

Electronic Supplementary Information

**Amines as Effective Ligands in Iridium-Catalyzed
Decarbonylative Dehydration of Biosourced Substrates**

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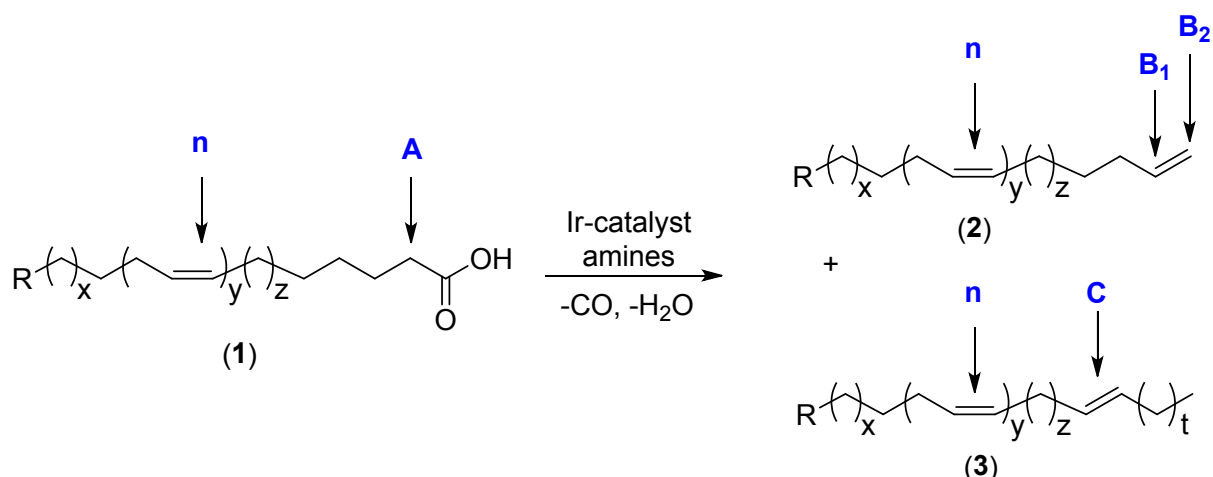
General Procedure

All reactions involving metal-amine catalysts were performed under inert atmosphere using standard Schlenk techniques. Ir precursor was purchased from Strem Chemicals and used as received. Fatty substrates were supplied by ITERG. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 spectrometer. ^1H and ^{13}C chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. SiMe_4 . Assignment of the signals was carried out using 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$) and 2D (COSY, HMBC, HMQC) NMR experiments. GLC-FID analyses were recorded on a Perkin Elmer Clarus 500 apparatus equipped with a Varian column (VF-1ms, 30m/0.25mm/0.25 μm , CP8912). All products were analyzed by GC using the same method : detector FID at 280°C; injection port temperature at 250°C; program : hold 1 min at 50°C, ramp 7°C/min to 150°C, ramp 4°C/min to 250°C and hold 10 min at 250°C. Hexadecane was used as internal standard. Transmission Electron Microscopy (TEM) images were collected on a FEI TECNAI G2-20 Twin microscope operating at 200 kV and supplied with a Bruker Energy Dispersive X-ray spectroscopy (EDX) detector. A drop of the crude reaction mixture diluted in acetone was deposited onto a carbon coated copper grid. The peaks of EDX spectra were labelled using Bruker software Esprit 1.9.

General procedure for decarbonylation-dehydration reactions. In a typical experiment, oleic acid 88% (**1**, 283 mg, 1.0 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (17 mg, 0.025 mmol), NPh_3 (36 mg, 0.15 mmol), KI (84 mg, 0.5 mmol) and a magnetic stirring bar were added under nitrogen in a test tube carousel. The test tube was evacuated and subsequently flushed several times with nitrogen. The reaction mixture was stirred at room temperature during 30 min. Then, anhydride acetic (204 mg, 2 mmol) was added and the reaction mixture was heated at 160°C for 8 hours. After the appropriate reaction time, the test tube was cooled to room

temperature and the mixture was purified by flash chromatography on silica gel (heptane) to give the corresponding olefins (78%, **2/3** = 63/37). The linear/branched (**2/3**) regioselectivity of olefins was determined by ^1H NMR spectroscopy and confirmed by GLC.

NMR determination of conversion and selectivity



For conversion: we firstly determine **C** which is the signal corresponding to CH=CH internal olefins (**Int** = total of internal alkenes in the mixture; **n** = number of substrate insaturations; **p** = substrate purity).

$$\boxed{C = \text{Int}} \quad \text{or} \quad \boxed{C = \frac{\text{Int} - A * n * p - B_2 * n * p}{n+1}}$$

saturated product unsaturated product

The conversion is determined by comparison between signal **A** (CH₂ in α-position to COOH) and signals **B₂** (CH₂ of terminal olefins) and **C** (CH=CH of internal olefins).

$$\text{Conv.(\%)} = \left[1 - \frac{A}{(A + B_2 + C)} \right] * 100$$

For selectivity:

- By NMR: comparison between signals **B₂** (CH₂ of terminal olefins) and **C** (CH=CH of internal olefins).

$$\text{Sel.(\%)} = \left[\frac{B_2}{(B_2 + C)} \right] * 100$$

- By GLC: comparison between the area of terminal product and the internal one.
- For **1e**, because of the presence of a terminal double bond:

$$\text{Sel.(\%)} = \left[\frac{B_2 - 2}{(B_2 - 2 + C)} \right] * 100$$

Table S1. Additional experiments for Ir-catalyzed decarbonylation of oleic acid.^a

Entry	Lewis acid (mol%)	Ligand (mol%)	Temp. (°C)	Time (h)	Conv. (%) ^b	Selectivity 2/3 ^b
1	-	-	240	12	<5	-
2^c	-	NPh ₃ (15)	200	4	< 5	-
3^{c,d}	-	NPh ₃ (15)	200	4	< 5	-
4	AlCl ₃ (50)	NPh ₃ (15)	200	4	< 5	-
5	B(C ₆ F ₅) ₃ (5)	NPh ₃ (15)	200	4	< 5	-
6	B(C ₆ F ₅) ₃ (5)	NPh ₃ (15)	200	20	< 5	-
7^c	B(C ₆ F ₅) ₃ (5)	NPh ₃ (15)	200	4	< 5	-

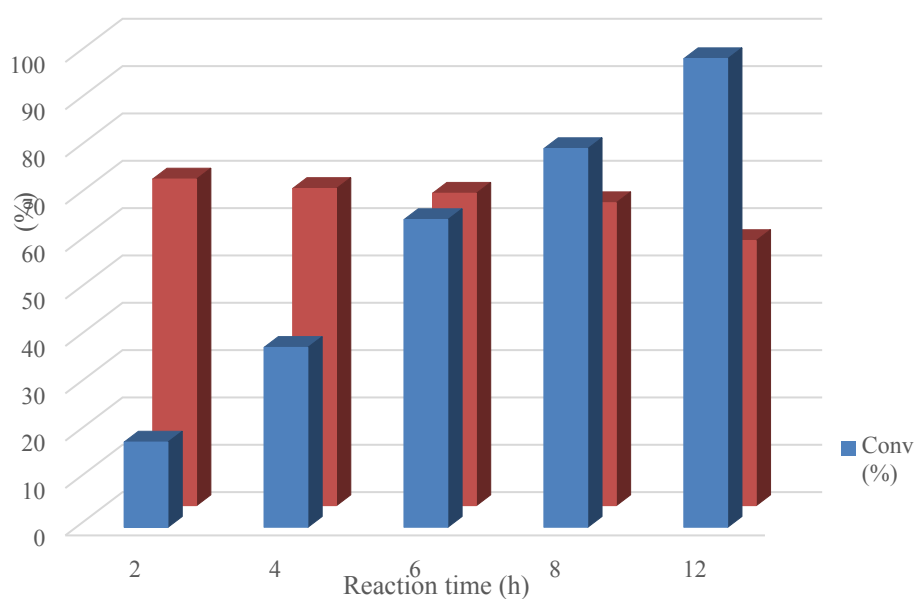
^aConditions: Oleic acid **1a** 88 wt% (2 mmol), [Ir(COD)Cl]₂ (0.050 mmol), KI (1 mmol).

^bConversions and selectivity determined by ¹H NMR. ^cunder vacuum. ^dzeolite Na-Y (CAS: 1318-02-1; SiO₂/Al₂O₃ Mole Ratio: 5.1; Nominal Cation Form: Sodium Unit Cell Size, A: 24.65; Surface Area, m²/g: 900): 70 mg.

Note that decarbonylation reaction could not be implemented without acetic anhydride. Very low conversions were obtained in that case, even at high reaction temperature (240 °C, entry 1). TEM images recorded from the crude reaction solution showed Ir-nanoparticles (Figure S22). According to entry 1, Ir nanoparticles could not catalyze the reaction. Hence, amines were required to stabilize the catalytic system.

Table S2. Variation of conversion and **2a/3a** selectivity over time in decarbonylation of oleic acid (**1a**) catalyzed by Ir-Amine system.^a

Time (h)	Conv (%) ^b	2a/3a Sel (%) ^b
2	18	69
4	38	67
6	65	66
8	80	64
12	99	56



^a Reaction conditions: **1a** 88 wt% (1.0 mmol), [Ir(COD)Cl]₂ (2.5 mol%), *N,N'*-TetraMePD (15 mol%), KI (0.5 mmol), acetic anhydride (2 mmol).^b Determined by ¹H NMR spectroscopy.

