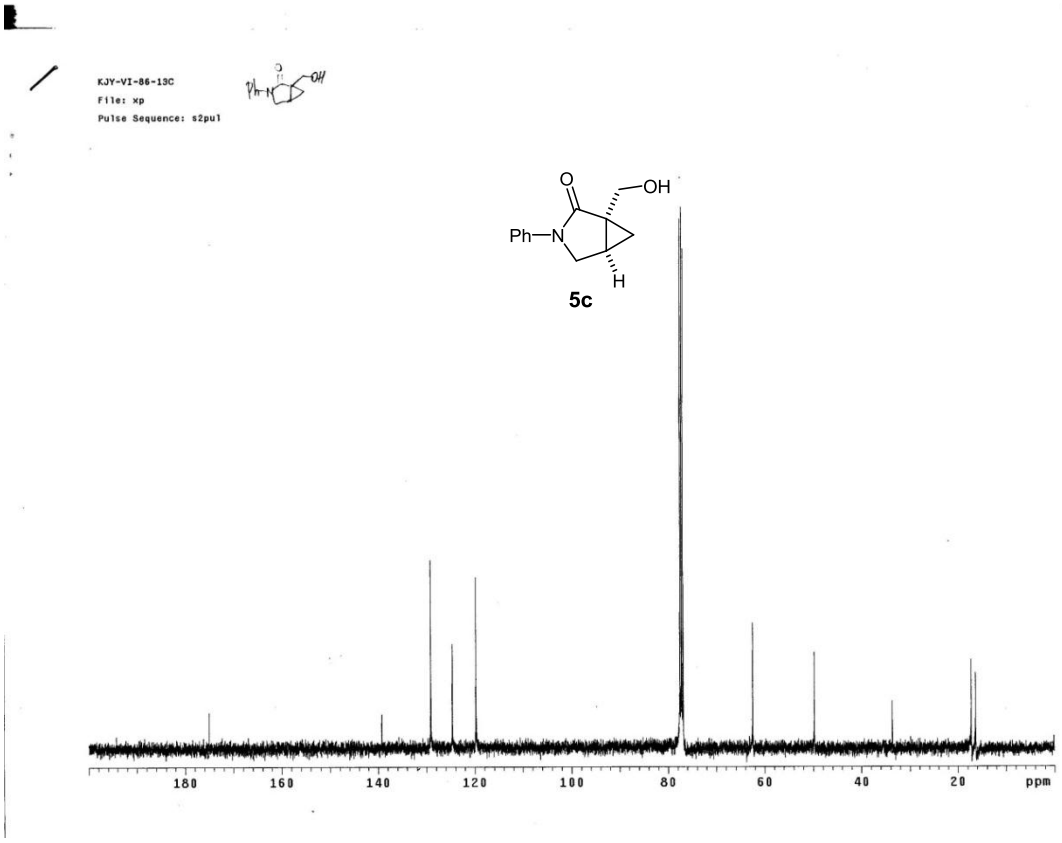


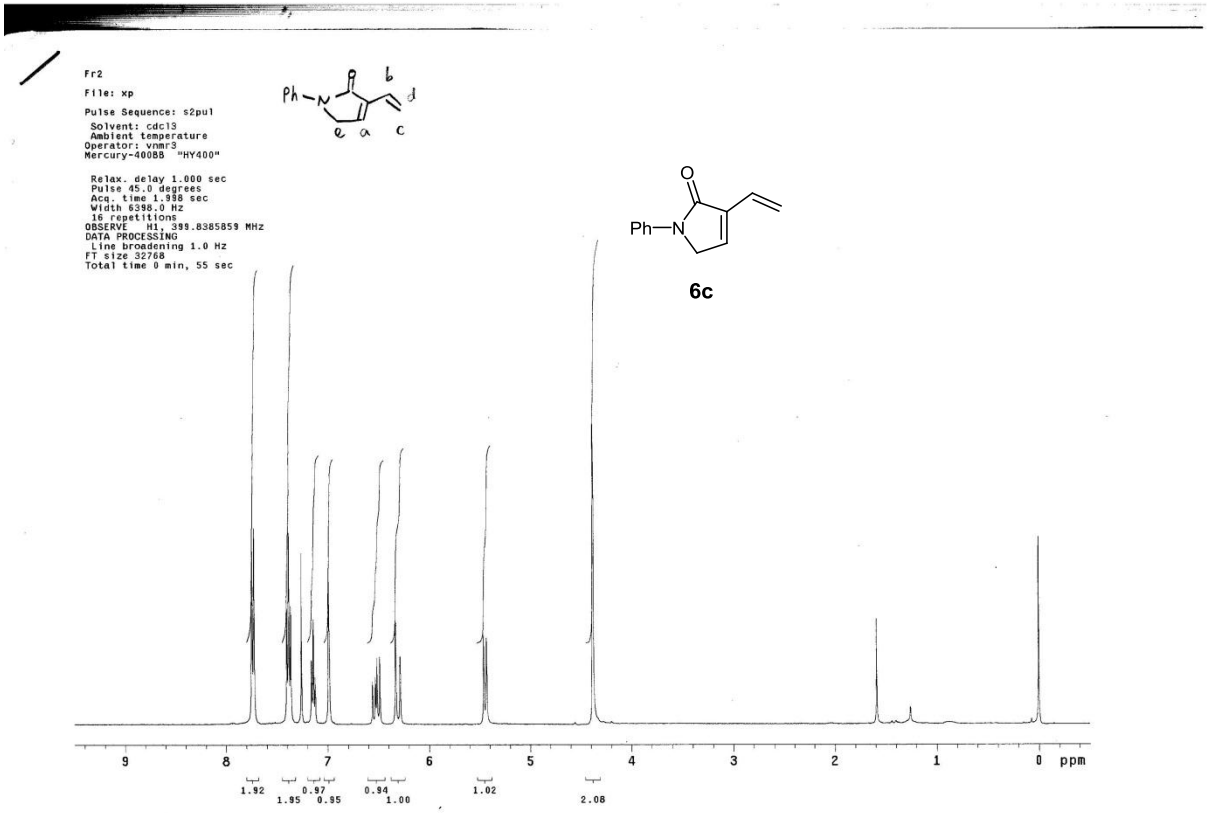








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Pulse 45.0 degrees
Acq. time 1.998 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.8385859 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 0 min, 55 sec
Ph
N
O
a
b
c
d
e
9
8
7
6
5
4
