Supporting Information

Stable Liquid Foams from a new Polyfluorinated Surfactant

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1. General Details

Reagents (Aldrich) were purchased as reagent grade and used without further purification. Reactions were performed in oven-dried glassware under Ar atmosphere. The water, used for characterization, was purified by distillation, deionization, and reserve osmosis (Milli-Q Plus). Flash column chromatography was performed using SiO_2 (60 Å, 230-400 mesh, particle size 0.040-0.063 mm, Merck). The solvent compositions are reported individually in parentheses. Analytical thin layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Macherey-Nagel) or with silica gel 60 RP-18 F_{254s} (Merck, Macherey-Nagel). Visualization was achieved using an alkaline aqueous solution of potassium permanganate ($KMnO_4$). Evaporation of solvents in vacuo was performed at 25-35 °C and 900-10 mbar. Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (0.1-0.05 mbar) before analytical characterization. ^{1}H, ^{13}C and ^{19}F and nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H), 101 MHz (^{13}C) and 376 MHz (^{19}F). Chemical shifts δ are reported in ppm upfield using the residual deuterated solvent signals as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; MeOD: δ_H = 3.31 ppm, δ_C = 49.00 ppm). For ^{1}H, ^{19}F and ^{13}C NMR, coupling constants *J* are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), pent (pentuplet), m (multiplet), and br (broad). All spectra were recorded at 298 K. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and are reported as wavenumbers ν (cm^{-1}). High resolution mass spectrometry (HRMS) and analyses were performed by the Laboratoire de Spectrométrie de Masse from Sorbonne Université, Paris. Gas Chromatography coupled to Mass Spectrometry (GC/MS) analyses were performed on a Shimadzu GC/MS-QP2010S using an electronic impact (EI) spectrometer. The abundance indicated for each mass number (*m/z* values) is given in percentage relative to the strongest peak of 100% abundance (base peak). Melting points were determined using a Büchi melting point apparatus in open capillaries. Nomenclature follows the suggestions proposed by the software ChemDraw Professional 16.0.

Surface tension of the surfactant aqueous solution was measured by using a Drop Shape Analyzer (DSA30 KRUSS).

Scanning Electron Microscopy SEM (FEI Magellan 400) at 10 kV, Transmission Electron Microscopy TEM (JEM2010F) at 200 kV were used to visualize the shape and the size of the synthesized surfactant in solution. Polydimethylsiloxane (PDMS) and the curing agent Sylgard 184 for the fabrication of the microfluidic device is bought from GMBH. In the microfluidic experiment, the gas flow is pressure-driven at a pressure p_{gas} using a MFCS™-EZ pressure controller Control Systems (Fluigent Smart Microfluidics) connected to a nitrogen tap.

Optical and Confocal microscope systems (Leica) were used to observe microfluidic fabricated foams over time. Confocal transmission images were analyzed by using a Matlab code.

2. Experimental procedures and characterization data

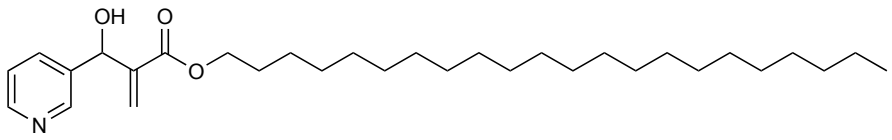
General procedure A for the Baylis-Hillman reaction

Nicotinaldehyde (1 equiv) and DABCO (1 equiv) were added to a solution of acrylate (1 equiv) in 1-octanol (2 equiv) at rt and the reaction mixture was stirred for 22 h. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography (CH_2Cl_2/EtOH = 99:1) to afford the expected compound.

General procedure B for the pyridine alkylation

Alkyl halide (1.5 equiv) was added to a solution of pyridine derivatives (1 equiv) in THF (*c* = 0.4 M). The reaction mixture was warmed to reflux and stirred for 18 h. THF was removed under reduced pressure to afford the expected pyridinium.

Docosyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 1'



Chemical Formula: $C_{31}H_{53}NO_3$
MW = 487.77 g.mol^{-1}

Nicotinaldehyde (74 µL, 0.788 mmol, 1 equiv) and DABCO (88 mg, 0.788 mmol, 1 equiv) were added to a solution of behenyl acrylate (300 mg, 0.788 mmol, 1 equiv) in 1-octanol (0.25 mL, 1.58 mmol, 2 equiv) following the general procedure **A**. Pure docosyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **1'** was isolated after purification by flash chromatography on silica gel (162 mg, 0.331 mmol, yield = 42%) as a white solid.

m.p.: 102 °C;

R_f = 0.73 (SiO_2, CH_2Cl_2/MeOH = 95:5);

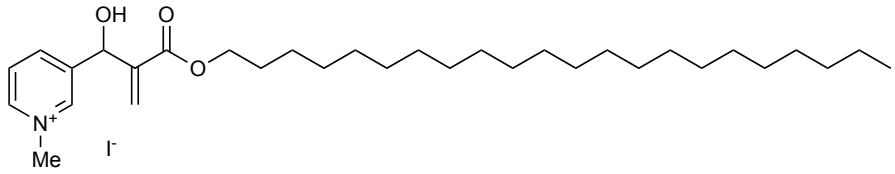
IR (ATR) ν = 3110, 2953, 2914, 2847, 1703, 1627, 1592, 1471, 1462, 1432, 1327, 1299, 1271, 1164, 1063, 1030, 956, 929 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (br s, 1H), 8.55 (br d, *J* = 4.9 Hz, 1H), 7.92 (br d, *J* = 7.9 Hz, 1H), 7.42 (dd, *J* = 7.9, 5.0 Hz, 1H), 6.41 (s, 1H), 5.92 (s, 1H), 5.36 (s, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.46 (br s, 1H, OH), 1.62 (pent$_{app}$, *J* = 6.6 Hz, 2H), 1.30-1.22 (m, 38H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 149.1, 148.6, 141.7, 137.3, 134.5, 126.5, 123.5, 71.5, 65.5, 32.1, 29.8 (11C), 29.7, 29.6, 29.5, 29.3, 28.6, 26.0, 22.8, 14.3;

HRMS (+ESI) *m/z* calcd for $C_{31}H_{54}NO_3$ $[M+H]^+$: 488.4098; found: 488.4096.

Iodo 3-(2-((docosyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 1



Chemical Formula: $C_{32}H_{56}NO_3I$
MW = 629.71 g.mol^{-1}

Iodomethane (19 μL, 0.300 mmol, 1.5 equiv) was added to a solution of docosyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **9** (100 mg, 0.205 mmol, 1 equiv) in THF (0.5 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(2-((docosyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium **1** was isolated without further purification (215 mg, 0.205 mmol, yield = quantitative) as a white solid.

m.p.: 56 °C;

R_f = 0.21 (SiO_2, CH_2Cl_2/MeOH = 96:4);

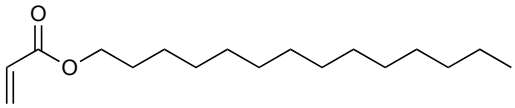
IR (ATR) ν = 3286, 3019, 2952, 2914, 2848, 1711, 1673, 1634, 1504, 1471, 1394, 1271, 1176, 1060, 973, 955, 940, 921 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (br d, *J* = 5.8 Hz, 1H), 8.97 (br s, 1H), 8.39 (br d, *J* = 8.0 Hz, 1H), 7.97 (m, 1H), 6.41 (s, 1H), 6.35 (s, 1H), 5.80 (s, 1H), 4.51 (s, 3H), 3.99 (m, 2H), 2.34 (br s, 1H, OH), 1.55 (m, 2H), 1.24-1.15 (m, 38H), 0.81 (br t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 145.1, 144.4, 143.8, 143.6, 139.7, 128.0, 127.7, 68.6, 65.4, 49.4, 31.9, 29.7 (9C), 29.6 (4C), 29.5, 29.3, 29.2, 28.4, 25.9, 22.6, 14.1;

HRMS (+ESI) *m/z* calcd for $C_{32}H_{56}NO_3$ $[M]^+$: 502.4255; found: 502.4253.

Tetradecyl acrylate, 2'



Chemical Formula: $C_{17}H_{32}O_2$
MW = 268.44 g.mol^{-1}

Triethylamine (0.13 mL, 0.931 mmol, 1 equiv) was added to a solution of 1-tetradecanol (200 mg, 0.931 mmol, 1 equiv) in THF (1.86 mL). The solution was cooled down to 0 °C, acryloyl chloride (91 μL, 1.117 mmol, 1.2 equiv) was added dropwise to the reaction media and allowed to warm up to rt for 3 h. The solvent of the reaction mixture was evaporated under reduced pressure and the crude product was diluted in CH_2Cl_2 (5 mL). The suspension was washed with an aqueous saturated NH_4Cl solution (2 x 5 mL) and brine (2 x 5 mL). The organic layer was dried over $MgSO_4$, filtrated and the solvent was evaporated under reduced pressure. The crude product was purified silica gel column chromatography (petroleum ether/CH_2Cl_2 = 60:40) to afford tetradecyl acrylate **2'** (150 mg, 0.559 mmol, yield = 60%) as a colorless oil. The spectral data were identical to those reported in the literature.[1]

R_f = 0.80 (SiO_2, Petroleum ether/CH_2Cl_2 = 50:50);

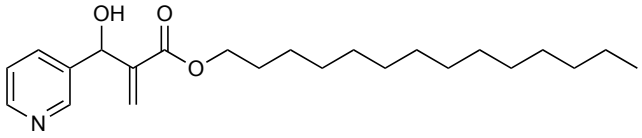
IR (ATR) ν = 2953, 2921, 2852, 2023, 1978, 1726, 1636, 1620, 1466, 1406, 1378, 1294, 1269, 1185, 1059, 984 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 16.8, 1.5 Hz, 1H), 6.12 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.67 ($pent_{App}$, *J* = 7.1 Hz, 2H), 1.26 (br s, 22H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 130.6, 128.8, 64.9, 32.1, 29.8 (4C), 29.7 (2C), 29.5, 29.4, 28.8, 26.1, 22.8, 14.3;

GC-MS (+ESI) *m/z*: 240 (M-$C_2H_4^{+\cdot}$, 0.2), 127 (14), 125 (7), 113 (14), 112 (5), 111 (17), 110 (6), 98 (10), 97 (35), 96 (9), 85 (9), 84 (17), 83 (43), 82 (17), 81 (6), 73 (41), 71 (18), 70 (33), 69 (46), 68 (13), 67 (10), 57 (41), 56 (33), 55 (100), 54 (7).

Tetradecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 2"



Chemical Formula: $C_{23}H_{37}NO_3$
MW = 375.55 $g.mol^{-1}$

Nicotinaldehyde (34 μL, 0.358 mmol, 1 equiv) and DABCO (40 mg, 0.358 mmol, 1 equiv) were added to a solution of tetradecyl acrylate **2'** (96 mg, 0.358 mmol, 1 equiv) in 1-octanol (0.12 mL, 0.716 mmol, 2 equiv) following the general procedure **A**. Pure tetradecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **2"** was isolated after purification by flash chromatography on silica gel (107 g, 0.283 mmol, yield = 79%) as a white solid.

m.p.: 80 °C;

R_f = 0.70 (SiO_2, CH_2Cl_2/MeOH = 95:05);

IR (ATR) ν = 3117, 2914, 2849, 1712, 1634, 1594, 1582, 1471, 1434, 1325, 1298, 1262, 1172, 1151, 1128, 1064, 1032, 974 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (br s_{App}, 1H), 8.53 (br s_{App}, 1H), 7.74 (br d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.39 (s, 1H), 5.86 (br s, 1H), 5.60 (br s, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.41 (br s, OH), 1.61 (m, 2H), 1.31-1.25 (m, 22H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 149.2, 148.6, 141.6, 137.1, 134.4, 126.7, 123.5, 71.6, 65.5, 32.1, 29.8 (4C), 29.7, 29.6, 29.5, 29.3, 28.6, 26.0, 22.8, 14.3;

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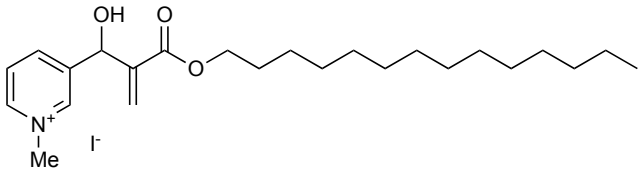
[1] Miller, J. B.; Zhang, S.; Kos, P.; Xiong, H.; Zhou, K.; Perelman, S. S.; Zhu, H.; Siegwart, D. J. *Angew. Chem. Int. Ed.* **2017**, *56*, 1059-1063.

HRMS (+ESI) *m/z* calcd for $C_{23}H_{37}NO_3$ $[M+H]^+$: 376.2846; found: 376.2846.

Iodo 3-(1-hydroxy-2-((tetradecyloxy)carbonyl)allyl)-1-methylpyridin-1-ium, 2



Chemical Formula: $C_{24}H_{40}NO_3I$
MW = 517.49 g.mol^{-1}

Iodomethane (13 μL, 0.200 mmol, 1.5 equiv) was added to a solution of tetradecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **2"** (50 mg, 0.133 mmol, 1 equiv) in THF (0.33 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(1-hydroxy-2-((tetradecyloxy)carbonyl)allyl)-1-methylpyridin-1-ium **2** was isolated without further purification (58 mg, 0.112 mmol, yield = 85%) as a yellowish solid.

m.p.: 82 °C;

R_f = 0.38 (SiO_2, CH_2Cl_2/MeOH = 95:05);

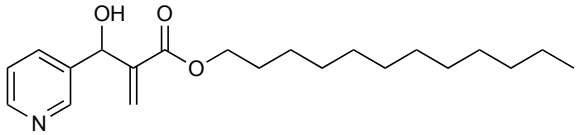
IR (ATR) ν = 3248, 3014, 2951, 2912, 2848, 1725, 1706, 1633, 1503, 1474, 1404, 1327, 1313, 1277, 1267, 1243, 1155, 1130, 1066, 973 (cm^{-1});

^{1}H NMR (400 MHz, MeOD) δ 8.99 (s, 1H), 8.82 (d, *J* = 6.0 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.04 (dd, *J* = 8.0, 6.1 Hz, 1H), 6.46 (s, 1H), 6.28 (s, 1H), 5.76 (s, 1H), 4.44 (s, 3H), 4.10 (m, 2H), 1.62 (m, 2H), 1.29 (m, 22H), 0.90 (t, *J* = 7.6 Hz, 3H), OH was not visible;

^{13}C NMR (101 MHz, MeOD) δ 166.5, 146.1, 145.4 (2C), 144.5, 142.7, 128.6, 128.0, 70.0, 66.2, 49.1, 33.1, 30.8 (2C), 30.7 (2C), 30.67, 30.6, 30.5, 30.3, 29.6, 27.0, 23.7, 14.4;

HRMS (+ESI) *m/z* calcd for $C_{24}H_{40}NO_3$ $[M+H]^+$: 390.3003; found: 390.3003.

Dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate, 3'



Chemical Formula: $C_{21}H_{33}NO_3$
MW = 347.50 g.mol^{-1}

Nicotinaldehyde (1 mL, 10.65 mmol, 1 equiv) and DABCO (1.20 g, 10.65 mmol, 1 equiv) were added to a solution of lauryl acrylate (2.56 g, 10.65 mmol, 1 equiv) in 1-octanol (3.36 mL, 21.31 mmol, 2 equiv) following the general procedure **A**. Pure dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **3'** was isolated after purification by flash chromatography on silica gel (2.63 g, 7.56 mmol, yield = 71%) as a white solid.
m.p.: 78 °C;

R_f = 0.63 (SiO_2, CH_2Cl_2/MeOH = 95:05);

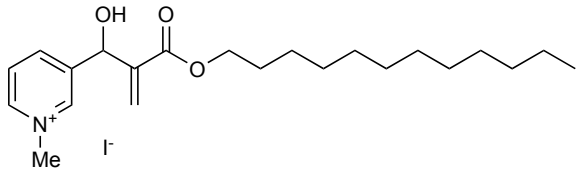
IR (ATR) ν = 3098, 2951, 2915, 2847, 1703, 1627, 1592, 1462, 1431, 1402, 1326, 1298, 1269, 1163, 1066, 954 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (br s, 1H), 8.53 (br d, *J* = 4.4 Hz, 1H), 7.75 (dt_{app}, *J* = 7.9, 1.7 Hz, 1H), 7.30 (dd, *J* = 7.8, 4.4 Hz, 1H), 6.39 (s, 1H), 5.87 (s, 1H), 5.60 (s, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.37 (br s, 1H, OH), 1.61 ($pent_{app}$, *J* = 6.6 Hz, 2H), 1.35-1.21 (m, 18H), 1.88 (t, *J* = 9.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 149.0, 148.5, 141.7, 137.3, 134.6, 126.5, 123.5, 71.4, 65.5, 32.0, 29.8, 29.7 (2C), 29.6, 29.5, 29.3, 28.6, 26.0, 22.8, 14.3;

HRMS (+ESI) *m/z* calcd for $C_{21}H_{34}NO_3$ $[M+H]^+$: 348.2533; found: 348.2532.

Iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 3



Chemical Formula: $C_{22}H_{36}NO_3I$
MW = 489.44 $g.mol^{-1}$

Iodomethane (105 μL, 1.68 mmol, 1.5 equiv) was added to a solution of dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **3'** (390 mg, 1.12 mmol, 1 equiv) in THF (2.81 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium **3** was isolated without further purification (530 mg, 1.09 mmol, yield = 97%) as a yellow oil.

R_f = 0.35 (SiO_2, CH_2Cl_2/MeOH = 95:5);

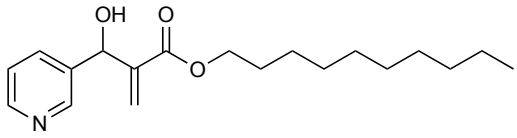
IR (ATR) ν = 3283, 2920, 2851, 1706, 1634, 1501, 1466, 1401, 1323, 1282, 1155, 1050, 960, 917 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05-9.00 (m, 2H), 8.43 (d, *J* = 8.1 Hz, 1H), 7.99 (dd, *J* = 7.9, 6.8 Hz, 1H), 6.48 (s, 1H), 6.42 (s, 1H), 5.86 (d, *J* = 5.1 Hz, 1H), 4.96 (d, *J* = 5.1 Hz, 1H, OH), 4.53 (s, 3H), 4.10-3.98 (m, 2H), 1.60 ($pent_{app}$, *J* = 6.7 Hz, 2H), 1.31-1.15 (m, 18H), 0.86 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 145.1, 144.8, 143.9, 143.7, 139.4, 128.5, 127.8, 68.8, 65.6, 49.6, 32.0, 29.7 (2C), 29.6, 29.4, 29.3, 28.6, 26.0, 25.5, 22.8, 14.2;

HRMS (+ESI) *m/z* calcd for $C_{22}H_{36}NO_3$ $[M]^+$: 362.2690; found: 362.2687.

Decyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 4'



Chemical Formula: $C_{19}H_{29}NO_3$
MW = 319.45 g.mol^{-1}

Nicotinaldehyde (0.14 mL, 1.50 mmol, 1 equiv) and DABCO (168 mg, 1.50 mmol, 1 equiv) were added to a solution of decyl acrylate (0.36 mL, 1.50 mmol, 1 equiv) in 1-octanol (0.47 mL, 3.00 mmol, 2 equiv) following the general procedure **A**. Pure decyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **4'** was isolated after purification by flash chromatography on silica gel (470 g, 1.41 mmol, yield = 94%) as a white solid.

m.p.: 81 °C;

R_f = 0.56 (SiO_2, CH_2Cl_2/MeOH = 95:5);

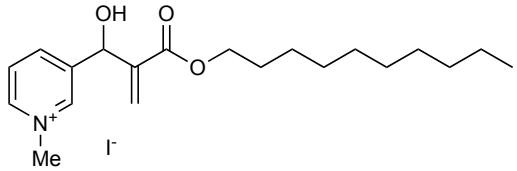
IR (ATR) ν = 3170, 2955, 2925, 2870, 1712, 1629, 1593, 1461, 1426, 1380, 1323, 1259, 1148, 1056, 1039, 1028, 956 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (br s, 1H), 8.46 (br d, *J* = 3.7 Hz, 1H), 7.74 (br dt_{app}, *J* = 7.9, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.38 (br s, 1H), 5.91 (br d, *J* = 1.0 Hz, 1H), 5.58 (br s, 1H), 4.09 (t, *J* = 3.7 Hz, 2H), 3.87 (br s, 1H, OH), 1.59 ($pent_{app}$, *J* = 6.5 Hz, 2H), 1.31-1.25 (m, 14H), 0.87 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 148.9, 148.5, 141.8, 137.4, 134.6, 126.4, 123.5, 71.3, 65.4, 32.0, 29.6 (2C), 29.4, 29.3, 28.6, 26.0, 22.8, 14.2;

HRMS (+ESI) *m/z* calcd for $C_{19}H_{30}NO_3$ $[M+H]^+$: 320.2220; found: 320.2223.

Iodo 3-(2-((decyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 4



Chemical Formula: $C_{20}H_{32}NO_3I$
MW = 461.39 g.mol^{-1}

Iodomethane (56 µL, 0.900 mmol, 1.5 equiv) was added to a solution of decyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **4'** (200 mg, 0.600 mmol, 1 equiv) in THF (1.5 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(2-((decyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium **4** was isolated without further purification (257 mg, 1.09 mmol, yield = 93%) as a yellow oil.

R_f = 0.13 (SiO_2, CH_2Cl_2/MeOH = 96:4);

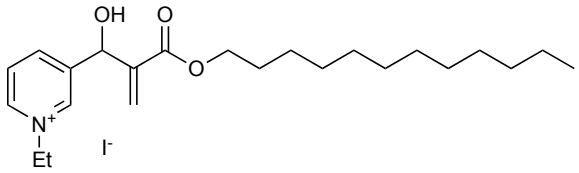
IR (ATR) ν = 3279, 3032, 2954, 2922, 2852, 2185, 1706, 1633, 1502, 1466, 1402, 1371, 1322, 1282, 1238, 1155, 1047, 962, 917 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (br d, *J* = 6.0 Hz, 1H), 8.92 (br s, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 7.95 (dd, *J* = 7.8, 6.2 Hz, 1H), 6.36 (br s, 1H), 6.30 (s, 1H), 5.77 (br s, 1H), 4.88 (br d, *J* = 4.7 Hz, 1H, OH), 4.46 (s, 3H), 3.94 (m, 2H), 1.50 (m, 2H), 1.24-1.06 (m, 14 H), 076 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 144.5, 144.1, 143.7, 143.5, 139.3, 128.2, 127.6, 68.3, 65.2, 49.4, 31.6, 29.3 (2C), 29.0 (2C), 28.2, 25.7, 22.4, 13.9;

HRMS (+ESI) *m/z* calcd for $C_{20}H_{32}NO_3$ $[M]^+$: 334.2377; found: 334.2377.

Iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium, 5



Chemical Formula: $C_{23}H_{38}NO_3I$
MW = 503.47 g.mol^{-1}

Iodoethane (0.14 mL, 1.73 mmol, 1.5 equiv) was added to a solution of dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **3'** (400 mg, 1.15 mmol, 1 equiv) in THF (2.88 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium **5** was isolated without further purification (580 mg, 1.15 mmol, yield = quantitative) as an orange oil.

R_f = 0.43 (SiO_2, CH_2Cl_2/MeOH = 95:5);

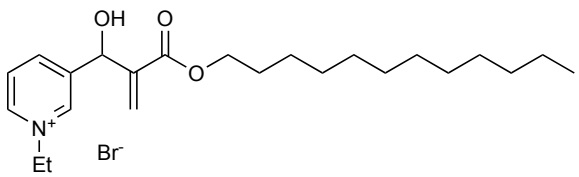
IR (ATR) ν = 3250, 2971, 2923, 2845, 1758, 1725, 1610, 1582, 1514, 1461, 1443, 1403, 1377, 1352, 1318, 1299, 1251, 1209, 1201, 1180, 1159, 1127, 1029, 996, 948, 931 (cm^{-1});

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 9.03 (m, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 7.99 (t_{app}, *J* = 6.1 Hz, 1H), 6.50 (s, 1H), 6.44 (s, 1H), 5.89 (d, *J* = 5.2 Hz, 1H), 5.05 (d, *J* = 5.2 Hz, 1H), 4.80 (q, *J* = 7.4 Hz, 2H), 4.13-4.98 (m, 2H), 1.72 (t, *J* = 7.4 Hz, 3H), 1.60 ($pent_{app}$, *J* = 6.6 Hz, 2H), 1.34-1.20 (m, 18H), 0.86 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 145.5, 143.8, 143.6, 142.7, 139.5, 128.1, 128.0, 68.7, 65.4, 57.7, 31.9, 29.7 (2C), 29.6 (2C), 29.4, 29.3, 28.5, 25.9, 22.7, 17.0, 14.2;

HRMS (+ESI) *m/z* calcd for $C_{23}H_{38}NO_3$ $[M]^+$: 376.2846; found: 376.2848.

Bromo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium, 6



Chemical Formula: $C_{23}H_{38}NO_3Br$
MW = 456.47 g.mol^{-1}

Bromoethane (0.13 mL, 1.73 mmol, 1.5 equiv) was added to a solution of dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **3'** (400 mg, 1.15 mmol, 1 equiv) in THF (2.88 mL) following the general procedure **B**. After evaporation of the solvent, the crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 80:20). Pure bromo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium **6** was obtained (580 mg, 1.15 mmol, yield = 41%) as a brown oil.

R_f = 0.42 (SiO_2, CH_2Cl_2/MeOH = 9:1);

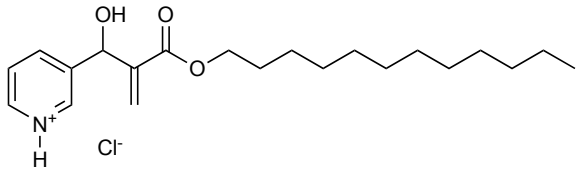
IR (ATR) ν = 3220, 2920, 2851, 1707, 1630, 1499, 1457, 1322, 1270, 1260, 1154, 1060, 959 (cm^{-1});

^{1}H NMR (400 MHz, MeOD) δ 9.09 (s, 1H), 8.92 (m, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.06 ($t_{app,}$ *J* = 7.4 Hz, 1H), 6.47 (s, 1H), 6.30 (s, 1H), 5.76 (br s, 1H), 4.71 (m, 2H), 4.10 (m, 2H), 1.66 (t, *J* = 7.4 Hz, 3H), 1.61 (m, 2H), 1.32-1.28 (m, 18H), 0.90 (t, *J* = 6.5 Hz, 3H), OH not visible;

^{13}C NMR (101 MHz, MeOD) δ 166.5, 146.5, 144.7, 144.3 (2C), 142.7, 129.0, 128.0, 70.1, 66.2, 58.6, 33.1, 30.7 (3C), 30.6, 30.5, 30.3, 29.6, 27.0, 23.7, 17.0, 14.5;

HRMS (+ESI) *m/z* calcd for $C_{23}H_{38}NO_3$ $[M]^+$: 376.2846; found: 376.2843.

Chloro 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)pyridin-1-ium, 7



Chemical Formula: $C_{21}H_{34}NO_3Cl$
MW = 383.76 $g.mol^{-1}$

Acetyl chloride (1.23 mL, 17.27 mmol, 15 equiv) was added at 0 °C to ethanol (1.21 mL, 20.72 mmol, 18 equiv) and the reaction mixture was warmed up to rt for 10 min. The reaction media was cooled to 0 °C and a solution of dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate **3'** (400 mg, 1.15 mmol, 1 equiv) in CH_2Cl_2/EtOH (9:1) (6.14 mL) was added. The reaction mixture was warmed up to rt and stirred for 18 h. The solvents were evaporated under reduced pressure to afford the expected chloro 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)pyridin-1-ium **7** without further purification (432 mg, 1.13 mmol, yield = 98%) as a white solid.

m.p: 86 °C;

R_f = 0.32 (SiO_2, CH_2Cl_2/MeOH 96:4);

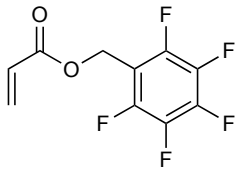
IR (ATR) ν = 3215, 3011, 2950, 2911, 2849, 2550, 2119, 1999, 1706, 1628, 1609, 1554, 1476, 1406, 1377, 1326, 1304, 1243, 1162, 1115, 1069, 968, 934 (cm^{-1});

^{1}H NMR (400 MHz, MeOD) δ 9.10 (br s, 1H), 8.73 (br d, *J* = 5.5 Hz, 1H), 8.83 (br d, *J* = 8.9 Hz, 1H), 8.26 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.64 (s, 1H), 6.47 (s, 1H), 5.95 (s, 1H), 5.09 (br s, NH + OH), 4.27 (m, 2H), 1.78 (m, 2H), 1.52-1.42 (m, 18H), 1.08 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (101 MHz, MeOD) δ 167.9, 147.7, 147.1, 144.3, 142.9, 142.8, 129.7, 129.2, 71.5, 67.6, 34.5, 32.2 (2C), 32.1, 32.0, 31.9, 31.7, 31.0, 28.4, 25.1, 15.9;

HRMS (+ESI) *m/z* calcd for $C_{21}H_{34}NO_3$ $[M]^+$: 348.2533; found: 348.2534.

(Perfluorophenyl)methyl acrylate, 8'[2]



Chemical Formula: $C_{10}H_5F_5O_2$
MW = 252.14 g.mol^{-1}

Triethylamine (0.20 mL, 2.40 mmol, 1.2 equiv) was added to a solution of pentafluorobenzyl alcohol (404 mg, 2.00 mmol, 1 equiv) in THF (4 mL). The reaction mixture was cooled down to 0 °C and acryloyl chloride (0.28 mL, 2 mmol, 1 equiv) was added dropwise. The media was warmed up to rt and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and washed with a saturated aqueous solution of NH_4Cl (2 x 5 mL) and brine (2 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (Petroleum ether/AcOEt = 95:5). Pure (perfluorophenyl)methyl acrylate **8'** was isolated (180 mg, 0.74 mmol, yield = 36%) as a colorless oil. The spectral data of **8'** were identical to those reported in the literature.[2]

R_f = 0.82 (SiO_2, Petroleum ether/AcOEt = 96:4);

IR (ATR) ν = 2969, 1731, 1657, 1635, 1522, 1502, 1407, 1376, 1309, 1294, 1259, 1169, 1129, 1050, 983, 964, 936 (cm^{-1});

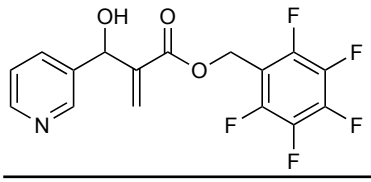
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.12 (dd, *J* = 10.5, 1.3 Hz, 1H), 5.85 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.28 (t_{app}, *J* = 1.5 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 145.8 (dm, *J* = 251.8 Hz, 2C), 141.9 (dm, *J* = 253.3 Hz), 137.6 (dm, *J* = 252.5 Hz, 2C), 132.2, 127.5, 109.6 (td, *J* = 17.8, 3.9 Hz), 53.5 (d = doublet);

^{19}F NMR (376 MHz, $CDCl_3$) δ -141.86 (m), -152.59 (td, *J* = 9.3, 22.9 Hz), -161.66 (tt, *J* = 9.1, 19.5 Hz);

MS (+EI) *m/z*: 252 ($M^{+\cdot}$, 17), 209 (16), 206 (11), 196 (8), 188 (13), 187 (6), 181 (69), 161 (11), 56 (7), 55 (100).

(Perfluorophenyl)methyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 8"



Chemical Formula: $C_{16}H_{10}F_5NO_3$
MW = 359.25 g.mol^{-1}

[2] Noy, J.-M.; Friedrich, A.-K.; Kyle Batten, K.; Bhebhe, M. N.; Busatto, N.; Batchelor, R. R.; Kristanti, A.; Pei, Y.; Roth P. J. *Macromolecules* **2017**, *50*, 7028-7040.

