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Bio-based aliphatic primary amines from alcohols through the ‘Nitrile route’ towards non-isocyanate polyurethanes

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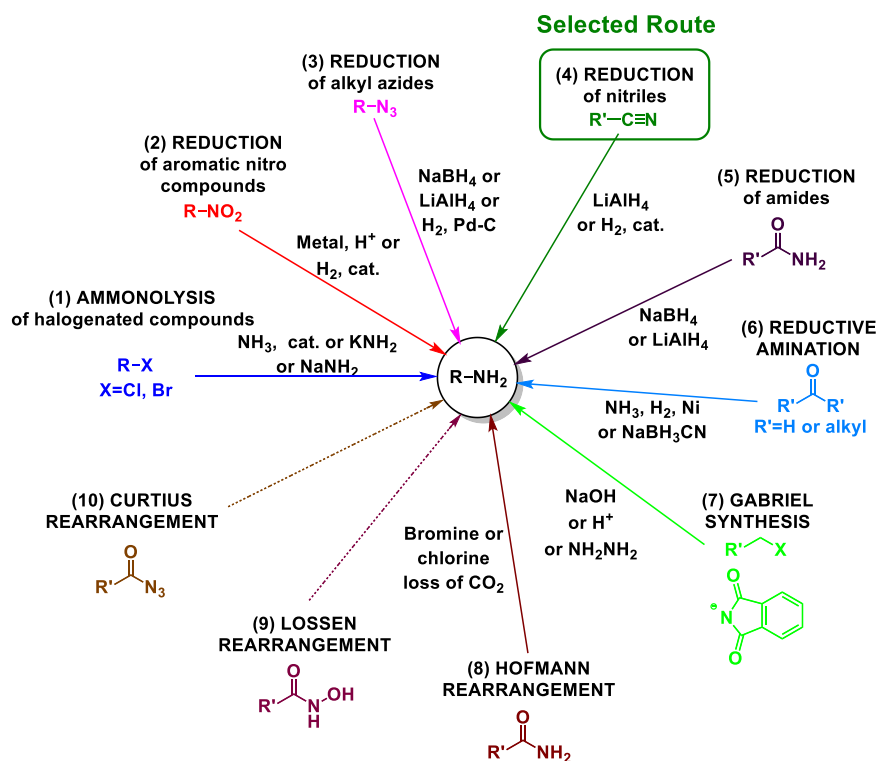
KEYWORDS: Amines, nitriles, alcohol, copper, oxidation, fatty acids, non-isocyanate polyurethanes, poly(hydroxyurethane)s

ABSTRACT: Bio-based primary amines obtained from the corresponding alcohols *via* nitrile intermediates and their subsequent polymerizations with cyclic carbonates are described. Nitrile compounds were synthesized under mild aerobic oxidation of primary aliphatic alcohols. CuI, bipyridine and TEMPO were used as a catalytic system, in the presence of aqueous ammonia and O₂. A series of bio-sourced alcohols were successfully oxidized into nitriles using this catalytic

system. The so-formed bio-based dinitriles were subsequently reduced into primary diamines under H_2 in the presence of Ni Raney. The latter were polymerized with fatty acid-based bis-cyclic carbonates for the design of fully bio-based poly(hydroxyurethane)s.

INTRODUCTION

Nowadays, amines and more specifically primary amines are extensively employed in the preparation of polymers and specially poly(hydroxyurethane)s (PHUs). The synthesis of poly(hydroxyurethane)s via the bis-cyclic carbonate / diamine route, allowing the replacement of toxic phosgene and isocyanates employed for the synthesis of classical polyurethanes is rising[1–4]. Due to the finite feedstock of fossil resources and to environmental issues, there is a growing need to develop sustainable chemical pathways and substrates[5–7]. In this purpose, multiple bis-cyclic carbonates have been developed from renewable resources and specially vegetable oils[8–10] but the development of ‘green’ amines and diamines appears to be crucial and need to be developed[11–16]. Numerous approaches are available in organic chemistry to prepare primary amines[17] (see Scheme 1). The latter can be either prepared by the ammonolysis of halogenated compounds (1) or by the reduction of nitro compounds (2), alkyl azides (3), nitriles (4) and amides (5) as well as by the reductive amination of ketones or aldehydes (6). Primary amines can also be obtained by Gabriel synthesis (7) and through Hofmann rearrangement (8); Lossen and Curtius (9-10) rearrangements can also indirectly lead to amines in the presence of water.



Scheme 1. Main approaches for the synthesis of amines

Various drawbacks can be pointed out from those reaction methods. First, the use of gaseous ammonia for ammonolysis (1) and reductive amination (6) is not safe and harsh conditions are usually requested. Moreover, the problems coming across with the alkylation of ammonia are the multiple alkylation reactions, which lead to a mixture of primary, secondary and tertiary amines together with quaternary ammonium salts. Among the main methods, the reduction of alkyl azide intermediates (3) involves a large number of steps and a nucleophilic addition with azide-based intermediates, such as NaN_3 , which are explosive and toxic substances. For the reduction of amides (5), toxic acyl chloride precursors need to be prepared. Finally, following the Gabriel procedure (7), the atom efficiency is not acceptable due to the generation of phthalimide derivatives and, in the case of Hofmann rearrangement (8), a decrease in the carbon chain length is observed due to CO_2 removal.

Among these routes, the reduction of nitriles (4) represents an attractive approach to prepare bio-based amines in mild conditions. While most of the procedures to synthesize nitrile compounds employ also toxic reagents or produce wastes,[18–20] the direct oxidation of primary alcohols with ammonia appears to be an attractive alternative approach for the preparation of nitriles[21]. Mizuno and coll. reported the direct oxidation of alcohol into nitrile using a heterogeneous $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$ catalyst and an excess of aqueous ammonia under air pressure (6 atm.) at 120°C . [22] Haruta *et al.* described a procedure using MnO_2 under pressurized oxygen (0.85 MPa) and NH_3 gas at 100°C . [23] These two approaches are quite efficient but are carried out at high temperature in autoclave. Besides, Cu/TEMPO system has been studied as a catalytic system for the oxidation of alcohols into aldehydes[24–27] with oxygen as the oxidant. Based on the work of Sheldon's group[24], Tao *et al.*[28] have developed a procedure to oxidize benzylic alcohols into nitrile in the presence of $\text{Cu}(\text{NO})_3/\text{TEMPO}$ as a catalytic system and aqueous ammonia under 1 atm of oxygen at 80°C . Aryl nitriles were synthesized in high yield but aliphatic alcohols could not be converted following these conditions. In the meantime, Yin *et al.*[29] described an aerobic oxidation of benzylic and few aliphatic alcohols under mild conditions using $\text{CuI}/\text{TEMPO}/\text{bipyridine}$ as a catalyst and an excess of aqueous ammonia under oxygen at room temperature. It should be mentioned that use of air instead of pure O_2 as oxidant is also reported. Yadav *et al.*[30] described an oxidation under air at 135°C of primary alcohols using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as a catalyst, in the presence of K_2CO_3 and ammonium formate as nitrogen source. This procedure does not permit the conversion of aliphatic alcohols that would require working at high temperature. To avoid the use of O_2 as oxidant, Dornan *et al.*[31] utilized another procedure under air at 50°C with $\text{Cu}(\text{OTf})_2/\text{TEMPO}/\text{bipyridine}$ and aqueous ammonia to oxidize aldehydes or alcohols into nitriles. Aliphatic alcohols could not be converted in nitriles

with this method but the authors could convert aliphatic alcohols by replacing the catalytic system with $[\text{Cu}(\text{MeCN})_4][\text{OTf}]/\text{TEMPO}/\text{bipyridine}$. This last catalytic system was applied on a petroleum-based aliphatic alcohol but was not fully optimized.

The approach of Yin et al.[29] employing $\text{CuI}/\text{TEMPO}/\text{bipyridine}$ under mild conditions, appears to be a desirable method to convert bio-based aliphatic alcohols into nitrile because copper catalyst is cheap, available and presents a low toxicity. Nevertheless, benzylic alcohols were mainly used as substrates for this oxidation reaction.

Herein, based on these recent developments in the course of sustainable primary amine synthesis, the latest process²¹ has been optimized for the design of fatty acid-based aliphatic dinitriles and extended to different bio-based alcohol substrates. The so-formed dinitriles were reduced into bio-based diamines and finally, the latest were reacted with fatty acid-based bis-cyclic carbonates in order to synthesize fully bio-based poly(hydroxyl urethane)s, PHUs.

EXPERIMENTAL SECTION

General procedure for nitrile synthesis

In an oven-dried Schlenk tube, the alcohol (3.0 mmol), CuI (0 to 10 mol% per moles of primary alcohol function (mol%)), bipyridine (bpy) (0 to 10 mol% per moles of primary alcohol function) and TEMPO (0 to 10 mol% per moles of primary alcohol function) were added. Then the Schlenk was capped with a rubber septum and flushed with oxygen three times. Acetonitrile was added and the reaction mixture was saturated in oxygen by bubbling for 20 minutes (for 0.5 g scale). Aqueous ammonia (25-28% w/w, 0.44 mL, 12 mmol, 2 eq. per moles of primary alcohol function (eq) was subsequently added. The resulting orange-brown solution was stirred from 30 to 70°C (depending on the reaction conditions, see Table 1) for 24 hours under oxygen balloons.

As the reaction is running, the reaction mixture turns to light blue. The crude reaction mixture was analyzed through ^1H NMR. The solvent was removed under vacuum and the residue was purified by alumina/celite column followed by flash chromatography (eluent: cyclohexane/ethyl acetate).

General procedure for diamine synthesis

In a jacketed pressurized reactor, decanedinitrile (0.5g, 3 mmol) or UndC20-dinitrile (0.9g, 3 mmol), Raney Nickel slurry in water (1 mL) and 15 mL of ethanol were successively added. The reactor was pressurized at 10 Bars of H_2 and stirred at 70°C overnight. After, the reactor was cooled down and slowly depressurized. The reaction media was then filtered over celite to remove the Raney nickel catalyst. The ethanol was evaporated and the obtained white powder was washed with ethyl acetate to remove the unreacted nitrile.

General procedure for bis-cyclic carbonates synthesis

The syntheses of fatty acid-based bis-cyclic carbonates follow the same procedures recently described in a paper published by our research team[10]. For more experimental details, refer to the supporting information.

General procedure for polymerization

PHUs were synthesized from Und-bCC-ether, Und-bCC-ester, and with 1,10-decanediamine (10DA) and UndC20-diamine (20DA) as comonomers. The polymerizations were performed in DMF at 1mol.L^{-1} at 70°C under nitrogen atmosphere without any catalyst, at the g/mg scale, and all monomers and resulting polymers were soluble in DMF.

RESULTS AND DISCUSSION

Synthesis of aliphatic primary amines

Based on the strategy developed by Yin *et al.*, the synthesis of nitrile was first optimized on 1,10-decanediol. The effect of the temperature on the conversion of 1,10-decanediol into decanedinitrile was first examined with 5 mol% of catalysts (CuI, bpy, TEMPO) per mole of substrate. Aliquots were collected and conversions were determined by ^1H NMR spectroscopy (See Fig S1 and S2).

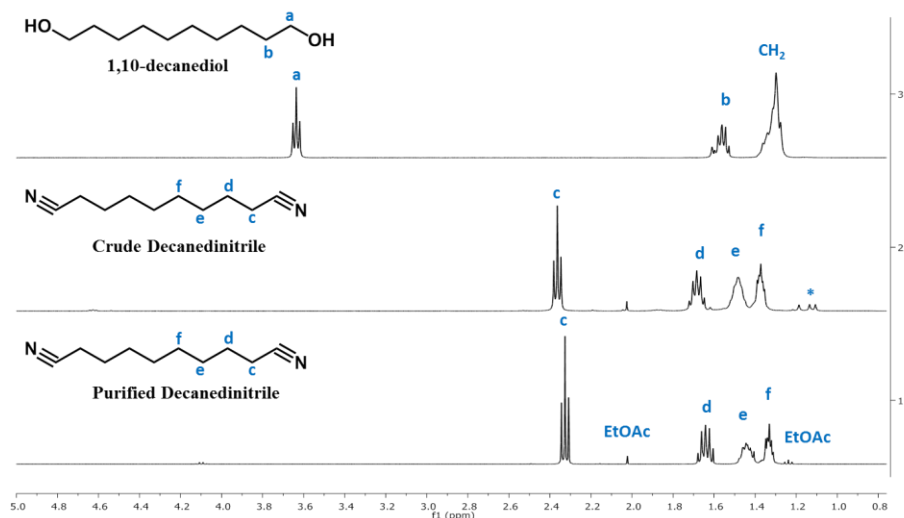


Figure 1. Stacked ^1H NMR spectra of 1,10-decanediol, crude decanedinitrile and purified decanedinitrile in CDCl_3 . (*) Impurity

The nitrile formation can be determined by quantifying the triplet corresponding to the methylene protons nearby the nitrile at 2.39 ppm. Results are summarized in Table 1.

Increase of the temperature until 50°C improved the conversion of 1,10-decanediol into decanedinitrile up to 41% but, above this temperature, the percentage of decanedinitrile

decreased and stabilized around 10 % (Table 1, entries 4 and 5). This feature can be explained by the evaporation of ammonia from the reaction medium. At 30°C and 60°C, aldehydes were also detected, by ^1H NMR spectroscopy with a triplet at 2.41 ppm (Figure S1 and S2). The presence of aldehydes can be logically explained according to the reaction mechanism[29] (Scheme S1). Indeed, in the oxidation cycle, the alcohol is first oxidized into aldehyde and the latter is then converted into imine in the presence of ammonia to finally afford the nitrile. In our case, no imines were observed at the end of the reaction.

Table 1. Effect of temperature on the nitrile conversion for 1,10-decanediol^a

Entry	Temperature (°C)	Alcohol (mol%) ^b	Nitrile (mol%) ^b	Aldehyde (mol%) ^b
1	30	93	5	2
2	40	82	18	0
3	50	59	41	0
4	60	81	9	10
5	70	90	10	0

^a Reaction conditions : 3.0 mmol of diol, 5 mol% CuI, 5 mol% bpy, 5 mol% of TEMPO, 2 eq of aqueous ammonia (25-28%, w/w), 5 mL of acetonitrile, oxygen balloon, 24h. ^b Determined by ^1H NMR in CDCl_3 .

