Supporting Information

Biodiesel production under a microwave-assisted approach using a glycerol-derived Zn bifunctional catalyst

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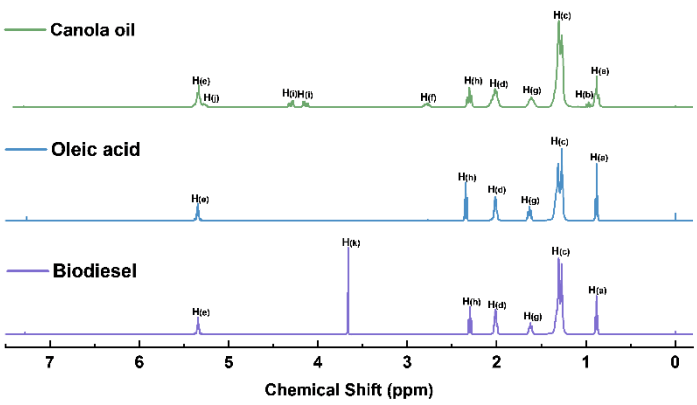
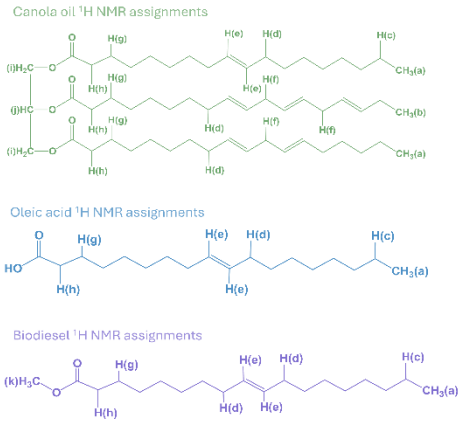
(a)



(b)



Assignments	Chemical shift (ppm)		
	Canola oil	Oleic acid	Biodiesel
H(a)	0.88	0.88	0.88
H(b)	0.97	-	-
H(c)	1.29	1.29	1.29
H(d)	2.01	2.02	2.02
H(e)	5.33	5.34	5.34
H(f)	2.77	-	-
H(g)	1.61	1.63	1.62
H(h)	2.30	2.34	2.30
H(i)	4.14; 4,29	-	-
H(j)	5.26	-	-
H(k)	-	-	3.66

Figure S.1 ^{1}H NMR of canola oil, oleic acid, and biodiesel obtained from the (trans)esterification reactions (300 MHz, $CDCl_3$). The quantification of the biodiesel yield is obtained by integrating the triplet associated with the α-carbonyl protons (H(k)) and the singlet associated with the methoxy protons (H(h)). (b) ^{1}H NMR assignments for canola oil, oleic acid, and biodiesel.

