

1 **Post-functionalized Monolithic Metal–Organic Frameworks for**
2 **Biodiesel Production: Mechanistic Insights from DFT, Process**
3 **Optimization via RSM, and Life Cycle Cost and Impact**
4 **Assessment**

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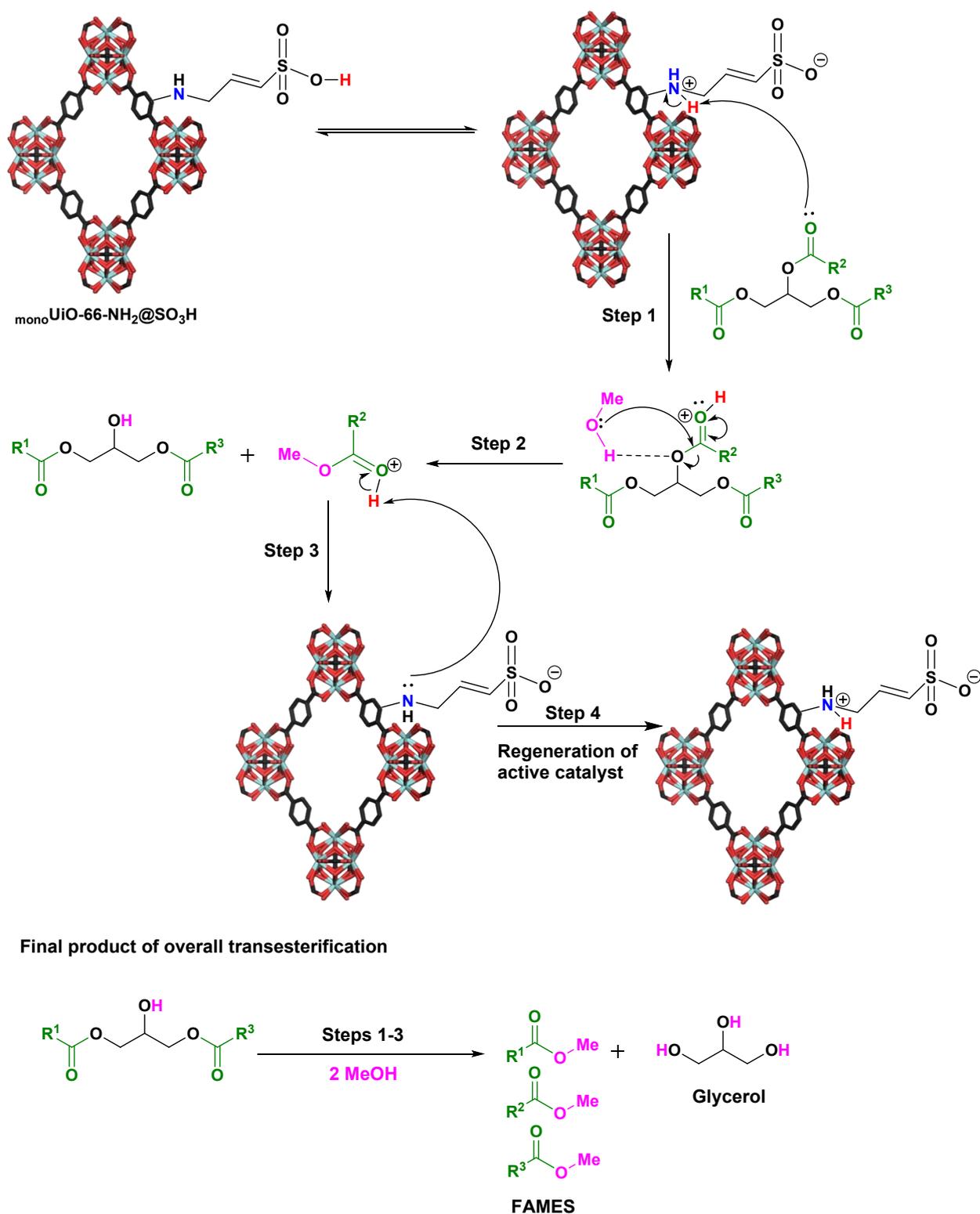


Fig. S1 Plausible mechanism for the transesterification of triglyceride by $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ catalyst.

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Table S1 ICP-OES data for mono UiO-66-NH_2 and $\text{mono UiO-66-NH}_2@\text{SO}_3\text{H}$

Elements	mono UiO-66-NH_2	$\text{mono UiO-66-NH}_2@\text{SO}_3\text{H}$	
	(Wt. %)	Fresh catalyst	Recovered catalyst (6 cycles)
Zr	23.4	22.03	21.8
S	-	4.47	4.09

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Table S2 Microanalysis data for mono UiO-66-NH_2 and $\text{mono UiO-66-NH}_2@\text{SO}_3\text{H}$

Elements	mono UiO-66-NH_2	$\text{mono UiO-66-NH}_2@\text{SO}_3\text{H}$	
	(Wt. %)	Fresh catalyst	Recovered catalyst (6 cycles)
C	30.4	28.1	32.3
H	1.8	2.4	2.8
N	4.9	4.7	4.1

