

LIST of SUPPORTING INFORMATION

An Efficient NO Equivalent for Activation of Molecular Oxygen and its Applications in Transition-Metal-Free Catalytic Aerobic Alcohol Oxidation

Yi Xie, Weimin Mo, Dong Xu, Zhenlu Shen, Nan Sun, Baoxiang Hu and Xinquan Hu *

College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou, 310014, People's Republic of China

*To whom correspondence should be address.

E-mail: xinquan@zjut.edu.cn

1. Complete ref. 12a .
2. Experimental Section-General (3 page).
3. Figure List (2 pages)
4. GC diagrams and NMR spectra (37 pages)

SUPPORTING INFORMATION

An Efficient NO Equivalent for Activation of Molecular Oxygen and its Applications in Transition-Metal-Free Catalytic Aerobic Alcohol Oxidation

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Complete ref. 12a

12. (a) Barvian, M.; Boschelli, D. H.; Cossrow, J.; Dobrusin, E.; Fattaey, A.; Fritsch, A.; Fry, D.; Harvey, P.; Keller, P.; Garrett, M.; La, F.; Leopold, W.; McNamara, D.; Quin, M.; Trumpp-Kallmeyer, S.; Toogood, P.; Wu, Z.; Zhang, E. *J. Med. Chem.* **2000**, *43*, 4606.

Experimental Section

General. Equipment and Material All experiments were carried out in a closed Teflon-lined 316L stainless steel autoclave (300 mL), the initial atmospheric air in the autoclave did not exchange for all oxidations. ¹H NMR spectrum was recorded (400MHz) CDCl₃ or d⁶-DMSO as the solvents with TMS as an internal reference. Conversions and selectivities were determined by GC analysis. Impurities were confirmed by GC-MS. Conversion and purity of the compound with a high melting point was detected via HPLC analysis. Benzyl alcohol, 1-octanol, 2-octanol were domestic reagents. Benzyl alcohol for high TON reactions was redistilled before using. TEMPO, *tert*-butyl nitrite (TBN), 4-methyl benzyl alcohol, 3-methyl benzyl alcohol, 2-methyl benzyl alcohol, 4-chloro benzyl alcohol, 3-chloro-benzyl alcohol, 2-chloro benzyl alcohol, 2-thiophene methanol, 3-pyridine methanol, 4-nitrobenzyl alcohol, α -methyl-benzyl alcohol were commercial products. 1-(4-Methylphenyl)-1-ethanol and 1-(4-chlorophenyl)-1-ethanol were reduced from their corresponding acetophenones and their purity was confirmed by GC analysis. 4-Amino-2-methylthio-pyrimidine-5-methanol was prepared according to the literature procedure (1, 2).

Typical procedure of aerobic oxidation alcohols with benzyl alcohol as an example (entry 1 in Table 2): To a Teflon-lined 316L stainless steel autoclave (300 mL), added 10.80 g (100 mmol) of benzyl alcohol, 15.6 mg (0.1 mmol, 0.1 mol%) of TEMPO, 48 μ L (70 mg, 0.4 mmol, 0.4 mol%) of 48% HBr ($d = 1.46$), 46 μ L (41 mg, 0.4 mmol, 0.4 mol%) of TBN, 1.0 mL of water. Then closed the autoclave and charged oxygen to 0.6 MPa. Put the autoclave into the oil bath, which was preheated to 80 $^{\circ}$ C. 4 hours later, the barometer dropped to 0.2 MPa indicated that the reaction was finished. The autoclave was taken out from the heating bath, cooled to room temperature and carefully depressurized the autoclave. Diluted the sample with CH_2Cl_2 and detected the conversion and selectivity by GC without any purification. GC result showed the reaction complete, the liquid in the autoclave was transferred into a separation funnel, washed with water (10 mL \times 2), the organic layer was dried over anhydrous Na_2SO_4 , concentrated to dryness to yield 10.25 g (96.7%) as an oil.

Procedure of oxidation of 4-nitrobenzyl alcohol (entry 10 in Table 2): To a Teflon-lined 316L stainless steel autoclave (300 mL), added 15.31 g (100 mmol) of 4-nitro benzyl alcohol, 78.0 mg (0.5 mmol, 0.5 mol%) of TEMPO, 350 mg (2.0 mmol, 2 mol%) of 48% HBr, 210 mg (2.0 mmol, 2 mol%) of TBN, 20 mL of acetonitrile (the minimum volume to form a slurry at room temperature). Then closed the autoclave and charged oxygen to 0.6 MPa. Put the autoclave into the oil bath, which was preheated to 80 $^{\circ}$ C. 6 hours later, the barometer, whose pressure was dropped to 0.2 MPa, indicated that the oxidation was complete. The autoclave was taken out from the heating bath, cooled to room temperature and carefully depressurized the autoclave. Sampling to GC analysis and the result showed it was a clean oxidation. Diluted the slurry with 20 mL of water and then filtered. The solid was washed with water (10 mL \times 2) and dried to yield 14.65 g (97.0%) as a pale yellow solid. The structure of 4-nitro benzaldehyde was confirmed by ^1H NMR (S-27).

Procedure of oxidation of 4-amino-2-methylthio-pyrimidine-5-methanol (entry 16 in Table 2): To a Teflon-lined 316L stainless steel autoclave (300 mL), added 16.40 g (96 mmol) of 4-amino-2-methylthio-pyrimidine-5-methanol, 0.30 g (1.92 mmol, 2 mol%) of TEMPO, 1.34 g (7.68 mmol, 8 mol%) of 48% HBr, 0.79 g (7.68 mmol, 8 mol%) of TBN, 40 mL of acetonitrile (the minimum volume to form a slurry at room temperature). Then closed the autoclave and charged oxygen to 0.6 MPa. Put the autoclave into the oil bath, which was preheated to 80 $^{\circ}$ C. 6 hours later, the barometer, whose pressure was dropped to 0.2 MPa, indicated that the oxidation was complete. The autoclave was taken out from the heating bath, cooled to room temperature and carefully depressurized the autoclave. Diluted the slurry with 40 mL of water and then filtered. The solid was washed with aqueous acetonitrile (1 : 1, v/v, 20 mL \times 2) and dried to yield 13.30 g (81.8%) as a yellow solid. The structure of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde was confirmed by ^1H NMR (S-42) and ^{13}C NMR (S-43), the purity of product was analysis by HPLC (S-41).

General GC conditions: FFAP column, 30m x 0.25mm (id); FID detector, 240 °C; injection: 240 °C; carrier gas: nitrogen; carrier gas rate: 1.0 mL / min; area normalization.

Benzyl alcohol, 4-methyl benzyl alcohol, 3-methyl benzyl alcohol, 2-methyl benzyl alcohol, 4-chloro benzyl alcohol, 3-chloro benzyl alcohol, 2-chloro benzyl alcohol, 2-thiophene methanol, 3-pyridine methanol, 4-nitro benzyl alcohol, α -methyl benzyl alcohol, 1-(4-methylphenyl)-1-ethanol, 1-(4-chlorophenyl)-1-ethanol and their corresponding carbonyl compounds were detected under a condition as: column temperature: 100 °C for 2 minutes, raising to 240 °C in a rate of 10 °C / min.

1-Octanol, 2-octanol and their corresponding carbonyl compounds were performed under a condition as: 80 °C for 5 minutes, raising to 240 °C in a rate of 10 °C / min.

HPLC condition for 4-amino-2-methylthio-pyrimidine-5-methanol: C18 column, 25cm x 4.6mm (id); UV detector at 254 nm; eluent phase: acetonitrile : water = 70 : 30; Flow rate = 0.8 mL / min.

Reference:

1. Ulbricht T. L. V.; Price, C. C. *J. Org. Chem.* **1956**, 21, 567.
2. Dymicky, M.; Caldwell, W. T. *J. Org. Chem.* **1962**, 27, 4211.

Figure List

- Figure 1: GC diagram of benzyl alcohol.
- Figure 2: GC diagram of benzaldehyde from oxidation of benzyl alcohol.
- Figure 3: GC diagram of 4-methyl benzyl alcohol.
- Figure 4: GC diagram of 4-methyl benzaldehyde from oxidation of 4-methyl benzyl alcohol.
- Figure 5: GC diagram of 3-methyl benzyl alcohol.
- Figure 6: GC diagram of 3-methyl benzaldehyde from oxidation of 3-methyl benzyl alcohol.
- Figure 7: GC diagram of 2-methyl benzyl alcohol.
- Figure 8: GC diagram of 2-methyl benzaldehyde from oxidation of 2-methyl benzyl alcohol.
- Figure 9: GC diagram of 4-chloro benzyl alcohol.
- Figure 10: GC diagram of 4-chloro benzaldehyde from oxidation of 4-chloro benzyl alcohol.
- Figure 11: GC diagram of 3-chloro benzyl alcohol.
- Figure 12: GC diagram of 3-chloro benzaldehyde from oxidation of 3-chloro benzyl alcohol.
- Figure 13: GC diagram of 2-chloro benzyl alcohol.
- Figure 14: GC diagram of 2-chloro benzaldehyde from oxidation of 2-chloro benzyl alcohol.
- Figure 15: GC diagram of 2-thiophene methanol.
- Figure 16: GC diagram of 2-thiophene carboxaldehyde from oxidation of 2-thiophene methanol.
- Figure 17: GC diagram of 3-pyridine methanol.
- Figure 18: GC diagram of 3-pyridine carboxaldehyde from oxidation of 3-pyridine methanol.
- Figure 19: GC diagram of 4-nitro benzyl alcohol.
- Figure 20: GC diagram of 4-nitro benzaldehyde from oxidation of 4-nitro benzyl alcohol.
- Figure 21: ^1H NMR spectrum of 4-nitrobenzaldehyde (isolated).
- Figure 22: GC diagram of α -methyl benzyl alcohol.
- Figure 23: GC diagram of acetophenone from oxidation of α -methyl benzyl alcohol.
- Figure 24: GC diagram of 1-(4-methylphenyl)-1-ethanol.
- Figure 25: GC diagram of 4-methyl acetophenone from oxidation of 1-(4-methylphenyl)-1-ethanol.
- Figure 26: GC diagram of 1-(4-chlorophenyl)-1-ethanol.
- Figure 27: GC diagram of 4-chloro acetophenone from oxidation of 1-(4-chlorophenyl)-1-ethanol.
- Figure 28: ^1H NMR spectrum of 4-chloro acetophenone (isolated).
- Figure 29: GC diagram of 2-octanol.
- Figure 30: GC diagram of 2-octanone from oxidation of 2-octanol.
- Figure 31: GC diagram of 1-octanol.
- Figure 32: GC diagram of oxidation of 1-octanol.
- Figure 33: GC diagram of 1-octanal (isolated via distillation).
- Figure 34: HPLC diagram of 4-amino-2-methylthio-pyrimidine-5-methanol.
- Figure 35: HPLC diagram of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated).
- Figure 36: ^1H NMR spectrum of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated).

Figure 37: ^{13}C NMR spectrum of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated).

