Supporting Information

Computational and experimental approach to evaluate the effect of initiator concentration, solvents, and enes on TEMPO driven thiol-ene reaction

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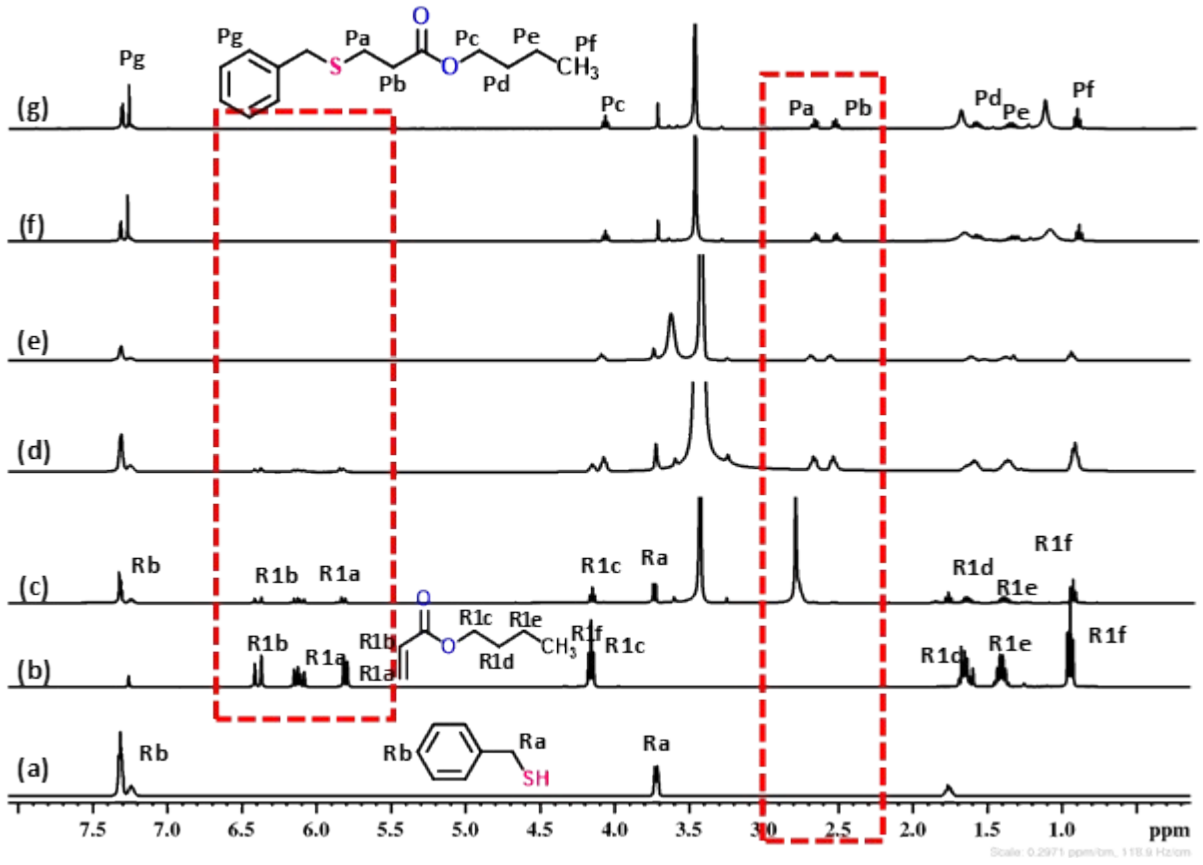


Figure S1. ^{1}H NMR spectra for the reaction between benzyl mercaptan and *n*-butyl acrylate at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a)

benzyl mercaptan, (b) *n*-butyl acrylate, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

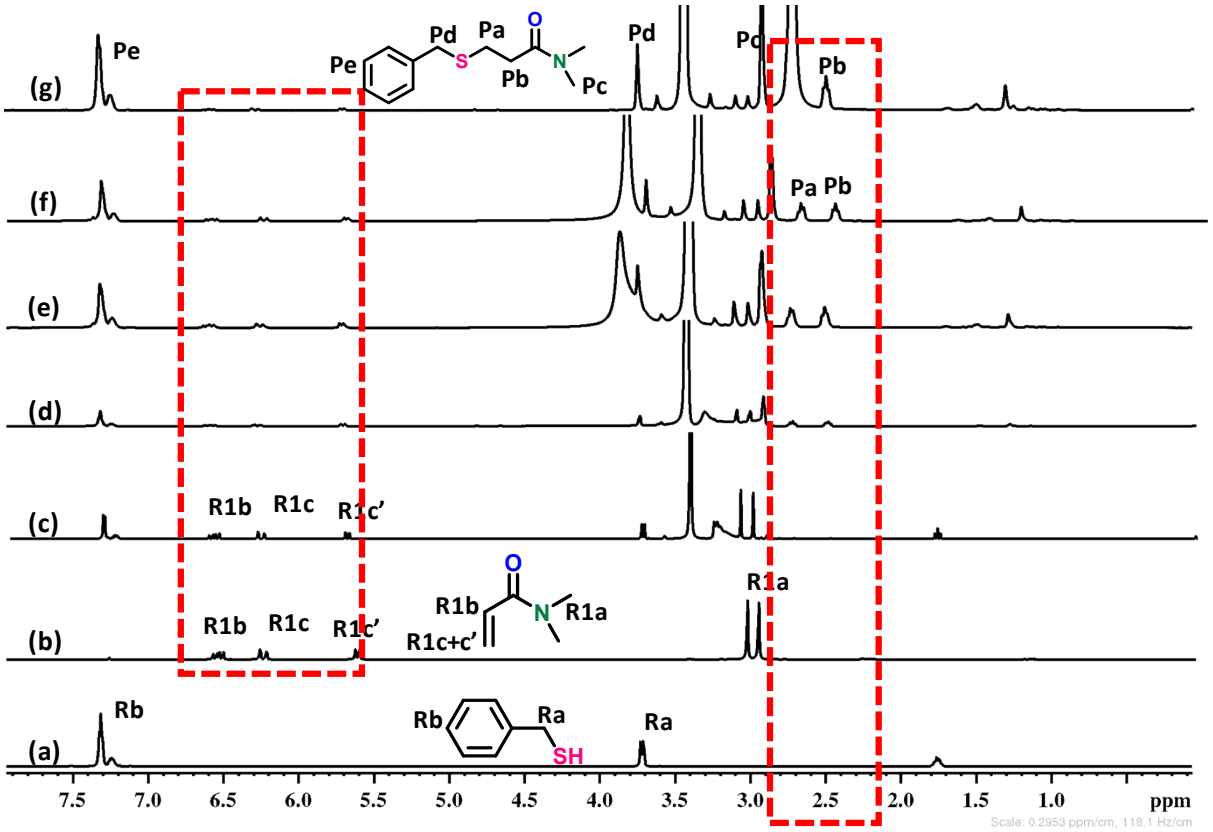


Figure S2. ^{1}H NMR spectra for reaction between benzyl mercaptan and *N,N*-dimethylacrylamide at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) *N,N*-dimethylacrylamide, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

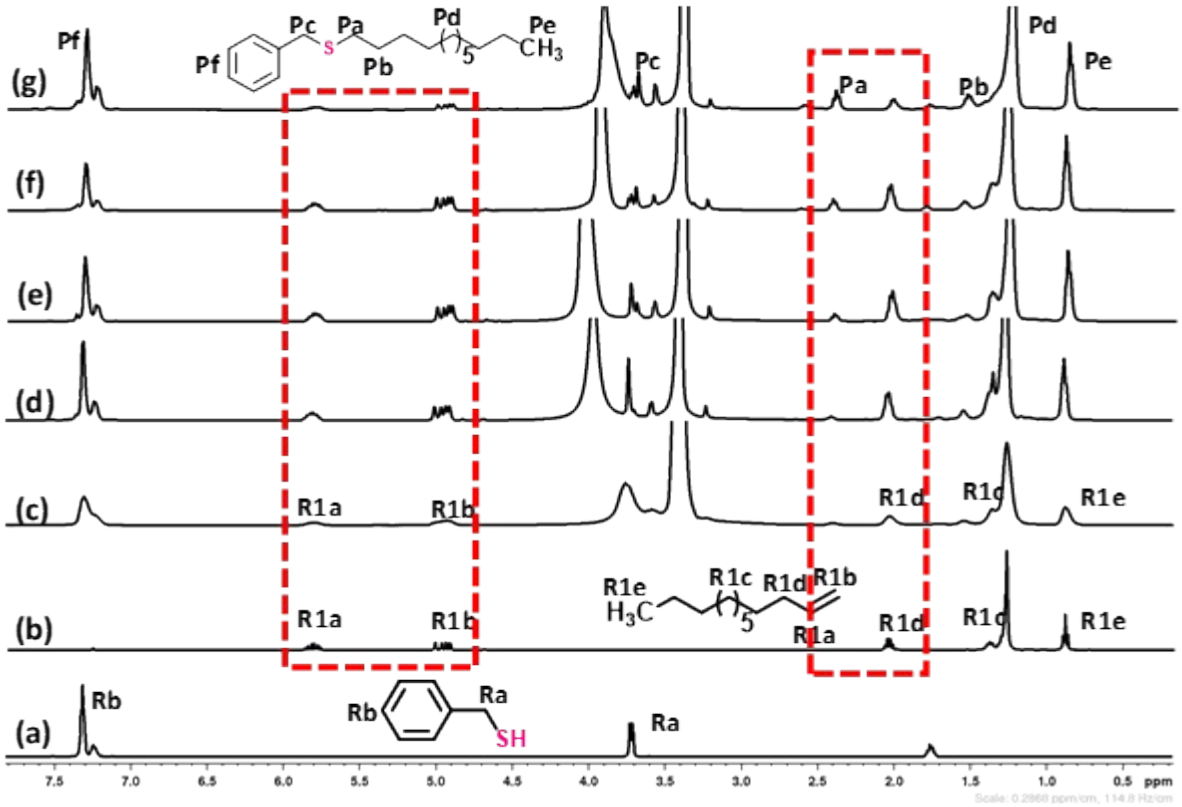


Figure S3. ^{1}H NMR spectra for the reaction between benzyl mercaptan and 1-dodecene at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) 1-dodecene, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

