Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

N-Alkylimidazolium carboxylates as a new type of Catanionic Surface Active Ionic Liquids: Synthesis, thermotropic behavior and micellization in water

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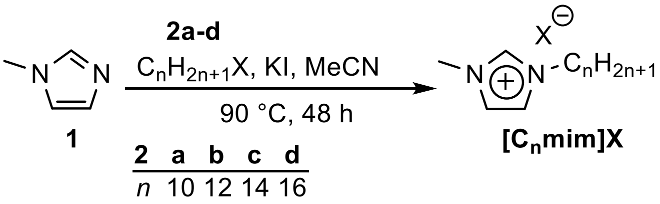
1. Materials and Equipment

All chemicals were obtained from the supplier and used without further purification. The following instruments were used for the characterization of the compounds. ^{1}H NMR spectra were recorded using *Bruker Avance 300*, *Avance 400* and *Avance 500* spectrometers at 300 MHz, 400 MHz and 500 MHz, respectively as well as ^{13}C NMR spectra at 75 MHz, 100 MHz and 126 MHz. As a solvent, deuterated chloroform (CDCl3) was used with tetramethylsilane as a reference for the chemical shift δ in ppm (parts per million). FT-IR spectra were recorded on a *Bruker Vektor 22* with a *MKII Golden Gate Single Reflection Diamond ATR*. Mass spectra (MS) as well as high resolution mass spectra (HRMS) were recorded by electrospray ionisation (ESI) with a *Bruker MicrOTOF-Q* spectrometer, and electron ionisation (EI) with a *Bruker Varian MAT 711* spectrometer. An *Elemental Analyzer Model 1106* from the company *Carlo Erba Strumentazione* was used for elemental analyses. Polarising optical microscopy measurements were realized with an *Olympus BX 50* polarising microscope combined with a *Linkam TP93* central controller. Differential scanning calorimetery was performed on a *DSC822e* from the company *Mettler Toledo*. Therefore, 40 µL sealed aluminium crucibles with heating and cooling rates of 5 K/min were used. The phase transition temperatures of the extrapolated onset values were determined using the software *STARe 7.01* from *Mettler Toledo*. Thermo gravimetric analysis was performed with a *STA 449C Jupiter* from *Netzsch* with a constant heating rate of 10 K/min starting at 25 to 450 °C. X-ray diffraction was measured using *Bruker AXS Nanostar C* with a ceramic tube generator (1500 W) and cross-coupled Goebel mirrors that provide monochromatic Cu $K_{\alpha 1}$ radiation (1.5405 Å). The samples were melted in a glass capillary from the company *Hilgenberg GmbH* (external diameter of 0.7 mm). Diffraction patterns were measured using a *Bruker HI-STAR* detector. For calibration, a diffraction pattern of silver behenate at room temperature was used before each measurement. Further analysis of measured values was performed with the software *SAXS (Version 4.1.51)* from the company *Bruker*. The obtained diffraction patterns were analyzed using the software *Datasqueeze (Version 2.2.8)* and *Origin*. The water content was determined via a Karl-Fischer Titrator *METTLER TOLEDO C10S* with a *DO308* oven. Therefore, 50 mg of the compound were heated within the device up to 120 °C and the evaporating water was titrated in a *CombiCoulomat fritless* solution. The surface tensions of the solutions of different concentrations were measured by a surface tensiometer *(Dataphysics DCAT 9)* equipped with a Wilhelmy plate. The solutions were prepared using ultrasound and an increased temperature in a volumetric flask. The solutions of the soapy ILCs were prepared in bidestilled water of the Institute for Physical Chemistry of the University of Stuttgart. For selected samples the surface tension was measured as a function of concentration. The surface-tension measurements were started with the highest concentration solution, and the subsequent concentrated solutions were prepared by adding the amount of water which was used to clean and fill the sample vessel. The vessel was cleaned with 5 mL of the solution and 15 mL were used for the measurement. The measurements were performed at 25 °C. The measurements were terminated by the *DCATS* program when the standard deviation of the last 100 measured values was less than 0.02 mN/m.

2. Synthesis

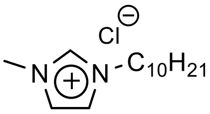
General procedure 1 (GP1): Synthesis of *N*-alkyl-*N*-methylimidazolium halides ([$C_n$mim]X)



Scheme 1

N-Methylimidazole **1** (8.00 g, 97.4 mmol) and the corresponding alkyl halide **2a-d** (21.6 g, 97.4 mmol) were mixed together in MeCN (200 mL). Then KI (0.01 g, 60.2 µmol) was added as a catalyst. The mixture was stirred at 90 °C for 24 h. Subsequently the solvent was removed under reduced pressure and the alkylated product was purified via recrystallization from EtOAc (3 x 100 mL).

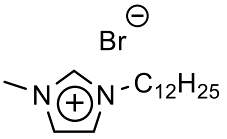
1-Decyl-3-methylimidazolium chloride ([C_{10}mim][Cl])



$C_{14}H_{30}ClN_2$
261.86

According to GP 1: *N*-Methylimidazole (8.00 g, 97.4 mmol), 1-bromodecane **2a** (21.6 g, 97.4 mol), KI (0.01 g, 60.2 µmol), MeCN (200 mL); reaction time: 72 h. Colorless liquid (95 %, 28.2 g, 93.0 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82–0.93 (t, *J* = 7.1 Hz, 3H), 1.19–1.39 (m, 14H), 1.93 (dt, *J* = 7.1 Hz, 7.5 Hz, 2H), 4.15 (s, 3H), 4.34 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 1.8 Hz, 1H), 7.77 (t, *J* = 1.8 Hz, 1H), 10.24 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.95 (1 × CH_3), 22.47, 26.08, 28.83, 29.05, 29.20, 29.27, 30.19, 31.65 (8 × CH_2), 36.58 (1 × NCH_3), 49.94 (1 × NCH_2), 122.06, 123.82 (2 x NCHC), 136.91 (1 × NCHN).The spectroscopic data were in accordance with ref[1].

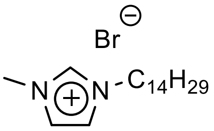
1-Dodecyl-3-methylimidazolium bromide ([C$_{12}$mim]Br)



$C_{16}H_{34}BrN_2$
334.37

According to GP 1: *N*-Methylimidazole (8.00 g, 97.4 mmol), 1-bromododecane **2b** (29.1 g, 97.4 mol), KI (0.01 g, 60.2 µmol), MeCN (200 mL); reaction time: 48 h. White solid (90 %, 29.00 g, 87.5 mmol); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.82–0.93 (t, *J* = 7.1 Hz, 3H), 1.24–1.37 (m, 25H), 1.92 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 4.13 (s, 3H), 4.32 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 1.8 Hz, 1H), 7.60 (t, *J* = 1.8 Hz, 1H), 10.48 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.07 (1 × $C\mathrm{H}_3$), 22.62, 26.23, 28.97, 29.27, 29.33, 29.45, 29.53, 30.29, 31.84 (10 × $C\mathrm{H}_2$), 36.58 (1 × $\mathrm{N}C\mathrm{H}_3$), 50.06 (1 × $\mathrm{N}C\mathrm{H}_2$), 121.70, 123.56 (2 x NCHC), 137.91 (1 × NCHN). The spectroscopic data were in accordance with ref[2].

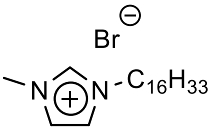
1-Tetradecyl-3-methylimidazolium bromide ([C$_{14}$mim]Br)



$C_{18}H_{38}BrN_2$
362.42

According to GP 1: *N*-Methylimidazole (6.00 g, 73.1 mmol), 1-bromotetradecane **2c** (20.3 g, 73.1 mmol), KI (0.01 g, 60.2 µmol), MeCN (200 mL); reaction time: 24 h. White solid (93 %, 24.53 g, 68.25 mmol); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.83–0.93 (t, *J* = 7.1 Hz, 3H), 1.22–1.33 (m, 27H), 1.90 (dt, *J* = 7.1, *J* = 7.4 Hz, 2H), 4.14 (s, 3H), 4.27–4.38 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 1.8 Hz, 1H), 7.51 (t, *J* = 1.8 Hz, 1H), 10.41 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.10 (1 × $C\mathrm{H}_3$), 22.66, 26.25, 28.98, 29.33, 29.36, 29.48, 29.57, 29.62, 29.65, 30.30, 31.89, 36.78 (12 × $\mathrm{N}C\mathrm{H}_3$), 50.20 (1 × $\mathrm{N}C\mathrm{H}_2$), 121.72, 123.46 (2 x NCHC), 137.67 (1 × NCHN). The spectroscopic data were in accordance with ref[3].

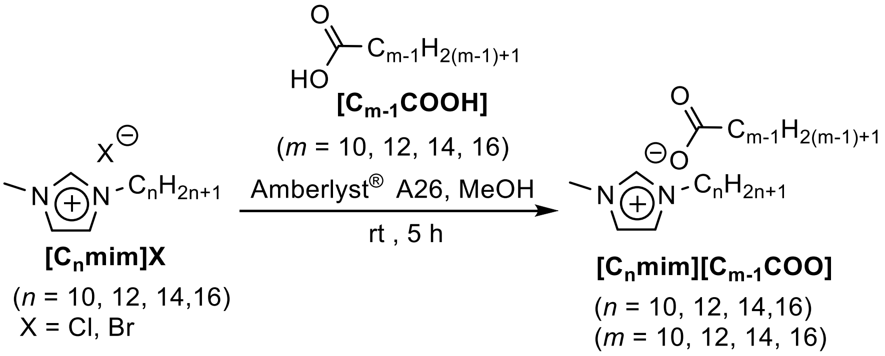
1-Hexadecyl-3-methylimidazolium bromide ([C$_{16}$mim]Br)



$C_{20}H_{42}BrN_2$
390.47

According to GP 1: *N*-Methylimidazole (2.00 g, 24.4 mmol), 1-bromohexadecane **2d** (7.44 g, 24.4 mol), KI (0.01 g, 60.2 µmol), MeCN (200 mL); reaction time: 48 h. White solid (79 %, 7.50 g, 19.4 mmol); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.83–0.93 (t, *J* = 7.1 Hz, 3H), 1.25-1.34 (m, 26H), 1.92 (dt, *J* = 7.1, *J* = 7.5 Hz, 2H), 4.14 (s, 3H), 4.32 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 1.8 Hz, 1H), 10.53 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.11 (1 × $C\mathrm{H}_3$), 22.68, 26.26, 28.98, 29.35, 29.49, 29.58, 29.64, 29.68, 30.29, 31.91 (14 × $\mathrm{N}C\mathrm{H}_3$), 36.79 (1 × $C\mathrm{H}_3$), 50.24 (1 × $\mathrm{N}C\mathrm{H}_2$), 121.58, 123.26 (2 x NCHC), 137.94 (1 × NCHN). The spectroscopic data were in accordance with ref[4].

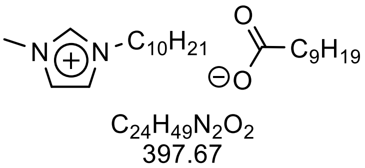
General procedure 2 (GP2): Synthesis of 1-Alkyl-3-methylimidazolium carboxylates ([$C_n$mim][C_{m-1}COO])



Scheme 2

A column was filled with ion exchange resin Amberlyst® A26 (20 mL). This was loaded with a carboxylic acid **[C_{m-1}COOH]** (m = 10, 12, 14, 16) (5 eq.) dissolved in MeOH (50 mL) with a dripping rate of 2 mL /min. Afterwards the column was thoroughly washed with water and MeOH to get rid of excess acid. Then, the 1-alkyl-3-methylimidazolium halide **[$C_n$mim]X** (n = 10, 12, 14, 16) (1 eq.) was dissolved in MeOH (100 mL) and the column was unloaded with a dripping rate of 0.5 mL /min. The solvent was evaporated under reduced pressure and the crude product recrystallized from acetone.

1-Decyl-3-methylimidazolium decanoate ([C_{10}mim][C_{10}COO])

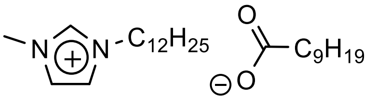


Synthesis according to GP 2. From 1-decyl-3-methylimidazolium chloride **[C_{10}mim]Cl**, decanoic acid **[C_9COOH]**, MeOH (50 mL); white solid (88 %, 2.29 g, 5.80 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.87 (m, 6H), 1.16–1.42 (m, 26H), 1.61–1.69 (dt, J = 7.8 Hz, 2H), 1.87 (dt, J = 7.1 Hz, J = 7.4 Hz, 2H), 2.21–2.28 (t, J = 7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, J = 7.4 Hz, 2H), 7.08 (s, 2H), 11.88 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.23 (2 × CH$_3$), 22.81, 26.38, 27.36, 29.14, 29.47, 29.50, 29.62, 29.71, 29.76, 29.79, 29.81, 29.87, 30.23, 30.41, 32.03, 32.05 (15 × CH$_2$), 36.40 (1 × CH$_3$), 39.53 (1 × CH$_2$), 50.00 (1 × NCH$_2$CH), 120.77, 122.28 (2 x NCHC), 181.21 (1 × COO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon NCHN could not be observed due to the poor signal to noise ratio; FT-IR: $\tilde{\nu}$ = 3382.34 (m), 3141.07 (m), 2955.80 (s), 2919.95 (vs), 2871.93 (m), 2849.65 (s), 2221.58 (w), 1560.74 (vs), 1465.33 (s), 1394.04 (s), 1334.40 (w), 1303.90 (w), 1270.23 (w), 1235.07 (w), 11689.64 (m), 1104.36 (w), 907.13 (m), 734.63 (vs), 663.85 (m), 628.20 (m), 506.77 (w), 456.46 (w) cm^{-1}**;** MS (ESI): Positive: m/z = 223.22 [M$^+$]; HRMS (ESI): m/z for

$C_{14}H_{27}N_2^+$ calc.: 223.2169 [M$^+$], found: 223.2169**;** MS (ESI): Negative: *m/z* = 171.14 [M$^-$]; HRMS (ESI): *m/z* for $C_{10}H_{19}O_2$- calc.: 171.1391 [M$^-$], found: 171.1398; DSC: Cr 61 °C [74.2 kJ mol^{-1}] SmA 108 °C [2.9 kJ mol^{-1}] I; Elemental analysis: calc.: C 73.04, H 11.74, N 7.10; found C 68.63, H 11.70, N 6.64 · 1.5; Water content: 0.33 ± 0.11 wt%.

1-Dodecyl-3-methylimidazolium decanoate ([C12mim][C9COO])

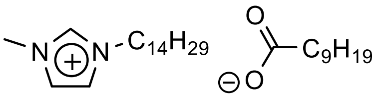
Synthesis according to GP 2. From 1-dodecyl-3-methylimidazolium bromide **[C12mim]Br,** decanoic acid **[C9COOH]**, MeOH (50 mL); white solid (69 %, 2.03 g, 4.79 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.87 (m, 6H), 1.16–1.43 (m, 30H), 1.62–1.71 (dt, *J* =7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.28 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 6.98–7.15 (m, 2H), 11.83 (s, 1H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 14.22, 14.24(2 × *C*H$_3$), 22.79, 22.82, 26.38, 27.36, 29.14, 29.44, 29.49, 29.52, 29.62, 29.71, 29.81, 29.87, 30.23, 30.41, 32.02, 32.08 (17 × *C*H$_2$), 36.41 (1 × *C*H$_3$), 39.53 (1 × *C*H$_2$), 50.01 (1 × N*C*H$_2$CH), 120.78, 122.28 (2 x N*C*HC), , 181.21 (1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio; FT-IR: $\tilde{\nu}$ = 3140.15 (m), 3033.92 (m9, 2955.46 (m), 2918.69 (vs), 2849.994 (s), 2199.75 (w), 1558.62 (vs), 1466.88 (m), 1397.10 (m), 1336.36 8 (w), 1304.05 (w), 1171.43 (m) 1105.19 8w), 609.38 (s), 727.66 (vs), 641.78 (m), 627.39 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 251.25 [M$^+$]; HRMS (ESI): *m/z* for $C_{16}H_{31}N_2^+$ calc.: 252.2482 [M$^+$], found: 251.2483; MS (ESI): Negative: *m/z* = 171.14 [M$^-$]; HRMS (ESI): *m/z* for $C_{10}H_{19}O_2^-$ calc.: 171.1391 [M$^-$], found: 171.1391; DSC: Cr 43 °C [63.4 kJ mol^{-1}] SmA 122 °C [3.5 kJ mol^{-1}] I; Water content: 1.11 ± 0.11 wt%.



$C_{26}H_{53}N_2O_2$
425.72

1-Tetradecyl-3-methylimidazolium decanoate ([C14mim][C9COO])

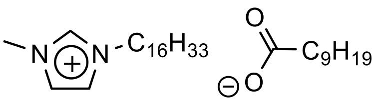
Synthesis according to GP 2. From 1-tetradecyl - 3-methylimidazolium bromide **[C14mim]Br**, decanoic acid **[C9COOH]**, MeOH (50 mL); white solid (79 %, 1.97 g, 4.38 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.84–0.91 (m, 6H), 1.18–1.39 (m, 34H), 1.66 (dt, *J* = 7.8f Hz, 2H), 1.83–1.90 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.28 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.07 (s, 2H), 11.87 (s, 1H) ppm.; ^{13}C NMR (101 MHz, CDCl$_3$) δ 14.23 (2 × *C*H$_3$), 22.79, 22.81, 26.38, 27.33, 29.14, 29.46, 29.49, 29.52, 29.62, 29.71, 29.75, 29.79, 29.80, 29.86, 30.21, 30.41, 32.03, 32.07 (19 × *C*H$_2$), 36.41 (1 × *C*H$_3$), 39.46 (1 × *C*H$_2$), 50.01 (1 × N*C*H$_2$CH), 120.80, 122.32 (2 x N*C*HC), 181.14 (1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed



$C_{28}H_{57}N_2O_2$
453.78

due to the poor signal to noise ratio; FT-IR: $\tilde{\nu}$ = 3144.73 (w), 2922.34 (s), 2852.80 (m), 2211.16 (w), 1557.35 (s), 1466.19 (m), 1392.08 (m), 1305.66 (w), 1170.37 (w), 907.15 (s), 728.98 (vs), 641.05 (m), 625.53 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 279.28 [M$^+$]; HRMS (ESI): *m/z* for $C_{18}H_{35}N_2^+$ calc.: 279.2795 [M$^+$], found: 279.2796; MS (ESI): Negative: *m/z* = 171.14 [M$^-$]; HRMS (ESI): *m/z* for C10$H_{19}O_2^-$ calc.: 171.1391 [M$^-$], found: 171.1399; DSC: Cr 47 °C [77.1 kJ mol^{-1}] SmA 126 °C [3.2 kJ mol^{-1}] I.; Water content: 0.56 ± 0.11 wt%.

1-Hexadecyl-3-methylimidazolium decanoate ([C_{16}mim][C_9COO])



$C_{30}H_{61}N_2O_2$
481.83

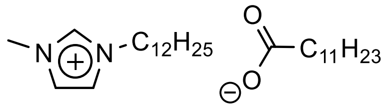
Synthesis according to GP 2. From 1-hexadecyl-3-methylimidazolium bromide **[C_{16}mim]Br**, decanoic acid **[C_9COOH]**, MeOH (50 mL); white solid (92 %, 2.28 g, 4.76 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.19–1.39 (m, 38H), 1.62–1.70 (dt, *J*=7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.20–2.30 (t, *J*=7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 11.80 (s, 1H) ppm.; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.24 (2 × CH_3), 22.81, 26.38, 27.35, 29.15, 29.48, 29.50, 29.53, 29.63, 29.72, 29.77, 29.81, 29.87, 30.22, 30.41, 32.04, 32.08 (21 × CH_2), 36.41 (1 × CH_3), 39.52 (1 × CH_2), 50.01 (1 × NCH_2CH), 120.77, 122.27 (2 x N*C*HC), 181.24 (1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio; FT-IR: $\tilde{\nu}$ = 2922.16 (s), 2851.59 (m), 2206.85 (w), 1558.22 (s), 1461.71 (m), 1309.59 (m), 1304.97 (w), 1168.59 (w), 907.07 (s), 727.93 (vs), 639.21 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 307.31 [M$^+$]; HRMS (ESI): *m/z* for $C_{20}H_{39}N_2^+$ calc.: 307.3108 [M$^+$], found: 307.3108; MS (ESI): Negative: *m/z* = 171.14 [M$^-$]; HRMS (ESI): *m/z* for $C_{10}H_{19}O_2^-$ calc.: 171.1391 [M$^-$], found: 171.1392; DSC: Cr 55 °C [90.1 kJ mol^{-1}] SmA 146 °C [3.6 kJ mol^{-1}] I.; Water content: 0.59 ± 0.11 wt%.

1-Decyl-3-methylimidazolium dodecanoate ([C_{10}mim][C_{11}COO])

$C_{26}H_{53}N_2O_2$
425.72

Synthesis according to GP 2. From 1-decyl-3-methylimidazolium chloride **[C_{10}mim]Cl**, dodecanoic acid **[C_{11}COOH]**, MeOH (50 mL); white solid (83 %, 1.15 g, 2.72 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.28 (m, 30H), 1.66 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.27 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.28–4.33 (t, *J* = 7.4 Hz, 2H), 7.06 (s, 2H), 11.84 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.21, 14.24 (2 × CH_3), 22.77, 22.81, 26.38, 27.36, 29.14, 29.36, 29.49, 29.57, 29.81, 29.87, 30.23, 30.41, 31.96, 32.06 (17 × CH_2), 36.41 (1 × CH_3), 39.53 (1 × CH_2), 50.01 (1 × NCH_2CH), 120.78, 122.28 (2 x N*C*HC), 181.24 (1 × *C*OO), The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 2923.99 (m), 2853.87 (m), 2212.85 (w), 1556.48 (m), 1466.02 (w), 1392.39 (m), 1170.97 (w), 906.45 (s), 726.77 (vs), 641.42 (m), 625.05 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 223.22 [M^+]; HRMS (ESI): *m/z* for $C_{14}H_{27}N_2^+$ calc.: 223.2169 [M^+], found: 223.2168; MS (ESI): Negative: *m/z* = 199.17 [M^-]; HRMS (ESI): *m/z* for $C_{14}H_{23}O_2^-$ calc.: 199.1704 [M^-], found: 199.1701; DSC: Cr 42 °C [68.0 kJ mol^{-1}] SmA 144 °C [3.7 kJ mol^{-1}] I.; Water content: 1.48 ± 0.11 wt%.

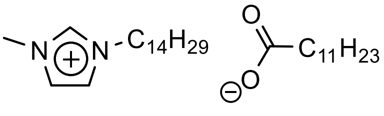
1-Dodecyl-3-methylimidazolium dodecanoate ([C_{12}mim][C_{11}COO])



$C_{28}H_{57}N_2O_2$
453.78

Synthesis according to GP 2. From 1-dodecyl-3-methylimidazolium bromide **[C_{12}mim]Br**, dodecanoic acid **[C_{11}COOH]**, MeOH (50 mL); white solid (95 %, 2.56 g, 5.68 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.91 (m, 6H), 1.16–1.39 (m, 34H), 1.63–1.71 (dt, *J* = 7.8 Hz, 2H), 1.84–1.90 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.28 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 2H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.06 (s, 2H), 11.87 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.22 (2 × $\mathit{C}H_3$), 22.79, 22.81, 26.38, 27.15, 29.14, 29.45, 29.50, 29.62, 29.71, 29.81, 29.84, 29.87, 30.15, 30.42, 32.02, 32.06 (19 × $\mathit{C}H_2$), 36.43 (1 × $\mathit{C}H_3$), 39.04 (1 × $\mathit{C}H_2$), 50.03 (1 × N$\mathit{C}H_2$CH), 120.81, 122.30 (2 x N*C*HC), 141.73 (1 × N*C*HN), 180.87 (1 × *C*OO); FT-IR: $\tilde{\nu}$ = 2923.57 (m), 2853.17 (m), 2221.68 (w), 1557.69 (m), 1466.19 (w), 1391.97 (w), 1171.59 (w), 905.93 (s), 726.35 (vs), 642.12 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 251.25 [M^+]; HRMS (ESI): *m/z* for $C_{16}H_{31}N_2^+$ calc.: 251.2482 [M^+], found: 251.2482; MS (ESI): Negative: *m/z* = 199.17 [M^-]; HRMS (ESI): *m/z* for $C_{12}H_{23}O_2^-$ calc.: 199.1693 [M^-], found: 199.1694; DSC: Cr 48 °C [79.6 kJ mol^{-1}] SmA 118 °C [3.0 kJ mol^{-1}] I; Water content: 1.95 ± 0.11 wt%.

1-Tetradecyl-3-methylimidazolium dodecanoate ([C_{14}mim][C_{11}COO])

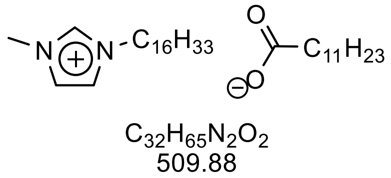


$C_{30}H_{61}N_2O_2$
481.83

Synthesis according to GP 2. From 1-tetradecyl-3-methylimidazolium bromide **[C_{14}mim]Br**, dodecanoic acid **[C_{11}COOH]**, MeOH (50 mL); white solid (93 %, 2.48 g, 5.18 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.19–1.39 (m, 38H), 1.66 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.27 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.03–7.08 (m, 2H), 11.89 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10 (2 × $\mathit{C}H_3$), 22.68, 26.25, 27.23, 29.01, 29.34, 29.37, 29.49, 29.58, 29.63, 29.66, 29.68, 29.74, 30.10, 30.28, 31.90, 31.92 (21 × $\mathit{C}H_2$), 36.27 (1 × $\mathit{C}H_3$), 39.40 (1 × $\mathit{C}H_2$), 49.87 (1 × N$\mathit{C}H_2$CH), 120.64, 122.15 (2 x N*C*HC), 181.08

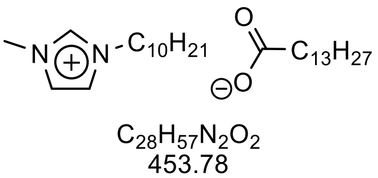
(1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 2919.53 (m), 2850.69 (m), 2194.98 (w), 1560.00 (m), 1466.43 (w), 1400.79 (w), 1169.83 (w), 906.35 (s), 724.68 (vs), 641.36 (m), 625.96 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 279.28 [M$^+$]; HRMS (ESI): *m/z* for $C_{18}H_{35}N_2^+$ calc.: 279.2795 [M$^+$], found: 279.2795; MS (ESI): Negative: *m/z* = 199.17 [M$^-$]; HRMS (ESI): *m/z* for $C12H_{23}O_2^-$ calc.: 199.1704 [M$^-$], found: 199.1709; DSC: Cr 57 °C [78.5 kJ mol^{-1}] SmA 139 °C [2.7 kJ mol^{-1}] I.; Water content: 0.66 ± 0.11 wt%.

1-Hexadecyl-3-methylimidazolium dodecanoate ([C$_{16}$mim][C$_{11}$COO])



Synthesis according to GP 2. From 1-hexadecyl-3-methylimidazolium bromide **[C$_{16}$mim]Br**, dodecanoic acid **[C$_{11}$COOH]**, MeOH (50 mL); white solid (76 %, 2.00 g, 3.95 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.88 (m, 6H), 1.19–1.39 (m, 42H), 1.62–1.70 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.20–2.27 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 11.79 (s, 1H) ppm.; ^{13}C NMR (101 MHz, CDCl$_3$) δ 14.19 (2 × *C*H$_3$), 22.77, 26.35, 27.28, 29.11, 29.44, 29.47, 29.60, 29.64, 29.69, 29.74, 29.78, 29.82, 29.84, 30.19, 30.38, 32.01, 32.02 (23 × *C*H$_3$), 36.38 (1 × *C*H$_3$), 39.37 (1 × *C*H$_2$), 49.97 (1 × N*C*H$_2$CH), 120.85, 120.88, 122.41 (2 x N*C*HC), 141.51 (1 × N*C*HN), 180.96 (1 × *C*OO); FT-IR: $\tilde{\nu}$ = 3373.84 (w), 3139.23 (w), 3030.54 (w), 2954.60 (m), 2915.28 (vs), 2849.12 (s), 1678.43 (w), 1557.17 (vs), 1467.27 (m), 1399.95 (s), 1335,79 (w), 1309.09 (w), 1281.34 (w),1252.77 (w), 907.78 (m), 776.23 (m), 734.27 (S), 664.98 (m), 628.51 (m), 519.24 (w), 466.41 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 307.31 [M$^+$]; HRMS (ESI): *m/z* for $C_{20}H_{39}N_2^+$ calc.: 307.3108 [M$^+$], found: 307.3112; MS (ESI): Negative: *m/z* = 199.17 [M$^-$]; HRMS (ESI): *m/z* for $C12H_{23}O_2^-$ calc.: 199.1704 [M$^-$], found: 199.1692; DSC: Cr 55 °C [76.6 kJ mol-1] SmA 126 °C [2.3 kJ mol-1] I.; Water content: 1.60 ± 0.11 wt%.

