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ARTICLE

Synthesis and characterization of new fully bio-based poly(acylhydrazone) vanillin vitrimers

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New acylhydrazone vitrimeric-type materials have been studied. These materials can be efficiently relaxed, without the addition of an external catalyst, through an exchange process that has been confirmed as imine metathesis, which differs from the previously reported transimination process in linear polymers. This is the first article that develops vitrimers with high T_g and easy relaxation based on poly(acylhydrazone)s. These materials have been prepared by condensing stoichiometric amounts of glycidyl vanillin and aliphatic dihydrazides of different chain lengths. The curing reaction takes advantage of the different reactivity of formyl and glycidyl groups and proceeds in two different steps: a first condensation of the formyl group of vanillin with dihydrazide monomers at low temperature followed by reaction of the remaining hydrazides with the epoxide, which requires temperatures above 150 °C. The complete disappearance of the initial reactive groups has been confirmed by FTIR spectroscopy. The thermomechanical characteristics have been evaluated by DMTA, obtaining T_gs above 100 °C for the materials prepared which present excellent vitrimeric characteristics with very short relaxation times. By using model compounds, we were able to demonstrate that imine metathesis is the responsible for the exchange process. The thermal stability of these materials has been rated by TGA. Poly(acylhydrazone) materials showed good recycling and self-healing abilities and the possibility to be hydrolyzed in acidic medium.

Introduction

Thermosets are a class of polymeric materials that have many advantages due to their excellent mechanical properties, dimensional stability and chemical resistance, which make them very interesting materials for several applications such as coatings,[1] adhesives,[2] electronics,[3] *etc*. However, their permanent cross-linked structure hampers them to be recycled or reprocessed once cured which can lead to serious environmental issues at the end of their lifetime due to the waste of resources. For this reason, the development of reshapable or recyclable materials has arisen as a promising solution to solve these issues.[4]

Covalent adaptable networks (CANs) behave as permanent cross-linked thermosets at a certain temperature but they have the ability to flow and therefore, to be reshaped or self-repaired when are subjected to an external stimulus such as heat or light due to the exchangeable bonds in their structure.[5] Since in 2011 Leibler and co-workers reported a specific type of CANs, named as vitrimers,[4] the interest in this research field has increased exponentially. Vitrimers have the particularity of exchanging bonds, while flowing, without losing their network integrity, meaning that the bonds rupture and formation occur in a concerted manner without any intermediate state but always keeping constant the crosslinking density.[6] Many examples of vitrimers have been reported regarding different types of reactions such as transesterification,[7-9] transcarbamoylation,[10,11] disulfide interchange,[12] olefin metathesis,[13] imine-amine exchange,[14-16] among many others.

In this last group of exchange reactions, acylhydrazone groups take part in a significant way. These groups are formed by a reversible condensation reaction of aldehydes or ketones with hydrazides, which spontaneously form the carbon-nitrogen double bond and water that can be eliminated, being a driving force in order to shift the equilibrium.[17] In 2004, Lehn and co-workers reported the ability of acylhydrazone dynamic bonds to produce dynamers.[18,19] They stated that the reversibility of these linear polymers relies on the imine group of the acylhydrazone while the amide group provides hydrogen bonding like in polyamides. They not only successfully reported the synthesis of different poly(acylhydrazone)s by mixing different dihydrazides with dialdehydes but also the exchangeable behaviour of these bonds upon heating by combining the synthesized poly(acylhydrazone)s with structurally different aldehydes or dihydrazides. They also reported the synthesis of dual dynamic acylhydrazones, with reversible covalent bonds and dynamic non-covalent hydrogen bonding interactions, by condensation of aromatic dialdehydes connected by a siloxane backbone, which imparts softness, with carbohydrazide. These materials revealed excellent self-healing properties.[20]

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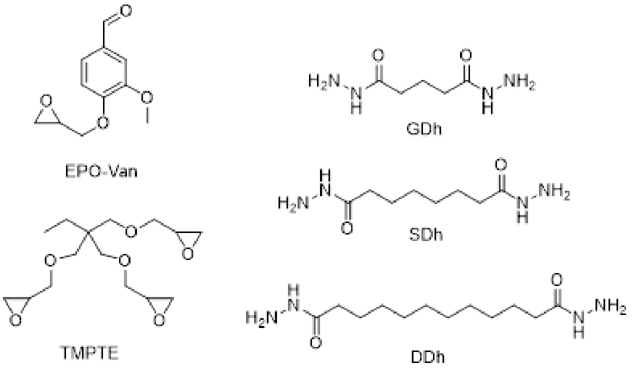
Later on, more studies of this type of materials were performed by Chen et al.[21] who reported a strategy to construct new reversible polymers by mixing poly(ethylene oxide) with terminal acylhydrazine end groups with trialdehydes to form dynamic gels in mild conditions. The gels formed could also be transformed into their starting monomers and re-form the gel again by increasing or decreasing the acidity of the water solution, respectively. In addition, these materials revealed interesting self-healing properties without using any external help. Afterwards, Deng et al.[22] went deeper in the topic and they successfully developed new dynamic hydrogels combining acylhydrazone and disulfide bonds in the same system. The obtained materials were able to repair themselves under hydrolytic acidic and basic conditions through acylhydrazones exchange or disulfide exchange reactions, respectively. It must be pointed out, that the exchange reaction is based in these cases on the hydrolysis and re-forming of the imine moiety and it is not related to any vitrimeric-type relaxation process.

To reach a high bond-exchange rate, many vitrimers required the addition of catalysts, being some of them toxic and easily leachable which makes difficult their reprocessing or reshaping. Consequently, there is a growing interest in new vitrimeric materials that do not require any type of catalyst.[23] Among them, vinylogous urethanes,[24] boroxines,[25] and imines[26] may be mentioned. As reported, the exchange reaction of poly(acylhydrazones) does not require the addition of any catalyst[18,21] and therefore the study and development of this type of vitrimers could be highly interesting.

In recent years, products derived from renewable resources have attracted a huge interest in materials science to reduce the use of petrochemical compounds as well as to find greener synthetic routes to avoid the depletion of fossil resources. The researchers have focused their attention on the synthesis of vitrimeric materials based on compounds derived from biomass such as catechol,[27] eugenol,[28,29] or vanillin.[30,31] In particular, vanillin (4-hydroxy-3-methoxybenzaldehyde) is not only one of the most important aromatic compounds used in food, beverages, perfumes and pharmaceuticals, but it is also very interesting as a feedstock for the development of materials due to its phenolic and aldehyde groups that can be further modified to get the suitable functionality. Moreover, the rigid structure due to the aromatic ring provides high thermal and mechanical properties to the obtained materials.[32]



Scheme 1. Monomers used in the preparation of the poly(acylhydrazone) vitrimers

Taking all of this into account, in the present article, we report the synthesis and characterization of a series of new bio-based poly(acylhydrazone) vitrimers. Three different dihydrazides derived from biobased glutaric, suberic and dodecandioic acids[33] were obtained in high yields via two-step synthesis as well as the glycidyl derivative of vanillin (EPO-Van) (see Scheme 1). Since dihydrazides are latent curing agents for epoxy resins and only react on heating above 150 °C,[34] they can condense specifically at lower temperatures with the aldehyde groups of EPO-Van, releasing water and leaving epoxy groups unreacted. At higher temperatures, the remaining dihydrazide groups in the mixture can react with epoxides leading to three-dimensional networks. To facilitate the processing and to improve the thermomechanical characteristics of the cross-linked materials, trimethylolpropane triglycidylether (TMPTE) has been added to the curing formulation. Stoichiometric mixtures of EPO-Van, dihydrazides (Dh) and TMPTE were used to get the final materials.

The completion of the reaction was evaluated by FTIR spectroscopy. The vitrimers obtained were characterized by thermogravimetric analysis to know the range of thermal stability, and by thermomechanical analysis to evaluate their relaxation behaviour. Poly(acylhydrazone)s were able to be recycled under determined conditions and proved to kept similar mechanical properties. Materials also revealed self-healing properties, which make them very interesting in many fields of application. As far as we know, this is the first time that the preparation and characterization of similar highly cross-linked poly(acylhydrazone) vitrimers have been reported and that imine metathesis is the exchange process responsible of the relaxation.

Experimental

Materials

(±)-Epichlorohydrin (ECH, ≥99%), triethylbenzylammonium chloride (TEBAC, 99%), glutaric acid (GA, 99%), suberic acid (SA, 98%), dodecandioic acid (DA, 99%), trimethylolpropane triglycidyl ether (TMPTE), benzaldehyde (B) and octanoic acid (OA) were purchased from Sigma Aldrich. Vanillin (Van, 99%) and hydrazine hydrate (HzH, 80%) were obtained from ACROS Organics. Ethyl acetate (EtOAc), 1,2-dichlorobenzene (DCB) and N,N-dimethylformamide (DMF) were purchased from VWR chemicals. Sodium hydroxide (granulated, NaOH) and absolute ethanol (EtOH) were purchased from Scharlau and sulphuric acid (H_2SO_4, ≥95 %) from Fisher Chemical.

Characterization techniques

^{1}H NMR and ^{13}C NMR spectra were registered in a Varian VNMR-S400 NMR spectrometer. $CDCl_3$ and DMSO-d_6 were used as the solvents. All chemical shifts are quoted on the δ scale in parts per million (ppm) using residual protonated solvent as internal standard (^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; ^{13}C NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm). Gas chromatography (GC) tests were performed in a gas chromatograph 6890 Series with automatic liquid sampler HP7683 Series and mass spectrometer 5973 (Hewlett Packard). The column used was an analytical column HP-5MS (30 m x 0.25 mm x 0.25 µm) (Agilent Technologies). Samples were dissolved in acetonitrile (GC grade) and 1µL was injected with a split ratio of 50:1 in a constant flow of 1.0 mL/min. DSC analyses were carried out on a Mettler DSC3+ instrument calibrated using indium (heat flow calibration) and zinc (temperature calibration) standards. Samples of approximately 8-10 mg were placed in aluminium pans with pierced lids and analysed in N_2 atmosphere with a gas flow of 50 cm^3/min. Dynamic studies between 30 and 250 °C at a heating rate of 10 °C/min were performed to determine the melting points. A Jasco FT/IR-680 Plus spectrometer equipped with an attenuated total reflection accessory (ATR) (Golden Gate, Specac Ltd. Teknokroma) was used to register the FTIR spectra of the mixtures after the curing procedure. Real-time spectra were registered in the wavenumber range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 20 scans. The disappearance of the characteristic absorbance peaks of epoxy and aldehyde groups at 915 cm^{-1} and 1715 cm^{-1}, respectively, as well as the appearance of the peaks corresponding to O-H at 3300 cm^{-1} and C=N at 1680 cm^{-1} were used to confirm the completion of the reactions. The thermal stability of the materials was evaluated using a Mettler Toledo TGA 2 thermobalance. Cured samples, weighting around 10 mg, were degraded between 30 and 600 °C at a heating rate of 10 °C/min in N_2 atmosphere with a flow of 50 cm^3/min. The thermomechanical properties were studied using a DMA Q800 (TA Instruments) equipped with a film tension clamp. Prismatic rectangular samples with dimensions around 30 x 5 x1.5 mm^3 were analysed from -25 °C to 200 °C at 1 Hz, 0.1% strain at a heating rate of 2 °C/min. Tensile stress-relaxation tests were conducted in the same instrument using the film tension clamp on samples with the same dimensions as previously defined. To obtain the activation energy (E_a) for the materials, the samples were firstly equilibrated at the relaxation temperature for 5 min and a constant strain of 1% was applied, measuring the consequent stress level as a function of time. The materials were tested only once at one temperature. The relaxation-stress $\sigma(t)$ was normalized by the initial stress σ_0, and the relaxation times (τ) were determined as the time necessary to relax $0.37\cdot\sigma_0$, i.e., ($\sigma = 1/e\cdot\sigma_0$). With the relaxation times obtained at each temperature, the activation energy values, E_a, were calculated by using an Arrhenius-type equation:

$$ln(\tau) = \frac{E_a}{RT} - \ln A \qquad (1)$$

where τ is the time needed to attain a given stress-relaxation value ($0.37\sigma_0$), A is the pre-exponential factor and R is the gas constant. From the Arrhenius relation, the topology freezing temperature (T_v) was obtained as the temperature at which the material reaches a viscosity of 10^{12} Pa·s. Using Maxwell's relation and E' determined from DMTA (assuming E' being relatively invariant in the rubbery state), τ^* was determined to be around 10^5 s in our systems. The Arrhenius relationship was then extrapolated to the corresponding value of τ^* to determine T_v in each sample.

The recycled samples were obtained by cutting the cross-linked polymers and hot-pressing in a Specac Atlas manual 15 T hydraulic press at 9.25 MPa into an aluminium mould, at 190 °C for 2 h. Recycled samples were die-cut in the same dimensions from the new film obtained, and tested again in the DMA analyser for their mechanical characterization at the same conditions previously described. Dissolution experiments of final materials were performed by the following procedure: pieces of poly (acylhydrazone) of 50-100 mg, weighted before the experiment, were placed in a 50 mL round bottom flask equipped with a magnetic stirrer. The flask was filled with 1,2-dichlorobenzene (DCB) closed and heated at 150 °C during 8 h. Then, the flask was cooled down to room temperature. The polymer sample was dried under reduced pressure, at 100 °C during 12 h. After cooling down to room temperature, the samples were weighted and the gel fraction was calculated. The chemical degradation of the materials was investigated by keeping a sample of the cured material in a 2 M HCl solution/THF 8:2 mixture for 24 h at 70 °C in a stirred flask in a thermostatized bad. To perform self-healing tests, samples were scratched and broken using a doctor blade, and subsequently heated in an oven at 190 °C for several hours exploring from time to time the evolution of the scratch by taking pictures with a Digital Microscope Leica DMS1000.

