Organic & Biomolecular Chemistry

Electronic Supplementary Information (ESI)

Synthesis of Guerbet ionic liquids and extractants as β-branched biosourceable hydrophobes

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Chemicals

L-Lysine (98%, 56-87-1) and tri-*N*-octylamine (97%, 1116-76-3) were purchased from Acros Organics (Geel, Belgium). *N*-Methylformamide (99%, 123-39-7) was purchased from Alfa Aesar (Karlsruhe, Germany). dimethyl carbonate (≥99.8%, 616-38-6) was purchased from Carl-Roth (Karlsruhe, Germany). formamide (99.5%, 75-12-7), calcium chloride anhydrous (95%+, 10043-52-4), and formic acid (99-100%, 64-18-6) were purchased from Chem-Lab (Zedelgem, Belgium). Palladium on activated carbon (10% Pd, unreduced, 7440-05-3) was purchased from J&K Scientific (Overpelt, Belgium). 1-hexanal (99.9%, 66-25-1), 1-heptanal (98.3%, 111-71-7), 1-octanal (99.8%, 124-13-0), 1-nonanal (99.2%, 124-19-6), 1-decanal (97.8%, 112-31-2), deuterochloroform (99.8 atom % D with 0.03 % (v/v) TMS, 865-49-6) and Raney®-Nickel 2800, slurry in water (≥89%, 7440-02-0) were purchased from Sigma-Aldrich (Diegem, Belgium). Sodium hydrogencarbonate (>99%, 144-55-8) was purchased from Fisher Scientific (Merelbeke, Belgium).

Petroleum ether (technical grade), methanol (technical grade), isopropanol (technical grade) and sodium hydroxide (Norma-pur) were obtained from VWR (Heverlee, Belgium). Petroleum ether was distilled prior to use to remove high boiling residues all other chemicals were used without any further purification.

Equipment

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 spectrometer. Fourier transform infrared spectra were recorded in ATR mode (attenuated total reflectance) on a Bruker Vertex 70 spectrometer equipped with a Bruker Platinum ATR module and a diamond crystal. HRMS spectra were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at 3 uL/min and spectra were obtained in positive (or negative) ionization mode with a resolution of 15000 (FWHM) using leucine enkephalin as lock mass. The water content in samples was measured using a Mettler-Toledo V30S volumetric Karl Fischer titrator. Viscosities and densities were measured on an Anton-Paar Lovis 2000 M/ME rolling-ball viscometer and DMA 4500 M densitometer. TGA and DSC analysis were carried out on a TA Instruments TGA Q500 and a TA Instruments DSC Q2000 respectively, with a heating/cooling rate of 10 °C min^{-1}. Ionic liquids were pre-dried for 120 min at 80 °C before of the TGA measurement. Vacuum measurement were carried out with the Pfeiffer TPG 201 digital manometer. For the dropping of the reagents it was used a Ismatec Reglo ICC peristaltic pump.

Experimental methods

General procedure 1: Solvent assay in NMR tube. The reaction was carried out on 1-hexanal (2 mmol, 0.2 g) catalysed by a L-lysine (0.5 mmol, 0.073 g) suspension in a solvent (2 mL) at 20-22 °C in a closed NMR tube. In absence of a deuterated analogue, the reaction was carried out in a non-deuterated solvent with an addition of deuterochloroform (100-200 µL) to allow the spectrometer signal lock-in. After 1.5, 6 and 24 h, the reaction was monitored via observation of the aldehyde peak shifting in the ^{1}H NMR spectra. Conversion and selectivity were determined via GC-MS analysis.

General procedure 2: Catalyst loading assay. The reaction was carried out at 20-22 °C in a closed reaction tube (10 mL), stirred with a stirring bar at 800-1200 rpm on a magnetic stirring plate. L-lysine (0.0125, 0.025, 0.05, 0.1, 0.2, and 0.5 mmol) was added to a solution of 1-hexanal (1 mmol, 0.1 g) in isopropanol (1 mL). At 1.5, 3 and 5 h at 20-22 °C, the reaction progression was monitored via ^{1}H NMR spectroscopy in deuterochloroform.

General procedure 3: Substrate concentration assay. The reaction was carried out at 20-22 °C in a closed reaction tube (10 mL), stirred with a stirring bar at 800-1200 rpm on a magnetic stirring plate. 1-Hexanal (1, 3, 5, 10, 20 mmol) was added to a suspension of L-lysine (0.05 eq) in isopropanol (1 mL). After 24 h at 20-22 °C, the reaction progression was monitored via ^{1}H NMR spectroscopy in deuterochloroform.

General procedure 4: Substrate scope assay. The reaction was carried out at 20-22 °C in a closed centrifugation tube (15 mL), shaken at 1000 rpm on an orbital thermo-shaker. An aldehyde was added (1 mmol) to a suspension of L-lysine (0.05 mmol, 0.073 g) in IPA (1 mL). After 24 h at 20-22 °C, the reaction progression was monitored via ^{1}H NMR spectroscopy in deuterochloroform.

General procedure 5: Optimised aldol condensation. The reaction was carried out in an Erlenmeyer conical flask (1 L). An aldehyde (2 mol) was added to a suspension of L-lysine (0.1 mol, 14.7 g) in isopropanol (260 mL, 156 g, 2.6 mol). After four hours at 40 °C, the reaction completion was verified via ^{1}H NMR spectroscopy in deuterochloroform.

Overtime, the crude adduct is unstable.[1–3] Purification could be achieved by flash chromatography with methyl-*tert*-butyl-ether as eluent phase (about 80% yield) or by discontinuous solvent extraction with petroleum ether and formic acid (about 50-85% yield).

General procedure 6: Catalyst loading assay. In a round bottom flask (1000 mL), 1-hexanal (24.6 mL, 200 mmol, 20 g) was added to a suspension of L-lysine (0.05 eq, 10 mmol, 1.46 g) in isopropanol (1.3 eq, 230 mmol, 20 mL). The reaction was stirred at 40C for 6 h. After reaction completion, Pd/C (10% loading) was added in various percentages to different batches (*i.e.* 10,5,2.5% w/w). The reaction showed complete conversion at about or above 5% and near completion at 2.5%. Folowing tests allowed the determination of the minimum needed loading at about 3% w/w.

General procedure 7: Catalyst reactivation. The recovered catalyst was shaken with methanol and filtered (SAFETY: catalyst pyrophoric, never dry on the filter). The process was repeated until the filtrate resulted colourless. Then, the catalyst was dried out at high vacuum. The dried catalyst must be handled under an inert atmosphere all the time (SAFETY: the drier, the more it is pyrophoric). If needed, the reactivated catalyst was topped up with a new one to even out recovery losses (about 10 to 15%).

General procedure 8: α,β-conjugated aldehyde selective reduction. In two Erlenmeyer conical flasks (0.5 L) the adduct of the aldol condensation was shaken on an orbital shaker (285 rpm, 55 mm orbit) with palladium over carbon (3% w/w, 10% w/w loading) under H_2 atmosphere, via a three-layered balloon (SAFETY: minimum two balloons are needed to avoid formation of explosive gas mixtures, hydrogen introduction was preceded by three nitrogen flushes of the reaction vessel). The reaction was carried out at 20-22 °C. Until full conversion, reaction progression was verified via ^{1}H NMR spectroscopy in deuterochloroform.

General procedure 9. Telescoped aldol condensation and ene-reduction. In an Erlenmeyer conical flask (1 L), L-lysine (14.7 g, 0.1 mol, 0.05 eq) was added to an isopropanol solution (260 mL, 2.6 mol, 1.3 eq) of aldehyde (2 mol, 1 eq). The flask was equipped with a stirring bar and flushed with nitrogen (3x). The flask was stirred under heating at 40 °C for 4 to 6 hours. The reaction completion was verified via ^{1}H NMR. Then, the stirring bar was removed and the General procedure 8 was followed.

General procedure 10: Aldehyde isolation. The reaction adduct was concentrated in a rotatory evaporator. The crude product was dissolved in an equivalent volume of petroleum ether and the resulting solution was shaken with formic acid (about 1/5 of the volume of the petroleum ether fraction). The formic acid layer was separed, re-extracted with petroleum ether, and then discarded. The combined petroleum ether fractions were washed with water and neutralised with saturated aqueous sodium hydrogencarbonate. The organic layer was rinsed with water, made anhydrous with magnesium sulphate, filtered, and dried at the rotatory evaporator. The product was left overnight at the Schlenk line (5 mbar, 22 °C, under stirring) and then distilled via vacuum distillation. The product was characterised via GC-MS, ^{1}H NMR, ^{13}C NMR, FTIR, HRMS, densitometry, and viscosimetry.

General procedure 11: *N*-methyl formamide Leuckart-Wallach reaction. The reaction was carried out in a 500 mL three-neck round bottom flask connected to a Dean-Stark apparatus and heated at 140 °C under a weak nitrogen flow and with vigorous stirring (1400 rpm, Octoval 38x16 mm PTFE stirrer bar), containing *N*-methyl-formamide (130 mL, 133 g, 2.25 mol, 4.5 eq.) and Raney nickel (0.15 g, 2.5 mmol). To the hot amide, the aldehyde (0.5 mol, 1 eq) and formic acid (56.59 mL, 69.05 g, 1.5 mol, 3 eq.) were added in a dropwise manner over 2.5 h. Afterwards, the reaction mixture was left stirring at 140 °C for another 1.5 h and then let to slowly cool. The reaction mixture was slowly added to a saturated solution of sodium hydrogencarbonate (300 mL) and shaken in a separatory funnel until the effervescence ceased (SAFETY: use oversized separator funnels and gentle shaking to counteract the vigorous effervescence caused by the neutralisation of the formic acid trapped in the organic phase). Then, the organic layer was washed with distilled water. The neutralised organic fractions were added to methanol in a separatory funnel (250 mL) for at least three times. The methanol fractions were collected, dried and stored to be recycled as a starting material in following batches. The remaining fraction that separated from methanol was tested at the GC-MS to determine if further purification with methanol was needed. The purification is sometimes strongly hindered by the presence of other solvents in the sample material and therefore prior to continue the purification process the material was fully dried at the high vacuum. Colour was a good indicator of the product purity. If further purification was needed, the product was shaken (3000 rpm, 25 °C) with methanol (3x40 mL). The product was dried at the Schlenk line overnight. The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, GCMS, HRMS, TGA, DSC, densitometry, and viscosimetry.

General procedure 12: Formamide Leuckart-Wallach reaction. The reaction was carried out in a 100 mL three-neck round bottom flask connected to a Dean-Stark apparatus and heated at 140 °C under a weak nitrogen flow and with vigorous stirring (1400 rpm, Octoval 19x10 mm PTFE stirrer bar), containing formamide (30 mL, g, 0.75 mol, 7.5 eq.) and Raney nickel (0.15 g, 2.5 mmol). To the hot amide, the aldehyde(0.1 mol, 1 eq) and formic acid (37 mL, g, 0.75 mol, 7.5 eq.) were added in a dropwise manner over 1.5 h. After the dropping was ceased, the reaction mixture was left stirring at 140 °C for another 2 h; after which stirring and heating were ceased and the round bottom flask was let to slowly cool. The reaction mixture was transferred into a 250 mL separatory funnel and the transparent bottom layer was carefully discarded. We transferred the remaining layer to a 1L separatory funnel and shaken with a saturated solution of sodium hydrogencarbonate until effervescence ceased. Then, the organic layer was washed with distilled water. The neutralised organic fractions were shaken on a shaker (3000 rpm, 25 °C) in 2 glass vials of 40 mL diluted with methanol. After shaking for few hours the vials were centrifuged(2500 rpm, 10 min) and the methanol fractions were

collected into another container. The procedure was repeated adding fresh methanol. The shaking time was increased to 6-8 h to facilitate the removal of trace impurities. Generally after 3/4 washes the product resulted pure (verified via GC-MS). If further purification was needed, first the product was concentrated in vacuo and then the methanol purification procedure was repeated. The pure product was dried at the Schlenk line overnight. The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, GCMS, HRMS, TGA, DSC, densitometry, and viscosimetry.

General procedure 13: Dimethyl carbonate quaternisation. Dimethyl carbonate (3 mL), methanol (1 mL), calcium chloride (0.6 g), and a tertiary amine (1 mL) were added to a 15 mL autoclave. Then, the autoclave was sealed and heated for 48 h in an oven preheated at 145 °C. After 48 h, the autoclave was cooled to 20-22 °C and slowly vented to allow the release of the build-up of carbon dioxide. The organic fractions were filtered over a filtering funnel (10 µm) and the solid residue was washed twice with petroleum ether. The collected fractions were then thoroughly dried at a rotatory evaporator and then at high vacuum overnight (5-10 mbar, 80 °C). The concentrated fractions were then dissolved in ethyl acetate and let to settle overnight. The liquid fraction was separated from the precipitate by filtration via a syringe filter (2 µm). The pure product was concentrated at a rotatory evaporator and at the Schlenk line overnight (5-10 mbar, 80 °C). The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, HRMS, TGA, DSC.

General procedure 14: Water solubility test. In a sealed vial, the sample (0.1 g) was added to 1 mL of Milli-Q water. The sample was stirred for 10 minutes at 20-22 °C. Until the sample was found soluble, the procedure was repeated raising the Milli-Q water volume to respectively .2, .5, 1, 2, 10, 100 ml (Table 1). After determining the approximate solubility of the sample, in a sealed vial a 100 mL saturated solution aqueous solution was prepared and shaken at 30 °C at 200 rpm for 24 h. Then, the saturated solution was left at the temperature of analysis (20-22 °C) for 24 h. Amines were titrated three times with a solution of sulphuric acid via an auto-titrator equipped with a potentiometric pH-meter electrode. Titrant exact title was determined via titration of a known amount of sodium carbonate dried over 48 h at 200 °C. The test was conducted in compliance to OECD guidelines.

Table 1. Tabulated values for the approximate solubility evaluation via a visual dissolution method.

Water / mL	0.1	0.5	1	2	10	100	>100
app. solubility / g L^{-1}	>1000	1000 to 200	200 to 100	100 to 50	50 to 10	10 to 1	<1

General procedure 15: Stability test towards aqueous sodium hydroxide solutions. In a sealed vial, the sample (100 µL) was added to 1 mL of a sodium hydroxide solution (20 g in 100 mL of Milli-Q water) and shaken at 2000 rpm for 24 h at 55 °C. Then, it was extracted deuterochloroform, separated and dried with magnesium sulphate and characterised via an ^{1}H NMR spectrum. The analyses were plotted via the library Matplotlib of Python.[4]

General procedure 16: Stability test towards methanol sodium hydroxide solutions. In a sealed vial, the sample (100 µL) was added to 1 mL of a sodium hydroxide solution (20 g in 100 mL of methanol) and shaken at 2000 rpm for 24 h at 55 °C. Then, it was diluted in water, extracted deuterochloroform, separated and dried with magnesium sulphate and characterised via an ^{1}H NMR spectrum. The analyses were plotted via the library Matplotlib of Python.[4]

General procedure 17: Rheological analysis. Viscosimetry and densitometry were measured on an Anto*N*-Paar Lovis 2000 M/ME rolling-ball viscometer and DMA 4500 M densitometer. The measurements were carried out between 20 and 60 °C via a scan of 2.5 °C per step. The analyses were plotted via the library Matplotlib of Python.[4]

General procedure 18: Thermogravimetric analysis. The thermogravimetric analysis was carried out with a TA Instruments TGA Q500 via a temperature ramped scan with a step of 10 °C min^{-1}. To assure complete water removal, the ionic liquid samples were heated prior to the analysis at 80 °C under a flow of nitrogen for 120 minutes. The analyses were carried out via TA universal analysis software suite and plotted via the library Matplotlib of Python.[4]

Chemical characterisation

2-Butyl-1-octanal

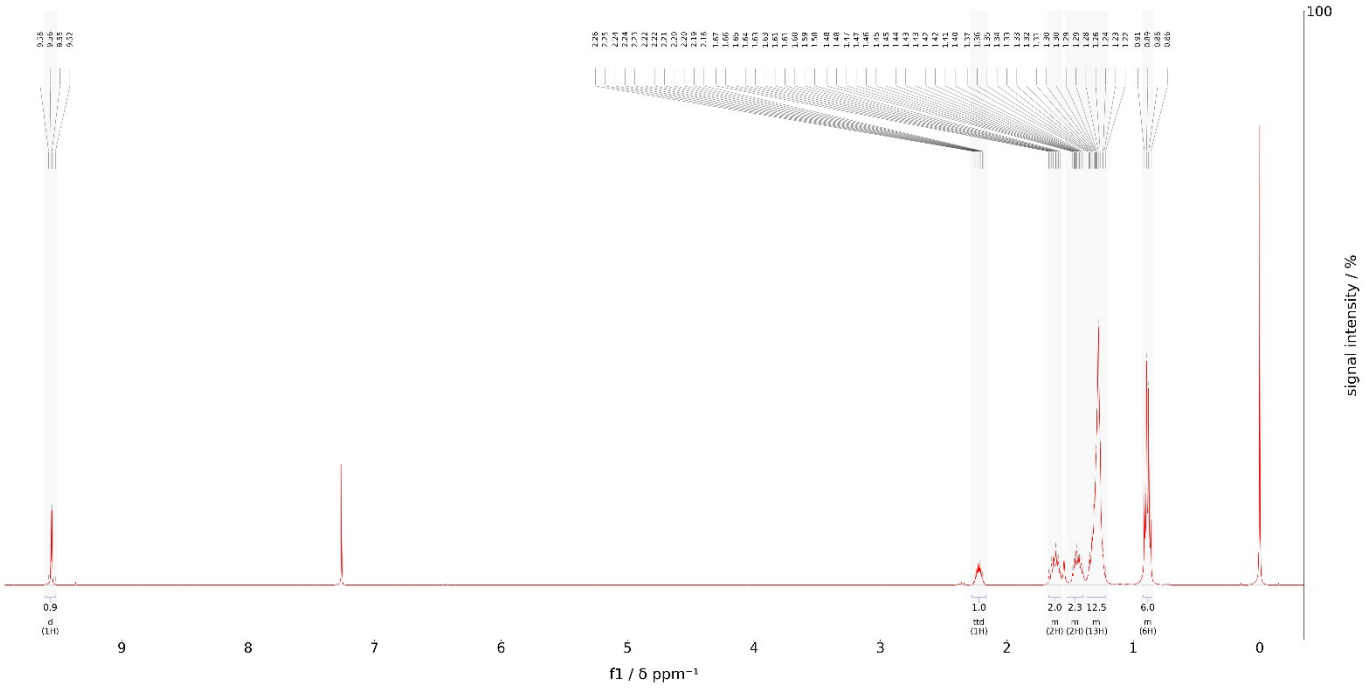

Figure S1. ^{1}H NMR of 2-butyl-1-octanal in deuterochloroform.

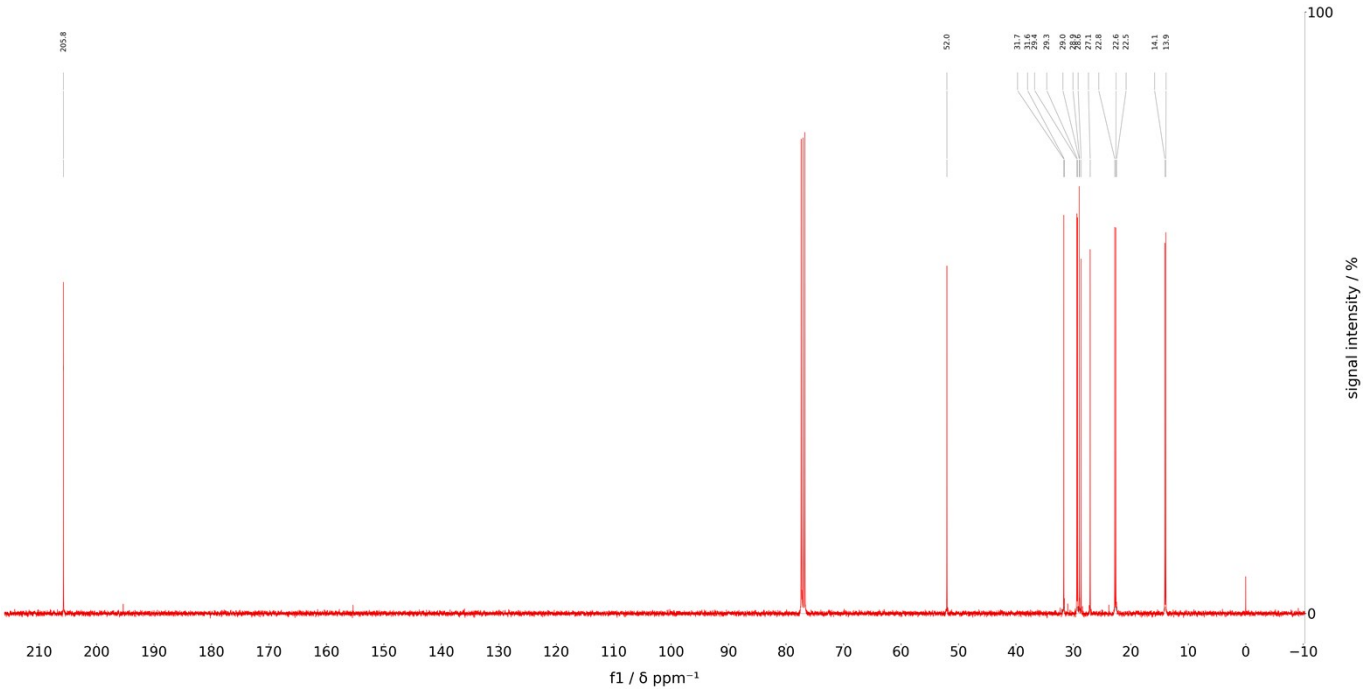

Figure S2. ^{13}C NMR of 2-butyl-1-octanal in deuterochloroform.

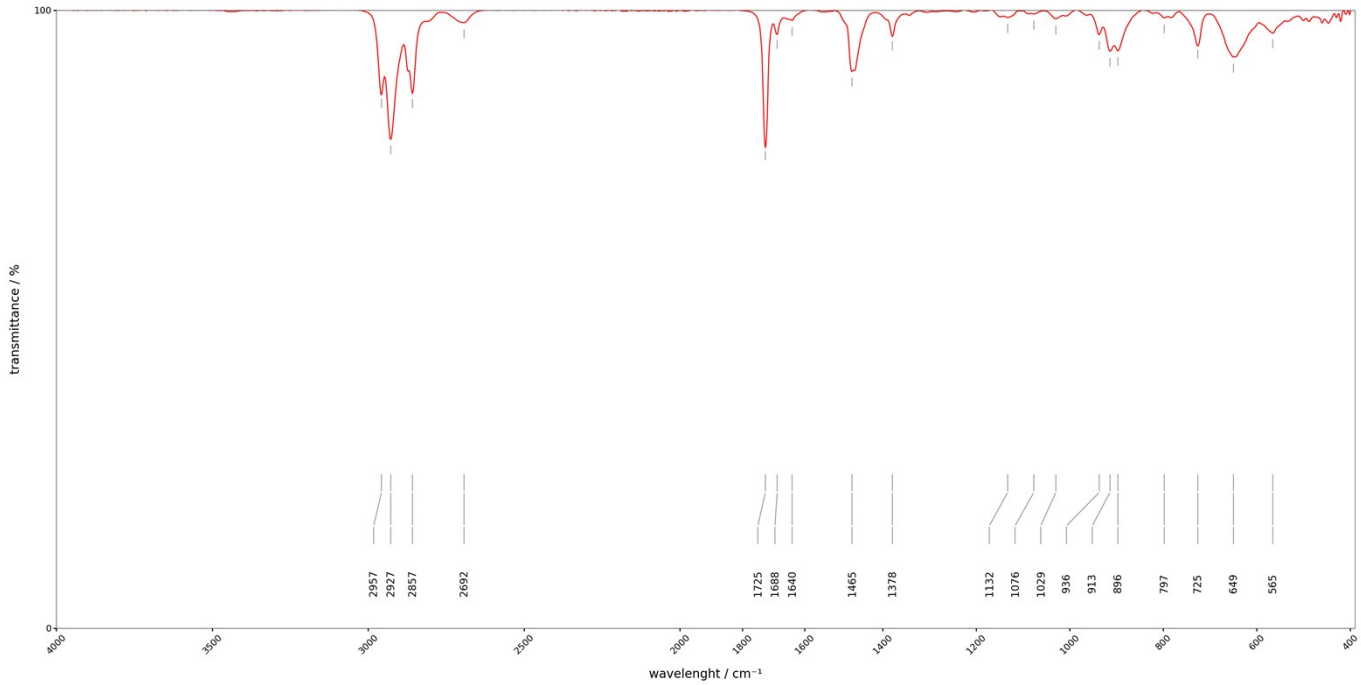

Figure S3. IR spectra of 2-butyl-1-octanal.

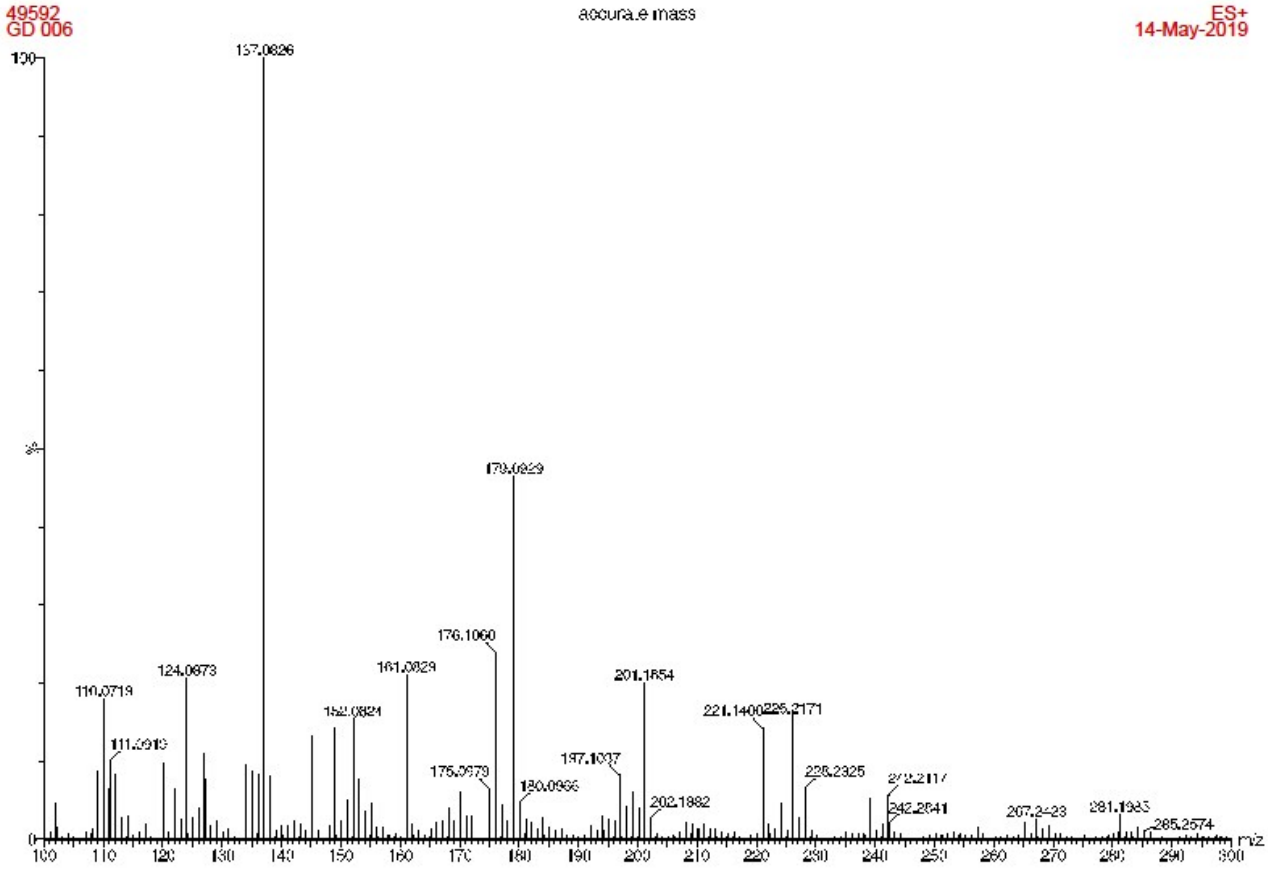

Figure S4. HRMS spectra of 2-butyl-1-octanal.

Table S1. Densitimetry and viscosimetry data for 2-butyl-1-octanal.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Coefficient Variation	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.59 Gold (20869052)
0.83050	20.02	2.432	2.929	20.00	0.03	0.25	Ø1.59 Gold (20869052)
0.82904	21.98	2.322	2.800	22.00	0.02	0.23	Ø1.59 Gold (20869052)
0.82756	23.98	2.220	2.682	24.00	0.07	0.23	Ø1.59 Gold (20869052)
0.82606	25.98	2.126	2.574	26.00	0.04	0.22	Ø1.59 Gold (20869052)
0.82457	27.98	2.036	2.470	28.00	0.02	0.27	Ø1.59 Gold (20869052)
0.82308	29.98	1.954	2.374	30.00	0.08	0.19	Ø1.59 Gold (20869052)
0.82159	31.98	1.879	2.287	32.00	0.07	0.23	Ø1.59 Gold (20869052)
0.82009	33.98	1.812	2.209	34.00	0.10	0.19	Ø1.59 Gold (20869052)
0.81860	35.98	1.747	2.134	36.00	0.12	0.24	Ø1.59 Gold (20869052)
0.81710	37.98	1.684	2.061	38.00	0.13	0.24	Ø1.59 Gold (20869052)
0.81561	39.98	1.616	1.982	40.00	0.10	0.31	Ø1.59 Gold (20869052)
0.81411	41.98	1.565	1.923	42.00	0.34	0.20	Ø1.59 Gold (20869052)
0.81261	43.98	1.518	1.869	44.00	0.28	0.19	Ø1.59 Gold (20869052)
0.81111	45.98	1.467	1.809	46.00	0.11	0.21	Ø1.59 Gold (20869052)
0.80961	47.98	1.430	1.767	48.00	0.40	0.25	Ø1.59 Gold (20869052)
0.80810	49.98	1.390	1.721	50.00	0.11	0.28	Ø1.59 Gold (20869052)
0.80660	51.98	1.339	1.660	52.00	0.64	0.23	Ø1.59 Gold (20869052)
0.80509	53.98	1.288	1.599	54.00	0.08	0.20	Ø1.59 Gold (20869052)
0.80358	55.98	1.245	1.549	56.00	0.30	0.22	Ø1.59 Gold (20869052)
0.80207	57.98	1.210	1.509	58.00	0.10	0.13	Ø1.59 Gold (20869052)
0.80056	59.98	1.180	1.474	60.00	0.33	0.15	Ø1.59 Gold (20869052)

2-Pentyl-1-nonanal

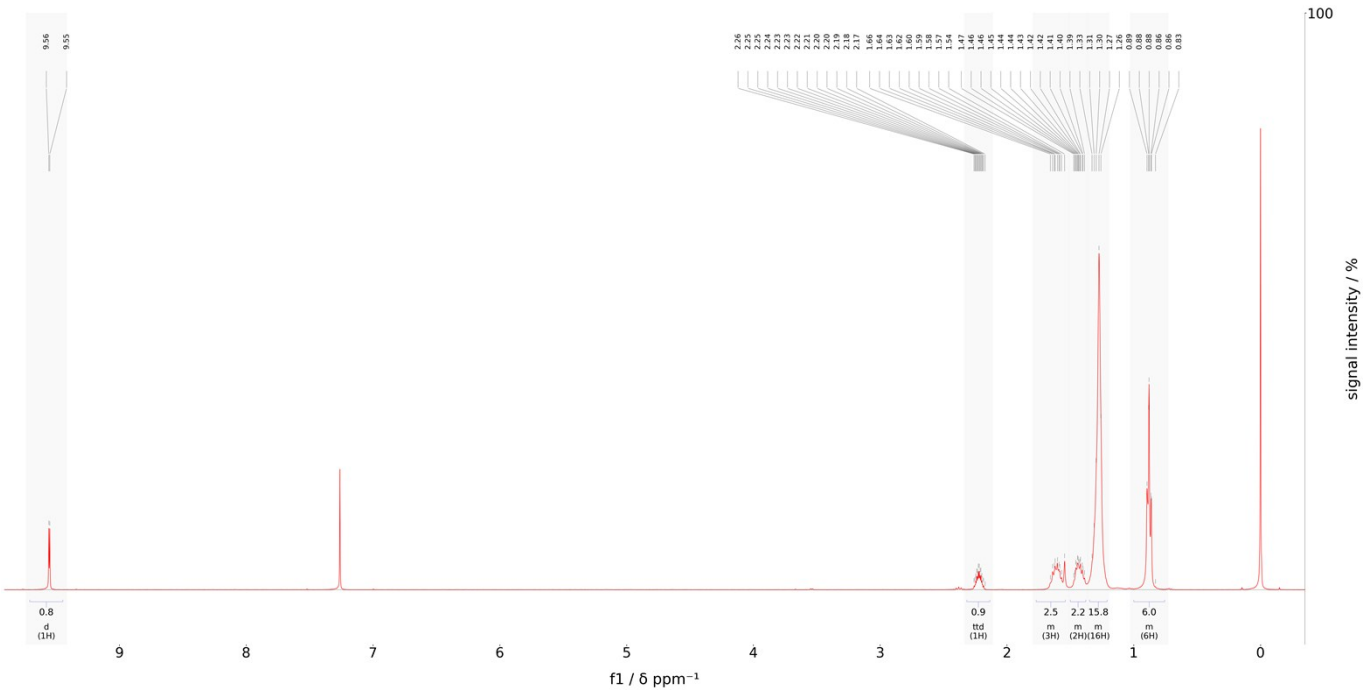

Figure S5. ^{1}H NMR of 2-pentyl-1-nonanal in deuterochloroform.

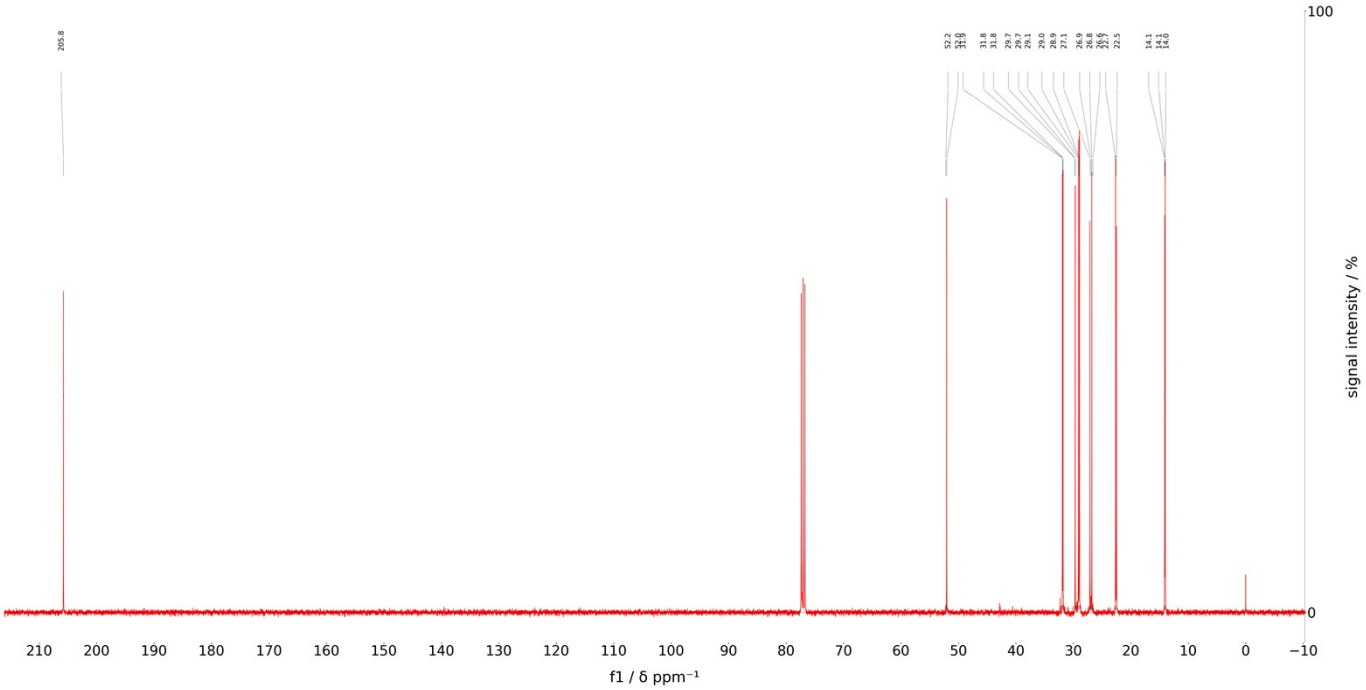

Figure S6. ^{13}C NMR of 2-pentyl-1-nonanal in deuterochloroform.

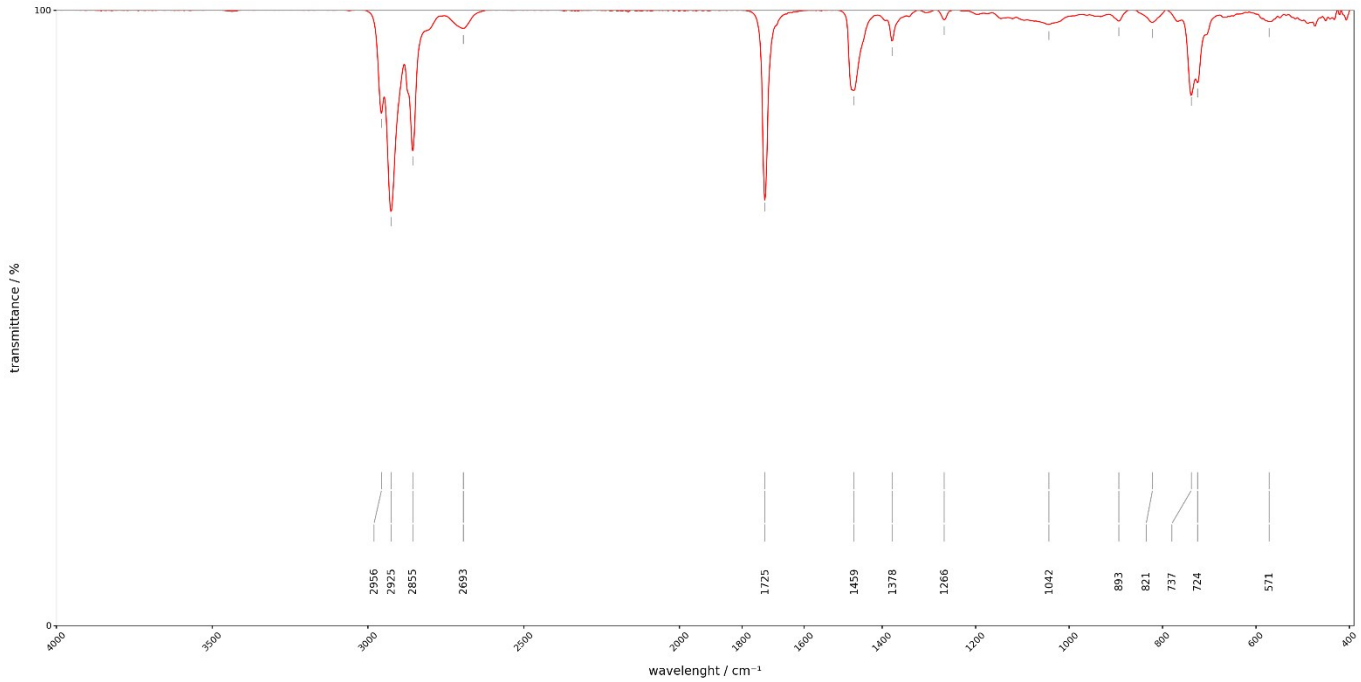

Figure S7. IR spectra of 2-pentyl-1-nonanal.

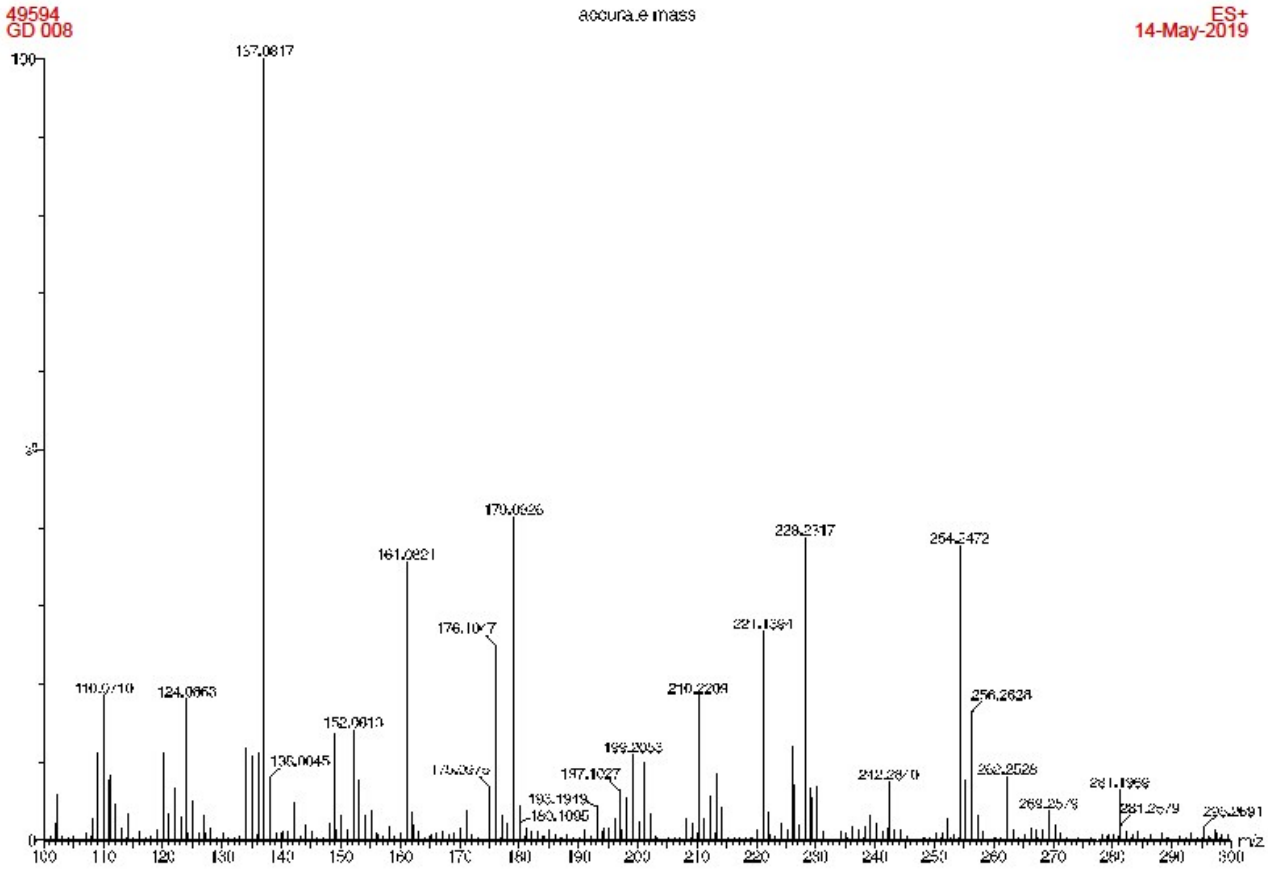

Figure S8. HRMS spectra of 2-pentyl-1-nonanal.

Table S2. Densitimetry and viscosimetry data for 2-pentyl-1-nonanal

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.59 Gold (20869052)
0.80234	59.98	1.696	2.113	60.00	0.03	0.07	Ø1.59 Gold (20869052)
0.80410	57.52	1.769	2.200	57.50	0.02	0.05	Ø1.59 Gold (20869052)
0.80590	55.02	1.850	2.296	55.00	0.02	0.06	Ø1.59 Gold (20869052)
0.80771	52.53	1.937	2.398	52.50	0.02	0.06	Ø1.59 Gold (20869052)
0.80952	50.03	2.031	2.509	50.00	0.03	0.02	Ø1.59 Gold (20869052)
0.81135	47.53	2.133	2.629	47.50	0.02	0.03	Ø1.59 Gold (20869052)
0.81317	45.03	2.244	2.759	45.00	0.02	0.05	Ø1.59 Gold (20869052)
0.81500	42.53	2.363	2.899	42.50	0.02	0.04	Ø1.59 Gold (20869052)
0.81683	40.03	2.493	3.053	40.00	0.02	0.06	Ø1.59 Gold (20869052)
0.81865	37.53	2.634	3.217	37.50	0.02	0.04	Ø1.59 Gold (20869052)
0.82048	35.03	2.787	3.397	35.00	0.01	0.02	Ø1.59 Gold (20869052)
0.82231	32.53	2.957	3.595	32.50	0.02	0.04	Ø1.59 Gold (20869052)
0.82414	30.03	3.141	3.811	30.00	0.02	0.06	Ø1.59 Gold (20869052)
0.82596	27.53	3.345	4.050	27.50	0.05	0.02	Ø1.59 Gold (20869052)
0.82779	25.02	3.567	4.309	25.00	0.03	0.07	Ø1.59 Gold (20869052)
0.82961	22.53	3.813	4.596	22.50	0.02	0.06	Ø1.59 Gold (20869052)
0.83144	20.02	4.085	4.913	20.00	0.07	0.08	Ø1.59 Gold (20869052)

2-Hexyl-1-decanal

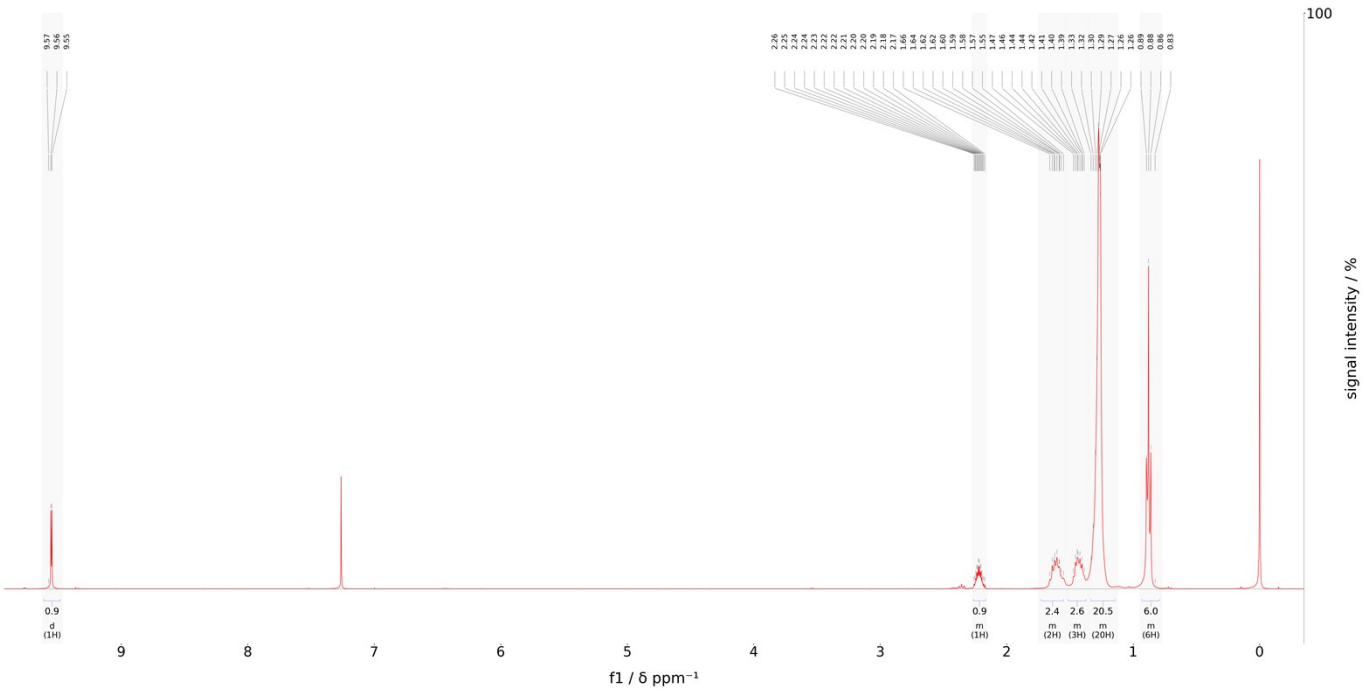

Figure S9. ^{1}H NMR of 2-hexyl-1-decanal in deuterochloroform.

