

## Supplementary Information

### Microkinetic Modeling of the Homogeneous Thermal Oligomerization of Ethylene to Liquid-Fuel Range Hydrocarbons

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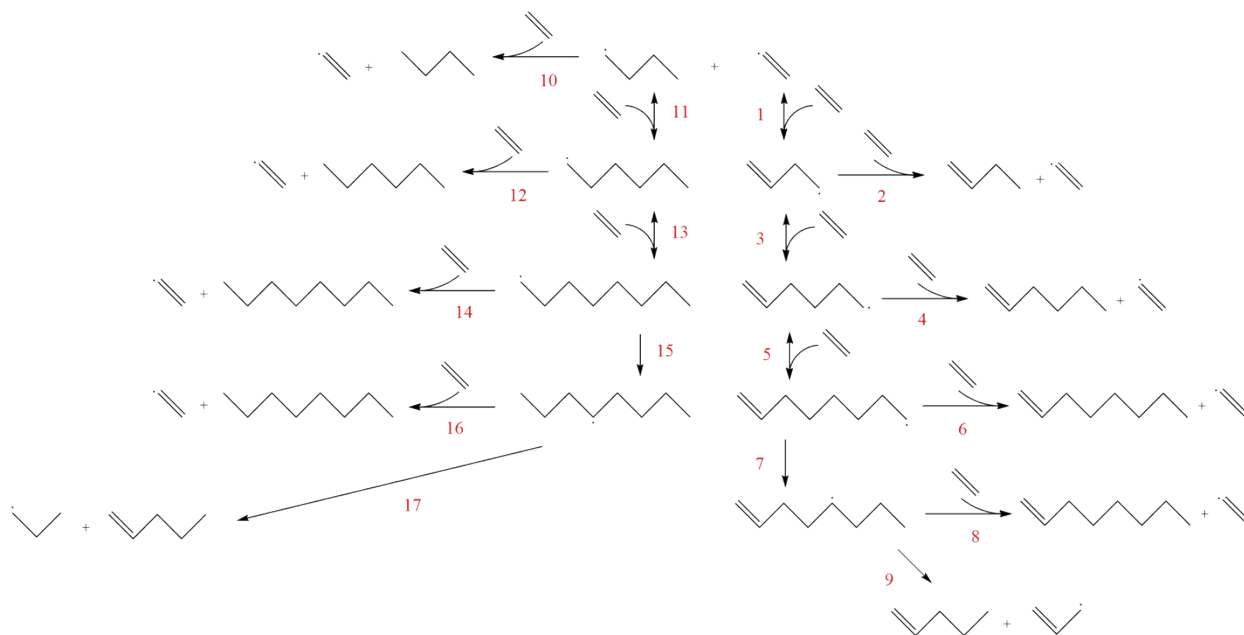
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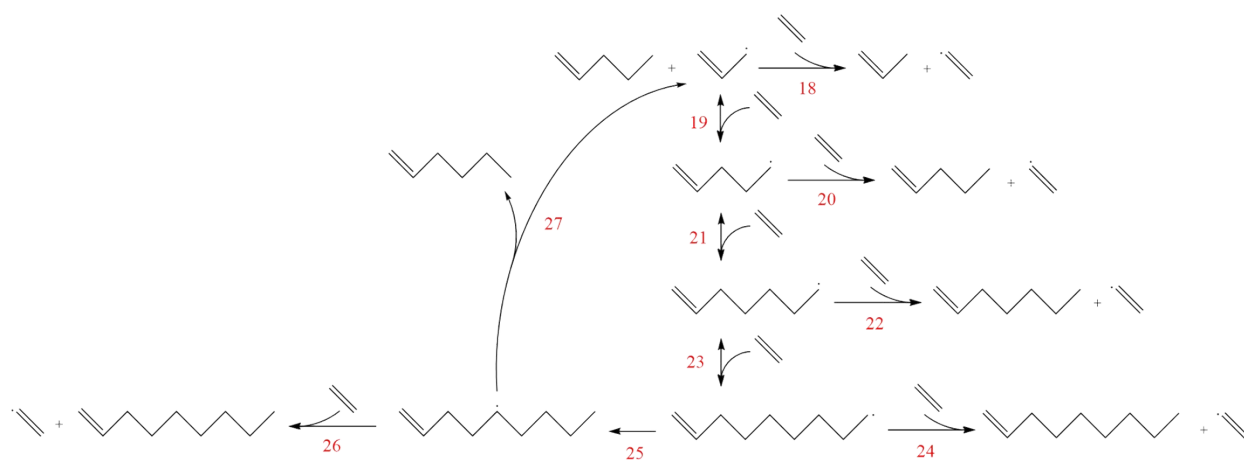
**Table S1:** Examples of heats of reaction used for the Evans-Polanyi approach within the microkinetic model.

