Supporting info

Efficient Continuous Flow Oxidation of Furfural to Maleic Anhydride Using O₂ as a Green Oxidant

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STARTING MATERIALS

Commercially available chemicals

Methylene blue, furfural (>98.5%) and Fe(NO₃)₃ · 9 H₂O were purchased from VWR chemicals. (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) was purchased from Acros organics. PIPO (Polymer-immobilised TEMPO, Mw ~2100-3250) was purchased from CLEA technologies. FeCl₃, 2-furoic acid and HNO₃ (25%) were purchased from Merck.

Synthesis of 5-hydroxy-2(5H)-furanone 3

vacuum-distilled furfural (4800 mg, 50 mmol, 1 eq.) and methylene blue (80 mg, 0.25 mmol, 0.005 eq.) are dissolved in MeOH in a volumetric flask (250 ml). The solution was then pumped through a dual piston pump (flow rate: 0.75 ml/min) and connected to an oxygen line controlled by a mass flow controller (flow rate:10 ml_N/min) via a Y-piece. The tubing of the resulting oxygen-reaction mixture Taylor flow, wrapped around a glass plate, was irradiated with a red LED (625 nm, 100W) while the pressure was kept at 17 bar with the help of a BPR at the end of the reactor. After 10 minutes reaction time, the reaction mixture was evaporated (temperature <30 °C) and redissolved in diethyl ether. The mixture was then filtrated over a small silica column (SiO₂) to remove the photosensitizer and recrystallized in chloroform (0°C) to afford a white crystalline solid (4655 mg, 93% yield). Experimental data was in accordance with literature.^[1]

LITERATURE OVERVIEW OF FURFURAL OXIDATION METHODS

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Н	Solvent, Cat., Temp.	0
1		2

Table S1 Vanadium-catalyzed aerobic oxidation of furfural to maleic a	anhydride in gas phase and solution
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Ref.	Solvent	Cat.	Temp. (°C)	Yield 2 (%)
[2]	/ (gas phase)	V ₂ O ₅	320	55 (0.65s) ^a
[3]	/ (gas phase)	$(VO)_2P_2O_7$	340	90 (0.5s) ^a
[4]	/ (gas phase)	V_2O_5/γ -Al_2O_3	300	68 (2.1s) ^a
[5]	/ (gas phase)	VO _x /Al ₂ O ₃	300	73
[6]	AcOH	Mo ₄ VO ₁₄	100	65 ^b (4h)
[7]	AcOH	VO-NH ₂ -Graphene oxide	90	62 ^b (8h)
[8]	MeCN/AcOH (2/1.3)	H ₅ PV ₂ Mo ₁₀ O ₄₀ · <i>x</i> H ₂ O/ Cu(CF ₃ SO ₃) ₂	110	54 (14h)

^aNumber between brackets reflects the contact time between gas phase and corresponding catalyst

^bYield is a combination of maleic anhydride and hydrolyzed maleic acid

EXPERIMENTAL PROCEDURES

One-step continuous flow oxidation of FUR



vacuum-distilled furfural 1 (4800 mg, 50 mmol, 1 eq., 0.2 M) with or without (in the case of UV light) methylene blue (80 mg, 0.25 mmol, 0.005 eq.) are dissolved in the appropriate solvent in a volumetric flask (250 ml). The solution was then pumped through a dual piston pump (flow rate: 0.15-3 ml/min) and connected to an oxygen line controlled by a mass flow controller (flow rate: 6-40 ml_N/min) via a Y-piece. The tubing of the resulting oxygen-reaction mixture Taylor flow, wrapped around a glass plate, was irradiated with a red LED (625 nm, 100W) or UV LED (365 nm, 50W) which was placed around 6 cm from the glass plate while the pressure was kept at 17 bar with the help of a BPR at the end of the reactor. (reactor set-up: see Fig. S1 – Fig. S3) After 3.5-90 minutes residence time, yield of oxidation products was determined. (see Analysis procedures)

