Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Direct RAFT Polymerization of an Unprotected Isocyanate-Containing Monomer and Subsequent Structopendant Functionalization Using "Click"-Type Reactions

Joel D. Flores, Junghwan Shin, Charles E. Hoyle and Charles L. McCormick*

Department of Polymer Science and Department of Chemistry and Biochemistry

The University of Southern Mississippi, Hattiesburg, Mississippi, 39406 USA

Model Reactions of Isocyanate with Amines, Thiols and Alcohols

To investigate the efficiency and selectivity of the reaction of isocyanate, model reactions using cyclohexylisocyanate (CHI) and various small molecule amines, thiols and alcohols were investigated. All the model reactions were conducted in $CDCl_3$. Briefly, to the solution containing CHI (~5 wt%, 0.37 M) and the catalyst (TEA - 0.5 wt% (50 mM) for reaction with thiols, DBTDL - 0.1 wt% (1.6 mM) for reaction with alcohol), a solution containing an equimolar amount of amine, thiol or alcohol was added dropwise being careful not to increase the reaction temperature. The reaction was allowed to proceed overnight at room temperature. The efficiency and selectivity of the reaction was probed by looking at the carbonyl signal in FT-IR and ^{13}C NMR spectra. For unambiguous peak assignment, signature signals for urea (NCO + amine), urethane (NCO + OH) and thiourethane (NCO + SH) in both FT-IR and ^{13}C NMR spectra were first identified using 3-propylamine, ethanol and ethanethiol, respectively (Figures S1 and S4). An identical procedure utilized ethanolamine and mercaptoethanol (Figures S2, S5-S6).

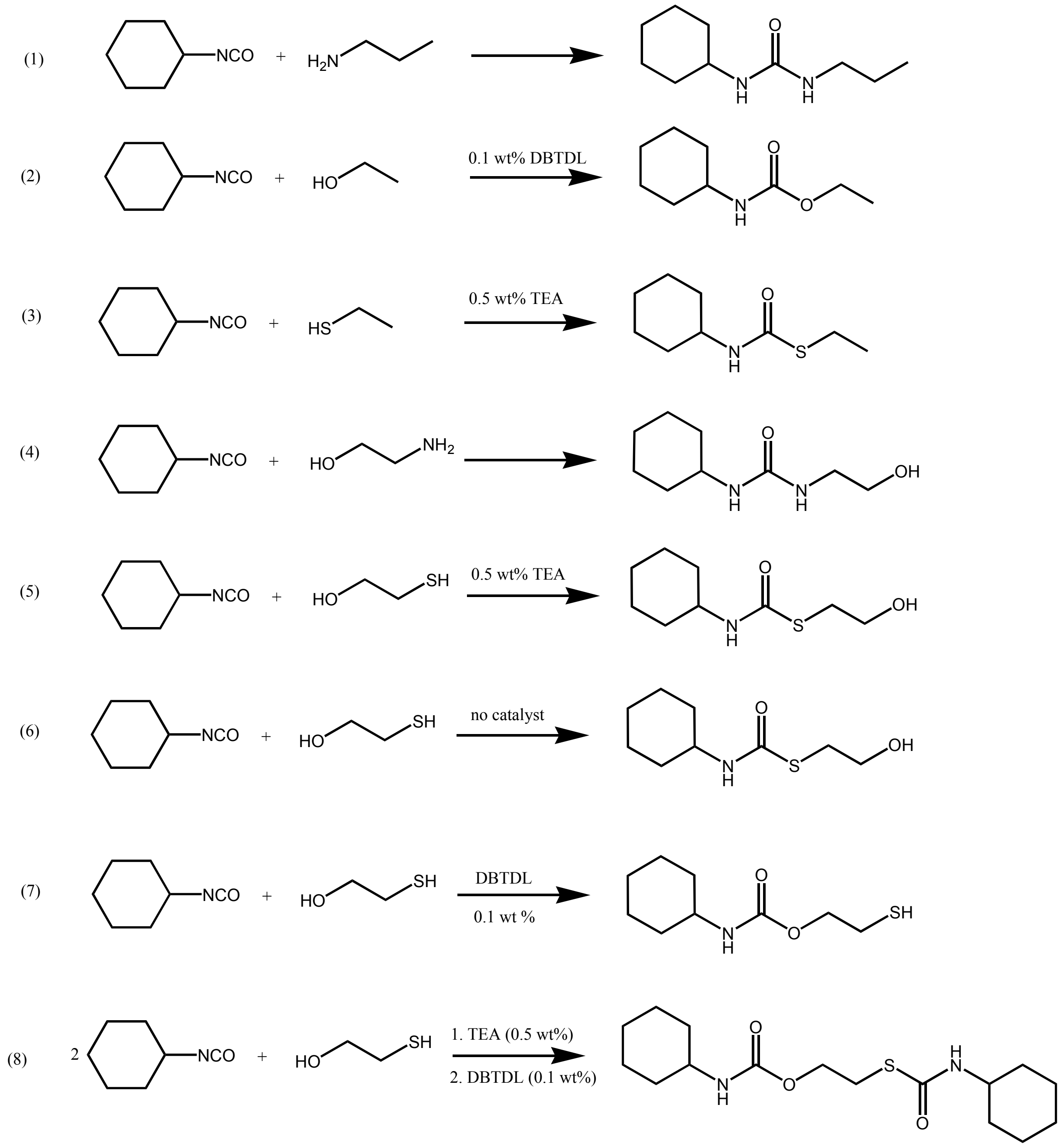
The reaction of an isocyanate and an amine does not require the addition of a catalyst and is selective over that of the alcohol. Similarly, base-catalyzed reaction of an isocyanate and a thiol is also highly efficient and selective over that of the alcohol. Urethane formation can be catalyzed by dibutyltin dilaurate (DBTDL) and proceeds at relatively slower rate compared to the reaction of amines and thiols. Unlike the reactions of more reactive aryl isocyanates,[1] we observed both the formation of urethane and thiourethane in the reaction of CHI and mercaptoethanol depending on the concentration of DBTDL catalyst with the latter preferentially formed in the absence of DBTDL (see Figures S3 and S7). There is contrasting evidence in literature regarding the role of tin(IV) catalyst in urethane formation.[2] Based on our limited experimental data, we speculate that, in the absence of the added catalyst, the initial addition of the hydroxyl group to the isocyanate may have resulted in deprotonation of some thiols as hydrogens of thiols are more abstractable (pKa ~ 10-11) than those of alcohols (pKa ~ 16-18). In accordance to previous reports, we also found that, under neutral conditions and even in the presence of DBTDL catalyst, free thiols are relatively unreactive towards isocyanates. This is not surprising as free thiols are less nucleophilic compared to hydroxyl groups. Once deprotonated, however, the thiolate anion becomes an excellent nucleophile and reacts immediately with isocyanate. When both the hydroxyl and the thiol are present in the reaction mixture, the latter has been shown to deactivate the DBTDL catalyst which affects urethane formation.[2] In our study, increasing the amount of DBTDL catalyst facilitated the reaction of hydroxyl groups in mercaptoethanol and minimized thiourethane formation.