(Z)-heptadeca-1,8-diene from Oleic acid 88% (1a): Obtained as an inseparable mixture (**2a/3a**); colorless oil. Some other by-products were observed resulting from other fatty acids present in the technical grade starting material. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **2a**: δ 5.92-5.75 (m, 1H, $\text{CH}=\text{CH}_2$), 5.42-5.26 (m, 2H, $\text{CH}=\text{CH}$), 5.07-4.90 (m, 2H, $\text{CH}=\text{CH}_2$), 2.18-1.91 (m, 6H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.48-1.15 (m, 18H, CH_2), 0.88 ppm (t, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **2a**: δ 139.1, 130.0, 129.7, 114.1, 33.8, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 28.9, 28.8, 27.0, 27.1, 22.7, 14.1. ppm ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **3a**: 5.52-5.26 (m, 4H, $\text{CH}=\text{CH}$), 2.18-1.91 (m, 6H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.65 (d, 3H, $J = 5.3$ Hz, $\text{CH}_3-\text{CH}=\text{CH}$), 1.48-1.15 (m, 16H, CH_2), 0.88 ppm (t, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **3a**: δ 131.6, 130.0, 129.8, 124.6, 33.8, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 28.9, 27.0, 27.1, 22.7, 17.9, 14.1. ppm

1-Heptadecene from Stearic acid 98% (1b): Obtained as an inseparable mixture (**2b/3b**); colorless oil. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **2b**: δ 5.90-5.74 (m, 1H, $\text{CH}=\text{CH}_2$), 5.05-4.88 (m, 2H, $\text{CH}=\text{CH}_2$), 2.12-2.02 (m, 2H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.45-1.18 (m, 26H, CH_2), 0.89 ppm (t, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **2b**: δ 139.1, 114.2, 33.9, 32.0, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0, 22.7, 14.1 ppm. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **3b**: δ 5.50-5.30 (m, 2H, $\text{CH}=\text{CH}$), 2.12-2.02 (m, 2H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.67 (d, 3H, $J = 5.3$ Hz, $\text{CH}_3-\text{CH}=\text{CH}$), 1.45-1.18 (m, 24H, CH_2), 0.89 ppm (t, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **3b**: δ 131.5, 124.7, 33.9, 32.0, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 22.7, 17.9, 14.1 ppm.

(8Z, 11Z, 14Z)-heptadeca-1,8,11,14-tetraene from Linolenic acid 47% (1c): Obtained as an inseparable mixture (**2c/3c**); colorless oil. Some other by-products were observed resulting from other fatty acids present in the technical grade starting material. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **2c**: δ 5.93-5.75 (m, 1H, $\text{CH}=\text{CH}_2$), 5.58-5.23 (m, 6H, $\text{CH}=\text{CH}$), 5.08-4.90 (m, 2H, $\text{CH}=\text{CH}_2$), 2.89-2.68 (m, 4H, $=\text{C}-\text{CH}_2-\text{C}=\text{C}$), 2.21-1.91 (m, 6H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.50-1.21 (m, 6H, CH_2), 0.92 ppm (t, $J = 7.5$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **2c**: δ 139.0, 131.8, 130.1, 128.3, 128.2, 127.7, 127.1, 114.1, 33.7, 29.5, 28.8, 28.7, 27.1, 25.6, 25.5, 20.5, 14.2 ppm. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **3c**: δ 5.55-5.23 (m, 8H, $\text{CH}=\text{CH}$), 2.89-2.68 (m, 4H, $=\text{C}-\text{CH}_2-\text{C}=\text{C}$), 2.21-1.91 (m, 4H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.54 (d, 3H, $J = 5.3$ Hz, $\text{CH}_3-\text{CH}=\text{CH}$), 1.50-1.21 (m, 4H, CH_2), 0.92 ppm (t, $J = 7.5$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **3c**: δ 132.0, 131.8, 130.1, 128.8, 128.5, 128.2, 127.7, 125.1, 33.7, 29.6, 29.5, 27.9, 25.6, 25.5, 20.5, 17.6, 14.2 ppm.

(Z)-Pentacos-1,12-diene from Erucic acid 87% (1d): Obtained as an inseparable mixture (**2d/3d**); colorless oil. Some other by-products were observed resulting from other fatty acids present in the technical grade starting material. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **2d**: δ 5.90-5.72 (m, 1H, $\text{CH}=\text{CH}_2$), 5.41-5.28 (m, 2H, $\text{CH}=\text{CH}$), 5.06-4.90 (m, 2H, $\text{CH}=\text{CH}_2$), 2.14-1.92 (m, 6H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.45-1.18 (m, 26H, CH_2), 0.89 ppm (t, $J = 6.6$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz, 23 °C) of **2d**: δ 139.3, 130.0, 129.9, 114.2, 33.9, 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.9, 27.2, 22.8, 14.2 ppm. ^1H NMR (CDCl_3 , 300 MHz, 23 °C) of **3d**: 5.46-5.28 (m, 4H, $\text{CH}=\text{CH}$), 2.14-1.92 (m, 6H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.68 (d, 3H, $J = 5.3$ Hz, $\text{CH}_3-\text{CH}=\text{CH}$), 1.45-1.18 (m, 24H, CH_2), 0.89 ppm (t, $J = 6.6$ Hz, 3H, CH_3). ^{13}C NMR

(CDCl₃, 75 MHz, 23 °C) of **3d**: δ 131.7, 130.0, 129.9, 124.6, 33.9, 32.7, 32.0, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.9, 22.8, 18.0, 14.2 ppm.

Deca-1,9-diene issued from Undecylenic acid 98% (1e): Obtained as an inseparable mixture (**2e/3e**); colorless oil. ¹H NMR (CDCl₃, 300 MHz, 23 °C) of **2e**: δ 5.96-5.78 (m, 2H, CH=CH₂), 5.09-4.98 (m, 4H, CH=CH₂), 2.21-1.99 (m, 4H, CH₂-CH=CH), 1.57-1.31 ppm (m, 8H, CH₂). ¹³C NMR (CDCl₃, 75 MHz, 23 °C) of **2e**: δ 139.3, 114.2, 33.8, 29.6, 29.5 ppm. ¹H NMR (CDCl₃, 300 MHz, 23 °C) of **3e**: δ 5.96-5.78 (m, 1H, CH=CH₂), 5.52-5.28 (m, 2H, CH=CH), 5.09-4.98 (m, 2H, CH=CH₂), 2.21-1.99 (m, 4H, CH₂-CH=CH), 1.65 (d, 3H, *J* = 5.3 Hz, CH₃-C=C), 1.57-1.31 ppm (m, 6H, CH₂). ¹³C NMR (CDCl₃, 75 MHz, 23 °C) of **3e**: δ 139.1, 130.4, 124.8, 114.2, 33.8, 32.7, 29.6, 29.5, 28.7, 17.6 ppm.

Diene issued from Pripol 1012 98% (1f): Obtained as an inseparable mixture (**2f/3f**); colorless oil. ¹H NMR (CDCl₃, 300 MHz, 23 °C) of **2f**: δ 5.96-5.74 (m, 2H, CH=CH₂), 5.09-4.92 (m, 4H, CH=CH₂), 2.14-1.92 (m, 4H, CH₂-CH=CH), 2.02-1.89 (m, 2H, CH), 1.49-1.04 (m, 50H, CH₂), 0.91 ppm (t, *J* = 6.6 Hz, 6H, CH₃). ¹³C NMR (CDCl₃, 75 MHz, 23 °C) of **2f**: δ 139.2 (2*H₂C=CH), 114.1 (2*H₂C=CH), 37.1, 35.3, 33.9, 33.8, 31.9, 31.9, 30.2, 30.0, 29.9, 29.9, 29.8, 29.6, 29.3, 29.3, 29.2, 29.1, 29.0, 29.0, 28.9, 28.7, 27.8, 27.8, 27.7, 27.7, 22.7 (2*CH₂-CH₃), 14.1 (2*CH₃) ppm. ¹H NMR (CDCl₃, 300 MHz, 23 °C) of **3f**: δ 5.62-5.22 (m, 4H, CH=CH₂), 2.14-1.92 (m, 4H, CH₂-CH=CH), 2.02-1.89 (m, 2H, CH), 1.75-1.50 (d, 6H, *J* = 5.3 Hz, CH₃-CH=CH), 1.49-1.04 (m, 44H, CH₂), 0.91 ppm (t, *J* = 6.6 Hz, 12H, CH₃). ¹³C NMR (CDCl₃, 75 MHz, 23 °C) of **3f**: δ 131.7, 130.9, 124.5, 123.6, 37.1, 35.3, 33.9, 33.8, 31.9, 31.9, 30.2, 30.0, 29.9, 29.9, 29.8, 29.6, 29.3, 29.3, 29.2, 29.1, 29.0, 29.0, 28.9, 28.7, 27.8, 27.8, 27.7, 27.7, 22.7 (2*CH₂-CH₃), 17.6 (2*CH₃-C=C), 14.1 (2*CH₃) ppm.

NMR spectroscopy

Figure S1. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of oleic acid 88% (**1a**).

Figure S2. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2a**, 61%) and internal (**3a**, 39%) olefins derived from oleic acid 88%.

Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2a**, 61%) and internal (**3a**, 39%) olefins derived from oleic acid 88%.

Figure S4. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of stearic acid 98% (**1b**).

Figure S5. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2b**, 60%) and internal (**3b**, 40%) olefins derived from stearic acid 98%.

Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2b**, 60%) and internal (**3b**, 40%) olefins derived from stearic acid 98%.

Figure S7. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of linolenic acid 47% (**1c**).

Figure S8. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2c**, 62%) and internal (**3c**, 38%) olefins derived from linolenic acid 47%.

Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2c**, 62%) and internal (**3c**, 38%) olefins derived from linolenic acid 47%.

Figure S10. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of erucic acid 87% (**1d**).

Figure S11. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2d**, 55%) and internal (**3d**, 45%) olefins derived from erucic acid 87%.

Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2d**, 55%) and internal (**3d**, 45%) olefins derived from erucic acid 87%.

Figure S13. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of undecylenic acid 98% (**1e**).

Figure S14. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2e**, 55%) and internal (**3e**, 45%) olefins derived from undecylenic acid 98%.

Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2e**, 55%) and internal (**3e**, 45%) olefins derived from undecylenic acid 98%.

Figure S16. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of Pripol 1012 98% (**1f**).

Figure S17. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2f**, 53%) and internal (**3f**, 47%) olefins derived from Pripol 1012 98%.

Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of terminal (**2f**, 53%) and internal (**3f**, 47%) olefins derived from Pripol 1012 98%.

Figure S1. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of oleic acid 88% (**1a**).

