Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Lignin Monomer Conversion into Biolubricant Base Oils

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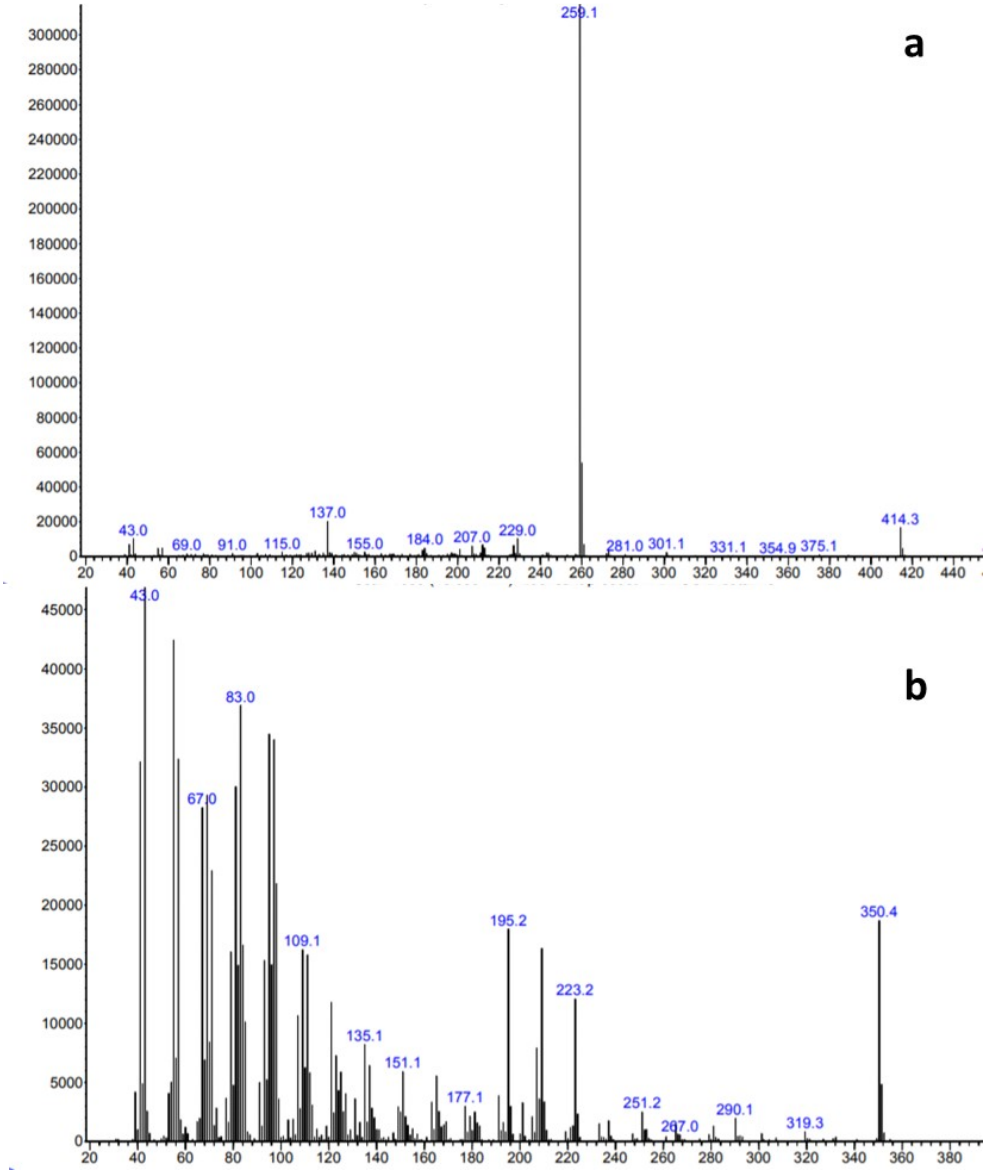


Figure S1: GCMS mass fragmentation of (a) branched benzene lubricant product (mass from GCMS – 414.3, calculated mass – 414) and (b) enal byproduct (mass from GCMS – 350.4, calculated mass – 350).

