Supplementary Material (ESI) for *Energy & Environmental Science*


Electronic Supplemental Information (ESI) for

# Production of Renewable Petroleum Refinery Diesel and Jet Fuel Feedstocks from Hemicellulose Sugar Streams

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## Supplementary Figures

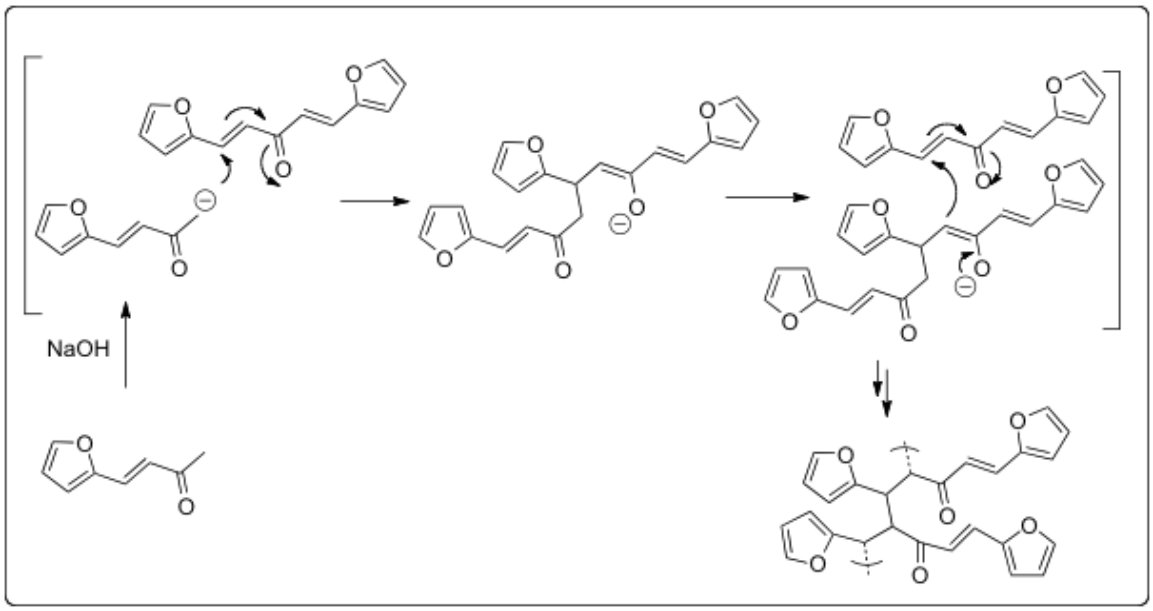


**Fig. S1.** Formation of FAF oligomers via Michael addition reactions in the presence of NaOH. These reactions are initiated by furfural-acetone (1:1) monomer (FA).

