Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Industrially scalable and cost-effective synthesis of 1,3-cyclopentanediol with furfuryl alcohol from lignocellulose

Guangyi Li,[a] Ning Li,*[a,b] Mingyuan Zheng,[a] Shanshan Li,[a,c] Aiqin Wang,[a,b] Yu Cong,[a] Xiaodong Wang[a] and Tao Zhang*[a,b]

[a]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China.*

[b]*iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[c]*University of Chinese Academy of Sciences, Beijing 100049, China.*

**Corresponding author:*

Tao Zhang, Tel.: +86-411-84379015, E-mail: taozhang@dicp.ac.cn;

Ning Li, Tel.:+86-411-84379738, E-mail: lining@dicp.ac.cn

1. CO_2-TPD

The basicity of the solid base catalysts used in the aqueous phase rearrangement of furfuryl alcohol were characterized by CO_2 temperature-programmed desorption (CO_2-TPD) experiments on a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System. For each test, 0.1 g sample was used. The catalyst was placed in a quartz reactor, pretreated in He flow at its preparation temperature for 1 h and cooled down in He flow to 353 K. After the saturated adsorption of CO_2, the sample was purged with He at 353 K for 45 min to remove the physically adsorbed CO_2. The desorption of CO_2 was carried out in He flow from 353 K to 1073 K at a heating rate of 10 K min^{-1}. The desorbed CO_2 molecules were detected by an OminiStar mass spectrometry (MS) equipped with the software quadstar 32-bit. The amounts of base sites on the surfaces of the solid base catalysts were illustrated in Table S5.

2. Purification of 4-hydroxycyclopent-2-enone and 1,3-cyclopentanediol

The 4-hydroxycyclopent-2-enone used in the hydrogenation tests was obtained from the aqueous phase rearrangement of furfuryl alcohol carried out in a one-gallon batch reactor. To do this, 2000 g water and 0.65 g MgAl-HT catalyst were put into stainless-steel autoclave (Parr 4553 reactor). The reactor was purged with Ar for six times then heated to 503 K. Subsequently, 500 mL 20wt.% aqueous solution of furfuryl alcohol (Sinopharm Chemical Reagent Co. Ltd.) was injected into the reactor with a HPLC pump (Elite P270, feeding time 6.25 min, feeding rate 80 mL min^{-1}). The mixture was stirred at rate of 800 rpm for 2 min and quenched to room temperature by cool water. The liquid product was taken out from the batch reactor and centrifuged to remove the MgAl-HT catalyst (and polymerization product). After removing the water (used as a solvent) in the solution by vacuum distillation, the 4-hydroxycyclopent-2-enone was obtained. According our analysis, the 4-hydroxycyclopent-2-enone prepared by this method has high purity (~97%) and can be used for the hydrogenation reaction without further purification. The carbon yield of 4-hydroxycyclopent-2-enone was calculated as 77.6%.

The 1,3-cyclopentanediol used in the polymerization experiment was purified by batch distillation. A packed distillation column (diameter: 15 mm, height: 1 m) filled with triangle auger fillers (2.5 cm height equivalent of theoretical plate) was used in this experiment. Typically, 250 g crude 1,3-cyclopentanediol was used for each experiment. The reboiler temperature was set as 423 K, the insulation temperature of column was fixed at 378 K, overhead vacuum was 96 kPa and total reflux time was 2 h. The overhead products were collected at the reflux ratio of 10:1.

According to the Table S6 in supporting information, 122.9 g 98wt.% 1,3-cyclopentanediol or 166.3 g 96wt.% 1,3-cyclopentanediol can be obtained from 253 g raw 1,3-cyclopentanediol, respectively. In real application, higher yield of high-purity 1,3-cyclopentanediol can be obtained by the recycling of low-purity 1,3-cyclopentanediol. It is worth mentioning that even *cis*- and *trans*- isomers of 1,3-cyclopentanediol can be separated (see ^{1}H and ^{13}C NMR spectra in Figure S7 and Figure S8) by this traditional distillation method. According to the result of differential scanning calorimetry (DSC), the melting points of *cis*- and *trans*-1,3-

cyclopentanediols were measured as 300.4 K and 314.4 K, respectively (see Figure S14).

3. Synthesis of polyurethane.

The polymerization of diphenyl-methane-diisocyanate and 1,3-cyclopentanediol were conducted under nitrogen atmosphere in a round bottom flask which was equipped with a magnetic stirrer and an addition funnel. Typically, 8 mmol 1,3-cyclopentanediol and 2.5 μL bis(lauroyloxy)dibutyl-stannan were introduced into the reactor and dried at room temperature under a vacuum (0.1 torr) for 30 min. Then, 20 g dimethyl formamide was added into the reactor which was filled with Argon. The mixture was heated at 323 K. Subsequently, 10 mmol diphenyl-methane-diisocyanate was added into the reactor. The pre-polymerization was carried out at 353 K for 2 h. Then, a dimethyl formamide solution of 1,3-cyclopentanediol (prepared by dissolving 3 mmol 1,3-cyclopentanediol in 6 g dimethyl formamide) was added drop wise to the aforementioned solution in 2 h. Reaction products were obtained by coagulating the polyurethane solution in methanol. The coagulated polyurethane was washed with methanol for three times and dried under vacuum at room temperature.

Gel permeation chromatography (GPC) analysis of the polyurethane obtained in this work were performed on a VISCOTED 270 gel chromatography equipped with a Malvern 270 Dual column (at 303 K) and a VE 3580 RI detector. The tetrahydrofuran (THF) (flow rate: 1.0 mL min^{-1}) was used as the mobile phase. Polystyrenes were used as the calibration standards.

Thermogravimetric analyses (TGA) of the polyurethane obtained in this work were carried out in nitrogen flow with a TGA-DSC NETZSCH STA 449 F3 instrument. About 6.4 mg of sample was heated from 313 K to 973 K at a rate of 10 K min^{-1}. Differential scanning calorimetry (DSC) experiments were performed on a DSC NETZSCH 204 HP instrument. The samples (5 mg) were enclosed in aluminum pans which were placed in the heating cell with empty pans as references and heated under nitrogen flow (20 mL min^{-1}) at a heating rate of 10 K min^{-1}.

Melting point of the polyurethane was measured by an X-4 Melting Point apparatus (Beijing Tech Instrument Co. Ltd.). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE Ⅲ 500 MHz. Chemical shifts (δ) were reported in parts per million (ppm). Fourier transform infrared spectra (FT-IR) were recorded on Tensor 27 in the range of 400-4000 cm^{-1}.

Wide-angle X-ray powder diffraction of the polyurethane was performed by X'pert Pro-1 X-ray diffractometer (XRD) using Ni-filtered Cu Kα radiation (40 kV, 30 mA). Diffraction intensity was measured in a range of $2\theta = 10\text{-}90\ ^{o}$.

