

Supplementary Information

Zinc monoglycerolate as a catalyst for the conversion of 1,3- and higher diols to diurethanes

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Materials and Methods:

¹H and ¹³C NMR spectra were recorded on either a Bruker DRK-400 or DRK 300MHz (100 and 75 MHz for carbon) instrument. GC-MS employed ThermoQuest TRACE DSQ GC-MS using an SGE BP5 column (30m x 0.22 mm ID) and an Electron Impact (EI) detector with ionization energy of 70 eV. Helium was used as a carrier gas at a flow-rate of 0.8 mL/min. ESI-MS was performed on an Agilent 6220 series Time of Flight Liquid chromatography mass spectrometry (LC/MS) (TOF) system with Agilent 1200 Series HPLC. Infrared spectra were obtained on an ATR-Perkin Elmer Spectrum RX1 series Fourier Transform infrared spectrometer with neat samples. Substrates, reagents and solvents were purchased from either Sigma-Aldrich or Merck and used directly. Commercial samples of zinc monoglycerolate (ZMG) was obtained from Micronisers Pty Ltd.

Glycerol carbonate^[14]: 10 g (0.109 mol) of glycerol, 9.78 g (0.163 mol) of urea and 5% wt. ZMG (0.5 g) to glycerol were heated to 140°C at 40 mbar for 7 h. ¹H-NMR (400 MHz, CDCl₃): δ_H 5.27 (br s, 1H, OH), 4.82-4.77 (m, 1H), 4.49 (t, 1H, J= 8.4 Hz), 4.28 (dd, 1H, J= 8 Hz, 6 Hz), 3.66 (dd, 1H, J= 12.8, 2.8 Hz), 3.51 (dd, 1H, J= 12.6, 3.6 Hz), FTIR (neat): ν/cm⁻¹ 3418(O-H_{str}), 2930, 1780(C=O_{str} cyclic), 1402, 1179, 1054. GC-MS: m/z 118(M-1, 3), 87.1(M-CH₂OH, 75), 71(5), 61(7), 55(10).

Ethylene carbonate^[15]: 5 g (0.081 mol) of ethylene glycol, 7.3 g (0.122 mol) of urea and ZMG (0.25 g) were heated to 140°C at ambient pressure for 24 h. ¹H-NMR (400 MHz, CDCl₃): δ_H 4.54 (s, 4H).

Propylene carbonate^[15]: 5 g (0.066 mol) of diol, 5.92 g (0.099 mol) of urea and 5% wt. ZMG (0.25 g) were heated to 140°C at 400 mbar for 24 h. ¹H-NMR (400 MHz, CDCl₃): δ_H 4.84 (sextuplet, 1H, 7.4 Hz), 4.54 (dd, 1H, J= 7.9, 7.8 Hz), 4.00 (dd, 1H, J= 7.3, 7.4 Hz), 1.46 (d, 3H, 6.2 Hz).

4-(2-Hydroxyethyl)-1,3-dioxolan-2-one^[16]: 5 g (0.047 mol) of diol, 4.23 g (0.071 mol) of urea and 5% wt. ZMG (0.25 g) were heated to 140°C at 40 mbar for 7 h. ¹H-NMR (300 MHz, CDCl₃): δ_H 4.98-4.88 (m, 1H), 4.59 (dd, 1H, J= 8.4, 7.8 Hz), 4.20 (dd, 1H, J= 8.7, 7.5 Hz), 3.84-3.79 (m, 2H), 2.12 (br s, 1H), 2.04-1.94 (m, 2H). FTIR (neat): ν/cm⁻¹ 3406(O-H_{str}), 2966(C-H_{str}), 2925(C-H_{str}), 1770(C=O_{str} cyclic), 1481, 1386, 1262, 1170, 1051, 774, 717 GC-MS: m/z 131.1(M-1, 3), 114.1(M-H₂O, 6), 101.1(M-

CH₂OH, 5), 90.1(M-CH₂CO, 14), 87.1(M-C₂H₄OH, 2), 70.1(M-HOCO₂H, 19), 59.1(87-CO, 39), 55.1(13). ESI-MS: m/z 133.1 (5%) [M+H]⁺ and m/z 155.1 (100%) [M+Na]⁺.

