Supporting Information for

Thermal Cyclodimerization of Isoprene for the Production of High Performance Sustainable Aviation Fuel

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Experimental

NMR spectroscopy. ^{1}H NMR spectra were recorded on a Bruker Avance III 500 spectrometer at 25 °C, operating at 500.46 MHz. Proton-decoupled $^{13}C\{1H\}$ NMR spectra were recorded with the same instrument at 25 °C, operating at 125.86 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane, and are referenced relative to the NMR solvent ($CDCl_3$), according to the literature values – $\delta(^{1}H) = 7.26$, $\delta(^{13}C) = 77.23$.

Kinematic viscosity and density studies. The kinematic viscosities and densities of the fuels were measured using a Stabinger Viscometer, SVM^{TM} 3001, connected to a TC-502 chiller to achieve temperatures down to -40 ^{o}C. Each sample was placed in a 5 mL syringe which was then attached to the viscometer through a Luer Lock adapter. Approximately 3 mL of each fuel was then slowly injected to prewet the measurement cells. The sample was allowed to equilibrate at the starting temperature (typically 20 °C). The method was then initiated and an additional 1 mL of sample was added. Each sample was then cooled to -40 ^{o}C (±0.002 °C), and at 5° C increments, both the kinematic viscosity and density were measured. Reported values were derived from the average of five determinations. After each run, the measuring cells were rinsed three times with hexanes and dried under a stream of nitrogen.

Heat of combustion studies. In a typical experiment, a pellet of high-purity benzoic acid (~950–1000 mg) was accurately weighed, and ~350–800 mg of fuel were added and allowed to fully saturate the pellet. The pellet was then re-weighed, and the gross heat of combustion was measured in a Parr 6200 Calorimeter. After combustion of the sample, the gross heat of combustion was corrected by subtracting the contribution due to benzoic acid and combusted wire. The NHOC was then calculated from the corrected gross HOC by taking into account the hydrogen content

[determined by elemental analysis (EA)] and the density of the fuel at 15 ˚C. The NHOC measurements were taken in triplicate and averaged.

Product distribution analysis. GC-FID was conducted with an Agilent Technologies 7820A GC system equipped with a DB-5 60m × 0.32mm × 0.25µm column. For entries 1- 7, volumes of 10, 15 and 20 mL of isoprene and 17.15 mL of myrcene were used. After 18 h, one µL (±0.2) of each sample solution was manually injected into the GC, with an inlet split ratio of 25:1, and inlet and detector temperatures of 250 °C and 300 °C, respectively. The column temperature was held at 40 °C for 3 min, followed by a temperature ramp of 10 °C min^{-1} to 300 °C. The fuel compositions were further analyzed with a Thermo Scientific Trace 1310 GC-MS equipped with an Orbitrap™ mass spectrometer, utilizing a TG-5SILMS, 30 mm x 0.25 mm x 0.25 µm column. The instrument was set to an injection volume of 1µL, held at 40 °C for 3 min, and then ramped at 20 °C min^{-1} to 300 °C.

Table S1. Kinematic viscosity and density of hydrogenated isoprene dimers

Cell Temperature °C	Kinematic Viscosity ($mm^2 s^{-1}$)	Density ($g mL^{-1}$)
20.00	1.42	0.802
15.00	1.53	0.806
10.00	1.65	0.810
5.00	1.80	0.814
0.00	1.97	0.818
-5.00	2.22	0.821
-10.00	2.47	0.825
-15.00	2.76	0.829
-20.00	3.10	0.832
-25.00	3.51	0.836
-30.00	4.00	0.840
-35.00	4.62	0.844
-40.00	5.45	0.847

