Electronic Supplementary Material (ESI) for RSC Advances.

Towards effective Lignin Conversion: HZSM-5 catalyzed one-pot solvolytic depolymerisation/hydrodeoxygenation of Lignin into Value added Hydrocarbons

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Supporting Information

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Table S-1 Calculated lattice parameters of HZSM-5.

HZSM-5 (ICDD[a] ref. code 00-044-0003)		**HZSM-5 (synthesised)**		**NiO (ICDD[a] ref. code 01-073-1523)**		**NiO impregnated on HZSM-5**	
Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
a (Å)	20.104	a (Å)	20.094	a (Å)	4.1800	a (Å)	4.18349
b (Å)	19.897	b (Å)	19.891	a (Å)	4.1800	a (Å)	4.18349
c (Å)	13.395	c (Å)	13.393	a (Å)	4.1800	a (Å)	4.18349
Cell volume (10^6 pm^3)	5358.12	Cell volume (10^6 pm^3)	5353.61	Cell volume (10^6 pm^3)	73.0300	Cell volume (10^6 pm^3)	73.2175

[a] ICDD-International Centre of Diffraction Data

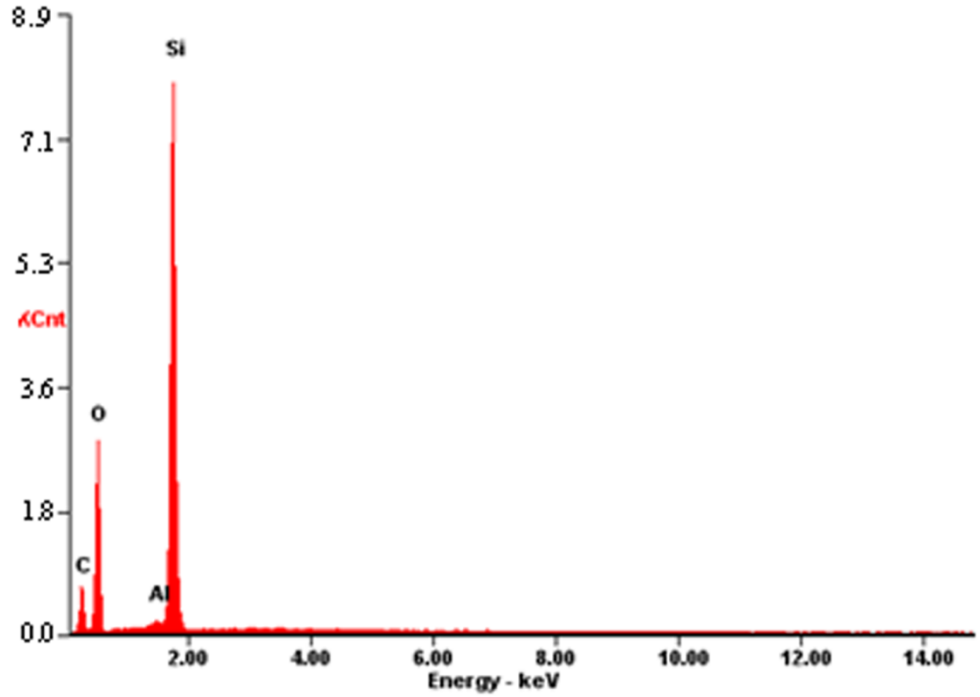

Figure S-1. EDS Spectra of HZSM-5

Table S-2 Gravimetric analysis of the catalyst recovered after catalytic runs (7 hr at 493 K) using 0.1 g of lignin, 1.7 mmol NaOH and 0.1 g of Ni-ZSM-5 catalyst in 10 mL of CH_3OH and 10 ml Water.[a]

Runs	Catalyst recovered (mg)	Deviation
1	99.8	-0.8
2	100.9	0.3
3	100.5	-0.1
4	101.2	0.6
Avg.	100.6	±0.45

[a]Few separate runs were conducted with 0.1 g lignin and 0.1 g Ni-ZSM-5 for 7 Hr. After the described solvent work-ups, the THF insoluble fraction was thoroughly washed with THF and dried in oven at 323 K for 6 hrs and measured gravimetrically. Results are shown in table S2, very little char (<1%), if any, was formed in the reaction with Solid catalyst. While without Solid catalyst and NaOH up to 40 % char was obtained.

Table S-3 FTIR bands assignment in lignin.

Wavenumber (cm^{-1})	Band origin
3400- 3600	Hydroxyl groups in phenolic and aliphatic structures
3000-3200	Aromatic C H stretching
2880-2968	C H stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains.
1720-1705	unconjugated carbonyl/carboxyl stretching
1600, 1515 and 1426	Aromatic skeleton vibrations
1460-1470	C H deformation; asym. in CH_3 and CH_2
1365-1370	Aliphatic C H stretch in CH_3, not in OCH_3
1325-1330	S ring plus G ring condensed
1266-1270	G ring plus C=O stretch
1215-1220	C–C plus C–O plus C=O stretching
1115	C–O–C linkages
1035	Aromatic in plane C–H deformation
855-865	aromatic out of plane C–H deformation

