Supporting Information

An efficient one-pot synthesis of $N,N'$-disubstituted urea and carbamates from $N$-Acylbenzotriazoles

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Table of Contents

1. $^1$H and $^{13}$C NMR spectrum of Aryl/alkyl-carbonylbenzotriazole (RCOBt, 2a-q) S2
2. $^1$H and $^{13}$C NMR spectrum of Carbamate (3a-t) & 4 S36
3. $^1$H and $^{13}$C NMR spectrum of Thiocarbamte (5a-b) S78
4. $^1$H and $^{13}$C NMR spectrum of urea (6a-g) S82
5. $^1$H and $^{13}$C NMR spectrum of azide (7b) S96
6. $^1$H and $^{13}$C NMR spectrum of triazoles (8a-c) S99
7. Single Crystal X-Ray data and structure of compounds 6a & 4. S104
1. $^1$H and $^{13}$C NMR Spectrum of Aryl/alkyl-carbonylbenzotriazole (RCOBt, 2a-p).
Spectrum 2: 75 MHz $^{13}$C NMR of compound 2a
Spectrum 3: 300 MHz $^1$H NMR of compound 2b
Spectrum 4: 75 MHz $^{13}$C NMR of compound 2b
Supplementary Information

Spectrum 5: 300 MHz $^1H$ NMR of compound 2c
Spectrum 6: 75 MHz $^{13}$C NMR of compound 2c
**Spectrum 7:** 300 MHz $^1$H NMR of compound 2d
Spectrum 8: 75 MHz $^{13}$C NMR of compound 2d
Spectrum 9: 300 MHz $^1$H NMR of compound 2e
Spectrum 10: 75 MHz $^{13}$C NMR of compound 2e
Spectrum 11: 300 MHz $^1$H NMR of compound 2f
Spectrum 12: 75 MHz $^{13}$C NMR of compound 2f
Spectrum 13: 300 MHz $^1$H NMR of compound 2g
Supplementary Information

Spectrum 14: 75 MHz $^{13}$C NMR of compound 2g
Spectrum 15: 300 MHz $^1$H NMR of compound 2h
Spectrum 16: 75 MHz $^{13}$C NMR of compound 2h
Spectrum 17: 300 MHz $^1$H NMR of compound 2i
Spectrum 18: 75 MHz $^{13}$C NMR of compound 2i
Spectrum 19: 300 MHz $^1$H NMR of compound 2j
Spectrum 20: 75 MHz $^{13}$C NMR of compound 2j
Spectrum 21: 300 MHz $^1$H NMR of compound 2k
Spectrum 22: 75 MHz $^{13}$C NMR of compound 2k
Spectrum 23: 300 MHz $^1$H NMR of compound 21
Spectrum 24: 75 MHz $^{13}$C NMR of compound 2l
Spectrum 25: 300 MHz $^1$H NMR of compound 2m
Spectrum 26: 75 MHz $^{13}$C NMR of compound 2m
Spectrum 27: 300 MHz $^1$H NMR of compound 2n
Spectrum 28: 75 MHz $^{13}$C NMR of compound 2n
Spectrum 29: 300 MHz $^1$H NMR of compound 2o
Spectrum 30: 75 MHz $^{13}$C NMR of compound 2o
Spectrum 31: 300 MHz $^1$H NMR of compound $2p$
Spectrum 32: 75 MHz $^{13}$C NMR of compound 2p
Spectrum 33: 300 MHz $^1$H NMR of compound 2q
Spectrum 34: 75 MHz $^{13}$C NMR of compound 2q
2. $^1$H and $^{13}$C NMR spectrum of Carbamates (3a-t).

**Spectrum 35:** 300 MHz $^1$H NMR of compound 3a
Spectrum 36: 75 MHz $^{13}$C NMR of compound 3a
Spectrum 37: 300 MHz $^1$H NMR of compound 3b
Spectrum 38: 75 MHz $^{13}$C NMR of compound 3b
Spectrum 39: 300 MHz $^1$H NMR of compound 3c
Spectrum 40: 75 MHz $^{13}$C NMR of compound 3c
Spectrum 41: 300 MHz $^1$H NMR of compound 3d
Spectrum 42: 75 MHz $^{13}$C NMR of compound 3d
Spectrum 43: 300 MHz $^1$H NMR of compound 3e
Spectrum 44: 75 MHz $^{13}$C NMR of compound 3e
Spectrum 45: 300 MHz $^1$H NMR of compound 3f
Spectrum 46: 75 MHz $^{13}$C NMR of compound 3f
**Spectrum 47: 300 MHz $^1$H NMR of compound 3g**