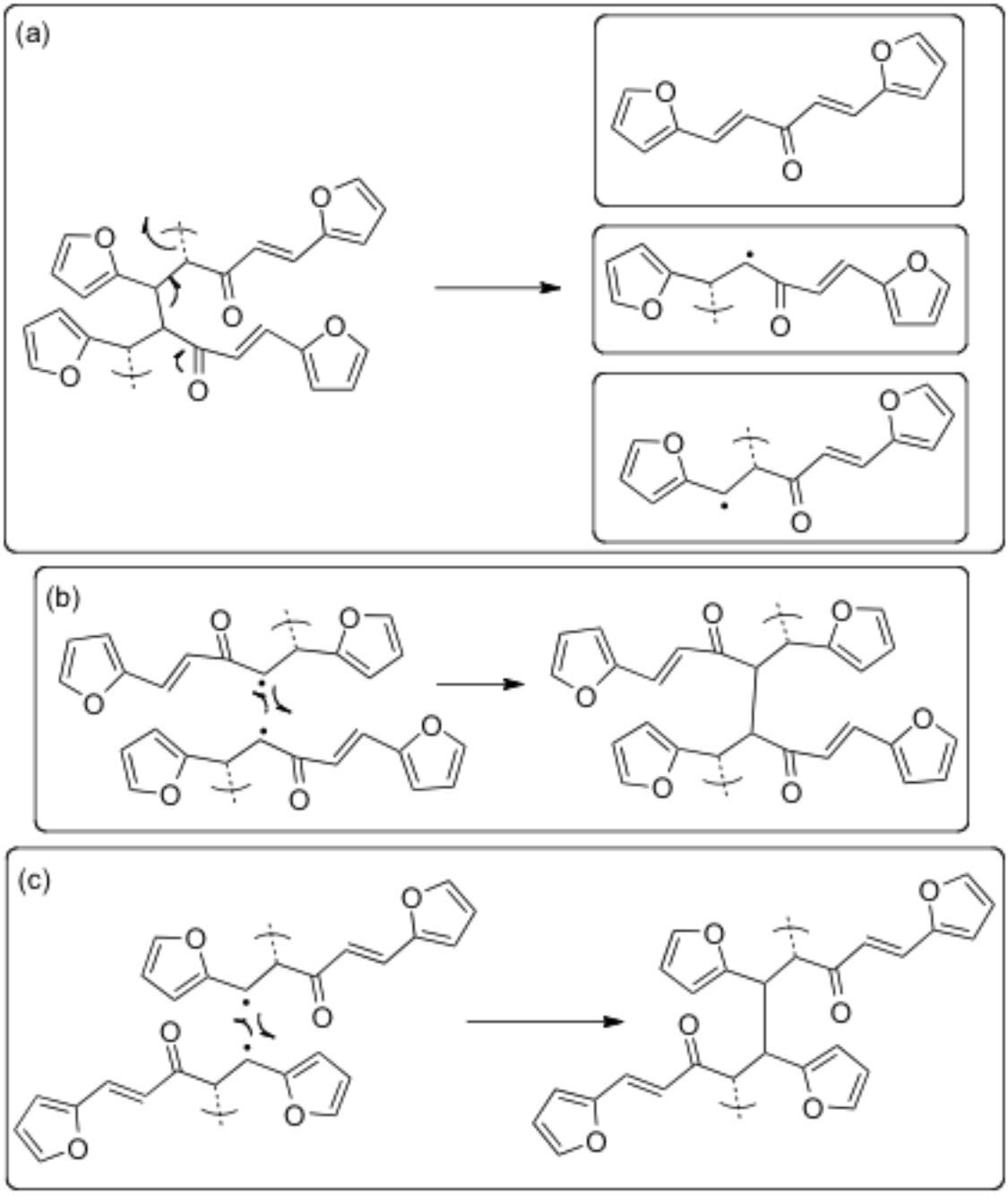


**Fig. S2.** Detailed mechanism of the radical polymerization of crude FAF when stored in the absence of any solvent. The mechanism takes place first by the decomposition of the oligomers formed via Michael addition reactions followed by the formation of radical species as shown in (a). These radical species can undergo two types of radical polymerization as presented in (b) and (c).

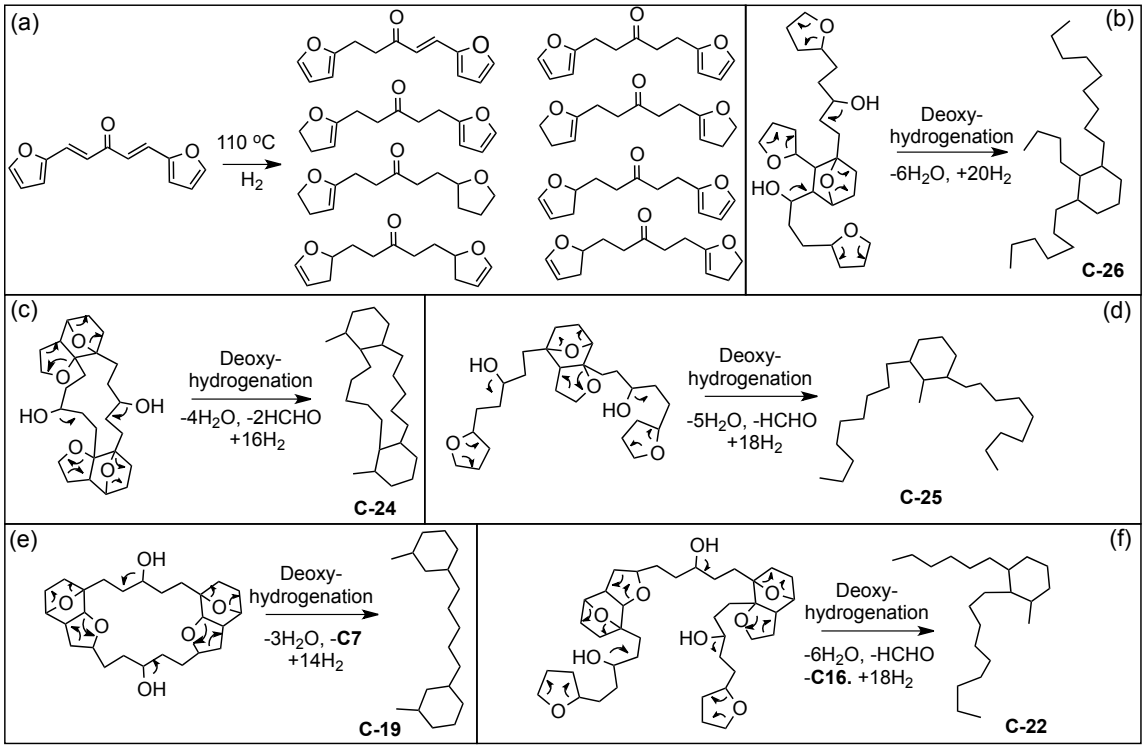


**Fig. S3.** Detailed mechanisms of the representative reactions taking place during hydrodeoxygenation: (a) Production of partially hydrogenated FAFs that participate in the Diels-Alder reactions during hydrocycloaddition. (b) $C_{26}$, (c) $C_{24}$, (d) $C_{25}$, (e) $C_{19}$ and (f) $C_{22}$ products formed during hydrodeoxygenation from hydrocycloadded products (shown in Section IV of Fig. 2) that are formed from the partially hydrogenated FAFs.

