Mechanistic Studies of Photochemical Grafting on H-terminated Silicon Surfaces

Q.C.W. van Dierendonck, BSc

890928182040

Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB,

Wageningen, The Netherlands

2014-06-13

Mechanistic Studies of Photochemical Grafting on H-terminated Silicon Surfaces

Quirijn C.W. van Dierendonck, Sidharam P. Pujari, and Han Zuilhof

Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB,
Wageningen, The Netherlands

Abstract

To study the mechanistic properties of photochemical grafting silicon surfaces, trifluoro-acetic acid-protected 10-aminodec-1-ene (TFAAD) was synthesized and UV-grafted to H-terminated Si(111). The prepared monolayers were analyzed by X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), ellipsometry and static water contact angle measurements. Experimental data indicates that UV-grafting of TFAAD to H-terminated Si(111) is prone to multilayer formation and Si-F bond formation, both of which are probably caused by the photodegradation of the TFA group.

Introduction

Technological advancements have driven the downscaling of micro-devices to the nanoscale.[1] However, surface properties gain more and more importance on this scale. The attachment of molecular layers to these surfaces becomes more than just a coating. Self-assembled monolayers (SAMs) can give very defined functionalities or properties to a bulk inorganic material, like silicon.[2,3] As the single material on which the entire computer industry worldwide has grown, this element has the ideal band gap, oxide surface chemistry and etching properties to enable the manufacture of incredibly powerful integrated circuitry. Combined with extra functionalities and properties provided by SAMs, the applications of silicon are even further increased and new technologies are rapidly developed.

Previous studies report that *ω*-functionalized 1-alkenes can be thermally grafted as well-ordered monolayers to hydrogen-terminated silicon.[4] These 1-alkenes are therefore widely used to add functionality to silicon surfaces and can also be grafted using UV or visible light.[5] However, the exact mechanism by which the Si-C bond is formed in the photochemical functionalization has been debated extensively.[6, 7]

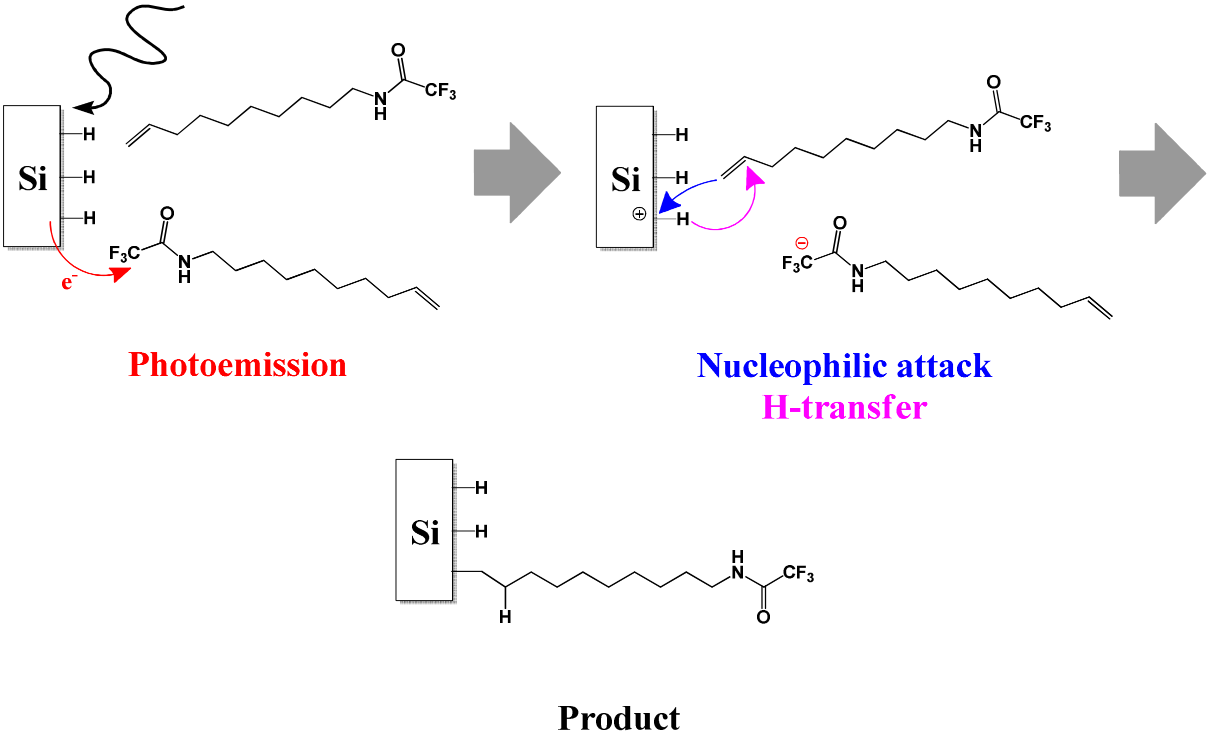


Figure 1. TFAAD UV-grafting mechanism proposed by Hamers et al. [8]

A recent study by Hamers et al. [8] proposed a new mechanism by which functionalized 1-alkenes are photochemically grafted to hydrogen-terminated silicon. Hamers et al. propose an exciton mechanism, where the functionalized headgroup of the 1-alkene, a trifluoroacetic acid group, facilitates the formation of an electron-hole pair, which is followed by a nucleophilic attack of the alkene. This mechanism (depicted in *Figure 1*), however, fails to explain what happens with the trifluoroacetic acid group that facilitated the formation of the electron-hole pair. Furthermore, precise characterisation of the resulting monolayers is not reported.

In this study, we attempted to replicate the trifluoroacetic acid-protected 10-aminodec-1-ene (TFAAD) monolayers on hydrogen-terminated Si(111) prepared by Hamers et al. to perform a mechanistic characterisation. To facilitate this, trifluoroacetic acid-protected 10-aminodec-1-ene (TFAAD) was synthesized and monolayers were grafted to Si(111) using thermal and photochemical methods. The resulting monolayers were characterized by X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), ellipsometry and static water contact angle measurements.

Experimental section

Materials

The synthesis procedure of the used trifluoroacetic acid-protected 10-aminodec-1-ene (TFAAD) and its NMR and IR spectra can be found in the Supplementary information. *Figure 2* shows the structure of the synthesized N-(dec-9-enyl)-trifluoroacetamide. All chemicals were used as received. Sulfuric acid (Sigma Aldrich, 95-97%), hydrogen peroxide (Acros Organics, 35%), ammonium fluoride (Riedel-de Haën, 40%, semiconductor grade VLSI PURANAL Honeywell 17600), deionized water (resistivity 18.3 MΩ cm). Hydrogen-terminated silicon wafers were (111)-orientated, n-type, phosphorus-doped with a resistance of 1-10 Ω cm and had a miscut angle of 0.2°. The wafers were bought from Siltronix (France).