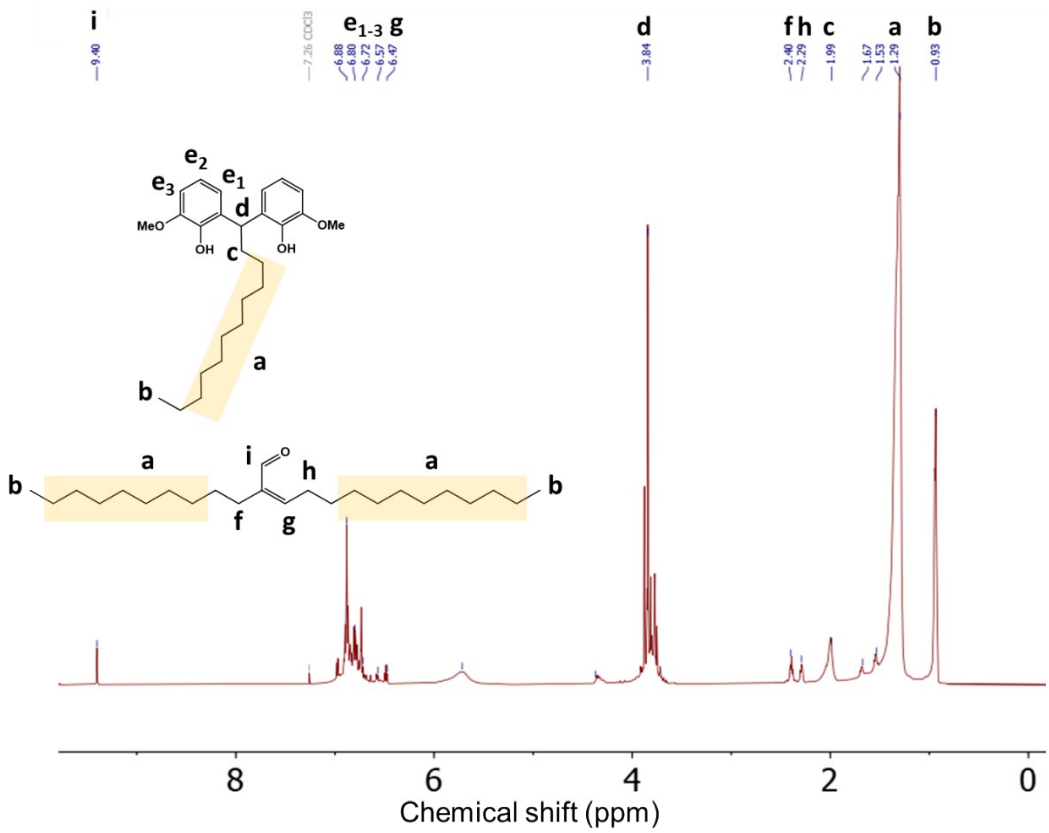
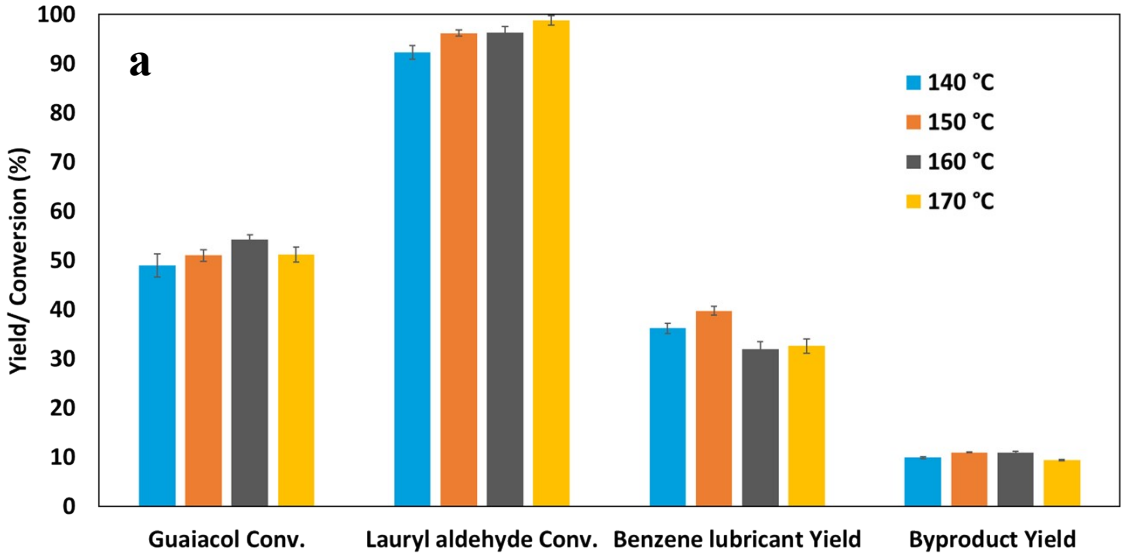


Figure S2: ^{1}H NMR spectrum of HAA reaction product. The sample was prepared in $CDCl_3$. The predominant product is the BBL followed by the enal product. The labels a-i are referencing the hydrogen atoms.



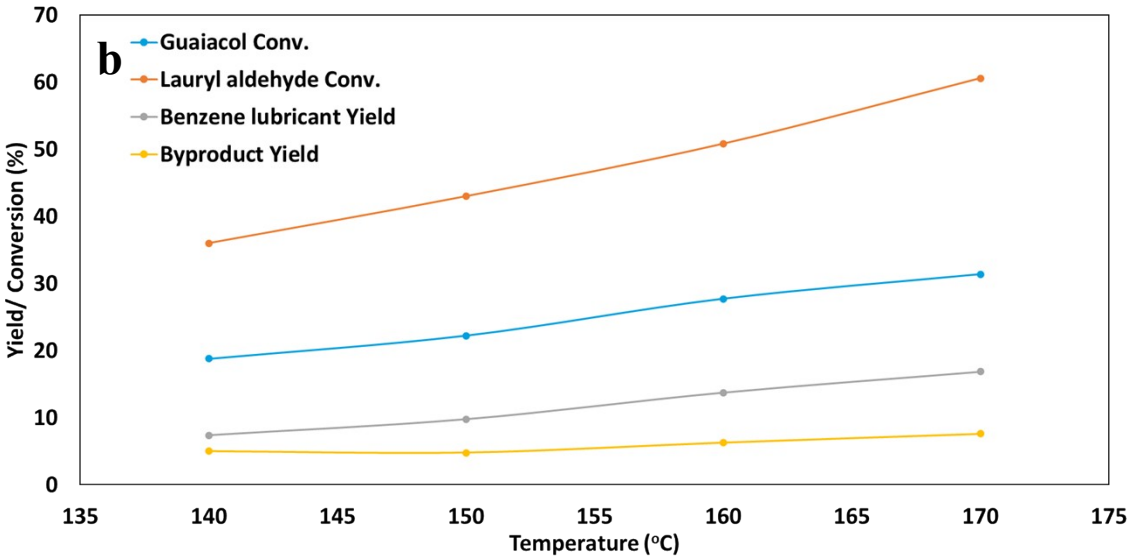


Figure S3: Effect of temperature on the yield of BBL and enal product and conversion of guaiacol and lauryl aldehyde reactants. A) Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 12 hr, 150 mg P-SiO_2. B) Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 1 hr, 150 mg P-SiO_2.

