Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A fluorous sodium L-prolinate derivative as low molecular weight gelator for perfluorocarbons

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1- Synthetic pathway to 1

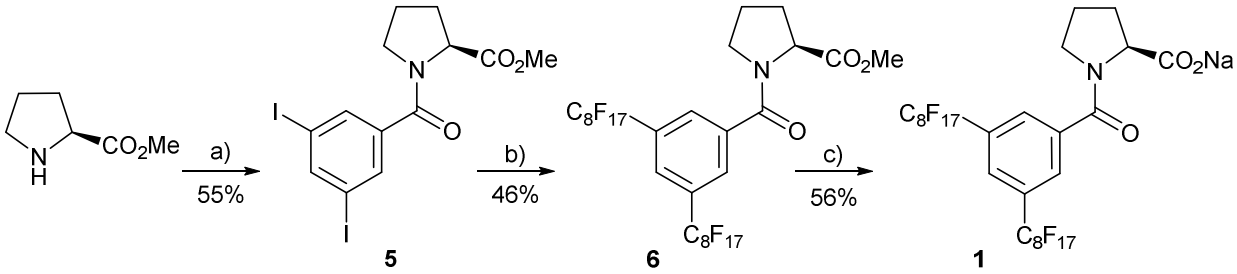

Fig. S1. Reaction pathway to **1**: a) 3,5-diiodobenzoic acid, DCC, DMAP, NEt_3, THF/DCM, rt; b) Copper powder, $C_8F_{17}I$, DMSO, 140 °C, 48 h; c) NaOH, H_2O/MeOH/DCM, rt, 24 h.

General experimental details. All reagents were obtained from commercial sources and used as received. NMR and Mass spectra were recorded at the CESAMO analytical center of the Institut des Sciences Moléculaires (University of Bordeaux, Talence, France). NMR analyses were carried out on a Bruker avanceIII-600 (600 MHz ^{1}H, 150 MHz ^{13}C). The chemical shifts (δ) for carbon and proton resonances are given compared to the residual solvent peak and are expressed in ppm.

Synthesis of (5) : To a stirred solution of 3,5-diiodobenzoic acid (3.50 g, 9.36 mmol) in 100 mL of dry THF, DCC (2.32 g, 11.26 mmol) and DMAP (23.00 mg, 0,19 mmol) were added sequentially. The mixture was stirred at room temperature under an argon atmosphere for 3 h. Then, a solution of L-proline methyl ester hydrochloride (2.32 g, 14.04 mmol) and NEt_3 (2 ml, 14.04 mmol) in 50 mL of dry CH_2Cl_2 was added to the reaction mixture via syringe. After being stirred overnight at room temperature, the mixture was filtered and the solvent evaporated under reduced pressure. The residue was taken up with EtOAc, filtered through celite, washed twice with brine and dried over magnesium sulfate. After filtration the organic solvent was removed using a rotary evaporator. The product was purified by column chromatography (Toluene/EtOAc, 98:2) to obtain the product as a white solid (2.51 g, 55 %).

^{1}H NMR ($CDCl_3$, 600 MHz, Rotamer 1/Rotamer 2 80/20): δ (ppm) R1 = 8.09 (d, J = 1.4 Hz, 1H), 7.81 (s, 2H), 4.60 (m, 1H), 3.75 (d, J = 1.7 Hz, 3H), 3.58 (m, 1H), 3.46 (m, 1H), 2.28 (m, 1H), 2.01 (m, 2H), 1.89 (m, 1H); δ (ppm) R2 = 8.05 (d, J = 1.4 Hz, 1H), 7.63 (s, 2H), 4.19 (m, 1H), 3.71 (m, 2H), 3.66 (bs, 3H), 2.20 (m, 1H), 2.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) R1 = 172.31, 166.17, 146.67, 139.55, 135.27, 94.63, 59.19, 52.46, 49.94, 29.37, 25.30;

δ (ppm) R2 = 172.56, 166.80, 146.28, 140.18, 134.64, 61.36, 52.78, 46.76, 31.41, 22.69; IR (KBr): 2986 (s, Csp^3-H), 2875 (s, Csp^3-H), 1747 (s, C=O ester), 1630 (s, C=O, amide), 1435 (s, C=C), 1198 (s, C-O), 866 (s, C-I), 763 (s, C-I) cm^{-1}; MS (m/z, FD^+): calcd for $C_{13}H_{13}I_2NO_3$: 484.8948, found: 484.8982; Rf = 0.32 (Toluene/EtOAc 98:2); M.p.: 116 -119 ºC.

Synthesis of (6) : An oven-dried tube was charged with copper (1g, 15.73 mmol), **2** (0.76 g, 1.57 mmol), perfluorooctyliodide (1.71 g, 3.14 mmol) and 10 ml of DMSO. The tube was sealed and kept at 140 ºC with stirring. After two days, the mixture was cooled to room temperature and ethyl acetate was added. The mixture was filtered and the solvent was removed by rotary evaporation. The solid was purified by column chromatography using ether petroleum/ ether (7:3). A white powder was obtained (0.77 g, 46%).

^{1}H NMR ($CDCl_3$, 600 MHz, Rotamer 1/Rotamer 2 80/20): δ (ppm) R1 = 8.04 (s, 2H), 7.88 (s, 1H), 4.70 (m, 1H), 3.81 (s, 3H), 3.63 (m, 1H), 3.48 (m, 1H), 2.37 (m, 1H), 2.09 (m, 2H), 1.97 (m, 1H); δ (ppm) R2 = 7.88 (s, 2H), 7.83 (s, 1H), 4.22 (m, 1H), 3.82 (m, 2H), 3.55 (s, 3H), 2.30 (m, 1H), 2.09 (m, 2H), 1.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) R1 = 172.28, 166.51, 137.95, 130.57, 129.70, 127.22, 118.20-109.00, 59.64, 52.66, 49.96, 29.53, 25.55; R2 = 172.14, 167.27, 138.78, 129.13, 126.71, 61.41, 52.47, 47.18, 31.77, 22.71; IR (KBr): 2978 (m, Csp^3-H), 1744 (s, C=O ester), 1639 (s, C=O amide), 1417 (s, C=C), 1202 (m, C-O), 902 (s, C-F) cm^{-1}; MS (m/z, FD^+): calcd for $C_{29}H_{13}F_{34}NO_3$: 1069.0262, found: 1069.0250 ; Rf = 0.4 (Ether petroleum/Et_2O 6:4); M.p.: 106 ºC.

Synthesis of (1). A solution of NaOH (0.073 g, 5.1 eq 1.90 mmol) in 10 ml of MeOH was added to a solution of the ester **3** (0.40 g, 0.37 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred at room temperature for 24 h. The solvents were then removed by rotary evaporation and the residue further dried under vacuum. The solid was taken up with H_2O (20 mL), sonicated, filtered, and washed wih water to afford **1** as a white powder (225 mg, 56%).

^{1}H NMR: (CD_3OD, 600 MHz, Rotamer 1/Rotamer 2 60/40): δ (ppm) R1 = 8.36 (s, 2H), 7.92 (s, 1H), 4.52 (dd, 1H), 3.63 (m, 1H), 3.34 (m, 1H), 2.33 (m, 1H), 2.07-1.95 (m, 2H), 1.86 (m, 1H); R2 = 8.15 (s, 2H), 7.87 (s, 1H), 4.08 (dd, 1H), 3.80 (m, 1H), 3.71 (m, 1H), 2.23 (m, 1H), 2.15 (m, 1H), 2.07-1.95 (m, 2H); ^{13}C NMR (CD_3OD, 150 MHz): δ (ppm) R1+R2 = 179.28, 178.15, 169.00, 168.01, 141.27, 140.97, 131.30, 130.98, 130.83, 127.20, 121.54-109.45, 65.81, 63.81, 51.27, 48.23, 33.04, 31.33, 26.25, 23.67.; M.p.: > 200 ºC (decomposed).

2- Gelation tests with water and organic solvents

Gelation tests were conducted in 2 mL vials using 5 mg of **1** and 0.250 mL of the solvents (18.5 mM). The heterogeneous mixtures were first sonicated, followed by heating at the solvent boiling point for 5-10 s to ensure the maximum solubilisation for **1**, and then let the solutions cooling down to room temperature. For water, isopropanol, acetonitrile, tetrahydrofuran, dimethylformamide, chloroform, toluene and heptane crystalline but not monocrystalline solids were formed. For dimethylsulfoxide an amorphous solid was formed.

