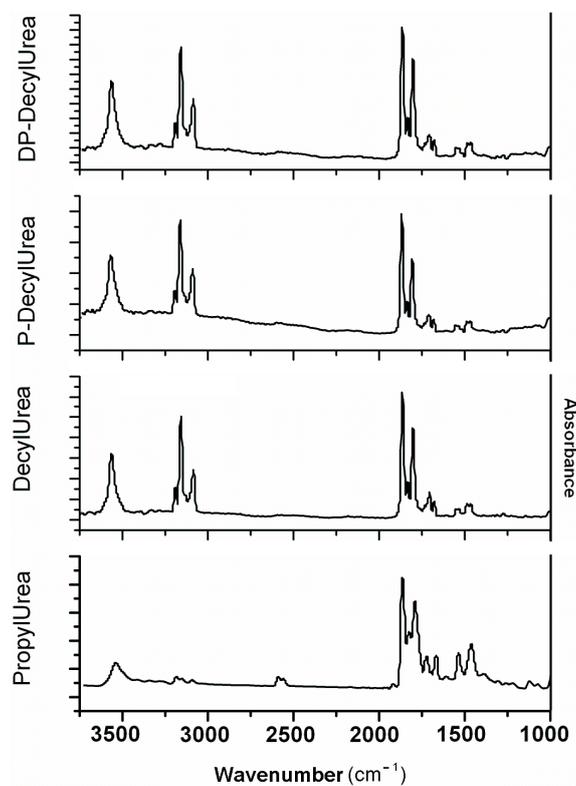
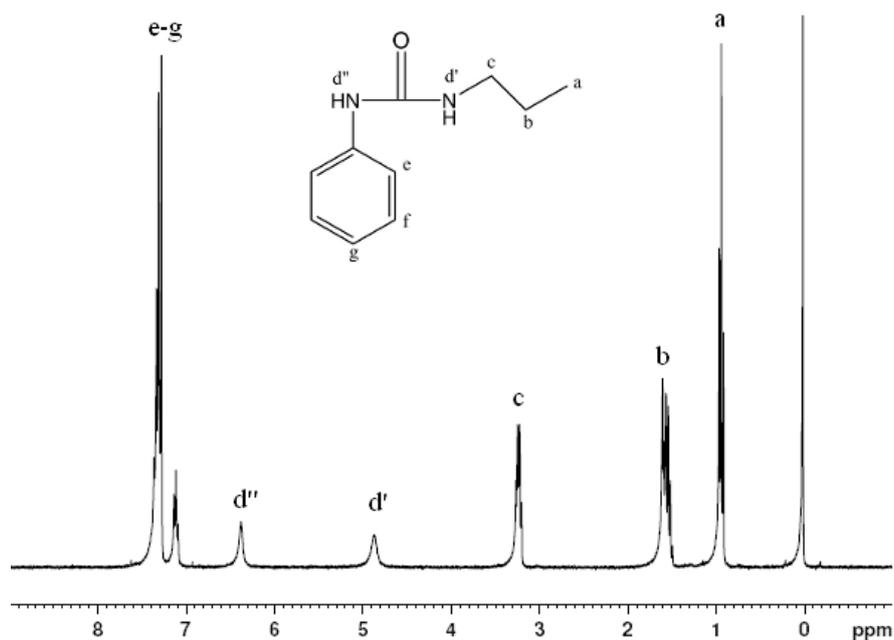


# Supplementary Materials: Reduced Reactivity of Amines against Nucleophilic Substitution via Reversible Reaction with Carbon Dioxide

Fiaz S. Mohammed and Christopher L. Kitchens \*



**Figure S1.** ATR-FTIR of *n*-phenyl, *n*-alkyl ureas showing the similar absorption spectra and characteristic carbonyl and secondary amine peak.



**Figure S2.**  $^1\text{H-NMR}$  of *n*-phenyl, *n*-propyl urea.  $\delta = 1.0$  (t, 3H), 1.6 (m, 2H), 3.3 (t, 2H), 4.9 (s, 1H), 6.4 (s, 1H), 7.1–7.5 (5H).

