

## SUPPLEMENTARY INFORMATION

# Nitrogen-doped carbon dots in transesterification reactions for biodiesel synthesis

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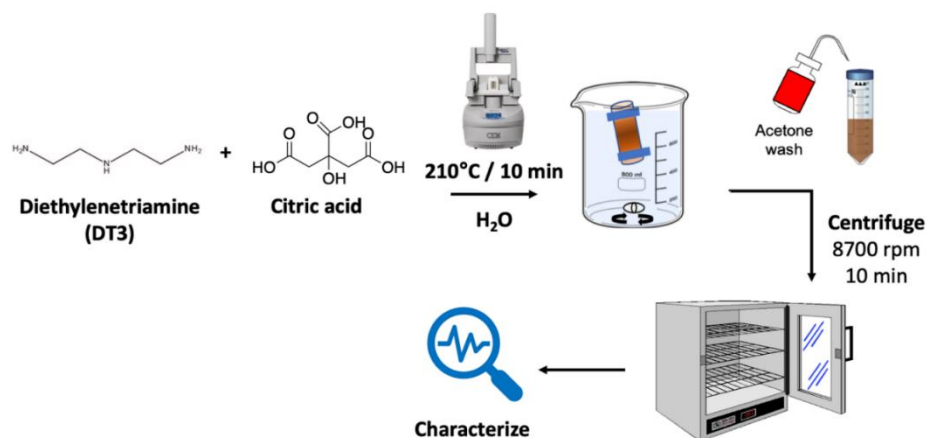
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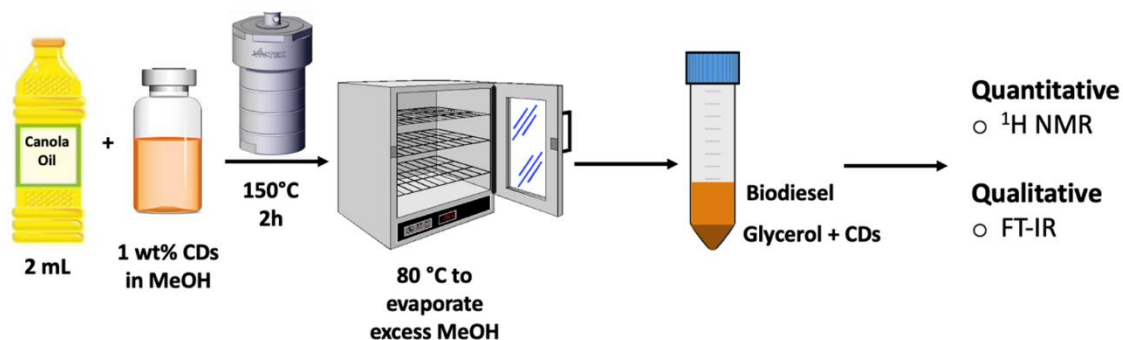
## 1. Synthesis Protocol



| [DT3] mM | Volume ( $\mu\text{L}$ ) | Passivating Agent - 375 mM | Volume ( $\mu\text{L}$ ) |
|----------|--------------------------|----------------------------|--------------------------|
| 125      | 216                      | ED2                        | 400                      |
| 250      | 432                      | TT4                        | 893                      |
| 375      | 648                      | TP5                        | 1138                     |
| 750      | 1296                     | PH6                        | 1468                     |

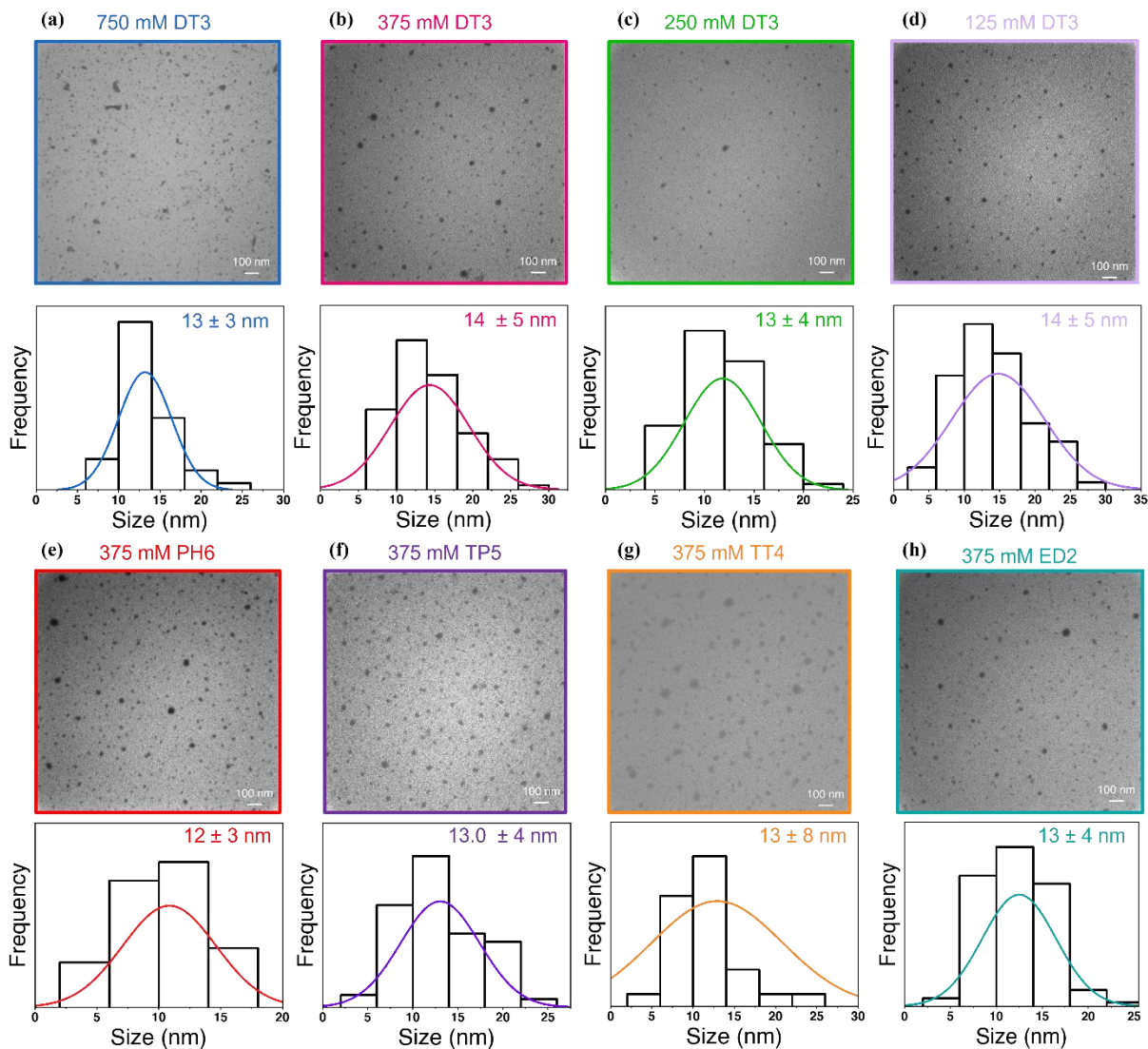
**Figure S1:** Schematic illustration of the synthesis of amine-passivated CDs. CDs were synthesized via a one-step microwave-assisted reaction of citric acid and the amine-passivating agent (ED2, DT3, TT4, TP5 or PH6) using a CEM Discover SP microwave reactor. Tabulated volumes required to prepare 16 mL of 125-, 250-, 375- and 750-mM amine-passivated CDs. Each sample contained 500 mM citric acid and was synthesized at 210°C.