General procedure for the poly(acylhydrazone)s preparation

Poly(acylhydrazone) materials were prepared by dissolving mixtures of EPO-Van/TMPTE in a molar percentage 3:1 with the corresponding dihydrazide in stoichiometric epoxy/aldehyde/NH_2 proportions in the minimum amount of DMF to solubilize the mixture. Then, the liquid formulations were magnetically stirred increasing the temperature up to 160 °C until most of the solvent was evaporated, and the mixture was poured into a Petri plate where it was maintained at the same temperature until a gel is formed. Obtained gels were cut into small pieces and placed in a vacuum oven for 2 h at 150 °C to ensure the elimination of the solvent and then the material was grinded to small particles. They were evenly spread in round aluminium moulds protected with an adhesive sheet of Teflon and thermally cured in the manual hydraulic hot press under 9.25 MPa at 160 °C for 1 h to obtain solid films with uniform thickness that were die-cut to get specimens of 30 x 5 x 1.5 mm^3.

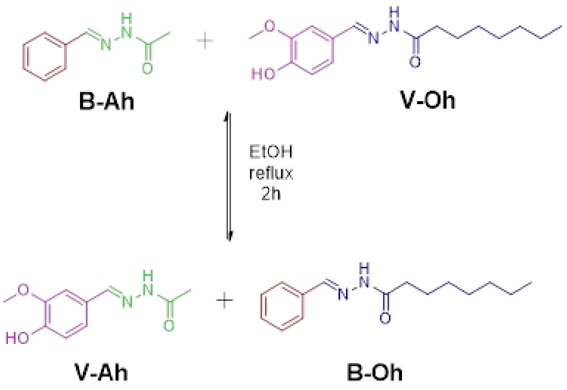
Results and discussion

Synthesis of starting compounds

Dihydrazides were prepared via two-step procedure including the synthesis of intermediate esters via Fischer esterification of dicarboxylic acids and further reaction with hydrazine hydrate. For the present work, glutaric (GA), suberic (SA) and dodecandioic (DDA) acids were selected as starting materials in order to achieve a series of bio-based dihydrazides (GDh, SDh and DDh, respectively) with different chain lengths. All the products synthesized were analyzed by NMR spectroscopy (Figures S1-S6). The disappearance of the characteristic proton signals of ethyl ester groups was observed, while newly formed hydrazide group signals appeared at around 8.9 and 4.1 ppm. ^{13}C NMR spectra also confirmed the purity of the compounds by the disappearance of the signals corresponding to the ethyl ester and the appearance of the carbonyl signal of hydrazide at around 171.1 ppm in all cases. Experimental details are presented in the SI. EPO-Van was synthesized by reacting vanillin with a large excess of epichlorohydrin, using NaOH as a base and TEBAC as a phase transfer catalyst maintained for 1.5 h at 80 °C. The procedure led to the formation of the expected glycidyl product as a yellowish-white solid in high yield. Its structure was confirmed by ^{1}H-NMR spectroscopy by the appearance of the signals corresponding to the glycidyl group between 4.5 and 2.6 ppm while the formyl proton signal remained unaltered (Figure S7). ^{13}C NMR spectrum showed the signals of the carbons corresponding to the glycidyl group between 44.0 and 70.0 ppm (Figure S8).

Demonstration of the exchange reaction

To confirm the possibility of exchange reaction between acylhydrazone groups four different acylhydrazones combining two aldehydes, benzaldehyde (B) and vanillin (V), with two synthesized hydrazides, octanoic hydrazide (Oh) and acetyl hydrazide (Ah) were synthesized. Thus, B-Oh, B-Ah, V-Oh and V-Ah acylhydrazones were successfully prepared in high yield and purity (see Figures S9-S20). Then, B-Ah and V-Oh were mixed, dissolved in absolute EtOH and maintained at reflux during 2 h. After that, the solvent was eliminated at the rotary evaporator obtaining a viscous oil. Scheme 2 depicts the structure of the model compounds and the structure of the rearranged compounds expected. The mixture after heating and each synthesized compound were investigated by gas chromatography coupled to a mass spectrometer detector by injecting samples dissolved in acetonitrile. The chromatograms are represented in Figure 1. As we can see in Figure 1b, after reaction of B-Ah and V-Oh, two new compounds that could be identified as the combination of both products (V-Ah and B-Oh) appeared in the chromatogram, concluding that the exchange reaction has taken place, which may indicate that the exchange mechanism occurs.



Scheme 2. Model compounds synthesized and structure of the compounds formed by the exchange reaction.

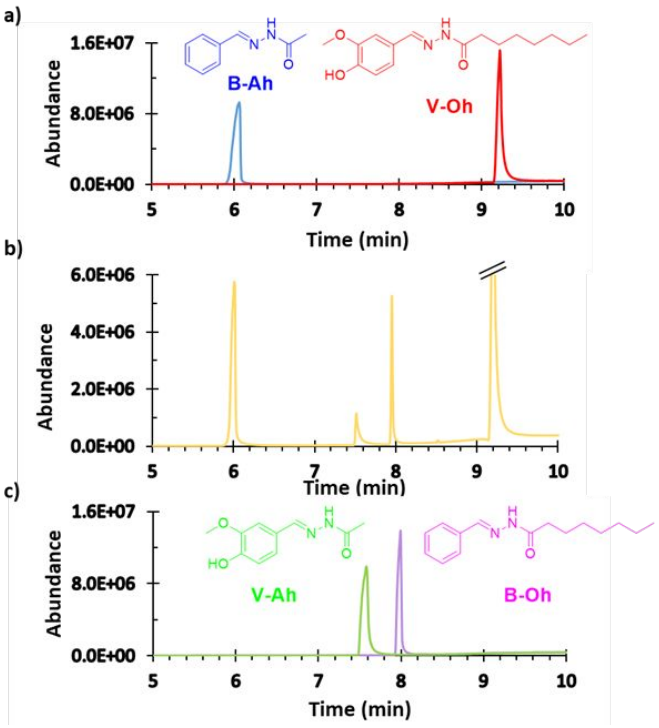
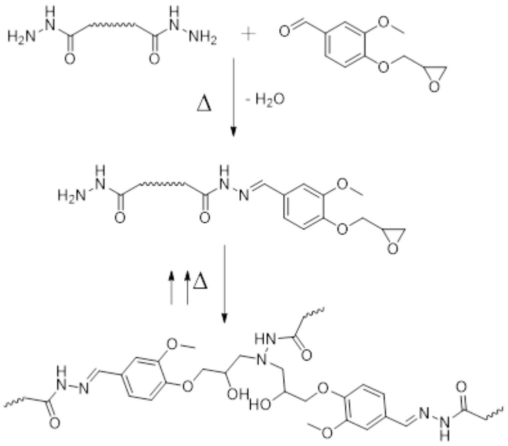


Figure 1. GC chromatograms of a mixture of pure B-Ah and V-Oh (a), after the reaction of B-Ah and V-Oh (b) and a mixture of pure V-Ah and B-Oh (c)

Moreover, it is possible to observe that no traces of any other compound referring to the hydrolysis of the acylhydrazone or any aldehyde are present in the chromatogram backing up the hypothesis of a concerted mechanism. Lehn and co-workers[18] explained that acylhydrazone groups were able to perform exchangeable reactions by the imine bond. They tested the exchange reaction by adding an excess of aldehydes or dihydrazides, which suggested that a transimination reaction was taking place on the acylhydrazone groups. In our case, as we added stoichiometric amounts of each pure acylhydrazone compound, an imine metathesis must be the only exchange reaction that occurs.

Study of the curing procedure

Synthesized dihydrazides and EPO-Van monomers were used in the preparation of sustainable vanillin-based vitrimers containing acylhydrazone dynamic covalent bonds. With the aim to achieve higher flexibility of the final networks, formulations were supplemented by aliphatic trimethylolpropane triglycidyl ether (TMPTE). DMF liquid mixtures of EPO-Van/TMPTE/Dh in stoichiometric epoxy/aldehyde/NH_2 proportions were cured as described in the experimental section. Cross-linked materials were successfully obtained as thin red films with high transparency. Since EPO-Van has epoxy and aldehyde reactive groups, in this curing system, before epoxy-amine reaction, aldehydes react with -NH_2 of



Scheme 3. Synthetic steps in the preparation of poly(acylhydrazone) thermosets

dihydrazides due to the latent character of these compounds as epoxy curing agents (Scheme 3).[34] This is the key point of the curing because otherwise the dihydrazides could react either with epoxides or with aldehydes. It should be noted that whereas epoxides firstly react with -NH_2, leaving free -NHR groups, aldehydes can only react with -NH_2 groups. Therefore, if epoxides were to react in the early stages of the curing process, a stoichiometric imbalance would occur that would leave unreacted aldehydes that would lead to materials with a lower degree of crosslinking and a lower proportion of exchangeable acylhydrazone moieties.

FTIR spectra were registered to determine if the complete curing has been reached forming a poly(acylhydrazone) network. Figure 2 shows as an example, the FTIR spectra of the initial monomers used and one of the final materials. As we can see, the bands corresponding to the aldehyde group at 1680 cm^{-1} and to the epoxy groups at 910 cm^{-1} have completely disappeared indicating the consumption of these groups. Moreover, the carbonyl dihydrazide band at 1626 cm^{-1} has vanished but at the same time, the broad absorption bands of the stretching of O-H and N-H at 3300 cm^{-1} visibly increase. In addition, in the spectrum of the final material, a peak at 1640 cm^{-1} corresponding to the imine of the formed acylhydrazone structure can be noticed. From these changes, it is evident that epoxy hydrazide and condensation reactions have been completed and subsequently a fully cured material has been achieved.

Thermal characterization of the materials

The thermal stability of the vitrimers was evaluated by thermogravimetry (TGA). Fig. 3 shows the TGA curves and their derivatives for the materials prepared and Table 1 collects the most significant thermogravimetric data. Whereas the degradation curves (Figure 3a) are quite similar for the three materials, the shapes of the first derivative (Figure 3b) present some differences.

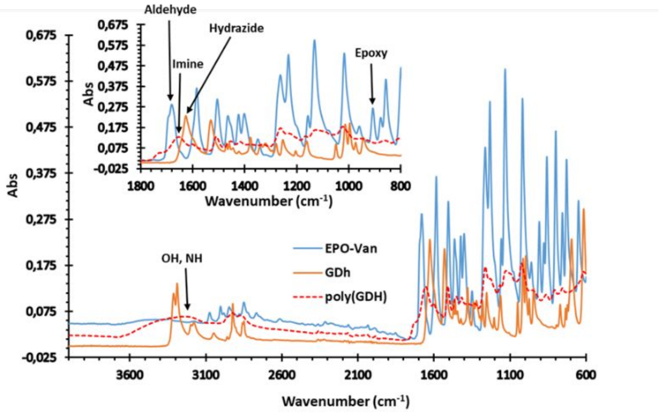


Figure 2. FTIR spectra of the initial monomers, EPO-Van (blue) and glutaric dihydrazide (GDh) (orange) and of the final material (polyGDH) (red).

As we can see, the degradation of poly(GDH) material has a broad peak with the maximum at 335 °C meaning that the breakage of different bonds and elimination of fragments take place simultaneously. However, in the case of poly(SDH) and poly(DDH) two different peaks can be observed, with the second one shifted to higher temperature on increasing the length of the aliphatic moiety in the network structure, which could be related to the breakage of acylhydrazone bonds.

The values in Table 1 reveal that these materials have a relatively high thermal stability, as the samples lose 2% of weight at temperatures above 234 °C. This high resistance to heat degradation is likely conferred by a high cross-linking density and aromatic content in the network structure. The temperatures, around 220 °C, at which the weight loss is only 1% accounts for the capability of safe recycling at temperatures below 200 °C. The presence of nitrogen and aromatic rings in the network structure leads to high char yields that decrease with the length of the aliphatic moiety of the dihydrazide monomer. The thermomechanical characteristics of the poly(acylhydrazone)s have been determined by DMTA analysis. Figure 4 shows the *tan δ* curves as well as the storage moduli (*E'*) as a function of temperature for all the materials and the corresponding data extracted from these studies are summarized in Table 2.

Table 1. Thermogravimetric data of all the poly(acylhydrazone)s prepared.

Sample	$T_{1\%}$[a] (°C)	$T_{2\%}$[b] (°C)	T_{max}[c] (°C)	Char yield [d] (%)
poly(GDH)	220.6	236.5	335.0	33.6
poly(SDH)	220.0	235.1	309.2/389.7	31.0
poly(DDH)	218.4	234.2	314.8/429.7	23.5

[a] Temperature of 1% of weight loss. [b] Temperature of 2% of weight loss. [c] Temperature at the maximum rate of degradation. [d] Char residue at 600 °C.

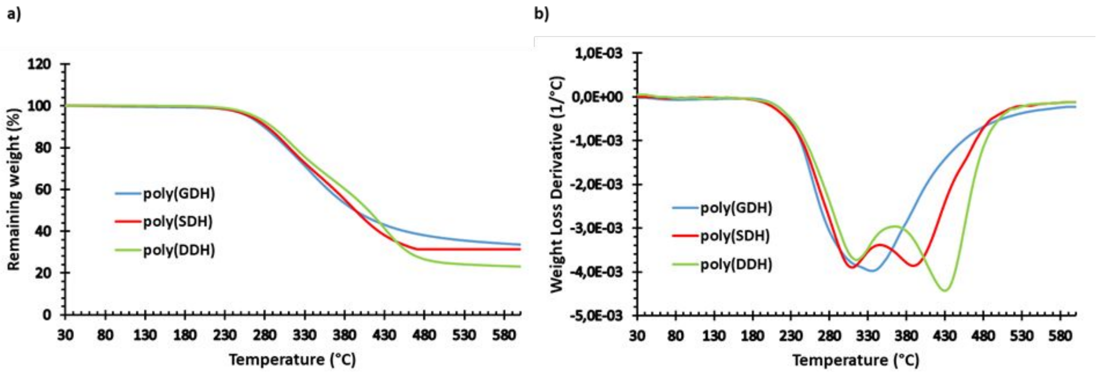


Figure 3. a) Thermogravimetric curves and b) DTG curves of the poly(acylhydrazone) materials

Table 2. Thermomechanical data of all the virgin and recycled poly(acylhydrazone)s prepared.

