Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Metal-acid nanoplates-supported ultrafine Ru nanoclusters for efficient catalytic fractionation of lignin into aromatic alcohols

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Part 1: Catalyst analysis

0.2. Characterization methods

i. X-ray Diffraction (XRD) Analysis

To examine the crystallinity of catalyst and lignin (alkaline, samples were analyzed by X-ray diffraction (XRD) performed on a Philips X'pert Pro Super diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). The samples were finely crushed and dried in vacuum over (10^{-4} MPa), the operation voltage was maintained at 40 kV, and the current at 200 mA and sample scanning was done from a 2θ value of 5° to 60° at the rate of 4.3 degree/min.

ii. Fourier Transform Infra-red (FT-IR) Spectroscopy

To assess the existence of functional group in catalyst, biomass feedstock and alkaline lignin FTIR spectra were recorded by using MAGNA-IR750 (Nicole instrument Co. USA) infrared spectrophotometer. The samples were measured using a KBr-pellet method (resolution of 4 cm^{-1}, wavenumber range 4000-400 cm^{-1}). Prior to the analysis samples were dried in vacuum over (10^{-4} Mpa) for 2 h.

iii. Scaning electon microscopy (SEM) analysis

Scanning electron microscopy (SEM) images were captured on a field-emission scanning electron microanalyzer (JEOL JSM-6700F, 15 kV).

iv. High-Resolution Transmission electron microscopy analysis

The structural morphology and microstructure of Ru/α-HfP catalyst samples was examined by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) on JEM-2010 transmission electron microscope at an acceleration voltage of 200kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and elemental mapping were taken on JEOL JEM-ARF200F atomic resolution analytical microscope. Powder samples were dispersed in ethanol by ultra-sonication and then deposited on carbon coated Cu grids. The elemental composition of the samples was determined by using the EDAX (JEOL X-ray micro analysis system TEM) installed on the same TEM machine.

v. Inductively coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis

The element content in Ru/HfP NPs catalyst was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a PerkinElmer Optima 8000 ICP-AES/ICP-OES spectrometer. Typically, 10 mg of Ru/α-HfP catalyst sample was dissolved in H_2SO_4:H_2O_2 (4:1). Then, the mixture solution was transferred to Teflon lined stainless steel autoclave and placed at 180 °C oven for 3 h. Later, the digested solution was filtered using 0.22 micron syringe filter and diluted with ultra pure H_2O after that the samples were analyzed by PerkinElmer Optima 8000 ICP-AES/ICP-OES spectrometer.

vi. X-ray photoeletron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) was carried out at the catalysis and surface science endstation in National Synchrotron Radiation Laboratory (NSRL), Hefei. The X-ray photoelectron spectroscopy (XPS) measurement were conducted on an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific, USA) at room temperature under vacuum of 10^{-8}-10^{-9} Torr using monochromatized Al Kα radiation (1486.92 eV). The sample was exposed to air before assessment. During analysis the residual pressure was kept below 1×10^{-7} Pa. Meanwhile, C 1s peak was used for binding energy correction for all XPS spectra.

vii. Thermo Gravimetric Analysis –Differential Thermal Analysis (TGA-DTA)

Thermal decomposition of catalyst and lignin samples were carried out under N_2 atmosphere with a heating rate of 10 °C min^{-1} with a Shimadzu TGA-50H thermogravimetric analyzer.

viii. Nuclear Magnetic resonance (NMR) analysis

Heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectra for extracted bio-oil sample were recorded on Bruker AVANCE 400MHz spectrometer. Bio-oil (60 mg) was dissolved deuterated chloroform ($CDCl_3$) 1 mL as solvent and tetramethylsilane (TMS) as reference. Chemical shifts were quoted as part per million (ppm) to 0.0 ppm for reference.

ix. Solid-state ^{13}C NMR analysis

The technique was involved to study the functional groups in lignin. ^{13}C NMR was done in Bruker Avance 400 , Germany ; at 10 kHz with a pulse program Cp, av and number of scans was 6214 . The sample was vacuum dried before analysis.

x. Nitrogen sorption studies

Nitrogen sorption measurement was performed using a Coulter SA 3100 adsorption analyzer, giving adsorption/desorption isotherm, specific surface area and pore volume automatically. The Brunauer, Emmett and Teller (BET) equation was used to calculate the surface area, while the pore size was calculated from the adsorption branch of the isotherm using thermodynamic based Barret-Joyner-Halenda (BJH) method.

xi. Temperature programmed Desorption (TPD-NH_3) analysis

Ammonia-temperature-programmed desorption (NH_3-TPD) was measured on a setup (micromeritics instrument corporation AutoChem II 2920 Version 5.01), sample was loaded into U-shaped quartz micro reactor and pretreated at 400 °C for 0.5 h in He gas. After pretreatment, the sample was cooled down to 80 °C and saturated with NH_3 (30 cm^3/min for 1 h and subsequently purged with He (60 cm^3/min), for 2 h to remove the physisorbed ammonia. Finally, TPD was performed by heating the sample from 80 °C to 800 °C at a heating rate of 10 °C/min under He flow (50 cm^3/min). The concentration of NH_3 in the exit gas was continuously detected by a gas chromatograph (SHIMADZU) with a thermal conductivity detector.

xii. Elemental analysis

The content of Carbon, Hydrogen, Nitrogen, and Sulfur elements in raw lignocellulose samples was determined by using a Vario EL elemental analyzer. The samples were first dried to remove moisture prior to analysis.

UV-Visible Spectroscopy

The UV-vis absorption spectrum was measured with a Shimadzu UV-2510 spectrophotometer in the region of 200 to 800 nm for alkaline lignin.

1.2. Supplementary figures

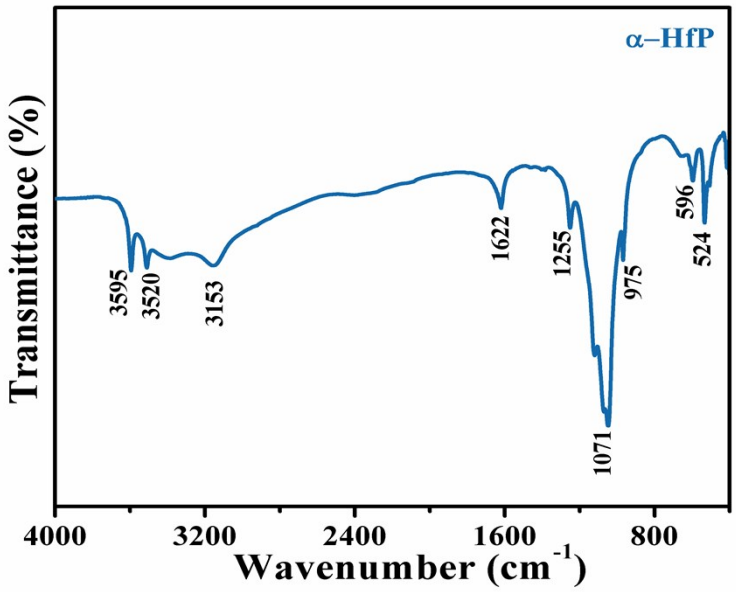

Fig. S1 FT-IR spectrum of α-HfP nanoplates.

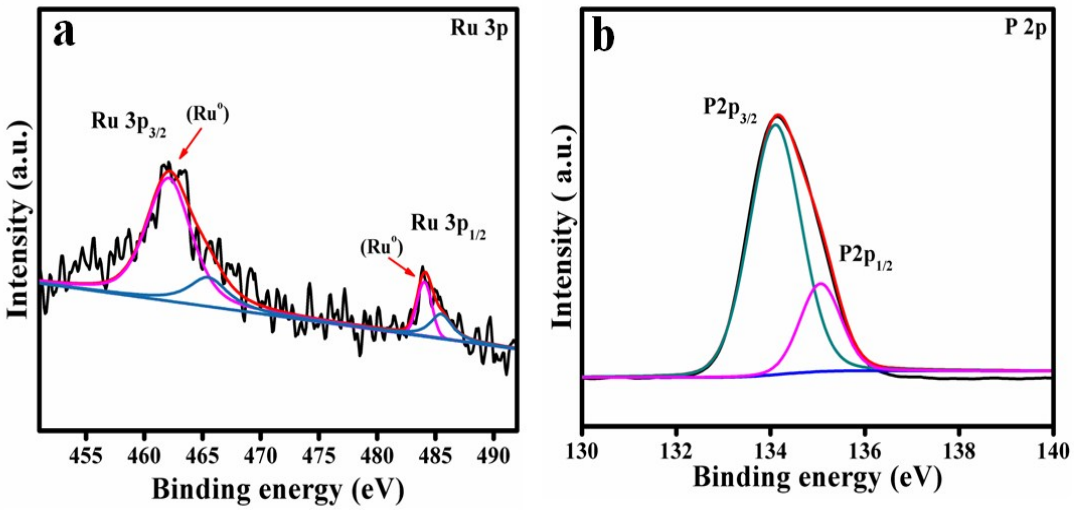

Fig. S2 XPS spectra of Ru 3p (a) and P 2p (b) of Ru/α-HfP nanocatalyst.

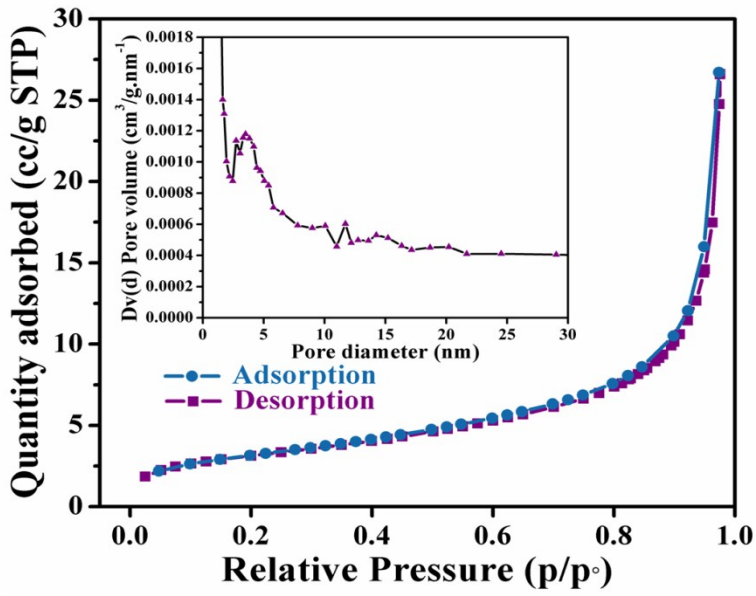

Fig. S3 N_2 adsorption-desorption isotherm and (inset) BJH pore-size distribution of Ru/α-HfP catalyst**.**

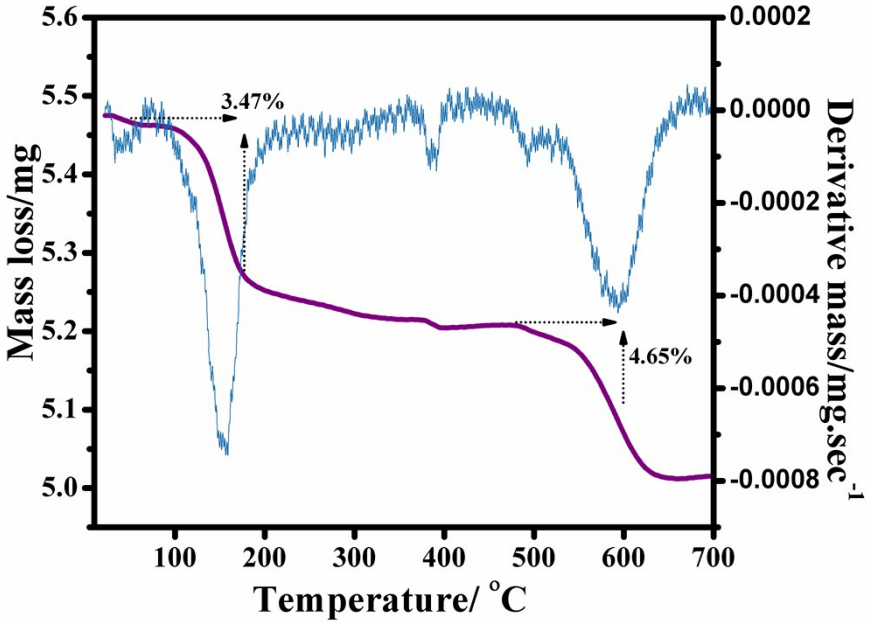

Fig. S4 TGA/DTG analysis of α-HfP sample.

