

# Evaluation of Cobalt, Nickel, and Palladium complexes as homogeneous catalysts for the hydrogenation and improvement of oxidative stability of biodiesel

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## Synthesis of ligand L2

The synthesis of compound **L2** was achieved in a 2-step reaction process. Step 1 is the acylation of picolinic acid using thionyl chloride to form an intermediate picolinium chloride as seen in Scheme 2.4. This is followed by the addition of equimolar amounts of 3-aminopropyltriethoxysilane and triethyl amine. The <sup>1</sup>H NMR in Figure S1 shows a broad singlet peak (e) at 8.01 ppm that is attributed to the presence of the N-H proton. The pyridyl protons labeled b, c, and d, are observed at 7.8, 7.5, and 7.47 ppm, giving integrals approximately equal to 1, which confirms the number of protons in each peak. The pyridyl imine proton is observed at 8.23 ppm, giving an integral of 0.91. The presence of the ethoxy functionality is confirmed by the peaks at j (1.02 ppm) and i (2.58 ppm), which give integrals of 6.01 and 8.52 correlating to the expected number of protons. The rest of the protons at positions h (0.49 ppm), g (1.2 ppm), and f (2.86 ppm) confirm the presence of the protons in the propyl chain. The corresponding carbon NMR spectra of **L2** in Figure S1 show the chemical shifts of the carbons in the ligand. The identified peaks are indexes a-k, as shown in the chemical structure. The chemical shifts correspond to carbons identified in the proposed indexed chemical structure. The vibrational frequencies of the functionalities present in ligand **L2** are shown in Figure S2. The broad peak at 3200-3300 cm<sup>-1</sup> is assigned to the N-H stretching, while the C=O is confirmed by a strong peak at 1734 cm<sup>-1</sup>. The element analysis of **L2** confirmed the proposed structure of the ligand, giving the element content of (predicted values in parenthesis) C, 54.9 (55.19); H, (7.58) 8.03; N, (7.55) 8.58. The ESI-MS of ligand **L2** in the positive mode shows a peak for [M+H]<sup>+</sup> ion at m/z 327.17, while the abundant peak at m/z 176.1 corresponds to [M+H+Na]<sup>+2</sup> (Figure S3), where [M] is the molecular cation (Henderson & McIndoe, 2005). To synthesize the corresponding amide complexes, a solution of **L2**; N-(3-(triethoxysilyl)propyl) picolinamide was dissolved in a minimum amount of dichloromethane and 0.001 mol NaOH in Methanol (Atkinson et al., 2012; Park et al., 2013). The metal precursors (CoCl<sub>2</sub>, PdCl<sub>2</sub>(NCME)<sub>2</sub>, or C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>NiBr<sub>2</sub>) were suspended in dichloromethane and added to a solution of ligand (**L2**) and stirred at room temperature for 24 h to afford complex **C4-Co**, **C5-Ni**, or **C6-Pd**, respectively (Scheme 1). The complexes were isolated over a minimum amount of hexane or diethyl ether.

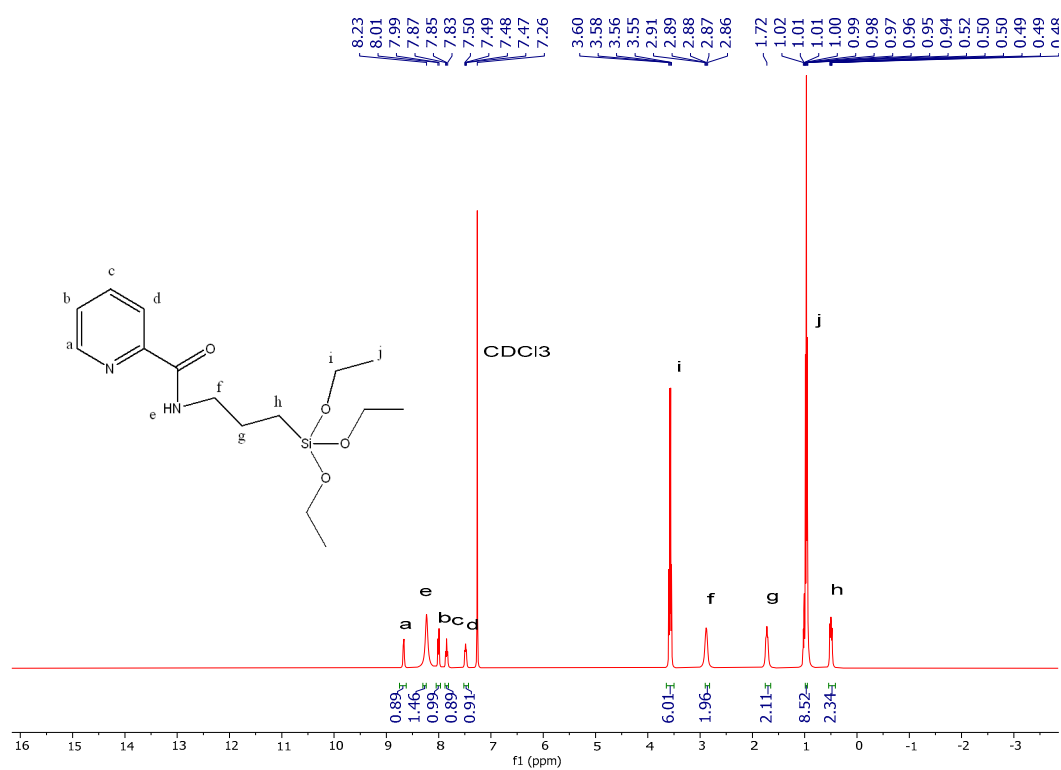


Figure S1: The <sup>1</sup>H NMR spectrum of ligand **L2** recorded in CDCl<sub>3</sub>.

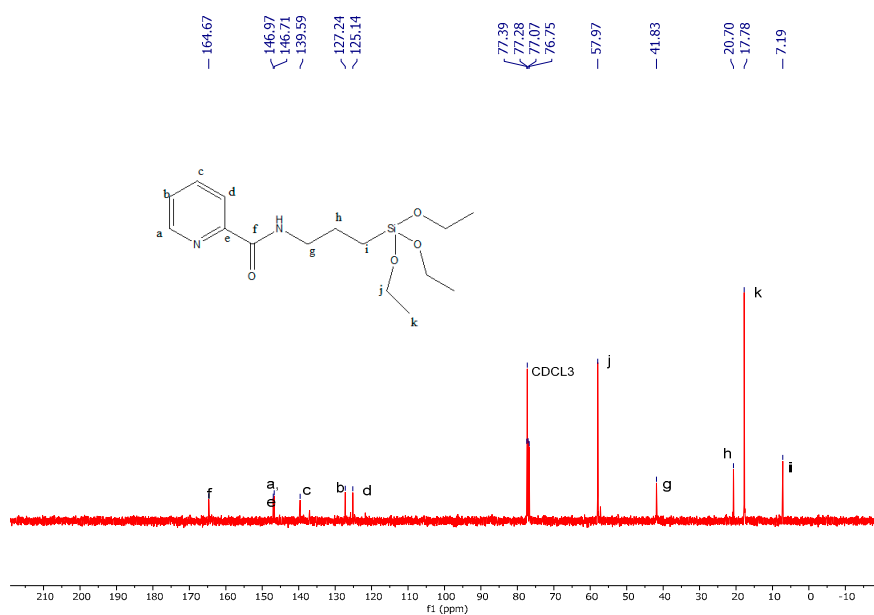


Figure S2: The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of ligand **L2** recorded in CDCl<sub>3</sub>.

