Supporting Information

Transformation of triolein to biogasoline by photo-chemo-biocatalysis

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1. Experimental procedures

1.1 Chemicals and analytical techniques

All chemical reagents used were purchased from standard commercial sources without purification unless otherwise noted.

The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data were recorded by a Bruker AMX400 MHz spectrometer with $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.34, 77.02, 76.70 ppm) as internal reference.

The EPR spectra were recorded by a Bruker EMX PLUS spectrometer at room temperature with open air. Standard test condition: center field (3498.00 G), sweep width (100.0 G), power (6.325 mW), power attenuation (15.0 dB), frequency Mon (9.828790 GHz), sweep time (30.00s), modulation amplitude (1.000 GHz), modulation frequency (100.00 kHz).

All compounds in the reactions were analyzed using a gas chromatography equipped with a flame ionization detector (FID) by SHIMADZU GC-2014 using CP-chirasil-Dex CB column (25 m × 0.25 mm × 0.25 μm).

Program 1 (for oleic acid): starting from 100 °C, holding 2 min; 10 °C /min heated to 200 °C; 200 °C, holding 10 min. The retention time of the methyl esterification product of oleic acid is 19.29 min, and the retention time of the methyl esterification product of pelargonic acid (internal standard) is 6.10 min.

Program 2 (for 8-hepatadecene, the decarboxylation product of oleic acid): 200 °C, holding 10 min. The retention time of 8-hepatadecene is 3.02 min, and the retention time of nonane (internal standard) is 1.60 min.

Program 3 (for short-chain fatty acids): starting from 100 °C, holding 2 min; 10 °C /min heated to 200 °C; 200 °C, holding 10 min. The retention time of the methyl esterification product of oleic acid is 19.29 min, methyl esterification product of hexanoic acid is 2.51 min, methyl esterification product of heptanoic acid is 3.50 min, methyl esterification product of octanoic acid is 4.79 min, methyl esterification product of pelargonic acid is 6.11 min, methyl esterification product of suberic acid is 9.31 min, methyl esterification product of azelaic acid is 10.50 min, methyl esterification product of myristic acid (internal standard) is 12.12 min.

Program 4: (for gasoline range hydrocarbons formed from oleic acid): starting from 60 °C, holding 4 min; 40 °C /min heated to 200 °C; 200 °C, holding 5 min. The retention time of pentane is 1.23 min, hexane is 1.47 min, heptane is 2.01 min, octane is 3.26 min, and nonane (internal standard) is 5.58 min.

Program 5: (for dodecane and tridecane formed from 9-trisosene): starting from 100 °C, holding 2 min; 10 °C /min heated to 200 °C; 200 °C, holding 10 min. The retention time of nonane is 2.51 min (internal standard), dodecane is 4.01 min, and tridecane is 5.33 min.

Yields were determined by using an internal standard against a standard curve of the purchased product.

1.2 Expression of WT *Cv*FAP and mutants

10 mL fresh LB medium (+ 50 μg/mL kanamycin) were inoculated with 10 μL WT *Cv*FAP or mutant and grown overnight at 37 °C. The pre-culture was subjected into 1 L TB (+ 50 μg/mL) for further induction. Cells were grown at 37 °C until OD_{600} reached 0.7-0.8. 0.2 mM IPTG was added to induce the *Cv*FAP production at 16 °C, 20 hours. Cells were harvested by centrifugation and resuspended in Tris-HCl buffer (100 mM, pH 8.5, containing 100 mM NaCl), and lysed by sonication. The cell crude was separated by centrifugation at 12,000 rpm for 30 min at 4 °C for further use.

1.3 Hydrolysis of triolein by lipases

Initially, we screened the highest hydrolysis activity of triolein to oleic acid by various lipases (PS-IM, CRL, AY-30, TL-IM, PPL, MML, ANL-A, PF-AL, Novozyme 435, CAL-A). The reaction was performed with 30 mg triolein and different amount lipases in 0.5 mL 100 mM Tris-HCl buffer (pH 8.5) at room temperature for different time. Then products were mixed with 50 μL 1M HCl and extracted with 0.5 mL ethyl acetate for 3 times. The obtained ethyl acetate solution was evaporated. Then 0.5 mL MeOH, 10 mg pelargonic acid (internal standard), and 50 μL H_2SO_4 were added into the residues for methyl esterification. The methyl esterification reaction was performed for 2 h at 50 °C, and then the solution was mixed with 0.5 mL H_2O and extracted with 1 mL ethyl acetate for 2 times. The yields of the triolein hydrolysis reactions catalysed by lipases were measured by GC analysis.

1.4 Photocatalytic oxidative cleavage of oleic acid

(1) Oxidative cleavage of oleic acid by various photocatalysts

At room temperature, we subjected 10 mg of oleic acid to 10% equivalent metal-photocatalysts or 20% equivalent organic-photocatalysts in 1 mL MeCN under the irradiation of 50 W blue LED for 24 h. Experiments were carried out under an O_2 atmosphere. Then 2 mL MeOH, 1 mg myristic acid (internal standard), and 10 μL H_2SO_4 were added into the residues for methyl esterification. The methyl esterification reaction was performed for 2 h at 50 °C, and then the solution was mixed with 2 mL H_2O and extracted with 2 mL ethyl acetate for 2 times. The yields of mixed acids were measured by GC analysis.

(2) The influence of solvents on the oleic acid oxidative cleavage catalysed by $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

In order to increase the overall yield of short-chain fatty acids, we further investigated the influence of solvents on the oxidative cleavage reaction. The reaction was performed under standard conditions. Then 2 mL MeOH, 1 mg myristic acid (internal standard), and 10 μL H_2SO_4 were added into

the residues for methyl esterification. The methyl esterification reaction was performed for 2 h at 50 °C, and then the solution was mixed with 2 mL H_2O and extracted with 2 mL ethyl acetate for 2 times. The yields of mixed acids were measured by GC analysis. As shown in Table S1, using DCM or MeCN as a solvent afforded the comparable yields (Table S1, entry 1 and 2). Reactions in DMF or MeOH provided the products in lower yields (Table S1, entry 3 and 4). While using DMSO and THF, no products were observed (Table S1, entries 5 and 6). Therefore, MeCN was selected as the solvent in this step.

(3) Optimization of the oleic acid oxidative cleavage catalysed by 4CzIPN

Considering non-metal photocatalysts might be more eco-friendly and economical, the organic photocatalyst 4CzIPN (Table S2) and riboflavin tetrabutyrate (Table S3) were also subjected to the optimization experiments. And the effects of solvents, the concentration of photocatalysts, reaction time, the intensity of the blue light, and O_2 concentration were investigated.

Indeed, increasing the dose of catalysts improved the reaction yields due to the attenuation of photocatalysts under blue LED (Table S2, entries 1-3). However, further loading of photocatalysts did not lead to any further improvement (Table S2, entry 4). The light intensity remarkably improved the yield of the reaction (Table S2, entries 5-6), and no product was formed without light (Table S2, entry 7). Reaction conducted in the air atmosphere yielded less product than in oxygen atmosphere (Table S2, entry 8), and there was no product detected in the nitrogen atmosphere (Table S2, entry 9). Furthermore, the screening of different solvents also did not improve the yields (Table S2, entries 10-13). Prolonging reaction time to 48 h provided 69% yield of total fatty acids (Table S2, entry 14). In comparison with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 4CzIPN could achieve comparable yield, however, the addition of 4CzIPN is 20 mol% and it took 48 h to obtain this result.

(4) Optimization of the oleic acid oxidative cleavage catalysed by riboflavin tetrabutyrate

Similar to 4CzIPN, increasing the dose of riboflavin tetrabutyrate improved the yields of the reaction (Table S3, entries 1-3). Further loading of 40 mol% riboflavin tetrabutyrate did not lead to any further improvement (Table S3, entry 4). The light intensity further improved the yields of the reaction (Table S3, entries 5-6) and no product was formed without light (Table S3, entry 7). Reaction conducted in the air atmosphere yielded less product than in the oxygen atmosphere (Table S3, entry 8), and there was no product detected in the nitrogen atmosphere (Table S3, entry 9). Other solvents also did not improve the yields (Table S3, entries 10-13), especially no fatty acids obtained when the reaction was conducted in DMSO and THF (Table S3, entries 12-13). 67.0% yield of total fatty acids were obtained after 48 h reaction time (Table S3, entry 14). It was noted that riboflavin tetrabutyrate exhibited unstable catalytic property under high power blue LED during experiments, and the 30 mol% addition of riboflavin tetrabutyrate was also not economical. In conclusion, both organic photocatalysts were not suitable for our sequential reaction.

1.5 Oxidative cleavage-decarboxylation sequential transformation of oleic acid into biogasoline

We tested the feasibility of the anticipated sequence comprising photocatalytic oxidative cleavage and photoenzymatic decarboxylation for the transformation of oleic acid into biogasoline (Scheme S2). Oxidative cleavage of oleic acid was performed with 10 mg oleic acid and 2.5 mol% Ir-photocatalyst in 0.4 mL MeCN at room temperature, blue LED 50 W for 24 h. The *Cv*FAP-catalyzed decarboxylation step was performed by adding 4 mL CvFAP mutant (I398L) crude extract into the oxidative reaction mixture with 10 W blue LED irradiation for 12 h. Then 0.5 mg nonane was added as internal standard and alkanes were extracted with 2 mL dodecane for 3 times. Productions were measured by GC analysis and showed in Scheme S2.

