

Supplementary Information for:

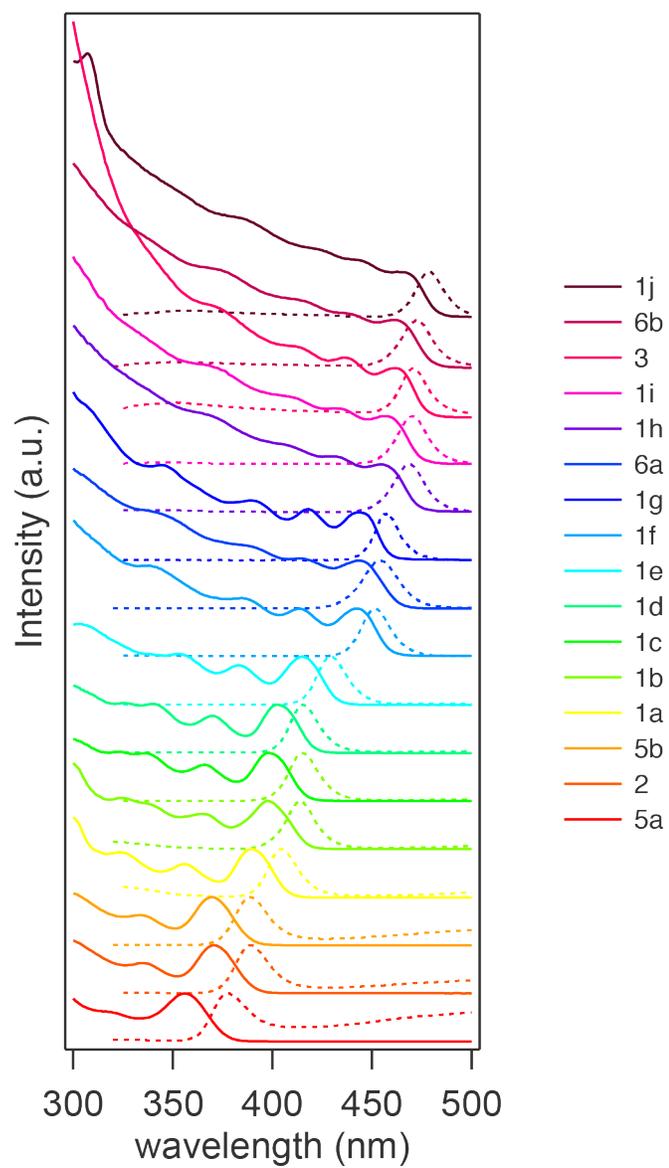
Kinetic Control over CdS Nanocrystal Nucleation Using a Library of Thiocarbonates, Thiocarbamates, and Thioureas

Leslie S. Hamachi, Ilan Jen-La Plante, Aidan C. Coryell, Jonathan De Roo, Jonathan S. Owen*
Department of Chemistry, Columbia University in the City of New York, New York, NY 10027,
United States.

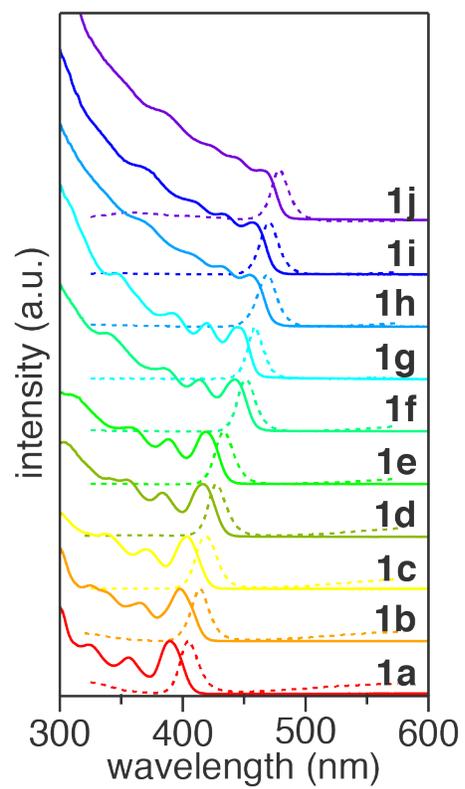
*Email: jso2115@columbia.edu

Sections:

- 1) Supplementary Figures (Pages S2-S22)
- 2) NMR Spectra of Precursors (Pages S23-S39)



SI Figure 1. Final CdS nanocrystal absorption and emission spectra from each compound tested in this manuscript.

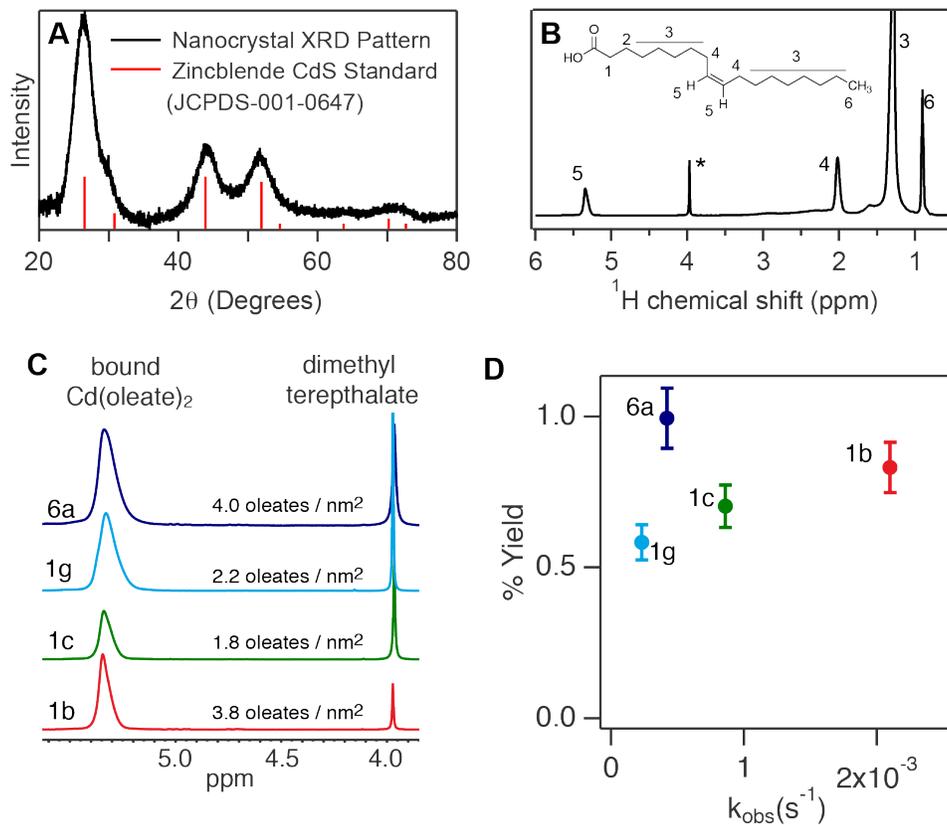


SI Figure 2. Final CdS nanocrystal absorption and emission spectra of nanocrystals made from thiocarbonate precursors.

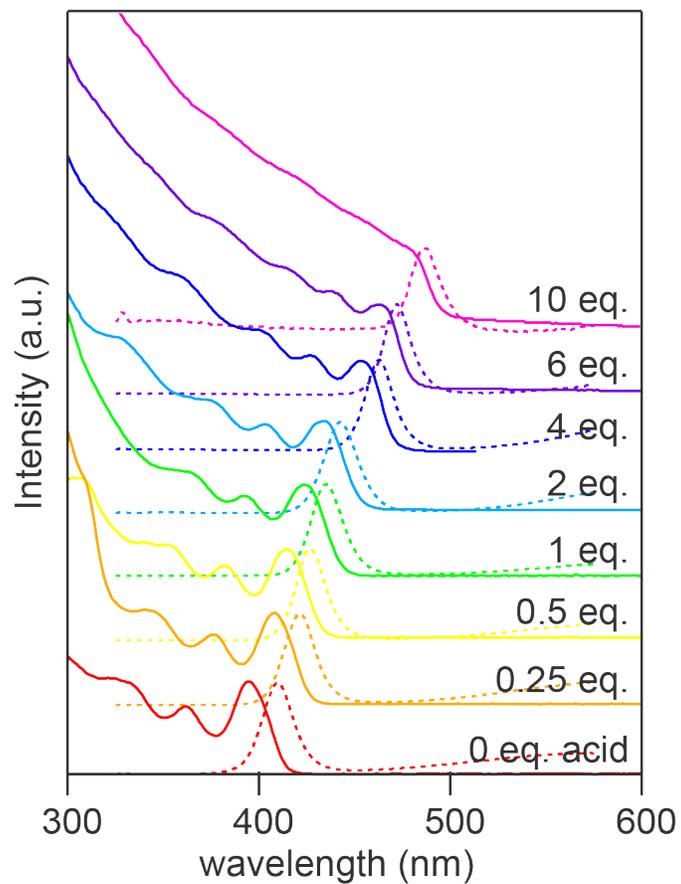


	X ₁	X ₂	k _{rel}	CdS yield	Diameter (nm)	Particle #	λ _{max}	time (min)	FWHM (eV)	Precursor Yield
1a	O-4-MeO-Ph	O-4-MeO-Ph	2.2 x 10 ⁻³	67%	3.13	1.53 x 10 ¹⁷	392	30	137	48%
1b	O-4-Me-Ph	O-4-MeO-Ph	2.1 x 10 ⁻³	75% (83%) ^a	3.26	1.57 x 10 ¹⁷	396	45	139	67%
1c	O-4-Me-Ph	O-4-Me-Ph	8.6 x 10 ⁻⁴	89% (70%) ^a	3.32	1.44 x 10 ¹⁷	398	60	132	76%
1d	O-4-Me-Ph	O-Ph	8.0 x 10 ⁻⁴	70%	3.86	9.78 x 10 ¹⁶	414	120	127	66%
1e	O-Ph	O-Ph	4.5 x 10 ⁻⁴	62%	4.04	7.17 x 10 ¹⁶	419	120	123	67%
1f	O-4-Me-Ph	O-4-Cl-Ph	2.9 x 10 ⁻⁴	73%	4.93	4.63 x 10 ¹⁶	442	240	112	68%
1g	O-4-Me-Ph	O-4-CF ₃ -Ph	2.3 x 10 ⁻⁴	57% (58%) ^a	5.02	3.22 x 10 ¹⁶	444	300	95	61%
1h	O-4-Me-Ph	O-Cy	2.1 x 10 ⁻⁴	66%	5.45	2.77 x 10 ¹⁶	454	305	114	62%
1i	O-Ph	O-4-Cl-Ph	8.2 x 10 ⁻⁵	56%	5.58	2.17 x 10 ¹⁶	457	720	108	60%
1j	O-4-Me-Ph	O-2,6-diMe-Ph	4.8 x 10 ⁻⁵	53%	5.85	1.51 x 10 ¹⁶	463	720	96	44%
2	O-4-Me-Ph	N-H(4-Me-Ph)	1.5 x 10 ⁻²	103%	2.73	3.98 x 10 ¹⁷	378	3	161	71%
3	O-4-Me-Ph	N-(CH ₃)Ph	8.1 x 10 ⁻⁵	62%	5.67	2.37 x 10 ¹⁶	459	1271	100	74%
4*	N-H(4-Me-Ph)	N-H(4-Me-Ph)	2.9 x 10 ⁻¹	---	---	---	---	---	---	---
5a	N-HPh	N-(n-Bu) ₂	5.3 x 10 ⁻²	93%	2.18	6.41 x 10 ¹⁷	355	1.5	175	---
5b	N-HPh	N-(CH ₃)Ph	1.4 x 10 ⁻²	110%	2.65	4.02 x 10 ¹⁷	375	4	169	92%
6a	N-(CH ₃) ₂	N-(CH ₃) ₂	4.2 x 10 ⁻⁴	98% (99%) ^a	4.98	5.54 x 10 ¹⁶	443	180	138	---
6b	N-(pyrr)	N-(pyrr)	2.9 x 10 ⁻⁴	103%	5.63	3.98 x 10 ¹⁶	458	245	106	49%

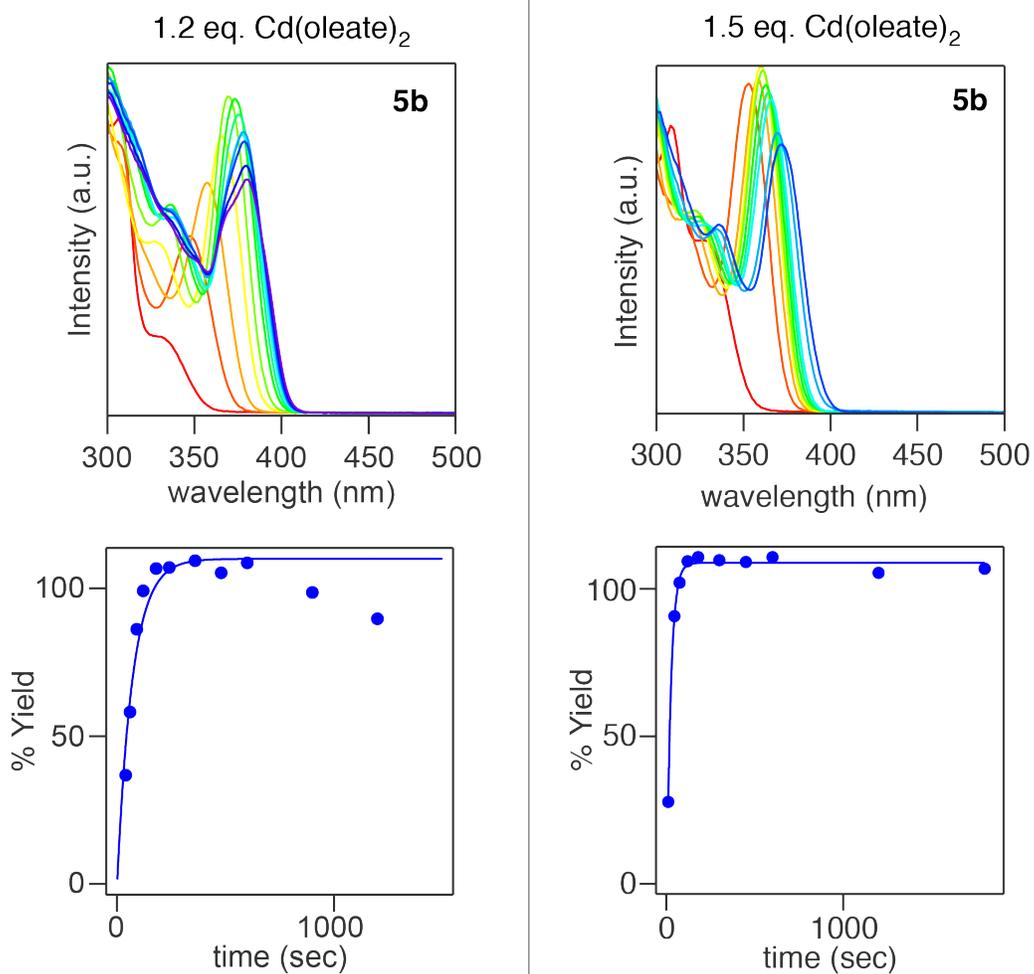
SI Figure 3. Table of all sulfur precursors, k_{rel} values, nanocrystal yields as determined via UV-vis and ^adetermined by weighing the isolated product and subtracting the known mass of ligands as determined by ¹H NMR, diameter, particle #, 1st excitonic feature, reaction time, FWHM of product, and precursor synthesis yield. See Nanocrystal Formation Kinetics and Cadmium Sulfide Reaction Yield Determination sections in the experimental for details.



