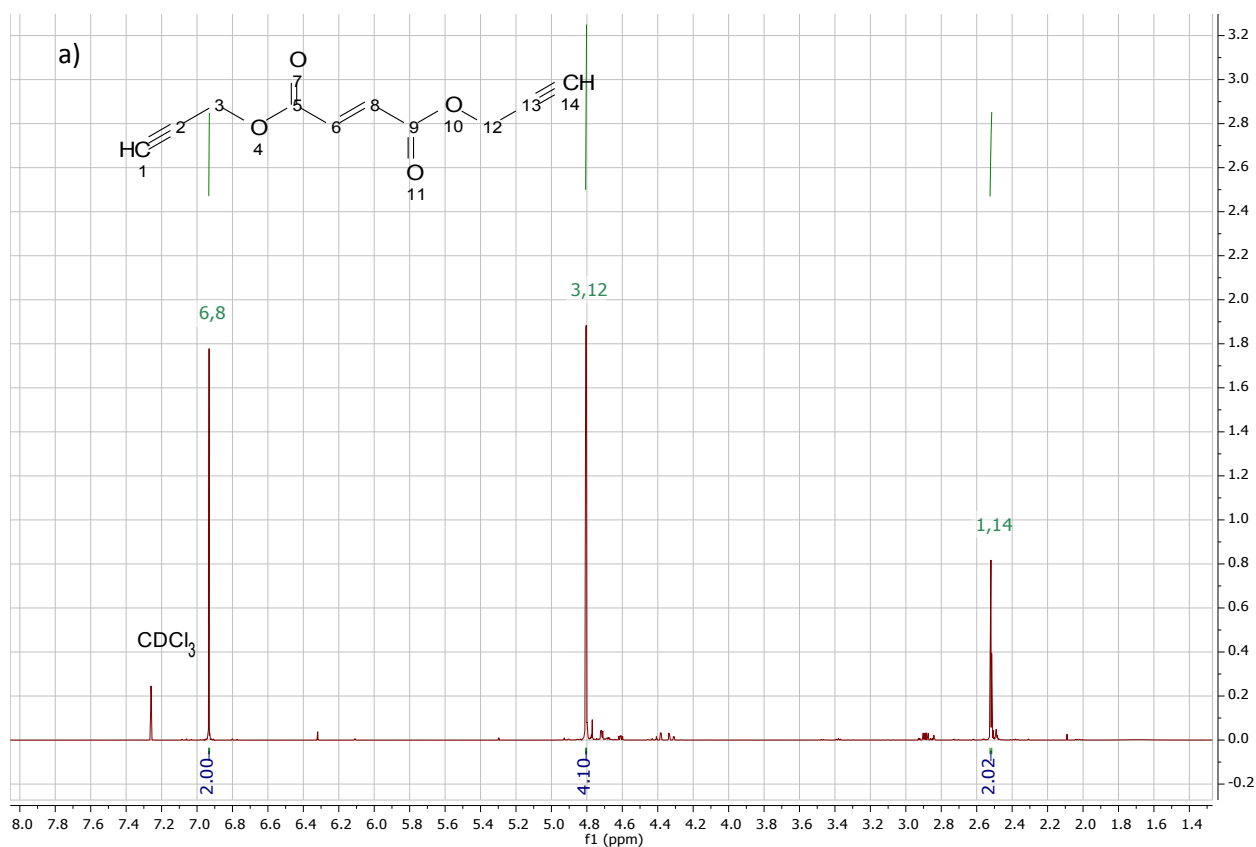


Thiol-yne chemistry for 3D printing: exploiting off stoichiometric route for selective functionalization of 3D objects