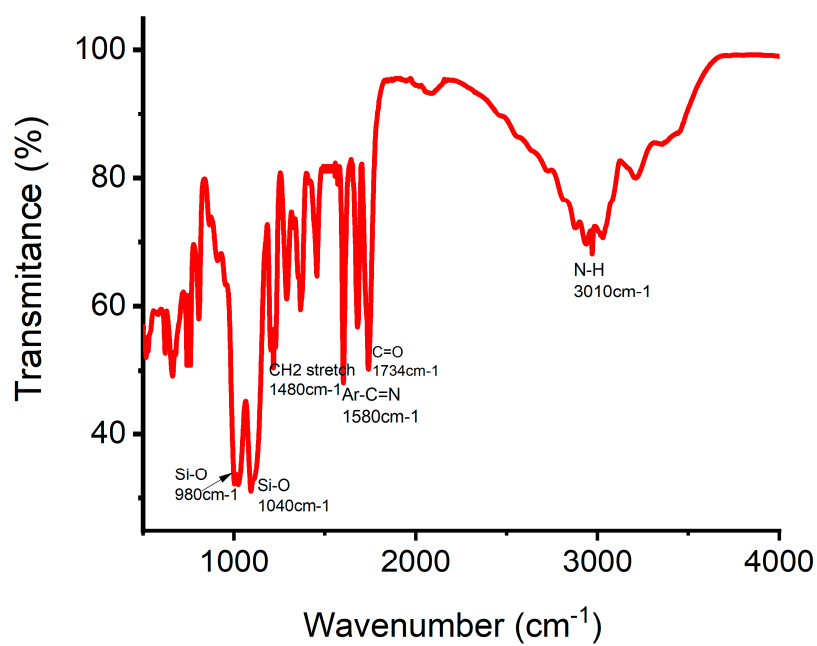


Figure S3: FTIR of ligand L2.

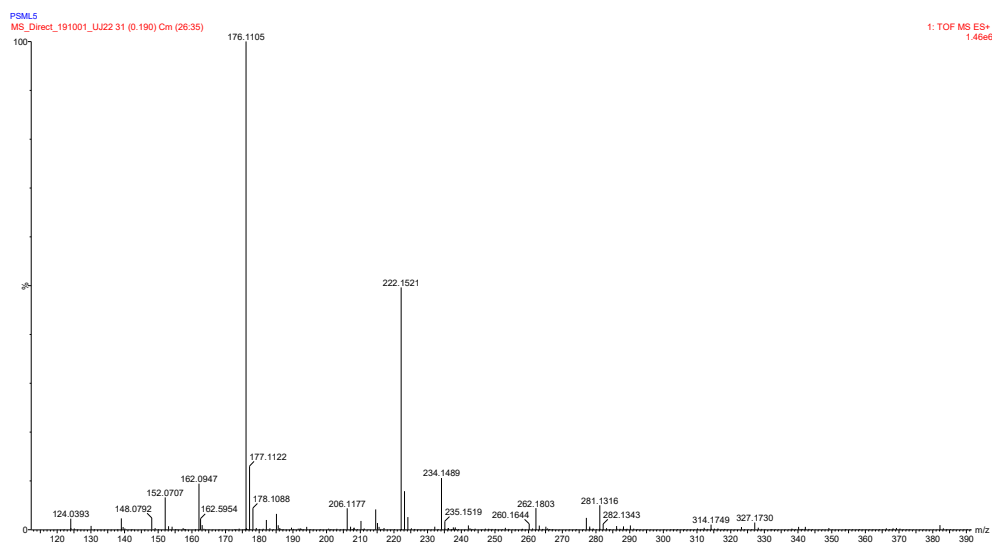


Figure S4: High-resolution ESI-MS of ligand L2.

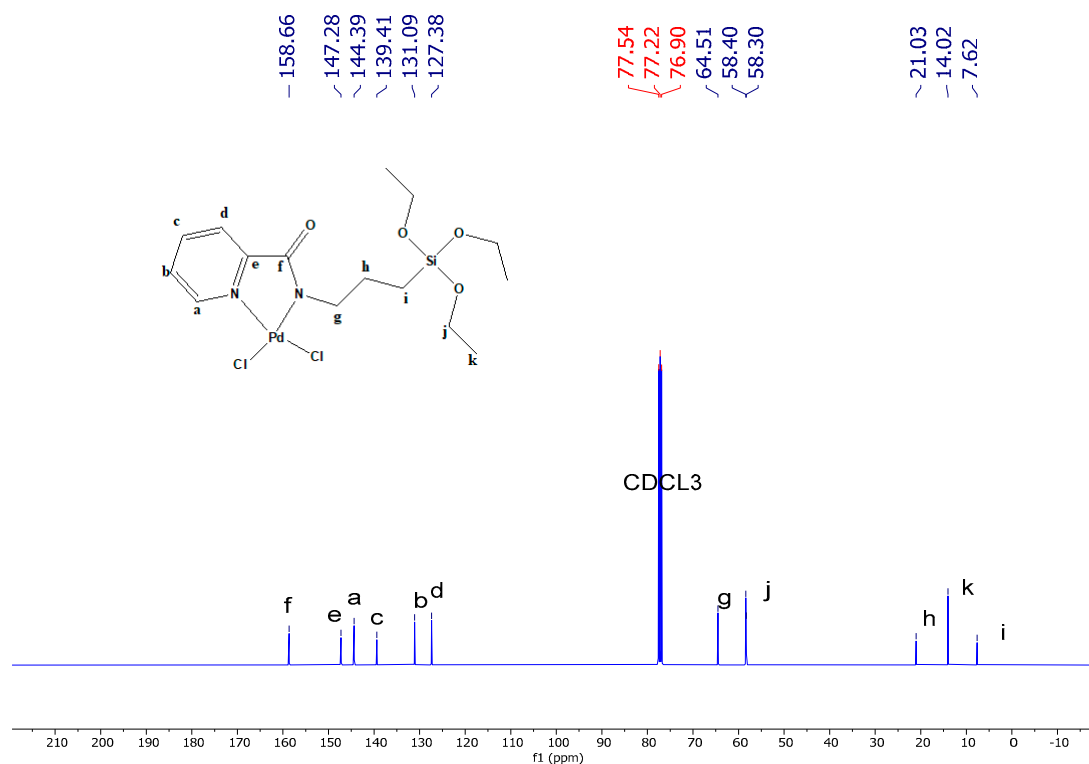


Figure S5: Structural determination of complex **C6-Pd** using <sup>13</sup>CNMR spectrometer recorded in CDCl<sub>3</sub>.

