

Electronic Supplementary information for

Two in one environment friendly chemical recycling of polycarbonate and harvesting preserved carbonyl for urea derivative synthesis.

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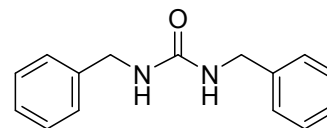
Materials and Methods

¹H/¹³C NMR (300/75 MHz; CDCl₃) spectra were recorded using commercial available deuterated solvents on multinuclear spectrometer Bruker 300 MHz. Data analysis was done by using MestReNova v8.1.0-11315 software. NMR is reported as follows: chemical shifts (multiplicity [singlet (s), doublet (d), double doublet (dd) triplet (t), quartet (q), AB quartet (ABq), broad (br), and multiplet (m)], coupling constant [Hz], integration). IR spectra were recorded on Jasco FTIR 6300 spectrophotometer only significant peaks are presented. Aligent 1200 series HPLC coupled with esquire 6000 mass spectrometer was used to investigate the reactions in LCMS. Thin layer chromatography (TLC) was performed on Merck (60F254, 0.2 mm) using an appropriate solvent system. The chromatograms were visualized under UV light. Most of the products crystallized in ethanol. All solvents and liquid reagents were dried with appropriate reagents before use. Commercially available amines, laboratory grade ethanol and polycarbonate used without any further purification. All the reactions we performed in Teflon capped 4 ml glass vials under shaking conditions.

Examples of N,N'-dibenzylureas

N,N'-bis-benzylurea 3a

Isolated yield 58%; white crystalline solid; [Found: C, 75.16; H, 6.97; N, 5.36. C₁₅H₁₆N₂O requires: C, 74.97; H, 6.71; N, 11.66 %]; ν_{\max} (neat)

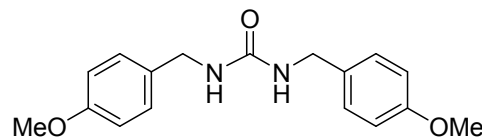


3317,1567, 1241 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 4.34 (s, 4H), 7.23- 7.34 (m, 10H); ¹³C NMR (75

MHz, CDCl₃): δ 44.5, 127.4, 128.6, 138.9, 158.1; MS (ESI) calcd. for C₁₅H₁₆N₂O (m/z): 240.13 found [MH]⁺ 241.2.

N,N'-bis-(4-methoxybenzyl)urea 3b

Isolated yield 62%; white solid; [Found: C, 68.30; H, 6.49; N, 9.85. C₁₇H₂₀N₂O₃ requires: C, 67.98; H, 6.71; N, 9.33 %]; ν_{\max}

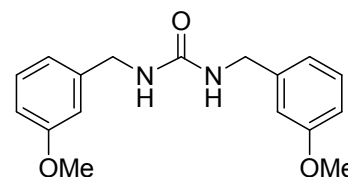


(neat) 3316, 1575, 1236 cm⁻¹; ¹H-NMR (300 MHz, DMSO): δ 3.73 (s, 6H), 4.15 (d, 4H, J 6.0 Hz), 6.30 (t, 2H, J 6.0 Hz), 6.87 (d, 4H, J 8.4), 7.17 (d, 4H, J 8.4 Hz); ¹³C NMR (75 MHz, DMSO): δ 42.3, 55.0, 113.5, 128.2, 132.7, 158.0; MS (ESI) calcd. for C₁₇H₂₀N₂O₃ (m/z): 300.15 found [MH]⁺ 301.3.

N,N'-bis-(3-methoxybenzyl)urea 3c

Isolated yield 60%; white solid; [Found: C, 68.21; H, 6.54; N, 10.27.

C₁₇H₂₀N₂O₃ requires: C, 67.98; H, 6.71; N, 9.33 %]; ν_{\max} (neat) 3307,

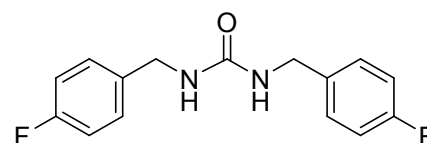


1568, 1261 cm⁻¹; ¹H-NMR (300 MHz, DMSO): δ 3.73 (s, 6H), 4.21 (d, 4H, J 6.0 Hz), 6.45 (t, 2H, J 6.0 Hz), 6.82 (m, 6H), 7.23 (m, 2H); ¹³C NMR (75 MHz, DMSO): δ 42.8, 54.8, 111.8, 112.4, 119.0, 129.2, 142.5, 144.1, 158.0; MS (ESI) calcd. for C₁₇H₂₀N₂O₃ (m/z): 300.15 found [MH]⁺ 301.4.

N,N'-bis-(4-fluorobenzyl)urea 3d

Isolated yield 52%; white solid; [Found: C, 65.26; H, 4.73; N,

11.09. C₁₅H₁₄F₂N₂O requires: C, 65.21; H, 5.11; N, 10.14 %]; ν_{\max}

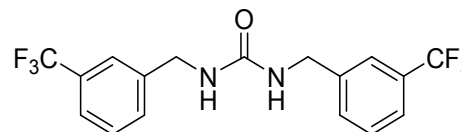


(neat) 3317, 1571, 1219 cm⁻¹; ¹H-NMR (300 MHz, DMSO): δ 4.21 (d, 4H, J 6.0 Hz), 6.49 (t, 2H, J 6.0 Hz), 7.11-7.31 (m, 8H); ¹³C NMR (75 MHz, DMSO): δ 42.2, 114.7, 115.0, 128.8, 128.9, 137.0, 157.9; MS (ESI) calcd. for C₁₅H₁₄F₂N₂O (m/z): 276.11 found [MH]⁺ 277.3.

N,N'-bis-(3-(trifluoromethyl)benzyl)urea 3f

Isolated yield 28%; white solid; [Found: C, 54.15; H, 3.80; N,

7.45. C₁₇H₁₄F₆N₂O requires: C, 54.26; H, 3.75; N, 7.44 %];



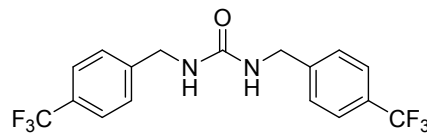
¹H-NMR (300 MHz, DMSO): δ 4.32 (d, 4H, J 6.0 Hz), 6.74 (t, 2H, J 6.0 Hz), 7.54-7.59 (m, 8H); ¹³C

NMR (75 MHz, DMSO): δ 42.4, 123.1, 129.1, 130.9, 142.6, 158.0; MS (ESI) calcd. for $C_{17}H_{14}F_6N_2O$ (m/z): 376.10 found $[MH]^+$ 377.3.

N,N'-bis-(4-(trifluoromethyl)benzyl)urea 3g

Isolated yield 48%; white solid; [Found: C, 54.19; H, 3.82; N,

7.39. $C_{17}H_{14}F_6N_2O$ requires: C, 54.26; H, 3.75; N, 7.44 %]; ν_{max}



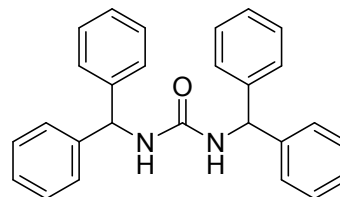
(neat) 3334, 1620, 1582, 1326, 1095 cm^{-1} ; 1H -NMR (300 MHz, DMSO): δ 4.32 (d, 4H, J 6.0 Hz), 6.71 (t, 2H, J 6.0 Hz), 7.46 (d, 4H, J 9.0 Hz), 7.70 (d, 4H, J 9.0 Hz); ^{13}C NMR (75 MHz, DMSO): δ 42.57, 125.0, 127.5, 134.4, 158.0; MS (ESI) calcd. for $C_{17}H_{14}F_6N_2O$ (m/z): 376.10 found $[MH]^+$ 377.3.

N,N'-dibenzhydrylurea 3h

Isolated yield 81%; white solid; [Found: C, 82.61; H, 6.28; N, 7.78.

$C_{27}H_{24}N_2O$ requires: C, 82.62; H, 6.16; N, 7.14 %]; ν_{max} (neat) 3306,

1560, 1270 cm^{-1} ; 1H -NMR (300 MHz, DMSO): δ 5.87 (d, 2H, J 8.4 Hz),

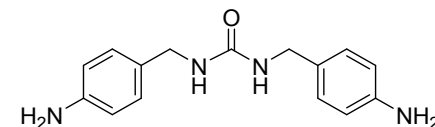


6.96 (d, 2H, J 8.4 Hz, D_2O exchangeable), 7.22-7.35 (m, 20H); ^{13}C NMR (75 MHz, DMSO): δ 56.8, 126.7, 128.3, 143.5, 156.2; MS (ESI) calcd. for $C_{27}H_{24}N_2O$ (m/z): 392.19 found $[MH]^+$ 393.5.

N,N'-bis-(4-aminobenzyl)urea 3j

Isolated yield 72%; white solid; [Found: C, 66.60; H, 6.87; N,

20.36. $C_{15}H_{18}N_4O$ requires: C, 66.64; H, 6.71; N, 20.73 %]; ν_{max}

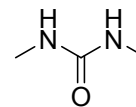


(neat) 3316, 1609, 1559, 1514, 1238 cm^{-1} ; 1H -NMR (300 MHz, DMSO): δ 4.03 (d, 4H, J 6.0 Hz), 4.94 (s, 4H, D_2O exchangeable), 6.05 (t, 2H, J 6.0 Hz, D_2O exchangeable), 6.50 (d, 4H, J 9.0 Hz), 6.91 (d, 4H, J 9.0 Hz); ^{13}C NMR (75 MHz, DMSO): δ 42.7, 113.6, 127.5, 128.0, 142.3, 157.9; MS (ESI) calcd. for $C_{15}H_{18}N_4O$ (m/z): 270.15 found $[MH]^+$ 271.3.

Examples of N,N'-dialkylureas

N,N'-dimethylurea 3k

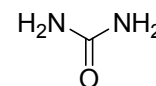
The NMR of the third crop is taken which contain little amount of BPA as well. The peaks corresponding to diemethyl urea are given. ¹H-NMR (300 MHz, DMSO): δ 2.53 (s,6H), 5.75 (s, 2H, D₂O exchangeable)



Urea 3l

Isolated yield 68%; white solid; [Found: C, 20.70; H, 6.66; N, 44.48. CH₄N₂O requires:

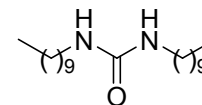
C, 20.00; H, 6.71; N, 46.65 %]; ν_{\max} (neat) 3428, 3333, 1673, 1589, 1458 cm⁻¹; ¹H-NMR



(300 MHz, DMSO): δ 5.47 (s, D₂O exchangeable); ¹³C NMR (75 MHz, DMSO): δ 159.6; MS (ESI) calcd. for CH₄N₂O (m/z): 60.03 found [MH]⁺ 61.1.

