

Supporting Information for :

Conversion of Biomass-derived Fatty Acids and Derivatives into Hydrocarbons Using a Meta-Free Hydrodeoxygenation Process

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S1 Chemicals

lauric acid (J&K, 98%), myristic acid (J&K, 99%), palmitic acid (J&K, 97%), stearic acid (Energy Chemical, 99%), methyl laurate (J&K, 99%), methyl myristate (J&K, 98%), methyl palmitate (J&K, 95%), methyl stearate (Energy Chemical, 95%), trilaurin (TCI, 98%), tripalmitin (TCI), tristearin (TCI, 80+%), oleic acid (SCR, AR), colza oil (SCR, CP), olive oil (Aladdin, CP), dodecane (aladdin, 98%), tetradecane (TCI, 99%), hexadecane (aladdin, 98%), octadecane (Energy Chemical, 99%), eicosane (Alfa Aesar, 98%), trispentafluorophenylborane ($B(C_6F_5)_3$) (TCI, 97+%), triethylamine (SCR, 99%), triethylsilane (J&K, 98%), triethoxysilane (Energy Chemical, 97%), diethylmethylsilane (J&K, 97%), diethylsilane (J&K, 98+%), poly(methylhydrosiloxane) (PMHS) (Alfa Aesar, CP), diphenylsilane (J&K, 99%). All superdry solvents were from J&K: dichloromethane (J&K, 99.9%), acetonitrile (J&K, 99.9%), 1,4-dioxane (J&K, 99.5%), N, N-dimethylformamide (J&K, 9.7%), N, N-Dimethylacetamide (J&K, 99.7%), dimethyl sulfoxide (J&K, 99.7%).

S2 Analysis Method

2.1 GC analysis. the samples were quenched by adding triethylamine, and then were directly analyzed (diluted to 10 mL) on GC. GC was performed with Shimadzu QP2010 Plus gas chromatograph equipped with an AT-65 capillary column. Homologous compounds were using as internal standard. Eicosane were internal standard when the product was octadecane, and hexadecane were internal standard when the product was tetradecane. Other examples were done in the same manner. The temperature program began with an isothermal step at 110 °C for 3 min. Then the temperature increased to 250 °C by 30 °C min⁻¹, and keep the temperature for 6 min. Identification of compounds was based on retention time and comparison mass spectrum of pure chemical. The FID was applied to the quantification.

2.2 GC-MS Analysis. the samples were quenched by adding triethylamine, and then were directly analyzed (diluted to 10 mL) on GC-MS (Thermal Trace GC Ultra with a PolarisQ ion trap mass spectrometer) with either a TR-5MS capillary column (30 m×0.25 mm×0.25 μm) and a Shimadzu GC equipped a AT-5 capillary column. Autosampler was used and split injection was performed at a split ratio of 50 using helium as carrier gas. The temperature program began with an isothermal step at 50 °C for 3 min. Then the temperature increased to 300 °C by 7 °C min⁻¹, and keep the temperature for 5 min. Identification of compounds was based on retention time and comparison mass spectrum of pure chemical.

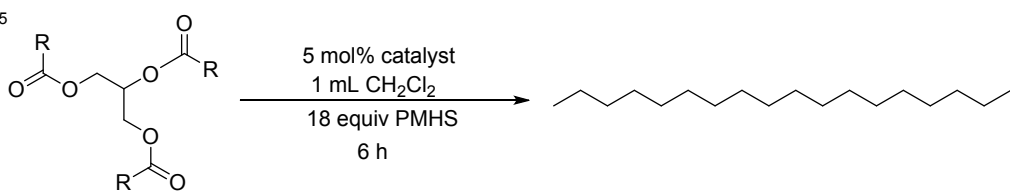
S3 Experiment Section

General Procedures. All reactions were performed using standard Schlenk-type glassware under argon. Glassware was dried 3 hours at 110°C before use. In a typical experiment, tristearin (0.1 mmol, 89.2 mg), $B(C_6F_5)_3$ (5 mol%, 2.5 mg) and anhydrous cyclohexane (1.0 mL) were added in a Schlenk tube (10 mL). Then PMHS (18.0 equiv, 110 μ L) were slowly (over 5 min) added via syringe. The mixture was stirred for 6 hours at room temperature followed by addition of triethylamine (0.1 mL) to quench the reaction. After the mixture was diluted to 10 mL, eicosane (0.3 mmol, 84.7 mg) was added as internal standard. The yield of product was analyzed by GC and GC-MS. To obtain the isolated yields, the reaction were processed under the same contions. After reaction, the mixture was diluted to 10 mL. The mixture was introduced directly onto a silica gel liquid chromatography column and purified by column chromatography using petroleum ether. Finally, solvent was removed in vacuo to obtain the pure product.

S4 Optimization of the reaction condition.

Table 1. The performances of $B(C_6F_5)_3$ and different metal Lewis acids ^a

R=C₁₇H₃₅



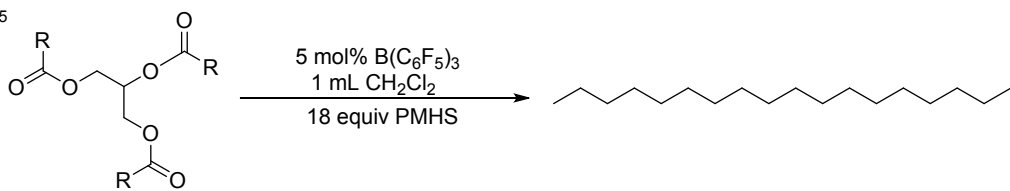
Entry	Catalyst	Time (h)	Yield (%) ^b
1	$B(C_6F_5)_3$	6	91
2	$(OTf)_2Zn(II)$	6	0
3	$(OTf)_2Zn(II)$	24	0
4	$(OTf)_2Fe(II)$	24	0
5	$AlCl_3$	24	0
6	$Fe(BF_4)_2$	24	0
7	$Fe(acac)_3$	24	0

^a Reaction conditions: Substrate 0.1 mmol, 1 atm Ar, under room temperature.