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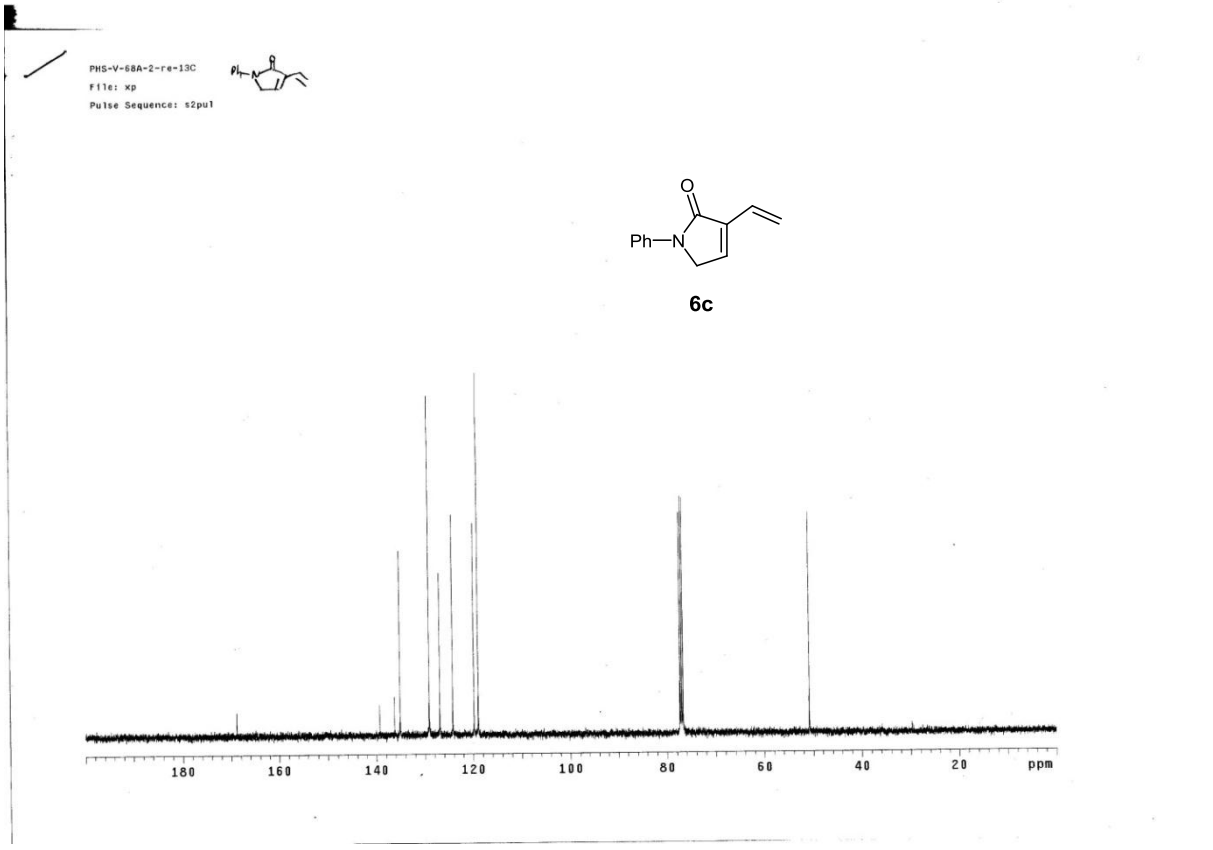
1.02
2.08

6c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120
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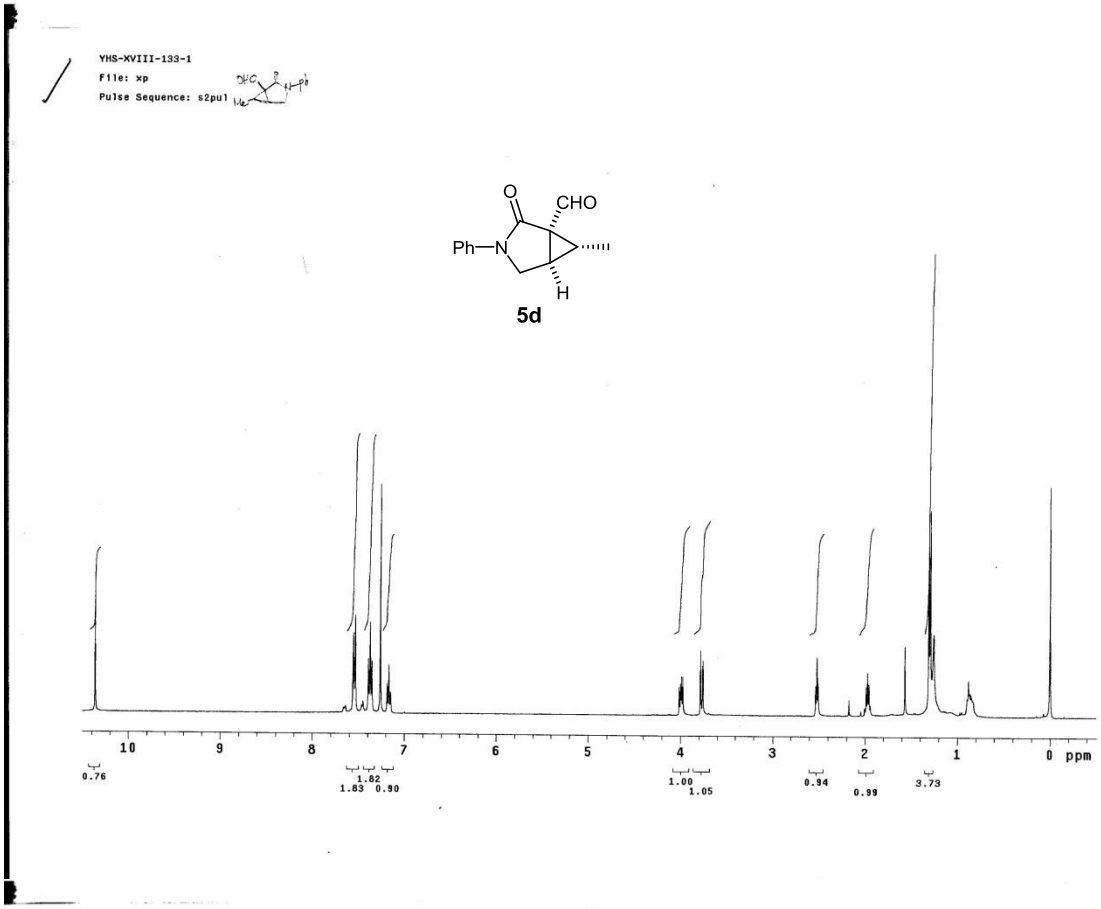
ppm

6c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H
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9
8
7
6