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SUPPORTING INFORMATION



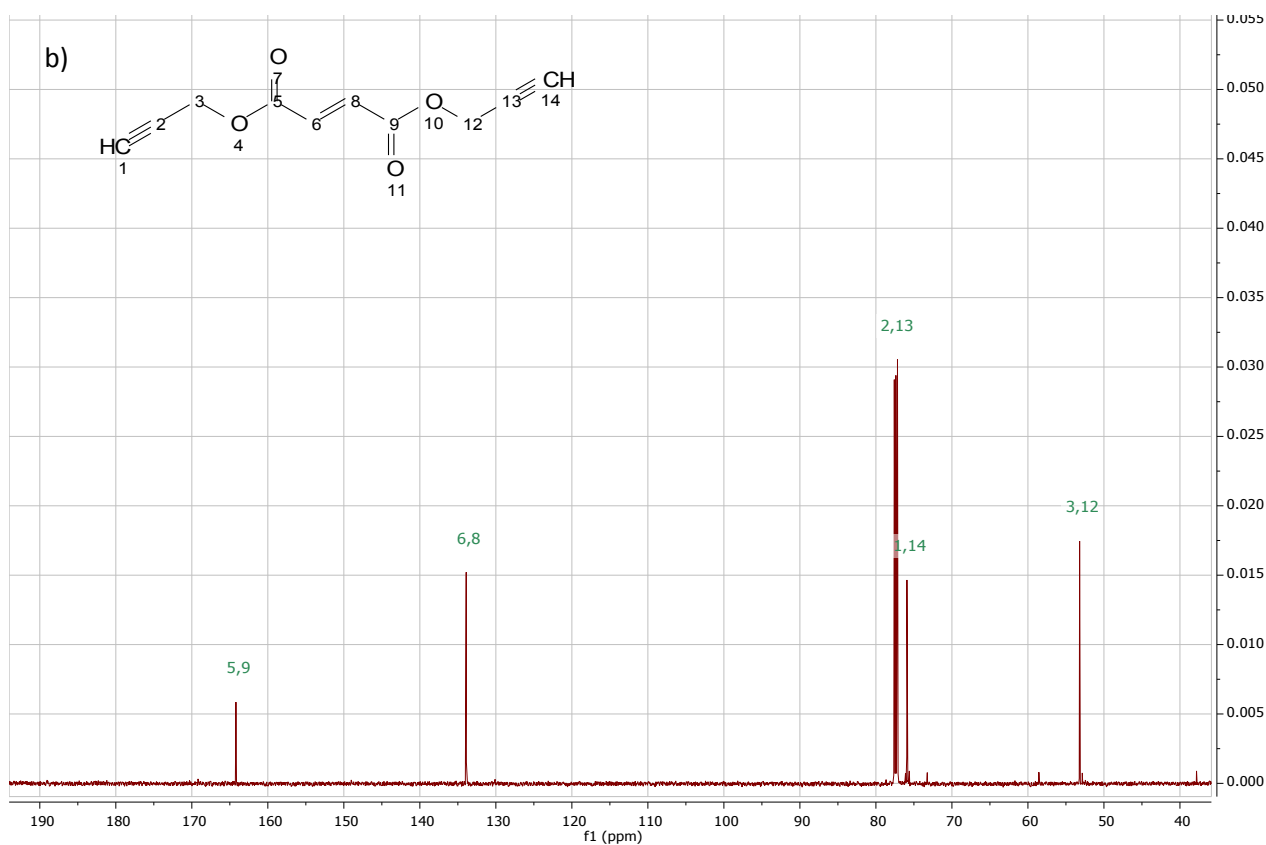


Figure S1 NMR Spectra. a) $^1\text{H-NMR}$ (CDCl_3); b) $^{13}\text{C-NMR}$ (CDCl_3)

SQ_N3_2#14 RT: 0.25 AV: 1 NL: 7.46E6
 F: FTMS - p ESI Full ms [600.0000-800.0000]