Supporting Information

C:\HS2000G\Oxidation\20061213-6.che

2007-01-31

GC REPORT

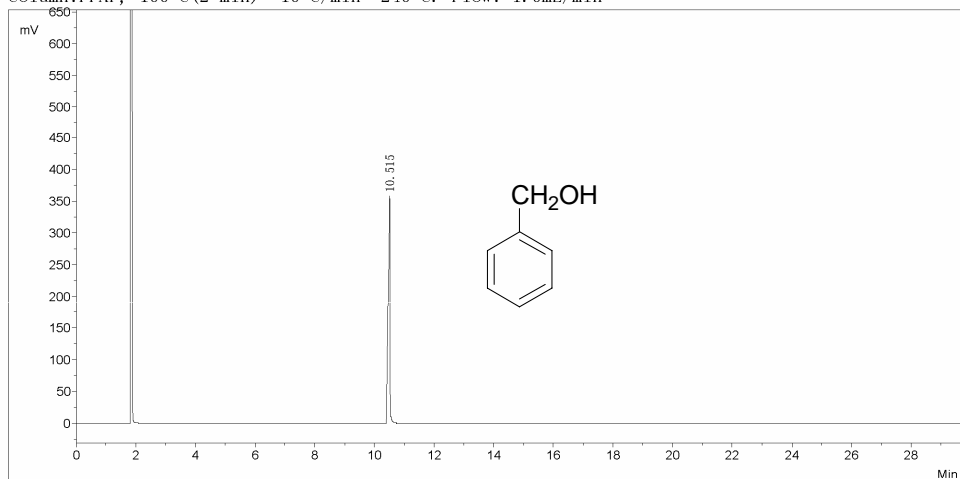
Sample Name:C6H5CH2OH

File Name:C:\HS2000G\Oxidation\20061213-6.che

Method:area normalization

Injection Date:2006.12.13 11.28

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		10.515	356014.4	1529523.4	100.0000
Total				356014.4	1529523.4	100.0000

Figure 1.
GC diagram of benzyl alcohol.

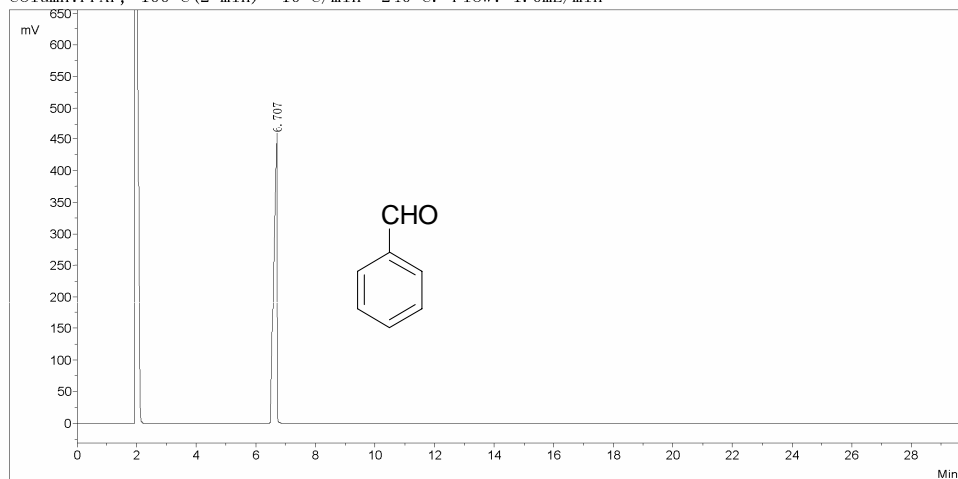
Supporting Information

C:\HS2000G\Oxidation\20061230-6.che

2007-01-29

GC REPORT

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Method: area normalization Injection Date: 2006.12.30 22:19
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		6.707	452312.3	3488300.7	100.0000
Total				452312.3	3488300.7	100.0000

Figure 2.
GC diagram of benzaldehyde from oxidation of benzyl alcohol

Supporting Information

C:\HS2000G\Oxidation\20070118-3.che

2007-01-29

GC REPORT

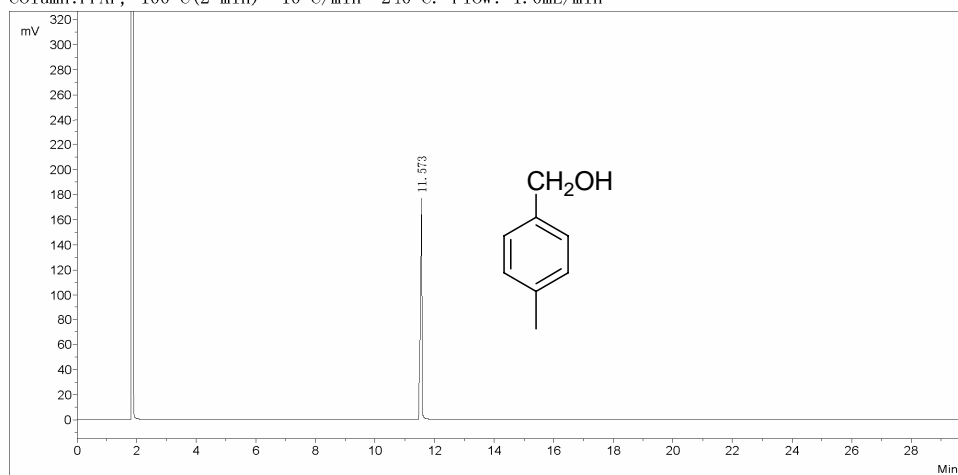
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File Name: C:\HS2000G\Oxidation\20070118-3.che

Method: area normalization

Injection Date: 2007.01.18 12:27

Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		11.573	176605.1	692903.4	100.0000
Total				176605.1	692903.4	100.0000

Figure 3.
GC diagram of 4-methyl benzyl alcohol.

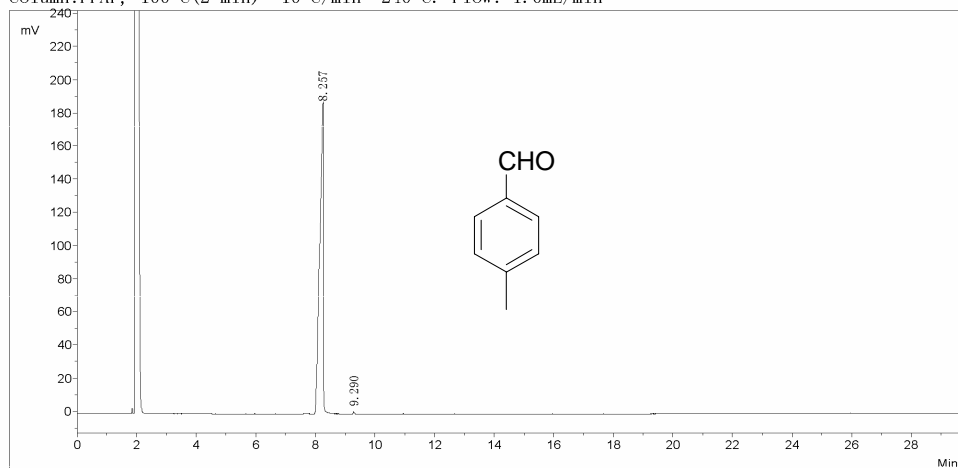
Supporting Information

C:\HS2000G\Oxidation\20070110-5.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070110-5.che
Method: area normalization Injection Date: 2007.01.10 18:29
Column: FFAP, 100 C(2 min)—10 C/min—240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		8.257	185659.4	1539971.4	99.7585
2	2		9.290	1410.5	3728.3	0.2415
Total				187069.9	1543699.6	100.0000

Figure 4.
GC diagram of 4-methyl benzaldehyde from oxidation of 4-methyl benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070110-2.che

2007-01-29

GC REPORT

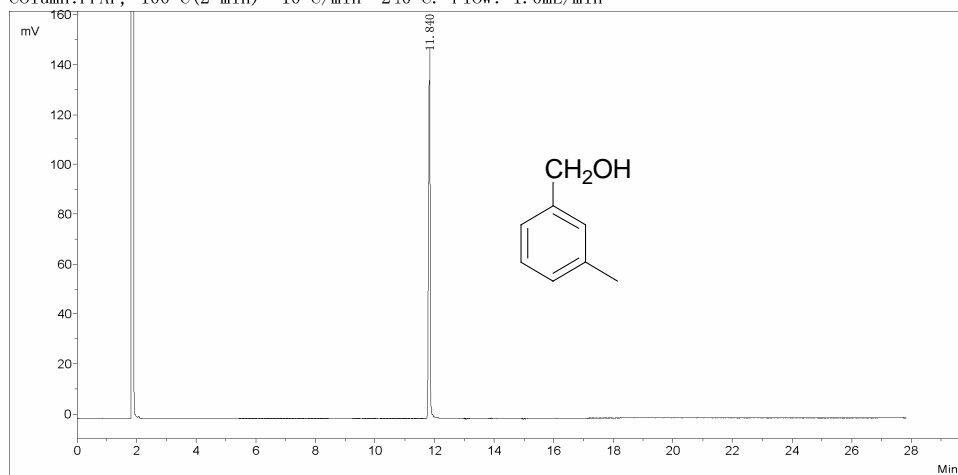
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File Name:C:\HS2000G\Oxidation\20070110-2.che

Method:area normalization

Injection Date:2007.01.10 12:25

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		11.840	146026.5	472435.8	100.0000
Total				146026.5	472435.8	100.0000

Figure 5.
GC diagram of 3-methyl benzyl alcohol.

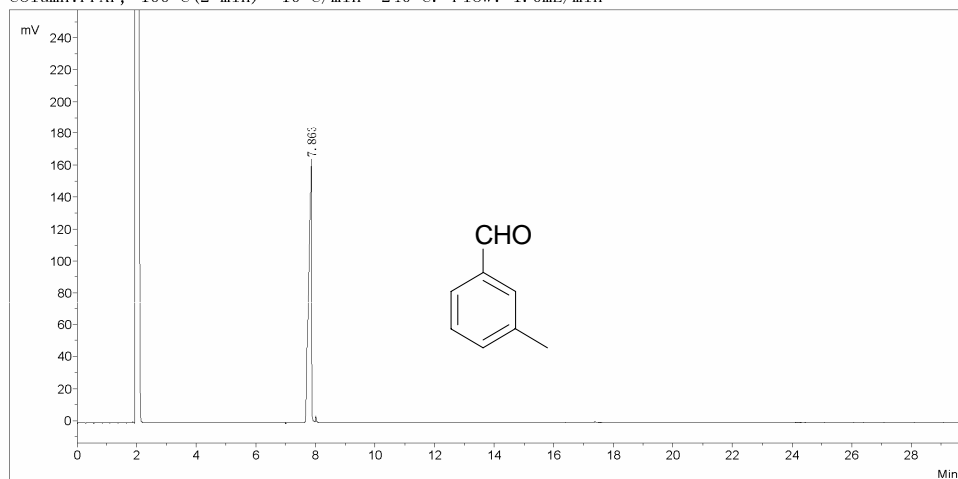
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2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070110-4.che
Method: area normalization Injection Date: 2007.01.10 17:49
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		7.863	162285.5	1060252.7	100.0000
Total				162285.5	1060252.7	100.0000

Figure 6.
GC diagram of 3-methyl benzaldehyde from oxidation of 3-methyl benzyl alcohol.