Then, the influence of the catalyst loading (CuI, bpy, TEMPO) on the nitrile conversion (see Figure 2 and Figure S3) of 1,10-decanediol at 50°C was investigated. As expected, no oxidation occurred in absence of any catalytic system. The conversion of alcohol into nitrile increased

when the quantity of catalyst was increased and, in all cases, no aldehyde was observed. Full conversion of alcohol was obtained with 7.5 mol. % of catalyst per mole of hydroxyl function.

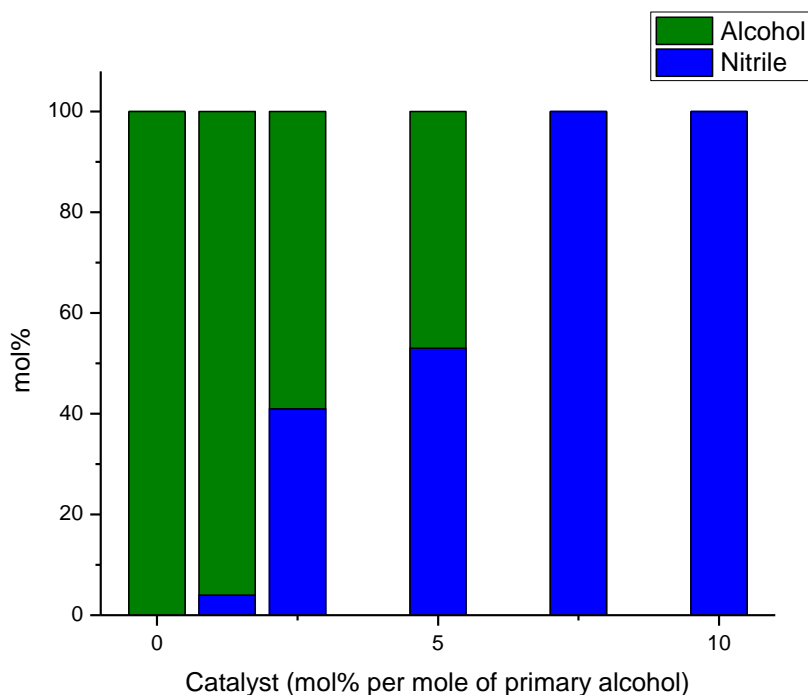


Figure 2. Effect of the catalyst percentage on the nitrile conversion for 1,10-decanediol^a

^a Reaction conditions : 3.0 mmol of diol, 2 eq of aqueous ammonia (25-28%, w/w), 5 mL of acetonitrile, oxygen balloon, 50°C, 24h. ^b Determined by ¹H NMR in CDCl₃.

The reaction conditions described above (10 mol% CuI per OH, 10 mol% bpy, 10 mol% of TEMPO, 2 eq of aqueous ammonia (25-28%, w/w), acetonitrile, oxygen balloon, 50°C, 24h) tested on 1,10-decanediol were extended to other renewable primary alcohols. In this purpose, vegetable oil derivatives (undecenol, oleyl alcohol and icos-10-ene-1,20-diol (UndC20-diol) obtained by metathesis of undecenol, terpenes (citronellol and phytol) and carbohydrates (glucose) were oxidized into nitrile at 50°C and 10 mol% of catalyst per mole of primary alcohol (Figure S5 to S11, Table 2). The percentage of nitrile formed was also determined by ¹H NMR

spectroscopy. The results are summarized in Table 2. Excellent conversions in nitrile compounds were obtained except for the glucose for which a conversion of 38% in nitrile was obtained. This low yield can be explained by a lower solubility of this substrate in acetonitrile, compared to the other alcohols. This oxidation reaction allowed the one-pot synthesis of various nitrile compounds from primary aliphatic alcohols. This protocol appears to be green (atom efficiency, catalyzed process, easy catalyst removal) but also highly efficient and versatile to produce bio-based nitrile compounds.

Table 2. Scope of bio-based primary alcohol substrates oxidized into nitrile derivatives^a

$$\text{R-OH} \xrightarrow[\text{MeCN, O}_2, 50^\circ\text{C}]{\substack{10 \text{ mol\% CuI, 10 mol\% bpy} \\ 10 \text{ mol\% TEMPO, aqueous ammonia}}} \text{R-CN}$$

Entry	Substrate	Product	Nitrile conv. (%) ^b
1			100
2			100
3			100
4			100
5			100
6			38 ^c

^a Reaction conditions : 3.0 mmol of alcohol, 10 mol% CuI, 10 mol% bpy, 10 mol% of TEMPO, 2 eq of aqueous ammonia (25-28%, w/w), 5 mL of acetonitrile, oxygen balloon, 24h. ^b Determined by ¹H NMR in CDCl₃. ^c Determined by ¹H NMR in D₂O.

The dinitrile derivatives were reduced in diamines as monomers for the synthesis of polymers. Two dinitrile compounds were thus completely reduced into amines in ethanol under 10 bars of H₂ at 70°C, for 16h and using Raney Nickel as hydrogenation catalyst. The formation of the two corresponding diamines has been demonstrated by FTIR-ATR and ¹H NMR spectroscopy. In FTIR-ATR, the stretching band of nitrile functions at 2243 cm⁻¹ disappeared and the stretching band of amine functions appeared in the range 3000-3500 cm⁻¹ (see Figures S12 and S13). In ¹H NMR spectrum, the triplet at 2.4 ppm corresponding to the proton nearby the nitrile function disappeared and a triplet at 2.6 ppm corresponding to the protons nearby the amine function appeared (see Figure S14 and S15). Thus, these two diamines 1,10-decanediamine (10DA) and UndC20-diamine (20DA) have been successfully synthesized by reduction of the corresponding dinitriles. Such a procedure can be easily applied to the all nitrile compounds platform.

Poly(hydroxyurethane)s synthesis

1,10-decanediamine (10DA) and UndC20-diamine (20DA) were directly polymerized with several bio-based bis-cyclic carbonates, Und-bCC-ester, Und-bCC-ether, and DGDC (see supporting information for the detailed synthesis and structures Scheme S2, Figure S16 to S19) in order to obtain fully bio-based poly(hydroxyurethane)s. The polymerizations were performed in DMF at 1 mol.L⁻¹ at 70°C under nitrogen atmosphere without any catalyst. Bulk polymerizations could not be achieved due to the high melting point of monomers. However, DMF was chosen thanks to its ability to solubilize all monomers and subsequent polymers. Then, PHUs were characterized without prior quenching and precipitation after 24h and 7 days. PHUs formation was followed by ¹H NMR with the disappearance of the signals in α -position nearby the cycle in the ranges 4.2-4.6 ppm, and with the presence of the characteristic protons CH₂-

NHC(O)O at 2.98 ppm (See Figure S20). The synthesized PHUs were also characterized by SEC in DMF (LiBr, PS standards, 25°C). SEC traces are shown in Figure 3. All the data are summarized in Table 3.

Table 3. Characterization of poly(hydroxyurethane)s obtained from diamines and bis-cyclic carbonates^a

PHUs	Diamine	Cyclic Carbonate	Conversion ^b (%)	M _n (g.mol ⁻¹) ^c [D]	DP _n	T _g ^d (°C)	T _f ^d (°C)	Td5% ^e (°C)
1	10DA	Und-bCC-ester	88	12000 [1.9]	16.8	-10	69/83	274
2		Und-bCC-ether	90	7500 [1.7]	10.9	-26	54/77	270
3		DGDC	83	12000 [1.4]	30.7	1	65/94	247
4	20DA	Und-bCC-ester	87	20500 [2]	23.9	10	80/84	229
5		Und-bCC-ether	82	8100 [1.5]	15.8	-6	73	234
6		DGDC	80	7600 [1.6]	14.3	26	92	200

^aReaction conditions: 1 eq of diamine, 1 eq of bis-cyclic carbonate, DMF (1 mol.L⁻¹), 70°C, no catalyst ^bDetermined by ¹H NMR after 24 h of polymerization, no significant evolution of the conversion after 7 days; ^cDetermined by SEC DMF (LiBr, 25°C, PS Std); ^dDetermined by DSC at 10°C.min⁻¹ from the second cycle. ; ^eDetermined by TGA at 10°C.min⁻¹ under nitrogen.;

The conversions of cyclic carbonates were above 80 % in 24 h but could not reach more than 90 % due to the abundant hydrogen bonding present in the polymer, avoiding a further polymerization. Additionally, side reactions such urea formation has already been reported in literature and could explained the limited conversions obtained for PHUs.[10] It is noteworthy to mention that the conversions were not significantly different after 7 days of polymerization.

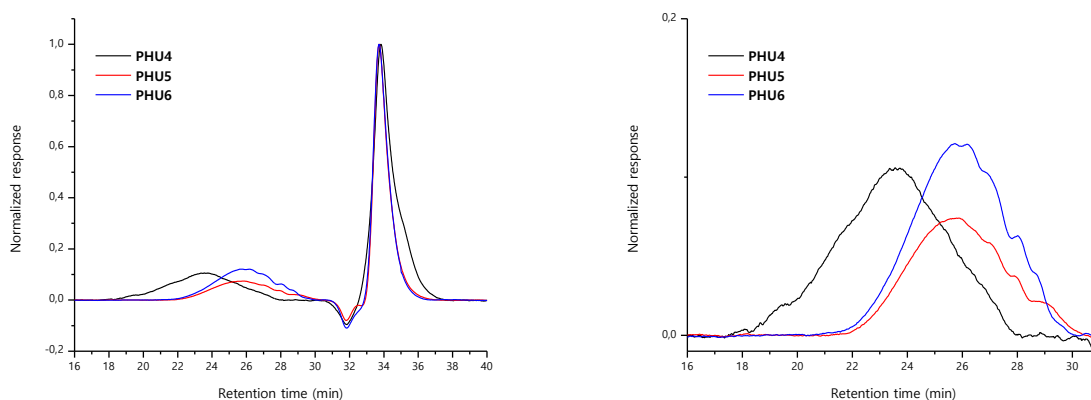


Figure 3. SEC traces of PHU 4 to PHU 6 (left) and corresponding zoom (right) (performed in DMF, LiBr, PS standards, 25°C).

Relatively high molar masses in the ranges 7500-20500 g.mol⁻¹ with dispersities comprised between 1.4 and 2 were achieved. This statement confirmed that the synthesized diamines and bis-cyclic carbonates were obtained pure enough for a polyaddition process. The thermal properties of the PHUs were examined by DSC and TGA, using a prior isothermal procedure at 160 °C for 15 min in order to remove DMF traces from the samples. The PHUs containing 20DA exhibited lower Td_{5%} compared to the one synthesized with 10DA. However, this statement could not be explained and was in contradiction with the general trends[32].

The PHUs were all semi-crystalline and some of them exhibited two melting peaks that could reveal two types of crystalline clusters or segregation between soft and hard segments (PHUs 1 to 4). Relatively low T_g in the ranges -26 to 26 °C conferred by the aliphatic monomer backbones were obtained. The ether-rotula structure of Und-bCC-ether conferred to PHU 2 and PHU 5 T_g of -26°C and -6°C, whereas PHU 3 and PHU 6 displayed a higher T_g imparted with a harder segmented monomer.

When 20DA was used as comonomer, the melting temperatures of PHUs were in the same range than the ones obtained with 10DA. However, the melting enthalpy and consequently the crystallinity were higher for the longer aliphatic diamine-based PHUs. Indeed, it has been reported that when the crystallinity increases in the PE-like polymers, an increase of the T_g is observed. [33] This statement could explain in our case that the T_g values obtained for the PHU4 to 6 synthesized with 20DA were globally 20°C above the ones obtained for 10DA-based PHUs.

CONCLUSION

In conclusion, we have optimized the efficient preparation of aliphatic and bio-based nitriles by a one-pot aerobic oxidation of primary alcohols. This oxidation was performed under mild condition using CuI, bipyridine and TEMPO as catalytic system under O₂ atmosphere. A catalyst ratio of 10 mol% per moles of primary alcohol at a temperature of 50°C permitted the complete oxidation of the 1,10-decanediol into decanedinitrile. This optimized process was successfully applied to different structures of alcohol derived from renewable resources. Then, the so-formed dinitriles were easily reduced into diamines. This optimized 'nitrile pathway' in the course of amine synthesis appears to be highly efficient, green and simple for the synthesis of bio-based amines from the corresponding primary alcohols.

The so-formed fatty acid-based primary diamines were polymerized with bio-based bis-cyclic carbonates and could enable the synthesis of poly(hydroxyurethane)s with relatively high carbonate function conversions and molar masses.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Bio-based aliphatic primary amines from alcohols through the ‘Nitrile route’ towards non-isocyanate polyurethanes

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Materials and methods

Copper Iodide (CuI, 98% dissolved in saturated aqueous sodium iodide solution and recrystallized by addition of distilled water prior to use), 2,2'-bipyridyl (bipyridine 98%), ammonium hydroxide solution (ACS reagent, 28.0-30.0% NH₃ basis), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%), 1-10-decanediol (98%), oleyl alcohol (85%), citronellol (>95%), phytol (97%), D-(+)-glucose (>99.5%), Raney®-Nickel (slurry in H₂O) N,N-dimethylformamide (DMF, anhydrous grade), sodium hydroxide (NaOH, pellet), tetrabutylammonium bromide

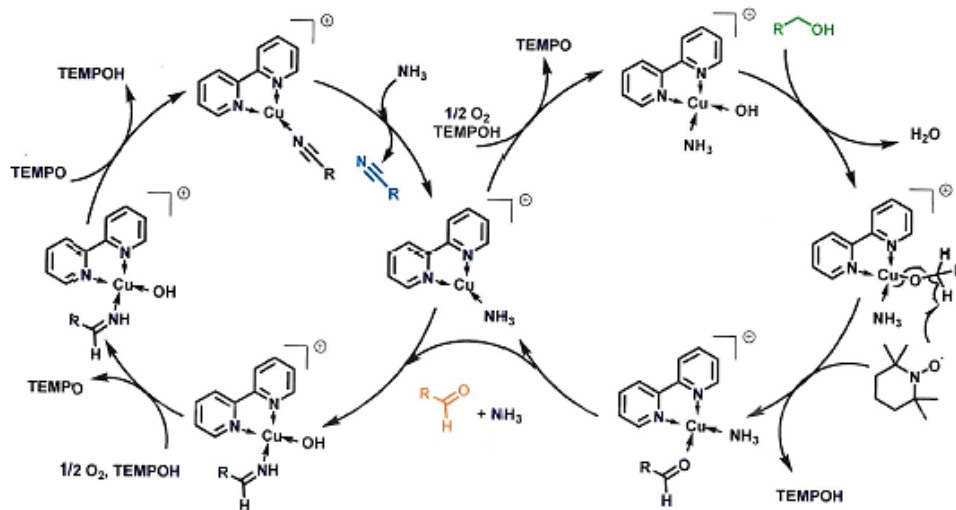
(TBABr, 99%), dimethyl carbonate (DMC, 99%), and Grubbs 1st and Grubbs 2nd generation metathesis catalysts were obtained from Sigma-Aldrich. 10-undecen-1-ol (99%), Lanthanum oxide (La₂O₃, 99%) and ethyl vinyl ether (99%) were purchased from Alfa Aesar. 10-undecen-1-ol (99%), epichlorohydrin (>99%) and diglycerol (>90%), were supplied by TCI, Europe. ITERG kindly provided 20 g of UndCC-ester. All products and solvents (reagent grade) were used as received except otherwise mentioned. The solvents were of reagent grade quality and were purified wherever necessary according to the methods reported in the literature.