<b>Reaction Label</b>	<b><math>\Delta H_{rxn}</math> (kcal/mol)</b>
1,4 Butyl H-Abstraction	25.0
Butene Diradical H-Abstraction	28.0
1, Vinyl Addition	-25.7
2, Butenyl H-Abstraction	1.8
3, Butenyl Addition	-21.6
4, Hexenyl H-Abstraction	1.6
5, Hexenyl Addition	-21.8
8, Shifted Octenyl H-Abstraction	4.7
18, Allyl H-Abstraction	16.5
19, Allyl Addition	-6.6
26, Shifted Nonenyl H-Abstraction	4.7
28, Propyl H-Abstraction	10.0
$\beta$ -scission reactions	7.6
Other addition reactions	-21.8
Other hydrogen abstraction reactions	1.6

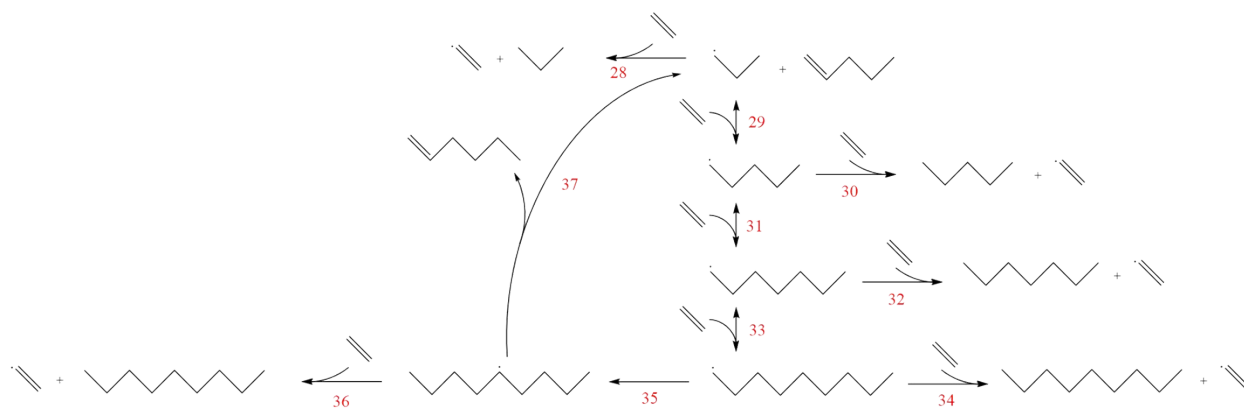
## Reaction Mechanism Labels



**Figure S1:** Numeric labels for events involving even-numbered carbon alkyl and alkenyl species, alkanes and alkenes: radical addition and hydrogen abstraction, and intramolecular hydrogen shift and β-scission of C<sub>8</sub> species.



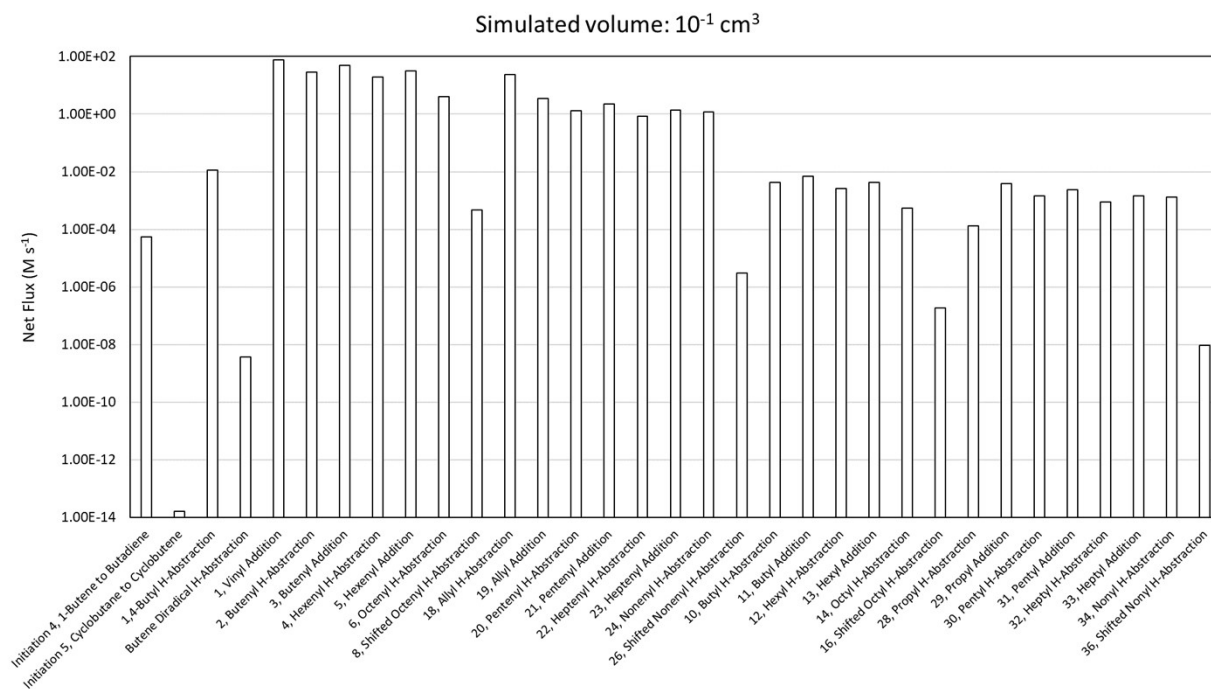
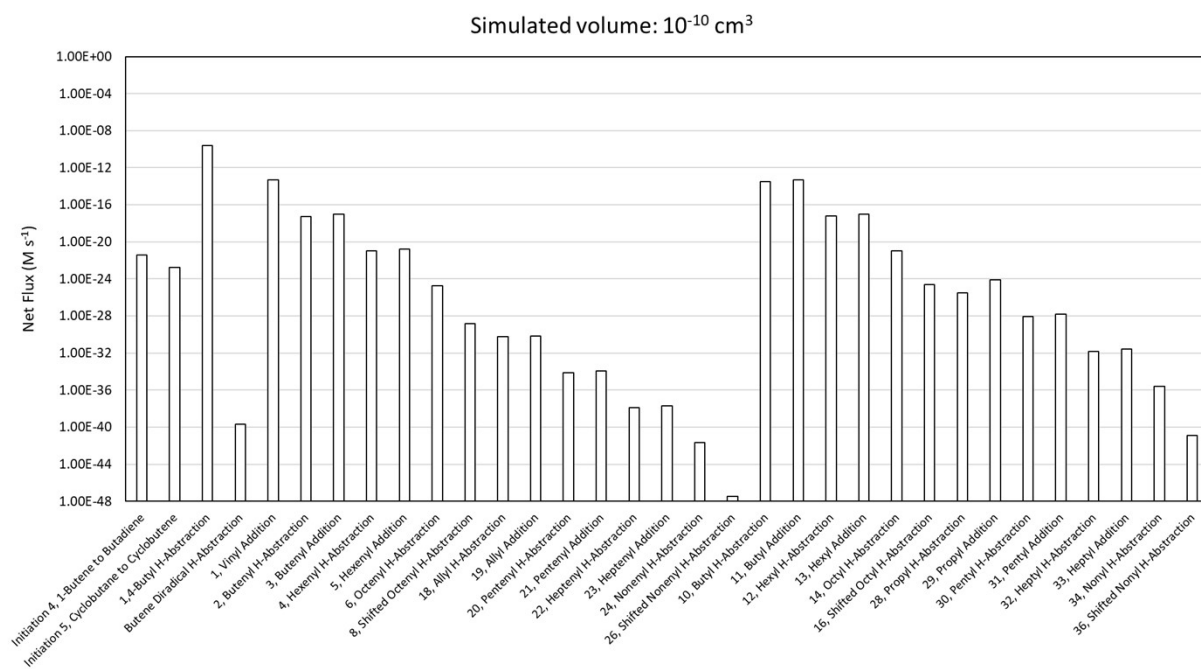
**Figure S2:** Numeric labels for events involving odd-numbered carbon alkenyl species and alkenes: radical addition, hydrogen abstraction, hydrogen shift, and β-scission.

