Ruthenium-catalyzed Hydrogen Generation from Glycerol and Selective Synthesis of Lactic Acid

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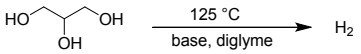
Supporting Information

General information: Gas phase GC samples were performed on Agilent 6890N (G1530N: HP Plot Q / FID – hydrocarbons, Carboxen / TCD - permanent gases, He carrier gas). The gas integration was calibrated using certified gas mixtures from commercial suppliers (Linde and Air Liquide). The systems allow for the determination of H_2, Ar, CO and CO_2 within the ranges: $H_2 \geq 0.5$ vol% - 100 vol%, CO ≥ 10 ppm, $CO_2 \geq 100$ ppm. $V(H_2)_m$ is used as 24.6 L/mol, based on 26.0 °C. ^{1}H NMR Spectra were recorded on Bruker 300 MHz, ^{13}C NMR Spectra were recorded on 75 MHz in the solvents CD_3OD; chemical shifts are reported in units (ppm) by assigning CD_3OD resonance in the ^{1}H spectrum as 3.31 ppm and CD_3OD resonance in the ^{13}C spectrum as 49.05 ppm. Compounds **3**,[1] **4**,[1] and **6**[1] were synthesized according to the reported procedure. All the solvents for reactions were used after the extrusion of air by argon. If no special indicated, regents were used as commercial sources and without further purification.

Standard reaction procedure:

The substrate was added to a double walled thermostated reaction vessel and evaporated and back-filled with argon for several times to remove air. Solvent, base were added under argon atmosphere. After heating to the specified temperature and stirring the solution for half an hour, the catalyst in a small teflon tube was added to the well stirred reaction mixture. The amount of gas generated over time was measured by manual gas burette (100 mL, and 1000 mL burettes were used). Subsequently, the gas purity was detected by GC analysis. After cooling to rt, the reaction mixture was treated with HCl (37%) until a pH to 3-4 was reached. In the reaction with glycerol using 200 ppm of catalyst and the reaction of sorbitol CO2 is observed as side-product.

Table S1. H_2 generation from glycerol: Variation of reaction conditions.



Entry	catalyst	µmol, ppm	base (M, equiv.)	V (1 h)	TOF (1 h)	V (2 h)	TOF (2 h)
1	**1**	4.00, 29.2	NaOH (2.00, 0.29)	56.0	569	109.5	556
2[a]	**1**	4.05, 29.6	NaOH (2.00, 0.29)	29.0	291	42.0	211
3	**1**	3.99, 29.1	CsOH[b](1.50, 0.22)	142.0	1447	272	1387
4	**1**	4.25, 31.0	K_2CO_3 (1.50, 0.22)	49.5	473.0	72.0	344

Reaction conditions: reactions were performed on glycerol (10.00 mL, 136.93 mmol) using diglyme (10.00 mL) as solvent. Calculated concerning to volumes were measured by gas burette with removal of blank volumes. [a] The reaction was performed at 95 °C. [b]15% H_2O was contained.

Analysis the products of glycerol.

Hydrogen generation from pure glycerol and industrial glycerol catalyzed by 0.5 ppm of catalyst **1**:

According to the standard reaction procedure after 12 h heating at 125 °C, 1-methylnaphthalene (9.725 mL, 68.47 mmol, 10 mol% to glyerol) was added as an internal standard for ^{1}HNMR, tetraglyme (75.413 mL, 342.33 mmol, 50 mol% to glyerol) was added as an internal standard for liquid phase GC. The reaction mixture was detected by crude ^{1}H NMR and ^{13}C NMR and MS (ethanol solution of reaction mixture). After comparison with the spectrum of glycerol, diglyme, and potassium lactate, which was synthesized by treatment with 2 equiv. of KOH in MeOH with a stirring overnight at room temperature, the major product was as identified as potassium lactate.

Hydrogen generation from glycerol catalyzed by 200 ppm of catalyst **1**:

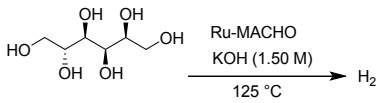
According to the standard reaction procedure after 200 minutes heating at 125 °C, no obvious gas volume was increased. After cooling to rt, 1-methylnaphthalene (1.95 mL, 13.69 mmol, 10 mol% to glyerol) was added as an internal standard for ^{1}HNMR, tetraglyme (21.12 mL, 95.85 mmol, 70 mol% to glyerol) was added as an internal standard for liquid phase GC. The reaction mixture was detected by ^{1}HNMR and GC. After comparison ^{1}H NMR and ^{13}C spectrum of reaction mixture with glycerol, diglyme, propane-1,2-diol (**10**), and potassium lactate (**9**), it is concluded that 11% of propane-1,2-diol (**10**), 12% of potassium lactate (**9**), trace amount of potassium acetate (**11**) and H_2 (10%) and CO_2 (2%) (reported data based on the increased volume

and the ratio of H_2 and CO_2 in gas phase, and the CO_2 trapped in liquid phase, which was released by addition of 37% HCl) were obtained. From GC result, it concluded that 35% conversion (65% of glycerol), 9% of propane-1,2-diol (**10**) were obtained.

Optimization H_2 generation from D-sorbitol.

When D-sorbitol was used as substrate in the optimal condition for glycerol, a TOF of 621^{-1} (1 h) and 472^{-1} (2 h) was obtained (Table S2, entry 1). Meanwhile, it was found that the reaction mixture was not a good soluiton. Water was tried using as solvent. Using mixture solvent of diglyme (8 mL) and water (2 mL) showed better result. Decreasing amout of catalyst from 29.7 ppm to 15.9 ppm, the reaction efficiency was imporved to a TOF of 1025^{-1} (1 h) and 765^{-1} (2 h). After the reaction mixture was cooled to rt, it was treated with HCl (37%) to pH to 3-4, 1.40 mL of CO_2 was released.

Table S2. H_2 generation from sorbitol: Variation of reaction conditions.



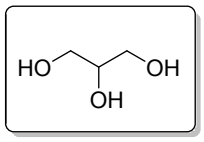
Entry	solvent (mL)	µmol, ppm	V (1 h)	TOF (1 h)	V (2 h)	TOF (2 h)
1	diglyme (10.0)	2.39, 29.2	36.5	621	55.5	472
2	H_2O (10.0)	2.42, 29.6	8.0	136	—	—
3	diglyme (5.0) + H_2O (5.0)	2.35, 28.7	47.5	823	65.8	569
4	diglyme (8.0) + H_2O (2.0)	2.43, 29.7	47.5	795	71.3	597

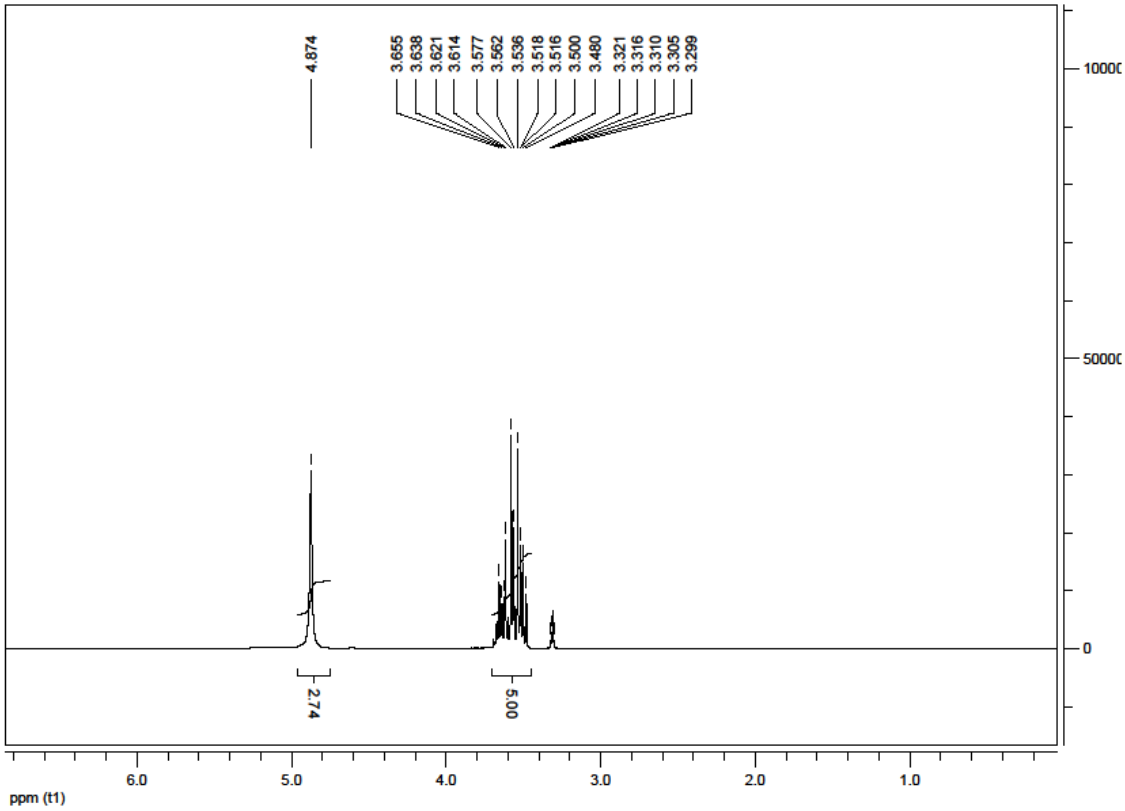
Reaction condtions: reactions were performed on (10.0 mL, 81.74 mmol), volumes (mL) were measured by gas burette with removal of blank volumes, TOFs (h^{-1}) were calculated with repect of volumes of H_2.