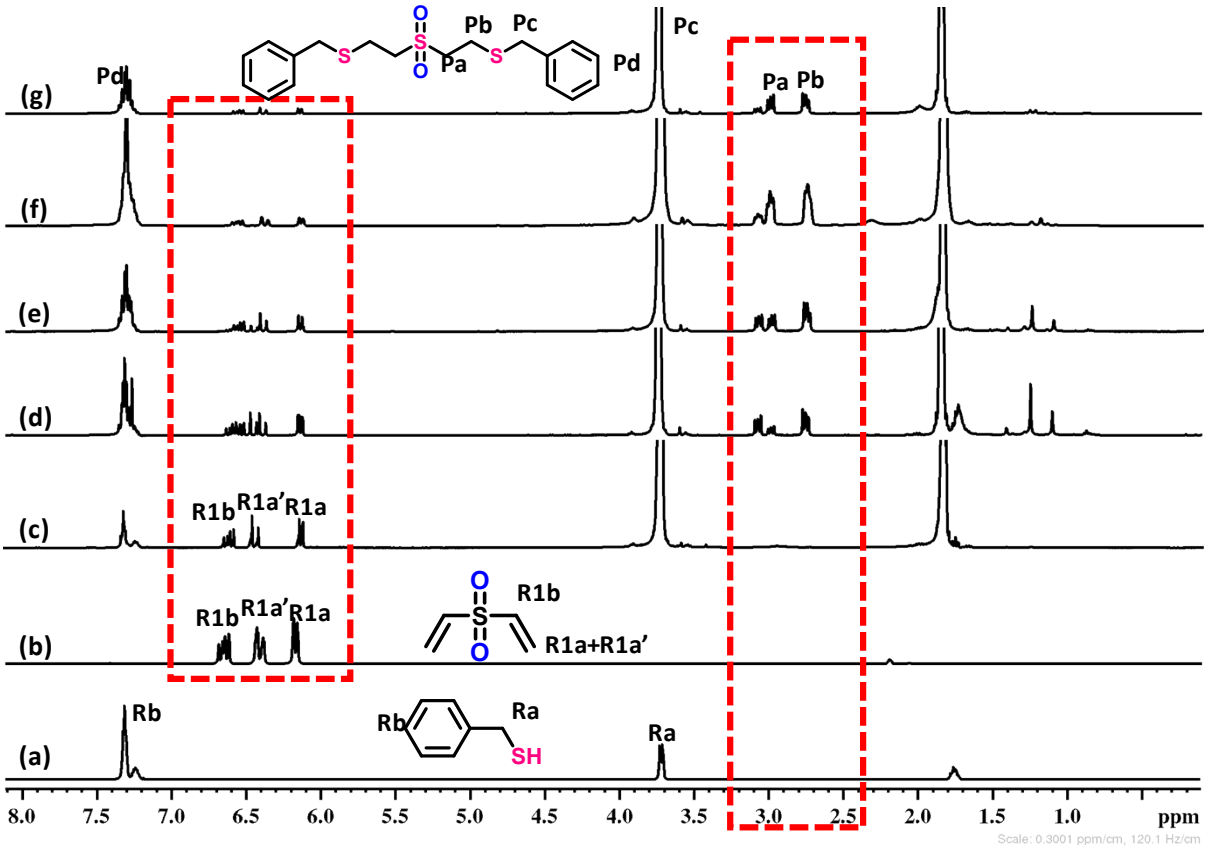


Figure S4. ^{1}H NMR spectra for the reaction between benzyl mercaptan and divinyl sulfone at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) divinyl sulfone, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

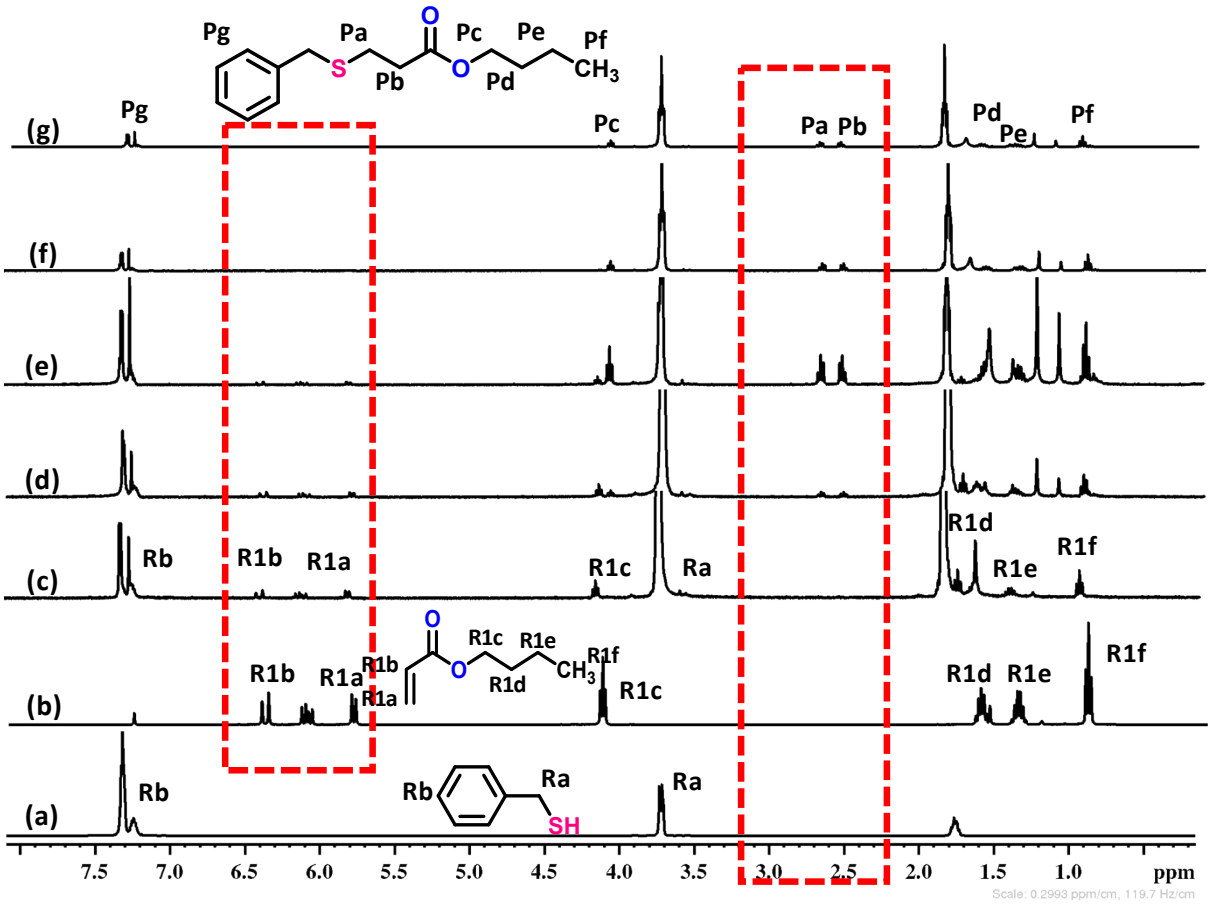


Figure S5. ^{1}H NMR spectra for the reaction between benzyl mercaptan and *n*-butyl acrylate at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) *n*-butyl acrylate, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

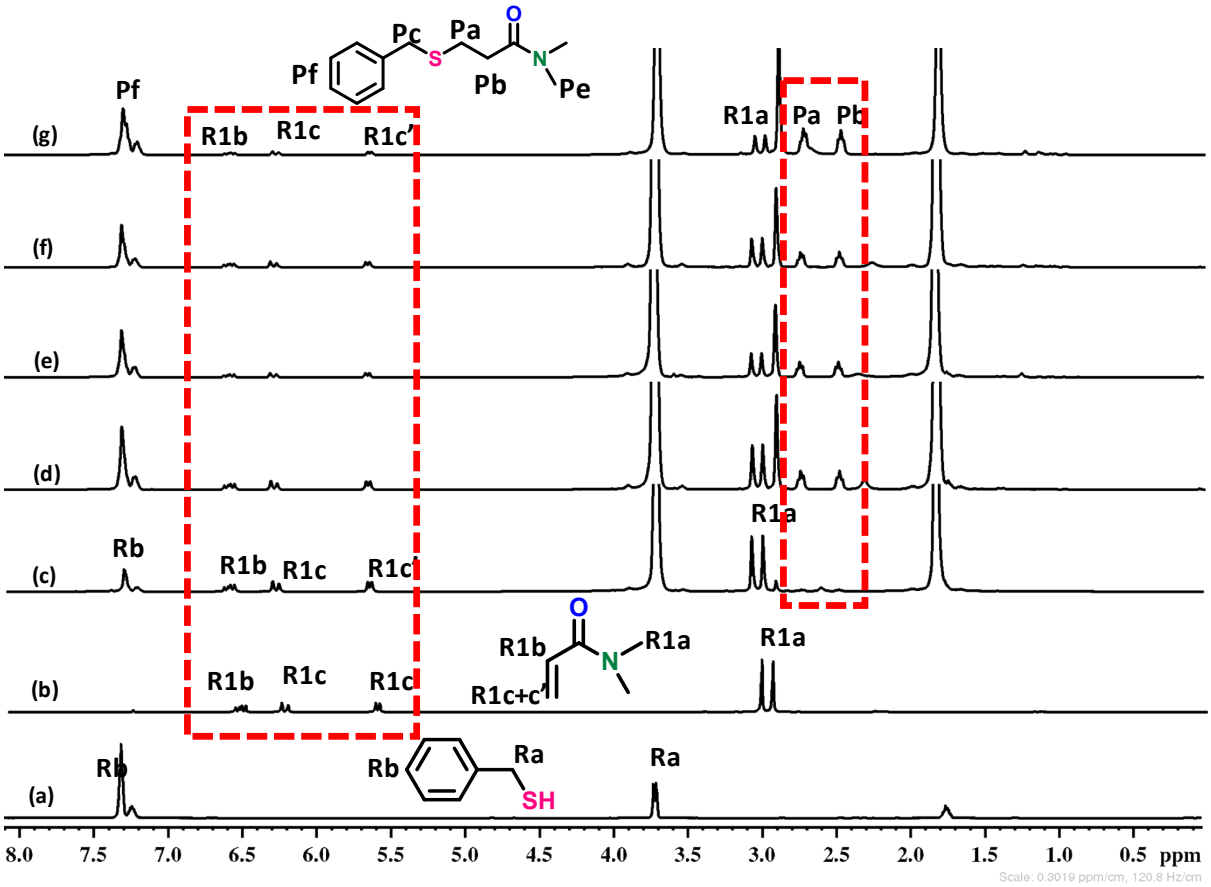


Figure S6. ^{1}H NMR spectra for reaction between benzyl mercaptan and *N,N*-dimethylacrylamide at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) *N,N*-dimethylacrylamide, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

