Supplementary Materials

Rhodium porphyrin molecule-based catalysts for the hydrogenation of biomass derived levulinic acid to biofuel additive γ-valerolactone

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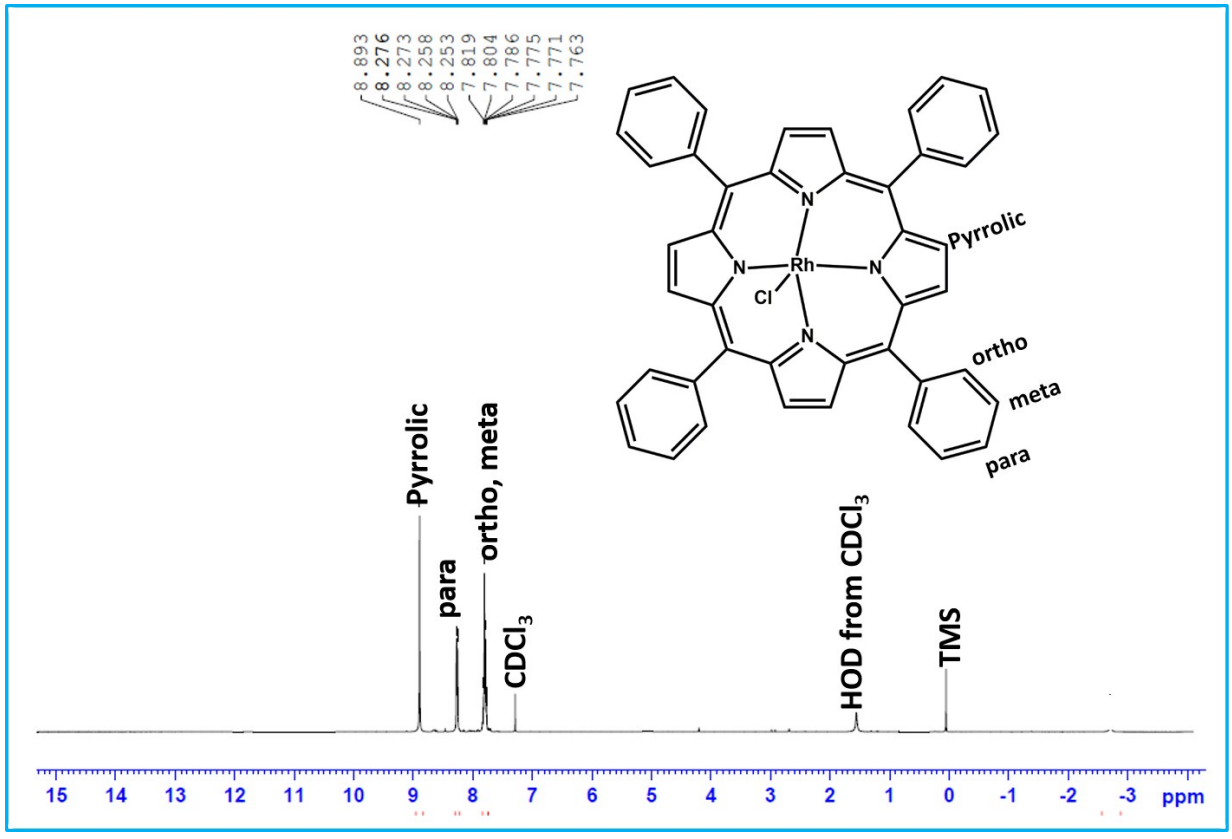

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Figure S1; ^{1}H NMR spectrum of RhTPP ($CDCl_3$, 400MHz)