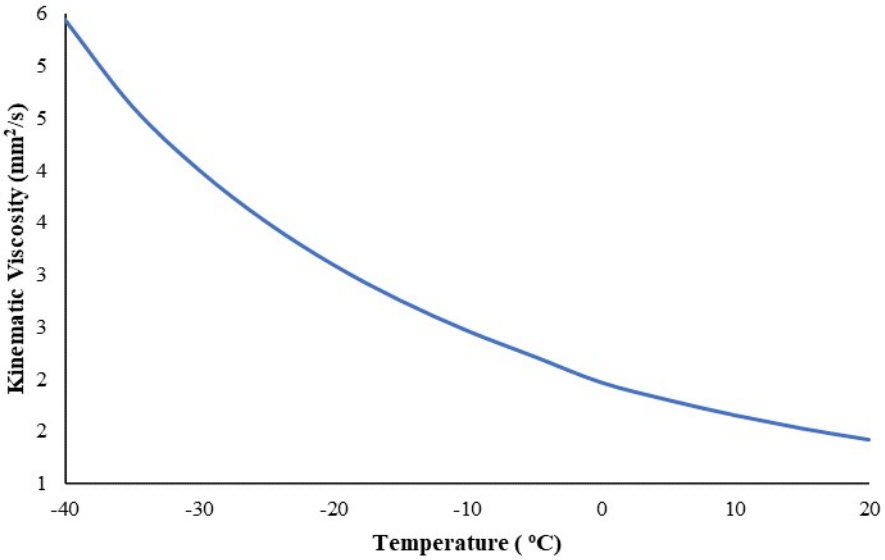


Figure S1. Kinematic viscosity of hydrogenated isoprene dimers (Pt catalyst) from 20 to - 40°C