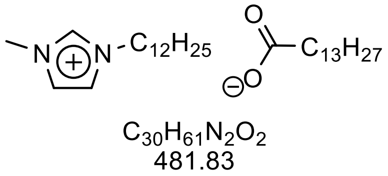
1-Decyl-3-methylimidazolium tetradecanoate ([C$_{10}$mim][C$_{13}$COO])



Synthesis according to GP 2. From 1-decyl-3-methylimidazolium chloride **[C$_{10}$mim]Cl**, tetradecanoic acid **[C$_{13}$COOH]**, MeOH (50 mL); white solid (94 %, 2.78 g, 6.17 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.88 (m, 6H), 1.19–1.39 (m, 34H), 1.62–1.70 (dt, *J*=7.8 Hz, 2H), 1.84–1.90 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.27 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.27–4.33 (t, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 11.76 (s, 1H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 14.17, 14.19 (2 × *C*H$_3$), 22.73, 22.77, 26.35, 27.17, 29.10, 29.33, 29.45, 29.54, 29.75, 29.82, 29.84, 30.15, 30.39, 31.92, 32.01 (19 × *C*H$_2$), 36.41(2 × *C*H$_3$), 39.12

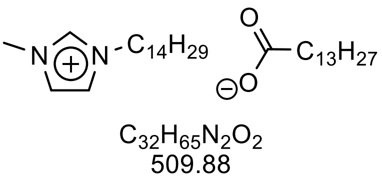
(2 × *C*H$_2$), 50.00 (1 × N*C*H$_2$CH), 122.48, 122.50 (2 x N*C*HC), 141.28 (1 × N*C*HN), 180.78 (1 × *C*OO); FT-IR: $\tilde{\nu}$ = 3383.37 (w), 3147.27 (w), 3073.71 (w), 2955.41 (m), 2921.61 (s), 2852.03 (s), 2190.05 (w), 1558.77 (s), 1465.42 (m), 1309.80 (m), 1306.64 (w), 1171.66 (m), 1090.55 (w), 907.37 (m), 728.03 (vs), 639.91 (m), 626.93 (m), 569.91 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 223.22 [M$^+$]; HRMS (ESI): *m/z* for $C_{14}H_{27}N_2^+$ calc.: 223.2169 [M$^+$], found: 223.2169; MS (ESI): Negative: *m/z* = 227.20 [M$^-$]; HRMS (ESI): *m/z* for C14H$_{27}$O$_2^-$ calc.: 227.2017 [M$^-$], found: 227.2017; DSC: Cr 37 °C [58.1 kJ mol^{-1}] SmA 132 °C [0.3 kJ mol^{-1}] I.; Water content: 0.89 ± 0.11 wt%.

1-Dodecyl-3-methylimidazolium tetradecanoate ([C$_{12}$mim][C$_{13}$COO])



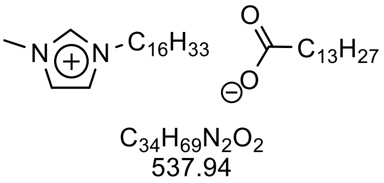
Synthesis according to GP 2. From 1-dodecyl-3-methylimidazolium bromide **[C$_{12}$mim]Br**, tetradecanoic acid **[C$_{13}$COOH]**, MeOH (50 mL); white solid (86 %, 2.26 g, 4.46 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.88 (m, 6H), 1.21–1.38 (m, 38H), 1.62–1.70 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.20–2.27 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 11.79 (s, 1H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 14.17 (2 × *C*H$_3$), 22.74, 22.76, 26.34, 27.35, 29.10, 29.40, 29.44, 29.45, 29.58, 29.66, 29.74, 29.80, 29.82, 29.84, 30.21, 30.37, 31.97, 32.00 (21 × *C*H$_2$), 36.34 (1 × *C*H$_3$), 39.53 (1 × *C*H$_2$), 49.94 (1 × N*C*H$_2$CH), 120.84, 122.42 (2 x N*C*HC), 181.02 (1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 2917.48 (s), 2849.98 (m), 2188.73 (w), 2015.08 (w), 1556.68 (s), 1466.31 (m), 1395.07 (m), 1172.36 (m), 906.54 (s), 726.96 (vs), 638.69 (m) cm^{-1}; MS (ESI): Positive: *m/z* = 251.25 [M$^+$]; HRMS (ESI): *m/z* for $C_{16}H_{31}N_2^+$ calc.: 251.2482 [M$^+$], found: 251.2473; MS (ESI): Negative: *m/z* = 227.20 [M$^-$]; HRMS (ESI): *m/z* for C14H$_{27}$O$_2^-$ calc.: 227.2017 [M$^-$], found: 227.2014; DSC: Cr 59 °C [145.7 kJ mol^{-1}] SmA 127 °C [5.2 kJ mol^{-1}] I.; Water content: 0.99 ± 0.11 wt%.

1-Tetradecyl-3-methylimidazolium tetradecanoate ([C$_{14}$mim][C$_{13}$COO])



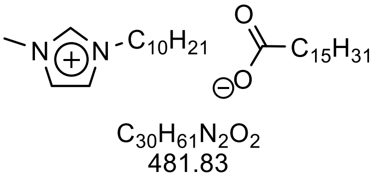
Synthesis according to GP 2. From 1-tetradecyl-3-methylimidazolium bromide **[C$_{14}$mim]Br**, tetradecanoic acid **[C$_{13}$COOH]**, MeOH (50 mL); white solid (84 %, 2.41 g, 4.75 mmol); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.88 (m, 6H), 1.22–1.38 (m, 42H), 1.62 (dt, *J* = 7.8 Hz, 2H), 1.88 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.27 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.29 (t, *J* = 7.4 Hz, 2H), 7.19-7.32 (m, 2H), 11.11 (s, 1H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.23 (2 × *C*H$_3$), 22.80, 26.38, 26.74, 29.13, 29.47, 29.49, 29.63, 29.72, 29.76, 29.79, 29.82, 29.85, 29.99, 30.41, 32.04 (23 × CH_2), 36.60 (1 × CH_3), 38.10 (1 × CH_2), 50.15 (1 × NCH_2CH), 121.14, 122.72 (2 x NCHC), 140.21 (1 × NCHN), 180.18 (1 × COO).; FT-IR: $\tilde{\nu}$ = 2921.73 (m), 2851.07 (m), 2198.76 (w9, 1560.13 (m), 1466.55 (w), 1400.51 (w), 1170.30 (w), 905.99 (s), 725.52 (vs), 641.67 (m), 625.84 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 279.28 [M$^+$]; HRMS (ESI): *m/z* for $C_{18}H_{35}N_2^+$ calc.: 279.2795 [M$^+$], found: 279.2795; MS (ESI): Negative: *m/z* = 227.20 [M$^-$]; HRMS (ESI): *m/z* for $C14H_{27}O_2^-$ calc.: 227.2018 [M$^-$], found: 227.2017; POM: Cr 70 °C, SmA 129 °C; Water content: 0.65 ± 0.11 wt%.

1-Hexadecyl-3-methylimidazolium tetradecanoate ([C_{16}mim][C_{13}COO])



Synthesis according to GP 2. From 1-hexadecyl-3-methylimidazolium bromide **[C_{16}mim]Br**, tetradecanoic acid **[C_{13}COOH]**, MeOH (50 mL); white solid (77 %, 2.13 g, 3.98 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 6H), 1.25 (m, 46H), 1.66 (dt, *J* = 7.8 Hz, 2H), 1.86 (dt, *J* = 7.1 Hz, 7.5 Hz, 2H), 2.21–2.28 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.27–4.34 (t, *J* = 7.5 Hz, 2H), 6.98–7.12 (m, 2H), 11.92 (s, 1H) ppm.; ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.23 (2 × CH_3), 22.81, 26.39, 27.38, 29.15, 29.48, 29.50, 29.64, 29.73, 29.78, 29.80, 29.82, 29.86, 29.87, 29.89, 30.25, 30.42, 32.05 (25 × CH_2), 36.43 (1 × CH_3), 39.55 (1 × CH_2), 50.03 (1 × NCH_2CH), 120.77, 122.27 (2 x NCHC), 181.24 (1 × COO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon NCHN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 3136.38m (w), 3031.85 (w), 2955.00 (m), 2914.78 (vs), 2848.63 (s), 1558.79 (s), 1466.80 (m), 1424.32 (w), 1401.04 (m), 1288.17 (w), 11171.14 (w), 905.87 (w), 778.17 (w), 720.50 (m), 664.00 (w), 627.95 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 307.31 [M$^+$]; HRMS (ESI): *m/z* for $C_{20}H_{39}N_2^+$ calc.: 307.3108 [M$^+$], found: 307.3099; MS (ESI): Negative: *m/z* = 227.20 [M$^-$]; HRMS (ESI): *m/z* for $C_{14}H_{27}O_2^-$ calc.: 227.2017 [M$^-$], found: 227.2033; DSC: Cr 58 °C [89.2 kJ mol^{-1}] SmA 150 °C [2.1 kJ mol^{-1}] I.; Water content: 0.89 ± 0.11 wt%.

1-Decyl-3-methylimidazolium hexadecanoate ([C_{10}mim][C_{15}COO])

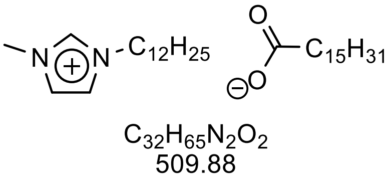


Synthesis according to GP 2. From 1-decyl-3-methylimidazolium chloride **[C_{10}mim]Cl**, hexadecanoic acid **[C_{15}COOH]**, MeOH (50 mL); white solid (89 %, 3.34 g, 6.98 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.18–1.40 (m, 38H), 1.62–1.70 (dt, *J*=7.8 Hz, 2H), 1.84–1.90 (dt, *J* = 7.1 Hz, 7.5 Hz, 2H), 2.20–2.27 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.27–4.33 (t, *J* = 7.5 Hz, 2H), 7.08 (s, 2H), 11.83 (s, 1H) ppm.; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.12 (2 × CH_3), 14.14, 22.67, 22.71, 26.28, 27.34, 29.05, 29.27, 29.39, 29.48, 29.68, 29.74, 29.78, 30.17, 30.33, 31.86, 31.95 (21 × CH_2), 36.25 (1 × CH_3), 39.56

(1 × CH_2), 49.86 (1 × NCH_2CH), 120.85, 122.45 (2 x NCHC), 180.92 (1 × COO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon NCHN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 3142.83 (m), 3029.11 (m), 2955.88 (m), 2917.17 (vs), 2847.36 (vs), 1669.60 (w), 1557.29 (vs), 1464.00 (m), 1424.45 (m), 1399.78 (s), 1286.67 (w), 1274.08 (w), 1170.73 (m), 1098.36 (w), 1021.81 (w), 904.88 (w), 777.53 (m), 738.15 (m), 721.53 (s), 663.83 (m), 627.46 (m), 520.01 (w), 490.04 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 223.22 [M^+]; HRMS (ESI): *m/z* for $C_{14}H_{27}N_2^+$ calc.: 223.2169 [M^+], found: 223.2168; MS (ESI): Negative: *m/z* = 255.23 [M^-]; HRMS (ESI): *m/z* for $C_{16}H_{31}O_2^-$ calc.: 255.2330 [M^-], found: 255.2331; DSC: Cr 54 °C [75.7 kJ mol^{-1}] SmA 128 °C [2.6 kJ mol^{-1}] I.; Water content: 0.17 ± 0.11 wt%.

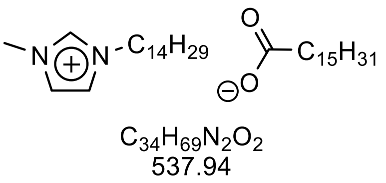
1-Dodecyl-3-methylimidazolium hexadecanoate ([C$_{12}$mim][C$_{15}$COO])

Synthesis according to GP 2. From 1-dodecyl-3-methylimidazolium bromide **[C$_{12}$mim]Br**, hexadecanoic acid **[C$_{15}$COOH]**, MeOH (50 mL); white solid (96 %, 3.38 g, 6.66 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.18–1.41 (m, 42H), 1.65 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, 7.4 Hz, 2H), 2.20–2.27 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 11.74 (s, 1H) ppm.; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.18 (2 × CH_3), 22.75, 26.33, 27.25, 29.10, 29.40, 29.44, 29.57, 29.66, 29.73, 29.79, 29.82, 30.17, 30.38, 31.97, 31.99 (23 × CH_2), 36.32 (1 × CH_3), 39.32 (1 × CH_2), 49.93 (1 × NCH_2CH), 120.84, 122.40 (2 x NCHC), 141.56 (1 × NCHN), 180.91 (1 × COO); FT-IR: $\tilde{\nu}$ = 3135.80 (m), 3029.15 (m), 2956.07 (m), 2915.15 (vs), 2848.20 (s), 2290.28 (w), 1673.16 (w), 1557.47 (s), 1464.35 (m), 1425.18 (m), 1400.41 (s), 1315.09 (w), 1287.94 (w), 1274.69 (w), 1253.53 (w), 1232.22 (w), 1172.29 (m), 1097.94 (w), 907.19 (m), 779.02 (m), 722.77 (s), 664.47 (m), 628.53 (m), 569.74 (w), 491.08 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 251.25 [M^+]; HRMS (ESI): *m/z* for $C_{16}H_{31}N_2^+$ calc.: 251.2482 [M^+], found: 251.2478; MS (ESI): Negative: *m/z* = 255.23 [M^-]; HRMS (ESI): *m/z* for $C_{16}H_{31}O_2^-$ calc.: 255.2330 [M^-], found: 255.2328; DSC: Cr 52 °C [98.9 kJ mol-1] SmA 138 °C [3.3 kJ mol^{-1}] I.; Water content: 0.66 ± 0.11 wt%.



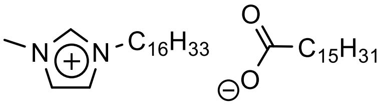
1-Tetradecyl-3-methylimidazolium hexadecanoate ([C$_{14}$mim][C$_{15}$COO])

Synthesis according to GP 2. From 1-tetradecyl-3-methylimidazolium bromide **[C$_{14}$mim]Br**, hexadecanoic acid **[C$_{15}$COOH]**, MeOH (50 mL); white solid (96 %, 2.86 g, 5.35 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 6H), 1.20–1.40 (m, 46H), 1.65 (dt, *J* = 7.8 Hz, 2H), 1.86 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.28 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.06 (m, 2H), 11.81 (s, 1H) ppm.; ^{13}C NMR



(75 MHz, $CDCl_3$) δ 14.20 (2 × *C*H_3), 22.77, 26.35, 27.35, 29.12, 29.44, 29.47, 29.60, 29.69, 29.73, 29.76, 29.81, 29.85, 30.22, 30.39, 32.01 (25 × *C*H_2), 36.35 (1 × *C*H_3), 39.53 (1 × *C*H_2), 49.95 (1 × N*C*H_2CH), 120.83, 122.38 (2 x N*C*HC), 181.09 (1 × *C*OO). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 3136.92 (m), 3029.84 (m), 2956.17 (m), 2914.66 (vs), 2848.50 (s), 1673.64 (w), 1558.74 (s), 1466.40 (m), 1424.78 (w),1401.29 (m), 1274.16 (w), 1170.36 (m), 903.81 (w), 771.93 (m), 720.70 (m), 665.15 (m), 628.04 (m), 520.72 (w), 489.24 (w), 456.17 (w), 421.74 (w) cm^{-1}; MS (ESI): Positive: *m/z* = 279.28 [M$^+$]; HRMS (ESI): *m/z* for $C_{18}H_{35}N_2^+$ calc.: 279.2795 [M$^+$], found: 279.2787; MS (ESI): Negative: *m/z* = 255.23 [M$^-$]; HRMS (ESI): *m/z* for $C16H_{31}O_2^-$ calc.: 255.2330 [M$^-$], found: 255.2336; DSC: Cr 64 °C [103.6 kJ mol^{-1}] SmA 150 °C [4.0 kJ mol-1] I.; Water content: 0.81 ± 0.11 wt%.

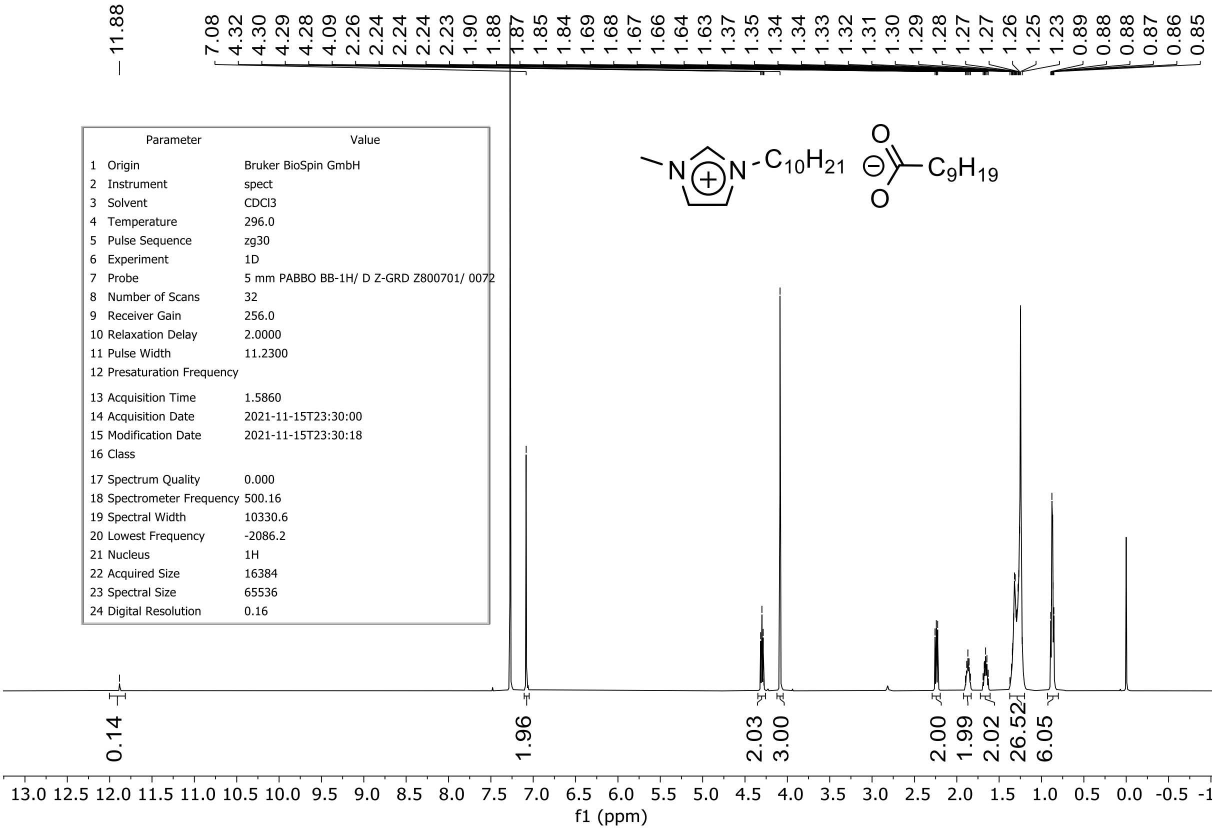
1-Hexadecyl-3-methylimidazolium hexadecanoate ([C_{16}mim][C_{15}COO])



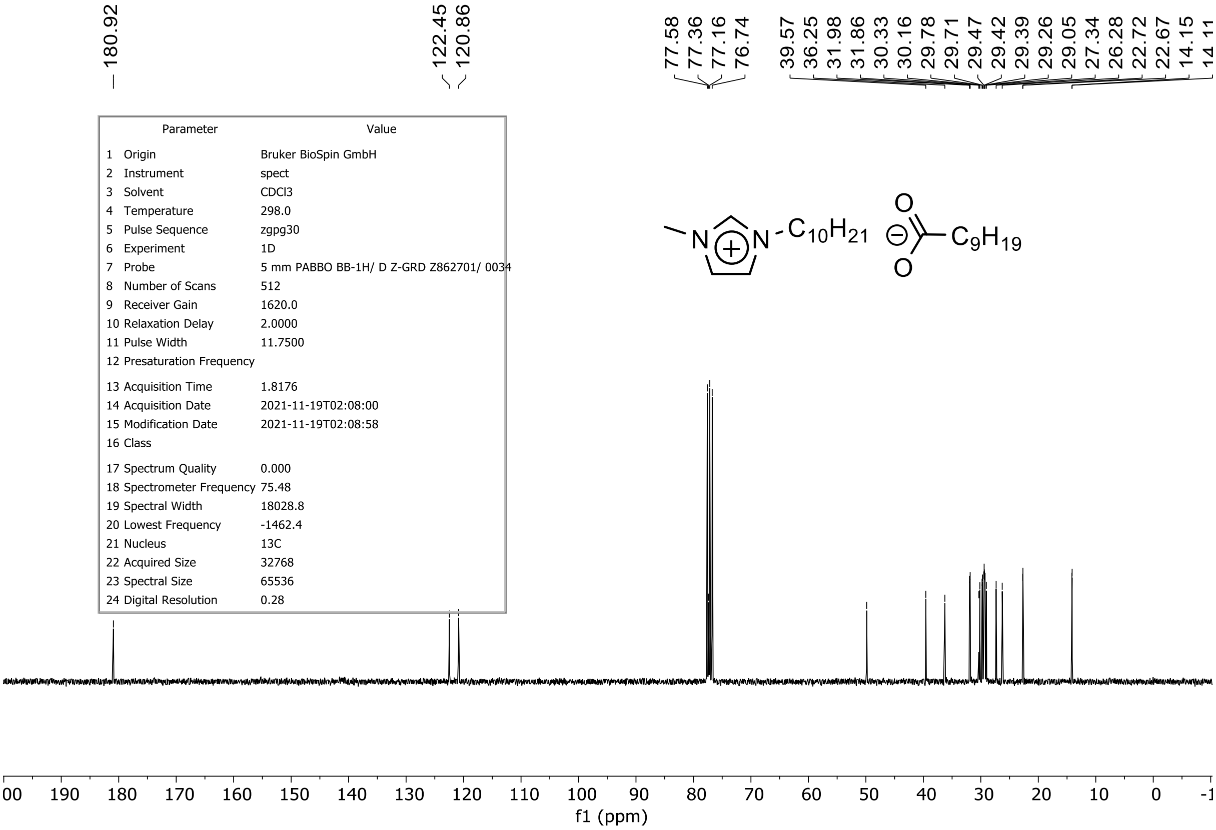
$C_{36}H_{73}N_2O_2$
565.99

Synthesis according to GP 2. From 1-hexadecyl-3-methylimidazolium bromide **[C_{16}mim]Br**, hexadecanoic acid **[C_{15}COOH]**, MeOH (50 mL); white solid (90 %, 1.43 g, 4.65 mmol), ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 6H), 1.21–1.33 (m, 50H), 1.66 (dt, *J* = 7.8 Hz, 2H), 1.87 (dt, *J* = 7.1 Hz, *J* = 7.4 Hz, 2H), 2.21–2.27 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 7.07 (m, 2H), 11.88 (s, 1H) ppm.; ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.24 (2 × *C*H_3), 22.82, 26.39, 27.39, 29.16, 29.50, 29.64, 29.74, 29.80, 29.83, 29.86, 29.89, 29.90, 30.26, 30.43, 32.06 (27 × *C*H_2), 36.41 (1 × *C*H_3), 39.57 (1 × *C*H_2), 50.02 (1 × N*C*H_2CH), 120.71, 122.18 (2 x N*C*HC), 181.27 (1 × *C*OO$^-$). The ^{13}C-peak at δ = 140 ppm for the imidazolium carbon N*C*HN could not be observed due to the poor signal to noise ratio.; FT-IR: $\tilde{\nu}$ = 3261.69 (w), 3140.68 (w), 2954.21 (m), 2914.12 (vs), 2872.25 (w), 2848.64 (s), 1688.00 (w), 1565.67 (s), 1470.85 (m), 1399.12 (m), 1176.83 (w), 1097.67 (w), 908.20 (w), 730.33 (m), 719.74 (m), 641.22 (w), 567.05 (w) cm^{-1}; -MS (ESI): Positive: *m/z* = 307.31 [M$^+$]; HRMS (ESI): *m/z* for $C_{20}H_{39}N_2^+$ calc.: 307.3108 [M$^+$], found: 307.3108; HRMS (ESI): Negative: *m/z* = 255.23 [M$^-$]; HRMS (ESI): *m/z* for $C16H_{31}O_2^-$ calc.: 255.2330 [M$^-$], found: 255.2333; DSC: Cr 79 °C [73.8 kJ mol^{-1}] SmA 133 °C [1.4 kJ mol^{-1}] I.; Water content: 0.09 ± 0.11 wt%.

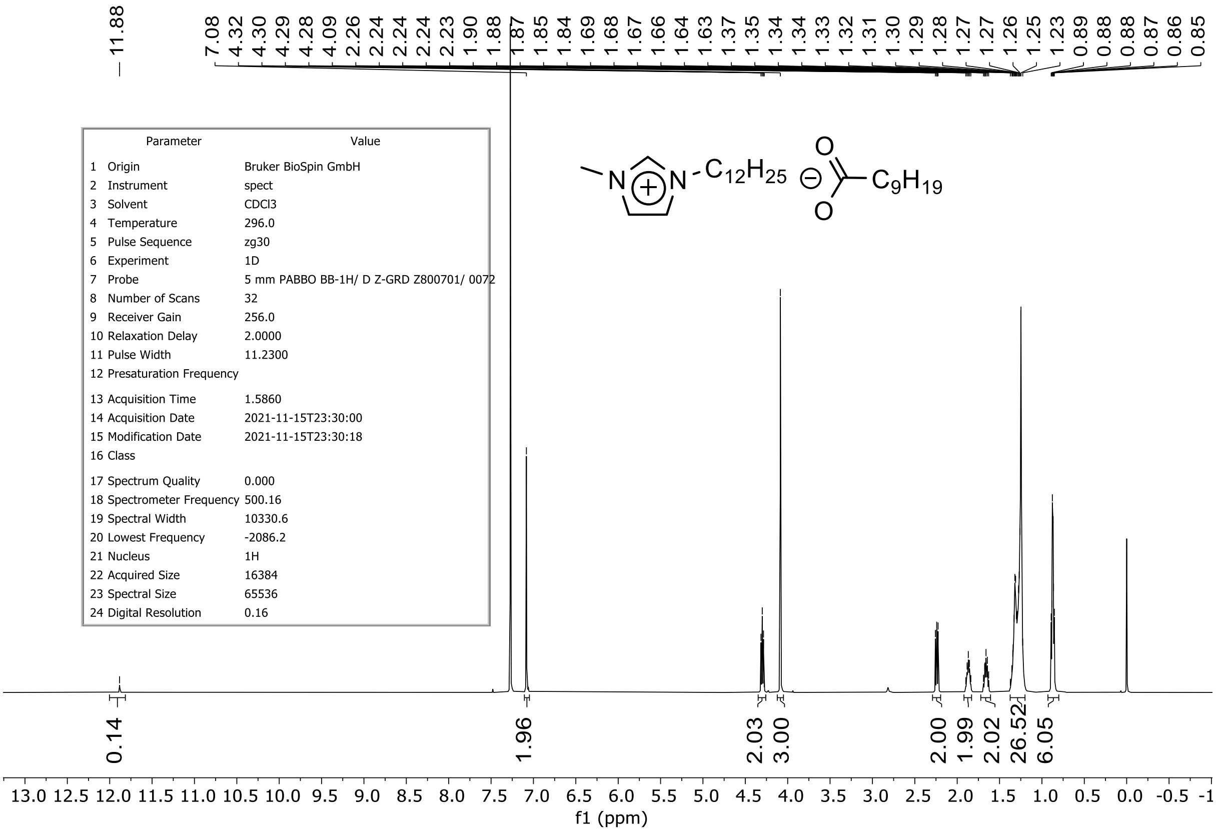
3. NMR spectra



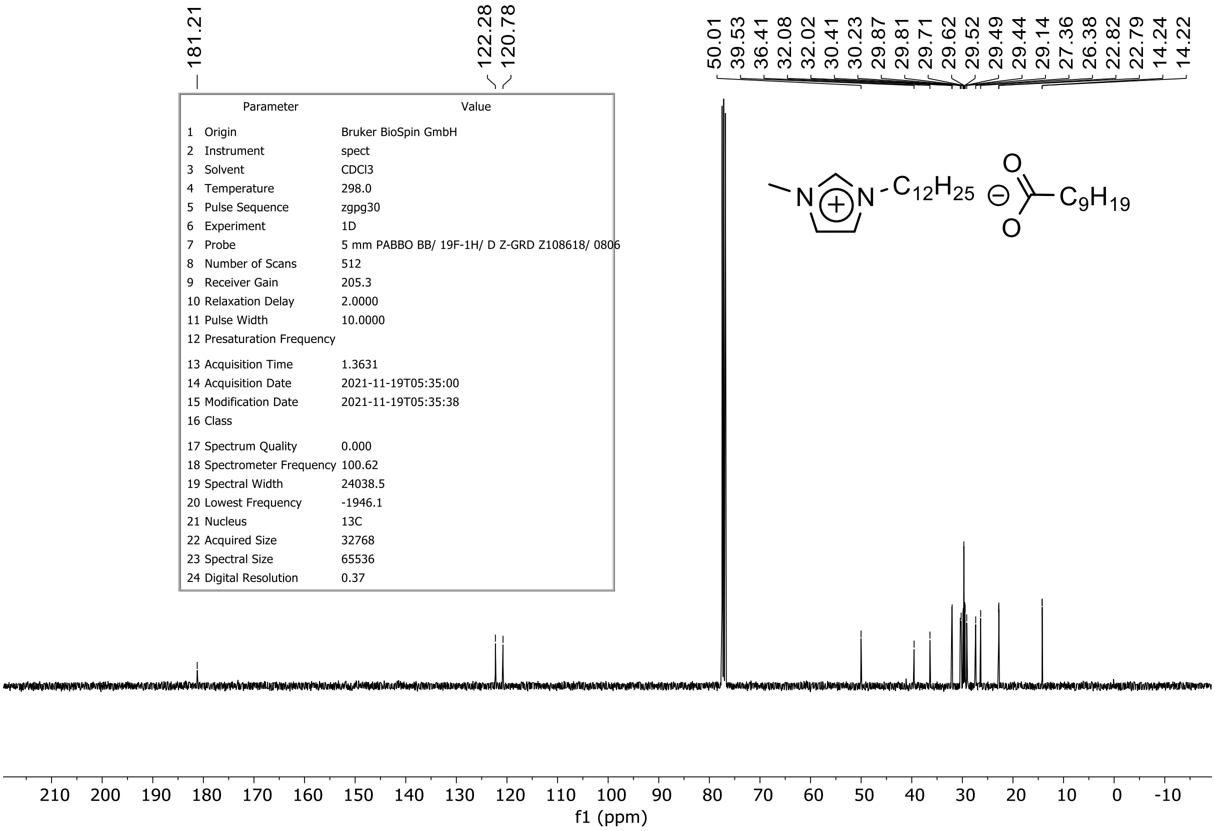
Parameter		Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	256.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-15T23:30:00
15	Modification Date	2021-11-15T23:30:18
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2086.2
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



