

Supporting Information

MnO₂/TiO₂ Catalyzed Synthesis of Coenzyme Pyridoxamine-5'-Phosphate Analogues : 3-deoxypyridoxamine-5'-phosphate

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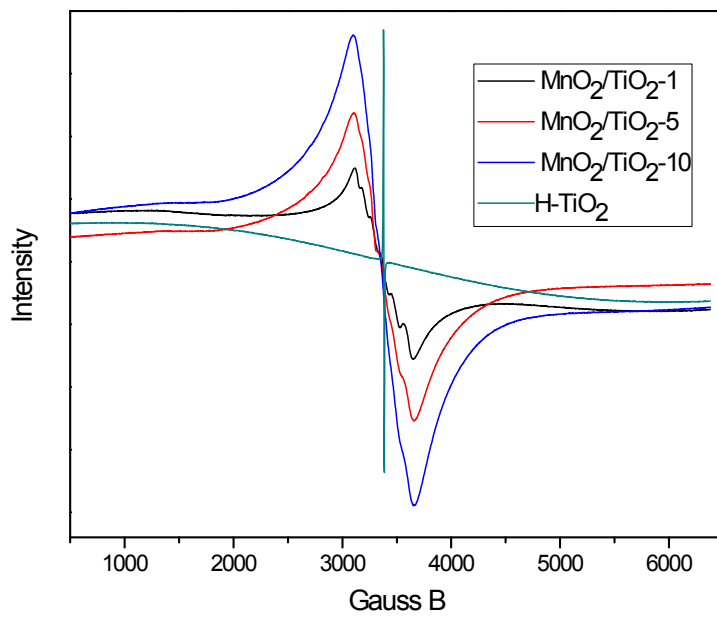


Figure 1. EPR Spectra of doped TiO₂NP

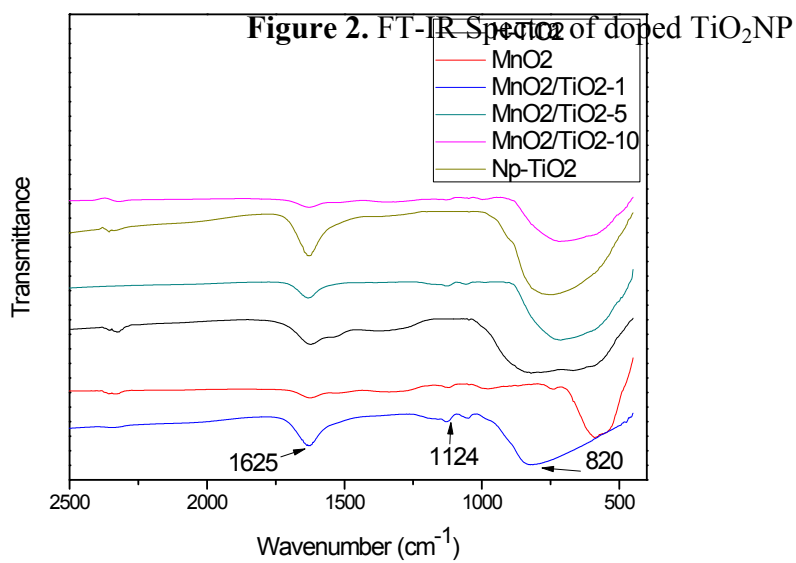


Figure 2. FT-IR Spectra of doped TiO₂NP

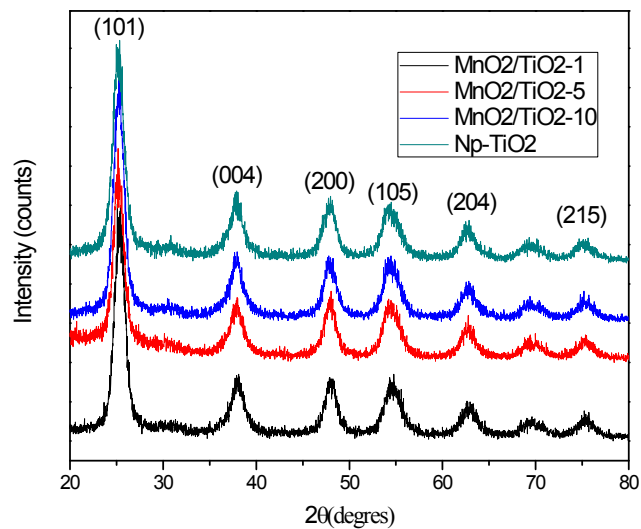


Figure 3.
XRD pattern

Powder

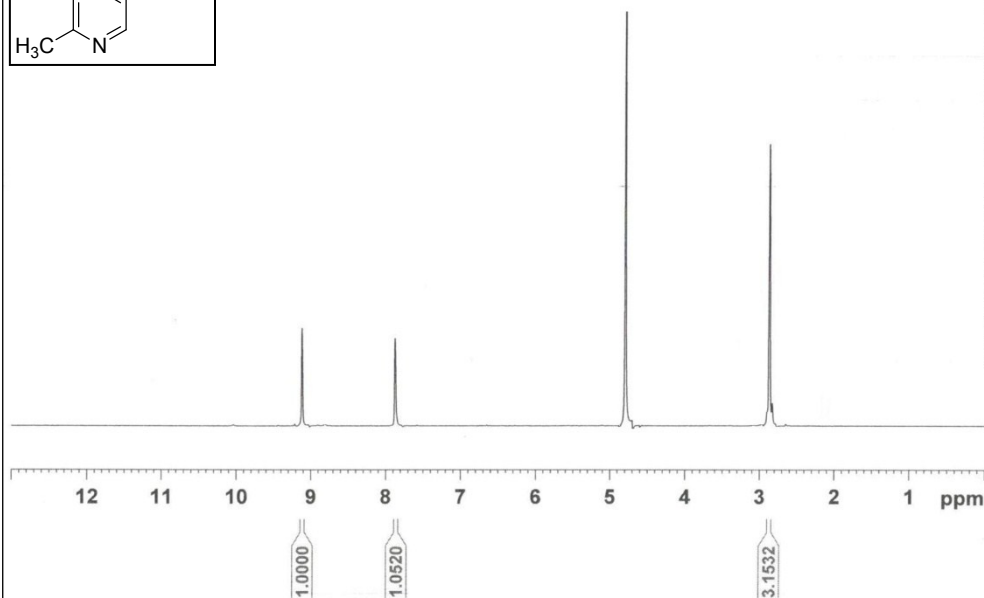
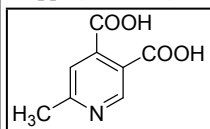
of doped TiO₂NP

Compound : **2-Methyl-4,5-pyridinedicarboxylic acid (2b)**

¹H NMR : 300 MHz

Solvent : D₂O

δ (ppm) = 9.07 (s, 1H, 6-H), 7.82 (s, 1H, 3-H), 2.82 (s, 3H, 2-Me)



Current Data Parameters
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PROCNO 1

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TD 32768
SOLVENT CDCl3
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FIDRES 0.137219 Hz
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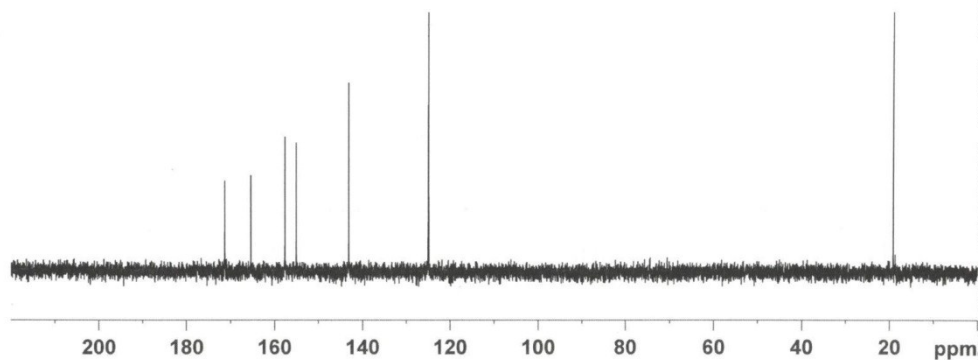
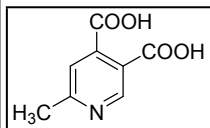
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Compound : **2-Methyl-4,5-pyridinedicarboxylic acid (2b)**

^{13}C NMR : 300 MHz

Solvent : D_2O

δ (ppm) = 171.3, 165.3, 157.6, 155.0, 143.1, 124.9, 20.3



Current Data Parameters
NAME 3M N acid 13C-1 D2O
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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SOLVENT DMSO
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PL1 0.00 dB
SFO1 75.4763978 MHz

CHANNEL f2
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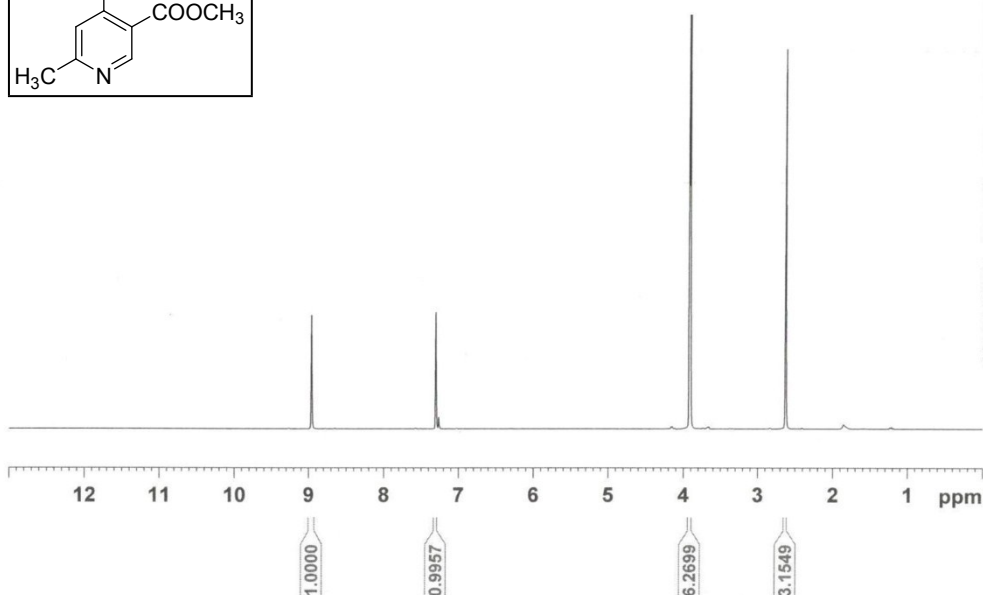
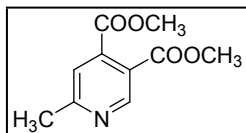
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PC 1.00