¹H NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ¹H and ¹³C, respectively) by using CDCl₃ as a solvent at room temperature, except otherwise mentioned. Infrared spectra (FTIR-ATR) were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired using 16 scans at a resolution of 4 wavenumbers. Size exclusion chromatography (SEC) analyses of PUs were performed in DMF (80°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from Polymer Laboratories (PLgel: PLgel 5µm Guard (guard column 7.5 mm ID x 5.0 cm L); PLgel 5µm MIXED-D (7.5 mm ID x 30.0 cm L) and PLgel 5µm MIXED-D (7.5 mm ID x 30.0 cm L)). In both cases, the elution times of the filtered samples were monitored using RI detectors. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -50 to 160 °C at 10 °C.min⁻¹ (additional isotherm of 15 min at 160°C at the end of the first cycle to remove the residual DMF) were performed and then the glass transition and melting temperatures were calculated from the second heating run. Thermogravimetric analyses (TGA) were performed on

TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ under nitrogen atmosphere from room temperature to 600°C, with an isotherm at 160°C for 15 min to remove the residual DMF.

Synthesis of nitriles

In an oven-dried Schlenk tube, the alcohol (3.0 mmol), CuI (0 to 10 mol% per moles of primary alcohol function (mol%)), bipyridine (bpy) (0 to 10 mol% per moles of primary alcohol function) and TEMPO (0 to 10 mol% per moles of primary alcohol function) were added. Then the Schlenk was capped with a rubber septum and flushed with oxygen three times. Acetonitrile was added and the reaction mixture was saturated in oxygen by bubbling for 20 min (for 0.5 g scale). Aqueous ammonia (25-28% w/w, 0.44 mL, 12 mmol, 2 eq. per moles of primary alcohol function (eq) were subsequently added. The resulting orange-brown solution was stirred from 30 to 70°C (depending on the reaction conditions, see Table 1) for 24 h under oxygen balloons. As the reaction is running, the reaction mixture turns to light blue. The crude reaction mixture was analyzed through ¹H NMR. The solvent was removed under vacuum and the residue was purified by alumina/celite column followed by flash chromatography (eluent: cyclohexane/ethyl acetate).



Scheme S1: Reaction mechanism proposed by Yin et al.²¹

Effect of the temperature

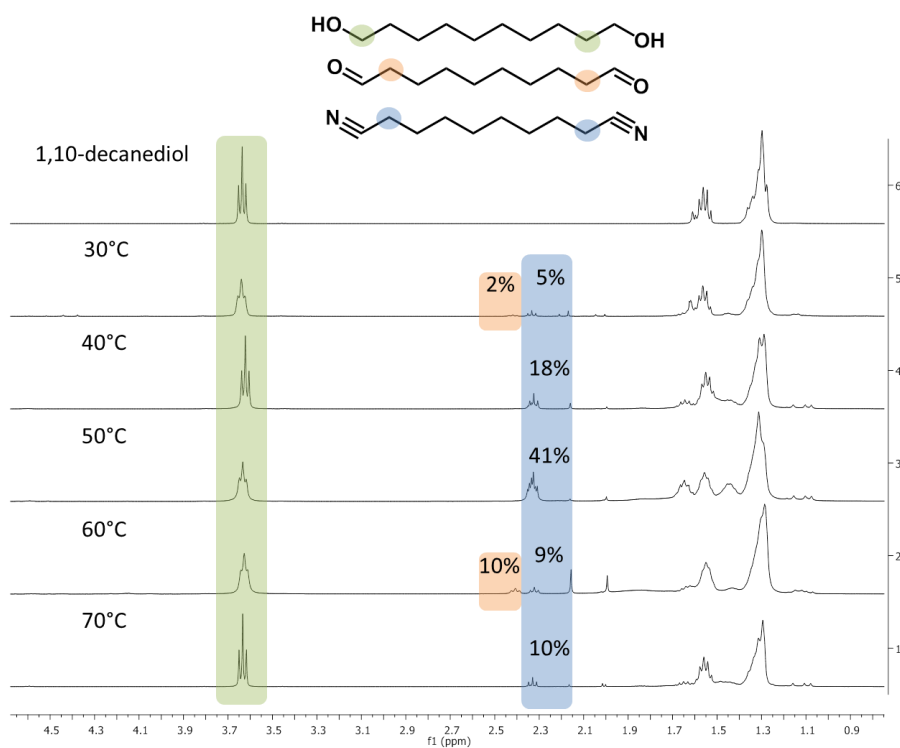


Figure S1: Stacked ¹H NMR spectra in CDCl₃ of crude mixture of oxidation reaction of 1,10-decanediol

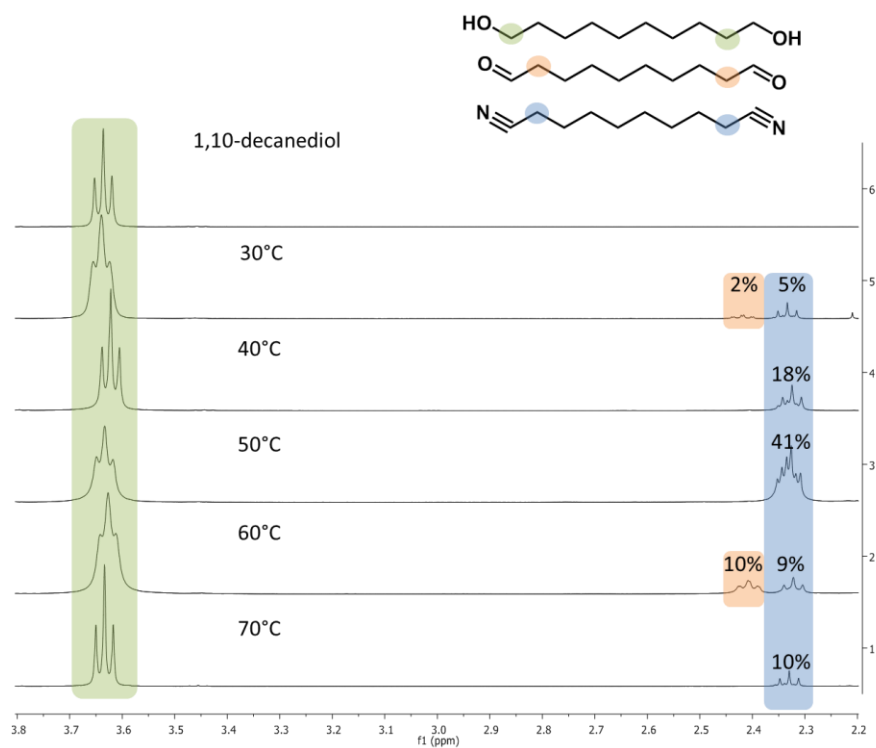


Figure S2: Stacked ^1H NMR spectra in CDCl_3 of crude mixture of oxidation reaction of 1,10-decanediol

Effect of the catalyst percentage

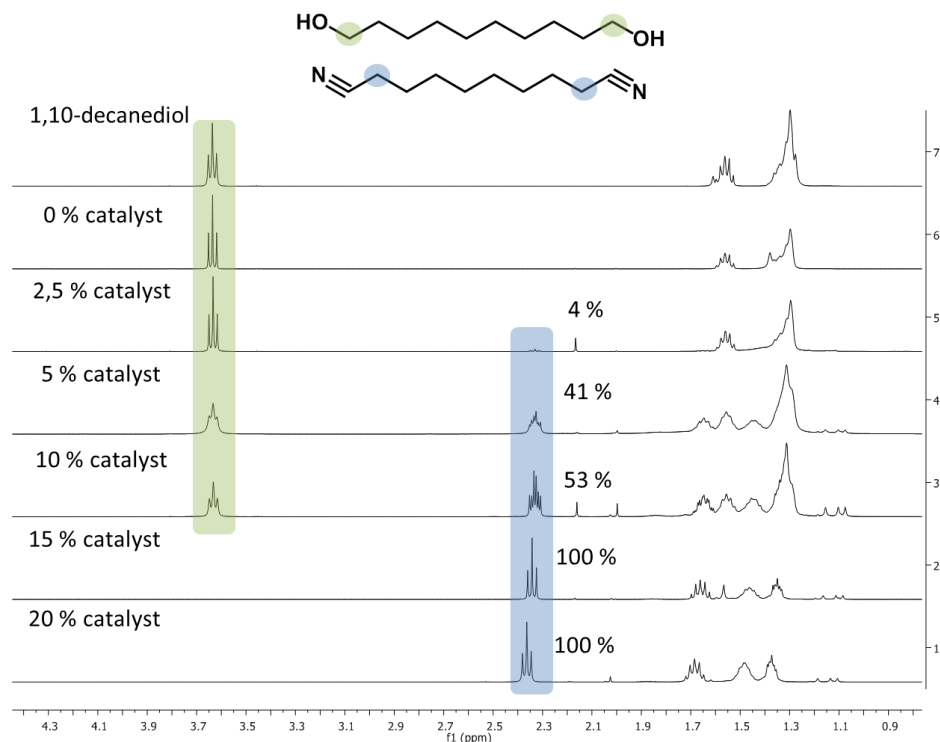


Figure S3: Stacked ^1H NMR spectra in CDCl_3 of crude mixture of oxidation reaction of 1,10-decanediol

From 1,10-decanediol: 1,10-decanediol (0.5 g, 2.9 mmol), CuI (110 mg, 0.58 mmol, 20 mol%), bpy (90 mg, 0.58 mmol, 20 mol%), TEMPO (90 mg, 0.58 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.44 mL). Decanedinitrile was obtained as a transparent liquid after flash chromatography (eluent: cyclohexane–ethyl acetate 90/10 to 43/57). Yield = 90%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 2.34 (t, 4H), 1.66 (m, 4H), 1.46 (m, 4H), 1.35 (m, 4H).

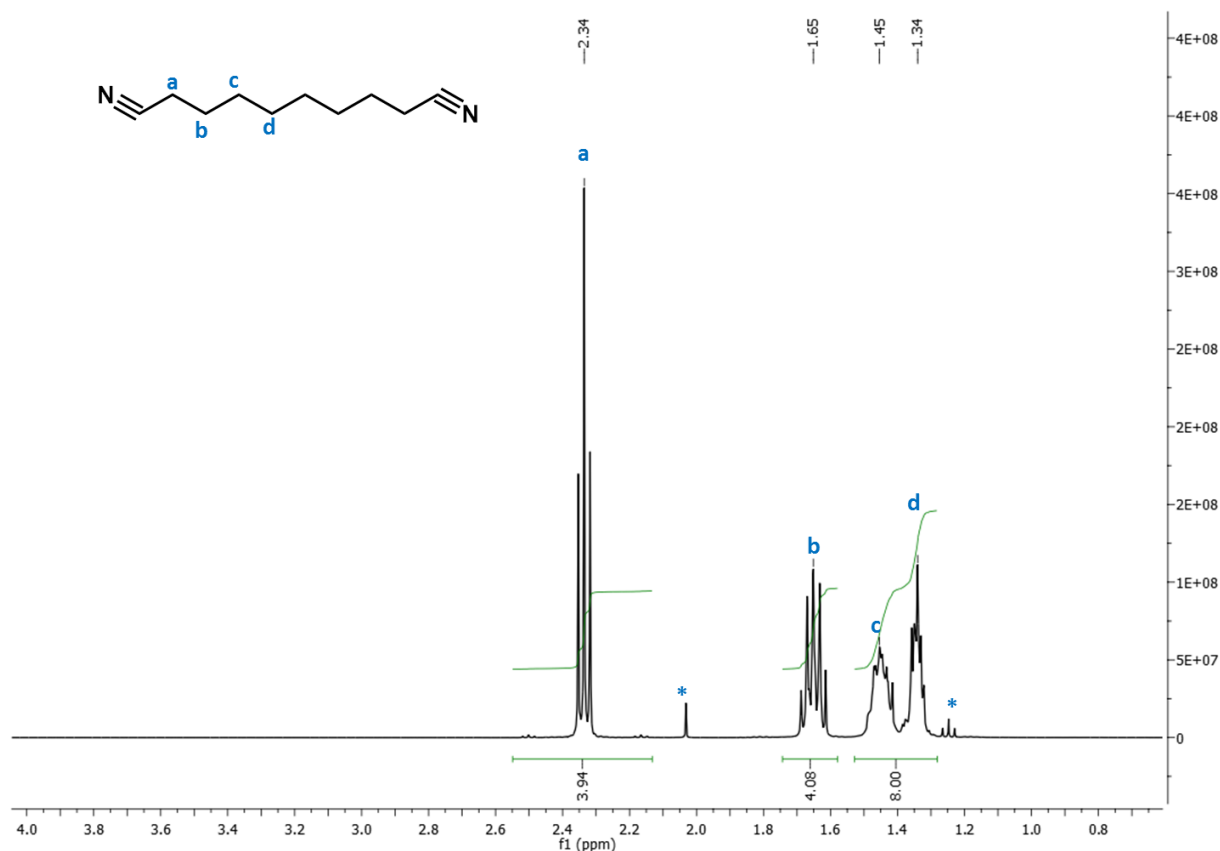


Figure S4: ^1H NMR spectrum in CDCl_3 of Decanedinitrile obtained from 1,10-decanediol.