## 2. Biodiesel Reaction Protocol



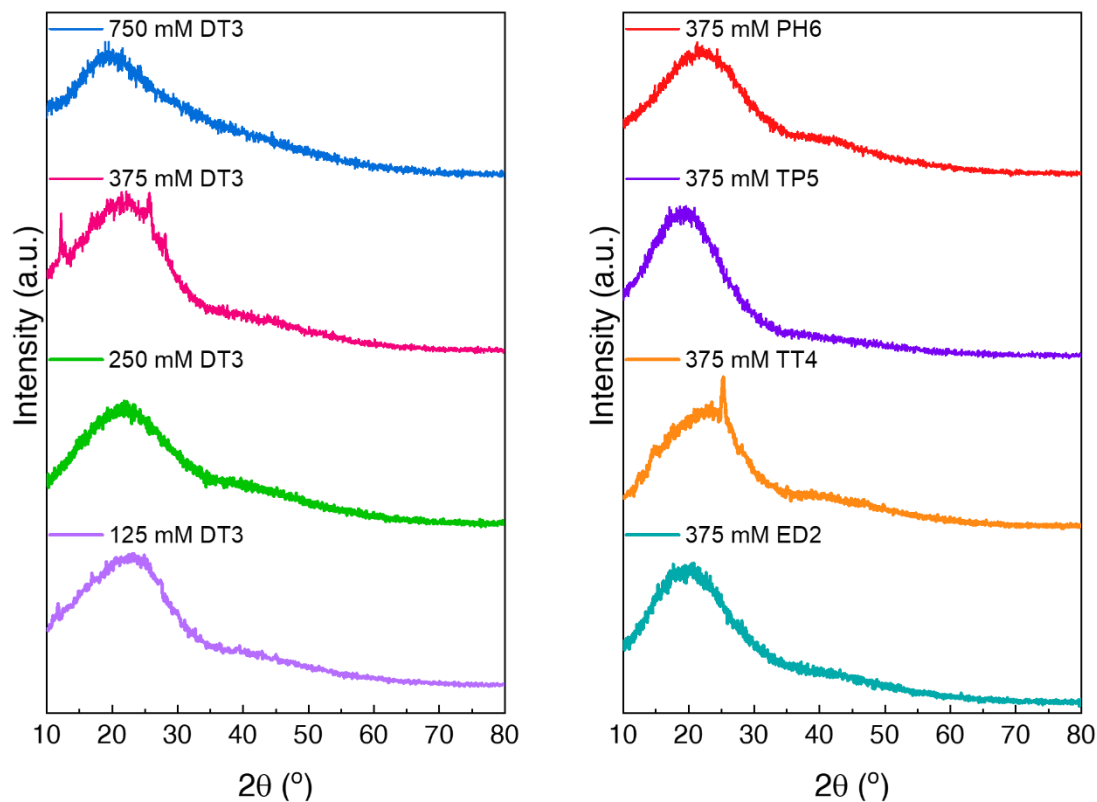
**Figure S2:** Schematic illustration of the transesterification of canola oil to biodiesel using the N-CD catalysts.