Compound : **Dimethyl 2-methyl-4,5-pyridinedicarboxylic acid (3b)**

^1H NMR : 300 MHz

Solvent : CDCl_3

δ (ppm) = 8.89 (s, 1H, 6-H), 7.55 (s, 1H, 3-H), 3.85 (s, 6H, OMe's), 2.58 (s, 3H, 2-Me)



Current Data Parameters
NAME 3M AB-ES 2 20150424
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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INSTRUM spect
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 20
DS 0
SWH 4496.403 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 362
DW 111.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

CHANNEL f1
NUC1 1H
P1 10.60 usec
PL1 0.00 dB
SFO1 300.1319508 MHz

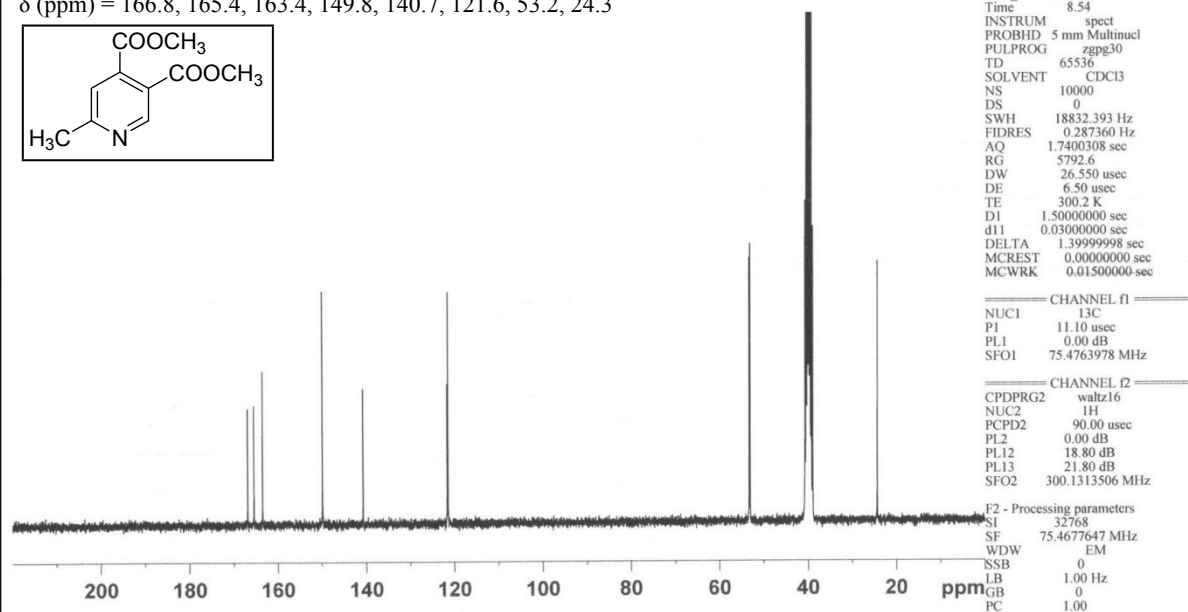
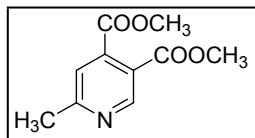
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PC 1.00

Compound : **Dimethyl 2-methyl-4,5-pyridinedicarboxylic acid (3b)**

^{13}C NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 166.8, 165.4, 163.4, 149.8, 140.7, 121.6, 53.2, 24.3

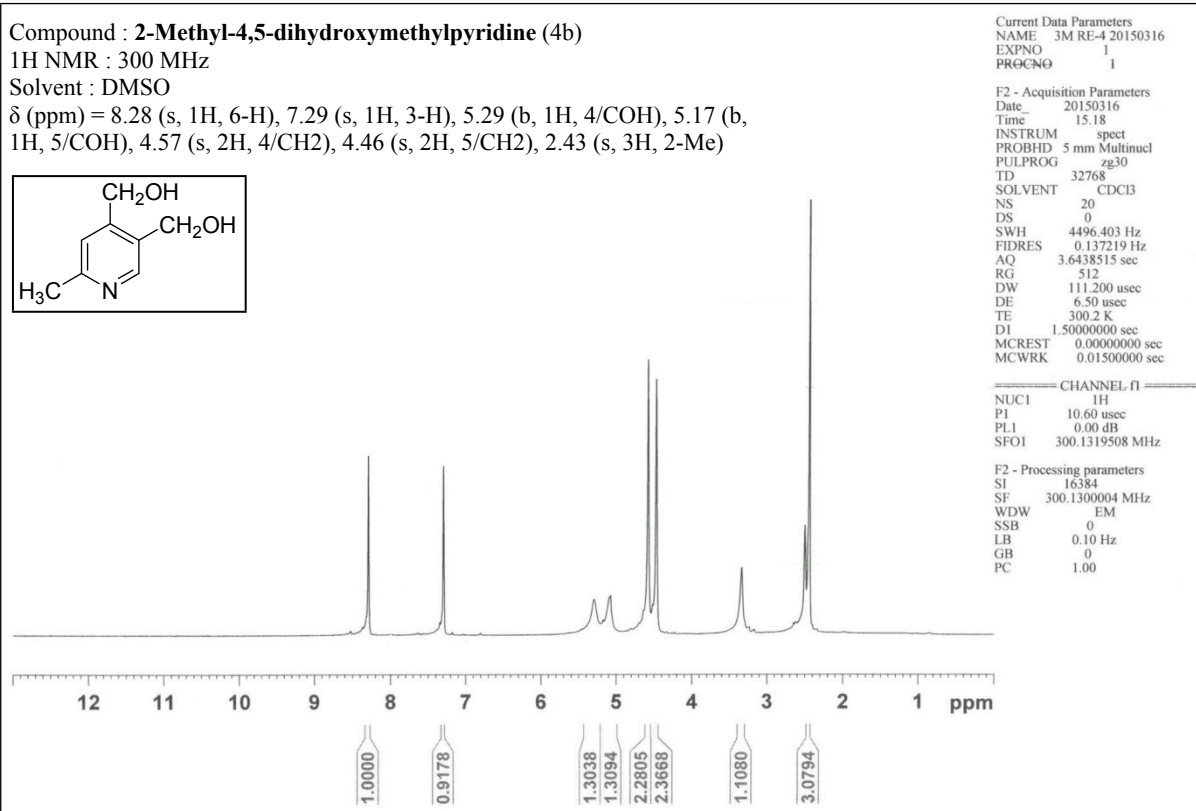
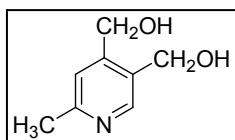


Compound : **2-Methyl-4,5-dihydroxymethylpyridine (4b)**

^1H NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 8.28 (s, 1H, 6-H), 7.29 (s, 1H, 3-H), 5.29 (b, 1H, 4/COH), 5.17 (b, 1H, 5/COH), 4.57 (s, 2H, 4/CH₂), 4.46 (s, 2H, 5/CH₂), 2.43 (s, 3H, 2-Me)

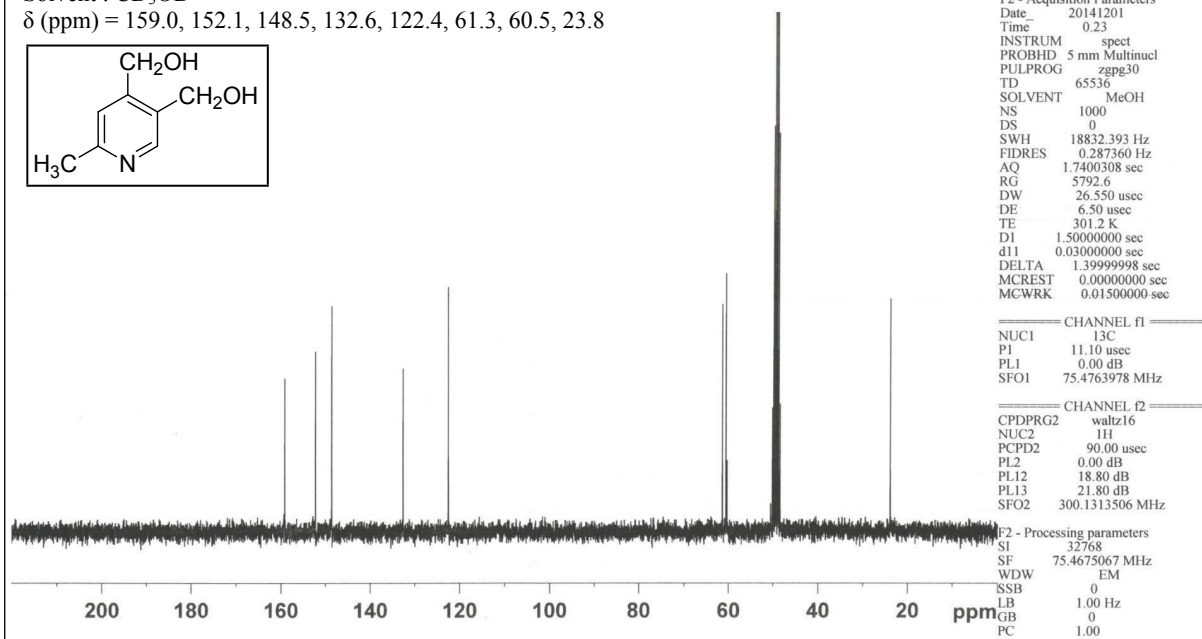
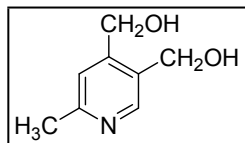