(*) Impurities

Metathesis reaction

Metathesis reaction procedure

In an oven-dried Schlenk tube, undecanol (20g, 117 mmol) was dissolved in pentane dried on CaH_2 . Afterwards, Grubbs 2nd generation metathesis catalyst (1 mol%, 0.99 g, 1.17 mmol) was added. The reaction was performed under inert atmosphere at room temperature for 72 hours. As the reaction was running, the product got precipitated, which allows the shift of the equilibrium toward the formation of diol. Then, ethyl vinyl ether was added to deactivate the Grubbs catalyst

and the reaction mixture was filtered to recover the solid diol. The product was purified by two recrystallizations in toluene.

UndC20-diol: 10-undecen-1-ol (20 g, 117 mmol), Grubbs II catalyst (0.99 g, 1.17 mmol) and pentane (100 mL). UndC20-diol was obtained as a white powder with a purity of 60.0% (determined by GC-FID, due to isomers) Yield = 43%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 3.63 (t, 4H), 1.97 (m, 4H), 1.56 (m, 4H), 1.28 (m, 24H).

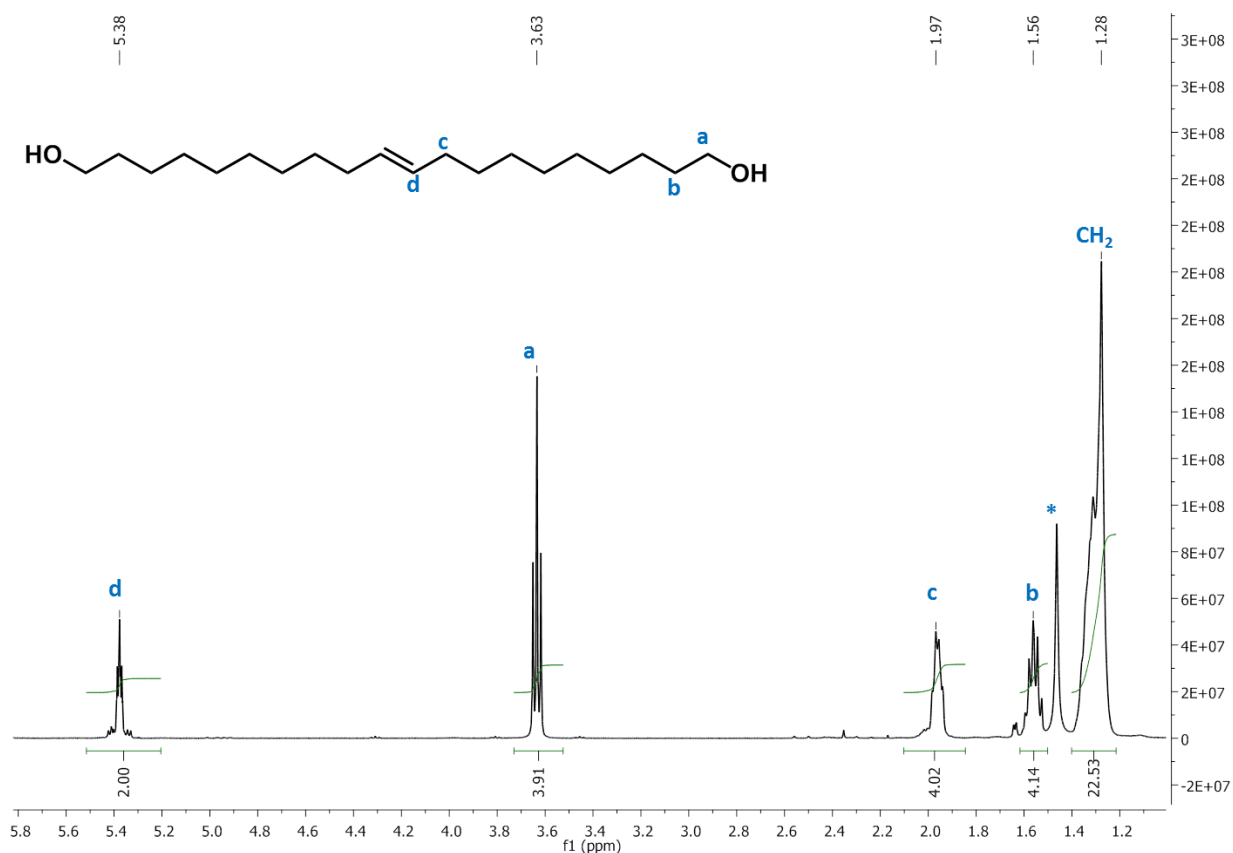


Figure S5: ^1H NMR spectrum of UndC20-diol in CDCl_3 . (*) Impurities

From UndC20-diol: UndC20-diol (0.5 g, 1.6 mol), CuI (61 mg, 0.32 mmol, 20 mol%), bpy (0.5 mg, 0.32 mmol, 20 mol%), TEMPO (0.5 mg, 0.32 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.25 mL). UndC20-dinitrile was obtained as a viscous transparent liquid after flash chromatography (eluent: cyclohexane–ethyl acetate 100/0 to 80/20). Yield = 76% OL205.

^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 2.33 (t, 4H), 1.96 (m, 4H), 1.66 (m, 4H), 1.45 (m, 4H), 1.30 (m, 16H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 119.94 (CN), 130.42 (CH=CH), 32.62 ($\text{CH}_2\text{-CH=CH}$), 29.63-28.74 (CH_2), 25.41 ($\text{CH}_2\text{-CH}_2\text{-CN}$), 17.22 ($\text{CH}_2\text{-CN}$). IR (cm^{-1}): 2924, 2855, 2244.

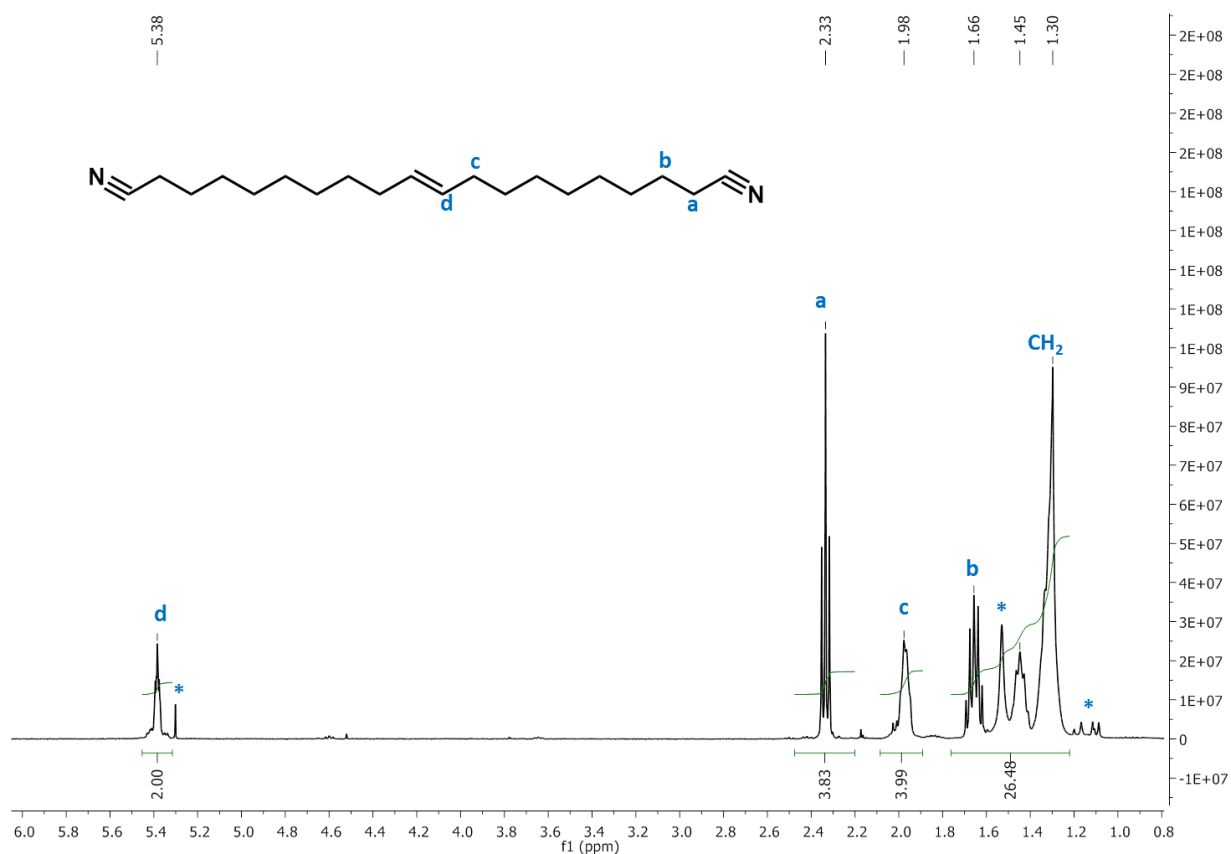


Figure S6: ^1H NMR spectrum in CDCl_3 of dinitrile obtained from UndC20-diol. (*)Impurities

From undecenol: undecenol (0.5 g, 2.9 mmol), CuI (112 mg, 0.59 mmol, 20 mol%), bpy (92 mg, 0.59 mmol, 20 mol%), TEMPO (92 mg, 0.59 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.45 mL). Und-nitrile was obtained as a viscous transparent liquid after flash chromatography (eluent: cyclohexane–ethyl acetate 100/0 to 93/7). Yield = 86%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.83 (m, 1H), 5.02 (m, 2H), 2.38 (t, 2H), 2.10 (m, 2H), 1.71 (m, 2H), 1.50-1.36 (m, 10H).

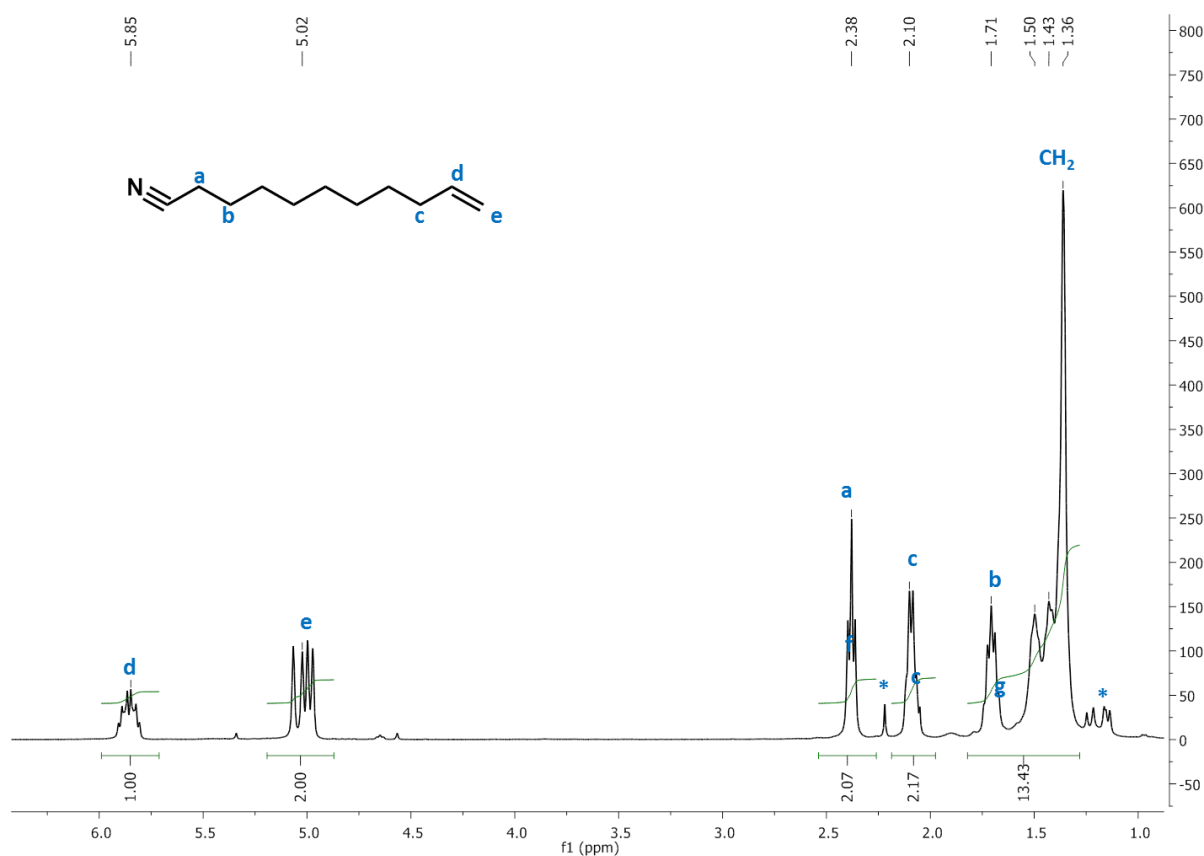


Figure S7: ^1H NMR spectrum in CDCl_3 of nitrile obtained from undecenol. (*)Impurities

From oleyl alcohol: oleyl alcohol (0.5 g, 1.9 mol), CuI (71 mg, 0.37 mmol, 20 mol%), bpy (58 mg, 0.37 mol, 20 mol%), TEMPO (58 mg, 0.37 mmol, 20 mol%), acetonitrile (5 mL) and

aqueous ammonia (0.29 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 2.35 (t, 2H), 2.04 (m, 4H), 1.68 (m, 2H), 1.47-1.29 (m, 22H), 0.91 (t, 3H).

