Supporting Information for

UV-Initiated Hydrosilylation on Hydrogen-Terminated Silicon (111): Rate Coefficient Increase of Two Orders-of-Magnitude in the Presence of Aromatic Electron Acceptors

L. A. Huck and J. M. Buriak

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton AB, T6G 2G2, and National Research Council Canada, National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton AB, T6G 2M9, Canada.

Figure S1a. UV-visible absorption spectra of (a) the Schott UG5 filter used to remove the 185 nm component from the Hg lamp (b) quartz slide placed over the alkene solution on the silicon surface. The dashed vertical lines = 254 nm.	S2
Figure S1b. UV absorption spectra (in hexanes) of 1-hexadecene and the aliphatic additives. Dashed vertical lines = 254 nm. Methyl-cyclohexane, chlorocyclohexane, and *t*-butyl chloride have no significant absorption > 200 nm.	S2
Figure S1c. UV absorption spectra (in hexanes) of the aromatic additives. Dashed vertical lines = 254 nm.	S3
Estimate of light absorption by solutions above the silicon surface	S4
Figure S2. Water contact angle (θ_w) of the surface of Si(111)-H coated with 0.25 M aliphatic additive (listed within each) in hexadecene and irradiated with 254 nm light. Data fit to eq 2.	S5
Figure S3. Water contact angle (θ_w) of the surface of Si(111)-H coated with 0.25 M aromatic additive (listed within each) in hexadecene and irradiated with 254 nm light. Data fit to eq 2.	S6
Figure S4. Effect of the concentration of PhCl added to 1-hexadecene on the rate coefficient of hydrosilylation on Si(111)-H.	S7
Figure S5. XPS F 1*s* spectra of Si(111)-H surfaces coated with (a) neat F-UD or (b) 0.25 M PhCl in F-UD and irradiated with 254 nm light. The numbers indicate the irradiation time in seconds. (c) Intensity of the fluorine 1*s* XPS signal from *a* and *b*.	S8
Figure S6. Cl(2*p*) XPS spectra of the surface of Si(111)-H coated with (a) 0.25 M BzCl, (b) 0.25 M PhCl, (c) 0.25 M C_2Cl_6, and (d) 0.25 M $CHCl_3$ in F-UD and irradiated with 254 nm light. The irradiation time for each is shown in the figure and corresponds to the approximate time in which maximum coverage is reached (as determined by θ_w).	S8
Figure S7. Si(2*p*) [left] and Cl(2*p*) [right] XPS spectra of the surface of Si(111)-H coated with (a,b) neat chlorobenzene, (c,d) neat benzyl chloride and irradiated with 254 nm light for 60 s. Spectra (e,f) are of the same benzyl chloride sample, except that it was exposed to air for 24 h prior to analysis. The arrows denote SiO_x.	S9

Figure S1a. UV-visible absorption spectra of (a) the Schott UG5 filter used to remove the 185 nm component from the Hg lamp (b) quartz slide placed over the alkene solution on the silicon surface. The dashed vertical lines = 254 nm.

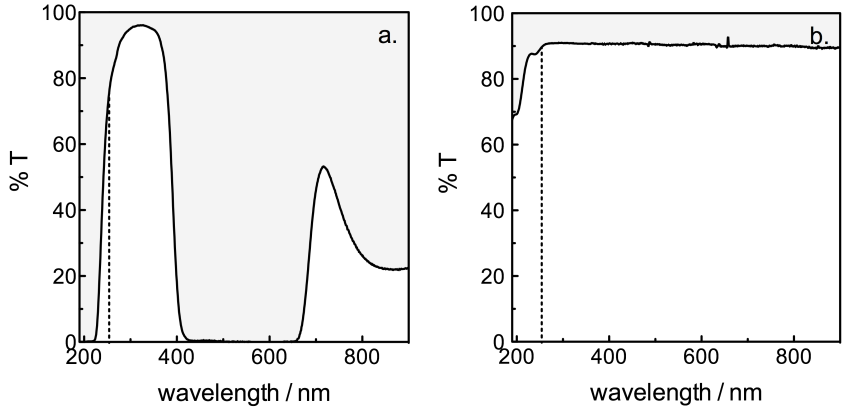


Figure S1b. UV absorption spectra (in hexanes) of 1-hexadecene and the aliphatic additives. Dashed vertical lines = 254 nm. Methyl-cyclohexane, chlorocyclohexane, and *t*-butyl chloride have no significant absorption > 200 nm.

