SUPPLEMENTARY INFORMATION

Photoinitiator-free light-mediated crosslinking of dynamic polymer and pristine protein networks

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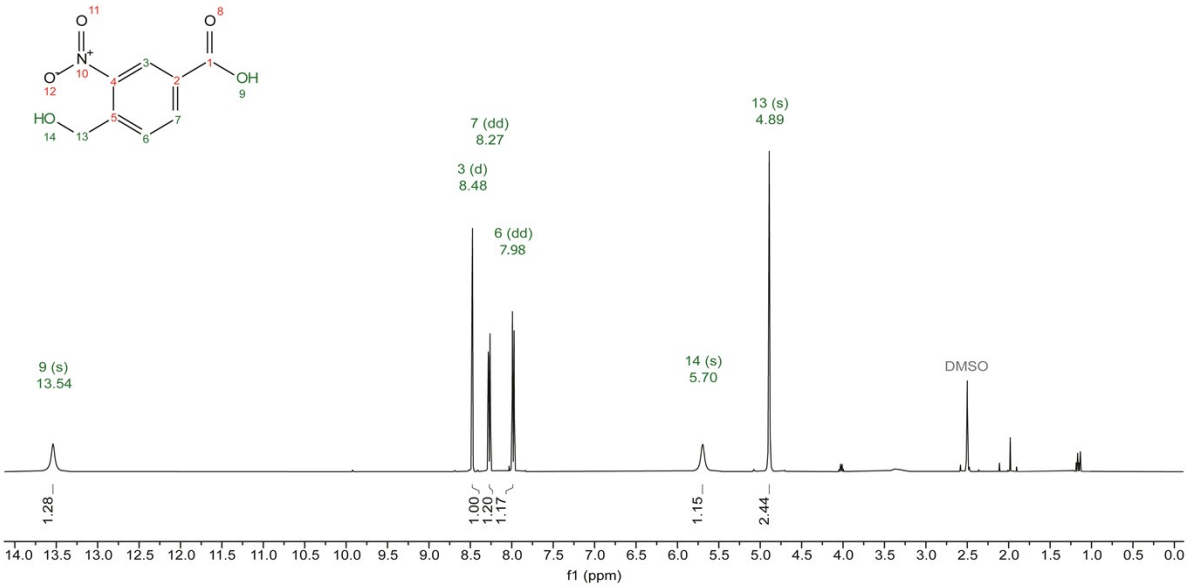

Figure S1. 4-(Hydroxymethyl)-3-nitrobenzoic acid (*o*NBA) ^{1}H NMR in DMSO-d_6.

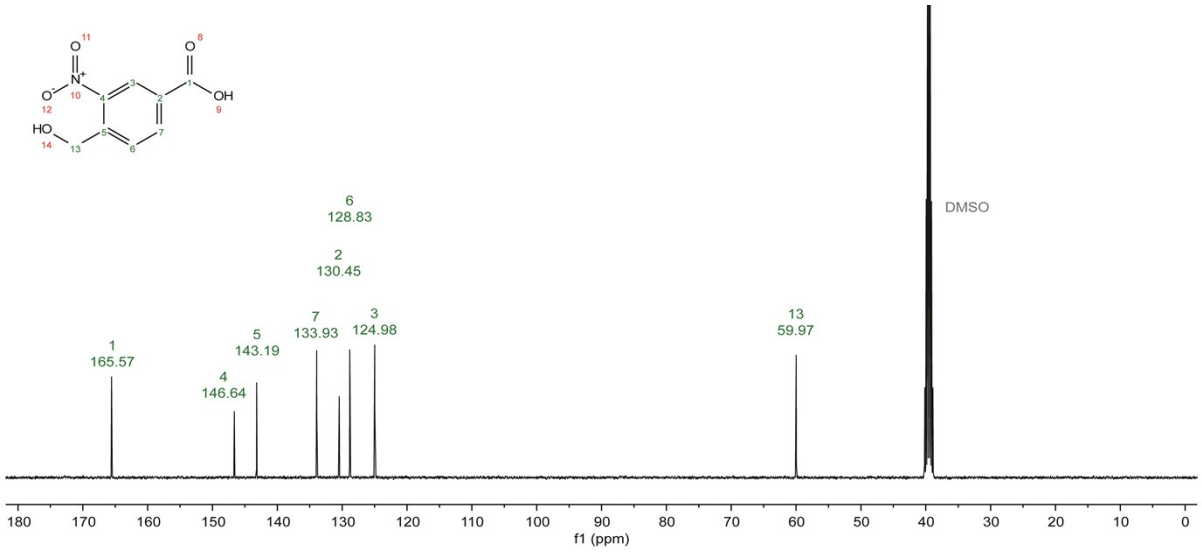

Figure S2. 4-(Hydroxymethyl)-3-nitrobenzoic acid (*o*NBA) ^{13}C NMR in DMSO-d_6.

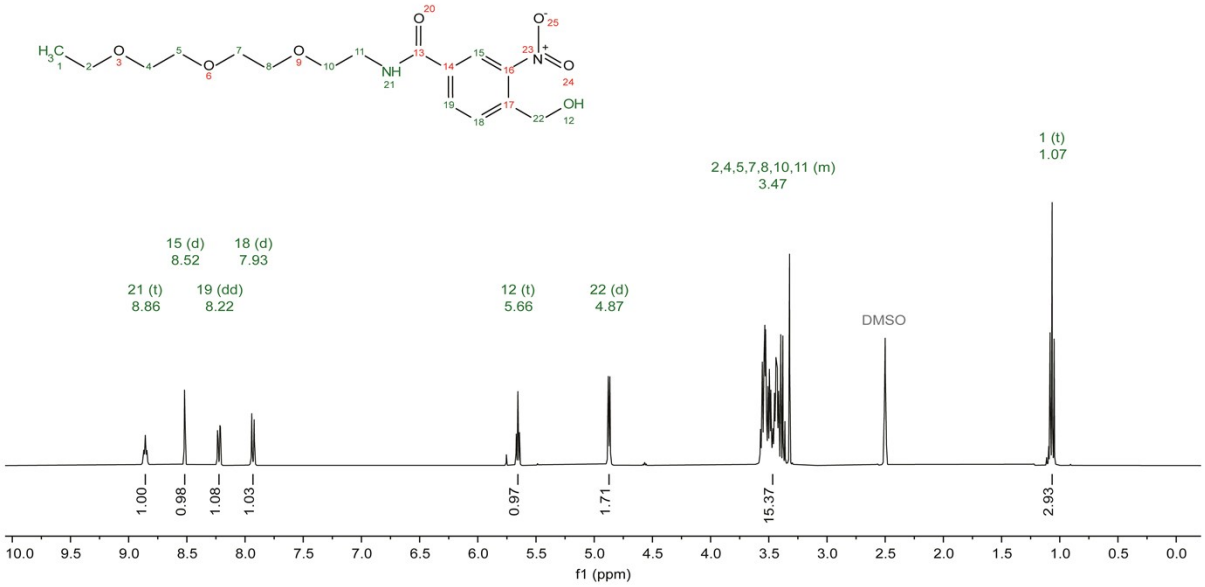

Figure S3. Monofunctional *o*NBA (m-*o*NBA) ^{1}H NMR in DMSO-d_6.

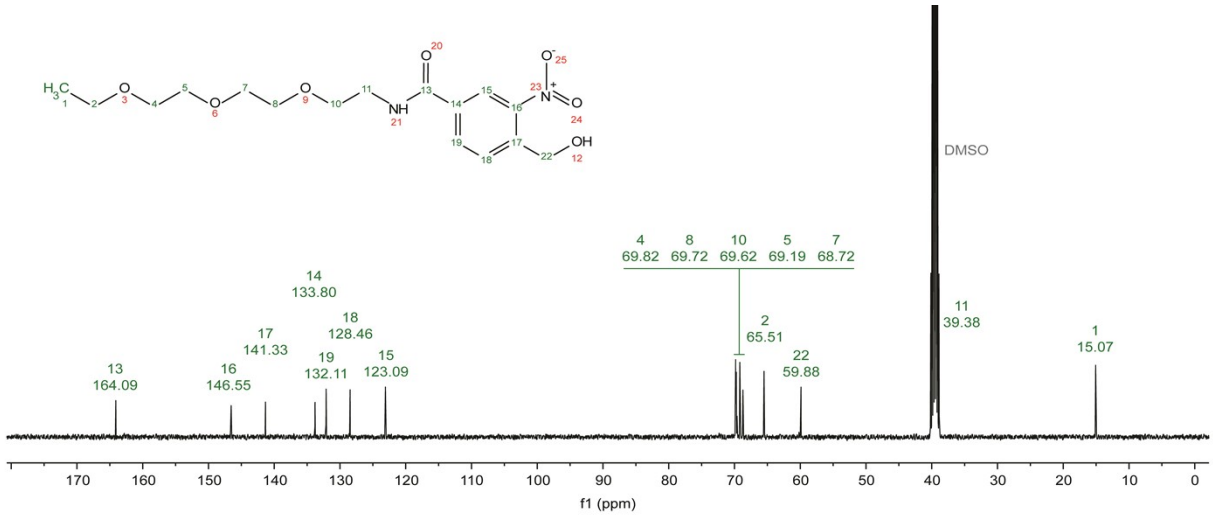

Figure S4. Monofunctional *o*NBA (m-*o*NBA) ^{13}C NMR in DMSO-d_6.