N,N'-didecylurea 3m

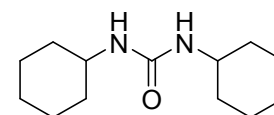
Isolated yield 78%; white solid; [Found: C, 74.00; H, 13.24; N, 7.96. C₃₉H₃₂N₂O requires: C, 74.06; H, 13.02; N, 8.23 %]; ν_{\max} (neat) 3335, 2955, 2918, 2848, 1610, 1570, 1465 cm⁻¹. The compound was not soluble in many organic solvents.



N,N'-dicyclohexylurea 3n

Isolated yield 81%; white solid; [Found: C, 69.55; H, 10.76; N, 12.37.

C₁₃H₂₄N₂O requires: C, 69.60; H, 10.78; N, 12.49 %]; ν_{\max} (neat) 3321, 2927,



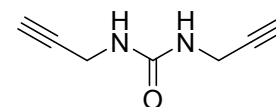
2850, 1623, 1567, 1241 cm⁻¹; ¹H-NMR (300 MHz, DMSO): δ 1.02-1.28 (m,

11H), 1.49-1.75 (m, 11H), 5.59 (d, 2H, J 9.0 Hz, D₂O exchangeable) ; MS (ESI) calcd. for C₁₃H₂₄N₂O (m/z): 224.19 found [MH]⁺ 225.3.

N,N'-dipropargylurea 3o

Isolated yield 72%; cream solid; [Found: C, 62.04; H, 6.04; N, 20.70. C₇H₈N₂O

requires: C, 61.75; H, 5.92; N, 20.58 %]; ν_{\max} (neat) 3316, 3293, 3271, 1592,

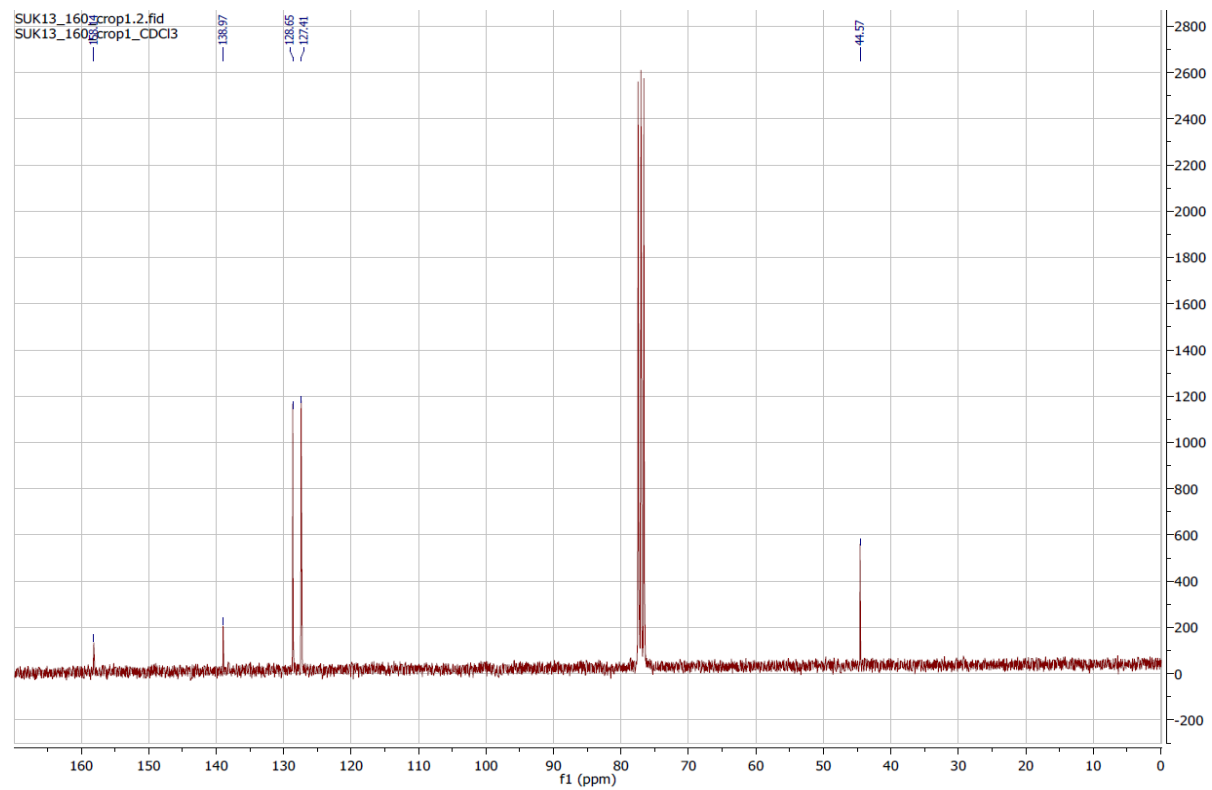
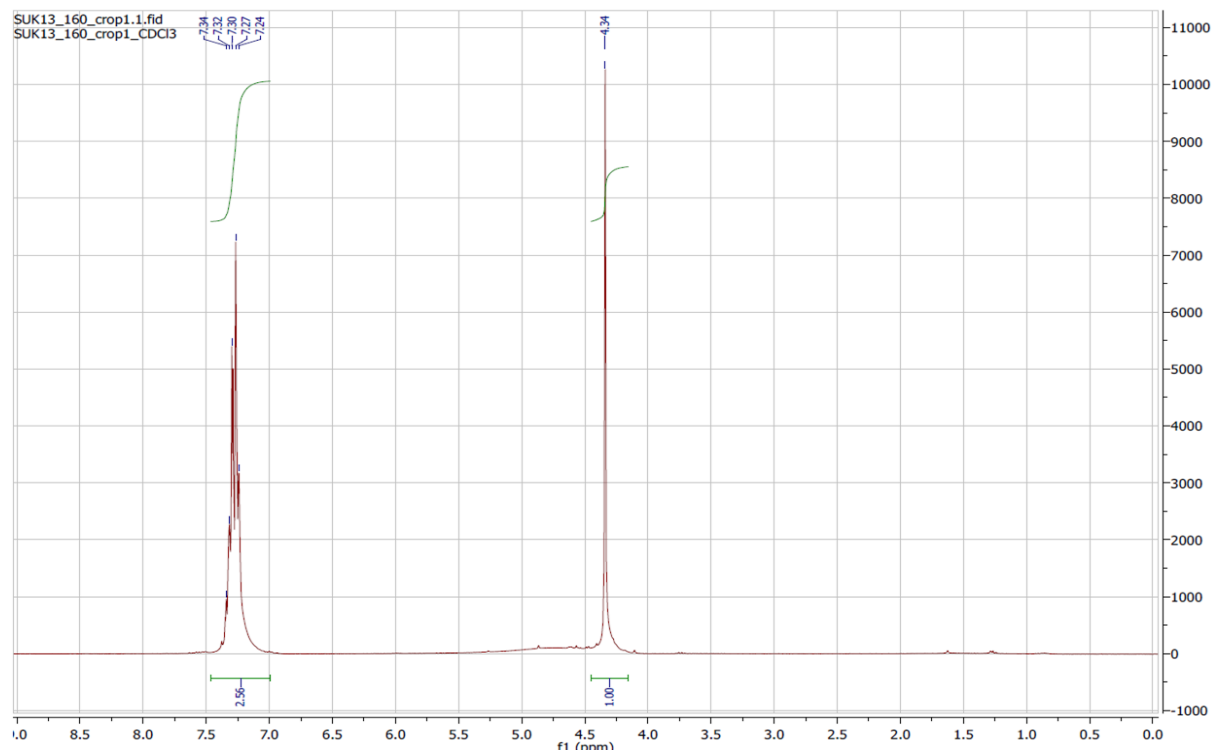


1250 cm⁻¹; ¹H-NMR (300 MHz, DMSO): δ 3.07 (t, 2H, J 2.4 Hz), 3.80 (dd, 4H, J 5.7 Hz, 2.4 Hz), 6.34 (t,