1.6 Large scale reaction for the photo-chemo-biocatalytic transformation of triolein to biogasoline

(1) Step 1: hydrolysis of triolein

Based on the optimization of each step in the analytic scale, we constructed the new sequence comprising lipase-catalyzed hydrolysis of triolein, fatty acid photodecarboxylase (*Cv*FAP)-catalyzed decarboxylation of oleic acid, photocatalytic oxidative cleavage of long-chain alkene, and the final decarboxylation of the medium- or short-chain fatty acids catalyzed by *Cv*FAP mutant. The scaled-up hydrolysis reaction of triolein was performed with 1.2 g triolein and 50 mg lipase PS-IM in 5 mL 100 mM Tris-HCl buffer (pH 8.5) at room temperature. During the reaction, sampling at different reaction time was performed to monitor the reaction progress. 50 μL samples were acidized with 50 μL 1M HCl and extracted with 0.5 mL ethyl acetate for 2 times. Evaporating the ethyl acetate and adding 1 mL MeOH, 10 mg pelargonic acid (internal standard), and 50 μL H_2SO_4 at 50°C for 2 h to methyl esterification. The reactions were mixed with 1 mL H_2O and extracted with 1 mL ethyl acetate for 2 times. Yield 1 was determined by GC and calculated as **Equation (1)**, and the results were shown in Fig. 2A.

$$\text{Yield 1\%} = \frac{\text{actual oleic acid (g)}}{\text{theoretical oleic acid (g)}} \times 100\%$$

Equation (1)

(2) Step 2: decarboxylation of oleic acid

The scaled-up *Cv*FAP-catalyzed decarboxylation of oleic acid was performed as following: Adding 20 mL WT *Cv*FAP crude extract into the products mixture of step 1 and the reaction was conducted at room temperature with the irradiation of 10 W blue LED. Because the catalytic efficiency of CvFAP is relatively stable when the pH value is in the range of 7.5-9.0 [1], thus we did not adjust the pH of the whole reaction system. During the reaction, sampling at different reaction time was performed to monitor the reaction progress. 200 μL samples were added with 2 mg nonane (internal

standard) and extracted with 200 μL ethyl ether for 3 times. Yield 2 was determined by GC and calculated as **Equation (2)**, and the results were shown in Fig. 2B.

$$\text{Yield } 2\% = \frac{\text{actual 8 - heptadecene (g)}}{\text{theoretical 8 - heptadecene (g)}} \times 100\%$$

Equation (2)

After completing the decarboxylation of oleic acid, an equal volume of ethyl ether was used to extract 8-heptadecene for 7 times. The organic phase was combined and dried over anhydrous Na_2SO_4 and then evaporated in vacuum to obtain crude product (about 2.1 g). The obtained crude product was subjected to silica gel column chromatography using ethyl acetate/petroleum ether (50/1) as eluent to provide 923 mg pure 8-heptadecene. 8-heptadecene was determined by ^{1}H NMR. Analysis results are consistent with the literature.[2]

(3) Step 3: oxidative cleavage of 8-hepetadecene

The reaction was performed with 923 mg 8-hepetadecene and 2.5 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in 5 mL MeCN at room temperature with the irradiation of 50 W blue LED. During the reaction, sampling at different reaction time was performed to monitor the reaction progress, 50 μL samples were added with 2 mg myristic acid (internal standard), 200 μL MeOH and 10 μL H_2SO_4 at 50 °C for 2 h to finish methyl esterification. The reactions were mixed with 300 μL H_2O and extracted with 200 μL ethyl acetate for 2 times. Productions and yields were determined by GC. Since one 8-heptadecene molecular would be eventually cleaved into two shorter-chain fatty acids molecules, Yield 3 represented the molar yields of the oxidative cleavage step and was calculated as **Equation (3)**, and the results were shown in Fig. 2C.

$$\text{Yield } 3\% = \frac{\sum \text{n mixed acids (mol)}}{\text{n practical 8 - heptadecene (mol)} \times 2} \times 100\%$$

Equation (3)

(4) Step 4: decarboxylation of short-chain fatty acids

The scaled-up *Cv*FAP-catalyzed decarboxylation of short-chain fatty acids produced from Step 3 was performed as following: Adding 40 mL *Cv*FAP mutant G462A crude extract into the products mixture of Step 3 and the reaction was conducted at room temperature with the irradiation of 10 W blue LED. During the reaction, sampling at different reaction time was performed to monitor the reaction progress, and the results were shown in Fig. 2D. For analysis process, 0.5 mL samples were added with 1 mg nonane (internal standard) and extracted with 200 μL dodecane for 3 times. Productions and yields were determined by GC. Yield 4 represented the molar yields from the decarboxylation step and was calculated as **Equation (4)**, and the results were shown in Fig. 2D.

$$\text{Yield } 4\% = \frac{\sum \text{n mixed alkanes (mol)}}{\sum \text{n mixed acids in step 3 (mol)}} \times 100\%$$

Equation (4)

1.7 Photo-chemo-biocatalytic sequential reaction of other substrates

(1) Synthesis of 7-pentadecene, 7-heptadecene, 9-nonadecene

50 Mg long-chain unsaturated fatty acids were dissolved in 200 μL MeOH, and 5 mL WT *Cv*FAP crude extract was added. The reaction was performed at room temperature for 3 h. Alkenes were extracted with 5 mL ethyl ether for 5 times. The organic phase was combined and dried over anhydrous Na_2SO_4 and then evaporated in vacuum to obtain the crude product. Crude products were subjected to silica gel column chromatography using ethyl acetate/petroleum ether (50/1) as eluent to provide pure products in almost quantitative yields, and the structure was characterized by ^{1}H NMR.

(2) Oxidative cleavage of long-chain alkenes

The reaction was performed with alkenes obtained from the last step and 2.5 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in 0.5 mL MeCN at room temperature with the irradiation of 50 W blue LED for 24 h. The production and yield of the mixed acids were measured by GC analysis. Since one long-chain alkene would be eventually cleaved into two shorter-chain fatty acids molecules, the molar yield of the oxidative cleavage step (Y2%) can be calculated as **Equation (5)**:

$$\text{Y } 2\% = \frac{\sum \text{n mixed acids (mol)}}{\text{n practical alkene (mol)} \times 2} \times 100\%$$

Equation (5)

(3) Decarboxylation of shorter-chain fatty acids

Adding 2 mL *Cv*FAP mutant G462A crude extract (For the 9-tricosene reaction, *Cv*FAP mutant I398L was used) into the products mixture of oxidative step, and the reaction was conducted at room temperature with the irradiation of 10 W blue LED for 2 h. The production and yield of the mixed alkanes were measured by GC analysis and calculated as **Equation (6)**:

$$Y\ 3\% = \frac{\sum n \text{ mixed alkanes (mol)}}{\sum n \text{ mixed acids in the last step (mol)}} \times 100\%$$

Equation (6)

The total yield (TY%) of biogasoline prepared from long-chain alkenes can be calculated as the equation: $TY(\text{total yield})\% = Y1\% \times Y2\% \times Y3\%$, **Equation (7)** or $\frac{\sum n \text{ mixed alkanes (mol)}}{n \text{ alkene (mol)} \times 2} \times 100\%$, **Equation (8)**, where 2 means that two alkane molecules were from one molecule of long-chain alkene.

In the oxidative cleavage-decarboxylation sequential reaction of one molecule alkene, two carbon atoms were lost during the decarboxylation step, we used TRC(total recovery of carbons)% to represent the carbon atoms recovery in this sequence and calculated as **Equation (9)**:

$$TRC\% = \frac{\sum n \text{ alkane (mol)} \times \text{carbon atom number of alkane}}{n \text{ alkene (mol)} \times (\text{carbon atom number of alkene} - 2)} \times 100\%$$

Equation (9)

1.8 Mechanism study

(1) Quencher study

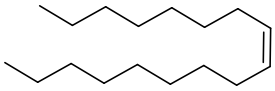
Different quenchers were added into the reaction of 8-heptadecene under standard conditions. Then adding 1 mg myristic acid and 10 μL conc. H_2SO_4 into the reaction mixtures to perform methyl esterification at 50 °C for 2 h. Yield was measured by GC analysis.

When 1.0 equivalent Tempo was added into the reaction of 8-heptadecene under the standard conditions, the product could be detected by GC-MS qualitative analysis (see Fig. S9), which implied the existence of the radical species.

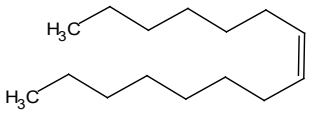
(2) EPR measurements

Reaction mixture contains 10 mg heptadecane, 0.025 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in 1 mL MeCN. 30 μL samples (without illumination and illumination for 5 min) were combined with 30 μL DMPO (200 mM in MeOH) individually, the mixtures were injected with capillary tube, then put into quartz tube for testing. The experimental EPR spectra were processed using Xenon.

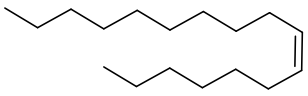
1.9 Characterization data



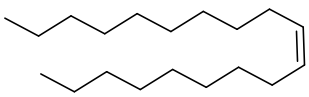
8-Heptadecene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (t, J = 4.78 Hz, 2H), 2.13 - 1.93 (q, J = 6.6 Hz, 4H), 1.41 - 1.20 (m, 22H), 0.99 - 0.80 (t, *J* = 6.8 Hz , 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9, 31.9, 31.9, 29.8, 29.5, 29.3, 29.3, 29.2, 27.2, 22.7, 14.1.



7-pentadecene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (t, *J* = 4.8 Hz, 2H), 2.08 - 1.93 (m, 4H), 1.28 (qd, *J* = 7.2, 4.7, 3.9 Hz, 18H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9, 31.9, 31.8, 29.8, 29.8, 29.3, 29.2, 29.0, 27.2, 22.7, 14.1.



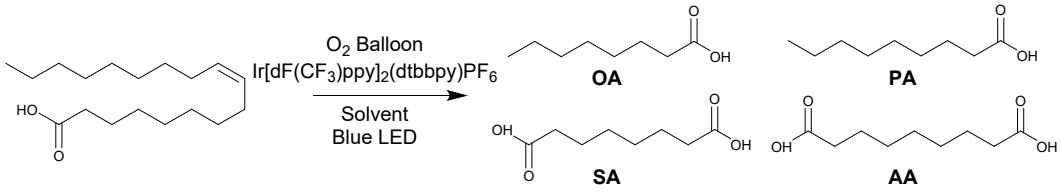
7-Heptadecene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (t, *J* = 3.7 Hz, 2H), 2.06 - 1.89 (m, 4H), 1.26 (d, 22H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.4, 32.6, 31.9, 31.8, 29.7, 29.6, 29.6, 29.4, 29.2, 28.9, 22.7, 22.7, 14.1.



9-Nonadecene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (t, *J* = 4.82 Hz, 2H), 2.01 (q, *J* = 6.36 Hz, 4H), 1.27 (s, 26H), 0.88 (t, *J* = 6.67 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9, 31.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 27.2, 22.7, 14.1.

2. Tables and figures

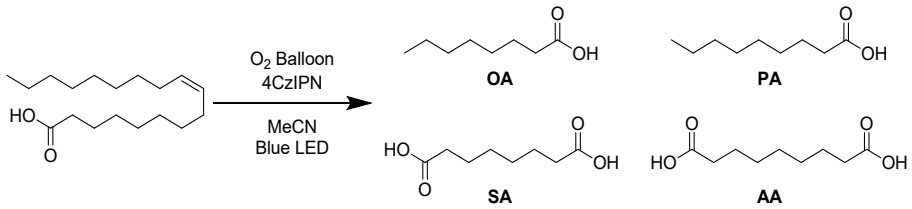
Table S1. Influence of solvents on the oxidative cleavage of oleic acid by $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ [a]



Entry	Solvent	Yield (%) [b]				
		OA	PA	SA	AA	Total
1	MeCN	20.5	18.8	19.5	16.5	75
2	DCM	17.9	16.0	19.0	17.6	71
3	MeOH	4.6	4.3	5.9	3.8	19
4	DMF	4.9	5.2	7.0	5.5	23
5	DMSO	trace	trace	trace	trace	-
6	THF	trace	trace	trace	trace	-

[a] Reaction conditions: 10 mg oleic acid, 5 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 1 mL solvent, blue LED 50 W, room temperature, reactions were conducted in Schlenk tubes. [b] Yield was measured by GC analysis and using myristic acid as internal standard. Samples were methylated prior to GC analysis. $\text{Yield\%} = \frac{\sum \text{n total fatty acids (mol)}}{\text{n oleic acid (mol)} \times 2} \times 100\%$.