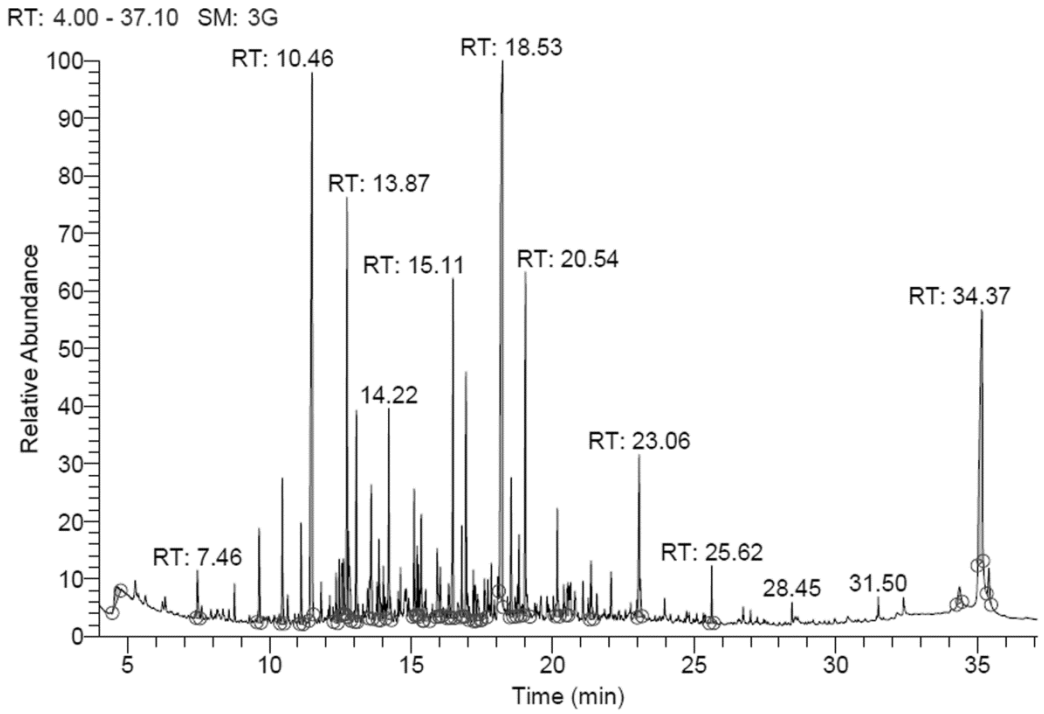

Figure S-2. Total ion chromatogram of Water soluble products of reaction with no solid catalyst.

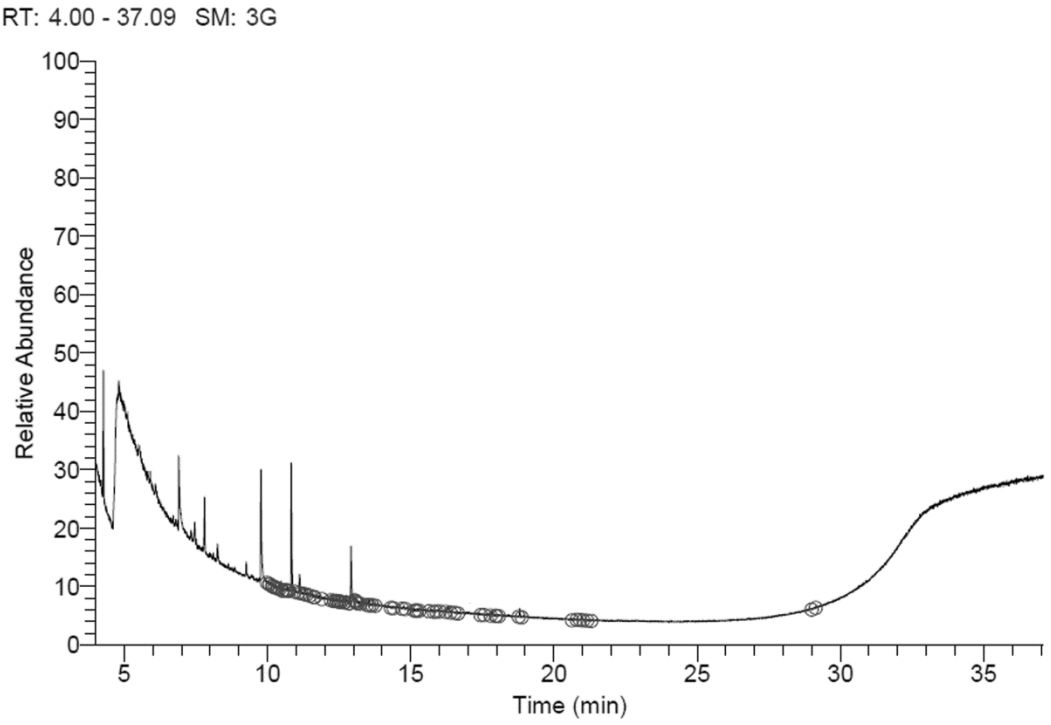

Figure S-3. Total ion chromatogram of EtOAc soluble products of reaction with no solid catalyst.