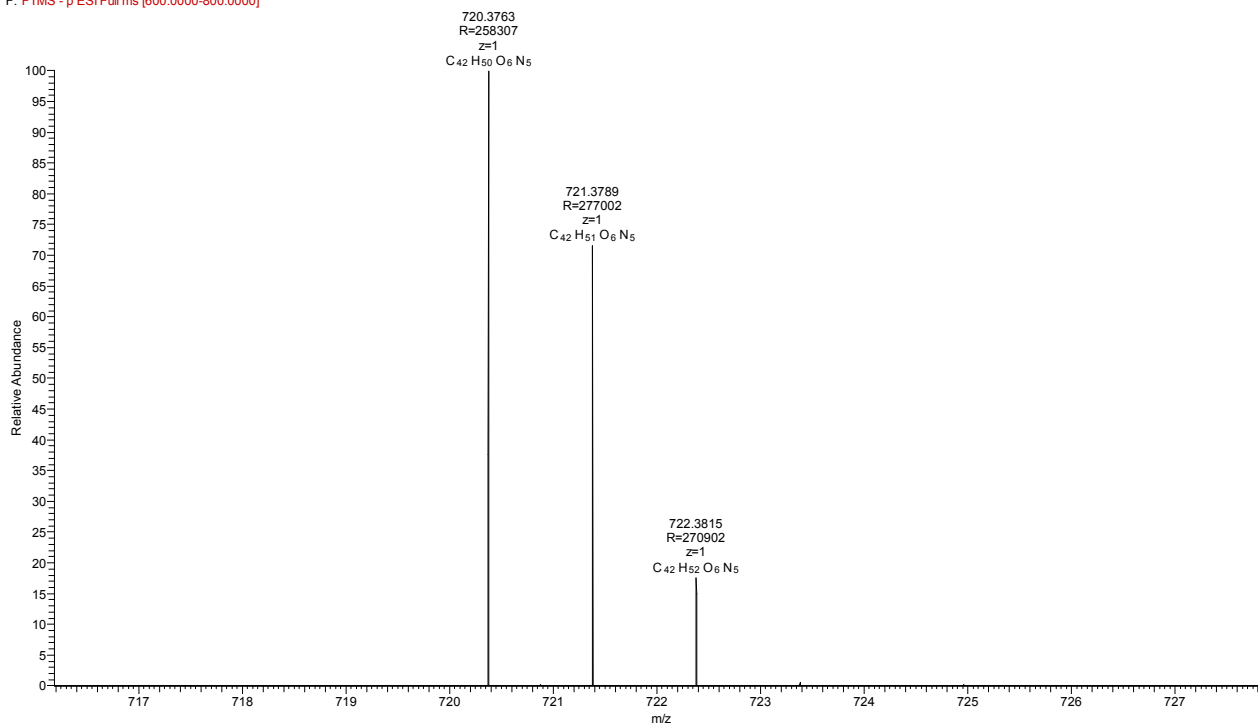
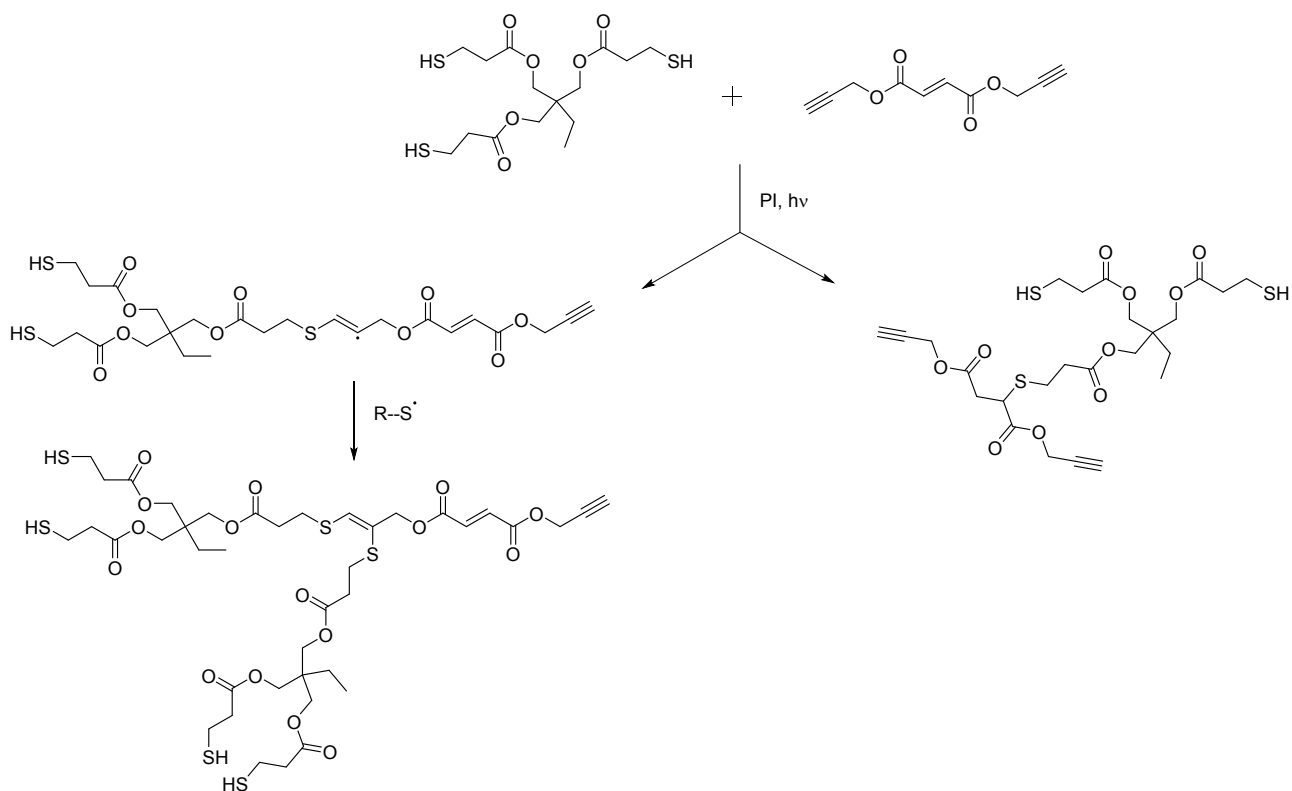


