#### Snehal A. Chavan\*, Avinash G. Ulhe and Baliram N. Berad

# Synthesis and characterization of *N*-glucosylated dithiadiazepine derivatives through carbon-sulfur bond formation

#### DOI 10.1515/hc-2015-0093

Received May 22, 2015; accepted June 8, 2015; previously published online September 16, 2015

**Abstract:** New 4,7-bis(arylamino)-2-tetra-O-acetyl- $\beta$ -D-glucopyranosylimino-1,3,5,6-dithiadiazepines were synthesized via reaction of *N*-tetra-O-acetyl- $\beta$ -D-glucopyranosyl isocyanodichloride with 1,6-diaryl-2,5-dithio-bis-ureas without using any catalyst. Thus, the synthesis of 7-membered heterocycles containing two sulfur and two nitrogen atoms through carbon-sulfur bond formation was explored. The chemical structures of these new compounds were elucidated by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectral, and elemental analyses.

**Keywords:** carbon-sulfur bond; dithiadiazepine; dithiobis-urea; glucopyranosyl isocyanodichloride.

#### Introduction

Heterocyclic ring systems that contain nitrogen and sulfur atoms are important scaffolds in medicinal chemistry [1–7]. Diazepines are seven-membered heterocyclic compounds with two nitrogen atoms. Such molecules possess a wide range of medicinal properties [8]. Substitution of the diazepine segment in the bioactive molecule often leads to improvement of pharmacological activities [9]. Some of 1,2-diazepine derivatives are used in the treatment of epilepsy, malignant gliomas, and amyotrophic lateral sclerosis [10–12]. Synthesis, ESR, and X-ray diffraction studies of 1,4,5,7-dithiadiazepine and 1,6,2,4-dithiadiazepine derivatives have been reported [13–15]. Although extensive synthetic studies have been published for various thiadiazepines [16–18], to our best knowledge, not much work has been reported for the synthesis of 1,3,5,6-dithiadiazepines.

Carbohydrates play a vital role in numerous biological processes including modification of proteins, molecular recognition, and immune response [19]. Carbohydrates are an important moiety in many natural antibiotics including bleomycin, neocarzinostatin, and other DNAtargeting drugs [20]. Introduction of carbohydrates into synthetic drugs leads to new hybrid molecules of considerable interest. For example, high levels of glucosylation imparts molecular changes that accompany malignant transformations, which is characteristic of cancer cells [21]. The carbohydrate moiety can be expected to act as drug carrier and improve the selectivity of compounds for cancerous cell lines.

In view of the biological importance of diazepine derivatives [22–24] and in continuation of our work on the synthesis of *N*-glucosylated heterocyclic compounds [25–28], *N*-glucosylated dithiadiazepine derivatives have been synthesized through the formation of carbon-sulfur bonds. The current study aims at the synthesis of new *N*-glucosylated dithiadiazepine derivatives, which are uncommon 7-membered heterocycles.

#### **Results and discussion**

1,6-Diaryl-2,5-dithio-bis-ureas **2a–e** have been synthesized by reacting two equivalents of aryl isothiocyanates **1a–e** with one equivalent of hydrazine hydrate at ambient temperature [29, 30]. The IR spectrum of **2c** shows an absorption band at 3210 cm<sup>-1</sup>, which indicates the presence of the NH functional group. The absence of an absorption band at 2800 cm<sup>-1</sup> and presence of an absorption band at 628 cm<sup>-1</sup> for C=S indicated that the symmetric dithio-bis-ureas **2a–e** exist in the thione tautomeric form. Further support for this structural feature comes from analysis of the <sup>1</sup>H NMR spectrum of **2c**, which does not show a peak attributable to the SH group [31] but shows a peak in the low field region at  $\delta$  9.60 for four NH protons [32]. Three signals

<sup>\*</sup>Corresponding author: Snehal A. Chavan, Department of Chemistry, Mahatma Jyotiba Phule Educational Campus, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440033, India, e-mail: i\_snehal123@yahoo.com

Avinash G. Ulhe and Baliram N. Berad: Department of Chemistry, Mahatma Jyotiba Phule Educational Campus, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440033, India

at  $\delta$  7.37, 7.20, and 6.96 belong to eight aromatic protons. The signal in the upfield region at  $\delta$  2.33 is attributed to the methyl protons.