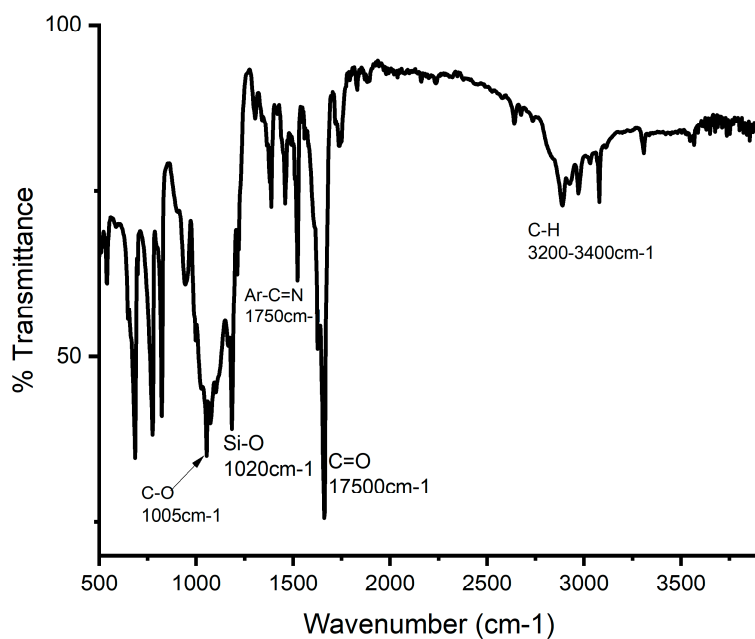
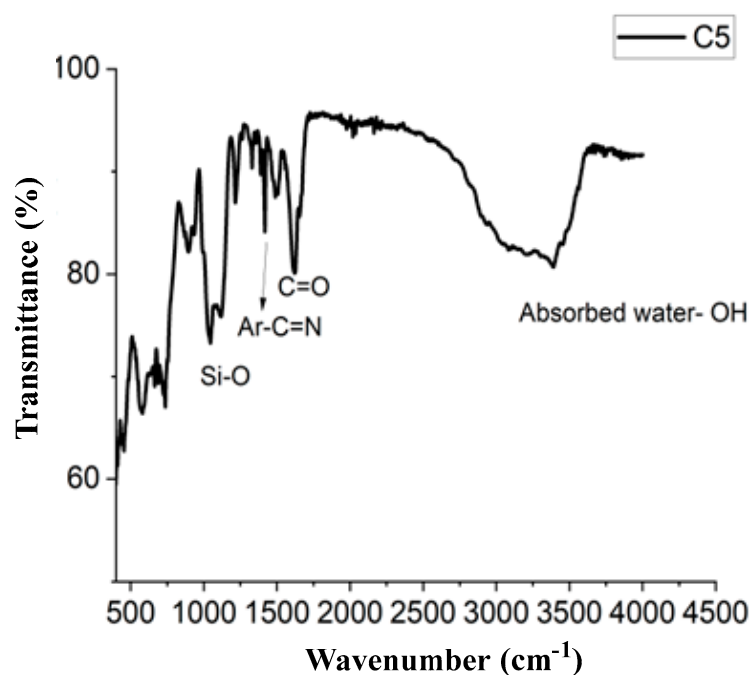
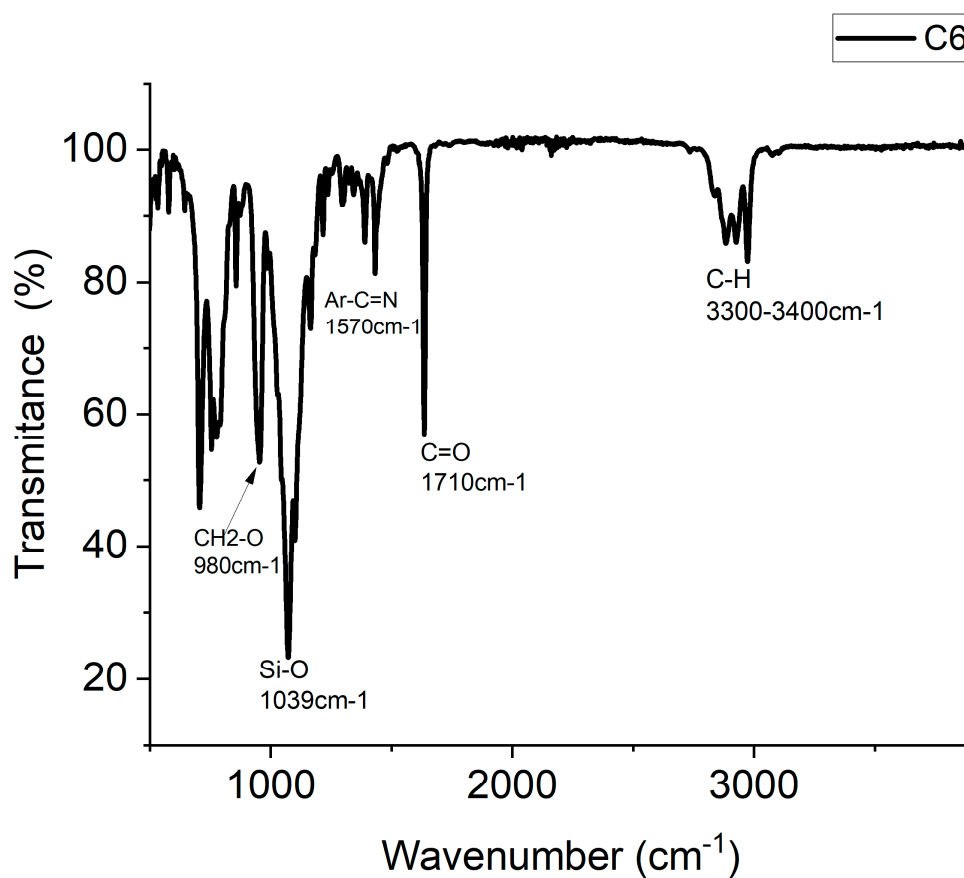