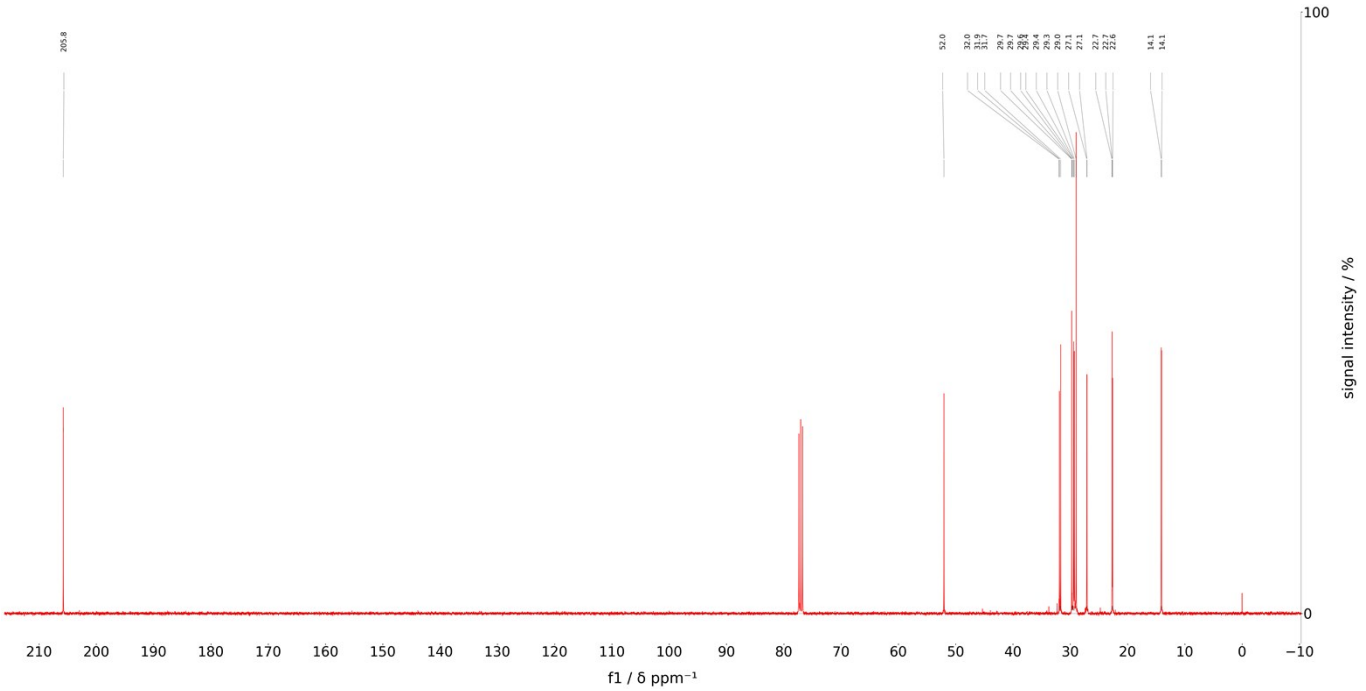

Figure S10. ^{13}C NMR of 2-hexyl-1-decanal in deuterochloroform.

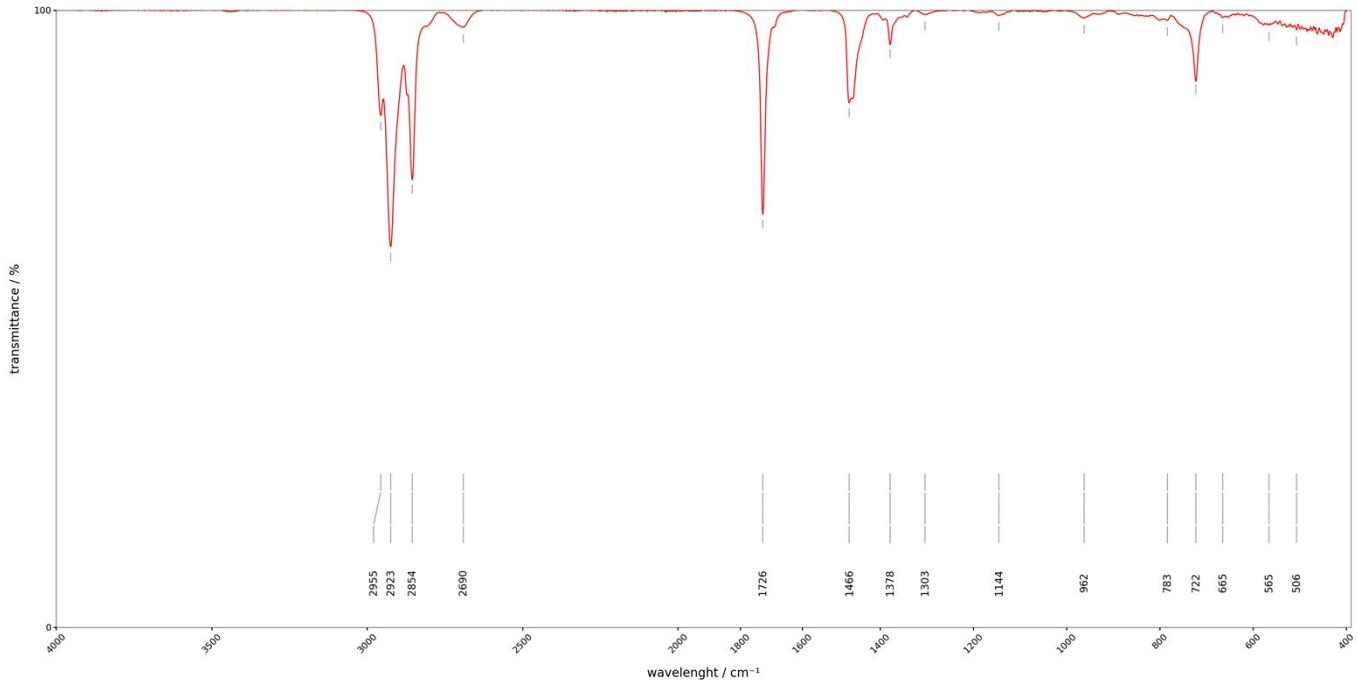

Figure S11. IR spectra of 2-hexyl-1-decanal.

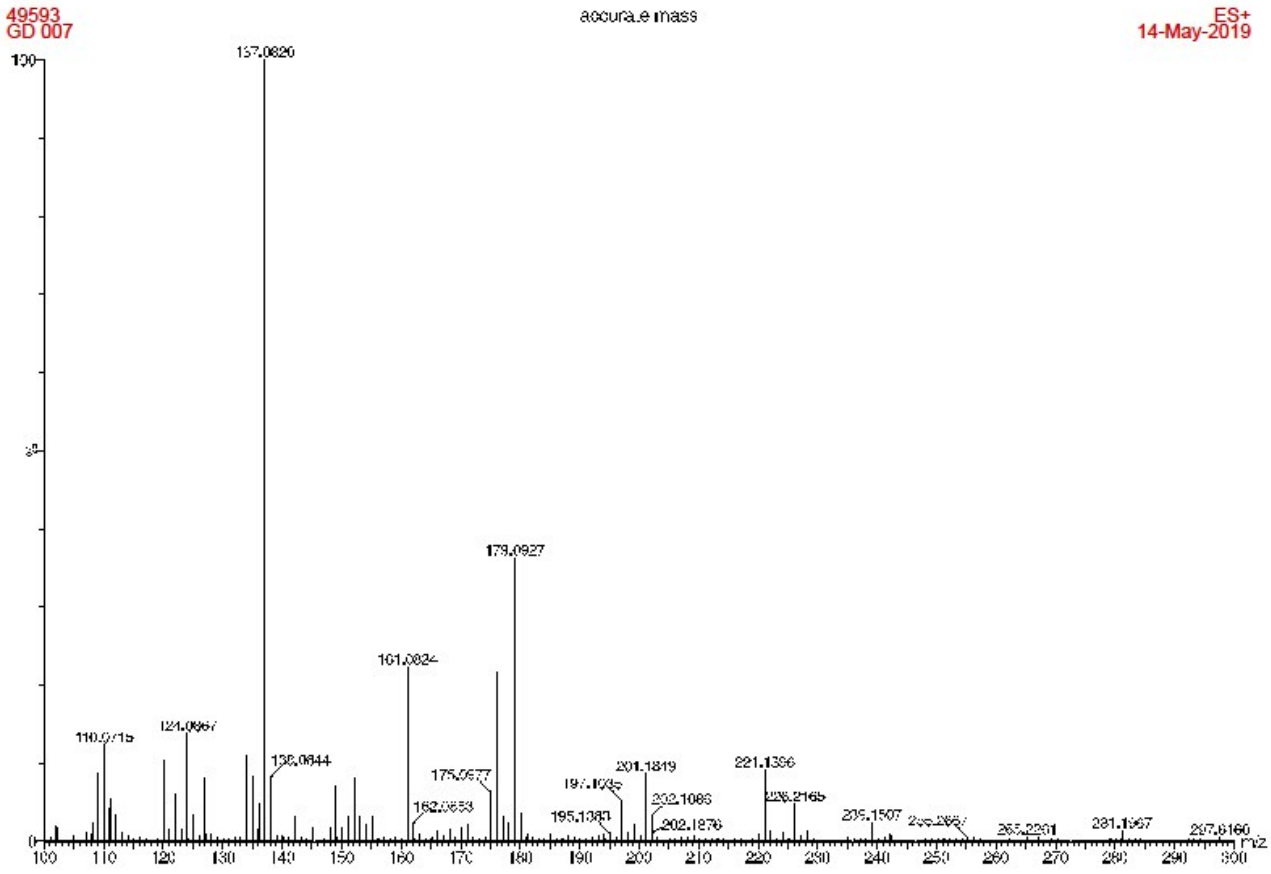

Figure S12. HRMS spectra of 2-hexyl-1-decanal.

Table S3. Densitimetry and viscosimetry data for 2-hexyl-1-decanal

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.59 Gold (20869052)
0.80345	59.98	2.128	2.649	60.00	0.03	0.04	Ø1.59 Gold (20869052)
0.80517	57.52	2.230	2.769	57.50	0.02	0.07	Ø1.59 Gold (20869052)
0.80694	55.02	2.339	2.899	55.00	0.02	0.10	Ø1.59 Gold (20869052)
0.80870	52.53	2.457	3.038	52.50	0.02	0.05	Ø1.59 Gold (20869052)
0.81046	50.03	2.584	3.188	50.00	0.01	0.08	Ø1.59 Gold (20869052)
0.81223	47.53	2.722	3.351	47.50	0.02	0.08	Ø1.59 Gold (20869052)
0.81399	45.03	2.868	3.524	45.00	0.01	0.09	Ø1.59 Gold (20869052)
0.81575	42.53	3.030	3.714	42.50	0.02	0.11	Ø1.59 Gold (20869052)
0.81752	40.03	3.207	3.923	40.00	0.03	0.06	Ø1.59 Gold (20869052)
0.81928	37.53	3.400	4.150	37.50	0.01	0.04	Ø1.59 Gold (20869052)
0.82104	35.03	3.610	4.397	35.00	0.01	0.03	Ø1.59 Gold (20869052)
0.82280	32.53	3.842	4.670	32.50	0.04	0.07	Ø1.59 Gold (20869052)
0.82457	30.03	4.096	4.968	30.00	0.04	0.06	Ø1.59 Gold (20869052)
0.82633	27.53	4.376	5.295	27.50	0.02	0.07	Ø1.59 Gold (20869052)
0.82810	25.03	4.685	5.657	25.00	0.01	0.06	Ø1.59 Gold (20869052)
0.82986	22.53	5.027	6.058	22.50	0.01	0.07	Ø1.59 Gold (20869052)
0.83162	20.02	5.409	6.504	20.00	0.04	0.11	Ø1.59 Gold (20869052)

2-Heptyl-1-undecanal

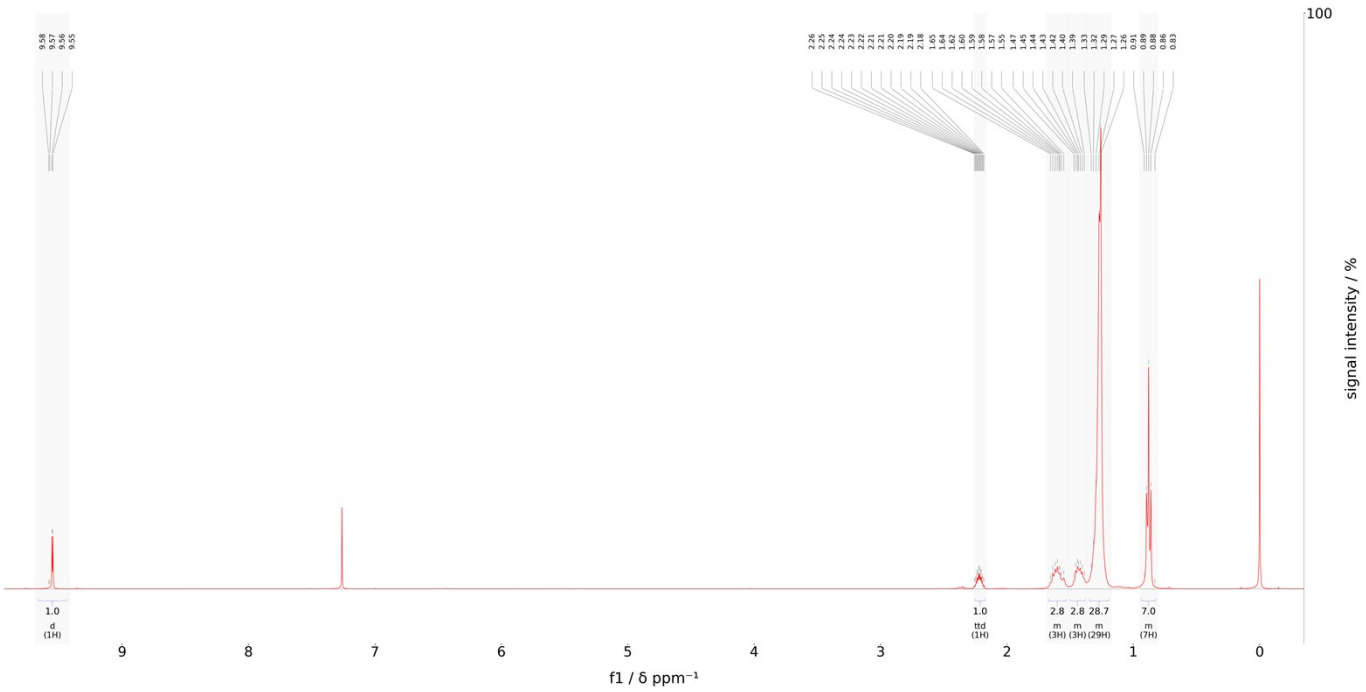

Figure S13. ^{1}H NMR of 2-heptyl-1-undecanal in deuterochloroform.

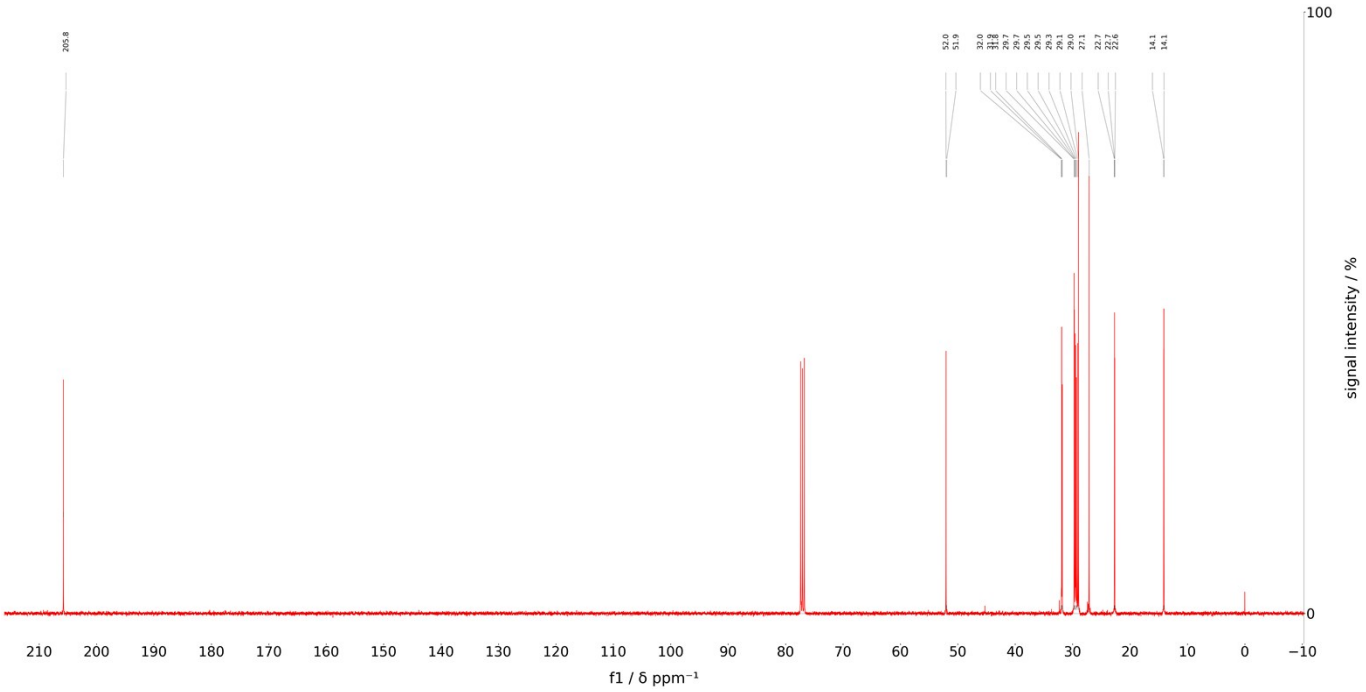

Figure S14. ^{13}C NMR of 2-heptyl-1-undecanal in deuterochloroform.

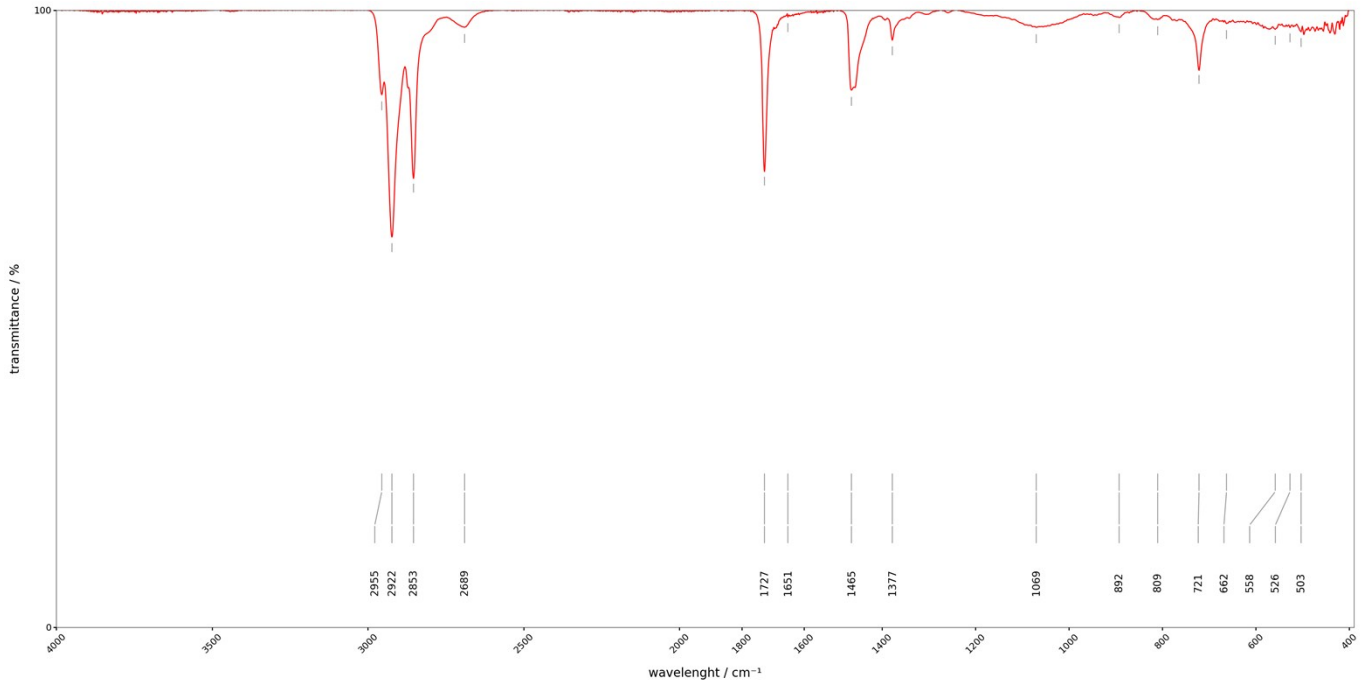

Figure S15. IR spectra of 2-heptyl-1-undecanal.

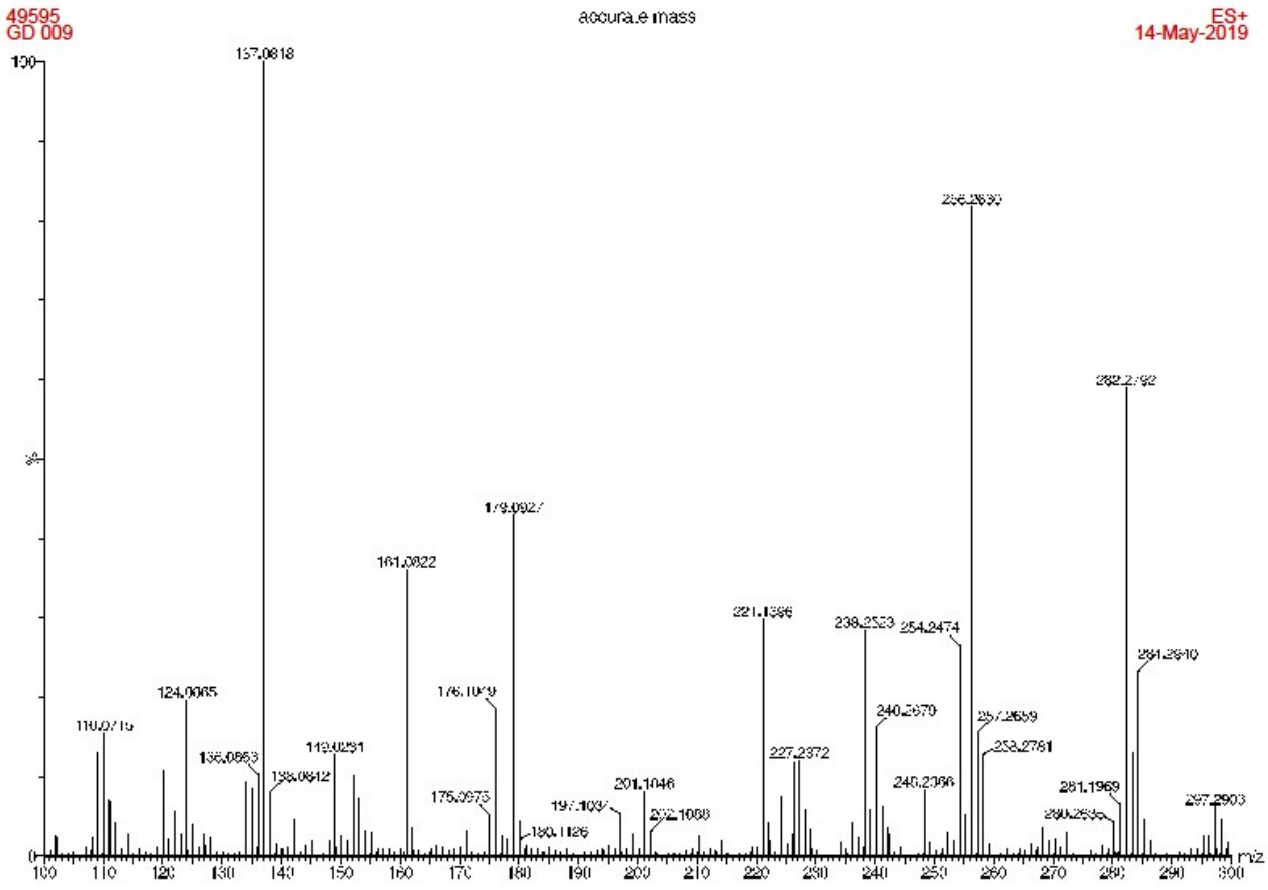

Figure S16. HRMS spectra of 2-heptyl-1-undecanal.

Table S4. Densitimetry and viscosimetry data for 2-heptyl-1-undecanal

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.59 Gold (20869052)
0.80548	59.98	2.614	3.245	60.00	0.02	0.01	Ø1.59 Gold (20869052)
0.80716	57.52	2.750	3.407	57.50	0.02	0.03	Ø1.59 Gold (20869052)
0.80888	55.03	2.899	3.583	55.00	0.15	0.21	Ø1.59 Gold (20869052)
0.81060	52.53	3.047	3.758	52.50	0.02	0.03	Ø1.59 Gold (20869052)
0.81232	50.03	3.219	3.963	50.00	0.02	0.02	Ø1.59 Gold (20869052)
0.81405	47.53	3.406	4.184	47.50	0.02	0.01	Ø1.59 Gold (20869052)
0.81578	45.03	3.610	4.425	45.00	0.00	0.02	Ø1.59 Gold (20869052)
0.81750	42.53	3.832	4.687	42.50	0.01	0.02	Ø1.59 Gold (20869052)
0.81923	40.03	4.076	4.975	40.00	0.02	0.02	Ø1.59 Gold (20869052)
0.82095	37.53	4.343	5.290	37.50	0.01	0.02	Ø1.59 Gold (20869052)
0.82268	35.03	4.637	5.636	35.00	0.01	0.03	Ø1.59 Gold (20869052)
0.82441	32.53	4.961	6.018	32.50	0.01	0.01	Ø1.59 Gold (20869052)
0.82614	30.03	5.319	6.439	30.00	0.01	0.04	Ø1.59 Gold (20869052)
0.82787	27.53	5.717	6.906	27.50	0.01	0.03	Ø1.59 Gold (20869052)
0.82960	25.02	6.159	7.423	25.00	0.01	0.03	Ø1.59 Gold (20869052)
0.83133	22.52	6.652	8.002	22.50	0.05	0.07	Ø1.59 Gold (20869052)
0.83306	20.02	7.201	8.645	20.00	0.02	0.01	Ø1.59 Gold (20869052)

2-Octyl-1-dodecanal

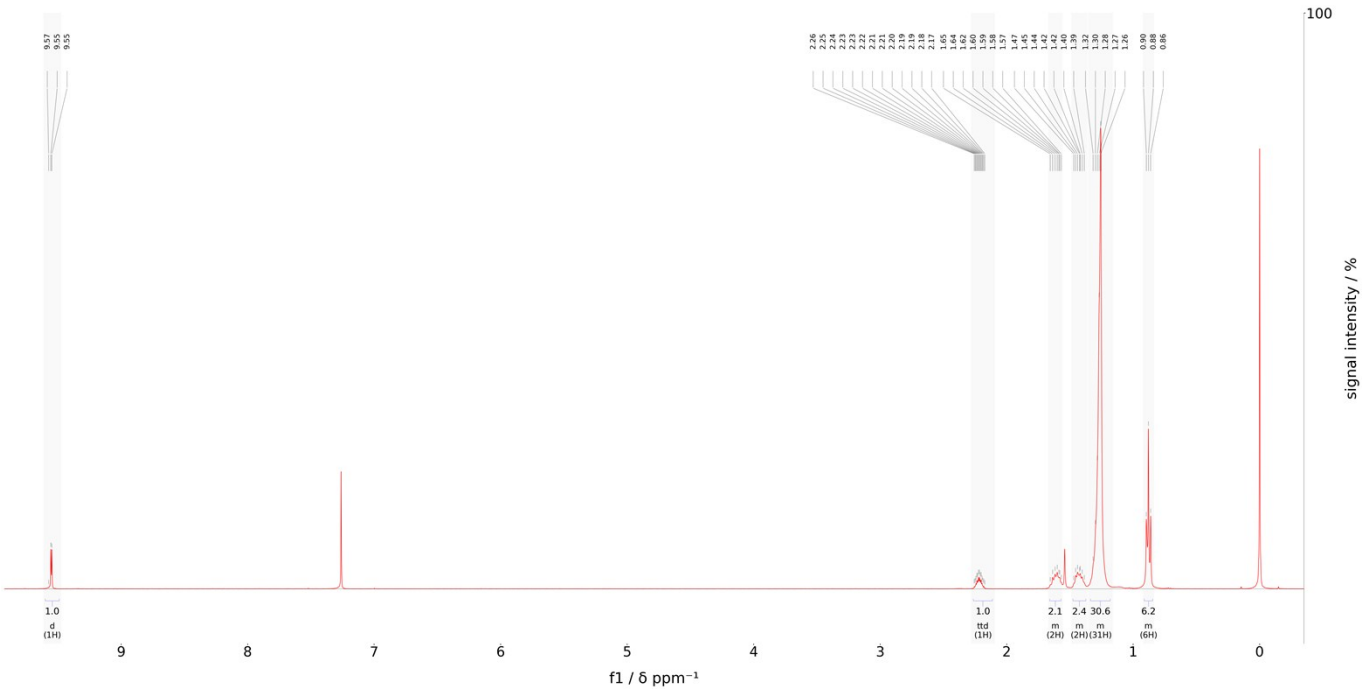

Figure S17. ^{1}H NMR of 2-octyl-1-dodecanal in deuterochloroform.

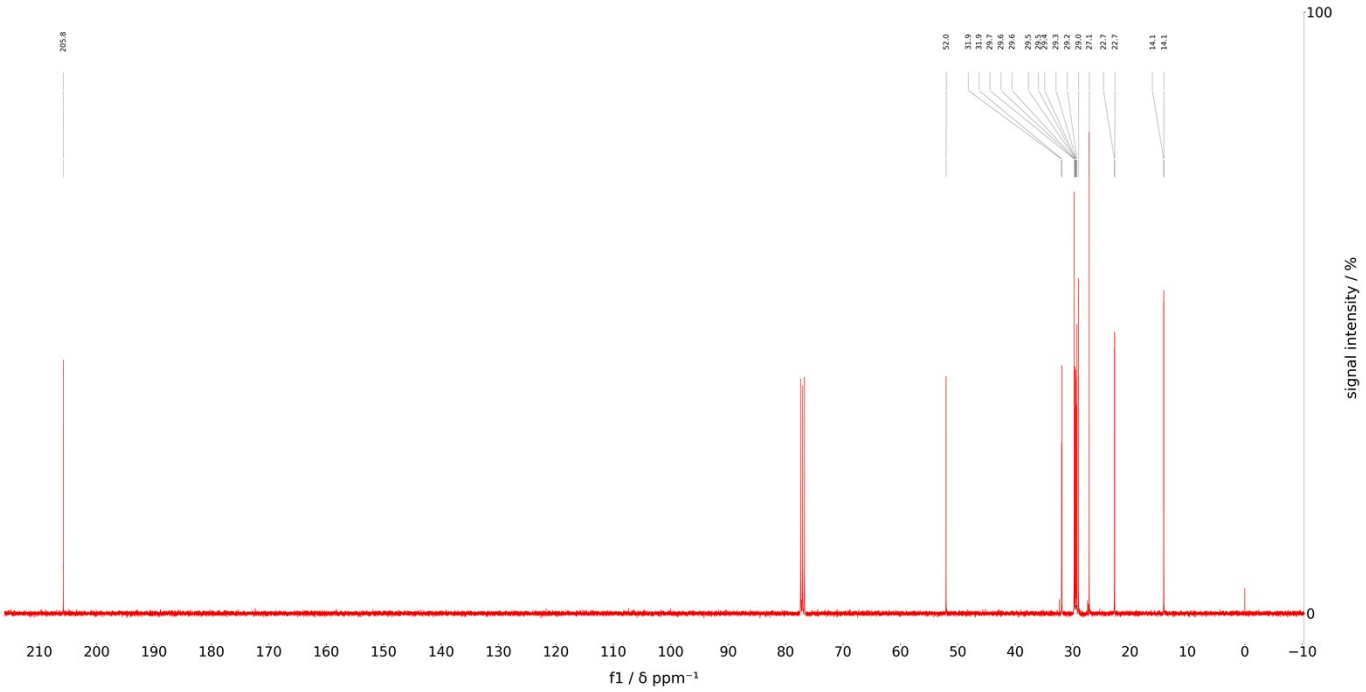

Figure S18. ^{13}C NMR of 2-octyl-1-dodecanal in deuterochloroform.

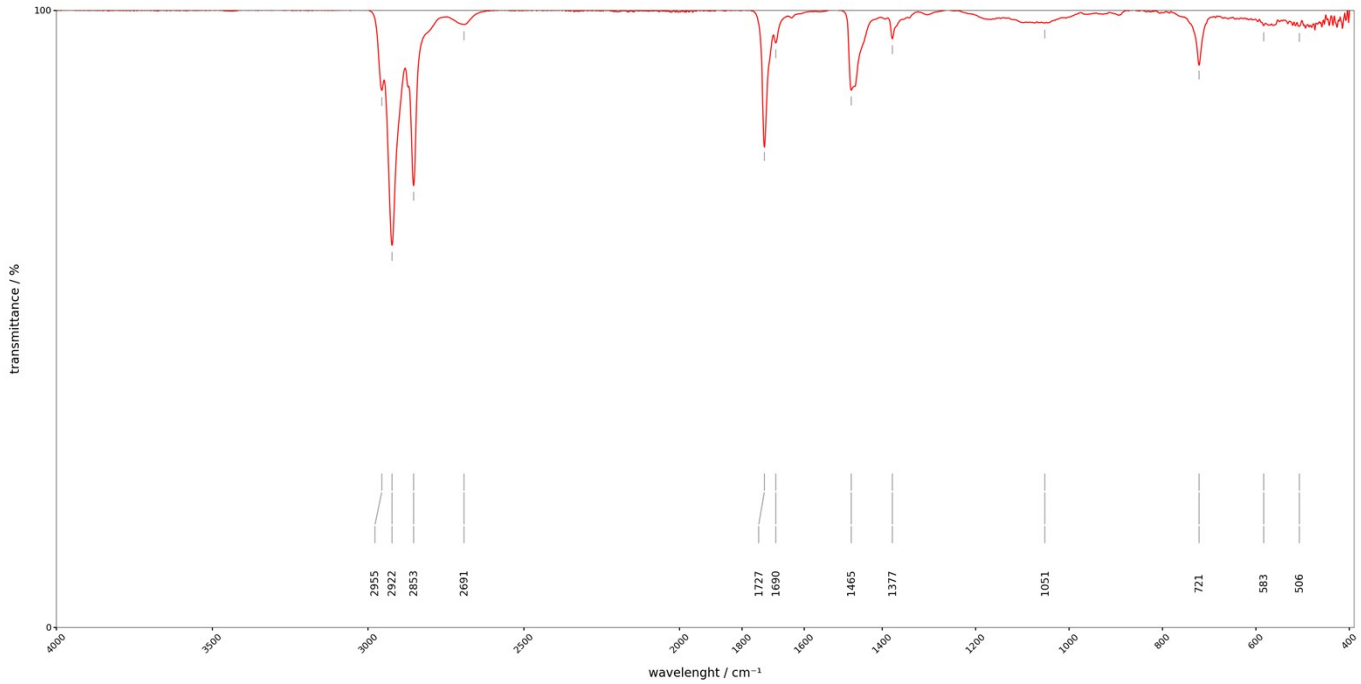

Figure S19. IR spectra of 2-octyl-1-dodecanal.

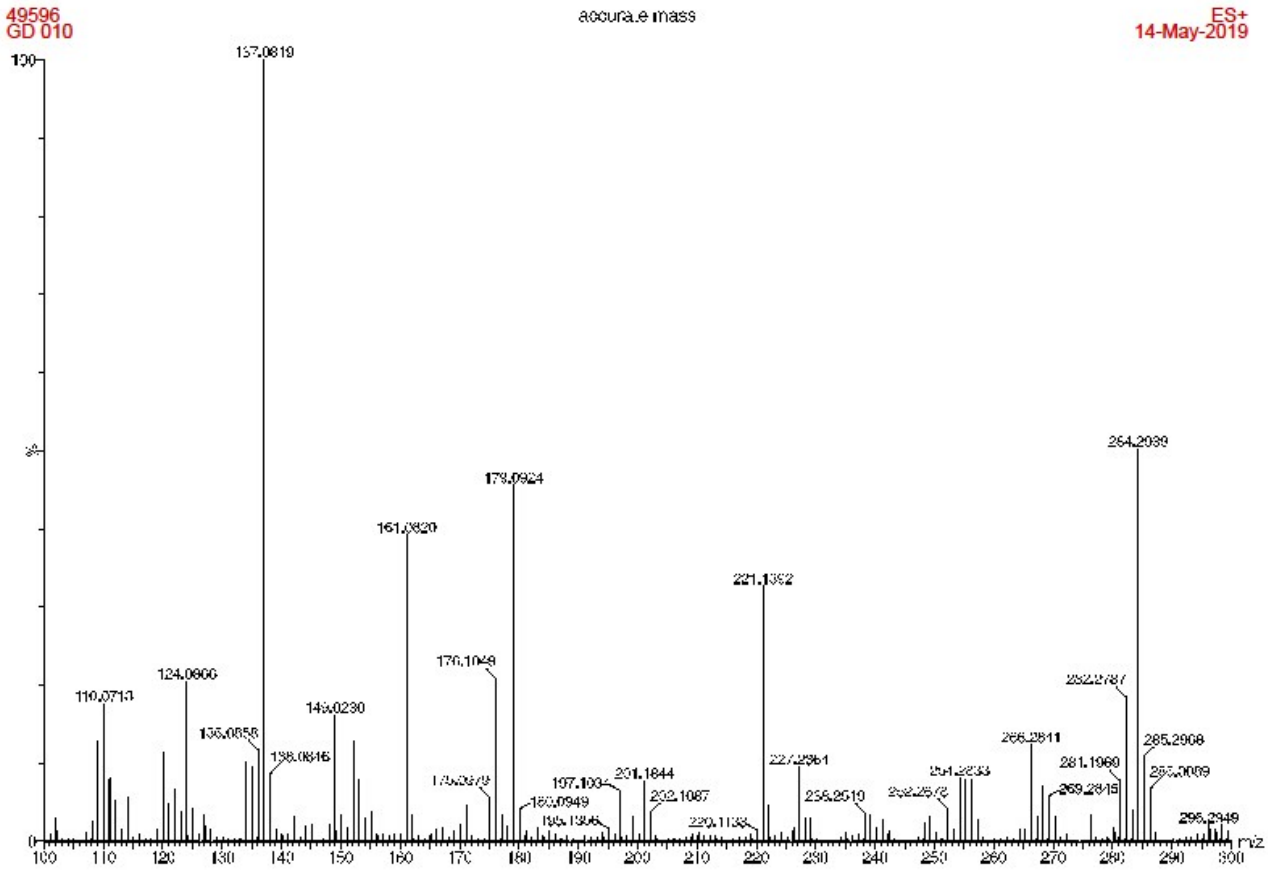

Figure S20. HRMS spectra of 2-octyl-1-dodecanal.

Table S5. Densitimetry and viscosimetry data for 2-octyl-1-dodecanal.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.81735	59.98	4.662	5.704	60.00	0.04	0.06	Ø1.8 Gold (20644413)
0.81901	57.52	4.952	6.046	57.50	0.03	0.09	Ø1.8 Gold (20644413)
0.82072	55.02	5.269	6.420	55.00	0.03	0.10	Ø1.8 Gold (20644413)
0.82242	52.53	5.619	6.832	52.50	0.03	0.06	Ø1.8 Gold (20644413)
0.82412	50.03	6.002	7.283	50.00	0.03	0.06	Ø1.8 Gold (20644413)
0.82583	47.53	6.424	7.779	47.50	0.03	0.06	Ø1.8 Gold (20644413)
0.82754	45.03	6.890	8.325	45.00	0.05	0.04	Ø1.8 Gold (20644413)
0.82925	42.53	7.405	8.929	42.50	0.05	0.05	Ø1.8 Gold (20644413)
0.83096	40.03	7.977	9.600	40.00	0.03	0.04	Ø1.8 Gold (20644413)
0.83267	37.53	8.612	10.34	37.50	0.03	0.05	Ø1.8 Gold (20644413)
0.83438	35.03	9.317	11.17	35.00	0.04	0.06	Ø1.8 Gold (20644413)
0.83609	32.53	10.11	12.09	32.50	0.04	0.06	Ø1.8 Gold (20644413)
0.83780	30.03	10.99	13.12	30.00	0.03	0.03	Ø1.8 Gold (20644413)
0.83952	27.53	11.99	14.29	27.50	0.04	0.06	Ø1.8 Gold (20644413)
0.84124	25.03	13.11	15.59	25.00	0.04	0.07	Ø1.8 Gold (20644413)
0.84295	22.52	14.38	17.06	22.50	0.02	0.05	Ø1.8 Gold (20644413)
0.84467	20.02	15.82	18.73	20.00	0.03	0.08	Ø1.8 Gold (20644413)

Di(2-butyl-octyl)methylamine

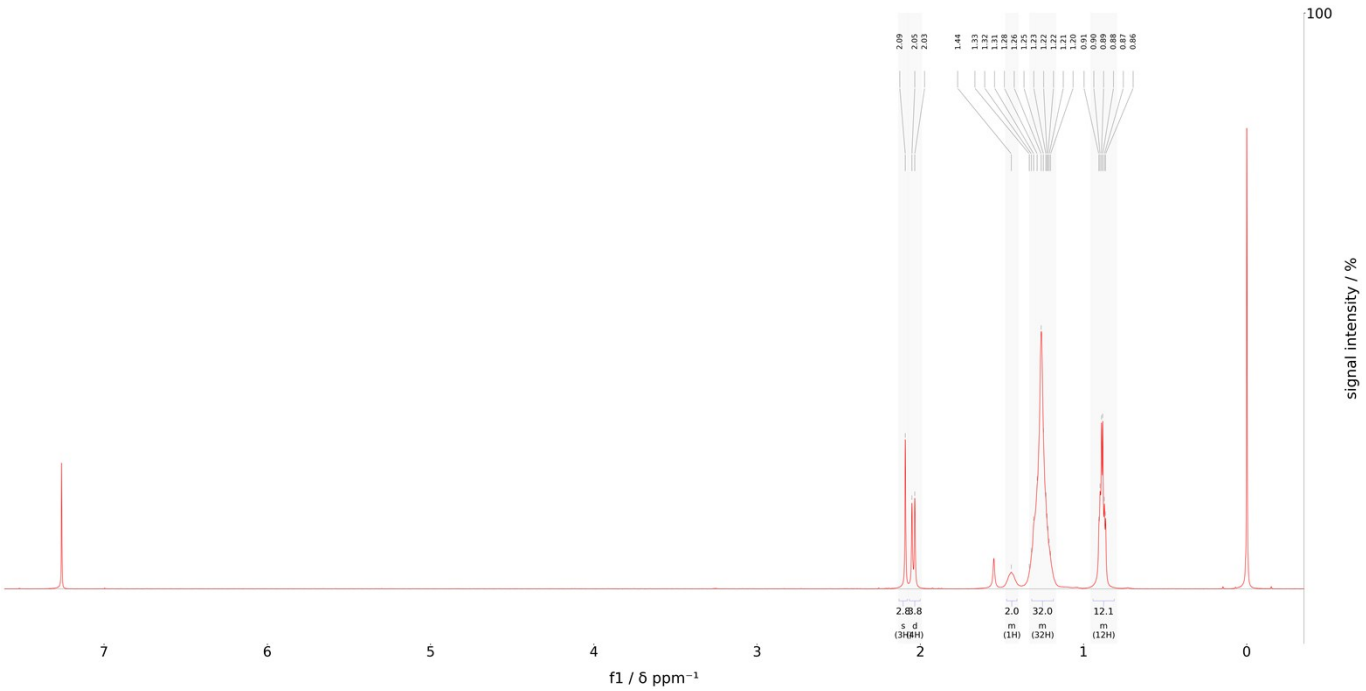

Figure S21. ^{1}H NMR of di(2-butyl-octyl)methylamine in deuterochloroform.

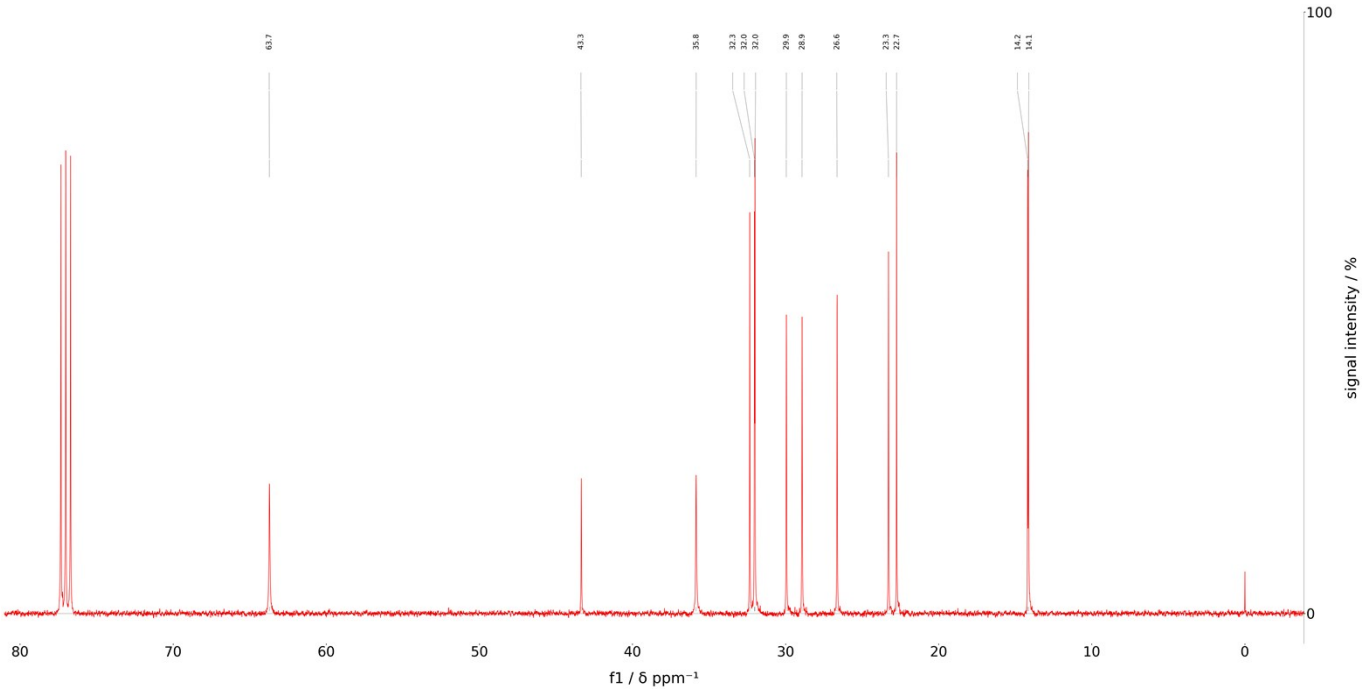

Figure S22. ^{13}C NMR of di(2-butyl-octyl)methylamine in deuterochloroform.

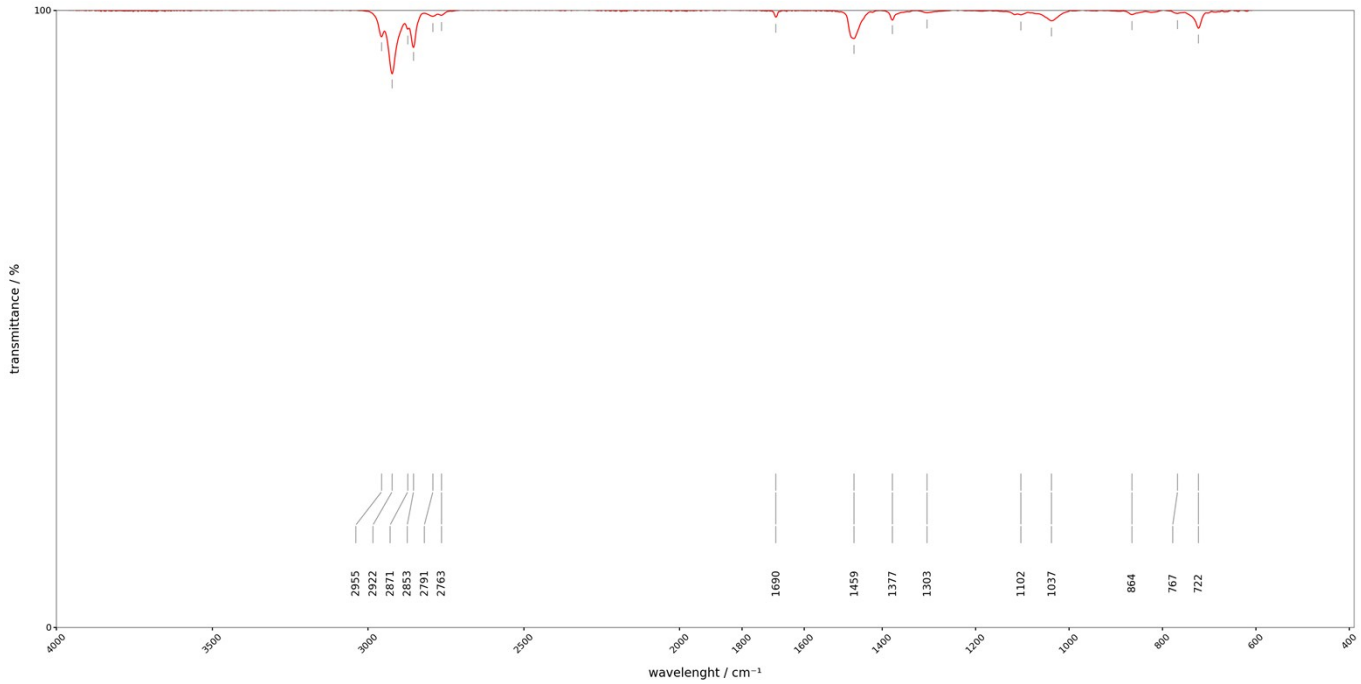

Figure S23. IR spectra of di(2-butyl-octyl)methylamine.

