

Supporting Information for

Rapid surface functionalization of hydrogen-terminated silicon by alkyl silanols

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1. EXPERIMENTAL SECTION

1.1. Chemicals.

Boron-doped silicon (111) wafers, with resistivity of 0.01-0.018 $\Omega\cdot\text{cm}$, were used in these experiments. Heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane (95% purum), (heptadecafluoro-1,1,2,2-tetrahydrodecyl)methyldichlorosilane (97% purum) and 1H,1H,2H,2H-perfluorodecyltrichlorosilane (97% purum, stabilized with copper) were purchased from abcr GmbH. Chloro-decyl-dimethylsilane, acetone, diethyl ether, CH_2Cl_2 and triethylamine (Et_3N) were purchased from Sigma-Aldrich. For surface modification, CH_2Cl_2 was dried in a PureSolv EN solvent purification system (Innovative Technology). Deionized (DI) water was obtained from a Milli-Q Integral water purification system (Merck-Millipore). Phosphate buffered saline (PBS, 10 mM, pH 7.4) was prepared from a solution of NaCl (8.01 g/L), Na_2HPO_4 (1.41 g/L), KH_2PO_4 (0.27 g/L) and KCl (0.20 g/L) in DI water.

1.2. Equipment.

Nuclear Magnetic Resonance (NMR). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Acance III 400 spectrometer (observation of ^1H nucleus 400 MHz and ^{13}C nucleus 100 MHz). Chemical shifts are reported in parts per million (PPM), calibrated on the residual peak of the solvent, whose values are referred to tetramethylsilane (TMS, $\delta_{\text{TMS}} = 0$ ppm), as the internal standard. ^{13}C NMR spectra were performed with proton decoupling.

X-ray Photoelectron Spectroscopy (XPS) Measurements. The XPS analysis of surfaces was performed using a JPS-9200 photoelectron spectrometer (JEOL, Japan). Survey and high-resolution spectra were obtained under UHV conditions using monochromatic Al $\text{K}\alpha$ X-ray radiation at 12 kV and 20 mA, and an analyzer pass energy of 50 eV for wide scans and 10 eV

for narrow scans. The X-ray incidence angle and the electron acceptance angle was 10° to the surface normal. The takeoff angle φ (angle between sample and detector) of 80° is defined to a precision of 1° . The intensity of the XPS core-level electron was measured as the peak area after standard background subtraction according to the linear procedure. All XPS spectra were evaluated using the Casa XPS software (version 2.3.15). The symmetrical GL(30) line shape was employed, which consists of a Gaussian (70%) and a Lorentzian (30%) component. The fwhm of each component was constrained to 1.0–1.1 eV. Atomic area ratios were determined after a baseline correction and normalizing the peak area ratios by the corresponding atomic sensitivity factors (1.00 for C 1s, 1.80 for N 1s, 2.93 for O 1s and 4.43 for F 1s). The binding energies were calibrated on the hydrocarbon (CH_2) peak with a binding energy of 285.0 eV.

Static Water Contact Angle (CA) Measurements. The wettability of the modified surfaces was determined by automated static water contact angle measurements with a Krüss DSA 100 goniometer (volume of the drop of deionized water was 3.0 μL). The reported values are the average of at least five droplets, and the relative error is less than $\pm 2^\circ$.

Atomic Force Microscopy (AFM) Characterization. AFM images ($1 \times 1 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$, and $20 \times 20 \mu\text{m}^2$) were obtained with a MFP3D atomic force microscope (Asylum Research, Santa Barbara, CA) at a scan speed of $50.08 \mu\text{m} \cdot \text{s}^{-1}$ at a resolution of 512×512 pixels. The imaging was performed in air in tapping mode using OLYMPUS OMCL-AC240TS-R3 microcantilevers with a spring constant of $2 \text{ N} \cdot \text{m}^{-1}$. Images were flattened with a first order using the MFP3D software.

Scanning Electron Microscopy (SEM). Morphologies of F1-functionalized patterns were analyzed by SEM. Measurements were performed at room temperature with a scanning Auger electron spectroscopy system (JEOL Ltd. JAMP-9500F field emission scanning Auger

microprobe). SEM images were acquired with a primary beam of 0.8 keV. The takeoff angle of the instrument was 0°.

Ellipsometry. The ellipsometric thickness of the modified surfaces was measured using a rotating Sentech Instruments (Type SE-400) ellipsometer, operating at 632.8 nm (He–Ne laser), and an angle of incidence of 70°. The optical constants of a freshly etched H-terminated Si(111) surface were taken as $n = 3.821$ and $k = 0.051$. The thicknesses of the monolayers were determined with a planar three layer (ambient, monolayer, substrate) isotropic model, with assumed refractive indices of 1.00 and 1.44 for ambient and the monolayer, respectively. The reported values are the average of at least 5 measurements on three different samples and the standard deviation is ≤ 0.1 nm.

1.3. General procedures.

1.3.1. Monolayer preparation. A piece of Si (111) wafer was first rinsed several times with acetone, followed by sonication for 15 min in acetone. The Si wafer was then oxidized in freshly prepared piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 3:1) for 30 min at 60 °C. After piranha treatment, the substrates were immersed immediately in water and rinsed thoroughly, followed by drying with a stream of argon. Subsequently, the Si (111) substrates were etched in an argon-saturated 40% aqueous NH_4F solution for 15 min under an argon atmosphere. After being etched, the samples were rinsed with water and finally blown dry with a stream of nitrogen. A three-necked flat-bottomed flask connected to a thin capillary as the argon inlet and to a reflux condenser connected to a vacuum pump was charged with individual neat silanol, flushed with argon in order to remove traces of oxygen and moisture. The freshly etched Si (111) substrate was placed in a flask containing the fluorinated silanol under an argon atmosphere. After the reaction had been stopped, the modified surfaces were rinsed and

sonicated with CH₂Cl₂ for 15 min to remove any physisorbed silanol compounds. The modified silicon substrates were directly used for surface characterization or stored in the glovebox prior to characterization. The monolayers were extensively analyzed by XPS, IR and contact angle measurements, as described elsewhere.

1.3.2. Hydrolytic Stability Experiments. Hydrolytic stability tests were carried out by placing the modified surfaces in rubber stopper glass vials. Four different aqueous environments were prepared containing deionized (DI) water, neutral PBS (pH 7.4), an acidic (HCl) solution at pH 3, and a basic (NaOH) solution at pH 11. The stability for all surfaces was investigated at constant temperature of 25 °C. The vials under study were continuously agitated at 25 rpm using an incubator shaker, benchtop Innova 4080, to mimic mechanical disturbances by flowing solvents; this approach also minimizes the deposition of adventitious carbon on the surface. The stability of the functionalized surfaces under acidic, basic, PBS, and neutral deionized water was monitored directly after preparation, and after 1 day, 7 days, and 30 days of immersion in the described medium in a laboratory environment. In all cases, before measurements, the samples were taken from the medium, rinsed with fresh DI water, sonicated in water, and dichloromethane for 5 min in each solvent, and finally rinsed with dichloromethane and dried in a flow of dry argon. The samples were returned to new vials filled with freshly prepared solutions for prolonged periods of this stability study. The reported values are the average of five surfaces.

1.3.3. Simulation of C 1s XPS spectra. The XPS spectra were simulated by M11/6-311G(d,p)-computed binding energies using Gaussian 09.¹ The core orbital energies were taken from the Natural Bond Analysis as described elsewhere.² Initially, a Monte Carlo conformational search using conformer distribution option available in Spartan'14 was used.³ With this option, a search without constraints was performed for every structure. The torsion angles were randomly varied and the obtained structures were fully optimized using the

MMFF force field. Thus, 100 minima of energy within an energy gap of 10 kcal/mol were generated. These structures were analyzed and ordered considering the relative energy, being the repeated geometries eliminated.

1.3.4.Fouling experiment. Clean and well-characterized monolayer-modified silicon surfaces were used for our fouling studies. For all experiments the concentration of fouling polymer was 10 mg/mL in DMF. The well-cleaned surface was immersed into the polymer solution for 12 h, and then taken out, washed with DMF for 2 min in an autoshaker (at 50 rpm), taken out, rinsed, and this washing step was performed in total three times. Next, the sample was dried in a 80 °C oven for 2 h. Unfouled monolayers are not affected in any observed manner by this sonication and drying treatment. The extent of absorption (fouling) and the morphology of the adhered polymer on these monolayers were characterized by ellipsometry, XPS and AFM measurements. For each monolayer, the fouling experiments were conducted on three different samples, and on each sample the ellipsometry, XPS and AFM measurements were carried out at least three different places. The reported data in this paper are the average results for all the measurements. Bare silicon was used as reference in this polymer absorption survey.

1.3.5.DFT calculations.

Calculations were performed using Gaussian'09. All geometries were fully optimized using density functional theory (DFT) by means of the M11L functional and the 6-311+G(d,p) basis set. Analytical frequencies were calculated at the same optimization level in all cases, and the natures of the stationary points were determined in each case according to the proper number of imaginary frequencies.

1.4. Synthesis of silanol derivatives.

Silanol derivatives were synthesized according to reported literature procedures.⁴

1.4.1. Synthesis of decyldimethylsilanol (A1).

Chloro-decyl-dimethylsilane (5.0 mL) was added to a cool (ice bath) solution of H₂O (1.0 mL), N(C₂H₅)₃ (5.0 mL) and ether (50 mL), and the mixture was stirred for 1 h at room temperature and filtered. The filtrate was concentrated to an oil by rotary evaporation (30 °C), and the yellowish oil was weighed. Yield = 81%; IR (cm⁻¹) = 3264, 2975, 2921, 2863, 1465, 1250, 1057, 837, 774. ¹H NMR (400 MHz, CDCl₃) δ = 3.10 (m, 1H), 1.45-1.39 (m, 16 H), 1.03-0.99 (t, *J* = 8.0 Hz, 3H), 0.73-0.69 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 33.5, 31.9, 29.7, 29.6, 29.4, 29.3, 23.1, 22.6, 17.9, 14.1, -0.13 ppm. MS calculated for C₁₂H₂₈OSi [M + H] 217.1988, found 217.1986.

1.4.2. Synthesis of heptadecafluoro-1,1,2,2-tetrahydrodecyl)-dimethylsilanol (F1).

This compound was synthesized from (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane following the described procedure. Yield = 98%; IR (cm⁻¹) = 3299, 2967, 2910, 1443, 1330, 1199, 1189, 1142, 1146, 1113, 1066, 956, 902, 842. ¹H NMR (400 MHz, CDCl₃) δ = 2.18-2.04 (m, 2H), 1.73 (s, 1H) 0.85-0.81 (dt, *J* = 4.4, 8.8 Hz, 2 H), 0.19 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 122.7-121.5, 119.8-119.0, 117.1-116.3, 115.2-113.4, 112.9-111.1, 110.8-108.2, 107.2-106.1, 26.2-26.0 (t), 25.8, 7.9, -0.3 ppm. MS calculated for C₁₂H₁₁F₁₇OSi [M + H] 523.0386, found 523.0389.

1.4.3. Synthesis of heptadecafluoro-1,1,2,2-tetrahydrodecyl)-dimethylsilanol (F2).

This compound was synthesized from (heptadecafluoro-1,1,2,2-tetrahydrodecyl)methyldichlorosilane following the described procedure. Yield = 95%; IR (cm⁻¹) = 3285, 2965, 2910, 1445, 1317, 1235, 1189, 1142, 1066, 889, 845. ¹H NMR (400 MHz, CDCl₃) δ = 2.48-2.34 (m, 2H), 1.56-1.48 (dt, *J* = 4.6, 8.7 Hz, 2 H), 0.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 120.4-120.2, 118.8-118.1, 115.7-115.3, 113.8-113.4, 111.4-110.8, 108.6-107.8, 25.0-24.5 (t), 11.6, 4.9 ppm. MS calculated for C₁₁H₉F₁₇O₂Si [M + H] 525.0179, found 525.0180.

1.4.4. Synthesis of (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)silanetriol (F3).

This compound was synthesized from 1H,1H,2H,2H-perfluorodecyltrichlorosilane following the described procedure. Yield = 97%; IR (cm⁻¹) = 3341, 2920, 2863, 1597, 1451, 1326, 1254, 1097, 1031, 948, 849. ¹H NMR (400 MHz, CDCl₃) δ = 3.01-2.94 (m, 2H), 1.27-1.23 (m, *J* = 16.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 121.6-121.0, 120.8-120.2, 118.86-117.6, 116.0-115.1, 114.1-109.9, 108.9-107.5, 105.9-105.4, 28.1-27.6, 4.38 (t), -3.81 ppm. MS calculated for C₁₀H₇F₁₇O₃Si [M + H] m/z: 526.9971, found 526.9970.

2. SUPPORTING FIGURES.

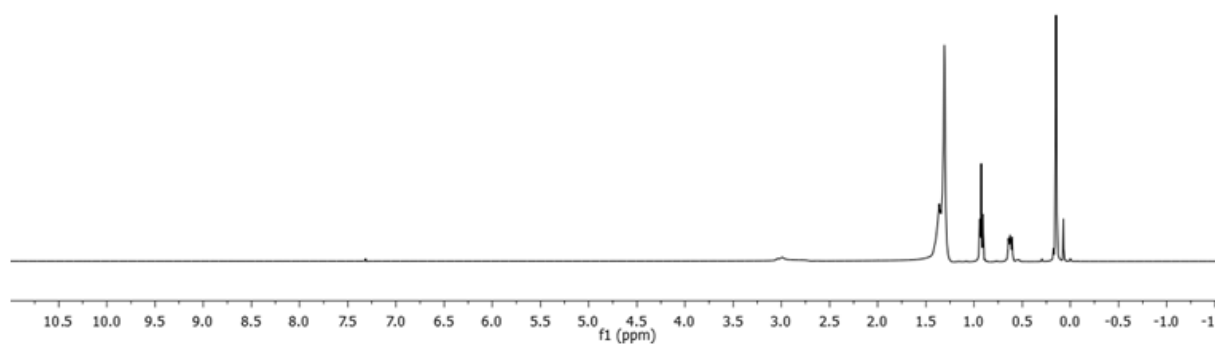


Figure S1. ^1H NMR spectrum of compound A1.

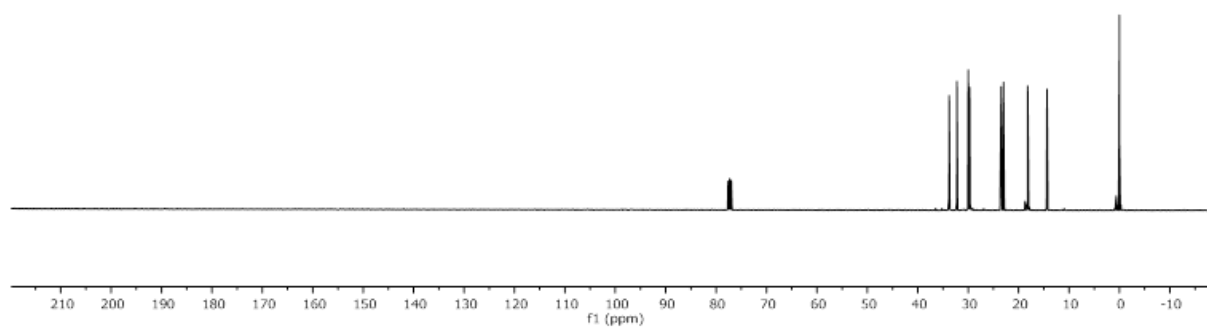


Figure S2. ^{13}C NMR spectrum of compound A1.

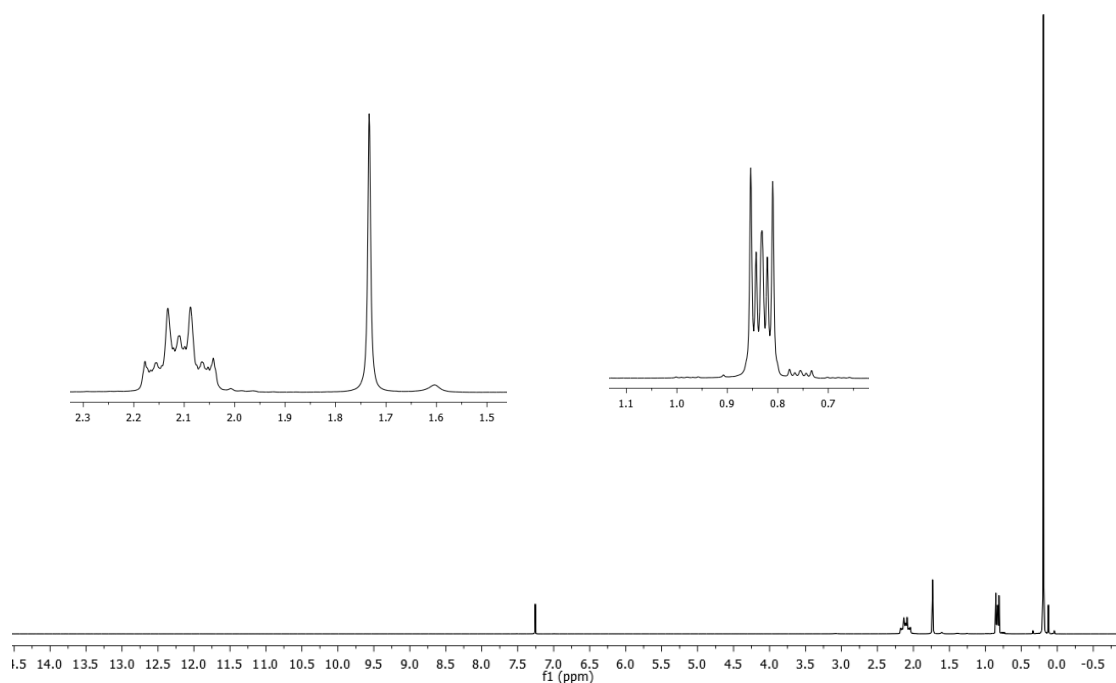


Figure S3. ^1H NMR spectrum of compound F1.