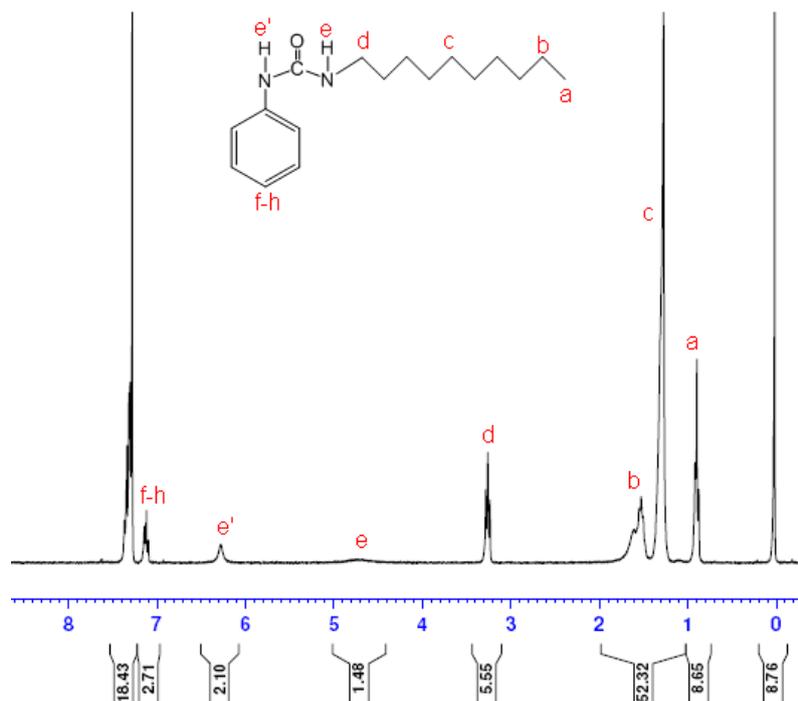


Figure S3.  $^1\text{H}$  NMR of *n*-phenyl, *n*-decyl urea.

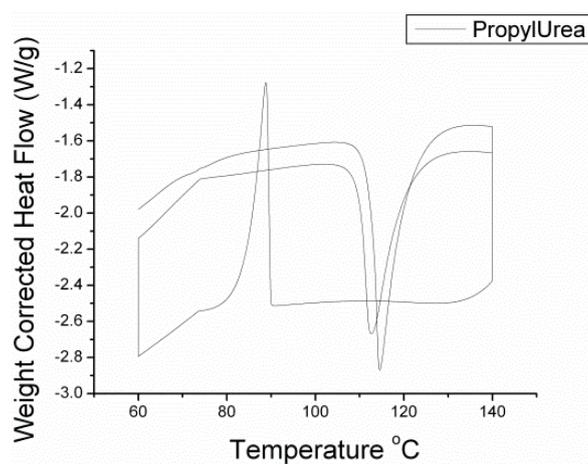
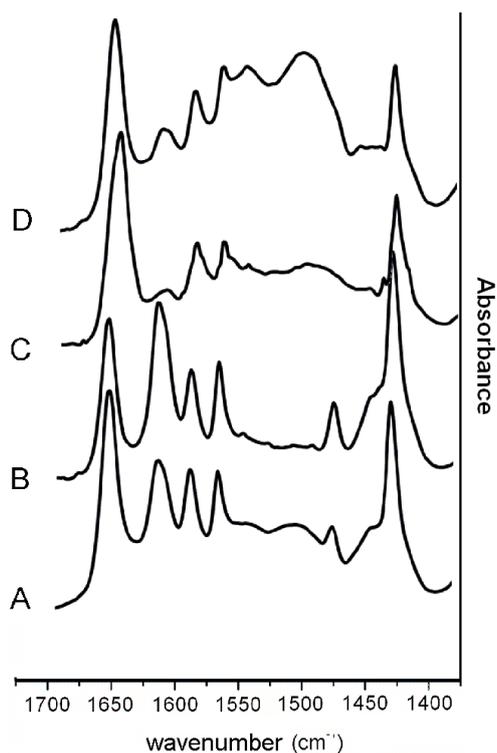
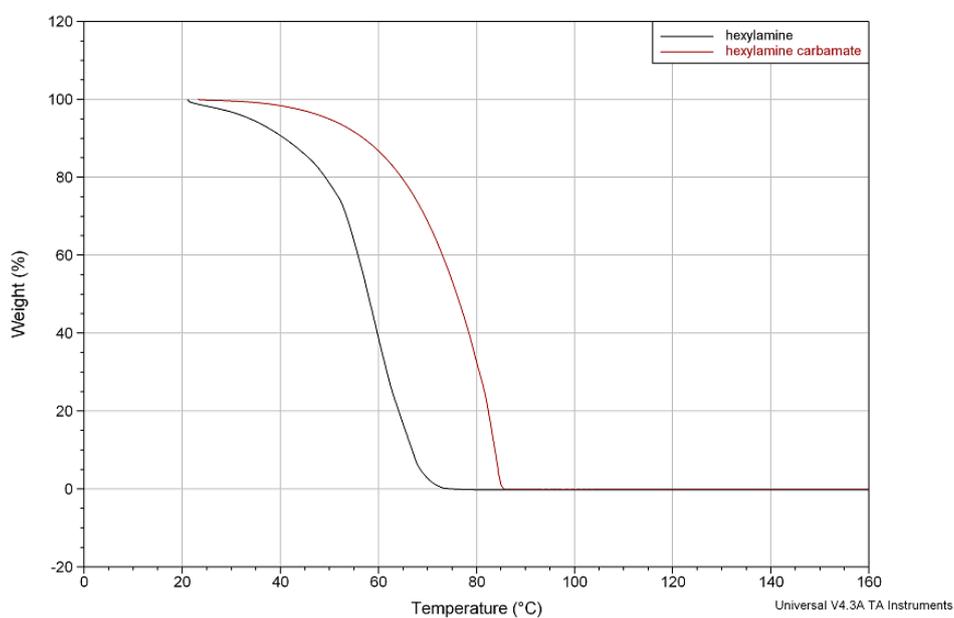