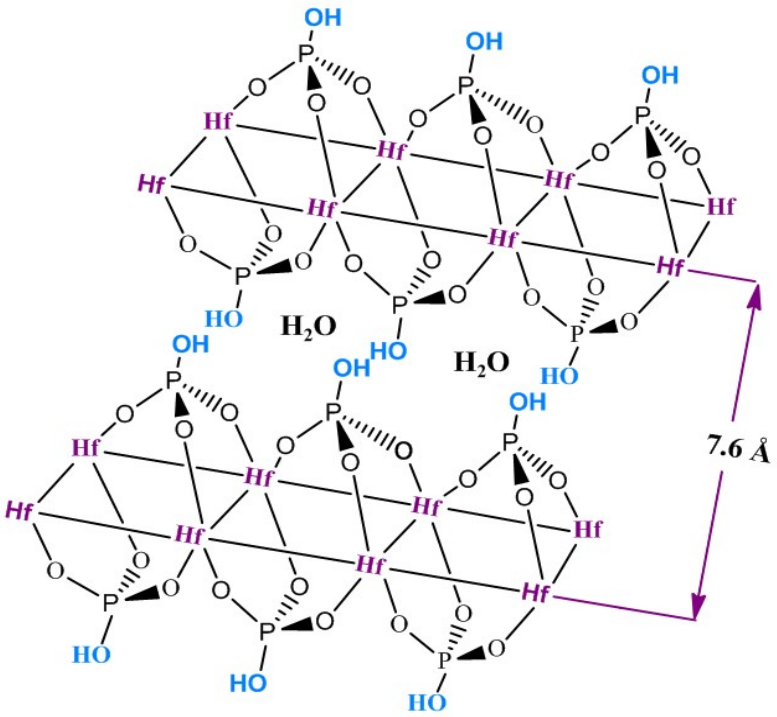

Fig. S5 Schematic structural representation of α-HfP.

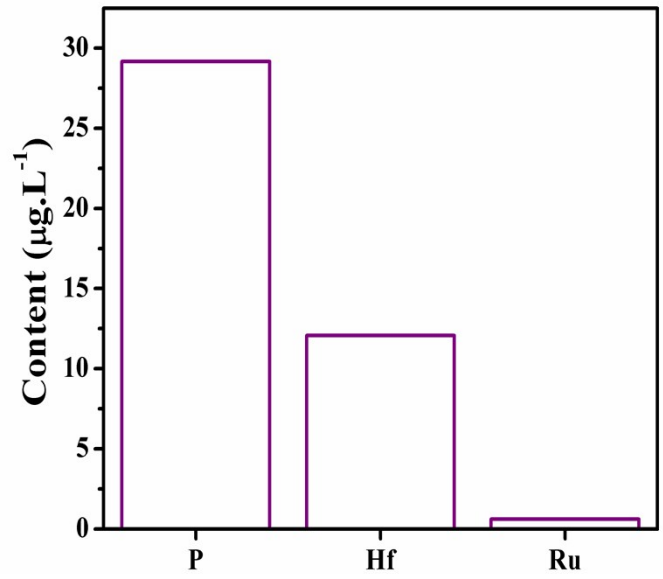

Fig. S6 ICP-MS analysis of catalyst elements.

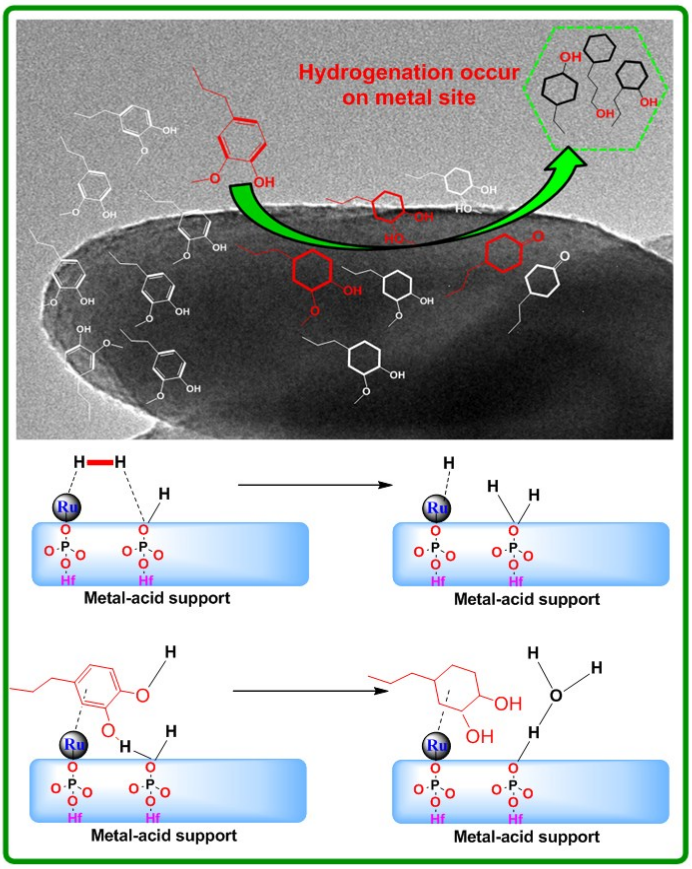

Fig. S7 Plausible reaction route from lignin-derived monomer to hydrogenated cyclic-alcohols upon metal/acid bifunctional Ru/α-HfP catalyst.

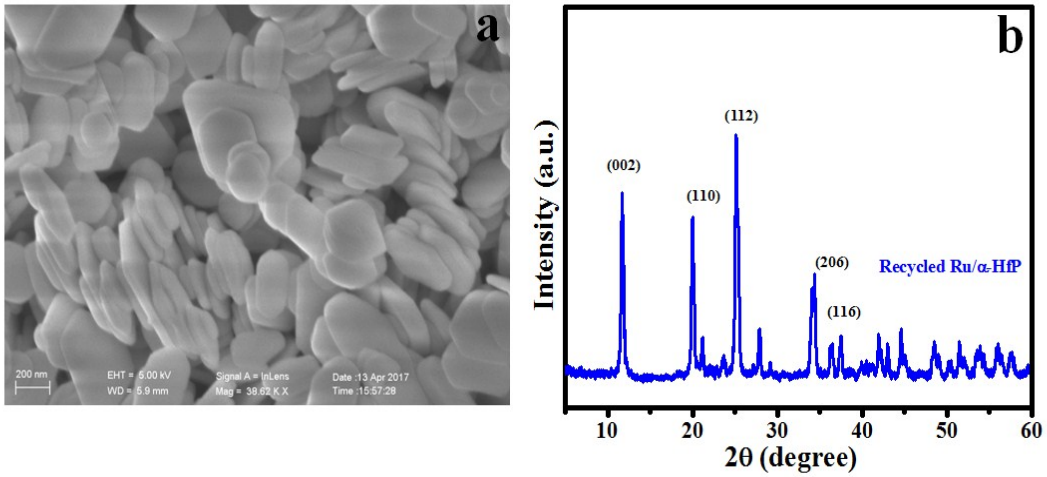

Fig. S8 (a) SEM image (b) XRD pattern of recycled Ru/α-HfP nanocatalyst.

Part 2: Substrate analysis

Table S1 The contents of C, H, N, S in different lignocellulosic biomass

Substrate	Analyze time	C (%)	H (%)	N (%)	S (%)
Pine	1	47.33	6.25	0.62	0.14
	2	47.12	6.28	0.59	0.11
	Average	**47.22**	**6.26**	**0.60**	**0.12**
Poplar	1	48.54	6.28	0.23	0.01
	2	46.83	6.23	0.21	0.02
	Average	**47.68**	**6.25**	**0.22**	**0.015**
Walnut	1	47.23	6.61	1.48	0.10
	2	48.01	6.55	1.48	0.10
	Average	**47.62**	**6.58**	**1.48**	**0.10**
Miscanthus	1	43.22	5.18	0.24	0.00
	2	43.31	5.14	0.22	0.00
	Average	**42.95**	**5.16**	**0.23**	**0.00**
Birch	1	48.26	6.43	0.10	0.05
	2	48.14	6.33	0.08	0.03
	Average	**48.2**	**6.38**	**0.09**	**0.04**
Oak	1	44.32	5.32	0.05	0.02
	2	43.88	5.33	0.04	0.03
	Average	**44.10**	**5.32**	**0.04**	**0.02**
Lignin, alkaline (commercial)	1	50.95	-	0.30	3.69
	2	51.12	-	0.21	3.12
	Average	**51.04**	**-**	**0.25**	**3.41**

The elemental compositions of wood material are based on the multiple ways of combining the basic elements carbon, hydrogen and oxygen obtained from the air. The chemical composition varies among the tree parts (root, stem, or branch), with geographic location, with climate or with soil conditions.[1]

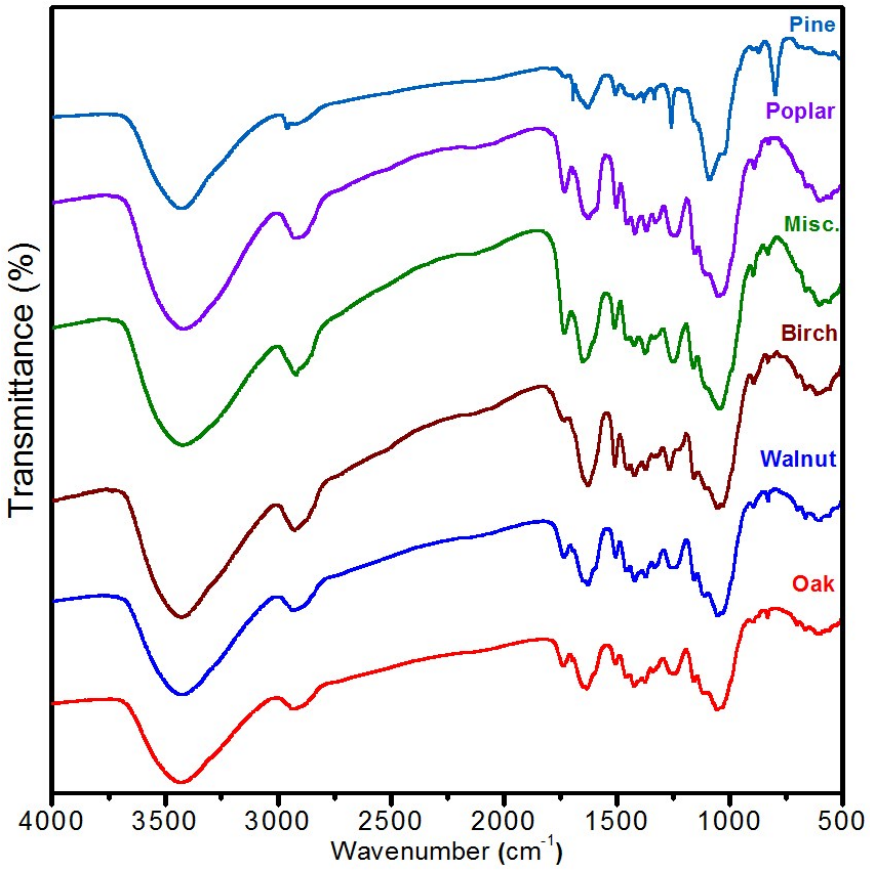

Fig. S9 FTIR spectra of different untreated lignocellulosic biomass

Table S2. Absorption peaks detected and corresponding functional groups in lignocellulosic biomass

