

Electronic Supplementary Information (ESI)

One-component rapid Norrish Type II photoinitiation of photo-CuAAC polymer networks

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Example FTIR of monomer resin and final crosslinked product

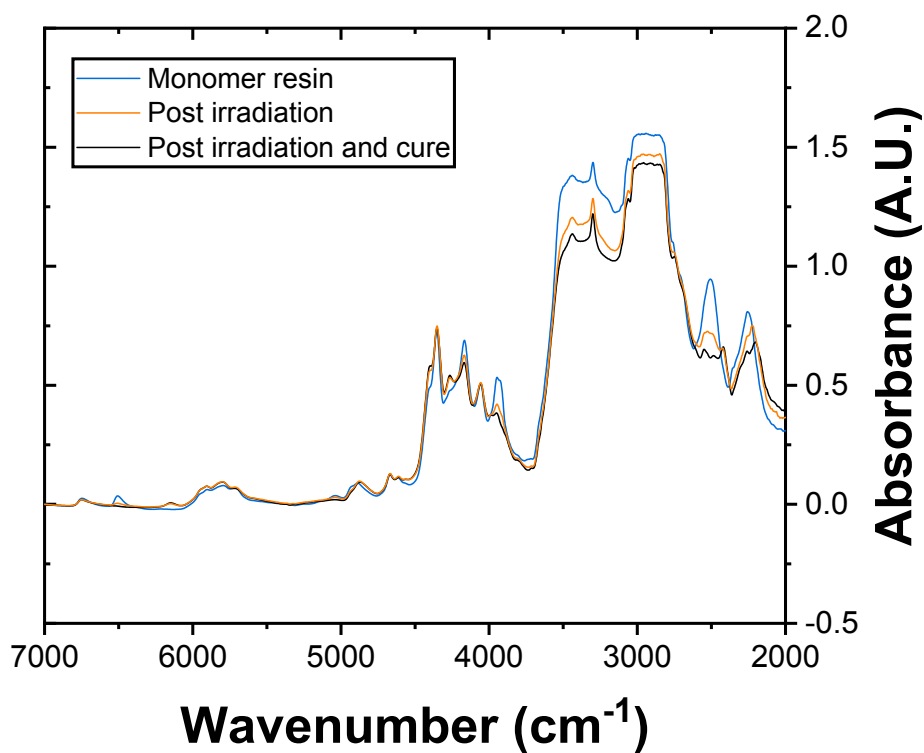


Figure S1. The resin contains N1 alkyne with the diazide monomer in a 1:1 functional group ratio. The formulations contain 1.5 mol% CuCl₂-PMDTA 0.6 mol% CQ. The IR spectra was collected of this monomer resin prior to polymerization. The monomer resin was then irradiated using blue-light (470 nm) at 30 mW cm⁻² intensity and a 'post-irradiation' spectra was collected after monitoring the polymerization kinetics. Upon irradiation, a post cure was performed at 70-80 °C and the final spectrum was collected of the photo-CuAAC bulk network film.