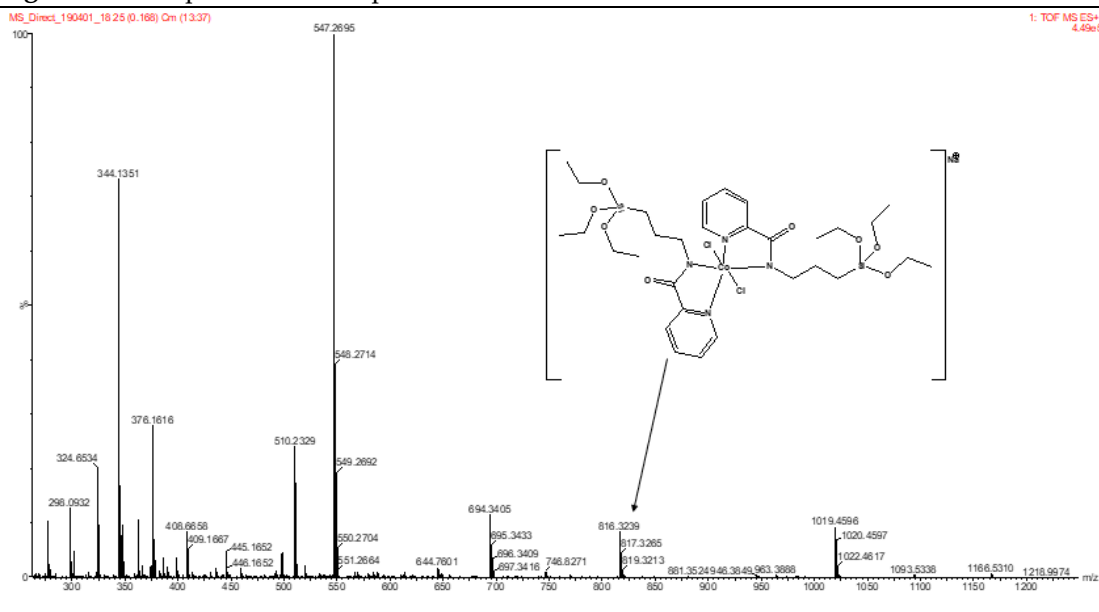
Figure S6a: IR spectrum of complex **C4-Co**.



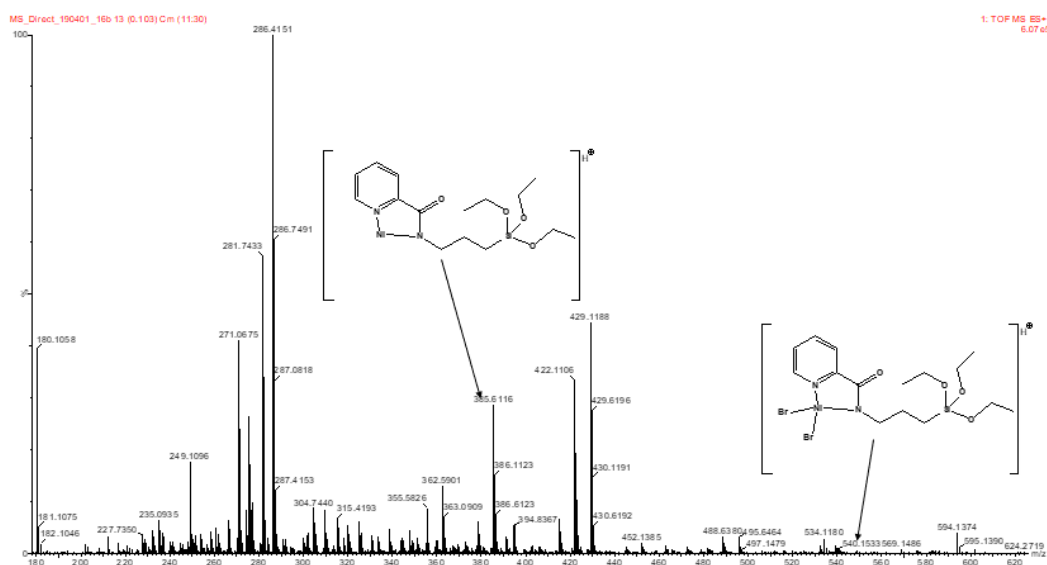
**Figure S6b:** IR spectrum of hygroscopic complex C5-Ni . The vibrational frequencies show absorbed water due to the hygroscopic nature of the nickel complex at 3400-3500 cm<sup>-1</sup>, C=O at 1738 cm<sup>-1</sup>, Ar-C=N at 1570 cm<sup>-1</sup>, Si-O at 1040 cm<sup>-1</sup>, and H<sub>2</sub>C-O at 1002 cm<sup>-1</sup>.



**Figure S6c:** IR spectrum of complex **C6-Pd**.



**Figure S7a:** Electrospray ionization mass spectrum for complex **C4-Co** recorded in negative ion mode.



**Figure S7b:** Electrospray ionization mass spectrum for complex **C5-Ni** recorded in positive ion mode.

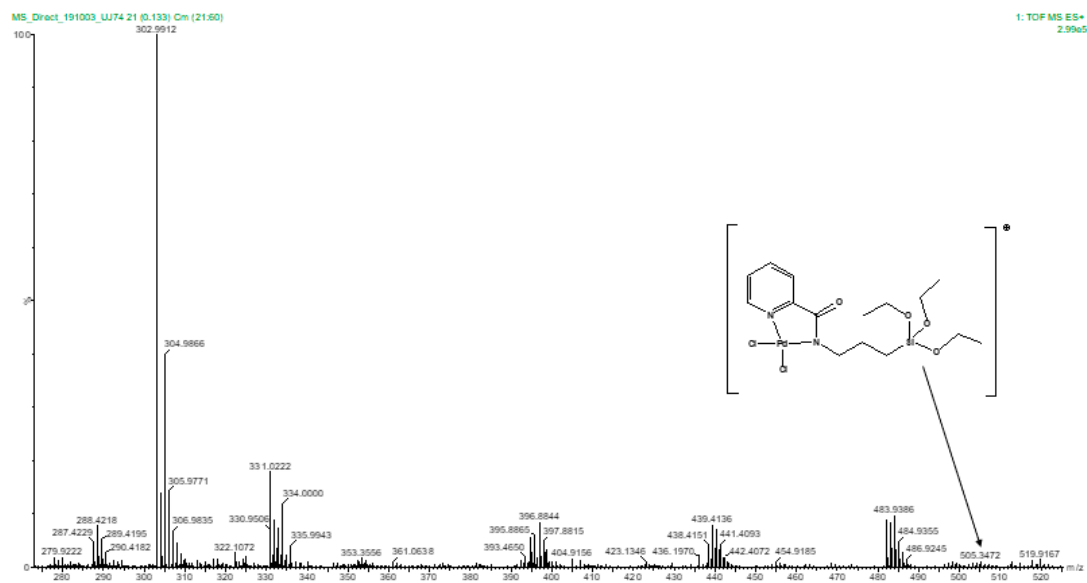


Figure S7c: Electrospray ionization mass spectrum for complex **C6-Pd** recorded in positive ion mode.

