

Green Chemistry

Highly Efficient Biobased Synthesis of Acrylic Acid

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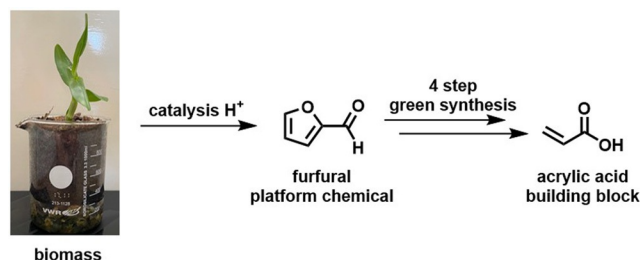
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Abstract: Petrochemical based polymers, paints and coatings are cornerstones of modern industry but our future sustainable society demands greener processes and renewable feedstock materials. A challenge is to access platform monomers from biomass resources while integrating the principles of green chemistry in their chemical synthesis. We present a synthesis route starting from biomass-derived furfural towards the commonly used monomers maleic anhydride and acrylic acid, implementing environmentally benign photooxygenation, aerobic oxidation and ethenolysis reactions. Maleic anhydride and acrylic acid, transformed into sodium acrylate, were isolated in yields of 85% (2 steps) and 81% (4 steps), respectively. With minimal waste and high atom efficiency, this biobased route provides a viable alternative to access key monomers.

Introduction

Changing the face of chemistry toward sustainable future processes and products, we are confronted with major challenges including the use of renewable feedstock and environmentally benign synthetic transformations based on the principles of green chemistry.^[1] Building blocks like maleic anhydride and acrylic acid are among the cornerstones of modern materials, widely used in various polymers and coatings.^[2] Current industrial production of both monomers, which globally exceeds several million metric tons per year,^[3] relies on traditional petrochemical transformations; oil derived hydrocarbons are converted into building blocks via gas-phase oxidations with multicomponent catalytic systems under forcing conditions.^[4] With the growing environmental awareness and the quest to replace traditional petroleum based monomers directly by those derived from renewable resources, alternative mild and no-waste producing chemical transformations leading to the same compounds have to be introduced (Scheme 1).^[5] In the past decade, several routes



Scheme 1. General strategy for biobased acrylic acid obtained via a 4-step green synthesis from the platform chemical furfural.

towards maleic anhydride have been proposed ranging from biomass derived platform chemicals hydroxymethylfurfural (HMF),^[6] furfural,^[7] 1-butanol^[8] and levulinic acid^[9] (Scheme 2). Similarly, advances towards biobased acrylic acid,^[10] originating from lactic acid,^[11] glycerol,^[12] 3-hydroxypropionic acid^[13] and acrylonitrile,^[14] indicate the importance of novel sustainable building blocks. Despite progress towards biobased routes towards these building blocks, applicability of these processes is still suffering from, among others, issues related to high temperatures, high pressures, low selectivities, low yields or catalyst instabilities. Very recently, Thomas et al. reported the further sustainable functionalization of acrylic acid towards various acrylate derivatives via a one-pot catalytic transformation using biobased alcohols.^[15]

Focusing on the monomer formation, we recently showed the synthesis and application of alkoxybutenolides as acrylate alternatives in the formation of biobased polymers and coatings.^[16] As part of our program on clean photocatalytic oxidation, the platform chemical furfural is photooxygenated using singlet oxygen to yield hydroxybutenolide quantitatively (Schemes 2 and 3). Singlet oxygen is generated via triplet-triplet annihilation of molecular oxygen upon excitation using a catalytic amount of photosensitizer and low-energy visible light irradiation. The furan moiety of furfural undergoes a [4+2] cycloaddition with ¹O₂, followed by transformation towards hydroxybutenolide.

It is worth noting that furfural is economically an attractive starting material with a price of \$1 kg⁻¹^[17] and has been listed by the U.S. Department of Energy as one of the most important (biobased) platform chemicals demonstrating the importance of discovering novel applications originating from furfural.^[18]

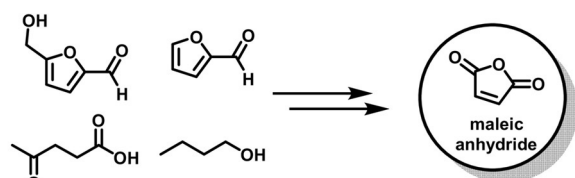
Here we report a green synthetic route to acrylic acid from biomass via furfural using sequential photochemical and catalytic oxidations with air and ethenolysis as major steps via hydroxybutenolide and maleic anhydride as key intermediates (Schemes 1 and 2).