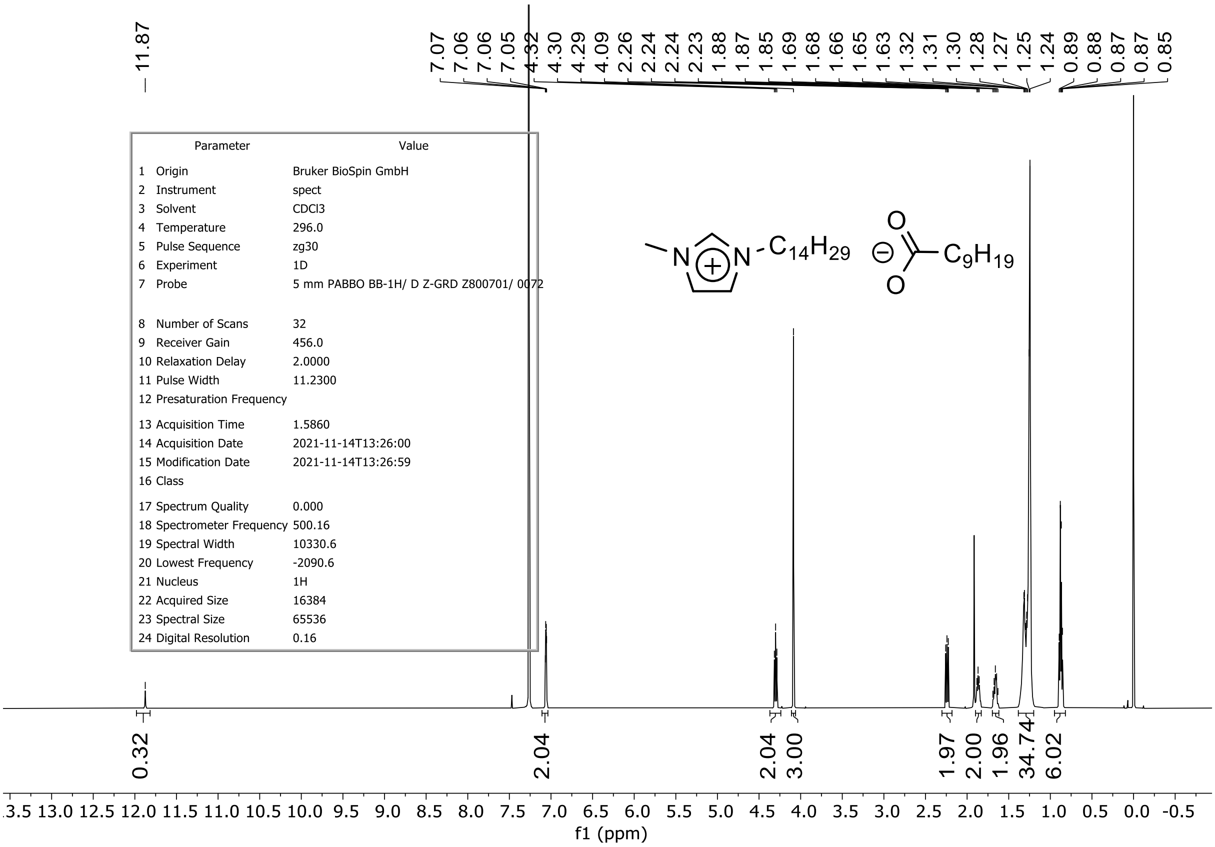
Parameter		Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1620.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-19T02:08:00
15	Modification Date	2021-11-19T02:08:58
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1462.4
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



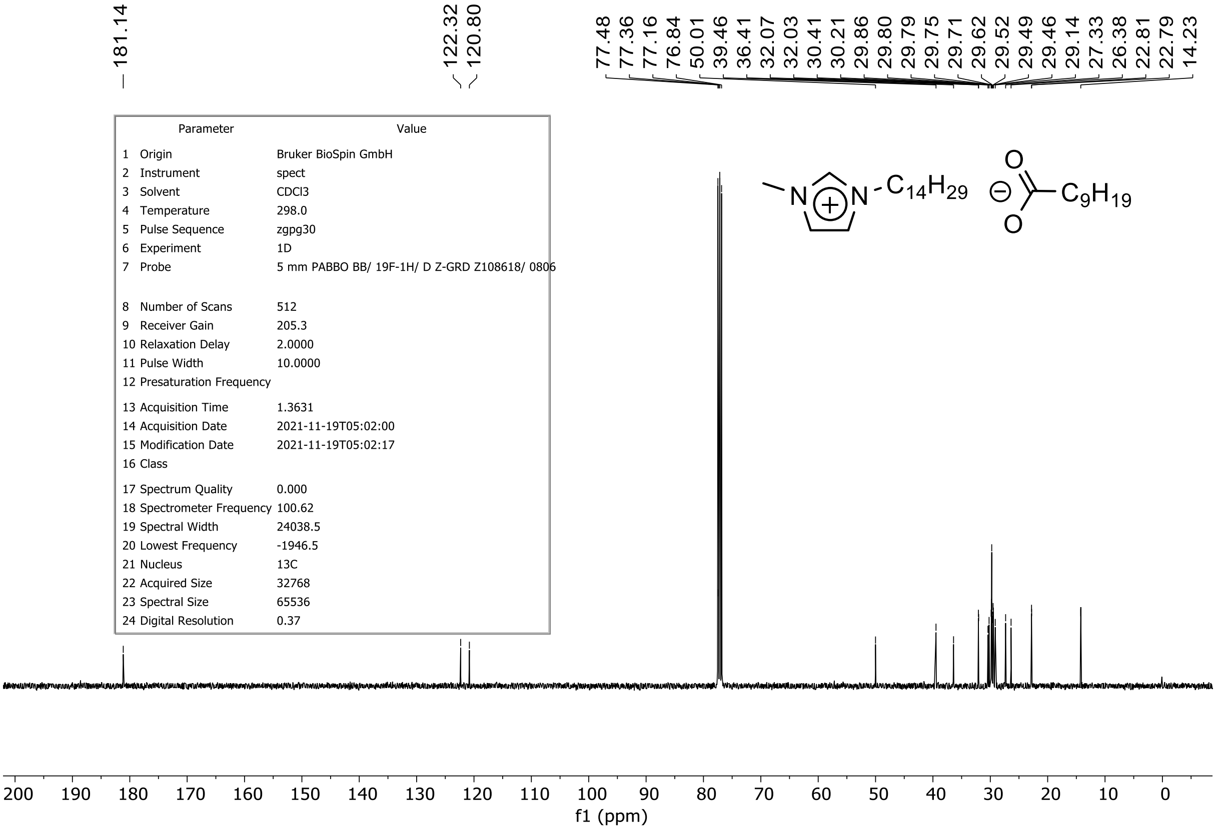
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	256.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-15T23:30:00
15	Modification Date	2021-11-15T23:30:18
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2086.2
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



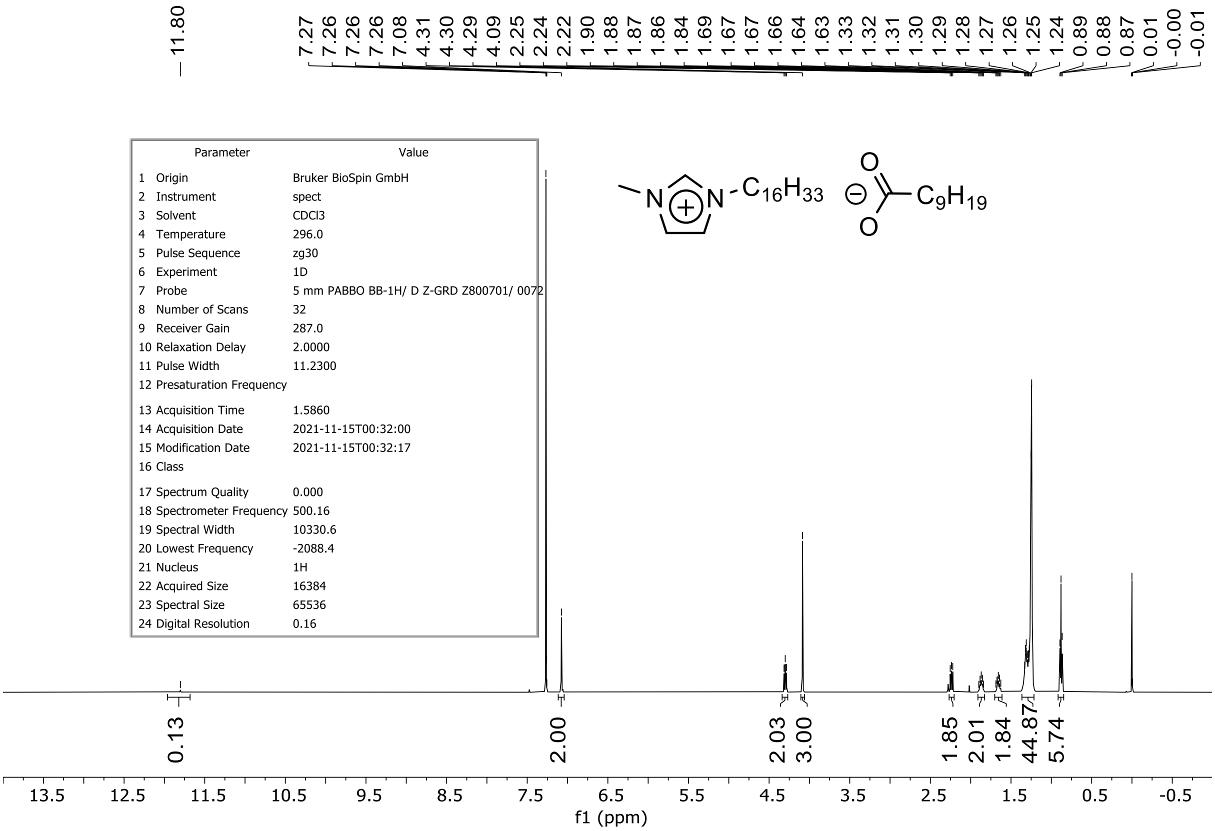
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8	Number of Scans	512
9	Receiver Gain	205.3
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Presaturation Frequency	
13	Acquisition Time	1.3631
14	Acquisition Date	2021-11-19T05:35:00
15	Modification Date	2021-11-19T05:35:38
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	100.62
19	Spectral Width	24038.5
20	Lowest Frequency	-1946.1
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.37



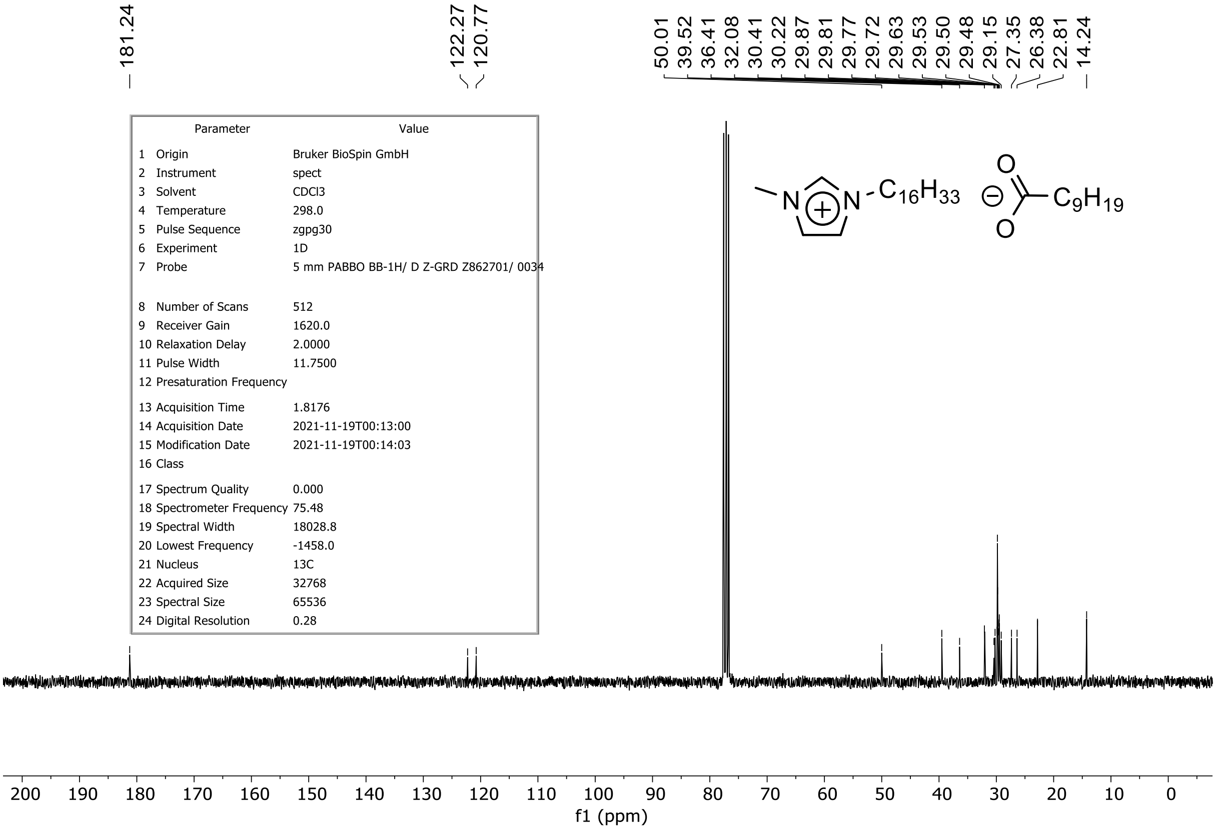
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	456.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-14T13:26:00
15	Modification Date	2021-11-14T13:26:59
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2090.6
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



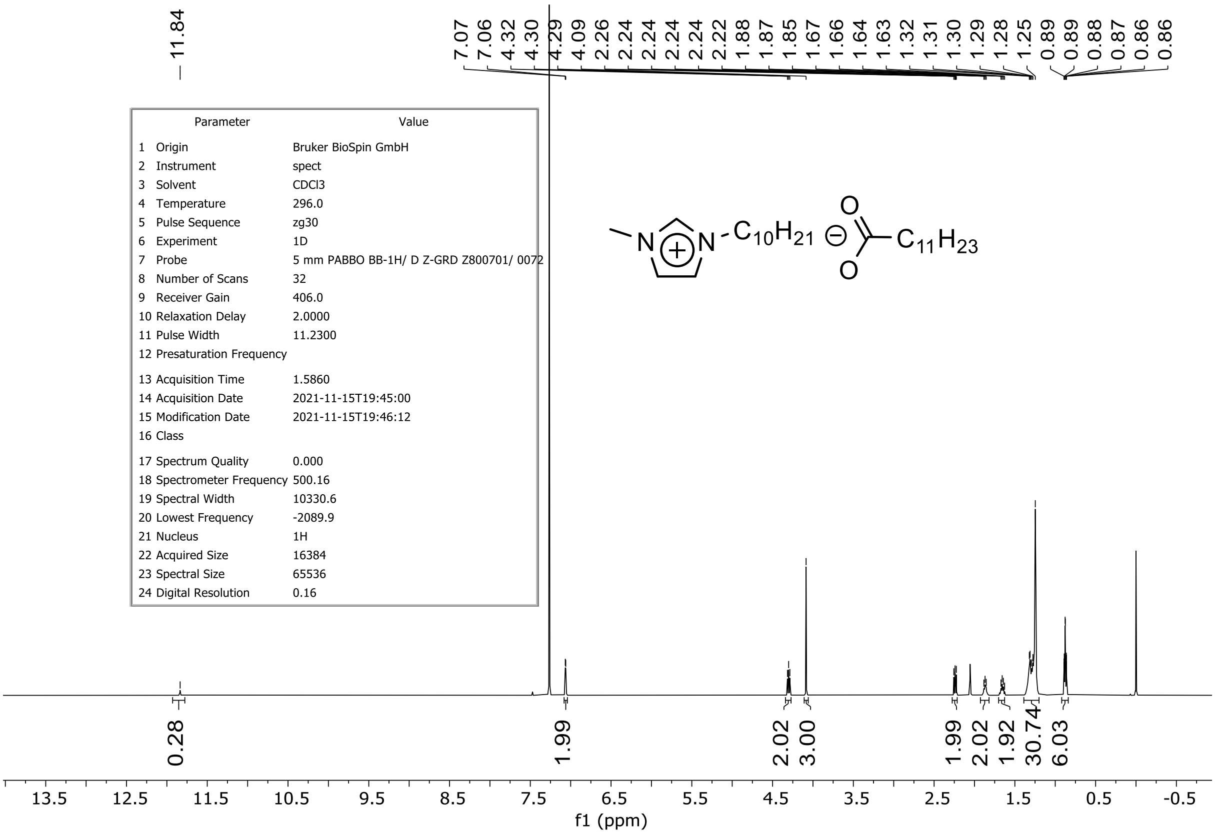
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8	Number of Scans	512
9	Receiver Gain	205.3
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Presaturation Frequency	
13	Acquisition Time	1.3631
14	Acquisition Date	2021-11-19T05:02:00
15	Modification Date	2021-11-19T05:02:17
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	100.62
19	Spectral Width	24038.5
20	Lowest Frequency	-1946.5
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.37



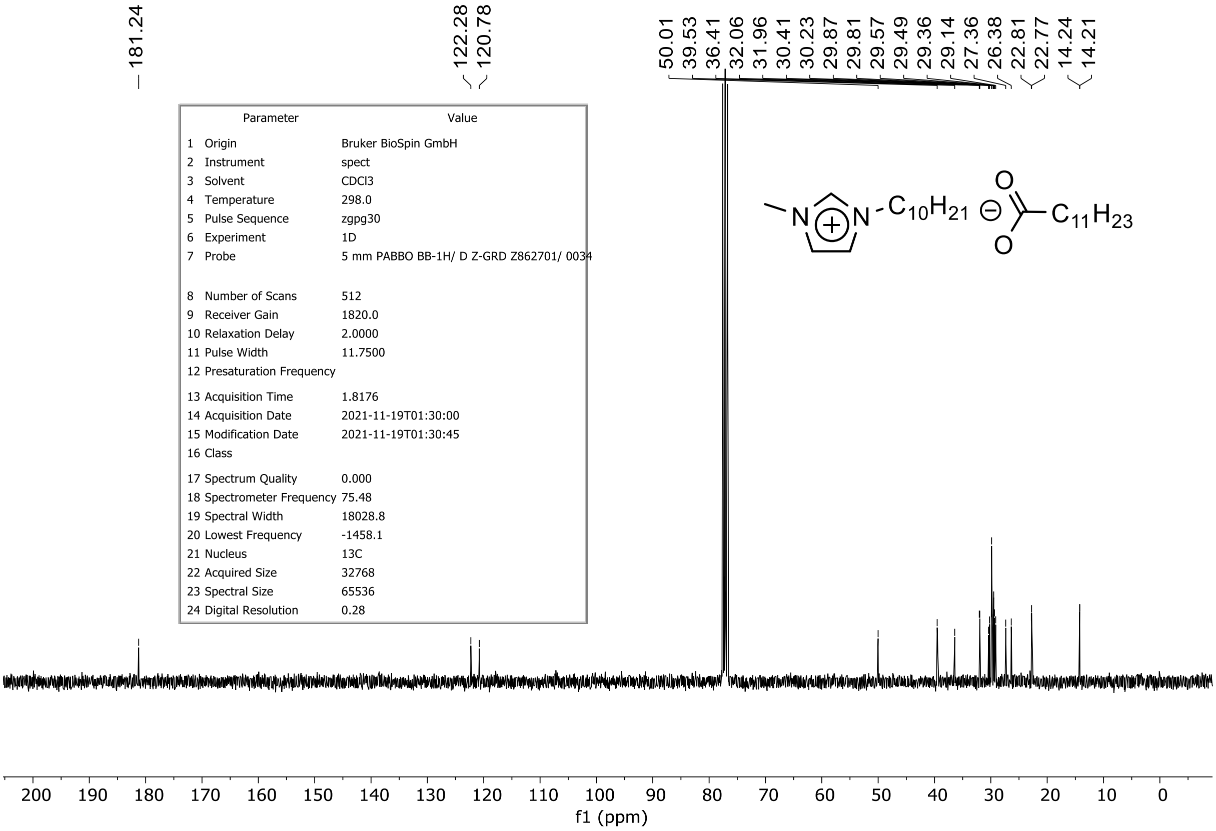
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8 Number of Scans	32
9 Receiver Gain	287.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.2300
12 Presaturation Frequency	
13 Acquisition Time	1.5860
14 Acquisition Date	2021-11-15T00:32:00
15 Modification Date	2021-11-15T00:32:17
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	500.16
19 Spectral Width	10330.6
20 Lowest Frequency	-2088.4
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	65536
24 Digital Resolution	0.16



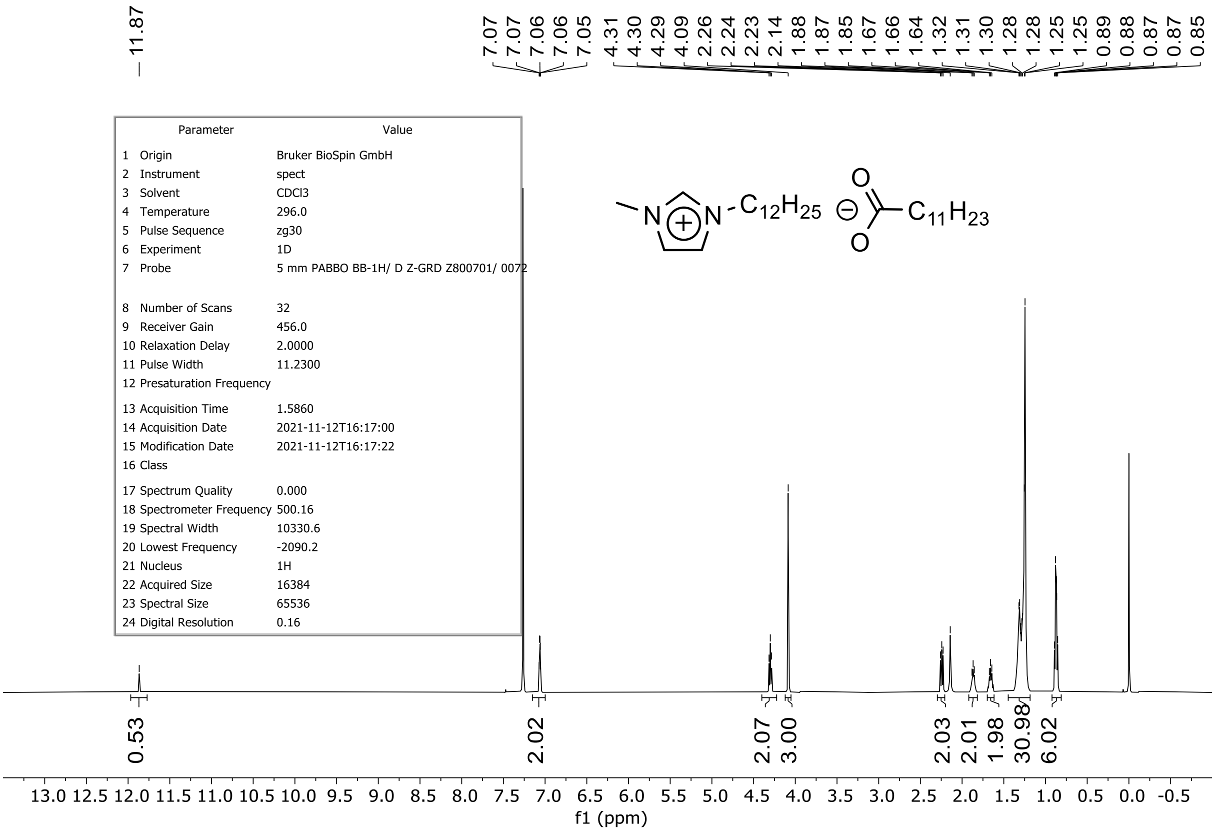
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.0
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8 Number of Scans	512
9 Receiver Gain	1620.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.7500
12 Presaturation Frequency	
13 Acquisition Time	1.8176
14 Acquisition Date	2021-11-19T00:13:00
15 Modification Date	2021-11-19T00:14:03
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	75.48
19 Spectral Width	18028.8
20 Lowest Frequency	-1458.0
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536
24 Digital Resolution	0.28



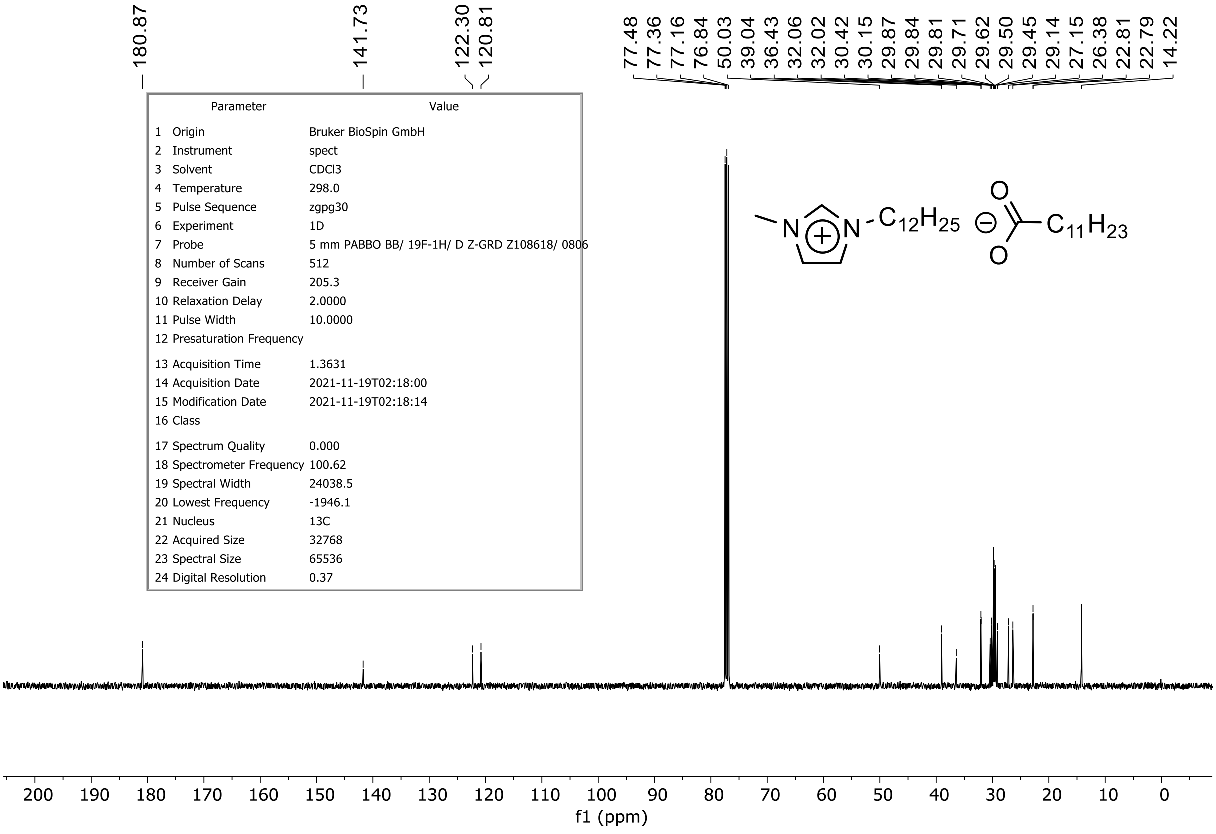
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	406.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-15T19:45:00
15	Modification Date	2021-11-15T19:46:12
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2089.9
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



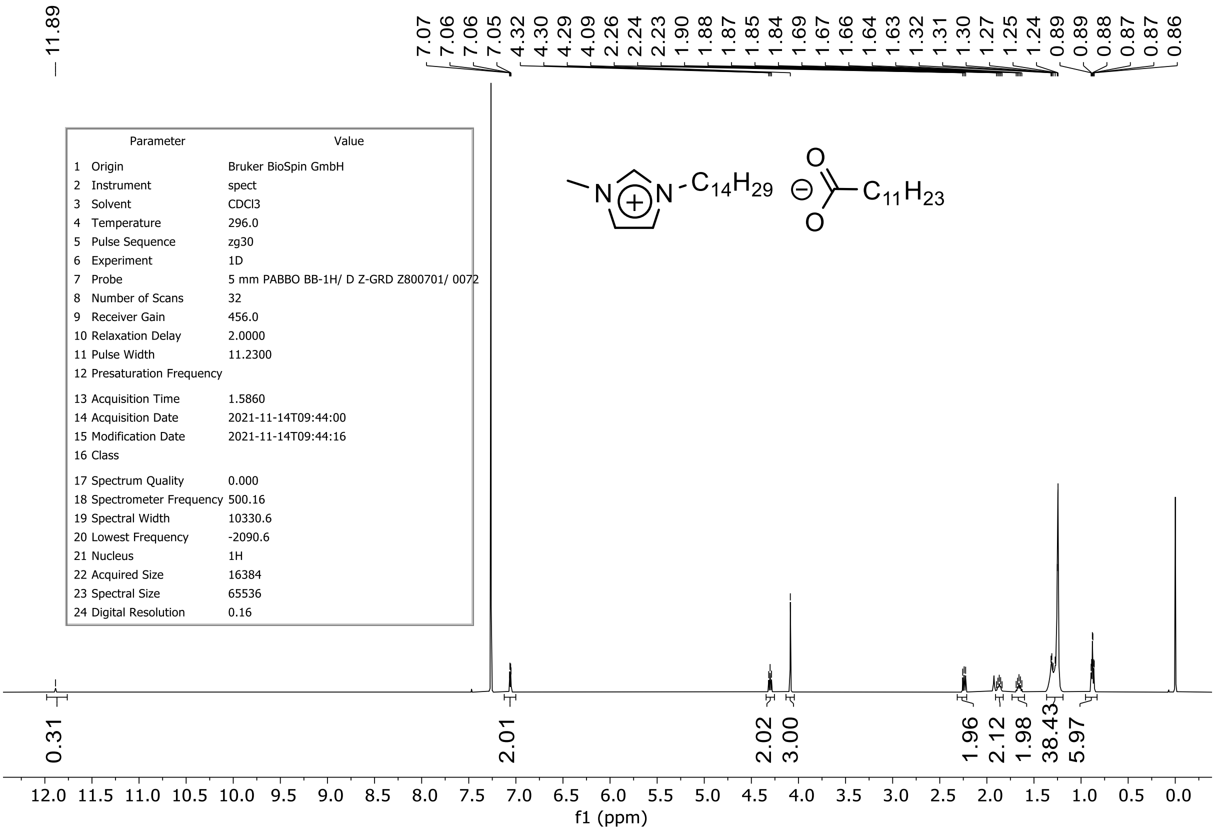
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1820.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-19T01:30:00
15	Modification Date	2021-11-19T01:30:45
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1458.1
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