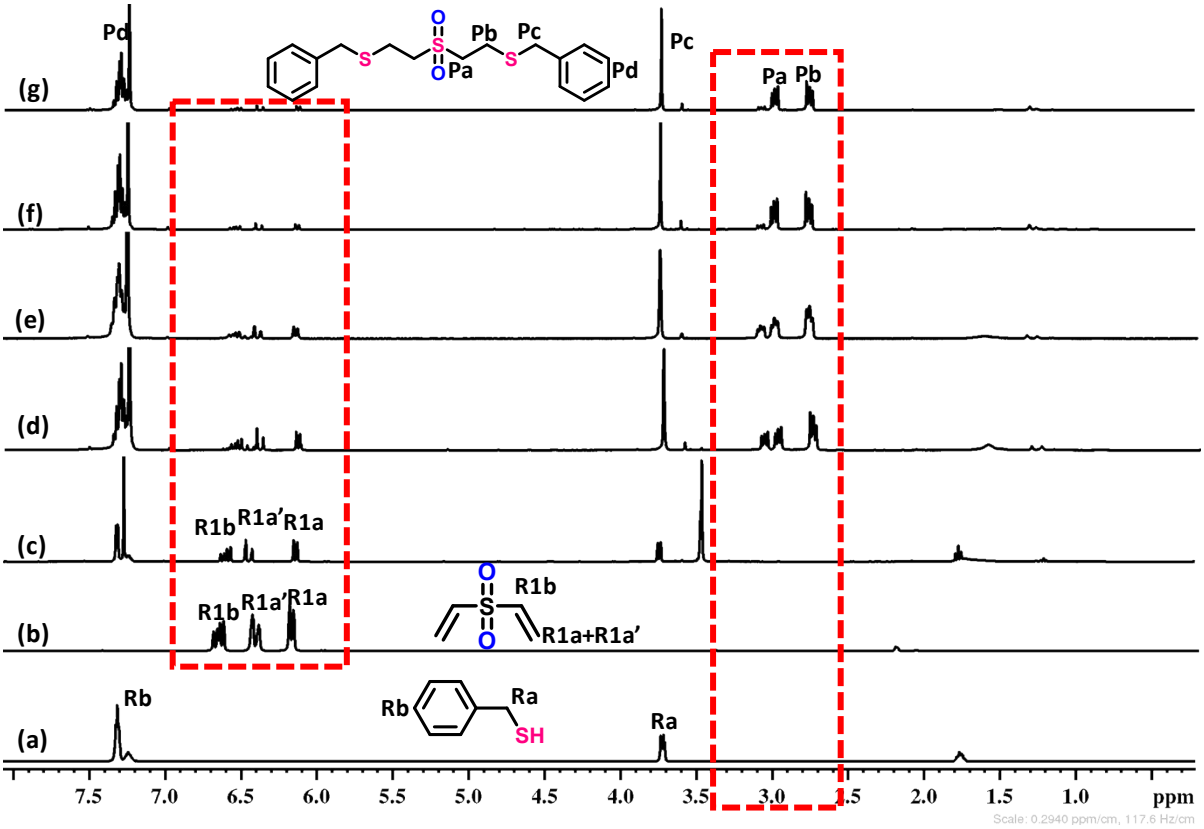


Figure S7. ^{1}H NMR spectra for the reaction between benzyl mercaptan and divinyl sulfone at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) divinyl sulfone, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

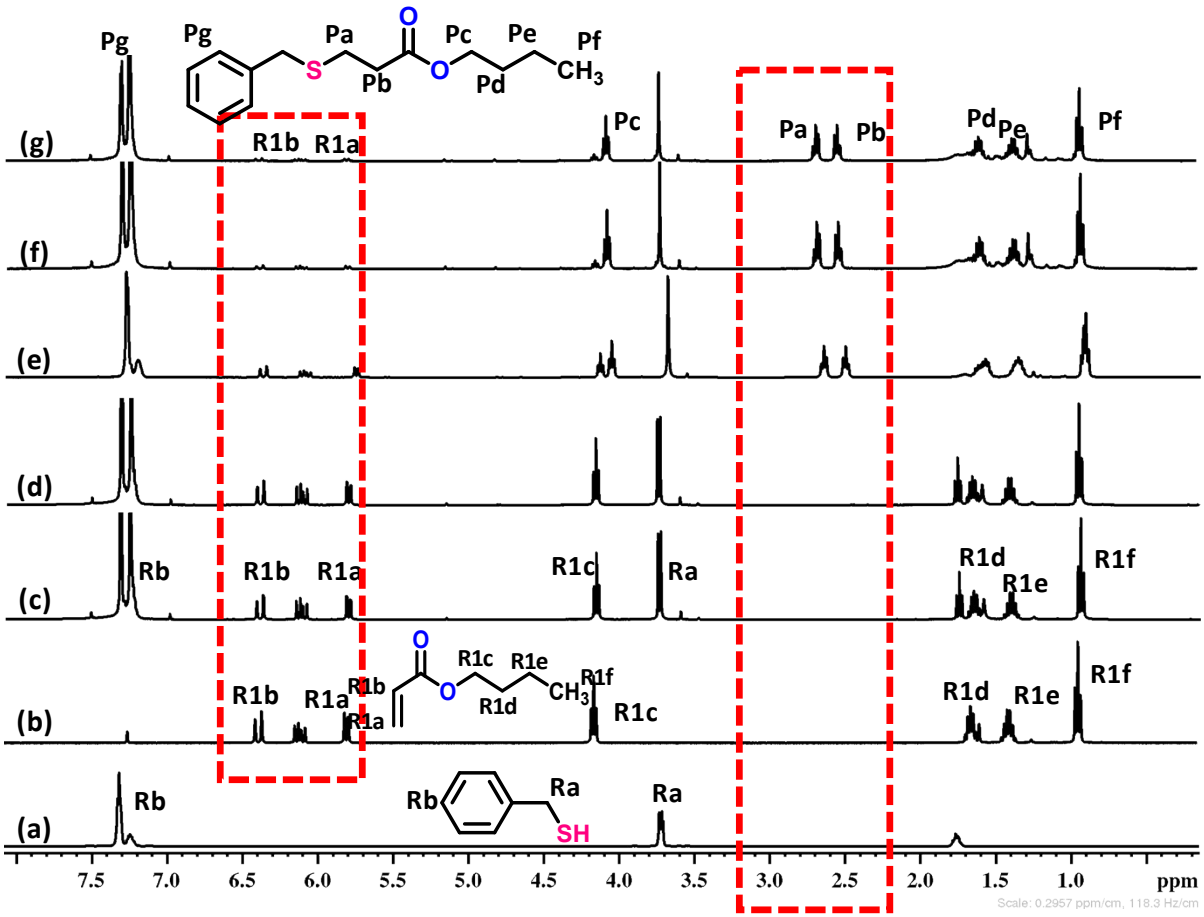


Figure S8. ^{1}H NMR spectra for the reaction between benzyl mercaptan and *n*-butyl acrylate at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) *n*-butyl acrylate, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

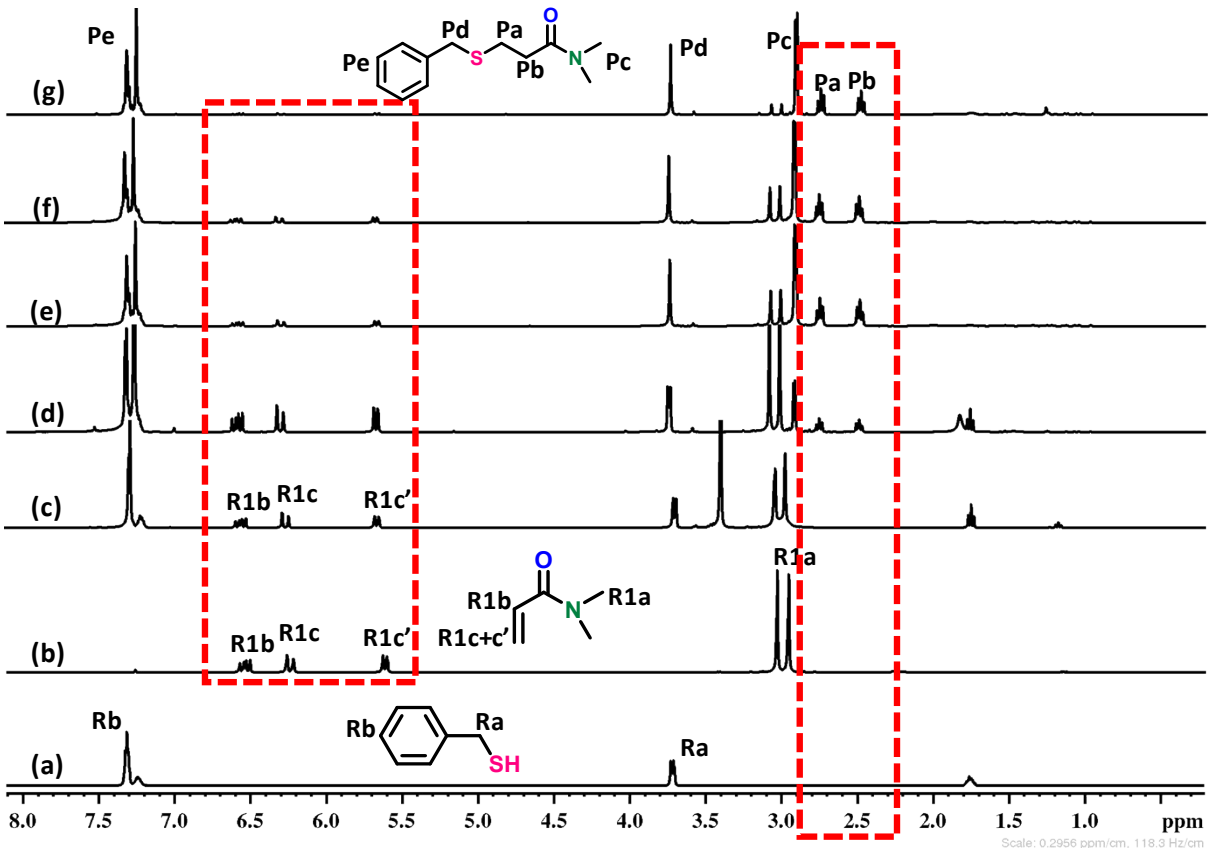


Figure S9. ^{1}H NMR spectra for reaction between benzyl mercaptan and *N,N*-dimethylacrylamide at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) *N,N*-dimethylacrylamide (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