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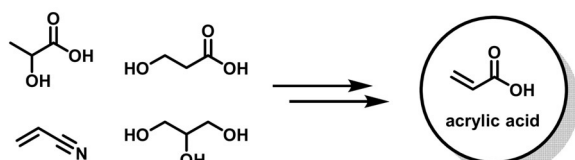
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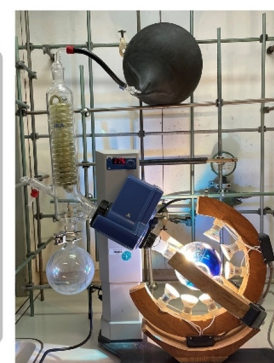
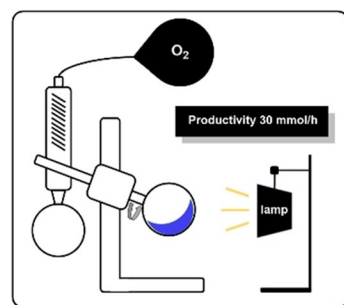
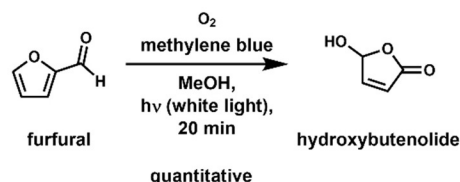
Previous biobased routes



Biobased platform chemicals

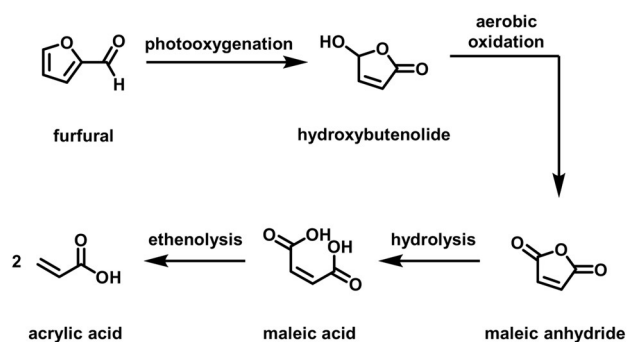


Biobased platform chemicals



Scheme 3. Photooxidation of furfural to hydroxybutenolide using a rotary photoreactor setup. Rotary photoreactor scheme (bottom left), rotary photoreactor in operation (bottom right). Reaction conditions: 1 L flask, 1 M furfural in MeOH (10 mL), 10×8 W LED, 0.5 mol% methylene blue.

This work



- 81% Yield over 4 steps
- Mild reaction conditions
- Aerobic oxidations
- High atom efficiency

Scheme 2. Previous described biobased synthesis routes towards maleic anhydride and acrylic acid starting from platform chemicals. General strategy, starting from furfural towards acrylic acid via maleic anhydride using aerobic oxidations and environmentally benign reaction conditions.

As hydroxybutenolide contains a hemiacetal moiety, specifically it features a single reduced anhydride, we envisioned a simple aerobic oxidation would suffice for the formation of the first building block maleic anhydride. For the synthesis of acrylic acid, one can recognize the similarities between the building block and maleic acid that is, the hydrolyzed form of maleic anhydride. It is worth noting that, although biobased routes towards maleic acid are known,^[19] hydrolysis of maleic anhydride towards maleic acid is a less energy intensive process than the formation of the anhydride from maleic acid as in the latter transformation higher temperatures (50°C vs. $> 130^\circ\text{C}$) are required for the removal of water.^[2,4] Direct ethenolysis of maleic acid would result in the production of two equivalents of acrylic acid starting from one equivalent of maleic acid (Scheme 2). Although ethylene is nowadays still produced on a scale exceeding hundred million tons annually from oil and gas,^[20] biobased ethylene gas can be directly obtained from the dehydration of bioethanol.^[21] Based on our design outlined here, we present

methodology to access the key monomers maleic anhydride and acrylic acid directly from the platform chemical furfural in an environmentally benign synthesis with excellent yields, mild reaction conditions and high atom efficiencies.