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3
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1.00
1.05
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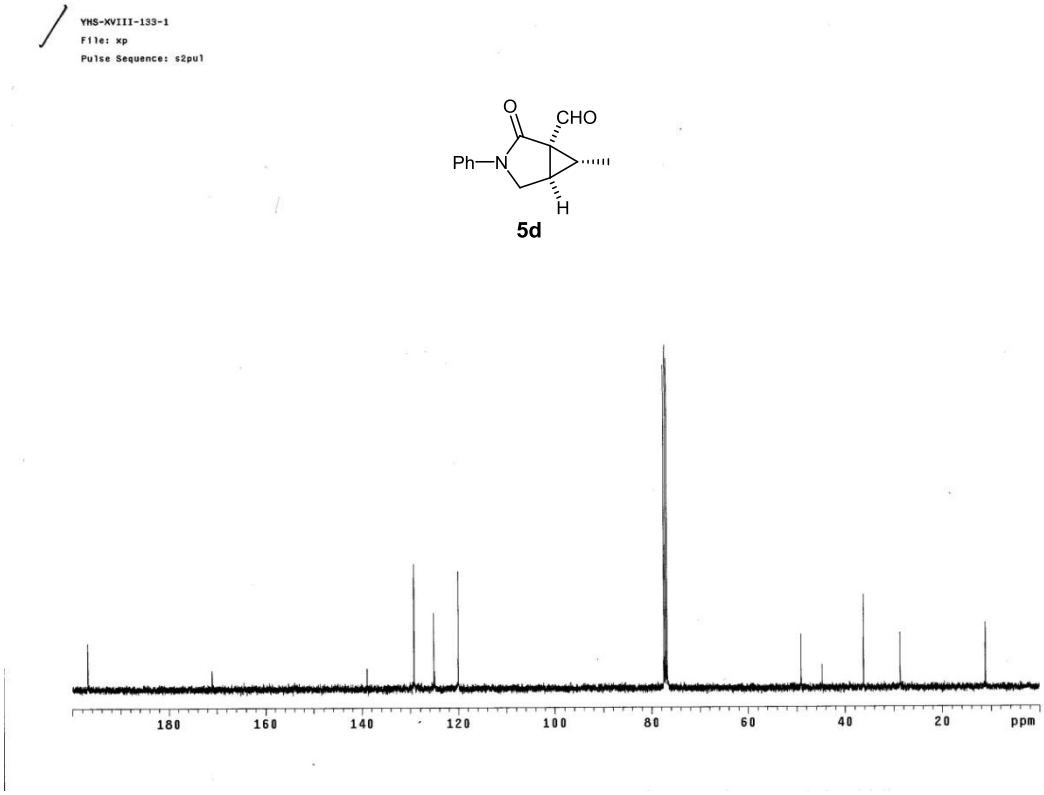
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File: xp
Pulse Sequence: s2pul
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Ph—N
H
5d