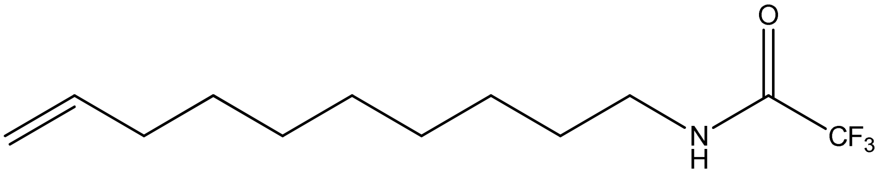


Figure 2. N-(dec-9-enyl)-trifluoroacetamide (TFAAD)

Monolayer formation

Thermal method

During the preparation of the Si(111) surfaces, the TFAAD was saturated with argon. The TFAAD was transferred to a 3-necked round bottom flask, a hollow glass tube was placed in the TFAAD and argon was bubbled through for a minimum of 60 minutes under vacuum. During the saturation, the TFAAD was heated to 80 °C, after which the vacuum was closed. Si(111) wafers were cut in pieces of 1 cm^2. The surfaces were sonicated for 10 minutes in semiconductor-grade acetone. After sonication, the surfaces were wiped with dust-free paper and dried with argon. The surfaces were transferred to freshly prepared Piranha solution (H_2SO_4/H_2O_2 3:1) to remove all organic contamination. After 20 minutes, the surfaces were thoroughly rinsed with argon-saturated deionised water and etched in an argon-saturated 40% aqueous ammonium fluoride solution for 15 minutes. After etching, the surfaces were rinsed with argon-saturated deionised water, dried with argon and, as quickly as possible, transferred to the argon-filled round bottom flask containing the argon-saturated TFAAD. After the surfaces were transferred to the round bottom flask, the set-up was closed. The vacuum was reengaged and the surfaces were left under constant heating, continuous argon flow and vacuum for a given time. After the heating was ended, the surfaces were rinsed with dichloromethane and acetone and dried under argon. The surfaces were directly used for surface characterization or stored in a glove box (MBRAUN MB 200B).

UV method

During the preparation of the Si(111) surfaces, the TFAAD was degassed using 3 freeze-pump-thaw cycles. The TFAAD was transferred to a quartz UV reaction chamber, filled with argon and frozen using liquid nitrogen. After the TFAAD was completely frozen, the argon flow was stopped and the chamber was put under vacuum until the TFAAD was liquid again. This cycle was then repeated 2 times. Si(111) wafers were cut in pieces of 1 cm^2. The surfaces were sonicated for 10 minutes in semiconductor-grade acetone. After sonication, the surfaces were wiped with dust-free paper and dried with argon. The surfaces were then cleaned using air plasma (Harrick Scientific Products, Inc. Pleasantville, NY) for 10 minutes and subsequently transferred to freshly prepared Piranha solution (H_2SO_4/H_2O_2 3:1) to remove all organic contamination. After 20 minutes, the surfaces were thoroughly rinsed with argon-saturated deionised water and etched in an argon-saturated 40% aqueous ammonium fluoride solution for 15 minutes. After etching, the surfaces were rinsed with argon-saturated deionised water, dried with argon and, as quickly as possible, transferred to the argon-filled quartz UV reaction chamber containing the degassed TFAAD. After the surfaces were transferred to the UV reaction chamber, the argon flow was stopped. The surfaces were then illuminated with a UV pen lamp (254 nm, low pressure mercury vapour, double bore lamp from Jelight Cie, California) with the output intensity of 9 mW cm^{-2}, which was placed approximately 4 mm above the surface and the sample was irradiated for a given time. After irradiation, the surfaces were rinsed with dichloromethane and acetone and dried under argon. The surfaces were directly used for surface characterization or stored in a glove box (MBRAUN MB 200B).

Monolayer characterization

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a JPS-9200 photoelectron spectrometer (JEOL, Japan). The analysis was performed under ultra-high vacuum conditions using a monochromatic Al Kα source at 12 kV and 20 mA and an analyzer pass energy of 10 eV. A takeoff angle ϕ (angle between the sample and the detector) of 80° was used, with a precision of ± 1°. All XPS spectra were evaluated with Casa XPS software (version 2.3.15). The binding energies were calibrated on the hydrocarbon (CH_2) peak with a binding energy of 285.0 eV.

Static water contact angle measurements were measured with an automated Krüss DSA 100 goniometer, at least 3 small droplets (3.0 μL of deionised water) were dispensed and the contact angles were determined by a Tangent 2 fitting model. The error in the determined contact angles is approximately 1°.

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 hydrogen terminated Si(111) surface were measured as $n = 3.750$ and $k = 0.073$ (average values from 15 independent measurements). The thickness of the monolayers was determined with a planar three layer (ambient, monolayer, substrate) isotropic model with assumed refractive indices for the ambient layer and monolayer of respectively 1.00 and 1.44. The reported values are the average of at least 7 measurements with an error of less than 1 Å. All samples were sonicated in CH_2Cl_2 for 5 minutes and washed with CH_2Cl_2 before measuring.

Infrared reflection absorption spectroscopy (IRRAS) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using a commercial variable angle reflection unit (Auto Seagull, Harrick Scientific). A Harrick grid polarizer was installed in front of the detector and was used to measure spectra with p-polarized (parallel) radiation with respect to the plane of incidence at the sample surface. All spectra were obtained at an incidence angle of 68° with respect to the sample using the Auto Seagull Pro v1.50 software. The resolution was set to 4 cm^{-1} per modulation centre and 2048 scans were made. All spectra were recorded at room temperature in dry atmosphere. A slight linear baseline correction was applied and the spectra were analysed using the Opus 6.5 software.

Results and Discussion

Monolayer formation

Monolayers of TFAAD were prepared using the thermal method as described. However, XPS data from the thermally prepared monolayers only showed statistically insignificant traces of the expected C=O and C-F peaks of the trifluoroacetamide (TFA) group, which indicated that the monolayer formation was too low for further measurements. Therefore, the thermal method was replaced by the UV method, which was used to prepare all the other monolayers used in this study, with the only variables being the duration that the sample was irradiated with a UV pen lamp and a 10 minute exposure of the sonicated Si(111) surfaces to air plasma during the surface preparation. These irradiation durations were chosen as 30 minutes, 2 hours, 4 hours and 10 hours.

Static water contact angles

The static water contact angles of monolayers is measured to provide an indication of the success of the modification and to quickly compare whether prepared monolayers possess approximately the same monolayer. Any differences in the measured contact angle between measured samples indicate that the monolayers are different. The obtained monolayers were analyzed by static water contact angle measurement. The results are shown in *Table 1*. As can be observed from the obtained contact angles, there appears to be no apparent trend between the different irradiation times and the observed contact angles, as all surfaces have relatively the same contact angle. This indicates that monolayer formation does not improve significantly when the samples are irradiated longer than 30 minutes.

Table 1*.* Static water contact angles of TFAAD monolayers on H-Si(111) at different UV irradiation times

UV irradiation time	Average contact angle (°) ±1
30 min	80
2 h	77
4 h	79
10 h	79

All surfaces show an increase in the contact angle, indicating that for all surfaces the hydrophobicity was decreased by the monolayer formation. However, when looking at the expected configuration of the TFAAD monolayer in *Figure 3*, one would predict that the terminal CF_3-groups would increase the hydrophobicity. Twisting the relatively bulky CF_3-groups to the surface of the monolayer seems the most favourable configuration. The measured contact angles can be explained by taking into account the fact that due to the relative bulkiness of the TFA group, the TFAAD monolayer will be a slightly disorganized monolayer. This could give the CF_3-group enough free space to twist slightly, explaining the decrease in hydrophobicity. There are no configuration calculations to support this however, thus this remains a hypothesis.