Figure S2 HR-ESI-MS of 4-((1-(10-azidodecyl)-5-carboxy-3,3-dimethyl-3H-indol-1-ium-2-yl)methylene)-2-(((E)-1-butyl-5-carboxy-3,3-dimethylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (5)



Scheme S1 Thiol-Yne and thiol-ene reactions that can occur between the two monomers.

The EQ formulation was calculated in order to have the same amount of SH groups from the thiol and possible bonds from the reactive groups present in the alkyne monomer.

The OSTY ones have a relative ratio of 60:40 and 40:60 between the number of SH and possible bonds in the alkyne monomer.

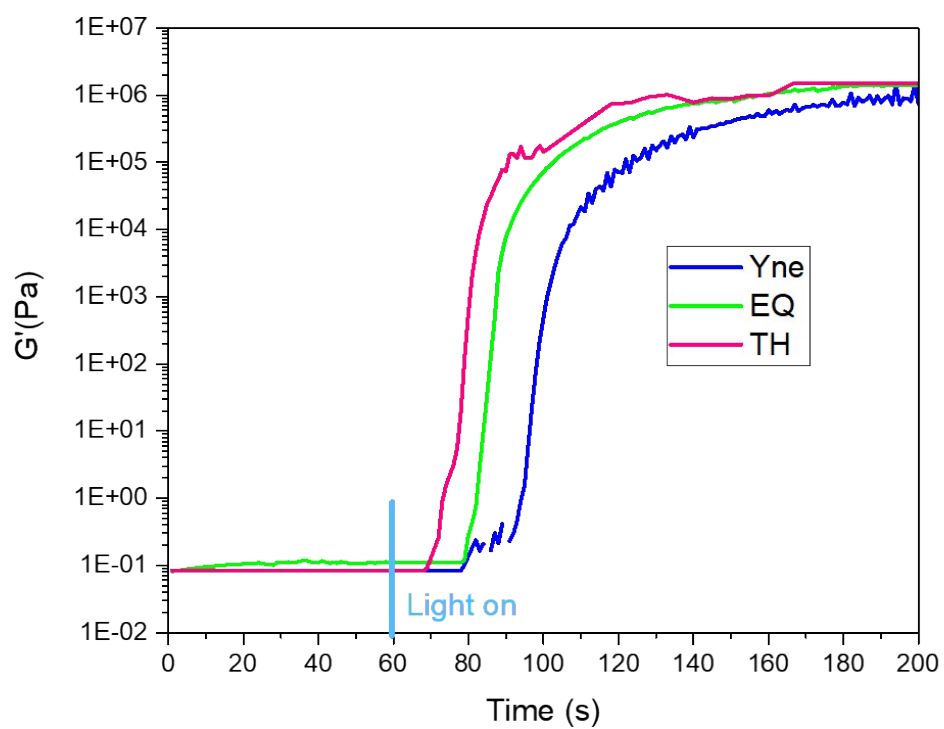


Figure S3 Photorheology test

Table S1. Layer exposure time for the different formulations.

