Supporting information:

Vinylidene fluoride polymerization by metal free selective activation of hydrogen peroxide: microstructure determination and mechanistic study

Nadim Eid[†], Bruno Améduri[†], Olinda Gimello[†], Anthony Bonnet,[§] Samuel Devisme,[§]

[†]Institut Charles Gerhardt, ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France.

[§]Centre de Recherche Rhône-Alpes (CRRA), Rue Henri Moissan - CS 42063, 69491 Pierre-Bénite Cedex, France.

Materials

VDF was kindly supplied by Arkema France (Pierre-Bénite, France). Azobisisobutyronitrile, isopropanol, dimethylcarbonate, and hydrogen peroxide (35 wt.% in water), methyl chloroformate, triethylamine, sulfuric acid and chromium trioxide were purchased from Sigma-Aldrich and used as received. Deuterated acetone (acetone-d_6) (purity>99.8%) and dimethylsulfoxide (DMSO-d_6) (purity>99.8%), used for ^{1}H and ^{19}F NMR spectroscopy, was purchased from Eurisotop (Grenoble, France). 2,2,3,3,3-pentafluoropropan-1-ol and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol were supplied by Atofina (Pierre-Bénite, France)

Preparation of methyl (2,2,3,3,3-pentafluoropropyl) carbonate:

In a 50 ml round bottom flask, 2,2,3,3,3-pentafluoropropan-1-ol (3.02g, 0.02 mol, 1 eq.) and triethylamine (2.8 ml, 0.06 mol, 3 eq.) were dissolved in dichloromethane (10 ml). Then the mixture was cooled to 0 °C using an ice bath. A solution of methyl chloroformate (3 ml, 0.04 mol, 2 eq.) in dichloromethane (10 ml) was added drop by drop to the fluoroalcohol solution. After that, the mixture was allowed to warm to room temperature (22 °C) and stirred (250 rpm) for 18 h. An additional 10 ml of dichloromethane was added to the crude mixture, and then the product was extracted with 200 ml of water. The left organic phase was dried over anhydrous sodium chloride and the solvent was evaporated using a rotavapor (40 °C, 100 Torr).

Methyl (2,2,3,3,3-pentafluoropropyl) carbonate: white solid.

^{1}H NMR (in acetone-$_{d6}$): 4.84 ppm ((tq,$^3J_{H\text{-}F}$= 13.3 Hz,$^4J_{H\text{-}F}$= 2 Hz, 2H), 3.78 ppm (s, 3H).

^{19}F NMR (in acetone-$_{d6}$): -84.30 ppm (3F), -124.7 ppm (2F).

The preparation of methyl (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) carbonate:

As above, in a 50 ml round bottom flask, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (7.3, 0.02 mol, 1 eq.) and triethylamine (2.8 ml, 0.06 mol, 3 eq.) dissolved in dichloromethane (10 ml) and cooled to 0 ^{o}C. Then, a solution of methyl chloroformate (3 ml, 0.04 mol, 2 eq.) in dichloromethane (10 ml) was added drop by drop. After that, the mixture was allowed to warm to room temperature (22 ^{o}C) and stirred for 18 h. An additional 10 ml of dichloromethane was added to the crude mixture, and then it was extracted with 200 ml of water. The left organic phase was dried and the solvent was evaporated.

methyl (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) carbonate: viscous, transparent oil.

^{1}H NMR (in acetone-$_{d6}$): 4.58 ppm (dt,$^{3}J_{H-H}$= 18.4 Hz,$^{3}J_{H-H}$= 6.1 Hz, 2H), 3.75 ppm (s, 3H), 2.78 ppm (q,$^{3}J_{H-H}$= 7.2 Hz, 2H)

^{19}F NMR (in acetone-$_{d6}$): -82.1 ppm (3F), -112.8 ppm (2F), -121.2 ppm (2F), -123.5 (2F), -127.0 ppm (2F).

Preparation of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoic acid:

In a 50 ml round bottom flask, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (3g, 0.008 mol) was dissolved in acetone (10 ml), and then the mixture was cooled to 0 ^{o}C using an ice bath. A solution of chrominum trioxide (5.02 g, 0.05 mol, 6 eq.), 5 ml of sulfuric acid, in water (25 ml) was cooled to 0 ^{o}C using an ice bath, an then added added drop by drop to the fluoroalcohol solution.The color of the medium changed from orange to green after 5 h. After 20 h, 20 ml of dichloromethane was added and the solution was extracted with water, untill clear and non colored aqueous phase was obtained (300 ml of water were used).The organic layer was dried over anhydrous sodium chloride and the solvent was evaporated using a rotavapor (40 ^{o}C, 100 Torr).