Nicotinaldehyde (30 µL, 0.321 mmol, 1 equiv) and DABCO (36 mg, 0.321 mmol, 1 equiv) were added to a solution of (perfluorophenyl)methyl acrylate **8'** (81 mg, 0.321 mmol, 1 equiv) in 1-octanol (0.10 mL, 0.642 mmol, 2 equiv) following the general procedure **A**. Pure (perfluorophenyl)methyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **8"** was isolated after purification by flash chromatography on silica gel (86 mg, 0.241 mmol, yield = 75%) as a white solid.

m.p.: 142 °C;

R_f = 0.29 (SiO_2, CH_2Cl_2/MeOH = 96:4);

IR (ATR) ν = 3180, 3067, 1709, 1661, 1627, 1526, 1504, 1434, 1392, 1326, 1308, 1289, 1148, 1133, 1047, 993, 972, 930 (cm^{-1});

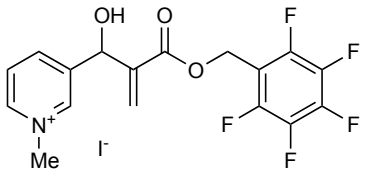
^{1}H NMR (400 MHz, MeOD) δ 8.63 (br s, 1H), 8.59 (br d, *J* = 3.9 Hz, 1H), 7.94 (dt_{app}, *J* = 7.9, 1.8 Hz, 1H), 7.54 (dd, *J* = 7.8, 4.9 Hz, 1H), 6.60 (t_{app}, *J* = 1.2 Hz, 1H), 6.38 (t_{app}, *J* = 1.3 Hz, 1H), 5.74 (br s, 1H), 5.47 (br d, J_{AB} = 14.4 Hz, 1H), 5.46 (br d, J_{AB} = 14.4 Hz, 1H), 5.06 (s, 1H, OH + H_2O);

^{13}C NMR (101 MHz, MeOD) δ 166.0, 149.3, 149.1, 146.3 (dm, *J* = 253.3 Hz, 2C), 143.4, 143.0 (dm, *J* = 252.0 Hz), 140.0, 138.8 (dm, *J* = 249.5 Hz, 2C), 136.8, 126.8, 125.0, 111.0 (td, *J* = 20.9, 4.2 Hz), 70.8, 54.4 (d = doublet);

^{19}F NMR (376 MHz, MeOD) δ -144.37 (dd, *J* = 8.4, 20.9 Hz), -156.12 (t, *J* = 23.3 Hz), -164.98 (td, *J* = 23.3, 7.3 Hz);

HRMS (+ESI) *m/z* calcd for $C_{16}H_{11}F_5NO_3$ $[M+H]^+$: 360.0654; found: 360.0653.

Iodo 3-(1-hydroxy-2-(((perfluorophenyl)methoxy)carbonyl)allyl)-1-methylpyridin-1-ium, 8



Chemical Formula: $C_{17}H_{13}F_5NO_3I$
MW = 501.19 g.mol^{-1}

Iodomethane (13 µL, 0.209 mmol, 1.5 equiv) was added to a solution of (perfluorophenyl)methyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **8"** (50 mg, 0.139 mmol, 1 equiv) in THF (0.35 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(1-hydroxy-2-(((perfluorophenyl)methoxy)carbonyl)allyl)-1-methylpyridin-1-ium **8** was isolated without further purification (76 mg, 0.139 mmol, yield = quantitative) as a yellow oil.

R_f = 0.09 (SiO_2, CH_2Cl_2/MeOH = 96:4);

IR (ATR) ν = 3282, 3026, 1716, 1658, 1635, 1522, 1503, 1379, 1306, 1254, 1129, 1050, 963, 937 (cm^{-1});

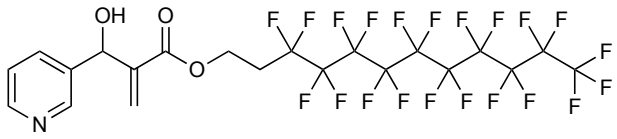
^{1}H NMR (400 MHz, MeOD) δ 9.19 (br s, 1H), 9.05 (br d, *J* = 6.0 Hz, 1H), 8.72 (br d, *J* = 8.1 Hz, 1H), 8.24 (dd, *J* = 8.1, 6.0 Hz, 1H), 6.66 (t_{app}, *J* = 0.8 Hz, 1H), 6.52 (t_{app}, *J* = 1.1 Hz, 1H), 5.95 (s, 1H), 5.49 (dt_{app}, J_{AB} = 12.5, 1.6 Hz, 1H), 5.45 (dt_{app}, J_{AB} = 12.5, 1.8 Hz, 1H) 4.99 (s, 1H, OH + H_2O), 4.65 (s, 3H);

^{13}C NMR (101 MHz, MeOD) δ 165.7, 147.1 (dm, *J* = 246.4 Hz, 2C), 145.7, 145.5, 145.4, 144.5, 143.1 (dm, *J* = 248.7 Hz), 141.8, 138.8 (dm, *J* = 250.4 Hz, 2C), 129.6, 128.7, 111.0 (td, *J* = 17.6, 3.7 Hz), 69.9, 55.0, 49.3 (determined by HSQC);

^{19}F NMR (376 MHz, MeOD) δ -144.20 (dd, *J* = 20.9, 12.2 Hz), -150.90 (t, *J* = 19.9 Hz), -164.85 (td, *J* = 21.8, 6.4 Hz);

HRMS (+ESI) *m/z* calcd for $C_{17}H_{13}F_5NO_3$ $[M]^+$: 374.0810; found: 374.0810.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafluorododecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 9'



Chemical Formula: $C_{21}H_{12}F_{21}NO_3$
MW = 725.30 g.mol^{-1}

Nicotinaldehyde (0.26 mL, 2.76 mmol, 1 equiv) and DABCO (309 mg, 2.76 mmol, 1 equiv) were added to a solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl acrylate (1.71 g, 2.76 mmol, 1 equiv) in 1-octanol (0.87 mL, 5.52 mmol, 2 equiv) and DMF (8.8 mL) and warmed up to 40 °C for 48 h following the general procedure **A**. Pure 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **9'** was isolated after purification by flash chromatography on silica gel (497 mg, 0.690 mmol, yield = 25%) as a white solid.

m.p.: 102 °C;

R_f = 0.50 (SiO_2, CH_2Cl_2/MeOH = 9:1);

IR (ATR) ν = 1717, 1427, 1373, 1342, 1198, 1147, 1083, 1056, 1002, 899 (cm^{-1});

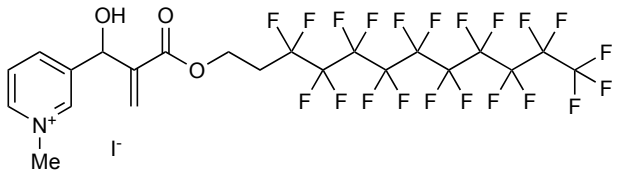
The product is unsoluble in most of the solvent (MeOD, DMSO-d_6, D_2O, THF-d_8, C_6D_6) but partially soluble in pyridine-d_5 with few drops of MeOD and in hexafluorobenzene aslo with few drops of MeOD.
^{1}H NMR (400 MHz, Pyridine-d_5 + MeOD) δ 8.64 (m, 1H), 7.83 (m, 1H), 7.17-7.09 (m, 1H), 6.48 (s, 1H), 6.42 (s, 1H), 5.99 (br s, 1H), 5.52 (br s, 3H, OH + H_2O), 4.38-4.27 (m, 2H), 2.58-2.45 (m, 2H);

^{1}H NMR (400 MHz, Hexafluorobenzene + MeOD) δ 8.54 (br s, 1H), 8.40 (br s, 1H), 7.80 (br s, 1H), 7.37 (br s, 1H), 6.45 (br s, 1H), 6.19 (br s, 1H), 5.58 (br s, 1H), 4.68 (br s, 3H, OH + H_2O), 4.45 (m, 2H), 2.56 (m, 2H);

^{19}F NMR (376 MHz, Pyridine-d_5 + MeOD) δ -79.7 (t, *J* = 9.6 Hz), -112.1 (t, *J* = 11.2 Hz), -120.6 (m), -121.6 (m), -122.3 (m), -125.0 (m);

HRMS (+ESI) *m/z* calcd for $C_{21}H_{13}F_{21}NO_3$ $[M+H]^+$: 726.0555; found: 726.0554.

Iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)oxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 9



Chemical Formula: $C_{22}H_{15}F_{21}NO_3I$
MW = 867.24 g.mol^{-1}

Iodomethane (13 μL, 0.138 mmol, 1.5 equiv) was added to a solution of (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **9'** (100 mg, 0.138 mmol, 1 equiv) in THF (0.35 mL) following the general procedure **B**. After evaporation of the solvent, the crude product was precipitated in CH_2Cl_2 and filtrated. Pure iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)oxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium **9** was isolated (77 mg, 0.090 mmol, yield = 65%) as a yellowish solid.

m.p.: 172 °C;

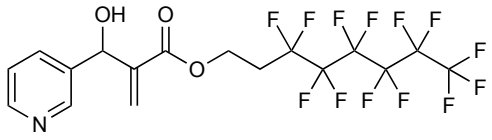
R_f = 0.28 (SiO_2, CH_2Cl_2/MeOH = 9:1);

IR (ATR) ν = 3371, 3044, 1707, 1637, 1502, 1476, 1342, 1307, 1199, 1146, 1112, 1087, 1055, 1007, 978 (cm^{-1});

The product is unsoluble in most of the solvent (MeOD, DMSO-d_6, D_2O, THF-d_8, C_6D_6, Pyridine-d_5) but partially soluble in hexafluorobenzene with few drops of MeOD.
^{1}H NMR (400 MHz, Hexafluorobenzene + MeOD) δ 9.13 (br s, 1H), 9.06 (br d, *J* = 5.5 Hz, 1H), 8.64 (br d, *J* = 8.0 Hz, 1H), 8.18 (t_{app}, *J* = 6.5 Hz, 1H), 6.61 (s, 1H), 6.46 (s, 1H), 5.87 (s, 1H), 4.64 (s, 3H), 4.53 (m, 2H), 2.68 (m, 2H).

HRMS (+ESI) *m/z* calcd for $C_{22}H_{15}F_{21}NO_3$ $[M]^+$: 740.0711; found: 740.0714.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 10'



Chemical Formula: $C_{17}H_{12}F_{13}NO_3$
MW = 525.27 g.mol^{-1}

Nicotinaldehyde (94 μL, 1.00 mmol, 1 equiv) and DABCO (112 mg, 1.00 mmol, 1 equiv) were added to a solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (0.28 mL, 1.00 mmol, 1 equiv) in 1-octanol (0.32 mL, 2.00 mmol, 2 equiv) following the general procedure **A**. Pure 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **10'** was isolated after purification by flash chromatography on silica gel (485 mg, 0.920 mmol, yield = 92%) as a white solid.

m.p.: 77 °C;

R_f = 0.58 (SiO_2, CH_2Cl_2/MeOH = 95:5);

IR (ATR) ν = 3173, 1711, 1332, 1319, 1298, 1242, 1228, 1186, 1156, 1138, 1078, 1058, 1001, 969, 922 (cm^{-1});

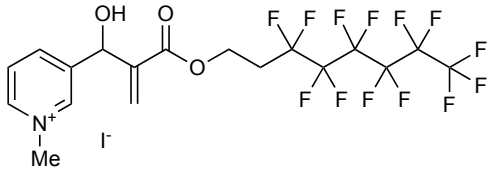
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (br s, 1H), 8.50 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.73 (dt_{app}, *J* = 7.9, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.43 (s, 1H), 6.00 (s, 1H), 5.61 (s, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 3.50 (br s, 1H, OH), 2.51-2.40 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 148.4, 148.3, 141.7, 138.1, 135.1, 126.6, 123.6, 121.9-105.3 (m, 6C), 70.1, 56.7 (br t, *J* = 6.7 Hz), 30.4 (t, *J* = 21.8 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.11 (t, *J* = 9.1 Hz), -113.85 (m), -122.08 (m), -123.09 (m), -123.76 (m), -126.40 (m);

HRMS (+ESI) *m/z* calcd for $C_{17}H_{13}F_{13}NO_3$ $[M+H]^+$: 526.0682; found: 526.0685.

Iodo 3-(1-hydroxy-2-(((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy)carbonyl)allyl)-1-methylpyridin-1-ium, 10



Chemical Formula: $C_{18}H_{15}F_{13}NO_3I$
MW = 667.21 g.mol^{-1}

Iodomethane (36 μL, 0.571 mmol, 1.5 equiv) was added to a solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **10'** (200 mg, 0.381 mmol, 1 equiv) in THF (0.95 mL) following the general procedure **B**. After evaporation of the solvent, iodo 3-(1-hydroxy-2-(((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy)carbonyl)allyl)-1-methylpyridin-1-ium **10** was isolated without further purification (270 mg, 0.381 mmol, yield = quantitative) as a yellow solid.

m.p.: 110 °C;

R_f = 0.12 (SiO_2, CH_2Cl_2/MeOH = 9:1);

IR (ATR) ν = 3371, 3044, 1706, 1637, 1504, 1477, 1365, 1310, 1232, 1190, 1163, 1139, 1121, 1089, 1057, 1007, 964, (cm^{-1});

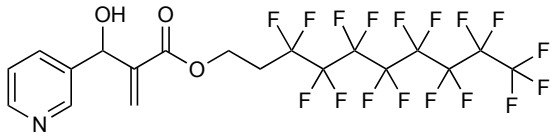
^{1}H NMR (400 MHz, MeOD) δ 9.02 (br s, 1H), 8.88 (br d, *J* = 6.1 Hz, 1H), 8.57 (br d, *J* = 8.1 Hz, 1H), 8.08 (dd, *J* = 8.1, 6.1 Hz, 1H), 6.51 (s, 1H), 6.34 (s, 1H), 5.81 (s, 1H), 4.48 (s, 3H), 4.50-4.40 (m, 2H), 2.64 (tt_{app}, *J* = 19.0, 6.0 Hz, 2H), OH not visible;

^{13}C NMR (101 MHz, MeOD) δ 166.0, 145.8, 145.5, 145.4, 144.6, 142.0, 129.1, 128.7, 123.1-106.6 (m, 6C), 69.8, 58.2 (t, *J* = 4.7 Hz), 49.4 (determined by HSQC), 31.1 (t, *J* = 21.4 Hz);

^{19}F NMR (376 MHz, MeOD) δ -82.43 (t, *J* = 10 Hz), -114.66 (m), -122.90 (m), -123.91 (m), -124.56 (m), -127.35 (m);

HRMS (+ESI) *m/z* calcd for $C_{18}H_{15}F_{13}NO_3$ $[M]^+$: 540.0839; found: 540.0833.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 11'



Chemical Formula: $C_{19}H_{12}F_{17}NO_3$
MW = 625.28 g.mol^{-1}

Nicotinaldehyde (0.47 mL, 5.00 mmol, 1 equiv) and DABCO (561 mg, 5.00 mmol, 1 equiv) were added to a solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (1.58 mL, 5.00 mmol, 1 equiv) in 1-octanol (1.57 mL, 10.0 mmol, 2 equiv) following the general procedure **A**. The crude product was precipitate in hexanes, filtrated and washed with CH_2Cl_2 (3 x 5 mL). After evaporation of the solvents, pure 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate **11'** was isolated (2.08 g, 3.30 mmol, yield = 66%) as a white solid.

m.p.: 89 °C;

R_f = 0.44 (SiO_2, CH_2Cl_2/MeOH = 9:1);

IR (ATR) ν = 3173, 1712, 1631, 1593, 1431, 1331, 1299, 1195, 1143, 1131, 1115, 1060, 1037, 967 (cm^{-1});

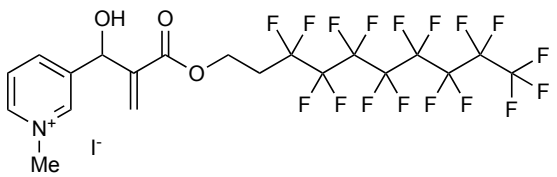
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (br s, 1H), 8.49 (br d, *J* = 4.8 Hz, 1H), 7.74 (dt, *J* = 7.8, 1.7 Hz, 1H), 7.29 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.43 (s, 1H), 6.02 (s, 1H), 5.62 (s, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 3.53 (br s, 1H, OH), 2.52-2.40 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 148.8, 148.5, 141.4, 137.6, 134.9, 127.0, 123.6, 121.9-105 (m, 8C), 70.5, 56.9 (t, $J^3_{C\text{-}F}$ = 4.3 Hz), 30.5 (t, $J^2_{C\text{-}F}$ = 21.8 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.72 (t, *J* = 8.8 Hz), -113.58 (br t, *J* = 12.9 Hz), -121.63 (m), -121.89 (m), -122.69 (m), -123.49 (m), -126.08 (m);

HRMS (+ESI) *m/z* calcd for $C_{19}H_{13}F_{17}NO_3$ $[M+H]^+$: 626.0618; found: 626.0618.

Iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 11



Chemical Formula: $C_{20}H_{15}F_{17}NO_3I$
MW = 767.22 g.mol^{-1}

Iodomethane (61 μL, 0.978 mmol, 1.5 equiv) was added to a suspension of acrylate **11'** (409 mg, 0.652 mmol, 1 equiv) in THF/DMF (50:50) (2.19 mL) following the general procedure **B**. After evaporation of the solvent, the crude product was precipitate in CH_2Cl_2 and filtrated. The expected iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy)carbonyl)-1-hydroxyallyl)-1 methylpyridin-1-ium **11** was isolated (367 mg, 0.476 mmol, yield = 73%) as a yellowish solid.

m.p.: 199 °C;

R_f = 0.36 (SiO_2, CH_2Cl_2/MeOH = 9:1);

IR (ATR) ν = 3369, 3044, 1706, 1637, 1506, 1477, 1371, 1311, 1199, 1165, 1142, 1132, 1115, 1057, 1007, 964, 936 (cm^{-1});

^{1}H NMR (400 MHz, MeOD) δ 9.00 (br s, 1H), 8.82 (br d, *J* = 6.0 Hz, 1H), 8.56 (br d, *J* = 8.0 Hz, 1H), 8.04 (dd, *J* = 8.0, 6.0 Hz, 1H), 6.51 (s, 1H), 6.34 (s, 1H), 5.77 (s, 1H), 4.43 (m, 2H), 4.44 (s, 3H), 2.62 (tt, *J* = 19.1, 6.0 Hz, 2H), OH not visible;

^{13}C NMR (101 MHz, MeOD) δ 166.0, 145.9, 145.5 (2C), 144.5, 142.1, 128.9, 128.7, 122.7-108.6 (m, 7C), 79.3 (t, *J* = 32.6 Hz), 69.9, 58.1 (t, *J* = 5.3 Hz), 49.1 (determined by HSQC), 31.1 (t, *J* = 21.2 Hz);

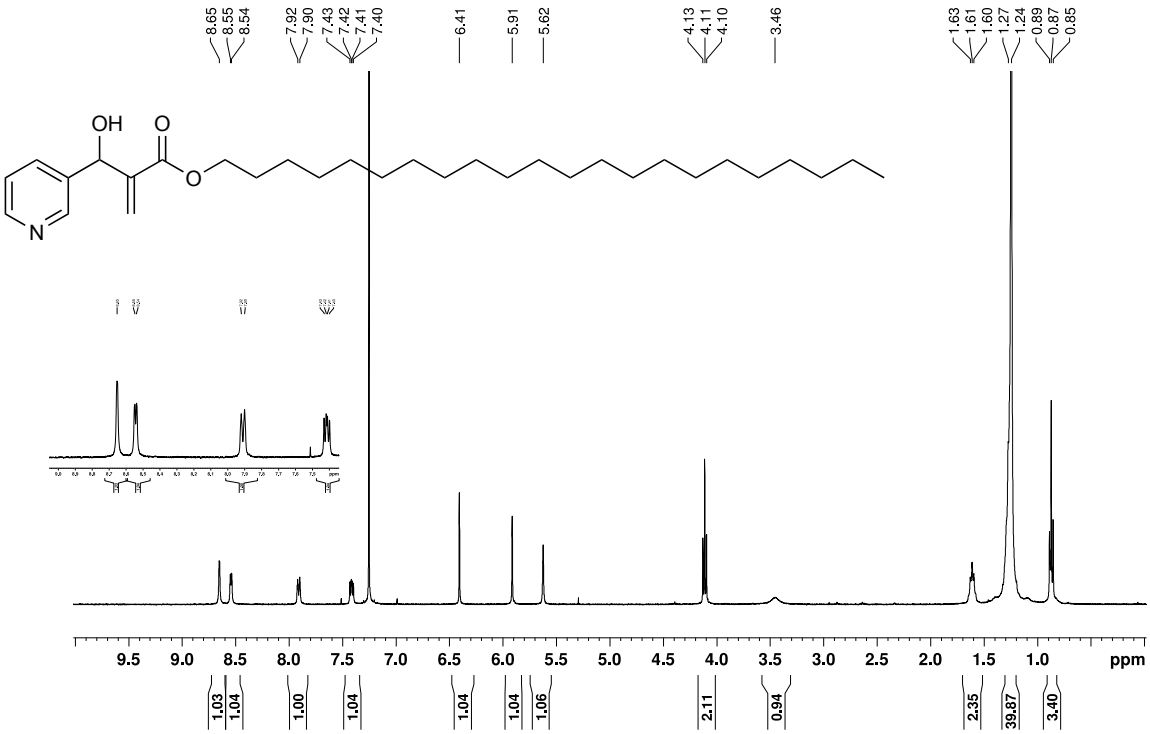
^{19}F NMR (376 MHz, MeOD) δ: -82.35 (t, *J* = 9.8 Hz), -114.68 (t, *J* = 14.1 Hz), -122.66 (m), -122.90 (m), -123.73 (m), -124.58 (m), -127.28 (m);

HRMS (+ESI) *m/z* calcd for $C_{20}H_{15}F_{17}NO_3$ $[M]^+$: 640.0775; found: 640.0759.

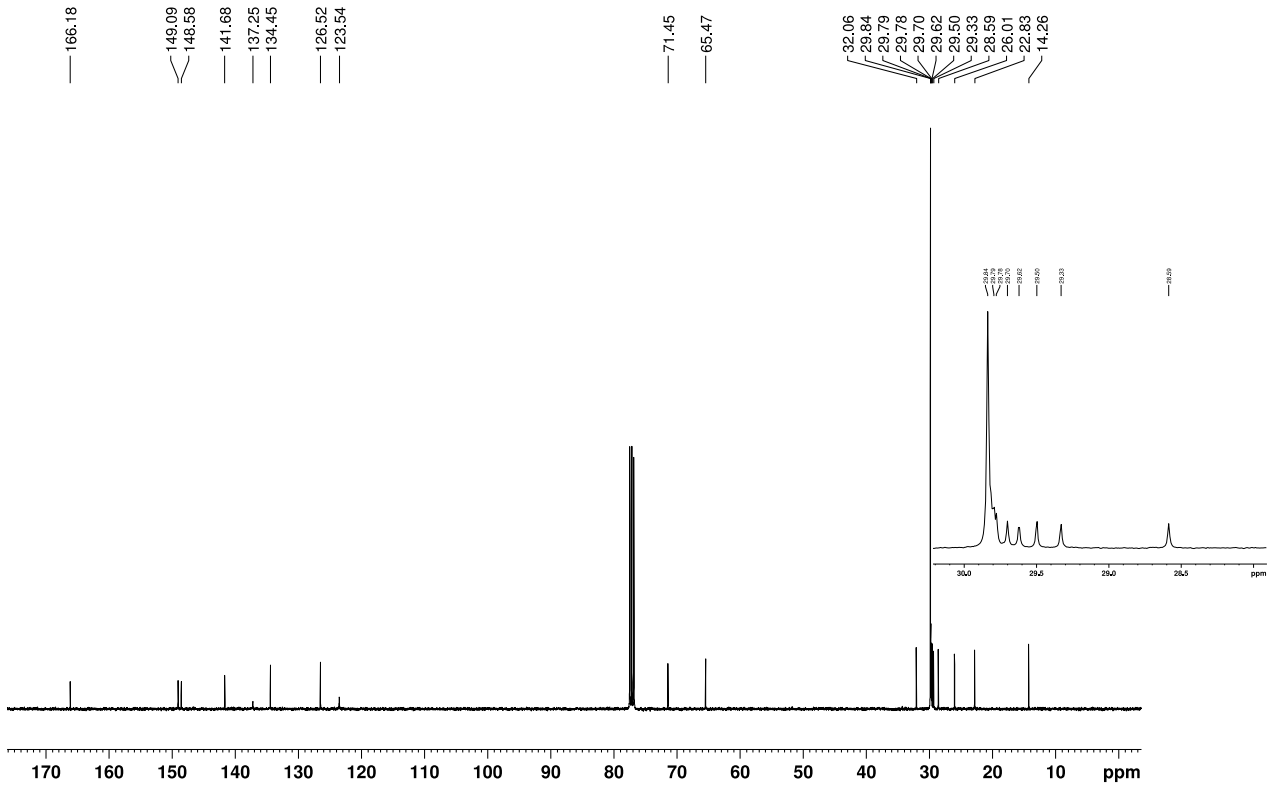
3. ^{1}H, ^{19}F and ^{13}C spectra

Docosyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 1'

^{1}H NMR (400 MHz, $CDCl_3$)

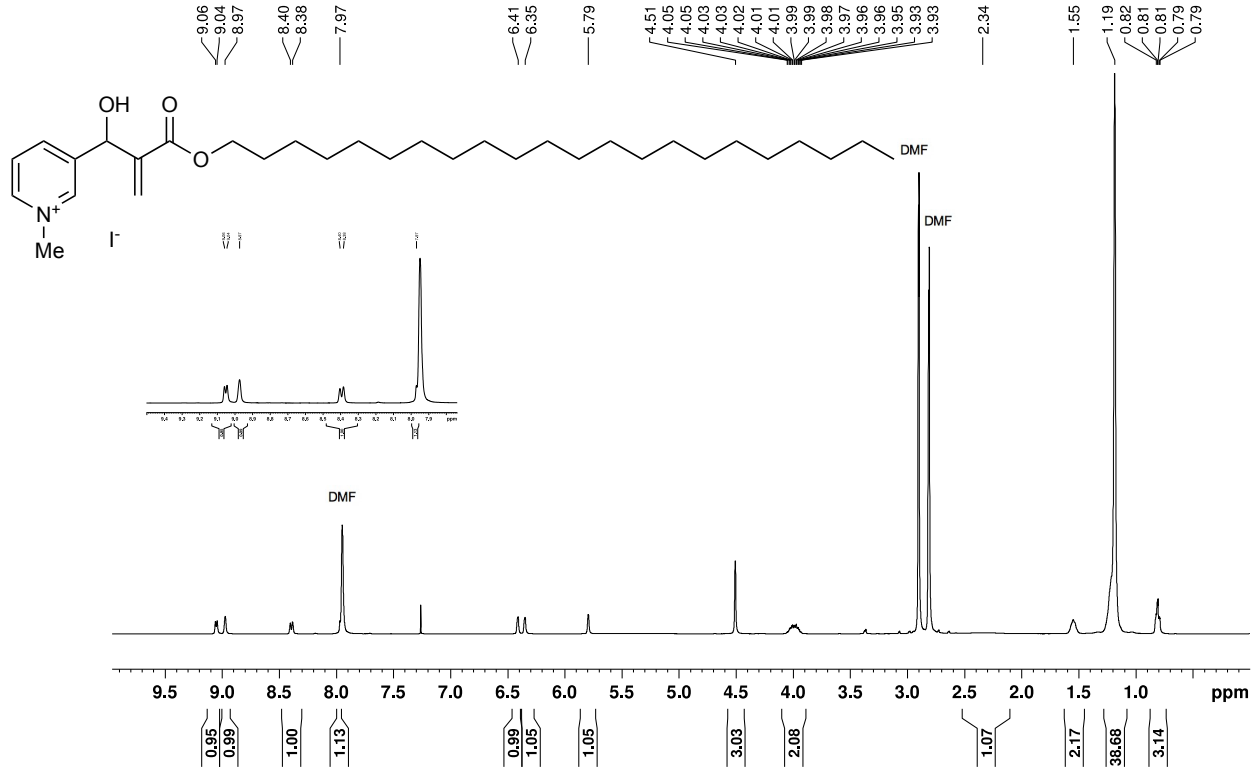


^{13}C NMR (101 MHz, $CDCl_3$)

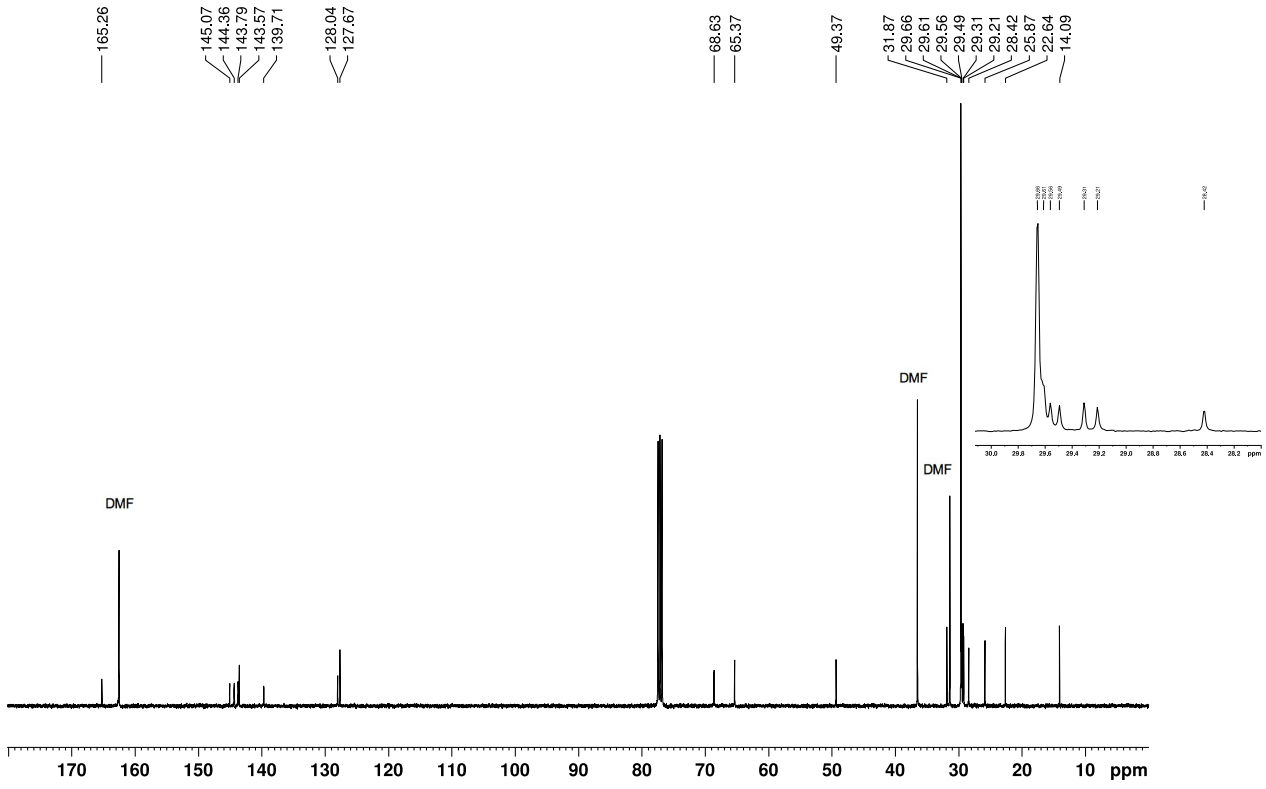


Iodo 3-(2-((docosyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 1

^{1}H NMR (400 MHz, $CDCl_3$)