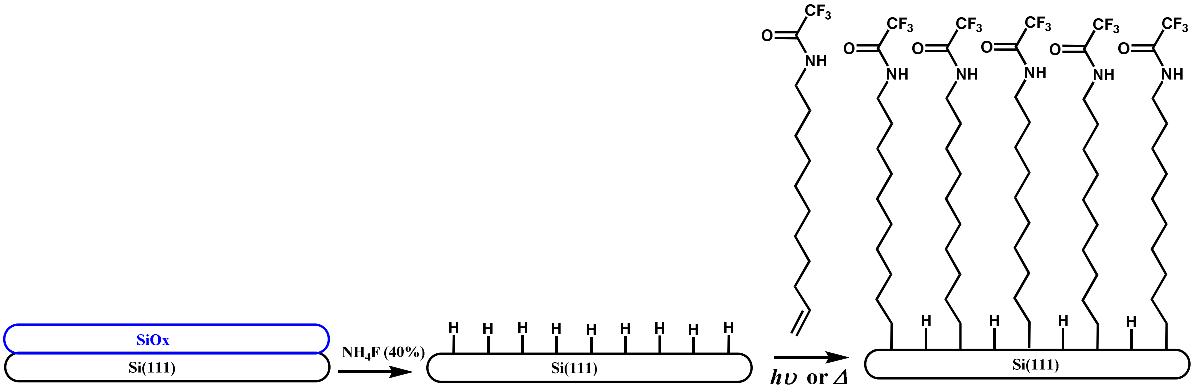


Figure 3. Schematic representation of the formation of TFAAD -derived organic monolayers on a hydrogen terminated silicon surface under photochemical or thermal modification.

Ellipsometry

Ellipsometry measurements are used to determine the thickness of a monolayer that has been grafted to a substrate. Ellipsometry uses the principle that light partially reflects from a boundary between two phases with different refractive indexes. By measuring the phase transition that occurs in the light waves because of this refraction, the thickness of the monolayer can be calculated.Several monolayers were analyzed by ellipsometry to determine the thickness of the TFAAD monolayers. The resulting data is shown in *Table 2*.

The measured thickness of the TFAAD monolayer corresponds with the length of the TFAAD molecule, as depicted in *Figure 4*. Although the length of the TFAAD molecule bound to Si(111) is 1.7 nm, the difference can be explained by assuming that the molecules are tilted at a slight angle on the surface. The thicknesses of the monolayers with 30 minutes and 2 hours of UV irradiation are comparable, indicating no additional monolayer formation in the additional 1.5 hours of irradiation. This strengthens the hypothesis that monolayer formation is complete after 30 minutes of UV irradiation, as could be seen in the results from the static water contact angle measurements.

Table 2. Thickness of TFAAD monolayers on H-Si(111) measured by ellipsometry at different UV irradiation times

UV irradiation time	Average monolayer thickness (nm)
30 min	1.6
2 h	1.4
2 h	1.6
4 h	2.4

As can be observed in the results, the monolayer thickness has increased beyond the maximum length of the TFAAD molecule after 4 hours of irradiation, indicating the formation of a multilayer. Studies performed by Hamers et al. have reported the formation of TFAAD multilayers on H-terminated amorphous carbon, observing that a maximum thickness of ~5 nm was reached after 15 hours of irradiation.[9] This multilayer formation is the result of a photodegradation process that involves fragmentation of the TFA group. The C-F bonds were found to be the most susceptible to cleavage. The photodegradation is explained using the TFAAD grafting mechanism proposed by Hamers et al. which involves electron photoemission from the substrate into the TFAAD, initiating the reaction with the surface as depicted in *Figure 1*.[8] This electron photoemission mechanism causes the fragmentation by photoinduced reduction of the TFA group to TFA$^{-\bullet}$, which subsequently fragmentizes. Although the maximum thickness of ~5 nm was not reached with the initial experiments, another modification of H-Si(111) using only a few drops of TFAAD to create a film between the Si(111) surface and the wall of the quartz reaction chamber, followed by 30 minutes of UV irradiation resulted in an average monolayer thickness of 4.7 nm. This might be caused by the a higher tendency of the photodegraded TFA fragments to react with TFAAD monolayer on the Si(111) because of the lower amount of available free TFAAD. Therefore, reaction of the fragmented TFA with free TFAAD molecules was less, resulting in a thinker multilayer.

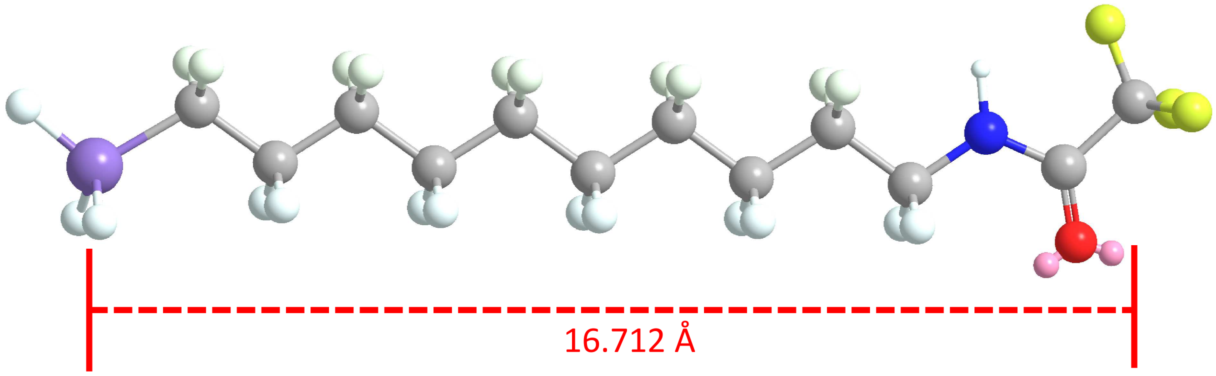


Figure 4. Model of a TFAAD molecule connected to H-Si(111) after MM2 minimized energy, created using ChemBio3D Ultra. The length of the TFAAD molecule (the distance from Si to CF_3) was estimated to be 16.712 Å.

IRRAS

IRRAS was used to determine the degree of organisation of the prepared TFAAD monolayers. The degree of organisation of a monolayer can be derived from the peak positions of the CH_2 stretch vibrations obtained by the IRRAS measurements. Highly ordered monolayers show their antisymmetric CH_2 stretching vibrations at 2918 ± 1 cm^{-1} and the symmetric vibrations at 2851 ± 1 cm^{-1}. For disordered monolayers, these vibrations increase until they reach the vibrations of the molecule in the liquid state.[10] For TFAAD, these liquid state antisymmetric and symmetric CH_2 stretch vibrations are approximately 2929 cm^{-1} and 2858 cm^{-1} respectively (the full spectrum can be found in the Supplemental Information).