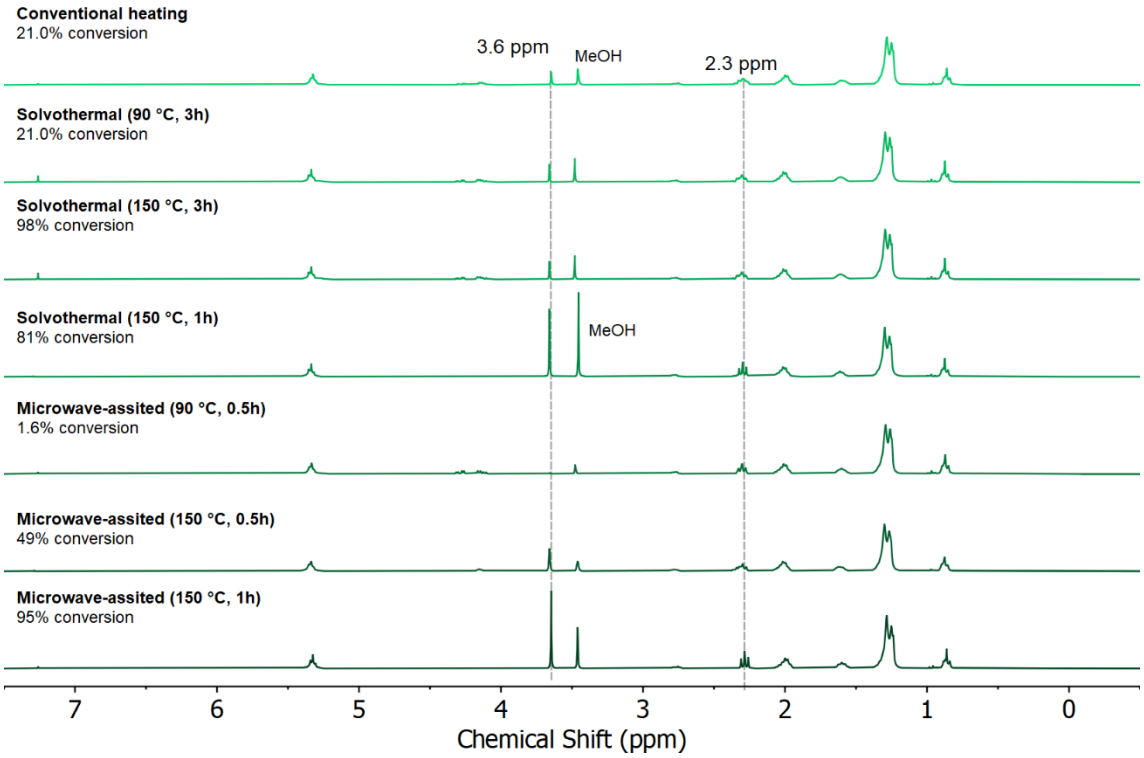


Figure S. 2 ^{1}H-NMR spectra of biodiesel obtained using Gly-Zn as a catalyst under different reaction approaches. Reactions were carried out under the conditions of a 1:36 molar ratio, and 5 wt.% catalyst loading (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

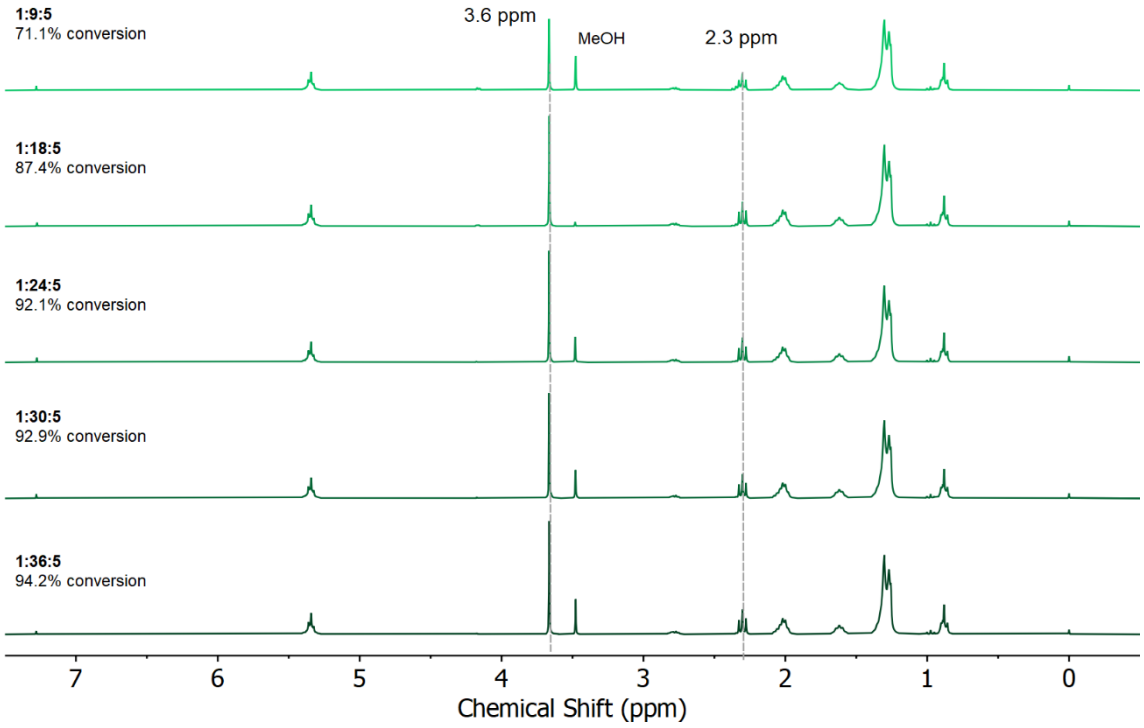


Figure S. 3 ^{1}H-NMR spectra of biodiesel obtained using Gly-Zn as catalyst under different oil:methanol molar ratios. Reactions were carried out under the conditions of 5 wt.% catalyst loading, 150 °C, 1 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