Sample	Virgin			Recycled		
	$T_{tan\ \delta}$ [a] (°C)	E'_{glassy} [b] (MPa)	$E'_{rubbery}$ [c] (MPa)	$T_{tan\ \delta}$ [a] (°C)	E'_{glassy} [b] (MPa)	$E'_{rubbery}$ [c] (MPa)
poly(GDH)	134.2	3637	12.8	133.2	3508	8.5
poly(SDH)	113.1	2656	11.4	112.8	1738	7.6
poly(DDH)	100.0	2149	9.9	98.9	1629	3.9

[a] Temperature at the maximum of tan δ peak at 1 Hz. [b] Glassy storage modulus at 25 °C determined by DMTA. [c] Rubbery storage modulus at Tg+50 °C determined by DMTA.

As it is observed, thermally cured poly(acylhydrazone) materials exhibit high T_g values (taken from the maximum of *tan δ* curves) reaching 134 °C. This can be essentially associated with the low network mobility arising from the presence of stiff benzene rings, the high functionality of dihydrazides that leads to high degree of cross-linking and the presence of hydrogen bonds. As expected, as the dihydrazide chain length increases, the T_g of the final material decreases due to the higher mobility and flexibility of the final material in accordance with the more open network structure.

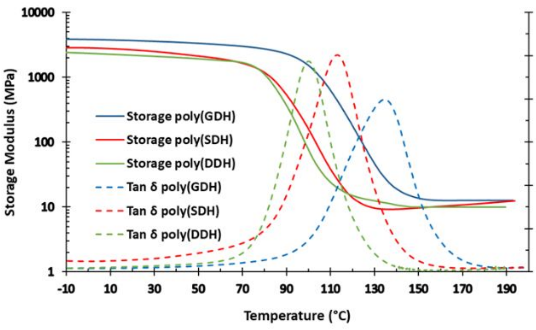


Figure 4. Evolution of *tan δ* and storage modulus with temperature of all poly(acylhydrazone) materials

Similarly, the rubbery modulus is reduced due to the longer distances between cross-links and the glassy modulus decreases indicating a less rigid network. Besides, single peaks in *tan δ* and well-defined transitions are indicative of homogenous network structures in all materials with a slightly broader network relaxation for poly(GDH).

To confirm the vitrimeric nature of the networked poly(acylhydrazone)s, the time and temperature dependent relaxation behaviour was investigated. With this purpose, stress relaxation tests were performed by DMTA and the results are shown in Figure 5 and in Table 3. The stress relaxation curves reveal that these materials are capable to rapidly relax stress, by reaching the reference relaxation value of 63% (σ/σ_0 = 0.37) in less than one minute at 185 °C for poly(GDH), in 1.5 min at 170 °C for poly(SDH) and in almost 3 min for poly(DDH) at 160 °C. From these experiments, it can also be calculated the time for almost total relaxation of the networks, which is reached in nearly 3.5, 5 and 10 min, respectively at 190 °C.

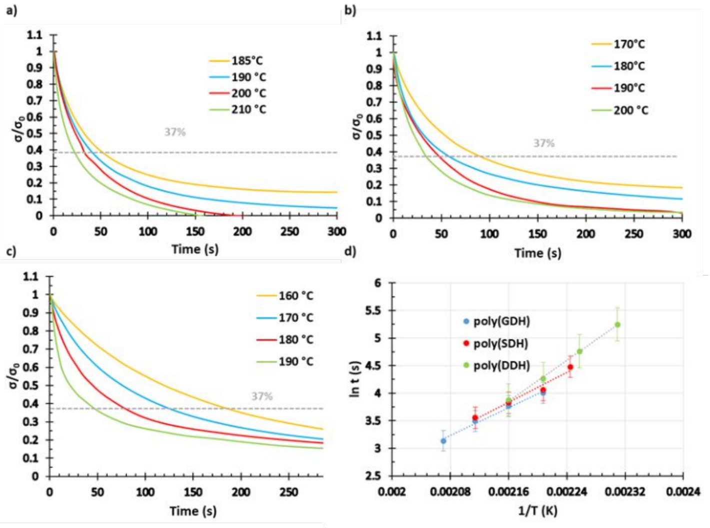


Figure 5. Normalized stress relaxation plots as a function of time at various temperatures during 300 s for poly(GDH) (a), poly(SDH) (b) and poly(DDH) (c) samples and Arrhenius plot of relaxation times against temperature for the different poly(acylhydrazones).

As we can see in Table 3, the time to reach the relaxed state of σ/σ_0 = 0.37 at 190 °C for the different materials slightly increases (from 43 to 48 s) on increasing the chain length of the dihydrazide. Although the material becomes more flexible, the distance between acylhydrazone moieties increases and their proportion in the network structure decreases, which makes the imine metathesis more difficult to occur.

Table 3. Relaxation times, topology freezing temperature, activation energy and adjusting parameters for the Arrhenius equation.

Material	$\tau_{0.37}$ [a] (s)	$\tau_{100\%}$ [a] (s)	T_v (°C)	E_a (kJ/mol)	*lnA* (s)	r^2
poly(GDH)	43	200	25.2	52.5	9.90	0.99
poly(SDH)	46	300	36.8	61.4	12.45	0.98
poly(DDH)	48	600	61.7	77.2	16.20	0.99

[a] Time to reach a value of σ/σ_0 = 0.37 at 190 °C. [b] Time to reach total relaxation at 190 °C.

It is well-known that vitrimeric materials follow an Arrhenius-type temperature dependence, when the viscosity is controlled by the chemical exchange reaction, leading to a temperature-viscosity relationship like inorganic silica materials.[37] According to that, to characterize the vitrimeric behaviour of poly(acylhydrazone) materials, the time required for the initial stress to decrease to e^{-1} (σ/σ_0 = 0.37) at different temperatures was obtained from the corresponding relaxation curves (Figures 5a-c). The Arrhenius-type equation derived when fitted to the data allows to calculate the activation energy (E_a) of the topological rearrangement (see Figure 5d and Table 3) for all the different vitrimers. Looking at the values presented in Table 3, it can be pointed out that the longer the chain in the poly(acylhydrazone)s prepared, the higher the activation energy, indicating a greater dependence with the temperature of the exchange kinetics of the network. Furthermore, when the relaxation temperature is increased, a significant acceleration of the relaxation process was observed in all cases. It is worthy to remind that these materials are prepared in absence of catalyst, which gives more importance to these low relaxation times.

It is also important to highlight the E_a values presented in Table 3, which are much lower than other reported values for different vitrimeric groups like polyester vitrimers[8] (90 kJ/mol), poly(urethane)s[35] (130.5 and 183.7 kJ/mol) or poly(thiourethane)s (72-102 kJ/mol)[36] without the need of adding catalyst.

The topology freezing temperatures defined as the temperature at which the transition from viscoelastic solid to viscoelastic liquid occurs, were also calculated by extrapolation of stress-relaxation experiments. This temperature accounts for the temperature below which chemical exchanges are negligible, and it can be used to qualitatively compare bond-exchanges capabilities in vitrimers. For these poly(acylhydrazone)s, the T_vs calculated by extrapolation are much lower than their T_gs and in this case the more important parameter to determine the relaxation behaviour is T_g, since below this temperature the network structure is frozen, without enough mobility to experiment the exchange reaction between imine units. Thus, in this case, T_vs are only hypothetical values, since below T_g no exchange reactions can occur being the network fixed due to the lack of segmental motions associated with T_g. Once T_g is overpassed and when the exchange kinetics change from a diffusion-controlled process to an exchange reaction-controlled process, the exchange reaction proceeds very fast.[37,38] Nevertheless, the fact that T_vs are lower than T_gs does not affect the applicability as thermosets at room temperature due to the high values of the T_g obtained for these materials, in contrast to what happens in others vitrimers where the creep resistance behaviour could be compromised.[40,41]

Recycling process

To investigate the recyclability of the cross-linked poly (acylhydrazone)s prepared, all the materials were grinded into small pieces and hot-pressed in the manual press under 9.25 MPa, in an aluminium mould. The temperature of the recycling process was set to 190 °C ensuring in all cases that the network rearrangement is taking place without any degradation. Figure 6 shows the pictures taken from the original, grinded and reprocessed samples where it can be clearly seen that the original and the recycled films preserve good transparency. To evaluate the recyclability of the poly(acylhydrazone)s, the thermomechanical behaviour of the original and recycled samples was compared. Results from the evolution of the storage modulus and *tan δ* curves with temperature, extracted from the DMTA analysis, are presented in Figure 7a-c and the most representative data presented in Table 2. From the values presented in Table 2 and the curves in Figure 7, it can be appreciated that recycled materials exhibit similar *tan δ* curves as the original ones, with almost the same $T_{tan\ \delta}$. Recycling slightly decreases the rubbery modulus, probably due to the break of covalent bonds during grinding, which reduces the cross-linking density. From these results, we can conclude that materials can be recycled without significant changes in their thermomechanical properties.

Solubility and chemical degradability

To further confirm the thermosetting nature of these materials, they were tried to dissolve in dichlorobenzene (DCB).

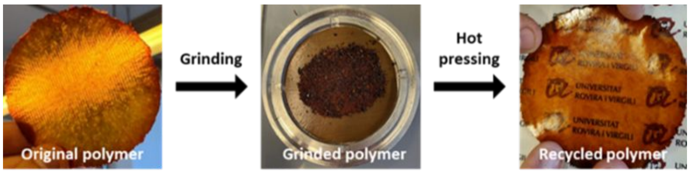


Figure 6. Photographs of the original, grinded and recycled samples of the poly(acylhydrazone)s.

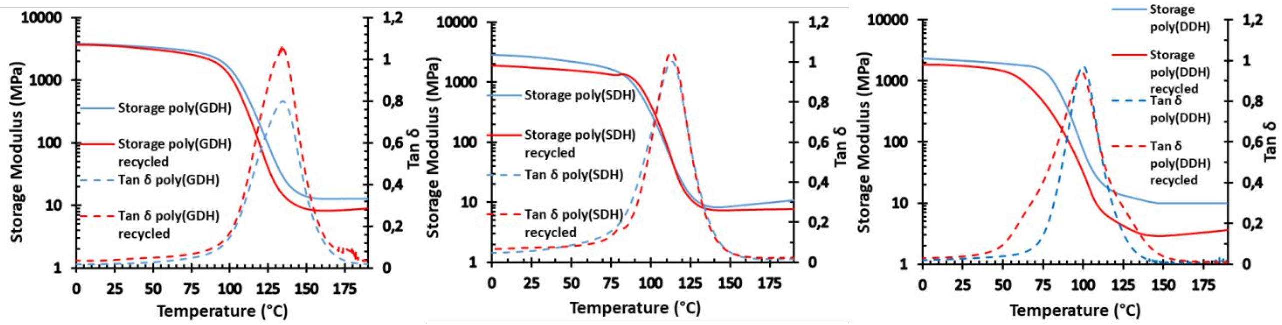


Figure 7. Dependence of tan δ and storage modulus versus temperature before and after recycling of poly(GDH) (a), poly(SDH) (b) and poly(DDH) (c).

Poly(acylhydrazone) samples were weighted and put at 150 °C for 12 h in DCB and dried in the vacuum oven for 12 h After that, the remaining sample was re-weighted noticing that in all cases the gel content of the materials was above 98.5% revealing a high resistance to be solubilized and their thermosetting character. Finally, we also attempt to perform a chemical degradation of the materials by leaving the poly(acylhydrazone) materials in a 2 M HCl solution/THF 8:2 mixture for 24 h at 70 °C. After that, the solution presented a high turbidity, so the supernatant solid was filtered in a Büchner funnel, washed 3 times with water, and dried in a vacuum oven at 80 °C during 6 h. We could prove by NMR spectroscopy that this solid corresponded to the starting dicarboxylic acid of the dihydrazide used, since the hydrolysis of the amide bond can occur in acidic media leading to the original diacid. In this way, starting acids can be recovered, although any quantitative recovery has been implemented. However, the reaction of the glycidyl group of the vanillin with NH_2 of dihydrazides prevents the fully recovery of the starting materials.

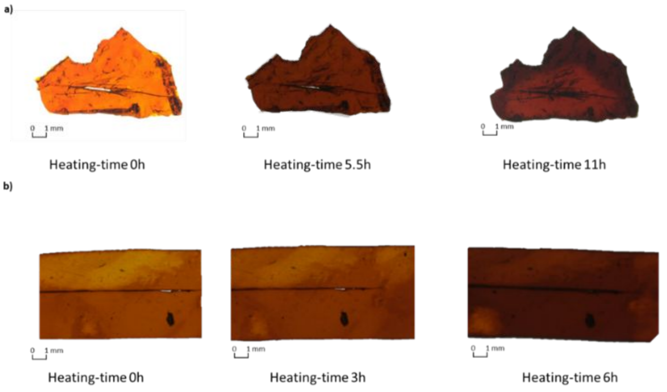


Figure 8. Pictures of the scratch made with a doctor blade on a poly (GDH) (a) and poly(DDH) samples maintained in an oven at 190 °C at different times.

Self-healing

It is already known that materials containing acylhydrazone groups can have self-healing properties.[42-44] Encouraged by these previous studies, we decided to test qualitatively if the poly(acylhydrazone) materials prepared in this work presented self-healing properties.

To do this, two samples of poly(GDH) and poly(DDH) were scratched and broken using a doctor blade, and subsequently heated in an oven at 190 °C for several hours exploring from time to time the evolution of the scratch by microscopy. The pictures taken of those materials at different times are shown in Figure 8.

As it can be clearly seen, the scratch was completely healed (even in the broken part) after 11 h in case of poly(GDH) and in only 6 h in poly(DDH), showing promising self-healing characteristics. The lower T_g of poly(DDH) facilitates the self-healing behaviour, but we have demonstrated that even poly(acylhydrazones) with T_gs higher than 100 °C can be self-healed in a short time.