Results and Discussion

Typically, photooxidation reactions, especially when performed on a larger scale, are limited by physical factors, such as light penetration and mass transfer of oxygen into the solution.^[22] Previously, we have shown the upscaling of the photooxidation of furfural to hydroxybutenolide by developing a photo flow reactor for continuous production and a rotary photoreactor for larger batch processes.^[16] The rotary photoreactor, modelled after Poliakoff and George,^[23] is a versatile setup that allows for fast conversion. Optimal light penetration is achieved due to the thin film that is created by rotation of the reaction flask containing a small volume with a high concentration of furfural. Concurrently, having an oxygen atmosphere applied simply with an O_2 filled balloon results in excellent mass transfer into the solution which allows a fast conversion of 10 mmol (1 g) furfural in 20 min.^[16,23] The photooxidation reaction was carried out under optimized conditions in methanol (MeOH) using methylene blue as photosensitizer.^[16] Although a 400 W halogen lamp can be used, we opted for a more sustainable home-built construction consisting of ten, 8 W (575 lm each) white Light Emitting Diodes (LEDs) (Scheme 3; Supporting Information, page 4).

In the route towards the first polymer building block, maleic anhydride, we aimed to utilize molecular oxygen as green oxidant taking advantage of a report by Stahl and co-workers on a copper-catalyzed aerobic oxidative conversion

of alcohols to esters proposed to involve hemiacetal intermediates.^[24]

We explored if a catalytic system based on copper(II), a 2,2-bipyridine (bpy) ligand, a *N*-methylimidazole (NMI) ligand, TEMPO and oxygen, would be suitable to oxidize hydroxybutenolide to maleic anhydride.

Initial experiments on this aerobic oxidation resulted in 58% conversion, determined by ¹H NMR spectroscopy, towards the desired maleic anhydride after 8 h of stirring under an O₂ atmosphere (balloon) at room temperature (Supporting Information, Table S1). When the reaction was conducted for an extended time, in contrast to our expectations, a lower conversion was observed. Moreover, reproduction of the oxidation reaction led to inconsistent results in terms of conversion and selectivity. Literature reports indicate that maleic anhydride can readily undergo polymerization by imidazoles.^[25] While NMI acts as a ligand for copper during the reaction, it is proposed that dissociation from the complex results to NMI acting as initiator for anionic polymerization of maleic anhydride. The oxidation reaction was monitored over time by ¹H NMR spectroscopy (Supporting Information, page 6, Figure S1) indicating that, while hydroxybutenolide is converted and the amount of maleic anhydride increases in the first few hours of the reaction (63%, 3 h), it subsequently decreases over a prolonged period (27%, 72 h), which is attributed to the anionic polymerization. In the attempt to prevent maleic anhydride from reacting, the oxidation was carried out in the absence of NMI. However, this resulted in low conversion (15%) that could be increased only to 30% after 16 h. Different bases were screened to enhance the conversion but resulted either in low conversion (Supporting Information, Table S1, entries 4, 7, and 8) or again resulted in conversion of maleic anhydride (Supporting Information, Table S1, entries 5, 6, and 9).

Moving away from copper catalyzed aerobic oxidations, while taking into account the twelve principles of green chemistry,^[1] we opted for iron catalyzed aerobic oxidation.^[26] Here use is made of the combination of TEMPO and molecular oxygen, catalyzed by a transition metal, in this case iron(III), to oxidize secondary alcohols in 1,2-dichloroethane (DCE).^[26] With these specific reaction conditions, full conversion of hydroxybutenolide towards maleic anhydride was achieved, as determined by ¹H NMR spectroscopy (Table 1, entry 1). Although promising, the use of a more environmentally benign solvent is highly warranted. Based on a list of solvents ranked regarding their environmental risk, acetonitrile was chosen as suitable candidate being considered a “green” solvent.^[27] Using acetonitrile as solvent, under the same conditions with molecular oxygen, quantitative conversion towards maleic anhydride was observed after 8 h at room temperature (Table 1, entry 2). Although the presence of sodium chloride has been shown to have a positive effect on the oxidation of allenols,^[26] full conversion was still achieved in our case employing hydroxybutenolide as substrate in the absence of NaCl (Table 1, entry 3, Figure 1A). Interestingly, the (relative) concentrations of both the iron catalyst and TEMPO are highly important (Table 1, entries 4–6). Lowering the TEMPO concentration to 5 mol% drastically lowers the conversion from >99% to 25%.

Table 1: Optimization table depicting oxidation of hydroxybutenolide to maleic anhydride with Fe(NO₃)₃. Reaction conditions: hydroxybutenolide (1 mmol, 0.05 M) in solvent (5 mL), room temperature, 1 atm O₂ (balloon), 8 h.