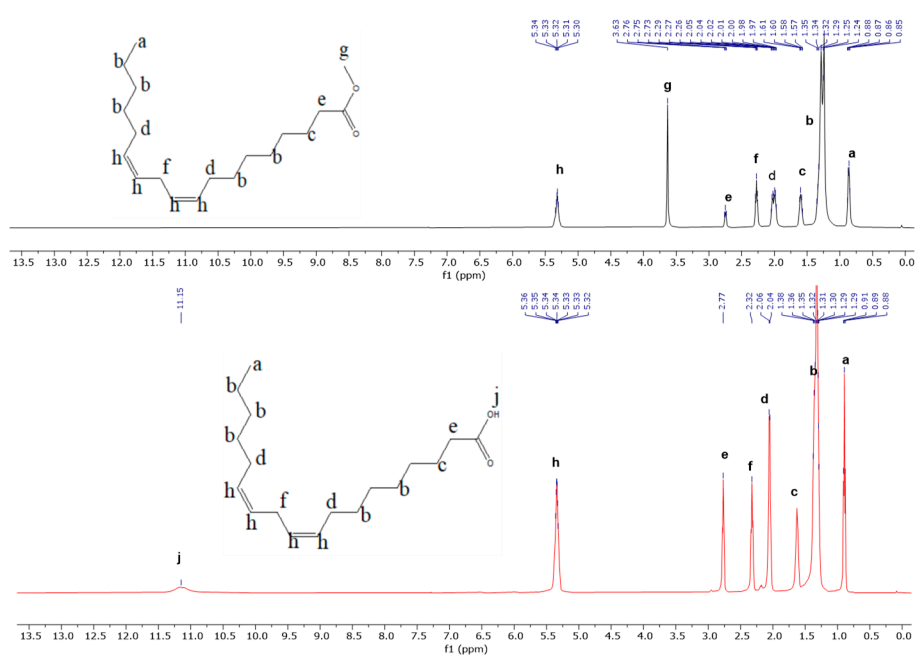


Figure S8: <sup>1</sup>H NMR spectrum showing the transesterification of linoleic acid using methanol to form methyl linoleate.

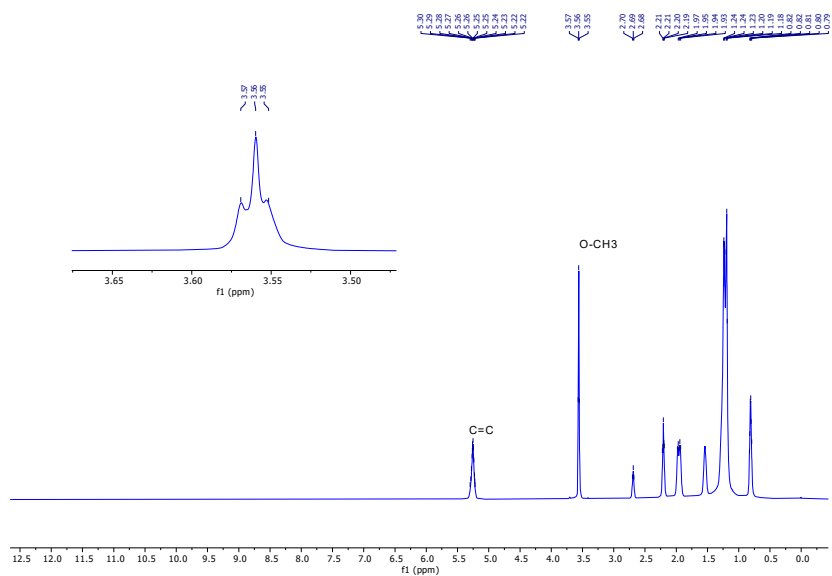


Figure S9: The  $^1\text{H}$ NMR spectrum of BD1.

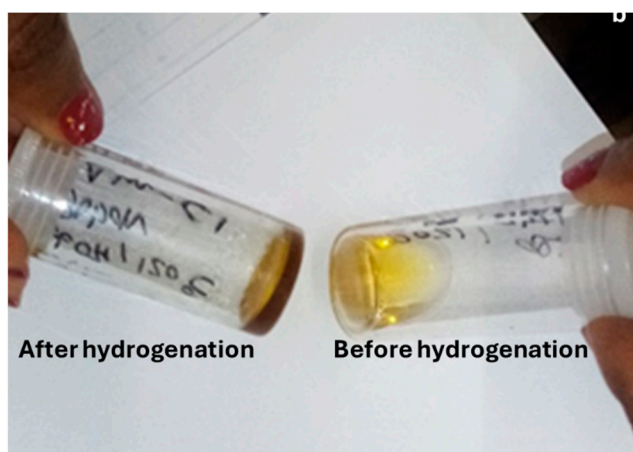


Figure S10: Visual of changes in the flow of the biodiesel after hydrogenation.



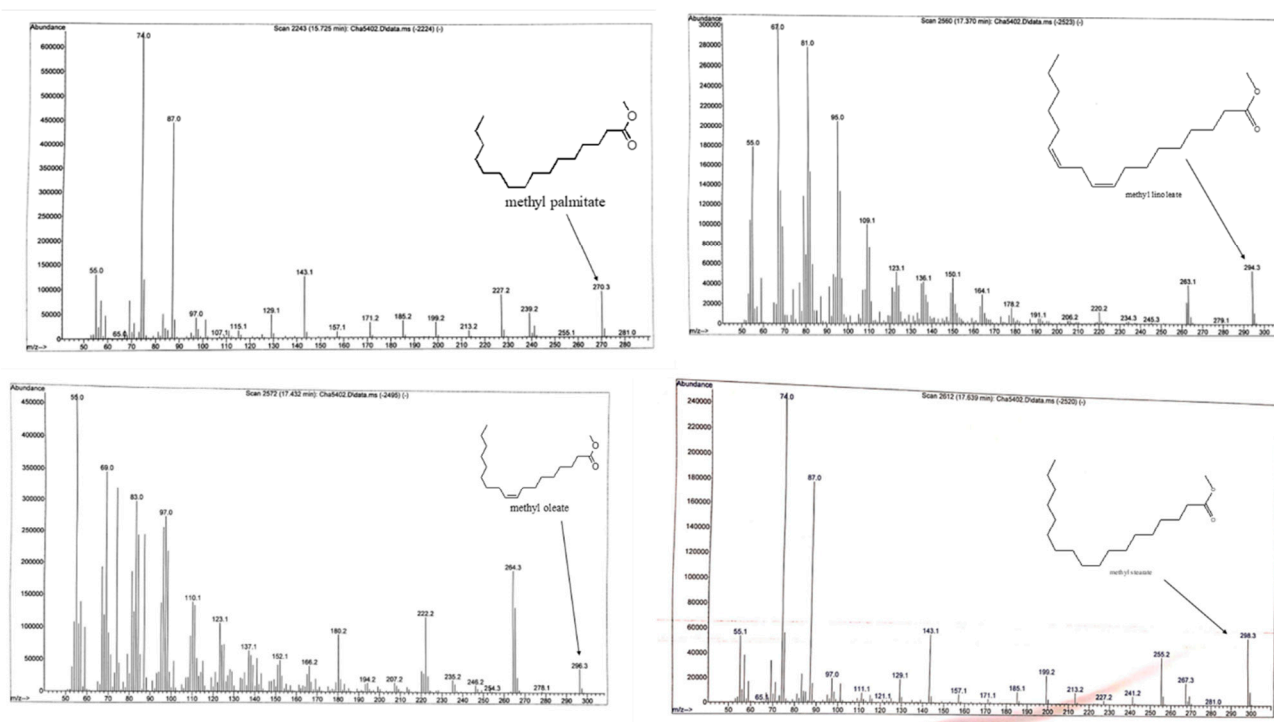


Figure S11: Mass spectrometer fragments of the components of BD1, in Figure 3.