Two-step oxidation of FUR to MA

Continuous flow O_2^1 oxidation of FUR to HFO

vacuum-distilled furfural 1 (4800 mg, 50 mmol, 1 eq., 0.2 M) and methylene blue (80 mg, 0.25 mmol, 0.005 eq.) are dissolved in MeOH in a volumetric flask (250 ml). The solution was then pumped through a dual piston pump (flow rate: 0.75-1.5 ml/min) and connected to an oxygen line controlled by a mass flow controller (flow rate: 10-20 ml_N/min) via a Y-piece. The tubing of the resulting oxygen-reaction mixture Taylor flow, wrapped around a glass plate, was irradiated with a red LED (625 nm, 100W) which was placed around 6 cm from the glass plate while the pressure was kept at 17 bar with the help of a BPR at the end of the reactor. After 10-20 minutes residence time, yield of HFO **3** was determined by quantitative HPLC (see **Analysis procedures**)



Fig. S1 schematic overview of the reaction setup for the O_2^1 oxidation of FUR 1 to HFO 3



Fig. S2 Full reaction setup



Fig. S3 Close-up of red LED irradiation on Reaction mixture-oxygen Taylor flow

Continuous flow Aerobic oxidation of HFO to MA

5-hydroxy-2(5*H*)-furanone **3** (2000 mg, 20 mmol, 1 eq.), $Fe(NO_3)_3 \cdot 9 H_2O$ (162 mg, 0.4 mmol, 0.02 eq.), TEMPO (64 mg, 0.4 mmol, 0.02 eq.) and a certain amount of mesitylene (internal standard) are dissolved in EtOAc in a volumetric flask (100 ml). The solution was then filtered^a and pumped through a dual piston pump (flow rate: 0.23-2.8 ml/min) and connected to an oxygen line controlled by a mass flow controller (flow rate: 2.66-32 ml_N/min) via a Y-piece. The pressure was kept at 17 bar with the help of a BPR at the end of the reactor. After 5-30 minutes residence time, yield of MA **2** was determined by quantitative ¹H-NMR with mesitylene as internal standard. (see **Analysis procedure**)

^aWhen $Fe(NO_3)_3 \cdot 9 H_2O$ was added to the mixture, it was seen that a small amount of an orange-brown product precipitated. As the pH decreased in the reaction mixture, we believe that $Fe(OH)_3$ was the precipitated product. (see **additional experiments**, **Table S6**) The reaction mixture was filtered to avoid clogging in the dual-piston pump and tubing



Fig. S4 Schematic overview of the reaction setup for the aerobic oxidation of HFO 3 to MA 2

Batch optimization of the Aerobic oxidation of HFO to MA

 $Fe(NO_3)_3 \cdot 9 H_2O$ (x eq.) and TEMPO (x eq.) are dissolved in 5 ml of the appropriate solvent. The solution was then flushed with an oxygen balloon for 30 minutes while stirring. Afterwards, 5-hydroxy-2(5*H*)-furanone **3** (25 mg, 0.25 mmol, 1 eq., 0.05 M), was added to the mixture to initiate the reaction while keeping the headspace saturated with an oxygen-filled balloon. Since prior experiments with internal standard showed that no side product is formed in this reaction, the yield is estimated with ¹H-

NMR	analysis	using	the	formula
Yield = final p	product/(starting materia	al + final product)		

ANALYSIS PROCEDURES

Analysis procedure for the one-step oxidation of FUR



When quantitatively analyzing the reaction mixture via ¹H-NMR, it is of utmost importance to not evaporate the solvent but analyze the reaction mixture as such. Evaporating the solvent under a nitrogen stream leads to the loss of several signals that are present in the unaltered mixture. (Fig. S5) These missing signals were later attributed to CBF 6.



Fig. S5 Results of ¹H-NMR analysis (CD₃Cl) before (above) and after (below) evaporation of the solvent.

Quantitative HPLC analysis of unreacted FUR

To quantify the unreacted furfural 1 in the reaction mixture, the mixture was diluted 20-fold in acetonitrile and analyzed using quantitative HPLC, employing calibration curves. (Fig. S6) To reduce equipment variability, the sample was analyzed three times, and the average value was recorded. The spectra were analyzed at a wavelength of 254,8 nm with an elution pattern of 90/10-0/100 H₂O/MeCN (C18 column).



Fig. S6 HPLC calibration curve to quantify the conversion of furfural 1

Quantitative GC-MS analysis of MA

In some experiments, the yield of MA **3** was determined via GC-MS. the mixture was diluted 20-fold in acetonitrile and analyzed using GC-MS, employing a calibration curve. (Fig. S7) The yield of the residual products was determined by ¹H-NMR of the crude reaction mixture using MA as reference.