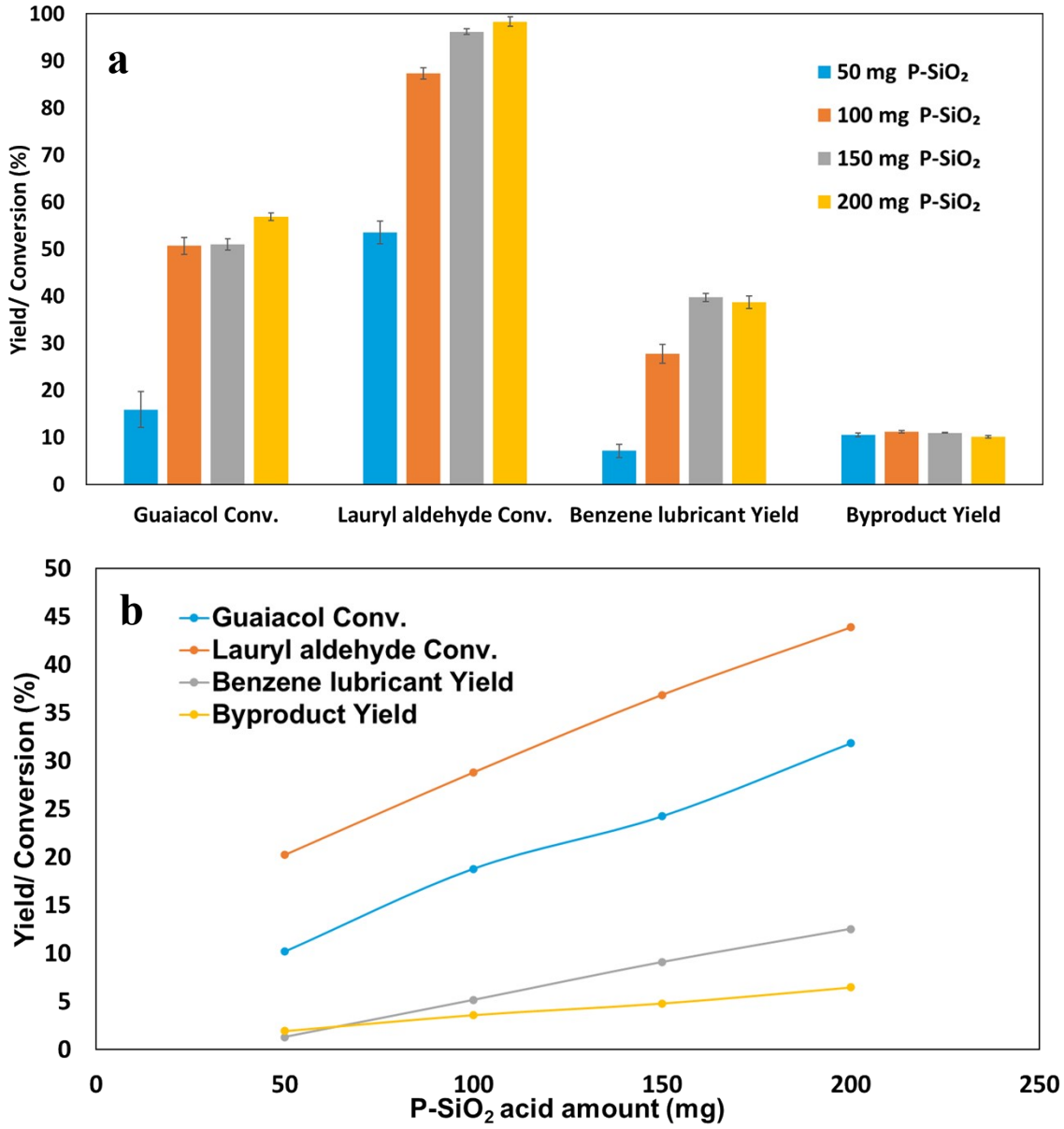


Figure S4: Effect of catalyst (P-SiO_2) amount on the yield of BBL and enal product and conversion of guaiacol and lauryl aldehyde reactants. A) Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 12 hr, 150 ^oC. B) Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 1 hr, 150 ^oC.

