

Supporting Information for

“Metafining” of Nerolidol with a Grubbs-Hoveyda Catalyst to Generate a High-Performance Sustainable Aviation Fuel

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Characterization.

NMR Parameters. ^1H NMR spectra were recorded on a Jeol ECZ400S spectrometer at 25 °C, operating at 400 MHz. Proton-decoupled $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with the same instrument at 25 °C, operating at 100 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 $-\delta(^1\text{H}) = 7.26$, $\delta(^{13}\text{C}) = 77.16$.

Kinematic Viscosity and Density Studies. The kinematic viscosities and densities of the fuels were measured using a Stabinger Viscometer, SVM 3001, connected to a TC-502 chiller to achieve temperatures down to -40 °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 sample was then slowly injected to pre-wet 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 °C (± 0.002 °C), and at 5 °C increments, both the kinematic viscosity and density were measured.

Fuel Characterization. All GC-FID spectra were collected on a Thermo Scientific Trace 1310 Gas Chromatograph (Santa Clara, CA). The GC oven method began at 40 °C for 3 min, then ramped to 300 °C at a rate of 10 °C \cdot min $^{-1}$, and was held at 300 °C for 1 min. The gas-phase separation was achieved using a Thermo Scientific TG-5 column, 30 m x .250 mm x 0.25 μm (Santa Clara, CA), the column was held at 12.59 PSI. An injection of 1 μL was injected for each run. The inlet's temperature was held at 250 °C at a pressure of 12.59 PSI. Eluted compounds were fed into the Flame Ionization Detection (FID) which was held at the following parameters: 300 °C, a hydrogen gas flow at 30 mL \cdot min $^{-1}$, an air flow at 350 mL \cdot min $^{-1}$, and a makeup gas flow at 35 mL \cdot min $^{-1}$.

All GC-MS spectra were collected on a Thermo Scientific Trace 1310 Gas Chromatograph Exactive GC orbitrap mass spectrometer (San Jose, CA). The GC oven method began at 40 °C for 3 min, then ramped to 300 °C at a rate of 20 °C \cdot min $^{-1}$, and was held at 300 °C for 30 min. The gas-phase separation was achieved using a Thermo Scientific TG-5SILMS column, 30 m x .25 mm x 0.25 μm (San Jose, CA). A split flow mode of injection was used at 25 mL \cdot min $^{-1}$ with a split ratio of 25.0. The inlet temperature was held at 300 °C. Eluted compounds passed through a heated auxiliary line (300 °C) and were directed toward the ion source region of the mass spectrometer, held at 305 °C, where they were subjected to electron impact ionization (EI). The mass range of the mass spectrometer was set from 50 to 600 amu.

Heat of Combustion Studies. The NHOCs of fuels derived from nerolidol were measured using the following procedure. A pellet of high-purity benzoic acid (~980-1020 mg) was accurately weighed, and ~200-400 mg of fuel were added and allowed to fully saturate the pellet. The pellet was then reweighed, and the gross heat of combustion (HOC) was measured in a Parr 6200 Calorimeter. After combustion of the sample, the HOC was corrected by subtracting the contribution due to benzoic acid and combusted wire. The NHOC was then calculated from the corrected HOC by taking into account the hydrogen content, measured independently by elemental analysis, and the density of the fuel at 15 °C. The NHOC measurements were taken in triplicate and averaged.

Table S1: Kinematic Viscosity and density of 2,6-dimethylheptane

Cell Temperature (°C)	Density (g/mL)	Kinematic Viscosity (mm ² /s)
20.000	0.70974	0.8659
15.000	0.71381	0.9186
10.000	0.71773	0.9789
5.000	0.72174	1.0427
0.000	0.72566	1.1191
-5.001	0.72950	1.2596
-10.000	0.73340	1.3755
-15.001	0.73733	1.5044
-20.001	0.74111	1.6552
-25.001	0.74511	1.8295
-30.001	0.74894	2.0366
-35.001	0.75286	2.2700
-40.000	0.75669	2.5453

Table S2. Kinematic viscosity and density of F1

Cell Temperature (°C)	Density (g/mL)	Kinematic Viscosity (mm ² /s)
19.999	0.77895	1.2797
14.999	0.78305	1.3747
9.999	0.78697	1.4867
4.999	0.79085	1.6171
-0.001	0.79478	1.7668
-5.000	0.79860	2.0332
-10.001	0.80247	2.2652
-15.001	0.80633	2.5409
-20.001	0.81019	2.8705
-25.001	0.81407	3.2511
-30.001	0.81794	3.7174
-35.002	0.82181	4.2884
-40.003	0.82563	5.0239