3- Rheology

Rheological experiments are conducted in a parallel-plate geometry. The upper rotating plate (diameter 40mm) is made of aluminum and connected to a stress-controlled rheometer (DHR-2, TA instrument). The bottom plate consists of a Teflon-coated Peltier unit that allows control of the temperature of the sample. The sample is introduced as a liquid at circa 120°C between the plates, which are separated by a gap of 500µm and preheated at 80°C. The sample is surrounded by a thin layer of sunflower seed oil to prevent solvent evaporation, and the gelation is induced by decreasing the temperature at 5°C/min down to 20°C. The experiment is conducted following the zero normal force protocol introduced in [1]. The normal force is maintained constant and equal to zero ($F_N = 0$N), while the gap width is modified by the rheometer to satisfy the latter condition. Therefore, if the sample dilates or contracts during the gelation, the gap will respectively increase or decrease to maintain $F_N = 0$N, which allows direct measurement of the dilation or the contraction of the sample. The evolution of the elastic and viscous modulus is determined by means of oscillations of small amplitude at a frequency of 1 Hz. The strain value applied to measure the elastic and viscous modulus is chosen to be large enough to be above the smallest torque accessible to the rheometer and below the strain at which the sample detaches from the plates and slip at the wall. Perfluorodecalin gels proved to be extremely prone to slip at the wall of the parallel-plate geometry, which makes the measurements quite challenging. We impose small strain values (typically 0.01%), which accounts for the noise associated with the data reported in Figure 1(b). After each gelation experiment, we systematically performed a strain sweep experiment to determine the critical strain γ_c beyond which the sample experiences wall slip (e.g. γ_c=0.4% for a 3% gel). In this way, it was ensured that the strain applied during gelation to determine G' and G" is smaller than the critical value beyond which the gel detaches from the wall.

4- IR and VCD measurements

The infrared (IR) and VCD spectra were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench.[1] In this optical bench, the light beam was focused on the sample by a BaF_2 lens (191 mm focal length), passing an optical filter (1850-800 cm^{-1}), a BaF_2 wire grid polarizer (Specac), and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1 mm focal length) onto a 1x1 mm^2 HgCdTe (ThermoNicolet, MCTA* E6032) detector. IR absorption and VCD spectra were recorded at a resolution of 4 cm^{-1}, by coadding 50 scans and 6000 scans (2h acquisition time), respectively. PFC gels obtained from 1 wt% of fluorous sodium or potassium L-prolinate in perfluorodecalin (PFD) were held in a demountable CaF_2 cell (Biotools) with fixed path length of 45 μm. Since the sample preparation may induce molecular orientation of the fibrils, the cell was placed on a rotating sample holder and the VCD spectra were measured with the cell rotated at four angles around the light beam axis (0°, 45°, 90° and 135°). Baseline corrections of the VCD spectra were performed by subtracting the raw VCD spectra of the PFD solvent. The photoelastic modulator was adjusted for a maximum efficiency in the mid-IR region at 1400 cm^{-1}. Calculations were performed via the standard ThermoNicolet software, using Happ and Genzel apodization, de-Haseth phase-correction and a zero-filling factor of one. Calibration spectra were recorded using a birefringent plate (CdSe) and a second BaF_2 wire grid polarizer, following the experimental procedure previously published.[2] IR spectra were shown with solvent absorption subtracted out. Reproducible IR and VCD spectra were obtained for four samples independently prepared (see Fig S4).

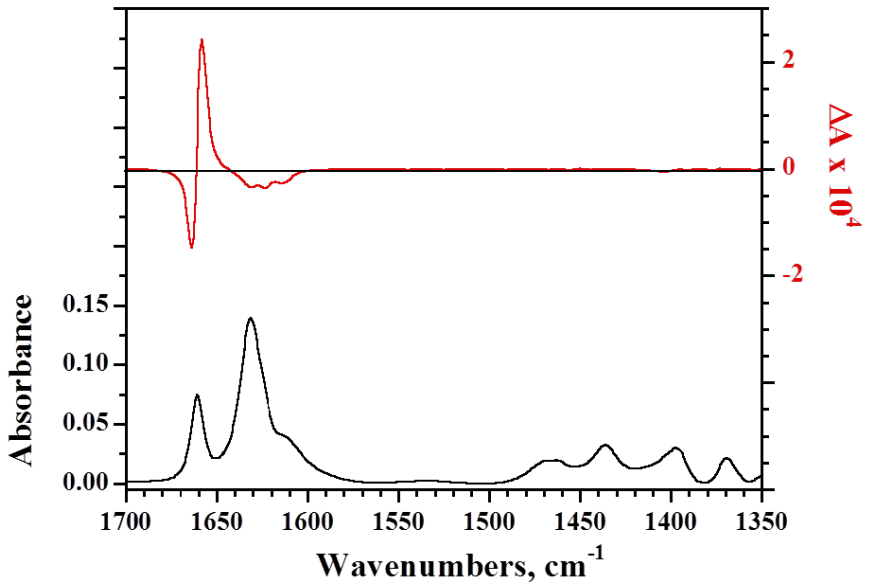

Fig. S2. IR and VCD spectra of a 1 wt% gel of **1** in PFD solvent in the 1700 – 1350 cm^{-1} spectral range.

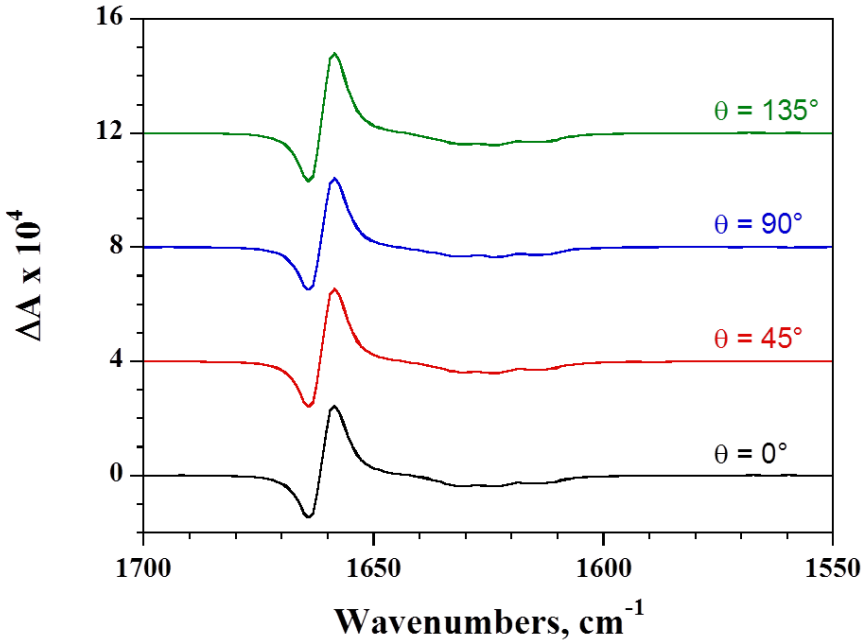

Fig. S3. VCD spectra of a 1 wt% gel of **1** in PFD solvent for four angles of the cell around the light beam axis.

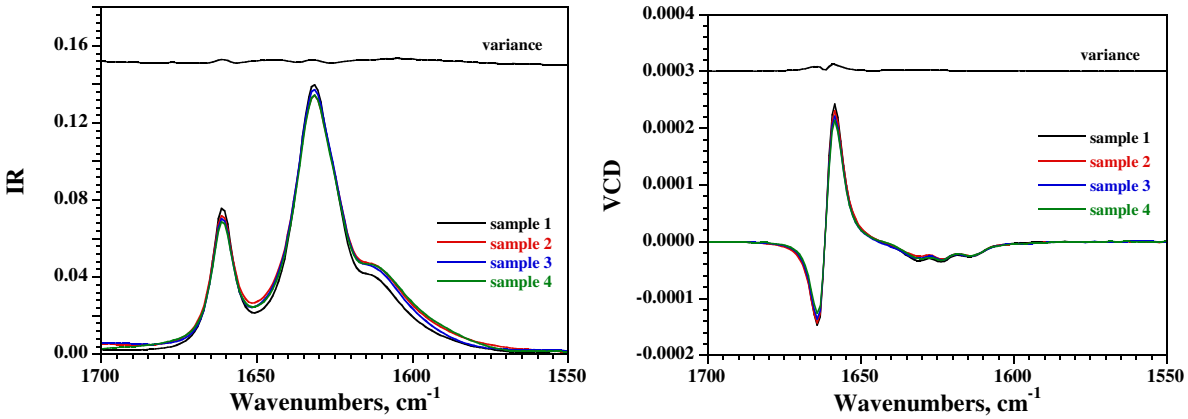

Fig. S4. IR and VCD spectra of 1 wt% gels of **1** in PFD solvent recorded from four different samples. Samples 1 and 2 were prepared from the same gel and samples 3 and 4 were prepared from two other gels.