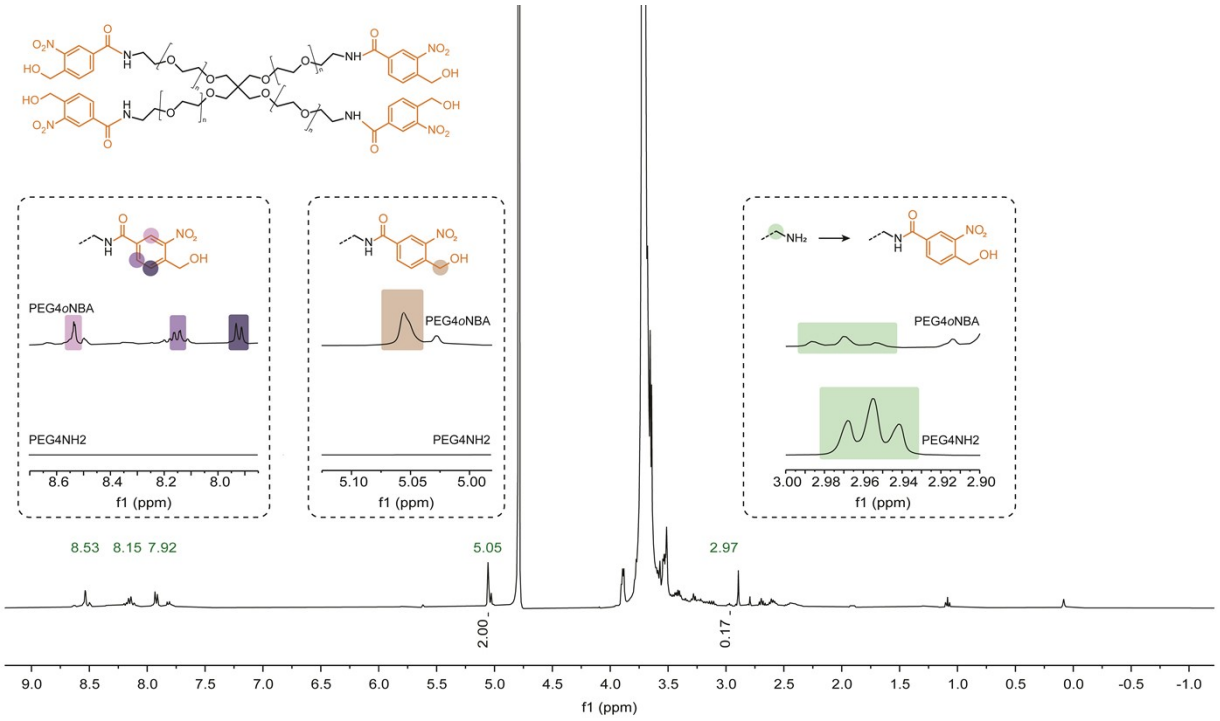

Figure S5. ^{1}H NMR of *o*NBA modified 4-arm PEG (PEG4*o*NBA) in D_2O revealing the presence of characteristic *o*NBA aromatic (purple highlights, details in left box) and CH_2-OH protons (brown highlight, middle box). The CH2-OH integral (~5.05 ppm) is compared with the terminal methylene protons of PEG4NH_2 at ~2.97 ppm (CH_2-NH_2, green highlight in right box) to determine the *o*NBA substitution degree (~92%).

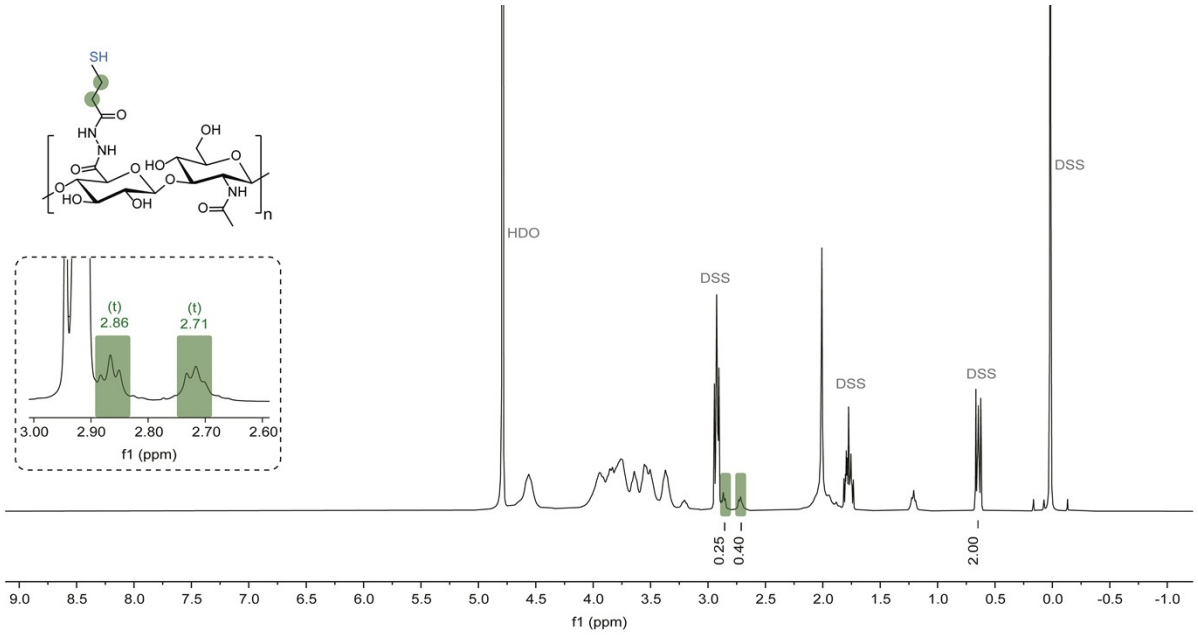

Figure S6. ^{1}H NMR of thiolated hyaluronic acid (HA-SH) in D_2O and in the presence of 3-(trimethylsilyl)-1-propanesulfonic acid (DSS), an internal standard. Highlighted in green are the methylene protons signals of grafted 3,3'-dithiobis(propionohydrazide) (DTPHY) used for quantification of the degree of substitution.

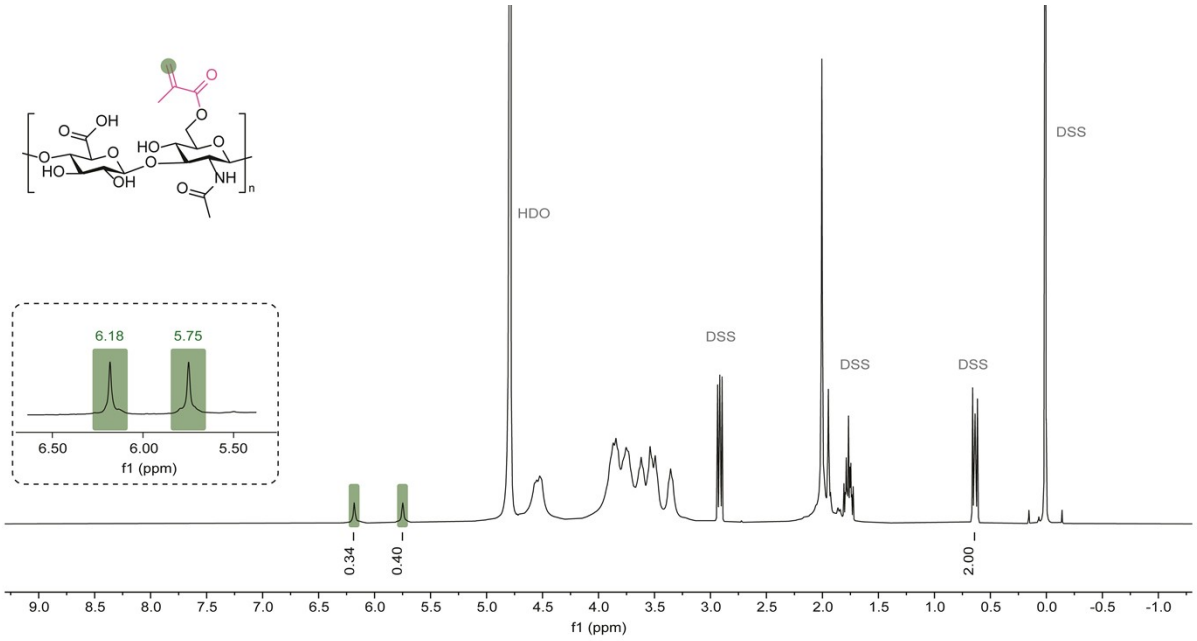

Figure S7. ^{1}H NMR of methacrylated hyaluronic acid (HA-MA) in D_2O, and in the presence of 3-(trimethylsilyl)-1-propanesulfonic acid (DSS) internal standard. Highlighted in green are the characteristic methacrylate protons signals used for the quantification of the degree of substitution.