Table S3. Kinematic viscosity and density of F2

Cell Temperature (°C)	Density (g/mL)	Kinematic Viscosity (mm ² /s)
20.000	0.72546	0.8828
15.000	0.72933	0.9440
9.999	0.73309	1.0133
4.999	0.73694	1.0701
0.000	0.74081	1.1546
-5.001	0.74456	1.3075
-10.001	0.74837	1.4340
-15.001	0.75219	1.5794
-20.000	0.75607	1.7488
-25.000	0.75989	1.9358
-30.002	0.76386	2.1556
-35.002	0.76787	2.4105
-40.000	0.77197	2.7104

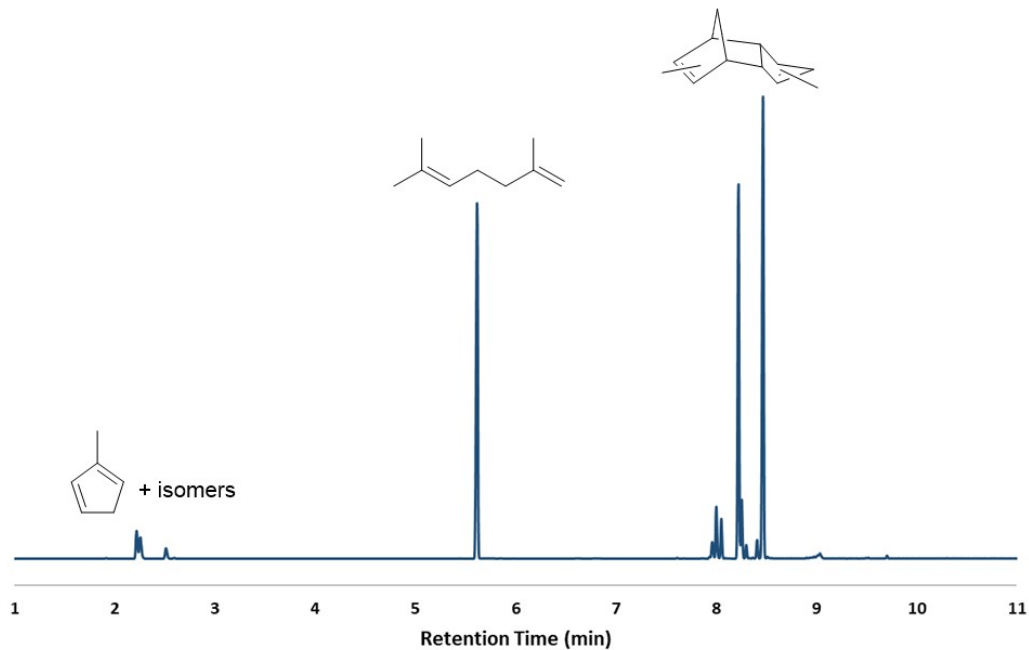


Figure S1. Gas chromatogram for the nerolidol ring-closing metathesis mixture after dehydration and dimerization

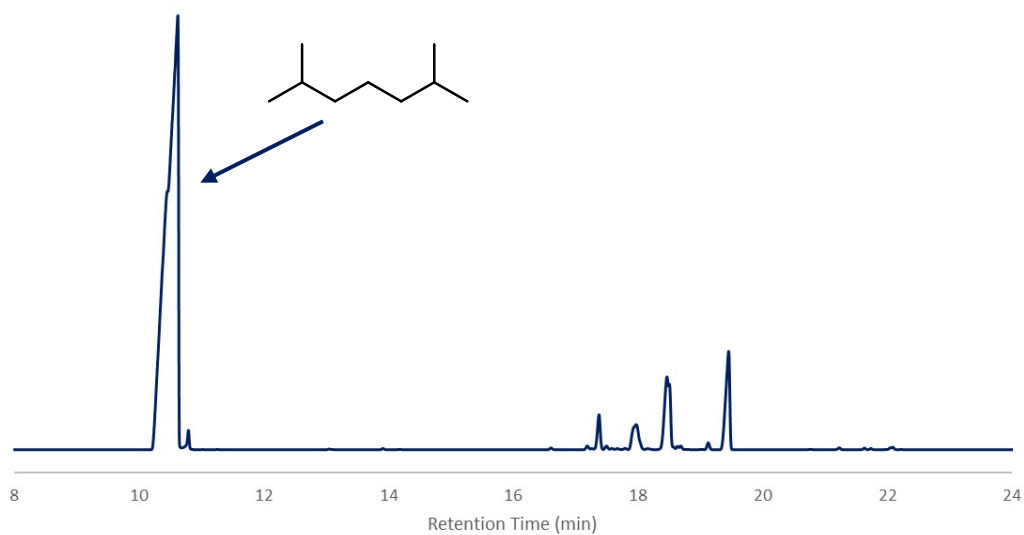


Figure S2. Gas chromatogram for 2,6-dimethylheptane along with some hydrogenated methylcyclopentadiene dimers