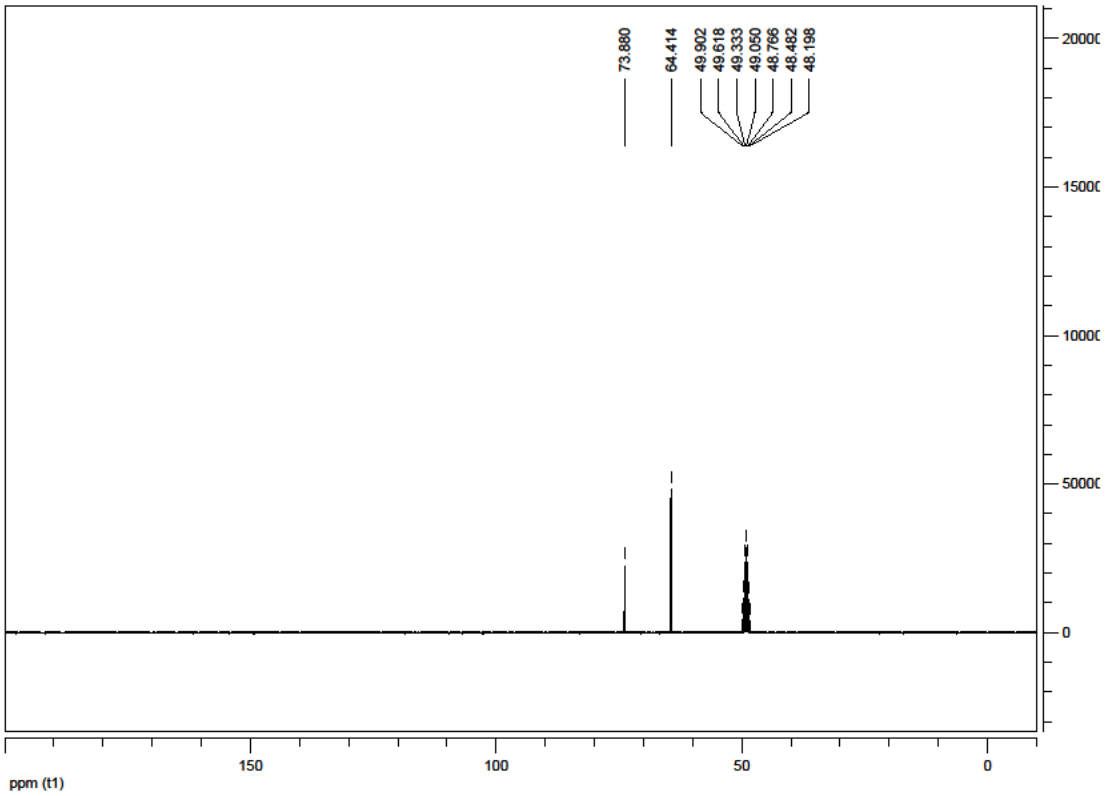
Prepartion of Lactic Acid from glycerol.

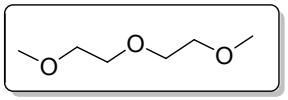
According to the standard reaction procedure after 24 h heating at 140 °C, 1-methylnaphthalene (9.725 mL, 68.47 mmol, 10 mol% to glyerol) was added as an internal standard for ^{1}HNMR to determine the yield of LA, tetraglyme (75.413 mL, 342.33 mmol, 50 mol% to glyerol) was added as an internal standard for liquid phase GC to determine the conversion of glycerol.