3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoic acid: viscous, transparent oil

^{1}H NMR (in acetone-$_{d6}$): 3.39 ppm (t,$^{3}J_{H-f}$= 18.5 Hz,2H)

^{19}F NMR (in acetone-$_{d6}$): -82.1 ppm (3F), -113.2 ppm (2F), -122.2 ppm (2F), -123.7 (2F), -127.0 ppm (2F).

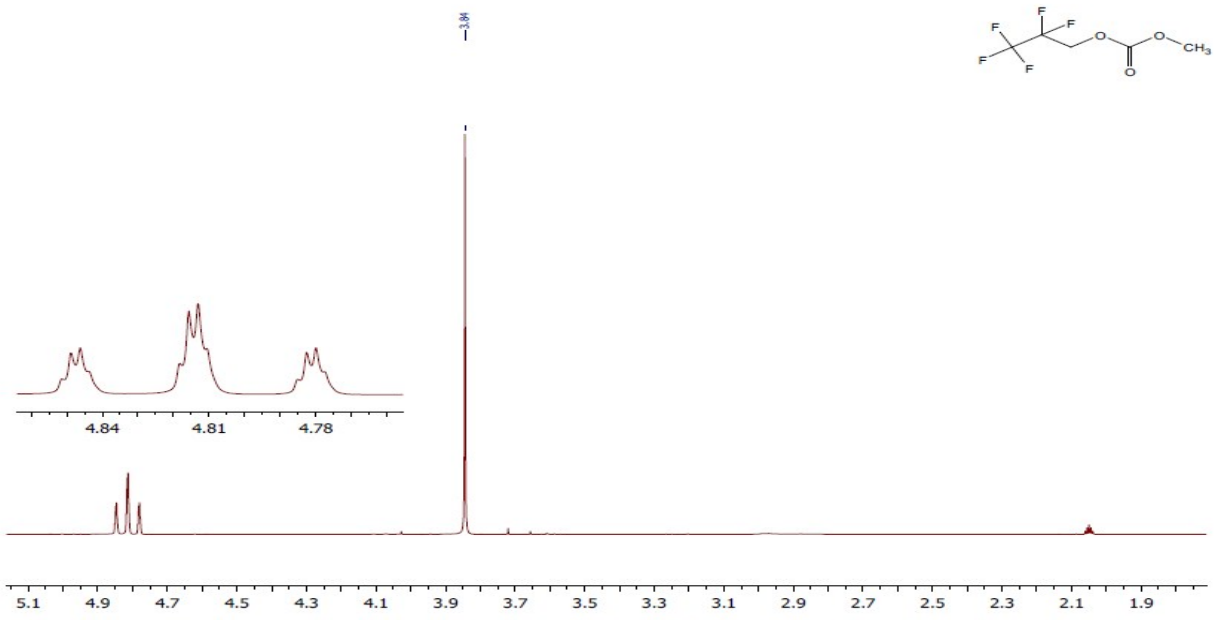

Figure S1: ^{1}H NMR spectrum of (2,2,3,3,3-pentafluoropropyl) carbonate (recorded in acetone-d_6)