### 3. Transmission Electronic Microscopy



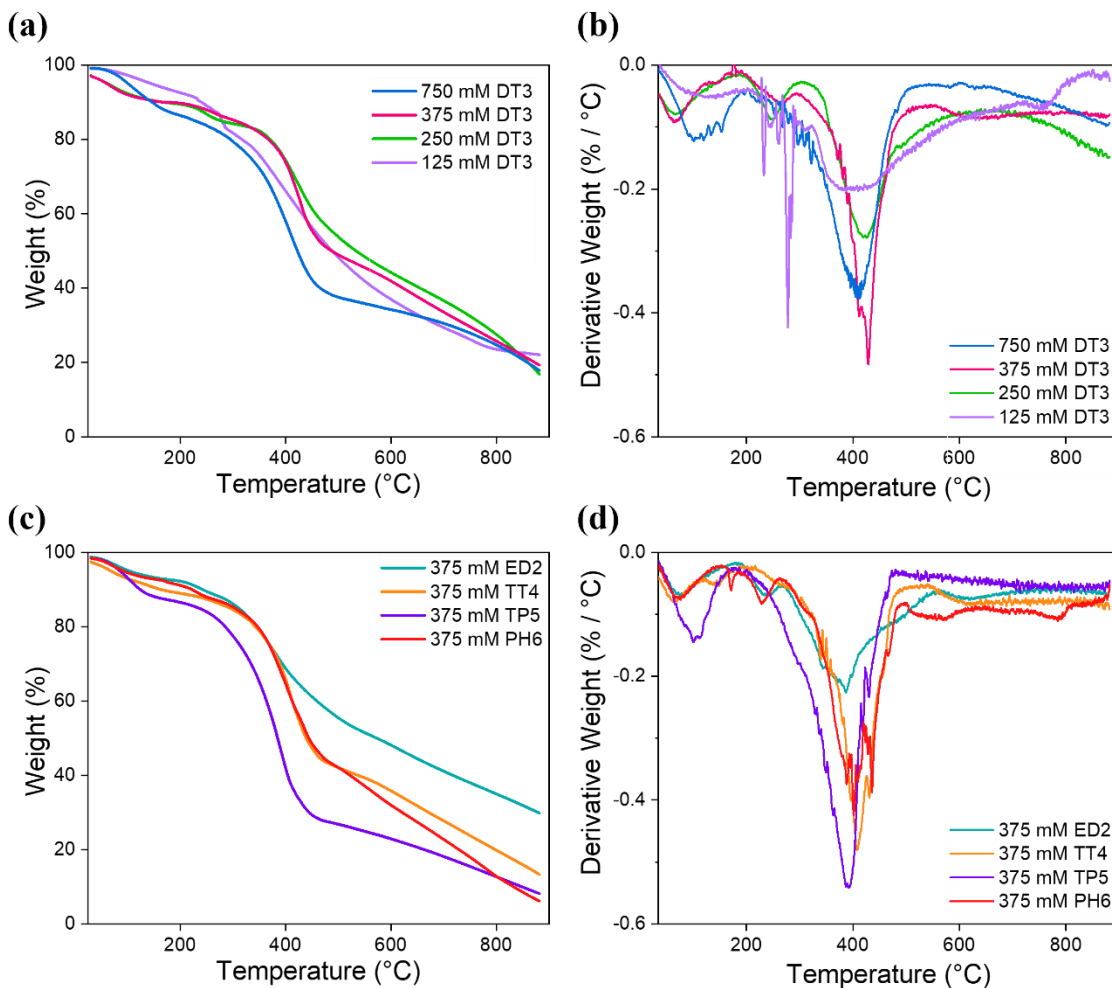
**Figure S3:** Transmission electronic microscopy (TEM) images for the N-CDs. All images present quasi-spherical carbon dots with minimal signs of aggregation. Statistical analysis for the samples synthesized with different concentrations of DT3 indicated a Gaussian size distribution, with average sizes of  $13 \pm 3$  nm,  $14 \pm 5$  nm,  $13 \pm 3$  nm, and  $14 \pm 5$  nm for (a) 750, (b) 375, (c) 250 and (d) 125 mM CDs, respectively. Similarly, the statistical analysis for the different amine passivating agents also displayed a Gaussian size distribution, with the average size distribution of  $12 \pm 3$  nm,  $13 \pm 4$  nm,  $13 \pm 8$  nm and  $13 \pm 4$  nm for 375 mM (e) PH6, (f) TP5, (g) TT4 and (h) ED2 CDs, respectively. Thus, the variation in concentration or amine-passivating agents did not present a significant variation in the morphology or size distribution of the N-CDs.

#### 4. Powder X-Ray Diffraction



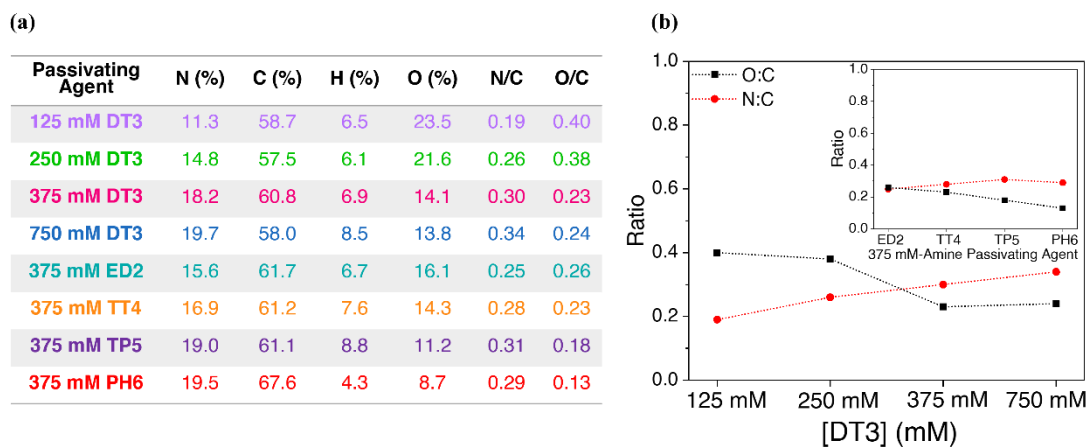
**Figure S4:** PXR D diffractograms for all synthesized protonated amine-passivated CDs. Diffraction patterns for all synthesized N-CDs exhibit an amorphous halo in the range 10–80°  $2\theta$  and lack any crystalline reflections, confirming that the prepared CDs were non-crystalline. The small peak centered at 26°  $2\theta$  observed for 375 mM DT3 and TT4 is likely associated with the presence of the aromatic graphitic structures in the core of the N-CDs.