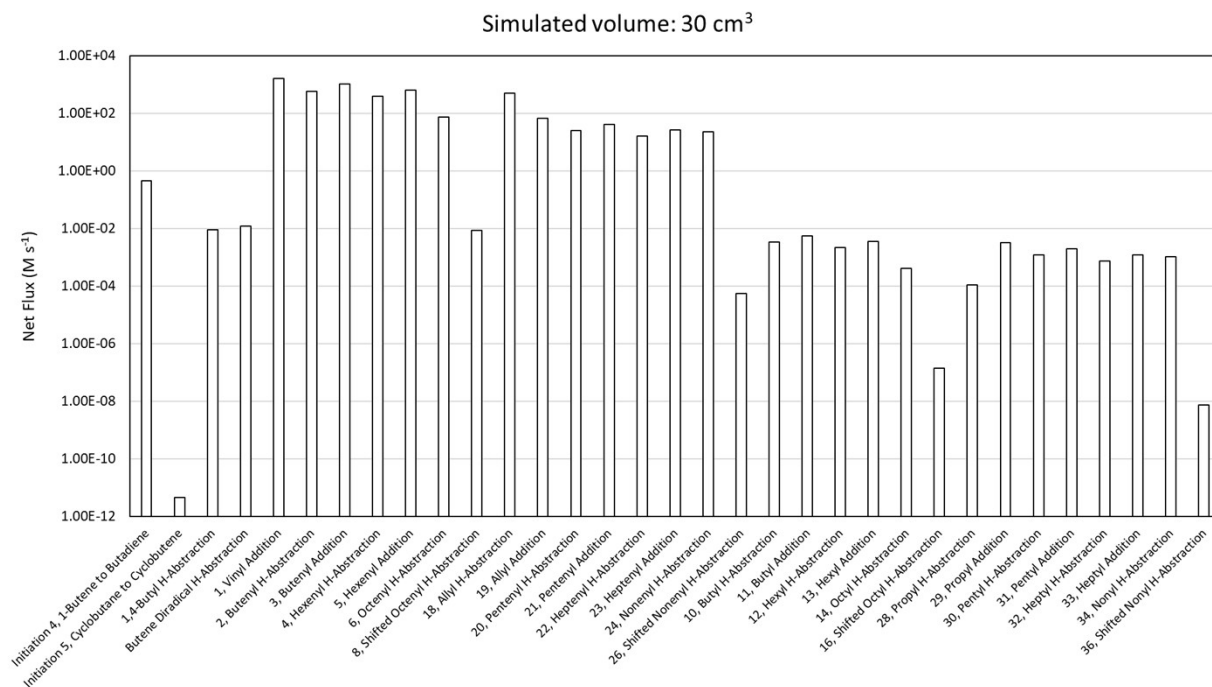


**Figure S3:** Numeric labels for events involving odd-numbered carbon alkyl species and alkenes: addition, hydrogen abstraction, hydrogen shift, and  $\beta$ -scission events.

