Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information for

Conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts

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Contents:

1. Characterization of Catalysts

N_2 physical adsorption/desorption measurement was carried out at liquid nitrogen temperature on an Autosorb-1 Quantachrome instrument. Samples were pre-degassed at 300 °C for about 10 h to remove water and other physically adsorbed species. The BET surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller equation (relative pressure between 0.05 and 0.25). The pore size and pore volume were calculated from the desorption branches of the nitrogen isotherms employing the Barrett-Joyner-Halenda (BJH) model.

Temperature programmed reduction (TPR) profiles were obtained on a Micromeritics AutoChem II 2920 Instrument with a thermal conductivity detector (TCD). Typically, 50 mg sample of the calcinated catalyst was degassed at 200 ^{o}C in an atmosphere of Ar for 2 h. After the sample was cooled to a temperature of 50 ^{o}C under Ar flow, the in-line gas was switched to 10% H_2/Ar, and the sample was heated to 800 ^{o}C at a rate of 10 ^{o}C min^{-1}. The H_2 consumption was monitored by a TCD detector.

The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 200 mA in a scanning rate of 5^{o}/min.

The microstructure of the materials was examined by transmission electron microscopy (TEM) on a JEOLJEM-2000EX electron microscopy.

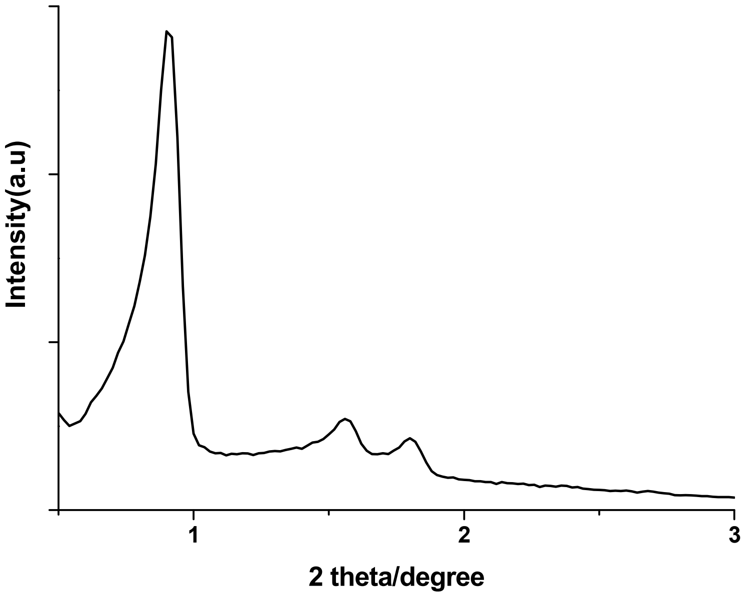


Fig S1. Small angle XRD pattern of as-synthesized SBA-15.

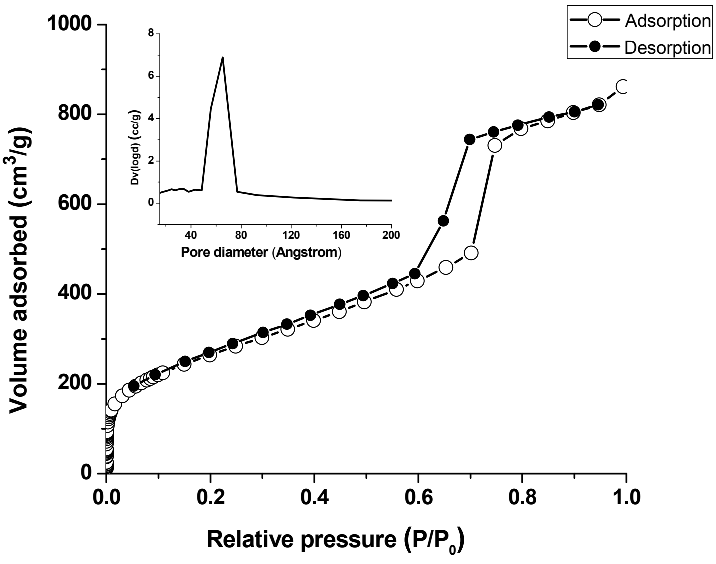


Fig S2. N_2 adsorption/desorption isotherms of as-synthesized SBA-15.

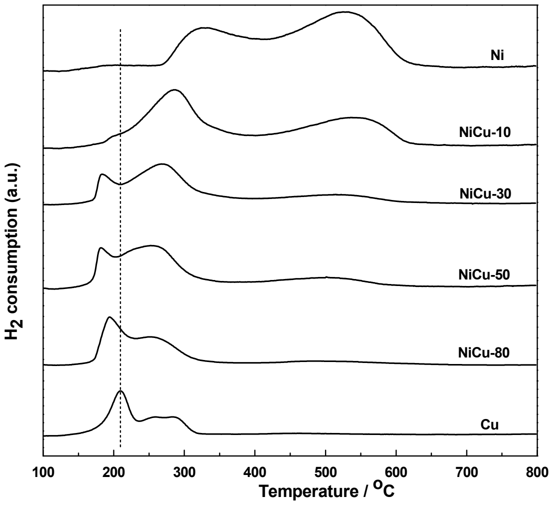


Fig. S3 TPR profiles of the monometallic Ni/SBA-15, Cu/SBA-15 and bimetallic NiCu/SBA-15 catalysts.

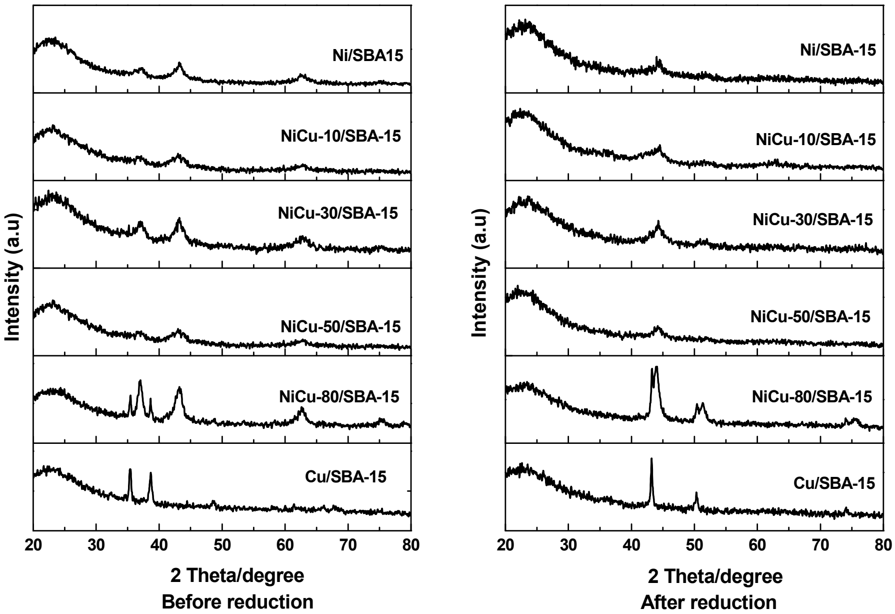


Fig S4. Wide angle XRD patterns before and after reduction.

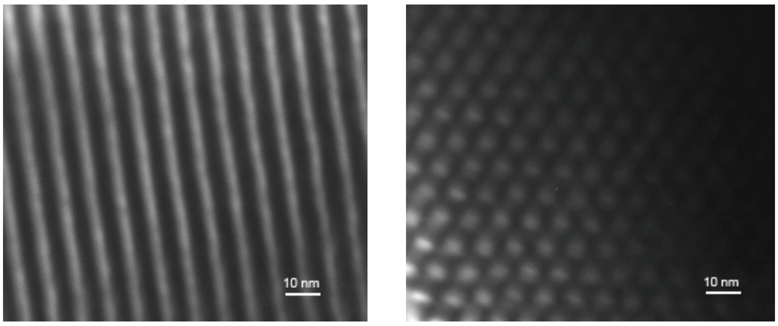


Fig S5. TEM images of as-synthesized SBA-15.

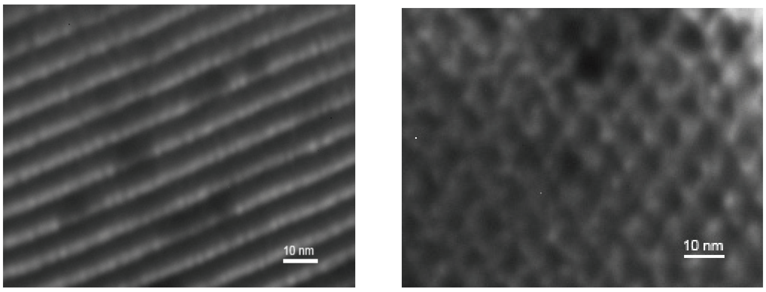


Fig S6. TEM images of NiCu-50/SBA-15.

Table S1 Physic properties of as-synthesized catalysts.

Sample	D_{Pore} (nm)	V_{Pore} (cm^3g^{-1})	S_{BET} (m^2g^{-1})
SBA-15	6.5	1.37	952
Ni/SBA-15	5.7	1.25	816
NiCu-10/SBA-15	5.6	1.25	672
NiCu-30/SBA-15	5.6	1.08	641
NiCu-50/SBA-15	5.6	1.09	691
NiCu-80/SBA-15	4.3	1.14	727
Cu/SBA-15	5.6	1.26	883

2. Isolation of Key Intermediates

2.1 Isolation of 4-Hydroxy-2-cyclopentenone

4-hydroxy-2-cyclopentenone was synthesized in water without any catalyst.

Typically, a solution of furfuryl alcohol (15.0 g, 0.15 mol) in water (300 mL) was loaded into a 600 mL Parr stainless steel autoclave. After sealed and purged with H_2 for 4 times to exclude air, the autoclave was heated to 160 ^{o}C and then purged with 2 MPa of H_2. After the reaction was completed (8 h), the solvent was removed under reduced pressure and red dark oil was obtained. The crude product was purified by silica gel chromatography using 3:1 *n*-hexane/ethyl acetate and then 1:1 *n*-hexane/ethyl acetate to afford the product, red yellow oil (Yield 52%, 7.78 g). ^{1}H NMR (400 MHz; $CDCl_3$;Me_4Si) δ = 7.58 (dd, *J* = 5.6Hz, 2.3Hz, 1H, CH), 6.25 (dd, *J* = 5.6Hz, 0.8Hz, 1H, CH), 5.08 (t, *J* = 5.6Hz, 1H, CH), 2.80 (dd, *J* = 18.5Hz, 6.1Hz, 1H, CH_2), 2.30 (dd, *J* = 18.5Hz, 2.1Hz, 1H, CH_2), 2.11 (d, *J* = 6.5Hz, 1H, OH); ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si) δ = 207.6 (C), 164.1(CH), 134.9(CH), 70.3(CH), 44.3(CH_2). m/z 98 (M+, 100%), 97 (41),70 (75), 55 (54), 44 (40), 43 (45), 42 (95).

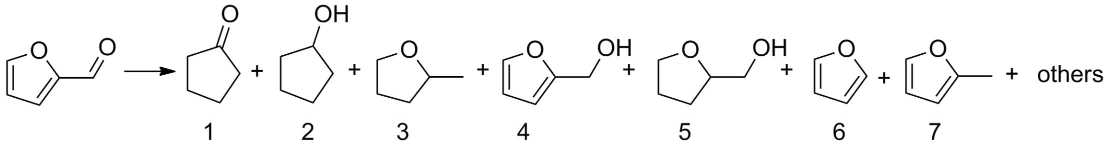
The corresponding ^{1}H NMR, ^{13}C NMR and MS are shown in Fig S10 and S13.

