

## Supporting Information

### Development of a microfluidic “click chip” incorporating an immobilized Cu(I) catalyst

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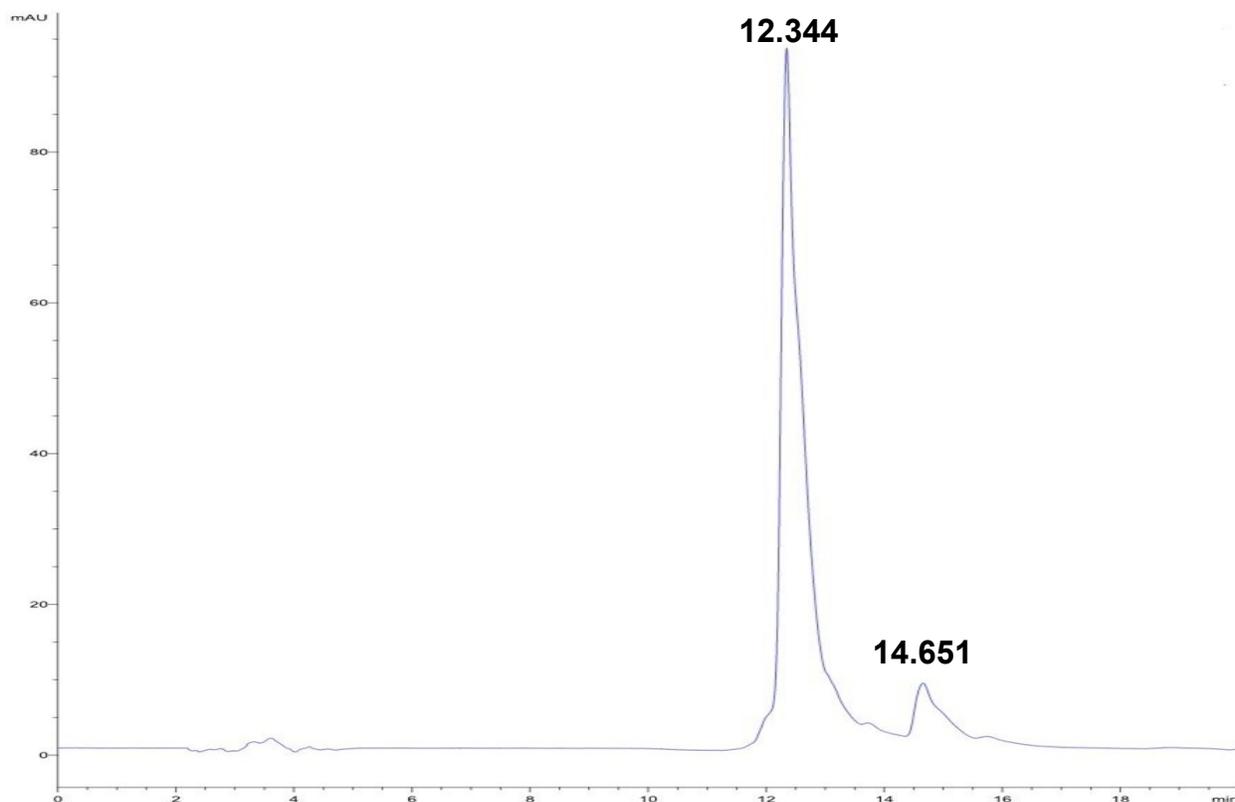
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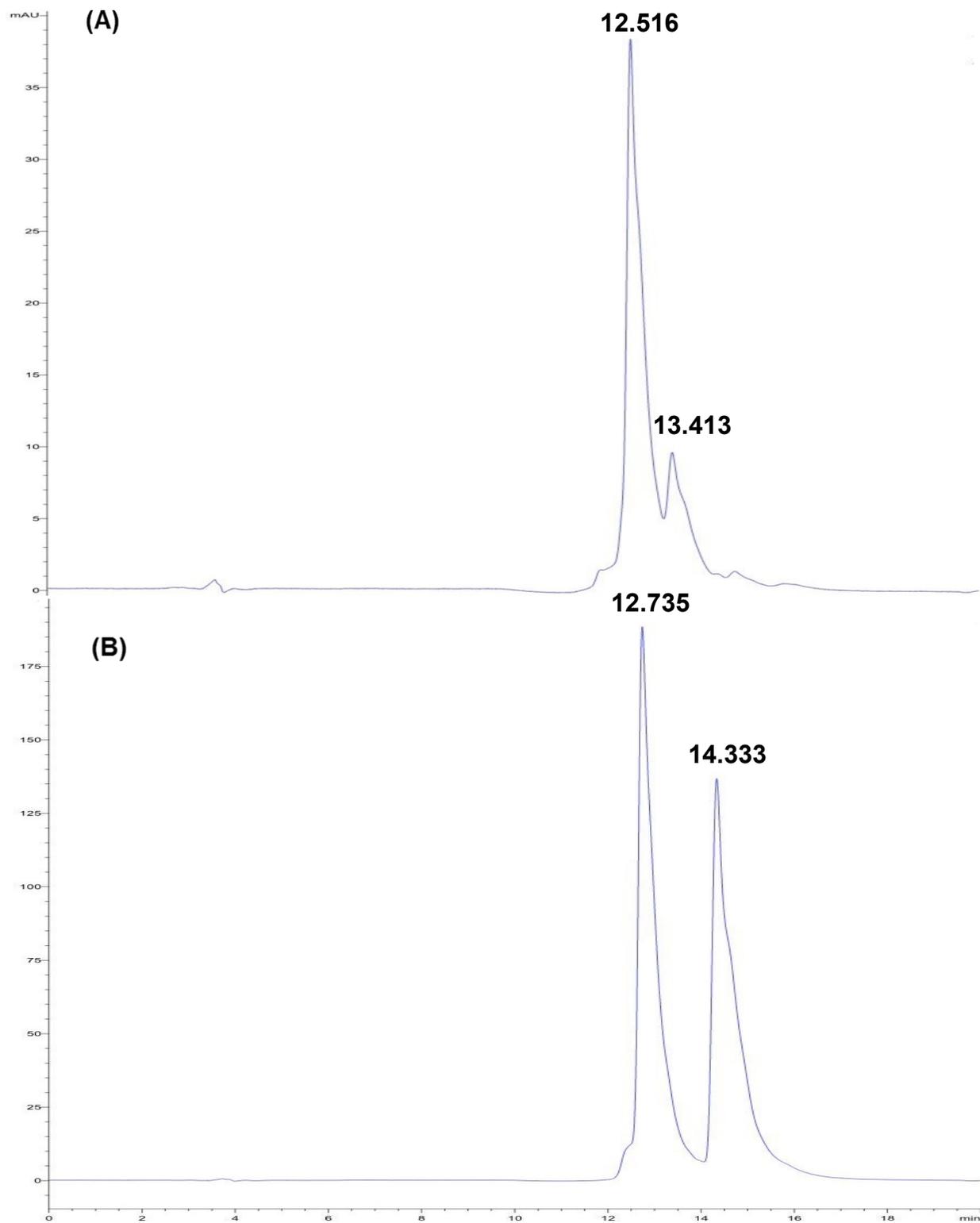