A close-up of the antisymmetric and symmetric methylene stretching vibrations of the monolayers prepared with 2 and 4 hours of UV irradiation is shown in *Figure 5*. The monolayer resulting from the 2 hour UV modification has an antisymmetric CH_2 stretch vibration of 2927 cm^{-1} and the symmetric stretch vibration at 2856 cm^{-1}. The 4 hour modification monolayer has an antisymmetric CH_2 stretch vibration of 2927 cm^{-1} and the symmetric stretch vibration at 2850 cm^{-1}. The values of the antisymmetric stretch vibrations of both monolayers indicate that the TFAAD monolayers are disorganized monolayers, although the symmetric stretch vibration of the monolayer from 4 hours UV irradiation is more indicative of an organized monolayer. This disorganization of the TFAAD monolayer is probably caused by to the relative bulky TFA group, which prevents a very tight packing of the chains in the monolayer. In contrast, TFAAD monolayers prepared by Hamers et al. show antisymmetric and symmetric CH_2 stretching at 2937 and 2861 cm^{-1} respectively.[8]

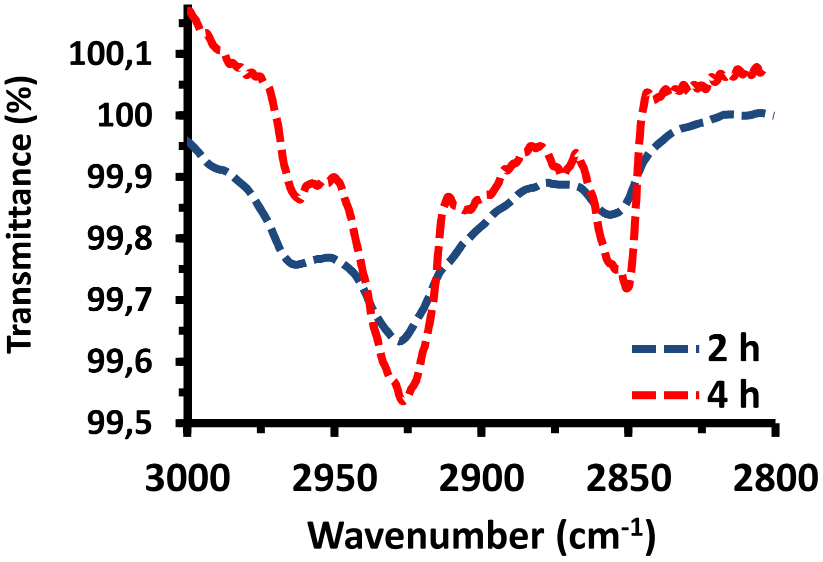


Figure 5. IRRAS spectra for TFAAD monolayers prepared with 2 and 4 hours of UV irradiation. Antisymmetric and symmetric methylene stretching vibrations are shown.

XPS

XPS was used to determine the elementary composition of the monolayer on the Si(111). By using the fact that chemical bonds emit an electron when hit by a photon, with a wavelength from the X-ray range, and the subsequent determination of the energy of the emitted electron, the composition of the chemical bond can be determined. The surfaces were analyzed by XPS and the wide scan and the C1s, Si2p, O1s, N1s and F1s narrow scans are depicted in *Figure 6*.

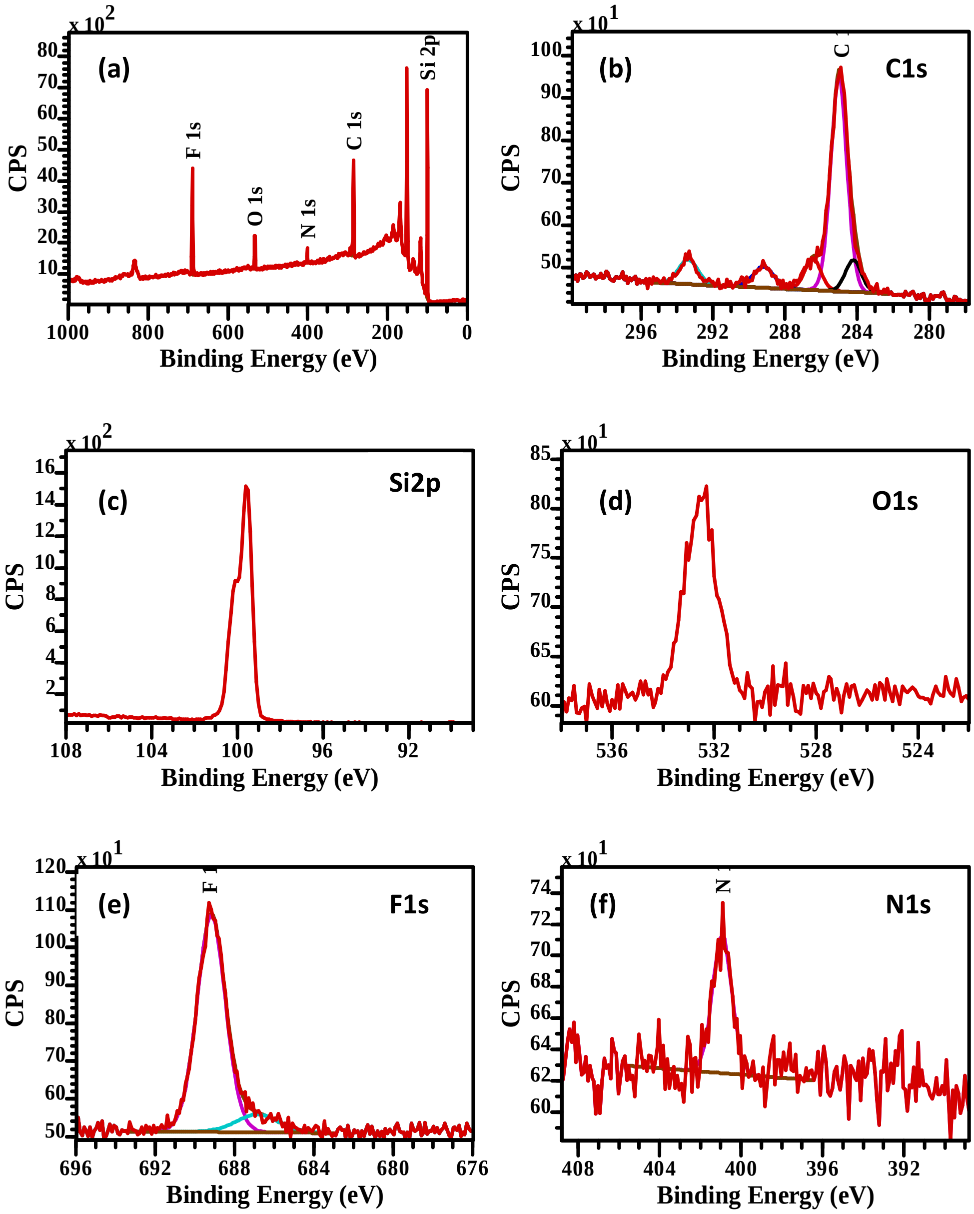


Figure 6. XPS spectra of a TFAAD monolayer on Si(111) after 2 h of UV irradiation with (a) the wide scan and (b)-(f) the narrow scans of C1s, Si2p, O1s, F1s and N1s respectively

The obtained spectra match the expectations of a TFAAD monolayer on H-terminated Si(111): in the C1s spectrum (Figure 6b) the C-bonds are visible with the ***C*****F$_3$** bond at 293.4 eV, the O=***C*****-N** bond at 289.2 eV, the ***C*****=O** bond at 286.5 eV, the ***C*****-H** bonds at 285.0 eV and a peak at 284.2 eV, that probably belongs to the **Si-*C*** bond; the Si2p spectrum shows no sign of oxidation of the H-terminated surface and the O1s and N1s both show the expected signals for the single oxygen and nitrogen atom of TFAAD.