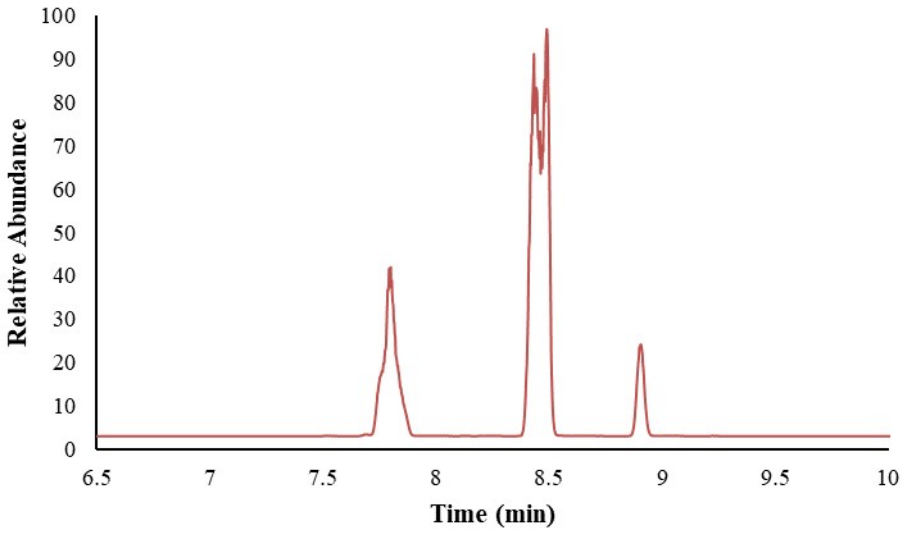


Figure S2. Gas chromatograph (GC-MS) of thermal isoprene dimers

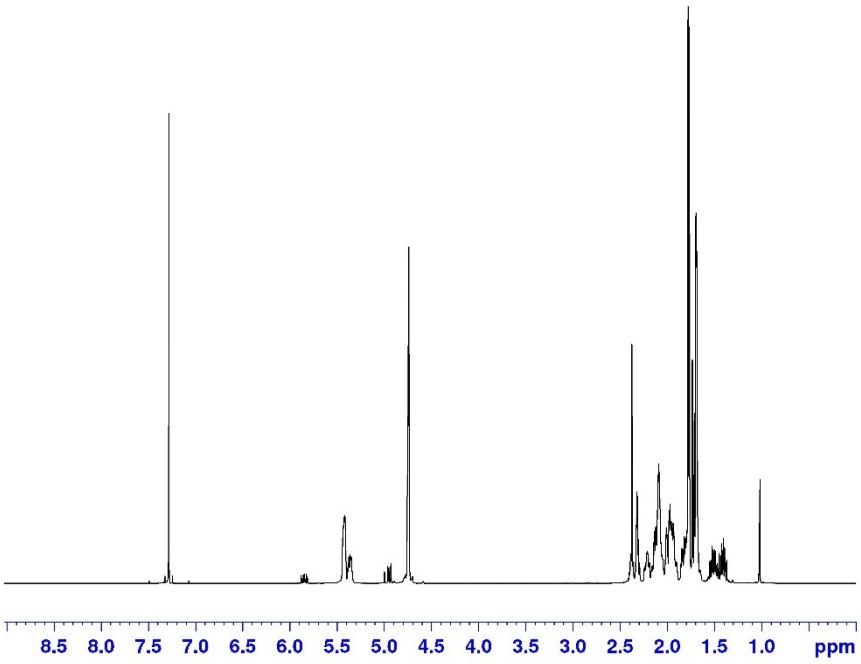


Figure S3. ^{1}H NMR spectrum of thermal isoprene dimers

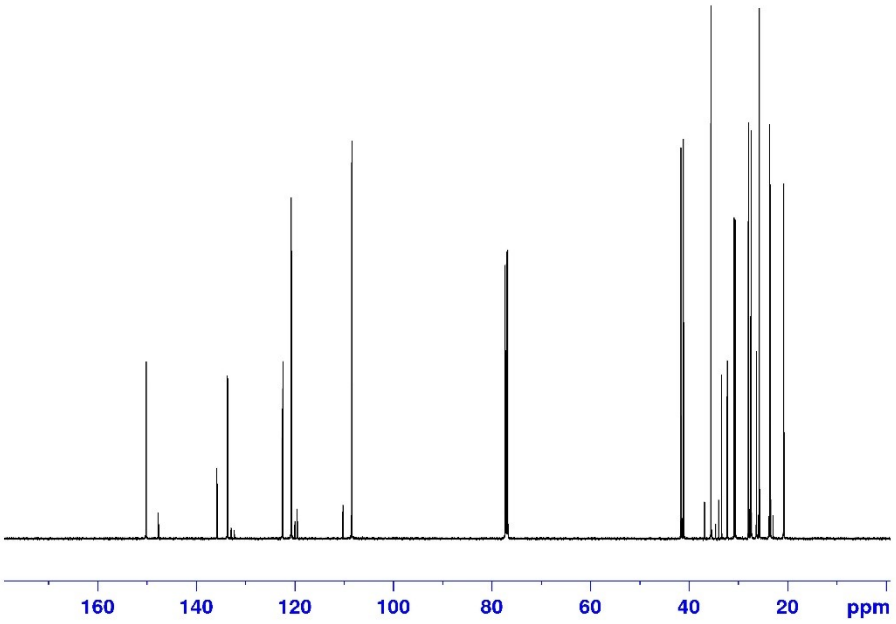


Figure S4. ^{13}C NMR spectrum of thermal isoprene dimers

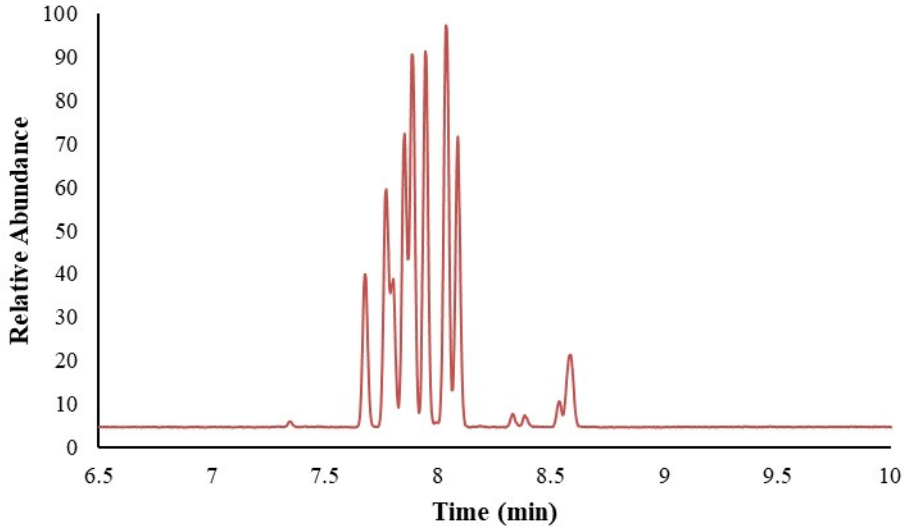


Figure S5. Gas chromatogram (GC-MS) of hydrogenated isoprene dimers (Pt catalyst)