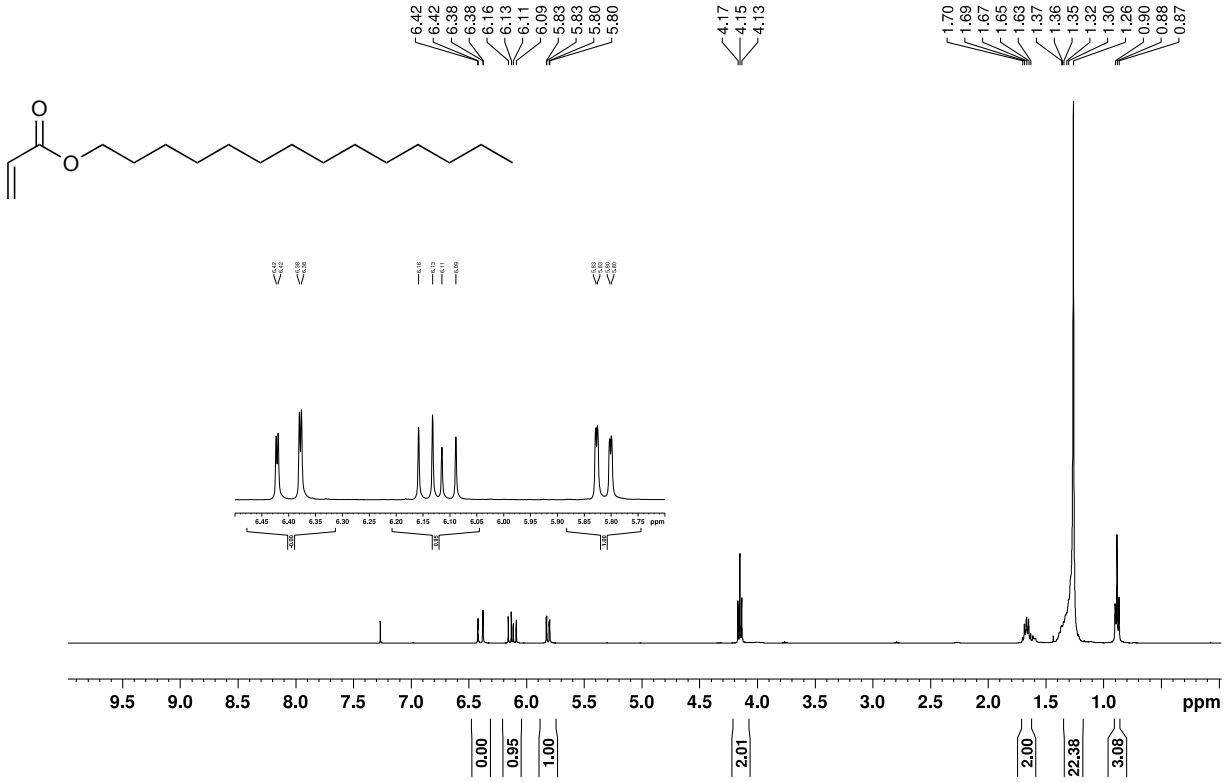


^{13}C NMR (101 MHz, $CDCl_3$)

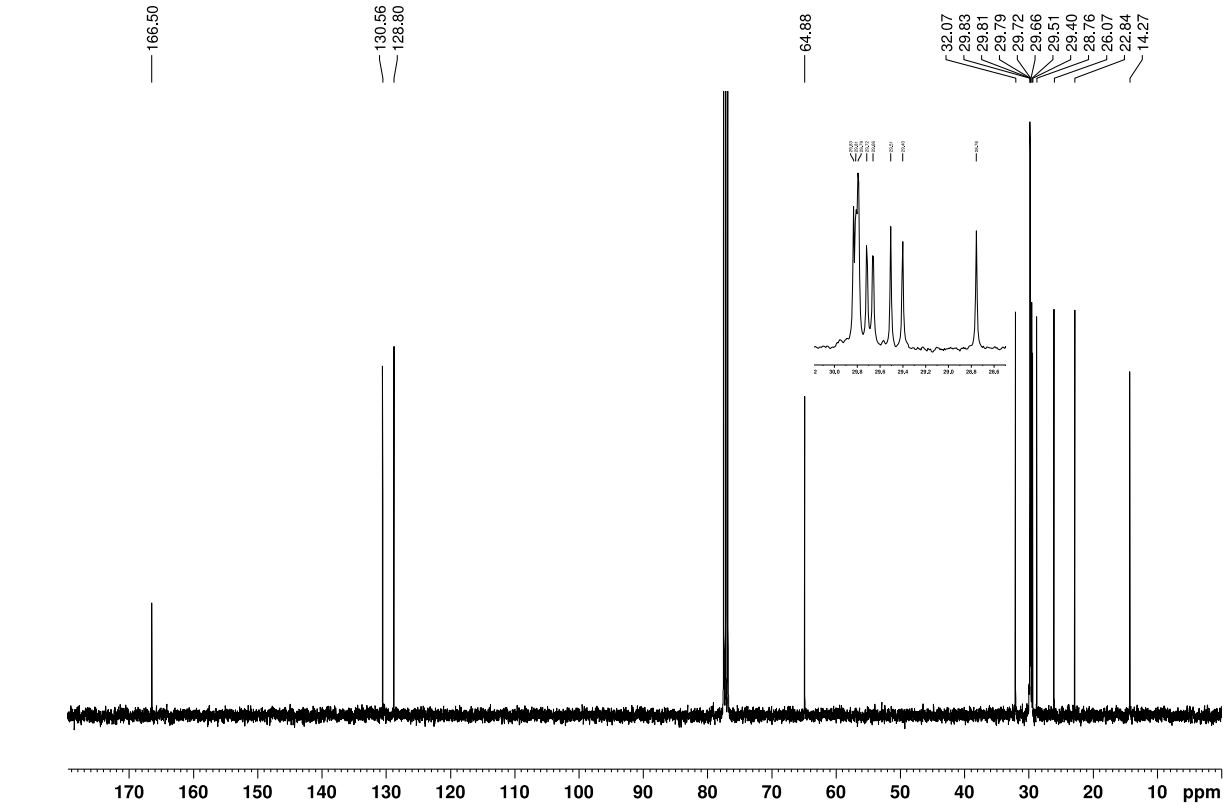


Tetradecyl acrylate, 2'

^{1}H NMR (400 MHz, $CDCl_3$)

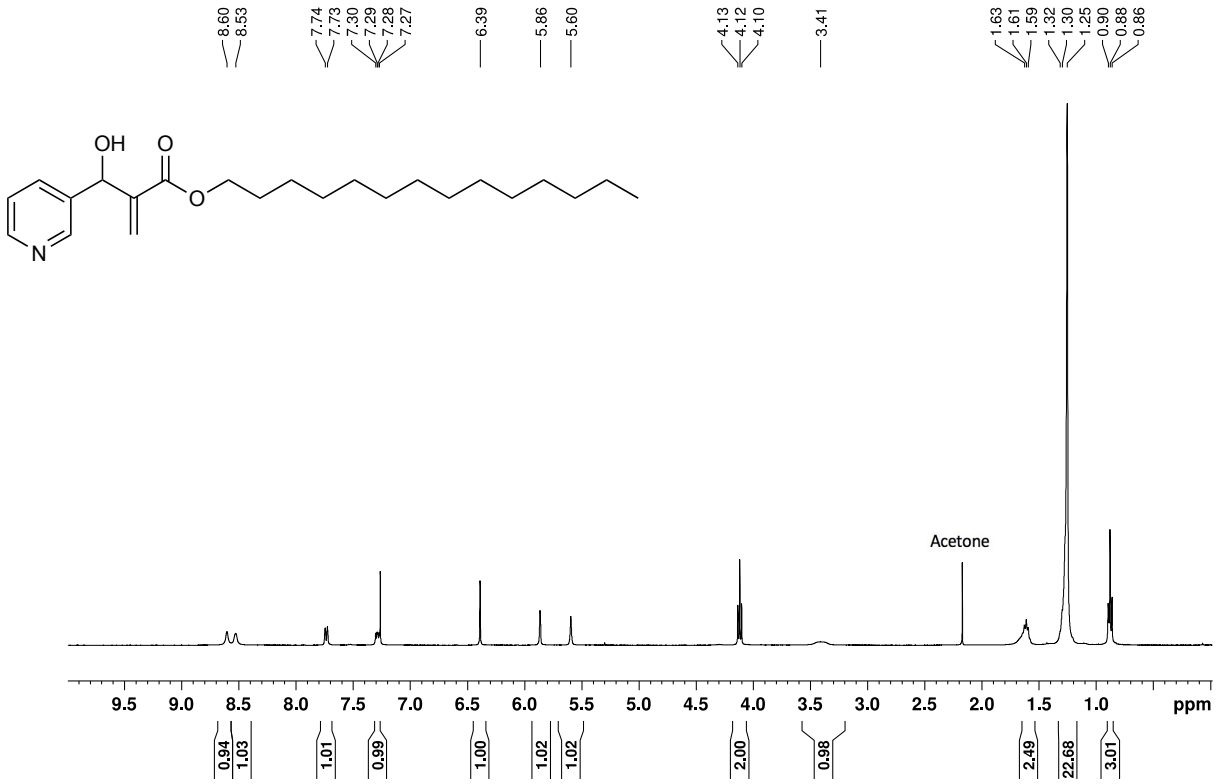


^{13}C NMR (101 MHz, $CDCl_3$)

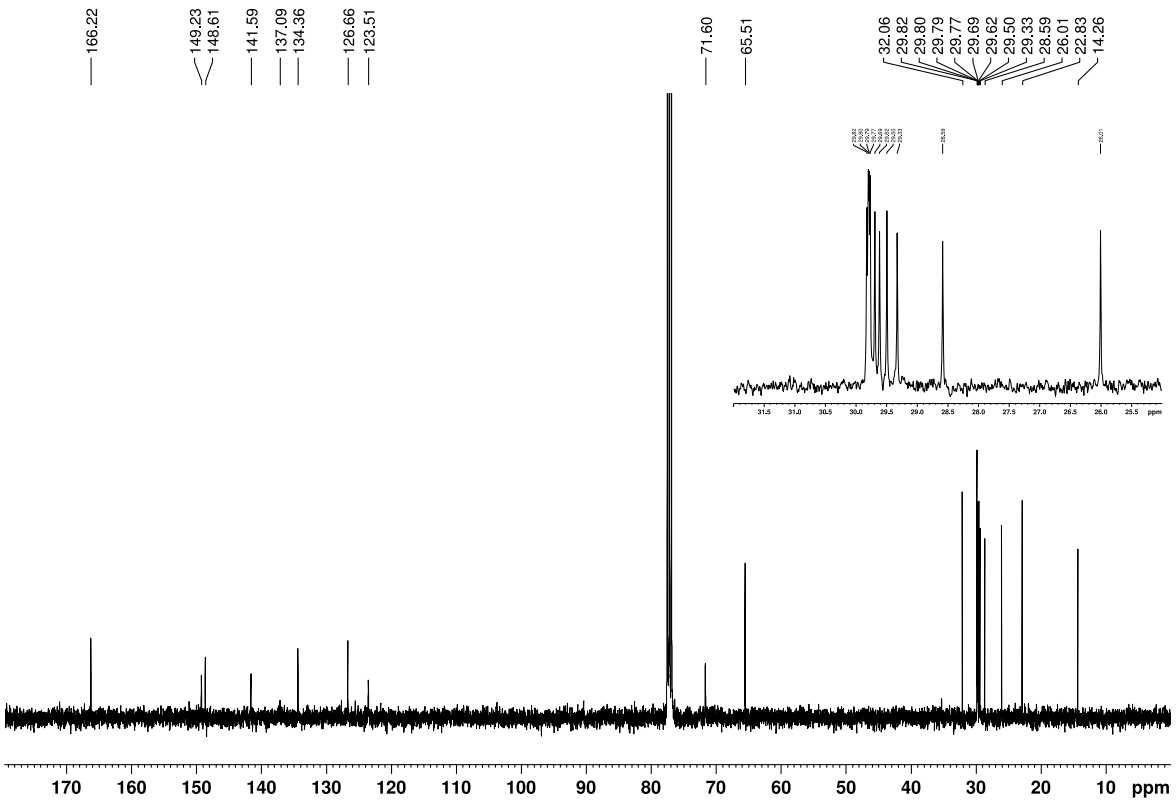


Tetradecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 2"

^{1}H NMR (400 MHz, $CDCl_3$)

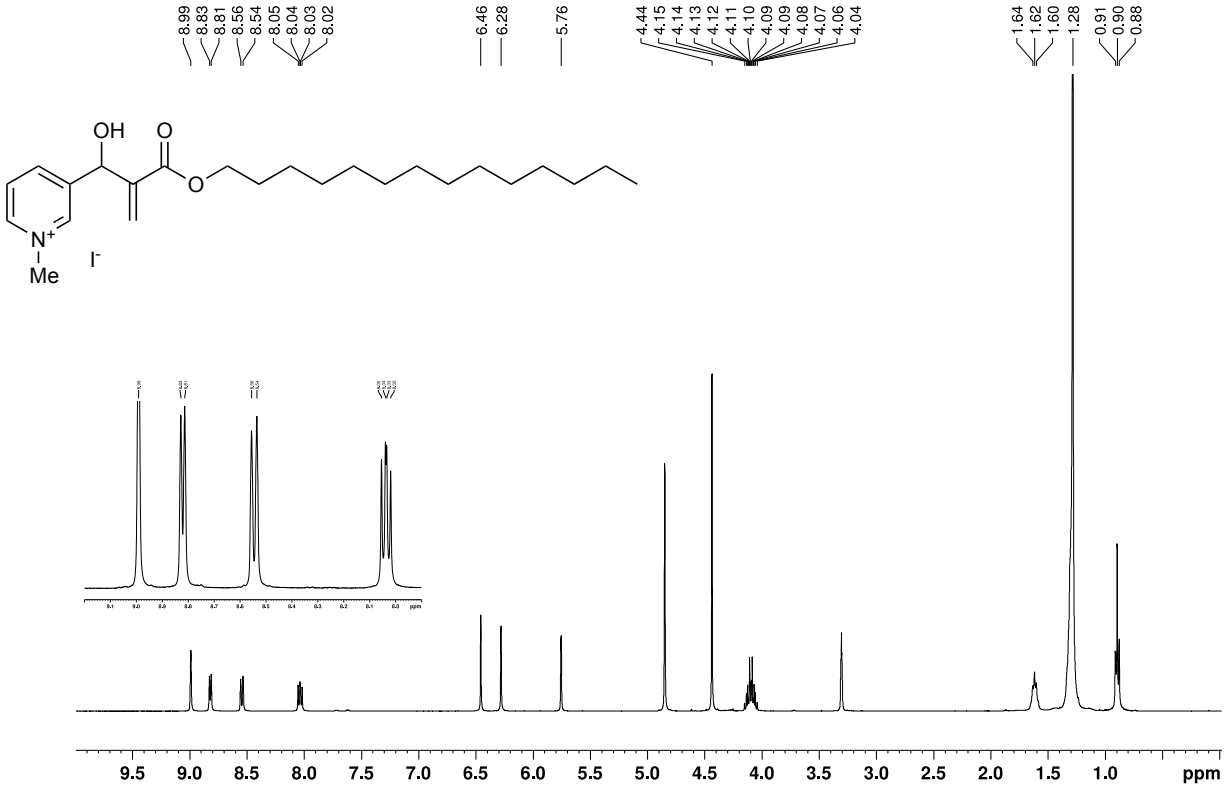


^{13}C NMR (101 MHz, $CDCl_3$)

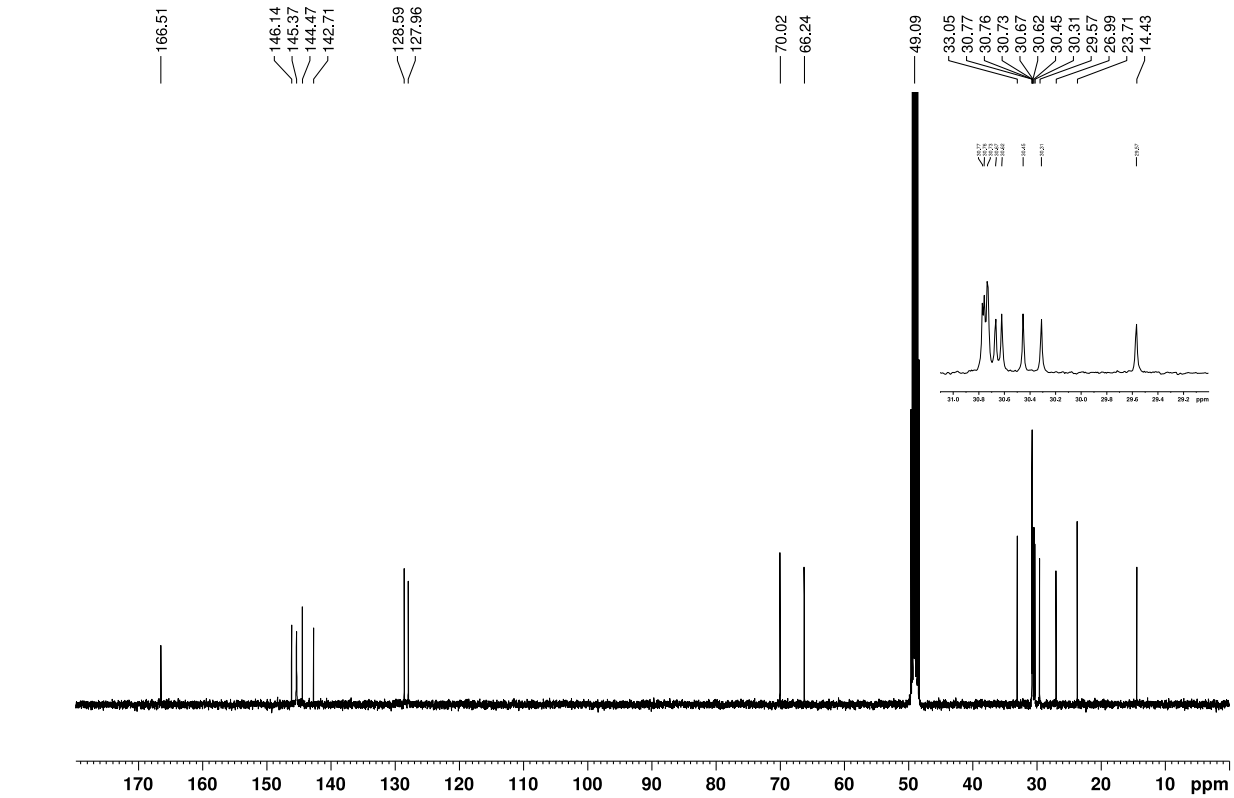


Iodo 3-(1-hydroxy-2-((tetradecyloxy)carbonyl)allyl)-1-methylpyridin-1-ium, 2

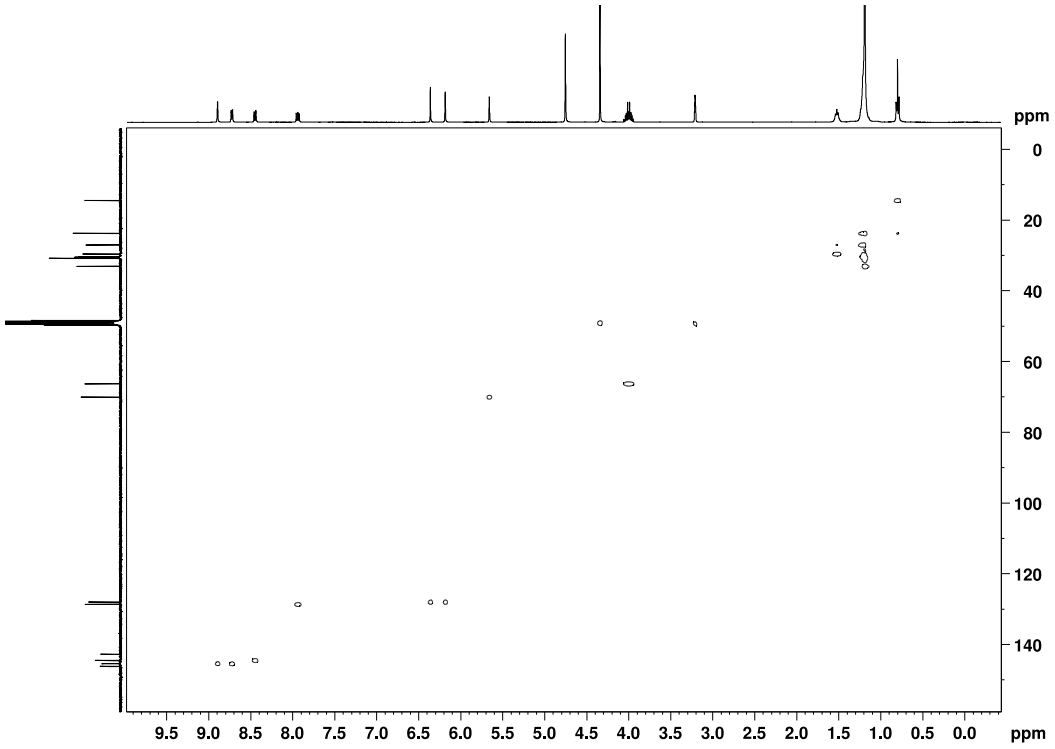
^{1}H NMR (400 MHz, MeOD)



^{13}C NMR (101 MHz, MeOD)

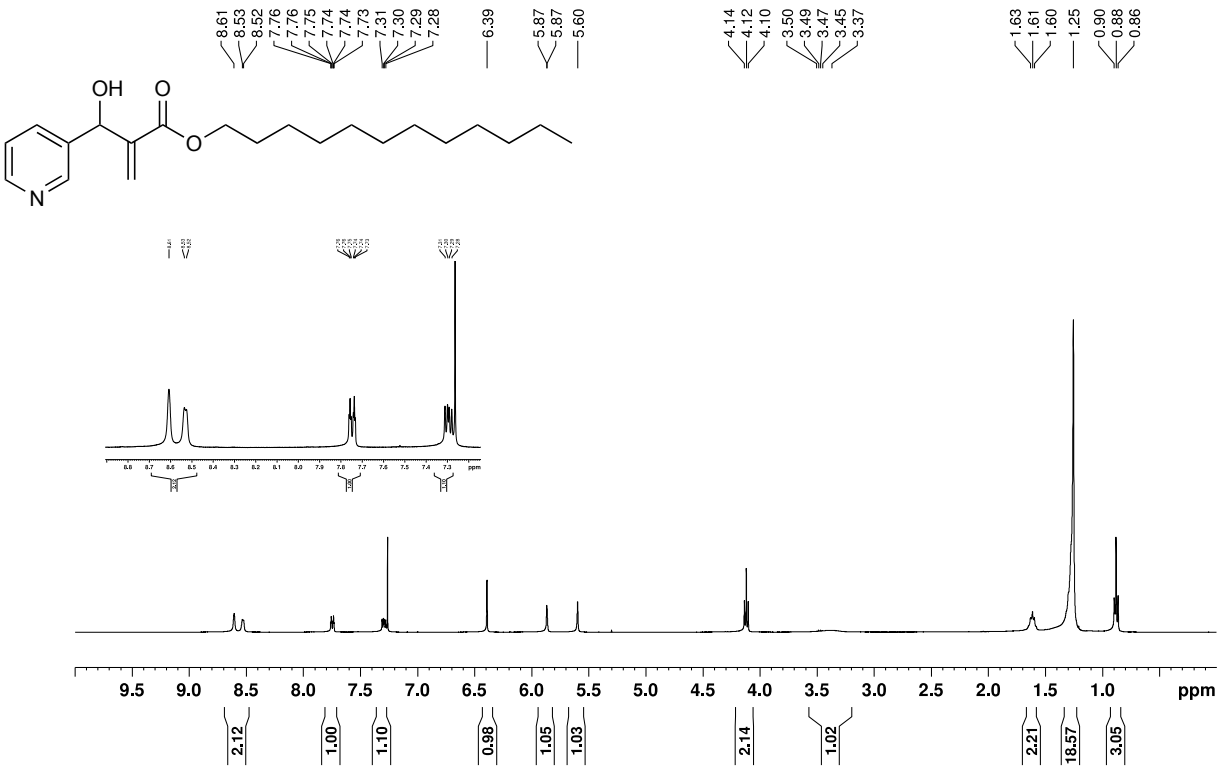


HSQC (MeOD)

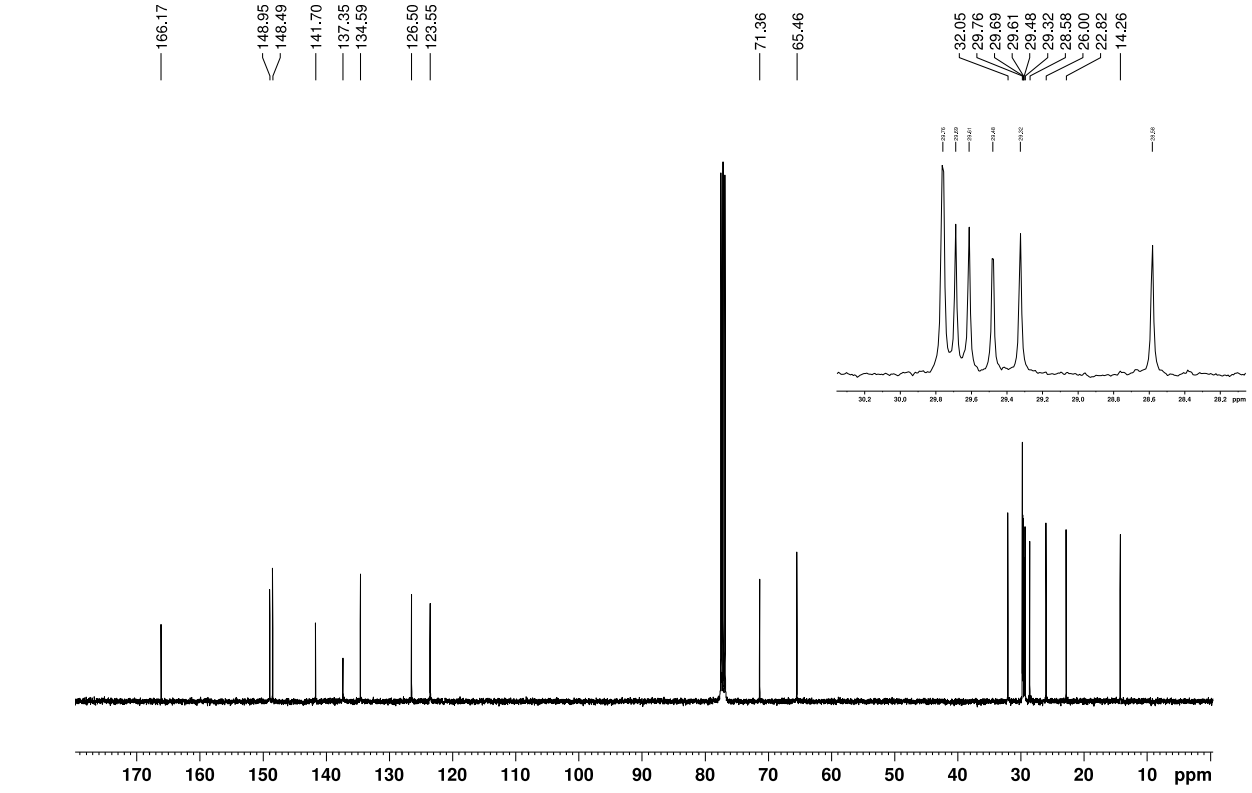

ppm
0
20
40
60
80
100
120
140
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

Dodecyl 2-(hydroxy(pyridine-3-yl)methyl)acrylate, 3'

^{1}H NMR (400 MHz, $CDCl_3$)

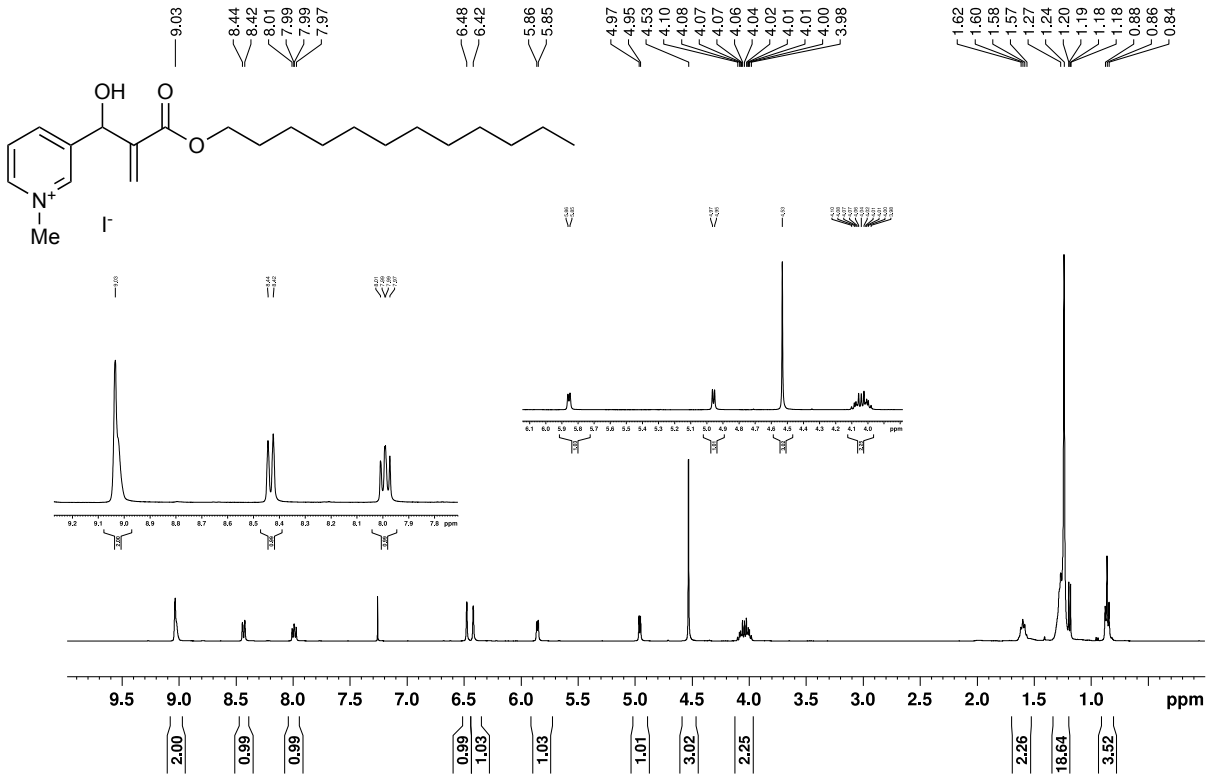


^{13}C NMR (101 MHz, $CDCl_3$)

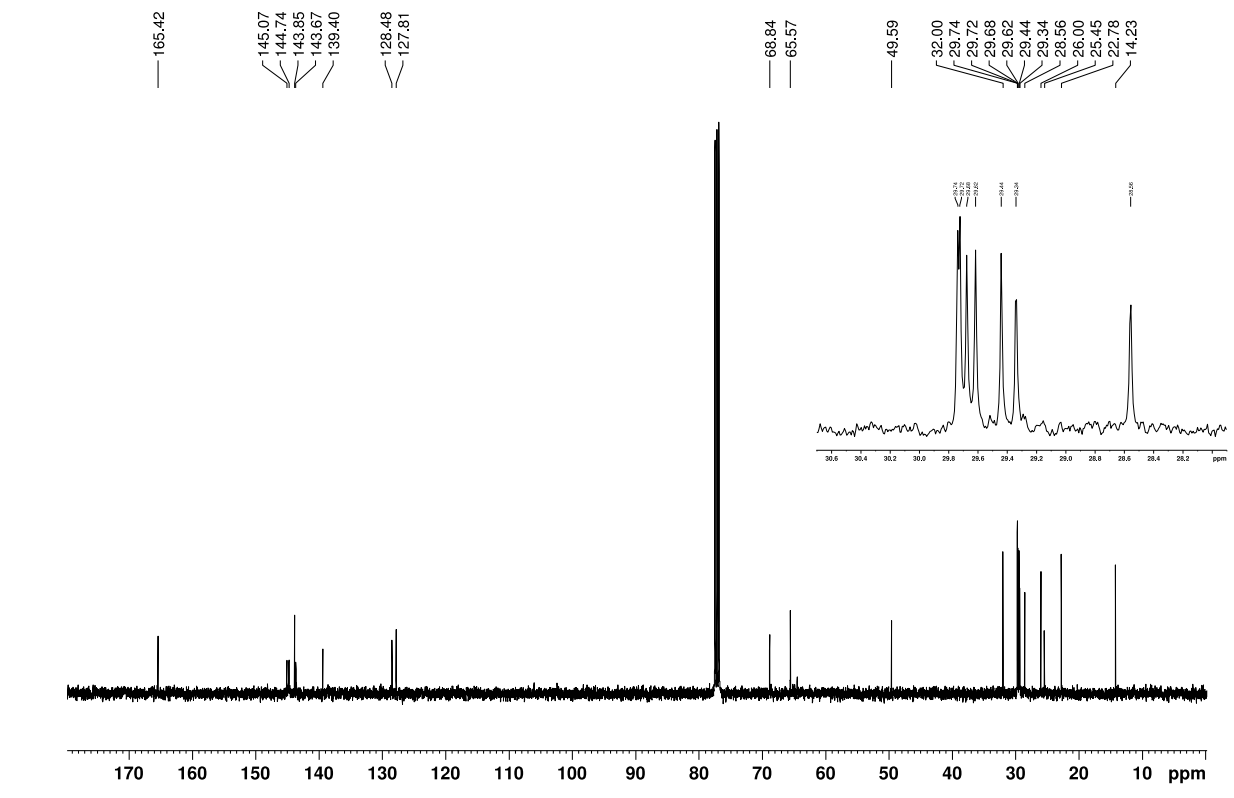


Iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 3

^{1}H NMR (400 MHz, $CDCl_3$)