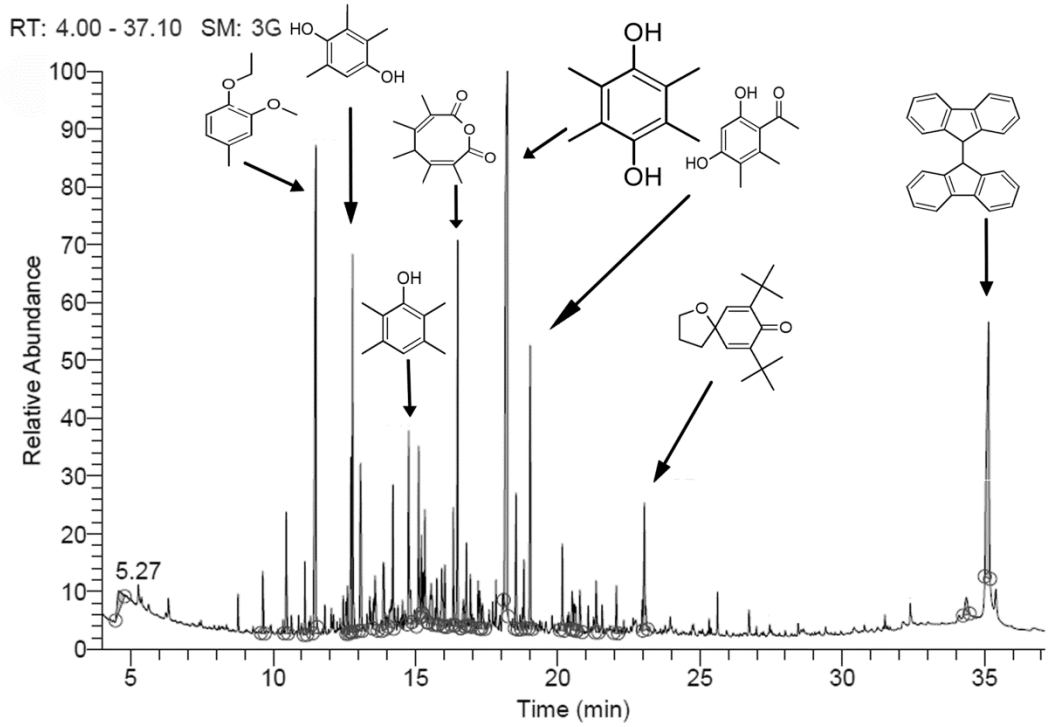

Figure S-4. Total ion chromatogram of water soluble products of reaction with HZSM-5.

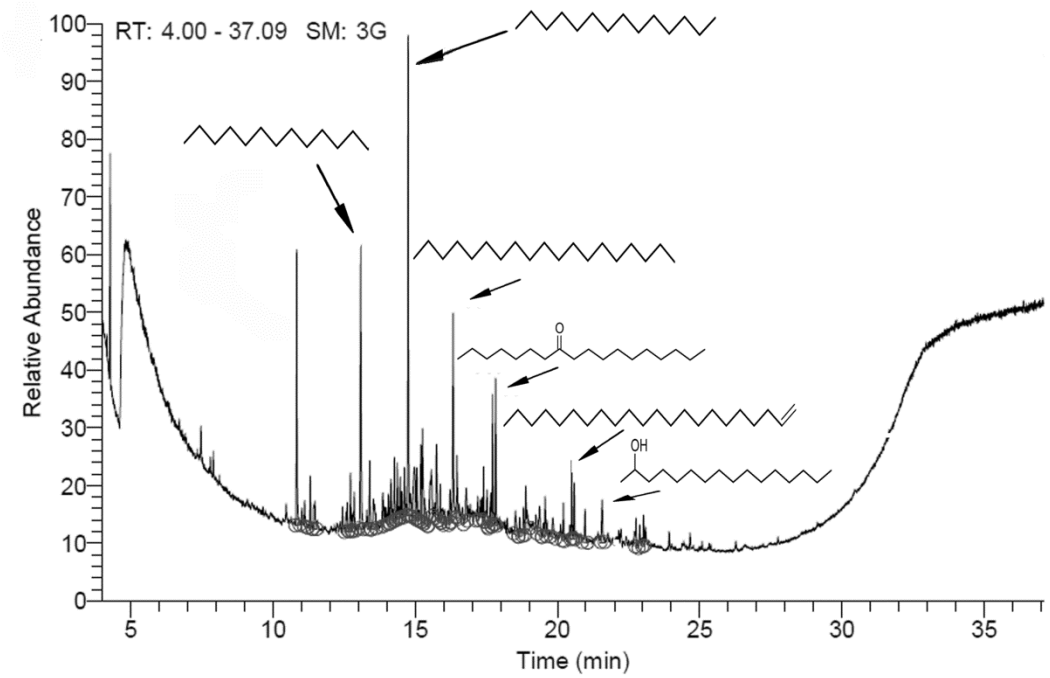

Figure S-5. Total ion chromatogram of EtOAc soluble products of reaction with HZSM-5.