The ^{13}C NMR spectrum of the product from the reaction of CHI and mercaptoethanol (NCO:SH:OH=2:1:1) with 0.5 wt% TEA and 0.1wt % DBTDL is shown in Figure S8 for comparison. The peaks positions are slightly shifted compared to the mono-capped adducts. Note that this spectrum was taken in a mixture of $CDCl_3$, CD_3COCD_3 and CD_3OD as solvent since the product was not completely soluble in $CDCl_3$ alone.

References:

1. Smith, J. F.; Friedrich, E. C. *J. Am. Chem. Soc.* **1959,** 81, 161-163.
2. Houghton, R. P.; Mulvaney, A. W. *J. Organomet. Chem.* **1996,** 518, 21-27.

Scheme S1: Model reactions of isocyanate with amines, thiols and alcohols.



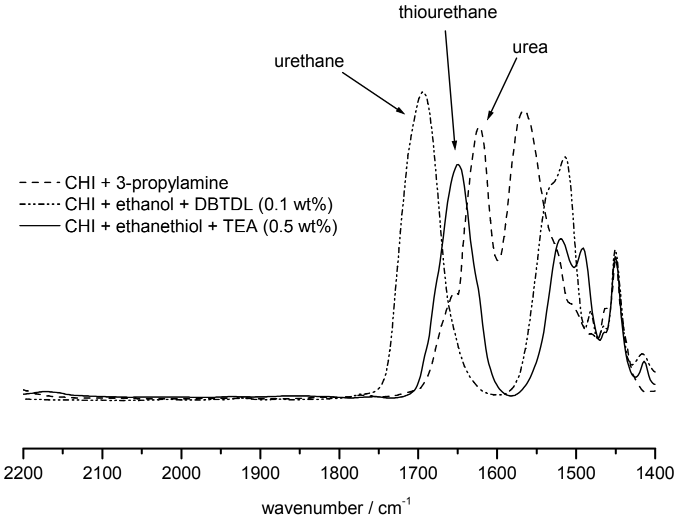


Figure S1. FT-IR spectra showing the carbonyl region of the product from the reaction of cyclohexylisocyanate (CHI) with 3-propylamine, ethanol (with 0.1 wt% DBTDL) and ethanethiol (with 0.5 wt% TEA).