Fig. S7 GC-MS calibration curve to quantify the yield of MA 3

Quantitative ¹H-NMR analysis of oxidation products

In some experiments, to quantify the yield of the oxidation products, the crude mixture was directly analyzed without evaporation of the solvent on ¹H-NMR in CDCl₃. The yields were calculated comparing the integration values with respect to the internal standard mesitylene, which was added at the start of the reaction. (Fig. S8) It should be noted that the signals are slightly shifted due to the presence of undeuterated solvent.





Fig. S8 Zoom-in (above: 6-7.2 ppm, below: 9.5-10 ppm) of a typical ¹H-NMR spectrum (CDCl₃) of reaction mixture after the one-step oxidation of furfural to MA (7.08 ppm, 2H), HFO (6.18-6.23 ppm, 2H), TBF (9.85 ppm, 1H), CBF (6.7 and 6.58 ppm, 2H) and FOF (6.36 ppm, 1H) with mesitylene (6.80 ppm, 3H) as internal standard. Signals are assigned to the hydrogen atoms in bold.

Analysis procedure for the two-step oxidation of FUR to MA

Quantitative HPLC analysis after the singlet oxygen oxidation of FUR to HFO

To quantify the unreacted furfural 1 and yield of 5-hydroxy-2(5*H*)-furanone 3 in the reaction mixture, the mixture was diluted 20-fold in acetonitrile and analyzed using quantitative HPLC, employing calibration curves. (Fig. S9, Fig. S10) To reduce equipment variability, the sample was analyzed three times, and the average value was recorded. The spectra were analyzed at a wavelength of 254,8 nm with an elution pattern of 90/10-0/100 H₂O/MeCN (C18 column), completely separating both products (Fig. S11, Fig. S12)



Fig. S9 HPLC calibration curve to quantify the conversion of furfural 1



Fig. S10 HPLC calibration curve to quantify the yield of HFO 3



Fig. S11 HPLC analysis (254.8 nm, 90/10-0/100 $H_2O/MeCN$) of furfural in MeCN (0.5 mg/ml, RT: 0.998 min)



Fig. S12 HPLC analysis (254.8 nm, 90/10-0/100 $H_2O/MeCN$) of HFO in MeCN (0.5 mg/ml, RT: 0.355 min)

Quantitative ¹H-NMR analysis after the aerobic oxidation of HFO to MA

To quantify the unreacted 5-hydroxy-2(5*H*)-furanone **3** and yield of MA **2** in the reaction mixture, the crude mixture was directly analyzed without evaporation of the solvent on ¹H-NMR in CDCl₃. The yields were calculated comparing the integration values with respect to the internal standard mesitylene, which was added at the start of the reaction. (Fig. S13) It should be noted that the signals are slightly shifted due to the presence of EtOAc.





Fig. S13 Zoom-in (5-8 ppm) of a typical ¹H-NMR spectrum (CDCl₃) of reaction mixture after aerobic oxidation of HFO (6.18-6.23 ppm, 2H) to MA (7.08 ppm, 2H) with mesitylene (6.80 ppm, 3H) as internal standard. Signals are assigned to the hydrogen atoms in bold.

ADDITIONAL EXPERIMENTS

Additional experiments for the one-step oxidation of FUR towards various products

Reaction kinetics





Fig. S14 Product formation of singlet oxygen-mediated furfural oxidation in batch over time. Yield of products was determined via quantitative ¹H-NMR analysis with mesitylene as internal standard

Additional experiments for the UV-mediated oxidation of FUR towards various products

Initial experiments

When performing control experiments, it was seen the reaction still proceeded when using different wavelengths without a photosensitizer, albeit in lower yield. While the precise mechanism of this reaction remains unclear, irradiation at 365 nm was identified as optimal. (Table S2, entry 2) irradiation with longer wavelengths led to lower yields. (Table S2, entry 1) Additionally, small-scale batch experiments confirmed a similar solvent trend to that observed with a photosensitizer. Specifically, nucleophilic solvents such as MeOH led to full conversion to HFO, whereas a mixture of MA/HFO was obtained when non-nucleophilic solvents like MeCN, EtOAc, or acetone were used. (Table S3) It is clear that this method – despite being catalyst-free - is not favourable due to the long

reaction times and incomplete conversion.



