## **Supporting Information**

## Direct patterning of covalent organic monolayers on silicon using nanoimprint lithography

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## XPS measurements

A full monolayer of 1-hexadecene on hydrogen-terminated silicon was investigated by X-ray Photoelectron Spectroscopy (XPS). The quality of full monolayers can generally be assessed by absence of a band for SiO<sub>2</sub> around 103 eV in the XPS Si<sub>2p</sub>-spectrum [12]. Figure S1 shows the Si<sub>2p</sub>- and C<sub>1s</sub>-spectra measured on a full hexadecyl monolayer. The maximum of the C<sub>1s</sub>-spectrum was set at 284.8 eV, the peak for aliphatic carbon. The averaged, fitted C<sub>1s</sub>-spectrum showed a ratio of C<sub>1s</sub>-electrons with a low binding energy to aliphatic C<sub>1s</sub>electrons of 1:15.6. This is indicative of formation of a Si-C-C bond. It must be noted however that the relative shift of  $C_{1s}$ -electrons with a low binding energy is very small and a visible peak for  $C_{1s}$ -electrons with a lower binding energy becomes much more apparent when the samples are prepared using 1-alkynes because of the relatively larger downfield shift [11].



**Figure S1.** XPS spectra of the  $C_{1s}$  region (a) and the  $Si_{2p}$  region (b) of a full hexadecyl monolayer on Si(111).



**Figure S2.** Contact mode AFM height (a;  $30 \ \mu m \ x \ 30 \ \mu m$ ) with height profile (c) and corresponding friction image (b) of a 100-µm patterned dot where native SiO<sub>2</sub> surrounding the spacings is still present.



**Figure S3.** a) Optical microscopy images of 100-µm diameter dots (a), 100-µm lines (b), 3-µm lines (c), and HR-SEM image of 100-nm lines (d), all after NIL.