2.2 Isolation of 2-Cyclopentenone

10.0 g aqueous solution of 4-hydroxy-2-cyclopentenone (10.2 mmol) and NiCu-50/SBA-15 (0.20 g) were loaded into a 60 mL stainless steel autoclave. After sealed and purged with H_2 for 4 times to exclude air, the autoclave was purged with 0.1 MPa of H_2 and then heated to 160 ^{o}C. 4 h later, the reactor was cooled and the mixture was centrifuged. Product was extracted by dichloromethane and purified by silica gel chromatography using 3:1 *n*-hexane/ether, 2:1 *n*-hexane/ether and then 1:1 *n*-hexane/ether to afford the product, colorless oil. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ = 7.74 (dt, *J* = 5.6 Hz, 2.7 Hz, 1H, CH), 6.22 (dt, *J* = 4.8 Hz, 2.1 Hz, 1H, CH), 2.71 (dq, *J* = 6.7 Hz, 2.2 Hz, 2H, CH_2), 2.40-2.33 (m, 2H, CH_2). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si) δ = 210.7 (C), 164.9 (CH), 134.7 (CH), 34.2 (CH_2), 29.1 (CH_2). m/z 82 (M+, 100%), 54 (29), 53 (30).

The corresponding ^{1}H NMR. ^{13}C NMR and MS, spectra are shown in Fig S12 and S14.

3. Optimization of Reaction Conditions



Scheme S1 Conversion of furfural in water.

Table S2 Conversion of furfural over nickel-based catalyst under H_2 atmosphere.[a]

Entry	Catalysts	Conv. (%)	Seletivity of products (%)				
			1	2	3	4	5
1	Ni/SiO_2	29	35	*n.d*	*n.d*	*n.d*	*n.d*
2	Ni/Al_2O_3	>99	3	17	*n.d*	*n.d*	44
3	Ni/AC	>99	2	5	*4*	*n.d*	18
4	Ni/ZSM-5	52	29	*n.d*	*n.d*	*n.d*	3
5	Ni/SBA-15	42	36	*n.d*	1	4	*n.d*

[a] Reaction conditions: 10 g 5 wt% furfural aqueous solution, 0.2 g catalyst (10 wt% nickel), 160 °C, 2 MPa H_2, 4 h. Results are based on carbon balance. *n.d*: not detected by GC.

Table S3 Effect of additives on the hydrogenation of furfural.[a]

Entry	Additives	pH [b]	Conv. (%)	Distribution of products (%)				
				1	2	3	4	5
1	Na_2CO_3	11.0	>99	*n.d*	*n.d*	*n.d*	40	36
2	Na_2HPO_4	9.2	>99	2	1	*n.d*	36	28
3	none	7.0	>99	62	3	17	*n.d*	*n.d*
4	NaH_2PO_4	4.8	>99	40	1	6	*n.d*	*n.d*
5	AcOH	3.3	94	40	2	3	*n.d*	*n.d*
6 [c]	H_3PO_4	1.4	-	*n.d*	*n.d*	*n.d*	40	36

[a] Reaction conditions: 10 g 5 wt% furfural aqueous solution, 0.2 g NiCu-50/SBA-15, 0.1 mmol additive, 160 °C, 4 MPa H_2, 4 h. AcOH: acetic acid. Results were based on carbon balance. *n.d*: not detected by GC.

[b] pH values were determined at room temperature. [c] 1 mmol H_3PO_4, black solid was observed.

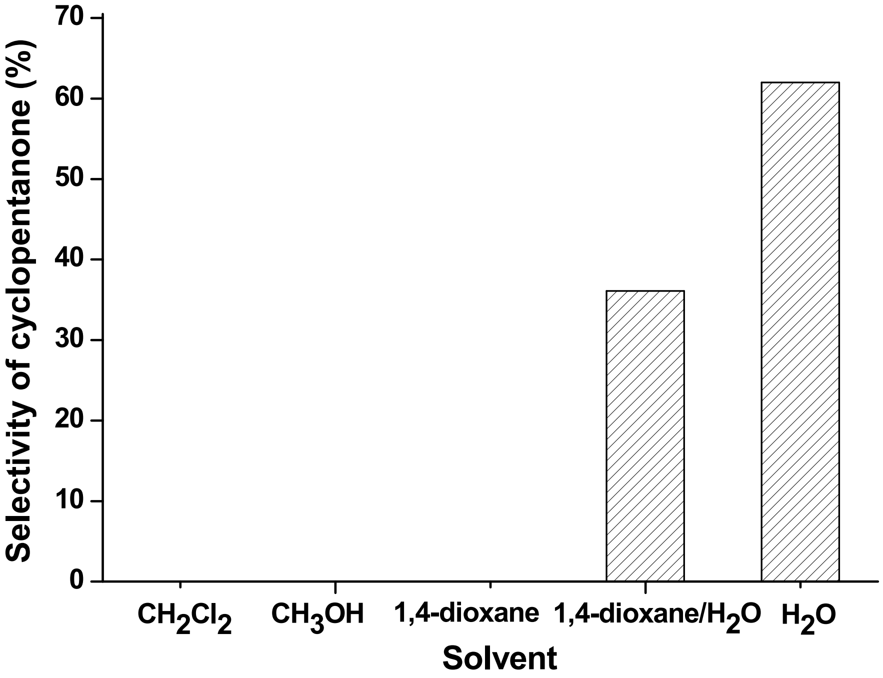


Fig S7. Hydrogenation of furfural over NiCu-50/SBA-15 in different solvents.

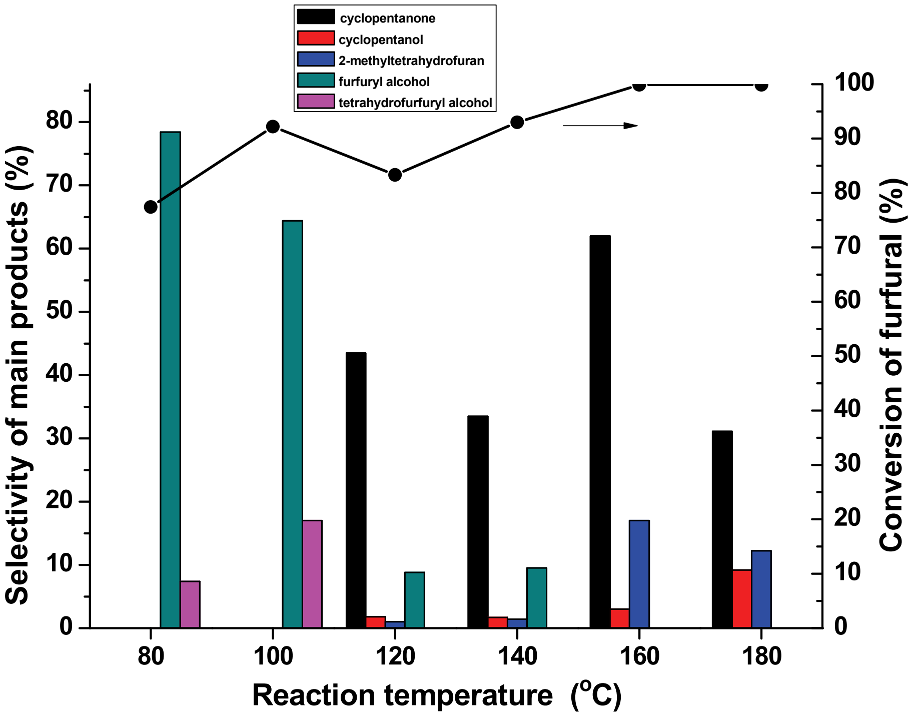


Fig S8. Hydrogenation of furfural over NiCu-50/SBA-15 at different reaction temperature.

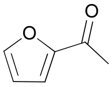
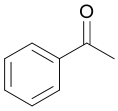
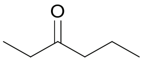
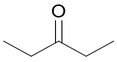
4. Control Experiments

Table S4 Control experiments under different reaction conditions.[a]

Entry	Substrates	Catalyst	Atmosphere	Yield of CPO+CPL (%)	Yield of HCP (%)
1	furfural	Y	H_2	65	*n.d*
2	furfural	Y	N_2	*n.d*	*n.d*
3	furfural	N	H_2	*n.d*	*n.d*
4	furfural	N	N_2	*n.d*	*n.d*
5	FA	Y	H_2	36	*n.d*
6	FA	Y	N_2	*n.d*	60
7	FA	N	H_2	*n.d*	52
8	FA	N	N_2	*n.d*	52
9[b]	FA	N	N_2	*n.d*	*n.d*
10[b]	furfural	Y	H_2	*n.d*	*n.d*
11[c]	FA	N	N_2	*trace*	*n.d*
12[c]	furfural	Y	H_2	*n.d*	*n.d*
13	THFA	Y	H_2	*n.d.*	*n.d.*
14	MF	Y	H_2	*n.d.*	*n.d.*

[a] Reaction conditions: 10 g 5 wt% aqueous solution, 0.2 g NiCu-50/SBA-15, 160 °C, 4 h, 0.1 MPa N_2 or 4 MPa H_2. FA: furfuryl alcohol. CPO: cyclopentanone. HCP: 4-hydroxy-2cyclopentenone. THFA: tetrahydrofurfuryl alcohol. MF: 2-methyl furan. Y: In the presence of NiCu-15/SBA-15. N: Without catalyst. *n.d*: not detected by GC. [b] in 1,4-dioxane. [c] at 80 °C.

Table S5 Conversion of furfuryl alcohol in the presence of different ketones.[a]

Entry	Additives [b]	Conv. (%)	Selectivity of products (%)			
			1	2	3	5
1		>99	*n.d*	20	1	13
2		>99	*n.d*	24	4	17
3		>99	*n.d*	8	3	17
4		>99	*n.d*	22	3	14

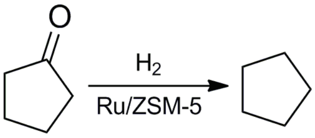
[a] Reaction condition*s*: 10 g 5 wt% furfural aqueous solution, 0.2 g NiCu-50/SBA-15, 160 °C, 4 MPa H_2, 4 h. *n.d*: not detected by GC. [b] The amount of ketone was equal to that of furfuryl alcohol.

Kinetic experiments

Kinetic experiments were performed in a Parr stainless steel autoclave. For a typical procedure, a solution of furfuryl alcohol (2.5 g, 0.025 mol) in water (50 mL, H_2O or D_2O) was put in a 600 mL Parr stainless steel autoclave. The reactor was sealed and purged with H_2 for 4 times to exclude air, and then it was heated to 120 ^{o}C. Samples were taken every six minutes and analyzed by GC based on internal standard method.