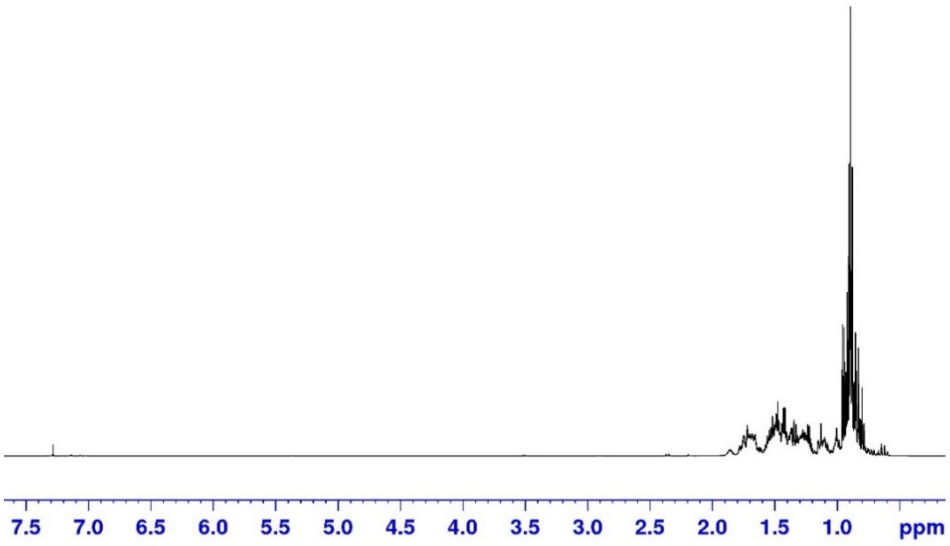


Figure S6. ^{1}H NMR spectrum of hydrogenated isoprene dimers (Pt catalyst)

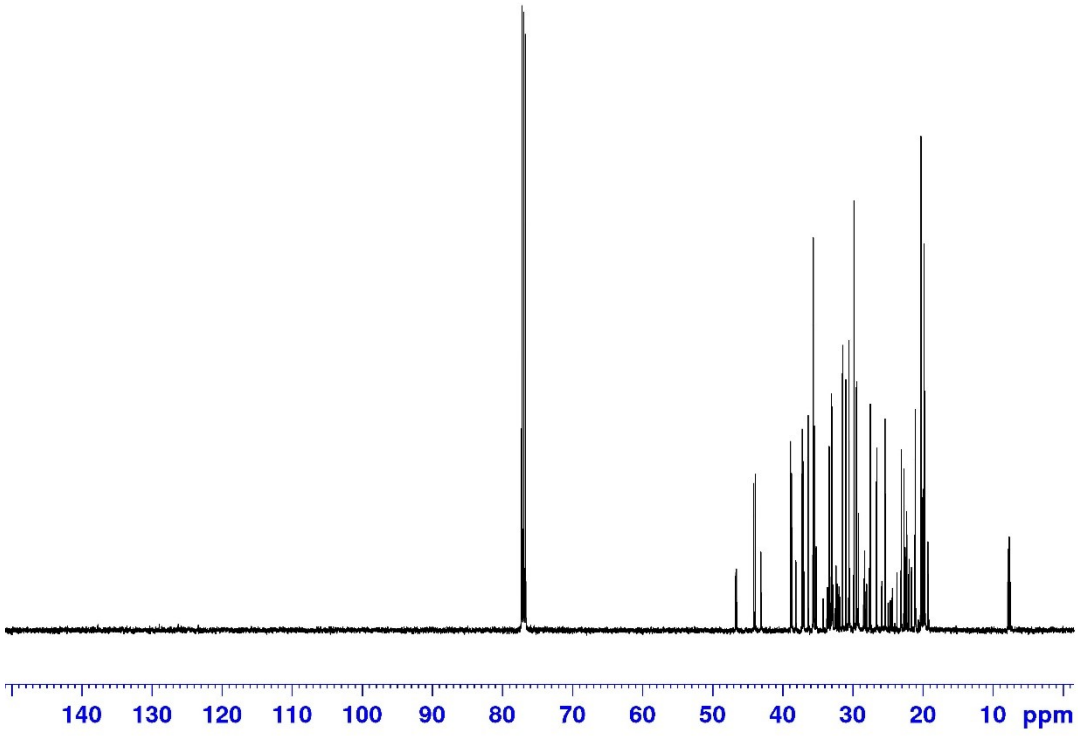


Figure S7. ^{13}C NMR spectrum of hydrogenated isoprene dimers (Pt catalyst)