^b Determined by GC using eicosane as an internal standard.

Table 2. Optimization of reaction time ^a

R=C₁₇H₃₅



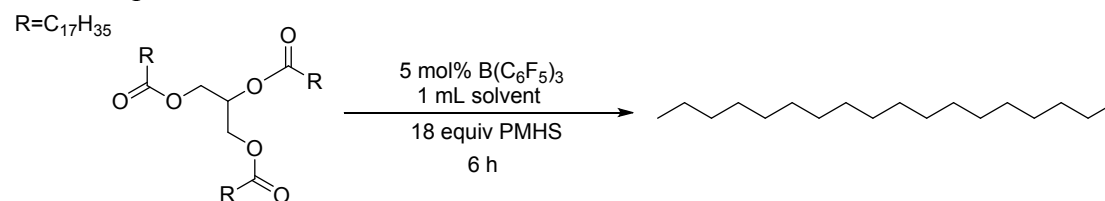
Entry	Time (h)	Yield (%) ^b
1	0.2	13
2	0.5	28

3	4	60
4	6	91
5	16	92
6	24	95

^a Reaction conditions: Substrate 0.1 mmol, 1 atm Ar, under room temperature.

^b Determined by GC using eicosane as an internal standard.

Table 3. Optimization of solvents ^a

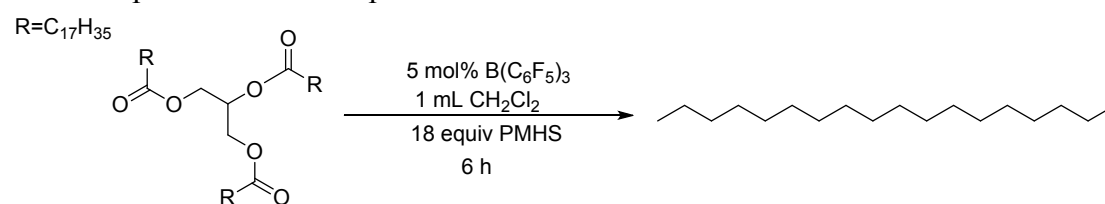


Entry	Solvent	Yield (%) ^b
1	CH ₃ CN	0
2	dioxane	5
3	DMF	0
4	DMA	0
5	DMSO	0
6	CH ₂ Cl ₂	91
7	cyclohexane	93
8	THF	0

^a Reaction conditions: Substrate 0.1 mmol, 1 atm Ar, under room temperature.

^b Determined by GC using eicosane as an internal standard.

Table 4. Optimization of temperature ^a



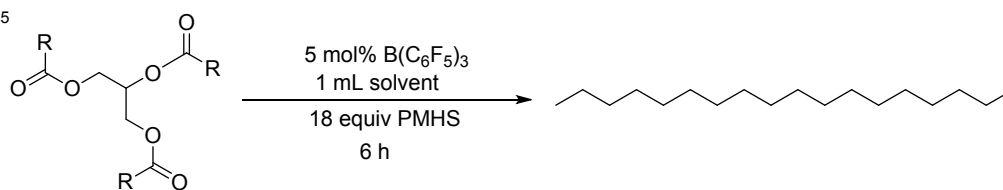
Entry	Temperature (°C)	Yield (%) ^b
1	room temperature	91
2	40	45
3	60	36
4	80	31
5	100	27

^a Reaction conditions: Substrate 0.1 mmol, 1 atm Ar.

^b Determined by GC using eicosane as an internal standard.

Table 5. The effect of water content on the reaction ^a

R=C₁₇H₃₅



Entry	Water content	Yield (%) ^b
1	5 wt.%	77
2	10 wt.%	10
3	15 wt.%	trace
4	20 wt.%	0
5	25 wt.%	0
6	30 wt.%	0

^a Reaction conditions: Substrate 0.1 mmol, 1 atm Ar, 1 mL solvent (CH₂Cl₂+H₂O).

^b Determined by GC using eicosane as an internal standard.