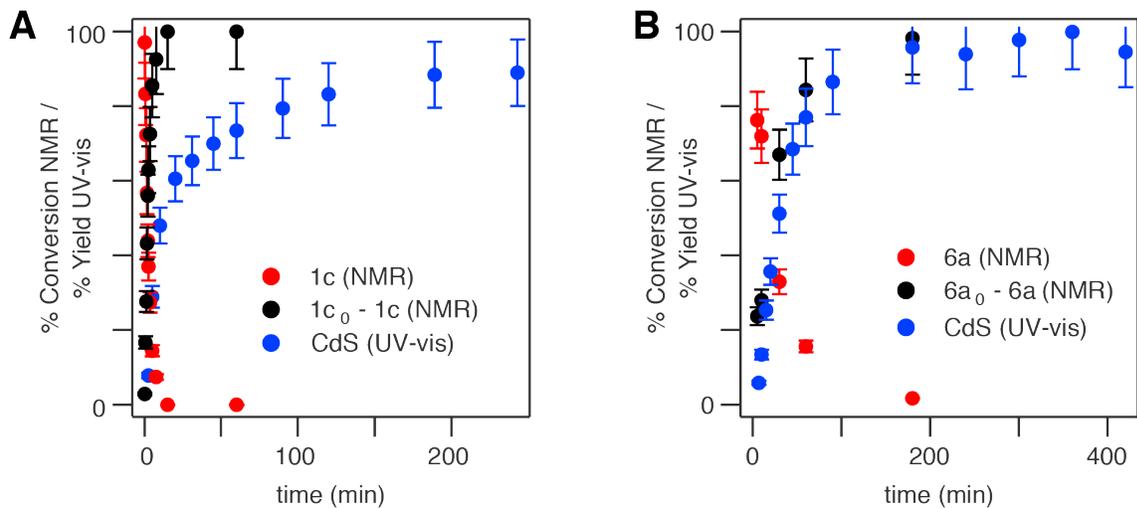
SI Figure 4. (a) PXRD of zincblende nanocrystal product. (b) Representative ^1H NMR of isolated nanocrystal sample. (c) Ligand coverages for several thiocarbonate and thiourea reactions. (d) % Yields as determined from ligand coverage and mass of isolated product.



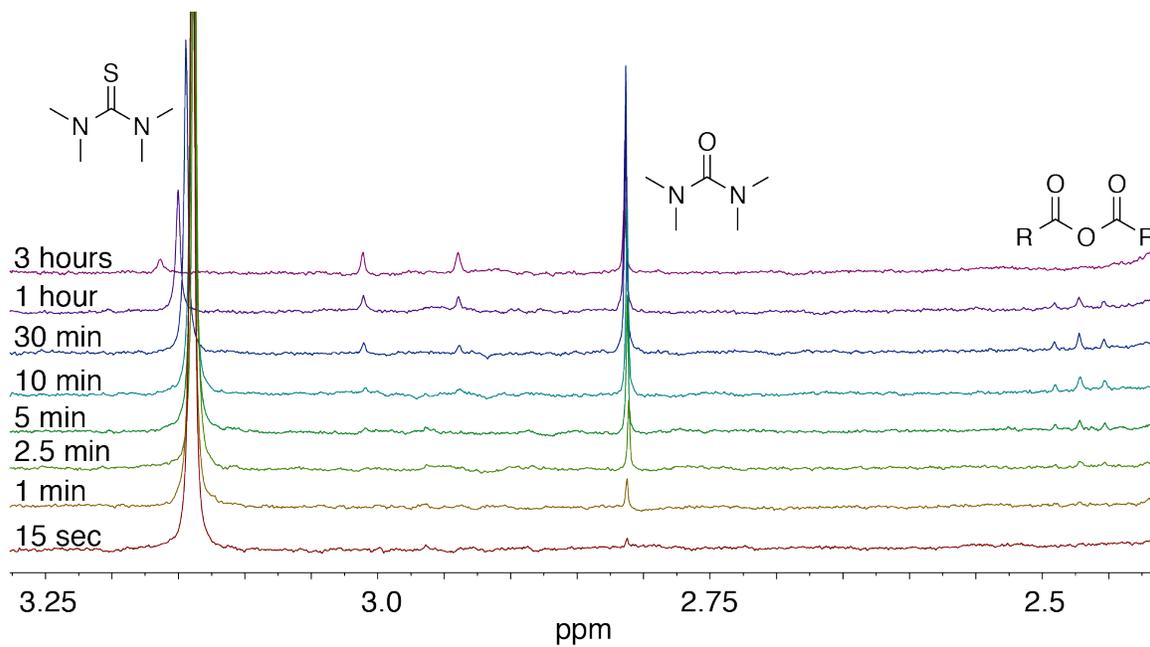
SI Figure 5. Final spectra of reactions of **6a** at standard reaction conditions with different equivalences of oleic acid added show size tunability.



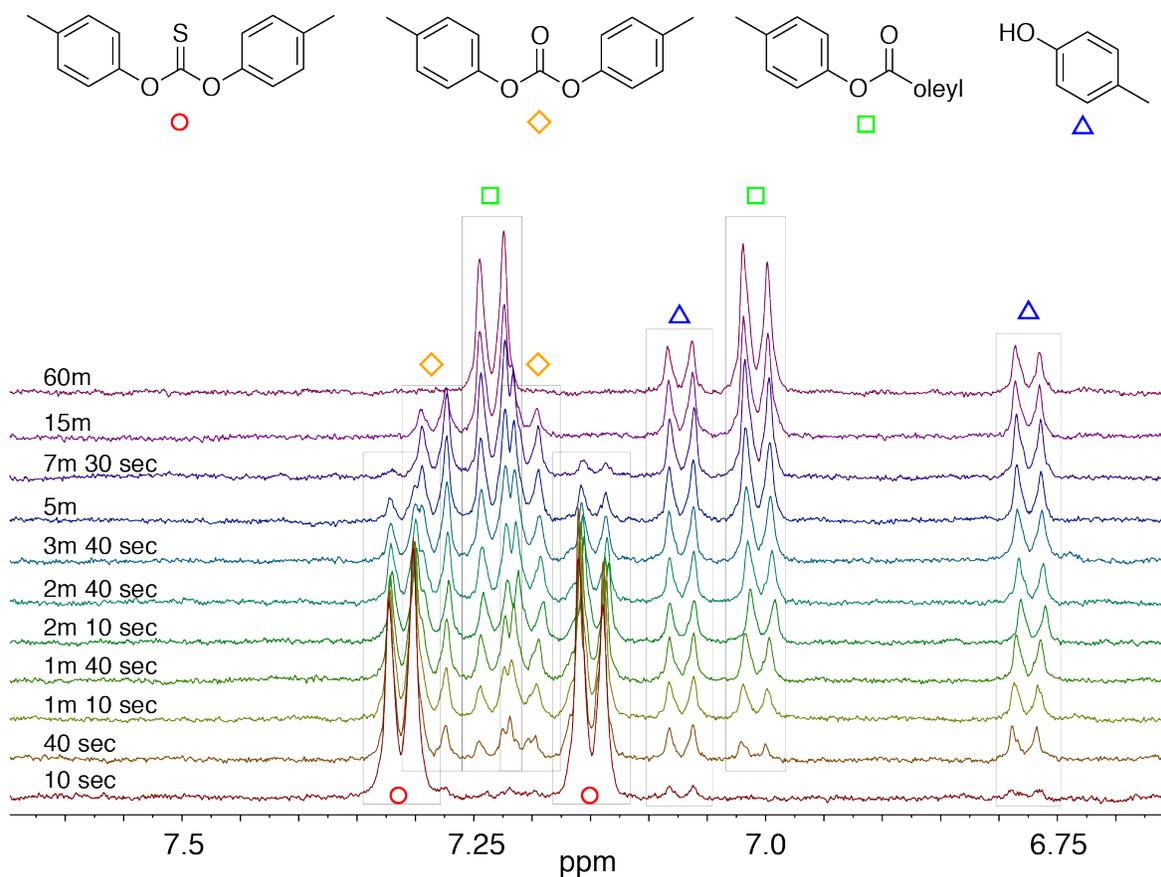
SI Figure 6. Comparing 1.2 and 1.5 equivalents of Cd(oleate)₂ precursor relative to sulfur precursor shows that more equivalents slow a ripening process that degrades the quality of the final nanocrystal product at small sizes.



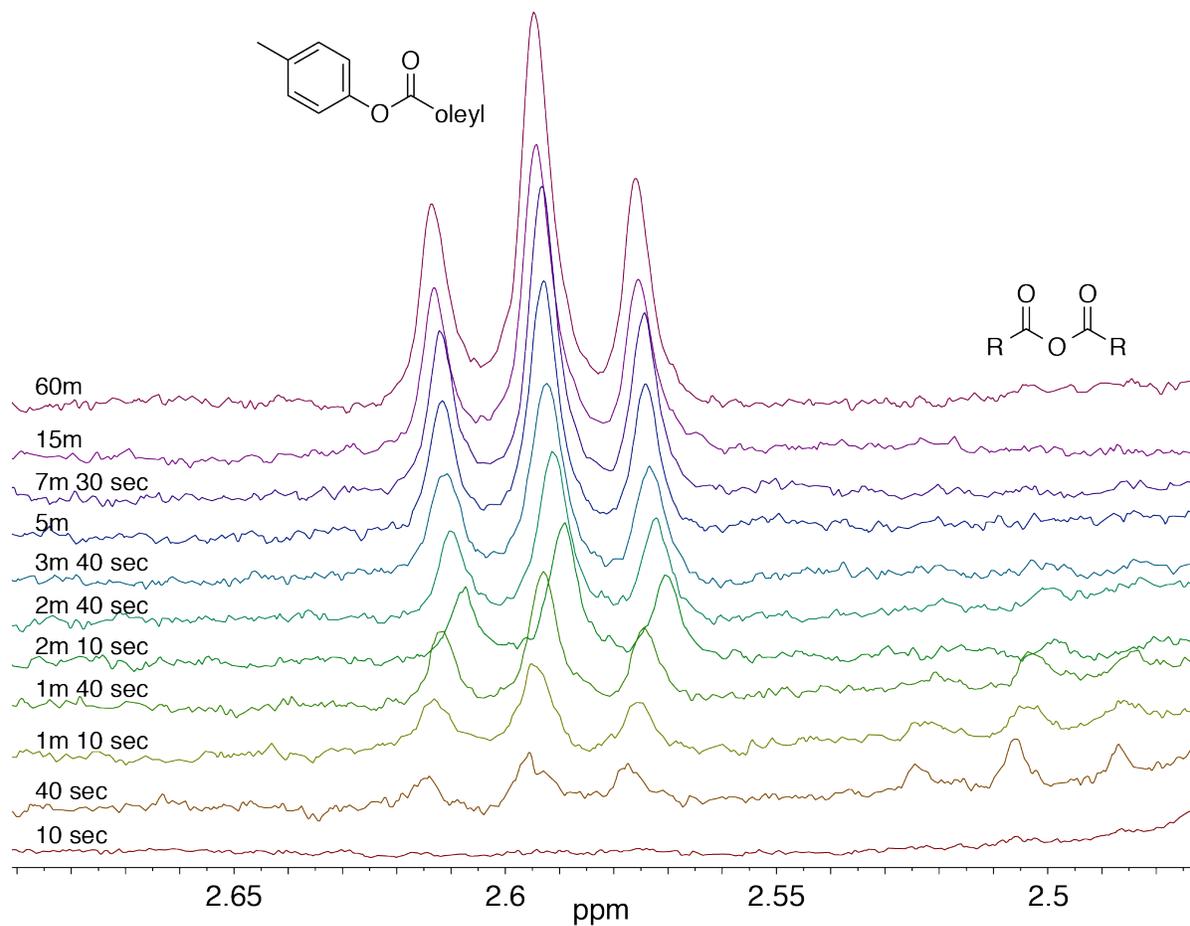
SI Figure 7. Reaction kinetics as measured by ¹H NMR spectroscopy (red), starting amount of precursor – red data (black), and UV-vis spectroscopy (blue) for (a) **1c** and (b) **6a**.



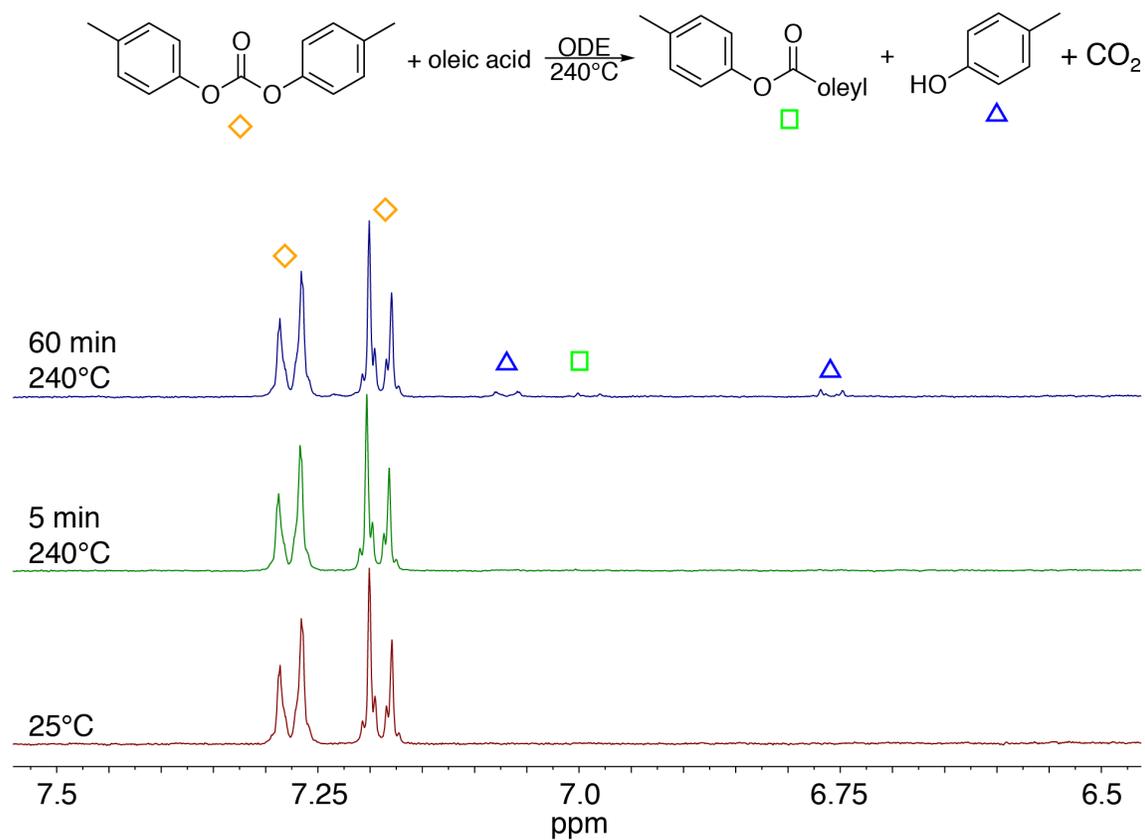
SI Figure 8. ¹H NMR spectra of the reaction of **6a** with cadmium oleate shows appearance of tetramethyl urea and oleic anhydride.