Wavenumber, cm^{-1}	Functional groups
1031	C-O, C=C, C-C-O vibrational stretching
1043	C-O, C-C and C-OH stretching vibrations of cellulose, hemicellulose and lignin
1060	C-OH stretching vibration (cellulose -hemicelluloses)
1157	C-O-C ring vibrational stretching (glycosidic linkage)
1266	Syringyl ring breathing and C-O stretching (lignin)
1319	C-H in plane bending (cellulose)
1370	Aliphatic C-H stretching (methyl and phenol alcohol)
1427	Aromatic skeletal combined with C-H in plane deformation
1457	The aliphatic part (lignin)
1511	C=C stretching vibration of the aromatic ring (lignin)
1640	C=O stretching vibrations in conjugated carbonyl
1730	C=O stretching (hemicellulose)
2855, 2890, 2923	C-H stretching
3392, 3412 (broad)	-OH bond stretching vibration

Table S3 Detailed compositional analysis of different lignocellulosic biomass

[a]Biomass	Weight fraction (wt%)[b]					Lignin		Extractives (wt%)[c]	Moisture (wt%)[c]
	Glu	Xyl	Gal	Ara	Man	ASL	KL		
Pine	39.70	6.17	0.86	0.29	9.53	1.55	28.35	8.53	9.50
Poplar	43.32	16.44	-	-	0.57	1.14	22.30	3.82	8.51
Birch	39.05	20.11	0.71	1.13	1.71	4.72	23.25	2.91	6.65
Walnut	41.02	17.22	3.4	2.73	4.27	2.10	49.30	3.62	7.44
Oak	47.21	15.14	1.5	1.33	3.02	3.71	22.39	3..31	7.23
Miscanthus	37.81	18.44	1.03	2.24	0.1	2.81	21.10	3.11	6.52

[a]Scotch pine (*Pinus sylvestris*), Poplar (*Populus*), Birch (Betula), Walnut (*Juglans regia*), Oak (*Quercus*) and Grass (Miscanthus)

[b]based on dried extracted biomass

[c]based on wet biomass (Moisture analyzer: Halogen-HB43-S, Mettler-Tolledo instruments, Shanghai, China)

Abbreviations: **Glu** (glucose); **Xyl** (xylose); **Gal** (galactose); **Ara** (arabinose); **Man** (mannose); **KL** (Klason lignin); and **ASL** (acid-soluble lignin).

The detailed compositional analysis can be approached to ref.[2]

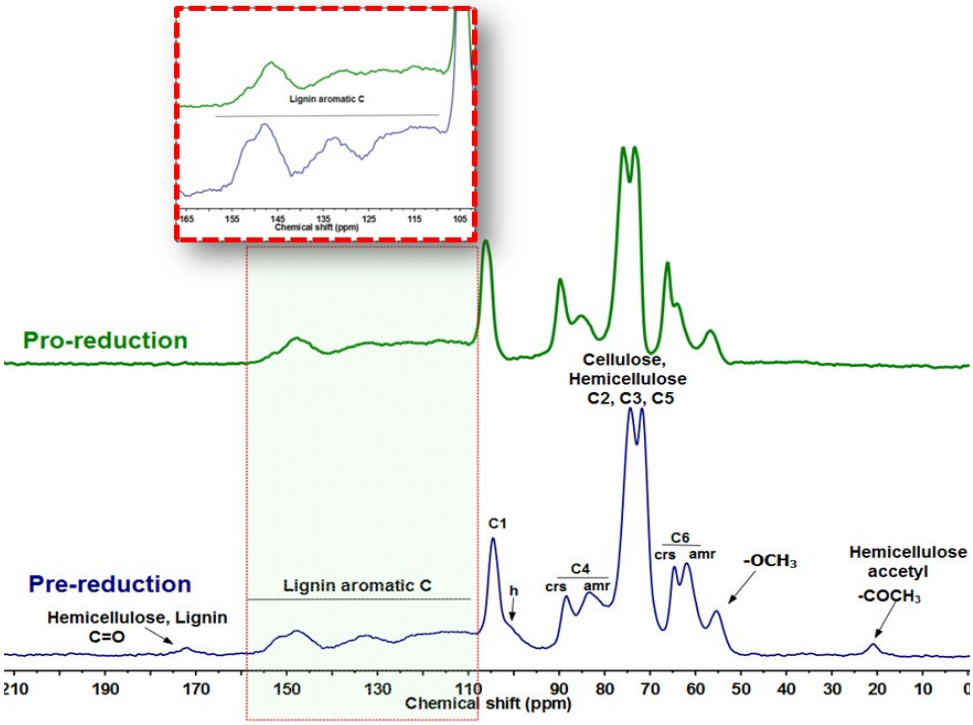

Fig. S10 Solid state ^{13}C CP MAS NMR analysis of pine sawdust.

Table S4 Signal assignment for the ^{13}C CPMAS NMR spectrum of pine sawdust

Chemical shift (ppm)	Assignment
173	CO_2 in acetyl groups of hemicelluloses
153	G 4e
148	G 3
146	G4f
136	G1e
133	G1f
120	G6
116	G5
112	G2
105	C-1 of cellulose
102	C-1 of hemicellulose
89	C-4 of crystalline of cellulose
84	C-4 of amorphous
72-75	C-2/C-3/C-5 of cellulose
65	C-6 of crystalline cellulose
62	C-6 of amorphous cellulose
56	$-OCH_3$ in lignin
21	CH_3 in acetyl groups of hemicellulose

G= guaiacyl, e=etherified C-4, f=free phenolic C-4, Crs (crystal), amr (amorphous)

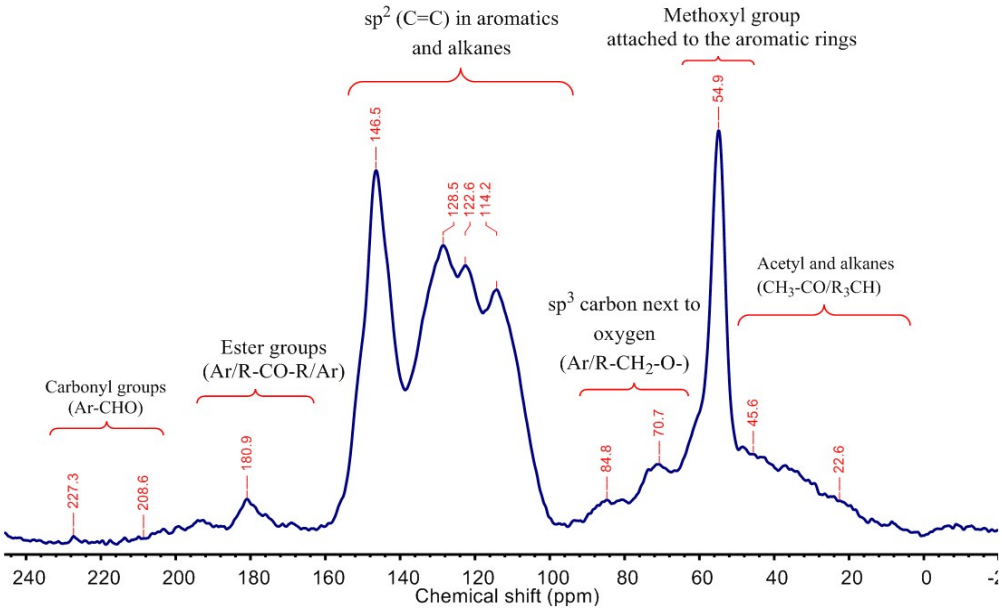

Fig. S11 Solid state ^{13}C NMR of alkaline lignin.

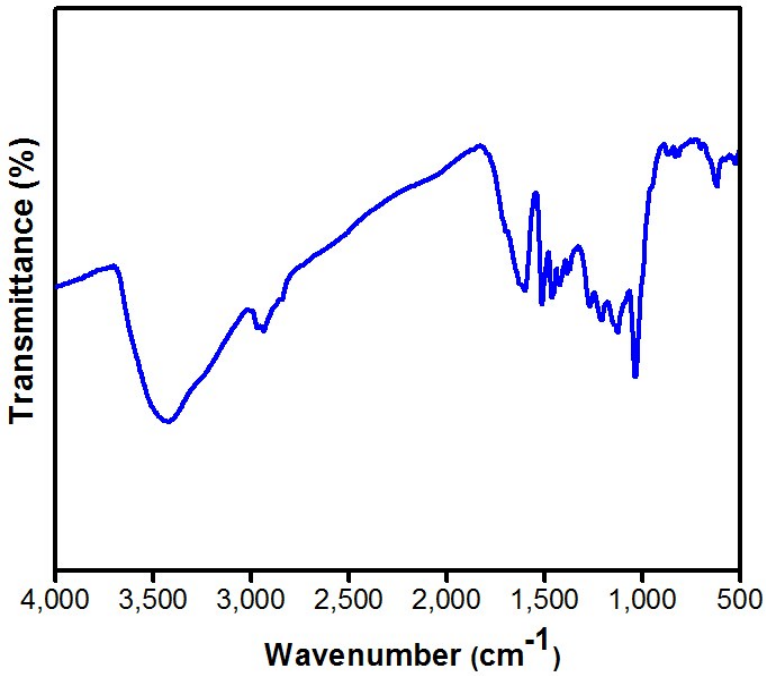

Fig. S12 FTIR analysis of alkaline lignin.

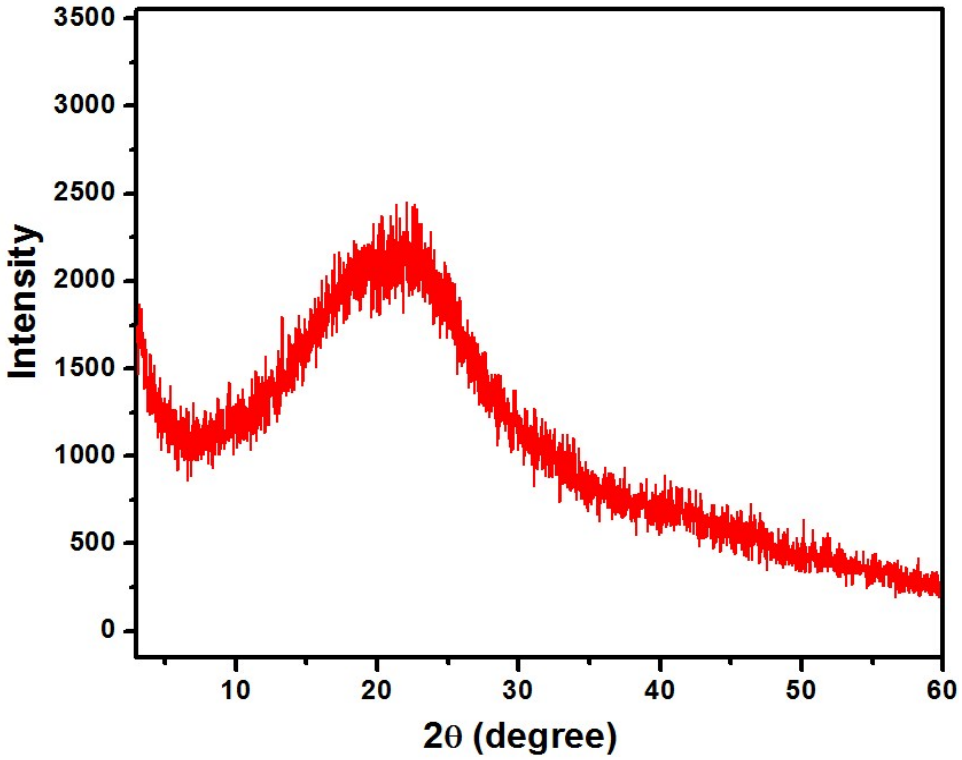

Fig. S13 XRD pattern of lignin alkaline.

