Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Synthesis of amino-functionalized metal-organic framework at nanoscale for highly dispersed gold nanoparticle deposition and catalysis

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Supporting Information

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General Information. The phase composition of the samples were investigated by X-ray powder diffraction (XRD, M21X, Cu Kα radiation, λ=0.154178 nm). Their morphology and structure of the as-obtained product was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Further information of the structure were revealed by transmission electron microscopy (TEM, TEI Tecnai F20) and high-resolution TEM (HRTEM, TEI Tecnai F20) using TEI Tecnai F20. The samples for the SEM, TEM and HRTEM measurements were first dispersed in ethanol and sonicated for a few minutes, and then supported onto the silicon slice and the holey carbon film on a Cu grid, respectively.The chemical compositions were analyzed using X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, Vavian 715-ES). Thermogravimetric analysis (TG) were conducted by a TGA instrument (Netzsch STA449F) at a heating rate of 10^oC/min under an N_2 flow. The specific surface areas were calculated by nitrogen sorption–desorption isotherms using a Micromeritics ASAP 2420 adsorption analyzer. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. Fourier transform Infrared spectra (FTIR) were acquired on a Nicolet 6700 using the KBr pellet technique. The catalytic results were analyzed by a gas chromatography-mass spectrum (GC-MS, Agilent7890/5975C-GC/MSD).

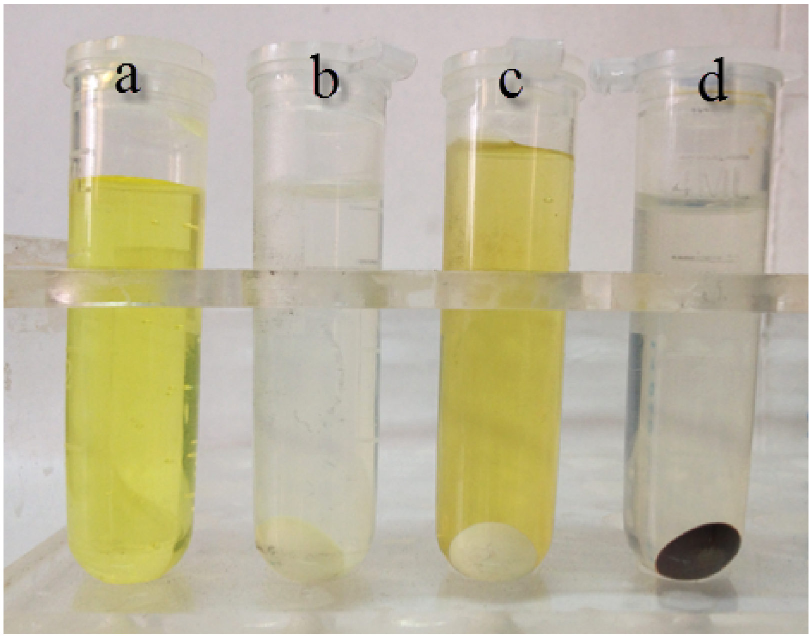


Figure S1. Amino functionalized MOFs for $HAuCl_4$ absorption. (a) $HAuCl_4$ solution. (b) Centrifuged UiO-66(NH_2) in solution (c) Time zero when UiO-66(NH_2) was added to $HAuCl_4$ solution (centrifuged) (d) 10 min after UiO-66(NH_2) was added to $HAuCl_4$ solution (centrifuged)

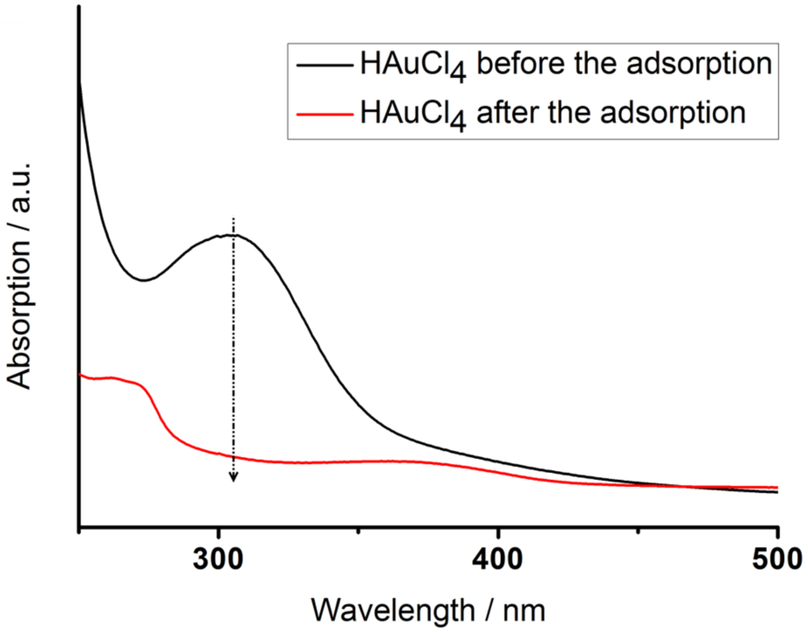


Figure S2. UV spectrum of $HAuCl_4$ before and after the adsorption.

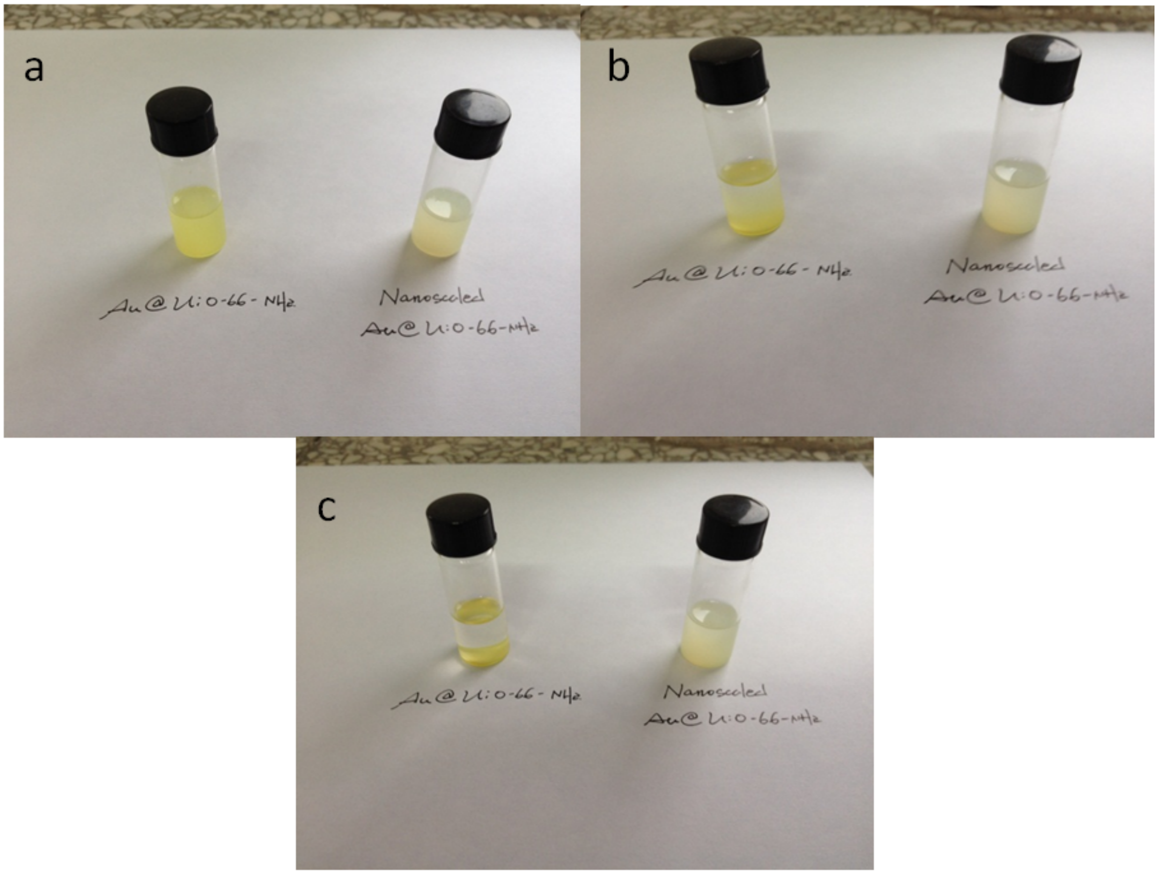
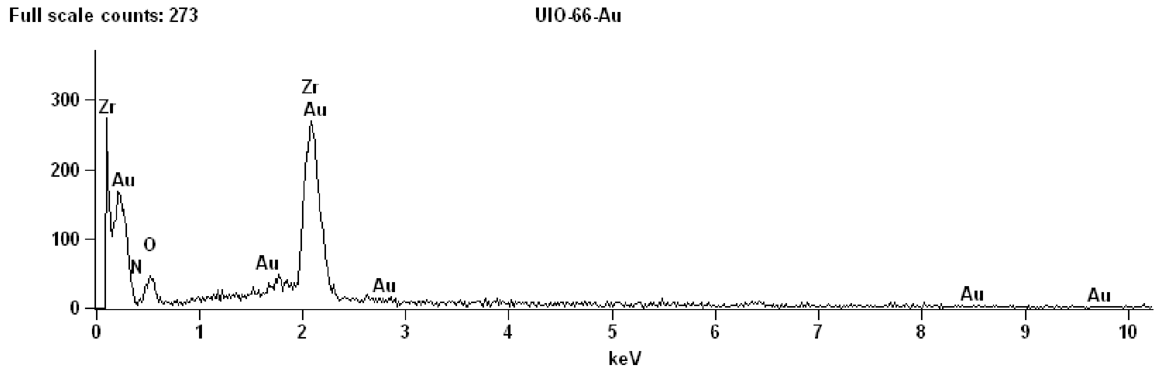


Figure S3. The dispersion of Au@UiO-66(NH_2) and Au@nano UiO-66(NH_2) in toluene solution. (a, 0 min, b, 5 min, c, 30 min)



Live Time: 30.0 sec.

Acc.Voltage: 15.0 kV Take Off Angle: 35.0 deg.

Quantitative Results

Element Line	***Net Counts***	***Net Counts Error***	***Weight %***	***Weight % Error***	***Atom %***	***Atom % Error***
N K	39	+/- 36	11.25	+/-10.39	22.32	+/-20.60
O K	527	+/- 33	36.11	+/- 2.26	62.71	+/- 3.93
Zr L	5273	+/- 145	46.15	+/- 1.27	14.06	+/- 0.39
Au L	19	+/- 22	6.49	+/- 7.51	0.91	+/- 1.06
Total			100.00		100.00	

Figure S4. EDX results of 1.8 wt% Au@UiO-66(NH_2)

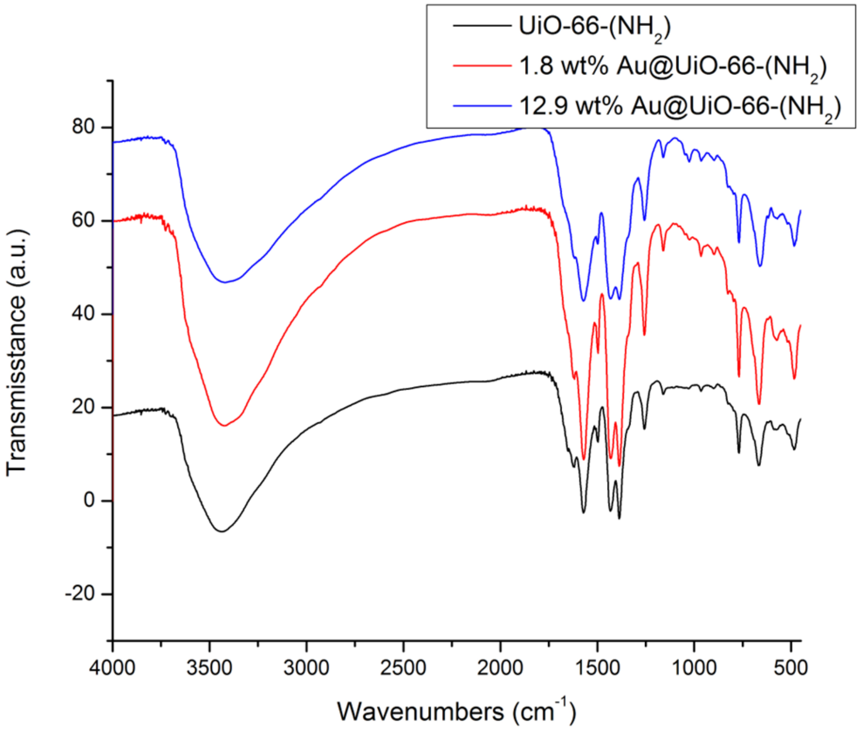


Figure S5. FTIR of UiO-66(NH$_2$) and various loading of Au@UiO-66(NH$_2$).

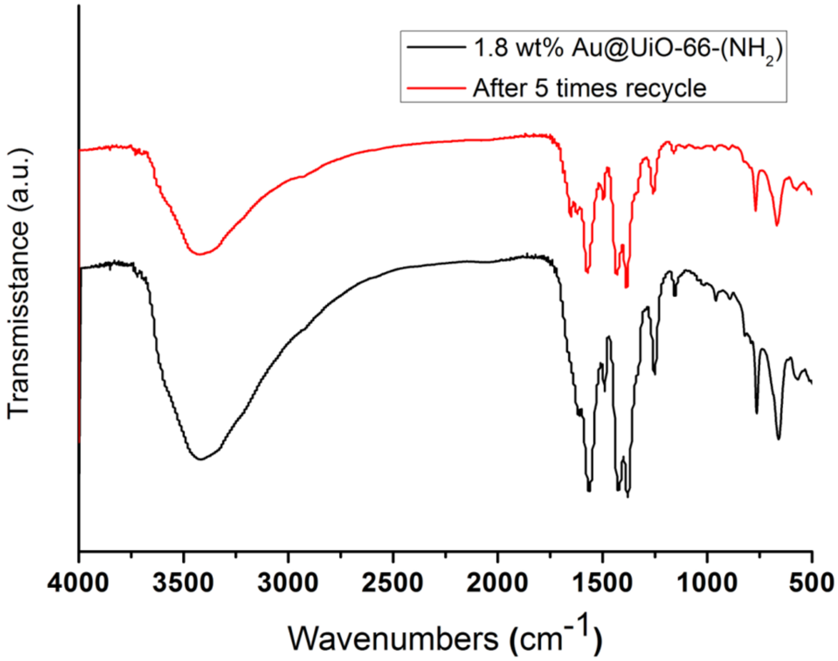


Figure. S6. FTIR of recycled 1.8 wt% Au@UiO-66(NH$_2$)

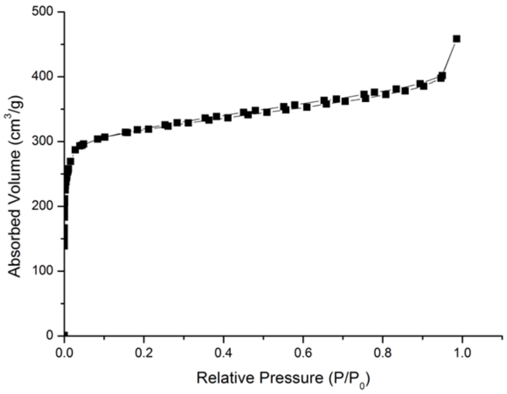


Figure S7. BET adsorption-desorption isotherms of UiO-66(NH_2)

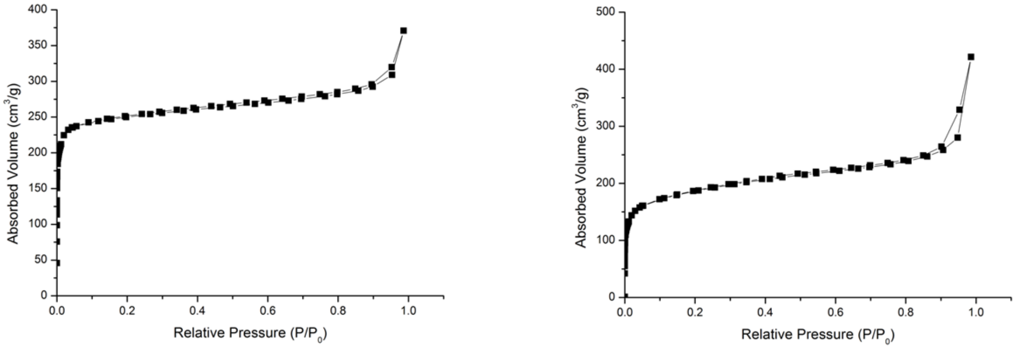


Figure S8. BET adsorption-desorption isotherms of (left) 1.8 wt% Au@UiO-66(NH_2) (right) 12.9 wt% Au@UiO-66(NH_2)

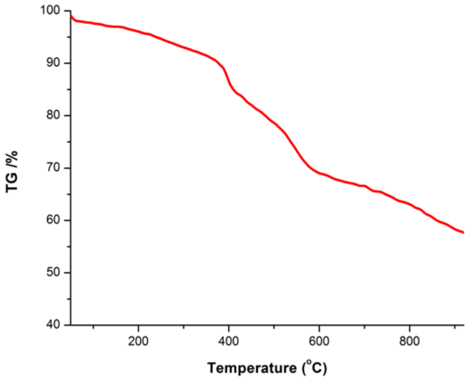


Figure S9. TGA curve for the as-synthesized nanosized UiO-66(NH_2)