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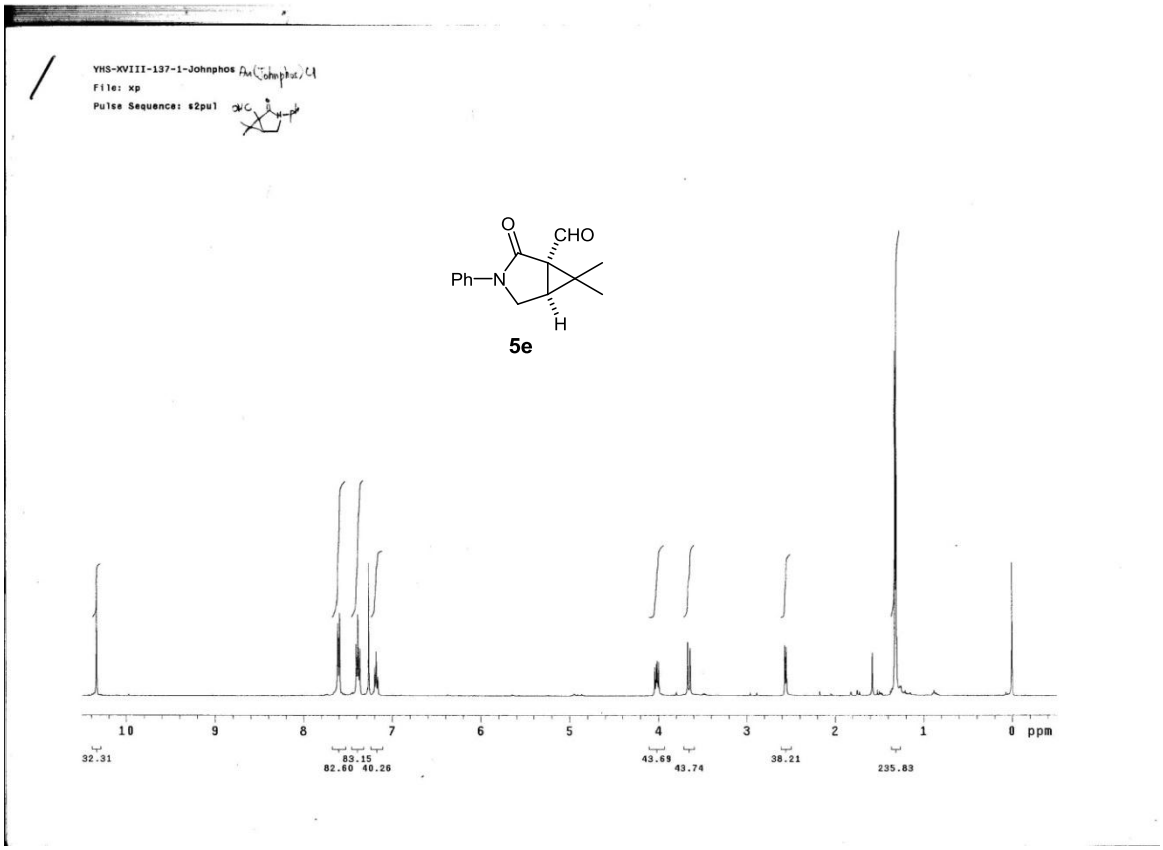
160
140
120
100
80
60
40
20
ppm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Ph—N
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5e
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9
8
7
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43.74
38.21