S5 Representative chromatogram

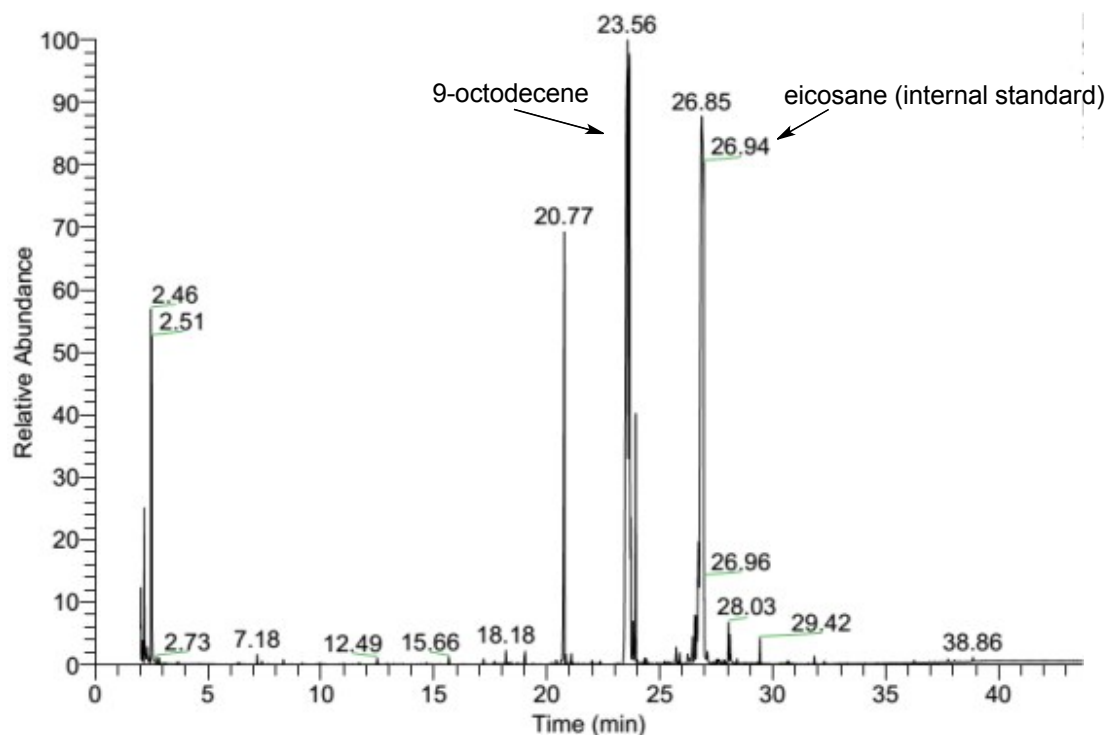


Figure S1. GC-MS analysis of the conversion of olive oil to 9-octadecene with internal standard

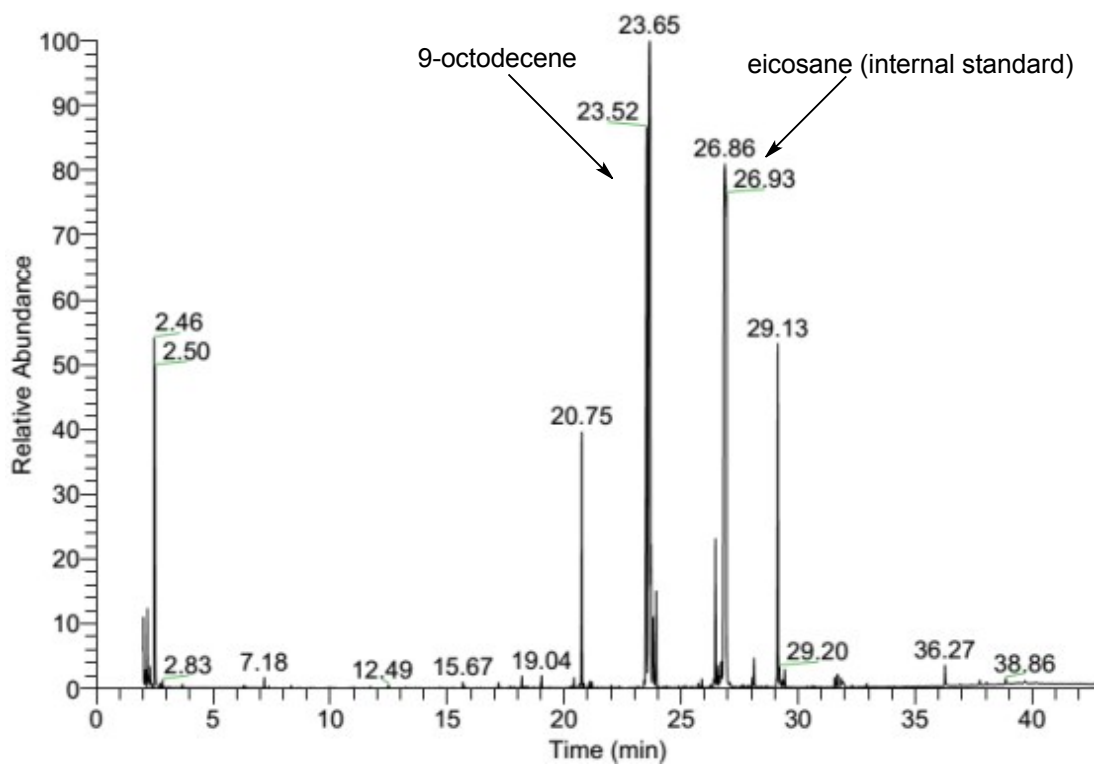


Figure S2. GC-MS analysis of the conversion of colza oil to 9-octadecene with internal standard