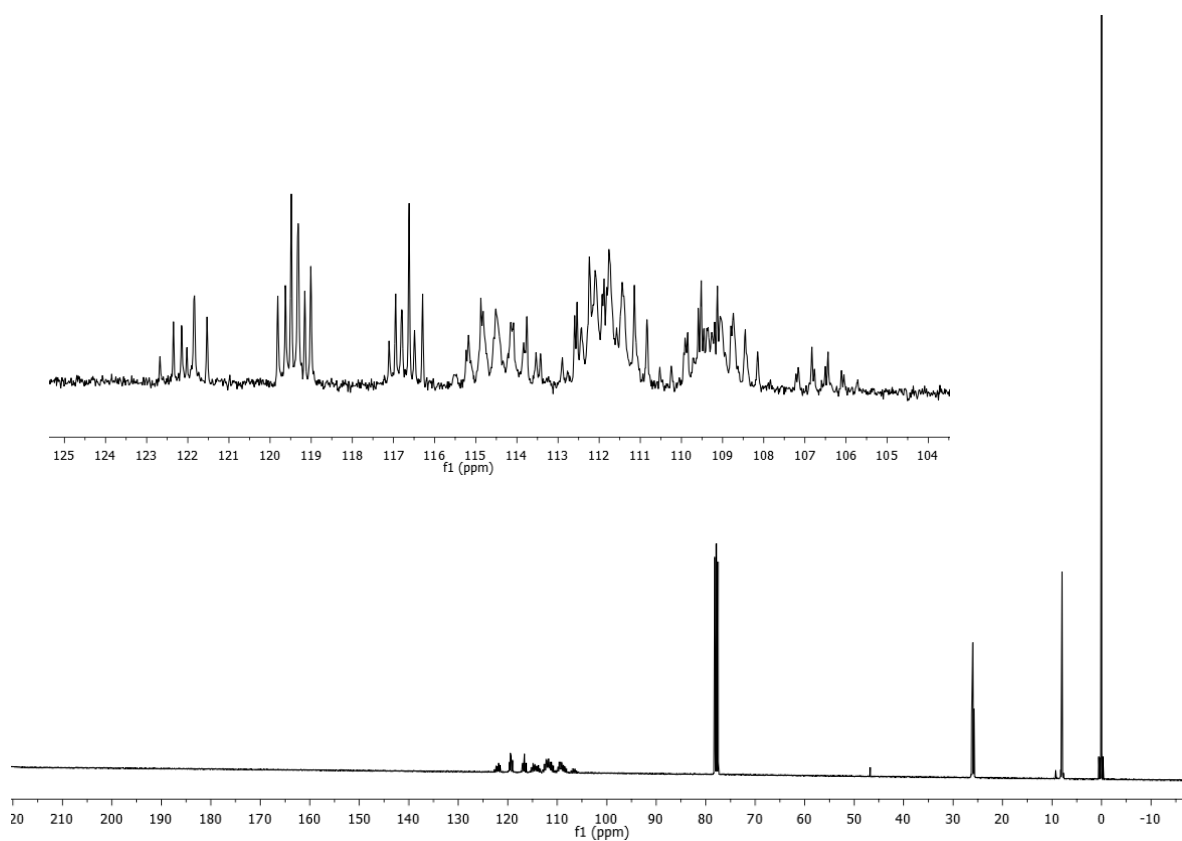


Figure S4. ^{13}C NMR spectrum of compound F1.

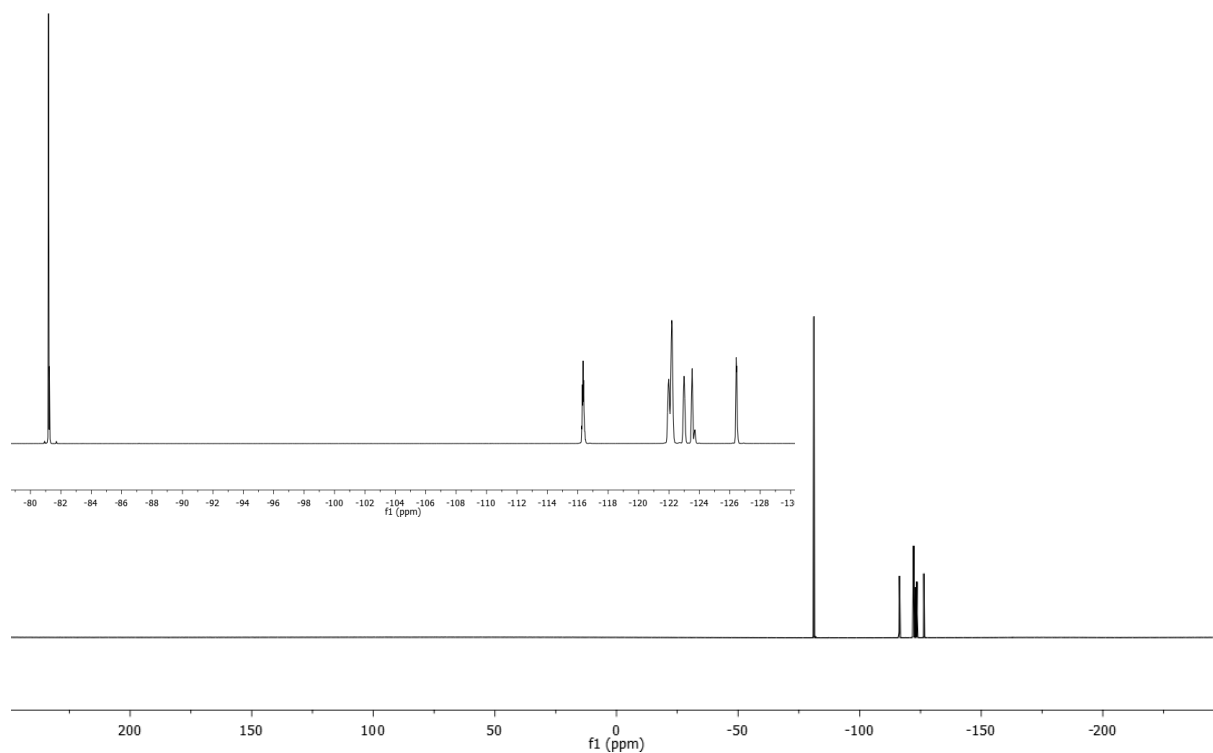


Figure S5. ^{15}F NMR spectrum of compound **F1**.

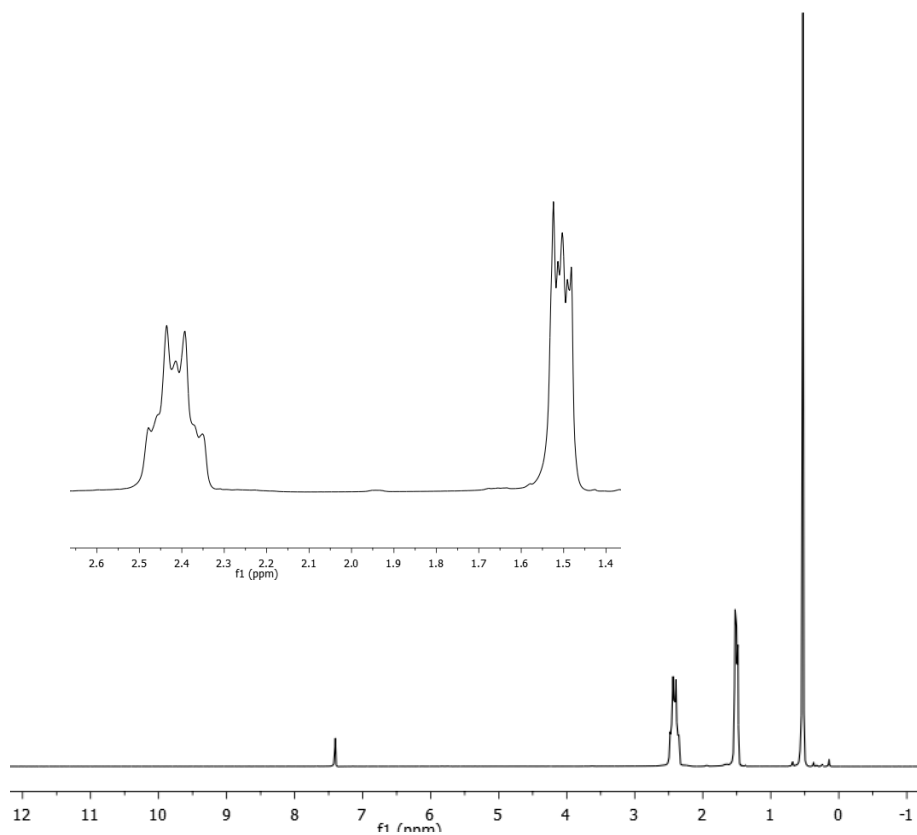


Figure S6. ^1H NMR spectrum of compound **F2**.

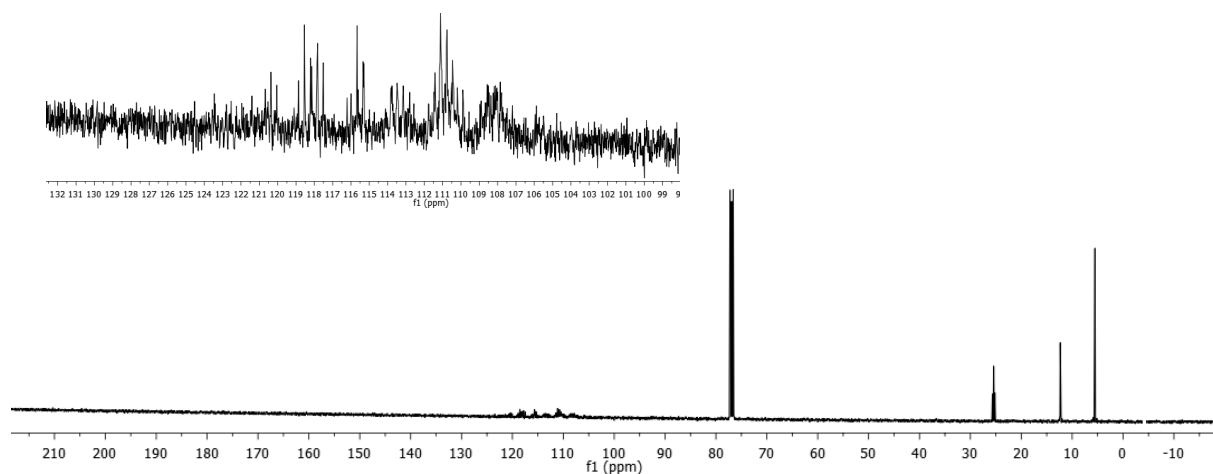


Figure S7. ^{13}C NMR spectrum of compound **F2**.

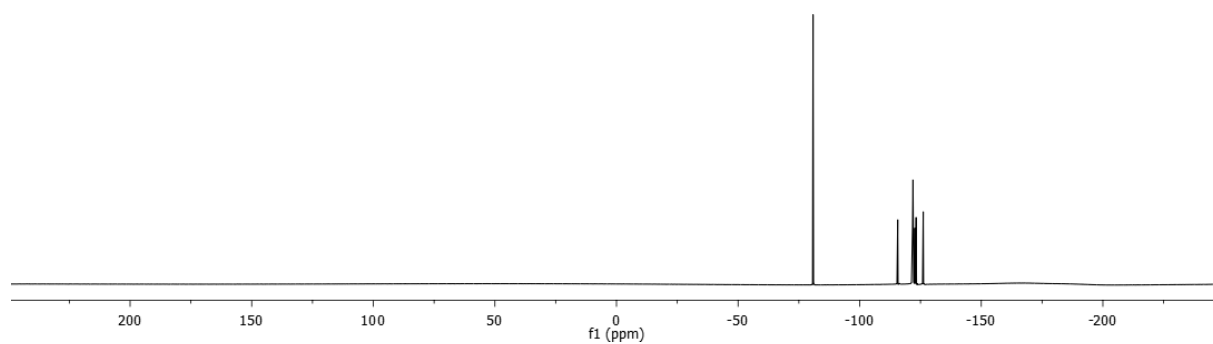


Figure S8. ^{15}F NMR spectrum of compound **F2**.

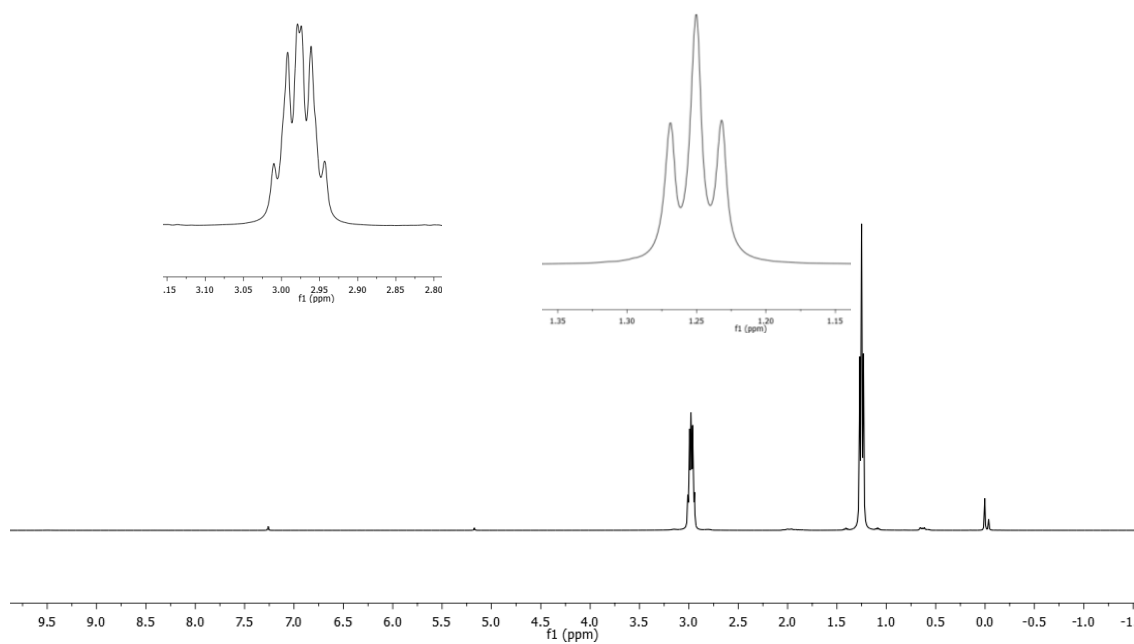


Figure S9. ^1H NMR spectrum of compound F3.