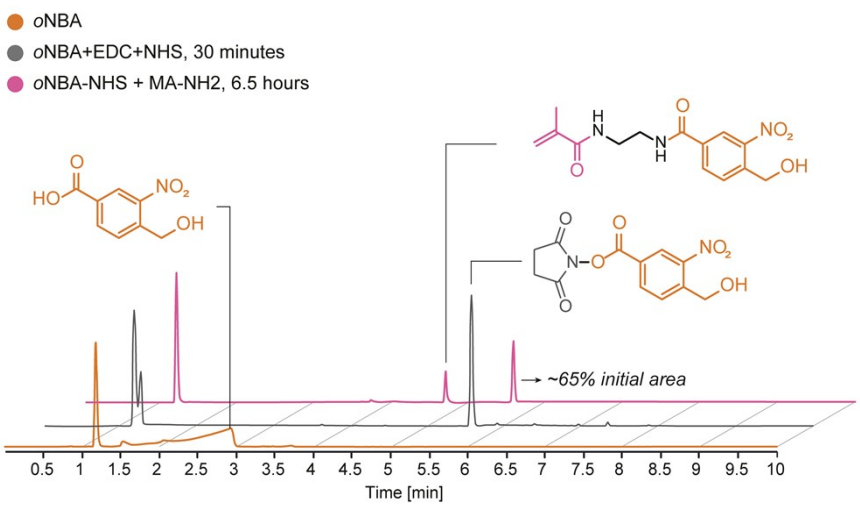

Figure S8. HPLC monitoring of *o*NBA-NHS and *o*NBA-MA synthesis.

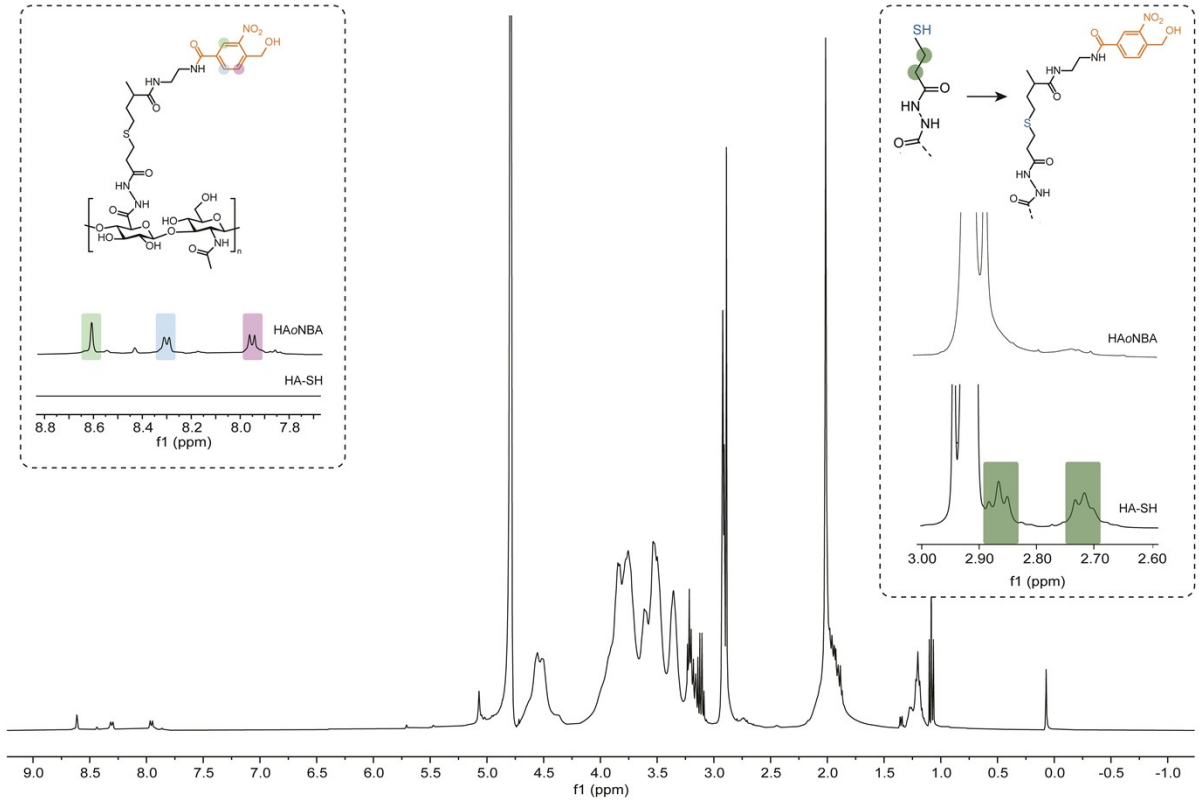

Figure S9. ^{1}H NMR of *o*NBA-modified hyaluronic acid (HA-*o*NBA) in D_2O revealing the presence of characteristic *o*NBA aromatic protons (green, blue, purple highlight, details in left box), and the consumption of methylene peaks characteristic of thiolated HA (HA-SH) (green highlights, details in right box).

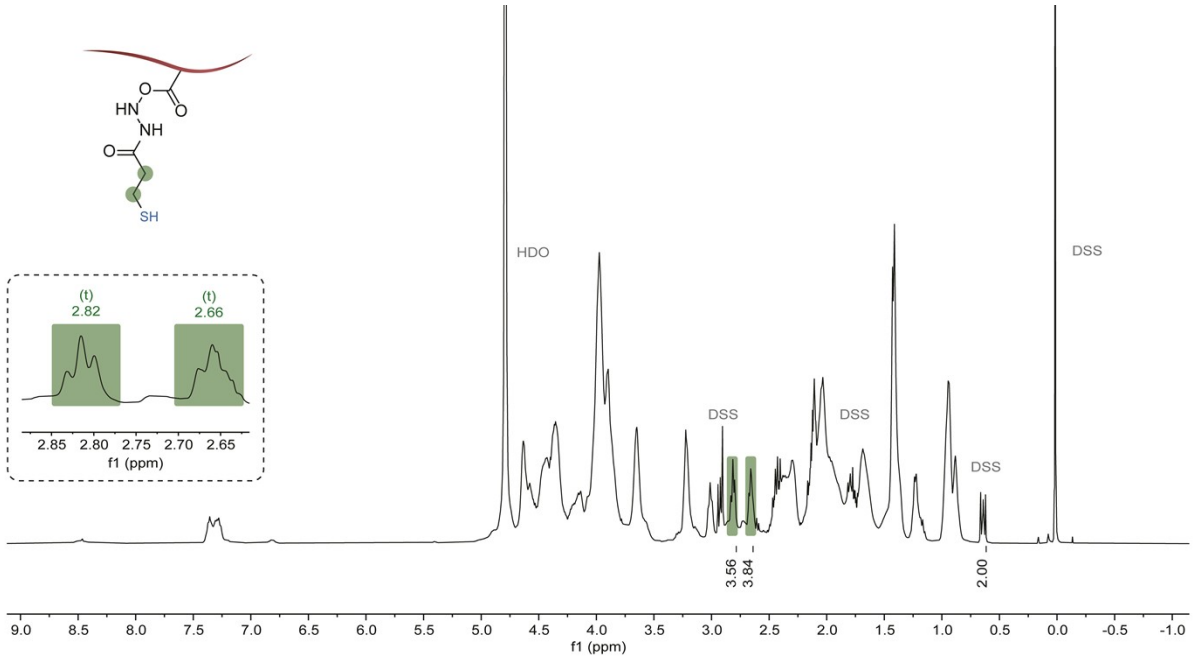

Figure S10. ^{1}H NMR of thiolated fish gelatin (fGel-SH) in D_2O, and in the presence of 3-(trimethylsilyl)-1-propanesulfonic acid (DSS), an internal standard. Highlighted in green the methylene protons signals of grafted 3,3'-dithiobis(propionohydrazide) (DTPHY) used for quantification of the degree of substitution.