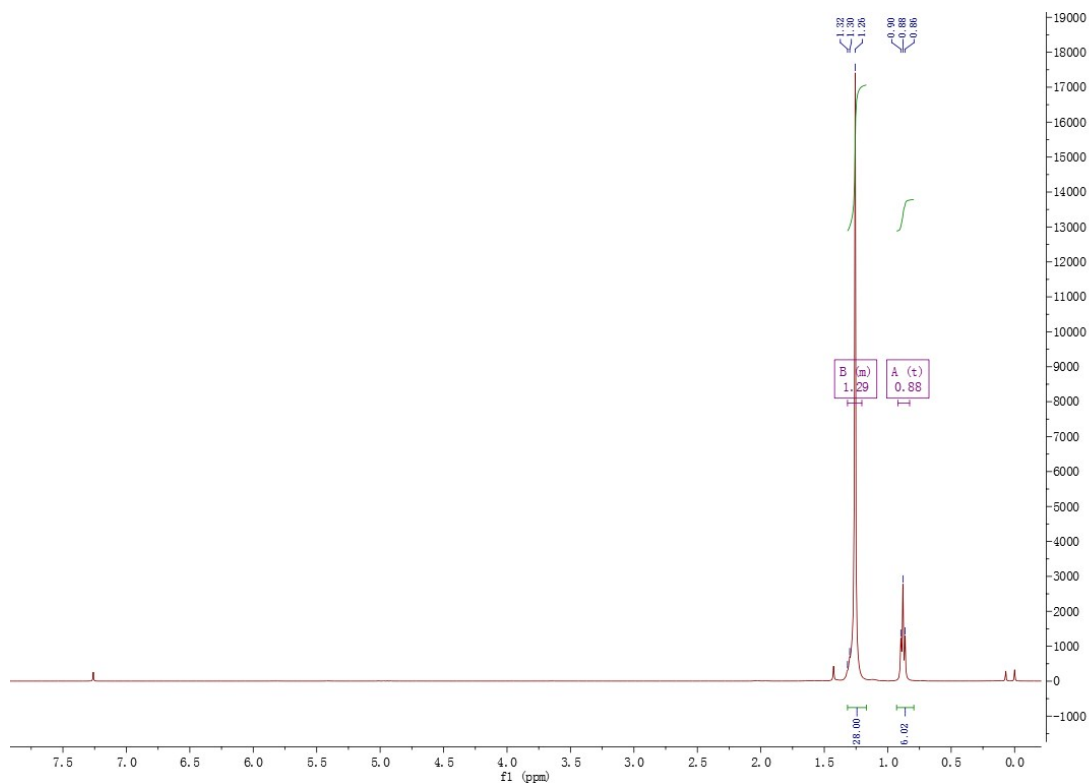


Figure S3. $^1\text{H-NMR}$ of hexadecane (C_{16}) from palmitic acid (cyclohexane as reaction solvent). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.32 - 1.20 (m, 28H), 0.88 (t, $J = 6.8$ Hz, 6H).

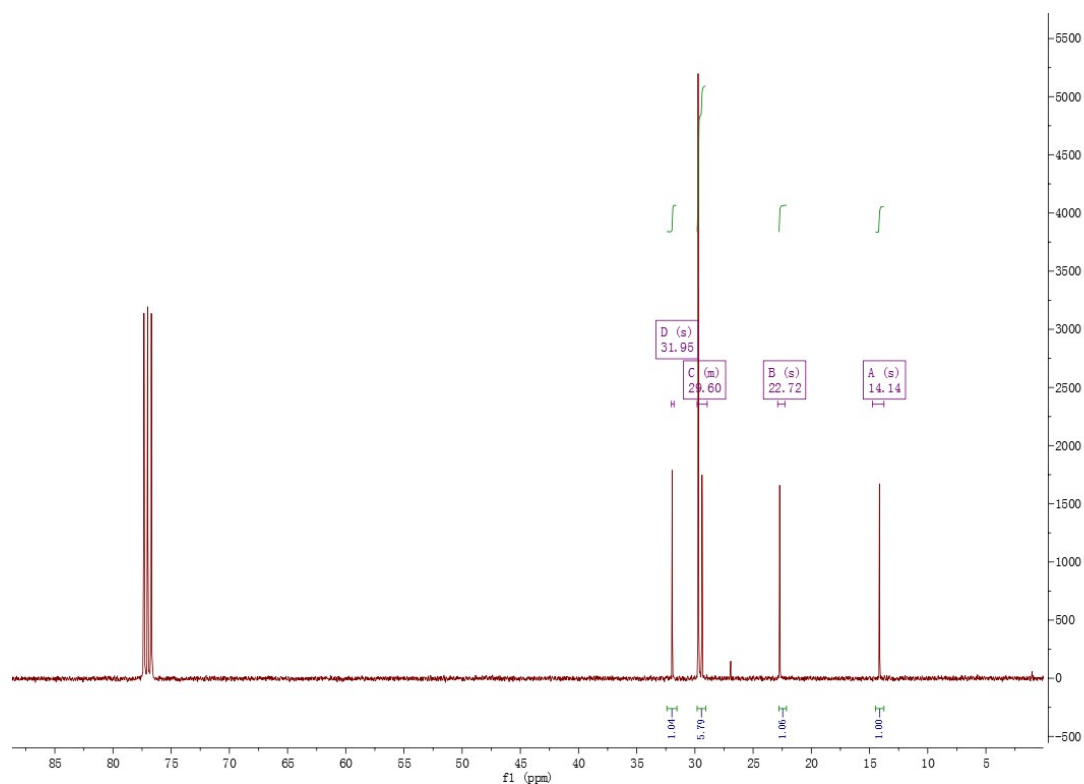


Figure S4. ^{13}C -NMR of hexadecane (C16) from palmitic acid (cyclohexane as reaction solvent). ^{13}C -NMR (101 MHz, CDCl_3) δ 31.95 (s), 29.81 - 28.95 (m), 22.72 (s), 14.14 (s).