The symmetrical dithio-bis-ureas **2a–e** were then allowed to react with *N*-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl isocyanodichloride **(4)** in a mixture of CHCl<sub>3</sub>-DMF (1:1) under reflux conditions to yield hydrochloride salts of 4,7-bis(arylamino)-2-tetra-*O*-acetyl- $\beta$ -D-glucopyranosylimino-1,3,5,6dithiadiazepines **5a–e**, as depicted in Scheme 1. During the intermolecular cyclocondensation reaction, evolution of the hydrogen chloride gas was clearly noticed by testing with moist blue litmus paper. The final compounds **5a–e** were found to be in the salt forms, which, upon treatment with saturated solution of sodium bicarbonate, were transformed into free bases **6a–e**. Formation of these products may be rationalized by the mechanism shown in Scheme 2.

For optimization of the cyclocondensation reaction, the preparation of **6a** was carried out in different solvents including CHCl<sub>3</sub>, DCM, a mixture of CHCl<sub>3</sub>-DMF, and DMF under reflux condition. The time needed for completion of the reaction varied from 5 to 10 h. The effect of solvent on the reaction time and product yield was observed. The yield of **6a** was found to increase significantly when the reaction was carried out in the 1:1 CHCl<sub>3</sub>-DMF mixture. The reaction conducted in other solvents gave the desired

product **6a** in a very low yield. The optimized solvent was used for the conversion of **2b–e** to **6b–e**.

Detailed analyses of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectra of compounds 6a-e were fully consistent with the given structures. The IR spectra of compounds 6a-e show two strong bands in the ranges of 3300-3100 cm<sup>-1</sup> and 1742–1753 cm<sup>-1</sup> due to the N-H and ester carbonyl stretching, respectively. The <sup>1</sup>H NMR spectra show a multiplet due to the glucosyl ring protons in the range of  $\delta$  5.35–3.83 ppm and a characteristic triplet or doublet for anomeric proton (H.) of the glucose moiety within the region of  $\delta$  5.30–5.40. Coupling constant (J) of H1/H2 within the range of 12.3– 9.3 Hz indicates that the glucosyl moiety exists as the  $\beta$ anomer [33]. The acetyl protons of the glucosyl moiety resonate as a multiplet within  $\delta$  2.06–1.83. In addition, the <sup>1</sup>H NMR spectra of compounds **6a-e** exhibit a broad singlet centered at  $\delta$  9.70 for the NH-aryl functionality. The aromatic protons also appear in the expected region as are other protons of the substituents. The <sup>13</sup>C NMR spectra of compounds **6a–e** show numbers of signals that are fully consistent with the number of carbon atoms in the molecules. The signal for  $\beta$  anomeric carbon is observed within the range of  $\delta$  83.50–84.06. The mass spectra of compounds **6a–e** show ion peaks  $[M+1]^+$  and the characteristic fragment ion peaks at 169, 331, and 413 for the glucosyl moiety.



Scheme 1 Synthetic route for the synthesis of compounds 6a-e from symmetrical dithio-bis-ureas (2a-e).



Scheme 2 Plausible mechanism for the formation of compound 6 through C-S bond formation.

#### Conclusions

We achieved the synthesis of 1,3,5,6-dithiadiazepine derivatives **6a–e** having glucosyl residue through a C-S bond formation in an efficient manner. The overall conversion was carried out in three steps in good yields.

### **Experimental**

Melting points were measured using an electro-thermal apparatus and are not corrected. FT-IR spectra were recorded using KBr disks on a Perkin Elmer FT-IR spectrophotometer. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (400 MHz) spectra were recorded on a Brucker Avance II 400 NMR spectrometer. Electron-impact mass spectra were obtained at an ionizing potential of 70eV. Optical rotations were measured using an Equip-Tronics Digital Polarimeter EQ-801. Purity of compounds was checked by thin layer chromatography, which was performed on aluminum sheet Silica Gel 60  $F_{254}$  (Merck). The spots were visualized by exposure to UV light and iodine vapor.

1,6-Diaryl-2,5-dithio-bis-ureas **2a–e** were synthesized by the previously described method and exhibited virtually identical physical properties as reported in the literature [29–31]. *N*-Tetra-*O*-acetyl- $\beta$ -Dglucopyranosyl isocyanodichloride **(4)** was synthesized by excessive chlorination of *N*-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate **(3)** using the previously reported method [25, 26].