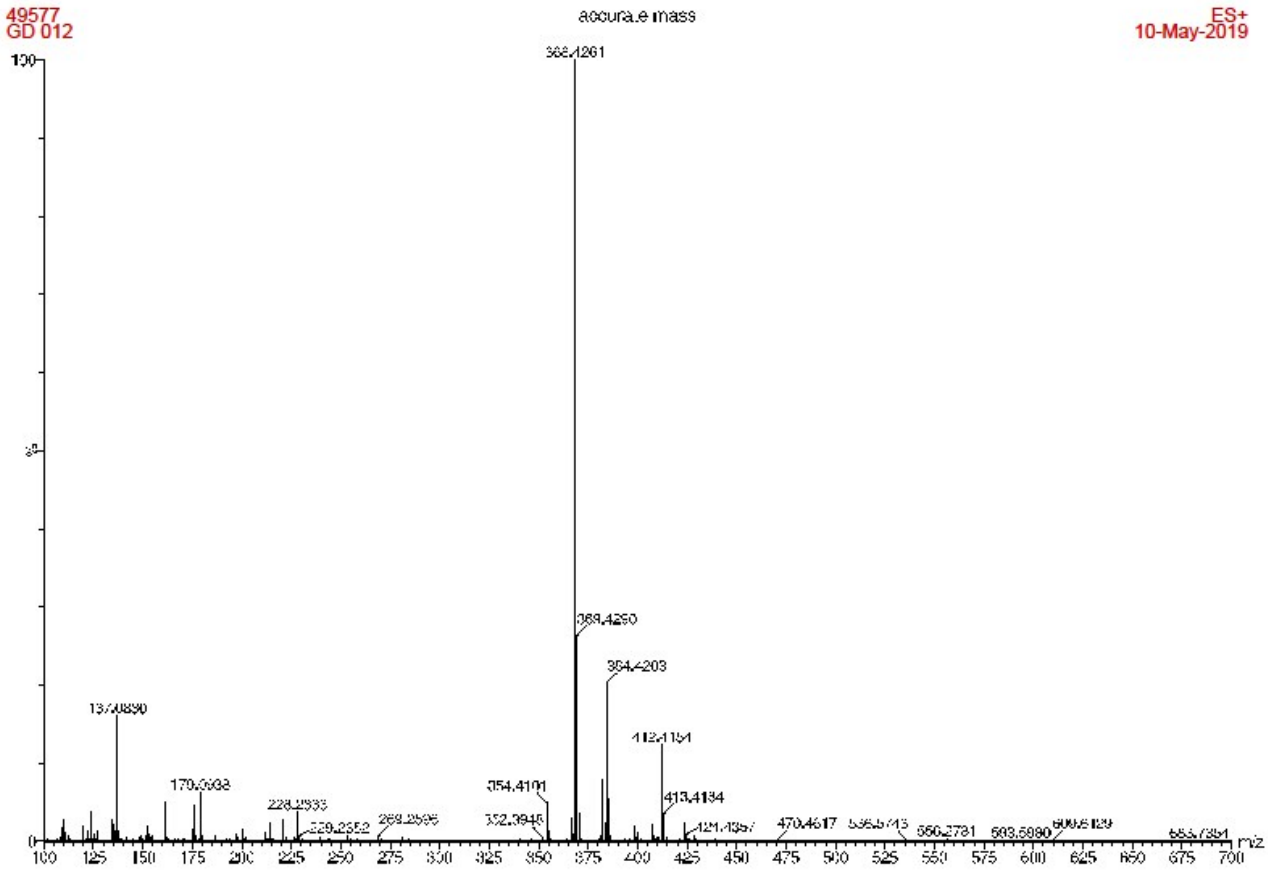

Figure S24. HRMS spectra of di(2-butyl-octyl)methylamine.

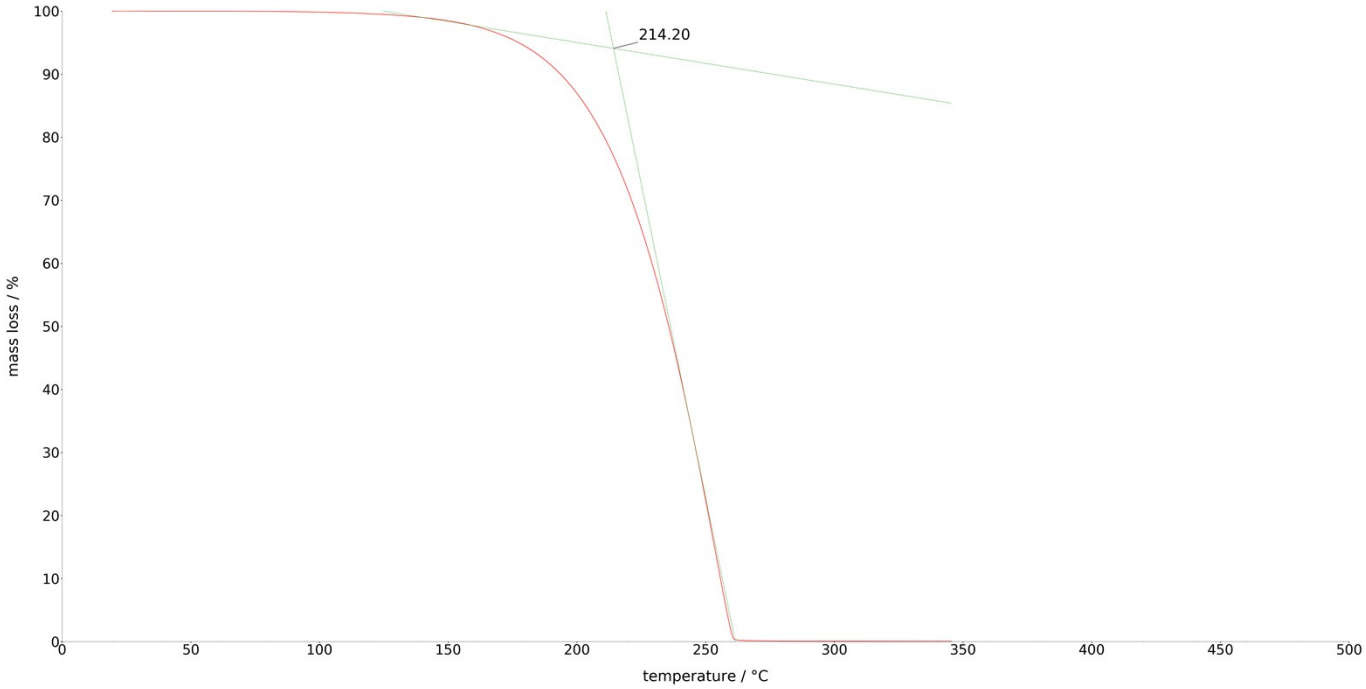

Figure S25. Thermogravimetric analysis for di(2-butyl-octyl)methylamine.

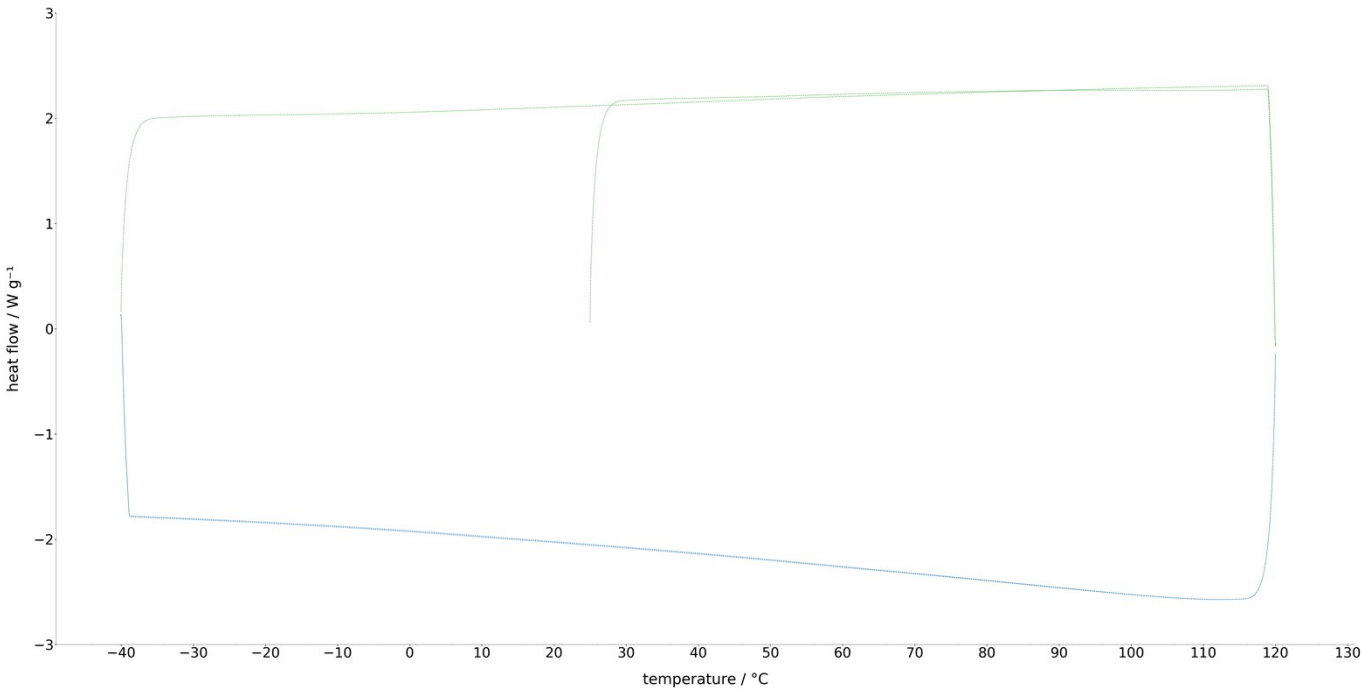

Figure S26. Differential scan calorimetry for di(2-butyl-octyl)methylamine.

Table S6. Densitimetry and viscosimetry data for di(2-butyl-octyl)methylamine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient
0.79093	59.98	4.433	5.605	60.00	0.03
0.79256	57.52	4.718	5.953	57.50	0.03
0.79423	55.02	5.039	6.345	55.00	0.03
0.79590	52.53	5.392	6.775	52.50	0.02
0.79757	50.03	5.784	7.252	50.00	0.04
0.79924	47.53	6.217	7.778	47.50	0.01
0.80092	45.03	6.699	8.364	45.00	0.04
0.80259	42.53	7.237	9.017	42.50	0.03
0.80427	40.03	7.837	9.744	40.00	0.03
0.80595	37.53	8.516	10.57	37.50	0.05
0.80762	35.03	9.273	11.48	35.00	0.06
0.80930	32.53	10.14	12.53	32.50	0.07
0.81097	30.03	11.11	13.70	30.00	0.06
0.81265	27.53	12.23	15.04	27.50	0.06
0.81433	25.03	13.49	16.57	25.00	0.04
0.81601	22.53	14.93	18.30	22.50	0.04
0.81769	20.02	16.57	20.26	20.00	0.02

Di(2-pentyl-nonyl)methylamine

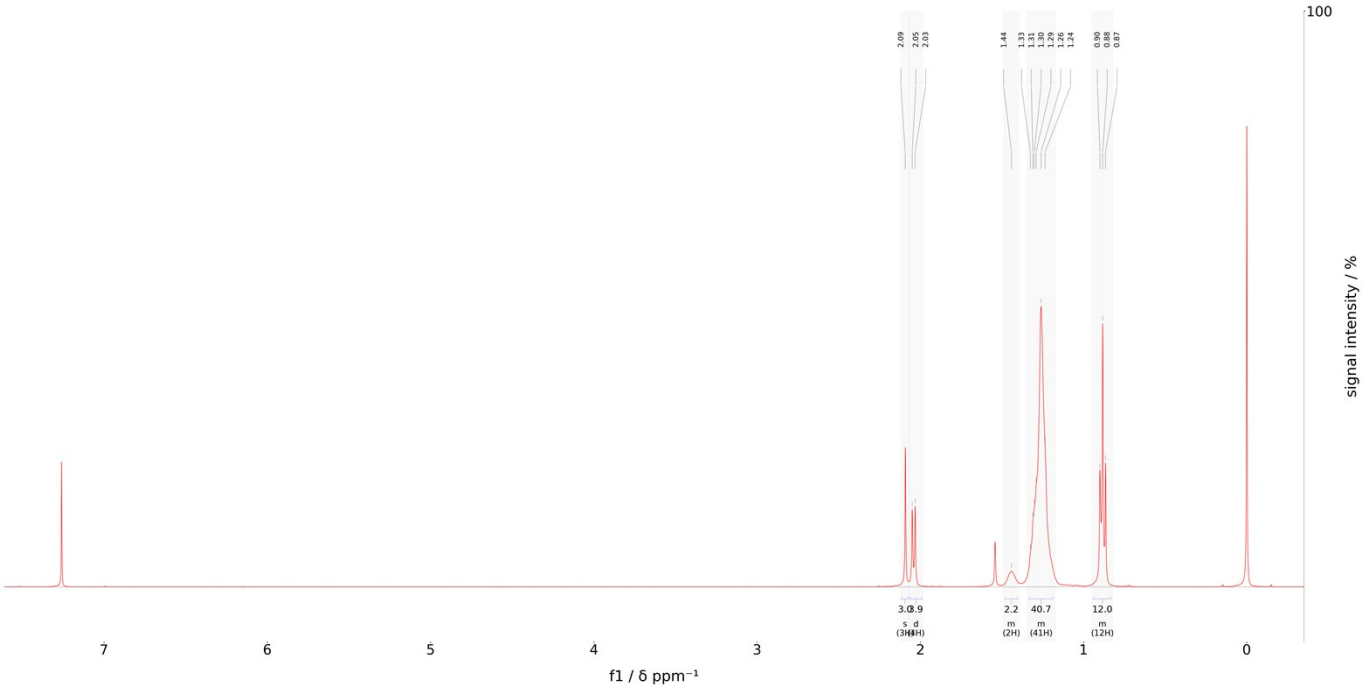

Figure S27. ^{1}H NMR of di(2-pentyl-nonyl)methylamine in deuterochloroform.

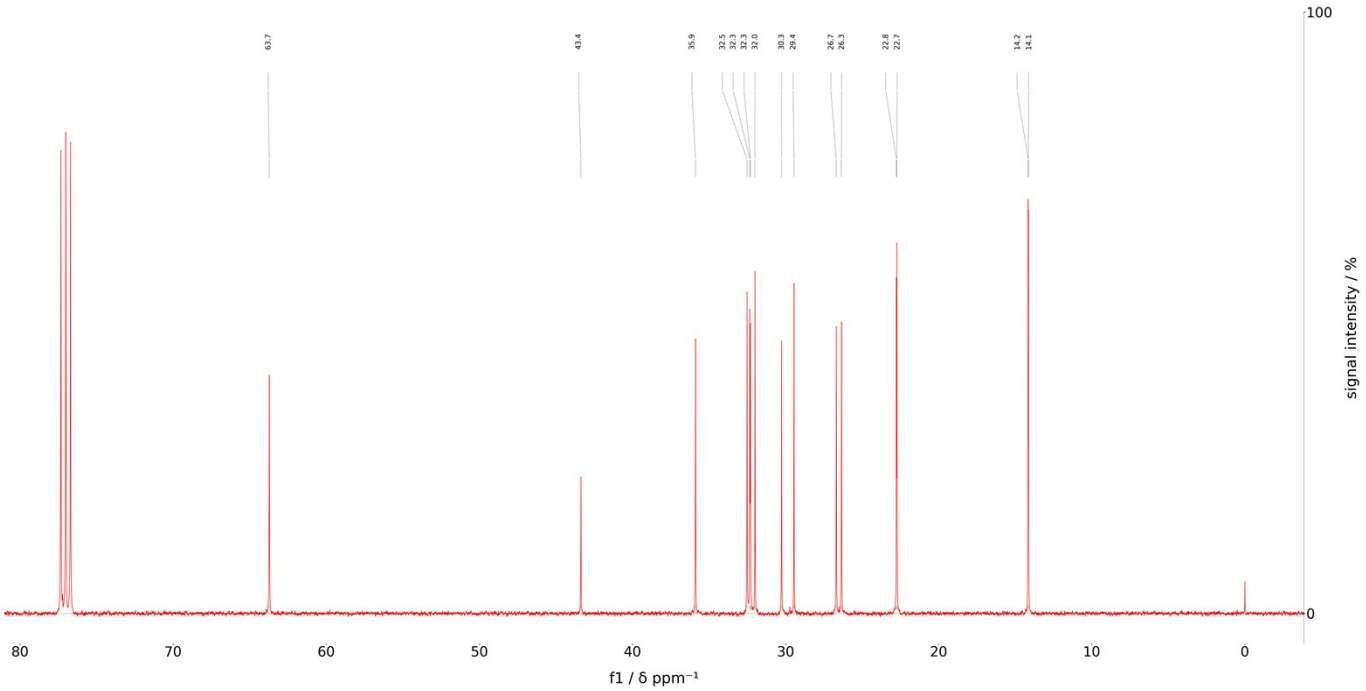

Figure S28. ^{13}C NMR of di(2-pentyl-nonyl)methylamine in deuterochloroform.

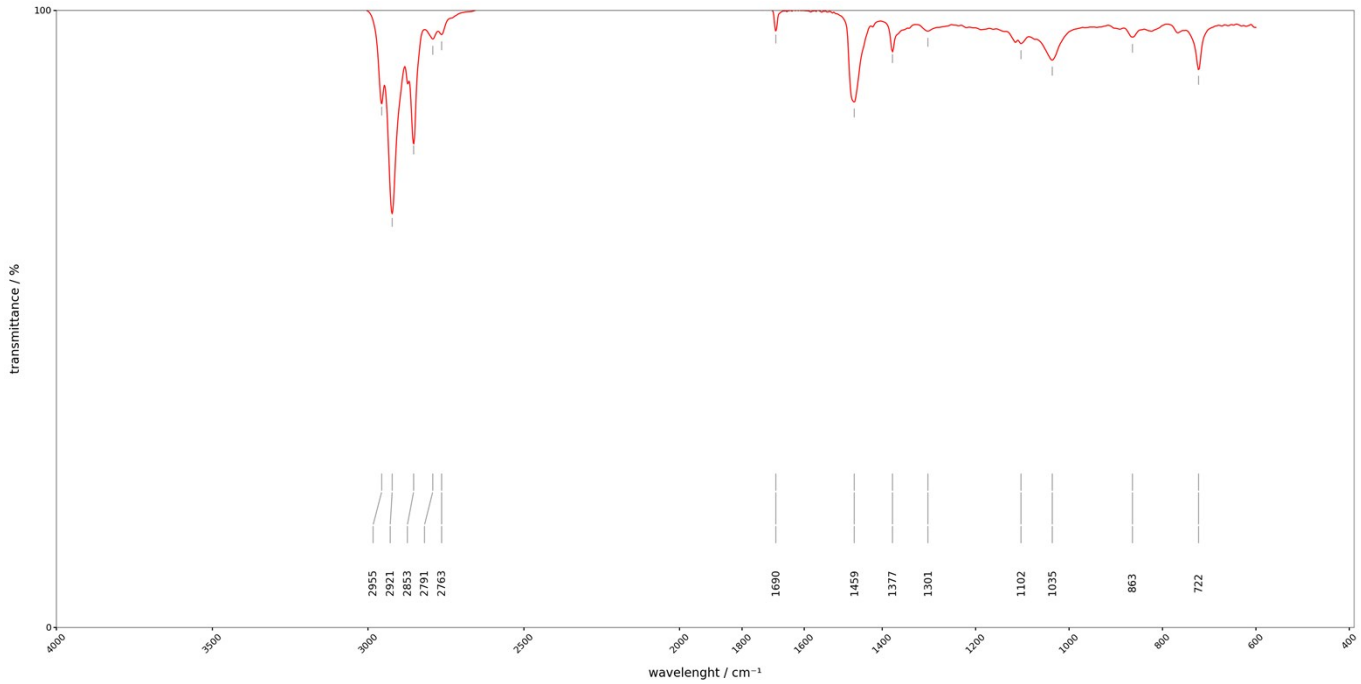

Figure S29. IR spectra of di(2-pentyl-nonyl)methylamine.

Figure S30. HRMS spectra of di(2-pentyl-nonyl)methylamine.

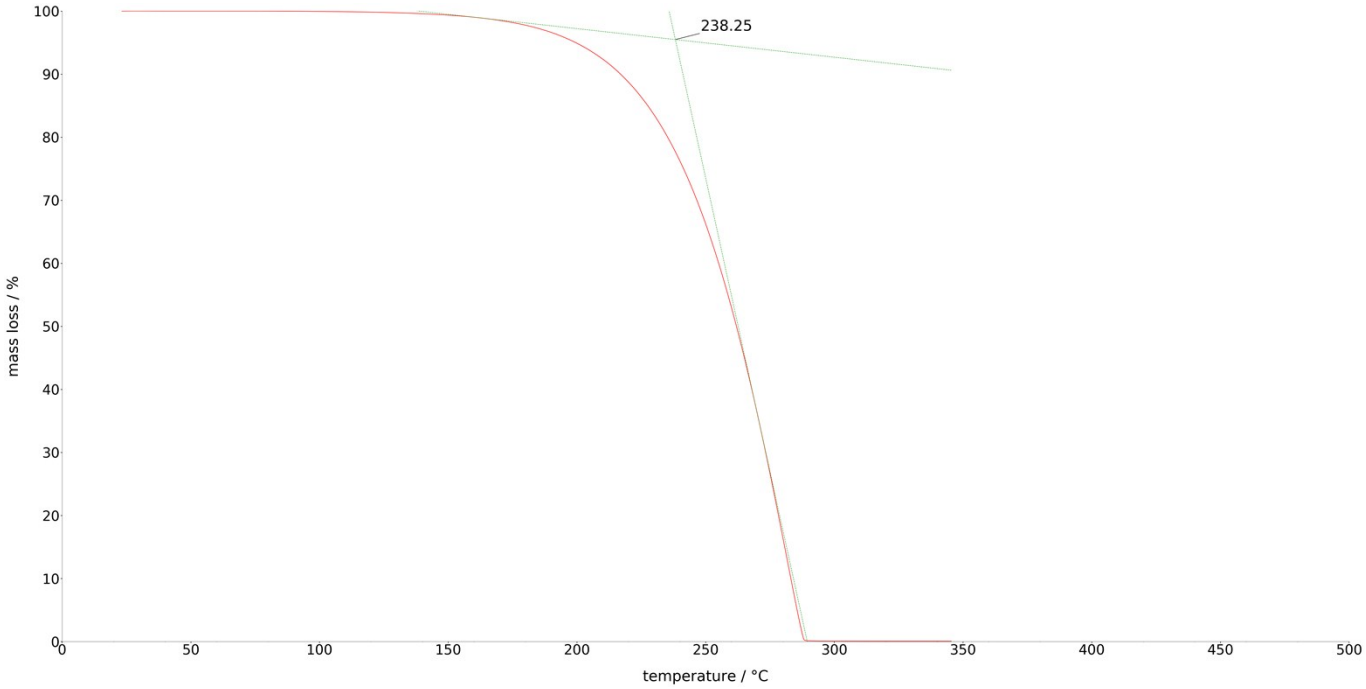

Figure S31. Thermogravimetric analysis for di(2-pentyl-nonyl)methylamine.

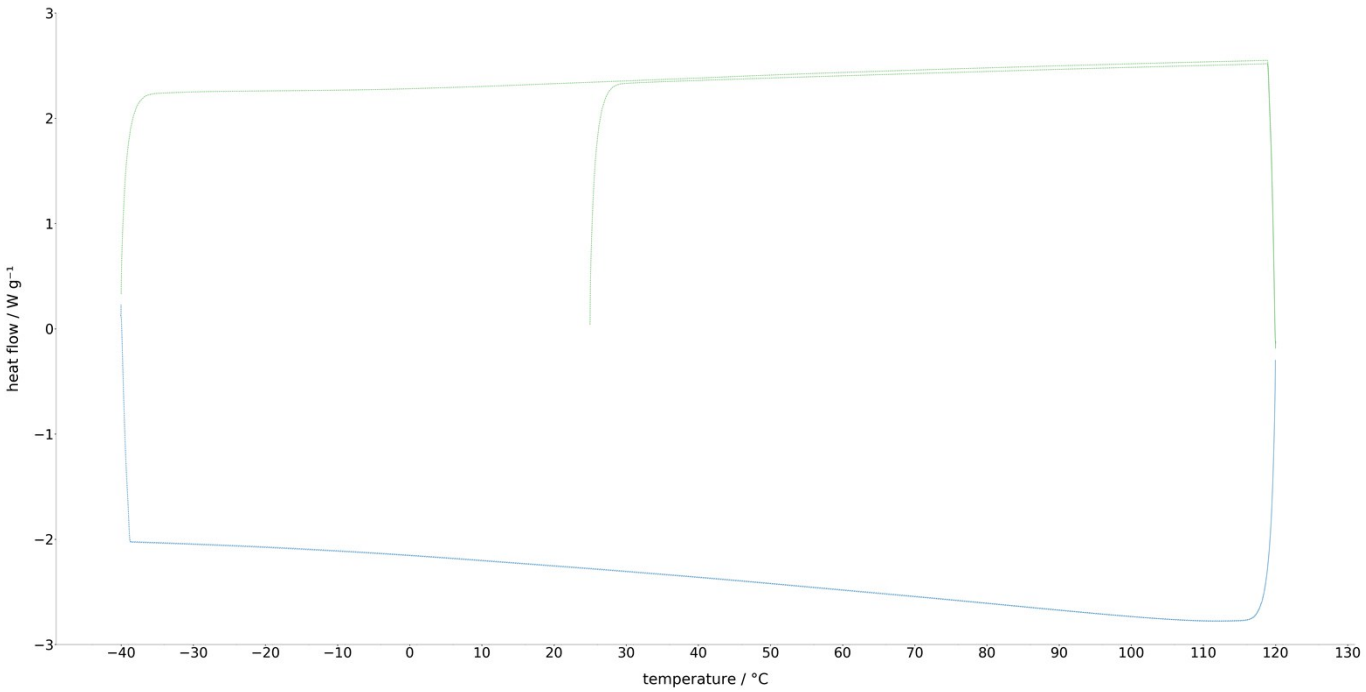

Figure S32. Differential scan calorimetry for di(2-pentyl-nonyl)methylamine.

Table S7. Densitimetry and viscosimetry data for di(2-pentyl-nonyl)methylamine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.79206	59.98	6.179	7.801	60.00	0.03	0.17	Ø1.8 Gold (20644413)
0.79365	57.52	6.615	8.335	57.50	0.04	0.13	Ø1.8 Gold (20644413)
0.79527	55.02	7.098	8.925	55.00	0.06	0.10	Ø1.8 Gold (20644413)
0.79690	52.53	7.637	9.583	52.50	0.02	0.08	Ø1.8 Gold (20644413)
0.79852	50.03	8.233	10.31	50.00	0.02	0.07	Ø1.8 Gold (20644413)
0.80015	47.53	8.893	11.11	47.50	0.03	0.02	Ø1.8 Gold (20644413)
0.80178	45.03	9.634	12.02	45.00	0.05	0.09	Ø1.8 Gold (20644413)
0.80341	42.53	10.46	13.02	42.50	0.04	0.04	Ø1.8 Gold (20644413)
0.80504	40.03	11.39	14.15	40.00	0.04	0.05	Ø1.8 Gold (20644413)
0.80667	37.53	12.43	15.41	37.50	0.06	0.04	Ø1.8 Gold (20644413)
0.80830	35.03	13.61	16.84	35.00	0.06	0.06	Ø1.8 Gold (20644413)
0.80993	32.53	14.94	18.45	32.50	0.06	0.10	Ø1.8 Gold (20644413)
0.81156	30.03	16.46	20.29	30.00	0.01	0.06	Ø1.8 Gold (20644413)
0.81320	27.52	18.20	22.38	27.50	0.04	0.07	Ø1.8 Gold (20644413)
0.81483	25.02	20.16	24.74	25.00	0.04	0.08	Ø1.8 Gold (20644413)
0.81647	22.52	22.43	27.48	22.50	0.01	0.10	Ø1.8 Gold (20644413)
0.81811	20.02	25.06	30.63	20.00	0.06	0.10	Ø1.8 Gold (20644413)

Di(2-hexyl-decyl)methylamine

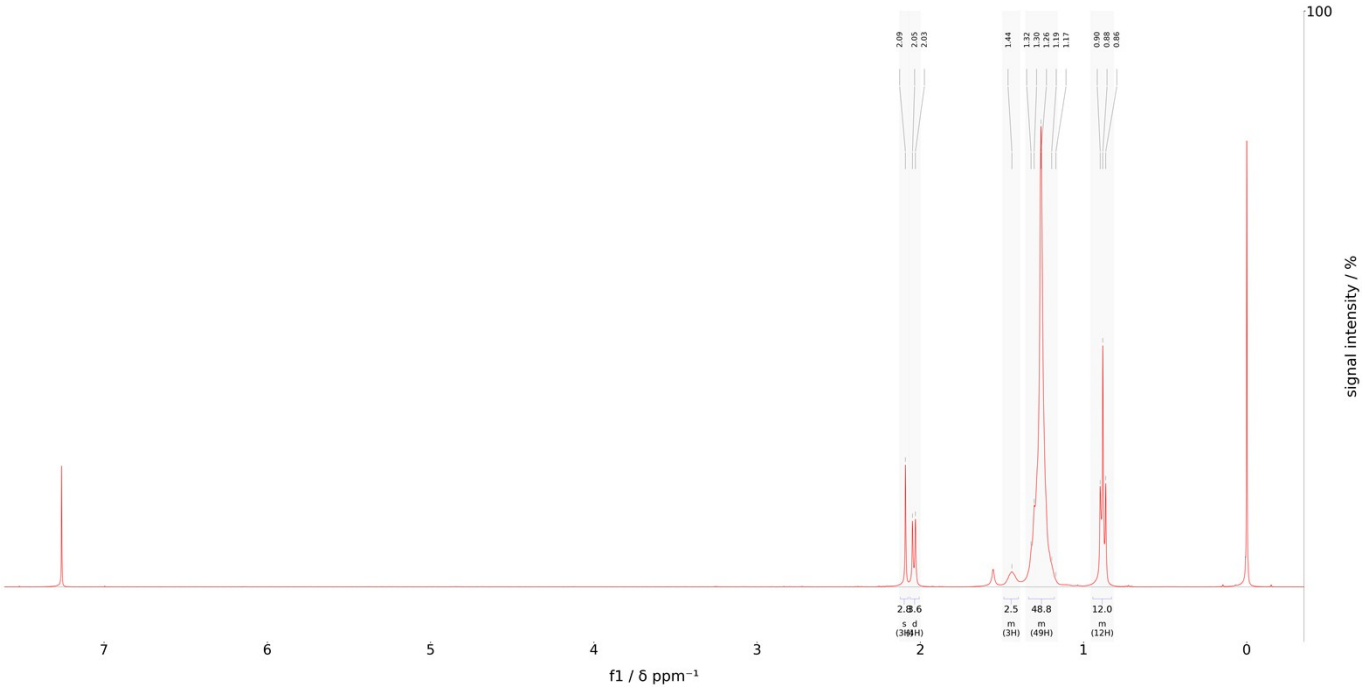

Figure S33. ^{1}H NMR of di(2-hexyl-decyl)methylamine in deuterochloroform.

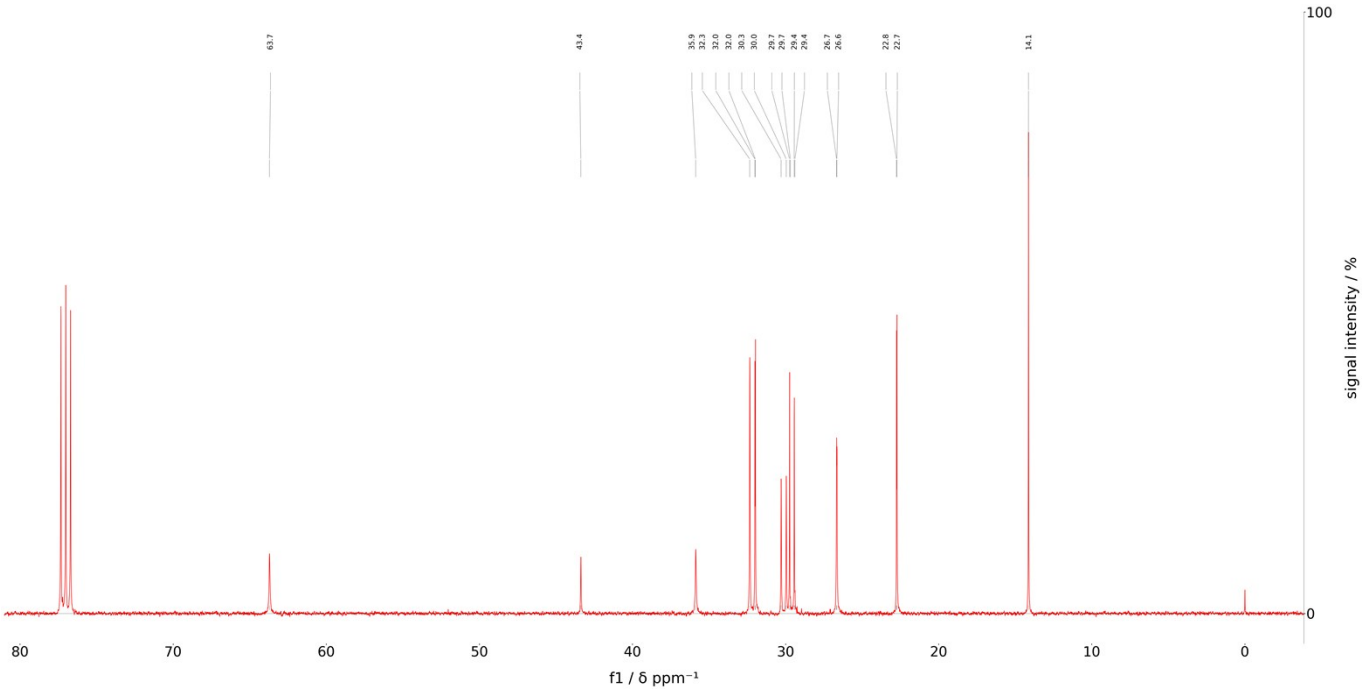

Figure S34. ^{13}C NMR of di(2-hexyl-decyl)methylamine in deuterochloroform.

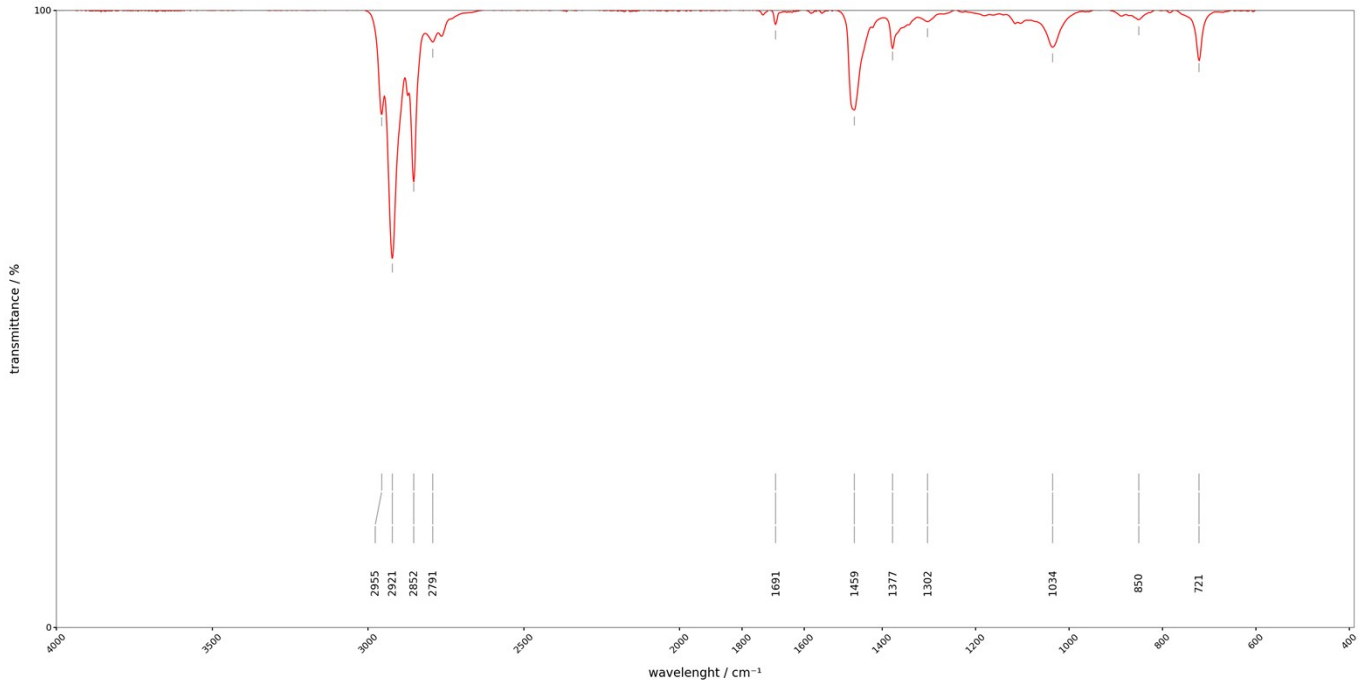

Figure S35. IR spectra of di(2-hexyl-decyl)methylamine.

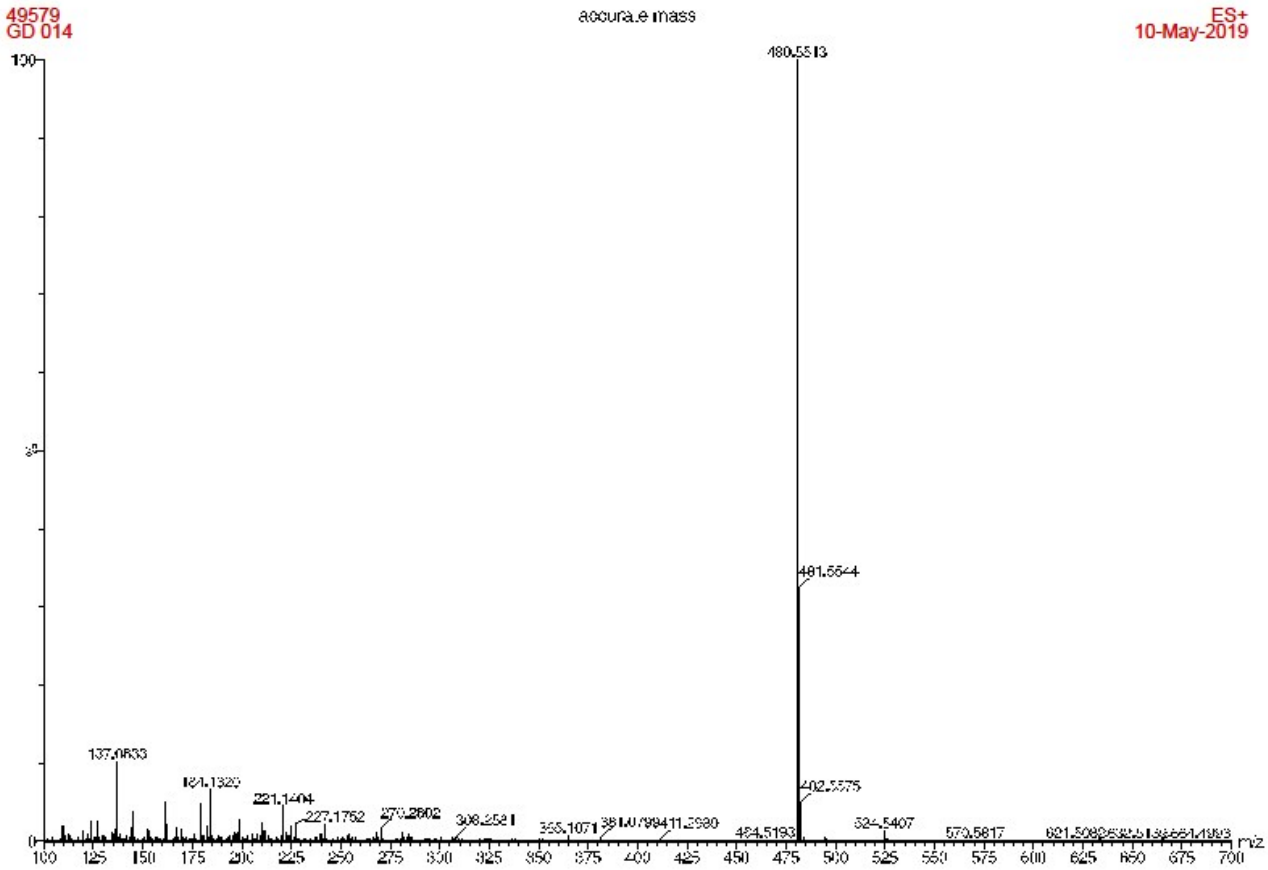

Figure S36. HRMS spectra of di(2-hexyl-decyl)methylamine.

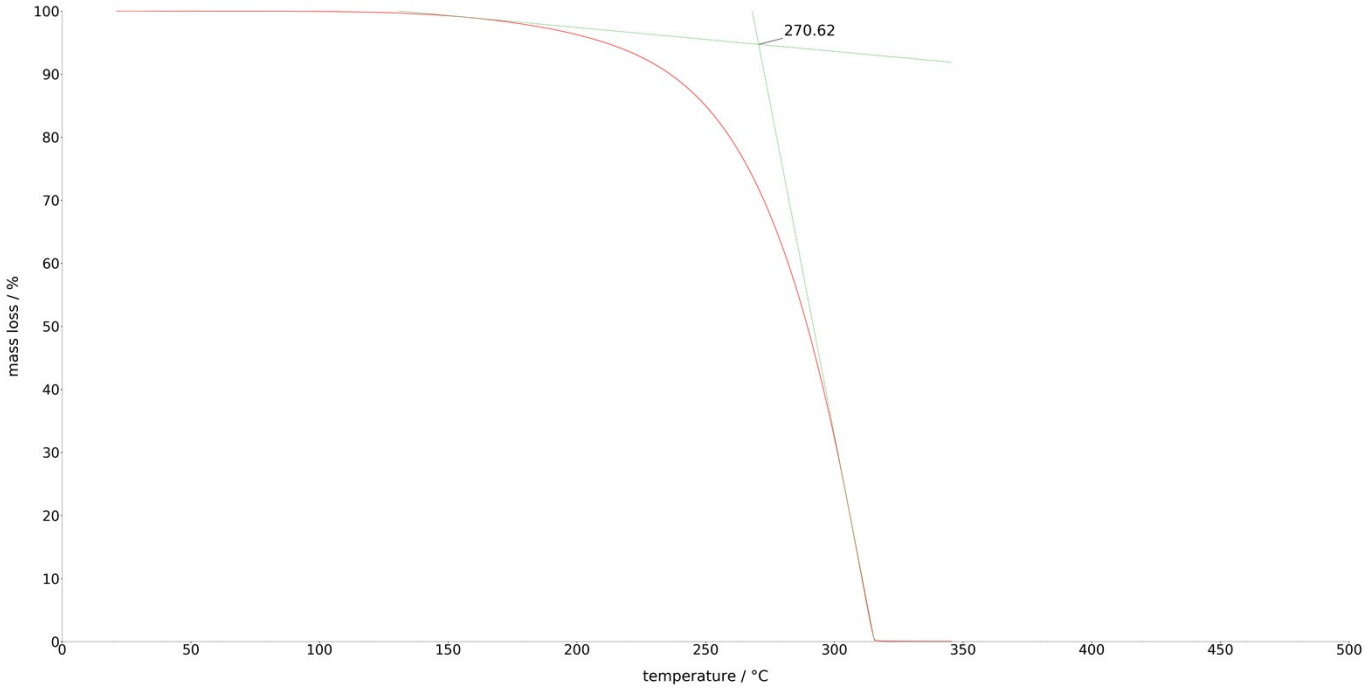

Figure S37. Thermogravimetric analysis for di(2-hexyl-decyl)methylamine.

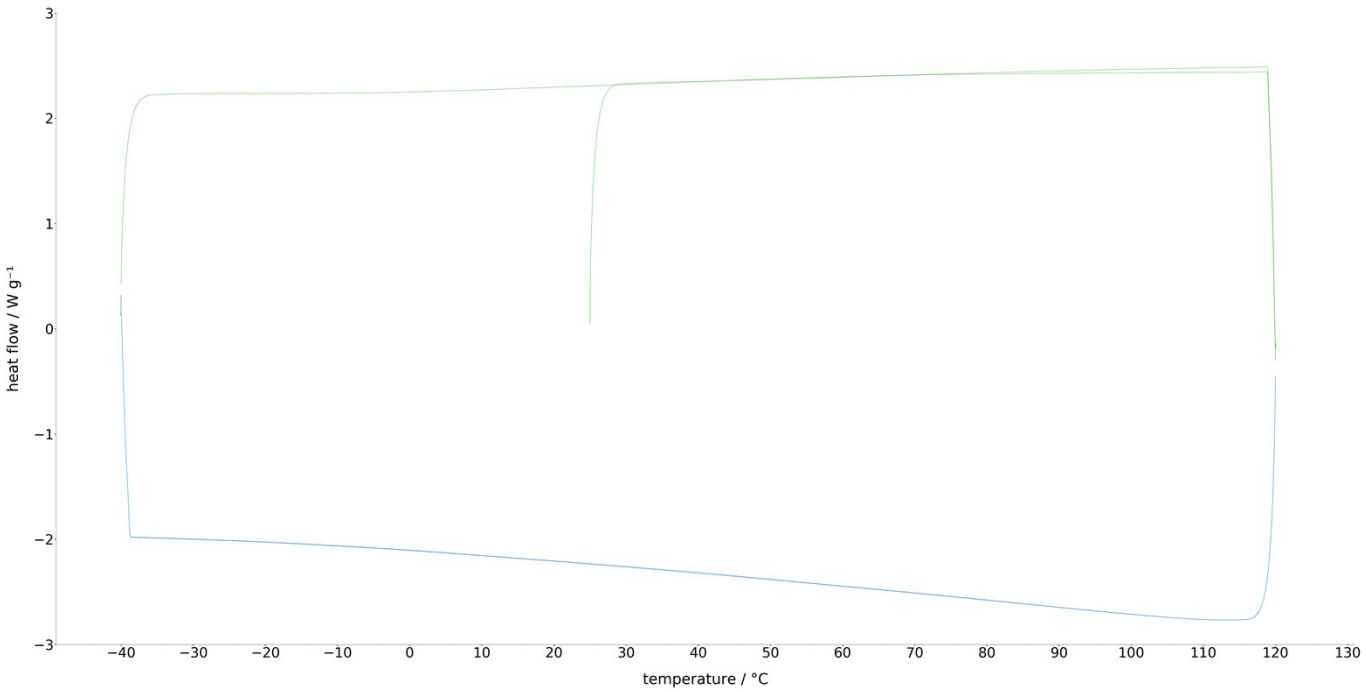

Figure S38. Differential scan calorimetry for di(2-hexyl-decyl)methylamine.