## 5. Thermogravimetric Analysis



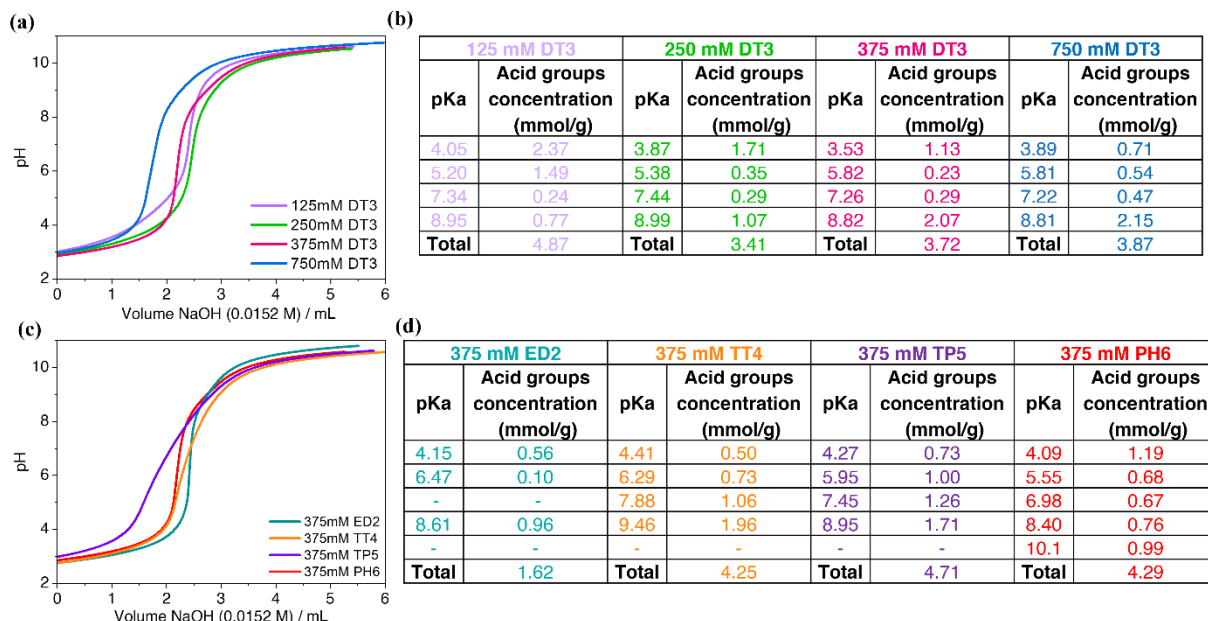
**Figure S5:** (a) Thermogravimetric analysis of the N-CDs synthesized using variable concentrations (125 to 750 mM) of DT3 and (c) 375 mM of different amine passivating agents and their differential thermogravimetric profiles (b) and (d), respectively. The differential thermogravimetry curves for all N-CDs display four-step decomposition profiles. The initial ~10% weight loss occurs at ~150°C, ascribed as the evaporation of water adsorbed CDs' surface. The second weight loss of 10-20% occurring at ~300°C is attributed to the decomposition of oxygenated surface groups. This inference is supported by a pronounced weight loss observed for the 125 mM DT3-CDs, containing the highest concentration of oxygenated surface groups relative to the other DT3-CDs based on the CHN results. The third weight loss of ~20-30% occurring at ~400°C is attributed to the decomposition of nitrogenated surface groups. This is supported by the intense weight losses for the 375 mM DT3-, 750 mM DT3-, 375 mM TT4-, 375 mM TP5- and 375 mM PH6-CDs, which contain higher concentrations of nitrogenated surface groups relative to the other amine-passivated CDs. The final weight loss of ~30-40% at ~800°C is related to the decomposition of the  $sp^2$  core. Finally, there is a ~10-20% residual weight remaining at 900°C caused by  $Na^+$  ions adsorbed to the surface of the N-CDs upon deprotonation with NaOH

## 6. Elemental Analysis



**Figure S6: (a)** Elemental analysis of the N-CDs. The percentage of oxygen was determined by subtraction, taking the percentage of sodium obtained by the TGA into account for this calculation. The CHN results indicate that the catalysts are primarily comprised of carbon, nitrogen, oxygen and hydrogen, as expected due to the precursors used in the synthesis of the N-CDs. **(b)** The increasing DT3 concentration increases the N:C ratio, while the O:C ratio decreases. Similarly, the N:C ratio augments with the increasing number of amines present in the passivating agent, with a concomitant decrease in the O:C ratio.

## 7. Potentiometric Titration



**Figure S7:** (a) Potentiometric titration curves obtained for the DT3-CDs using different concentrations of the passivating agent and (c) 375 mM of the different passivating agents. Results obtained by the non-linear fitting of the titration curves for the former (c) and the latter. According to the functional groups observed in the FT-IR results, the N-CDs moieties presenting pKa ranging from 2 to 6 were scribed as associated with carboxylic acids and from 7 to 9 to amines. According to the titration results, the increase in DT3 concentration from 125 to 750 mM leads to a decrease in the concentration of carboxylic acids from 80 to 32%, with a concomitant increase in the amines from 20 to 67%. The variations in the passivation agent did not present major effects on the concentration of carboxylic acids that remained fairly constant from 30 to 40%. Nonetheless, a major variation in the amines percentage was observed, decreasing from 60% for ED2 to 33% for PH6.