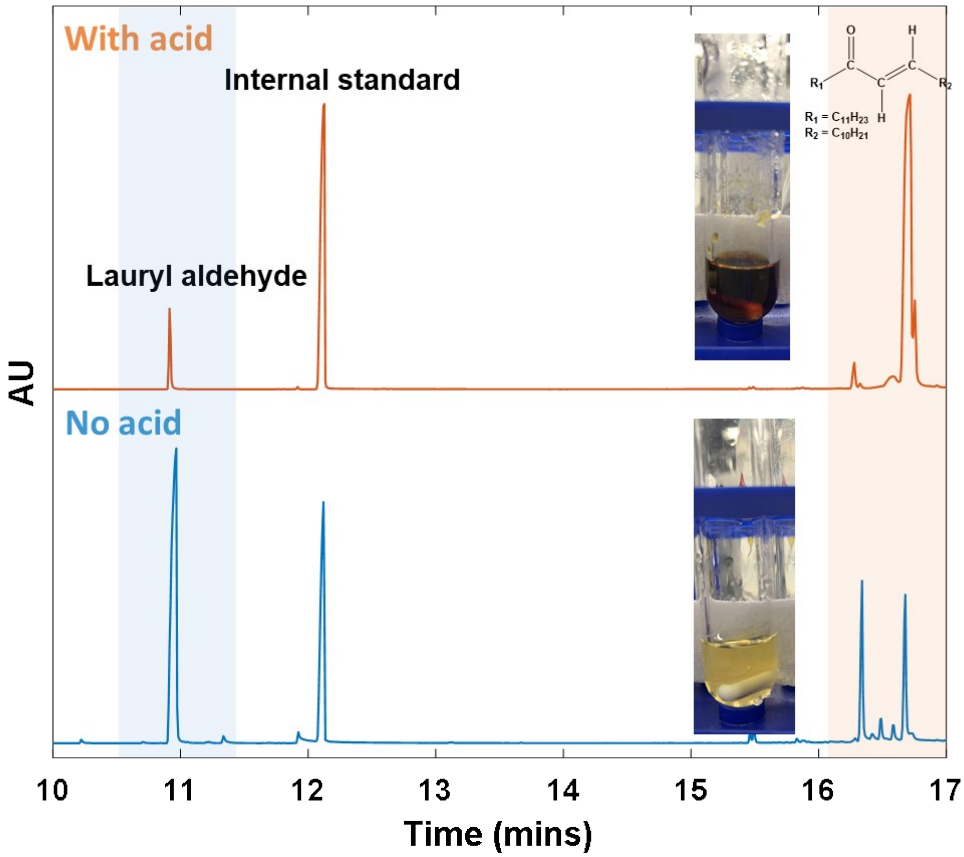


Figure S5: GC Chromatogram after heating lauryl aldehyde with and without acid catalyst. Reaction conditions: 5 mmol lauryl aldehyde, 100 mg P-SiO_2, 150 °C, 15 hr. Pictures inset from lauryl aldehyde condensation with and without acid catalyst.

Table S1: Initial reaction rate data.

	Reaction rates (M/min)		
	130 °C	140 °C	150 °C
r_{BBL}	0.0000381	0.0000453	0.0000784
$r_{Byproduct}$	0.00000676	0.0000109	0.0000189

Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 100 mg P-SiO_2.

Table S2: Comparison of guaiacol and lauryl aldehyde HAA in batch and semi-batch system.

	Batch system	Semi-batch system
Guaiacol conversion (%)	51.0	59.6
Lauryl aldehyde conversion (%)	96.2	94.0

BBL yield (%)	39.8	53.8
Byproduct yield (%)	11.0	6.8
Carbon balance (%)	85.0	92.0

Reaction conditions. Batch system: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 150 mg P-SiO_2, 12 hr, 150 ^oC. Semi-batch system: 10 mmol guaiacol, 1.25 mmol lauryl aldehyde,150 mg P-SiO_2, 12 hr, 150 ^oC, 1.25 mmol lauryl aldehyde was added at an interval of 4 hr thrice.

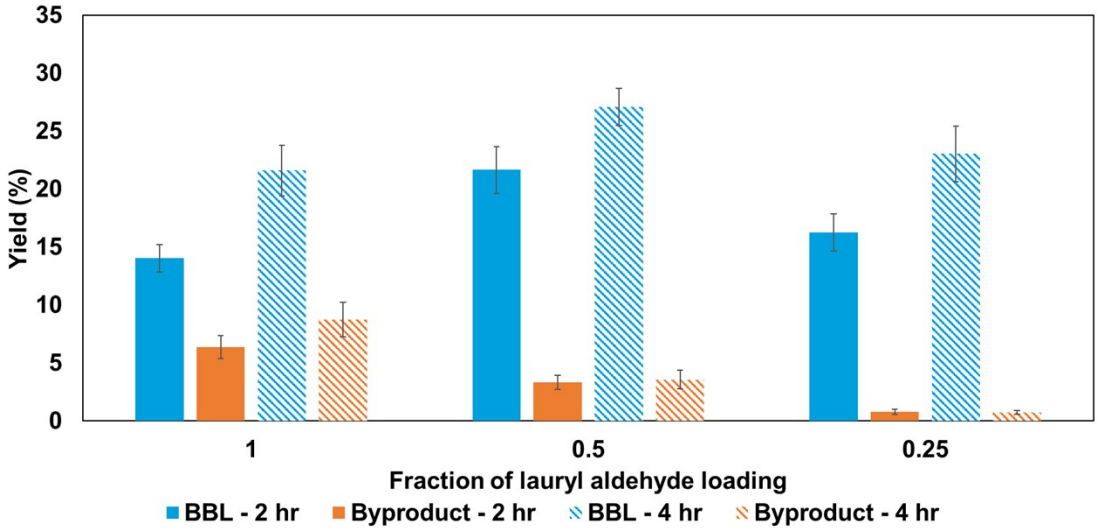


Figure S6: Yield of branched benzene lubricant (BBL) and condensation byproduct at various fractional loadings of lauryl aldehyde at 2 hr (solid bars) and 4 hr (slashed bars) reaction time. Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde (batch) 150 mg P-SiO_2, 150 ^oC