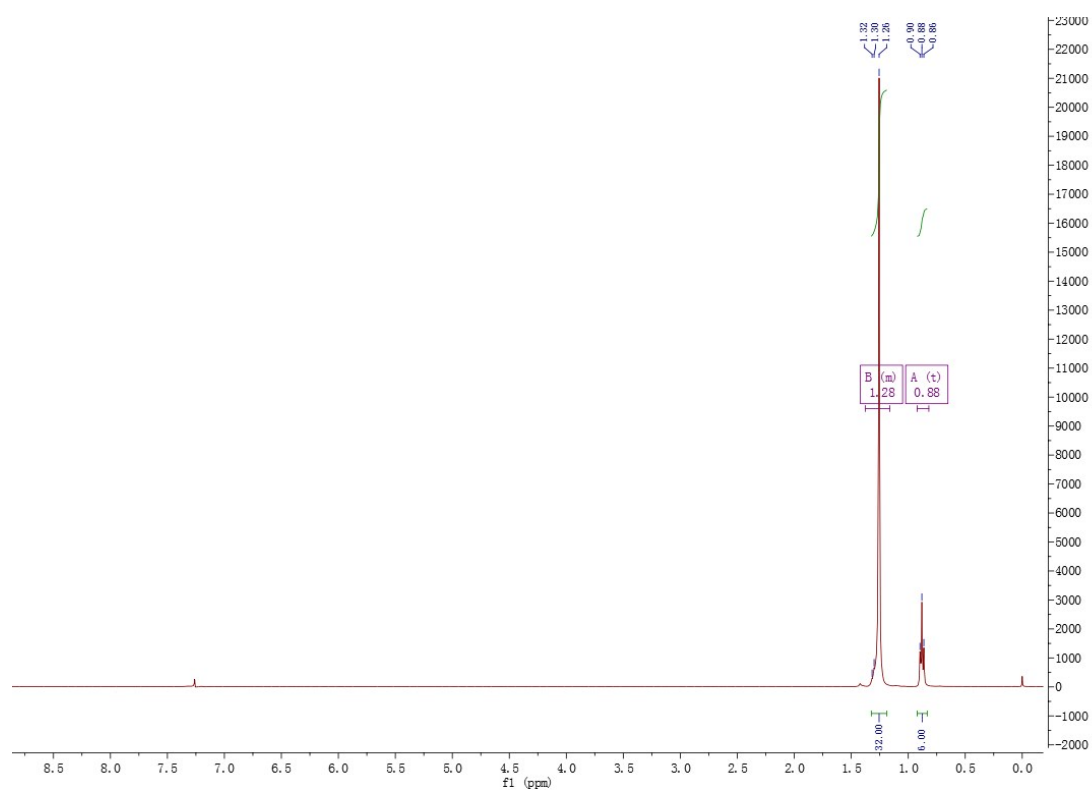


Figure S5. ^1H -NMR of octadecane (C18) from stearic acid (cyclohexane as reaction solvent). ^1H -NMR (400 MHz, CDCl_3) δ 1.38- 1.16 (m, 32H), 0.88 (t, $J = 6.8$ Hz, 6H).

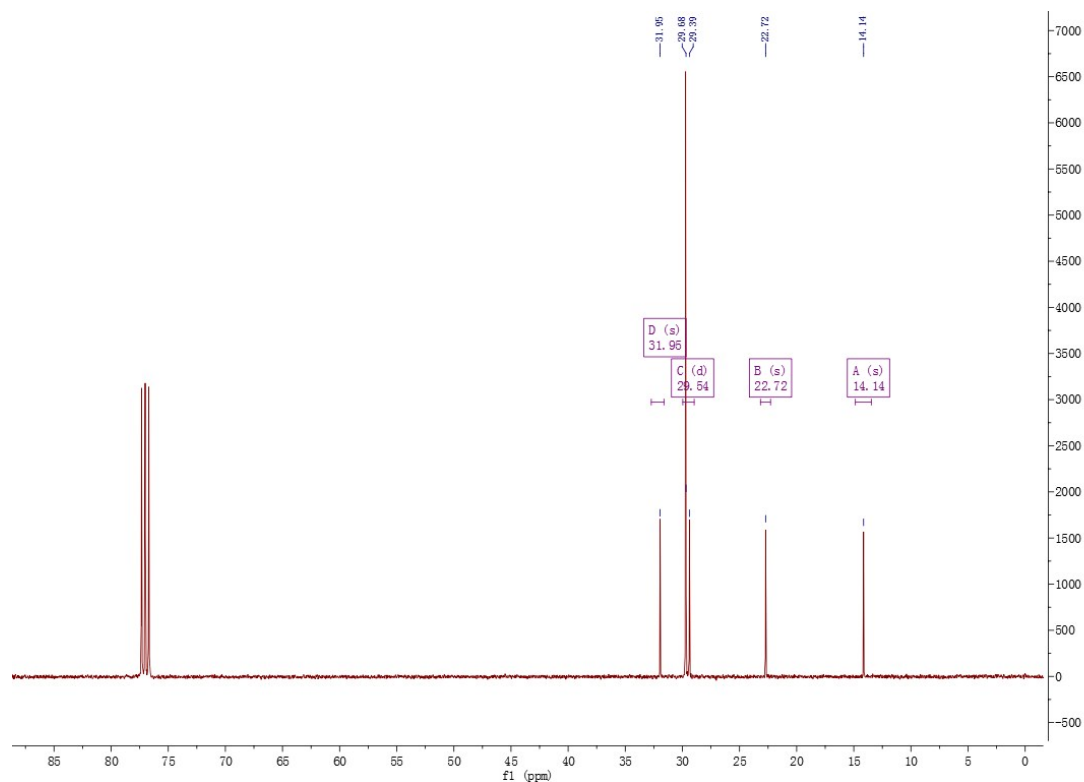


Figure S6. ^{13}C -NMR of octadecane (C18) from stearic acid (cyclohexane as reaction solvent). ^{13}C -NMR (101 MHz, CDCl_3) δ 31.95 (s), 29.54 (d, $J = 29.6$ Hz), 22.72 (s), 14.14 (s).