Supporting Information

C:\HS20006\Oxidation\20070117-5.che

2007-01-29

GC REPORT

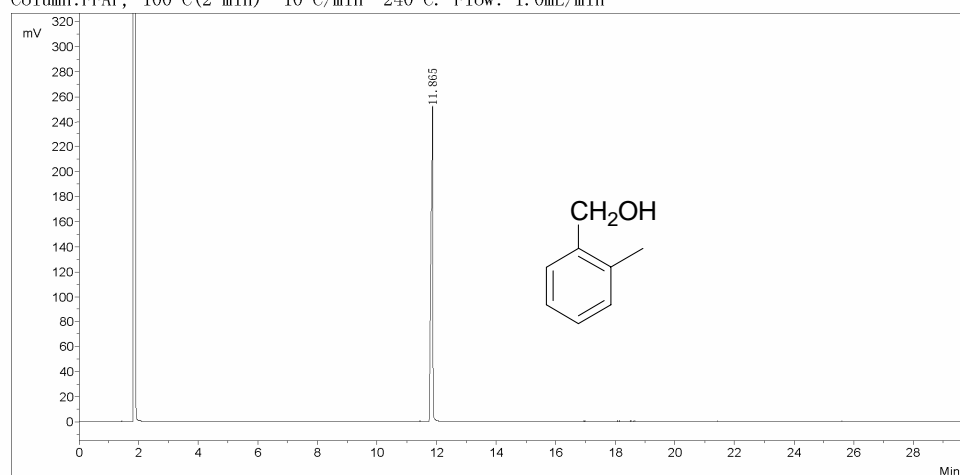
Sample Name: 2-CH₃C₆H₄CH₂OH

File Name: C:\HS20006\Oxidation\20070117-5.che

Method: area normalization

Injection Date: 2007.01.17 20:20

Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		11.865	248479.6	1065711.1	100.0000
Total				248479.6	1065711.1	100.0000

Figure 7.
GC diagram of 2-methyl benzyl alcohol.

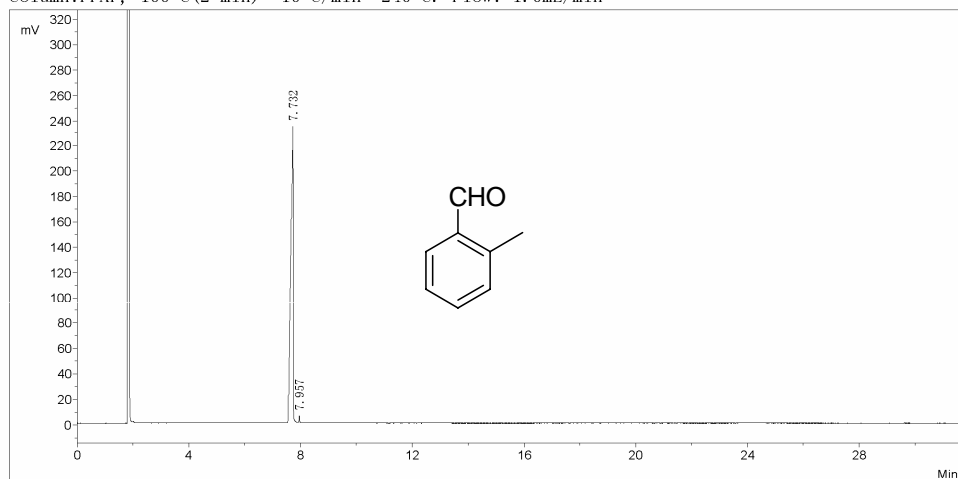
Supporting Information

C:\HS2000G\Oxidation\20070115-2.che

2007-01-29

GC REPORT

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Method: area normalization Injection Date: 2007.01.15 14:56
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		7.732	234640.8	1411849.2	99.1711
2	2		7.957	5511.3	11801.2	0.8289
Total				240152.1	1423650.4	100.0000

Figure 8.
GC diagram of 2-methyl benzaldehyde from oxidation of 2-methyl benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20061213-8.che

2007-01-29

GC REPORT

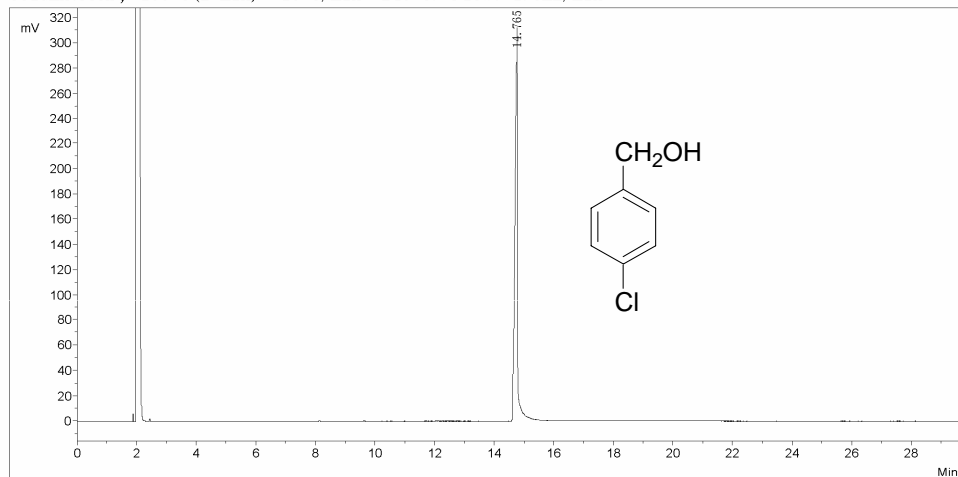
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File Name:C:\HS2000G\Oxidation\20061213-8.che

Method:area normalization

Injection Date:2006.12.13 14:52

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		14.765	312358.8	1839284.6	100.0000
Total				312358.8	1839284.6	100.0000

Figure 9.
GC diagram of 4-chloro benzyl alcohol.

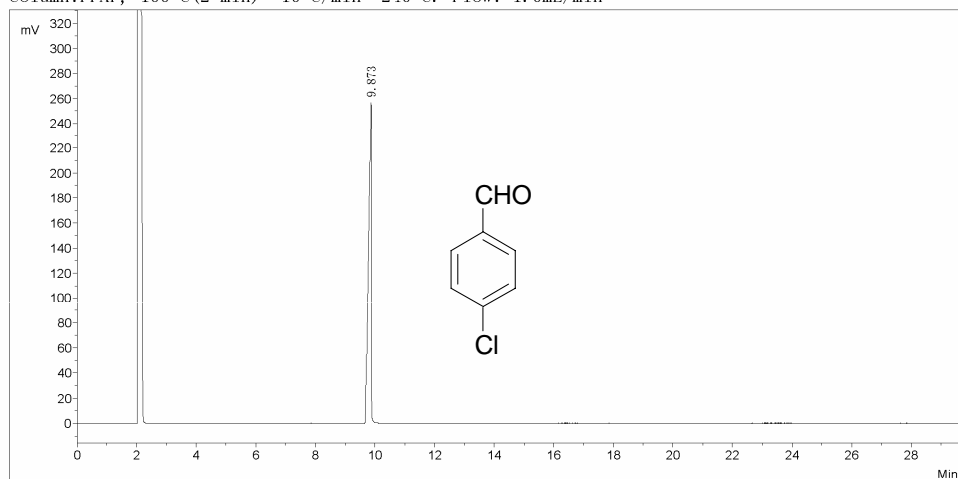
Supporting Information

C:\HS2000G\Oxidation\20070111-1.che

2007-01-29

GC REPORT

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Method: area normalization Injection Date: 2007.01.11 12:43
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		9.873	256775.2	1661398.3	100.0000
Total				256775.2	1661398.3	100.0000

Figure 10.
GC diagram of 4-chloro benzaldehyde from oxidation of 4-chloro benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070109-3.che

2007-01-29

GC REPORT

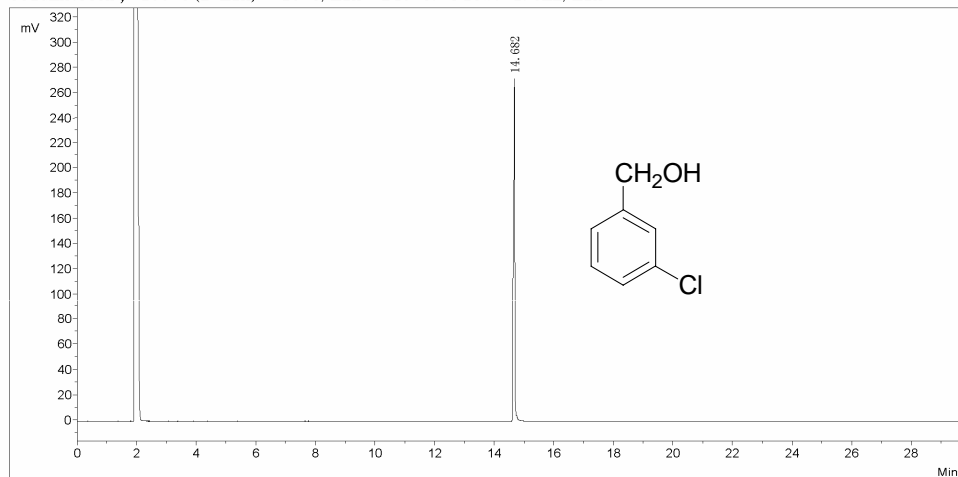
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File Name:C:\HS2000G\Oxidation\20070109-3.che

Method:area normalization

Injection Date:2007.01.09 13:48

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		14.682	272119.8	889526.9	100.0000
Total				272119.8	889526.9	100.0000

Figure 11.
GC diagram of 3-chloro benzyl alcohol.

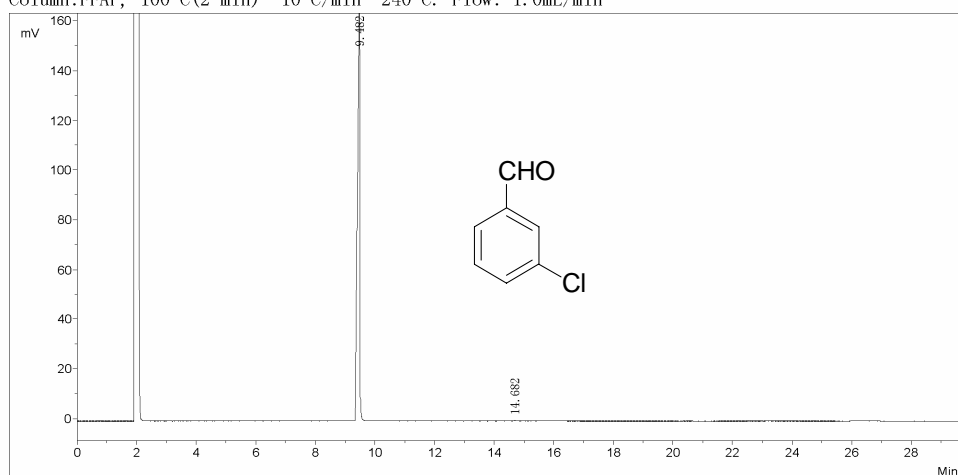
Supporting Information

C:\HS2000G\Oxidation\20070109-5.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070109-5.che
 Method: area normalization Injection Date: 2007.01.09 17:42
 Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		9.482	182865.4	981607.1	99.8648
2	2		14.682	394.0	1328.9	0.1352
Total				183259.4	982936.0	100.0000

Figure 12.
GC diagram of 3-chloro benzaldehyde from oxidation of 3-chloro benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070111-3. che