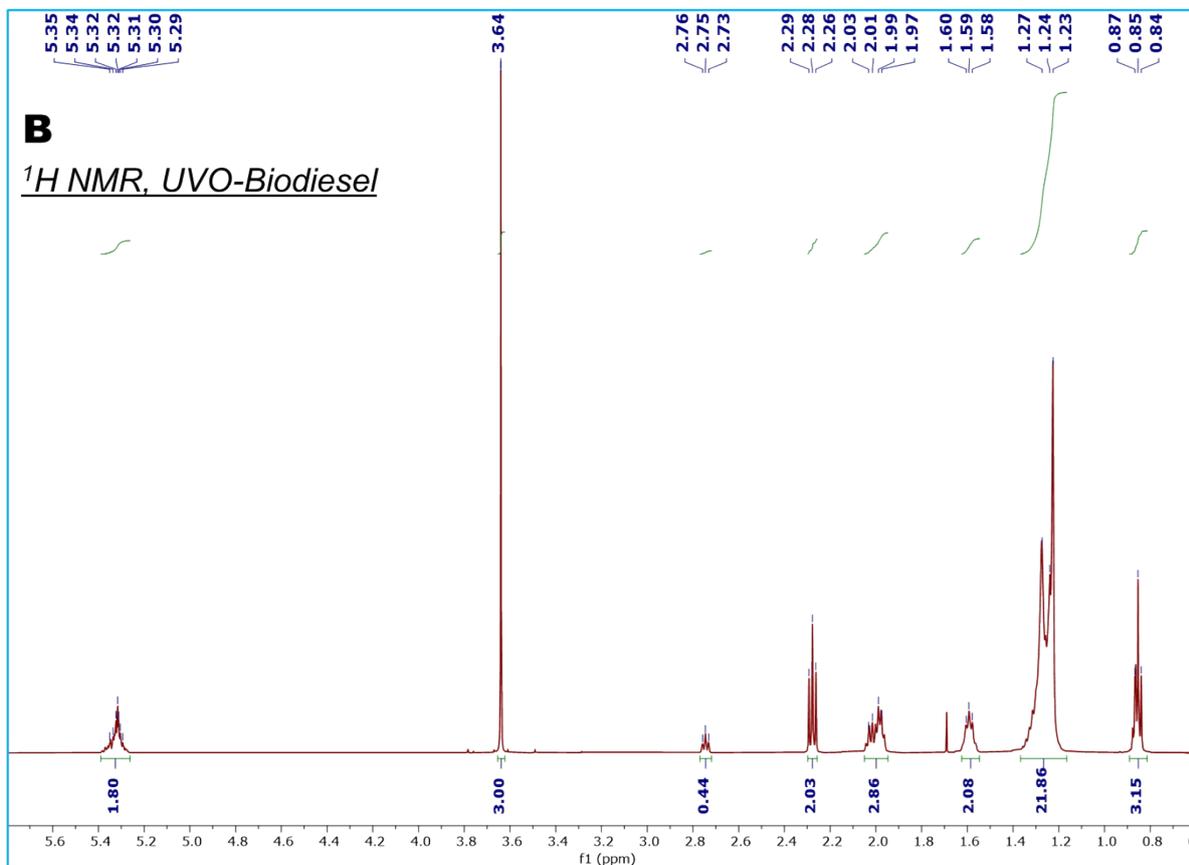
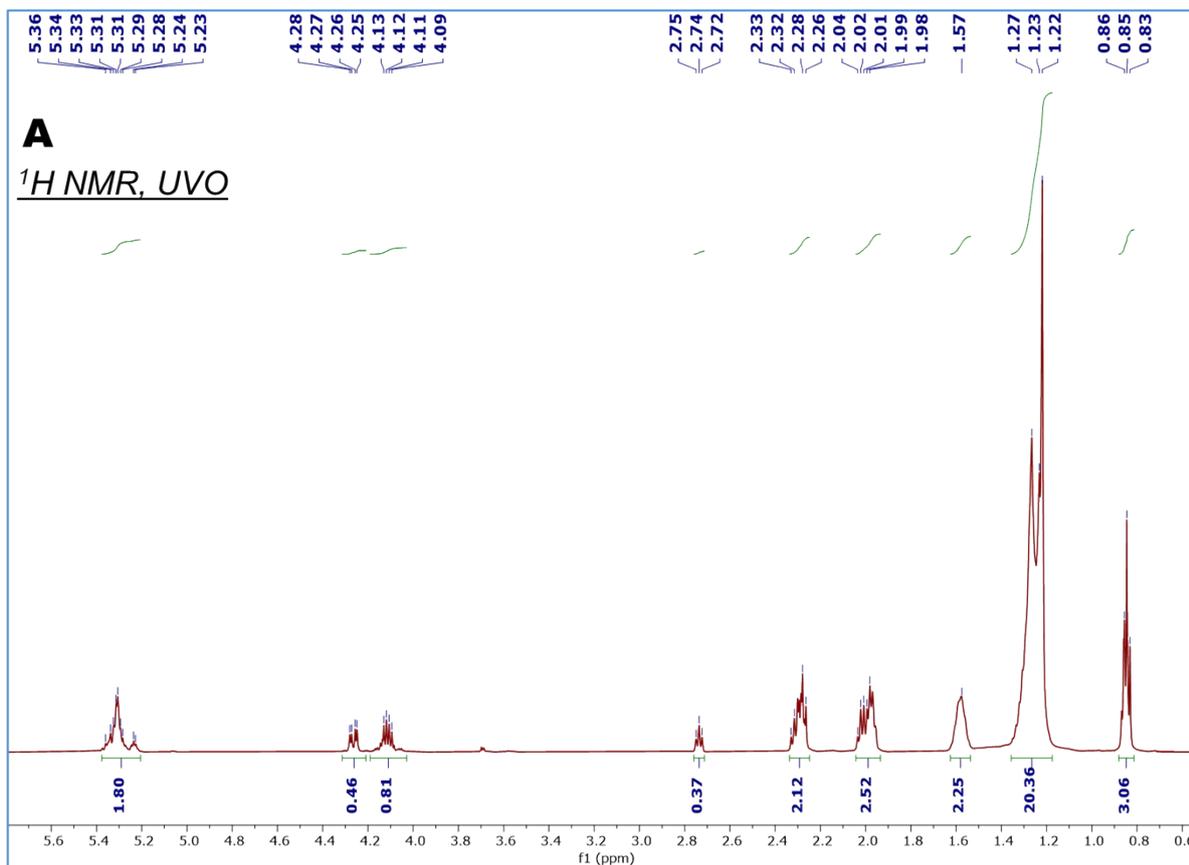
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