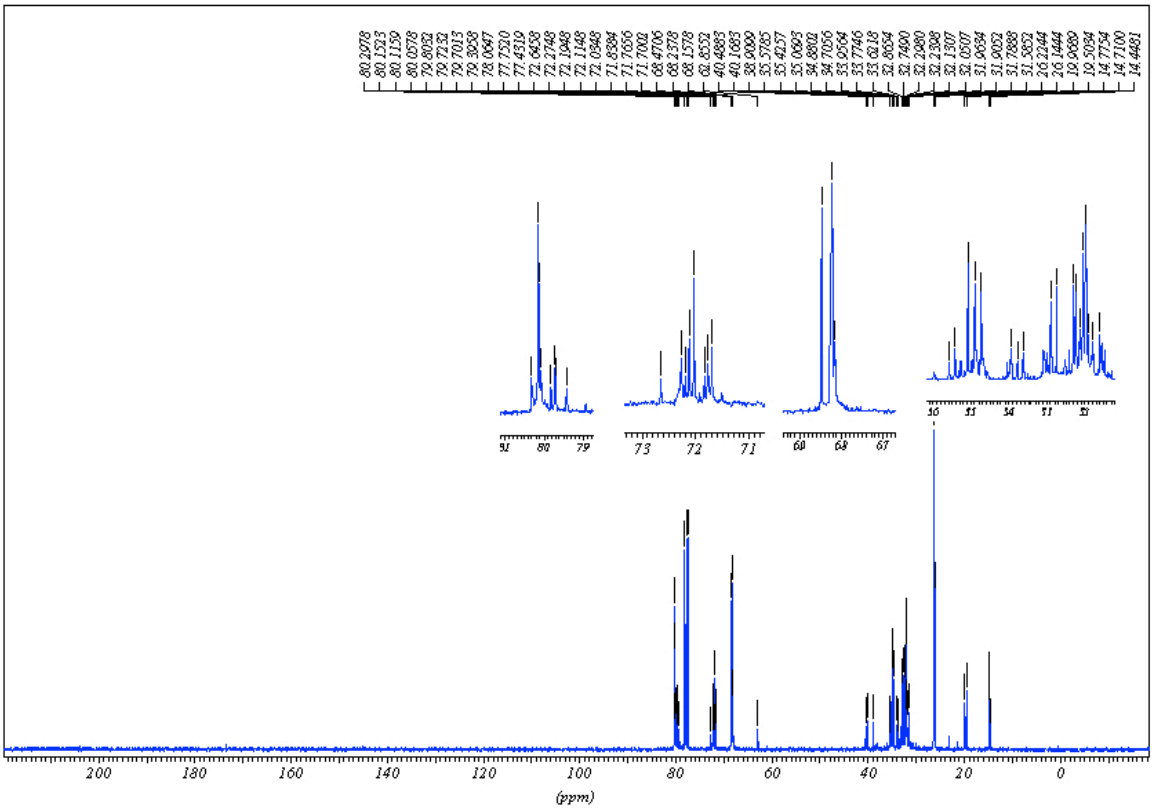


**Fig. S4.** $^{13}$C-NMR spectrum of the hydrocycloaddition product of Run 3 of Table 1. The spectrum shows no peaks at chemical shifts greater than 100 ppm, which indicates presence of no C=C bonds in the product. Hydrocycloaddition reaction was conducted at 140°C and 8.27 MPa (1200 psi) using 30% purified feed over 15 g 2% Ru/alumina catalyst in a 160-cm$^3$ batch reactor for 6 h. Total amount of feed in THF was 100 cm$^3$.