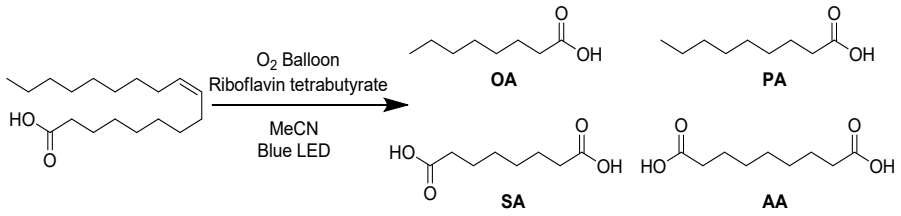
Table S2. Optimization of the oxidative cleavage of oleic acid by 4CzIPN [a]



Entry	Equivalents	Light (W)	Solvent	Yield (%) [f]				
				OA	PA	SA	AA	Total
1	0.05	40	MeCN	3.3	3.2	2.7	2.8	12
2	0.1	40	MeCN	4.3	5.1	4.0	4.8	18
3	0.2	40	MeCN	5.4	6.1	4.9	5.8	22
4	0.3	40	MeCN	4.6	5.2	5.8	4.9	21
5	0.2	60	MeCN	11.0	13.0	11.0	14.5	49
6	0.2	80	MeCN	12.5	11.1	14.0	13.8	51
7[b]	0.2	-	MeCN	nd	nd	nd	nd	-
8[c]	0.2	80	MeCN	8.6	9.7	6.7	9.9	35
9[d]	0.2	80	MeCN	nd	nd	nd	nd	-
10	0.2	80	MeOH	2.5	8.4	2.5	9.0	22
11	0.2	80	DCM	4.0	8.6	6.8	10.2	30
12	0.2	80	THF	10.7	12.2	11.2	13.1	47
13	0.2	80	DMF	6.5	7.1	4.8	6.2	25
14[e]	0.2	80	MeCN	16.9	19.0	15.2	17.5	69

[a] Reaction condition: 10 mg oleic acid, 1 mL solvent, room temperature. [b] Reaction was conducted without light.; [c] Air balloon; [d] N_2 balloon. [e] Reaction time was prolonged to 48 h. [f] Yield was measured by GC analysis using myristic acid as internal standard. Samples were methylated prior to GC analysis. $\text{Yield\%} = \frac{\sum \text{n total fatty acids (mol)}}{\text{n oleic acid (mol)} \times 2} \times 100\%$.

Table S3. Optimization of the oxidative cleavage of oleic acid by Riboflavin retrabutyrate[a]



Entry	Equivalents	Light (W)	Solvent	Yield (%)[f]				
				OA	PA	SA	AA	Total
1	0.1	40	MeCN	3.3	5.9	2.7	5.6	18
2	0.2	40	MeCN	6.0	8.7	4.8	9.3	29
3	0.3	40	MeCN	7.2	9.0	5.0	9.7	31
4	0.4	40	MeCN	6.7	7.2	5.1	8.5	28
5	0.3	60	MeCN	8.2	8.9	7.8	10.1	35
6	0.3	80	MeCN	11.5	12.0	11.4	13.6	48
7[b]	0.3	-	MeCN	nd	nd	nd	nd	nd
8[c]	0.3	80	MeCN	8.1	8.7	8.0	8.2	33
9[d]	0.3	80	MeCN	nd	nd	nd	nd	nd
10	0.3	80	MeOH	3.2	8.4	3.4	8.8	24
11	0.3	80	DCM	3.9	9.5	4.0	9.9	27
12	0.3	80	THF	nd	nd	nd	nd	nd
13	0.3	80	DMSO	nd	nd	nd	nd	nd
14[e]	0.3	80	MeCN	16.8	17.1	15.7	17.4	67

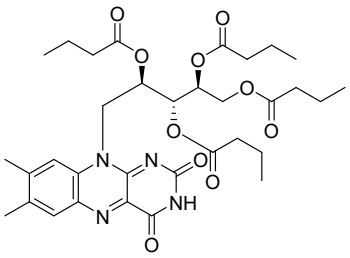
[a] Reaction condition: 10 mg oleic acid, 1 mL solvents, room temperature. [b] Reaction was conducted without light.; [c] Air balloon; [d] N_2 balloon. [e] Reaction time was prolonged to 48 h. [f] Yield was measured by GC analysis, using myristic acid as internal standard. Samples were methylated prior to GC analysis. $\text{Yield\%} = \frac{\sum \text{n total fatty acids (mol)}}{\text{n oleic acid (mol)} \times 2} \times 100\%$.

Table S4. Literature data for oleic acid oxidation with a variety of oxidants

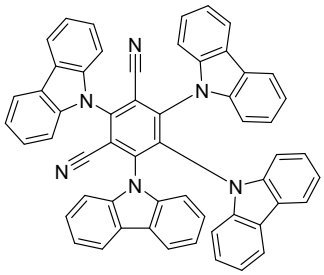
Entry	Media	Catalyst	Oxidant	Temp. (°C)	Time (h)	Other requirements	Yield (%) [a]	Ref.
1	MeCN	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	O_2	r.t.	24	blue LED	75	This work [b]
2	supercritical CO_2	CrMCM-41	10 bar O_2	81	8	100 bar CO_2 specialized equipment	84	3
3	*tert*-butanol	WO_3	H_2O_2	130	4	Na_2SnO_3 as additive	93	4
4	-	H_2WO_4	H_2O_2	100	8	H_2O_2 (60 % v/v)	80	5
5	MeCN/H_2O	Fe(6-Me-PyTACN)	$NaIO_4$	r.t.	48	H_2SO_4	43	6
6	Acetone/H_2O	-	O_2/O_3	0	>10	continuous flow setup	82	7

[a] Yield was calculated as the equation: $\text{Yield\%} = \frac{\sum \text{n mixed acids (mol)}}{\text{n oleic acid (mol)} \times 2} \times 100\%$. [b] From Table 3, entry 11 in the text.

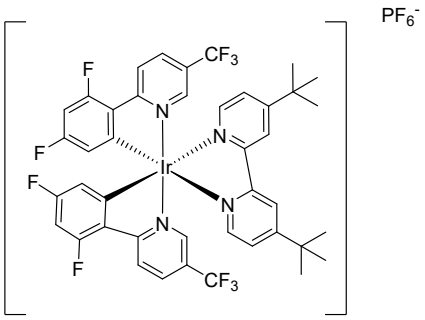
Scheme S1. The structure of representative photocatalysts



Riboflavin tetrabutyrate

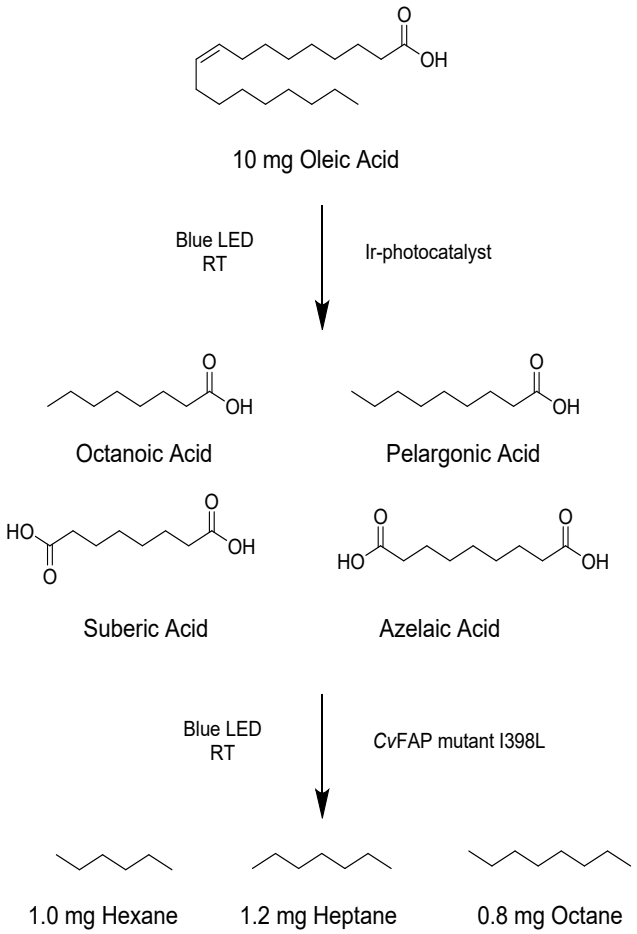


4CzIPN



$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

Scheme S2. The oxidative cleavage-decarboxylation sequential transformation of oleic acid into biogasoline



Reaction conditions: Oxidative cleavage step: 10 mg oleic acid, 2.5 mol% Ir-photocatalyst, 0.4 mL MeCN, room temperature, blue LED 50 W, 24 h. Decarboxylation: Adding 4 mL *Cv*FAP mutant I398L crude extract into the products mixture from oxidative cleavage step, room temperature, blue LED 10 W, Yields were determined by GC, using nonane as internal standard.