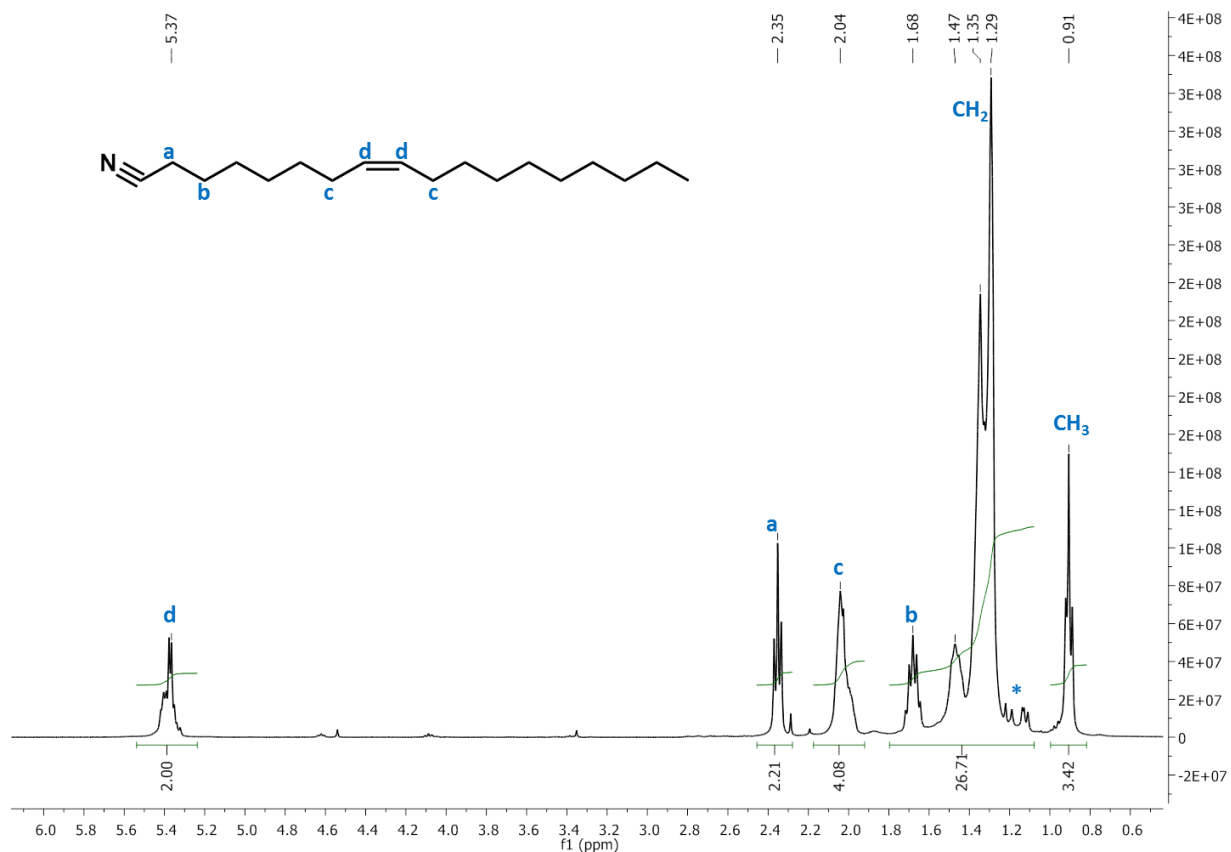


Figure S8: ^1H NMR spectrum in CDCl_3 of nitrile obtained from oleyl alcohol. (*) Impurities

From citronellol: citronellol (0.5 g, 3.2 mmol), CuI (122 mg, 0.64 mmol, 20 mol%), bpy (100 mg, 0.64 mmol, 20 mol%), TEMPO (100 mg, 0.64 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.5 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.09 (t, 1H), 2.32 (m, 2H), 2.02 (m, 2H), 1.89 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.47-1.39 (m, 2H), 1.10 (d, 3H).

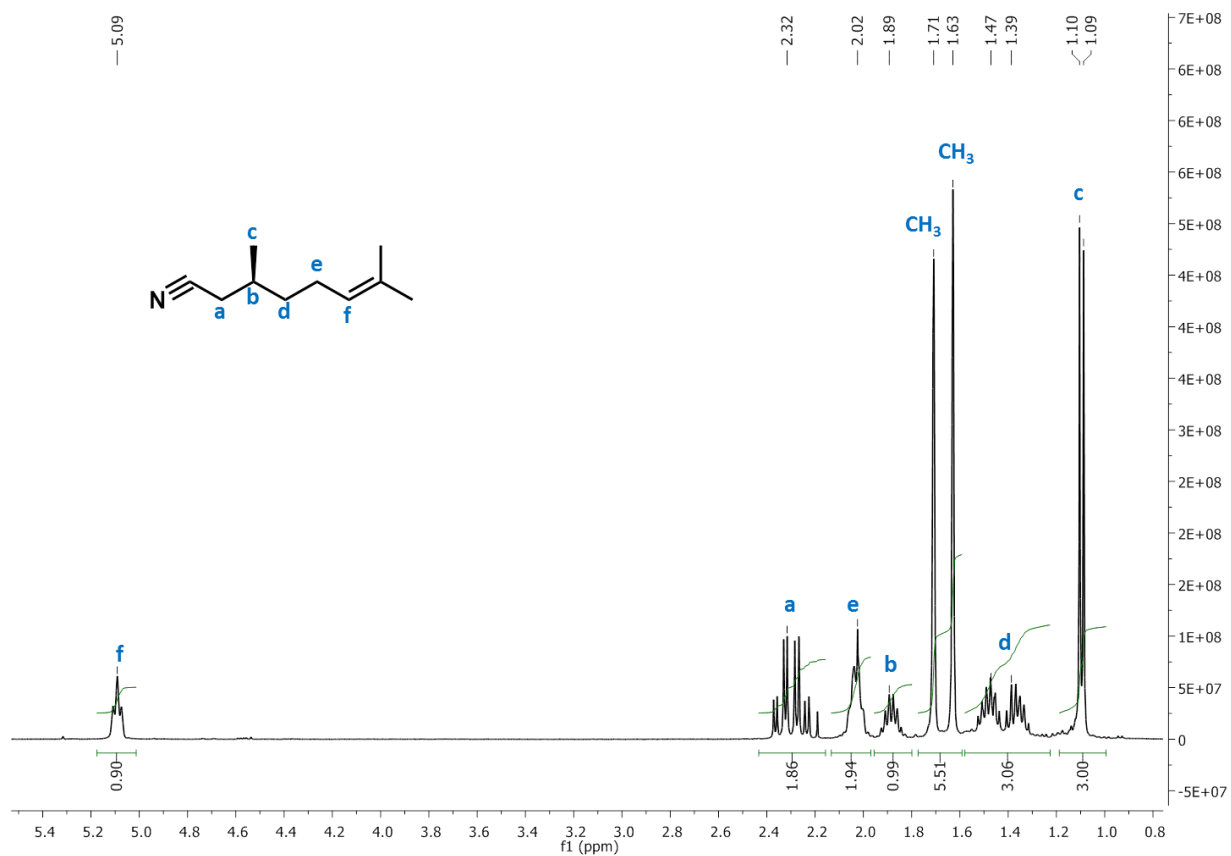


Figure S9: ^1H NMR spectrum in CDCl_3 of nitrile obtained from citronellol. (*)Impurities

From phytol: phytol (0.5 g, 1.7 mmol), CuI (64 mg, 0.34 mmol, 20 mol%), bpy (53 mg, 0.34 mmol, 20 mol%), TEMPO (53 mg, 0.34 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.26 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.12 (s, 1H), 2.40 and 2.17 (2.t, 2H), 2.06 and 1.92 (2.s, 3H), 1.52-1.09 (m, 19H), 0.89 (m, 12H).

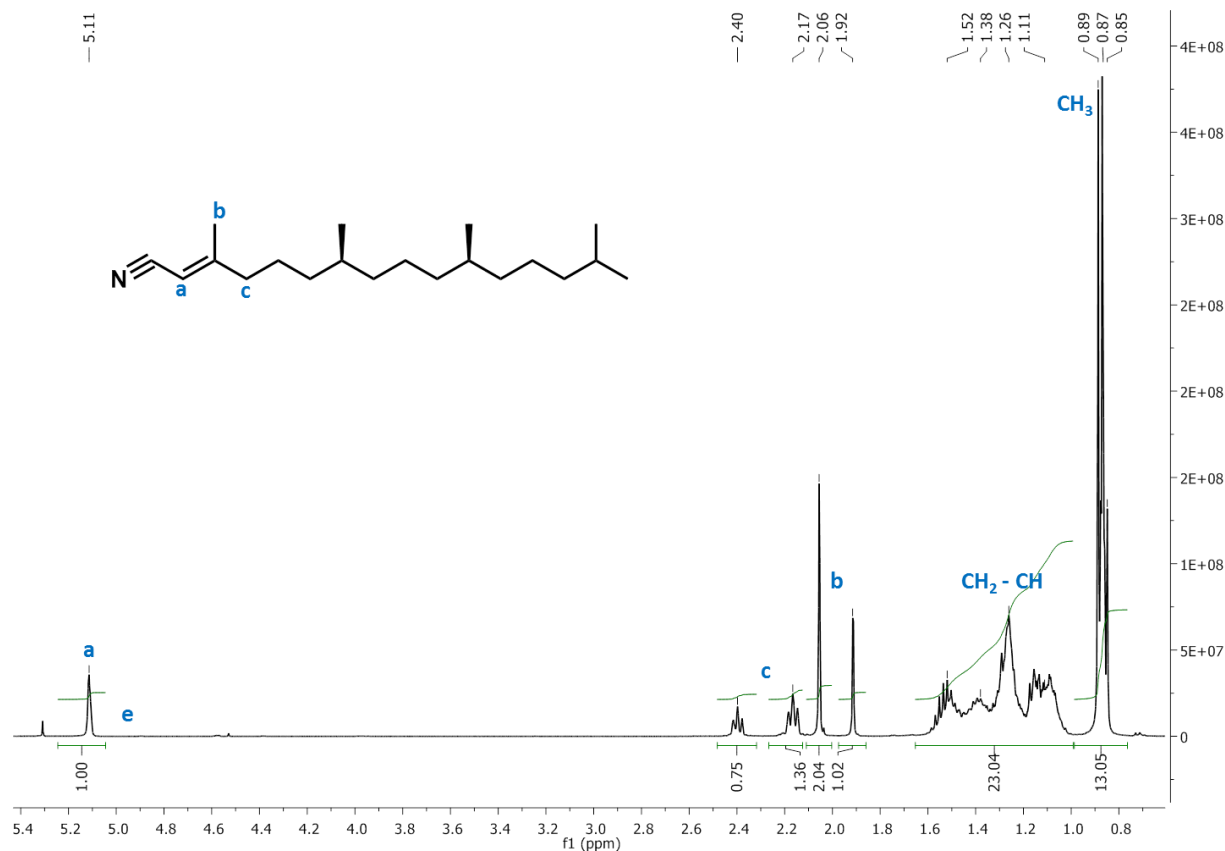


Figure S10: ^1H NMR spectrum in CDCl_3 of nitrile obtained from phytol. (*)Impurities

From glucose: glucose (0.5 g, 2.8 mmol), CuI (106 mg, 0.56 mmol, 20 mol%), bpy (87 g, 0.56 mol, 20 mol%), TEMPO (87 mg, 0.56 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.43 mL). ^1H NMR (D_2O , 25 °C, 400 MHz) δ (ppm): 5.25 and 4.61 (2.d, 1H), 4.25-3.59 (m, 6H).

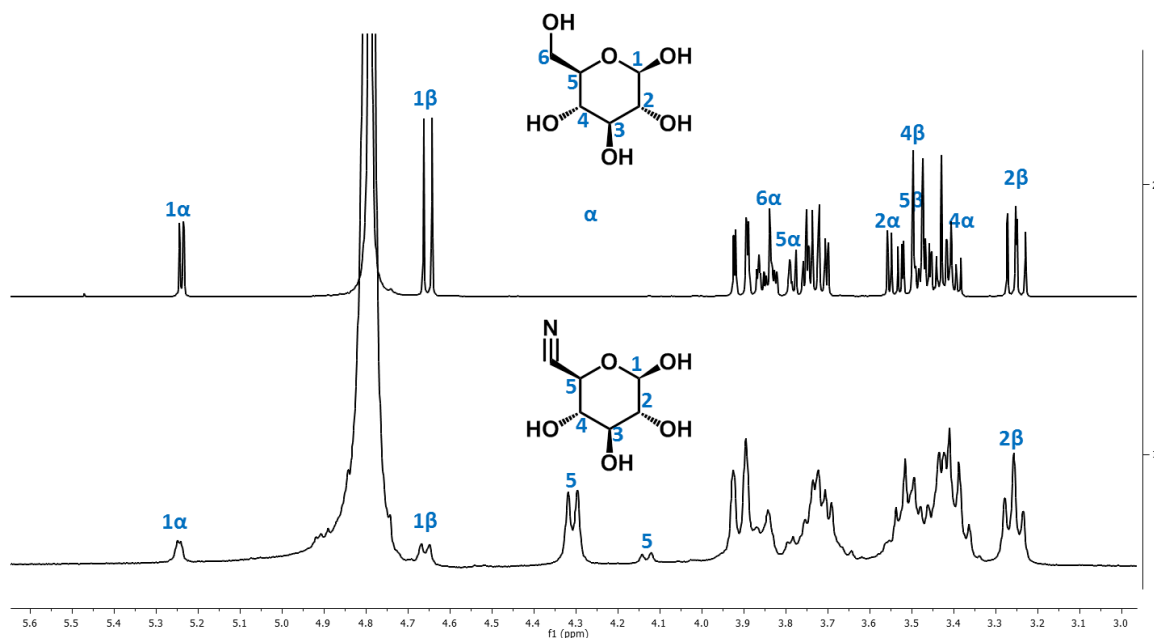


Figure S11: Stacked ^1H NMR spectra in CDCl_3 of glucose and nitrile obtained from glucose

Synthesis of amines

In a jacketed pressurized reactor, decanedinitrile (0.5g, 3 mmol) or UndC20-dinitrile (0.9g, 3 mmol), Raney Nickel slurry in water (1 mL) and 15 mL of ethanol were successively added. The reactor was pressurized at 10 Bars of H_2 and stirred at 70°C overnight. After, the reactor was cooled down and slowly depressurized. The reaction media was then filtered over celite to remove the Raney nickel catalyst. The ethanol was evaporated and the obtained white powder was washed with ethyl acetate to remove the unreacted nitrile.