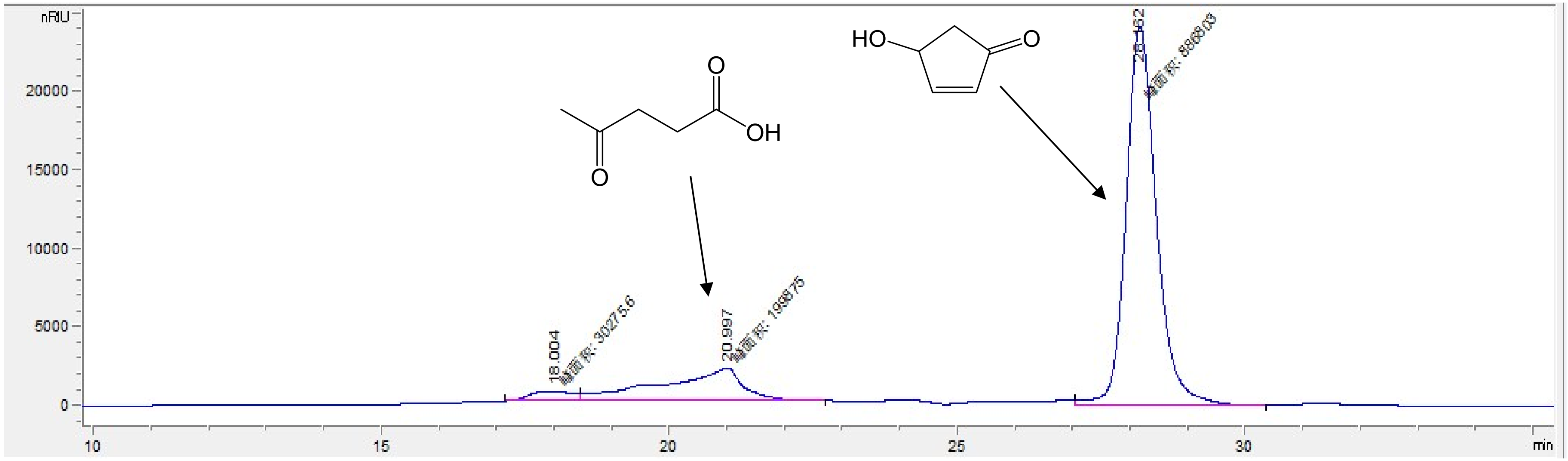


Figure S1. HPLC chromatogram of the liquid products from the aqueous phase rearrangement of furfuryl alcohol in the absence of catalyst. Reaction conditions: 513 K, 1 min; 10.0 g 10wt.% aqueous solution of furfuryl alcohol, 40 g water and catalyst were used for the reaction.

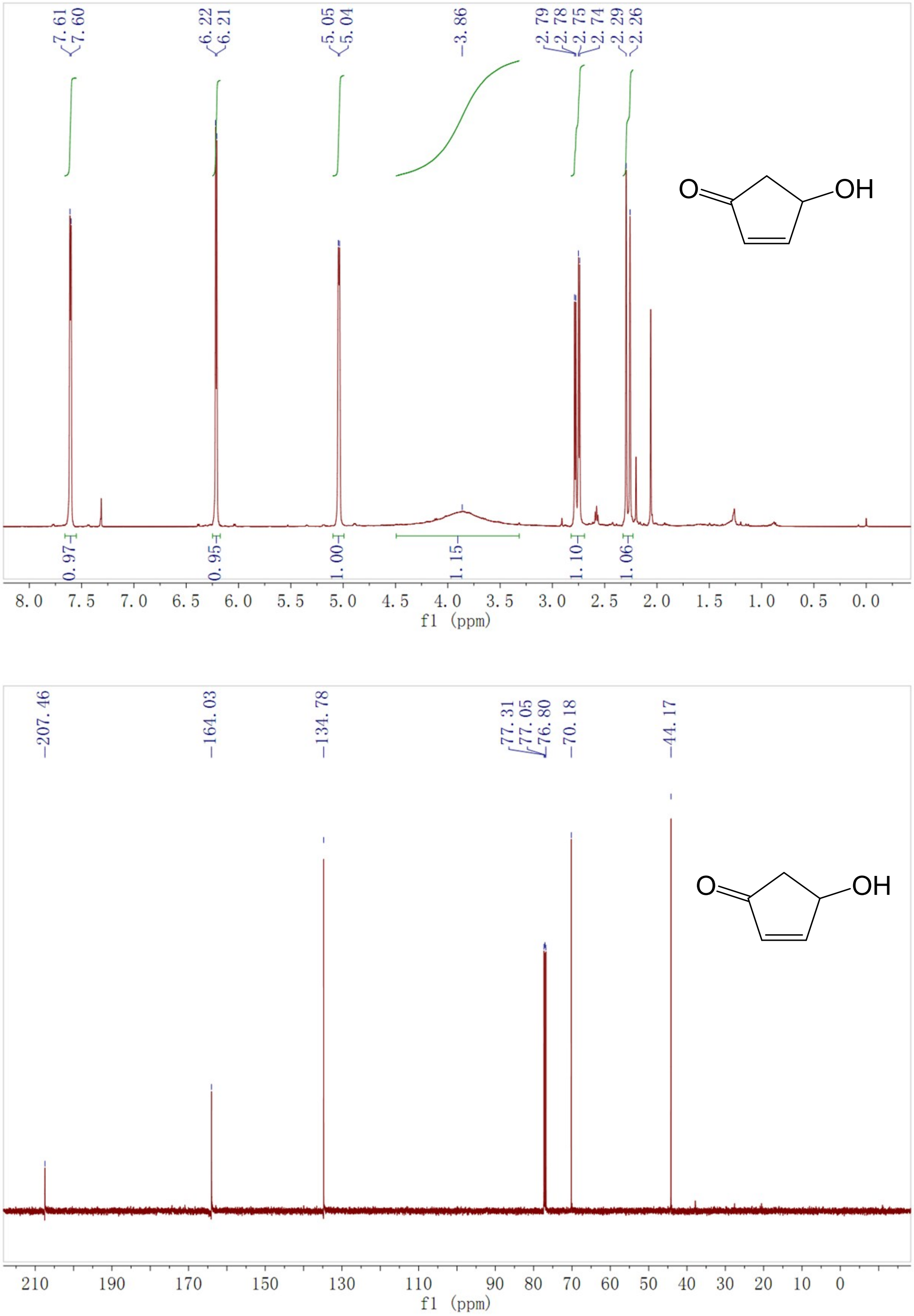


Figure S2. ^{1}H and ^{13}C NMR spectra of the 4-hydroxycyclopent-2-enone from the aqueous phase rearrangement of furfuryl alcohol.

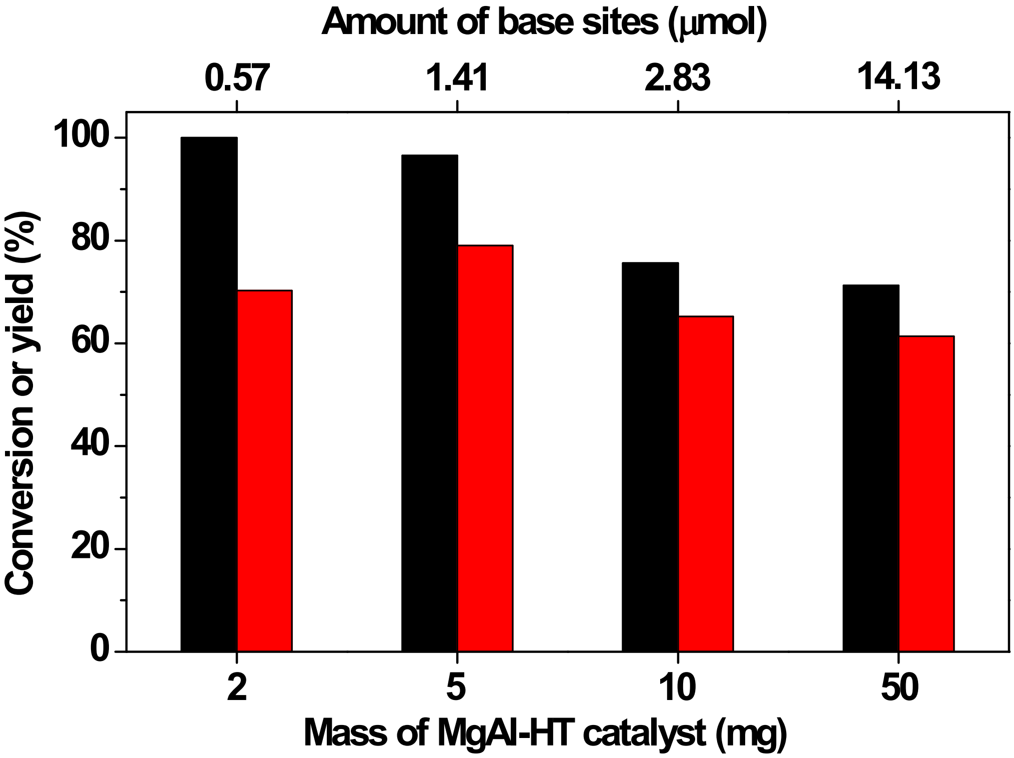


Figure S3. Effect of catalyst dosage on the furfuryl alcohol conversion (black bars) and the carbon yield of 4-hydroxycyclopent-2-enone (red bars) over MgAl-HT. Reaction conditions: 513 K, 1 min; 10.0 g 10wt.% furfuryl alcohol aqueous solution and 40 g water were used for each reaction.