2007-01-29

GC REPORT

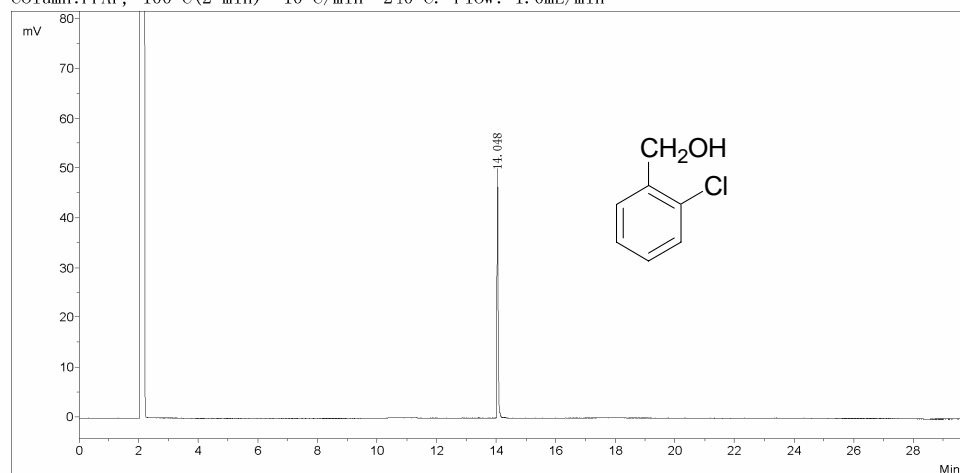
Sample Name: 2-ClC₆H₄CH₂OH

File Name: C:\HS2000G\Oxidation\20070111-3. che

Method: area normalization

Injection Date: 2007.01.11 14:18

Column: FFAP, 100 C (2 min) -- 10 C/min -- 240 C. Flow: 1.0 mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		14.048	48716.5	126257.7	100.0000
Total				48716.5	126257.7	100.0000

Figure 13.
GC diagram 2-chloro benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070111-2. che

2007-01-29

GC REPORT

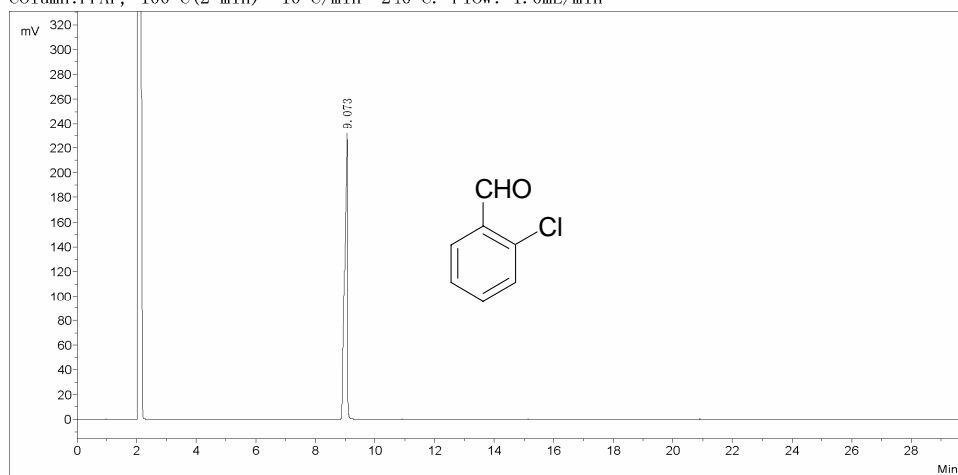
Sample Name:

File Name: C:\HS2000G\Oxidation\20070111-2. che

Method: area normalization

Injection Date: 2007.01.11 13:30

Column: FFAP, 100 C (2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		9.073	231374.7	1524662.0	100.0000
Total				231374.7	1524662.0	100.0000

Figure 14.
GC diagram of 2-chloro benzaldehyde from oxidation of 2-chloro benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070117-6. che

2007-01-29

GC REPORT

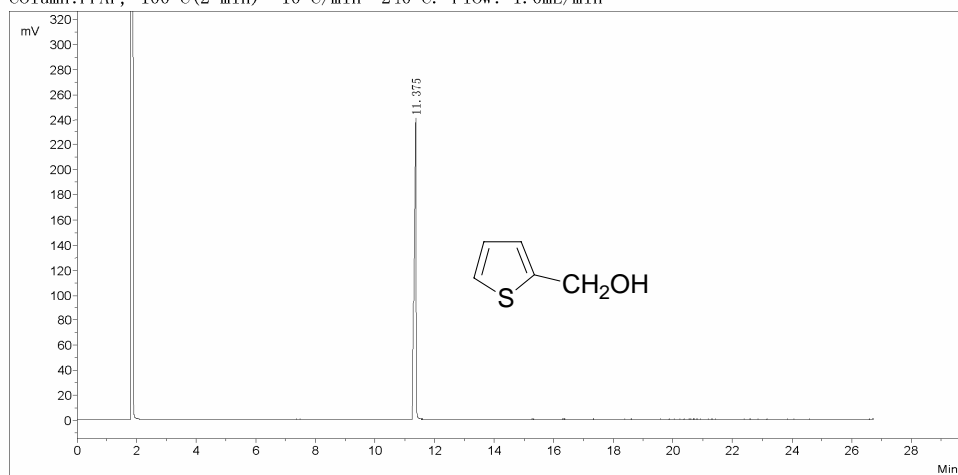
Sample Name: C₄H₃S-2-CH₂OH

File Name: C:\HS2000G\Oxidation\20070117-6. che

Method: area normalization

Injection Date: 2007.01.17 21:04

Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		11.375	239177.8	1149982.3	100.0000
Total				239177.8	1149982.3	100.0000

Figure 15.
GC diagram of 2-thiophene methanol.

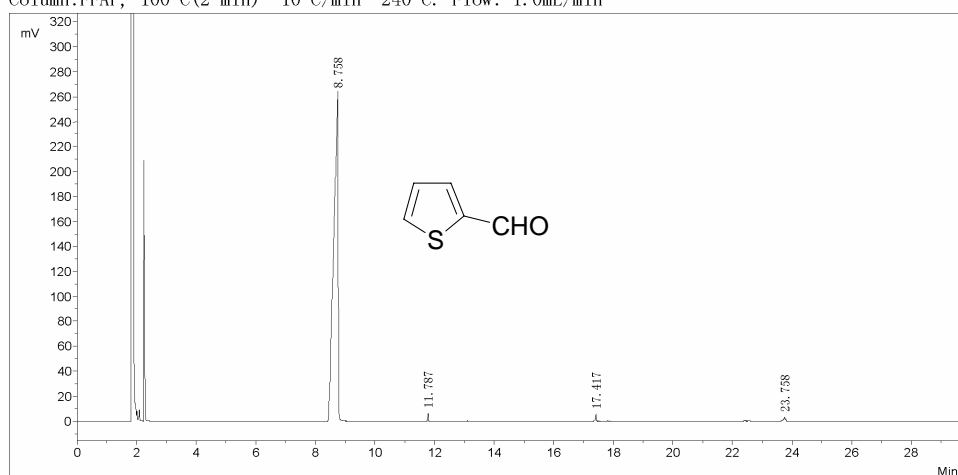
Supporting Information

C:\HS2000G\Oxidation\20070113-5.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070113-5.che
 Method: area normalization Injection Date: 2007.01.13 19:13
 Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		8.758	262757.5	2694568.7	98.8182
2	2		11.787	6228.5	12278.1	0.4503
3	3		17.417	4704.1	9068.0	0.3326
4	4		23.758	2659.5	10878.7	0.3990
Total				276349.5	2726793.6	100.0000

Figure 16.
GC diagram of 2-thiophene carboxaldehyde from oxidation of 2-thiophene methanol.

C:\HS2000G\Oxidation\20070118-2. che

2007-01-29

GC REPORT

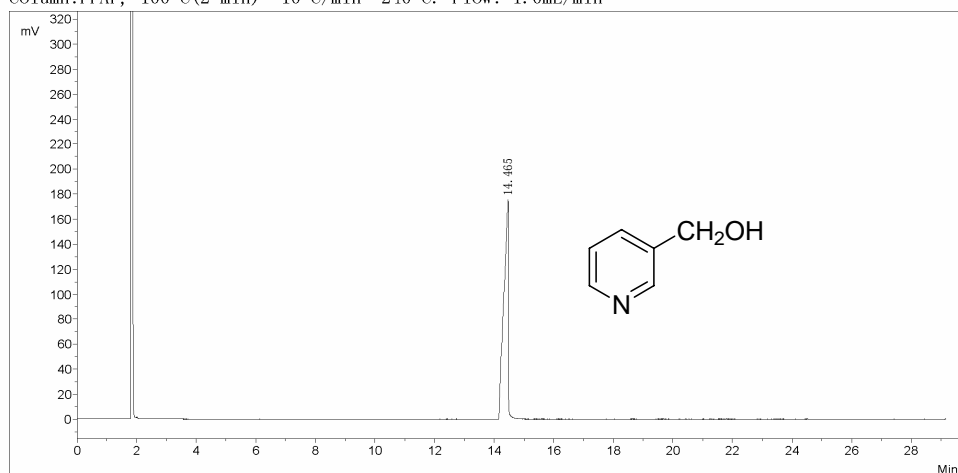
Sample Name: C₅H₄N-3-CH₂OH

File Name: C:\HS2000G\Oxidation\20070118-2. che

Method: area normalization

Injection Date: 2007.01.18 10:29

Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		14.465	174492.5	1802519.2	100.0000
Total				174492.5	1802519.2	100.0000

Figure 17.
GC diagram of 3-pyridine methanol.