Table S8. Densitimetry and viscosimetry data for di(2-hexyl-decyl)methylamine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.79623	59.98	8.310	10.44	60.00	0.04	0.33	Ø1.8 Gold (20644413)
0.79779	57.52	8.898	11.15	57.50	0.07	0.25	Ø1.8 Gold (20644413)
0.79938	55.02	9.554	11.95	55.00	0.06	0.22	Ø1.8 Gold (20644413)
0.80098	52.53	10.28	12.83	52.50	0.02	0.23	Ø1.8 Gold (20644413)
0.80259	50.03	11.08	13.80	50.00	0.06	0.22	Ø1.8 Gold (20644413)
0.80419	47.53	11.97	14.88	47.50	0.03	0.24	Ø1.8 Gold (20644413)
0.80579	45.03	12.97	16.09	45.00	0.00	0.22	Ø1.8 Gold (20644413)
0.80740	42.53	14.12	17.49	42.50	0.08	0.24	Ø1.8 Gold (20644413)
0.80900	40.03	15.41	19.05	40.00	0.04	0.23	Ø1.8 Gold (20644413)
0.81061	37.53	16.89	20.84	37.50	0.06	0.21	Ø1.8 Gold (20644413)
0.81222	35.03	18.59	22.89	35.00	0.05	0.18	Ø1.8 Gold (20644413)
0.81382	32.53	20.54	25.24	32.50	0.05	0.10	Ø1.8 Gold (20644413)
0.81543	30.03	22.71	27.85	30.00	0.07	0.10	Ø1.8 Gold (20644413)
0.81705	27.53	25.00	30.59	27.50	0.31	0.08	Ø1.8 Gold (20644413)
0.81866	25.03	27.29	33.33	25.00	0.47	0.07	Ø1.8 Gold (20644413)
0.82027	22.53	29.96	36.53	22.50	0.28	0.07	Ø1.8 Gold (20644413)
0.82189	20.02	33.28	40.50	20.00	0.08	0.21	Ø1.8 Gold (20644413)

Di(2-heptyl-undecyl)methylamine

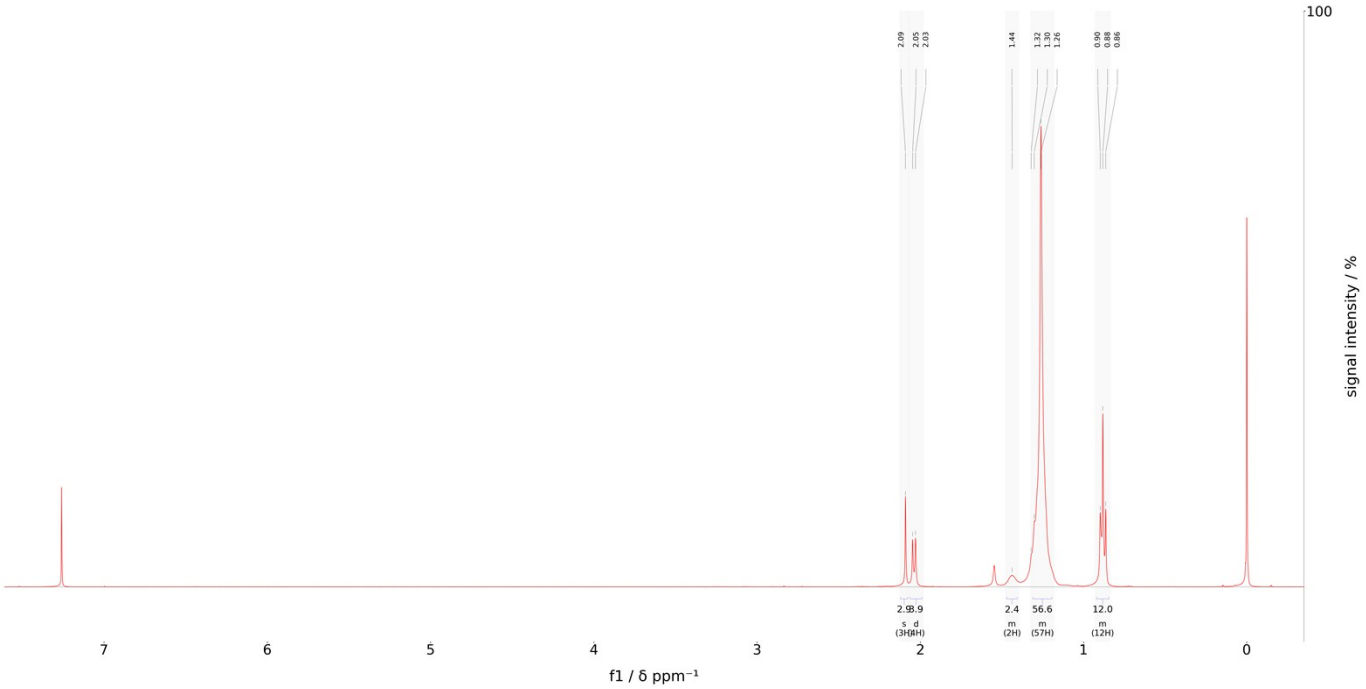

Figure S39. ^{1}H NMR of di(2-heptyl-undecyl)methylamine in deuterochloroform.

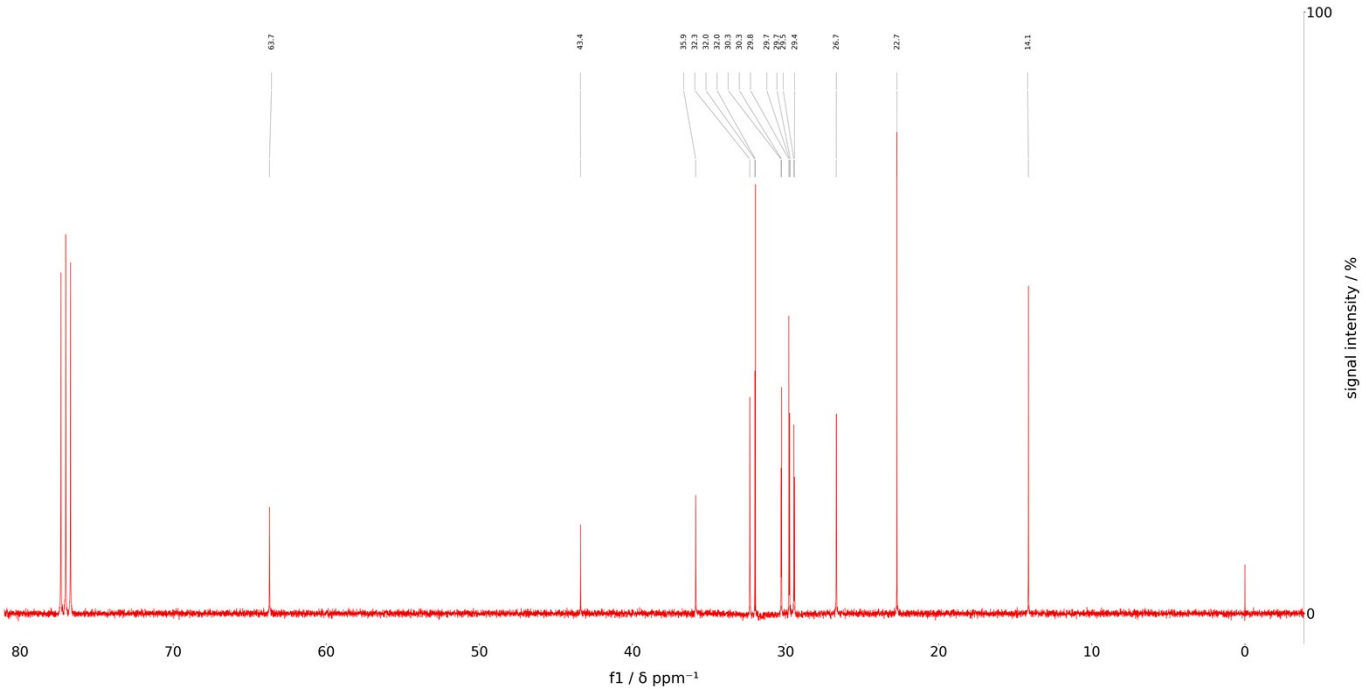

Figure S40. ^{13}C NMR of di(2-heptyl-undecyl)methylamine in deuterochloroform.

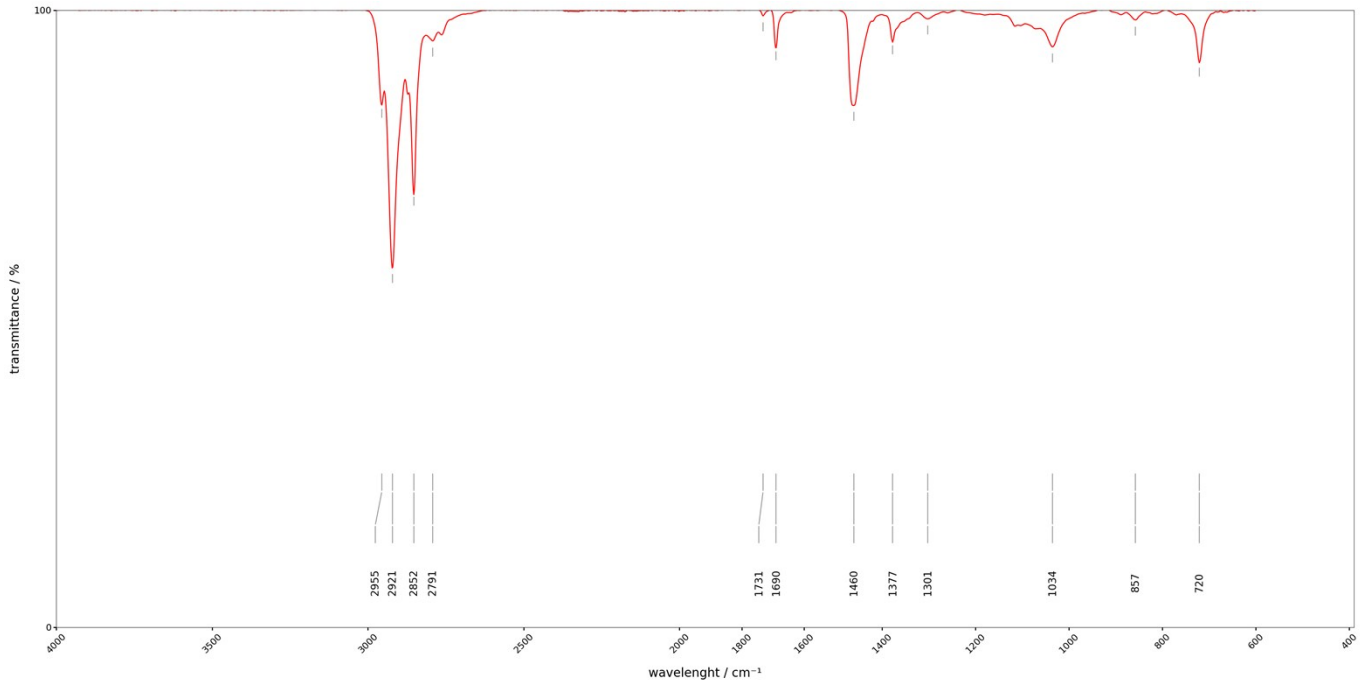

Figure S41. IR spectra of di(2-heptyl-undecyl)methylamine.

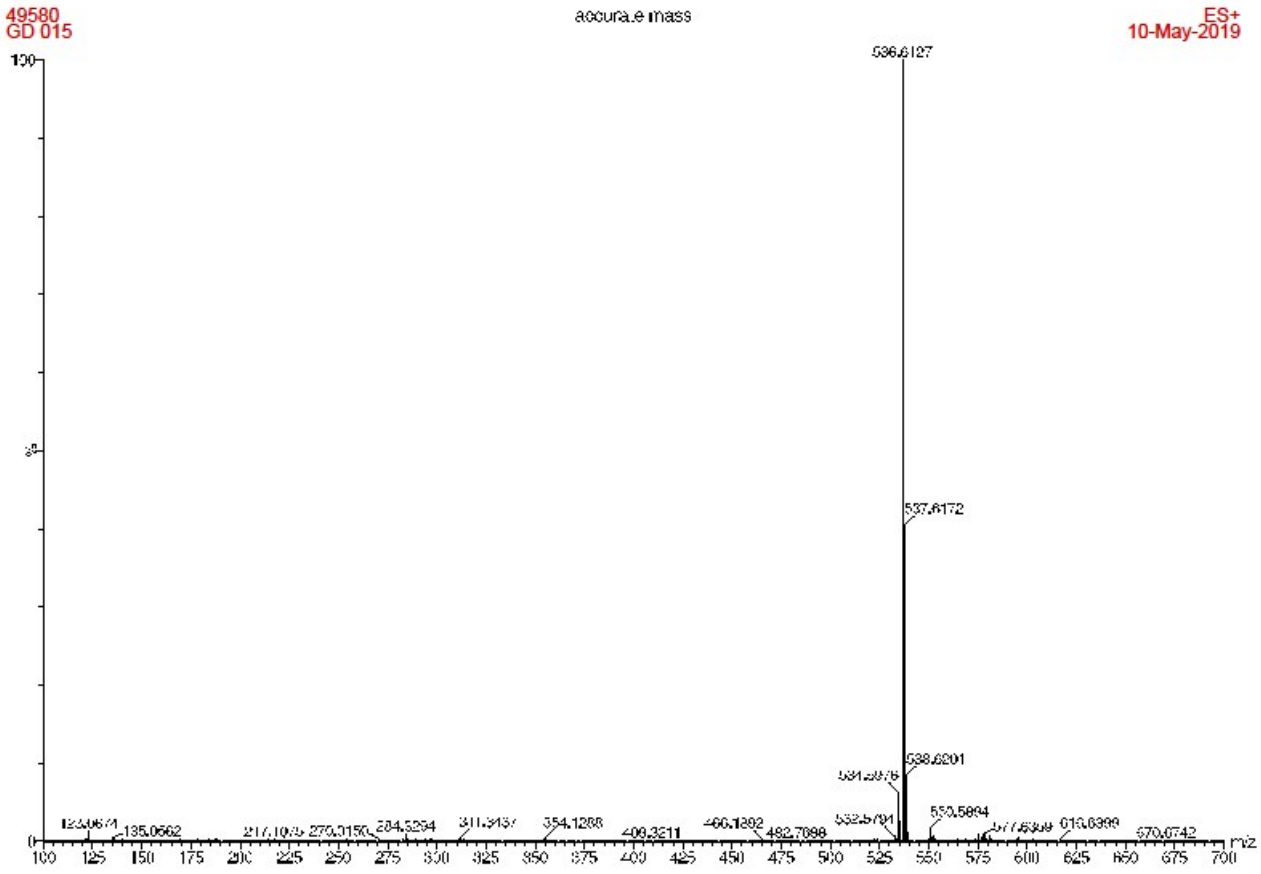

Figure S42. HRMS spectra of di(2-heptyl-undecyl)methylamine.

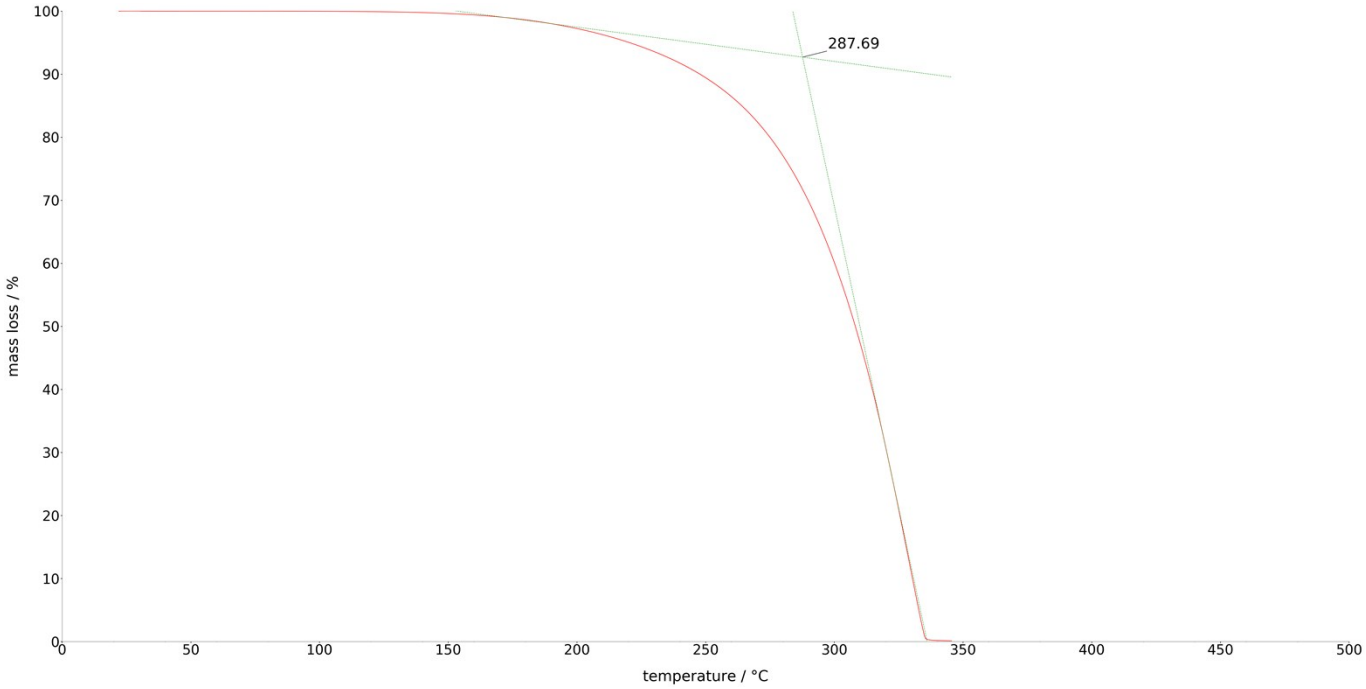

Figure S43. Thermogravimetric analysis for di(2-heptyl-undecyl)methylamine.

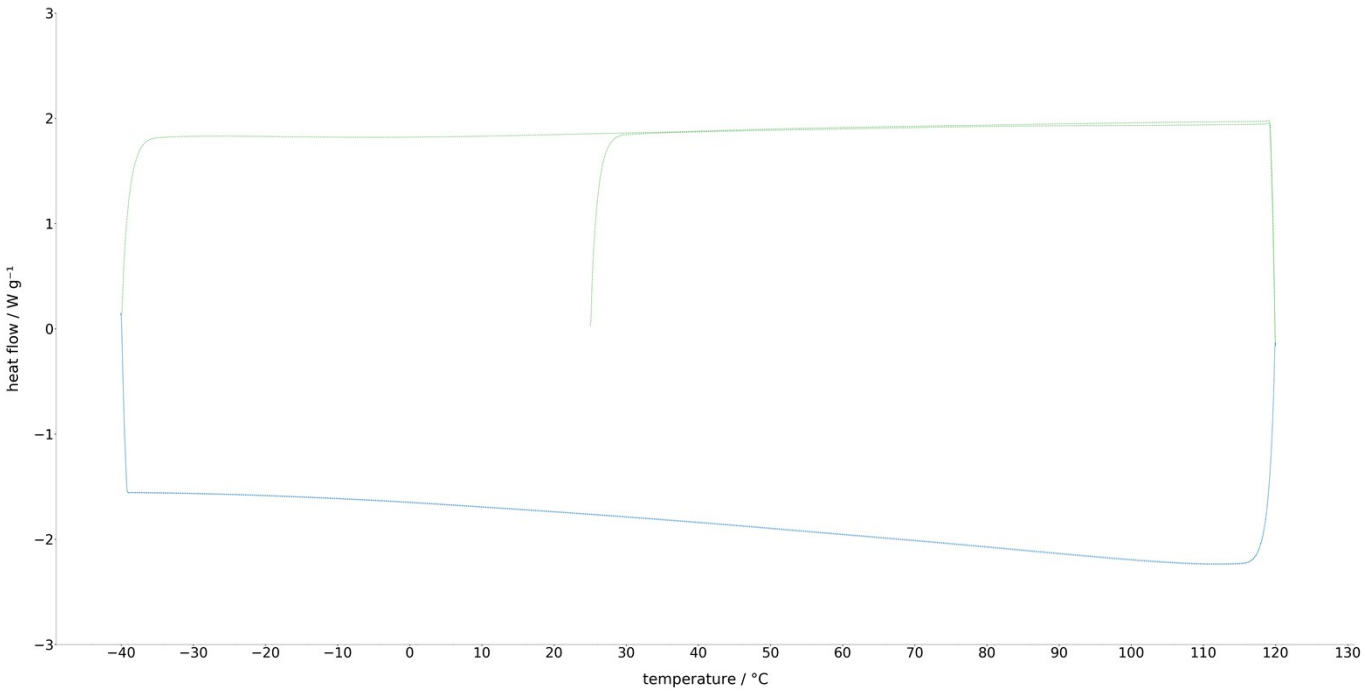

Figure S44. Differential scan calorimetry for di(2-heptyl-undecyl)methylamine.

Table S9. Densitimetry and viscosimetry data for di(2-heptyl-undecyl)methylamine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.79982	59.98	10.29	12.87	60.00	0.01	0.25	Ø1.8 Gold (20644413)
0.80137	57.52	11.01	13.74	57.50	0.10	0.33	Ø1.8 Gold (20644413)
0.80295	55.02	11.86	14.77	55.00	0.03	0.28	Ø1.8 Gold (20644413)
0.80453	52.53	12.78	15.89	52.50	0.05	0.25	Ø1.8 Gold (20644413)
0.80612	50.03	13.82	17.15	50.00	0.04	0.28	Ø1.8 Gold (20644413)
0.80770	47.53	14.99	18.55	47.50	0.07	0.31	Ø1.8 Gold (20644413)
0.80932	44.99	16.36	20.22	45.00	0.04	0.30	Ø1.8 Gold (20644413)
0.81091	42.48	17.86	22.03	42.50	0.05	0.21	Ø1.8 Gold (20644413)
0.81246	40.03	19.46	23.96	40.00	0.06	0.34	Ø1.8 Gold (20644413)
0.81405	37.53	21.37	26.25	37.50	0.02	0.23	Ø1.8 Gold (20644413)
0.81564	35.03	23.49	28.80	35.00	0.03	0.28	Ø1.8 Gold (20644413)
0.81723	32.53	25.90	31.69	32.50	0.05	0.20	Ø1.8 Gold (20644413)
0.81882	30.03	28.56	34.87	30.00	0.11	0.22	Ø1.8 Gold (20644413)
0.82042	27.53	31.43	38.31	27.50	0.27	0.22	Ø1.8 Gold (20644413)
0.82201	25.02	34.64	42.14	25.00	0.24	0.18	Ø1.8 Gold (20644413)
0.82361	22.52	38.41	46.64	22.50	0.16	0.19	Ø1.8 Gold (20644413)
0.82521	20.02	42.96	52.06	20.00	0.02	0.28	Ø1.8 Gold (20644413)

Di(2-octyl-dodecyl)methylamine

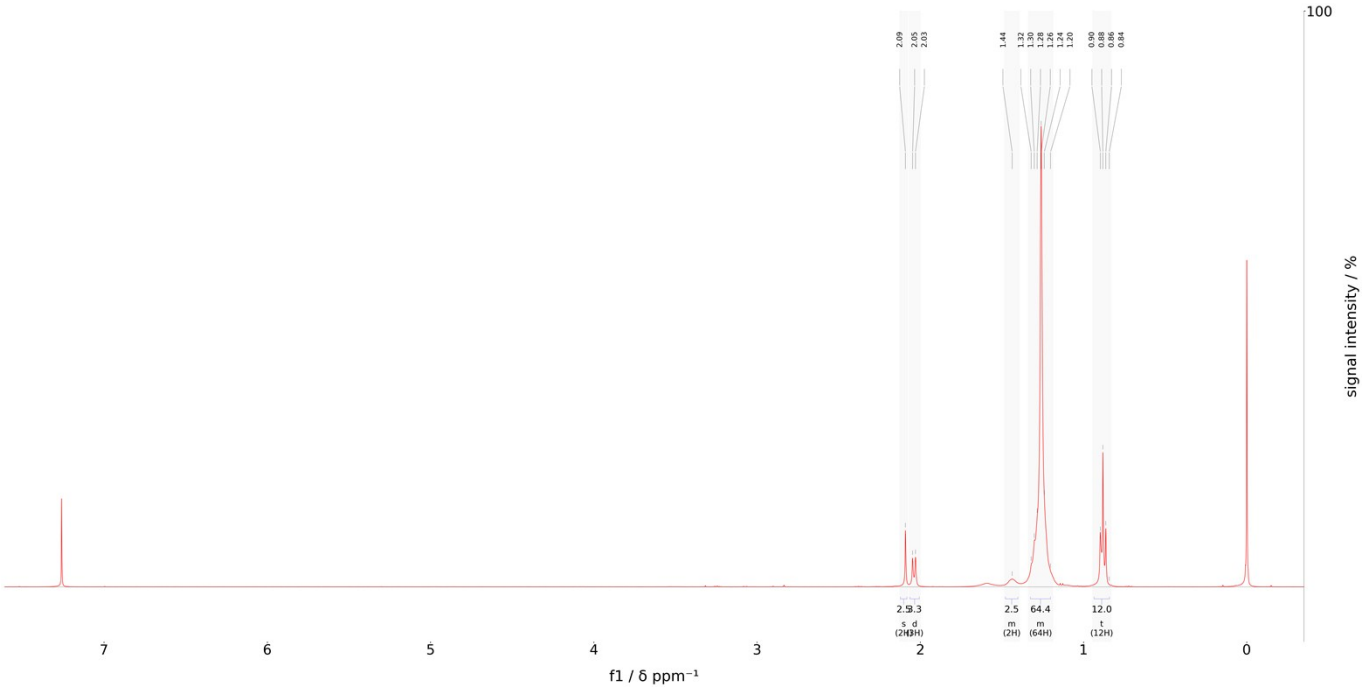

Figure S45. ^{1}H NMR of di(2-octyl-dodecyl)methylamine in deuterochloroform.

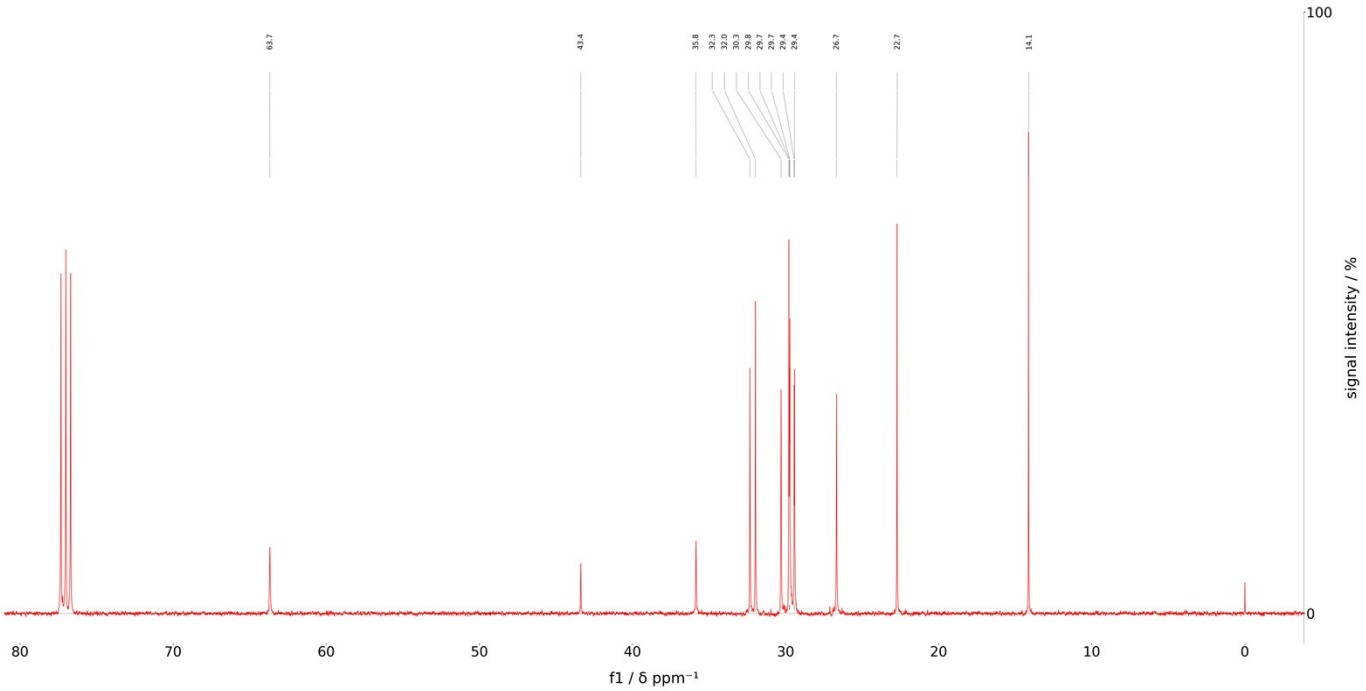

Figure S46. ^{13}C NMR of di(2-octyl-dodecyl)methylamine in deuterochloroform.

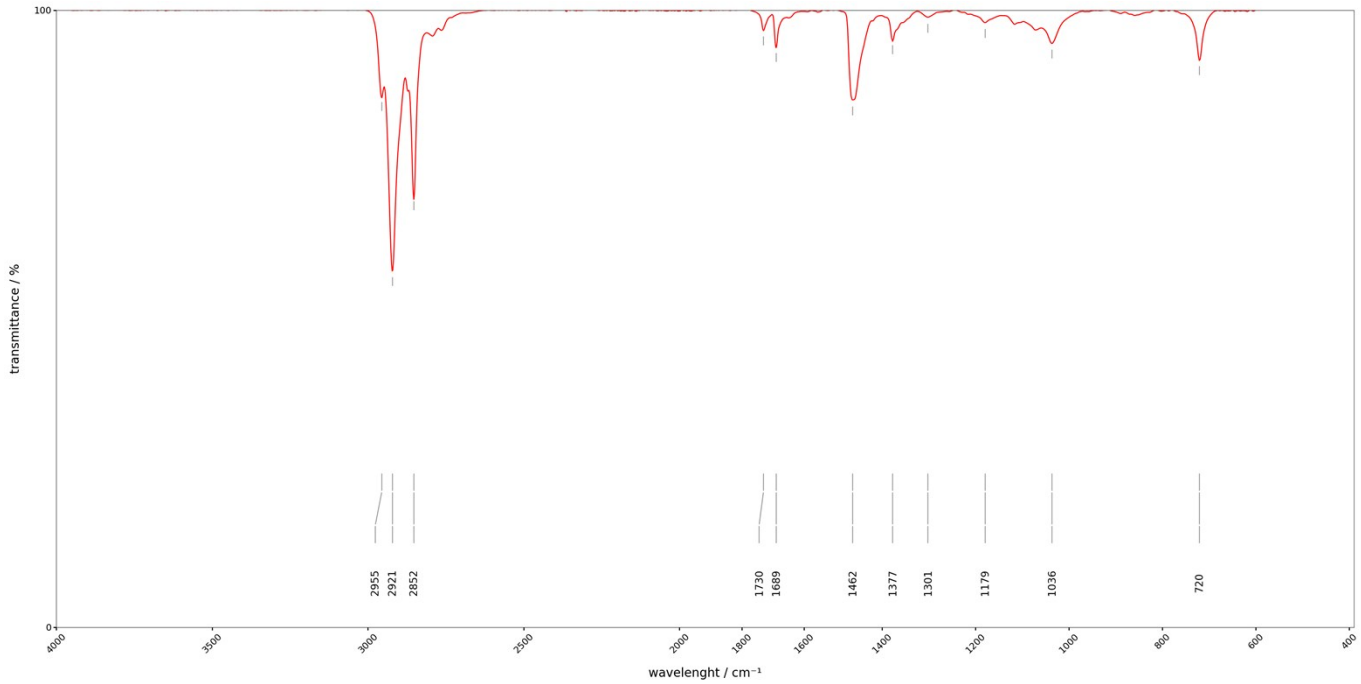

Figure S47. IR spectra of di(2-octyl-dodecyl)methylamine.

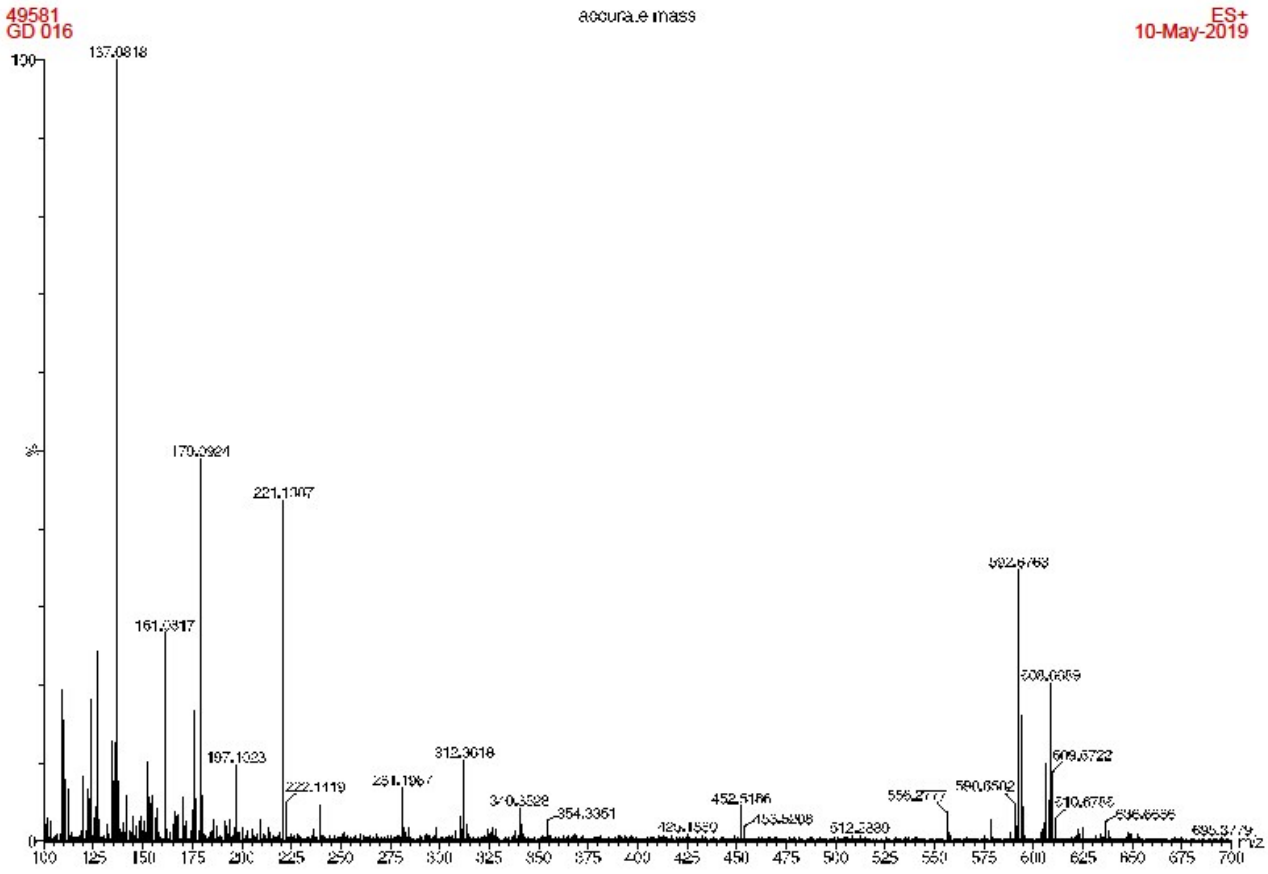

Figure S48. HRMS spectra of di(2-octyl-dodecyl)methylamine.

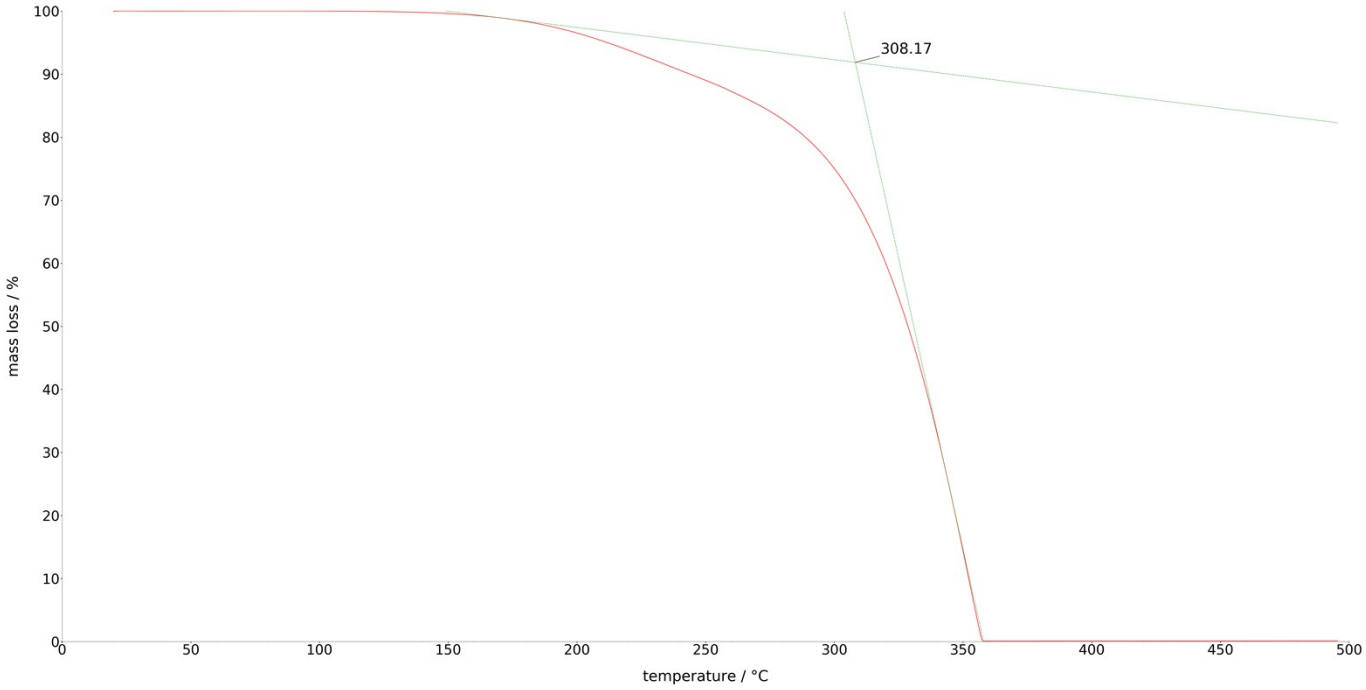

Figure S49. Thermogravimetric analysis for di(2-octyl-dodecyl)methylamine.

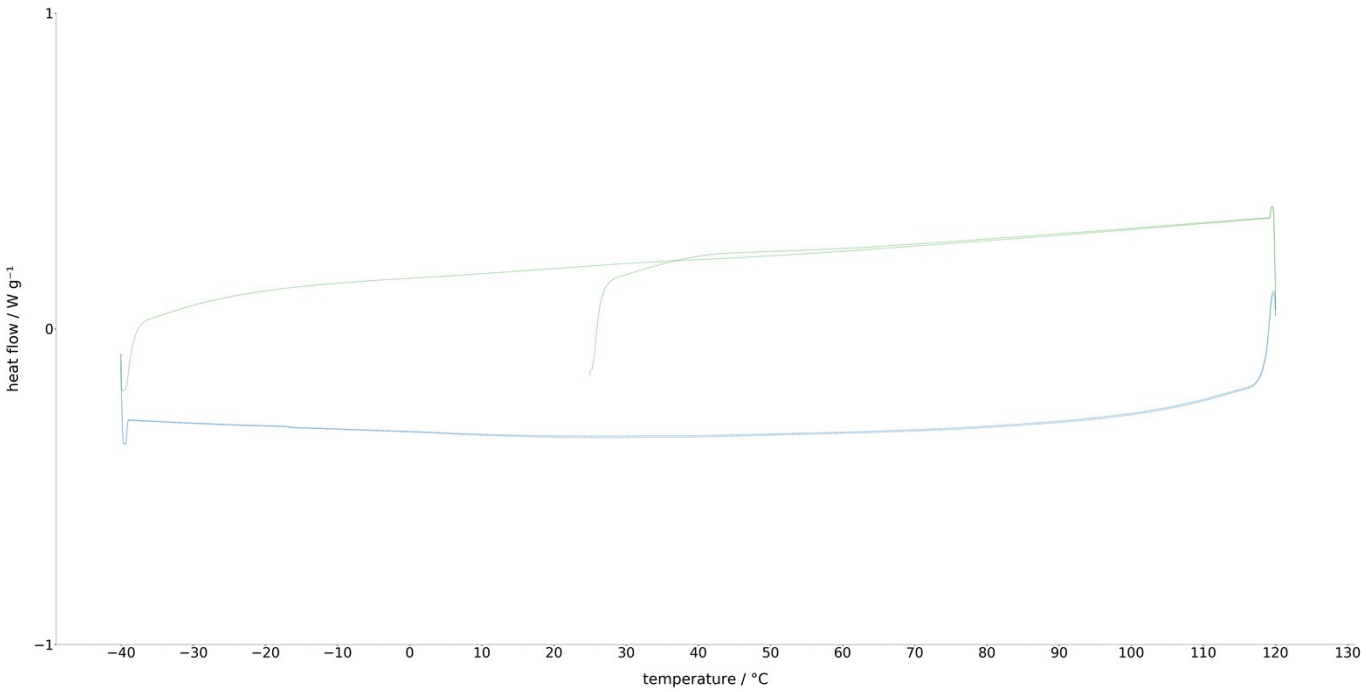

Figure S50. Differential scan calorimetry for di(2-octyl-dodecyl)methylamine.

Table S10. Densitimetry and viscosimetry data for di(2-octyl-dodecyl)methylamine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.80102	59.98	11.00	13.73	60.00	0.02	0.01	Ø1.8 Gold (20644413)
0.80256	57.52	11.82	14.73	57.50	0.03	0.08	Ø1.8 Gold (20644413)
0.80412	55.02	12.73	15.83	55.00	0.01	0.06	Ø1.8 Gold (20644413)
0.80569	52.53	13.75	17.07	52.50	0.03	0.12	Ø1.8 Gold (20644413)
0.80726	50.03	14.88	18.43	50.00	0.01	0.03	Ø1.8 Gold (20644413)
0.80884	47.53	16.15	19.96	47.50	0.02	0.04	Ø1.8 Gold (20644413)
0.81042	45.03	17.58	21.69	45.00	0.02	0.03	Ø1.8 Gold (20644413)
0.81199	42.53	19.16	23.59	42.50	0.02	0.03	Ø1.8 Gold (20644413)
0.81358	40.03	20.94	25.74	40.00	0.05	0.05	Ø1.8 Gold (20644413)
0.81516	37.53	22.94	28.14	37.50	0.04	0.03	Ø1.8 Gold (20644413)
0.81674	35.03	25.22	30.88	35.00	0.02	0.03	Ø1.8 Gold (20644413)
0.81833	32.53	27.83	34.01	32.50	0.01	0.06	Ø1.8 Gold (20644413)
0.81991	30.03	30.81	37.58	30.00	0.02	0.05	Ø1.8 Gold (20644413)
0.82150	27.52	34.41	41.88	27.50	0.02	0.15	Ø1.8 Gold (20644413)
0.82309	25.02	38.39	46.64	25.00	0.05	0.03	Ø1.8 Gold (20644413)
0.82469	22.52	42.93	52.06	22.50	0.02	0.08	Ø1.8 Gold (20644413)
0.82628	20.02	48.27	58.42	20.00	0.05	0.08	Ø1.8 Gold (20644413)

Tri(2-butyl-octyl)amine

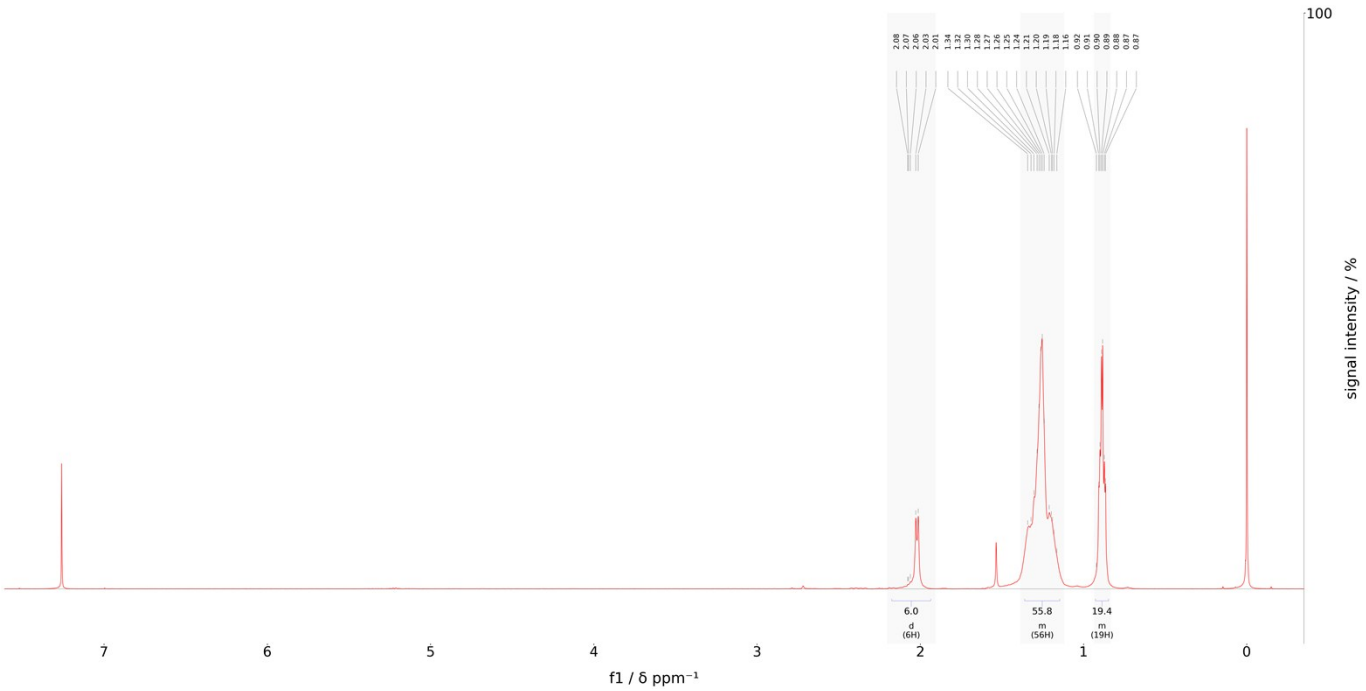

Figure S51. ^{1}H NMR of tri(2-butyl-octyl)amine in deuterochloroform.

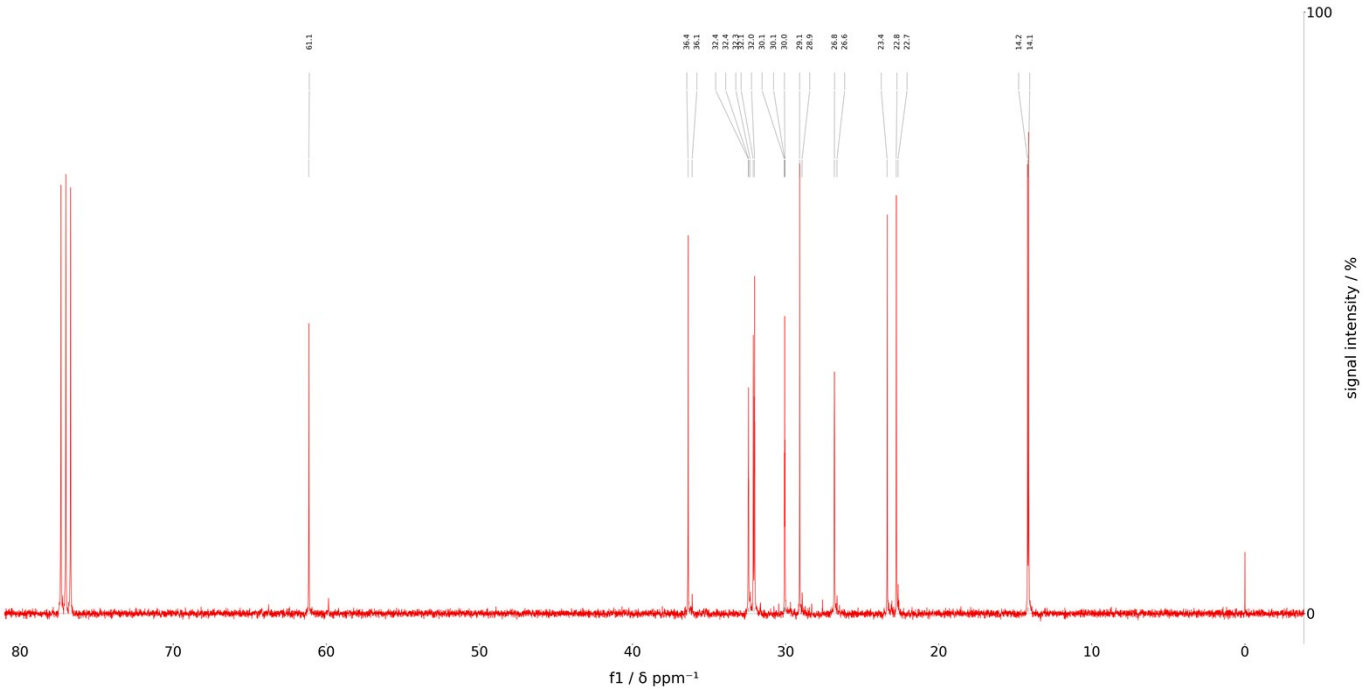

Figure S52. ^{13}C NMR of tri(2-butyl-octyl)amine in deuterochloroform.