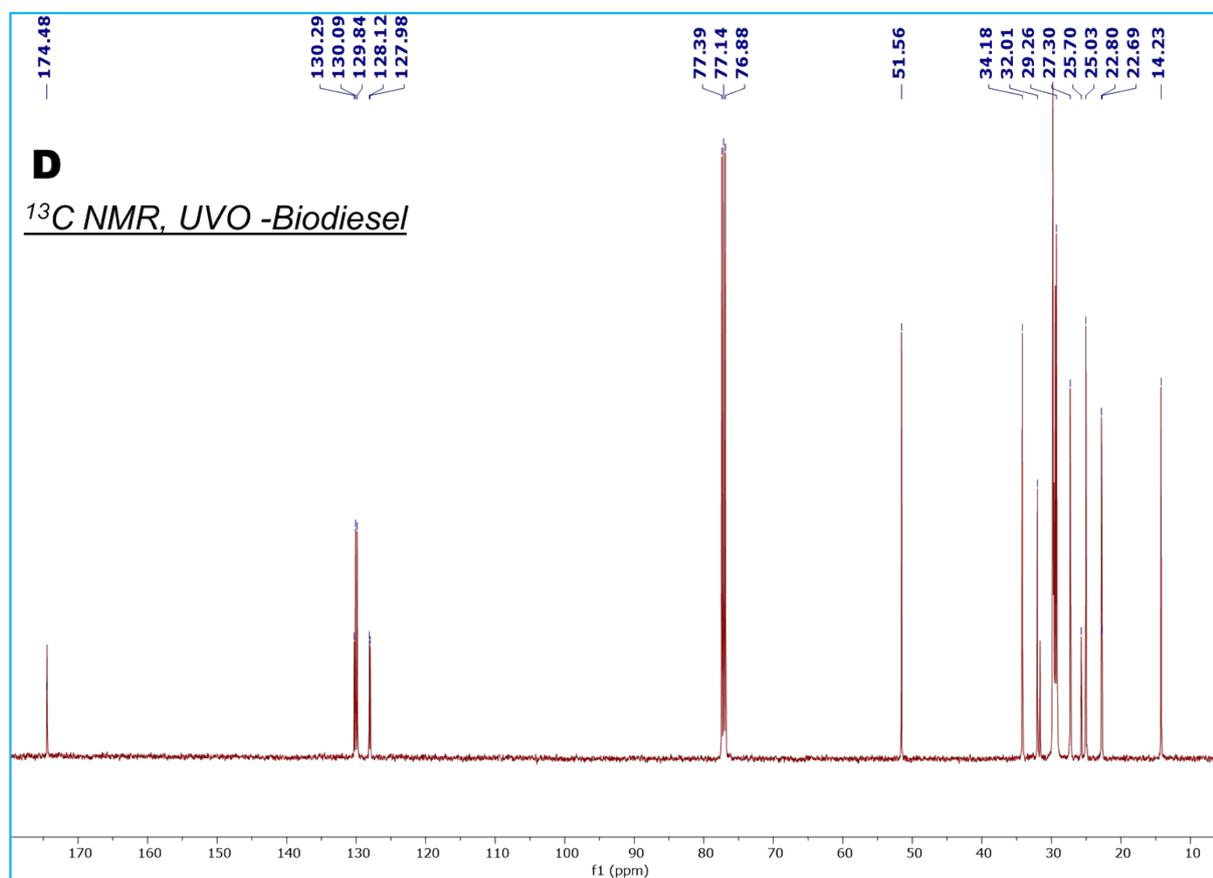
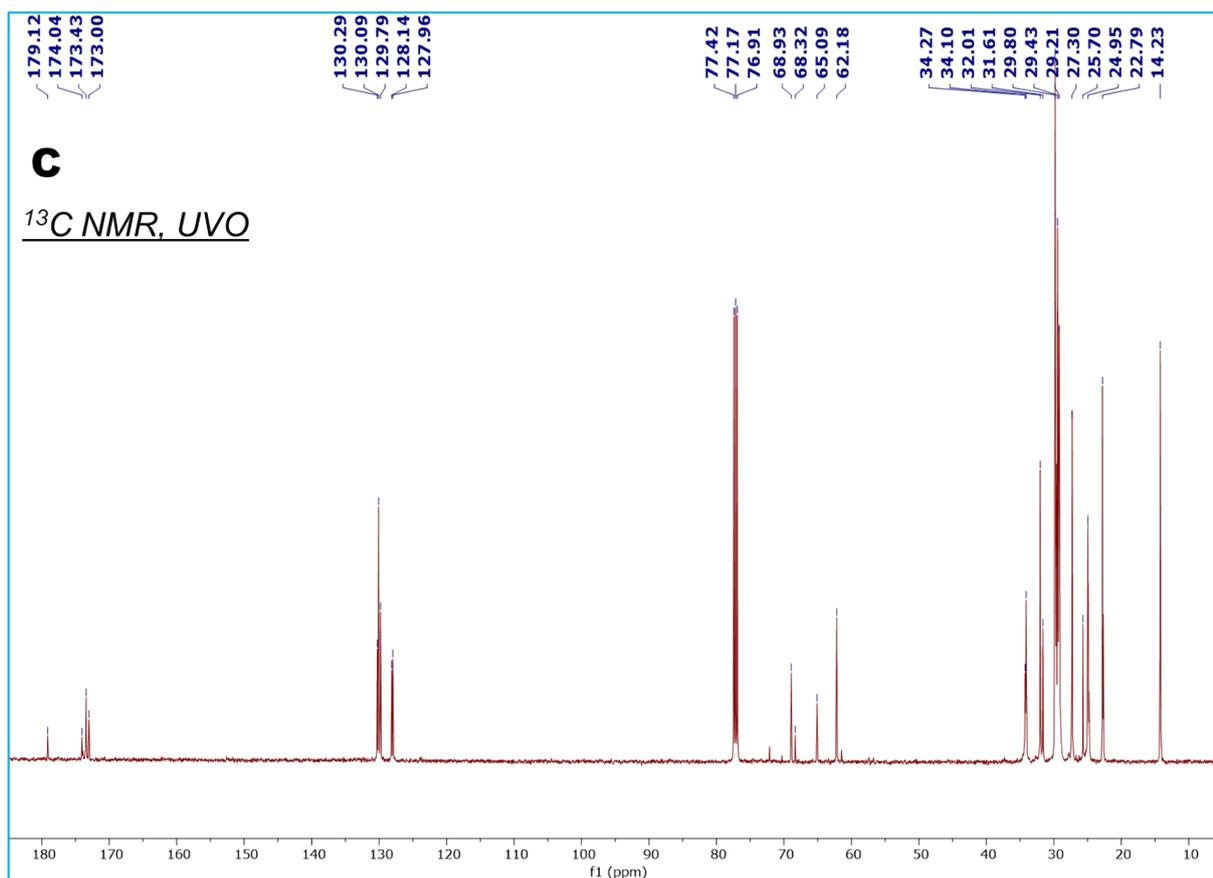
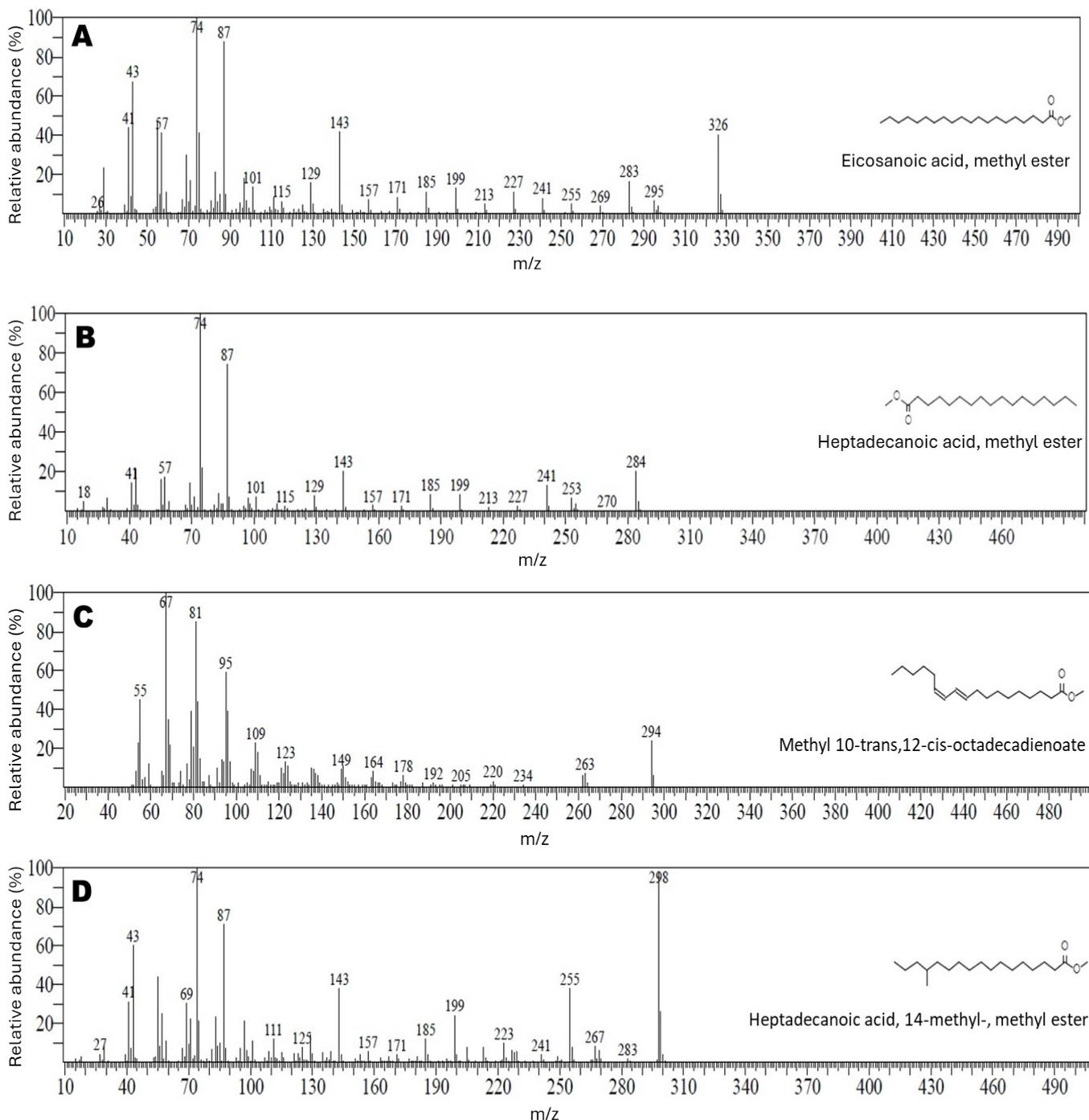