Solvated networks of N1 exhibiting final conversion increase from vitrification

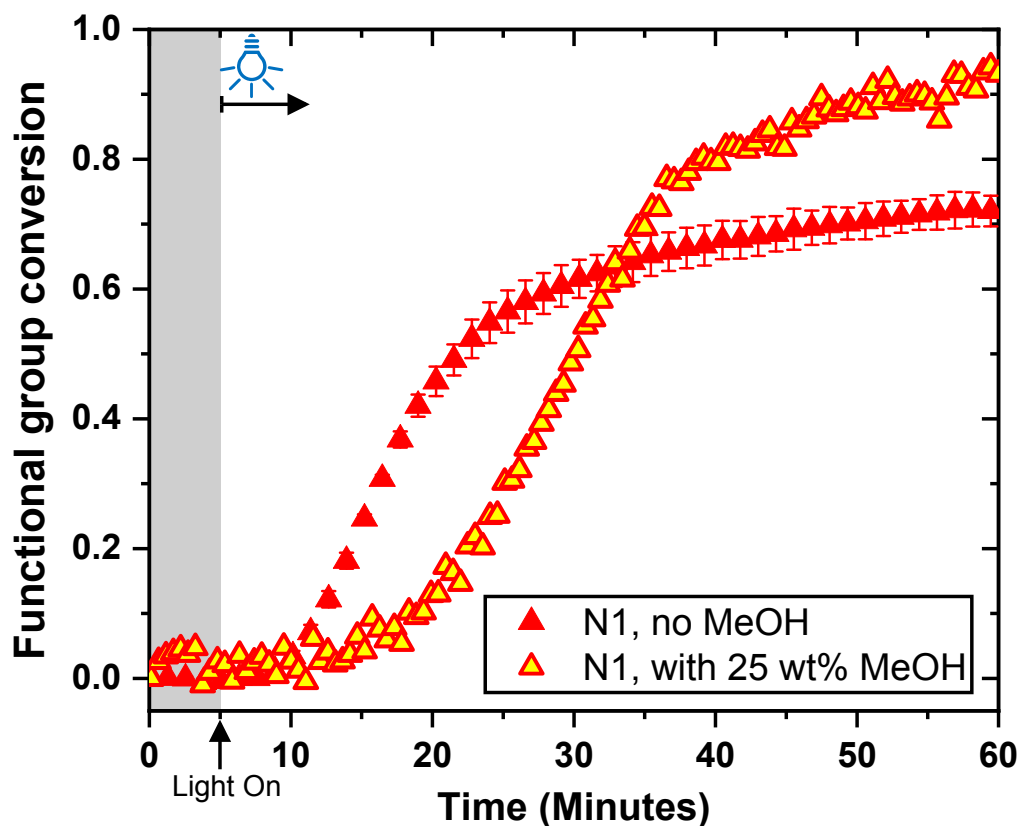


Figure S2. Real-time functional group conversions of photoCuAAC reaction between the diazide monomer and N1 (i.e., tripropargyl amine) in neat (red filled triangle) and 25 wt% methanol (yellow filled triangle) to assess vitrification. The formulation was mixed as described in section 2. Functional group conversions are determined using real-time near-infrared spectroscopy by monitoring the overtone of the C-H stretch of the alkyne functional group (i.e., $6540\text{--}6460\text{ cm}^{-1}$). All formulations are continuously irradiated after 5 minutes in dark (marked by the shaded region) with 470 nm blue-light at an intensity of 30 mW cm^{-2} .