However, the F1s spectrum (Figure 6e) stands out, because it contains 2 peaks, where only one is expected for the C-F bond at 689.0 eV. The second peak at 686.7 eV was first thought to be caused by the etching procedure, because of the use of NH_4F, which could have resulted in the formation of Si-F bonds on the H-terminated Si(111) surface. This was disproven by a control experiment where a freshly etched Si(111) surface was measured with XPS before a monolayer was grafted. The XPS spectra from this experiment are depicted in *Figure 7*.

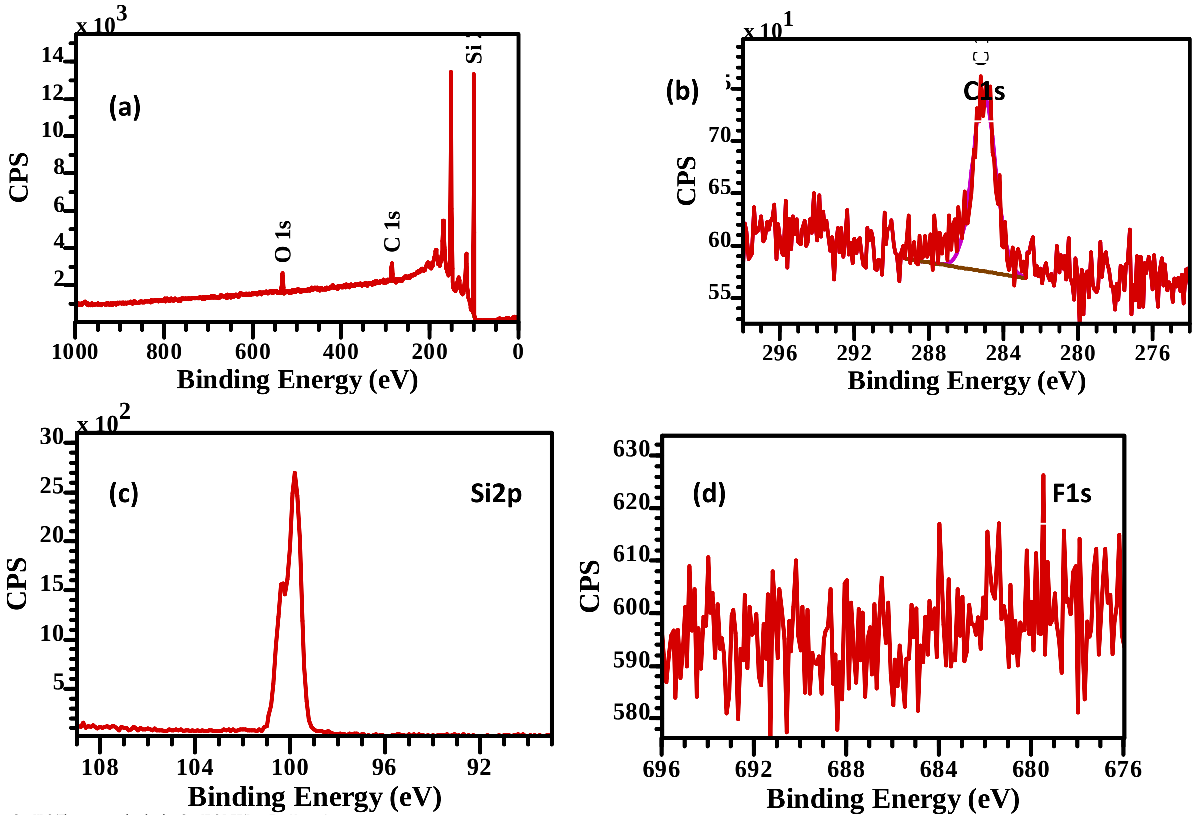


Figure 7. XPS spectra of a freshly etched H-terminated Si(111) surface with (a) the wide scan and (b)-(d) the narrow scans of C1s, Si2p and F1s respectively

As can be seen from the F1s spectrum of Figure 7d, there is no evidence of a Si-F peak visible after the etching procedure. This indicates that the Si-F peak forms during the UV-induced monolayer formation. Further evidence of this hypothesis is given by the fact that all TFAAD monolayers show this second Si-F peak in their F1s spectrum. This can be seen in *Figure 8*.