Hexahydrobenzo[d][1,3]dioxol-2-one^[17]: *cis*-1,2-cyclohexanediol (750 mg, 6 mmol), urea (580 mg, 9.6 mmol) and 5% wt ZMG (37.5 mg) were heated at 140°C/40 mbar. The product was purified by recrystallization from methanol. Yield = 56% (400 mg). ¹H-NMR (400 MHz, CDCl₃): δ_H 4.63 (t, 2H, 4 Hz), 1.86 (m, 4H), 1.58-1.53 (m, 2H), 1.38-1.34 (m, 2H). ¹³C-NMR (400 MHz, CDCl₃): δ_C 155.3, 70.6, 26.7, 19.1. FTIR (film): ν/cm⁻¹ 1788, 1172, 1076. GC-MS: m/z 142 [M]⁺, 81, 69, 55, 41(base peak).

Cyclohexane-1,2-diyl dicarbamate : *trans*-1,2-cyclohexanediol (5 g, 0.043 mol), urea (3.88 g, 0.065 mol) and 5% wt ZMG (0.25 g) were heated for 7h at 140°C under 40 mbar reduced pressure. ¹H-NMR (400 MHz, CDCl₃): δ_H 7.86 (br s, 2H), 4.62 (t, 2H, 4 Hz), 1.85 (m, 4H), 1.57-1.52 (m, 2H), 1.39-1.34 (m, 2H). ¹³C-NMR (400 MHz, CDCl₃): δ_C 157.1, 70.5, 26.8, 19.2. FTIR (film): ν/cm⁻¹ 1753, 1690, 1491, 1389, 1229, 1068. GC-MS: m/z 344 [M]⁺, 98 (base peak), 83, 70.1, 57.1.

2-Hydroxyphenyl carbamate^[18]: 5 g (0.045 mol) of diol, 4.09 g (0.068 mol) of urea and 5% wt. ZMG (0.25 g) were heated to 140°C at 40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 9.45 (s, 1H), 6.99 (dd, 1H, J= 7.8, 7.6Hz), 6.95 (d, 1H, J=8.1 Hz), 6.87 (d, 1H, J= 8.1 Hz), 6.74 (dd, 1H, J= 7.8, 7.3 Hz).

Propane-1,3-diyl dicarbamate^[19]: 5 g (0.066 mol) of diol, 7.93 g (0.132 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C at ambient pressure for 24 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.47 (br. s), 3.94 (t, 4H, J= 6.5Hz), 1.80 (pentuplet, 2H, J =6.6 Hz).

Butane-1,4-diyl dicarbamate^[19]: 5 g (0.055 mol) of diol, 6.61 g (0.11 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 24 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.42 (br. s), 3.91 (m, 4H), 1.56 (m, 4H).

Hexane-1,6-diyl dicarbamate^[19] : 5 g (0.042 mol) of diol, 5.05 g (0.084 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.37 (br. s), 3.88 (t, 4H, J= 6.7Hz), 1.52 (m, 4H), 1.30 (m, 4H).

Octane-1,8-diyl dicarbamate^[19]: 5 g (0.034 mol) of diol, 4.08 g (0.068 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.39 (br. s), 3.88 (t, 4H, J= 6.5Hz), 1.52 (m, 4H), 1.28 (m, 8H).

Decane-1,10-diyl dicarbamate^[19]: 5 g (0.029 mol) of diol, 3.48 g (0.058 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.38 (br. s), 3.87 (t, 4H, J= 6.4Hz), 1.51 (pentuplet, 4H, J =7.1 Hz), 1.26 (m, 12H).

Oxybis(ethane-2,1-diyl) dicarbamate^[20] : 5 g (0.047 mol) of diol, 5.65 g (0.094 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.50 (br. s), 4.01 (t, 4H, J= 4.3Hz), 3.56 (t, 4H, J =4.7 Hz).

(Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) dicarbamate^[21]: 5 g (0.033 mol) of diol, 3.96 g (0.066 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.51 (br. s), 4.01 (t, 4H, J= 4.4Hz), 3.56 (t, 4H, J =4.6 Hz), 3.53 (m, 4H).