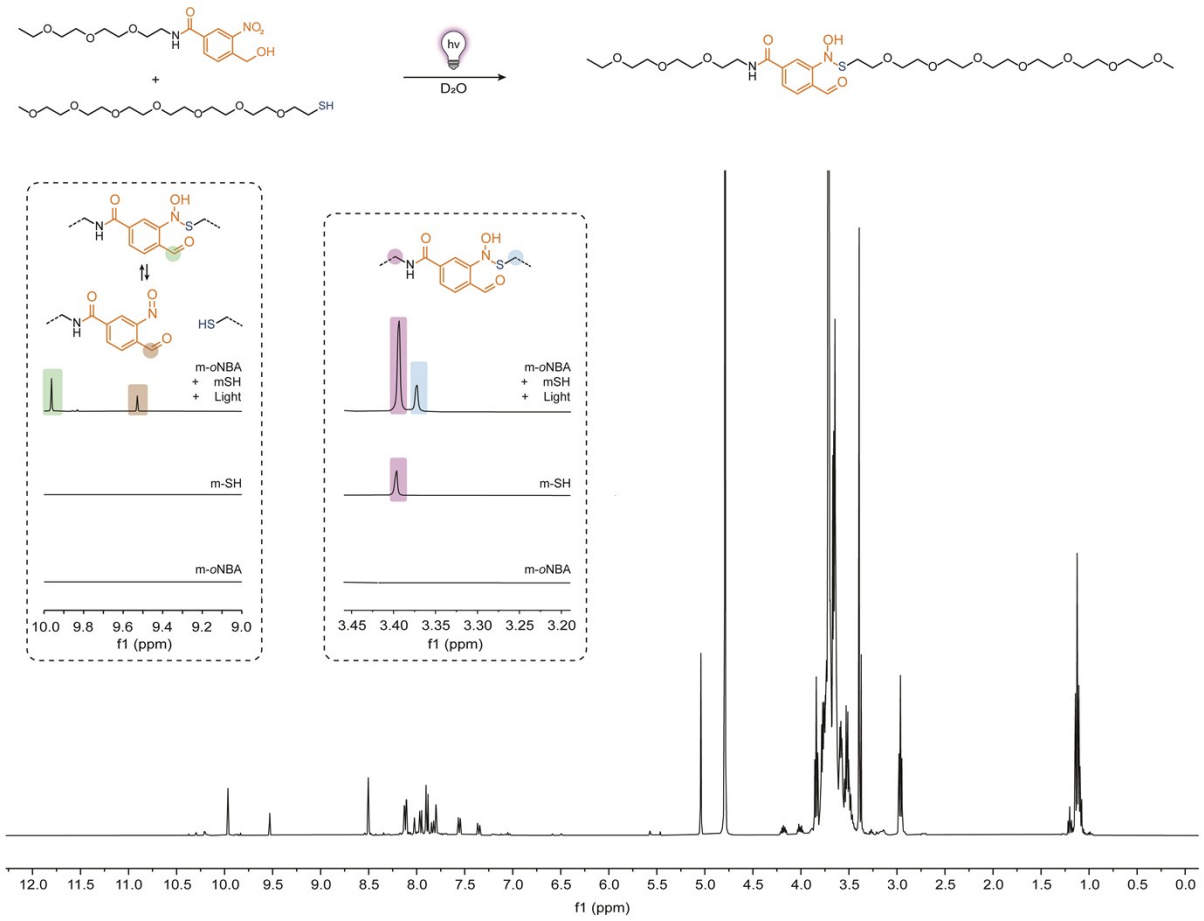

Figure S11. ^{1}H NMR of a 10 mM m-*o*NBA + 10 mM m-SH solution reacted in D_2O (365 nm, 20 mW cm^{-2} for 15 min) revealing the appearance of benzaldehyde peaks of activated *o*NBA (brown highlight) and N-semimercaptal adduct (green highlight) (details in left box). A shift of terminal methylene protons of m-SH (CH_2-SH) is also observed due to the formation of N-semimercaptal bond (blue highlight, details in right box).

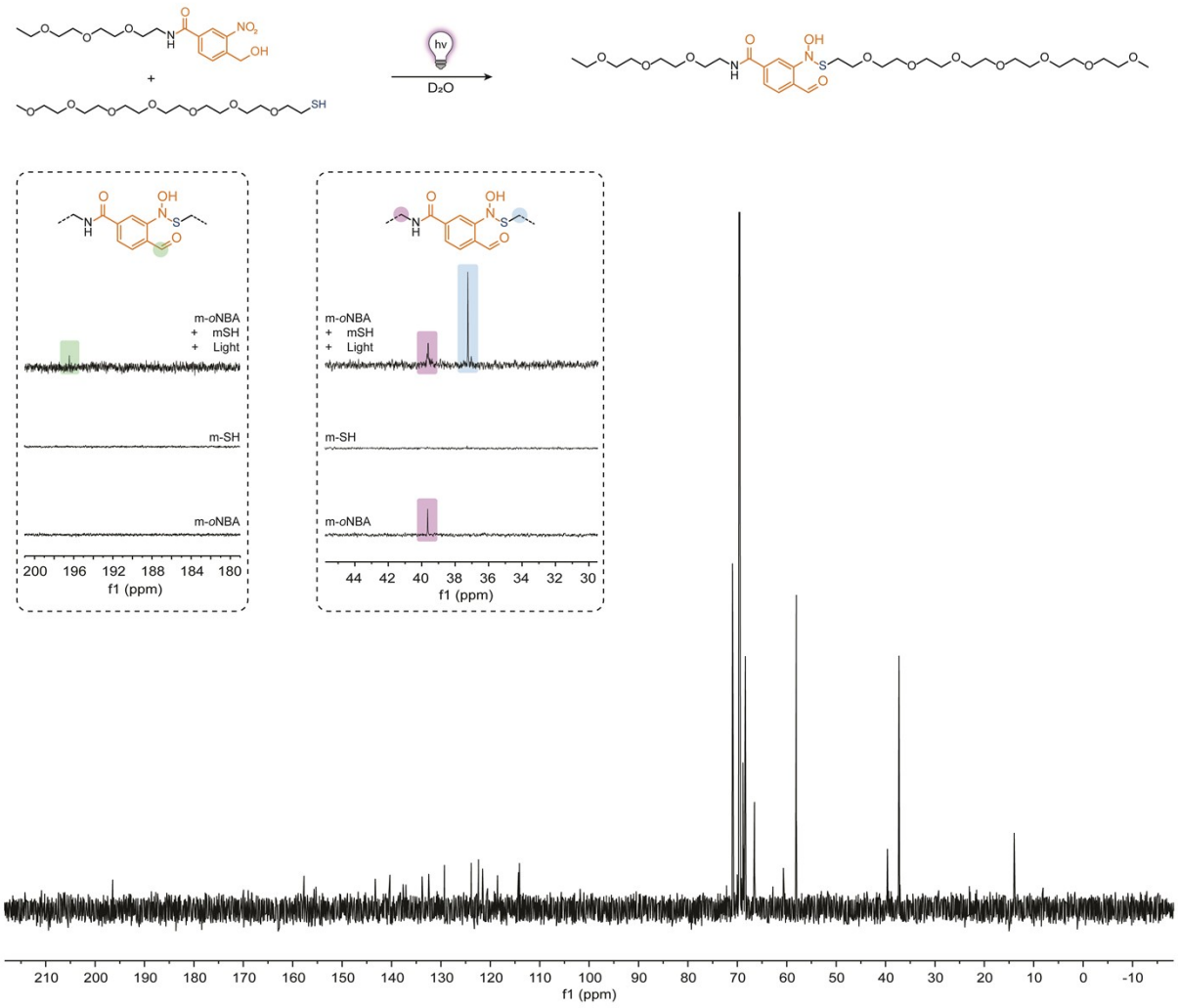

Figure S12. ^{13}C NMR of a 10 mM m-*o*NBA + 10 mM m-SH solution reacted in D_2O (365 nm, 20 mW cm^{-2} for 15 min) revealing the appearance of benzaldehyde peaks of activated *o*NBA or N-semimercaptal adduct (green highlight) (details in left box). A shift of terminal methylene carbon of m-SH (CH_2-SH) is also observed due to the formation of N-semimercaptal bond (blue highlight, details in right box).