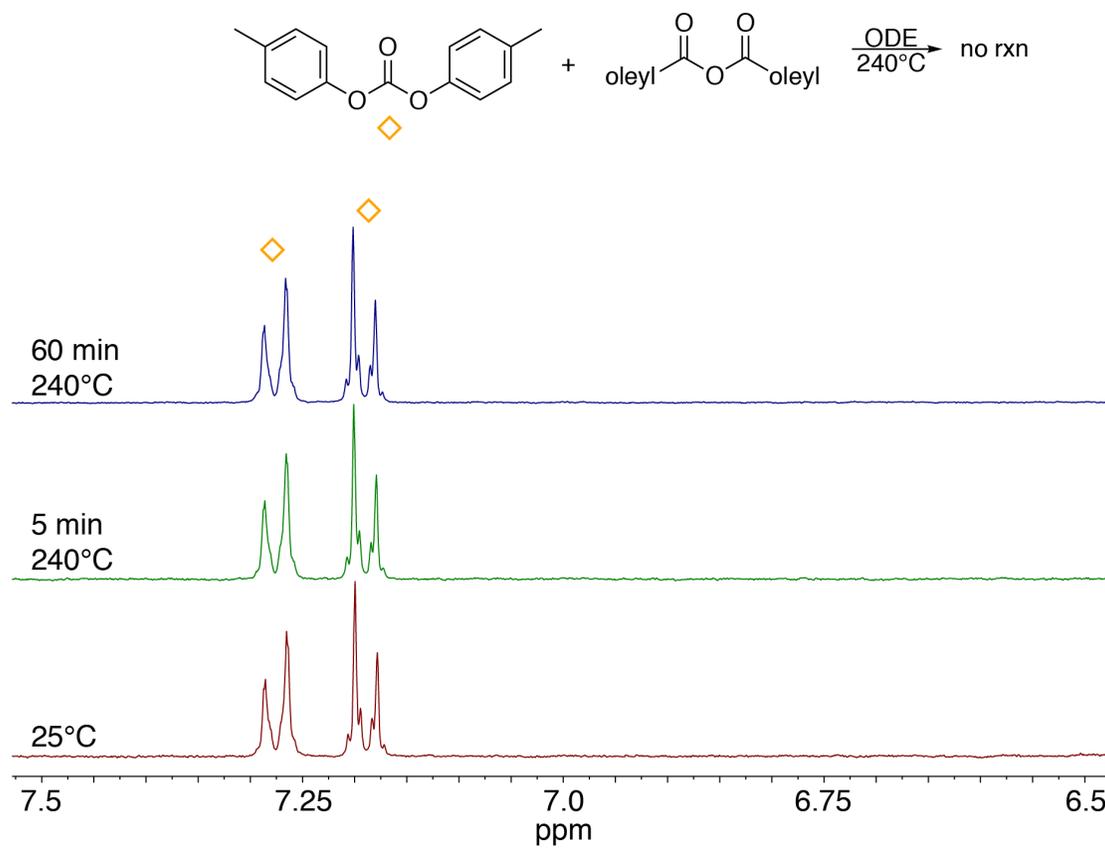
SI Figure 9. ¹H NMR for coproduct identification and tracking over the course of the reaction of **1c** with cadmium oleate.



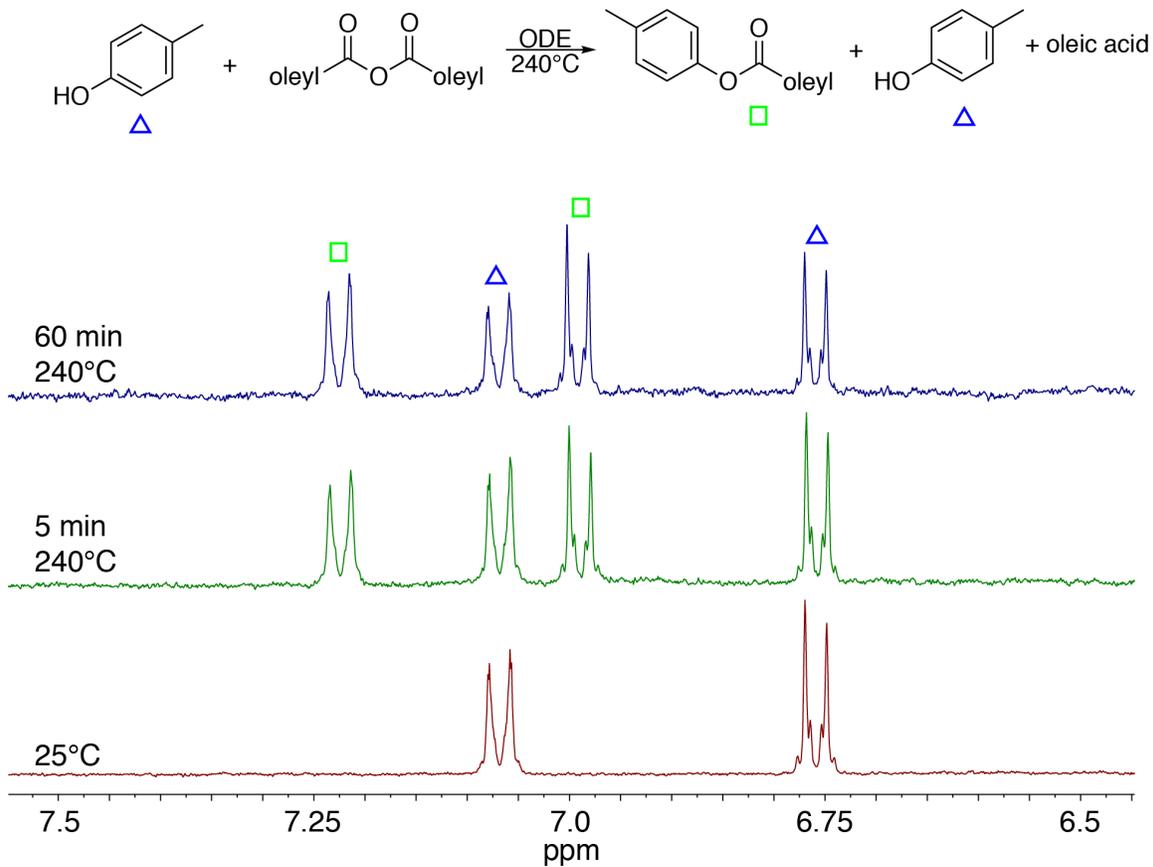
SI Figure 10. ^1H NMR for the reaction of **1c** with cadmium oleate shows appearance of oleic anhydride at early times which is consumed to produce tolyl oleate.



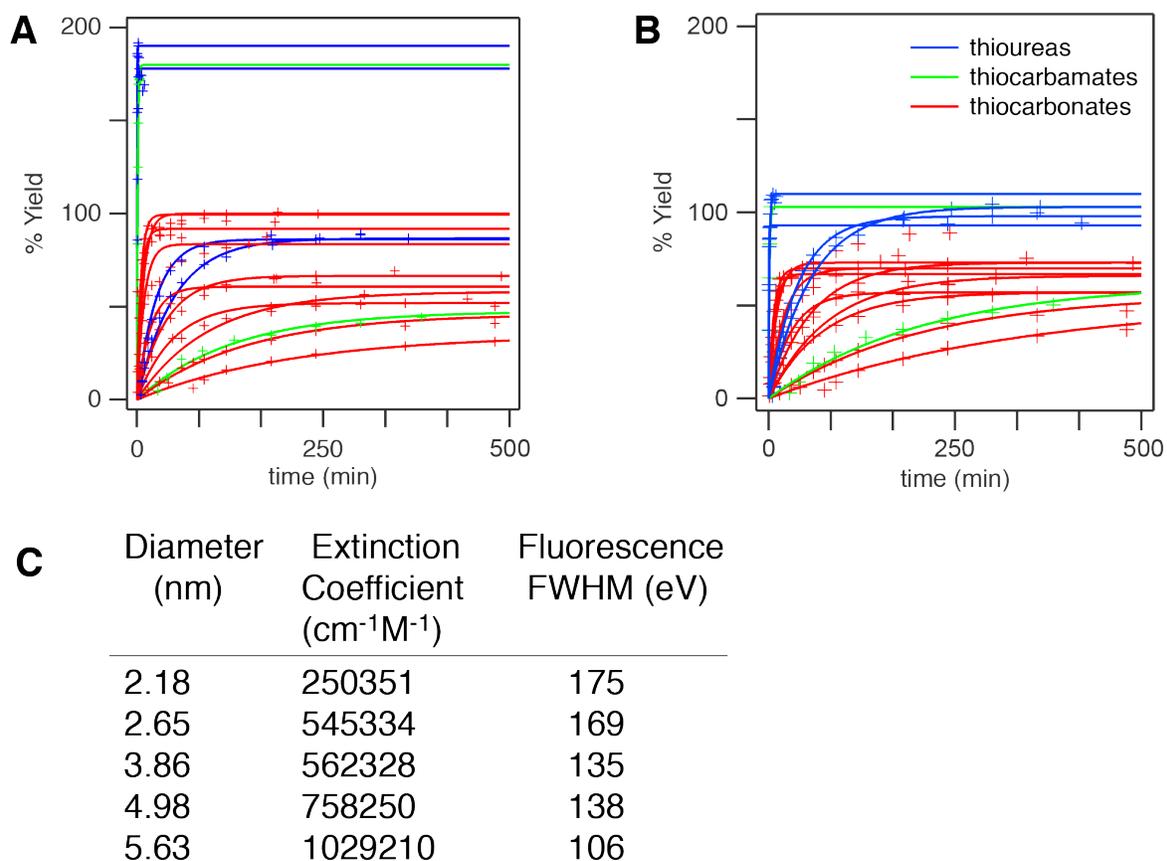
SI Figure 11. ¹H NMR spectra of the reaction between **7c** and oleic acid. The formation of tolyl oleate and *p*-cresol is observed.



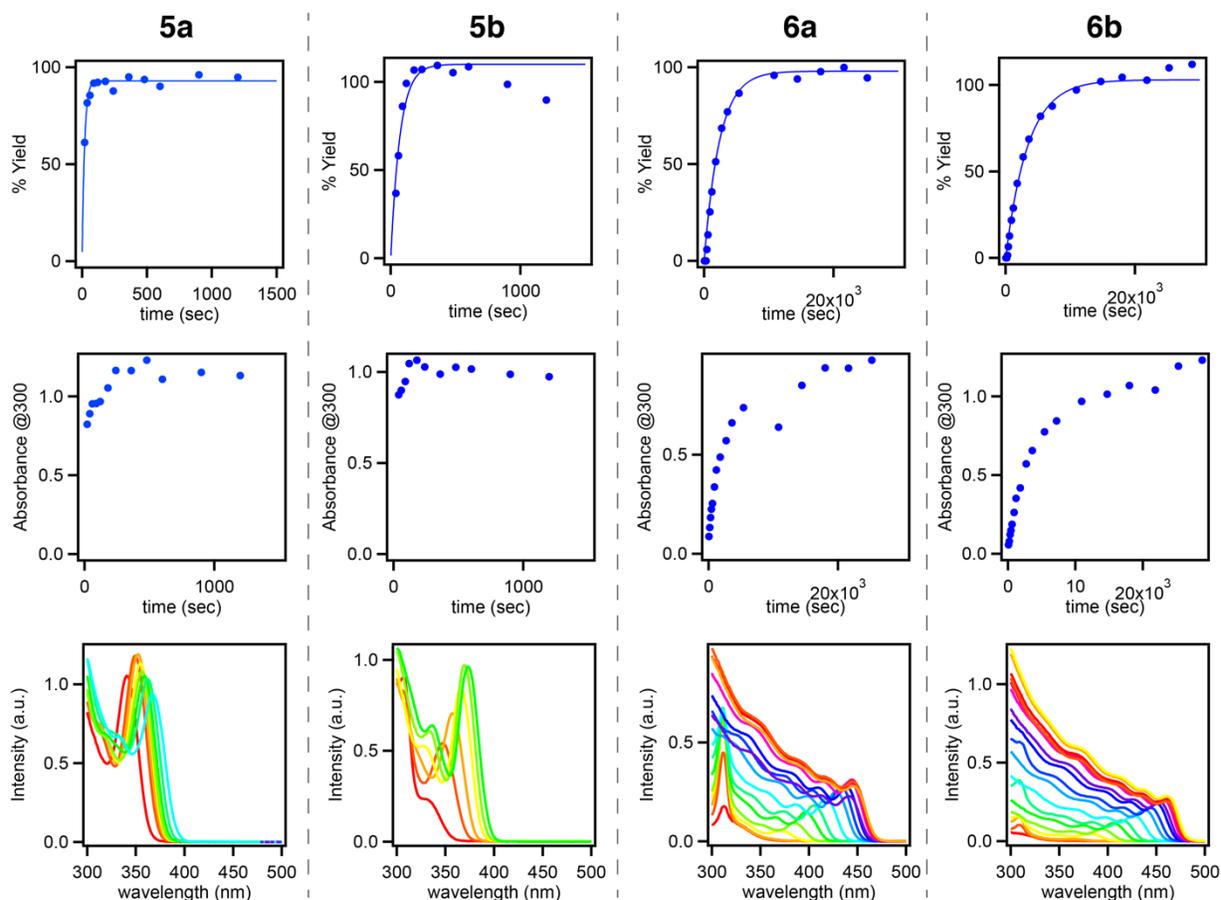
SI Figure 12. ^1H NMR to monitor the reaction of **7c** and oleic anhydride. No reaction is observed.



SI Figure 13. ¹H NMR spectroscopic monitoring of the reaction between *p*-cresol and oleic anhydride. The formation of *p*-tolyl oleate is observed.