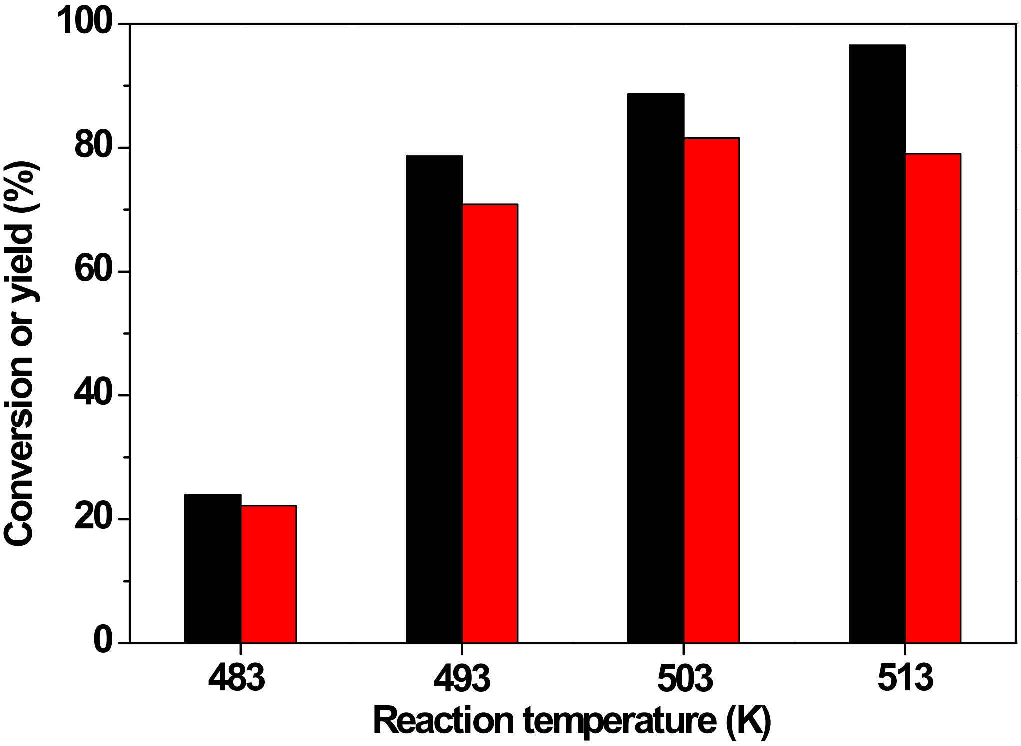


Figure S4. Furfuryl alcohol conversion (black bars) and the carbon yield of 4-hydroxycyclopent-2-enone (red bars) over the MgAl-HT catalyst as the function of reaction temperature. Reaction conditions: 1 min, 10.0 g 10wt.% furfuryl alcohol aqueous solution, 40 g water and 5 mg MgAl-HT catalyst were used for each reaction.

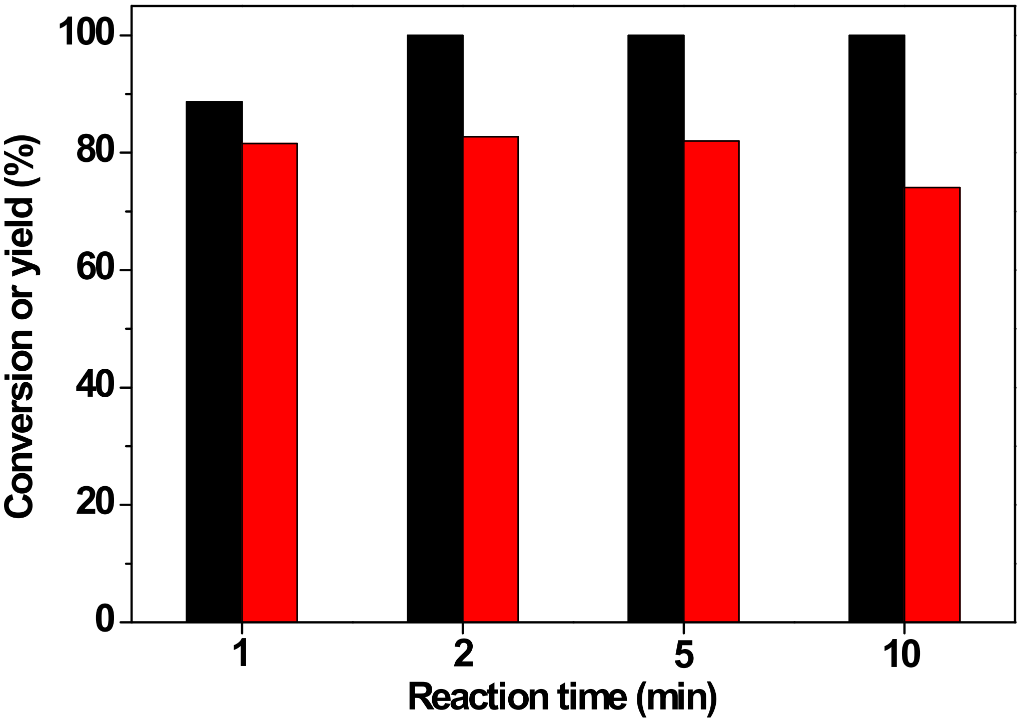


Figure S5. Furfuryl alcohol conversion (black bars) and the carbon yield of 4-hydroxycyclopent-2-enone (red bars) over MgAl-HT catalyst as the function of reaction time. Reaction conditions: 503 K; 10.0 g 10wt.% furfuryl alcohol aqueous solution, 40 g water and 5 mg MgAl-HT catalyst were used for each reaction.