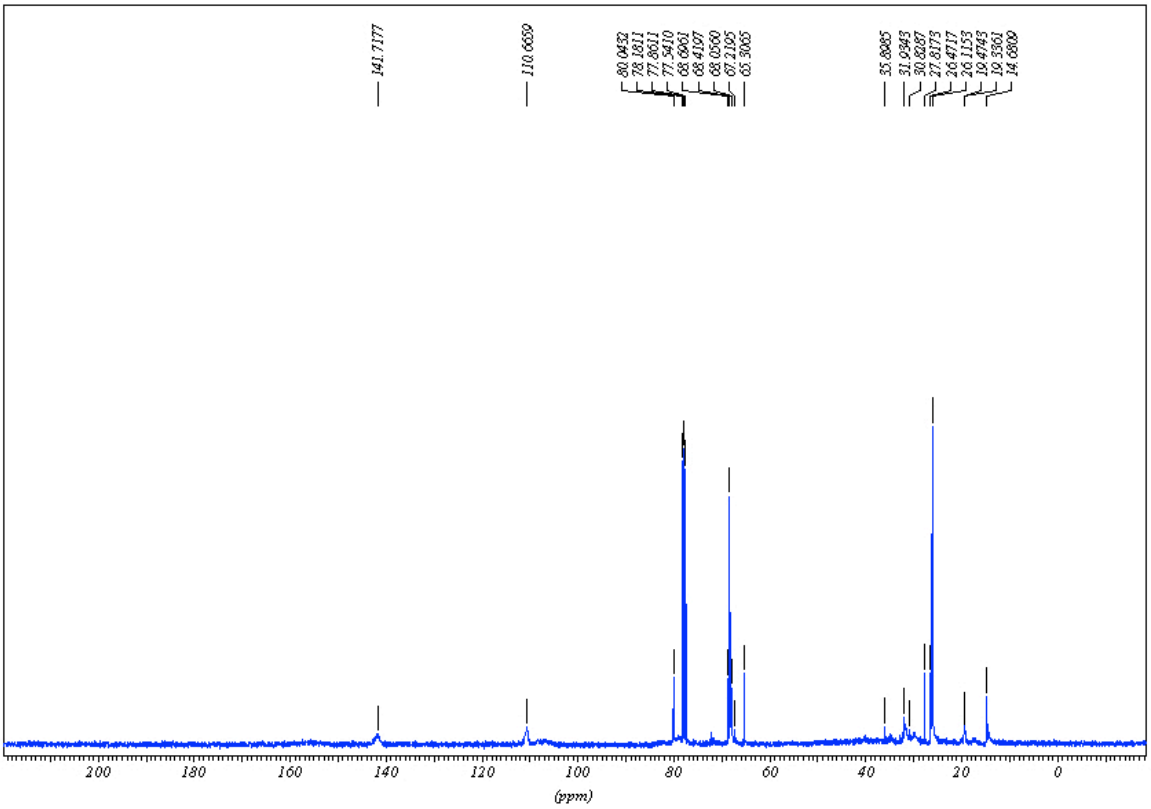


**Fig. S5.** $^{13}$C-NMR spectrum of the hydrocycloaddition product of Run 4 of Table 1. The spectrum shows two small peaks at chemical shifts greater than 100 ppm, which indicates the presence of some C=C bonds in the product. Hydrocycloaddition reaction was conducted at 110°C and 8.27 MPa (1200 psi) using 30% crude feed over 15 g 2% Ru/alumina catalyst in a 160-cm$^3$ batch reactor for 6 h. Total amount of feed in THF was 100 cm$^3$.