Table S2 UV-mediated oxidation of FUR 1 towards MA 2 and HFO 3

Entry	Light	Solvent	Pump flow rate (ml/min)	O ₂ flow rate (ml _N /min)	Residence time (min) ^a	Conv. 1 (%) ^b	Yield 2/3/8 (%) ^c
1	390 nm, 50W	MeCN	0.15	6	75	11	5/2/0
2	365 nm, 50W	MeCN	0.3	7.5	37	33	15/8/2
3	365 nm, 50W	MeCN	0.15	6	80	69	29/16/4
4	365 nm, 50W	EtOAc	0.3	7.5	45	25	14/6/1
5	365 nm, 50W	EtOAc	0.15	6	90	53	23/10/2
6	365 nm, 2 x 50W	EtOAc	0.15	6	90	65	30/13/3

^aResidence time determined experimentally

^bConversion determined via quantitative HPLC analysis

^cYield determined via quantitative GC-MS analysis (2) and quantitative ¹H-NMR analysis (3 and 8)

Solvent effect on product ratio



Table S3 Control experiments for the UV-mediated oxidation of furfural

Solvent	Ratio 2/3
MeOH	Only 3 formed
Et ₂ O	none

THF	none
DMF	none
Acetone	1.33/1

Additional experiments for the aerobic oxidation of HFO to MA

All additional experiments were conducted with 25 mg HFO in 5 ml EtOAc (0.05 M) in a batch setup in accordance with prior reaction and analysis procedure. (see **experimental procedures**)

Control experiments



Table S4 Control experiments for the aerobic oxidation of HFO to MA

Entry	TEMPO (mol%)	Fe(NO ₃) ₃ · 9 H ₂ O (mol%)	Yield 2 (%)
1	10	5	100
2	/	5	0
3	10	/	0
4	/	/	0

Influence of reaction mixture filtering

To prevent clogging of the tubing in the continuous flow reactor and the dual piston pump, the mixture was filtered before the reaction. This filtration step was found to have no significant effect on the overall yield in a batch set-up. (Table S5)



Table S5 Control experiments for the reaction mixture filtering

Entry	Deviation of normal procedure	Yield 2 (%)
1	/	42 (2h) 73 (4,5h)
2	Addition of both catalyst, 30 minutes stirring, then filtration over syringe filter (0.22 μ m)	48 (2h) 73 (4,5h)

Ph dependency

When adding $Fe(NO_3)_3 \cdot 9 H_2O$ to EtOAc, it was seen that a small amount (<10 mass%) precipitated as an orange-brown product. As the pH decreased in the reaction mixture, we believe that $Fe(OH)_3$ was the precipitated product. To exclude any pH-dependency of the TEMPO-catalyzed aerobic oxidation, we first replaced $Fe(NO_3)_3 \cdot 9 H_2O$ to HNO₃ in the mixture. (**Table S6, entry 2**) At first, we were surprised to see that 25% yield was obtained after 0.5h. After two more hours of stirring however, the yield stagnated at 25%, indicating that HNO₃, a strong oxidant, can replace the O₂/iron catalyst system as final oxidant in stoichiometric amounts. To verify whether the pH had anything to do with the oxidation, the non-oxidizing acid HCl was added to the mixture and did not result in any conversion towards MA. (**Table S6, entry 4**)



Table S6 Control experiments to examine the possible pH dependency for the oxidation of HFO to MA

Entry	Catalyst (mol%)	Yield 2 (%)
1	TEMPO (7.5), $Fe(NO_3)_3 \cdot 9 H_2O(7.5)$	90 (0,5h)
		100 (1h)
2	TEMPO (7.5), HNO ₃ (7.5) ^a	25 (0,5h)
		25 (2,5h)
3	$HNO_{3}(7.5)^{a}$	0 (0.5h)
		0 (2,5h)
4	TEMPO (7.5) HCl (7.5) ^b	0 (0 5h)
·		0 (2,5h)
4	TEMPO (7.5), HCl (7.5) ^b	0 (0,5h) 0 (2,5h)