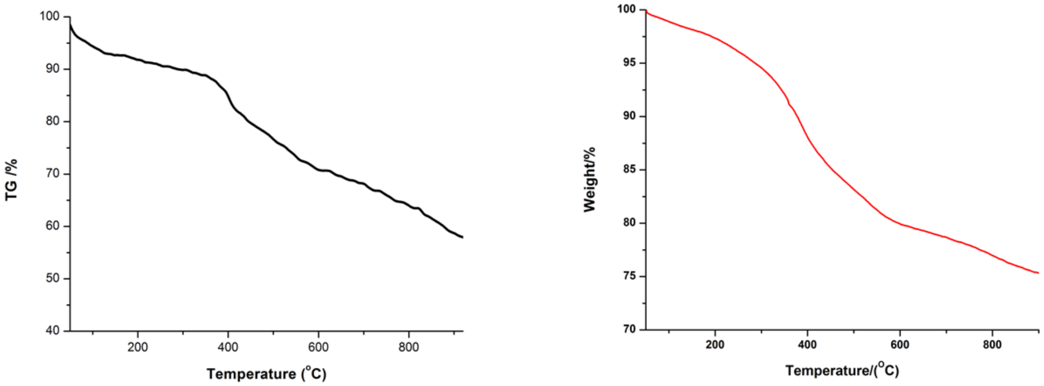


Figure S10. TGA curve for 1.8 wt% Au@UiO-66(NH_2) (left) and 12.9 wt% Au@UiO-66(NH_2)

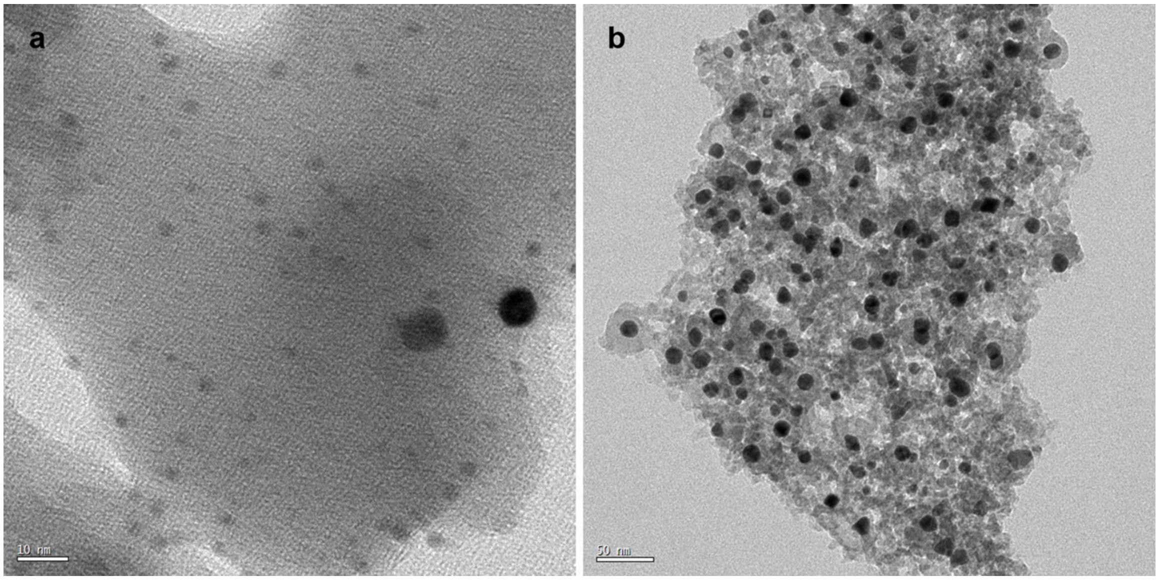


Figure S11. HRTEM images Au@IRMOF-3.

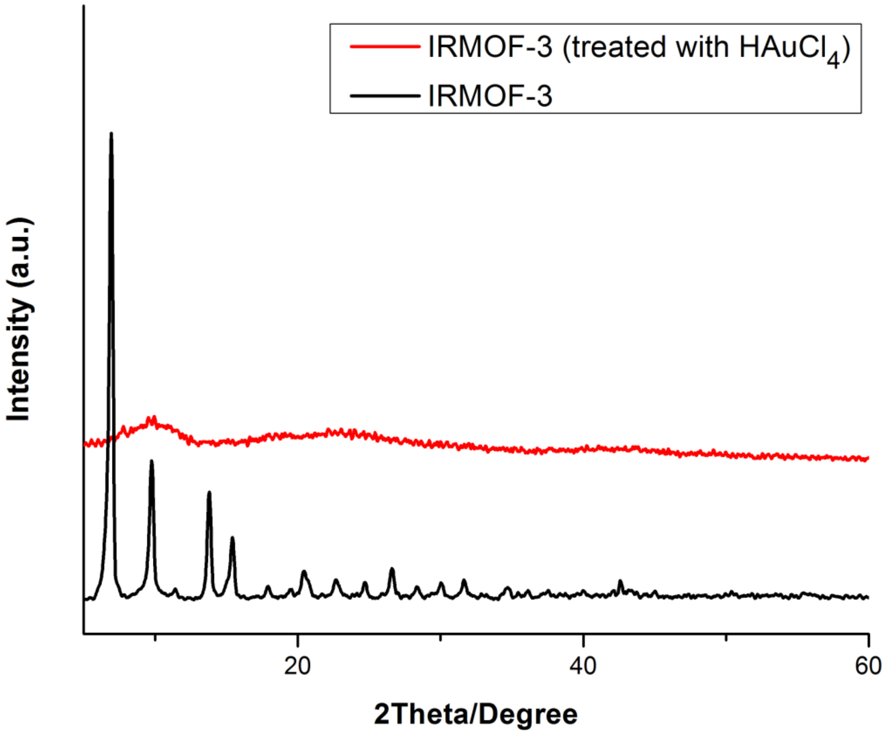


Figure S12. PXRD of IRMOF-3 and IRMOF-3 after $HAuCl_4$ and $NaBH_4$ treatment.

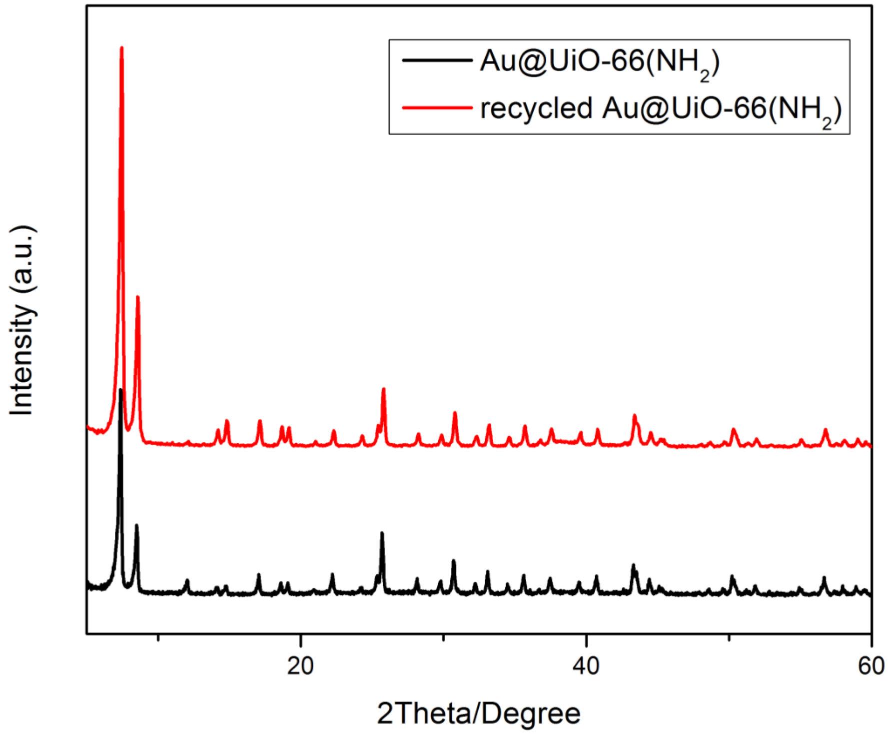


Figure S13. PXRD of recycled 1.8 wt% Au@UiO-66(NH$_2$) catalyst after five times. 1.8 wt% Au@UiO-66(NH$_2$) (Bottom), recycled 1.8 wt% Au@UiO-66(NH$_2$) (Top).

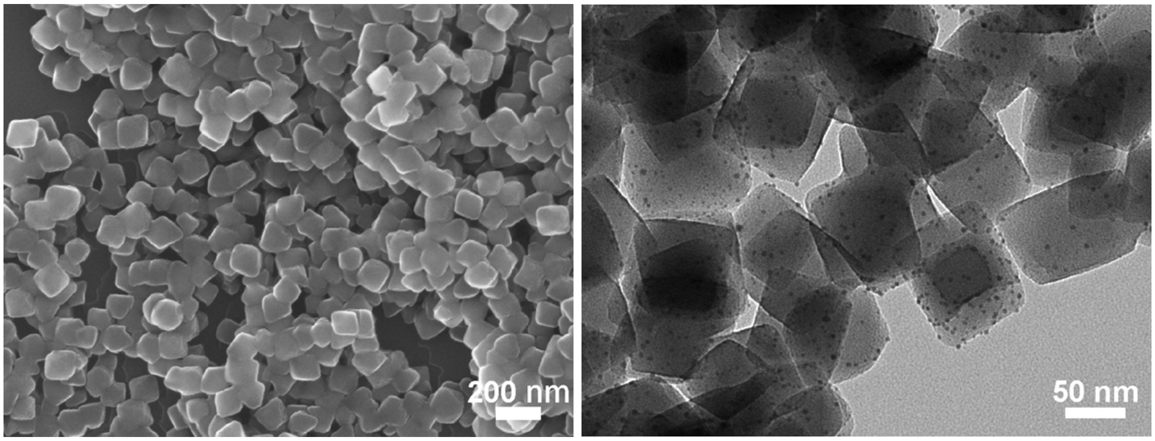


Figure S14. SEM and TEM of 1.8 wt% Au@UiO-66(NH$_2$) after recycled for 5 times in the aerobic oxidation.

Synthesis of unsupported gold stabilized by citrate

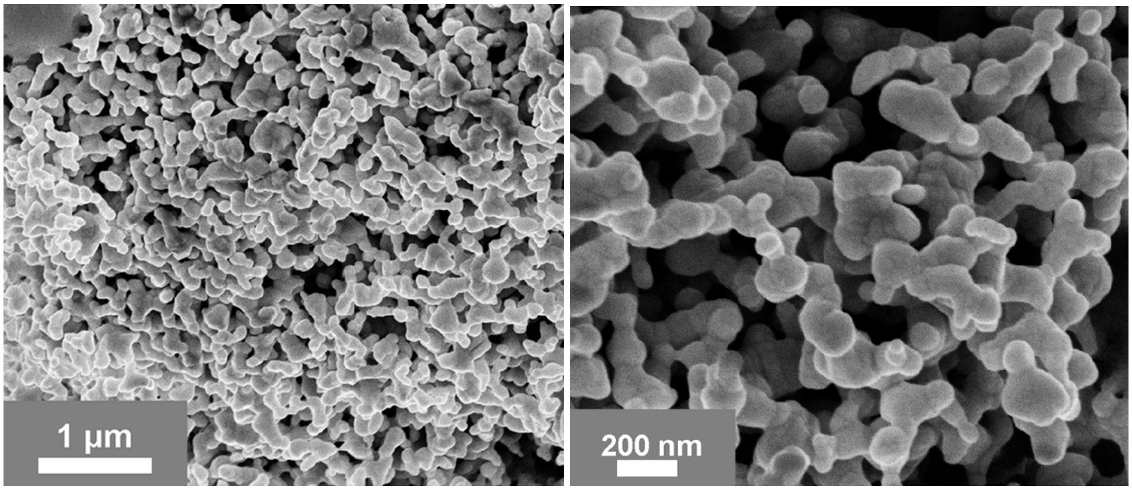


Figure S15. SEM images of citrate stabilized unsupported gold.

Procedure of citrate stabilized gold nanoparticles synthesis

Citrate stabilized gold nanoparticles were prepared according to the literature procedure.[1] A 50 mL aqueous solution of $HAuCl_4$ (2.5×10^{-3} M) was heated to boiling, then 2 mL of trisodium citrate solution (1% by wt) was added to it under continuous stirring. After 20s, the solution turned faint blue. The reaction solution was boiled for another 30 min in order to achieve complete reduction of Au(III) ions. The resulting unsupported gold was separated through centrifugation and washed with water (3 x 15 mL).

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[1] Tarasankar Pal, etc. J. Phys. Chem. C, 2007, 111 (12), pp 4596–4605

Synthesis of Au@TiO$_2$

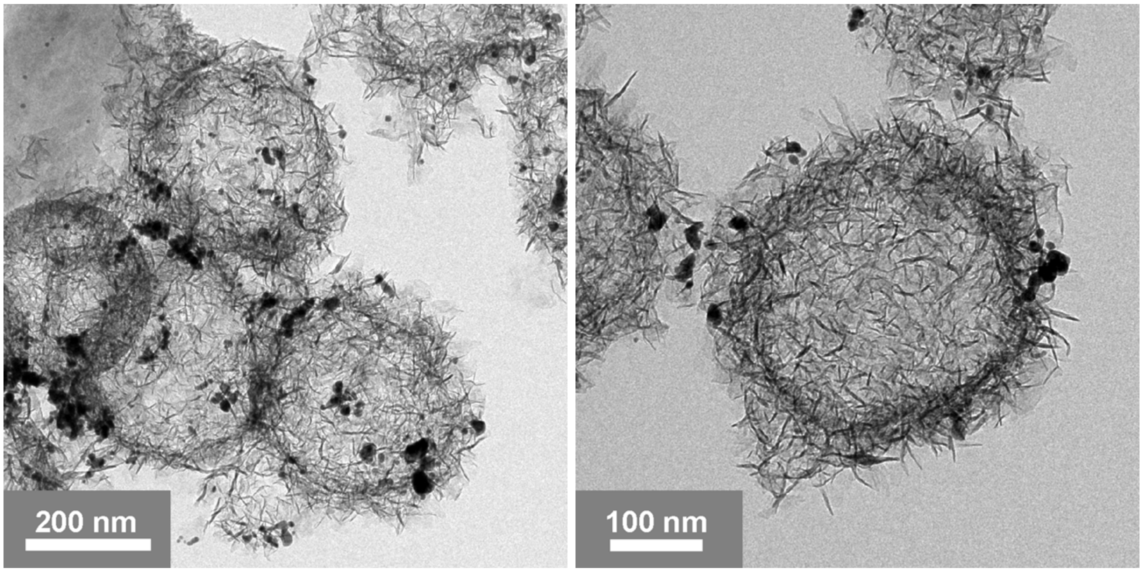

Figure S16. TEM images of Au@TiO$_2$

Procedure of Au@TiO$_2$ synthesis[2]

Synthesis of hierarchical titanate 3D nanospheres

0.8 mL of 0.1 M aqueous potassium chloride was injected into a mixture of 160 mL ethanol and 0.05 g hydroxypropyl cellulose (HPC), and added 4.4 mL tetrabutyl titanate at ambient temperature under magnetic stirring until a white precipitate appeared. Then the suspension was sit in static condition for 24 h in a closed container at room temperature. The TiO$_2$ precipitation was collected by centrifugation and washed with ethanol for 3 times and deionized water for 3 times. An amount of 0.025 g of the TiO$_2$ precipitation was added in aqueous NaOH solution (15 mL, 1 M), and then transferred into a 25 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated in an oven at 150 °C for 12 h, and then cooled to room temperature. The resultant precipitate was collected by filtration, washed thoroughly with deionized water and ethanol for 3 times, respectively.

Synthesis of Au@TiO$_2$

Hierarchical titanate 3D nanospheres (0.05 g) were dispersed in 10 mL deionized water and then placed in a 250 mL three-necked round bottom flask with a mechanical stirrer. An aqueous solution of HAuCl$_4$ (2.5 mL, 0.025 M aqueous solution) was added and the

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[2] Y. Qi and G. Wang, etc. Applied Surface Science, 2014, 293, 359–365.

mixture was stirred at 300 rpm for 4 h in an ice-bath. Subsequently $NaBH_4$ aqueous solution (10 mL, 0.05 M aqueous solution) was rapidly added and the reaction continued for 0.5 h at 0 °C with vigorous stirring. The Au@TiO_2 product was separated by centrifugation, washed three times with deionized water to remove excess $NaBH_4$ and dried under vacuum. ICP-AES analysis shows a gold content of 2.8 wt% for Au@TiO_2.

Synthesis of Au@PANI

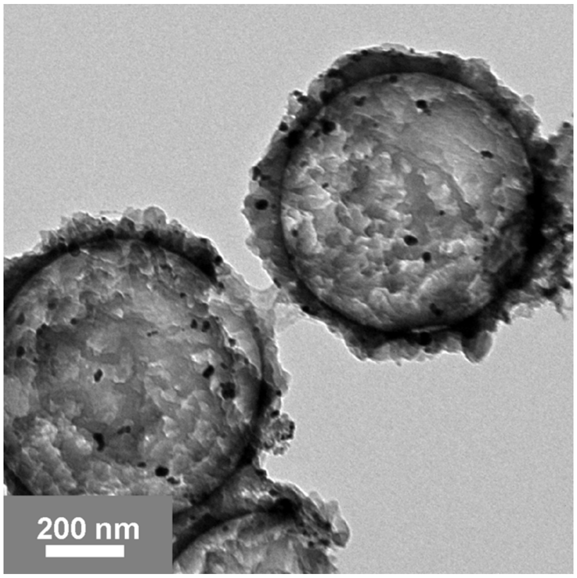

Figure S17. TEM image of Au@PANI

Procedure of Au@PANI synthesis[3]

Synthesis of polystyrene (PS) template

In a 250 mL four-necked round-bottom flask, 140 mL of deionized water and 10 g of styrene were placed in with a mechanical stirrer, a N_2 inlet and a reflux condenser. Then N_2 was bubbled through the solution to remove oxygen for 10 min while stirring (300 rpm), and heated to 70 °C via oil bath. At this time, 10 mL of KPS aqueous solution (0.023 g/mL) was injected into the flask to initiate the polymerization. The reaction mixture was stirred at 70 °C for 24 h, then PS microspheres were collected by

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[3] Au@PANI preparation is achieved according to the literature procedure. W. C. Guo and G. Wang, etc. Chemistry – An Asian Journal, 2013, 8, 1160–1167.

centrifugation and washed with water and ethanol three times. The PS microspheres precipitate was then dried under vacuum.