Figure S4. DSC spectra of *n*-propyl urea at ramp rate 5  $^{\circ}\text{C}$  per minute to 140  $^{\circ}\text{C}$  followed by equilibration to 60  $^{\circ}\text{C}$  and repeated heating.

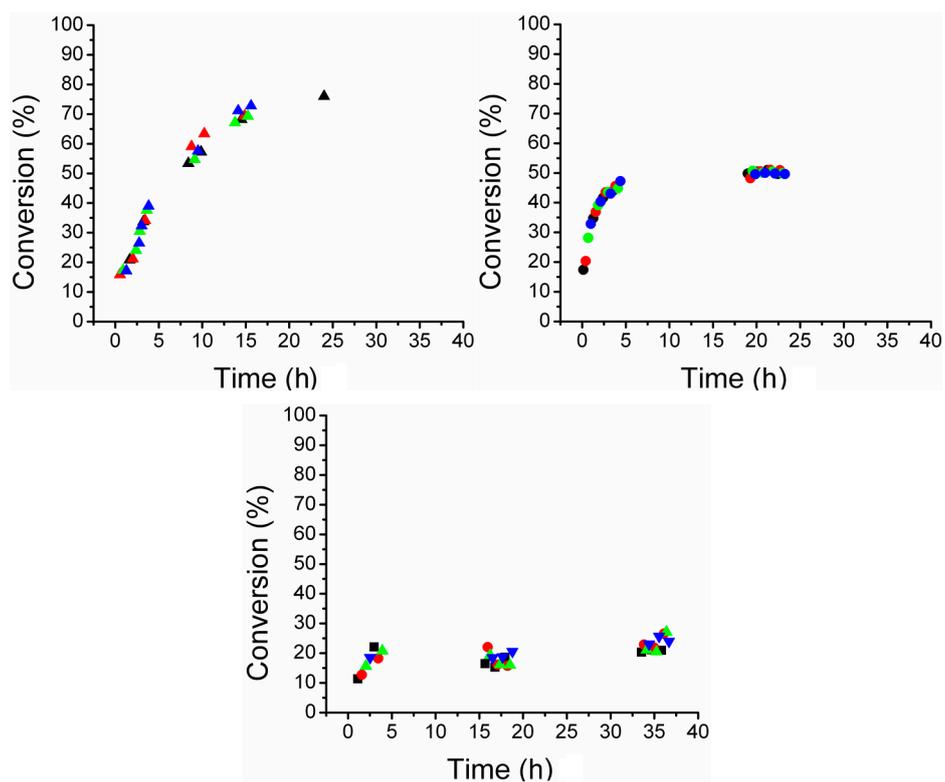


**Figure S5.** ATR-FTIR spectra of non-protected BP reactions at 3 h (A) and at 12 h (B). ATR-FTIR of protected BP reaction at 3 h (C) and at 12 h (D)



**Figure S6.** Thermogravimetric analysis is (TGA) of hexylamine and hexylamine carbamate.

The temperature at which the CO<sub>2</sub> evolves from neat hexylammonium carbamate powder is higher than that temperature at which the neat hexylamine will volatilize. Hence, it is very important to control the de-protection technique as some starting amine can be lost due to vaporization. This also applies to a greater extent for propyl amine which is more volatile than the hexylamine.



**Figure S7.** BP conversion % of Non-protected (**top**), Protected (**middle**) and De-protected (**bottom**) reactions monitored in-situ from 4reaction vials.