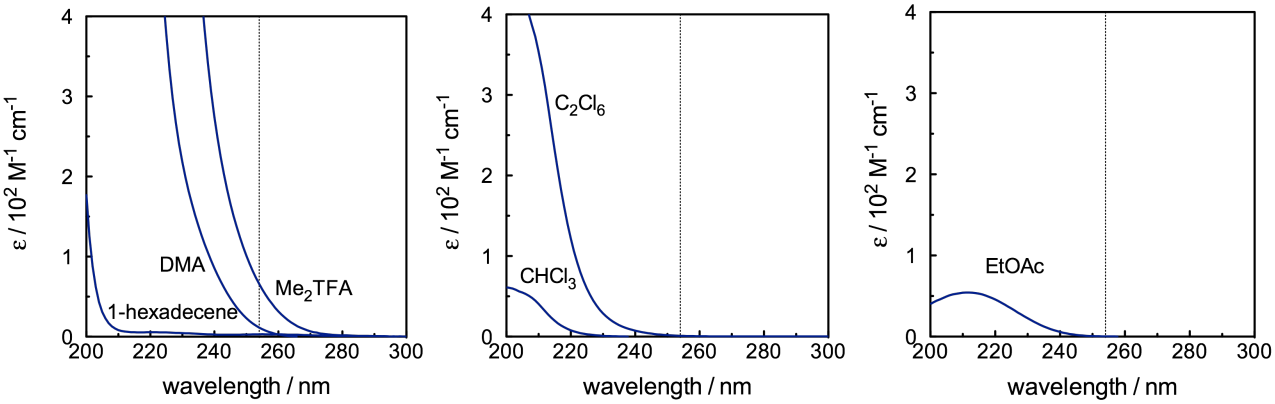
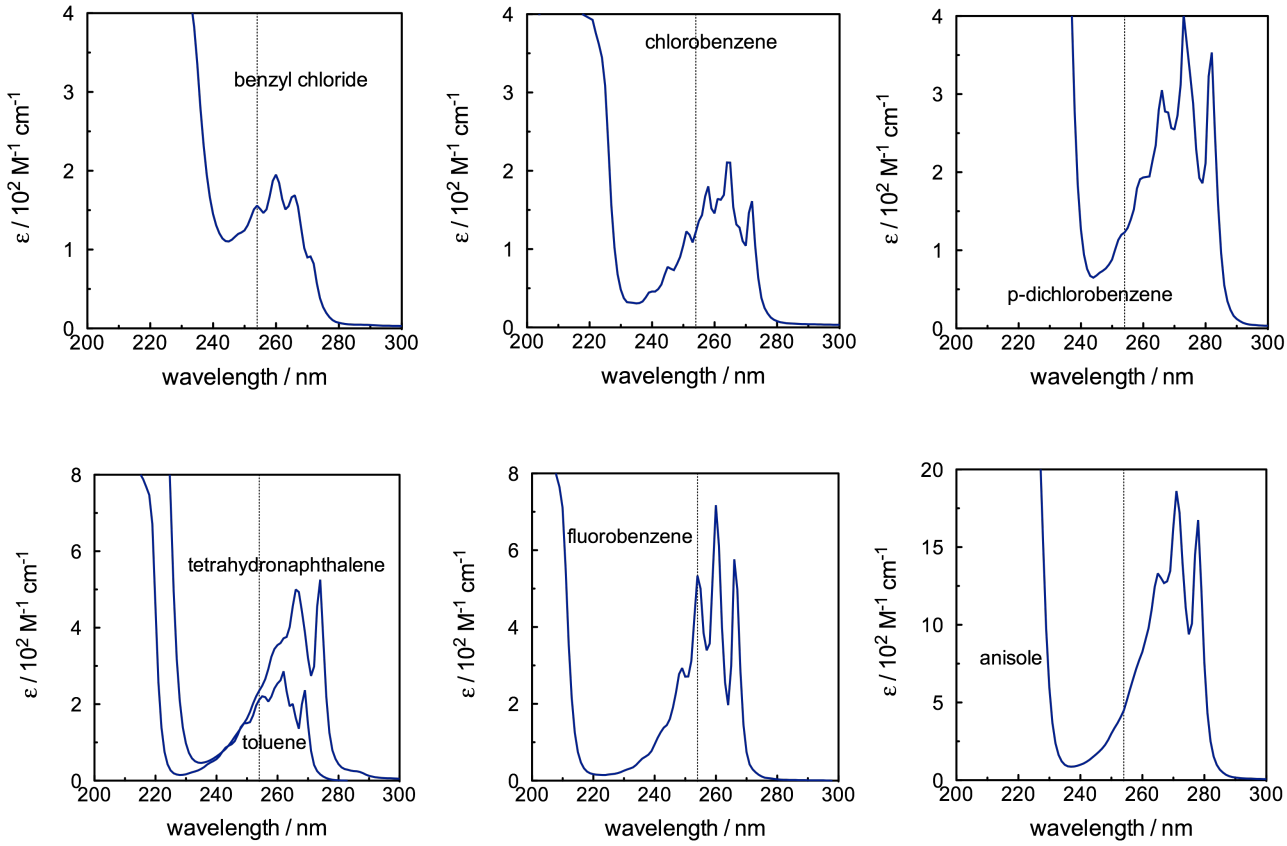
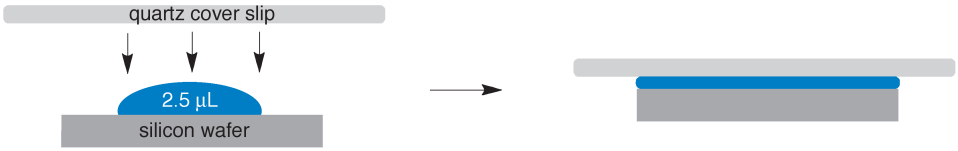