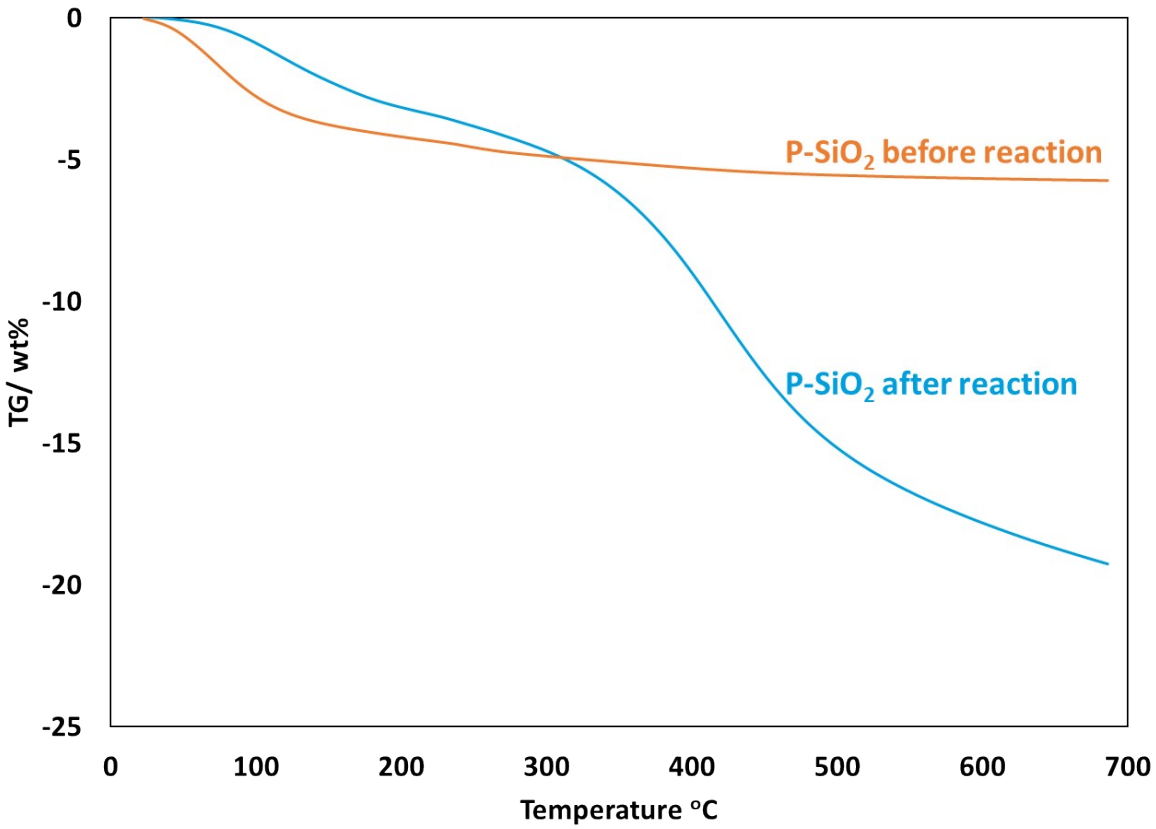


Figure S7: TGA profile of fresh and spent P-SiO_2 catalyst. Heating from 30 to 700 °C at a heating rate of 10 K min^{-1} under air (30 mL min^{-1}).

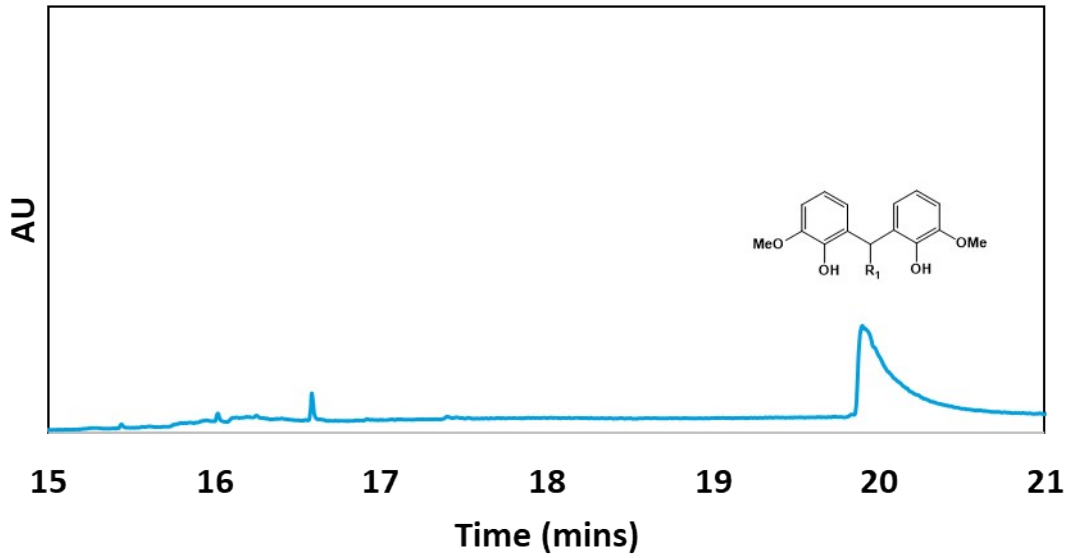


Figure S8: GC Chromatogram of THF wash of spent catalyst after HAA reaction.