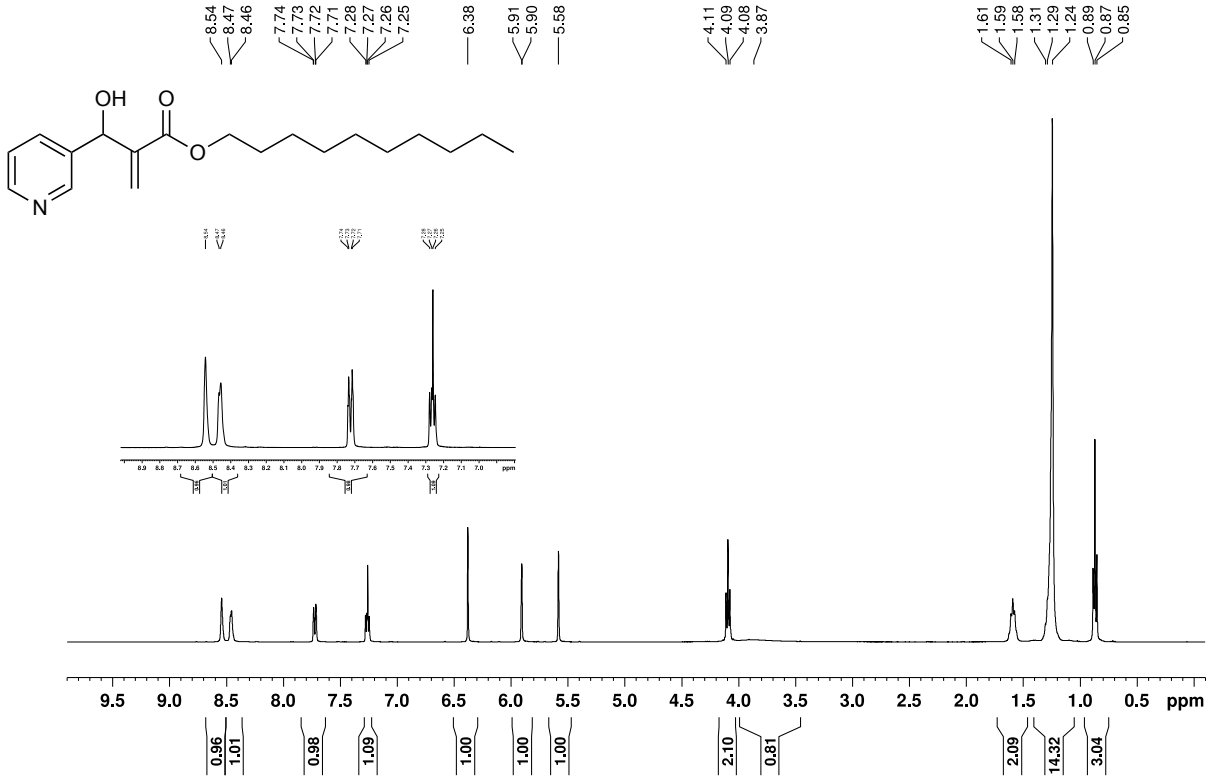


^{13}C NMR (101 MHz, $CDCl_3$)

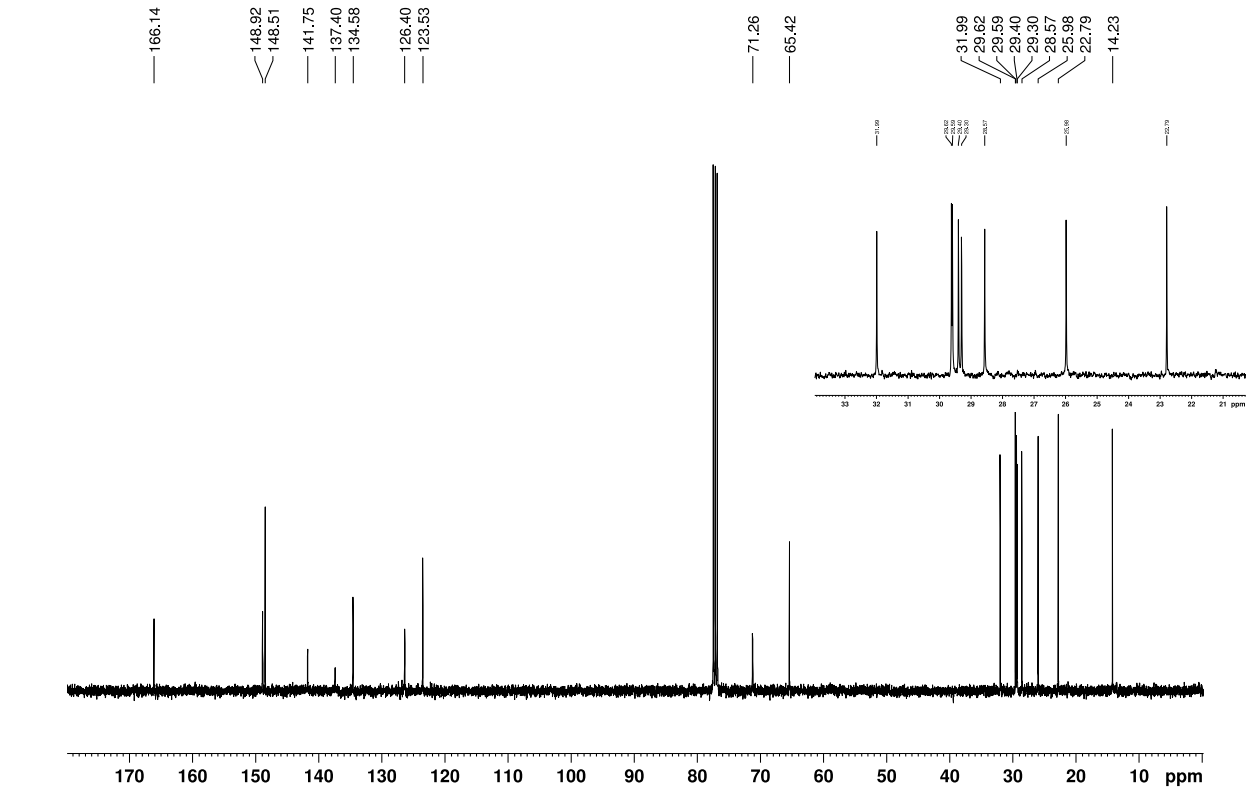


Decyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 4'

^{1}H NMR (400 MHz, $CDCl_3$)

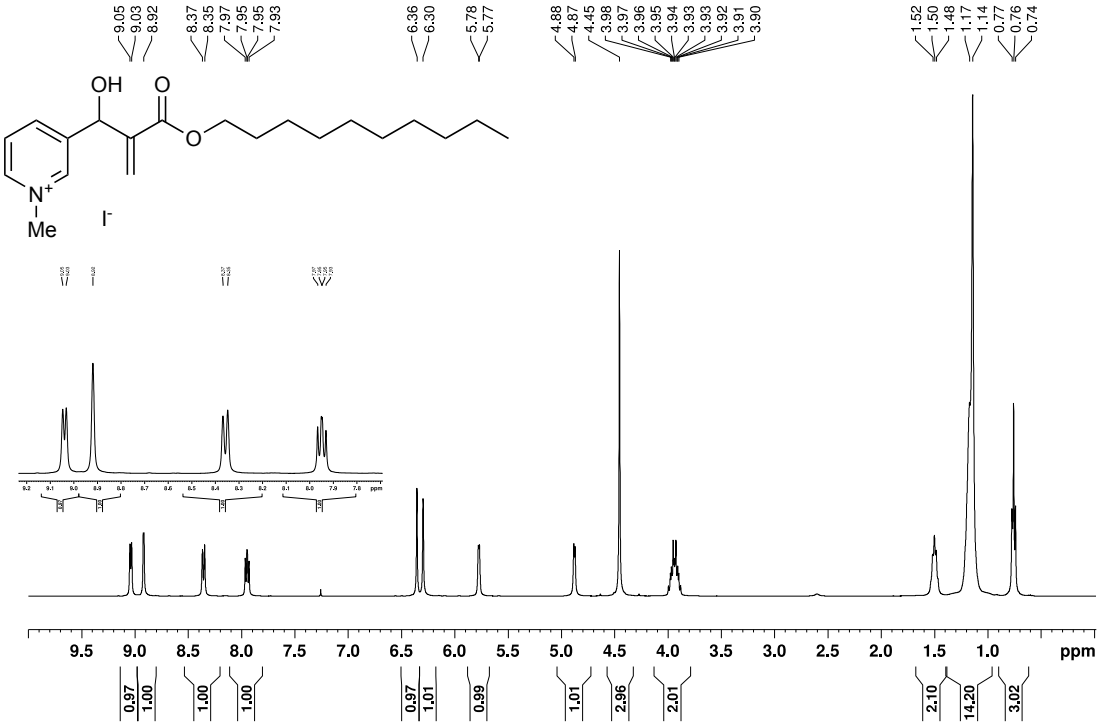


^{13}C NMR (101 MHz, $CDCl_3$)

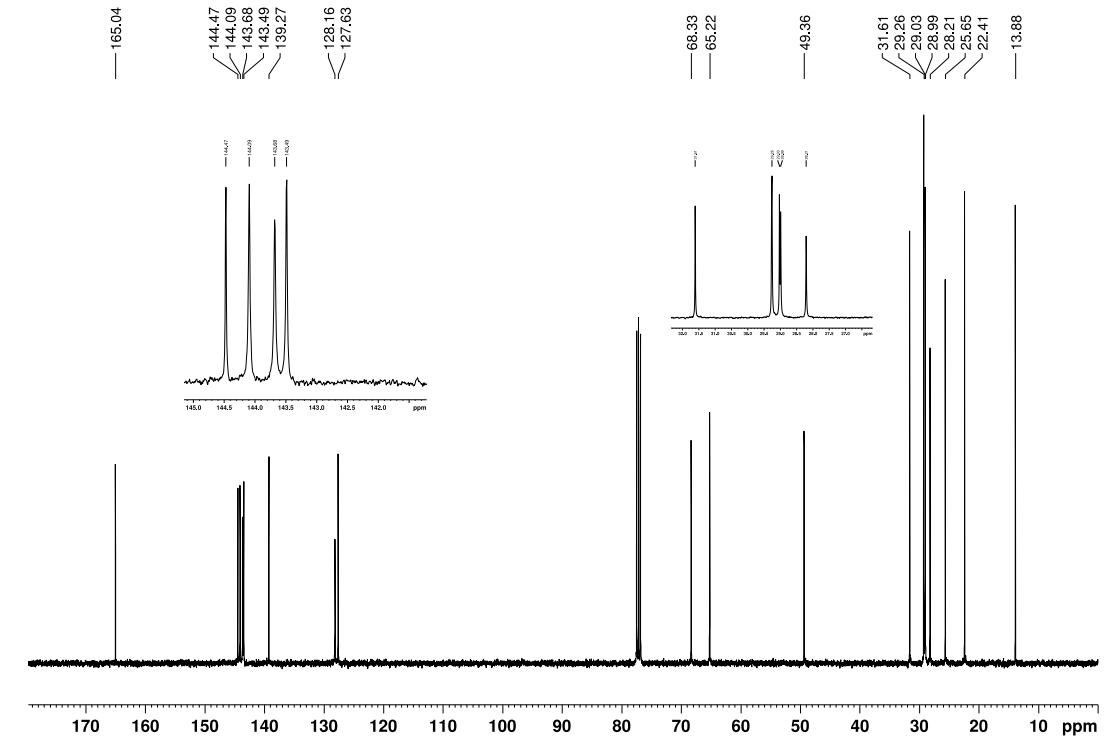


Iodo 3-(2-((decyloxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 4

^{1}H NMR (400 MHz, $CDCl_3$)

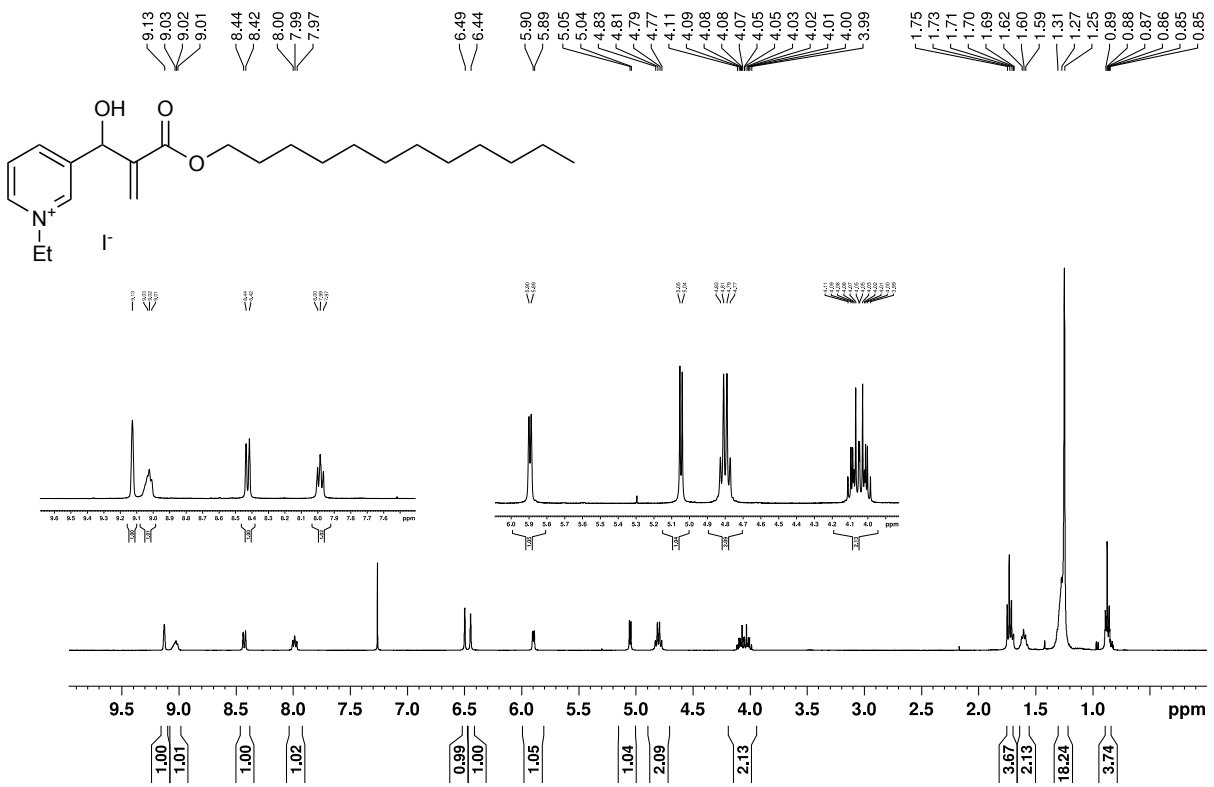


^{13}C NMR (101 MHz, $CDCl_3$)

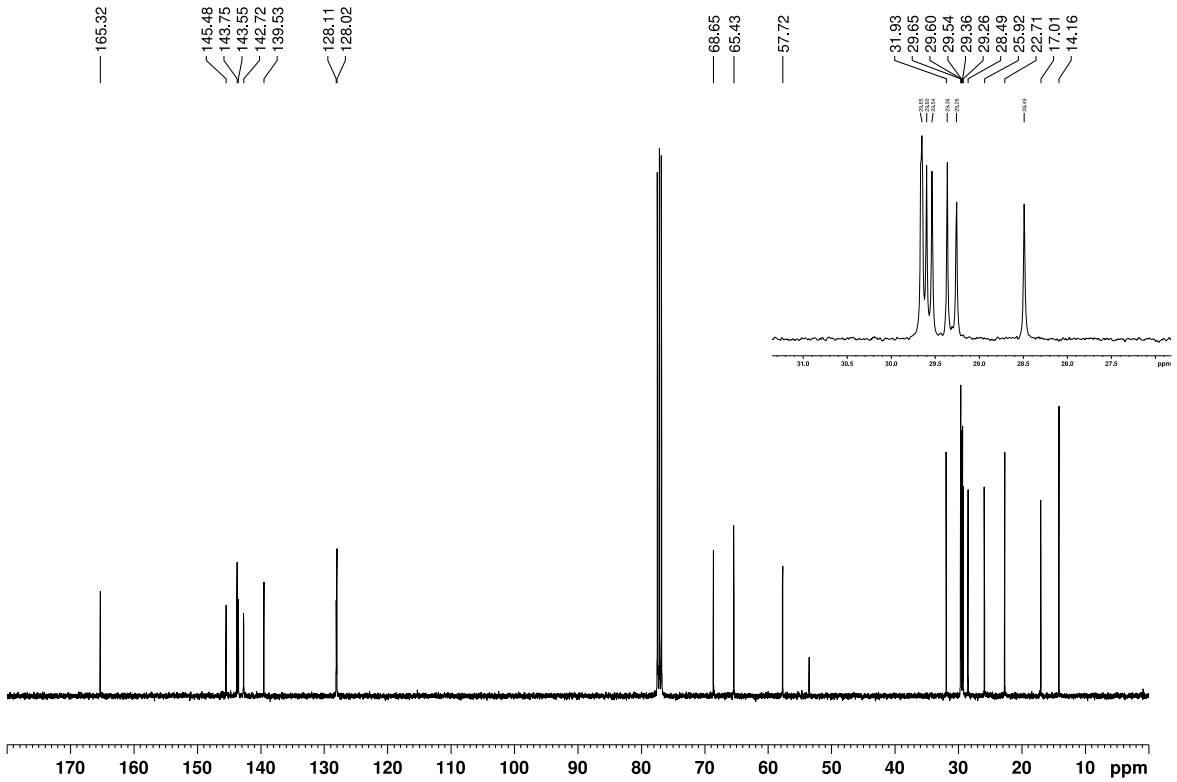


Iodo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium, 5

^{1}H NMR (400 MHz, $CDCl_3$)

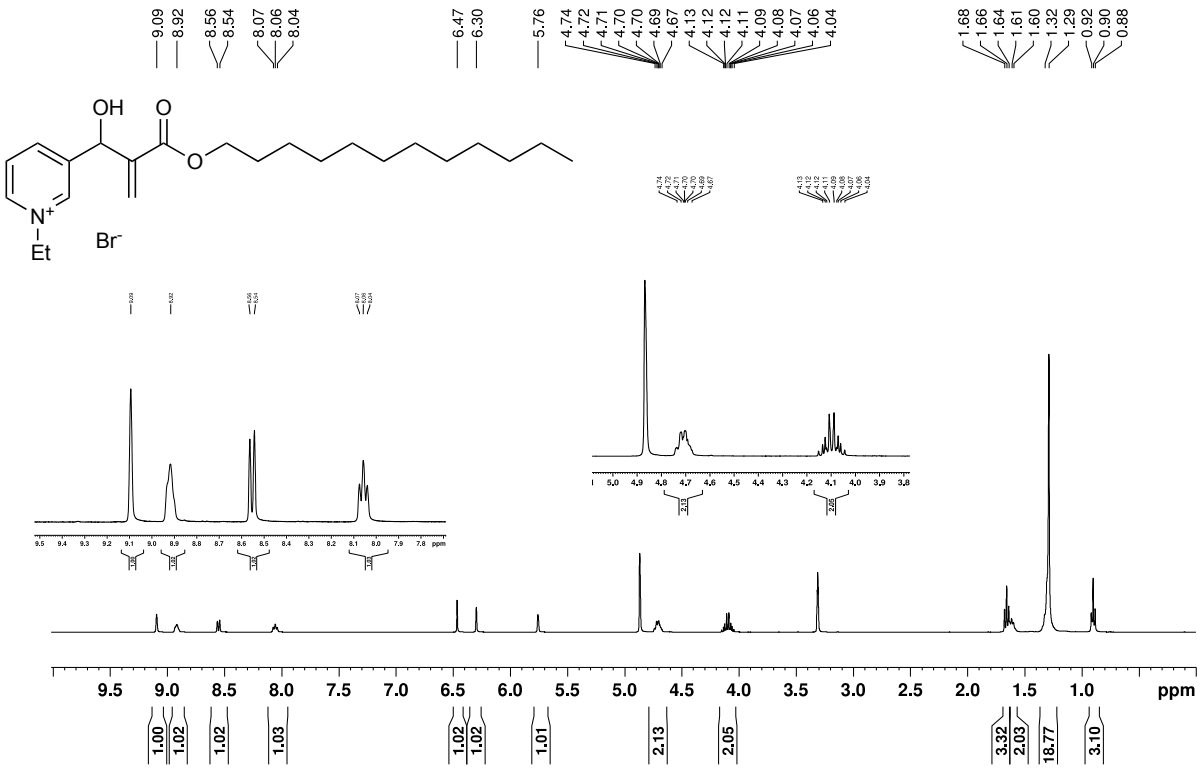


^{13}C NMR (101 MHz, $CDCl_3$)

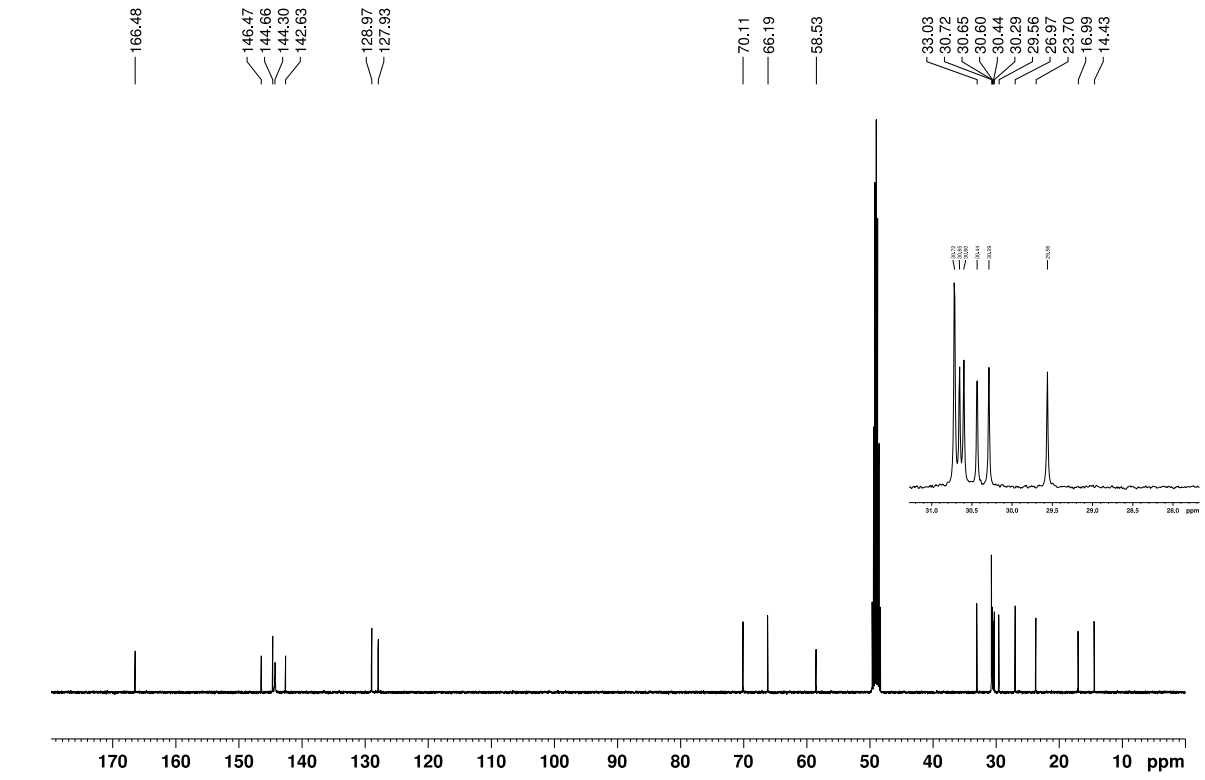


Bromo 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)-1-ethylpyridin-1-ium, 6

^{1}H NMR (400 MHz, MeOD)

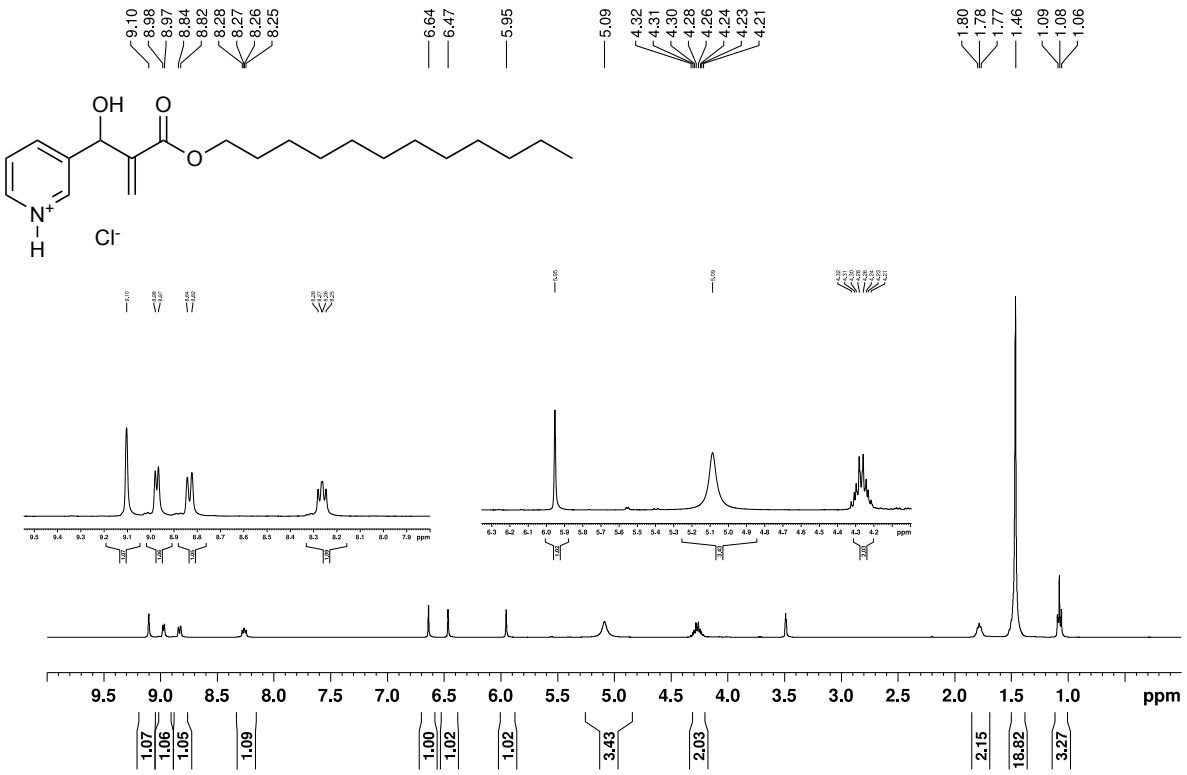


^{13}C NMR (101 MHz, MeOD)

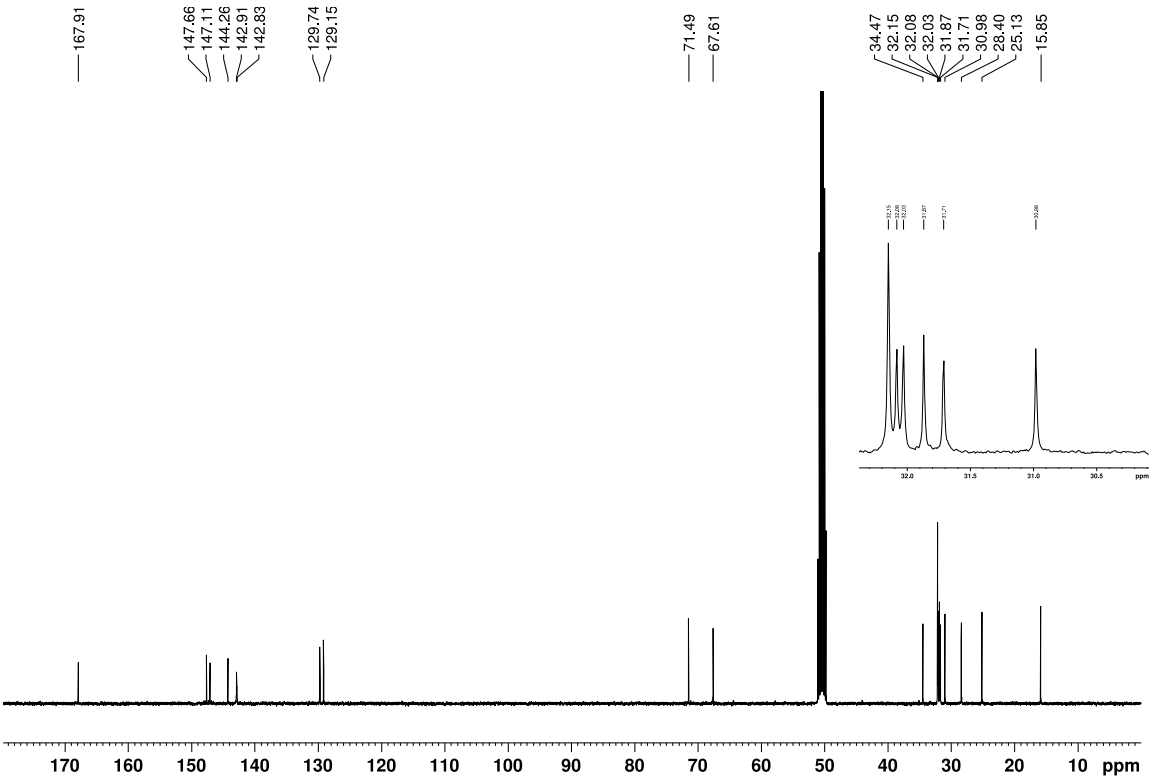


Chloro 3-(2-((dodecyloxy)carbonyl)-1-hydroxyallyl)pyridin-1-ium, 7

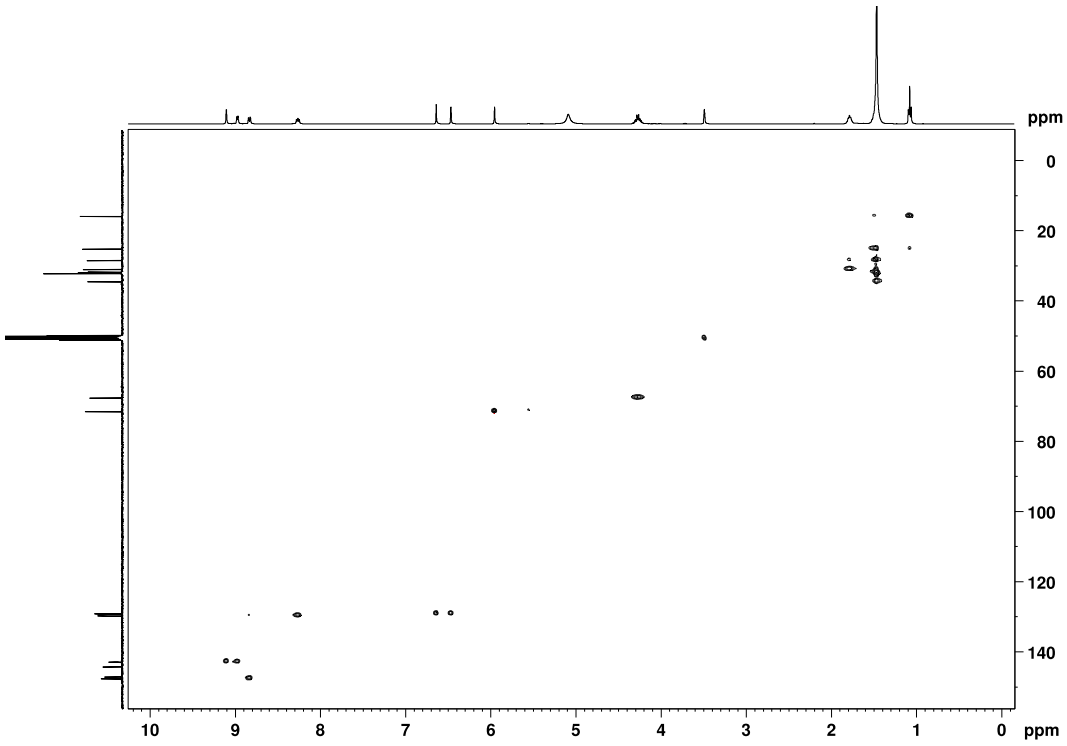
^{1}H NMR (400 MHz, MeOD)