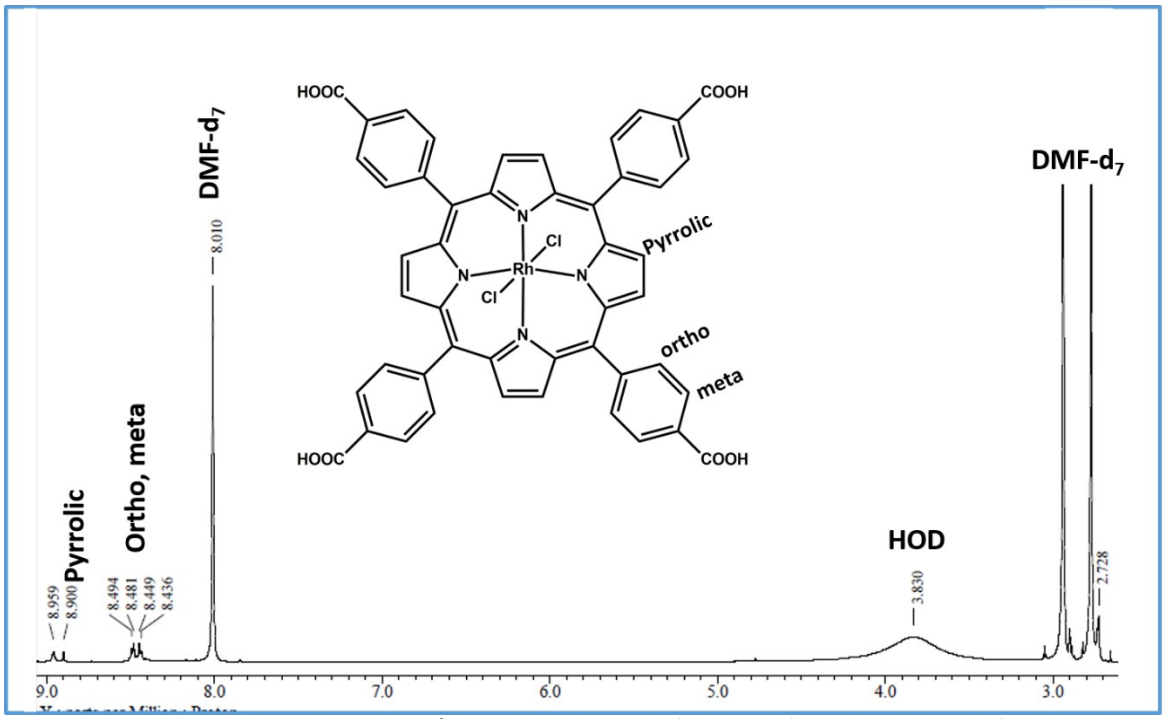

Figure S2; ^{1}H NMR spectrum of RhTCPP (DMF-d_7, 400MHz)

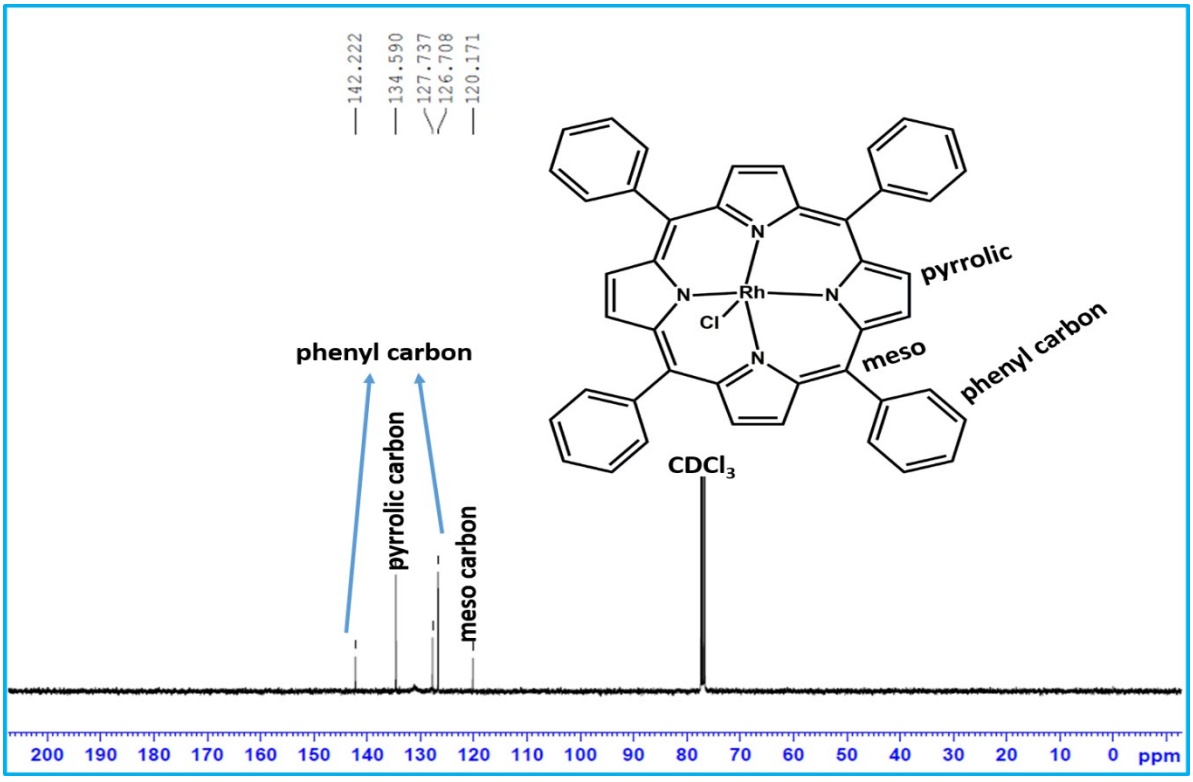

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Figure S3; ^{13}C NMR spectrum of RhTPP