Compound : **2-Methyl-4,5-dihydroxymethylpyridine (4b)**

^{13}C NMR : 300 MHz

Solvent : CD_3OD

δ (ppm) = 159.0, 152.1, 148.5, 132.6, 122.4, 61.3, 60.5, 23.8

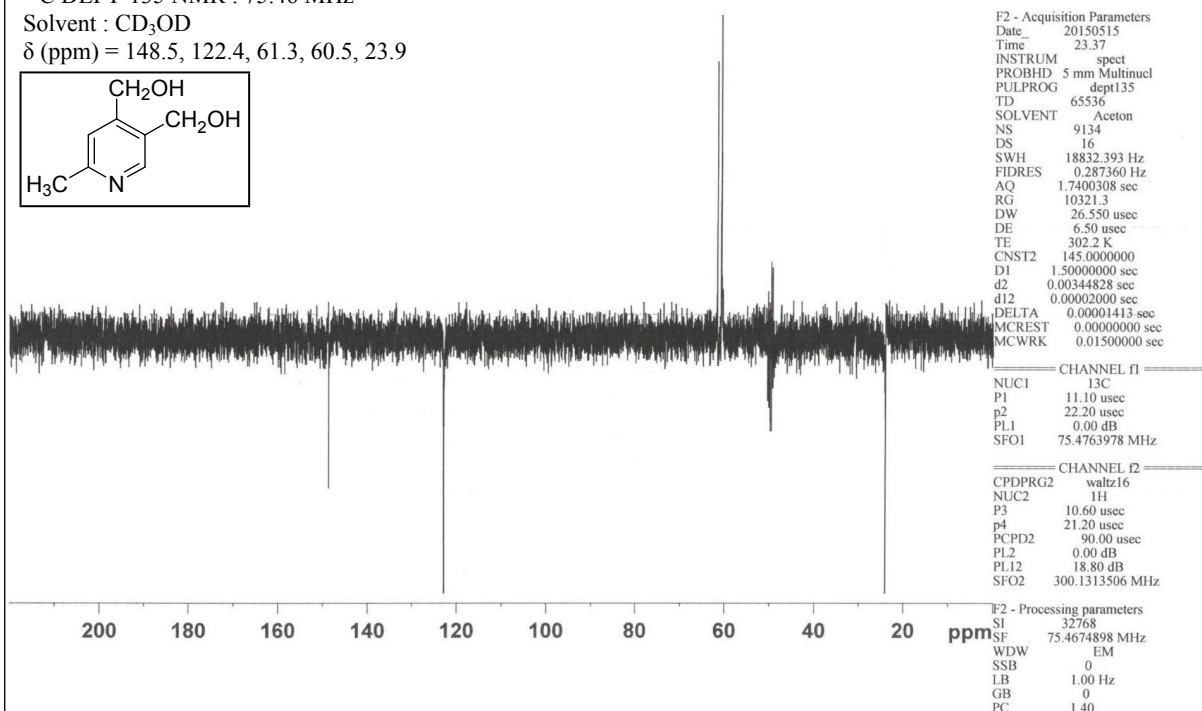
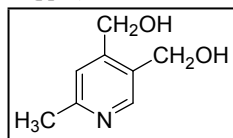


Compound : **2-Methyl-4,5-dihydroxymethylpyridine (4b)**

^{13}C DEPT-135 NMR : 75.46 MHz

Solvent : CD_3OD

δ (ppm) = 148.5, 122.4, 61.3, 60.5, 23.9

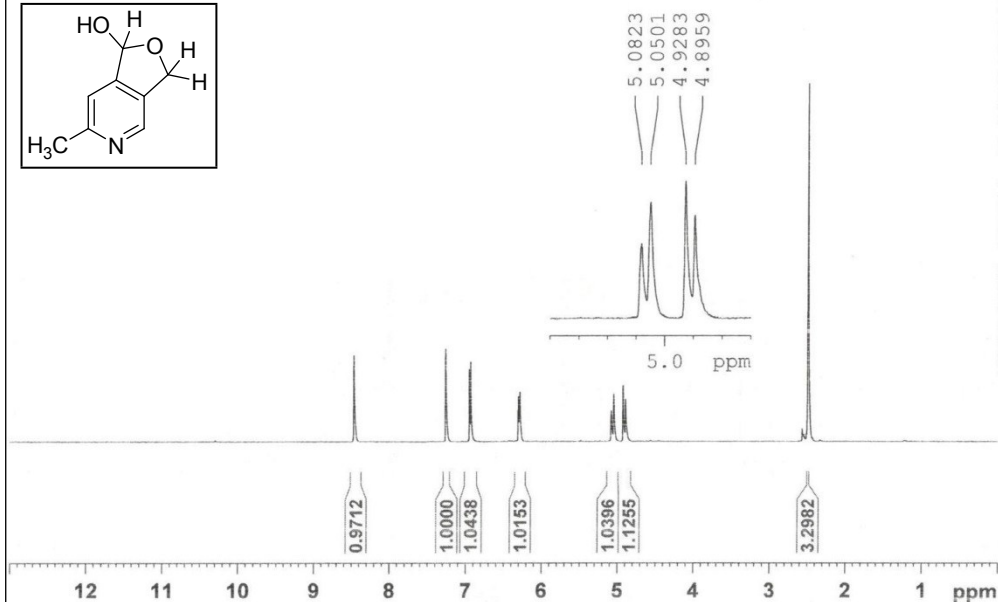
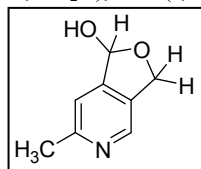


Compound : **5-Hydroxymethyl-2-Methyl-4-pyridinecarboxaldehyde hemiacetal (7b)**

¹H NMR : 400 MHz

Solvent : DMSO

δ (ppm) = 8.46 (s, 1H, 6-H), 7.25 (s, 1H, 3-H), 6.94 (d, J = 7.6 Hz, OH), 6.29 (d, J = 5.7 Hz, CH of hemiacetal form), 5.06 (d, 1H, J = 12.8 Hz, CH₂O), 4.91 (d, 1H, J = 12.9 Hz, CH₂O), 2.49 (s, 3H, 2-Me)



Current Data Parameters
NAME 3MAB19cy
EXPNO 1
PROCNO 1

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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
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SWH 6393.862 Hz
FIDRES 0.195125 Hz
AQ 2.5625076 sec
RG 4
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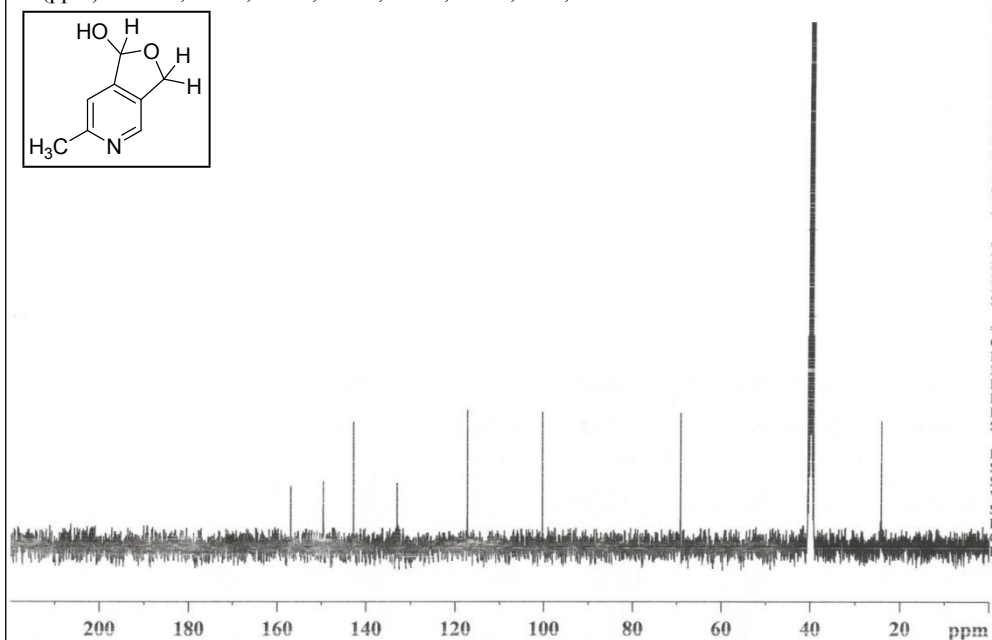
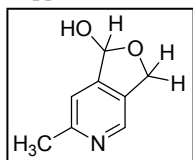
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Compound : **5-Hydroxymethyl-2-Methyl-4-pyridinecarboxaldehyde hemiacetal (7b)**

¹³C NMR : 400 MHz

Solvent : DMSO

δ (ppm) = 157.0, 149.6, 142.8, 133.0, 117.3, 100.3, 69.3, 24.3



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EXPNO 1
PROCNO 1

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SOLVENT CDCl3
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FIDRES 0.389255 Hz
AQ 1.2845556 sec
RG 4
DW 19.600 usec
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TE 295.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 9.80 usec
PL1 0.00 dB
SFO1 100.6248425 MHz

CHANNEL f2
CPDPRG2 waltz16
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PL13 17.00 dB
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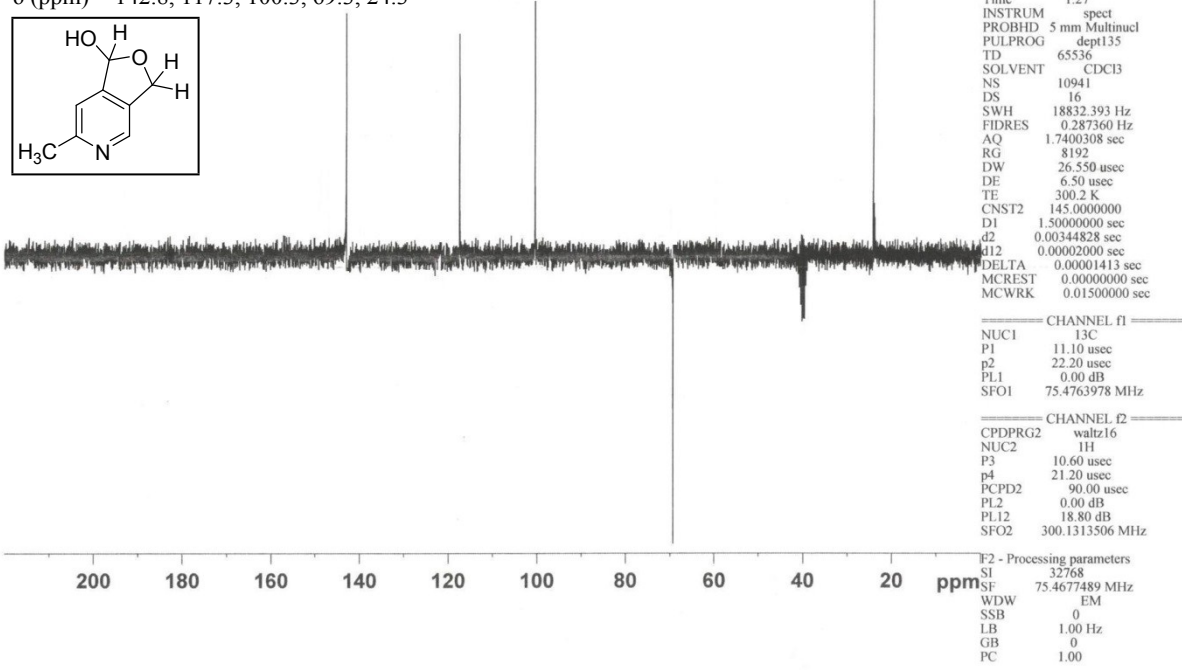
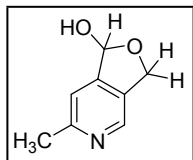
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Compound : **5-Hydroxymethyl-2-Methyl-4-pyridinecarboxaldehyde hemiacetal (7b)**