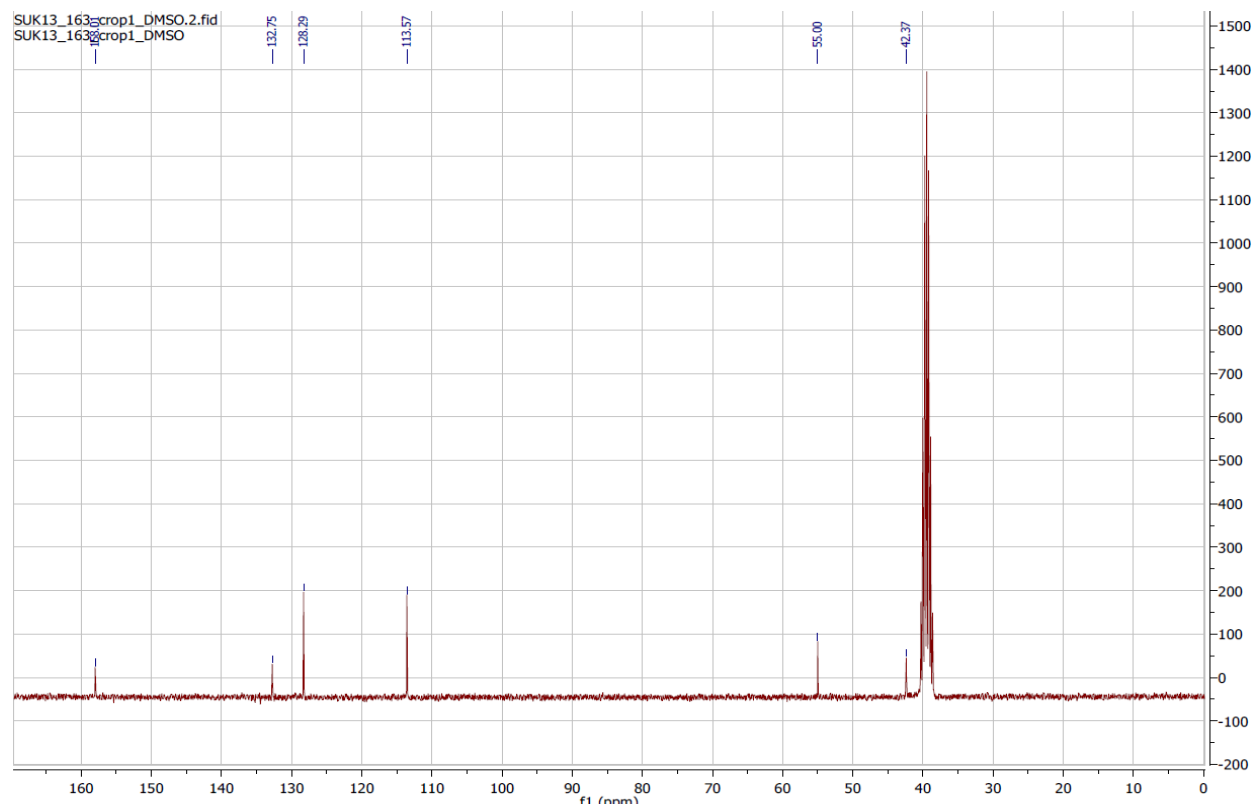
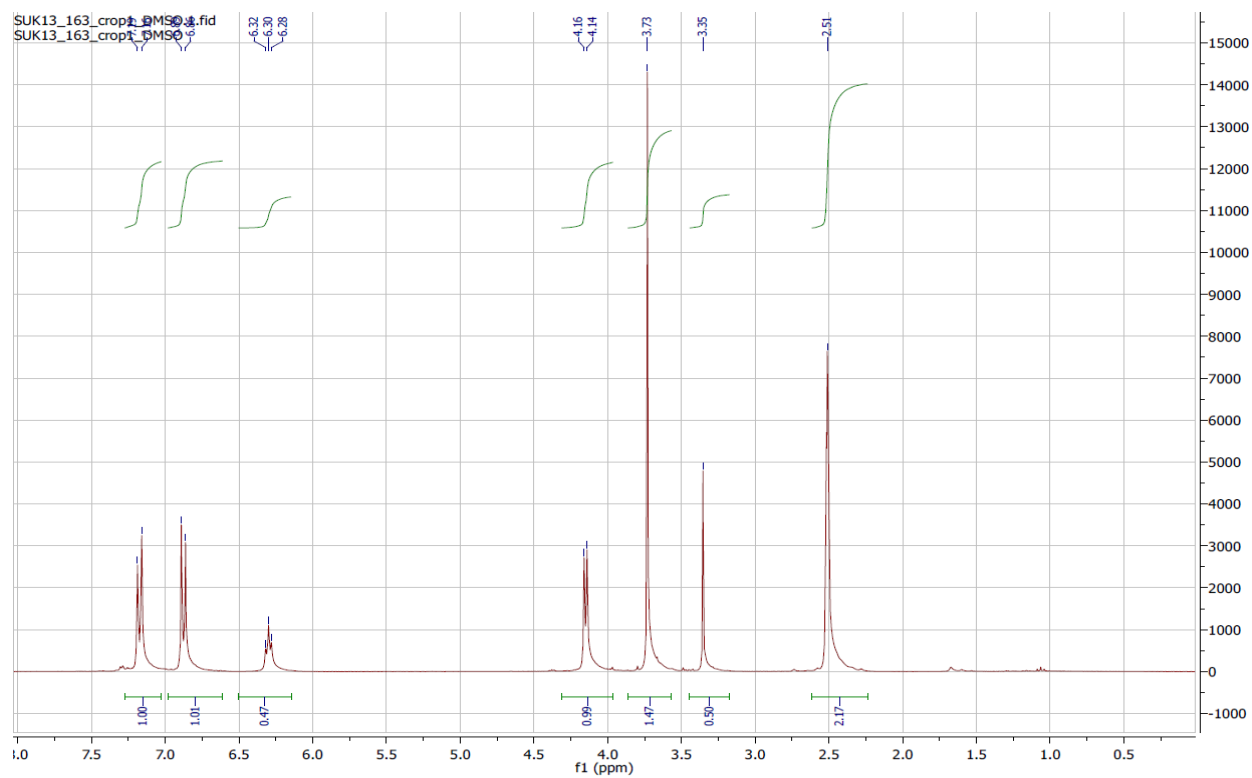
2H, J 5.7 Hz, D₂O exchangeable); ¹³C NMR (75 MHz, DMSO): δ 28.8, 72.6, 82.3, 156.9; MS (ESI)
calcd. for C₇H₈N₂O (m/z): 136.06 found [MH]⁺ 137.1.

Copy of NMR spectra

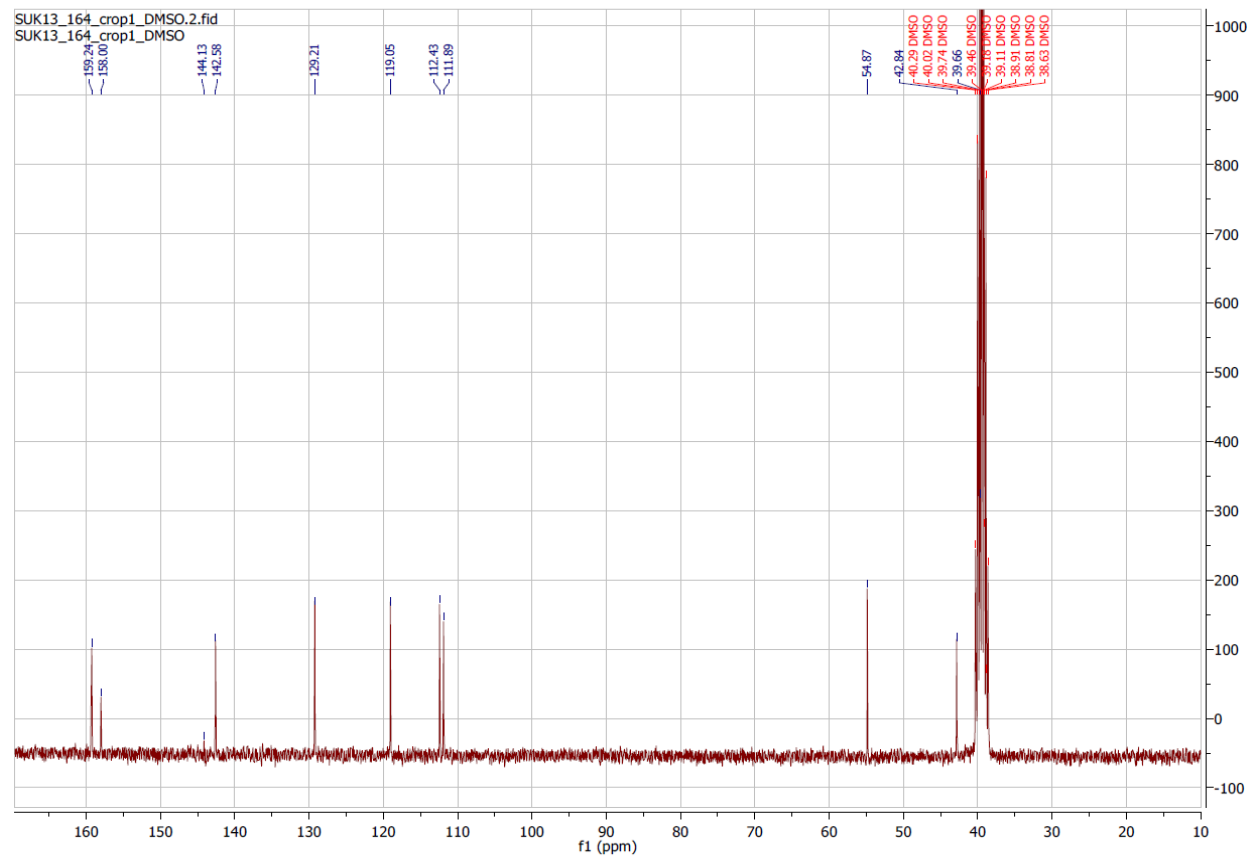
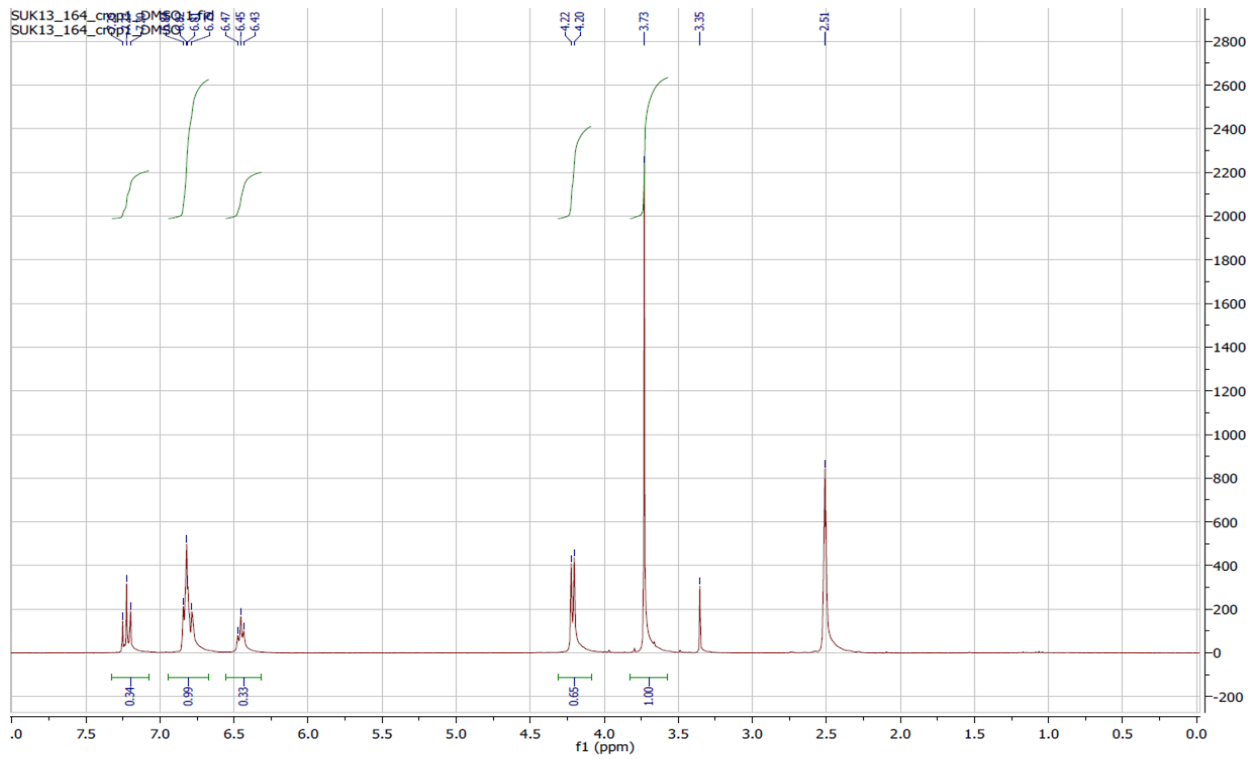
N,N'-bis-benzylurea 3a