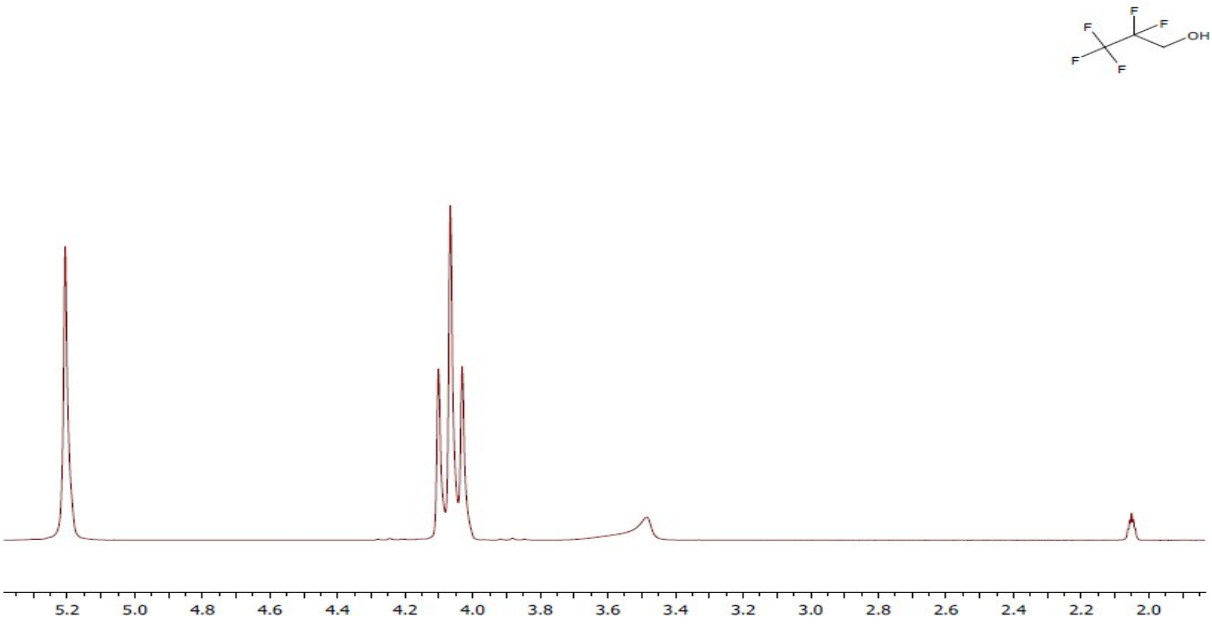

Figure S2: ^{1}H NMR spectrum of 2,2,3,3,3-pentafluoropropan-1-ol (recorded in acetone-d_6)

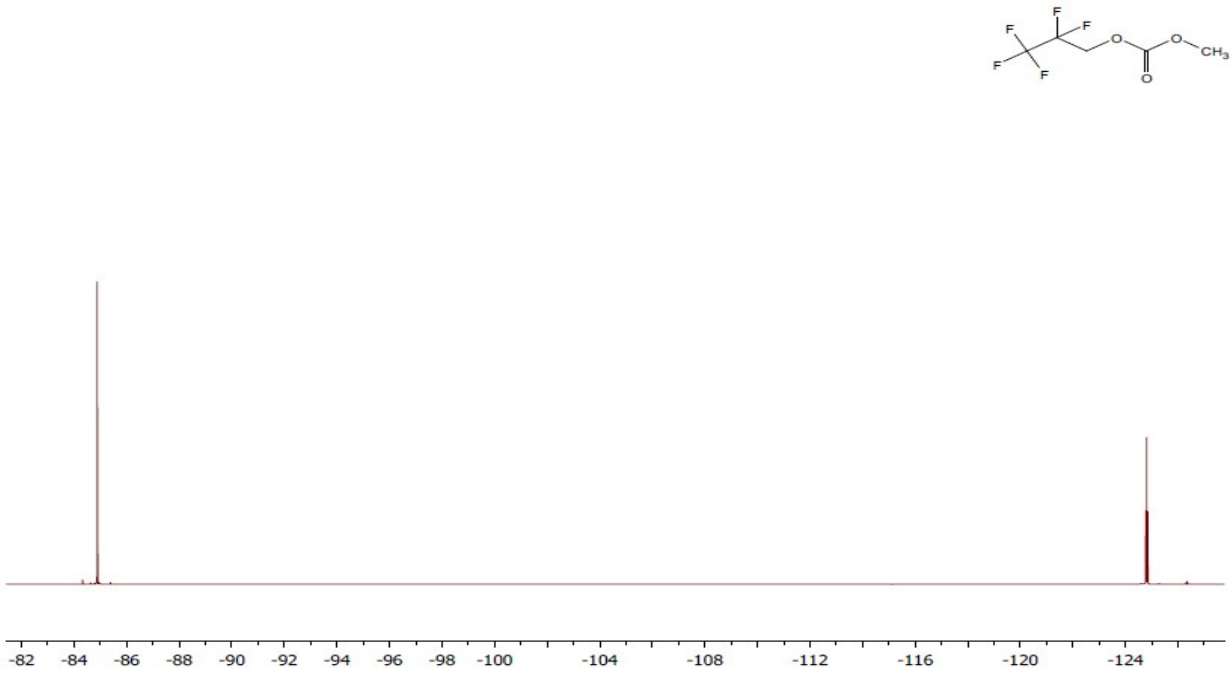

Figure S3: ^{19}F NMR spectrum of (2,2,3,3,3-pentafluoropropyl) carbonate (recorded in acetone-d_6)