¹³C DEPT-135 NMR : 75.46 MHz

Solvent : DMSO

δ (ppm) = 142.8, 117.3, 100.3, 69.3, 24.3

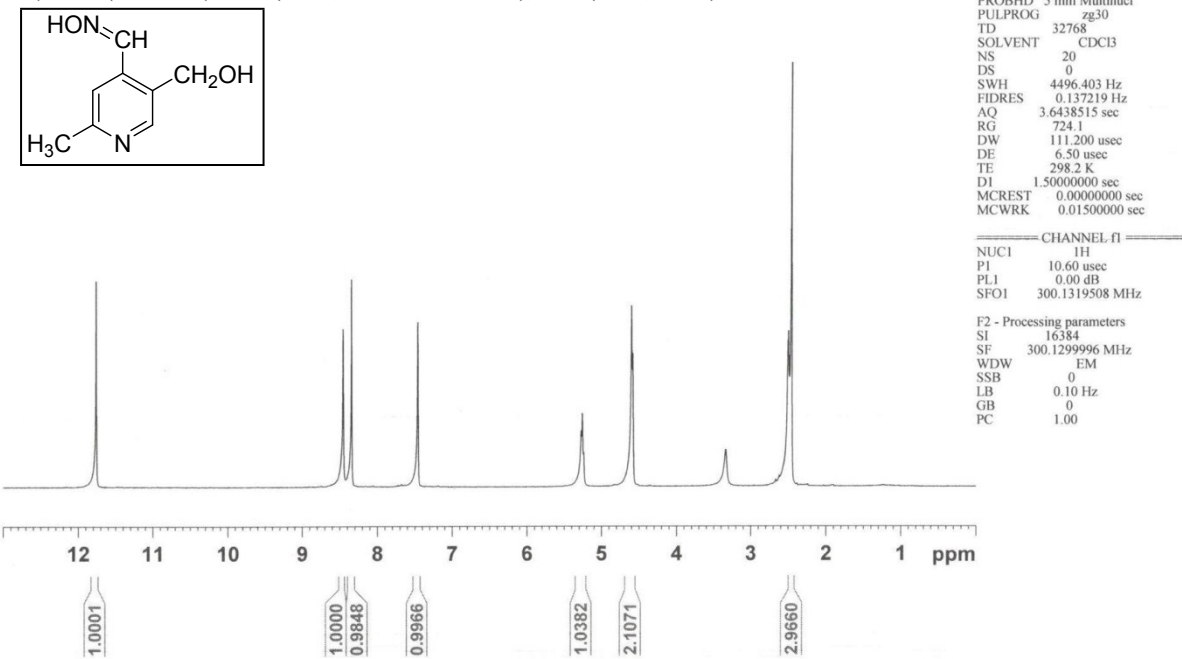
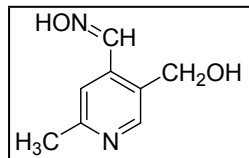


Compound : **5-Hydroxymethyl-2-Methyl-4-pyridinecarboxaldehyde oximes (8b)**

¹H NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 11.76 (s, 1H, NOH), 8.45 (s, 1H, 4'-CH), 8.33 (s, 1H, 6-H), 7.45 (s, 1H, 3-H), 5.26 (s, 1H OH), 4.58 (d, 2H, J = 4.4 Hz, CH₂O), 2.45 (s, 3H, 2-Me)

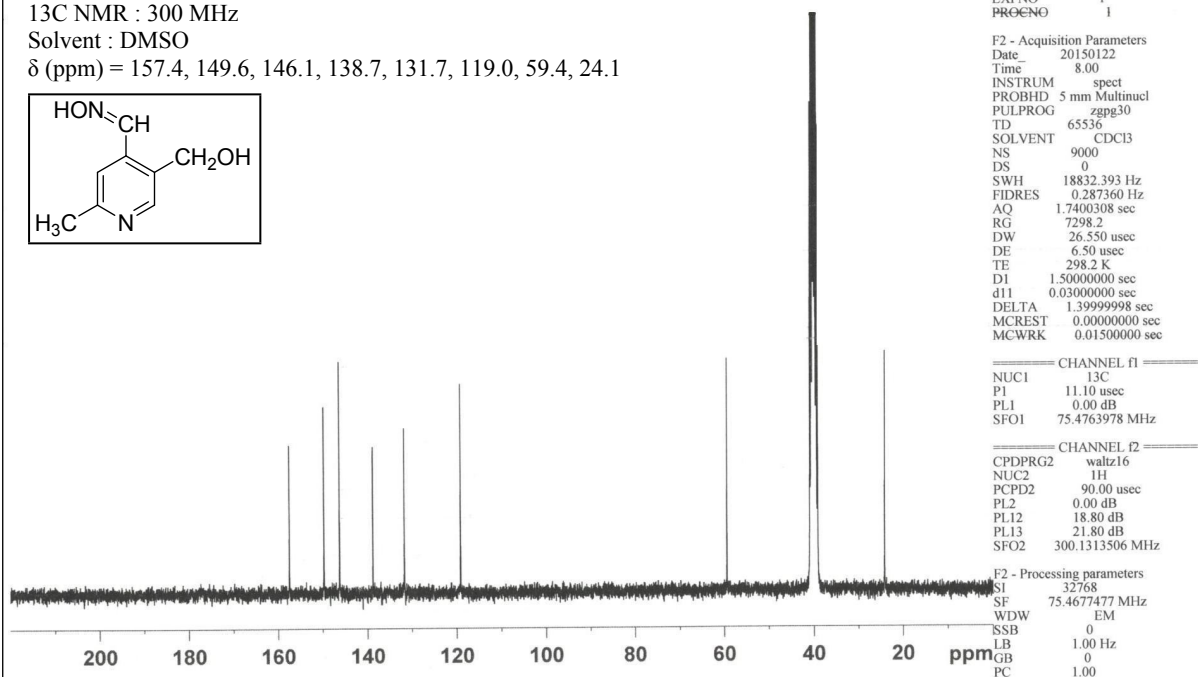
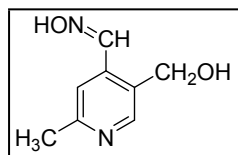


Compound : **5-Hydroxymethyl-2-Methyl-4-pyridinecarboxaldehyde oximes (8b)**

¹³C NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 157.4, 149.6, 146.1, 138.7, 131.7, 119.0, 59.4, 24.1

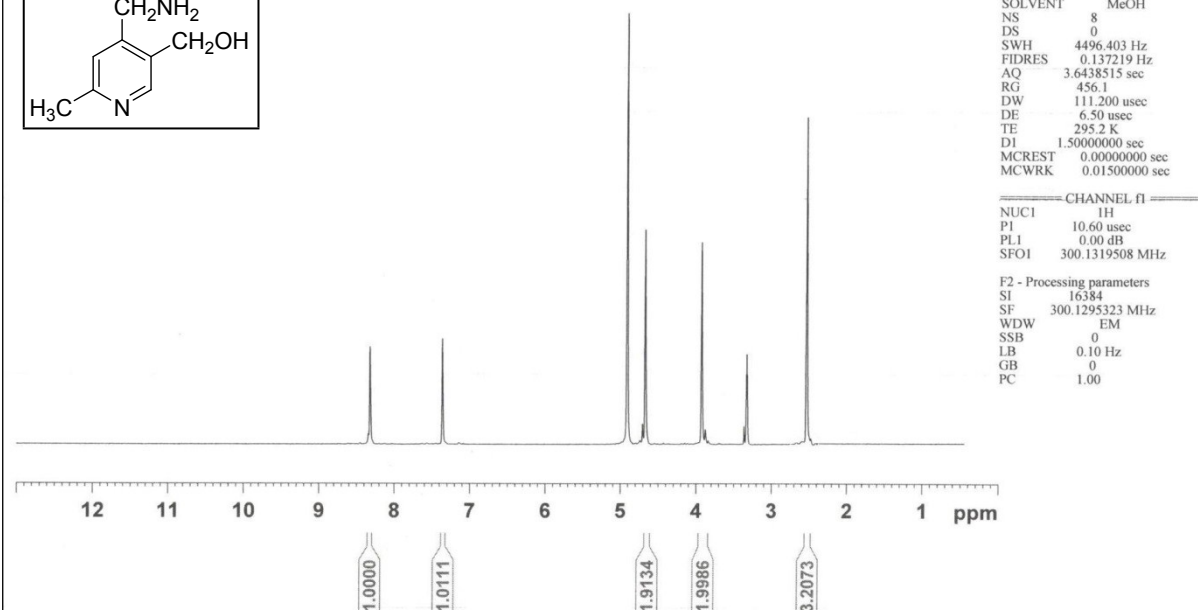
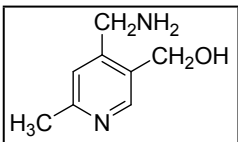