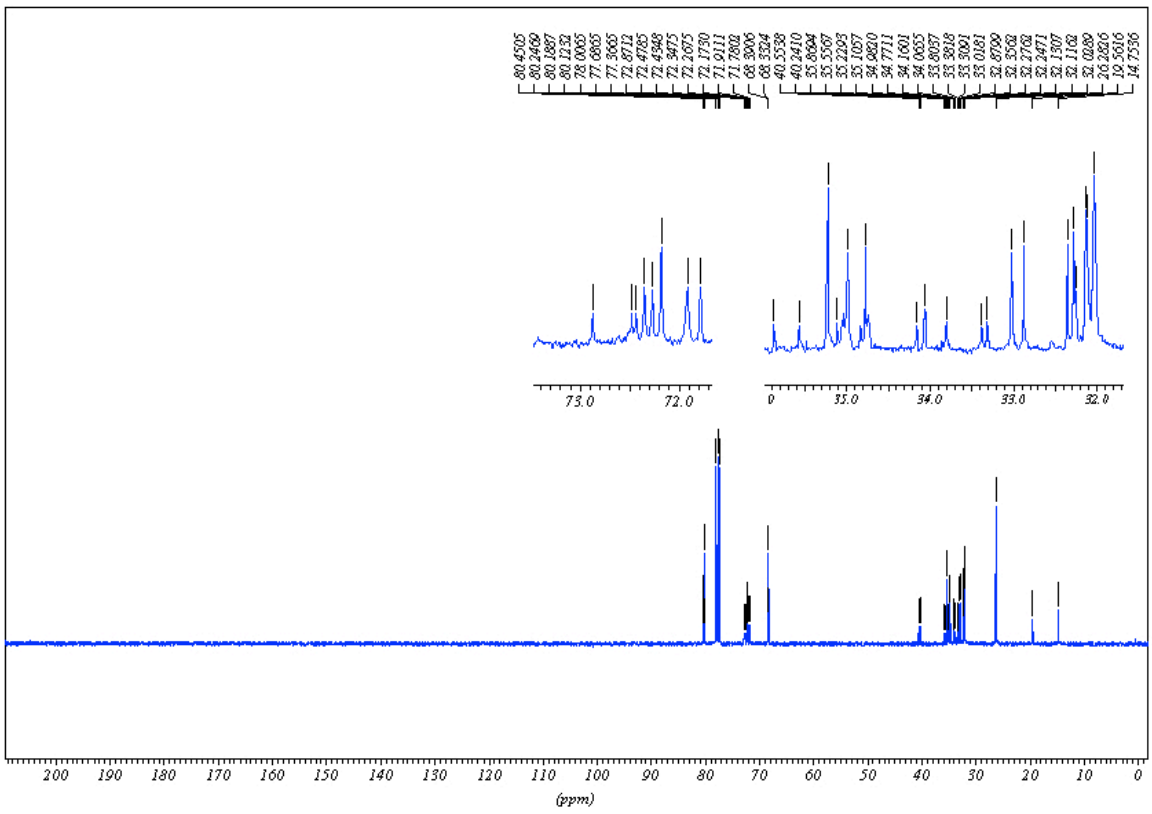


**Fig. S6.** $^{13}$C-NMR spectrum of the hydrocycloaddition product of Run 7 of Table 1. The spectrum shows no peaks at chemical shifts greater than 100 ppm, which indicates presence of no C=C bonds in the product. Hydrocycloaddition reaction was conducted at 110°C and 5.52 MPa (800 psi) using 10% purified feed over 15 g 2% Ru/alumina catalyst in a 160-cm$^3$ batch reactor for 6 h. Total amount of feed in THF was 100 cm$^3$.

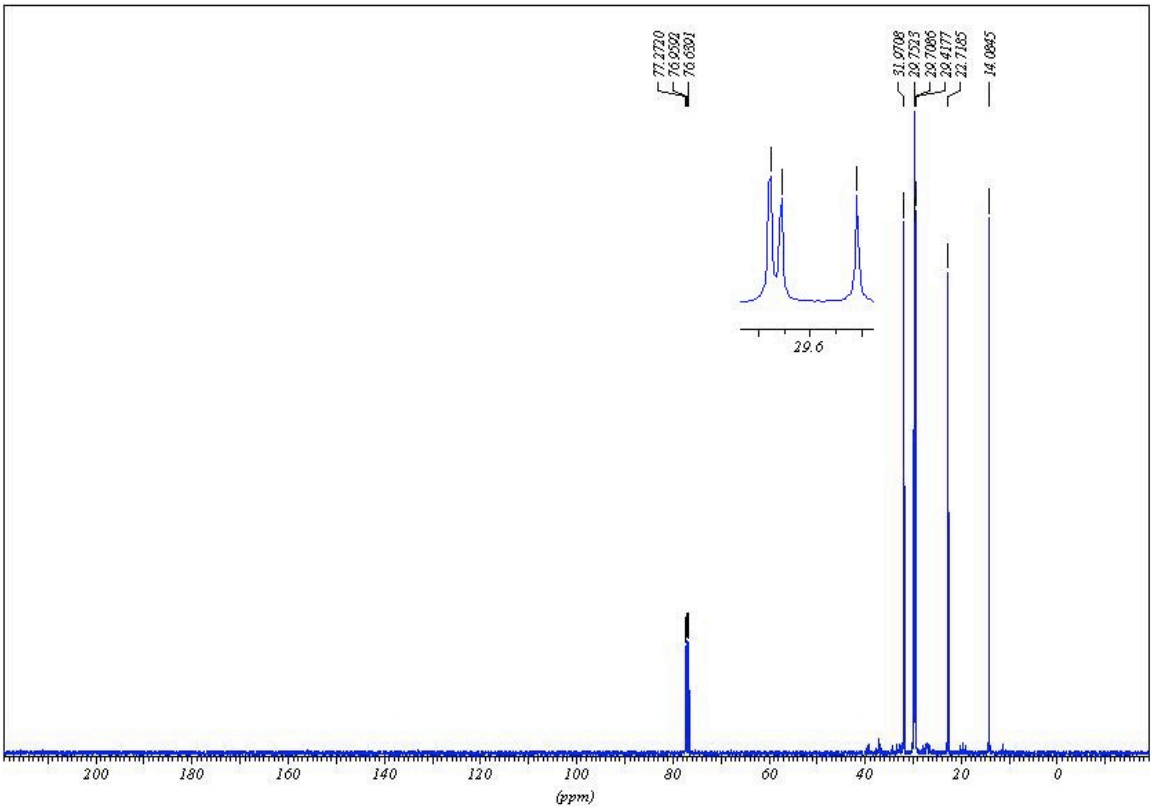


**Fig. S7.** $^{13}$C-NMR spectrum of the hydrodeoxygenation product that is indicated with blue data in Fig. 1. The group of peaks given at 76-78 ppm belongs to $CDCl_3$. The spectrum shows no peaks at chemical shifts greater than 100 ppm, which indicates presence of no C=C bonds in the product. Hydrodeoxygenation reactions were conducted at 300°C and 8.27 MPa (1200 psi) over 2.5 g 4% Pt/silica-alumina catalyst in a continuous flow reactor.

