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Supporting Materials for

Renewable High-Density Spiro-fuel from Lignocellulose-Derived Cyclic Ketones

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1 Materials

Cyclohexanone (99.5%), cyclopentanone (99.5%) were obtained from Tianjin Guangfu Fine Chemical Research Institute. Titanium tetrachloride, Zn powder, anhydrous magnesium sulfate, sodium carbonate, sodium bicarbonate, sodium chloride, diethylene glycol, n-Pentane, methanol, tetrahydrofuran, ether, dichloromethane were purchased from Tianjin Yuanli Chemical Co., China. Potassium tert-butoxide (99%), hydrazine hydrate (80%), Tin tetrachloride (99.9%), were obtained from Beijing Bailingwei Technology Co., China. Acetonitrile was supplied by Shanghai Aladdin Biochemical Technology Co., China. All chemicals were used without further purification.

2 Experiment

2.1 Reductive coupling of cyclic ketones

To a gray suspension of Zn powder (26 g, 0.4 mol) and ethyl ether (300 mL) was added TiCl₄ (11 mL, 0.1 mol) under nitrogen atmosphere. After stirring for 10 min, cyclohexanone (9.814 g, 0.1 mol) or cyclopentanone (8.412 g, 0.1 mol) was added dropwise. Then the reaction mixture was stirred under reflux and nitrogen atmosphere for 15h. The reaction mixture was quenched with 400mL of 10 wt% Na₂CO₃ aqueous solution followed by 100 mL ether. The suspension was filtered, and the filtrate was twice extracted with 100 mL ether. The extracts were washed with saturated NaC1, dried over anhydrous MgSO₄, and finally purified by recrystallization from ether.

2.2 Pinacol rearrangement

Bicyclopentyl-1,1-'diol (7.828 g. 39.5 mmol) or bicyclohexyl-1,1'-diol (6.715 g. 39.5 mmol) was dissolved in 200 mL of CH_2Cl_2 , stirred with 10 g anhydrous magnesium sulfate at room temperature under nitrogen for 2h, treated with 5 mL $SnCI_4$ in an ice bath and stirred for 10 min. Then 100 mL CH_2Cl_2 and 100 mL saturated aqueous NaHCO₃ was added and stirred for 10 min. After filter, the organic layer was separated, and the trace organics in aqueous layer was extracted with CH_2Cl_2 , then The organics was washed with brine, dried over anhydrous MgSO₄, and concentrated.

2.3 Wolff-Kishner-Huang reduction of spiro ketones

A mixture of spiro[5, 6]dodecan-7-one (6.098 g, 31.08 mmol) or spiro[4, 5]decan-6-one (4.724 g, 31.08 mmol), 80% hydrazine hydrate (30 mL) in diethylene glycol (100 mL) was refluxed for 1.5 h. Then the excess hydrazine hydrate was distilled off. After cooling to room temperature, t-BuOK (10 g) was added and heated at 190-200°C for another 3 h. The reaction mixture was extracted with pentane (100 mL×3), and the extracts was distillated to obtain the spirocycloalkane.

3 Analytical method

The products were determined qualitatively using an Agilent 6890/5975 gas chromatography-mass spectrometry (GC-MS) equipped with HP-5 capillary column (30 m × 0.5 mm) and ¹³C and ¹H NMR spectra were collected using Bruker Avance 400M or Bruker Avance 500M Spectrometers spectrometer. The concentration of each compounds was analyzed by a gas chromatography (Agilent-7820A) equipped with an FID detector and a capillary column HP-1 capillary column (30 m × 0.53 mm). Fourier transform infrared (FTIR) spectra of the samples were recorded using a Bruker Vertex 70 IR spectrometer (4 cm⁻¹) in potassium bromide media.

4 Conversion and selectivity calculation

The conversion and selectivity were calculated as follows:

 $conversion (wt\%) = \frac{m(reactant converted)}{m(original reactant)} \times 100\%$ $selectivity (wt\%) = \frac{m(product produced)}{m(reactant converted)} \times 100\%$ $yield (wt\%) = conversion \times selectivity$

Take the following reaction as example:



$$conversion of cyclohexanone(wt\%) = \frac{m(cyclohexanone \ converted)}{m(original \ cyclohexanone)} \times 100\%$$

$$selectivity of \ bicyclohexyl - 1,1' - diol \ (wt\%) = \frac{m(bicyclohexyl - 1,1' - diol)}{m(cyclohexanone \ converted)} \times 100\%$$

$$selectivity \ of \ cyclohexanol \ (wt\%) = \frac{m(cyclohexanol)}{m(cyclohexanone \ converted)} \times 100\%$$

5 Yield of by-products

Cyclohexanol and cyclopentanol by-products are produced with 21.5% and 23.9% yield in reductive coupling of cyclohexanone and cyclopentanone, respectively. 1,1'-bicyclohexene and 1,1'-bicyclopentene by-products are produced with 20.6% and 5.6% yield in pinacol rearrangement of bicyclohexyl-1,1'-diol and bicyclopentyl-1,1'-diol. In Wolff-Kishner-Huang reduction of spiro[5, 6]dodecan-7-one and spiro[4, 5]decan-6-one produces by-products with yield of 16.6% and 9.9%, respectively.