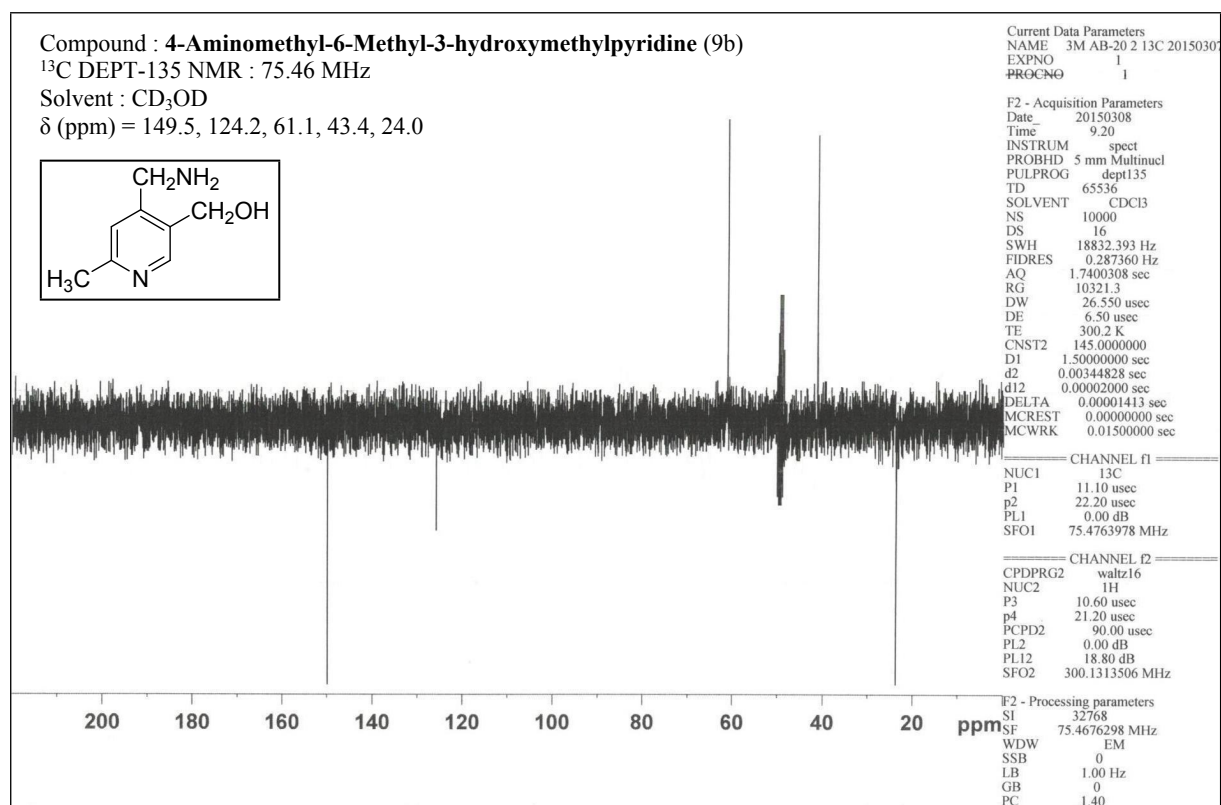
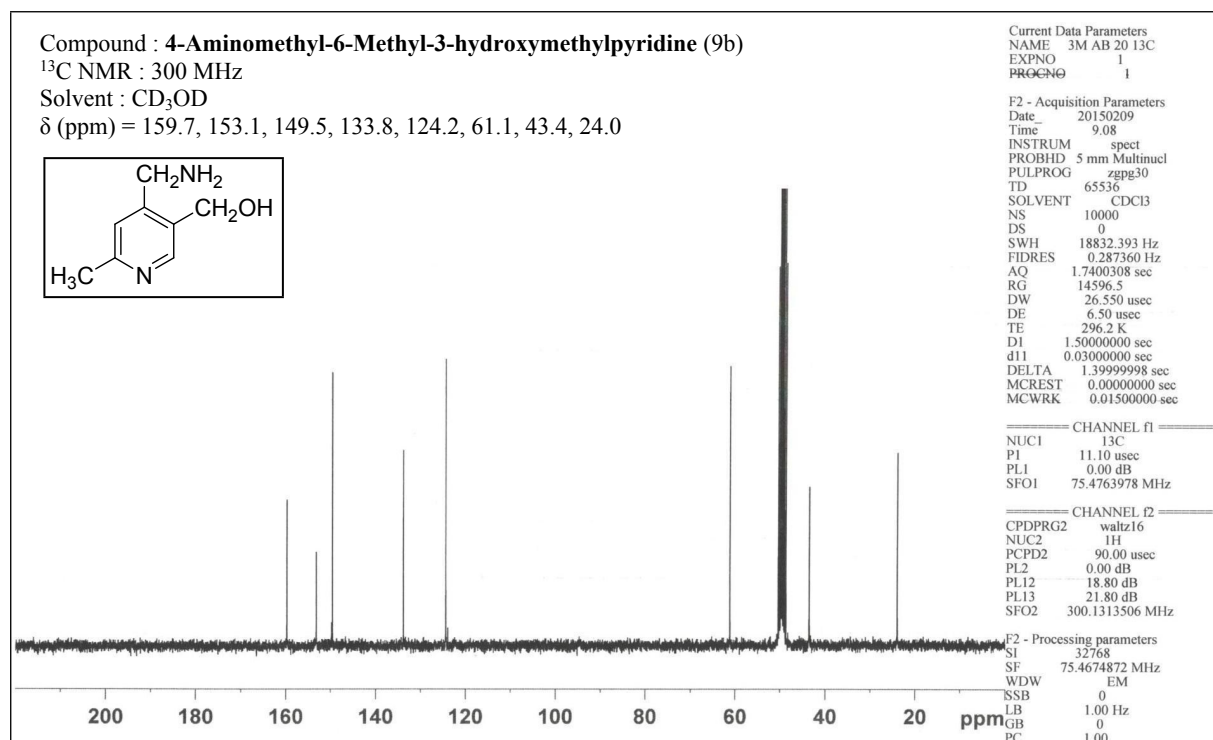
Compound : **4-Aminomethyl-6-Methyl-3-hydroxymethylpyridine (9b)**

¹H NMR : 300 MHz

Solvent : CD₃OD

δ (ppm) = 8.31 (s, 1H, 6-H), 7.35 (s, 1H, 3-H), 4.65 (s, 2H, 5'-CH₂), 3.95 (s, 2H, 4'-CH₂), 2.53 (s, 3H, 2-Me)



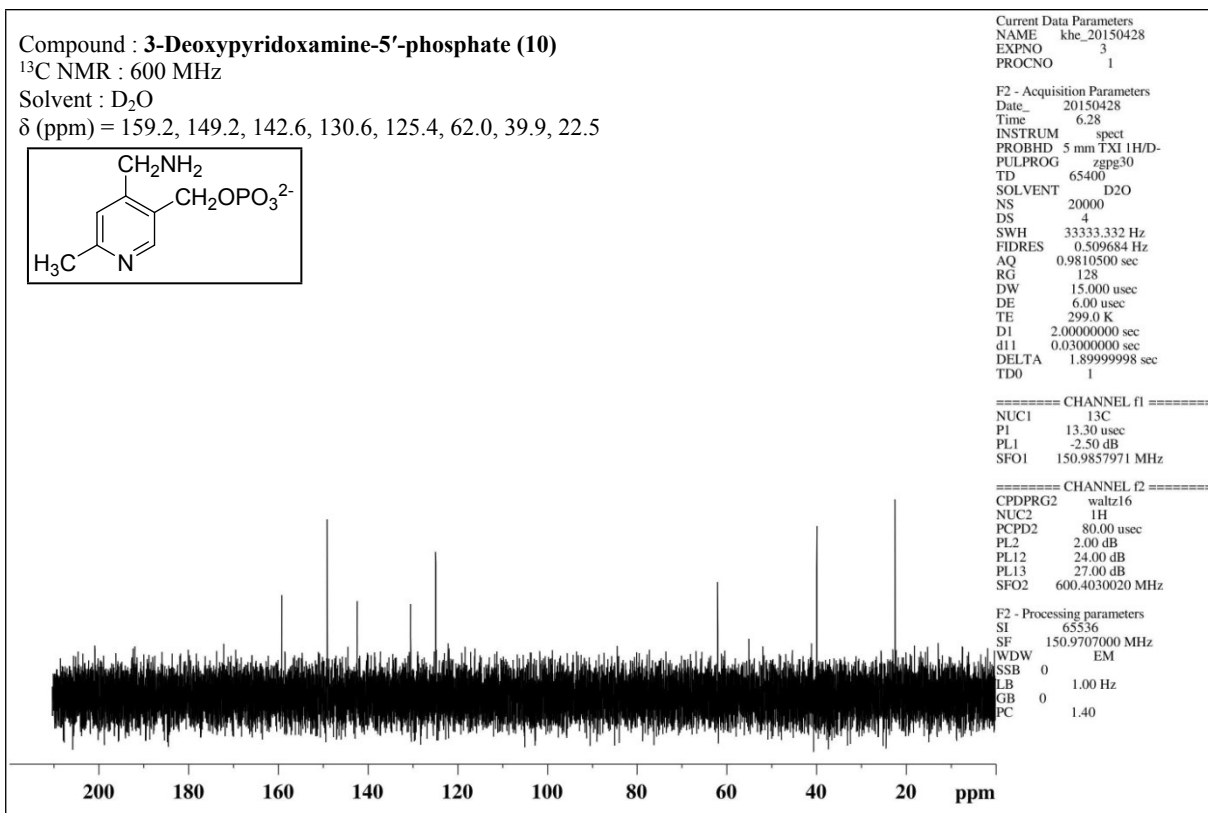
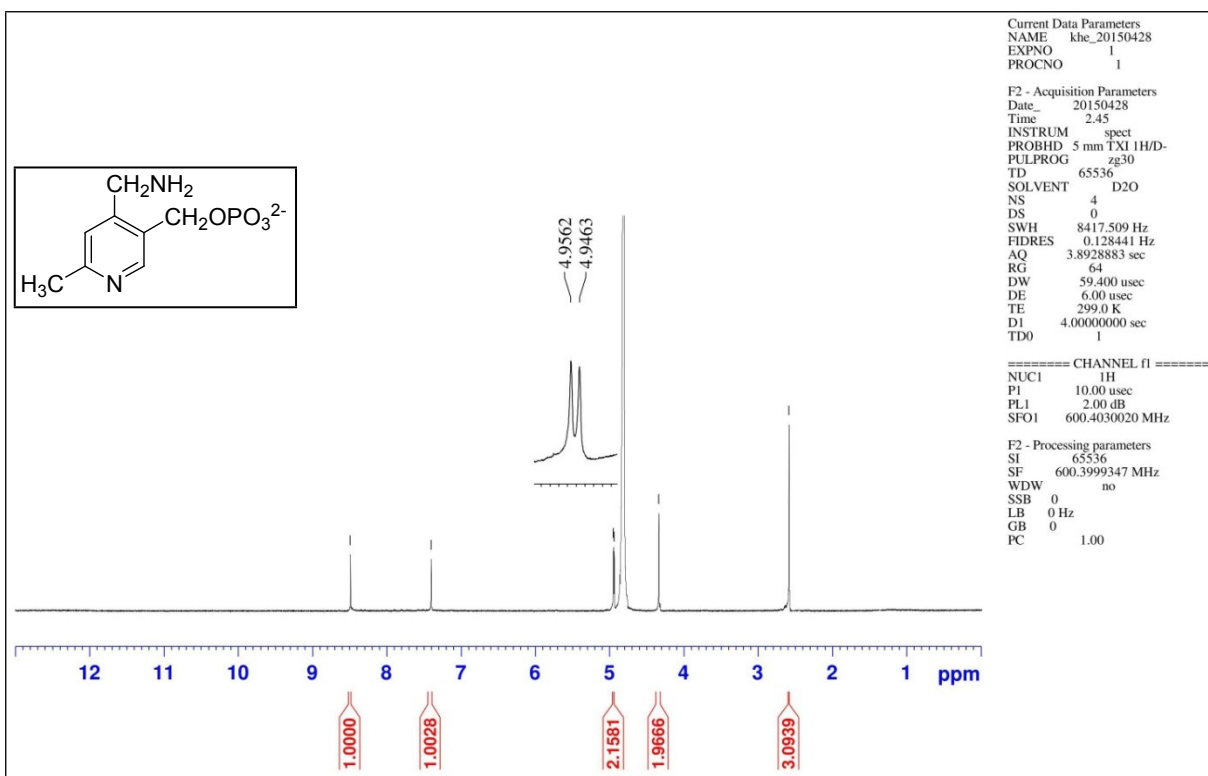