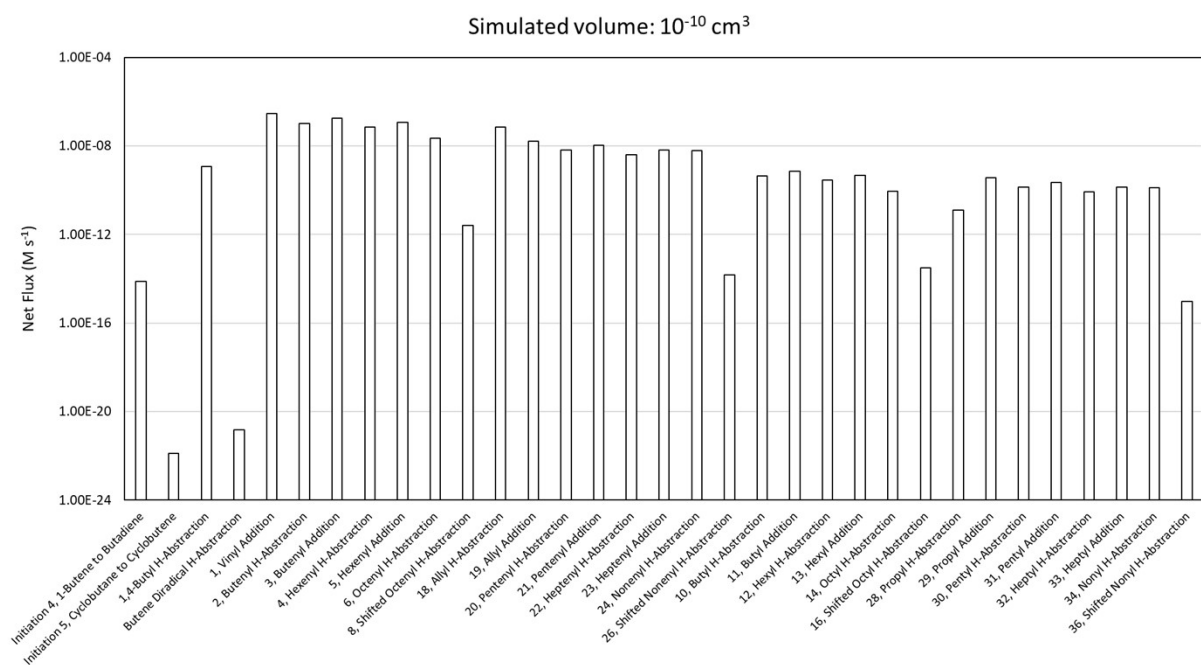
## Ethylene Consumption Figures

a) 15 bar:





b) 25 bar:





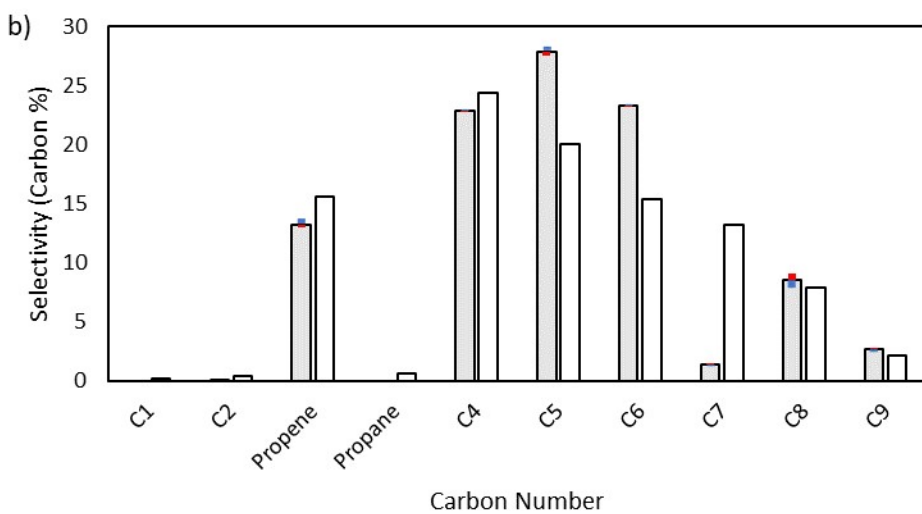
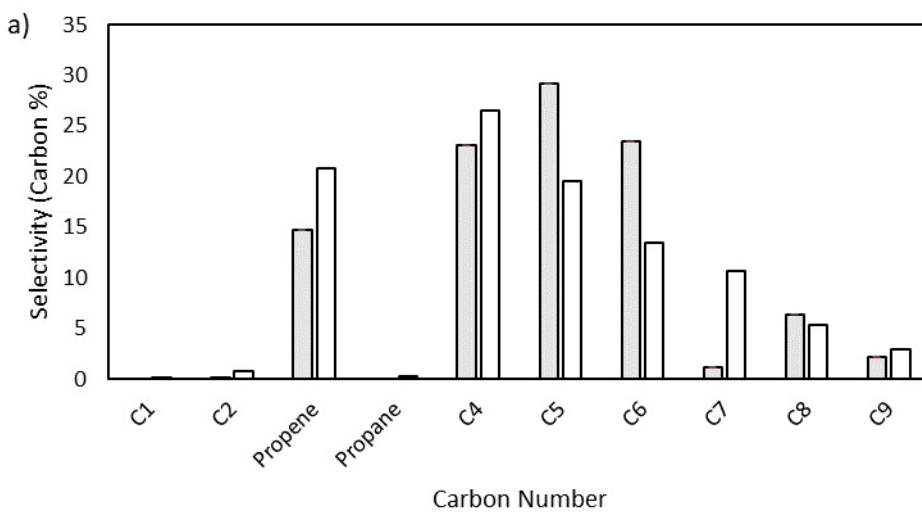
## Computer Specifications