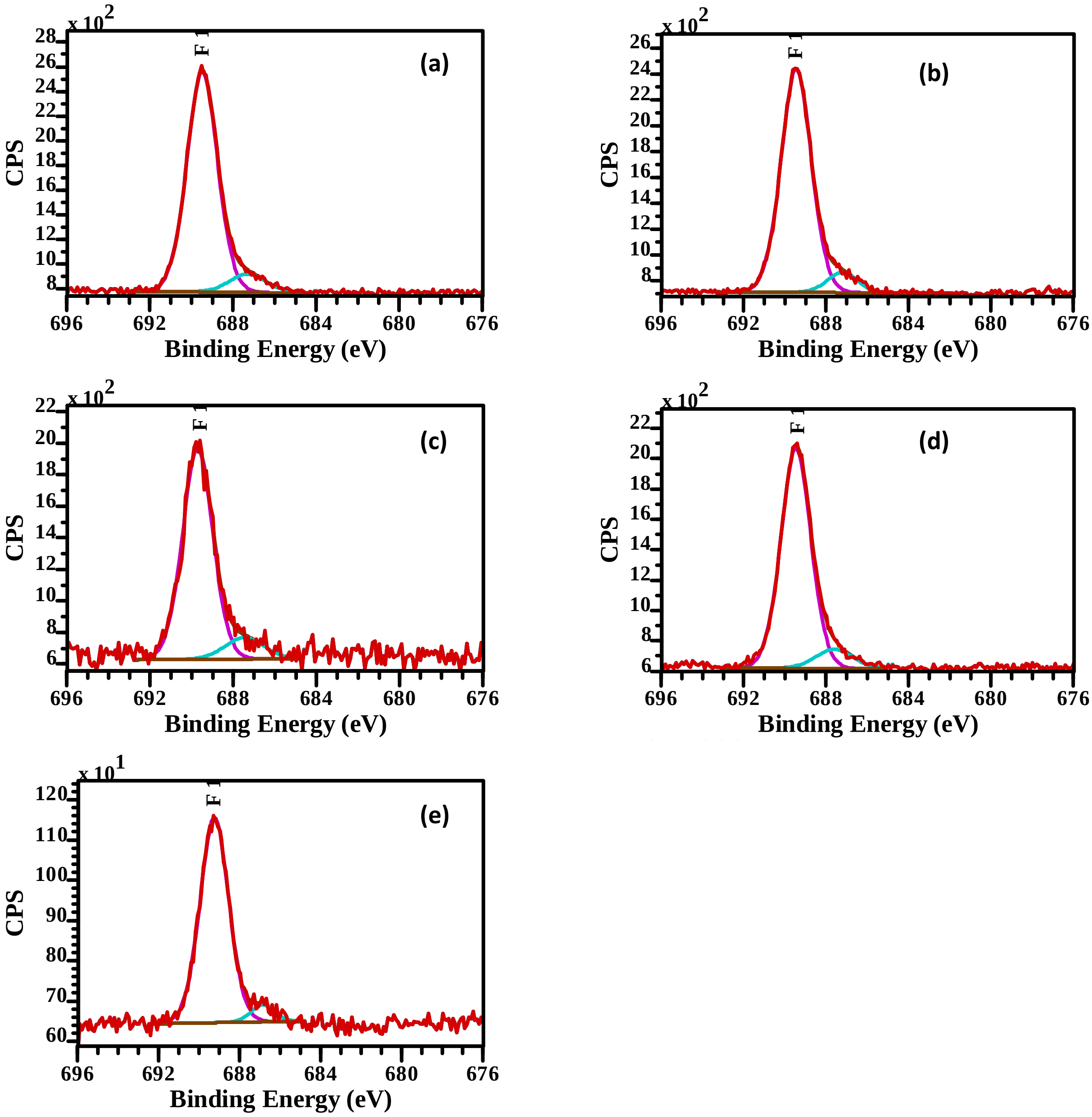


Figure 8. F1s spectra of a TFAAD monolayer on Si(111) after (a)-(b) 30 minutes, (c)-(d) 2 hours and (e) 4 hours of UV irradiation

Although we can see a Si-F peak in the XPS spectra of the prepared monolayers, we were unable to determine how it was created during the procedure. It could be caused by a contamination in the synthesized TFAAD, which reacts with the H-terminated surface as soon as it is introduced or during the UV irradiation. It could also be a side product of the fragmentation by photoinduced reduction of the TFA group of TFAAD molecules in solution mentioned in the previous section. This data demonstrates the importance of a previously unrecognized initiation process, photoelectron ejection (photoemission), as an easily accomplished way of initiating photochemical grafting of liquid alkenes to silicon surfaces when using UV. These results indicate that photoemission is an effective way of initiating grafting, caused by the irreversible nature of photoemission, which leaves the sample with a net excess of holes that have no corresponding electrons with which to recombine, while in a competing exciton mechanism, the net concentration of holes is limited by recombination processes. This might be photoemission-driven hydrosilylation, as was proposed and explained by Hamers et al.[8] Another possible explanation is that UV-grafting of TFAAD to H-terminated Si(111) can lead to the photodegradation of the TFA groups in the monolayer, resulting in multilayer formation or the formation of Si-F bonds on the surface.[9]

Conclusions

Grafting oxide-free monolayers of TFAAD on H-terminated Si(111) was attempted by thermal and UV methods. Only the UV method resulted in the successful formation of desired monolayer, whereas the performed thermal method yielded no significant results. Static contact angle and ellipsometry results show that monolayer formation is completed after 30 minutes of UV irradiation. Longer exposure of these monolayers to UV irradiation, such as 4 hours or longer, can result in multilayer formation caused by the photodegradation of the TFA group. IRRAS measurements showed that TFAAD forms disorganized monolayers on Si(111), which is most likely caused by the bulky nature of the TFA group.

XPS measurements of the obtained monolayers showed an unexpected peak in the F1s spectrum, which was contributed to Si-F bonds that formed during the UV irradiation. This might be photoemission-driven hydrosilylation instead of Si–H dissociation for UV light promoted hydrosilylation. These results also suggest that UV-grafting of TFAAD to H-terminated Si(111) can lead to the photodegradation of the TFA group, resulting in multilayer formation or the formation of unwanted Si-F bonds on the surface. The source of this bond formation was not found, but could be contributed to either impurities in the synthesized TFAAD or reaction of the photodegraded TFA fragments with the Si(111) substrate. However, more experiments need to be performed to be certain of the fact that the Si-F bond formation is caused by the photodegradation.

Associated Content

Supplementary information: synthesis procedure of TFAAD and its IR and NMR spectra; XPS spectra of the TFAAD monolayers on Si(111).

Acknowledgement

The author wants to thank Sidharam Pujari, Han Zuilhof and many of my close friends and family for the help, support, understanding and patience they provided during the thesis period. Without their support and understanding, it is unlikely this project would be where it is now. Furthermore, Frank Claassen and Barend van Lagen for their extensive help with the measurements. Luc Scheres and Remco Regeling for their interesting discussions and ideas. All lab mates for the great atmosphere and friendship at the Organic Chemistry group.

References

1. Bhushan, B., *Handbook of Nanotechnology*. Springer-Verlag: New York, **2007**.
2. Ciampi, S.; Harper, J. B.; Gooding, J. J., Wet chemical routes to the assembly of organic monolayers on silicon surfaces via the formation of Si-C bonds: surface preparation, passivation and functionalization. *Chem. Soc. Rev.* **2010,** *39*, 2158-2183.
3. Li, Y.; Calder, S.; Yaffe, O.; Cahen, D.; Haick, H.; Kronik, L.; Zuilhof, H., Hybrids of Organic Molecules and Flat, Oxide-Free Silicon: High-Density Monolayers, Electronic Properties, and Functionalization. *Langmuir* **2012,** *28* (26), 9920-9929.
4. Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; van der Maas, J. H.; de Jeu, W. H.; Zuilhof, H.; Sudhölter, E. J. R., Highly Stable Si-C Linked Functionalized Monolayers on the Silicon (100) Surface. *Langmuir* **1998,** *14*, 1759-1768.
5. Sun, Q.-Y.; de Smet, L. C. P. M.; van Lagen, B.; Wright, A.; Zuilhof, H.; Sudhölter, E. J. R., Covalently Attached Monolayers on Hydrogen-Terminated Si(100): Extremely Mild Attachment by Visible Light. *Angew. Chem. Int. Ed.* **2004,** *43* (11), 1352-1355.
6. Buriak, J. M., Illuminating Silicon Surface Hydrosilylation: An Unexpected Plurality of Mechanisms. *Chem. Mater.* **2014,** *26* (1), 763-772.
7. Scheres, L.; Giesbers, M.; Zuilhof, H., Self-Assembly of Organic Monolayers onto Hydrogen-Terminated Silicon: 1-Alkynes Are Better Than 1-Alkenes. *Langmuir* **2010,** *26* (13), 10924-10929.
8. Wang, X.; Ruther, R. E.; Streifer, J. A.; Hamers, R. J., UV-Induced Grafting of Alkenes to Silicon Surfaces: Photoemission versus Excitons. *J. Am. Chem. Soc.* **2010,** (132), 4048-4049.
9. Colavita, P. E.; Streifer, J. A.; Sun, B.; Wang, X.; Warf, P.; Hamers, R. J., Enhancement of Photochemical Grafting of Terminal Alkenes at Surfaces via Molecular Mediators: The Role of Surface-Bound Electron Acceptors. *J. Phys. Chem. C* **2008,** *112,* 5102-5112.
10. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D., Spontaneously organized molecular assemblies. 4. Structural characterization of n-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy, and electrochemistry. *J. Am. Chem. Soc.* **1987,** *109* (12), 3559-3568.