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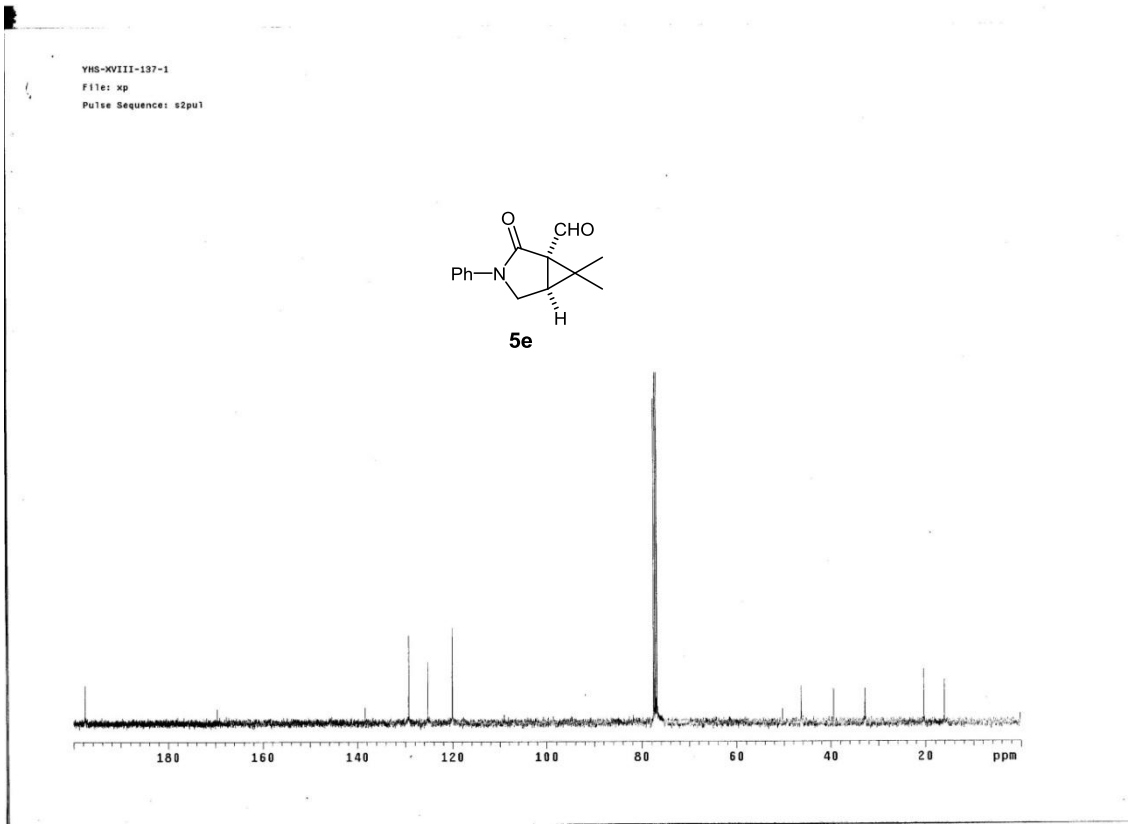
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160
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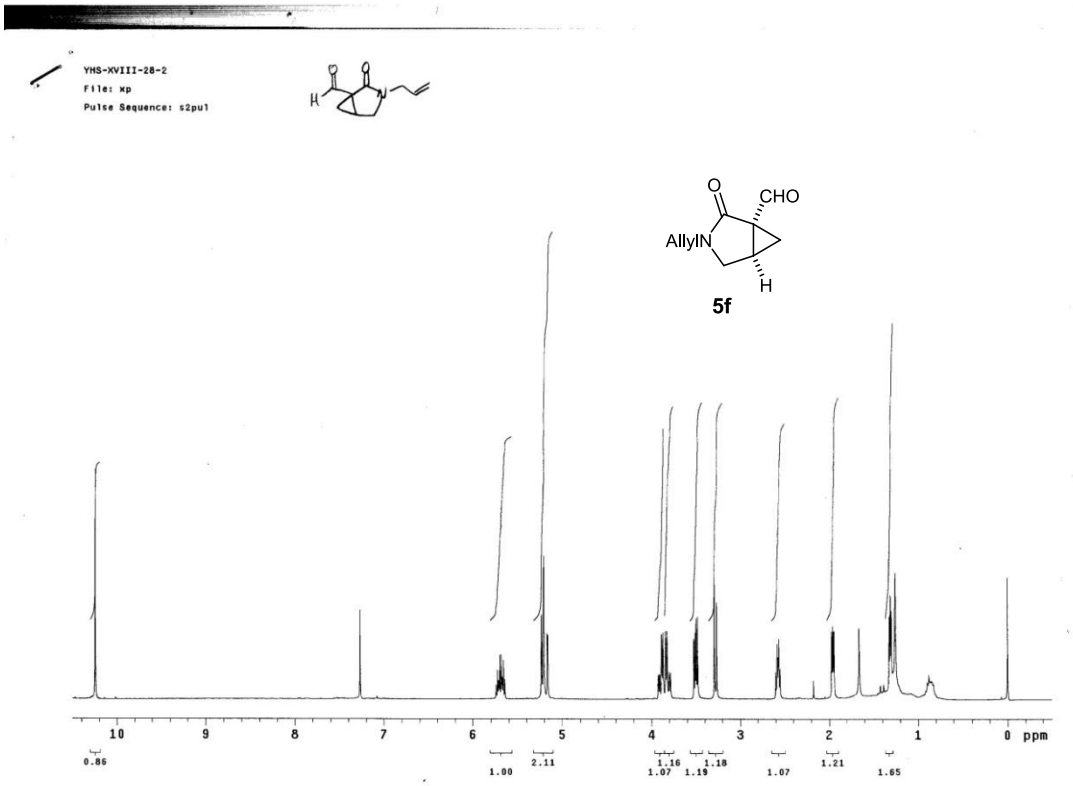
60
40
20
ppm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9
8
7
6
5
4
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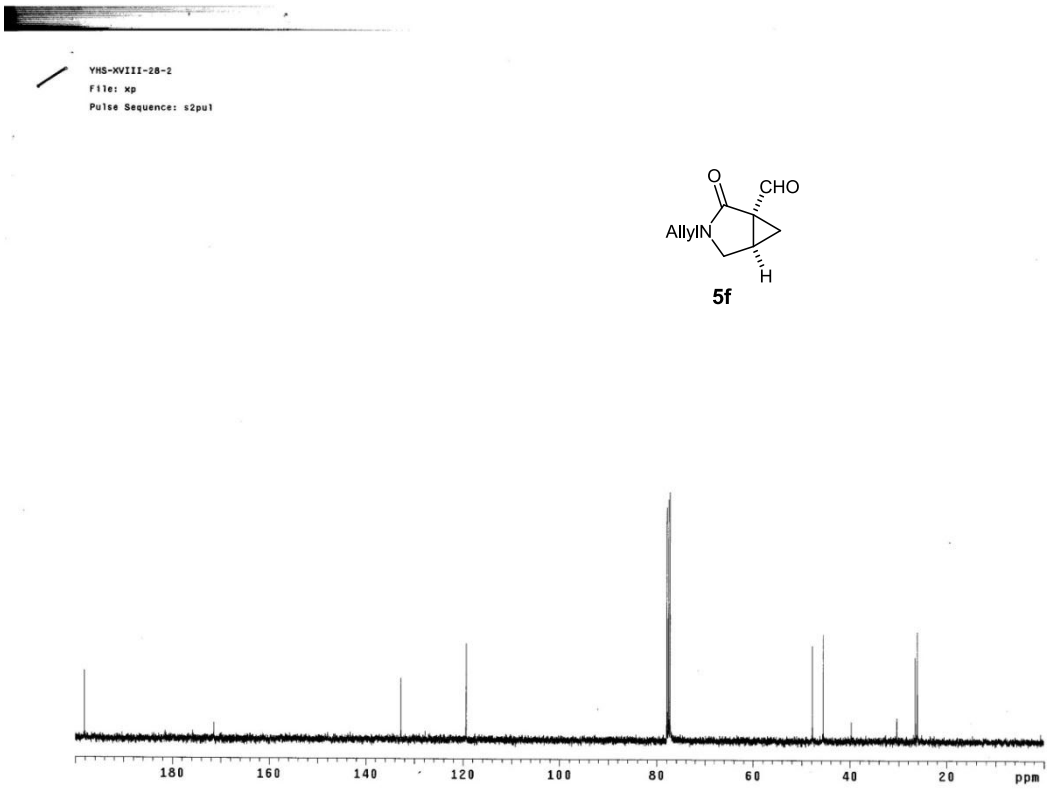