SI Figure 14. (a) % Yields of reaction aliquots using previously reported extinction coefficient,¹ (b) % Yields of reaction aliquots using the size dependent extinction coefficients determined in this work. (c) Properties of particles used in calibration curve

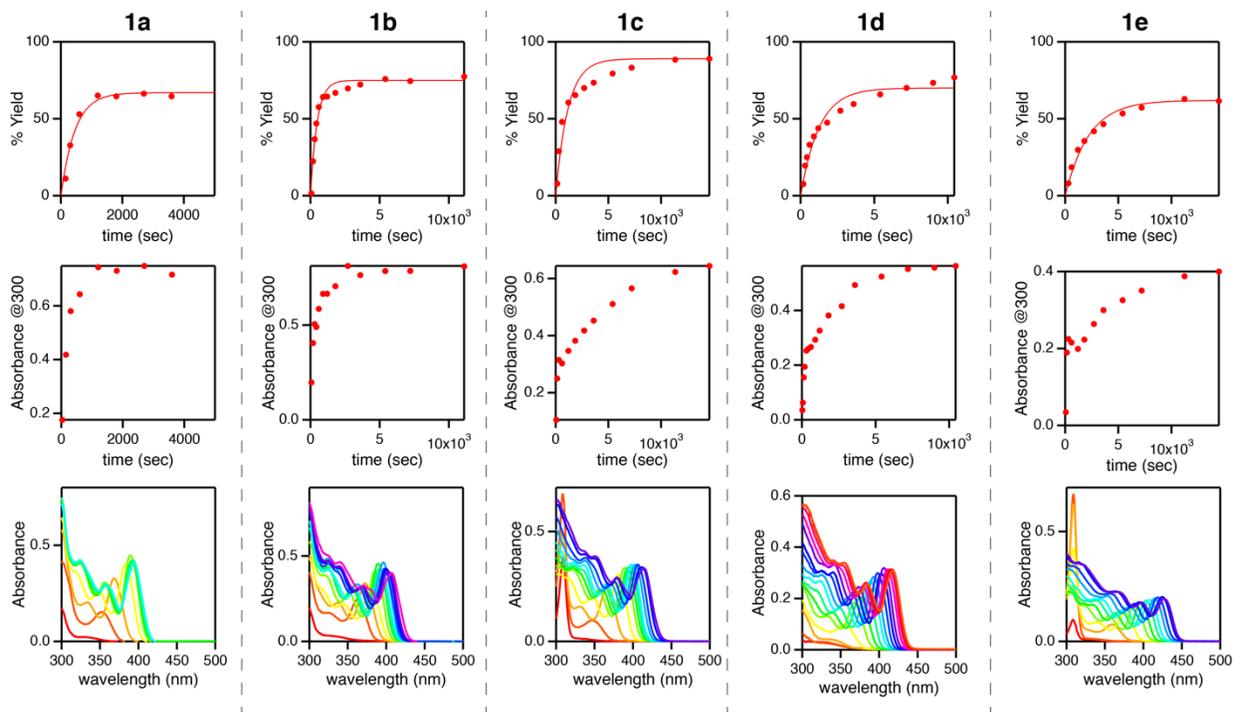


SI Figure 15. Yield Data using corrected size dependent extinction coefficients, absorbance at 300nm, and UV-vis spectra of reaction aliquots for thioureas **5a–6b**.

Selection of the endpoint for each of these reactions for incorporation into the extinction coefficient correction is nontrivial. In most cases, the precursor is considered done reacting when the % Yield starts to plateau. However, for precursor **5b**, a decrease in % Yield is observed as particles ripen after the reaction has reached completion. Additionally, % Yields are compared with the absorbance at 300nm, which while not a perfect size independent wavelength to measure conversion of CdS, serves as a rough measure of conversion. Precursor **6b**, shows a plateau and then increase in % yield at extended reaction times. The endpoint was selected during the plateau region since at very large sizes when the 1st excitonic feature is hard to identify, there is more error incorporated into the % yield calculation.

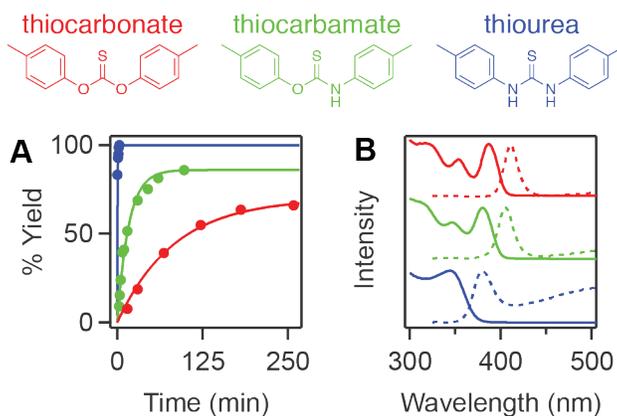
With the absorbance data at each reaction endpoint and a calculated theoretical concentration of CdS nanocrystals at 100% conversion, extinction coefficients could be calculated. These are plotted and compared against the empirical curve reported by Peng's group.¹ These data points are fit to a second order polynomial and used in subsequent % Yield calculations for thiocarbonate and thiocarbamate precursors.

It is worth noting that some reactions result in the formation of magic size clusters (peak around 321 nm), however a correlation between their appearance and precursor structure could not be determined.

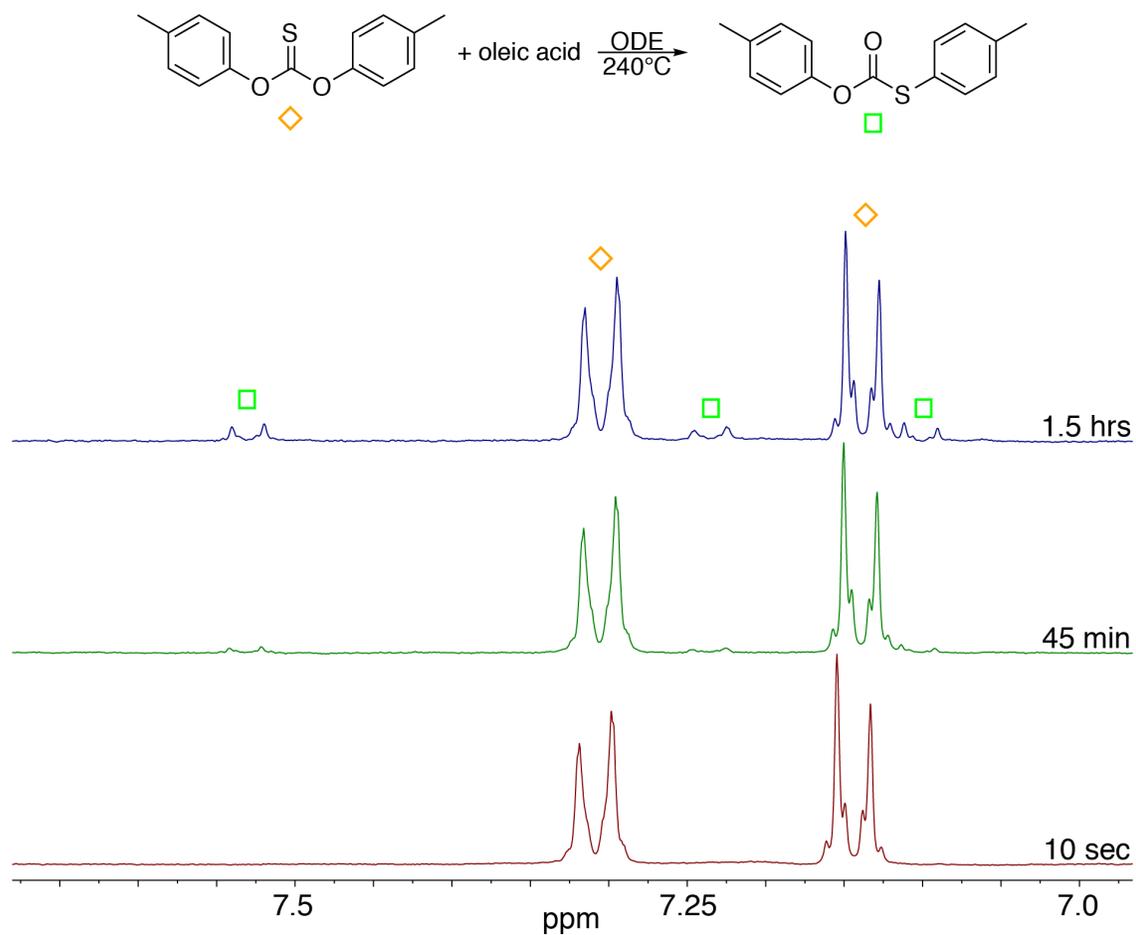


SI Figure 16. Yield Data using corrected size dependent extinction coefficients, absorbance at 300nm, and UV-vis spectra of reaction aliquots for thioureas **1a-1e**.

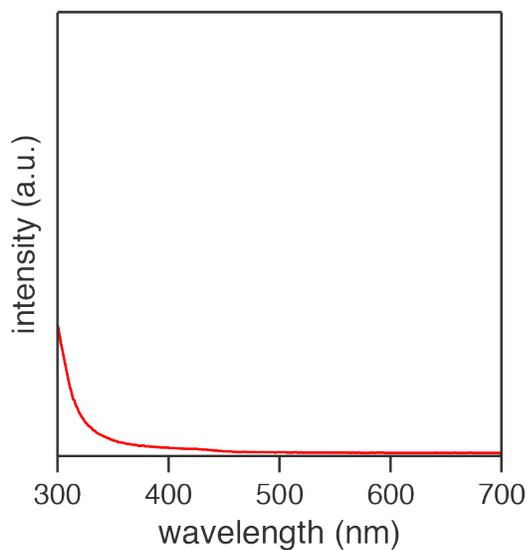
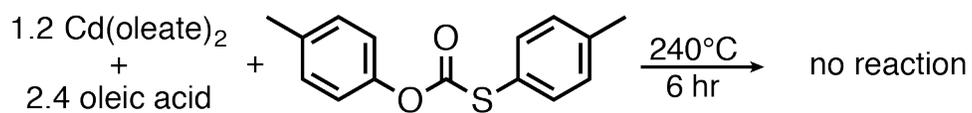
This is a representative data set where some data can be fit well to a first order fit (**1a** and **1e**) but other data may be fit better by a second order fit (**1b**, **1c**, and **1d**). The reaction endpoints were determined by comparing where the % Yield data plateaus and the absorbance at 300nm stops increasing.



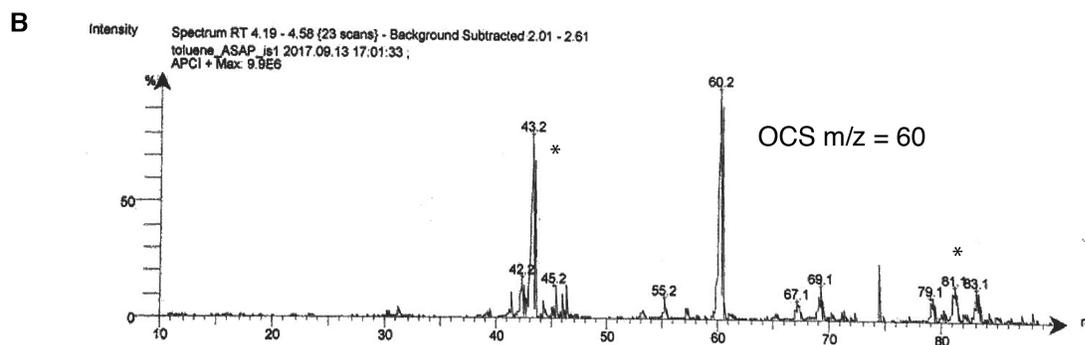
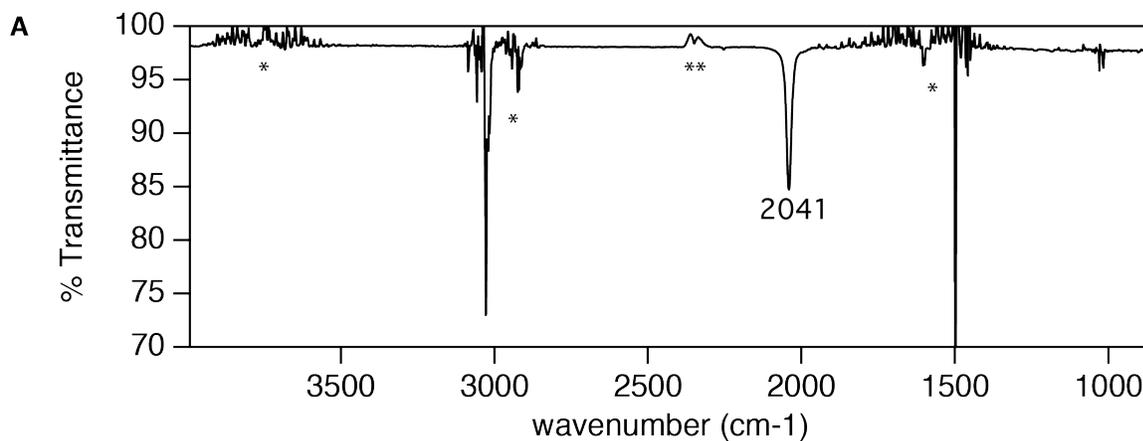
SI Figure 17. (a) Precursor conversion kinetics of **1c**, **2**, and **4** as determined via UV-vis. (b) UV-vis and fluorescence spectra of final nanocrystal products.



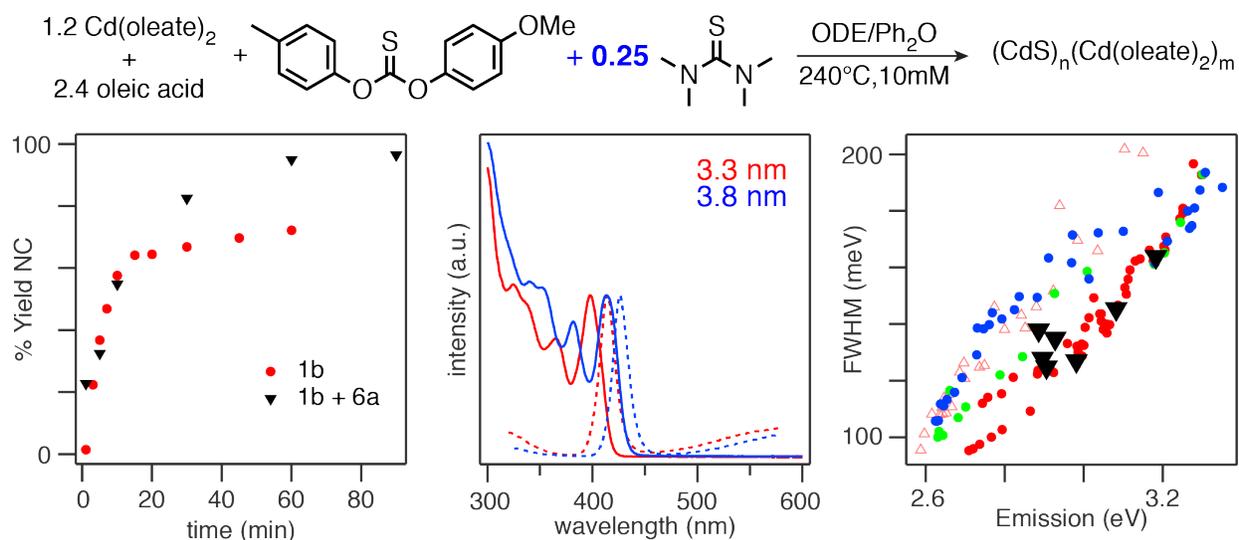
SI Figure 18. ¹H NMR of thiocarbonate **1c** and oleic acid at reaction temperature shows isomerization in the absence of cadmium to O,S-di-*p*-tolyl thiolcarbonate.