Entry	Fe(NO ₃) ₃ [mol %]	TEMPO [mol %]	Solvent	Yield [%] ^[a]
1 ^[b]	5	10	DCE	> 99
2 ^[b]	5	10	CH ₃ CN	> 99
3	5	10	CH ₃ CN	> 99
4	5	5	CH ₃ CN	25
5	2.5	5	CH ₃ CN	48
6	1.25	2.5	CH ₃ CN	20
7 ^[c]	5	10	CH ₃ CN	98

[a] Yield determined by ¹H NMR spectroscopy in CDCl₃ using mesitylene (0.66 equiv.) as an internal standard. [b] 10 mol% NaCl added. [c] Reaction performed under air atmosphere.

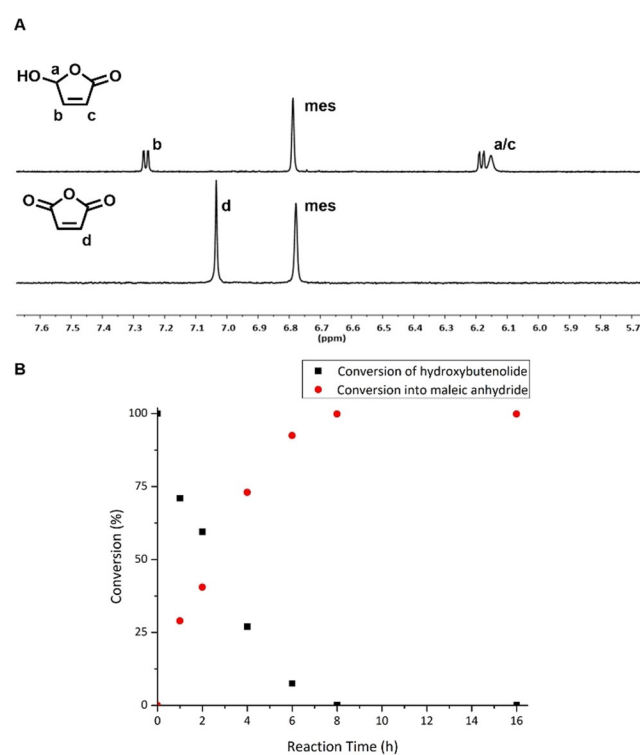


Figure 1. A) Stacked ¹H NMR in CD₂Cl₂ showing full conversion of the iron-catalyzed aerobic oxidation of hydroxybutenolide (6.15 ppm and 7.25 ppm) into maleic anhydride (7.05 ppm) using mesitylene (mes) (0.66 equiv.) as an internal standard. B) Conversion of hydroxybutenolide into maleic anhydride over time followed by ¹H NMR spectroscopy in CDCl₃ (bottom). Reaction conditions: hydroxybutenolide (1 mmol), Fe(NO₃)₃·9 H₂O (5 mol%), TEMPO (10 mol%), mesitylene (0.66 equiv.) in acetonitrile (5 mL) under 1 atm O₂ (balloon).

Surprisingly, when lowering the iron catalyst simultaneously to 2.5 mol% the conversion was only lowered to 48%. Although not fully understood yet, the ratio of 1:2 between Fe(NO₃)₃ and TEMPO is of major importance. Decreasing both the concentrations further to 1.25 mol% and 2.5 mol%,

respectively, decreases the conversion to 20%. Finally, the oxidation was also carried out under ambient air instead of oxygen, which resulted in a slightly lower but still excellent and highly selective conversion of 98% (Table 1, entry 7).

The conversion of hydroxybutenolide to maleic anhydride was also followed over time by taking aliquots at certain timestamps, and measuring these by ^1H NMR spectroscopy, using the optimized conditions (Table 1, entry 3). These results (Figure 1) complement the results of the optimization showing that 8 h of stirring at room temperature with our Fe-based catalytic system provides full conversion towards maleic anhydride and no decomposition of the product was observed afterwards. It should be noted that several control experiments were performed to confirm the essential role of the key components (Fe-catalyst, TEMPO) in this oxidative transformation (for experimental details and discussion, see Supporting Information, pages 8 and 9). Using the optimized conditions (Table 1, entry 3), pure maleic anhydride was isolated by sublimation under reduced pressure as a white crystalline solid in 85% yield.