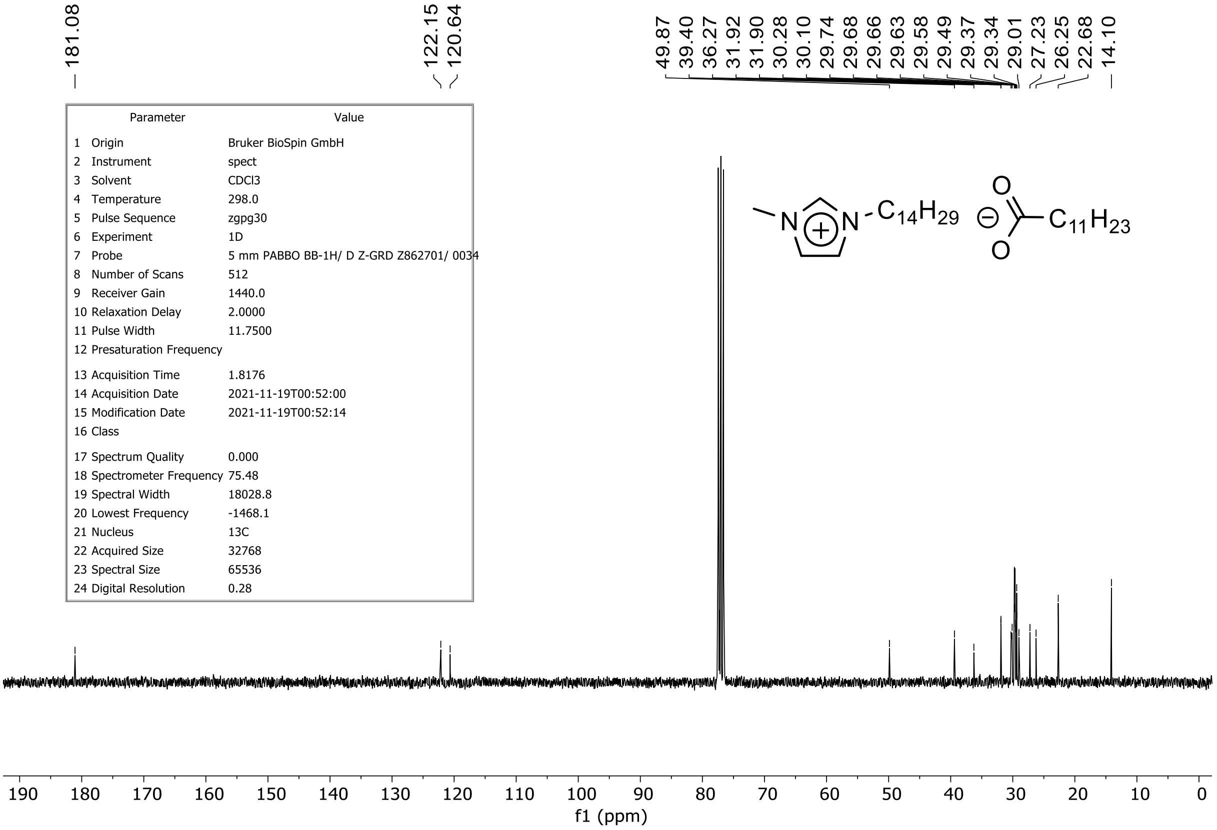
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8 Number of Scans	32
9 Receiver Gain	456.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.2300
12 Presaturation Frequency	
13 Acquisition Time	1.5860
14 Acquisition Date	2021-11-12T16:17:00
15 Modification Date	2021-11-12T16:17:22
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	500.16
19 Spectral Width	10330.6
20 Lowest Frequency	-2090.2
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	65536
24 Digital Resolution	0.16



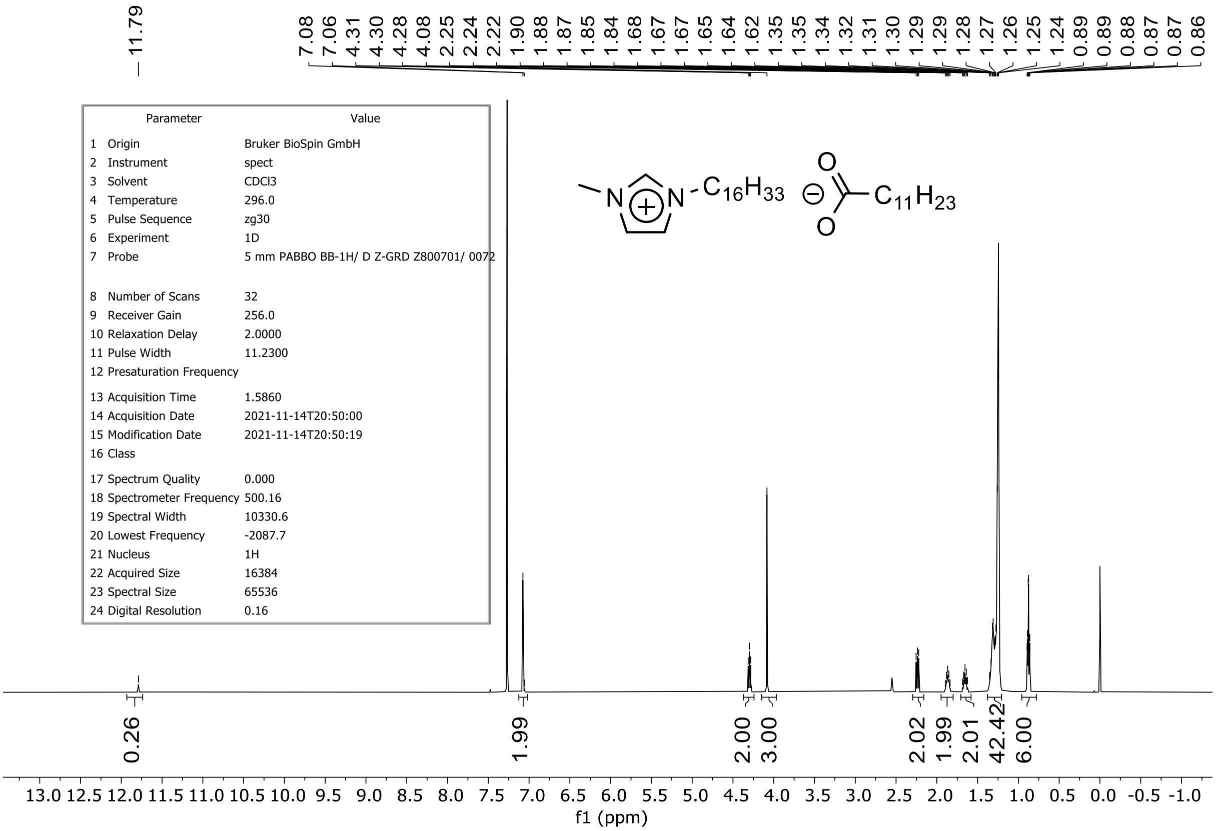
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.0
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8 Number of Scans	512
9 Receiver Gain	205.3
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Presaturation Frequency	
13 Acquisition Time	1.3631
14 Acquisition Date	2021-11-19T02:18:00
15 Modification Date	2021-11-19T02:18:14
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	100.62
19 Spectral Width	24038.5
20 Lowest Frequency	-1946.1
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536
24 Digital Resolution	0.37



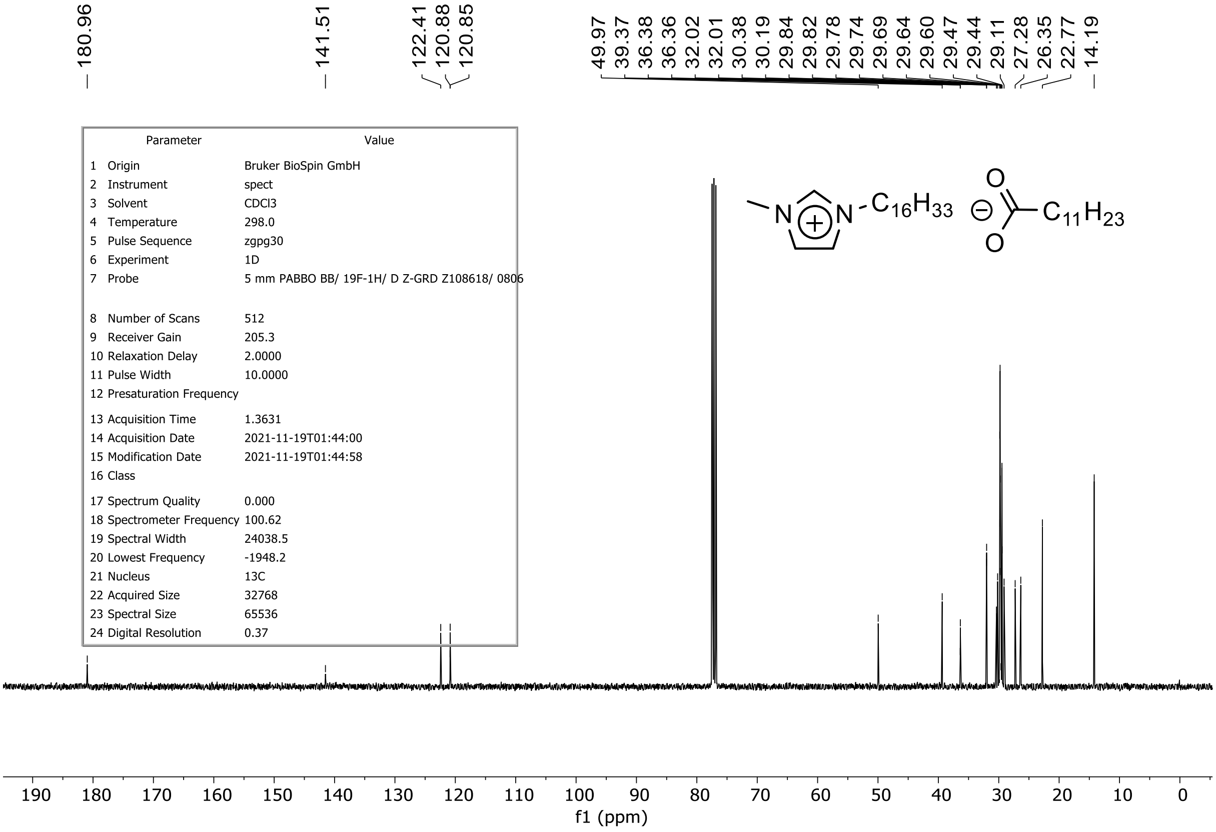
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	456.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-14T09:44:00
15	Modification Date	2021-11-14T09:44:16
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2090.6
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



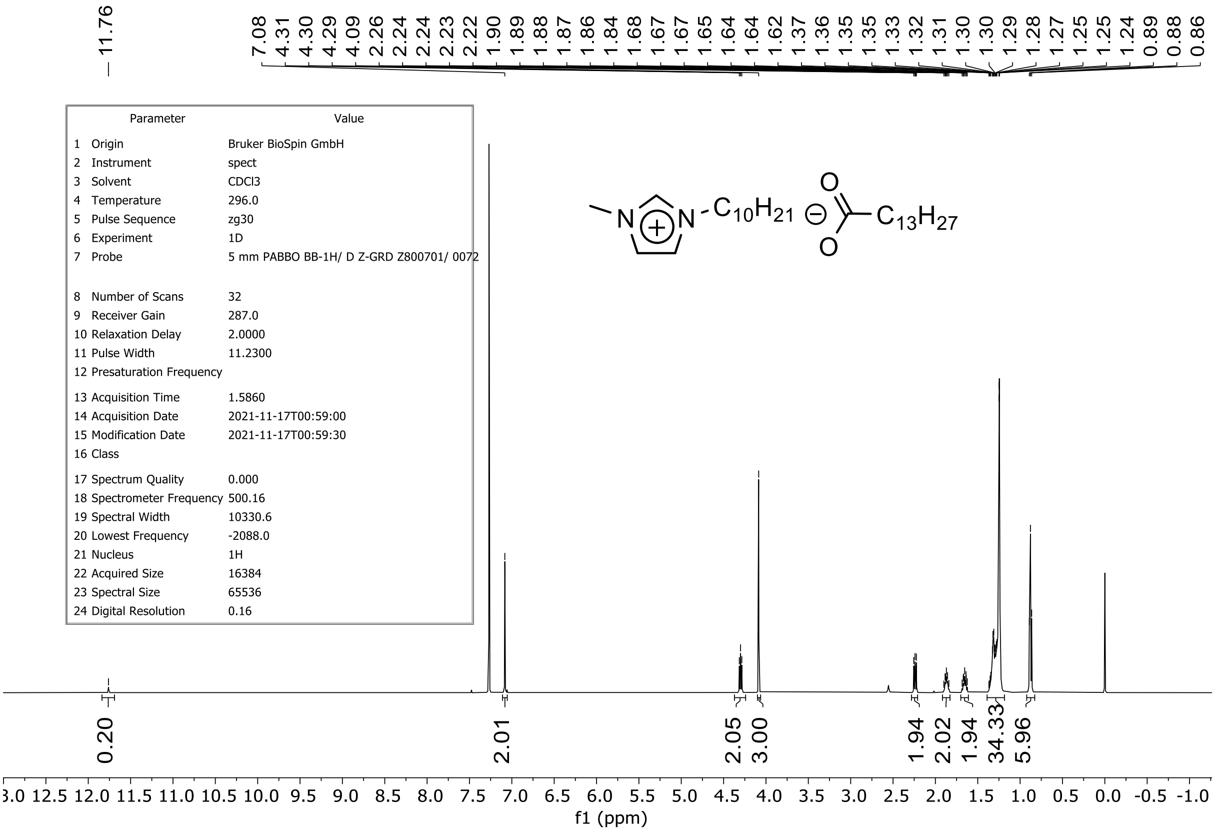
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1440.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-19T00:52:00
15	Modification Date	2021-11-19T00:52:14
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1468.1
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



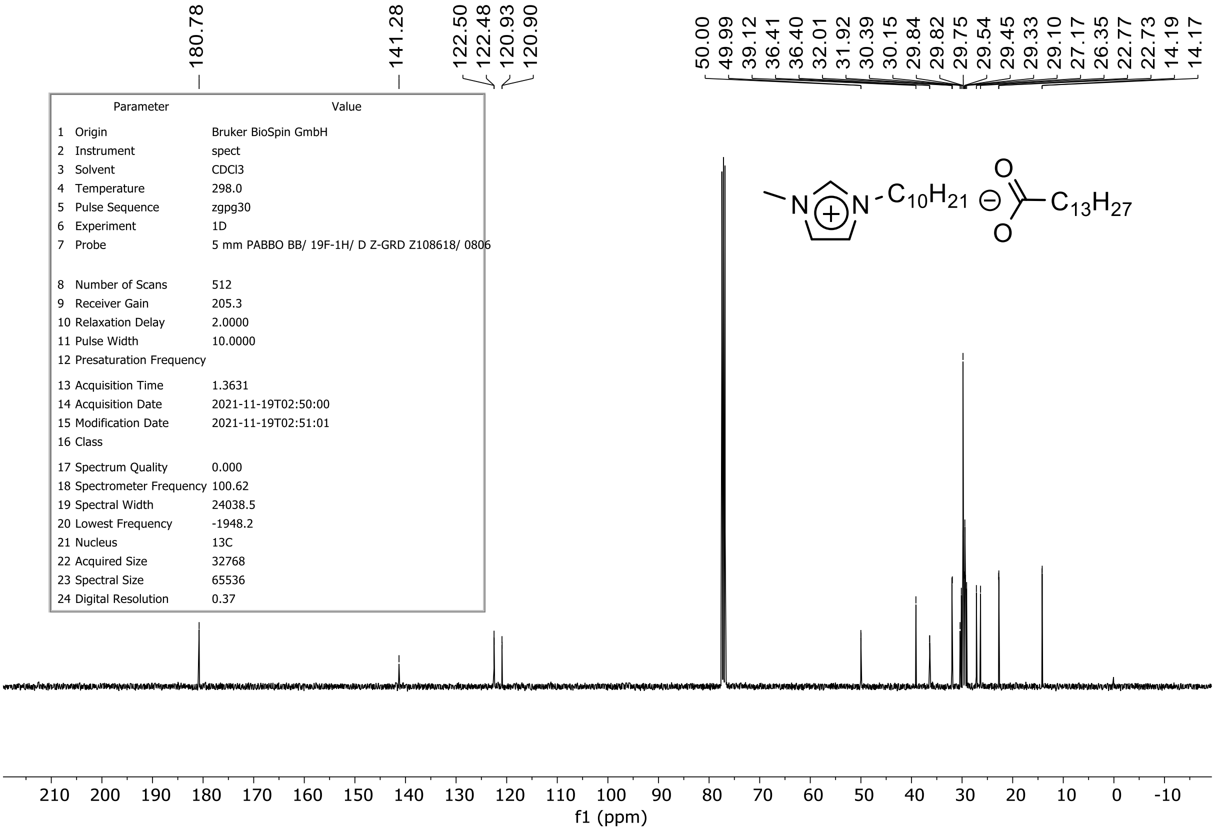
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	256.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-14T20:50:00
15	Modification Date	2021-11-14T20:50:19
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2087.7
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



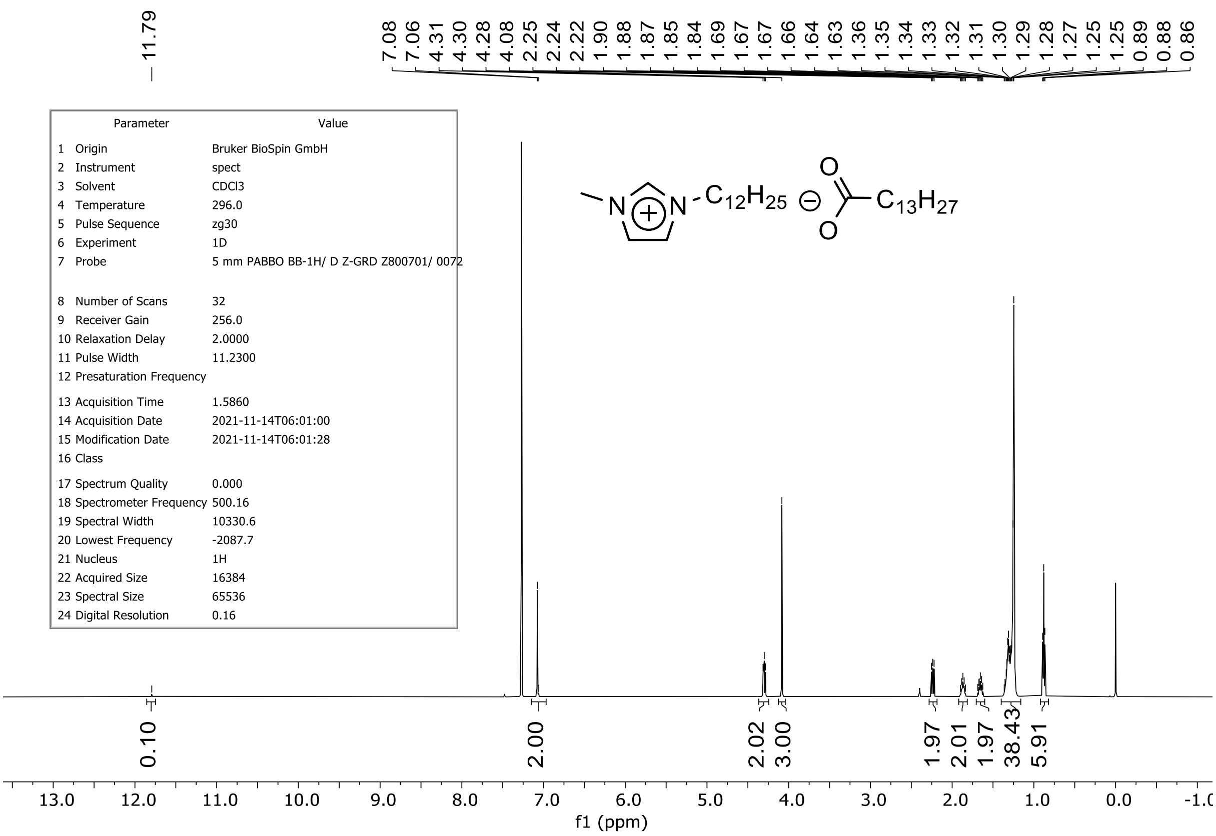
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8	Number of Scans	512
9	Receiver Gain	205.3
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Presaturation Frequency	
13	Acquisition Time	1.3631
14	Acquisition Date	2021-11-19T01:44:00
15	Modification Date	2021-11-19T01:44:58
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	100.62
19	Spectral Width	24038.5
20	Lowest Frequency	-1948.2
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.37



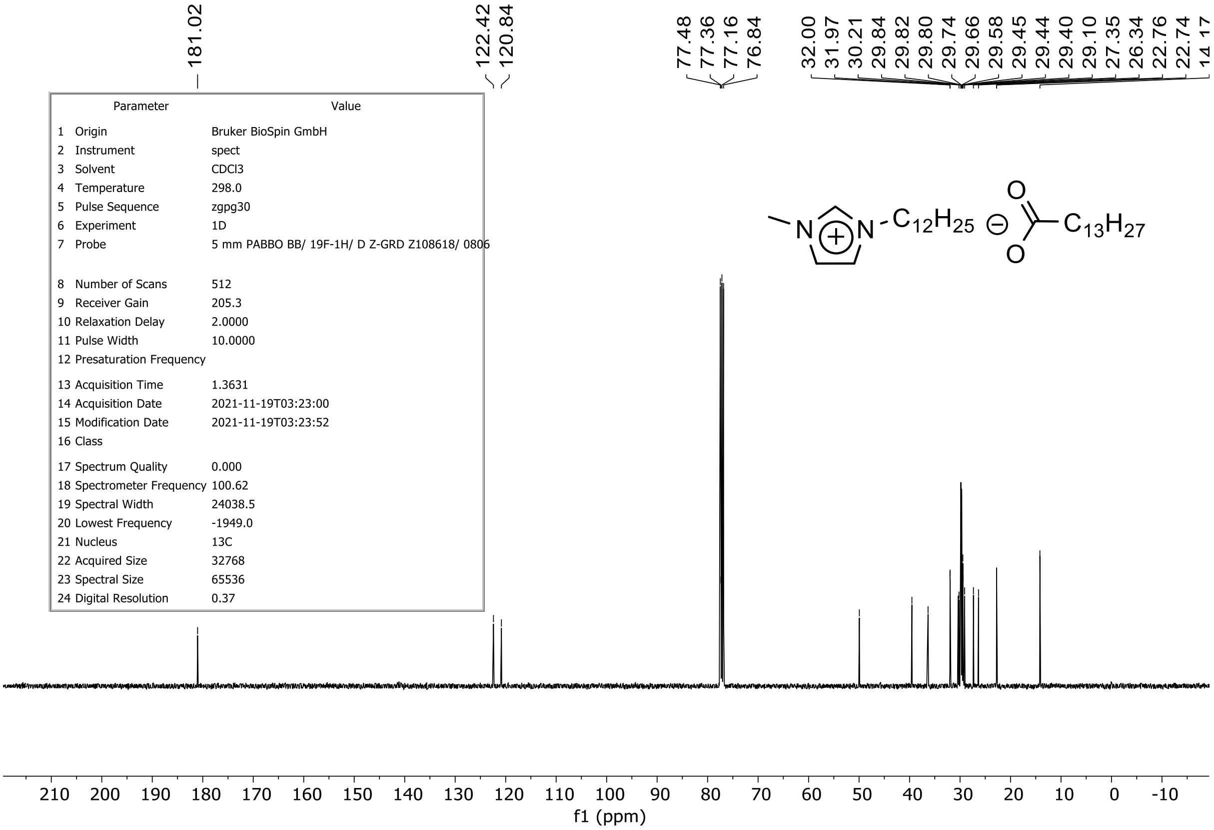
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8 Number of Scans	32
9 Receiver Gain	287.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.2300
12 Presaturation Frequency	
13 Acquisition Time	1.5860
14 Acquisition Date	2021-11-17T00:59:00
15 Modification Date	2021-11-17T00:59:30
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	500.16
19 Spectral Width	10330.6
20 Lowest Frequency	-2088.0
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	65536
24 Digital Resolution	0.16



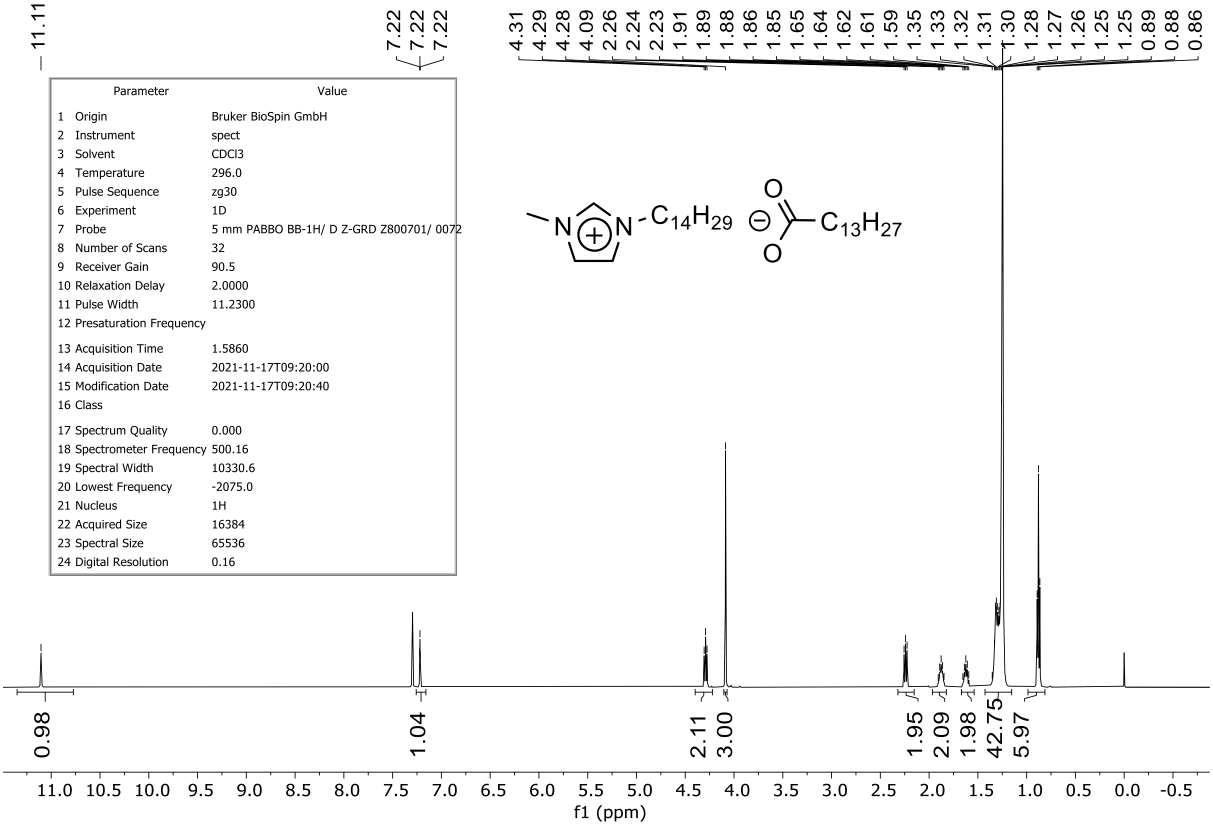
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.0
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8 Number of Scans	512
9 Receiver Gain	205.3
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Presaturation Frequency	
13 Acquisition Time	1.3631
14 Acquisition Date	2021-11-19T02:50:00
15 Modification Date	2021-11-19T02:51:01
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	100.62
19 Spectral Width	24038.5
20 Lowest Frequency	-1948.2
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536
24 Digital Resolution	0.37