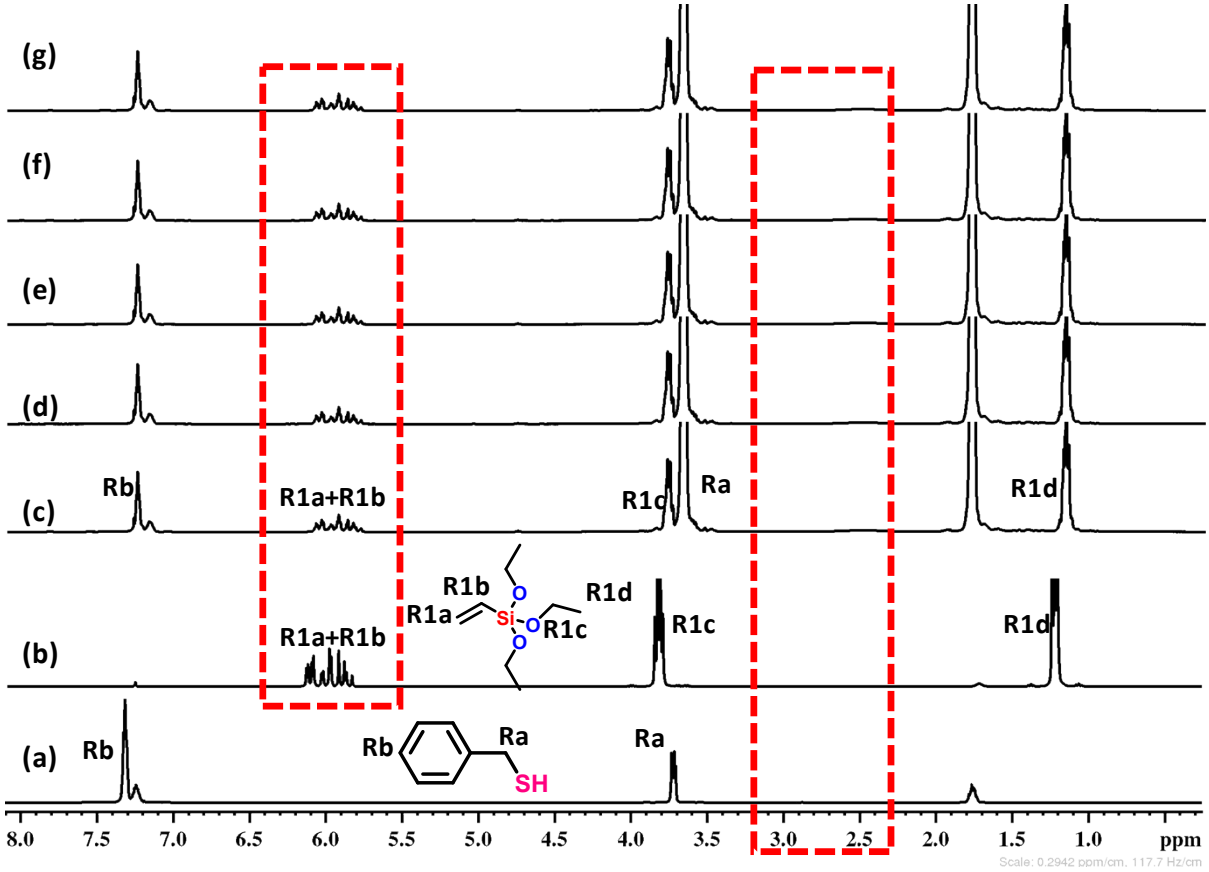


Figure S10. ^{1}H NMR spectra for the reaction between benzyl mercaptan and vinyltriethoxysilane at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) vinyltriethoxysilane, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

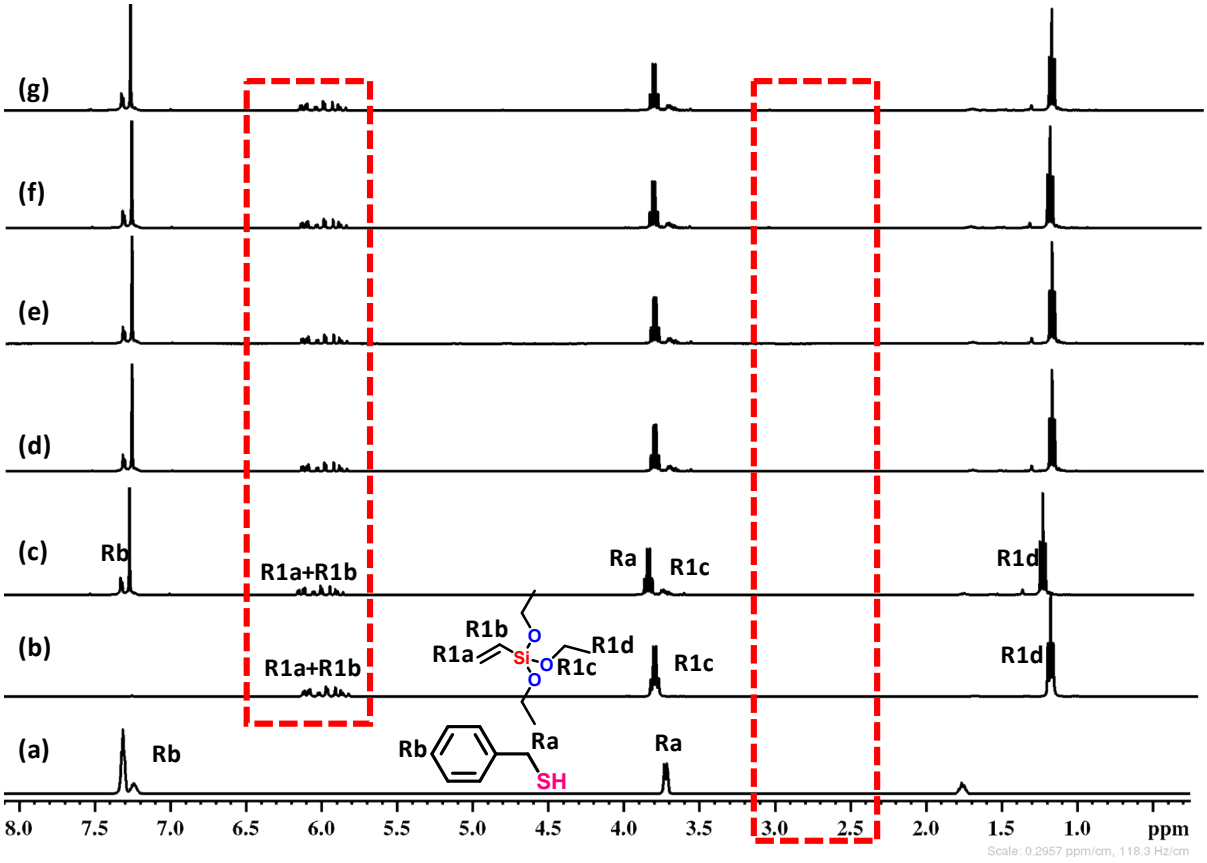


Figure S11. ^{1}H NMR spectra for the reaction between benzyl mercaptan and vinyltriethoxysilane at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) vinyltriethoxysilane, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

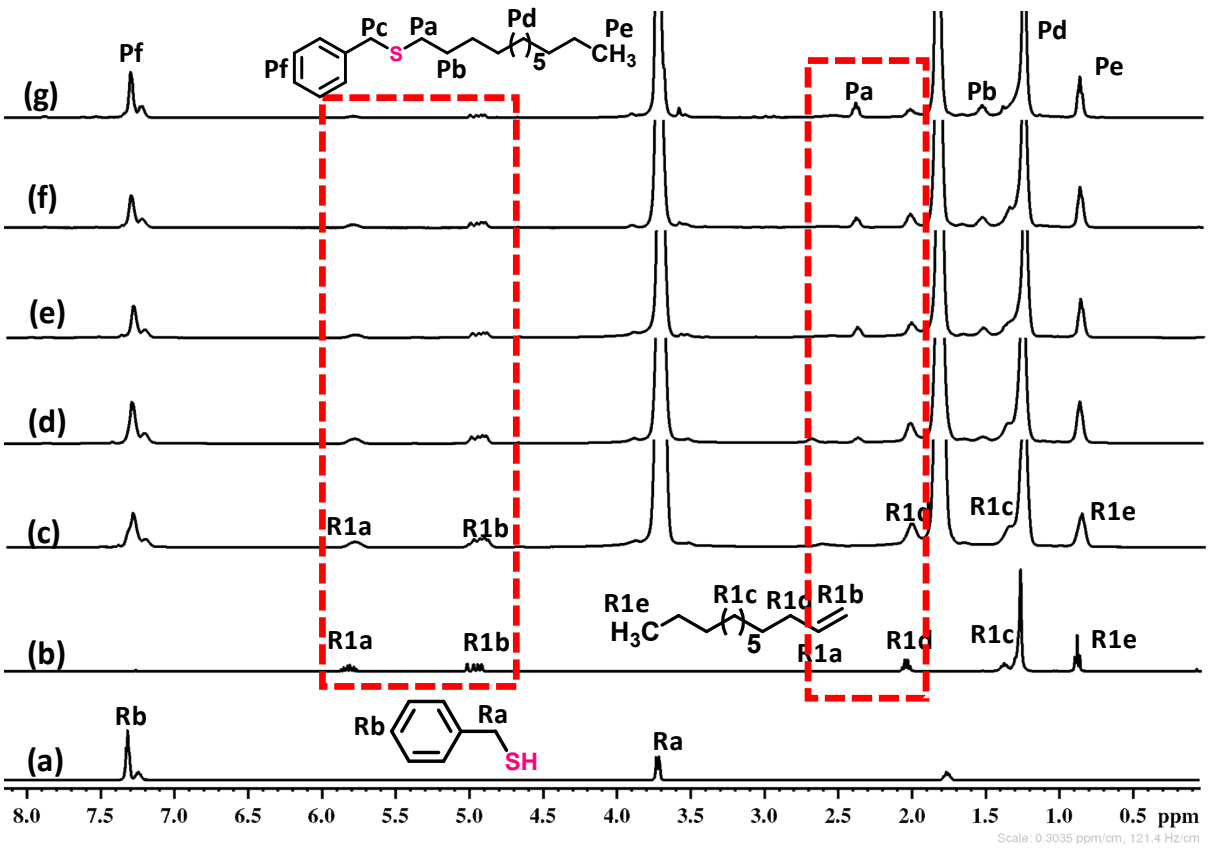


Figure S12. ^{1}H NMR spectra for the reaction between benzyl mercaptan and 1-dodecene at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) 1-dodecene, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