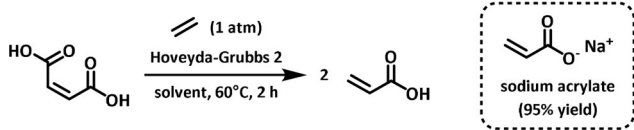
In the path towards the first biobased building block, maleic anhydride was obtained in a two-step catalytic oxidation process (i.e. photocatalytic oxidation, Fe-catalyzed oxidation, both using O_2), starting from the platform chemical furfural, with a total yield of 85%. It should be noted that this synthetic route meets multiple requirements of the twelve principles of green chemistry (vide infra).^[1]

The next step in the journey towards biobased acrylic acid, maleic anhydride was hydrolyzed to maleic acid by heating (50°C) in water overnight (Supporting Information, Figure S2).^[4] Subsequent evaporation of the water layer resulted in quantitative amounts of the white solid maleic acid. Control experiments showed that fumaric acid was not formed confirming the selective and quantitative hydrolysis of maleic anhydride at 50°C to maleic acid (Supporting Information, pages 10 and 11, Figures S2 and S3).

With a short route to maleic acid in hand, we focused on the final step that is, metathesis of ethylene and maleic acid to produce directly two acrylic acid molecules.

Realizing that high ethylene pressures might inhibit the activity of commonly used Ru-catalyst based cross metathesis,^[28] we decided to use a Schlenk technique similar to the one used in the aerobic oxidation of hydroxybutenolide to maleic anhydride, however, now equipped with an ethylene atmosphere. Starting at a high concentration of 3.3 M maleic acid, the reaction was carried out using the bench-stable Hoveyda-Grubbs II catalyst (5 mol%) in toluene. However, in view of the very poor solubility of maleic acid in organic solvents commonly used for metathesis reactions that is, toluene, dichloromethane (DCM), which resulted in no conversion, it was important to identify a solvent in which all the components, maleic acid, Hoveyda-Grubbs II and ethylene, were soluble. Tetrahydrofuran (THF) qualified as such a solvent, and gratifying a yield of 76% (NMR analysis) of acrylic acid was obtained (Table 2, entry 3). Based on the promising results, extensive optimization of the reaction conditions was performed. Taking notice that olefin metathesis is an equilibrium reaction,^[29] it is essential to know if equilibrium has been reached. Prolonging the reaction

Table 2: Optimization table for ethenolysis of maleic acid towards acrylic acid. Reaction conditions: maleic acid, Hoveyda-Grubbs II, 60°C, 1 atm ethylene (balloon), 2 h.



Entry	Conc. [M]	Cat. [mol %]	Solvent	Yield [%] ^[a]
1	3.3	5	Toluene	0
2	3.3	5	DCM	0
3	3.3	5	THF	76
4	1.7	5	THF	75
5	0.8	5	THF	91
6	0.4	5	THF	97
7	0.2	5	THF	> 99
8	0.2	3	THF	> 99
9	0.2	1	THF	92
10	0.1	1	THF	89
11 ^[b]	0.2	3	THF	51

[a] Conversion determined by ^1H NMR spectroscopy in CDCl_3 using mesitylene (0.66 equiv.) as an internal standard. [b] Reaction performed at room temperature.

beyond 2 h did not have any effect on the conversion, indicating that the equilibrium was reached. According to Le Chatelier's principle,^[29] the equilibrium can be pushed towards acrylic acid by increasing the ethylene:maleic acid ratio. In practice, this is done by simply lowering the concentration of maleic acid, which allows for an excess of ethylene in the liquid phase (for which the saturation concentration remains unchanged) with respect to maleic acid. Retaining a similar ethylene pressure, while lowering the concentration of maleic acid to 0.83 M, increased the conversion (Table 2, entry 5) and at a concentration of 0.2 M full conversion towards acrylic acid was observed (Table 2, entries 6 and 7).

Studying catalyst loading, it was established that full conversion was still achieved using 3 mol%, while at 1 mol% catalyst loading the conversion was only slightly lower (92%) (Table 2, entries 8 and 9). Further lowering the concentration, while still using 1 mol% catalyst loading, did not result in a higher conversion (Table 2, entry 10). Performing the reaction at room temperature resulted in a large drop in conversion, emphasizing that the temperature of 60°C is necessary (Table 2, entry 11). Under optimal conditions (3 mol% Ru-catalyst, conc. 0.2 M, THF, 60°C) the selective and high yield formation (> 99%) to acrylic acid was achieved (Figure 2). It should be pointed out that direct ethenolysis of maleic anhydride (which would shorten our route by one step) to yield acrylic anhydride is ineffective, presumably due to the equilibrium favoring the ring structure.