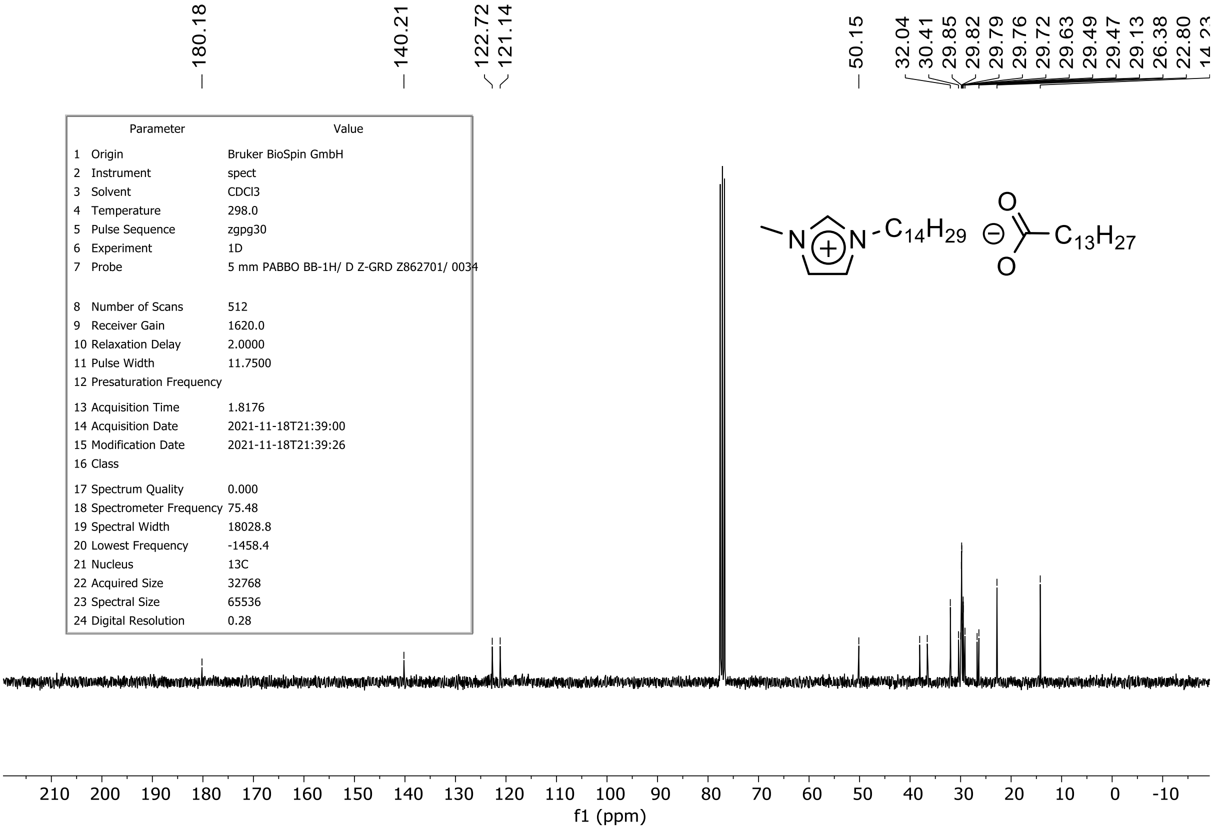
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	256.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-14T06:01:00
15	Modification Date	2021-11-14T06:01:28
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2087.7
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



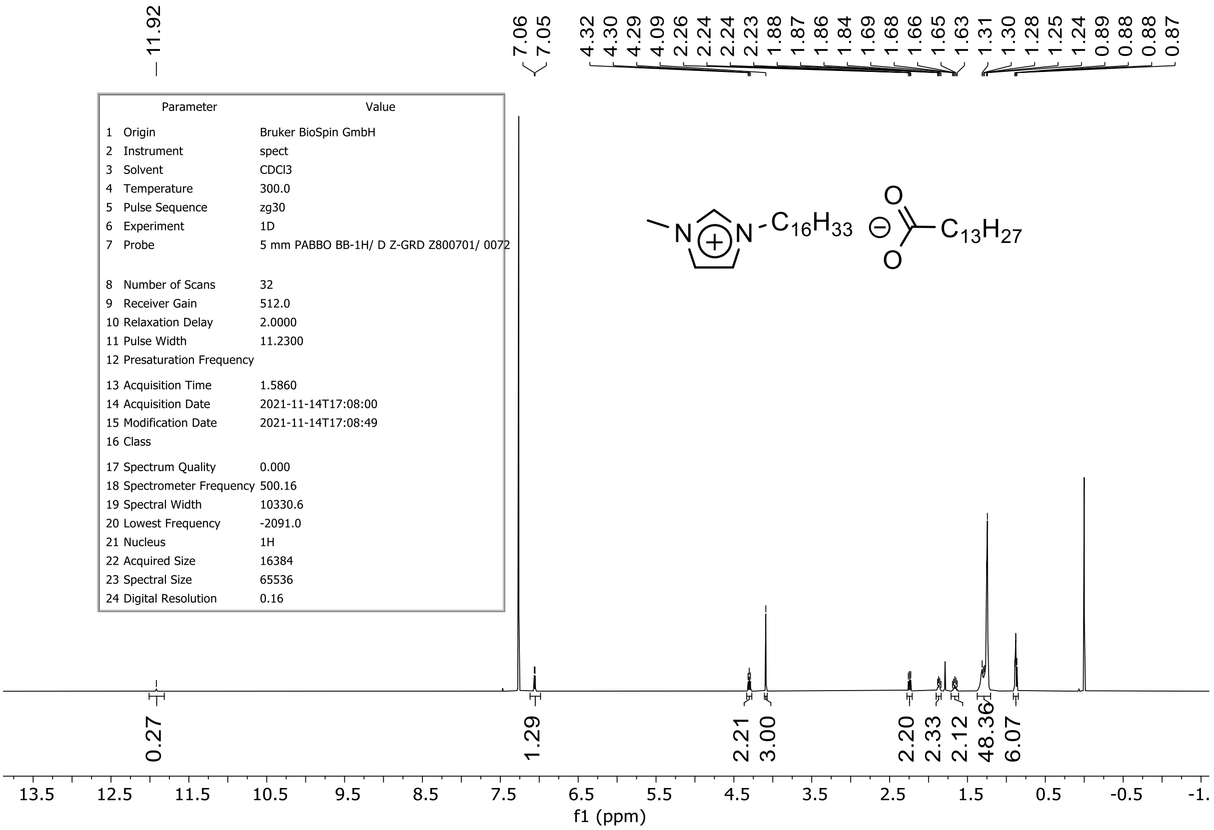
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8	Number of Scans	512
9	Receiver Gain	205.3
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Presaturation Frequency	
13	Acquisition Time	1.3631
14	Acquisition Date	2021-11-19T03:23:00
15	Modification Date	2021-11-19T03:23:52
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	100.62
19	Spectral Width	24038.5
20	Lowest Frequency	-1949.0
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.37



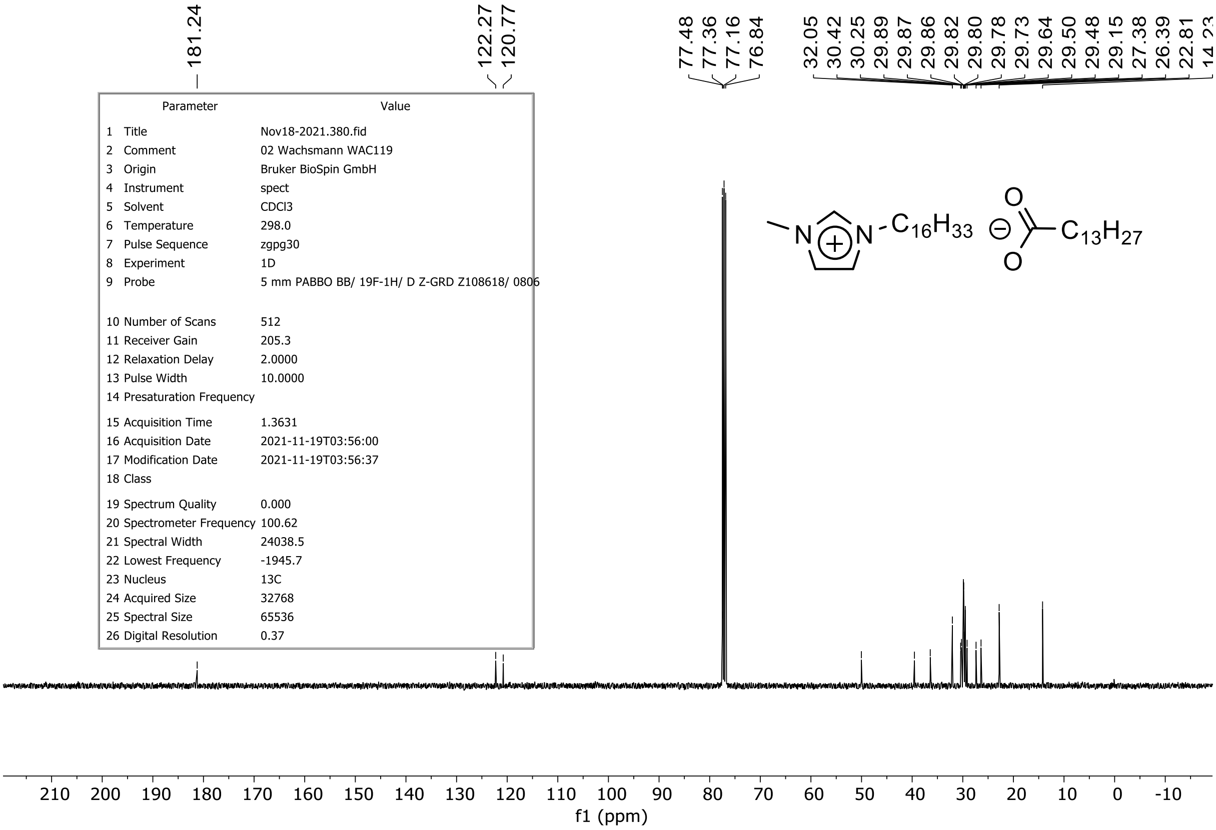
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	90.5
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-17T09:20:00
15	Modification Date	2021-11-17T09:20:40
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2075.0
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



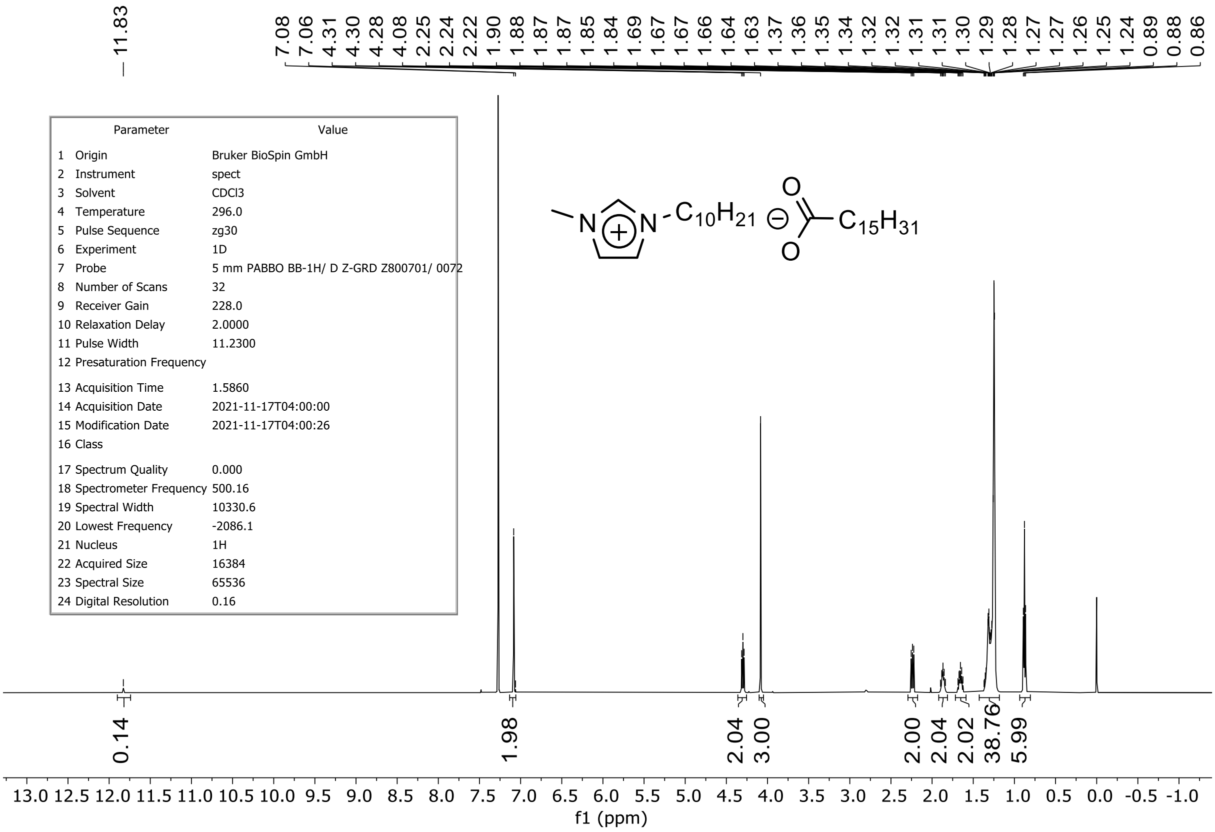
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1620.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-18T21:39:00
15	Modification Date	2021-11-18T21:39:26
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1458.4
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



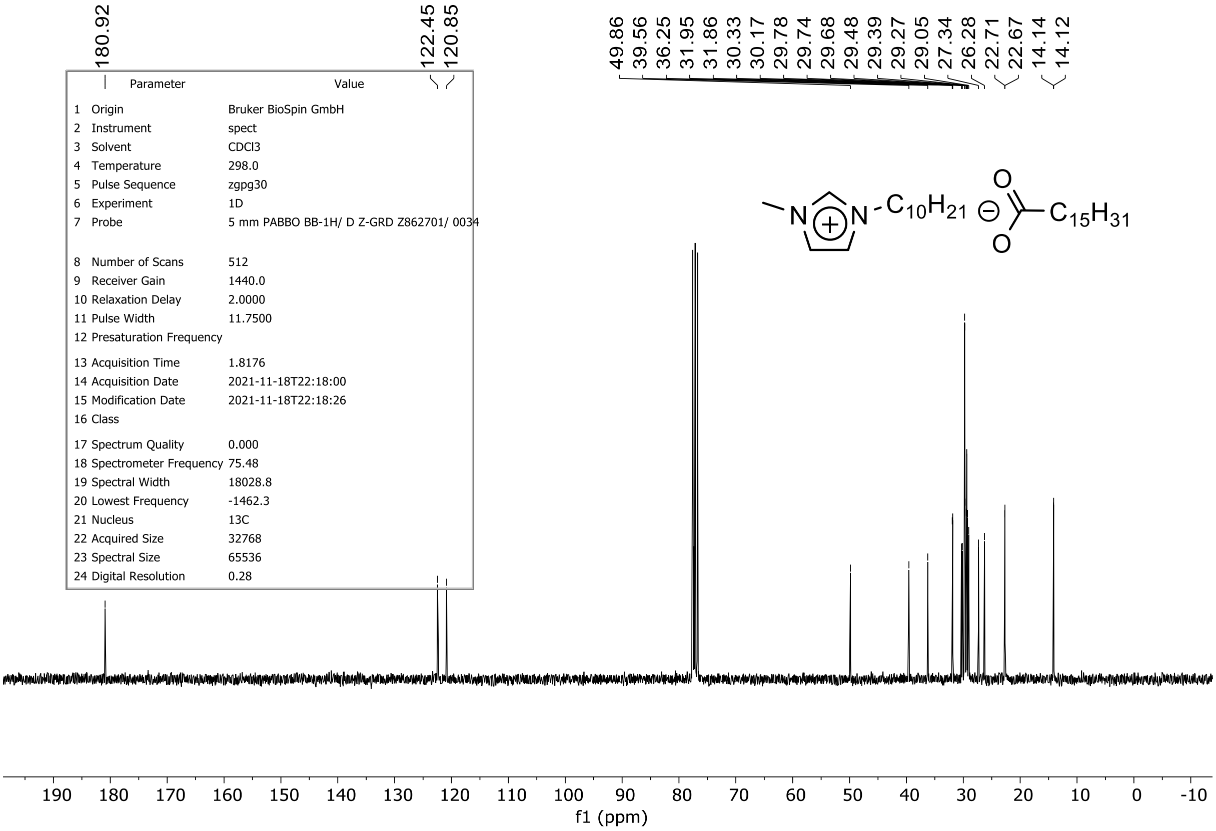
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	512.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-14T17:08:00
15	Modification Date	2021-11-14T17:08:49
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2091.0
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



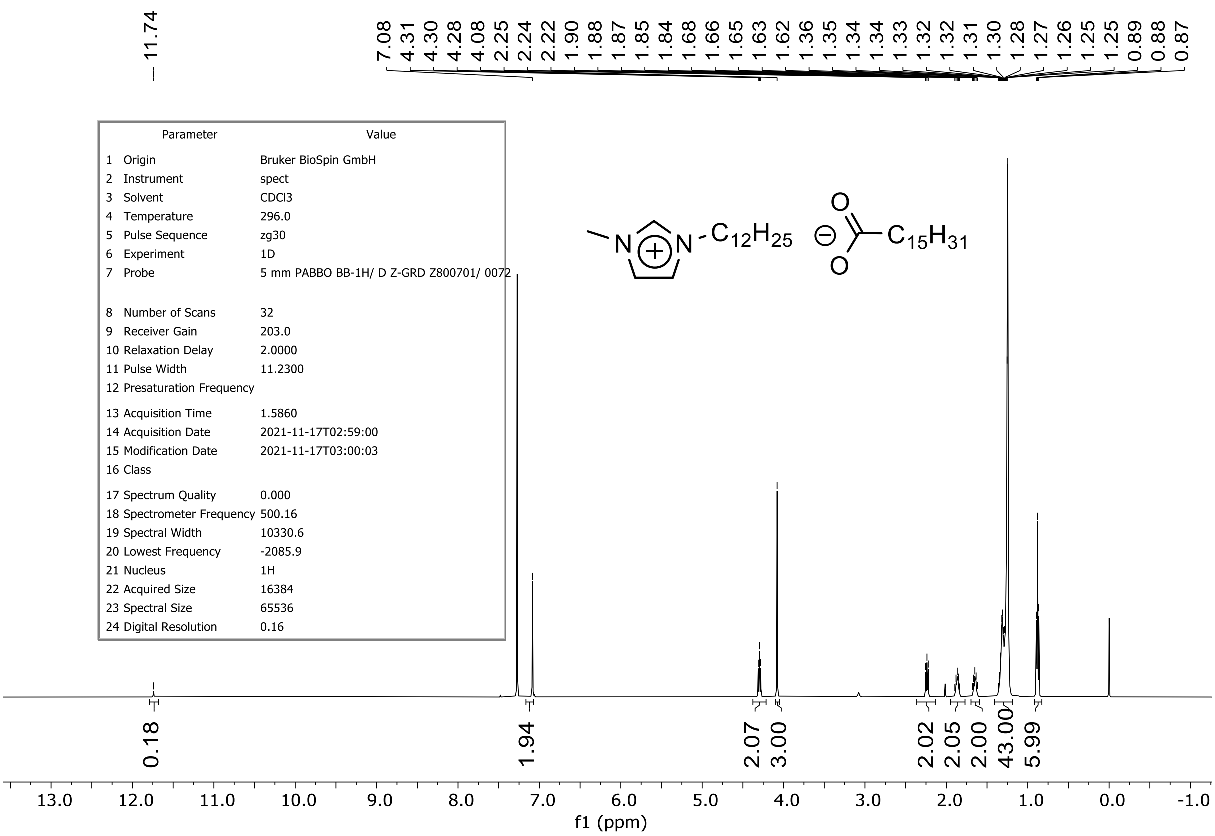
	Parameter	Value
1	Title	Nov18-2021.380.fid
2	Comment	02 Wachsmann WAC119
3	Origin	Bruker BioSpin GmbH
4	Instrument	spect
5	Solvent	CDCl3
6	Temperature	298.0
7	Pulse Sequence	zgpg30
8	Experiment	1D
9	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
10	Number of Scans	512
11	Receiver Gain	205.3
12	Relaxation Delay	2.0000
13	Pulse Width	10.0000
14	Presaturation Frequency	
15	Acquisition Time	1.3631
16	Acquisition Date	2021-11-19T03:56:00
17	Modification Date	2021-11-19T03:56:37
18	Class	
19	Spectrum Quality	0.000
20	Spectrometer Frequency	100.62
21	Spectral Width	24038.5
22	Lowest Frequency	-1945.7
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536
26	Digital Resolution	0.37



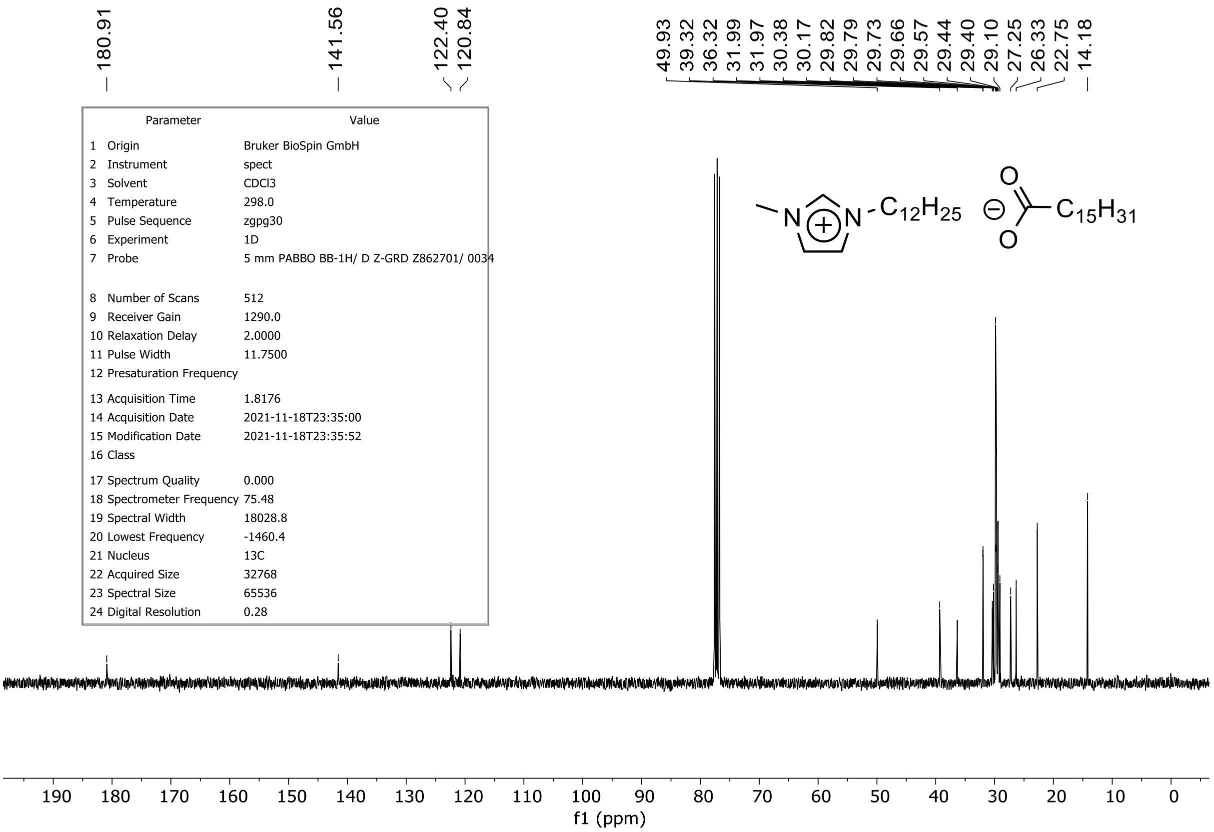
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8 Number of Scans	32
9 Receiver Gain	228.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.2300
12 Presaturation Frequency	
13 Acquisition Time	1.5860
14 Acquisition Date	2021-11-17T04:00:00
15 Modification Date	2021-11-17T04:00:26
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	500.16
19 Spectral Width	10330.6
20 Lowest Frequency	-2086.1
21 Nucleus	1H
22 Acquired Size	16384
23 Spectral Size	65536
24 Digital Resolution	0.16



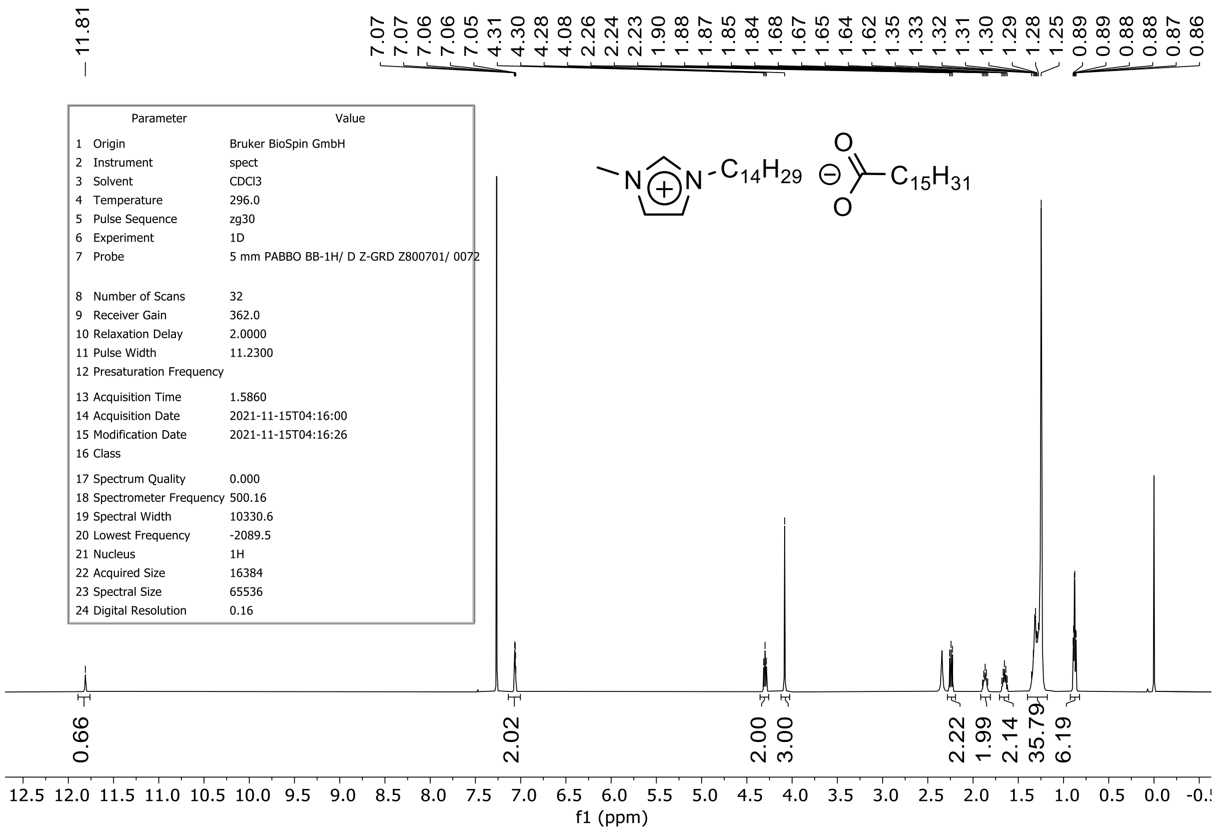
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.0
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8 Number of Scans	512
9 Receiver Gain	1440.0
10 Relaxation Delay	2.0000
11 Pulse Width	11.7500
12 Presaturation Frequency	
13 Acquisition Time	1.8176
14 Acquisition Date	2021-11-18T22:18:00
15 Modification Date	2021-11-18T22:18:26
16 Class	
17 Spectrum Quality	0.000
18 Spectrometer Frequency	75.48
19 Spectral Width	18028.8
20 Lowest Frequency	-1462.3
21 Nucleus	13C
22 Acquired Size	32768
23 Spectral Size	65536
24 Digital Resolution	0.28



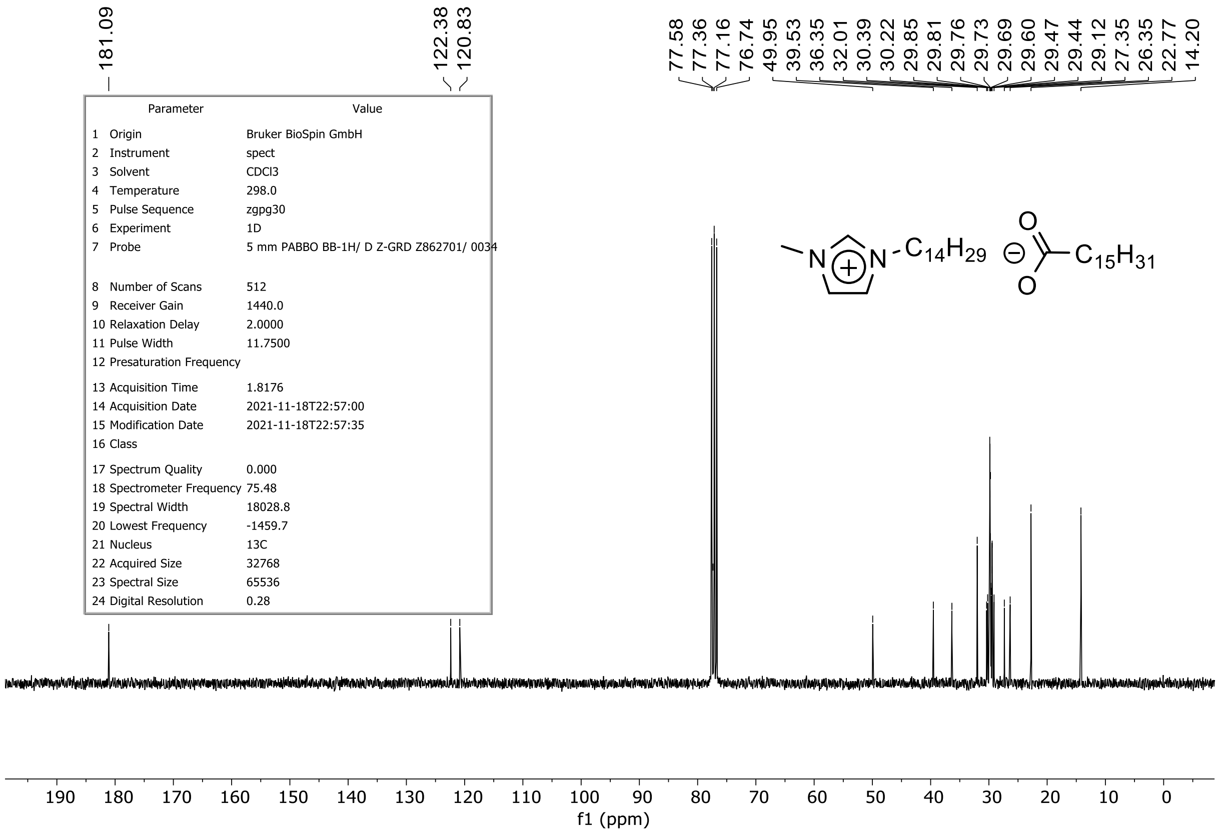
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	203.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-17T02:59:00
15	Modification Date	2021-11-17T03:00:03
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2085.9
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