Tetra carbamate of pentaerythritol^[22]: 5 g (0.037 mol) of polyol, 11.11 g (0.185 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 6.52 (br. s), 3.93 (s, 8H).

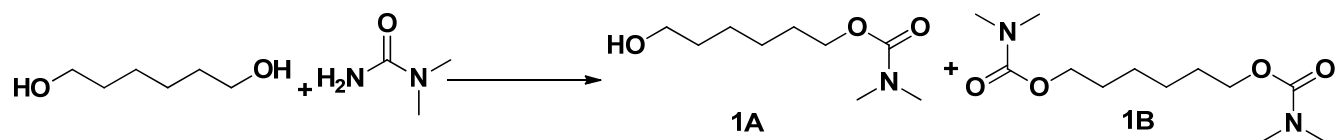
2-(Hydroxymethyl)phenyl carbamate: 5 g (0.040 mol) of polyol, 3.6 g (0.06 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 7.94 (br. s), 7.28 (appt, 1H, J=7.4 Hz), 7.24 (d, 1H, J= 7.4Hz), 7.12 (appt, 1H, J= 7.4 Hz), 7.00 (d, 1H, J= 7.8 Hz,), 4.40 (s, 2H). ¹³C-NMR (400 MHz, *d*₆-DMSO): δ_c 150.1, 149.8, 128.6, 126.2, 123.9, 118.1, 115.7, 41.2. GC-MS: m/z (minor peak on chromatogram ret.time 13.3 min.) 166 [19%, M-H]⁺, 149 (9%), 122 (52%), 106 (64%), 78 (100%); m/z (major peak on chromatogram ret.time 14.3 min.) 149 [60%, M-H₂O]⁺, 106 (75%), 78 (100%).

6-Hydroxyhexyl carbamate^[23]: 5 g (0.042 mol) of 1,6-hexanediol, 6.5 g (0.06 mol) of urea and 5% wt. ZMG (0.25 g) were heated at 140°C/40 mbar for 7 h. ¹H-NMR (400 MHz, *d*₆-DMSO): δ_H 9.79 (br. s, 1H), 6.40 (br. s, 2H), 4.05 (t, 2H, J= 6.5 Hz), 3.88 (t, 2H, J= 6.8 Hz), 1.55 (m, 4H), 1.31 (m, 4H).

Mono N,N-dimethyl carbamate

Reaction of N,N dimethyl urea with 1,6-hexanediol.

2.5 g of 1,6-hexanediol (0.021 mol) was reacted with 3.73 g of N,N dimethyl urea (0.042 mol) using 10% wt ZMG (250 mg). The mixture was heated at 140° C under 40 mbar for 7h with sampling at t=1,3,5 and 7h. On heating the mixture formed a suspension. After 7h, 20 mL methanol was added to precipitate out ZMG, filtered and the filtrate concentrated. The conversion was low due to volatile nature of reactants.



¹H-NMR (400 MHz, DMSO): δ_H 4.96 (br s, 1H), 3.89 (t, 2H), 3.62(t, 2H), 3.34 (s, 6H), 1.65-1.53 (m, 8H). GC-MS: m/z 62 (base peak), 82, 102, 116, 131.

Figure S1: GC-MS for reaction mixture - N,N dimethyl urea with 1,6-hexanediol.