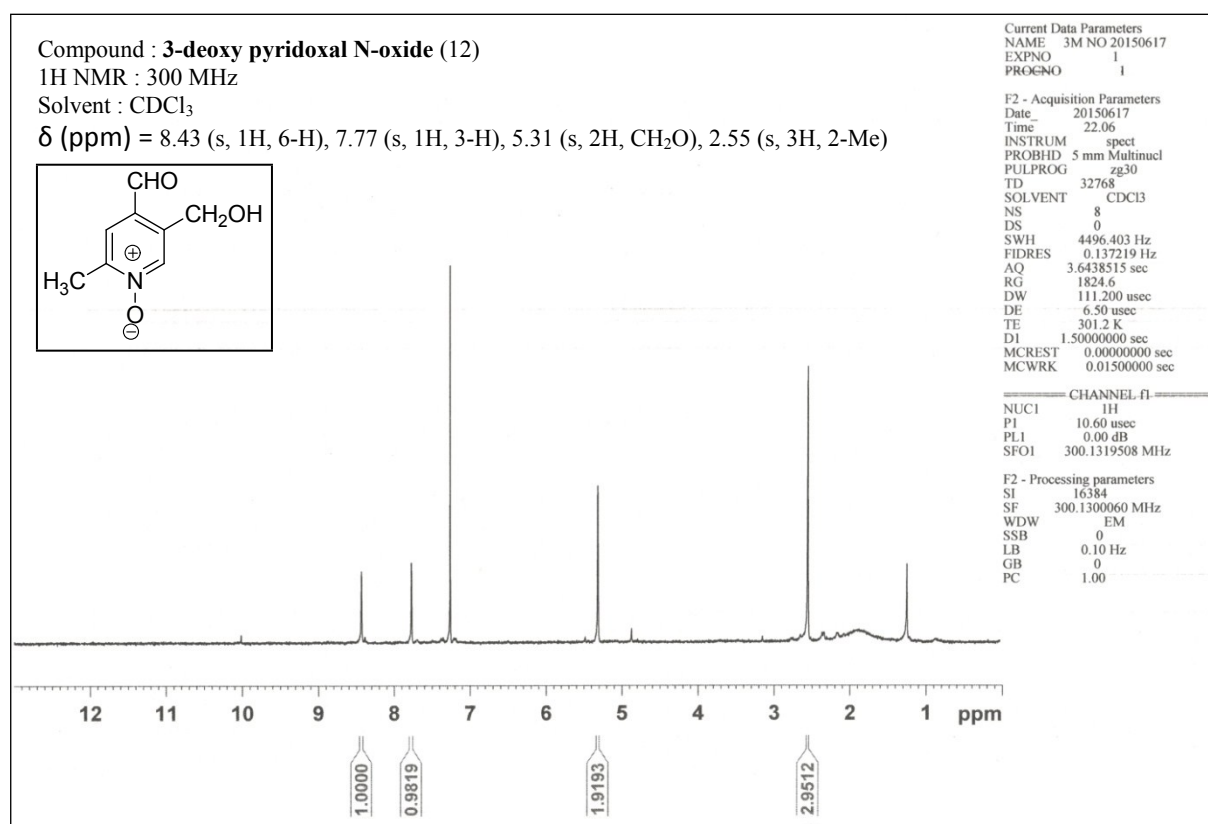
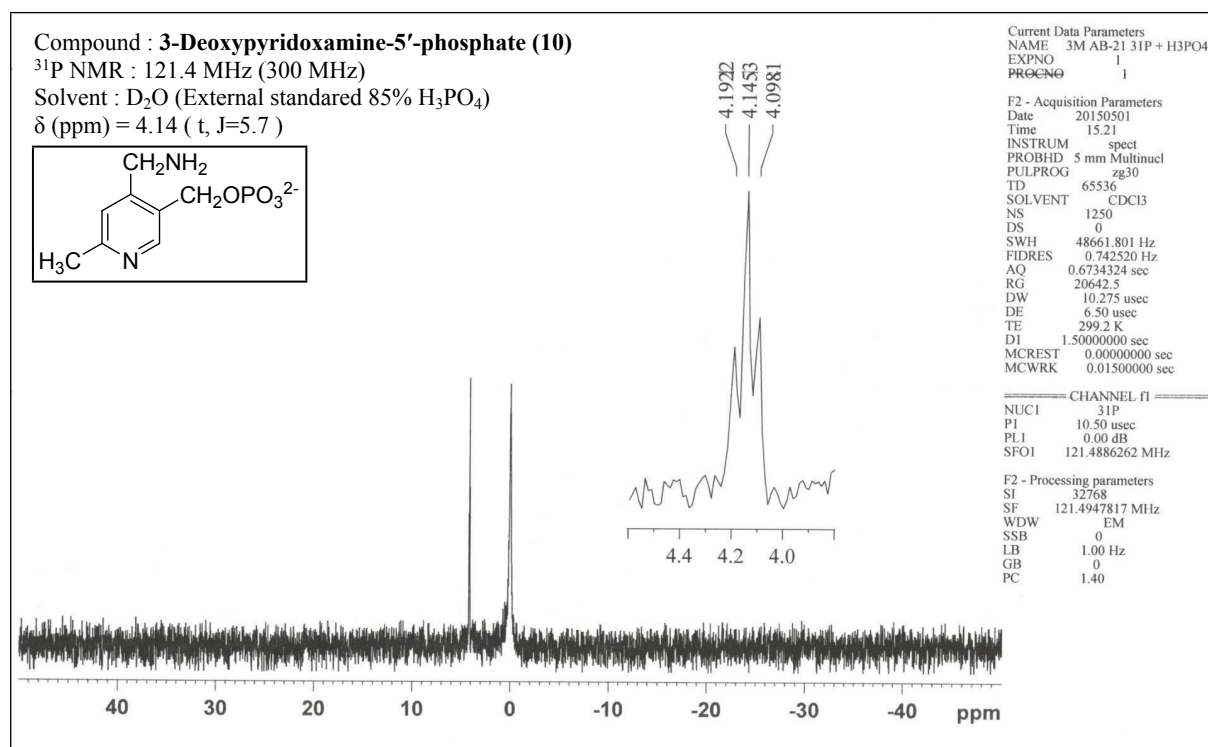
Compound : **3-Deoxypyridoxamine-5'-phosphate (10)**