## Synthesis of 4,7-bis(arylamino)-2-tetra-*O*-acetyl-β-D-glucopyranosylimino-1,3,5,6-dithiadiazepines 6a–e

*N*-Tetra-*O*-acetyl-β-D-glucopyranosyl isocyanodichloride (**4**, 0.43 g, 1.0 mmol) was added to a stirred solution of **2a–e** (1.0 mmol) in a mixed solvent of CHCl<sub>3</sub>-DMF (1:1) and the mixture was heated under reflux for 5 h. The evolution of hydrogen chloride gas was observed with moist blue litmus paper. Progress of the reaction was monitored by TLC analysis. The mixture was cooled and diluted with dichloromethane. The organic layer was washed with water and dried with anhydrous sodium sulfate. The organic layer was evaporated under reduced pressure to afford a salt form of the product **5a–e**. The crude product **5a–e** was triturated with aqueous saturated solution of sodium bicarbonate for 10 min. The free base **6a–e** was extracted with ethyl acetate. The extract was dried with anhydrous sodium sulfate and concentrated under reduced pressure to afford a free base **6a–e** as a creamy solid, which was crystallized from CHCl<sub>3</sub>-petroleum ether.

**4,7-Bis(phenylamino)-2-tetra-O-acetyl-β-D-glucopyranosylimino-1,3,5,6-dithiadiazepine (6a)** The free base was obtained in 81% yield; mp 140°C;  $[\alpha]_{D}^{25}+200°$  (*c* 0.1, EtOH);  $R_f$  0.50 (50% EtOAc-hexane); IR:  $v_{max}$  3462 (N-H), 1743 (O=C-O), 1601 (C=N), 1380 (C-N), 744 cm<sup>-1</sup> (C-S); <sup>1</sup>H NMR (DMSO- $d_o$ ): δ 9.73 (s, 2H, 2×NH), 7.62–6.89 (m, 10H, ArH), 5.33 (t, J = 12.3 Hz, 1H,  $H_1$ ), 5.38–3.97 (m, 7H,  $H_{1-7}$ ), 2.07–1.93 (m, 12H, acetyl protons); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 170.9, 170.7, 170.0, 169.6, 137.1, 134.2, 130.1, 129.5, 129.3, 128.1, 128.0, 127.6, 127.4, 123.5, 123.3, 122.1, 83.9, 73.2, 72.8, 70.8, 7.18, 69.7, 20.7, 20.6; MS: m/z 658 [M+1]<sup>+</sup>. Anal. Calcd for  $C_{29}H_{31}N_5O_9S_2$ : C, 52.96; H, 4.75; N, 10.65; S, 9.75. Found: C, 52.72; H, 4.45; N, 10.54; S, 9.80.

**4**,7-**B**is(4-methylphenylamino)-2-tetra-*O*-acetyl-β-Dglucopyranosylimino-1,3,5,6-dithiadiazepine (6b) The free base was obtained in 79% yield; mp 110°C;  $[\alpha]_{D}^{25}$ +150° (*c* 0.1, EtOH); *R<sub>f</sub>* 0.52 (50% EtOAc-hexane); IR:  $v_{max}$  3460 (N-H), 1742 (O=C-O), 1607 (C=N), 1380 (C-N), 746 cm<sup>-1</sup> (C-S); <sup>1</sup>H NMR (DMSO-*d<sub>g</sub>*): δ 9.64 (s, 2H, NH), 747– 7.04 (m, 8H, ArH), 5.36 (d, *J* = 9.3 Hz, 1H, H<sub>1</sub>), 5.00–3.98 (m, 6H, H<sub>2–7</sub>), 2.26 (s, 6H, 2×CH<sub>3</sub>), 2.11–1.83 (12H, m, 4×CH<sub>3</sub>CO); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 169.7, 169.3, 169.0, 155.6, 138.8, 130.1, 129.6, 129.3, 129.1, 125.5, 117.6, 116.8, 89.0, 79.0, 78.7, 78.4, 72.6, 70.8, 21.1, 20.9, 20.4, 20.4, 20.3; MS: *m/z* 686 [M+1]<sup>+</sup>. Anal. Calcd for C<sub>31</sub>H<sub>35</sub>N<sub>5</sub>O<sub>9</sub>S<sub>2</sub>: C, 54.29; H, 5.14; N, 10.21; S, 9.35. Found: C, 54.15; H, 5.28; N, 10.09; S, 9.22.