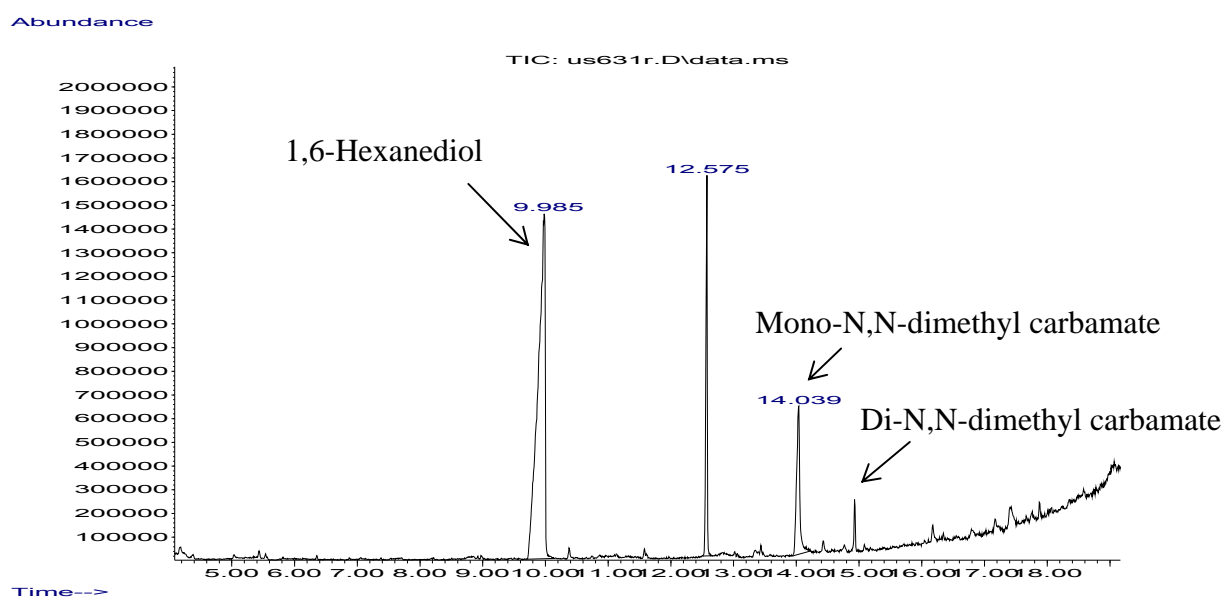


Figure S2: Mass spectrum of mono substituted N,N-dimethyl carbamate (rt= 14.04 min)

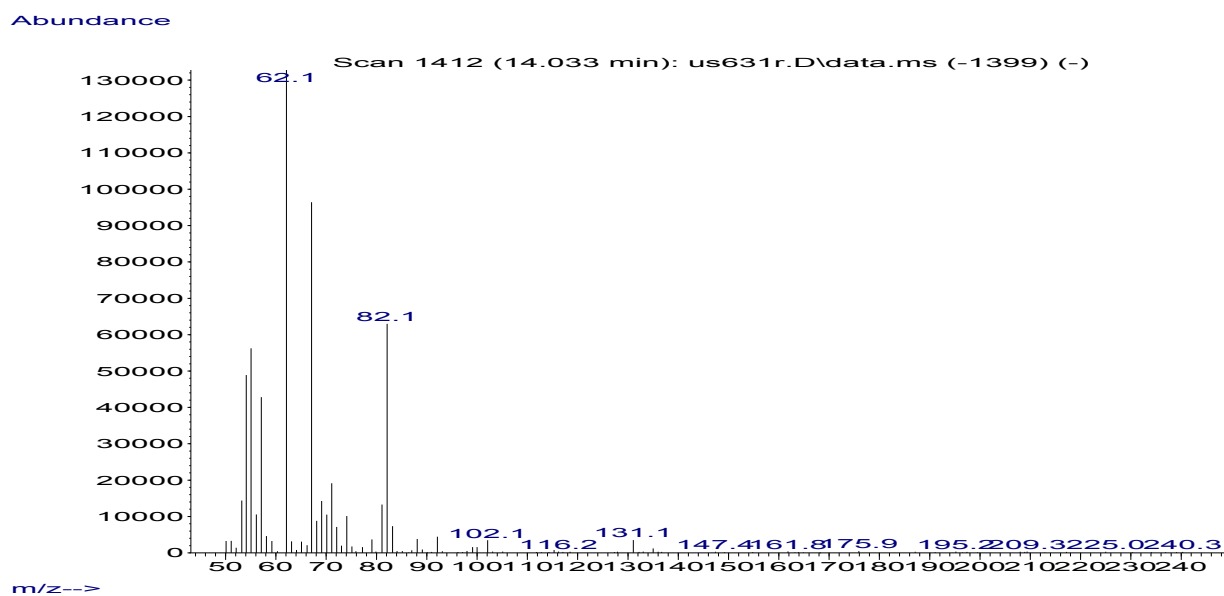


Figure S3: Mass spectrum of disubstituted N,N-dimethyl carbamate (rt= 14.9 min)