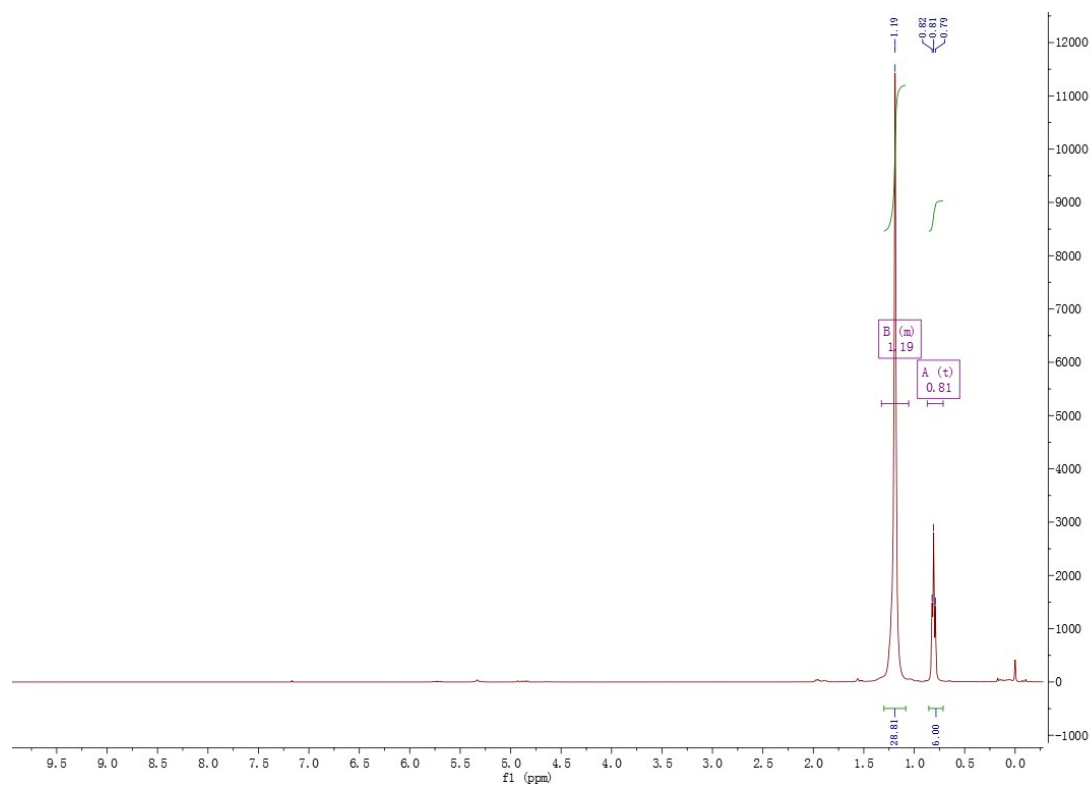


Figure S7. ^1H -NMR of hexadecane (C16) from methyl palmitate (cyclohexane as reaction solvent). ^1H -NMR (400 MHz, CDCl_3), δ 1.19 (m, 28H), 0.81 (t, $J = 6.6$ Hz, 6H).

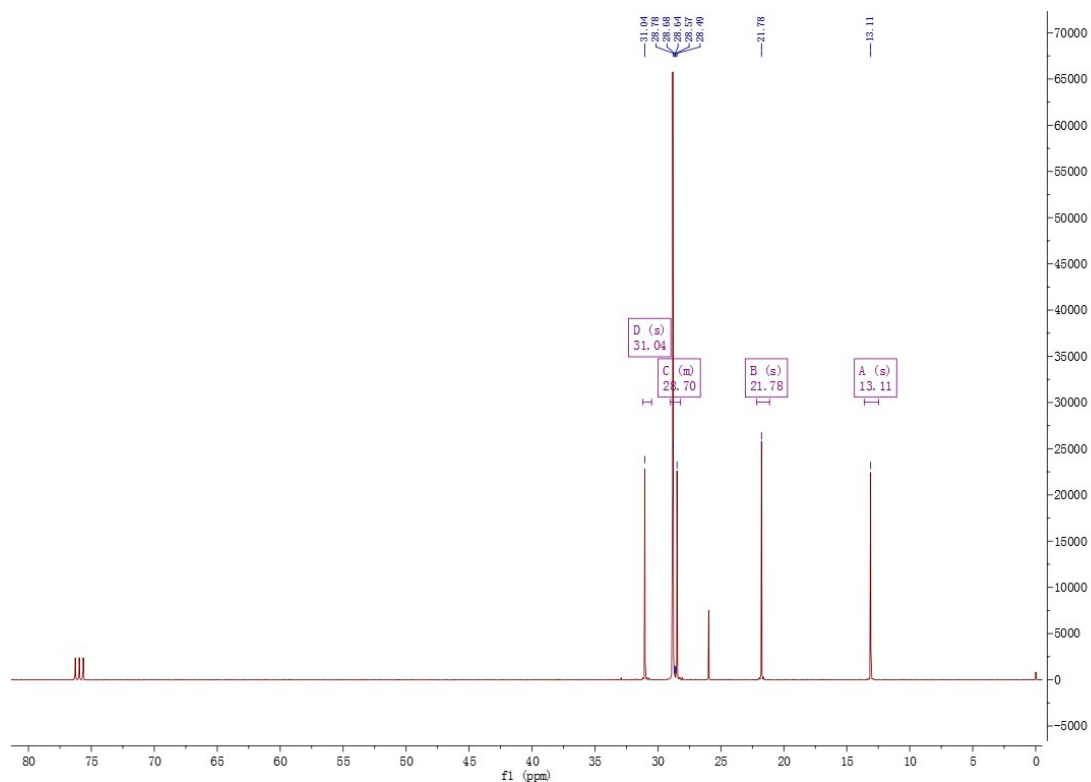


Figure S8. ¹³C-NMR of hexadecane (C₁₆) from methyl palmitate (cyclohexane as reaction solvent). ¹³C-NMR (101 MHz, CDCl₃), δ 31.04 (s), 28.78- 28.49 (m), 21.78 (s), 13.11 (s).