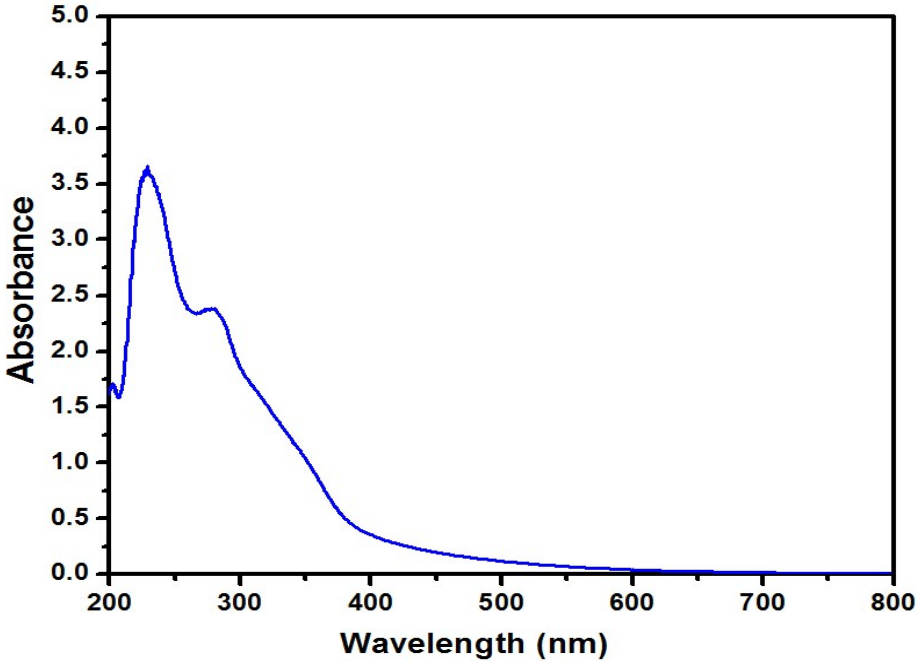

Fig. S14 UV-Vis absorption spectra of alkali lignin.

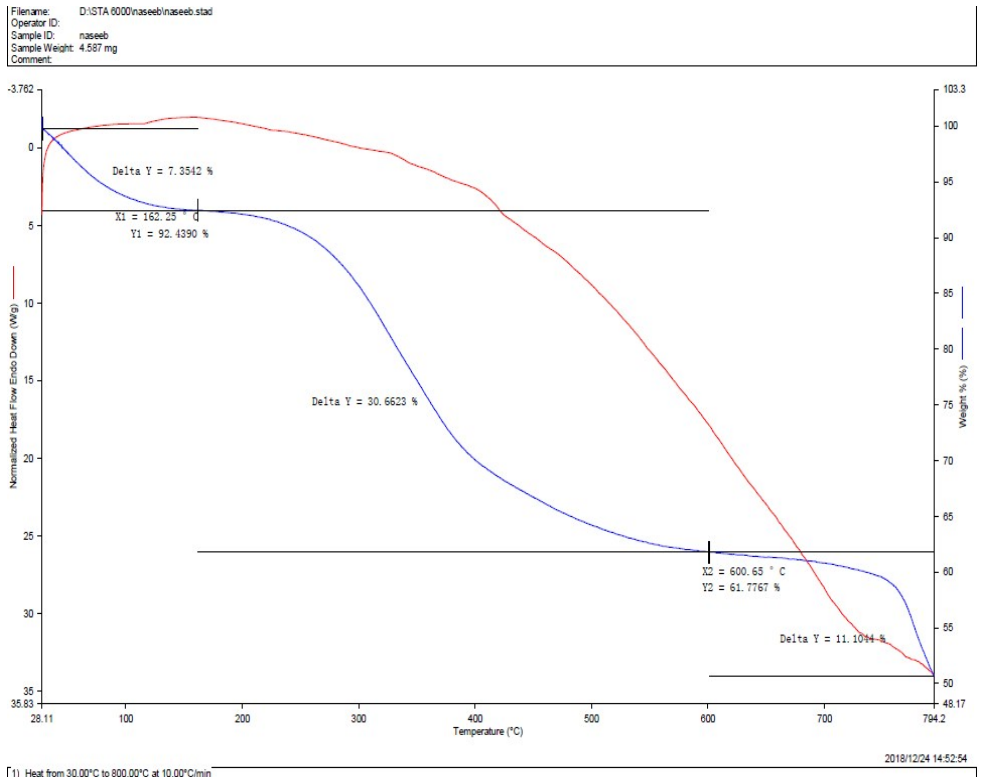

Fig. S15 TGA analysis of alkaline lignin

Specification

Dec 31, 2018 (JST)

TOKYO CHEMICAL INDUSTRY CO.,LTD.
4-10-1 Nihonbashi-Honcho, Chuo-ku, Tokyo 103-0023 Japan

Chemical Name: Lignin (Alkaline)	
Product Number: L0082	CAS RN: 8068-05-1

Tests	Specifications
pH	8.0 to 10.0(50g/L, 20 deg-C)
Methoxyl Group	10.0 to 12.0 %(calcd.on anh.substance)
Ignition residue(Sulfate)	20.0 to 29.0 %(calcd.on anh.substance)
Water	max. 10.0 %

The contents of the specifications are subject to change without advance notice. The specification values displayed here are the most up to date values. There may be cases where the product labels display a different specification, however, the product quality still meets the latest specification.

Customer service:

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Specifications file of commercially acquired lignin (TCI Chemicals Tokyo Chemical Industry UK Ltd.)[3]

Part 3: Product analysis

Product analysis

In literature, the product yields are typically based on the amount of acid insoluble lignin in lignocellulose depolymerization, also called Klason lignin. For the determination of the Klason lignin content of pine lignocellulose standard NREL method was adopted.[2] Initially, a suitable mass of lignocellulose samples were milled and sieved to particle size below <0.5 mm and then dried at 105 °C overnight before study. A soxtec extraction method was adopted initially to remove any extractives like fat, waxes, resins and terpenoids/steroids, which can manipulate the Klason lignin determination. The detailed composition of lignocellulose samples can be found in **Table S2**.

After the reductive fractionation reaction the aqueous phase mixture was subjected to threefold liquid-liquid extraction by using diethyl ether (DEE) as an extractant to separate the soluble sugar and lignin-derived products. Afterward, the extracted DEE phase was dried under reduced pressure in a rotary evaporator at 40 °C and the final obtained lignin-oil was used to determine the degree of delignification (based on Klason lignin weight). Preliminary, monomer identification was performed by (Thermo Fisher Scientific) gas chromatography equipped with ISQ mass spectrometry (GC-MS). The compounds were separated by using an ISQ HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The detailed program was as follow: 1.0 μL of the sample was injected into the GC at an inlet temperature of 280 °C and was operated in a split mode (split flow of 30 mL/min, split ratio = 50). Helium (99.99%) was used as a carrier gas with a constant flow rate of 1 mL/min. The temperature of the GC was held at 40 °C for 5 min, then increased at a rate 5 °C/min up to 280 °C, and held at this temperature for 5 min. The MS was used until the end of GC run with a solvent delay of 5.0 min. The ion source was maintained at temperature of 250 °C, and the MS was operated in scan mode. The instrument control and data processing were carried out using the installed Thermo Xcalibur 2.2 software to identify each appeared peak by National Institute of Standards and Technology library (NIST MS). All results were based on the average value of three reactions. Given the complexity of lignin monomer mixtures, whenever possible, we compared the GC retention time and GC-MS spectra of the lignin monomer mixture with authenticated standards. Quantification of liquid extracted product was performed by using GC-FID (Thermo Scientific TRACE 1300 GC), weighted amount of external standard (accetophenone) was added to the lignin-oil after which the content was completely re-solublized in 2 mL DEE. The products peak sequence in the GC-FID appears in the same orders as are those in GC-MS due to keeping same GC conditions and the use of a similar capillary column. The sensitivity factors of products were obtained by calibration with commercial standards or attained by ECN-based calculations,[4,5] due to lack of commercial standards. The yield of monomer was calculated based on the peak area of monomer and peak area of external standard (accetophenone) in GC chromatogram. Calculations are based on the following equations:

$$\text{Conversion (wt\%)} = \frac{W_b - W_a}{W_b} \; x\ 100\%$$

Whereas, W_b is the weight of feedstock before reaction, W_a is weight of solid residue after reaction.

$$Yield\ monomer\ (wt\%) = \frac{m_{product\ A}}{\left(m_{lignocellulose}\right) x \left(wt\%_{Klason\ lignin}\right)}\ x\ 100\%$$

In the above descriptions, $m_{product\ A}$ is the mass of product A, $m_{lignocellulose}$ is the mass of the initial lignocellulose substrate, $wt\%_{Klason\ lignin}$ is the weight percentage of Klason lignin in the feedstock lignocellulose.

$$Selctivity\ (\%) = \frac{yield_{\ monomer\ A}}{\sum Yield_{\ all\ monomers}}\ x\ 100\%$$

After liquid-liquid organic phase separation by DEE, the remanant H_2O phase was analyzed to detect the sugar contents. Following standard NREL procedure,[6] the sample was analyzed by HPLC (Hitachi-L 2130 pumps, a Shodex Sugar SH-1011 column (ø 8 × 300 mm), using water as mobile phase at flow rate of 0.6 mL/min.

Table S5 Complete overview of GC-MS identified compounds in bio-oil obtained from depolymerisation of pine lignocellulose feedstock by using Ru/α-HfP catalyst

Entry	RT[a] (min)	Identification	Formula	Match (%)
1	5.16	2-Methyl Cyclopentanone	$C_6H_{10}O$	45
2	6.2	2 methyl-2-cyclopentenone	C_6H_8O	53
3	7.06	3,3-Dimethyl-2-oxo butanal, hemihydrate	$C_6H_{10}O_2$	67
4	7.60	Phenol	C_6H_6O	85
5	8.18	3 methyl Cyclopentenedione	$C_6H_8O_2$	65
6	9.27	2-methoxyphenol	$C_7H_8O_2$	92
7	11.85	4-Propylphenol	$C_9H_{12}O$	81
8	12.14	4-ethyl-2-methoxyphenol	$C_9H_{12}O_2$	90
9	13.41	2-Methoxy-4-propylphenol	$C_{10}H_{14}O_2$	98
10	14.61	2-(Octadecyloxy)ethanol	$C_{20}H_{42}O_2$	48
11	15.26	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O$	79
12	16.69	4-hydroxy-3-methoxy-Benzenepropanol	$C_{10}H_{14}O_3$	83
13	23.41	2-Methoxy-6-methylaniline	$C_8H_{11}NO$	66

[a]Retention time

Reaction conditions: 1 g feedstock (pine), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S6 Complete overview of GC-MS identified compounds in bio-oil obtained from depolymerisation of pine lignocellulose feedstock by using Ru/α-HfP catalyst

Entry	RT[a] (min)	Identification	Formula	Match (%)
1	6.22	Hydroperoxide, heptyl	$C_7H_{16}O_2$	20
2	7.31	2-ethylhexanol	$C_8H_{18}O$	40
3	-	unknown	-	-
4	7.76	1,4-dimethyl-2-octadecyl cyclohexane	$C_{26}H_{52}$	55
5	8.35	1,2-dimethylcyclohexane	C_8H_{16}	45
6	8.70	2-ethylcyclohexyl ester hexanoic acid	$C_{14}H_{28}O_2$	35
7	9.23	1-cyclohexylbutan-1-ol	$C_{10}H_{20}O$	55
8	9.35	unknown	-	-
9	9.42	2-propylcyclohexanol	$C_9H_{18}O$	75
10	10.26	Cyclohexanepropanol	$C_9H_{18}O$	95
11	11.29	4-ethylcyclohexanol	$C_8H_{16}O$	90
12	11.33	2-decanol (2-hydroxy decane)	$C_{10}H_{22}O$	35
13	11.91	5-Methoxymethoxyhex-3-yn-2-ol	$C_8H_{12}O_2$	35
14	12.56	1-Penten-3-ol, 2-methyl-	$C_6H_{12}O$	33
15	13.17	1-Hepten-4-ol	$C_7H_{14}O$	28
16	13.39	unknown	-	-
17	13.43	2-methoxy-4-propylphenol	$C_{10}H_{14}O_2$	68
18	13.60	trans-1,4-Cyclohexanedicarboxylic acid dimethyl ester	$C_{10}H_{16}O_4$	35
19	14.03	2-Octanone, 1-nitro-	$C_8H_{15}NO_3$	40
20	14.32	Heptanal	$C_7H_{14}O$	45
21	14.39	2,4-bis(1,1-dimethylethyl)-5-methylphenol,	$C_{15}H_{24}O$	30
22	14.46	3-Hepten-1-ol, acetate	$C_9H_{16}O_2$	35
23	14.90	Unknown	-	-
24	15.21	1,2-dicyclohexylpropane	$C_{15}H_{28}$	38
25	17.57	unknown	-	-

[a]Retention time

Reaction conditions: 1 g feedstock (pine), 0.2 g Ru/α-HfP catalyst, 6 h, 190 °C, 3.5 MPa H_2.