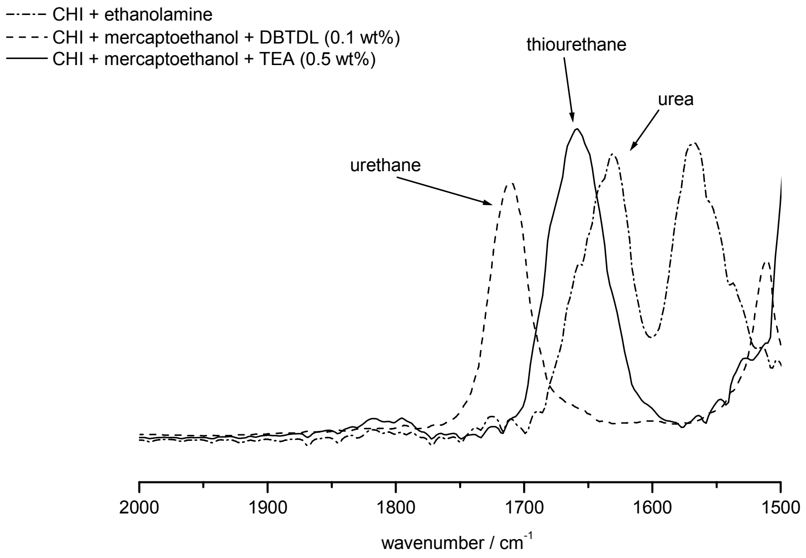


Figure S2. FT-IR spectra showing the carbonyl region of the product from the reaction of cyclohexylisocyanate (CHI) with ethanolamine and mercaptoethanol with DBTDL (0.1 wt%) and TEA (0.5 wt%).

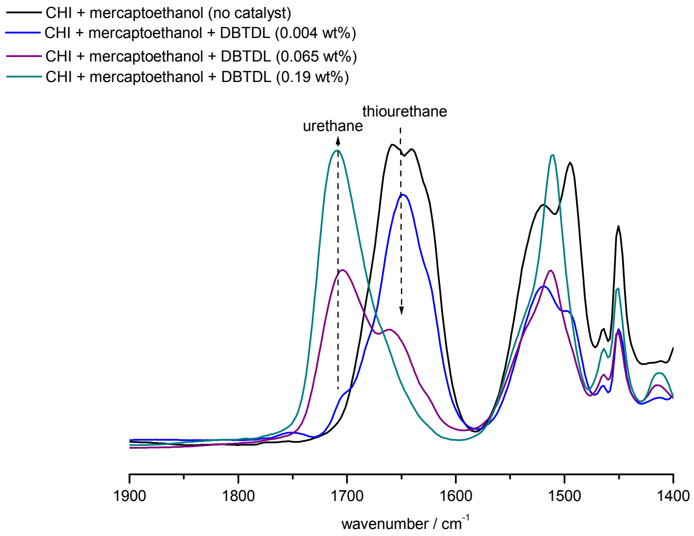
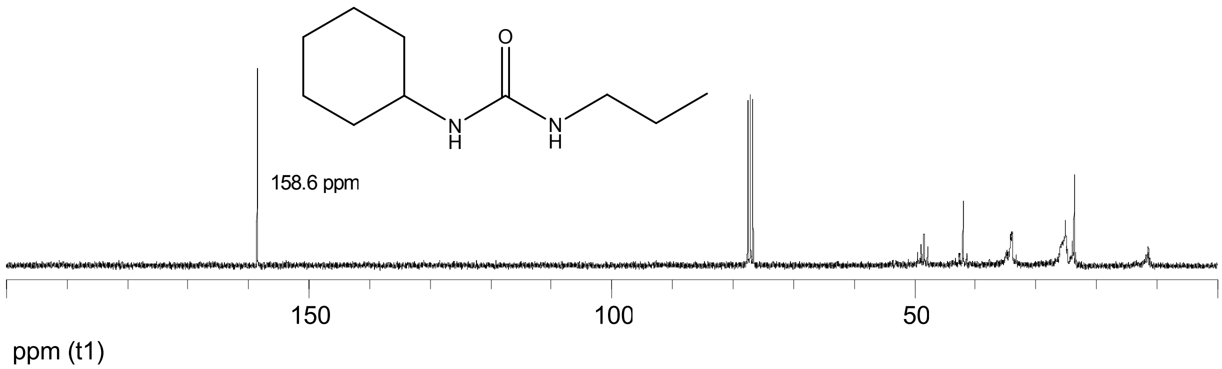


