Supporting Information

Synthetic middle-distillate-range hydrocarbons via catalytic dimerization of branched C_6 - C_8 olefins derived from renewable dimethyl ether *Mayank Behl¹*, *Joshua A. Schaidle¹*, *Earl Christensen² and Jesse E. Hensley^{1,*}*

¹National Bioenergy Center, ²Transportation and Hydrogen Systems Center, National Renewable Energy Laboratory, Golden, Colorado 80401 (USA) *Email: jesse.hensley@nrel.gov

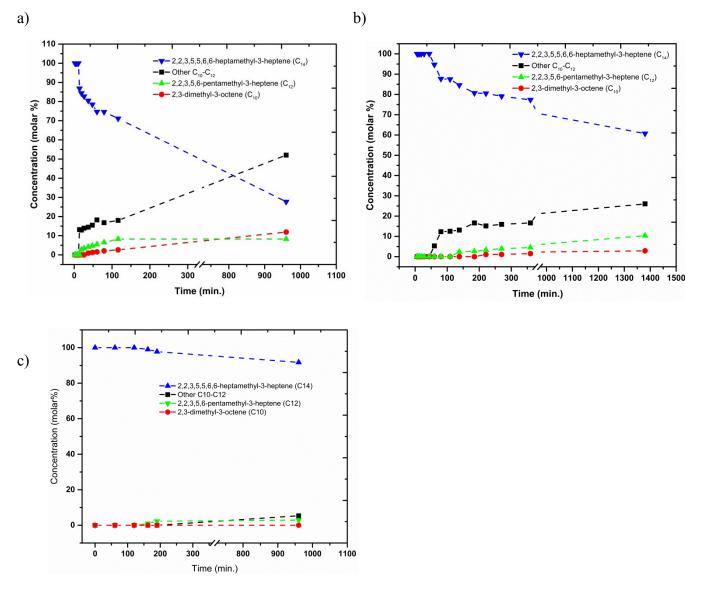


Figure S1: Evolution of different $C_{10} - C_{14}$ range products (as percentage) obtained from triptene dimerization over Amberlyst-35 at (a) 100 °C, (b) 80 °C and (c) 60 °C

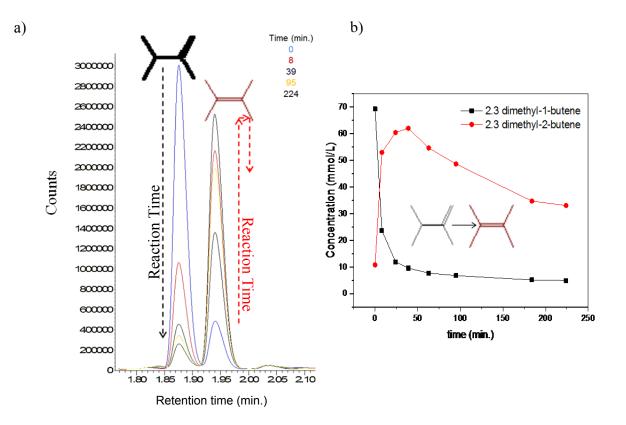


Figure S2: (a) FID signal and (b) Concentration-time profile corresponding to 2,3-dimethyl-1butene during its reaction over Amberlyst-35 displaying quick initial isomerization to nonterminal 2,3-dimethyl-2-butene that converts at a relatively slower rate.



Figure S3: Photographs of Amberlyst-35 before and after exposure to solvent (from left to right: Amberlyst-35 with no solvent, with added water, nonane and pentadecane). In nonane and pentadecane, Amberlyst-35 exhibits negligible swelling as compared to swelling caused by water.