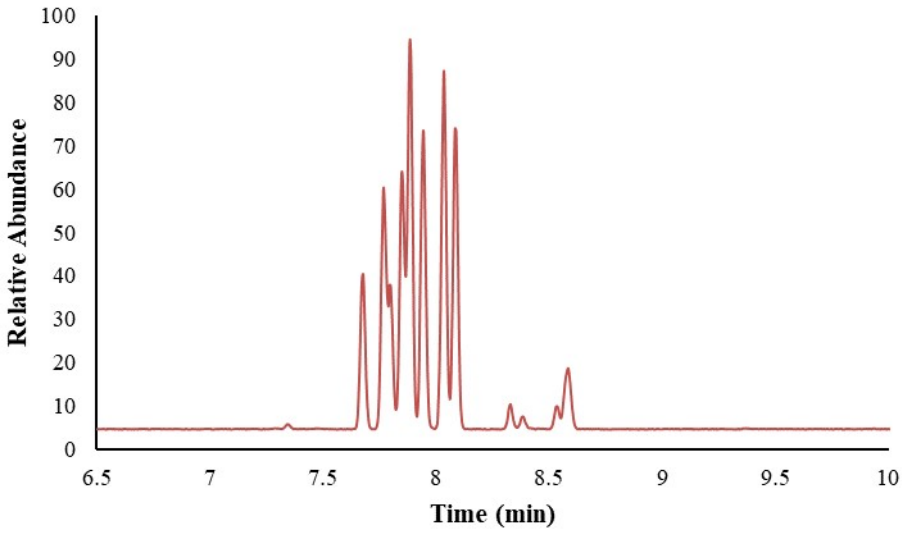


Figure S8. Gas chromatogram (GC-MS) of hydrogenated isoprene dimers (Raney nickel)

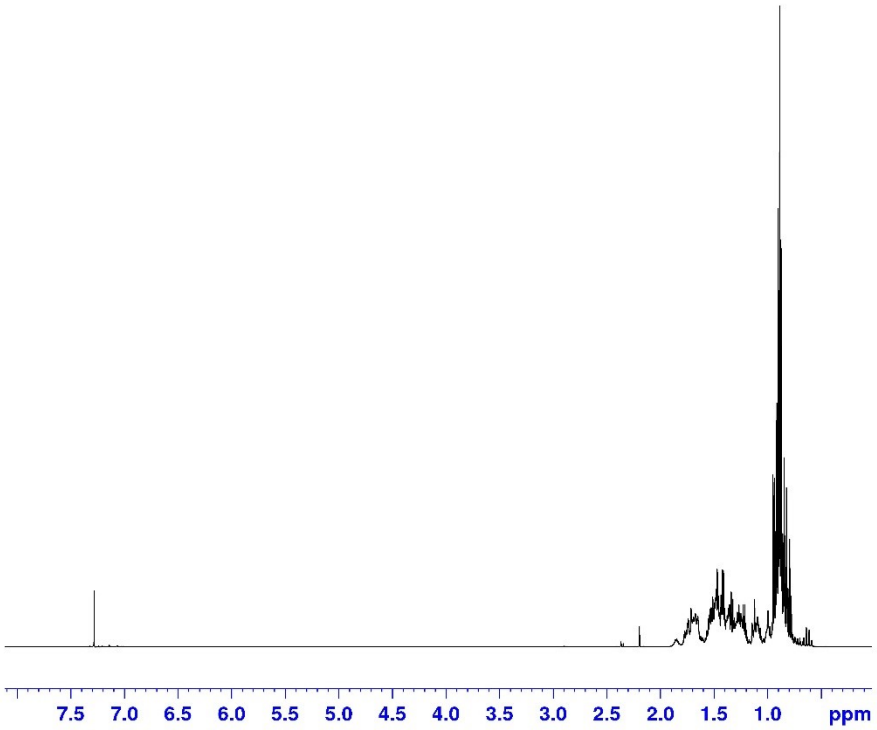


Figure S9. ^{1}H NMR spectrum of hydrogenated isoprene dimers (Raney nickel)