5- Cryo SEM

A small piece of the gel was put onto an aluminium stub and fixed on the cryo holder. The latter was rapidly plunged in a liquid Nitrogen slush. After transferring the holder to the preparation chamber (Quorum PP3010 preparation device from Quorum technologies; The description of the preparation chamber and procedure to prepare the fractured/sublimed samples could be found here: https://www.quorumtech.com/quorum-product/pp3010t-cryo-sem-preparation-system) attached to the microscope (HITACHI SU 8010), a first metallization was performed followed by fracturing of the upper surface. Fracturing is performed with a scalpel blade inserted in the preparation chamber. A short sublimation (2 min at -90°C) was undergone and then a second metallization of a thin layer of Pt. Finally, the holder was transferred into the SEM and maintained at -160°C during the full time of observation. The samples were observed at 1kV with a current of 10µA.

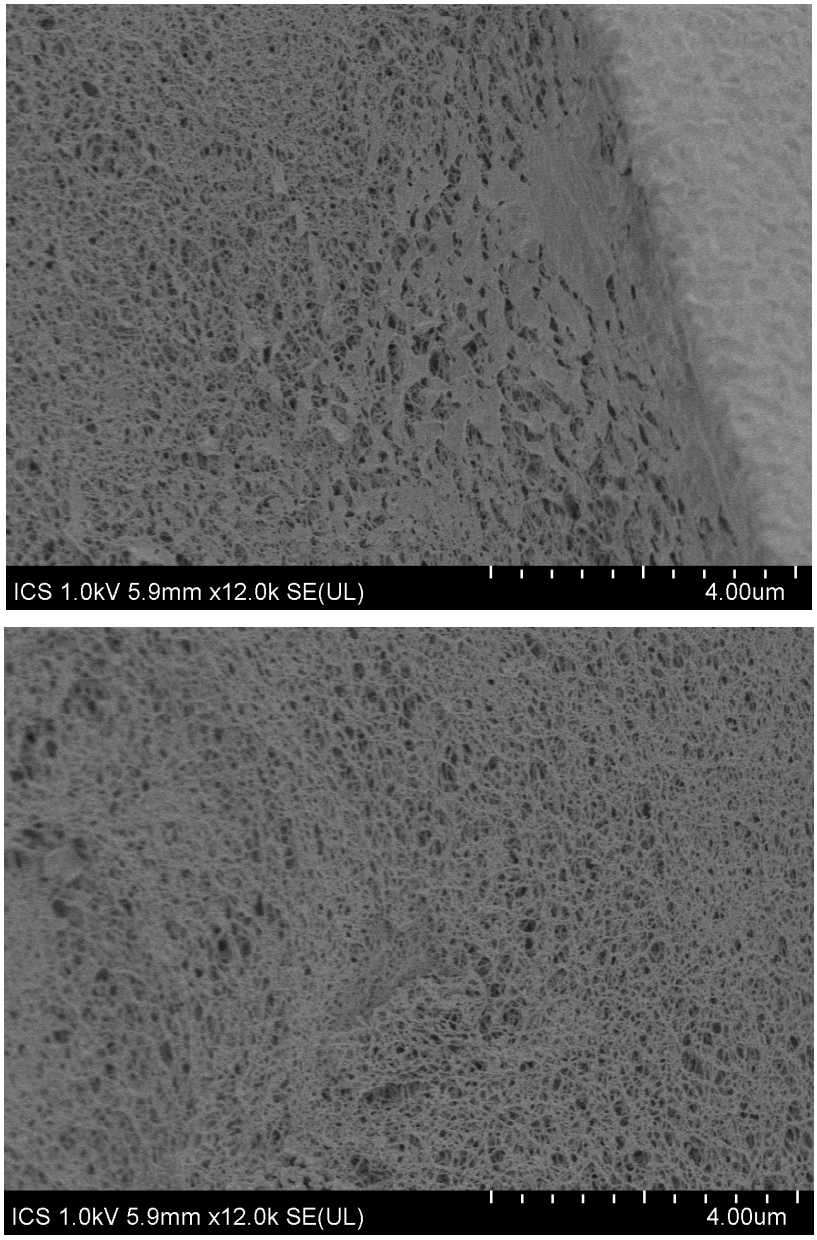

Fig. S5. Cryo-SEM images of a perfluorodecalin gel of **1** (0.5 wt%).

6- AFM

Samples were prepared by deposition of ca. 5 µL of an already formed gel onto a glass microscope slide, followed by solvent evaporation under vacuum during at least 2 hours. For imaging, an Asylum Research MFP3D AFM was used in alternative contact mode with an Olympus AC240TS silicon tip (7 nm radius of curvature, lever spring constant of 1.6 $N.m^{-1}$). The calibrated free amplitude was set to 90 nm at resonance frequency, and very small amplitude reduction setpoint together with slow scan rates of ca. 0.5 to 1.0 $\mu m.s^{-1}$ were used.

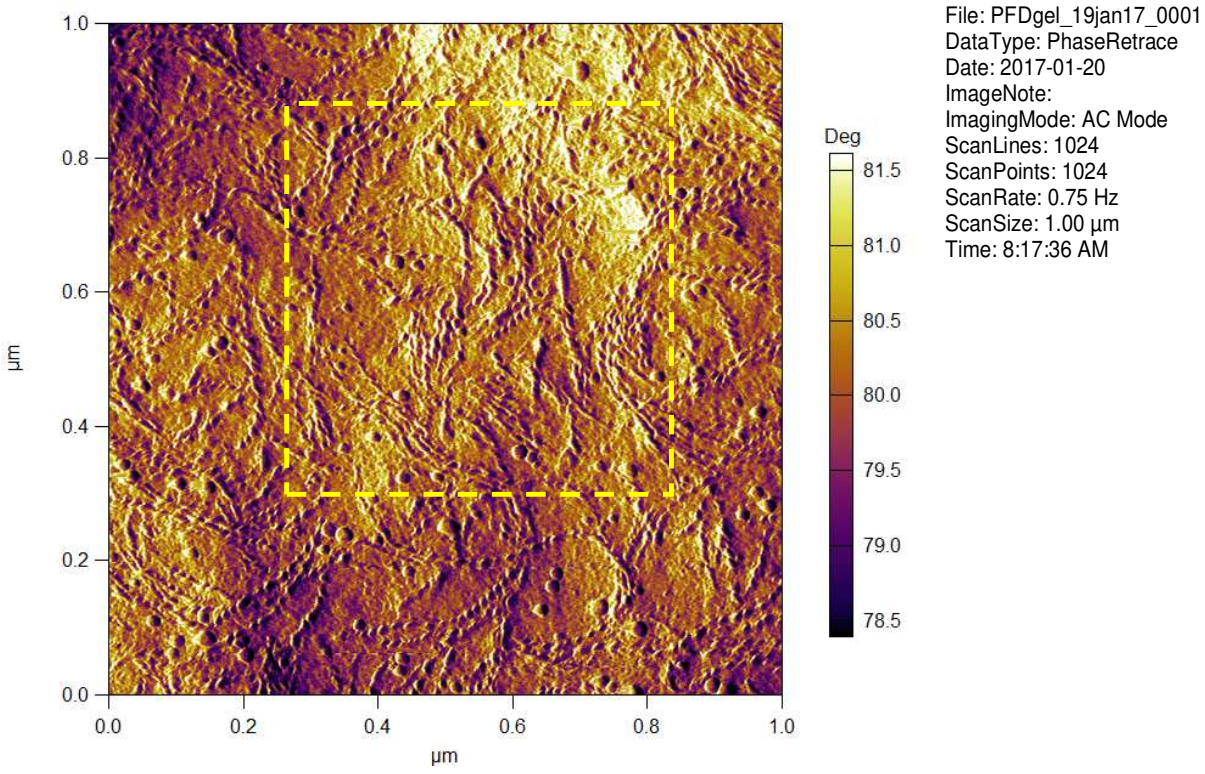

Fig. S6. AFM phase image of a perfluorodecalin gel of **1** (1 wt%) recorded during solvent evaporation.