Figure S3. FT-IR spectra showing the carbonyl region of the product from the reaction of cyclohexylisocyanate (CHI) and mercaptoethanol with selected amounts of added DBTDL as catalyst. Direction of arrow indicates increasing catalyst concentration.

(A) CHI + 3-propylamine



(B) CHI + ethanol + DBTDL (0.1 wt%)

(C) CHI + ethanethiol + TEA (0.5 wt%)

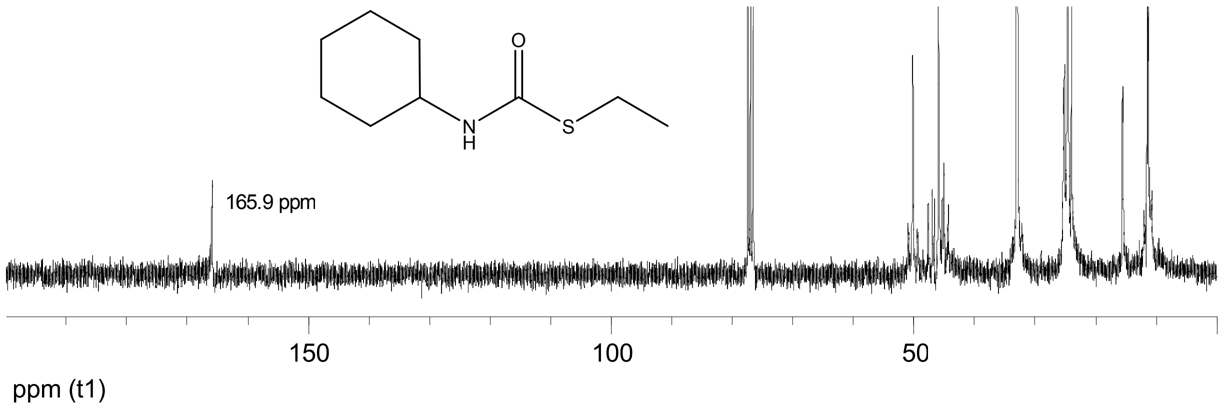


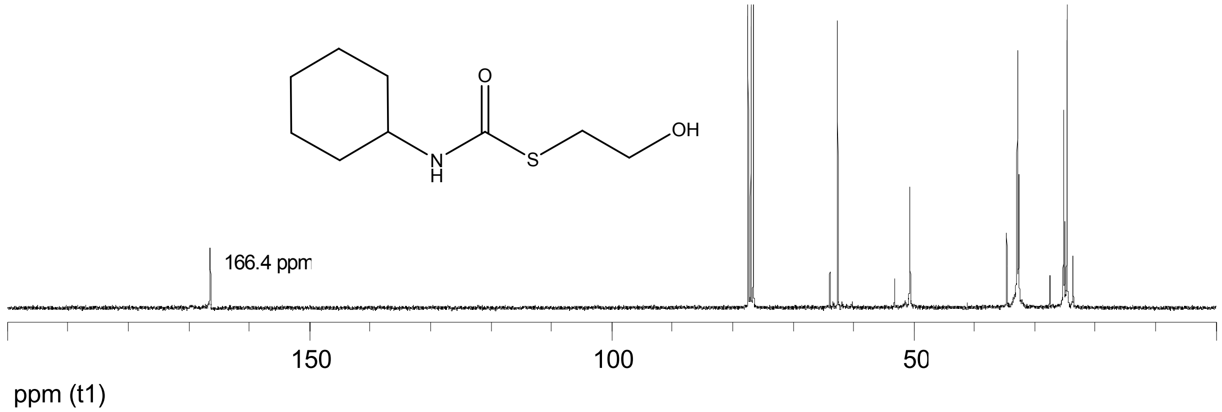
Figure S4. ^{13}C NMR spectra (in $CDCl_3$) of the product from the reaction of (A) cyclohexylisocyanate and 3-propylamine, (B) cyclohexylisocyanate and ethanol (with 0.1 wt%

DBTDL as catalyst) and (C) cyclohexylisocyanate and ethanethiol (with 0.5 wt% TEA as catalyst).