## 8. Zeta Potential

(a)

| Amine-Passivating Agent | Protonated          |                                   | Deprotonated        |                                   |
|-------------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|
|                         | Zeta-Potential (mV) | Conductivity ( $\mu\text{S/cm}$ ) | Zeta-Potential (mV) | Conductivity ( $\mu\text{S/cm}$ ) |
| 375 mM ED2              | -4.5                | -0.32                             | -10.3               | -0.73                             |
| 375 mM TT4              | -2.2                | -0.16                             | -5.2                | -0.37                             |
| 375 mM TP5              | 0.3                 | 0.02                              | -4.7                | -0.33                             |
| 375 mM PH6              | 1.2                 | 0.08                              | -14.2               | -1.01                             |

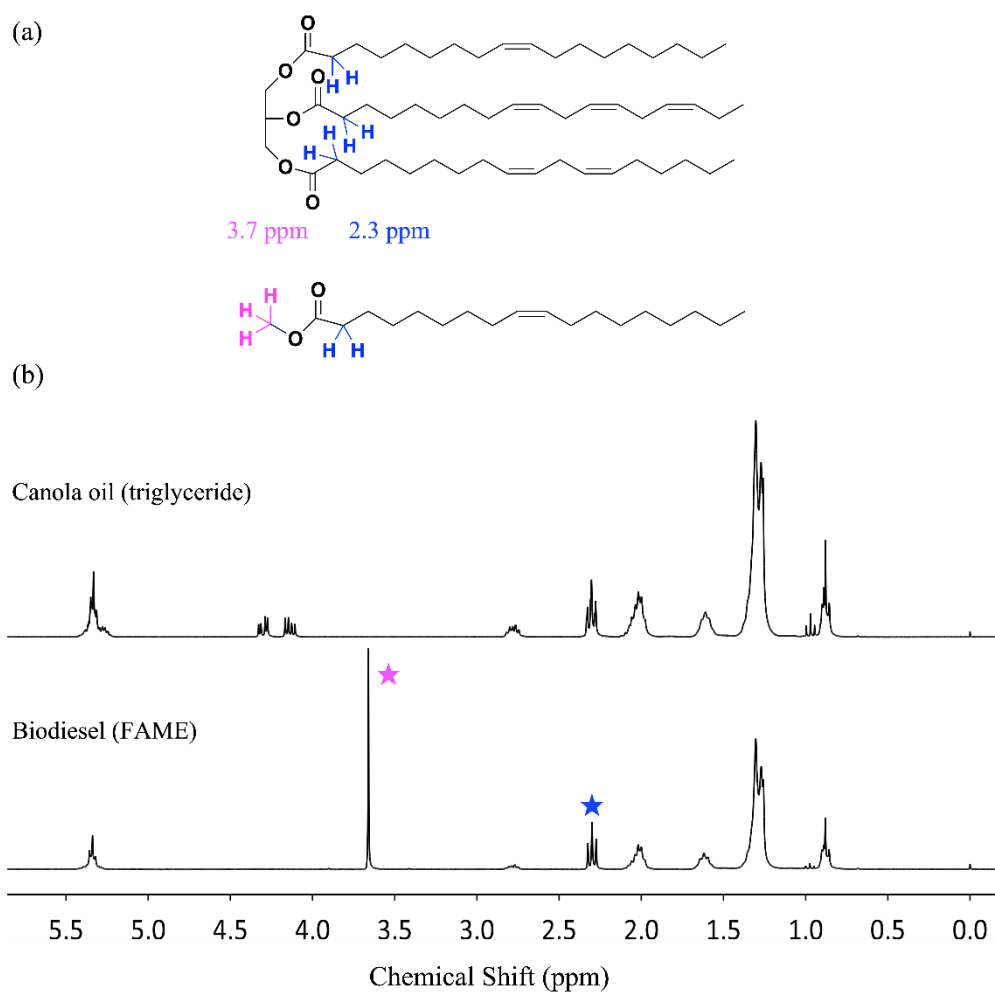
(b)

| Amine-Passivating Agent | Protonated          |                                   | Deprotonated        |                                   |
|-------------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|
|                         | Zeta-Potential (mV) | Conductivity ( $\mu\text{S/cm}$ ) | Zeta-Potential (mV) | Conductivity ( $\mu\text{S/cm}$ ) |
| 125 DT3                 | 7.4                 | 0.52                              | -29.6               | -2.10                             |
| 250 DT3                 | 9.4                 | 0.66                              | -26.0               | -1.85                             |
| 375 DT3                 | 0.5                 | 0.04                              | -16.1               | -1.14                             |
| 750 DT3                 | 1.4                 | 0.10                              | -20.0               | -1.42                             |

**Figure S6:** The surface charge of the N-CDs was investigated by zeta potential analysis, indicating that all materials present a negative surface charge. **(a)** For the N-CDs synthesized using different concentrations of DT3, a surface charge of -29.6, -26.0, -26.1 and -20.0 mV was observed for 125, 250, 375 and 750 mM of DT3, respectively. **(b)** When the surface passivating agent was varied, an increase in the surface charge was observed, with values of -10.3, -5.2, -4.7 and -14.2 mV for 375 mM of ED2, TT4, TP5 and PH6-CDs.