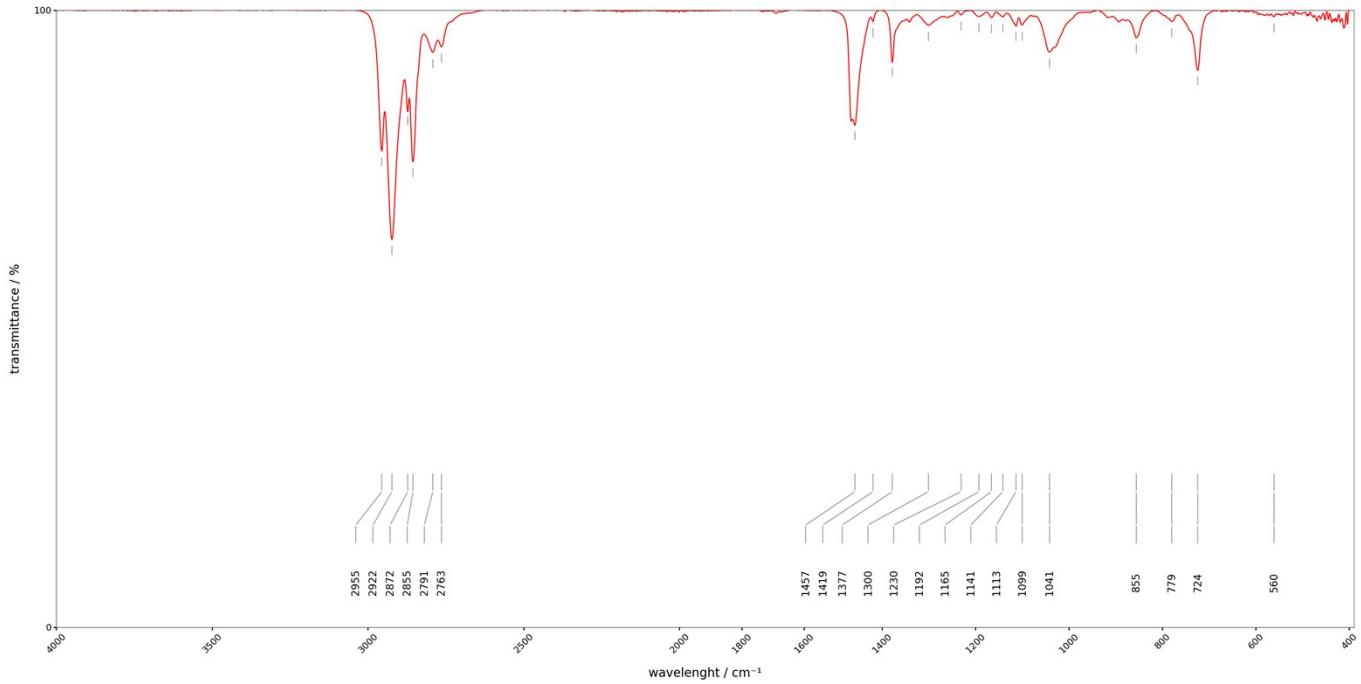

Figure S53. IR spectra of tri(2-butyl-octyl)amine.

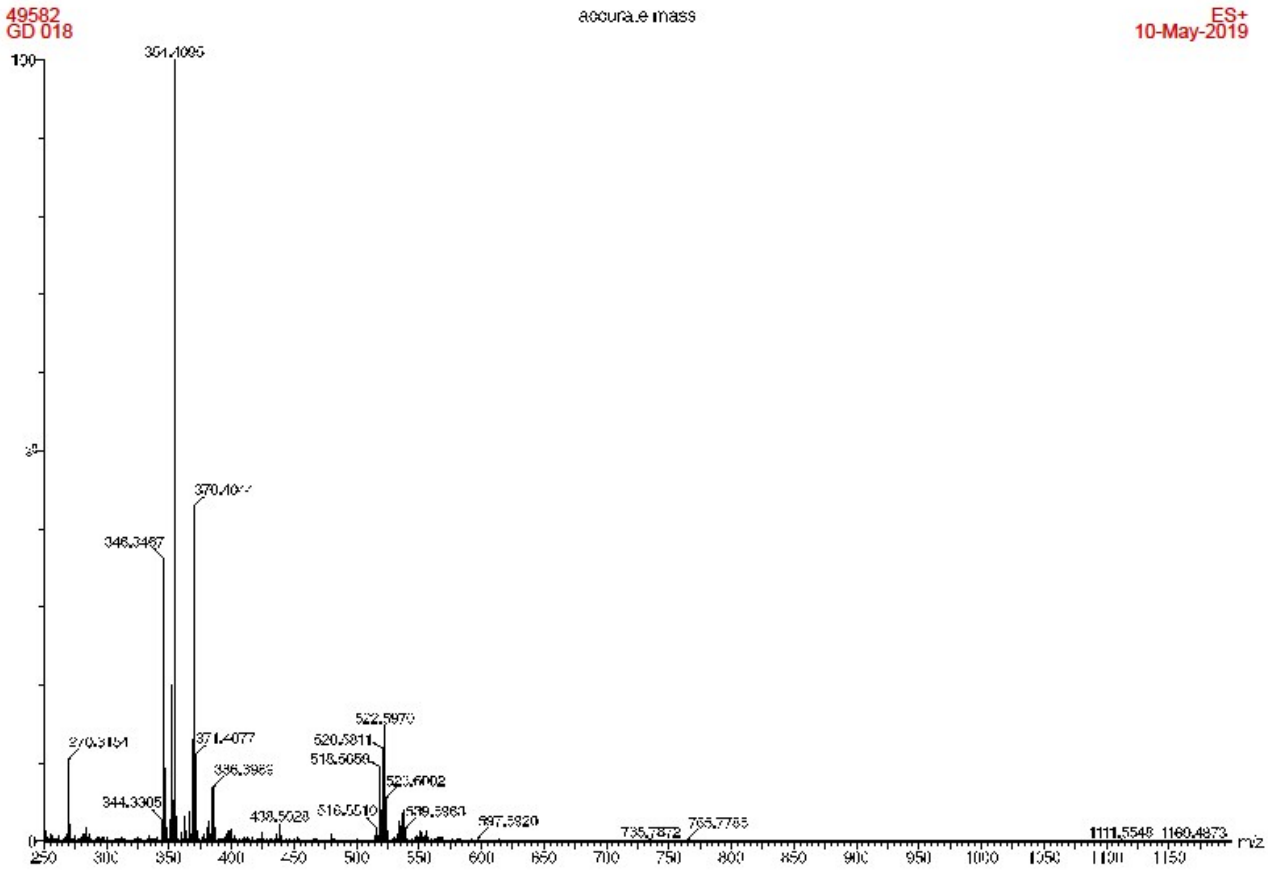

Figure S54. HRMS spectra of tri(2-butyl-octyl)amine.

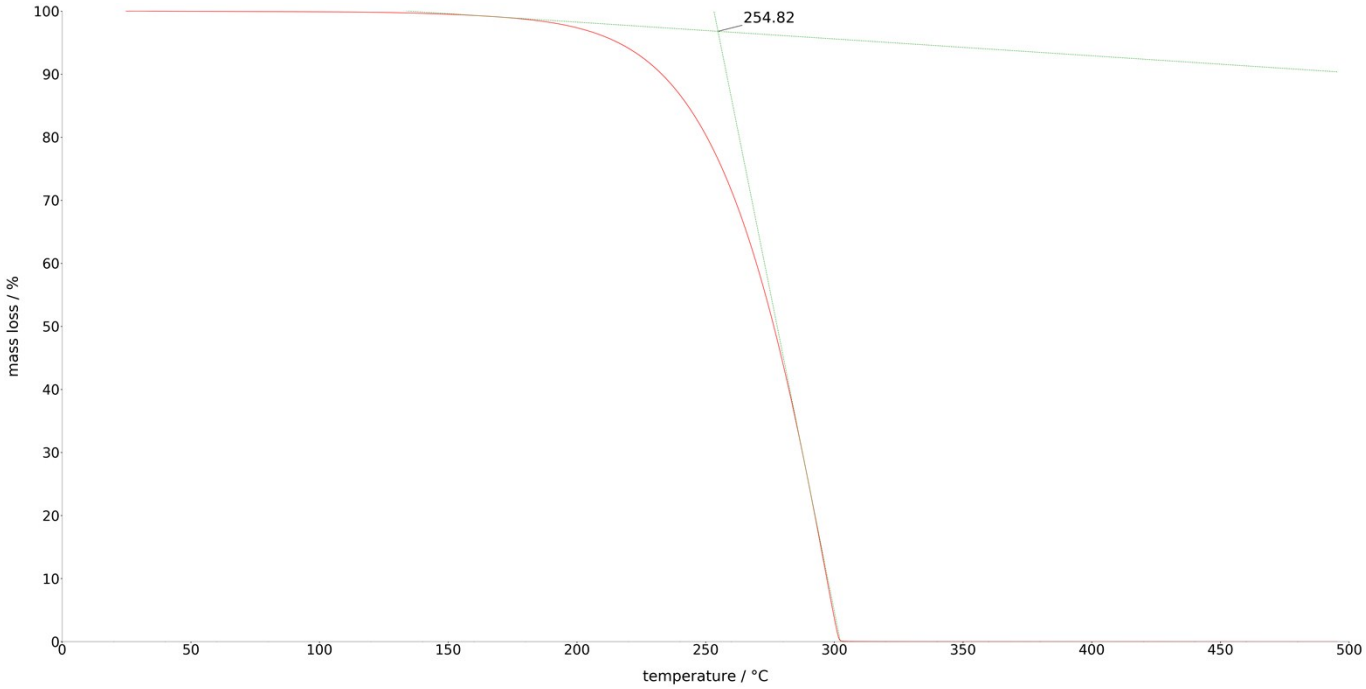

Figure S55. Thermogravimetric analysis for tri(2-butyl-octyl)amine.

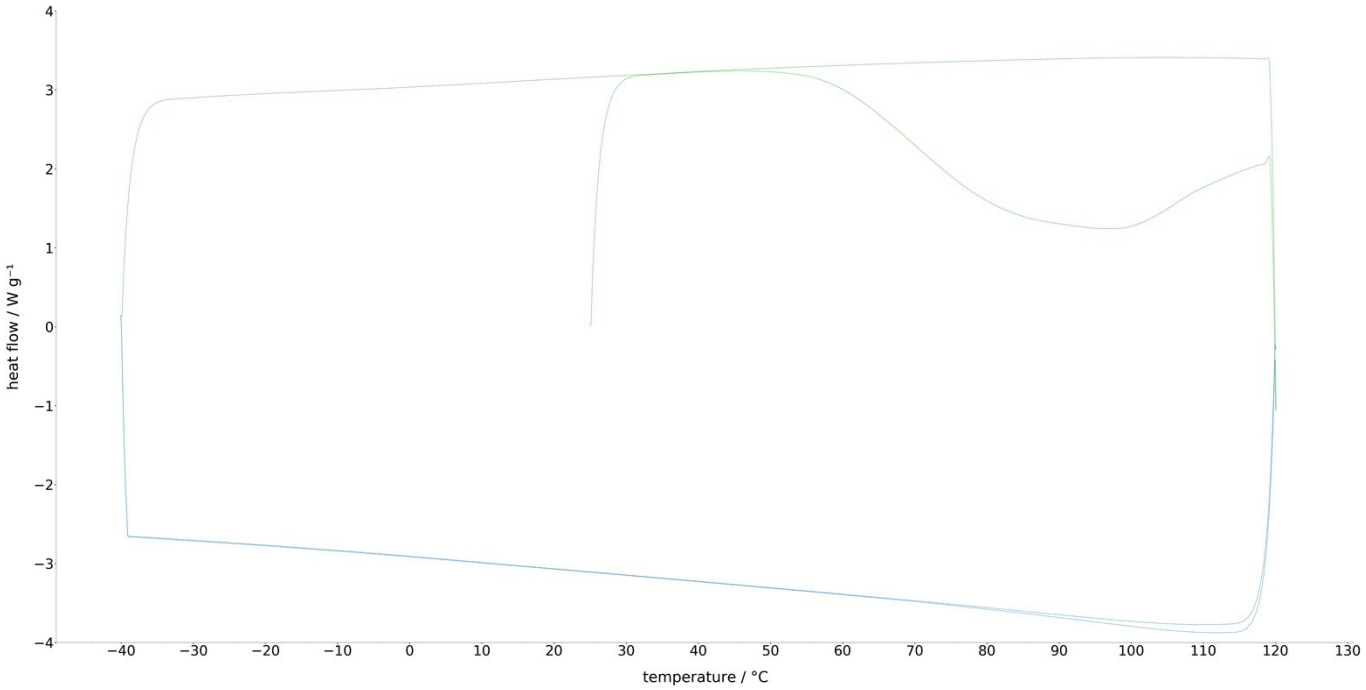

Figure S56. Differential scan calorimetry for tri(2-butyl-octyl)amine.

Table S11. Densitimetry and viscosimetry data for tri(2-butyl-octyl)amine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.80302	59.98	13.12	16.34	60.00	0.11	0.34	Ø1.8 Gold (20644413)
0.80458	57.52	14.32	17.80	57.50	0.06	0.17	Ø1.8 Gold (20644413)
0.80617	55.02	15.55	19.29	55.00	0.06	0.21	Ø1.8 Gold (20644413)
0.80777	52.53	16.97	21.01	52.50	0.03	0.19	Ø1.8 Gold (20644413)
0.80937	50.03	18.54	22.91	50.00	0.06	0.11	Ø1.8 Gold (20644413)
0.81097	47.53	20.36	25.11	47.50	0.02	0.09	Ø1.8 Gold (20644413)
0.81256	45.03	22.43	27.60	45.00	0.00	0.13	Ø1.8 Gold (20644413)
0.81416	42.53	24.83	30.50	42.50	0.04	0.09	Ø1.8 Gold (20644413)
0.81577	40.03	27.54	33.76	40.00	0.03	0.16	Ø1.8 Gold (20644413)
0.81737	37.53	30.67	37.53	37.50	0.02	0.15	Ø1.8 Gold (20644413)
0.81897	35.03	34.35	41.95	35.00	0.07	0.12	Ø1.8 Gold (20644413)
0.82058	32.53	38.51	46.93	32.50	0.06	0.06	Ø1.8 Gold (20644413)
0.82218	30.03	43.34	52.71	30.00	0.07	0.17	Ø1.8 Gold (20644413)
0.82378	27.52	48.99	59.47	27.50	0.06	0.17	Ø1.8 Gold (20644413)
0.82538	25.02	55.30	67.00	25.00	0.16	0.10	Ø1.8 Gold (20644413)
0.82698	22.52	63.20	76.42	22.50	0.13	0.24	Ø1.8 Gold (20644413)
0.82859	20.02	72.16	87.09	20.00	0.06	0.32	Ø1.8 Gold (20644413)

Tri(2-pentyl-nonyl)amine

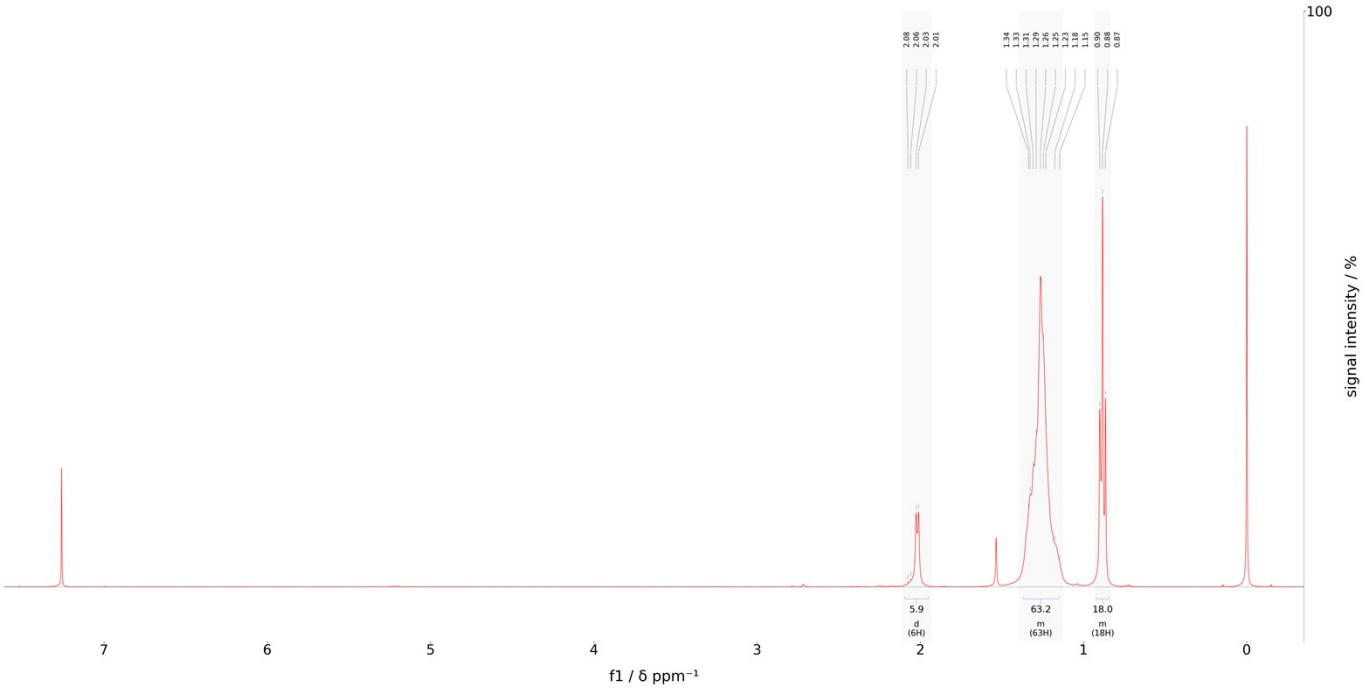

Figure S57. ^{1}H NMR of tri(2-pentyl-nonyl)amine in deuterochloroform.

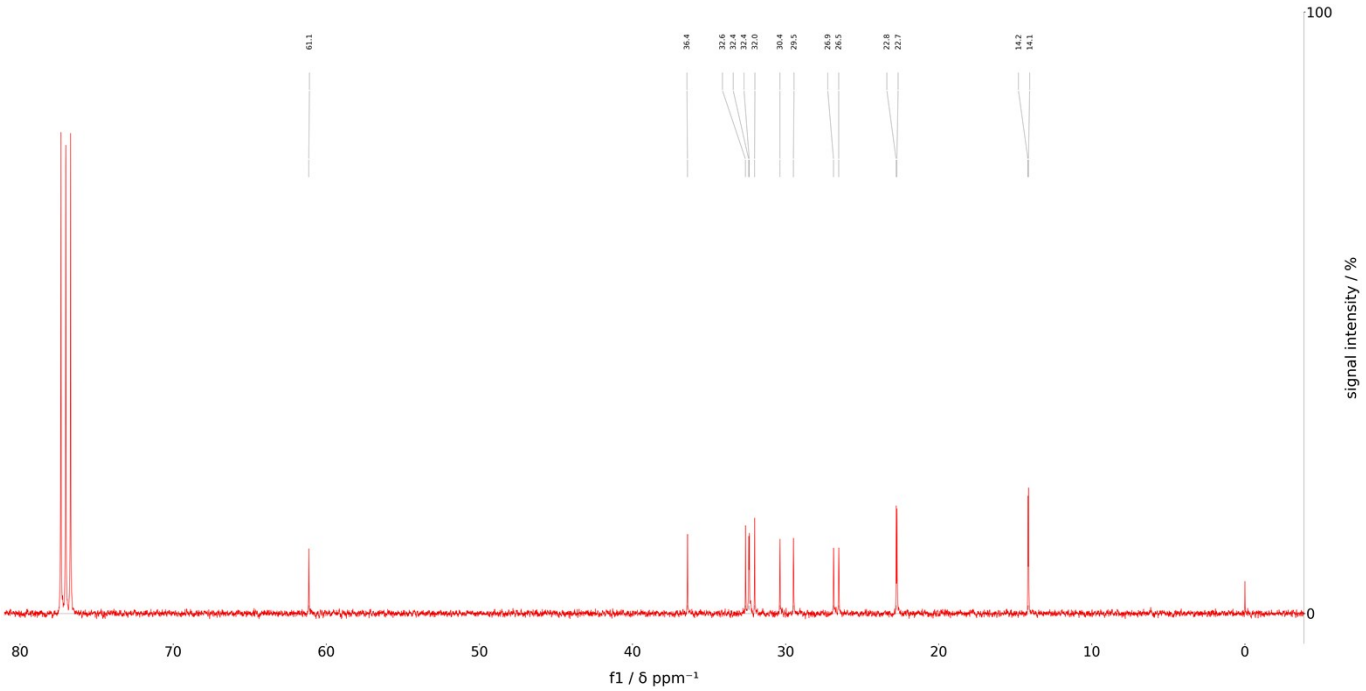

Figure S58. ^{13}C NMR of tri(2-pentyl-nonyl)amine in deuterochloroform.

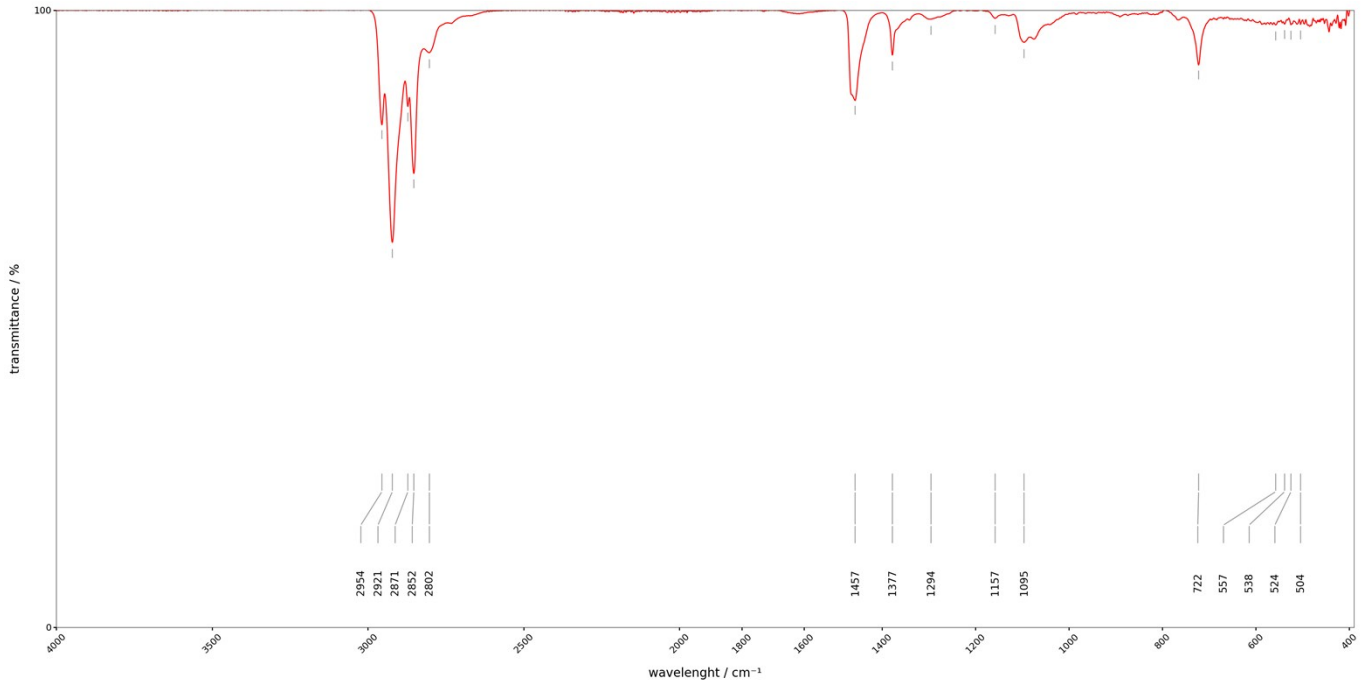

Figure S59. IR spectra of tri(2-pentyl-nonyl)amine.

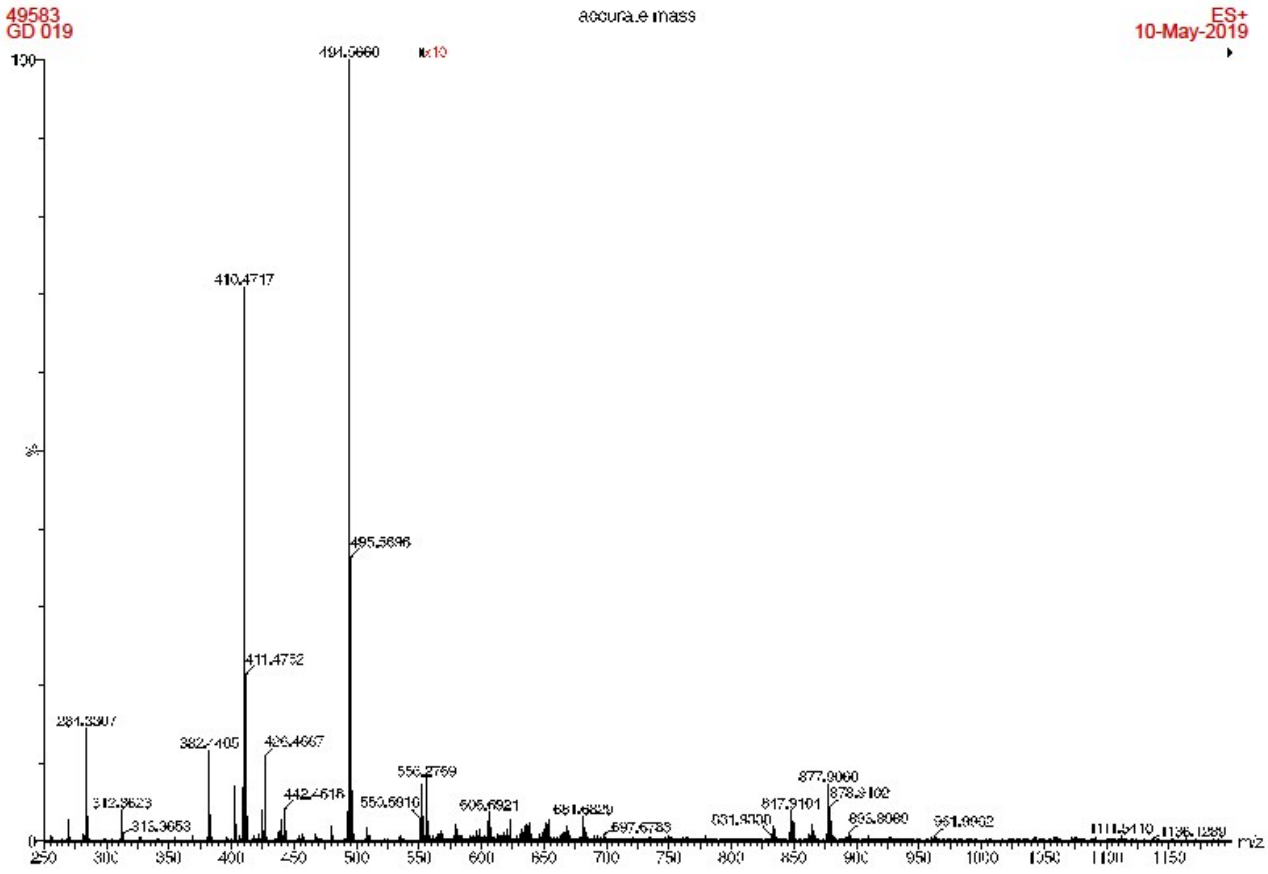

Figure S60. HRMS spectra of tri(2-pentyl-nonyl)amine.

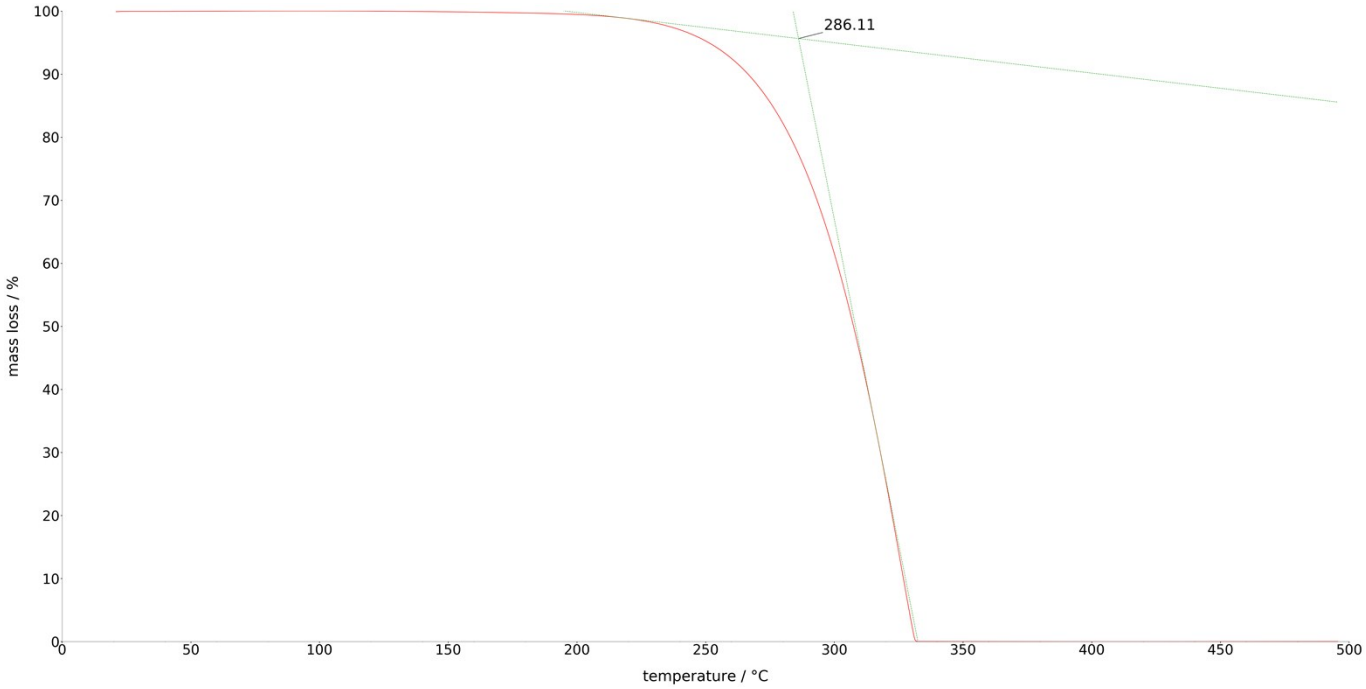

Figure S61. Thermogravimetric analysis for tri(2-pentyl-nonyl)amine.

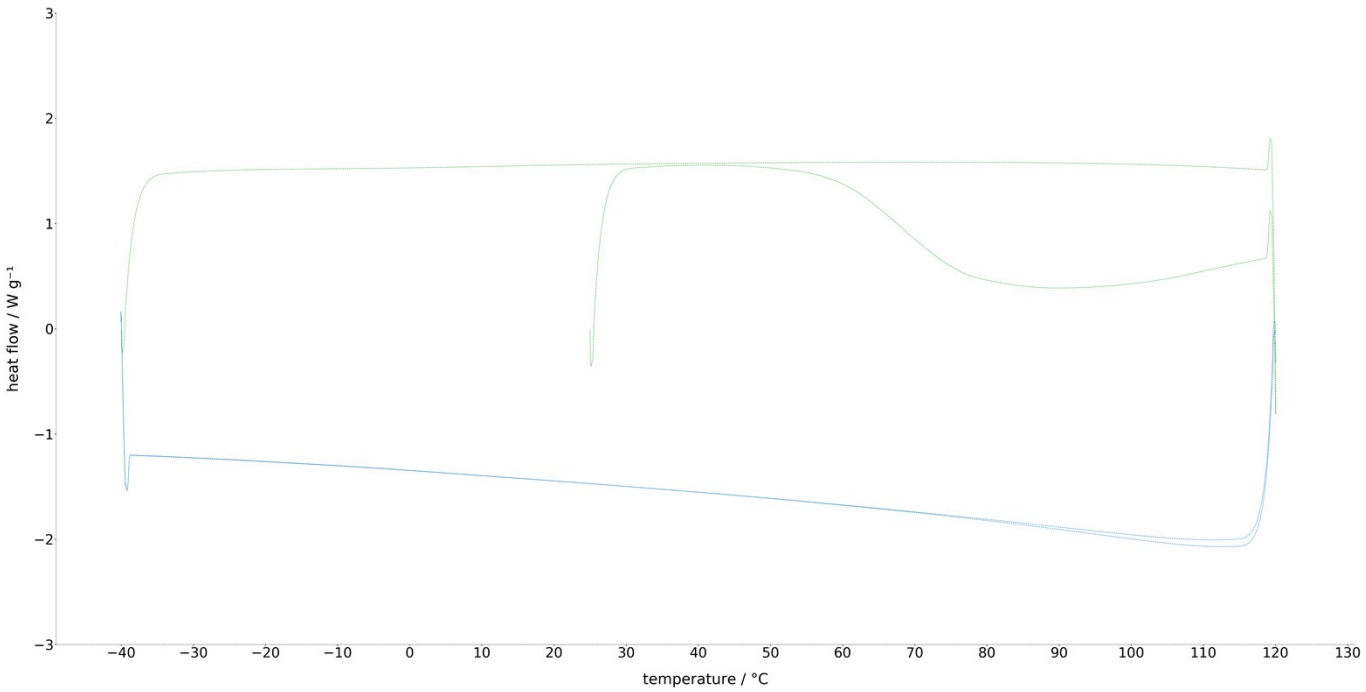

Figure S62. Differential scan calorimetry for tri(2-pentyl-nonyl)amine.

Table S12. Densitimetry and viscosimetry data for tri(2-pentyl-nonyl)amine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.80489	59.98	15.90	19.75	60.00	0.04	0.35	Ø1.8 Gold (20644413)
0.80642	57.52	17.23	21.37	57.50	0.16	0.43	Ø1.8 Gold (20644413)
0.80799	55.02	18.75	23.20	55.00	0.03	0.24	Ø1.8 Gold (20644413)
0.80955	52.53	20.43	25.24	52.50	0.05	0.26	Ø1.8 Gold (20644413)
0.81112	50.03	22.33	27.53	50.00	0.05	0.34	Ø1.8 Gold (20644413)
0.81269	47.53	24.48	30.13	47.50	0.02	0.24	Ø1.8 Gold (20644413)
0.81426	45.03	26.88	33.01	45.00	0.07	0.20	Ø1.8 Gold (20644413)
0.81583	42.53	29.64	36.33	42.50	0.02	0.15	Ø1.8 Gold (20644413)
0.81740	40.03	32.84	40.18	40.00	0.07	0.21	Ø1.8 Gold (20644413)
0.81897	37.53	36.47	44.53	37.50	0.05	0.18	Ø1.8 Gold (20644413)
0.82055	35.03	40.58	49.45	35.00	0.08	0.29	Ø1.8 Gold (20644413)
0.82212	32.53	45.34	55.15	32.50	0.10	0.21	Ø1.8 Gold (20644413)
0.82370	30.03	50.92	61.82	30.00	0.02	0.09	Ø1.8 Gold (20644413)
0.82528	27.52	57.53	69.72	27.50	0.06	0.08	Ø1.8 Gold (20644413)
0.82685	25.02	65.18	78.83	25.00	0.04	0.20	Ø1.8 Gold (20644413)
0.82843	22.52	73.76	89.04	22.50	0.09	0.06	Ø1.8 Gold (20644413)
0.83001	20.02	83.45	100.5	20.00	0.02	0.17	Ø1.8 Gold (20644413)

Tri(2-hexyl-decyl)amine

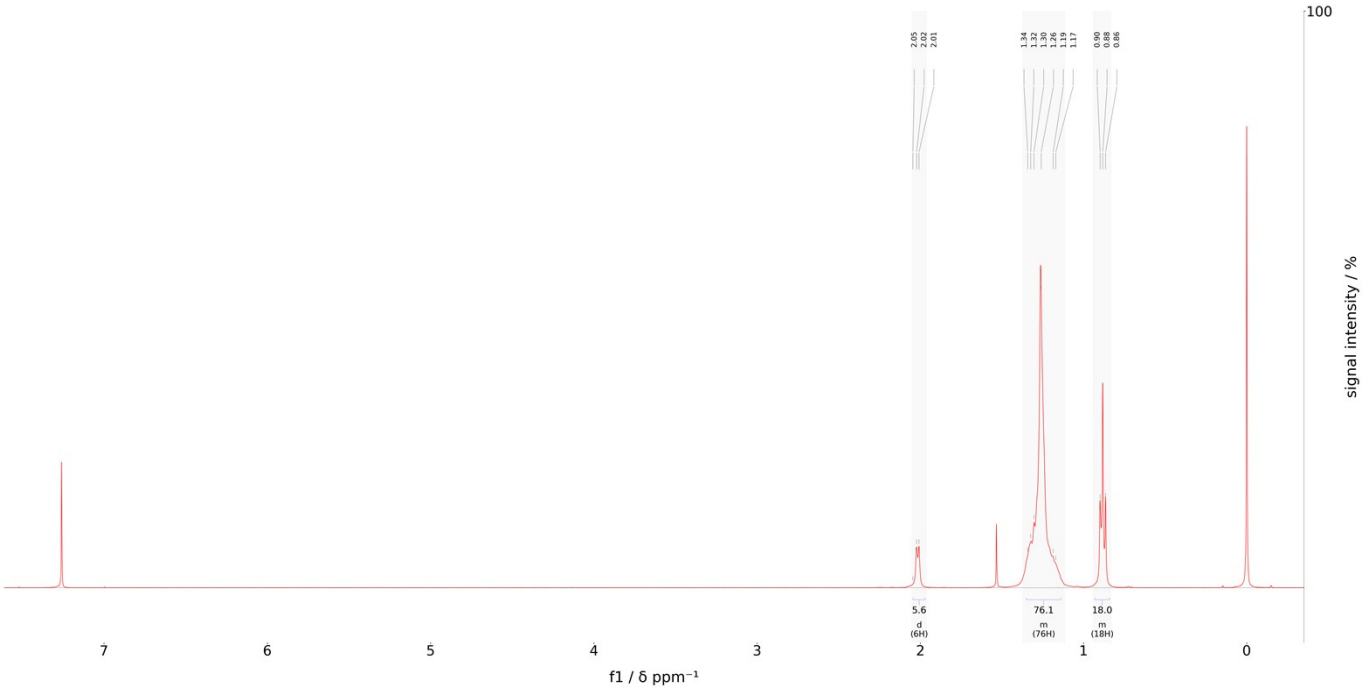

Figure S63. ^{1}H NMR of tri(2-hexyl-decyl)amine in deuterochloroform.

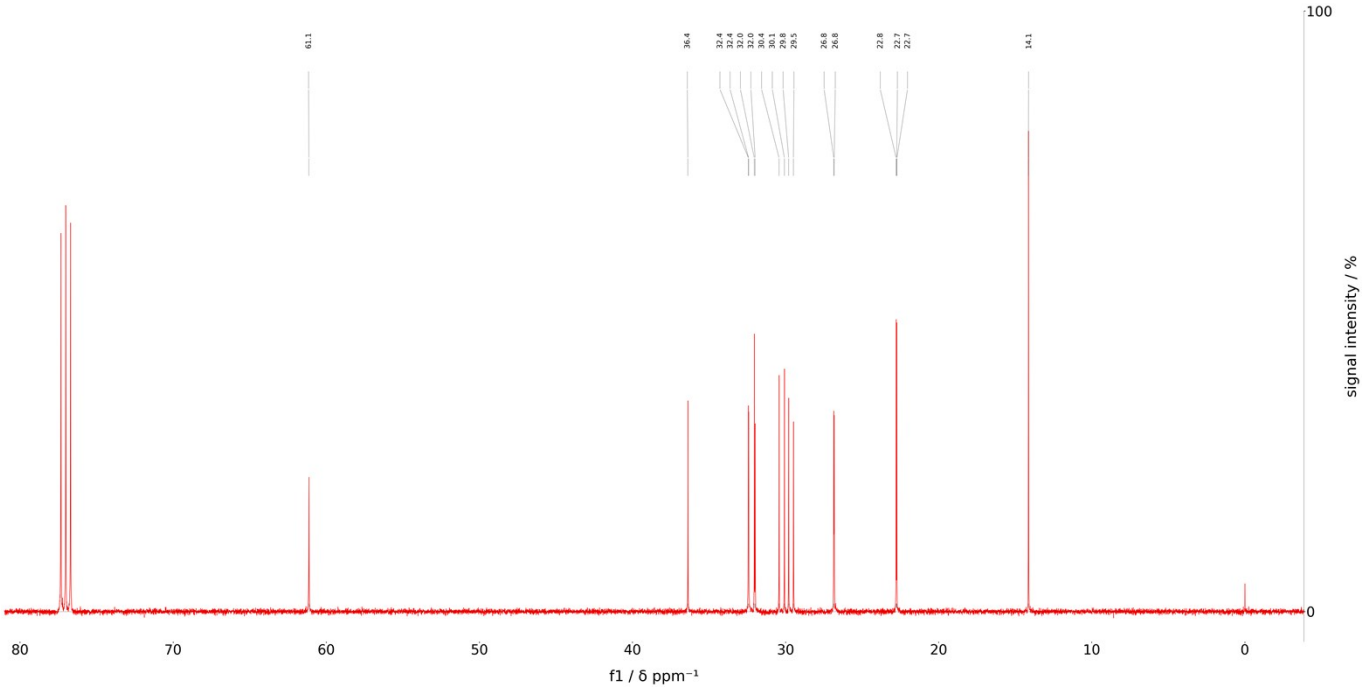

Figure S64. ^{13}C NMR of tri(2-hexyl-decyl)amine in deuterochloroform.

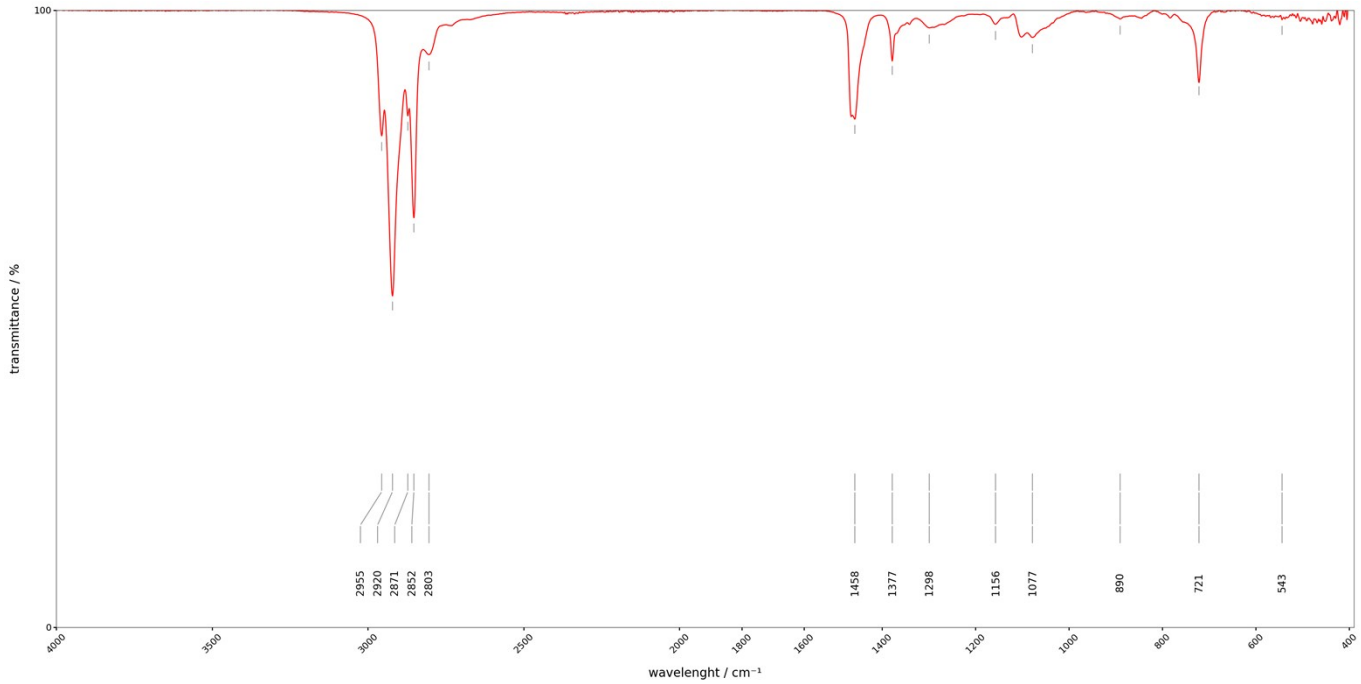

Figure S65. IR spectra of tri(2-hexyl-decyl)amine.

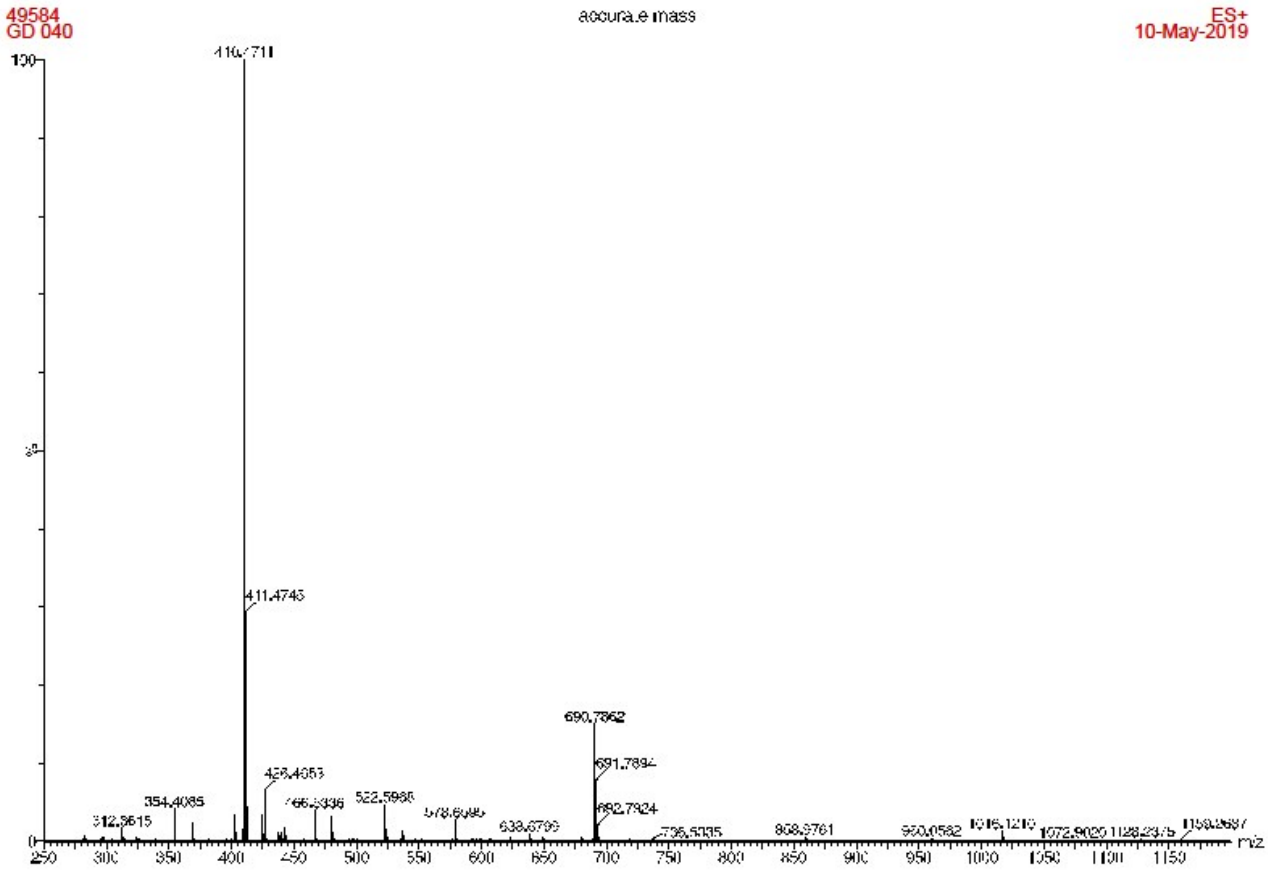

Figure S66. HRMS spectra of tri(2-hexyl-decyl)amine.