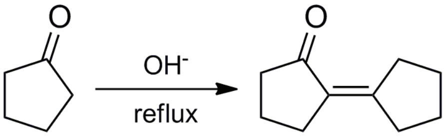
5. Preparation of Cycloalkanes

5.1 Hydrodeoxygenation of Cyclopentanone into Cyclopentane



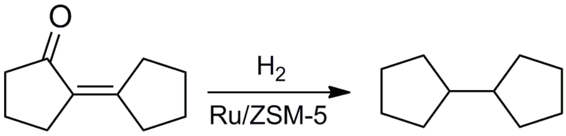
Hydrogenation of cyclopentanone was carried out in a 60 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. A typical procedure was as follows: the reactor was initially loaded with cyclopentanone (10.0 g, 0.2 mol) and Ru/ZSM-5 (3.0 g) catalyst. After the reactor was sealed and purged with H_2 for 4 times to exclude air, the reactor was heated to 180 ^oC and purged with 4 MPa of H_2. 36 h later, the reactor was cooled down to room temperature. The conversion and selectivity of cyclopentane were determined by area normalization method (conversion: 89%, selectivity: 96%).

5.2 Self-condensation of Cyclopentanone



A typical procedure was as follows: Cyclopentanone (1100 mL) and sodium hydroxide aqueous solution (110 mL, 10 wt %) was loaded in reactor, and stirred for 10 h under reflux. Then the mixture was cooled and allowed to separate in two layers. The organic phase was analyzed (conversion: 67%, selectivity: 97%), then distilled under reduced pressure to offer 2-cyclopentylidenecyclopentanone (554.9 g, yield 60%).

5.3 Production of Bicyclopentyl via Catalytic Hydrogenation



Hydrogenation of 2-cyclopentylidenecyclopentanone was carried out in a 600 mL batch autoclave reactor (Parr Instrument Co.) equipped with an external temperature and stirring controller. A typical procedure was as follows: the reactor was initially loaded with 2-cyclopentylidenecyclopentanone (30.0 g, 0.2 mol) and Ru/ZSM-5 (3.0 g) catalyst. After the reactor was sealed and purged with H_2 for 4 times to exclude air, the reactor was heated to 180 ^{o}C and purged with 4 MPa of H_2. 36 h later, the reactor was cooled down to room temperature. The mixture was filtrated and dried by anhydrous sodium sulfate to afford the product (colorless oil, 25.2 g, yield 91%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.72$ (s, 4H), 1.59-1.49 (m, 10H), 1.12 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 46.5$, 32.0, 25.5. m/z 138 (M+, 13%), 96 (67), 95 (65), 82 (68), 81 (47), 69 (43), 68 (98), 67 (100) The corresponding MS, ^{1}H NMR and ^{13}C NMR spectra are shown in Fig S15 and S11.

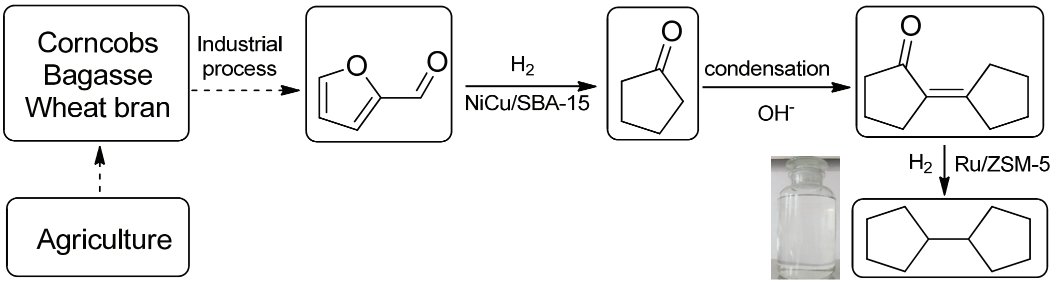


Fig S9. Total schematic description for the production of cycloalkanes.

Table S6 Chemical and physical properties of bicyclopentyl.

Property	Value	Reference
Chemical Formula	$C_{10}H_{18}$	-
Molecular weight	138.2 g/mol	Calculated
Freezing Point	-35 ^{o}C (1 atm, air)	[S1]
Boiling Point	190 ^{o}C	[S2,S4]
Density	0.8664 g/cm^{-3} (30 ^{o}C)	[S5]
Viscosity	4.22 cs (-34 ^{o}C)	[S3]
	1.35 cs (38 ^{o}C)	
	0.72 cs (99 ^{o}C)	
Aniline point	36.5 ^{o}C	[S4]
Thermal Decomp temp	399 ^{o}C	[S3]
Luminometer number	52.2	[S3]
Net Heat of Combustion	18297 b.t.u/lb	[S3]
	132864 b.t.u./gal	
	42.530 MJ/kg	Calculated from [S3]
	37.029 MJ/L	

References:

[S1] A. J. Streiff, A. R. Hulme, P. A. Cowie, N. C. Krouskop, F. D. Rossini, *Anal. Chem.,* 1955, **27**, 411-415.

[S2] A. R. Lepley, *Anal. Chem.,* 1962, **34**, 322-325.

[S3] L. I. B. M. H. Gollis, B. J. Gudzinowicz, S. D. Koch, J. O. Smith, R. J. Wineman, *J. Chem. Eng. Data,* 1962, **7**, 311-316.

[S4] G. E. Goheen, *J. Am. Chem. Soc*., 1941, **63**, 744-749.

[S5] A. Weissler, *J. Am. Chem. Soc.,* 1949, **71**, 419-421.

6. NMR, MS and GC Traces

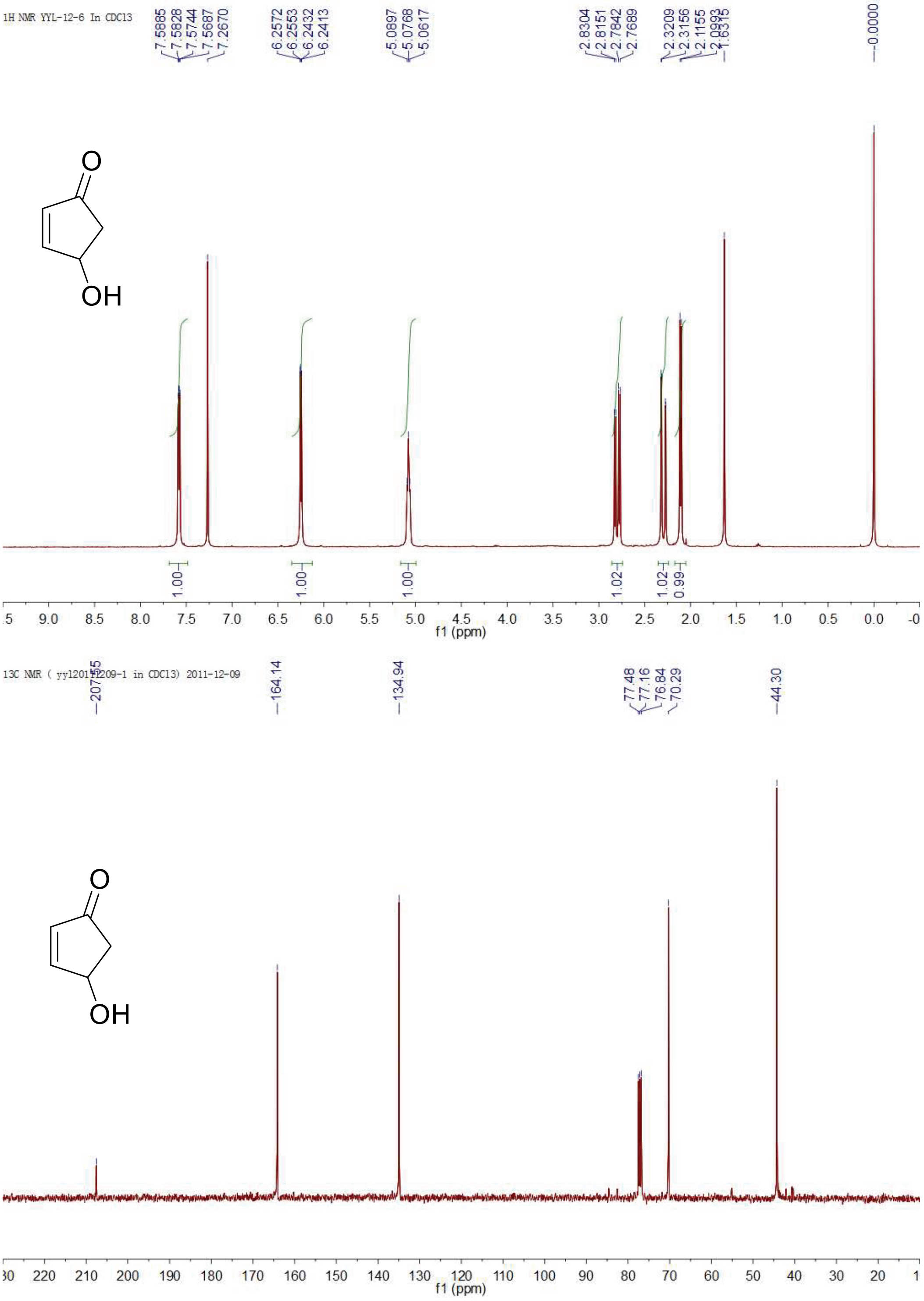


Fig S10. ^{1}H and ^{13}C NMR spectra of 4-hydroxy-2-cyclopentenone.