Network polymerization with N1 and external tertiary amine

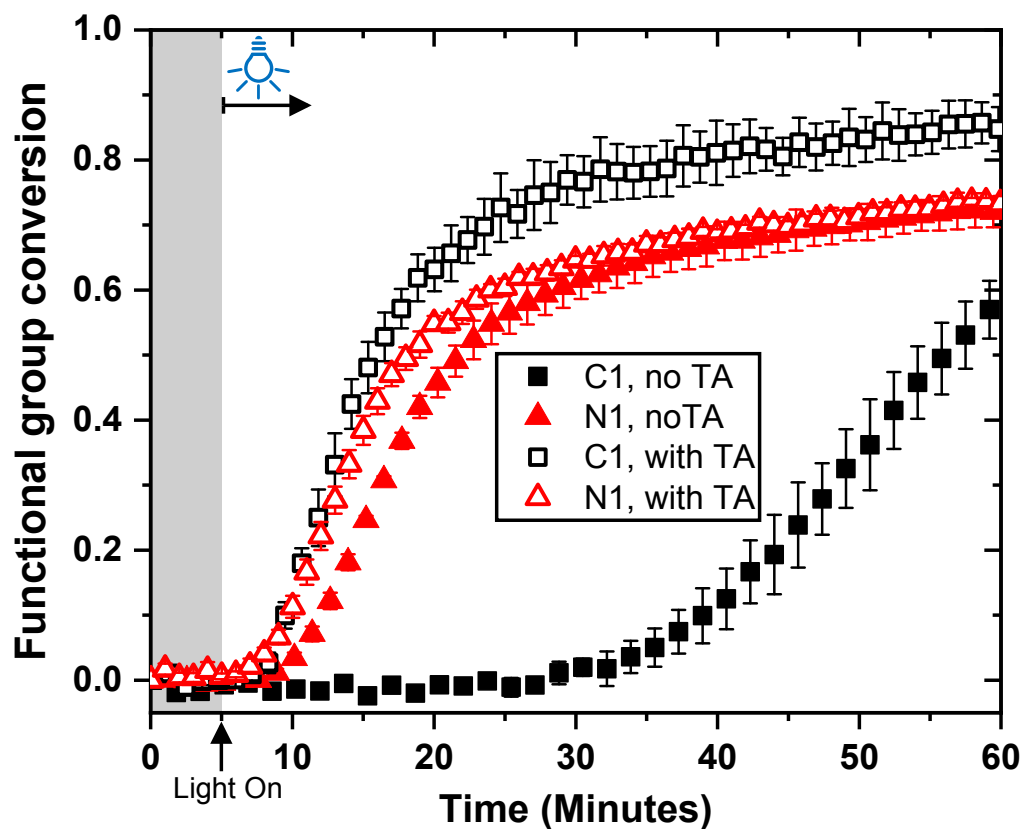


Figure S3. Functional group conversion of a resin containing the diazide monomer and N1 or C1 with and without the presence of a tertiary amine. Polymerization kinetics were monitored using real-time near infrared (NIR) spectroscopy. Functional group conversions are determined by monitoring the overtone in the C-H alkyne stretch ($6540\text{-}6460\text{ cm}^{-1}$). All formulations are irradiated with 470 nm blue-light at 30 mW cm^{-2} after 5 minutes in dark (marked by the shaded region).

Hybrid network polymerization with C1 and N1

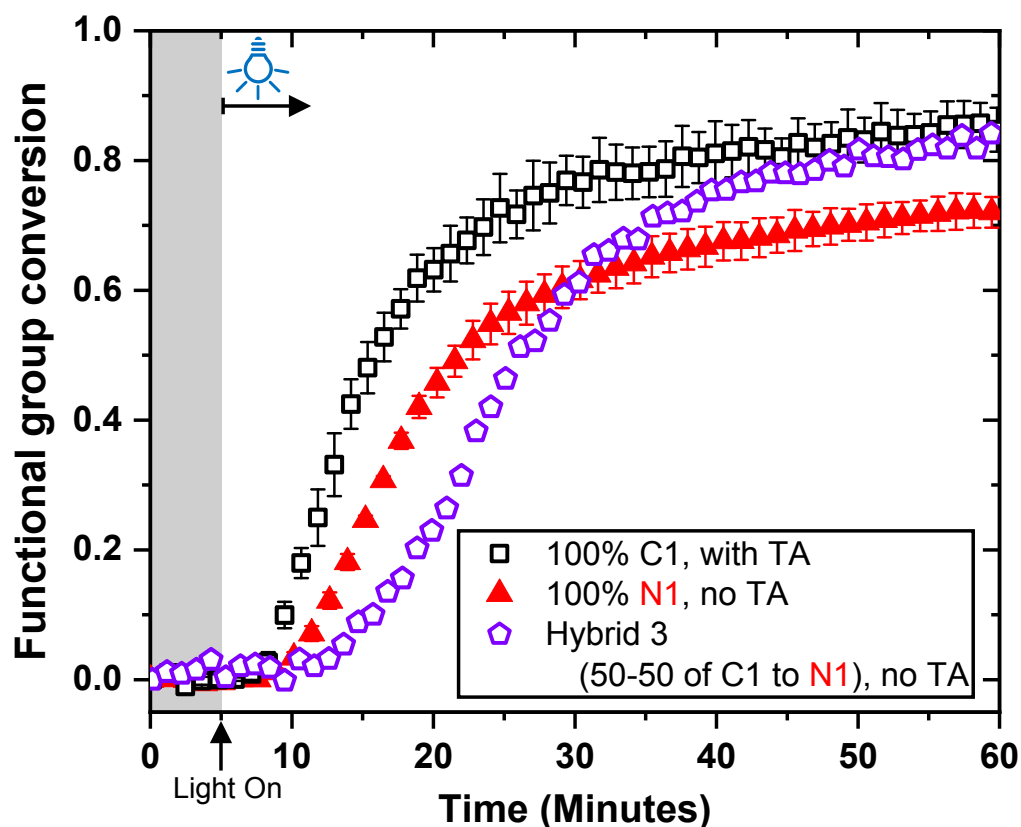


Figure S4. Functional group conversion for copolymerization of the diazide monomers and both C1 and N1 (i.e., a 'hybrid' system) as compared with formulations with diazide monomer and only C1 and TA or diazide monomer and only N1 and no TA. Photo-CuAAC network polymerization kinetics with hybrid networks using alkyne C1 and N1, in presence or absence of catalytic amount of accelerating amine (1.2 mol% of amine to total functional groups). Functional group conversions are determined by monitoring the C-H overtone of the alkyne ($6540\text{--}6460\text{ cm}^{-1}$) functional group. All formulations are irradiated with 470 nm blue-light at 30 mW cm^{-2} after 5 minutes in dark (marked by the shaded region).