C:\HS2000G\Oxidation\20070113-1.che

2007-01-29

GC REPORT

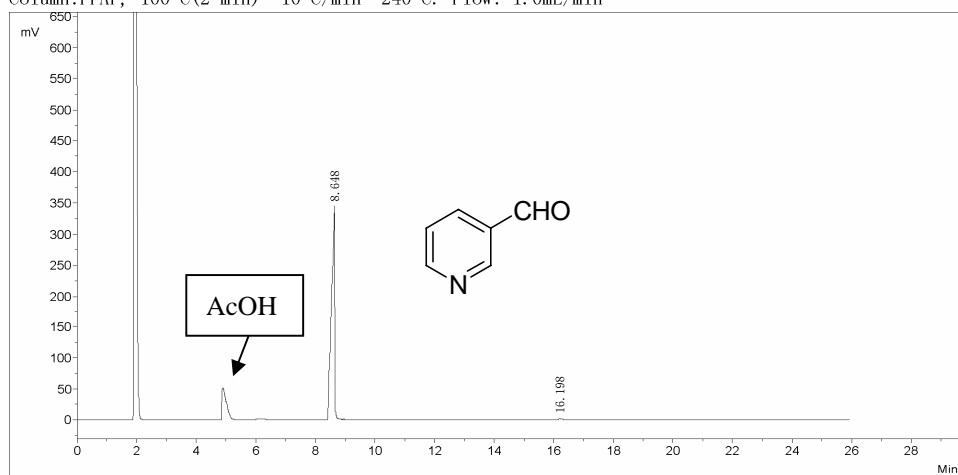
Sample Name:

File Name:C:\HS2000G\Oxidation\20070113-1.che

Method:area normalization

Injection Date:2007.01.13 10:14

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		8.648	343971.3	2678102.0	99.6182
2	2		16.198	1617.9	10264.0	0.3818
Total				345589.2	2688366.1	100.0000

Figure 18.
GC diagram of 3-pyridine carboxaldehyde from oxidation of 3-pyridine methanol

Supporting Information

C:\HS20006\Oxidation\20061214-3.che

2007-01-29

GC REPORT

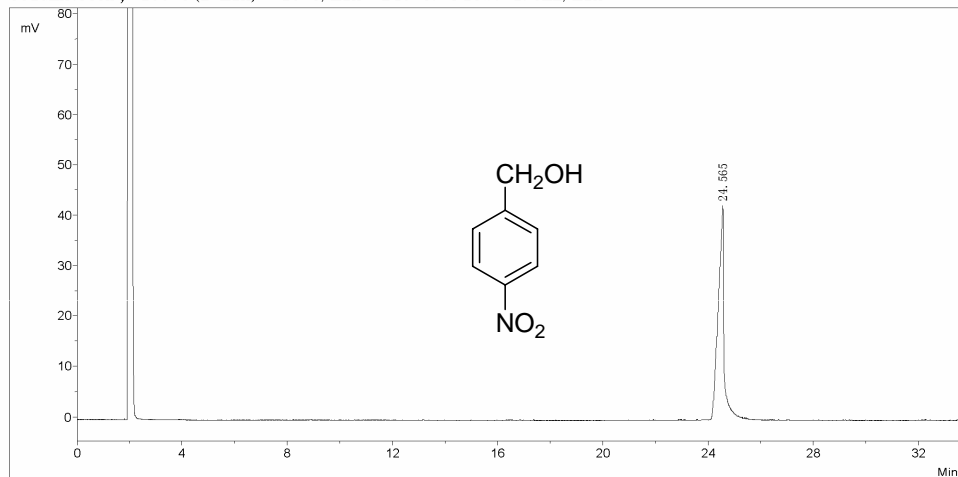
Sample Name:4-NO₂C₆H₄CH₂OH

File Name:C:\HS20006\Oxidation\20061214-3.che

Method:area normalization

Injection Date:2006.12.14 13:33

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		24.565	42228.7	653143.7	100.0000
Total				42228.7	653143.7	100.0000

Figure 19.
GC diagram of 4-nitrobenzyl alcohol

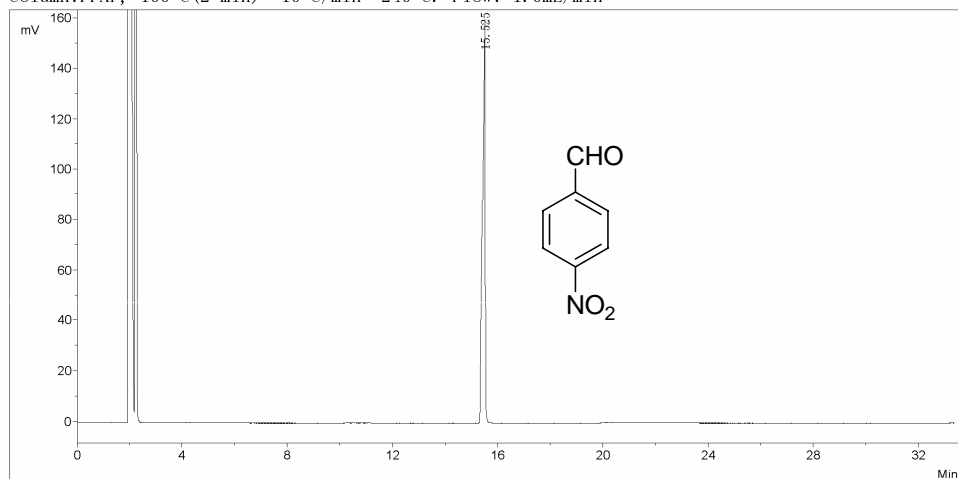
Supporting Information

C:\HS2000G\Oxidation\20070107-4.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070107-4.che
Method: area normalization Injection Date: 2007.01.07 18:24
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		15.525	159982.6	1144521.7	100.0000
Total				159982.6	1144521.7	100.0000

Figure 20.
GC diagram of 4-nitro benzaldehyde from oxidation of 4-nitro benzyl alcohol.

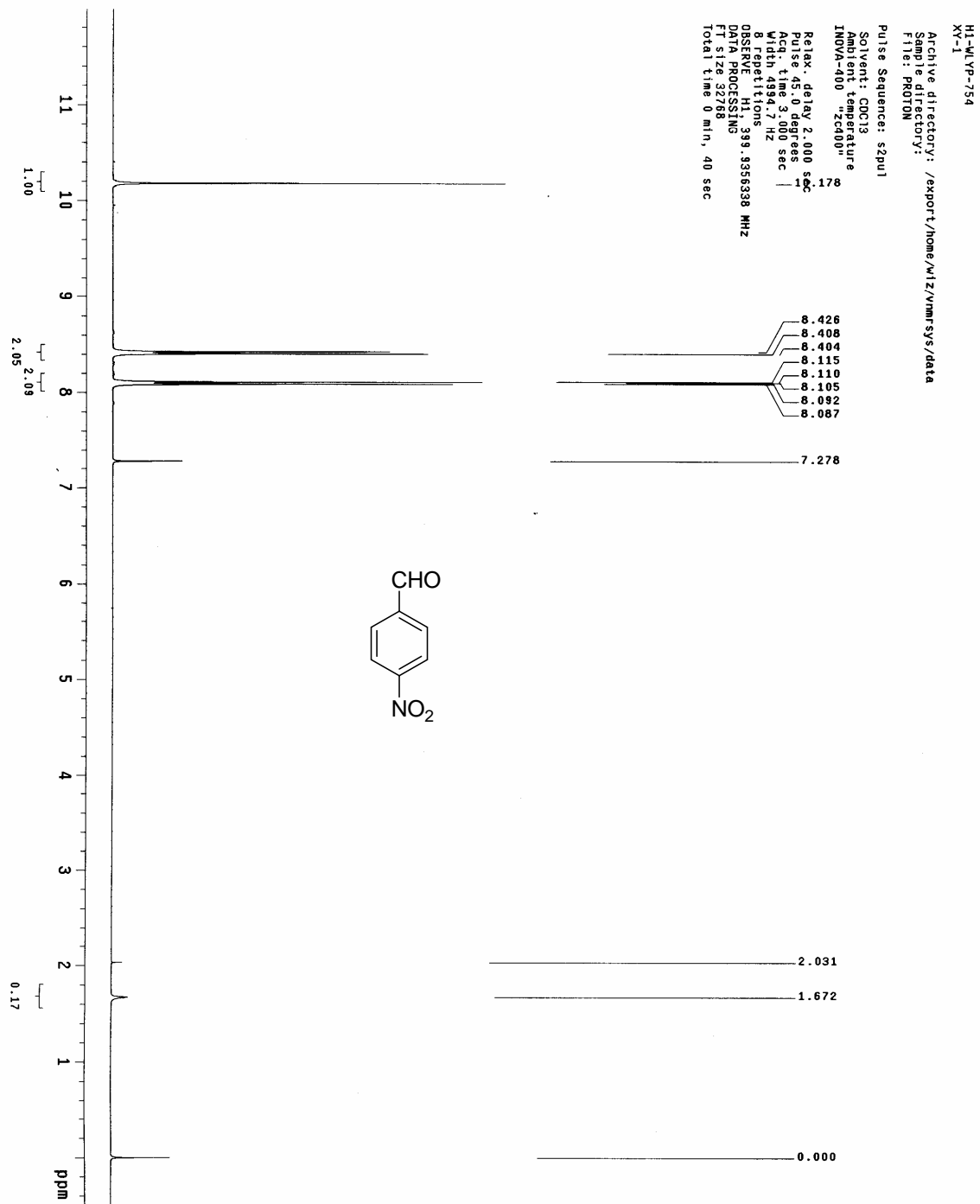


Figure 21.
¹H NMR spectrum of 4-nitro benzaldehyde

Supporting Information

C:\HS2000G\Oxidation\20070108-6.che

2007-01-29

GC REPORT

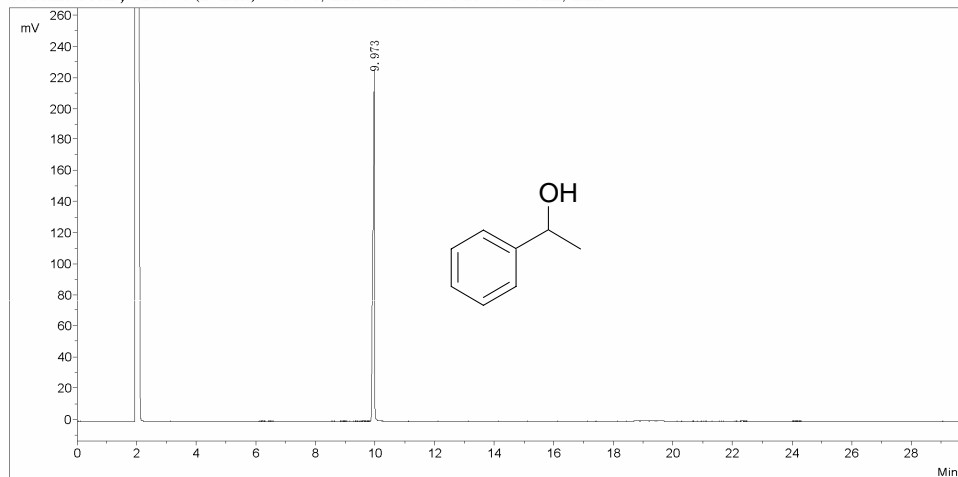
Sample Name: C₆H₅CH(CH₃)OH

File Name: C:\HS2000G\Oxidation\20070108-6.che

Method: area normalization

Injection Date: 2007.01.08 20:06

Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		9.973	221748.2	849120.2	100.0000
Total				221748.2	849120.2	100.0000

Figure 22.
GC diagram of α -methyl-benzyl alcohol

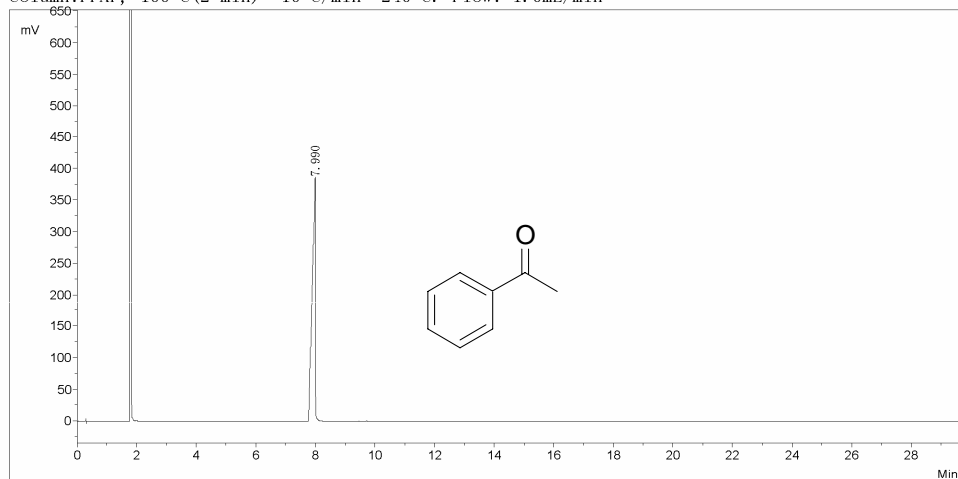
Supporting Information

C:\HS2000G\Oxidation\20070110-1.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070110-1.che
Method: area normalization Injection Date: 2007.01.10 09:01
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		7.990	378598.3	2812109.3	100.0000
Total				378598.3	2812109.3	100.0000

Figure 23.
GC diagram of acetophenone from oxidation of α -methyl benzyl alcohol.