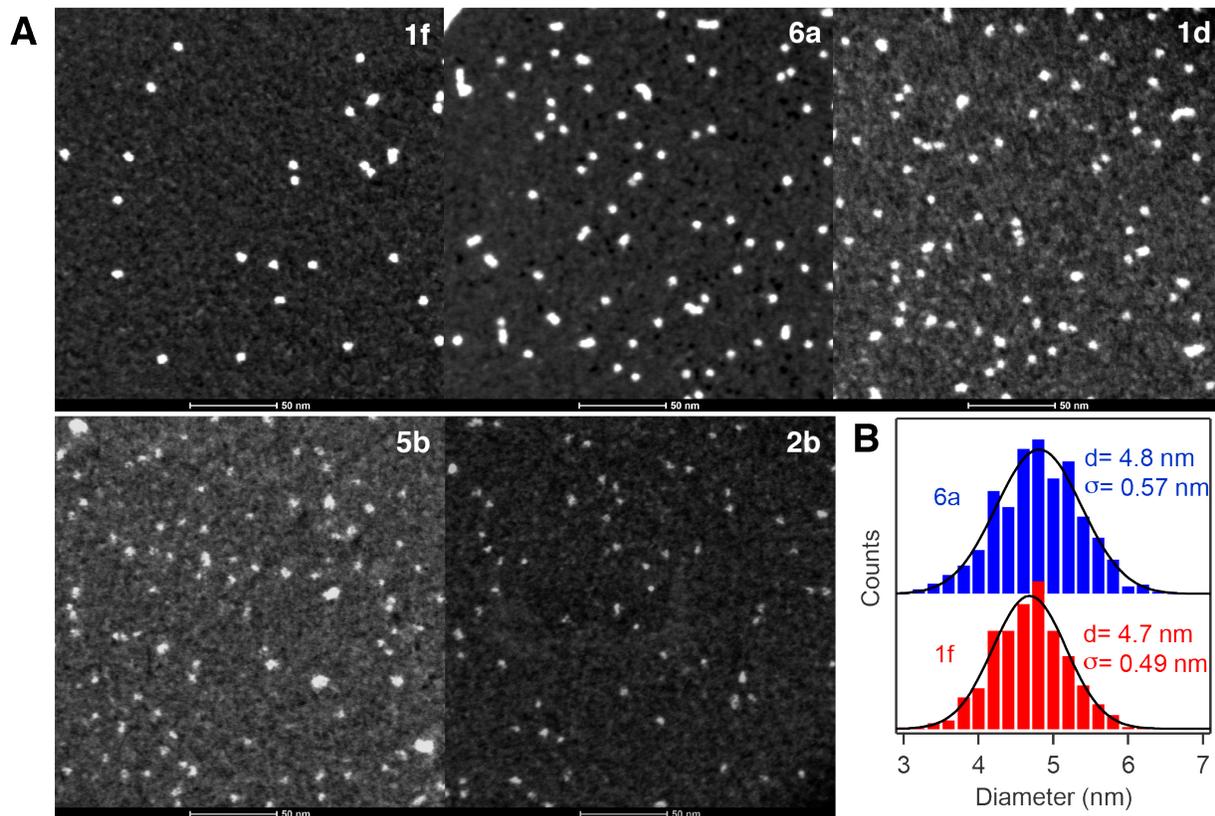
SI Figure 19. The reaction of cadmium oleate with O,S-di-*p*-tolyl thiolcarbonate shows no formation of CdS nanocrystals over the course of 6 hours.



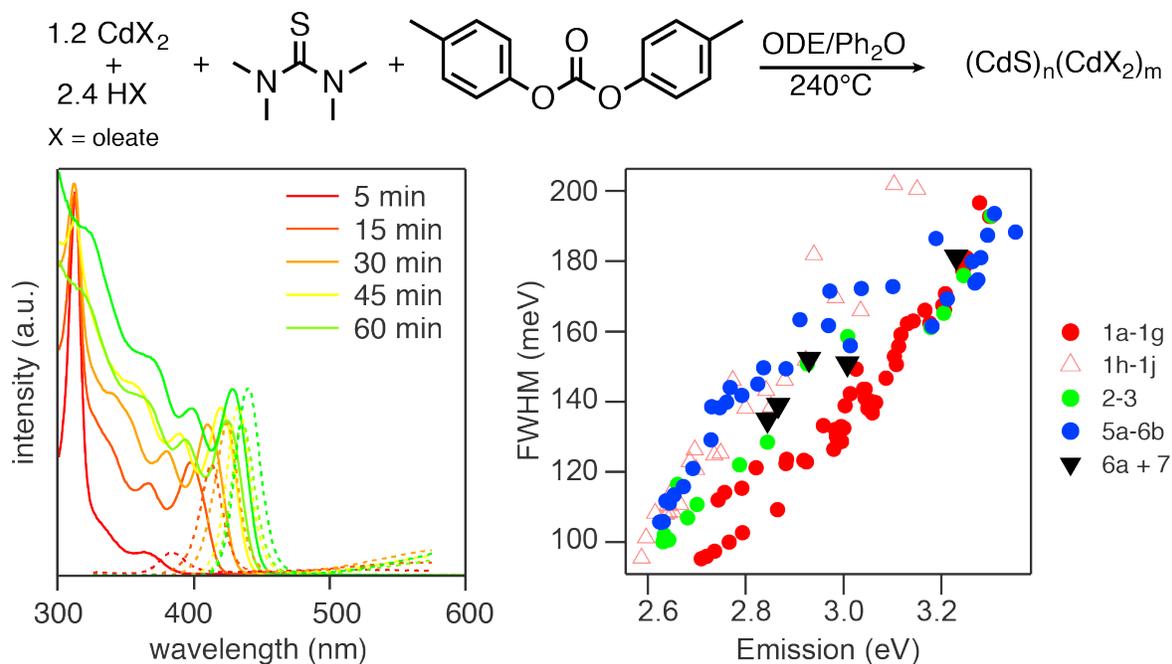
SI Figure 20. (a) FT-IR of volatile coproducts obtained from the reaction of **1e** with cadmium oleate. The volatiles were vac transferred into toluene. *Instrument artifacts **CO₂ background subtraction makes it difficult to characterize if CO₂ is present in the sample. (b) ASAP+ mass spectrum of volatile coproducts dissolved in toluene. *These peaks were also present in a toluene blank and are not though to be associated with the sample.



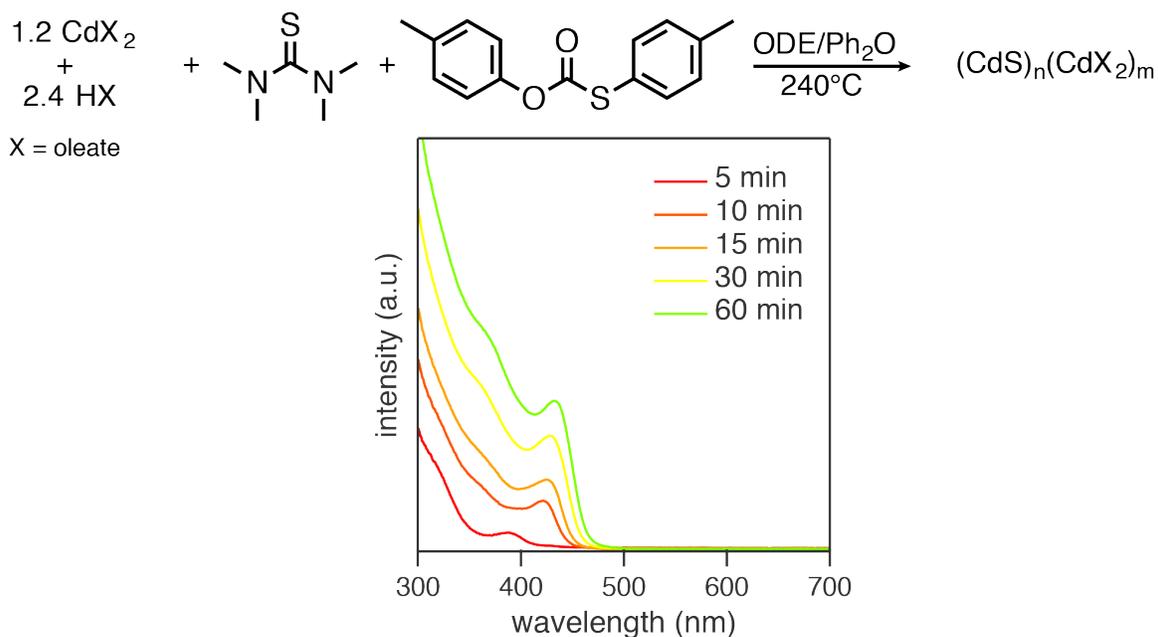
SI Figure 21. (a) yield versus time for thiocarbonate **1b** and the combined reaction of **1b + thiourea 6a** for comparison. (b) A thiocarbonate reaction can be run with additional thiourea added to boost the yield up to 100%. (c) the FWHM of particles nucleated by thiocarbonates shelled by a slow thiourea maintains narrow size dispersities typical of thiocarbonate reactions.



SI Figure 22. (a) HAADF-STEM (high angle annular dark field scanning transmission electron microscope) images of nanocrystal samples used for sizing and FWHM analysis. (b) FWHM comparison of 619 and 1081 CdS nanocrystals synthesized from **1f** and **6a**, respectively.



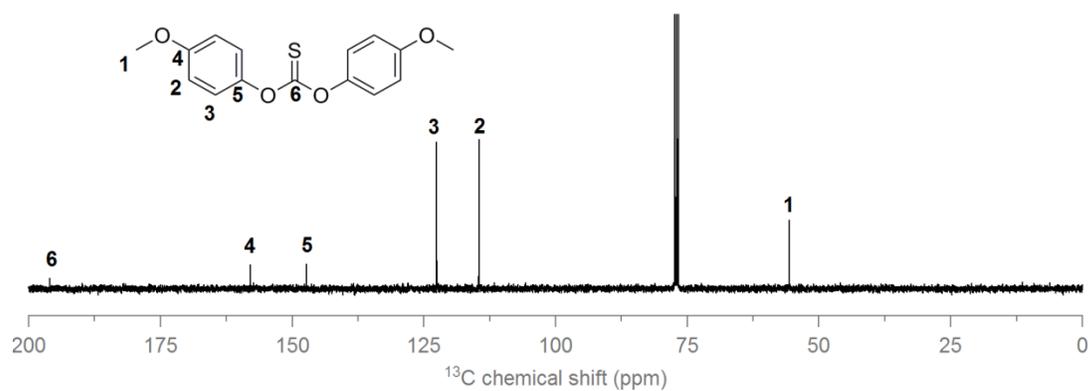
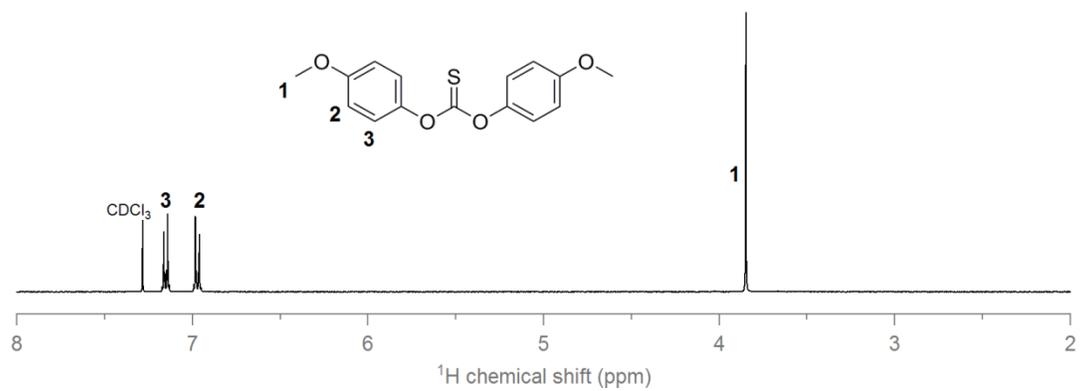
SI Figure 23. Spiking **7c** into a thiourea CdS reaction has no noticeable impact on particle size dispersity.



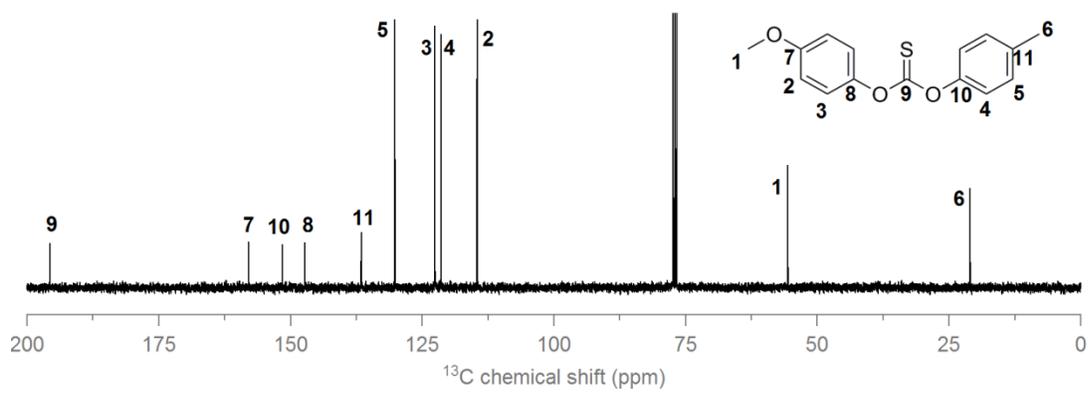
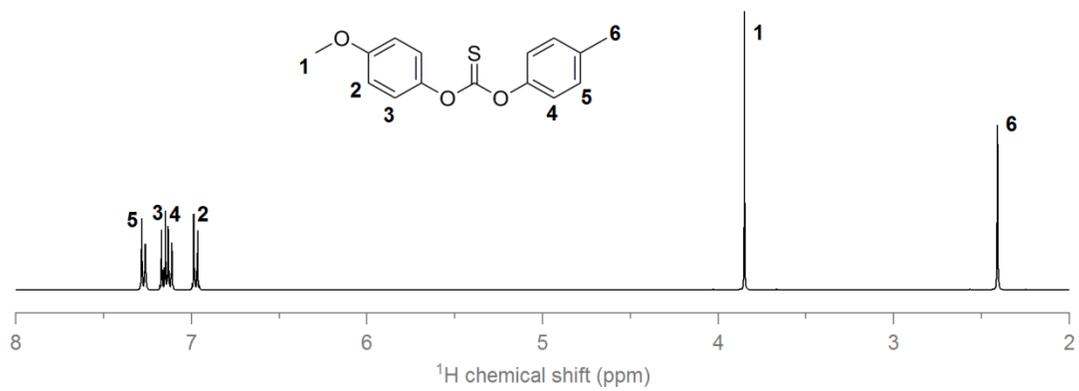
SI Figure 24. Reaction of **6a** in the presence of O,S-di-*p*-tolyl thiocarbonate results in a decrease in quality of the nanocrystal sample.