Supplementary information

Experimental section

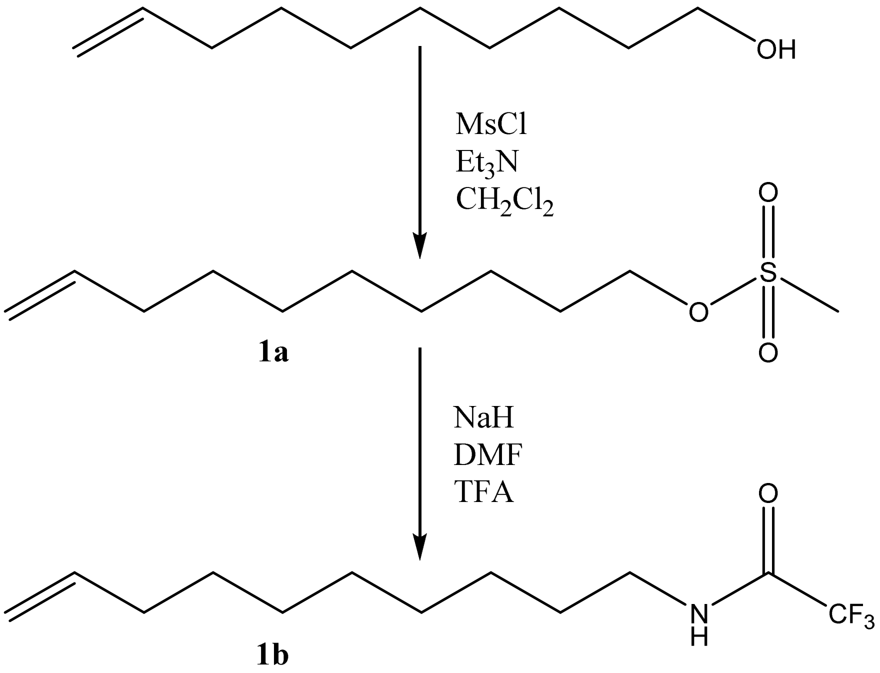
Materials

9-decen-1-ol (Aldrich, 90%), triethylamine (Et3N, Acros Organics, 99%), methanesulfonyl chloride (MsCl, Janssen Chimica, 99%), N,N-dimethylformamide (DMF, Aldrich, +99.5%), trifluoroacetamide (TFAA, Aldrich, 97%), 60% sodium hydride in mineral oil (NaH, Aldrich, 60%) and silica gel 60 (Fluka) were all used as received. Dichloromethane (CH_2Cl_2 , Fisher Chemical, +99%) was distilled before use.

Analysis

All reactions were monitored by thin layer chromatography (TLC) and carried out on 0.25 mm silica gel PET foil plates with a medium pore size of 60 Å and a fluorescent indicator of 254 nm. Molybdate coloring reagent and heat were used as developing agents. The synthesized compound was purified by automatic column chromatography with the Biotage Isolera One UV-VIS Flash Purification System using Biotage SNAP Cartridges (KP-Sil 50 or 100 g). ^{1}H-NMR (400 MHz) and ^{13}C-NMR (400 MHz) spectra were recorded on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvent and internal standard (^{1}H-NMR: 7.26 ppm and ^{13}C-NMR: 77.16 ppm). In the reported data below, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, ddt = doublet of doublets of triptlets, m = multiplet. Chemical shifts are reported in ppm. High resolution mass spectra were recorded using Direct Analysis in Real Time (DART) ionization coupled to a high resolution mass spectrometer from Thermo Scientific. Samples were measured in acetone. Attenuated total reflectance (ATR) infrared spectra of pure compound were recorded on a Alpha-P spectrometer from Brucker. The wavenumbers are reported in reciprocal centimeters and the appearance is denoted as weak (w), medium (m) or strong (s). The purities of the synthesized compound was checked with GC-MS using an Agilent HP-5MS column (30 m x 0.250 mm x 0.25 µm).

Synthesis of trifluoroacetic acid-protected 10-aminodec-1-ene



Scheme S1. Synthetic route of 9-decen-1-ol to trifluoroacetic acid-protected 10-aminodec-1-ene

Dec-9-en-1-yl methanesulfonate (1a)

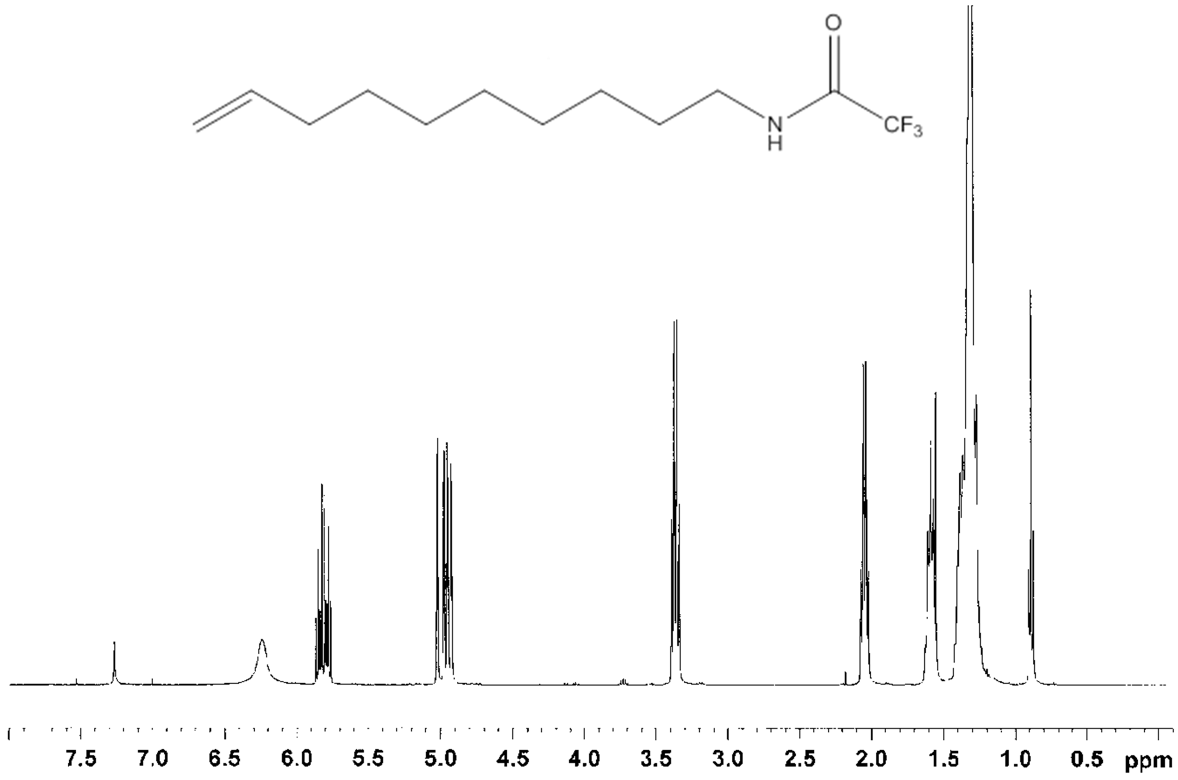
To a solution of 9-decen-1-ol (30.143 g, 0.192 mol) and Et_3N (54.0 mL, 0.386 mol) in dry CH_2Cl_2 (450 mL) stirring at 0 °C was added methanesulfonyl chloride (30.0 mL, 0.386 mol) via a syringe. The reaction mixture was stirred at 0 °C for 2 h. The mixture was poured into a separation funnel and ice cold 1 N HCl (500 mL) was added. The water layer was extracted with CH_2Cl_2 (2 x 200 mL). The organic layers were combined, washed with a saturated aqueous $NaHCO_3$ solution (2 x 200 mL), dried over $MgSO_4$ and filtered. The resulting filtrate was evaporated under reduced pressure to give a yellow oil. The crude product mesylate **1a** was used in the next step without purification.