Preparation of polystyrene/polyaniline (PS/PANI) support

PS microspheres (0.3 g) were added to 20 mL deionized water and dispersed to form an emulsion. 3 mmol of aniline was subsequently added to the emulsion under vigorous stirring with a magnetic stir bar at room temperature for 12 h to swell the monomer into the PS templates. After the swelling of the templates, the $Fe(NO_3)_3 \cdot 9H_2O$ was added as oxidant. The reaction was stirred for 12 h, the composite microspheres were centrifuged, washed with water until the supernatant became colorless, and dried under vacuum.

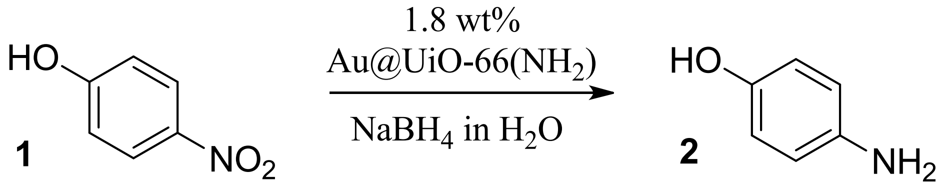
Gold nanoparticles immobilization on PS/PANI support

PS/PANI (0.05 g) composite microspheres were dispersed in 10 mL deionized water and then placed in a 250 mL three-necked round bottom flask with a mechanical stirrer. An aqueous solution of $HAuCl_4$ (2.5 mL, 0.025 M aqueous solution) was added and the mixture was stirred at 300 rpm for 4 h in an ice-bath. Subsequently $NaBH_4$ aqueous solution (10 mL, 0.05 M aqueous solution) was rapidly added and the reaction continued for 0.5 h at 0 ^{o}C with vigorous stirring. The product was separated by centrifugation, washed three times with deionized water to remove excess $NaBH_4$ and dried under vacuum.

Preparation of hollow Au@PANI catalyst

0.03 g PS/PANI@Au nanocatalyst was dispersed in 5 mL of THF and stirred for 24 h at room temperature to remove the PS template. The product was centrifuged, washed with ethanol, and dried under vacuum. ICP-AES analysis shows a gold content of 2.4 wt%.

Reduction of 4-Nitrophenol using $NaBH_4$.



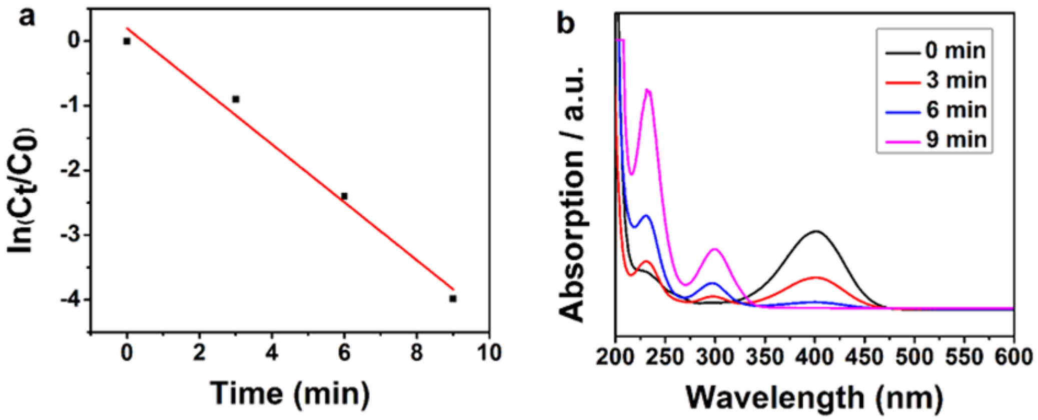


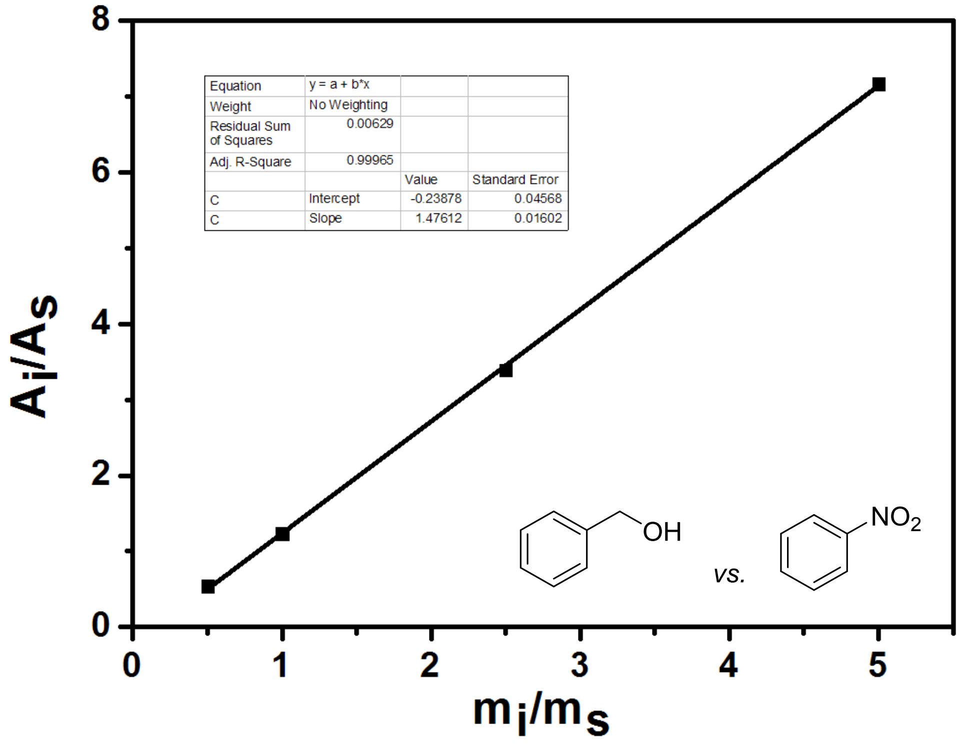
Figure S18. Catalytic reduction of 4-nitrophenol by $NaBH_4$ over Au@UiO-66(NH_2).

The reduction of 4-NP was carried out in a centrifuge tube and was monitored by UV/Vis spectroscopy at room temperature. The alcohol solution of 4-NP (0.005 M, 2 mL) was added to an ethanol dispersion of the Au@UiO-66(NH_2) catalyst (1.8 wt%, 0.01 g). Then, freshly prepared $NaBH_4$ (0.2 M, 10 mL) was added rapidly. The catalytic reaction solution was monitored by UV/Vis spectroscopy every 3 min until the solution became colorless. The linear relationship between $\ln(C_t/C_0)$ and reaction time was elucidated, which showed the 4-nitrophenol reduction occurred under first-order reaction kinetics (Fig. 18b). Here C_t was definited as absorbance of 4-nitrophenol at the fixed intervals, and C_0 as absorbance of 4-nitrophenol at the initial stage. The first-order rate constant (k) was calculated to be -0.45 min^{-1} for Au@UiO-66(NH_2).

However, it is observed that the crystalline structure of MOF support tended to decompose slowly over the course of the reaction according to the XRD analysis, which has not been reported in other Au@MOF reduction systems. The 4-nitrophenol reduction was designed to be finished within 15 minutes in order to avoid the loss of the crystalline of the MOF support. The $NaBH_4$-promoted slow decomposition of UiO-66(NH_2) support should be taken into consideration for future catalytic reaction design.

Compound versus internal standard for GC-MS calibration.

Table 3, entry 1



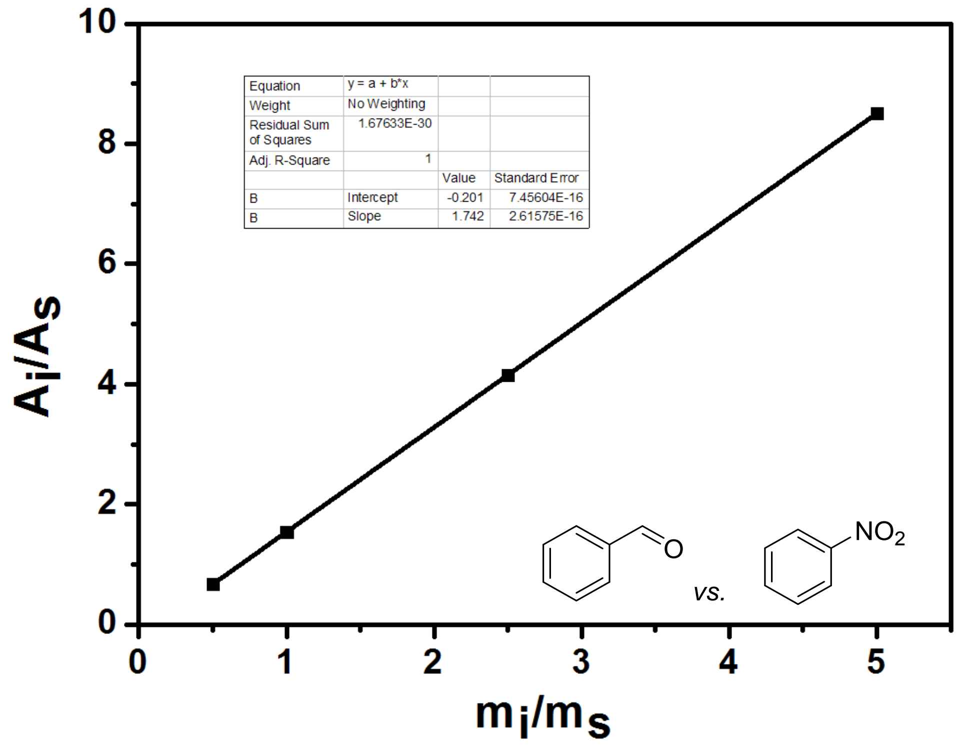
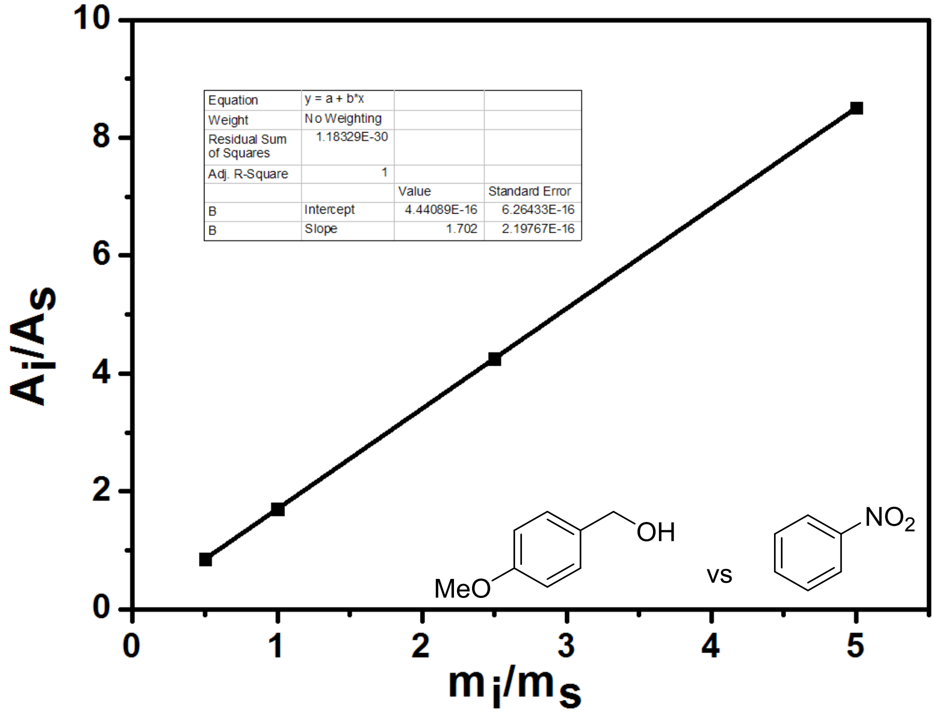
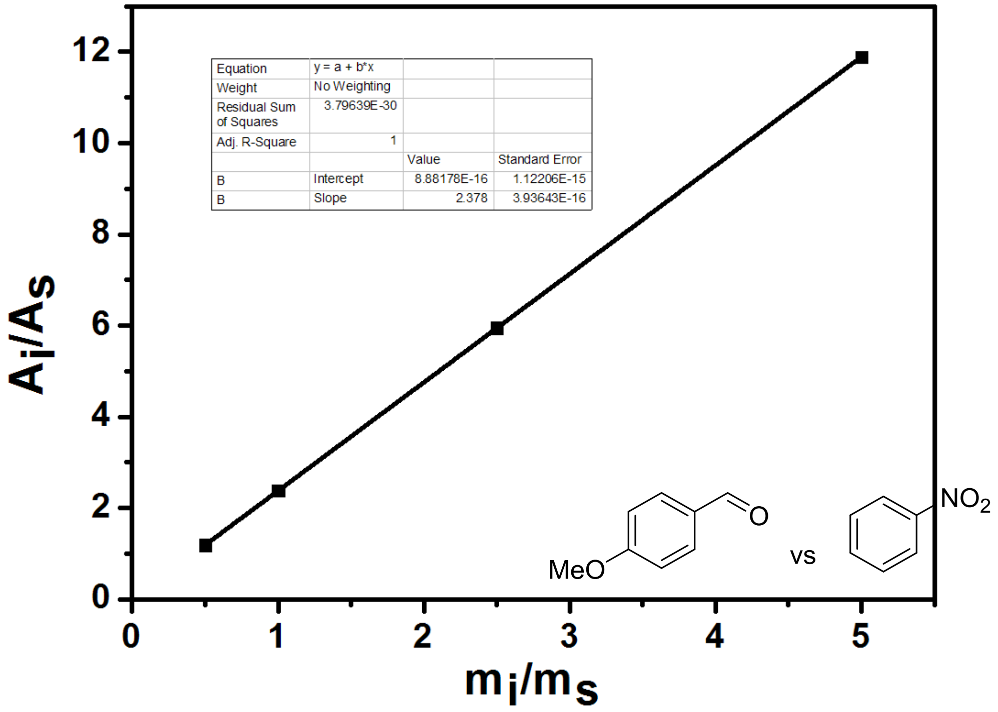


Table 3, entry 2

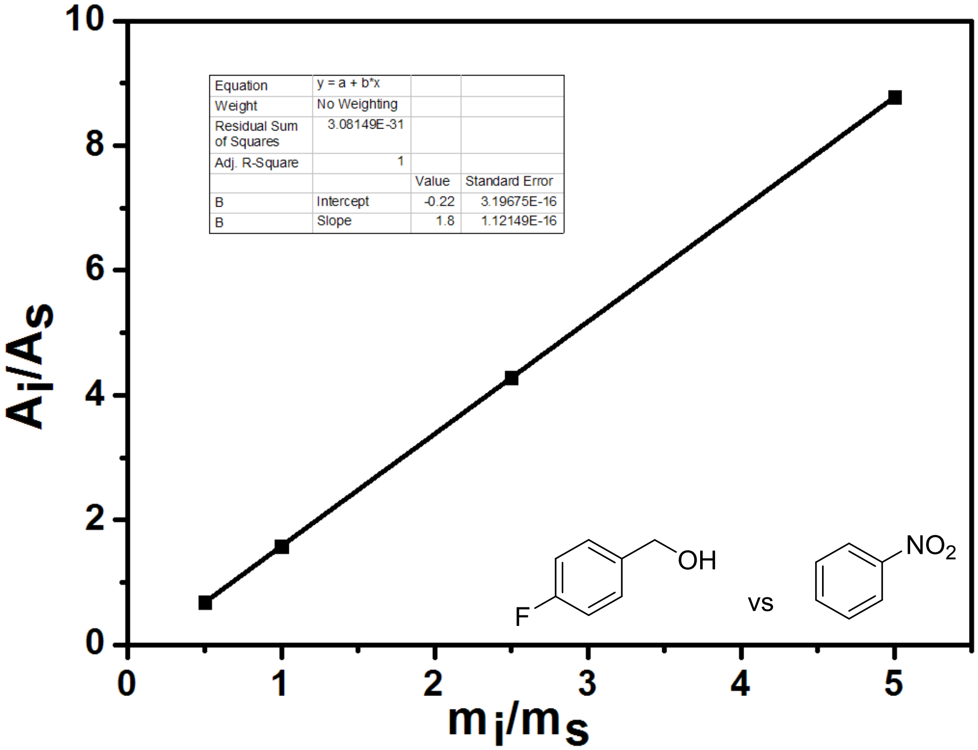


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.18329E-30		
Adj. R-Square	1		
		Value	Standard Error
B	Intercept	4.44089E-16	6.26433E-16
B	Slope	1.702	2.19767E-16



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3.79639E-30		
Adj. R-Square	1		
		Value	Standard Error
B	Intercept	8.88178E-16	1.12206E-15
B	Slope	2.378	3.93643E-16