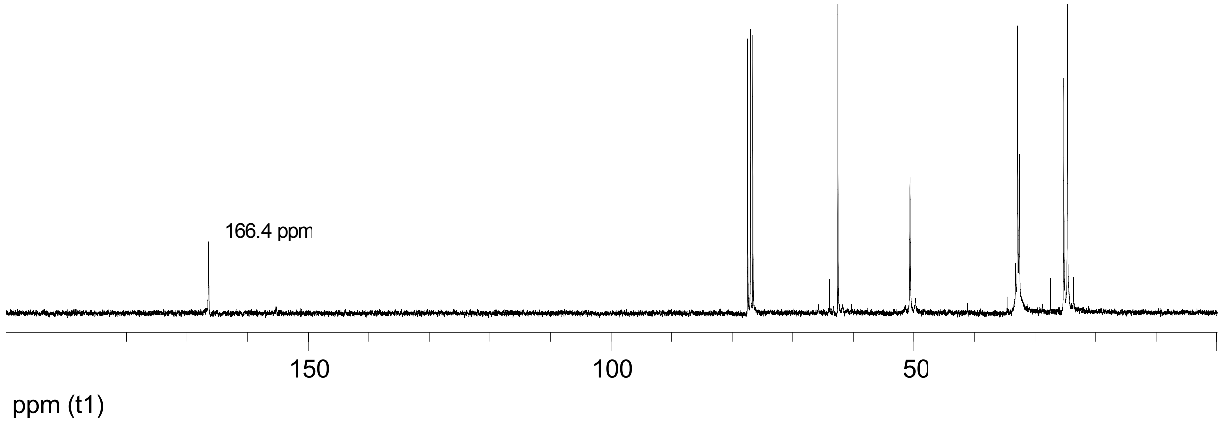
Figure S5. ^{13}C NMR spectrum (in $CDCl_3$) of the product from the reaction of cyclohexylisocyanate and ethanolamine.

Figure S6. ^{13}C NMR spectrum (in $CDCl_3$) of the product from the reaction of cyclohexylisocyanate and mercaptoethanol with 0.5 wt% TEA as catalyst.

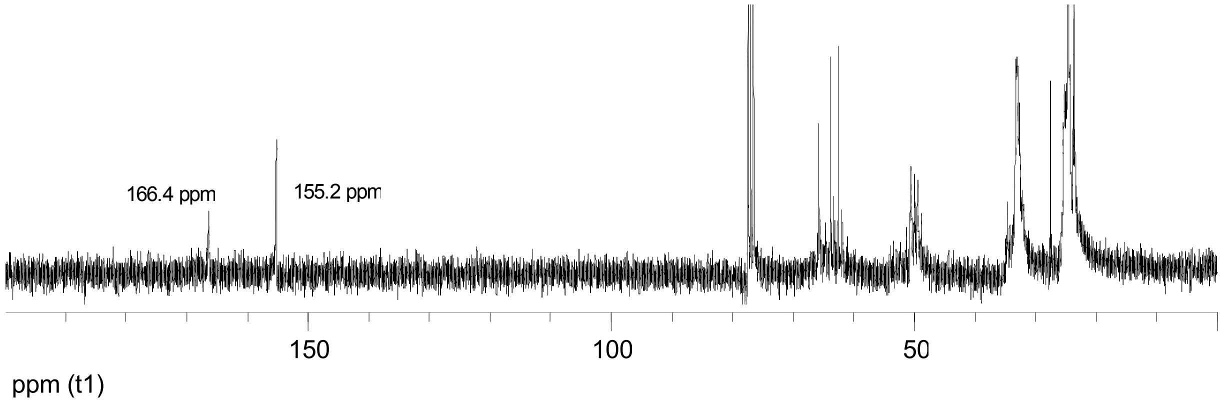
(A) CHI + mercaptoethanol (no catalyst)



(B) CHI + mercaptoethanol + DBTDL (0.004 wt%)



(C) CHI + mercaptoethanol + DBTDL (0.065 wt%)