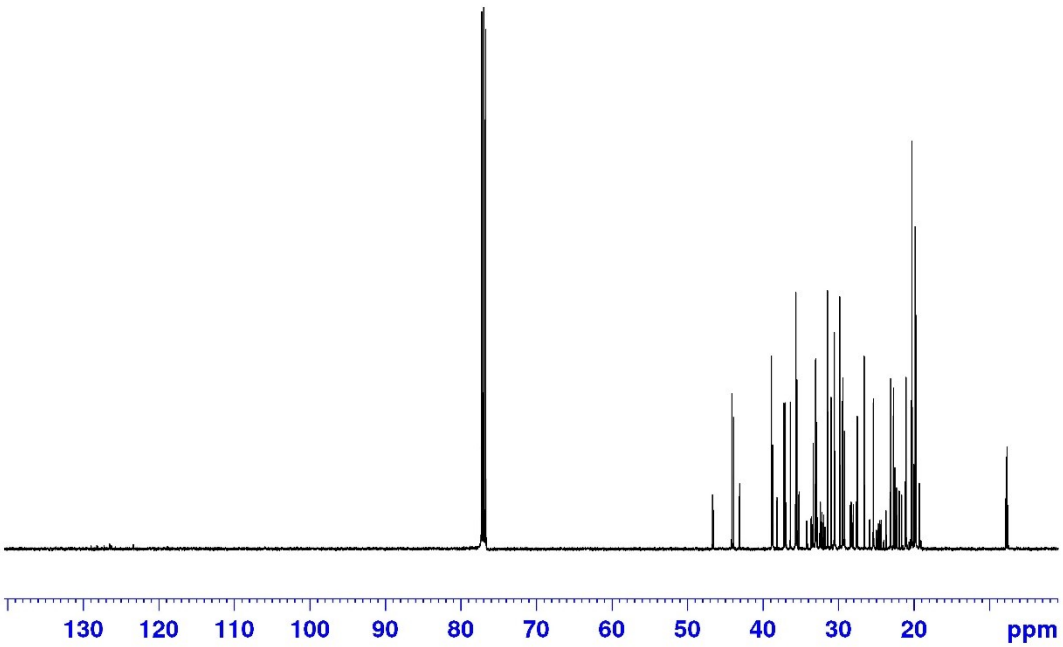


Figure S10. ^{13}C NMR spectrum of hydrogenated isoprene dimers (Raney nickel)

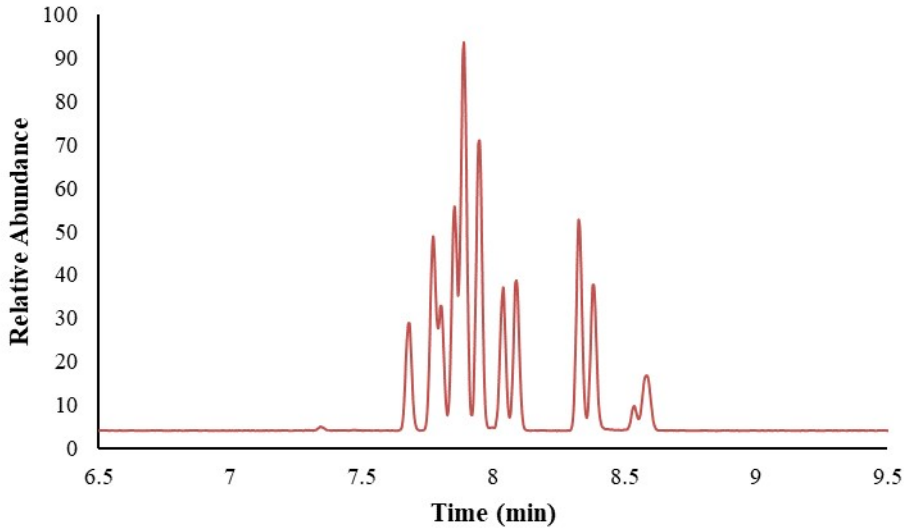


Figure S11. Gas chromatogram (GC-MS) of hydrogenated isoprene dimers (Pd/C)