Polymerized photoCuAAC film post irradiation

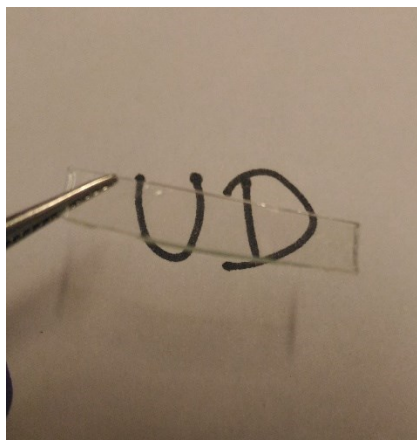


Figure S5. The image of a bulk photo-CuAAC network film generated using N3 alkyne and azide from **Figure 3** without the addition of TA. Irradiation was performed using 470 nm blue-light at an intensity of 30 mW/cm². The resultant glassy material is completely defect (bubble) free and clear, evident of its transparent nature.

NMR spectroscopy of the synthesized monomers

Note: Materials and synthetic procedures are shown in the main text.

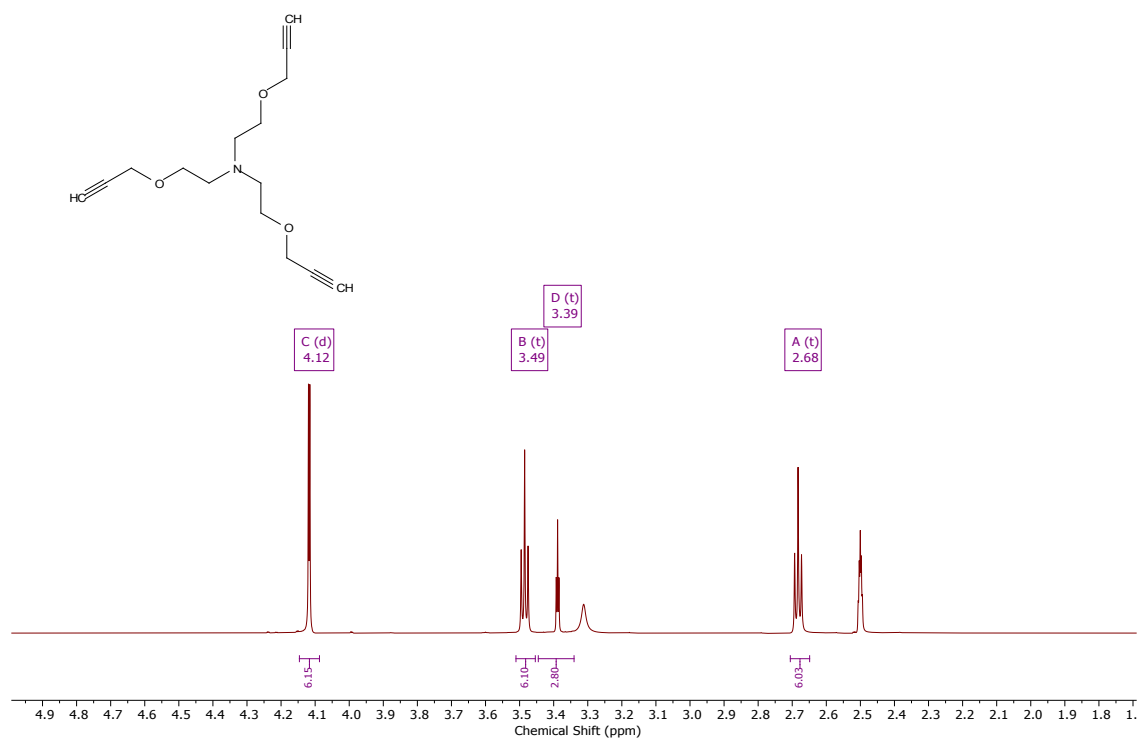


Figure S6. ¹H NMR spectrum of alkyne monomer N2