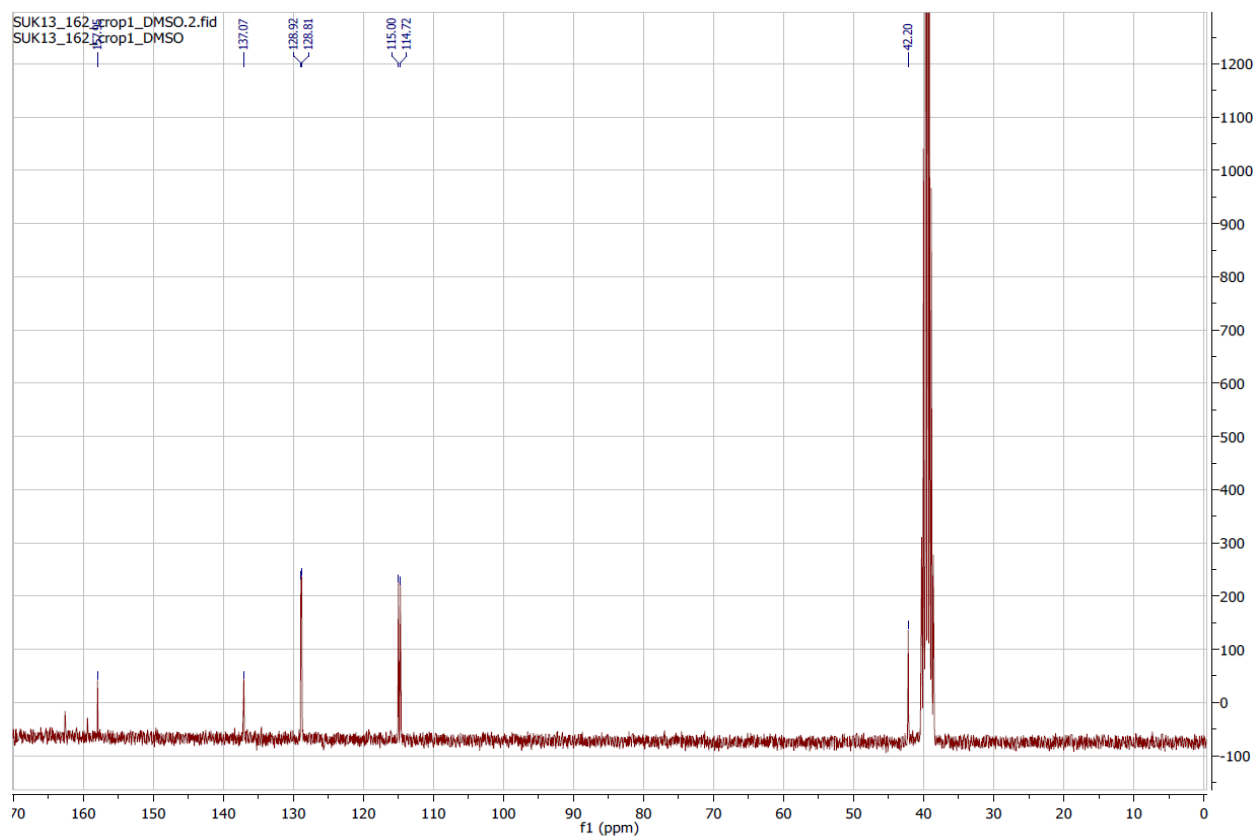
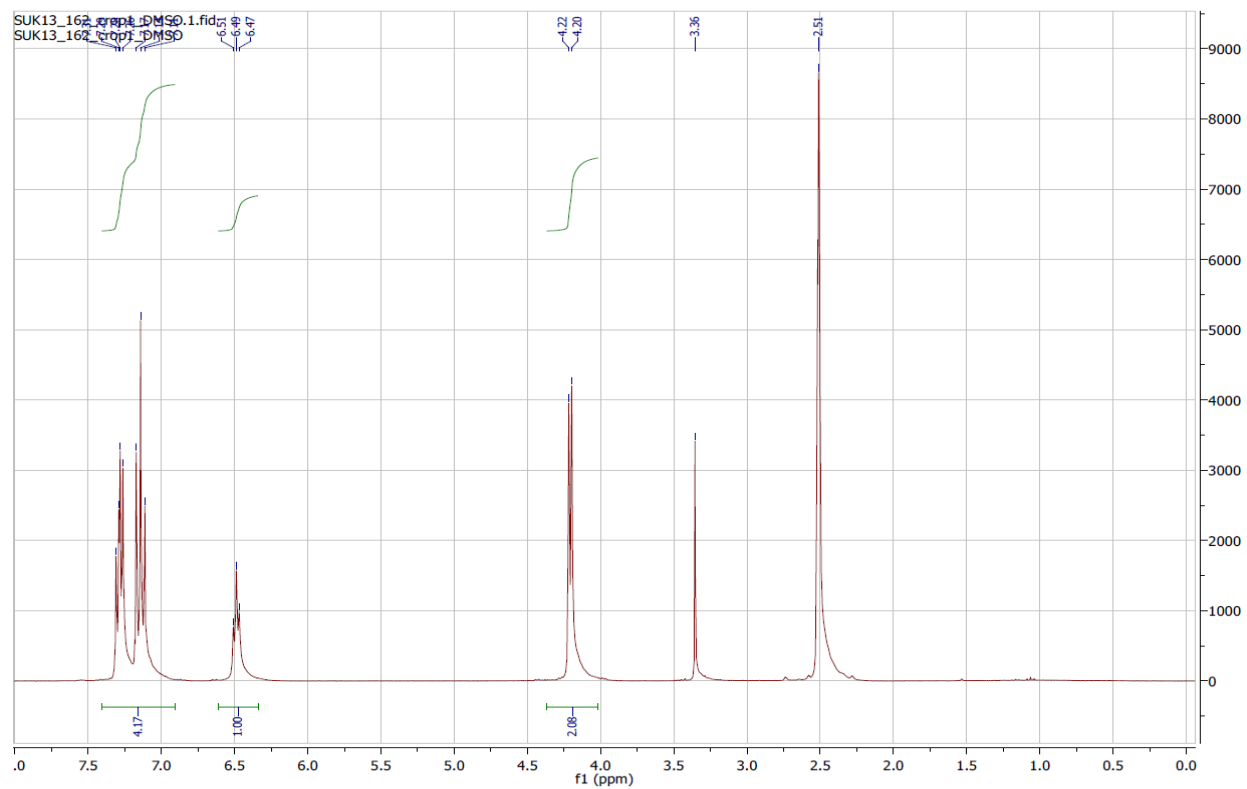
N,N'-bis-(4-methoxybenzyl)urea 3b



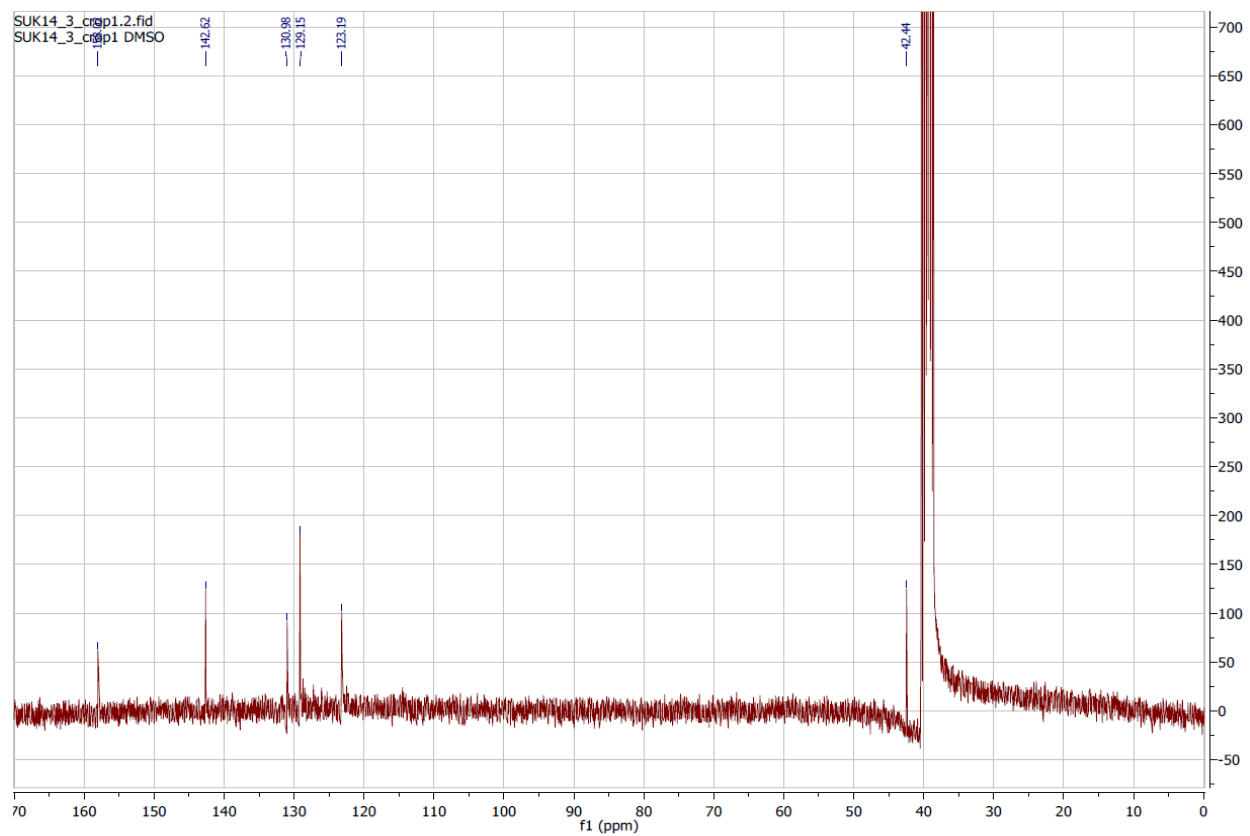
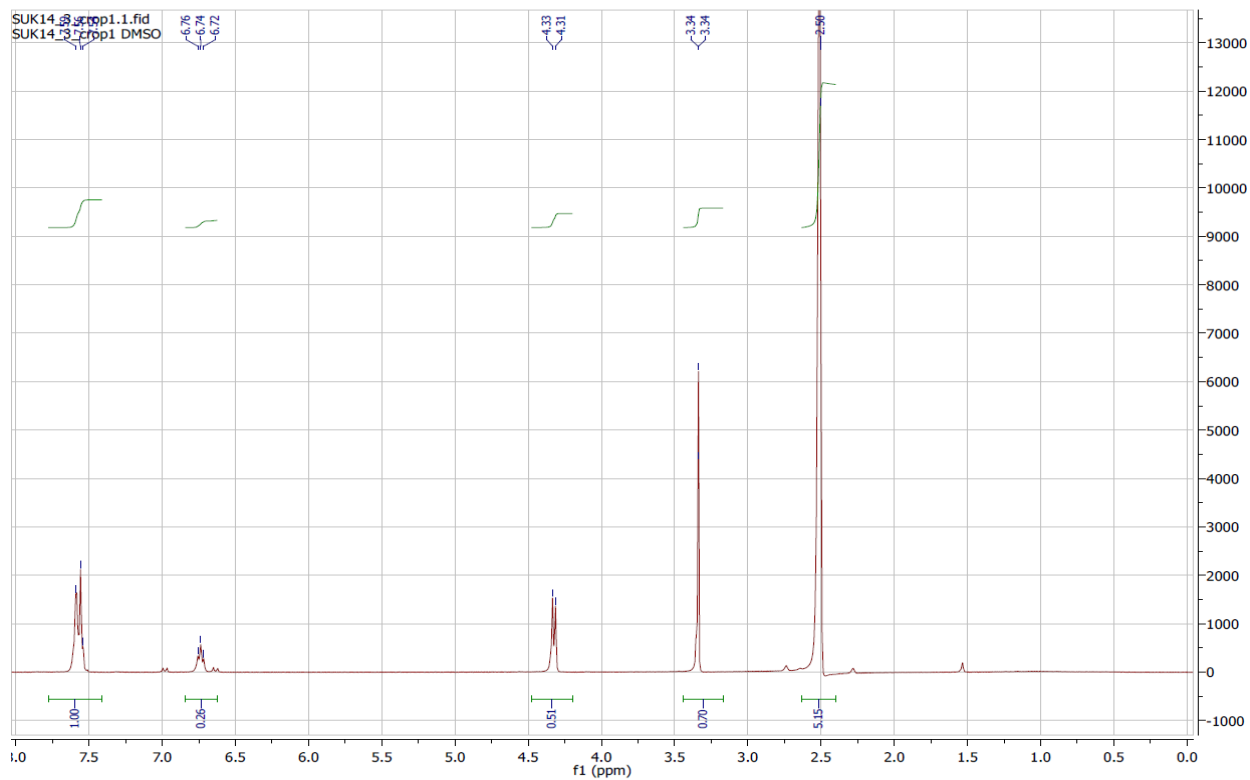
N,N'-bis-(3-methoxybenzyl)urea 3c