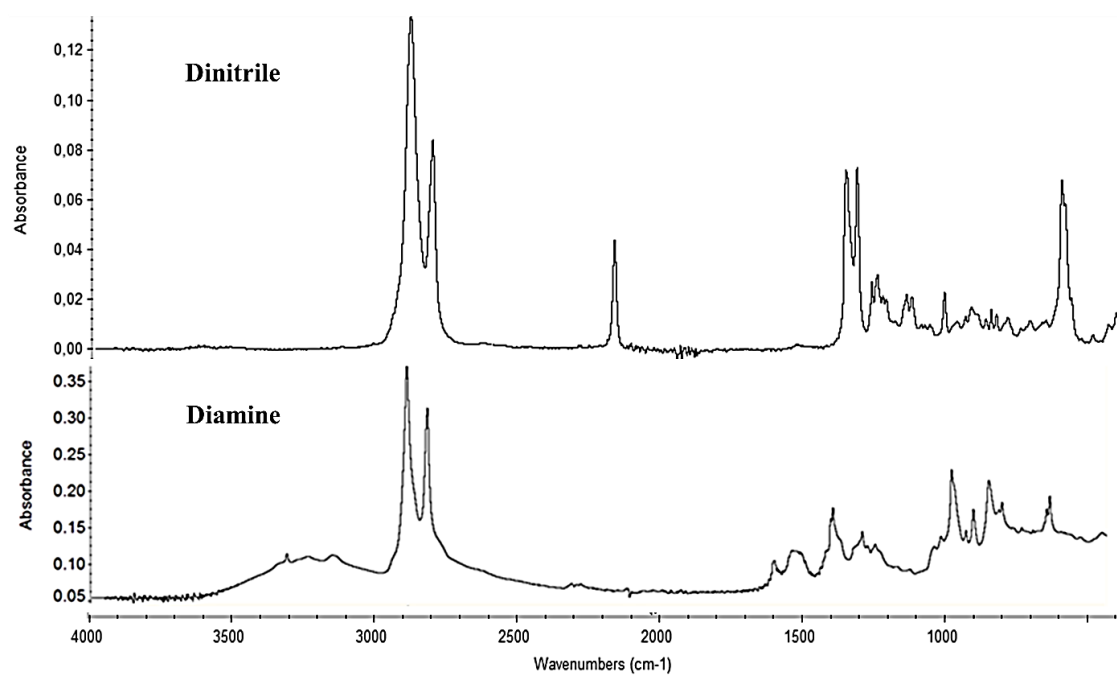


Figure S12: Stacked FTIR-ATR spectrum of Decanediamine and decanedinitrile

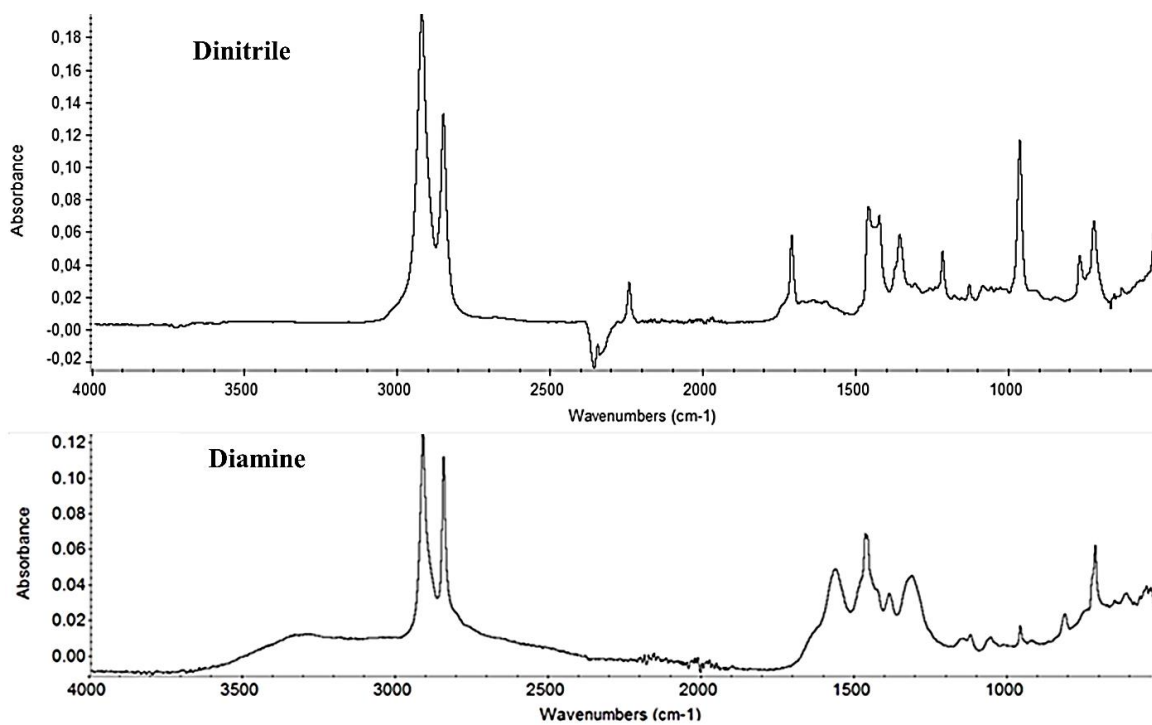


Figure S13: FTIR-ATR spectrum of UndC20-dinitrile and UndC20-diamine

Decanediamine: Decanediamine was obtained as a white powder. conversion = 93%. Y=51%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 2.64 (t, 4H), 1.40 (m, 4H and 2.NH $_2$), 1.25 (m, 12H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 42.30 ($\text{CH}_2\text{-NH}_2$), 29.72-27.04 (CH_2). IR (cm^{-1}): 3330, 3257, 3163, 2919, 2848.

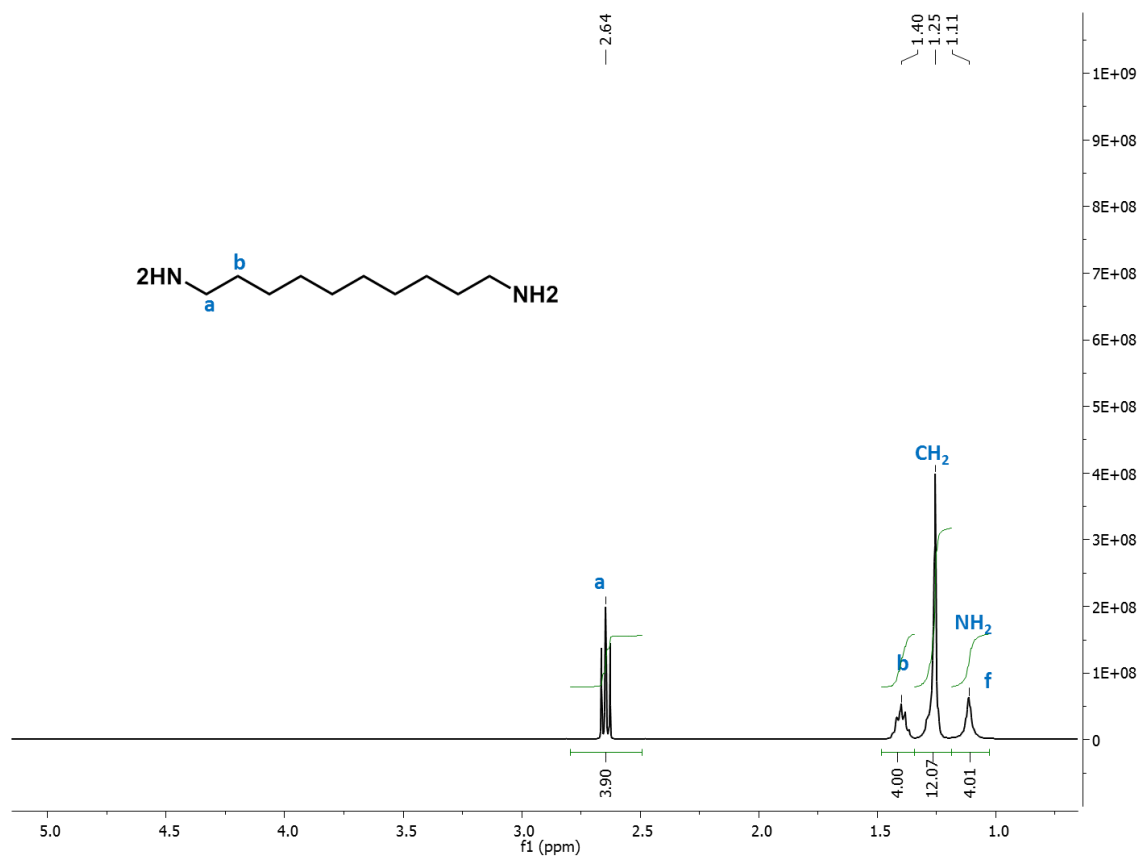


Figure S14: ^1H NMR spectra in CDCl_3 of decanedinitrile in CDCl_3

UndC20-diamine: UndC20-diamine was obtained as a white/yellow powder. Y=71%. ^1H NMR (CD_3OD , 25 °C, 400 MHz) δ (ppm): 2.72 (t, 4H), 1.53 (m, 4H), 1.29 (m, 32H). ^{13}C NMR

(CD₃OD, 25 °C, 100 MHz) δ (ppm): 41.96 (CH₂-NH₂), 32.06-27.86 (CH₂). IR (cm⁻¹): 3299, 2916, 2850).

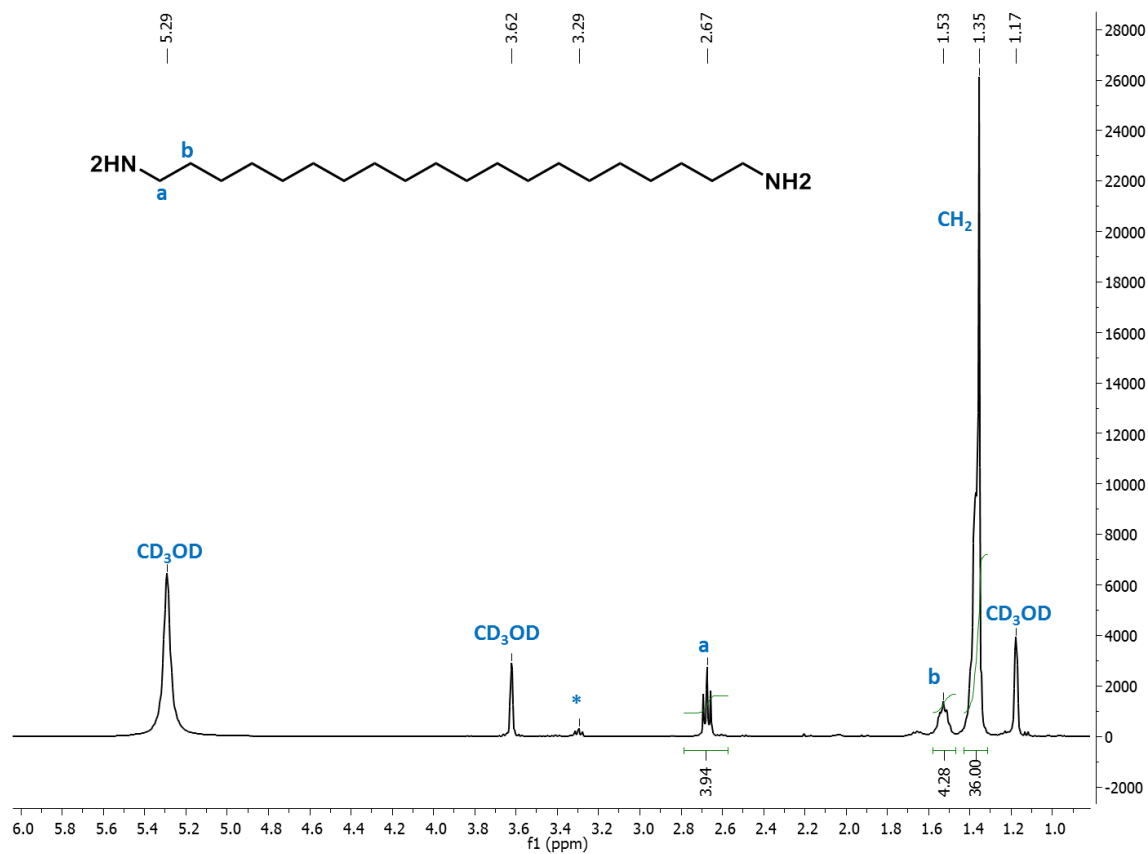
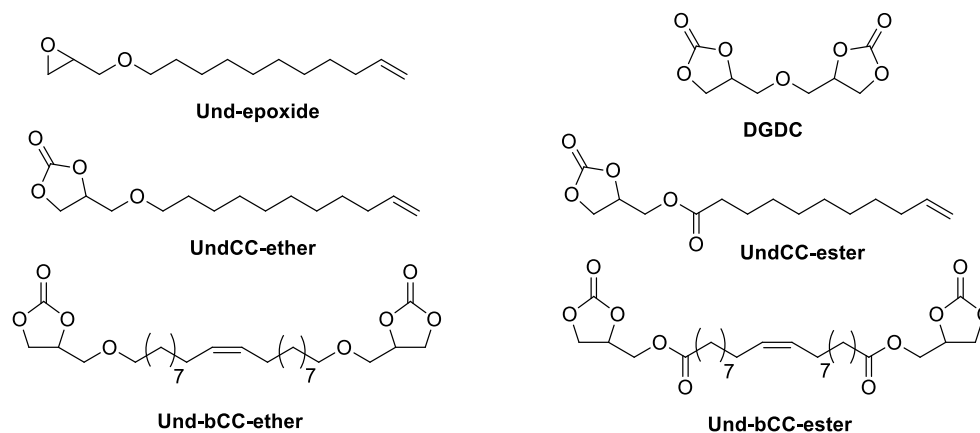


Figure S15: ¹H NMR spectra in CD₃OD of UndC20-diamine. (*) Impurities

Cyclic Carbonate synthesis



Scheme S2: Abbreviations and structures of epoxides, mono-cyclic carbonates, bis-cyclic carbonates