^{13}C NMR (101 MHz, MeOD)

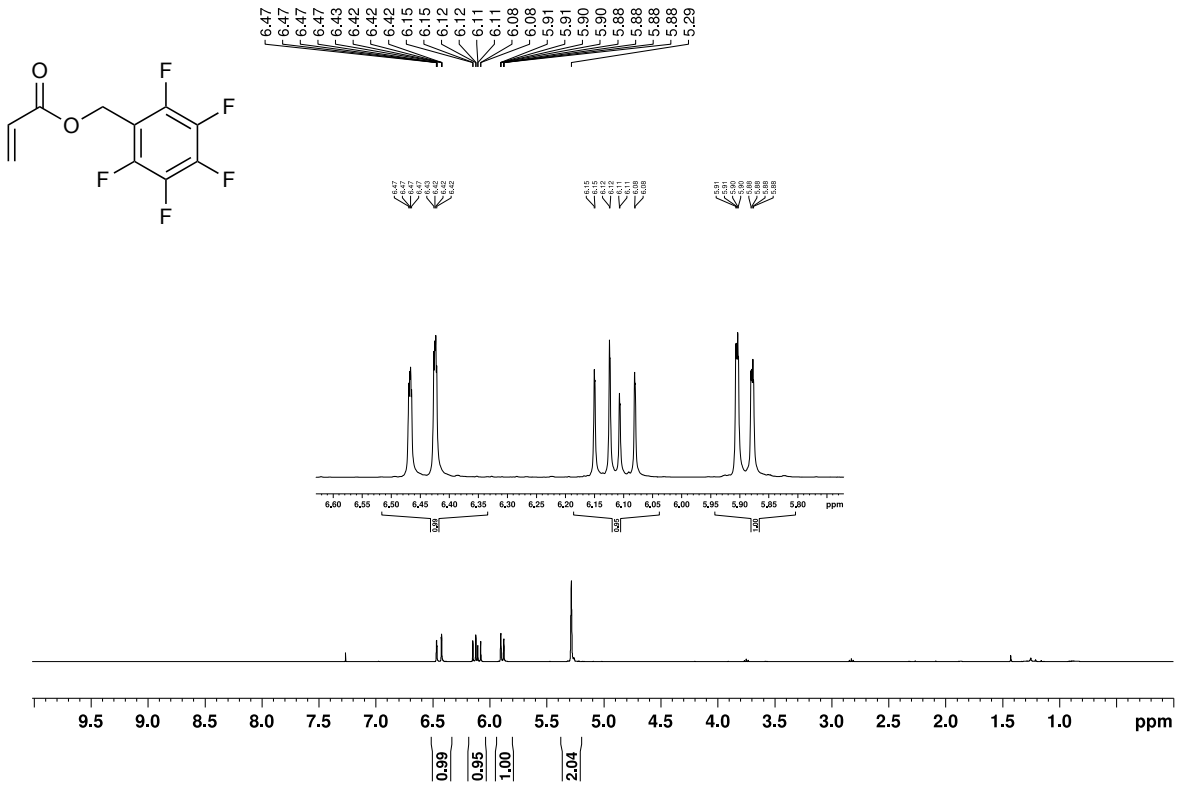


HSQC (MeOD)

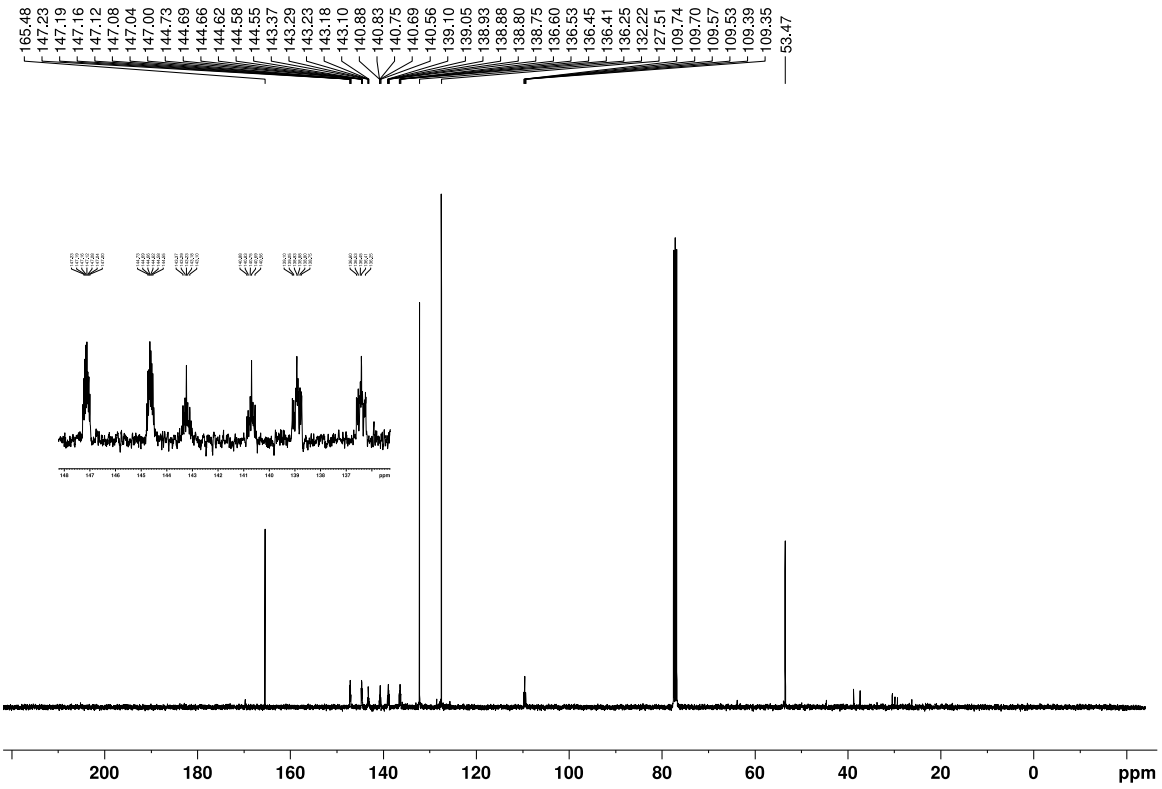


luorophenyl)methyl acrylate, 8'

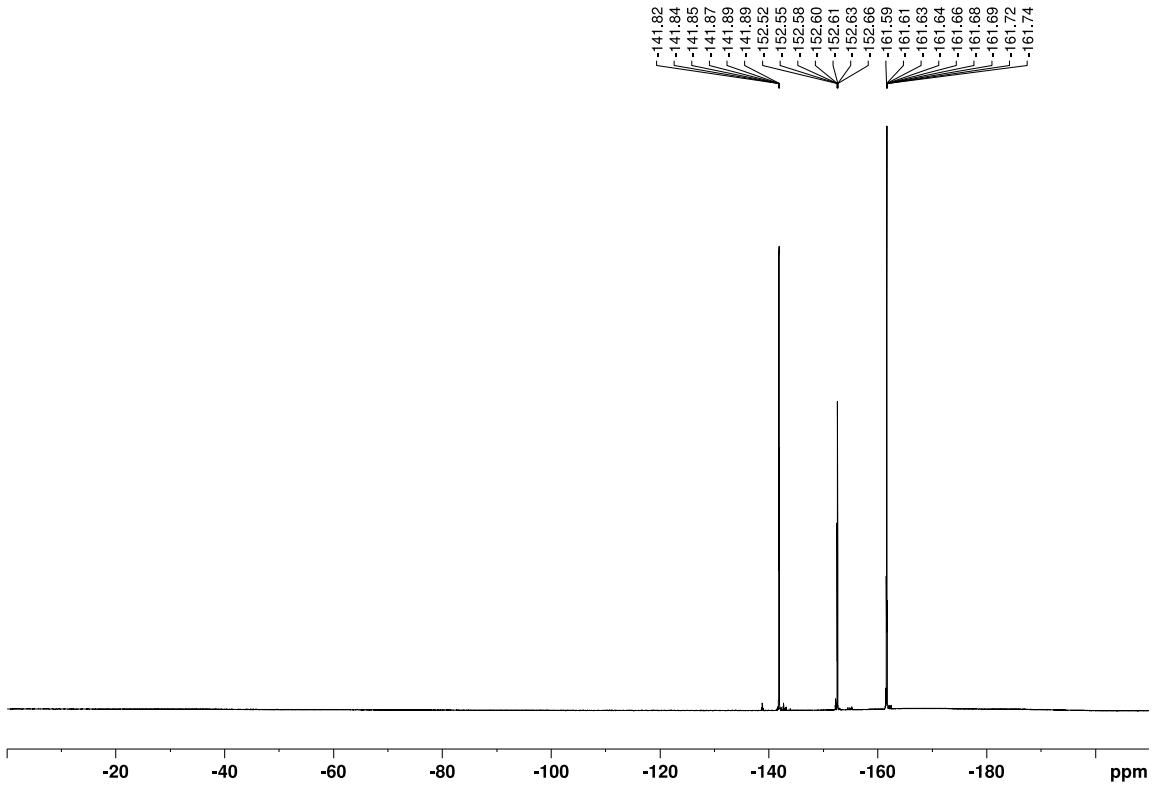
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

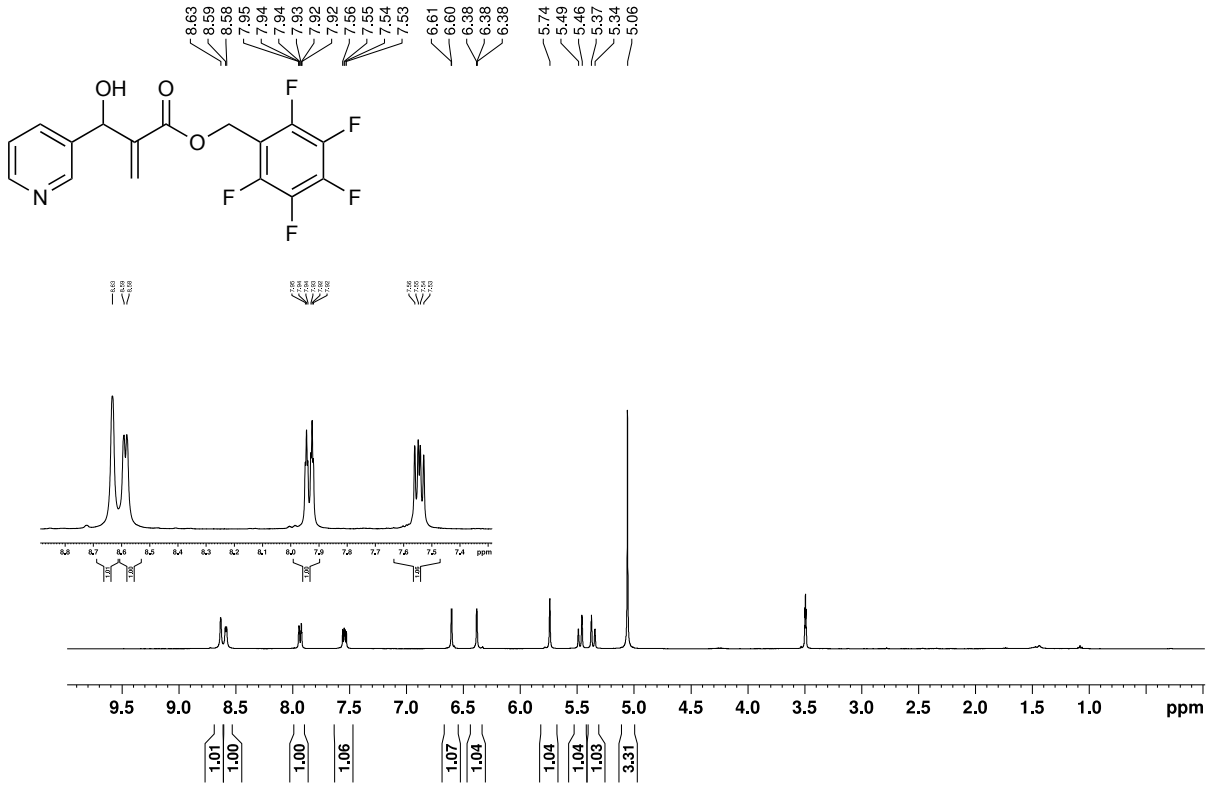


^{19}F NMR (376 MHz, $CDCl_3$)

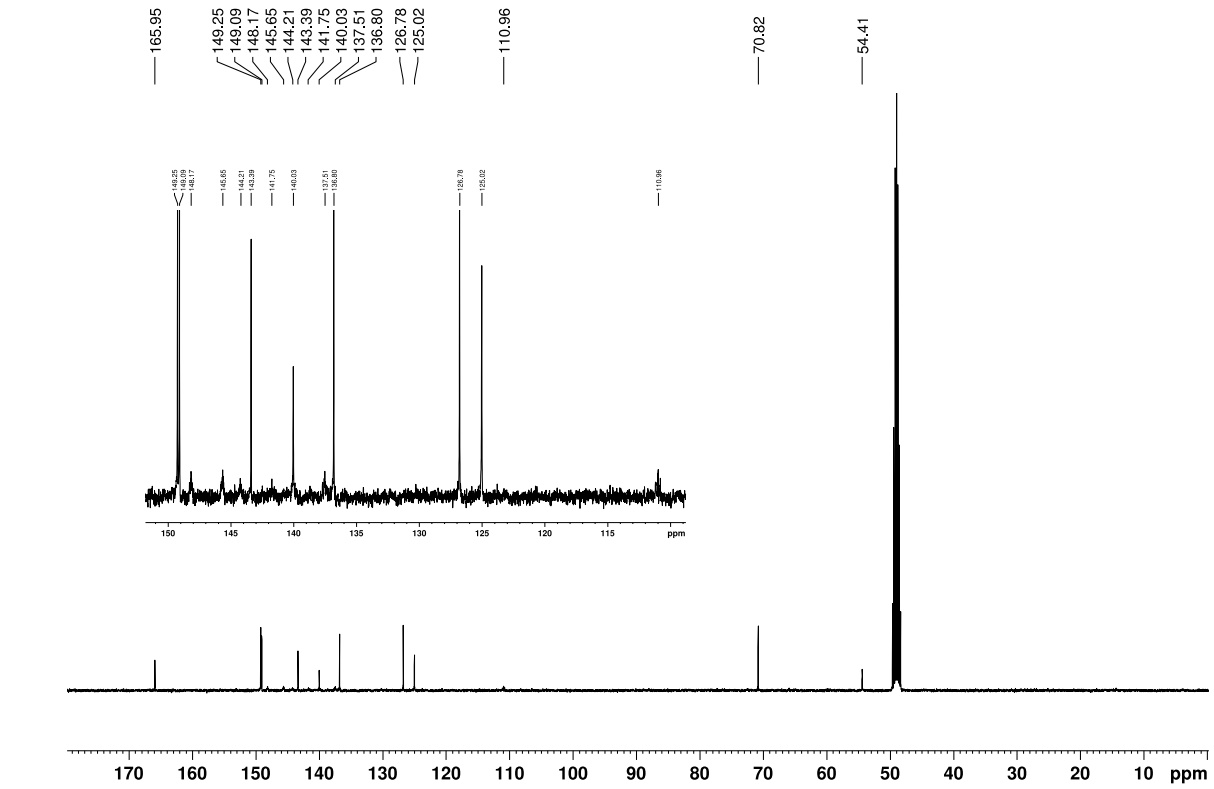


(Perfluorophenyl)methyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 8"

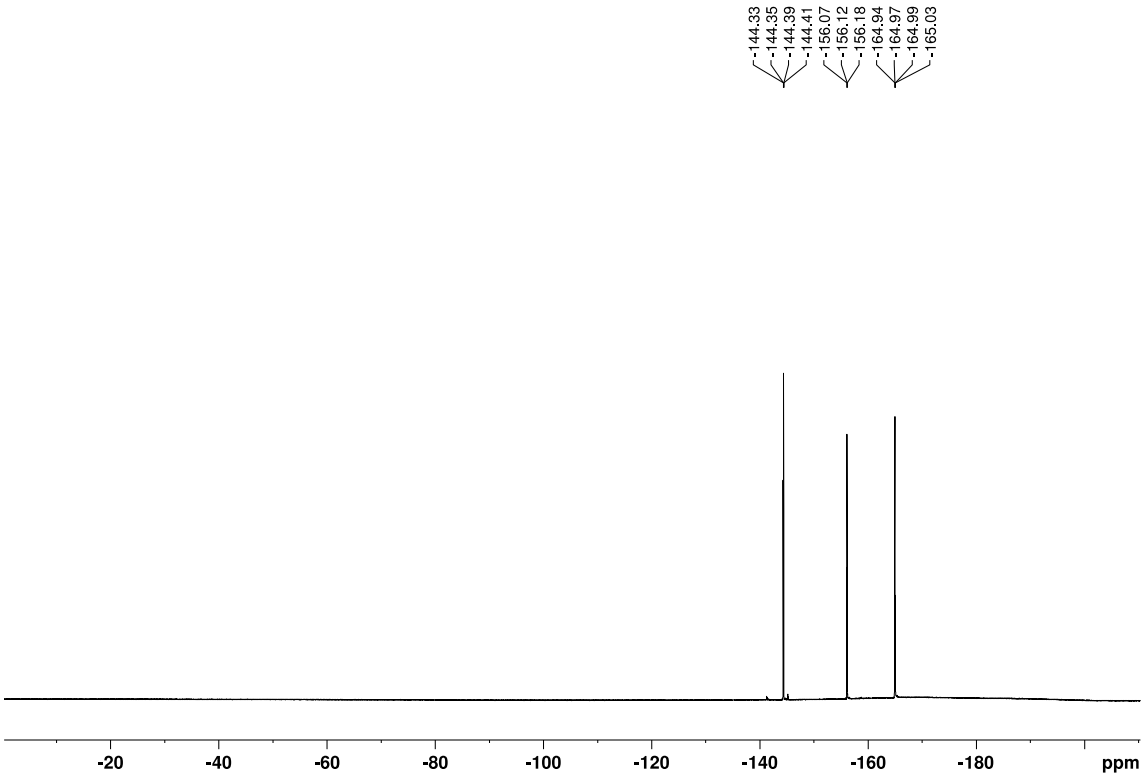
^{1}H NMR (400 MHz, MeOD)



^{13}C NMR (101 MHz, MeOD)

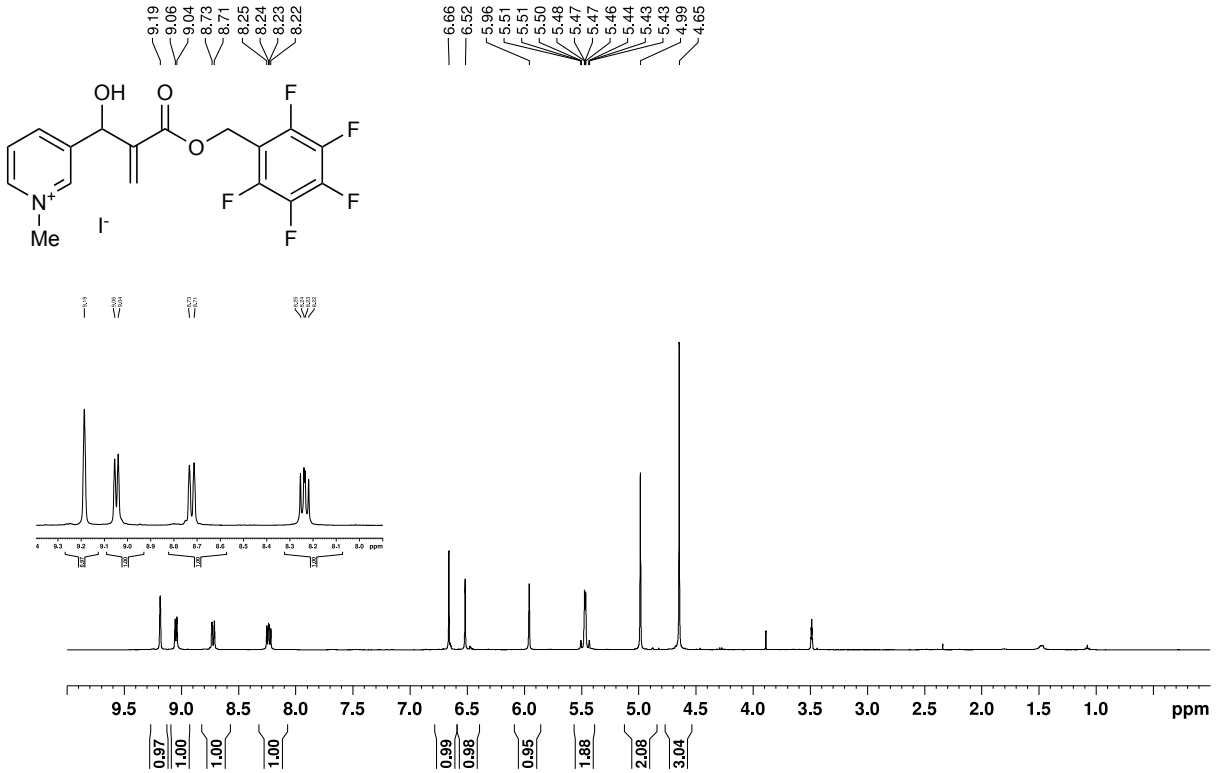


^{19}F NMR (376 MHz, MeOD)

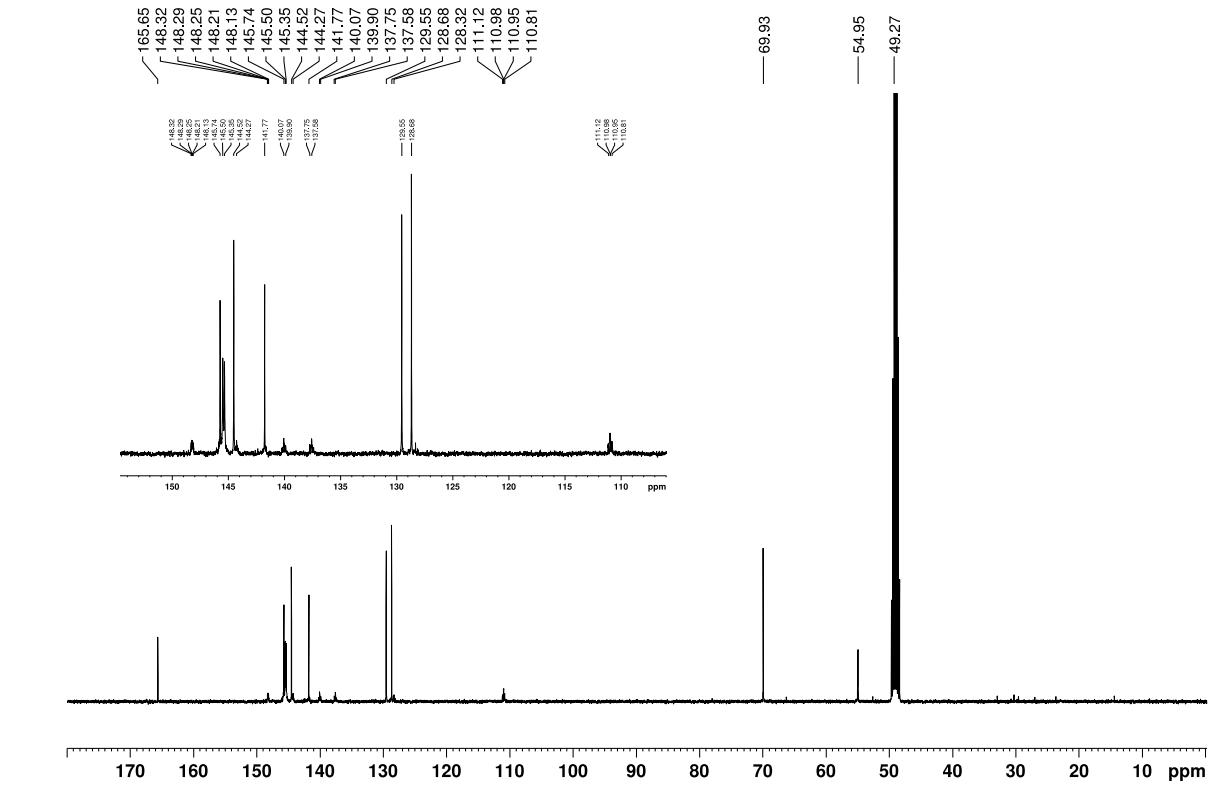


Iodo 3-(1-hydroxy-2-(((perfluorophenyl)methoxy)carbonyl)allyl)-1-methylpyridin-1-ium, 8

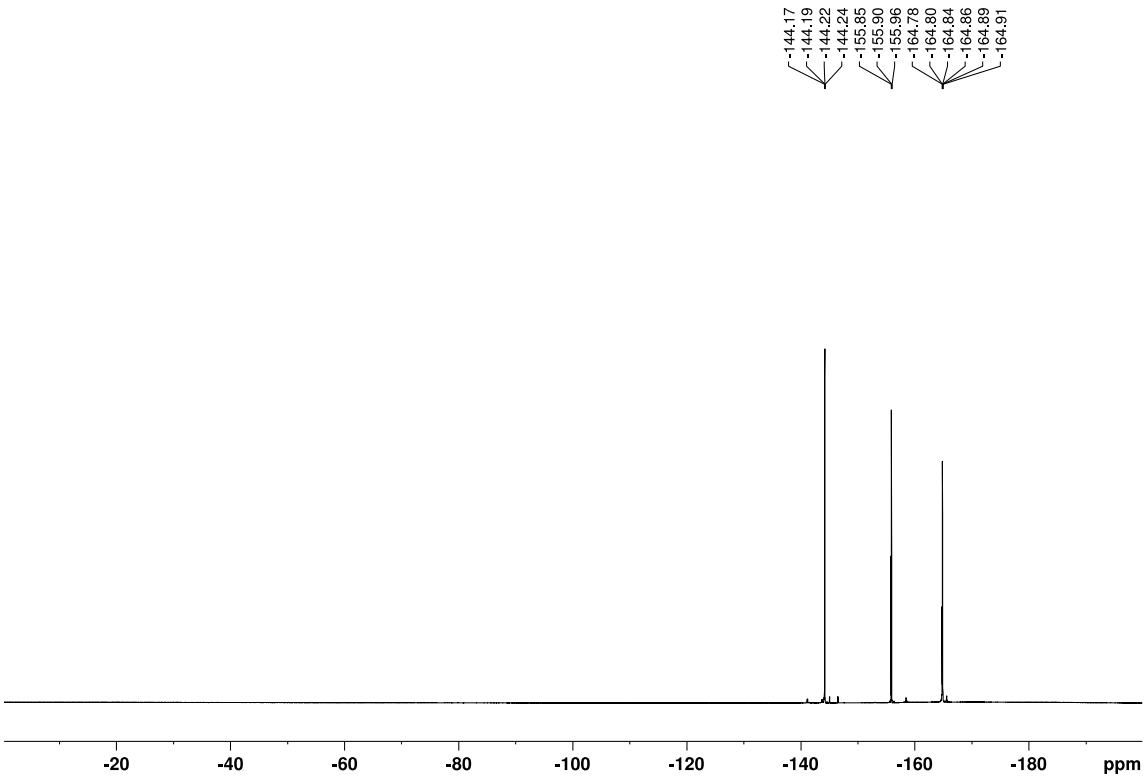
^{1}H NMR (400 MHz, MeOD)



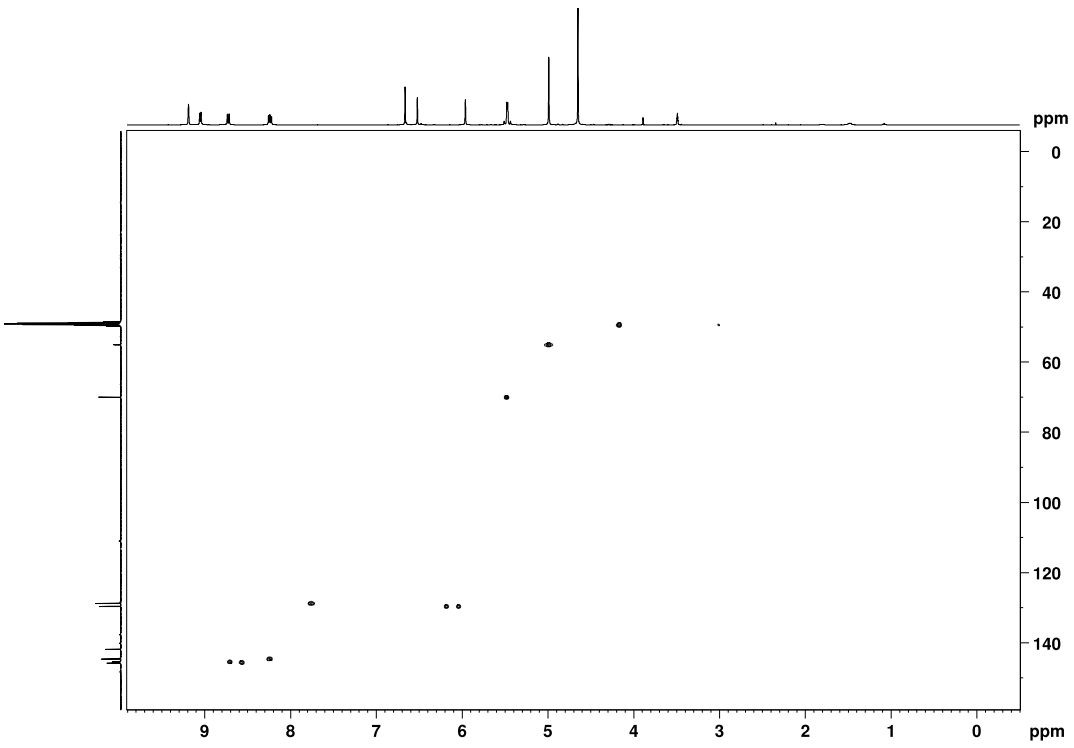
^{13}C NMR (101 MHz, MeOD)



^{19}F NMR (376 MHz, MeOD)