| Sample | LAYER EXPOSURE TIME (sec) |
|--------|---------------------------|
| YNE | 15 |
| EQ | 6 |
| TH | 5 |

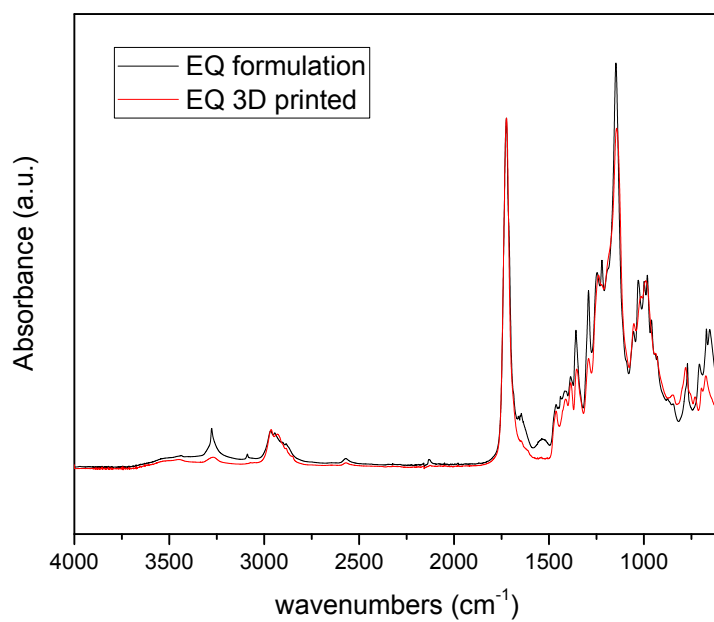


Figure S4 ATR spectra of EQ liquid formulation and EQ 3D printed sample

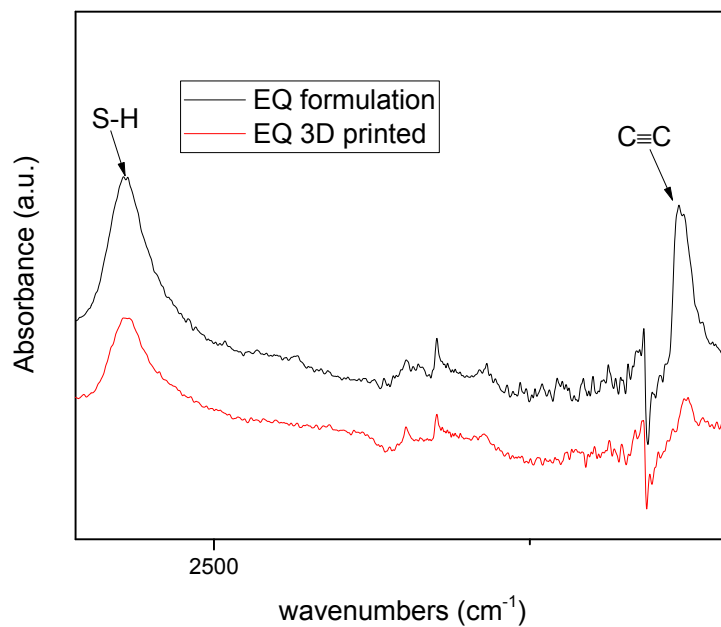


Figure S5 ATR spectra of EQ liquid formulation and EQ 3D printed sample in the SH and C≡C range