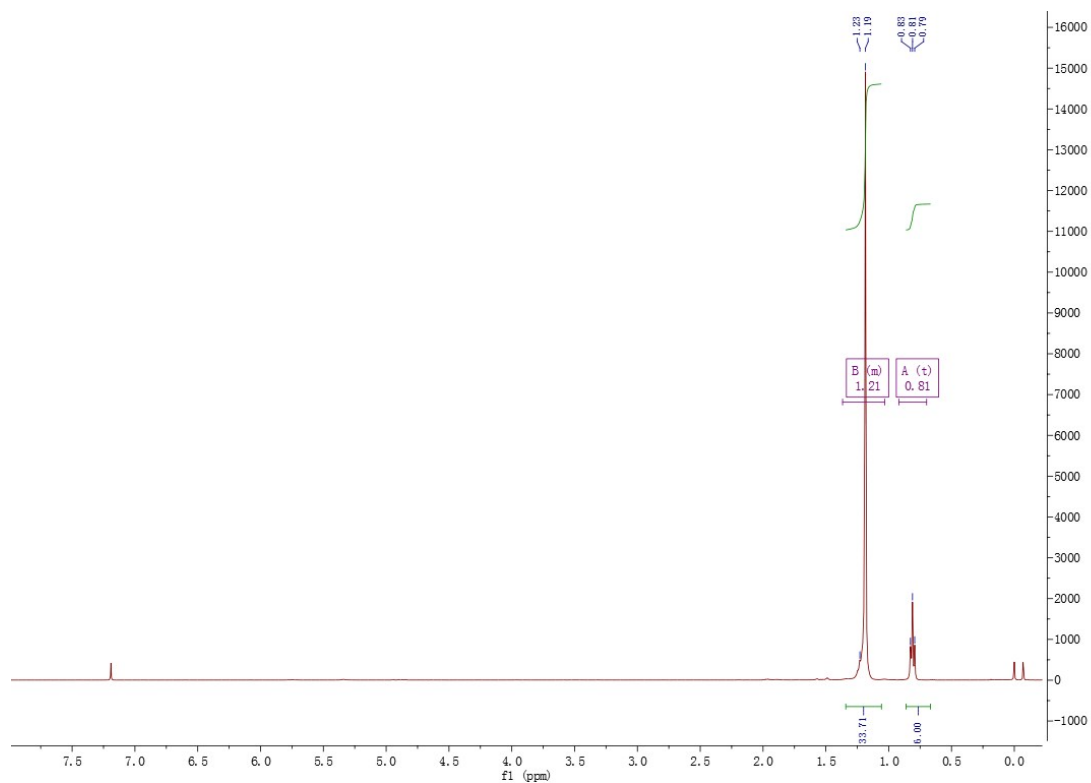


Figure S9. ¹H-NMR of octadecane (C₁₈) from methyl stearate (cyclohexane as reaction solvent). ¹H-NMR (400 MHz, CDCl₃), δ 1.37-1.03 (m, 32H), 0.81 (t, J = 6.7 Hz, 6H).

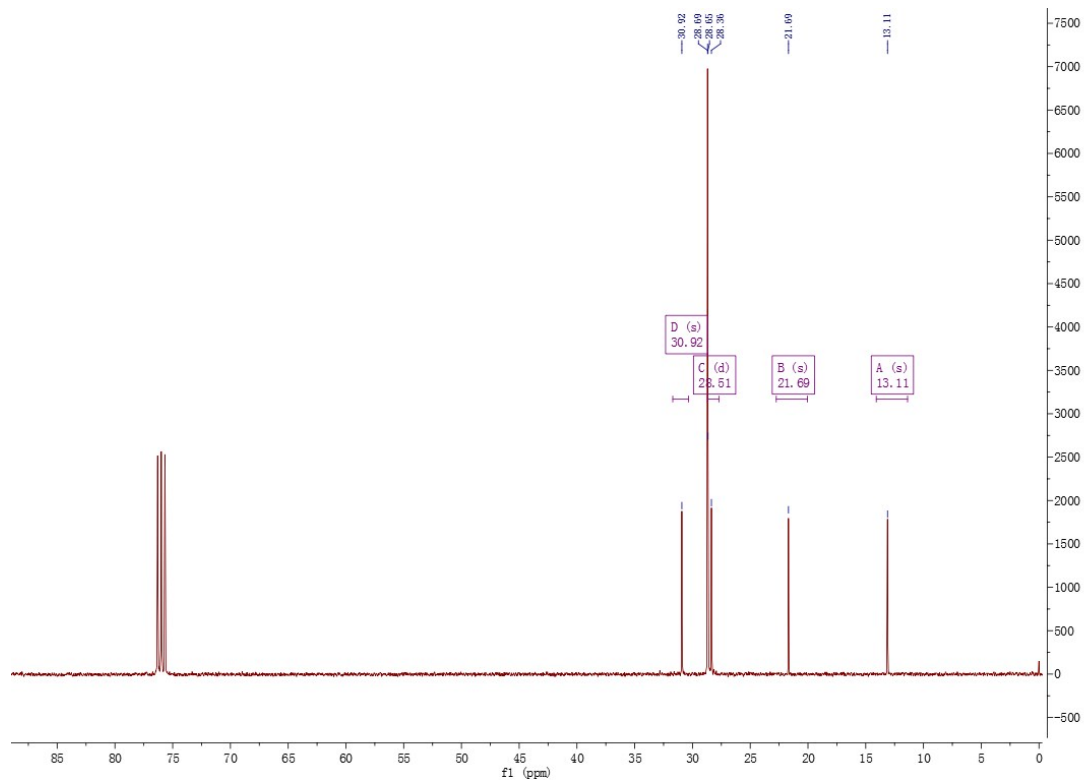


Figure S10. ^{13}C -NMR of octadecane (C18) from methyl stearate (cyclohexane as reaction solvent). ^{13}C -NMR (101 MHz, CDCl_3), δ 30.92 (s), 28.51 (m, $J = 29.6$ Hz), 21.69 (s), 13.11 (s).

