

Electronic Supplementary Information (ESI)

Robust biocatalyst for the green continuous flow synthesis of esters from biomass-derived furfuryl alcohol and C₈-C₁₈ carboxylic acids

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Space-time-yield (STY) for batch process

$$STY = m_{\text{product}} / t_{\text{reaction time}} V_{\text{biocatalyst}} \text{ (gh}^{-1}\text{L}^{-1}\text{)}$$

$$STY = 0.0884\text{g} / 0.75\text{h} \cdot 0.000368\text{L} = 320.7 \text{ (gh}^{-1}\text{L}^{-1}\text{)}$$

Specific productivity (SP) for batch process

$$SP = m_{\text{product}} / t_{\text{reaction time}} m_{\text{protein}} \text{ (gh}^{-1}\text{mg}^{-1}\text{)}$$

$$SP = 0.0884\text{g} / 0.75\text{h} \cdot 6.36\text{mg} = 0.019 \text{ (gh}^{-1}\text{mg}^{-1}\text{)}$$

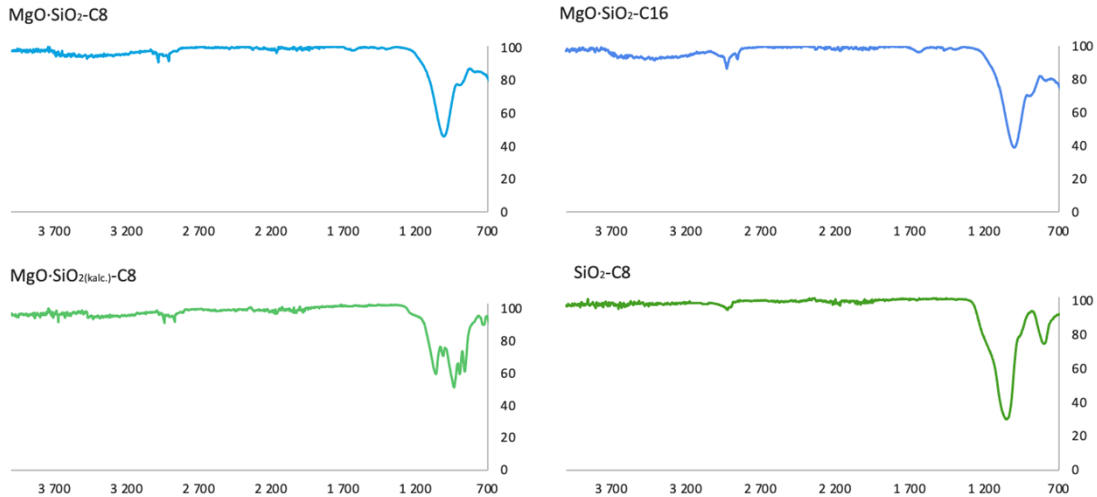


Fig. S1. FT-IR analysis of $\text{MgO} \cdot \text{SiO}_2\text{-C}_8$, $\text{MgO} \cdot \text{SiO}_2\text{-C}_{16}$, $\text{MgO} \cdot \text{SiO}_2\text{-C}_8(\text{calc.})$, $\text{SiO}_2\text{-C}_8$.

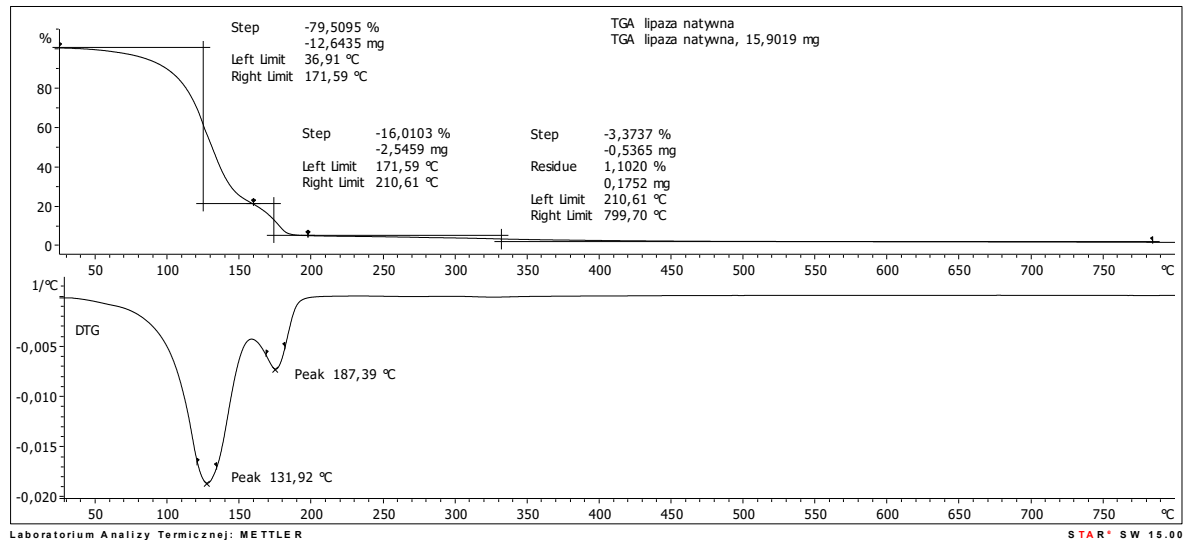


Fig. S2. TG/DTG analysis of LAO.

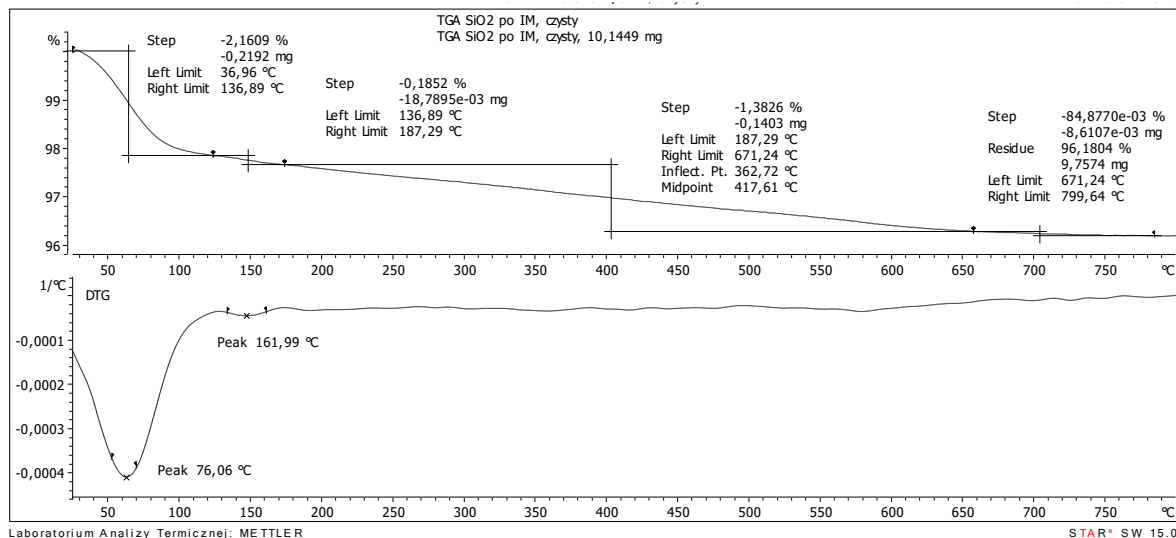


Fig. S3. TG/DTG analysis of SiO₂.

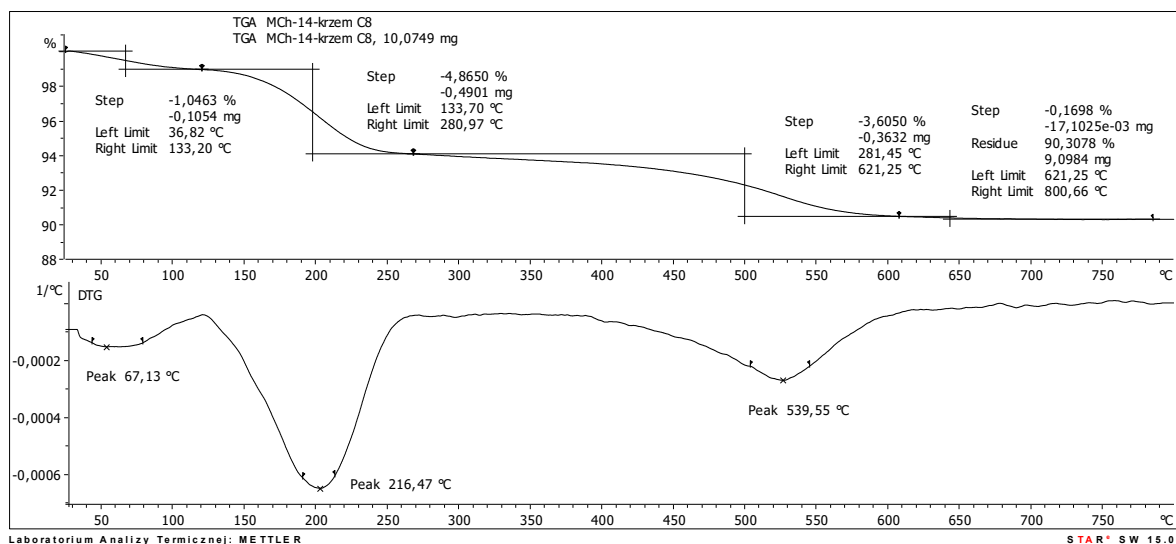


Fig. S4. TG/DTG analysis of SiO₂-C₈.

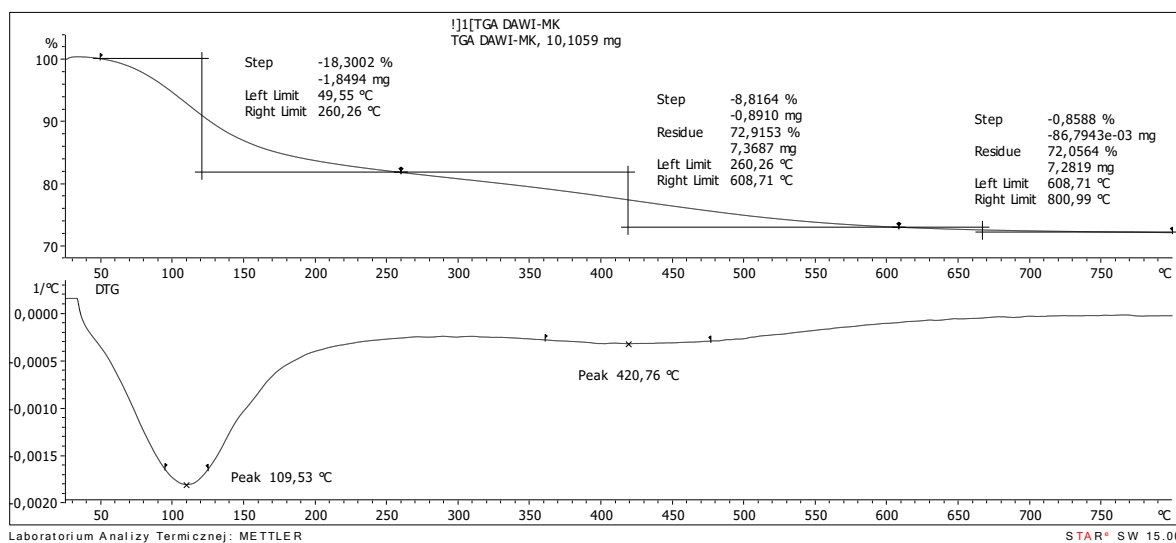


Fig. S5. TG/DTG analysis of MgO · SiO₂.