Figure S1c. UV absorption spectra (in hexanes) of the aromatic additives. Dashed vertical lines = 254 nm.



Estimate of light absorption by solutions above the silicon surface:

The maximum volume of hexadecene that can be compressed between the square silicon wafer (0.9 cm × 0.9 cm) and the larger quartz cover slip is ~2.5 µL. At smaller volumes, the surface is not completely covered, while at larger volumes liquid is expelled from between the silicon and quartz.



Using this volume, we estimate a solution height (h) (*i.e.* path length for the light) of about 30 µm, as shown:

$2.5\ \mu L = (2.5\times10^{-6}\ L)(10^{3}\ cm^{3}/L) = 2.5\times10^{-3}\ cm^{3}$

$2.5\times10^{-3}\ cm^{3} = (Area)(h) = (0.81\ cm^{2})(h)$
$\boldsymbol{h = 0.0031\ cm}$

This leads to the following absorption and transmission values for various hexadecene solutions used throughout the experiments:

	[ ] / M	$\varepsilon_{254\ nm}$ / $M^{-1}\ cm^{-1}$	$A_{254\ nm}$	$\%\ T_{254\ nm}$
PhF	0.25	530	0.41	39
PhOMe	0.25	480	0.37	42
THN	0.25	240	0.19	65
toluene	0.25	210	0.16	69
BzCl	0.25	160	0.12	75
p-DCB	0.25	120	0.09	81
PhCl	0.25	120	0.09	80.7
	0.05	120	0.02	95.8
	0.01	120	0.00	99.1
	0.006	120	0.00	99.5
	0.001	120	0.00	99.9
Me_2TFA	0.25	60	0.05	90
DMA	0.25	12	0.01	98
C_2Cl_6	0.25	1	0.00	99.82
	0.05	1	0.00	99.96
$CHCl_3$	0.25	< 0.5	~ 0	>99.9
t-BuCl	0.25	< 0.5	~ 0	>99.9
EtOAc	0.25	< 0.5	~ 0	>99.9
Me(*c*Hx)	0.25	< 0.5	~ 0	>99.9

Figure S2. Water contact angle (θ_w) of the surface of Si(111)-H coated with 0.25 M aliphatic additive in hexadecene and irradiated with 254 nm light. Data fit to eq 2. The dashed line in (d) is the fit of the neat hexadecene curve shown in Figure 1a.