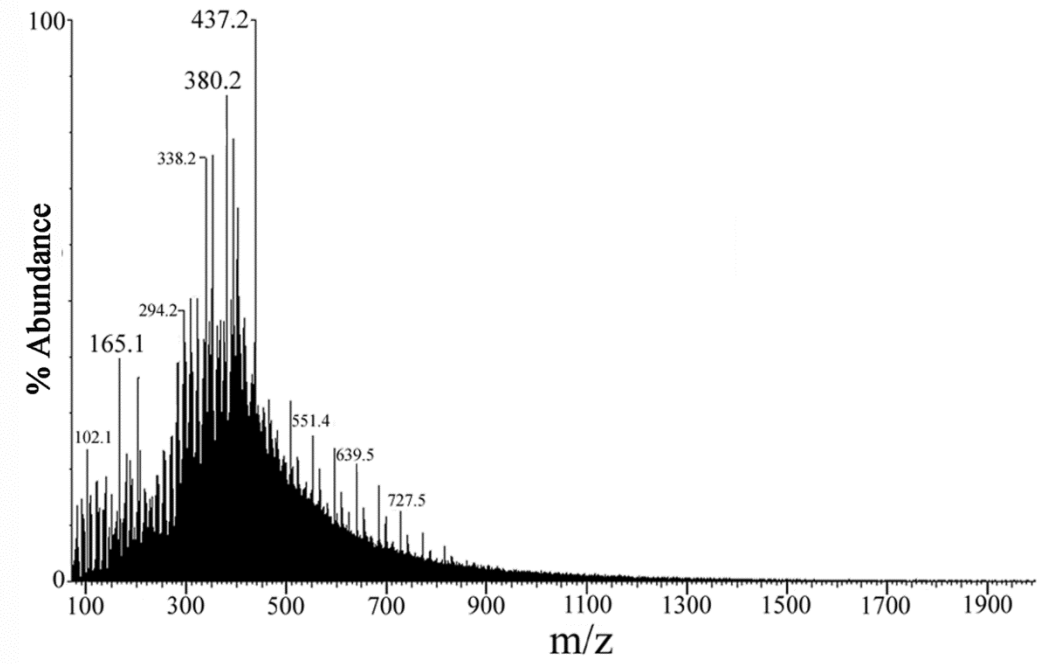

Figure S-6. ESI-MS spectra of lignin conversion products of reaction with HZSM-5.

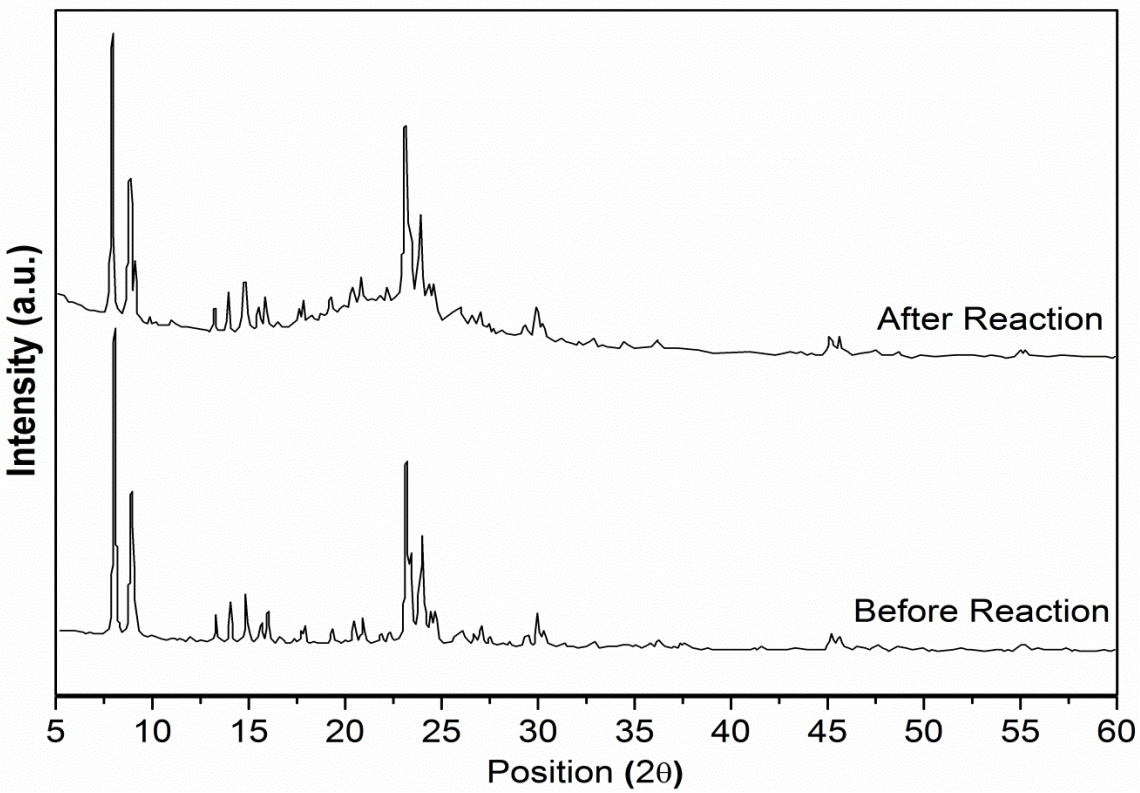

Figure S-7. XRD spectra of HZSM-5 after and before reaction.