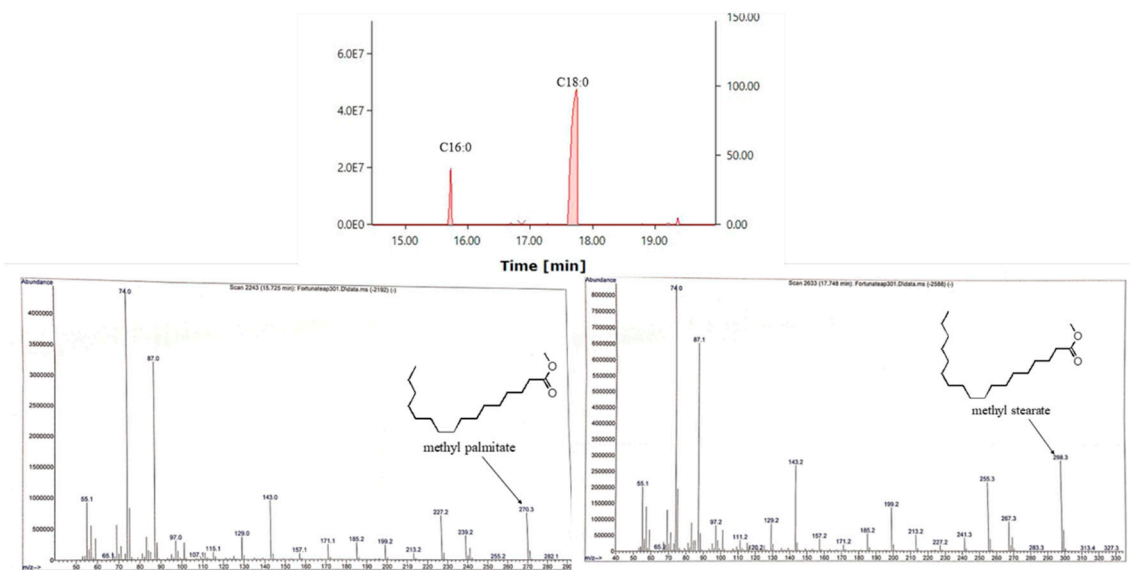


Figure S12: An example of a chromatogram and the corresponding mass fragments for all the detected peaks for entry 2 Table 3. No C18:1 is detected.

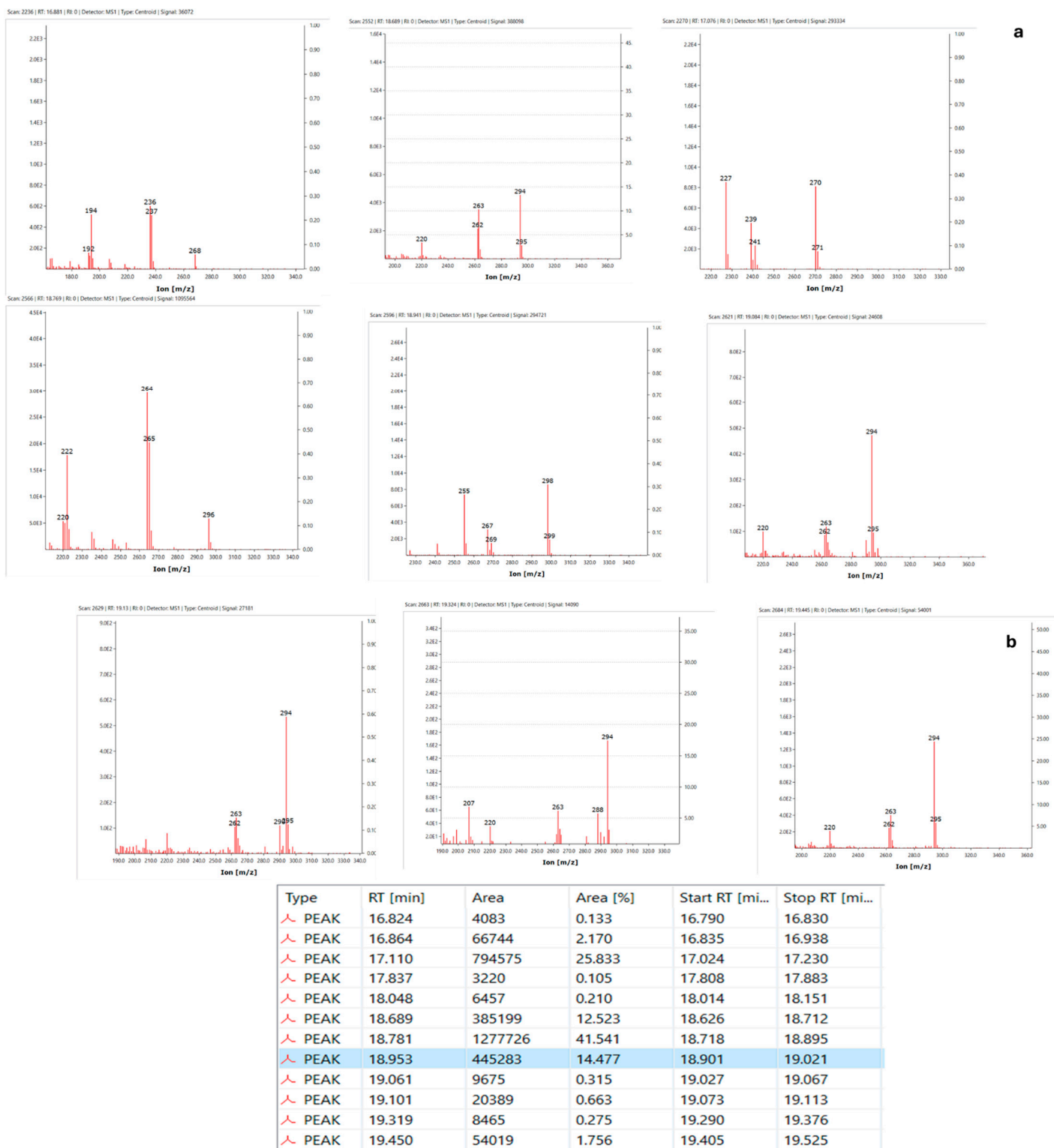


Figure S13: Corresponding mass fragments for the detected peaks for Figure 5, where C16:0=m/z 270, C18:2=m/z 294, C18:1=m/z 296, and C18:0=m/z 298.