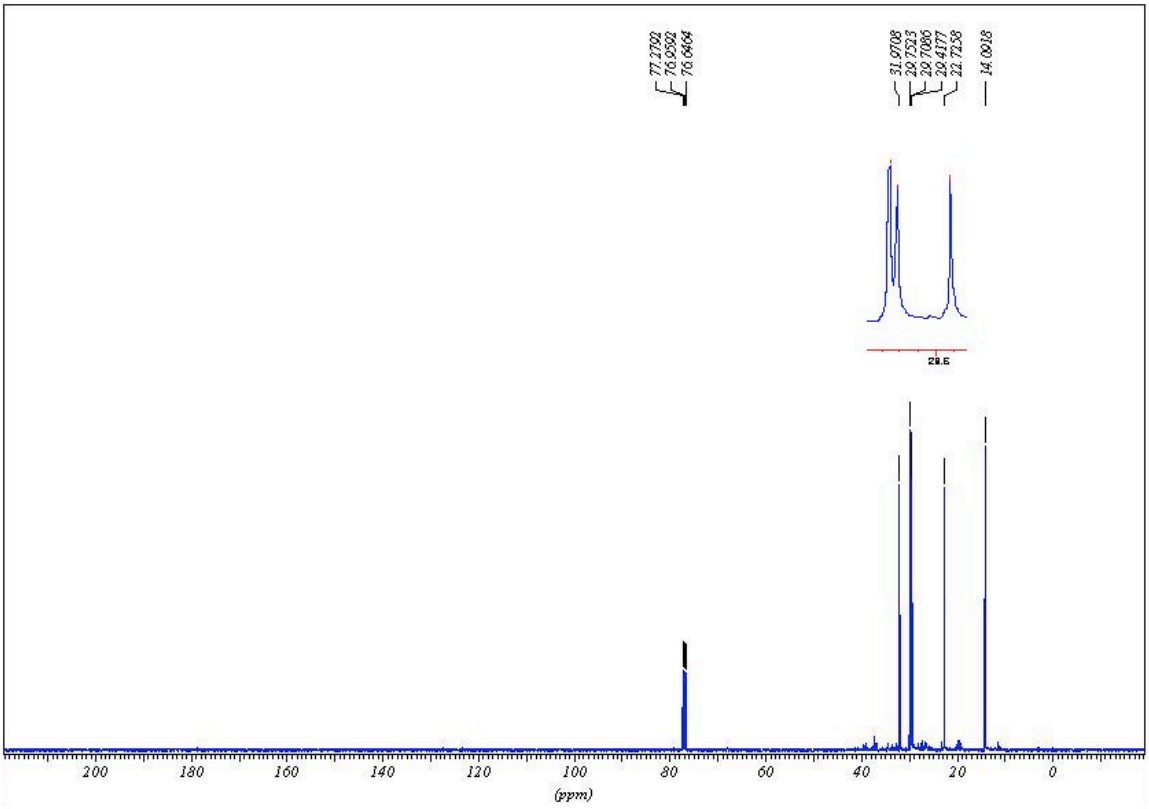


**Fig. S8.** $^{13}$C-NMR spectrum of the hydrodeoxygenation product that is indicated with green data in Fig. 1. The group of peaks given at 76-78 ppm belongs to $CDCl_3$. The spectrum shows no peaks at chemical shifts greater than 100 ppm, which indicates presence of no C=C bonds in the product. Hydrodeoxygenation reactions were conducted at 300°C and 8.27 MPa (1200 psi) over 2.5 g 4% Pt/silica-alumina catalyst in a continuous flow reactor.