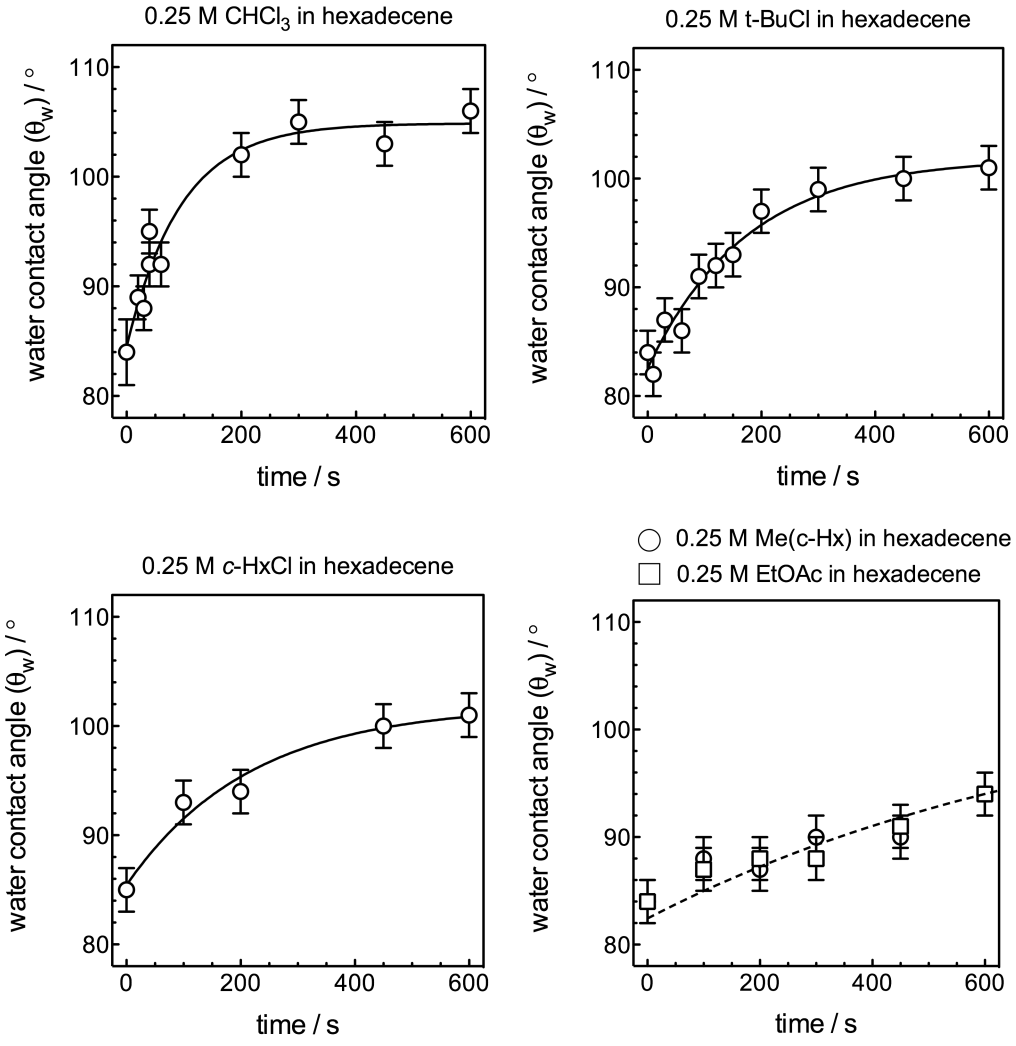


Figure S3. Water contact angle (θ_w) of the surface of Si(111)-H coated with 0.25 M aromatic additive (listed within each) in hexadecene and irradiated with 254 nm light. Data fit to eq 2.