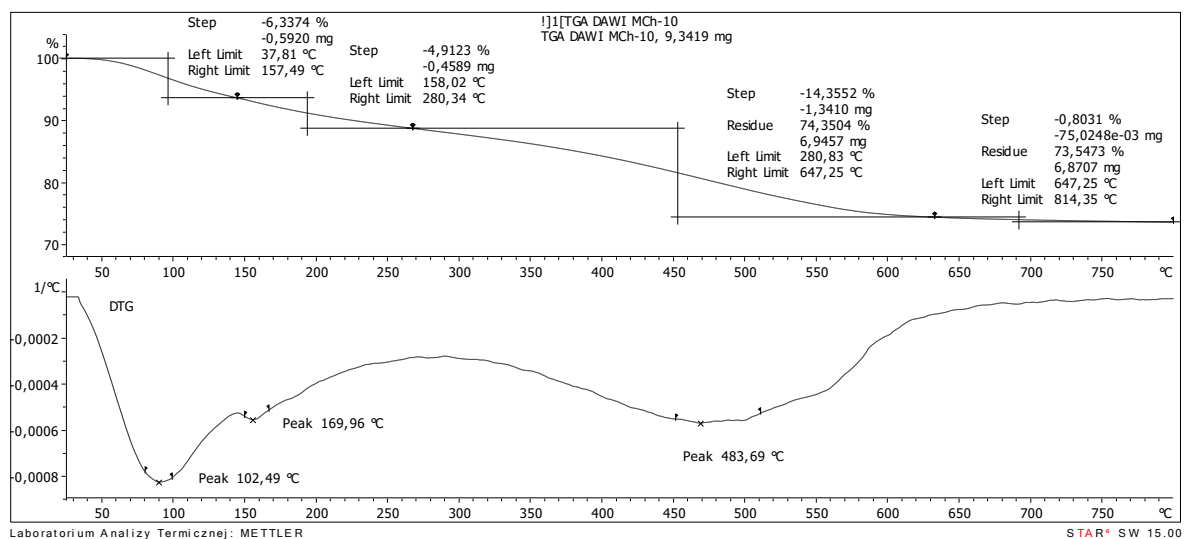


Fig. S6. TG/DTG analysis of MgO · SiO₂ · C₈.

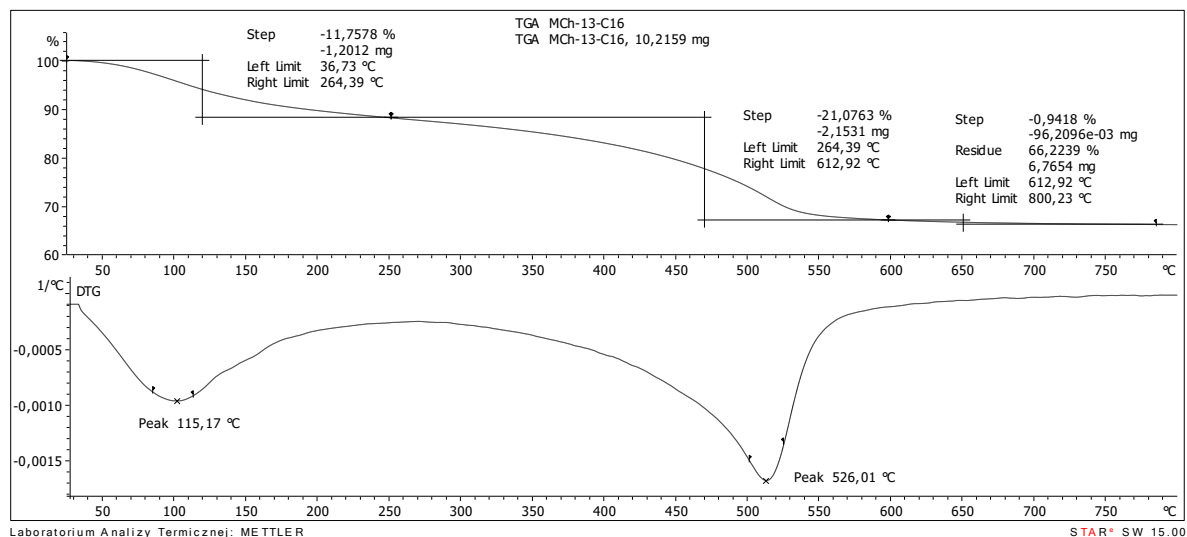


Fig. S7. TG/DTG analysis of MgO · SiO₂ · C₁₆.

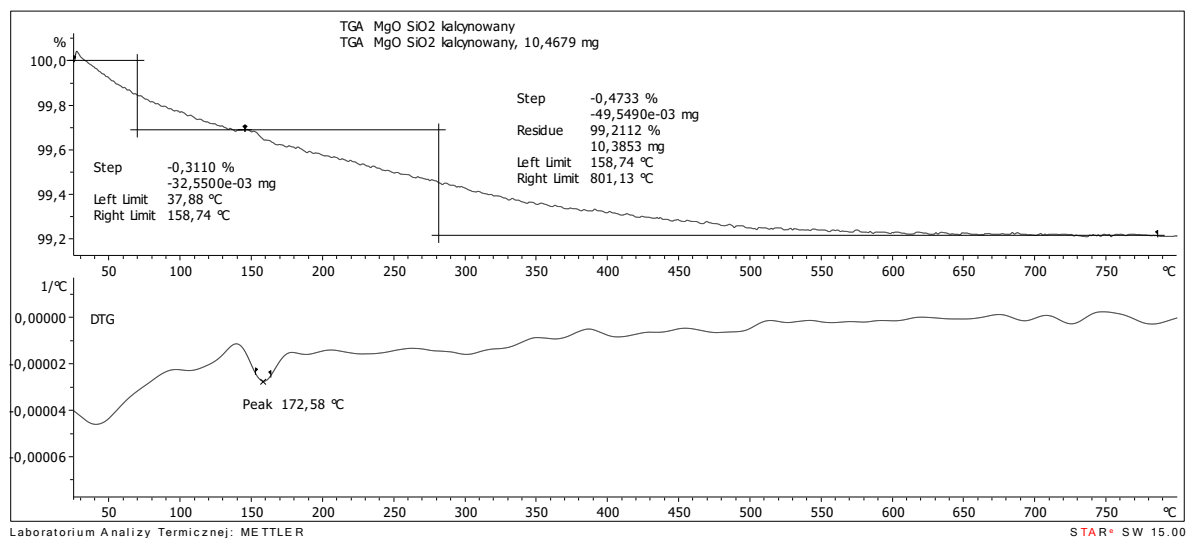


Fig. S8. TG/DTG analysis of $\text{MgO} \cdot \text{SiO}_2(\text{calc.})$.

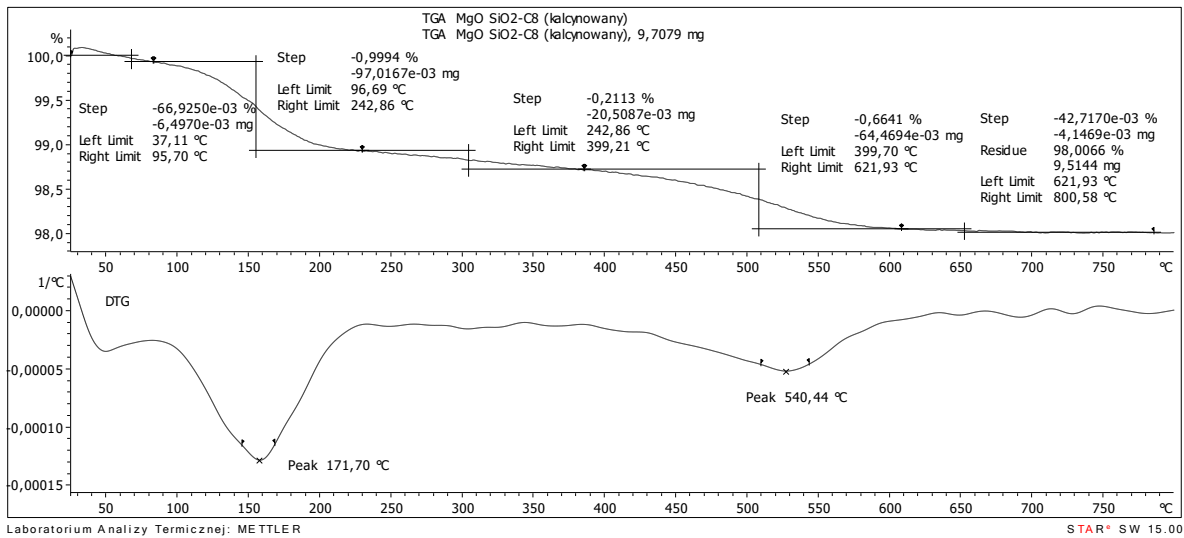


Fig. S9. TG/DTG analysis of $\text{MgO} \cdot \text{SiO}_2(\text{calc.})\text{-C}_8$.



Fig. S10. SEM-EDS analysis SiO_2 .

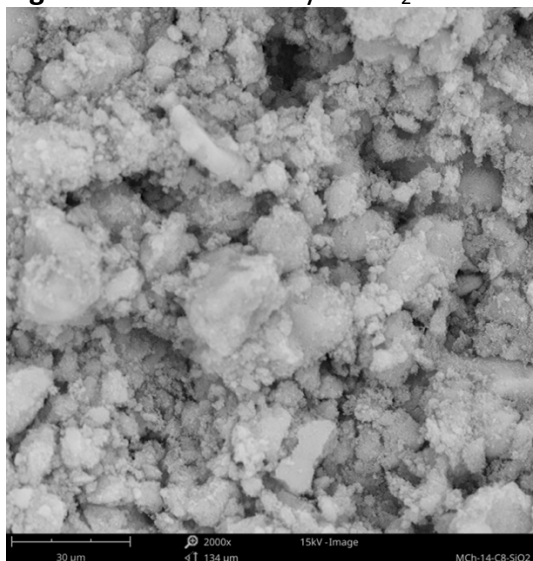
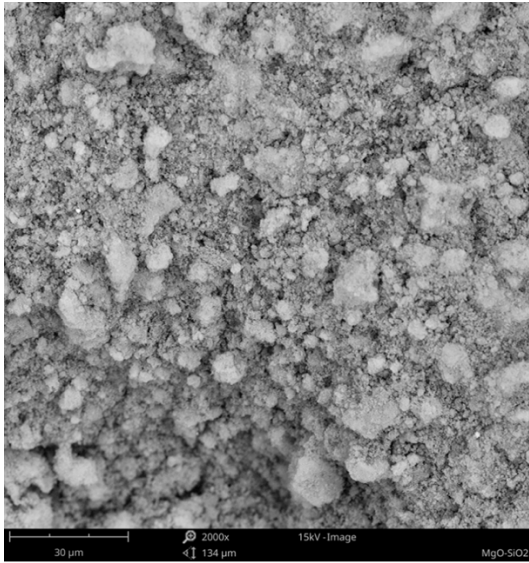
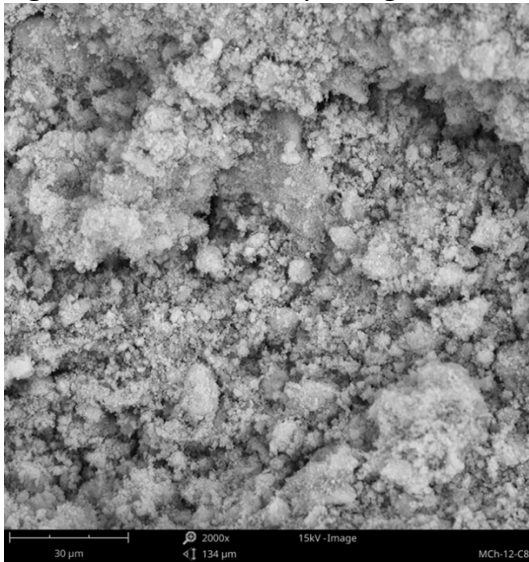


Fig. S11. SEM-EDS analysis $\text{SiO}_2\text{-C}_8$.