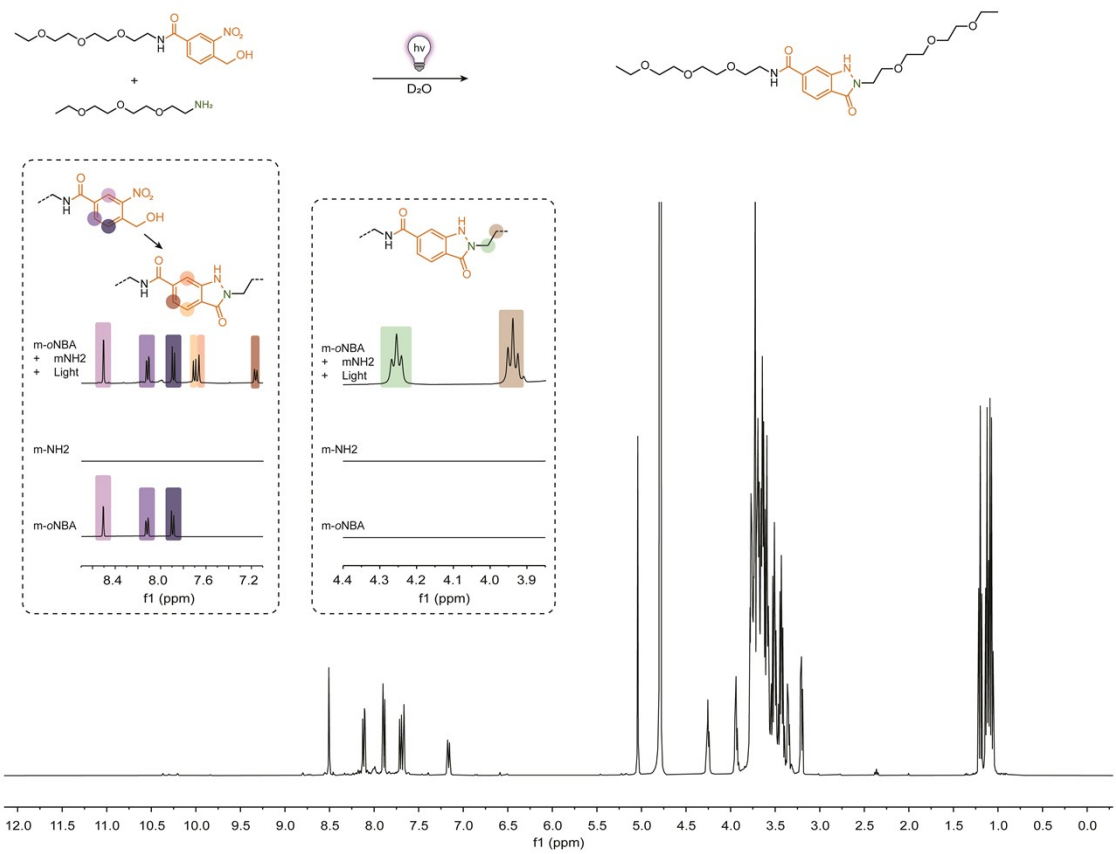

Figure S13. ^{1}H NMR of a 10 mM m-*o*NBA + 10 mM m-NH_2 solution reacted in D_2O (365 nm, 20 mW cm^{-2} for 15 min) showing shifts of the aromatic protons signals due to the formation of the indazolone bond (purple vs orange highlights, details in left box). Note: No benzaldehyde signals are observed (typical range 9-10 ppm), in accordance with the cyclization process resulting in the formation of an indazolone bond (see Figure 4A). The shifts of terminal methylene protons of m-NH_2 (CH_2-CH_2-NH_2) are observed due to the formation of the indazolone bond (green and brown highlights, details in the right box).

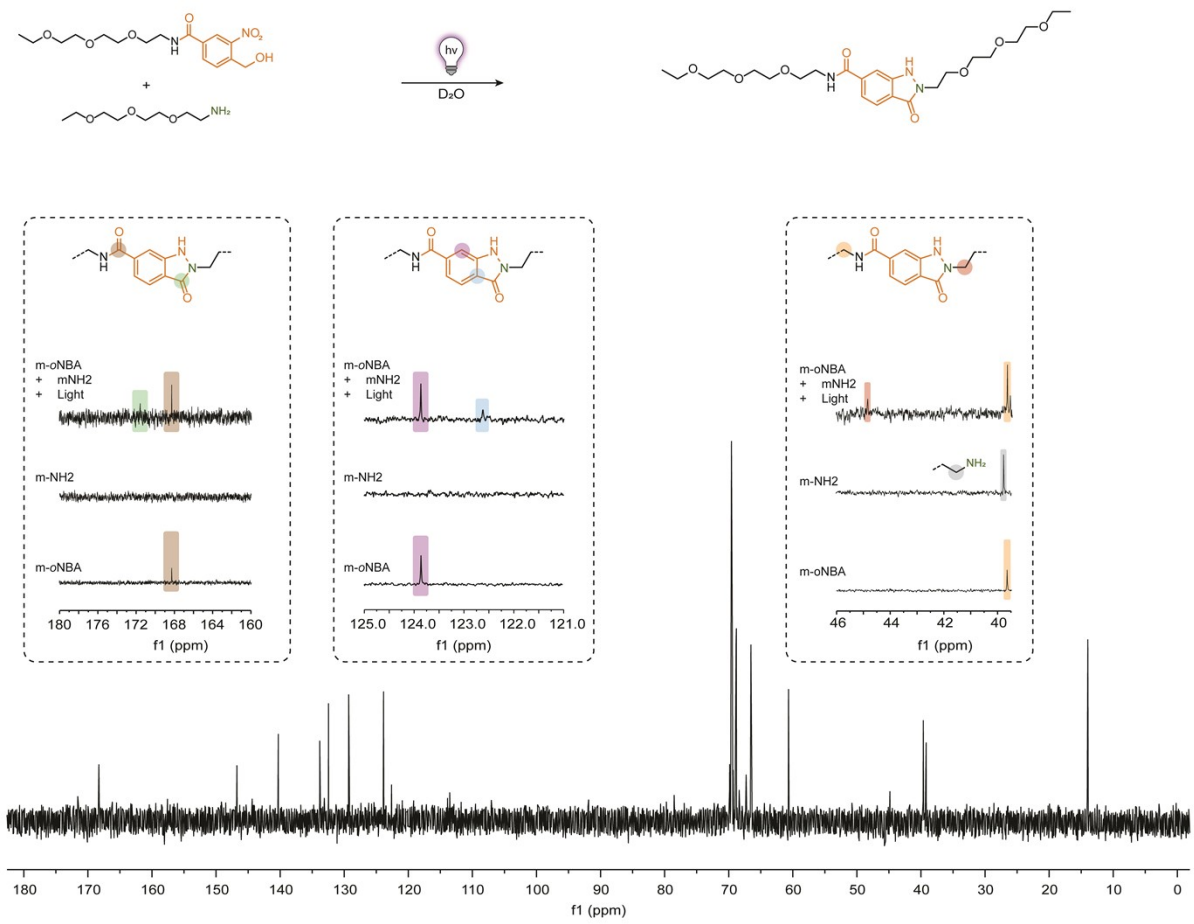

Figure S14. ^{13}C NMR of a 10 mM m-*o*NBA + 10 mM m-NH_2 solution reacted in D_2O (365 nm, 20 mW cm^{-2} for 15 min) showing the appearance of the indazolone carbonyl peak (green highlight, left box). A shift of an aromatic carbon was also observed upon reaction (blue highlight, middle box). The terminal methylene carbon signal of m-NH_2 (CH_2-NH_2) shifts (grey to red highlight, right box) due to the formation of an indazolone bond.