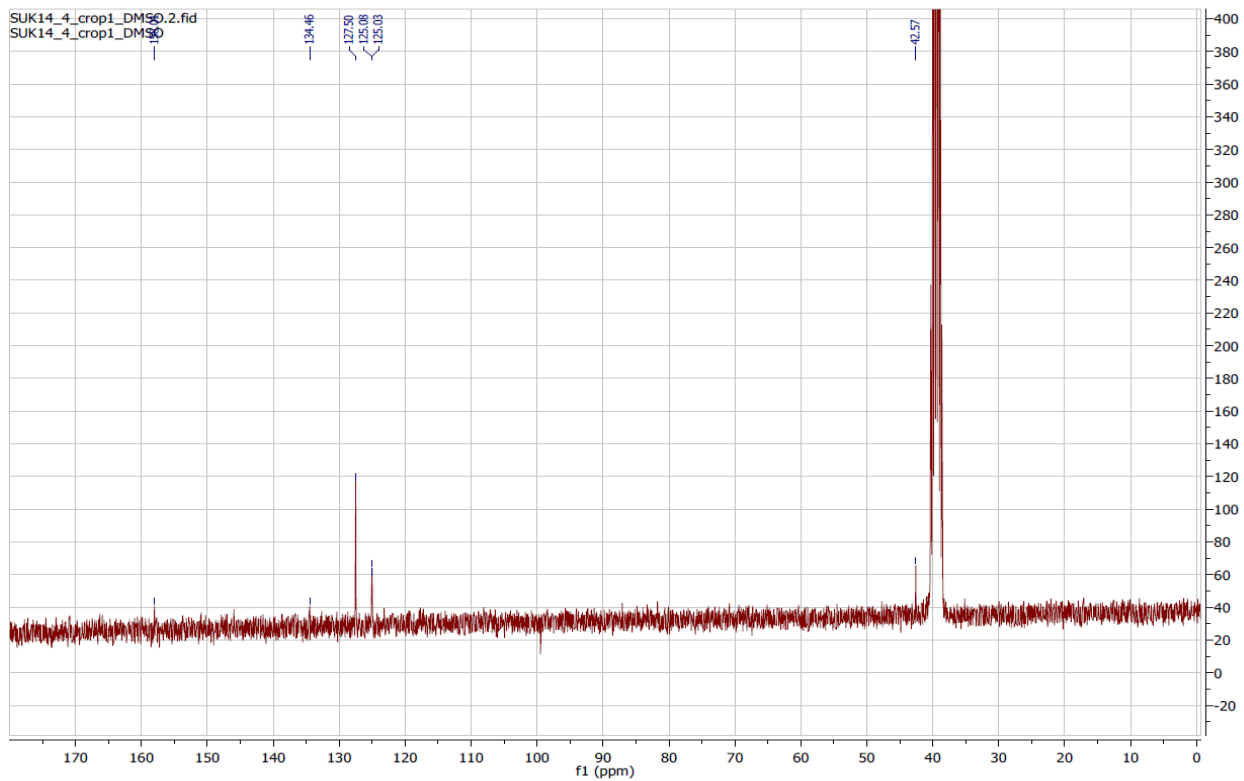
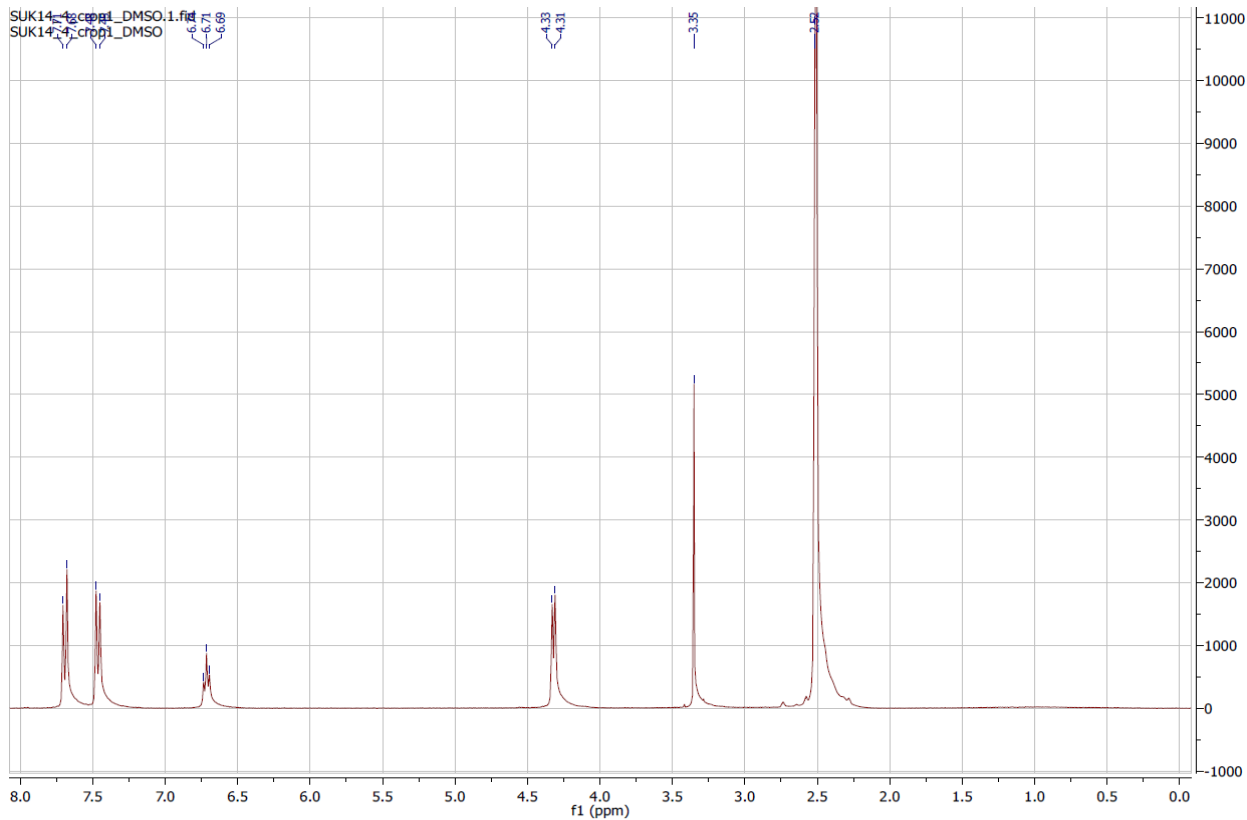
N,N'-bis-(4-fluorobenzyl)urea 3d