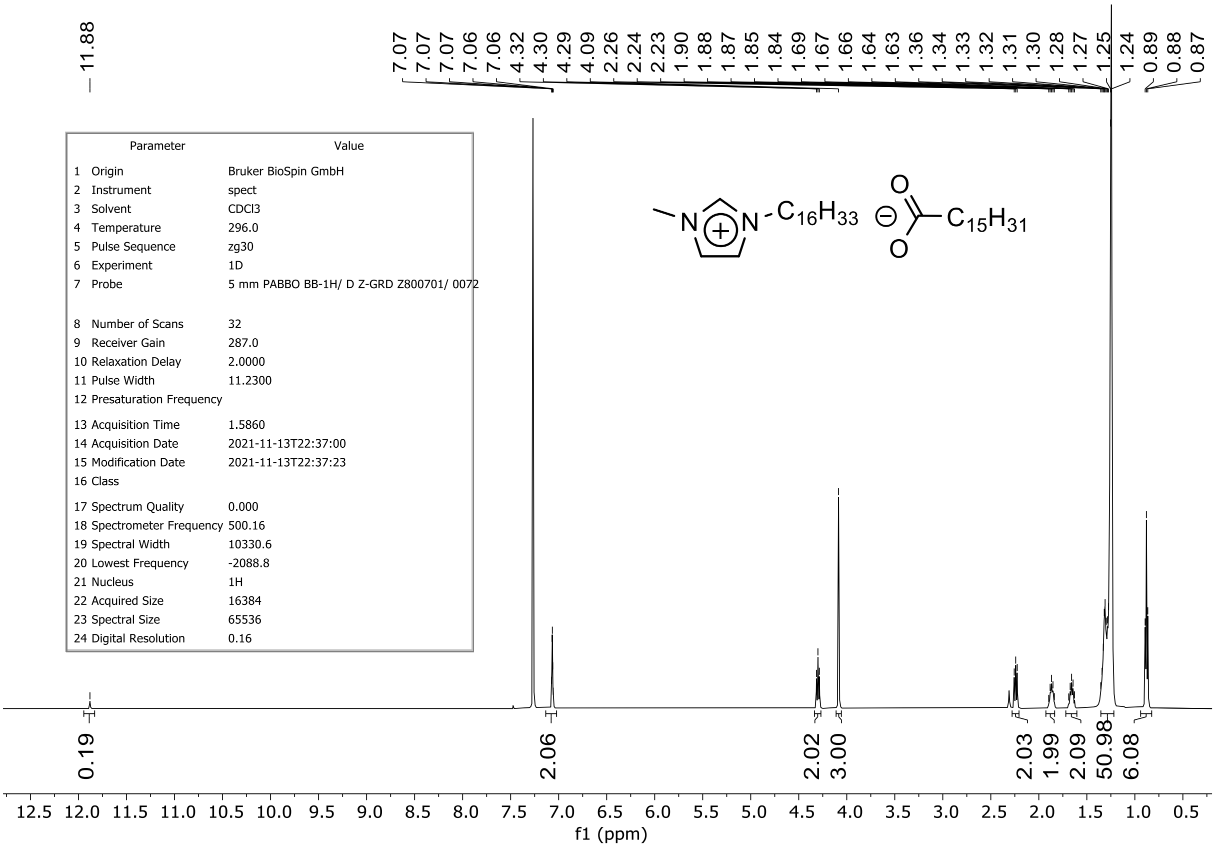
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1290.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-18T23:35:00
15	Modification Date	2021-11-18T23:35:52
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1460.4
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



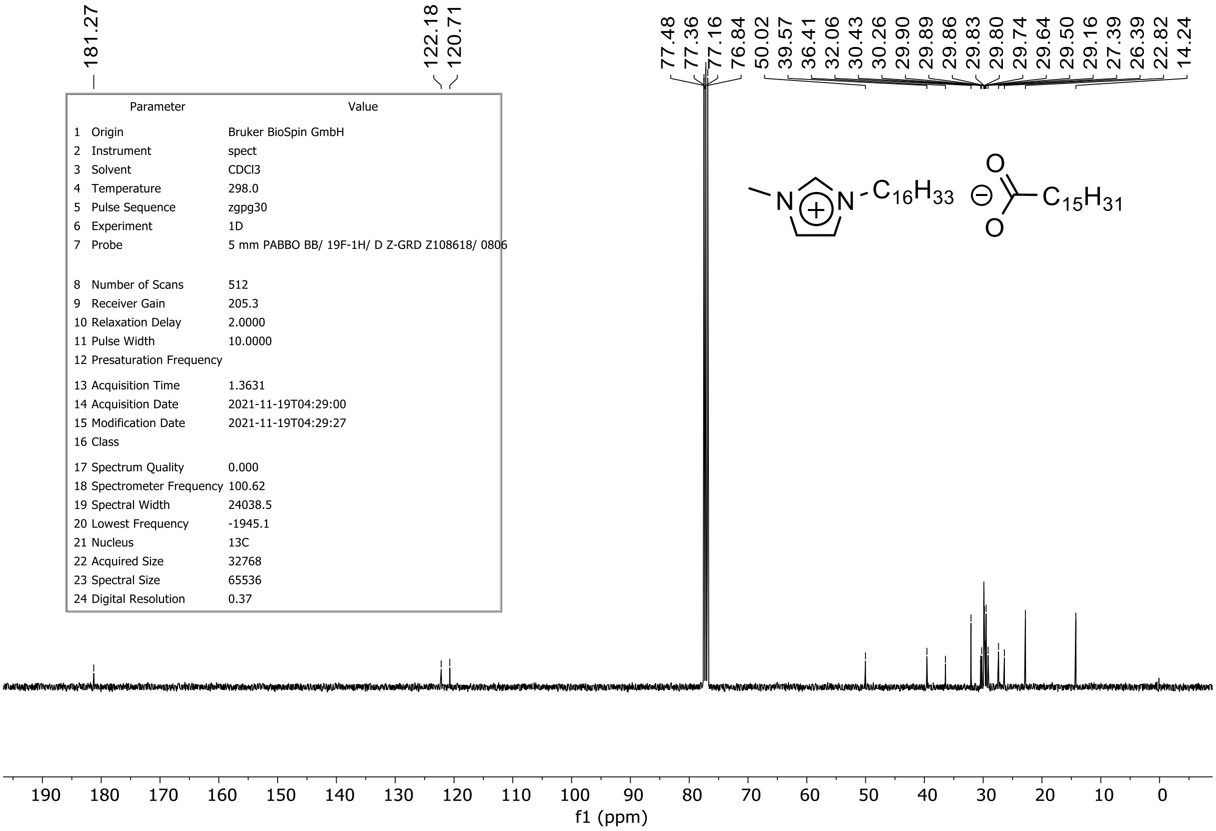
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	362.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-15T04:16:00
15	Modification Date	2021-11-15T04:16:26
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2089.5
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z862701/ 0034
8	Number of Scans	512
9	Receiver Gain	1440.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.7500
12	Presaturation Frequency	
13	Acquisition Time	1.8176
14	Acquisition Date	2021-11-18T22:57:00
15	Modification Date	2021-11-18T22:57:35
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	75.48
19	Spectral Width	18028.8
20	Lowest Frequency	-1459.7
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.28



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	296.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
8	Number of Scans	32
9	Receiver Gain	287.0
10	Relaxation Delay	2.0000
11	Pulse Width	11.2300
12	Presaturation Frequency	
13	Acquisition Time	1.5860
14	Acquisition Date	2021-11-13T22:37:00
15	Modification Date	2021-11-13T22:37:23
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	500.16
19	Spectral Width	10330.6
20	Lowest Frequency	-2088.8
21	Nucleus	1H
22	Acquired Size	16384
23	Spectral Size	65536
24	Digital Resolution	0.16



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0806
8	Number of Scans	512
9	Receiver Gain	205.3
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Presaturation Frequency	
13	Acquisition Time	1.3631
14	Acquisition Date	2021-11-19T04:29:00
15	Modification Date	2021-11-19T04:29:27
16	Class	
17	Spectrum Quality	0.000
18	Spectrometer Frequency	100.62
19	Spectral Width	24038.5
20	Lowest Frequency	-1945.1
21	Nucleus	13C
22	Acquired Size	32768
23	Spectral Size	65536
24	Digital Resolution	0.37

4. DSC and mesophase analysis

Table S1: Phase transition temperatures i.e. melting temperatures T_{m} [°C], clearing temperatures T_{Cl} and corresponding enthalpies ΔH [kJ/mol] of alkylimidazolium carboxylates **[C$_{n}$mim][C$_{m-1}$COO]**. Values were taken out of the DSC curves of the first heating/cooling cycle due to degradation and additionally verified via POM. • was found in the DSC, * was found via POM investigation; - not observed. The following phases were observed: Cr: crystallin; SmA: smectic A; I: isotropic; *n* = chain length of cation, *m* = chain length of anion.

n	m	Cr	T_{m} (ΔH)	SmA	T_{Cl} (ΔH)	I	Cycle
10	10	•	61 (74.2)	•	108 (2.9)	•	1th heat
		•	45 (38.7)	•	105 (2.7)	•	1th cool
12	10	•	43 (63.4)	•	122 (3.5)	•	1th heat
		•	43 (50.7)	•	98 (2.3)	•	1th cool
14	10	•	47 (77.1)	•	126 (3.2)	•	1th heat
		•	35 (31.4)	•	128 (2.3)	•	1th cool
16	10	•	55 (90.1)	•	146 (3.6)	•	1th heat
		•	37 (85.6)	•	145 (2.9)	•	1th cool
10	12	•	42 (68.0)	•	144 (3.7)	•	1th heat
		•	30 (53.6)	•	139 (3.3)	•	1th cool
12	12	•	48 (79.6)	•	118 (3.0)	•	1th heat
		•	59 (20.0)	•	102 (1.9)	•	1th cool
14	12	•	57 (78.5)	•	139 (2.7)	•	1th heat
		•	54 (34.1)	•	123 (1.8)	•	1th cool
16	12	•	55 (76.6)	•	126 (2.3)	•	1th heat
		•	52 (40.1)	•	96 (1.6)	•	1th cool
10	14	•	37 (58.1)	•	132 (0.3)	•	1th heat
		•	35 (15.6)	•	129 (2.3)	•	1th cool
12	14	•	59 (145.7)	•	127 (5.2)	•	1th heat
		•	35 (49.4)	•	123 (4.4)	•	1th cool
14	14	•	70 (75.9)	*	120* (-)	*	1th heat
		*	64 (-)	*	115* (-)	*	1th cool
16	14	•	58 (89.2)	•	150 (2.1)	•	1th heat
		•	46 (40.0)	•	143 (1.5)	•	1th cool
10	16	•	45 (75.7)	•	128 (2.6)	•	1th heat
		•	46 (45.9)	•	99 (1.7)	•	1th cool
12	16	•	52 (98.9)	•	138 (3.3)	•	1th heat
		•	56 (26.7)	•	129 (2.1)	•	1th cool
14	16	•	64 (103.6)	•	150 (4.0)	•	1th heat
		•	43 (37.0)	•	148 (1.9)	•	1th cool
16	16	•	79 (73.8)	•	133 (1.4)	•	1th heat
		•	78 (33.8)	•	126 (1.2)	•	1th cool

[a] Additional Cr–Cr transitions were observed for **[C$_{14}$mim][C$_{9}$COO]** at 37 °C 1th cooling (7.2 kJ/mol), **[C$_{16}$mim][C$_{11}$COO]** at 63 °C 1th cooling (14.2 kJ/mol), **[C$_{14}$mim][C$_{11}$COO]** at 60 °C 1th cooling (11.8 kJ/mol), **[C$_{12}$mim][C$_{13}$COO]** at 56 °C 1th cooling (50.7 kJ/mol), **[C$_{16}$mim][C$_{13}$COO]** at 60 °C 1th cooling (10.1 kJ/mol), 65 °C 1th cooling (14.5 kJ/mol) and **[C$_{14}$mim][C$_{15}$COO]** at 65 °C 1th cooling (28.6 kJ/mol), at 74 °C 1th cooling (1.5 kJ/mol).

Table S2: Phase transition temperatures i.e. melting temperatures T_m [°C], clearing temperatures T_Cl [°C] and corresponding enthalpies ΔH [kJ/mol] of alkylimidazolium derivatives **[C$_n$mim]**. Values were taken out of the DSC curves of the first heating/cooling cycle due to degradation and additionally verified via POM. • was found in the DSC;- not observed. The following phases were observed: Cr: crystallin; I: isotropic. The mesophase was not further investigated.

Compound	Cr	T_m (ΔH)	Mesophase	T_Cl (ΔH)	I	Cycle
[C$_{10}$mim]Br	•	17 (1.0)	-	-	•	1th heat
	•	-3 (0.1)	-	-	•	1th cool
[C$_{12}$mim]Br	•	45 (46.2)	•	130 (0.5)	•	1th heat
	•	13 (32.5)	•	129 (0.5)	•	1th cool
[C$_{14}$mim]Br	•	55 (53.5)	•	180 (1.2)	•	1th heat
	•	20 (56.9)	•	174 (1.0)	•	1th cool
[C$_{16}$mim]Br	•	54 (60.2)	•	223 (1.3)	•	1th heat
	•	39 (19.1)	•	205 (1.2)	•	1th cool

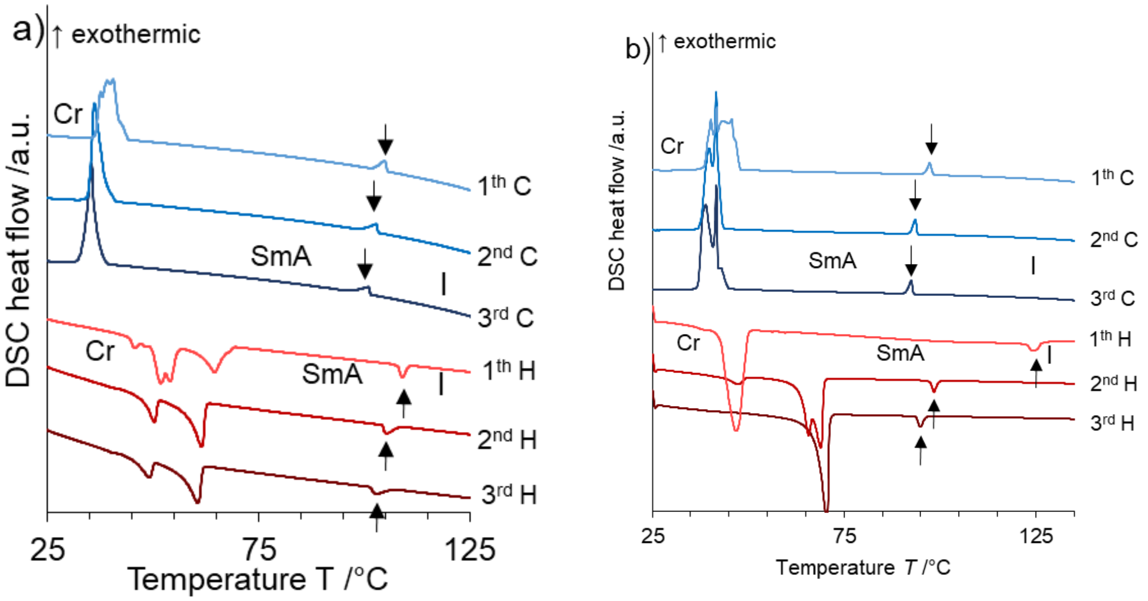


Figure S1: DSC-curves of a) **[C$_{10}$mim][C$_9$COO]** and b) **[C$_{12}$mim][C$_9$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

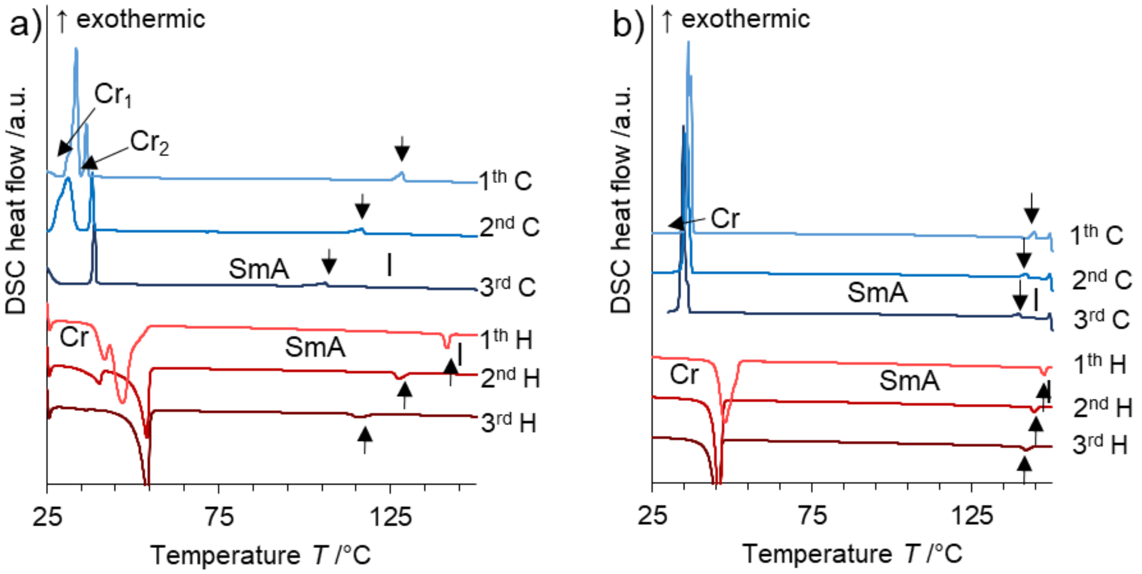


Figure S2: DSC-curves of a) **[C_{14}mim][C_9COO]** and **b) [C_{16}mim][C_9COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

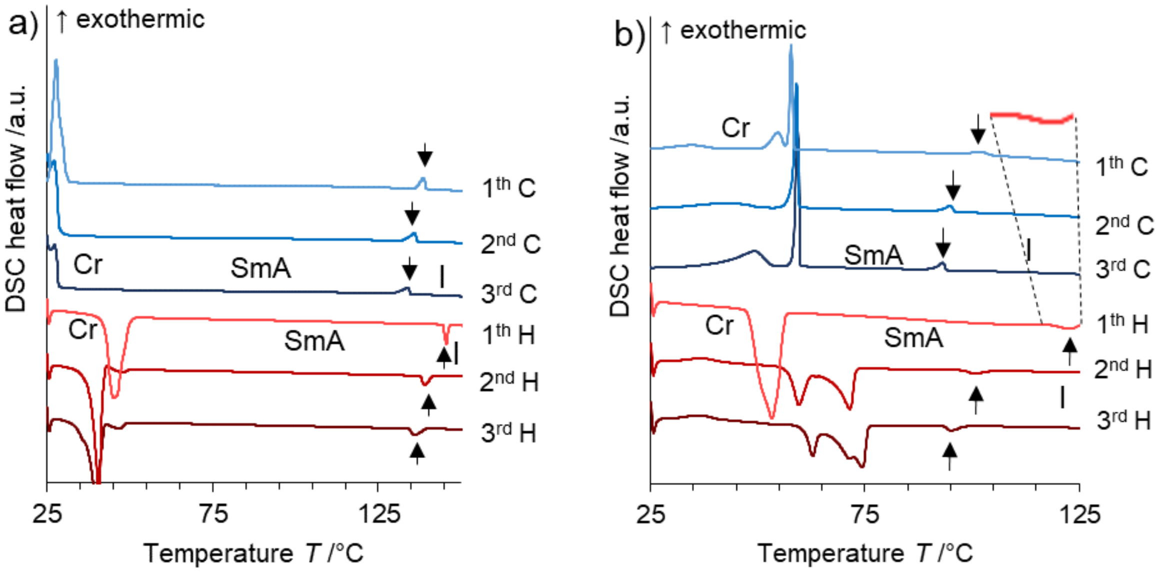


Figure S3: DSC-curves of a) **[C_{10}mim][C_{11}COO]** and b) **[C_{12}mim][C_{11}COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

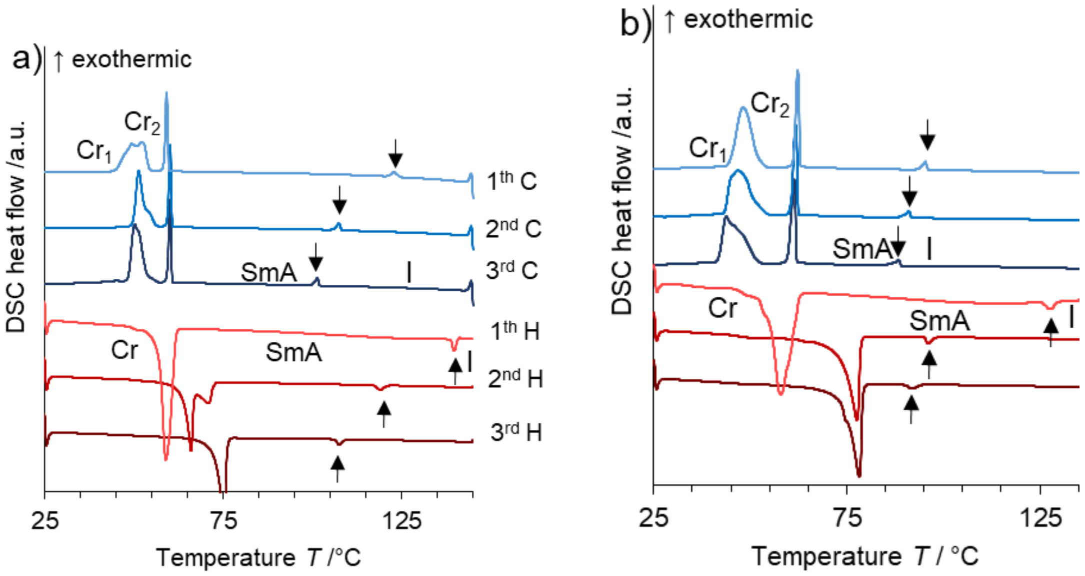


Figure S4: DSC-curves of a) **[C$_{14}$mim][C$_{11}$COO]** b) **[C$_{16}$mim][C$_{11}$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

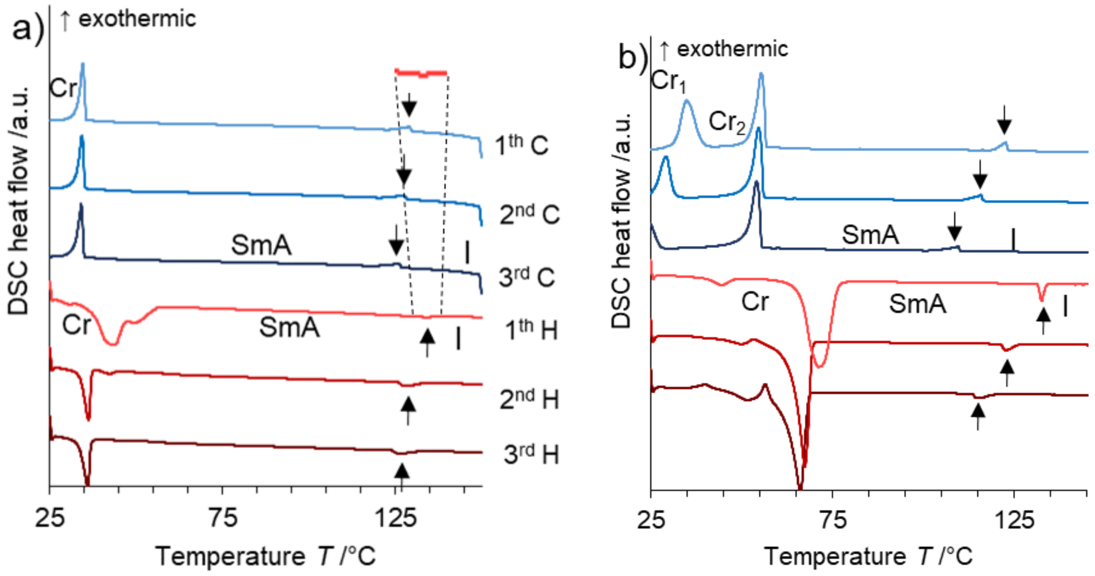


Figure S5: DSC-curves of a) **[C$_{10}$mim][C$_{13}$COO]** and b) **[C$_{12}$mim][C$_{13}$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

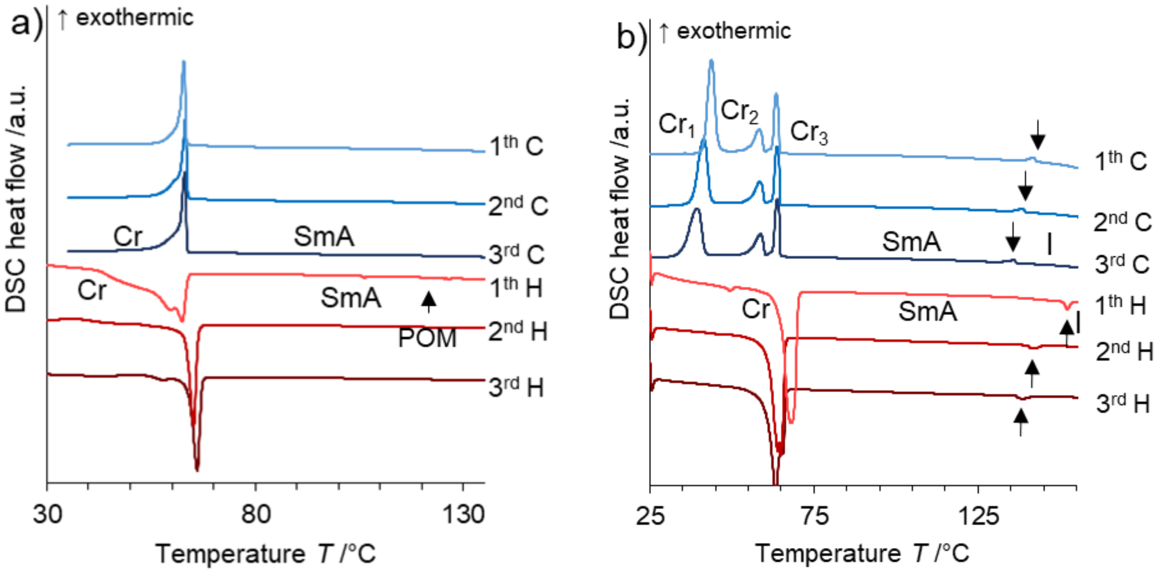


Figure S6: DSC-curves of a) **[C$_{14}$mim][C$_{13}$COO]** and b) **[C$_{16}$mim][C$_{13}$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

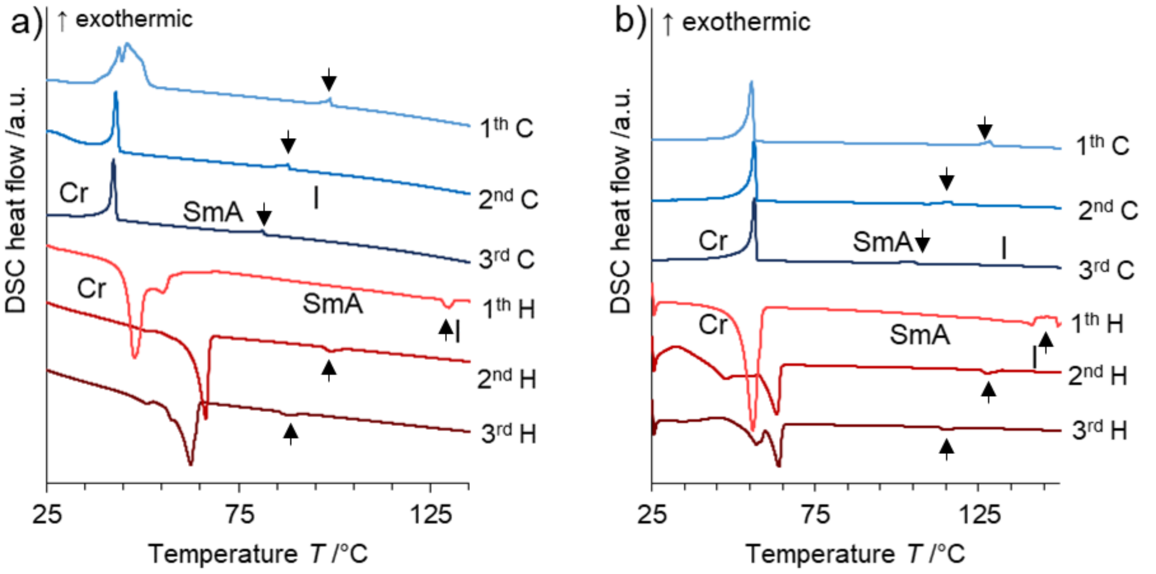


Figure S7: DSC-curves of a) **[C$_{10}$mim][C$_{15}$COO]** and b) **[C$_{12}$mim][C$_{15}$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