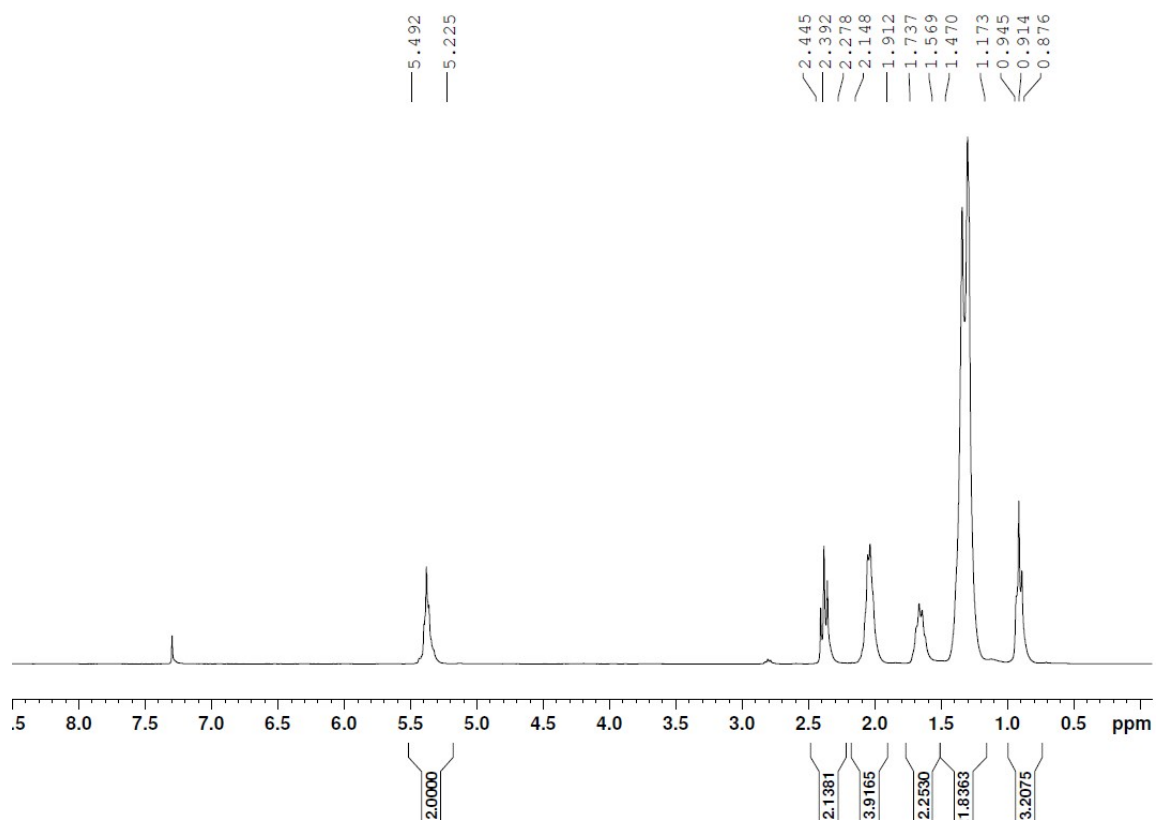


Figure S2. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of the terminal (**2a**, 61%) and internal (**3a**, 39%) olefins derived from oleic acid 88%.

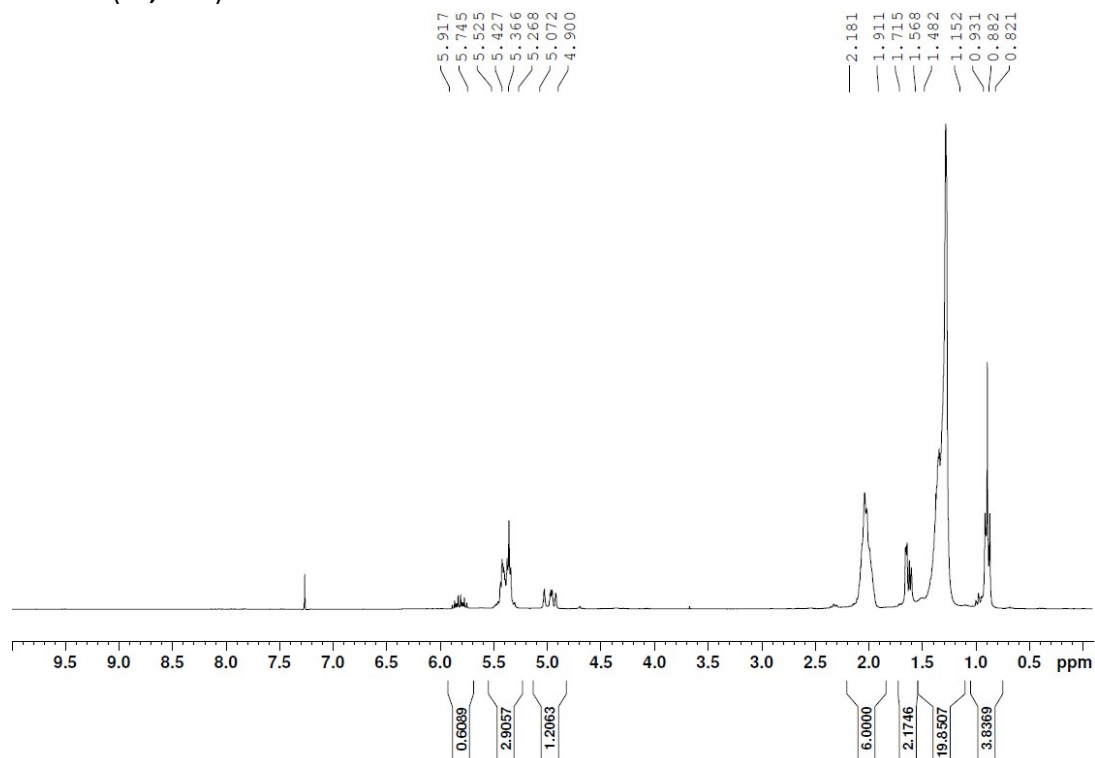


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C, AE952JT) of a mixture of the terminal (**2a**, 61%) and internal (**3a**, 39%) olefins derived from oleic acid 88%.

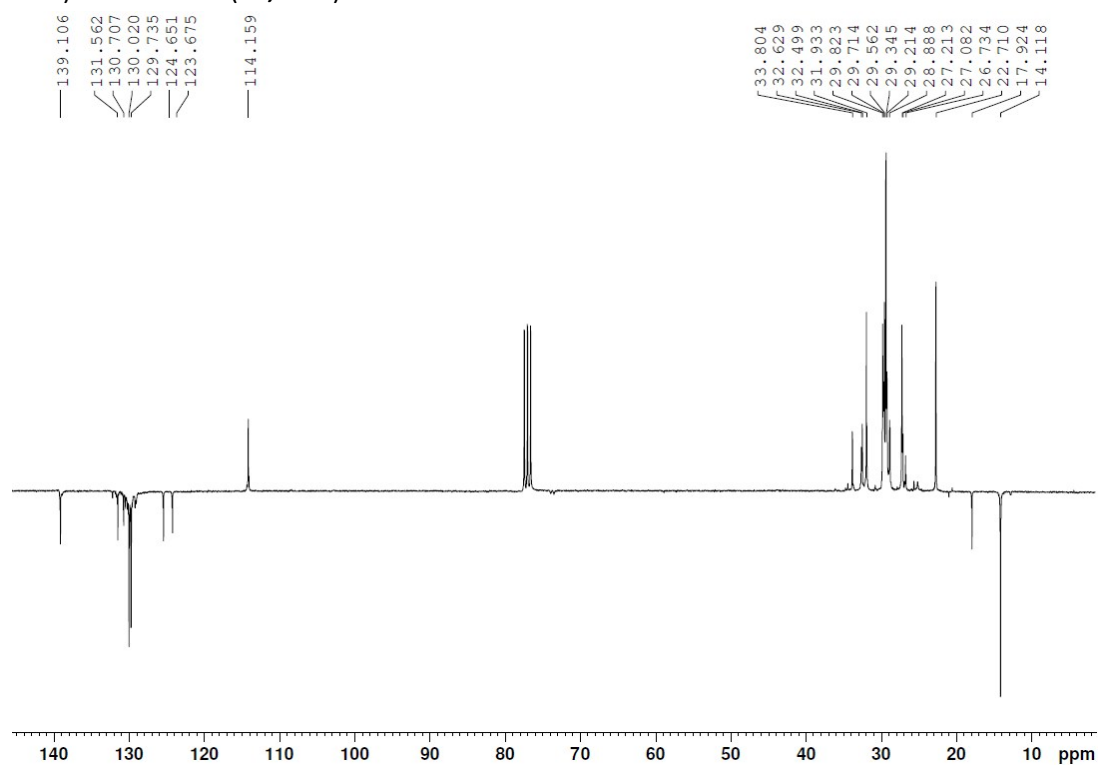


Figure S4. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of stearic acid 98% (**1b**).

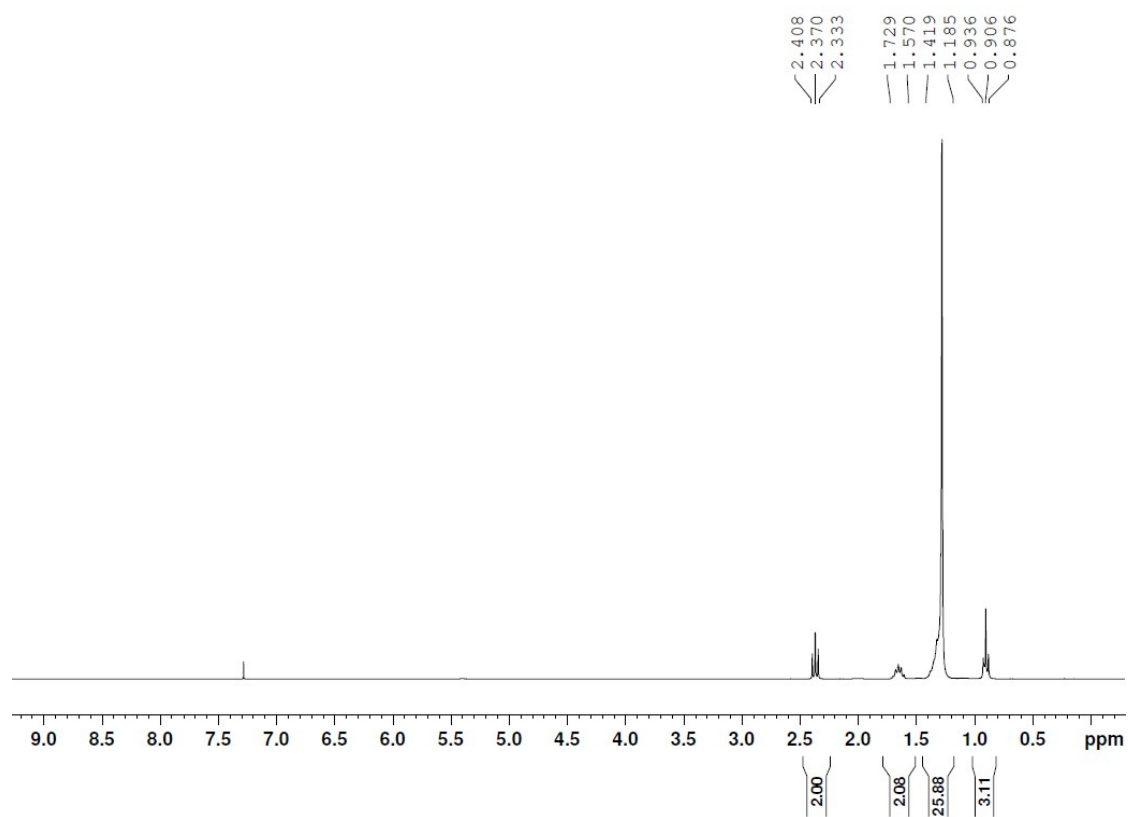


Figure S5. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of a mixture of the terminal (**2b**, 60%) and internal (**3b**, 40%) olefins derived from stearic acid 98%.