Isolation of acrylic acid was not performed directly as it is hard to completely remove traces of Ru-catalyst at this stage and prevent polymerization. As the catalyst is still active after the reaction, evaporation of the solvent increased the concentration in which the equilibrium shifted towards maleic acid. Although catalyst deactivation is a known strategy,^[30] we decided to isolate acrylic acid as sodium acrylate. Further-

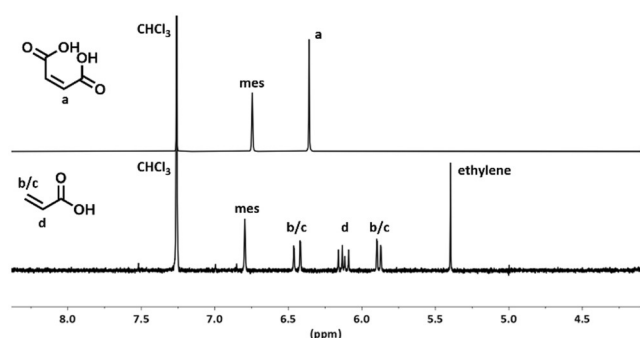


Figure 2. Stacked ^1H NMR spectrum in CDCl_3 showing full conversion of the ethenolysis of maleic acid (top) to acrylic acid (0.2 M, bottom) using mesitylene (mes) (0.66 equiv.) as an internal standard.

more, acrylic acid has to be typically stored with an inhibitor to prevent radical polymerization, whereas sodium acrylate is bench stable. By addition of a 0.2 M solution of NaOH in water, acrylic acid was easily extracted from the organic layer and subsequent removal of the water led to pure sodium acrylate, which was isolated in 95% yield (Supporting Information, Figures S10 and S11).

We have shown here that acrylic acid can be prepared in a four-step environmentally benign route from the platform

Table 3: Relevant principles of green chemistry and their justification for the synthesis of maleic anhydride and acrylic acid.

Principles of green chemistry ^[1]	Justification
Atom economy	<i>In the synthesis of maleic anhydride and acrylic acid, only methyl formate is produced as a side product during the photooxidation of furfural.</i>
Design for energy efficiency	<i>The oxidation of furfural is performed using visible-light photocatalysis at room temperature. Scalable setups have been designed with energy-efficient lamps (LED).^[16]</i>
Safer solvents and auxiliaries	<i>In the synthesis towards maleic anhydride and acrylic acid, methanol, acetonitrile, water and THF are used. These solvents are ranked high in terms of environmentally safe solvents.^[27]</i>
Use of renewable feedstocks	<i>The platform chemical furfural, derived from the acid-mediated dehydration of lignocellulose (H_2O as waste), is used as the starting material for the synthesis of maleic anhydride and acrylic acid.^[31]</i>
Catalysis	<i>The photooxidation of furfural, the aerobic oxidation of hydroxybutenolide and the ethenolysis of maleic acid are catalytic methods in which only molecular oxygen is used as a stoichiometric reagent. No high-energy oxidants are required.</i>
Inherently safer chemistry for accident prevention	<i>All reactions have been optimized to allow safer handling (ambient or lowered temperatures, atmospheric pressures).</i>

chemical furfural with a total yield 81%. The excellent atom efficiency is worth noting as no waste is produced in the oxidation, hydrolysis or ethenolysis, which above all generates two molecules of acrylic acid from a single molecule of maleic acid. Overall, this complementary biobased route towards these building blocks meets multiple requirements of the principles of green chemistry as illustrated by an analysis of this process based on key parameters as presented in Table 3.

Conclusion

In conclusion, we have demonstrated a novel synthetic route towards two commonly used building blocks in the polymer, paint and coatings industry and omnipresent in materials that sustain modern society. It is shown that, starting from the biomass-derived platform chemical furfural, by applying photooxidation, aerobic oxidation, hydrolysis and ethenolysis, the important monomer acrylic acid can be accessed in a mild and straightforward manner. The methodology presented incorporates many important features of green chemistry, by applying catalytic reactions, producing minimal waste, and providing high yields with excellent atom efficiency, proving the viability of alternative sustainable chemical routes for future chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acrylic acid · biobased polymers · furfural · maleic anhydride · sustainability

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