Section 2. NMR spectra of newly synthesized compounds in this study.

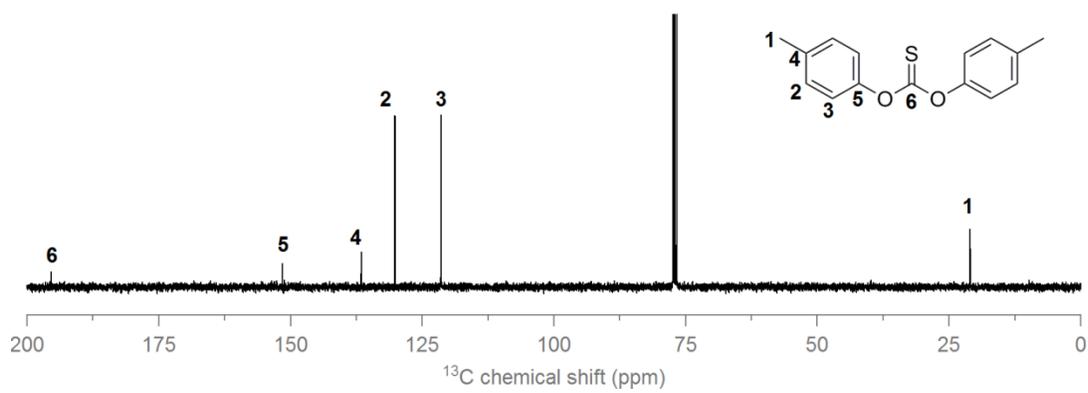
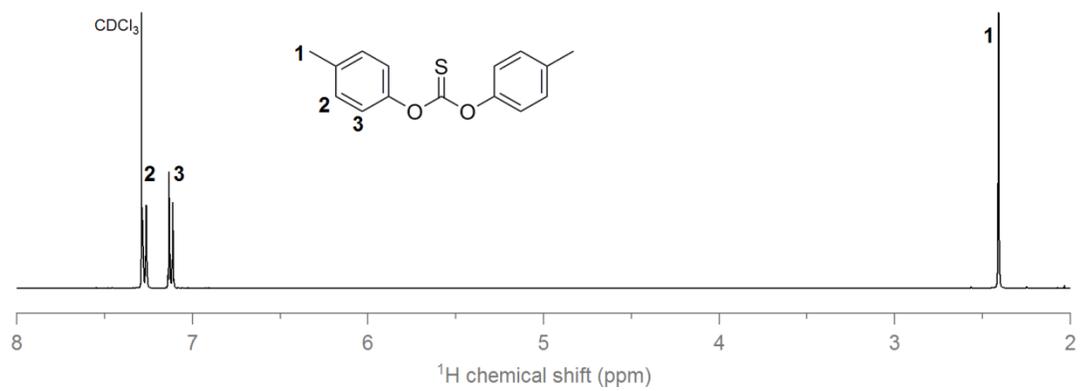
O,O'-bis(4-methoxyphenyl) thiocarbonate (1a).



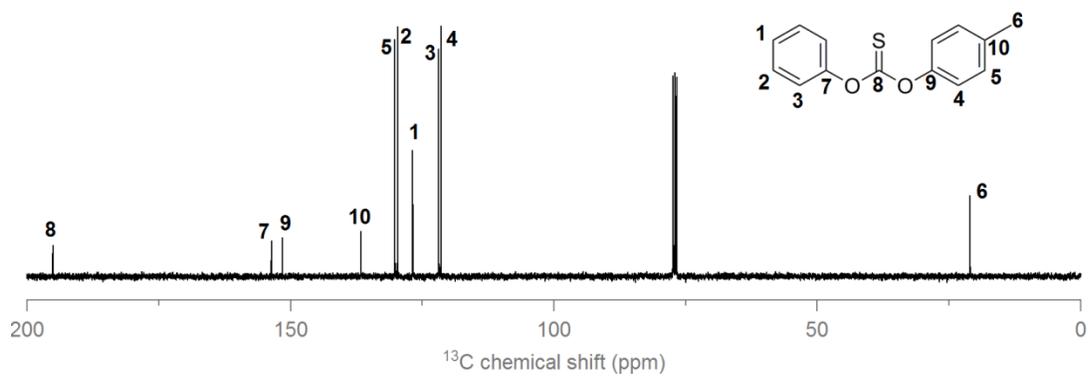
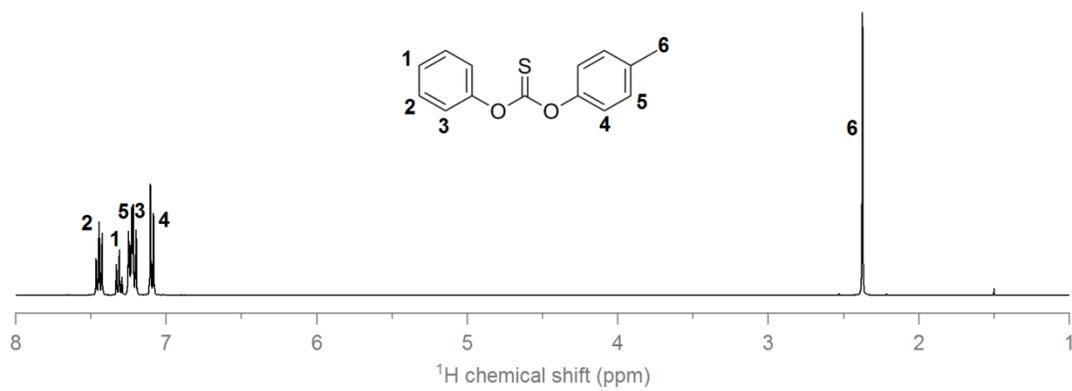
***O*-(4-methoxyphenyl)-*O'*-(*p*-tolyl) thiocarbonate (1b).**



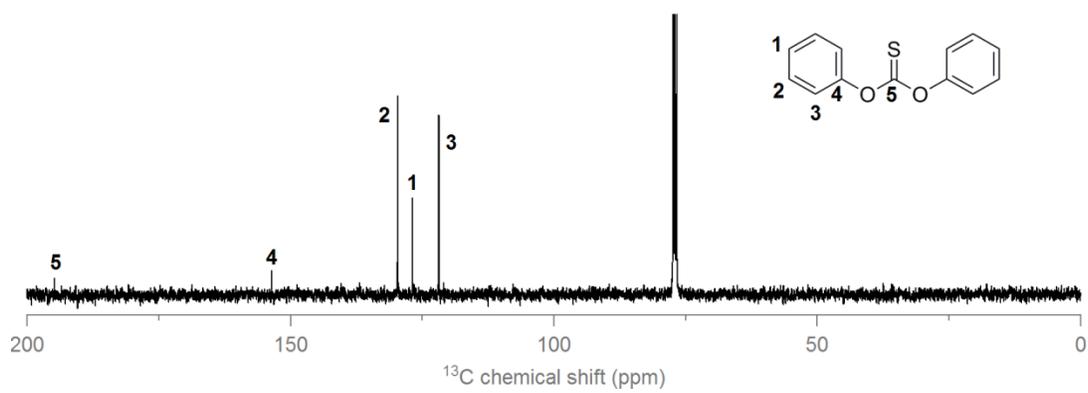
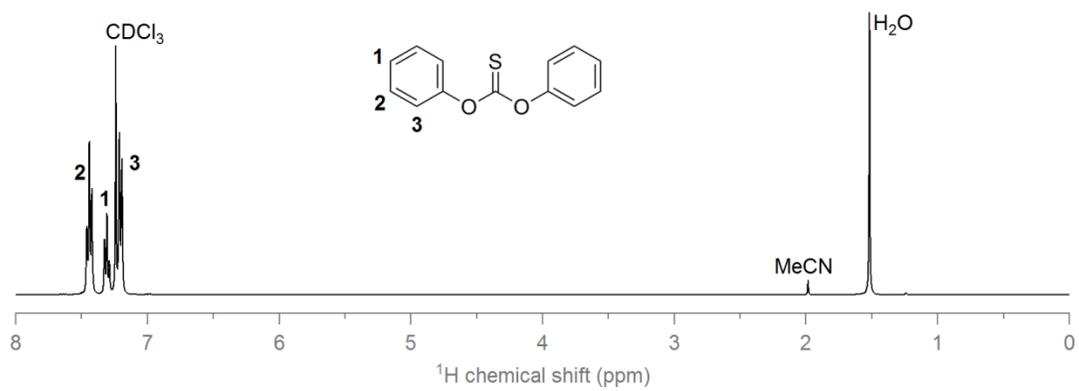
***O,O'*-di-*p*-tolyl thiocarbonate (1c).**



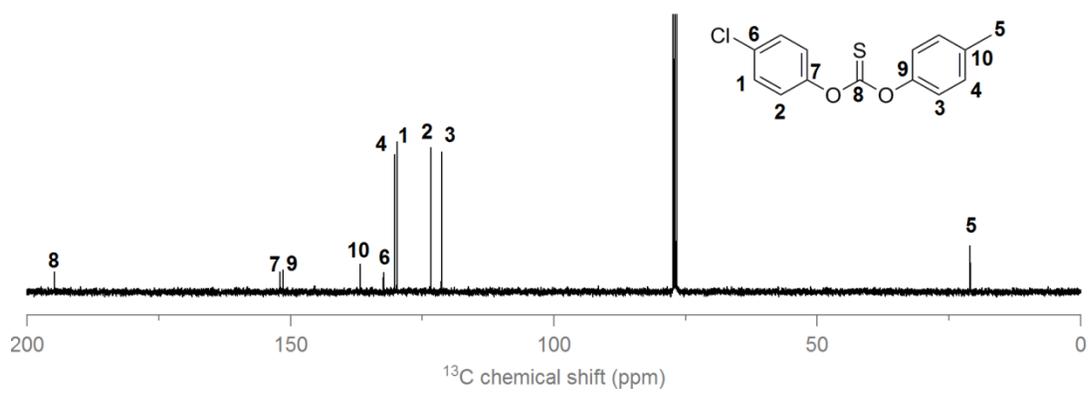
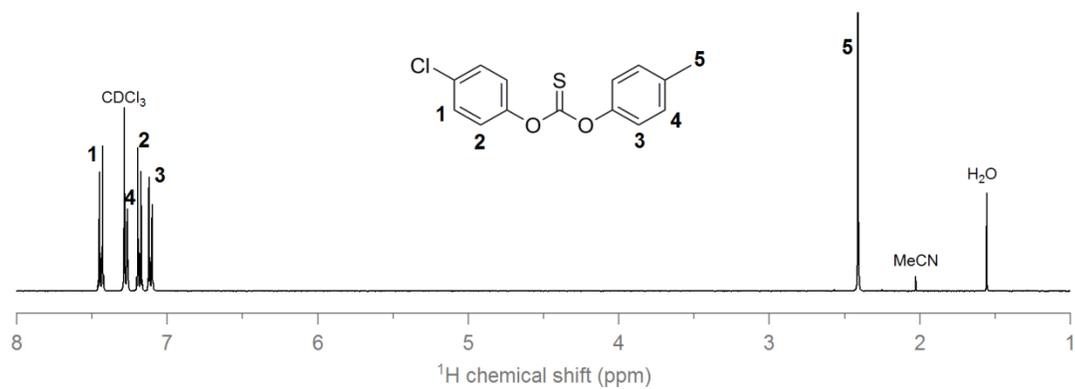
***O*-phenyl-*O'*-(*p*-tolyl) thiocarbonate (1d).**



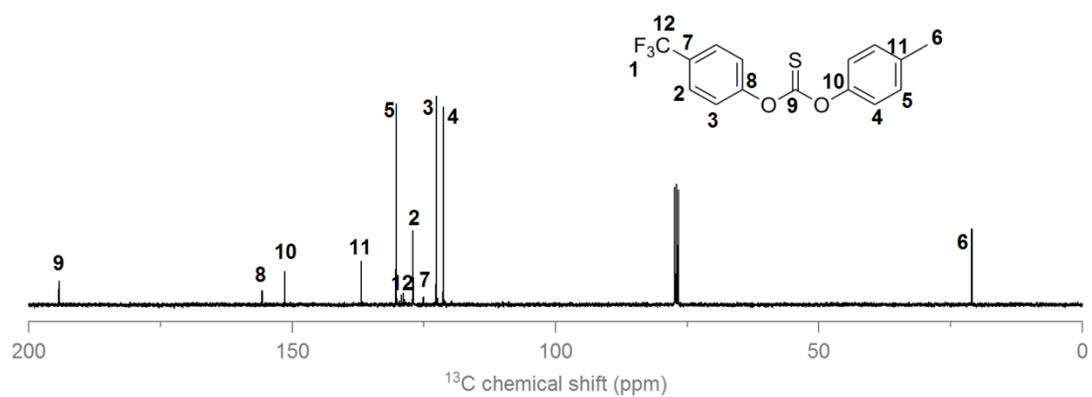
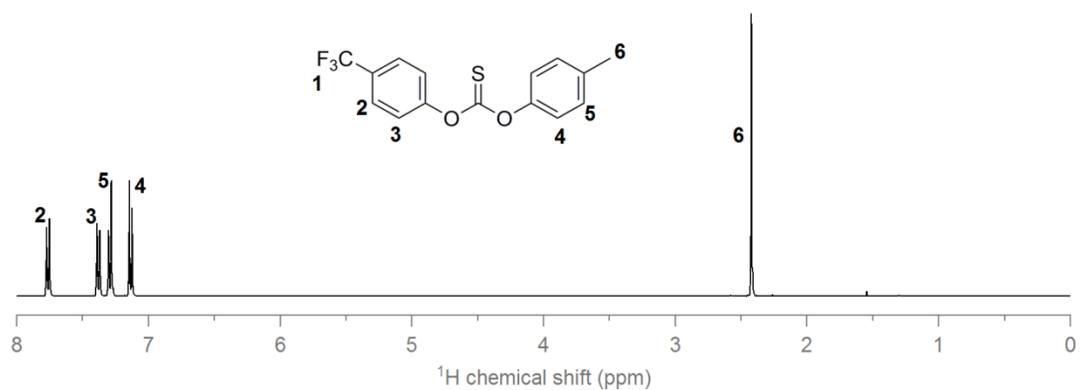
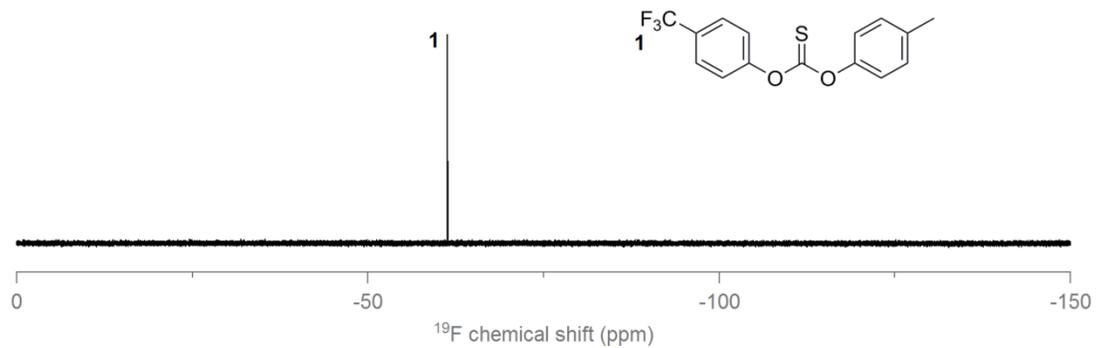
***O,O'*-di-phenyl thiocarbonate (1e).**