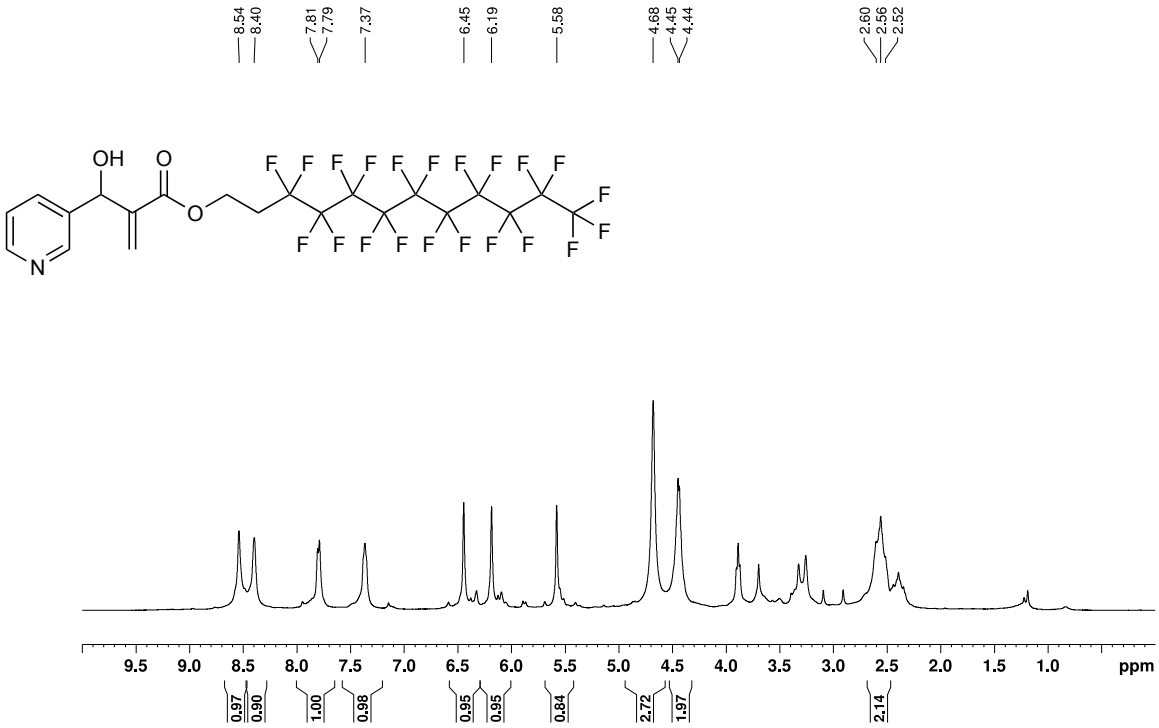


HSQC (MeOD)

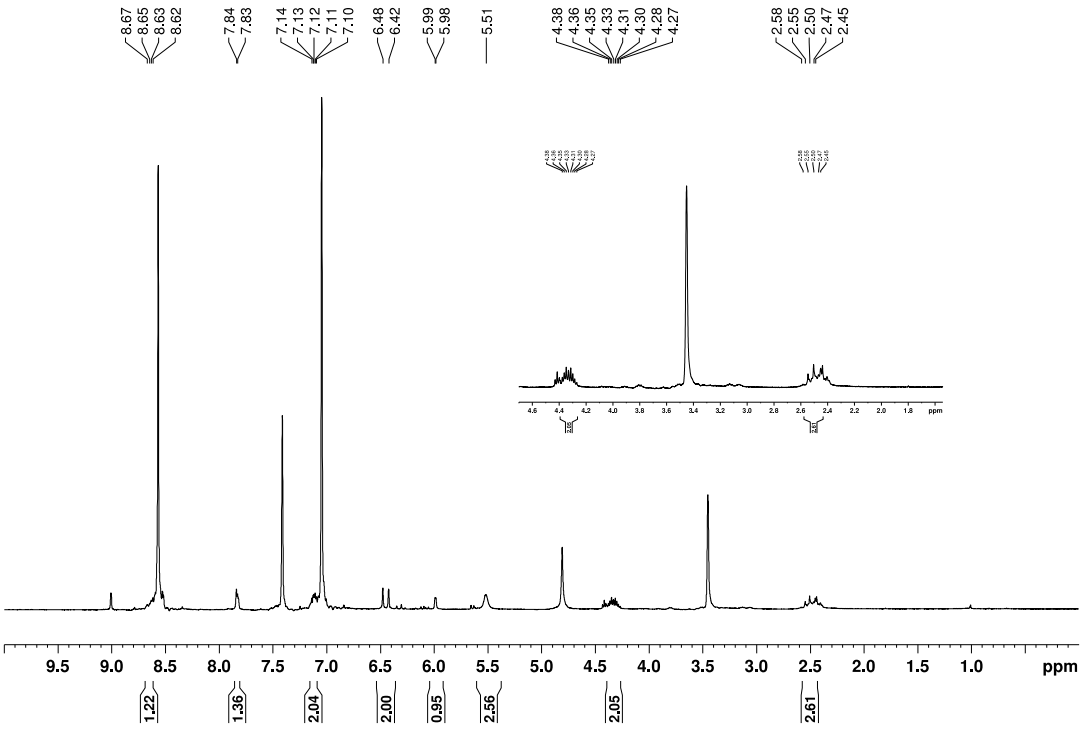


3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafluorododecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 9'

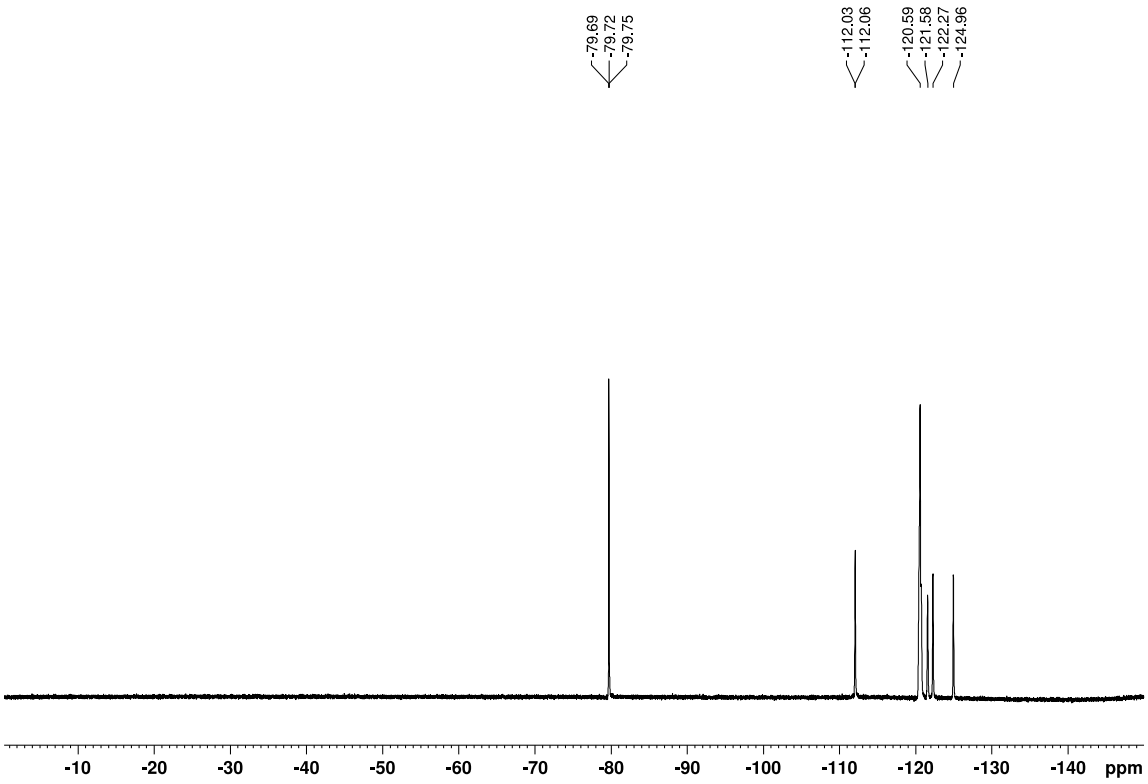
^{1}H NMR (400 MHz, Hexafluorobezene + MeOD)



^{1}H NMR (400 MHz, Pyridine-d_5 + MeOD)

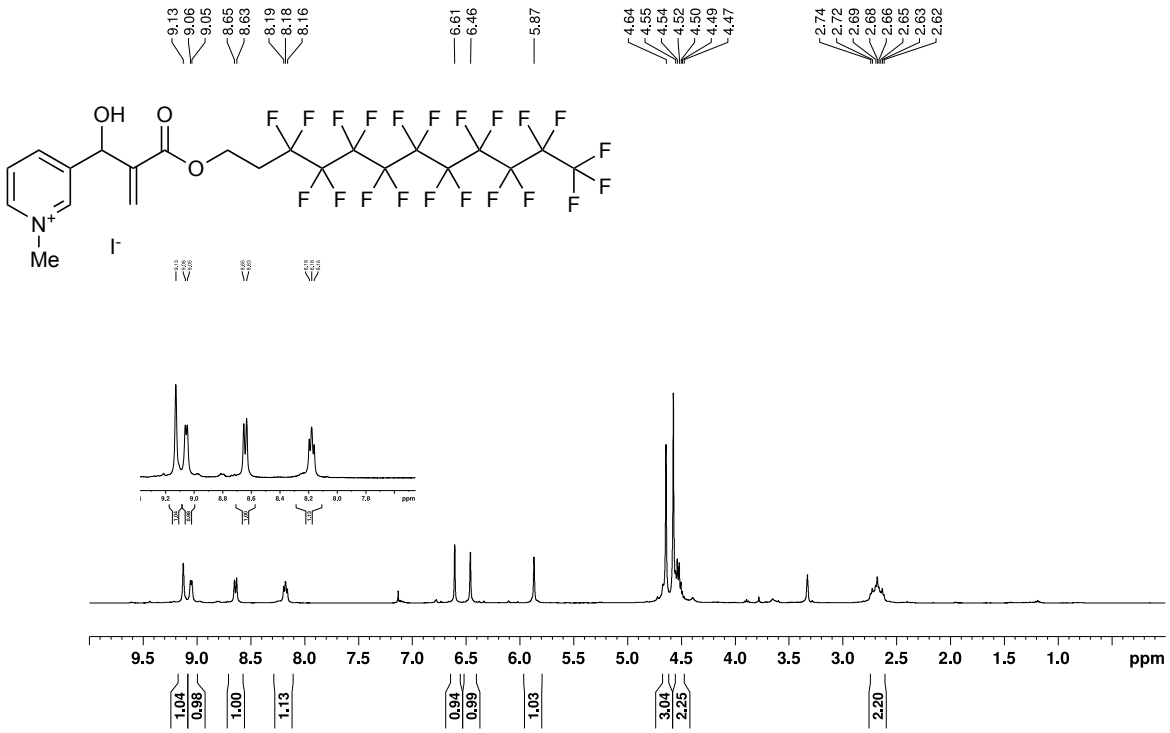


^{19}F NMR (376 MHz, Pyridine-d_5 + MeOD)



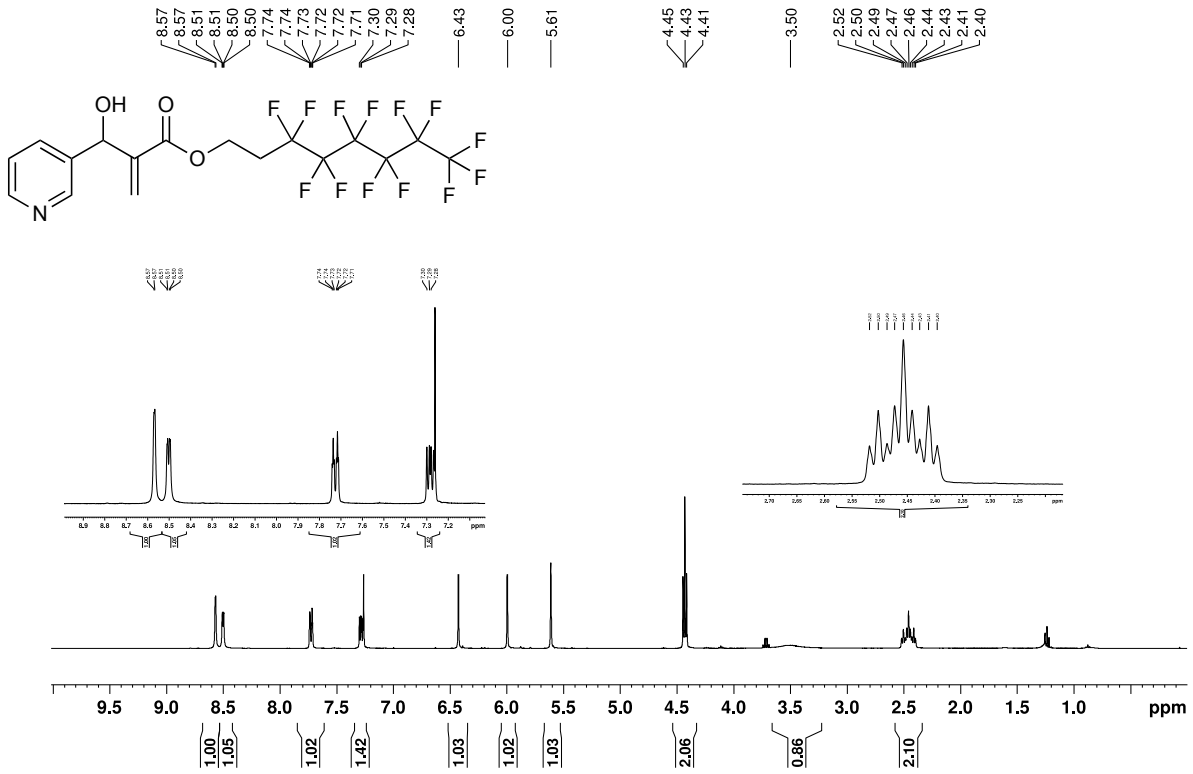
Iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)oxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 9

^{1}H NMR (400 MHz, Hexafluorobenzene + MeOD)

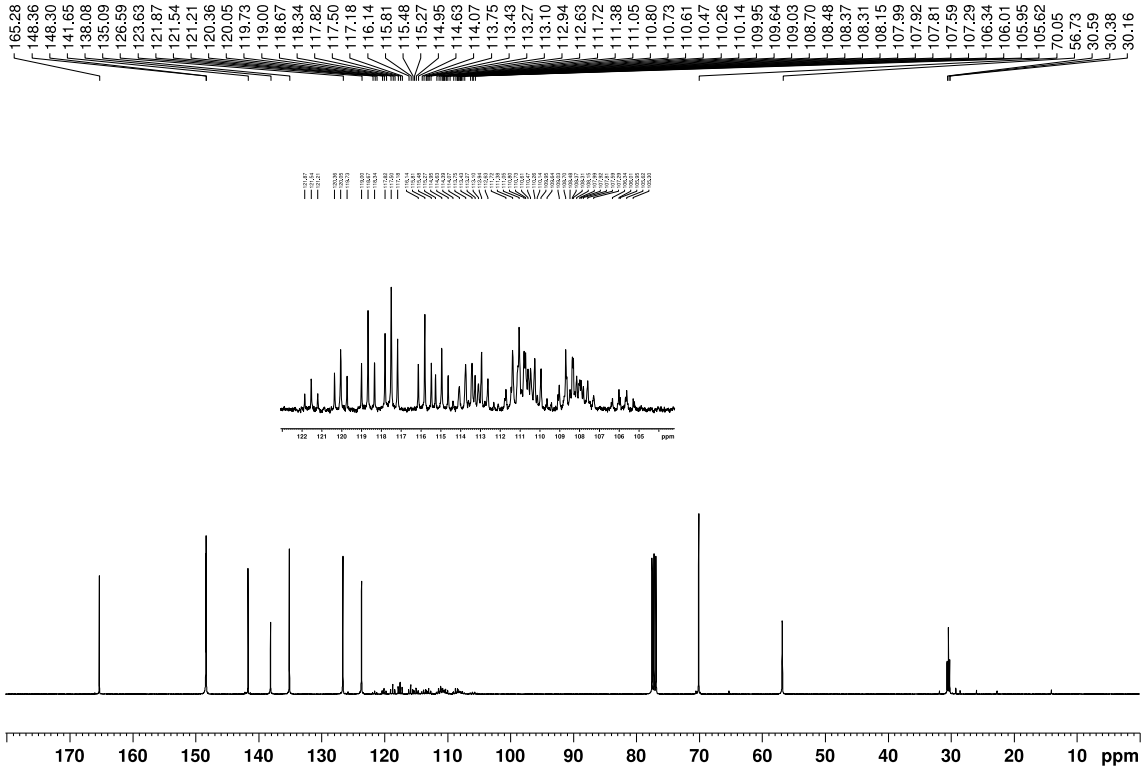


3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 10'

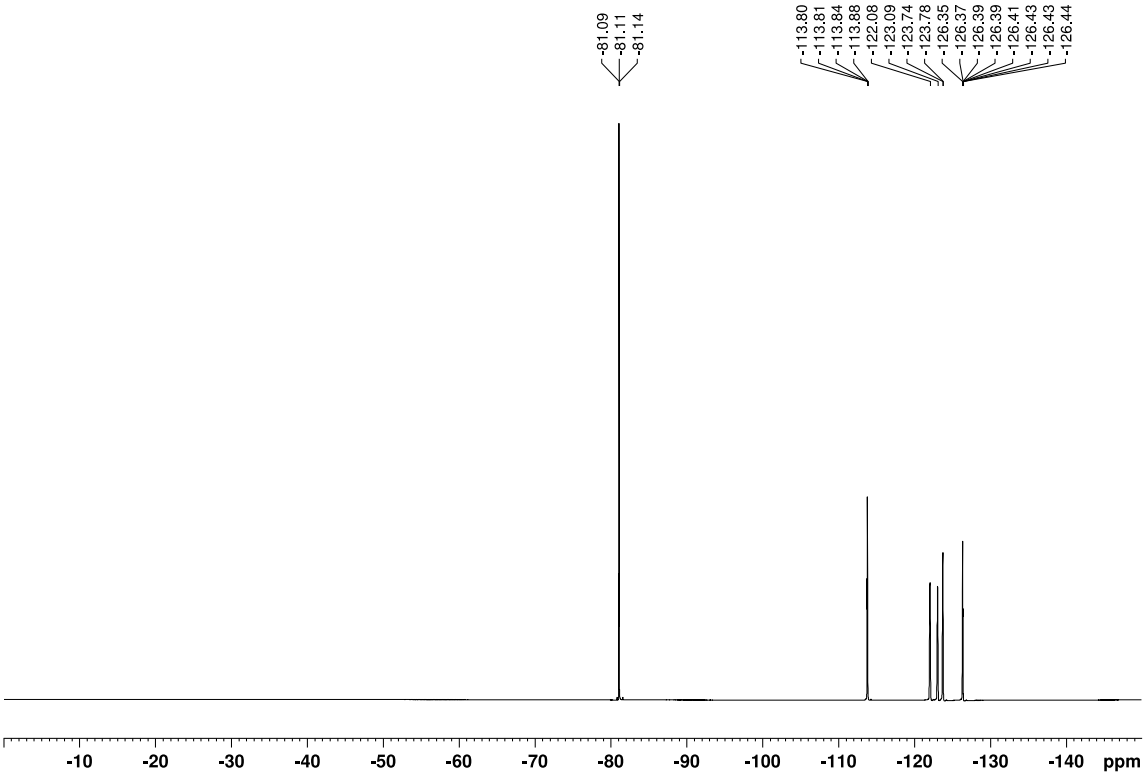
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

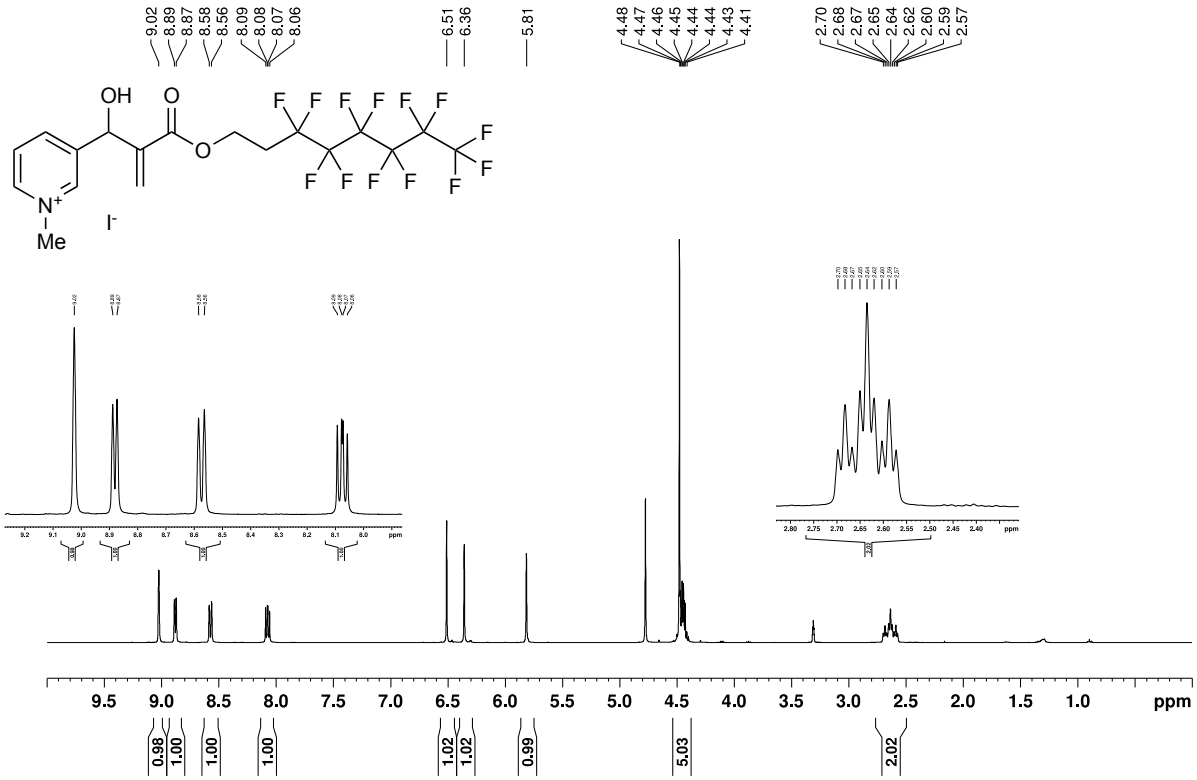


^{19}F NMR (376 MHz, $CDCl_3$)

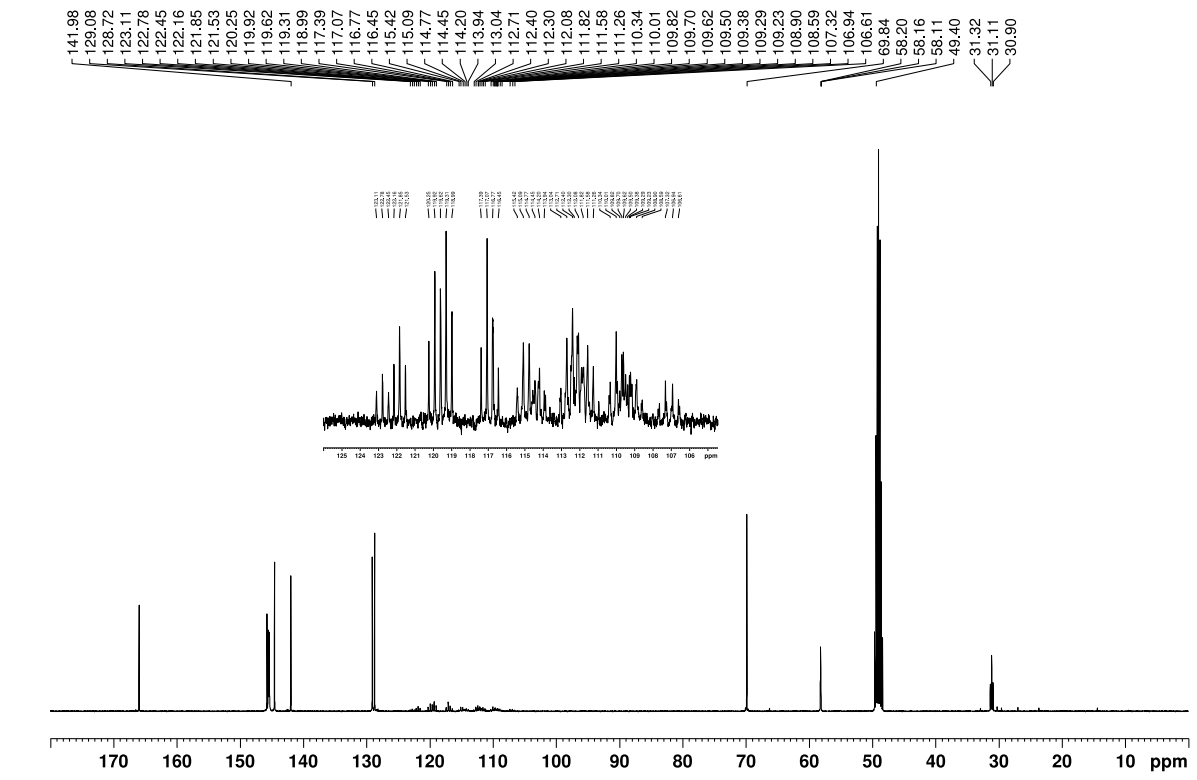


Iodo 3-(1-hydroxy-2-(((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy)carbonyl)allyl)-1-methylpyridin-1-ium, 10

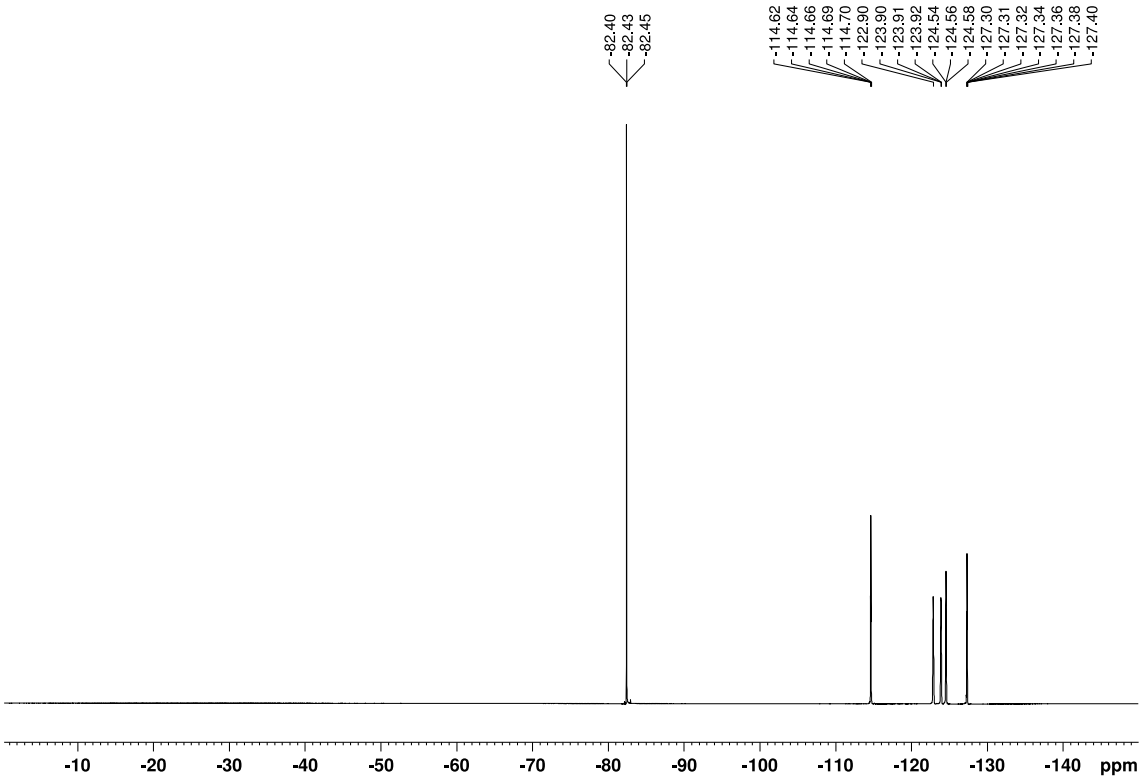
^{1}H NMR (400 MHz, MeOD)



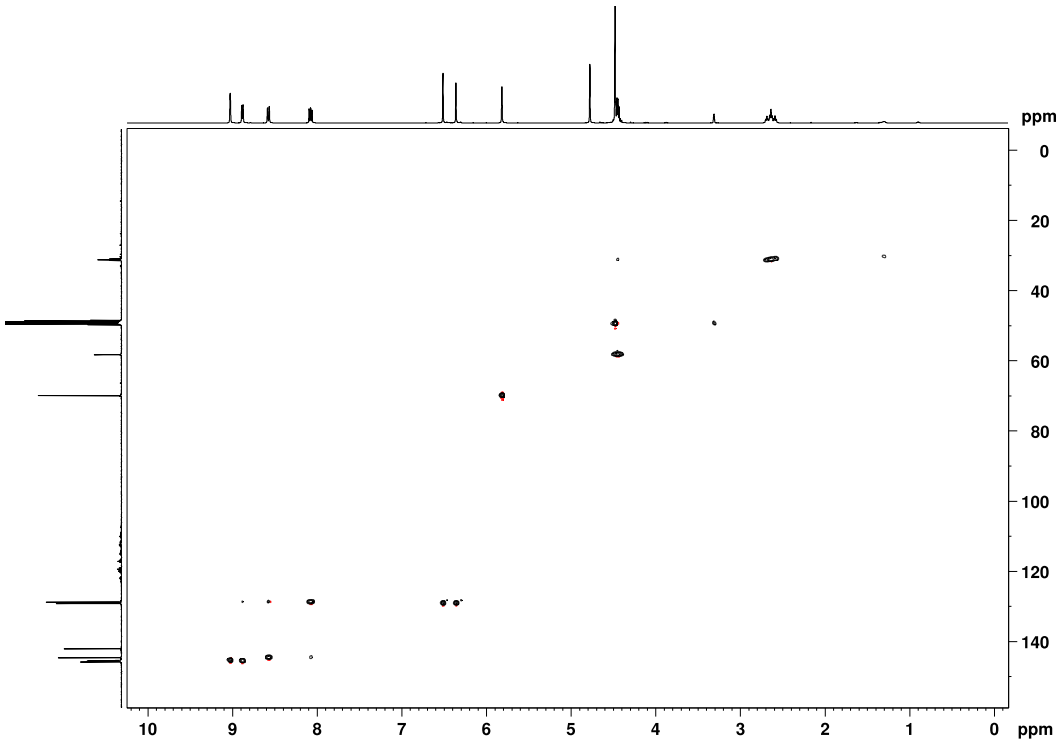
^{13}C NMR (101 MHz, MeOD)



^{19}F NMR (376 MHz, MeOD)

