Supporting Information for

Decoupling Amine Evolution from Sulfur Delivery in High-Temperature Metal Sulfide Nanocrystal Synthesis

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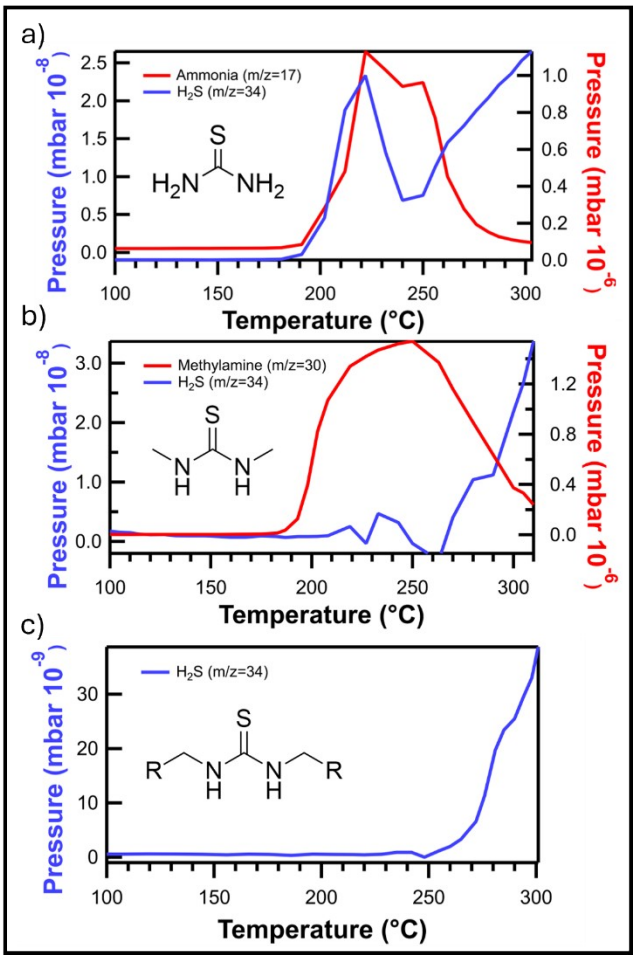

Figure S1. In situ mass spectrometry monitoring of gaseous products during thermal decomposition of (a) thiourea, (b) N,N'-dimethylthiourea, and (c) N,N'-dioleylthiourea (DOlTU) in oleylamine. The plots show the evolution of characteristic mass fragments corresponding to amine species and H_2S as a function of temperature. Thiourea and N,N'-dimethylthiourea exhibit early amine evolution prior to sulfur release, whereas DOlTU shows no detectable amine evolution before H_2S formation.