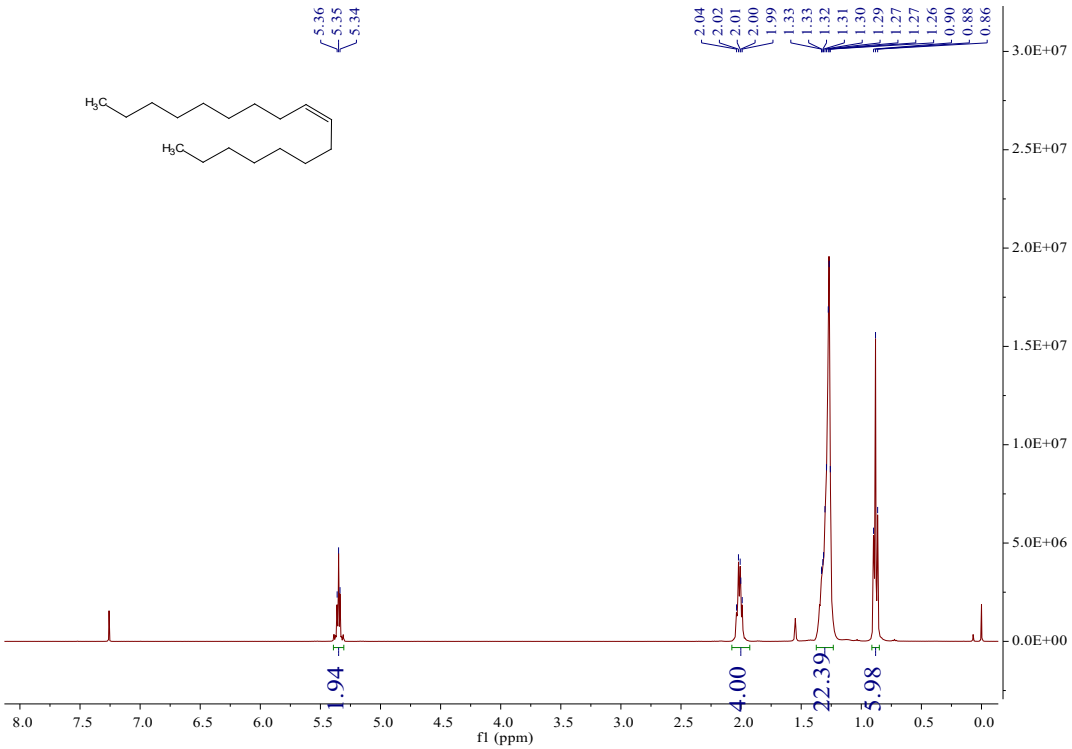


Fig. S1. [1] H spectrum of 8-heptadecene

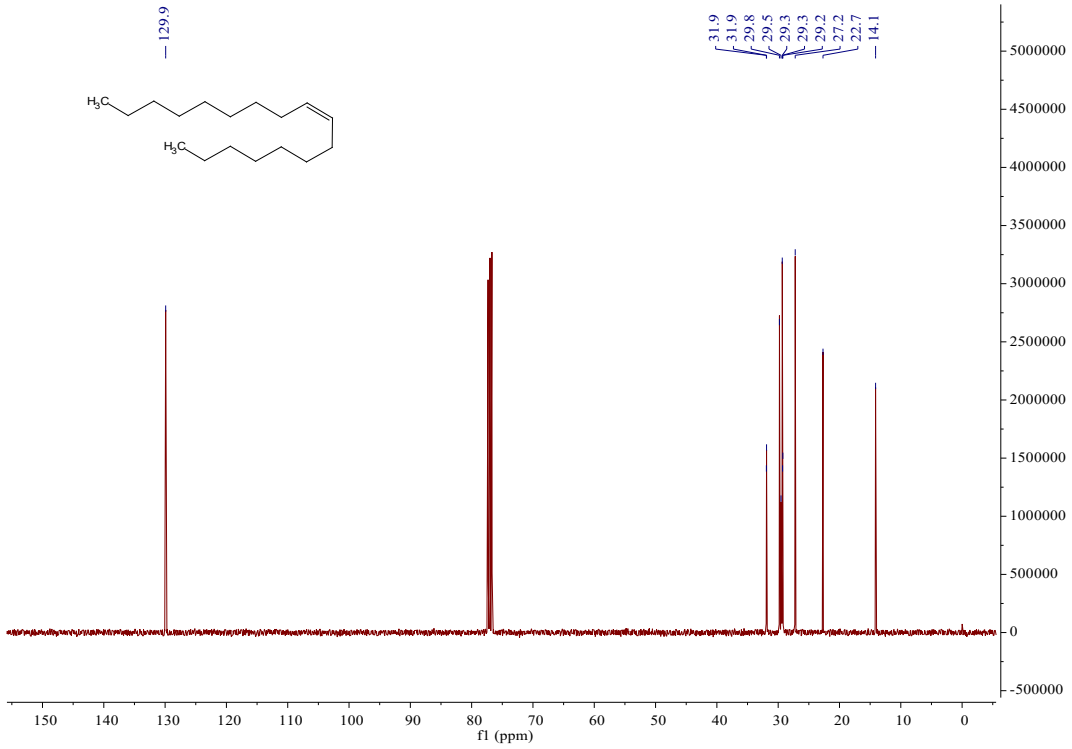


Fig. S2. [13] C spectrum of 8-heptadecene

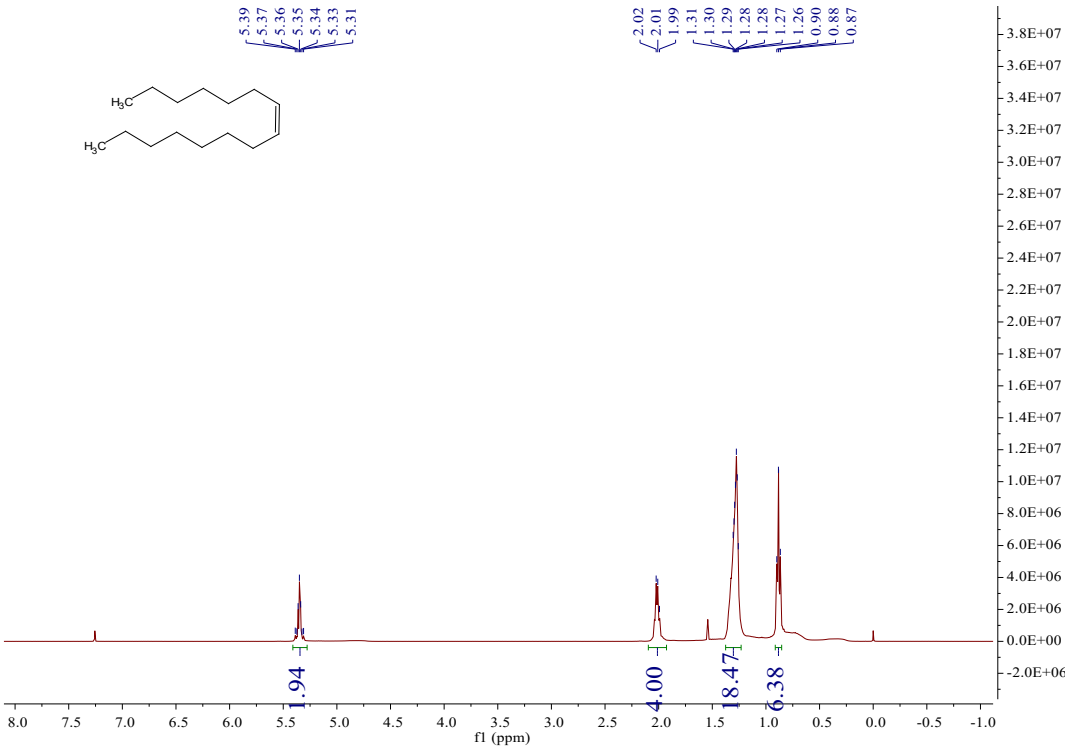


Fig. S3. [1] H spectrum of 7-pentadecene

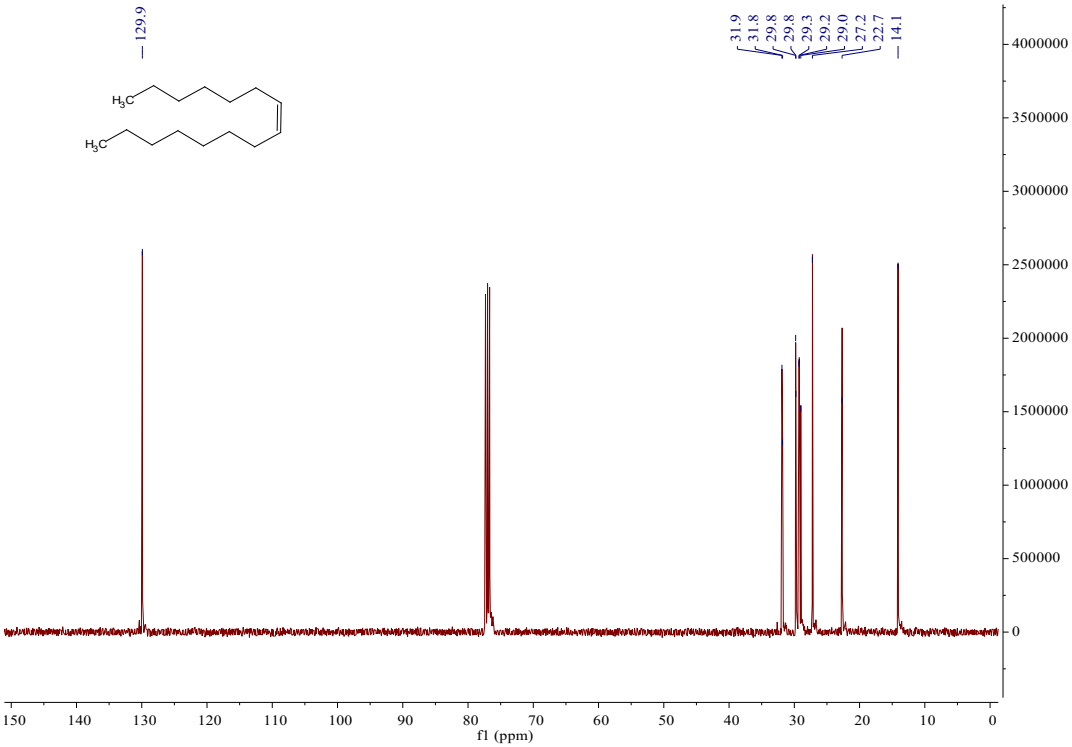


Fig. S4. [13] C spectrum of 7-pentadecene

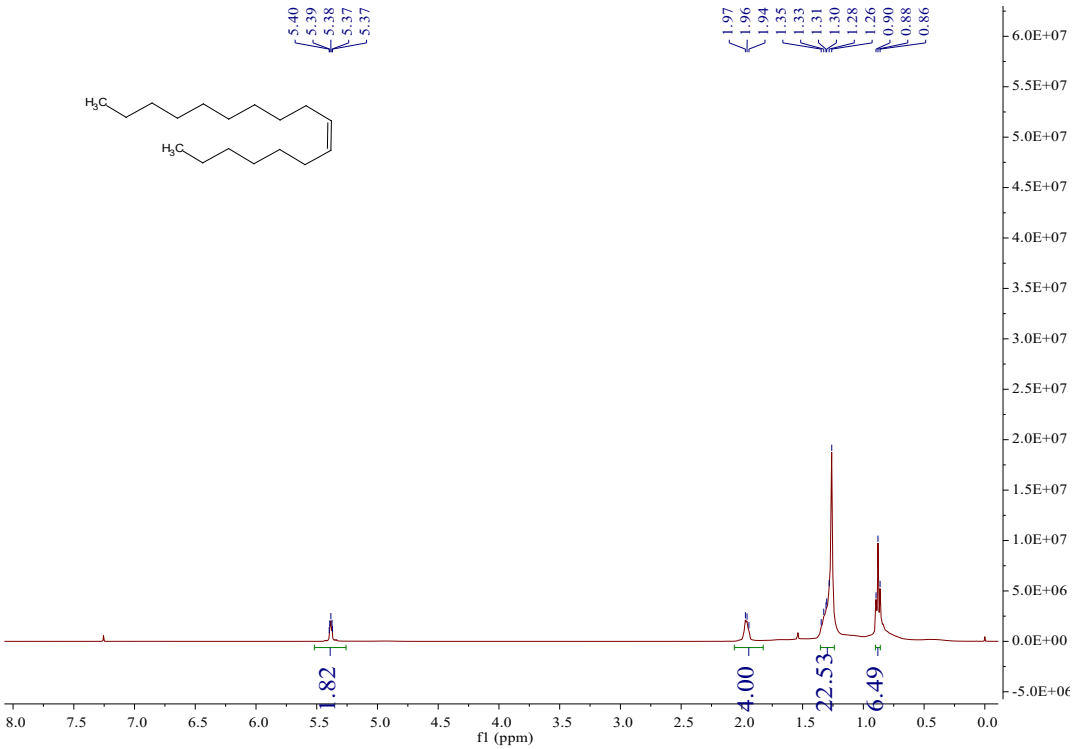


Fig. S5. [1] H spectrum of 7-heptadecene

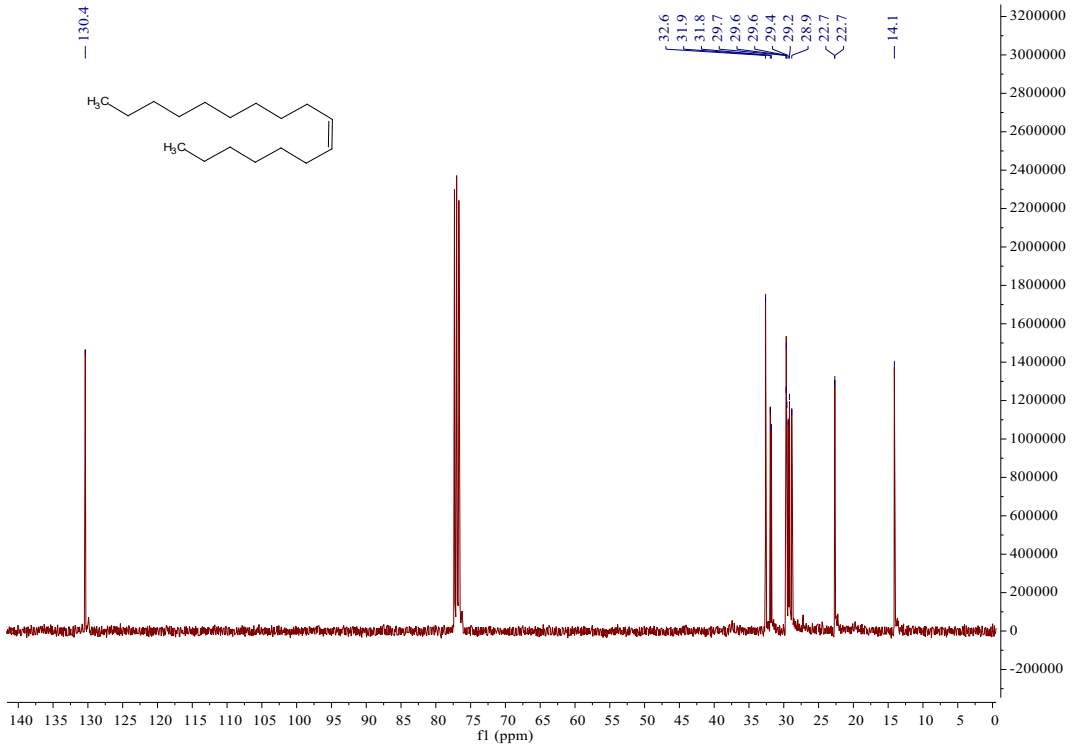


Fig. S6. [13] C spectrum of 7-heptadecene

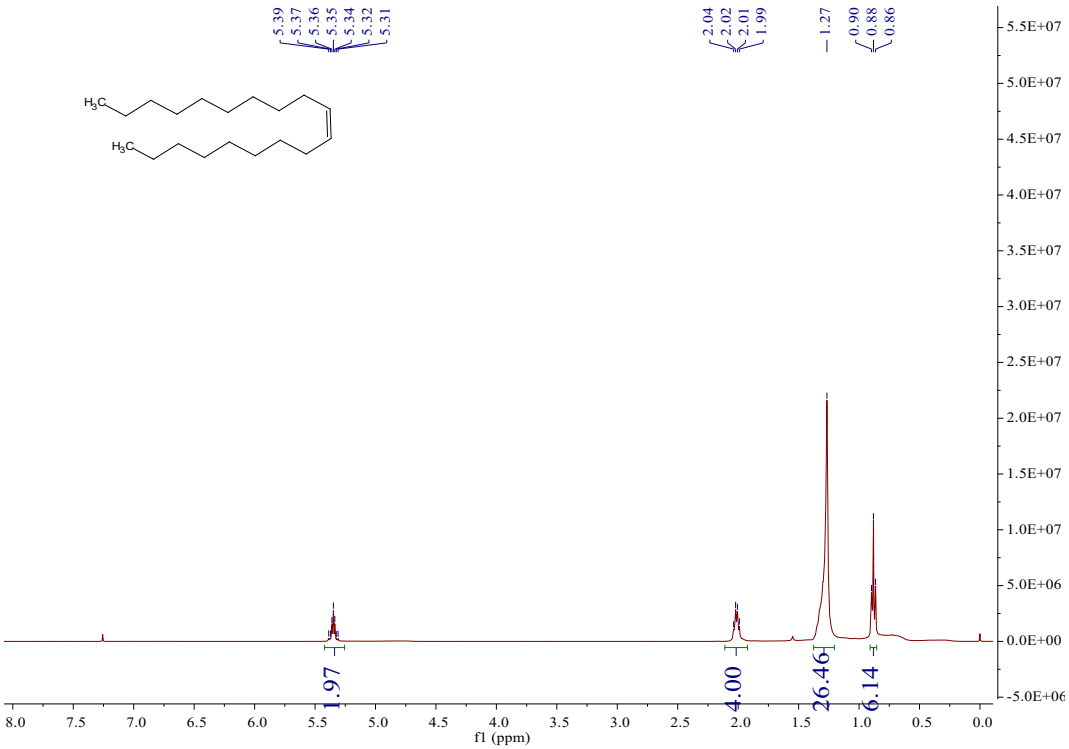


Fig. S7. [1] H spectrum of 9-nonadecene

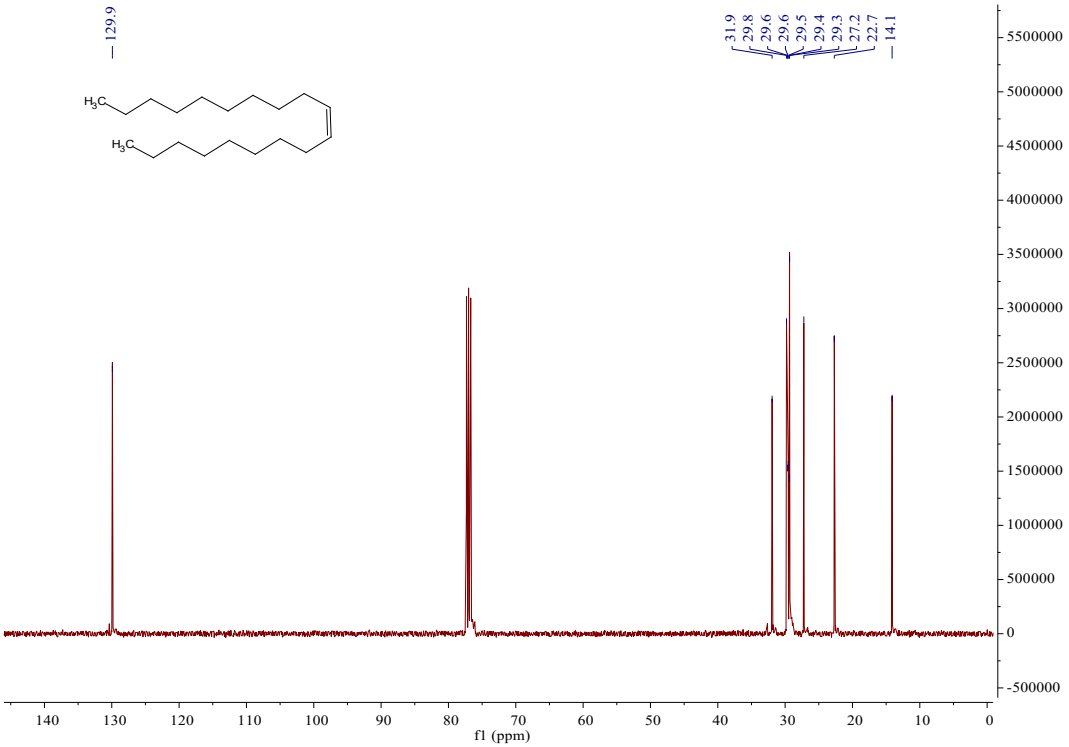
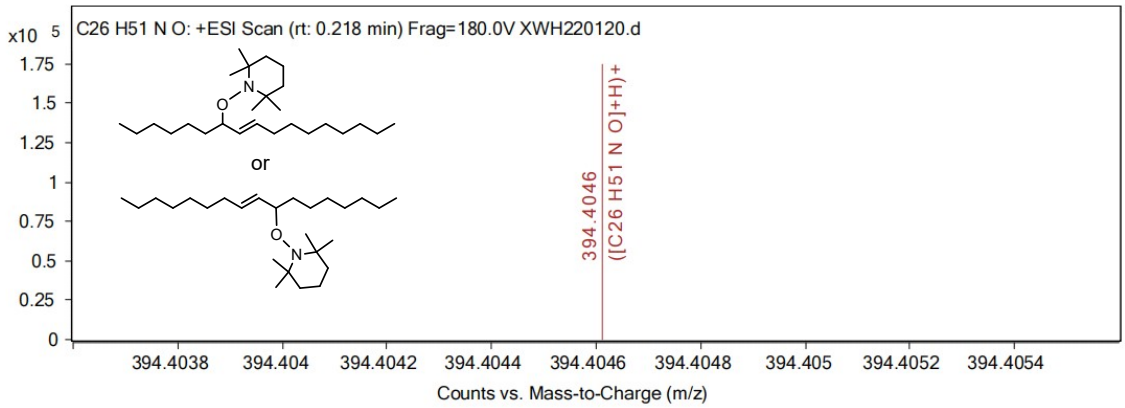


Fig. S8. [13] C spectrum of 9-nonadecene



Formula Calculator Element Limits