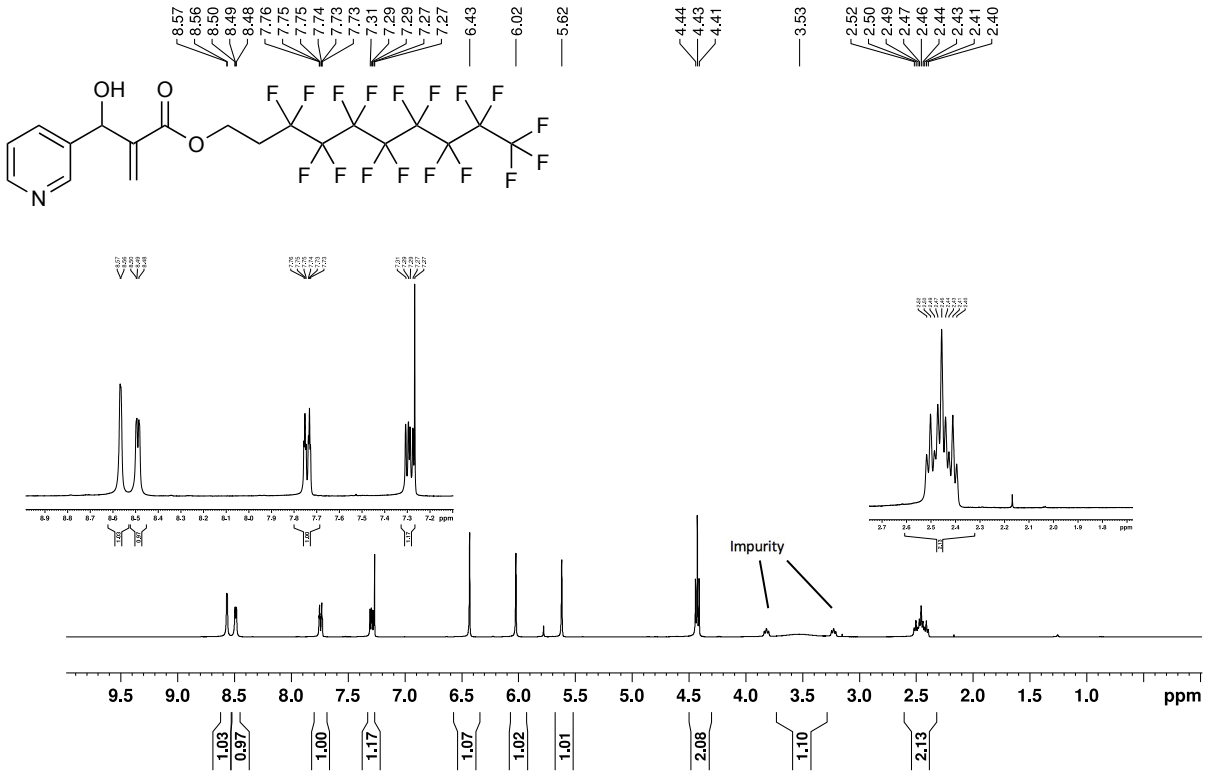


HSQC (MeOD)

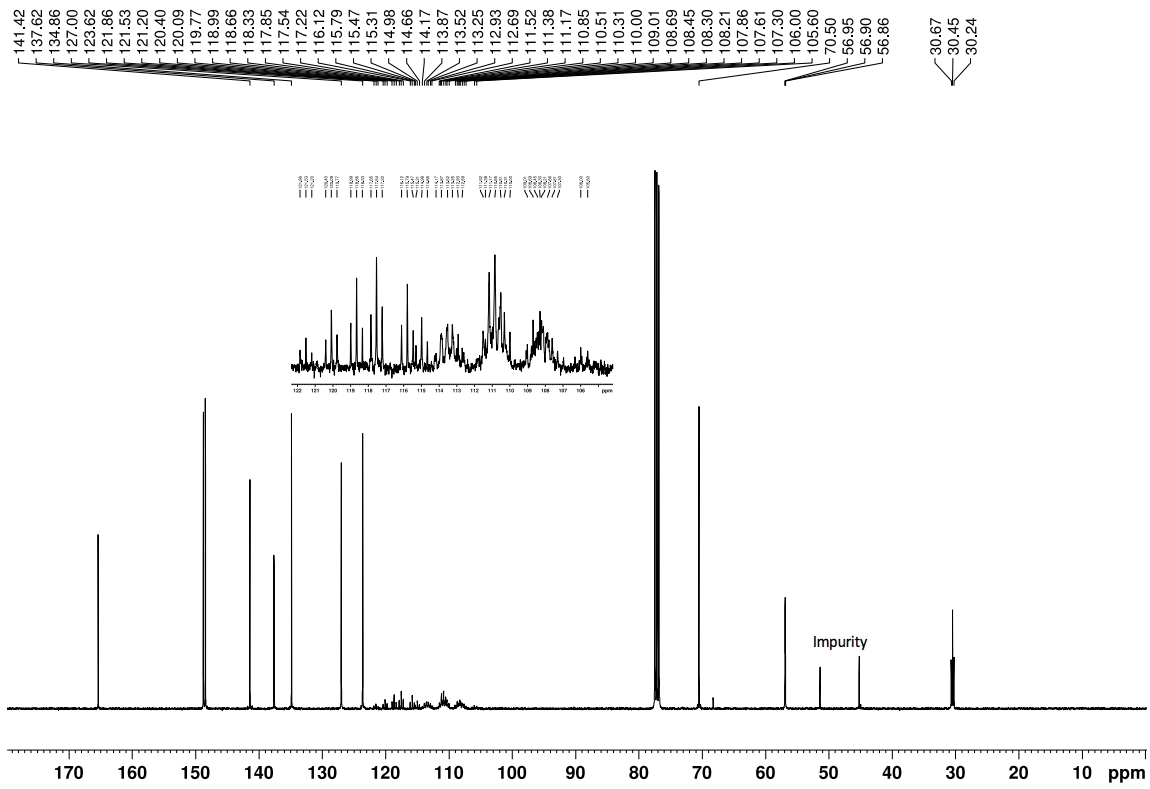


3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl 2-(hydroxy(pyridin-3-yl)methyl)acrylate, 11'

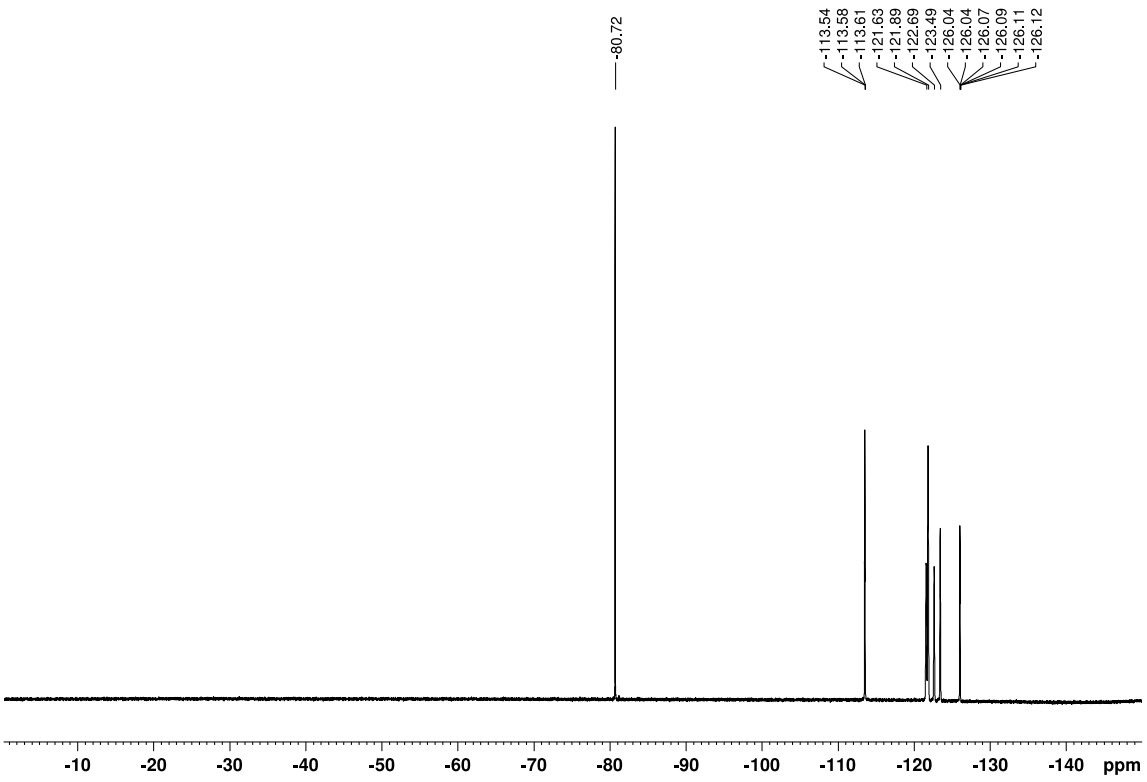
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

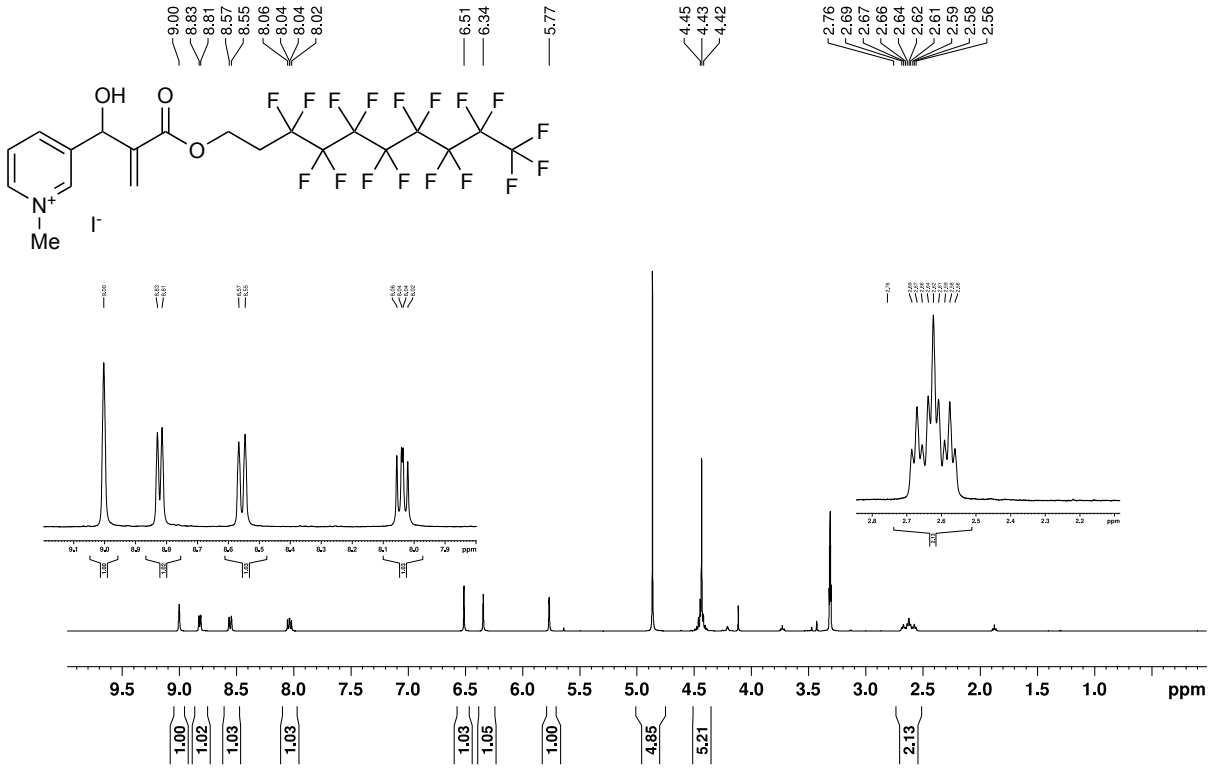


^{19}F NMR (376 MHz, $CDCl_3$)

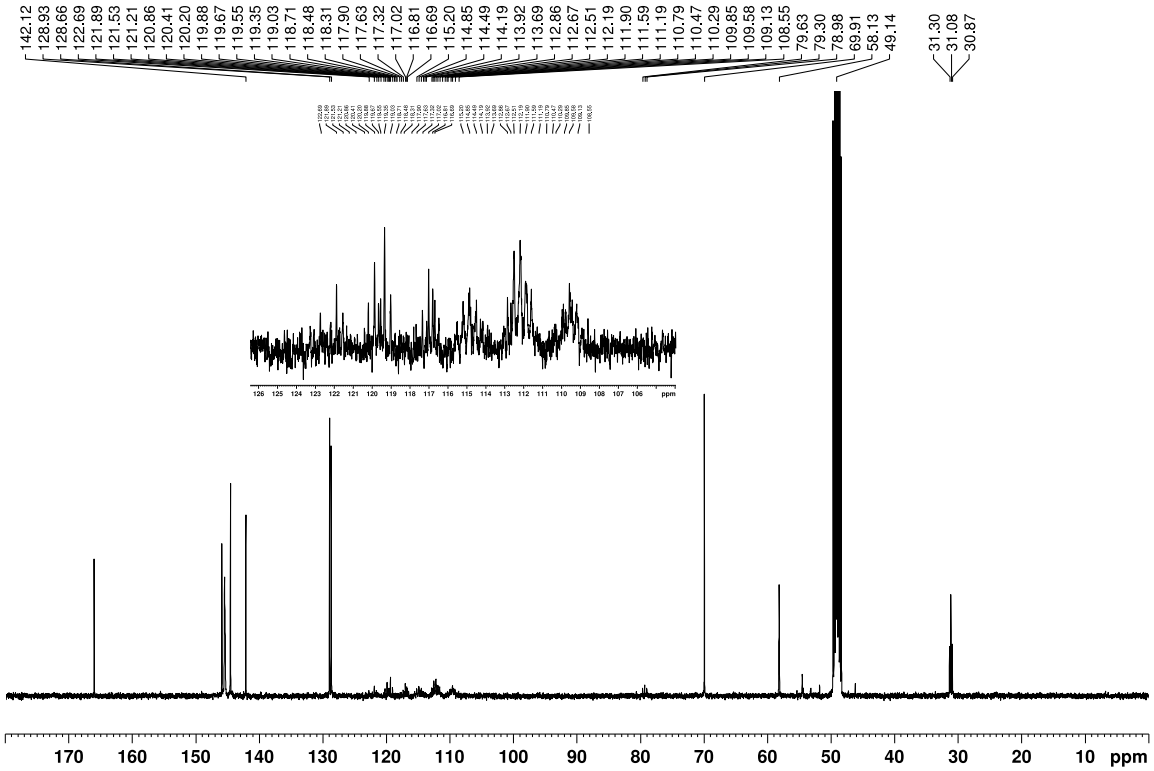


Iodo 3-(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy)carbonyl)-1-hydroxyallyl)-1-methylpyridin-1-ium, 11

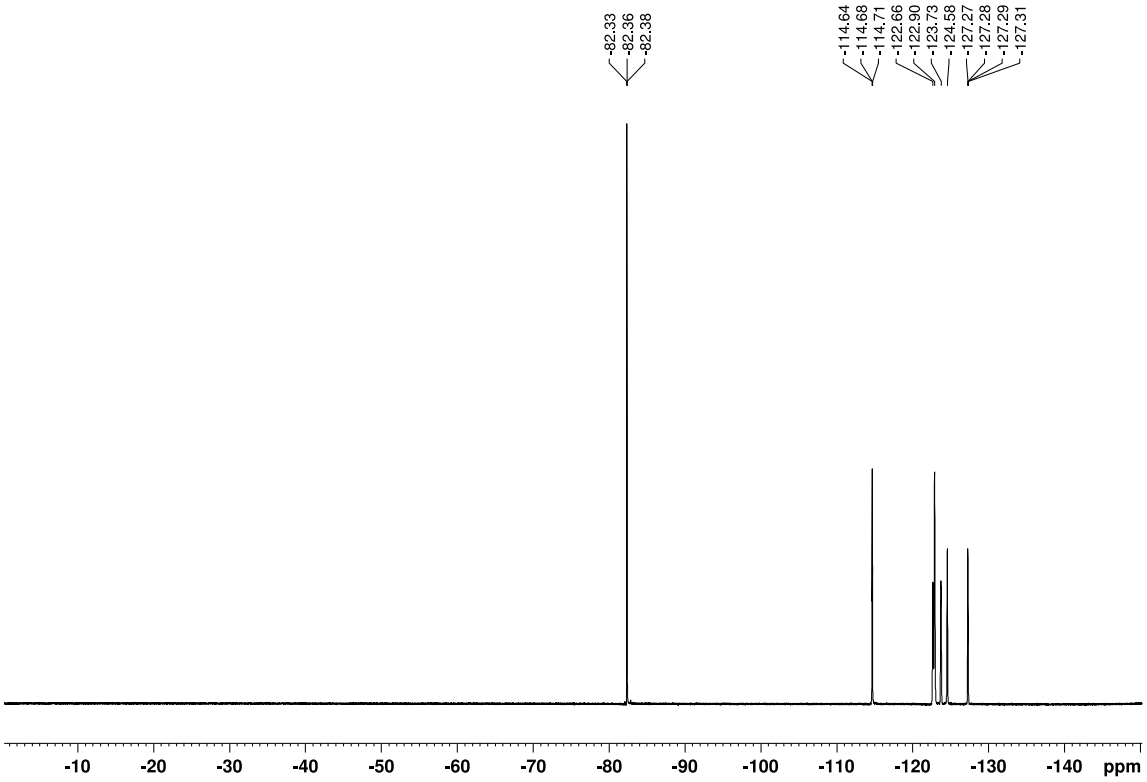
^{1}H NMR (400 MHz, MeOD)



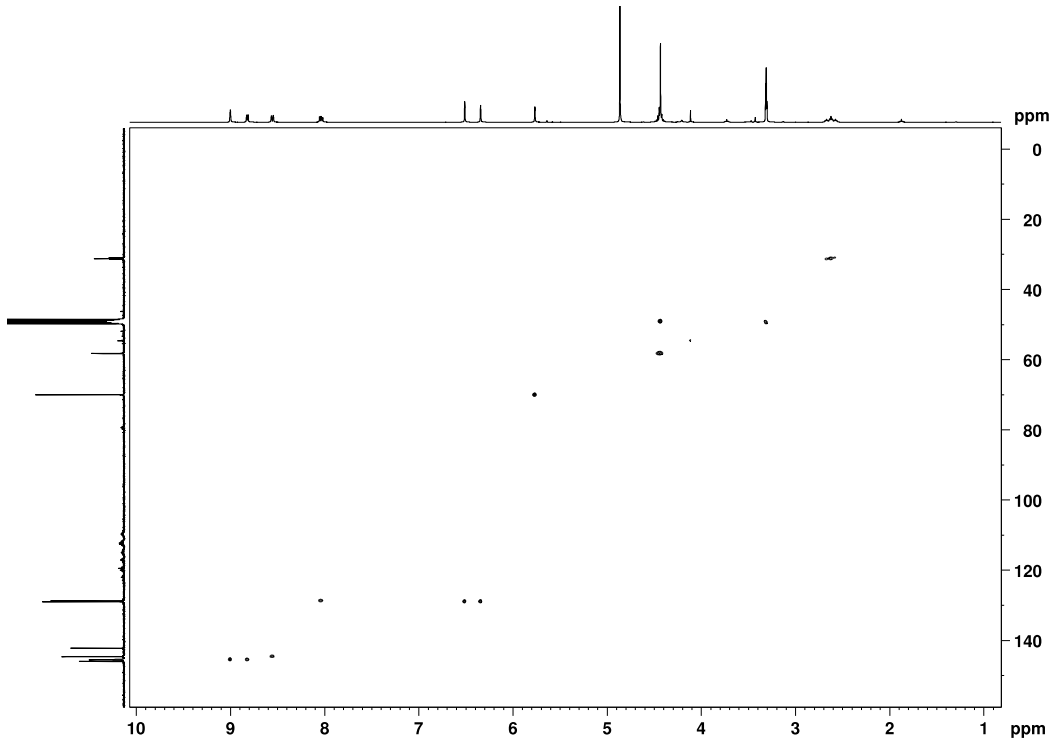
^{13}C NMR (101 MHz, MeOD)



^{19}F NMR (376 MHz, MeOD)



HSQC (MeOD)



4. Physical characterization of the synthetized surfactants

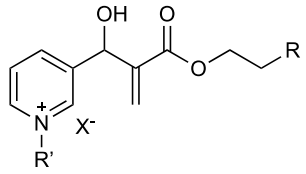
a. Preparation of aqueous surfactant dispersions and macroscopic evaluation

The surfactants were dispersed in deionized water at different concentrations (*c* = 0.1 to 6 g/L). The solutions were mixed using a magnetic stirrer at 700 rpm for 10 min and then an ultrasonic bath for 15 min. Solutions at different concentrations (*c* = 0.05 – 10 g/L) of the commercially available surfactant SDS (Sodium Dodecyl Sulfate) were also prepared for comparison.

Macroscopic evaluations and the minimum value of the Surface Tension (ST_{min}) of all the synthetized surfactants are reported in Tables S1 and S2.

Table S. 1. Macroscopic evaluation and minimal surface tension measurement for the synthetized surfactants of *class 1* (alkyl lipophilic chain).

Class 1: Alkyl lipophilic chain

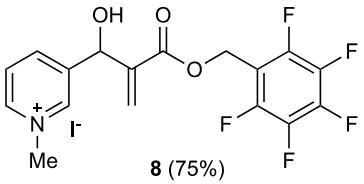


1, R = -$(CH_2)_{19}$-CH_3, R' = Me, X^- = I^- (42%)
2, R = -$(CH_2)_{11}$-CH_3, R' = Me, X^- = I^- (67%)
3, R = -$(CH_2)_9$-CH_3, R' = Me, X^- = I^- (69%)
4, R = -$(CH_2)_7$-CH_3, R' = Me, X^- = I^- (87%)
5, R = -$(CH_2)_9$-CH_3, R' = Et, X^- = I^- (71%)
6, R = -$(CH_2)_9$-CH_3, R' = Et, X^- = Br^- (29%)
7, R = -$(CH_2)_9$-CH_3, R' = H, X^- = Cl^- (70%)

entry	compounds (R, R', X^-)	foam ability	average foam stability	ST_{min} (mN/m)
1	**1** (-$(CH_2)_{19}$-CH_3, Me, I^-)	-	-	-
2	**2** (-$(CH_2)_{11}$-CH_3, Me, I^-)	+	few hours	n.d.
3	**3** (-$(CH_2)_9$-CH_3, Me, I^-)	+	few hours	~ 36
4	**4** (-$(CH_2)_7$-CH_3, Me, I^-)	+	-	~ 36
5	**5** (-$(CH_2)_9$-CH_3, Et, I^-)	+	few hours	~ 35
6	**6** (-$(CH_2)_9$-CH_3, Et, Br^-)	+	few hours	~ 38
7	**7** (-$(CH_2)_9$-CH_3, H, Cl^-)	-	-	-

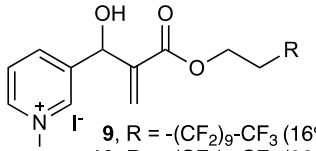
Table S. 2. Macroscopic evaluation and minimal surface tension measurement of the synthetized surfactants of *class 2* (pentafluorobenzyl lipophilic part) and *class 3* (polyfluoroalkyl lipophilic chain).

Class 2: Pentafluorobenzene lipophilic part



8 (75%)

Class 3: Perfluorinated alkyl lipophilic chain



9, R = -$(CF_2)_9$-CF_3 (16%)
10, R = -$(CF_2)_5$-CF_3 (92%)
11, R = -$(CF_2)_7$-CF_3 (48%)

entry	compounds (R, R', X^-)	foam ability	average foam stability	ST_{min} (mN/m)
1	**8** (-C_6F_5, Me, I^-)	-	-	-
2	**9** (-$(CF_2)_9$-CF_3, Me, I^-)	-	-	-
3	**10** (-$(CF_2)_5$-CF_3, Me, I^-)	+	several days	~ 19
4	**11** (-$(CF_2)_7$-CF_3, Me, I^-)	+	several weeks	~ 19

b. Critical Micellar Concentration measurements of aqueous surfactant dispersions

Surface Tension (ST) measurements were performed using pendant drop shape analysis technique (Drop Shape Analyzer) at different surfactant concentrations (*c* = 0.1 – 6 g/L) at 20 °C.

The pendant drop is a drop suspended from a needle in a bulk liquid or gaseous phase (air). The shape of the drop results from the relationship between the surface tension or interfacial tension and gravity. Consequently, the surface tension or interfacial tension is calculated from the shadow image of a pendant drop using drop shape analysis. The pendant drop shape was determined by the factors: droplet volume; density and the surface tension.

c. Characterization of the synthesized surfactants

In the case of the surfactant **11**, this latter was also characterized by using electron microscopes to visualize it (Figure S1). For Scanning Electron Microscope (SEM), the powdered sample was directly placed on a carbon impregnated self-adhesive disc. It was then coated with 3 nm of pure gold. Otherwise, for Transmission Electron Microscope (TEM) characterization, it was dispersed in water using an ultrasonic bath for 5 min and drops on carbon-coated grids and allowed to air dry.

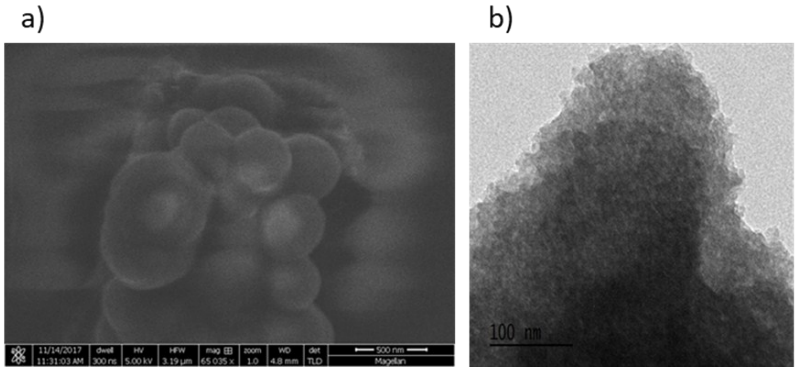


Figure S. 1 *Scanning Electron Microscope (SEM) image and b) Transmission Electron Microscope (TEM) image of the perfluorinated surfactant* ***11*** *in water at 1.5 g/L.*

d. Preparation and measurement of aqueous foams

Foams were initially prepared by hand shaking (in bulk) in order to select the correct formulation. Then, microfluidic was used to optimize the production of the foam.

1) Hand-shaking.
   The aqueous surfactant dispersion was transferred to Falcon tubes 50 mL filled with 10 mL of an aqueous solution of surfactant at a concentration ranging between 0.1 and 6 g/L. The Falcon tubes were stoppered and then shaken up and down vigorously for about 30 times. The foam volumes just after shaking were taken as the measure of foamability of the aqueous surfactant solution. The foam stability was evaluated measuring the foam volume at different times.
   When the foam is generated, the volume of the foam sample (which is the total volume minus the pure liquid volume) was tracked using a camera and pictures are taken at time 0 to measure the foamability and at regular time lapses to evaluate the stability over time.

The best hand shaking tests (at concentration close to the CMC) are showed for surfactant **10** in Figures S.2 and S.3.

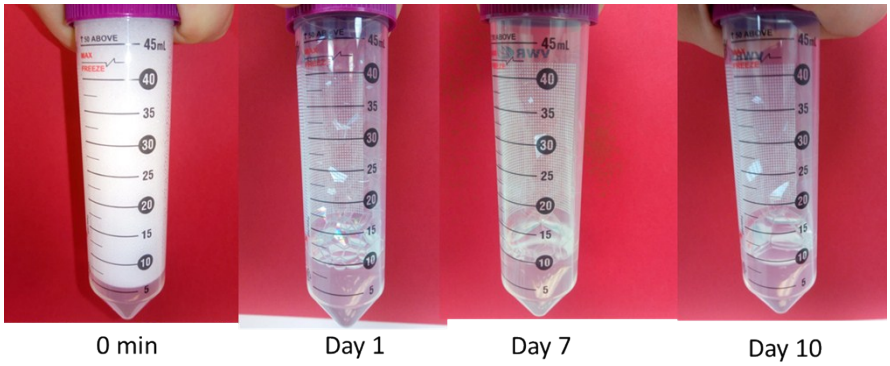


Figure S. 2 *Pictures of perfluorinated surfactant* ***10*** *foams (c=2 g/L) taken at different times*

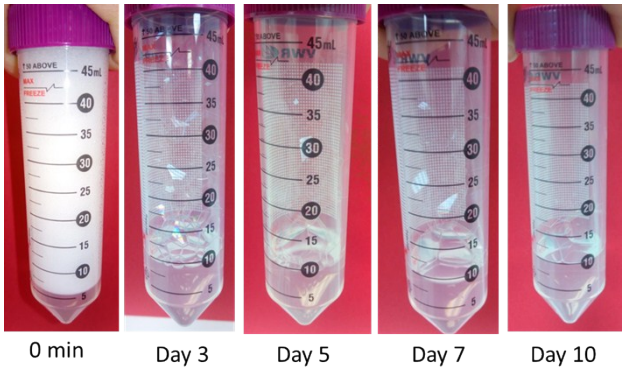
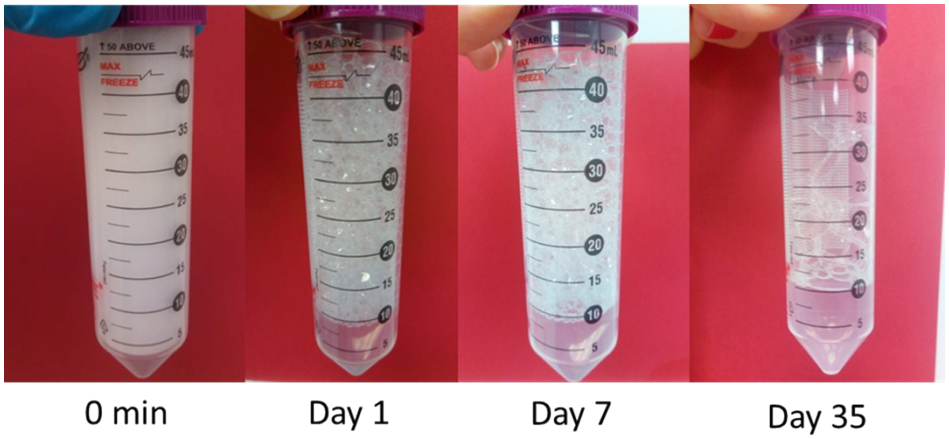


Figure S. 3 *Pictures of perfluorinated surfactant* ***10*** *foams (c=3 g/L) taken at different times*

The hand shaking tests for three different concentrations (0.15; 0.5; 1.5 g/L) are showed for surfactant **11** in Figures S. 4- 6.

Figure S4 (bottom) shows the comparison between surfactant **11** and SDS foams, both generated by the hand-shaking method. For the polyfluorinated surfactant **11** in water at 0.15 g/L, shaking tests showed outstanding foamability which was comparable to the one obtained with commercial surfactant SDS (Figure S4, time 0). More interestingly, after 1 day, the SDS foam totally disappeared while the total foam volume obtained with surfactant **11** only slightly decreased, showing a very good stability (Figure S4, time= 1 day).