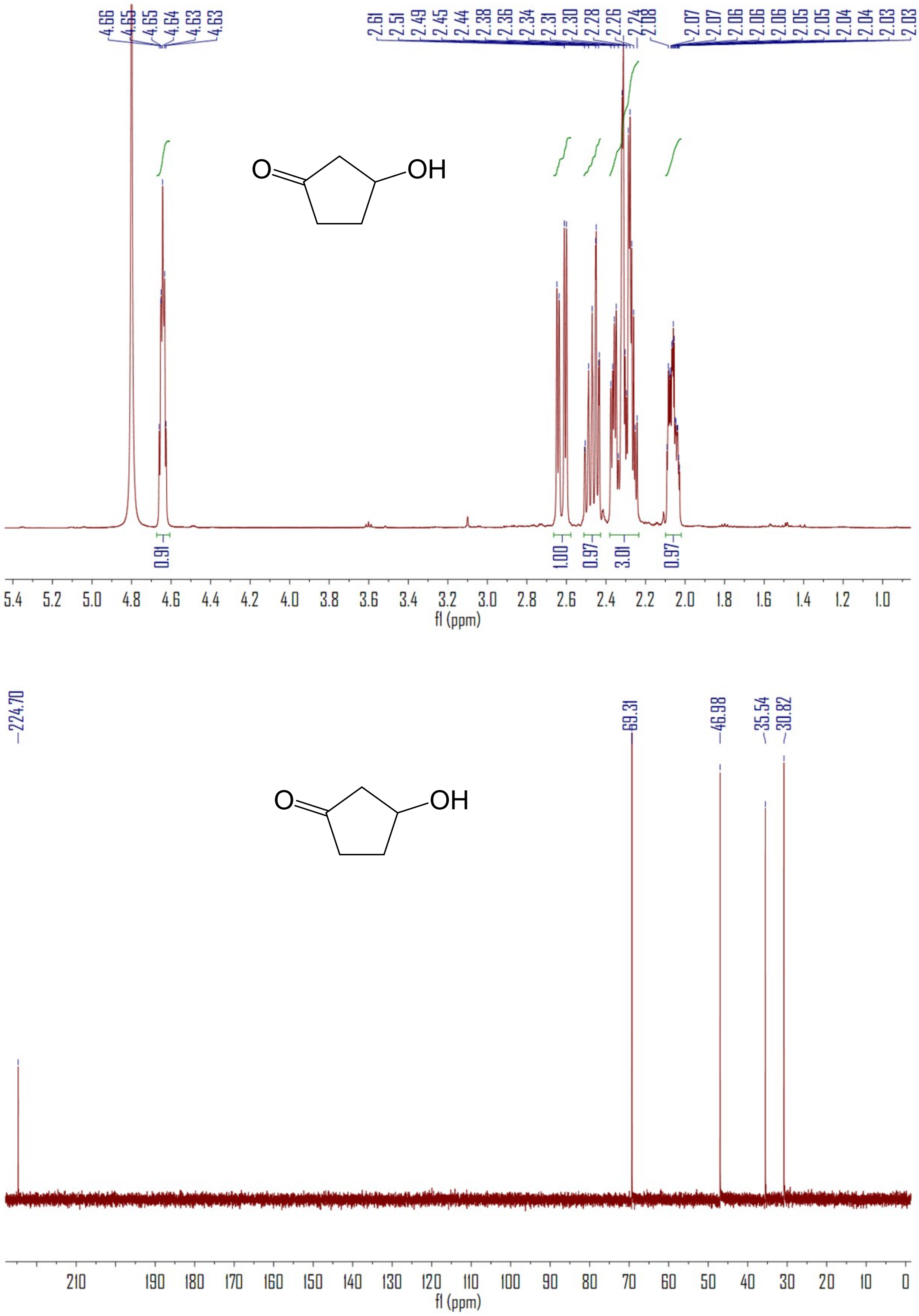


Figure S6. ^{1}H and ^{13}C NMR spectra of 3-hydroxycyclopentanone from the hydrogenation of 4-hydroxycyclopent-2-enone at room temperature.

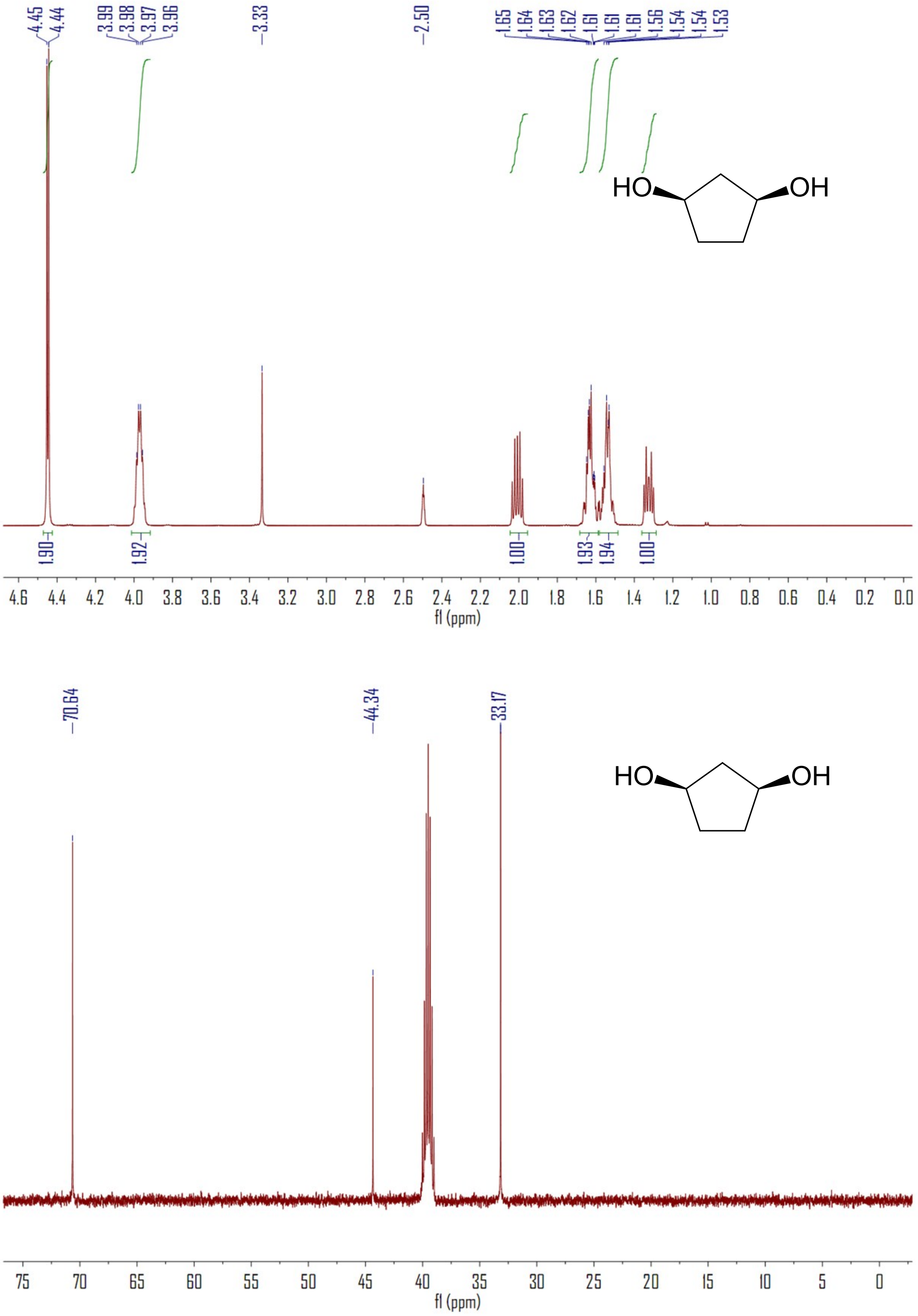


Figure S7. ^{1}H and ^{13}C NMR spectra of the *cis*-1,3-cyclopentanediol from the hydrogenation of 4-hydroxycyclopent-2-enone.