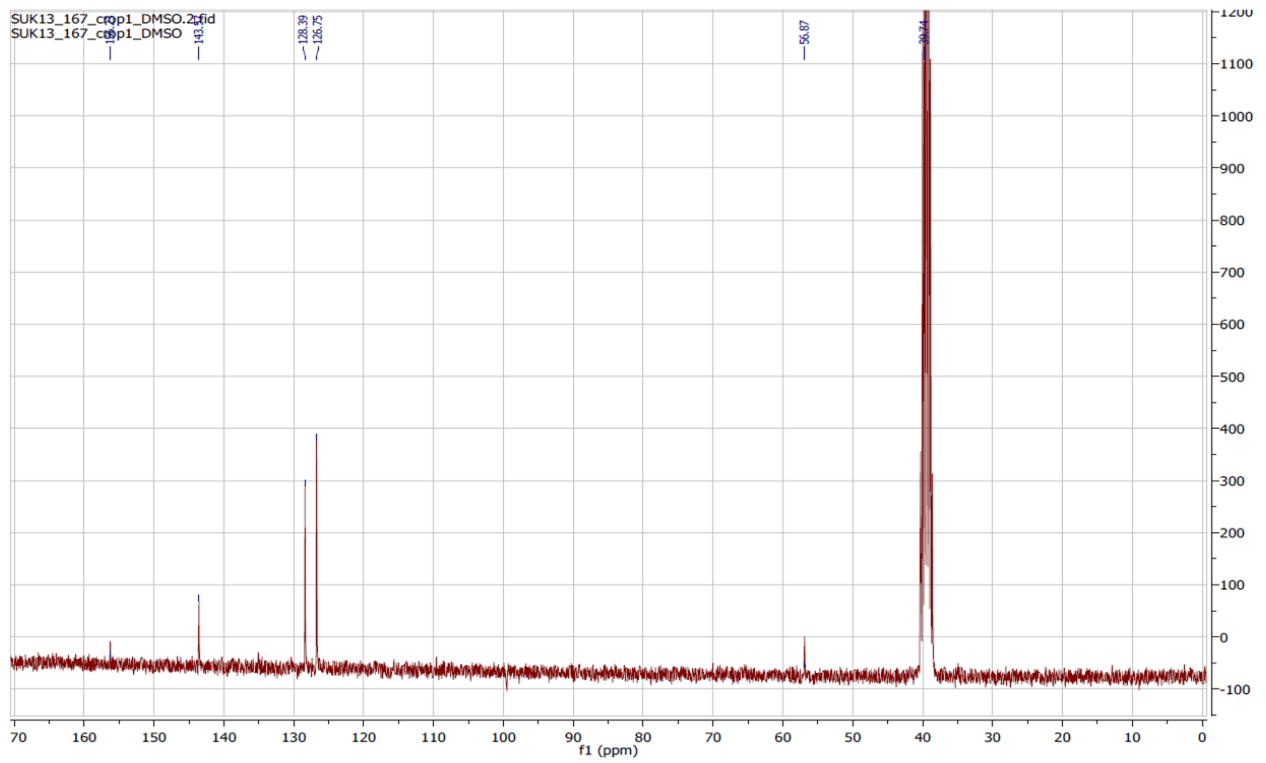
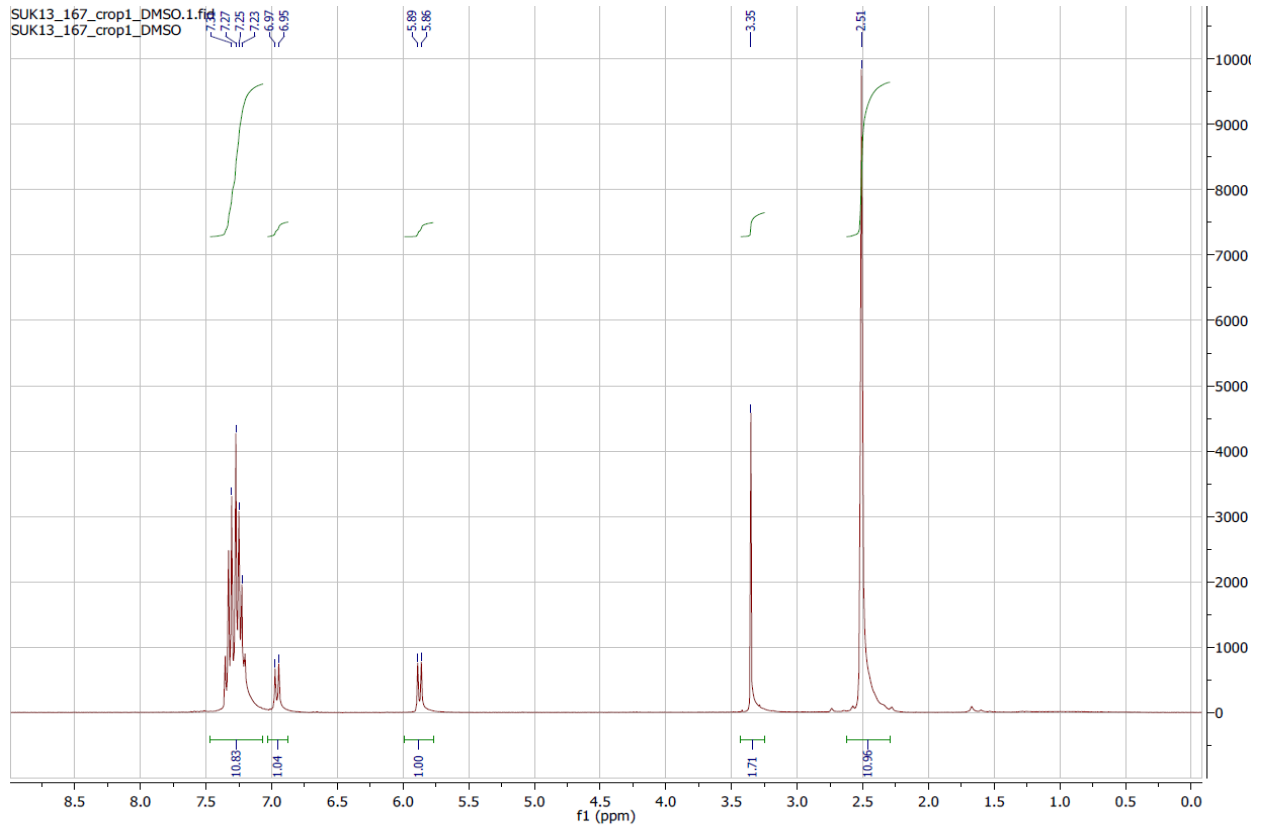
N,N'-bis-(3-(trifluoromethyl)benzyl)urea 3f



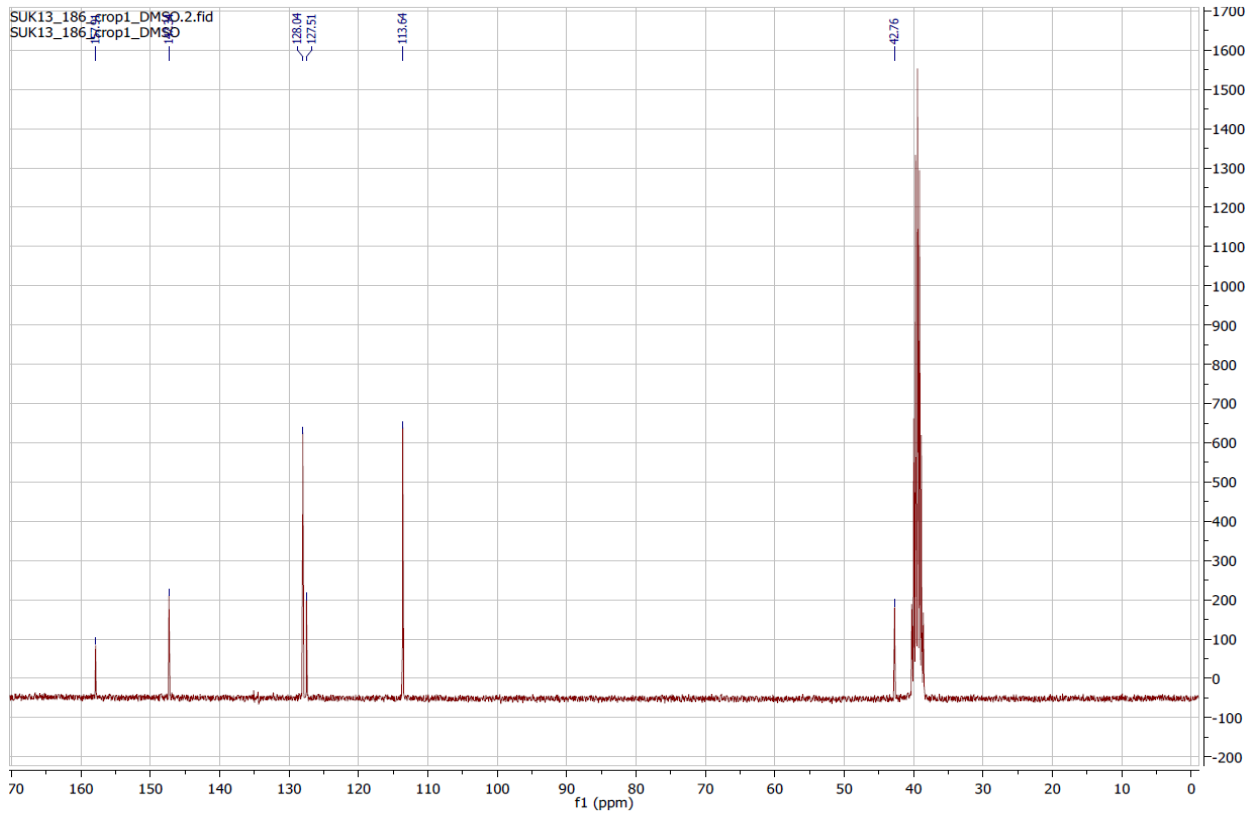
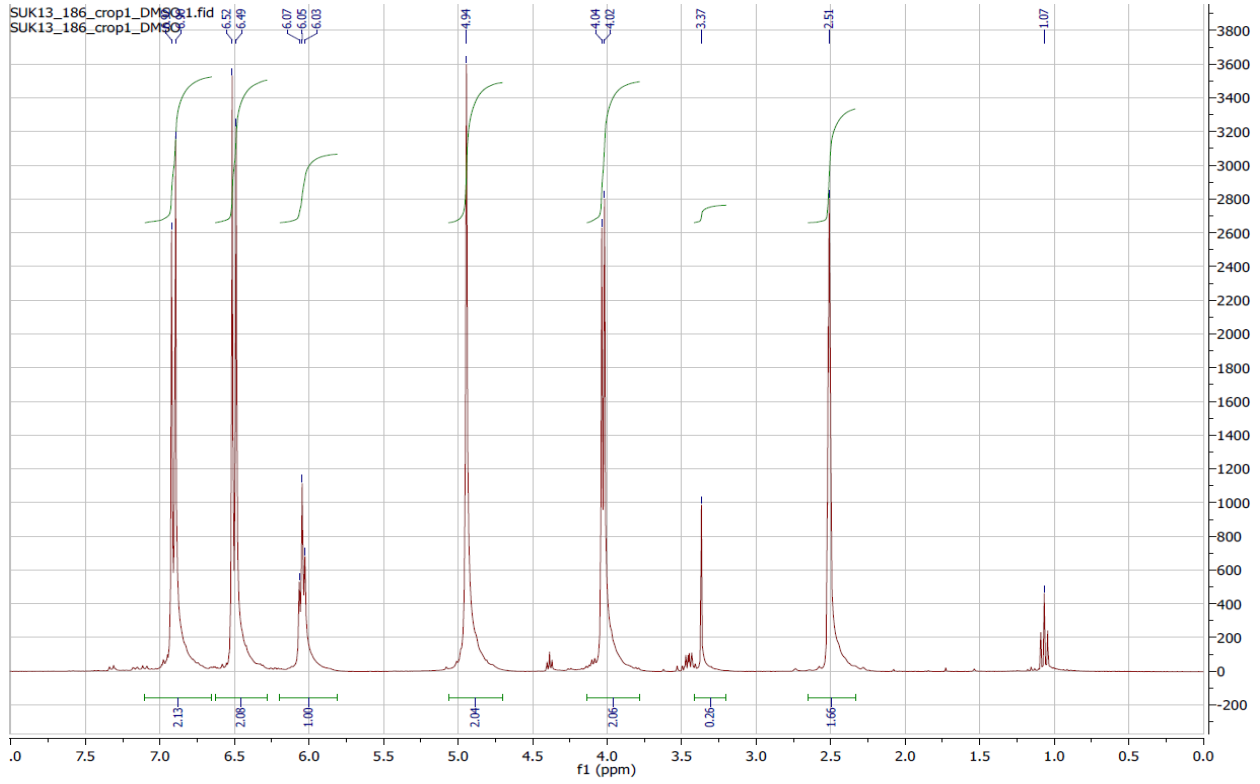
N,N'-bis-(4-(trifluoromethyl)benzyl)urea 3g