1.07
1.18
1.19
1.07
1.21
1.65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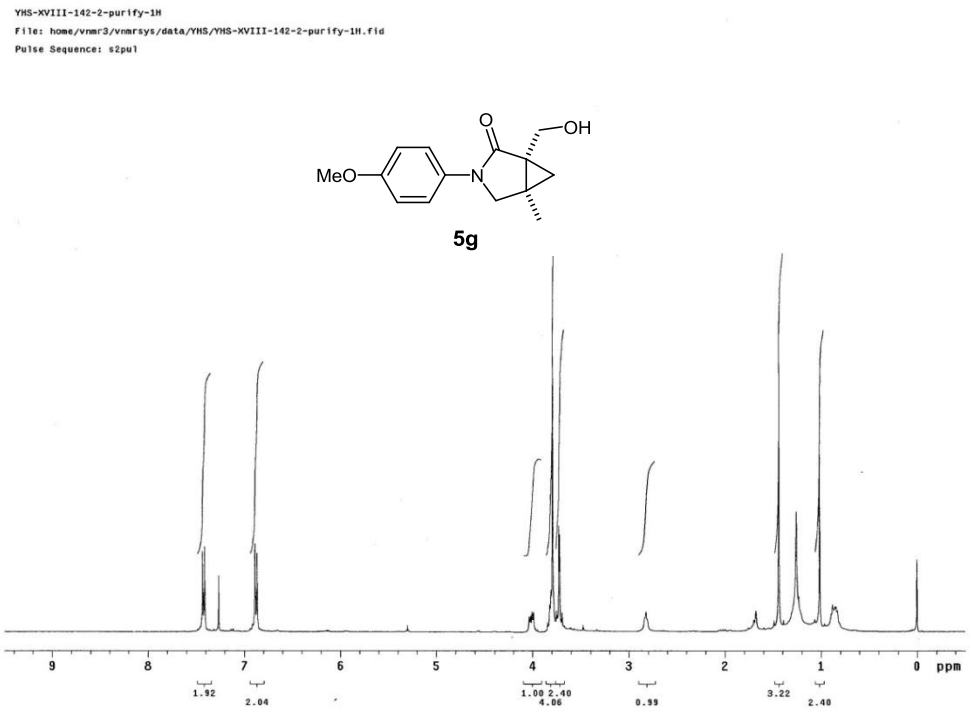
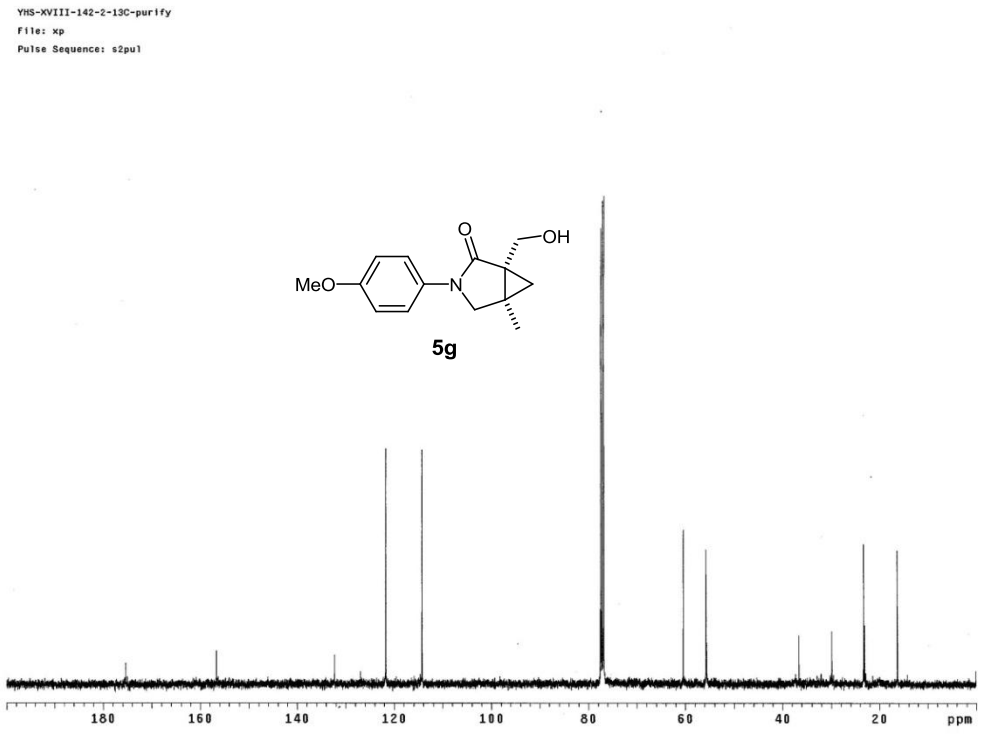
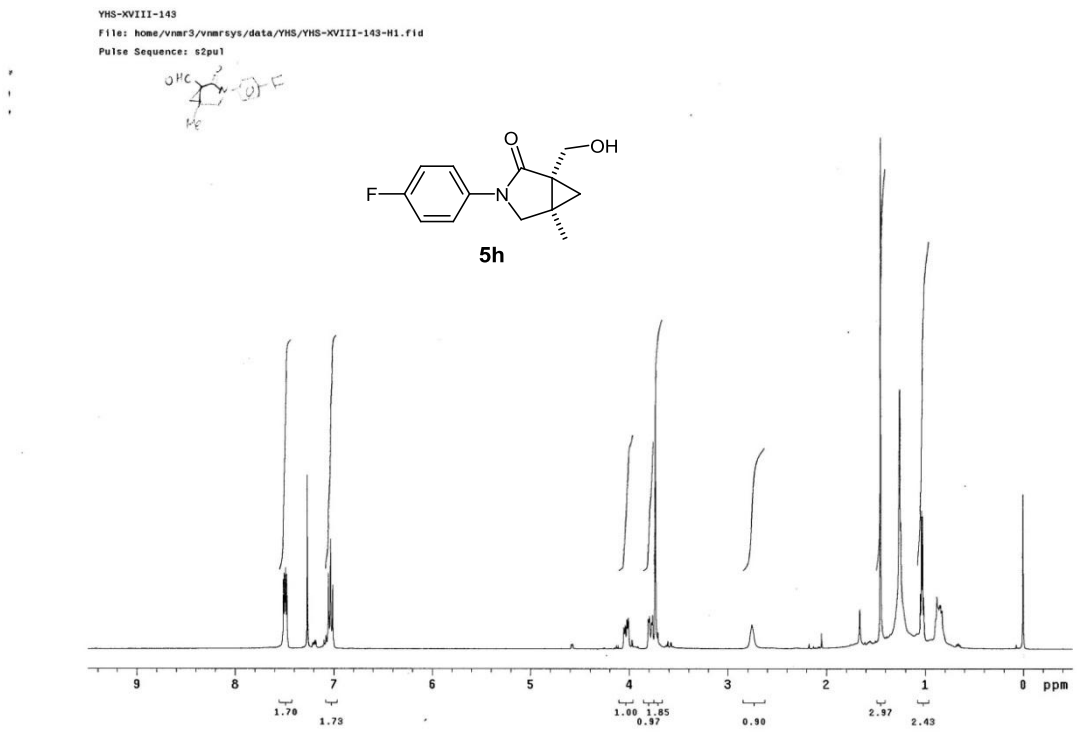
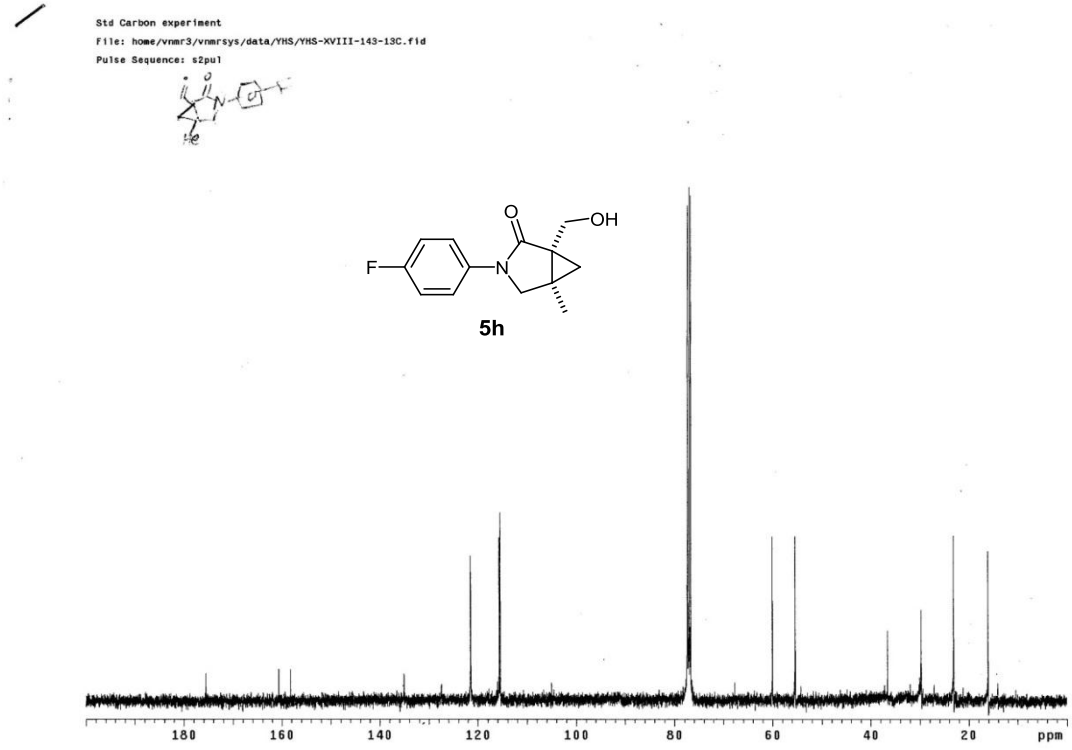
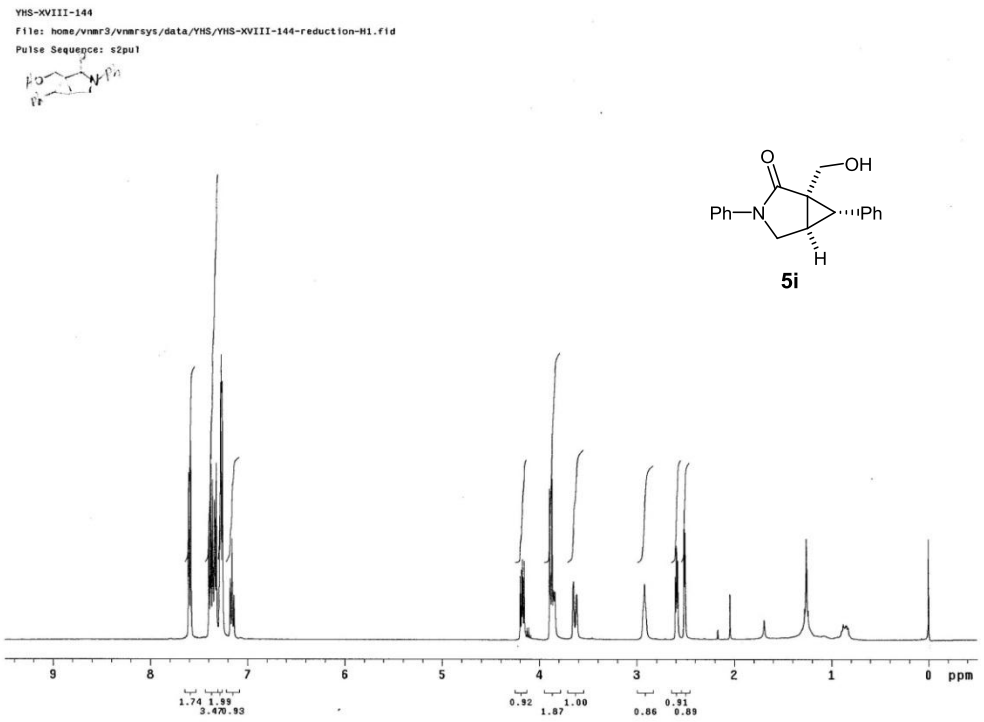
CHO
AllylN
H
5f
180
160
140
120
100
80
60
40
20
ppm