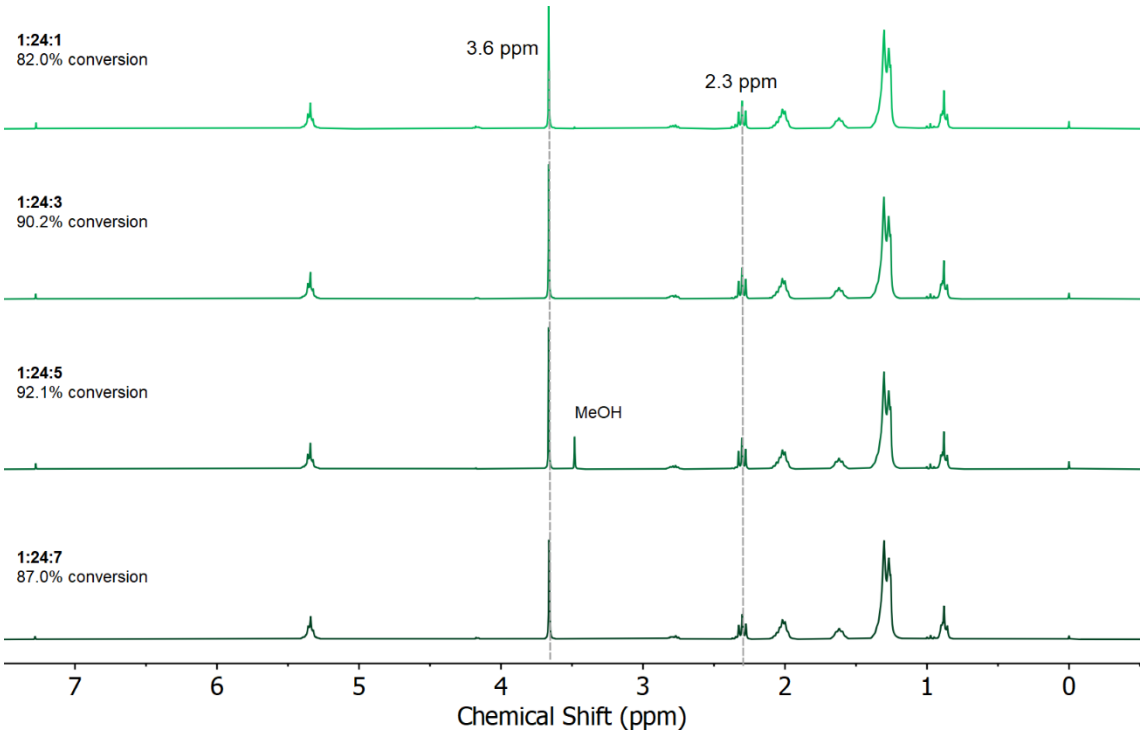


Figure S. 4 ^{1}H-NMR spectra of biodiesel obtained using Gly-Zn as a catalyst at different catalyst loadings. Reactions were carried out under the conditions of 1:24 oil-to-methanol molar ratio, 150 °C, 1 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