6 Measurements of fuel properties

The density was measured by Mettler Toledo DE40 density meter according to ASTM D4052. Freezing point was measured according to ASTM D2386, and kinematic viscosity was determined using capillary viscometer according to ASTM D445. The net heat of combustion was measured by the IKA-C6000 isoperibol Package 2/10 Calorimeter according to ASTM D240-02. Differential scanning calorimetry (DSC) was performed on a NETZSCH-DSC 200 F3 Maia differential scanning calorimeter using hermetically sealed aluminum pans with a nitrogen flow of 50 mL/min. High purity indium was used to calibrate the calorimeter. Sample sizes were between 5-10 mg and the samples were ramped from -100 °C to 50 °C, down to -100 °C and then back to 50 °C, all at 10 °C /min.

Scheme S1. Reaction pathway of reductive coupling



vicinal dialkoxides intermediate



Scheme S2. Side reaction of reductive coupling



Scheme S3. Reaction pathway of pinacol rearrangement



Scheme S4. Side reaction of pinacol rearrangement



n=1 bicyclopentyl-1,1'-diol n=2 bicyclohexyl-1,1'-diol

n=1 1,1'-bicyclopentene n=2 1,1'-bicyclohexene

Figure S1. 1 H (a) and 13 C (b) NMR spectra of pinacols.

bicyclohexyl-1,1'-diol ^{1}H NMR $\delta_{\rm H}$ (500 MHz, CDCl_3) δ 1.84 (2H, s), 1.72-1.62 (6H, m), 1.61-1.50 (8H, m), 1.38-1.27 (4H, m), 1.14-1.02 (2H, m) ¹³C NMR δ_C (500MHz, CDCl₃) δ 75.90, 30.93, 26.12, 22.01. 1a012016-12-30-1HCDCL3-XJJ-4 STANDARD PROTON PARAMETERS а 2.964 2.00<u>4</u> 1.084 0.0 .0 7.5 7.0 6.5 6.0 5. 5 5.0 4.5 4.0 3.5 f1 (ppm) 3. 0 2.5 2.0 1.5 1. 0 0.5 1a2017-01-03-1HCDCL3-XJJ-4# 2017-01-03-13CCDCL3-XJJ-5# -26.12 -22.01 -75.90 b

55 50 f1 (ppm)

40

35

45

30

25

15

20

90

85

80

75

70

65

60

-32

-30

-28 -26 -24 -22 -20 18 16 14 12 10

--2

-8.0

-7.5 -7.0 -6.5 -6.0 -5.5 5.0 4.5 4.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0 0.5 0.0 --0.5

-0.5



1 H NMR δ_{H} (400 MHz, CDCl₃) δ 1.98 (2H, brs), 1.97, 1.90-1.55 (16H, m)



Figure S2. Mass spectra of pinacols.



Spectrum of bicyclohexyl-1,1'-diol synthesized in this work.

Standard spectrum of bicyclohexyl-1,1'-diol in NIST.



Prob is 87.7 % with NIST# 156581. Name: 1,1'-Bicyclohexyl-1,1'-diol MW: 198 CAS#: 2888-11-1 NIST#: 156581



Spectrum of bicyclopentyl-1,1'-diol synthesized in this work. $\pm \underline{c}$

The molecular ion peak m/z 170.1 isn't detected because the structure is unstable under the electronic flow bombardment. The m/z 152.1 and m/z 134.1 can generate by losing one or two –OH. Prob is 88.4 % with NIST# 154712. Name: 1,1'-Bicyclopentyl-1,1'-diol MW: 170 CAS#: 5181-75-9 NIST#: 154712 Figure S3. Mass spectra of by-products in reductive coupling.

100-ОH 50-62 65 (Text File) Component at scan 799 (4.913 min) [Model = +57u] in E:\A\\\XJJ\20160627\0625NA.D\DAT

Spectrum of cyclohexanol synthesized in this work.

Standard spectrum of cyclohexanol in NIST.