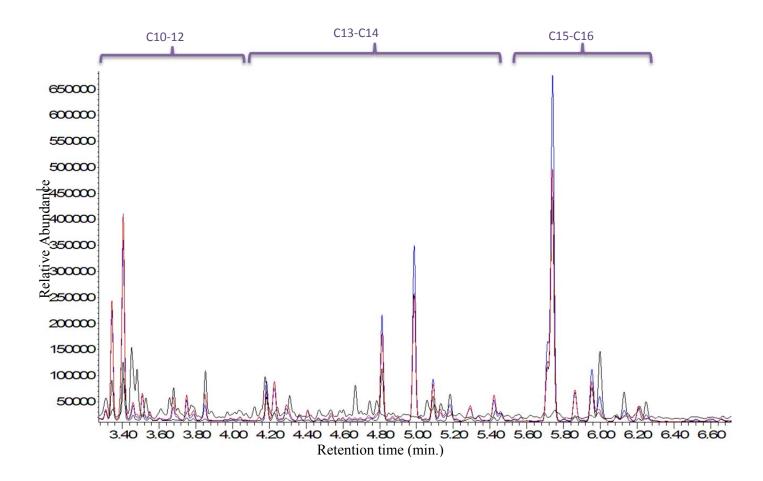
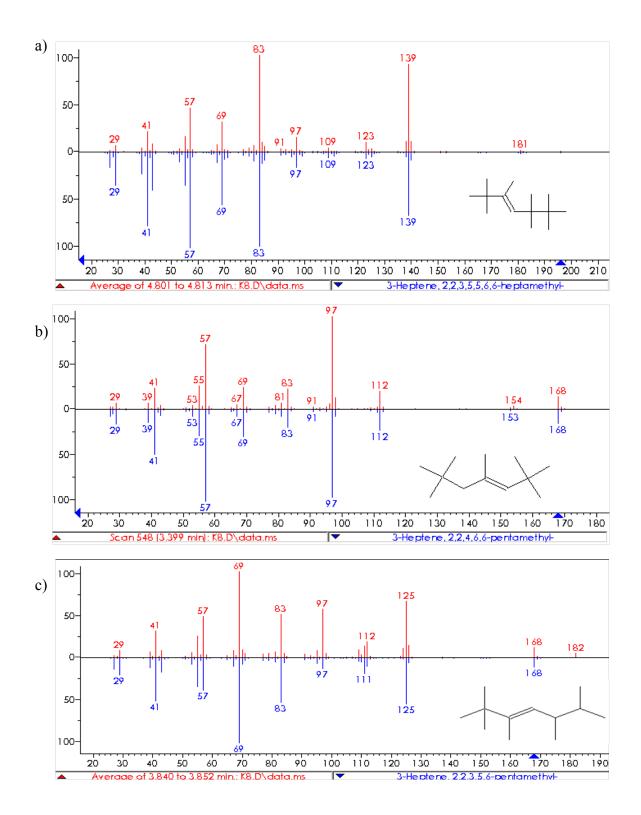


Figure S4: Representative gas chromatograms of major products from the dimerization and cross-coupling of mixed olefin feed during the first hours of reaction (t = 0.5h (blue trace); t = 2h (red trace); t = 3h (black trace)).