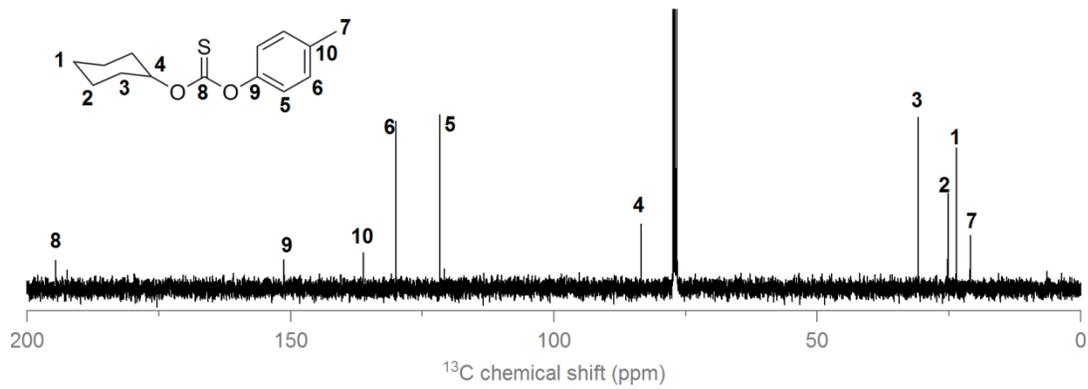
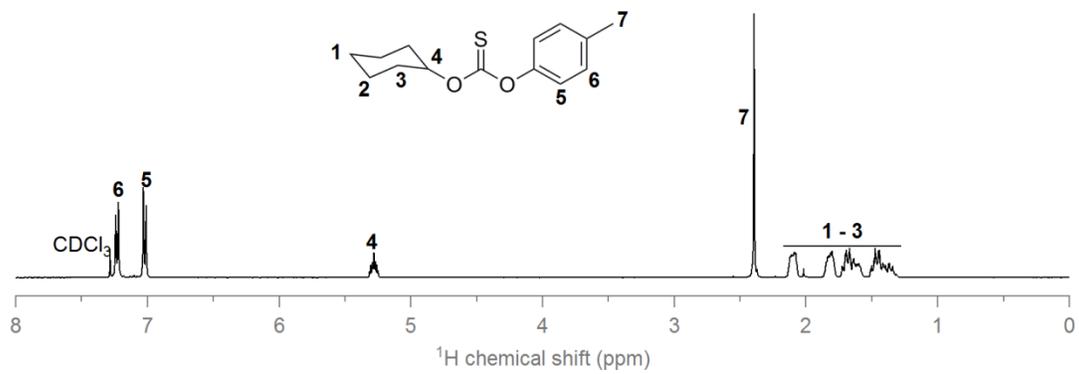
***O*-(4-chlorophenyl)-*O'*-(*p*-tolyl) thiocarbonate (1f).**



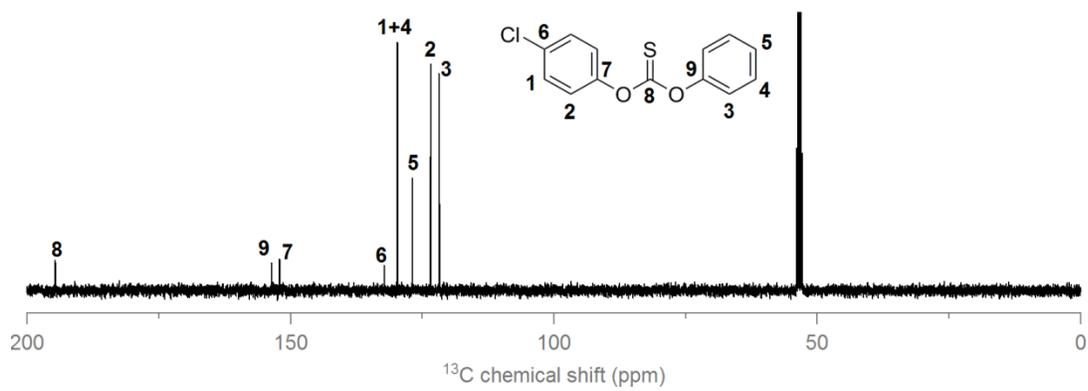
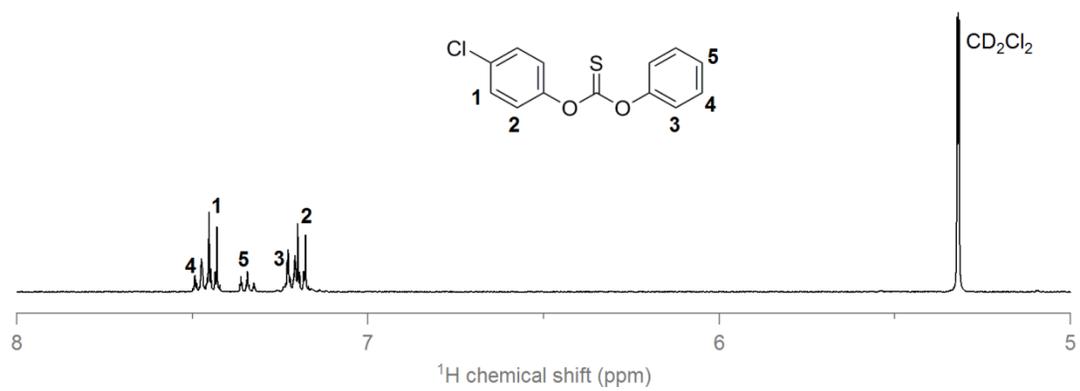
***O*-(*p*-tolyl)-*O*'-(4-(trifluoromethyl)phenyl) thiocarbonate (1g).**



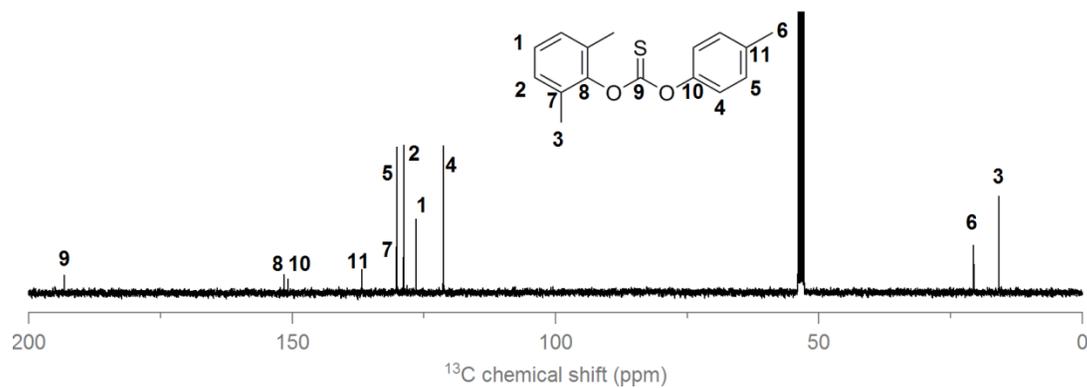
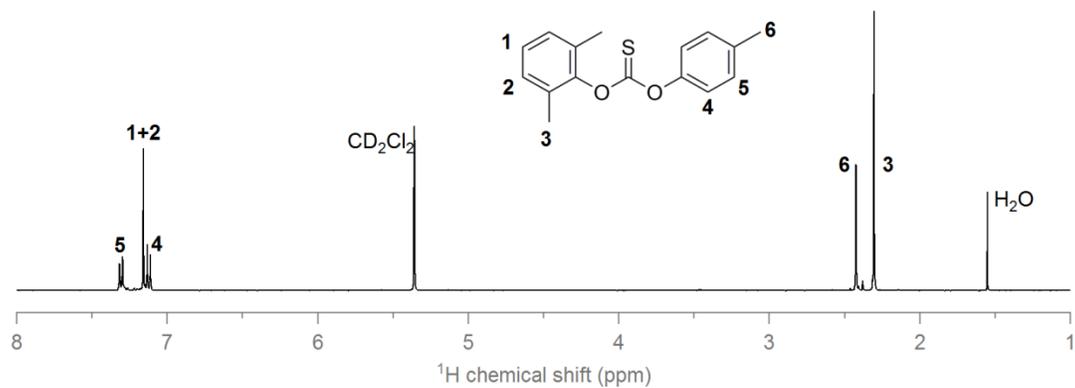
***O*-cyclohexyl-*O'*-(*p*-tolyl) thiocarbonate (1h).**



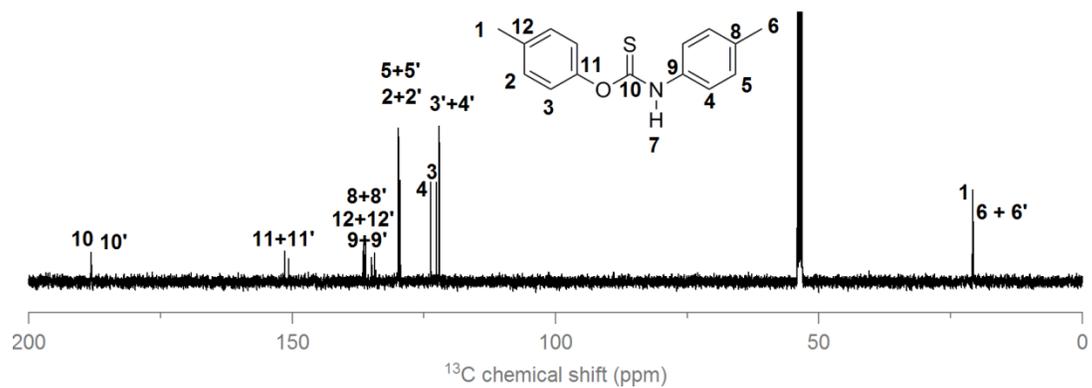
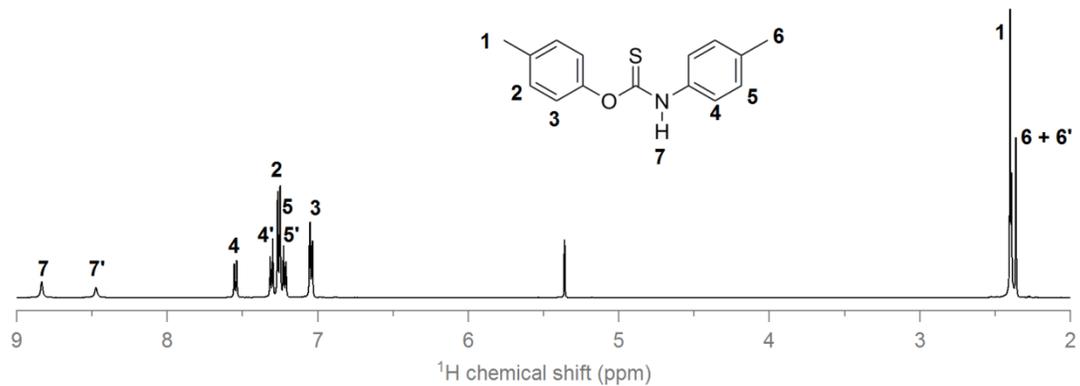
***O*-(4-chlorophenyl)-*O'*-phenyl thiocarbonate (1i).**



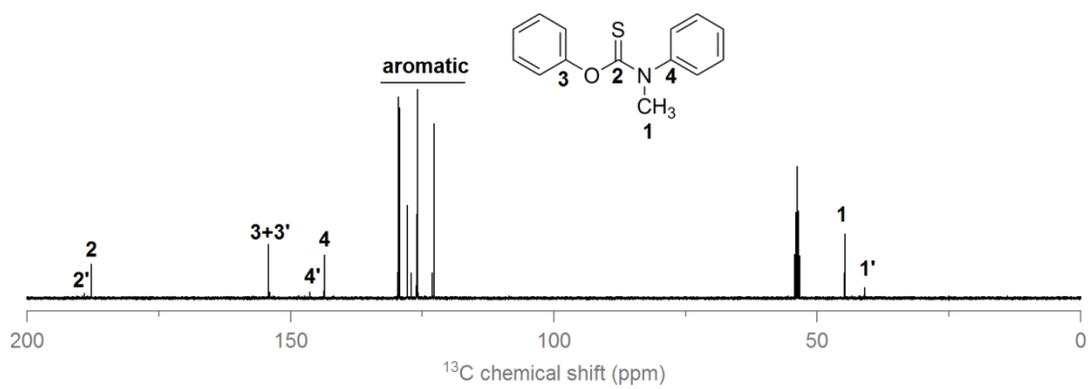
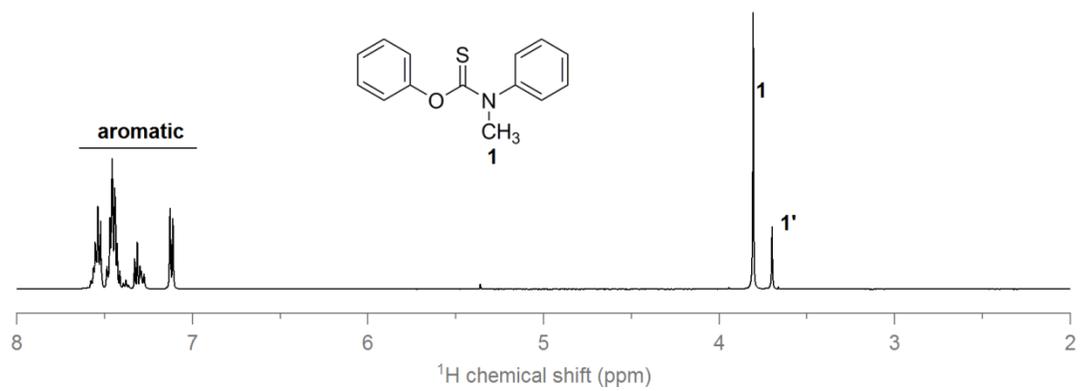
***O*-(2,6-dimethylphenyl)-*O'*-(*p*-tolyl) thiocarbonate (1j).**