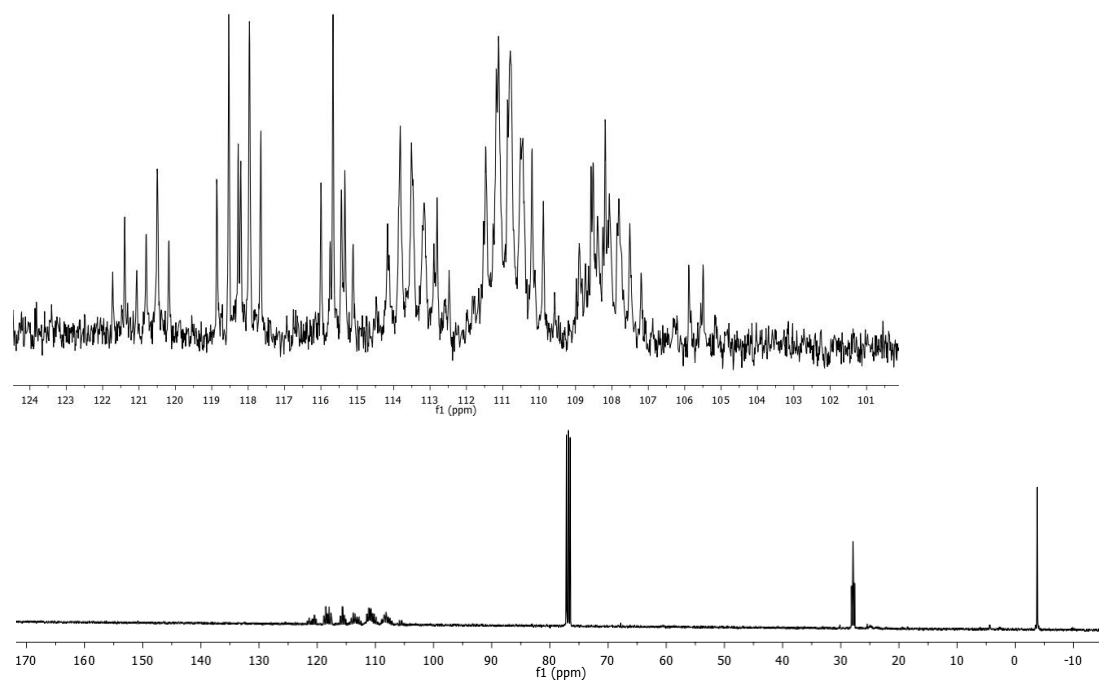


Figure S10. ^{13}C NMR spectrum of compound F3.

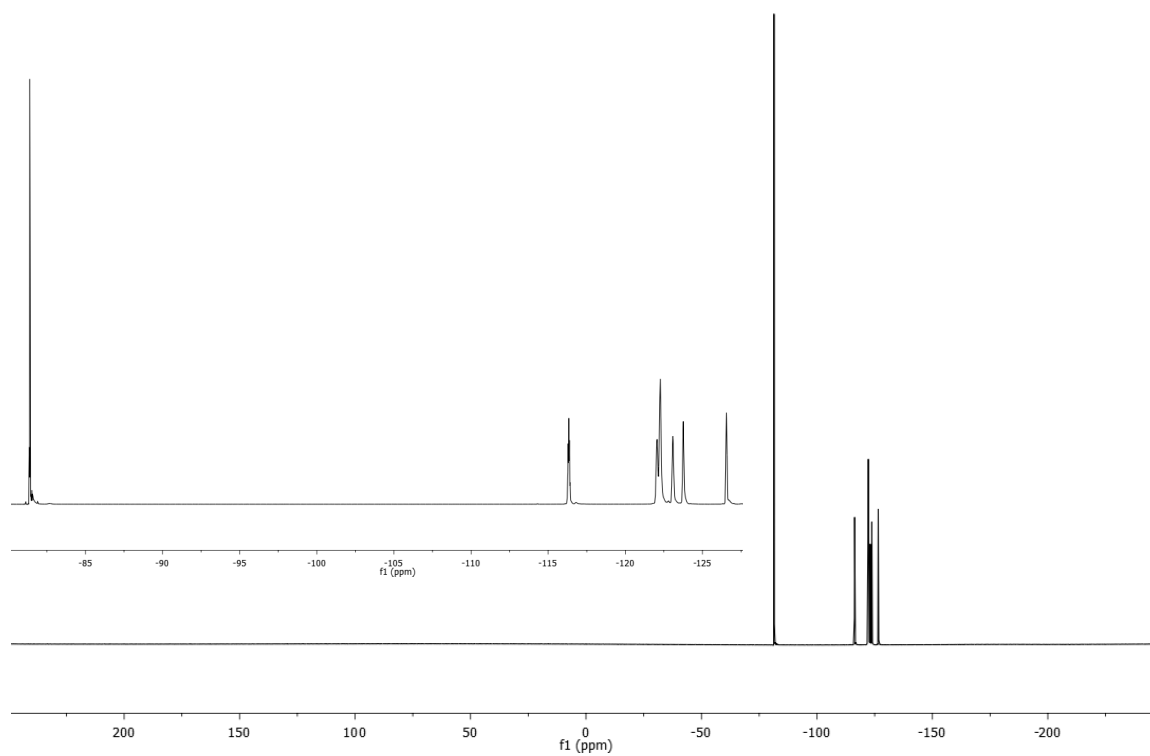


Figure S11. ^{15}F NMR spectrum of compound **F3**.

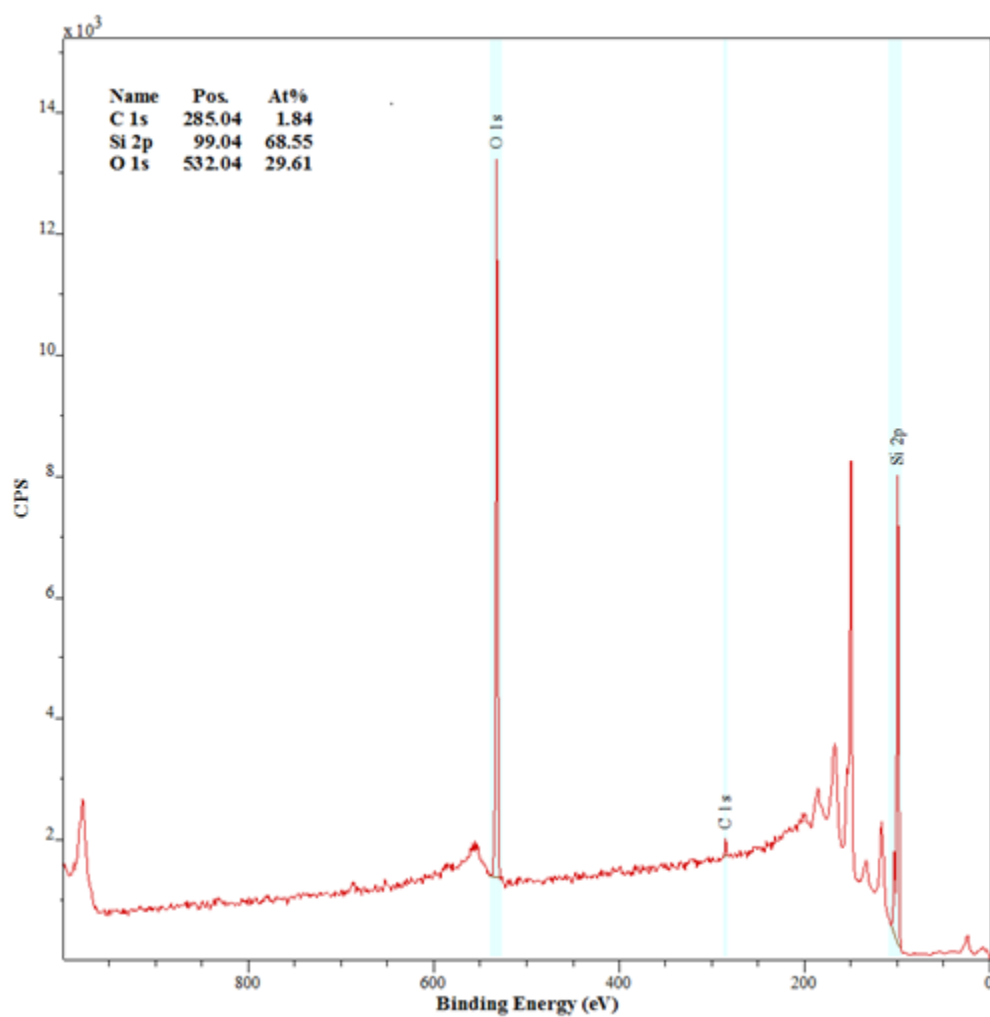


Figure S12. XPS spectra sample after piranha cleaning (30 min).

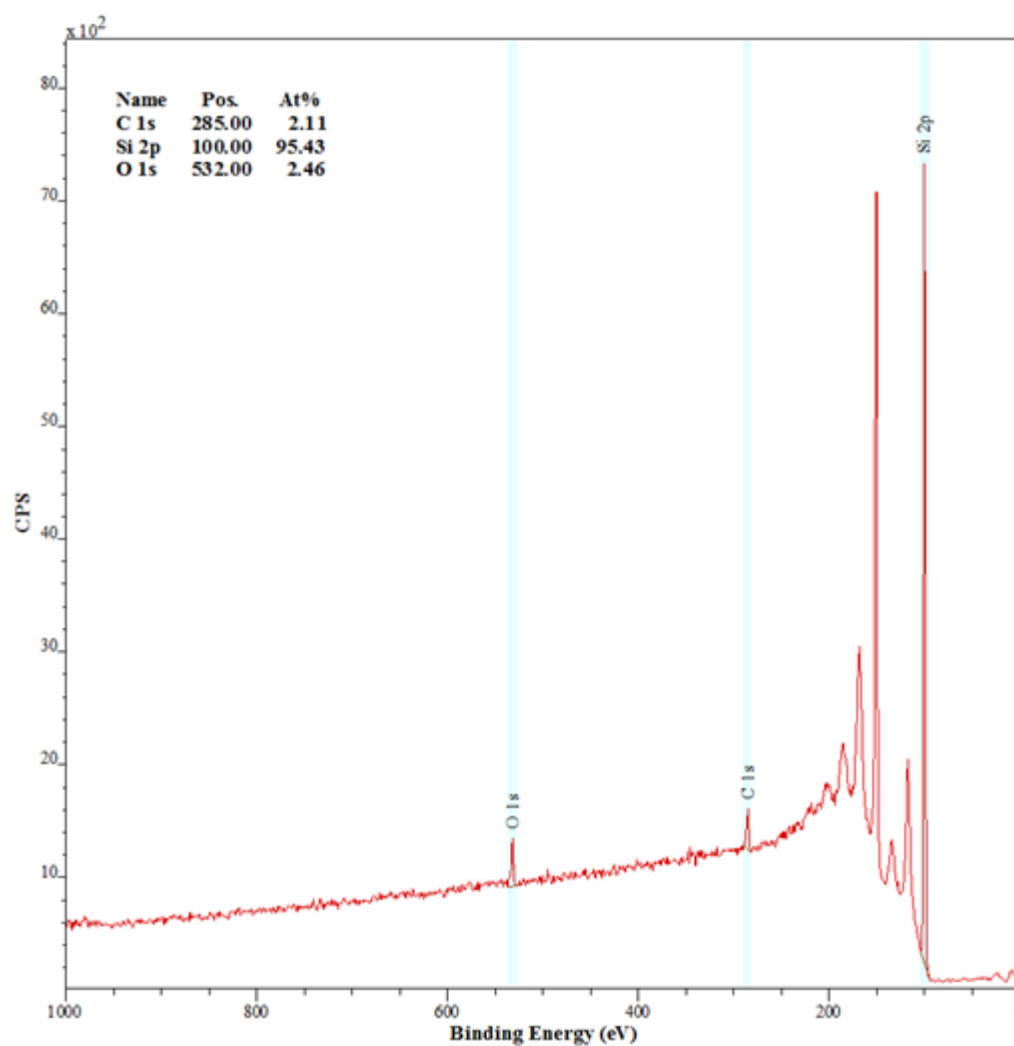


Figure S13. XPS spectra sample after NH_4 etching (15 min).

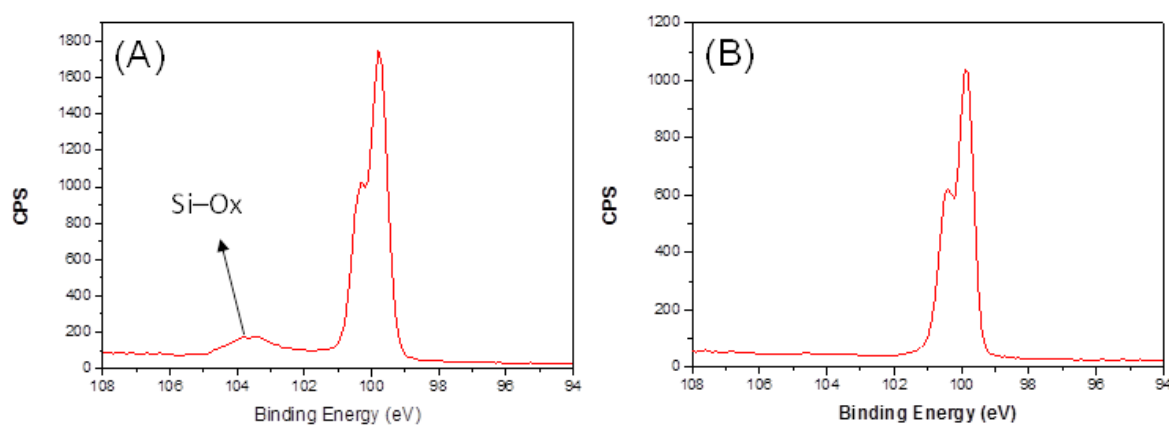


Figure S14. High-resolution Si 2p spectra, for the (A) piranha cleaned silicon surface (30 min) and (B) after NH_4 etching (15 min).

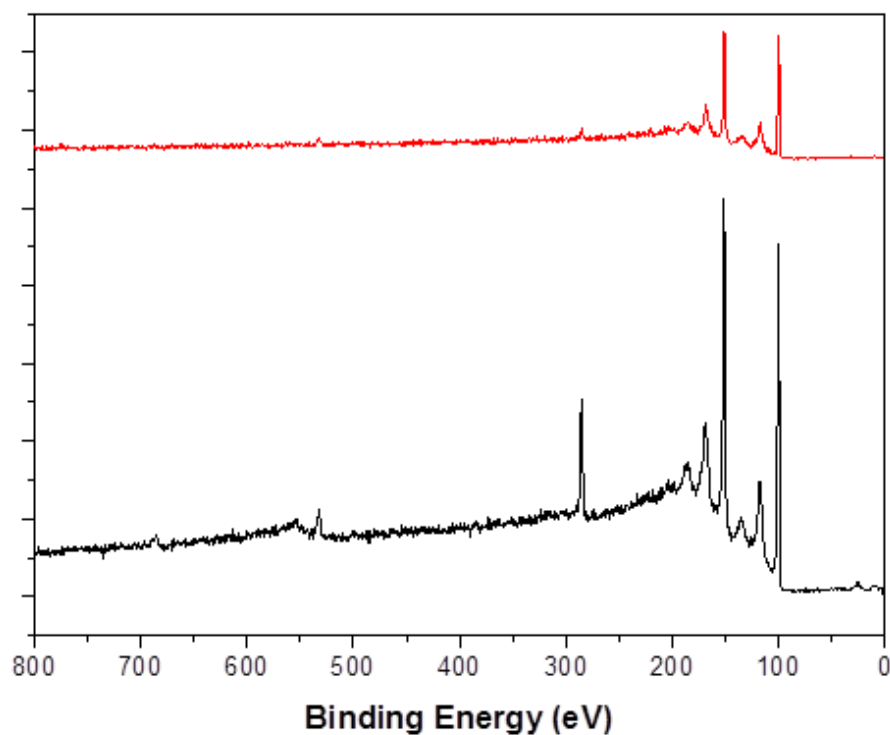


Figure S15. Comparison of XPS spectra of reaction of silanol **A1** and H-terminated Si (111) in the presence of 1 mol % of borane catalyst (red line) and without catalyst (black line).

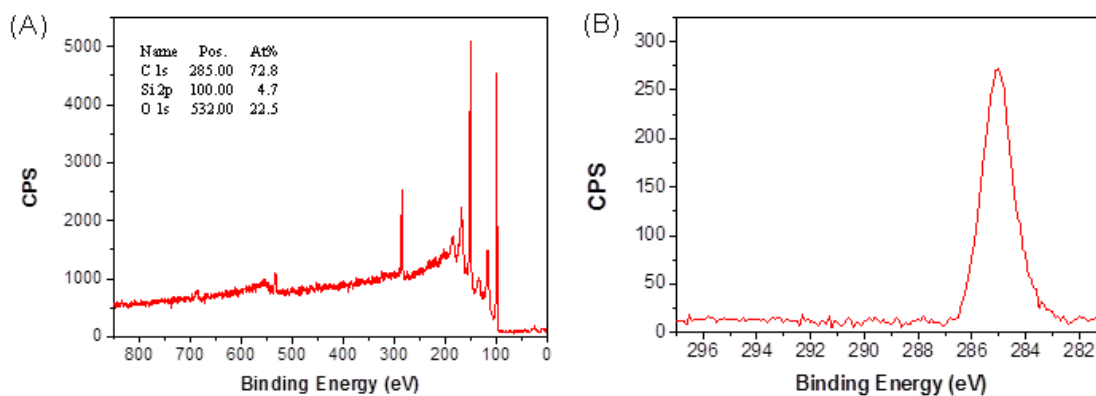


Figure S16. XPS spectra of silanol **A1**: (A) wide scan and (B) C 1s narrow scan.