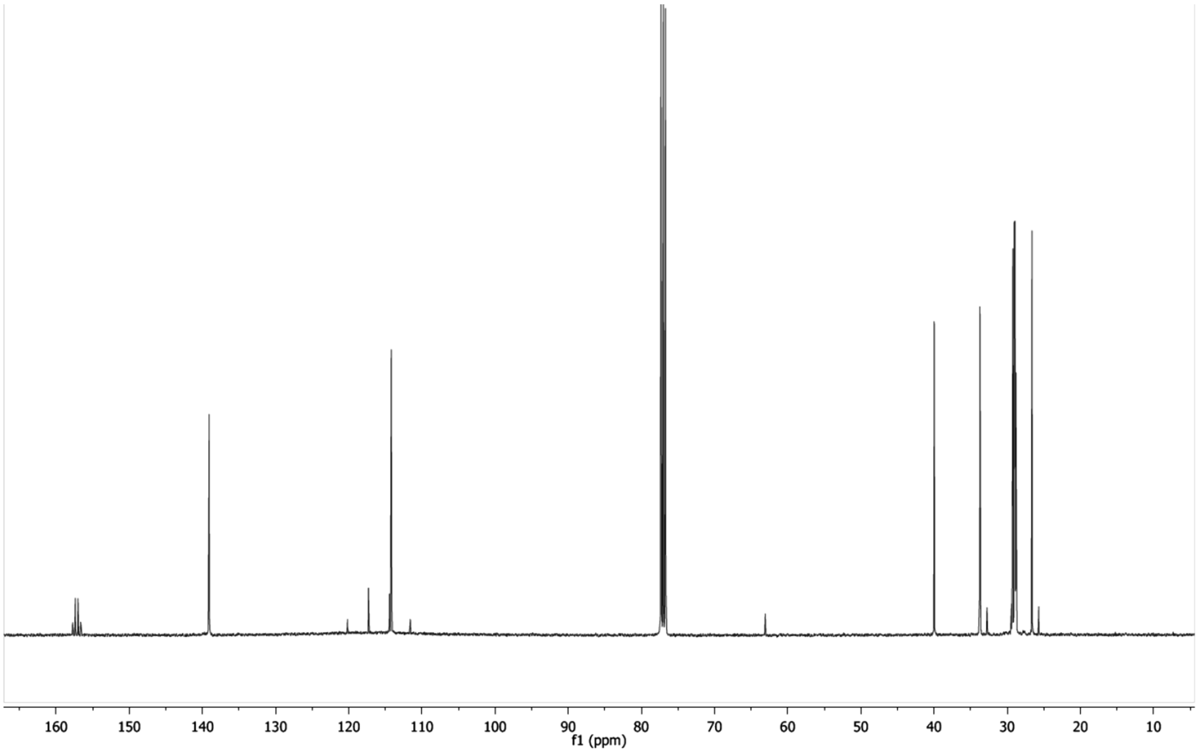
Trifluoroacetic acid-protected 10-aminodecene (1b)

To a suspension of NaH (60% wt in mineral oil, 15.81 g, 0.395 mol) in anhydrous N,N-dimethylformamide (450 mL) was added trifluoroacetamide (33.52 g, 0.297 mol). The reaction mixture was stirred until H_2 evolution ceased. To this solution was added a solution of crude mesylate **1a** (46.33 g, ±0.198 mol) in N,N-dimethylformamide (120 mL). The reaction mixture was heated to 70 °C for 24 h. The reaction mixture was diluted with Et_2O (1000 mL) and washed with H_2O (3 x 500 mL). The organic layer was washed with brine (2 x 400 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a crude oil. Purification of the crude oil by silica gel column chromatography (heptane/EtOAc 96%:4%) gave title compound **1b** (41.809 g, 86%). ^{1}H-NMR: δ 6.23 (s, 1H, F_3C-(C=O)-N*H*-R), 5.87-5.76 (ddt, *J*=6.7, 8.5, 5.1 Hz, 1H, H_2C=C*H*-R), 5.03-4.97 (ddt, *J*=17.2, 2.0, 1.6 Hz, 1H, H_A-CH=CH-R), 4.96-4.92 (dquin, *J*=10.2, ~1.4 Hz, 1H, H_B-CH=CH-R), 3.37 (t, *J*=6.8 Hz, 2H, F_3C-(C=O)-NH-CH_2-R), 2.08-2.01 (qt, *J*=7.2, ~1.2 Hz, 2H, H_2C=CH-CH_2-R), 1.59 (quin, *J*=7.2 Hz, 2H, F_3C-(C=O)-NH-CH_2-CH_2-R), 1.45-1.20 (m, 10H, H_2C=CH-CH_2-(CH_2)$_5$-R). ^{13}C-NMR: δ 157.73-156.64 (q, 1C, F_3C-(*C*=O)-R), 139.08 (1C, H_2C=*C*H-R), 121.29-111.58 (q, 1C, F_3*C*-R), 114.11 (1C, H_2*C*=CH-R), 39.98 (1C, R_1-NH-*C*H_2-R_2), 33.77, 29.24, 29.05, 28.95, 28.89, 28.82, 25.69 (7C, alkyl). IR (cm^{-1}): 3301 (m, NH), 3078, 2976 (w, w, C=C-*H*), 2926, 2856, 1463 (s, s, m, CH_2), 1701 (s, C=O), 1640 (m, C=C), 1160 (s, CF_3). MS (DART): calculated for $C_{12}H_{20}ONF_3$ (M + NH_4) 269.18, found 269.1834; (M + H) 252.16, found 252.1570; (M – H) 250.14, found 250.1422.

NMR-spectra

Trifluoroacetic acid-protected 10-aminodecene (1b)





IR-spectra

Trifluoroacetic acid-protected 10-aminodecene (1b)