Conclusions

Fully renewable poly(acylhydrazone) materials have been easily prepared by condensation of glycidyl vanillin and dihydrazides. The addition of trimethylolpropane triglycidyl ether to the formulation facilitates the preparation of materials with good mechanical characteristics. The latent character of the reaction of hydrazide groups with epoxies, which occurs at high temperatures, facilitates the complete condensation of hydrazide groups with the formyl group of the vanillin. The disappearance of all reactive groups was confirmed by FTIR spectroscopy.

The materials obtained show excellent vitrimeric characteristics, without the need of any type of catalyst, with very short relaxation times (between 200 and 600 s for almost a total relaxation), that increase on increasing the length of the dihydrazide used as monomer. The thermomechanical and relaxation behaviour of these vitrimers can be tailored only by changing the dihydrazide structure, obtaining very low values of activation energy in all of them.

The reactive process behind the vitrimeric exchange is based on the imine metathesis, since the materials prepared do not have any excess of hydrazide or aldehyde groups. The occurrence of imine metathesis has been proved by means of gas chromatography coupled to mass spectroscopy using acylhydrazone model compounds synthesized for this purpose. This is the first time that this type of highly cross-linked materials has shown its vitrimeric characteristics.

Poly(acylhydrazone) materials have also demonstrated good recycling and self-healing abilities at temperatures not much higher than their T_g. These compounds can be chemically degraded in acidic medium, which allows to recover the corresponding starting diacids.

Author Contributions

Adrià Roig conducted some experiments and wrote the original draft. Aina Petrauskaitė performed the synthesis of the monomers and materials. Xavier Ramis validated the studies and developed some methodologies. Silvia De la Flor and Àngels Serra made conceptualization and supervised the work. Silvia De la Flor, Xavier Ramis and Àngels Serra reviewed and edited the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supporting information

Additional experimental procedures and structural characterization of monomers and model compounds.

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Prof. Filip Du Prez
Ghent University
Belgium

Tarragona, December 23th2021

Dear Prof. Du Prez:

Hereby, I submit our manuscript entitled "Synthesis and characterization of new fully bio-based poly(acylhydrazone) vanillin vitrimers" to be considered for publication in Polymer Chemistry.

In recent times, great attention has been paid to the development of new vitrimeric materials that can rapidly relax the stresses without the addition of an external catalyst. On the other hand, the use of bio-based monomers to prepare materials with good characteristics is today one of the key points as the alternative to the petrol-based ones.

The manuscript is of great interest, from our point of view, since it is the first article that develops vitrimers with high T_g and easy relaxation based on poly(acylhydrazone)s without the need of any catalyst. Using model compounds, we have proved that the chemical exchange mechanism responsible for the stress relaxation is the imine metathesis, which differs from the mechanism reported by Prof. J. M. Lehn in dynamers. The materials are prepared by condensation reaction of glycidyl vanillin with dihydrazides of different chain length, derived of bio-based diacids. Th synthetic procedure takes advantage of the latent character of the reaction of hydrazide-epoxy reaction. The prepared materials have shown good potentiality for recycling, self-healing and chemical degradation.

We thank you for considering our submission.

I take this opportunity to wish you a happy Christmas and New Year holidays and a year 2022 better than the present

Looking forward to your reply, I send my regards.

Prof. Angels Serra

Supplementary Information for

Synthesis and characterization of new fully bio-based poly(acylhydrazone) vanillin vitrimers

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- Total number of pages: 17
- Total number of figures: 20

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1. Additional experimental procedures

Synthesis of epoxy compound from Vanillin (EPO-Van)

EPO-Van was prepared following a previously reported procedure.[1] Vanillin (7.6 g, 50.0 mmol), TEBAC (1.1 g, 5.0 mmol) and ECH (46.3 g, 500.0 mmol) were added to a 250 mL three-necked round bottom flask under magnetic stirring. The mixture was first stirred for 1.5 h at 80 °C and then cooled down to room temperature. A mixed solution of TEBAC (1.1 g, 5.0 mmol) and NaOH (8 g, 200.0 mmol, 5 M) was added and stirred for 30 min at room temperature. After the reaction was completed, ethyl acetate (EtOAc) and distilled water were poured and stirred, and the aqueous phase extracted three times with EtOAc. The organic phase was collected, dried over anhydrous $MgSO_4$ and concentrated in a vacuum rotary evaporator. The residual amount of ECH was eliminated by mixing the product with EtOAc and evaporating it under vacuum multiple times. The monoglycidyl compound was obtained as a yellowish-white solid with a 93 % of yield (9.7 g). M.p. 97.0 °C.

^{1}H NMR ($CDCl_3$, δ in ppm): 9.84 (s, 1H), 7.43 (d, 1H), 7.41 (s, 1H), 7.02 (d, 1H), 4.37 (dd, 1H), 4.08 (dd, 1H), 3.92 (s, 3H), 3.40 (m, 1H), 2.92 (dd, 1H) and 2.77 (dd, 1H). ^{13}C NMR ($CDCl_3$, δ in ppm): 190.99, 153.51, 150.07, 130.78, 126.61, 112.37, 109.61, 70.05, 56.13, 50.00 and 44.86.

Synthesis of diesters of dicarboxylic acids

Diesters were synthesized following a previous procedure reported by Mills *et al.*[2] In a 250 mL three-necked round bottom flask equipped with a magnetic stirrer, 15 g of the corresponding diacid were dissolved in absolute EtOH (150 mL). Then, concentrated H_2SO_4 (80 µL, 1.3 mmol) was added and the mixture was heated up to 80 °C and kept it during 4 h under reflux. The mixture was cooled down to room temperature and concentrated. The concentrate was dissolved in EtOAc (150 mL) and the organic fraction was washed three times, once with a saturated solution of $NaHCO_3$, once with water and finally with brine, dried over anhydrous $MgSO_4$ and concentrated by rotary evaporator to yield the corresponding products as colorless oils.

Diethyl glutarate (DEG) was obtained in 85% yield. ^{1}H NMR (CDCl$_3$, δ in ppm): 4.11 (q, 4H), 2.34 (t, 4H), 1.93 (m, 2H) and 1.23 (t, 6H). ^{13}C NMR (CDCl$_3$, δ in ppm): 173.06, 60.47, 33.45, 20.28 and 14.32.

Diethyl suberate (DES) was obtained in 89% yield. ^{1}H NMR (CDCl$_3$, δ in ppm): 4.10 (q, 4H), 2.26 (t, 4H), 1.60 (m, 4H), 1.32 (m, 4H) and 1.23 (t, 6H). ^{13}C NMR (CDCl$_3$, δ in ppm): 173.83, 60.28, 34.36, 28.84, 24.86 and 14.34.

Diethyl dodecanoate (DEDD) was obtained in 90% yield. ^{1}H NMR (CDCl$_3$, δ in ppm): 4.10 (q, 4H), 2.26 (t, 4H), 1.59 (m, 4H), 1.26 (m, 12H) and 1.23 (t, 6H). ^{13}C NMR (CDCl$_3$, δ in ppm): 174.05, 60.25, 34.47, 29.46, 29.32, 29.22, 25.06 and 14.35.

Synthesis of dihydrazides

Dihydrazides were synthesized following a previous procedure reported by Tomuta *et al.*[3] In a 100 mL three-necked round bottom flask provided with a magnetic stirrer, 5.6 g of the corresponding diester were added and dissolved in 25 mL of absolute EtOH. Then, hydrazine hydrate (80%, 6.7 g, 107.6 mmol) was added drop by drop. When the addition was complete, the mixture was kept 6 h under reflux. The precipitate formed was filtered through a Büchner funnel, washed twice with cold EtOH and dried in the vacuum oven at 60 ˚C during 4 h. All products were obtained as white powders with yields higher than 90%.

Glutaric dihydrazide (GDh): ^{1}H NMR (DMSO-d_6, δ in ppm): 8.91 (s, 2H), 4.13 (s, 4H), 1.99 (t, 4H) and 1.69 (m, 2H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171.17, 32.87 and 21.48. M.p. 181.8 ˚C.

Suberic dihydrazide (SDh): ^{1}H NMR (DMSO-d_6, δ in ppm): 8.89 (s, 2H), 4.13 (s, 4H), 1.98 (t, 4H), 1.46 (m, 4H) and 1.20 (m, 4H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171.58, 33.37, 28.39 and 25.10. M.p. 188.1 ˚C.

Dodecandioic dihydrazide (DDh): ^{1}H NMR (DMSO-d_6, δ in ppm): 8.91 (s, 2H), 4.13 (s, 4H), 1.98 (t, 4H), 1.46 (m, 4H) and 1.22 (m, 12H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171.64, 33.42, 28.92, 28.77, 28.67 and 25.24. M.p. 192.0 ˚C.

Synthesis of model compounds

Ethyl octanoate was synthesized following the same procedure previously described.[2]

^{1}H NMR ($CDCl_3$, δ in ppm): 4.11 (q, 2H), 2.27 (t, 2H), 1.60 (m, 2H), 1.27 (m, 8H), 1.24 (t, 3H) and 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 173.83, 60.13, 34.39, 31.66, 29.10, 28.93, 24.99, 22.59, 14.25 and 14.05.

Hydrazides were synthesized following the same procedure previously described for the synthesis of dihydrazide compounds.[3]

Acetyl hydrazide (Ah): ^{1}H NMR (DMSO-d_6, δ in ppm): 8.94 (s, 1H), 4.13 (s, 2H) and 1.74 (s, 3H). ^{13}C NMR (DMSO-d_6, δ in ppm): 168.75 and 20.55. M.p. 60.1 °C.

Octanoyl hydrazide (Oh): ^{1}H NMR (DMSO-d_6, δ in ppm): 8.91 (s, 1H), 4.14 (s, 2H), 1.98 (t, 2H), 1.46 (m, 2H), 1.23 (m, 8H) and 0.85 (t, 3H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171. 65, 33.44, 31.22, 28.65, 28.48, 25.27, 22.11 and 14.00. M.p. 88.3 °C.

Acylhydrazones were synthesized by the following procedure. In a 50 mL three-necked round bottom flask provided with a magnetic stirrer 10 mmol of aldehyde (vanillin or benzaldehyde) were added. After that, 10 mL of EtOH were poured followed by the addition of 10 mmol of the corresponding hydrazide (acetyl hydrazide or octanoyl hydrazide). When the addition was completed, the mixture was kept under reflux during 12 h. The precipitate formed was filtered through a Büchner funnel, washed twice with cold EtOH and dried in the vacuum oven at 60 ˚C during 4 h. All products were obtained as white powders with yields higher than 90%.

Benzylideneacetohydrazide (B-Ah) mixture of *cis*/*trans* isomers 1:2: ^{1}H NMR (DMSO-d_6, δ in ppm): 11.37 (s, 1H), 11.25 (s, 1H_a), 8.14 (s, 1H), 7.98 (s, 1H_a), 7.66 (m, 2H, 2H_a), 7.41 (m, 3H, 3H_a), 2.20 (s, 3H_a) and 1.95 (s, 3H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171.99, 165.61, 145.57, 142.51, 134.38, 134.31, 129.88, 129.67, 128.81, 128.79, 126.97, 126.64, 21.66 and 20.27.

(4-Hydroxy-3-methoxybenzylidene)octanehydrazide (V-Oh) mixture of *cis*/*trans* isomers 1:1: ^{1}H NMR (DMSO-d_6, δ in ppm): 11.15 (s, 1H), 11.04 (s, 1H_a), 9.49 (s, 1H, 1H_a), 8.02 (s, 1H), 7.85 (s, 1H_a), 7.24 (d, 1H), 7.20 (d, 1H_a), 7.03 (dd, 1H), 7.02 (dd, 1H_a), 6.81 (d, 1H), 6.80 (d, 1H_a), 3.80 (s, 3H), 3.79 (s, 3H_a), 2.58 (t, 2H_a), 2.15 (t, 2H), 1.56 (m, 2H, 2H_a), 1.26 (m, 8H, 8H_a), 0.86 (t, 3H_a) and 0.84 (t, 3H). ^{13}C NMR (DMSO-d_6, δ in ppm): 174.16, 168.30, 148.79, 148.51, 148.00, 147.93, 146.25, 142.78, 125.83, 125.77, 121.89, 120.83, 115.56, 115.38, 109.31, 108.83, 55.52, 55.46, 34.23, 31.92, 31.22, 28.82, 28.66, 28.51, 28.50, 25.17, 24.41, 22.11 and 13.98.

(4-Hydroxy-3-methoxybenzylidene)acetohydrazide (V-Ah) mixture of *cis*/*trans* isomers 2:3: ^{1}H NMR (DMSO-d_6, δ in ppm): 11.17 (s, 1H), 11.07 (s, 1H_a), 8.01 (s, 1H), 7.86 (s, 1H_a), 7.24 (d, 1H), 7.21 (d, 1H_a), 7.04 (d, 1H), 7.02 (d, 1H_a), 6.81 (d, 1H_a), 6.79 (d, 1H), 3.81 (s, 3H), 3.80 (s, 3H_a), 2.17 (s, 3H_a) and 1.91 (s, 3H). ^{13}C NMR (DMSO-d_6, δ in ppm): 171.68, 165.28, 148.79, 148.53, 148.01, 147.95, 146.14, 142.99, 125.77, 121.88, 120.97, 115.54, 115.40, 109.29, 108.93, 55.55, 55.53, 21.65 and 20.28.

Benzylideneoctanehydrazide (B-Oh) mixture of *cis*/*trans* isomers 2:3: ^{1}H NMR (DMSO-d_6, δ in ppm): 11.32 (s, 1H), 11.21 (s, 1H_a), 8.15 (s, 1H), 7.97 (s, 1H_a), 7.65 (m, 2H, 2H_a), 7.42 (m, 3H, 3H_a), 2.61 (t, 2H_a), 2.18 (t, 2H), 1.57 (m, 2H, 2H_a), 1.27 (m, 8H, 8H_a), 0.86 (t, 3H) and 0.85 (t, 3H_a). ^{13}C NMR (DMSO-d_6, δ in ppm): 174.89, 169.11, 146.12, 142.78, 135.07, 134.83, 130.30, 130.08, 129.97, 129.64, 129.27, 129.24, 127.39, 127.03, 34.66, 32.32, 31.63, 29.18, 29.09, 28.93, 28.92, 25.48, 24.75, 22.54, 14.41.