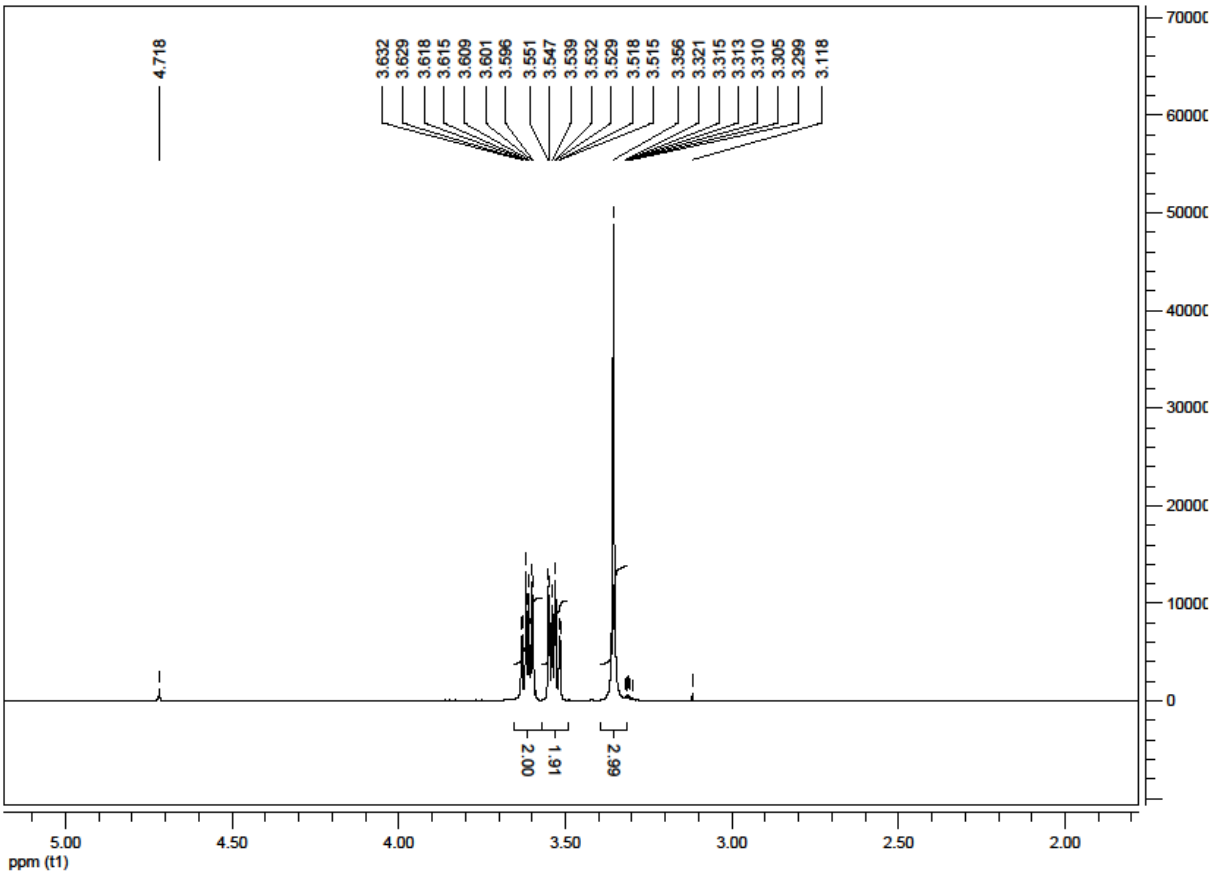
NMR spectrum

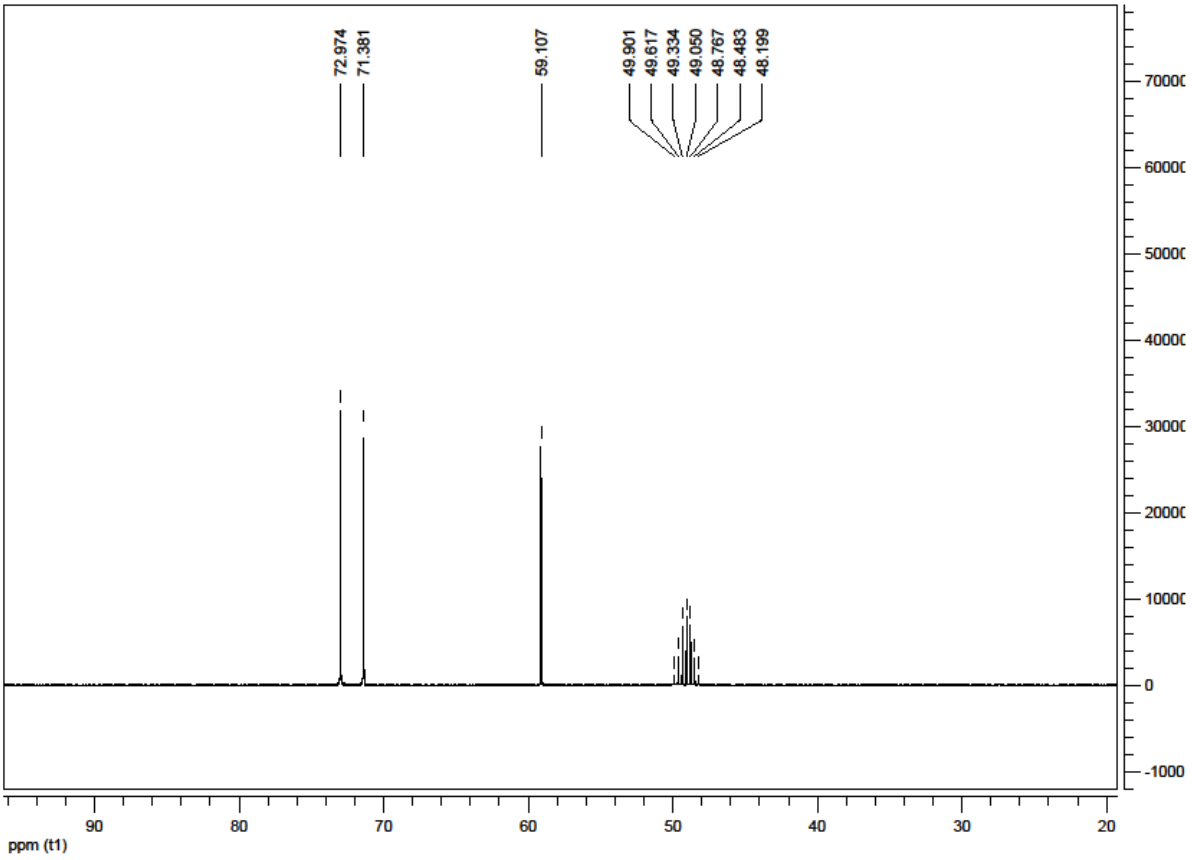









4.718
3.632
3.629
3.618
3.615
3.609
3.601
3.596
3.551
3.547
3.539
3.532
3.529
3.518
3.515
3.356
3.321
3.315
3.313
3.310
3.305
3.299
3.118
2.00
1.91
2.99
ppm (t1)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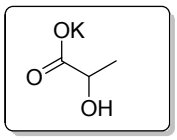
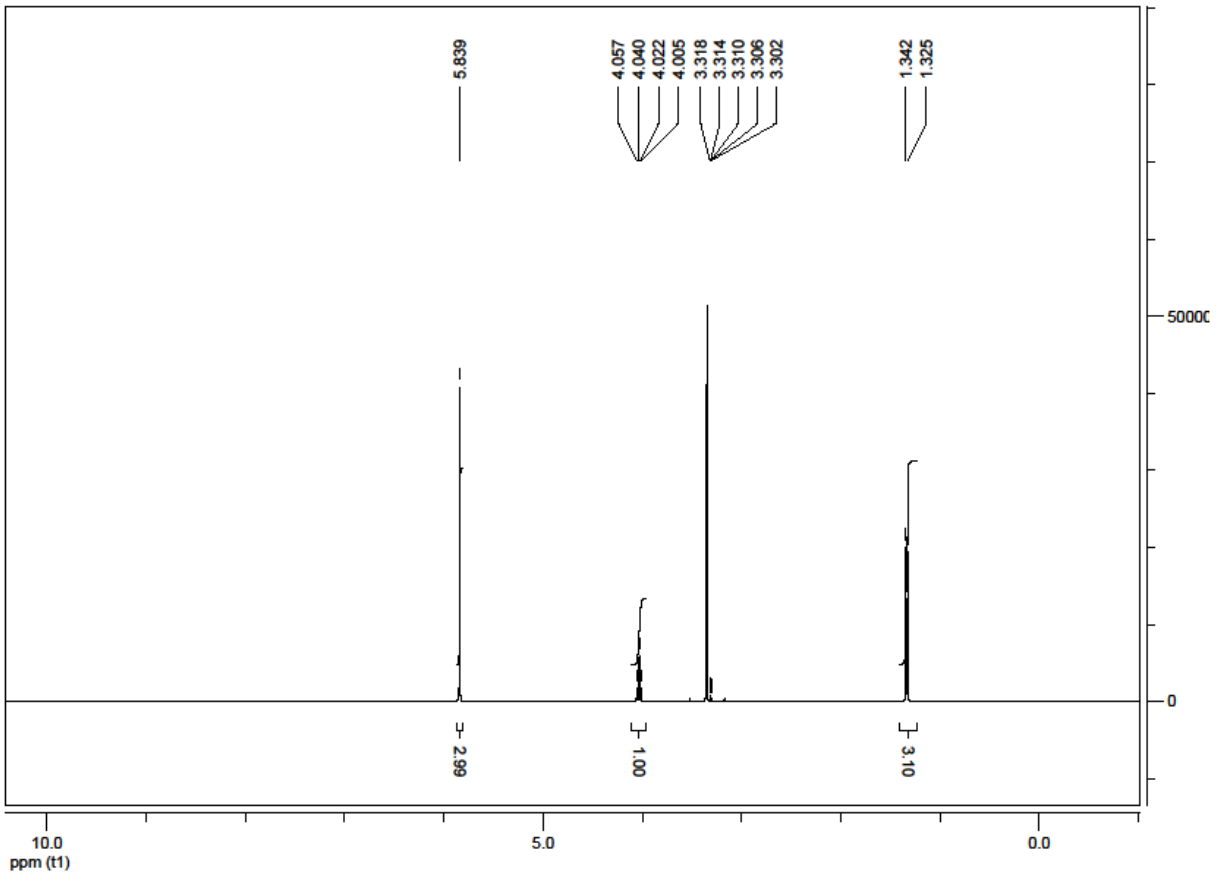
71.381
59.107
49.901
49.617
49.334
49.050
48.767
48.483
48.199
ppm (t1)


OK
O
OH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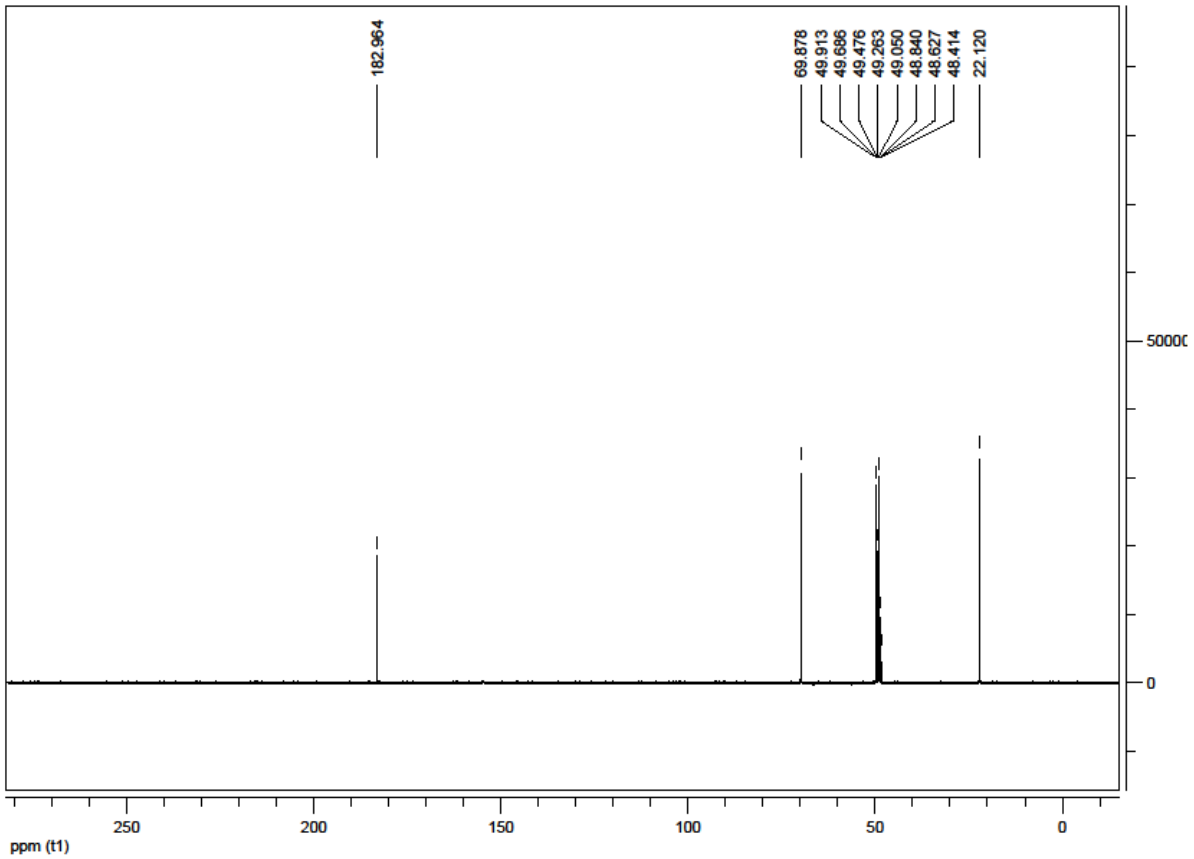
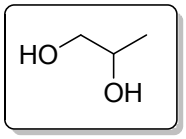
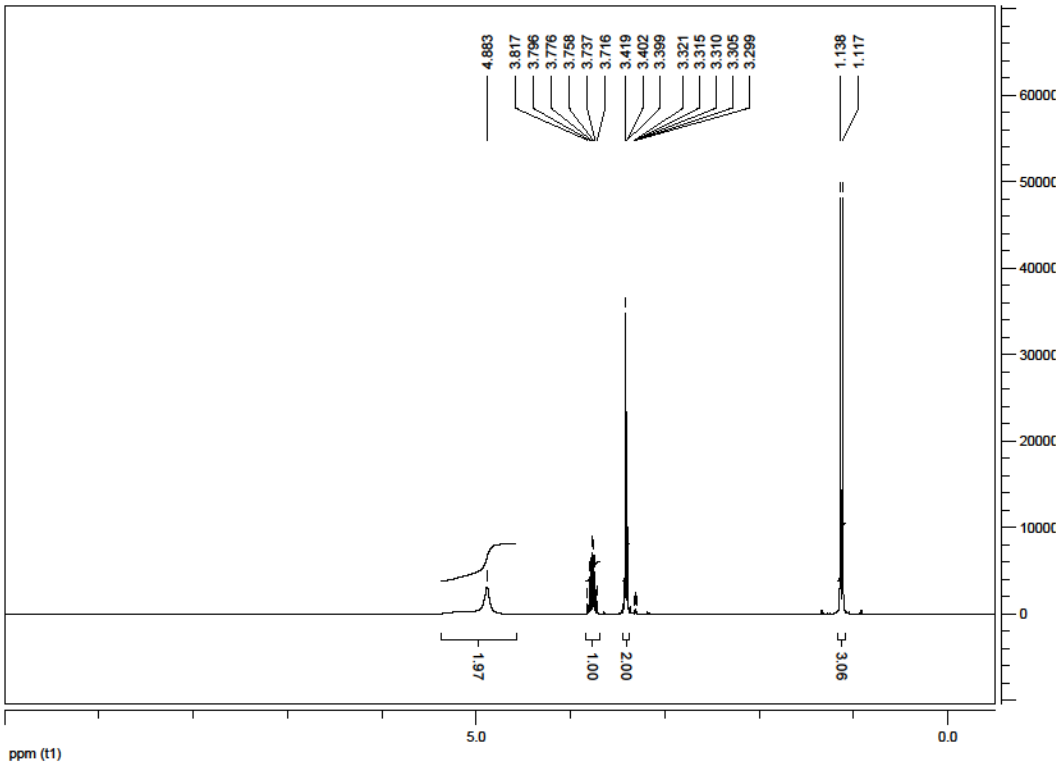
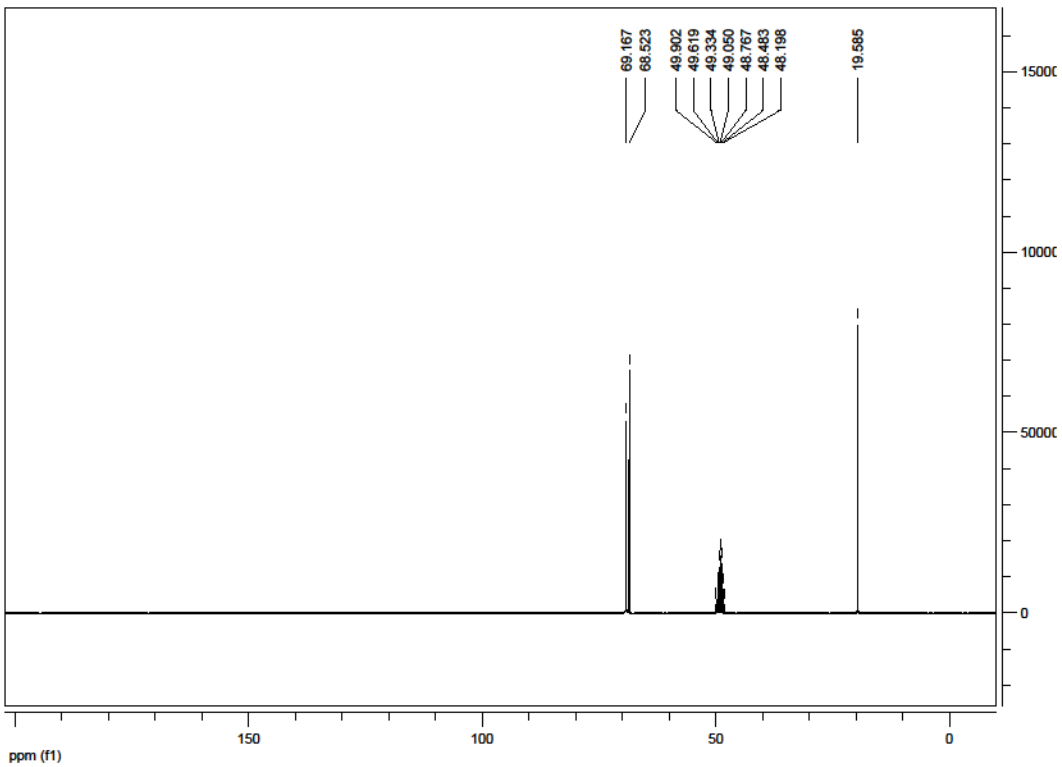
4.057
4.040
4.022
4.005
3.318
3.314
3.310
3.306
3.302
1.342
1.325
50000
0
2.99
1.00
3.10
10.0
5.0
0.0
ppm (t1)