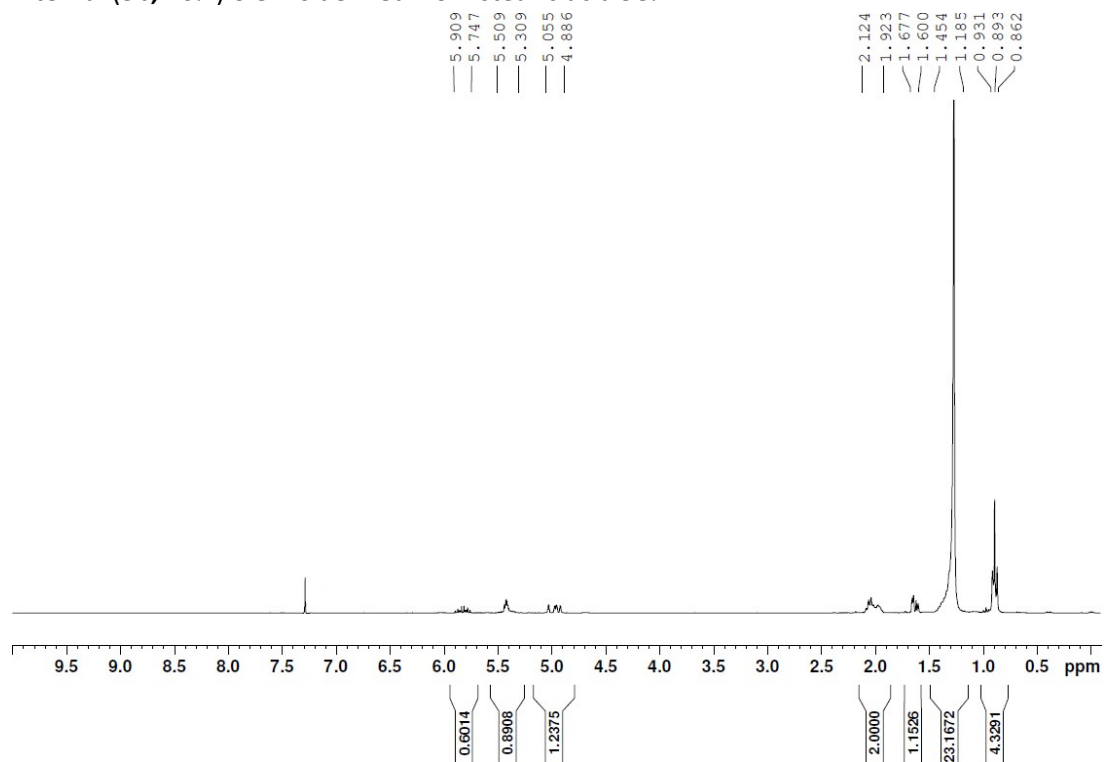


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of the terminal (**2b**, 60%) and internal (**3b**, 40%) olefins derived from stearic acid 98%.

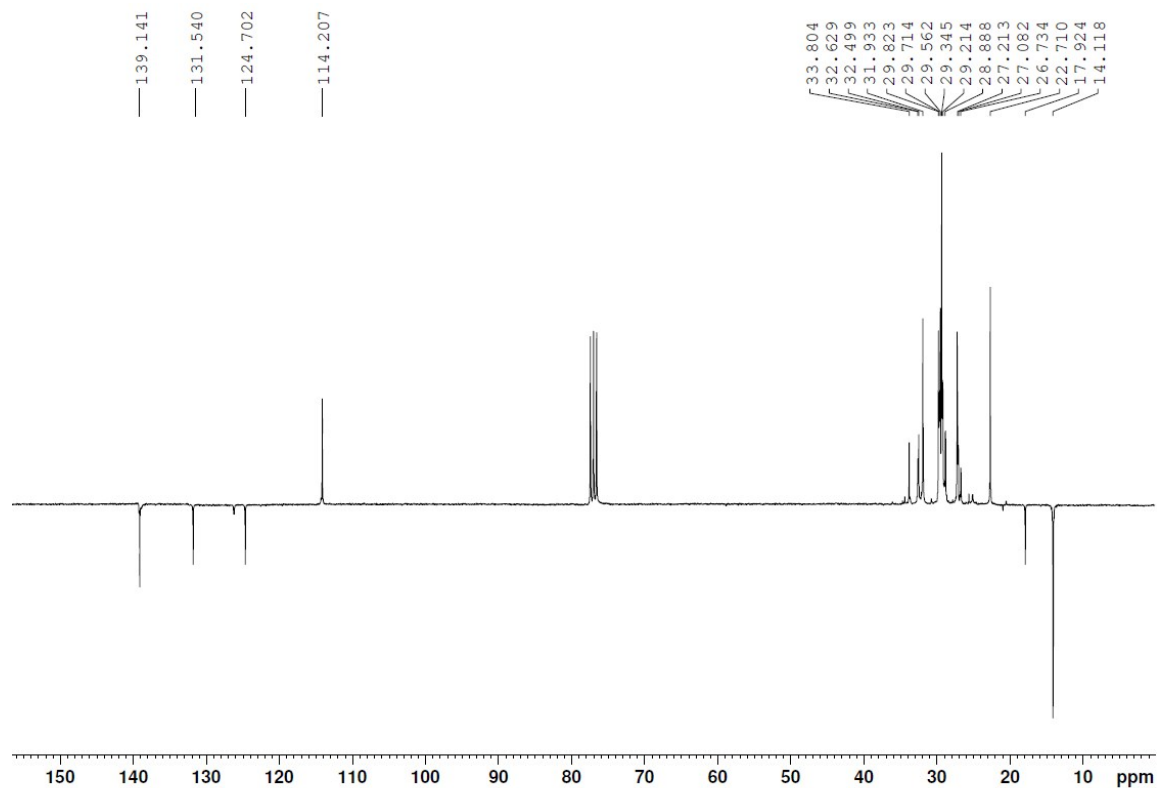


Figure S7. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of linolenic acid 47% (**1c**).

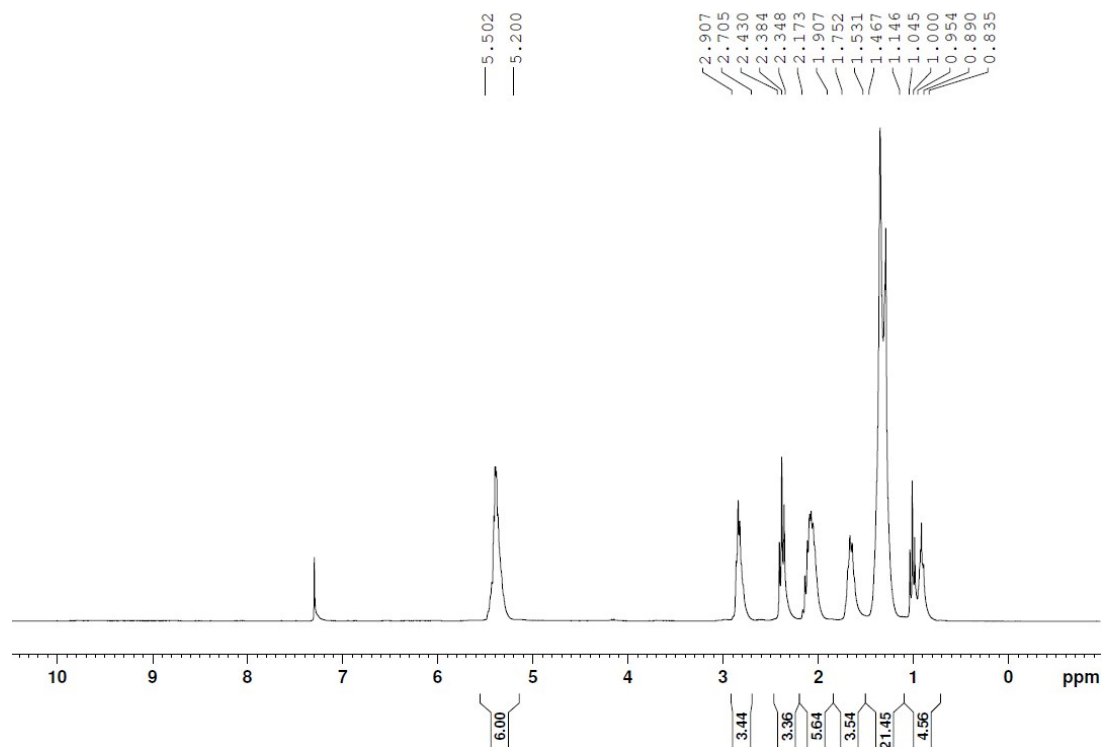


Figure S8. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2c**, 62%) and internal (**3c**, 38%) olefins derived from linolenic acid 47%.