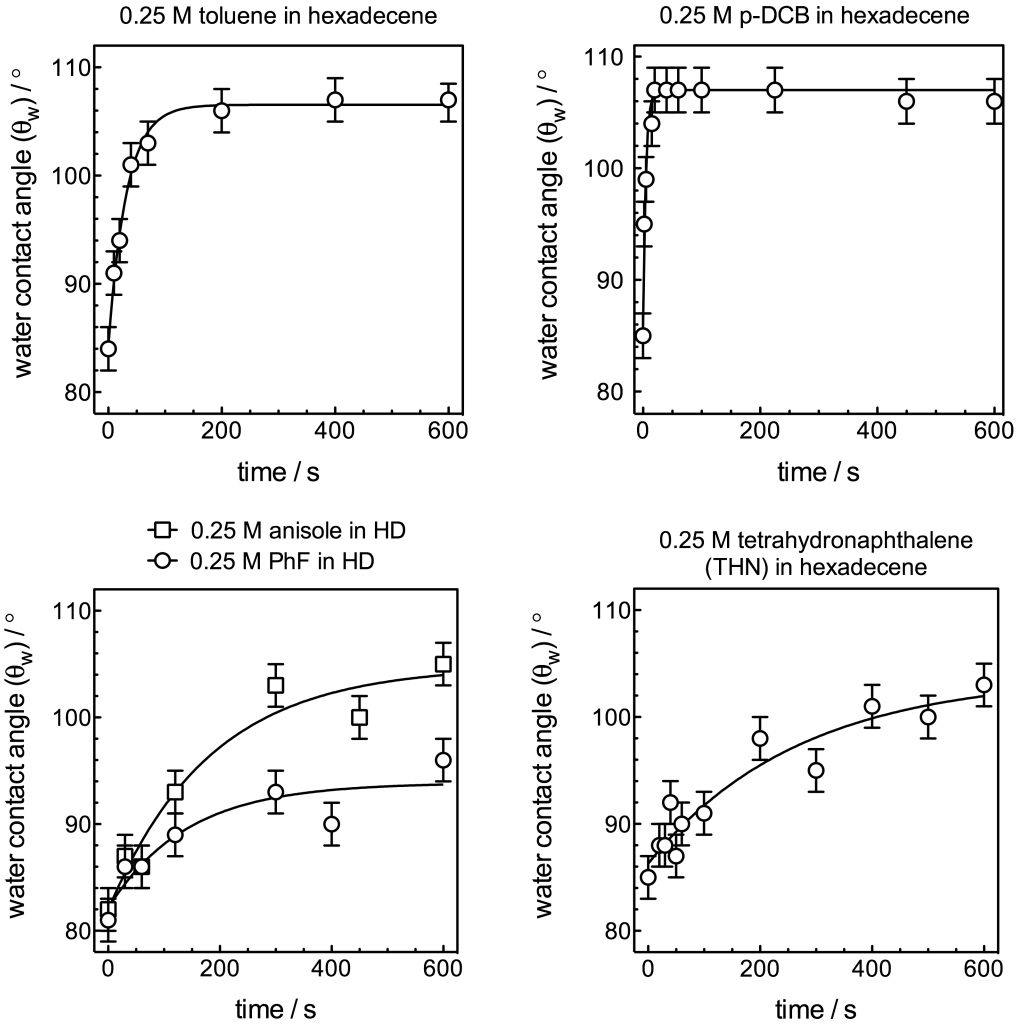


Figure S4. Effect of the concentration of PhCl added to 1-hexadecene on the rate coefficient of hydrosilylation on Si(111)-H.