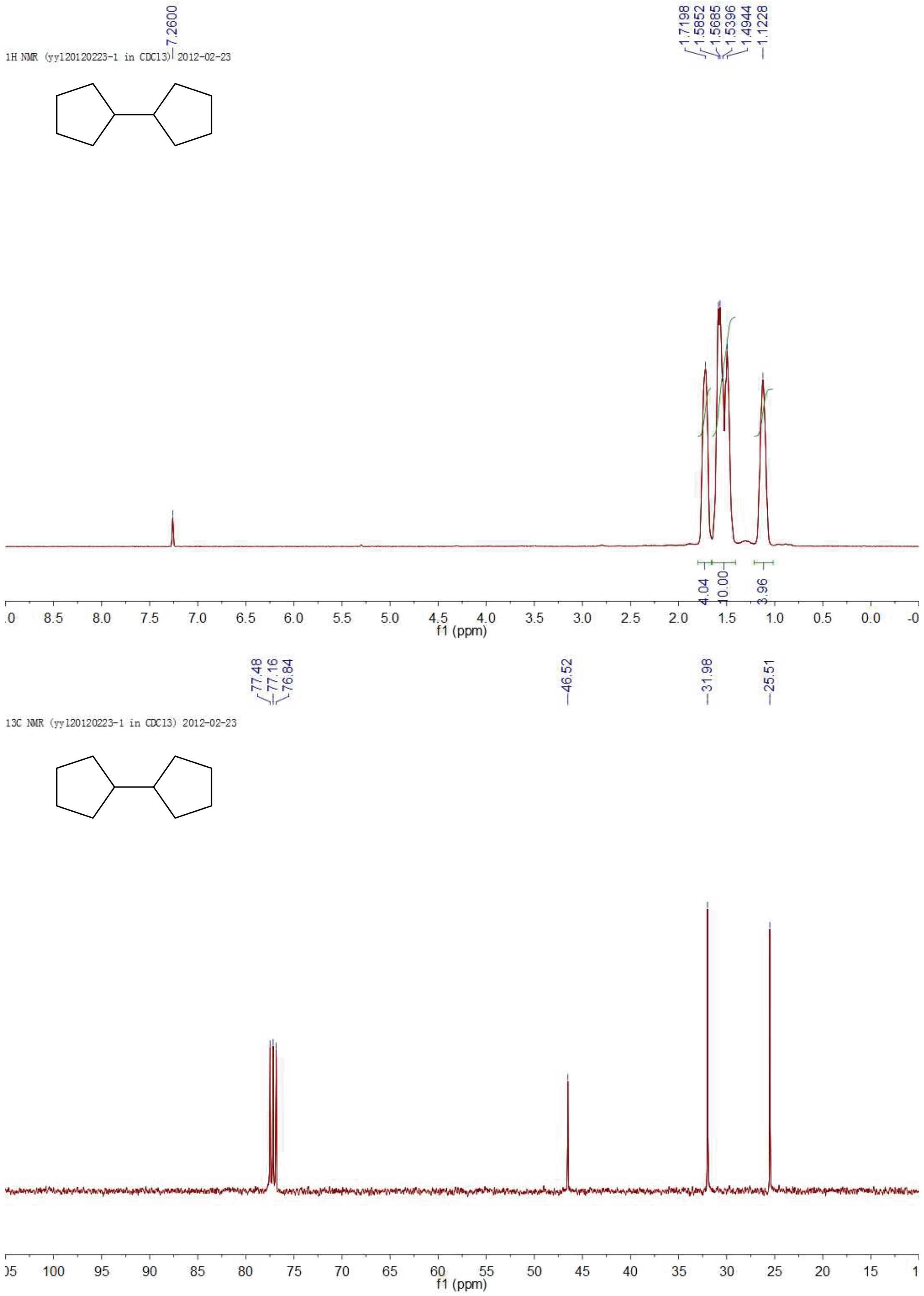
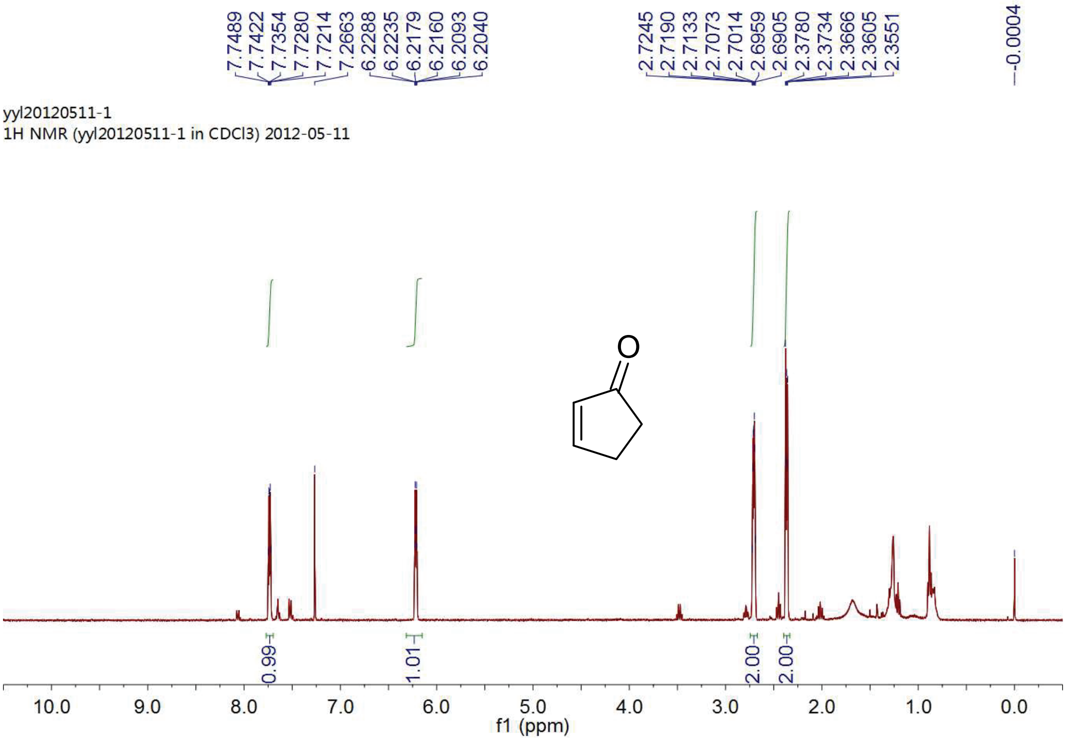


Fig S11. ^{1}H NMR and ^{13}C NMR spectra of bicyclopentyl.



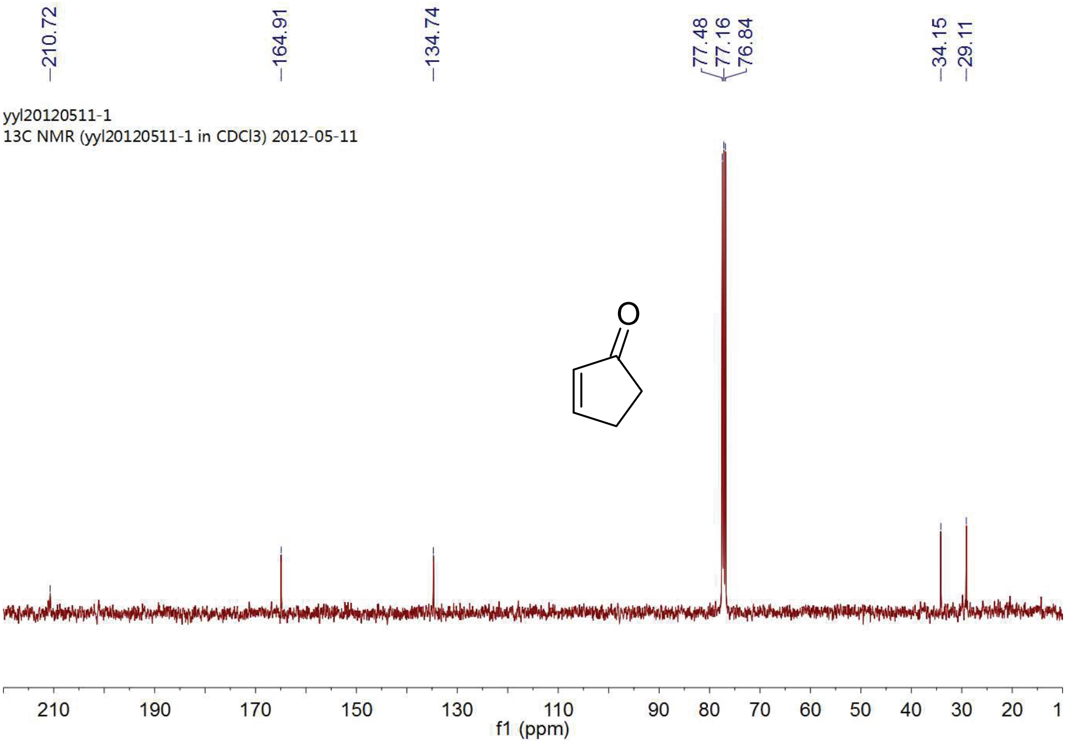


Fig S12. ^{1}H and ^{13}C NMR spectra of 2-cyclopentenone.

m/z 98 (M+, 100%), 97 (41), 70 (75), 55 (54), 44 (40), 43 (45), 42 (95)

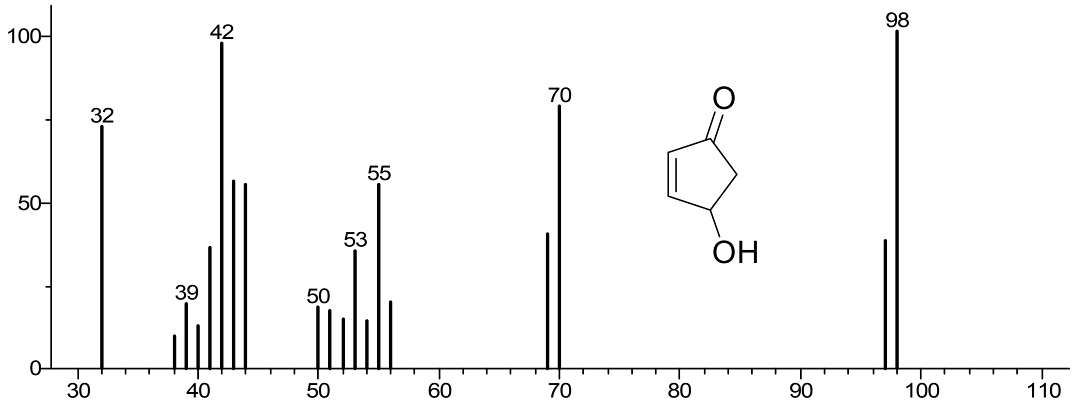


Fig S13. Mass spectrum of 4-hydroxy-2-cyclopentenone.

m/z 82 (M+, 100%), 54 (29), 53 (30)

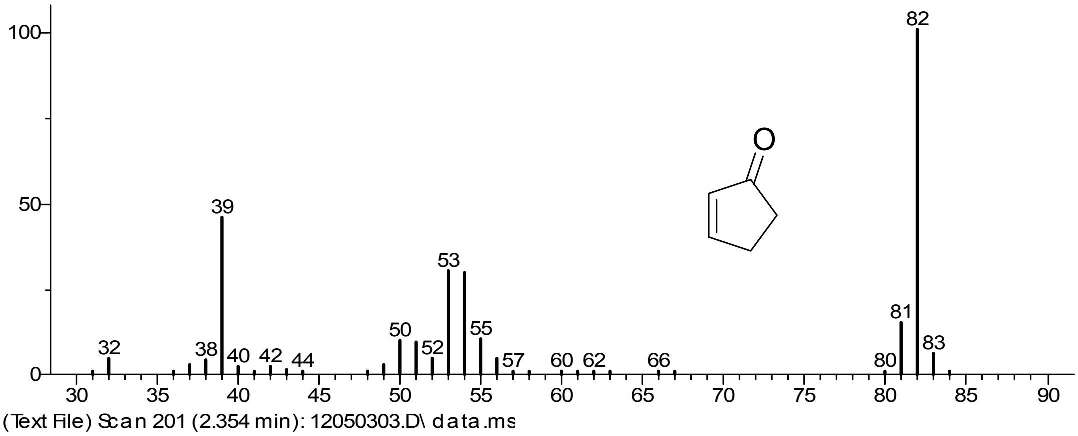


Fig S14. Mass spectrum of 2-cyclopentenone.

m/z 138 (M+, 13%), 96 (67), 95 (65), 82 (68), 81 (47), 69 (43), 68 (98), 67 (100)