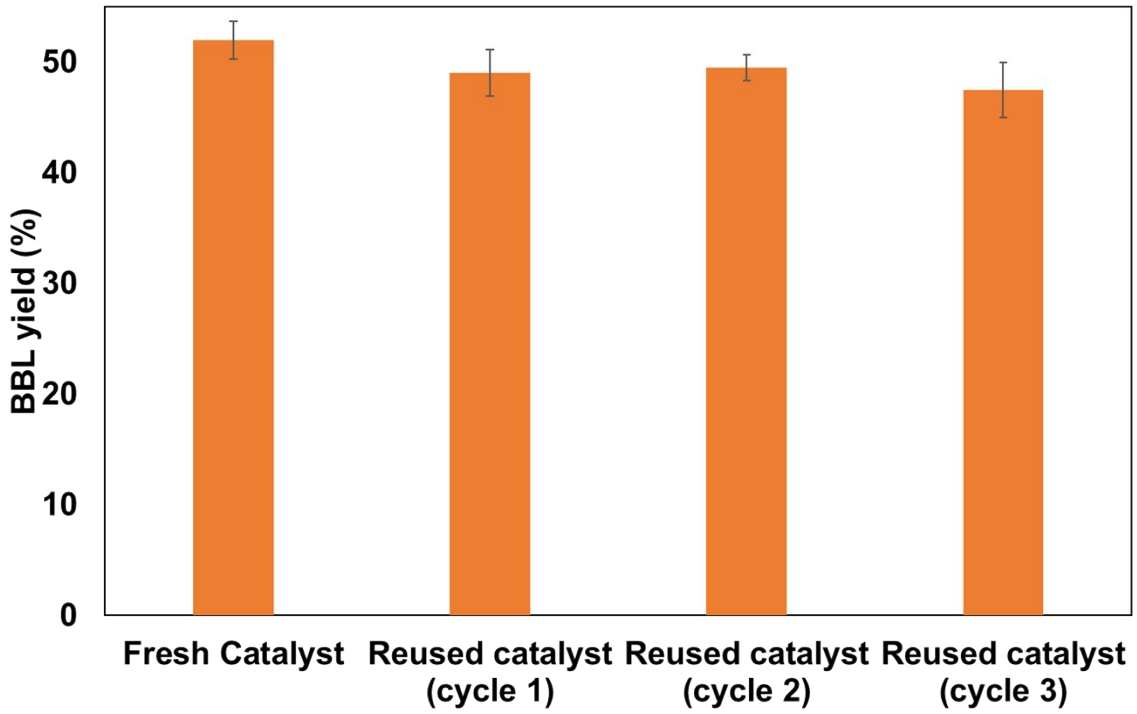


Figure S9: Recyclability of P-SiO_2 for the synthesis of branched benzene lubricant. Reaction conditions: 10 mmol guaiacol, 5 mmol lauryl aldehyde, 150 mg P-SiO_2, 150 ^oC, 24 hr, semi-batch system.

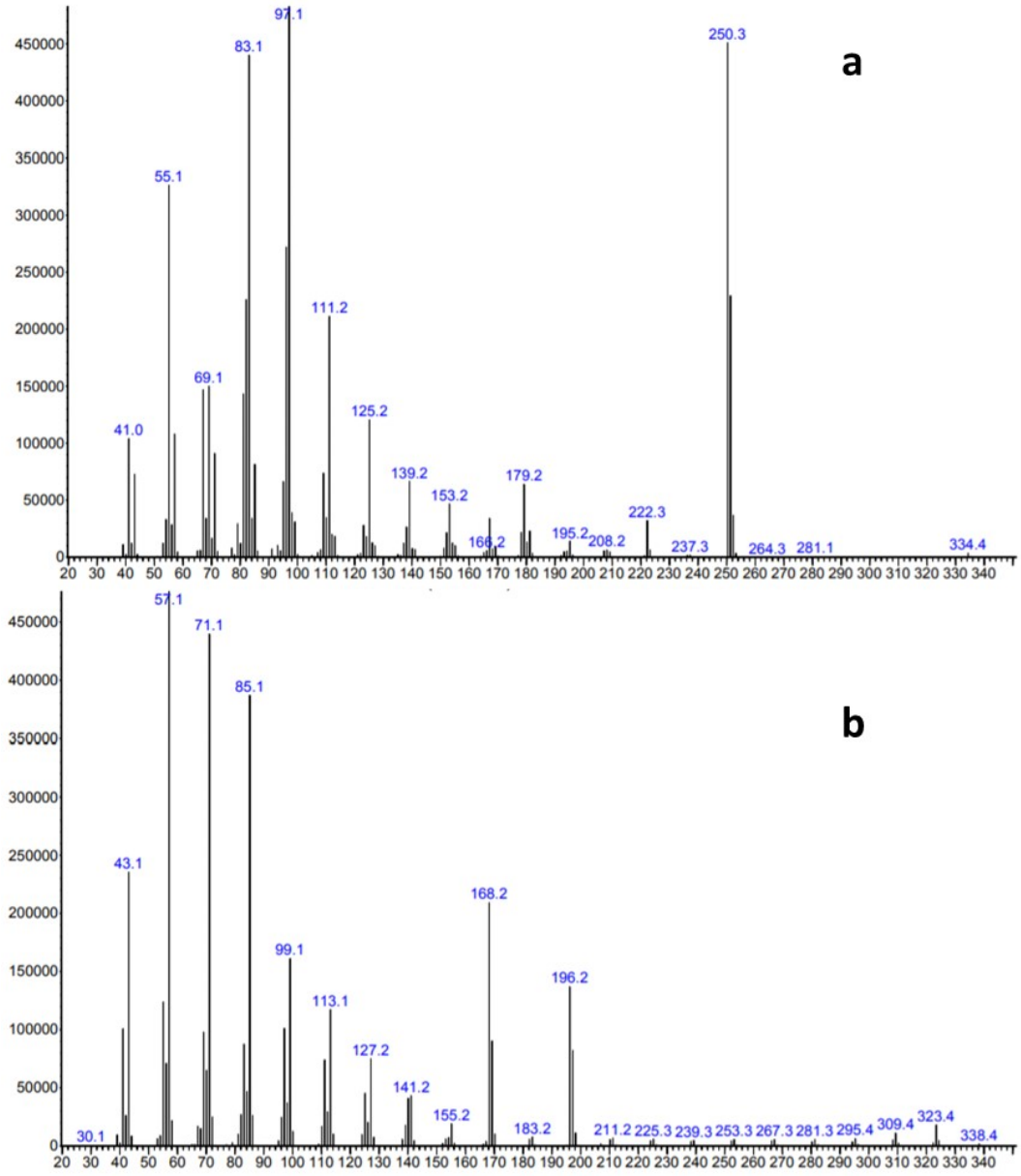


Figure S10: GCMS mass fragmentation of (a) cyclic C_{24} alkane base oil (mass from GCMS – 334.43, calculated mass – 334) and (b) branched C_{24} alkane base oil (mass from GCMS – 338.4, calculated mass – 338).