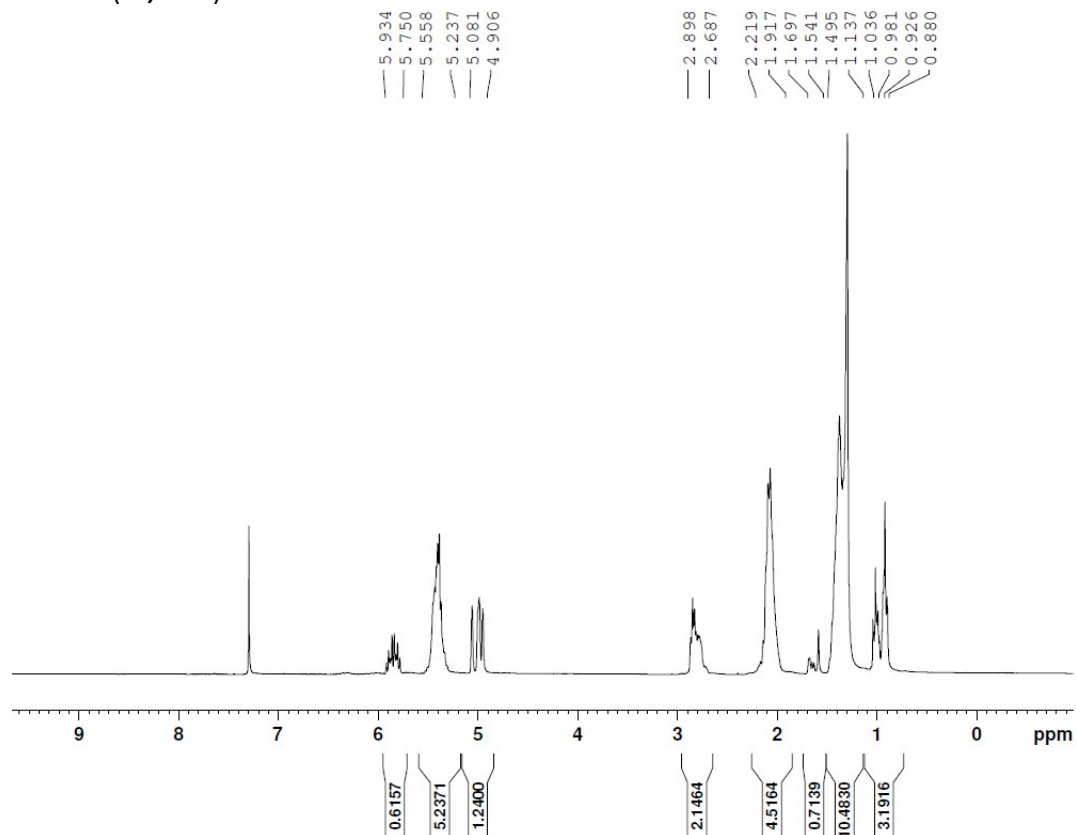


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2c**, 62%) and internal (**3c**, 38%) olefins derived from linolenic acid 47%.

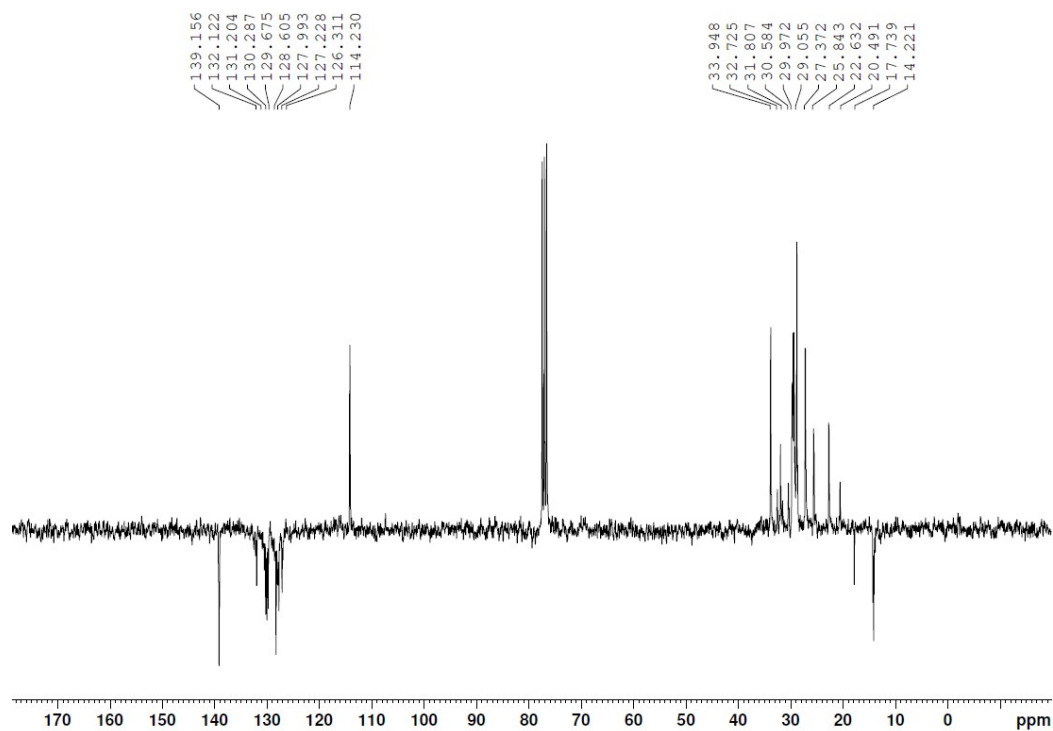


Figure S10. ^{13}C NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of erucic acid 87% (**1d**).

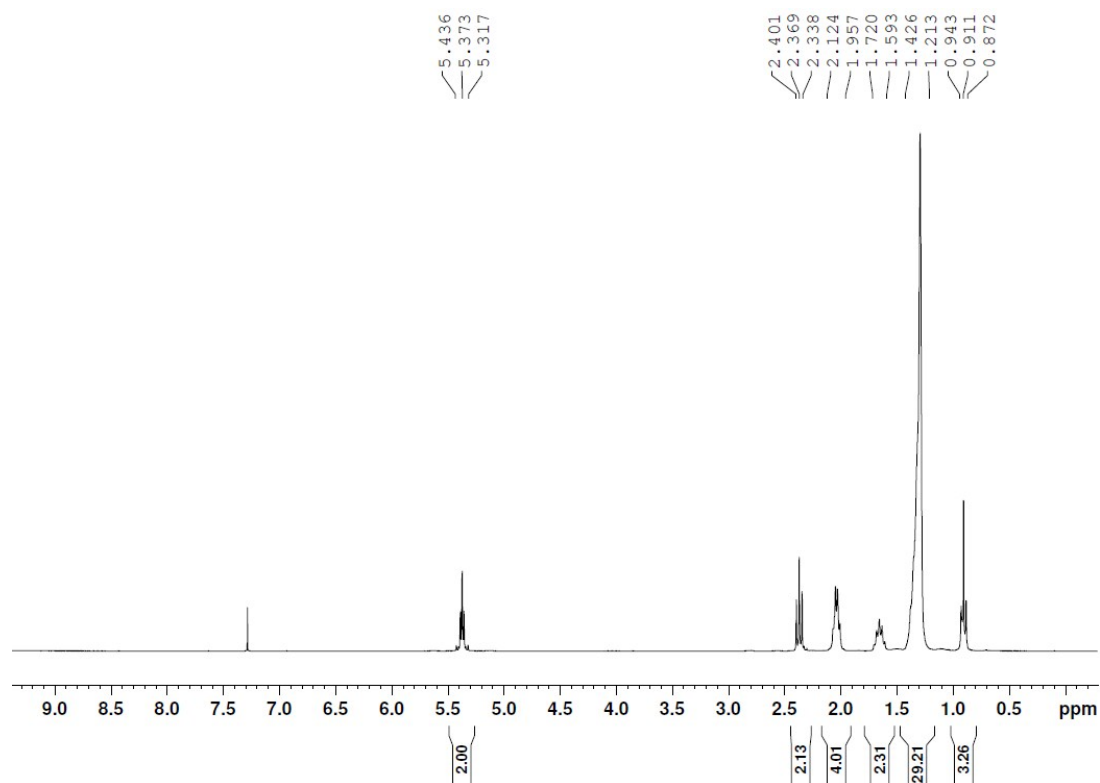


Figure S11. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2d**, 55%) and internal (**3d**, 45%) olefins derived from erucic acid 87%.

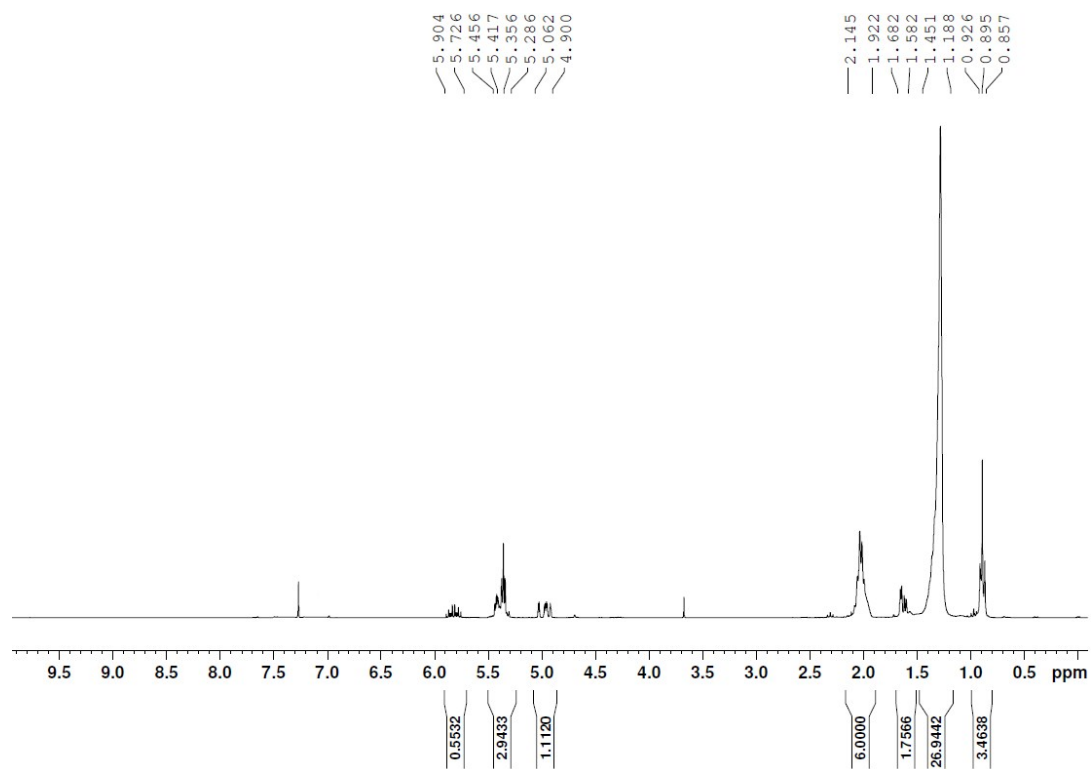


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of the terminal (**2d**, 55%) and internal (**3d**, 45%) olefins derived from erucic acid 87%.