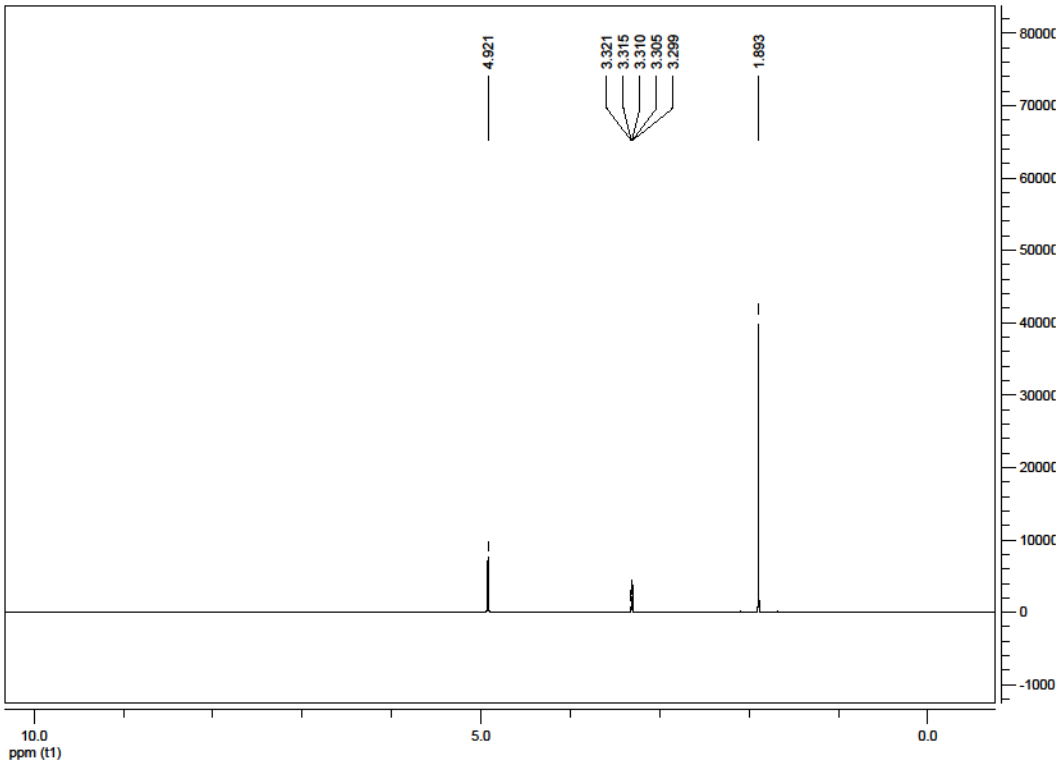

182.964
69.878
49.913
49.686
49.476
49.263
49.050
48.840
48.627
48.414
22.120
50000
0
250
200
150
100
50
0
ppm (t1)


HO
OH


4.883
3.817
3.796
3.776
3.758
3.737
3.716
3.419
3.402
3.399
3.321
3.315
3.310
3.305
3.299
1.138
1.117
1.97
1.00
2.00
3.06
5.0
0.0
ppm (t1)


69.167
68.523
49.902
49.619
49.334
49.050
48.767
48.483
48.198
19.585
150
100
50
0
ppm (f1)

KOAc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3.321
3.315
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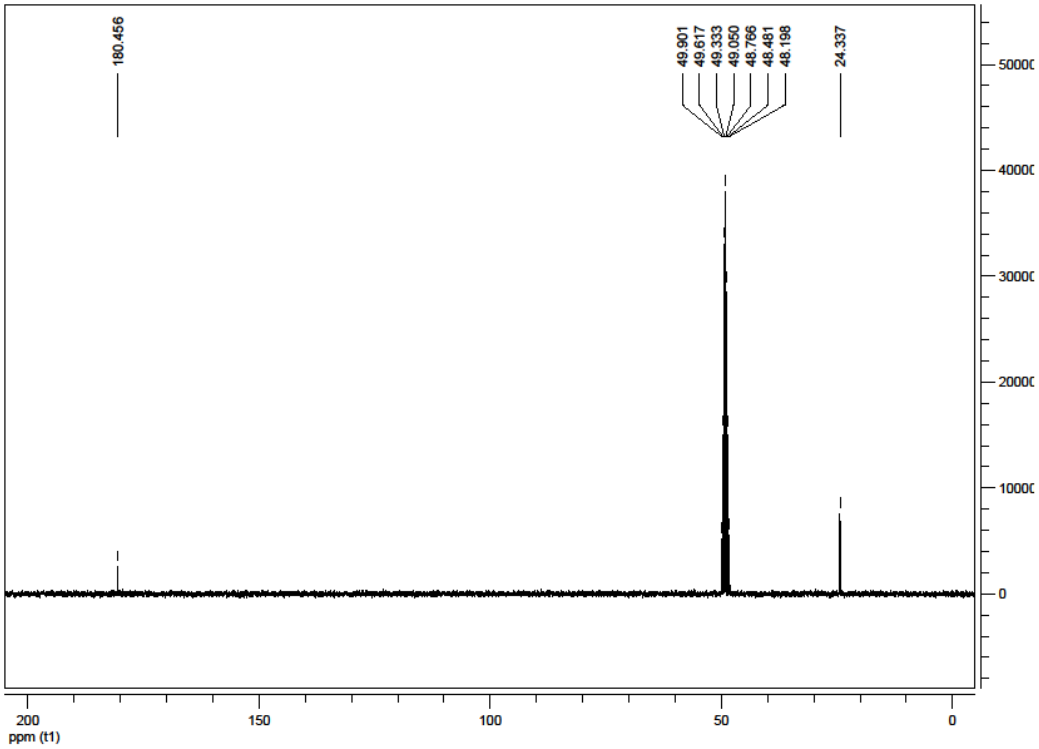
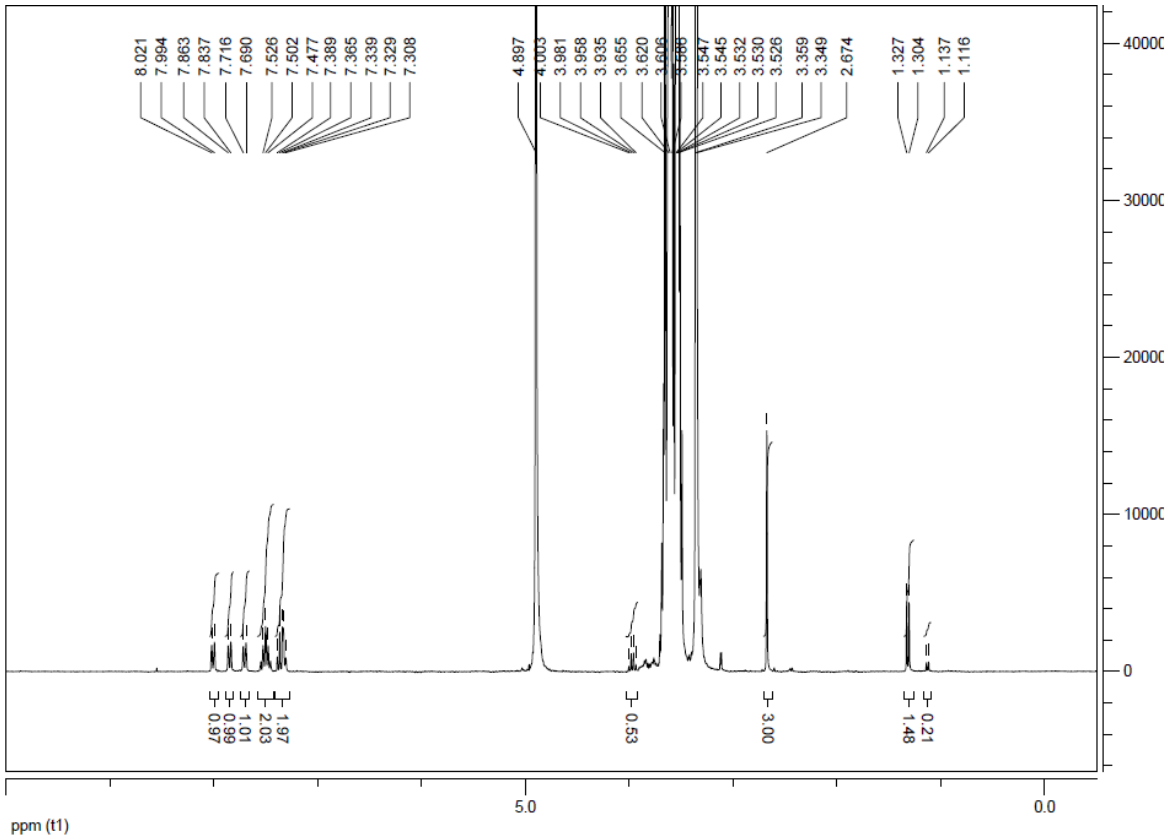
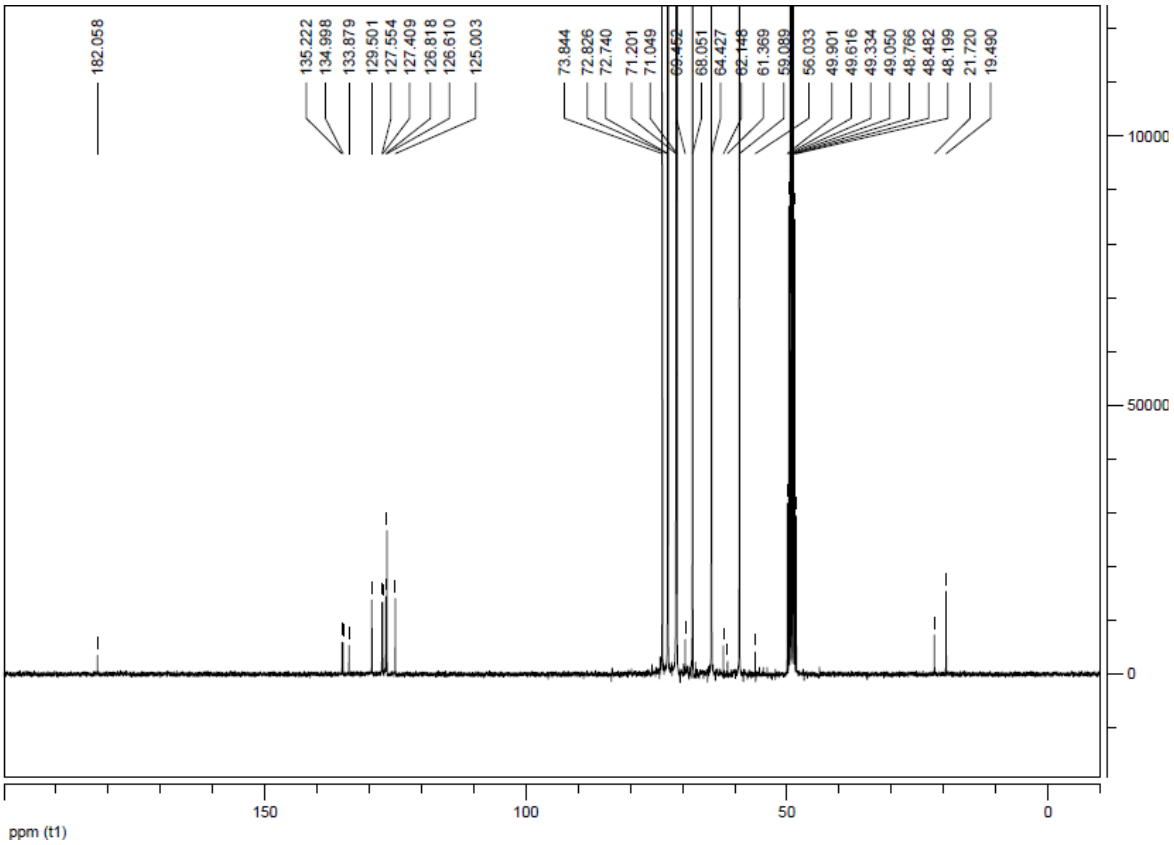
3.305
3.299
1.893
10.0
ppm (t1)
5.0
0.0