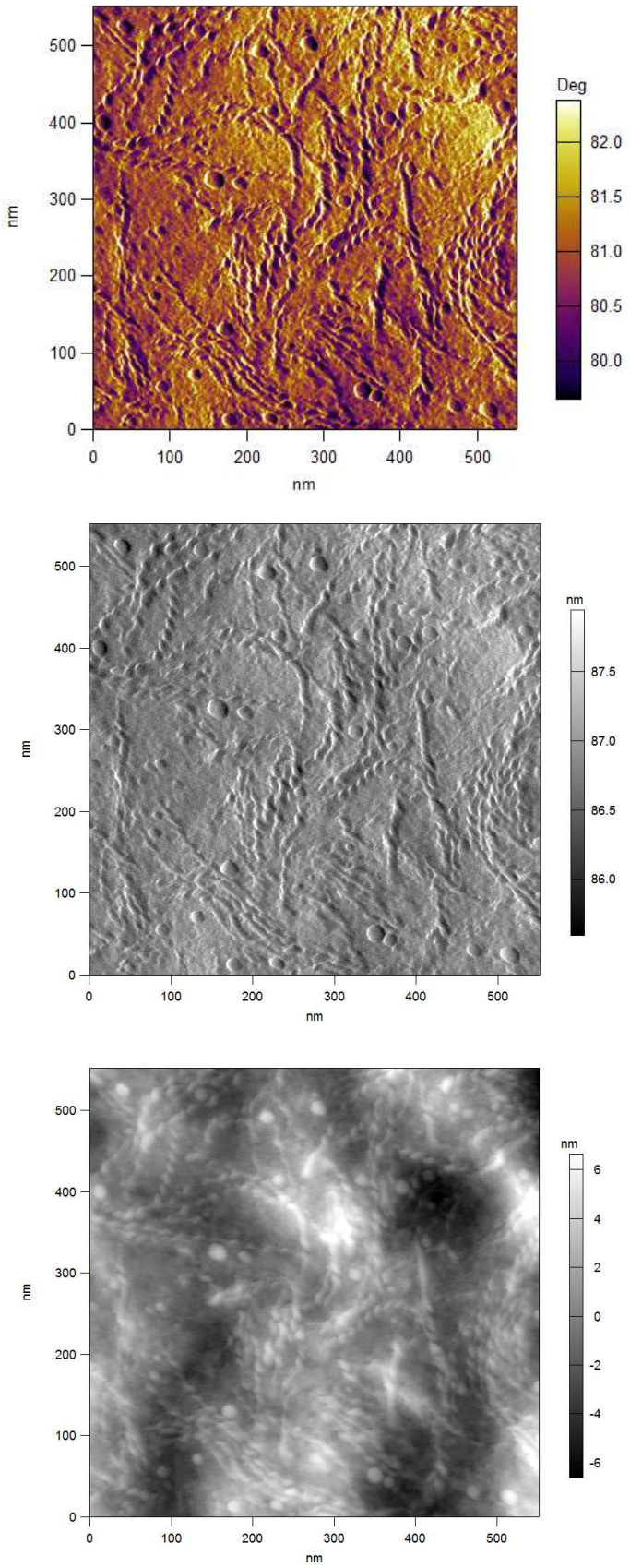

Fig. S7. From top to bottom, AFM phase, amplitude and height (flattened) images of the area highlighted in yellow on the image of Fig. S6.

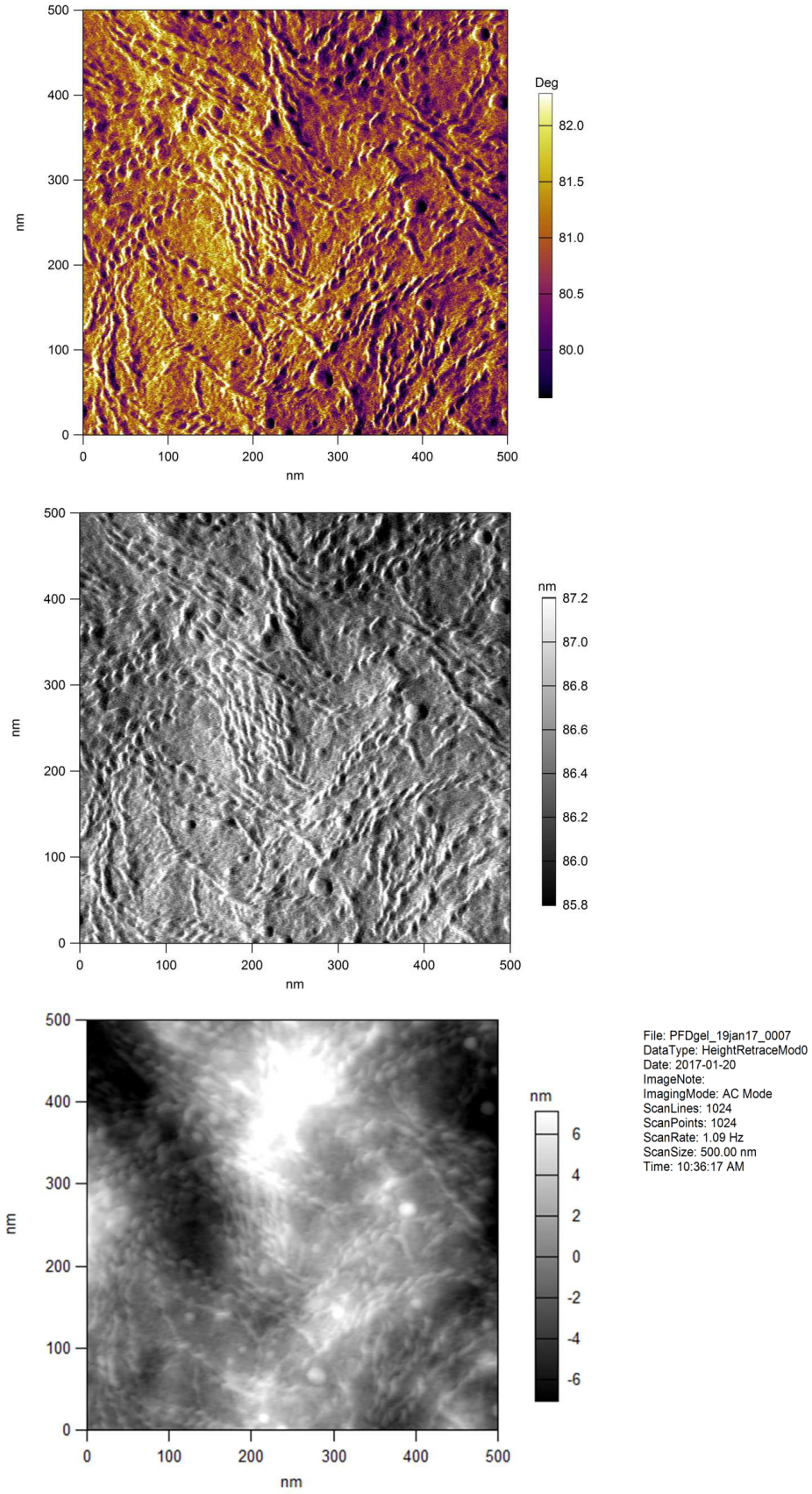

Fig. S8. From top to bottom, AFM phase, amplitude and height (flattened) images recorded in a different area of the sample used for the Fig. S6.

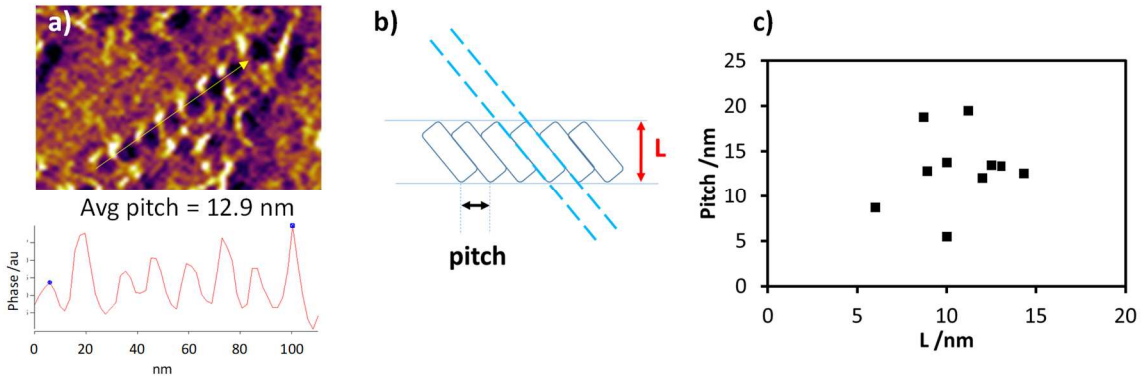

Fig. S9. a) AFM phase image showing an individual helical fiber on top of the cross section profile along the yellow arrow. The 12.9 nm average pitch was calculated by measuring the series of distances between successive maxima, and calculating the average of the series. b) Schematic showing the measured dimensions. c) Statistical analysis of 10 individual fibers that affords an average width of 10.6 ± 2.4 nm, and average pitch of 13.1 ± 4.1 nm.

7- Theoretical Calculations

Molecular structures and vibrational harmonic frequencies were obtained at the DFT level using the B3LYP exchange-correlation functional and the 6-31G(d,p) basis set. Dispersion effects were added by using the Grimme's D3 correction with Becke-Johnson damping (GD3BJ).[3] Solvent effects were taken into account by using the non-equilibrium Polarizable Continuum Model (PCM) in its integral equation formalism (IEF).[4] Perfluorobenzene was used as solvent since its dielectric constant (ε_0 = 2.03) is close to that of perfluorodecalin (ε_0 = 1.86) used experimentally. All calculations were performed using the Gaussian16 package.