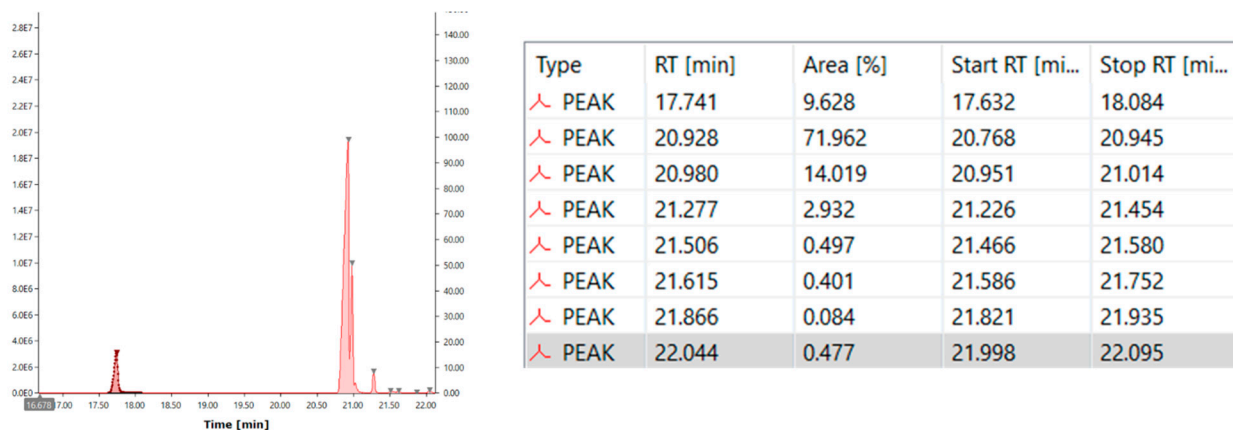


Figure S14: Identification of compounds in biodiesel sample BD3 after hydrogenation and the corresponding mass fragments.

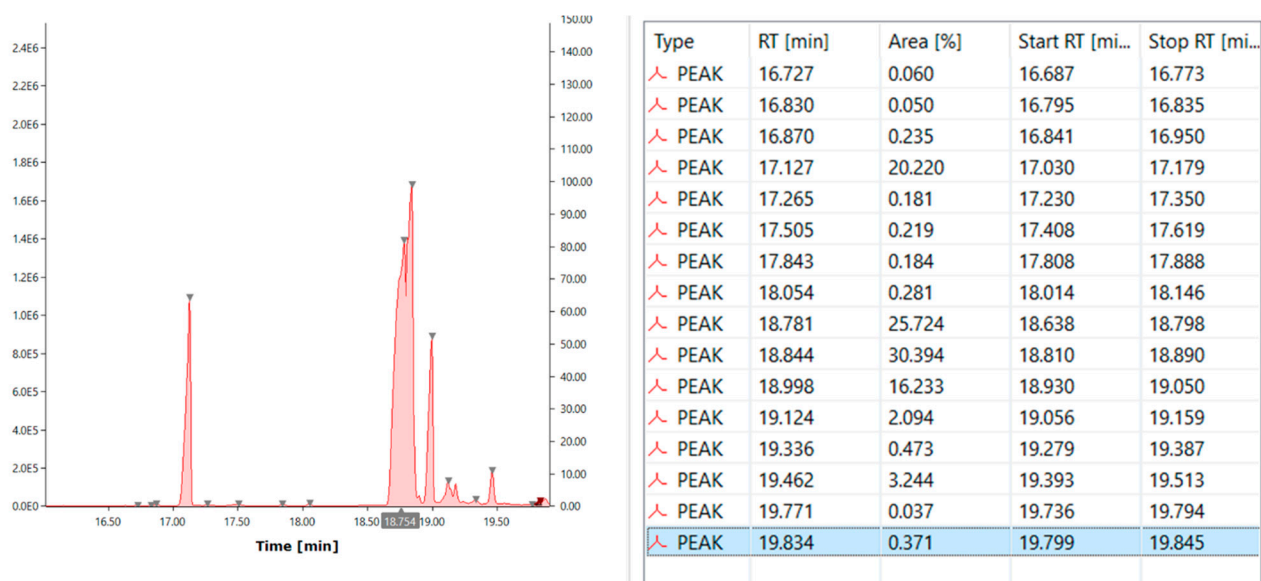


Figure S15: Identification of compounds in biodiesel sample BD2 after hydrogenation and the corresponding mass fragments.

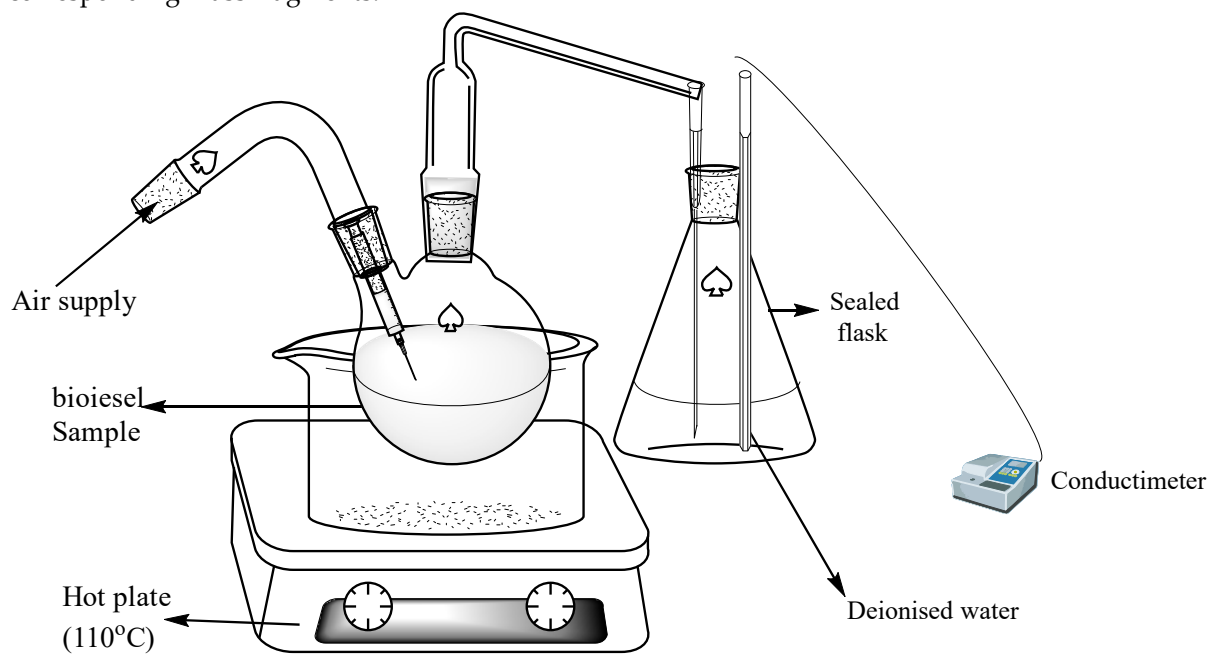


Figure S16: Experimental setup for the conductivity measurements.