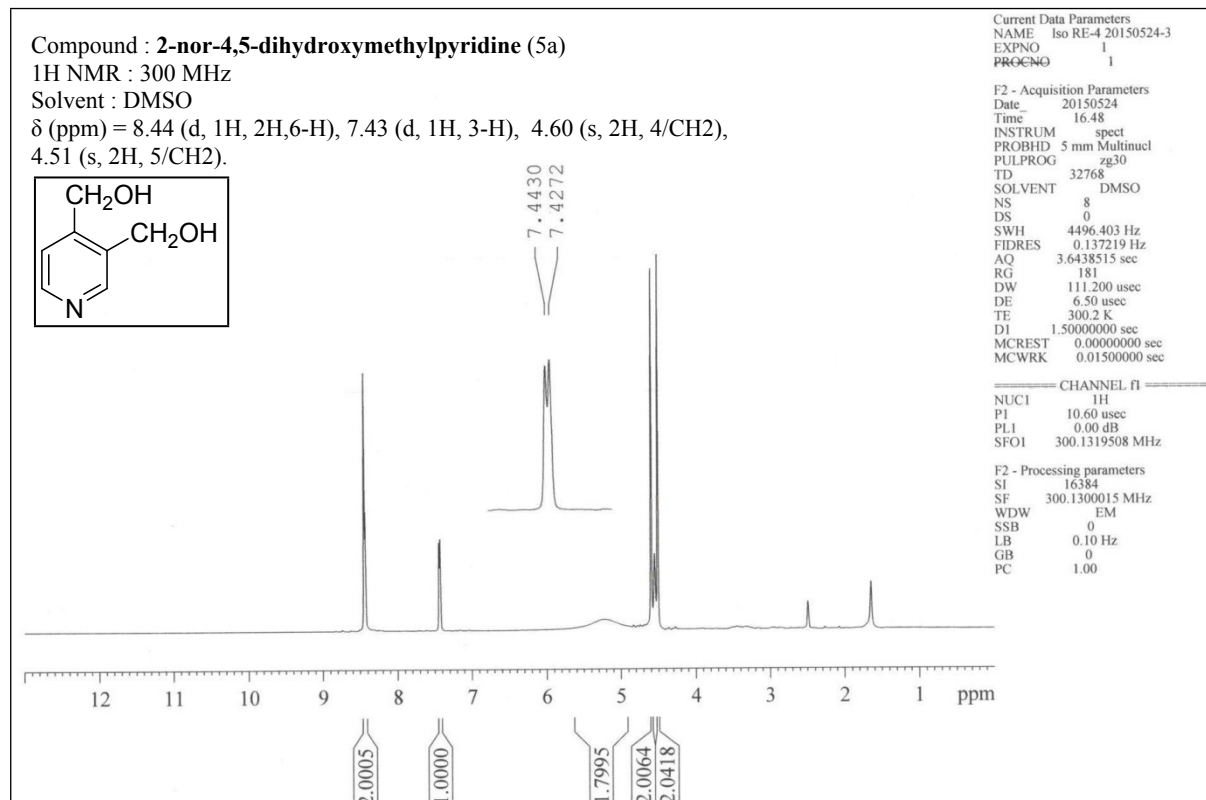
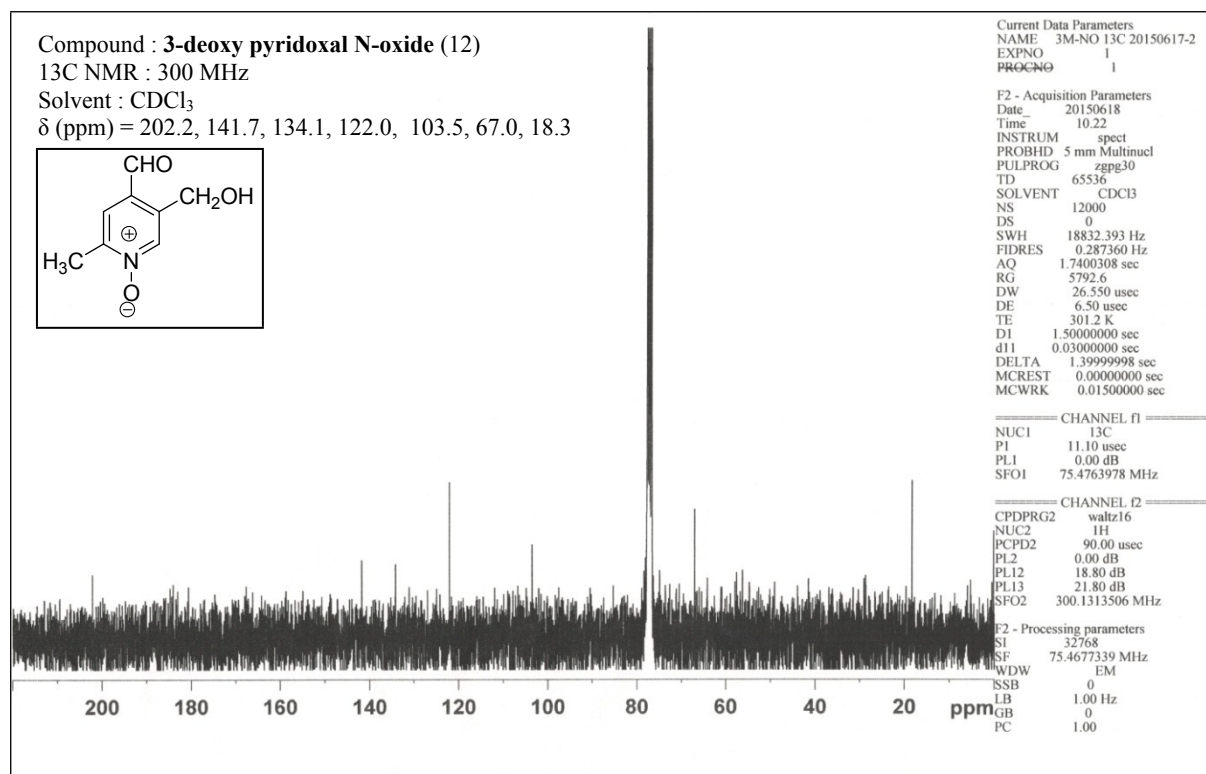
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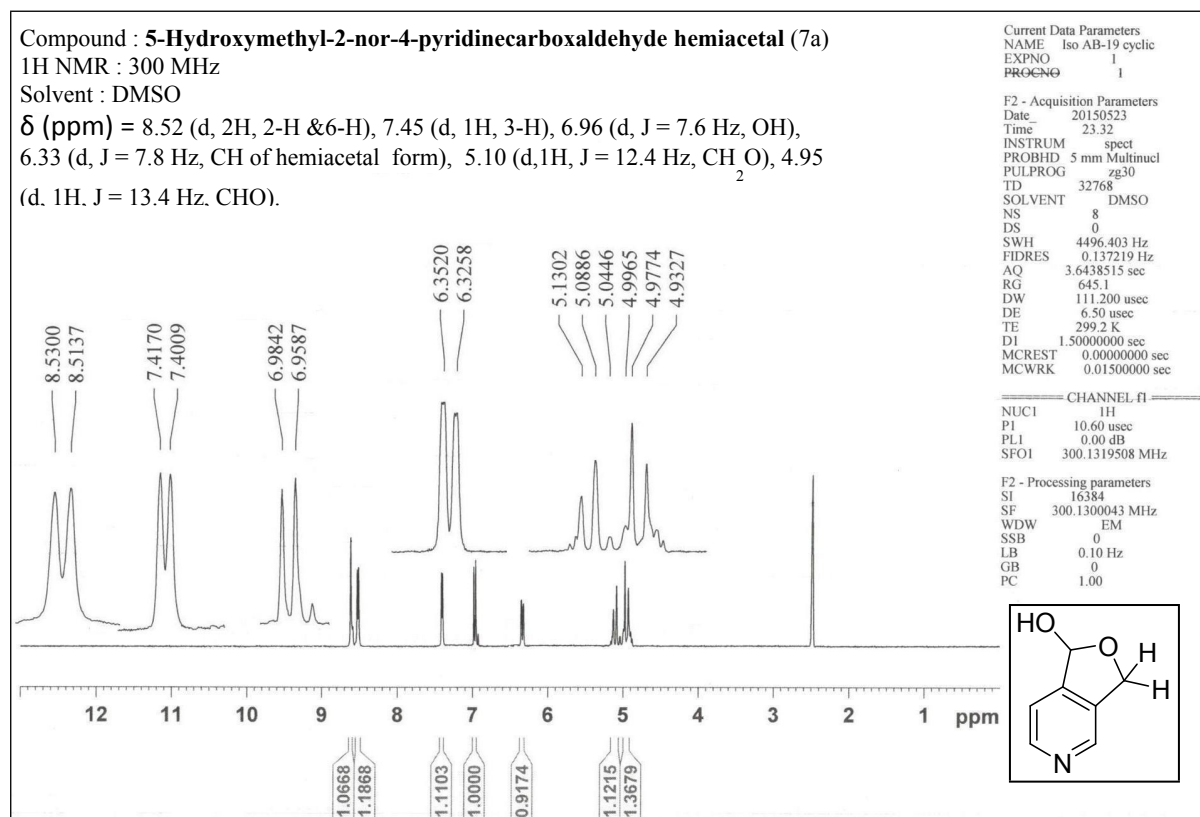
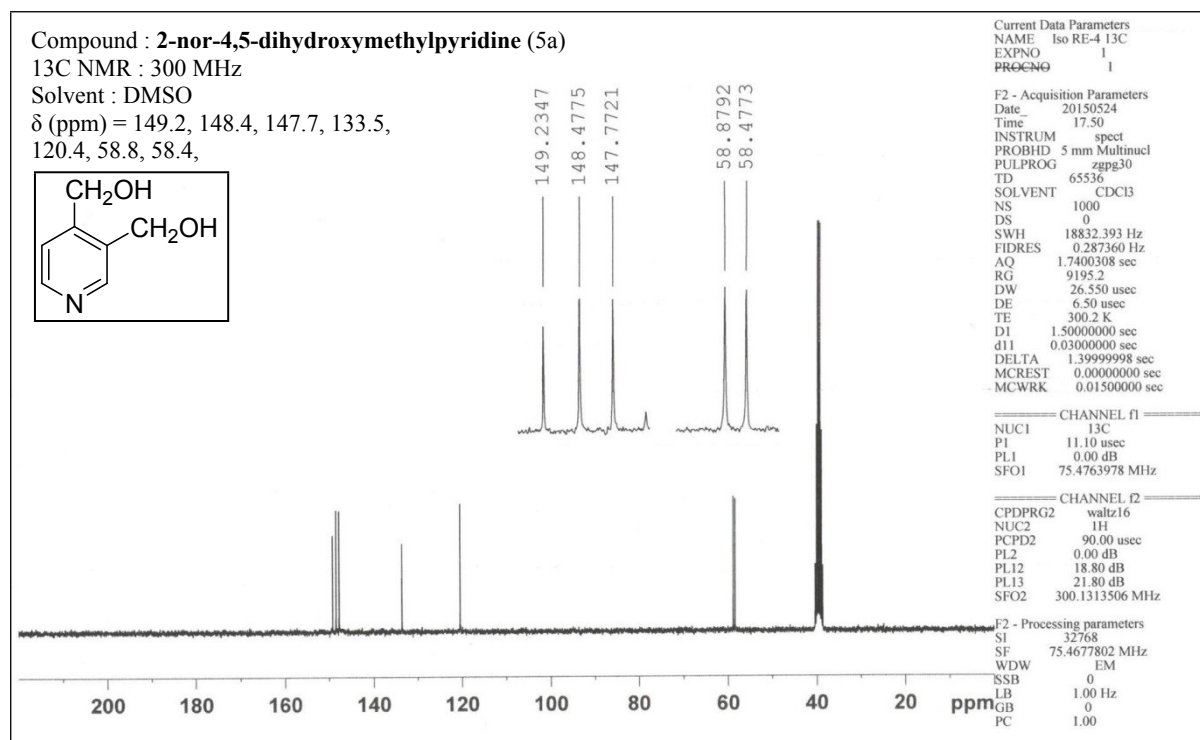
Solvent : D₂O

δ (ppm) = 8.49 (s, 1H, 6-H), 7.41 (s, 1H, 3-H), 4.95 (d, 2H, 5'CH₂ J= 5.94), 4.34 (s, 2H, 4'CH₂), 2.59 (s, 3H, 2-Me)







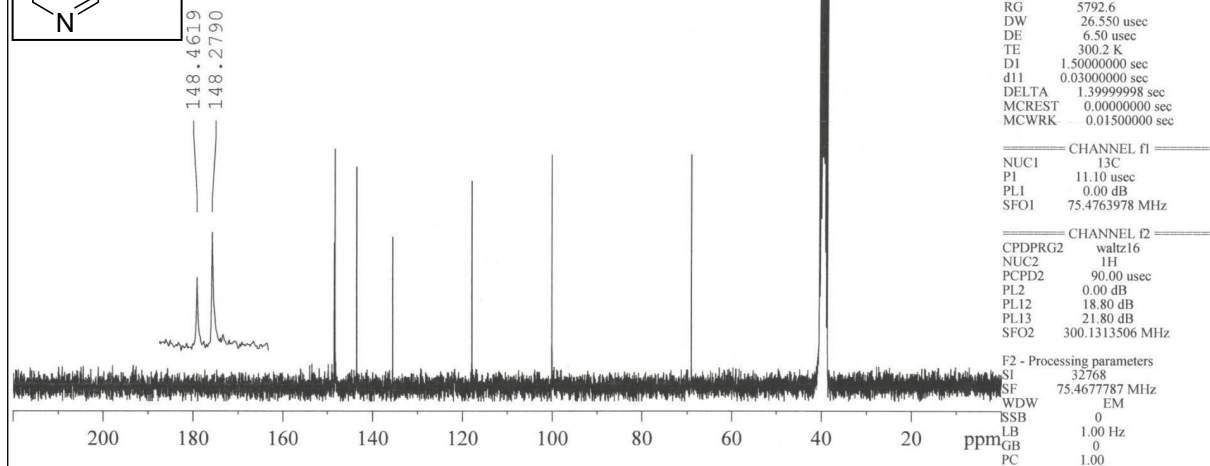
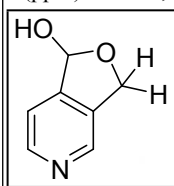


Compound : **5-Hydroxymethyl-2-nor-4-pyridinecarboxaldehyde hemiacetal (7a)**

¹³C NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 148.4, 148.2, 143.4, 135.5, 117.9, 100.0, 69.0