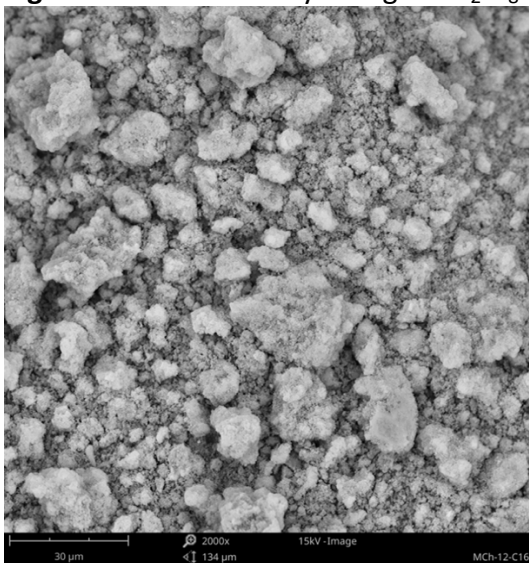
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	68.42	56.74
14	Si	Silicon	17.80	25.90
12	Mg	Magnesium	13.78	17.36

Fig. S12. SEM-EDS analysis $\text{MgO}\cdot\text{SiO}_2$.



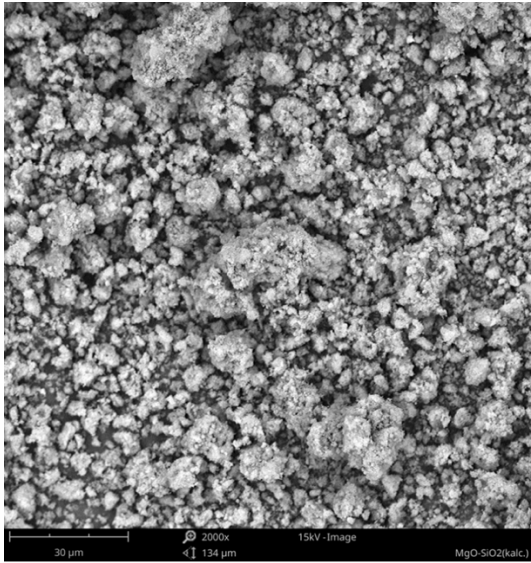
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	62.92	53.67
14	Si	Silicon	16.98	25.42
12	Mg	Magnesium	12.27	15.90
6	C	Carbon	7.83	5.01

Fig. S13. SEM-EDS analysis $\text{MgO}\cdot\text{SiO}_2\text{-C}_8$.



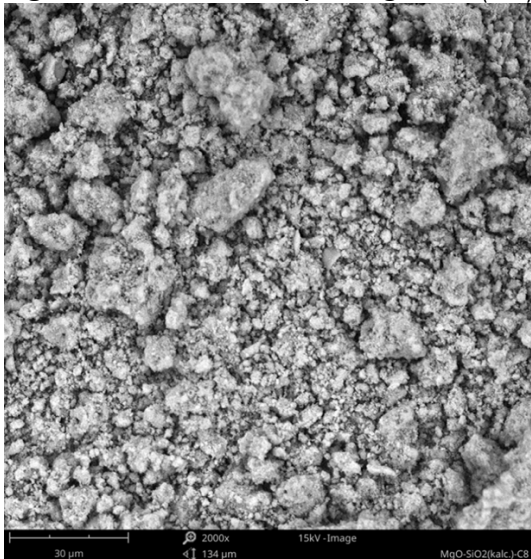
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	67.57	59.21
14	Si	Silicon	14.07	21.64
12	Mg	Magnesium	10.52	14.00
6	C	Carbon	7.84	5.16

Fig. S14. SEM-EDS analysis $\text{MgO}\cdot\text{SiO}_2\text{-C}_{16}$.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	54.43	41.83
14	Si	Silicon	27.34	36.88
12	Mg	Magnesium	18.24	21.29

Fig. S15. SEM-EDS analysis $\text{MgO}\cdot\text{SiO}_2(\text{calc.})$.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	65.28	56.13
14	Si	Silicon	15.10	22.80
12	Mg	Magnesium	12.72	16.61
6	C	Carbon	6.90	4.46

Fig. S16. SEM-EDS analysis $\text{MgO}\cdot\text{SiO}_2(\text{calc.})\text{-C}_8$.

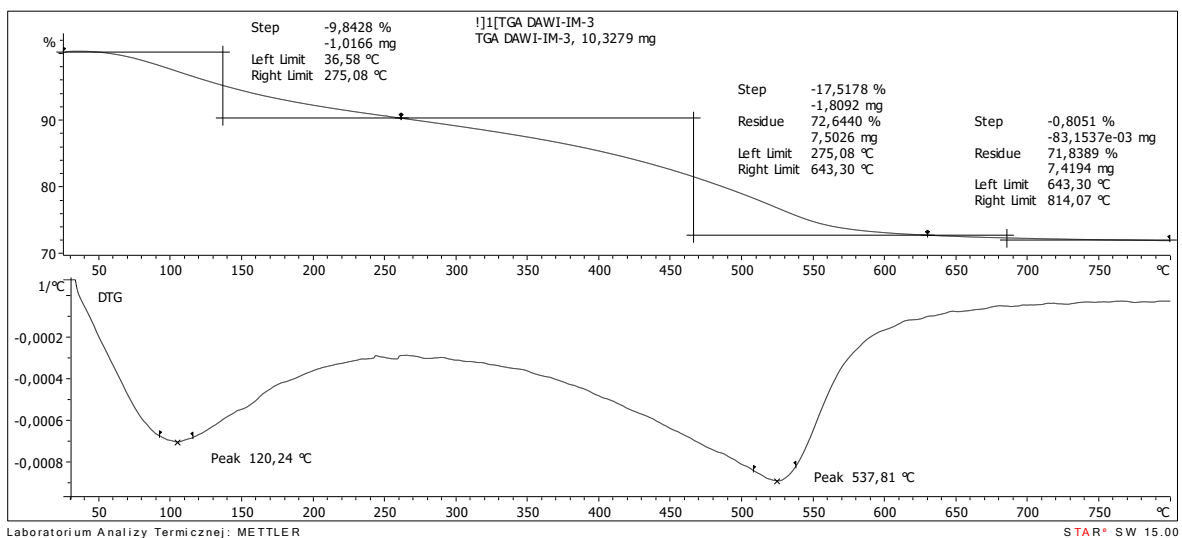


Fig. S17. TG/DTG analysis of $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$.

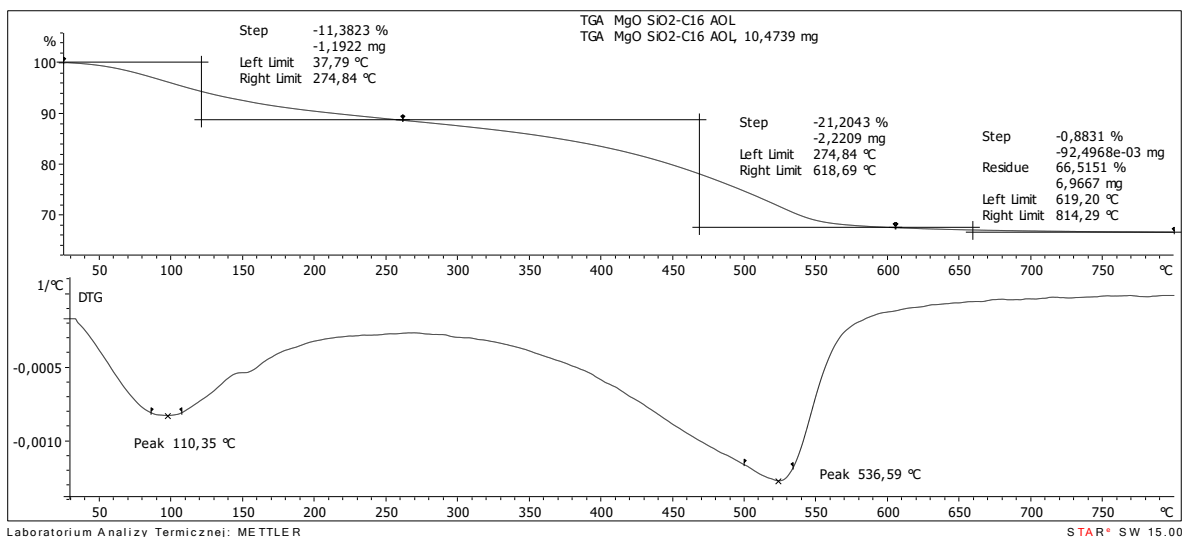


Fig. S18. TG/DTG analysis of MgO · SiO₂-C₁₆-LAO.

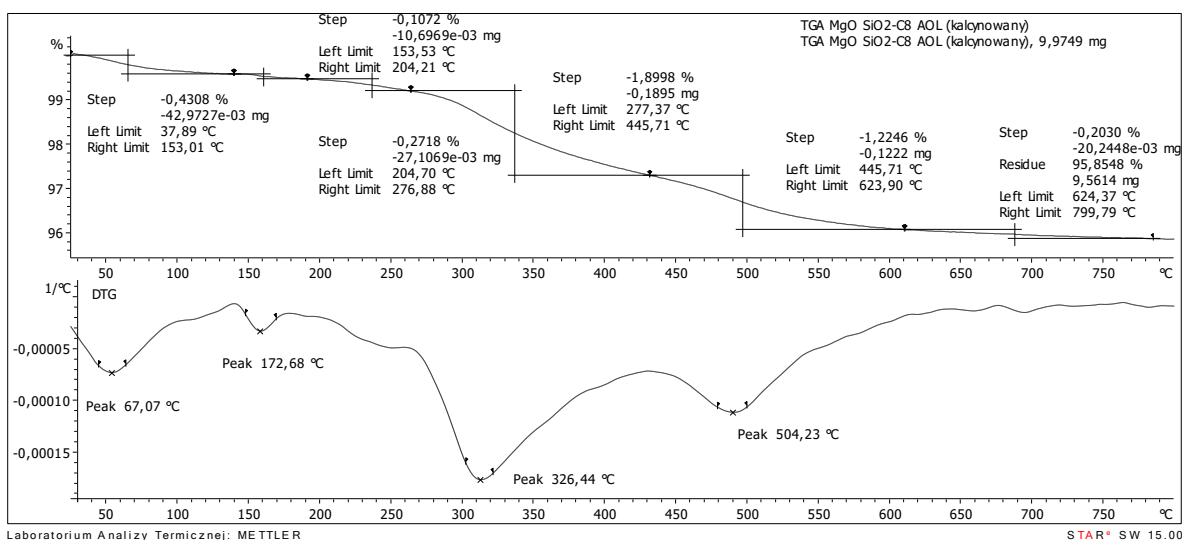


Fig. S19. TG/DTG analysis of MgO · SiO₂(calc.)-C₈-LAO.