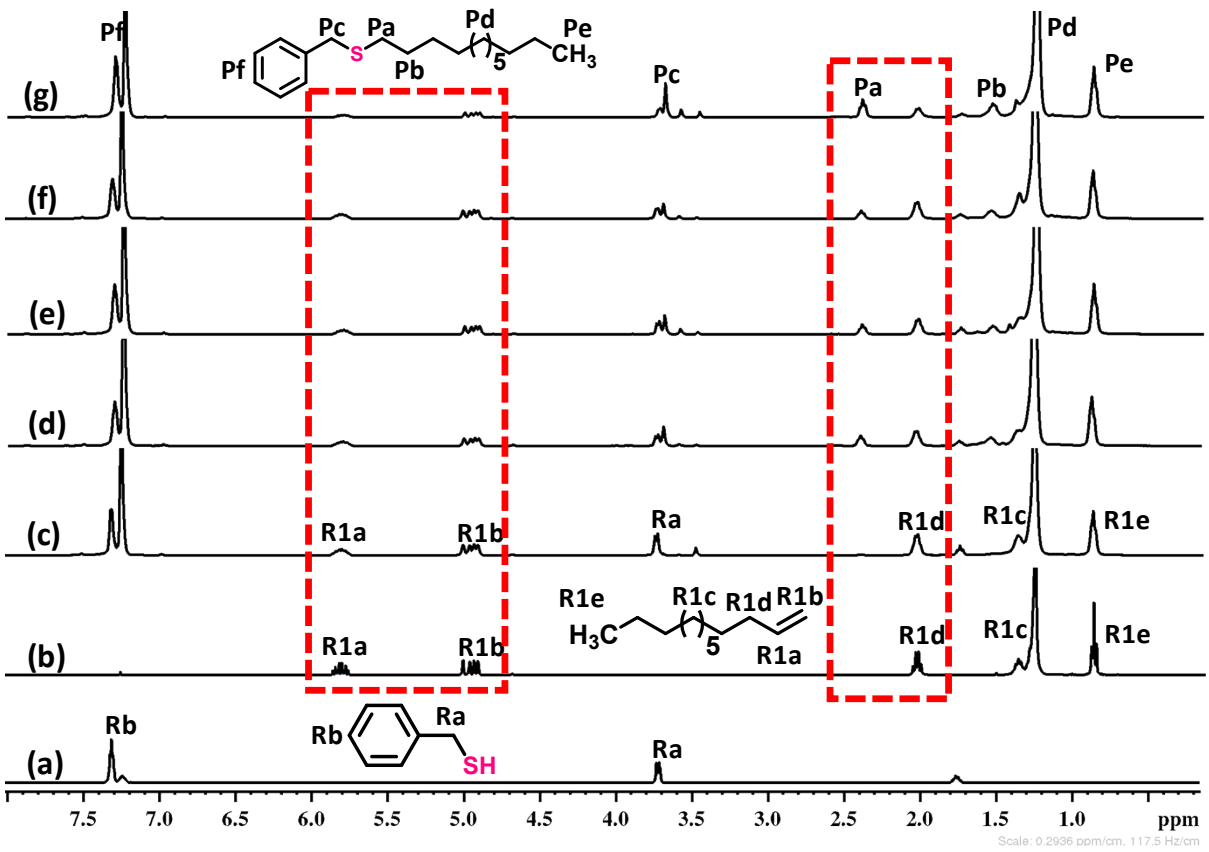


Figure S13. ^{1}H NMR spectra for the reaction between benzyl mercaptan and 1-dodecene at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) benzyl mercaptan, (b) 1-dodecene, (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO, (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO, and (g) 0.1 mmol TEMPO.

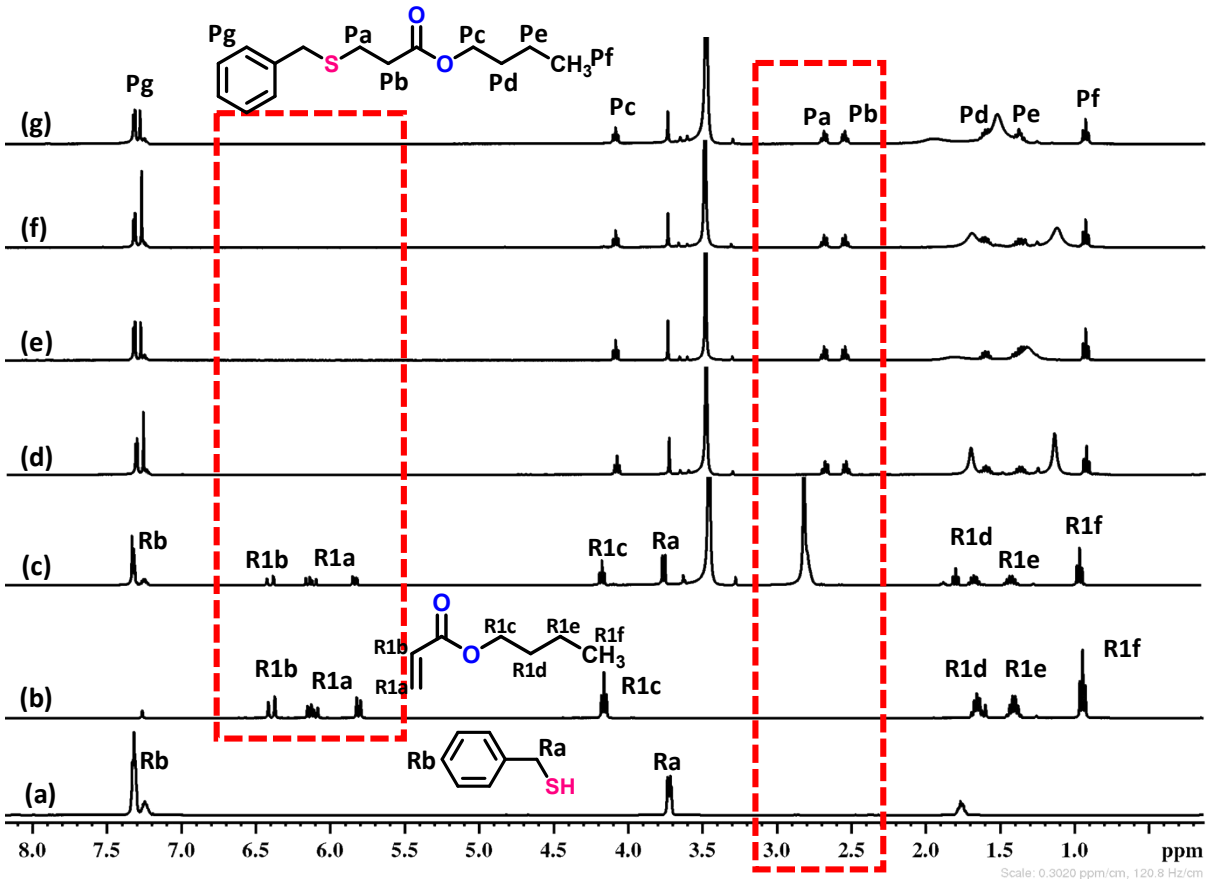


Figure S14. ^{1}H NMR spectra for the reaction between benzyl mercaptan and *n*-butyl acrylate at 35 °C using methanol as solvent and varying time (a) benzyl mercaptan, (b) *n*-butyl acrylate, (c) 0 h, (d) 4 h, (e) 8 h, (f) 12 h, and (g) 16 h.