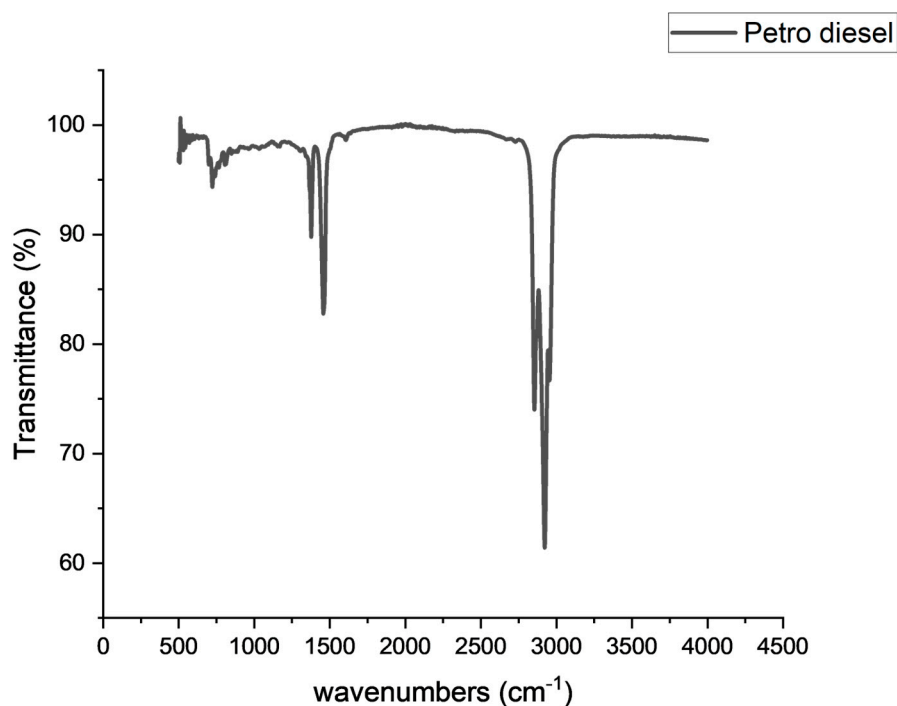


Figure S17: FTIR spectrum of commercial diesel.

Degree of Unsaturation (DU)

=%Wt of the monounsaturated + 2(% wt of the poly unsaturated) Equation Error! No text of specified style in document..1

**Table S1:** Different oil components of jatropha and methyl linoleate.

Component	Jatropha biodiesel (BD1) (%)	Methyl- Linoleate (ML) (%)
C18:0	4.70	0
C18:1	64.10	0
C18:2	18.10	100
C17:0	13.10	0
<b>Total unsaturation</b>	82.20	100

## Sample analysis procedure and techniques

### Gas chromatography:

Sample Inlet: GC, Injection Source: GC ALS, Mass Spectrometer: Enabled, Oven, Equilibration, time 0.25 min, Max Temperature 325 °C, Slow Fan, Disabled, Oven Program, On, 100 °C for 3 min, then 10 °C/min to 300 °C for 3 min, Run Time 26 min, 1 min (Post Run), 50 °C, Front SS Inlet He, Mode: Splitless, Heater On 280 °C, Pressure, On 72.553 kPa, Total Flow, On 64 mL/min, Septum Purge Flow, On 3

mL/min, Gas Saver Off, Purge Flow to Split Vent 60 mL/min at 0.75 min, Thermal Aux 2 {MSD Transfer Line}, Heater On, Temperature Program On, 280 °C for 0 min, Run Time, 26 min, Column #1, Agilent 19091S-433: 469.51938, HP-5MS 5% Phenyl Methyl Silox, 325 °C: 30 m x 250 µm x 0.25 µm, In: Front SS Inlet He, Out: Vacuum, (Initial) 100 °C, Pressure 72.553 kPa, Flow, 1 mL/min, Average Velocity 37.293 cm/sec, Holdup Time 1.3407 min, Flow Program Off, 1 mL/min for 0 min, Run Time 26, in, 1 min (Post Run) 1.2 mL/min, Low Mass: 50.0, High Mass: 550.0, Threshold: 0, Sample #2 A/D Samples 4, Plot 2 low mass: 50.0, Plot 2 high mass: 500.0, [MSZones], MS Source: 250 C maximum 350 C, MS Quad: 150 C, maximum 200 C, Injection Source: GC Automatic Liquid Sampler (ALS), Mass Spectrometer. *Oven parameters:* Equilibration Time: 0.25 min, Max Temperature 325 °C. *Oven Program:* 100 °C for 3 min, then 10 °C/min to 300 °C for 3 min, run time 26 min, 1 min (Post Run) 50 °C. *Column parameters:* Agilent 19091S-433: 1469.51938, HP-5 MS 5% Phenyl Methyl Silox, 325 °C: 30 m x 250 µm x 0.25 µm. *Front SS Inlet* He, Spitless injection, Injection temp: 280 °C, *Pressure* 72.553 kPa, Total Flow 64 mL/min, Septum Purge GC-MS: Flow 3 mL/min. Low Mass: 50.0, High Mass: 550.0, MS Source: 250 °C maximum 350 °C, MS Quad 150 °C maximum of 200 °C. At the end of the reaction, the reactor vessel was cooled, and excess gas was released. The sample from the reactor was then dissolved in hexane, and the catalyst was removed by decanting. The filtrate was dried in an oven at 70 °C for an hour to remove the solvent (hexane).

**NMR:** A sample of the mixture was analyzed. NMR: Spectra were recorded on a Bruker Ultrashield-400 MHz spectrometer (<sup>1</sup>H: 400 MHz, <sup>13</sup>C{<sup>1</sup>H}:100 MHz, in chloroform, using tetramethylsilane (TMS) as an internal standard (δ ppm). All the chemical shifts were reported in ppm using TMS as a reference.

**FTIR:** The functional groups of the ligands, metal precursors, and complexes were confirmed using infrared spectroscopy that was recorded using a Thermo Nicolet FTIR instrument fitted with an ATR probe and a diamond stage.

**Elemental analysis:** A Thermo Scientific Flash 2000 Series CHNO element analyzer was used. Mass spectrometry was carried out on a Water Synapt G2 electrospray ionization mass spectrometer in negative or positive ion mode. The metal complexes were completely dissolved in the appropriate solvent before analysis.

## References

1. Atkinson, B. N., Chhatwal, A. R., & Williams, J. M. J. (2012). Catalytic amide bond forming methods. In *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Three Volumes*. <https://doi.org/10.1002/9783527651733.ch27>
2. Henderson, W., & McIndoe, J. S. (2005). Mass Spectrometry of Inorganic and Organometallic Compounds: Tools - Techniques - Tips. In *Mass Spectrometry of Inorganic and Organometallic Compounds: Tools - Techniques - Tips* (Vol. 9). <https://doi.org/10.1002/0470014318>
3. Park, J. K., Shin, W. K., & An, D. K. (2013). New and efficient synthesis of amides from acid chlorides using diisobutyl(amino)aluminum. *Bulletin of the Korean Chemical Society*, 34(5), 1592–1594. <https://doi.org/10.5012/bkcs.2013.34.5.1592>