2. Structural characterization of monomers

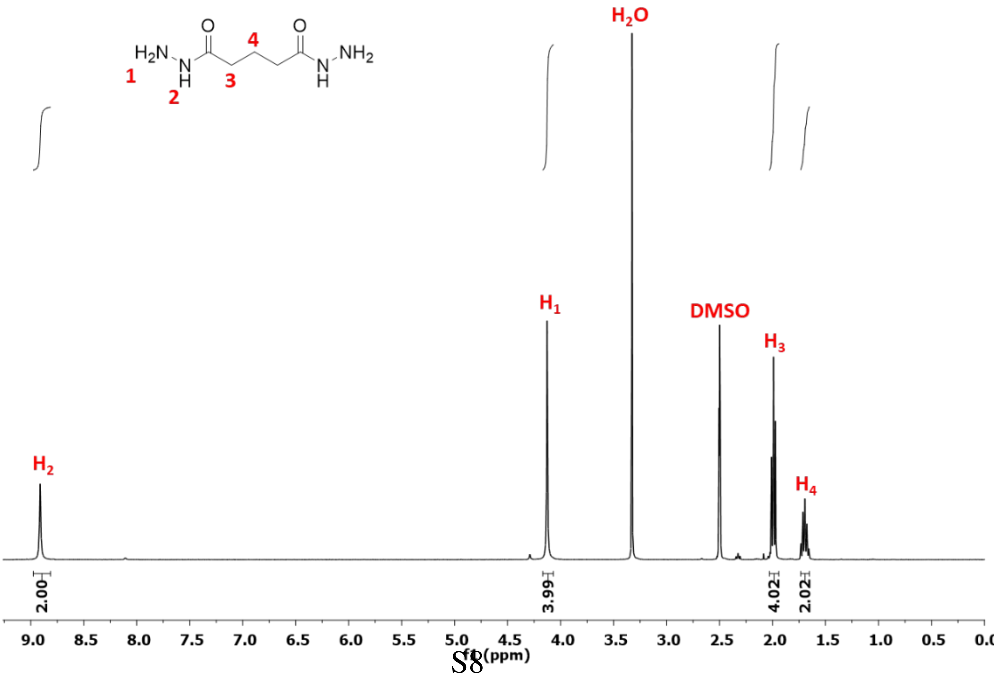


Figure S1. ^{1}H NMR spectrum of glutaric dihydrazide (GDh) in DMSO-d_6.

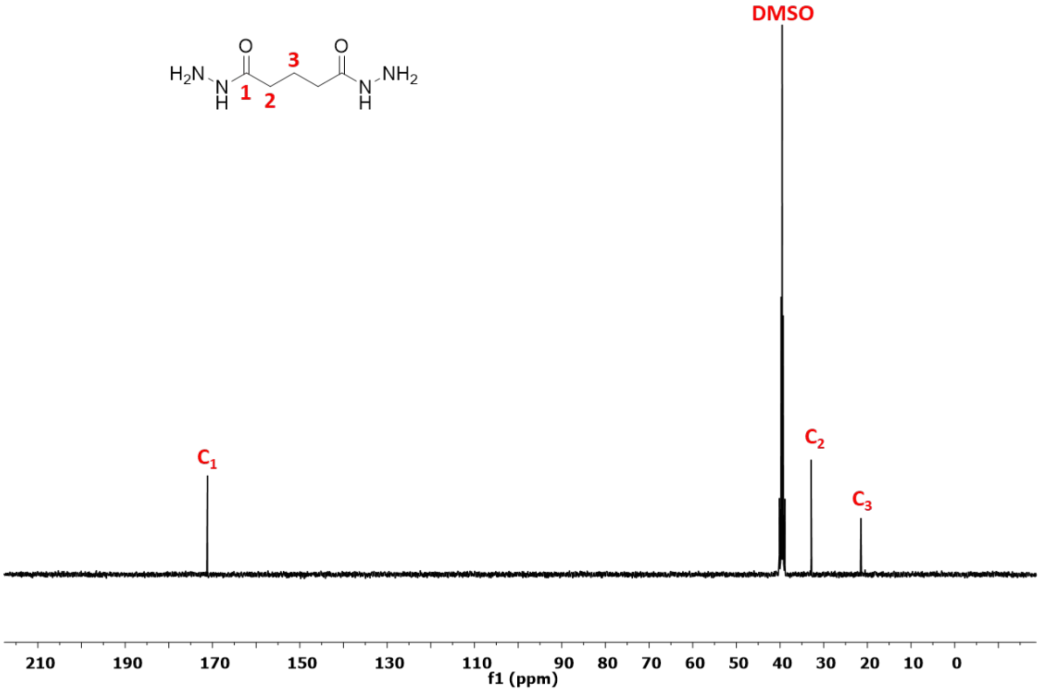


Figure S2. ^{13}C NMR spectrum of glutaric dihydrazide (GDh) in DMSO-d_6.

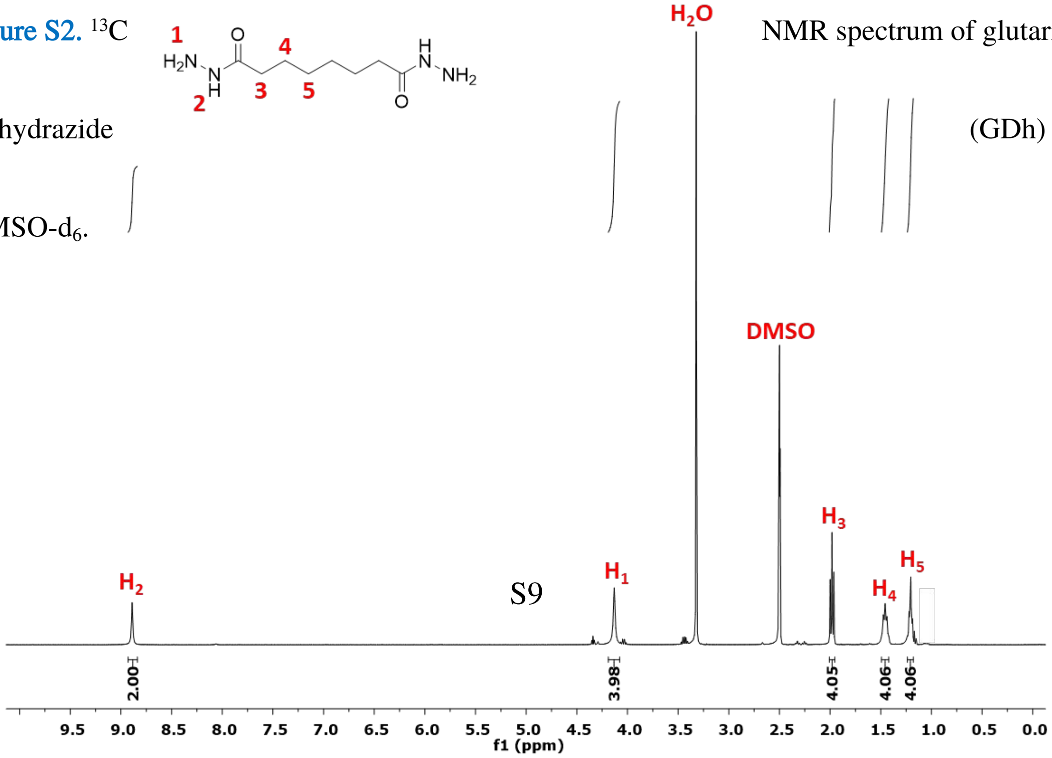


Figure S3. ^{1}H NMR spectrum of suberic dihydrazide (SDh) in DMSO-d_6.

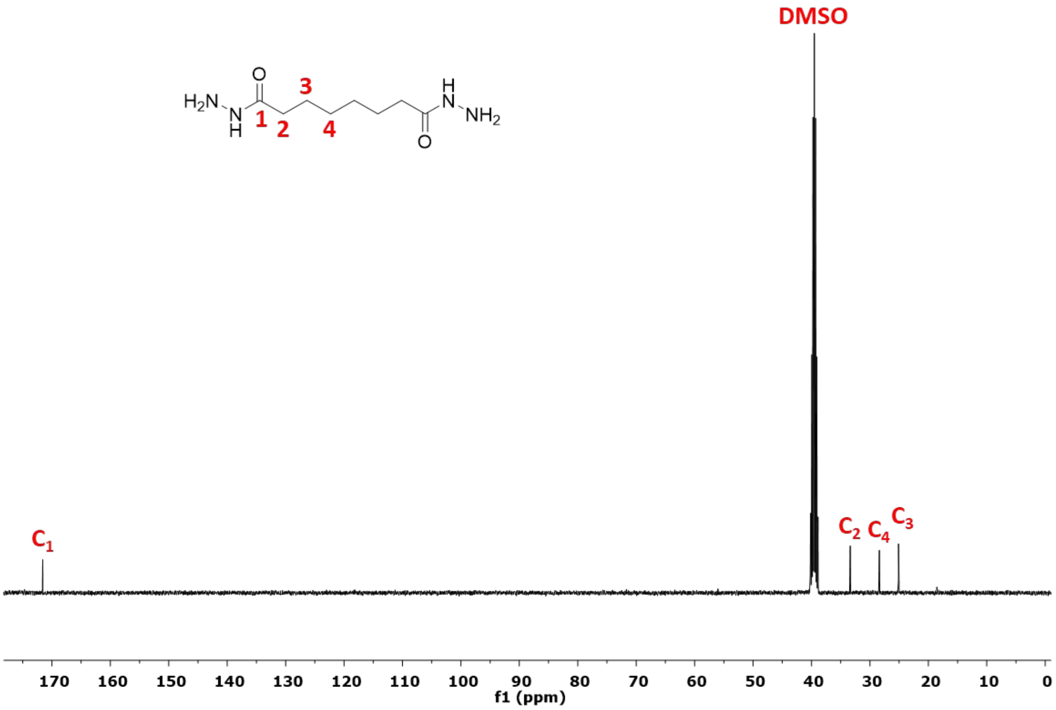


Figure S4. ^{13}C NMR spectrum of suberic dihydrazide (SDh) in DMSO-d_6.

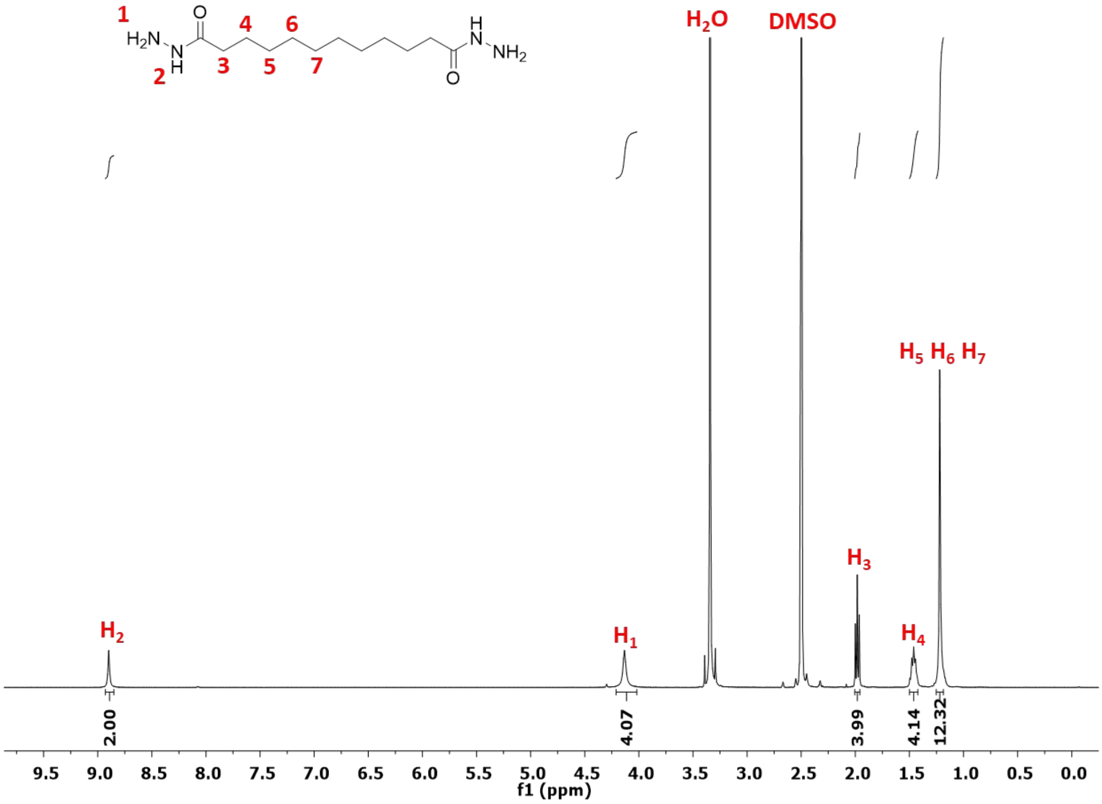


Figure S5. ^1H NMR spectrum of dodecandioic dihydrazide (DDh) in DMSO-d_6.