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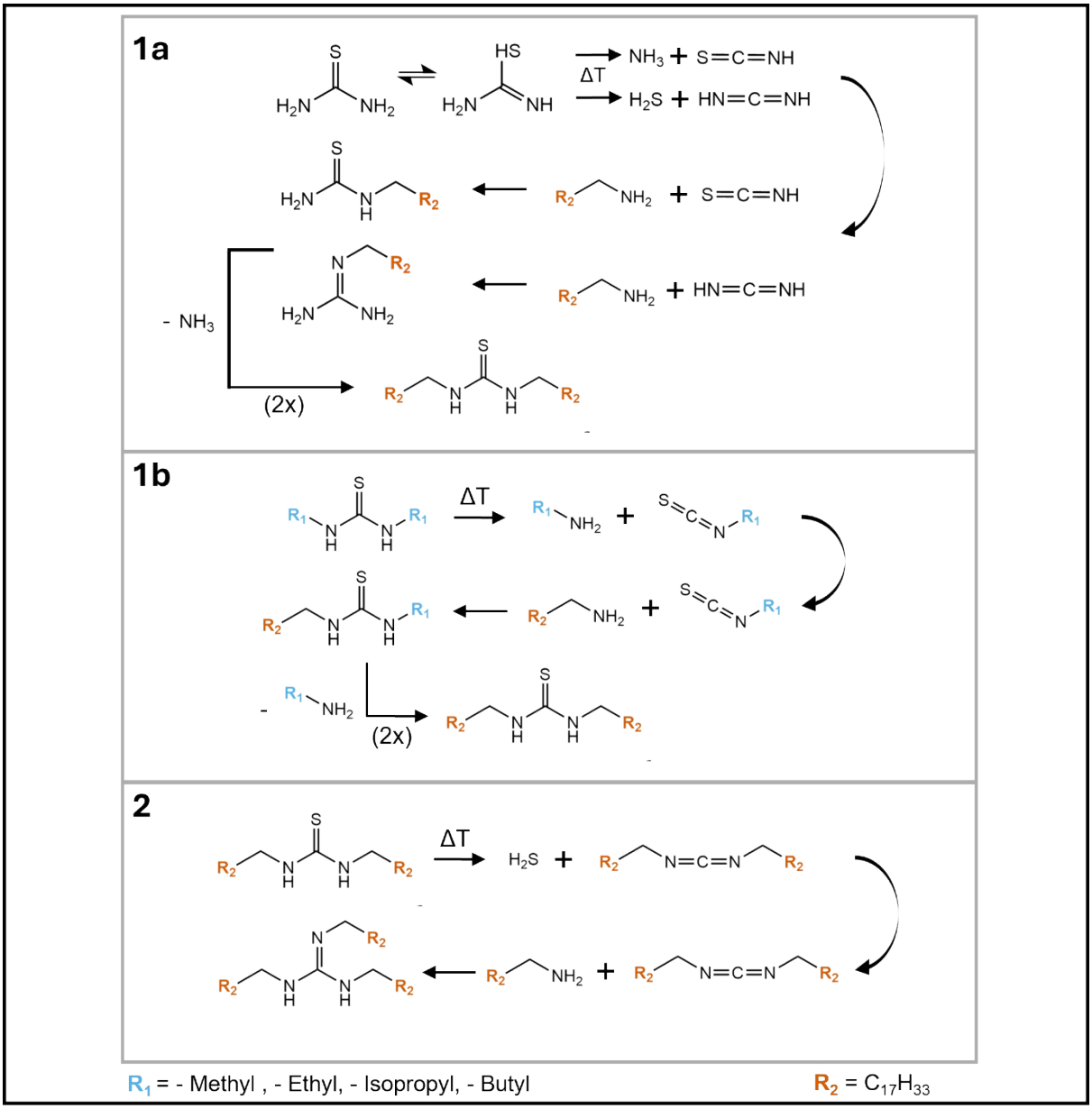

Figure S2. Proposed detailed thermal decomposition pathways of thiourea (1a) and N,N'-substituted thiourea derivatives (1b) in oleylamine. Both pathways converge through formation of asymmetric oleylthiourea intermediates that subsequently transform into N,N'-dioleylthiourea (DOlTU). At elevated temperature, DOlTU decomposes to release H_2S and dioleylcarbodiimide, which can further react with oleylamine to form 1,2,3-trioleylguanidine.

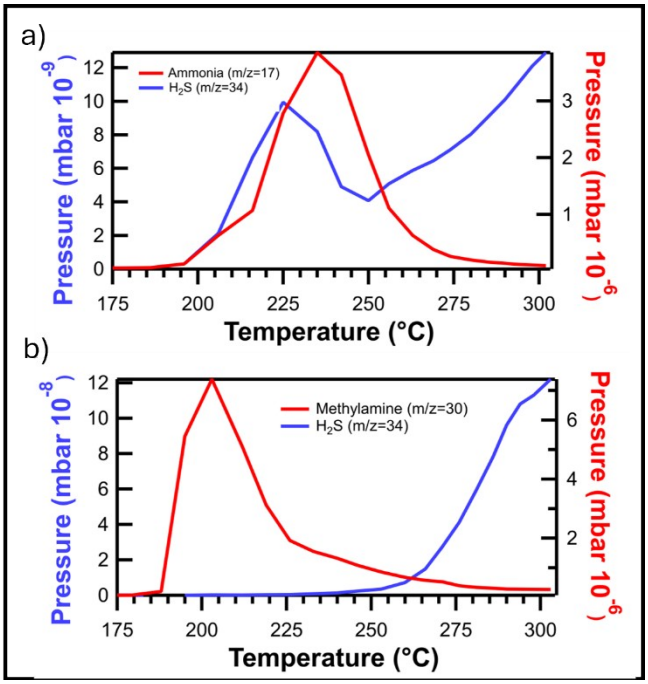

Figure S3. In situ mass spectrometry analysis of gaseous species during SrS nanocrystal synthesis using (a) thiourea and (b) N,N′-dimethylthiourea as sulfur precursors. The evolution profiles demonstrate that precursor decomposition in the presence of metal precursor follows the same sequence observed in neat oleylamine, with amine evolution preceding H_2S formation.