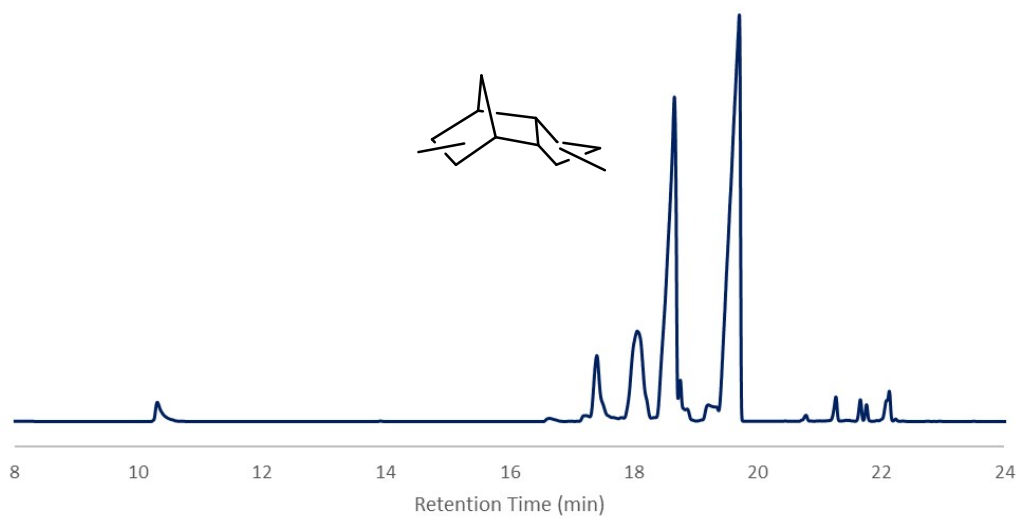


Figure S3. Gas chromatogram of hydrogenated methylcyclopentadiene dimers

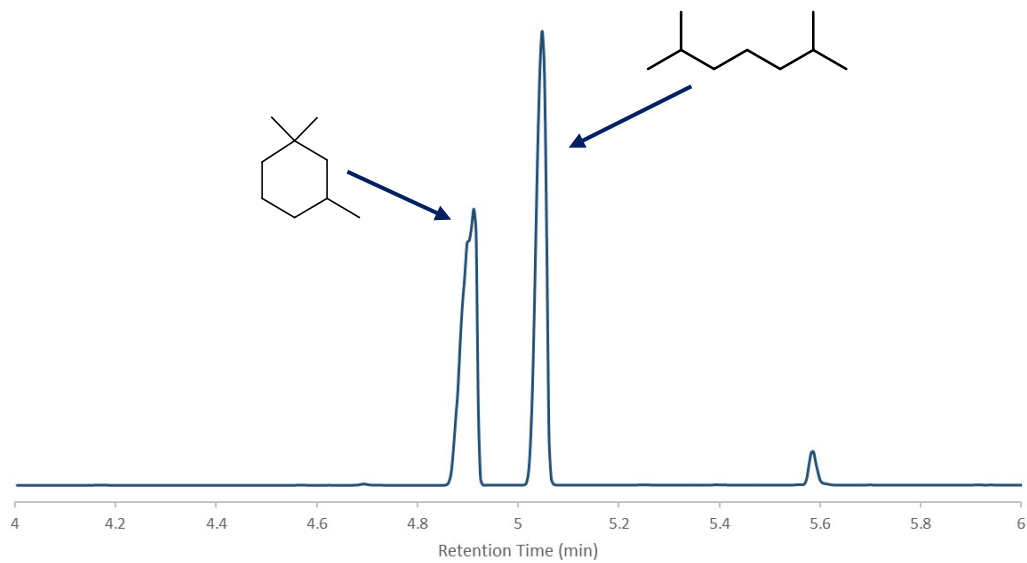


Figure S4. Gas chromatogram of F2

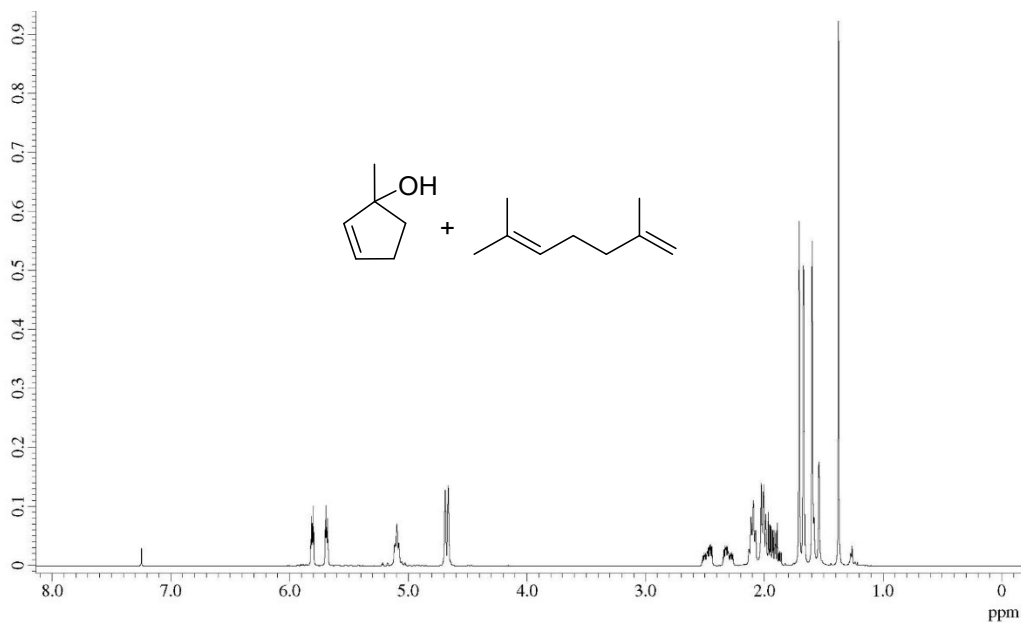