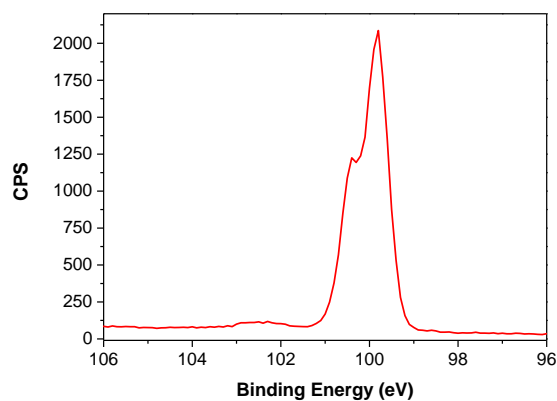


Figure S17. High-resolution Si 2p spectra for the A1-modified surface.

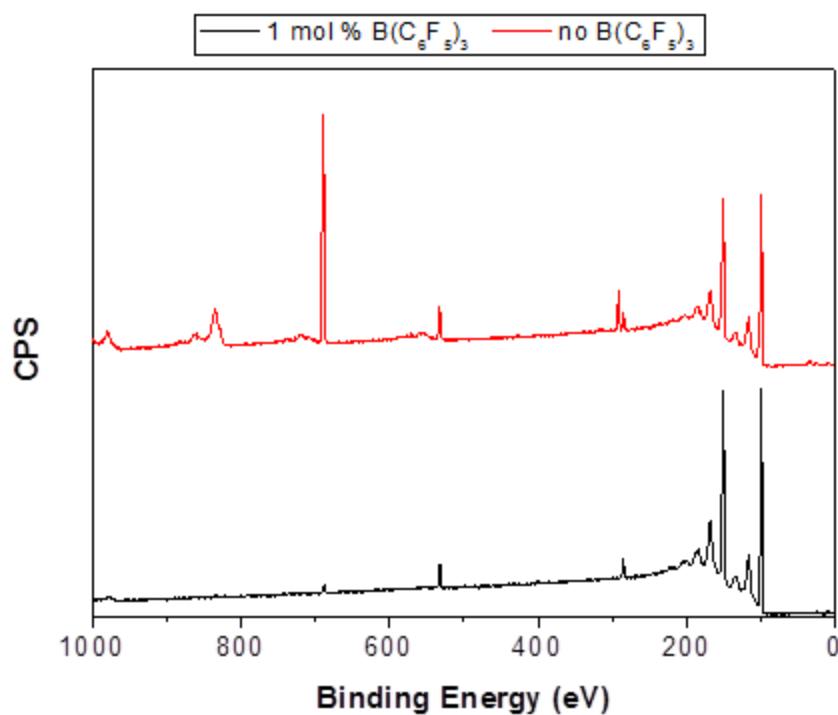


Figure S18. Comparison of XPS spectra of reaction of silanol **F1** and H-terminated Si (111) in the presence of 1 mol % of borane catalyst (black line) and without catalyst (red line).

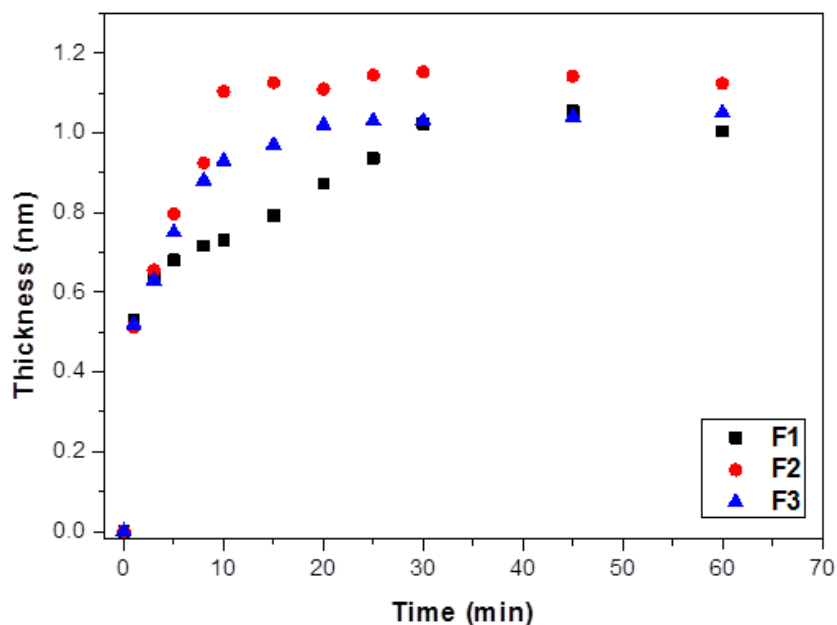


Figure S19. Layer ellipsometric thicknesses (± 0.1 nm) of fluorinated silanol compounds **F1**, **F2** and **F3** derived monolayers versus reaction time (lines connecting data points are a mere guide to the eye). Each data point represents the average value of three separately prepared monolayers.

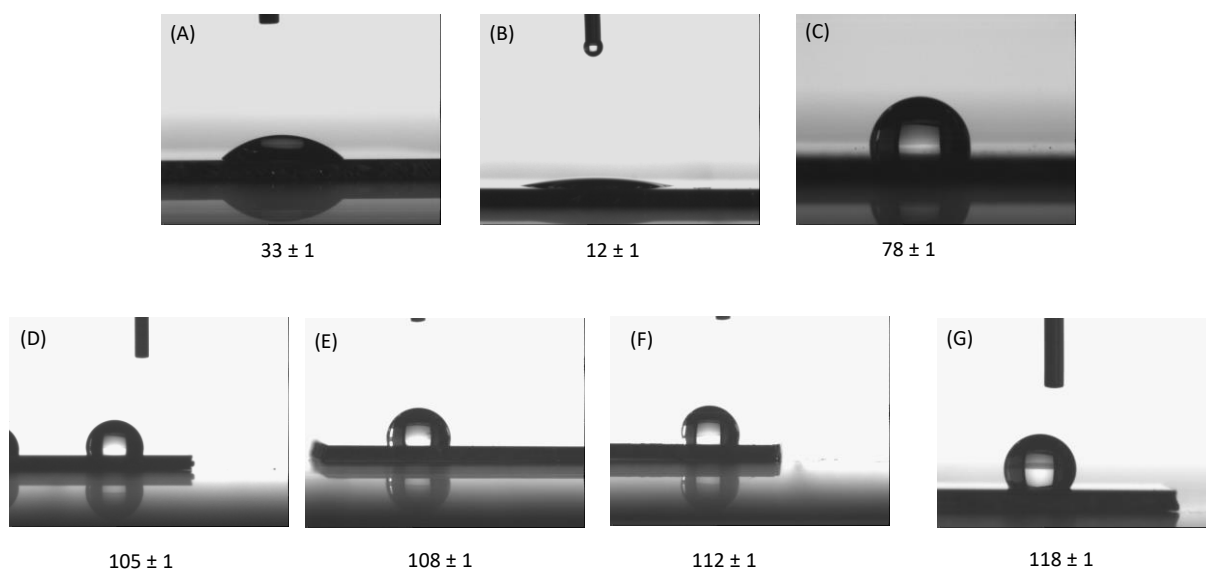


Figure S20. SCA of reaction of Si (111) surface after (A) acetone cleaning, (B) piranha cleaning, (C) NH_4 etching and after reaction (30 min) with (D) **A1**, (E) **F1**, (F) **F2**, and (G) **F3**.

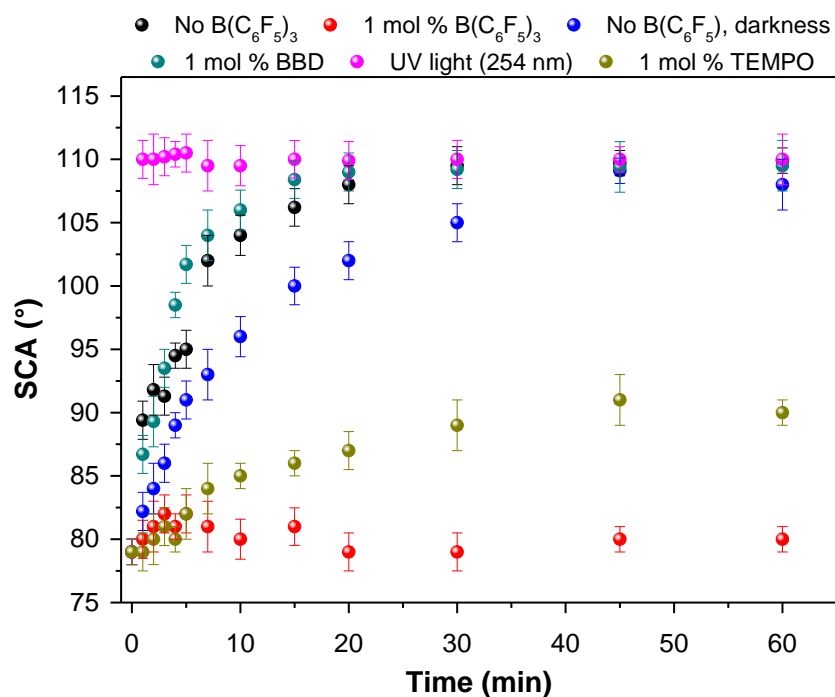


Figure S21. SCA of silanol **F1** grafting vs reaction time under different reaction conditions. Each data point represents the average of five separately prepared monolayers.

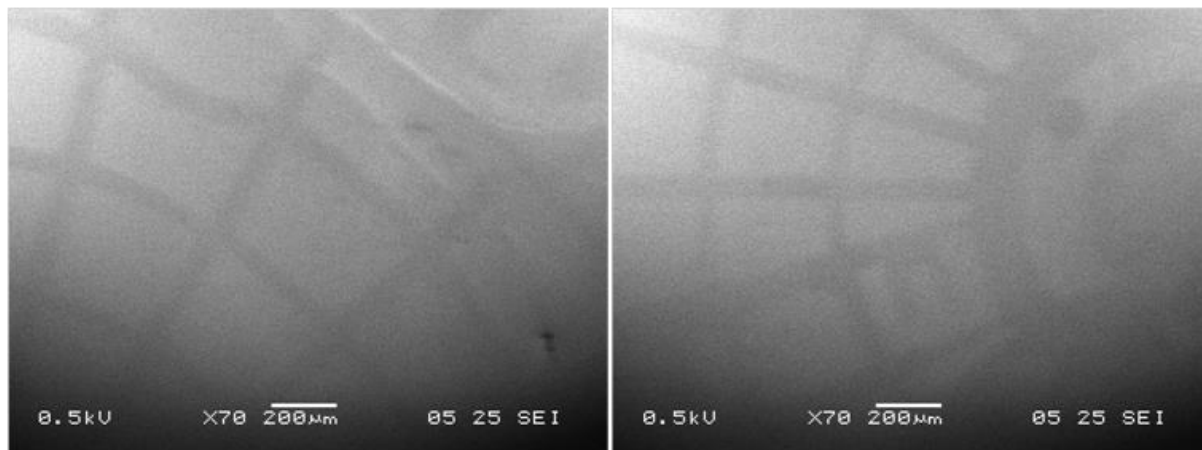


Figure S22. Scanning electron microscopy (SEM) image obtained using a gold photomask.

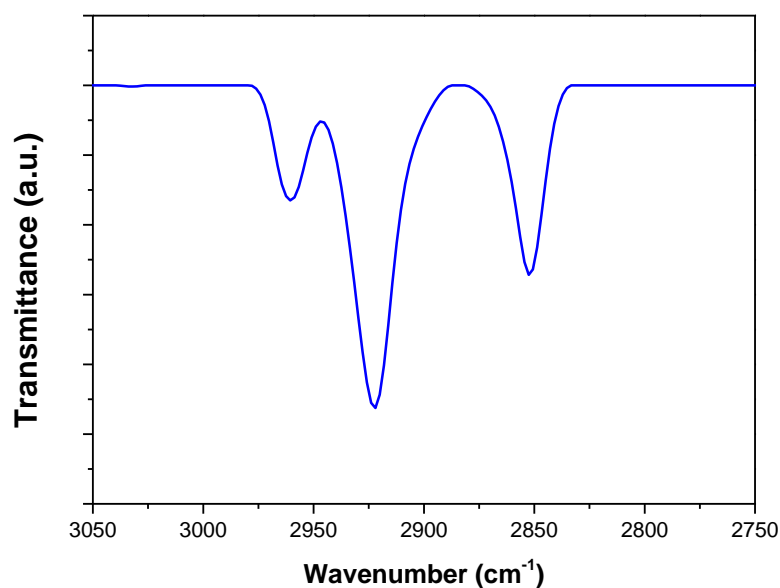


Figure S23. IRRAS spectrum of **A1**-modified surface. Only C-H stretching region is shown after baseline correction. The symmetric and antisymmetric -C-H stretching peaks of -CH₂ groups appear at 2851 cm⁻¹ and 2921 cm⁻¹, respectively. The peak at 2963 cm⁻¹ corresponds to the -C-H stretching peak of -CH₃.

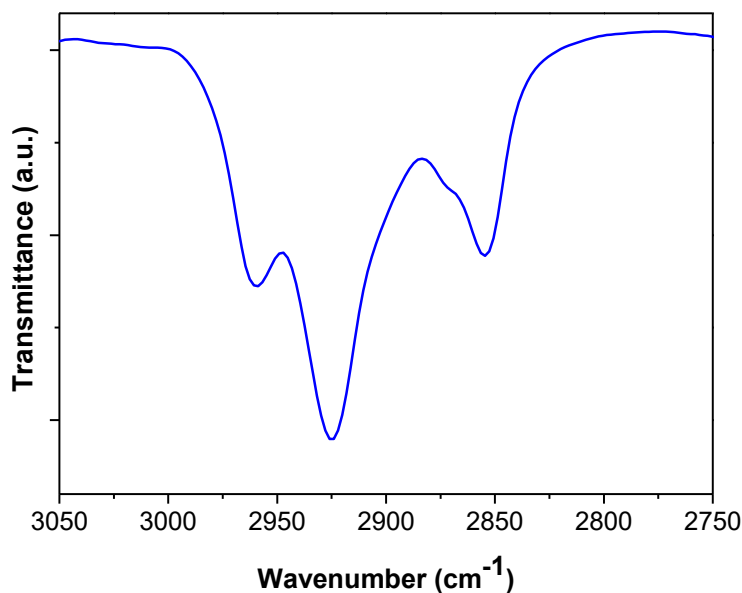


Figure S24. IRRAS spectrum of **F1**-modified surface. Only C-H stretching region is shown after baseline correction. The symmetric and antisymmetric -C-H stretching peaks of -CH₂ groups appear at 2852 cm⁻¹ and 2923 cm⁻¹, respectively. The peak at 2959 cm⁻¹ corresponds to the -C-H stretching peak of -CH_{3.5}.

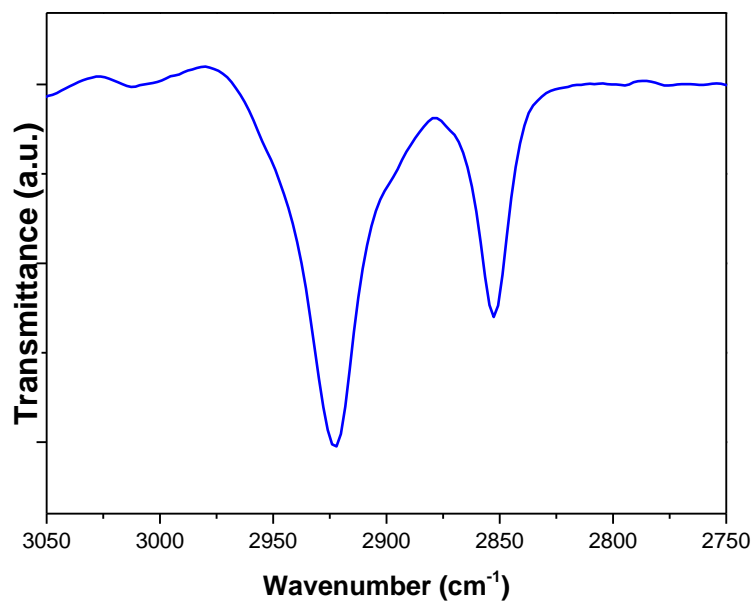


Figure S25. IRRAS spectrum of **F2**-modified surface. Only C-H stretching region is shown after baseline correction. The symmetric and antisymmetric -C-H stretching peaks of -CH₂ groups appear at 2851 cm⁻¹ and 2921 cm⁻¹, respectively.