Element	Min	Max
C	0	100
H	0	200
O	0	10
N	0	10

Formula Calculator Results

Formula	Best	Measured Mass	Tgt Mass	Diff (ppm)	Score
C26 H52 N O	True	394.4046	394.4043	-0.77	99.48

Fig. S9. Qualitative analysis report of the TEMPO-8-heptadecene complex ($C_{26}H_{51}NO$)

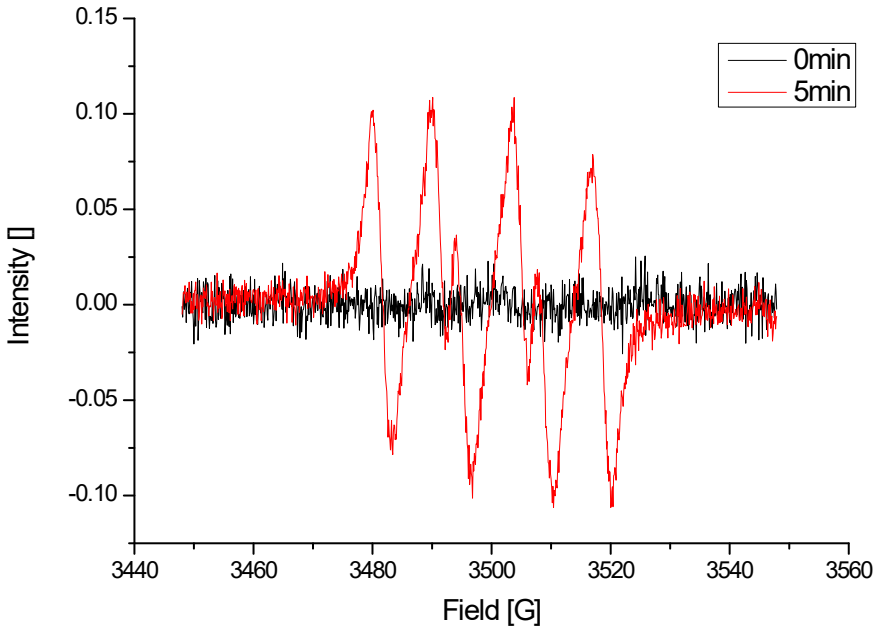


Fig. S10. EPR spectra of $O_2^{\bullet-}$ in the oxidative cleavage reaction mixture of heptadecene with the blue LED illumination at 0 min (without illumination) and 5 min (blue LED illumination). Reaction mixture contains 10 mg heptadecene and 2.5 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, dissolved in 1 mL MeCN. 30 µL Samples were combined with 30 µL DMPO (200 mM in MeOH) individually prior to analysis.