Table 3, entry 3



Equation	y = a + b*x		
Weight	No Weighting		
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Adj. R-Square	1		
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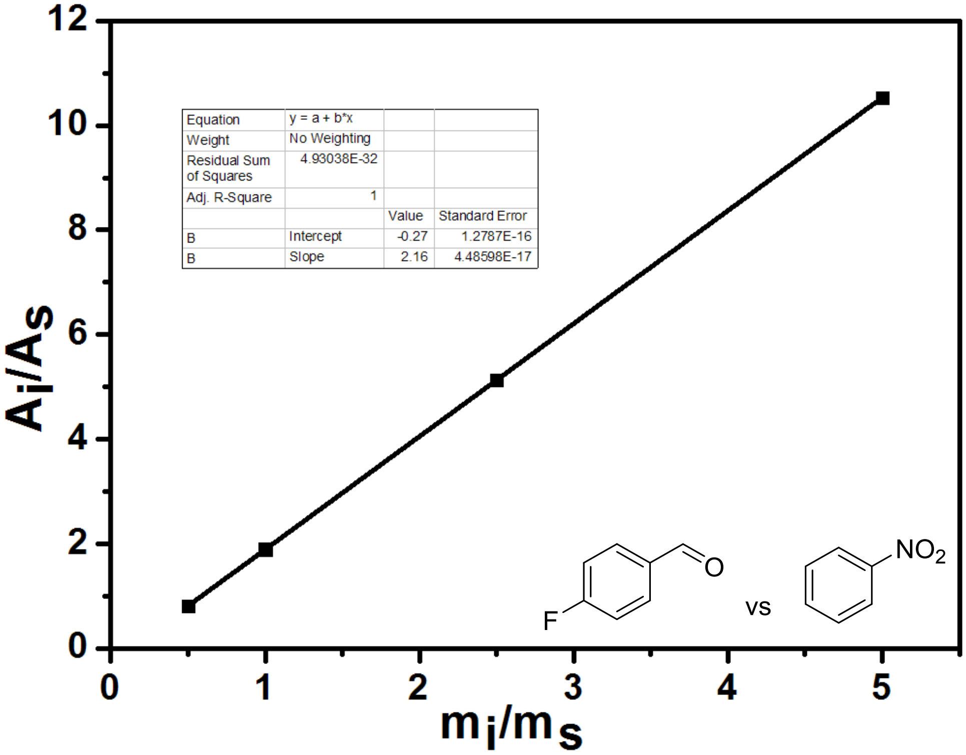
B	Intercept	-0.22	3.19675E-16
B	Slope	1.8	1.12149E-16



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4.93038E-32		
Adj. R-Square	1		
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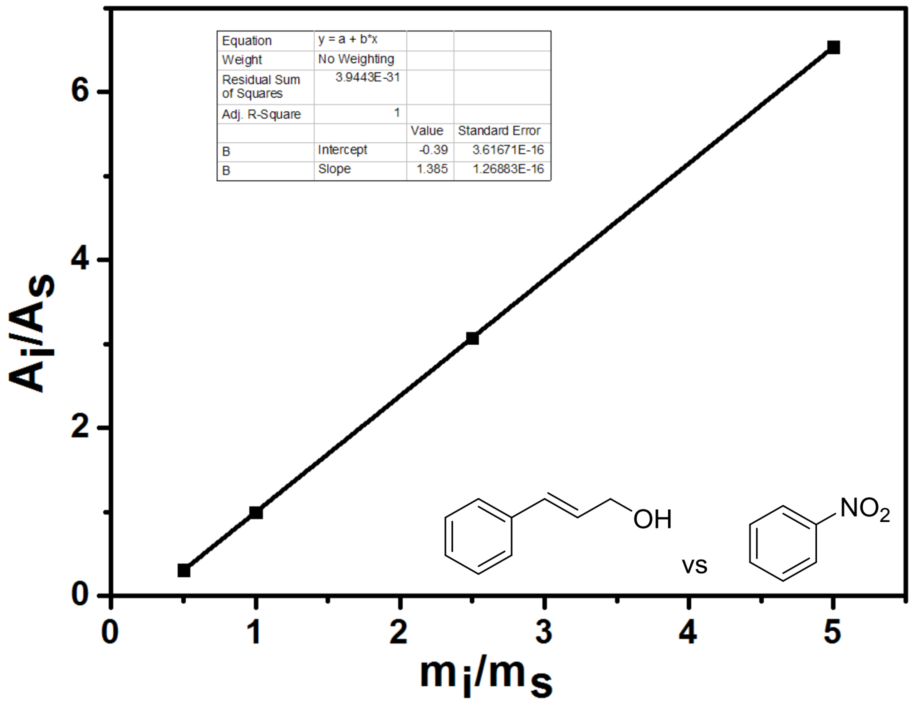
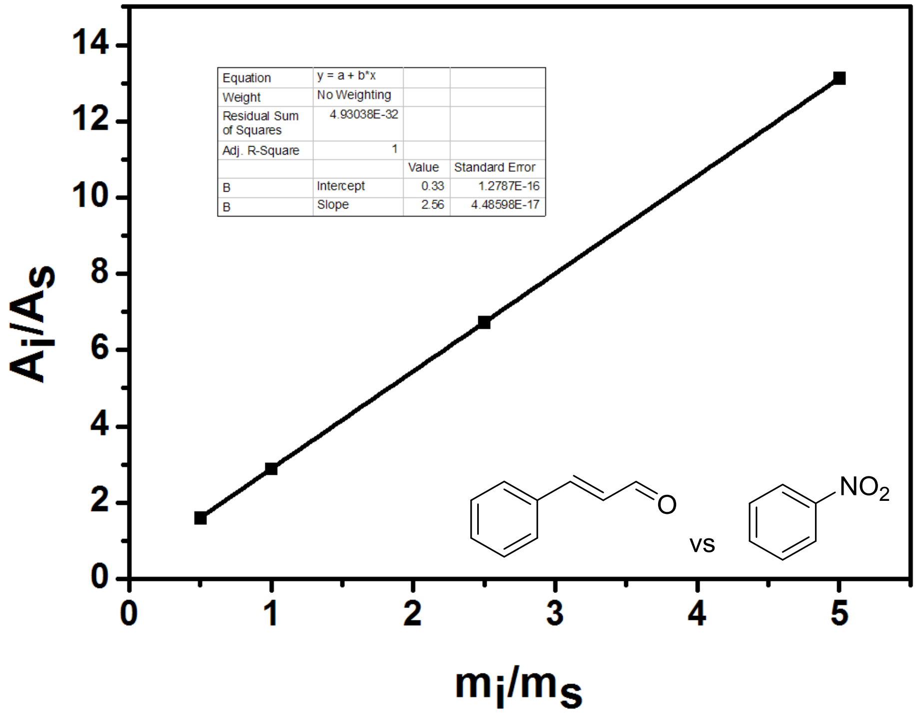
B	Intercept	-0.27	1.2787E-16
B	Slope	2.16	4.48598E-17

Table 3, entry 4





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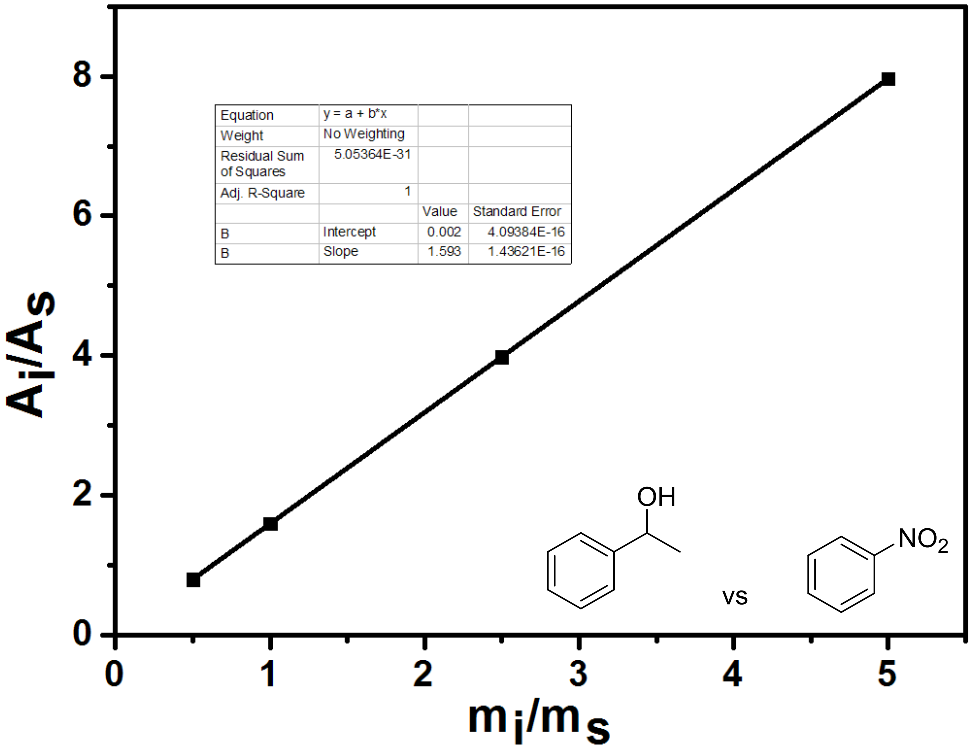
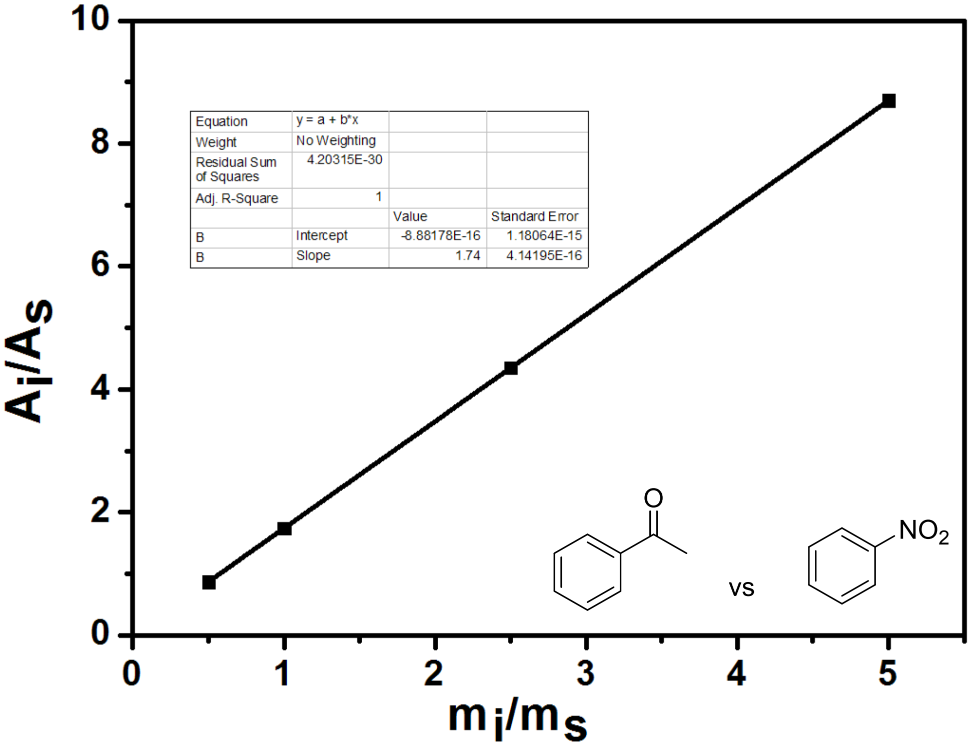
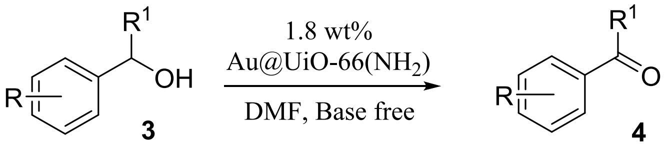


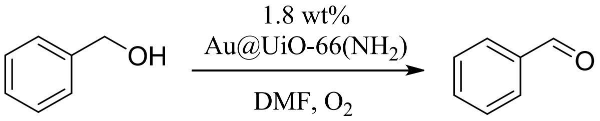


In-situ monitoring of aerobic oxidation reaction for Table 3.

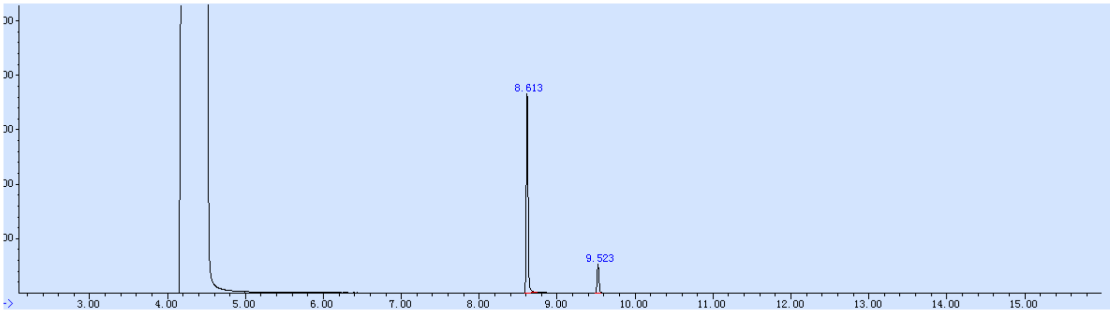


The in-situ GC-MS monitoring of conversion and yield was performed through direct injection of reaction solution after 10 times dilution. The in-situ ^{1}H NMR monitoring of reaction conversion and yield was performed in DMF d$_7$ solvent. The crude sample was filtered through a sodium sulfate layer and transferred to a NMR tube for direct ^{1}H NMR analysis. There is no aqueous work-up for GC-MS and ^{1}H NMR in-situ monitoring.

Table 3, entry 1



GC-MS at 0 min



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 #   min  Scan Scan  Scan  Type         Area      %      area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1  8.613  1135 1140  1165   M  1878216  30479347 100.00%  87.972%
 2  9.523  1293 1300  1309   M   265613   4167240  13.67%  12.028%
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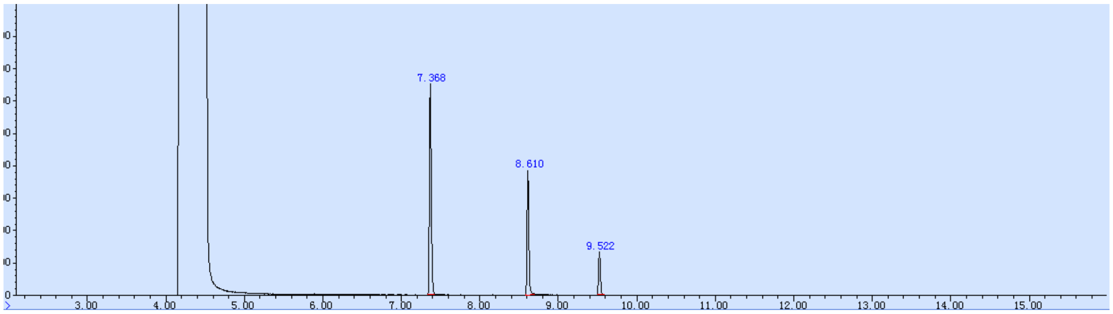
GC-MS at 20 min



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 1   7.368   918  923  935   M  1301407  20330557 100.00%  55.192%
 2   8.610  1136 1140 1157   M   772170  12386745  60.93%  33.627%
 3   9.522  1295 1299 1311   M   271372   4118954  20.26%  11.182%
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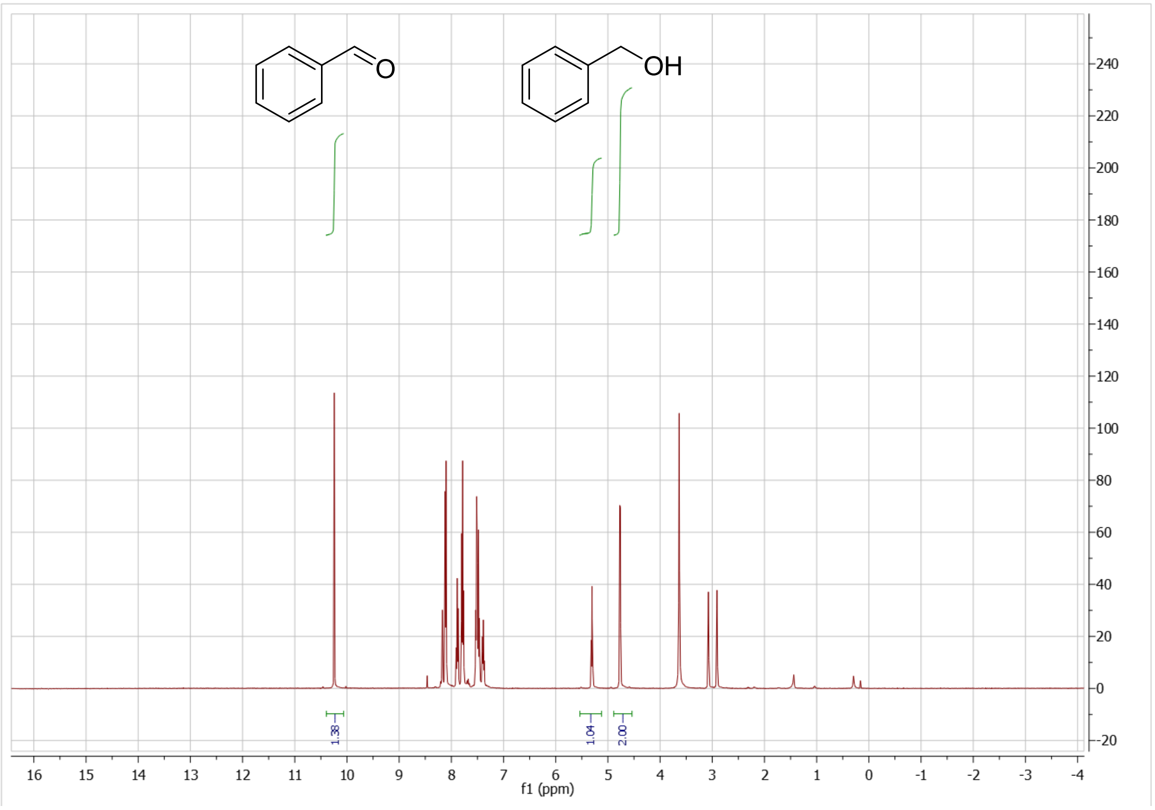
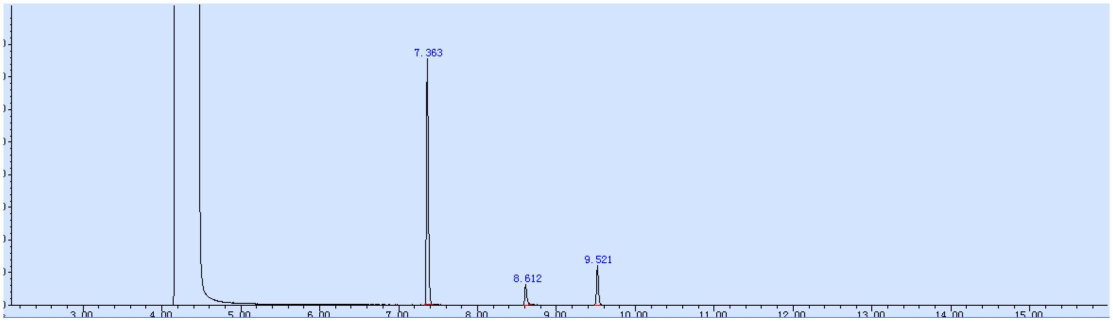
^{1}H NMR at 20 min