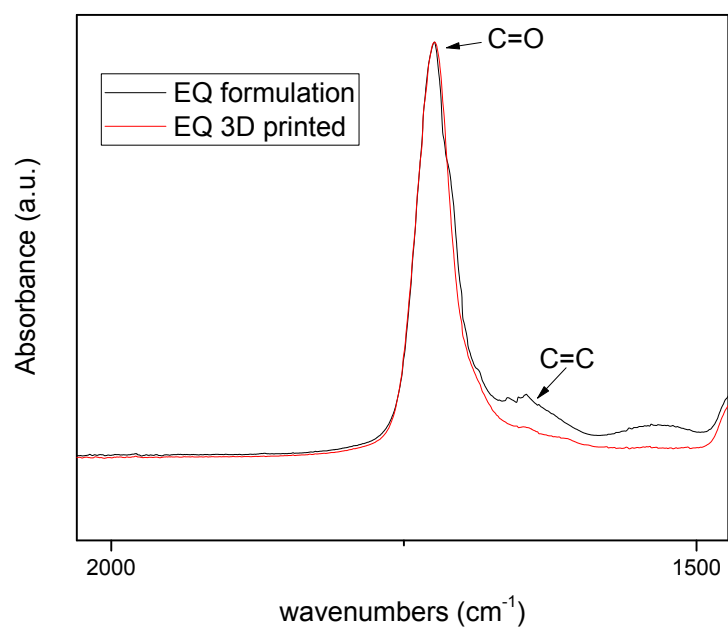


Figure S6 ATR spectra of EQ liquid formulation and EQ 3D printed sample in the carbonyl and C=C range

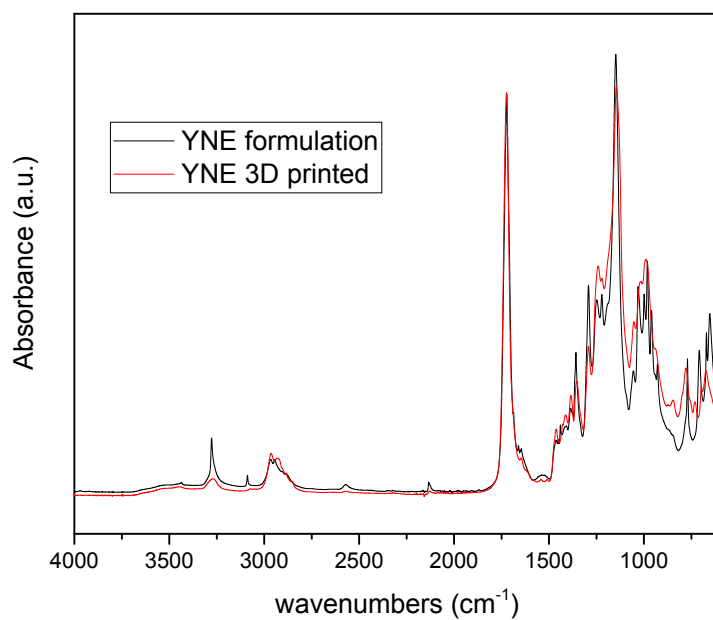


Figure S7 ATR spectra of YNE liquid formulation and YNE 3D printed sample

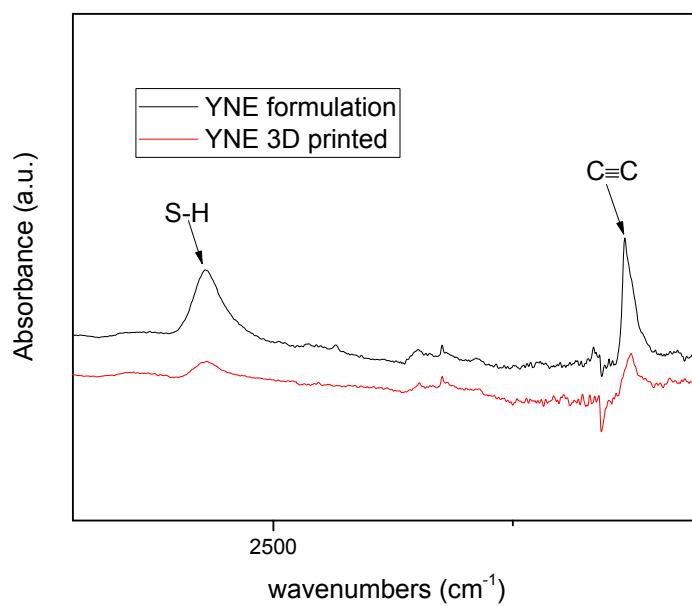


Figure S8 ATR spectra of YNE liquid formulation and YNE 3D printed sample in the SH and C≡C range