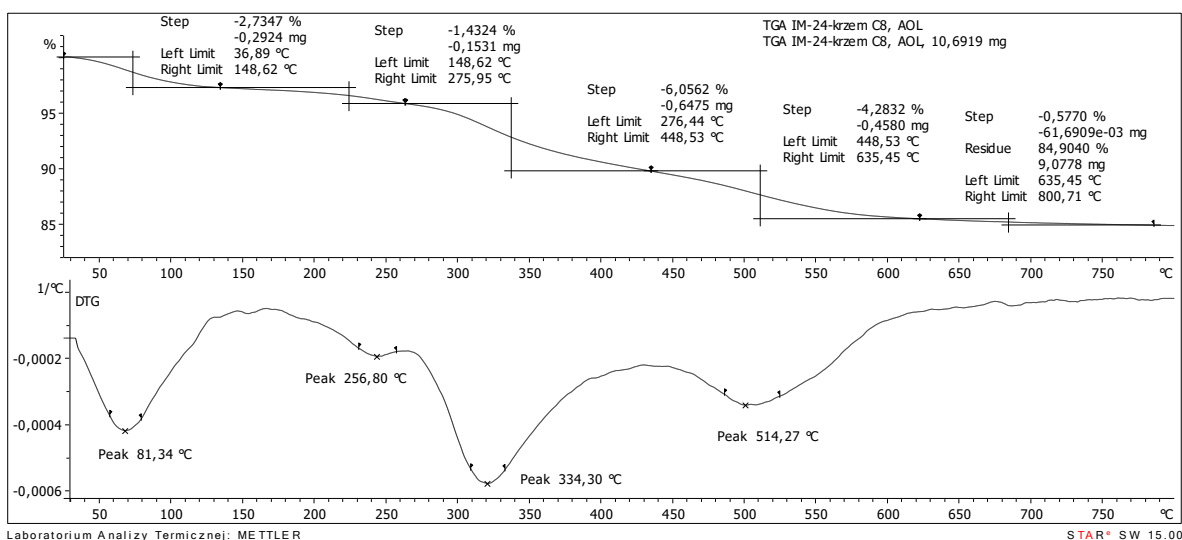


Fig. S20. TG/DTG analysis of SiO₂-C₈-LAO.

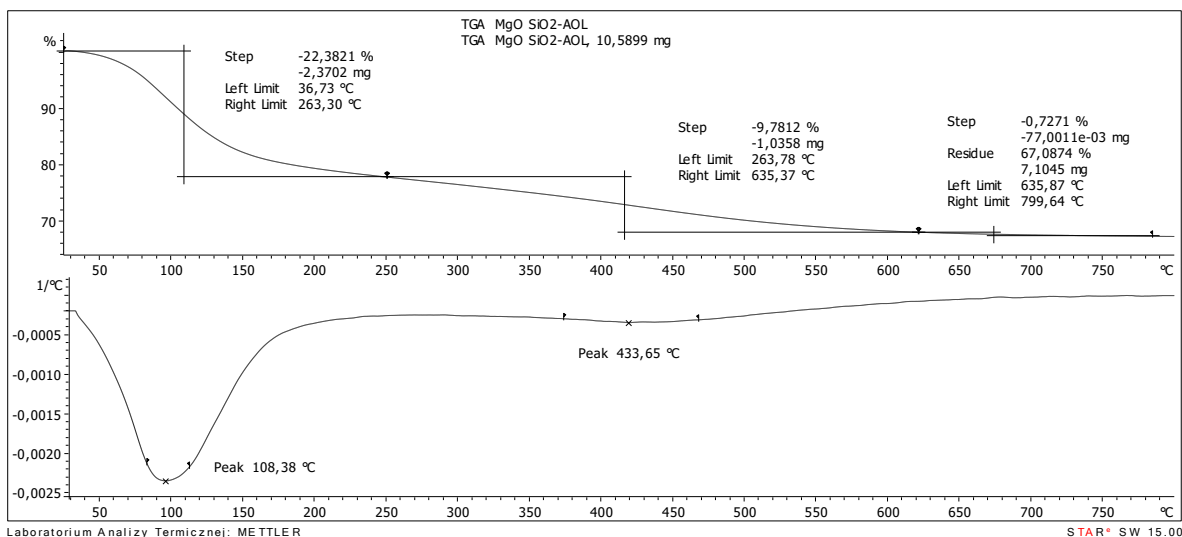
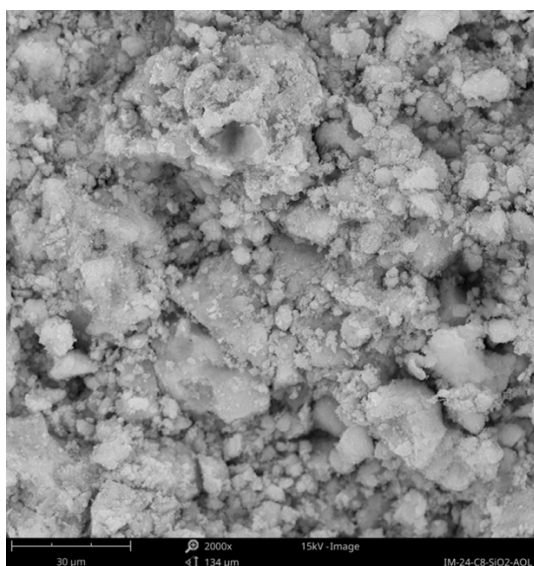
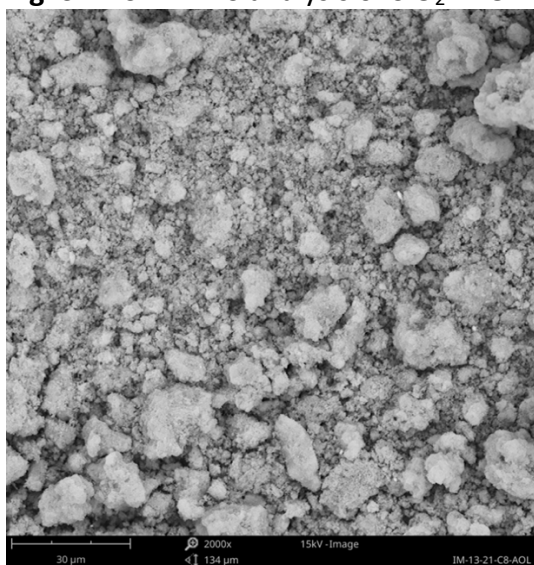


Fig. S21. TG/DTG analysis of MgO · SiO₂-LAO.



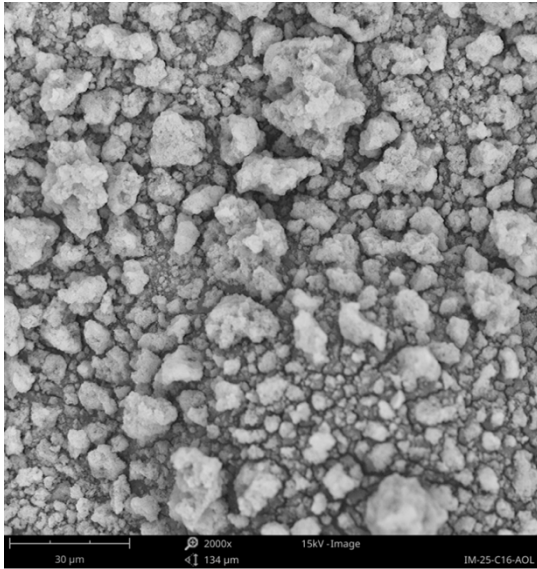
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	66.04	58.09
14	Si	Silicon	21.39	33.03
6	C	Carbon	8.53	5.63
7	N	Nitrogen	3.61	2.78
9	F	Fluorine	0.41	0.43
16	S	Sulfur	0.02	0.04

Fig. S22. SEM-EDS analysis of SiO₂-LAO.



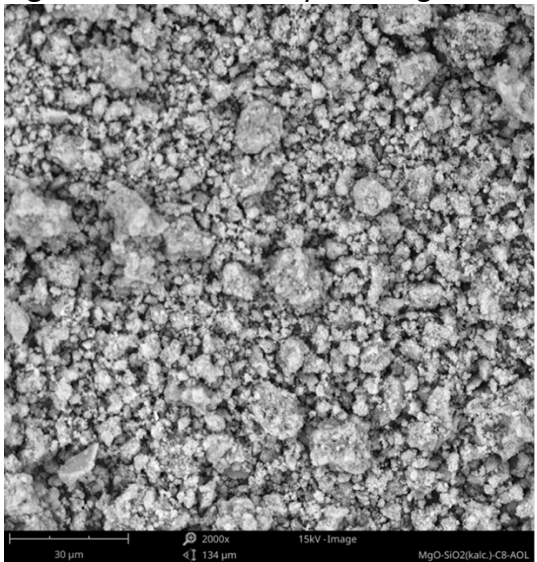
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	69.29	60.30
14	Si	Silicon	13.34	20.38
12	Mg	Magnesium	11.34	14.99
6	C	Carbon	3.85	2.52
7	N	Nitrogen	1.81	1.38
9	F	Fluorine	0.29	0.30
15	P	Phosphorus	0.06	0.10
16	S	Sulfur	0.02	0.04

Fig. S23. SEM-EDS analysis of MgO·SiO₂-C₈-LAO.



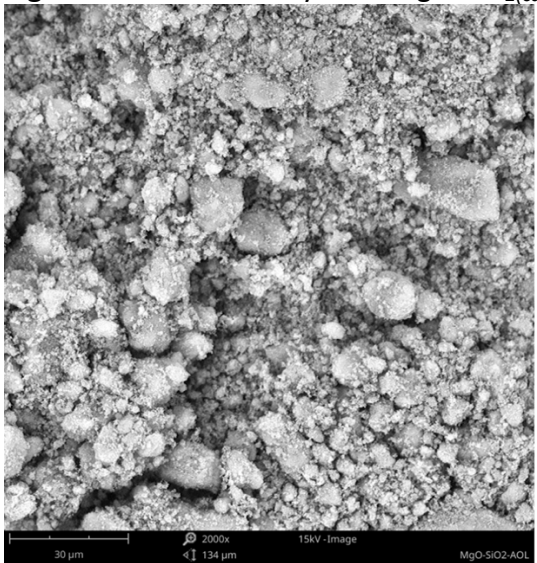
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	65.74	58.63
14	Si	Silicon	12.23	19.15
12	Mg	Magnesium	10.33	14.00
6	C	Carbon	9.52	6.38
7	N	Nitrogen	1.79	1.39
9	F	Fluorine	0.32	0.33
15	P	Phosphorus	0.04	0.06
16	S	Sulfur	0.03	0.05

Fig. S24. SEM-EDS analysis of MgO·SiO₂-C₁₆-LAO.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	60.27	53.24
14	Si	Silicon	13.79	21.38
12	Mg	Magnesium	11.33	15.21
6	C	Carbon	10.12	6.71
7	N	Nitrogen	4.49	3.47

Fig. S25. SEM-EDS analysis of MgO·SiO₂(calc.)-C₈-LAO.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	56.58	48.77
14	Si	Silicon	17.52	26.51
12	Mg	Magnesium	11.12	14.56
6	C	Carbon	9.19	5.94
7	N	Nitrogen	5.59	4.22

Fig. S26. SEM-EDS analysis of MgO·SiO₂-LAO.