GC-MS at 40 min



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Peak    R.T.  Ini. TOP  Stp.  Peak  Height                        %
 #    min  Scan Scan  Scan  Type          Area      %        area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   7.363   916  922  937   M  1513945  24053393 100.00%  80.415%
 2   8.612  1136 1140 1154   M   124965   2164264   9.00%   7.236%
 3   9.521  1293 1299 1308   M   241647   3694011  15.36%  12.350%
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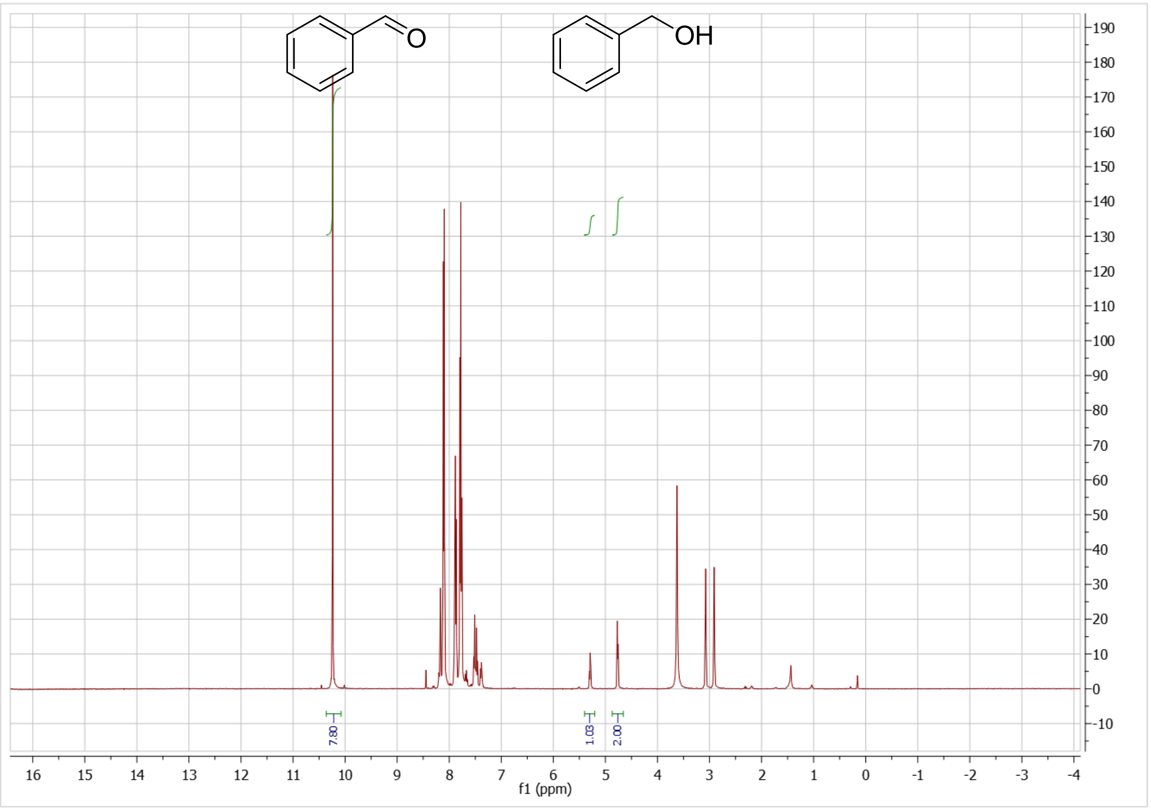
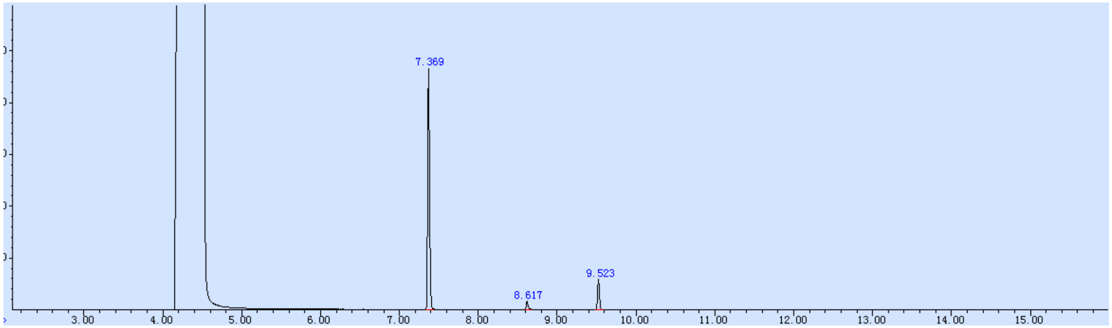
^{1}H NMR at 40 min



GC-MS at 60 min



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Peak    R.T.  Ini. TOP  Stp.  Peak  Height                    %
 #    min  Scan Scan  Scan  Type          Area       %       area
---  ----- ----- ---- ---- ---  -------    -------  ------  -------
 1   7.369   918  923  933   M  2332653  36933739 100.00%  86.089%
 2   8.617  1138 1141 1153   M    77303    1347104   3.65%   3.140%
 3   9.523  1294 1300 1313   M   295166    4620844  12.51%  10.771%
```

^{1}H NMR at 60 min

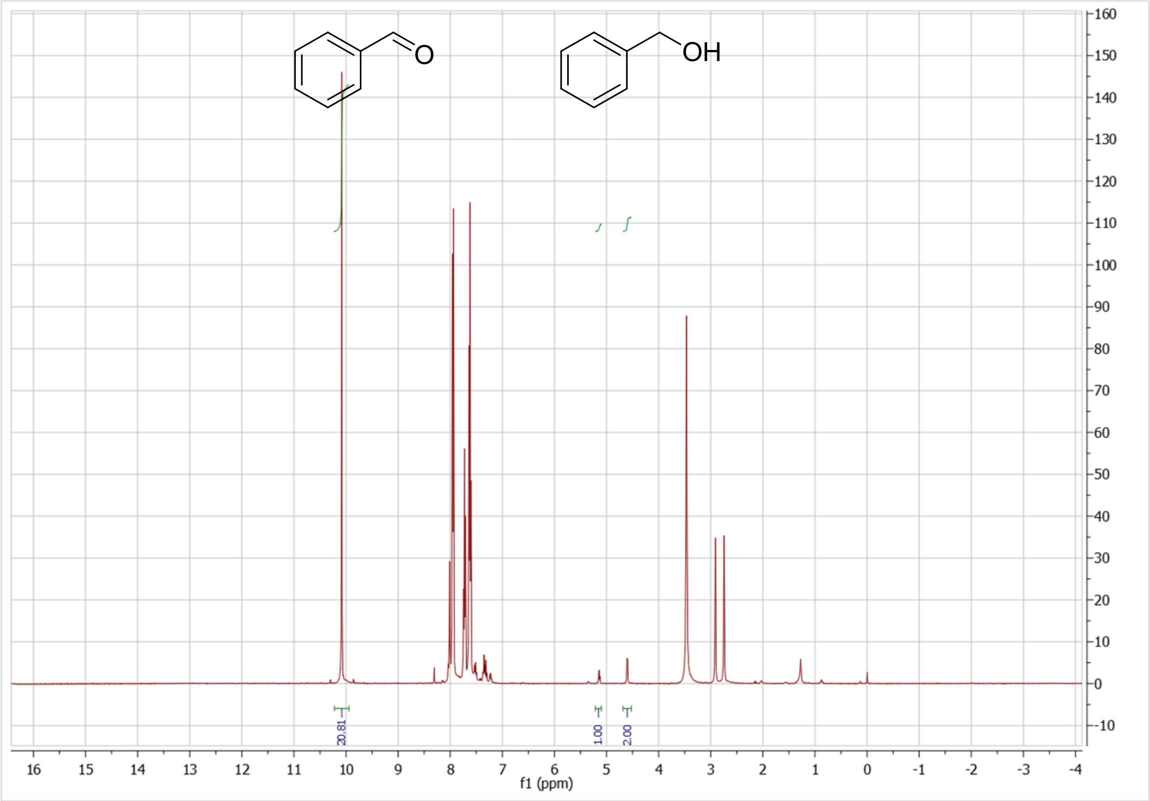
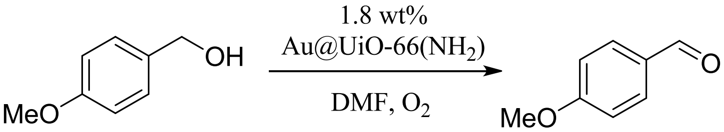
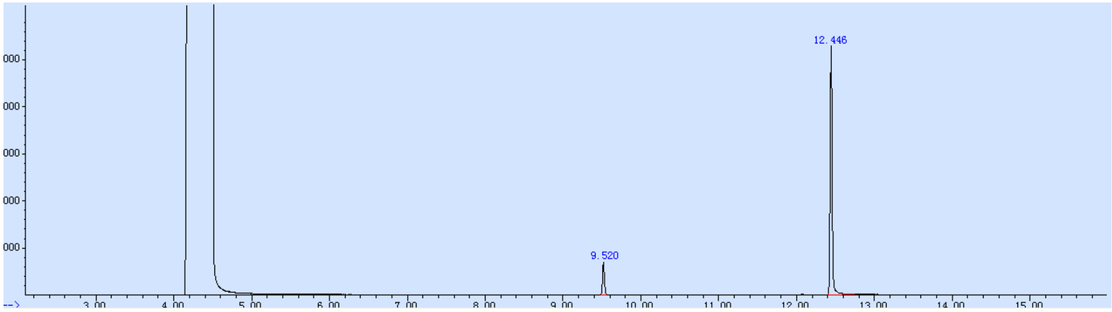


Table 3, entry 2

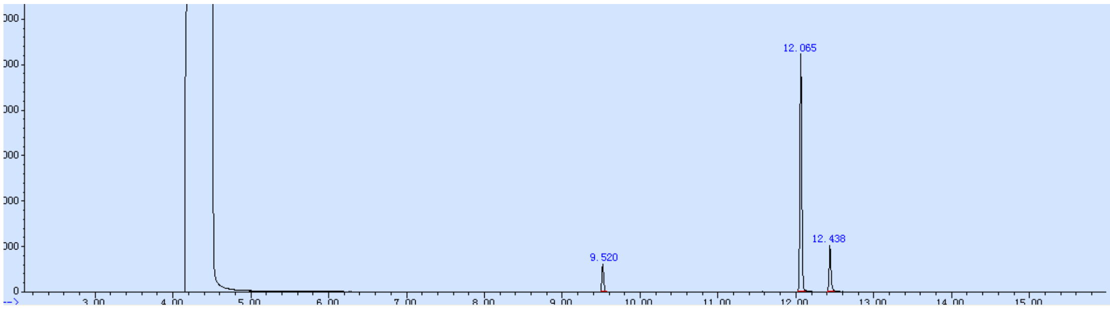


GC-MS at 0 min



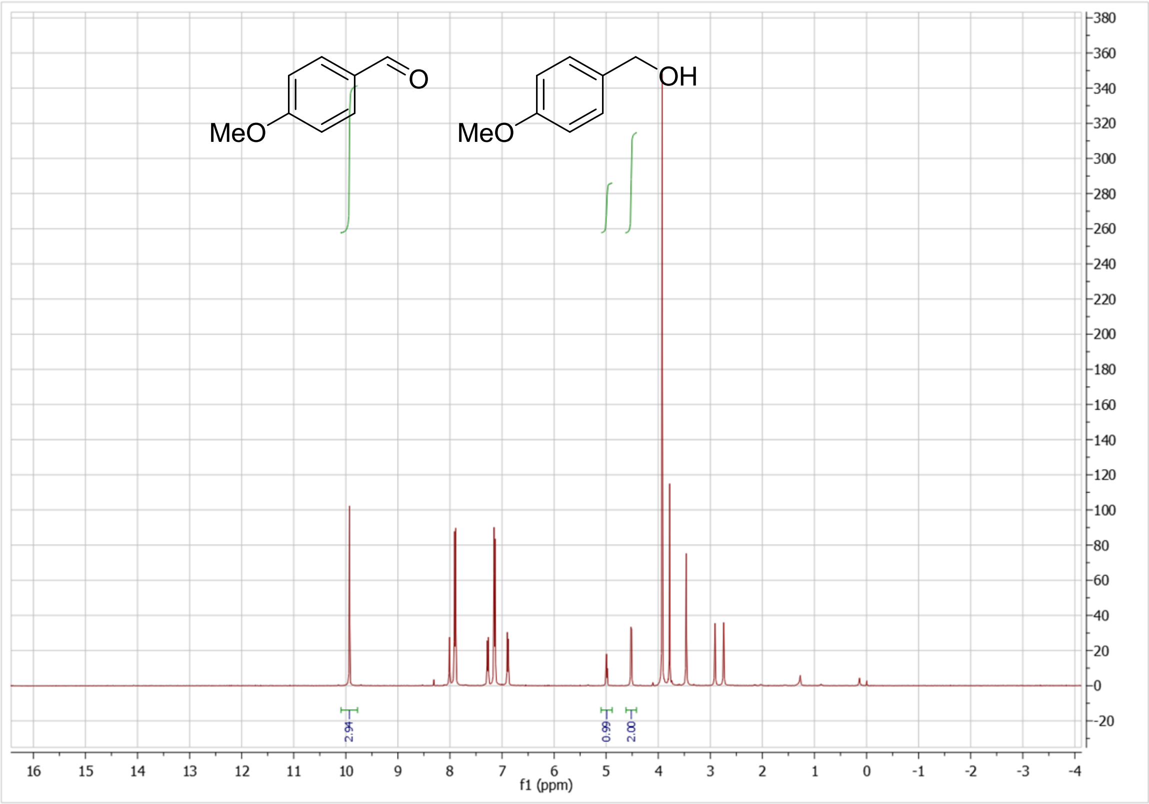
```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                        %
 #    min  Scan Scan  Scan  Type          Area       %       area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   9.520  1293 1299 1308   M   350796   5410317  11.75%  10.516%
  2  12.446  1804 1810 1865   M  2693349  46037063 100.00%  89.484%
```

GC-MS at 20 min

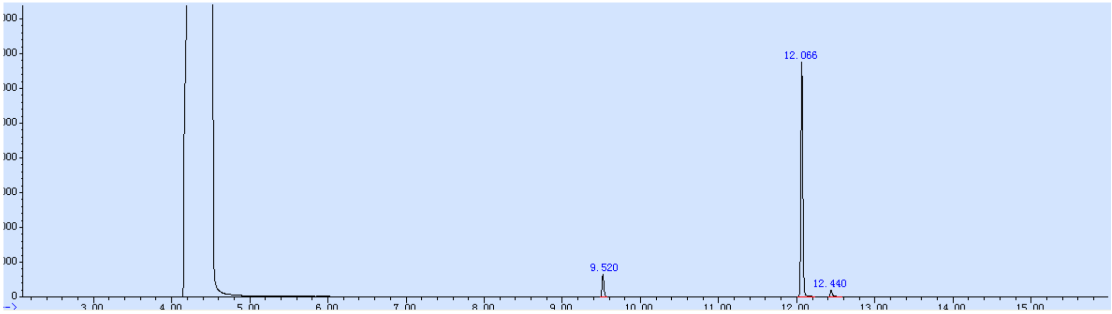