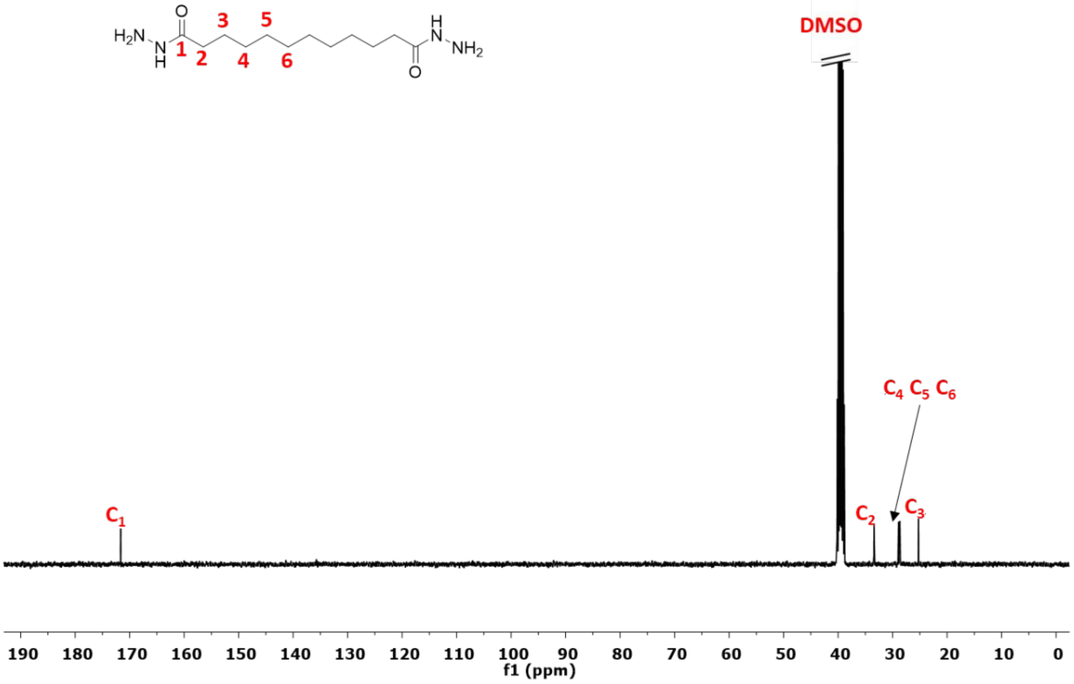


Figure S6. ^{13}C NMR spectrum of dodecandioic dihydrazide (DDh) in DMSO-d$_6$.

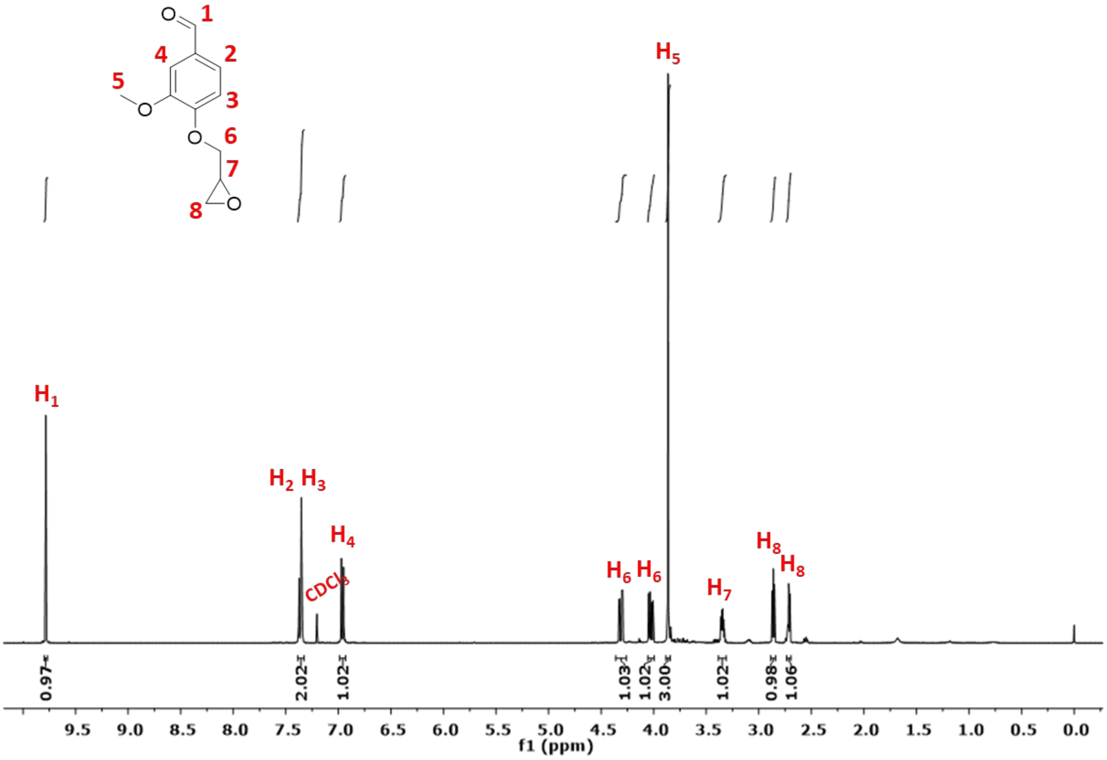


Figure S7. ^1H NMR spectrum of EPO-Van in CDCl$_3$.

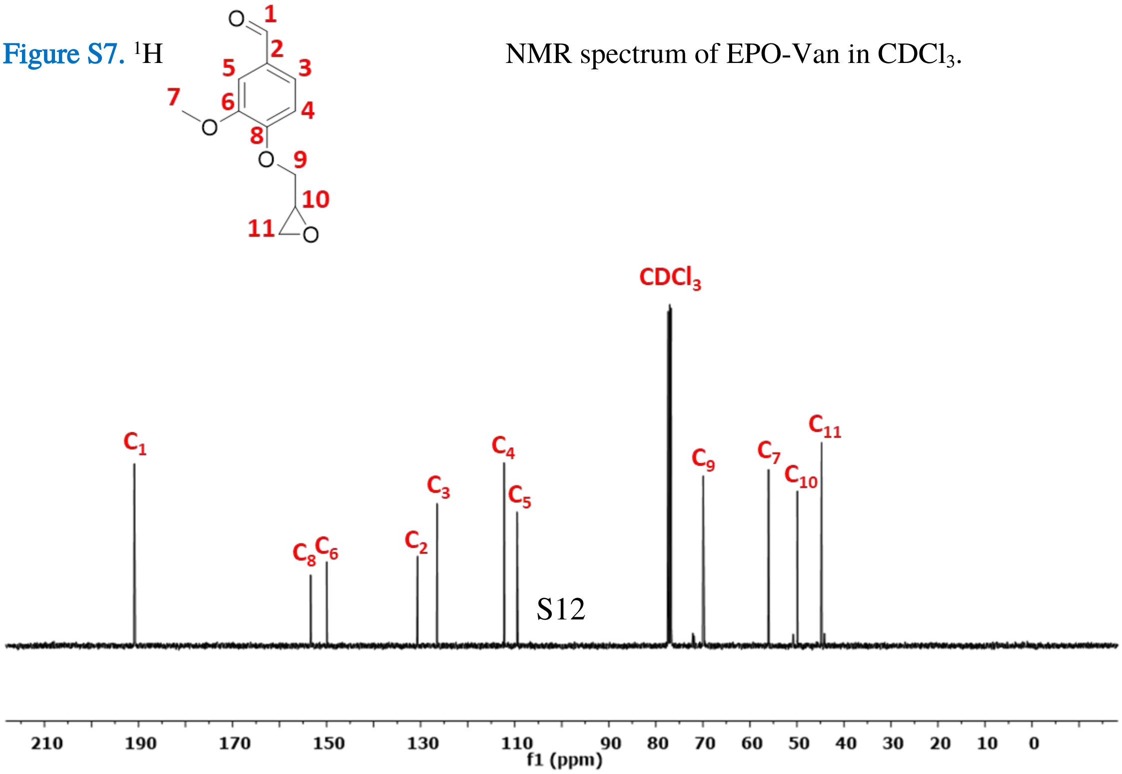


Figure S8. ^{13}C NMR spectrum of EPO-Van in DMSO-d_6.

3. Structural characterization of model compounds

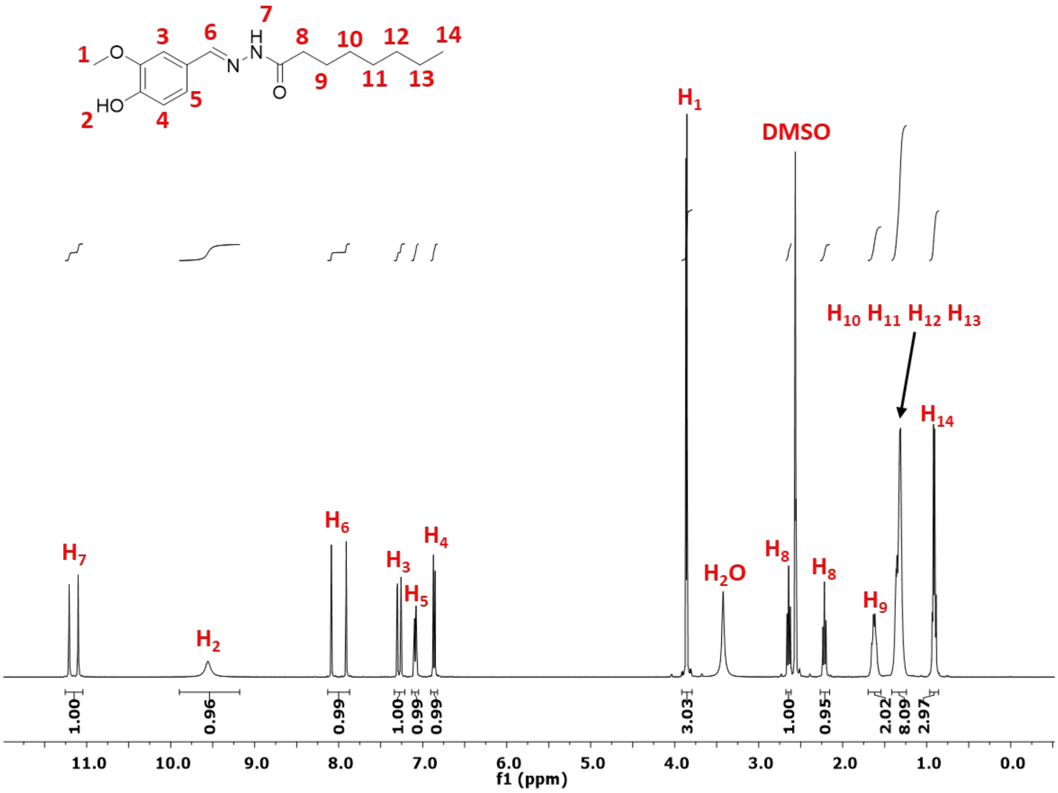


Figure S9. ^{1}H NMR spectrum of V-Oh in DMSO-d_6.

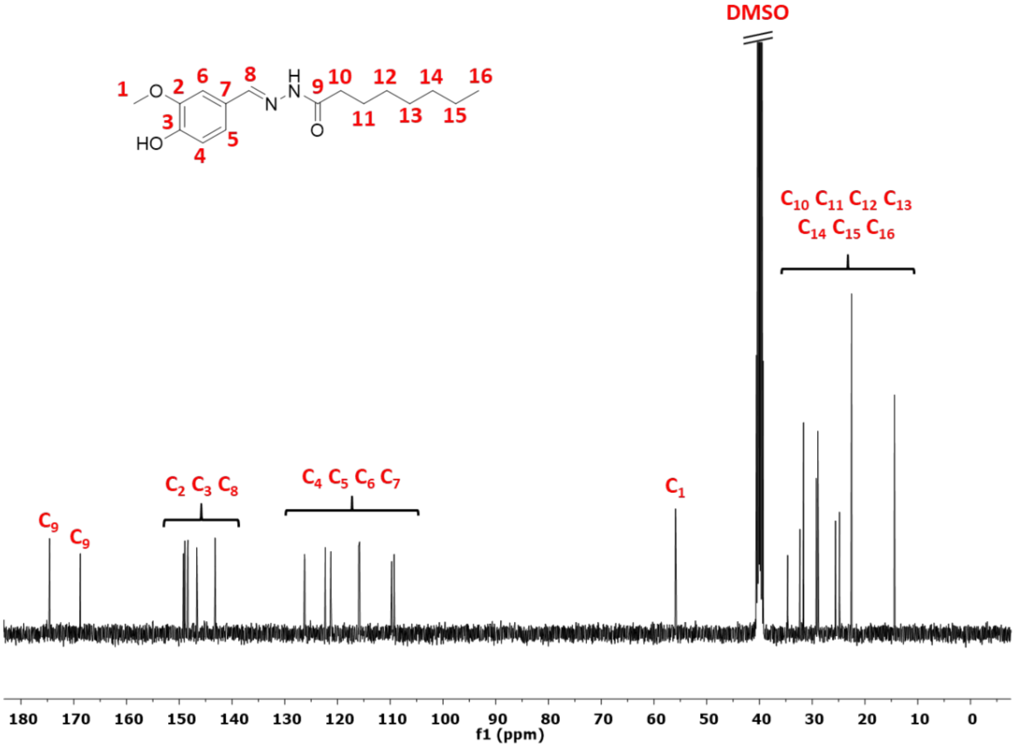


Figure S10. ^{13}C NMR spectrum of V-Oh in DMSO-d$_6$.