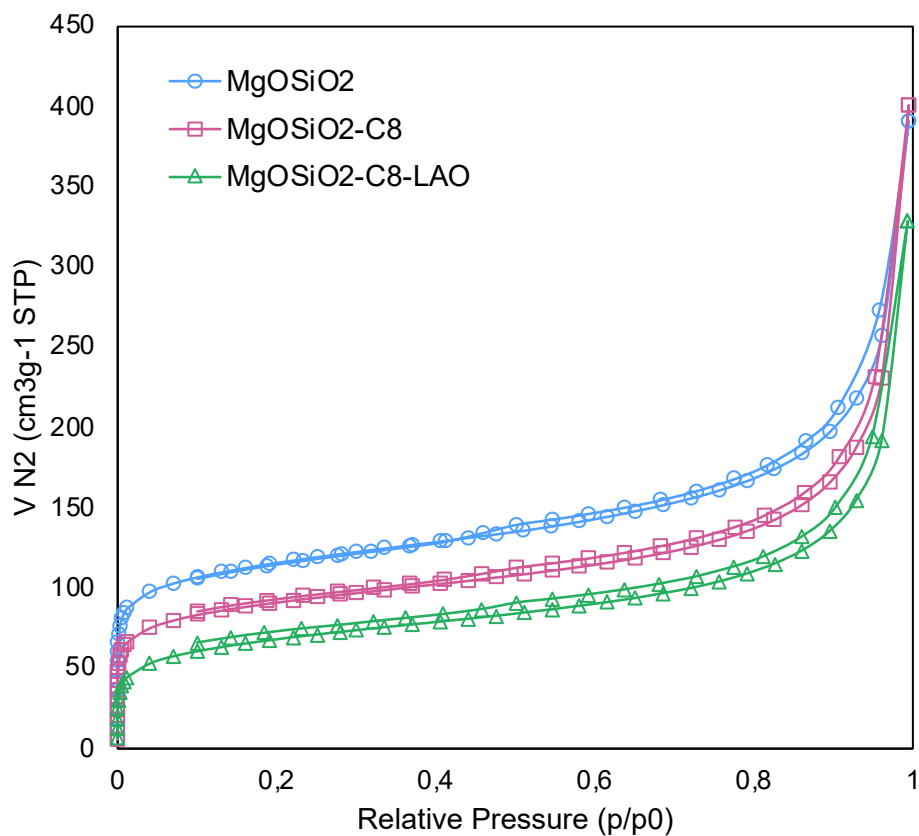


Fig. S27. Adsorption-desorption isotherms of $\text{MgO}\cdot\text{SiO}_2$, $\text{MgO}\cdot\text{SiO}_2\text{-C}_8$, $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$.

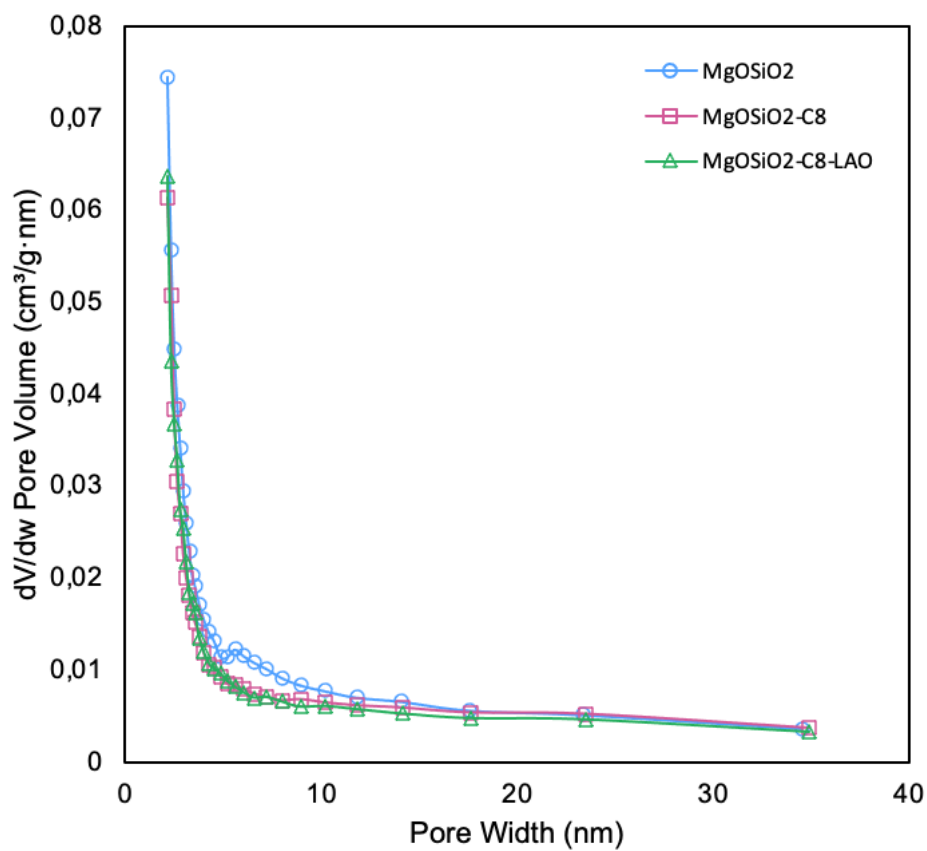


Fig. S28. Pore size distributions of $\text{MgO}\cdot\text{SiO}_2$, $\text{MgO}\cdot\text{SiO}_2\text{-C}_8$, $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$.

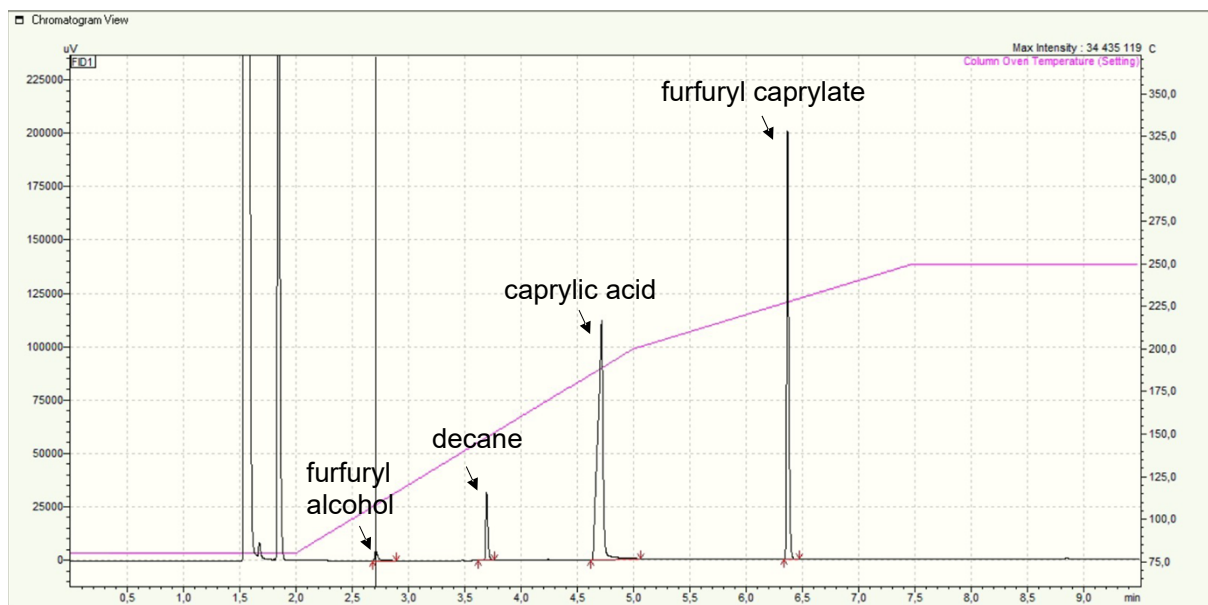


Fig. S29. Chromatogram GC analysis of esterification of furfuryl alcohol and caprylic acid.

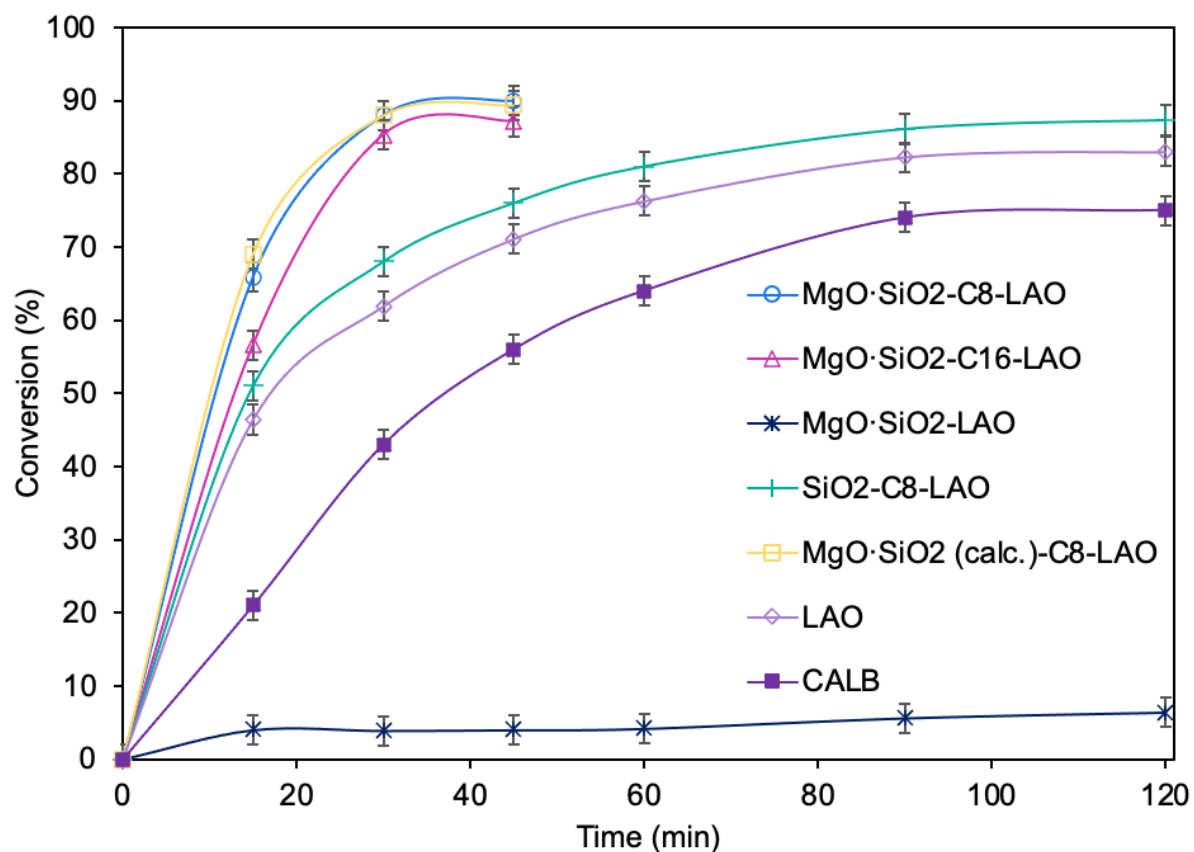


Fig. S30. The influence of siliceous support modification on biocatalyst performance on furfuryl alcohol esterification.