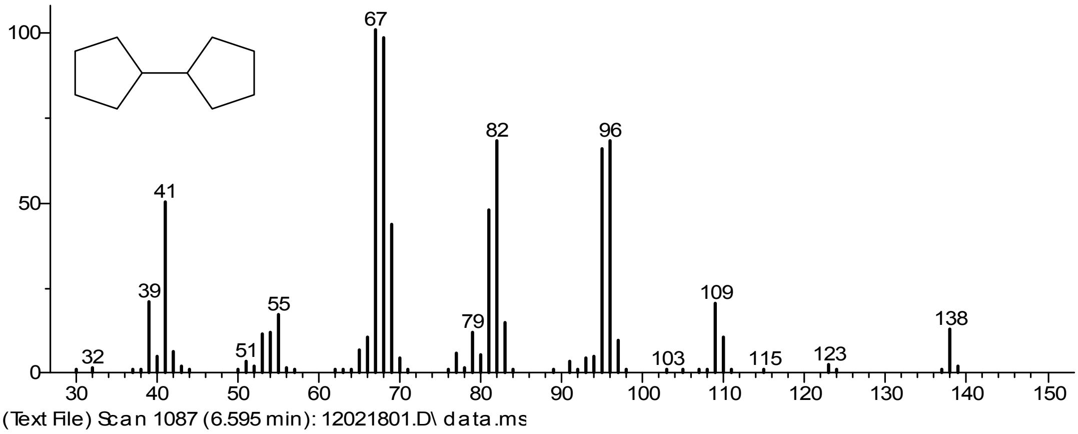
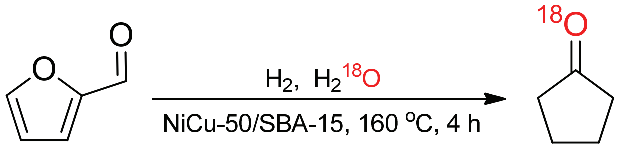
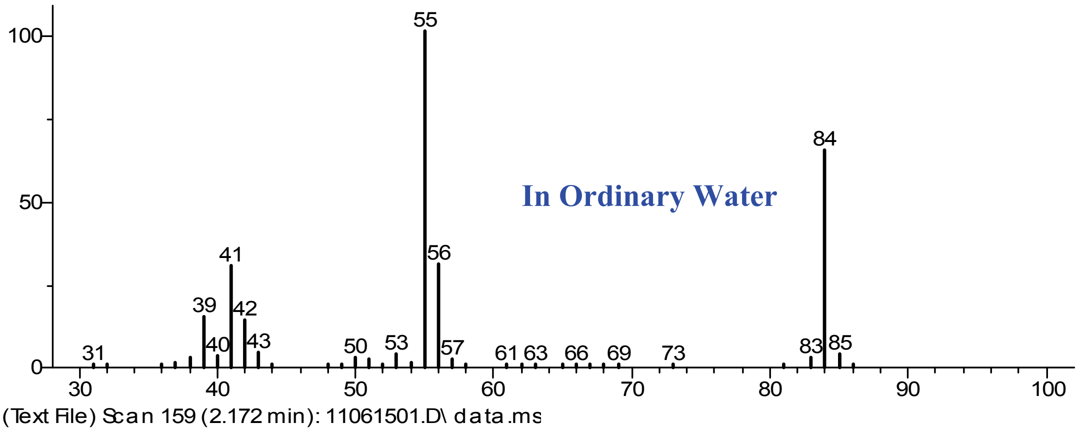


Fig S15. Mass spectrum of bicyclopentyl.



m/z 84 (M+, 65%), 56 (31), 55 (100)



m/z 86 (M+, 74%), 84 (4), 58 (27), 57 (100)

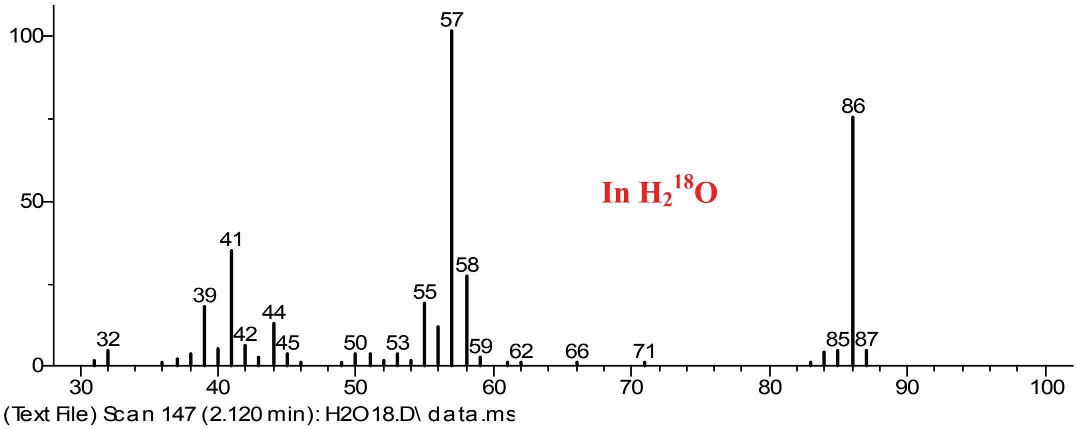
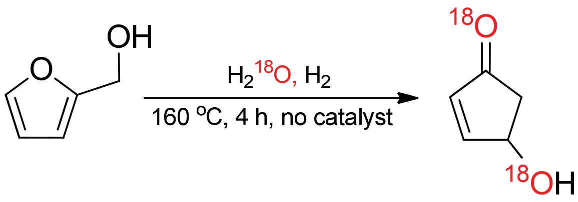
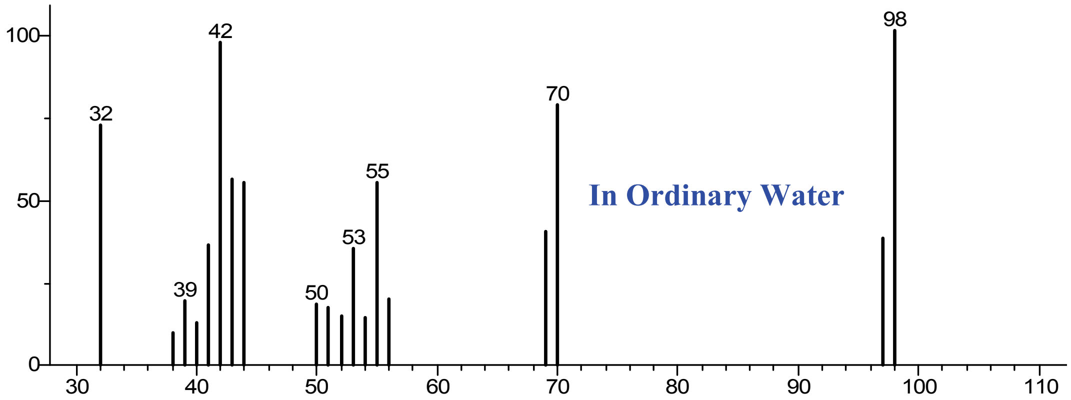


Fig S16. MS traces of cyclopentanone obtained in ordinary water and $H_2{}^{18}O$.



m/z 98 (M+, 100%), 97 (32), 70 (73), 55 (51), 44 (42), 43 (46), 42 (80)



m/z 102 (M+, 100%), 100 (28), 98 (2), 72 (80), 57 (68), 45 (54), 44 (59), 42 (62)

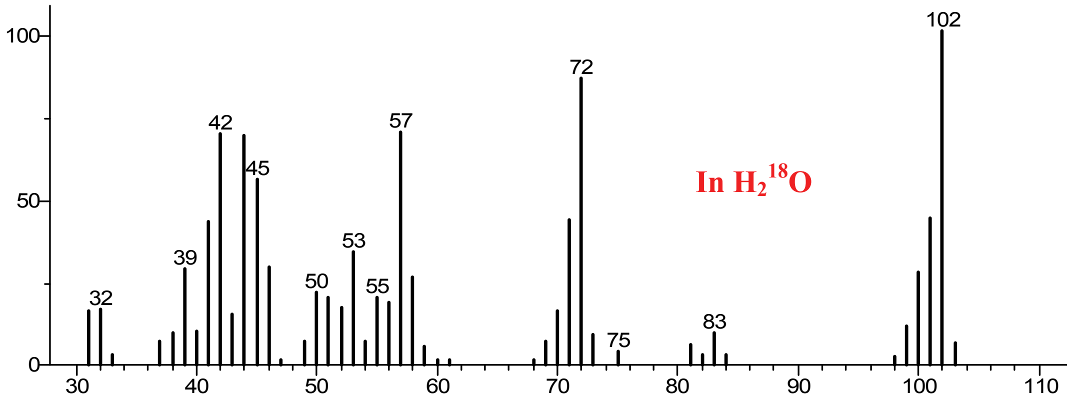
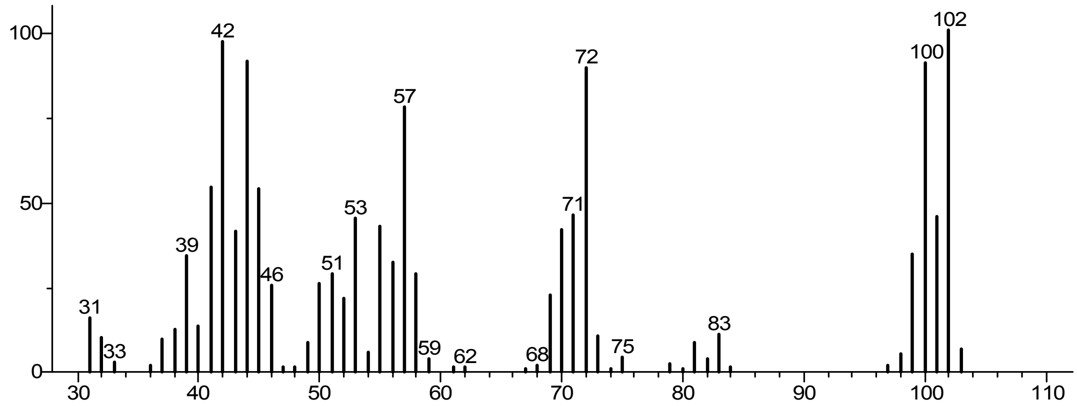


Fig S17. MS traces of 4-hydroxy-2-cyclopentenone obtained in ordinary water and $H_2{}^{18}O$.

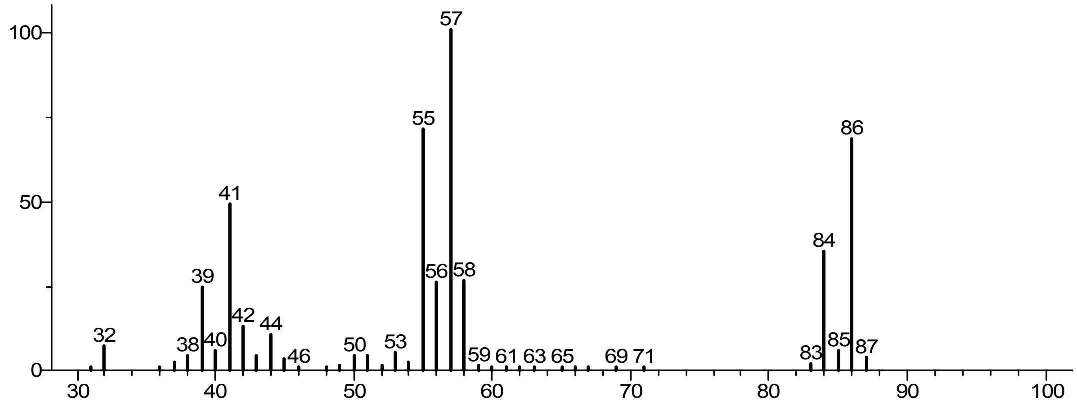
m/z 102 (M+, 100%), 100 (90), 98 (5),72 (89), 57 (77), 45 (54), 44 (91), 42 (96)



(Text File) Scan 950 (5.601 min): 11082201.D\ data.ms

Fig S18. The oxygen exchange between 4-hydroxy-2-cyclopentenone and water (160 °C, 4 h, no catalyst, H_2 atmosphere).

m/z 86 (M+, 68%), 84 (35), 57 (100), 55 (71), 41 (49)



(Text File) Scan 134 (2.063 min): 12041240.D\ data.ms

Fig S19. The oxygen exchange between cyclopentanone and water (160 °C, 4 h, no catalyst, H_2 atmosphere).

m/z 68 (M+, 100%), 39 (76)