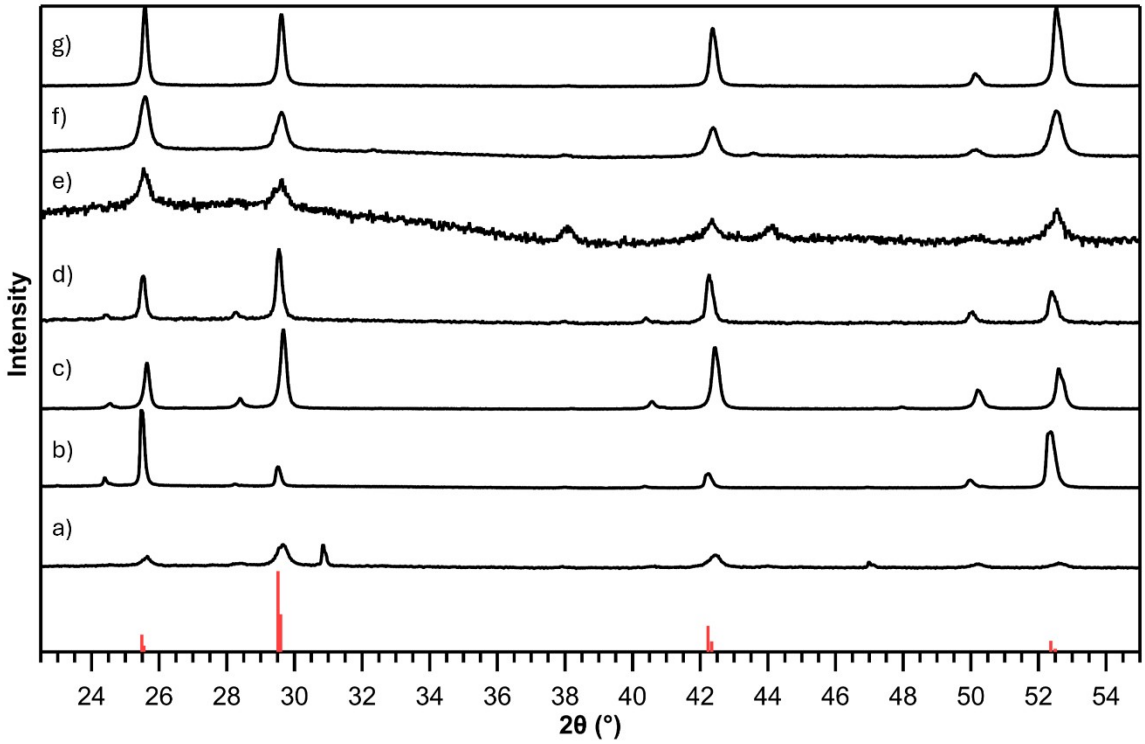

Figure S4. Powder X-ray diffraction patterns of products obtained after 5 min reactions at different temperatures using (a,b) thiourea, (c,d) N,N′-dimethylthiourea, and (e–g) N,N′-dioleylthiourea as sulfur precursors. The reference pattern of SrS is included for comparison. Reactions conducted near the temperature of peak amine evolution for conventional thioureas show little or no crystalline SrS formation, whereas DOlTU consistently produces crystalline material across the temperature range.

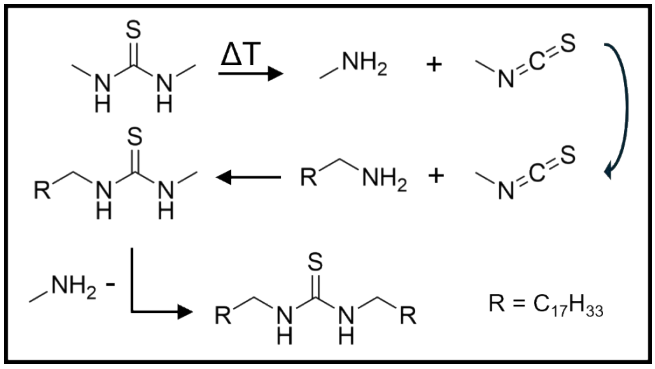

Figure S5. Proposed reaction pathway for the formation of N,N'-dioleylthiourea (DOlTU) from N,N'-dimethylthiourea in oleylamine during thermal treatment.