Fig. S2 Representative ^1H NMR (500 MHz, CDCl_3 , 27 °C) for (A) UVO, (B) as-synthesized biodiesel from UVO, and ^{13}C NMR (126 MHz, CDCl_3 , 27 °C) spectra for (C) UVO, and (D)

as-synthesized biodiesel from UVO, produced using $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ catalyst (MOMR 21.7:1, catalyst loading 7.4 wt. %, temperature 97.3 °C, and reaction time 0.96 h). The corresponding numerical spectroscopic data for as-synthesized biodiesel from UVO are: $^1\text{H NMR}$: δ 5.32 (m, 2H), 3.64 (s, 3H), 2.75 (t, 2H), 2.28 (t, 2H), 2.01 (m, 2H), 1.59 (m, 2H), 1.24 (m, 20H), 0.85 (t, 3H). $^{13}\text{C NMR}$: 174.48, 130.29, 130.09, 129.84, 128.12, 127.98, 51.56, 34.18, 32.01, 29.26, 27.30, 25.70, 25.03, 22.80, 22.69, 14.23

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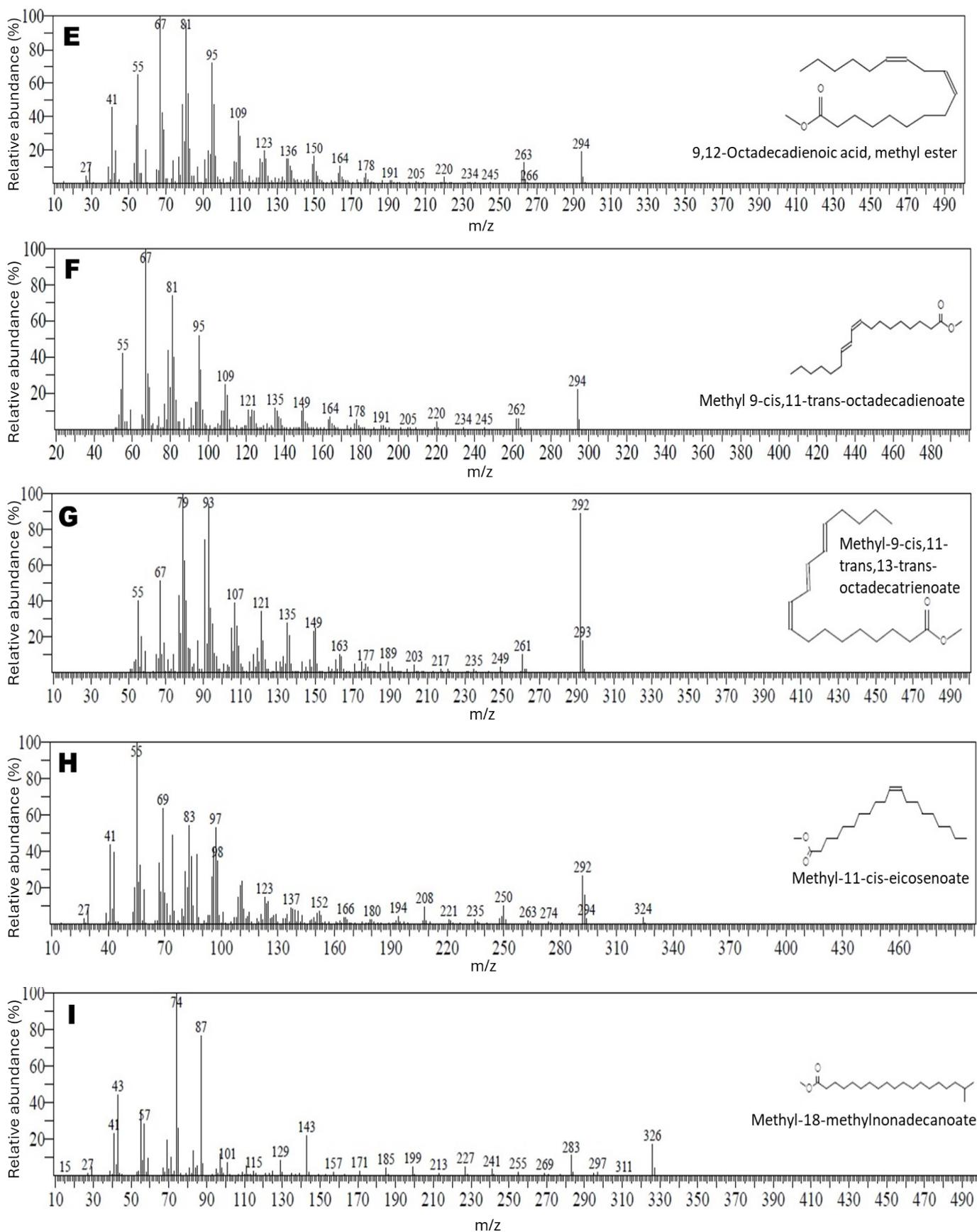