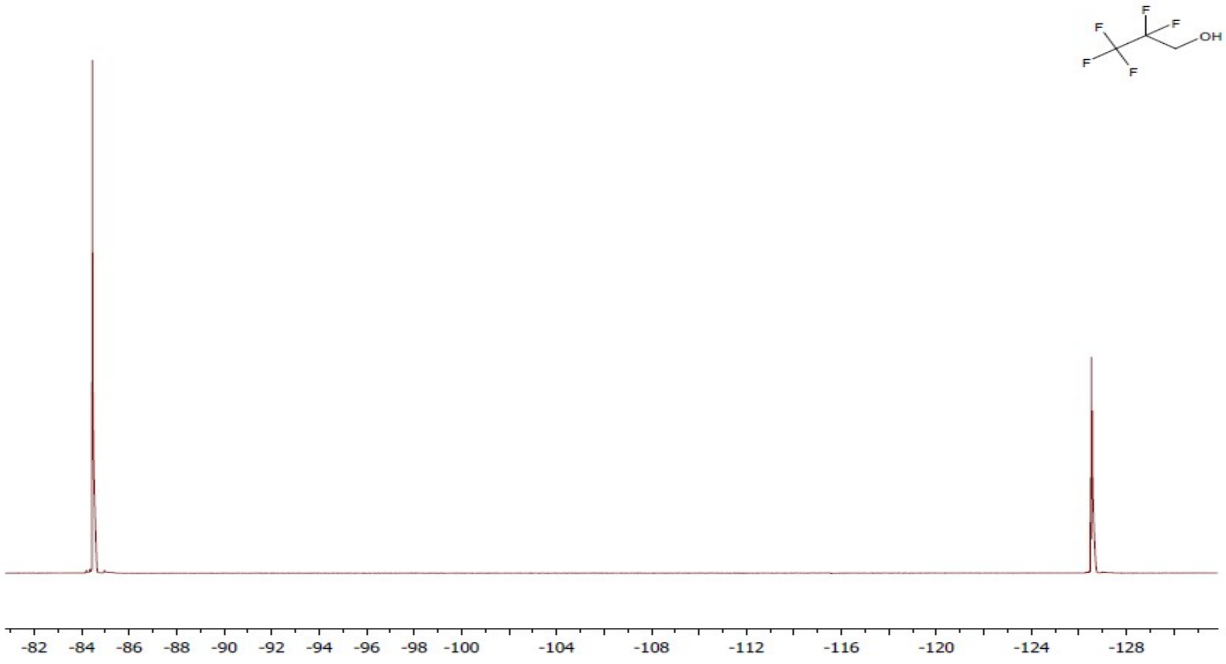

Figure S4: ^{19}F NMR spectrum of 2,2,3,3,3-pentafluoropropan-1-ol (recorded in acetone-d_6)