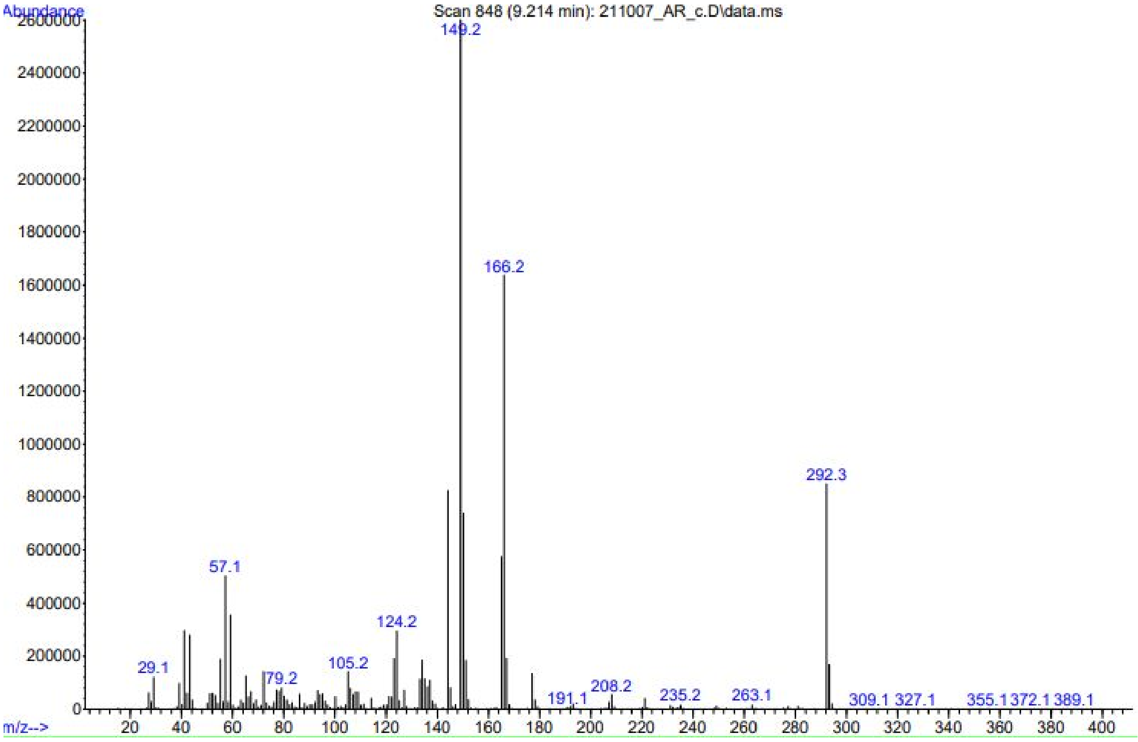


Figure S11. Mass spectrum of pure V-Oh.

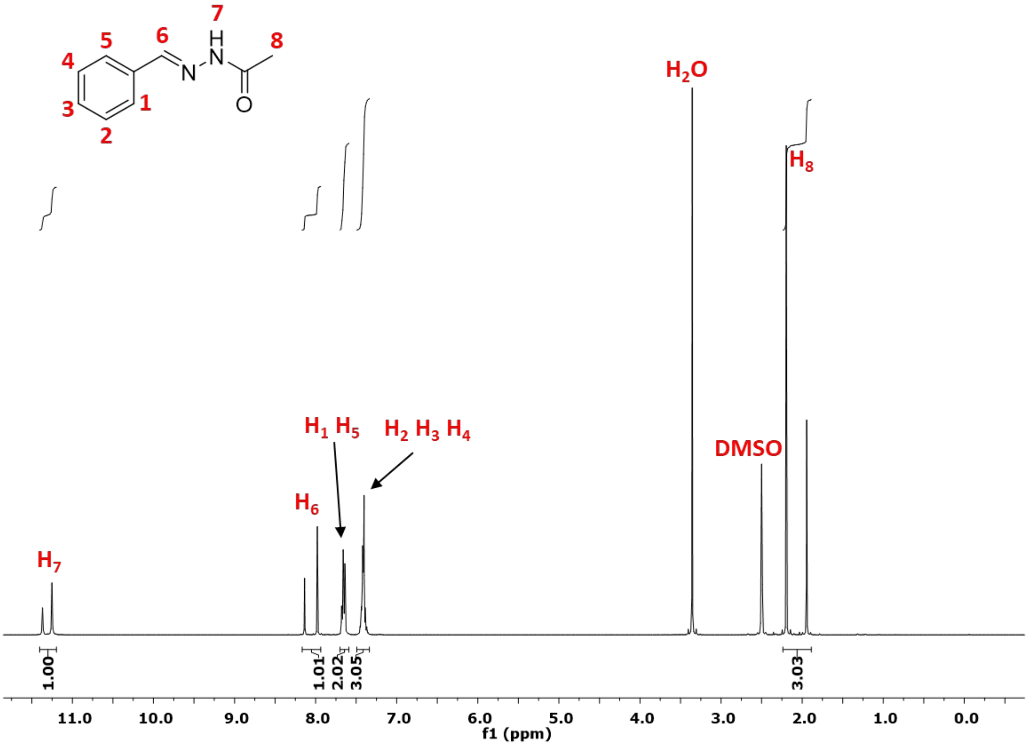


Figure S12. ^{1}H NMR spectrum of B-Ah in DMSO-d_6.

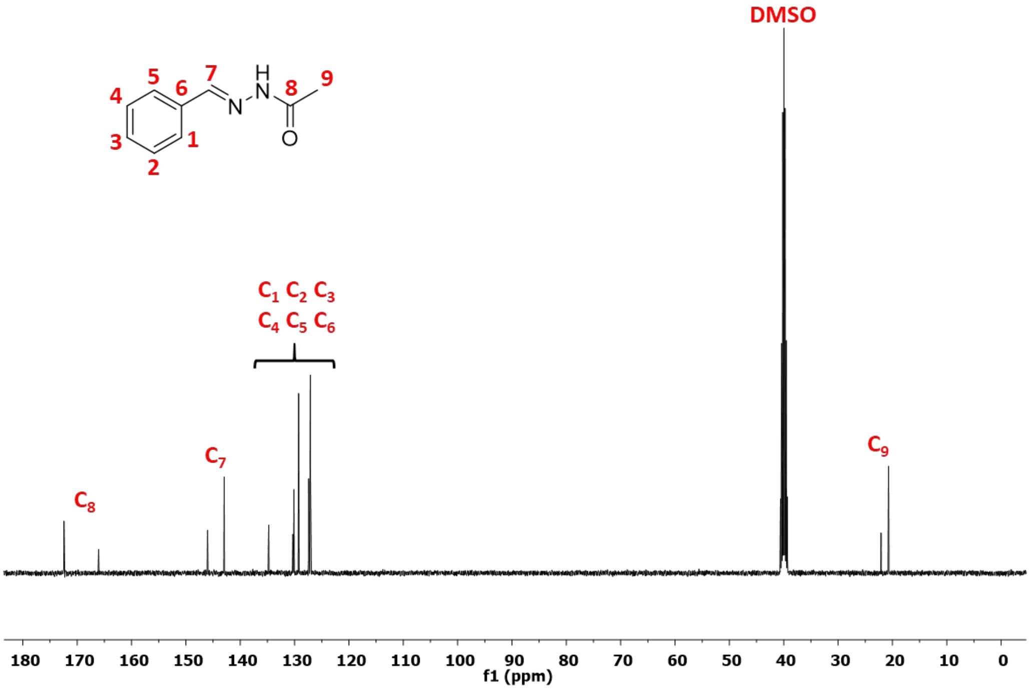


Figure S13. ^{13}C NMR spectrum of B-Ah in DMSO-d$_6$.

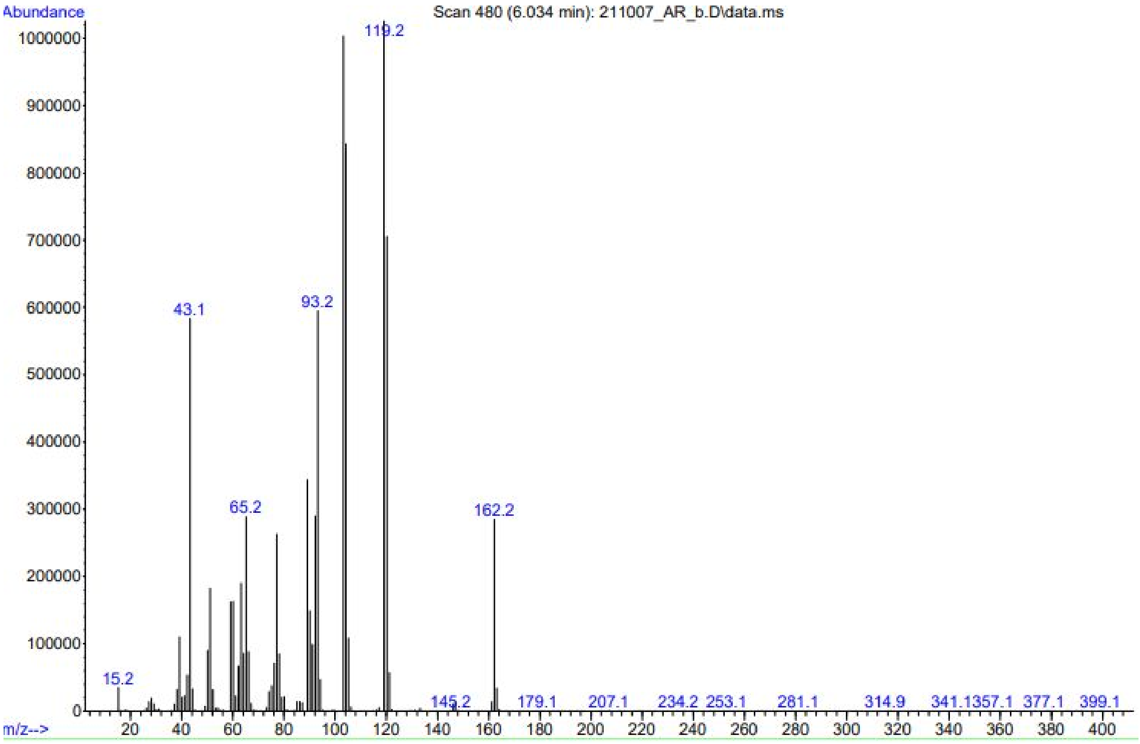


Figure S14. Mass spectrum of pure B-Ah.

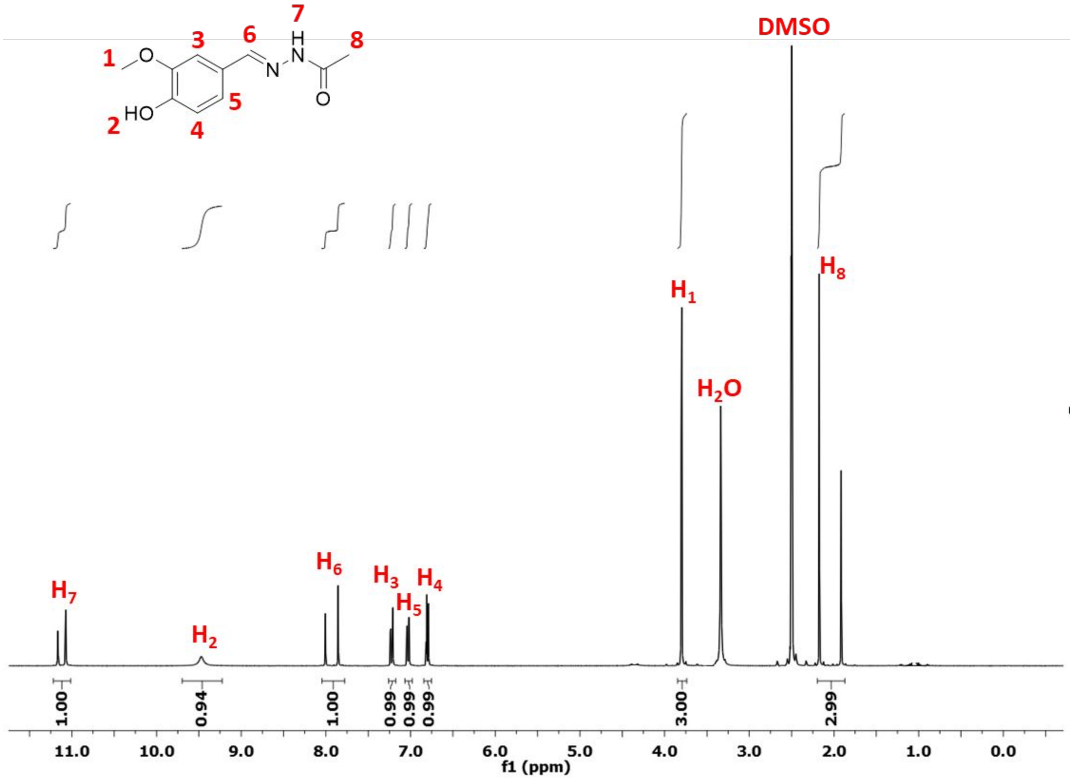


Figure S15. ^{1}H NMR spectrum of V-Ah in DMSO-d_6.

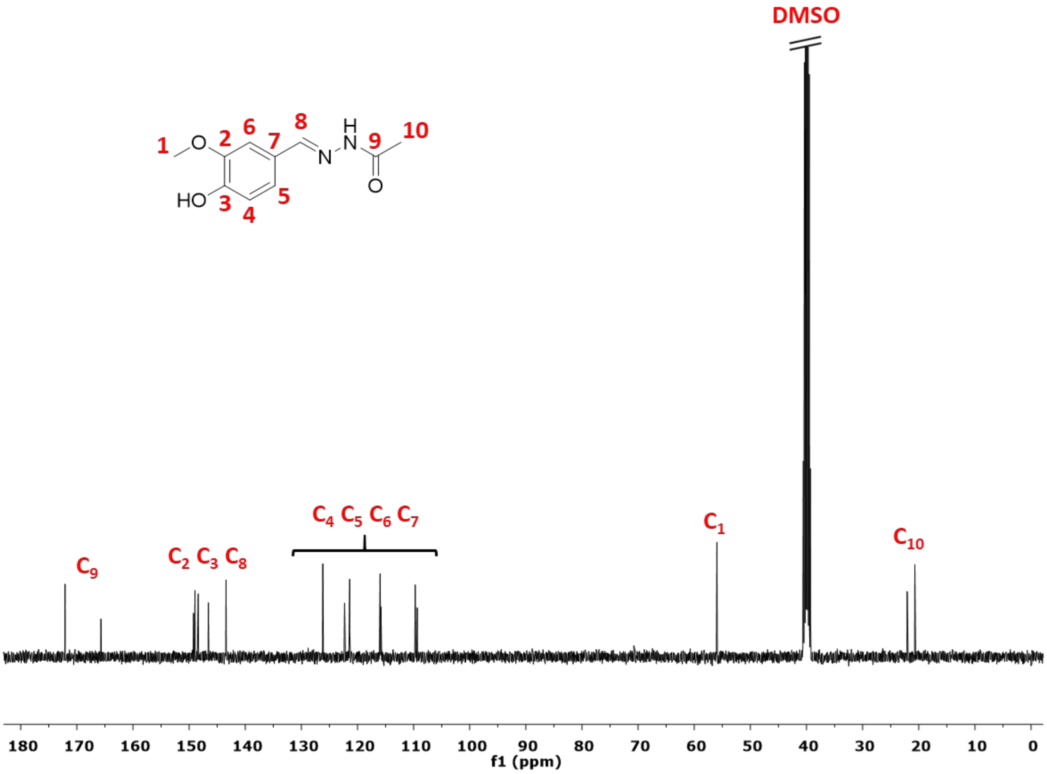


Figure S16. ^{13}C NMR spectrum of V-Ah in DMSO-d_6.

