Supporting Information

^{1}H NMR identification of butyl 3-(oct-1-enylthio)propanoate

^{1}H NMR (500MHz, CDCl$_3$, δ): 0.87 (t, 3H, *n*), 0.92 (t, 3H, *a*), 1.27 (m, 6H, *j*, *k* and *l*), 1.36 (m, 4H, *b* and *m*), 1.61 (m, 2H, *c*), 2.08 (m, 2H, *i*), 2.62 (m, 2H, *e*), 2.89 (m, 2H, *f*), 4.09 (t, 2H, *d*), 5.60 and 5.69 (m, 1H, *h*), 5.87 (m, 1H, *g*). A triplet at 1.92 ppm, arising from the –C≡CH in 1-octyne, was not observed in the NMR spectrum; a peak centered at 2570 cm^{-1}, arising from the SH stretch in butyl 3-mercaptopropionate, was not observed in the IR spectrum.
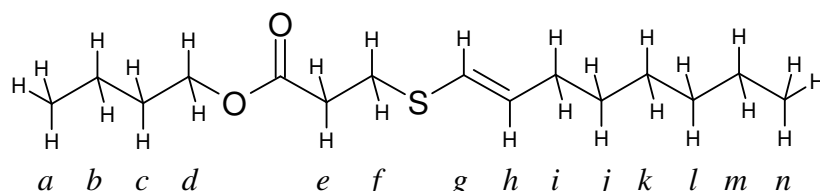

Figure 1. ^{1}H designation for butyl 3-(oct-1-enylthio)propanoate.

Verification of butyl 3-(oct-1-enylthio)propanoate via ESI+-MS

Notable peaks, MH+=273.2, MNa+=295.2, MK+=311.1, are all consistent with the expected product, butyl 3-(oct-1-enylthio)propanoate MW=272.4.

Molar absorptivity determination for the vinyl thioether functionality

Butyl 3-(oct-1-enylthio)propanoate (BOETP) was synthesized according to the procedure described in the manuscript. BOETP was sandwiched between two NaCl crystals separated by polyester shims with thicknesses ranging from 25 to 127 µm. The infrared spectrum, at a resolution of 2 cm^{-1}, was collected using a Nicolet Magna-IR 750 Series II FTIR spectrometer. The molar absorptivity was determined by linear regression of the peak area centered at 1609 cm^{-1} versus pathlength, utilizing the Beer-Lambert law.
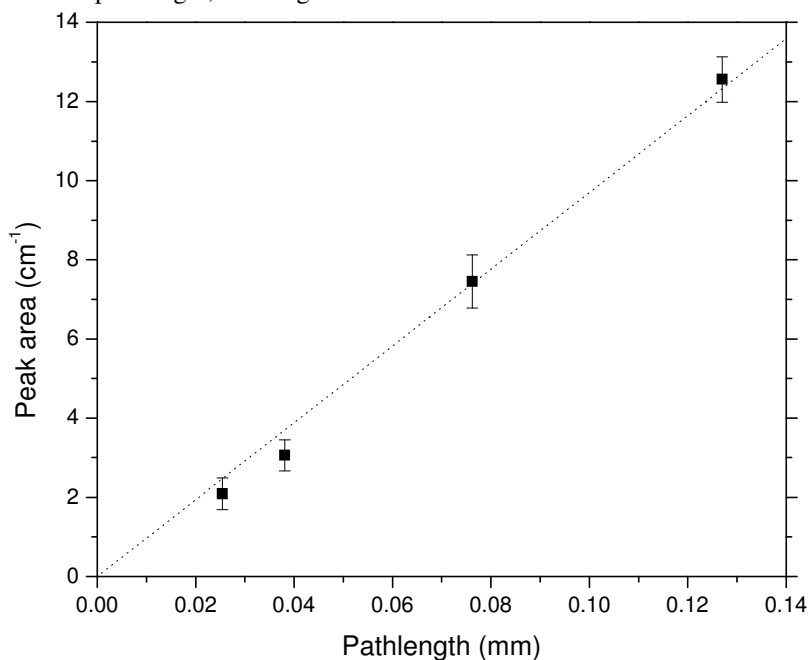

Figure 2. Linear regression of peak area centered at 1609 cm^{-1} versus pathlength (slope = 970 cm^{-2}).

The rate constant ratio ($k_{P,2}/k_{P,1}$) was determined as described in the manuscript. Numerically integrating the rate expression ratio (Equation 3), a least squares analysis was performed to find the rate constant ratio that provided the best fit to experimental data up to a 30% conversion. This best fit was found at $k_{P,2}/k_{P,1}=3.3$.
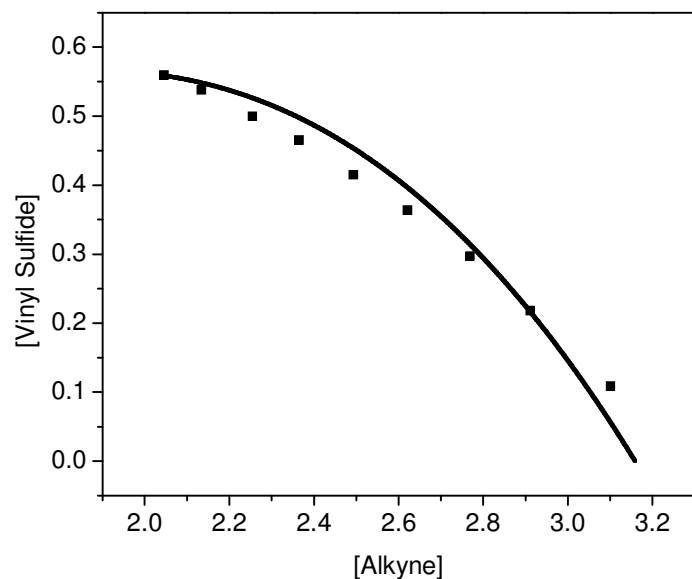

Figure 3. Experimental data (■) and numerical integration of reaction rate expression ratio with $r_{CT,2}/r_{CT,1}$ as the fitting parameter for a least squares regression. Best fit is achieved for $k_{P,2}/k_{P,1}=3.3$.