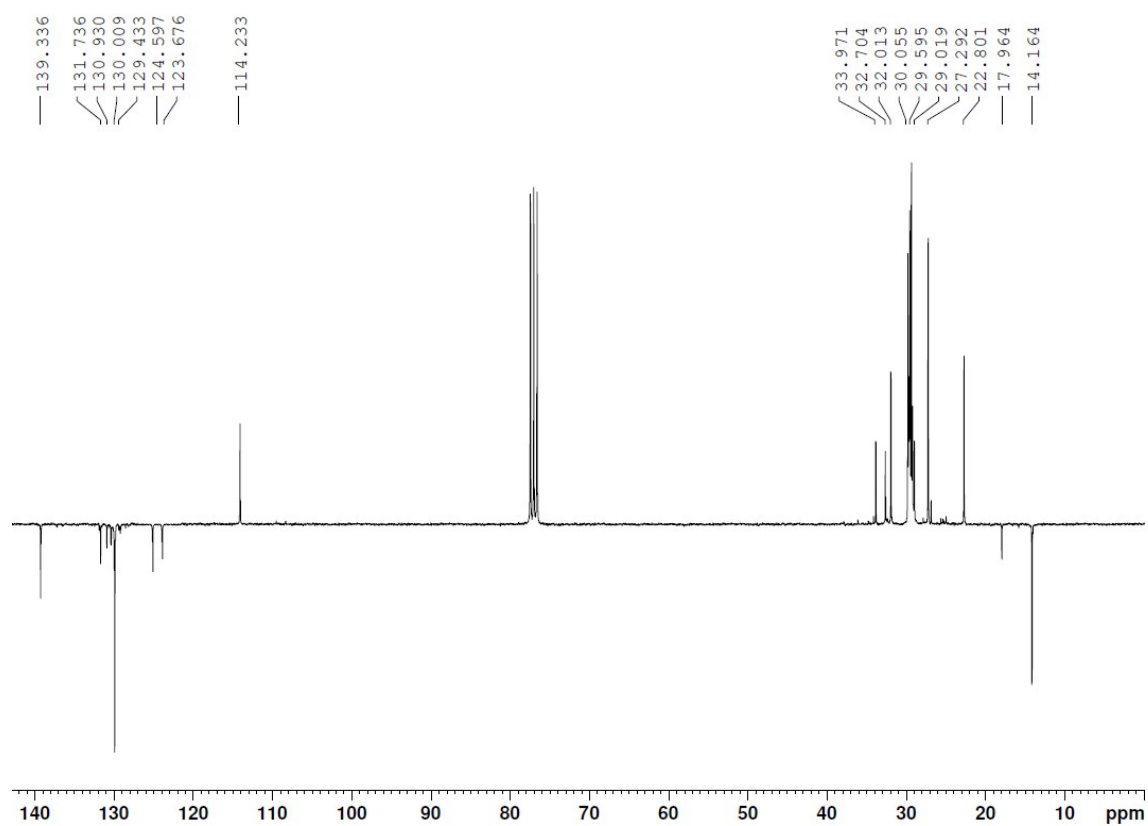


Figure S13. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of undecylenic acid 98% (**1e**).

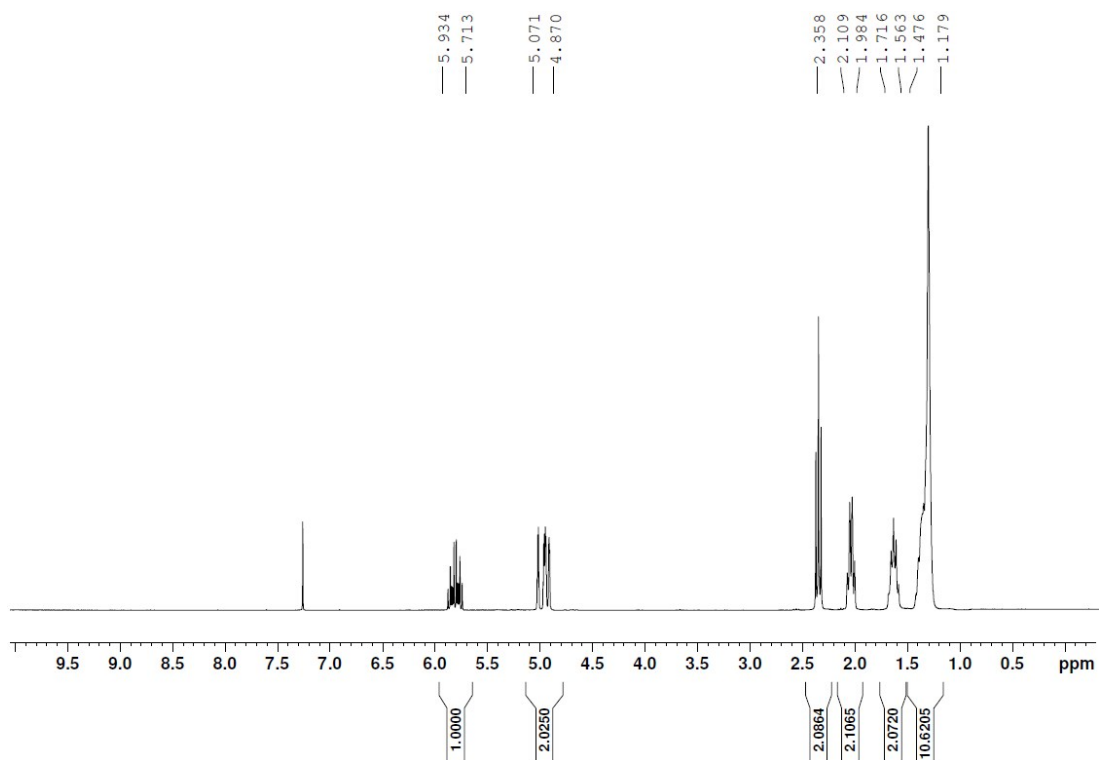


Figure S14. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2e**, 55%) and internal (**3e**, 45%) olefins derived from undecylenic acid 98%.

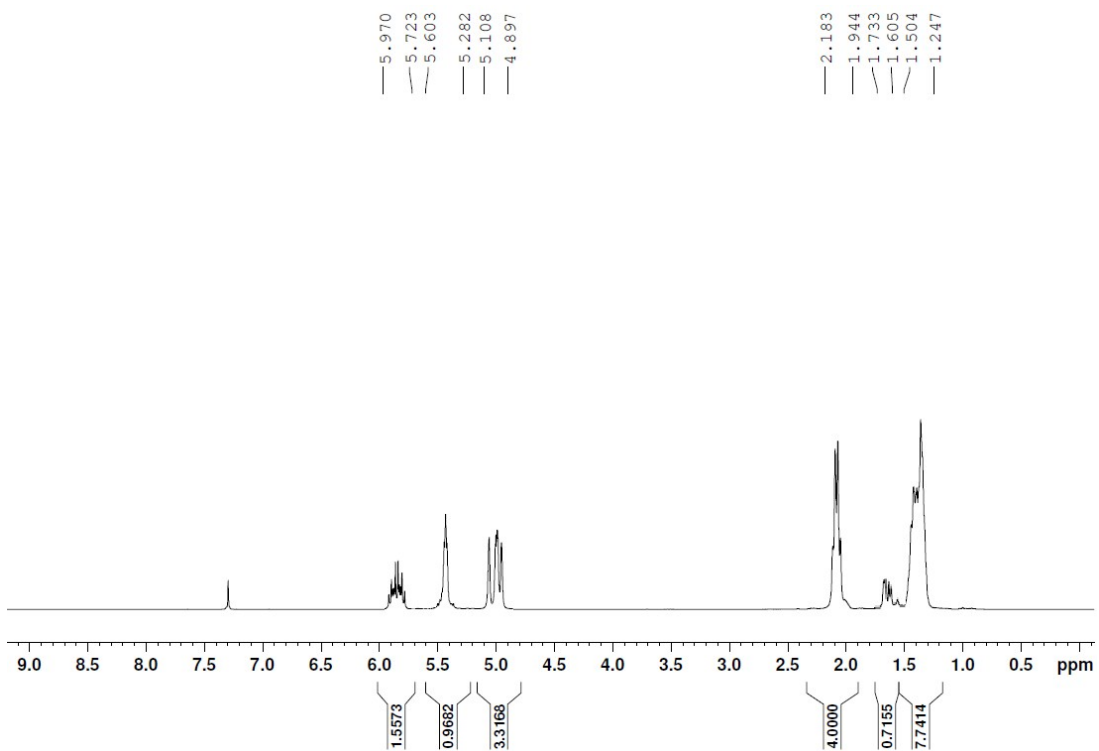


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 °C) of a mixture of the terminal (**2e**, 55%) and internal (**3e**, 45%) olefins derived from undecylenic acid 98%.