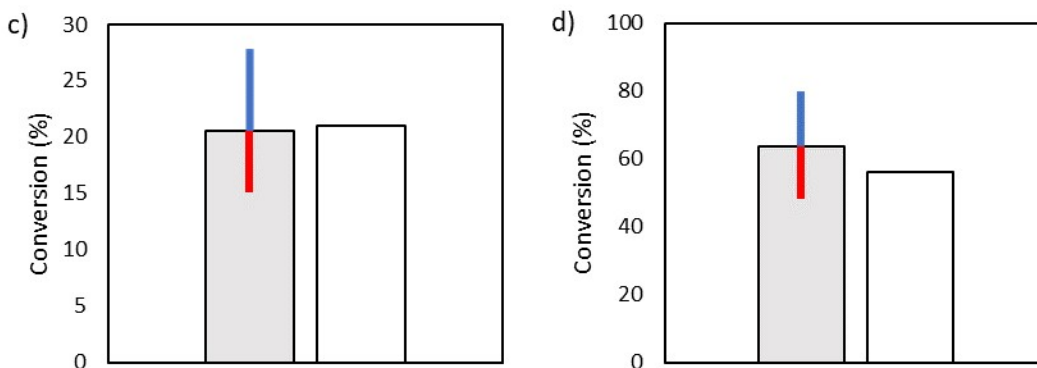
The simulations were run on a Linux node of 8 CPUs with a memory of approximately 32 GB. Runs completed nearly instantaneously for simple model solutions, but fitting of model parameters took 30 minutes – 2 hours per attempt depending on tolerances used, of which several hundred fits were tested throughout model iteration.



## Results of Sensitivity Analysis

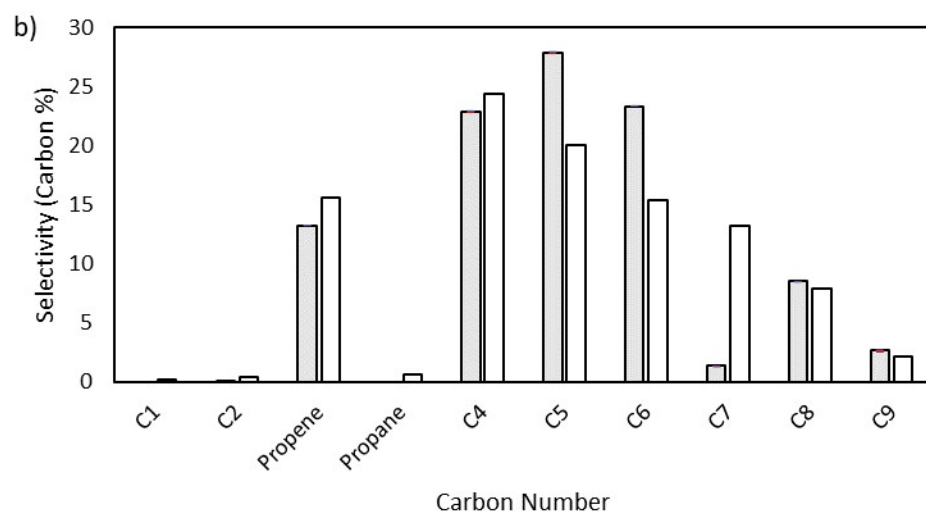
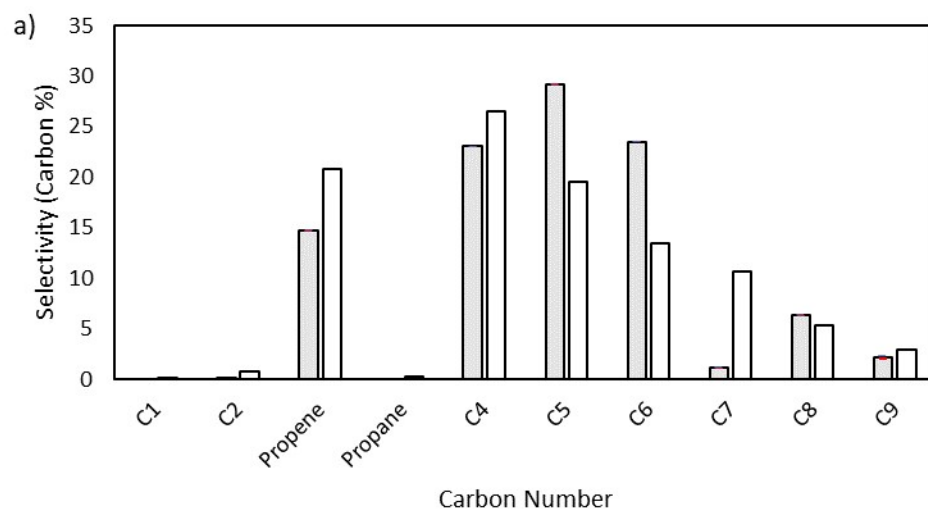
### *Recombination*