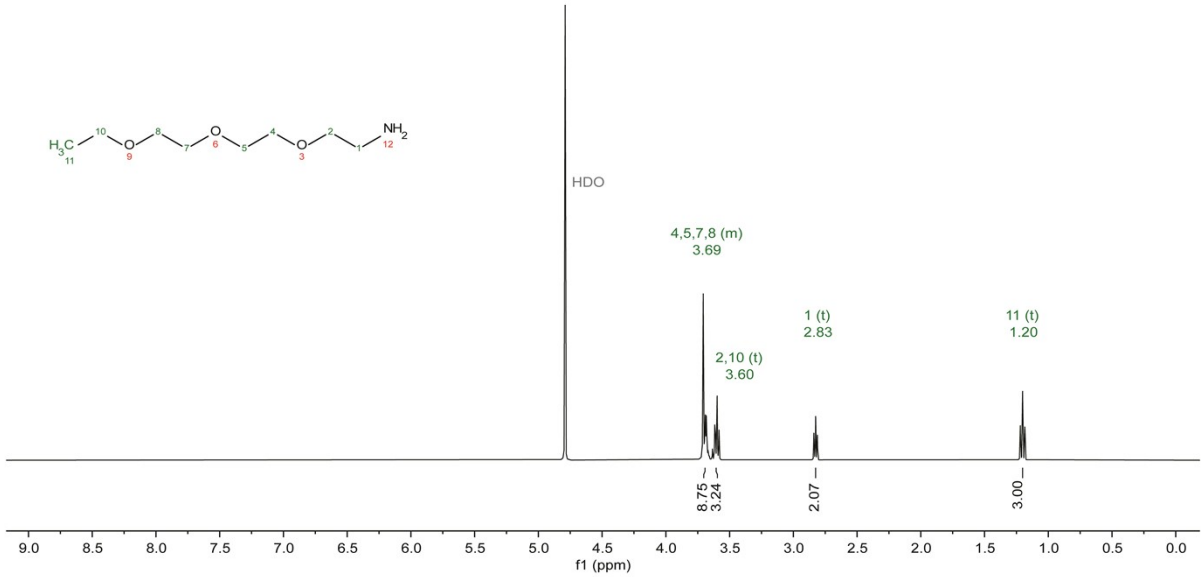

Figure S15. 2-(2-(2-ethoxyethoxy)ethoxy)ethanamine (m-NH_2) ^{1}H NMR in D_2O.

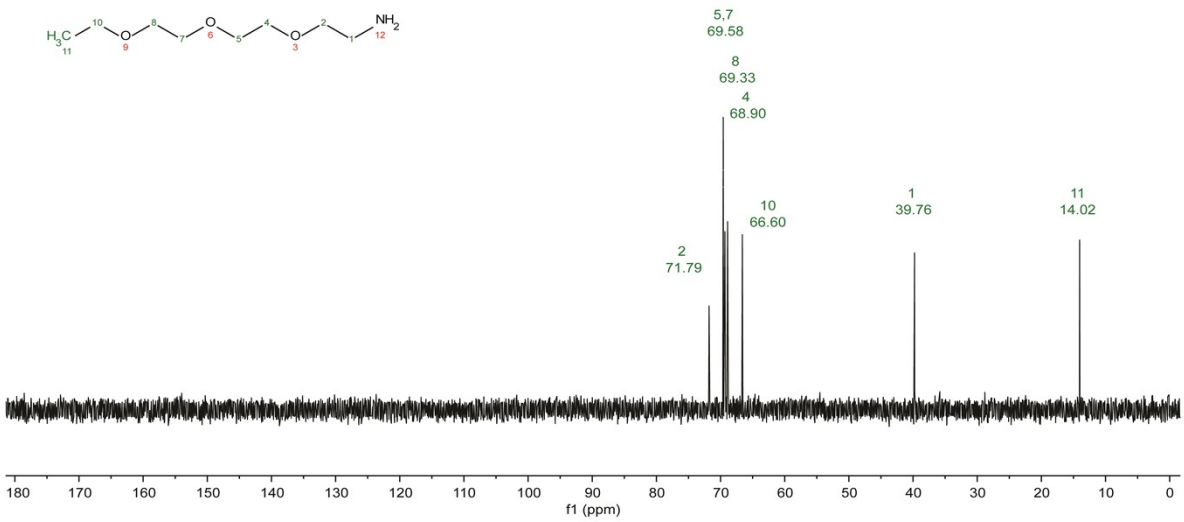

Figure S16. 2-(2-(2-ethoxyethoxy)ethoxy)ethanamine (m-NH_2) ^{13}C NMR in D_2O.

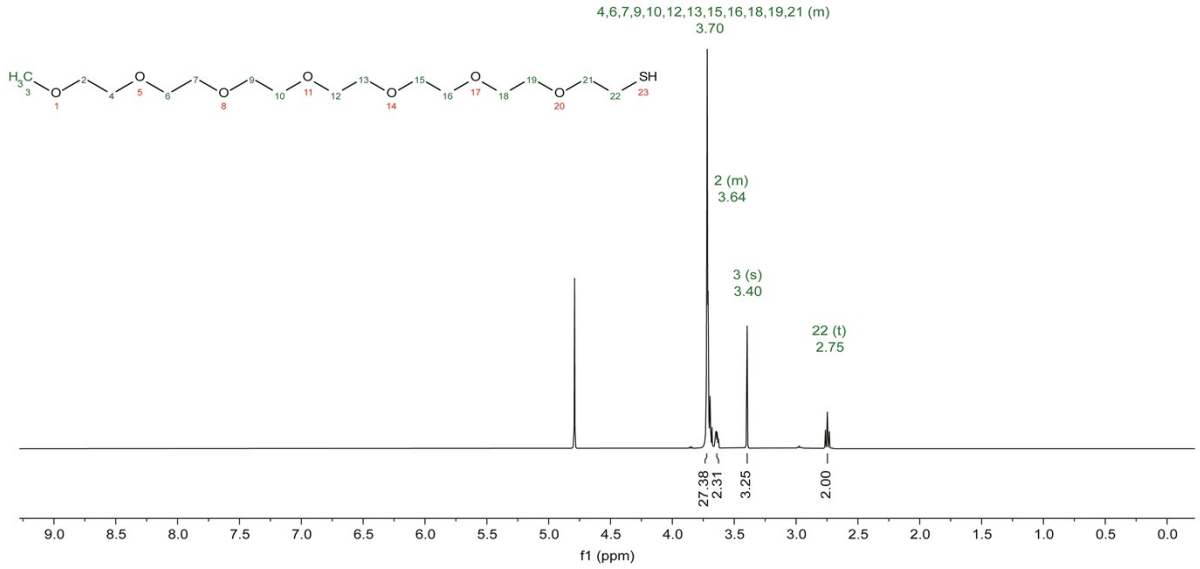

Figure S17. O-(2-mercaptoethyl)-O'-methyl-hexa(ethylene glycol) (m-SH) ^{1}H NMR in D_2O.

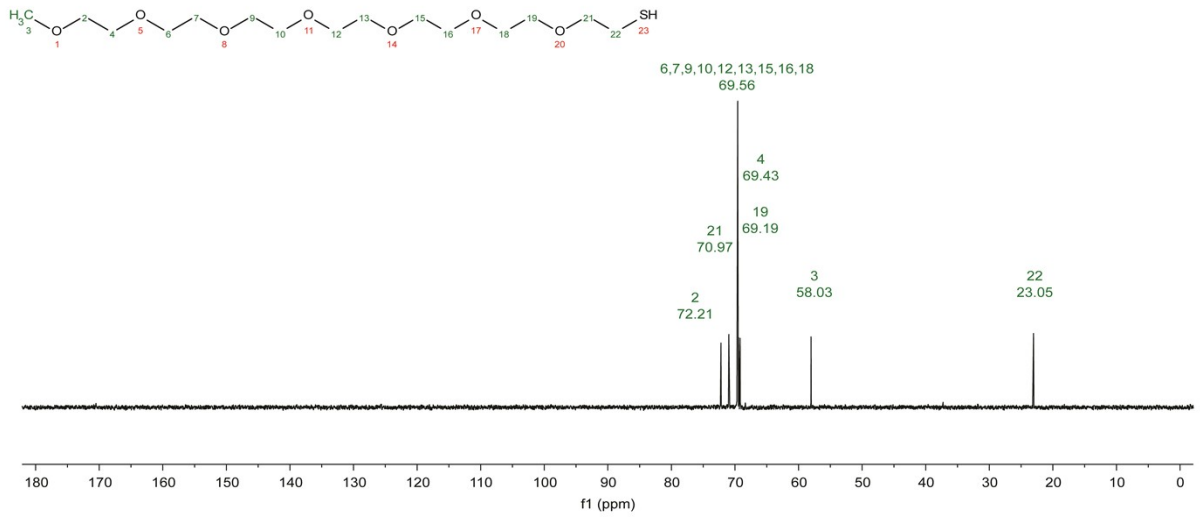

Figure S18. O-(2-mercaptoethyl)-O'-methyl-hexa(ethylene glycol) (m-SH) ^{13}C NMR in D_2O.