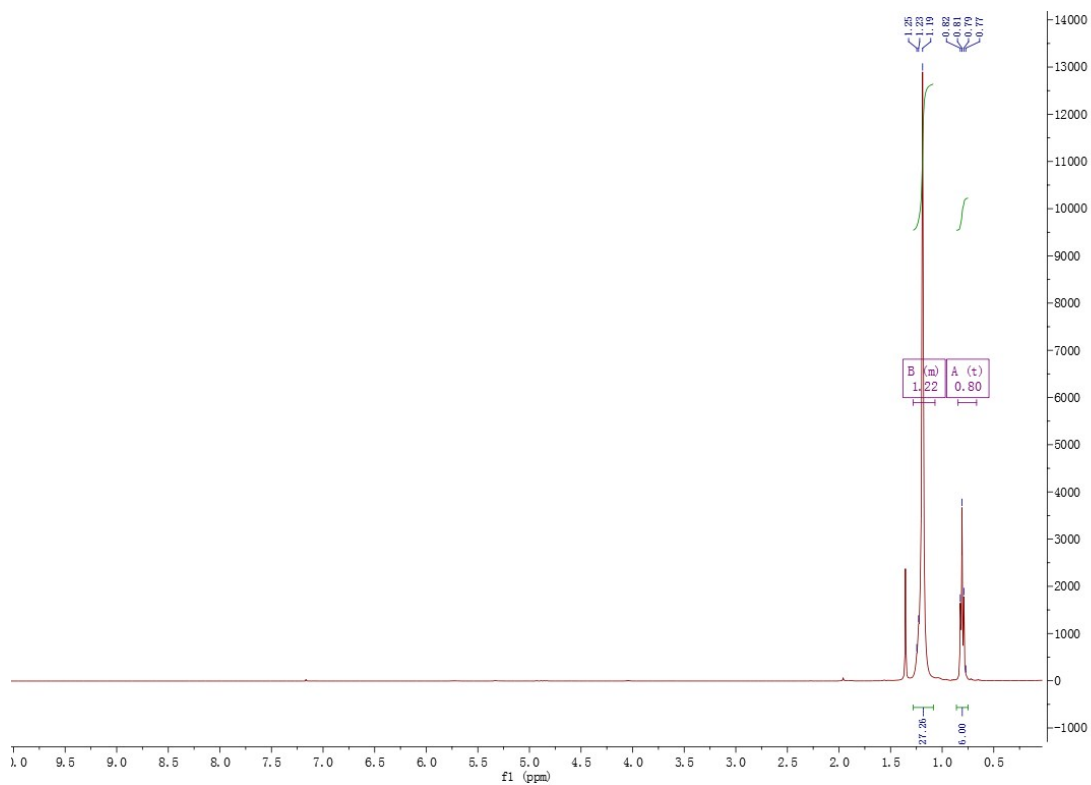


Figure S11. $^1\text{H-NMR}$ of hexadecane (C16) from palmitin (dichloromethane as reaction solvent).
 $^1\text{H-NMR}$ (400 MHz, CDCl_3), δ 1.20-1.17 (m, 28H), 0.80 (t, 6H).

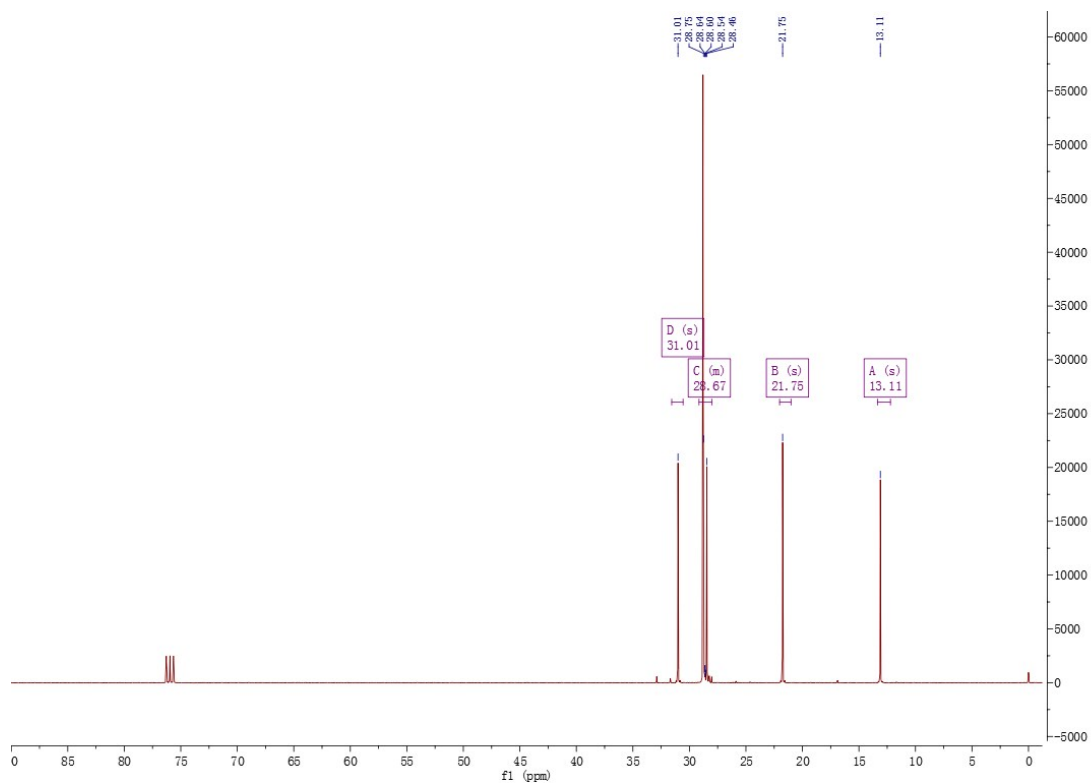


Figure S12. $^{13}\text{C-NMR}$ of hexadecane (C16) from palmitin (dichloromethane as reaction solvent).
 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3), δ 31.01 (s), 29.15- 28.00 (m), 21.75 (s), 13.11 (s).