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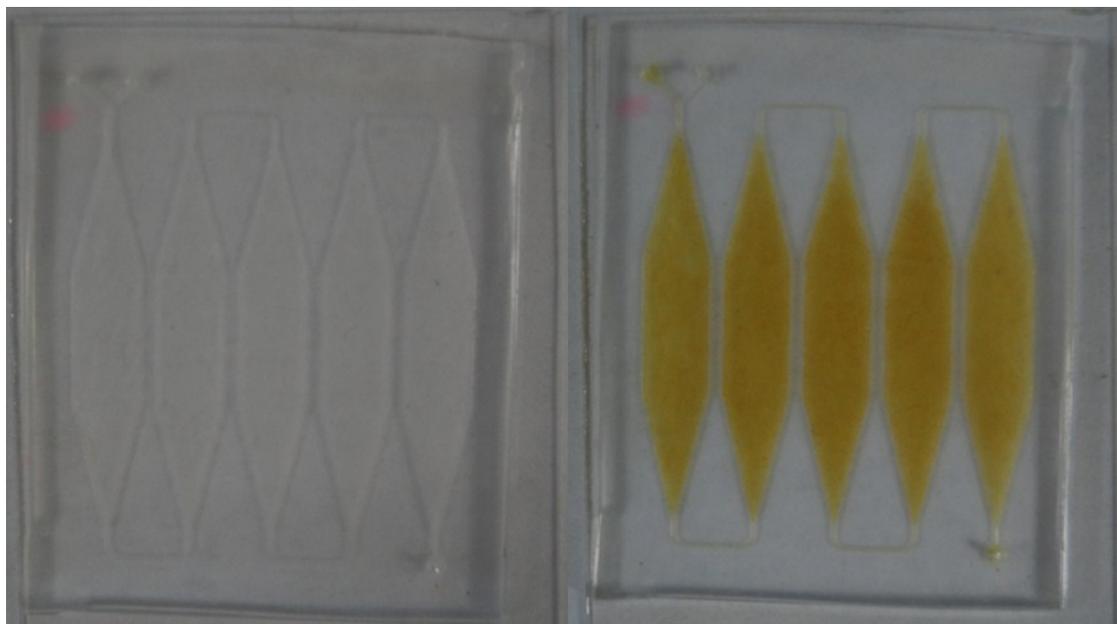
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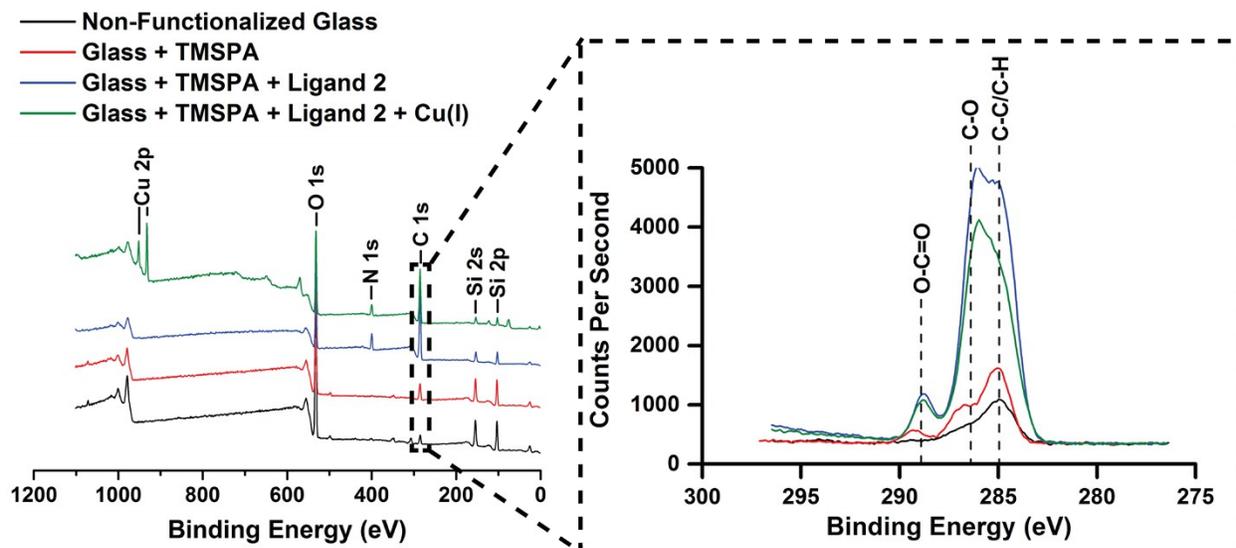
**Figure S1.** HPLC analysis of “click” reaction between Flu568-azide and propargylamine for 30 min on a functionalized microchip.