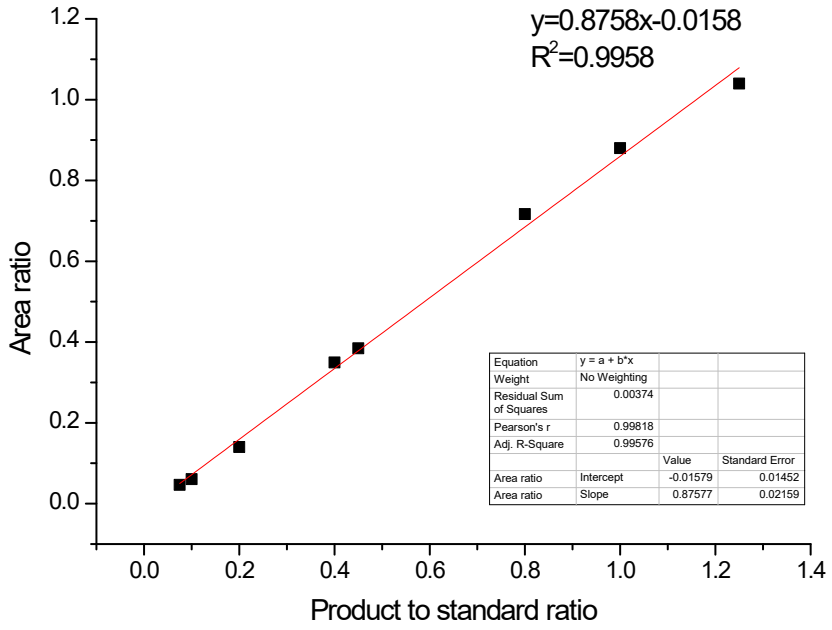


Fig. S11. Calibration curve of pentane (nonane as internal standard)

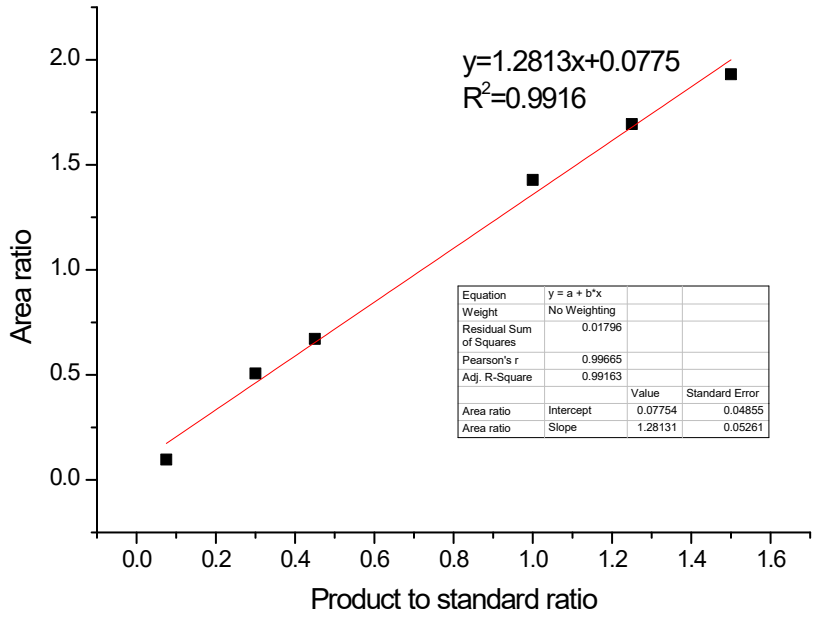


Fig. S12. Calibration curve of hexane (nonane as internal standard)

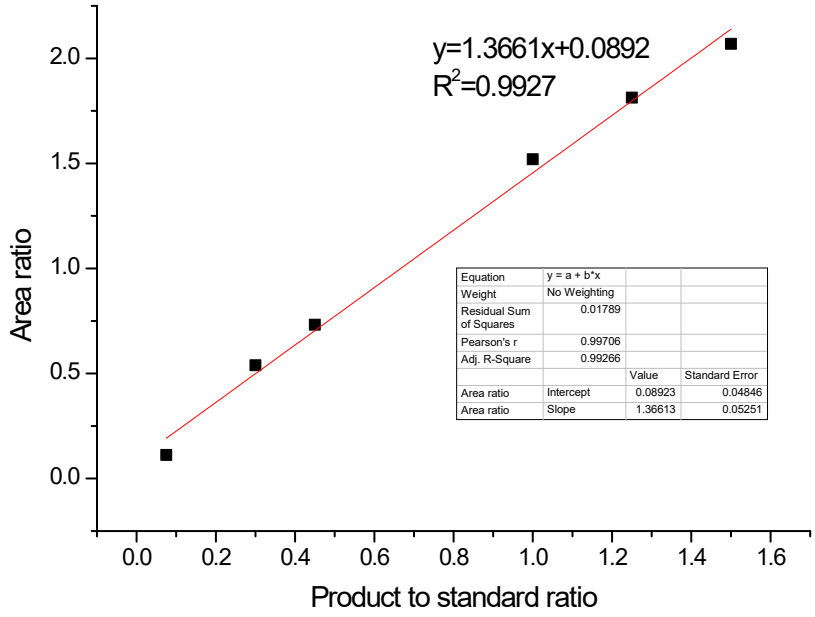


Fig. S13. Calibration curve of heptane (nonane as internal standard)

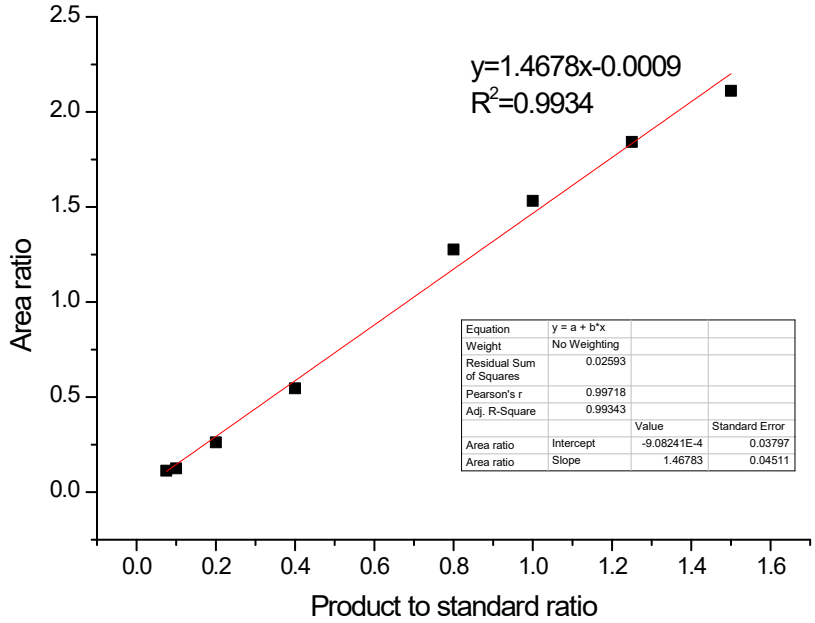


Fig. S14. Calibration curve of octane (nonane as internal standard)

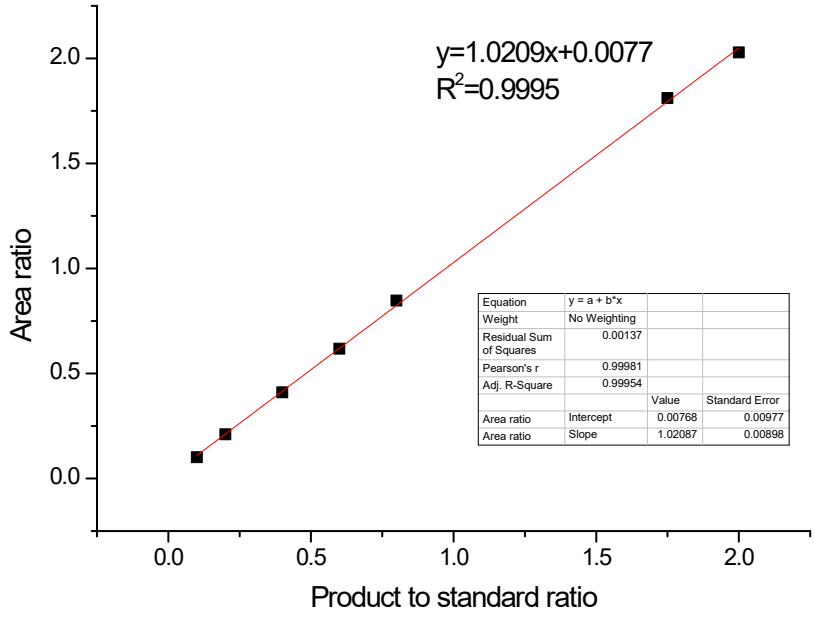


Fig. S15. Calibration curve of nonane (heptadecane as internal standard)

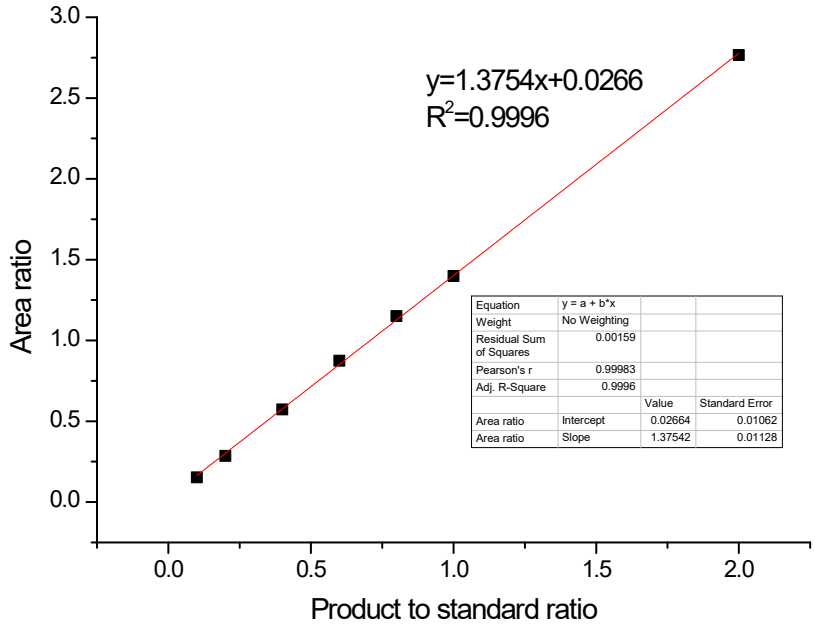


Fig. S16. Calibration curve of dodecane (nonane as internal standard)