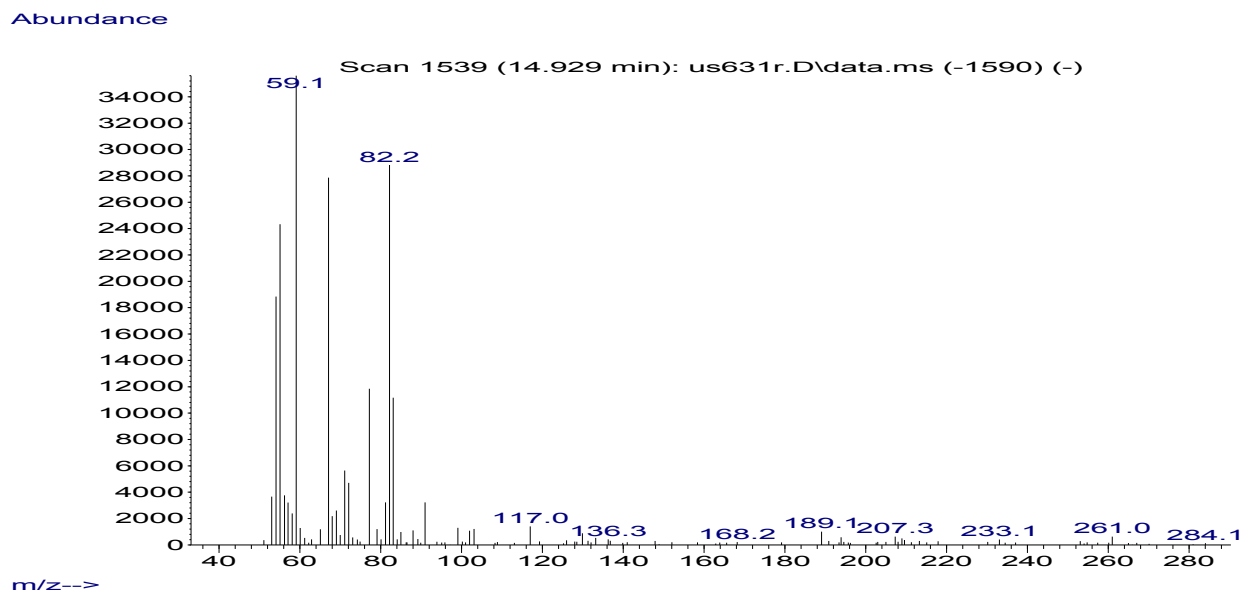


Figure S4: Mass spectrum of 1,6-hexanediol (rt= 9.97 min)