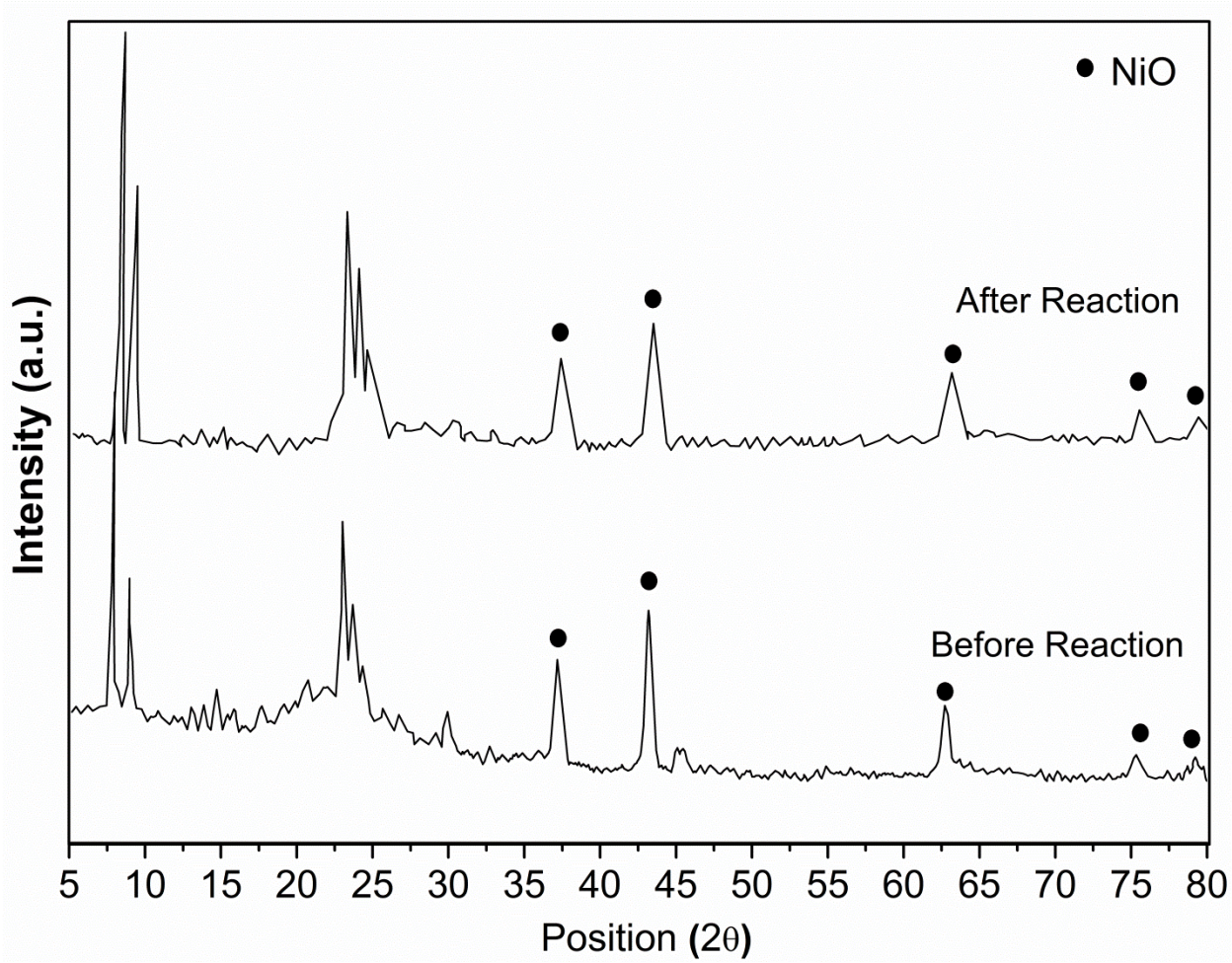

Figure S-8. XRD spectra of Ni-ZSM-5 after and before reaction.

Table S-4 Compound identified in EtOAc soluble products of reaction with HZSM-5.