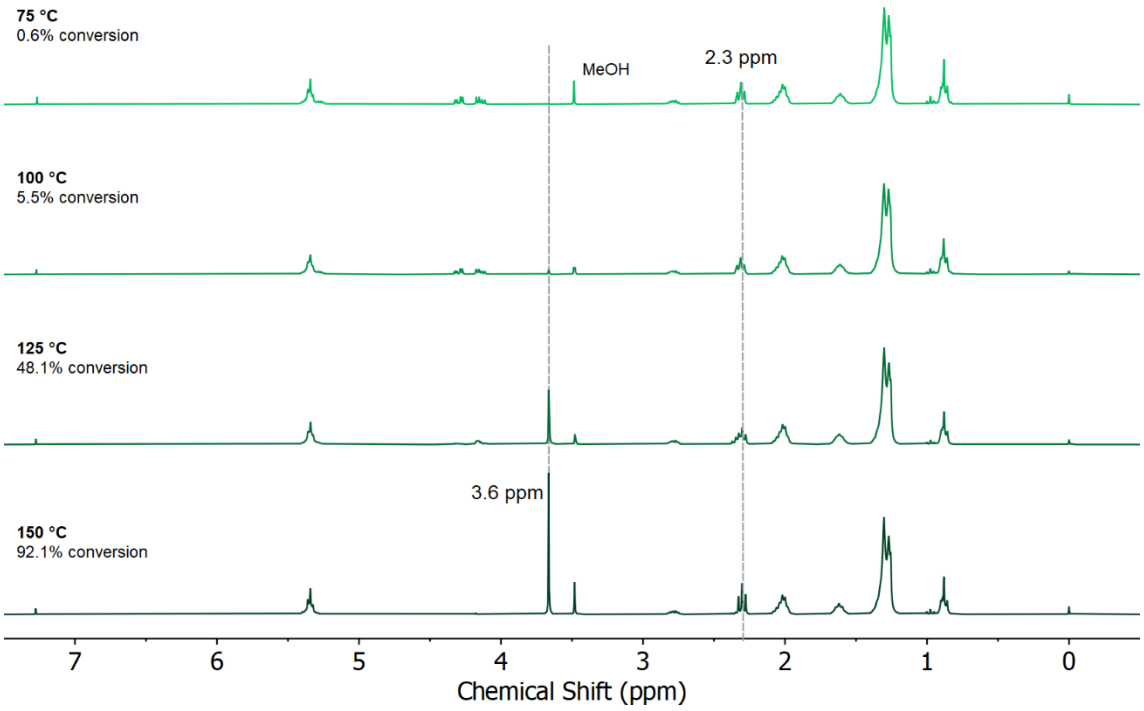


Figure S. 5 ^{1}H-NMR spectra of biodiesel obtained using Gly-Zn as a catalyst at different temperatures. Reactions were carried out under the conditions of 1:24 oil-to-methanol molar ratio, 5 wt.%, 1 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

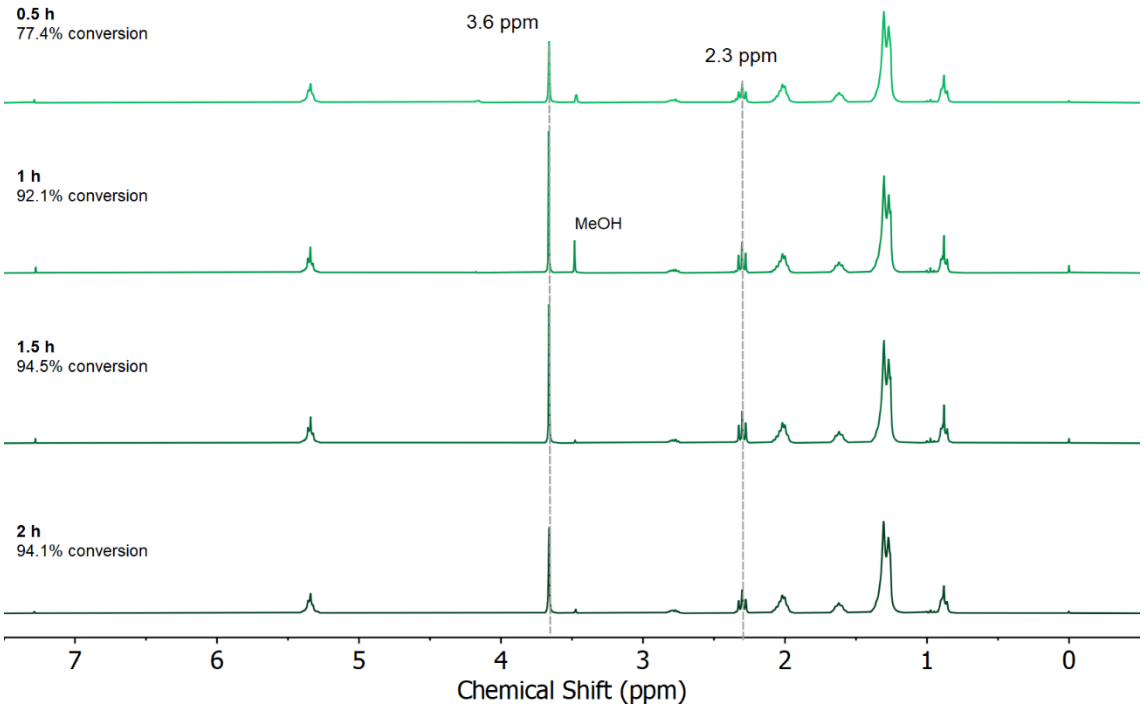


Figure S. 6 ^{1}H-NMR spectra of biodiesel obtained using Gly-Zn as a catalyst at different reaction times. Reactions were carried out under the conditions of 1:24 oil-to-methanol molar ratio, 5 wt.%, 150 °C (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