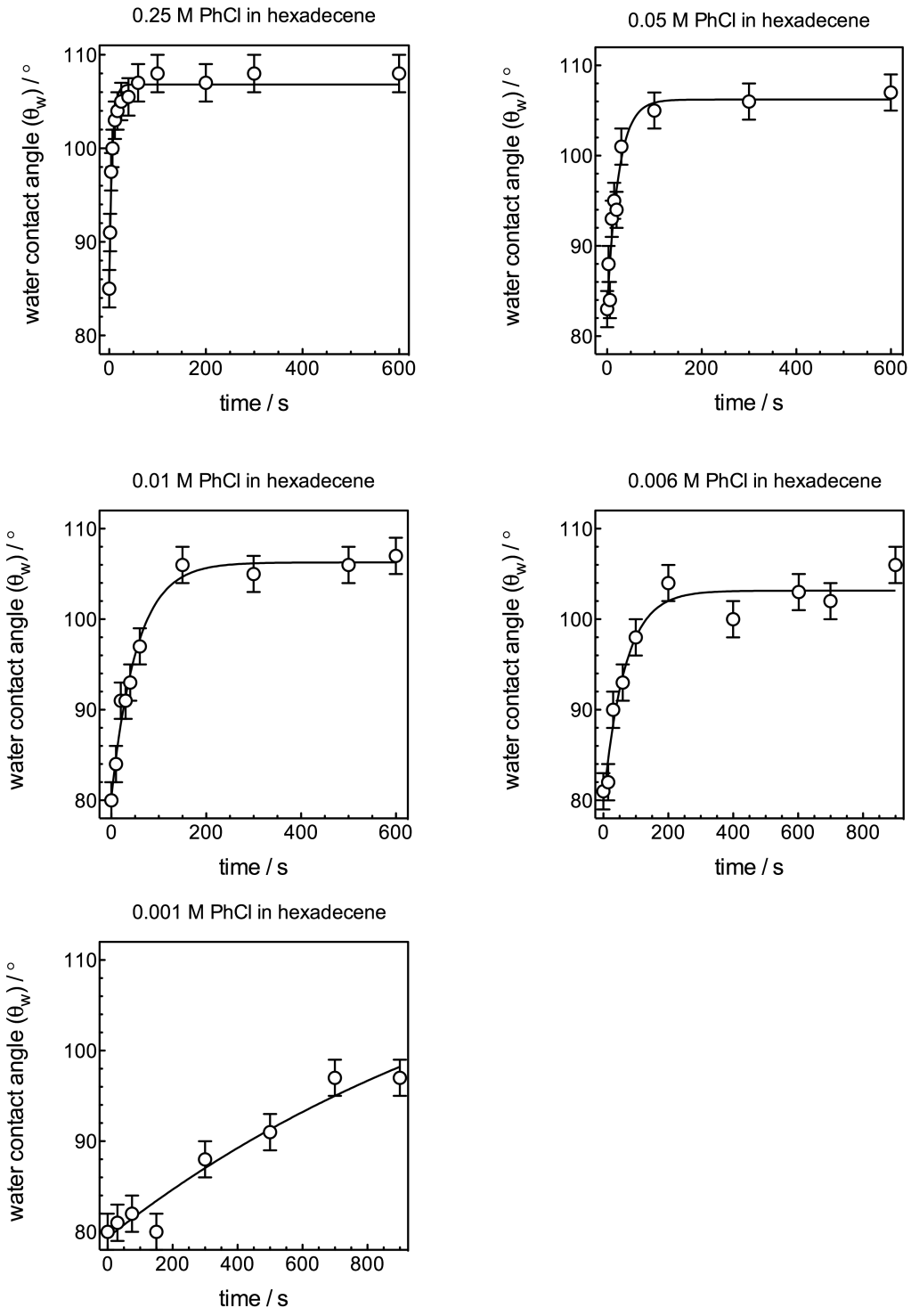


Figure S5. XPS F 1*s* spectra of Si(111)-H surfaces coated with (a) neat F-UD or (b) 0.25 M PhCl in F-UD and irradiated with 254 nm light. The numbers indicate the irradiation time in seconds. (c) Intensity of the fluorine 1*s* XPS signal from *a* and *b*.