RT	Compound Name	Molecular Formula	Molecular Weight	Area %
11.12	2-Naphthalenol, 1,2-dihydro-,acetate	$C_{12}H_{12}O_2$	188	0.78
11.31*	**Dodecane**	**$C_{12}H_{26}$**	**170**	**1.34**
11.47	à-Irone	$C_{14}H_{22}O$	206	1.48
12.61**	**Cyclopropanetetradecanoic acid,2-octyl-, methyl ester**	**$C_{26}H_{50}O_2$**	**394**	**4.75**
12.72	2-Cyclopenten-1-one, 2-(2-butenyl)-4-hydroxy-3-methyl,(Z)	$C_{10}H_{14}O_2$	166	1.46
13.53	**2-hydroxy-6-hexadecenoic acid, methyl ester**	**$C_{17}H_{41}O_3$**	**356**	**1.91**
13.86	Trans-Z-à-Bisabolene epoxide	$C_{15}H_{24}O$	220	1.11
14.27	**1-Hexadecanol, 2-methyl-**	**$C_{17}H_{36}O$**	**256**	**1.67**
14.38	**Dodecane, 2,6,10-trimethyl-**	**$C_{15}H_{32}$**	**212**	**1.47**
14.48	à-acorenol	$C_{15}H_{26}O$	222	0.90
14.75	**Tetradecane**	**$C_{14}H_{30}$**	**198**	**19.04**
15.06	**5-Isopropylidene-6-methyl deca-3,6,9-trien-2-one**	**$C_{14}H_{20}O$**	**204**	**1.33**
15.26	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$	156	5.10
15.33	2H-Cyclohepta[b]furan-2-one, 6-[1-(acetyloxy)-3-oxobutyl]-3,3a, 4,7,8,8a-hexahydro-7-methyl-3-methylene	$C_{17}H_{22}O_5$	306	1.26
15.75	**Tetradecane, 2,6,10-trimethyl-**	**$C_{17}H_{36}$**	**240**	**3.94**
15.96	Cyclohexane,1,1,3-trimethyl-2,3-epoxy-2(3-methylcyclobuten-2-yl)-4-acetyloxy-	$C_{16}H_{24}O_3$	264	0.76
16.33	**Hexadecane**	**$C_{16}H_{34}$**	**226**	**5.58**
16.47	3-tert-Butyl-4-hydroxyanisole	$C_{11}H_{16}O_2$	180	1.65
17.40	**1-Dodecanol,3,7,11-trimethyl-**	**$C_{15}H_{32}O$**	**228**	**3.48**
17.52	2-Butenal, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	$C_{14}H_{22}O$	206	1.19
17.72	**1-Hexadecanol, acetate**	**$C_{18}H_{36}O_2$**	**284**	**8.89**
17.83	**Nonadecane**	**$C_{19}H_{40}$**	**268**	**3.17**
18.52	Xanthatin,1'-acetoxy-3-methyl-3-demethylene-1',2'-dihydro-	$C_{17}H_{24}O_5$	308	1.18
18.89	**8-Octadecanone**	**$C_{18}H_{36}O$**	**268**	**2.04**
20.21	**Heptadecane, 3methyl-**	**$C_{18}H_{38}$**	**254**	**0.90**
20.50	**1-Docosene**	**$C_{22}H_{44}$**	**308**	**1.74**
20.59	**Heptacosane**	**$C_{27}H_{56}$**	**380**	**2.04**
21.57	2-Myristynoyl pantetheine	$C_{25}H_{44}N_2O_5S$	484	1.55
23.03	**2-Hexadecanol**	**$C_{16}H_{34}O$**	**242**	**4.73**

*** Acyclic deoxygenated hydrocarbons (marked in bold red), ** Acyclic Oxygenated hydrocarbons (marked in bold blue)**

Table S-5 Compound identified in EtOAc soluble product of reaction with Ni-ZSM-5.

RT	Compound Name	Molecular Formula	Molecular Weight	Area %
11.11	2-Naphthalenol, 1,2-dihydro-,acetate	$C_{12}H_{12}O_2$	188	1.03
11.31*	**Decane, 4-methyl-**	**$C_{11}H_{24}$**	**156**	**2.93**
11.47	à-Irone	$C_{14}H_{22}O$	206	1.64
12.73	2-Cyclopenten-1-one, 2-(2-butenyl)-4-hydroxy-3-methyl, (Z)	$C_{10}H_{14}O_2$	166	1.23
14.07**	**Methoxyacetic acid, 2-tridecyl ester**	**$C_{16}H_{32}O_3$**	**272**	**0.88**
14.15	**Tetradecane, 2,6,10-trimethyl-**	**$C_{17}H_{36}$**	**240**	**3.54**
14.27	**1-Hexadecanol, 2-methyl-**	**$C_{17}H_{36}O$**	**256**	**5.48**
14.37	**Dodecane, 2,6,10-trimethyl-**	**$C_{15}H_{32}$**	**212**	**1.74**
14.47	à-acorenol	$C_{15}H_{26}O$	222	0.95
14.53	Benzene, (2,4-cyclopentadien-1-ylidenemethyl-)	$C_{12}H_{10}$	154	0.75
14.75	**Tetradecane**	**$C_{14}H_{30}$**	**198**	**20.64**
15.06	1H-Benzocycloheptene, 2,4a,5,6,7,8,9,9a-octahydro-3,5,5-trimethyl-9-methylene,(4aScis)	$C_{15}H_{24}$	204	1.14
15.26	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$	156	4.17
15.55	**9,12,15-Octadecatrienoic acid,2-(acetyloxy)-1-[(acetyloxy)methyl]ethyl ester, (Z,Z,Z)**	**$C_{25}H_{40}O_6$**	**436**	**3.27**
15.75	**Heptadecane, 2,6,10,14-tetramethyl-**	**$C_{21}H_{44}$**	**296**	**2.51**
16.33	**Nonadecane**	**$C_{19}H_{40}$**	**268**	**6.56**
16.47	3-tert-Butyl-4-hydroxyanisole	$C_{11}H_{16}O_2$	180	1.63
17.34	**Cyclopropanetetradecanoic acid, 2-octyl-, methyl ester**	**$C_{26}H_{50}O_2$**	**394**	**7.44**
17.40	**2-Hexadecanol**	**C16H34O**	**242**	**4.87**
17.52	Naphtho-[2,3b]-furan-2-(3H)-one,-4-(acetyloxy)decahydro-8-hydroxy-3,8a-dimethyl-5-methylene,[3R(3à,3aà,4à,4aà,8á,8aá,9aá)]	$C_{17}H_{24}O_5$	308	1.11
17.66	**1-Hexadecanol, acetate**	**$C_{18}H_{36}O_2$**	**284**	**3.61**
17.72	**Acetic acid, n-octadecyl ester**	**$C_{20}H_{40}O_2$**	**312**	**2.50**
18.52	2H-Cyclohepta-[b]-furan-2-one, 6-[1-(acetyloxy)-3-oxobutyl]-3,3a,4,7,8,8a-hexahydro-7-methyl-3-methylene	$C_{17}H_{22}O_5$	306	1.10
18.89	**8-Octadecanone**	**C18H36O**	**268**	**2.13**
20.21	**Heptadecane, 2,3dimethyl-**	**$C_{19}H_{40}$**	**268**	**1.15**
20.50	**1-Docosene**	**$C_{22}H_{44}$**	**308**	**1.35**
20.59	**Octadecane**	**$C_{18}H_{38}$**	**254**	**1.69**
22.76	**Nonadecane, 2,3-dimethyl-**	**$C_{21}H_{44}$**	**296**	**1.02**