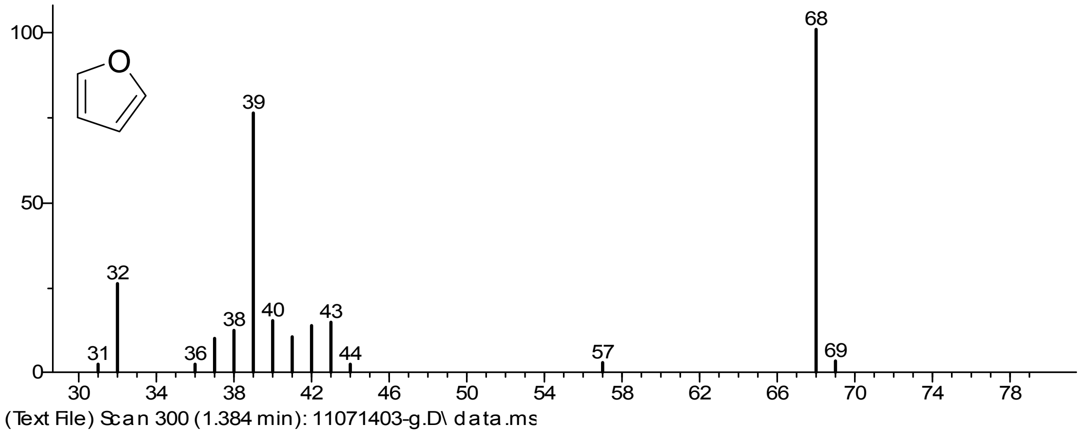


Fig S20. Mass spectrum of furan.

m/z 82 (M+, 100%), 81 (61), 53 (49)

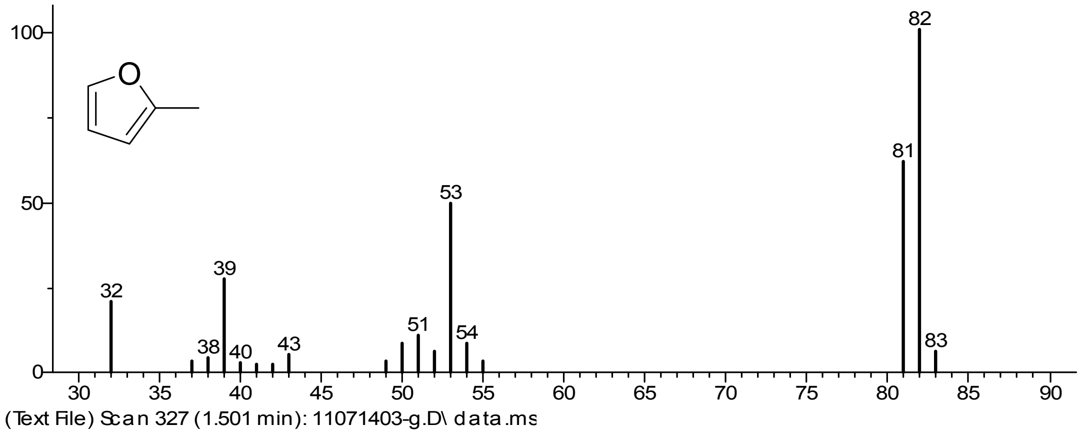


Fig S21. Mass spectrum of 2-methyltetrahydrofuran.

m/z 86 (M+, 8%), 57 (100)

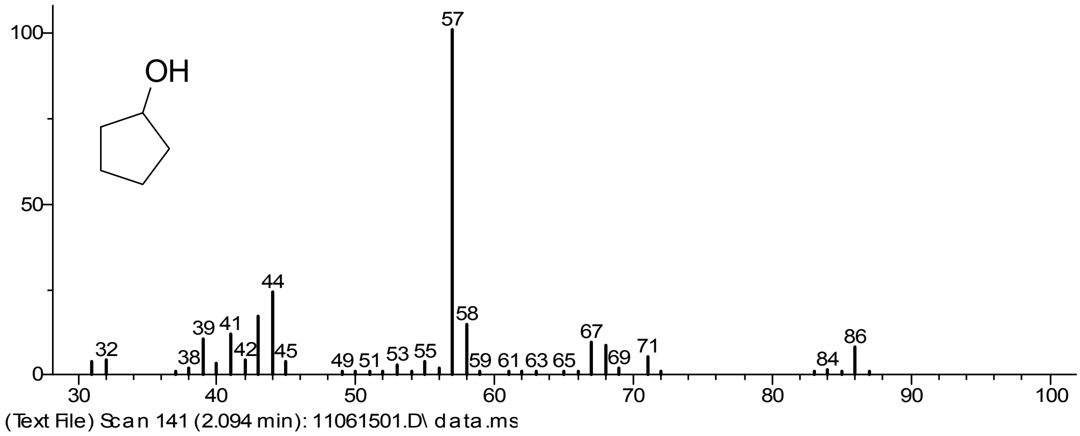


Fig S22. Mass spectrum of cyclopentanol.

m/z 84 (M+, 63%), 56 (31), 55 (100)

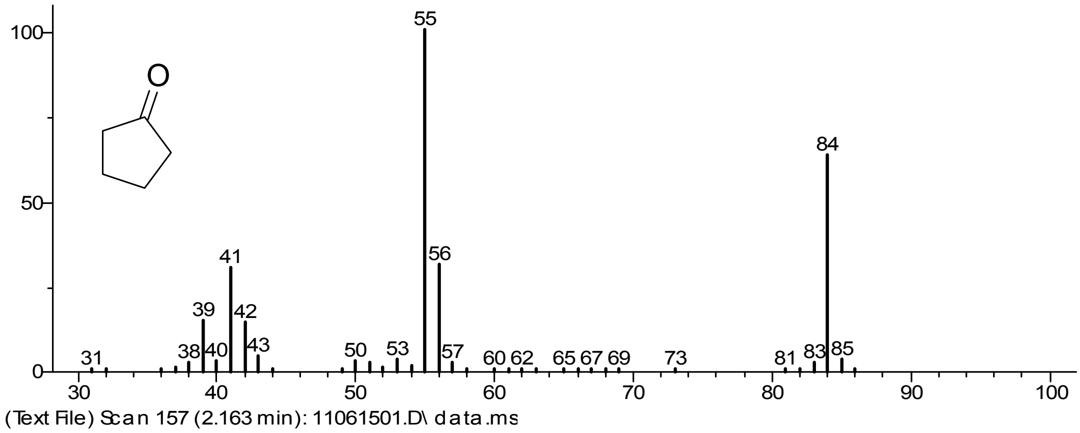


Fig S23. Mass spectrum of cyclopentanone.

m/z 98 (M+, 100%), 97 (53), 96 (49), 95 (54), 81 (49), 69 (29), 53 (33), 41 (31)

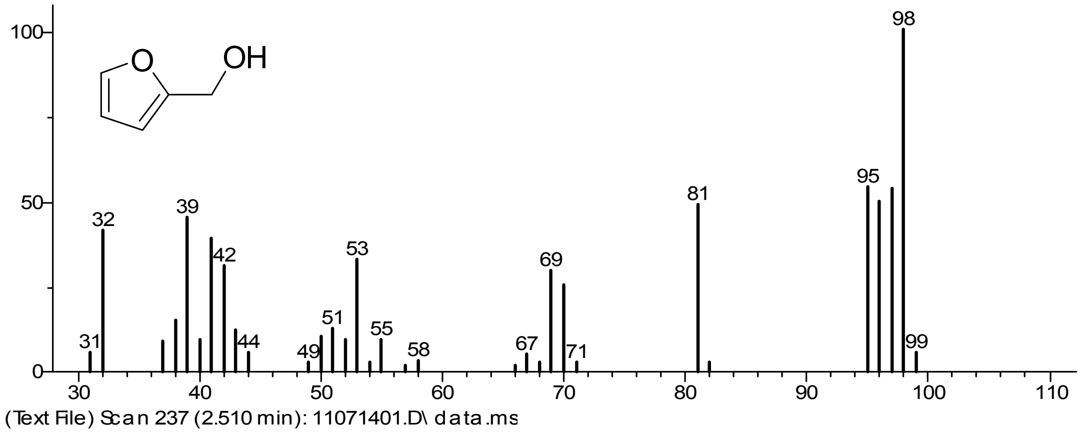


Fig S24. Mass spectrum of furfuryl alcohol.

m/z 102 (M+, 0%), 71 (100), 43 (43)

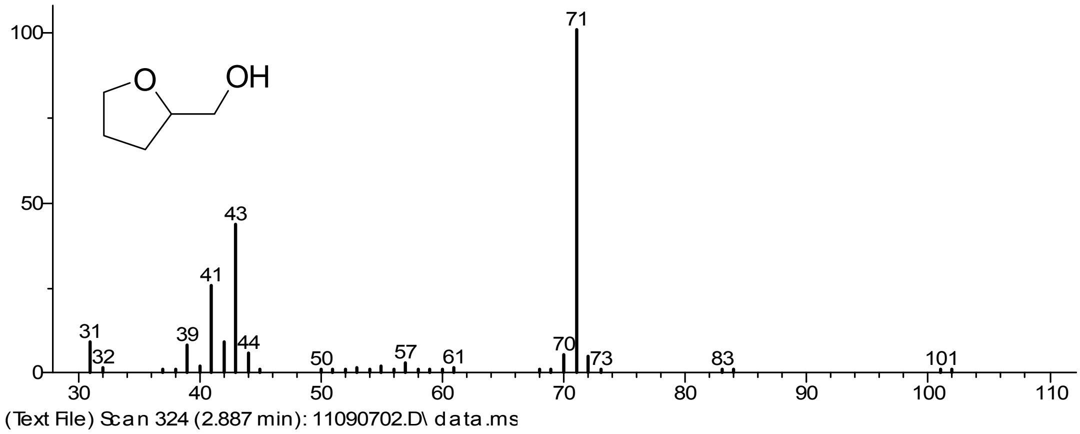


Fig S25. Mass spectrum of tetrahydrofurfuryl alcohol.

m/z 132 (M+, 0%), 101 (94), 83 (25), 57 (100), 55 (34)

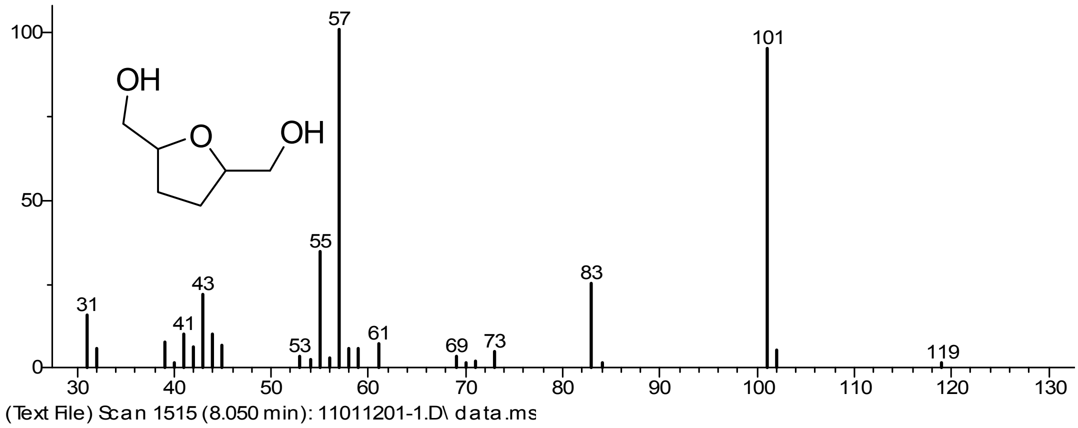


Fig S26. Mass spectrum of (tetrahydrofuran-2,5-diyl)dimethanol.