The spectrum shows the NMR signals for the compound 3g at 300 MHz. The peaks are labeled with their corresponding chemical shifts and assignments. The compound structure is also shown, indicating the presence of a phenyl group, an acetamide group, and an ethyl group (Et).
Spectrum 48: 75 MHz $^{13}$C NMR of compound 3g
Spectrum 49: 300 MHz $^1$H NMR of compound 3h
Spectrum 50: 75 MHz $^{13}$C NMR of compound 3h
Spectrum 51: 300 MHz $^1$H NMR of compound 3i
Spectrum 52: 75 MHz $^{13}$C NMR of compound 3i
Spectrum 53: 300 MHz $^1$H NMR of compound 3j
Spectrum 54: 75 MHz $^{13}$C NMR of compound 3j
Spectrum 55: 300 MHz $^1$H NMR of compound 3k
Spectrum 56: 75 MHz $^{13}$C NMR of compound 3k
Spectrum 57: 300 MHz $^1$H NMR of compound 3l
**Spectrum 58**: 75 MHz $^{13}$C NMR of compound 31
Spectrum 59: 300 MHz $^1$H NMR of compound 3m
Spectrum 60: 75 MHz $^{13}$C NMR of compound 3m
Spectrum 61: 300 MHz $^1$H NMR of compound 3n
**Spectrum 62: 75 MHz $^{13}$C NMR of compound 3n**
**Spectrum 63**: 300 MHz $^1$H NMR of compound 3o
Spectrum 64: 75 MHz $^{13}$C NMR of compound 30
Spectrum 65: 300 MHz $^1$H NMR of compound 3p
Spectrum 66: 75 MHz $^{13}$C NMR of compound 3p
Spectrum 67: 300 MHz $^1$H NMR of compound 3q
Spectrum 68: 75 MHz $^{13}$C NMR of compound 3q
Spectrum 69: 300 MHz $^1$H NMR of compound 3r
Spectrum 70: 75 MHz $^{13}$C NMR of compound 3r
Spectrum 71: 500 MHz $^1$H NMR of compound 3s
Spectrum 72: 125 MHz $^{13}$C NMR of compound 3s
Spectrum 73: 500 MHz $^1$H NMR of compound 3t
Spectrum 74: 125 MHz $^{13}$C NMR of compound 3t
3. $^1$H and $^{13}$C NMR spectrum of compound 4

*Spectrum 75: 300 MHz $^1$H NMR of compound 4*
Spectrum 76: 75 MHz $^{13}$C NMR of compound 4
4. $^1$H and $^{13}$C NMR spectrum of thiocarbamates (5a-g)

**Spectrum 77: 500 MHz $^1$H NMR of compound 5a**
Spectrum 78: 125 MHz $^{13}$C NMR of compound 5a
Spectrum 79: 500 MHz $^1$H NMR of compound 5b
Spectrum 80: 125 MHz $^{13}$C NMR of compound 5b
5. $^1$H and $^{13}$C NMR spectrum of urea (6a-g)
Supplementary Information

Spectrum 82: 75 MHz $^{13}$C NMR of compound 6a
Spectrum 83: 300 MHz $^1$H NMR of compound 6b
Spectrum 84: 75 MHz $^{13}$C NMR of compound 6b
Spectrum 85: 300 MHz $^1$H NMR of compound 6c
Supplementary Information

Spectrum 86: 75 MHz $^{13}$C NMR of compound 6c
Spectrum 87: 300 MHz $^1$H NMR of compound 6d
Spectrum 88: 75 MHz $^{13}$C NMR of compound 6d
Spectrum 89: 300 MHz $^1$H NMR of compound 6e
Spectrum 90: 75 MHz $^{13}$C NMR of compound 6e
Spectrum 91: 300 MHz $^1$H NMR of compound 6f
Spectrum 92: 75 MHz $^{13}$C NMR of compound 6f
Spectrum 93: 300 MHz $^1$H NMR of compound 6g
Spectrum 94: 75 MHz $^{13}$C NMR of compound 6g

Ammonia gas was passed for 3 h into a stirring solution of glycosyl-β-olefinic ester (10.0 g, 0.028 mol) in dry ethanol (100 ml). The mixture was stirred at room temperature. After 12 hours a diastereomeric mixture of ethyl-[5-amino-3-O-benzyl-5,6-dideoxy-1,2-O-isopropylidene]-α-D-gluco- and β-L-ido-heptofuranurate was obtained as colourless oil (9.42 g, 90% yield). To this mixture imidazole-1-sulphonyl azide (5.34 g, 0.030 mol), K$_2$CO$_3$ (7.12 g, 0.050 mol) and ZnCl$_2$ (5 mol%) were added and allowed to stir for 5 hours at room temperature 5 hrs. Purification by flash chromatography afforded glycosyl-β-azido ester 7b as major product. White crystals, mp 82-84°C; yield 60%; $R_f$= 0.52 (10% ethyl acetate/n-hexane); MS: $m/z$ 392 [M+H]$^+$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.35 (m, 5H), 5.87 (d, $J$ = 3.0 Hz, 1H), 4.69-4.62 (m, 3H), 4.28 (dd, $J$ = 9.9, 19.2 Hz, 1H), 4.18 (q, $J$ = 6.9 Hz, 2H), 4.06 (m, 1H), 3.99 (d, $J$ = 9.6 Hz, 1H), 2.90 (d, $J$ = 16.5 Hz, 1H), 2.46 (dd, $J$ = 10.2, 16.8 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H), 1.27 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.8, 136.9, 128.4 (2C), 128.0, 127.9 (2C), 111.9, 105.1, 81.8, 81.4, 80.8, 71.9, 60.7, 56.5, 37.4, 26.8, 26.1, 14.0 ppm; IR (KBr) $\nu_{max}$: 2980, 2933, 2134 (azide- N$_3$), 2906, 1742 (C=O), 1465, 1399, 1081, 1037, 731 cm$^{-1}$. 