 $^aa\,25\%$ HNO_3/H2O solution was used

^ba 37% HCl solution was used

Batch experiments on catalyst loading variation at higher temperature



Table S7 Effect of different catalyst loading at higher temperatures

Entry	TEMPO (mol%)	Fe(NO ₃) ₃ · 9 H ₂ O (mol%)	Reaction time (h)	Yield 2 (%)
1	2,5	2,5	0,5	21
			1	31
			2	43
2	5	5	0,5	75
			1	90
			2	100
3	7,5	7,5	0,5	90
			1	100
			2	100

Different catalysts

$$\begin{array}{c} O_2 \\ Catalysts \\ \hline \\ O \\ O \\ O \\ O \\ \hline \\ O \\ \hline \\ Catalysts \\ \hline \\ EtOAc, 50 ^{\circ}C \\ \hline \\ 2 \end{array}$$

Table S8 Varying the catalysts to see the influence on the aerobic oxidation of HFO to MA

Entry	Catalysts	Reaction time	Yield 2 (%)
1	FeCl ₃ (7,5 mol%), TEMPO (7,5	0,5	0
	mol%)	2	0
2	$Fe(NO_3)_3 \cdot 9 H_2O$ (7,5 mol%),	0,5	45
	PIPO (15 mg) ^a	2	80

^aPIPO = Polymer-immobilised TEMPO

Reaction kinetics

To learn more about the reaction kinetics, the yield of maleic anhydride **2** was determined at different points in time.



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Reaction time (min)	Yield 2 (%)
0	0
1	10
2	13
4	19
9	27
18	37
35	49

55	66	
75	76	
95	81	



Graph S1 MA yield as a function of time

Catalyst loading



2h reaction time

		Fe(NO ₃) ₃ (mol%)	2,5	5	7,5	10
TEMPO (mol%)	25		12	10	20	34
	2,5		22	42	55	61
	7,5		26	54	73	76
	10		39	60	74	93

4,5h reaction time

		Fe(NO ₃) ₃ (mol%)	2,5	5	7,5	10
TEMPO (mol%)	2,5		22	41	48	55
	5		30	73	73	91
	7,5		44	79	97	100
	10		62	80	100	100

Fig. S15 Catalyst loading optimization for the aerobic oxidation of HFO **3** to MA **2** in batch. The yield (%) was estimated using the following formula: yield = MA / (FUR + MA) via ¹H-NMR analysis

ASSIGNMENT OF ¹H-NMR SIGNALS

Assignment of FOF 8

5-(formyloxy)-2(5H)-furanone **8** has not been previously described in literature. Being unable to fully purify prior product, it has been characterized via a mixture of FOF **8**, MA **2** and HFO **3**. (Fig. S16)





Fig. S16 full overview of ¹H-NMR spectrum (CDCl₃) used for characterization of FOF 8

Fig. S17 Zoom-in (6-8.5 ppm) of ¹H-NMR spectrum (CDCl₃) used for characterization of FOF 8







Fig. S18 full overview of ¹³C-NMR spectrum (CDCl₃) used for characterization of FOF 8

Fig. S19 Zoom-in on HSQC spectrum (CDCl₃) used for characterization of FOF 8



Fig. S20 Zoom in on HMBC spectrum (CDCl₃) used for characterization of FOF 8



Fig. S21 Zoom-in on COSY spectrum (CDCl₃) used for characterization of FOF 8

The positive identification of FOF **8** is also strengthened by the very similar C and H signals of corresponding 5-(acetyloxy)-2(5H)-furanone **9**.^[9] (Fig. S22)



Fig. S22 Comparison of ¹H-NMR and ¹³C-NMR signals of FOF **8** and the very similar corresponding 5-(acetyloxy)-2(5H)-furanone **9**

Assignment of TBF 7 and CBF 6

Trans- β -formylacrylic acid (TBF) 7 was identified via ¹H-NMR, showing signals consistent with reported literature values.^[10] Minor shifts were observed, attributed to the use of a different deuterated solvent, though the coupling constants aligned precisely with the literature values. Cis- β -formylacrylic acid CBF **6** has never been characterized, probably due to it's volatile nature, as previously discussed. This compound was therefore identified directly from the reaction mixture via ¹H-NMR without solvent evaporation. (**Fig. S23, Fig. S24**) as expected, a decrease in coupling constant was observed, consistent with the cis-formation. On top of that, MS spectra obtained from GC-MS analysis of the mixture revealed similar fragmentation patterns to those reported in the literature.^[11]





Fig. S23 Zoom-in (6.45-7.2 ppm) on the ¹H-NMR spectrum (CDCl₃) used for identification of TBF 7 and CBF 6.