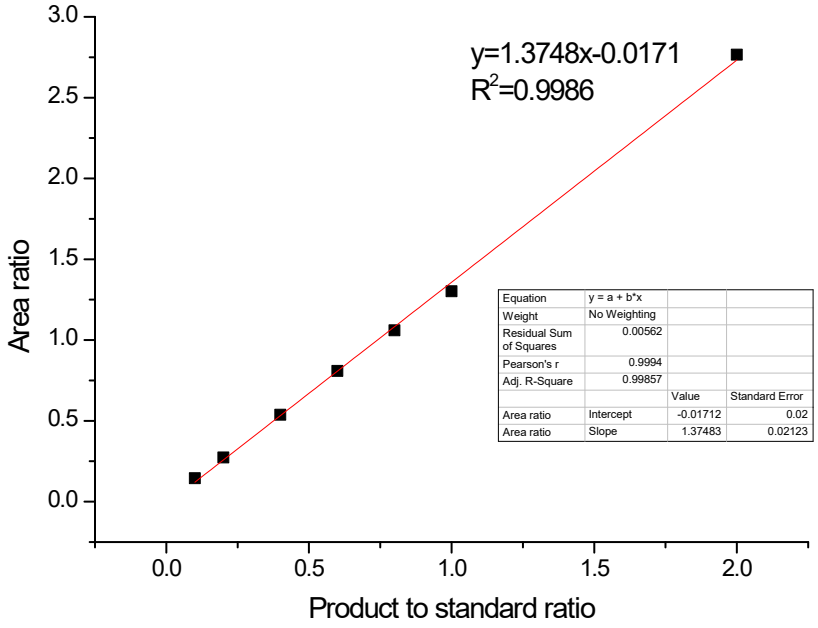


Fig. S17. Calibration curve of tridecane (nonane as internal standard)

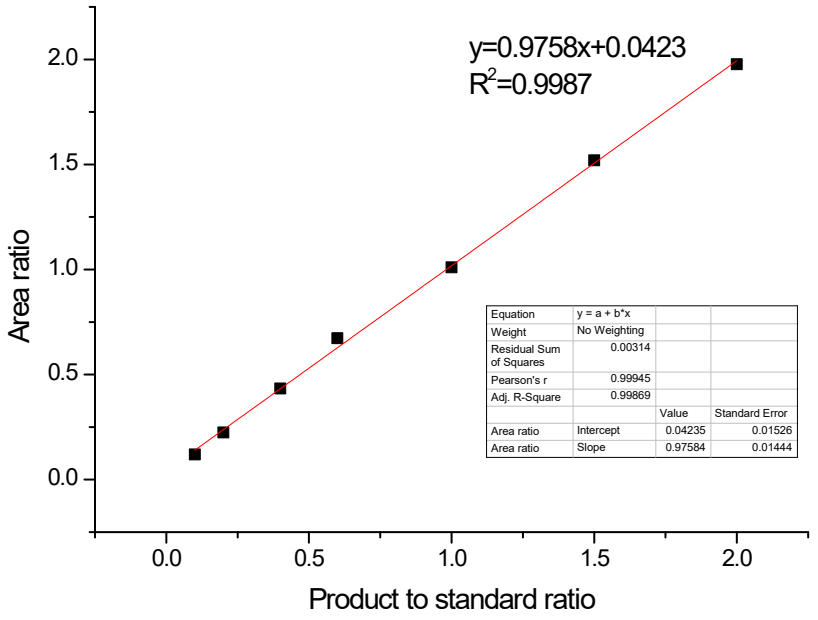


Fig. S18. Calibration curve of 8-heptadecene (nonane as internal standard)

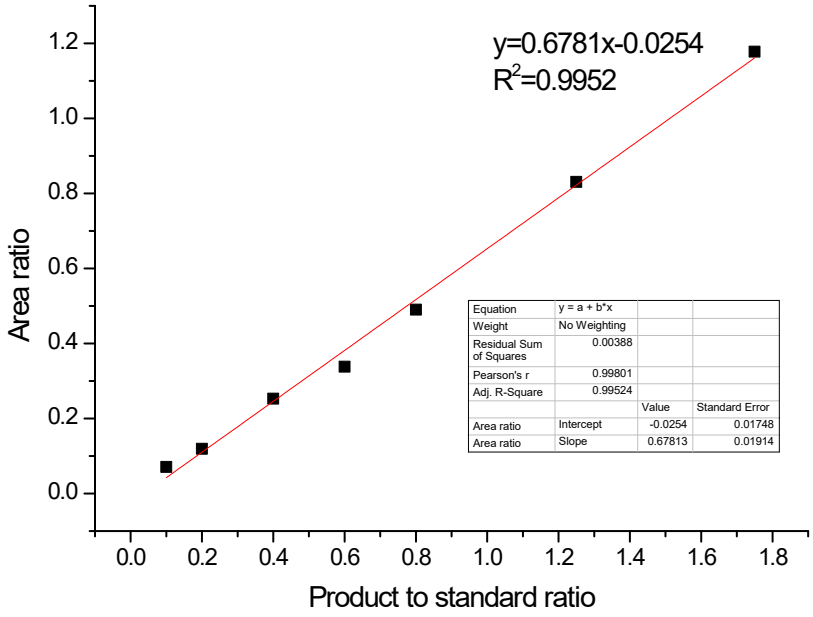


Fig. S19. Calibration curve of hexanoic acid (myristic acid as internal standard)

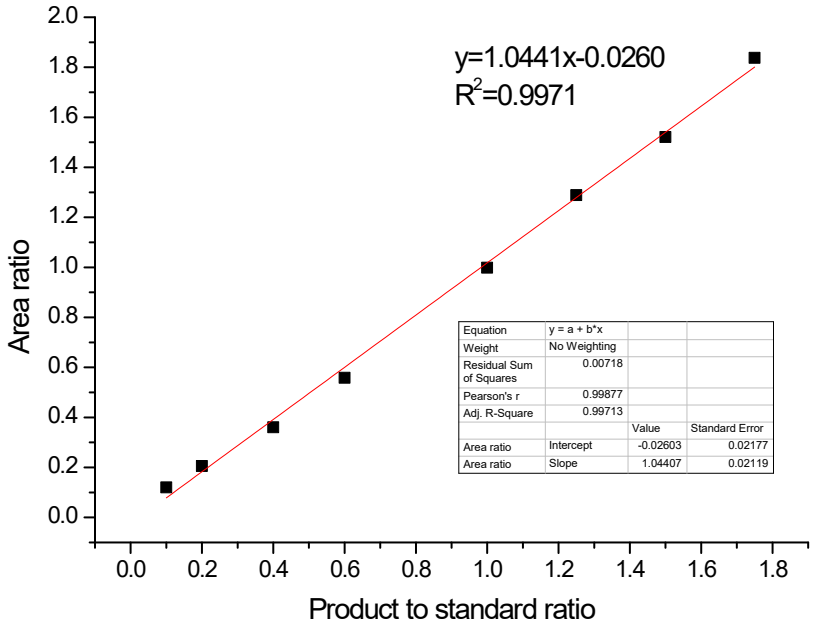


Fig. S20. Calibration curve of heptanoic acid (myristic acid as internal standard)

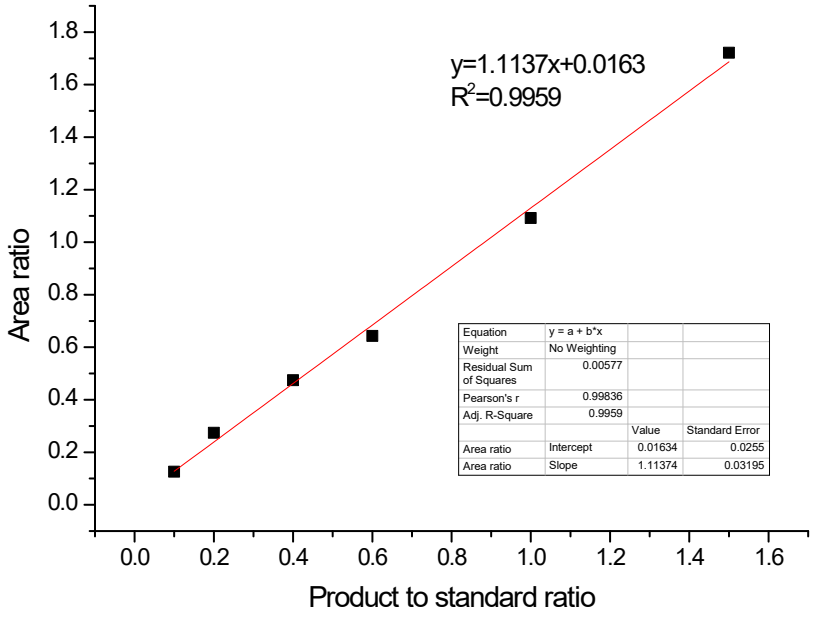


Fig. S21. Calibration curve of octanoic acid (myristic acid as internal standard)

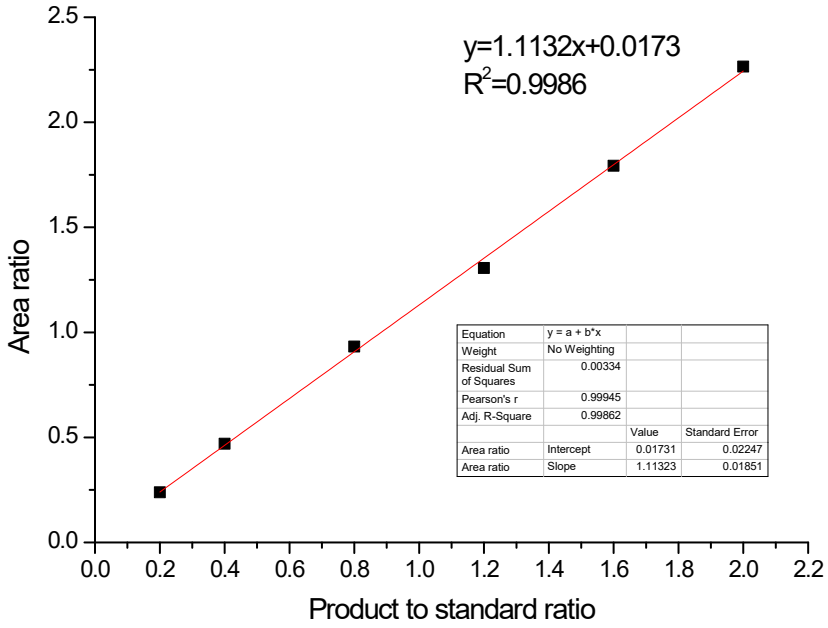


Fig. S22. Calibration curve of pelargonic acid (myristic acid as internal standard)