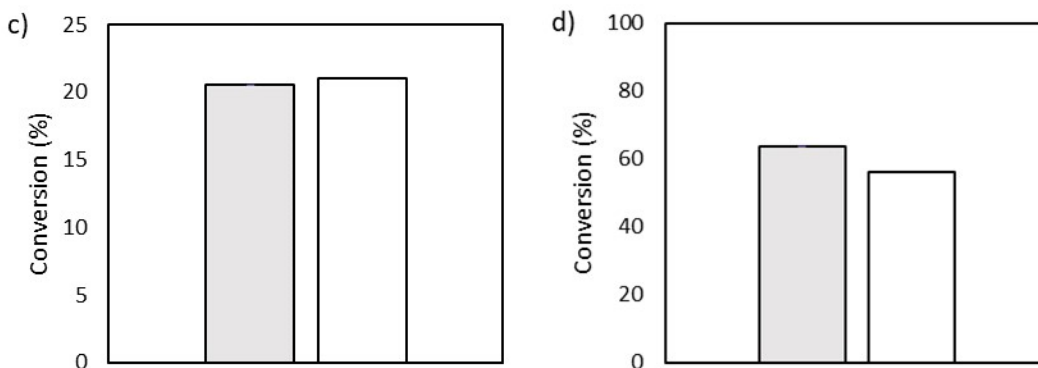




**Figure S5:** Sensitivity analysis of the impact of varying the base activation energy of recombination reactions by  $\pm 1$  kcal/mol. The shaded bars are the model results based on the optimized parameters in Table 2, and the sensitivity to changes in the activation energy are denoted by colored error bars. The blue error bar indicates the change resulting from increasing the base activation energy by 1 kcal/mol, whereas the red error bar indicates the change resulting from decreasing the base activation energy by 1 kcal/mol. a) Product selectivities at a total pressure 15 bar. b) product selectivities at a total pressure 25 bar. c) ethylene conversion at a total pressure 15 bar. d) ethylene conversion at a total pressure 25 bar.

As anticipated, changing the activation energy for recombination does not have major influence on the product distribution, but as a key determinant of the length of the kinetic chain, it does have a measurable influence over conversion, as it effectively controls the lifetime of radicals that are produced. Longer radical lifetimes as the activation energy for recombination is increased, thereby decreasing the rate coefficient, results in a longer kinetic chain with a higher rate of propagation, thereby increasing conversion.

*1,5 Hydrogen Shift*

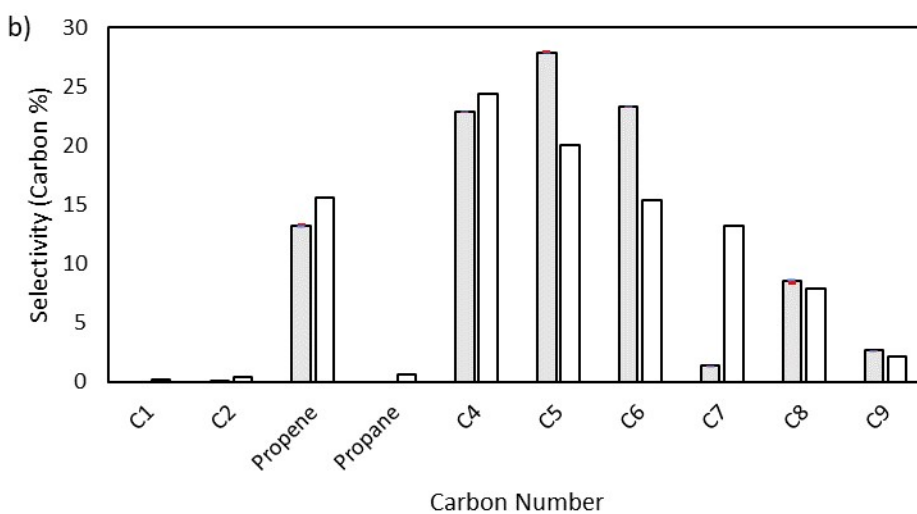
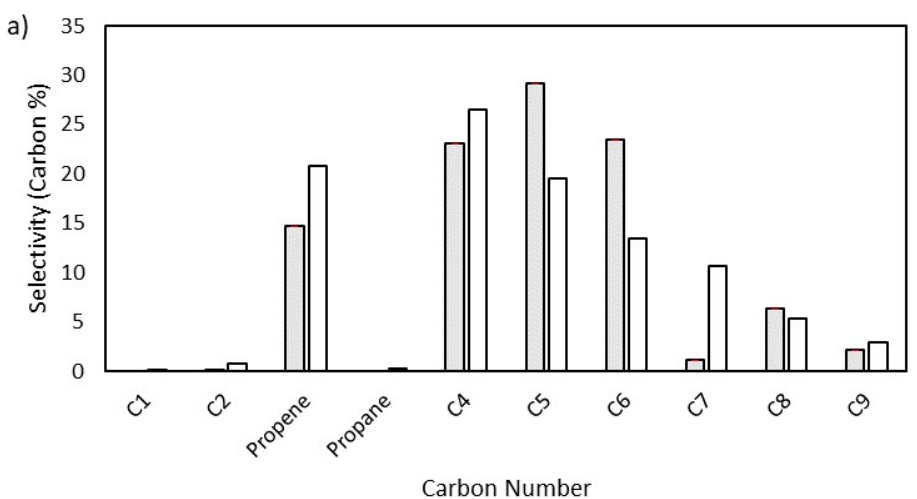