Figure S5. ^1H NMR spectrum of nerolidol after ring-closing metathesis

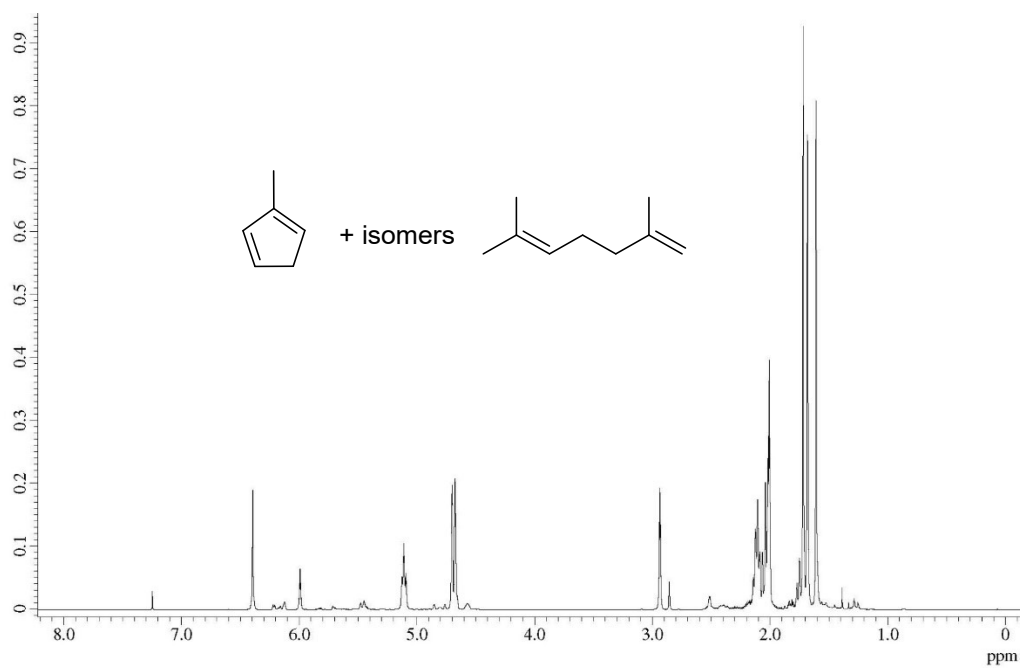


Figure S6. ^1H NMR Spectrum of nerolidol after ring-closing metathesis and dehydration