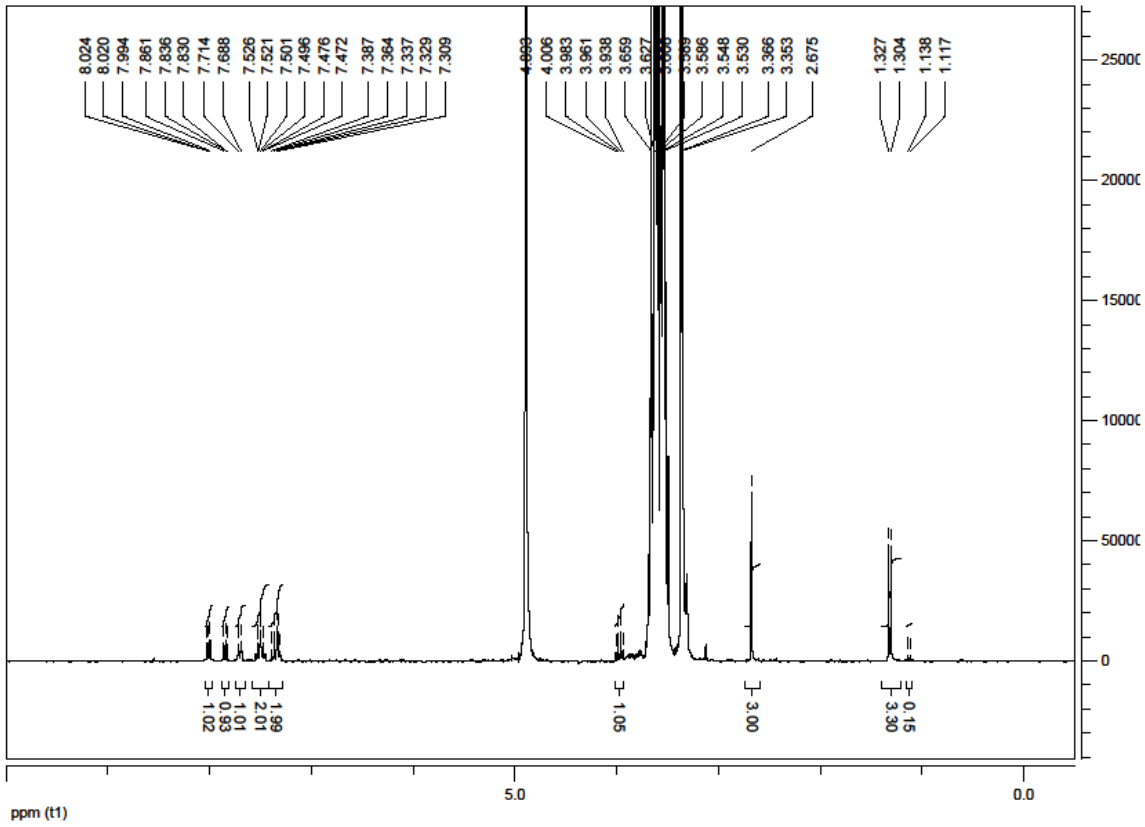

180.456
49.901
49.617
49.333
49.050
48.766
48.481
48.198
24.337
200
ppm (t1)
150
100
50
0

H_2 generation from pure glycerol (0.5 ppm catalyst, 12 h)