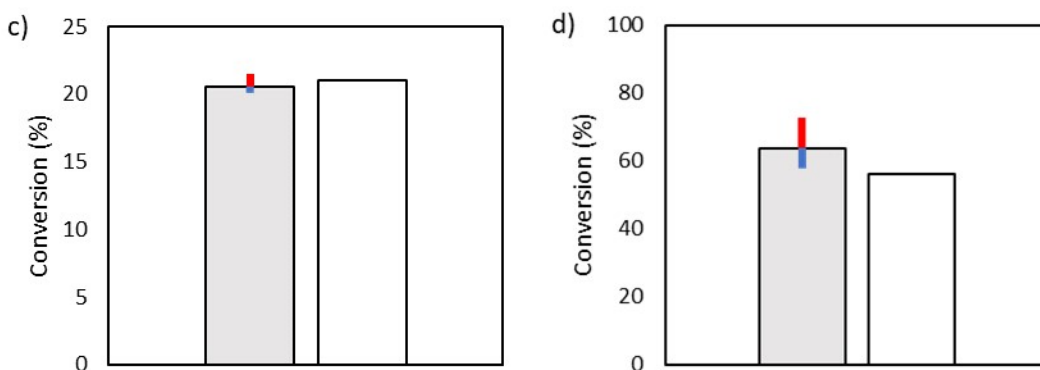
**Figure S6:** Sensitivity analysis of the impact of varying the activation energy of 1,5 hydrogen shift reactions by  $\pm 1$  kcal/mol. The shaded bars are the model results based on the optimized parameters in Table 2, and the sensitivity to changes in the activation energy are denoted by colored error bars. The blue error bar indicates the change resulting from increasing the base activation energy by 1 kcal/mol, whereas the red error bar indicates the change resulting from decreasing the base activation energy by 1 kcal/mol. a) Product selectivities at a total pressure 15 bar. b) product selectivities at a total pressure 25 bar. c) ethylene conversion at a total pressure 15 bar. d) ethylene conversion at a total pressure 25 bar.

The sensitivity of the model results to the activation energy for 1,5-hydrogen shift is less pronounced than that to the activation energy of 1,4-hydrogen shift. As formulated in the model, 1,5-hydrogen shift reactions only allow for nonenyl, nonyl, and octyl radicals as reactants, thereby impacting the subsequent  $\beta$ -scission reactions of the radicals that are formed as products of 1,5-hydrogen shift. However, 1,5-hydrogen shift was not implemented for octenyl radical, as it was assumed to lead to a species that resulted in futile reaction pathways. Specifically, the formation of the 1-octenyl-4-radical would result in a diene for  $\beta$ -scission in one direction, and dienes were not observed in the product distribution. Note that no radicals that were generated were allowed to lead to dienes through propagation steps, although butadiene was a species in one of the initiation pathways. In the other direction, vinyl radical would be formed, and given its relative stability, the heat of reaction, and thus the  $E_a$  value for this reaction channel, would be high, leading to low rates. Thus, it was simply excluded from this compact model. In adjusting