Reaction conditions: furfuryl alcohol 1.0 mmol, caprylic acid 3.0 mmol, cyclohexane 0.5 mL, biocatalyst containing 6.36 mg of LAO, (146 μL of LAO solution (43.7 mg mL^{-1}); 530 μL of CALB solution (12 mg mL^{-1}); 300 mg of $\text{MgO}\cdot\text{SiO}_2\text{-LAO}$; 69 mg of $\text{SiO}_2\text{-C}_8\text{-LAO}$; 150 mg of $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$; 294 mg of $\text{MgO}\cdot\text{SiO}_2(\text{calc})\text{-C}_8\text{-LAO}$; 413 mg of $\text{MgO}\cdot\text{SiO}_2\text{-C}_{16}\text{-LAO}$); 25°C, 250 rpm; determined using GC).

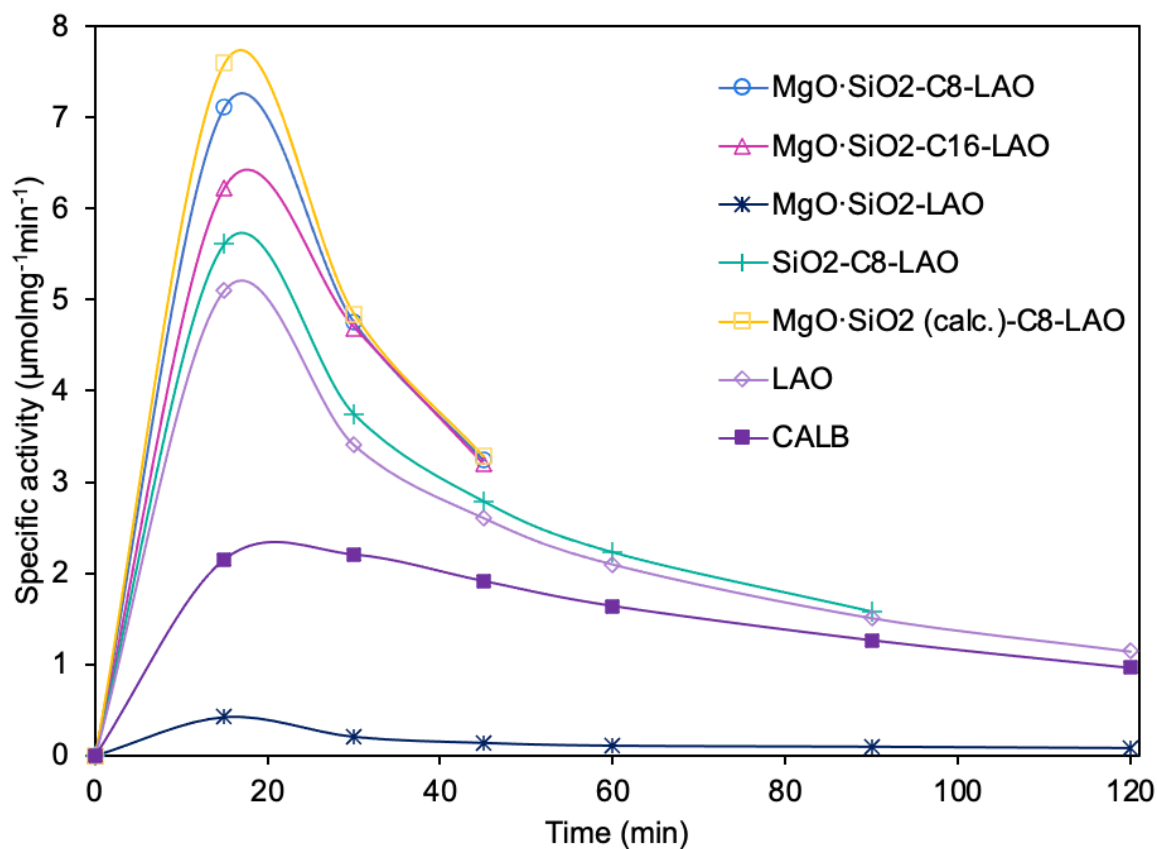


Fig. S31. The influence of siliceous support modification on biocatalyst performance on furfuryl alcohol esterification.

Reaction conditions: furfuryl alcohol 1.0 mmol, caprylic acid 3.0 mmol, cyclohexane 0.5 mL, biocatalyst containing 6.36 mg of LAO, (146 μL of LAO solution (43.7 mg mL^{-1}); 530 μL of CALB solution (12 mg mL^{-1}); 300 mg of $\text{MgO}\cdot\text{SiO}_2\text{-LAO}$; 69 mg of $\text{SiO}_2\text{-C}_8\text{-LAO}$; 150 mg of $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$; 294 mg of $\text{MgO}\cdot\text{SiO}_2(\text{calc})\text{-C}_8\text{-LAO}$; 413 mg of $\text{MgO}\cdot\text{SiO}_2\text{-C}_{16}\text{-LAO}$), 25°C , 250 rpm; determined using GC).

Fig. S32. TG/DTG analysis of $\text{MgO}\cdot\text{SiO}_2\text{-C}_8\text{-LAO}$ after recycling.

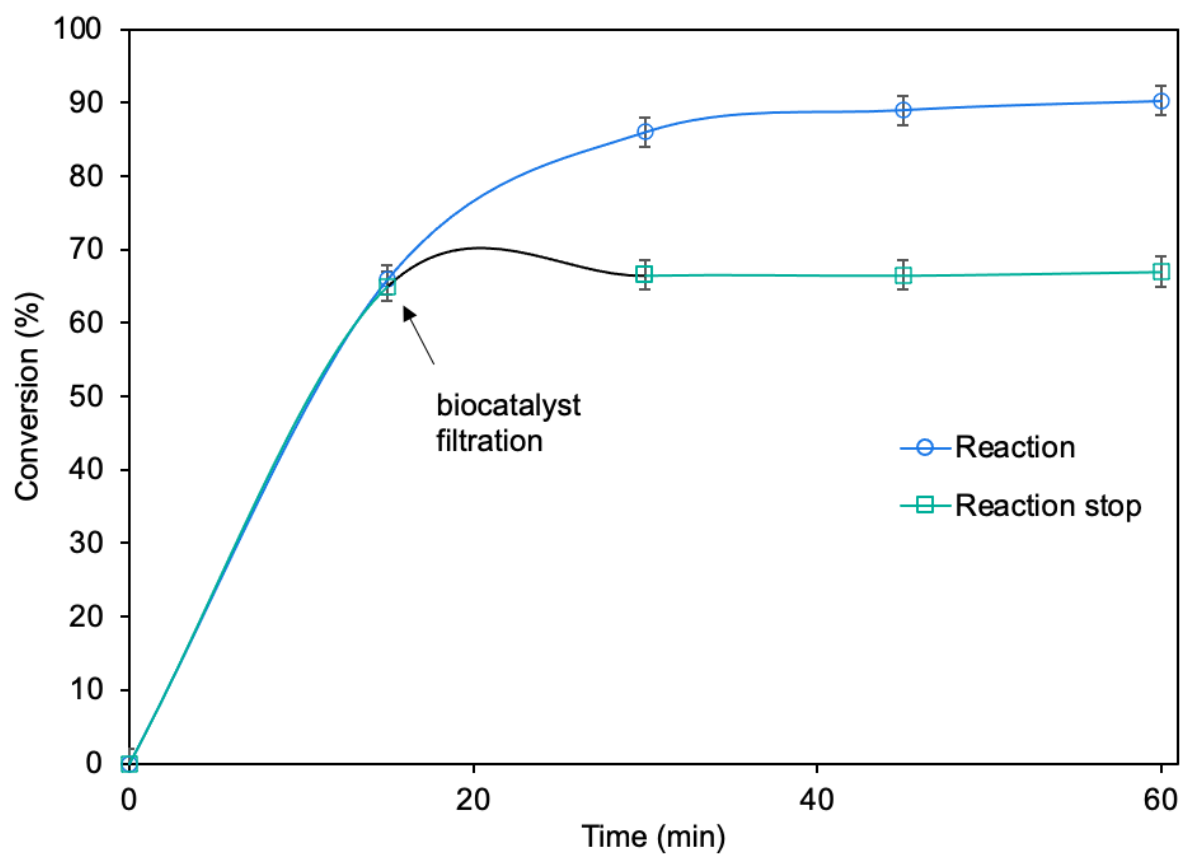


Fig. S33. Fast biocatalyst filtration from reaction mixture. “Reaction stop” experiment.

Reaction conditions: furfuryl alcohol 1.0 mmol, caprylic acid 3.0 mmol, cyclohexane 0.5 mL, biocatalyst (6.36 mg of lipase, e.g. 150 mg of MgO·SiO₂-C₈-LAO), 25°C, 250 rpm.

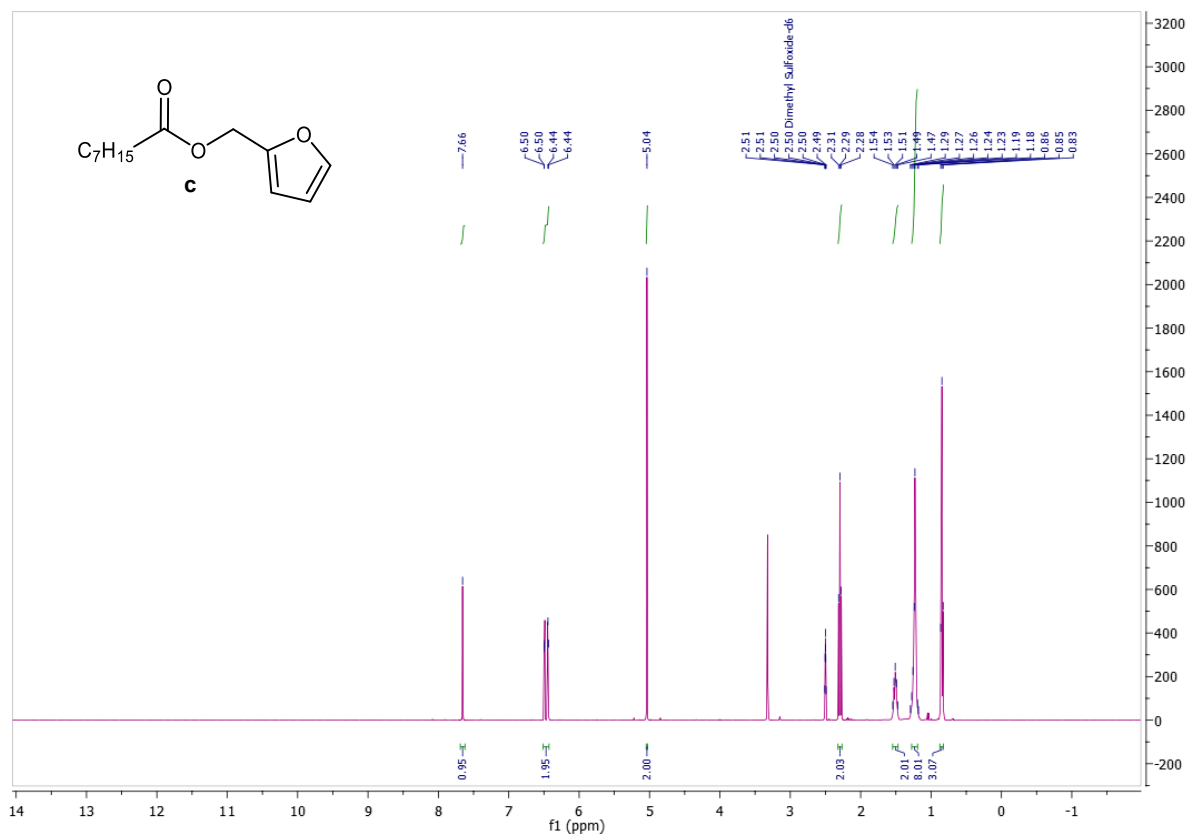


Fig. S34. ^1H NMR spectra of furfuryl caprylate (c).