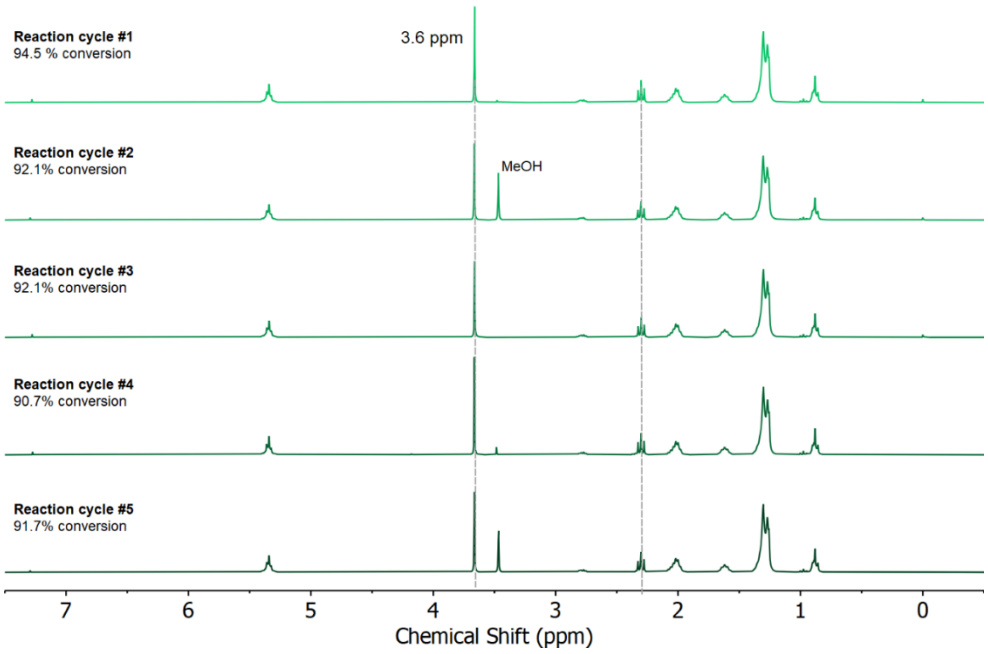


Figure S. 7 ^{1}H-NMR spectra of biodiesel obtained during the reusability test. Reactions were carried out under the conditions of a 1:24 molar ratio, 5 wt.% catalyst loading, 150 °C and 1.5 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

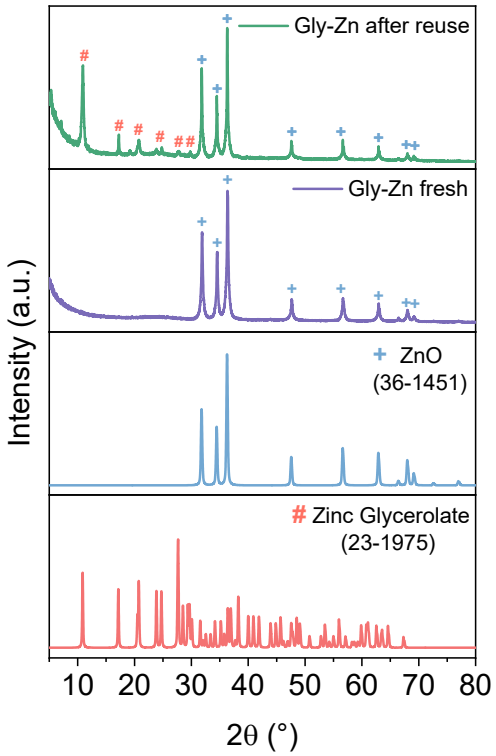


Figure S. 8 PXRD diffractograms of Gly-Zn after reuse and fresh Gly-Zn. The appearance of reflections associated with zinc glycerolate (JCDPS-23-1975) in the reused catalyst confirms the in-situ formation of this phase on the catalyst surface.