Supporting Information

C:\HS2000G\Oxidation\20070118-4.che

2007-01-29

GC REPORT

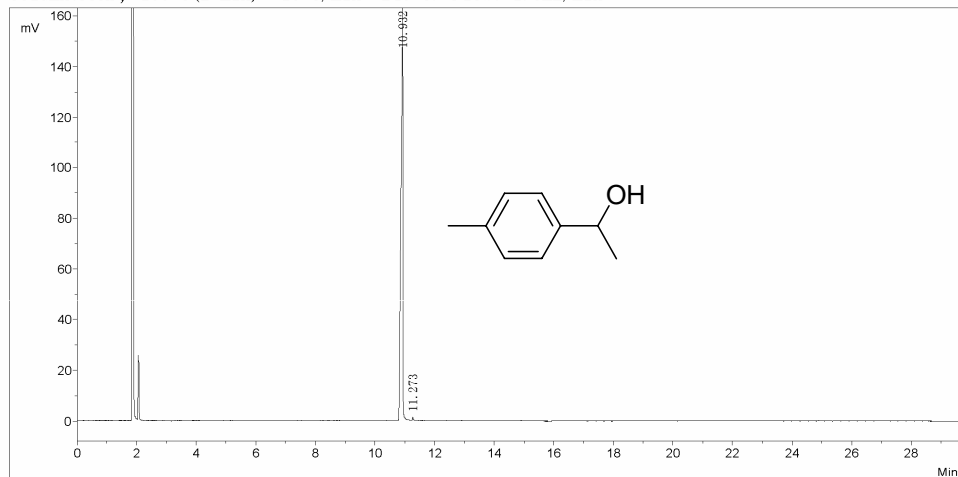
Sample Name: 4-CH₃C₆H₄CH(CH₃)OH

File Name: C:\HS2000G\Oxidation\20070118-4.che

Method: area normalization

Injection Date: 2007.01.18 14:20

Column: FFAP, 100 C (2 min) -- 10 C/min -- 240 C. Flow: 1.0 mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		10.932	167371.0	728294.5	99.6720
2	2		11.273	1203.0	2396.8	0.3280
Total				168574.0	730691.4	100.0000

Figure 24.
GC diagram of 1-(4-methylphenyl)-1-ethanol

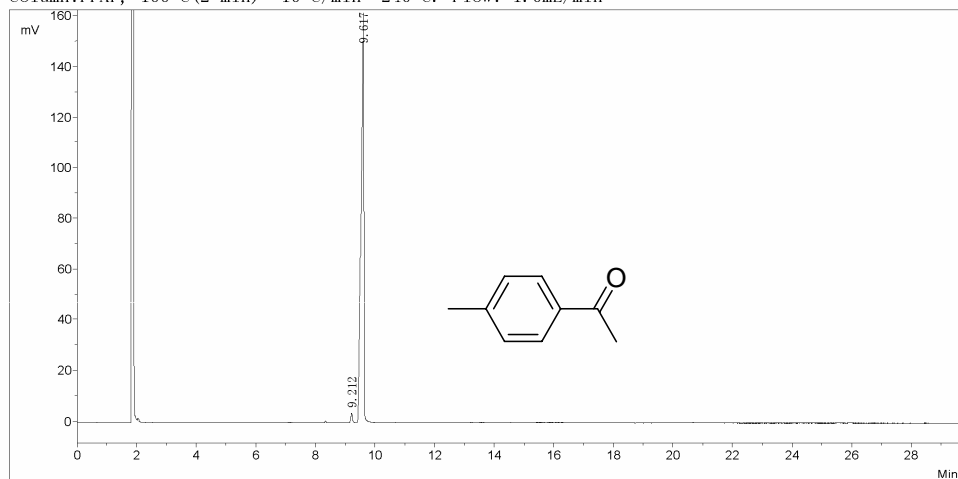
Supporting Information

C:\HS2000G\Oxidation\20070118-6.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070118-6.che
Method: area normalization Injection Date: 2007.01.18 19:24
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		9.212	3349.7	11963.7	1.2062
2	2		9.617	161383.1	979878.9	98.7938
Total				164732.9	991842.5	100.0000

Figure 25.
GC diagram of 4-methyl acetophenone from oxidation of 1-(4-methylphenyl)-1-ethanol.

Supporting Information

C:\HS2000G\Oxidation\20061231-8.che

2007-01-29

GC REPORT

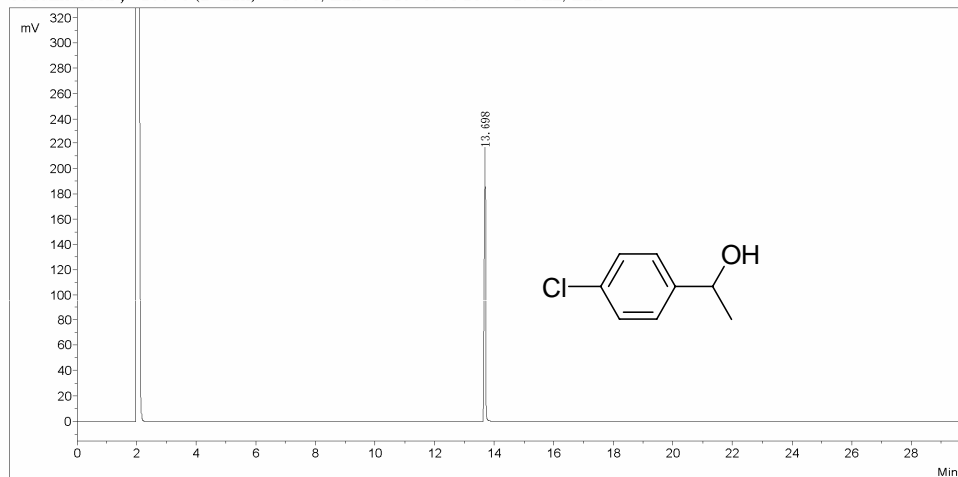
Sample Name:4-ClC₆H₄CH(CH₃)OH

File Name:C:\HS2000G\Oxidation\20061231-8.che

Method:area normalization

Injection Date:2006.12.31 19:46

Column:FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		13.698	212065.3	665964.3	100.0000
Total				212065.3	665964.3	100.0000

Figure 26.
GC diagram of 1-(4-chlorophenyl)-1-ethanol

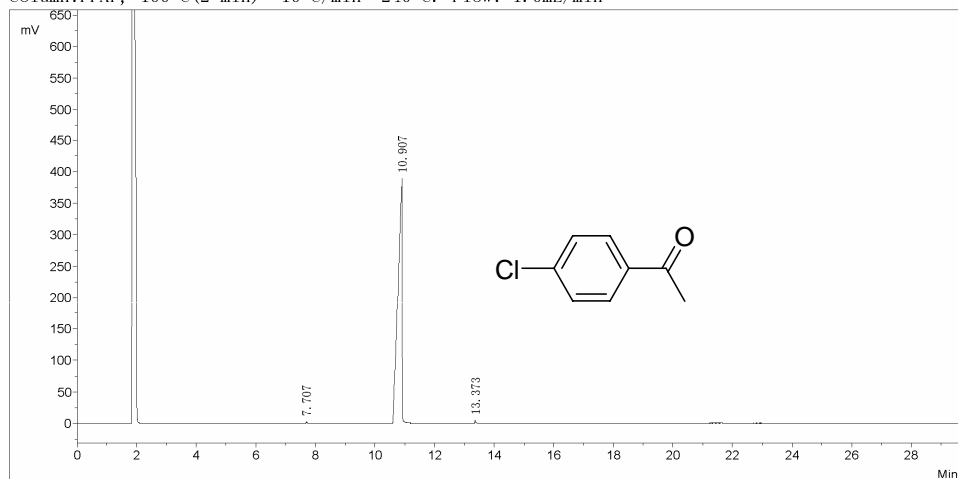
Supporting Information

C:\HS2000G\Oxidation\20070104-1.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070104-1.che
Method: area normalization Injection Date: 2007.01.04 08:57
Column: FFAP, 100 C(2 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		7.707	2139.0	3491.0	0.0935
2	2		10.907	389143.7	3715883.6	99.5524
3	3		13.373	4987.3	13216.4	0.3541
Total				396270.0	3732591.0	100.0000

Figure 27.
GC diagram of 4-chloro acetophenone from oxidation of 1-(4-chlorophenyl)-1-ethanol.

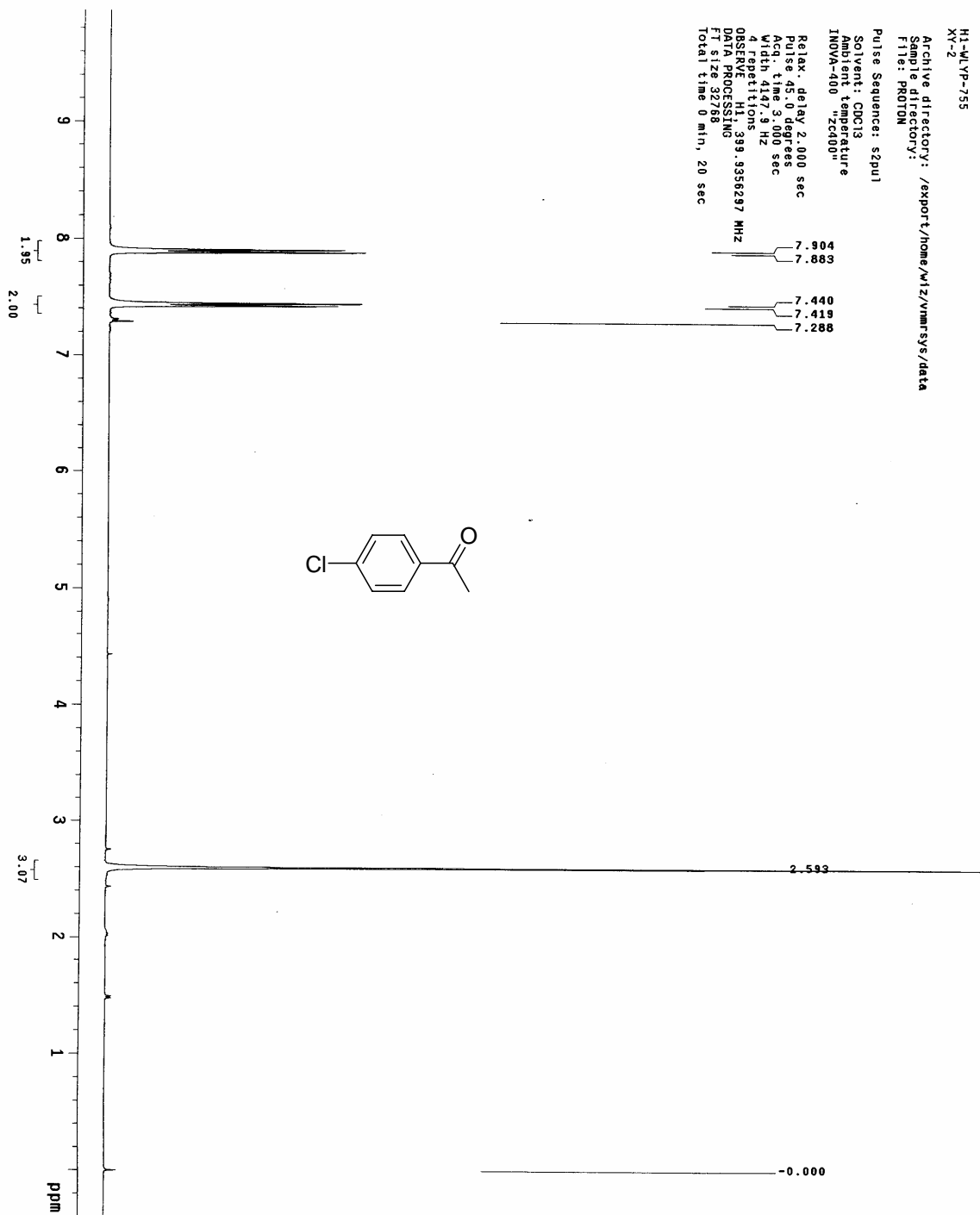


Figure 28.
¹H NMR spectrum of 4-chloroacetophenone (isolated)