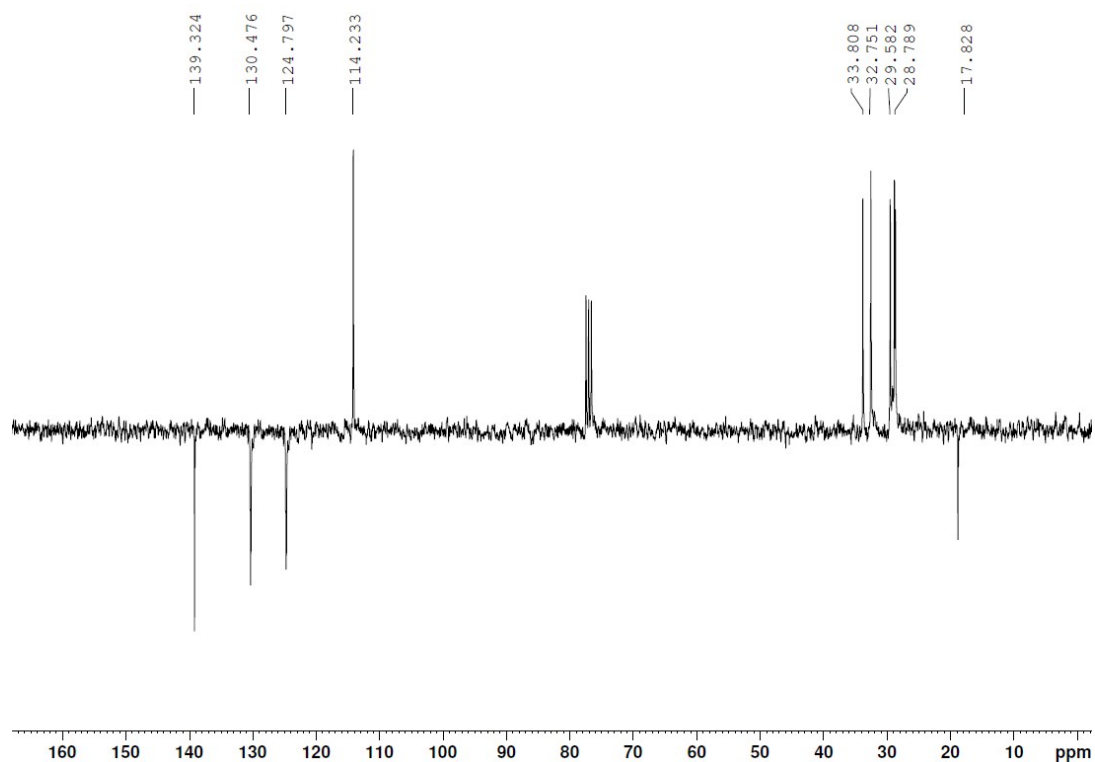


Figure S16. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 °C) of Pripol 1012 98% (**1f**).

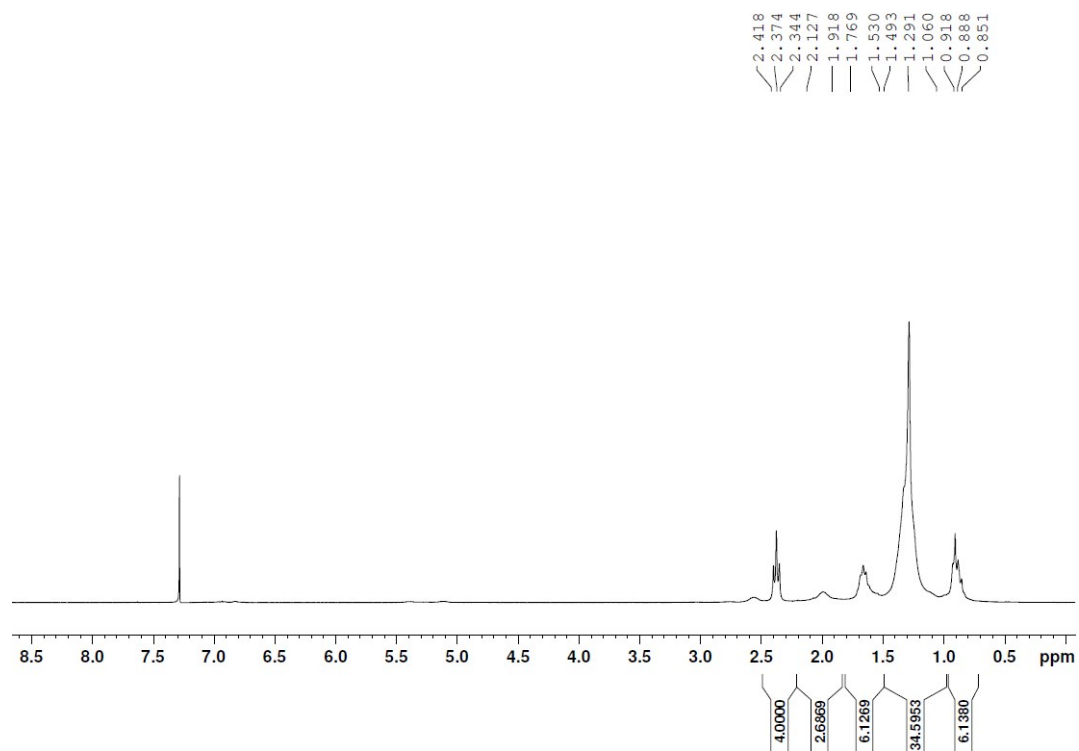


Figure S17. ^1H NMR spectrum (300 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2f**, 53%) and internal (**3f**, 47%) olefins derived from Pripol 1012 98%.

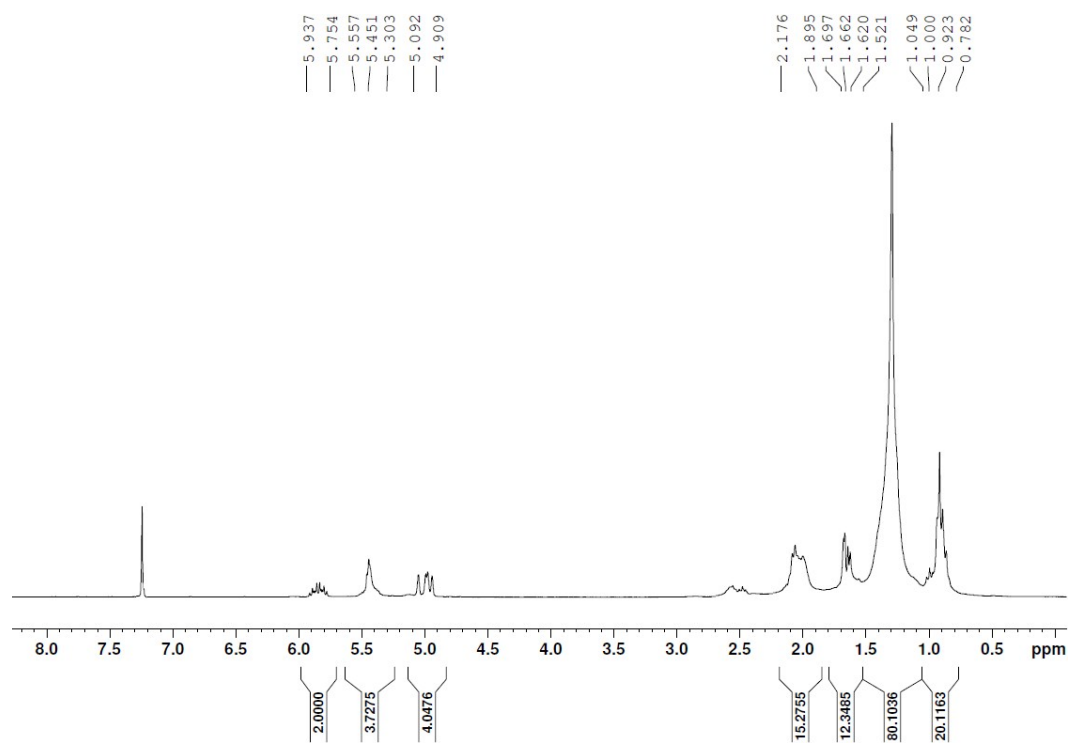
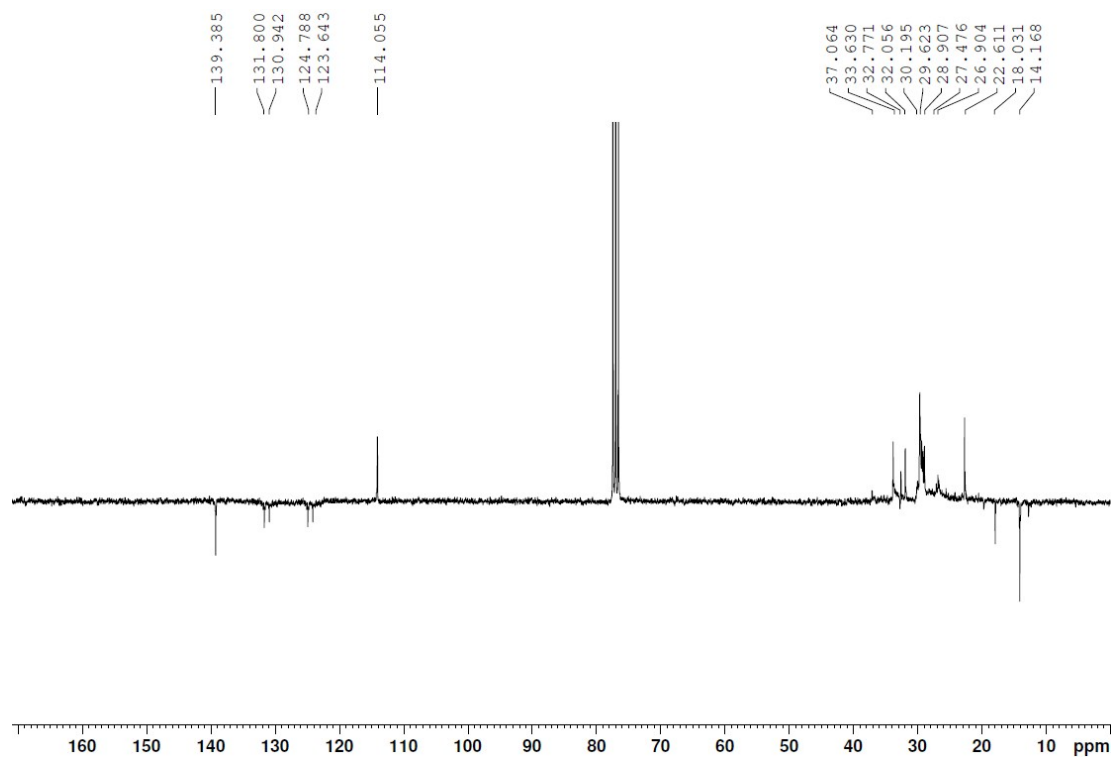