*** Acyclic deoxygenated hydrocarbons (marked in bold red), ** Acyclic Oxygenated hydrocarbons (marked in bold blue)**

Table S6 Compound identified in water soluble product of reaction with HZSM-5.

RT	Compound Name	Molecular Formula	Molecular Weight	Area %
9.64	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	$C_9H_{14}O$	138	0.90
10.46	1,4-Benzenediol, 2,5-dimethyl-	$C_8H_{10}O_2$	138	1.93
11.12	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	$C_{10}H_{16}O$	152	0.93
11.50	Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	136	10.37
12.62	2-Cyclopenten1one, 2-(2-butenyl)- 4-hydroxy-3-methyl-,(Z)	$C_{10}H_{14}O_2$	166	0.77
12.74	Benzene, 1-ethoxy-2-methoxy-4-methyl-	$C_{10}H_{14}O_2$	166	2.08
12.80	1,4-Benzenediol, 2,3,5-trimethyl-	$C_9H_{12}O_2$	152	5.17
13.07	Phenol, 2-ethyl-4,5-dimethyl-	$C_{10}H_{14}O$	150	3.08
13.58	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy-	$C_{11}H_{16}O_2$	180	1.41
13.87	Phenol, 3-methoxy-2,5,6-trimethyl-	$C_{10}H_{14}O_2$	166	1.57
14.21	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	150	2.59
15.11	2,5-Heptadienoic anhydride, 2,3,4,5,6-pentamethyl, Z,Z-	$C_{12}H_{16}O_3$	208	2.47
15.21	3-Buten-2-one,3-methyl-4-(1,3,3-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl)-	$C_{14}H_{22}O_2$	222	0.98
15.33	Phenol, 5-methoxy-2,3,4-trimethyl-	$C_{10}H_{14}O_2$	166	1.58
15.55	1,4-Benzenediol, 2,3,5-trimethyl-	$C_9H_{12}O_2$	152	1.36
15.76	2-Oxabicyclo[3.3.0] oct-7-en-3-one, 7-(-1-hydroxypentyl)-	$C_{12}H_{18}O_3$	210	0.70
15.93	5,6,7,8-Tetramethylbicyclo[4.1.0]Hept-4-en-3-one	$C_{11}H_{16}O$	164	1.53
16.03	Carbofurane	$C_{12}H_{15}NO_3$	221	0.99
16.49	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	$C_{11}H_{16}O_2$	180	5.53
16.69	Phenol, 5-methoxy-2,3-dimethyl-	$C_9H_{12}O_2$	152	0.69
16.79	Phenol, 4-methoxy-2,3,6-trimethyl-	$C_{10}H_{14}O_2$	166	1.22
16.94	Phenol, 2-(1,1-dimethylethyl)-3-methyl-	$C_{11}H_{16}O$	164	0.68
17.26	àTetralol, 2-amino-5,6-dimethoxy-	$C_{12}H_{17}NO_3$	223	0.74
17.34	Benzene,	$C_{12}H_{18}O_2$	194	0.65

	1,4-dimethoxy-2,3,5,6-tetramethyl-			
18.24	Durohydroquinone	$C_{10}H_{14}O_2$	166	19.05
18.53	Phenol, 2-methoxy-4-methyl-6-[propenyl]-	$C_{11}H_{14}O_2$	178	1.86
18.81	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	$C_{11}H_{16}O_2$	180	1.08
19.03	4',6'-Dihydroxy-2',3'-dimethylacetophenone	$C_{10}H_{12}O_3$	180	4.11
20.17	2-Hydroxy-4,5-methylene dioxypropiophenone	$C_{10}H_{10}O_4$	194	1.28
20.51	3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl) cyclohex-2-enone	$C_{14}H_{22}O$	206	0.75
20.59	4(3,3-Dimethylbut-1-ynyl) 4-hydroxy-2,6,6-trimethylcyclohex-2-enone	$C_{15}H_{22}O_2$	234	0.68
20.78	4,7-Dimethoxy-2-methyl indan-1-one	$C_{12}H_{14}O_3$	206	0.73
21.35	Phenol, 2,5-bis(1,1-dimethylethyl)-	$C_{14}H_{22}O$	206	0.79
22.06	Trimethyl-3,4-methylene dioxychromane	$C_{13}H_{16}O_3$	220	0.69
23.05	7,9-Ditert-butyl-1-oxaspiro-[4,5]-deca-6,9-dien-8-one	$C_{17}H_{26}O_2$	262	2.41
34.36	9H-Xanthene-1,4-(4ah,9ah)-dione,-7-hydroxy-2,3,4a,5,6,8,9a-heptamethyl	$C_{20}H_{24}O_4$	328	0.81
35.15	9,9'-Bi-9H-fluorene	$C_{26}H_{18}$	330	9.75