```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                      %
 #    min  Scan Scan  Scan  Type          Area       %        area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   9.520  1295 1299 1307   M   302964   4484677  10.58%   8.136%
  2  12.065  1738 1744 1756   M  2627309  42388701 100.00%  76.897%
  3  12.438  1803 1809 1821   M   509048   8250405  19.46%  14.967%
```

^{1}H NMR at 20 min

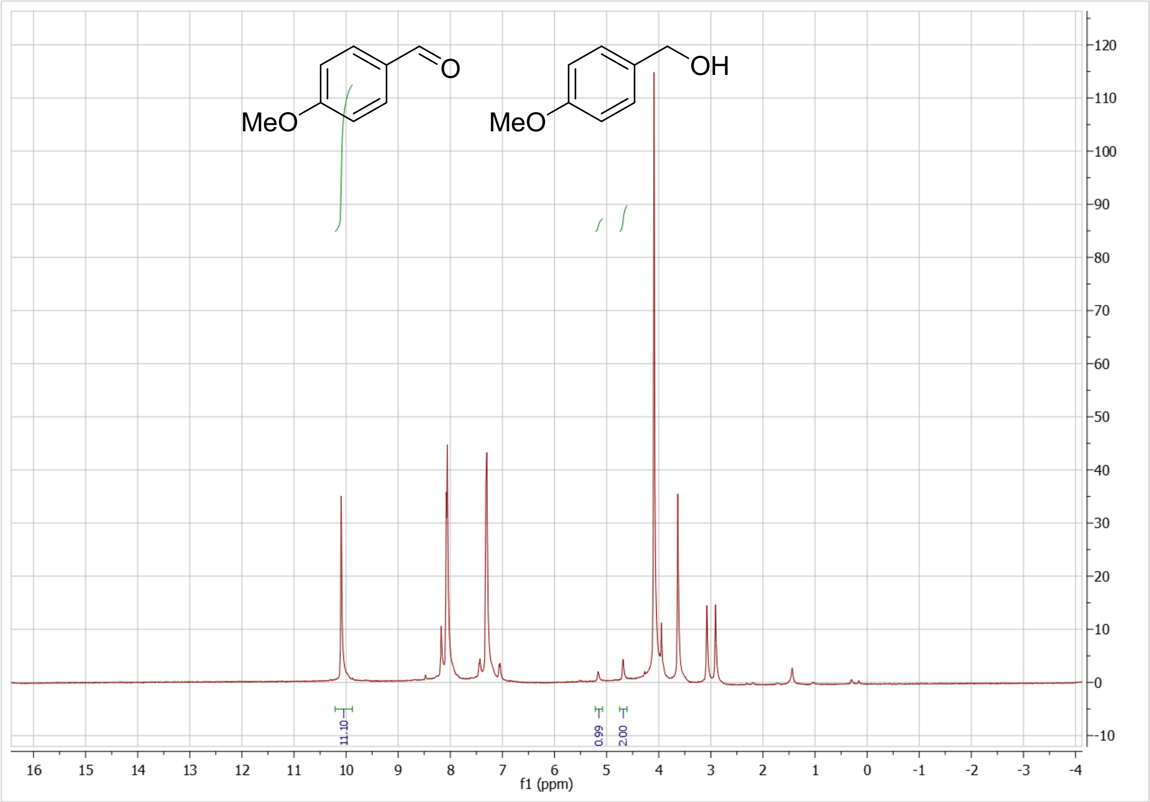


GC-MS at 40 min

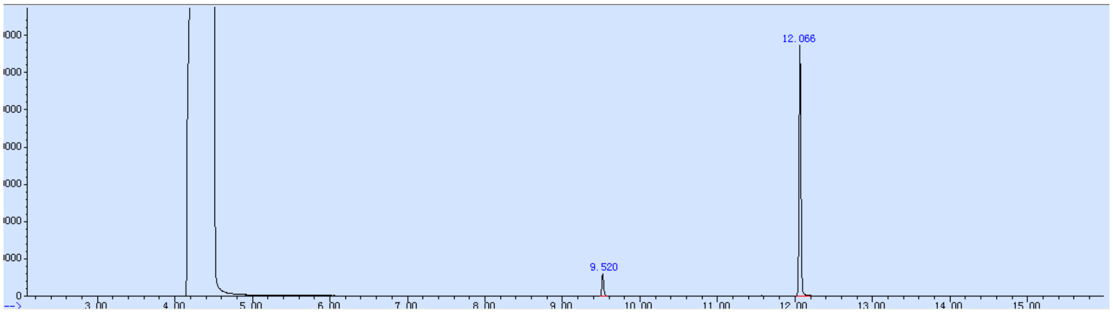


```
Peak   R.T.  Ini. TOP  Stp.  Peak  Height                          %
 #    min    Scan Scan  Scan  Type                Area      %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.520  1294 1299 1309   M   327004    5200959   9.36%   8.307%
 2  12.066  1735 1744 1775   M  3382429  55537159 100.00%  88.709%
 3  12.440  1804 1809 1836   M    99156   1867702   3.36%   2.983%
```

^{1}H NMR at 40 min



GC-MS at 60 min



```
Peak   R.T.  Ini. TOP  Stp.  Peak  Height                      %
 #    min    Scan Scan  Scan  Type              Area      %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.520  1294 1299 1309   M   301825   4607792   8.41%   7.757%
 2  12.066  1737 1744 1769   M  3370816  54793557 100.00%  92.243%
```

^{1}H NMR at 60 min

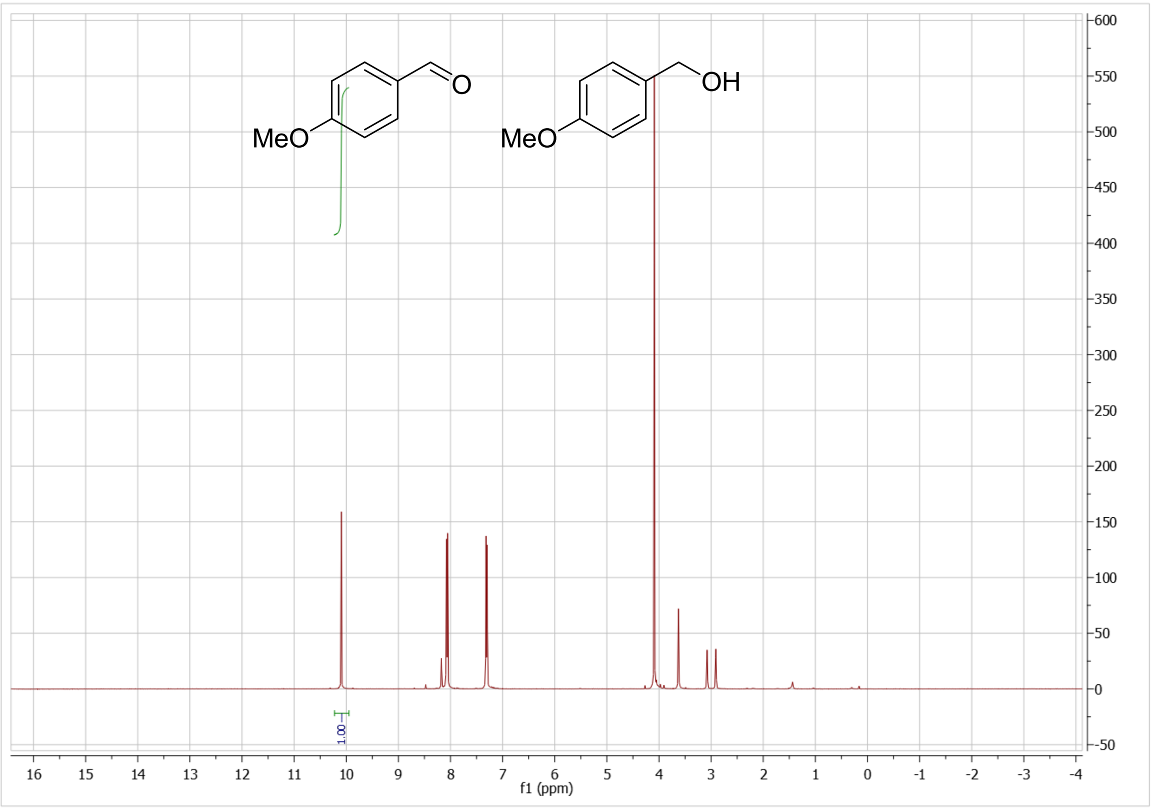
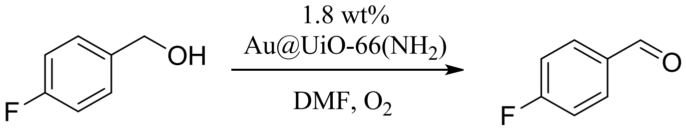
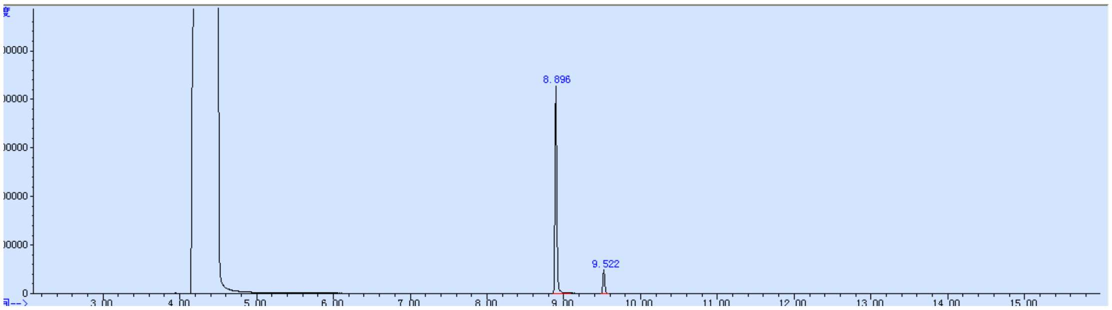


Table 3, entry 3

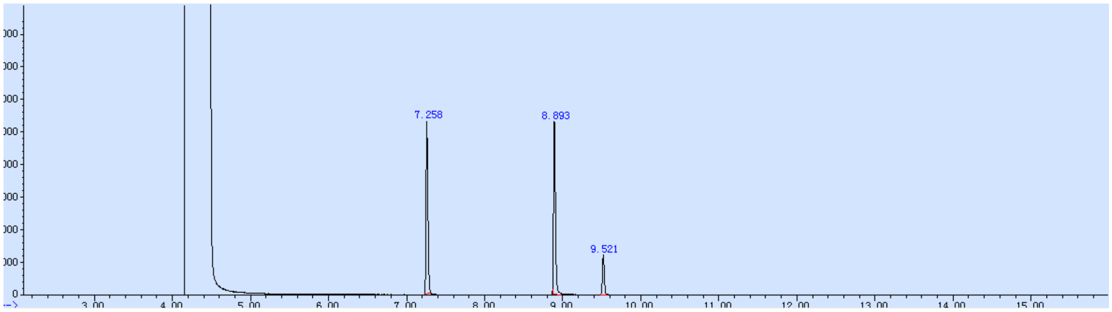


GC-MS at 0 h



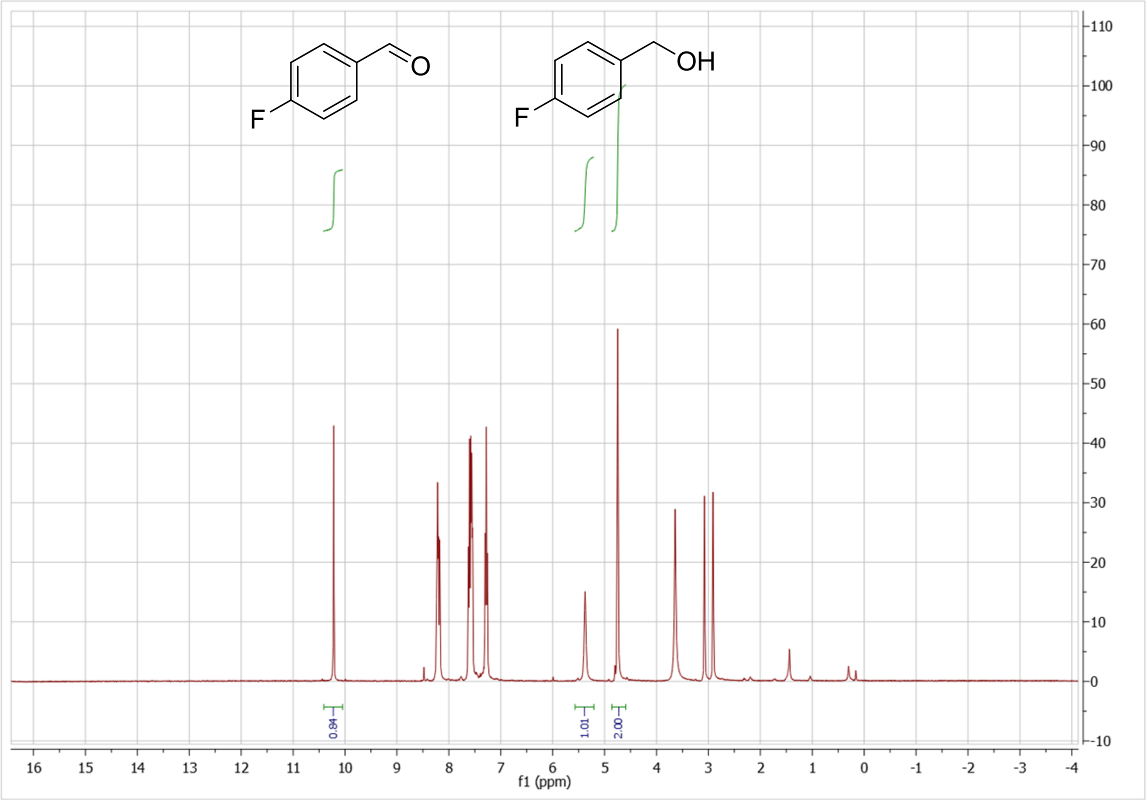
```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                          %
 #    min    Scan Scan  Scan  Type                 Area      %      area
 ---  ----- ----- ---- ---- ---  -------    -------  ------  -------
  1   8.896  1185 1190 1227   M  2138599  34206279 100.00%  89.981%
  2   9.522  1293 1299 1311   M   249018   3808757  11.13%  10.019%
```

GC-MS at 2 h

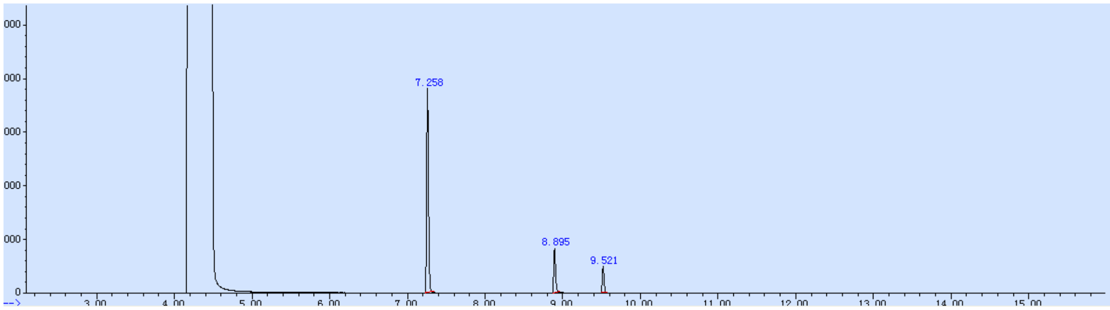


```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                              %
 #    min    Scan Scan  Scan  Type                  Area       %       area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   7.258   899  904  912   M  1064574  16435718  95.15%  43.712%
  2   8.893  1186 1189 1206   M  1100531  17273744 100.00%  45.940%
  3   9.521  1294 1299 1309   M   246024   3890891  22.52%  10.348%
```

^{1}H NMR at 2 h

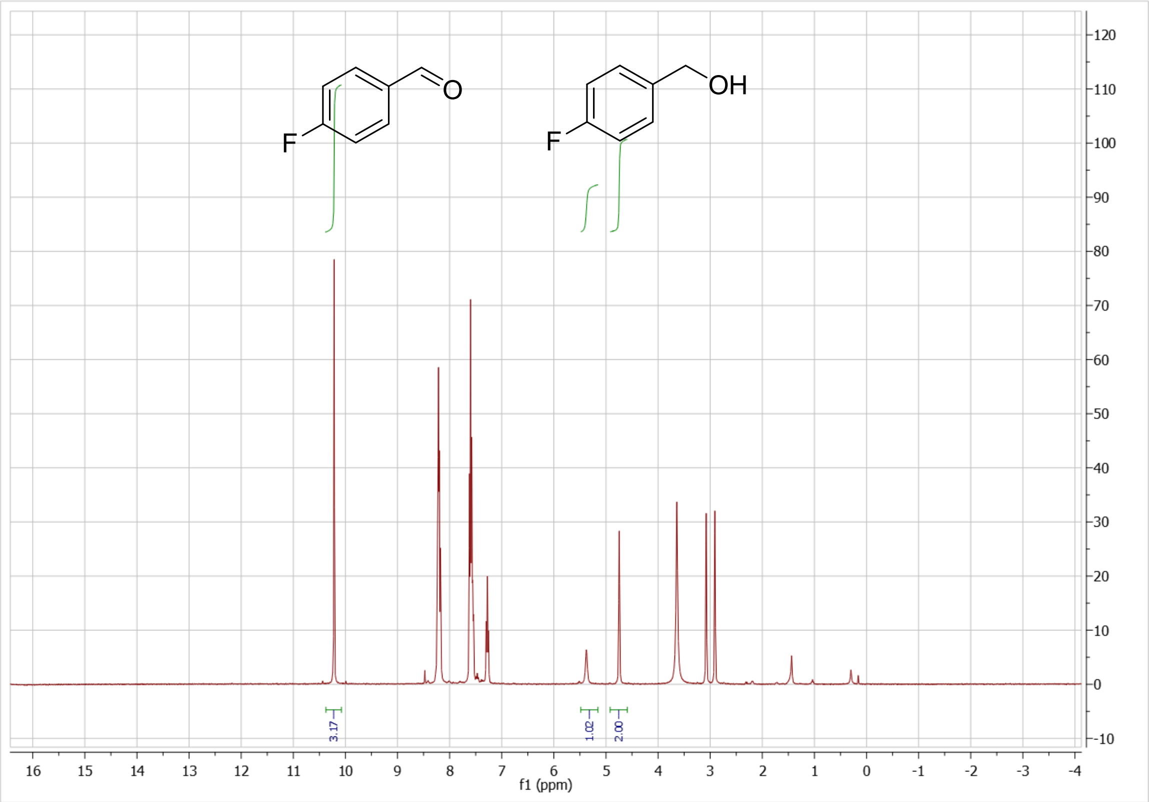


GC-MS at 4 h

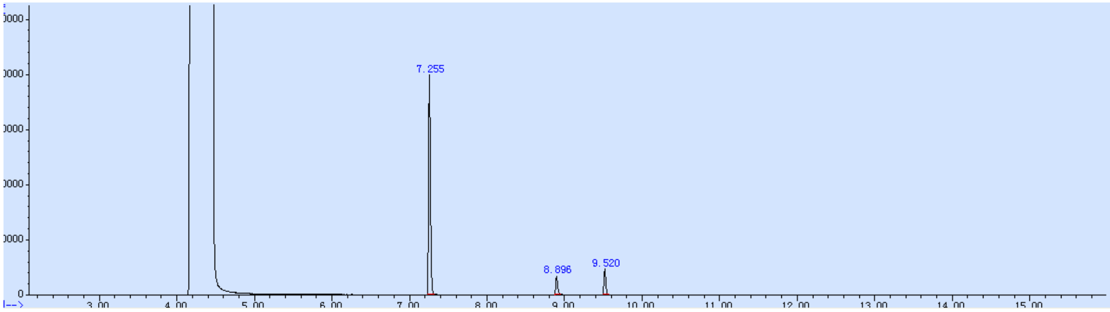


Peak #	R.T. min	Ini. Scan	TOP Scan	Stp. Scan	Peak Type	Height	Area	%	% area
1	7.258	898	904	918	M	1927979	29717153	100.00%	74.738%
2	8.895	1185	1190	1200	M	415092	6407205	21.56%	16.114%
3	9.521	1295	1299	1307	M	244450	3637198	12.24%	9.148%

^{1}H NMR at 4 h



GC-MS at 6 h