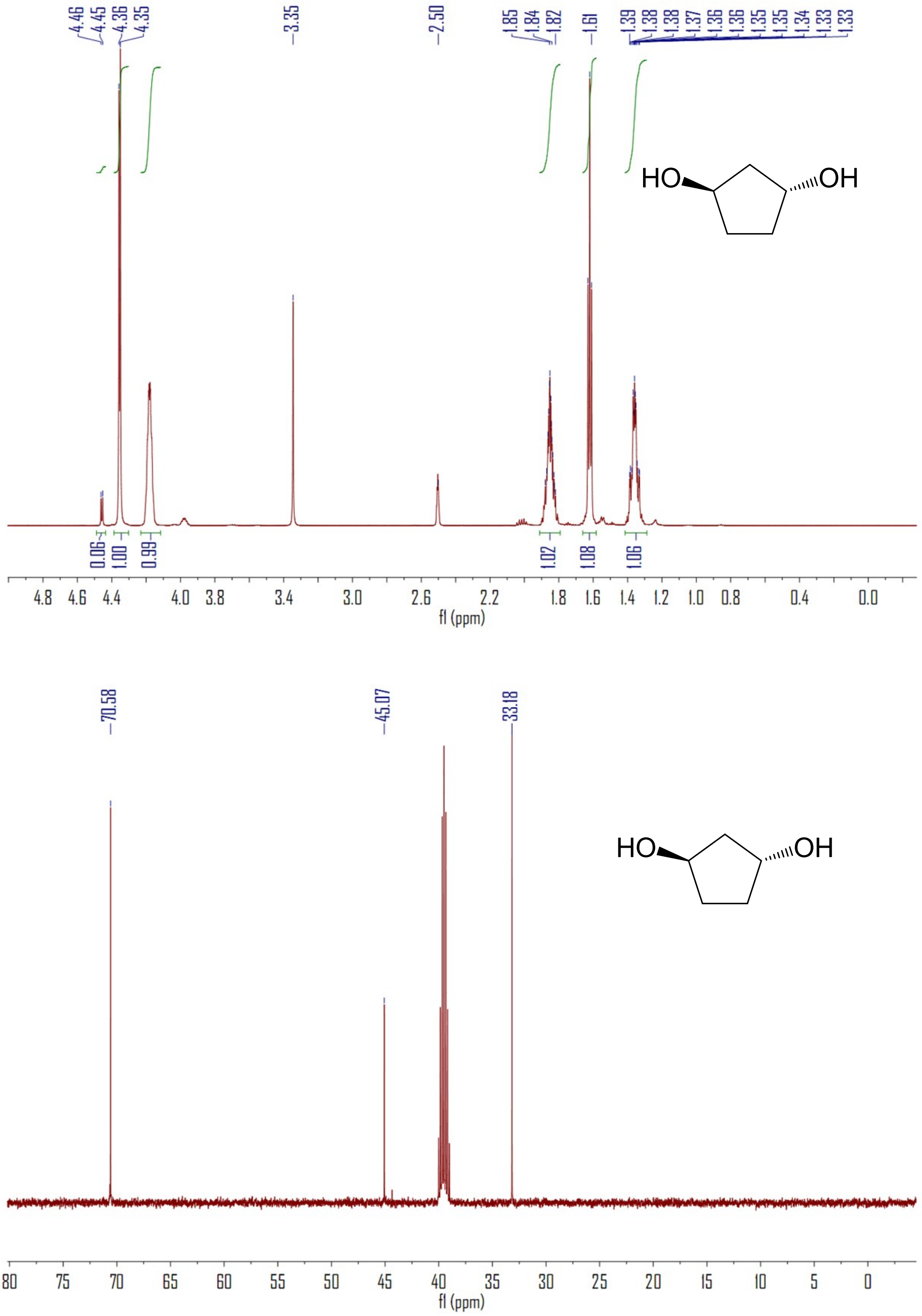


Figure S8. ^{1}H and ^{13}C NMR spectra of the *trans*-1,3-cyclopentanediol from the hydrogenation of 4-hydroxycyclopent-2-enone.

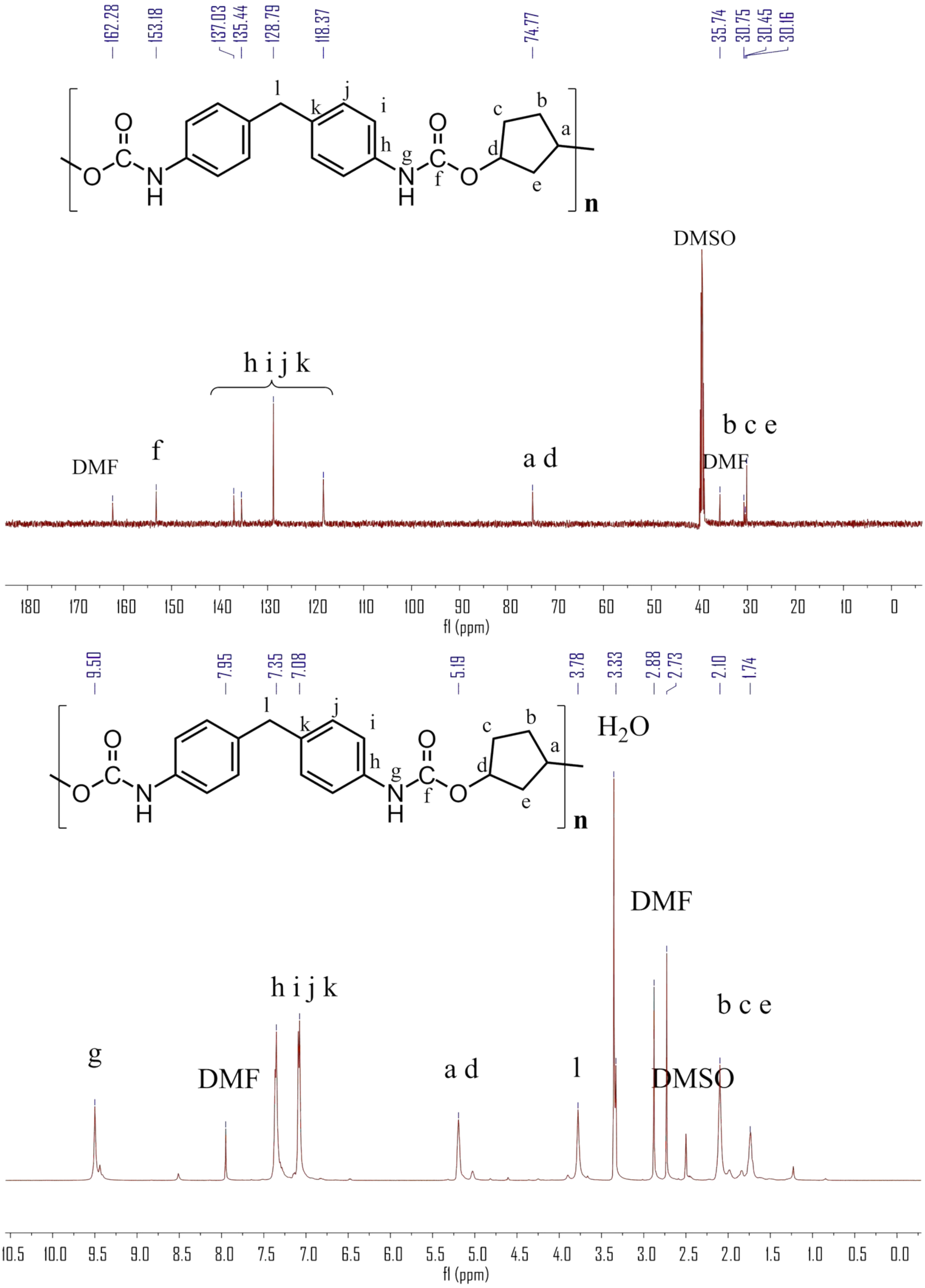


Figure S9. ^1H and ^{13}C NMR spectra of the polyurethane obtained in this work.

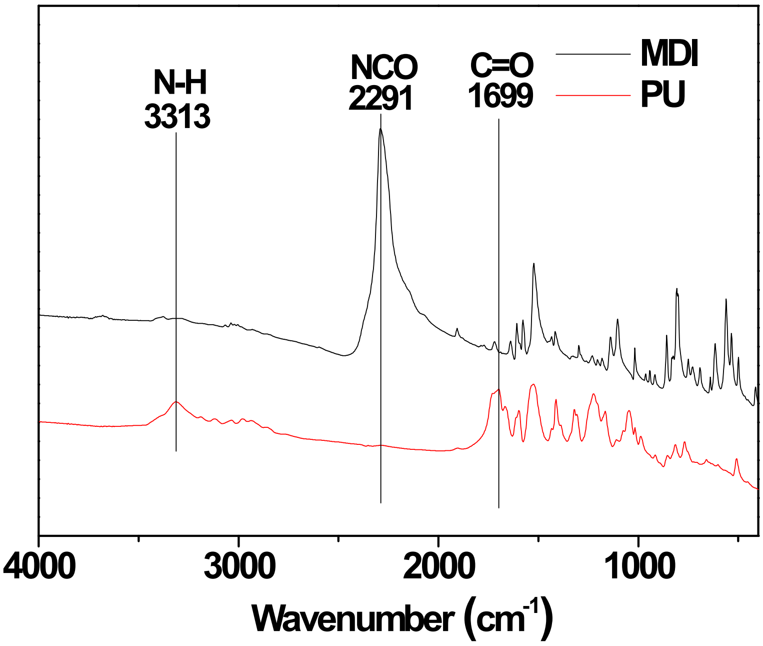


Figure S10. FT-IR spectra of diphenyl-methane-diisocyanate (black line) and the polyurethane obtained in this work (red line). According to literature,[1] the disappearance of the NCO peak at 2291 cm^{-1} and the appearance of N-H peak at 3313 cm^{-1} can be considered as the evidence for the formation of polyurethane.