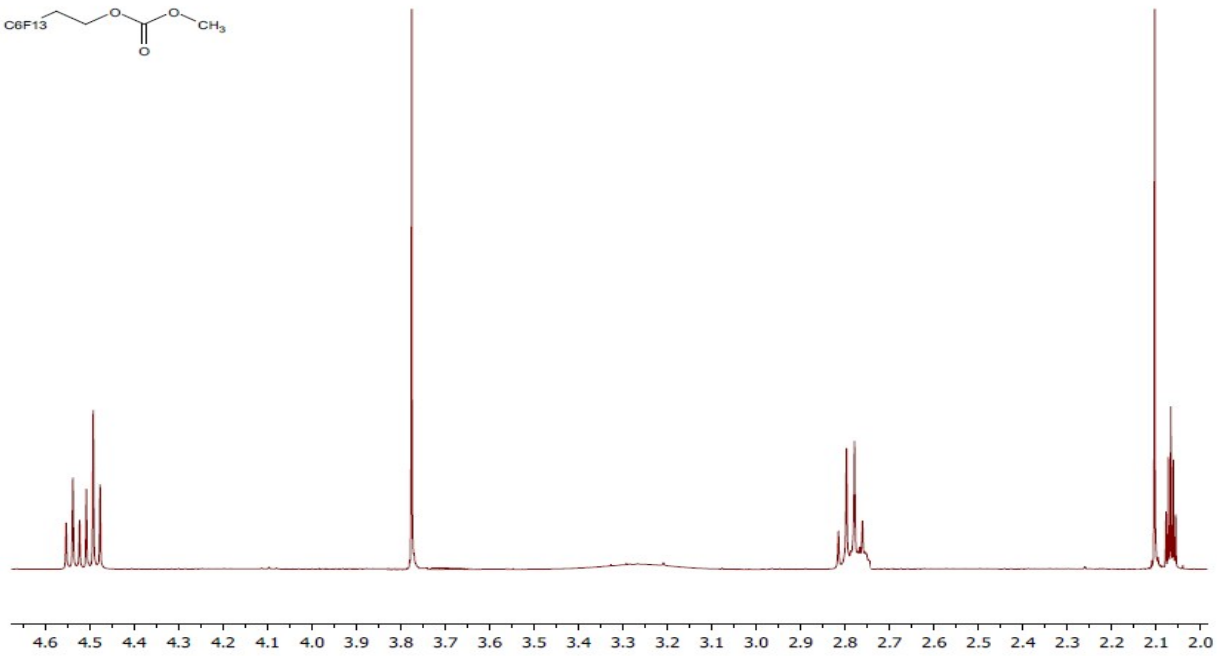

Figure S5: ^{1}H NMR spectrum of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) carbonate (recorded in acetone-d_6)

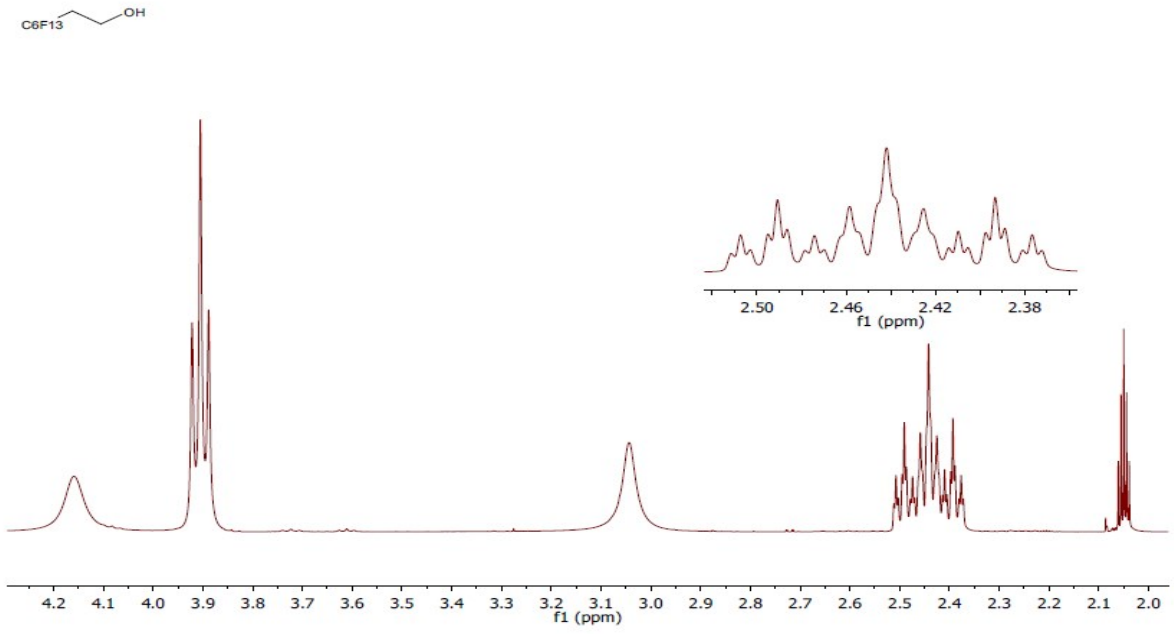

Figure S6: ^{1}H NMR spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (recorded in acetone-d_6)