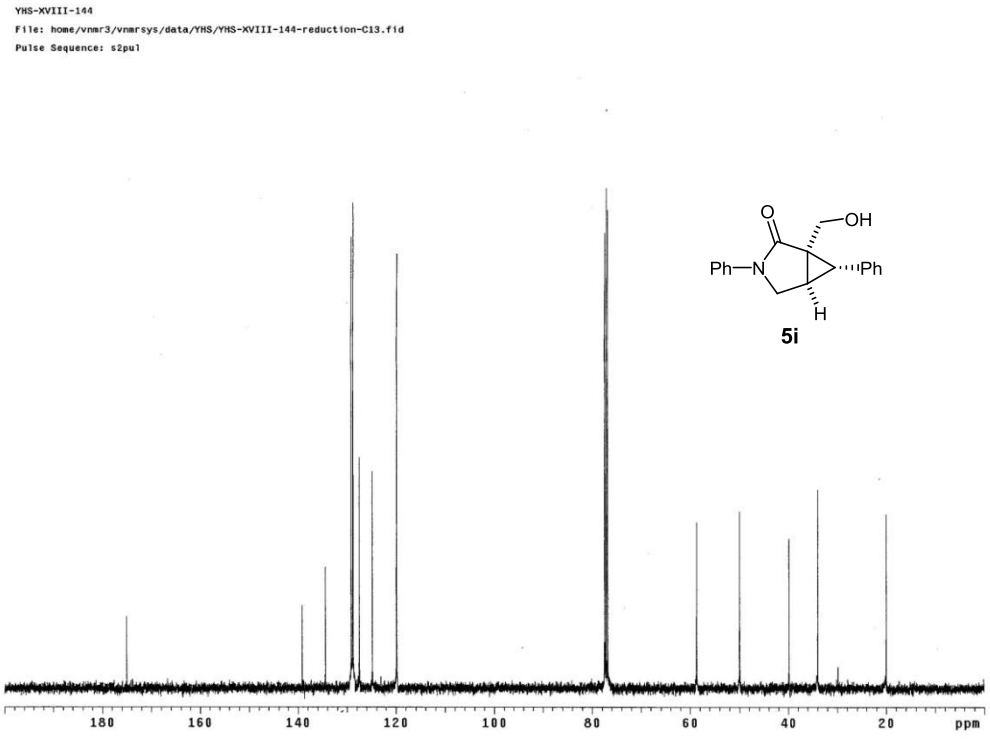





YHS-XVIII-144
File: home/vnmr3/vnmrsys/data/YHS/YHS-XVIII-144-reduction-H1.fid
Pulse Sequence: s2pul
9
8
7
6
5
4
3
2
1
0
ppm
1.74
1.89
3.47
0.93
0.92
1.00
1.87
0.86
0.91
0.89

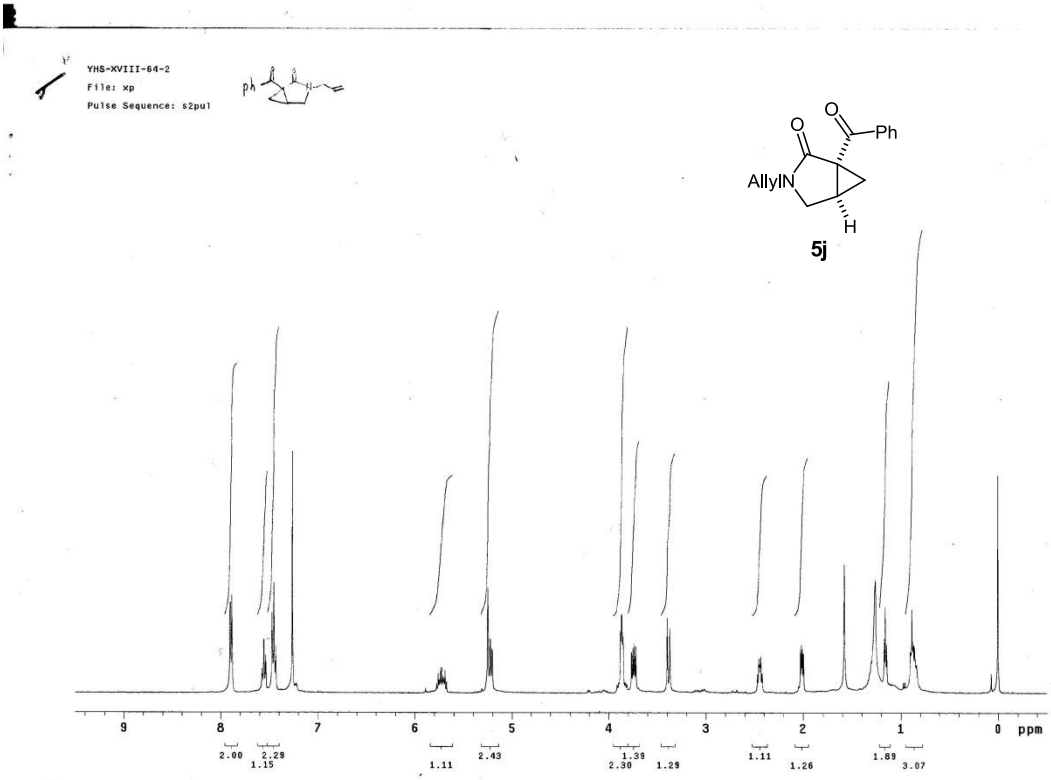
O
OH
Ph
N
Ph
H

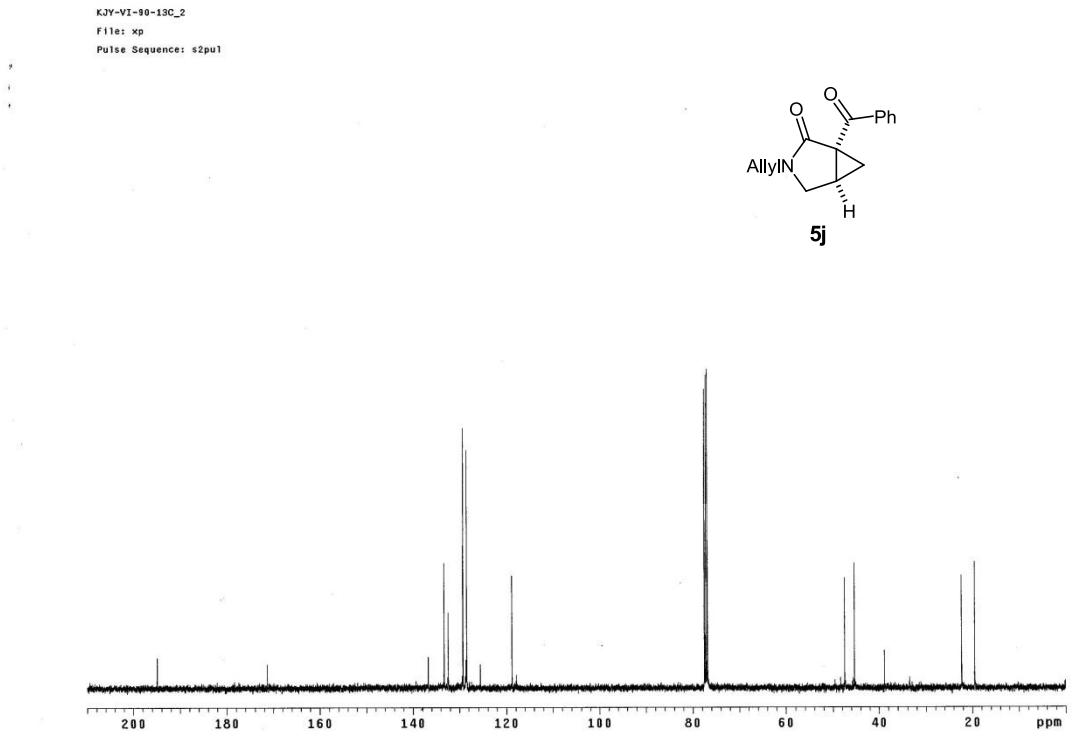
5i


YHS-XVIII-144
File: home/vnmr3/vnmrsys/data/YHS/YHS-XVIII-144-reduction-C13.fid
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
ppm

O
OH
Ph
N
Ph
H

5i


YHS-XVIII-64-2
File: xp
Pulse Sequence: s2pul
Ph
AllylN
H
5j
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.29
1.15
1.11
2.43
1.39
2.30
1.29
1.11
1.26
1.89
3.07


KJY-VI-90-13C_2
File: xp
Pulse Sequence: s2pul
Ph
AllylN
H
5j
200
180
160
140
120
100
80
60
40
20
ppm