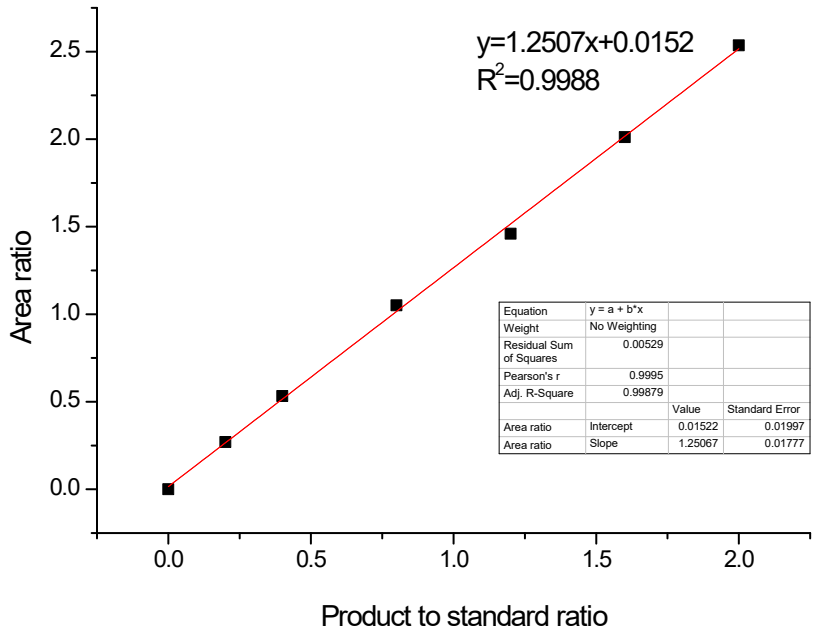


Fig. S23. Calibration curve of capric acid (myristic acid as internal standard)

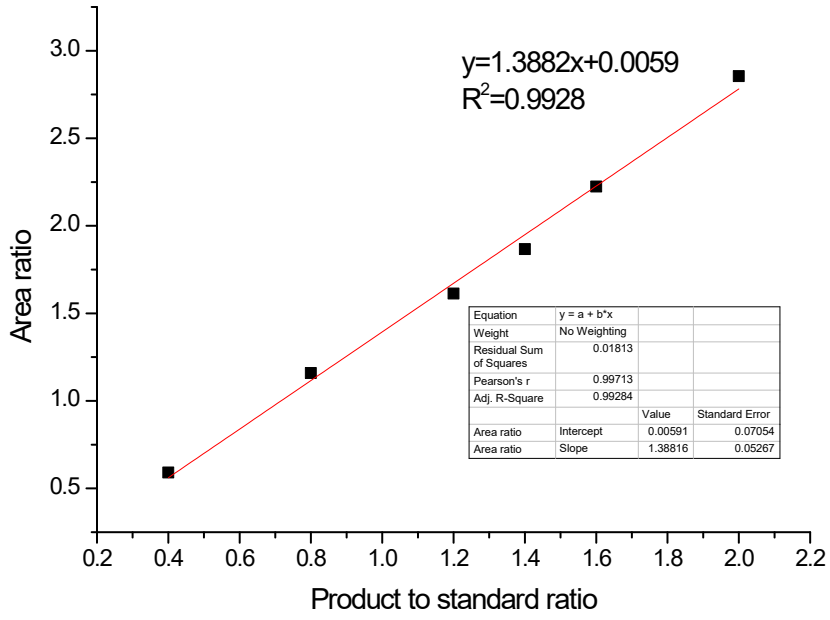


Fig. S24. Calibration curve of tridecanoic acid (myristic acid as internal standard)

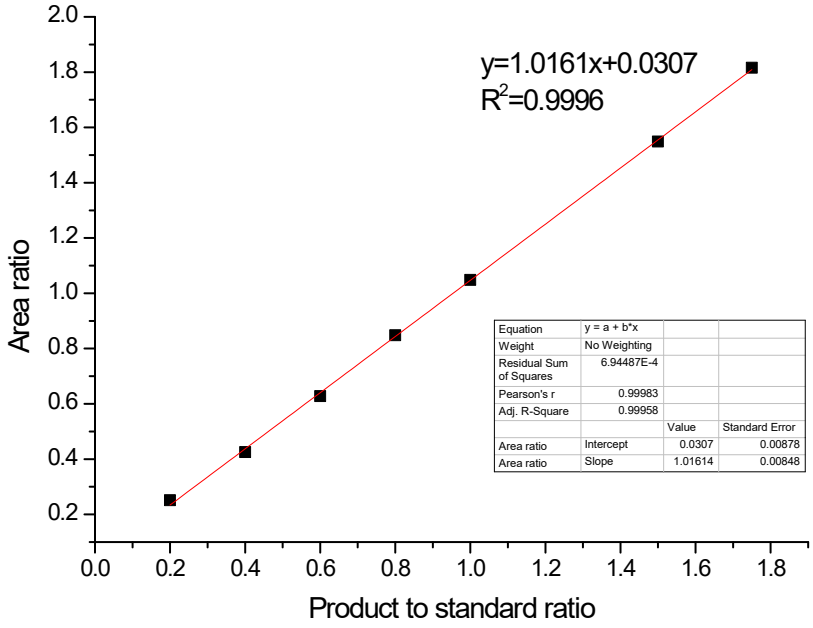


Fig. S25. Calibration curve of myristic acid (nonanoic acid as internal standard)

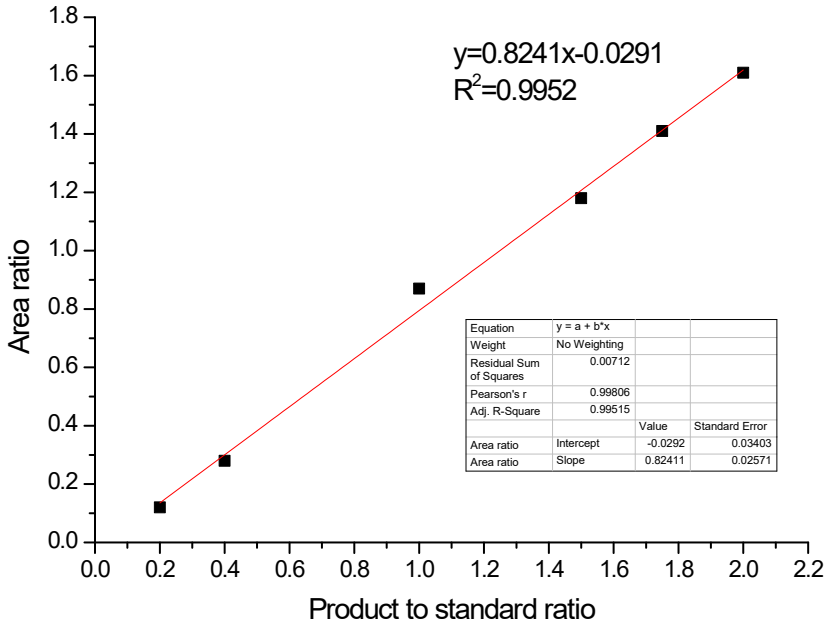


Fig. S26. Calibration curve of oleic acid (pelargonic acid as internal standard)

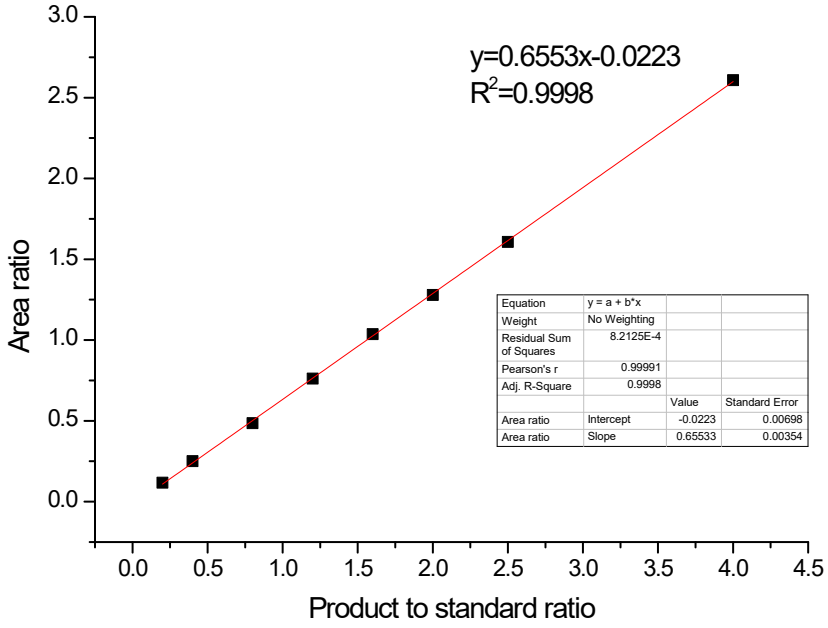


Fig. S27. Calibration curve of suberic acid (myristic acid as internal standard)

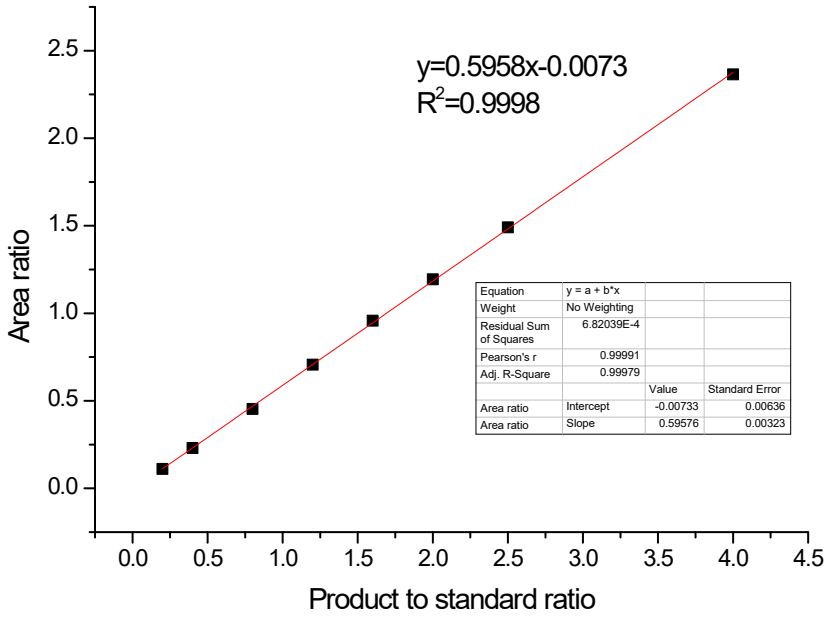


Fig. S28. Calibration curve of azelaic acid (myristic acid as internal standard)

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