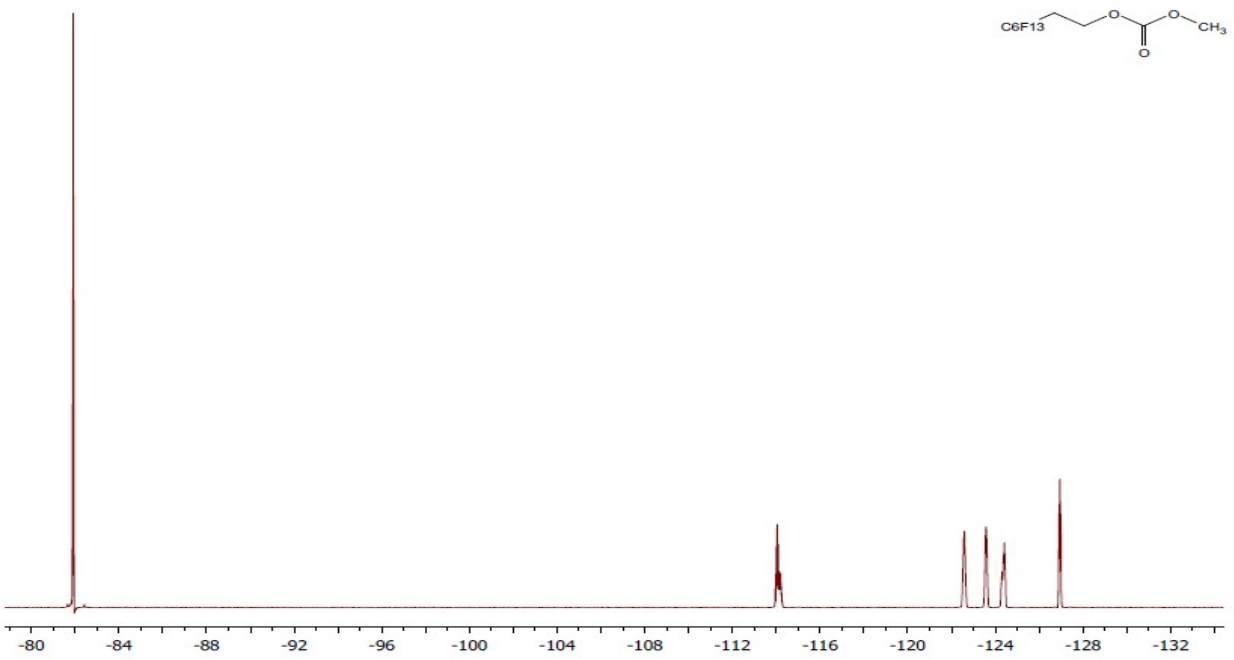

Figure S7: ^{19}F NMR spectrum of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) carbonate (recorded in acetone-d_6)

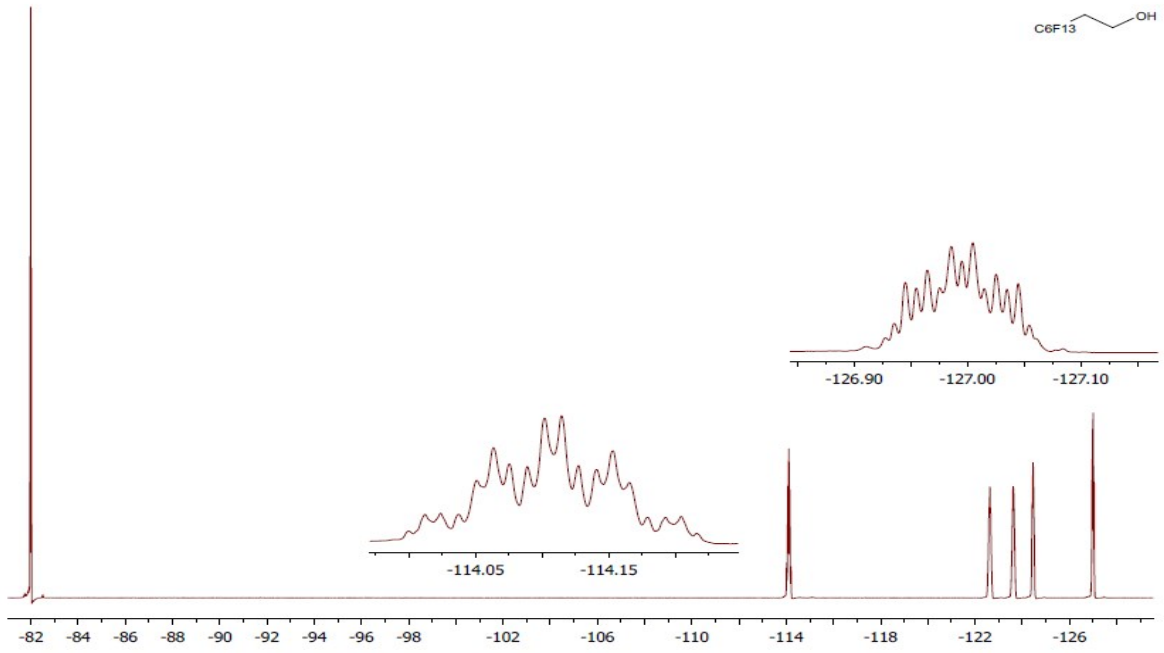

Figure S8: ^{19}F NMR spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (recorded in acetone-d_6)