UndCC-ether synthesis : (i) In a round-bottom flask, 10-undecen-1-ol (10 g, 58.7 mmol) was stirred with epichlorohydrin (54.35g, 587 mmol, 10 eq) and TBABr (1.89 g, 5.87 mmol, 0.1 eq) at room temperature for 30 min. NaOH was added via a 50% concentrated aqueous solution (70 mL, 0.88 mol, 15eq). After 24 hours of reaction at room temperature, the mixture reaction was diluted with 4 volumes of distilled water. The aqueous phase was extracted 3 times with 100 mL of ethyl acetate. The organic phase was then washed twice with 75 mL of water, dried over anhydrous magnesium sulfate, filtered and the remaining epichlorohydrin was removed on rotary evaporator. The ^1H NMR spectrum revealed a conversion of 72%. The compound **Und-epoxide** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 88:12) and obtained as a viscous transparent liquid. Yield=58%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.80 (m, 1H), 4.96 (m, 2H), 3.70 and 3.37 (dd, 2H), 3.49 (m, 2H), 3.14(m, 1H),

2.78 and 2.59 (t, 2H), 2.02 (m, 2H), 1.58-1.28 (m, 16H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 137.9 ($\text{CH}=\text{CH}_2$), 113.2 ($\text{CH}=\text{CH}_2$), 70.7 ($\text{OCH}_2\text{-CH}_2$), 70.4 ($\text{CH}_2\text{O-CH}_2\text{CH}_2$), 49.9 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 43.4 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 32.7 ($\text{CH}_2\text{-CH=CH}_2$), 28.7-25.1 (CH_2). (ii) The **Und-epoxide** (7.72g, 34.2 mmol) was first pre-mixed with the TBABr (0.24 g, 0.7 mmol, 3 wt%) in 5 mL of acetone. Then the mixture was placed in a reactor and heated up at 80°C . Once the temperature got stabilized, CO_2 was slowly introduced into the reactor until 50 bars. After 3 days, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The mixture was reconcentrated on rotary evaporator. The ^1H NMR of the final mixture revealed a conversion of 98%. The **UndCC-ether** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 81:19), and obtained as a viscous transparent liquid. Yield=82%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.72 (m, 1H), 4.90 (m, 2H), 4.73 (m, 1H), 4.42-4.32 (t, 2H), 3.58 (m, 2H), 3.41 (t, 2H), 1.98 (dd, 2H), 1.48 (m, 2H), 1.21 (m, 14H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 155.3 (OCO), 138.8 ($\text{CH}=\text{CH}_2$); 114.2 ($\text{CH}=\text{CH}_2$), 74.7 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 71.8 ($\text{CH}_2\text{O-CH}_2\text{-CH}_2$), 68.8 ($\text{CH-CH}_2\text{O-CH}_2$), 66.1 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 33.6 ($\text{CH}_2\text{-CH=CH}_2$), 28.7-26.2 (CH_2). IR (cm^{-1}): 3075, 2979, 2928, 2850, 1760.

Und-bCC-ether synthesis: Into a round-bottom flask, the **UndCC-ether** (5g, 18.5 mmol) and 1st generation Grubbs catalyst (76.2 mg, 0.093 mmol, 0.5% mol) were charged under nitrogen. The contents were vigorously stirred at 35°C for 24 hours. The equilibrium was driven thank to the removal under vacuum of the produced ethylene. The product was then purified with flash chromatography using a mixture of dichloromethane and methanol as eluent (100:0 to 95:5).

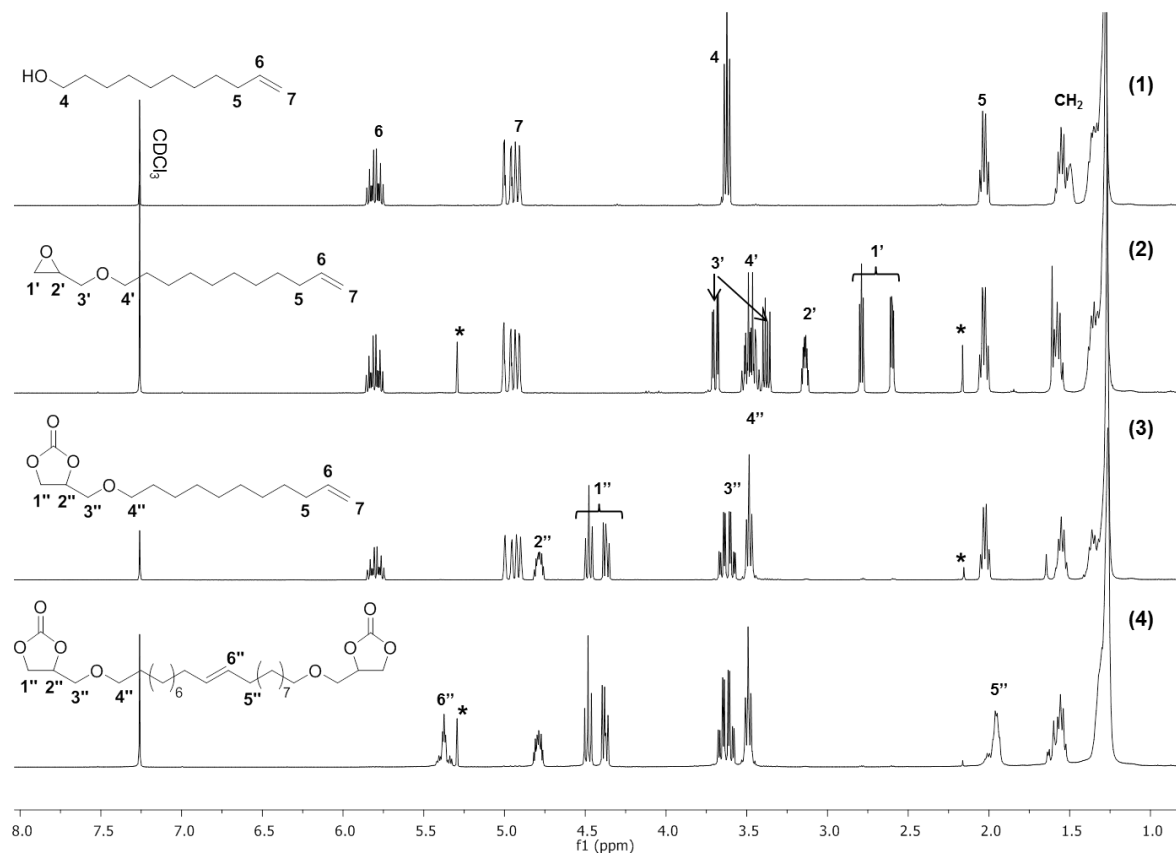


Figure S16: Stacked ^1H NMR spectra of (1) undecen-1-ol, (2) Und-epoxide, (3) UndCC-ether and (4) Und-bCC-ether (All analyses were performed in CDCl_3 .) (* : residual solvents)

Und-bCC-ether was obtained as a grey solid. Yield=53%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.38 (m, 2H), 4.80 (m, 2H), 4.49 and 4.39 (t, 4H), 3.64 (m, 4H), 3.50 (t, 4H), 1.97 (m, 4H), 1.56 (m, 6H), 1.27 (m, 26H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 154.5 (OCOO), 130.9 ($\text{CH}=\text{CH}$), 75.2 ($\text{CH}_2-\underline{\text{CH}}-\text{CH}_2\text{O}$), 72.2 ($\text{CH}-\text{CH}_2-\text{O}\underline{\text{CH}}_2$), 69.6 ($\text{CH}_2-\text{CH}-\underline{\text{CH}}_2\text{O}$), 66.3 ($\underline{\text{CH}}_2\text{CH}-\text{CH}_2\text{O}$), 32.7 ($\underline{\text{CH}}_2-\text{CH}=\text{CH}$), 29.9-26.1 (CH_2). IR (cm^{-1}): 2923, 2850, 1792, 1141. $T_m=54^\circ\text{C}$.

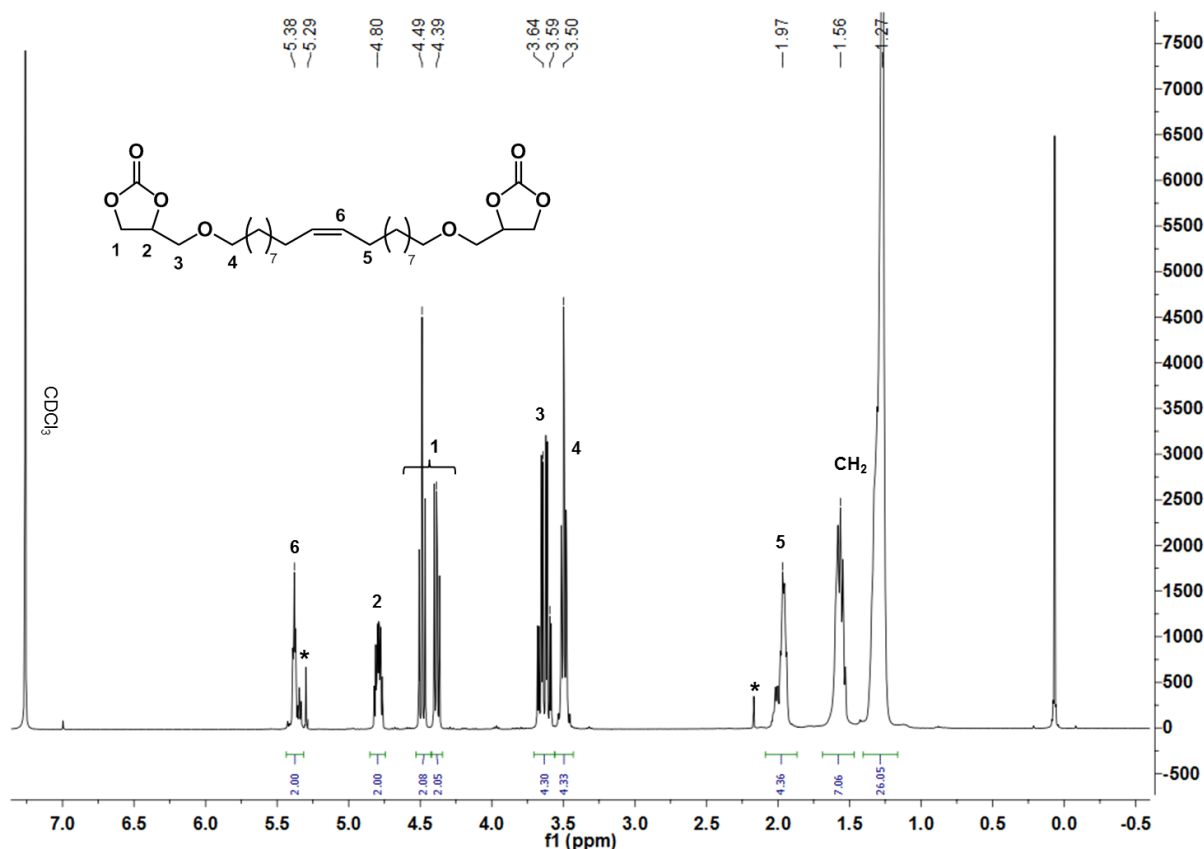


Figure S17: ^1H NMR spectrum of Und-bCC-ether (Analysis performed in CDCl_3 .)

(* : residual solvents)

Und-bCC-ester synthesis: Into a round-bottom flask equipped with a mineral oil bubbler, the **UndCC-ester** (3g, 5.6 mmol) was mixed with 2 mL of dichloromethane. 1st generation Grubbs catalyst (42.6 mg, 0.028 mmol, 0.5% mol) was then charged under nitrogen. The contents were vigorously stirred at room temperature for 24 hours. The ^1H NMR revealed of conversion of 80%. The product was purified by recrystallization in 10 mL of cold dichloromethane (-80°) followed by a filtration and a washing with 30 mL of dichloromethane. **Und-bCC-ester** was obtained as a grey powder. Yield=44%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.36 (m, 2H), 4.92 (m, 2H), 4.55 and 4.32 (t, 4H), 4.28 (t, 4H), 2.35 (t, 4H), 1.95 (m, 4H), 1.63-1.28

(24H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 173.0 ($\text{CH}_2\text{-OCO-CH}_2$), 154.5 (OCOO), 130.5 (CH=CH), 73.7 ($\text{CH-CH}_2\text{-OCO}$), 65.7 ($\text{CH}_2\text{-CH-CH}_2\text{-OCO}$), 62.7 ($\text{CH-CH}_2\text{-OCO}$), 34.2 ($\text{OCO-CH}_2\text{-CH}_2$), 32.0 ($\text{CH}_2\text{-CH=CH}$), 29.4-28.5 (CH_2), 24.5 ($\text{OCO-CH}_2\text{-CH}_2$). IR (cm^{-1}): 2917, 2850, 1784, 1736. $T_m=111^\circ\text{C}$.