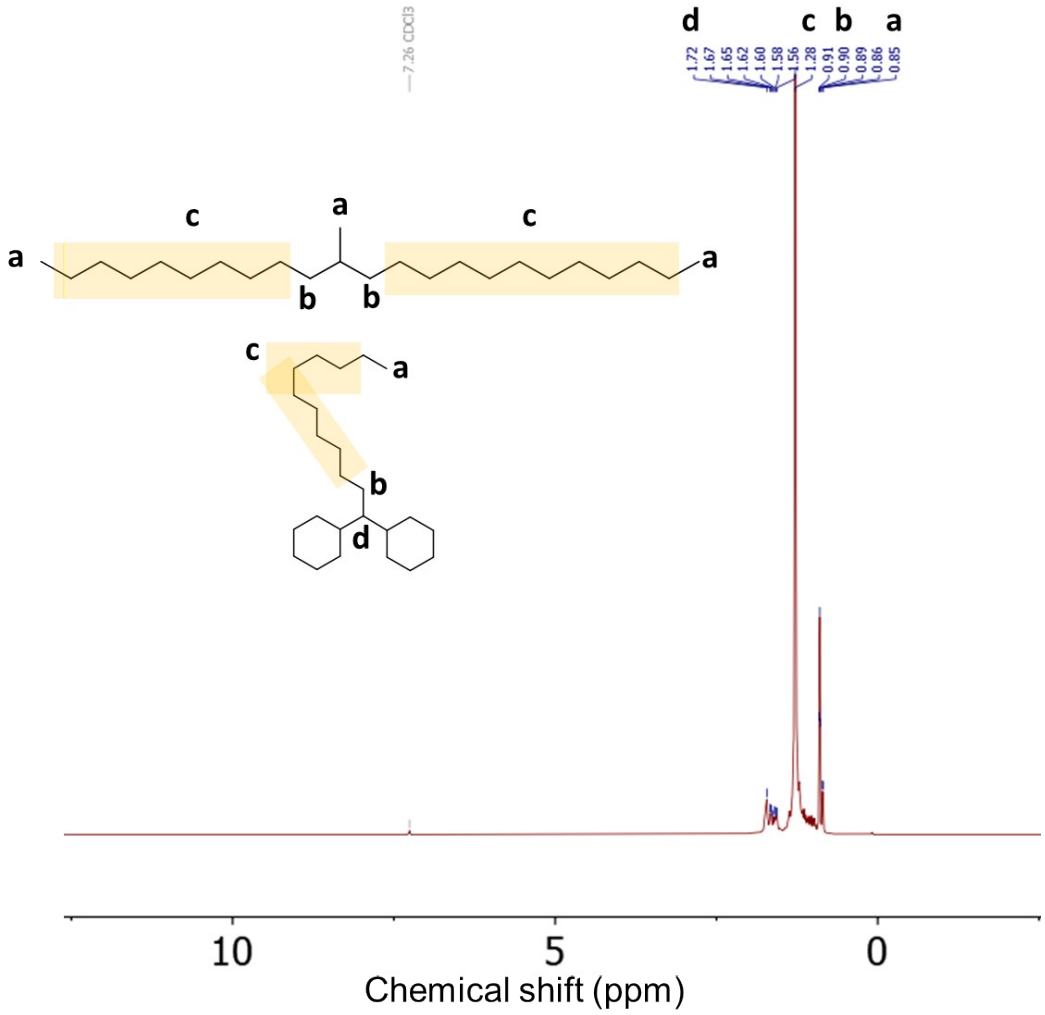


Figure S11: ^{1}H NMR spectrum of C_{24} alkane lubricant mix. Sample was prepared in $CDCl_3$. The predominant product is the C_{24} cyclic alkane lubricant, followed by the C_{24} branched alkane lubricant. The labels a-d are referencing the hydrogen atoms.