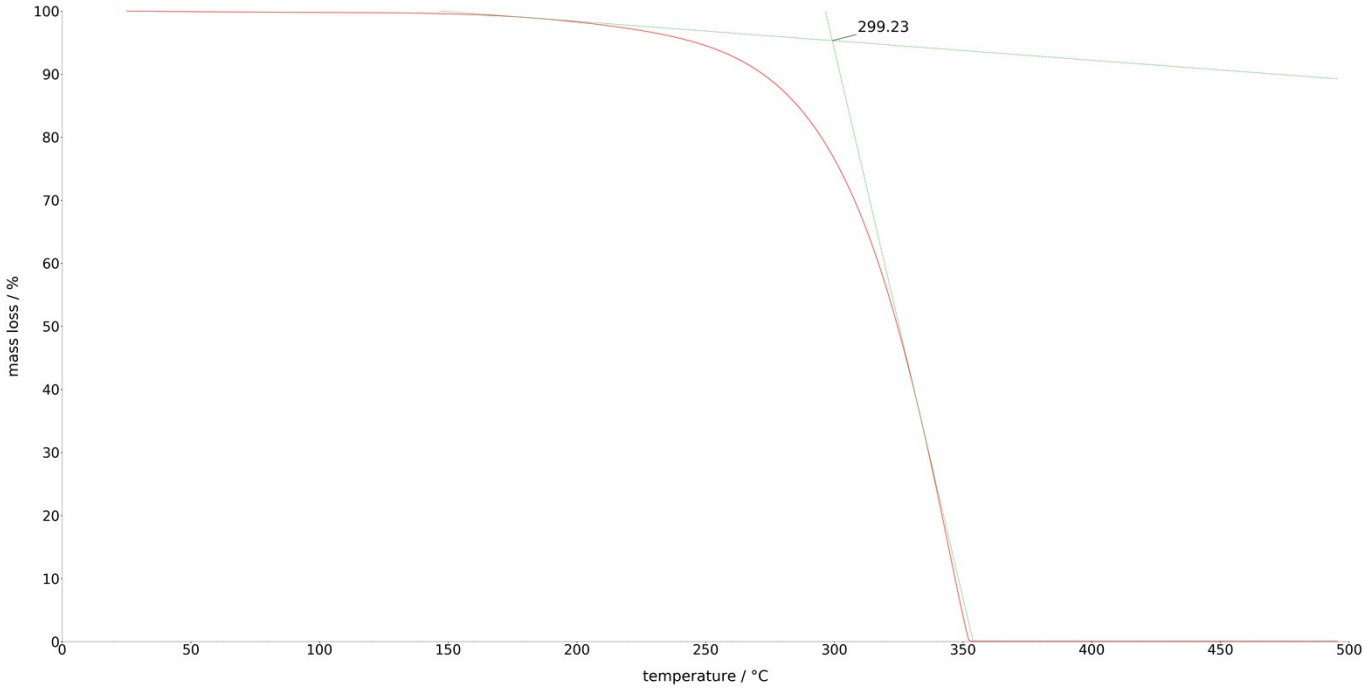

Figure S67. Thermogravimetric analysis for tri(2-hexyl-decyl)amine.

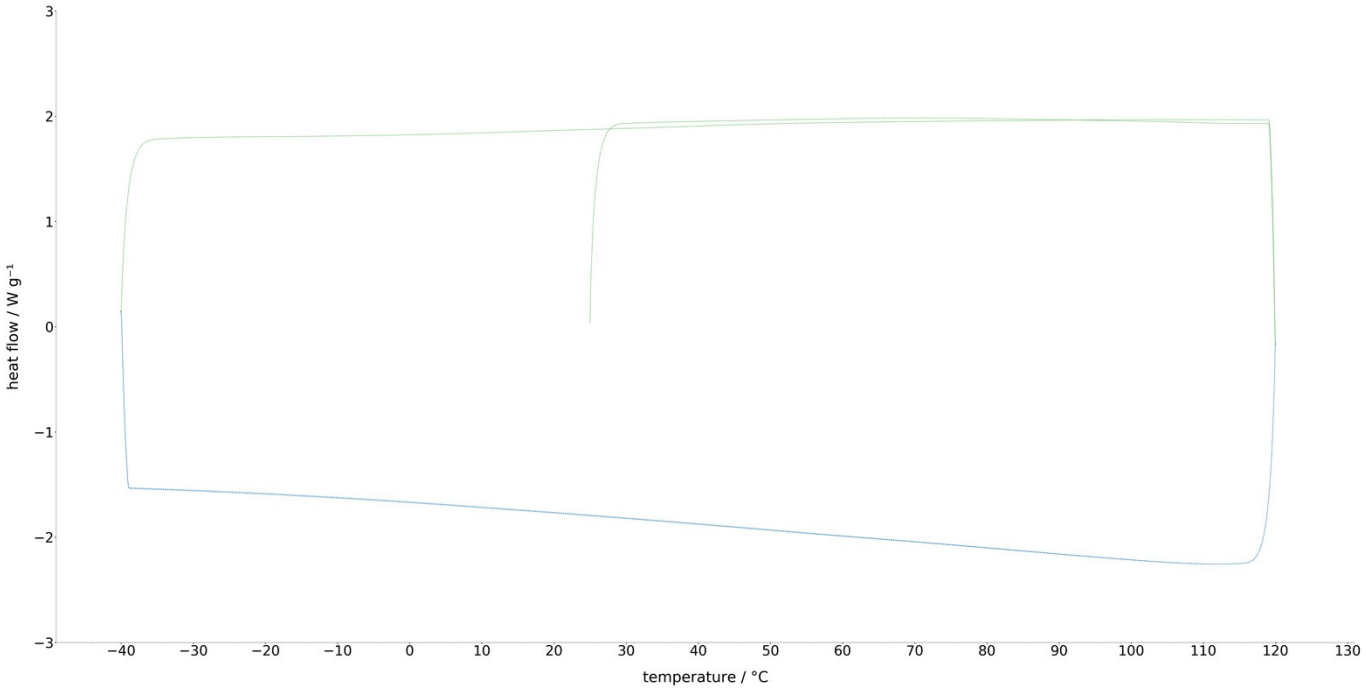

Figure S68. Differential scan calorimetry for tri(2-hexyl-decyl)amine.

Table S13. Densitimetry and viscosimetry data for tri(2-hexyl-decyl)amine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.82979	20.03	90.09	108.6	20.00	0.36	0.53	Ø1.8 Gold (20644413)
0.82827	22.49	79.01	95.40	22.50	0.40	0.32	Ø1.8 Gold (20644413)
0.82671	24.98	70.08	84.77	25.00	0.46	0.34	Ø1.8 Gold (20644413)
0.82515	27.48	62.55	75.80	27.50	0.13	0.43	Ø1.8 Gold (20644413)
0.82360	29.98	55.62	67.53	30.00	0.14	0.89	Ø1.8 Gold (20644413)
0.82204	32.48	49.97	60.79	32.50	0.64	0.31	Ø1.8 Gold (20644413)
0.82049	34.98	44.59	54.35	35.00	0.10	0.48	Ø1.8 Gold (20644413)
0.81893	37.48	40.15	49.02	37.50	0.10	0.74	Ø1.8 Gold (20644413)
0.81738	39.98	36.27	44.37	40.00	0.23	0.59	Ø1.8 Gold (20644413)
0.81583	42.48	32.79	40.19	42.50	0.07	0.35	Ø1.8 Gold (20644413)
0.81428	44.98	29.74	36.52	45.00	0.17	0.80	Ø1.8 Gold (20644413)
0.81273	47.48	27.09	33.33	47.50	0.22	0.42	Ø1.8 Gold (20644413)
0.81118	49.98	24.63	30.36	50.00	0.22	0.74	Ø1.8 Gold (20644413)
0.80963	52.48	22.54	27.84	52.50	0.20	0.68	Ø1.8 Gold (20644413)
0.80808	54.98	20.65	25.56	55.00	0.27	0.50	Ø1.8 Gold (20644413)
0.80654	57.48	18.97	23.52	57.50	0.27	0.61	Ø1.8 Gold (20644413)
0.80499	59.98	17.45	21.68	60.00	0.11	0.68	Ø1.8 Gold (20644413)

Tri(2-heptyl-undecyl)amine

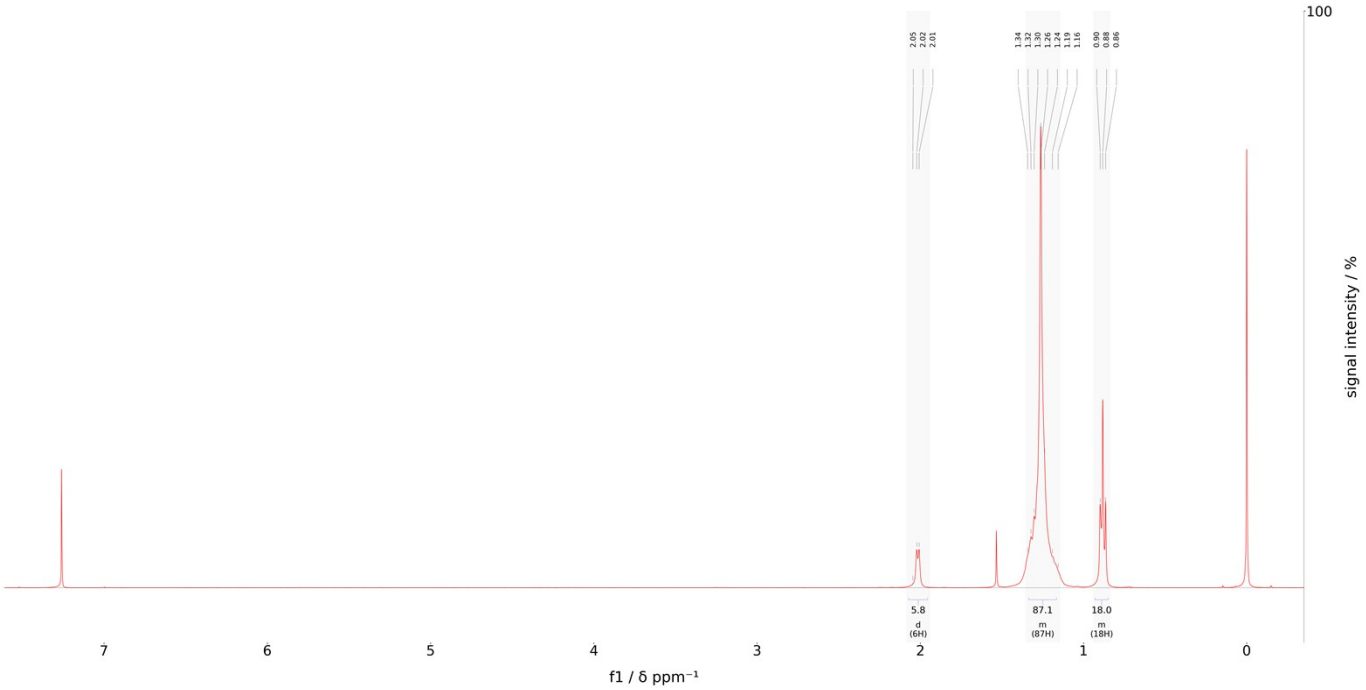

Figure S69. ^{1}H NMR of tri(2-heptyl-undecyl)amine in deuterochloroform.

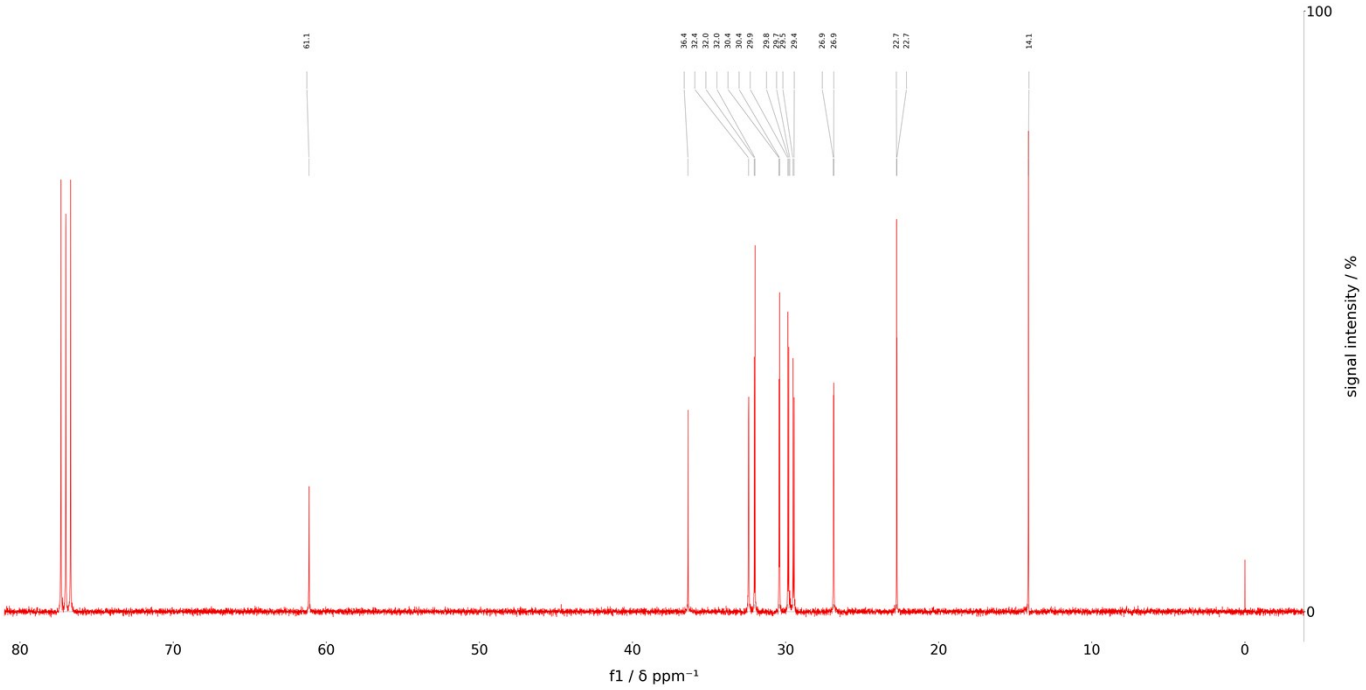

Figure S70. ^{13}C NMR of tri(2-heptyl-undecyl)amine in deuterochloroform.

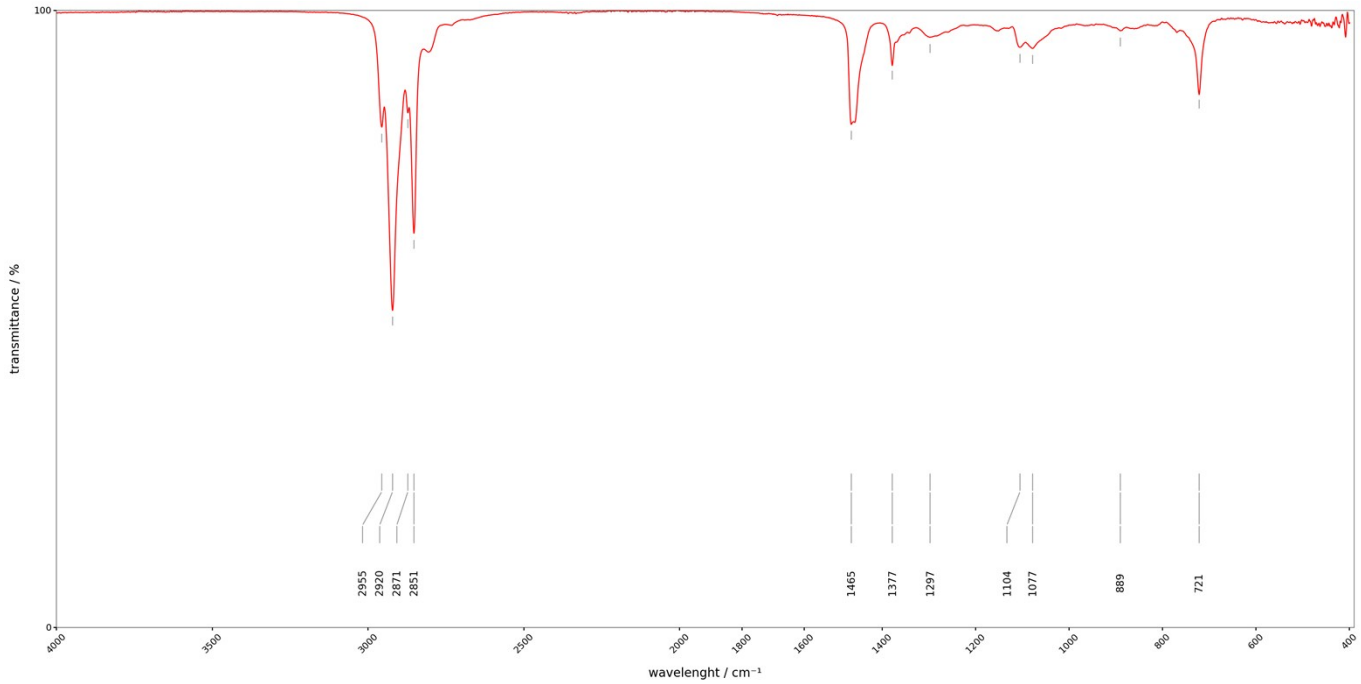

Figure S71. IR spectra of tri(2-heptyl-undecyl)amine.

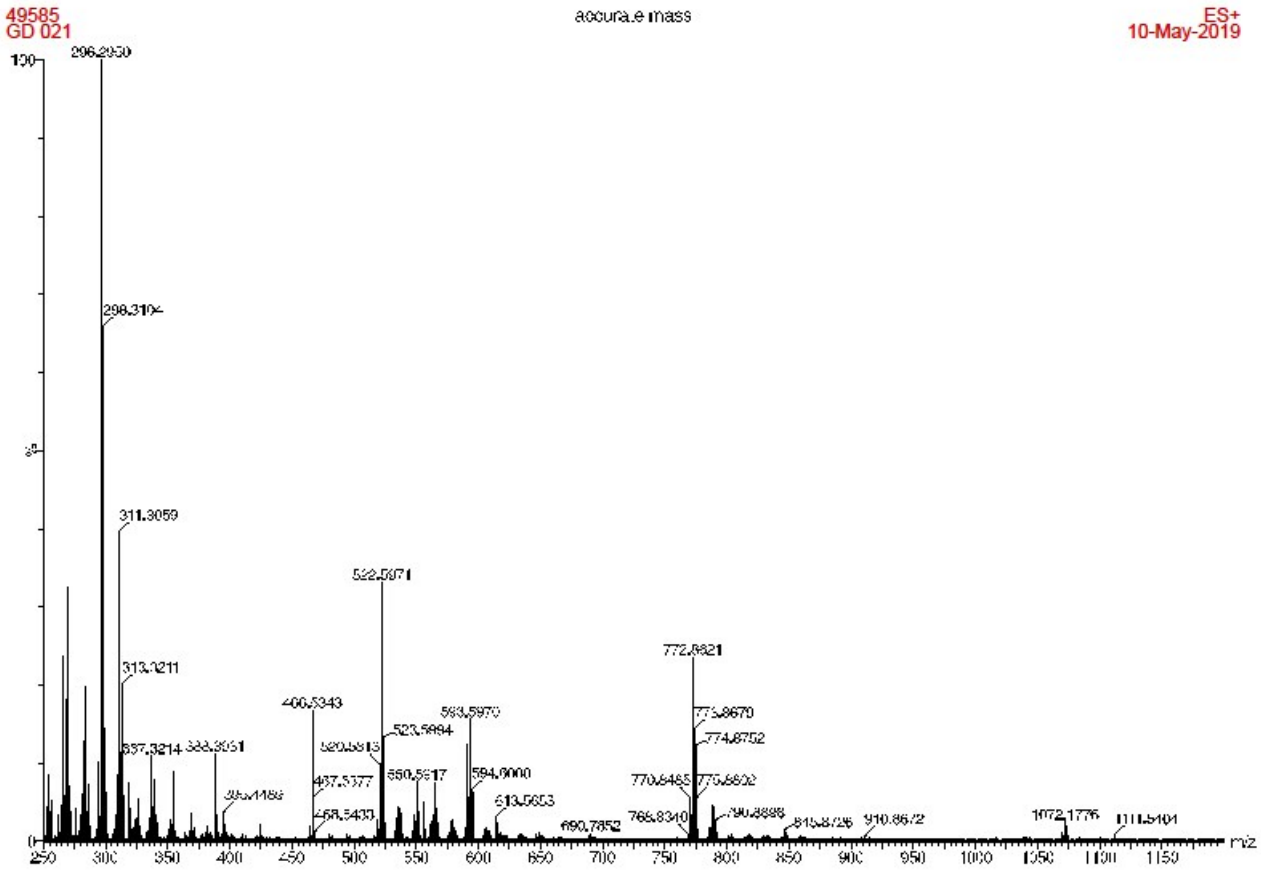

Figure S72. HRMS spectra of tri(2-heptyl-undecyl)amine.

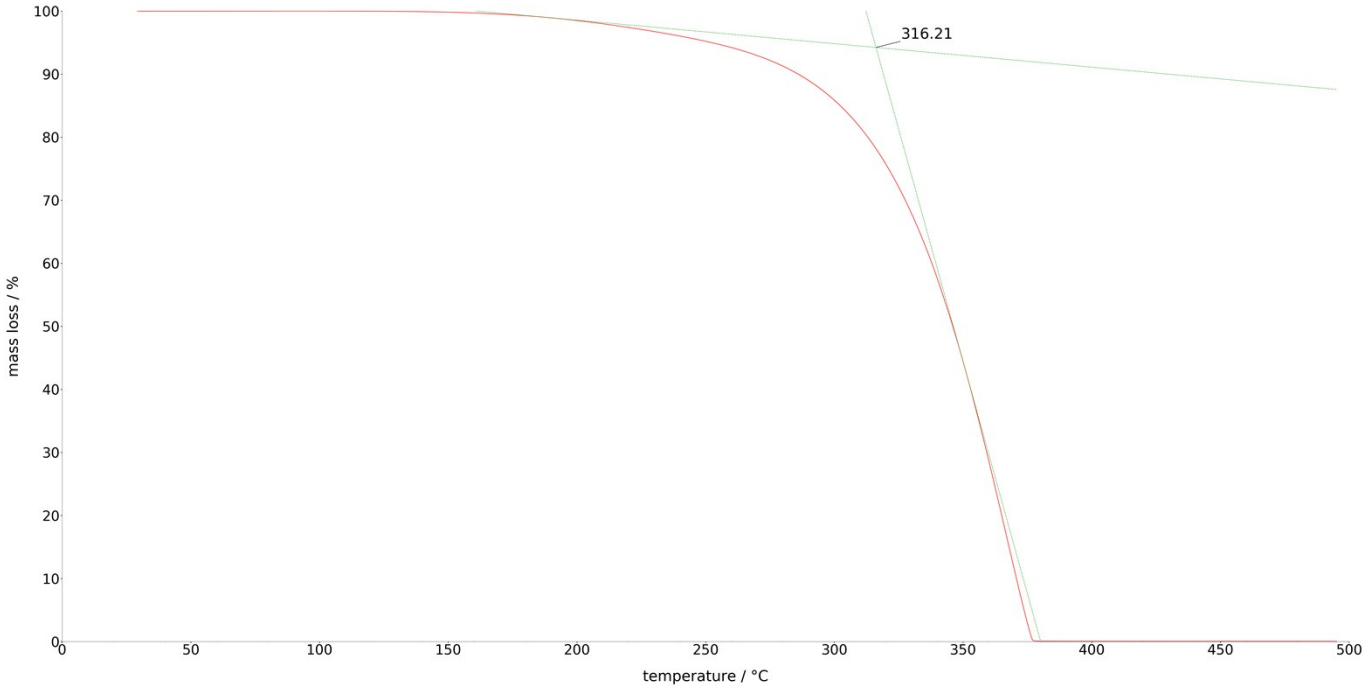

Figure S73. Thermogravimetric analysis for tri(2-heptyl-undecyl)amine.

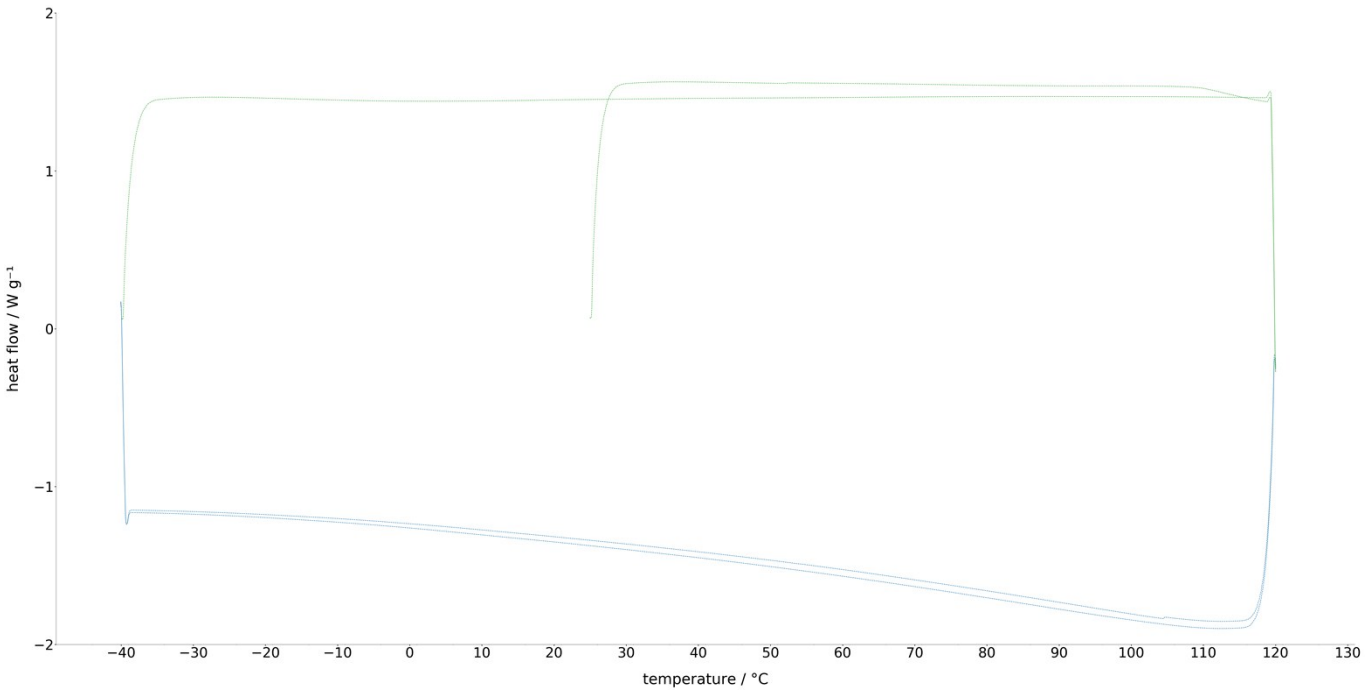

Figure S74. Differential scan calorimetry for tri(2-heptyl-undecyl)amine.

Table S14. Densitimetry and viscosimetry data for tri(2-heptyl-undecyl)amine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
---	---	---	---	---	---	---	Ø1.8 Gold (20644413)
0.83287	20.02	103.2	123.9	20.00	0.13	0.14	Ø1.8 Gold (20644413)
0.83136	22.48	90.64	109.0	22.50	0.02	0.46	Ø1.8 Gold (20644413)
0.82980	24.98	79.90	96.29	25.00	0.11	0.26	Ø1.8 Gold (20644413)
0.82825	27.48	71.00	85.72	27.50	0.06	0.33	Ø1.8 Gold (20644413)
0.82671	29.98	63.11	76.33	30.00	0.07	0.36	Ø1.8 Gold (20644413)
0.82516	32.48	56.50	68.47	32.50	0.17	0.37	Ø1.8 Gold (20644413)
0.82361	34.98	51.06	62.00	35.00	0.11	0.52	Ø1.8 Gold (20644413)
0.82207	37.48	45.88	55.81	37.50	0.08	0.62	Ø1.8 Gold (20644413)
0.82053	39.98	41.47	50.54	40.00	0.01	0.65	Ø1.8 Gold (20644413)
0.81899	42.48	37.60	45.91	42.50	0.04	0.64	Ø1.8 Gold (20644413)
0.81744	44.98	34.22	41.86	45.00	0.07	0.58	Ø1.8 Gold (20644413)
0.81590	47.48	31.21	38.25	47.50	0.14	0.62	Ø1.8 Gold (20644413)
0.81436	49.98	28.50	35.00	50.00	0.04	0.77	Ø1.8 Gold (20644413)
0.81282	52.48	26.09	32.09	52.50	0.02	0.65	Ø1.8 Gold (20644413)
0.81128	54.98	23.93	29.49	55.00	0.12	0.59	Ø1.8 Gold (20644413)
0.80975	57.48	21.96	27.12	57.50	0.07	0.74	Ø1.8 Gold (20644413)
0.80821	59.98	20.23	25.03	60.00	0.05	0.54	Ø1.8 Gold (20644413)

Tri(2-octyl-dodecyl)amine

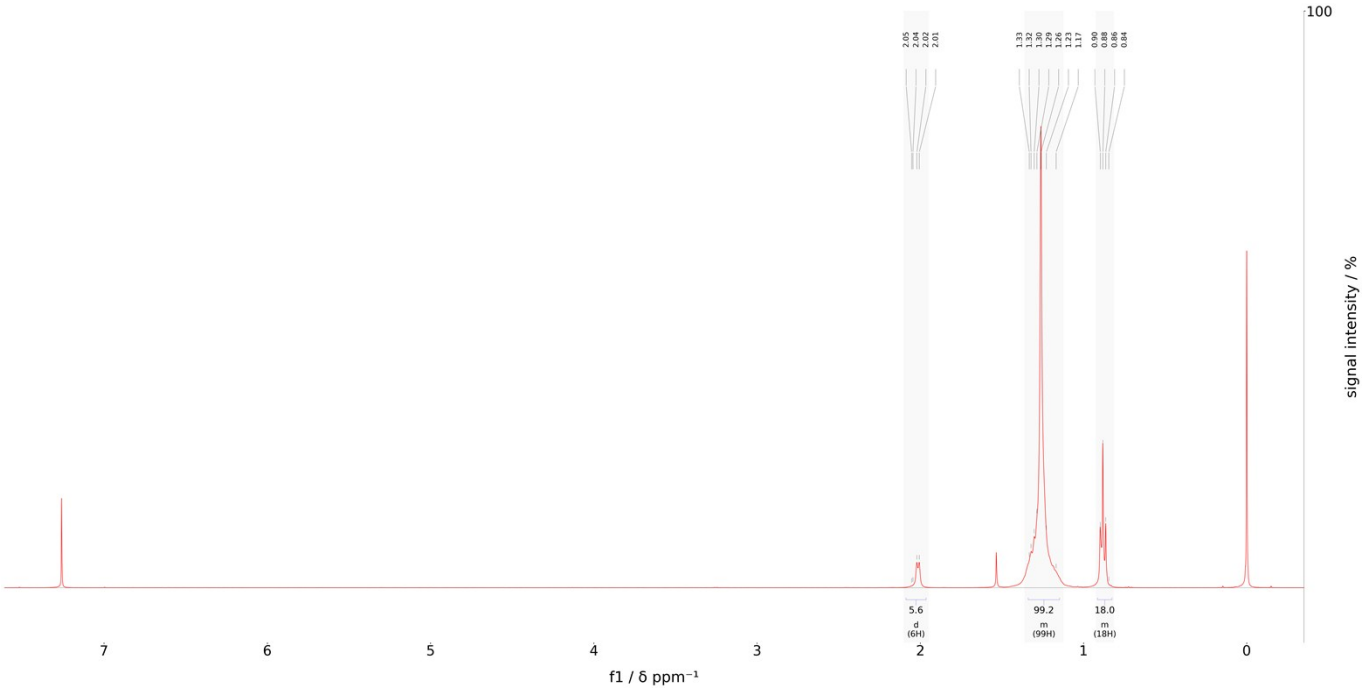

Figure S75. ^{1}H NMR of tri(2-octyl-dodecyl)amine in deuterochloroform.

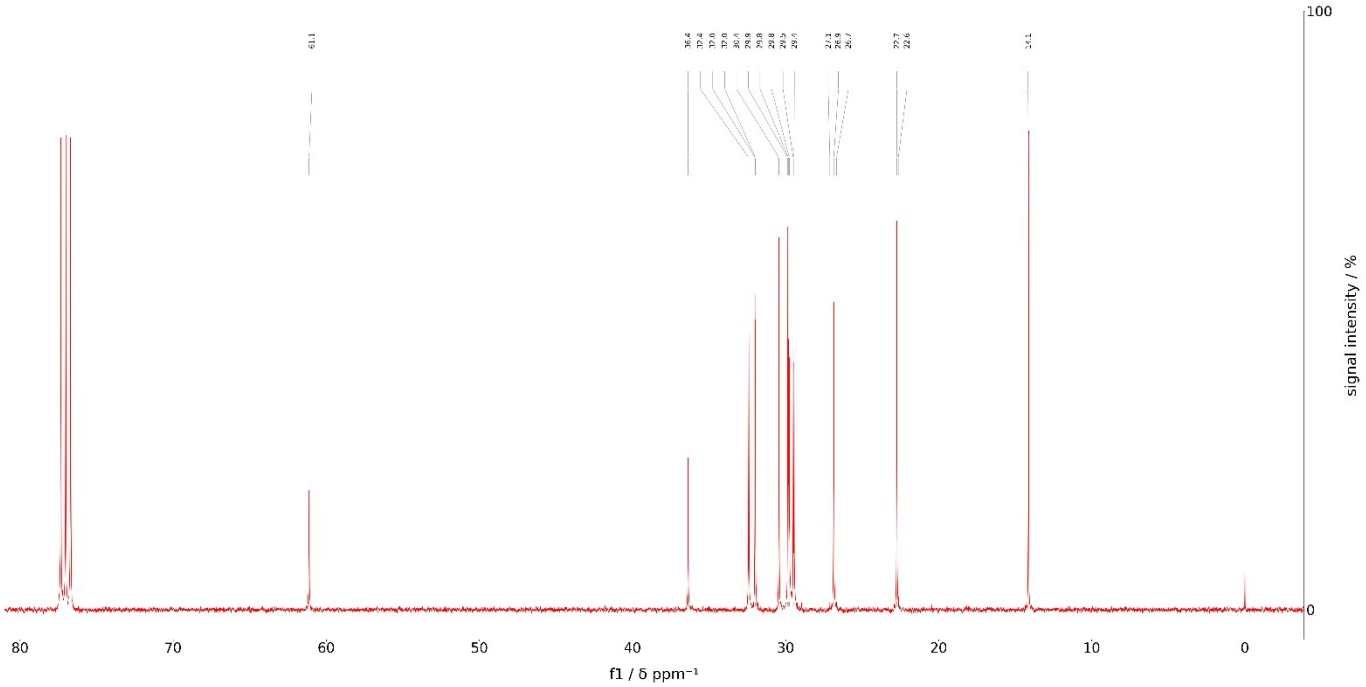

Figure S76. ^{13}C NMR of tri(2-octyl-dodecyl)amine in deuterochloroform.

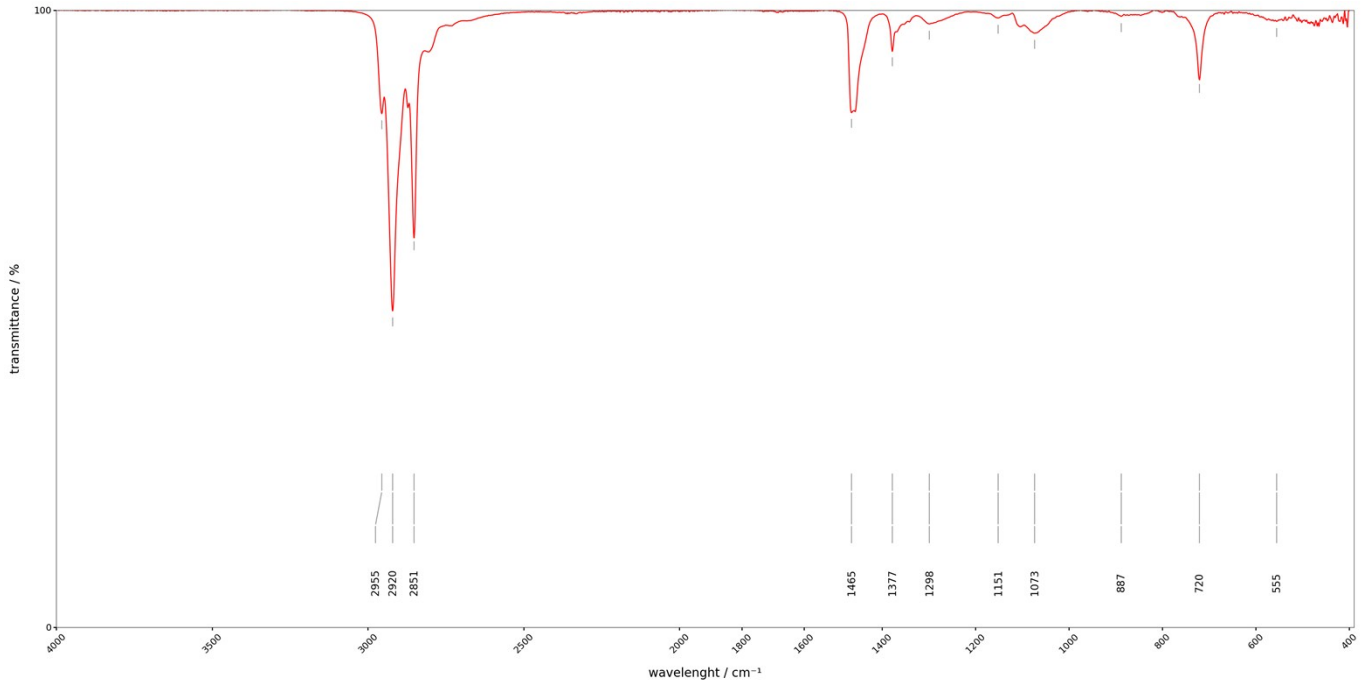

Figure S77. IR spectra of tri(2-octyl-dodecyl)amine.

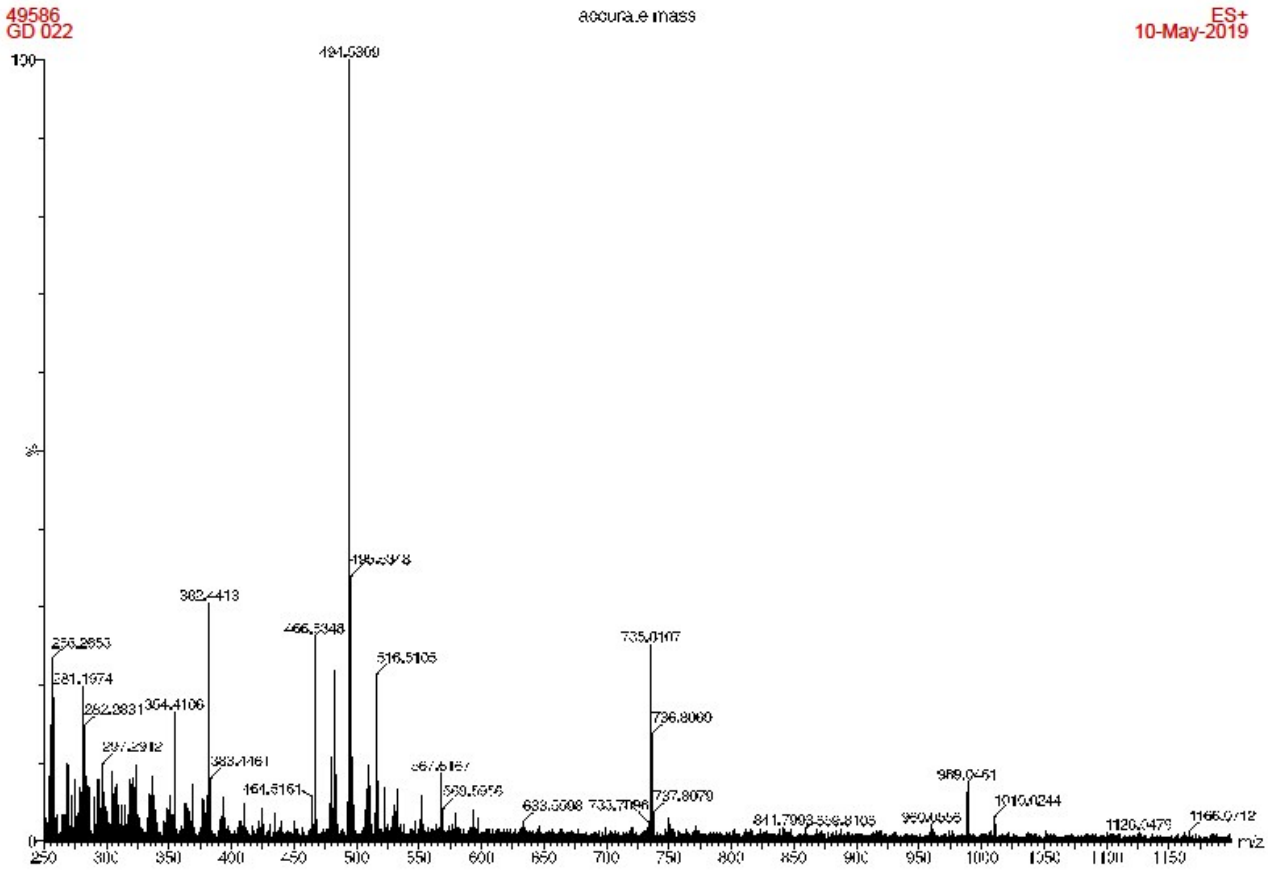

Figure S78. HRMS spectra of tri(2-octyl-dodecyl)amine.

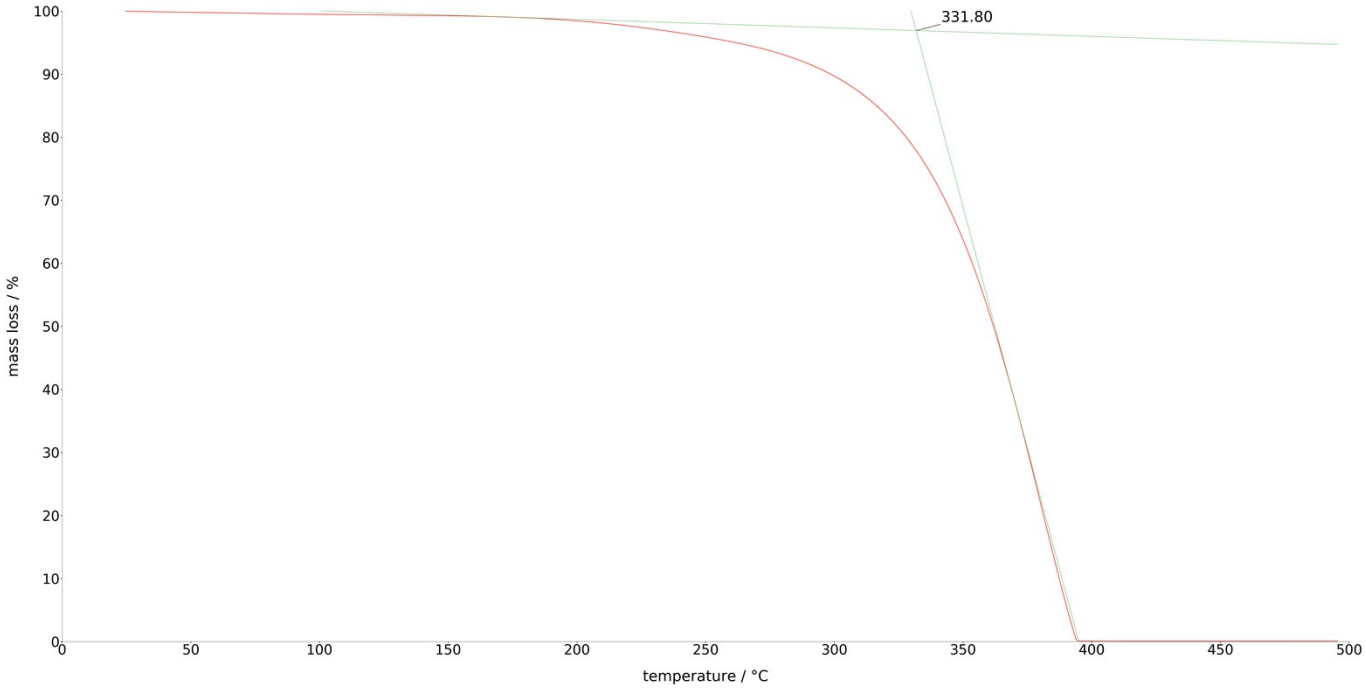

Figure S79. Thermogravimetric analysis for tri(2-octyl-dodecyl)amine.

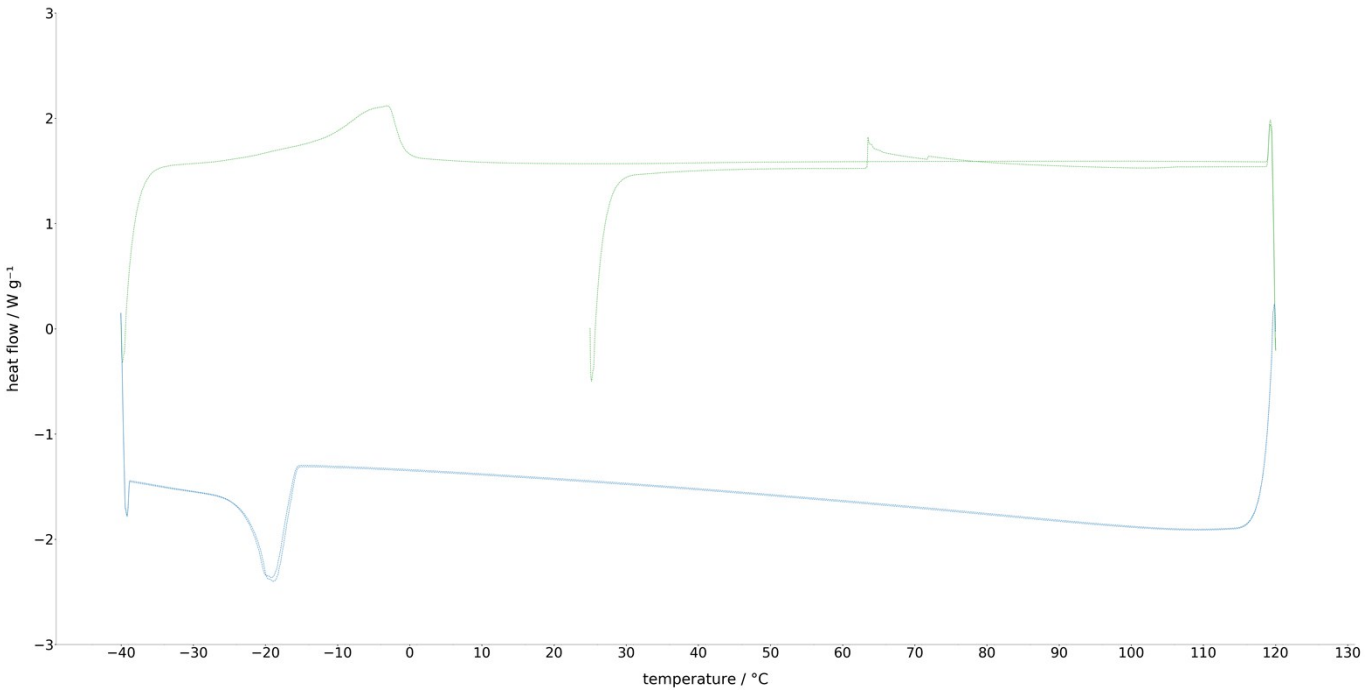

Figure S80. Differential scan calorimetry for tri(2-octyl-dodecyl)amine.

Table S15. Densitimetry and viscosimetry data for tri(2-octyl-dodecyl)amine.