m/z 98 (M+, 100%), 83 (24), 70 (35), 69 (57), 56 (27), 55 (83)

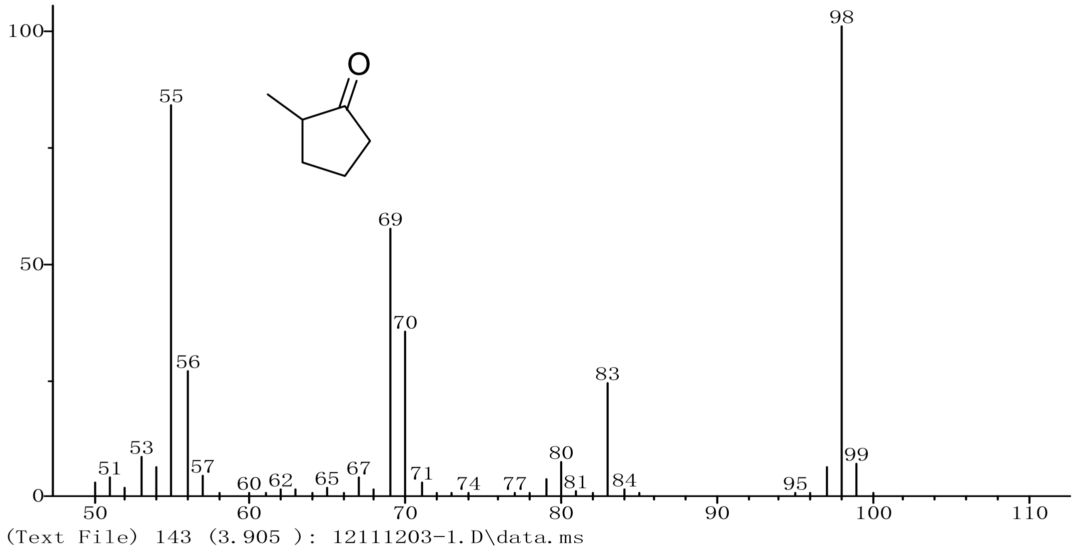


Fig S27. Mass spectrum of 2-methylcyclopentanone.

m/z 112 (M+, 86%), 111 (29), 97(40), 95 (100)

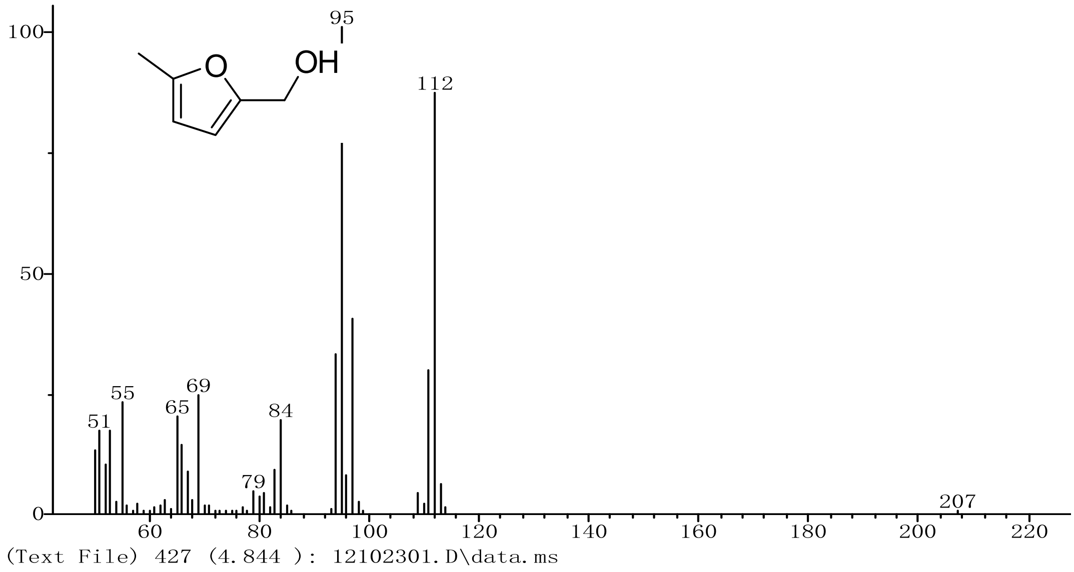


Fig S28. Mass spectrum of (5-methylfuran-2-yl)methanol.

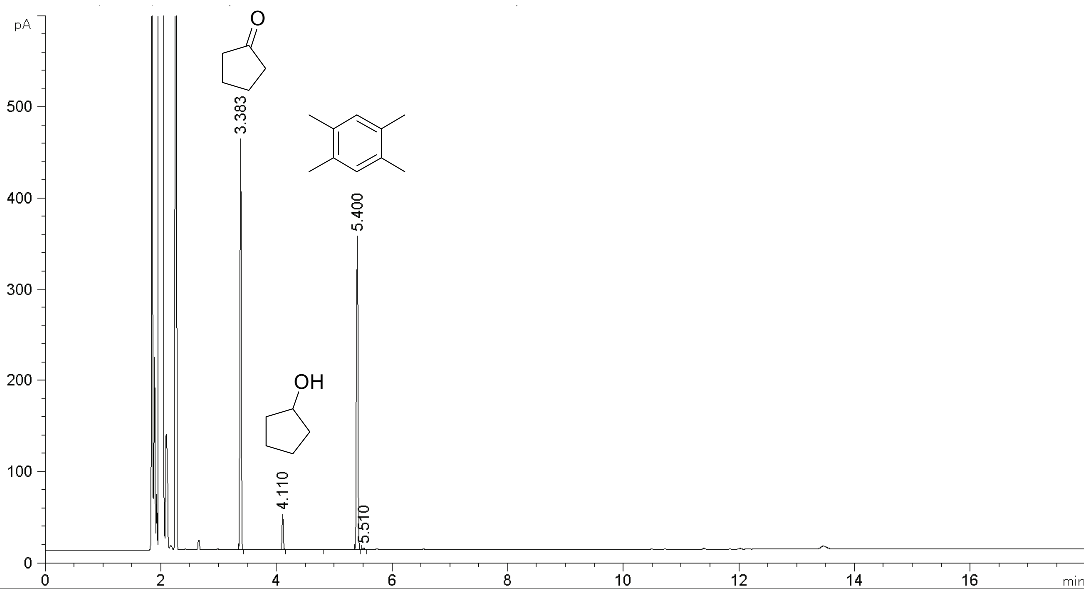


Fig S29. GC trace of furfural hydrogenation (Fig 4, line *a*, left).

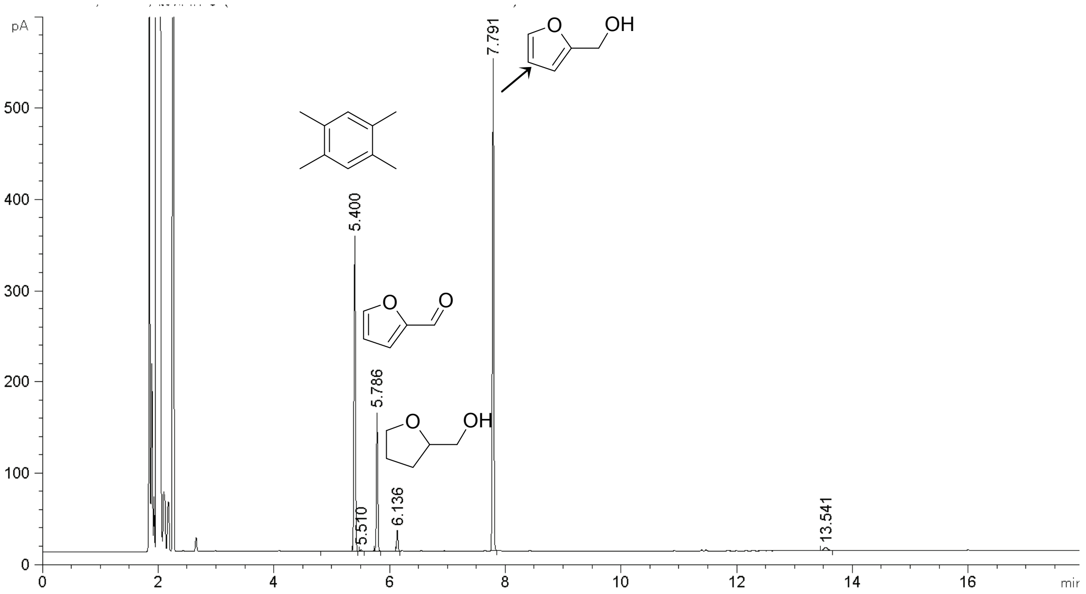


Fig S30. GC trace of furfural hydrogenation at 80 °C (Fig 4, line *b*, left).

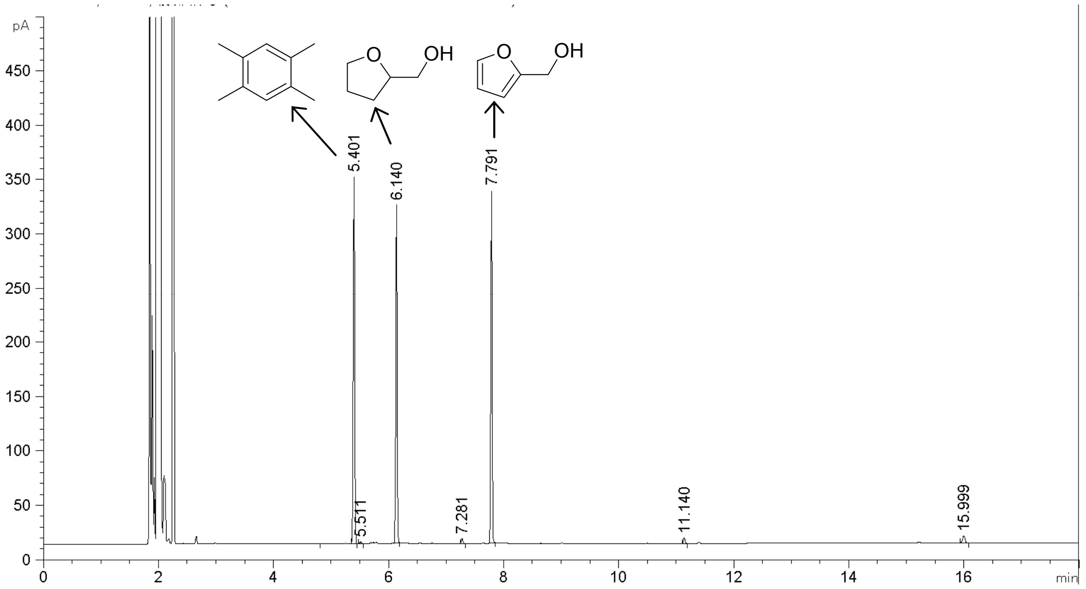


Fig S31. GC trace of furfural hydrogenation with Na_2CO_3 as additive (Fig 4, line *c*, left).

Fig S32. GC trace of furfural hydrogenation in 1,4-dioxane (Fig 4, line *d*, left).

