ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Photocatalyzed Hydrodecarboxylation of Fatty Acids: A Prospective Method to Produce Drop-in Biofuels.

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1. General Information

All reagents and solvents were purchased (Dinâmica, Neon, Nuclear, Petroquímios, Quimex, Sigma Aldrich, Synth, Vetec) and used as received without further purification.

Gas Chromatography with Flame Ionization Detection (GC-FID) analyses were performed using a Shimadzu GC 2010 instrument equipped with a DB-5 column (0.25 mm x 30 m, Film: 0.25 µm, Agilent). Gas chromatography mass spectra (GC-MS) were taken at Thermo Scientific ISQ Quadrupole GCMS with Trace GC Ultra equipped with a DB-5MS column (0.25 mm x 30 m, Film: 0.50 µm, Agilent).

2. General procedure for the hydrodecarboxylation of lauric acid

The reaction preparation was carried out following a standard procedure: a clean and dry 10 mL glass flask was placed in an oven, and the reagents (fatty acid, photocatalyst, hydrogen transfer agent, and base) were added in predefined quantities according to the experimental plan. Since all reactions were conducted under stirring, the flasks were equipped with magnetic stir bars to promote constant homogenization of the reaction medium. Based on literature findings, it was observed that the reaction atmosphere influenced the process; thus, all flasks were sealed and purged with nitrogen gas. Subsequently, the solvent also purged with N_2 in a separate container, was added to the reaction flask using a syringe and needle. Each magnetic stirrer supported one reaction, placed under the irradiation of a single 7W blue LED lamp (~450 nm) positioned approximately 3 cm away from the flask for 24 hours. As the lamps heated over time, the system was placed under ventilation to maintain room temperature (Figure 1).

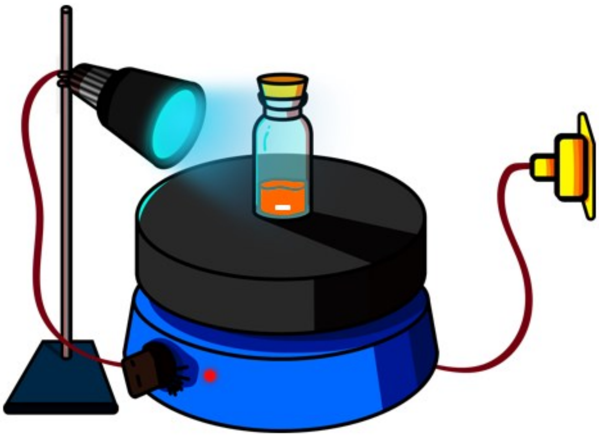


Figure 1 - Reaction scheme used to develop the methodology.

After this time, the reaction mixture was analyzed by GC-MS to determine relative yield using hexadecane as the internal standard. The samples were prepared for analysis by diluting an aliquot of the reaction mixture in hexane HPLC and then sent directly for GC-MS analysis.

3. General procedure for the hydrodecarboxylation of fatty acids

Into a clean and oven-dried 10 mL glass flask, equipped with a magnetic stir bar, fatty acid (0.2 mmol), acridinium salt (0.01 mmol), thiophenol (0.02 mmol), and sodium bicarbonate (0.02 mmol) were added. Subsequently, the flasks were sealed and purged with argon gas. Following this, the solvent (toluene/water (9:1), 2 mL), also purged with argon in a separate container, was added to the reaction flask using a syringe and needle. Finally, the flasks were placed on a magnetic stirrer under the irradiation of two 7W blue LED lamps (~450 nm), positioned approximately 3 cm away from the flask for 24 hours. Absolute yield and conversion of these reactions were determined by GC-FID with hexadecane as the internal standard.