Density	Density Temperature	Lovis Dyn. Viscosity	Lovis Kin. Viscosity	Lovis Temperature	Lovis Variation Coefficient	Lovis Fw/Bw Deviation	Lovis Current Capillary
0.83355	20.02	104.6	125.4	20.00	0.08	0.37	Ø1.8 Gold (20644413)
0.83203	22.48	92.67	111.4	22.50	0.16	0.39	Ø1.8 Gold (20644413)
0.83047	24.98	81.65	98.32	25.00	0.17	0.46	Ø1.8 Gold (20644413)
0.82892	27.48	72.30	87.22	27.50	0.09	0.44	Ø1.8 Gold (20644413)
0.82737	29.98	64.33	77.76	30.00	0.08	0.36	Ø1.8 Gold (20644413)
0.82582	32.48	57.55	69.69	32.50	0.09	0.60	Ø1.8 Gold (20644413)
0.82427	34.98	52.00	63.08	35.00	0.05	0.61	Ø1.8 Gold (20644413)
0.82273	37.48	46.88	56.98	37.50	0.05	0.59	Ø1.8 Gold (20644413)
0.82118	39.98	42.40	51.64	40.00	0.03	0.63	Ø1.8 Gold (20644413)
0.81964	42.48	38.52	46.99	42.50	0.03	0.59	Ø1.8 Gold (20644413)
0.81810	44.98	35.14	42.95	45.00	0.24	0.70	Ø1.8 Gold (20644413)
0.81656	47.48	32.19	39.42	47.50	0.12	0.54	Ø1.8 Gold (20644413)
0.81501	49.98	29.46	36.14	50.00	0.08	0.56	Ø1.8 Gold (20644413)
0.81347	52.48	26.97	33.15	52.50	0.03	0.50	Ø1.8 Gold (20644413)
0.81194	54.98	24.75	30.49	55.00	0.10	0.47	Ø1.8 Gold (20644413)
0.81040	57.48	22.75	28.07	57.50	0.06	0.61	Ø1.8 Gold (20644413)
0.80886	59.98	20.89	25.83	60.00	0.13	0.62	Ø1.8 Gold (20644413)

Di(2-butyl-octyl)dimethylammonium chloride

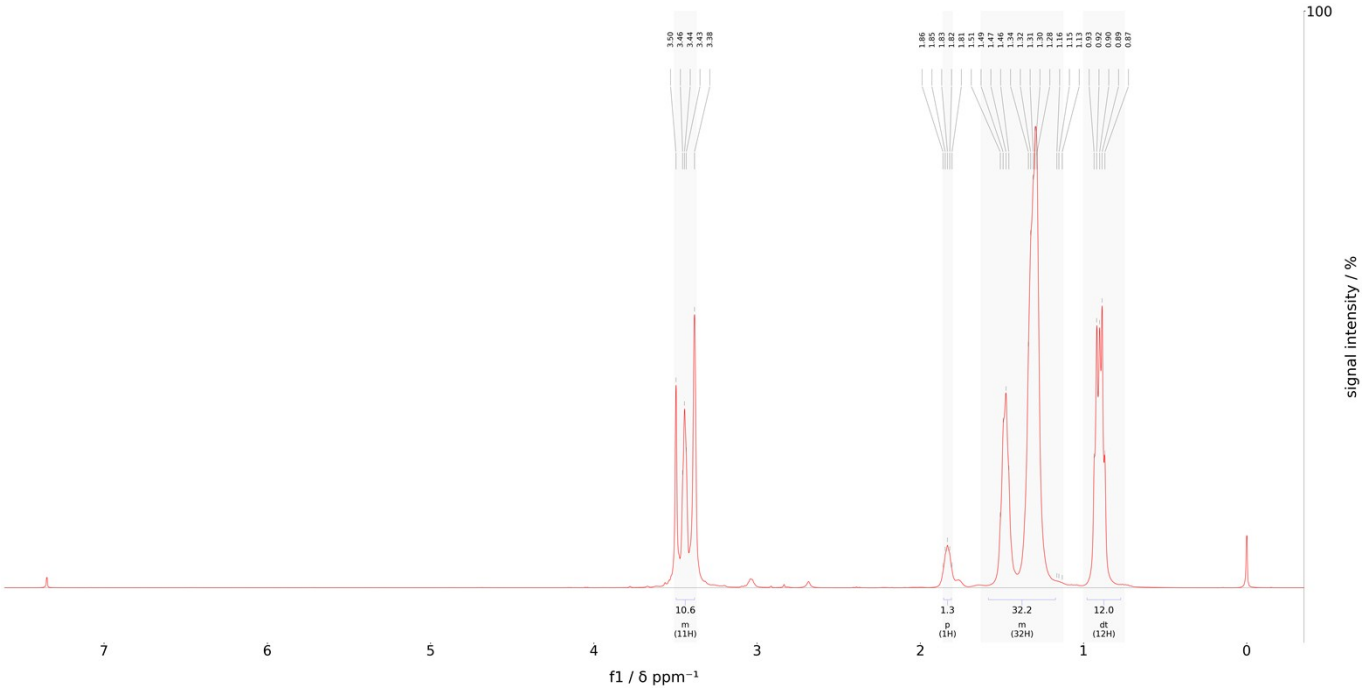

Figure S81. ^{1}H NMR of di(2-butyl-octyl)dimethylammonium chloride in deuterochloroform.

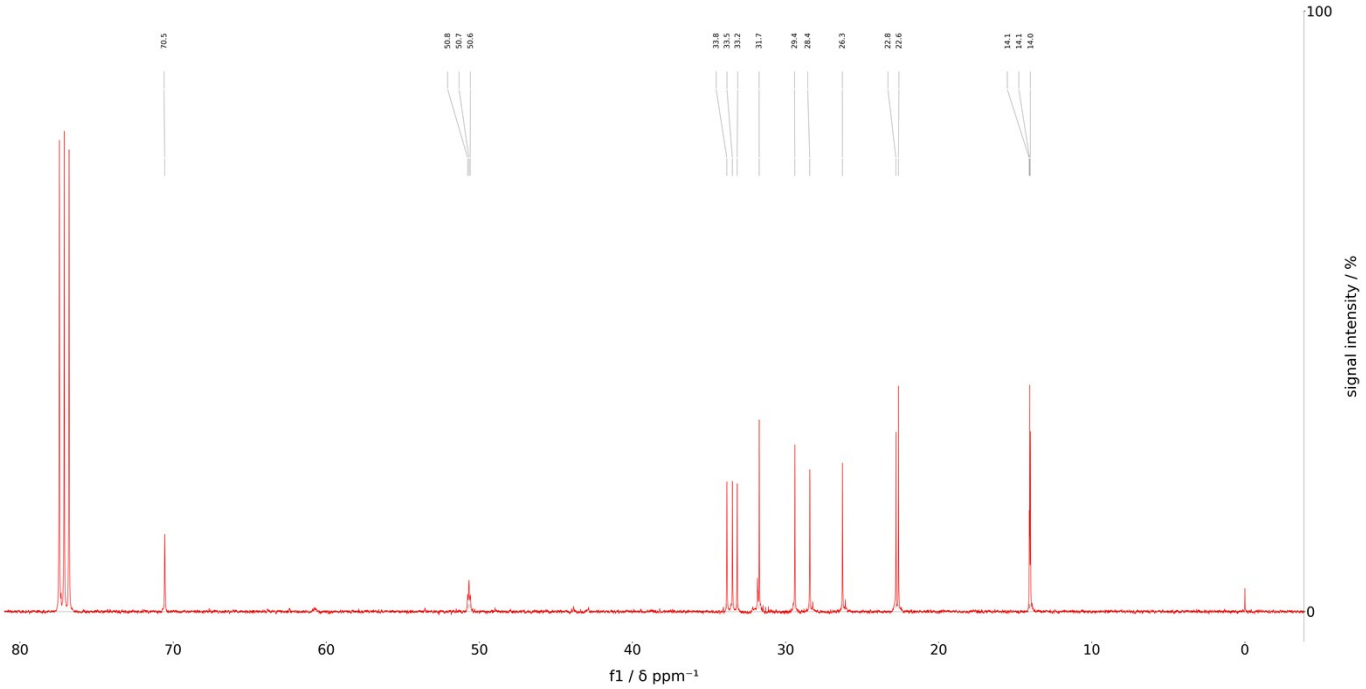

Figure S82. ^{13}C NMR of di(2-butyl-octyl)dimethylammonium chloride in deuterochloroform.

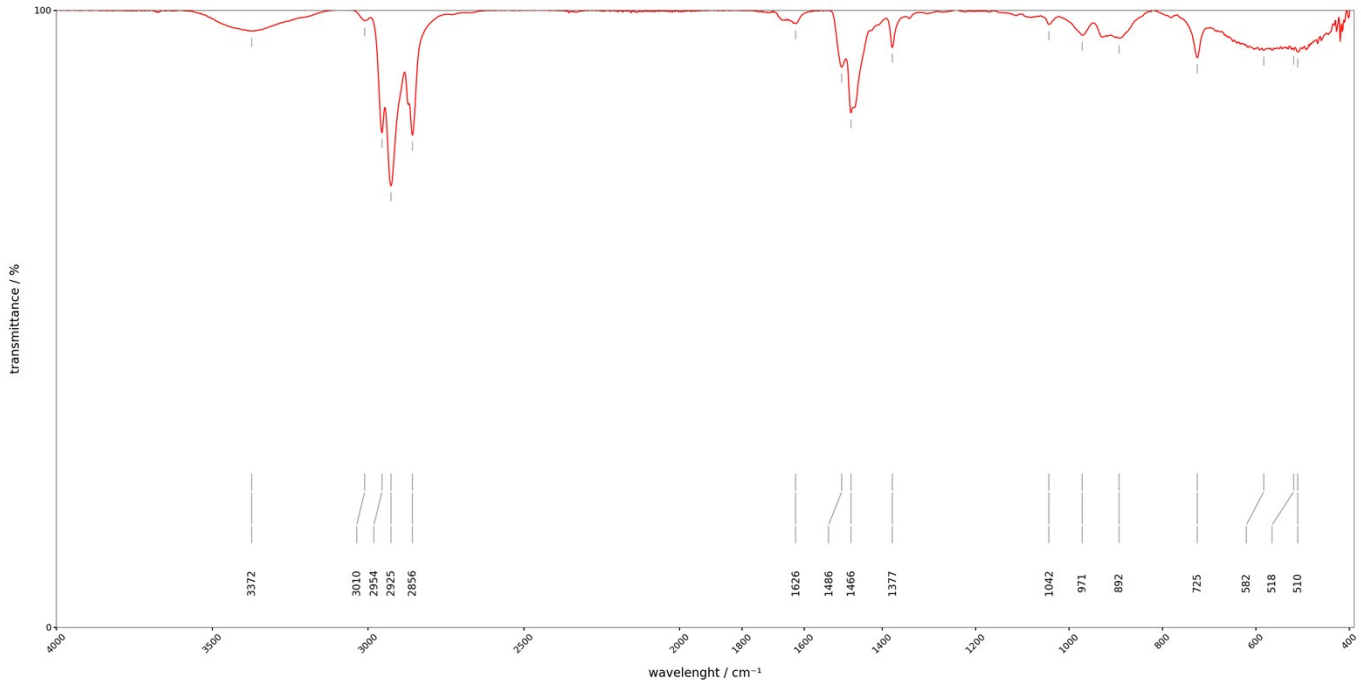

Figure S83. IR spectra of di(2-butyl-octyl)dimethylammonium chloride.

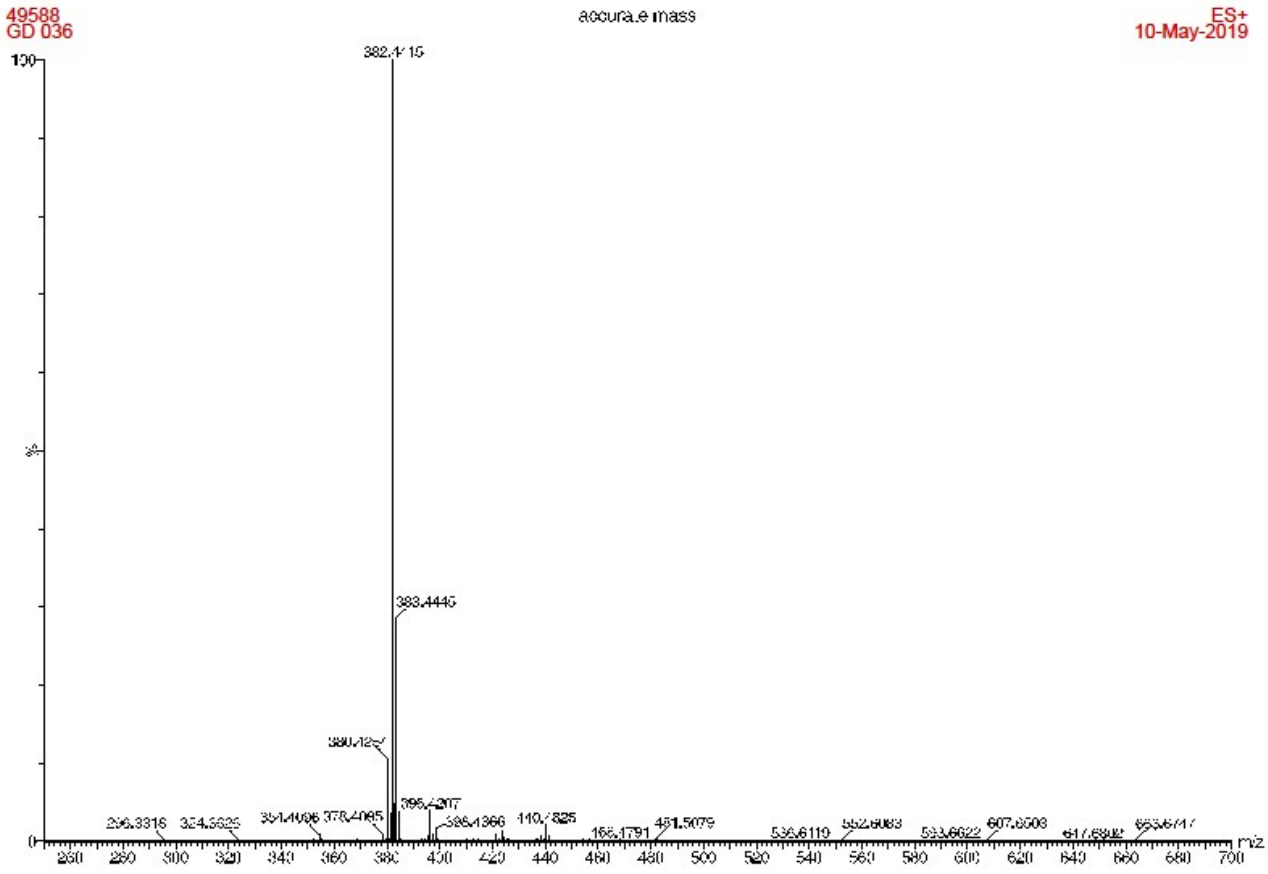

Figure S84. HRMS spectra of di(2-butyl-octyl)dimethylammonium chloride.

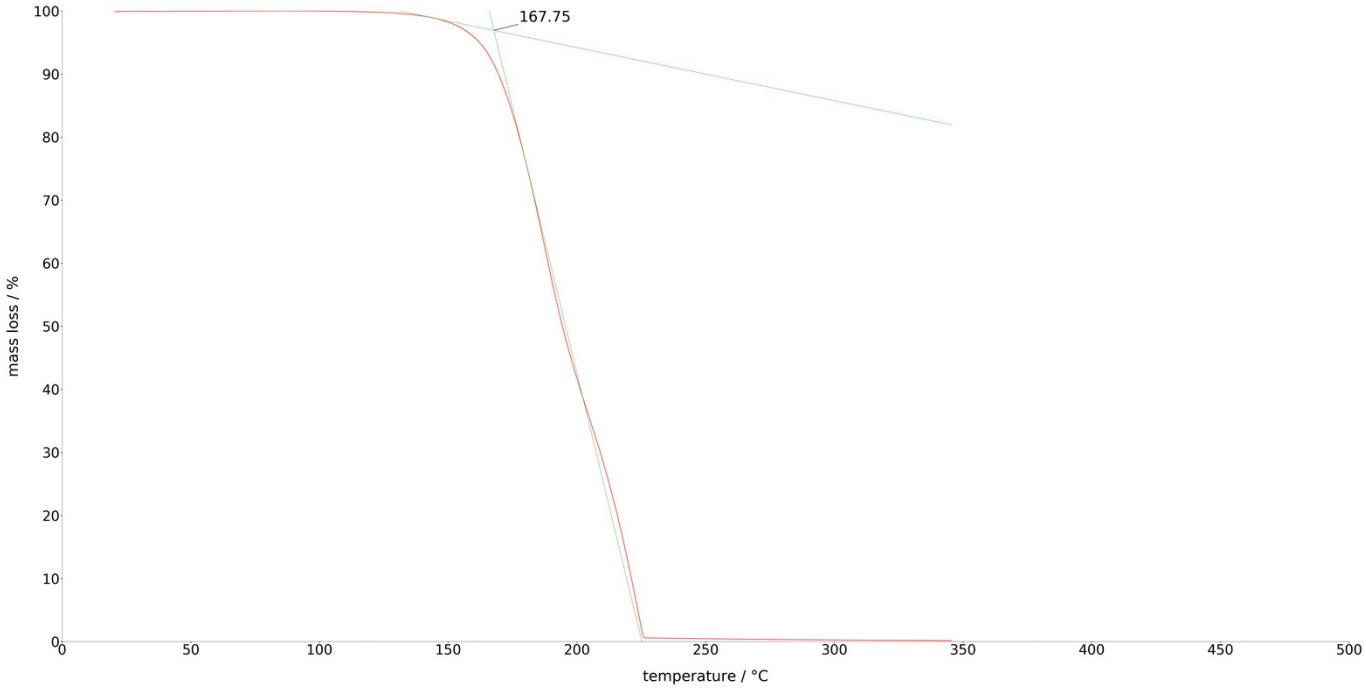

Figure S85. Thermogravimetric analysis for di(2-butyl-octyl)dimethylammonium chloride.

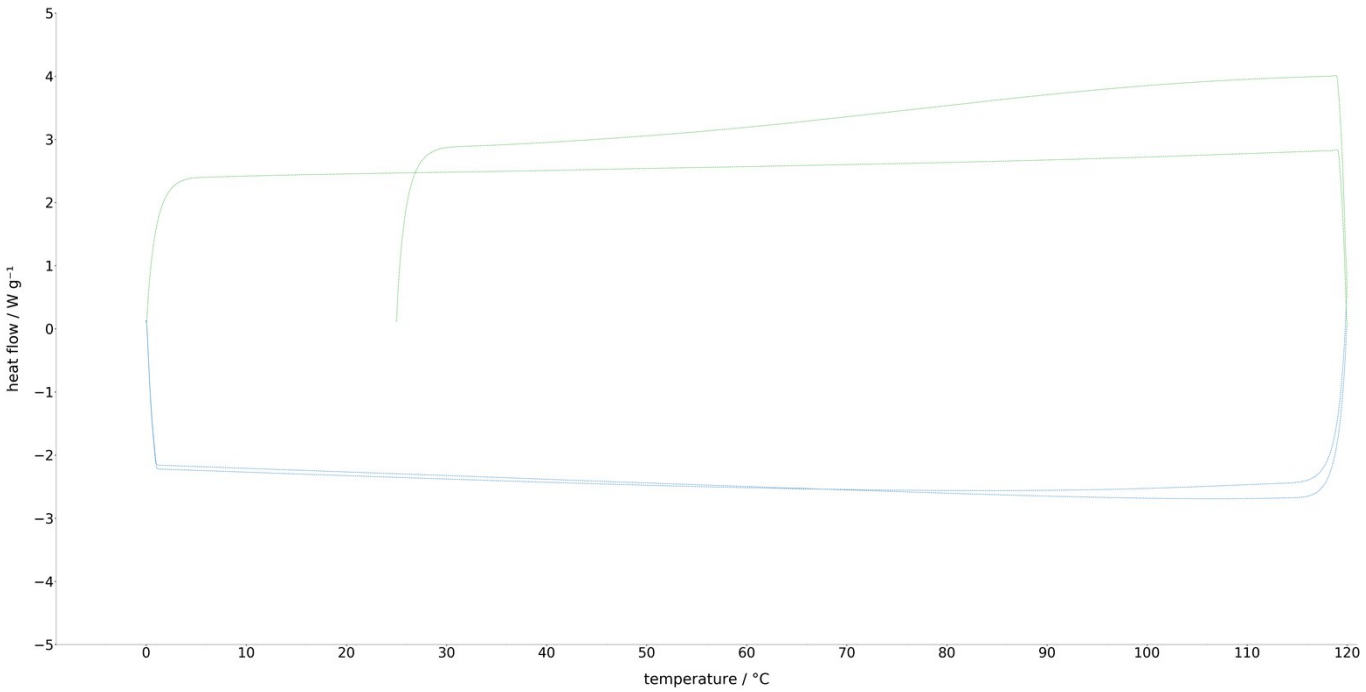

Figure S86. Differential scan calorimetry for di(2-butyl-octyl)dimethylammonium chloride.

Di(2-pentyl-nonyl)dimethylammonium chloride.

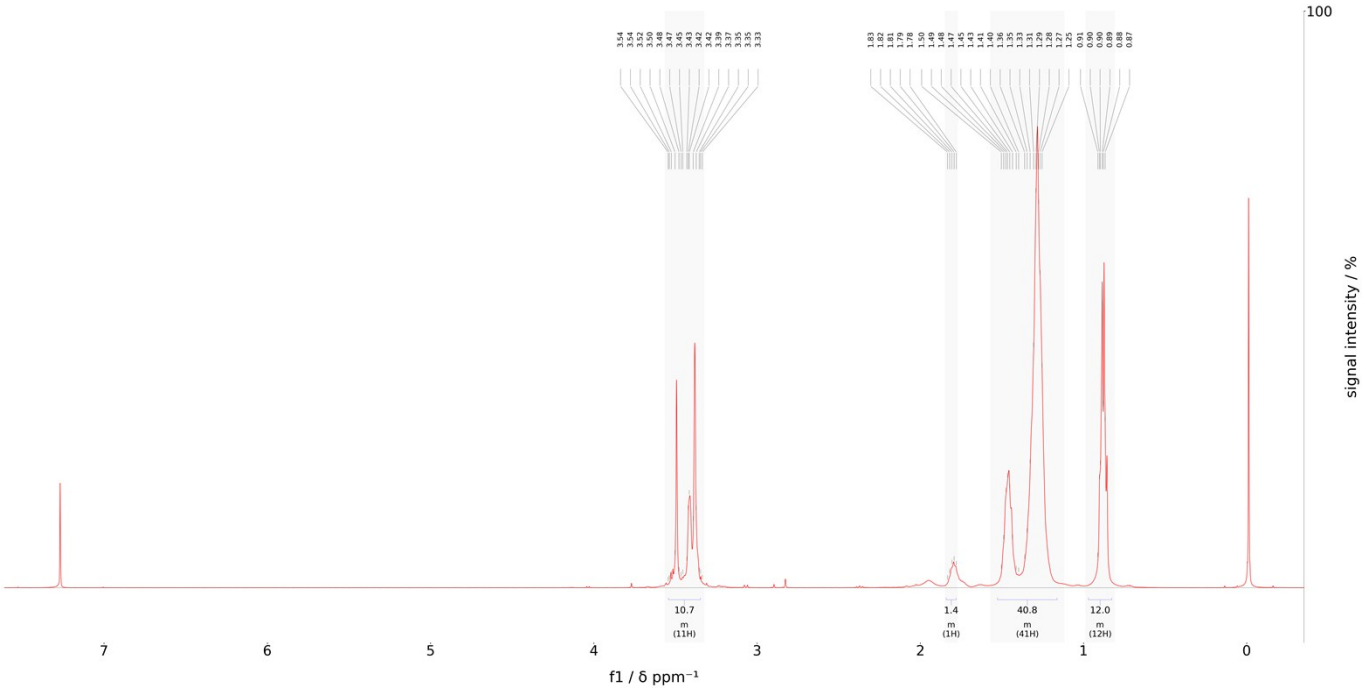

Figure S87. ^{1}H NMR of di(2-pentyl-nonyl)dimethylammonium chloride in deuterochloroform.

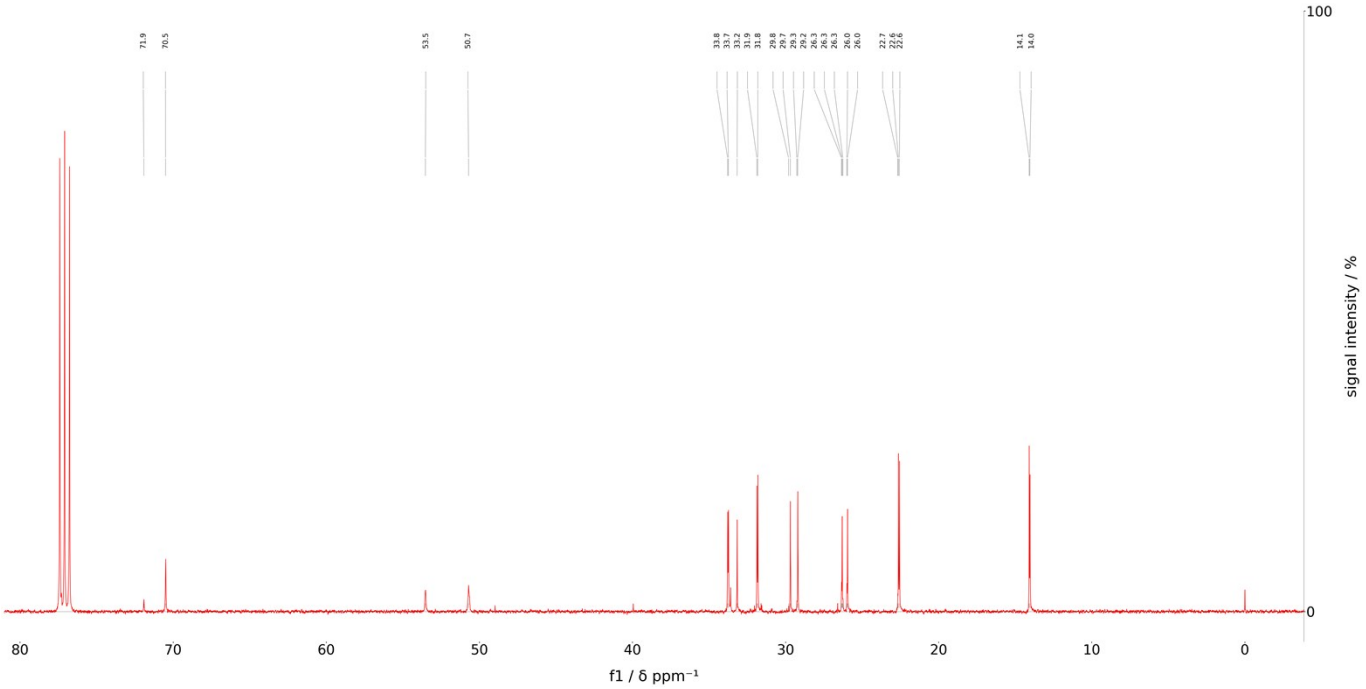

Figure S88. ^{13}C NMR of di(2-pentyl-nonyl)dimethylammonium chloride in deuterochloroform.

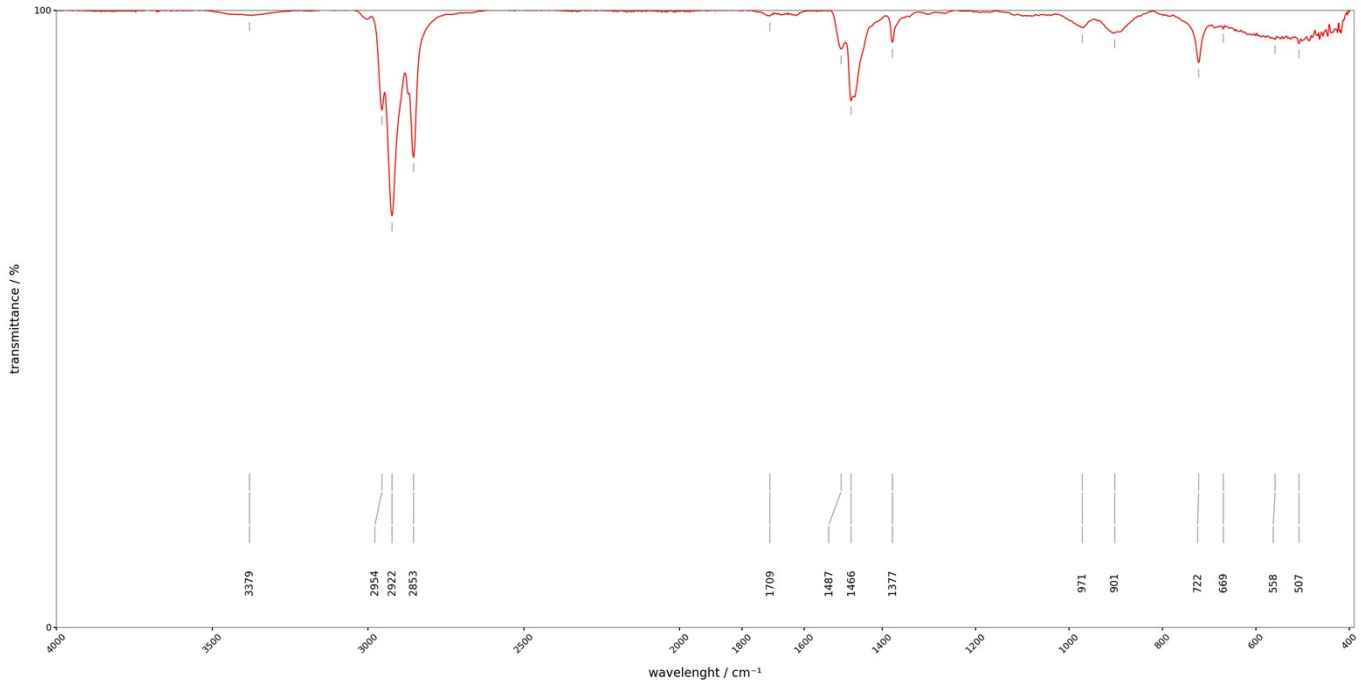

Figure S89. IR spectra of di(2-pentyl-nonyl)dimethylammonium chloride.

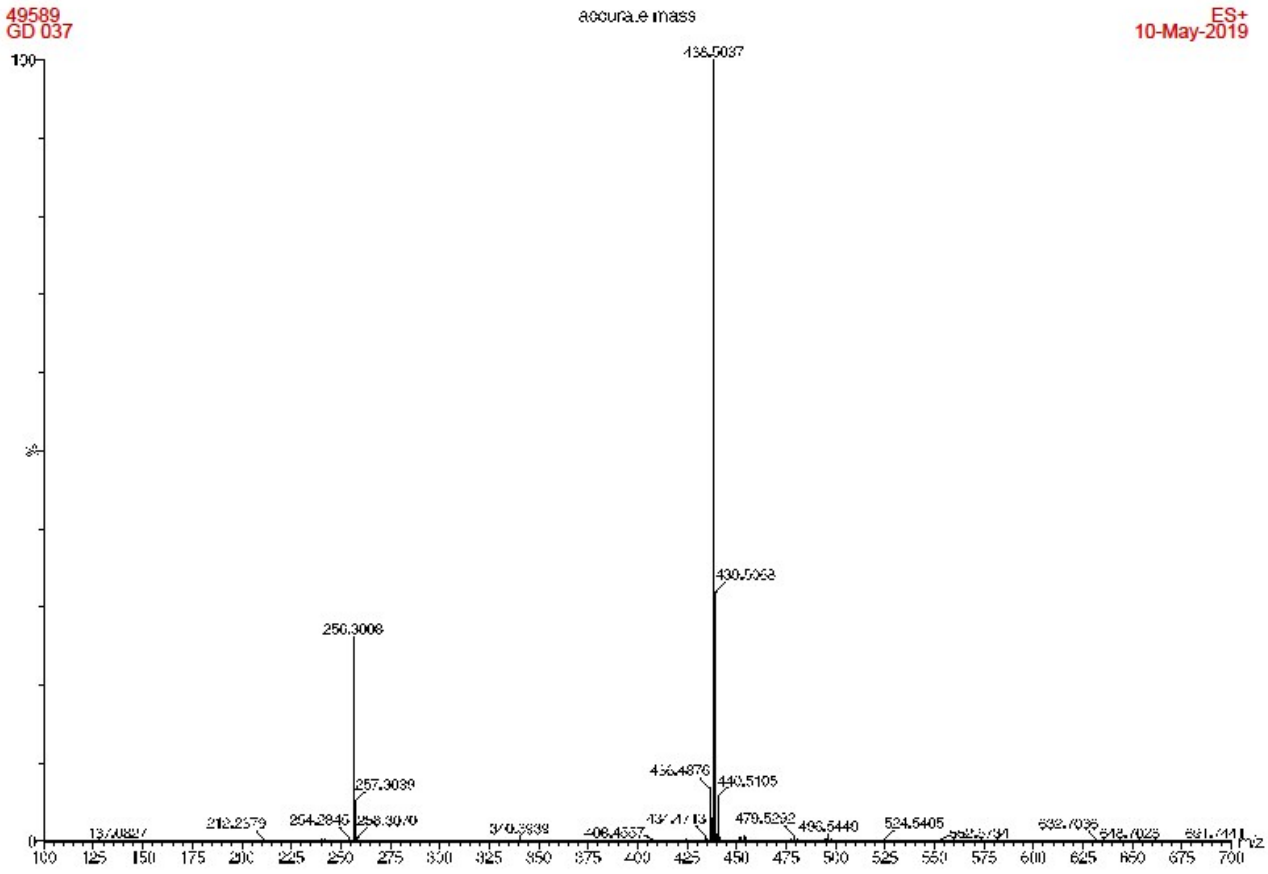

Figure S90. HRMS spectra of di(2-pentyl-nonyl)dimethylammonium chloride.

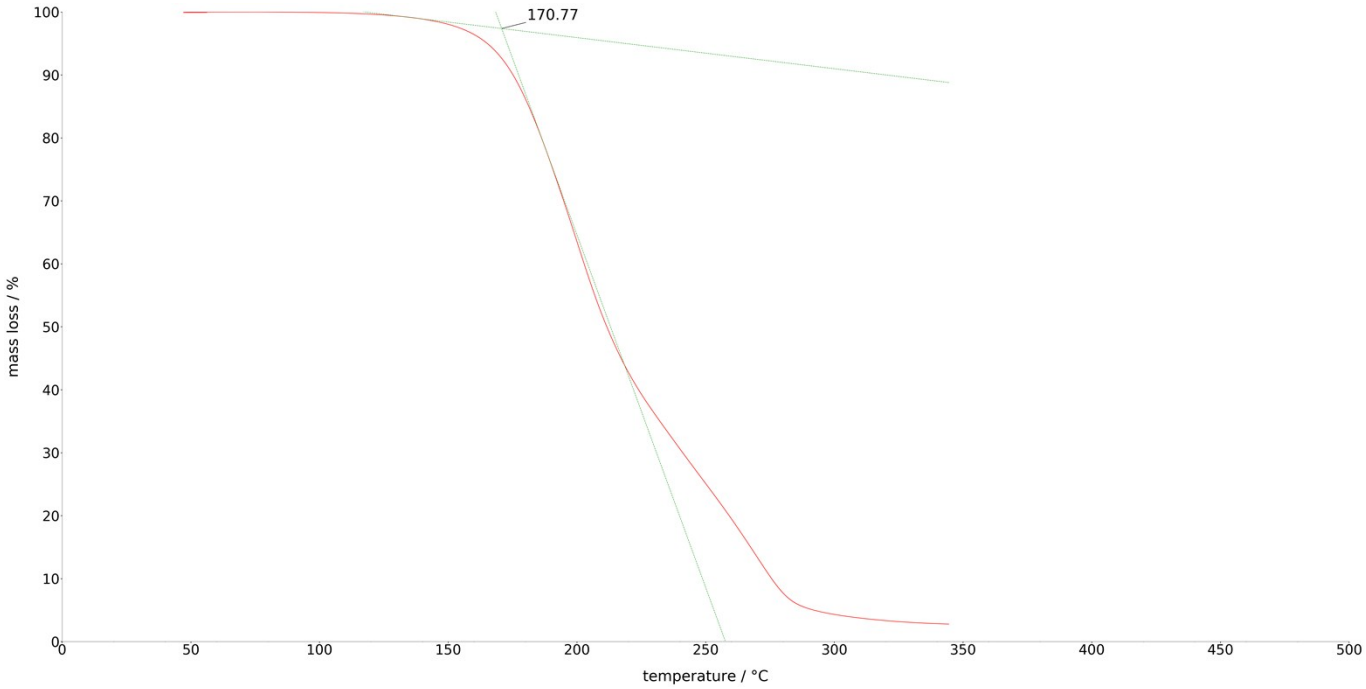

Figure S91. Thermogravimetric analysis for di(2-pentyl-nonyl)dimethylammonium chloride.

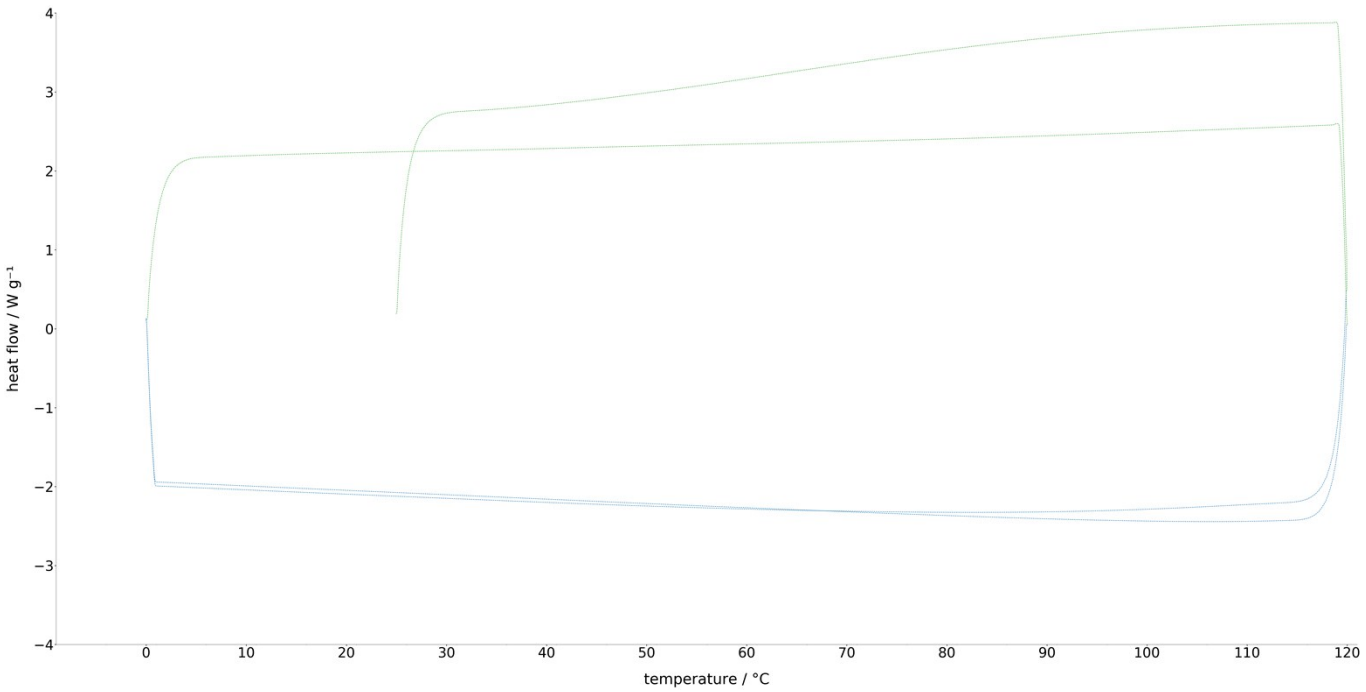

Figure S92. Differential scan calorimetry for di(2-pentyl-nonyl)dimethylammonium chloride.

Di(2-hexyl-decyl)dimethylammonium chloride

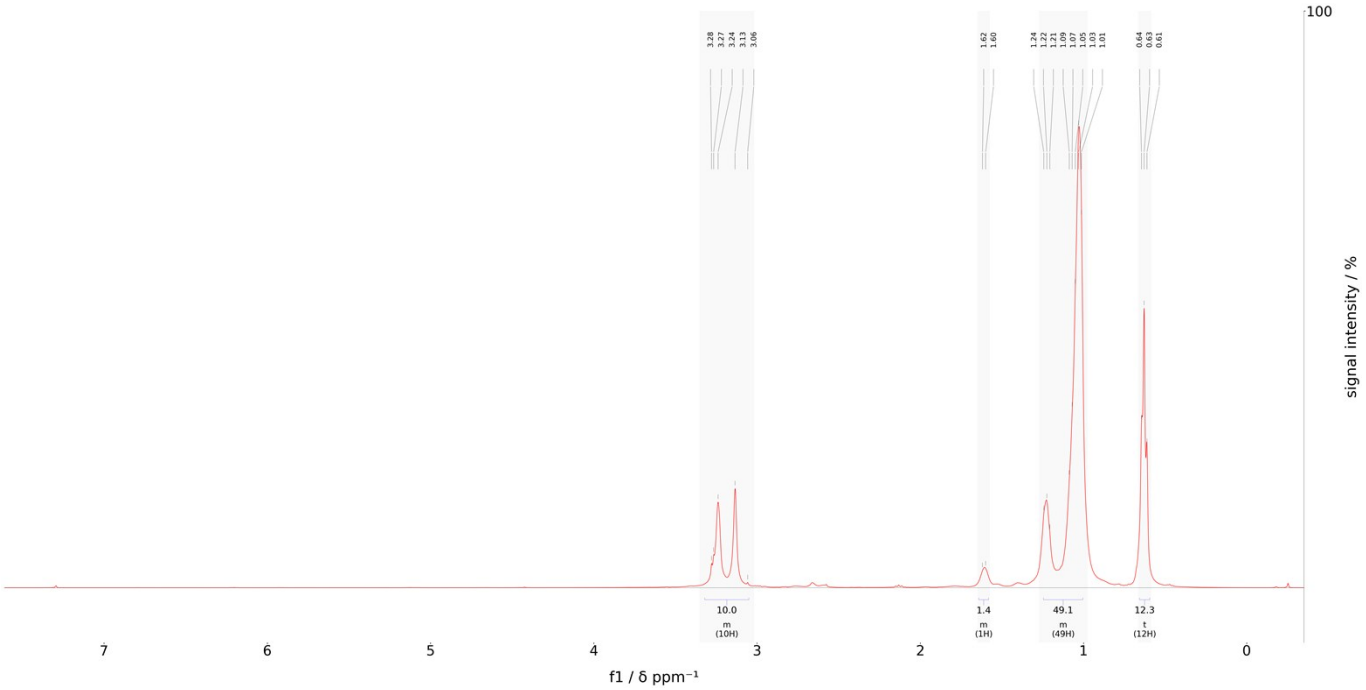

Figure S93. ^{1}H NMR of di(2-hexyl-decyl)dimethylammonium chloride in deuterochloroform.

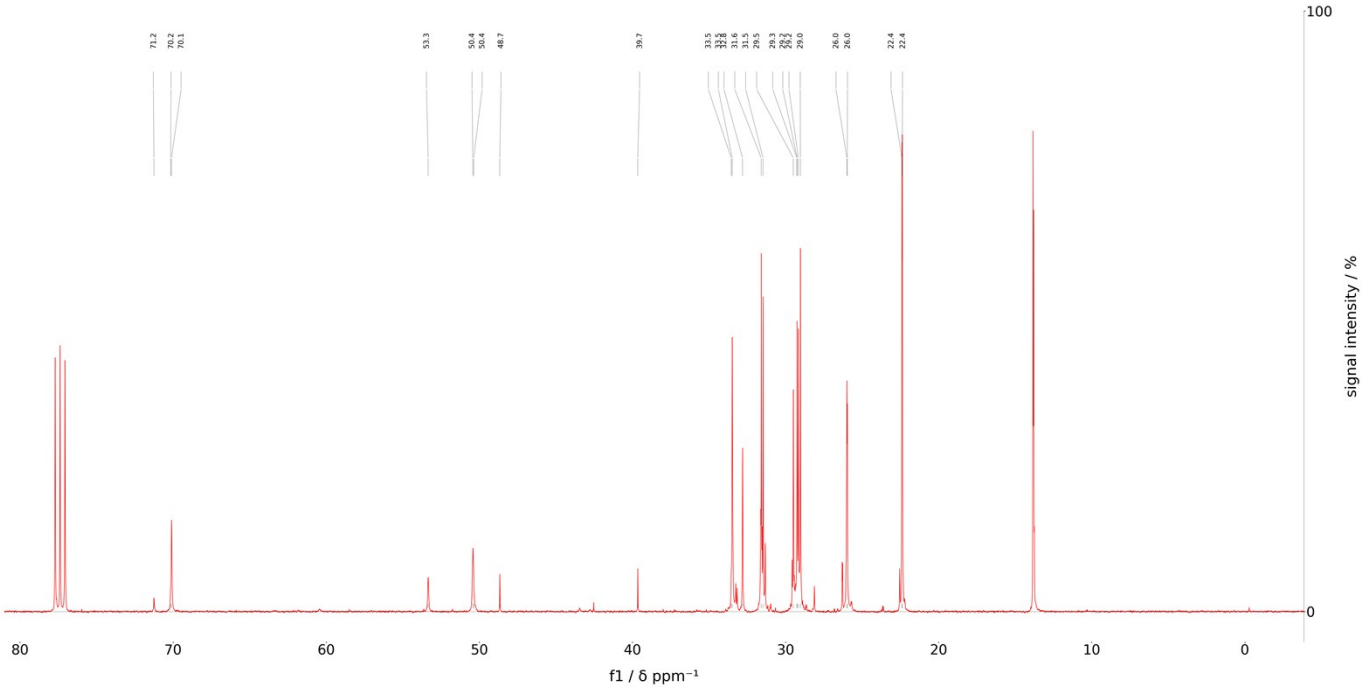

Figure S94. ^{13}C NMR of di(2-hexyl-decyl)dimethylammonium chloride in deuterochloroform.

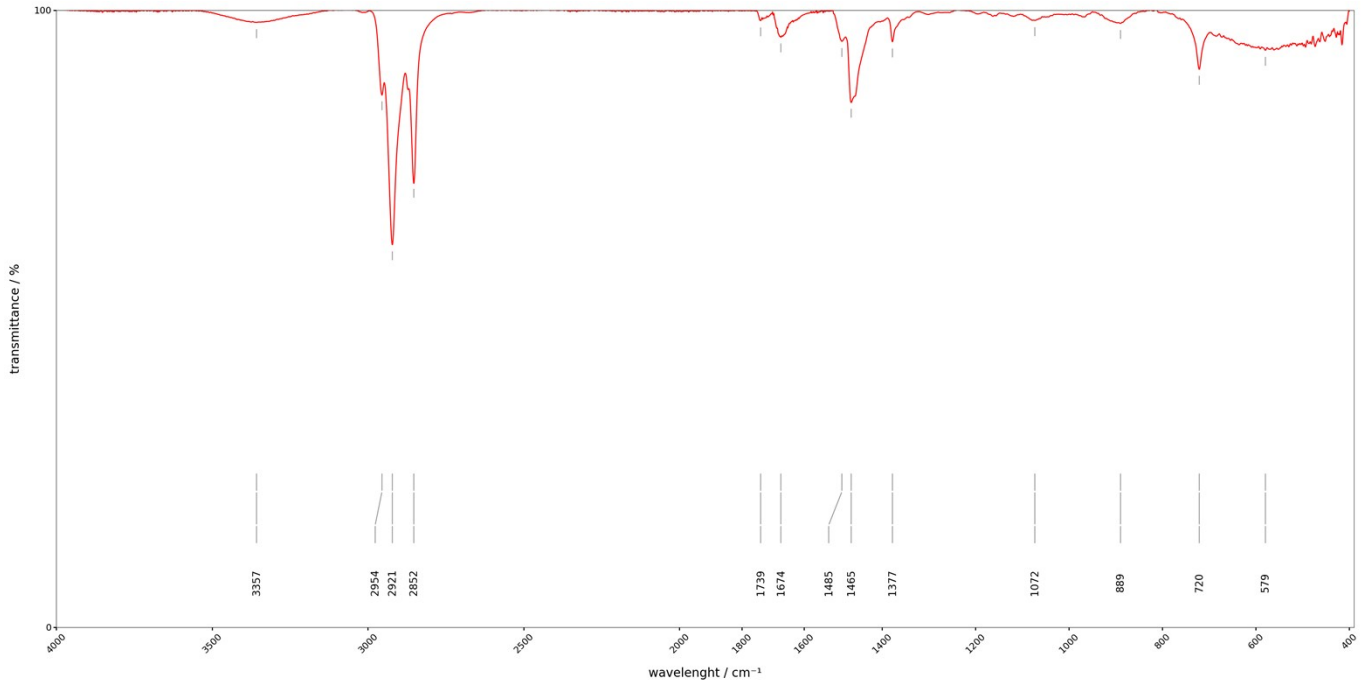

Figure S95. IR spectra of di(2-hexyl-decyl)dimethylammonium chloride.