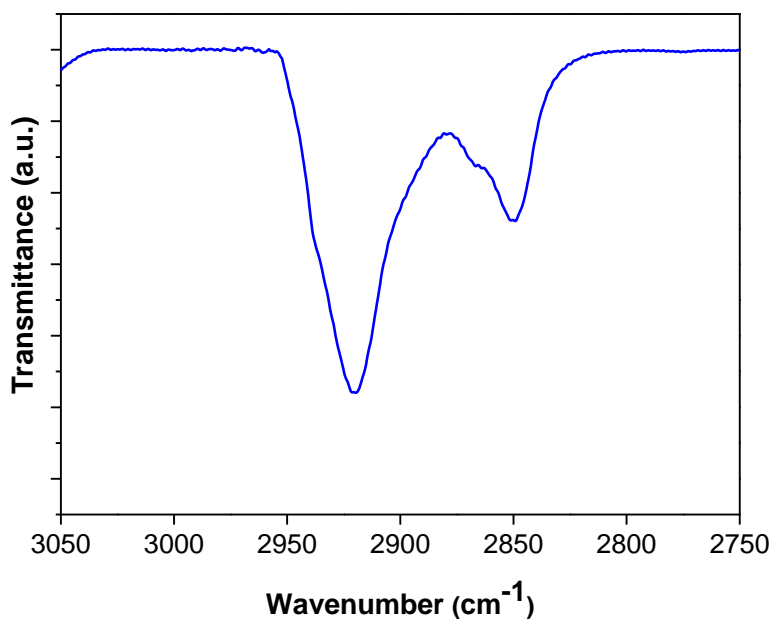


Figure S26. IRRAS spectrum of **F3**-modified surface. Only C-H stretching region is shown after baseline correction. The symmetric and antisymmetric -C-H stretching peaks of -CH₂ groups appear at 2851 cm⁻¹ and 2920 cm⁻¹, respectively.

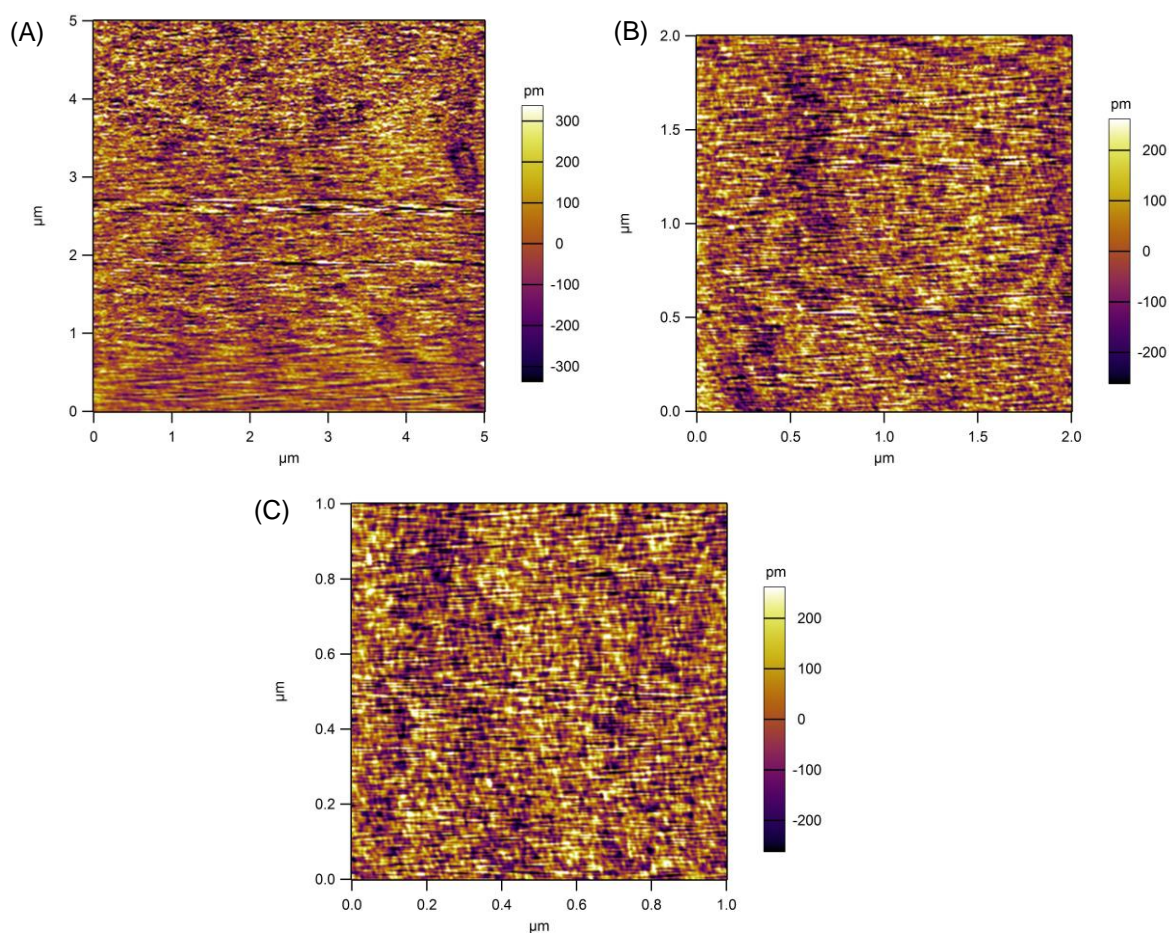


Figure S27. Tapping AFM images of piranha cleaned Si (111) over scan sizes of 5×5 μm (A, rms roughness 0.33 nm), 2×2 μm (B, rms roughness 0.28 nm) and 1×1 μm (C, rms roughness 0.21 nm).

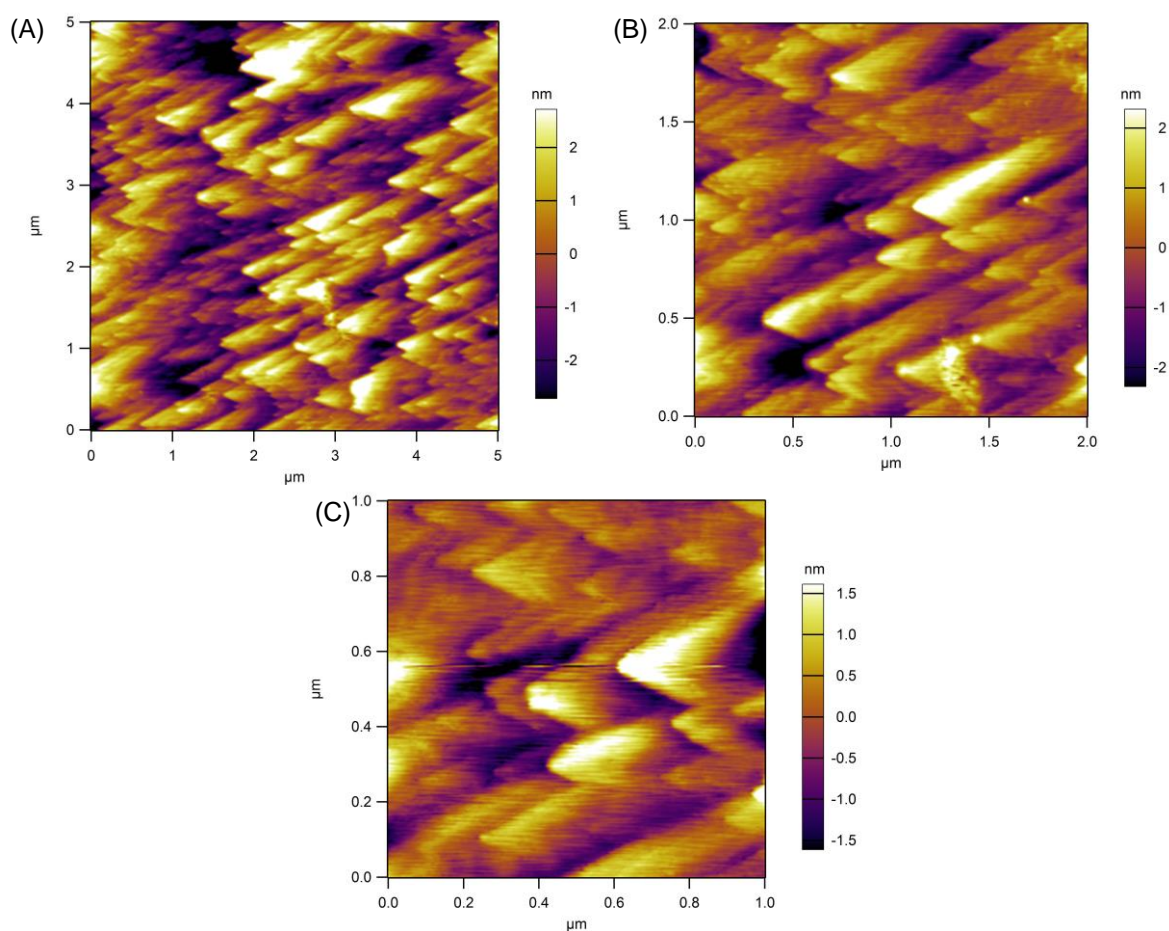


Figure S28. Tapping AFM images of NH₄ etched Si (111) over scan sizes of 5 × 5 μm (A, rms roughness 0.45 nm), 2 × 2 μm (B, rms roughness 0.37 nm) and 1 × 1 μm (C, rms roughness 0.31 nm).

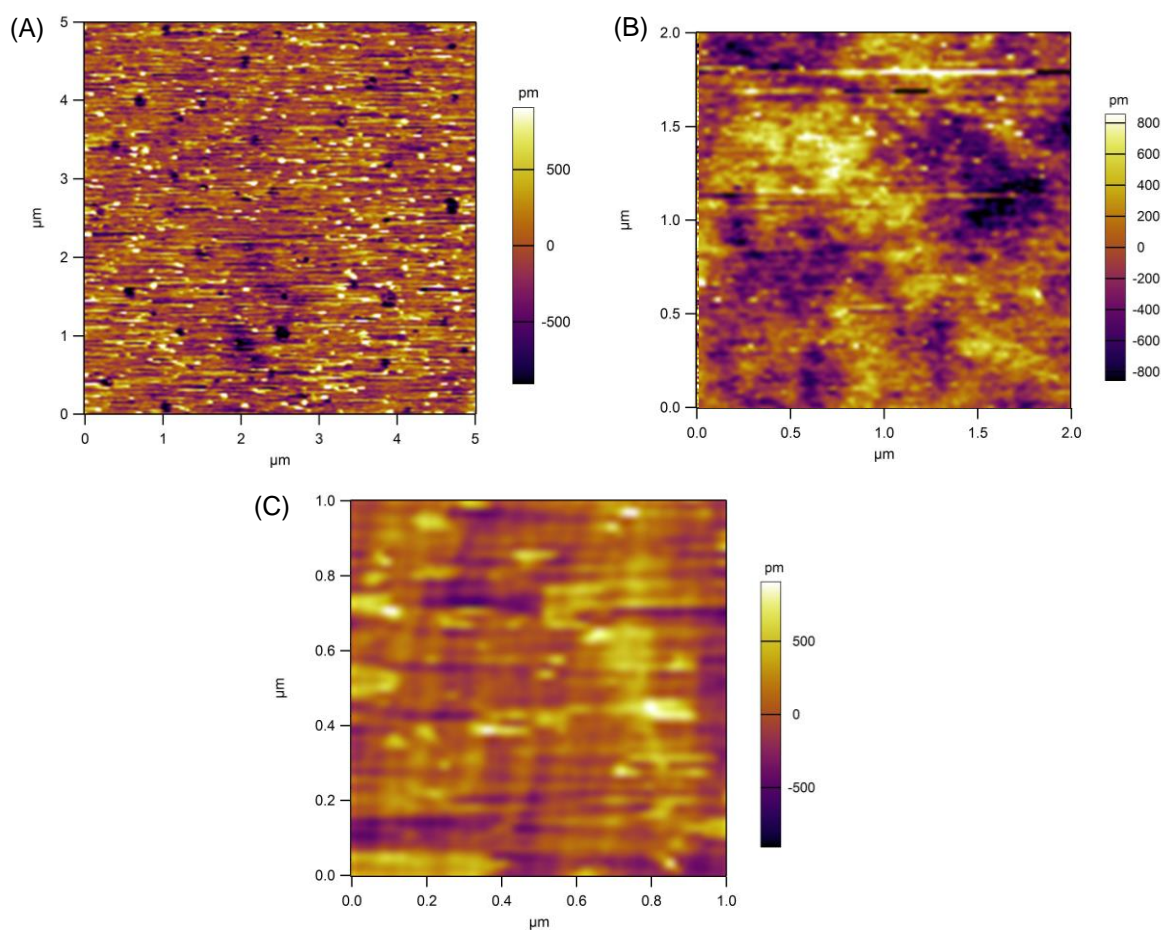


Figure S29. Tapping AFM images of A1-modified Si (111) over scan sizes of 5×5 μm (A, rms roughness 0.31 nm), 2×2 μm (B, rms roughness 0.32 nm) and 1×1 μm (C, rms roughness 0.28 nm).

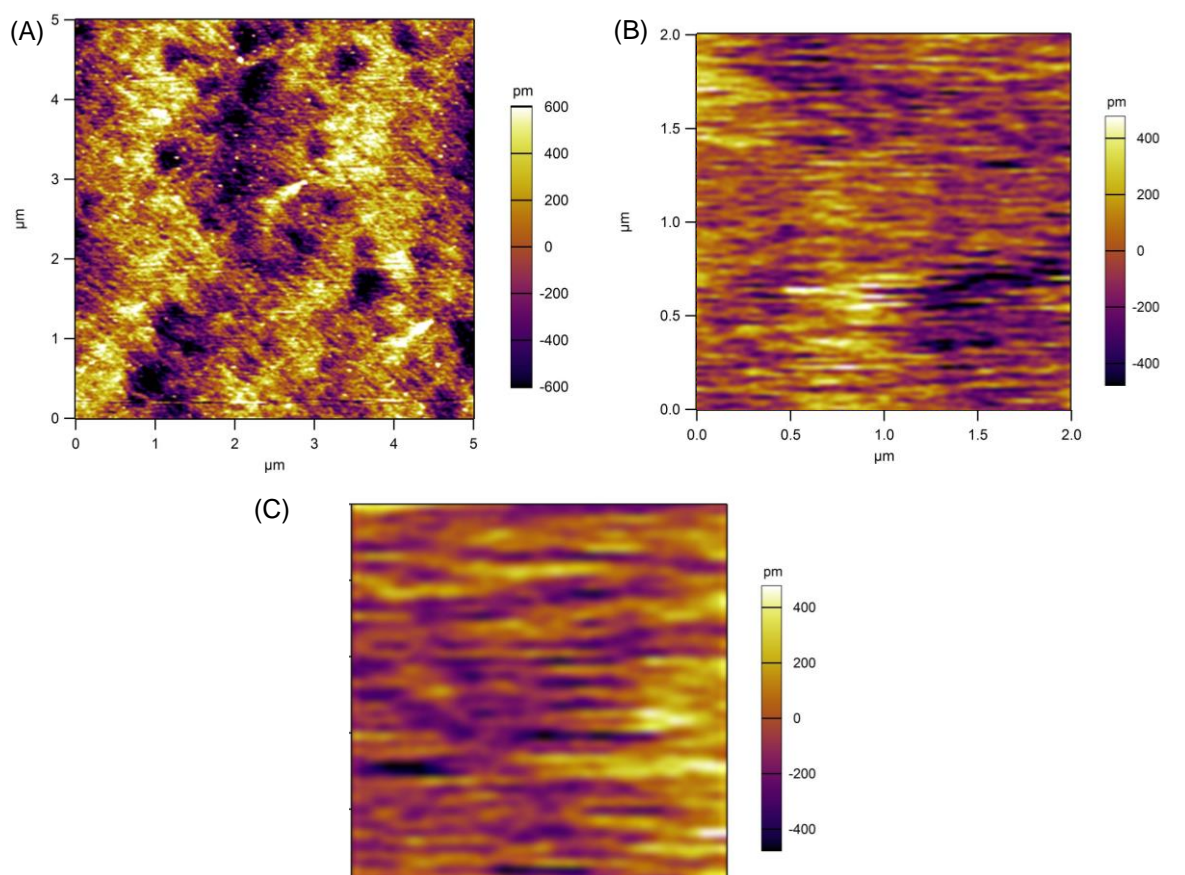


Figure S30. Tapping AFM images of **F1**-modified Si (111) over scan sizes of 5×5 μm (A, rms roughness 0.36 nm), 2×2 μm (B, rms roughness 0.31 nm) and 1×1 μm (C, rms roughness 0.31 nm).