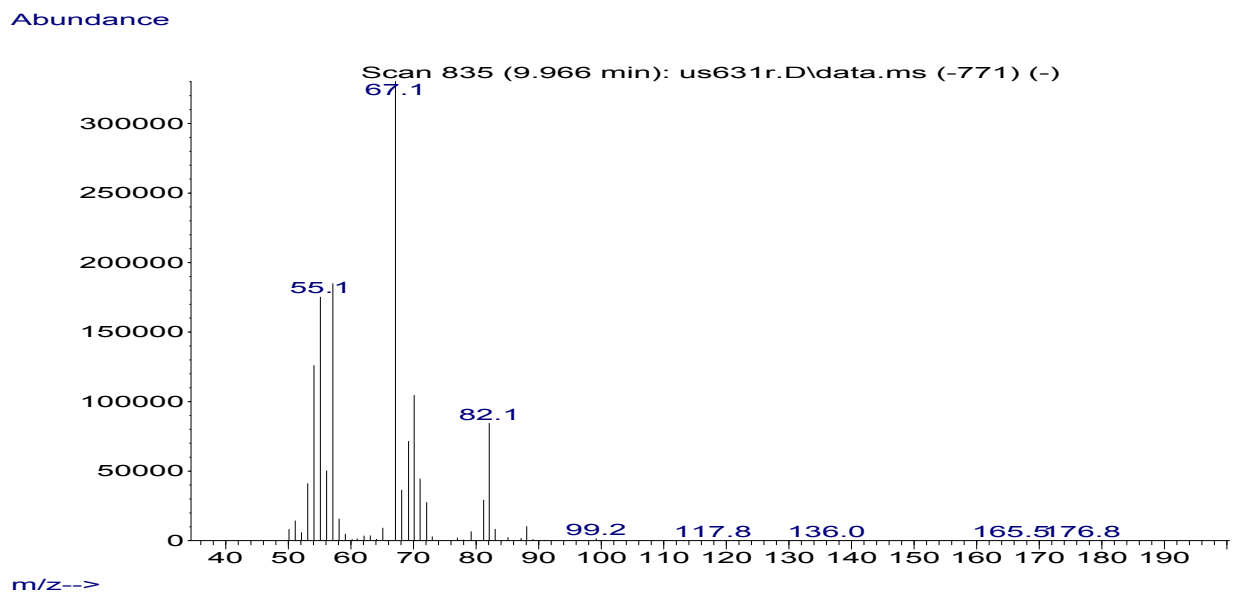
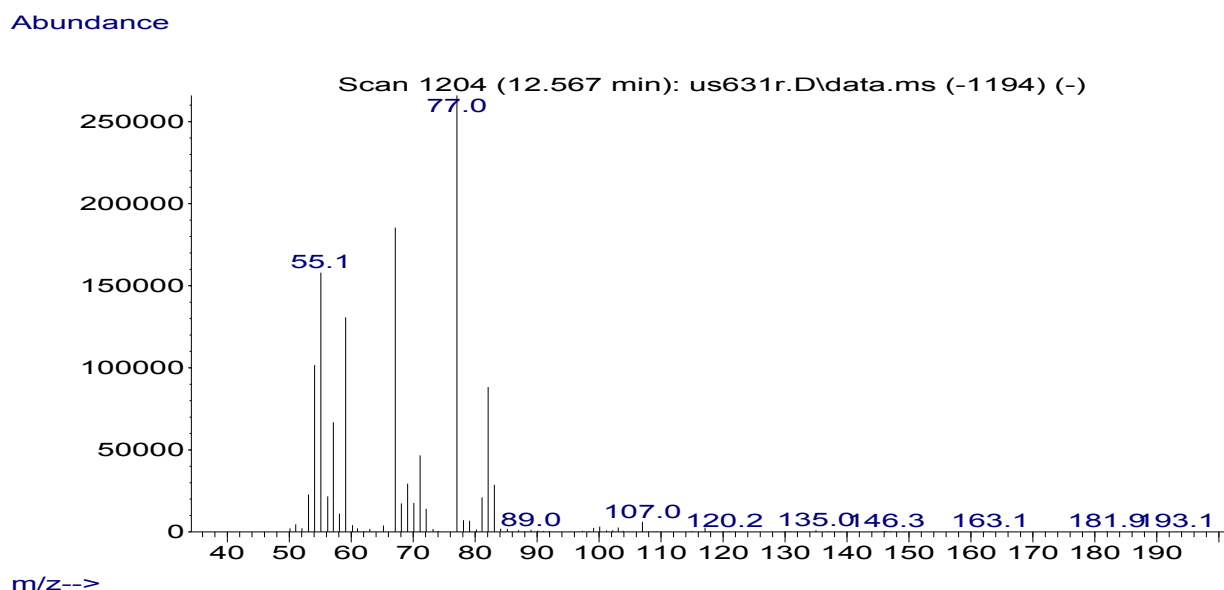


Figure S5: Mass spectrum of N,N-dimethyl urea (rt= 12.57min)



Attempted reaction of thiourea with 1,6-hexanediol

5 g of 1,6-hexanediol (0.042 mol) was reacted with 4.8 g of tetramethyl urea (0.063 mol) using 10% wt ZMG (250 mg). The mixture was heated at 140° C under 40 mbar (to form a white suspension) for 7h with sampling at t=1.5 and 3 hrs by FTIR. Product formation was not visible at this stage or in the residue at 7 hrs.

Attempted reaction of tetramethyl urea with 1,6-hexanediol

2.5 g of 1,6-hexanediol (0.021 mol) was reacted with 4.92 g of tetramethyl urea (0.042 mol) using 10% wt ZMG (250 mg). The mixture was heated at 140° C under 40 mbar (to form a white suspension) for 7h with sampling at t=1,3,5 and 7h. No product formation occurred.

References – as in manuscript