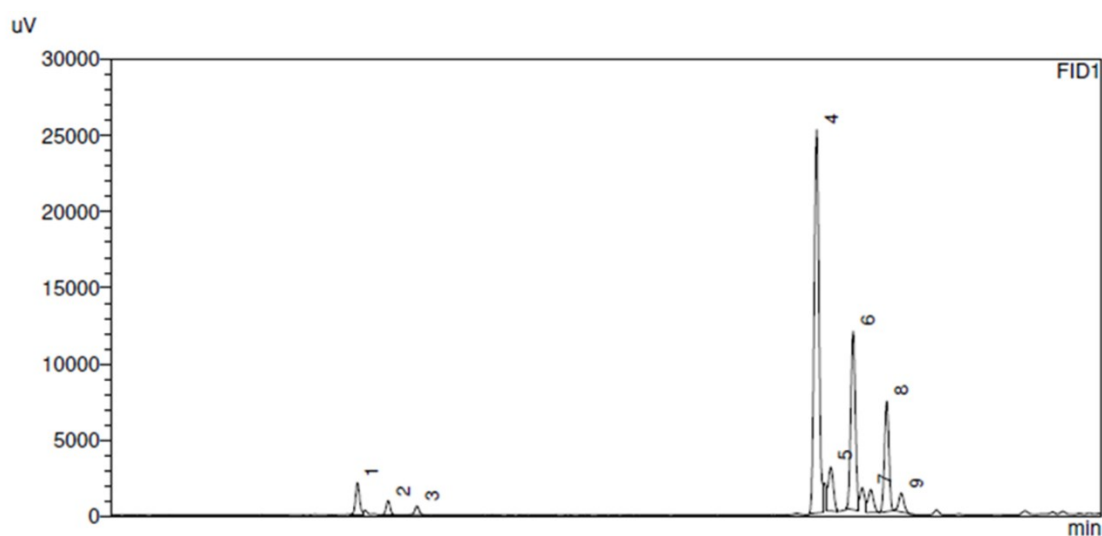
Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a mixture of the terminal (**2f**, 53%) and internal (**3f**, 47%) olefins derived from Pripol 1012 98%.



GLC-FID analyses

The GLC-FID analysis of (Z)-heptadeca-1,8-diene obtained as an inseparable mixture (**2a/3a**) from oleic acid 88% (**1a; C18:1**) confirms that the mixture contains only few products as only two different internal olefins are detected (peaks **6** and **8**). Other by-products resulting from other fatty acids (**C18:0, C18:2,...**) are also observed.

Figure S19. Chromatogram of purified mixture **2a/3a** (peaks **4** for **2a** and **6, 8** for **3a**) obtained from **1a (C18:1)**. The other peaks are relative to decarbonylation of by-products such as stearic acid **C18:0** (peaks **1, 2, 3**) and linoleic acid **C18:2** (peaks **5,7,9**)

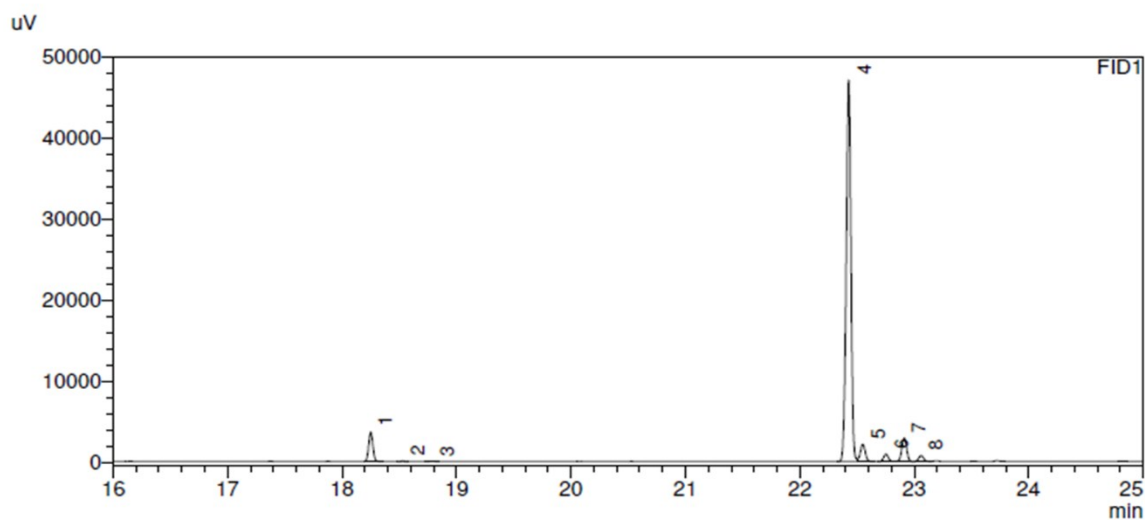


Peak Table

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.238	5177	2051	0.000			2b
2	18.516	2420	939	0.000			3b (internal isomer)
3	18.777	1487	565	0.000			3b (internal isomer)
4	22.411	75338	25026	0.000		M	2a
5	22.539	9223	2871	0.000		M	2c
6	22.742	33946	11583	0.000		M	3a (internal isomer)
7	22.902	5091	1499	0.000		M	3c (internal isomer)
8	23.048	20417	7232	0.000			3a (internal isomer)
9	23.179	3993	1232	0.000		M	3c (internal isomer)
Total		157093	52997				

To confirm the attribution of the signal of terminal olefin **3a**, we inject the product obtained in our previous work catalyzed by Ir-phosphine system.¹ The purified mixture was obtained with a selectivity **2a/3a** of 89/11.

Figure S20. Chromatogram of purified mixture **2a/3a** (peaks **4** for **2a** and **5, 7** for **3a**) obtained from **1a** (**C18:1**) in our previous work, and others by-products due to the presence of **C18:0** (peaks **1, 2** and **3**) and **C18:2** (peaks **6** and **8**).



Peak Table

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.250	9232	3617	0.000			2b
2	18.529	184	80	0.000		M	3b (internal isomer)
3	18.788	234	71	0.000		M	3b (internal isomer)
4	22.428	134424	46826	0.000			2a
5	22.551	6456	2111	0.000		V	3a (internal isomer)
6	22.753	2545	896	0.000		M	3c
7	22.913	8527	2893	0.000			3a (internal isomer)
8	23.059	2097	719	0.000		M	3c (internal isomer)
Total		163699	57213				

¹ J. Ternel, T. Lebarbé, E. Monflier and F. Hapiot, *ChemSusChem*, 2015, **8**, 1585-1592.

TEM images

Figure S21. Transmission electron microscopy (TEM) and Energy Dispersive X-Ray Analysis (EDX) of the crude reaction solution (diluted in acetone) resulting from the catalytic test described in Table 1, entry 4.

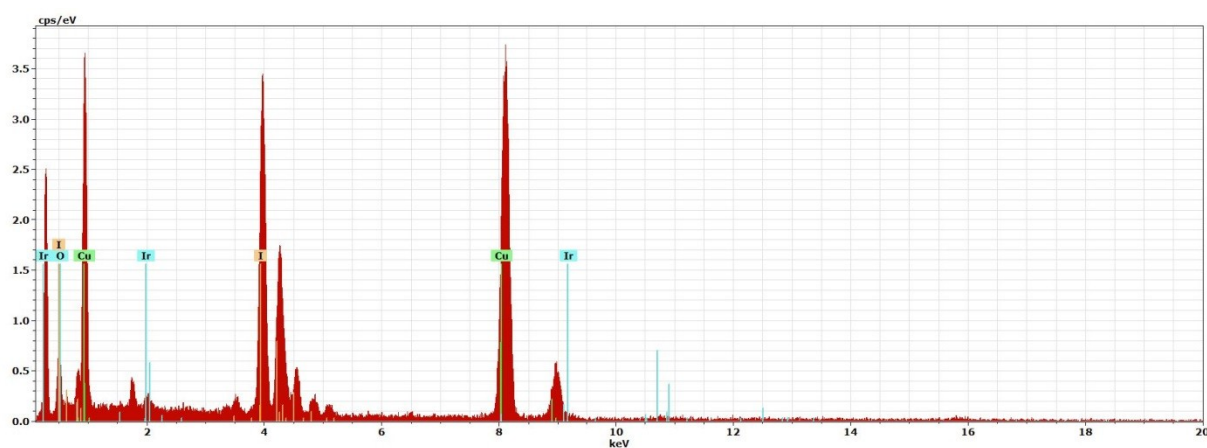
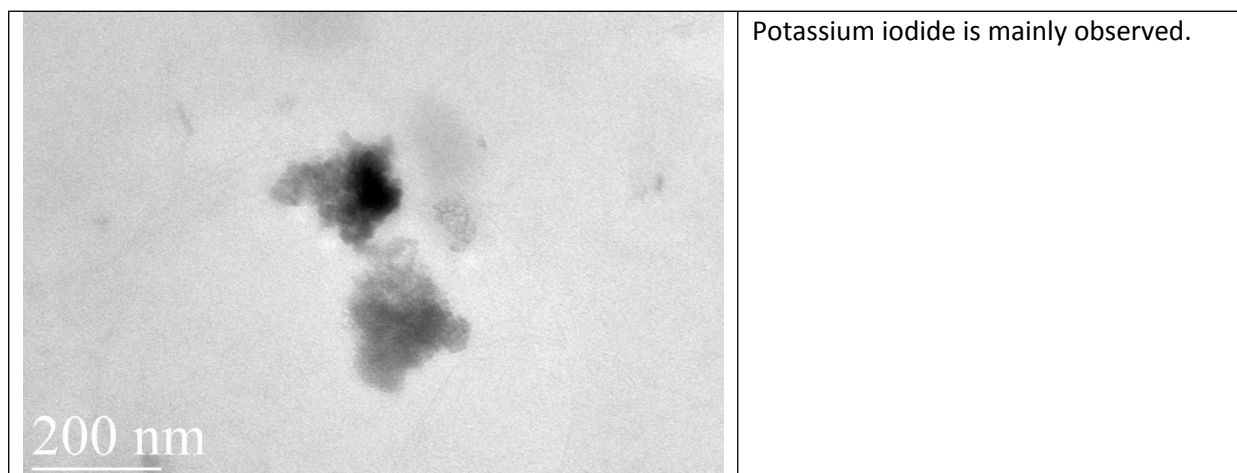


Figure S22. Transmission electron microscopy (TEM) and Energy Dispersive X-Ray Analysis (EDX) of the crude reaction solution (diluted in acetone) resulting from the catalytic test described in Table S1, entry 1.