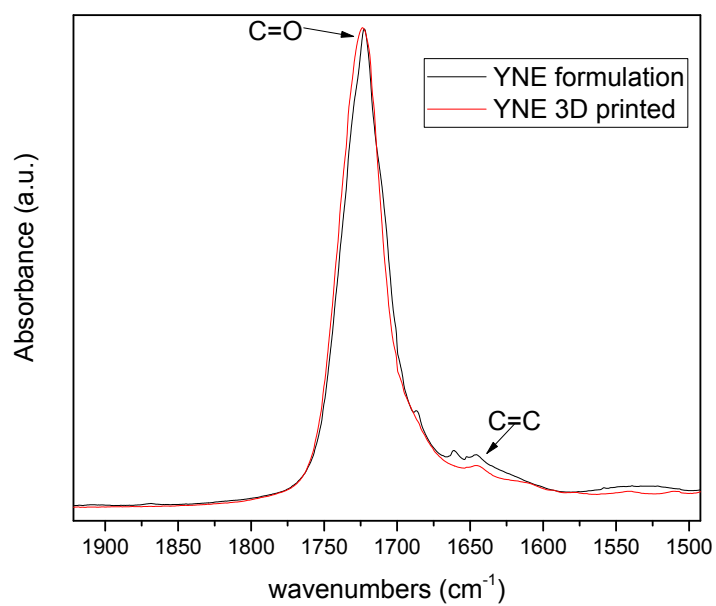


Figure S9 ATR spectra of YNE liquid formulation and YNE 3D printed sample in the carbonyl and C=C range