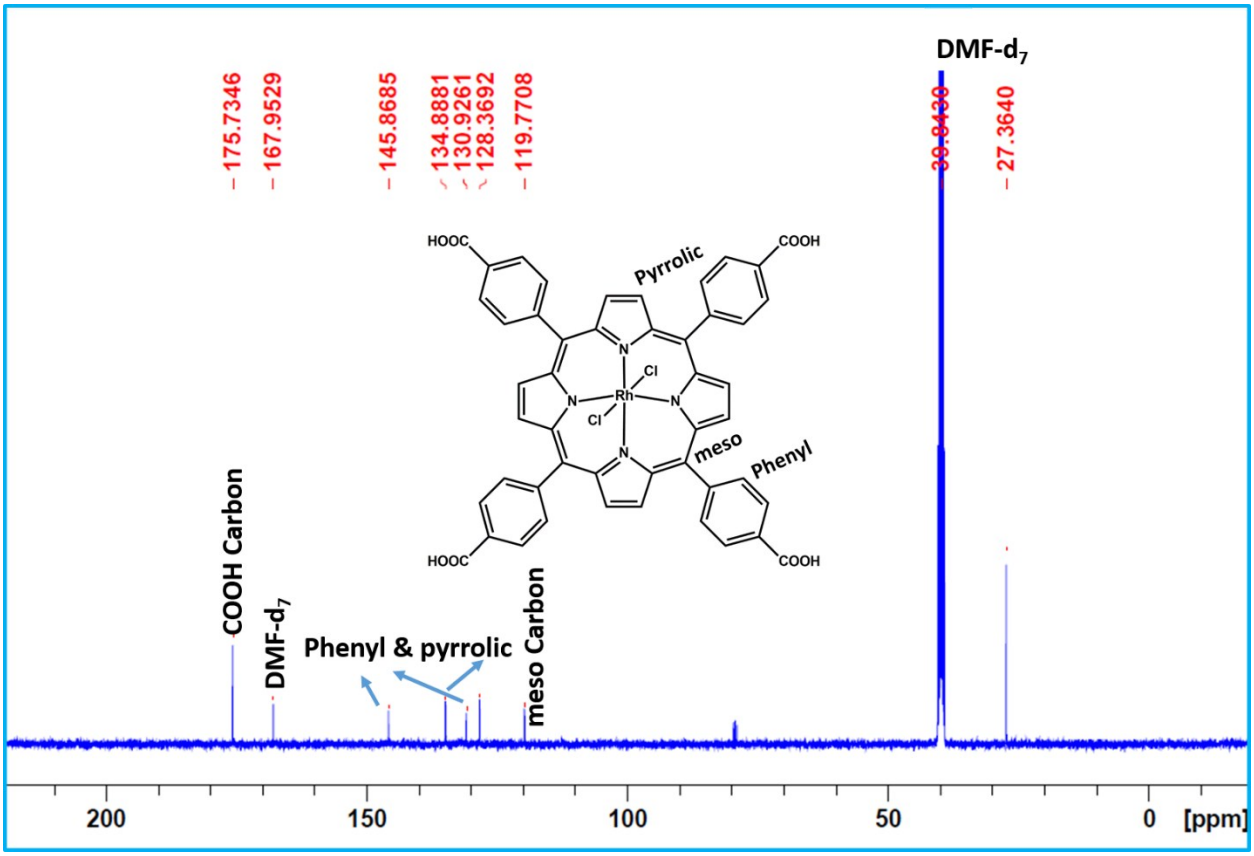

Figure S4; ^{13}C NMR spectrum of RhTCPP

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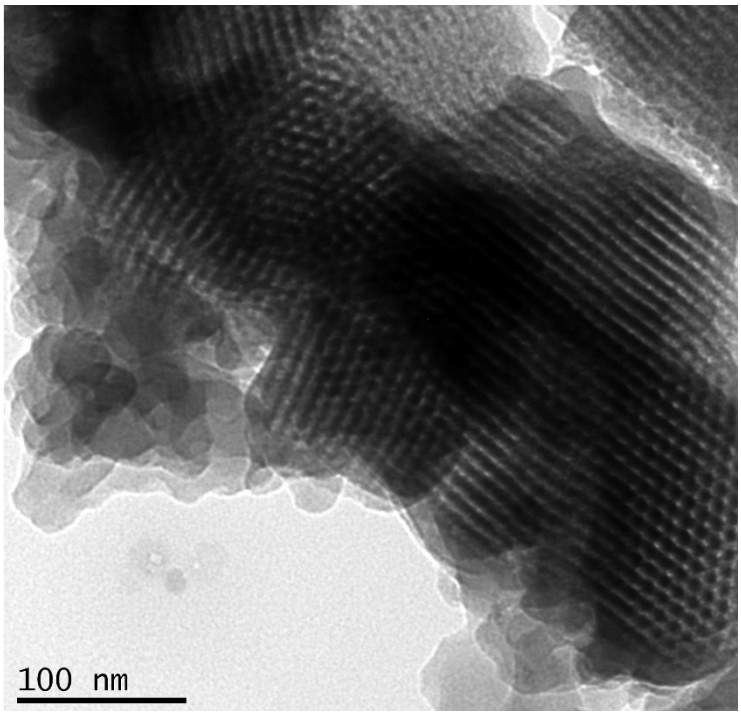

Figure S5; High resolution transmission electron microscopy (HR-TEM) micrographs of RhTPP-SBA-AM

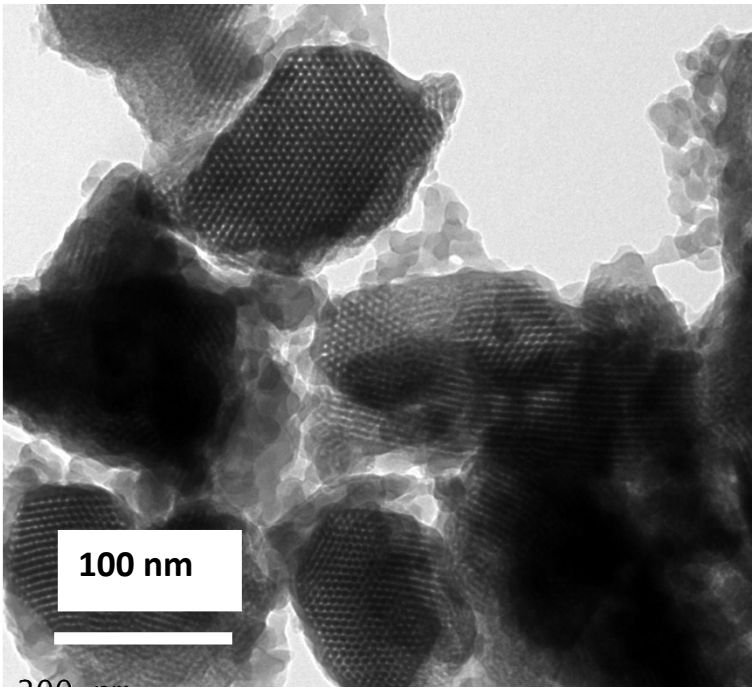

Figure S5; High resolution transmission electron microscopy (HR-TEM) micrographs RhTCPP-SBA-AM

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Table S1: Quenching studies by filtering the solution (Hot filtration study).

Catalysts	Conversion (%)	Selectivity (%)	
		GVL	Diol
RhTPP-SBA-AM	1.4	92	8
RhTCPP-SBA-AM	1.6	86	12

Reaction Conditions: LA = 5mmol, Solvent (IPA) = 3mL, Pressure = 10 bar H_2, time = 12 hrs, Temperature = 100 °C, Catalyst RhTPP-SBA-AM/RhTCPP-SBA-AM= 0.1g.

Table S2; Levulinic acid hydrogenation using ruthenium porphyrin and iridium porphyrin complex.

Catalysts	Conversion (%)	Selectivity (%)		
		GVL	Diol	Valeric acid
IrTPP	93.8	87	9	4
RuTPP	89	62	30	8
RhTPP	100	100	--	

Reaction Conditions: LA = 5mmol, Solvent (IPA) = 3mL, Pressure = 10 bar H_2, time = 12 hrs, Temperature = 100 °C, Catalyst RhTPP/ IrTPP/RhTPP = 0.01g.

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Table S3; Comparison of levulinic acid hydrogenation reaction by various reported catalysts.