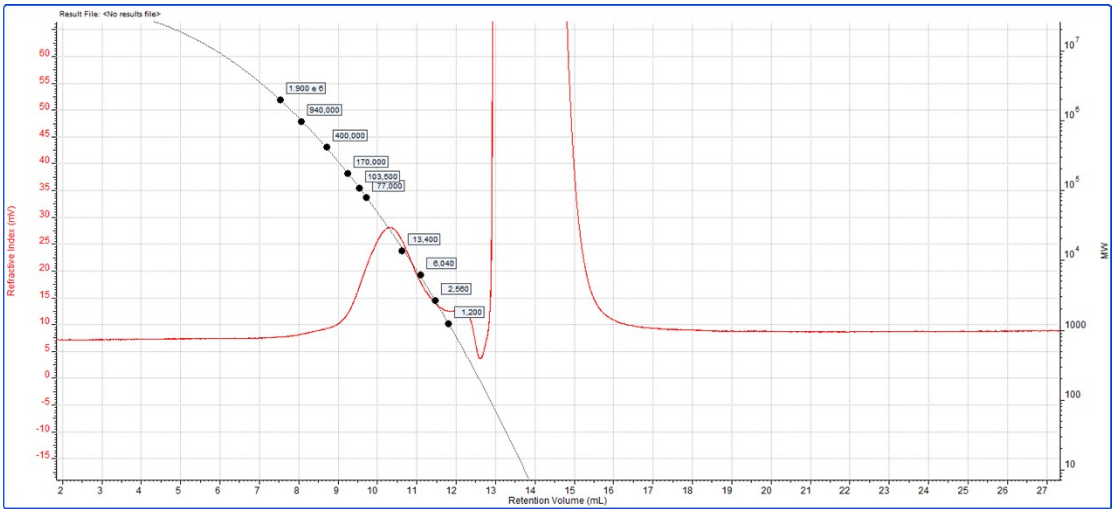


Figure S11. Gel permeation chromatography (GPC) pattern of the polyurethane obtained in this work (Mn = 17200 g mol^{-1}, PDI = 2.3).

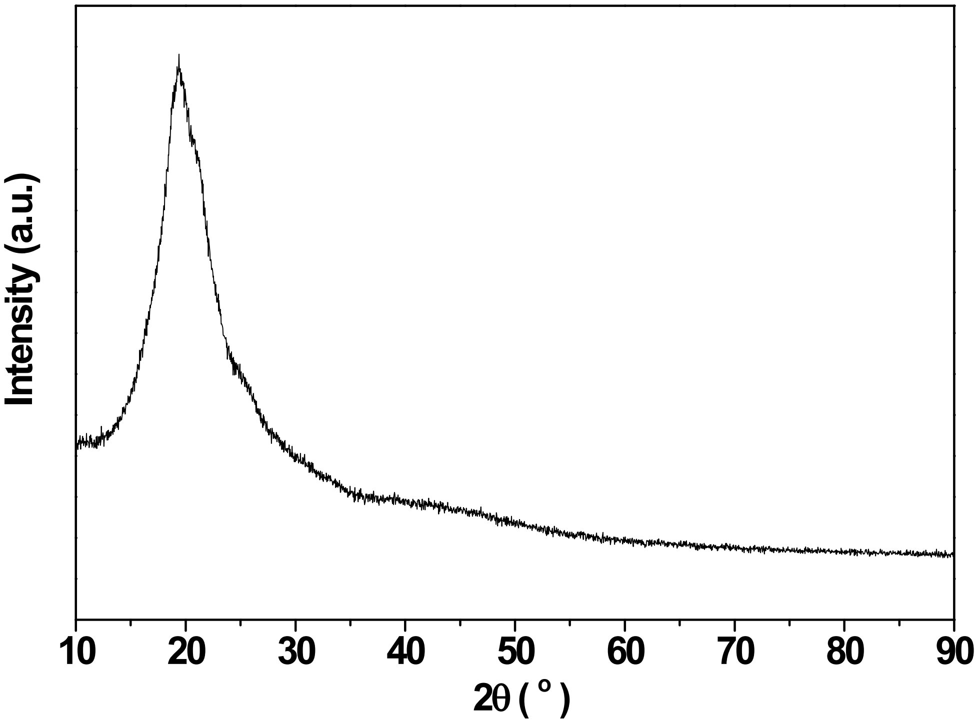
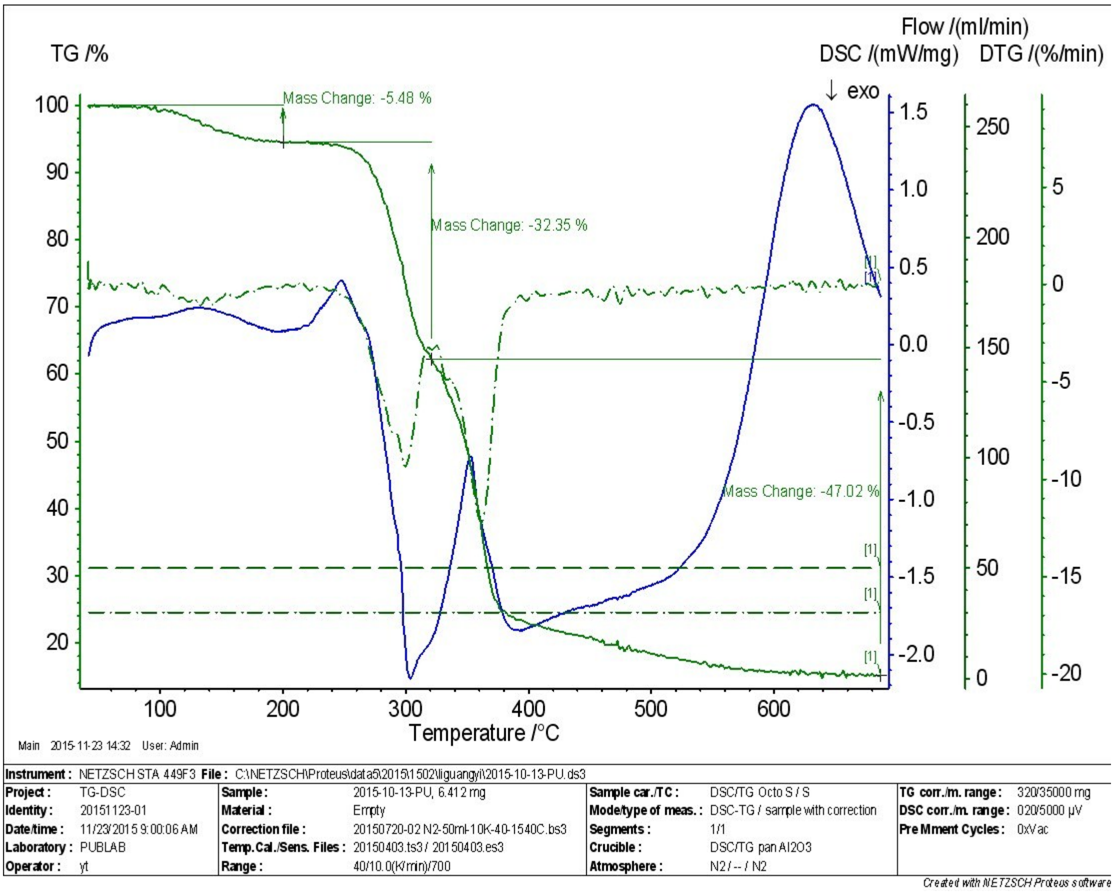


Figure S12. XRD pattern of the polyurethane obtained in this work.