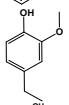
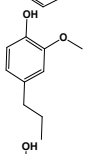
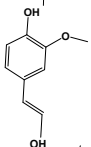
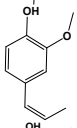
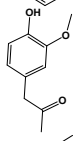
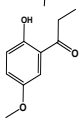
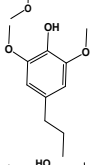
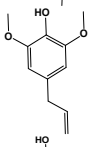
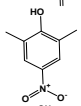
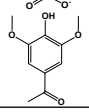
Table S7 Complete overview of GC-MS identified compounds in bio-oil obtained from depolymerisation of commercial lignin feedstock by using Ru/α-HfP catalyst

Entry	RT (min)	Identification	Formula	Match (%)
1	5.41	2-(1-Isopropoxyethoxy)propane	$C_8H_{18}O$	45.1
2	5.54	2-hydroxy-, 1-methylethyl ester propanoic acid,	$C_6H_{12}O_3$	62.3
3	6.00	Trans-2-methylcyclopentanol	$C_6H_{12}O$	52.9
4	6.43	2-butoxyethanol	$C_6H_{14}O_2$	76.2
5	7.06	1-methylhexyl Hydroperoxide,	$C_7H_{16}O_2$	41.8
6	7.54	3-methyloxirane-2-carboxylic Acid	$C_4H_6O_3$	40.5
7	7.60	Carbamic acid, phenyl ester	$C_7H_7NO_2$	43.1
8	7.60	3-methylpyridazine	$C_5H_6N_2$	35.2
9	8.22	3,6-octadecadiynoic acid, methyl ester	$C_{19}H_{30}O_2$	44.6
10	8.40	3-thioxobutanoate benzyl	$C_{11}H_{12}O_2S$	24.4
11	8.95	4-methoxyphenol	$C_7H_8O_2$	80.1
12	9.28	2-methoxyphenol	$C_7H_8O_2$	83.4
13	10.55	2-methoxy-5-methylphenol	$C_8H_{10}O_2$	60.2
14	10.77	2-methoxy-6-methylphenol	$C_8H_{10}O_2$	59.1
15	10.89	2-methoxy-4-methylphenol	$C_8H_{10}O_2$	75.6
16	11.65	2,4-dimethyl-1,3-dioxolane-2-methanol	$C_6H_{12}O_3$	35.4
17	12.12	4-ethyl-2-methoxyphenol	$C_9H_{12}O_2$	82.7
18	12.56	2-methoxy-4-vinylphenol	$C_9H_{10}O_2$	56.9
19	12.95	2,6-dimethoxyphenol	$C_8H_{10}O_3$	63.2
20	13.21	4-formyl-2-methoxyphenyl acetate	$C_{10}H_{10}O_4$	50.2
21	13.36	2-methoxy-4-propylphenol	$C_{10}H_{14}O_2$	88.4
22	13.69	4-hydroxy-3-methoxybenzaldehyde	$C_8H_8O_3$	92.2
23	13.77	1-phenyl-2-propanone	$C_9H_{10}O$	66.3
24	14.26	Unknown	-	-
25	14.39	4-allyl-2-methoxyphenol, acetate	$C_{12}H_{14}O_3$	53.5
26	14.80	1-(4-Hydroxy-3-methoxyphenyl)ethanone	$C_9H_{10}O_3$	76.5
27	15.00	3,4-dimethoxy-, methylmonoacetal benzaldehyde,	$C_{10}H_{14}O_4$	73.3
28	15.11	4-hydroxy-3-methoxybenzyl alcohol, di(isopropyl) ether	$C_{14}H_{22}O_3$	70.8
29	15.27	1-(4-hydroxy-3-methoxyphenyl)propan-2-one	$C_{10}H_{12}O_3$	65.7
30	15.31	9-octadecen-12-ynoic acid, methyl ester	$C_{19}H_{32}O_2$	34.3
31	15.36	2-methyldecane	$C_{11}H_{24}$	44.5
32	15.93	1-propanone, 1-(2-hydroxy-5-methoxyphenyl)-	$C_{10}H_{12}O_3$	36.4
33	16.33	4-hydroxy-3-methoxy-, benzoic acid	$C_8H_8O_4$	48.8
34	16.79	4-(3-hydroxypropyl)-2-methoxyphenol	$C_{10}H_{14}O_3$	44.6
35	16.90	3-methoxy-4-hydroxy-phenylacetic acid	$C_9H_{10}O_4$	39.6
36	17.11	2-isopropenyl-5,5-dimethyl-cyclohexanone	$C_{11}H_{18}O$	19.4
37	17.32	2-cyclopropyl-2-methylspiro[2.2]pentane-1-carboxylic acid	$C_{10}H_{14}O_2$	32.9
38	17.55	Unknown	-	-
39	17.88	2,3,5,8-tetramethyldecane	$C_{14}H_{30}$	34.8
40	18.12	N-(2-cyano-1-methylethyl)-4-nitro-benzenesulfonamide,	$C_9H_{10}N_2O_2S$	61.9
41	18.23	4,7-dimethyl-5-decyne-4,7-diol	$C_{12}H_{22}O_2$	29.4
42	18.62	Unknown	-	-
43	19.13	1-(1-Hydroxy-2,6,6-trimethyl-2,4-cyclohexadien-1-yl)ethanone	$C_{11}H_{16}O_2$	31.9
44	19.24	1-(4,5-Diethyl-2-methylcyclopenten-1-yl)ethanone	$C_{12}H_{20}O$	17.3
45	20.19	N-hexadecanoic acid	$C_{16}H_{32}O_2$	45.6
46	22.19	Unknown	-	-
47	22.94	3,6-dinitro-4-cyclohexene-1,2-dicarboxylic acid	$C_8H_8N_2O_8$	35.2
48	23.40	3,5,7-cycloheptatriene-1,3-dimethanol	$C_9H_{12}O_2$	41.5
49	25.17	Diisooctyl phthalate	$C_{24}H_{38}O_4$	55.2
50	27.30	9-octadecenamide, (Z)-	$C_{18}H_{35}NO$	41.2

[a]Retention time

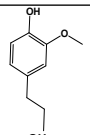
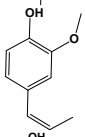
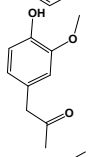
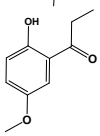
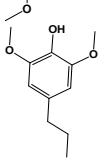
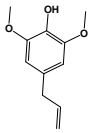
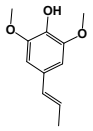
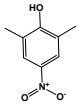
Reaction conditions: 0.4 g feedstock (alkali lignin), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S8 GC-MS identification, peak area contribution of monomers in bio-oil fractionated from Poplar feedstock by using Ru/α-HfP catalyst (Fig. S17 for corresponding gas chromatogram)

RT	Identification	Structure	Relative content (area%)
7.57	Phenol		8.12
9.23	2-methoxyphenol		0.64
12.15	4-ethyl-2-methoxyphenol,		0.71
12.95	2,6-dimethoxyphenol		0.24
13.37	2-methoxy-4-propylphenol,		18.02
13.89	2-methoxy-4-(1-propenyl)-phenol,		0.51
14.38	2-methoxy-4-(1-propenyl)-, (Z)-phenol,		3.97
15.29	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-		2.18
15.91	1-Propanone, 1-(2-hydroxy-5-methoxyphenyl)-		0.52
16.31	2,6-dimethoxy-4-propylphenol,		23.29
17.29	2,6-dimethoxy-4-(2-propenyl)-phenol,		3.97
18.04	2,6-dimethyl-4-nitrophenol,		0.68
18.61	1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone,		0.94

area%: the relative contents in percentage calculated with area normalization method.
Reaction conditions: 1 g feedstock (Poplar), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S9 GC-MS identification, peak area contribution of monomers in bio-oil fractionated from Oak feedstock by using Ru/α-HfP catalyst (Fig. S17 for corresponding gas chromatogram)

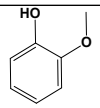
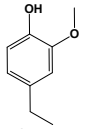
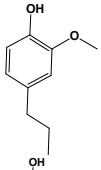
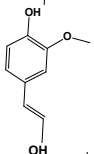
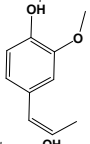
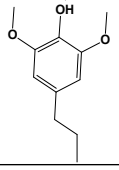
RT[a]	Identification	Structure	Relative content (area%)
13.37	2-methoxy-4-propylphenol		0.88
14.39	2-methoxy-4-(1-propenyl)-phenol,		1.13
15.25	1-(4-hydroxy-3-methoxyphenyl)-2-propanone		0.8
15.90	1-(2-hydroxy-5-methoxyphenyl)-1-propanone		0.24
16.30	2,6-dimethoxy-4-propylphenol		41.35
16.74	2,6-dimethoxy-4-(2-propenyl)-phenol,		1.02
17.30	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol		29.91
17.94	2,6-dimethyl-4-nitrophenol,		0.99

area%: the relative contents in percentage calculated with area normalization method.

[a]Retention time

Reaction conditions: 1 g feedstock (Oak), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S10 GC-MS identification, peak area contribution of monomers in bio-oil fractionated from Birch feedstock by using Ru/α-HfP catalyst (Fig. S17 for corresponding gas chromatogram)

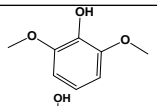
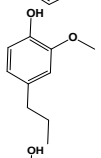
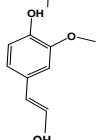
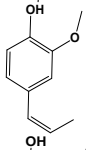
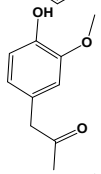
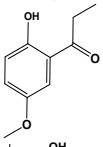
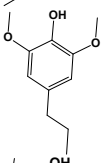
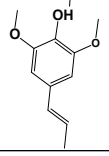
RT[a]	Identification	Structure	Relative content (area%)
9.24	2-methoxyphenol		0.21
12.12	4-ethyl-2-methoxyphenol		0.10
13.37	2-methoxy-4-propylphenol		35.33
13.86	2-methoxy-4-(1-propenyl)-phenol,		31.65
14.36	2-methoxy-4-(1-propenyl)-, (Z)-phenol		0.29
16.29	2,6-dimethoxy-4-propylphenol		4.7

area%: the relative contents in percentage calculated with area normalization method.

[a]Retention time

Reaction conditions: 1 g feedstock (Birch), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S11 GC-MS identification, peak area contribution of monomers in bio-oil fractionated from Walnut feedstock by using Ru/α-HfP catalyst (Fig. S17 for corresponding gas chromatogram)

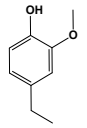
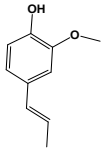
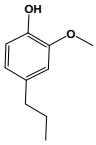
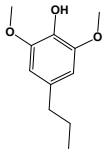
RT[a]	Identification	Structure	Relative content (area%)
12.99	2,6-dimethoxyphenol,		0.26
13.42	2-methoxy-4-propylphenol,		30.42
13.86	2-methoxy-4-(1-propenyl)-phenol,		0.07
14.42	2-methoxy-4-(1-propenyl)-, (Z)-phenol,		4.23
15.31	1-(4-hydroxy-3-methoxyphenyl)-2-propanone,		0.43
15.96	1-(2-hydroxy-5-methoxyphenyl)-1-propanone,		0.03
16.34	2,6-dimethoxy-4-propylphenol,		32.67
17.33	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol		4.95

area%: the relative contents in percentage calculated with area normalization method.

[a]Retention time

Reaction conditions: 1 g feedstock (Walnut), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S12 GC-MS identification, peak area contribution of monomers in bio-oil fractionated from Miscanthus feedstock by using Ru/α-HfP catalyst (Fig. S17 for corresponding gas chromatogram)

RT[a]	Identification	Structure	Relative content (area%)
12.12	4-ethyl-2-methoxyphenol,		1.48
14.39	2-methoxy-4-(1-propenyl) phenol,		1.12
13.38	2-methoxy-4-propyl phenol,		44.99
16.29	2,6-dimethoxy-4-propyl-phenol,		1.86

area%: the relative contents in percentage calculated with area normalization method.