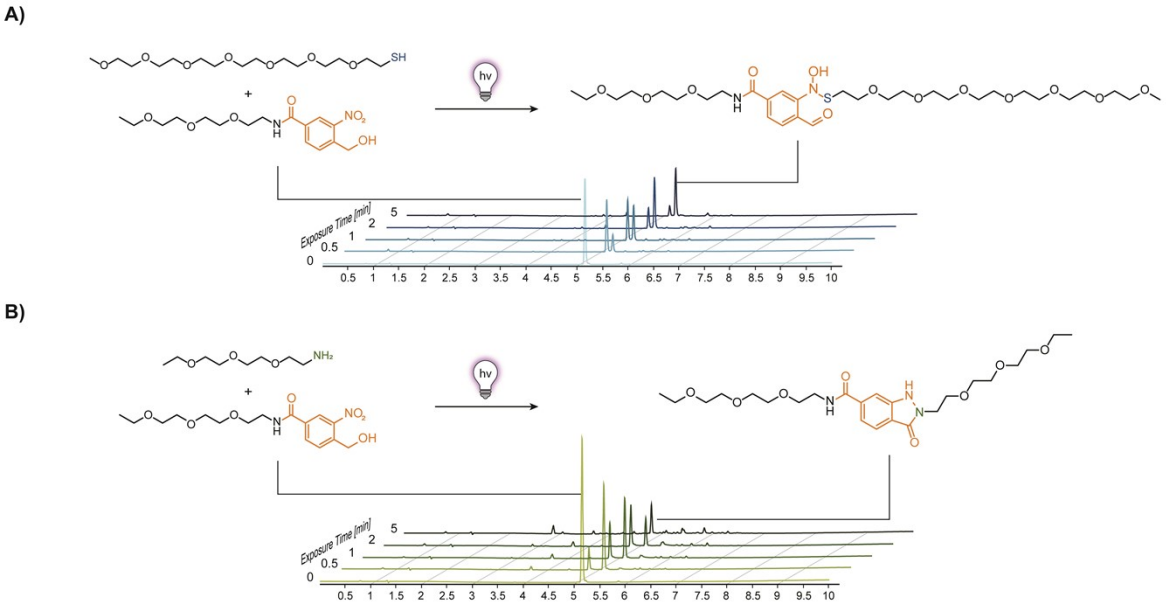

Figure S19. HPLC monitoring of 10 mM m-*o*NBA + 10 mM m-SH reaction (A) and 10 mM m-*o*NBA + 10 mM m-NH_2 reaction (B) in H_2O (365 nm, 20 mW cm^{-2} for 5 min) revealing consumption of reagents to form N-semimercaptal (A) and indazolone (B) adducts.

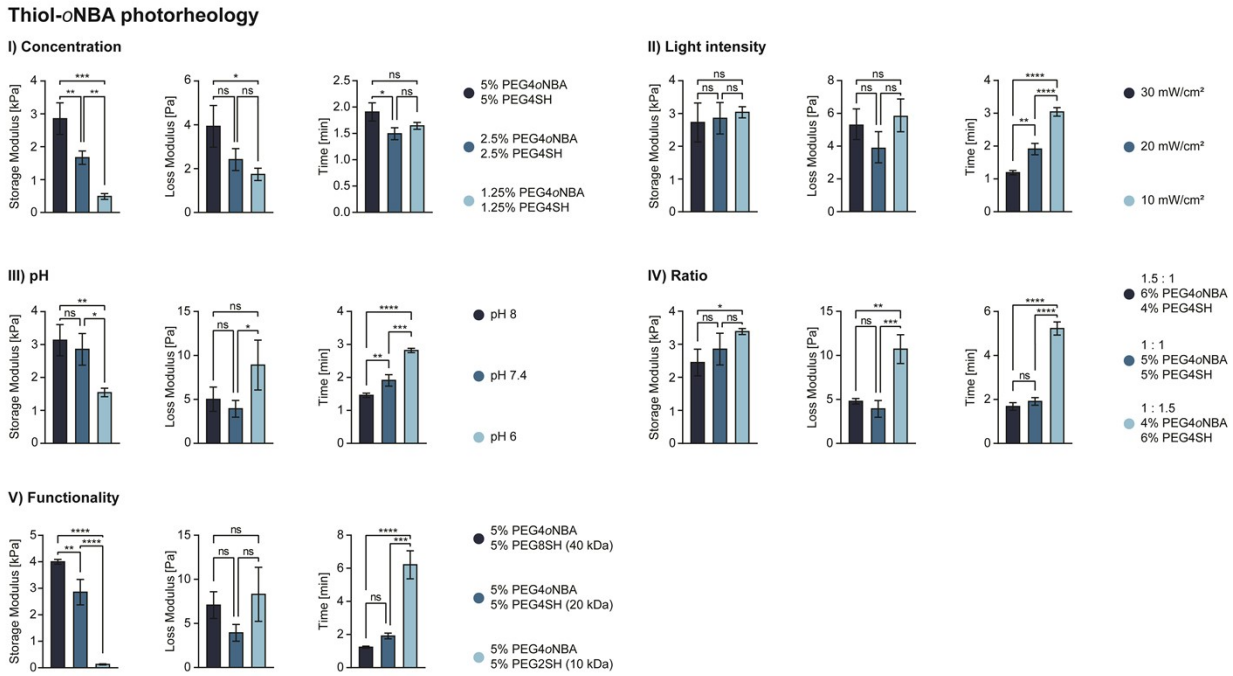

Figure S20. Photorheology of PEG-based thiol-*o*NBA photoresins.

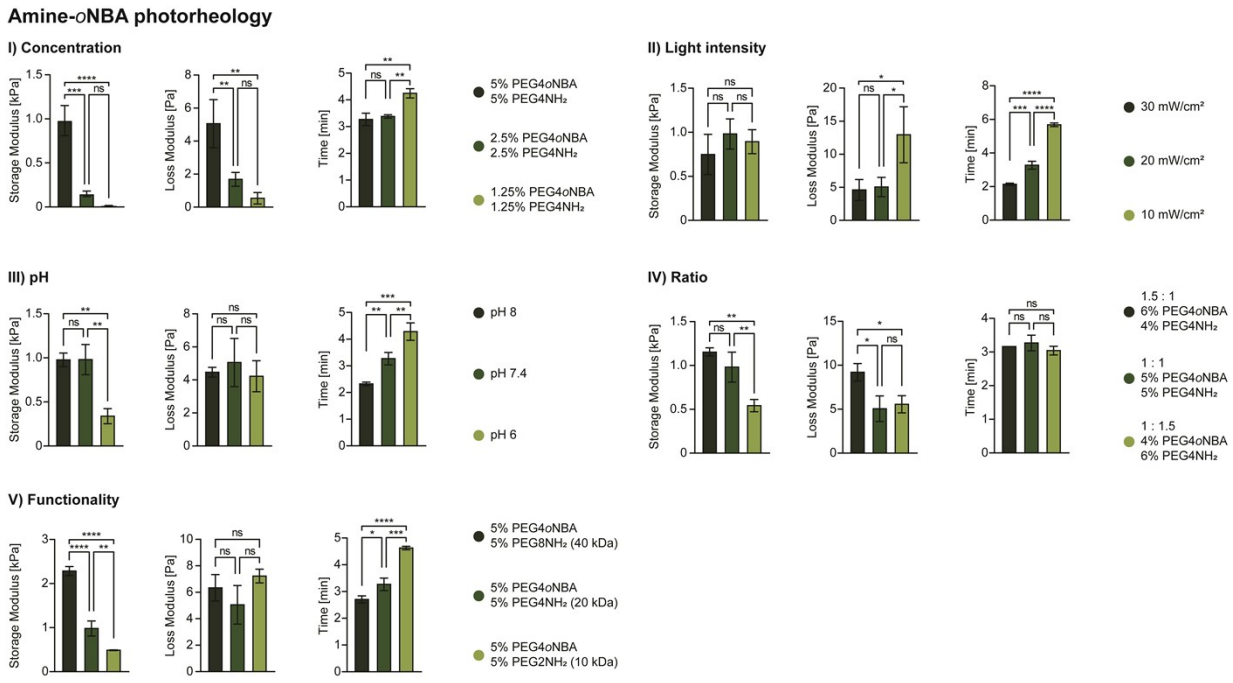

Figure S21. Photorheology of PEG-based amine-*o*NBA photoresins.