Catalysts	Reaction condition	Conversion / GVL selectivity(%)	Reference
Hybrid Ru-containing catalysts, based on poly(propylene imine) (PPI) dendrimers, immobilized in silica	Reaction conditions are: 0.3 mL levulinic acid, 0.3 mL of water, substrate/Ru ~ 1700, Time = 1 h., H_2 pressure = 30 bars, Temp = 80 ^{0}C.	80/95	10
Nickel Catalysts Supported on Aluminum Oxide	30%Ni/Al_2O_3 = 0.1g, Levulinic acid = 1g , Solvent = water, Time = 3 hr Temp= 200 ^{o}C, H_2 pressure = 3MPa	96.2/90.3	14
Nickel Catalysts Supported on Aluminum Oxide	30%Ni/Al_2O_3 = 0.1g, Levulinic acid = 1g , Solvent = dioxane, Time = 2 hr, Temp= 180 ^{o}C, H_2 pressure = 3MPa	100/98.3	14
Ru(acac)3,with alkyl-bis(m-sulfonated-phenyl)- and dialkyl-(m-sulfonated-phenyl)phosphine ligands	Levulinic acid = 34.02 g, Catalysts Ru(acac)3 =0.046 mmol, Time = 1.8 hr, Temp = 140 °C, H_2 pressure = 100 bar	99.9	12
Ru supported on Carbon	Levulinic acid = 34.02 g, Catalysts Ru(acac)3 =0.046 mmol, Time = 1.8 hr, Temp = 150 °C, H_2 pressure = 55 bar	80/90	27
iridium pincer complexes	Levulinic acid = 3 mmol, Catalyst 0.15 mol% ligand, 1.2 eqv base KOH, Solvent = 4ml methanol, Time = 15 hr, Temp = 100 °C, H_2 pressure = 50 bar	89/96	93
Ru-PP/CNT based catalyst (	Levulinic acid = 1.0 mmol, catalyst = 50 mg,		

Polymeric ruthenium porphyrin-functionalized carbon nanotubes)	base, $NaHCO_3$50 mg, solvent methanol = 5 mL, H_2 pressure = 3.0 MPa,Tepm = 100°C time = 10 h		
[Ru(triphos)(TMM) catalysts ([Ru(Triphos)(TMM)] (Triphos= 1,1,1-tris(diphenylphosphinomethyl)ethane, TMM = tri-methylene methane)	Levulinic acid = 1.0 mmol, catalyst = 50 mg, base, solvent methanol = 5 mL, H_2 pressure = 50 bar,Tepm = 140°C, time = 18 h	99	94
Ruthenium−N-Triphos Complexes	Levulinic acid = 10 mmol LA, Solvent THF = 20 mL, 0.5 mol % complex or 0.5 mol % [Ru(acac)3] and 1.0 mol % ligand, time = 25 h, H_2 pressure = 65 bar,Tepm = 150°C	85	95
Rh based catalysts	Levulinic acid = 5mmol, Catalyst RhTPP = 0.01g, Solvent (IPA) = 3mL, H_2 Pressure = 10 bar, time = 12 hrs, Temperature = 100 °C,	100/100	Present work

Table S4: Conversion of various substrates using the RhTPP, RhTPP−SBA-AM, RhTCPP and RhTCPP−SBA-AM Catalysts‡.

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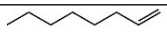
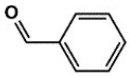
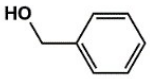
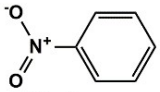
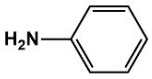
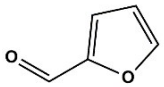
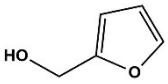
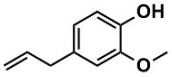
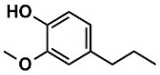
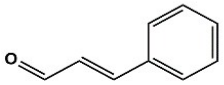
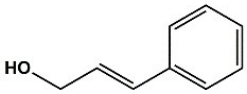
Substrate	Product	Product Yield (%)			
		RhTPP	RhTPP-SBA-AM	RhTCPP	RhTCPP-SBA-AM
 1-Octene	 Octane	100	100	100	100
 CycloOctene	 cyclooctane	100	100	100	100
 Benzaldehyde	 Benzyl alcohol	61	76	100	96
 Nitrobenzene	 Aniline	82	54	70	72
 Furfural	 Furfuryl Alcohol	80	87	85	68
 Eugenol	 2-methoxy-4-propylphenol	83	85	100	99
 Cinnamylaldehyde	 Cinnamylalcohol	58	98	96	85

‡ Reaction Conditions: LA = 5mmol, Solvent (IPA) = 3mL, Pressure = 10 bar H_2, time = 12 hrs, Temperature = 100 °C, Catalyst RhTPP/ RhTCPP = 0.01g, RhTPP-SBA-AM/ RhTCPP-SBA-AM= 0.1g