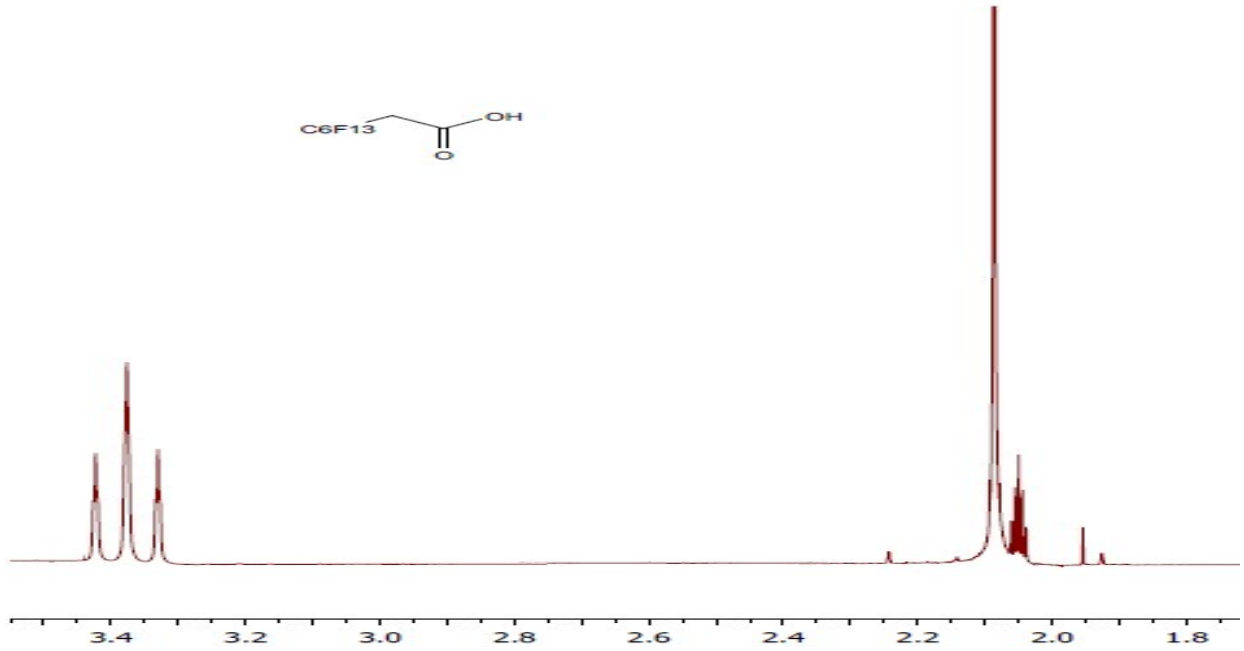

Figure S9: ^{1}H NMR spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoic acid (recorded in acetone-d_6)