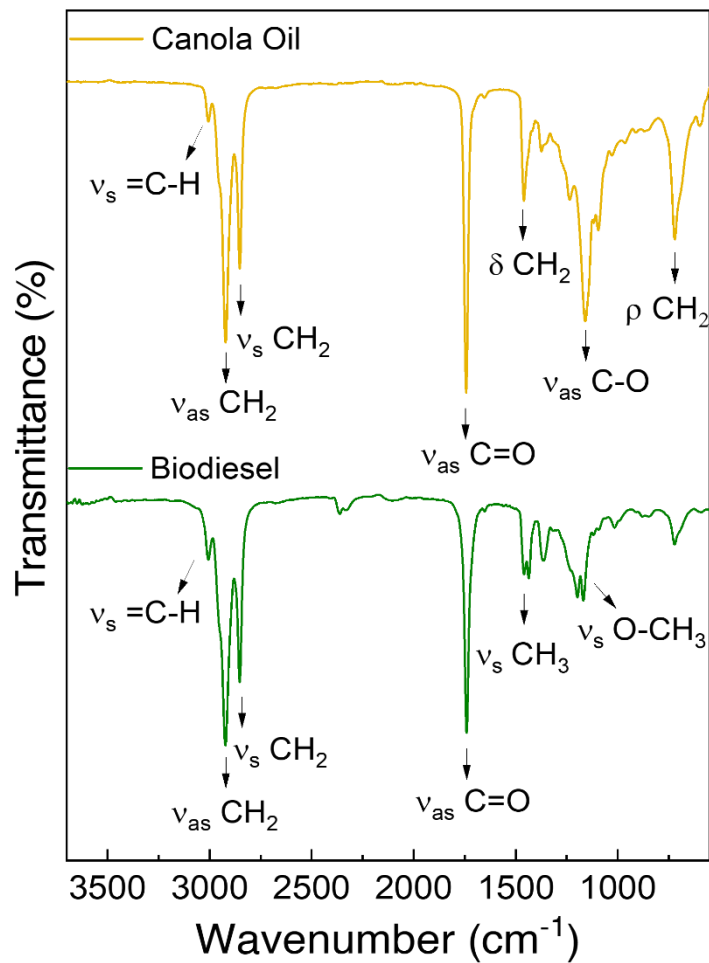


## 9. Quantitative Analysis of Biodiesel Yield by $^1\text{H}$ NMR



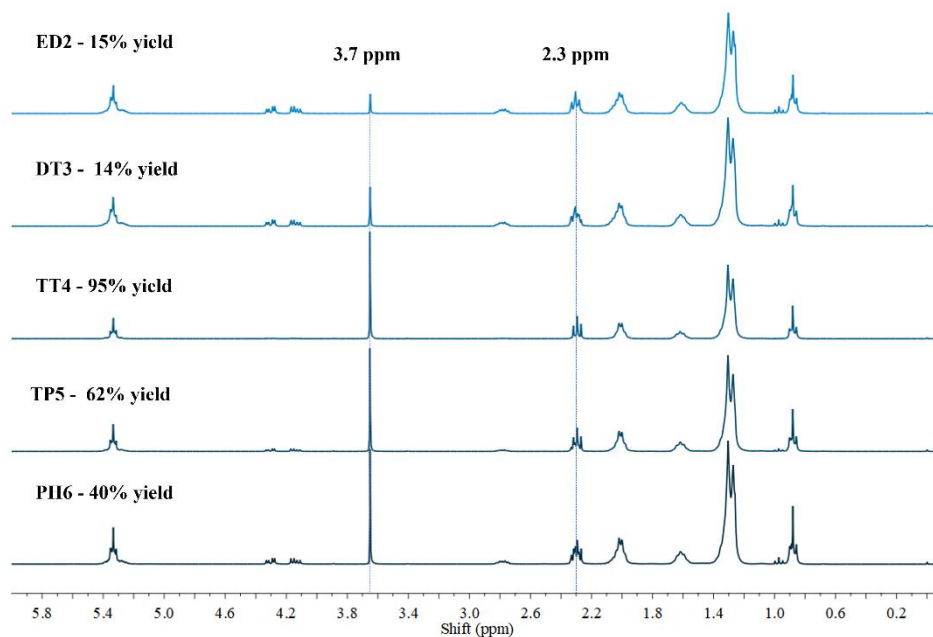
**Figure S7:** (a) Structures of triglyceride and FAME depicting the alpha-methylene and methoxy protons. (b)  $^1\text{H}$  NMR spectra of canola oil and biodiesel illustrating the singlet at 3.7 ppm pertaining to the methoxy protons of FAME.

## 10. Qualitative Analysis of Biodiesel by FT-IR

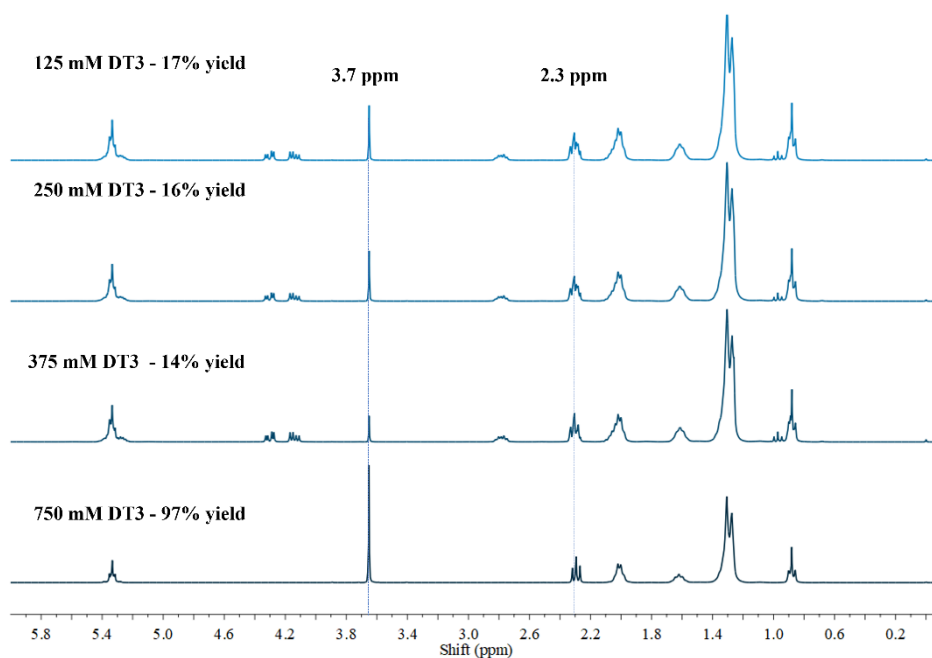


**Figure S8:** FTIR spectra of canola oil and biodiesel, representing the characteristic vibrations associated with each material. Both biodiesel and triglyceride functional groups exhibit cis sp<sup>2</sup> C-H stretching at  $\sim 3010$  cm<sup>-1</sup>, asymmetrical and symmetrical methylene stretching at  $\sim 2930$  cm<sup>-1</sup> and  $\sim 2860$  cm<sup>-1</sup>, and ester carboxyl stretching at  $\sim 1,750$  cm<sup>-1</sup>. However, significant changes are observed at  $\sim 1450$  cm<sup>-1</sup> and  $1196$  cm<sup>-1</sup>, where the characteristic splitting exhibited by the asymmetric methyl and methoxy stretching peaks, respectively, are observed in biodiesel