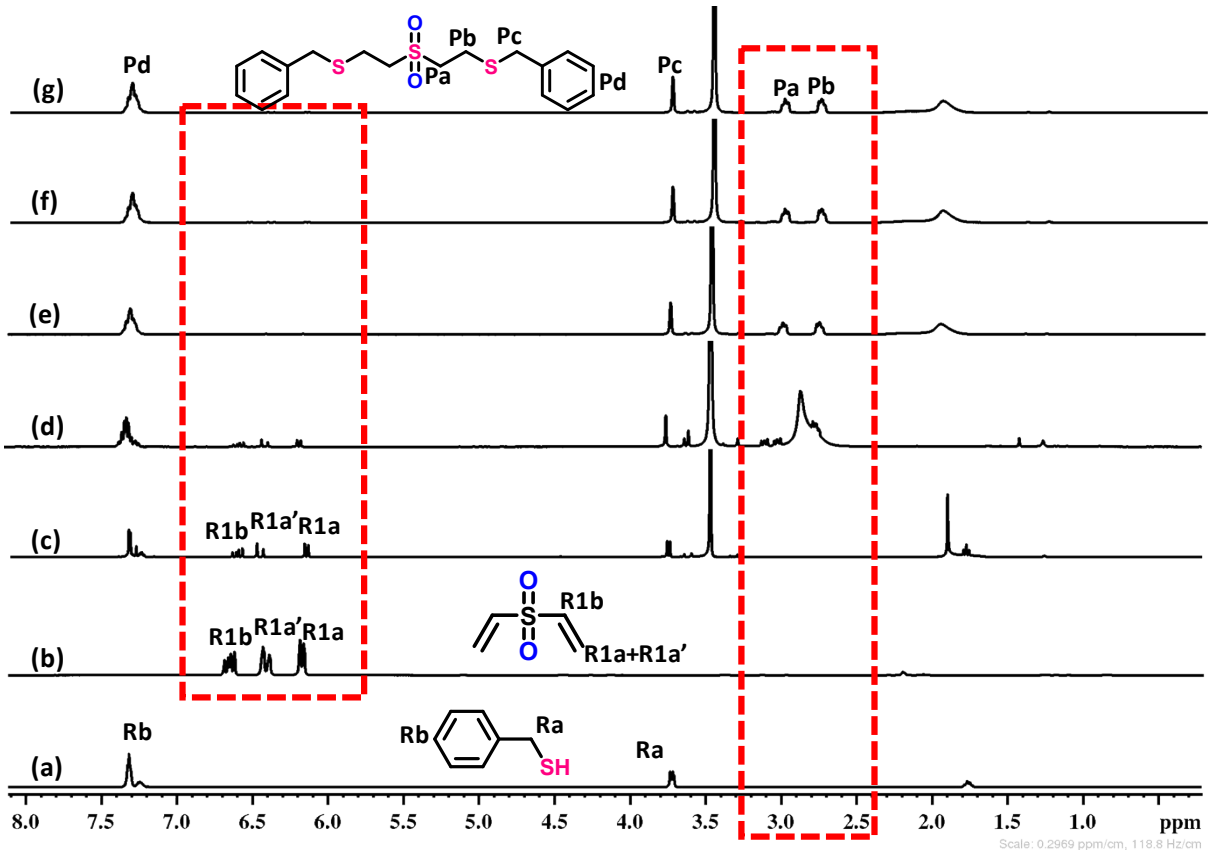


Figure S15. ^{1}H NMR spectra for the reaction between benzyl mercaptan and divinyl sulfone at 35 °C using methanol as solvent and varying time (a) benzyl mercaptan, (b) divinyl sulfone, (c) 0 h, (d) 4 h, (e) 8 h ,(f) 12 h, and (g) 16 h.

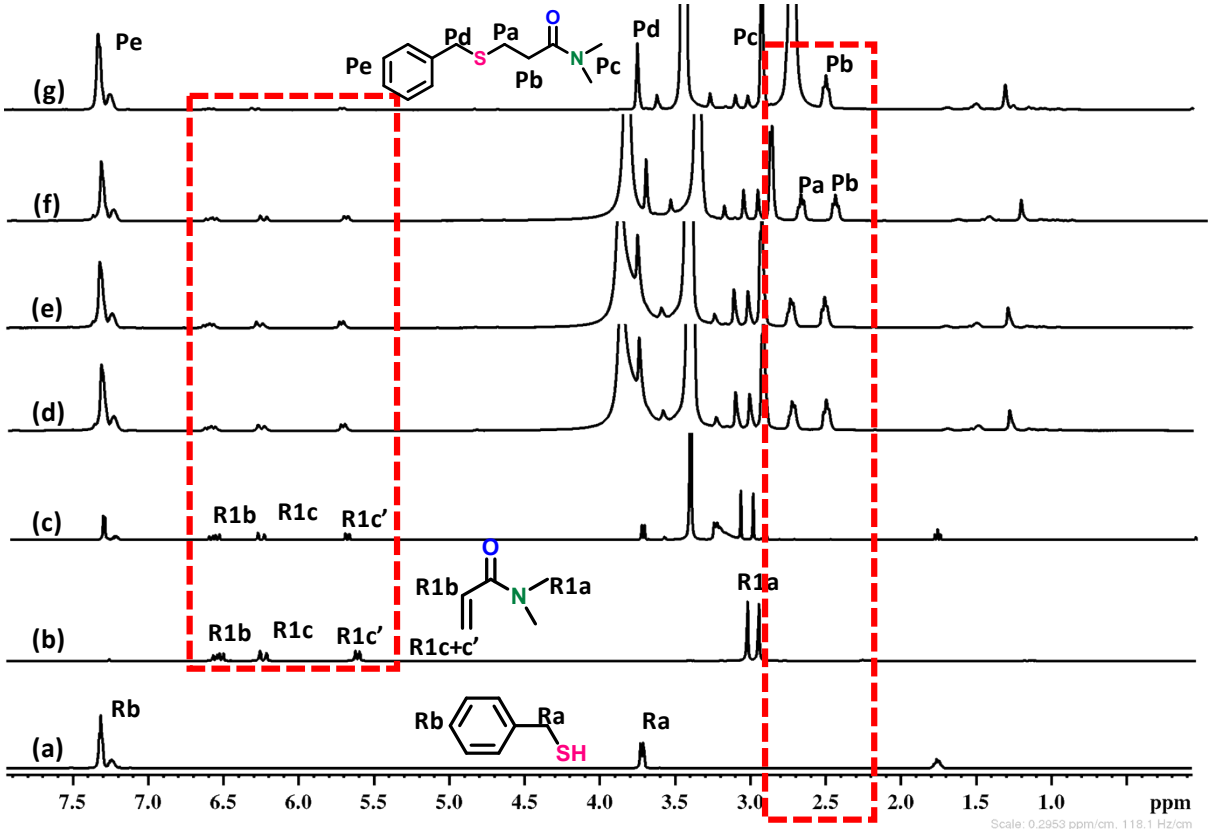


Figure S16. ^{1}H NMR spectra for reaction between benzyl mercaptan and *N,N*-dimethylacrylamide at 35 °C using methanol as solvent and varying time (a) benzyl mercaptan, (b) *N,N*-dimethylacrylamide, (c) 0 h, (d) 4 h, (e) 8 h, (f) 12 h, and (g) 16 h.

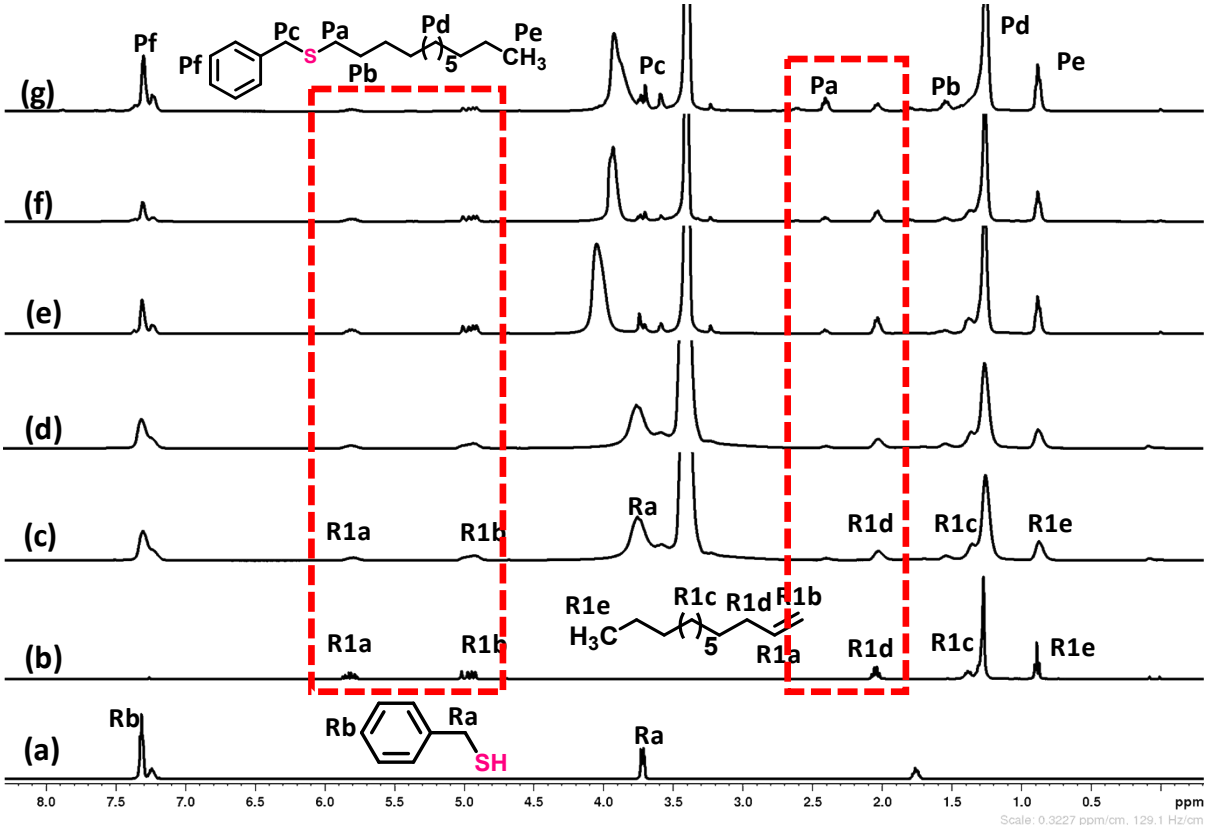


Figure S17. ^{1}H NMR spectra for the reaction between benzyl mercaptan and 1-dodecene at 35 °C using methanol as solvent and varying time (a) benzyl mercaptan, (b) 1-dodecene, (c) 0 h, (d) 4 h, (e) 8 h, (f) 12 h, and (g) 16 h.