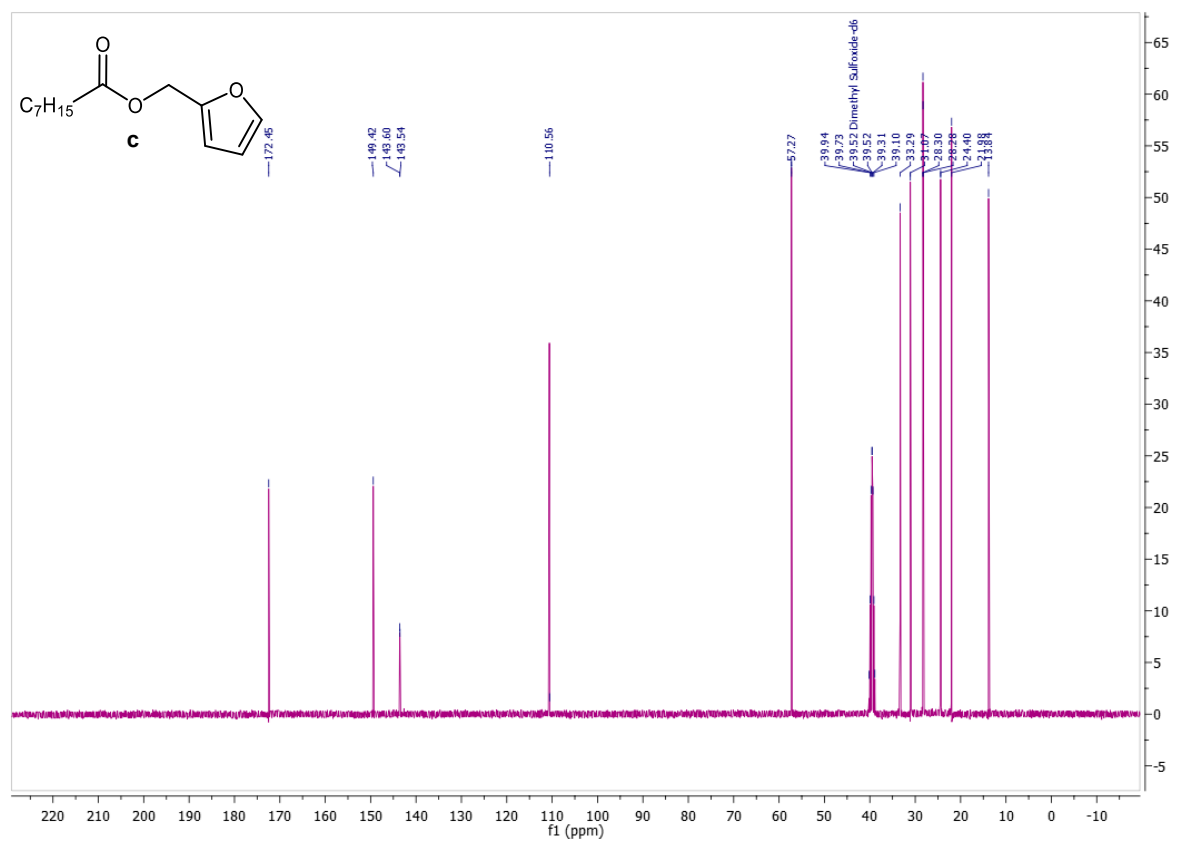


Fig. S35. ^{13}C NMR spectra of furfuryl caprylate (c).

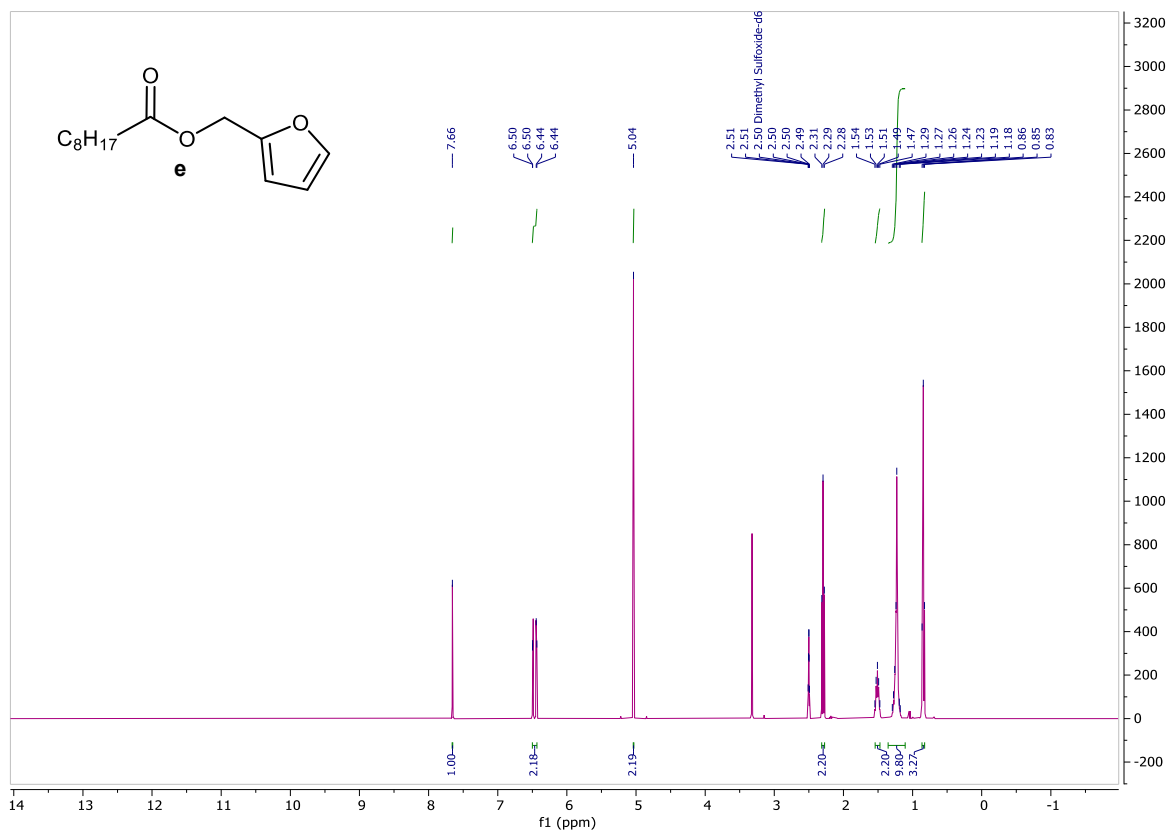


Fig. S36. ¹H NMR spectra of furfuryl nonanoate (e).



Fig. S37. ¹³C NMR spectra of furfuryl nonanoate (e).

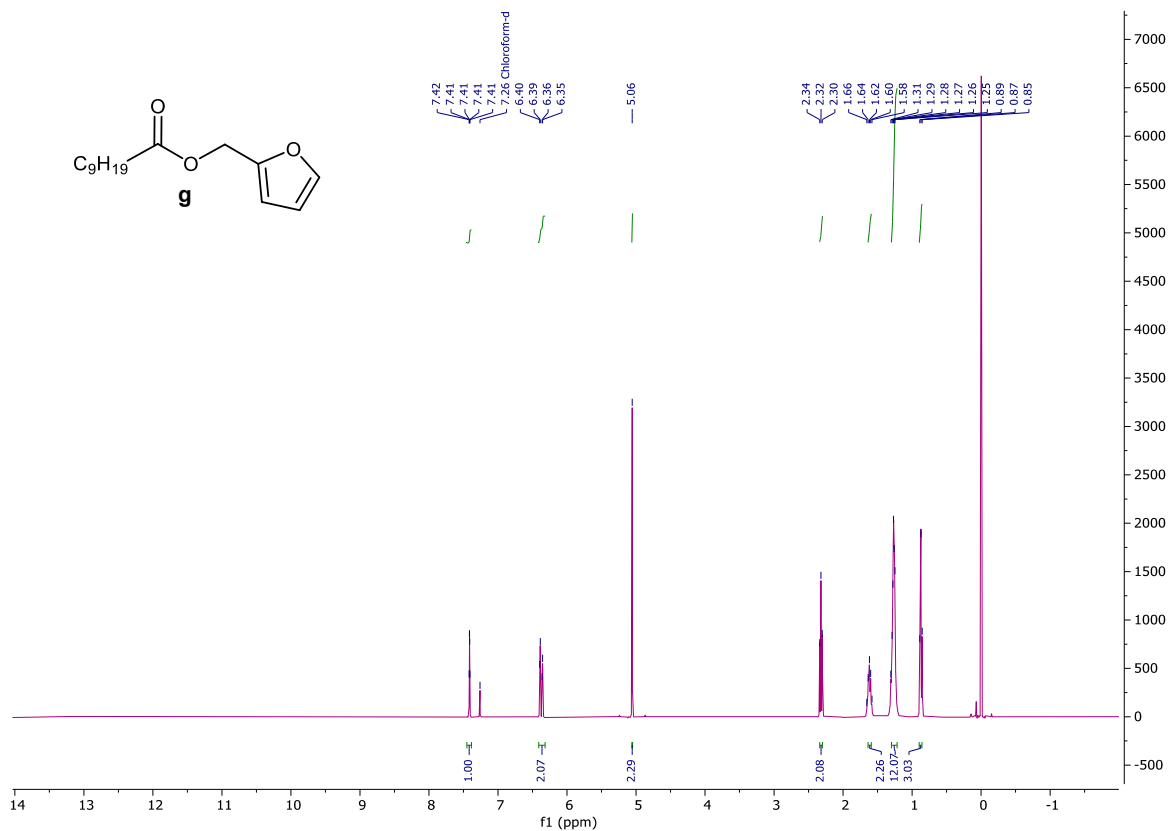


Fig. S38. ¹H NMR spectra of furfuryl decanoate (g).

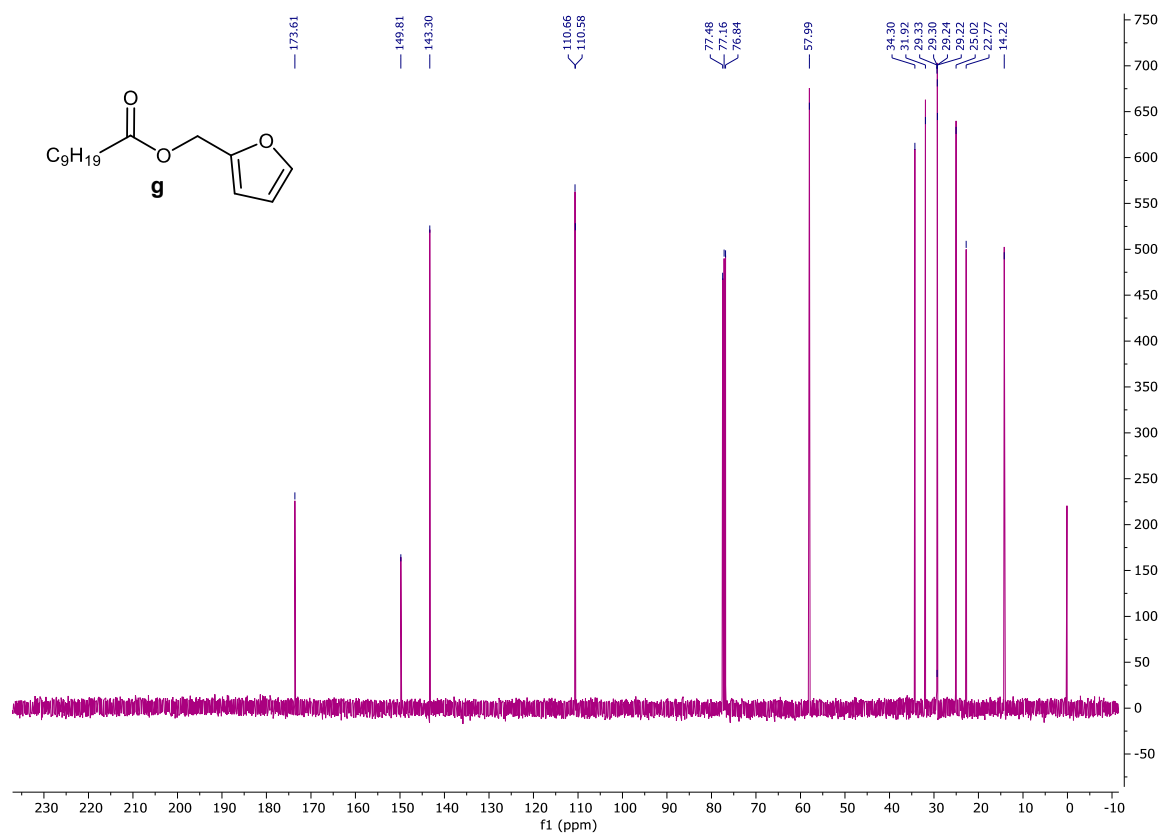


Fig. S39. ¹³C NMR spectra of furfuryl decanoate (g).