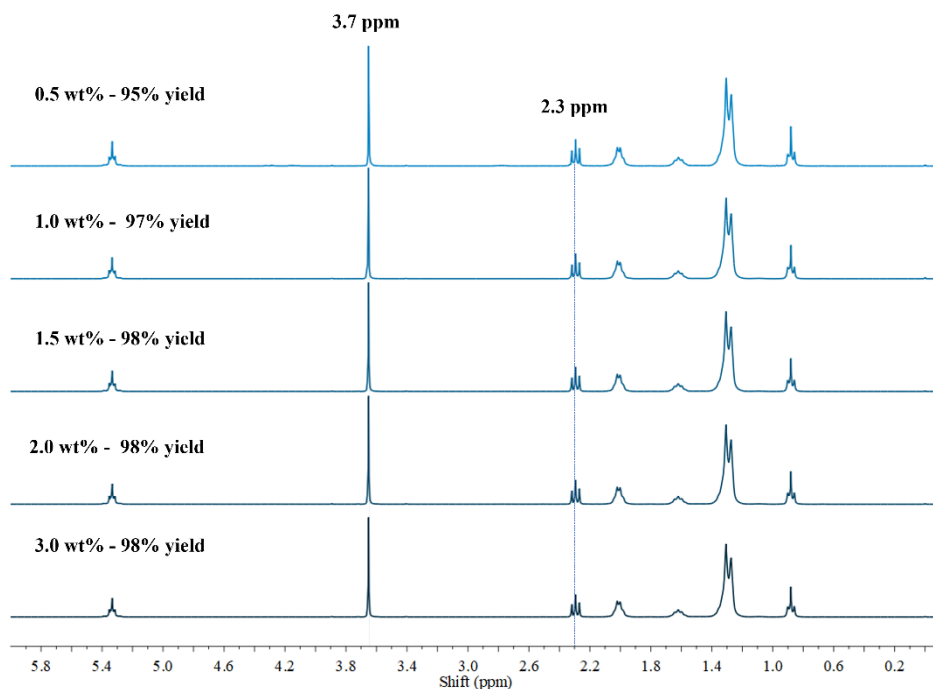
## 11. $^1\text{H}$ NMR Spectra



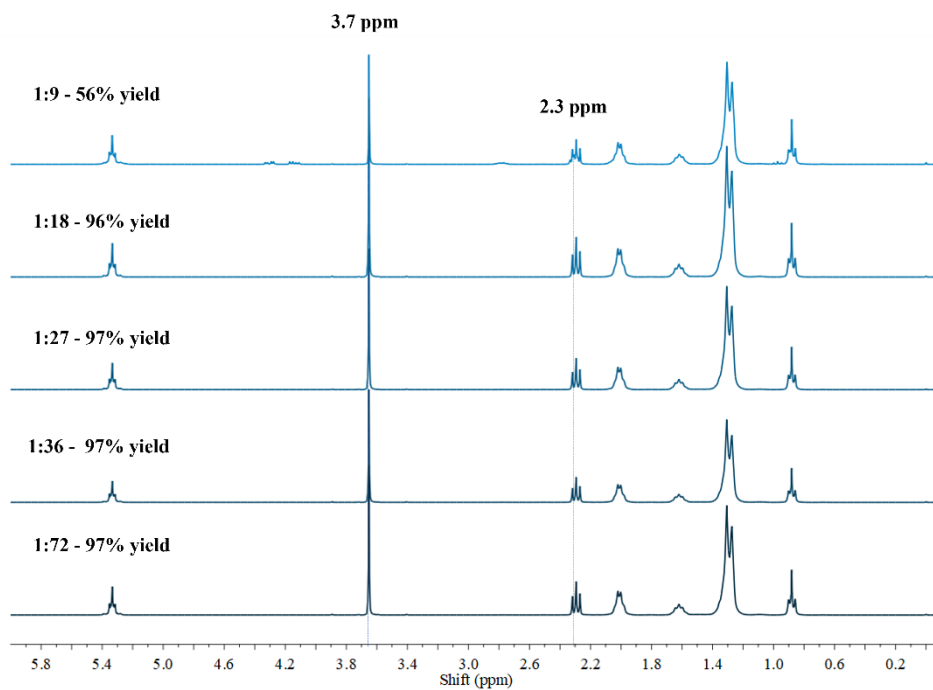
**Figure S11a:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using N-CDs with different 375 mM of amine-passivating agents. The N-CDs were loaded at a 10 wt% content with oil to methanol ratio of 1:72, and the reaction mixtures were heated at 150°C for 3 hours.