\[ \text{OEt} \quad \text{NH}_3 \text{(g), ethanol, 24 h then ZnCl}_2\text{, } \text{K}_2\text{CO}_3\text{, 5 h, RT} \]

\[
\begin{array}{c}
\text{Major Isomer}
\end{array}
\]
6. $^1$H and $^{13}$C NMR spectrum of glycosyl-$\beta$-azido ester 7b

Spectrum 95: 300 MHz $^1$H NMR of compound 7b
Spectrum 96: 75 MHz $^{13}$C NMR of compound 7b
7. $^1$H and $^{13}$C NMR spectrum of triazoles (8a-c)

Spectrum 97: 300 MHz $^1$H NMR of compound 8a
Spectrum 98: 75 MHz $^{13}$C NMR of compound 8a
Spectrum 99: 300 MHz $^1$H NMR of compound 8b
Spectrum 100: 75 MHz $^{13}$C NMR of compound 8b
Spectrum 101: 300 MHz $^1$H NMR of compound 8c
Spectrum 102: 75 MHz $^{13}$C NMR of compound 8c

Data Collection and Refinement

Single-crystal X-ray data of compound 6a were collected on Xcalibur Eos (Oxford) CCD-Diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). The data integration and reduction were processed with CrysAlis Pro software. Data of compound 4 was collected on Bruker SMART CCD-Diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by the direct method and then refined on $F^2$ by the full matrix least-squares technique with the SHELX-97 set of software using the WinGX (version 1.80.05) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software. Further information on the crystal structure (excluding structure factors) has been given in table 1-5 (Supporting Information) and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications numbers 1482293 (6a) and 1482294 (4). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

Procedure for crystallization of compound 6a and 4

For crystallization a mixture of ethyl acetate and hexane (2:8) has been used and kept in dark place at temperature 25 °C. The single crystal appeared after three days was isolated in its initial state of growth.
**Selected bond length (Å):** O1-C7 1.230(3), N1-C8 1.406(4), N1-C7 1.367(4), N1-HN1 0.86(3), N2-C1 1.421(4), N2-C7 1.342(4), N2-HN2 0.87(3);  
**Selected bond angles:** C8 N1 C7 125.4(3), C8 N1 HN1 116(2), C7 N1 HN1 116(2), N1 C8 C13 118.7(3), N1 C8 C9 123.0(3), C1 N2 C7 126.2(3), C1 N2 HN2 121(2), C7 N2 HN2 113(2), N2 C1 C6 118.7(3), N2 C1 C2 120.9(3), O1 C7 N1 121.6(3), O1 C7 N2 124.0(3), N1 C7 N2 114.4(3)

**Figure S1.** Molecular structure of compound 6a. Thermal ellipsoids of carbon, nitrogen, sulfur and oxygen are set at 40% probability.
### Table S1. Crystallographic refinement data for compound 6a

<table>
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<th><strong>Compound 6a</strong></th>
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<td>Formula Weight</td>
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<td>Crystal System</td>
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<td>$a$ (Å)</td>
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<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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<td>$V$ (Å$^3$)</td>
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<td>$Z$</td>
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<td>Density (calc)</td>
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<td>$\mu$ (mm$^{-1}$)</td>
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<td>Crystal Size [mm]</td>
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<td>Temperature (K)</td>
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<td>Radiation</td>
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<td>$\theta$ Min-Max [°]</td>
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<td>Tot., UniqData, R(int)</td>
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<td>R1, wR2, S</td>
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<td>Min. - Max. resid. dens. [e/ Å$^3$]</td>
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Selected bond length (Å): O1-C1 1.380(2), O1-C4 1.369(2), N1-H1 0.860(1), N1-C2 1.385(2), N1-C4 1.347(2), O2-C4 1.206(2); Selected bond angles (°): C1 O1 C4 107.0(1), H1 N1 C2 125.1(1), H1 N1 C4 125.1(1), C2 N1 C4 109.8(1), O1 C1 C2 109.3(1), O1 C1 C6 127.5(1), N1 C2 C1 105.5(1), N1 C2 C3 133.7(1), O1 C4 N1 108.2(1), O1 C4 O2 121.7(1), N1 C4 O2 130.1(2)

Figure S2. Molecular structure of compound 4. Thermal ellipsoids of carbon, nitrogen and iron are set at 40 % probability.
**Table S2. Crystallographic refinement data for compound 4**

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<td><strong>Formula Weight</strong></td>
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<td><strong>Space group</strong></td>
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<td><strong>c (Å)</strong></td>
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<td><strong>µ (mm&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
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<tr>
<td><strong>Crystal Size [mm]</strong></td>
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<tr>
<td><strong>Temperature (K)</strong></td>
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<tr>
<td><strong>Radiation</strong></td>
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<tr>
<td><strong>θ Min-Max [°]</strong></td>
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