Fig. S3 Mass spectra of the corresponding methyl esters of the produced biodiesel tabulated in **Table S1**.

Table S3: Design of experiments for modelling biodiesel yield based on the RSM-CCD methodology

Std	Run	MeOH: Oil (molar ratio) (A)	Catalyst loading (wt. %) (B)	Temperature (°C) (C)	Time (min) (D)	Actual Yield (%)	Predicted Yield (%)
11	1	15	10	80	70	78.6	78.13
19	2	20	1	100	50	68.3	68.18
6	3	25	4	120	30	73.5	74.78
28	4	20	7	100	50	96.5	95.95
4	5	25	10	80	30	86.2	87.33
13	6	15	4	120	70	83.1	82.78
2	7	25	4	80	30	81.9	81.51
14	8	25	4	120	70	80.2	79.83
24	9	20	7	100	90	90.6	90.44
26	10	20	7	100	50	95.1	95.95
18	11	30	7	100	50	90.3	89.64
29	12	20	7	100	50	95.8	95.95
8	13	25	10	120	30	88.7	87.9
10	14	25	4	80	70	86.4	86.66
20	15	20	13	100	50	75.5	74.91
17	16	10	7	100	50	81.8	81.74
3	17	15	10	80	30	76.2	76.48
30	18	20	7	100	50	96.4	95.95

12	19	25	10	80	70	87.4	88.03
15	20	15	10	120	70	83.4	83.7
9	21	15	4	80	70	83.8	84.51
5	22	15	4	120	30	77.5	76.78
7	23	15	10	120	30	81.6	82.15
16	24	25	10	120	70	88.2	88.5
1	25	15	4	80	30	77.9	78.41
23	26	20	7	100	10	84.3	83.74
21	27	20	7	60	50	86.6	85.63
22	28	20	7	140	50	84.2	84.46
27	29	20	7	100	50	96.1	95.95
25	30	20	7	100	50	95.8	95.95

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Table S4 ANOVA results showing the significance of each process variable and its interaction effects

Source	Sum of squares	df	Mean square	F-value	p-value	status
Model	1595.4	14	113.96	172.18	< 0.0001	significant
A-MOMR	93.62	1	93.62	141.45	< 0.0001	
B-CL	68.01	1	68.01	102.75	< 0.0001	
C-Temp	2.04	1	2.04	3.08	0.0994	
D-Time	67.34	1	67.34	101.74	< 0.0001	
AB	60.06	1	60.06	90.75	< 0.0001	
AC	26.01	1	26.01	39.3	< 0.0001	
AD	0.9025	1	0.9025	1.36	0.2611	
BC	53.29	1	53.29	80.52	< 0.0001	
BD	19.8	1	19.8	29.92	< 0.0001	
CD	0.01	1	0.01	0.0151	0.9038	
A ²	180.4	1	180.4	272.58	< 0.0001	
B ²	1021.31	1	1021.31	1543.16	< 0.0001	
C ²	203.99	1	203.99	308.21	< 0.0001	
D ²	134.52	1	134.52	203.25	< 0.0001	
Residual	9.93	15	0.6618			
Lack of Fit						Not significant
Fit	8.63	10	0.8632	3.33	0.0981	
Pure Error	1.3	5	0.259			
Cor Total	1605.33	29				

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Table S5 Estimation of statistical parameters from the ANOVA analysis

Std. Dev.	0.8135	R ²	0.9938
Mean	85.06	Adjusted R ²	0.988
C.V. %	0.9564	Predicted R ²	0.9679
		Adequate Precision	48.2831