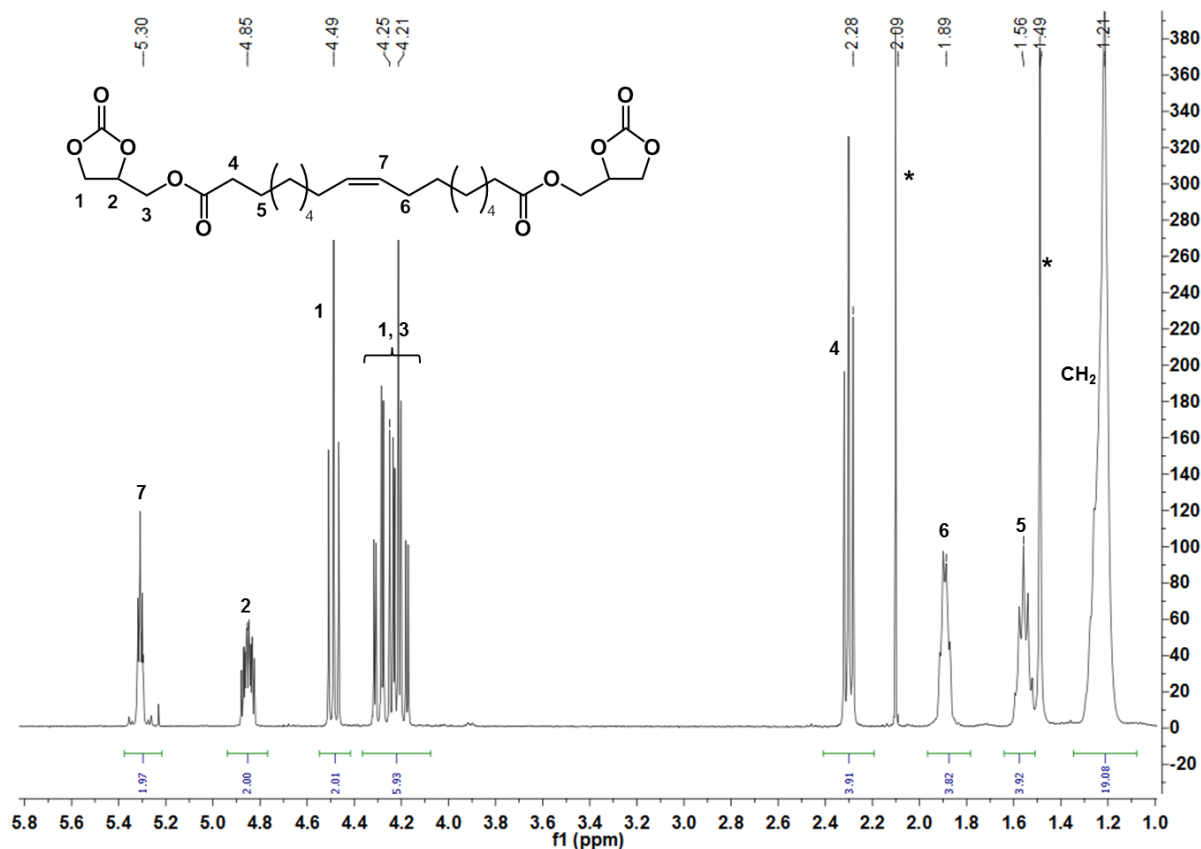


Figure S18: ^1H NMR spectrum of Und-bCC-ether (Analysis performed in CDCl_3 .)

(* : residual solvents)

DGDC synthesis : Into a round-bottom flask equipped with a refrigerant, 1 eq of dried diglycerol (5 g, 30 mmol) was mixed with 15 eq of dimethyl carbonate (40.7 g, 452 mmol) and heated up to 90°C . 0.05 eq of La_2O_3 (0.49 g, 1.5 mmol) was then inserted and the contents were

vigorously stirred at 120°C for 48 hours. The mixture reaction was then filtered and reconcentrated. The product was purified by recrystallization in cold methanol. The ^1H NMR (DMSO, 25°C, 400 MHz) δ (ppm): 4.93 (m, 2H), 4.54 and 4.23 (t, 4H), 3.76 and 3.68 (m, 4H). ^{13}C NMR (DMSO, 25°C, 100 MHz) δ (ppm): 154.9 (OCOO), 74.8 ($\text{CH}_2\text{-}\underline{\text{CH}}\text{-CH}_2\text{O}$), 69.8 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 66.1 ($\underline{\text{CH}}_2\text{CH-CH}_2\text{O}$), IR (cm^{-1}): 2928, 1773, 1176. $T_m=73^\circ\text{C}$.

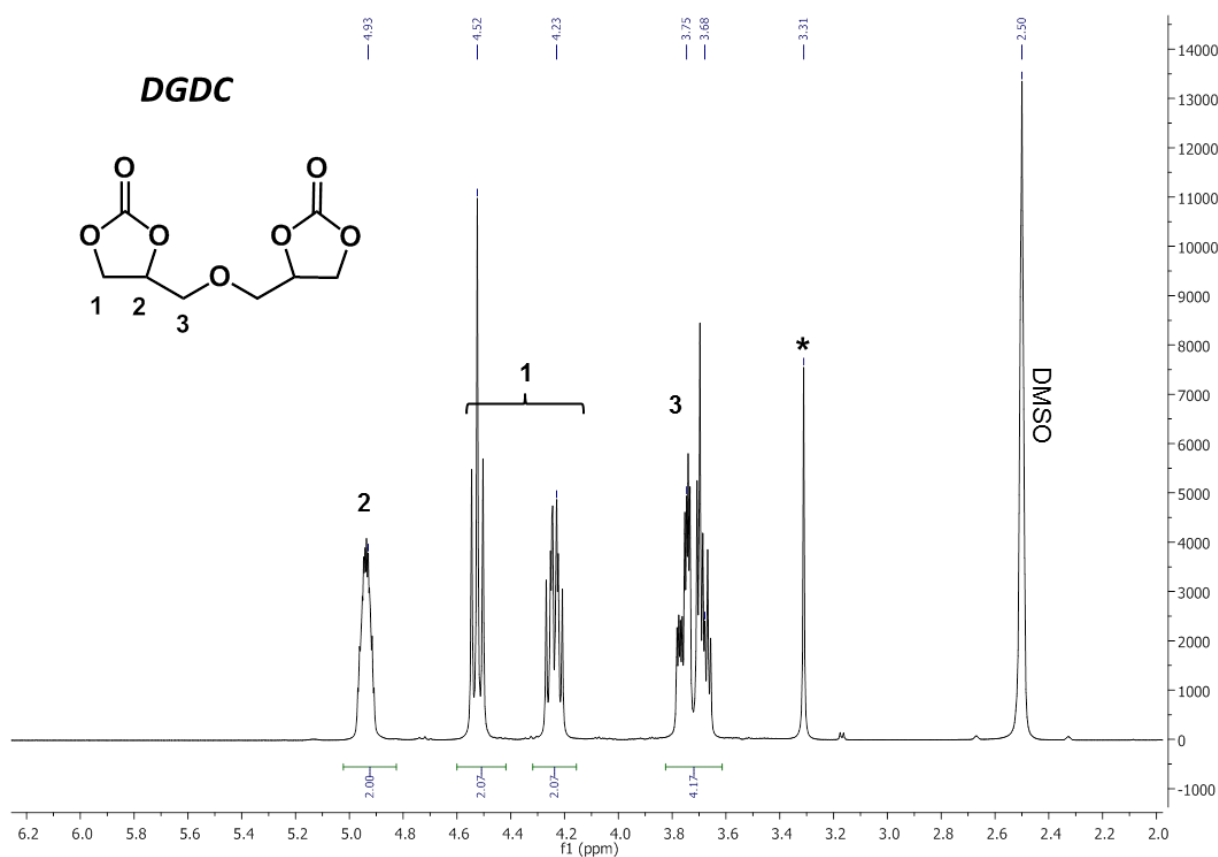


Figure S19: ^1H NMR spectrum of DGDC (Analysis performed in DMSO.)

(* : residual solvents)

PHUs synthesis

DMF at 1mol.L⁻¹ at 70°C under nitrogen atmosphere without any catalyst.

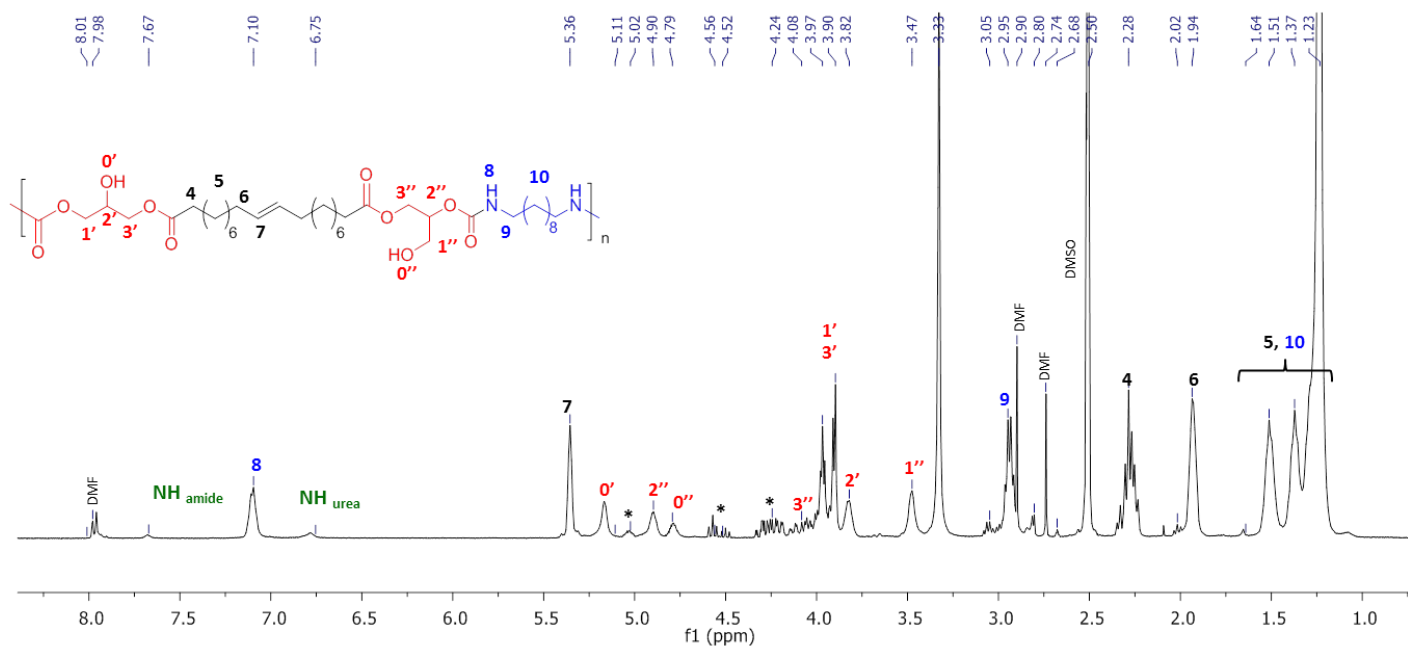


Figure S20: ^1H NMR spectrum of PHU1 from 10 DA and Und-bCC-ester. Analysis performed in DMSO) (* : residual monomers)

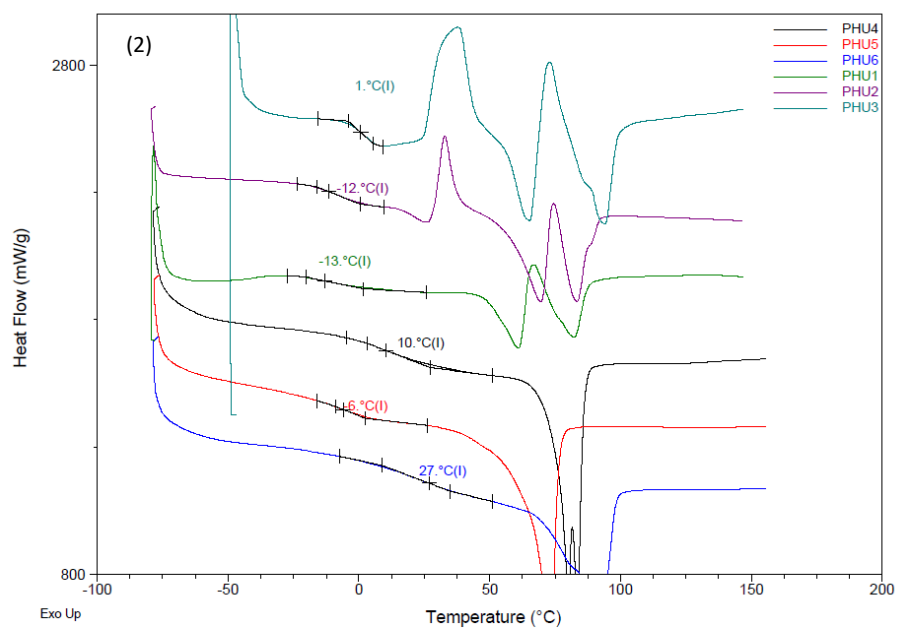
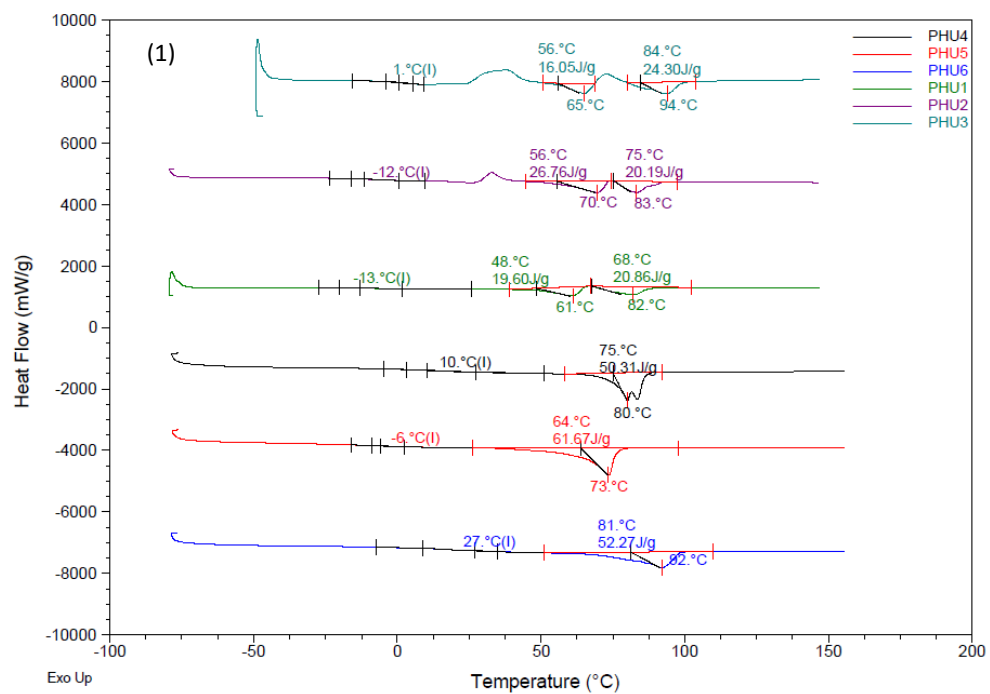


Figure S21: DSC profiles of PHU1 to PHU6 (1) with T_g, melting enthalpies and temperatures and (2) zoomed on T_g values.