```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                          %
 #    min    Scan Scan  Scan  Type                 Area      %      area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   7.255   899  903  916   M  2016669  31045347 100.00%  84.090%
  2   8.896  1186 1190 1201   M2  162510   2557408   8.24%   6.927%
  3   9.520  1295 1299 1308   M   225876   3316271  10.68%   8.983%
```

^{1}H NMR at 6 h

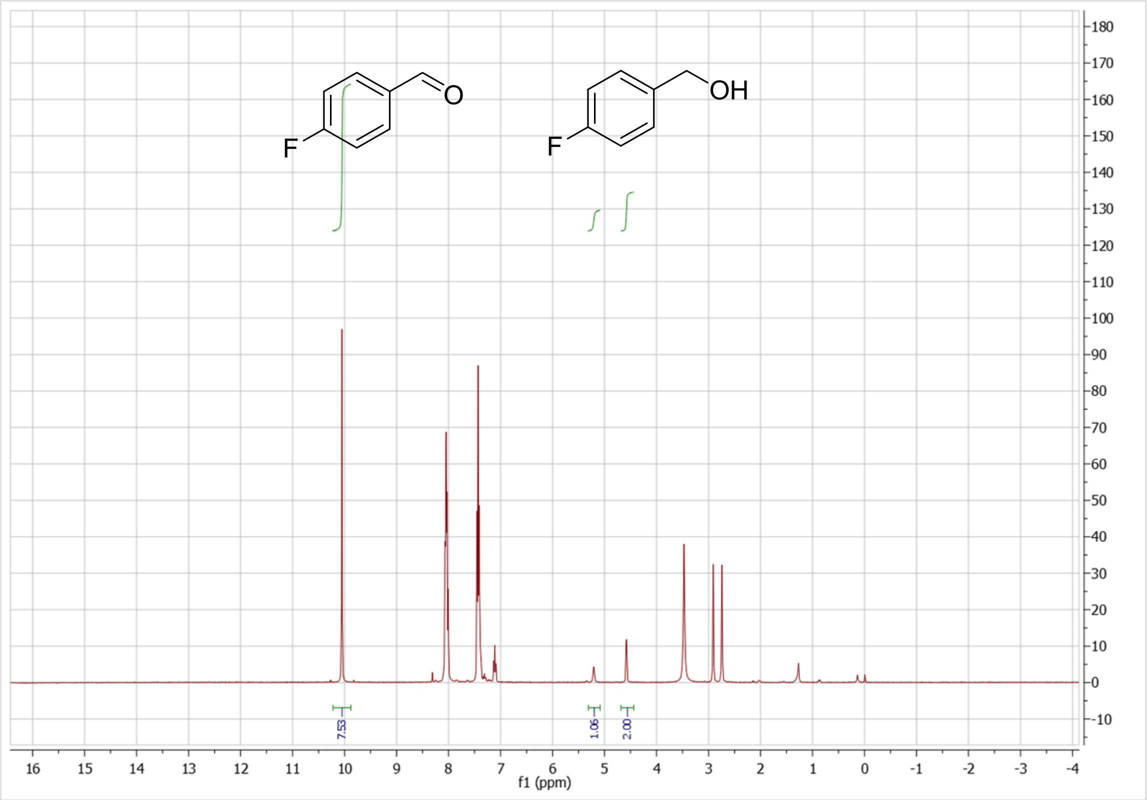
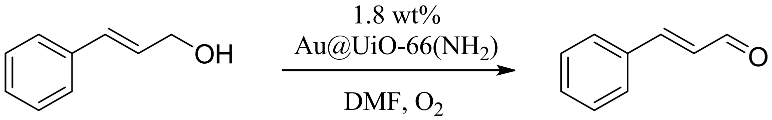
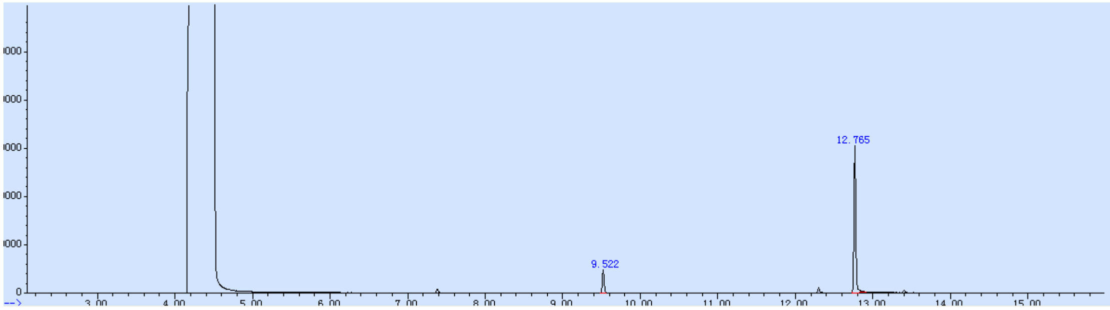


Table 3, entry 4

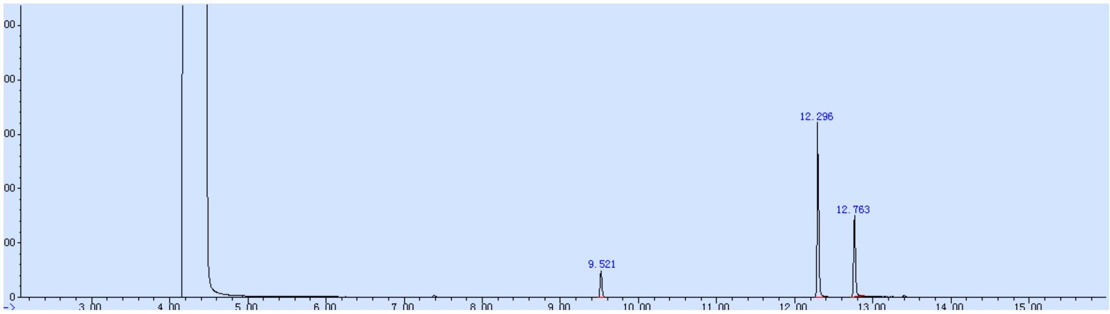


GC-MS at 0 min



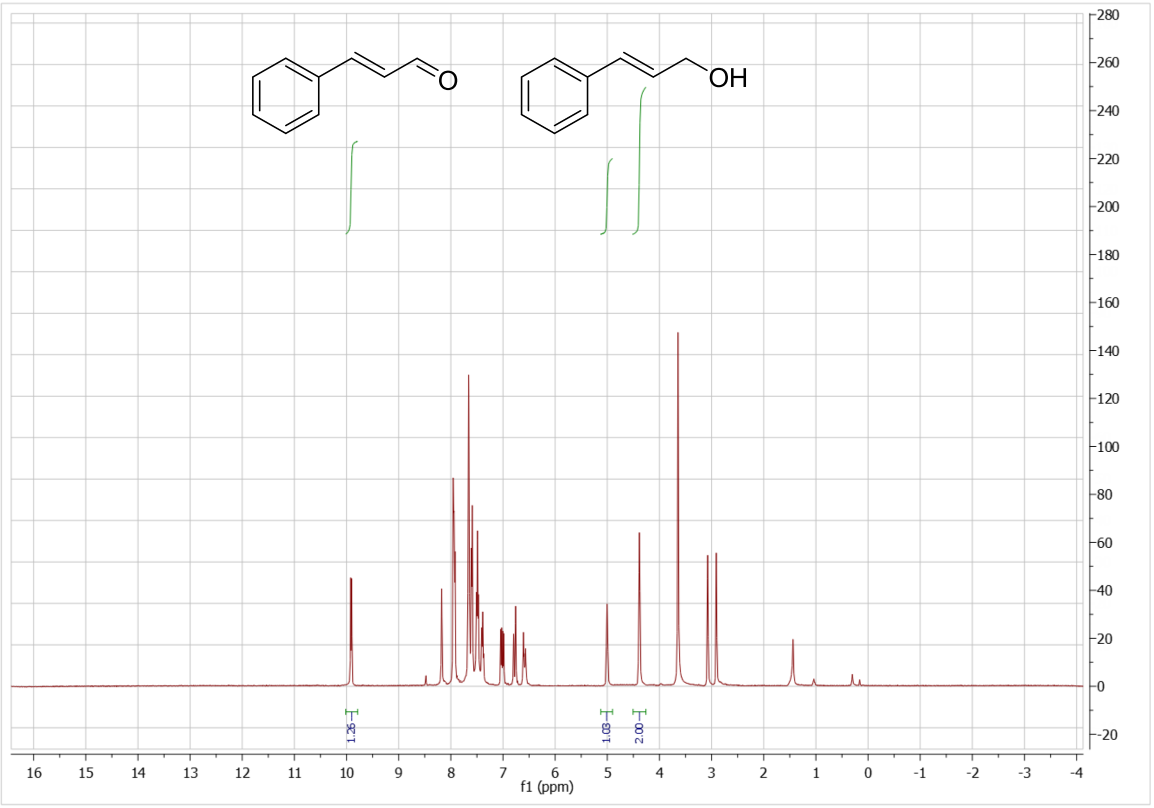
```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                              %
 #    min    Scan Scan  Scan  Type                   Area       %        area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.522  1294 1299 1305   M   244250   3749702  15.30%  13.273%
 2  12.766  1861 1866 1894   M  1538590  24500995 100.00%  86.727%
```

GC-MS at 20 min

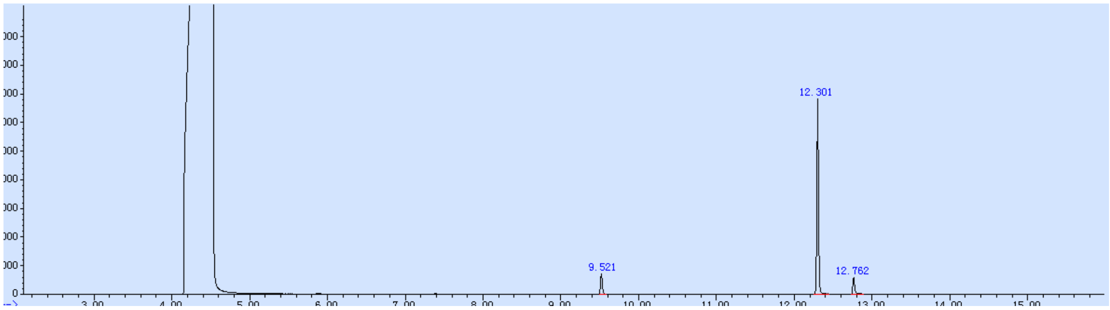


```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                        %
 #    min    Scan Scan  Scan  Type              Area      %     area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.521  1294 1299 1306   M   247451   3847271  14.87%   9.268%
 2  12.296  1778 1784 1798   M  1621320  25864479 100.00%  62.308%
 3  12.763  1859 1866 1888   M   753183  11799011  45.62%  28.424%
```

^{1}H NMR at 20 min

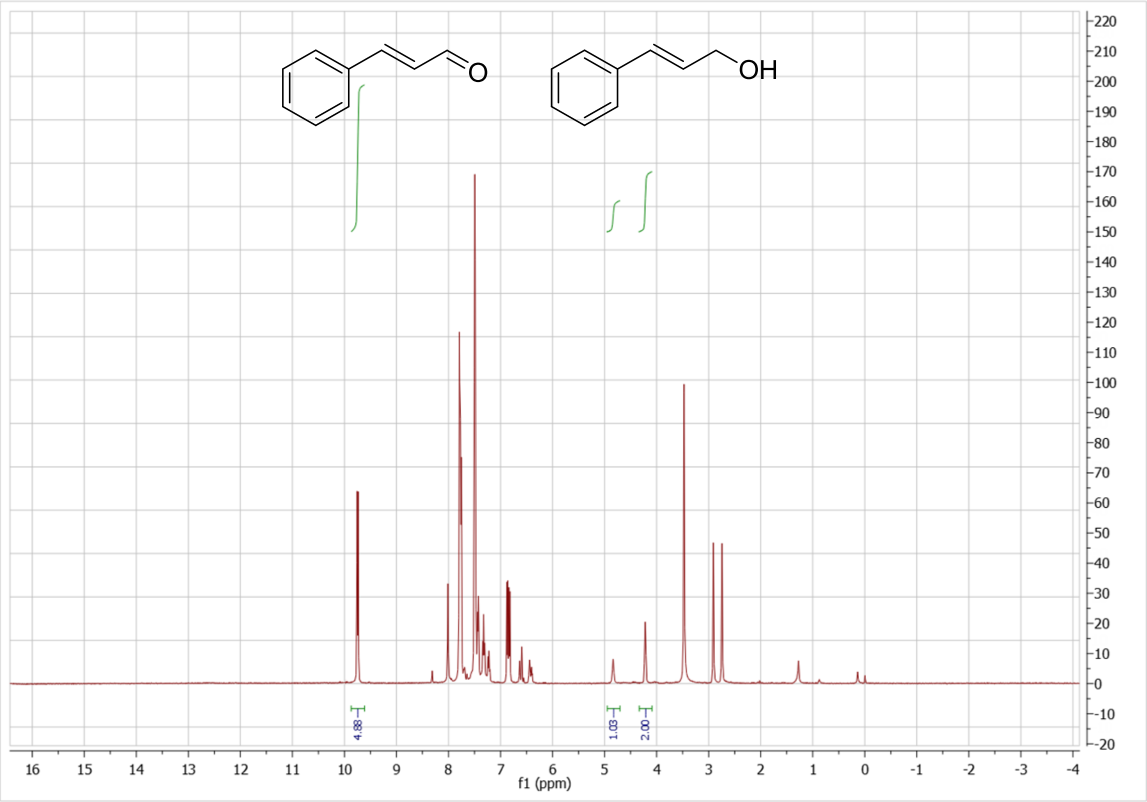


GC-MS at 40 min

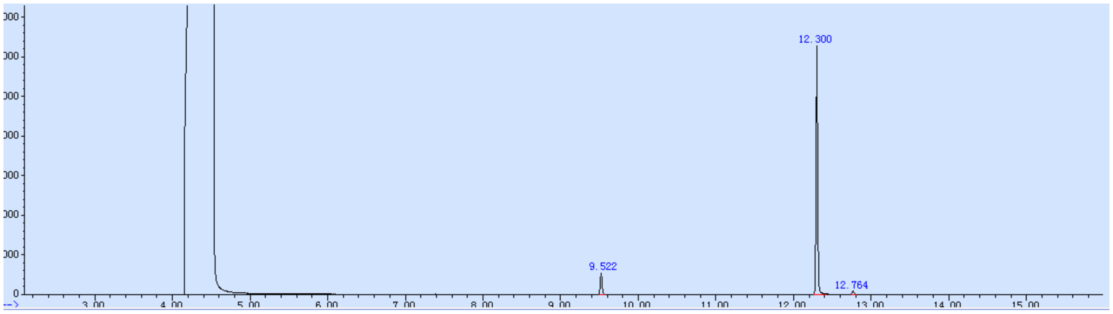


```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                              %
 #    min    Scan Scan  Scan  Type                 Area       %       area
 ---  ----- ----- ---- ---- ---  -------   -------  ------  -------
  1   9.521  1295 1299 1312   M   366038   5754978  10.17%   8.537%
  2  12.301  1776 1785 1812   M  3413211  56569689 100.00%  83.913%
  3  12.762  1860 1866 1890   M   296222   5089806   9.00%   7.550%
```

^{1}H NMR at 40 min



GC-MS at 60 min