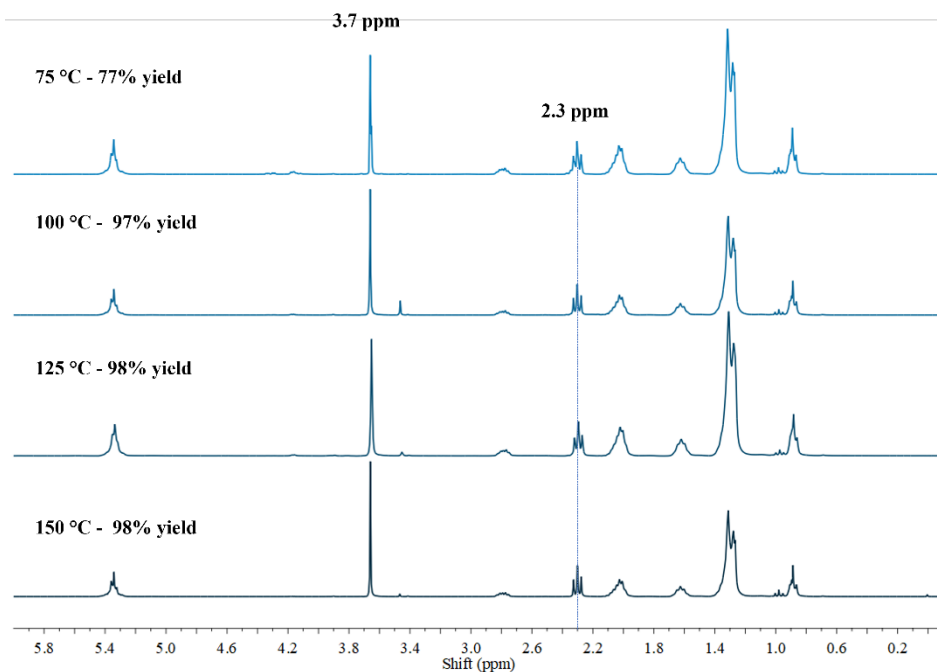
**Figure S9b:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using N-CDs with different concentration of DT3 as passivating agents. The N-CDs were loaded at a 10 wt% content with oil to methanol ratio of 1:72, and the reaction mixtures were heated at 150°C for 3 hours.



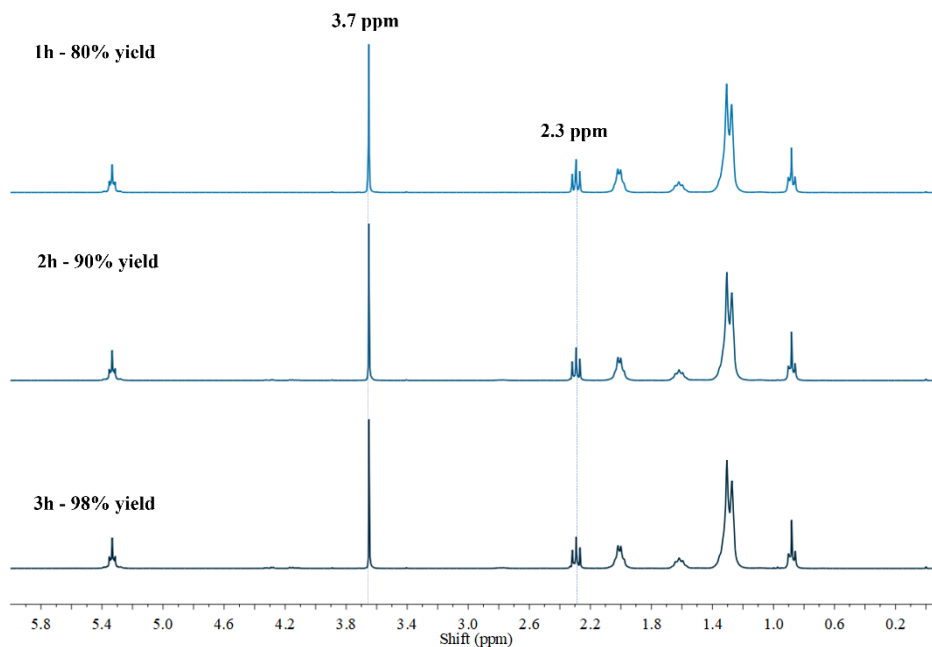
**Figure S11c:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using 750 mM DT3 CDs. The reaction was performed using an oil to methanol ratio of 1:72, and the reaction mixtures were heated at  $150^\circ\text{C}$  for 3 hours.



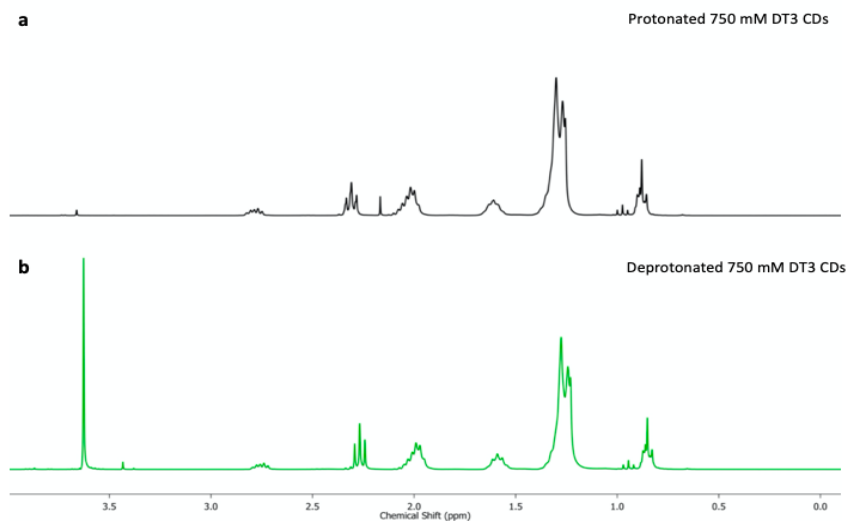
**Figure S11d:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using 750 mM DT3 CDs. The N-CDs were loaded at a 1 wt% content, and the reaction mixtures were heated at  $150^\circ\text{C}$  for 3 hours.



**Figure S11e:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using 750 mM DT3 CDs. The N-CDs were loaded at a 1 wt% content with oil to methanol ratio of 1:18, and the reaction mixtures were heated for 3 hours.



**Figure S11f:**  $^1\text{H}$  NMR Spectra for the transesterification reaction products obtained using 750 mM DT3 CDs. The N-CDs were loaded at a 1 wt% content with oil to methanol ratio of 1:18, and the reaction mixtures were heated at 100 °C.



**Figure S11g:** <sup>1</sup>H NMR Spectra for the transesterification reaction products obtained using 750 mM DT3 CDs. Representative results using protonated and deprotonated 750 DT3 CDs, demonstrating that no significant biodiesel conversion was achieved when using the protonated CDs.