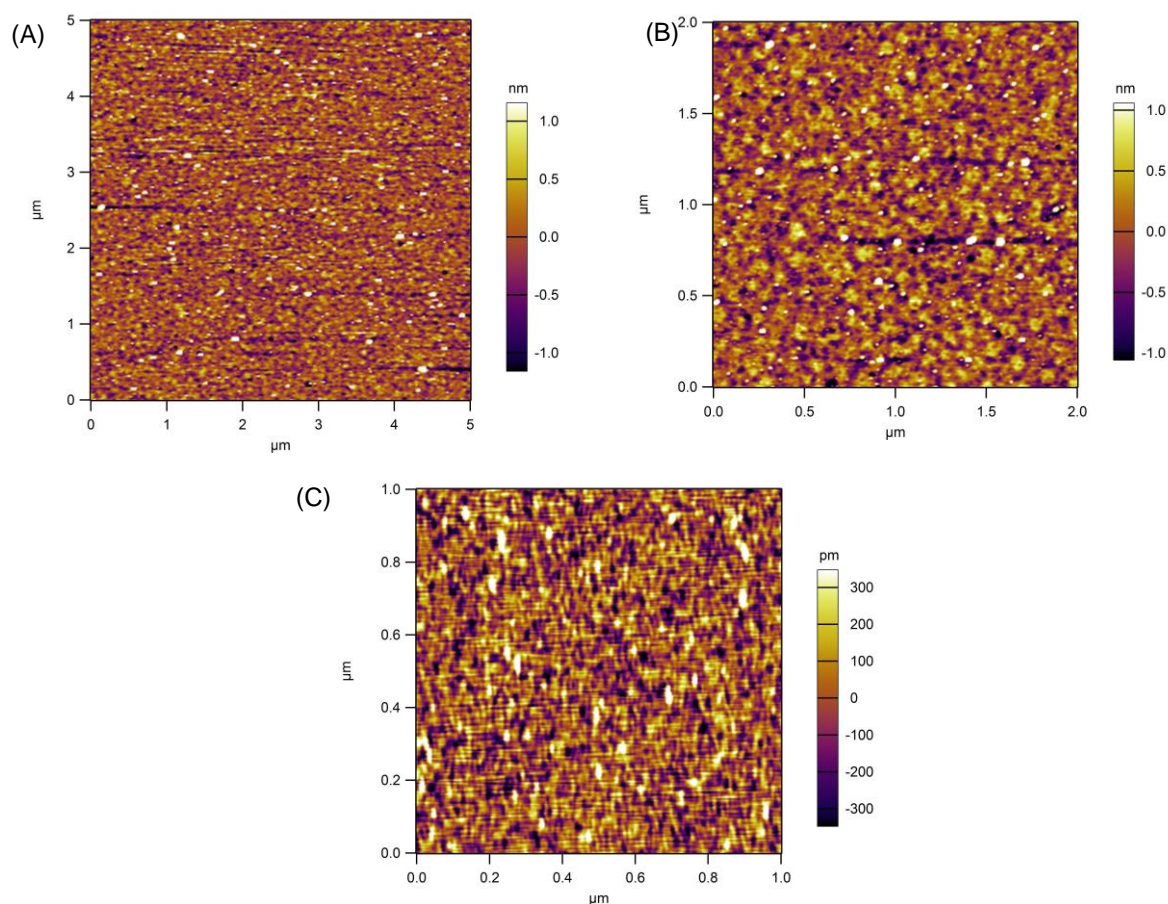


Figure S31. Tapping AFM images of **F2**-modified Si (111) over scan sizes of $5 \times 5 \mu\text{m}$ (A, rms roughness 0.33 nm), $2 \times 2 \mu\text{m}$ (B, rms roughness 0.27 nm) and $1 \times 1 \mu\text{m}$ (C, rms roughness 0.21 nm).

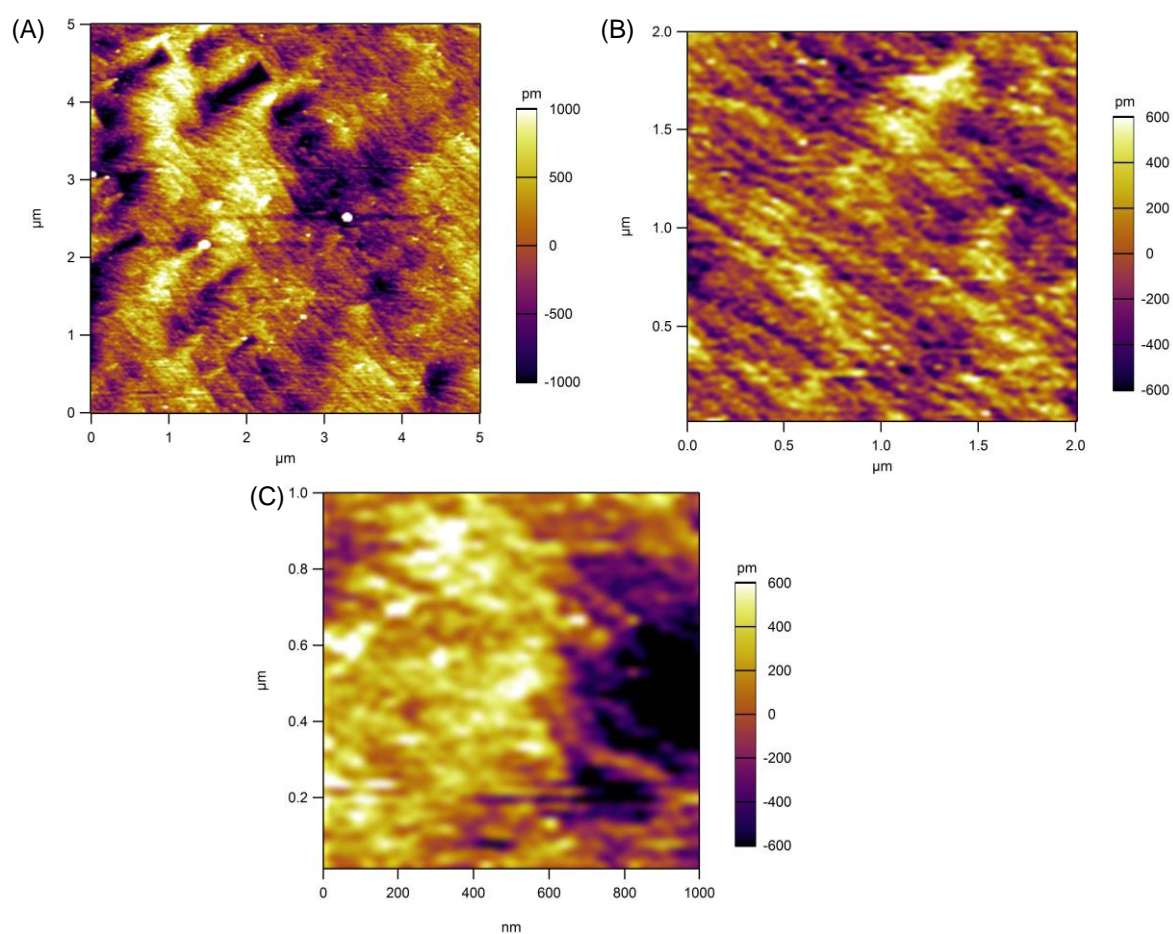


Figure S32. Tapping AFM images of **F3**-modified Si (111) over scan sizes of $5 \times 5 \mu\text{m}$ (A, rms roughness 0.31 nm), $2 \times 2 \mu\text{m}$ (B, rms roughness 0.31 nm) and $1 \times 1 \mu\text{m}$ (C, rms roughness 0.29 nm).

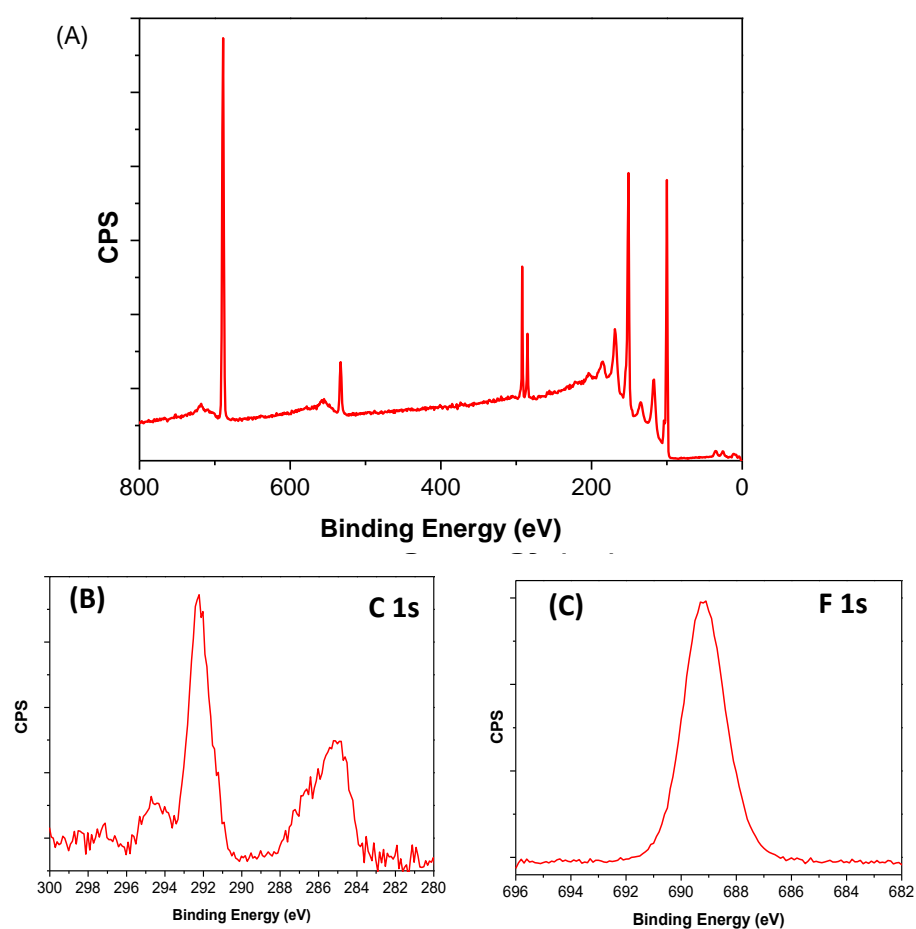


Figure S33. XPS spectra of silanol **F1**: (A) wide scan, (B) C 1s narrow scan and (C) F 1s narrow scan.

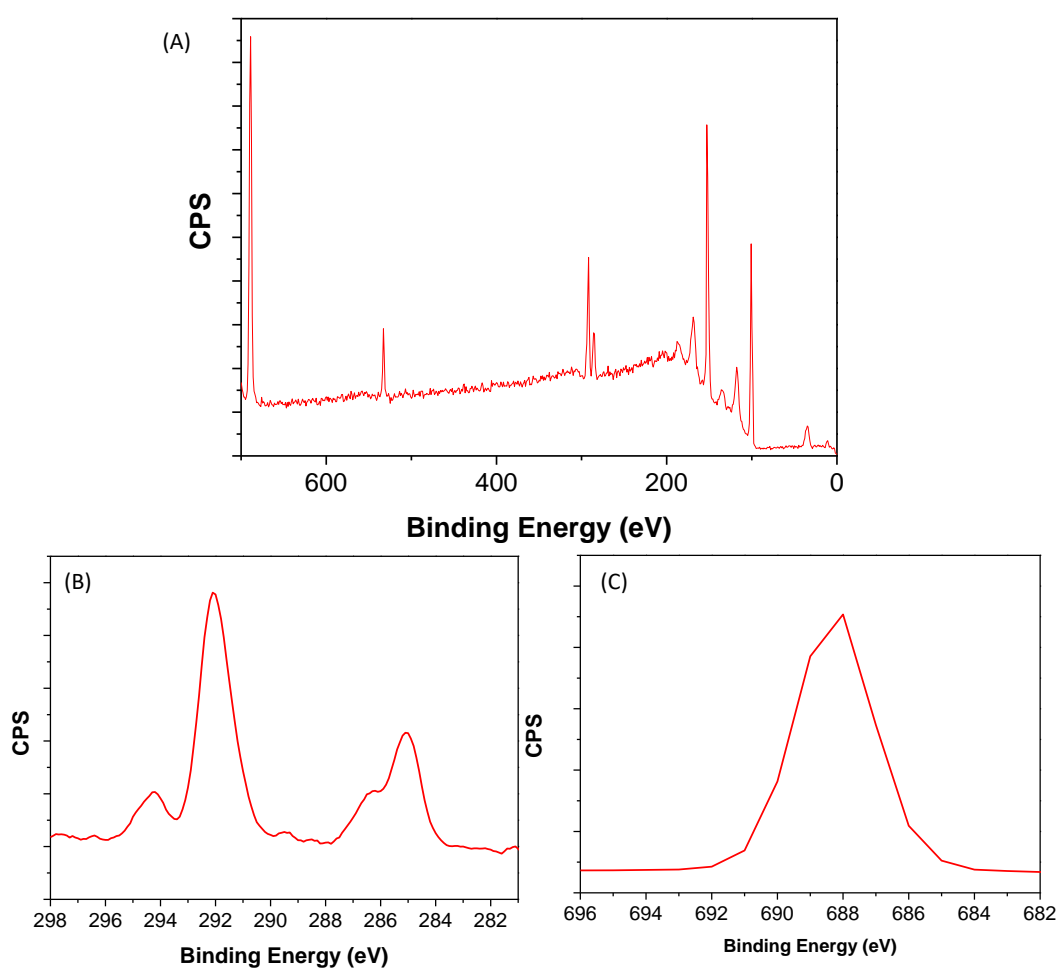


Figure S34. XPS spectra of silanol **F2**: (A) wide scan, (B) C 1s narrow scan and (C) F 1s narrow scan.

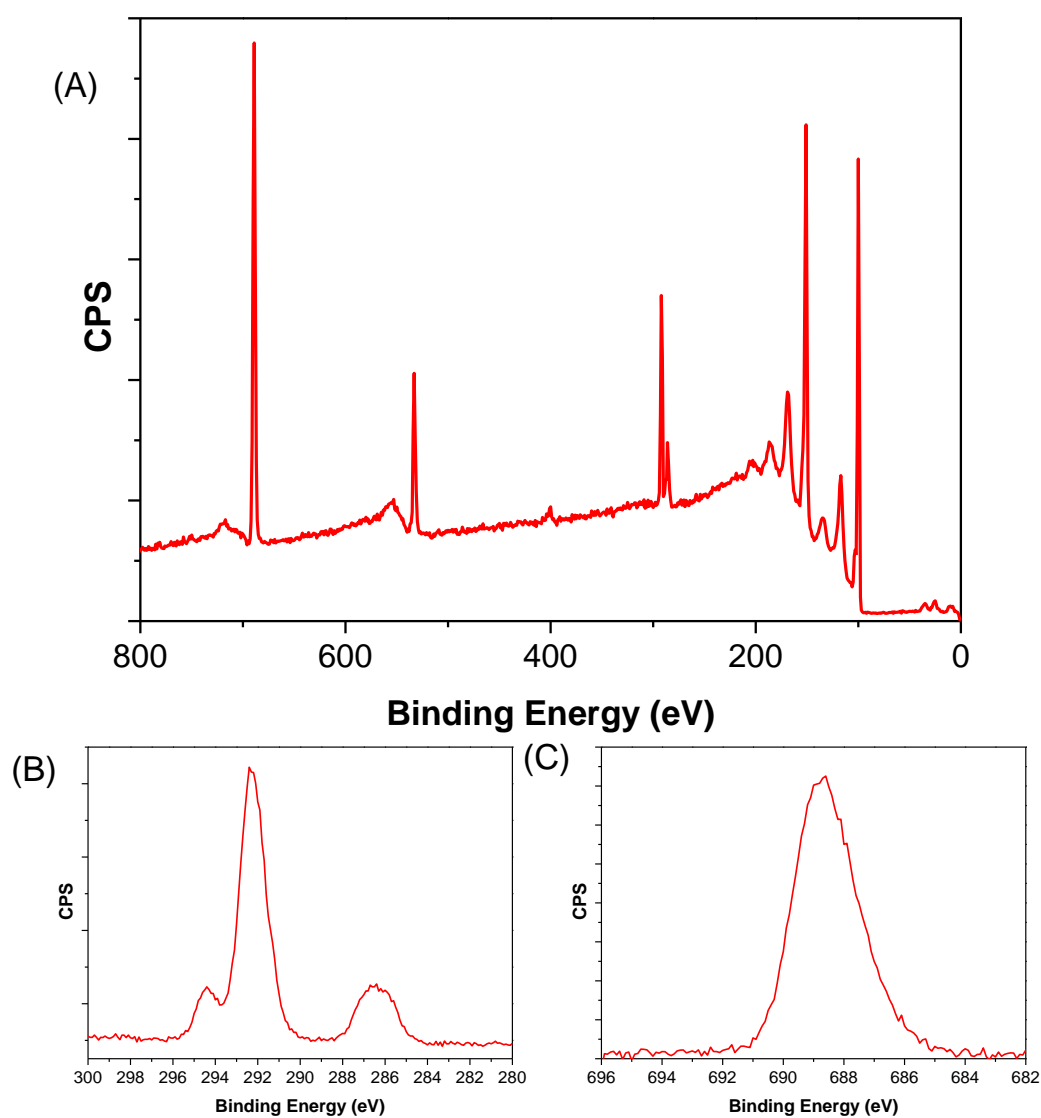


Figure S35. XPS spectra of silanetriol **F3**: (A) wide scan, (B) C 1s narrow scan and (C) F 1s narrow scan.