```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                              %
 #    min    Scan Scan  Scan  Type                  Area      %       area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.522  1294 1299 1311   M   278893   4224710   8.27%   7.545%
 2  12.300  1779 1785 1806   M  3136942  51083523 100.00%  91.229%
 3  12.764  1862 1866 1873   M2   41453    686521   1.34%   1.226%
```

^{1}H NMR at 60 min

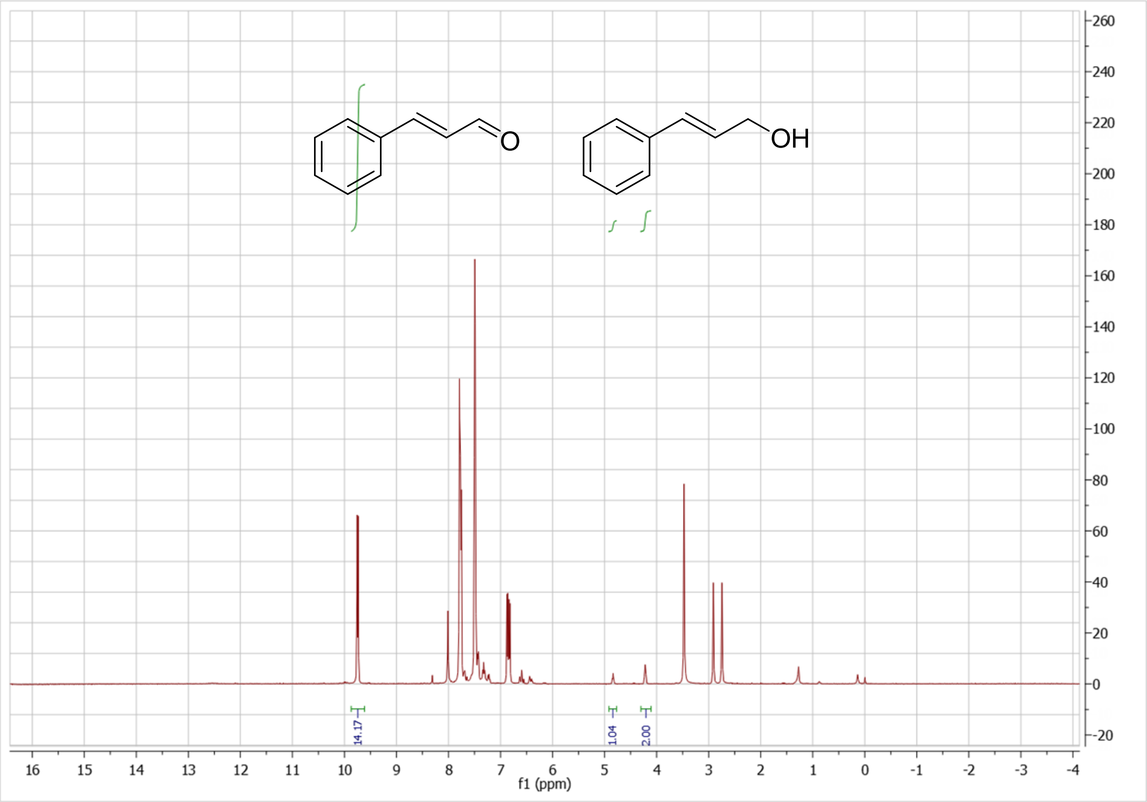
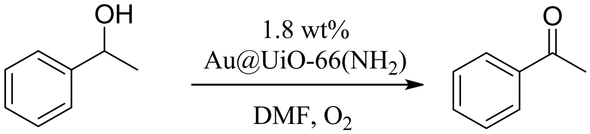
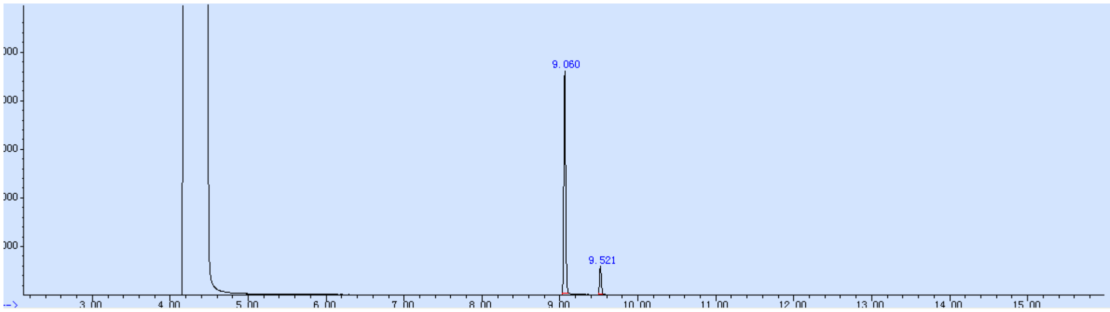


Table 3, entry 5

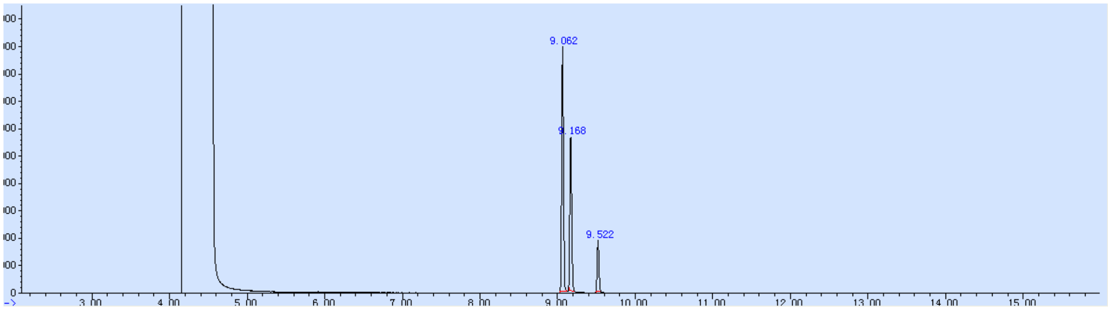


GC-MS at 0 min



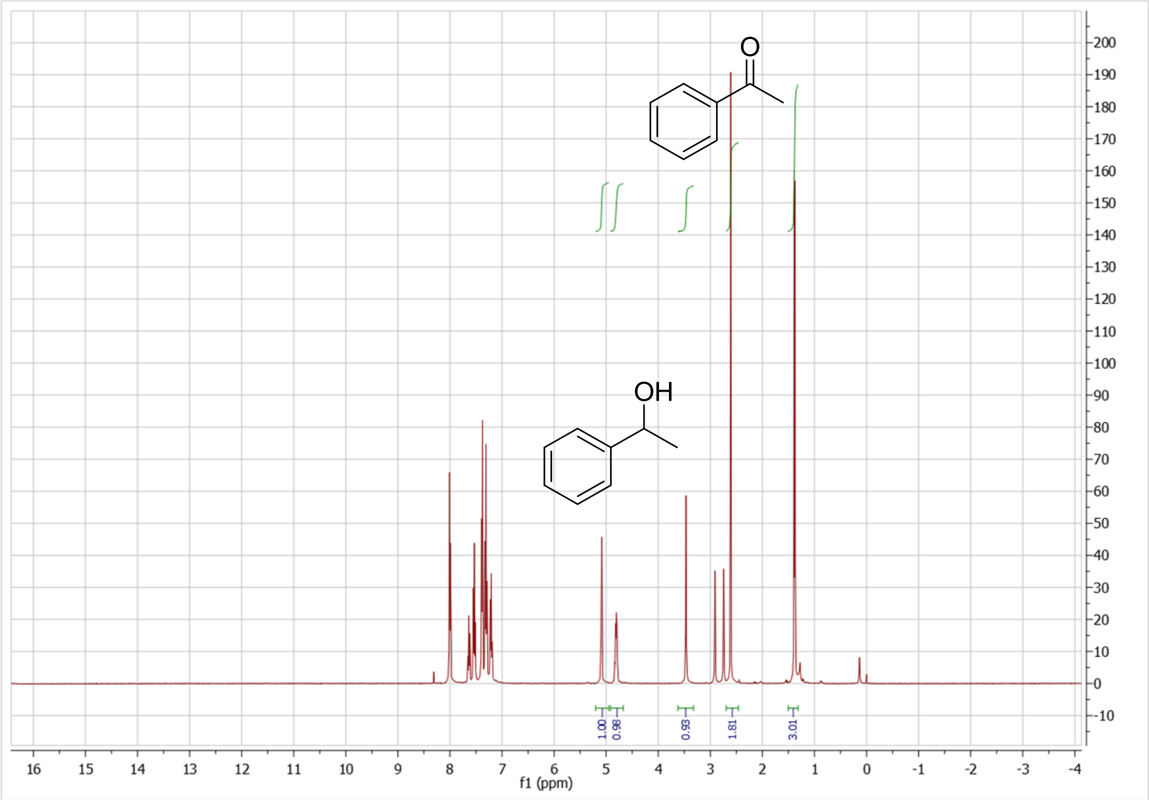
```
Peak   R.T.  Ini. TOP  Stp.  Peak  Height                      %
 #    min    Scan Scan  Scan  Type              Area     %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.060  1213 1219 1229   M  2335862  35392009 100.00%  88.854%
 2   9.521  1295 1299 1305   M   289328   4439595  12.54%  11.146%
```

GC-MS at 20 min

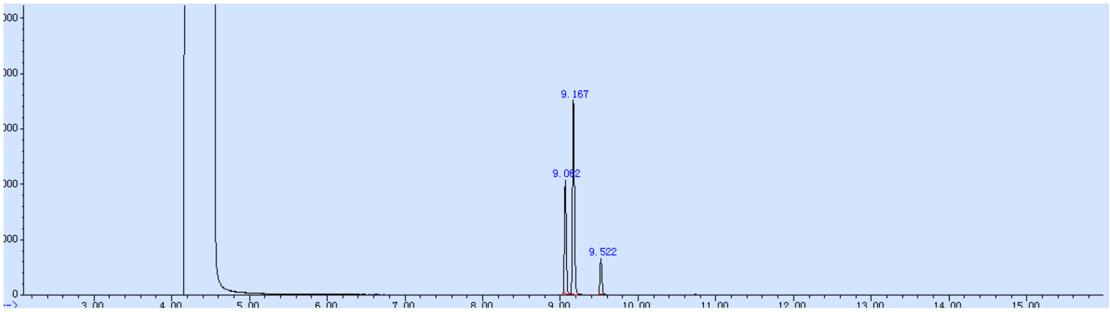


```
Peak    R.T.  Ini. TOP  Stp.  Peak  Height                          %
 #     min    Scan Scan  Scan  Type                 Area      %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.062  1214 1219 1227   M  1787123  27687799 100.00%  53.687%
 2   9.168  1233 1238 1245   M  1148264  18195177  65.72%  35.281%
 3   9.522  1294 1299 1306   M   379622   5689528  20.55%  11.032%
```

^{1}H NMR at 20 min

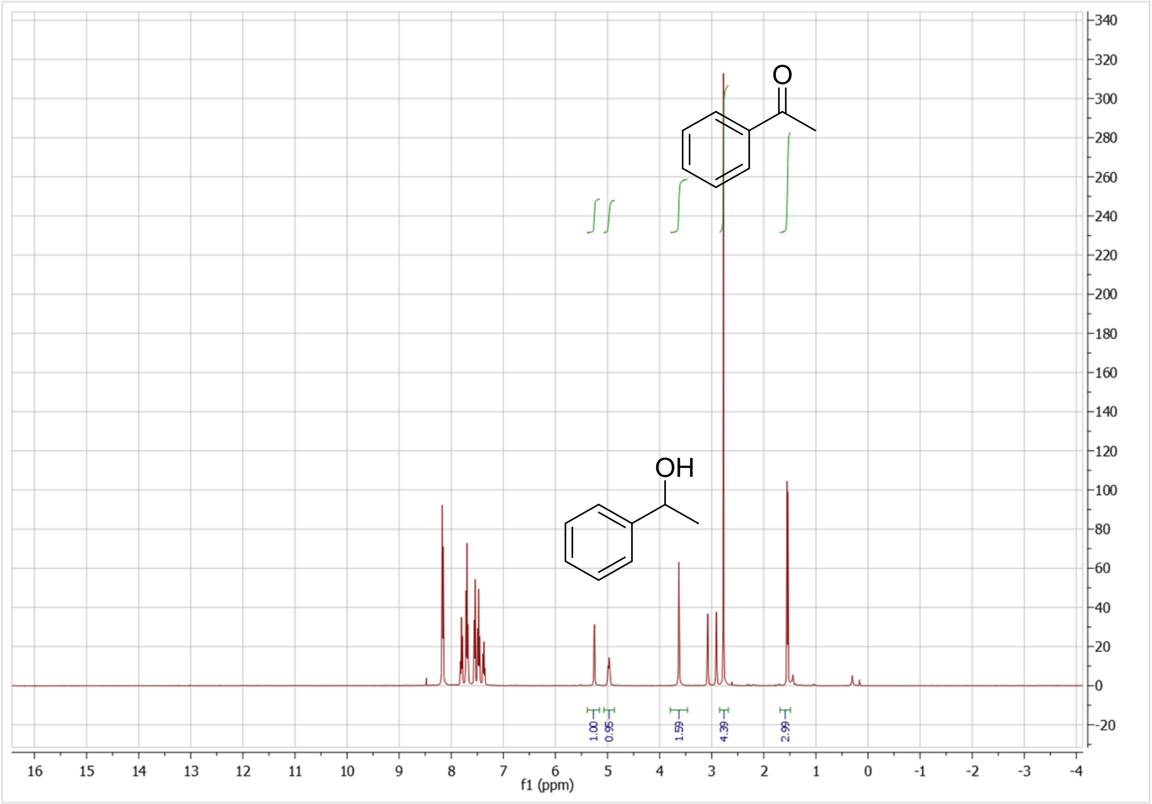


GC-MS at 40 min

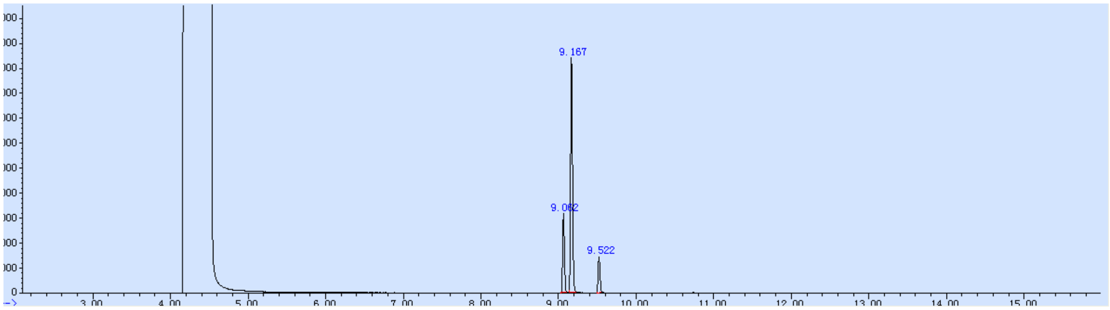


```
Peak   R.T.  Ini. TOP  Stp.  Peak  Height                          %
 #    min    Scan Scan  Scan  Type                Area      %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.062  1214 1219 1227   M  1027226  15920609  56.17%  32.236%
 2   9.167  1232 1237 1246   M  1792650  28344888 100.00%  57.393%
 3   9.522  1294 1299 1308   M   333241   5121751  18.07%  10.371%
```

^{1}H NMR at 40 min

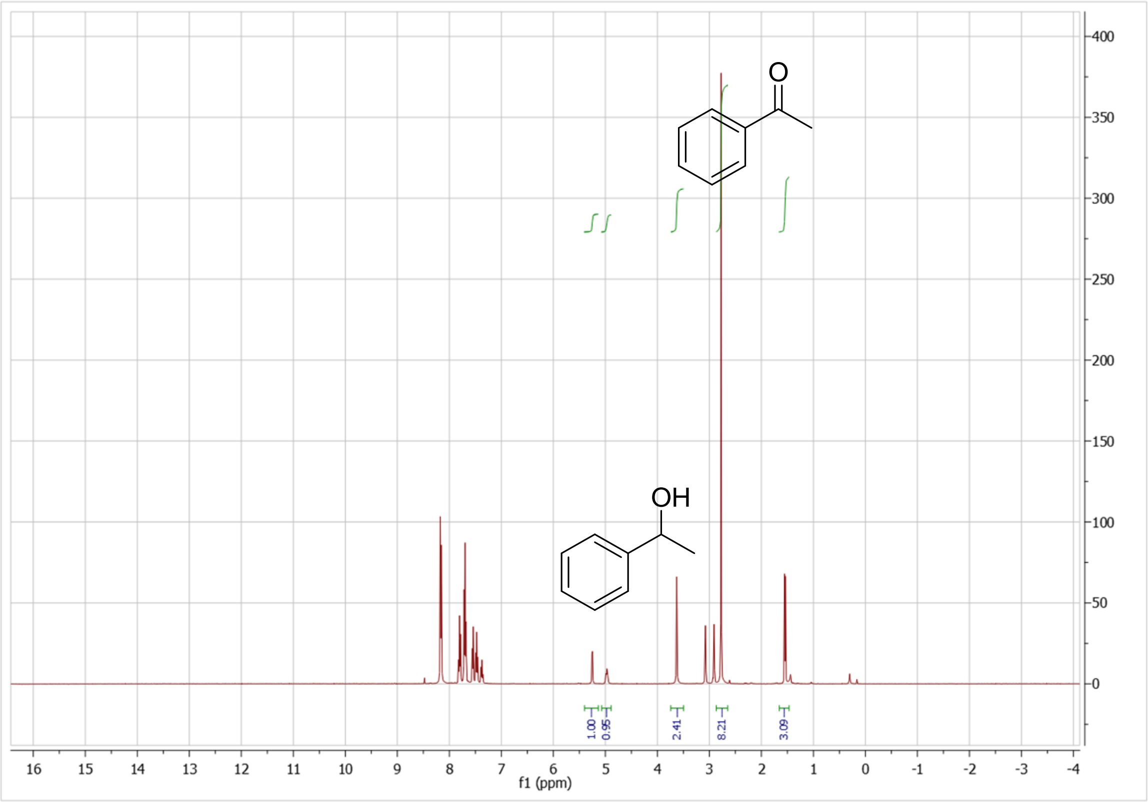


GC-MS at 60 min

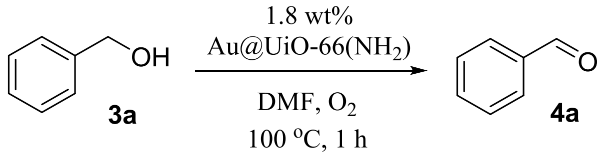


```
Peak   R.T.  Ini. TOP  Stp.  Peak  Height                             %
 #    min    Scan Scan  Scan  Type                   Area      %      area
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1   9.062  1214 1219 1226   M   629345   9572670  31.65%  21.506%
 2   9.167  1232 1237 1247   M  1904920  30241199 100.00%  67.941%
 3   9.522  1295 1299 1306   M   299303   4696915  15.53%  10.552%
```

^{1}H NMR at 60 min



The isolated yield determination for aerobic oxidation of alcohol



The reaction was run in a 25 mL flask with reflux condenser. In a typical reaction, the flask was first charged with desired amount of alcohol, DMF solvent and Au@UiO-66(NH_2) catalyst. After purging three times with oxygen and set up with the oxygen balloon, the closed vessel was heated rapidly to reach 100 ºC. After 1 h, the flask was cooled to room temperature. The reaction was purified without work-up by flash chromatography over silica gel column (2% EtOAc in hexanes) to afford the aldehyde product **4a** as a clear oil (96.5 mg, 91% yield). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel.