Supplementary Information (SI) for Green Chemistry.

Supporting Information

Synthesis of novel bio-based amines from vanillin and guaiacol for high performance epoxy thermosets

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Materials

Chemicals

All chemicals were used as received unless otherwise stated. Vanillin (99%) was provided by Borregaard Group as EuroVanillin. Guaiacol (>99%) was purchased as bio-based guaiacol natural from Sigma-Aldrich. Hexamethylenetetramine (HMTA), Trifluoroacetic acid (TFA), hydrochloric acid (HCl), dichloromethane (DCM), magnesium sulfate, toluene, potassium carbonate, tetrabutylammonium iodide (TBAI), dimethyl sulfate, sodium hydroxide (NaOH), dimethylformamide (DMF), sodium acetate, hydroxylamine, ethanol and 1,4-dioxane were purchased from Sigma-Aldrich. Bisphenol A diglycidyl ether was purchased as Araldite® GY 250 (EEW 187 g/eq) and bisphenol F diglycidyl ether was purchased as Araldite® GY 281 (EEW 165 g/eq) from Huntsman. 1,4-Butane diglycidyl ether was purchased as Syna-Epoxy 27(HQ) from Synasia. C12-C14 alkyl glycidyl ether was purchased as Grilonit® Epoxide 8 from EMS. MXDA (AEW 34 g/eq) was purchased from Mitsubishi Gas Chemical.

NMR

The ^{1}H-NMR spectra were recorded on a Bruker AscendTM 400 spectrometer at 400 MHz. The ^{13}C-NMR spectra were recorded on a Bruker AscendTM 400 spectrometer at 100 MHz. Chemical shifts are reported as ppm downfield from TMS. Coupling constants are reported in Hz.

ATR FT-IR

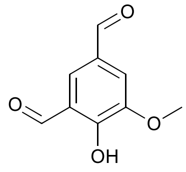
Infrared spectroscopy was performed on a Thermo Fischer Scientific iD5 ATR NicoletTM iS5 FT-IR spectrometer.

GC

Gas chromatography was carried out on a Thermo Fischer Scientific Trace 1300 gas chromatograph equipped with Zebron ZB-5 column and a gas flow of 1.5 mL/min. Temperature ranged from 60 to 320 °C with a heating rate of 15 °C/min and a 10-minute hold time at 320 °C. The injector temperature was 250 °C. Detection was performed using flame ionization (FID).

Synthetic procedure

4-Hydroxy-5-methoxyisophthalaldehyde (5-Formyl vanillin) (1)



1

Original Synthesis: 100.61 g (0.661 mol) vanillin (1 eq.) and 110.96 g (0.791 mol) hexamethylenetetramine (1.2 eq.) were charged to a 2000 ml triple-necked round-bottomed flask equipped with magnetic stirring bar, condenser, nitrogen inlet and dropping funnel. 500 ml of trifluoroacetic acid was added dropwise. The solution was heated to reflux and stirred vigorously for 5 h. Then, 800 ml of aq. hydrochloric acid (4 M) was added. The solution was again heated to reflux and stirred for 1 h. After cooling down, the solution was extracted with a total of 600 ml dichloromethane. The combined organic phase was dried over magnesium sulfate and concentrated under reduced pressure. Recrystallization in toluene and drying to constant mass afforded 98.15 g (0.54 mol) of a yellow solid as a pure product (yield 96 %).

Improved Greener Synthesis: 10.00 g (0.066 mol) vanillin (1 eq.) and 11.10 g (0.079 mol) hexamethylenetetramine (1.2 eq.) were charged to a 250 ml triple-necked round-bottomed flask equipped with magnetic stirring bar, condenser, nitrogen inlet and dropping funnel. 25 ml of glacial acetic acid and 25 ml of trifluoroacetic acid were added dropwise. The solution was heated to reflux and stirred for 5 h. Then, 80 ml of aq. hydrochloric acid (4 M) was added. The solution was again heated to reflux and stirred for 40 min. Then, the reaction was left to cool down in an ice bath. After cooling down the solution was extracted a total of 250 ml dichloromethane. The combined organic phase was washed with 80 ml of brine and dried over magnesium sulfate and concentrated in the rotary evaporator. Recrystallization in toluene and drying to constant mass afforded 7.9 g (0.044 mol) of a yellow solid as a pure product (yield 66 %).

Molecular weight = 180.16 g/mol.

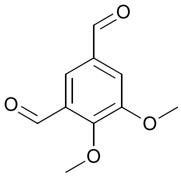
^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 11.30 (br s, 1 H, Ar-OH), 10.36 (s, 1H, O=CH, ipso), 9.89 (s, 1H, O=CH, meta), 7.88 (d, 1 H, Ar-H, J = 1.8 Hz), 7.61 (d, 1 H, Ar-H, J = 1.8 Hz), 3.96 (s, 3 H, OCH3).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 55.46 (OCH$_3$), 113.26 (Ar-CH), 119.00 (Ar-CH), 128.08 (Ar-C-CH, meta), 128.46 Ar-C-CHO, ortho), 148.42 (Ar-C-OCH$_3$), 156.09 (Ar-C-OH), 188.56 (CHO, meta), 194.83 (CH, ipso).

ATR FT-IR (cm^{-1}): 3073, 3032, 2991, 2939, 2873, 2733, 2508, 2559, 1683, 1640, 1615, 1588, 1557, 1538, 1502, 1467, 1453, 1435, 1407, 1385, 1323, 1293, 1276, 1200, 1183, 1145, 1090, 1029, 1015, 982, 956, 908, 883, 830, 809, 797, 763, 732, 666.

GC (EtOAc): R_t = 11.12 min.

4,5-Dimethoxy-1,3-benzenedicarboxyaldehyde (2)



2

5.01 g (27.8 mmol) 4-hydroxy-5-methoxyisophthalaldehyde (1 eq.) was dissolved in 130 ml DMF and charged to a 250 ml two-necked round-bottomed flask equipped with stirring bar, condenser, dropping funnel and nitrogen inlet. 11.53 g (83.4 mmol) potassium carbonate (3 eq.) and 0.46 g (1.25 mmol) tetrabutylammonium iodide (cat.) were added. The mixture was stirred at room temperature for 2 h. Then, 8.09 g (55.6 mmol) of dimethyl sulfate was added dropwise. The reaction was stirred at room temperature for 24 h. The reaction was quenched with 40 ml aq. NaOH (1 M). DMF was distilled off on the rotary evaporator and the remaining solid dissolved in deionized water and extracted with a total of 300 ml ethyl acetate. The combined organic phase was dried over magnesium sulfate and concentrated under reduced pressure. Drying to constant mass afforded 5.61 g (26.7 mmol) of a yellow solid as a pure product (yield 88 %).

Molecular weight = 194.18 g/mol.

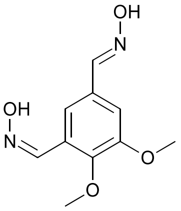
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 10.38 (s, 1H, O=CH, meta), 9.87 (s, 1H, O=CH, ipso), 7.86 (d, 1 H, Ar-H, J = 1.92 Hz), 7.59 (d, 1 H, Ar-H, J = 1.92 Hz), 4.05 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3).

^{13}C-NMR ($CDCl_3$): δ (ppm) 55.24 (OCH_3), 61.35 (OCH_3), 113.26 (Ar-CH), 123.42 (Ar-CH), 128.42 (Ar-C-CHO, meta), 131.13 (Ar-C-CHO, ipso), 152.64 (Ar-C-O), 156.49 (Ar-C-O), 188.02 (CHO, meta), 189.46 (CHO, ipso).

ATR FT-IR (cm^{-1}): 3020, 2954, 2873, 2849, 1682, 1597, 1581, 1516, 1485, 1463, 1428, 1386, 1335, 1284, 1248, 1227, 1190, 1133, 1071, 1009, 982, 934, 891, 873, 786, 764, 751.

GC (EtOAc): R_t = 11.49 min.

4,5-Dimethoxy isophthalaldehyde dioxime



49.22 g (0.6 mol) sodium acetate (3 eq.) and 29.09 g (0.44 mol) aq. hydroxylamine (50 wt. %, 2.2 eq.) were charged to a 1000 ml triple-necked round-bottomed flask equipped with magnetic stirring bar, condenser and nitrogen inlet. 500 ml of deionized water was added so that the hydroxylamine concentration was roughly 100 g/l. Then, 38.83 g (0.2 mol) 4,5-Dimethoxy-1,3-benzenedicarboxaldehyde (1 eq.) was added. The reaction was heated to reflux and stirred for 1.5 hour. The reaction was monitored by IR. The solution was cooled down in an ice-bath. The white precipitate was suction-filtered and washed with 300 ml of ice-cold deionized water. Drying to constant mass afforded 35.54 g (0.16 mol) of a white solid as a pure product (yield 80 %).

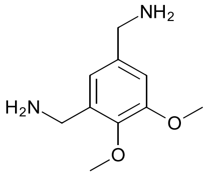
Molecular weight = 224.21 g/mol.

^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 11.37 (br s, 2 H, 2 x OH-N), 8.24 (s, N=CH, meta), 8.11 (s. N=CH, ipso), 7.48 (d, 1 H, Ar-H, *J* = 1.87 Hz), 7.29 (d, 1 H, Ar-H, *J* = 1.87 Hz), 3.85 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3).

^{13}C-NMR (100 MHz, DMSO-d6): δ (ppm) 56.18 (OCH_3), 61.49 (OCH_3), 110.48 (Ar-CH), 116.34 (Ar-CH), 126.99 (Ar-C-C=N-OH, meta), 129.73 (Ar-C-C=N-OH, ipso), 143.47 (OH-N=C, ipso), 147.96 (OH-N-C, meta), 148.12 (Ar-C-O), 153.25 (Ar-C-O).

ATR FT-IR (cm^{-1}): 3398, 3209, 3095, 3002, 2972, 2937, 2826, 1581, 1493, 1477, 1457, 1416, 1353, 1313, 1291, 1279, 1241, 1226, 1196, 1147, 1082, 1017, 997, 971, 962, 954, 935, 863, 836, 794, 757, 731; GC (THF): R_t = 14.62 min.

4,5-Dimethoxy-1,3-benzenedimethanamine / Dimethoxy-MXDA (3)



3

20 g (0.089 mol) of 4,5-dimethoxy isophthalaldehyde dioxime was dissolved in a solvent mixture consisting of 100 ml EtOH and 1200 ml 1,4-dioxane, corresponding to a concentration of roughly 9 g/l resp. 0.02 M/l. The solution was then introduced to the H-cube® carrying a Raney Nickel catalyst. The flowrate was adjusted to 5 ml/min with pressure at 80 bar and temperature at 80 °C. The reduction was monitored by IR. The crude product was then concentrated on the rotary evaporator. Drying to constant mass afforded 16.12 g (0.086 mol) of a yellow oil (yield 92 %). The amine value was determined to be 519 mg KOH/g.

Molecular weight 196.25 g/mol.

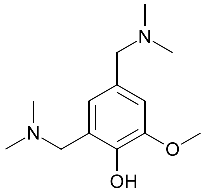
^{1}H-NMR (400 MHz, DMSO-d_6): 6.92 (s, 1 H, Ar-H), 6.90 (s, 1 H, Ar-H), 3.79 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.67 (s, 2 H, CH_2-N), 3.66 (s, 2 H, CH_2-N), 1.81 (br s, 4 H, 2x NH_2).

^{13}C-NMR (100 MHz, DMSO-d_6): 41.04 (CH_2-N), 46.22 (CH_2-N), 56.00 (OCH_3), 60.48 (OCH_3), 110.32 (Ar-CH), 119.02 (Ar-CH), 137.31 (Ar-C-CH_2), 140.33 (Ar-C-CH_2), 144.89 (Ar-C-O), 152.30 (Ar-C-O).

ATR FT-IR (cm^{-1}): 3367, 3284, 3189, 2994, 2932, 2831, 1588, 1488, 1462, 1428, 1383, 1338, 1309, 1225, 1185, 1139, 1080, 1051, 1005, 838, 775, 741, 706.

GC (EtOAc): R_t = 14.59 min.

2,4-Bis(dimethylaminomethyl)-6-methoxyphenol / Methoxy-K54 (4)



4

24.83 g (0.2 mol) guaiacol (1 eq.) and 81.96 g (0.6 mol) dimethylamine solution (33 wt. % in ethanol, 3 eq.) together with 250 ml ethanol were charged to a 1000 ml triple-necked round-bottomed flask equipped with magnetic stirring bar, condenser and nitrogen inlet. 18.20 g (0.6 mol) paraformaldehyde (3 eq.) was added. The reaction mixture was heated to reflux and stirred for 10 hours. The crude reaction mixture was then concentrated on the rotary evaporator. Vacuum distillation at 120 °C afforded 45.3 g (0.19 mol) of a clear, yellow liquid (yield 72 %). A minor side product identified was 2(4)-dimethylaminomethyl-6-methoxyphenol. The amine number was determined to be 452 mg KOH/g.

Molecular weight = 238.33 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$): 6.75 (d, 1 H, Ar-H), 6.57 (d, 1 H, Ar-H), 3.74 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2N), 3.24 (s, 2 H, CH_2N), 2.21 (s, 6 H, $(CH_3)_2N$), 2.11 (2, 6 H, $(CH_3)_2N$).

Characterization

4-Hydroxy-5-methoxyisophthalaldehyde (5-Formyl vanillin) (1)

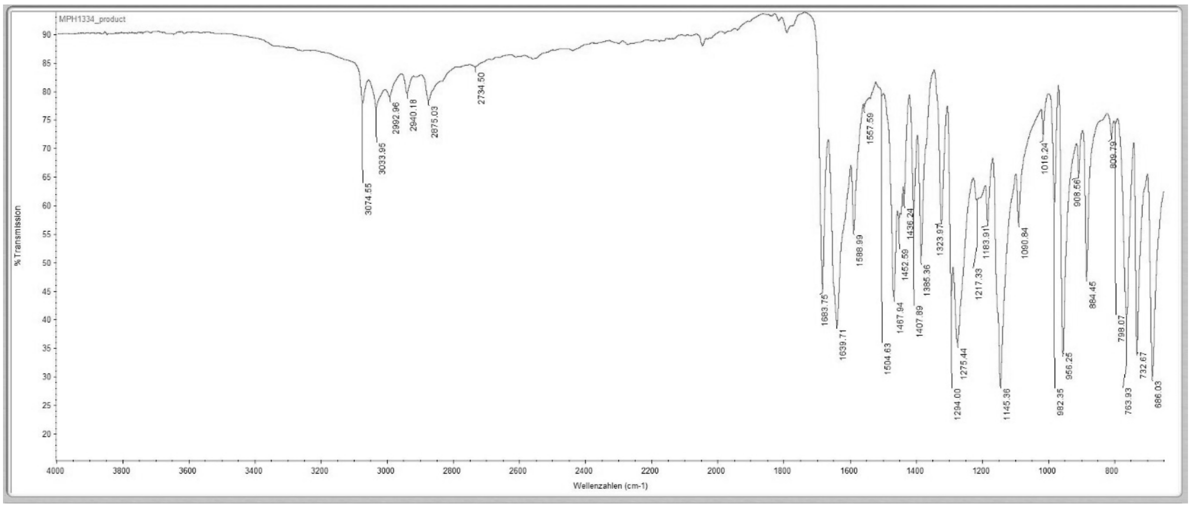


Fig. S1 FT-IR Spectrum of **1**.

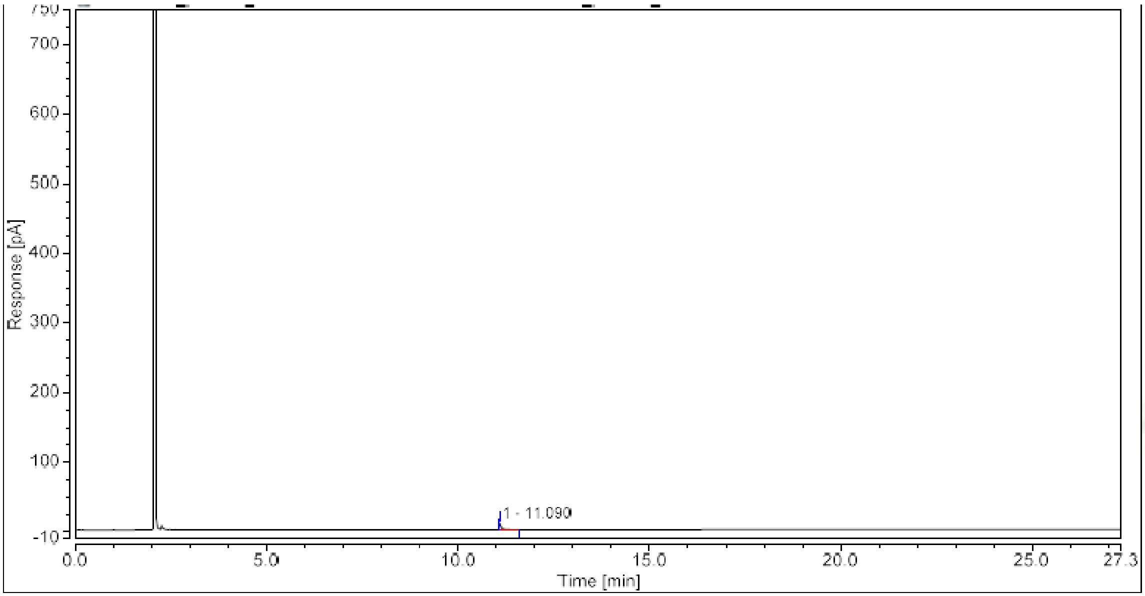


Fig. S2 GC Chromatogram of **1**.

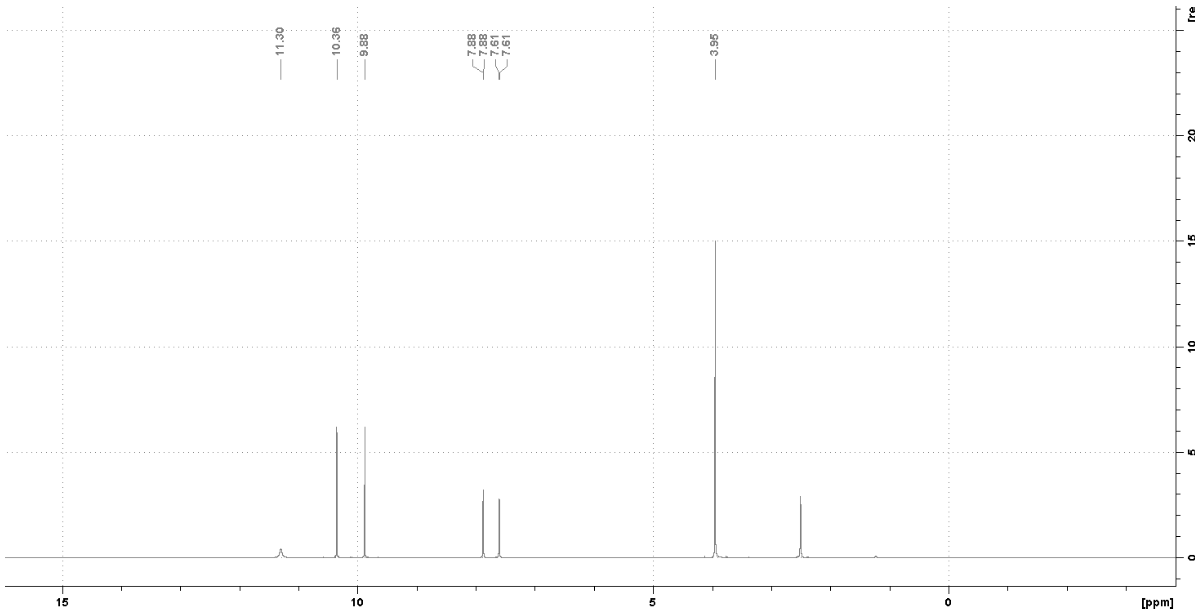


Fig. S3 ^{1}H NMR spectrum of **1**.

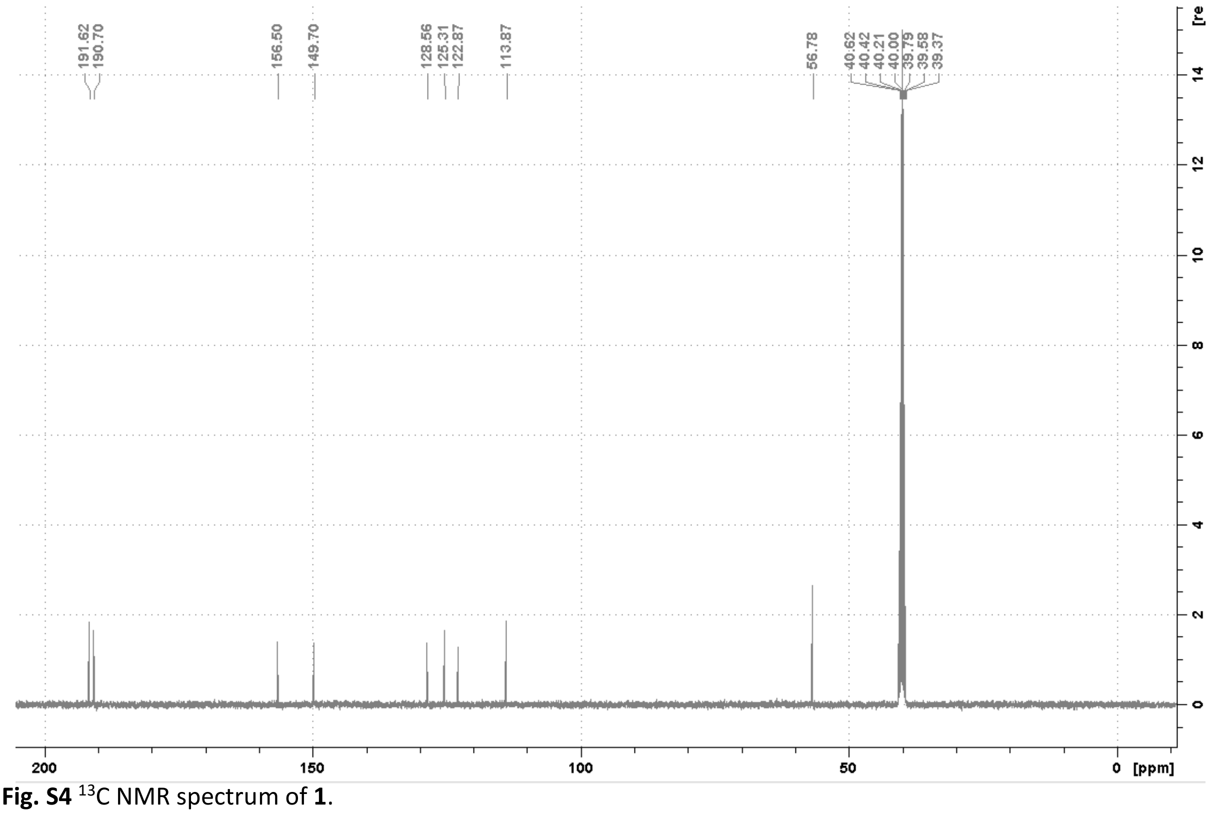


Fig. S4 ^{13}C NMR spectrum of **1**.

4,5-Dimethoxy-1,3-benzenedicarboxyaldehyde (2)

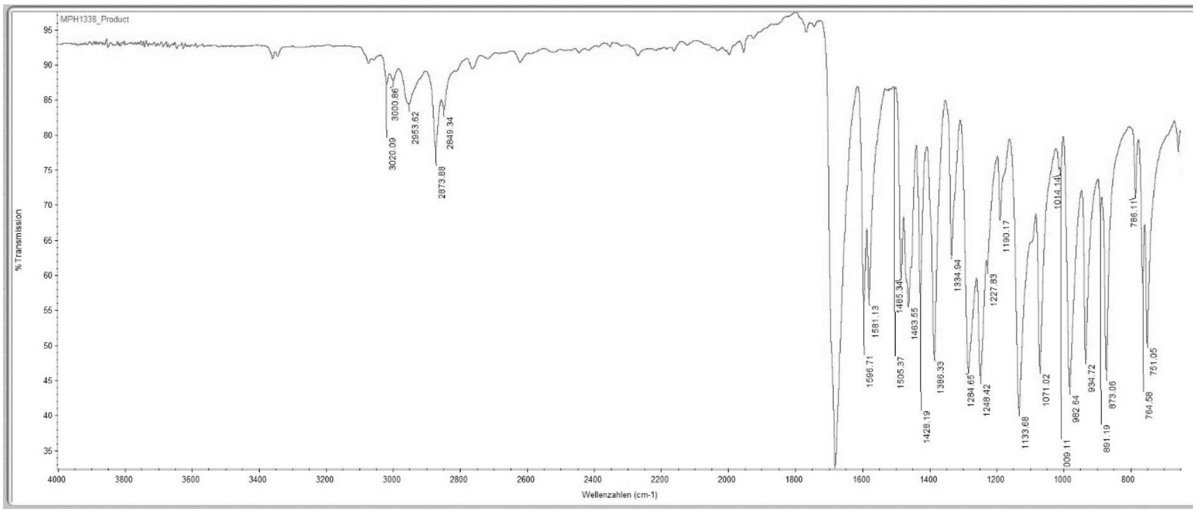


Fig. S5 FT-IR spectrum of **2**.

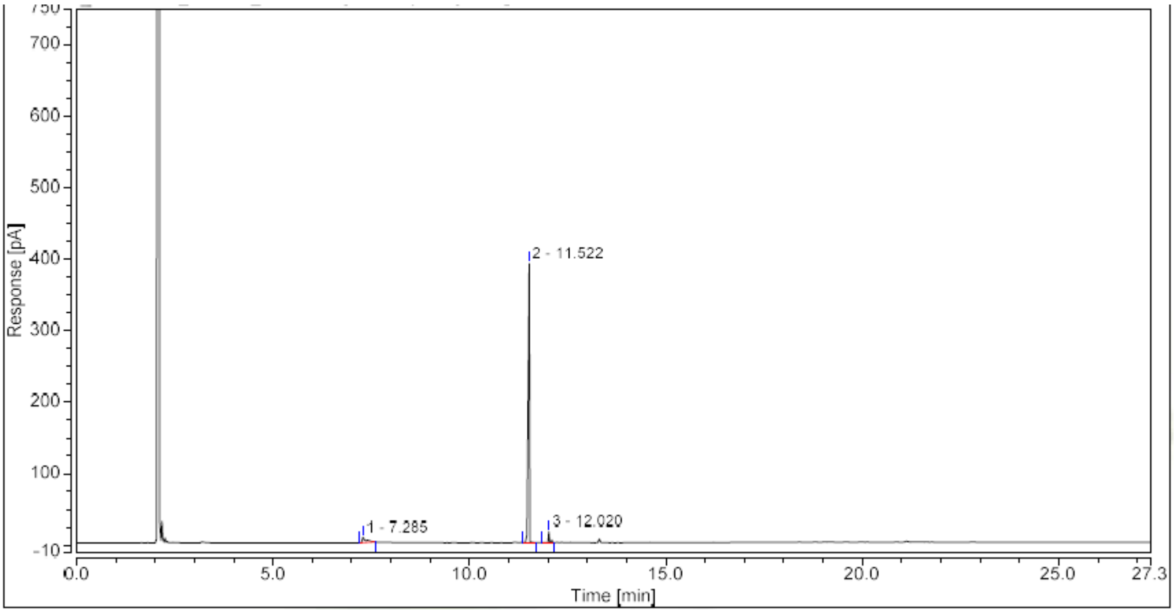


Fig. S6 GC chromatogram of **2**.

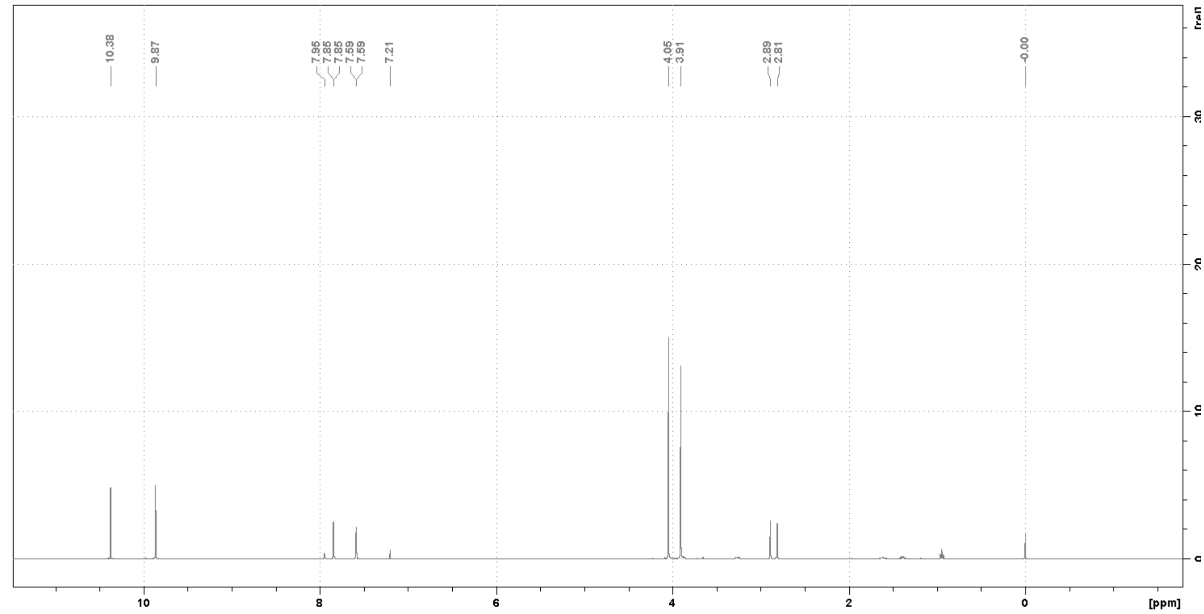


Fig. S7 ^{1}H NMR spectrum of **2**.

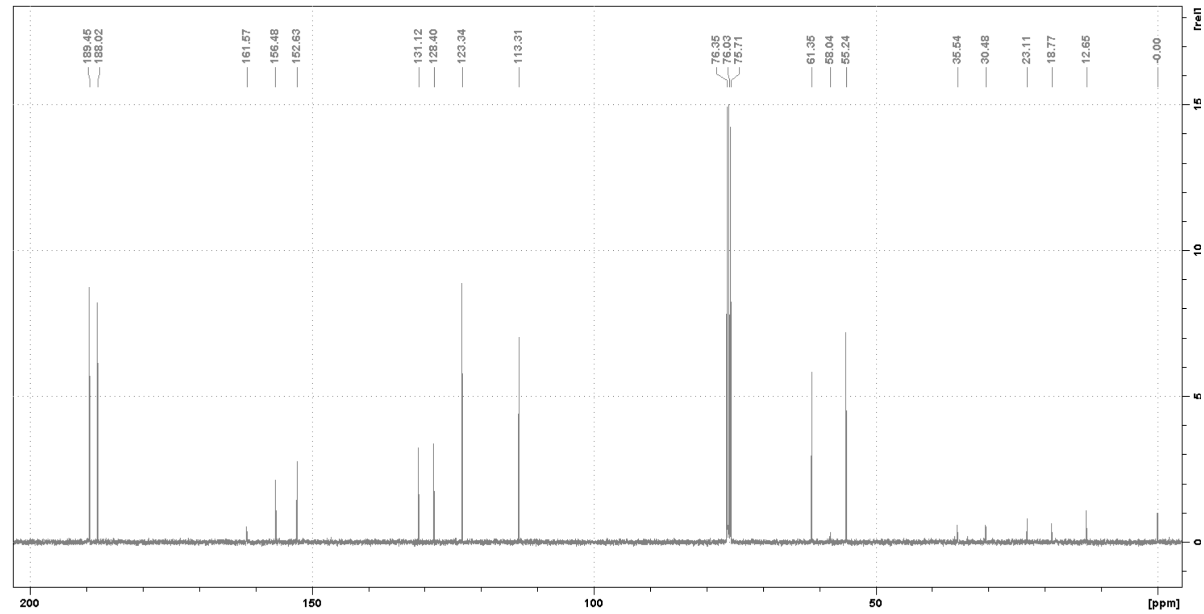


Fig. S8 ^{13}C NMR spectrum of **2**.

4,5-Dimethoxy isophthalaldehyde dioxime

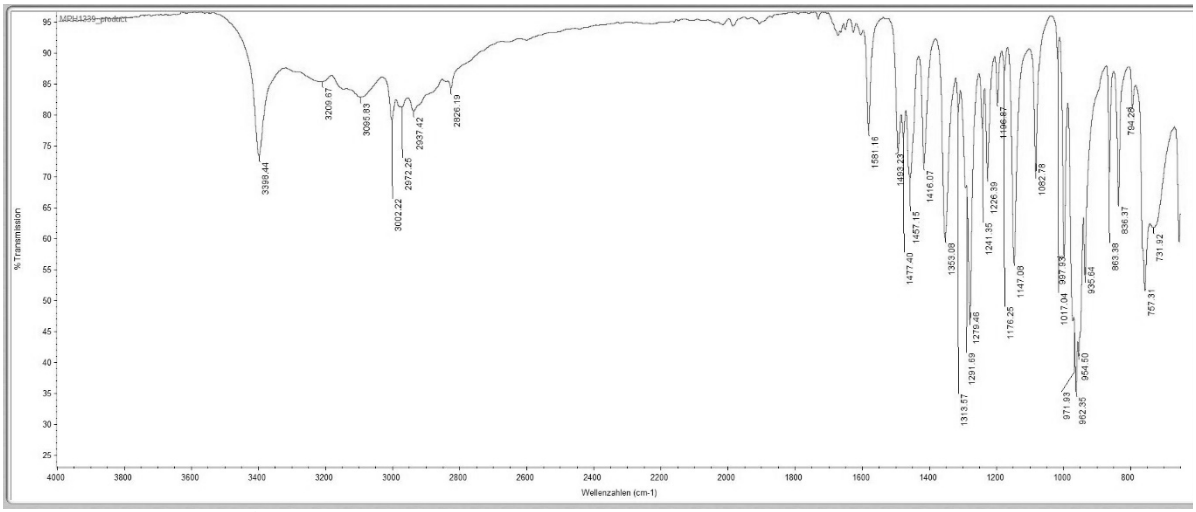


Fig. S9 FT-IR spectrum of 4,5-dimethoxy isophthalaldehyde dioxime.

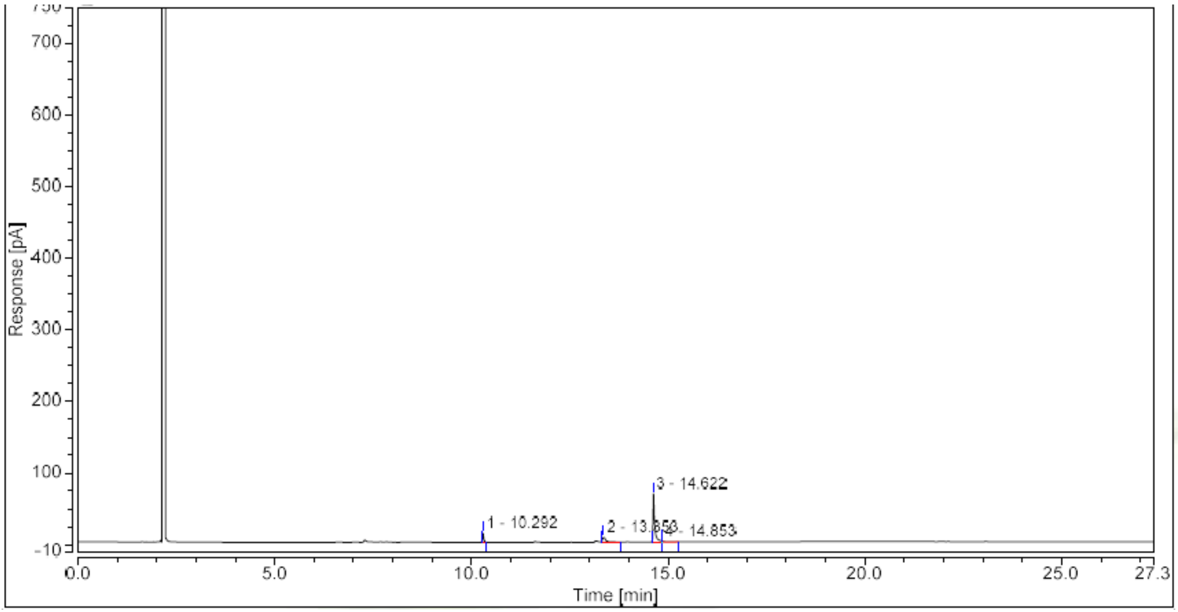


Fig. S10 GC chromatogram of 4,5-dimethoxy isophthalaldehyde dioxime.

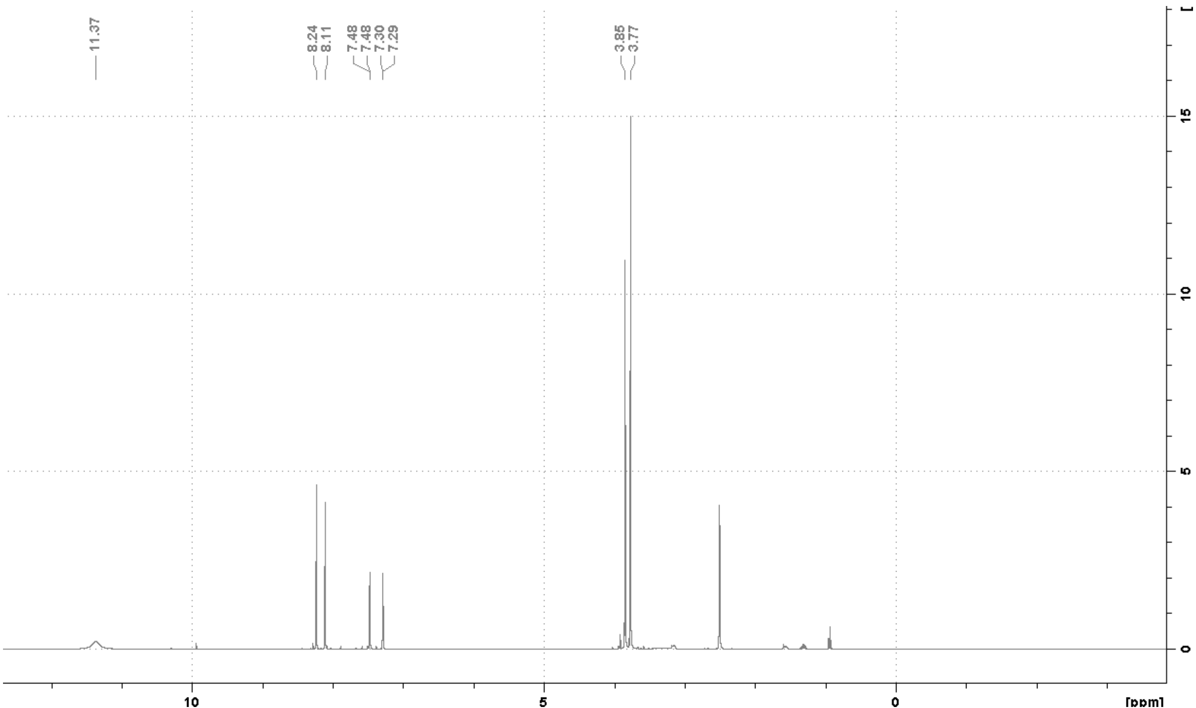


Fig. S11 ^{1}H NMR spectrum of 4,5-dimethoxy isophthalaldehyde dioxime.

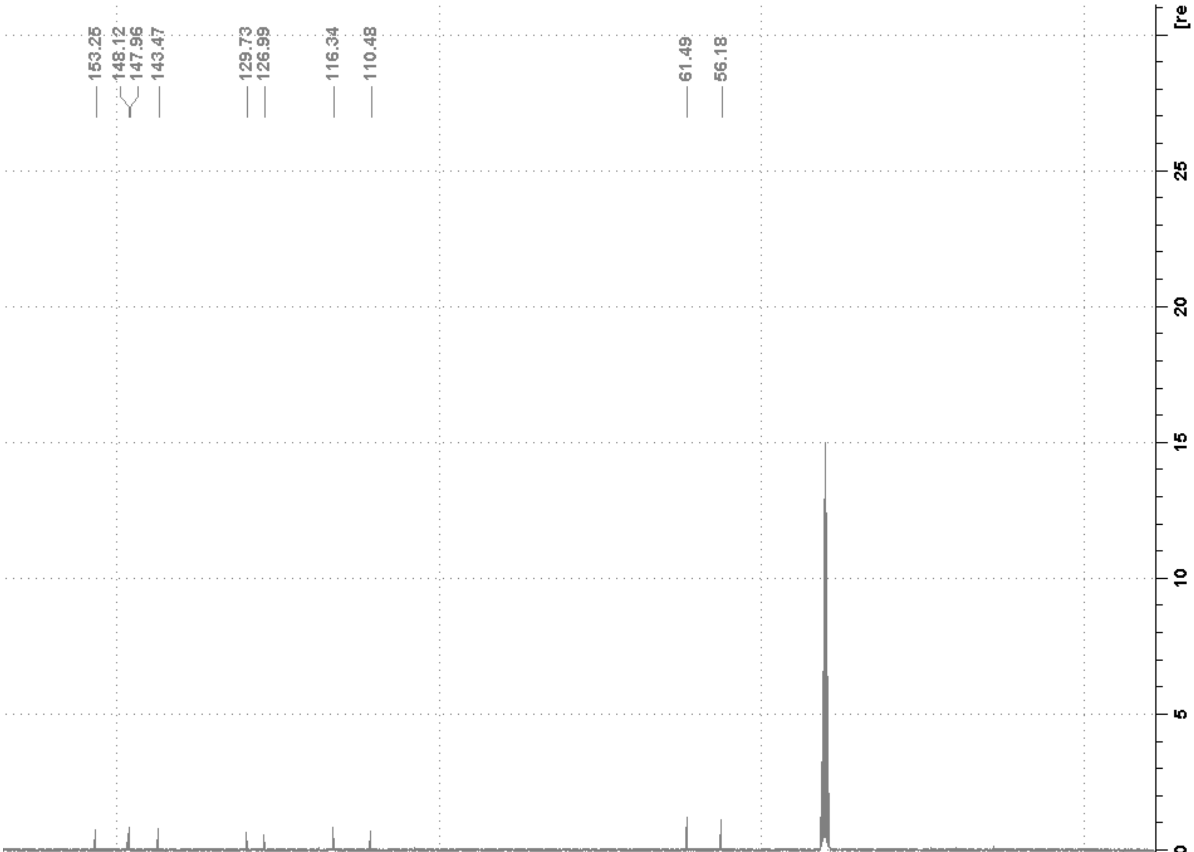


Fig. S12 ^{13}C NMR spectrum of 4,5-dimethoxy isophthalaldehyde dioxime.

4,5-Dimethoxy-1,3-benzenedimethanamine / Dimethoxy-MXDA (3)

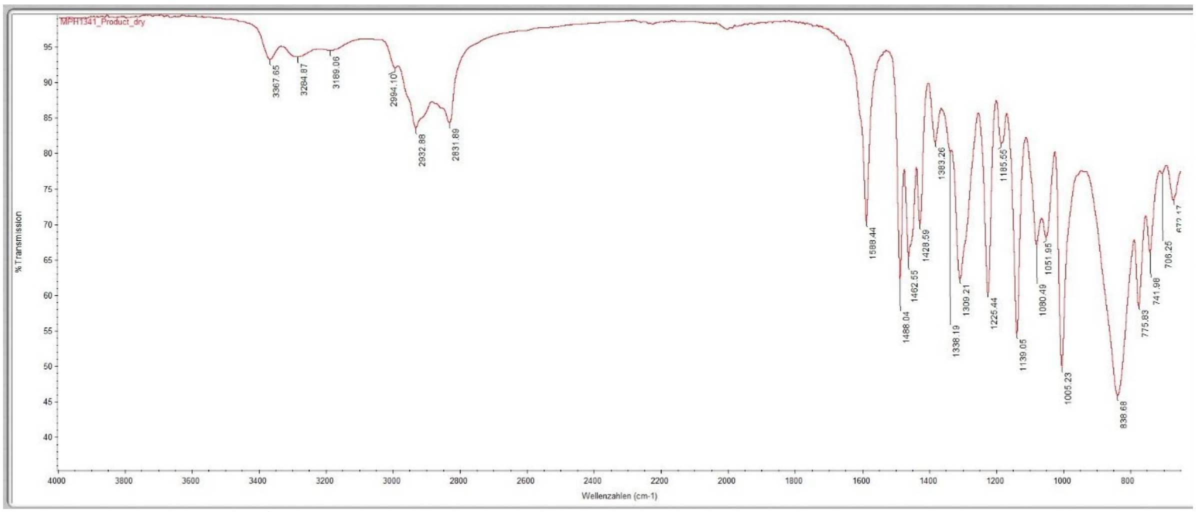


Fig. S13 FT-IR spectrum of **3**.

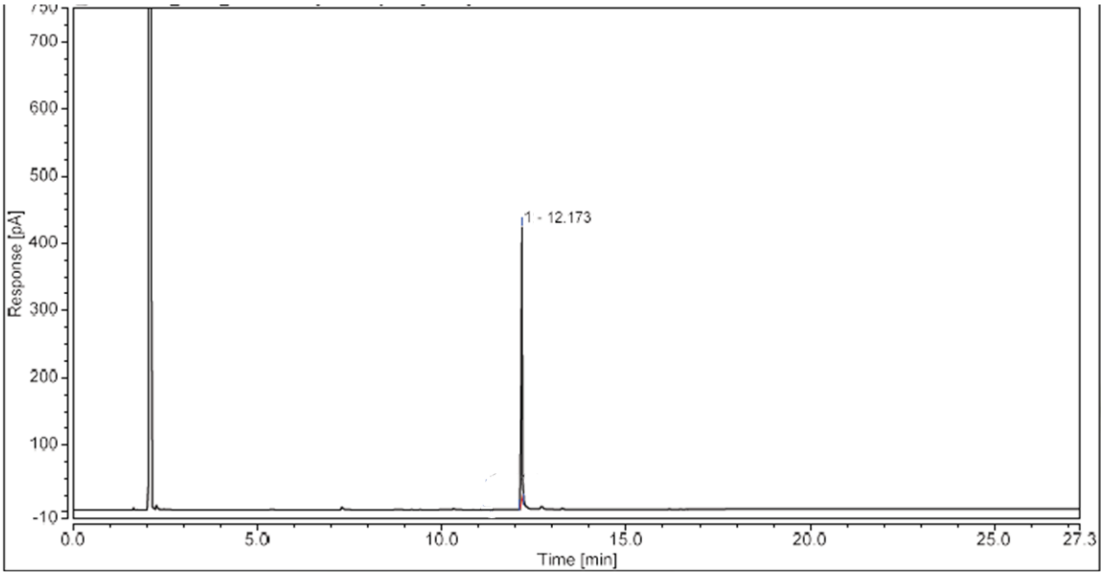


Fig. S14 GC chromatogram of **3**.

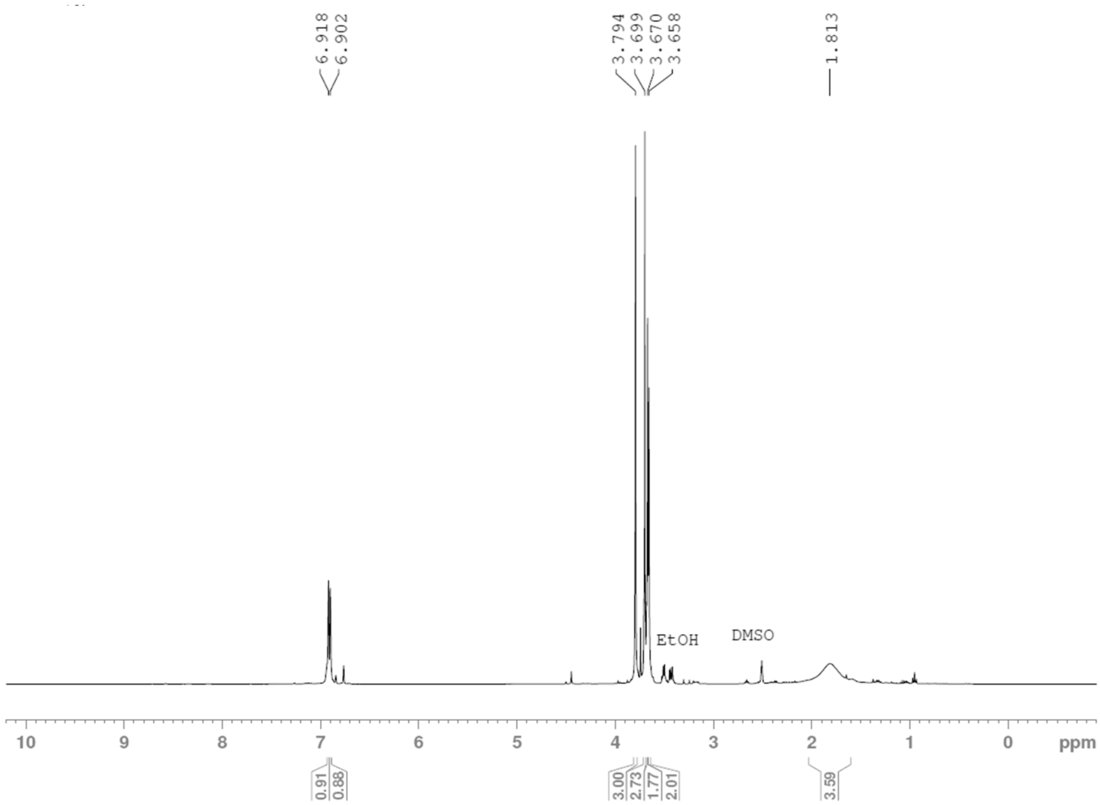


Fig. S15 ^{1}H NMR spectrum of **3**.

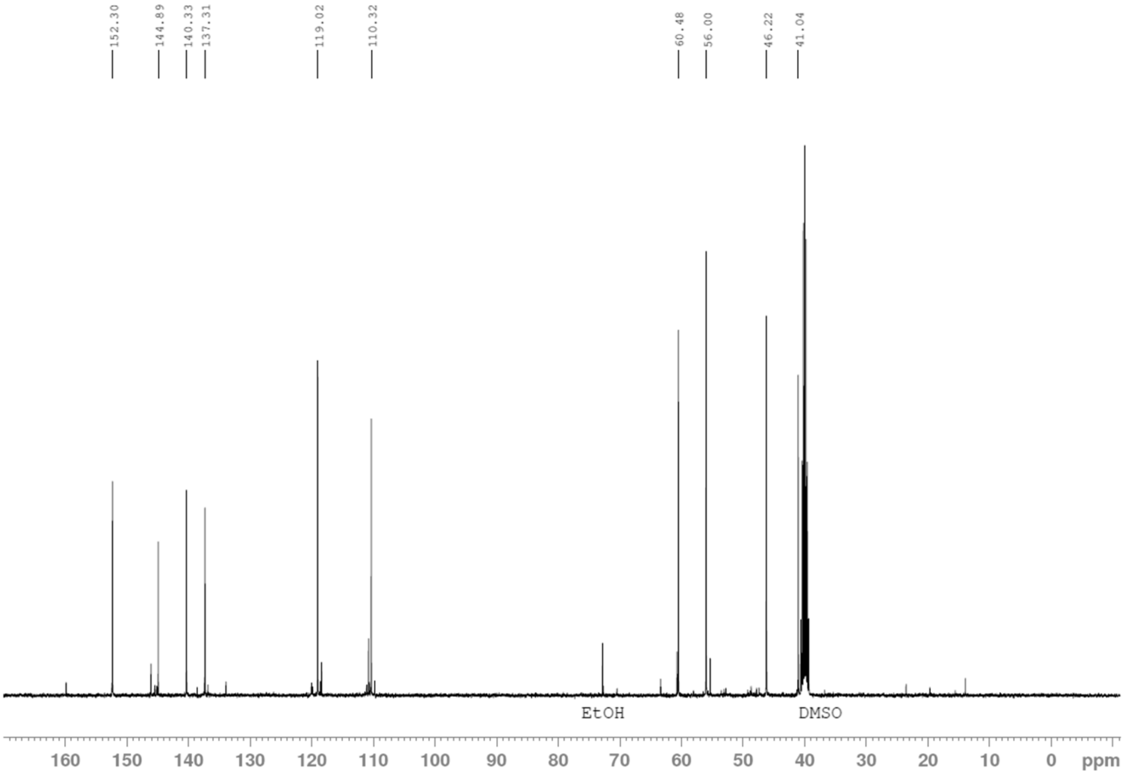


Fig. S16 ^{13}C NMR spectrum of **3**.

2,4-Bis(dimethylaminomethyl)-6-methoxyphenol / Methoxy-K54 (4)

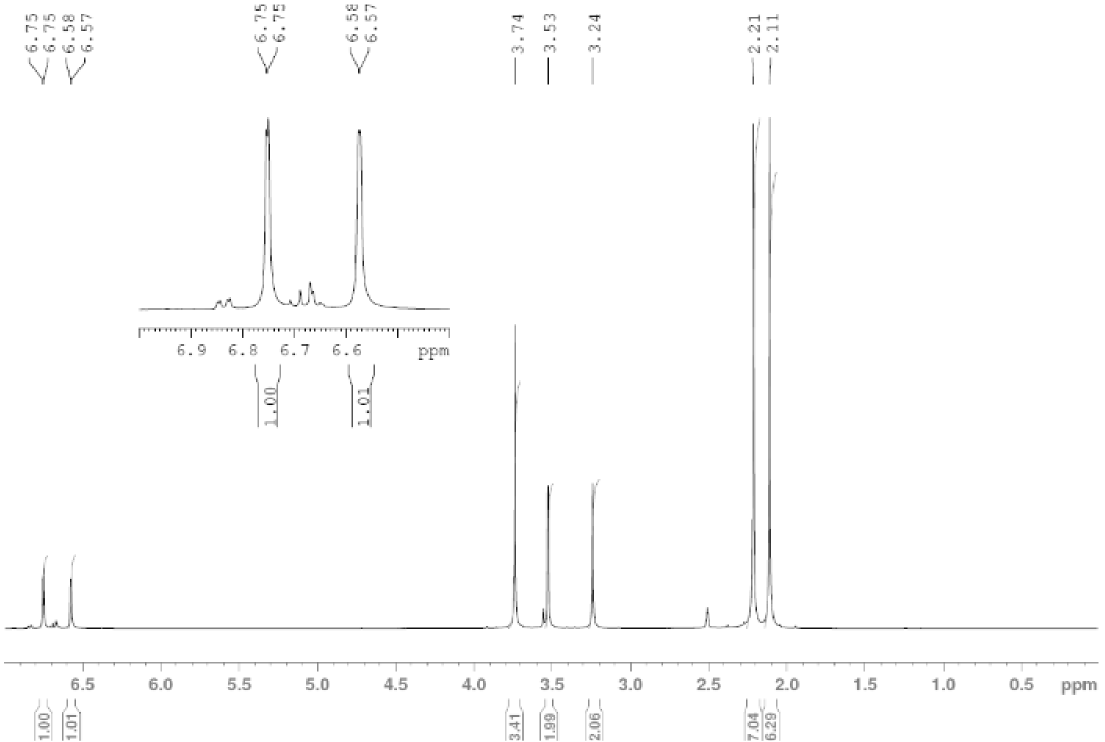


Fig. S17 ^{1}H NMR spectrum of **4**.

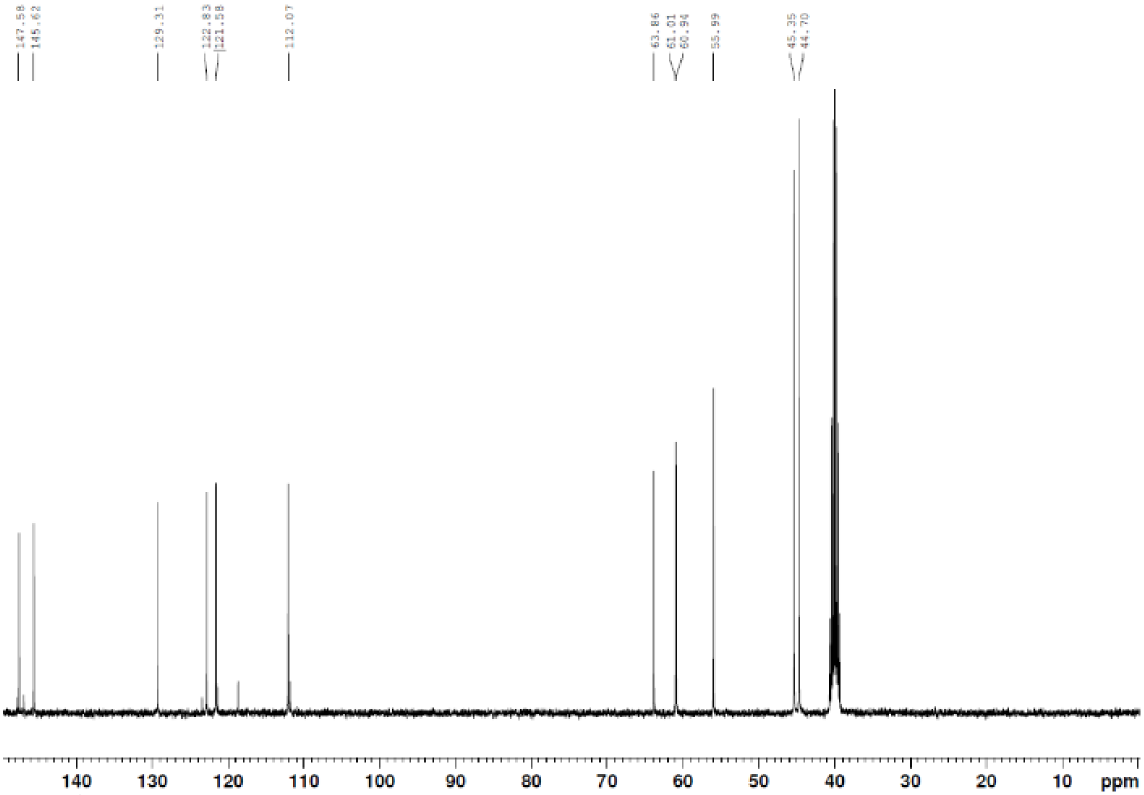


Fig. S18 ^{13}C NMR spectrum of **4**.

Epoxy thermosets

Material properties

Viscosity

The viscosity was measured 5 minutes after the start of the curing reaction at 20 °C using a thermostatically controlled cone-plate viscometer Rheotec RC30 (cone diameter 50 mm, cone angle 1°, cone-plate gap 0.005 mm, shear rate 10 s^{-1}).

Tack free time

The gelation of the polymer was determined via tack free times as a qualitative measure of the progress of the overall crosslinking process. All tack free times were measured in a climate room at 23 °C and 50 % relative humidity by tapping the surface of a freshly mixed sample of approximately 3 g at regular intervals with the head of a plastic pipette, until no residue remained on the pipette for the first time.

Glass transition temperature

The glass transition temperature (T_g) was determined by means of DMTA measurements on cylindrical samples (height 2 mm, diameter 10 mm), which were stored as described for mechanical test samples, using a Mettler DMA/SDTA 861e instrument, measuring in shear mode with a 10 Hz excitation frequency and a heating rate of 5 K/min. The samples were cooled to -70 °C and then heated to 200 °C while determining the storage G' and loss modulus G'' as well as the complex modulus of elasticity G*, with the value of T_g being read as the maximum in the curve of the loss angle tan δ.

Tensile tests

Tensile strength, elongation at break (E break) and the modulus of elasticity at 0.05-0.25 % strain (E modulus) were measured according to EN ISO 527 at 23 °C and 50 % r. h. at a rate of 10 mm/min.

Pendulum hardness

The pendulum hardness according to König (DIN EN ISO 1522) was determined on the thin films.

Blushing and yellowing

The blushing and yellowing behaviour was determined on the thin films.

Preparation of epoxy thermosets

Table S1 EP-bulk formulation.

Amount	Chemical
60 wt.-%	Bisphenol A diglycidyl ether
20 wt.-%	Bisphenol F diglycidyl ether
15 wt.-%	1,4-Butane diglycidyl ether
5 wt.-%	C12-C14-Alkyl glycidyl ether

The used amine hardener was Dimethoxy-MXDA (**3**) for the bio-based epoxy thermoset and MXDA for the petrol-based epoxy thermoset. EP-bulk and the corresponding amine hardener was used for production of specimens for mechanical tests.

Table S2 EP-coat formulation.

Amount	Chemical
84 wt.-%	Bisphenol A diglycidyl ether
16 wt.-%	C12-C14-Alkyl glycidyl ether

The used amine hardener was Dimethoxy-MXDA (**3**) for the bio-based epoxy thermoset and MXDA for the petrol-based epoxy thermoset. EP-coat and the corresponding amine hardener was used for the production of thin film plates.

Table S3 EP-coat-accelerated formulation.

Amount	Chemical
84 wt.-%	Bisphenol A diglycidyl ether
16 wt.-%	C12-C14-Alkyl glycidyl ether

The used amine hardener was N-benzyl-1,2-ethandiamine (B-EDA) with an AEW of 50.1 g/Val and prepared by reductive alkylation of 1 ,2-ethanediamine and benzaldehyde in a molar ratio of 3:1 and subsequent purification by distillation.

Methoxy-K54 (**4**) was used as an accelerator in the bio-based system and Ancamine® K54 was used in the petrol-based benchmark system.

Material properties data

Table S4 Comparison of material properties between molecule **3** and MXDA.

Conditions	Dimethoxy-MXDA (**3**)	MXDA
AEW (exp.)	49.06 g/Val	34.05 g/Val
Hardener Viscosity	277 mPa s	14 mPa s
Mixing Viscosity	1470 mPa s	740 mPa s
Tack free time	1-2 h	> 4 h
Skin Formation	No	Yes

Cured bio-based epoxy thermoset

Table S5 Pendulum Hardness according to König for bio-based epoxy thermoset.

Conditions	Pendulum Hardness according to König
1d 23 °C /50 % r.h.	74 s
2d 23 °C /50 % r.h.	148 s
7d 23 °C /50 % r.h.	167 s
14d 23 °C /50 % r.h.	167 s
7d 8 °C /80 % r.h.	39 s
7d 8 °C /80 % r.h. + 7d 23 °C / 50 % r.h.	50 s
7d 8 °C /80 % r.h. + 7d 23 °C / 50 % r.h.	76 s

Table S6 Yellowing and blushing for bio-based epoxy thermoset.

Q Sun (72h) (ΔE)	Blushing
17.3	Slightly cloudy

Cured petrol-based epoxy thermoset

Table S7 Pendulum Hardness according to König for petrol-based epoxy thermoset.

Conditions	Pendulum Hardness according to König
1d 23 °C /50 % r.h.	11 s
2d 23 °C /50 % r.h.	13 s
7d 23 °C /50 % r.h.	16 s
14d 23 °C /50 % r.h.	22 s
7d 8 °C /80 % r.h.	4 s
7d 8 °C /80 % r.h. + 7d 23 °C / 50 % r.h.	4 s
7d 8 °C /80 % r.h. + 7d 23 °C / 50 % r.h.	4 s

Table S8 Yellowing and blushing for petrol-based epoxy thermoset.

Q Sun (72h) (ΔE)	Blushing
10.3	Sticky cloudy