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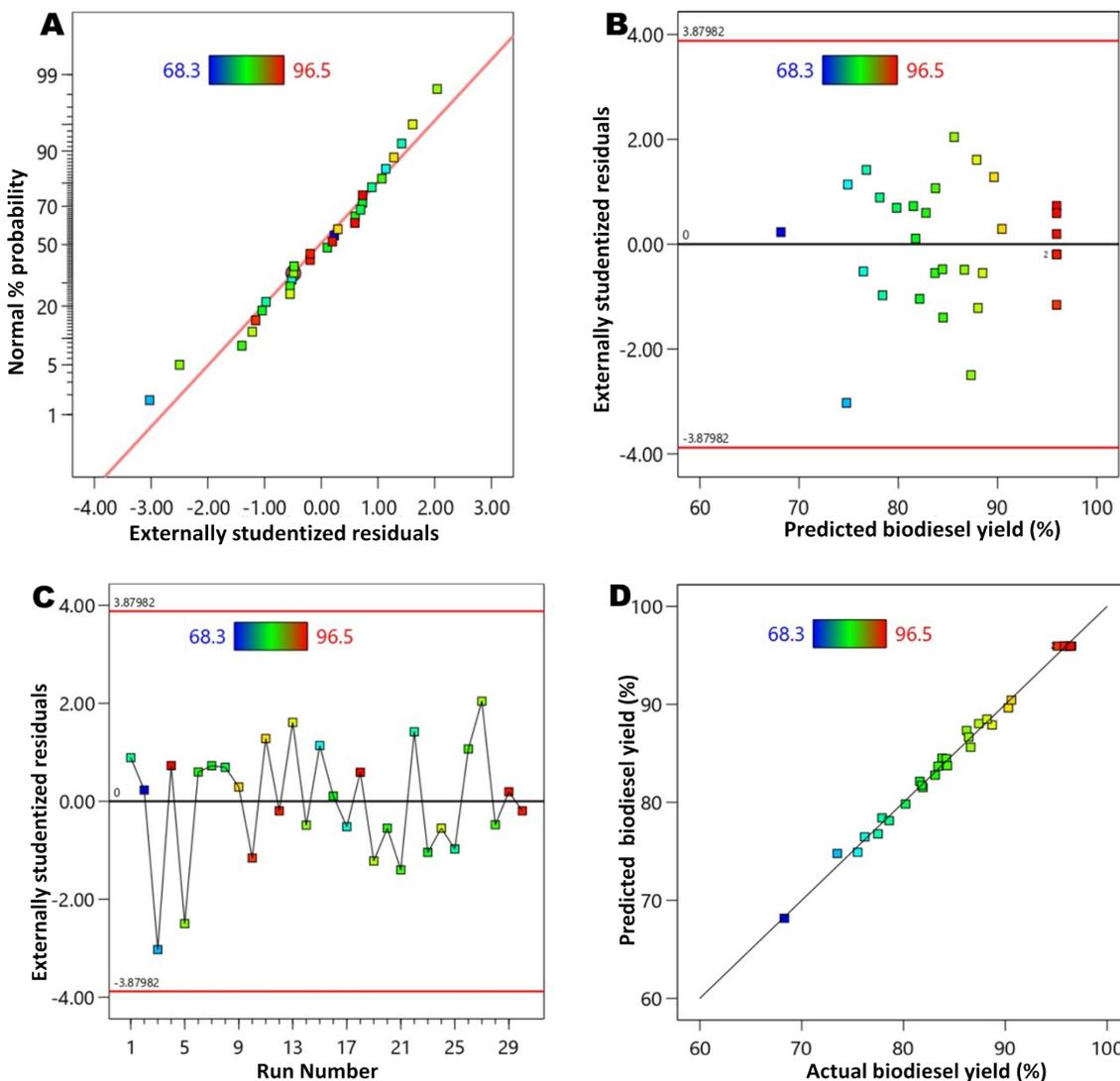


Fig. S4 Diagnostic plots for the 30 run experiments displaying the assessment of (A) normal percentage probability vs. externally studentized residuals, (B) externally studentized residuals vs. predicted biodiesel yield, (C) externally studentized residuals vs. run numbers, and (D) predicted vs. actual biodiesel yield.

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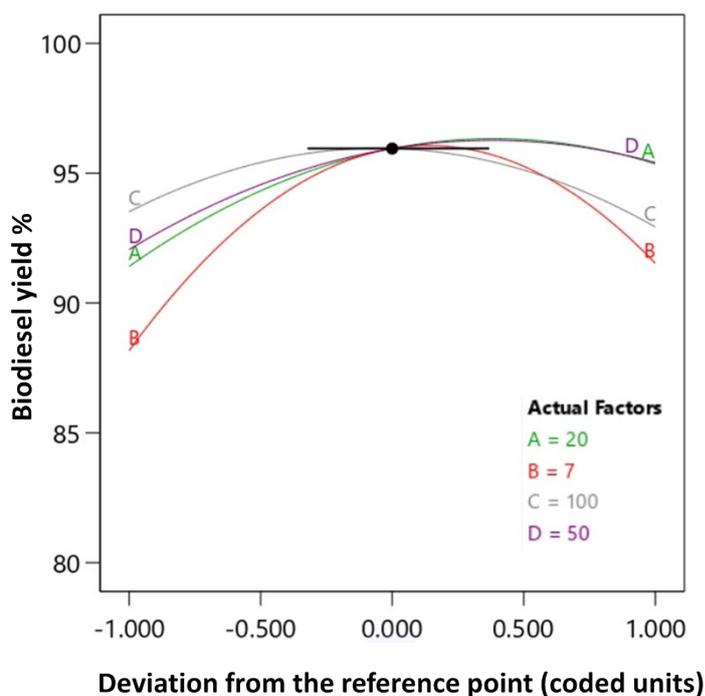


Fig. S5 Perturbation plot displaying the influence of four variables at the center values of MOMR (A) = 20:1, catalyst loading (B) = 7 wt. %, reaction temperature (C) = 100 °C, reaction time (D) = 50 min. on biodiesel yield %.

55 Comparison of heterogeneous catalysts for biodiesel production from UVO

56 A range of heterogeneous catalysts has been explored for biodiesel production from diverse
 57 feedstocks, as summarized in **Table S6**. The current catalyst, $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$, offers
 58 several advantages over others, particularly in biodiesel yield (97.8 %) and recyclability across five
 59 cycles with minimal yield loss (95.8 %). Among the MOFs listed, MOF-801¹ shows a notably lower
 60 yield (60 %) under more energy-intensive conditions. Similarly, MOF-5² achieves 90.8 % yield
 61 but requires a significantly longer reaction time of 12 h with limited reusability (27.7 %). HPA-
 62 ZIF-8³ delivers an impressive yield of 98 %, but its stability after multiple cycles remains inferior
 63 (54 % yield after reuse). Additionally, HPW-ZIF-67⁴ achieves a high yield (98.5 %) using
 64 microalgal lipids but involves difficulties associated with the recovery process unlike the current
 65 monolithic formulation, which simplifies recycling. In comparison to Cr-EDTA⁵, which catalyzes
 66 the conversion of oleic acid with a yield of 91%, $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ offers higher efficiency
 67 and a greater number of reuse cycles while requiring only moderate operating conditions. Other
 68 catalysts, such as CuO/ZnO⁶ and $\text{K}_2\text{CO}_3/\text{MgFe}_2\text{O}_4$ ⁷, yield 93.5 % and 92.9 % biodiesel,
 69 respectively, but require higher temperatures and longer reaction durations. In terms of reusability,
 70 $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ outperforms many conventional catalysts. For instance, $\text{NaFeTiO}_4/\text{Fe}_2\text{O}_3$ -

71 FeTiO_3 ⁸ shows good catalytic performance initially (93.24 %), but it loses efficiency quickly over
72 subsequent cycles (47.54 %). Although CuO/ZnO ⁶ maintains moderate reusability (81.4 %), its
73 starting yield is still lower than that achieved by the current catalyst. The monolithic nature of
74 $\text{monoUiO-66-NH}_2@\text{SO}_3\text{H}$ offers distinct advantages over other powdered MOFs, which often suffer
75 from diffusion limitations. Consistent with this trend, $\text{powUiO-66-NH}_2@\text{SO}_3\text{H}$ yields 92.4 ± 0.2 %
76 biodiesel with modest recyclability (60.4 % yield after 3 cycles). In contrast, monoUiO-66-
77 $\text{NH}_2@\text{SO}_3\text{H}$ achieves a higher initial yield of 97.8 % and 89.8 % yield even after five reaction
78 cycles, demonstrating a clear advantage in stability and reuse.