4. Determination of product conversion and yield by GC-FID

Product yield was determined by USEPA 8015C method[1] using a calibration curve prepared with certified *n*-alkanes standards from Accusstandard (DRH-008S-R2) which was specifically developed for the analysis of hydrocarbons in the range from *n*-C_8 to *n*-C_{40}. Conversion of the starting materials was calculated by comparing the areas associated with the fatty acids in the initial and final obtained chromatograms. The conversion and the yield of each fatty acid were calculated using the following equations (1) and (2).

$$\text{Conversion (\%)} = \left(1 - \frac{\mathrm{C_{FA}}}{\mathrm{C_{FA}^{0}}}\right) \text{x } 100 \quad (1)$$

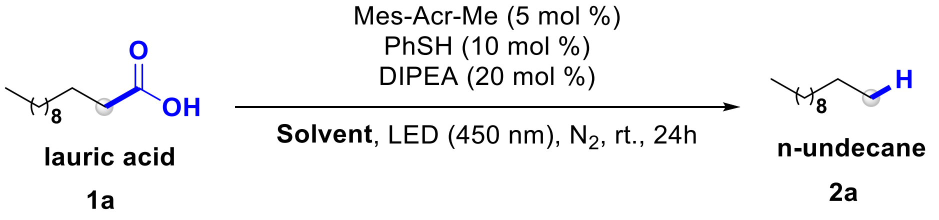
where C_F and $C_F{}^0$ are the contents of fatty acids after reaction and before reaction, respectively.

$$\text{Yield (\%)} = \left(\frac{C_H}{C_{Hmax.}}\right) \text{x } 100 \quad (2)$$

where C_H and C_{Hmax} are the contents of hydrocarbons in the product and the maximum theoretical content, respectively.

5. Optimization Studies

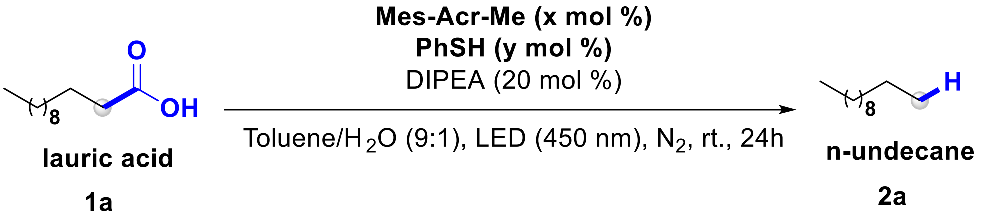
5.1 Solvent Screening



Entry	**Solvent**	Yield (%)[b]
1	DCM	<5
2	MeCN	<5
3	AcOEt	<5
4	Hexane	21
5	Toluene	22
6	$CHCl_3$	16
7	Ethanol	12
8	Methanol	16
9	DMF	-
10	THF	-
11	DCM/H_2O (9:1)	<5
12	MeCN/H_2O (9:1)	9
13	Hexane/H_2O (9:1)	35
14	Toluene/H_2O (9:1)	44
15	$CHCl_3$/H_2O (9:1)	17
16	MeOH/H_2O (9:1)	-

[a] Reactions carried out on a 0.2 mmol scale in N_2-sparged solvents [0.1M] at ambient temperature for 24 h. [b] Yields determined by GC-MS using hexadecane as internal standard.

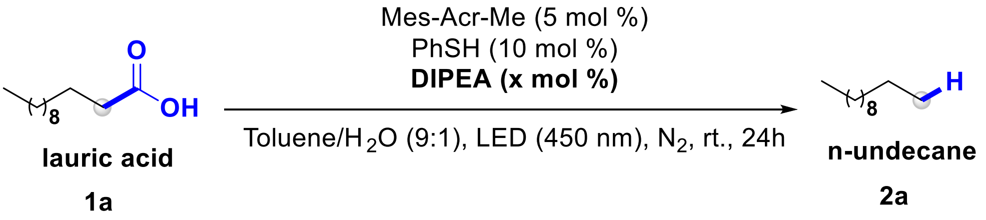
5.2 Optimization of catalyst stoichiometry



Entry	**Catalyst (x mol %)**	**PhSH (y mol %)**	Yield (%)[b]
1	1	10	20
2	2.5	10	28
3	3	10	25
4	5	5	40
5	5	20	61
6	10	10	53
7	10	20	65

[a]Reactions carried out on a 0.2 mmol scale in N_2-sparged solvents [0.1M] at ambient temperature for 24 h. [b]Yields determined by GC-MS using hexadecane as internal standard.