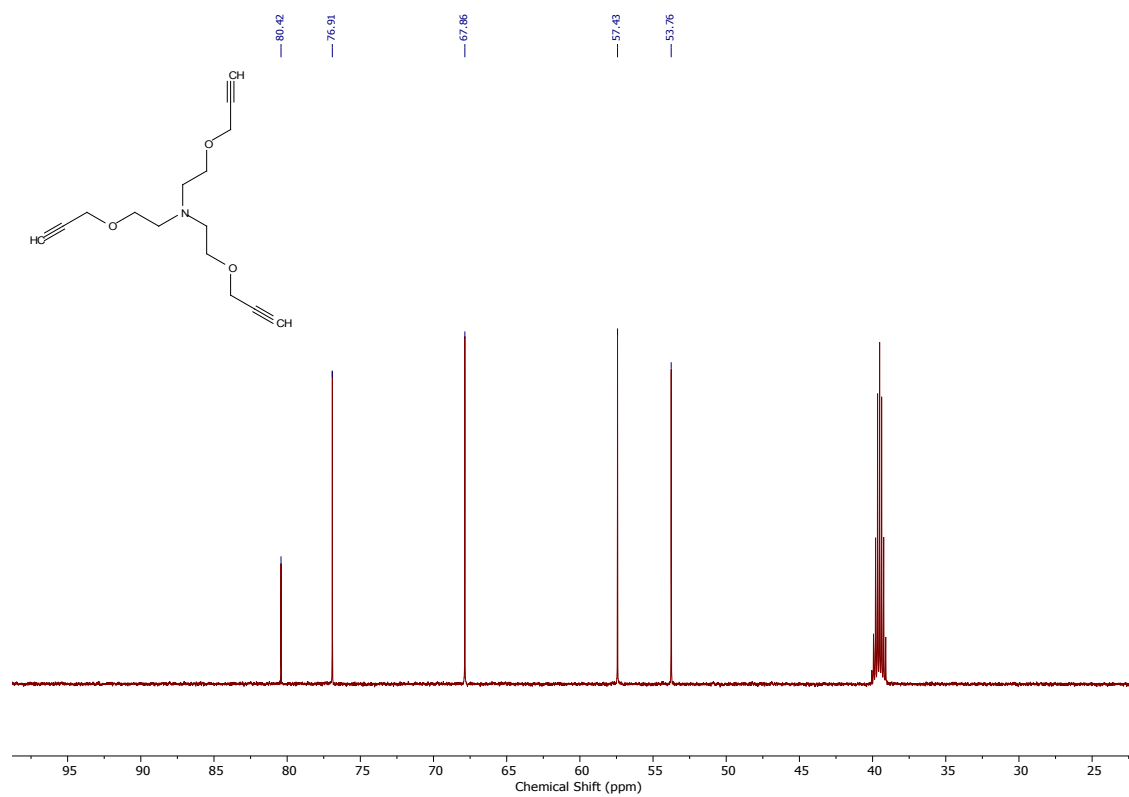


Figure S7. ^{13}C NMR spectrum of alkyne monomer N2

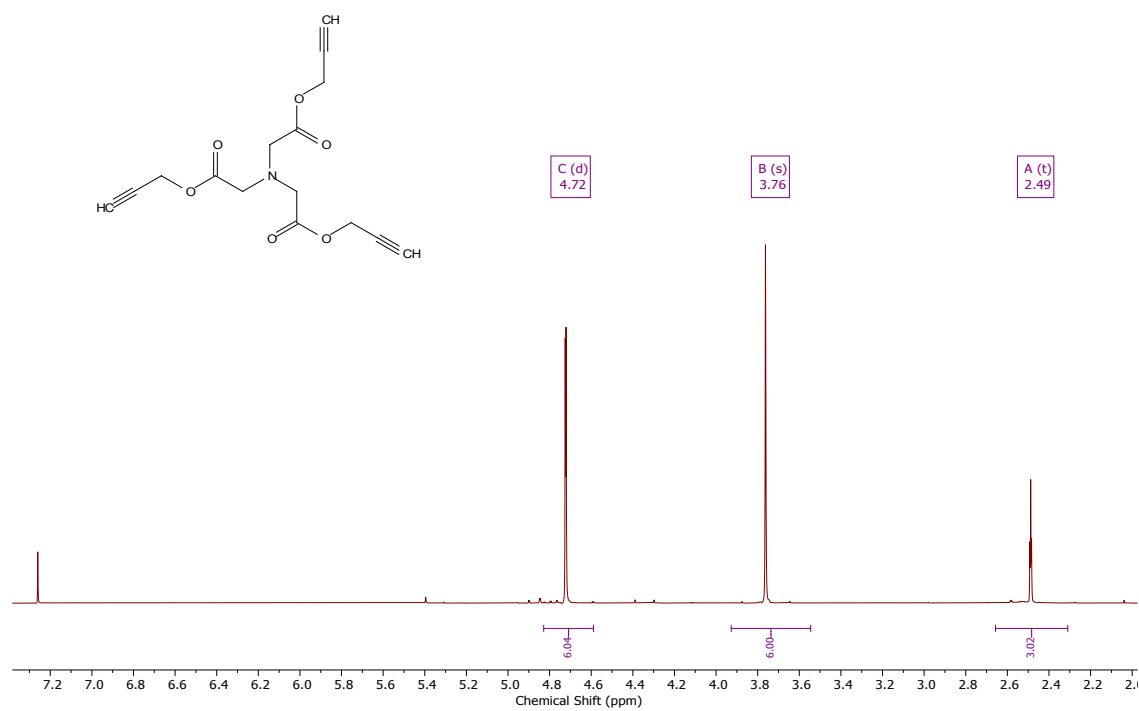


Figure S8. ¹H NMR spectrum of alkyne monomer N3

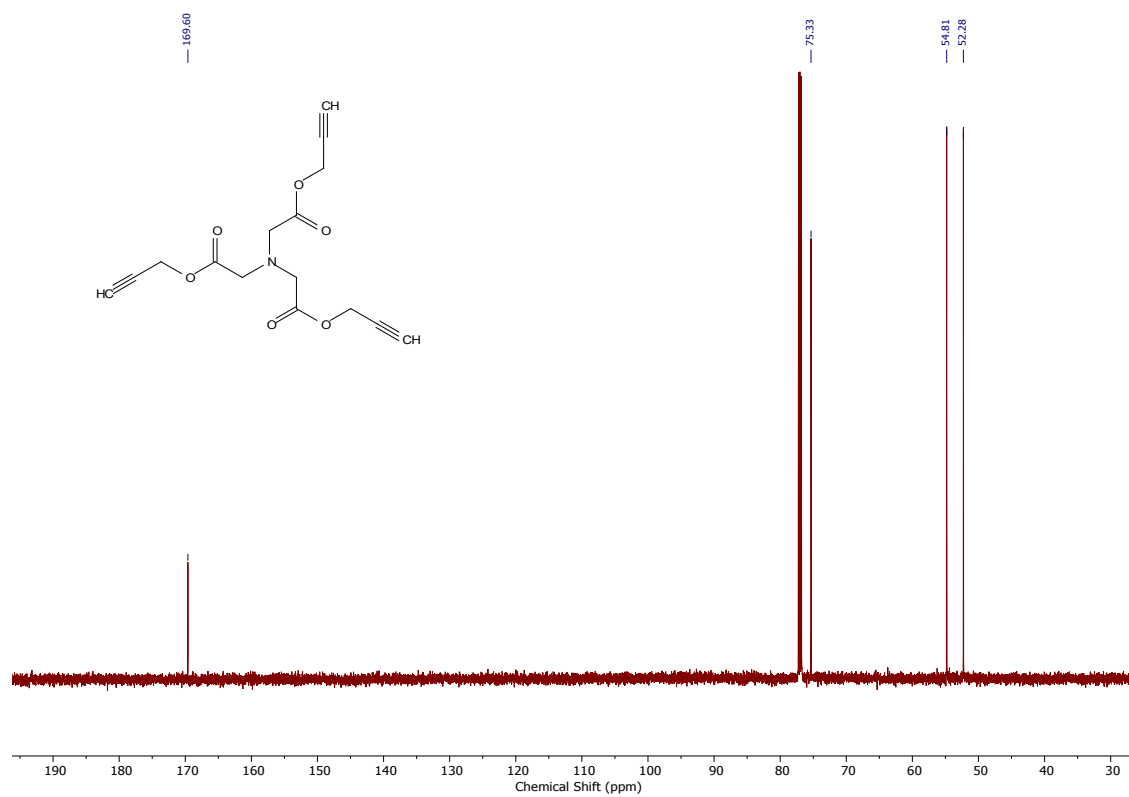


Figure S9. ¹H NMR spectrum of alkyne monomer N3