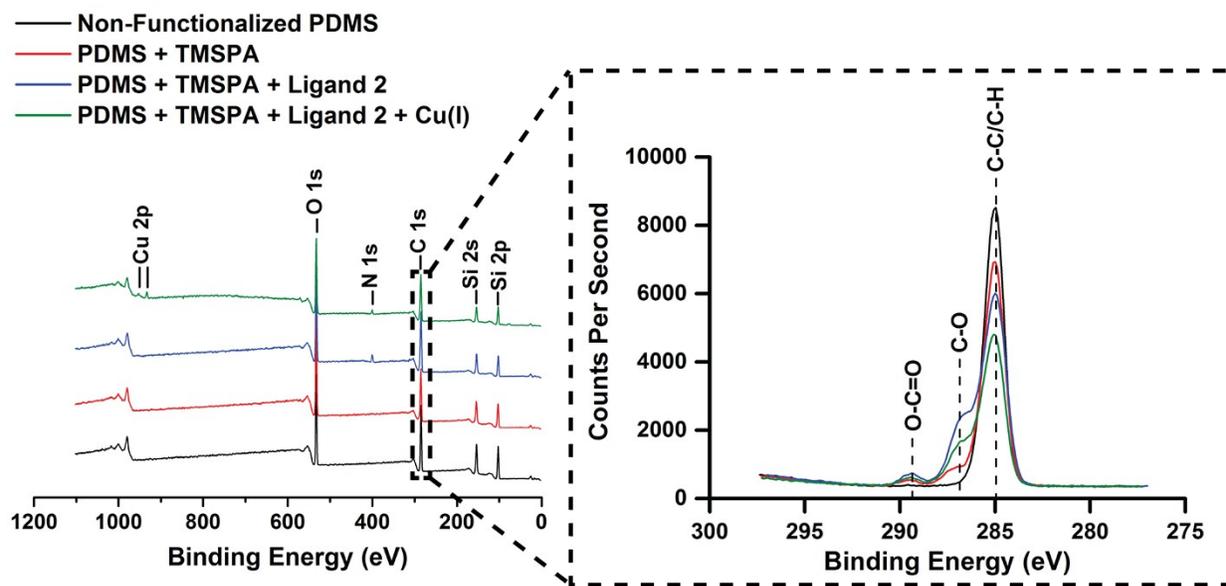
**Figure S2.** HPLC analysis of "click" reaction between Flu568-acetylene and cyclo(RGDfK)-N<sub>3</sub> for 30 min: (A) on a functionalized microchip; (B) conventionally (cat. 60%).