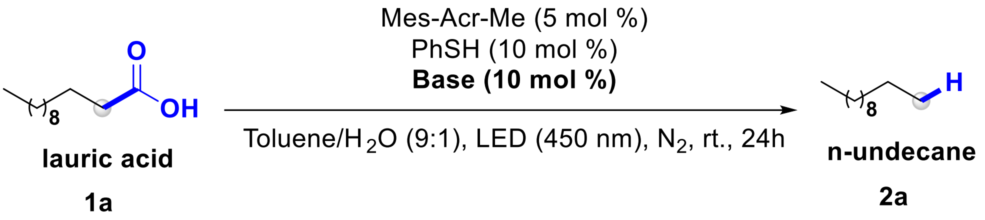
5.3 Optimization of base stoichiometry



Entry	**DIPEA (x mol %)**	Yield (%)[b]
1	10	59
2	50	60
3	100	35

[a]Reactions carried out on a 0.2 mmol scale in N_2-sparged solvents [0.1M] at ambient temperature for 24 h. [b]Yields determined by GC-MS using hexadecane as internal standard.

5.4 Base optimization



lauric acid

1a

n-undecane

2a

Entry	**Base (10 mol %)**	Yield (%)[b]
1	Et_3N	60
2	DMAP	38
3	Piridine	33
4	K_2CO_3	59
5	K_2HPO_4	29
6	$NaHCO_3$	57

[a]Reactions carried out on a 0.2 mmol scale in N_2-sparged solvents [0.1M] at ambient temperature for 24 h. [b]Yields determined by GC-MS using hexadecane as internal standard.

6. Determination of the catalyst's turnover number (TON) and turnover frequency (TOF)[3]

To calculate the turnover number (TON) and turnover frequency (TOF) of the homogeneous photocatalyst, the equations below were used:

$$\mathrm{TON} = \left(\frac{\text{Moles of desired product formed}}{\text{Moles of catalyst}}\right) \quad (3)$$

$$\mathrm{TOF} = \left(\frac{\text{Turnover number (TON)}}{\text{Time of reaction (s)}}\right) \quad (4)$$

7. Procedure for Licuri oil hydrolysis

The hydrolysis reaction to obtain free fatty acids was adapted from the methodology found in the literature.[2] Initially, 30 mL of ethanolic potassium hydroxide solution (90% v/v, 1.75 mol/L) was added to 5.0 g of vegetable oil. In a round-bottom flask, the mixture was subjected to 65°C with constant stirring, and the reaction progress was monitored by thin-layer chromatography (TLC). The average reaction time was 5 hours. Once the process was completed, approximately 30 mL of distilled water was added to the reaction mixture, and the unsaponifiables were extracted with hexane (2 × 20 mL). Next, the alcoholic phase was collected and acidified with a HCl 6 M to reach a pH close to 1. Afterward, the resulting fatty acids were recovered by extraction with hexane. Subsequently, the extract was washed with distilled water until it reached a neutral pH. Finally, the organic fraction was dried with anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation to obtain the free fatty acids.

8. Supplementary references

1 USEPA, United States Environmental Protection Agency. "Method 8015C (SW-846): Nonhalogenated Organics by Gas Chromatography " Revision 3, February 2007. Washington, DC.
2 J. Salimon, B. M. Abdullah, N. Salih, Chem. Cent. J. 2011, 5, 1–9.
3 S. Kozuch and J. M. L. Martin, *ACS Catal*, 2012, 2, 2787–2794.