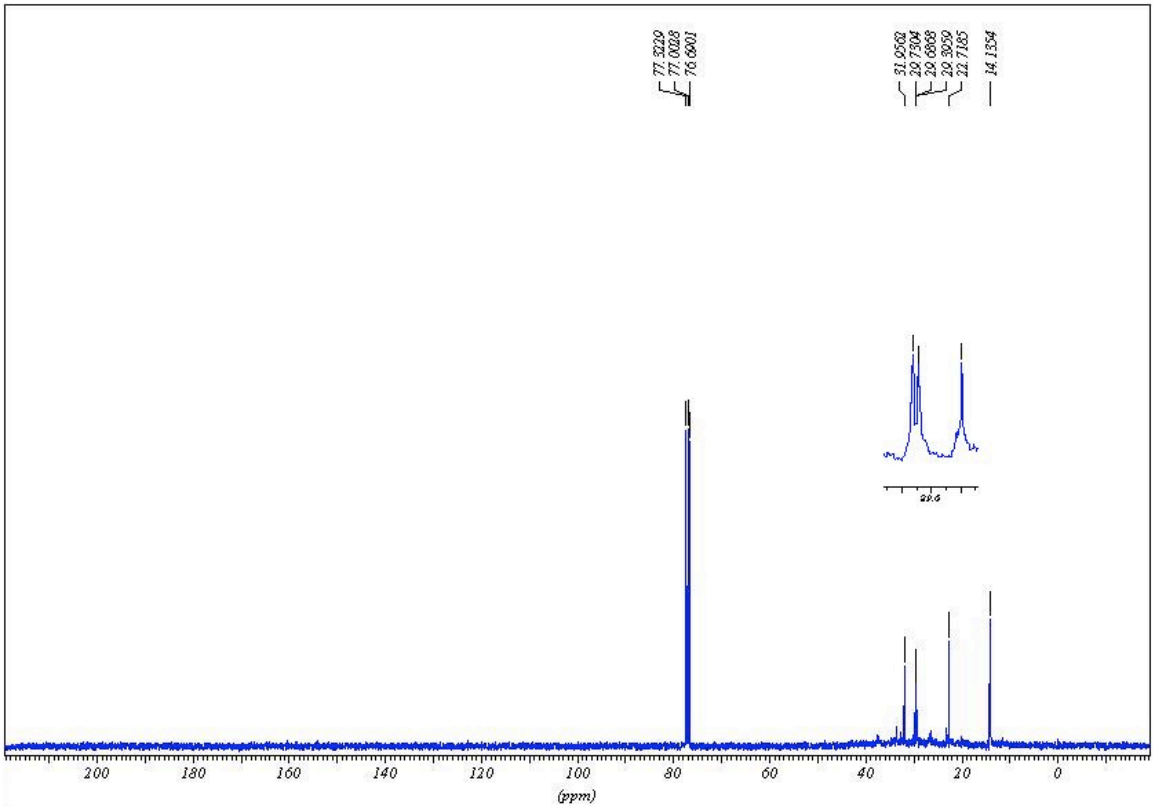


**Fig. S9.** $^{13}$C-NMR spectrum of the hydrodeoxygenation product that is indicated with red data in Fig. 1. The group of peaks given at 76-78 ppm belongs to $CDCl_3$. The spectrum shows no peaks at chemical shifts greater than 100 ppm, which indicates presence of no C=C bonds in the product. Hydrodeoxygenation reactions were conducted at 300°C and 8.27 MPa (1200 psi) over 2.5 g 4% Pt/silica-alumina catalyst in a continuous flow reactor.

## Supplemental Tables

**Table S1.** Blue data (% molar carbon selectivities) of Fig. 11.

| C Number | n-Paraffin | i-Paraffin | Naphthene | Aromatic | TOTAL |
|---|---|---|---|---|---|
| 1 | 3.55 | 0.00 | 0.00 | 0.00 | 3.55 |
| 2 | 1.69 | 0.00 | 0.00 | 0.00 | 1.69 |
| 3 | 0.54 | 0.00 | 0.00 | 0.00 | 0.54 |
| 4 | 3.96 | 0.00 | 0.00 | 0.00 | 3.96 |
| 5 | 0.38 | 0.05 | 0.00 | 0.00 | 0.43 |
| 6 | 0.17 | 0.33 | 0.10 | 0.00 | 0.60 |
| 7 | 0.04 | 0.75 | 0.90 | 0.00 | 1.70 |
| 8 | 2.04 | 1.13 | 1.00 | 0.00 | 4.17 |
| 9 | 0.93 | 1.29 | 1.45 | 0.00 | 3.67 |
| 10 | 0.48 | 0.94 | 1.40 | 0.00 | 2.82 |
| 11 | 0.72 | 0.67 | 1.57 | 0.01 | 2.97 |
| 12 | 8.86 | 1.57 | 2.14 | 0.00 | 12.56 |
| 13 | 33.50 | 9.91 | 7.21 | 0.00 | 50.62 |
| 14 | 1.00 | 0.74 | 1.49 | 0.00 | 3.23 |
| 15 | 0.10 | 0.56 | 1.46 | 0.00 | 2.13 |
| 16 | 0.06 | 0.41 | 1.19 | 0.01 | 1.67 |
| 17 | 0.03 | 0.41 | 0.69 | 0.01 | 1.14 |
| 18 | 0.02 | 0.39 | 0.55 | 0.00 | 0.95 |
| 19 | 0.00 | 0.34 | 0.46 | 0.00 | 0.80 |
| 20 | 0.00 | 0.15 | 0.07 | 0.00 | 0.22 |
| 21 | 0.00 | 0.18 | 0.04 | 0.00 | 0.23 |
| 22 | 0.00 | 0.33 | 0.03 | 0.00 | 0.35 |
| 23 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 24 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 25 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 26 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 29 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 31 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 58.08 | 20.15 | 21.74 | 0.03 | |