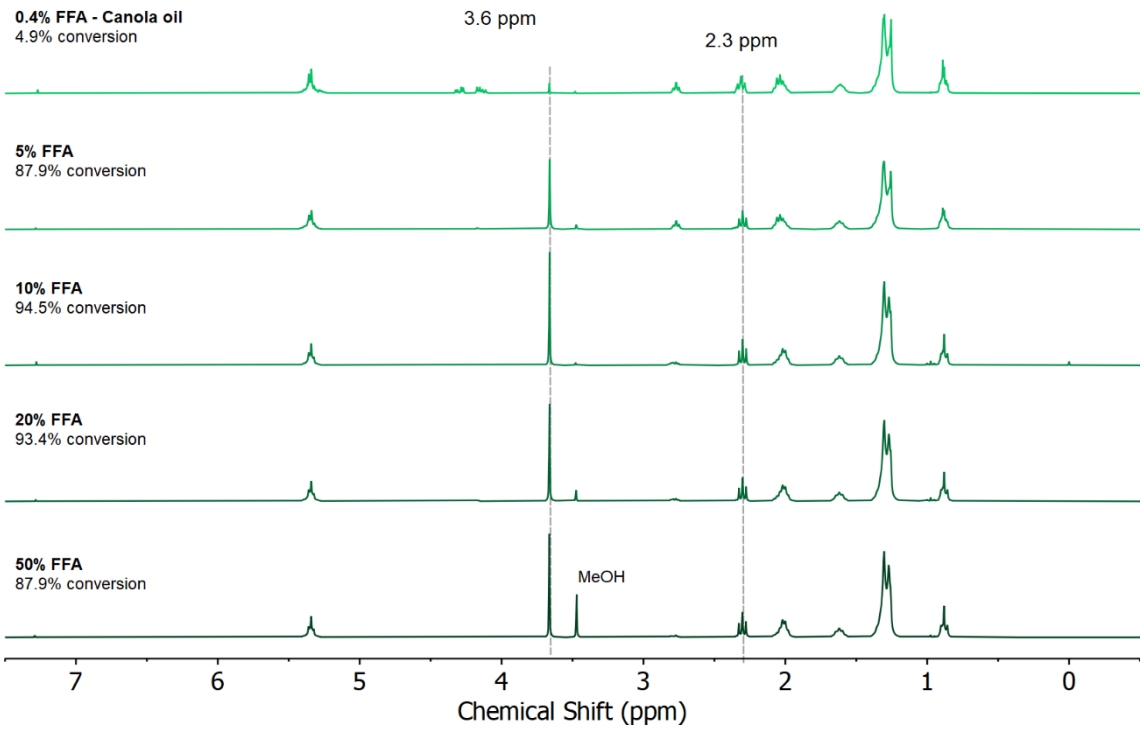


Figure S. 9 ^{1}H-NMR spectra of biodiesel obtained during acid tolerance studies using Gly-Zn as catalyst. Reactions were carried out under the conditions of a 1:24 molar ratio, 5 wt.% catalyst loading, 150 °C and 1.5 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2).