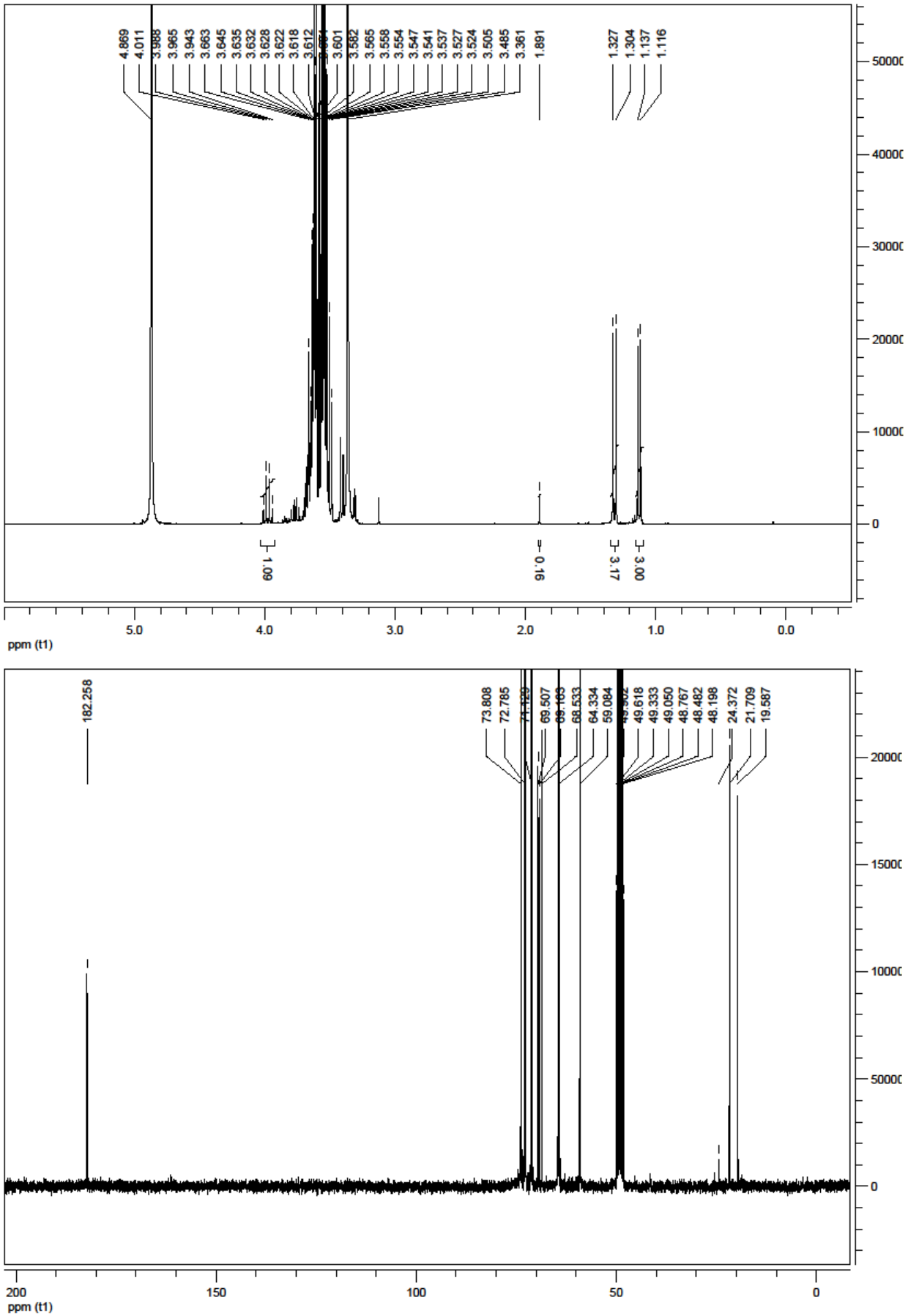




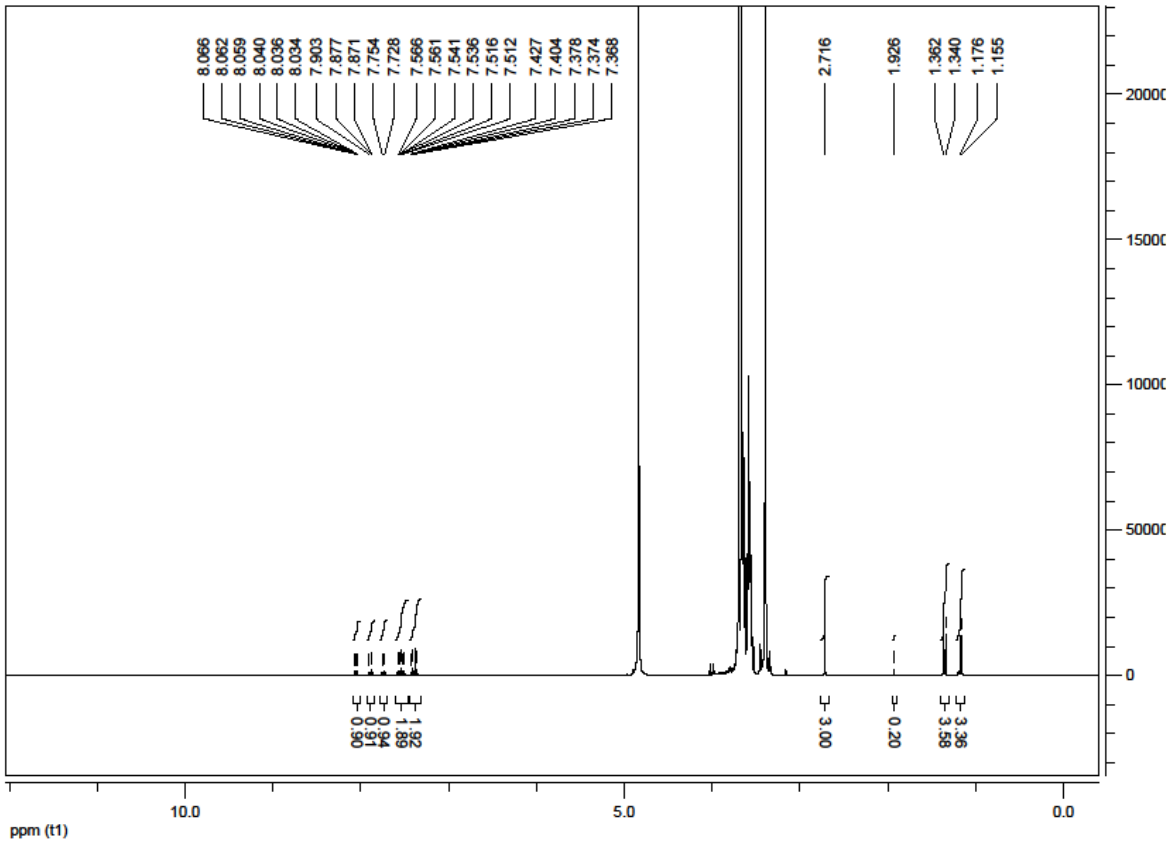
H_2 generation from industrial glycerol (0.5 ppm catalyst, 12 h)



H_2 generation from glycerol (200 ppm catalyst, 200 minutes)

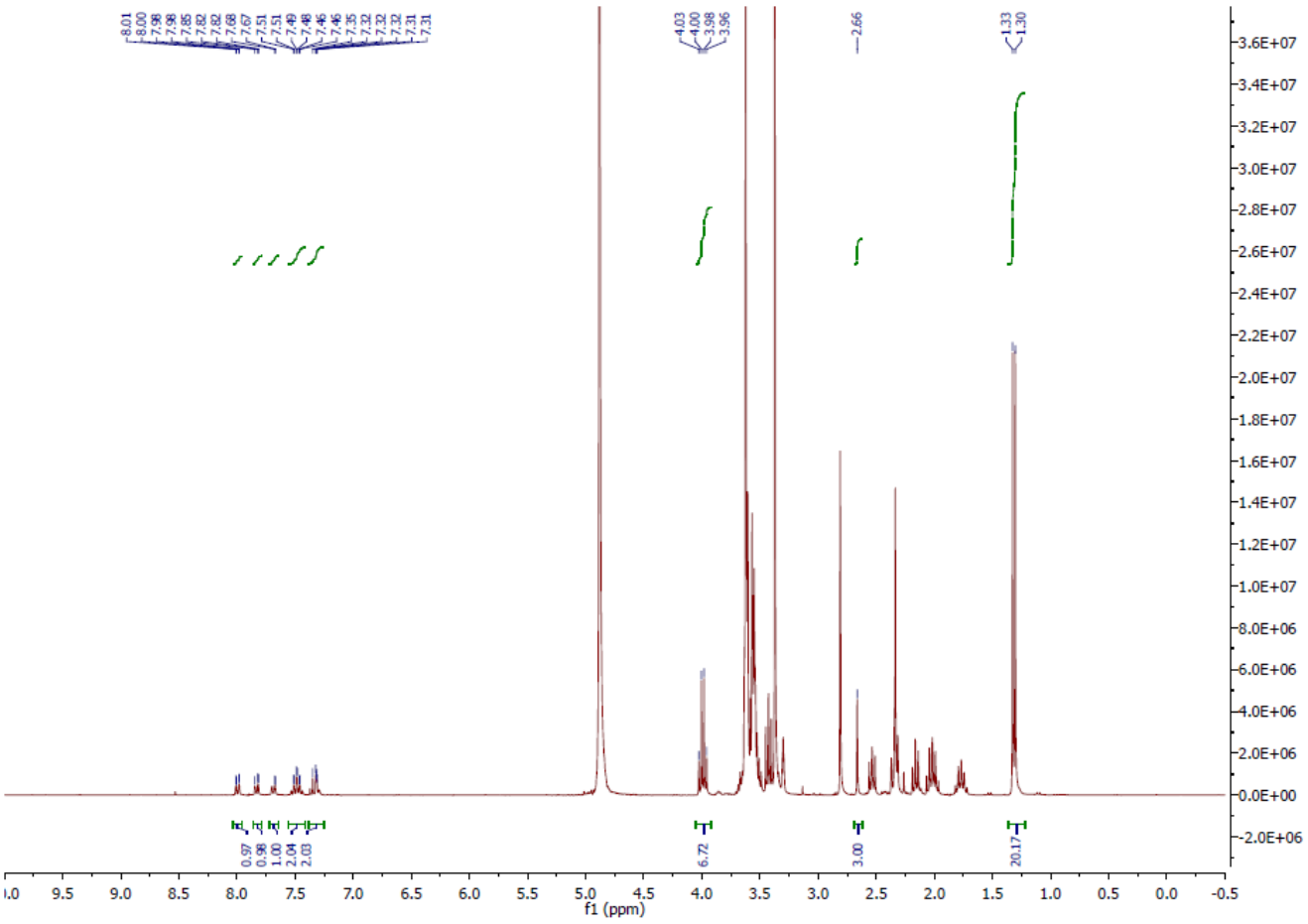


^{1}H NMR with 1-methylnaphthalene (10%) as internal standard



H_2 generation from industrial glycerol at 140 °C (Determine the yield of LA)

^{1}H NMR with 1-methylnaphthalene (10%) as internal standard


8.01
8.00
7.98
7.98
7.85
7.82
7.82
7.68
7.67
7.51
7.51
7.49
7.48
7.46
7.46
7.35
7.32
7.32
7.31
7.31
4.03
4.00
3.98
3.96
2.66
1.33
1.30
0.97
0.96
1.00
2.04
2.03
6.72
3.00
20.17
f1 (ppm)

Selected Gas phase GC spectrum:

H_2 generation from pure glycerol with 0.5 ppm of catalyst **1** (12 h).

Data File C:\HPCHEM\1\DATA\2013\1309\130911\SIG14782.D Sample Name: LY5-190

12 h

```
==========================================================================
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Acq. Operator   : LY                                    Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\WASSERST.M
Last changed    : 11/09/2013 19:52:35 PM by AR
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Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 12/09/2013 08:28:59 PM by LY
                  (modified after loading)
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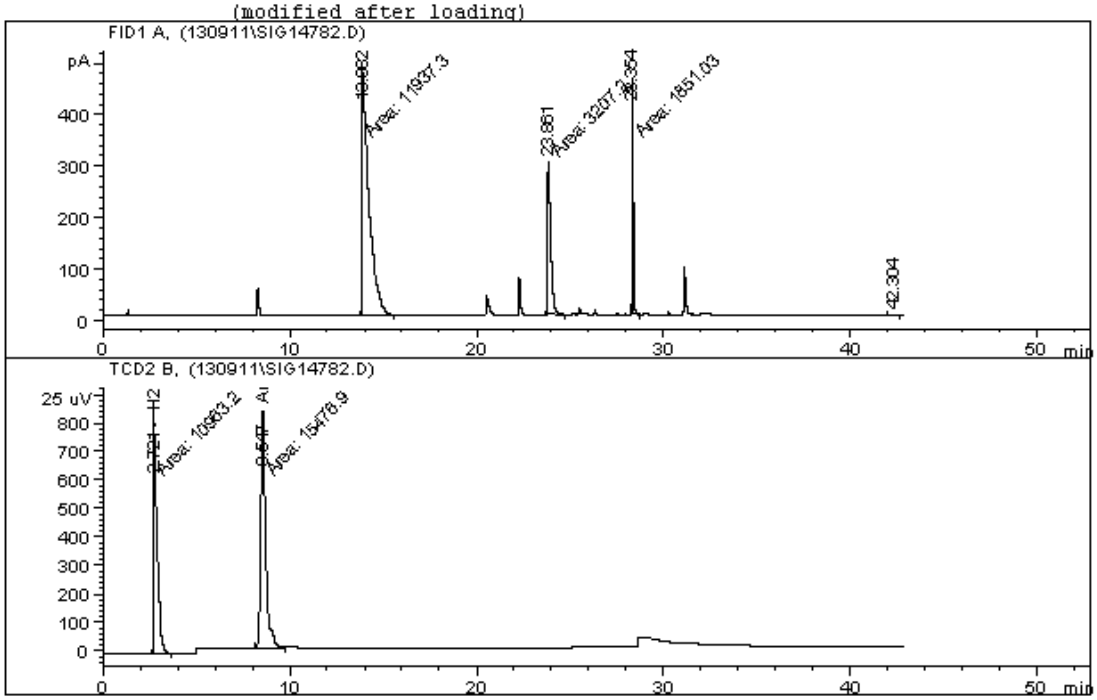


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                        External Standard Report
==========================================================================

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Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.721  2 MM     1.09632e4  9.10863e-3   99.85930    H2
  8.547  2 MM     1.54769e4  2.15715e-4    3.33859    Ar
 10.800  2           -          -            -        CO
 18.900  2           -          -            -        CH4
 25.890  2           -          -            -        CO2

Totals :                                  103.19789

 Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
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Gas GC 12/09/2013 08:29:30 PM LY Page 1 of 2

Blank reaction of industrial glycerol (12 h)

Data File C:\HPCHEM\1\DATA\2013\1308\130829\SIG14754.D Sample Name: ly5-174-4

12 h