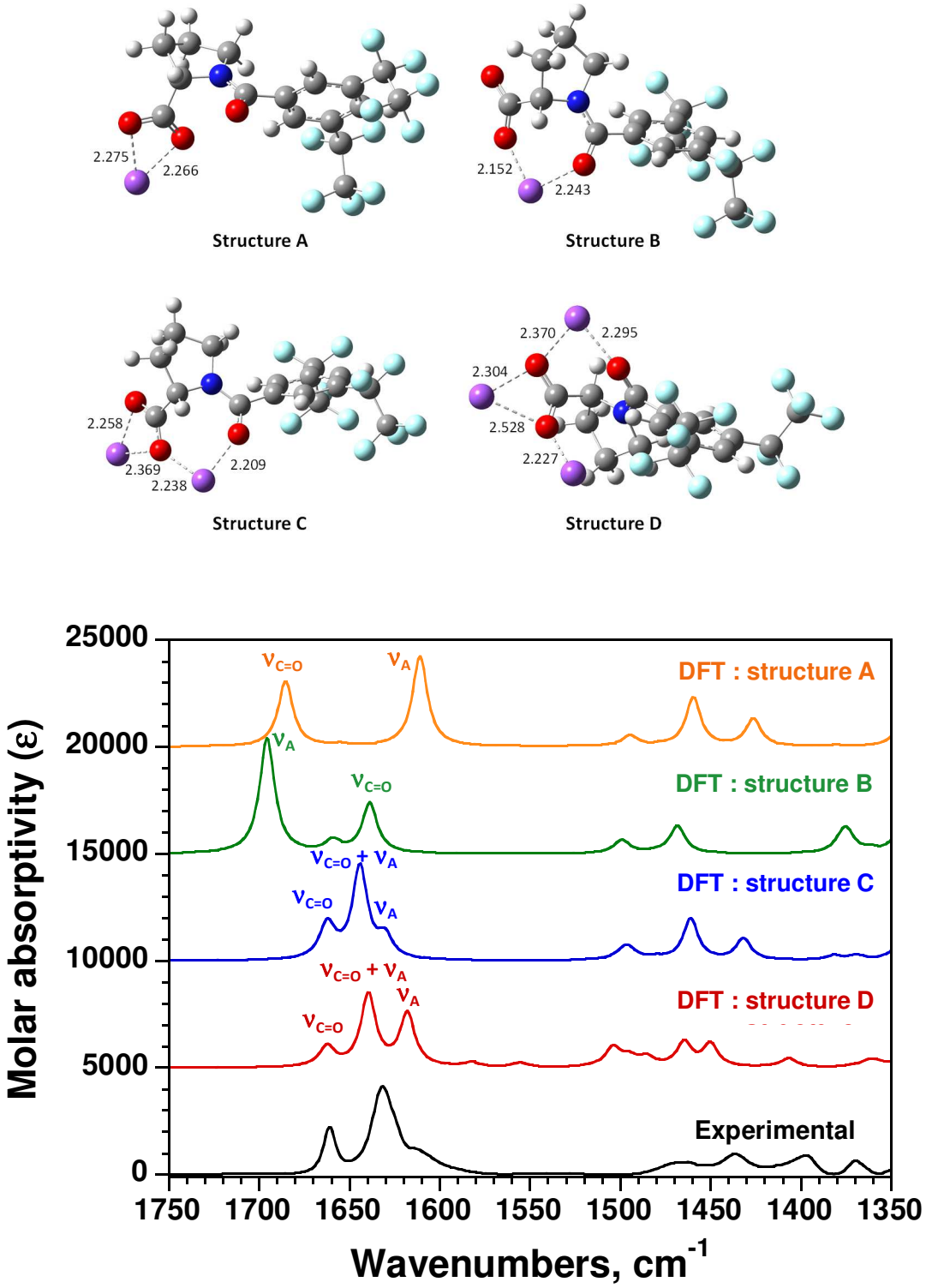

Fig. S10. Minimized molecular structures of "**1**" (the C_8F_{17} chains have changed to C_2F_5 chains) having different carboxylate/Na coordination modes (C: grey, H: white, O: red, N: dark blue, F: light blue, Na: purple), and their calculated IR spectra compared to the experimental spectrum of the perfluorodecalin gel of **1** (ν_A = antisymmetric stretching vibration of the carboxylate group, $\nu_{C=O}$ = stretching vibration of carbonyl amide group, ν_S = symmetric stretching vibration of the carboxylate group).

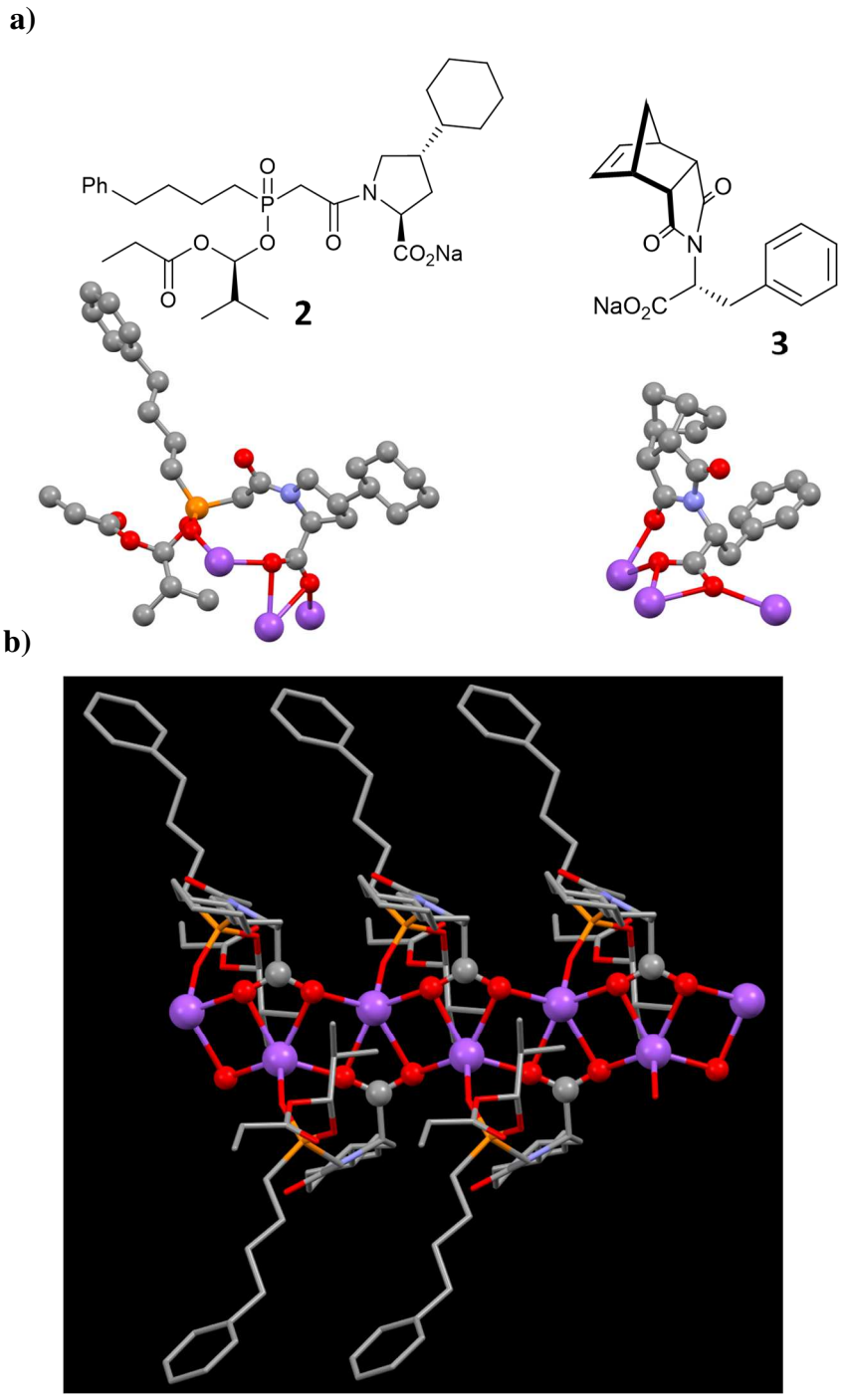

Fig. S11. a) Chemical structures of fosinopril sodium **2** (CCDC 1276464) and of the sodium salt of the (*R*)-Phenylalanine functionalized norbornene **3** (CCDC 1826288), with the sodium-carboxylate bonding highlighted as found in their X-ray structures. Atoms: O (red), C (grey), Na (purple), P (orange); b) View of the 1D coordination polymer observed in the crystal of **2**, highlighting the carboxylates bridging the sodium ions.