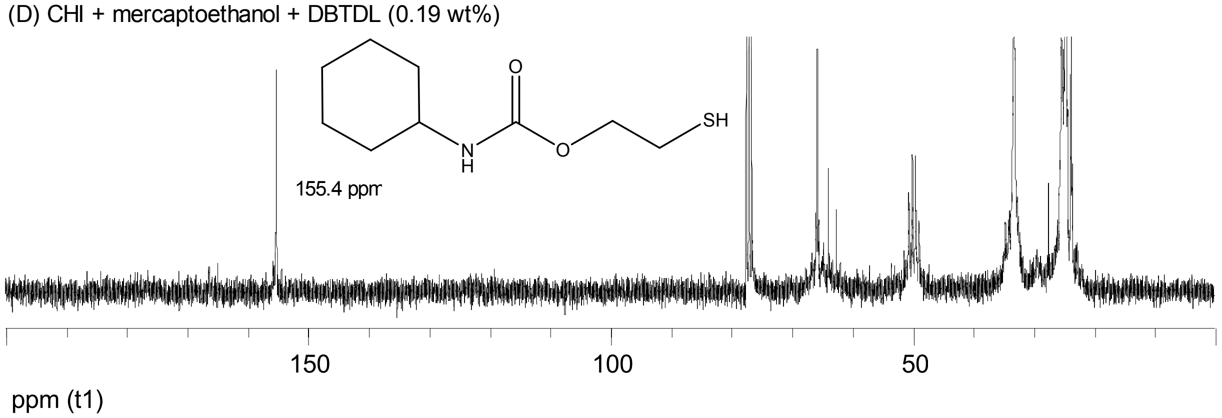


Figure S7. ^{13}C NMR spectra (in $CDCl_3$) of the product from the reaction of cyclohexylisocyanate and mercaptoethanol with selected amounts of added DBTDL catalyst: (A) no catalyst (spectrum taken after 3 days), (B) 0.004 wt% (after 24 hrs), (C) 0.065 wt% (after 24 hours) and (D) 0.19 wt% (24 hrs).

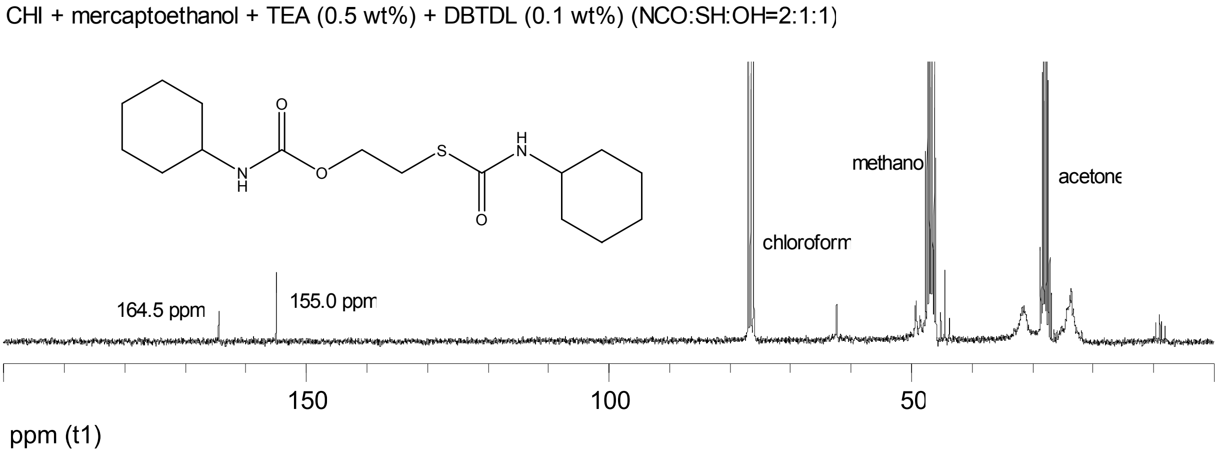


Figure S8. ^{13}C NMR spectrum (in $CDCl_3/CD_3COCD_3/CD_3OD$) of the product from the reaction of cyclohexylisocyanate and mercaptoethanol with TEA (0.5 wt%) and DBTDL (0.1 wt%) (NCO:SH:OH=2:1:1). The reaction was conducted in $CDCl_3$. The product precipitated out. After completion of the reaction, the precipitate was dissolved in $CDCl_3/CD_3COCD_3/CD_3OD$ for NMR analysis.