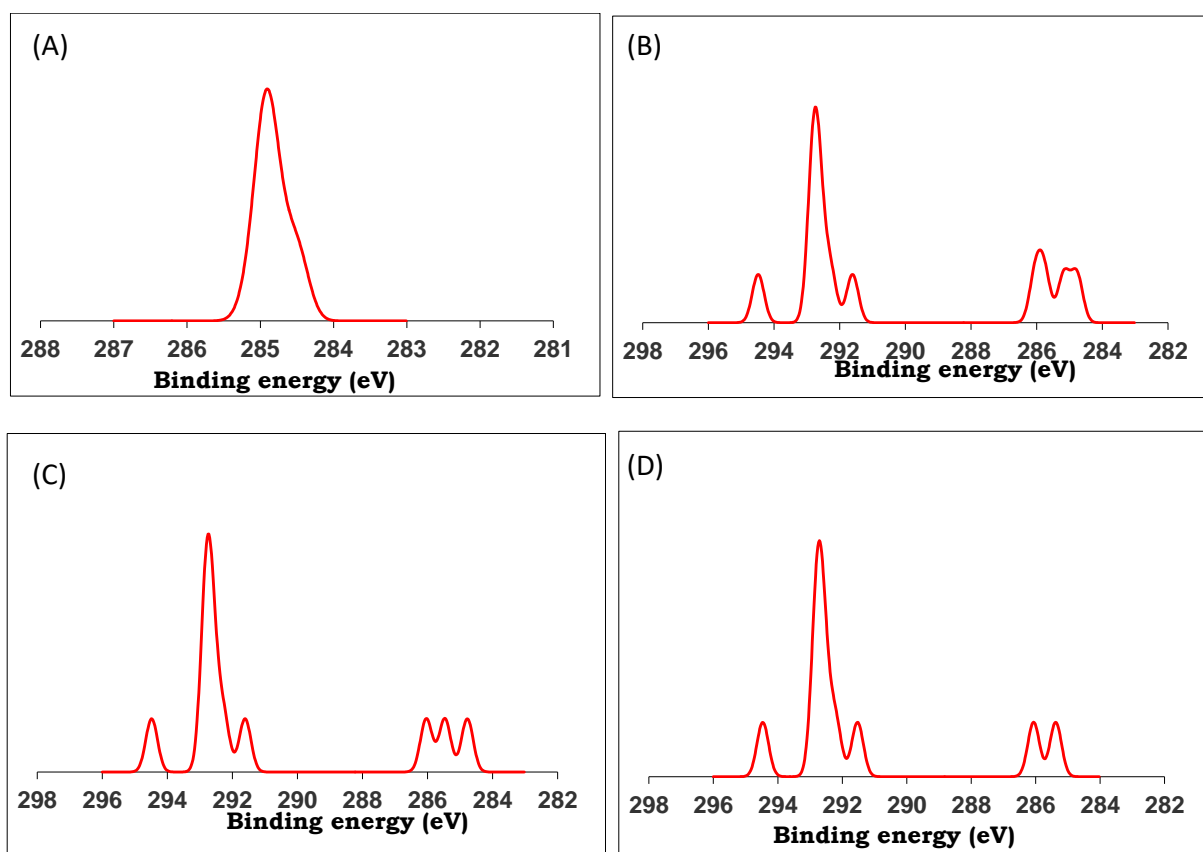


Figure S36. Simulated XPS spectra of silanol **A1** (A) and fluorinated compounds **F1** (B), **F2** (C) and **F3** (D) using the B3LYP/6-311G(d,p).

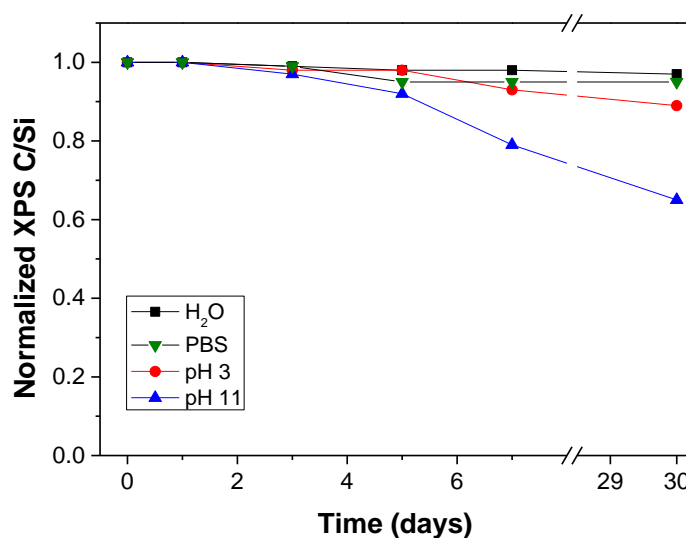


Figure S37. Hydrolytic stability of **A1**-modified surfaces as followed by normalized C/Si ratio from XPS. Measurements were performed on cleaned surfaces after taking them out from H_2O , PBS, pH 3, and pH 11 at the indicated time period (lines connecting data points are a mere guide to the eye).

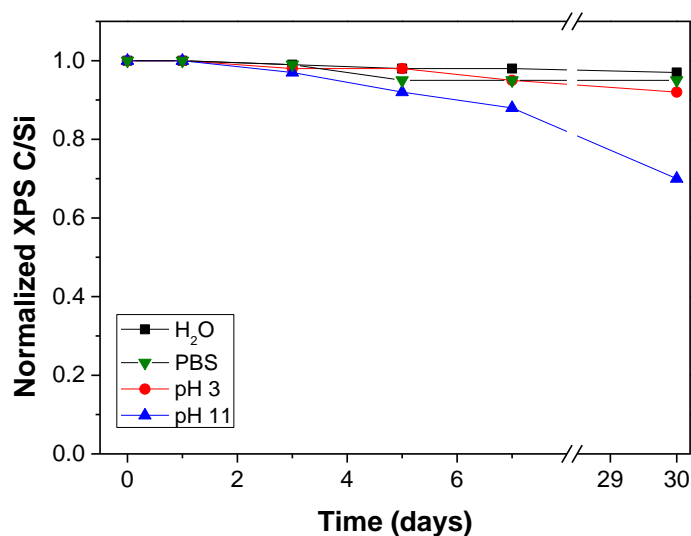


Figure S38. Hydrolytic stability of **F1**-modified surfaces as followed by normalized C/Si ratio from XPS. Measurements were performed on cleaned surfaces after taking them out from H₂O, PBS, pH 3, and pH 11 at the indicated time period (lines connecting data points are a mere guide to the eye).

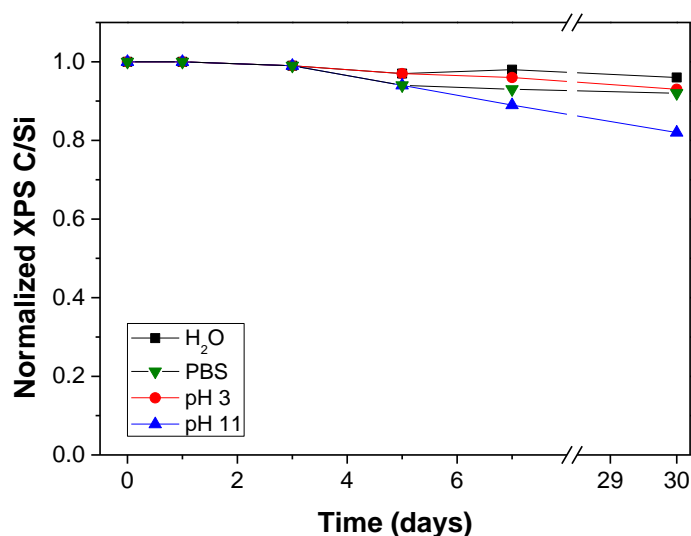


Figure S39. Hydrolytic stability of **F2**-modified surfaces as followed by normalized C/Si ratio from XPS. Measurements were performed on cleaned surfaces after taking them out from H₂O, PBS, pH 3, and pH 11 at the indicated time period (lines connecting data points are a mere guide to the eye).

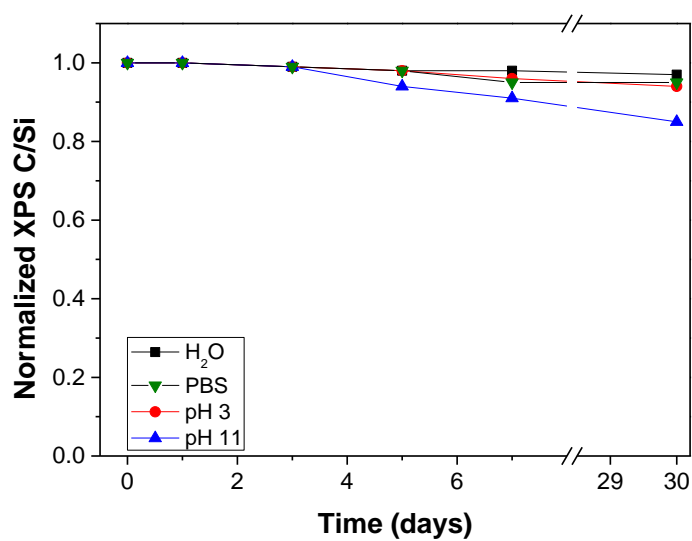


Figure S40. Hydrolytic stability of **F3**-modified surfaces as followed by normalized C/Si ratio from XPS. Measurements were performed on cleaned surfaces after taking them out from H₂O, PBS, pH 3, and pH 11 at the indicated time period (lines connecting data points are a mere guide to the eye).

3. SUPPORTING TABLES.

Table S1. Calculated binding energies (eV) for C atoms in compounds **F1**, **F2** and **F3** using the B3LYP/6-311G(d,p) as implemented in Gaussian 09.

Carbon	F1	F2	F3
Si-CH ₃	284.5	284.8	-----
-CH ₂ -Si	285.2	285.1	285.4
-CH ₂ -CH ₂ -Si	286.1	286.0	286.1
-CF ₂ -CH ₂	291.6	291.6	291.5
-CF ₂ -	292.3	292.3	292.2
-CF ₂ -	292.6	292.6	292.5
-CF ₂ -	292.67	292.7	292.7
-CF ₂ -	292.7	292.8	292.7
-CF ₂ -	292.7	292.8	292.8
-CF ₂ -	292.7	292.8	292.8
-CF ₃	294.6	294.5	294.4

Table S2. SCA variation of monolayers containing **A1** compound on Si (111) surfaces. Each SCA value point represents the average of five separately prepared monolayers.

Days	H ₂ O	PBS	pH 3	pH 11
0	105.4 ± 0.9	105.4 ± 0.9	105.4 ± 0.9	105.4 ± 0.9
1	105.2 ± 1.2	105.3 ± 0.9	106.2 ± 1.1	105.4 ± 0.8
3	105.4 ± 1.0	105.1 ± 1.2	105.3 ± 1.0	105.3 ± 1.2
5	104.9 ± 0.9	105.4 ± 1.2	102.8 ± 0.9	103.2 ± 1.0
7	105.5 ± 1.0	104.3 ± 1.0	103.7 ± 1.0	97.2 ± 1.0
30	104.3 ± 1.2	104.4 ± 1.0	103.2 ± 1.2	93.2 ± 1.0

Table S3. SCA variation of monolayers containing **F1** compound on Si (111) surfaces. Each SCA value point represents the average of five separately prepared monolayers.

Days	H ₂ O	PBS	pH 3	pH 11
0	109.6 ± 0.8	109.6 ± 0.8	109.6 ± 0.8	109.6 ± 0.8
1	109.2 ± 1.2	109.3 ± 0.8	109.2 ± 1.1	109.4 ± 0.8
3	109.4 ± 0.9	108.1 ± 1.1	108.4 ± 1.0	107.3 ± 1.2
5	108.7 ± 1.1	107.4 ± 1.3	107.8 ± 1.2	106.2 ± 1.0
7	108.3 ± 1.0	107.9 ± 0.9	106.3 ± 1.0	100.7 ± 1.0
30	108.1 ± 0.9	105.4 ± 1.0	103.2 ± 1.1	95.2 ± 1.1

Table S4. SCA variation of monolayers containing **F2** compound on Si (111) surfaces. Each SCA value point represents the average of five separately prepared monolayers.

Days	H ₂ O	PBS	pH 3	pH 11
0	112.5 ± 0.9	112.5 ± 0.9	112.5 ± 0.9	112.5 ± 0.9
1	112.4 ± 1.1	112.0 ± 1.0	111.7 ± 1.0	111.5 ± 1.1
3	112.3 ± 1.0	111.7 ± 0.9	109.3 ± 0.9	111.4 ± 0.9
5	112.1 ± 0.8	111.0 ± 1.0	107.2 ± 1.0	112.0 ± 1.0
7	112.4 ± 0.9	110.0 ± 1.1	105.6 ± 1.0	110.5 ± 0.8
30	111.9 ± 1.2	107.0 ± 0.9	102.1 ± 1.1	108.5 ± 1.0

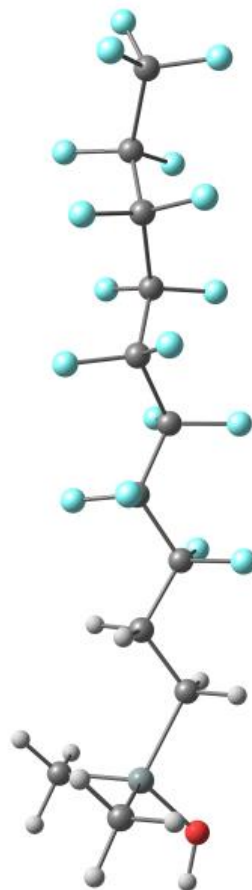
Table S5. SCA variation of monolayers containing **F3** compound on Si (111) surfaces. Each SCA value point represents the average of five separately prepared monolayers.

Days	H ₂ O	PBS	pH 3	pH 11
0	117.1 ± 1.0	117.1 ± 1.0	117.1 ± 1.0	117.1 ± 1.0
1	117.0 ± 1.1	116.0 ± 0.9	116.4 ± 0.9	116.2 ± 1.1
3	117.0 ± 0.8	116.2 ± 1.0	114.4 ± 0.9	116.3 ± 0.9
5	116.8 ± 1.0	115.7 ± 0.8	112.7 ± 1.1	115.5 ± 0.8
7	116.6 ± 1.2	115.4 ± 1.2	109.1 ± 1.0	114.7 ± 1.0
30	115.4 ± 1.3	111.2 ± 0.9	105.6 ± 0.8	111.3 ± 1.1

4. CARTESIAN COORDINATES FOR OPTIMIZED COMPOUNDS

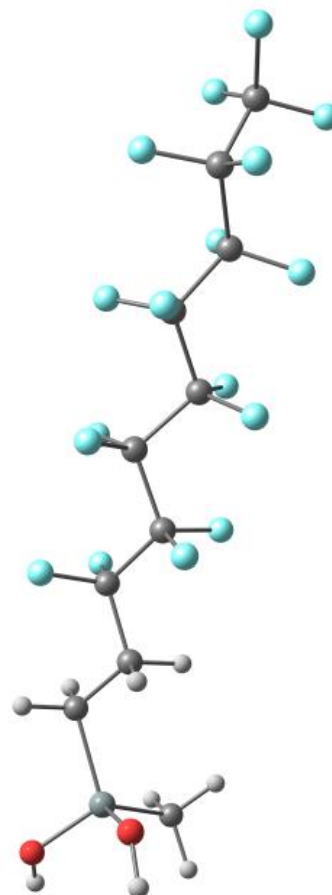
Silanol F1

Si	7.006456000000	0.231067000000	0.091770000000
C	5.400369000000	-0.573448000000	-0.447736000000
H	5.365908000000	-0.577727000000	-1.541042000000
H	5.412410000000	-1.619499000000	-0.127206000000
C	4.163708000000	0.130122000000	0.116435000000
H	4.126760000000	1.182378000000	-0.183378000000
H	4.150532000000	0.094843000000	1.208205000000
C	2.885675000000	-0.512634000000	-0.374516000000
C	1.615988000000	0.207722000000	0.134526000000
C	0.289261000000	-0.561739000000	-0.105420000000
C	-0.958673000000	0.358482000000	-0.007238000000
C	-2.272825000000	-0.444576000000	0.200679000000
C	-3.535457000000	0.386700000000	-0.157409000000
C	-4.827381000000	-0.204445000000	0.467861000000
C	-6.125798000000	0.288178000000	-0.218648000000
F	-4.886506000000	0.143174000000	1.757487000000
F	-4.795392000000	-1.541781000000	0.370998000000
F	-3.674759000000	0.417673000000	-1.489906000000
F	-3.376391000000	1.638495000000	0.295085000000
F	-2.358952000000	-0.816112000000	1.485374000000
F	-2.244397000000	-1.535556000000	-0.575913000000
F	-0.803608000000	1.197451000000	1.026510000000
F	-1.068629000000	1.067303000000	-1.140145000000
F	1.740477000000	0.414521000000	1.458836000000
F	1.536259000000	1.407141000000	-0.475013000000
F	2.802435000000	-1.805355000000	0.030615000000
F	2.841631000000	-0.510632000000	-1.727329000000
F	0.307009000000	-1.122384000000	-1.320374000000
F	0.175250000000	-1.525423000000	0.822062000000
F	-6.108844000000	1.611648000000	-0.329977000000
F	-6.254936000000	-0.250398000000	-1.421567000000
F	-7.165380000000	-0.069464000000	0.523391000000
C	7.112452000000	0.296769000000	1.960051000000
H	6.348016000000	0.957667000000	2.378700000000
H	6.979128000000	-0.696378000000	2.396272000000
H	8.082884000000	0.678556000000	2.288947000000
C	7.148244000000	1.959565000000	-0.614161000000
H	7.061151000000	1.945173000000	-1.703261000000
H	6.367649000000	2.616422000000	-0.220262000000
H	8.109497000000	2.414864000000	-0.360228000000
O	8.179758000000	-0.768231000000	-0.540160000000
H	9.106818000000	-0.552265000000	-0.438000000000