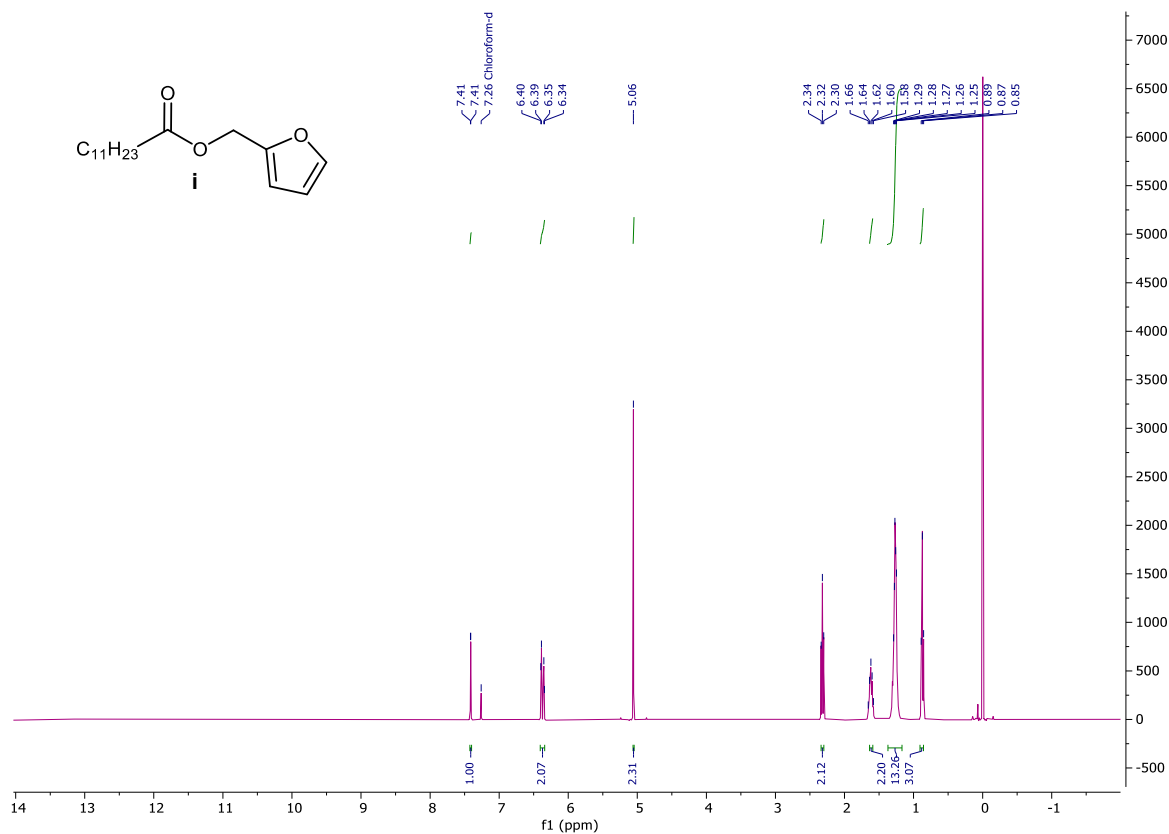


Fig. S40. ¹H NMR spectra of furfuryl laurate (i).



Fig. S41. ¹³C NMR spectra of furfuryl laurate (i).

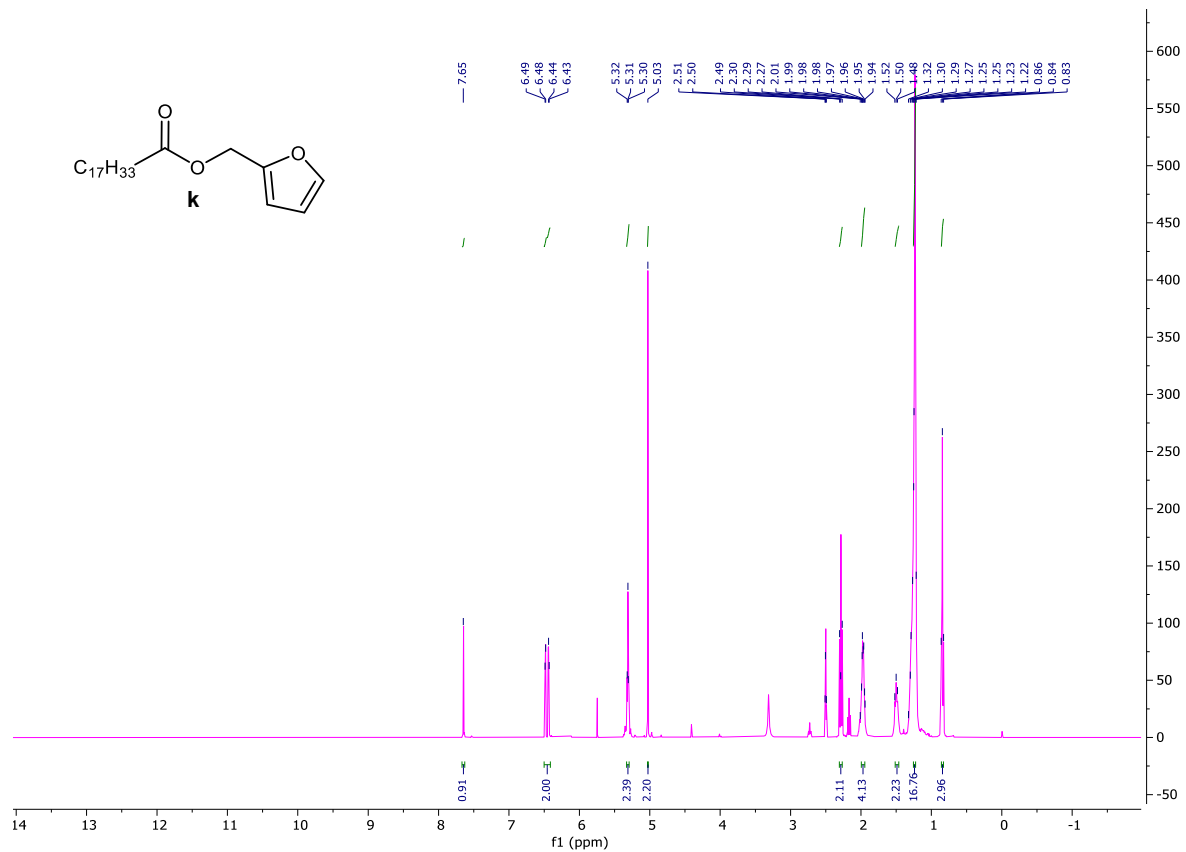


Fig. S42. ¹H NMR spectra of furfuryl oleate (k).

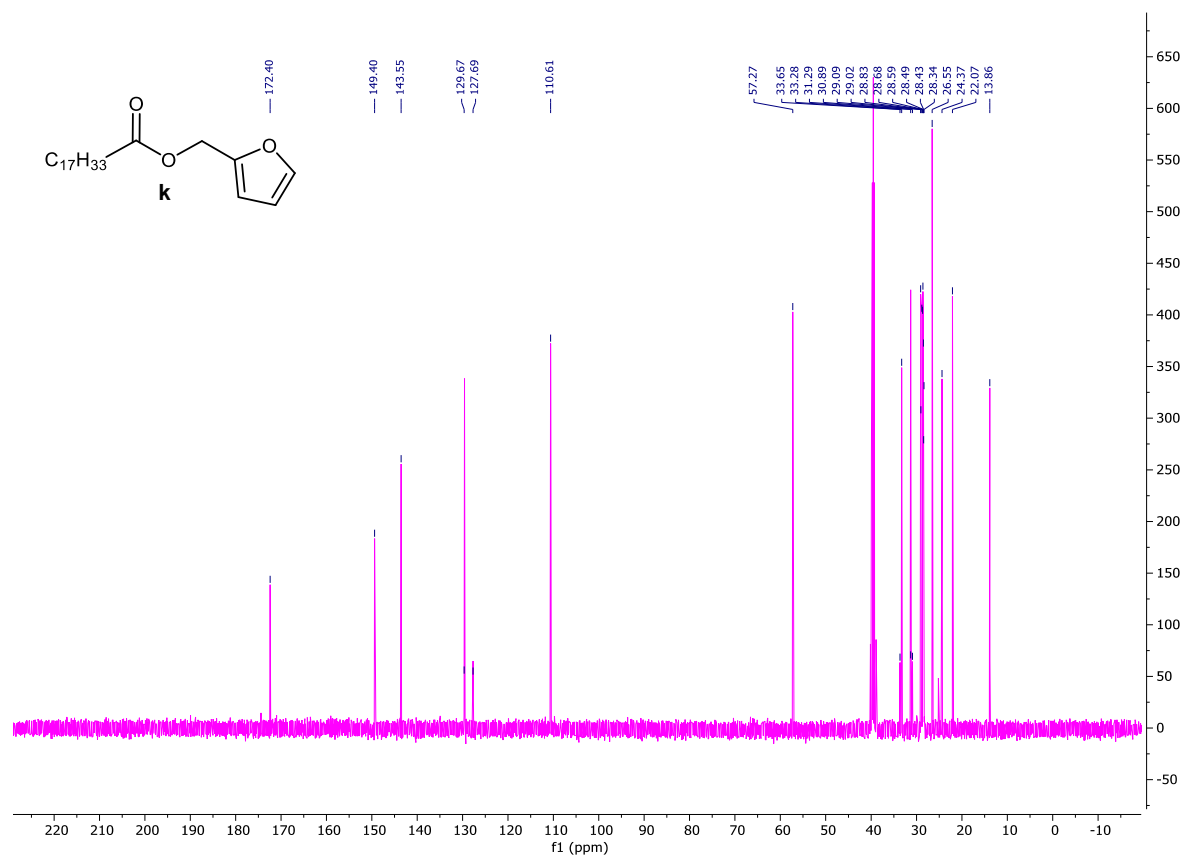


Fig. S43. ¹³C NMR spectra of furfuryl oleate (k).