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Table S6: Comparison of heterogeneous catalysts for biodiesel production from various feedstocks

Entry	Catalyst	Feedstock	^a Conditions	Biodiesel yield (%)	^d CRC (Y %)	Ref.
1.	HPW-ZIF-67	Microalgal lipids	20:1, 1, 200, 1.5	98.50 ^c	4 (91.30) ^c	4
2.	Cr-EDTA	Oleic acid	11:1, 17.7, 60, 5	91.00	3 (89.00)	5
3.	Heteropanax fragrans	JCO	12:1, 7, 65, 1.08	91.00	2 (90.22)	9
4.	NaFeTiO ₄ /Fe ₂ O ₃ -FeTiO ₃	JCO	12.47:1, 13.8, 65, 1	93.24 ^c	4 (47.54) ^c	8
5.	CuO/ZnO	WCO	9:1, 5, 65, 2	93.50 ^c	5 (81.40) ^c	6
6.	MOF-5	WCO	36:1, 0.75, 145, 12	90.80 ^c	2 (27.70) ^c	2
7.	K ₂ CO ₃ /MgFe ₂ O ₄	WCO	6.6:1, 4.4, 50, 1.8	92.90 ^c	2 (91.80) ^c	7
8.	CuO/ZnO	WCO	9:1, 5, 65, 2	93.50 ^c	5 (81.40) ^c	6
9.	HPA-ZIF-8	Rapeseed oil	10:1, 4, 200, 2	98.00	5 (54.00)	3
10.	MOF-801	UVO	50:1, 10, 180, 8	60.00	3 (50.00)	1
11.	_{pow} UiO-66-NH ₂ @SO ₃ H	UVO	21.7, 7.4, 97.3, 0.96	92.40	3 (60.40)	This work
12.	_{mono} UiO-66-NH ₂ @SO ₃ H	UVO	21.7, 7.4, 97.3, 0.96	97.80	5 (89.80)	This work

^a MOMR, Catalyst loading (wt. %), Temperature (°C), Time (h)

^b Microwave heating, ^c Conversion (%)

^d CRC (Y %) – Catalyst reusability cycles (Yield %); PSF – Polysulfonic acid-formaldehyde; WCO – Waste cooking oil

AIL – Acidic ionic liquid; SAFACAM – Sulfonic acid functionalized aromatic carbonaceous material, UVO – Used vegetable oil

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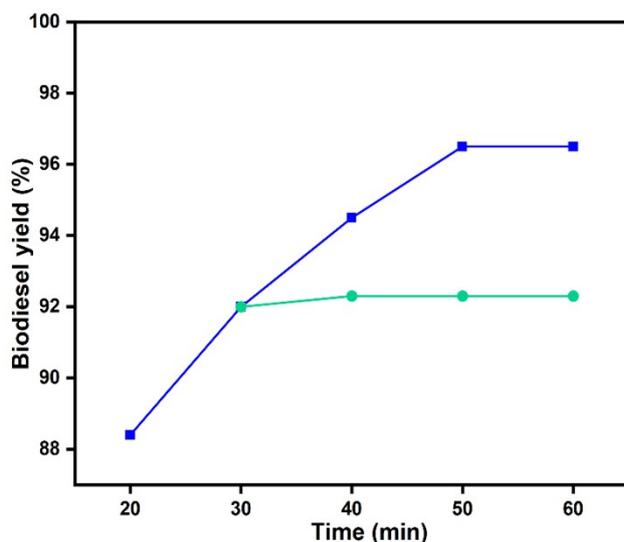


Fig. S6 Biodiesel yield obtained using $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ under the reaction conditions of MOMR 20:1, catalyst loading 7 wt. %, temperature 100 °C, and reaction time 20-60 min (blue line) and after removal of catalyst at 30 min. and continuation of reaction under otherwise identical conditions (green line).

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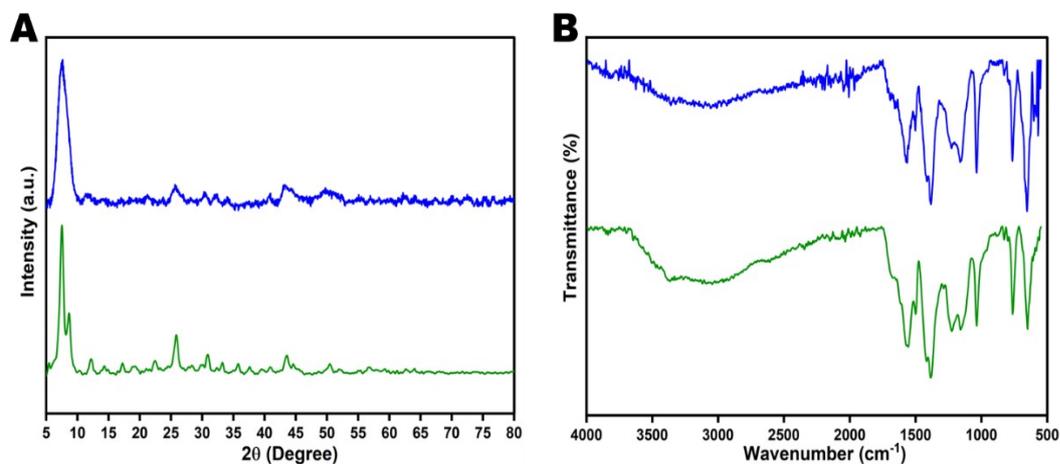


Fig. S7 XRD and FTIR of fresh (green) and reused (blue) catalyst after 6-transesterification cycles.

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Table S7 Overview of expenditure, covering raw materials, workforce, energy, research, and operational overheads, in $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ catalyst synthesis.