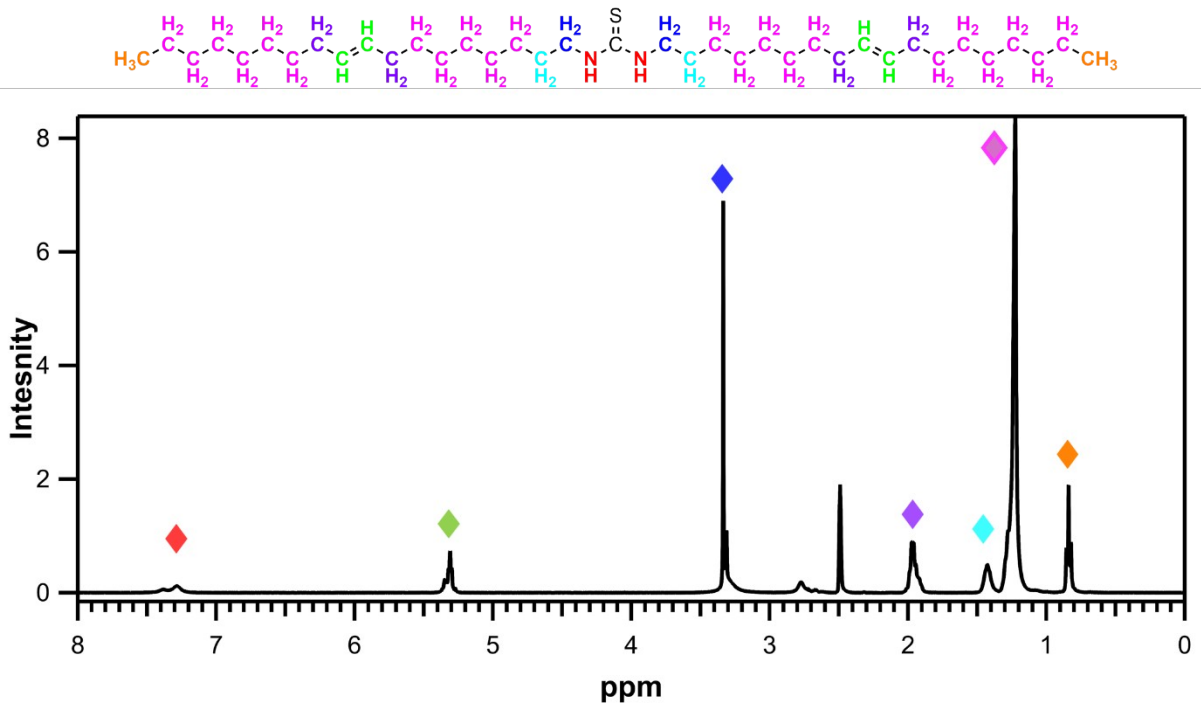

Figure S6. ^{1}H NMR spectrum of N,N'-dioleylthiourea (DOlTU) recorded in DMSO-d_6, confirming successful synthesis of the precursor. Characteristic resonances corresponding to the oleyl chains and thiourea NH groups are observed; minor signals originate from residual oleylamine and solvent. δ = 7.38 (s, 2H, NH_2, residue oleylamine), δ = 7.30 (s, 2H, NH, N,N'-dioleylthiourea), δ = 5.30 (m, 4H, CH, N,N'-dioleylthiourea), δ = 3.35 (s, 2H, H_2O, H_2O from DMSO-d_6), δ = 3.31 (s, 4H, CH_2, N,N'-dioleylthiourea), δ = 2.77 (s, 2H, CH_2, residue oleylamine), δ = 2.50 (s, 1H, CH_3, DMSO-d_6), δ = 1.96 (m, 8H, CH_2, N,N'-dioleylthiourea), δ = 1.43 (t, 4H, CH_2, N,N'-dioleylthiourea), δ = 1.24 (m, 22H, CH_2, N,N'-dioleylthiourea), δ = 0.83 (t, 6H, CH_3, N,N'-dioleylthiourea).