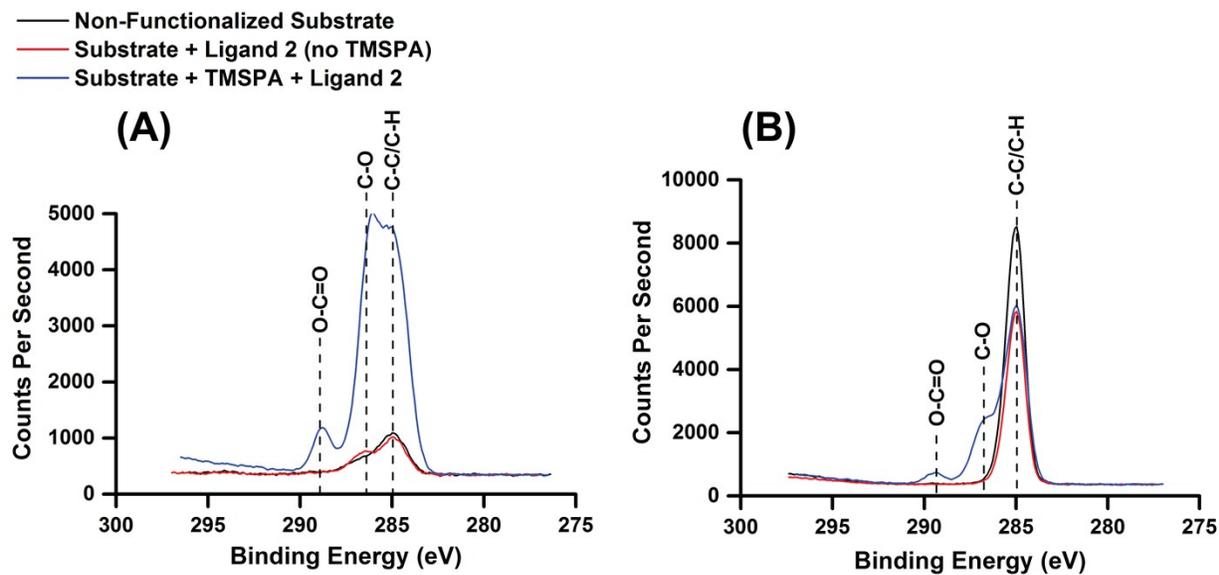
**Figure S3.** Picture of a functionalized PDMS microchip: (left) microchip functionalized with water-soluble TBTA ligand **2**; (right) a microchip functionalized with Cu(I)-ligand **2** complex.