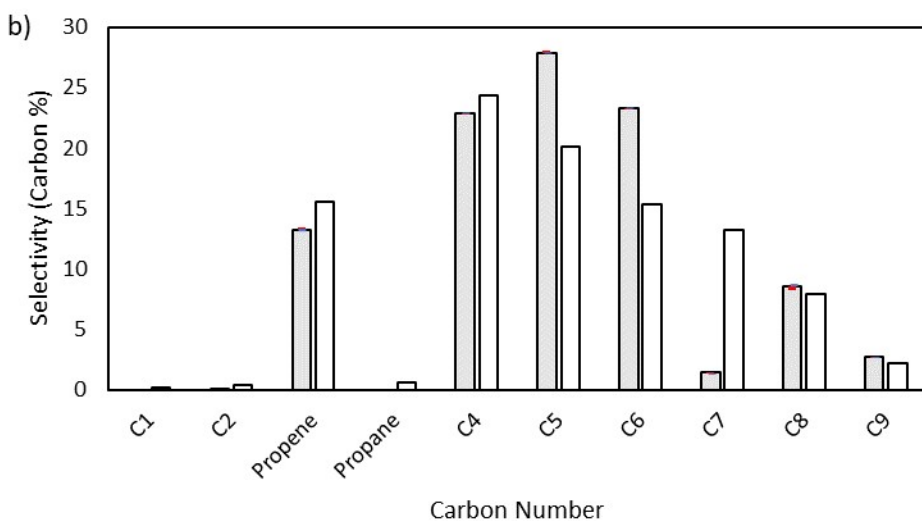
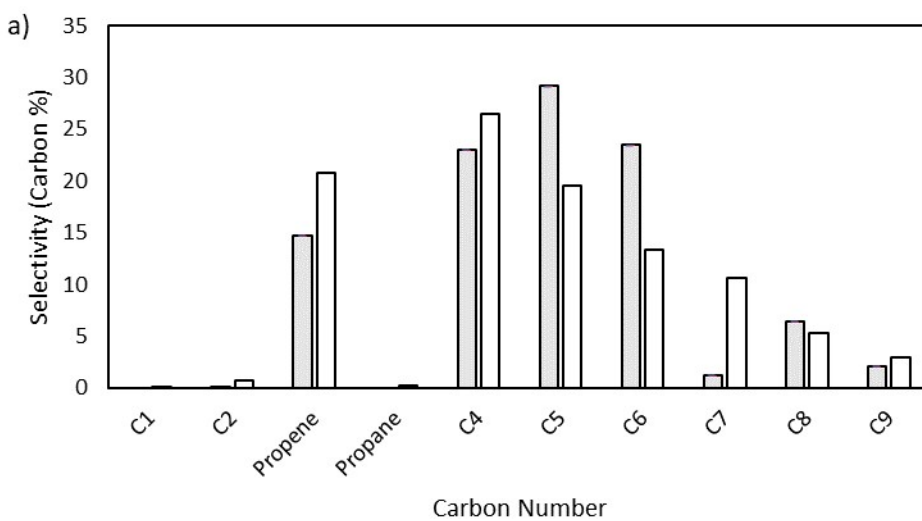
the activation energy for 1,5-hydrogen shift, there is a small effect on the C<sub>9</sub> selectivity, but overall, 1,4-hydrogen shift, despite its less favorable kinetics than 1,5-hydrogen shift, guides the formation of odd-number carbon species through the octenyl  $\beta$ -scission pathway in this truncated reaction network.

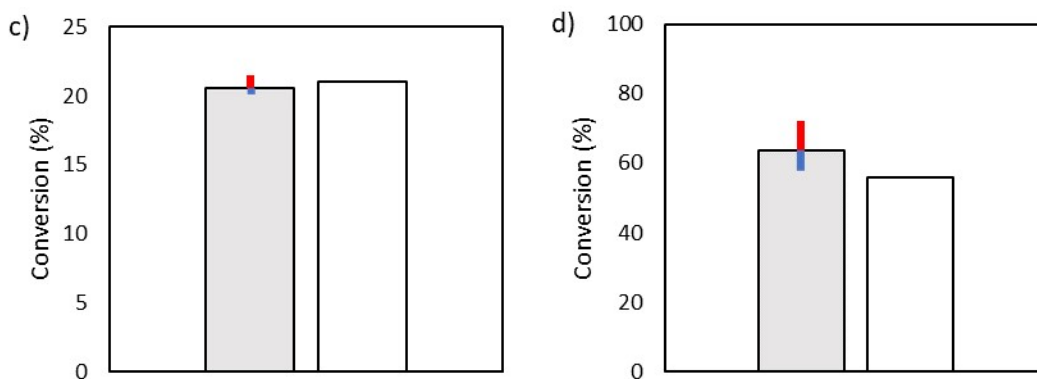
*Initiation Label 4 (Figure 2 main text)*





**Figure S7:** Sensitivity analysis of the impact of varying the activation energy of the *Initiation Label 4* (Figure 2 main text) reaction, the conversion of 1-butene to butadiene, by  $\pm 1$  kcal/mol. The shaded bars are the model results based on the optimized parameters in Table 2, and the sensitivity to changes in the activation energy are denoted by colored error bars. The blue error bar indicates the change resulting from increasing the base activation energy by 1 kcal/mol, whereas the red error bar indicates the change resulting from decreasing the base activation energy by 1 kcal/mol. a) Product selectivities at a total pressure 15 bar. b) product selectivities at a total pressure 25 bar. c) ethylene conversion at a total pressure 15 bar. d) ethylene conversion at a total pressure 25 bar.

*Initiation Label 6 (Figure 2 main text)*



**Figure S8:** Sensitivity analysis of the impact of varying the activation energy of the *Initiation Label 6* (Figure 2 main text) reaction, the conversion of butadiene to a resonance-stabilized diradical, by  $\pm 1$  kcal/mol. The shaded bars are the model results based on the optimized parameters in Table 2, and the sensitivity to changes in the activation energy are denoted by colored error bars. The blue error bar indicates the change resulting from increasing the base activation energy by 1 kcal/mol, whereas the red error bar indicates the change resulting from decreasing the base activation energy by 1 kcal/mol. a) Product selectivities at a total pressure 15 bar. b) product selectivities at a total pressure 25 bar. c) ethylene conversion at a total pressure 15 bar. d) ethylene conversion at a total pressure 25 bar.