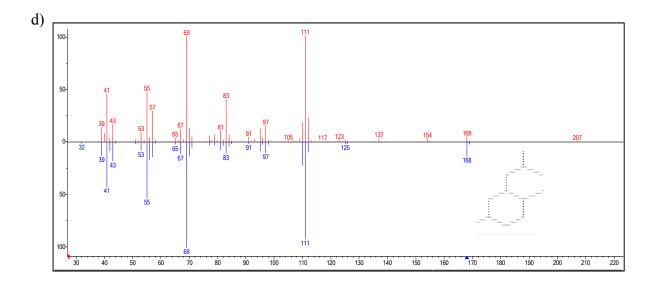
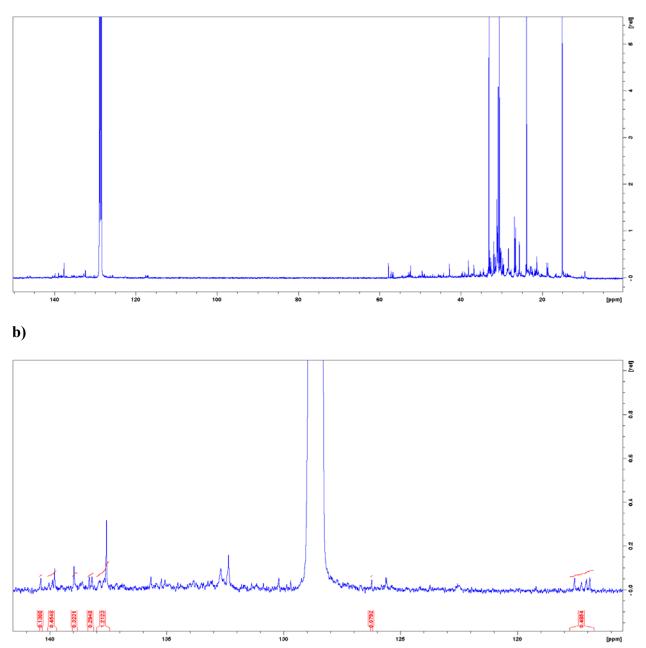
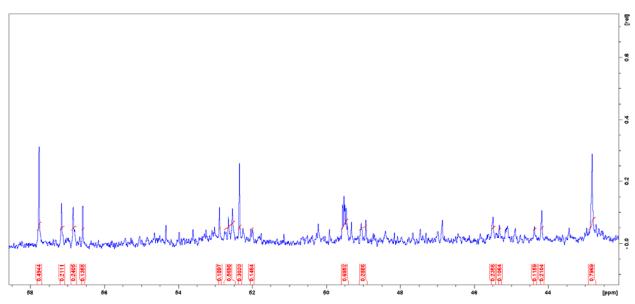
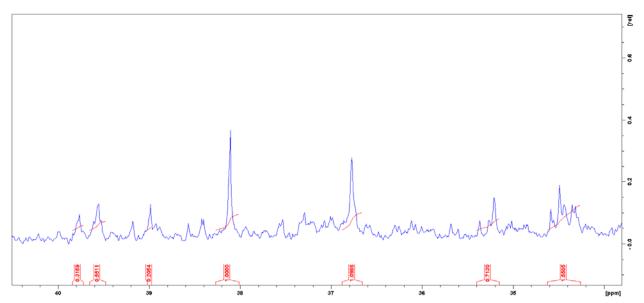


Figure S5: a) Mass spectrum of the major product from triptene dimerization co-located over the mass spectrum of 2,2,3,5,5,6,6-heptamethyl-3-heptene as provided in the NIST library. b) A mass spectrum of a C12 product co-located over the mass spectrum of 2,2,4,6,6-pentamethyl-3-heptene. c) A mass spectrum of another product co-located over the mass spectrum of 2,2,3,5,6-pentamethyl-3-heptene. d) A mass spectrum of another product co-located over the mass spectrum of 2,2,3,5,6-pentamethyl-3-heptene. d) A mass spectrum of another product co-located over the mass spectrum of 2-isobutyl-1,4-dimethylcyclohexane.





d)



c)

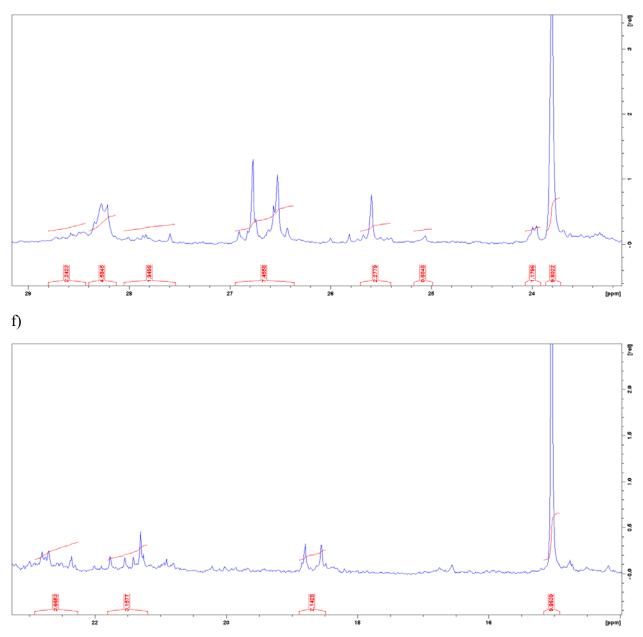


Figure S6: Representative 13C-NMR spectra of the product from coupling of mixed olefin feed: (a) Full 13C-NMR spectrum (the large peak at 128.6 ppm is Benzene (i.e., carrier medium)). An expanded view of (a) in the region of (b) 115-142 ppm, in the region of (c) 40-59 ppm, in the region of (d) 30-42 ppm, in the region of (e) 20-30 ppm and in the region of (f) 12-23 ppm.