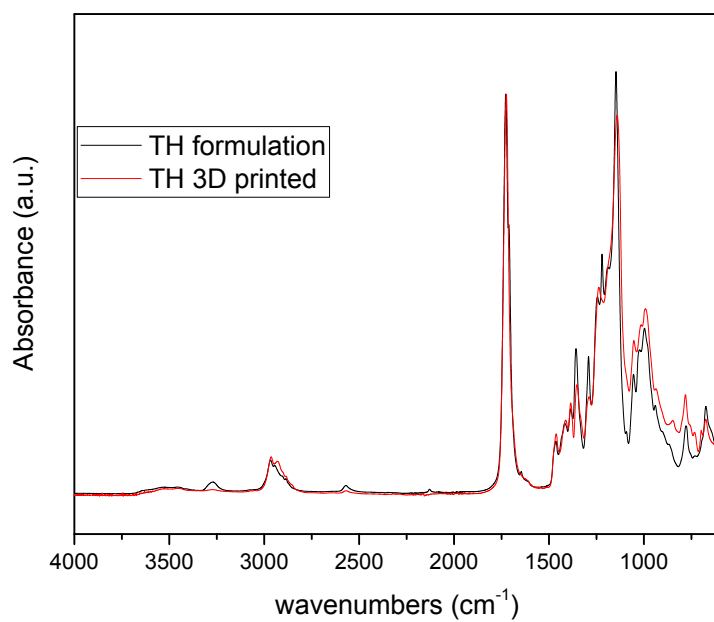


Figure S10 ATR spectra of TH liquid formulation and TH 3D printed sample

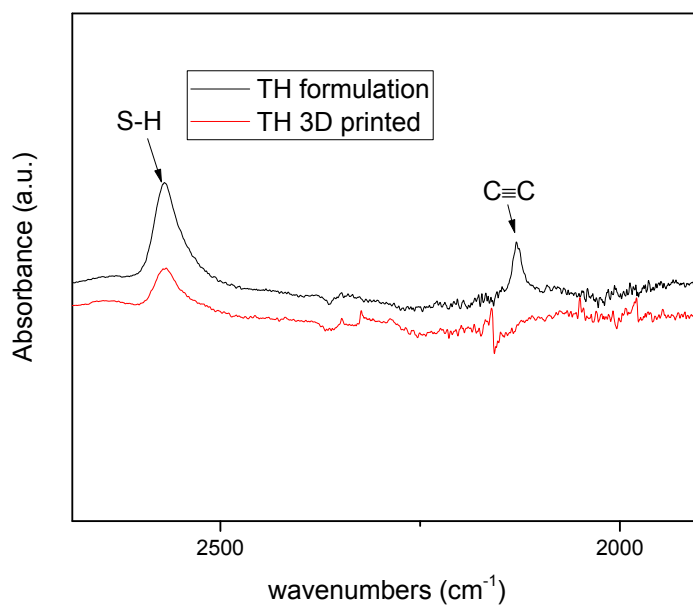


Figure S11 ATR spectra of TH liquid formulation and TH 3D printed sample in the SH and C≡C range

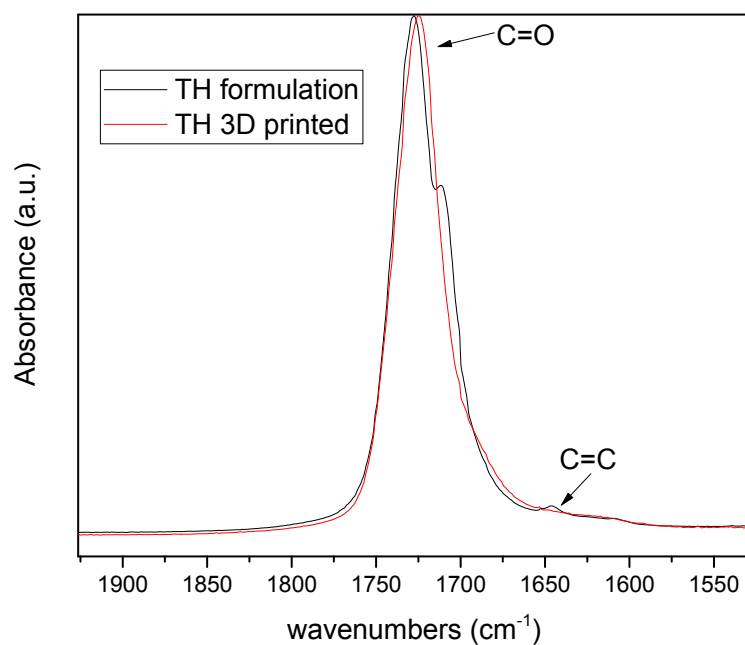
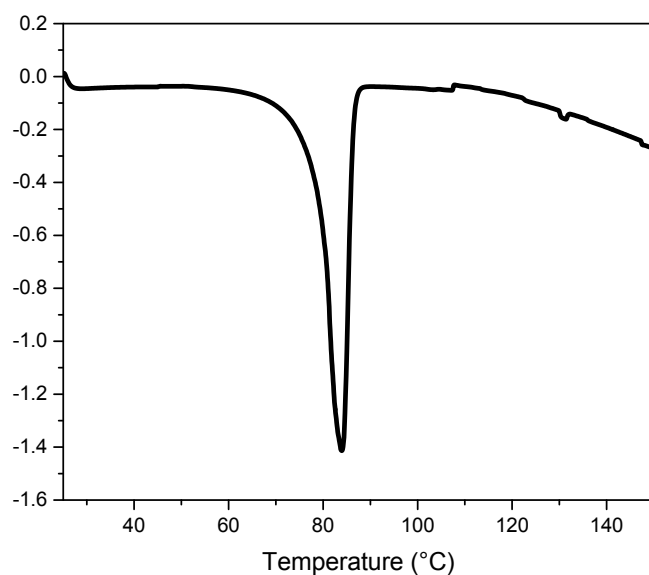


Figure S12 ATR spectra of TH liquid formulation and TH 3D printed sample in the carbonyl and C=C range



FigureS13 DSC plot of the alkyne monomer