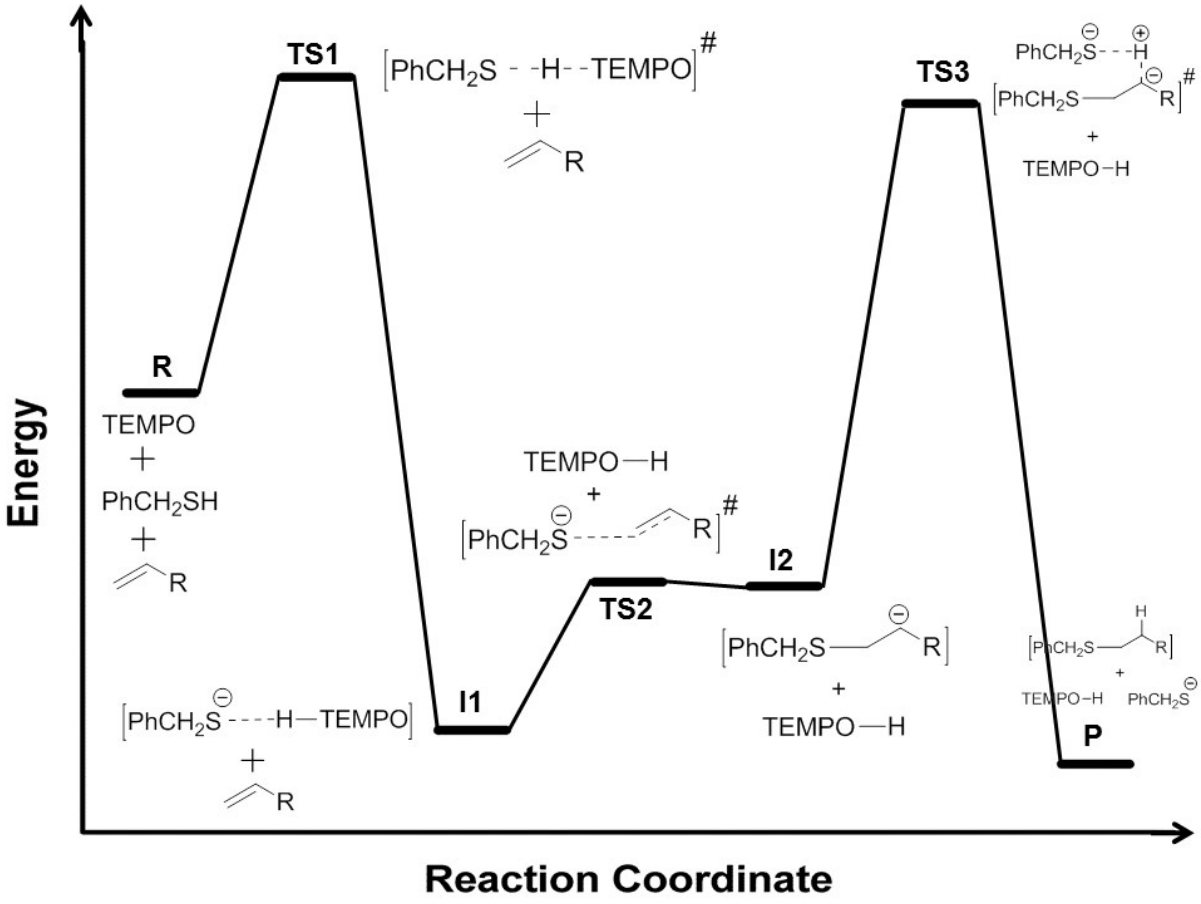


Figure S18. General mechanism adapted for the kinetics of TEMPO initiated thiol-ene reaction in the present study.

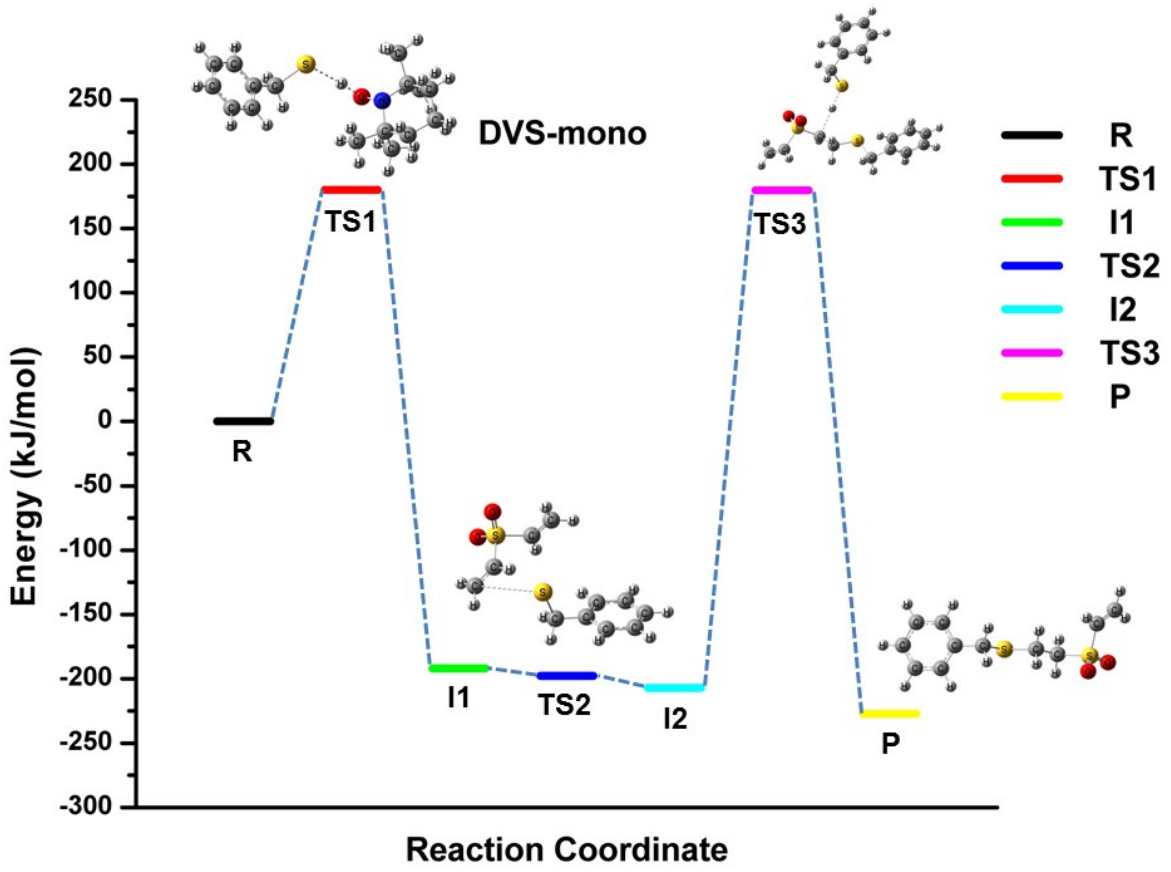


Figure S19. Energy profiles for the kinetics of reaction between thiol and DVS considering attack on one group of DVS. The structures of only transition states and product are shown in the figure.

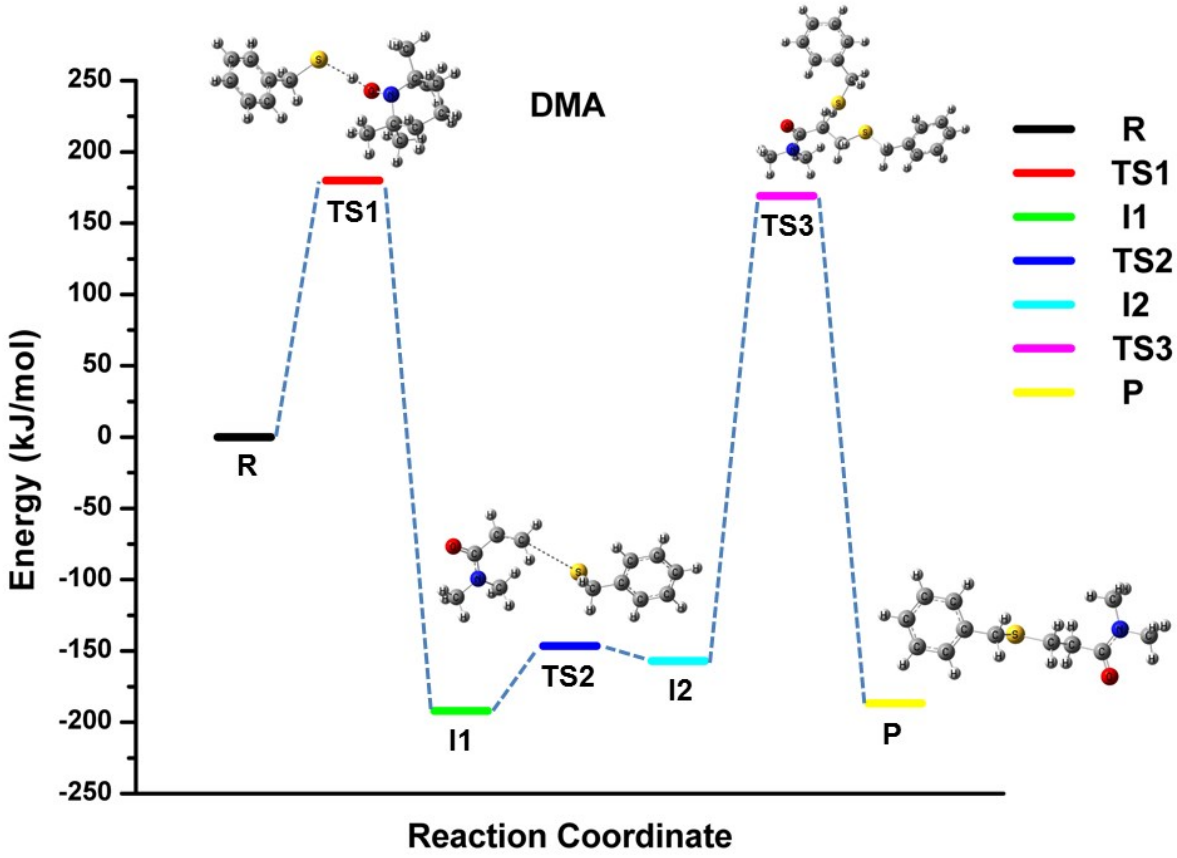


Figure S20. Energy profiles for the kinetics of reaction between thiol and DMA. The structures of only transition states and product are shown in the figure.