Supporting Information

C:\HS2000G\Oxidation\20070117-3. che

2007-01-29

GC REPORT

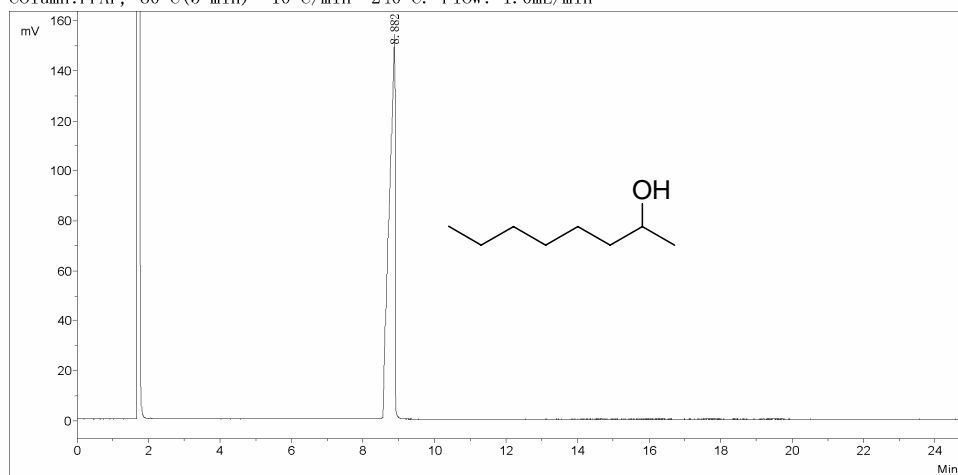
Sample Name:2-Octanol

File Name:C:\HS2000G\Oxidation\20070117-3. che

Method:area normalization

Injection Date:2007.01.17 19:04

Column:FFAP, 80 C(5 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		8.882	151633.1	1694121.9	100.0000
Total				151633.1	1694121.9	100.0000

Figure 29.
GC diagram of 2-octanol.

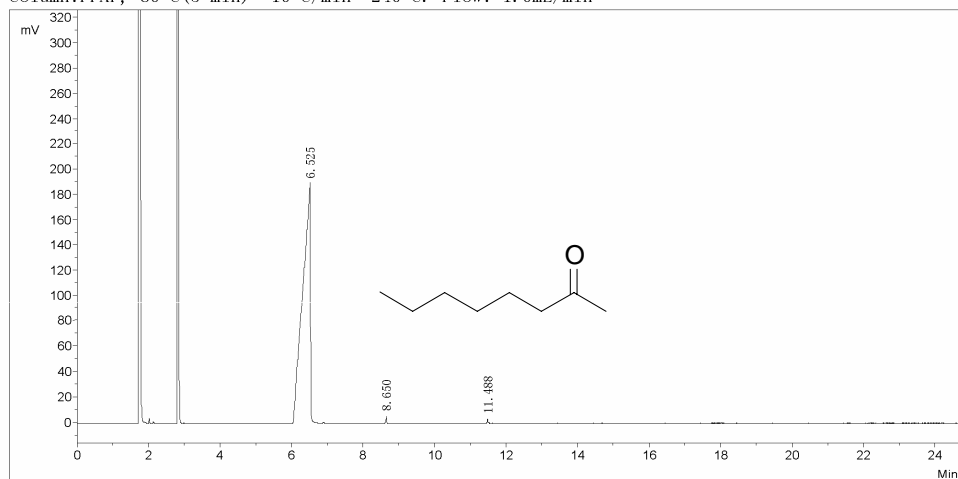
Supporting Information

C:\HS2000G\Oxidation\20070116-2.che

2007-01-29

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070116-2.che
Method: area normalization Injection Date: 2007.01.16 18:49
Column: FFAP, 80 C (5 min)—10 C/min—240 C. Flow: 1.0 mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		6.525	188927.8	2805217.3	99.5546
2	2		8.650	5243.2	8297.1	0.2945
3	3		11.488	3063.5	4252.4	0.1509
Total				197234.6	2817766.7	100.0000

Figure 30.
GC diagram of 2-octanone from oxidation of 2-octanol.

Supporting Information

C:\HS2000G\Oxidation\20070117-2. che

2007-01-29

GC REPORT

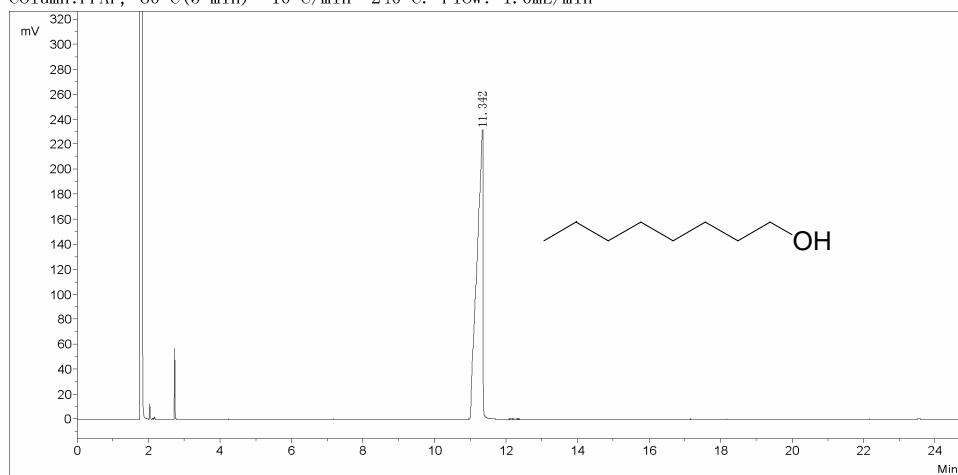
Sample Name:1-Octanol

File Name:C:\HS2000G\Oxidation\20070117-2. che

Method:area normalization

Injection Date:2007.01.17 10:45

Column:FFAP, 80 C(5 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		11.342	229509.1	2601290.9	100.0000
Total				229509.1	2601290.9	100.0000

Figure 31
GC diagram of 1-octanol.

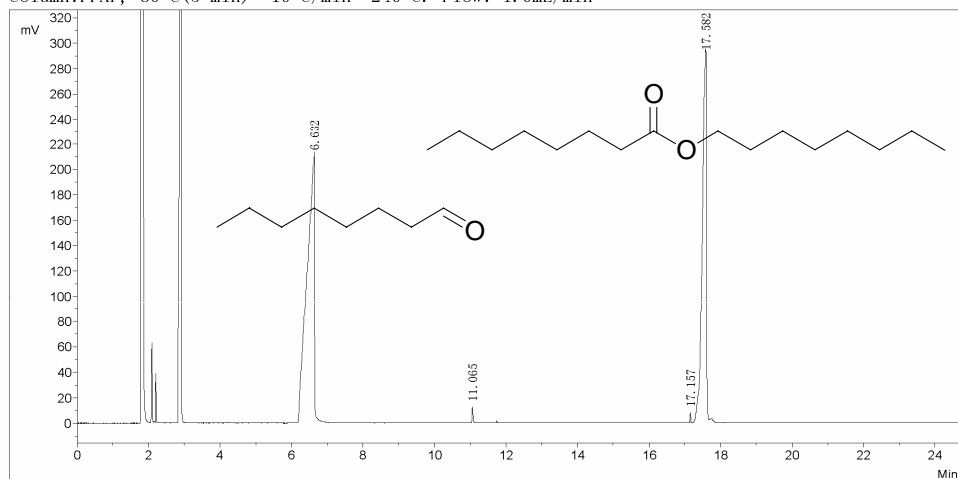
Supporting Information

C:\HS2000G\Oxidation\20070124-2.che

2007-01-31

GC REPORT

Sample Name: File Name: C:\HS2000G\Oxidation\20070124-2.che
Method: area normalization Injection Date: 2007.01.24 20:39
Column: FFAP, 80 C(5 min)—10 C/min—240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		6.632	210770.9	3058737.1	54.3029
2	2		11.065	12716.5	26946.9	0.4784
3	3		17.157	8231.4	13413.5	0.2381
4	4		17.582	295592.7	2533636.6	44.9806
Total				527311.6	5632734.2	100.0000

Figure 32
GC diagram of oxidation of 1-octanol.

Supporting Information

C:\HS2000G\Oxidation\20070125-2.che

2007-01-29

GC REPORT

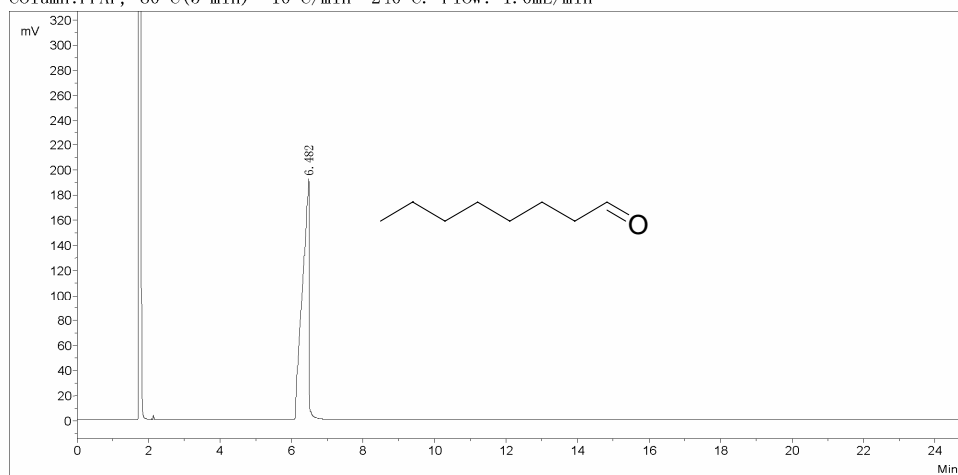
Sample Name:

File Name:C:\HS2000G\Oxidation\20070125-2.che

Method:area normalization

Injection Date:2007.01.25 20:54

Column:FFAP, 80 C(5 min)--10 C/min--240 C. Flow: 1.0mL/min



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	Conc (%)
1	1		6.482	190312.7	2459320.5	100.0000
Total				190312.7	2459320.5	100.0000

Figure 33
GC diagram of 1-octanal (isolated via distillation).