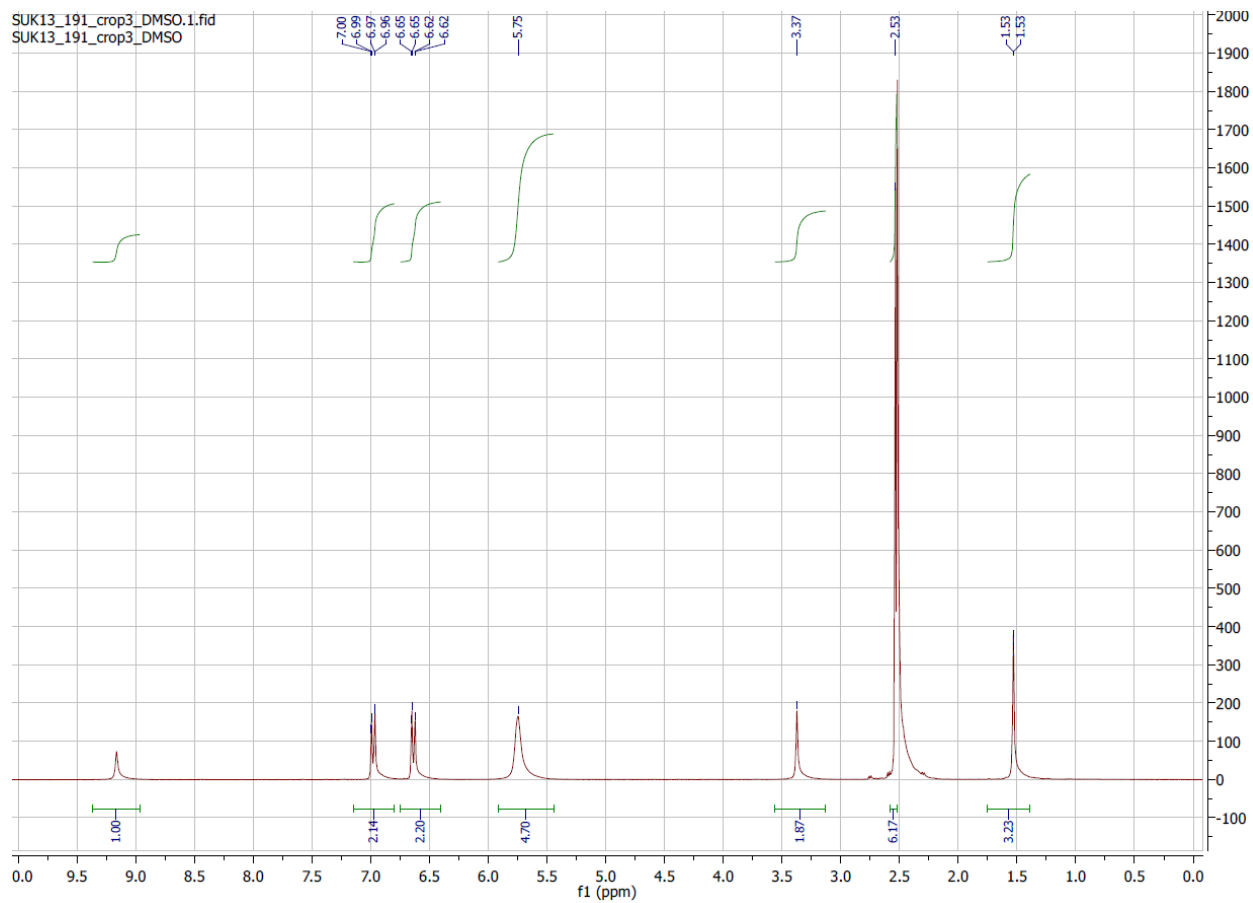
N,N'-dibenzhydrylurea 3h



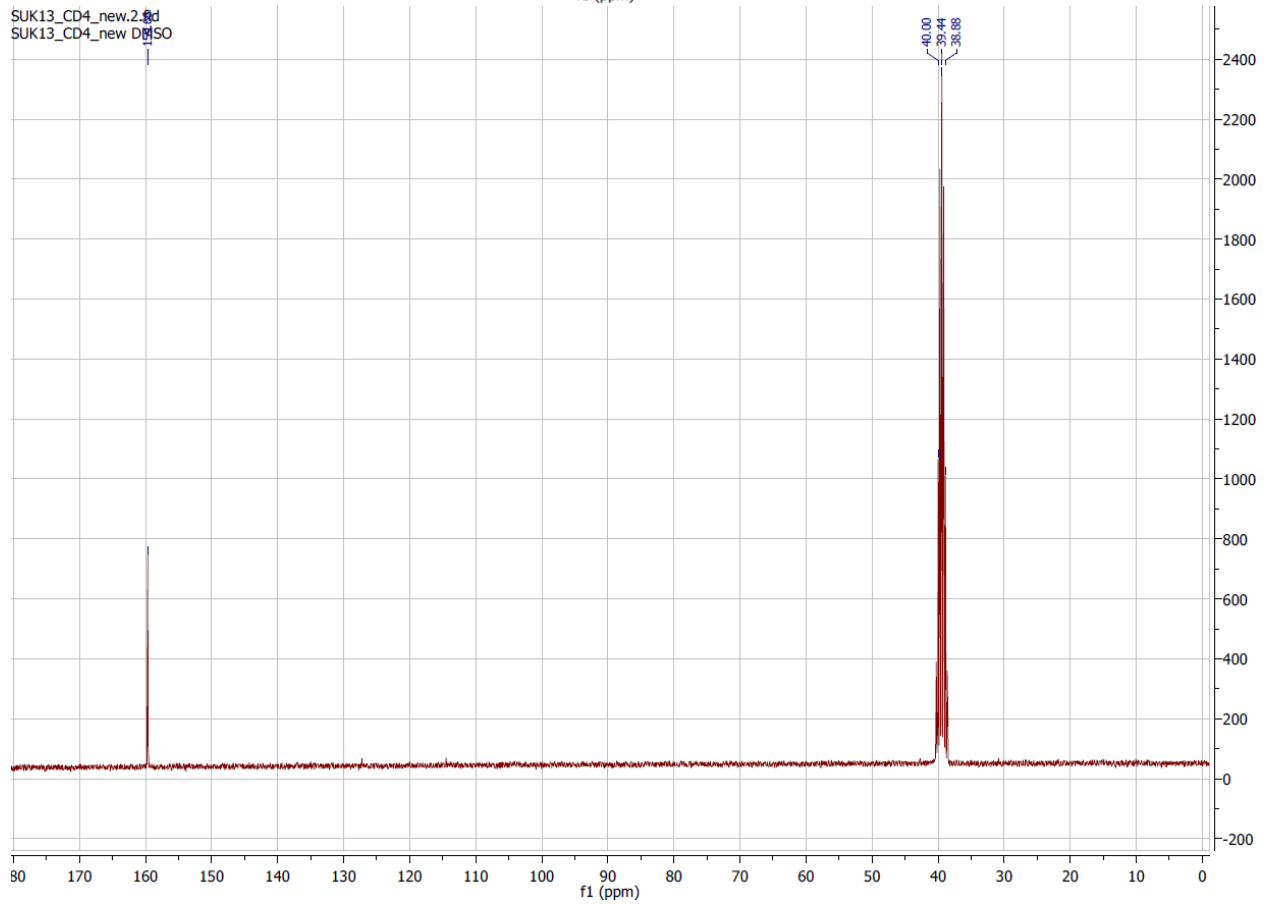
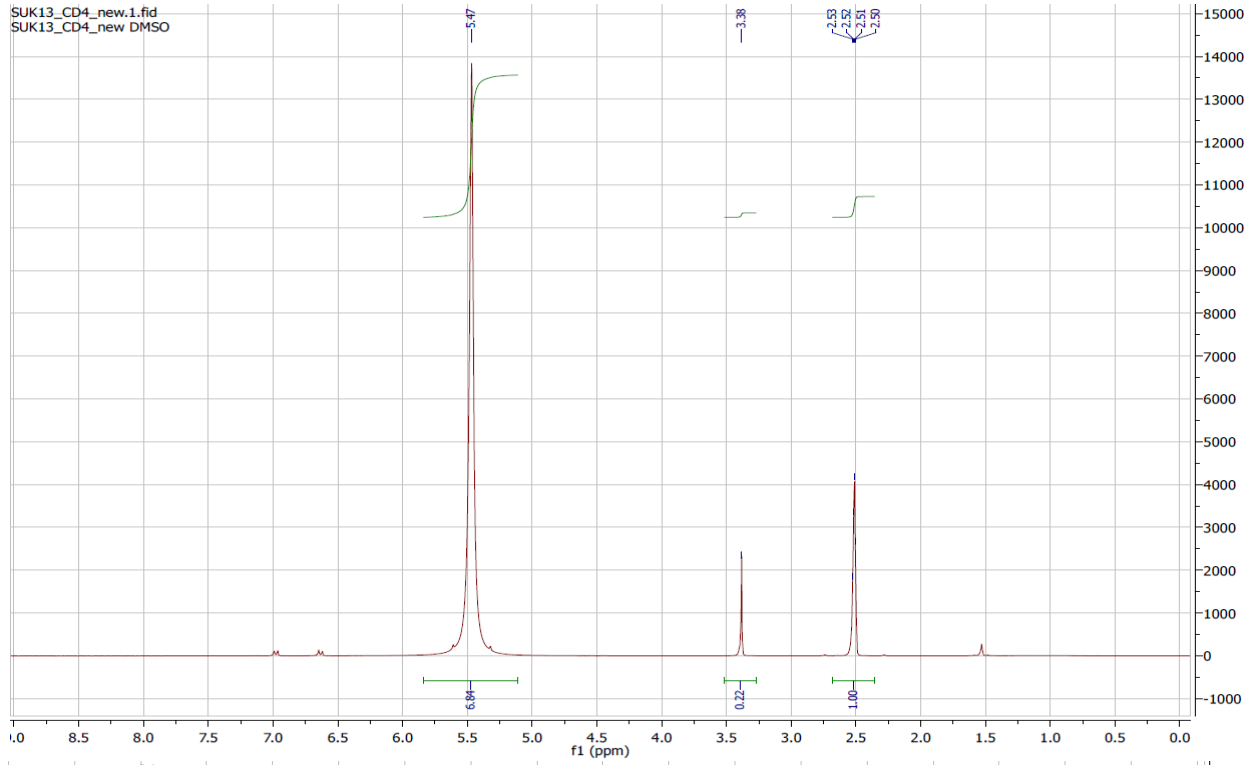
N,N'-bis-(4-aminobenzyl)urea 3j