```
==========================================================================
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Sample Name     : ly5-174-4                          Location : Vial 1
Acq. Operator   : LY                                    Inj :   1
                                                   Inj Volume : Manually
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Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 04/09/2013 16:41:15 PM by AK
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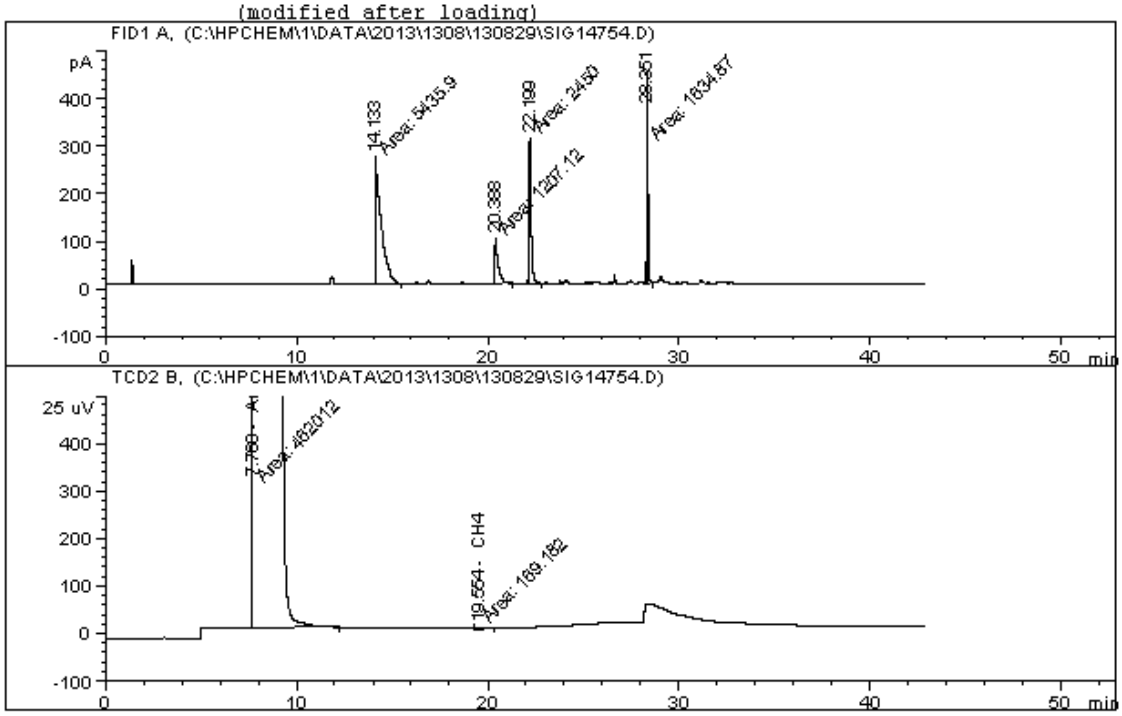


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Dilution              :      1.0000
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Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  3.000  2            -          -          -         H2
  7.760  2 MM     4.62012e5  2.18032e-4  100.73347    Ar
 11.275  2            -          -          -         CO
 19.554  2 MM      169.18150 2.76108e-4 4.67124e-2    CH4
 25.872  2            -          -          -         CO2

Totals :                                 100.78018

 Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
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H_2 generation from industrial glycerol (12 h).

Data File C:\HPCHEM\1\DATA\2013\1308\130814\SIG14699.D Sample Name: ly5-152-3

12 h

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Acq. Operator   : lv                                  Inj :   1
                                                  Inj Volume : Manually
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Last changed    : 14/08/2013 16:11:09 PM by ly
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 04/09/2013 16:53:40 PM by AK
                  (modified after loading)
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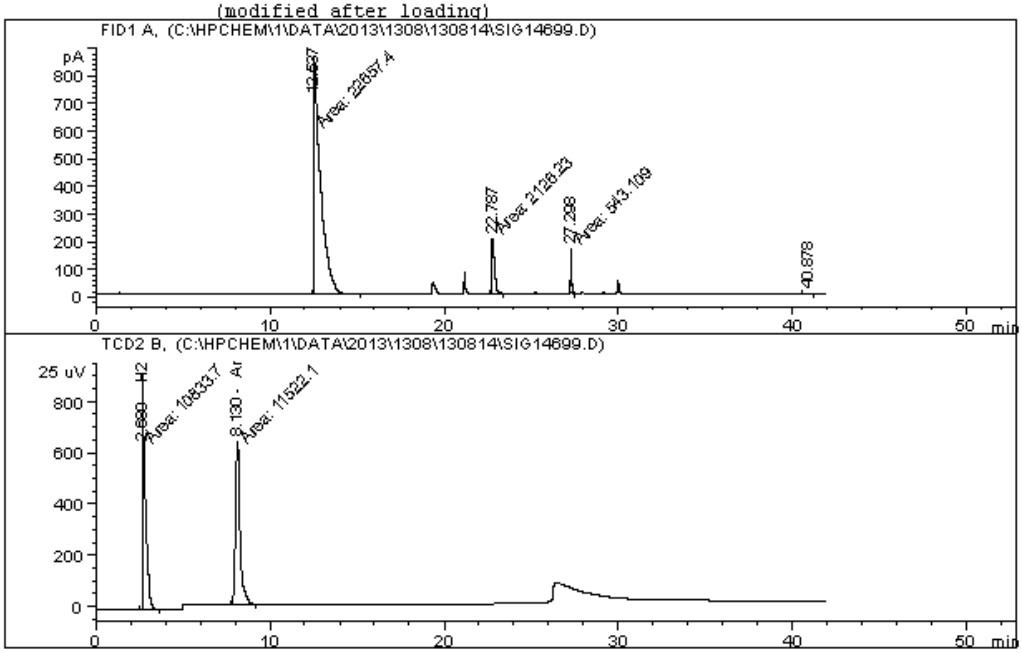


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==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Retention Time
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Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.689  2 MM     1.08337e4  9.14322e-3   99.05516    H2
  8.130  2 MM     1.1522le4  2.15695e-4    2.48527    Ar
 11.275  2            -          -           -        CO
 19.000  2            -          -           -        CH4
 25.872  2            -          -           -        CO2

Totals :                                  101.54042

 Results obtained with enhanced integrator!
2 Warnings or Errors :

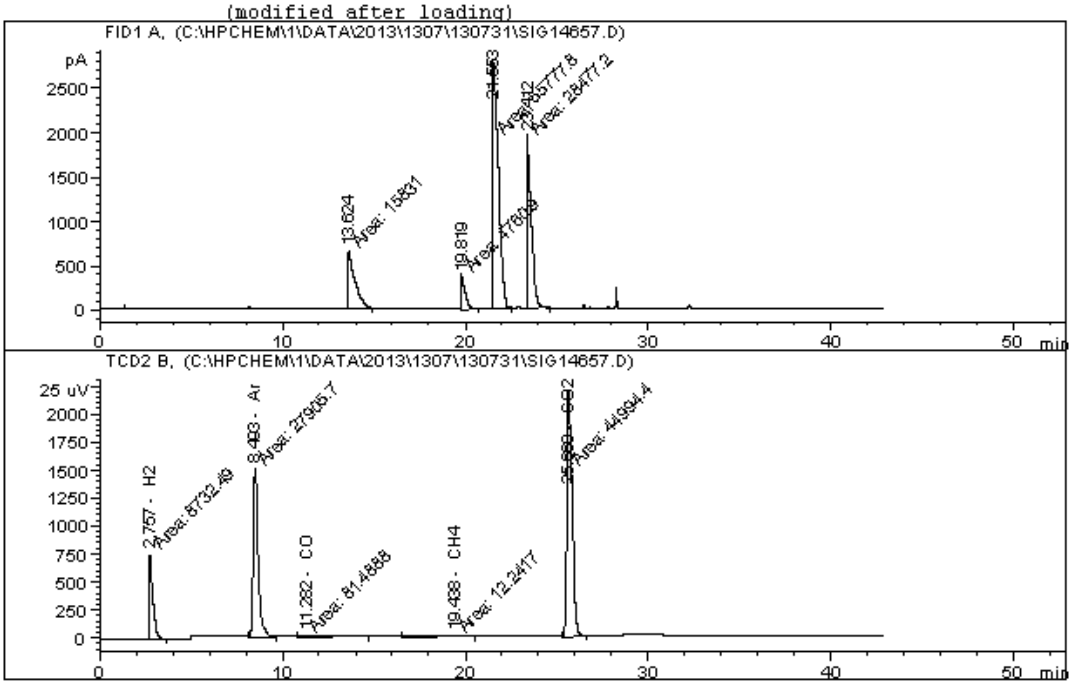
Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
```

H_2 generation from glycerol with 200 ppm of catalyst **1** (200 mins).

Data File C:\HPCHEM\1\DATA\2013\1307\130731\SIG14657.D Sample Name: LY5-135

200 mins

```
======================================================================
Injection Date  : 31/07/2013 14:09:53 PM
Sample Name     : LY5-135                       Location : Vial 1
Acq. Operator   : LY                               Inj :   1
                                                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\WASSERST.M
Last changed    : 31/07/2013 13:47:21 PM by AK
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 04/09/2013 17:00:04 PM by AK
                  (modified after loading)
```




```
======================================================================
                      External Standard Report
======================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      04/09/2013 16:59:50 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.757  2 MM     8732.48633 9.77617e-3   85.37030    H2
  8.493  2 MM     2.79057e4  2.15778e-4    6.02144    Ar
 11.282  2 MM       81.48878 2.52189e-4 2.05505e-2    CO
 19.438  2 MM       12.24173 2.76108e-4 3.38004e-3    CH4
 25.660  2 MM     4.49944e4  1.8798le-4    8.45809    CO2