Prob is 84.3 % with NIST# 291439. Name: Cyclohexanol MW: 100 CAS#: 108-93-0 NIST#: 291439

Spectrum of cyclopentanol synthesized in this work.



Standard spectrum of cyclopentanol in NIST.



Prob is 90.7% with NIST# 233847. Name: Cyclopentanol MW: 86 CAS#: 96-41-3 NIST#: 233847

Figure S4. 1 H (a) and 13 C (b) NMR spectra of spiro ketones.

spiro[5, 6]dodecan-7-one ¹H NMR $\delta_{\rm H}$ (500 MHz, CDCl₃) δ 2.47(2H, t), 1.76-1.27 (18H, m), ¹³C NMR $\delta_{\rm C}$ (500 MHz, CDCl₃) δ 218.17, 50.88, 39.56, 34.91, 33.38, 30.37, 26.62, 25.92, 24.15, 22.00.



spiro[4, 5]decan-6-one

¹**H NMR** $\delta_{\rm H}$ (500 MHz, CDCl₃) δ 2.38 (2H, t), 2.10-1.99 (2H, m), 1.86-1.76 (2H, m), 1.74-1.67 (4H, m), 1.63-1.52 (4H, m), 1.44-1.33 (2H, m).

 ^{13}C NMR δ_{C} (500 MHz, CDCl₃) 214.87, 57.08, 40.18, 39.67, 35.68, 27.57, 25.46, 23.14.





Figure S5. Mass spectra of spiro ketones.

Spectrum of spiro[5, 6]dodecan-7-one synthesized in this work.



Standard spectrum of spiro[5, 6]dodecan-7-one in NIST.



Prob is 93.3 % with NIST# 187784. Name: Spiro[5, 6]dodecan-7-one MW: 180 CAS#: 4728-90-9 NIST#: 187784





Standard spectrum of spiro[4, 5]decan-6-one in NIST.



Prob is 94.3 % with NIST#190202. Name: Spiro[4, 5]decan-6-one MW: 152 CAS#: 13388-94-8 NIST#: 190202

Figure S6. Mass spectra of by-products in pinacol rearrangement.

Spectrum of 1,1'-bicyclohexene synthesized in this work.



The molecular ion peak is 162. 81 is a fragment ion of

Spectrum of 1,1'-bicyclopentene synthesized in this work.



The molecular ion peak is 134.

67 is the fragment ion of



Figure S7. ¹H (a) and ¹³C (b) NMR spectra of spirocycloalkanes.



spiro[4, 5]decane ¹H NMR $\delta_{\rm H}$ (400 MHz, CDCl₃) δ 1.63-1.25 (18 H, m). ¹³C NMR $\delta_{\rm C}$ (400 MHz, CDCl₃) 42.59, 38.59, 38.44, 26.53, 24.50, 23.83.



Figure S8. Mass spectra of spirocycloalkanes.



Spectrum of spiro[5, 6]dodecane synthesized in this work. 丰度

Standard spectrum of spiro[5, 6]dodecane in NIST.



Prob is 89.4% with NIST# 6224. Name: Spiro[5, 6]dodecane MW: 166 CAS#: 181-15-7 NIST#: 6224



Spectrum of sample spiro[4, 5] decane synthesized in this work. $\pm g$

Standard spectrum of spiro[4, 5]decane in NIST.



Prob is 85.8 % with NIST# 39290.. Name: Spiro[4, 5]decane MW: 138 CAS#: 176-63-6 NIST#: 39290 In Wolff-Kishner-Huang reduction of spiro ketones, by-products should be some bridged compound that we do not know its exact structure (Bulletin of the Chemical Society of Japan, 1969, 42, 1351-1353).

Figure S9. FTIR spectra of spiro[4, 5]decane (A) and spiro[5, 6]dodecane (B)



spiro[4, 5]decane characteristic peaks: 1448, 2854, 2923 cm^{-1.}







2923 cm⁻¹ and 2850 cm⁻¹ belongs to the stretching vibration of C-H in $-CH_2$ -.1452 cm⁻¹ is the rocking vibration of methyl and methine.

Figure S10. Mass spectra of products synthesized from cycloheptanone.



Spectrum of bicycloheptyl-1,1'-diol synthesized in this work.

Spectrum of spiro[6.7]tetradecan-8-one synthesized in this work.



100-50-190 200 (Text File) Component at scan 1223 (10.475 min) [Model = +81u] in E:\A\\\XJJ\170823\170823HUANG

Spectrum of spiro[6.7]tetradecane synthesized in this work.

Figure. S11 Differential scanning calorimetry (DSC) of spiro[5, 6]dodecane (A) and spiro[4, 5]decane (B).