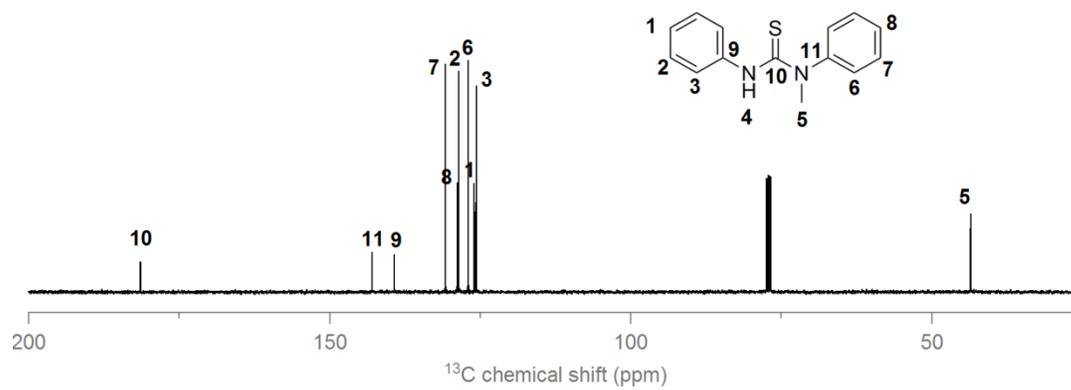
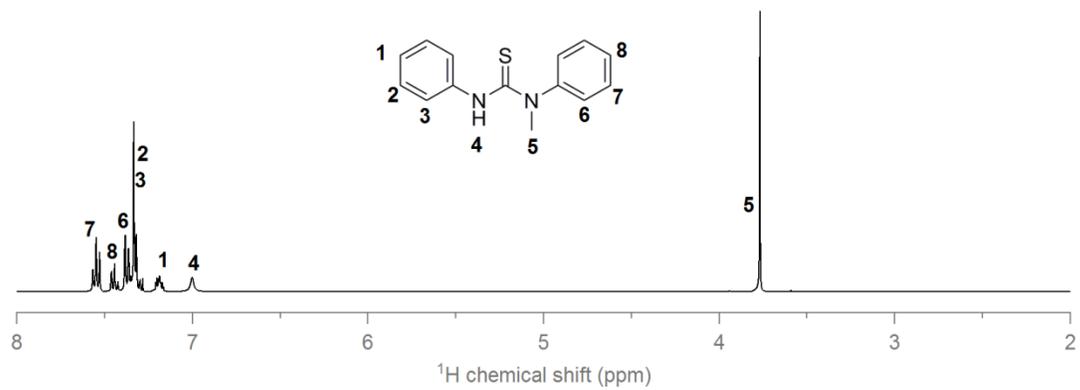
***O*-(*p*-tolyl)-*N*-*p*-tolyl thiocarbamate (2).**



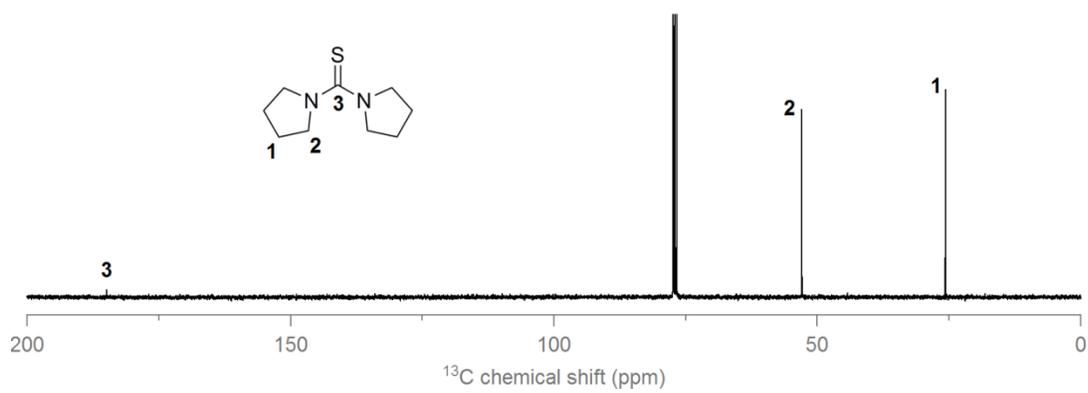
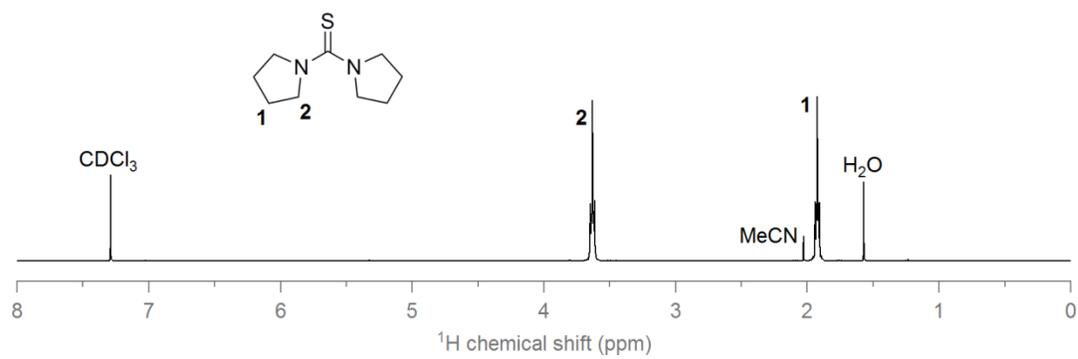
***O*-phenyl-*N*-methyl(phenyl) thiocarbamate (3).**



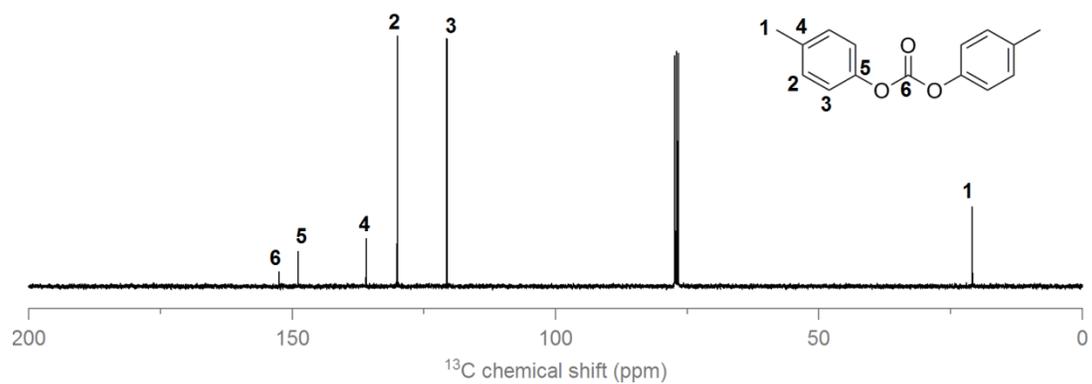
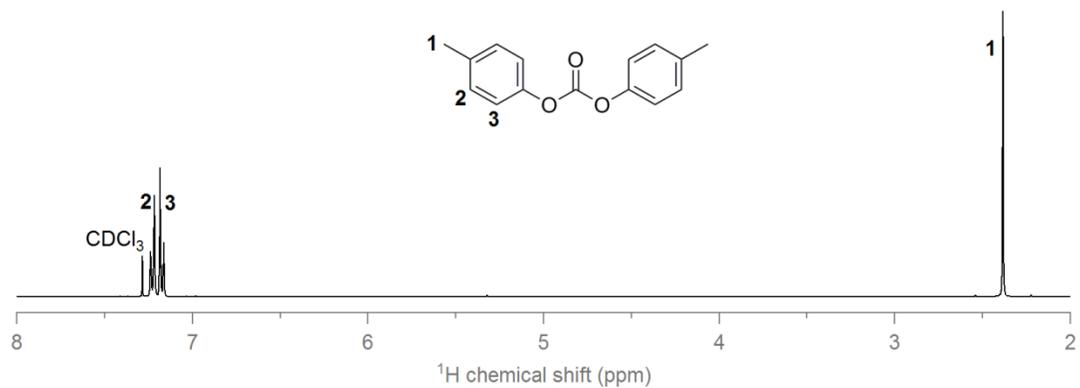
***N*-methyl-*N,N'*-diphenyl thiourea (5b).**



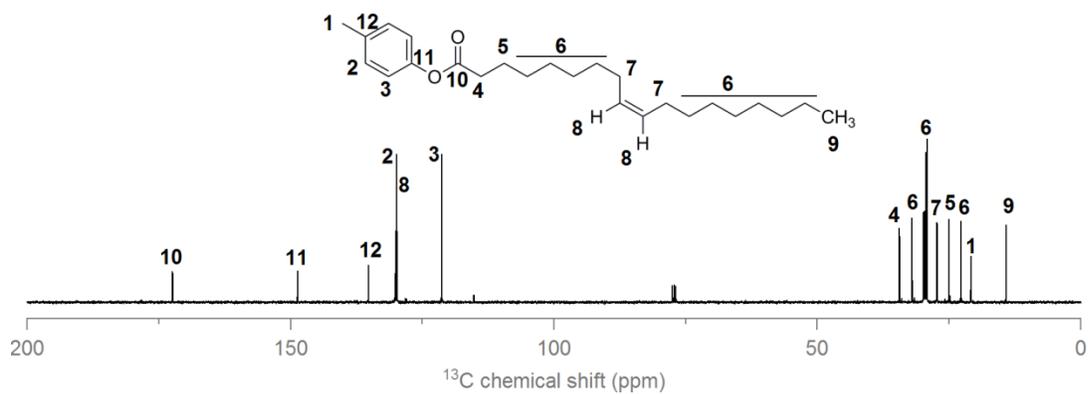
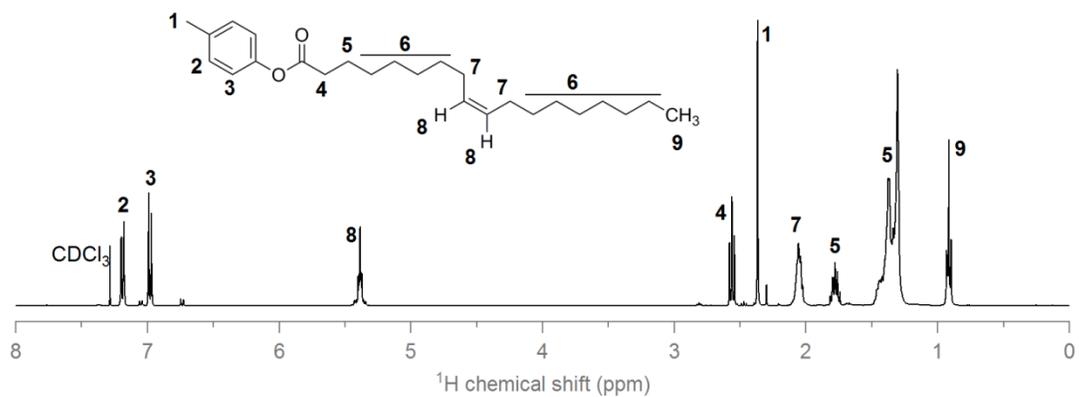
di(pyrrolidin-1-yl)methanethione (6b).



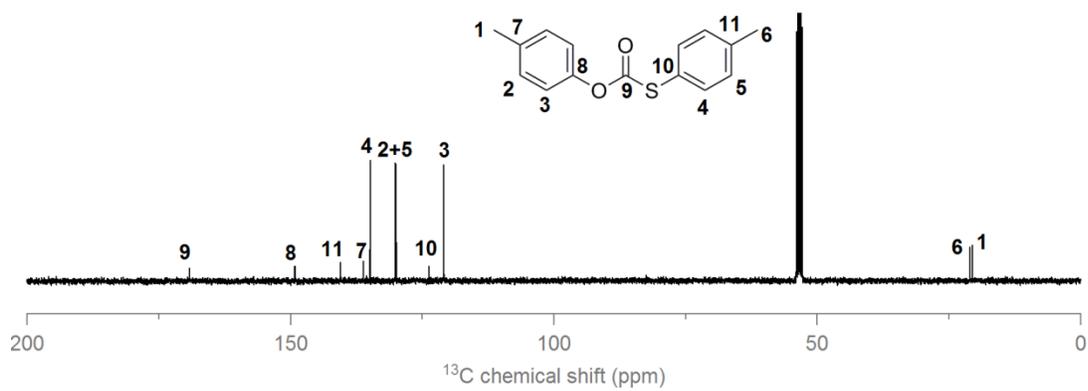
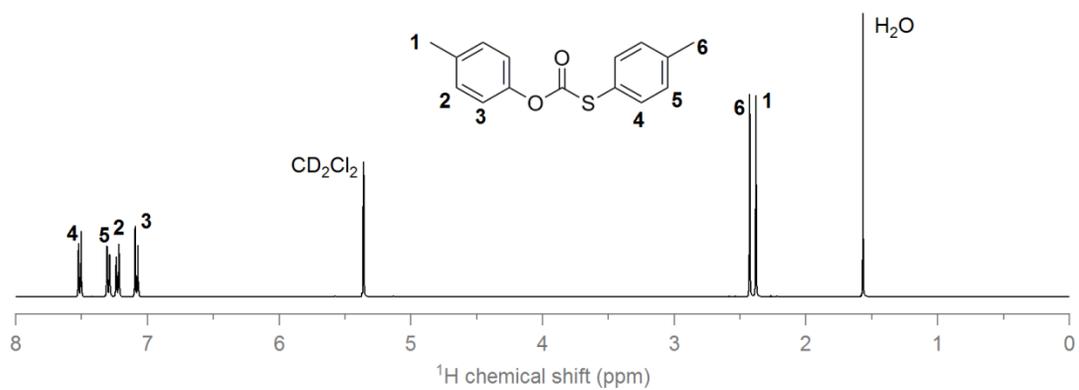
di-*p*-tolyl carbonate (7c).



p-tolyl Oleate.



***O,S*-di-*p*-tolyl thiolcarbonate.**



References:

- (1) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854-2860.