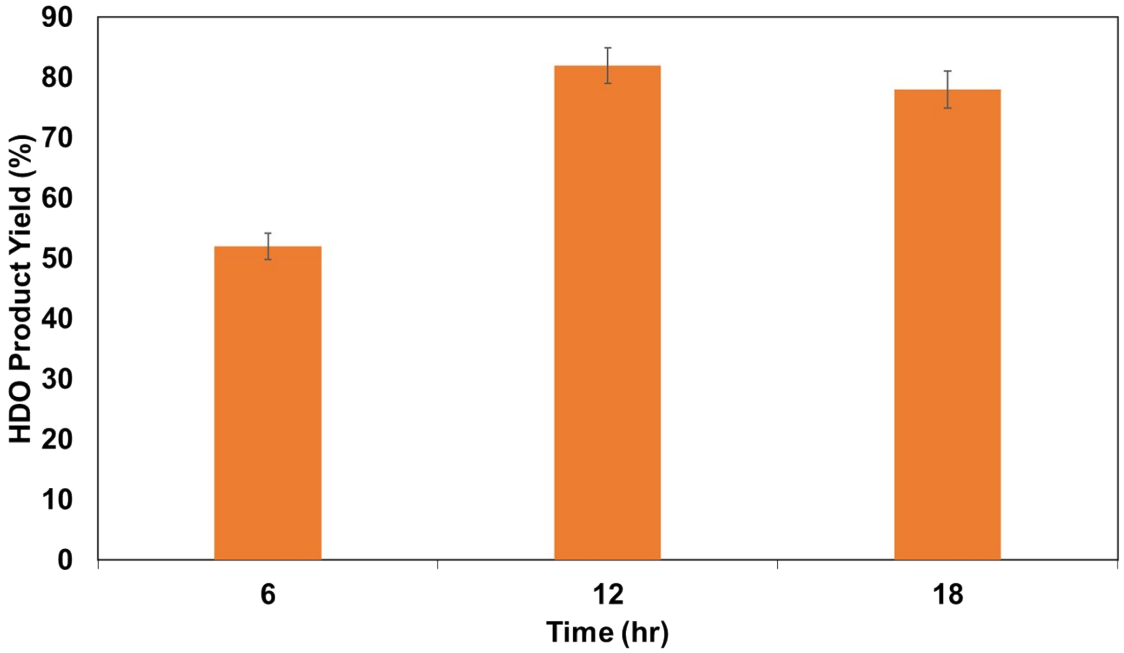


Figure S12: Branched cyclic lubricant yield at different reaction times (0.3 g HAA reaction product, 0.2 g Ir-ReOx on silica, 20 ml cyclohexane, 500 rpm, 200 °C, 5 MPa H_2).

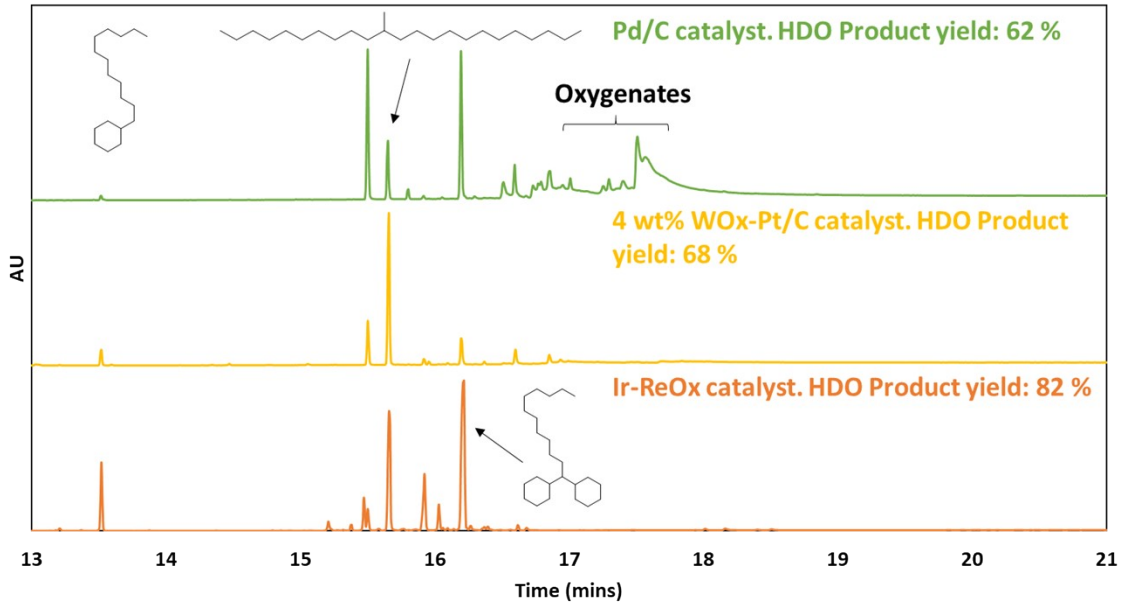


Figure S13: Chromatogram of HDO of benzene lubricant over different catalysts (0.3 g HAA reaction product, 0.2 g catalyst, 20 ml cyclohexane, 500 rpm, 200 °C, 12 hr, 5 MPa H_2).

Table S3. Summary of experimental settings and lubricant product yields for the HDO reaction. Reaction conditions: 0.3 g HAA reaction product, 0.2 g catalyst, 20 ml cyclohexane, 500 rpm, 5 MPa H_2.

Time (hr)	Temperature (°C)	Catalyst	C_{24} lubricant mix yield* (%)
6	200	Ir-ReOx	54
12	200	Ir-ReOx	82
18	200	Ir-ReOx	78
18	180	Ir-ReOx	52
18	220	Ir-ReOx	70
18	250	Ir-ReOx	67
12	200	Pd/C	62
12	200	4 wt.% WOx-Pt/C	68

*contains C_{24} cyclic alkane lubricant, C_{24} branched alkane lubricant and dodecyl cyclohexane

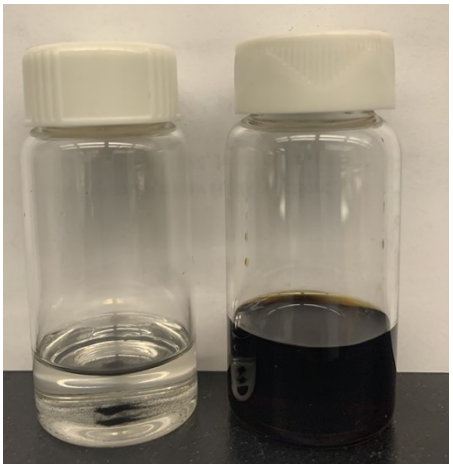


Figure S14: Lubricant products. Left (clear) –cyclic and branched C_{24} alkane base oil from HDO reaction. Right (dark) – BBL and byproduct mixture from HAA reaction.