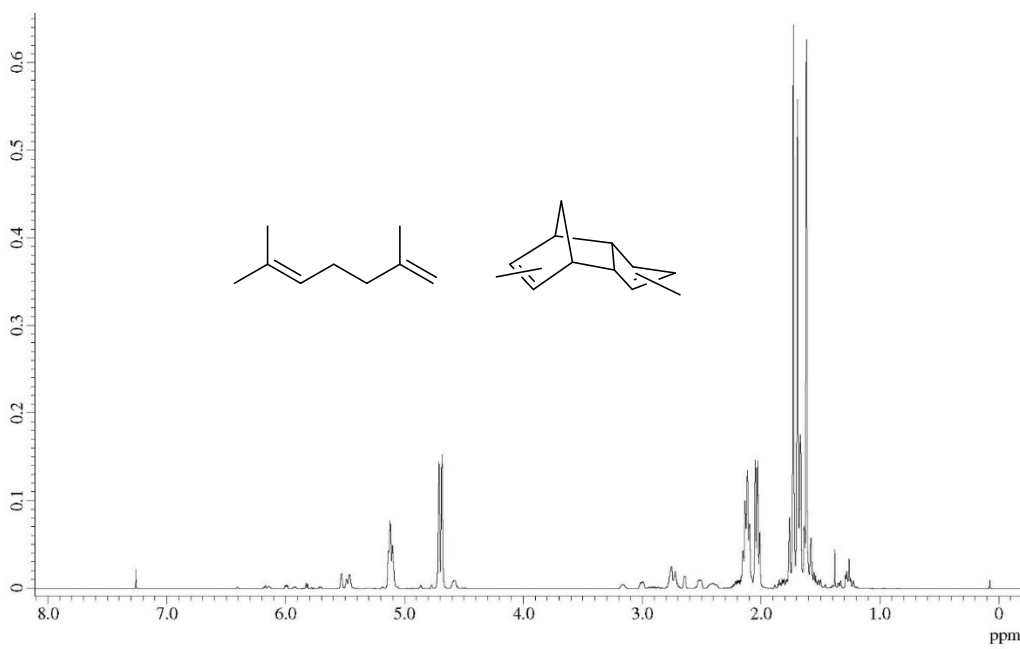


Figure S7. ^1H NMR Spectrum of nerolidol product mixture after ring closing metathesis, dehydration, and dimerization