Fig. S24 Zoom-in (9.8-10.6 ppm) on the ¹H-NMR spectrum (CDCl₃) used for identification of TBF 7 and CBF 6.

MATERIALS AND METHODS

High Performance Liquid Chromatography (HPLC)

To quantify yield, high performance liquid chromatography was used with the help of a calibration curve. The 1200 Series LC/MSD SL is equipped with a Supelco ascentis express C18 column with an internal diameter of 4.6 mm. Additionally, the instrument possesses a UV-DAD detector and there was an Agilent 1100 Series MSD SL mass spectrometer with electrospray ionisation (ESI, 4000 V, 70 eV) and with a single quadrupole detector coupled to the machine. To elute the components, a solvent mixture of acetonitrile and water in different ratios is used.

Nuclear Magnetic Resonance Spectroscopy (NMR)

The spectra were taken by a Bruker Avance Nanobay III NMR spectrometer with a ¹H/BB z-gradient high resolution probe. The ¹H NMR was taken at 400 MHz. The software used to process and display the spectra was TOPSPIN version 3.6.4. To prepare the samples for usage, the compounds were dissolved in CDCl₃.

Continuous flow pumps

The continuous flow reactions were carried out using a Knauer AZURA P 4.1S pump, equipped with a pressure sensor and a stainless steel pump head. The pump is capable of delivering a maximum flow rate of 10 mL/min and operating at pressures up to 200 bar.

Mass flow controller (MFC)

An EL-FLOW metal-sealed F-201 CM mass flow controller from Bronkhorst® was employed to regulate the oxygen flow to the continuous flow reactor. This controller is capable of handling gas pressures up to 30 bar and allows for precise control of oxygen flow, with a maximum setpoint of 80 mL_N/min .

Continuous flow tubing

To build the continuous flow reactor, PFA (polyfluoroalkoxy) tubing with an internal/external diameter of 0.8/1.6 mm was used.

Back pressure regulator

To maintain a constant pressure, BPR cartridges of IDEX Health & Science of 17 bar were placed at the end of the reactor and regularly exchanged.

LED irradiation setup

For the singlet oxygen oxidation reactions, a red LED light of Chanzon (625-630 nm, 100W) was used. The LED was glued with thermal paste on the surface of a Tesfish aluminum heatsink with a cooling fan to ensure the Led temperature is kept below 60°C. The LED was connected to a MEAN WELL LED driver of type HLG-150H-36B AC-DC Single output Mix mode (CV+CC) with built-in PFC; Output 36Vdc at 4.2A to ensure the LEDs are operated at 100W.

REFERENCES

- [1] H. Urakami, K. Zhang, F. Vilela, *Chemical Communications* **2013**, *49*, 2353–2355.
- [2] P. Santander, L. Bravo, G. Pecchi, A. Karelovic, *Appl Catal A Gen* 2020, 595, Article 117513.
- [3] X. Li, J. Ko, Y. Zhang, *ChemSusChem* **2018**, *11*, 612–618.
- [4] N. Alonso-Fagúndez, M. Ojeda, R. Mariscal, J. L. G. Fierro, M. López Granados, J Catal 2017, 348, 265–275.
- [5] N. Alonso-Fagúndez, M. L. Granados, R. Mariscal, M. Ojeda, *ChemSusChem* 2012, 5, 1984– 1990.
- [6] X. Li, B. Ho, Y. Zhang, Green Chemistry 2016, 18, 2976–2980.
- [7] G. Lv, C. Chen, B. Lu, J. Li, Y. Yang, C. Chen, T. Deng, Y. Zhu, X. Hou, RSC Adv 2016, 6, 101277–101282.
- [8] J. Lan, Z. Chen, J. Lin, G. Yin, Green Chemistry 2014, 16, 4351–4358.
- [9] J. Lan, Z. Chen, J. Lin, G. Yin, *Green Chemistry* **2014**, *16*, 4351–4358.
- [10] L. J. Zhang, X. X. Deng, F. S. Du, Z. C. Li, *Macromolecules* 2013, 46, 9554–9562.
- [11] D. K. Chauhan, V. R. Battula, A. Giri, A. Patra, K. Kailasam, Catal Sci Technol 2022, 12, 144–153.