[a]Retention time

Reaction conditions: 1 g feedstock (Miscanthus), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

Table S13 Literature yields comparison of dihydroeugenol as product by using reductive fractionation using metal-acid catalyst unless indicated otherwise

Catalyst system	Feedstock	Lignin	Yield monomer	Selectivity	$Yield_{dihydroeugenol}$		Reaction conditions (solvent, temp. P_{H2})	Ref.
		wt%	wt% lignin	$S_{dihydroeugenol}$ %	wt% lignin	wt% wood		
	Softwood							
Ru/α-HfP	Pine (*Pinus sylvesteris*)	28.3 [a]	19.86	83	18.54	5.2	Water, 190 °C, 3.5 MPa, 3 h	This work
Ru/C , $LiTaMoO_6$, H_3PO_4	Pine	26.5[a]	21.2	31	6.5	1.4	Water, 230 °C, 6 MPa, 24 h	7
Ru/C	Pine /Spruce	27 [a]	20.5[d]	80	16.3	4.4	Methanol, 250 °C, 3 MPa, 3 h	8
Rh/C, HCl	Spruce (*Picea glauca*)	27.3 [a]	-	-	13.4[e]	3.7	HCl, dioxane, water	9
Pd/C, $ZnCl_2$	Pine (*Pinus concorta*)	31[b]	19	100	19.0	5.9	Methanol, 250 °C, 5 MPa, 12 h	10
	Hardwood							
Rh/C, H_3PO_4	Birch (*Betula platyphylla*)	19 [a]	45.5	22	9.9	1.9	dioxane, water	11
Ru/C	Poplar	21.2[a]	43.9[d]	29	12.8	2.7	Methanol, 250 °C, 3 MPa, 3 h	9
Ru/C	Birch (betula pendula)	19.1[a]	51.4[d]	20	10.3	2.0	Methanol, 250 °C, 3 MPa, 3 h	12
Pd/C, $ZnCl_2$	Poplar	19[c]	54	45	24.3	4.6	Methanol, 250 °C, 5 MPa, 12 h	10
	Grasses							
Ru/C , $LiTaMoO_6$, H_3PO_4	Wheat straw	20.2[a]	39.0	17	6.7	1.4	Water, 230 °C, 6 MPa, 24 h	7
Ru/C	Miscanthus	24.3 [a]	26.8	24	6.3	1.5	Methanol, 250 °C, 3 MPa, 3 h	9
Ni/C	Miscanthus	13	67.0	33	22	2.9	Methanol, 225 °C, 3.5 MPa, 12 h	13
MoS_2	Corn stover	18.15 [a]	18.67	20.3	3.39	-	Methanol, 250 °C, 5 MPa, 2h	14

[a]Klason lignin method, [b]Acetyl bromide-soluble lignin (ABSL) analysis, [c]Kraft pulping, [d]expressed as carbon yield, [e]reported as percentage of Klason lignin

Table S14 Literature yields comparison of aromatic monomers derived from technical lignin by using metal-acid catalyst unless indicated otherwise

Entry	Catalyst system	Feedstock	Reaction condition (solvent, temp. P_{H2}, t)	Monomer yield Wt% lignin	Ref.
1[a]	Ru/ α-HfP	Alkaline lignin	Isopropanol, 190 °C, 3.5 MPa, 3 h	27.97	This study
2	Ru/Al_2O_3	Kraft lignin	Water, 450 °C, 10 MPa, 4 h	22	[15]
3	Ru/TiO_2	Organosolv lignin	Water, 400 °C, 10 MPa, 4 h	22.1	[16]
4[b]	Ru/C-$HTaMoO_6$	Kraft lignin	Dioxane/water,320 °C, 2 MPa, 2 h	8.2	[17]
5	Ru/C, MgO/ZrO	Kraft lignin	Ethanol, 350 °C, 3 MPa, 1 h	4.52	[18]
6	Ru/C, Al_2O_3/ZrO	Kraft lignin	Ethanol, 350 °C, 3 MPa, 1 h	6.10	[18]
7	Pt/Al_2O_3	Kraft lignin	Water, 450 °C, 10 MPa, 4 h	29.8	[15]
9	PtMgAlOx	Protobind alkali lignin	Ethanol, 300 °C, 1 MPa, 4 h	6	[16]
8[c]	Ru/C	Kraft lignin	Water, 450 °C, 10 MPa,4 h	27.30	[15]
10[d]	TiO_2	Protobind alkali lignin	Ethanol, 340 °C, 1 MPa, 1 h	9	[19]
11[e]	Ru	Organosolv lignin	Water, 130 °C, 1 MPa, 12 h	1.50	[20]
12[f]	Ru/Ni	Organosolv lignin	Water, 130 °C, 1 MPa, 12 h	6.8	[20]

[a] acid-supported, [b]acid co-cat., [c]non-acid support, [d]non-supported, [e]single metal, [f] bi-metalic

Part 4: Figures

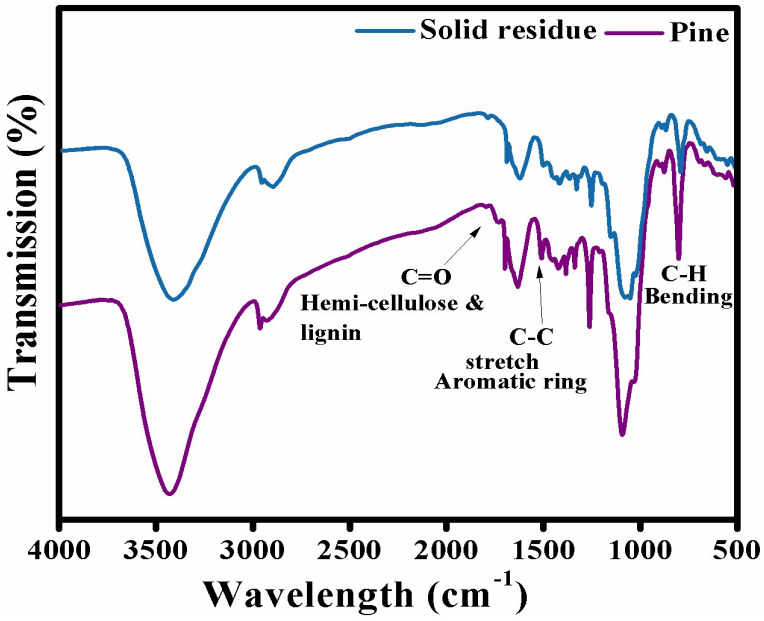


Fig. S16 FTIR spectra of feedstock lignocellulose (pine and solid residue) before and after Ru/α-HfP reductive fractionation.

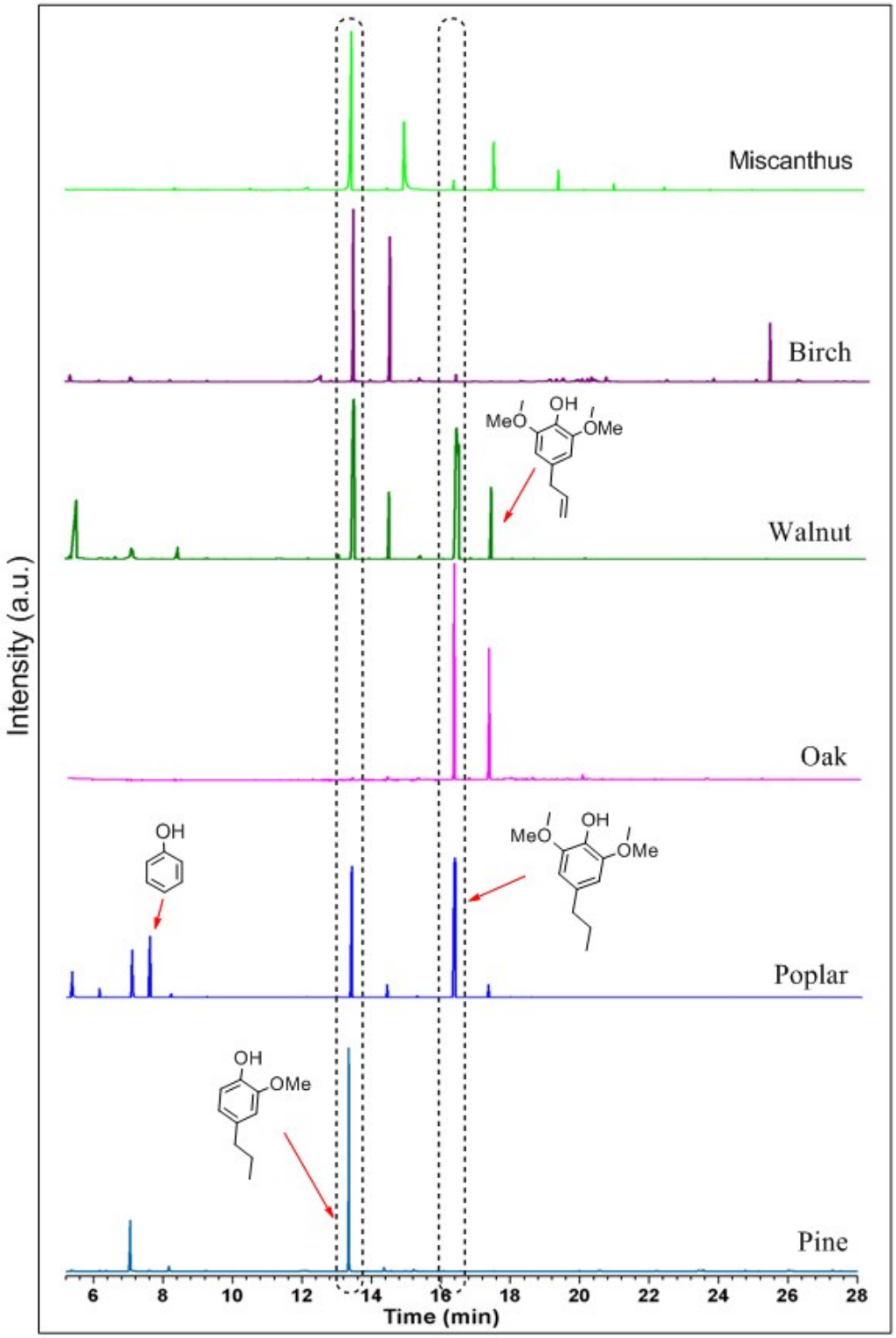


Fig. S17 Gas chromatograms and peak identification of monomers in bio-oil derived from different lignocellulose by Ru/α-HfP catalyst.

Reaction conditions: 1 g feedstock, 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

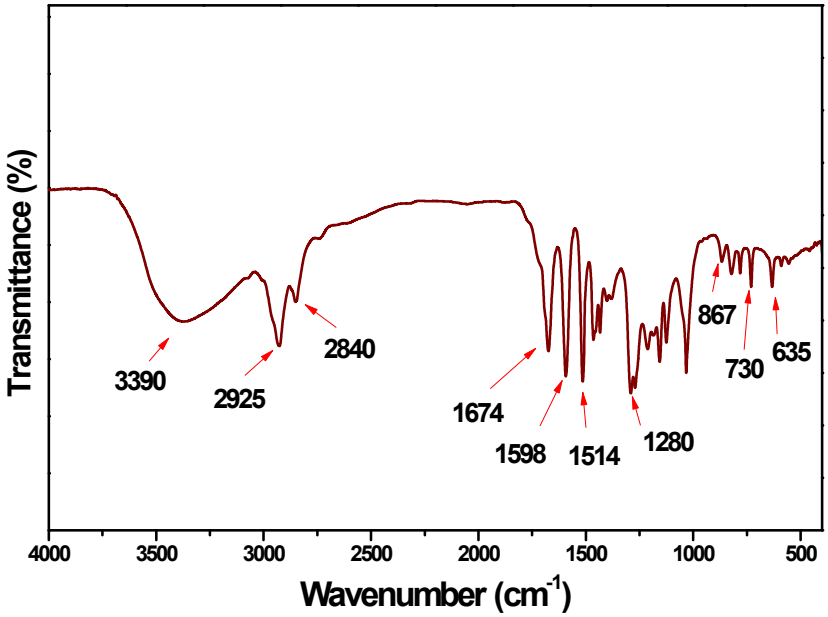


Fig. S18 FTIR spectrum of bio-oil from alkaline lignin depolymerisation by Ru/α-HfP NPs.