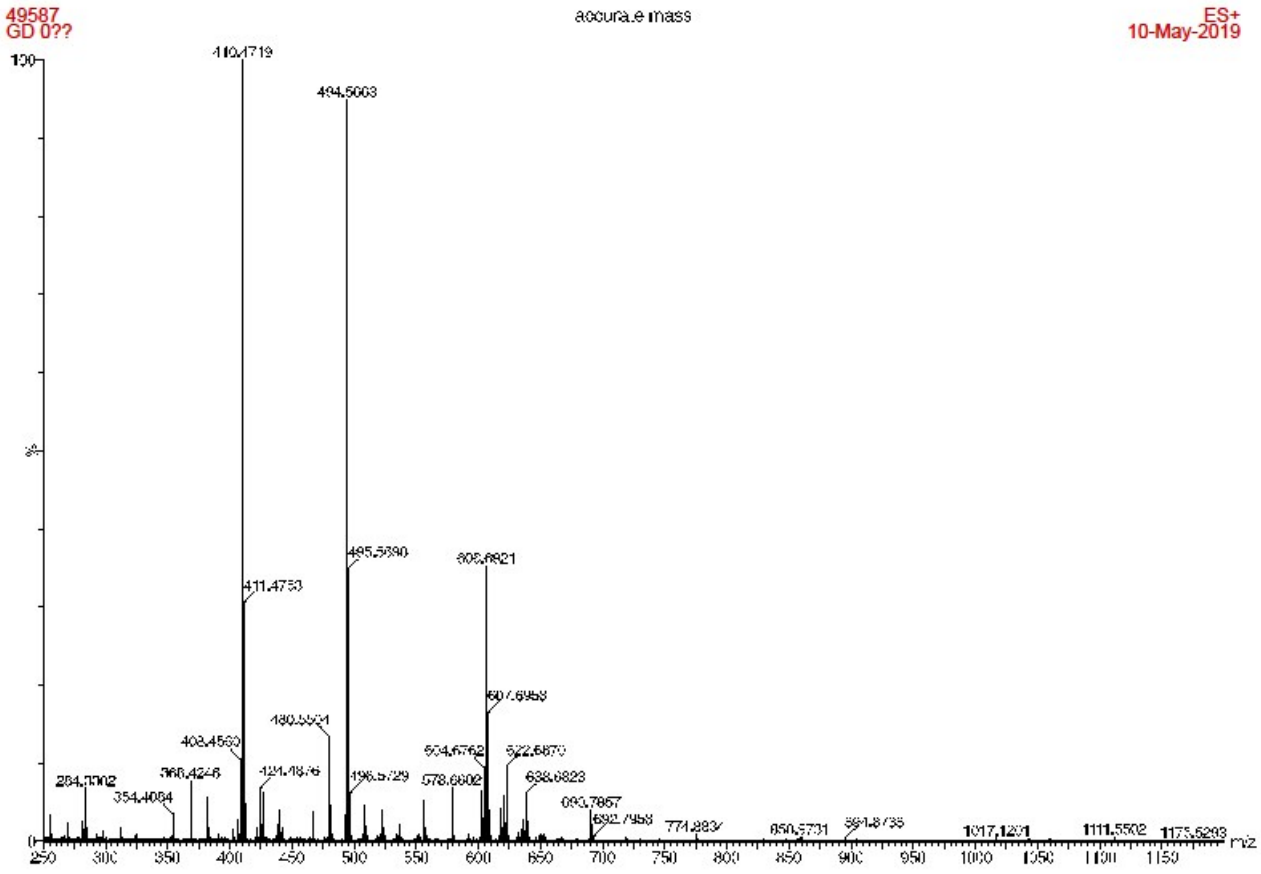

Figure S96. HRMS spectra of di(2-hexyl-decyl)dimethylammonium chloride.

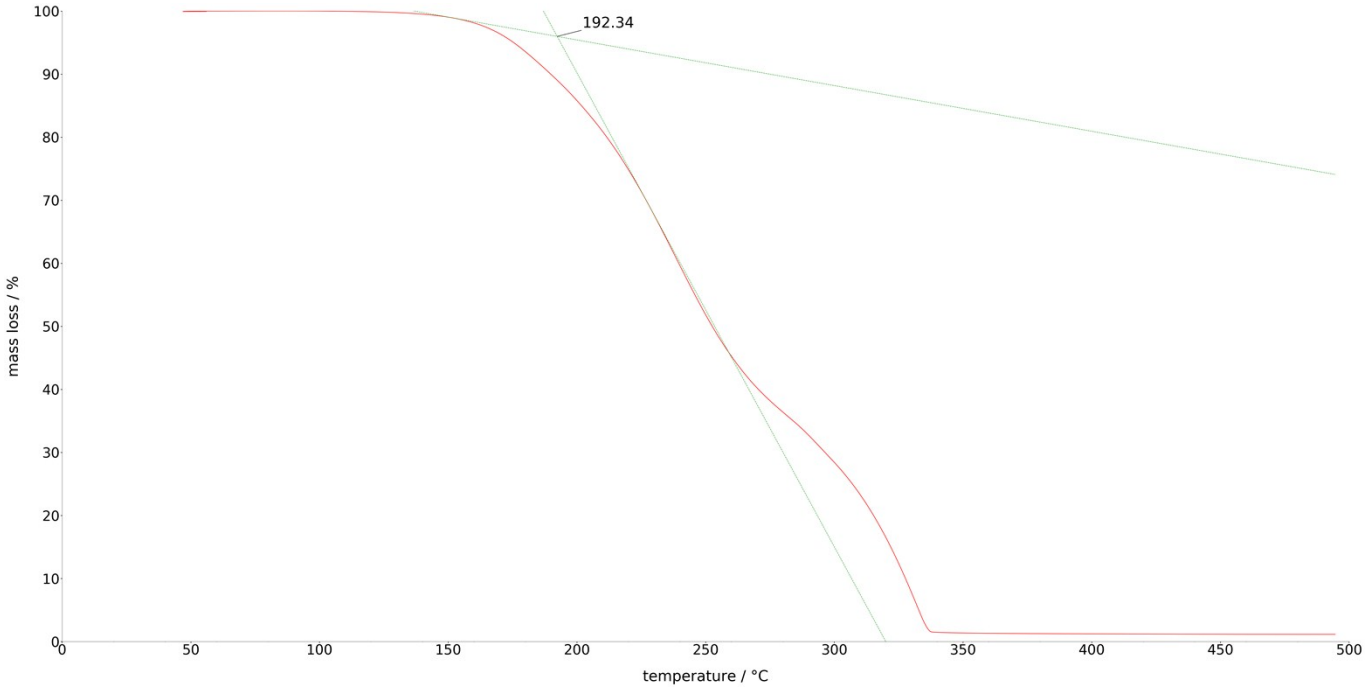

Figure S97. Thermogravimetric analysis for di(2-hexyl-decyl)dimethylammonium chloride.

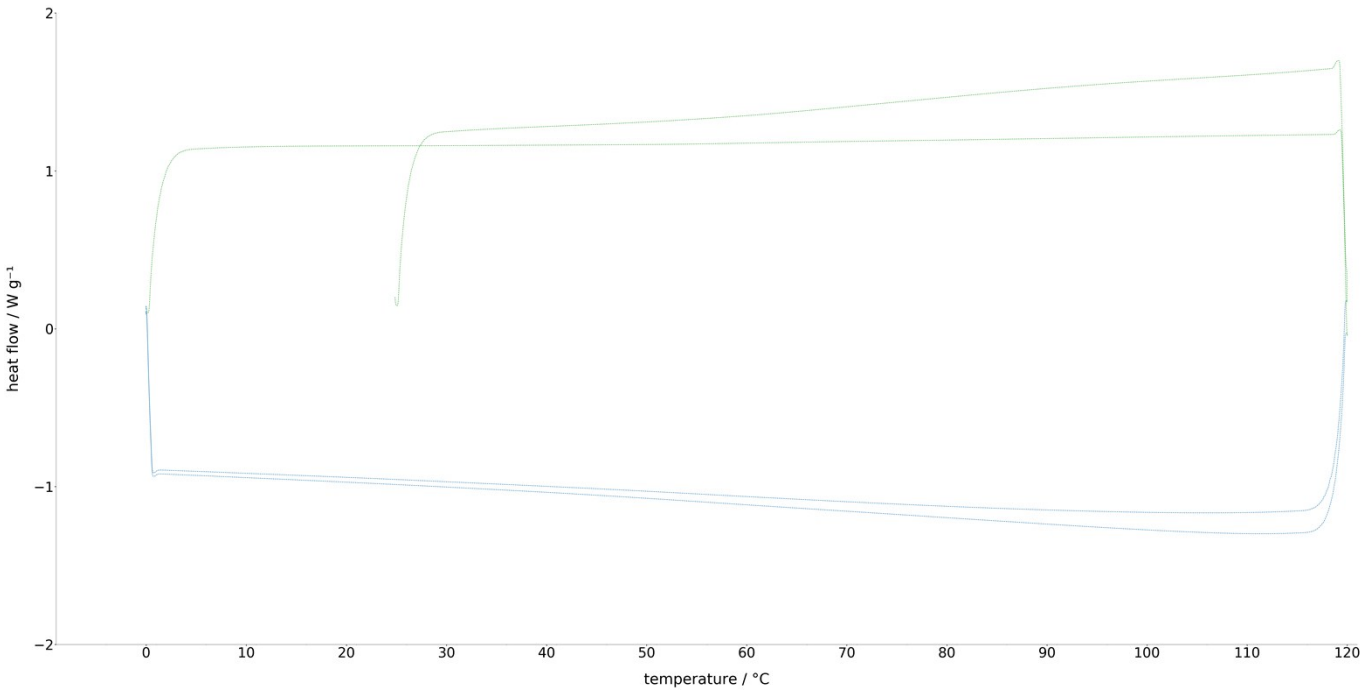

Figure S98. Differential scan calorimetry for di(2-hexyl-decyl)dimethylammonium chloride.

Di(2-heptyl-undecyl)dimethylammonium chloride

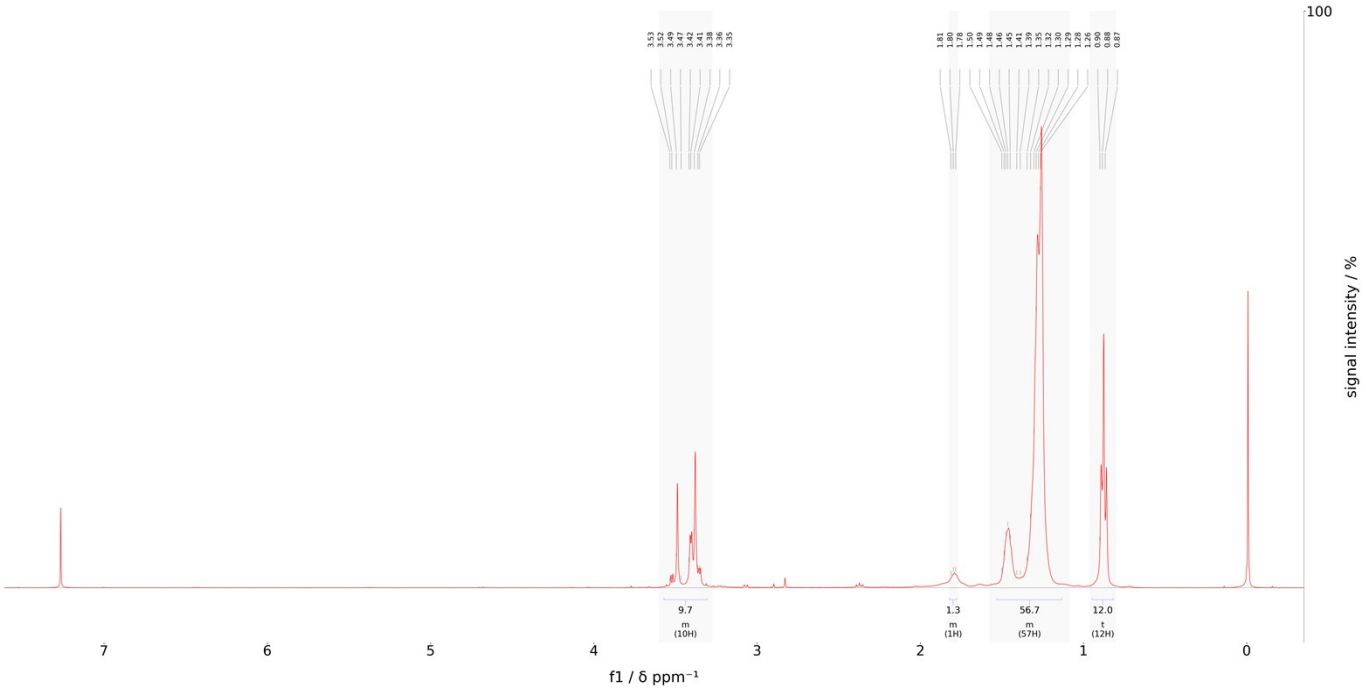

Figure S99. ^{1}H NMR of di(2-heptyl-undecyl)dimethylammonium chloride in deuterochloroform.

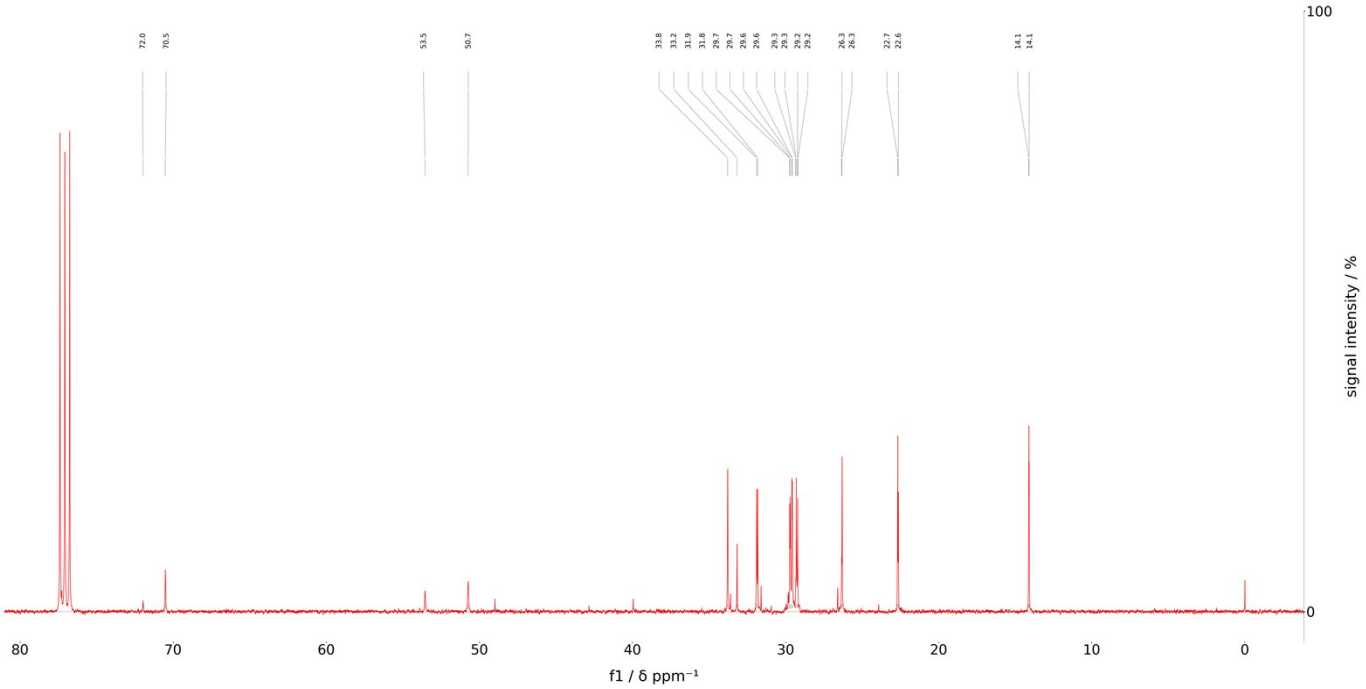

Figure S100. ^{13}C NMR of di(2-heptyl-undecyl)dimethylammonium chloride in deuterochloroform.

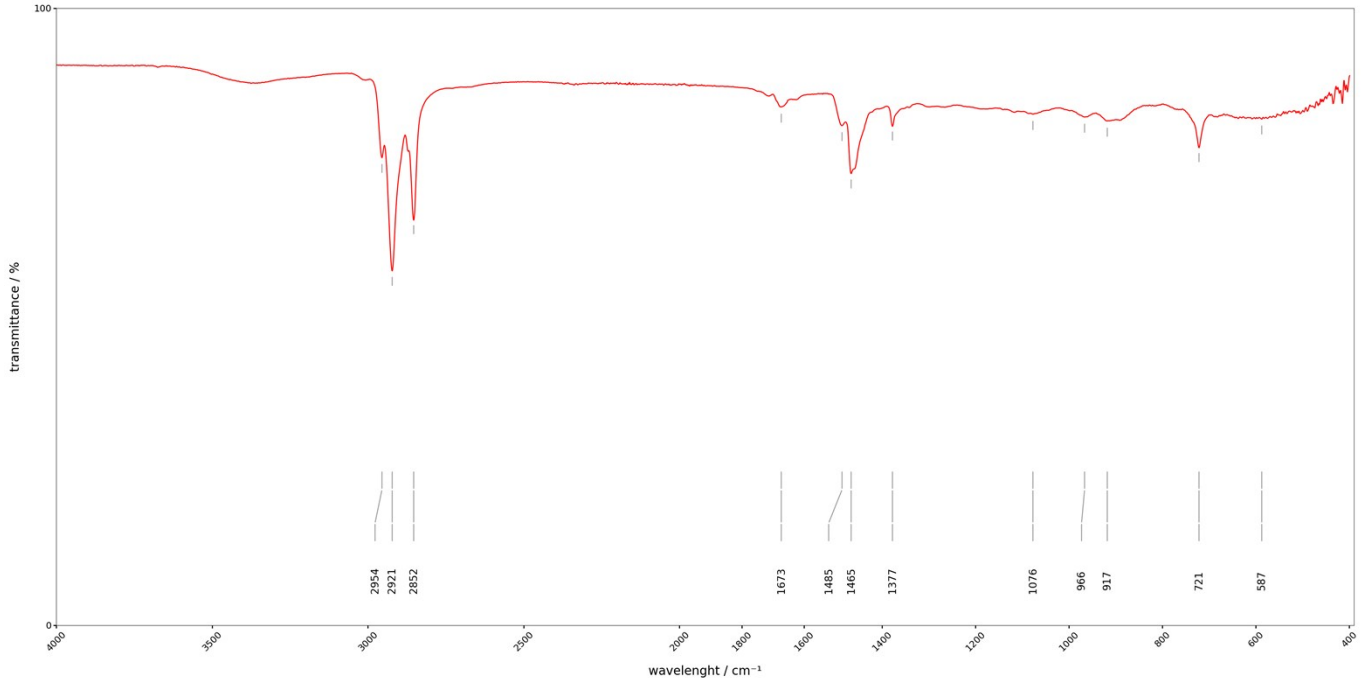

Figure S101. IR spectra of di(2-heptyl-undecyl)dimethylammonium chloride.

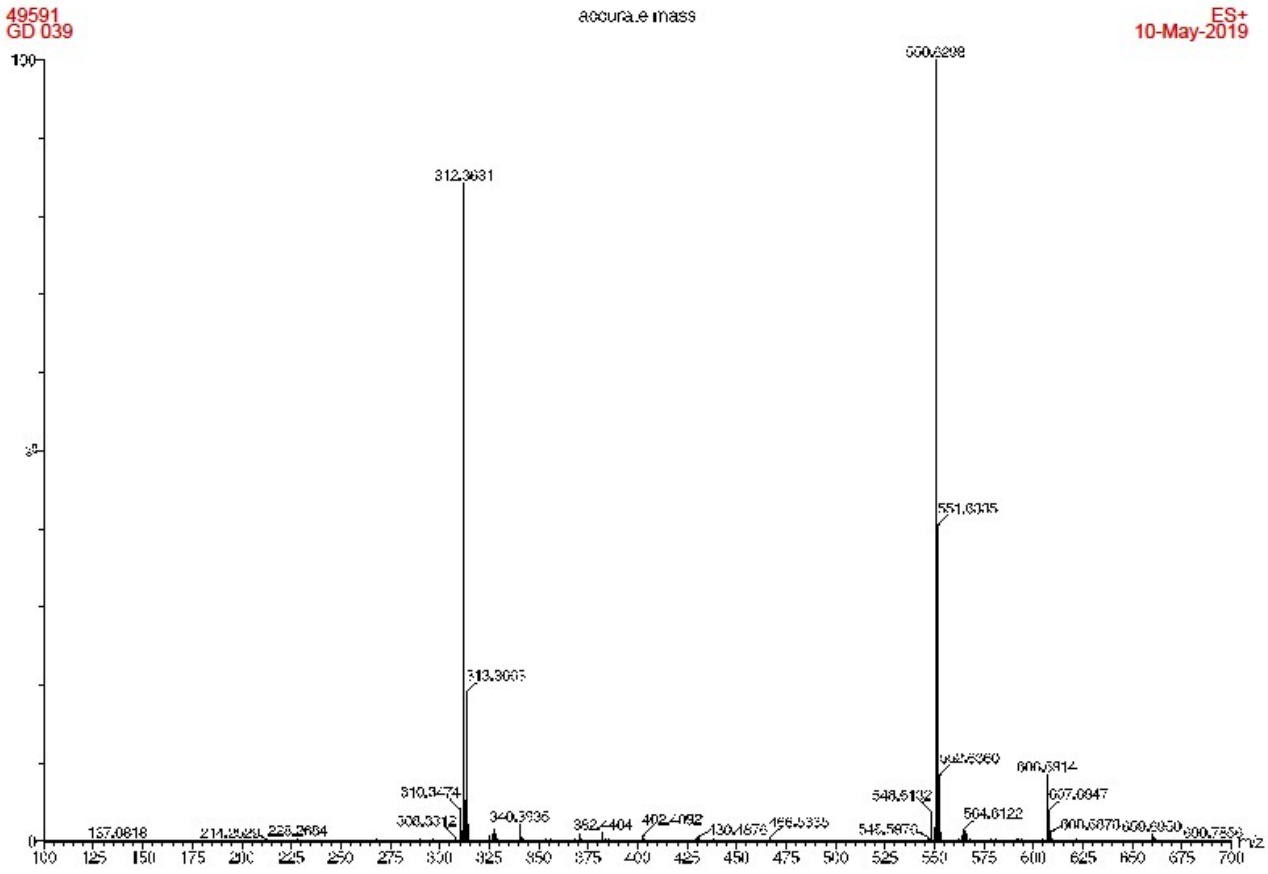

Figure S102. HRMS spectra of di(2-heptyl-undecyl)dimethylammonium chloride.

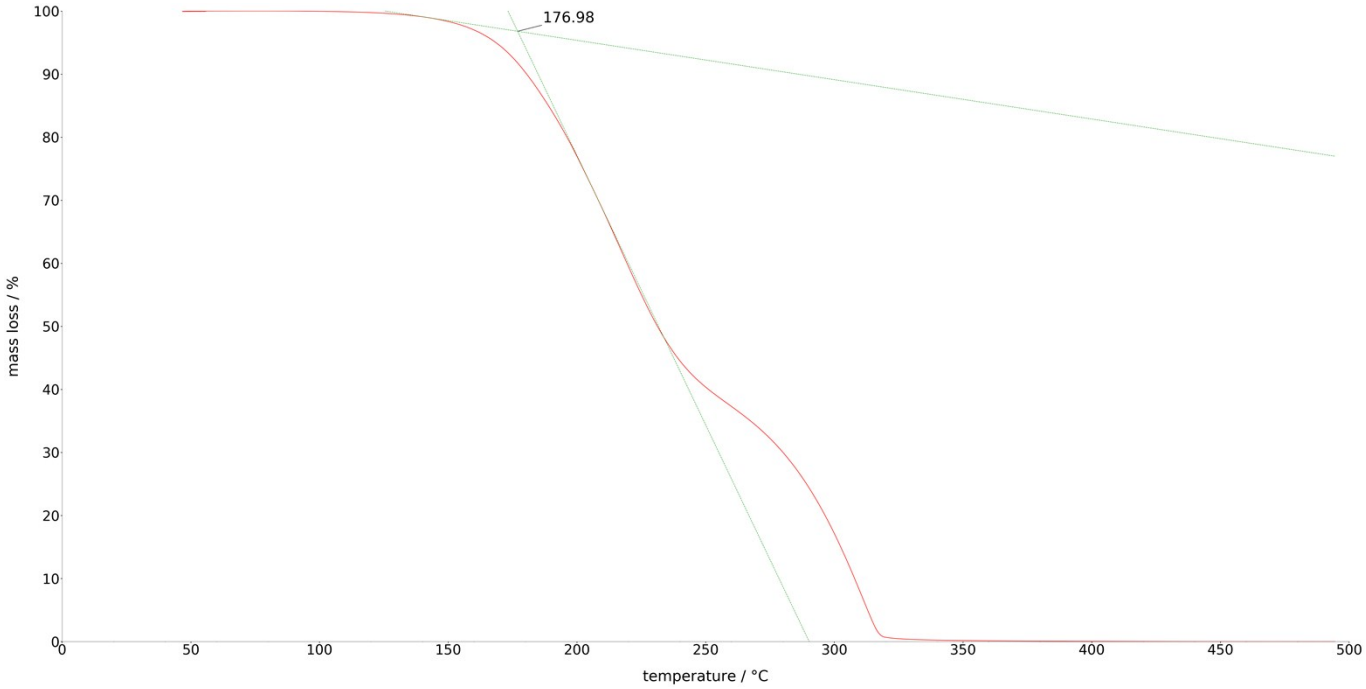

Figure S103. Thermogravimetric analysis for di(2-heptyl-undecyl)dimethylammonium chloride.

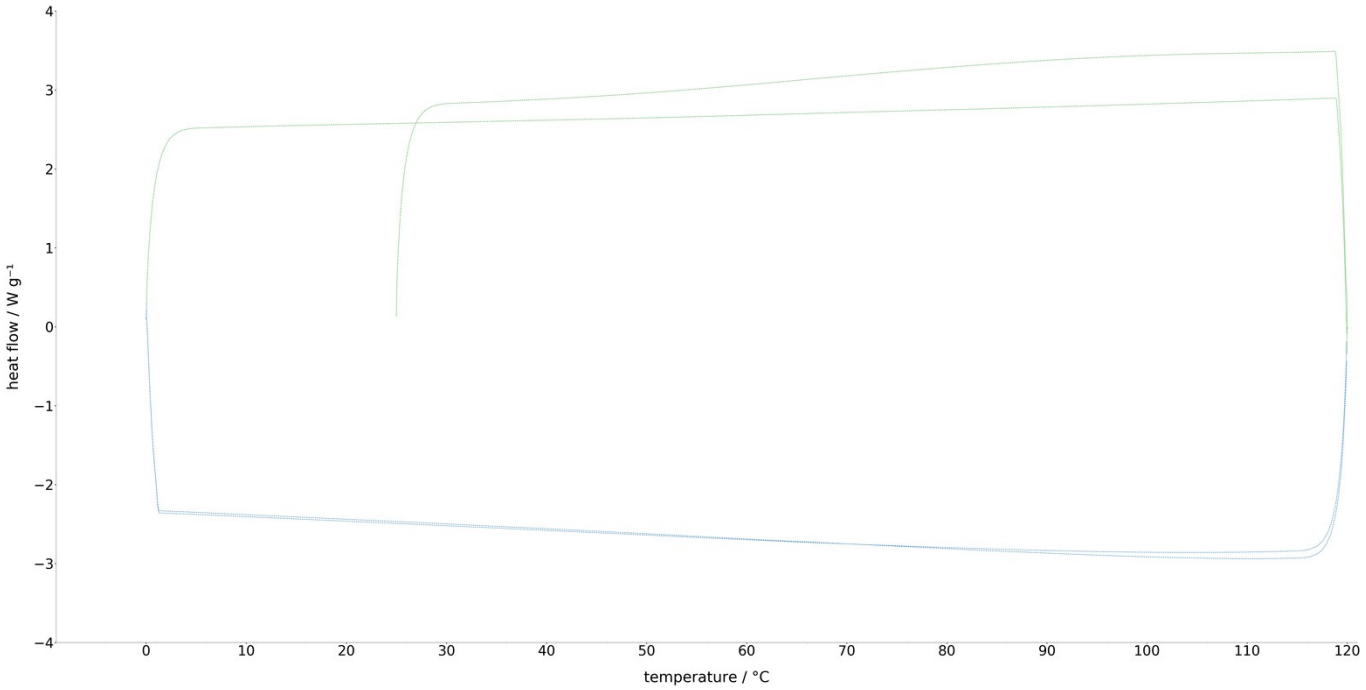

Figure S104. Differential scan calorimetry for di(2-heptyl-undecyl)dimethylammonium chloride.

Di(2-octyl-dodecyl)dimethylammonium chloride

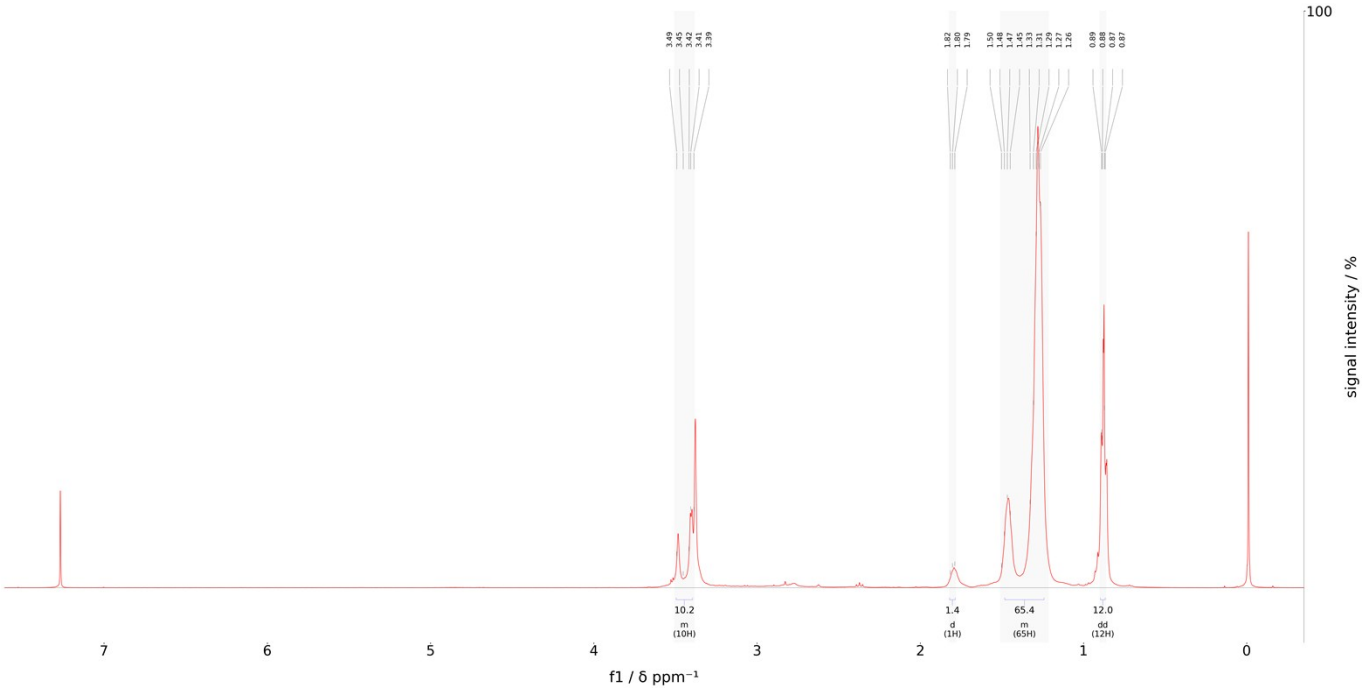

Figure S105. ^{1}H NMR of di(2-octyl-dodecyl)dimethylammonium chloride in deuterochloroform.

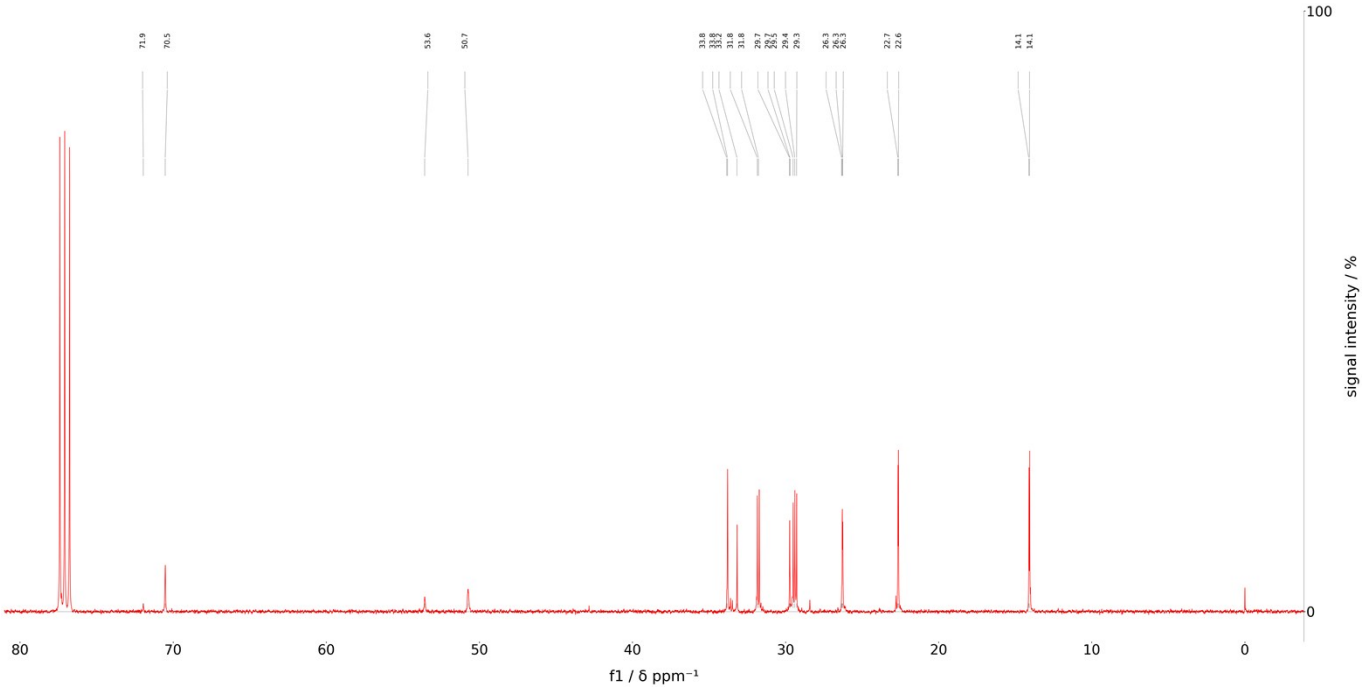

Figure S106. ^{13}C NMR of di(2-octyl-dodecyl)dimethylammonium chloride in deuterochloroform.

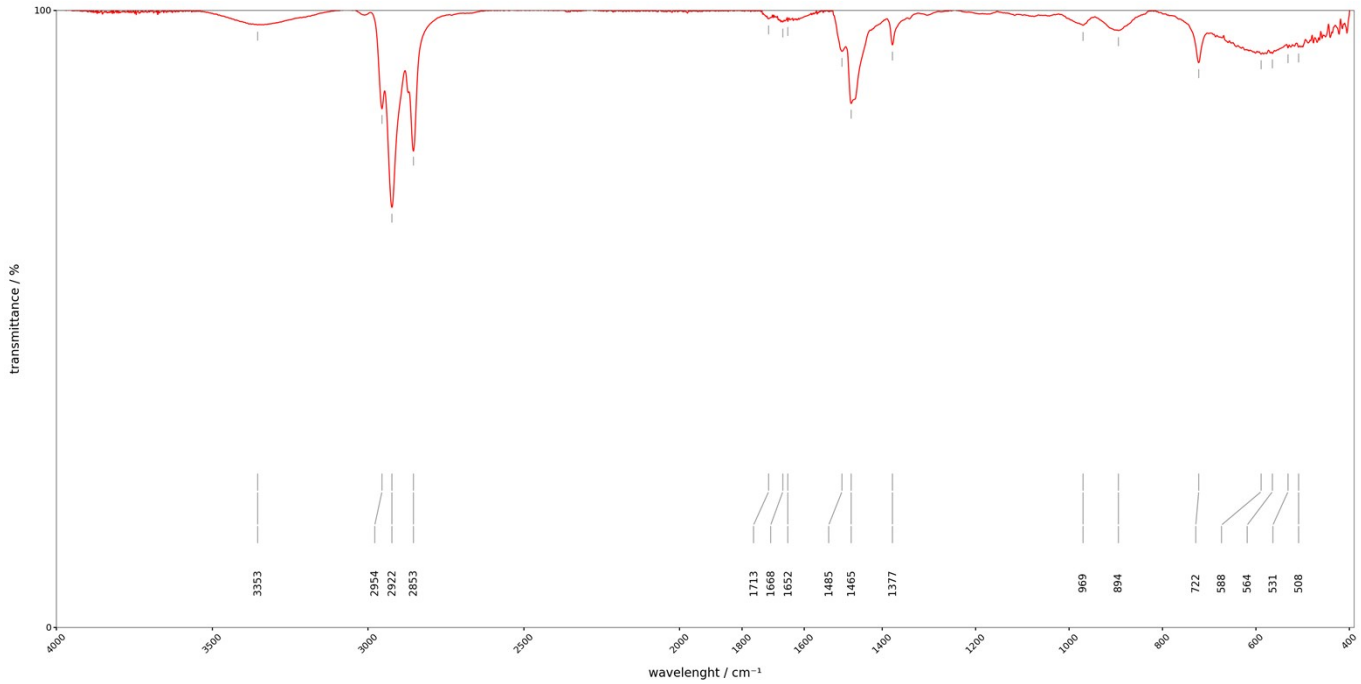

Figure S107. IR spectra of di(2-octyl-dodecyl)dimethylammonium chloride.

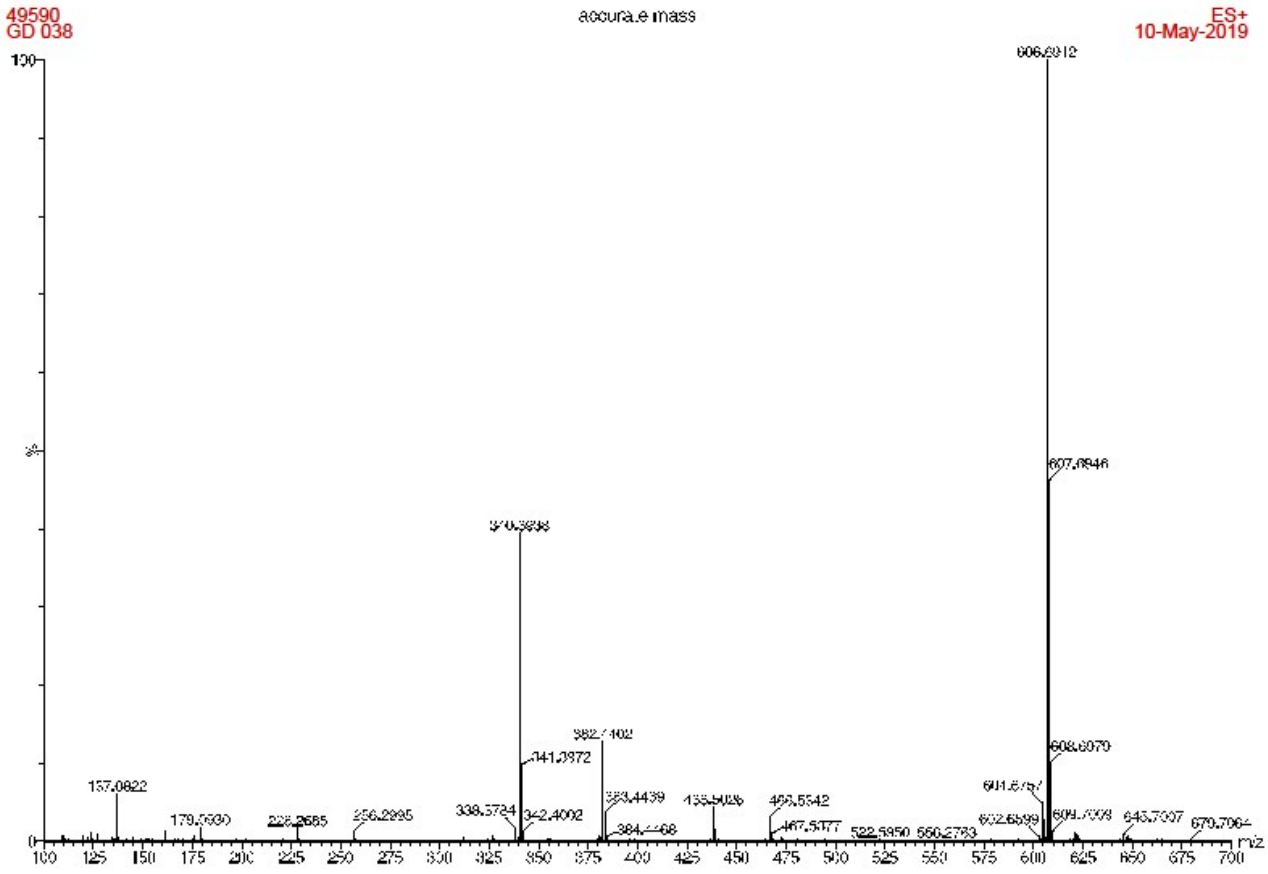

Figure S108. HRMS spectra of di(2-octyl-dodecyl)dimethylammonium chloride.

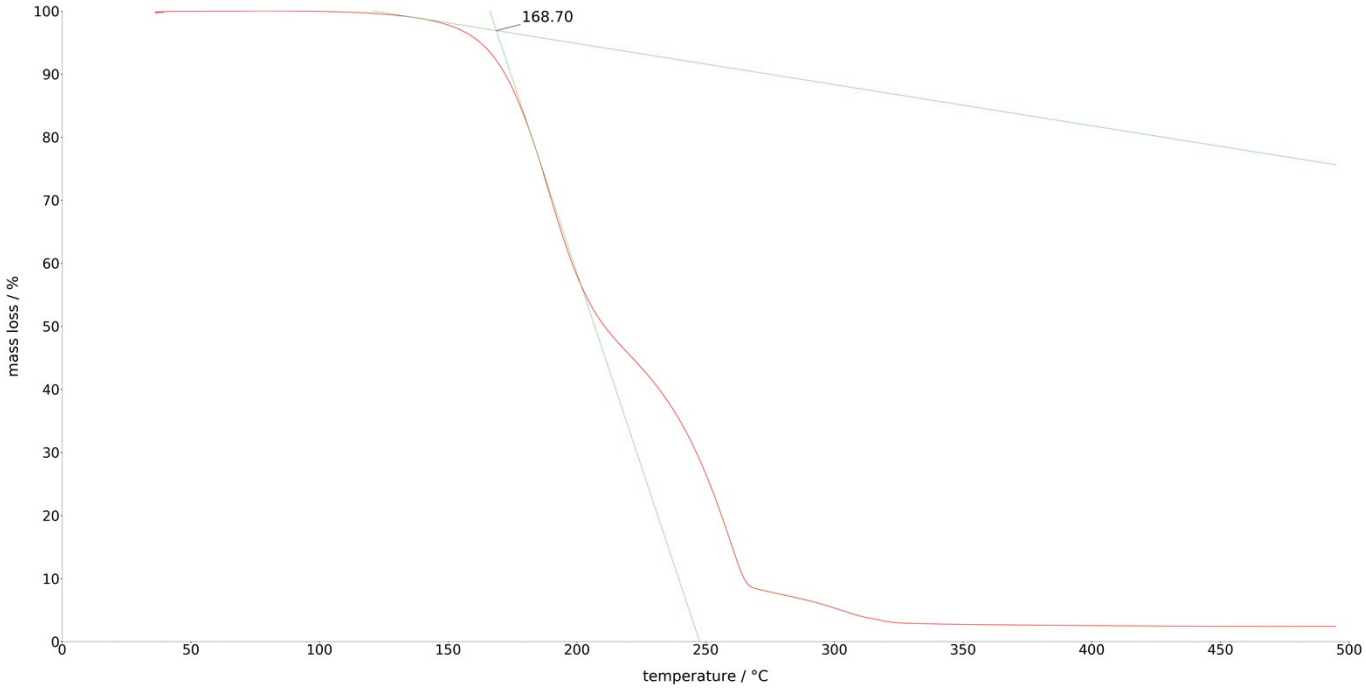

Figure S109. Thermogravimetric analysis for di(2-octyl-dodecyl)dimethylammonium chloride.

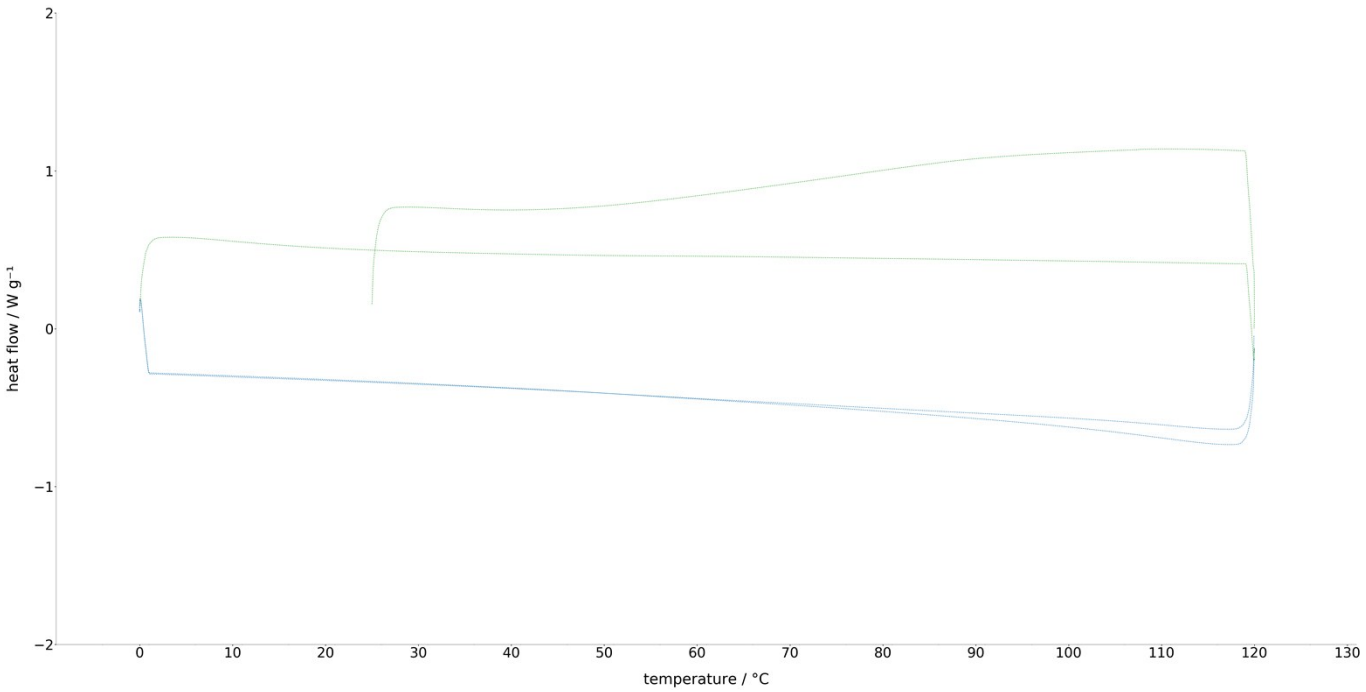

Figure S110. Differential scan calorimetry for di(2-octyl-dodecyl)dimethylammonium chloride.

References

1 A. T. Nielsen, *J. Am. Chem. Soc.*, 1957, **79**, 2518–2524.
2 A. T. Nielsen, *J. Am. Chem. Soc.*, 1957, **79**, 2524–2530.
3 A. T. Nielsen, *J. Org. Chem.*, 1963, **28**, 2115–2119.
4 J. D. Hunter, *Comput. Sci. Eng.*, 2007, **9**, 90–95.