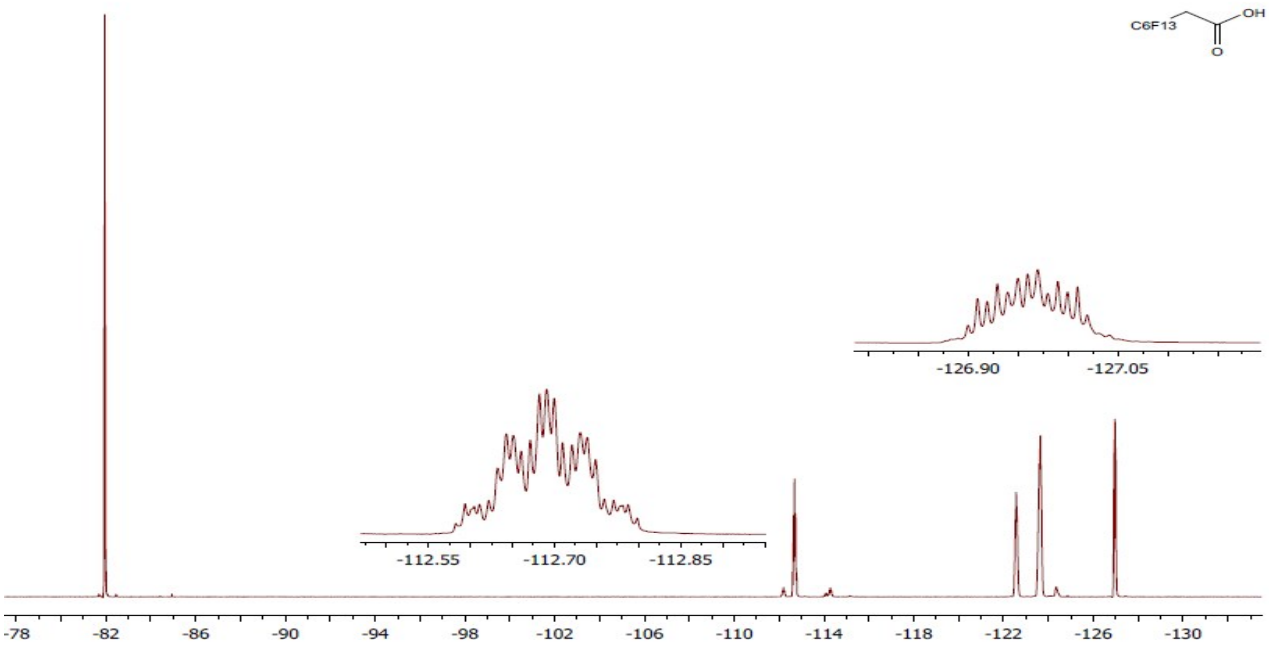

Figure S10: ^{19}F NMR spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoic acid (recorded in acetone-d_6)

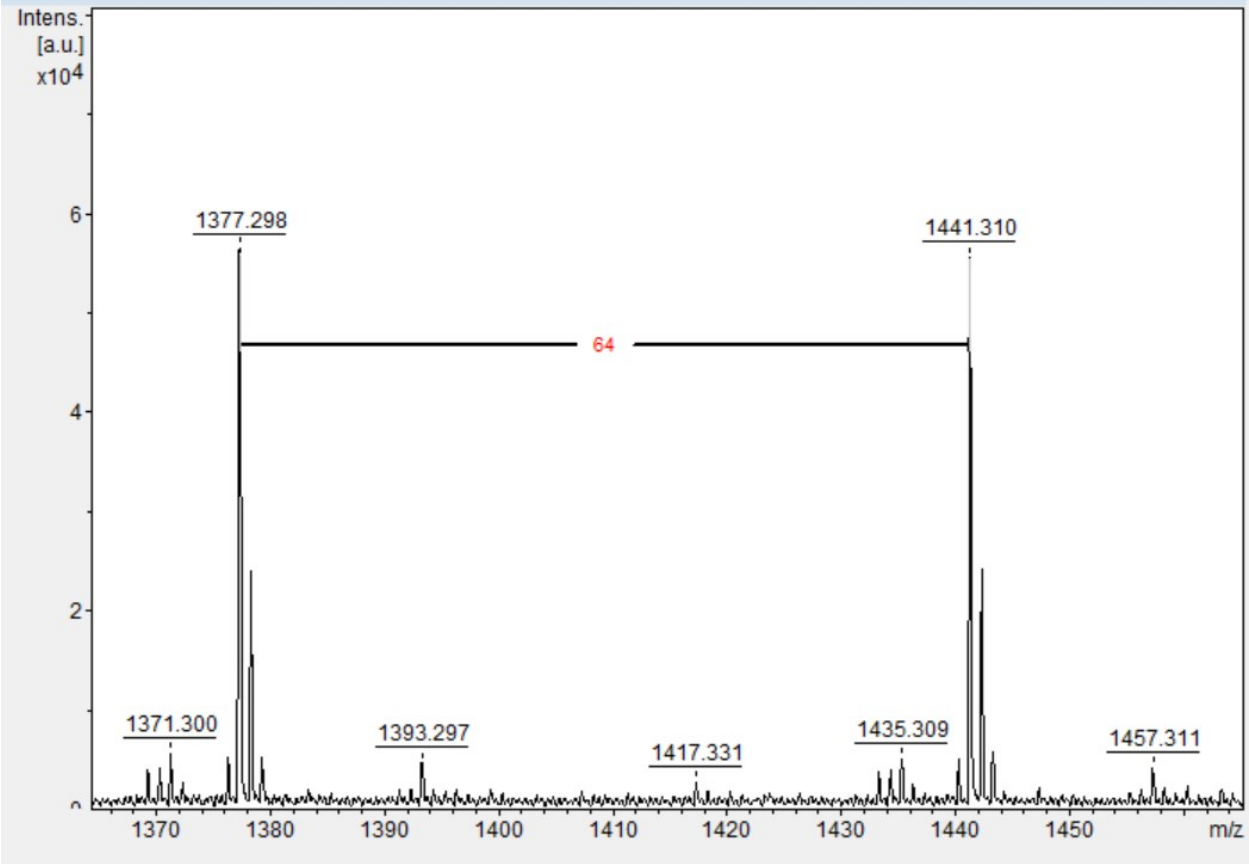

Figure S11: Zoom of MALDI-TOF spectrum between 1370<m/z<1460