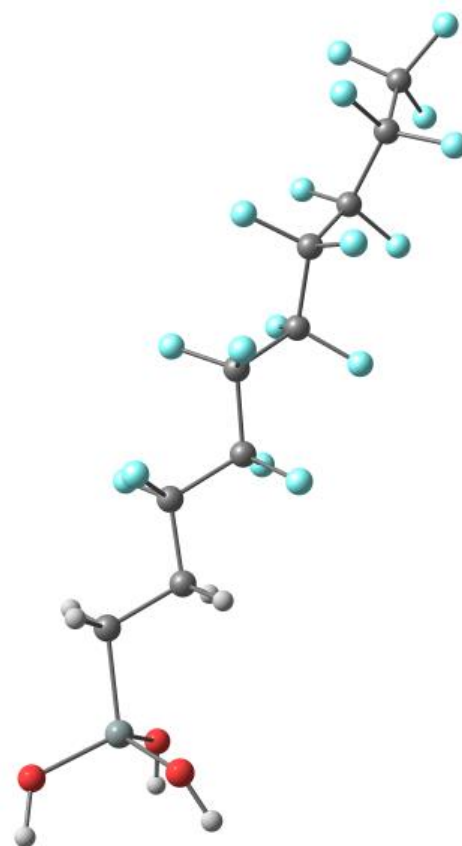
Silanol F2

Si	6.987823000000	0.199961000000	0.161964000000
C	5.401042000000	-0.553205000000	-0.461488000000
H	5.388516000000	-0.521610000000	-1.554960000000
H	5.393557000000	-1.608151000000	-0.172503000000
C	4.166109000000	0.148061000000	0.111530000000
H	4.139510000000	1.208708000000	-0.157755000000
H	4.161398000000	0.084467000000	1.200983000000
C	2.890159000000	-0.469379000000	-0.411278000000
C	1.618162000000	0.223348000000	0.129869000000
C	0.294736000000	-0.539550000000	-0.146647000000
C	-0.957936000000	0.368611000000	-0.001790000000
C	-2.266762000000	-0.450936000000	0.172627000000
C	-3.535456000000	0.388290000000	-0.143637000000
C	-4.821337000000	-0.236744000000	0.460195000000
C	-6.127212000000	0.286014000000	-0.188181000000
F	-4.871142000000	0.045489000000	1.766229000000
F	-4.787177000000	-1.567450000000	0.295463000000
F	-3.680769000000	0.478606000000	-1.472468000000
F	-3.381331000000	1.619617000000	0.364231000000
F	-2.346997000000	-0.881450000000	1.439020000000
F	-2.234588000000	-1.504698000000	-0.653955000000
F	-0.804694000000	1.159896000000	1.068804000000
F	-1.076796000000	1.128724000000	-1.100011000000
F	1.739385000000	0.370137000000	1.461164000000
F	1.533668000000	1.448626000000	-0.426009000000
F	2.805725000000	-1.781178000000	-0.073829000000
F	2.848330000000	-0.400557000000	-1.764435000000
F	0.312813000000	-1.040780000000	-1.387450000000
F	0.185742000000	-1.548374000000	0.732706000000
F	-6.116601000000	1.613523000000	-0.229661000000
F	-6.267158000000	-0.188163000000	-1.417024000000
F	-7.158273000000	-0.115182000000	0.543507000000
C	7.409367000000	1.814274000000	-0.672417000000
H	7.597168000000	1.660751000000	-1.738624000000
H	6.594854000000	2.536016000000	-0.577687000000
H	8.301345000000	2.272501000000	-0.236496000000
O	8.220786000000	-0.881277000000	-0.074413000000
H	9.042331000000	-0.617282000000	-0.487159000000
O	6.705312000000	0.405080000000	1.781067000000
H	7.416531000000	0.590950000000	2.394239000000



Silanol F3

Si	6.977695000000	0.237803000000	0.114631000000
C	5.397428000000	-0.618990000000	-0.309753000000
H	5.403748000000	-0.812637000000	-1.386825000000
H	5.403550000000	-1.592032000000	0.190898000000
C	4.163868000000	0.184587000000	0.091978000000
H	4.151534000000	1.163092000000	-0.397417000000
H	4.142360000000	0.342876000000	1.171185000000
C	2.895466000000	-0.530895000000	-0.315704000000
C	1.616257000000	0.255295000000	0.056900000000
C	0.298557000000	-0.558100000000	-0.048176000000
C	-0.957799000000	0.350569000000	-0.147834000000
C	-2.261162000000	-0.395872000000	0.252026000000
C	-3.538941000000	0.344396000000	-0.235607000000
C	-4.804526000000	-0.096040000000	0.544119000000
C	-6.127973000000	0.204723000000	-0.204301000000
F	-4.838622000000	0.549163000000	1.715231000000
F	-4.749257000000	-1.419079000000	0.764614000000
F	-3.725339000000	0.089062000000	-1.537824000000
F	-3.374473000000	1.663750000000	-0.062881000000
F	-2.309429000000	-0.498928000000	1.586696000000
F	-2.245315000000	-1.622816000000	-0.285881000000
F	-0.804082000000	1.401520000000	0.669223000000
F	-1.085704000000	0.785055000000	-1.410104000000
F	1.731655000000	0.693483000000	1.324050000000
F	1.525767000000	1.325232000000	-0.756513000000
F	2.807530000000	-1.749140000000	0.271950000000
F	2.877249000000	-0.728666000000	-1.654867000000
F	0.339658000000	-1.343427000000	-1.131040000000
F	0.175673000000	-1.323935000000	1.048130000000
F	-6.120574000000	1.448049000000	-0.672139000000
F	-6.303196000000	-0.637281000000	-1.210900000000
F	-7.139352000000	0.067644000000	0.644853000000
O	8.219706000000	-0.756540000000	-0.310643000000
H	9.113493000000	-0.577551000000	-0.016680000000
O	6.990019000000	0.537361000000	1.740075000000
H	7.500333000000	1.251122000000	2.119706000000
O	7.019580000000	1.667684000000	-0.709942000000
H	7.816064000000	2.172619000000	-0.866900000000



Immobilized Silanol F1

C	3.429383000000	-0.155328000000	0.041550000000
H	3.485168000000	0.340829000000	1.015628000000
H	3.488217000000	0.637373000000	-0.711640000000
C	2.083888000000	-0.884996000000	-0.089509000000
H	1.994515000000	-1.384171000000	-1.056582000000
H	1.968124000000	-1.648507000000	0.684827000000
C	0.903364000000	0.064454000000	0.036331000000
C	-0.474007000000	-0.660082000000	-0.019983000000
C	-1.722304000000	0.270640000000	-0.178159000000
C	-3.071747000000	-0.425135000000	0.208389000000
C	-4.335813000000	0.303365000000	-0.352601000000
C	-5.671175000000	-0.105287000000	0.341642000000
F	-5.756354000000	-1.451489000000	0.396262000000
F	-5.699965000000	0.398607000000	1.593745000000
F	-4.452228000000	0.018441000000	-1.665615000000
F	-4.193490000000	1.638702000000	-0.202254000000
F	-3.158211000000	-0.466617000000	1.556862000000
F	-3.076407000000	-1.689965000000	-0.266990000000
F	-1.577558000000	1.359286000000	0.604784000000
F	-1.794212000000	0.665831000000	-1.468895000000
F	-0.466135000000	-1.518055000000	-1.071884000000
F	-0.606202000000	-1.388767000000	1.118185000000
F	0.924964000000	0.994035000000	-0.967214000000
F	0.961015000000	0.743234000000	1.218689000000
Si	4.960609000000	-1.252522000000	-0.148898000000
O	6.272316000000	-0.248798000000	-0.023270000000
Si	7.700790000000	0.586627000000	0.081789000000
Si	7.232533000000	2.905663000000	0.143275000000
H	6.398291000000	3.247681000000	1.326699000000
H	8.506889000000	3.670244000000	0.226270000000
H	6.505855000000	3.330535000000	-1.083652000000
Si	8.854114000000	-0.040672000000	2.053228000000
H	8.027865000000	0.227764000000	3.261379000000
H	9.196635000000	-1.489034000000	2.034295000000
H	10.116818000000	0.739640000000	2.161896000000
Si	9.054437000000	0.098483000000	-1.799377000000
H	9.346727000000	-1.359069000000	-1.877063000000
H	8.385408000000	0.508060000000	-3.063966000000
H	10.345231000000	0.831431000000	-1.690173000000
C	-6.859797000000	0.452038000000	-0.463446000000
C	-8.168249000000	0.190645000000	0.305467000000
C	5.004416000000	-2.585236000000	1.260199000000
H	4.843734000000	-2.110281000000	2.205450000000
H	4.235720000000	-3.309798000000	1.089858000000
H	5.957955000000	-3.070681000000	1.262471000000
C	4.948067000000	-2.117917000000	-1.885140000000
H	4.165530000000	-2.847074000000	-1.914576000000
H	4.782103000000	-1.385637000000	-2.647454000000
H	5.889649000000	-2.598344000000	-2.051006000000
F	-8.245832000000	-1.117462000000	0.630025000000
F	-9.220886000000	0.524859000000	-0.470907000000
F	-8.185049000000	0.935394000000	1.431329000000
F	-6.699762000000	1.780749000000	-0.640691000000
F	-6.914786000000	-0.158966000000	-1.666006000000

Immobilized Silanol F2

C	3.484732000000	-0.282114000000	-0.431724000000
H	3.587032000000	0.697208000000	0.045946000000
H	3.490090000000	-0.103701000000	-1.511803000000
C	2.151663000000	-0.920715000000	-0.012243000000
H	2.004769000000	-1.889034000000	-0.495172000000
H	2.126622000000	-1.084348000000	1.067587000000
C	0.962679000000	-0.048858000000	-0.376962000000
C	-0.399901000000	-0.649659000000	0.078542000000
C	-1.675230000000	0.057102000000	-0.490827000000
C	-2.984186000000	-0.281155000000	0.303738000000
C	-4.295678000000	0.045002000000	-0.491683000000
C	-5.564567000000	0.145174000000	0.422472000000
F	-5.527947000000	-0.839622000000	1.346031000000
F	-5.540385000000	1.338504000000	1.055162000000
F	-4.493124000000	-0.929872000000	-1.405003000000
F	-4.146494000000	1.224028000000	-1.131213000000
F	-2.982453000000	0.432363000000	1.450648000000
F	-2.995248000000	-1.597382000000	0.604719000000
F	-1.503957000000	1.394312000000	-0.457541000000
F	-1.837256000000	-0.332651000000	-1.775366000000
F	-0.444830000000	-1.950452000000	-0.307751000000
F	-0.441261000000	-0.608576000000	1.434454000000
F	0.898761000000	0.139058000000	-1.731689000000
F	1.081770000000	1.183713000000	0.196043000000
Si	4.996024000000	-1.297941000000	0.020562000000
O	6.354574000000	-0.423650000000	-0.319211000000
Si	7.600448000000	0.628822000000	0.036424000000
Si	7.042114000000	2.800284000000	-0.720097000000
H	5.791634000000	3.274403000000	-0.068532000000
H	8.142741000000	3.741546000000	-0.377365000000
H	6.844476000000	2.818240000000	-2.194247000000
Si	7.985349000000	0.667321000000	2.374604000000
H	6.865586000000	1.310963000000	3.110045000000
H	8.150089000000	-0.720925000000	2.889455000000
H	9.237375000000	1.419388000000	2.660897000000
Si	9.538263000000	-0.150611000000	-1.071871000000
H	9.921069000000	-1.500835000000	-0.576157000000
H	9.310755000000	-0.235653000000	-2.539356000000
H	10.670185000000	0.782110000000	-0.820370000000
C	-6.909833000000	0.019960000000	-0.363904000000
C	-8.161296000000	0.516283000000	0.423015000000
C	5.128819000000	-2.917945000000	-0.903081000000
H	4.256728000000	-3.556149000000	-0.735834000000
H	5.217986000000	-2.742342000000	-1.978769000000
H	6.016678000000	-3.475548000000	-0.590128000000
F	-8.197135000000	-0.031171000000	1.642730000000
F	-9.260342000000	0.151972000000	-0.243819000000
F	-8.154444000000	1.845158000000	0.539857000000
F	-6.834430000000	0.740481000000	-1.504799000000
F	-7.109053000000	-1.276868000000	-0.674290000000
O	4.848799000000	-1.538602000000	1.664321000000
H	5.435672000000	-2.152970000000	2.110599000000

Immobilized Silanol F3

C	3.453660000000	-0.036459000000	-0.304673000000
H	3.536848000000	0.745945000000	0.455775000000
H	3.474894000000	0.468926000000	-1.275222000000
C	2.125934000000	-0.790645000000	-0.133694000000
H	2.016476000000	-1.565458000000	-0.894489000000
H	2.081887000000	-1.278968000000	0.842590000000
C	0.929669000000	0.138213000000	-0.238347000000
C	-0.430580000000	-0.590592000000	-0.030242000000
C	-1.707601000000	0.246949000000	-0.373077000000
C	-3.026010000000	-0.347326000000	0.233938000000
C	-4.325744000000	0.199784000000	-0.451813000000
C	-5.618122000000	-0.018779000000	0.406807000000
F	-5.583710000000	-1.250642000000	0.959326000000
F	-5.633716000000	0.902738000000	1.394623000000
F	-4.479277000000	-0.429641000000	-1.636566000000
F	-4.188264000000	1.524427000000	-0.671104000000
F	-3.065588000000	-0.040208000000	1.548750000000
F	-3.015071000000	-1.690369000000	0.096507000000
F	-1.564715000000	1.503232000000	0.096027000000
F	-1.834722000000	0.293193000000	-1.718464000000
F	-0.445731000000	-1.699251000000	-0.812361000000
F	-0.497649000000	-0.984412000000	1.267090000000
F	0.891606000000	0.742617000000	-1.466160000000
F	1.014555000000	1.130018000000	0.695864000000
Si	4.953340000000	-1.136351000000	-0.179679000000
O	6.306440000000	-0.240129000000	-0.432308000000
Si	7.708834000000	0.514928000000	0.087376000000
Si	7.382805000000	2.856509000000	0.017822000000
H	6.249236000000	3.253714000000	0.895080000000
H	8.616056000000	3.539782000000	0.493290000000
H	7.092259000000	3.309814000000	-1.368609000000
Si	8.248392000000	-0.168853000000	2.290642000000
H	7.236707000000	0.297162000000	3.273890000000
H	8.344600000000	-1.651906000000	2.368159000000
H	9.571324000000	0.405827000000	2.657748000000
Si	9.443242000000	-0.113424000000	-1.391740000000
H	9.669490000000	-1.583645000000	-1.342146000000
H	9.099068000000	0.259259000000	-2.790549000000
H	10.706990000000	0.574452000000	-1.013941000000
O	4.924167000000	-1.818983000000	1.323695000000
H	5.344010000000	-2.674394000000	1.442256000000
O	4.938490000000	-2.376192000000	-1.278176000000
H	5.433235000000	-2.258558000000	-2.092015000000
C	-6.941320000000	0.104601000000	-0.416878000000
C	-8.220374000000	0.307486000000	0.451766000000
F	-9.296526000000	0.168862000000	-0.328103000000
F	-8.240167000000	1.526880000000	0.992399000000
F	-8.275559000000	-0.605827000000	1.427190000000
F	-6.851687000000	1.156571000000	-1.260574000000
F	-7.108835000000	-1.023549000000	-1.135789000000

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