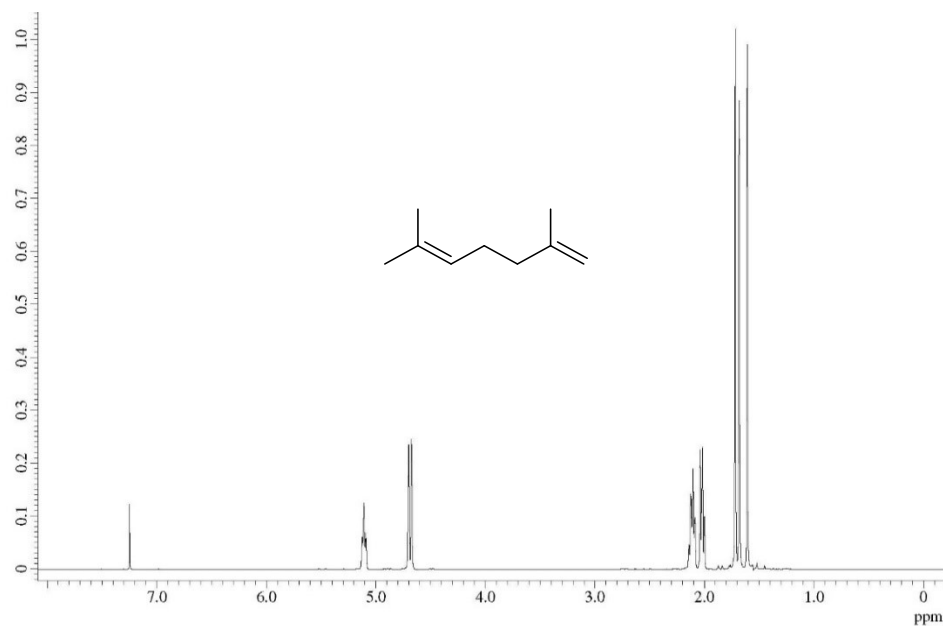


Figure S8. ^1H NMR Spectrum of 2,6-dimethyl-1,5-heptadiene

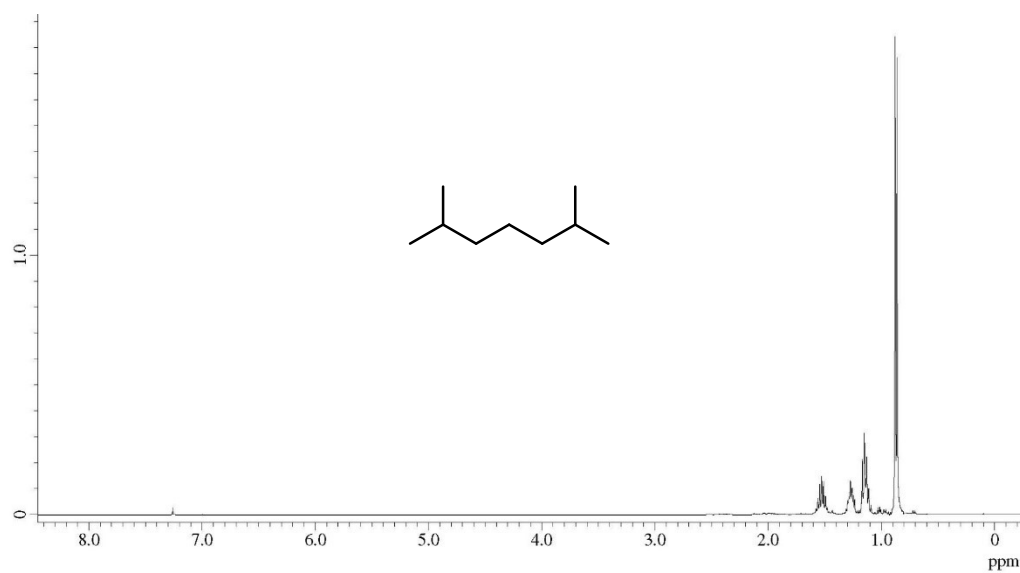


Figure S9. ^1H NMR Spectrum of 2,6-dimethylheptane

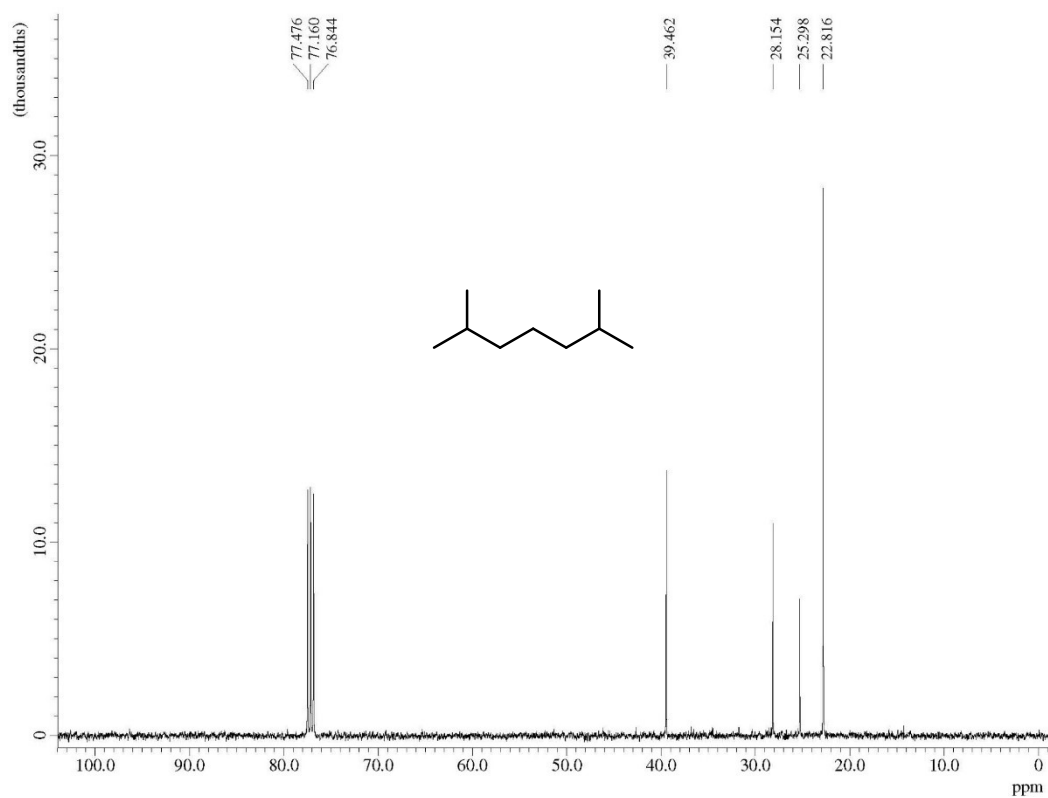