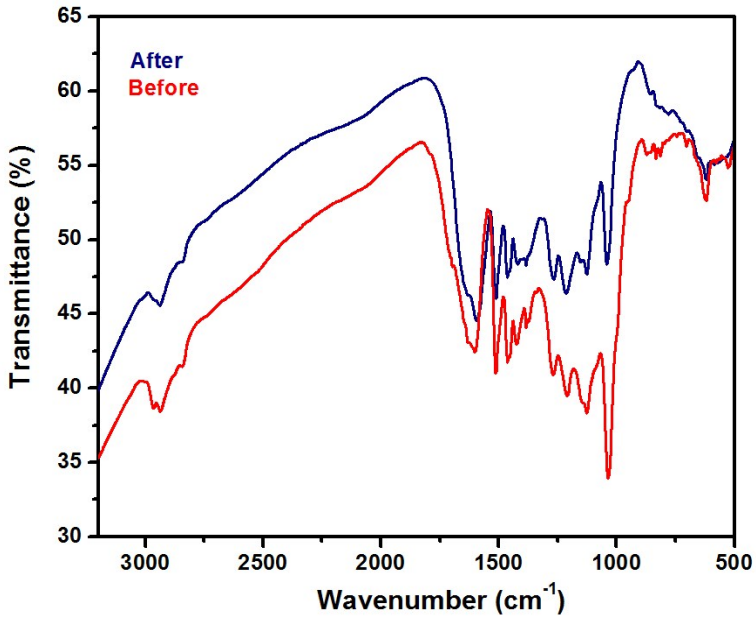


Fig. S19 FTIR spectra of alkaline lignin before and after depolymerisation by using Ru/α-HfP NPs.

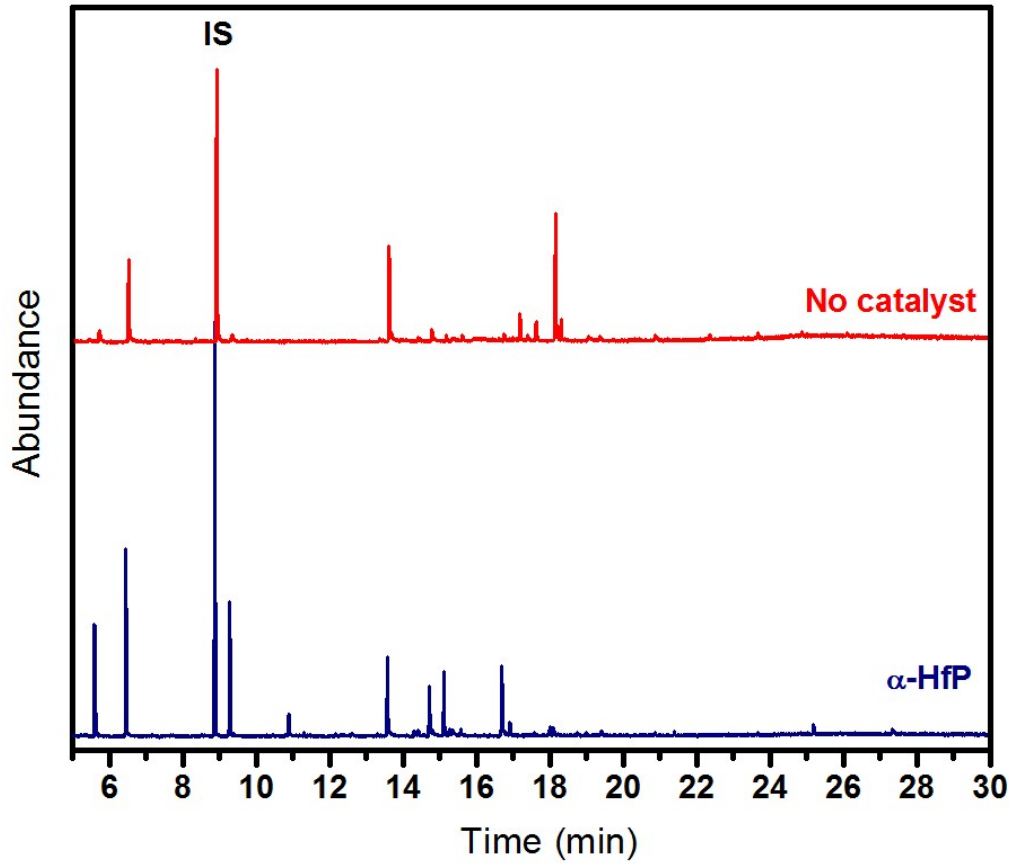


Fig. S20 Gas chromatographic comparison of liquid phase products of comparative experiments with bare α-HfP and without any catalyst.

Reaction conditions: 0.4 g of lignin, initial 3.5 MPa of H_2, 40 mL of isopropanol, 190 °C, 3 h.

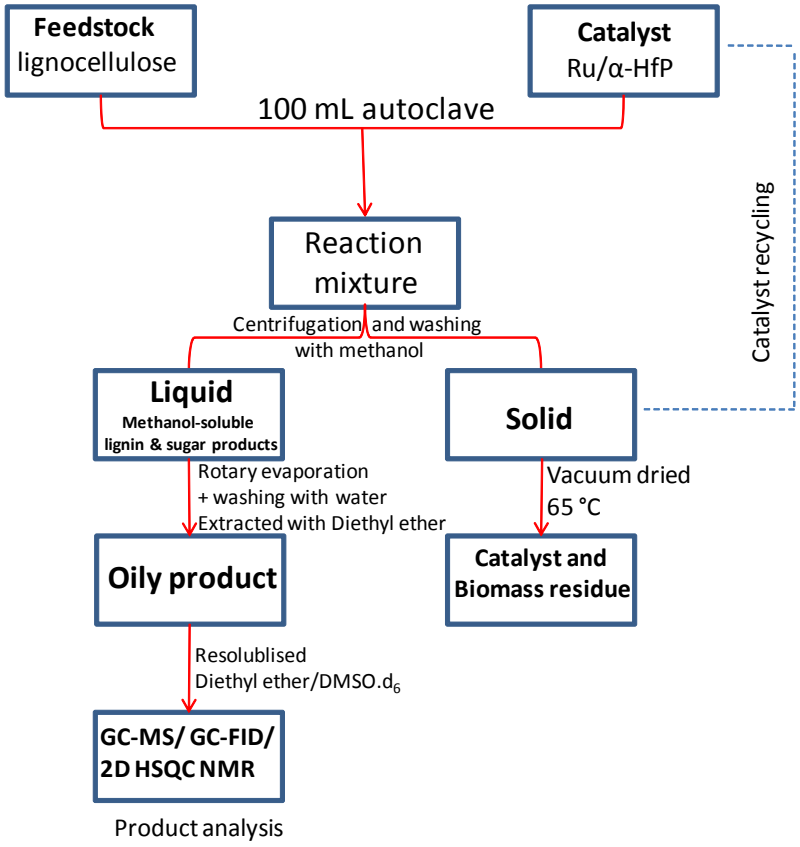


Fig. S21 The post-processing flowchart of catalytic reductive fractionation of lignocellulose with Ru/α-HfP catalyst.

Fig. S22a Mass spectrogram of major monomeric products from pine sawdust.

Reaction conditions: 1 g feedstock (pine), 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2.

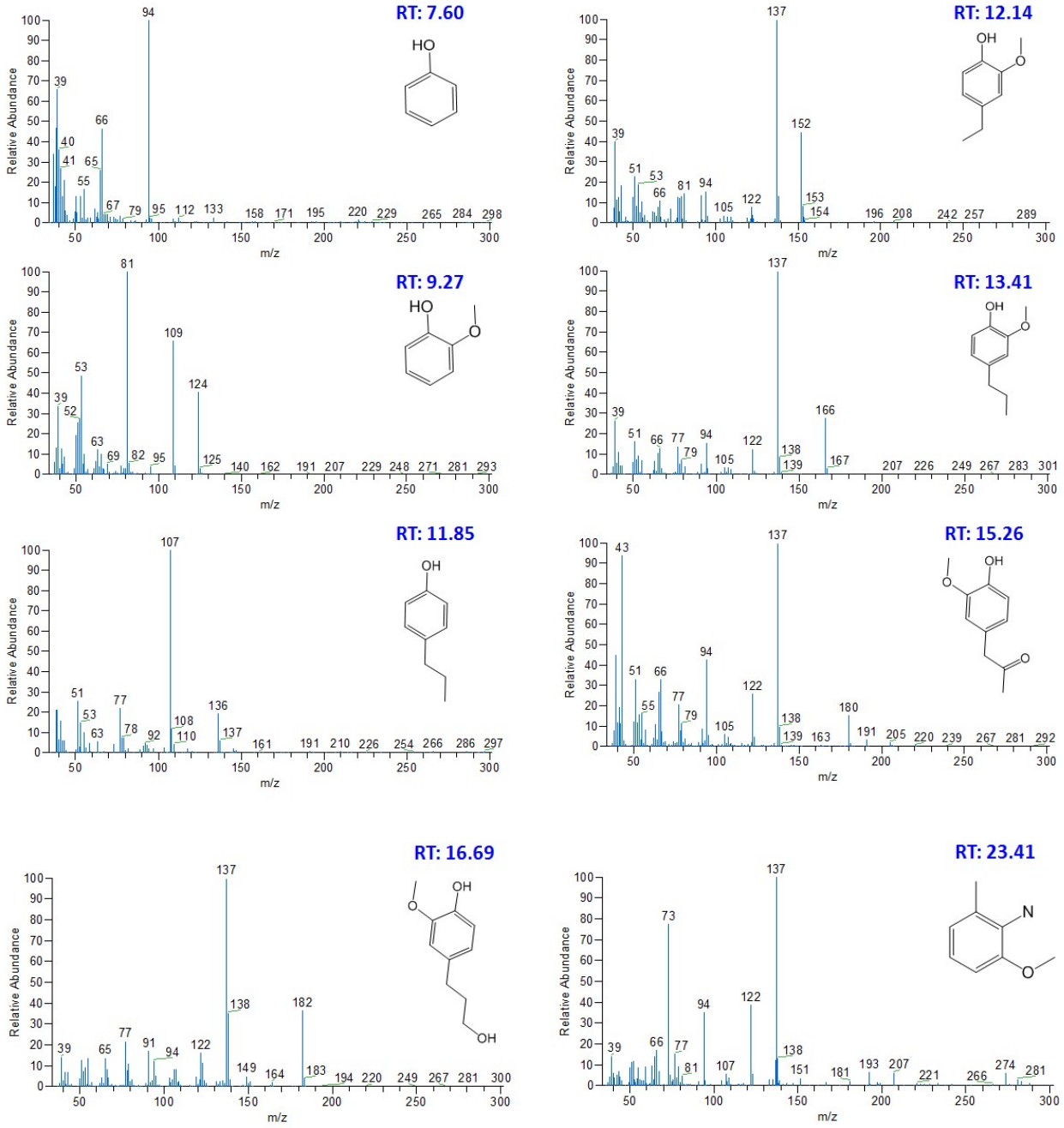


Fig. S22b Mass spectrogram of major monomeric products from pine sawdust.

Reaction conditions: 1 g feedstock (pine), 0.2 g Ru/α-HfP catalyst, 6 h, 190 °C, 3.5 MPa H_2.