Totals :                                 99.87376

 Results obtained with enhanced integrator!
1 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
```

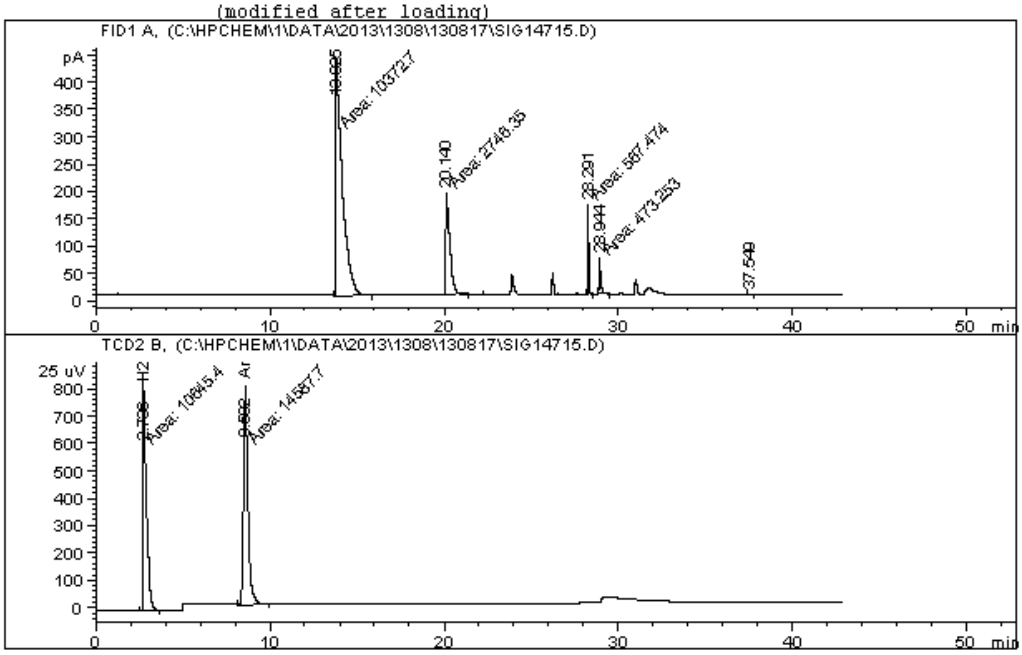
Gas GC 04/09/2013 17:00:05 PM AK Page 1 of 2

H_2 generation from ethylene glycol (2 h).

Data File C:\HPCHEM\1\DATA\2013\1308\130817\SIG14715.D Sample Name: LY5-157

2 h

```
==========================================================================
Injection Date  : 17/08/2013 18:03:18 PM
Sample Name     : LY5-157                          Location : Vial 1
Acq. Operator   : LY                                  Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\WASSERST.M
Last changed    : 15/08/2013 09:03:30 PM by AK
Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 12/09/2013 12:20:31 PM by LY
                  (modified after loading)
```




```
==========================================================================
                        External Standard Report
==========================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      12/09/2013 08:28:15 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.736  2 MM     1.06454e4  9.19437e-3   97.87750    H2
  8.582  2 MM     1.45877e4  2.15711e-4    3.14672    Ar
 10.800  2            -          -           -        CO
 18.900  2            -          -           -        CH4
 25.890  2            -          -           -        CO2

Totals :                                  101.02422

 Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
```

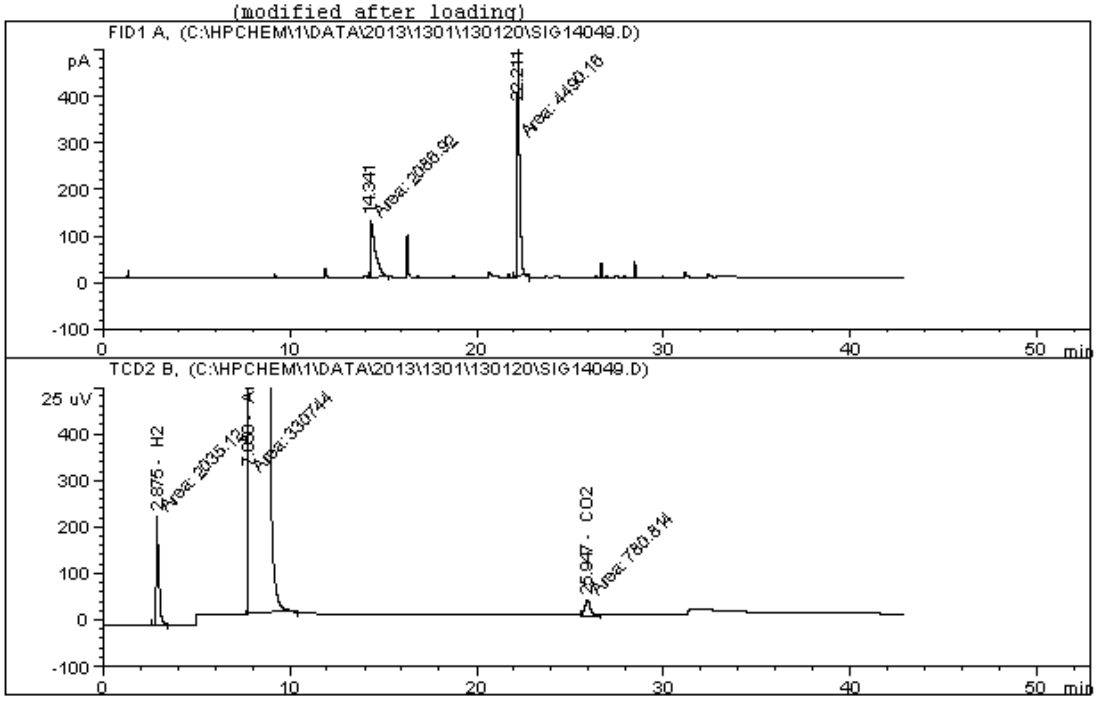
Gas GC 12/09/2013 12:22:06 PM LY Page 1 of 2

H_2 generation from sorbitol (2 h).

Data File C:\HPCHEM\1\DATA\2013\1301\130120\SIG14049.D Sample Name: LY4-074

2h

```
==================================================================
Injection Date  : 20/01/2013 19:32:11 PM
Sample Name     : LY4-074                        Location : Vial 1
Acq. Operator   : LY                                Inj :   1
                                                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\WASSERST.M
Last changed    : 20/01/2013 11:23:32 PM by CC
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\CAL1210.M
Last changed    : 04/09/2013 17:14:55 PM by AK
                  (modified after loading)
```




```
==================================================================
                    External Standard Report
==================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      04/09/2013 17:14:26 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,

RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                   [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.875  2 MM     2035.12170 1.39182e-2   28.32517    H2
  7.850  2 MM     3.30744e5  2.17341e-4   71.88409    Ar
 11.275  2           -          -            -        CO
 19.000  2           -          -            -        CH4
 25.947  2 MM      780.81372 1.87399e-4 1.46323e-1    CO2

Totals :                                 100.35558

 Results obtained with enhanced integrator!
2 Warnings or Errors :

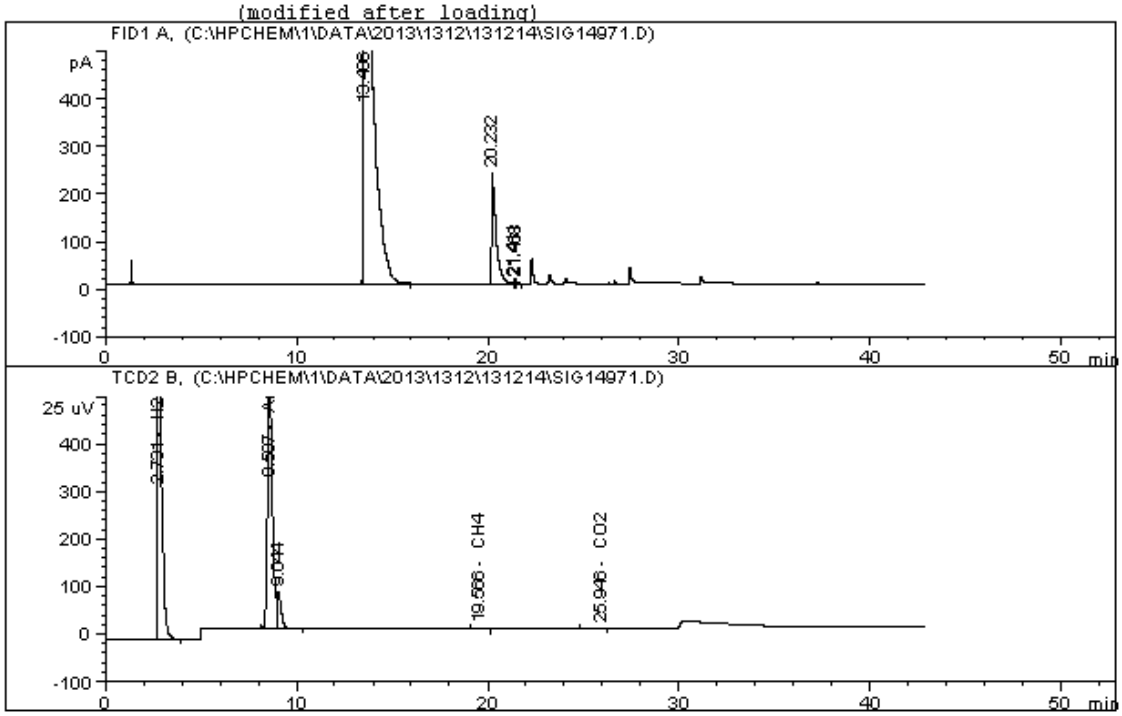
Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
```

Gas GC 04/09/2013 17:14:56 PM AK Page 1 of 2

H_2 generation from industrial glycerol at 140 °C (24 h).

24 h

```
======================================================================
Injection Date  : 14/12/2013 10:55:42 PM
Sample Name     : ly6-106-3                        Location : Vial 1
Acq. Operator   : LY                                  Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\WASSERST.M
Last changed    : 14/12/2013 10:47:22 PM by LY
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\CAL1109.M
Last changed    : 06/03/2014 16:43:09 PM by PS
                  (modified after loading)
```




```
======================================================================
                      External Standard Report
======================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      06/03/2014 16:41:55 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [vol%]   (not used in calc.)

Signal 1: FID1 A,
Signal 2: TCD2 B,
```

RetTime [min]	Sig	Type	Area	Amt/Area	Amount [vol%]	Grp	Name
2.731	2	BP	1.04392e4	9.71277e-3	101.39340		H2
8.587	2	PV	9663.10059	2.15686e-4	2.08419		Ar
11.447	2		-	-	-		CO
19.566	2	BP	12.97576	2.85033e-4	3.69851e-3		CH4
25.946	2	PV	20.64616	1.87007e-4	3.86097e-3		CO2

```
Totals :                                 103.48515

 Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
```

References

(1) M. Bertoli, A. Choualeb, A. J. Lough, Moore, B. D. Spasyuk and D. G. Gusev,*Organometallics* **2011**, *30*, 3497.

(2) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, and P. Rigo, *Organometallics* **2005**, *24*, 1660.