Figure S10. ^{13}C NMR spectrum of 2,6-dimethylheptane

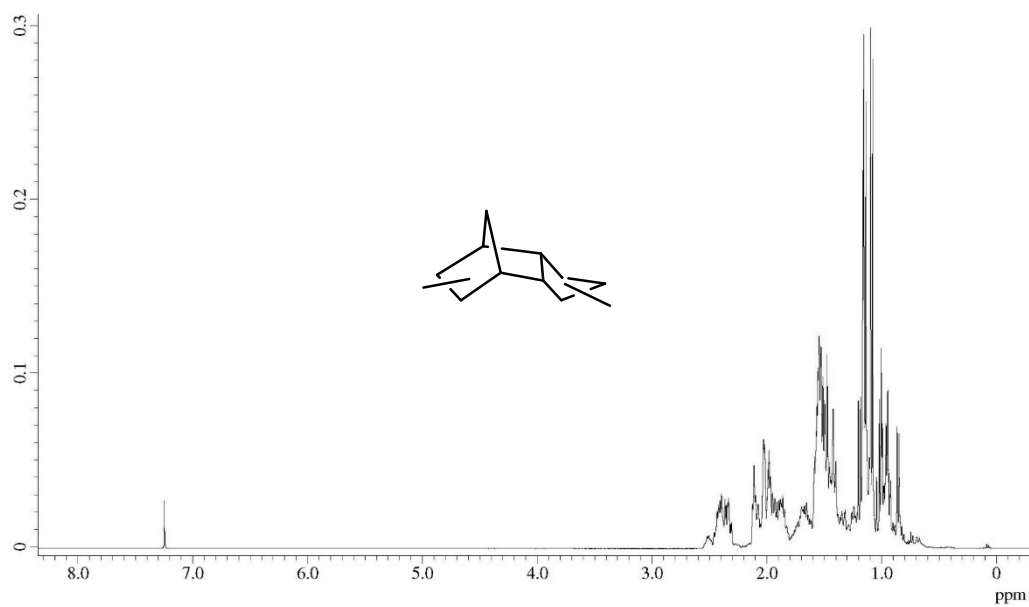


Figure S11. ^1H NMR spectrum of hydrogenated methylcyclopentadiene dimers

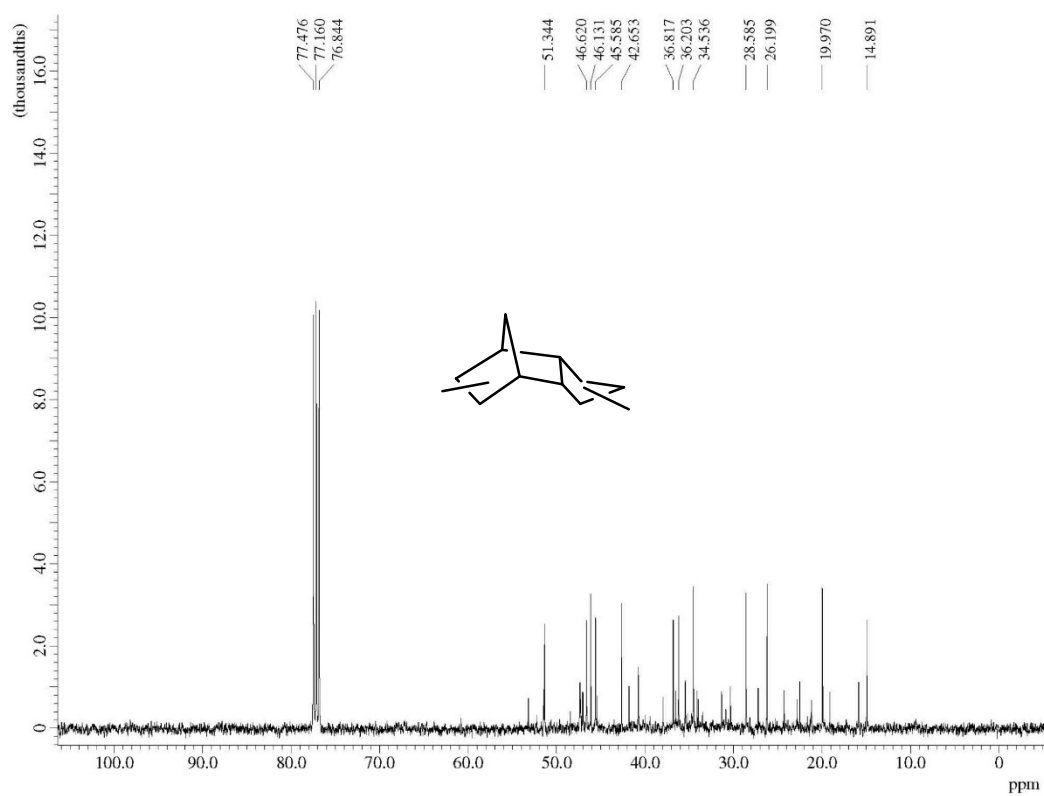