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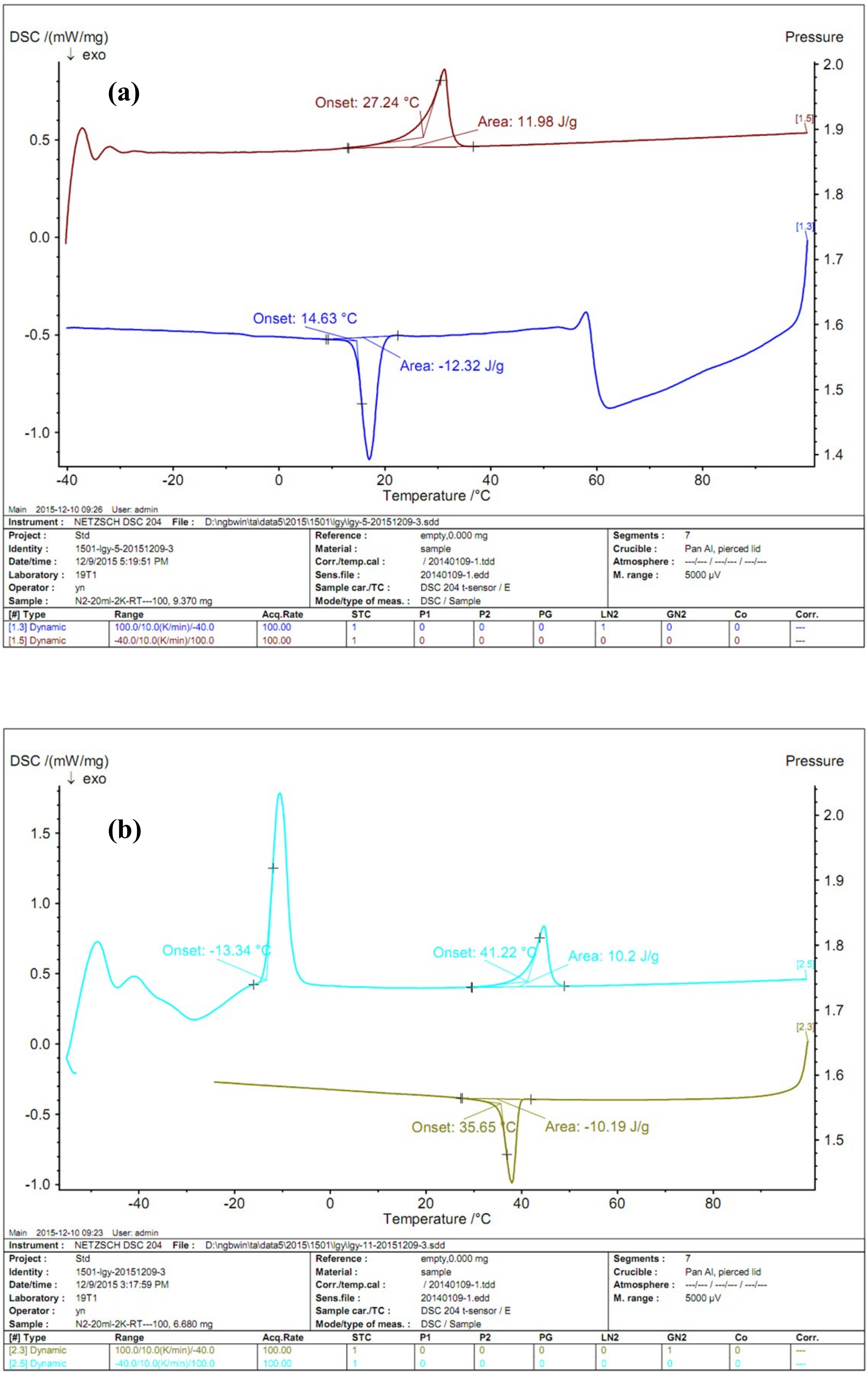
Date/time :	11/23/2015 9:00:06 AM	**Correction file :**	20150720-02 N2-50ml-10K-40-1540C.bs3	**Segments :**	1/1	**Pre Mment Cycles :**	0xVac
Laboratory :	PUBLAB	**Temp.Cal./Sens. Files :**	20150403.ts3 / 20150403.es3	**Crucible :**	DSC/TG pan Al2O3		
Operator :	yt	**Range :**	40/10.0(K/min)/700	**Atmosphere :**	N2 / -- / N2		

Created with NETZSCH Proteus software

Figure S13. TG-DSC pattern of the polyurethane obtained in this work. The first weight loss peak is caused by the evaporation of residual dimethyl formamide. In the calculation of the yield and thermal properties of polyurethane, the portion of this weight loss was deduced.



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Date/time :	12/9/2015 5:19:51 PM	**Corr./temp.cal :**	/ 20140109-1.tdd	**Atmosphere :**	---/--- / ---/--- / ---/---
Laboratory :	19T1	**Sens.file :**	20140109-1.edd	**M. range :**	5000 µV
Operator :	yn	**Sample car./TC :**	DSC 204 t-sensor / E		
Sample :	N2-20ml-2K-RT---100, 9.370 mg	**Mode/type of meas. :**	DSC / Sample		

[#] Type	Range	Acq.Rate	STC	P1	P2	PG	LN2	GN2	Co	Corr.
[1.3] Dynamic	100.0/10.0(K/min)/-40.0	100.00	1	0	0	0	1	0	0	---
[1.5] Dynamic	-40.0/10.0(K/min)/100.0	100.00	1	0	0	0	0	0	0	---

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Instrument : NETZSCH DSC 204 **File :** D:\ngbwin\ta\data5\2015\1501\lgy\lgy-11-20151209-3.sdd

Project :	Std	**Reference :**	empty,0.000 mg	**Segments :**	7
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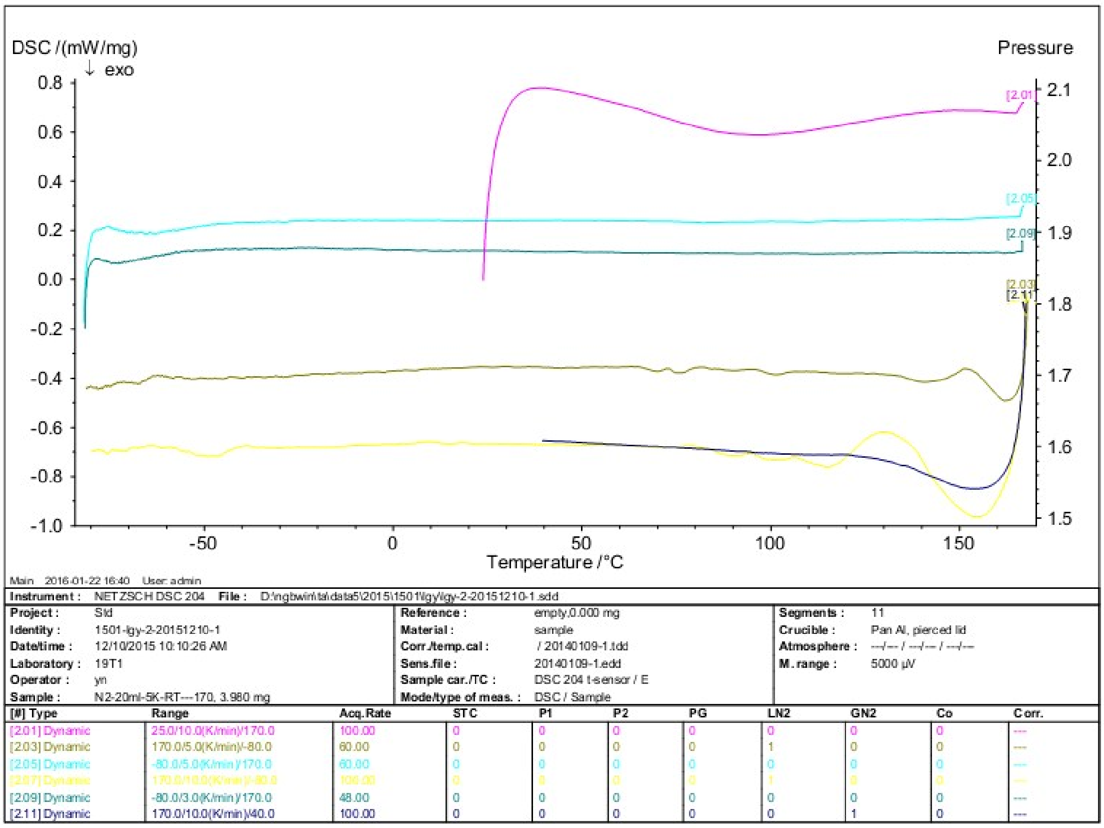
Date/time :	12/9/2015 3:17:59 PM	**Corr./temp.cal :**	/ 20140109-1.tdd	**Atmosphere :**	---/--- / ---/--- / ---/---
Laboratory :	19T1	**Sens.file :**	20140109-1.edd	**M. range :**	5000 µV
Operator :	yn	**Sample car./TC :**	DSC 204 t-sensor / E		
Sample :	N2-20ml-2K-RT---100, 6.680 mg	**Mode/type of meas. :**	DSC / Sample		