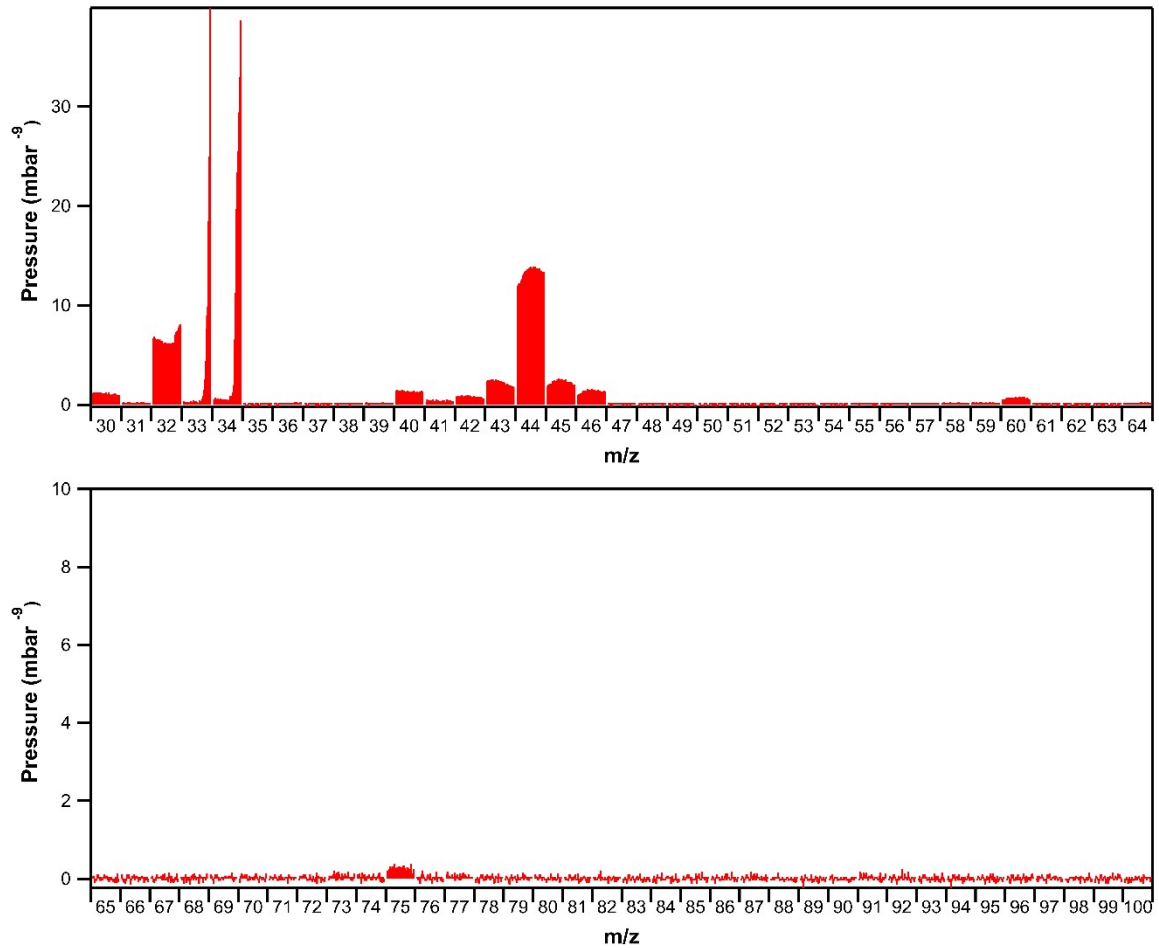

Figure S7. Full mass spectrometry scan (m/z 30–100) recorded during thermal decomposition of N,N'-dioleylthiourea in oleylamine. The absence of signals corresponding to low-mass amine fragments confirms that DOlTU does not release amines prior to sulfur evolution. Signals at m/z 30–46, 60, and 75 originate from background air contamination and remain constant during the experiment.