**Table S2.** Green data (% molar carbon selectivities) of Fig. 11.

| C Number | n-Paraffin | i-Paraffin | Naphthene | Aromatic | TOTAL |
|---|---|---|---|---|---|
| 1 | 2.93 | 0.00 | 0.00 | 0.00 | 2.93 |
| 2 | 1.61 | 0.00 | 0.00 | 0.00 | 1.61 |
| 3 | 0.68 | 0.00 | 0.00 | 0.00 | 0.68 |
| 4 | 4.40 | 0.00 | 0.00 | 0.00 | 4.40 |
| 5 | 0.42 | 0.06 | 0.00 | 0.00 | 0.48 |
| 6 | 0.21 | 0.26 | 0.08 | 0.00 | 0.56 |
| 7 | 0.02 | 0.64 | 0.55 | 0.00 | 1.20 |
| 8 | 0.95 | 1.03 | 1.08 | 0.00 | 3.05 |
| 9 | 0.72 | 1.25 | 1.74 | 0.00 | 3.70 |
| 10 | 0.60 | 1.19 | 1.90 | 0.00 | 3.70 |
| 11 | 1.33 | 1.04 | 2.22 | 0.00 | 4.59 |
| 12 | 9.02 | 1.80 | 3.07 | 0.00 | 13.88 |
| 13 | 26.40 | 5.99 | 5.76 | 0.00 | 38.15 |
| 14 | 1.01 | 0.97 | 2.14 | 0.00 | 4.11 |
| 15 | 0.17 | 1.12 | 2.22 | 0.00 | 3.52 |
| 16 | 0.10 | 0.67 | 1.79 | 0.01 | 2.57 |
| 17 | 0.06 | 0.70 | 1.40 | 0.01 | 2.17 |
| 18 | 0.04 | 0.86 | 1.45 | 0.00 | 2.35 |
| 19 | 0.01 | 0.82 | 1.30 | 0.00 | 2.13 |
| 20 | 0.01 | 0.35 | 0.40 | 0.00 | 0.77 |
| 21 | 0.00 | 0.60 | 0.38 | 0.00 | 0.99 |
| 22 | 0.00 | 1.20 | 0.43 | 0.00 | 1.63 |
| 23 | 0.00 | 0.06 | 0.01 | 0.00 | 0.07 |
| 24 | 0.00 | 0.07 | 0.00 | 0.00 | 0.07 |
| 25 | 0.00 | 0.30 | 0.01 | 0.00 | 0.31 |
| 26 | 0.00 | 0.39 | 0.00 | 0.00 | 0.39 |
| 27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 29 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 31 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 50.68 | 21.35 | 27.94 | 0.03 | |

**Table S3.** Red data (% molar carbon selectivities) of Fig. 11.

| C Number | n-Paraffin | i-Paraffin | Naphthene | Aromatic | TOTAL |
|---|---|---|---|---|---|
| 1 | 3.19 | 0.00 | 0.00 | 0.00 | 3.19 |
| 2 | 1.81 | 0.00 | 0.00 | 0.00 | 1.81 |
| 3 | 1.89 | 0.00 | 0.00 | 0.00 | 1.89 |
| 4 | 7.27 | 0.00 | 0.00 | 0.00 | 7.27 |
| 5 | 1.57 | 0.10 | 0.00 | 0.00 | 1.67 |
| 6 | 0.33 | 0.28 | 0.41 | 0.00 | 1.01 |
| 7 | 0.05 | 0.50 | 1.97 | 0.00 | 2.53 |
| 8 | 0.36 | 0.62 | 2.08 | 0.00 | 3.06 |
| 9 | 0.26 | 0.52 | 2.53 | 0.00 | 3.31 |
| 10 | 0.43 | 0.49 | 3.48 | 0.00 | 4.40 |
| 11 | 0.47 | 0.52 | 4.11 | 0.04 | 5.14 |
| 12 | 1.20 | 0.38 | 4.10 | 0.05 | 5.73 |
| 13 | 4.28 | 0.62 | 6.44 | 0.06 | 11.41 |
| 14 | 0.14 | 0.28 | 5.86 | 0.07 | 6.35 |
| 15 | 0.03 | 0.13 | 5.29 | 0.12 | 5.57 |
| 16 | 0.01 | 0.09 | 4.34 | 0.19 | 4.63 |
| 17 | 0.01 | 0.13 | 4.73 | 0.36 | 5.23 |
| 18 | 0.01 | 0.19 | 4.45 | 0.39 | 5.03 |
| 19 | 0.00 | 0.05 | 4.29 | 0.44 | 4.78 |
| 20 | 0.00 | 0.02 | 3.01 | 0.35 | 3.39 |
| 21 | 0.00 | 0.03 | 3.93 | 0.44 | 4.39 |
| 22 | 0.00 | 0.03 | 2.99 | 0.37 | 3.38 |
| 23 | 0.00 | 0.00 | 0.95 | 0.17 | 1.12 |
| 24 | 0.00 | 0.00 | 0.69 | 0.12 | 0.81 |
| 25 | 0.00 | 0.01 | 0.95 | 0.10 | 1.05 |
| 26 | 0.00 | 0.02 | 1.27 | 0.12 | 1.41 |
| 27 | 0.00 | 0.00 | 0.25 | 0.02 | 0.27 |
| 28 | 0.00 | 0.00 | 0.09 | 0.01 | 0.10 |
| 29 | 0.00 | 0.00 | 0.05 | 0.00 | 0.05 |
| 30 | 0.00 | 0.00 | 0.02 | 0.00 | 0.02 |
| 31 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 |
| | 23.31 | 5.01 | 68.29 | 3.40 | |