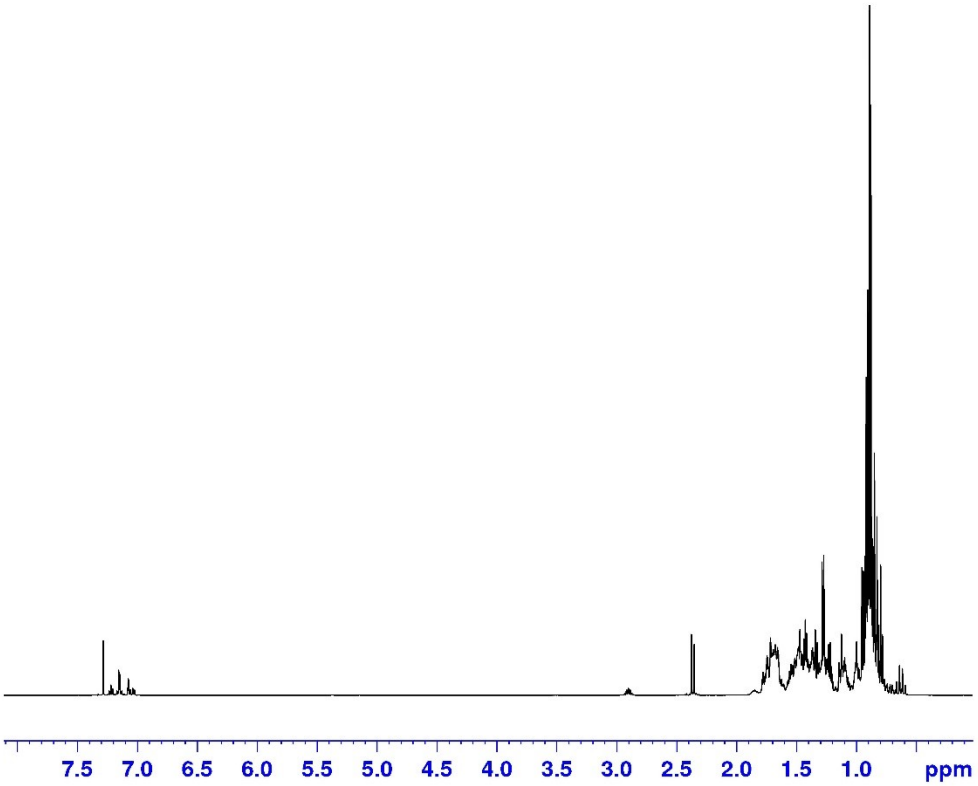
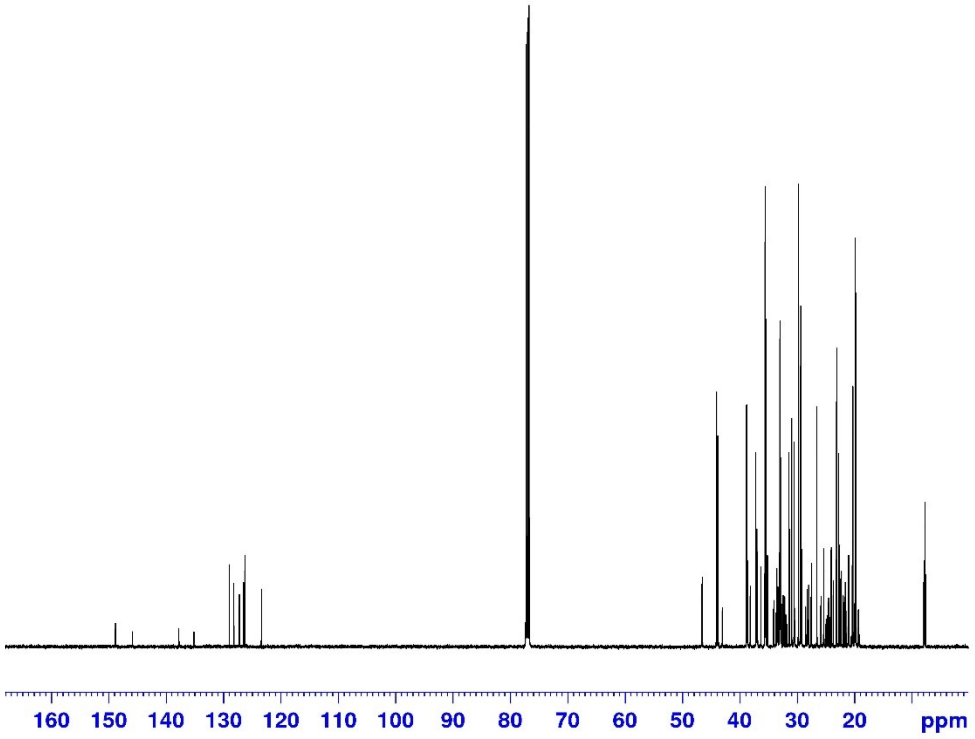


Figure S12. ^{1}H NMR spectrum



of hydrogenated isoprene dimers (Pd catalyst)

Figure S13. ^{13}C NMR spectrum of hydrogenated isoprene dimers (Pd catalyst)