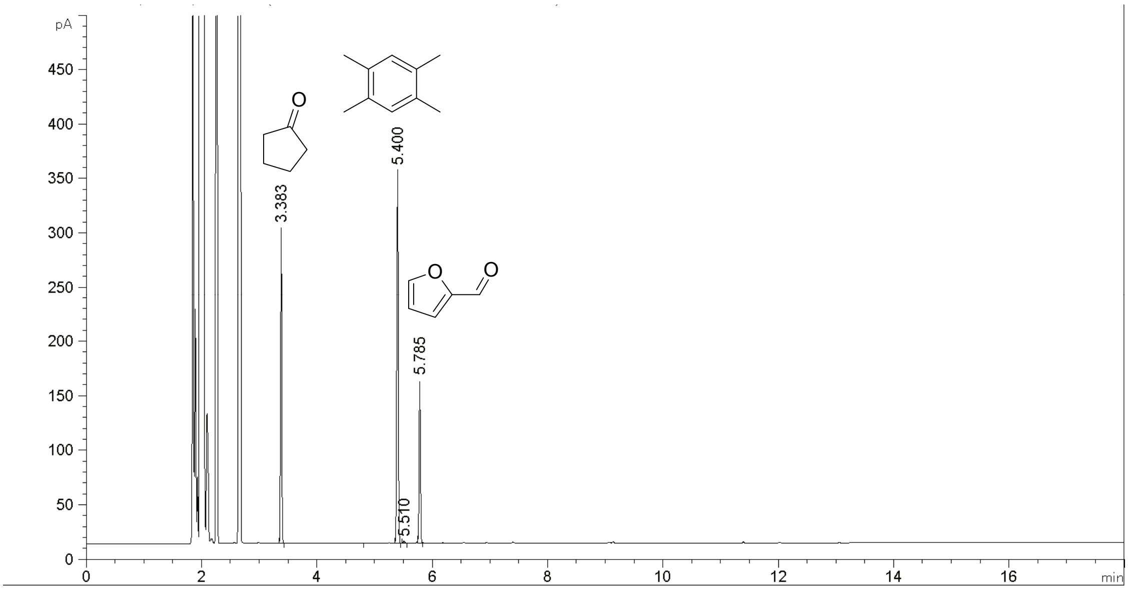


Fig S33. GC trace of furfural hydrogenation in 1,4-dioxane / water (Fig 4, line *e*, left).

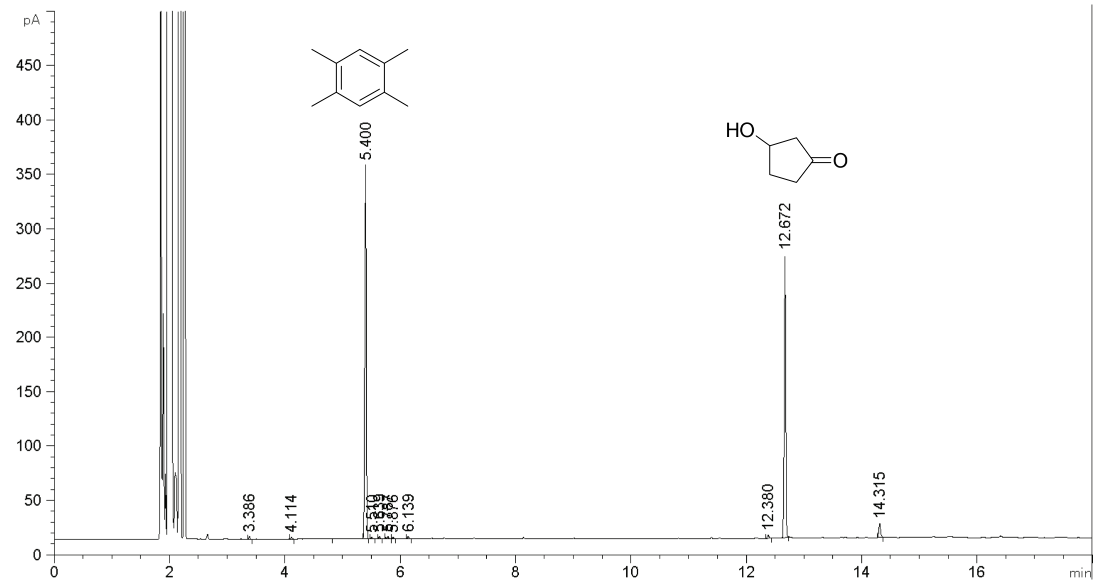


Fig S34. GC trace of furfuryl alcohol conversion in water (Fig 4, line *a* right).

Fig S35. GC trace of furfuryl alcohol conversion at 80 °C (Fig 4, line *b*, right).

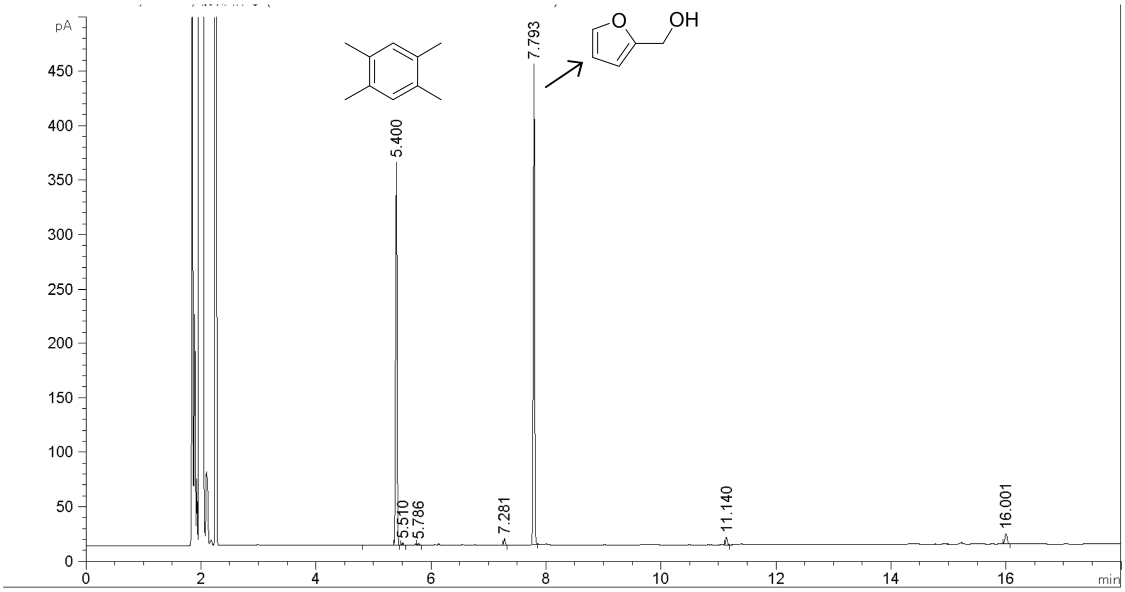


Fig S36. GC trace of furfuryl alcohol conversion using Na_2CO_3 as additive (Fig 4, line *c*, right).

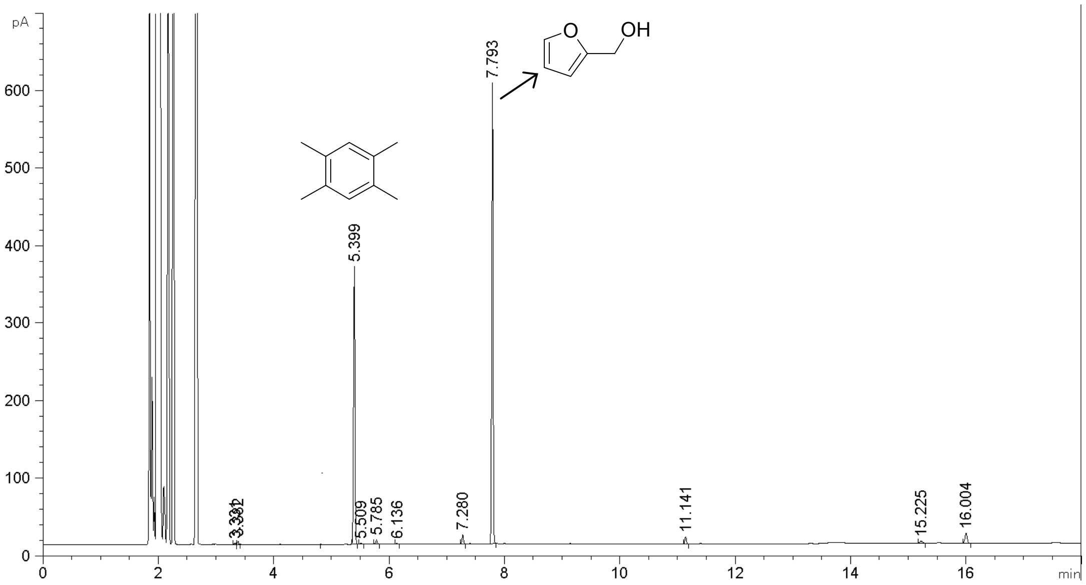


Fig S37. GC trace of furfuryl alcohol conversion in 1,4-dioxane (Fig 4, line *d*, right).

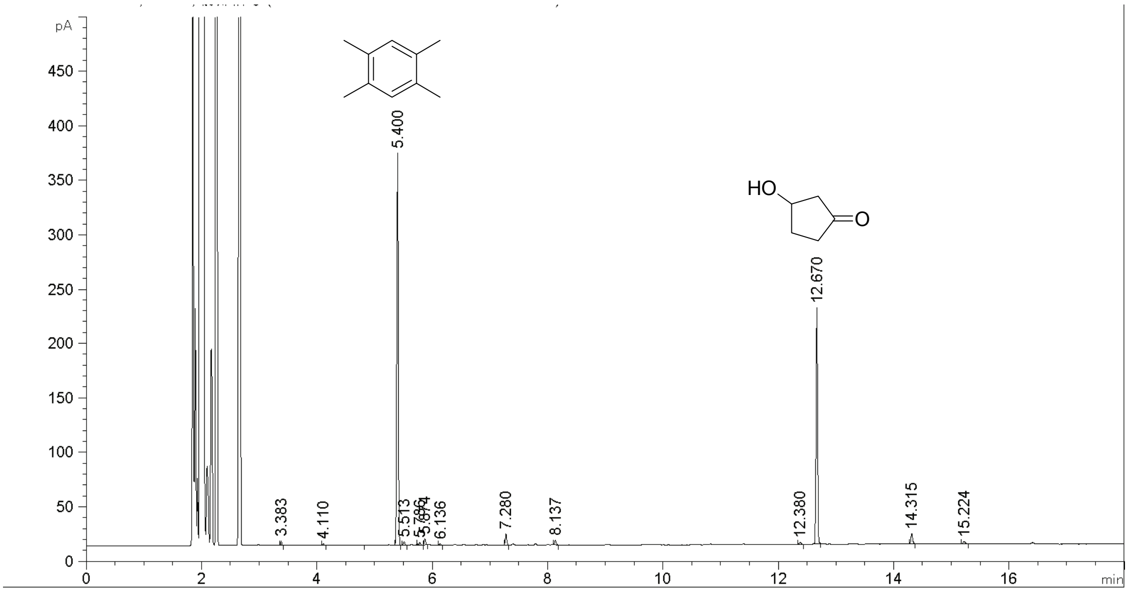


Fig S38. GC trace of furfuryl alcohol conversion in 1,4-dioxane / water (Fig 4, line *e*, right).

Fig S39. The photo of the black solid observed (Table 1, entry 6).