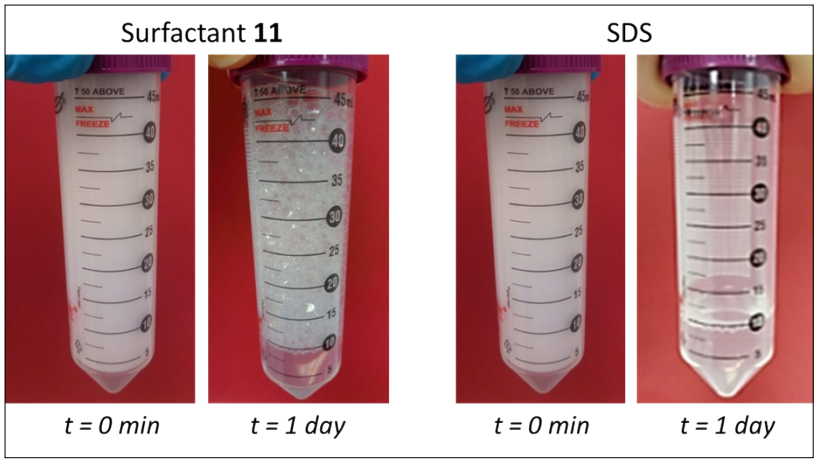


Figure S. 4 *Pictures of perfluorinated surfactant* ***11*** *foams taken at different times for a concentration of 0.15 g/L in water, close to the CMC (top). Pictures of the foam of the polyfluorinated surfactant 11 at 0.15 g/L and SDS at 7 mM after 1 day (bottom).*

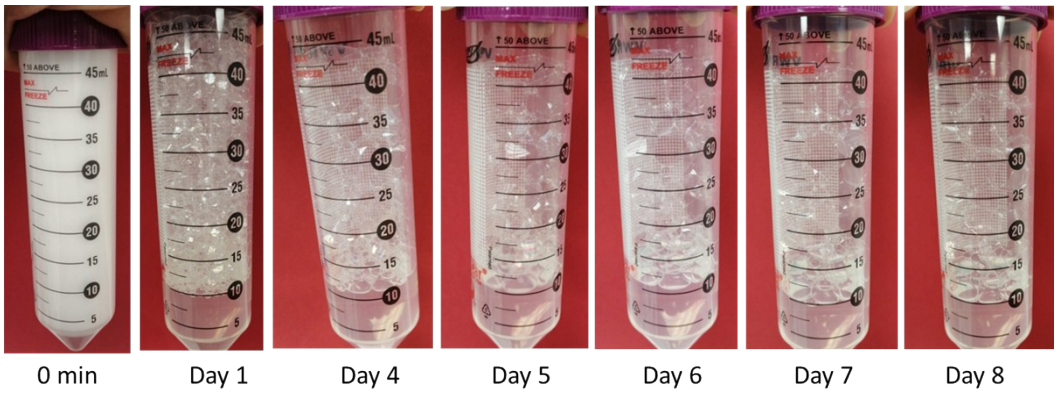


Figure S. 5 *Pictures of perfluorinated surfactant* ***11*** *foams taken at different times for a concentration of 0.5 g/L in water.*

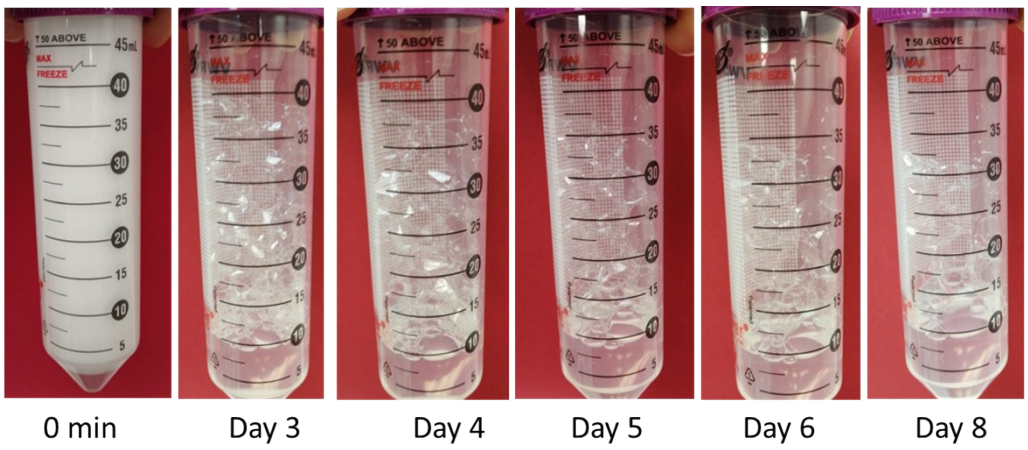


Figure S. 6 *Pictures of perfluorinated surfactant* ***11*** *foams taken at different times for a concentration of 1.5 g/L in water, close to the CMC.*

Hand-shaking tests were not highly reproducible and the estimation of the exact foam evolution in time in order to have quantitative information has been very difficult to perform. Hand-shaking was a preliminary step before the controlled microfluidic experiments that are described below.

2) Microfluidic set-up.

Foam generation was carried out using a classical Flow-Focusing microfluidic geometry (Figure S. 7). The device was made by standard soft photolithography and replica-molding techniques using polydimethylsiloxane (PDMS). The PDMS device is then irreversibly bonded to a microscope glass slide by corona discharge. The channels have a depth of 50 µm and a width of 100 µm and meet each other at a FF junction of 30 µm wide. The gas flow is pressure-driven at a pressure p_{gas} using a MFCS™-EZ pressure controller Control Systems connected to a nitrogen tap. Using a pressure-driven flow, rather than a flow-rate-driven one, gas flow ensured rapid stabilization of the viscous two-phase flow in the microfluidic chip since the gas is compressible at the characteristic pressures encountered in the device. The gas phase was nitrogen with traces of perfluorohexane, a gas which is used in many studies about liquid foams in order to hinder Ostwald ripening. Different gas pressures were tested, and the influence of the pressure ratio, defined as the ratio between the gas and the liquid phase, was determined. For the feasibility study, an aqueous solution containing surfactant concentrations ranging from 0.1 to 1.5 g/L was used to explore the effects on the bubble formation. The flow-focusing behaviour on the microchannel was observed using an Optical Microscope with a 4x scanning objective. The foam was generated and collected on microscope glass slides to be then characterized by using confocal microscopy.

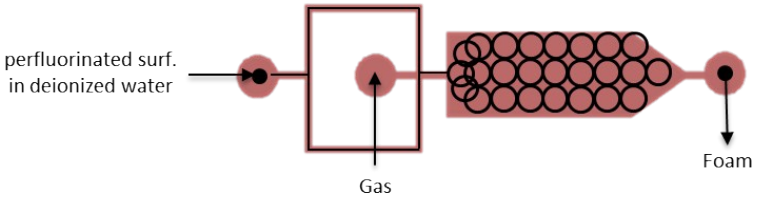


Figure S. 7 *Flow Focusing Microfluidic set-up to produce foams from the polyfluorinated surfactants.*

e. Bubble size evolution in a FF microfluidic device

Figures S. 8-10 show the range of bubble sizes that can be generated in a FF microfluidic chip with a constriction of 30 µm wide by using an aqueous solution of surfactant **11** at 0.15 g/L.

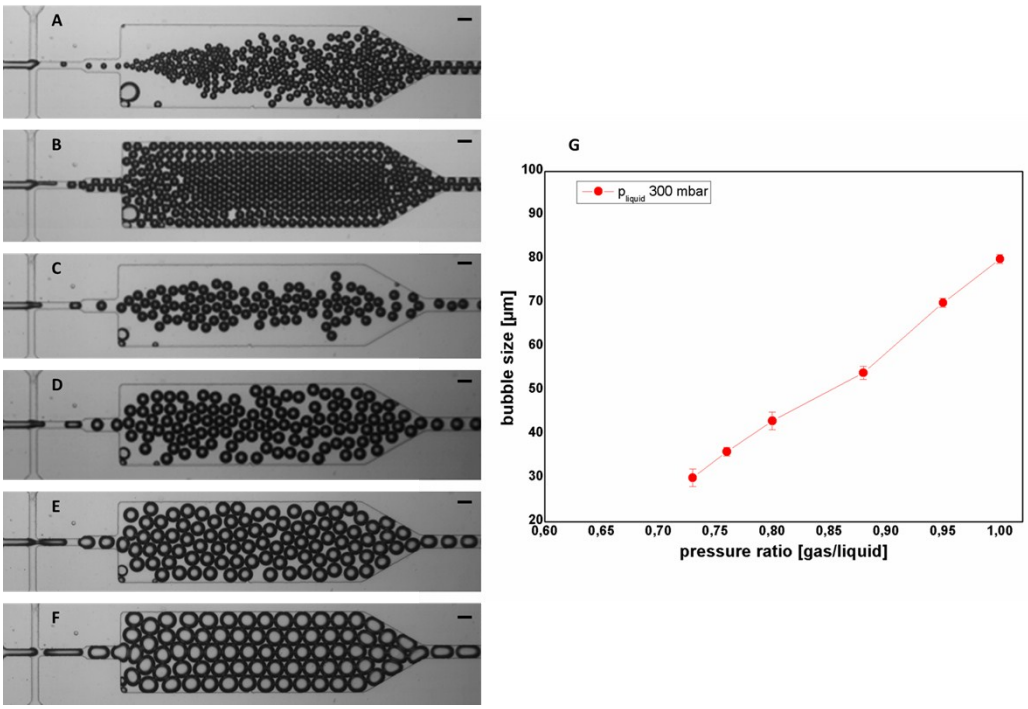


Figure S. 8 *Bubble size evolution at different pressure ratios (gas/liquid) when the* p_{liquid} *is 300 mbar.*
A-F) Optical images of the bubble generation in a FF microfluidic device with a constriction of 30 µm by changing the pressure ratio from 0.73 to 1. Scale bar 50 µm; G) Bubble size varies from 30 to 80 µm increasing the pressure ratio.

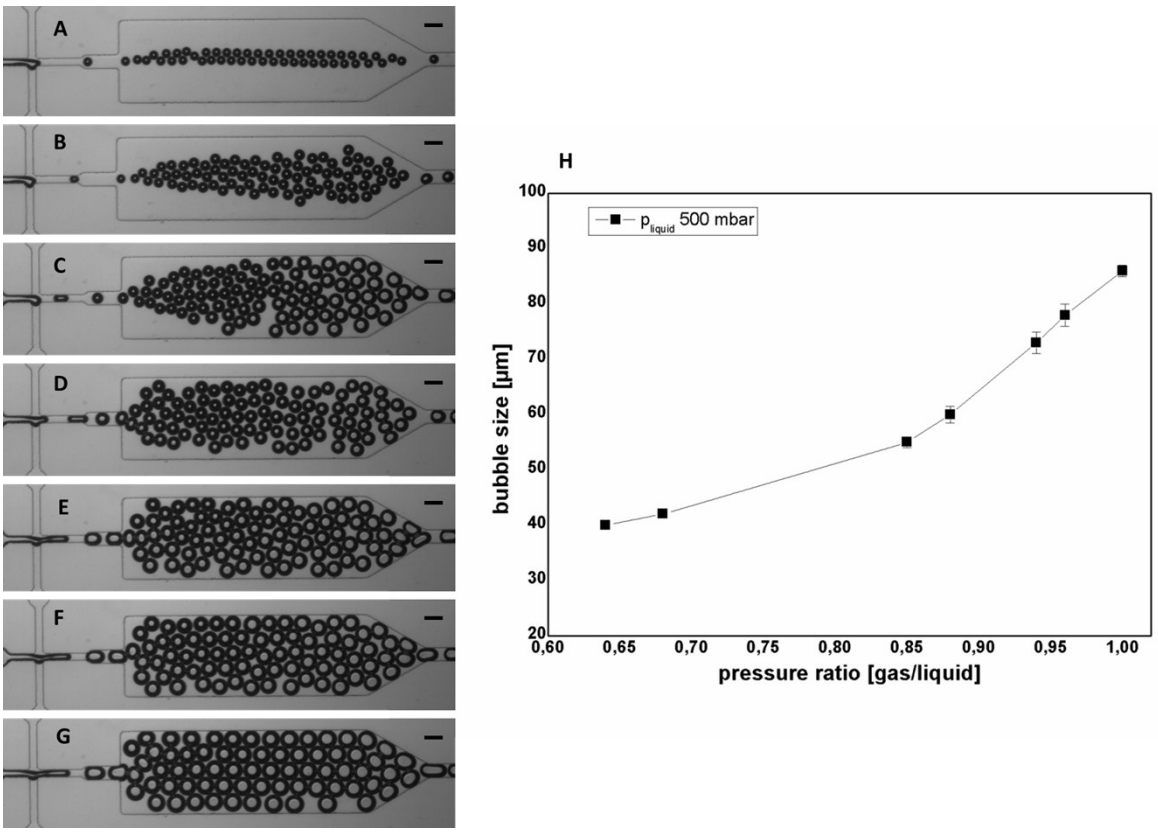


Figure S. 9 *Bubble size evolution at different pressure ratios (gas/liquid) when the* p_{liquid} *is 500 mbar.*
A-F) Optical images of the bubble generation in a FF microfluidic device with a constriction of 30 µm by changing the pressure ratio from 0.64 to 1. Scale bar 50 µm; G) Bubble size varies from 40 to 85 µm increasing the pressure ratio.

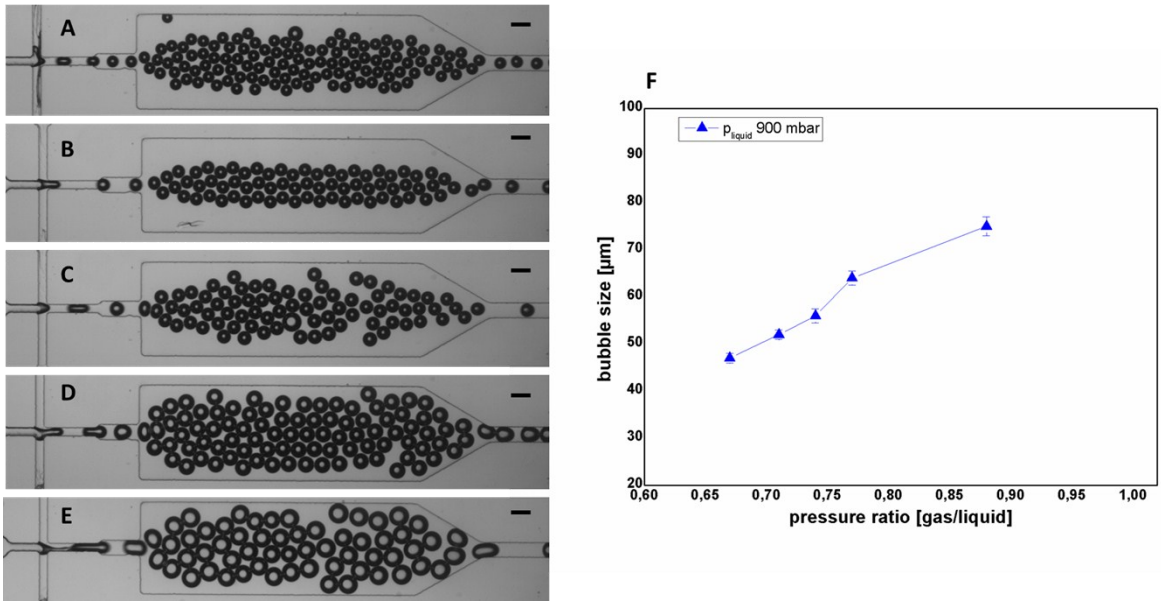


Figure S. 10 *Bubble size evolution at different pressure ratios (gas/liquid) when the* p_{liquid} *is 900 mbar.*
A-F) Optical images of the bubble generation in a FF microfluidic device with a constriction of 30 µm by changing the pressure ratio from 0.67 to 0.88. Scale bar 50 µm; G) Bubble size varies from 47 to 75 µm increasing the pressure ratio.

Most of the microfluidic experiments were conducted at p_{gas}/p_{liquid} = 0.95 with a p_{liquid} = 500 mbar producing foams with 80-85 µm in bubble size. Different surfactant concentrations of **11** (from 0.15 to 1.5 g/L) have been tested.

f. Characterization of aqueous foams fabricated in microfluidics

To observe foams, stabilized by the surfactant **11**, the foam was placed on a microscope glass slide, and micrographs were taken (before moisture evaporated) using Optical and in particular Confocal Microscope systems (Leica).

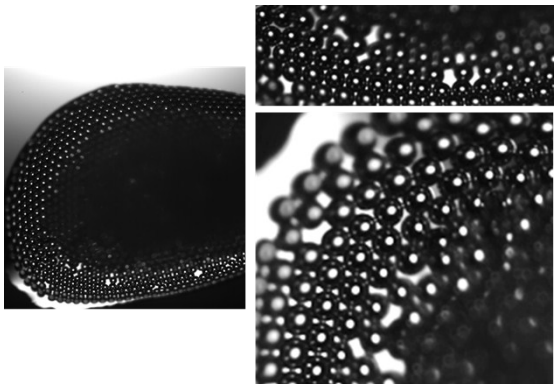


Figure S. 11 *Optical microscope images of typical obtained foams after the collection on a microscope glass plate.*

Most of the foam images were taken by using confocal microscopy. None of the fluorescent dyes is added to the surfactant solution in water. Confocal images are taken in transmission by using a laser light (visible 458 nm). Automatically, images are captured every 30 seconds like in the following Figures (Figure S. 12, S.13, S. 14).

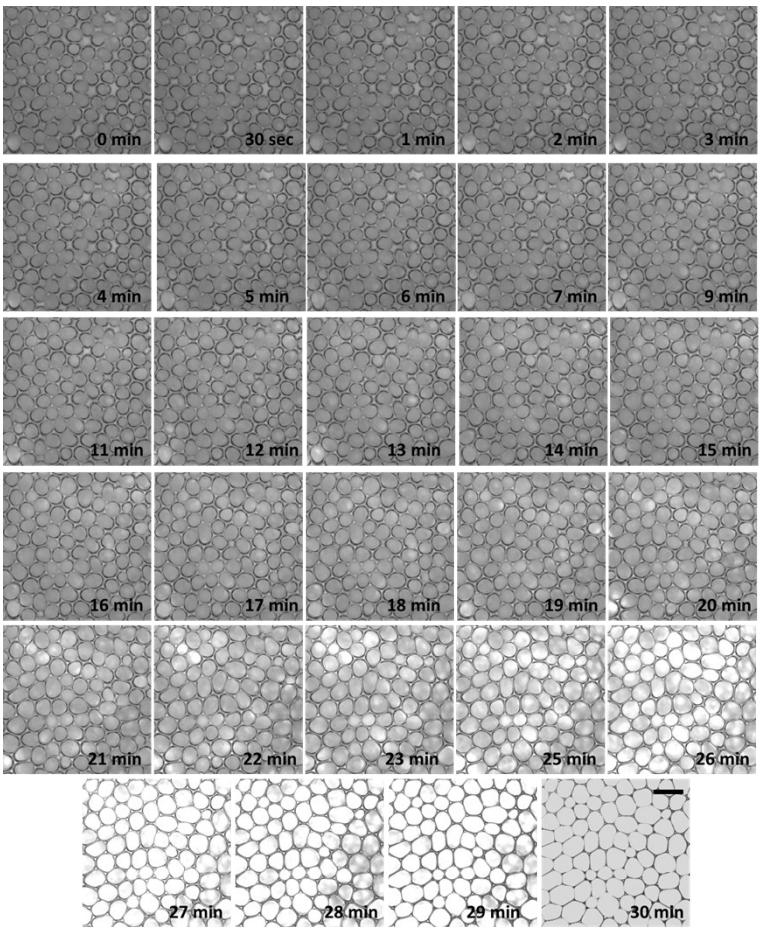


Figure S. 12 *Evolution of the bubbles during the drying process of the foam (c = 0.15 g/L) by confocal microscope analysis. Scale bar 100 µm.*

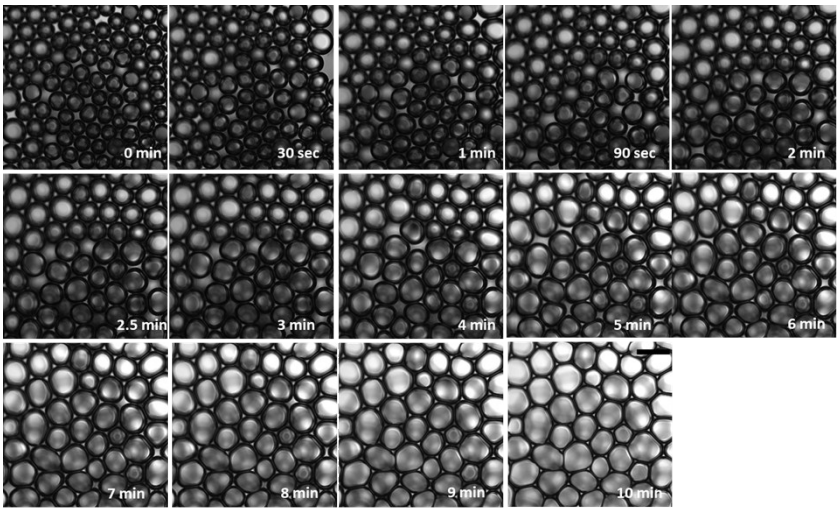


Figure S. 13 *Evolution of the bubbles during the drying process of the foam (c = 0.5 g/L) by confocal microscope analysis. Scale bar 100 µm.*

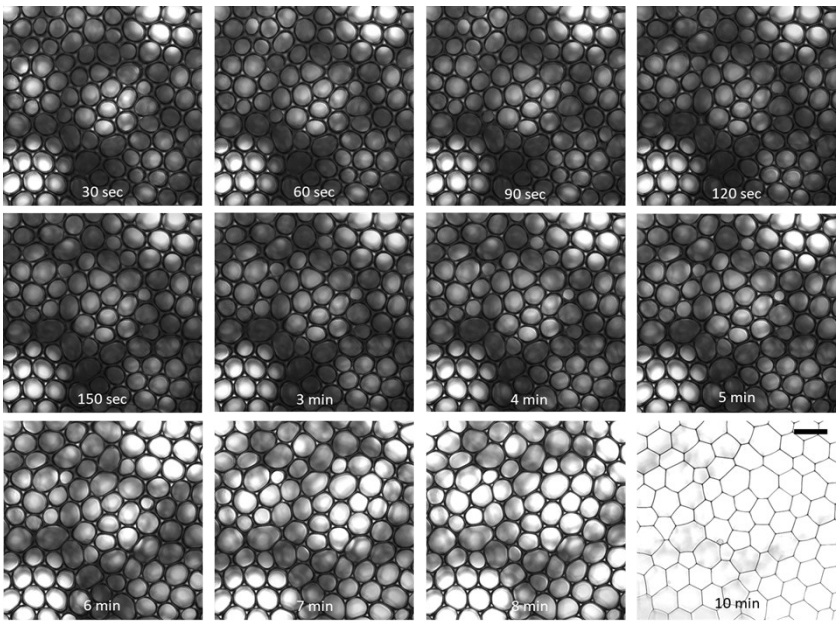


Figure S. 14 *Evolution of the bubbles during the drying process of the foam (c = 1.5 g/L) by confocal microscope analysis. Scale bar 100 µm.*

g. MATLAB analysis

Confocal transmission images (Figures S. 12-14) are analyzed by using a Matlab code that detects the bubbles, calculates their areas and their numbers over time.

Below, the number of bubbles over time is analysed for three different concentrations 0.15, 0.5 and 1.5 g/L. Another concentration is added compared to the main text, 0.5 g/L. The drying behaviour of the foam at 0.5 g/L is very similar to 1.5 g/L already discussed in the main text.

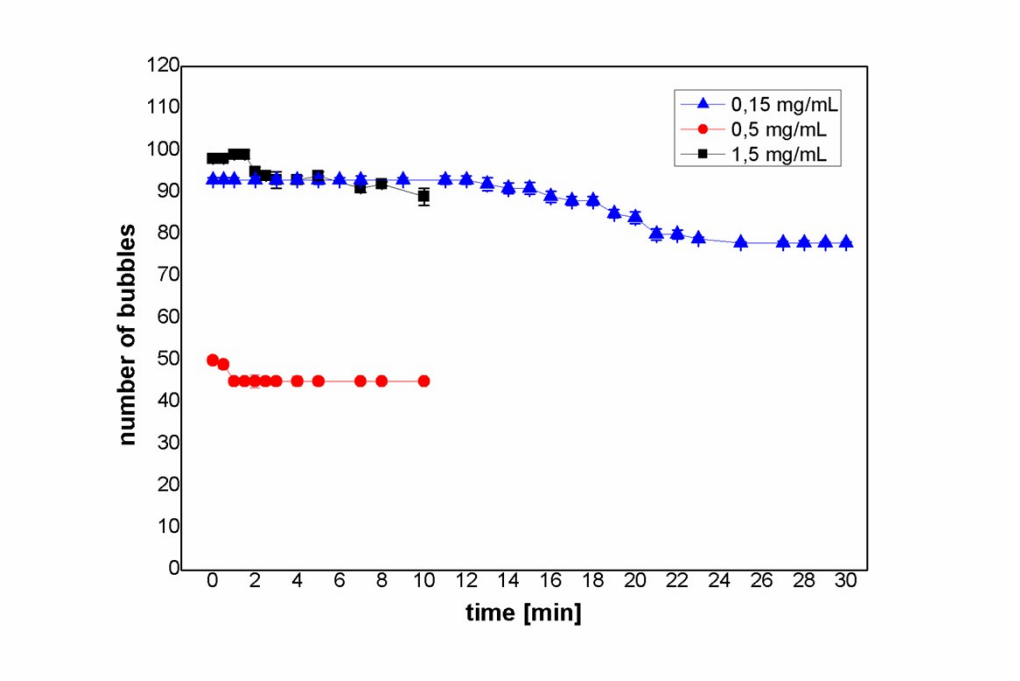


Figure S. 15 *Microscale evolution of the bubbles during the drying process of the foam at 0.15 g/L, 0.5 g/L and 1.5 g/L. Number of bubbles over time of the foam using confocal transmission images processed with MATLAB.*

Some aging phenomena are set out below for the case of 1.5 g/L. The results reported in Figure S. 16 provide a set of observations about the dynamics of the foam aging. In this experiment, the liquid fraction dropped from 45% to 17% due to the drying process of the foam. As a result of the liquid fraction drop, the plateau borders went thinner, explaining why the average area of the bubbles increased. Most importantly, the number of the bubbles only slightly varied in time, providing an argument that coalescence and coarsening do not intervene much, even though both are most likely favoured by the visualization conditions. Some aging events were recorded (see Figures S. 16 and S. 17) but these remained rare and isolated.

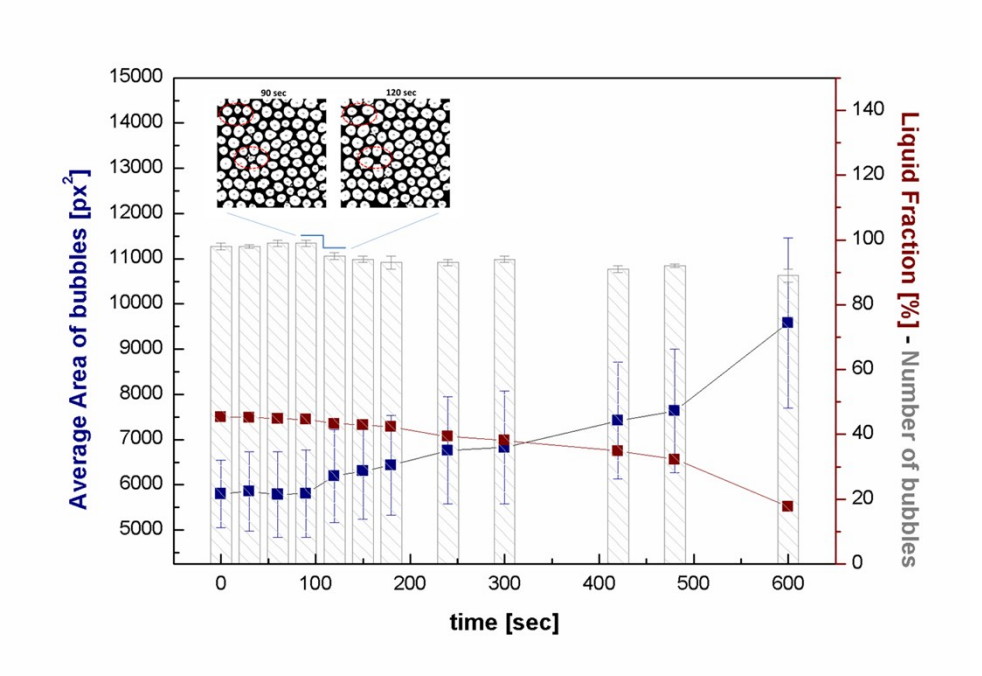


Figure S. 16 *Microscale evolution of the foam (c=1.5 g/L) using confocal transmission images processed with MATLAB: in blue (■), the average area of the bubbles; in red (■), the liquid fraction; In columns, the number of bubbles over time; Illustration of an aging phenomenon (some bubbles merging due to the coarsening between t = 90 and t = 120 sec).*

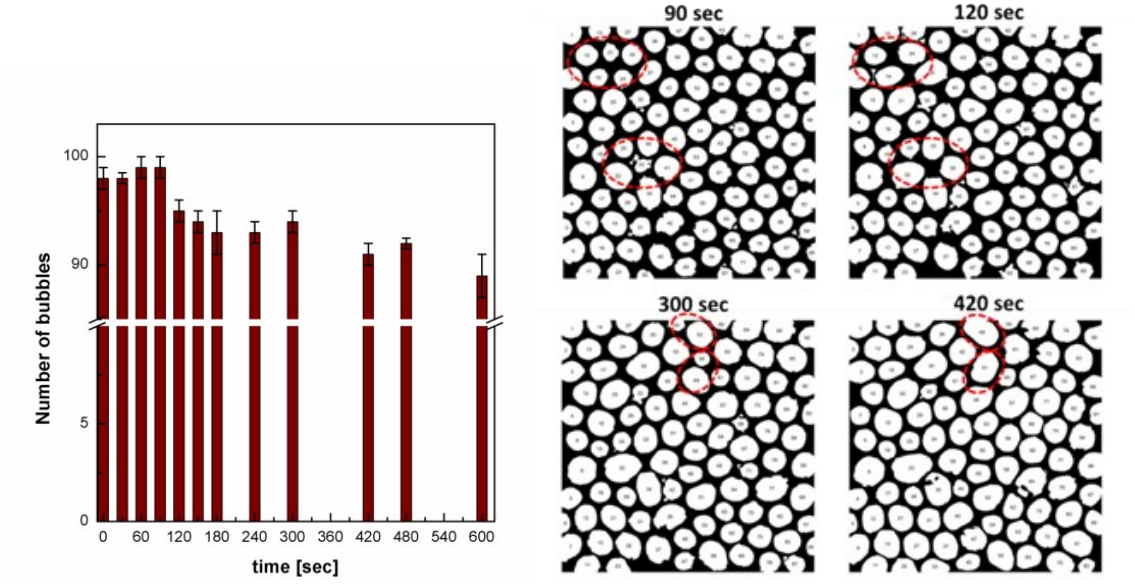


Figure S. 17 *Number of the bubbles (white area) of the foam (c=1.5 g/L) over time calculated by counting the white area in the confocal transmission images with MATLAB (on the left); Analysis of some bubbles merging (coarsening) between 90 and 120 sec and between 300 and 420 sec (on the right).*

In order to have quantitative information about the drying process, circularity value was evaluated to measure how close a bubble is to a perfect sphere (Fig. S. 18). Indeed, when the circularity is equal to one, bubbles are like a circle in shape indicating wet foam; otherwise, when circularity approaches zero, bubbles are more polyhedral-like in shape, as in a dry foam.
The quality of the image analysis conducted here can be further improved increasing the number of bubbles and using images with a higher quality, like it is generally recommended in such studies.

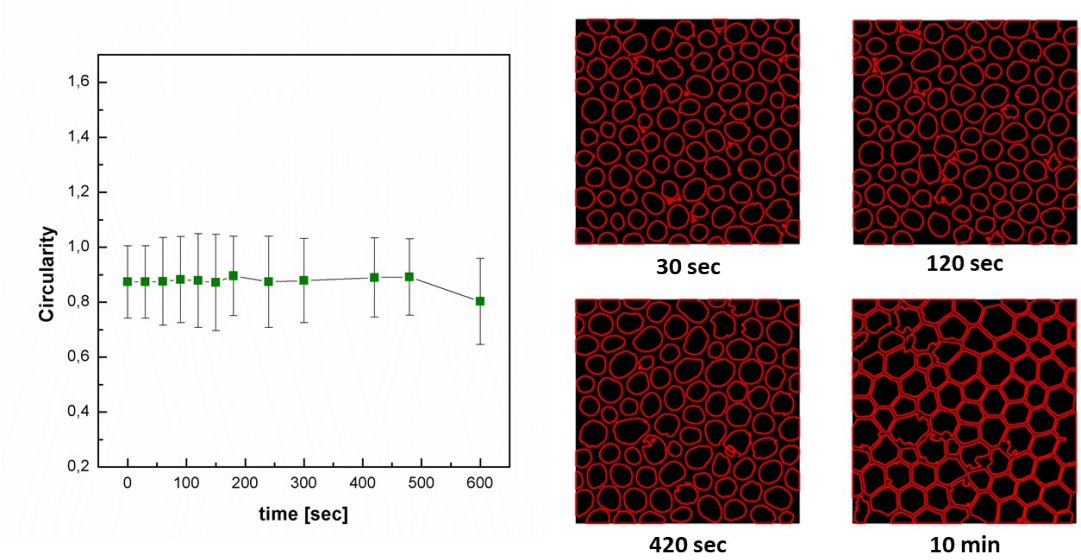


Figure S. 18 *Circularity (defined as $4\pi A/p^2$) of the bubbles (white area) of the foam (c=1.5 g/L) over time (on the left) calculated by analyzing the grey scale of the confocal transmission images with MATLAB (on the right).*