SI. No	Item	Quantity	^a Price (USD)	Cost (USD)
1.	Zirconium oxychloride octahydrate	1.30 g	1.15/500 g	0.003
2.	2-aminobenzenedicarboxylic acid	1.0 g	2.1/500 g	0.004
3.	N, N-dimethylformamide	50 mL	0.34/1 L	0.017
5.	Propene-1,3-sultone	0.4 g	10/500 g	0.008
6.	Chloroform	15 mL	0.43/1 L	0.006
7.	The total amount of catalyst	1 g	-	0.038
8.	Cost price of chemicals required for catalyst preparation for 1 kg biodiesel	72.3 g	-	2.74
9.	Electricity required in the preparation of the catalyst	1.2 units	-	0.1
10.	Preparatory cost of 71.4 g catalyst	-	-	2.84
11.	No. of cycles of reactions	6	-	-
12.	Cost of catalyst per cycle	-	-	0.47

⁸⁶Cost of raw materials is as per the purchased quotation price (2024-2025) from India Mart and Sisco

⁸⁷Research Lab, India. 1 USD = 87.19 INR (September 2025)

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Table S8: Cost analysis for the preparation of biodiesel from $\text{mono UiO-66-NH}_2\text{@SO}_3\text{H}$ catalyst, providing a systematic view of the financial aspects throughout the process

Sl. No.	Item	Quantity	^a Price (USD)	Cost (USD)
1.	Total amount of biodiesel	1 kg	-	-
2.	Cost UVO per kg biodiesel production	0.978 kg	Collected from canteens of NIT Silchar	0.0
3.	Pretreatment cost (Filtration and water removal)	0.978 kg	-	0.08
3.	Amount of catalyst for 1 kg biodiesel production	72.3 g	-	0.47
4.	Methanol for 1 kg biodiesel production	933.0 mL	0.6/5 L	0.12
5.	Electricity	1.3 units	-	0.1
6.	Total cost	-	-	0.77
7.	^b Overhead cost	15 %	-	0.12
8.	Total cost of 1 kg biodiesel production			0.89

92 ^aCost of raw materials is as per the purchased quotation price (2024-2025) from India Mart and
93 Sisco Research Lab, India. 1 USD = 87.19 INR (September 2025)

94 ^bOverhead cost in biodiesel production = 15 % of the net charge and includes indirect expenses
95 such as administrative, utility, and facility costs.

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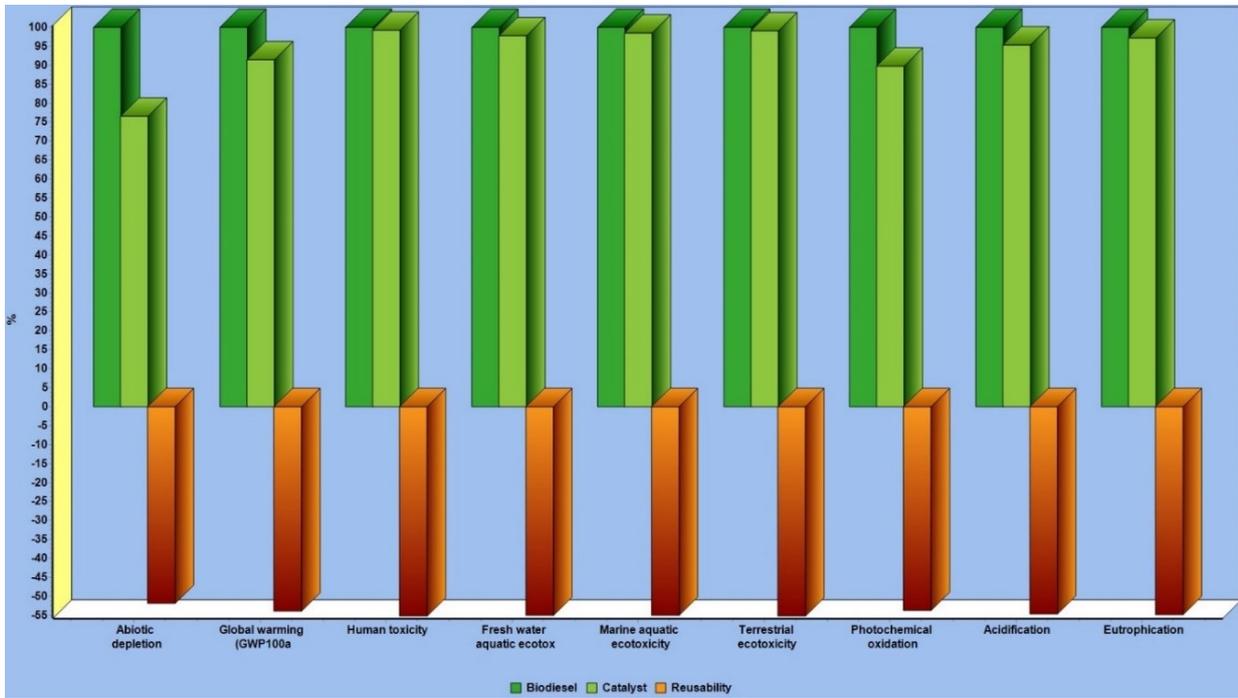


Fig. S8 Percentage variation attributed to potential environmental impacts assessed using the CML-IA baseline method (Version 3.10).

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Table S9: Environmental impact assessment in 1 kg biodiesel production from $\text{monoUiO-66-NH}_2\text{@SO}_3\text{H}$ catalyst

Sl No.	Impact category	Unit	Catalyst preparation (a)	Biodiesel production (b)	Recycling (c)	Total [b+c]
1.	Abiotic depletion	kg C ₂ H ₄ eq	2.02E-6	2.64E-6	-1.37E-6	1.27E-6
2.	Global warming	kgCO ₂ eq	12.1	13.3	-7.17	6.13
3.	Human toxicity	kg 1,4-DB eq	19.3	19.5	-10.8	8.7
4.	Freshwater aquatic ecotoxicity	kg 1,4-DB eq	3.72	3.81	-2.09	5.9
5.	Marine aquatic ecotoxicity	kg 1,4-DB eq	1.37E3	1.39E4	-7.65E+3	6.25E3
6.	Terrestrial ecotoxicity	kg 1,4-DB eq	0.123	0.124	-0.0685	0.055
7.	Photochemical oxidation	kg C ₂ H ₄ eq	0.0004	0.00446	-0.0024	0.002
8.	Acidification	kg SO ₂ eq	0.0352	0.0369	0.0202	0.0167
9.	Eutrophication	kg PO ₄ ³⁻ eq	0.0155	0.016	-0.00878	0.0072

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