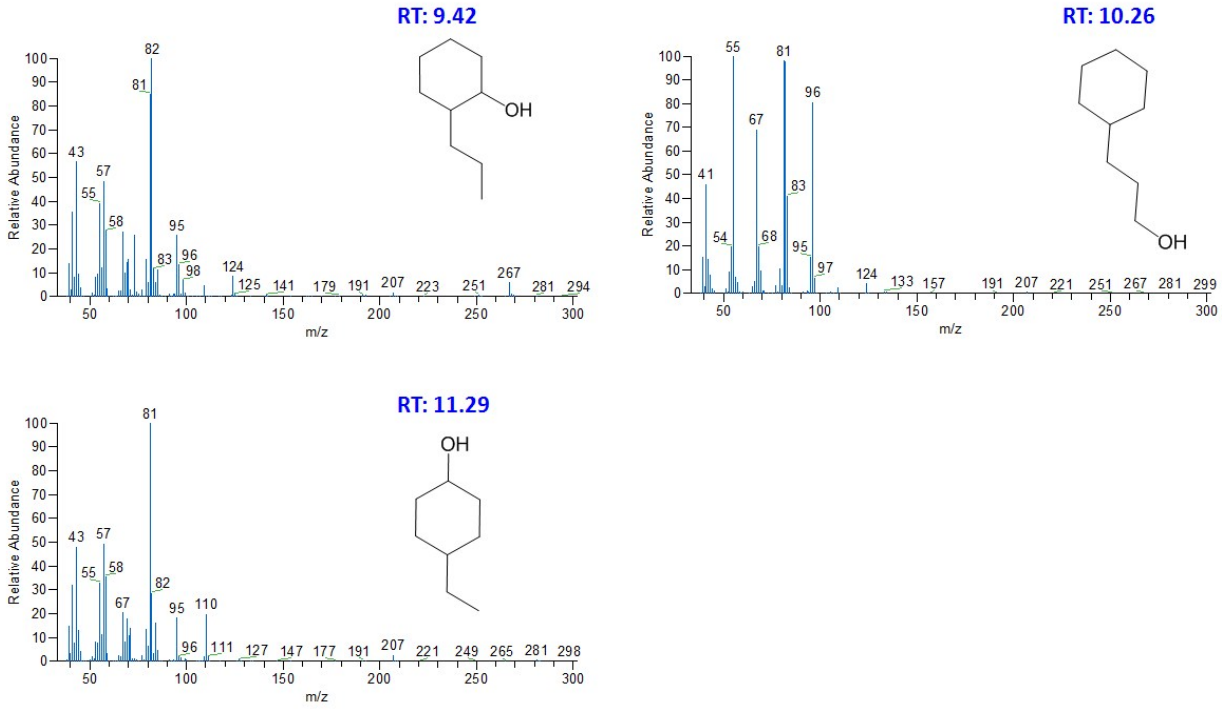
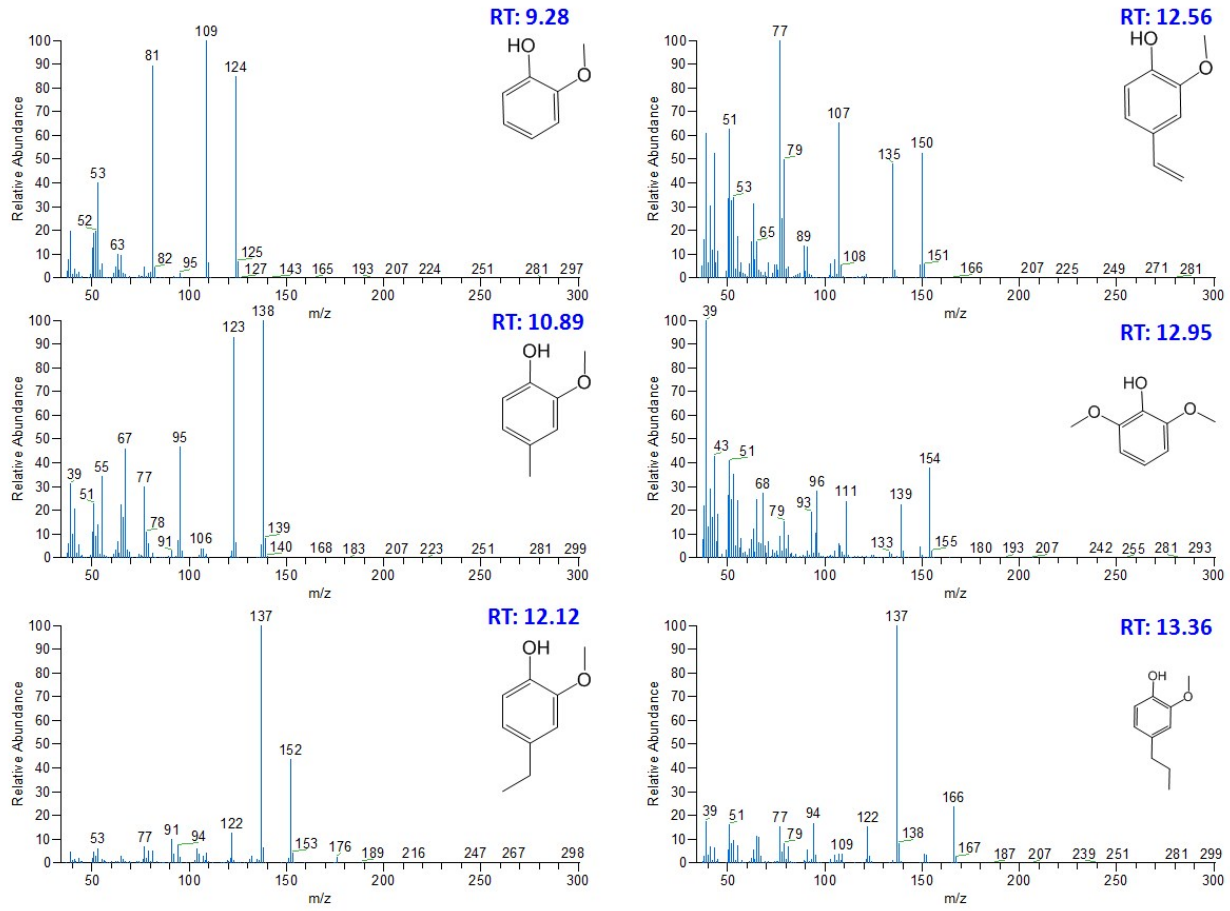
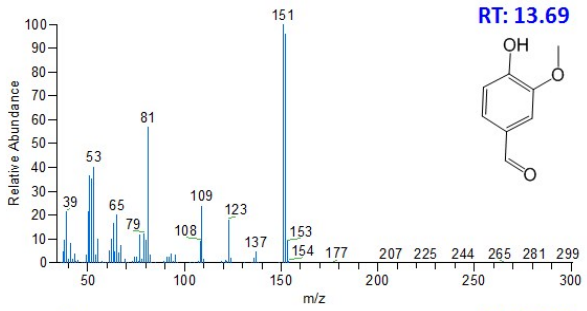


Fig. S23 Mass spectrogram of major monomeric products from technical lignin.

Reaction conditions: 0.4 g lignin, 0.2 g Ru/α-HfP catalyst, 3 h, 190 °C, 3.5 MPa H_2, Isopropanol (solvent).

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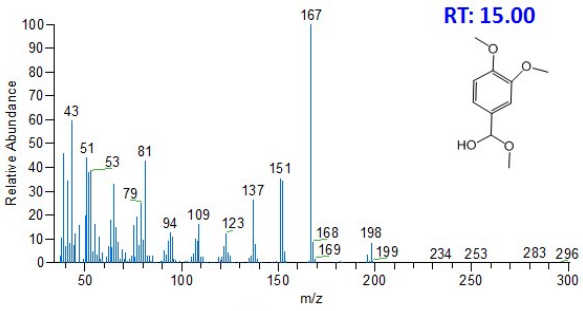
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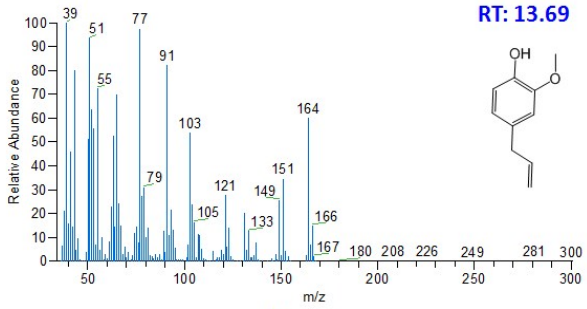
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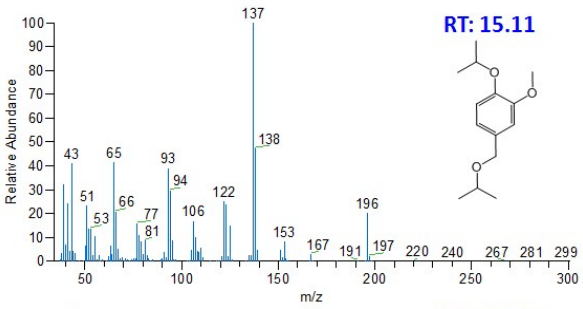
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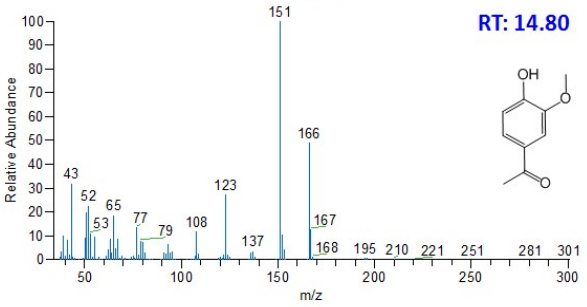
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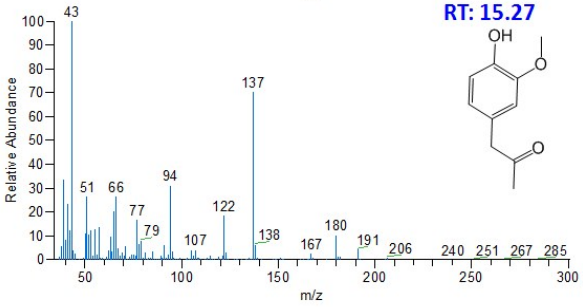
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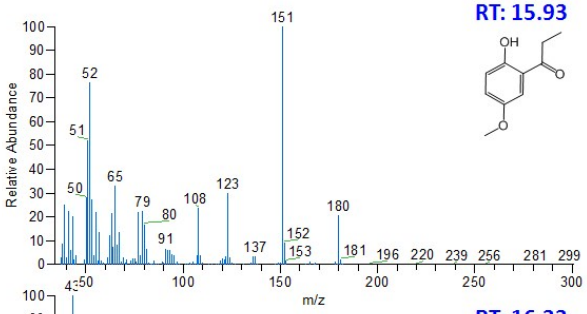
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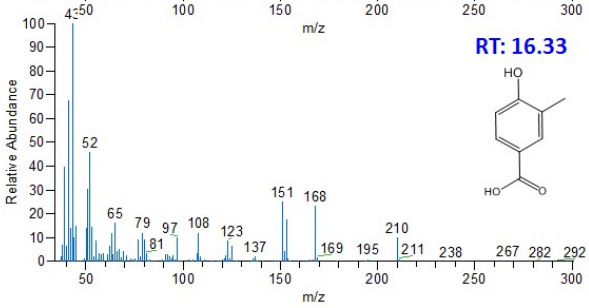
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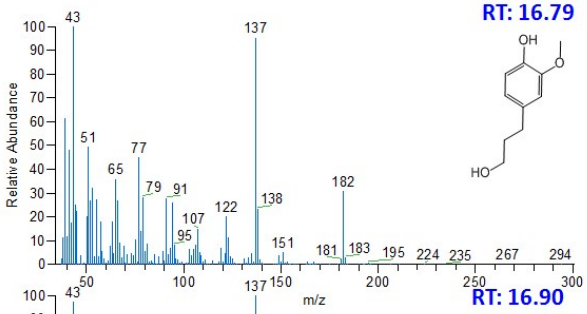
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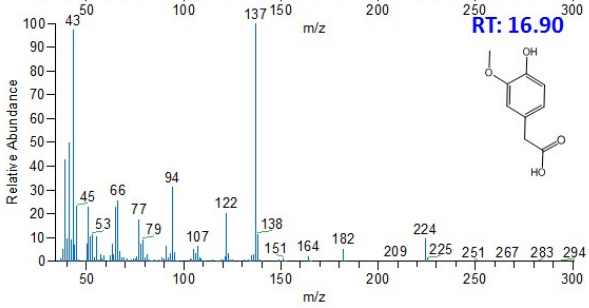
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Relative Abundance
m/z

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