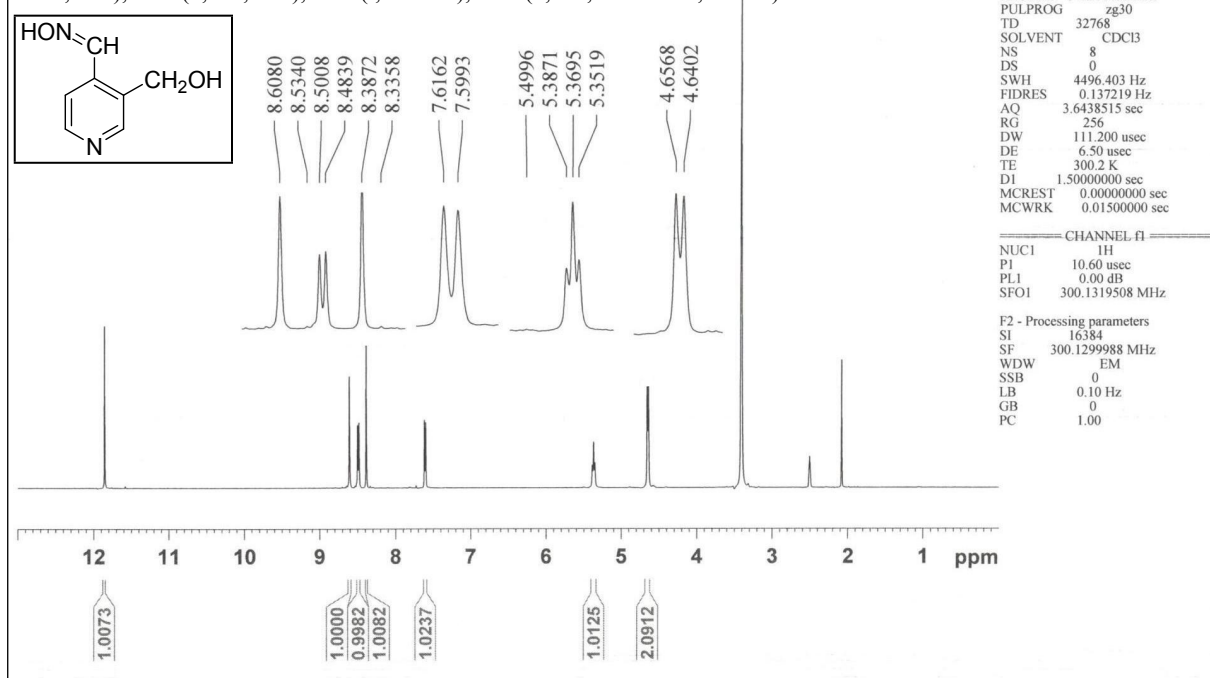
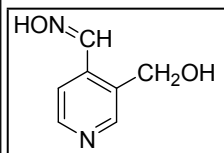


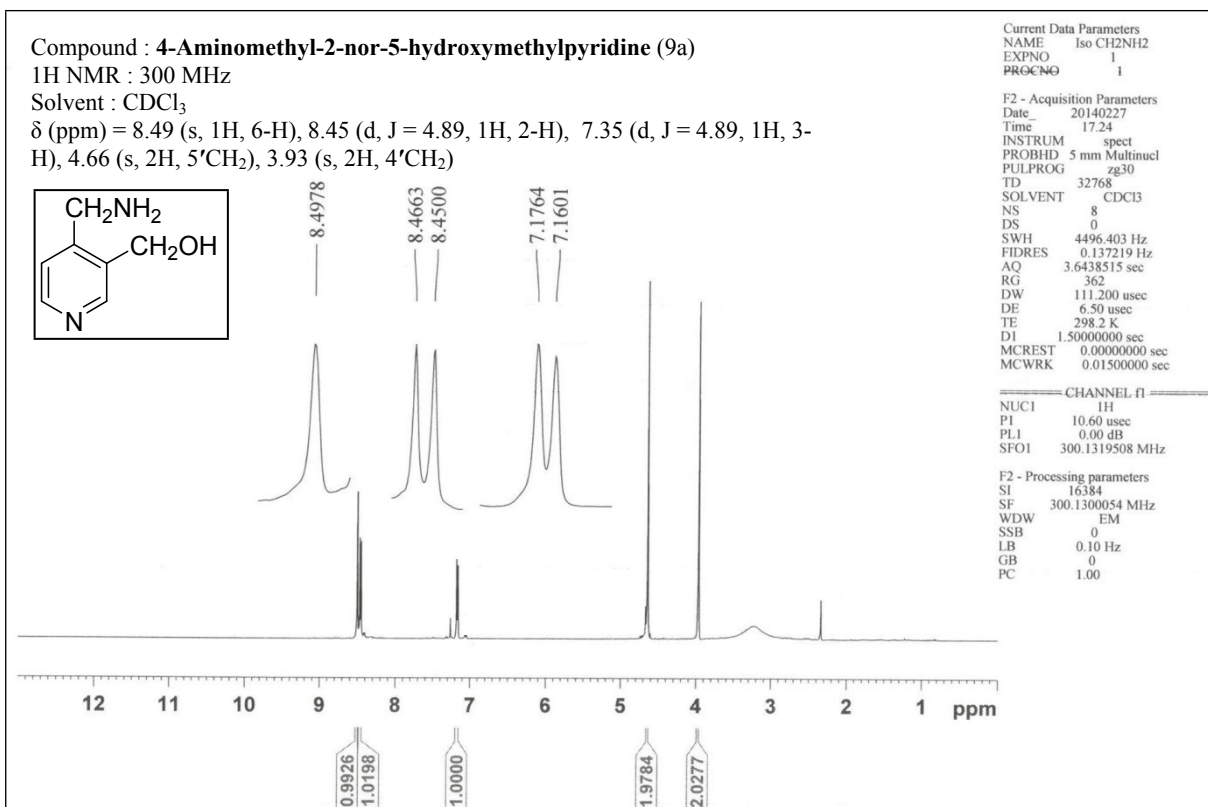
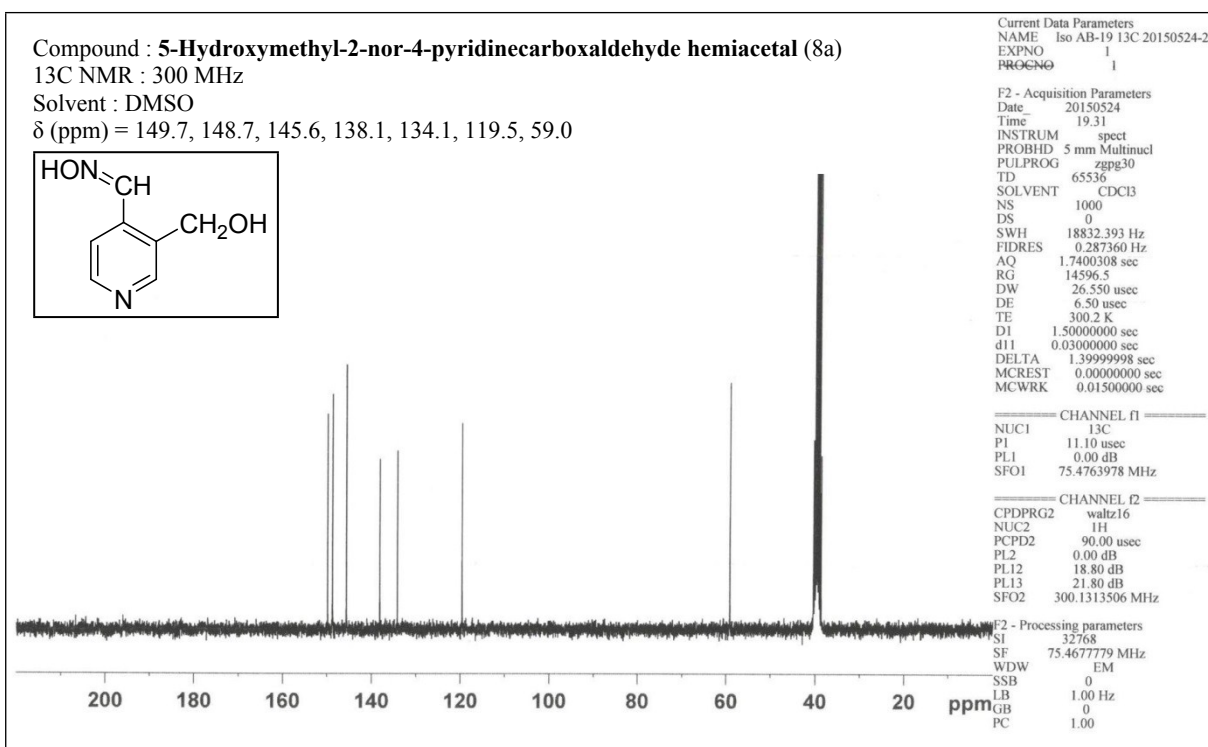
Compound : **5-Hydroxymethyl-2-nor-4-pyridinecarboxaldehyde oximes (8a)**

¹H NMR : 300 MHz

Solvent : DMSO

δ (ppm) = 11.81 (s, 1H, NOH), 8.60 (s, 1H, 4'-CH), 8.49 (d, 1H, 2-H), 8.38 (s, 1H, 6-H), 7.60 (d, 1H, 3-H), 5.36 (t, 1H OH), 4.58 (d, 2H, J = 4.4 Hz, CH₂O)



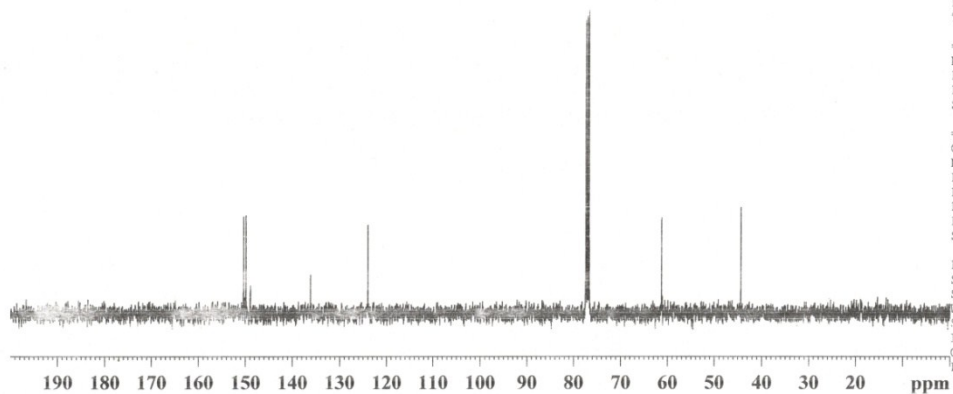
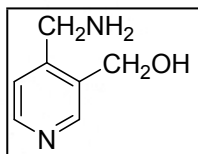


Compound : 4-Aminomethyl-2-nor-5-hydroxymethylpyridine (9a)

^{13}C NMR : 400 MHz

Solvent : CDCl_3

δ (ppm) = 150.3, 149.8, 148.8, 136.1, 123.9, 61.3, 44.4



Current Data Parameters
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EXPNO 328011
PROCNO 1

F2 - Acquisition Parameters
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Time 17.31
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 0
SWH 25510.203 Hz
FIDRES 0.389255 Hz
AQ 1.2845556 sec
RG 1150
DW 19.600 usec
DE 7.00 usec
TE 296.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.80 usec
PL1 0.00 dB
SFO1 100.6248425 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 14.00 dB
PL13 17.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
FC 1.00