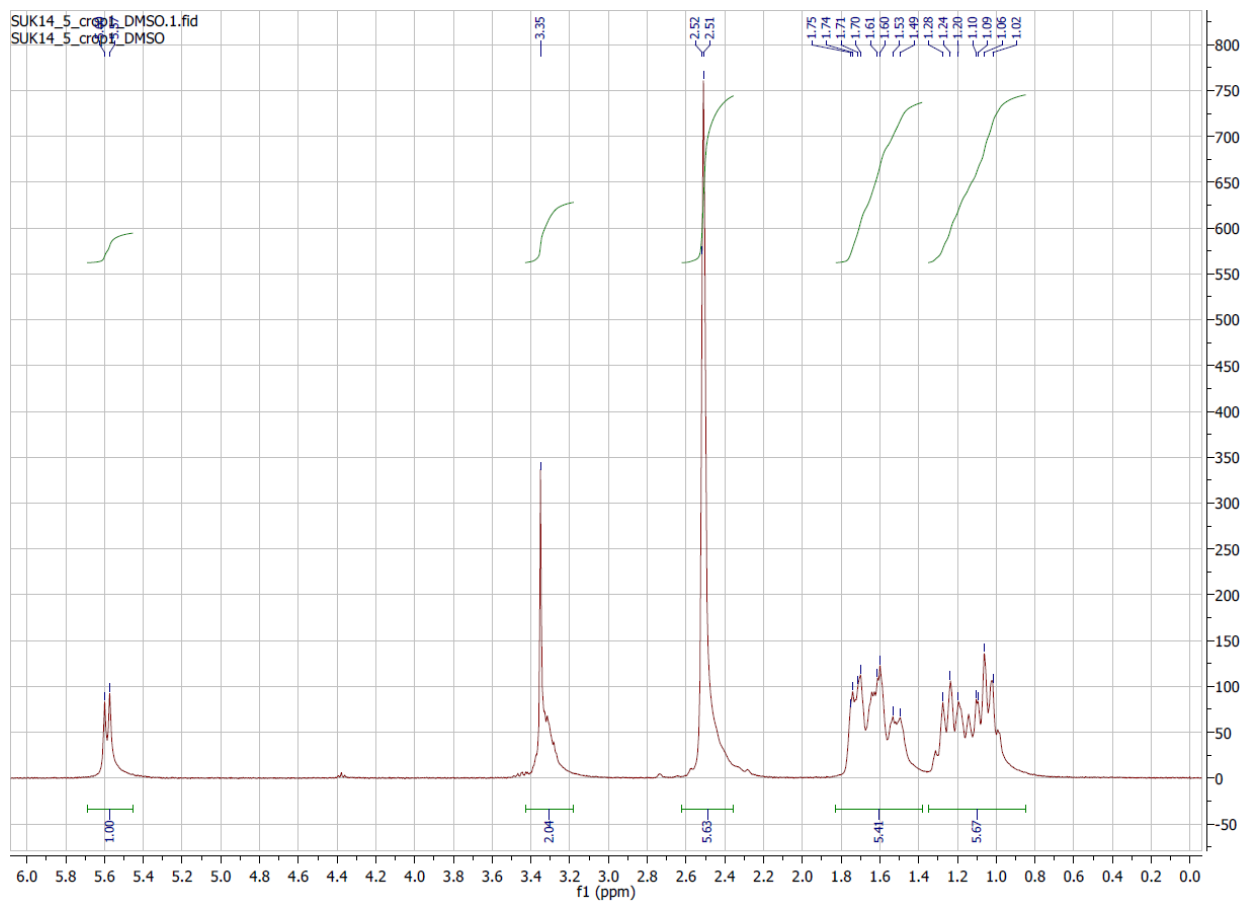
N,N'-dimethylurea + Bisphenol A mixture 3k



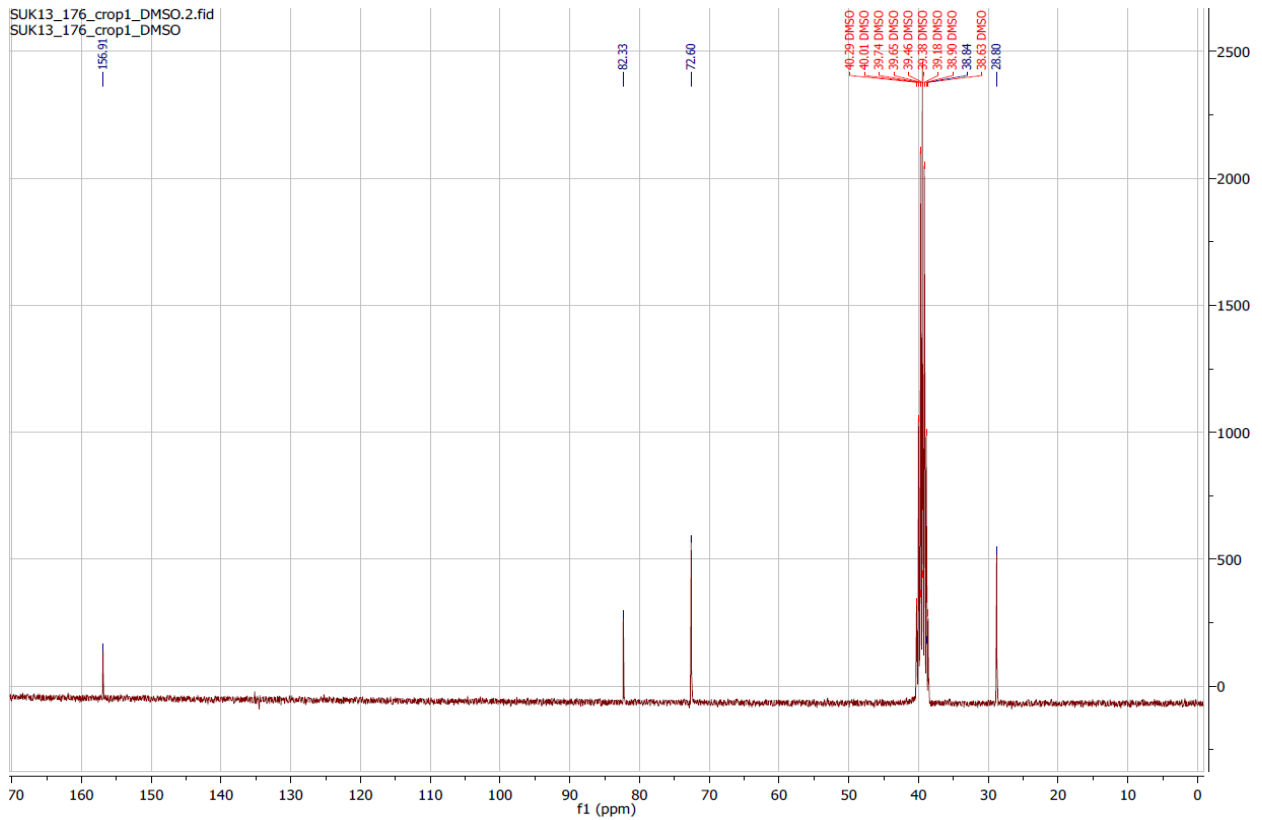
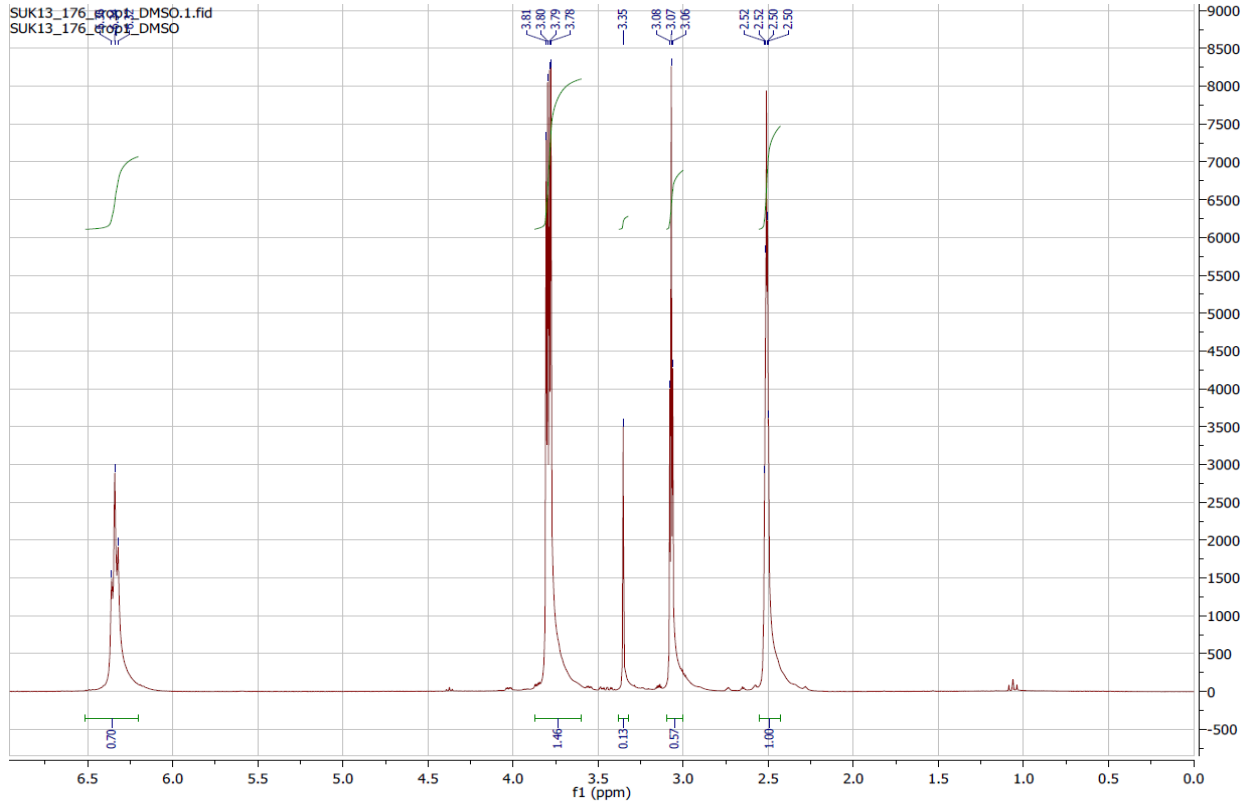
Urea 3I



N,N'-dicyclohexylurea 3n



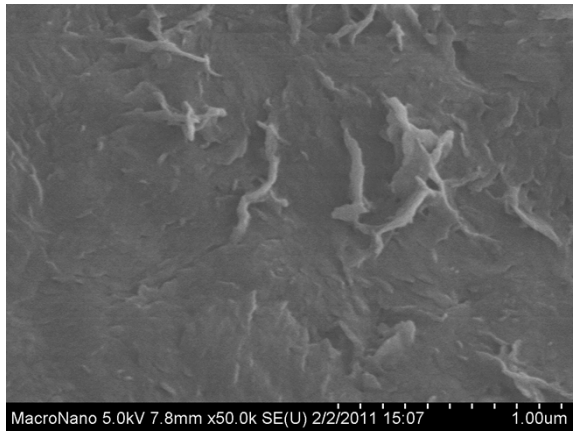
N,N'-dipropargylurea 3o



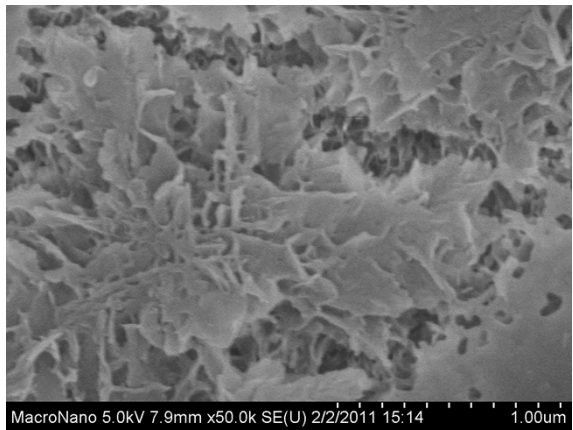
SEM Images



(A) Treatment of polycarbonate with 0.5% propargyl amine solution in ethanol



(B) Treatment of polycarbonate with 2% propargyl amine solution in ethanol



(C) Treatment of polycarbonate with 5% propargyl amine solution in ethanol