HS 色谱数据工作站分析报告

样品名称:

文件名:-20070115-5

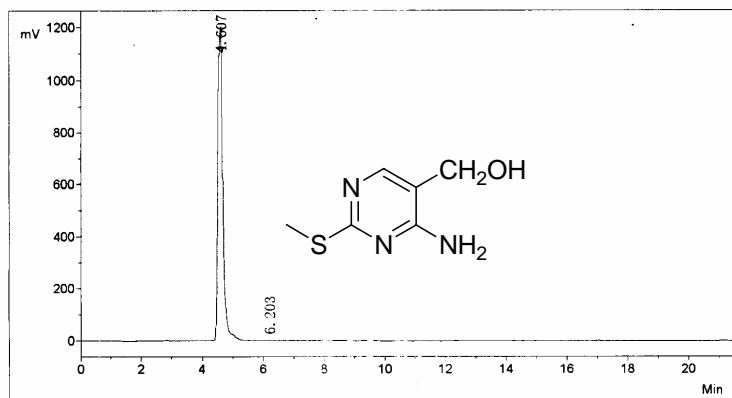
进样时间:2007年01月15日

半峰宽:5 斜率:50

分析方法:面积 归一法

色谱仪:

检测器:



序号	峰号	组份名	保留时间	峰高	峰面积	含量
1	1		4.607	1201915.4	14008640.4	99.9167
2	2		6.203	872.9	11685.1	0.0833
合计				1202788.3	14020325.5	100.0000

Figure 34.
HPLC diagram of 4-amino-2-methylthio-pyrimidine-5-methanol.

HS 色谱数据工作站分析报告

样品名称:

文件名:-20070118-1

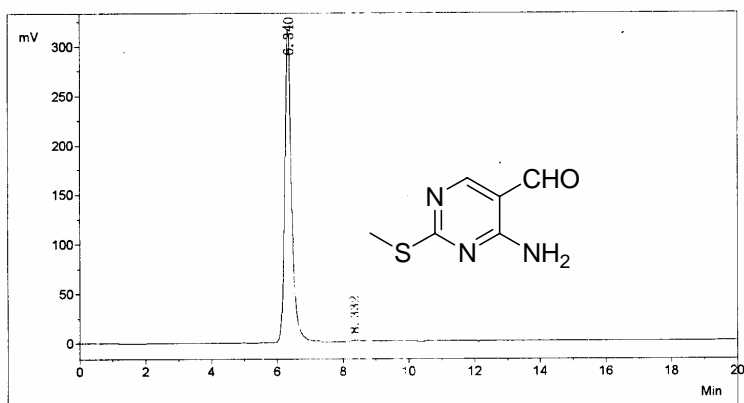
进样时间:2007年01月18日

半峰宽:5 斜率:50

分析方法:面积 归一法

色谱仪:

检测器:



序号	峰号	组份名	保留时间	峰高	峰面积	含量
1	1		6.340	35503.9	4507693.2	99.6782
2	2		8.332	683.7	14553.1	0.3218
合计				36187.6	4522246.3	100.0000

Figure 35.
HPLC diagram of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated)

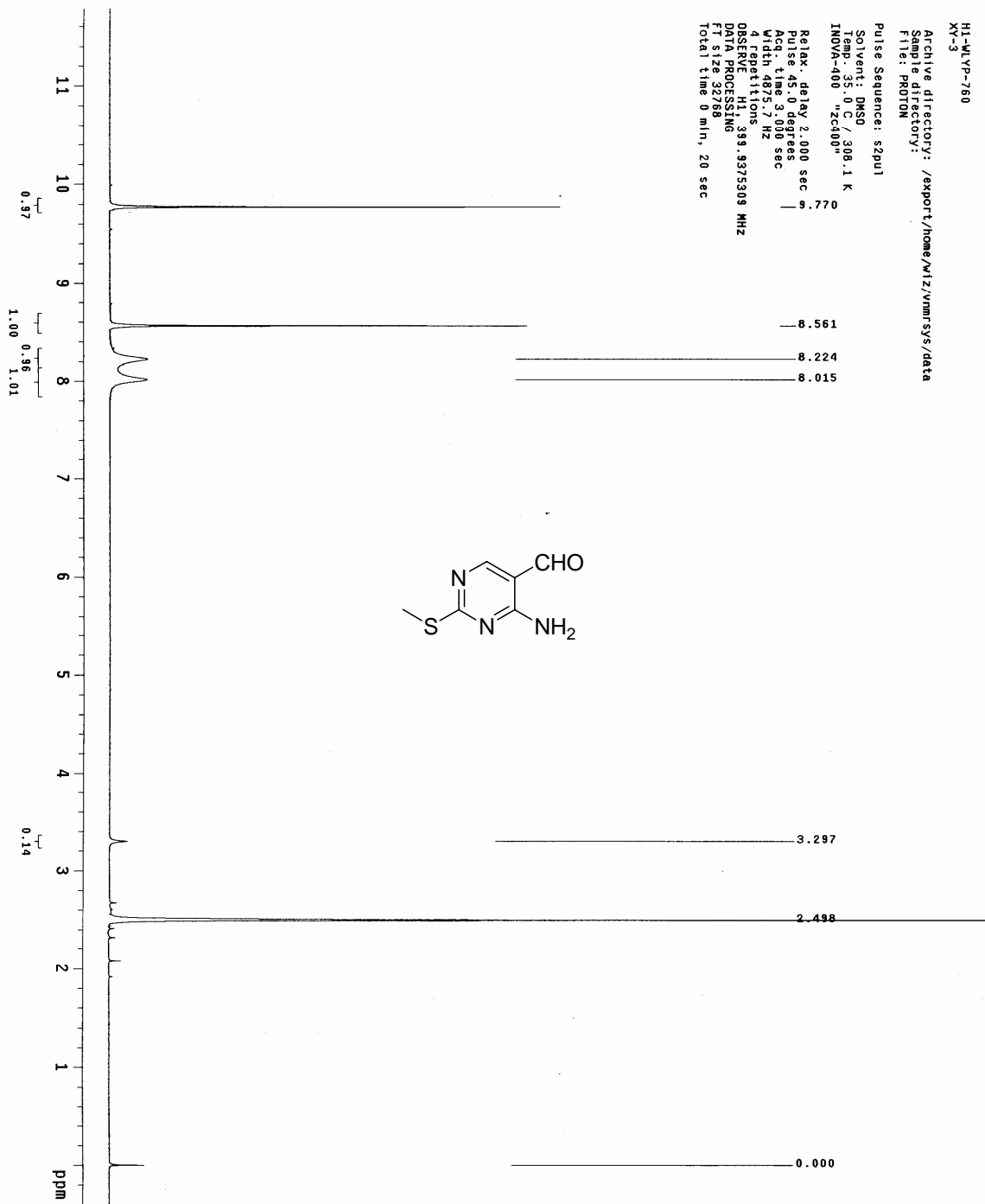


Figure 36
¹H NMR spectrum of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated).

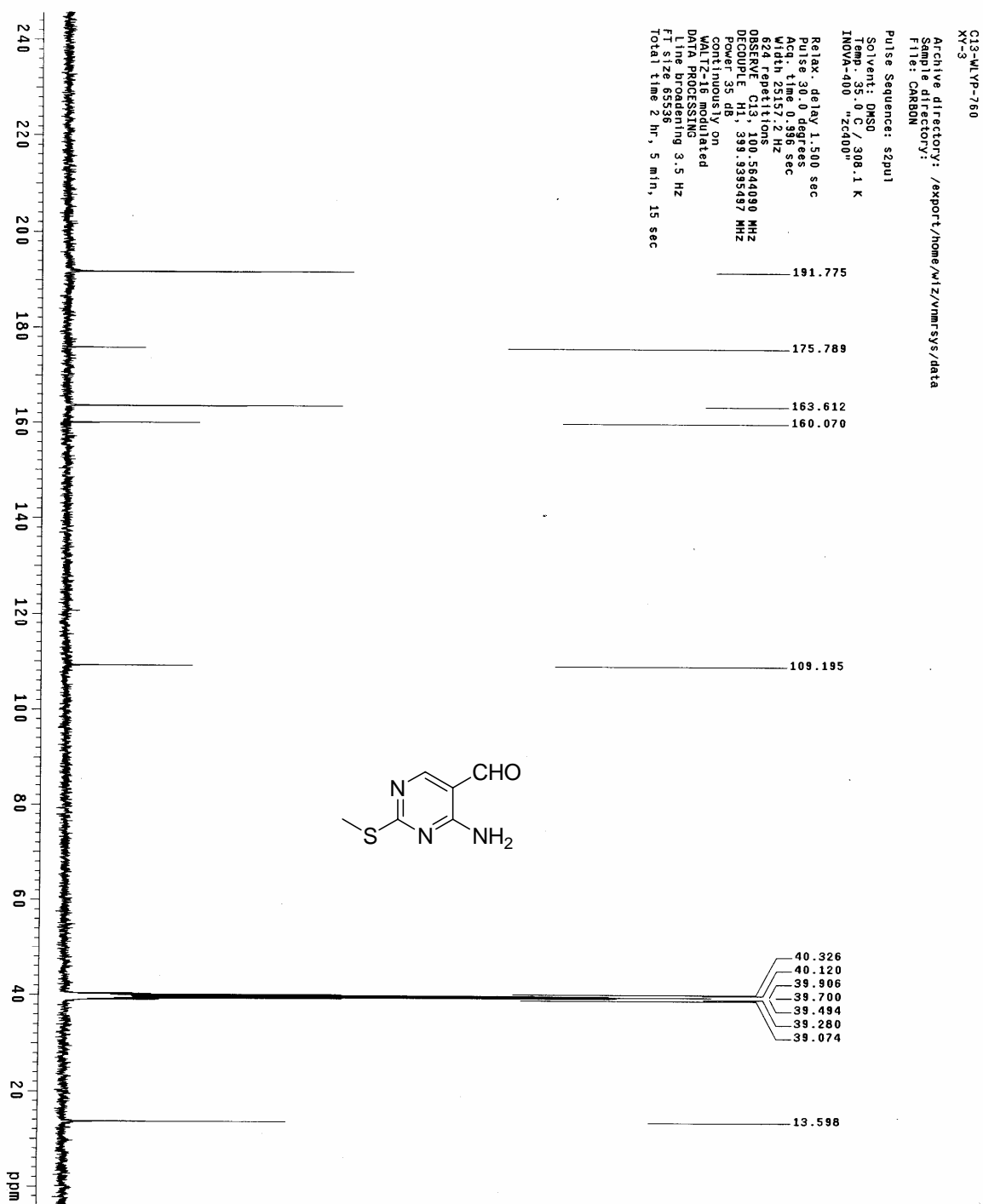


Figure 37.
¹³C NMR spectrum of 4-amino-2-methylthio-pyrimidine-5-carboxaldehyde (isolated)