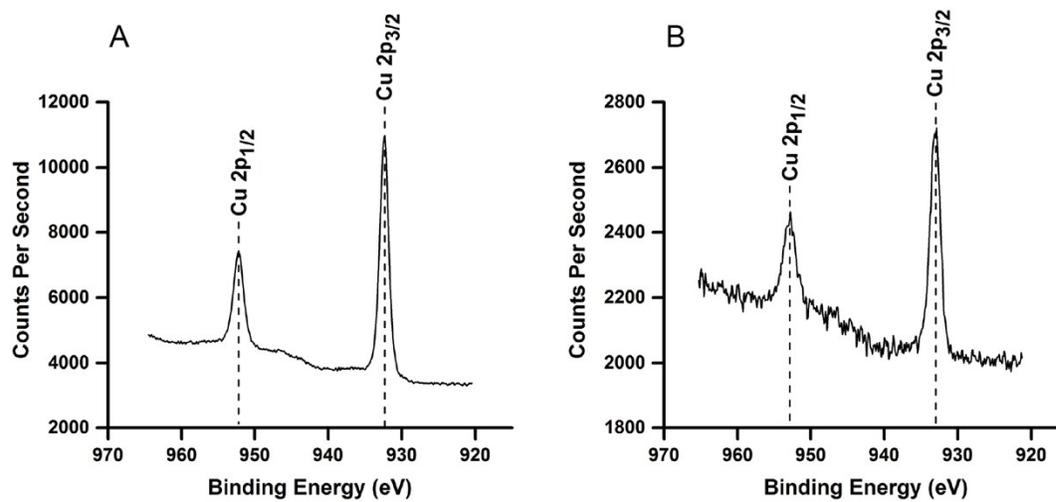
**Figure S4.** XPS survey spectra and carbon narrow scan spectra (inset) of glass sample at each stage of functionalization: (black) non-functionalized glass; (red) glass+TMSPA; (blue) glass+TMSPA+ligand 2; (green) glass+TMSPA+ligand 2+Cu(I).