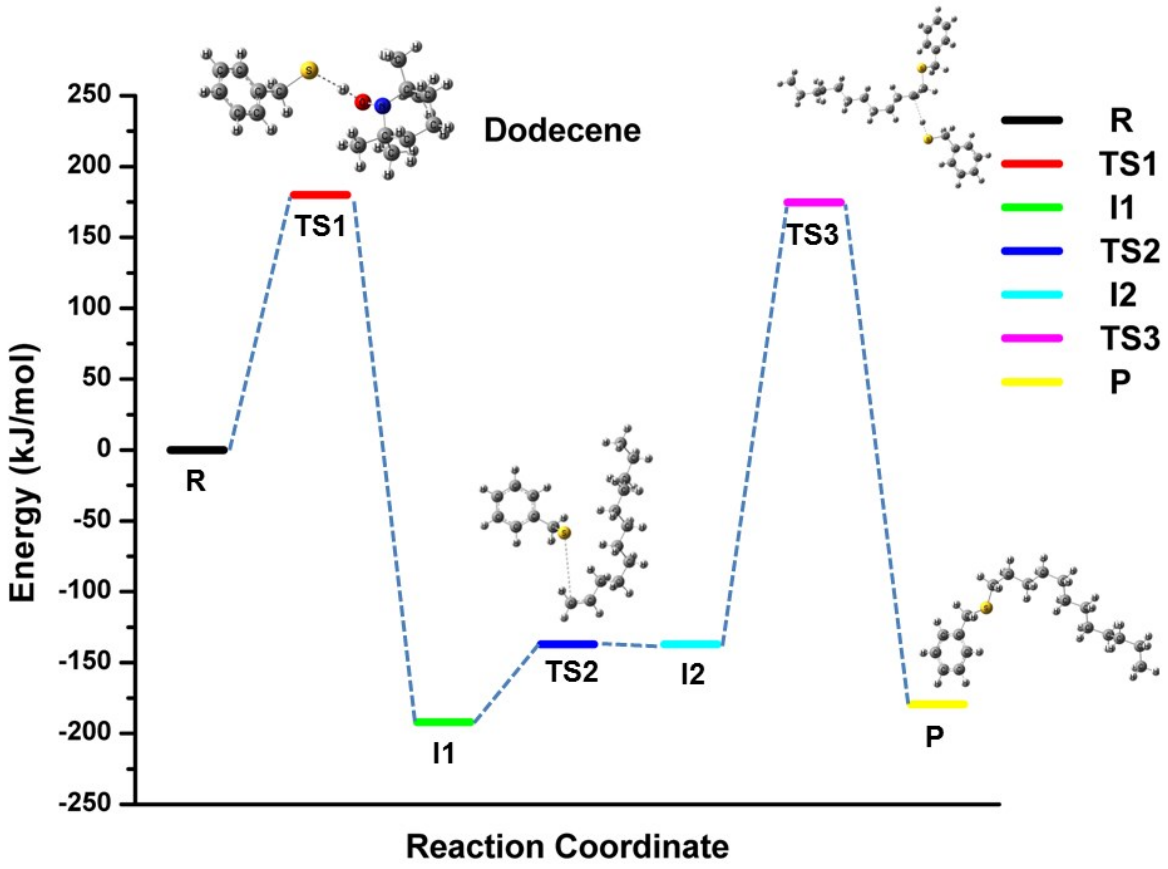


Figure S21. Energy profiles for the kinetics of reaction between thiol and 1-dodecene. The structures of only transition states and product are shown in the figure.

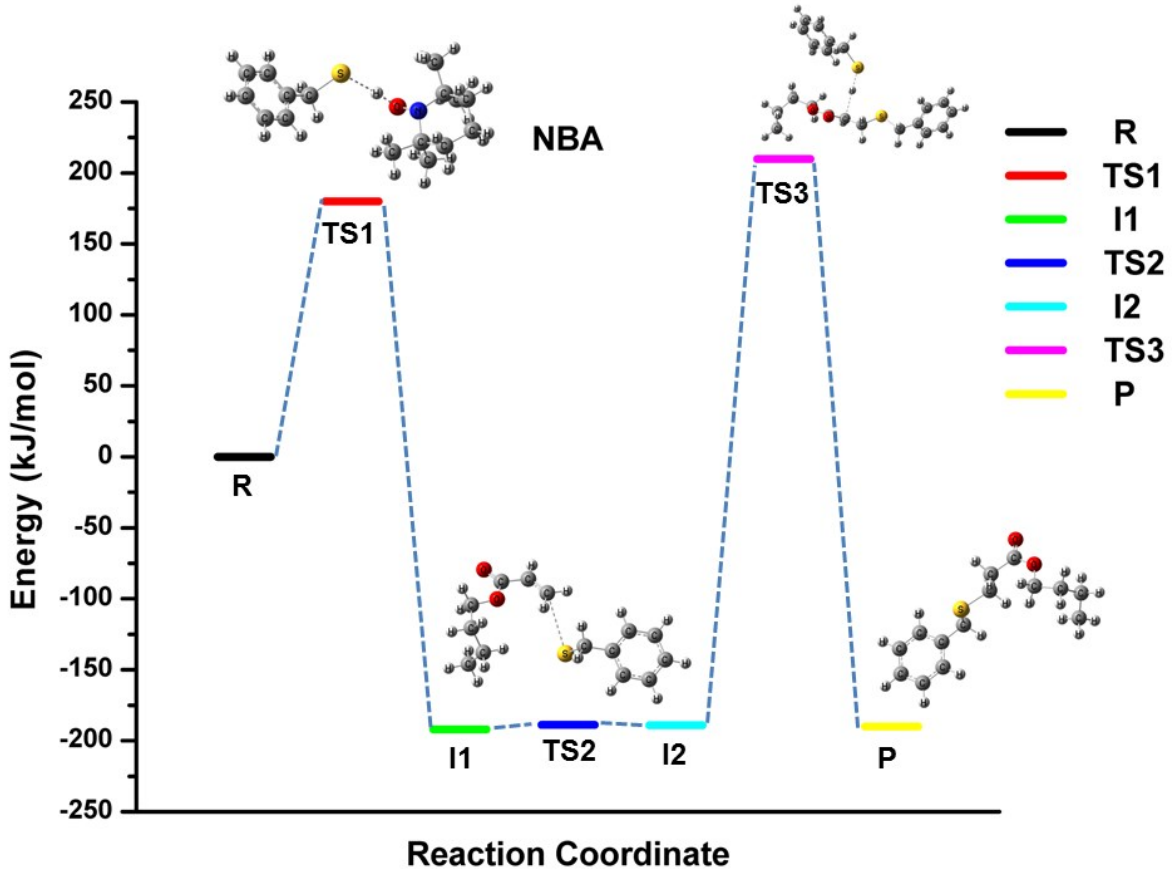
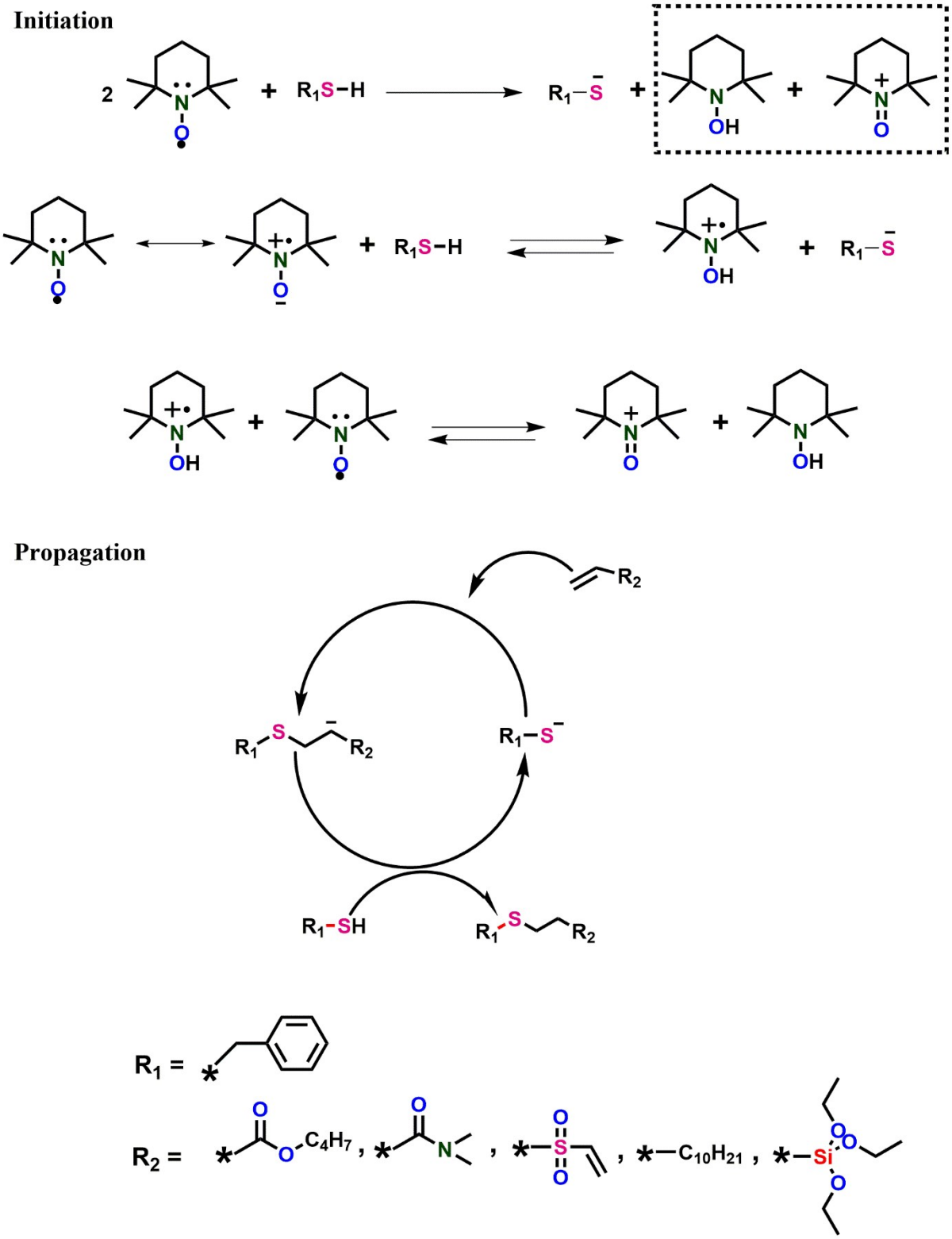


Figure S22. Energy profiles for the kinetics of reaction between thiol and NBA. The structures of only transition states and product are shown in the figure.



Scheme S1. Mechanism for thiol-ene reaction initiated by TEMPO showing detail initiation step.