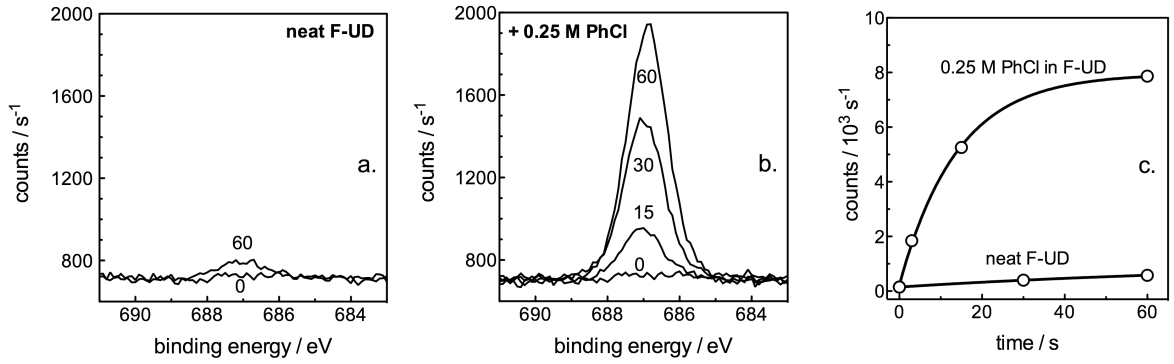


Figure S6. Cl(2*p*) XPS spectra of the surface of Si(111)-H coated with (a) 0.25 M BzCl, (b) 0.25 M PhCl, (c) 0.25 M C_2Cl_6, and (d) 0.25 M $CHCl_3$ in F-UD and irradiated with 254 nm light. The irradiation time for each is shown in the figure and corresponds to the approximate time in which maximum coverage is reached (as determined by θ_w).

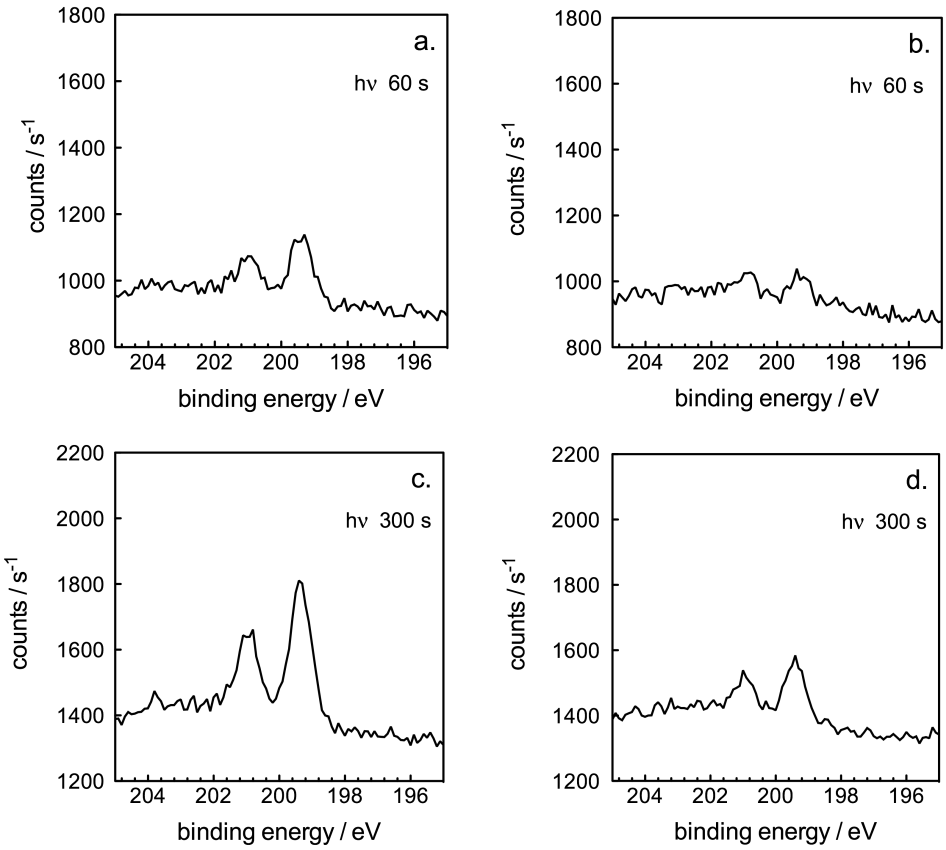


Figure S7. Si(2*p*) [left] and Cl(2*p*) [right] XPS spectra of the surface of Si(111)-H coated with (a,b) neat chlorobenzene, (c,d) neat benzyl chloride and irradiated with 254 nm light for 60 s. Spectra (e,f) are of the same benzyl chloride sample, except that it was exposed to air for 24 h prior to analysis. The arrows denote SiO_x.