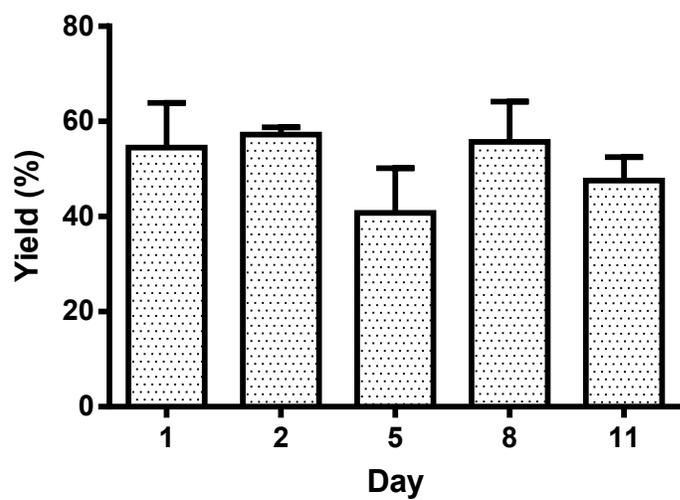
**Figure S5.** XPS survey spectra and carbon narrow scan spectra (inset) of PDMS sample at each stage of functionalization: (black) non-functionalized PDMS; (red) PDMS+TMSPA; (blue) PDMS+TMSPA+ligand 2; (green) PDMS+TMSPA+ligand 2+Cu(I).



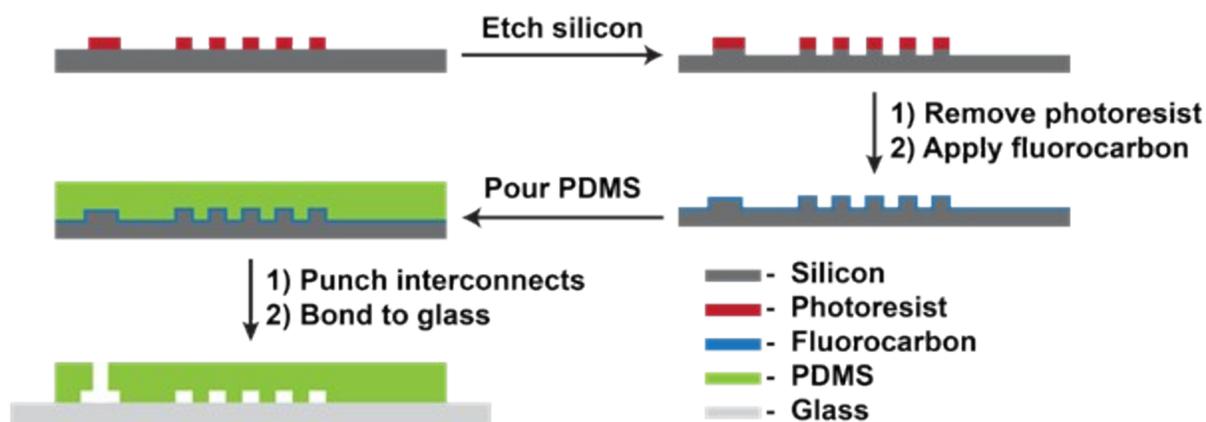
**Figure S6.** XPS carbon narrow scan spectra of (A) glass and (B) PDMS for (black) non-functionalized samples; (red) samples functionalized with ligand **2** without prior functionalization with TMSPA; (blue) samples functionalized with ligand **2** with prior functionalization with TMSPA.



**Figure S7.** Copper narrow scan spectra for (A) glass and (B) PDMS substrate functionalized with TMSPA, ligand **2**, and Cu(I).



**Figure S8.** “Click” reaction between Flu568-azide and propargylamine on a functionalized microchip for 15 min at 37 °C on different days (n=3-4).



**Figure S9.** Fabrication steps for making PDMS-glass microreactors: PDMS master was made by etching a silicon wafer with patterned photoresist by DRIE technique; the photoresist was removed and a PTFE-like layer (fluorocarbon) was applied to the etched silicon surface to prevent PDMS from adhering to the wafer; PDMS was poured onto the master and polymerized in an oven; interconnects were punched for inserting inlet and outlet tubing, and finally the PDMS imprint was bonded to glass.