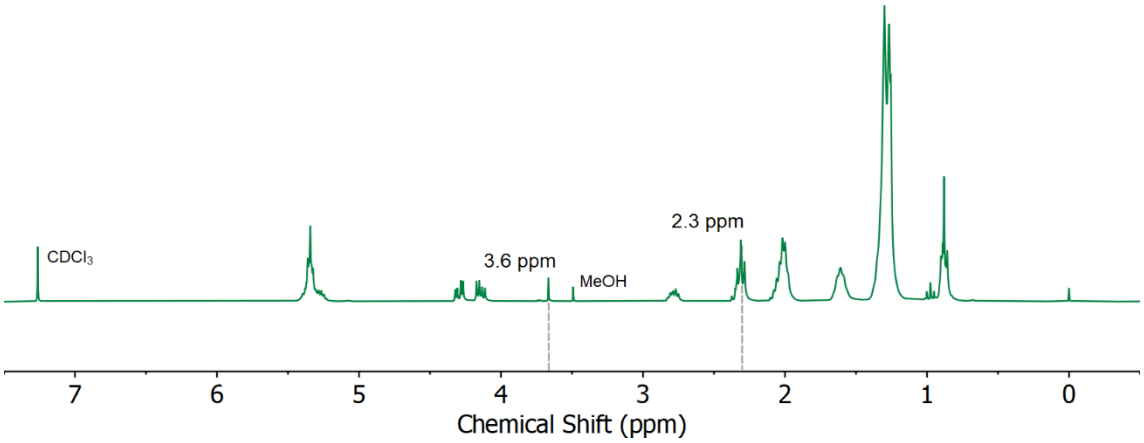


Figure S. 10 ^{1}H-NMR spectrum obtained during control reactions. Reactions were carried out without the presence of the catalyst under the conditions of 1:24 molar ratio, 150 °C, and 1.5 h (300 MHz, $CDCl_3$, δ 3.6 (s, 3H) from -OCH_3, and δ 2.3 (t, 2H) from -αCH_2). A conversion of 4.3% was observed, associated with the ability of oleic acid to perform autocatalysis.

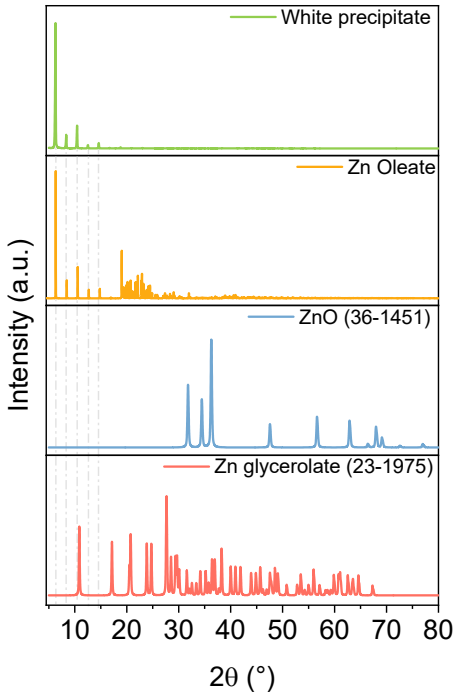


Figure S. 11 PXRD diffractogram of the white precipitate recovered from reactions performed with high acidity feedstocks (>20% FFA). When compared with the diffractograms of zinc oleate, ZnO (JCPDS 36-1451), and zinc glycerolate (JCPDS 23-1975), its identity was confirmed as zinc oleate.

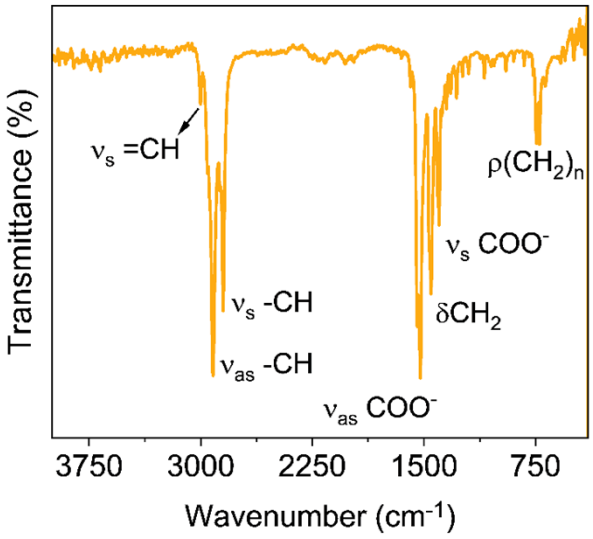


Figure S. 12 FTIR spectrum of the white precipitate recovered from reactions performed with high acidity feedstocks (>20% FFA). A weak stretching vibration at 3001 cm^{-1} is attributed to the =CH bond of the unsaturated oleate chain. Asymmetric and symmetric stretching vibrations associated with CH were observed at 2915 cm^{-1} and 2848 cm^{-1}, respectively. The strong vibration associated with carbonyl stretching is not observed, instead two intense vibrations characteristic of the zinc carboxylate are observed, confirming the conversion of oleic acid into zinc oleate. The asymmetric COO^- stretching is observed at 1529 cm^{-1} while the symmetric one is observed at 1396 cm^{-1}. Moreover, $\Delta\nu$ is about 140 cm^{-1}, suggesting a bidentate bridging coordination of zinc. Vibration at 1450 cm^{-1} characteristic of CH_2 bending was also observed. Furthermore, a bending attributed to the methylene groups (-$(CH2)_n$-) vibration at 731 cm^{-1} was observed.