8- Singlet oxygen phosphorescence measurements

The steady state NIR emission spectra of air-equilibrated samples were recorded on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer, which is equipped with an iHR-320 spectrograph (150-1500 nm range, 1200 gr/mm grating, blazed at 500 nm), Hamamatsu NIR detector 10330-45 (950-1400 nm range), as well as an integration sphere.

Singlet oxygen luminescence decays were recorded, following pulsed laser excitation at 532 nm with an Innolas MOPA-1 (variable repetition rate : 1-5000 Hz). The Hamamatsu H10330-45 NIR detector was configured with a Fastcom P7889 100 ps multistep TDC acquisition card operating at 10 GHz.

Preparation of gels:

The porphyrin photosensitizer concentration was adjusted to give an absorbance of around 0.2 at 532 nm (concentration of 68 µM). This solution was used for studies in solutions and gels Table S1, Fig. S12-S13).

In order to obtain a 0.6 wt% (11 mM) gel, 5.3 mg of gelator was added to 0.45 mL of the photosensitizer solution, then dispersing **1** by sonication, followed by rapid heating to the solvent boiling point to obtain a transparent solution, before cooling down to 20 °C. The gels were prepared directly in a cuvette for studies in an integrating sphere.

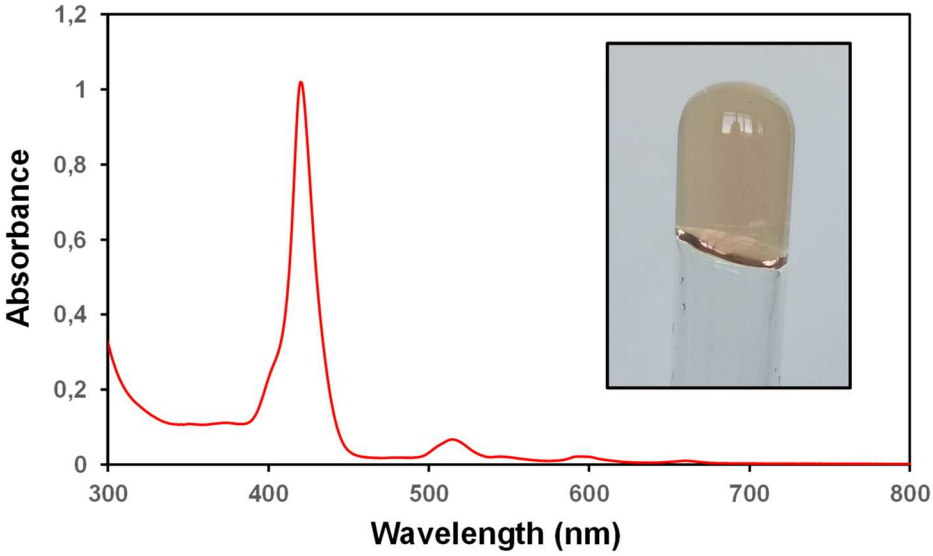

Fig. S12. UV-vis spectrum of a PFD gel of **1** (0.6 wt%) containing the porphyrin **4** (68 µM) prepared and recorded in a 0.1 cm pathlength cuvette. The inset shows a photograph (inverted tube) of the reddish transparent gel (1 mL).

Table S1. $^1O_2$ lifetimes in PFD gels of **1** and corresponding solution containing the porphyrin **4** (68 μM).

wt% of **1**	-	0.29 wt%	0.61 wt%	0.83 wt%
$^1O_2$ lifetimes in gels	-	6.5 ms	3.7 ms	2.8 ms
$^1O_2$ lifetimes in solutions[a)]	17.3 ms (τ_0)	6.2 ms	3.6 ms	2.8 ms

a) The gels were prepared, and then vigorously disrupted with a spatula to afford viscous solutions.

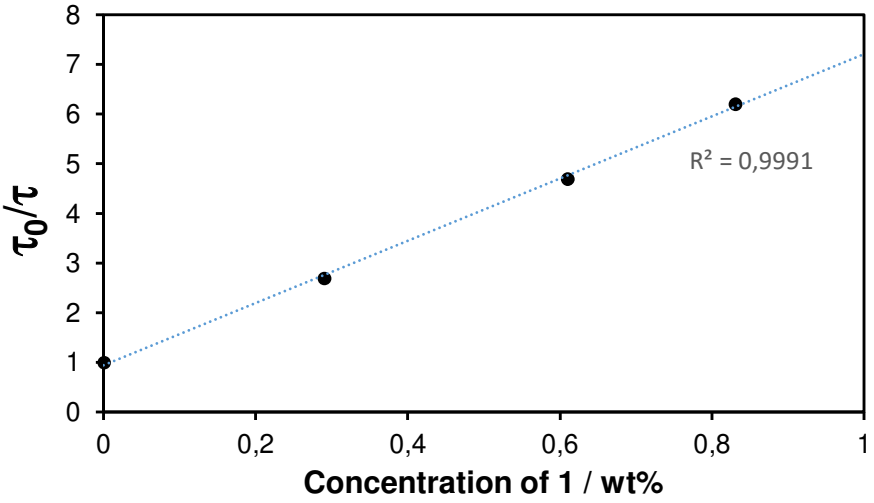

Fig. S13. Singlet oxygen quenching in PFD gels of **1** containing the porphyrin **4** (68 μM).

9- References:

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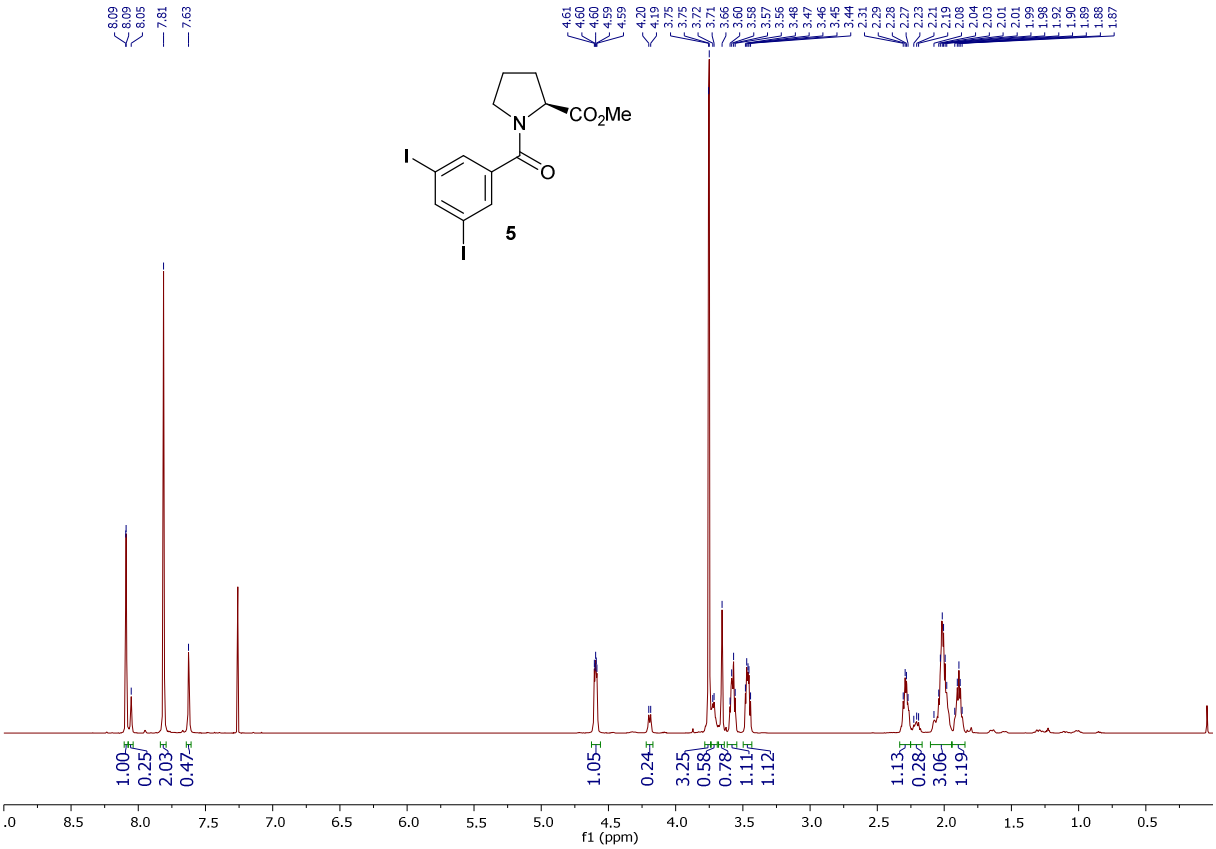
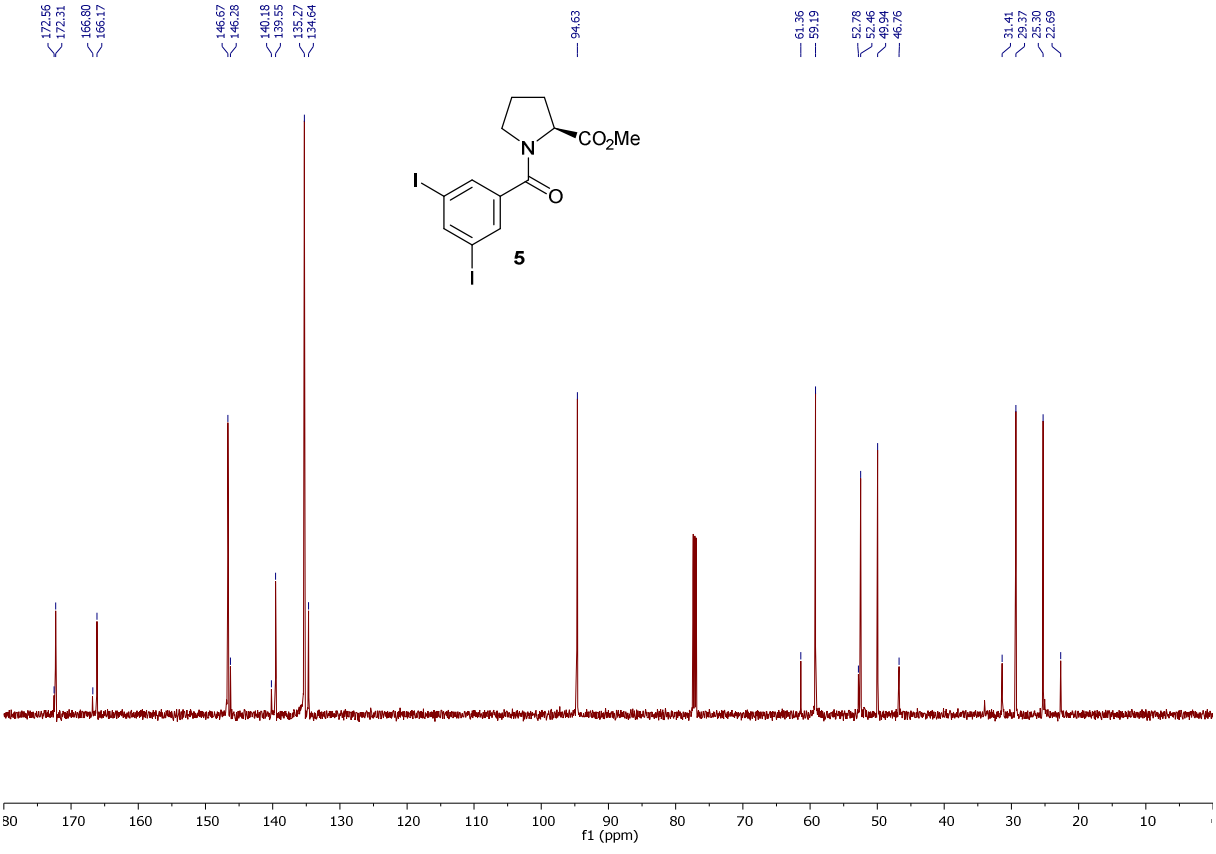
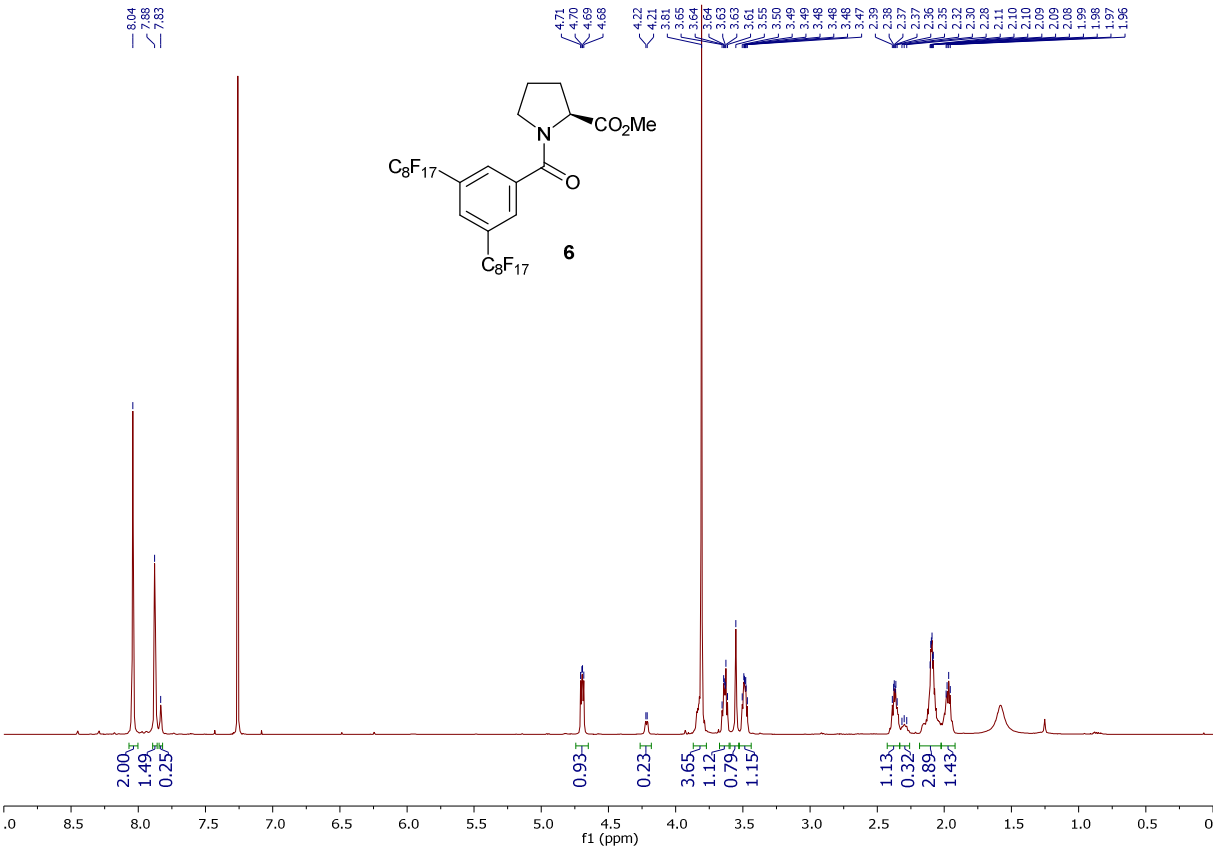
10- ^{1}H, ^{13}C NMR spectra