Table S7 Compound identified in water soluble product of reaction with Ni-ZSM-5

RT	**Compound Name**	**Molecular Formula**	**Molecular Weight**	**Area %**
9.64	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl	$C_9H_{14}O$	138	0.87
10.46	1,4-Benzenediol, 2,5-dimethyl-	$C_8H_{10}O_2$	138	1.81
11.12	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	$C_{10}H_{16}O$	152	0.82
11.50	Phenol, 2,3,5-trimethyl-	$C_9H_{12}O$	136	10.84
12.62	2-Cyclopenten-1-one, 2-(2-butenyl)4-hydroxy-3-methyl,(Z)-	$C_{10}H_{14}O_2$	166	0.74
12.74	Benzene, 1-ethoxy-2-methoxy-4-methyl-	$C_{10}H_{14}O_2$	166	2.22
12.80	3,4-Dimethoxytoluene	$C_9H_{12}O_2$	152	4.99
13.07	Phenol, 2-ethyl-4,5-dimethyl-	$C_{10}H_{14}O$	150	2.56

13.59	3-Acetyl-2,4,4-trimethyl cyclohex-2-en-1-one	$C_{11}H_{16}O_2$	180	1.07
13.88	Phenol, 3-methoxy-2,5,6-trimethyl-	$C_{10}H_{14}O_2$	166	1.42
14.12	Phenol, 3-methoxy-2,5,6-trimethyl-	$C_{10}H_{14}O_2$	166	0.62
14.21	Phenol, 2,3,5,6-tetramethyl-	$C_{10}H_{14}O$	150	1.68
15.11	2,5-Heptadienoic anhydride, 2,3,4,5,6-pentamethyl, Z,Z	$C_{12}H_{16}O_3$	208	0.96
15.21	6-(3-Hydroxybut-1-enyl) 1,5,5-trimethyl-7-oxabicyclo -[4.1.0]-heptan-2-ol	$C_{13}H_{22}O_3$	226	0.64
15.33	Phenol, 3-methoxy-2,5,6-trimethyl-	$C_{10}H_{14}O_2$	166	1.38
15.56	1,4-Benzenediol, 2,3,5-trimethyl-	$C_9H_{12}O_2$	152	1.32
15.93	5,6,7,8-Tetramethylbicyclo -[4.1.0]-hept-4-en-3-one	$C_{11}H_{16}O$	164	1.58
16.04	Carbofurane	$C_{12}H_{15}NO_3$	221	0.92
16.49	Phenol, 3-(1,1-dimethylethyl) 4-methoxy-	$C_{11}H_{16}O_2$	180	5.64
16.69	Phenol, 5-methoxy-2,3-dimethyl	$C_9H_{12}O_2$	152	0.69
16.79	2',4'-Dihydroxy-3'-methylacetophenone	$C_9H_{10}O_3$	166	1.36
16.94	Phenol, 2-(1,1-dimethylethyl)-3-methyl-	$C_{11}H_{16}O$	164	0.72
17.20	1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)	$C_{14}H_{22}O_2$	222	0.68
17.26	à-Tetralol, 2-amino-5,6-dimethoxy1	$C_{12}H_{17}NO_3$	223	0.75
17.34	Benzene,1,4-dimethoxy -2,3,5,6-tetramethyl-	$C_{12}H_{18}O_2$	194	0.57
18.26	Durohydroquinone	$C_{10}H_{14}O_2$	166	23.73
18.54	Phenol, 2-methoxy-4-methyl-6-[propenyl]-	$C_{11}H_{14}O_2$	178	1.99
18.81	Phenol, 3-(1,1-dimethylethyl) -4-methoxy-	$C_{11}H_{16}O_2$	180	1.38
19.04	4',6'-Dihydroxy-2', 3'-dimethylacetophenone	$C_{10}H_{12}O_3$	180	5.10
20.17	2-Hydroxy-4,5-methylene dioxypropiophenone	$C_{10}H_{10}O_4$	194	1.56
20.60	3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl) cyclohex-2-enone	$C_{14}H_{22}O$	206	0.58

20.79	4,7-Dimethoxy-2-methyl indan-1-one	$C_{12}H_{14}O_3$	206	0.74
21.36	Phenol, 2,5-bis (1,1-dimethylethyl)-	$C_{14}H_{22}O$	206	0.92
22.07	Trimethyl-3,4-methylene dioxychromane	$C_{13}H_{16}O_3$	220	0.72
23.04	7,9-Ditertbutyl-1-oxaspiro[4,5]-deca-6,9-dien-8-one-	$C_{17}H_{26}O_2$	262	2.32
25.62	4,6-Dimethoxy-1-naphthaldehyde-	$C_{13}H_{12}O_3$	216	0.66
35.13	9,9'-Bi-9H-fluorene	$C_{26}H_{18}$	330	8.47