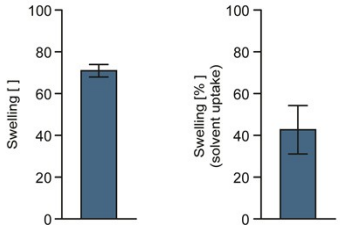

Figure S22. Swelling behavior of thiol-*o*NBA photoresin 1.3% PEG4oNBA / 1% HA-SH (250 kDa, DS: 10%).

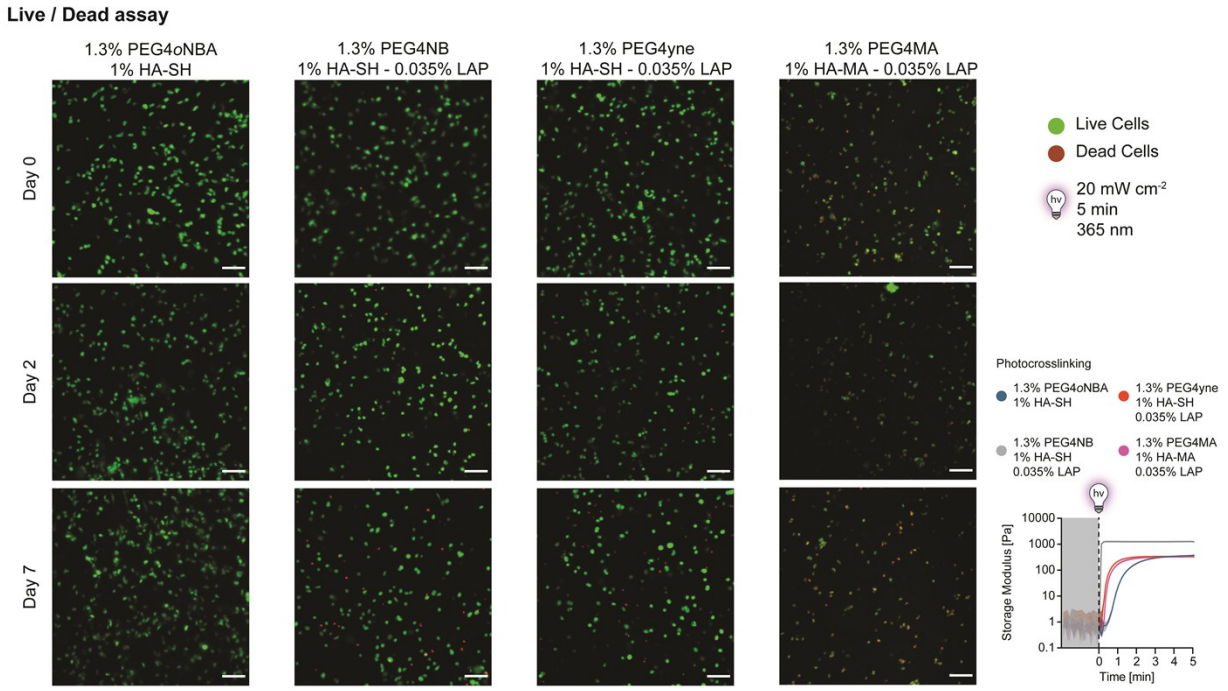

Figure S23. Live/dead assay of photocrosslinked bioresins (2.5M cells mL^{-1}, human neonatal dermal fibroblasts) over 1 week of culture. Step-growth chemistries exhibit high cell viability (>95%) upon photocrosslinking (day 0) compared to the chain-growth methacrylated hydrogel (~50%) (see also Figure 3BII). Over 1 week of culture, thiol-*o*NBA maintained the highest viability (>95%), followed by thiol-NB (~87%) and thiol-yne (~75%) chemistries (see also Figure 3BII). By contrast, methacrylate-based resins resulted in lower (~50%) cell viability, due to the generation of reactive oxygen species (ROS, see also Figure 3BI). Photorheology for different photoresins is also shown (bottom right).

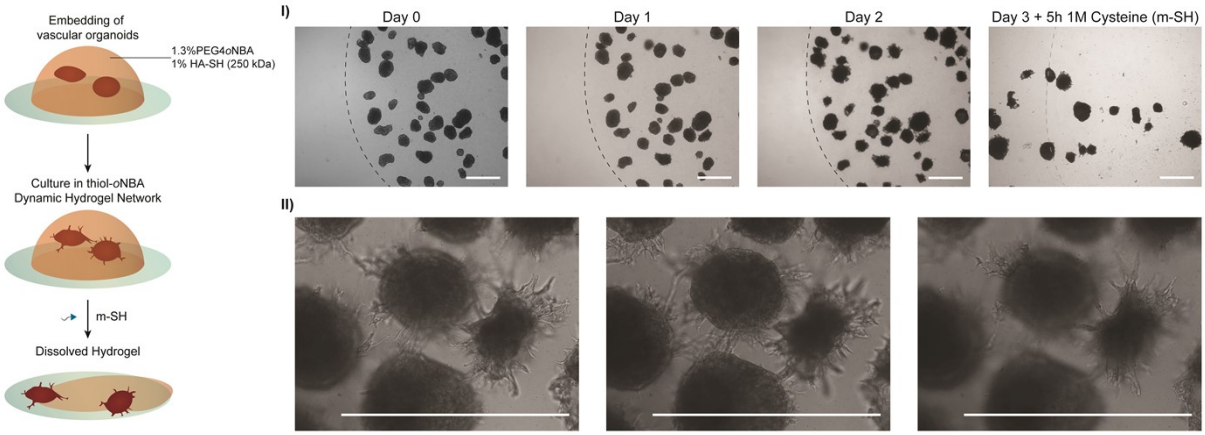

Figure S24. Example of thiol-*o*NBA hydrogel use as a dynamic, transient matrix for vascular organoid culture. Vascular organoids are embedded in 1.3% PEG4*o*NBA / 1% HA-SH (DS:10%, 250 kDa) (photocrosslinking conditions: 365 nm, 20 mW cm^{-2} for 5 min). After 3 days of culture, the organoids are retrieved by immersing the hydrogel in culture media containing an excess of monofunctional thiols (*i.e.*, cysteine, see also Figure 3C VI) (I). Although lacking integrin cell-adhesion sites, the soft and permissive nature of the matrix, which arises from the dynamic nature of the N-semimercaptal linkages enabled extensive vascular sprouting and spreading after 3 days of culture (II). Scale bars: 500 µm.

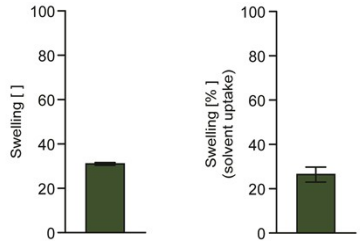

Figure S25. Swelling behavior of amine-*o*NBA photoresin 2.5% HA*o*NBA (250 kDa) / 10% fGel.

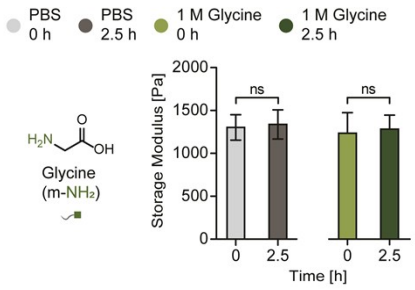

Figure S26. Stability of the indazolone bond confirmed by unchanged storage modulus upon 2.5 h exposure to excess of monofunctional amine (m-NH_2, glycine).

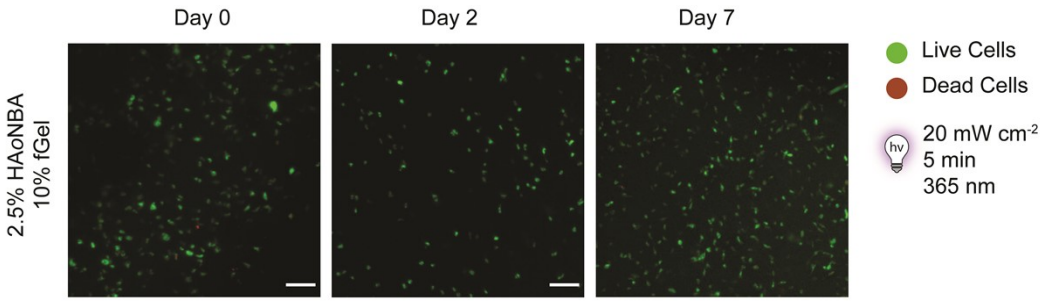

Figure S27. Live/dead assay for amine-*o*NBA bioresin (2.5 million cells mL^{-1}, human neonatal dermal fibroblasts) showing excellent viability upon crosslinking (~92%) and after 2 (~97%) and 7 days (~99%) of culture (see also Figure 4B-II).