Figure S12. ^{13}C NMR spectrum of hydrogenated methylcyclopentadiene dimers

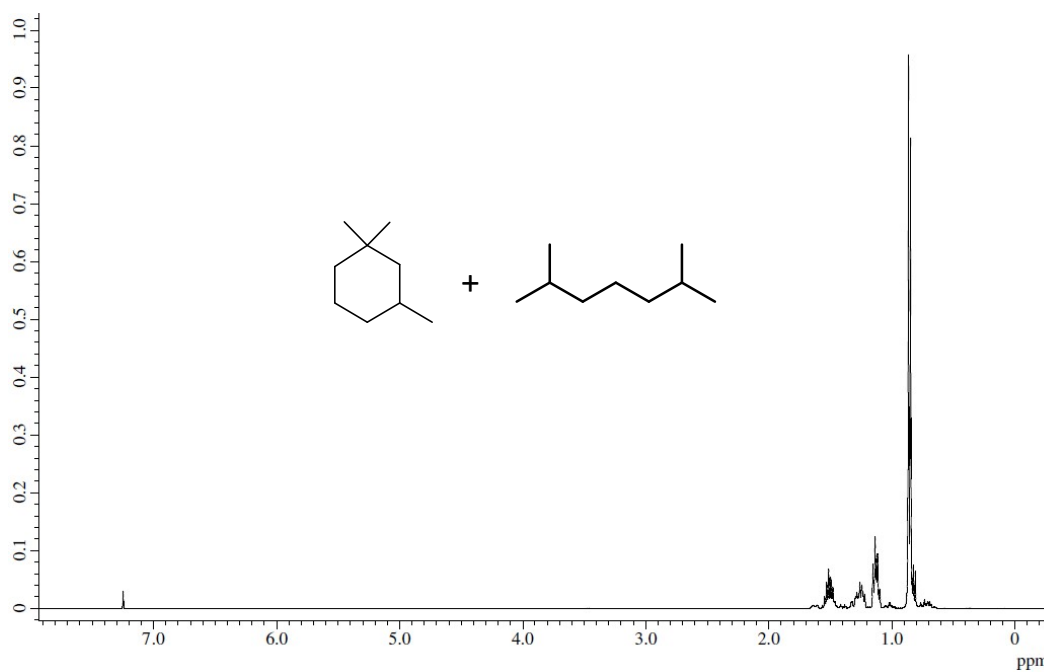


Figure S13. ^1H NMR spectrum of F2

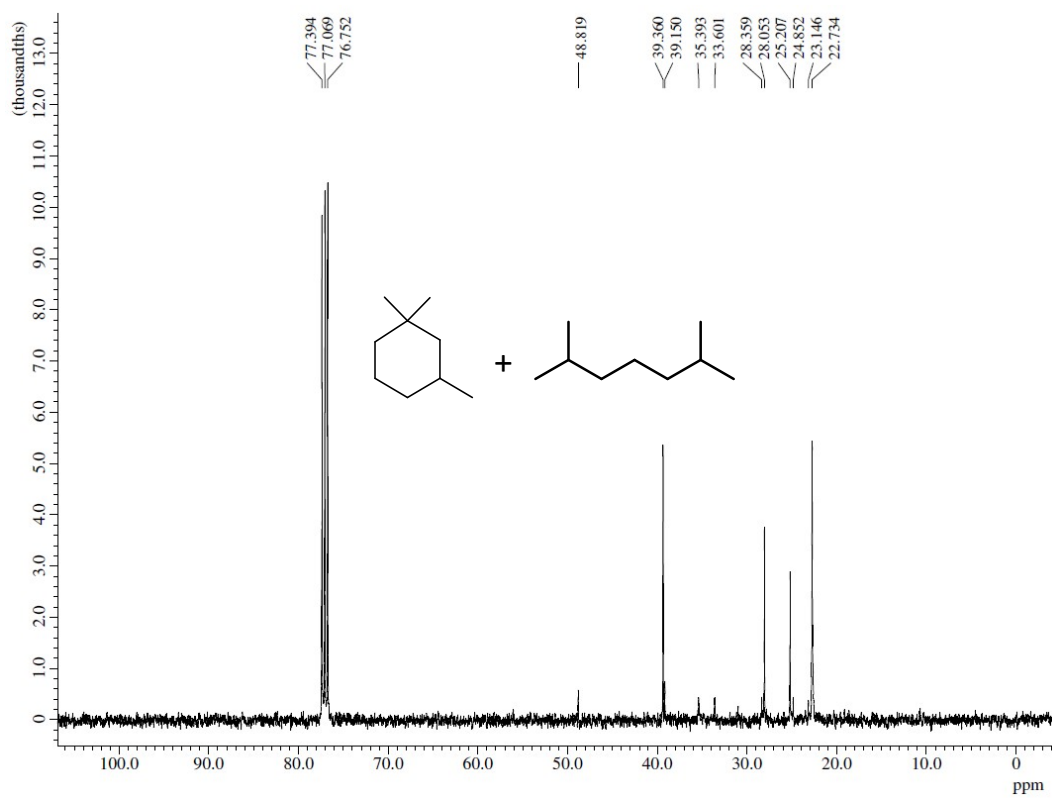


Figure S14. ^{13}C NMR spectrum of F2