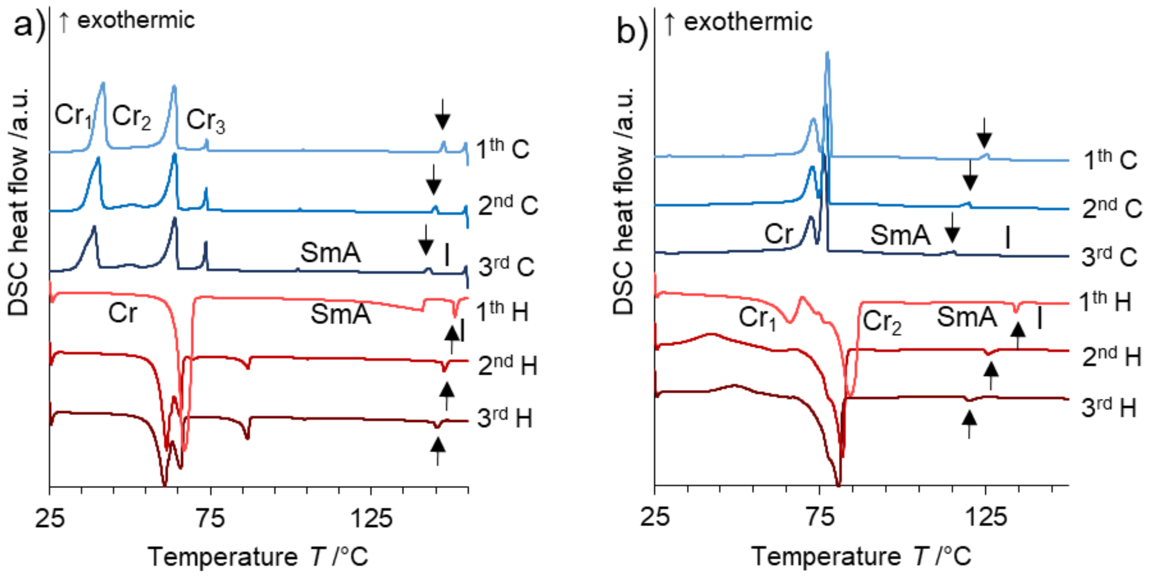


Figure S8: DSC-curves of a) **[C$_{14}$mim][C$_{15}$COO]** and b) **[C$_{16}$mim][C$_{15}$COO]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

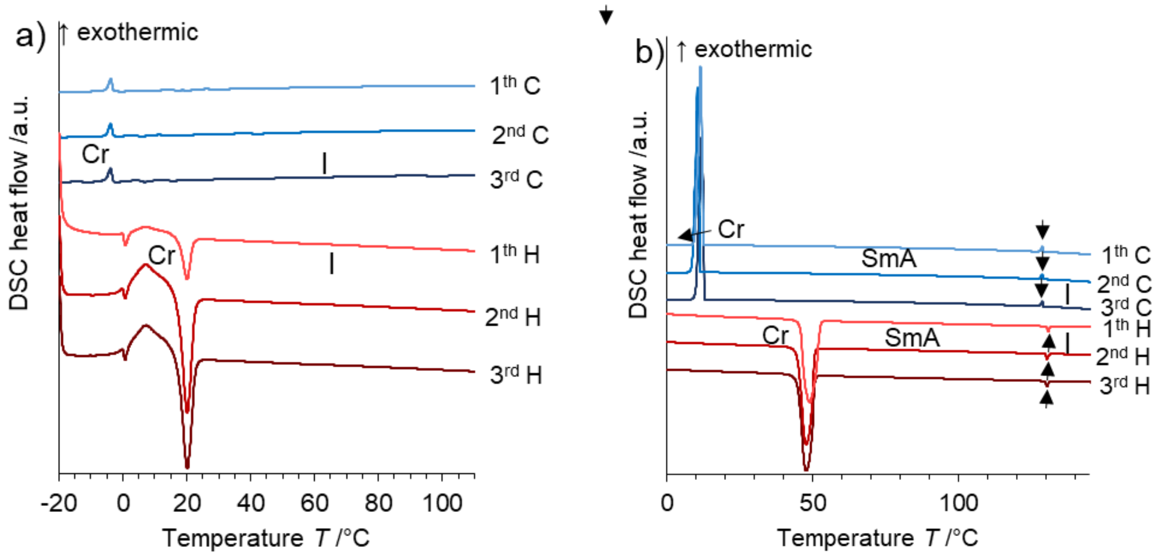


Figure S9: DSC-curves of a) **[C$_{10}$mim]** and b) **[C$_{12}$mim]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

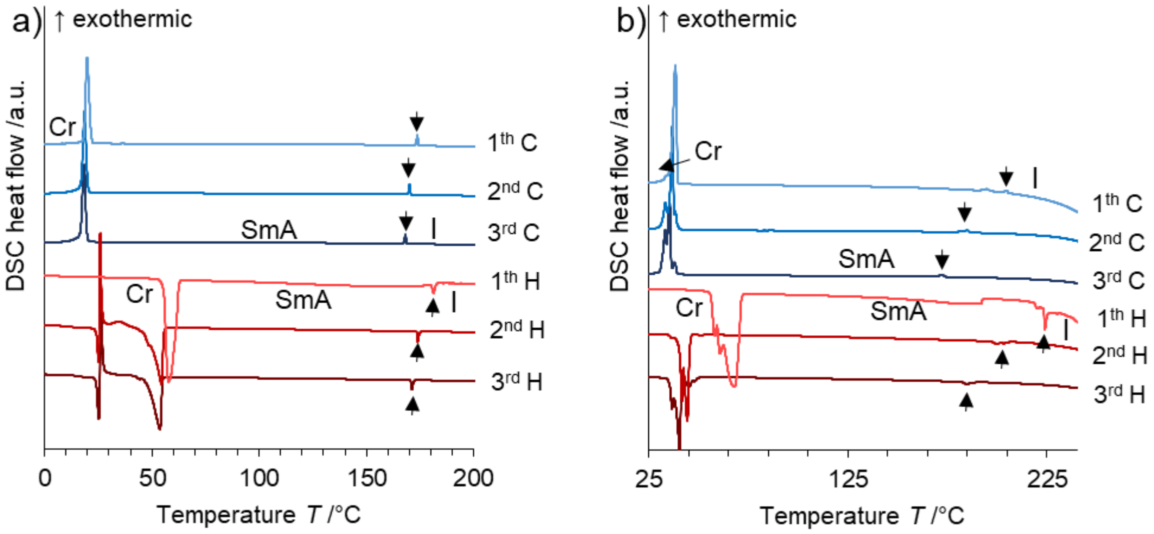


Figure S10: DSC-curves of a) **[C$_{14}$mim]** and b) **[C$_{16}$mim]**. Cr: crystallin; SmA: smectic A; I: isotropic. H/C: Heating/Cooling (rate 5 K/min).

5. Polarization microscopy studies

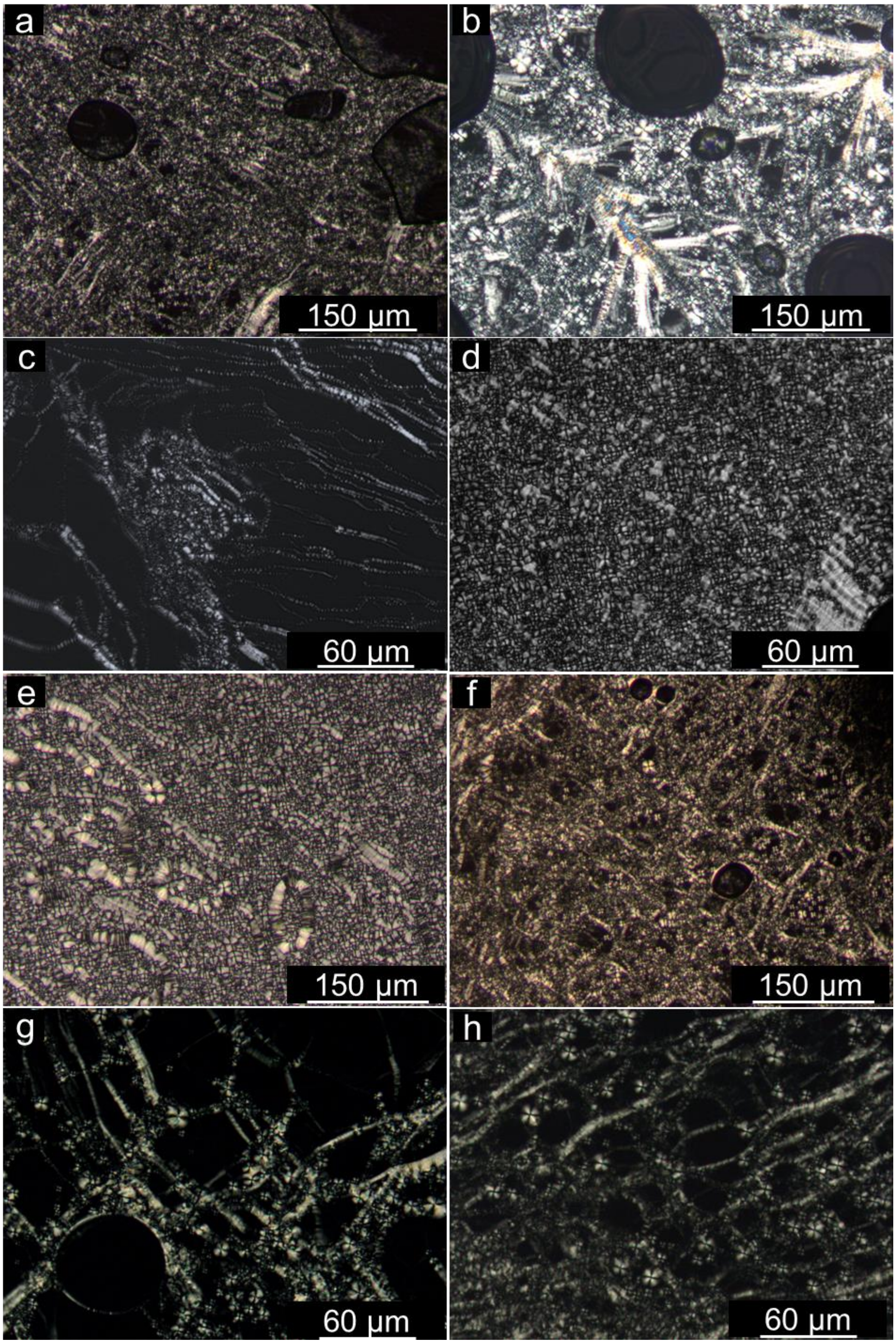


Figure S11: POM textures as seen between crossed polarizers upon cooling from the isotropic liquid (cooling rate 2K/min) of imidazolium carboxylates **[$C_n$mim][C_{m-1}COO]**. a) **[C_{10}mim][C_9COO]** temp. 100 °C, magnification 100x, b) **[C_{12}mim][C_9COO]** temp. 110 °C, magnification 100x, c) **[C_{14}mim][C_9COO]** temp. 110 °C, magnification 200x, d) **[C_{16}mim][C_9COO]** temp. 90 °C, magnification 200x, e) **[C_{10}mim][C_{11}COO]** temp. 100 °C, magnification 100x, f) **[C_{12}mim][C_{11}COO]** temp. 100 °C, magnification 100x, g) **[C_{14}mim][C_{11}COO]** temp. 110 °C, magnification 200x, h) **[C_{16}mim][C_{11}COO]** temp. 120 °C, magnification 100x.

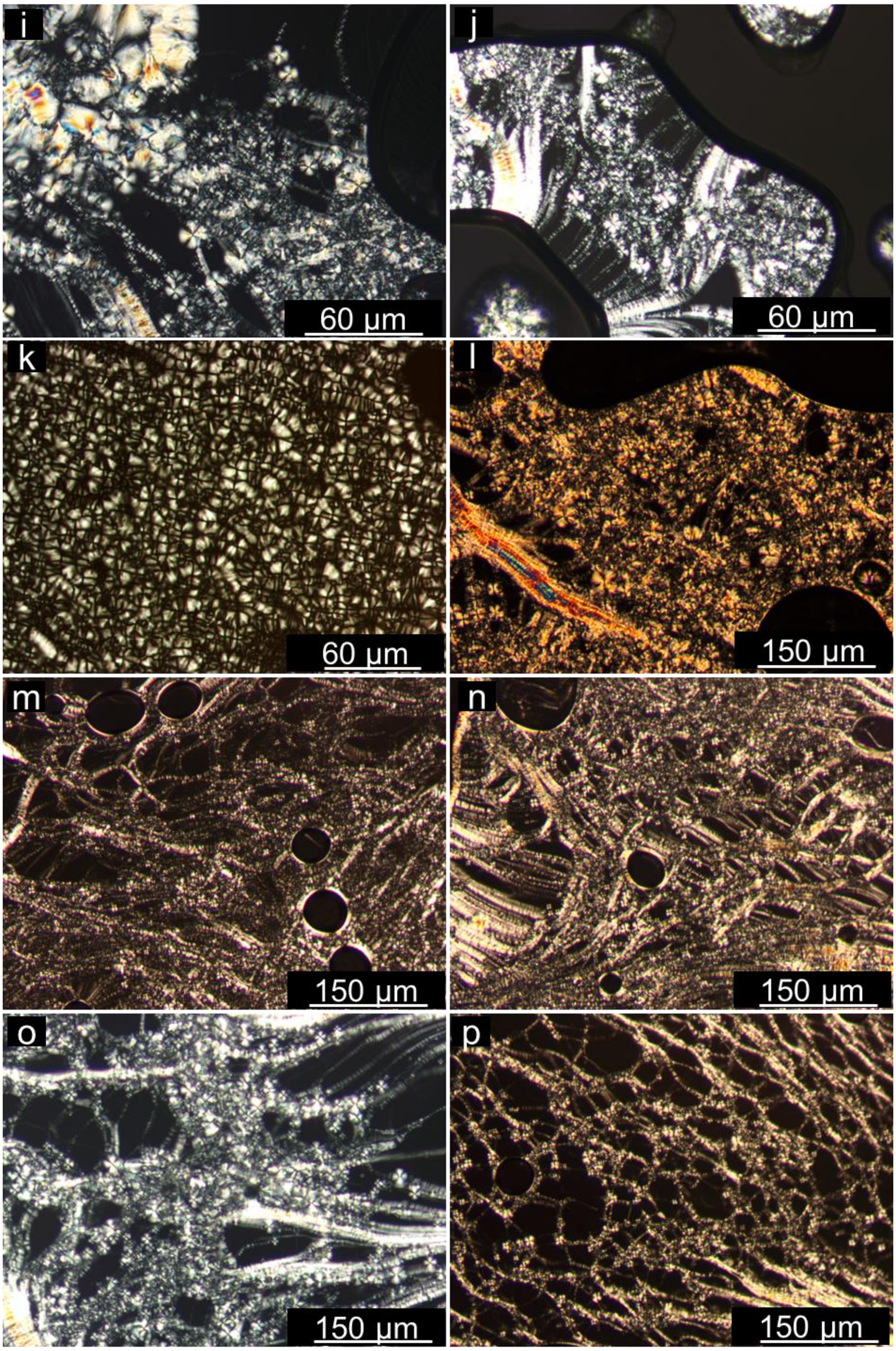


Figure S12: POM textures as seen between crossed polarizers upon cooling from the isotropic liquid (cooling rate 2K/min) of imidazolium carboxylates **[C$_{n}$mim][C$_{m-1}$COO]**. i) **[C$_{10}$mim][C$_{13}$COO]** temp. 110 °C, magnification 200x, j) **[C$_{12}$mim][C$_{13}$COO]** temp. 100 °C, magnification 200x, k) **[C$_{14}$mim][C$_{13}$COO]** temp. 84 °C, magnification 200x, l) **[C$_{16}$mim][C$_{13}$COO]** temp. 90 °C, magnification 100x, m) **[C$_{10}$mim][C$_{15}$COO]** temp. 80 °C, magnification 100x, n) **[C$_{12}$mim][C$_{15}$COO]** temp. 90 °C, magnification 100x, o) **[C$_{14}$mim][C$_{15}$COO]** temp. 110 °C, magnification 100x, p) **[C$_{16}$mim][C$_{15}$COO]** temp. 90 °C, magnification 100x.

6. Thermogravimetric analysis

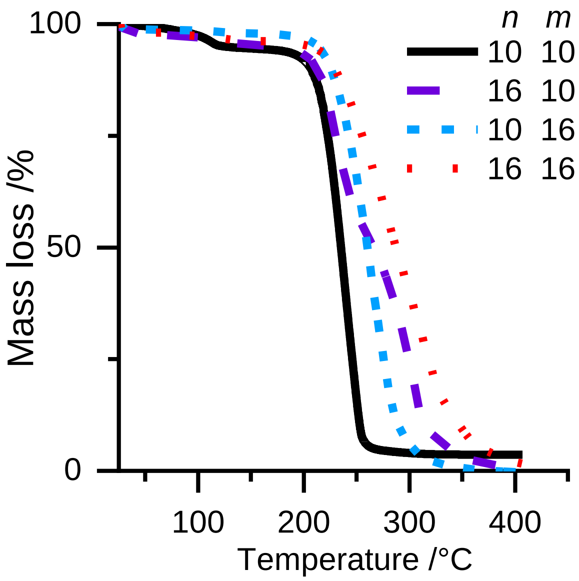


Figure S13: TGA diagram of exemplaric samples **[C$_{10}$mim][C$_9$COO]**, **[C$_{16}$mim][C$_9$COO]**, **[C$_{10}$mim][C$_{15}$COO]** and **[C$_{16}$mim][C$_{15}$COO]**. The measurements were performed from 25 to 450 °C with a constant heating rate of 10 K/min.

7. Surface tension measurements

For the determination of the minimum headgroup area a_{min} of the salt-free new catanionic **[C$_n$mim][C$_{m-1}$COO]**'s the surface tension data were analyzed with the Gibbs adsorption isotherm (eq. 1, see manuscript) using a prefactor of $\nu = 2$. In more detail, the decrease of the surface tension data was described with a polynomial (quadratic) fit^5 to determine the surface excess concentration Γ and the head group area a as a function of the **[C$_n$mim][C$_{m-1}$COO]** concentration according to eqs. 1 and 2 (see manuscript), respectively. Figure S14 a) shows, by means of **[C$_{10}$mim][C$_9$COO]**, that Γ systematically increases with increasing concentration of the **[C$_{10}$mim][C$_9$COO]**'s, while the head group area a systematically decreases (b)). As can be seen, the values of the maximum surface excess concentration Γ_{max} and the minimum headgroup area a_{min} can be determined nicely from these plots by extrapolation to the critical micelle concentration (indicated by the stars).

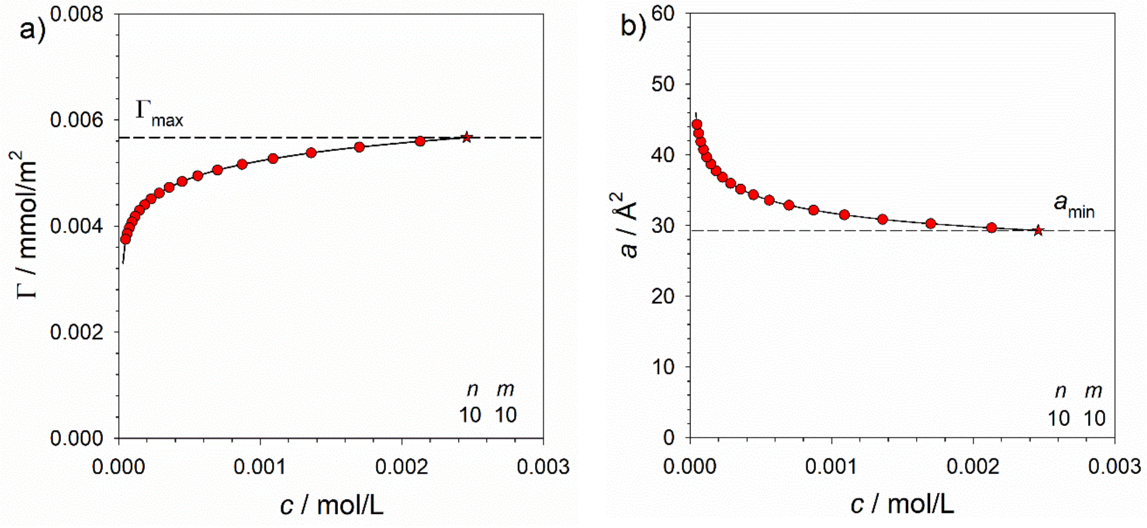


Figure S14: a) Surface excess concentration Γ and b) head group area a as a function of the **[C$_{10}$mim][C$_9$COO]** concentration determined from the analysis of the surface tension data (T=25 °C) according to eqs. 1 and 2, respectively. Γ_{max} and a_{min} were determined by extrapolation to the critical micelle concentration (indicated by the stars).

The cmc values obtained from the intersection of the quadratic fit describing the decrease of the surface tension data[5] and a linear extrapolation of the plateau data are compiled in the Table S3.

Table S3: Critical micelle concentration cmc, minimum surface tension γ_{min} and minimum head group area a_{min} for various salt-free imidazolium carboxylates **[C$_n$mim][C$_{m-1}$COO]** at T=25 °C.

n	m	cmc / mol/L	γ_{min} / mN/m	a / Å^2
10	10	$(1.2 \pm 0.1)\ 10^{-3}$	23.1 ± 0.3	58.6 ± 4.1
10	12	$(1.6 \pm 0.2)\ 10^{-4}$	22.5 ± 0.2	66.6 ± 10.1
10	14	$(3.4 \pm 0.4)\ 10^{-5}$	21.2 ± 0.3	51.2 ± 12.4
12	10	$(3.9 \pm 0.2)\ 10^{-4}$	23.2 ± 0.3	60.7 ± 3.2
14	10	$(1.3 \pm 0.2)\ 10^{-4}$	23.9 ± 0.2	55.0 ± 4.3
16	10	$(4.1 \pm 0.5)\ 10^{-5}$	25.4 ± 0.3	53.5 ± 4.5

8. X-Ray data

Table S4: XRD-data of imidazolium carboxylates **[$C_n$mim][C_{m-1}COO]**. Difference between experimental and calculated layer thickness *d* is caused by interdigitation.

n	*m*	Mesophase	Layer thickness *d*/ Å exp. (calcd.)	Miller indices
10	10	SmA	26.5 (29.1)	(001)
12	10	SmA	28.4 (30.7)	(001)
14	10	SmA	28.5 (34.0)	(001)
16	10	SmA	29.2 (36.4)	(001)
10	12	SmA	27.4 (32.1)	(001)
12	12	SmA	28.4 (33.7)	(001)
14	12	SmA	29.7 (37.0)	(001)
16	12	SmA	34.5 (39.4)	(001)
10	14	SmA	30.2 (34.0)	(001)
12	14	SmA	29.9 (35.6)	(001)
14	14	SmA	32.1 (38.9)	(001)
16	14	SmA	32.9 (41.3)	(001)
10	16	SmA	29.8 (37.4)	(001)
12	16	SmA	34.3 (39.0)	(001)
14	16	SmA	35.9 (42.3)	(001)
16	16	SmA	37.8 (44.7)	(001)

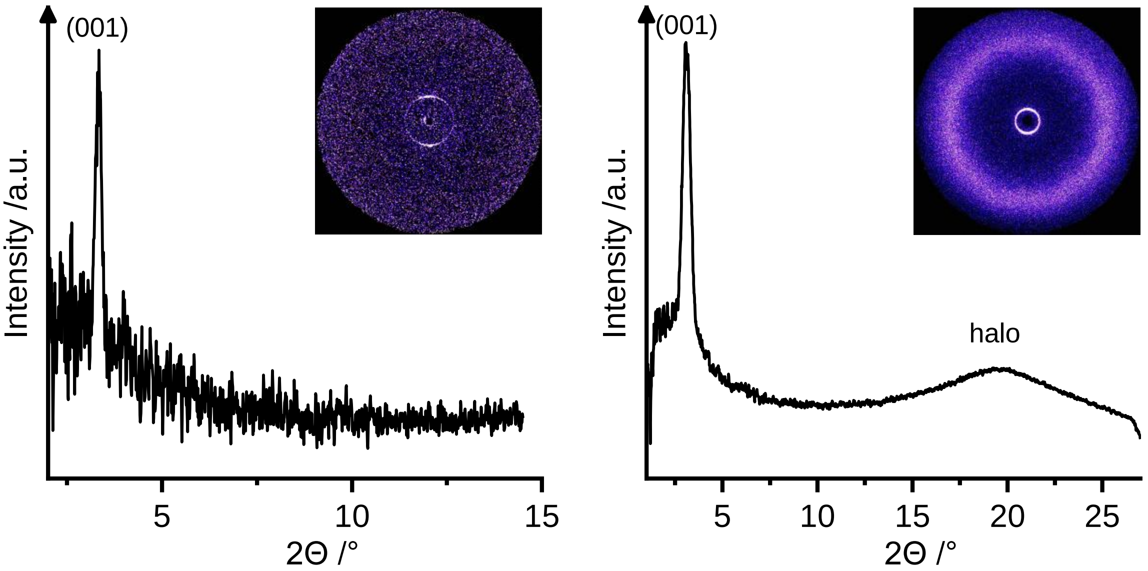


Figure S15: X-Ray scattering profile of **[C$_{10}$mim][C$_{9}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 78 °C.

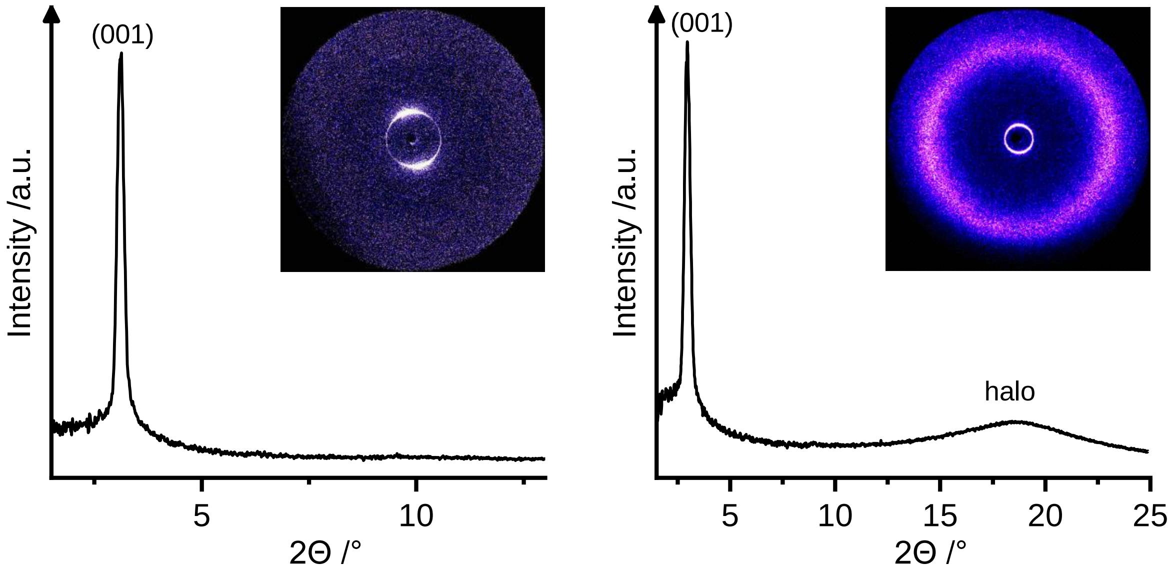


Figure S16: X-Ray scattering profile of **[C$_{12}$mim][C$_{9}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 87 °C.

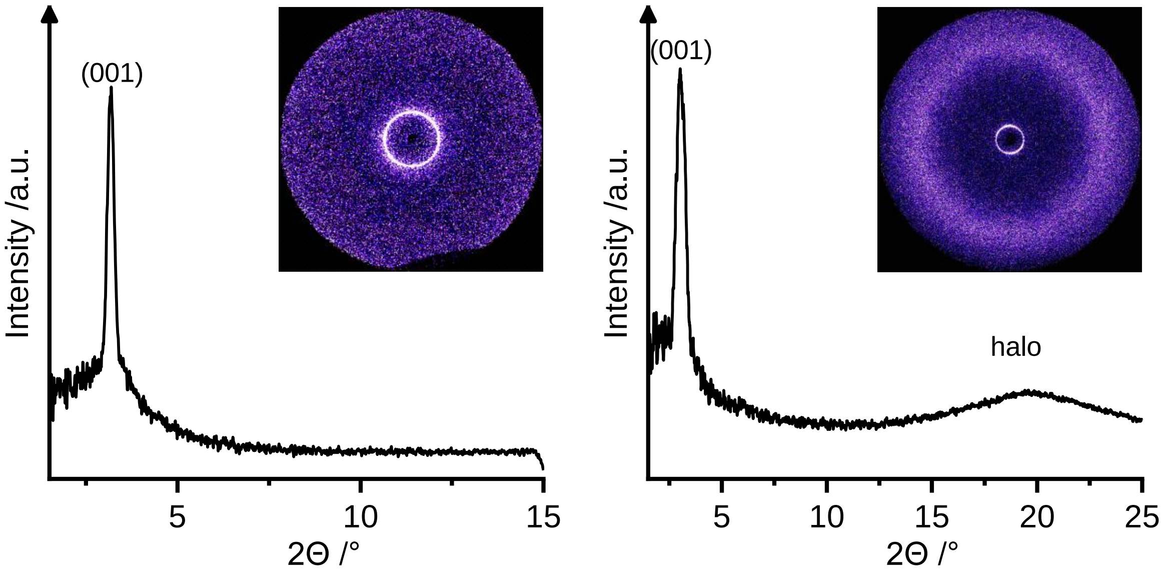


Figure S17: X-Ray scattering profile of **[C$_{14}$mim][C$_9$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 90 °C.