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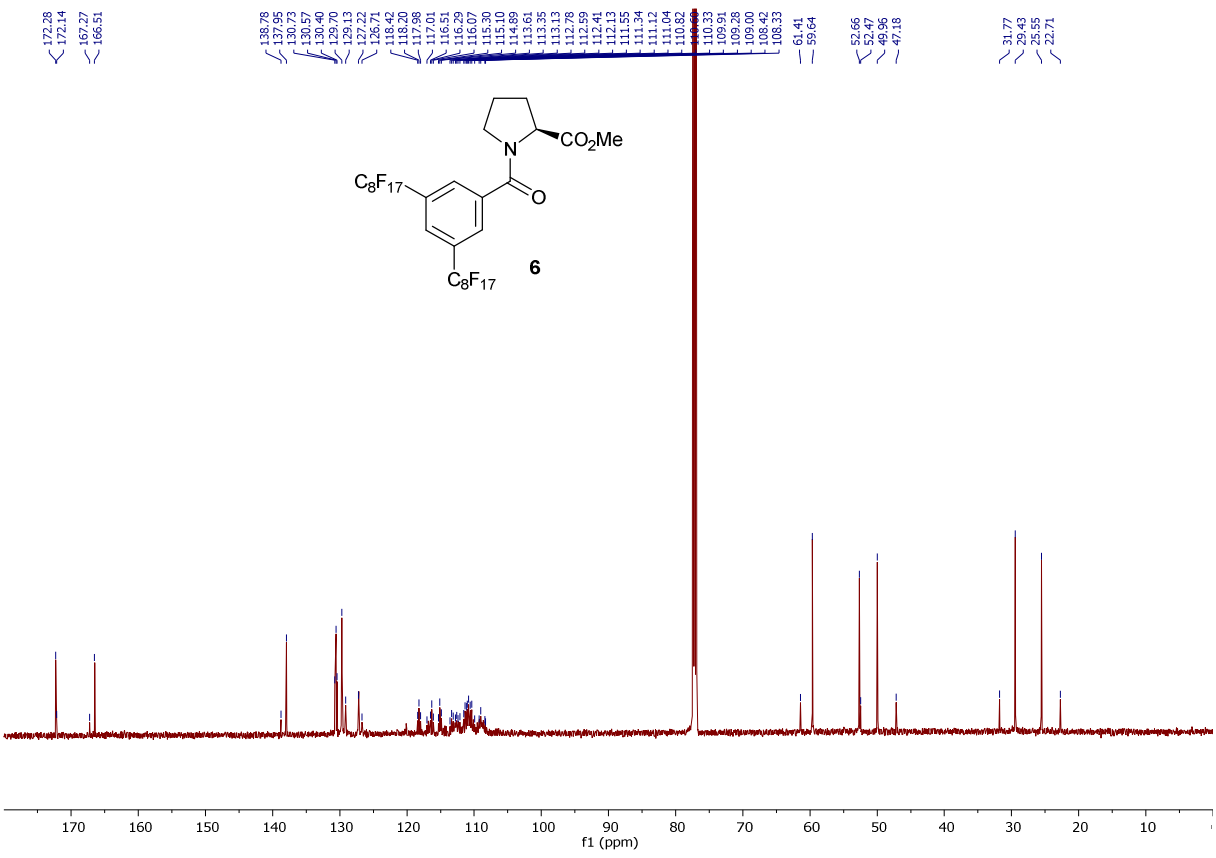
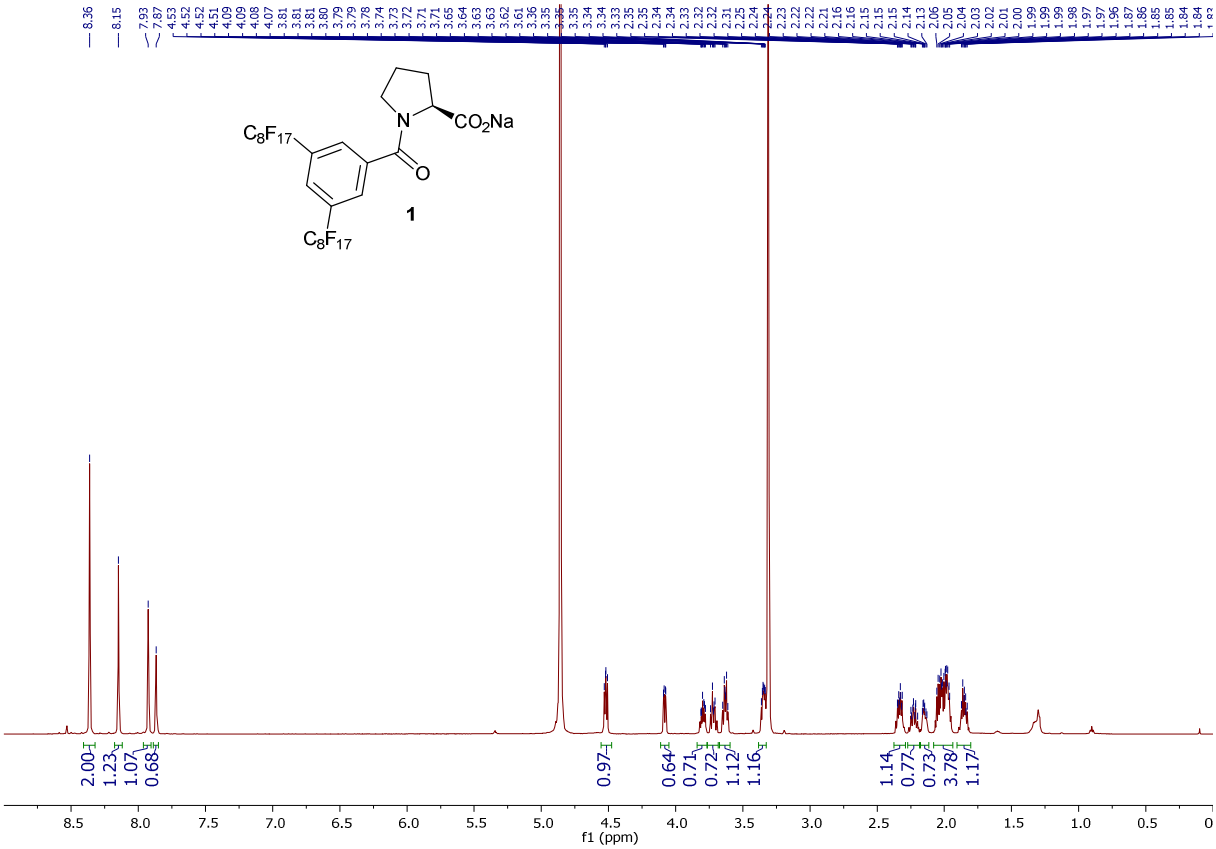
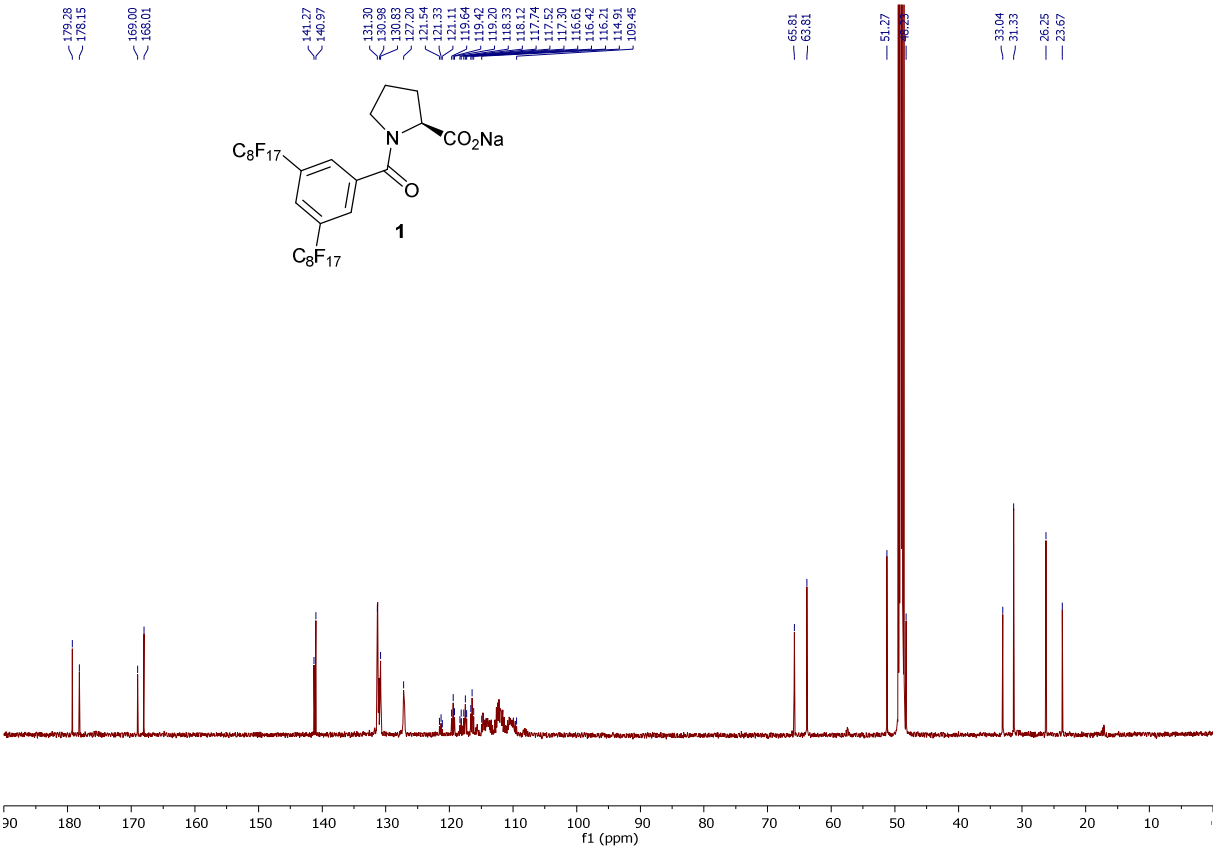
2.89
1.43
f1 (ppm)


172.28
172.14
167.27
166.51
138.78
137.95
130.73
130.57
130.40
129.70
129.13
127.22
126.71
118.42
118.20
117.89
117.01
116.51
116.29
116.07
115.30
115.10
114.89
113.61
113.35
113.13
112.78
112.59
112.41
112.13
111.55
111.34
111.12
111.04
110.82
110.33
109.91
109.28
109.00
108.42
108.33
61.41
59.64
52.66
52.47
49.96
47.18
31.77
29.43
25.55
22.71
CO2Me
N
O
C8F17
C8F17
6
f1 (ppm)


C8F17
N
CO2Na
O
1
C8F17
f1 (ppm)


C8F17
N
CO2Na
O
1
C8F17
f1 (ppm)