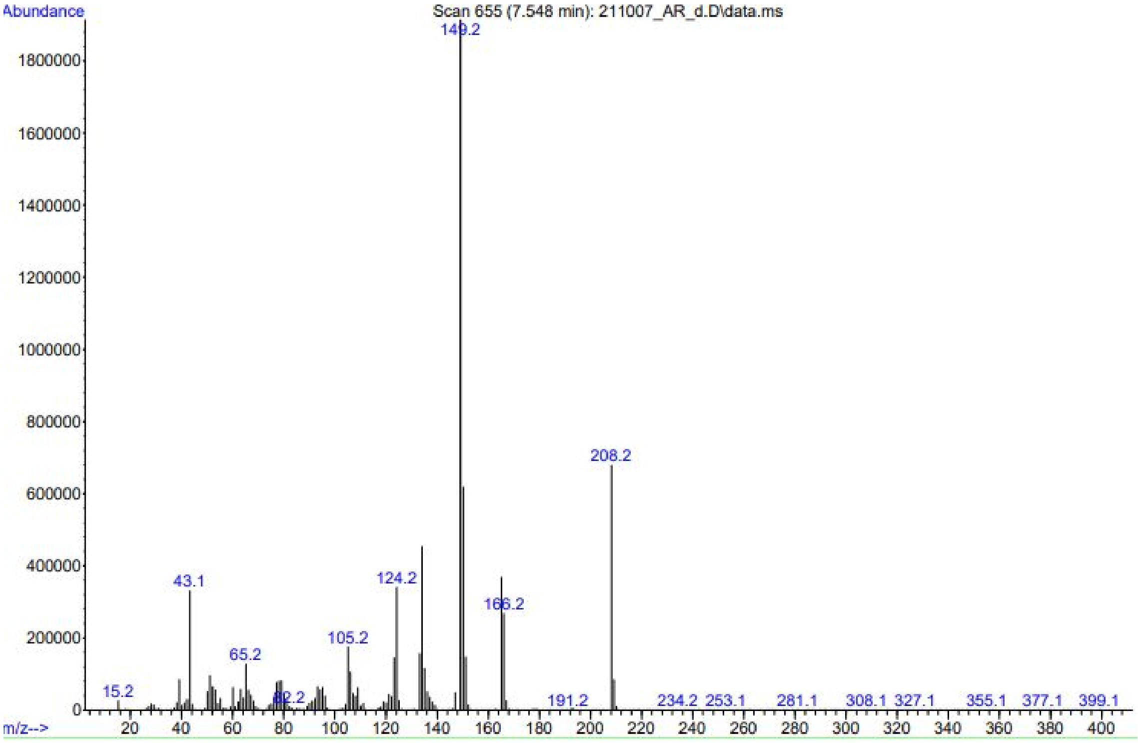


Figure S17. Mass spectrum of pure V-Ah.

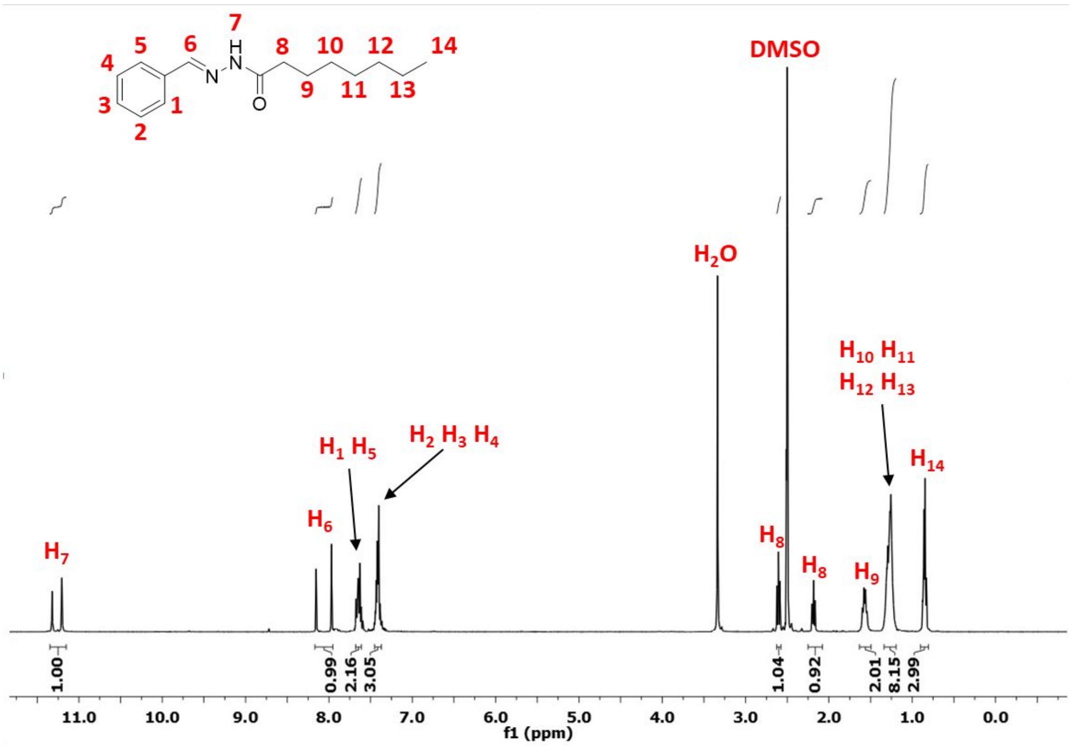


Figure S18. ^{1}H NMR spectrum of B-Oh in DMSO-d$_6$.

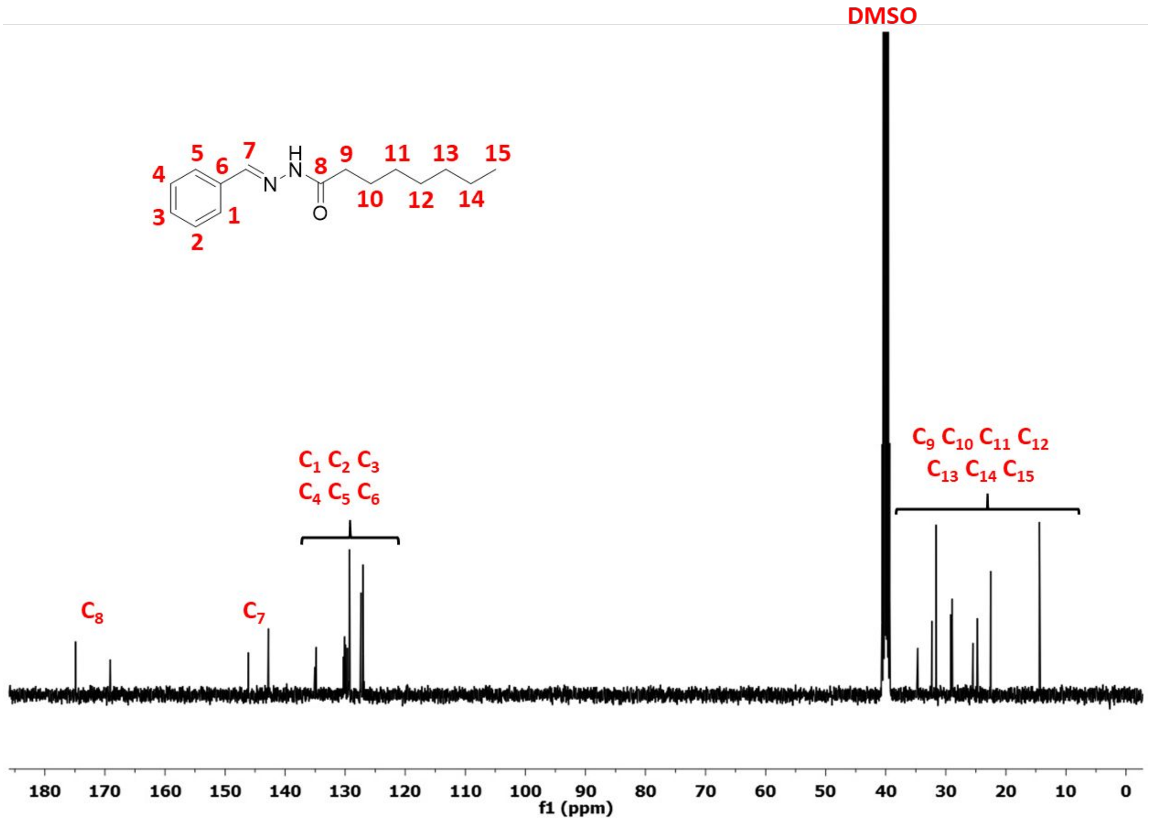


Figure S19. ^{13}C NMR spectrum of B-Oh in DMSO-d_6.

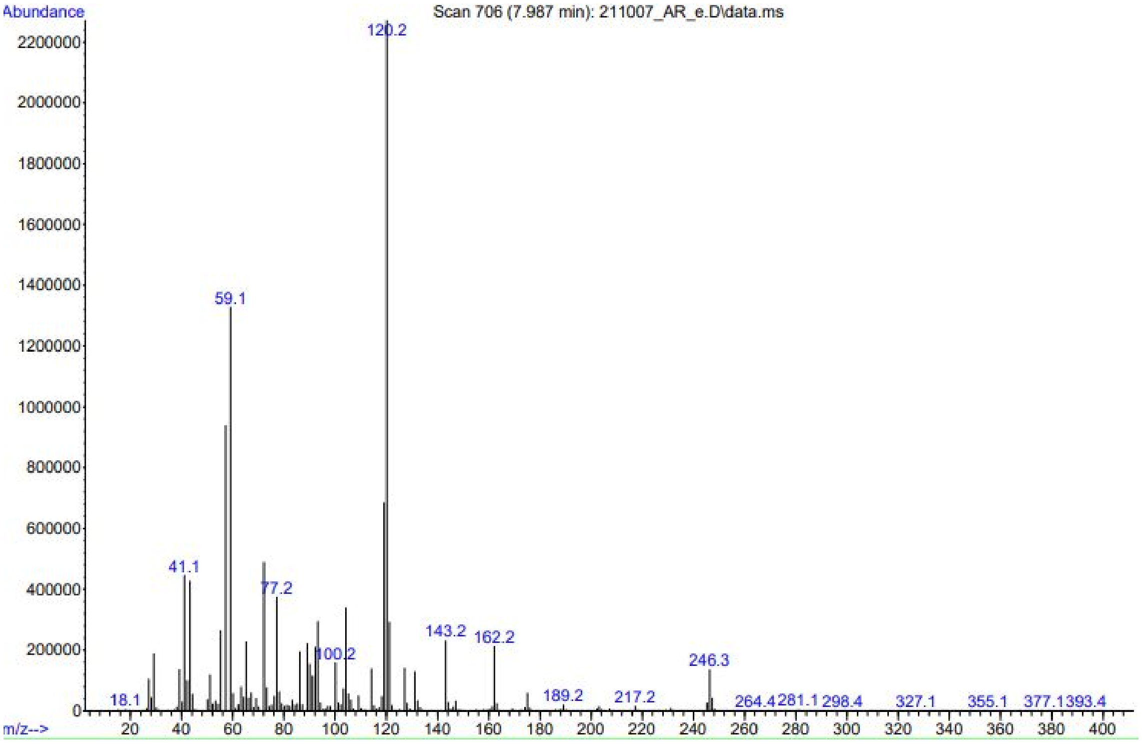


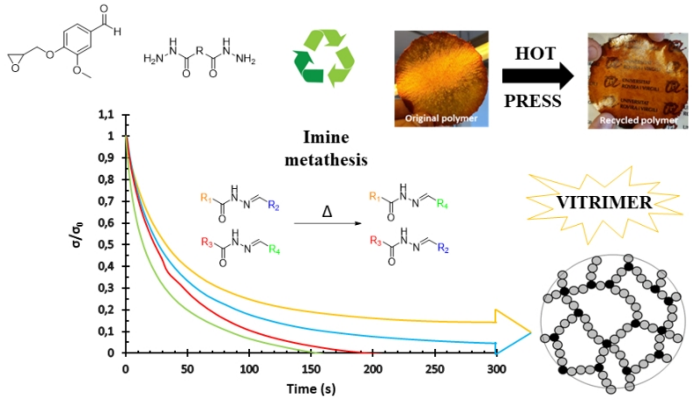
Figure S20. Mass spectrum of pure B-Oh.

Supporting References

[1] Yu, Q.; Peng, X.; Wang, Y.; Geng, H.; Xu, A.; Zhang, X.; Xu, W.; Ye, D. Vanillin-based degradable epoxy vitrimers: Reprocessability and mechanical properties study. *Eur. Polym. J.*, **2019**, *117*, 55-63. https://doi.org/10.1016/j.eurpolymj.2019.04.053.

[2] Mills, L.R.; Zhou, C.; Fung, E. Rousseaux, S.A.L. Ni-Catalyzed β-Alkylation of Cyclopropanol-Derived Homoenolates. *Org. Lett.*, **2019**, *21*, 8805-8809. https://doi.org/10.1021/acs.orglett.9b03435.

[3] Tomuta, A.M.; Ramis, X.; Ferrando, F. Serra, A. The use of dihydrazides as latent curing agents in diglycidyl ether of bisphenol A coatings. *Prog. Org. Coat.,* **2012**, *74*, 59-66. https://doi.org/10.1016/j.porgcoat.2011.10.004.



Graphical Abstracts

338x190mm (96 x 96 DPI)