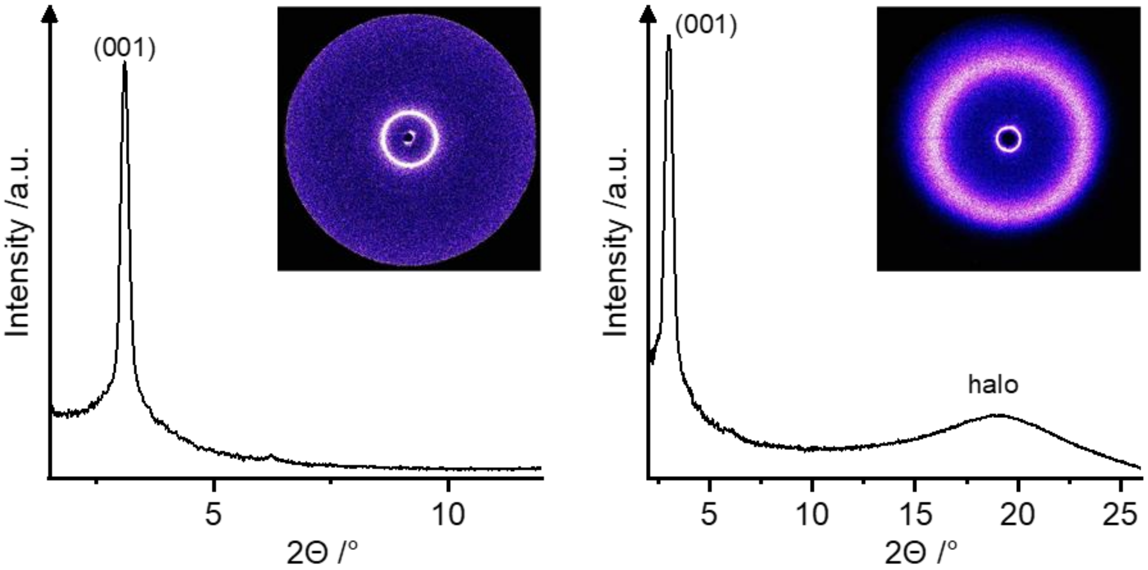


Figure S18: X-Ray scattering profile of **[C$_{16}$mim][C$_9$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 100 °C.

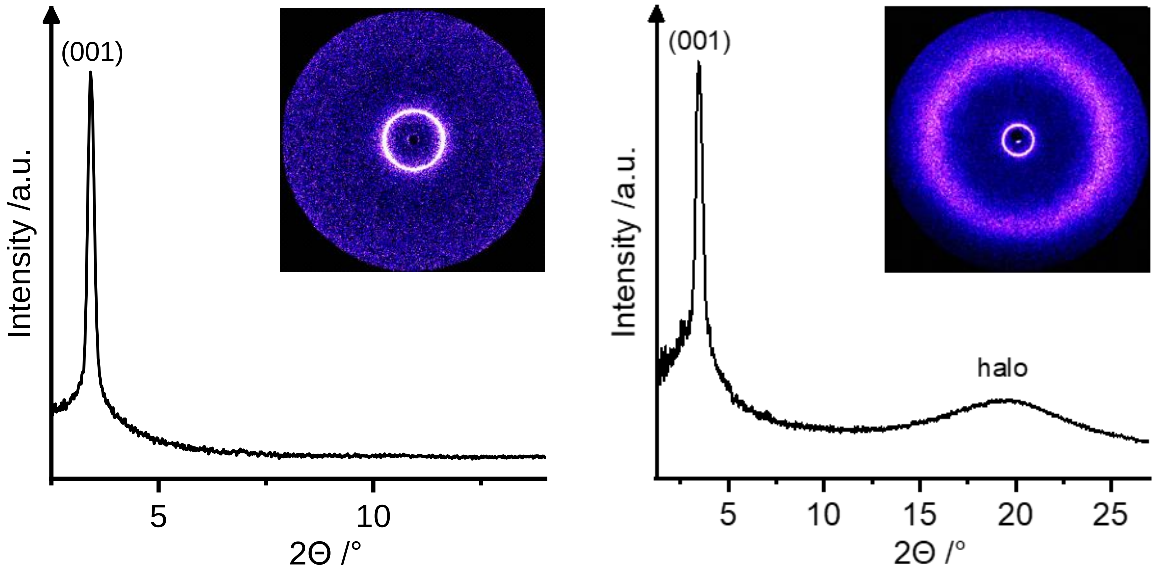


Figure S19: X-Ray scattering profile of **[C$_{10}$mim][C$_{11}$COO]** and corresponding diffraction pattern (SAXS (left) at 118 °C; WAXS (right)) at 128 °C.

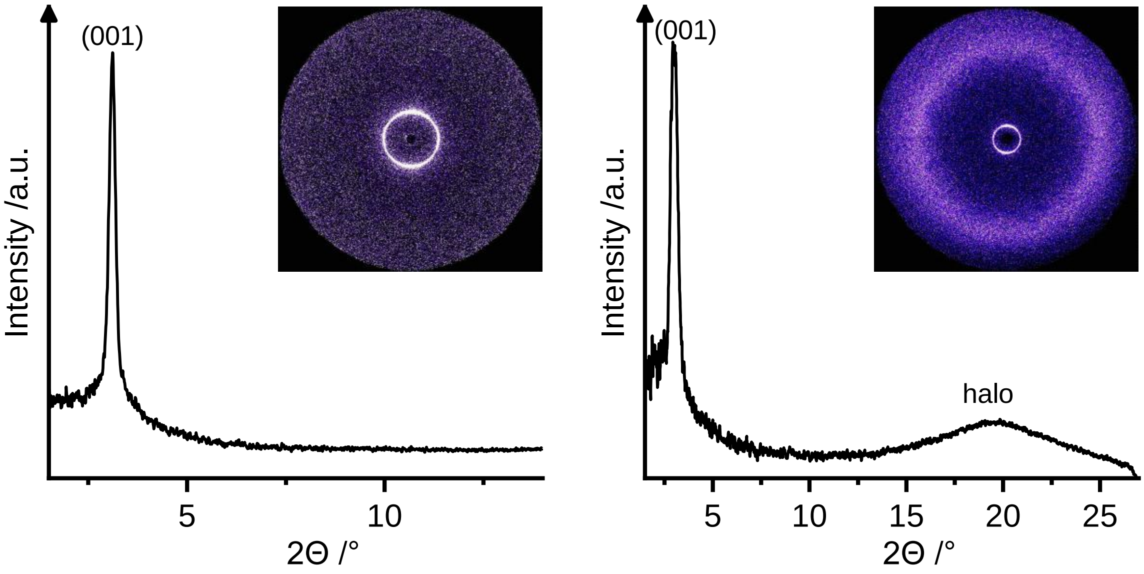


Figure S20: X-Ray scattering profile of **[C$_{12}$mim][C$_{11}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 87 °C.

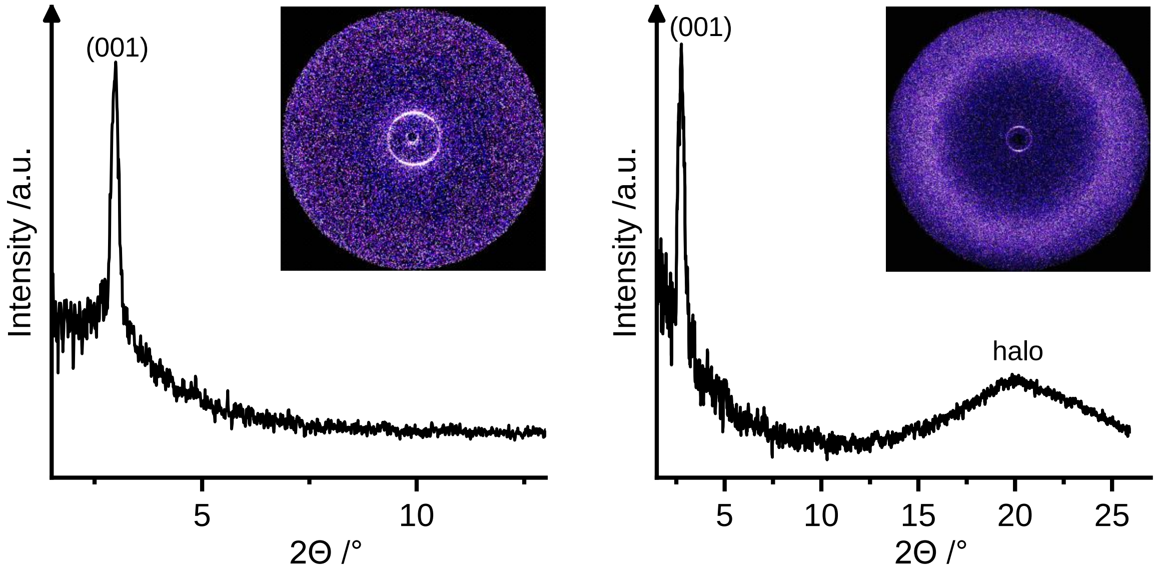


Figure S21: X-Ray scattering profile of **[C$_{14}$mim][C$_{11}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 97 °C.

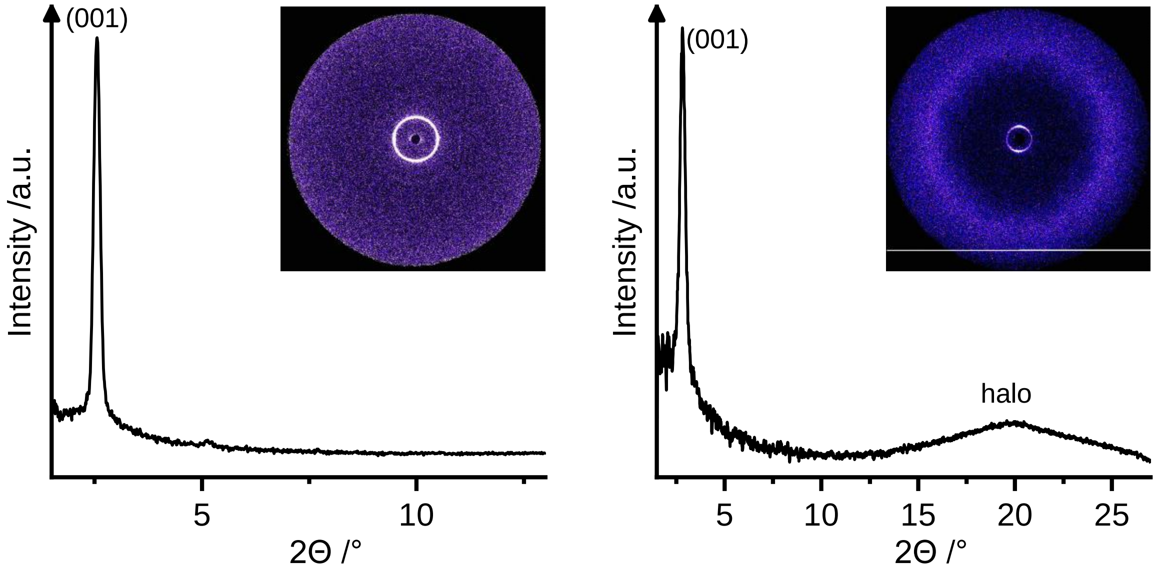


Figure S22: X-Ray scattering profile of **[C$_{16}$mim][C$_{11}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 75 °C.

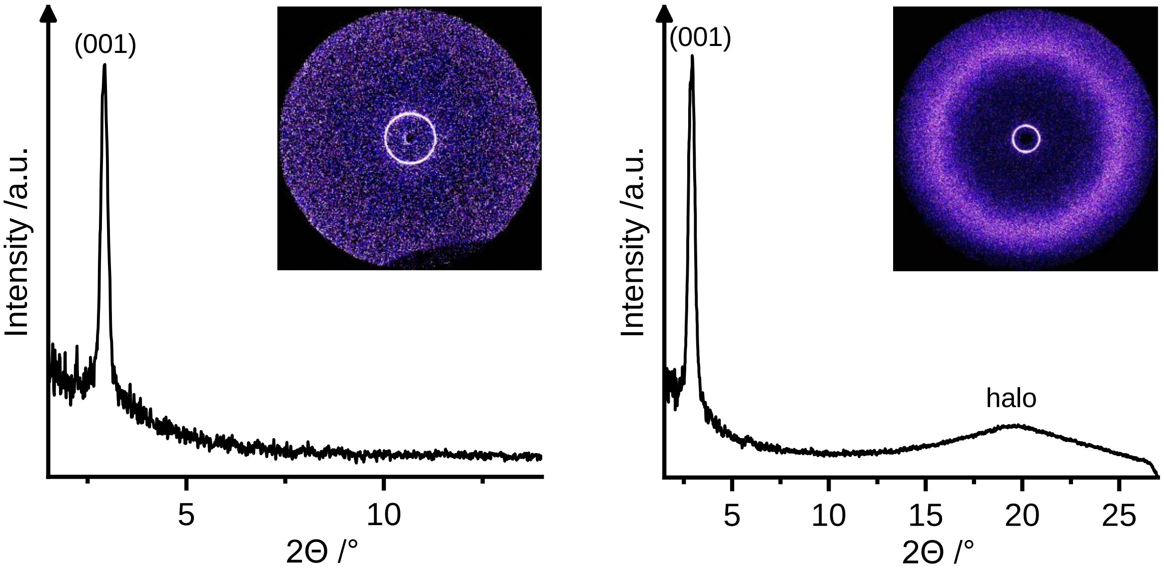


Figure S23: X-Ray scattering profile of **[C$_{10}$mim][C$_{13}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 76 °C.

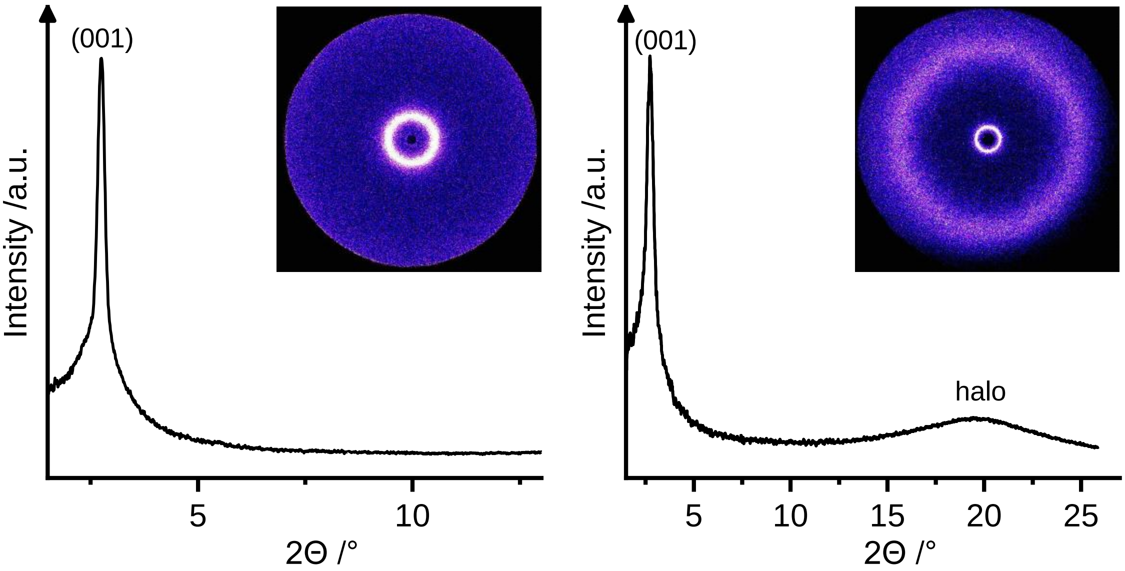


Figure S24: X-Ray scattering profile of **[C$_{12}$mim][C$_{13}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 83 °C.

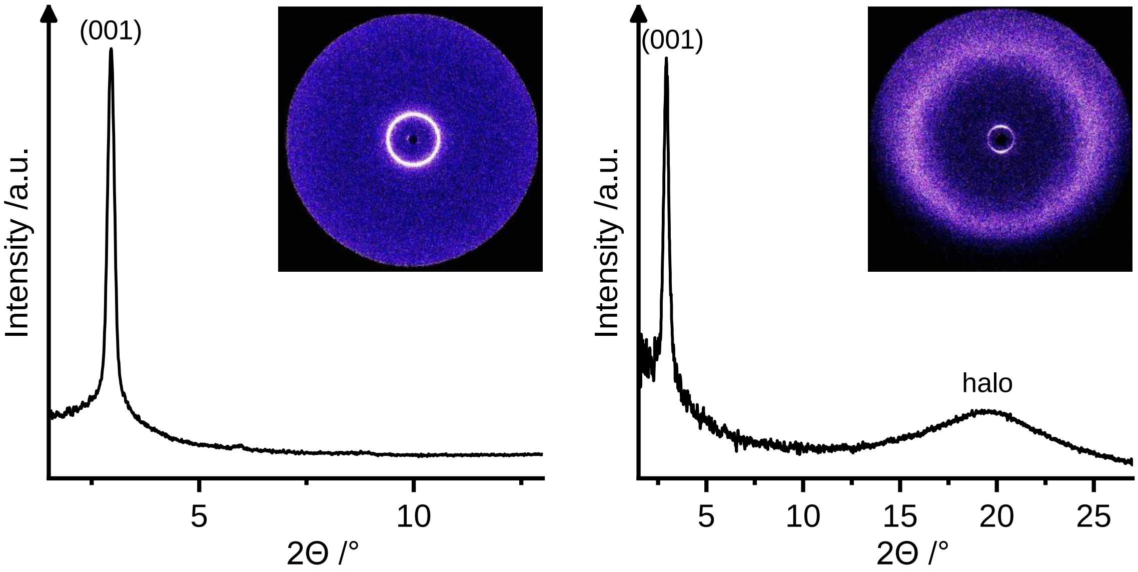


Figure S25: X-Ray scattering profile of **[C$_{14}$mim][C$_{13}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 74 °C.

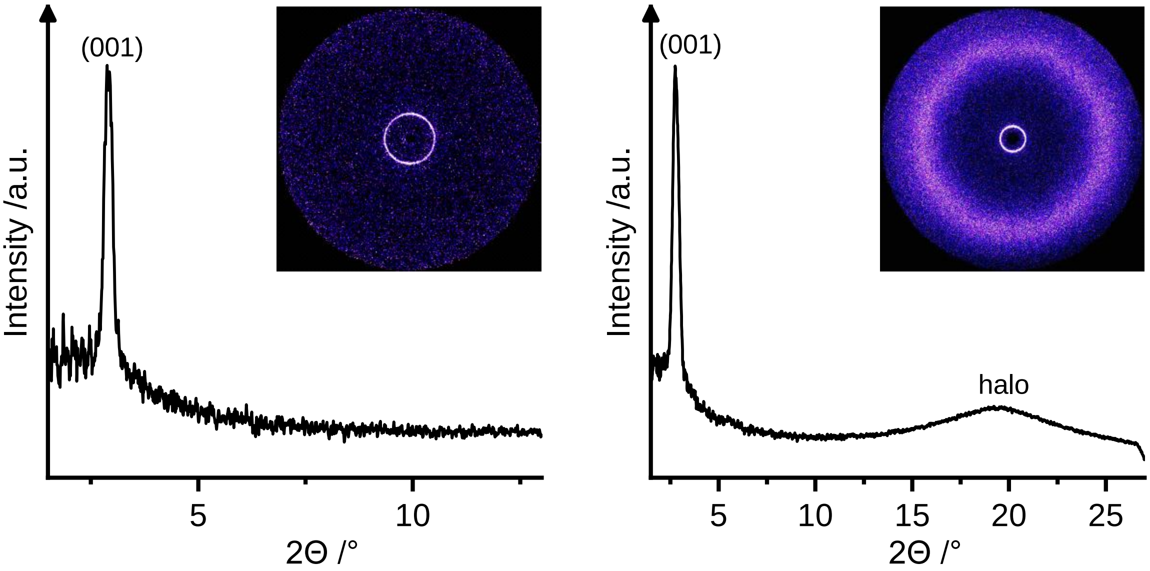


Figure S26: X-Ray scattering profile of **[C$_{16}$mim][C$_{13}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 95 °C.

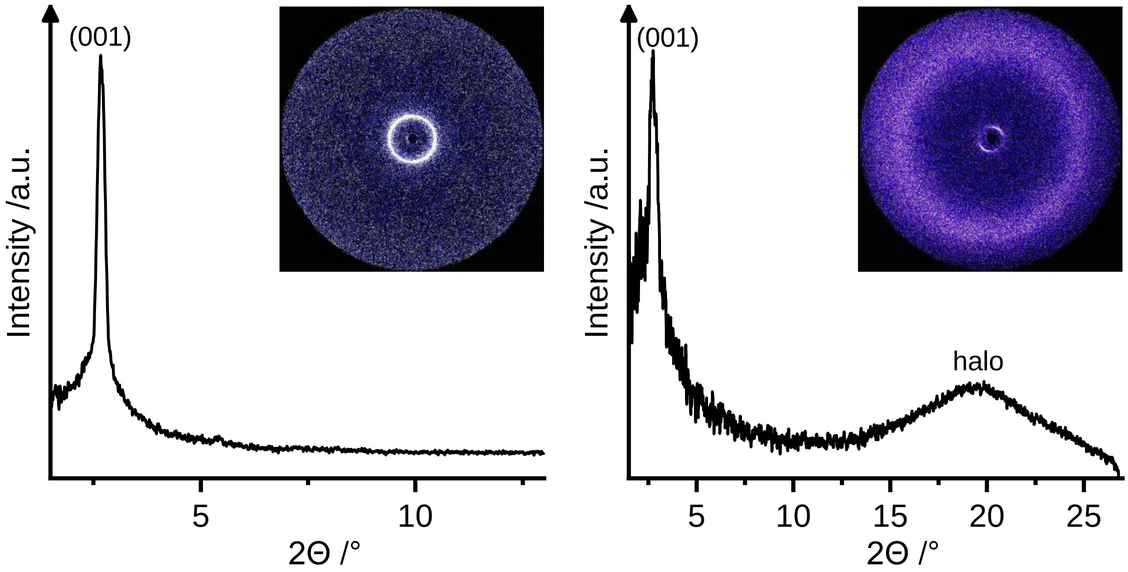


Figure S27: X-Ray scattering profile of **[C$_{10}$mim][C$_{15}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 78 °C.

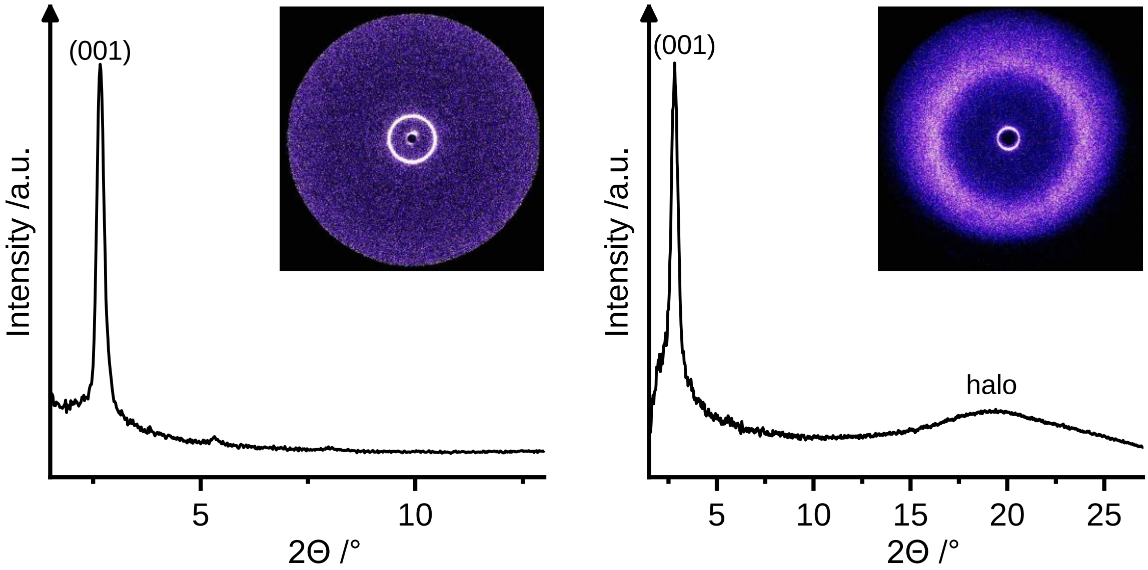


Figure S28: X-Ray scattering profile of **[C$_{12}$mim][C$_{15}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 87 °C.

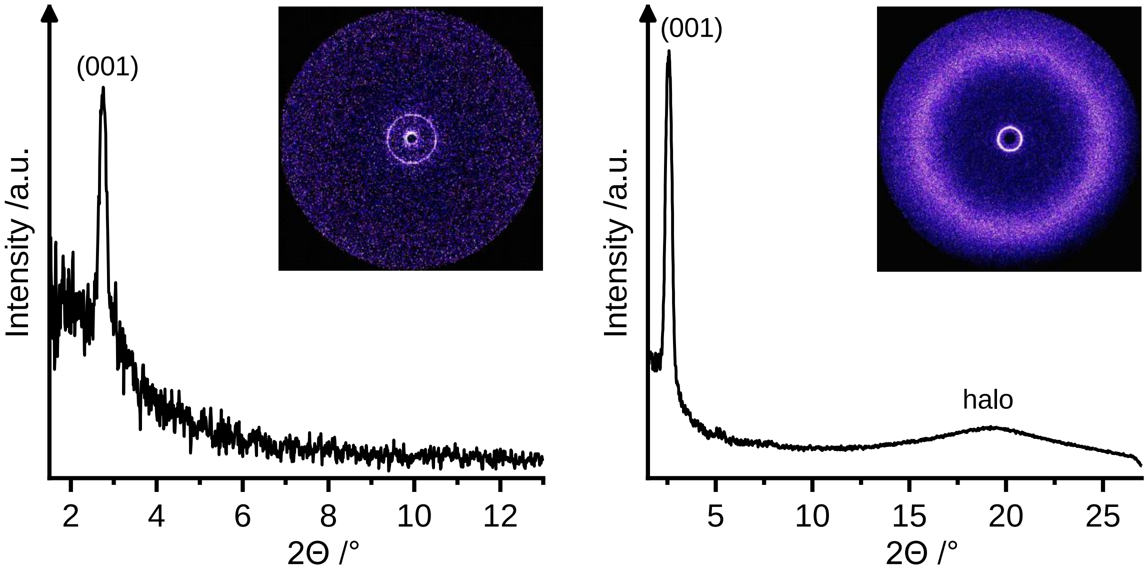


Figure S29: X-Ray scattering profile of **[C$_{14}$mim][C$_{15}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 92 °C.

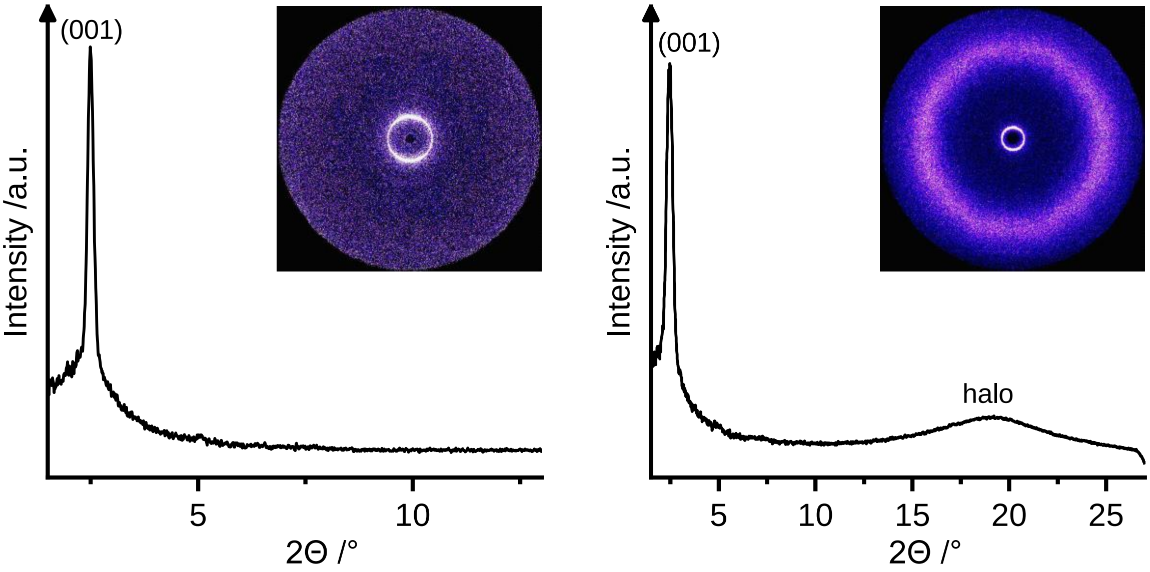


Figure S30: X-Ray scattering profile of **[C$_{16}$mim][C$_{15}$COO]** and corresponding diffraction pattern (SAXS (left); WAXS (right)) at 97 °C.

9. References

1 E. Alcalde, I. Dinarès, A. Ibáñez and N. Mesquida, *Chem. Commun.*, 2011, **47**, 3266.

2 A. Pal and S. Yadav, *J. Mol. Liq.*, 2017, **229**, 309–318.

3 H. Kumar and P. Sharma, *J. Mol. Liq.*, 2021, **322**, 114851.

4 A. A. Salman, M. Tabandeh, T. Heidelberg, R. S. D. Hussen, H. M. Ali, *Carbohydr. Res.*, 2015, **412**, 28–33.

5 E. A. Simister, R. K. Thomas, J. Penfold, R. Aveyard, B. P. Binks, P. Cooper, P. D. I. Fletcher, J. R. Lu, and A. Sokolowski, *J. Phys. Chem.*, 1992, **96**, 1383–1388.