[#] Type	Range	Acq.Rate	STC	P1	P2	PG	LN2	GN2	Co	Corr.
[2.3] Dynamic	100.0/10.0(K/min)/-40.0	100.00	1	0	0	0	0	1	0	---
[2.5] Dynamic	-40.0/10.0(K/min)/100.0	100.00	1	0	0	0	0	0	0	---

Figure S14. DSC results of the *cis*-1,3-cyclopentanediol (a) and *trans*-1,3-cyclopentanediol (b) obtained in this work.



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Laboratory : 19T1
Operator : yn
Sample : N2-20ml-5K-RT---170, 3.980 mg

Reference : empty,0.000 mg
Material : sample
Corr./temp.cal : / 20140109-1.tdd
Sens.file : 20140109-1.edd
Sample car./TC : DSC 204 t-sensor / E
Mode/type of meas. : DSC / Sample

Segments : 11
Crucible : Pan Al, pierced lid
Atmosphere : ---/--- / ---/--- / ---/---
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1	P2	PG	LN2	GN2	Co	Corr.
[2.01] Dynamic	25.0/10.0(K/min)/170.0	100.00	0	0	0	0	0	0	0	---
[2.03] Dynamic	170.0/5.0(K/min)/-80.0	60.00	0	0	0	0	1	0	0	---
[2.05] Dynamic	-80.0/5.0(K/min)/170.0	60.00	0	0	0	0	0	0	0	---
[2.07] Dynamic	170.0/10.0(K/min)/-80.0	100.00	0	0	0	0	1	0	0	---
[2.09] Dynamic	-80.0/3.0(K/min)/170.0	48.00	0	0	0	0	0	0	0	---
[2.11] Dynamic	170.0/10.0(K/min)/40.0	100.00	0	0	0	0	0	1	0	---

Figure S15. DSC results of the polyurethane obtained in this work.

Table S1. Carbon yields of 4-hydroxycyclopent-2-enone from the aqueous phase rearrangement of furfuryl alcohol reported in the literature.

Reaction conditions	Carbon yield (%)	Reference
0.443 mol L^{-1} aqueous solution of furfuryl alcohol 433 K, 15 min.	38.3	[2]
15.0 g furfuryl alcohol in 300 mL water; 433 K, 2 MPa H_2, 8 h.	52	[3]
0.25 mol L^{-1} aqueous solution of furfuryl alcohol under microwave irradiation (300 W). 473-483 K, 1.55-1.76 MPa.	80	[4]
0.25 mol L^{-1} aqueous solution of furfuryl alcohol (pH adjusted to 4 with acetic acid), 1.8 mol min^{-1}, feed with toluene at 0.2 mL min^{-1} to a micro-reactor. Residence time: 53 s.	87	[4, 5]
0.4 mol L^{-1} furfuryl alcohol, 1 mol L^{-1} N-methyl pyrrolidinone, 0.031 mol L^{-1} acetic acid in water; microreactor; 513 K, 1.5 min.	98	[6]

Table S2. Carbon yields of 3-hydroxycyclopentanone from the room-temperature aqueous phase hydrogenation of 4-hydroxycyclopent-2-enone reported in the previous work of Ulbrich.[5]

Catalyst	Hydrogen pressure (MPa)	Reaction time (h)	Carbon yield of 3-hydroxycyclopentanone (%)
10wt.% Pd/C	0.1	18	53
10wt.% Pd/C	0.5	0.25	86
10wt.% Pt/C	0.5	0.25	54
5wt.%Pd/Al_2O_3	0.5	0.25	92
10-20wt.% $Pd(OH)_2$/C	0.5	0.25	59

Table S3. 4-Hydroxycyclopent-2-enone conversion and the carbon yield of 1,3-cyclopentanediol from the hydrogenation of 4-hydroxycyclopent-2-enone over the Raney Ni catalyst. Reaction conditions: 433 K, 5 MPa H_2, 1 h; 300 g crude 4-hydroxycyclopent-2-enone in 1600 g tetrahydrofuran and 35.0 g Raney Ni catalyst were used in the test.

Initial concentration of 4-hydroxycyclopent-2-enone (wt.%)	15.8
Conversion of 4-hydroxycyclopent-2-enone (%)	100
Carbon yield of 1,3-cyclopentanediol (%)	92.8

Table S4. Thermal properties of polyurethane obtained in this work.

Sample	$T_{d\ 5\%}$ (K)	$T_{d\ 10\%}$ (K)	$T_{d\ max}$ (K)	T_g (K)	T_m (K)
Polyurethane	547	559	572	-[a]	519-522

$T_{d\ 5\%}$ and $T_{d\ 10\%}$ mean the temperatures when 5% and 10% polyurethane were degraded. $T_{d\ max}$ means the temperature when the maximum degradation rate of the polyurethane was reached. T_g means the glass state temperature of the polyurethane. T_m means the melting point of the polyurethane.

[a] T_g was not observed (see Figure S15).

Table S5. The amounts of base sites on the surfaces of solid base catalysts (measured by CO_2-TPD).

Catalyst	Amount of base sites (mmol kg^{-1})
CeO_2	1.08
MgO	91
CaO	140
MgAl-HT	282.60

Table S6. The output quantity and purity of batch distillation

Entry	Quantity of distillate (g)	Purity of 1,3-cyclopentanediol[a]	Cumulative quantity of distillate (g)
1	11.9	9.1%	11.9
2	6.7	97.1%	18.6
3	7.3	98.5%	25.9
4	8.3	98.8%	34.2
5	10.2	-[b]	44.4
6	9.1	-	53.5
7	11.4	99.5%	64.9
8	10.8	-	75.7
9	11.9	-	87.5
10	9.9	-	97.4
11	10.6	99.2%	108.0
12	7.0	-	115.0
13	10.7	-	125.7
14	8.2	98.1%	133.8
15	7.7	98.3%	141.5
16	8.9	97.8%	150.4
17	10.1	97.8%	160.5
18	9.1	97.7%	169.5
19	8.7	96.7%	178.2
20	8.3	91.0%	186.6

Experimental conditions: 253 g crude 1,3-cyclopentanediol, rebolier temperature 423 K, overhead vacuum was 96 kPa. Reflux time: 2 h. The overhead products were collected at the specified reflux ratio of 10:1. The crude 1,3-cyclopentanediol was prepared by the vacuum distillation of tetrahydrofuran solution of 1,3-cyclopentanediol from the hydrogenation of 4-hydroxycyclopent-2-enone with a rotary evaporator.

[a] The purity was measured by GC analysis. [b] This sample purity wasn't analyzed.

References

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