**4**, **7**-**B** is (3-methylphenylamino)-2-tetra-*O*-acetyl-β-Dglucopyranosylimino-1,3,5,6-dithiadiazepine (6c) The free base was obtained in 73% yield;  $[\alpha]_{D}^{25}$ +50° (*c* 0.1, EtOH); mp 100°C; <sup>1</sup>H NMR (DMSO-*d<sub>e</sub>*): δ 9.70 (bs, 2H, 2×NH),743–6.73 (m, 8H, ArH), 5.38 (d, *J* = 9.28 Hz, 1H, H<sub>1</sub>), 5.33–3.99 (m, 6H, H<sub>2-7</sub>), 2.38 (s, 6H, 2×CH<sub>3</sub>), 2.15–1.97 (12H, m, 4×CH<sub>3</sub>CO); <sup>13</sup>C NMR (DMSO-*d<sub>e</sub>*) δ: 169.7, 169.2, 169.0, 155.7, 141.1, 138.0, 128.5, 122.6, 121.6, 117.8, 117.3, 114.0, 79.1, 78.8, 78.5, 21.3, 20.4, 20.39, 20.28; Anal. Calcd for C<sub>31</sub>H<sub>35</sub>N<sub>5</sub>O<sub>9</sub>S<sub>2</sub>: C, 54.29; H, 5.14; N, 10.21; S, 9.35. Found: C, 54.40; H, 4.98; N, 9.91; S, 9.55; IR: v<sub>max</sub> 3462 (N-H), 1742 (O=C-O), 1594 (C=N), 1380 (C-N), 774 cm<sup>-1</sup> (C-S); MS (*m/z*): 686 [M+1]<sup>-</sup>; *R<sub>f</sub>* 0.52 (50% EtOAc-hexane).

**4**,**7**-**Bis**(**4**-**methoxyphenylamino**)-**2**-**tetra**-**0**-**acetyl**-**β**-**D**-**glucopyranosylimino**-**1**,**3**,**5**,**6**-**dithiadiazepine** (**6d**) The free base was obtained in 75% yield; mp 115°C;  $[\alpha]_D^{25}$ +100° (*c* 0.1, EtOH);  $R_f$  0.56 (30% EtOAc-hexane); IR:  $v_{max}$  3393 (N-H), 1751 (O=C-O), 1604 (C=N), 1370 (C-N), 668 cm<sup>-1</sup> (C-S); <sup>1</sup>H NMR (DMSO- $d_6$ ) δ: 9.46 (s, 2H, 2×NH), 7.52–6.80 (m, 8H, ArH), 5.35–3.83 (m, 7H, H<sub>1-7</sub>), 3.73 (s, 6H, 2×OCH<sub>3</sub>), 2.06–1.93 (12H, m, 4×CH<sub>3</sub>CO); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 174.9, 174.4, 174.2, 161.8, 161.1, 159.0, 140.0, 137.1, 131.3, 124.3, 124.1, 123.6, 119.0, 118.6, 84.1, 83.7, 83.4, 78.3, 73.1, 60.2, 25.6, 25.5; MS: m/z 169, 331, 413. Anal. Calcd for C<sub>31</sub>H<sub>35</sub>N<sub>5</sub>O<sub>10</sub>S<sub>2</sub>: C, 51.87; H, 4.91; N, 9.76; S, 8.93. Found: C, 51.99; H, 4.66; N, 9.50; S, 9.08.

**4**, **7**-**B** is (2-chlorophenylamino)-2-tetra-*O*-acetyl-β-Dglucopyranosylimino-1,3,5,6-dithiadiazepine (6e) The free base was obtained in 95% yield; mp 83°C;  $[\alpha]_D^{25}$ +50° (*c* 0.1, EtOH); *R<sub>f</sub>* 0.55 (50% EtOAc-hexane); IR: v<sub>max</sub> 3461 (N-H), 1742 (O=C-O), 1592 (C=N), 1381 (C-N), 747 cm<sup>-1</sup> (C-S); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.96–6.98 (m, 8H, ArH), 5.35 (t, *J* = 9.5 Hz, 1H, H<sub>1</sub>), 5.14–3.85 (m, 6H, H<sub>2–7</sub>), 2.12–1.95 (12H, m, 4×CH<sub>3</sub>CO); <sup>13</sup>C NMR (DMSO-*d<sub>b</sub>*): δ169.7, 169.23, 169.0, 155.7, 141.1, 128.7, 128.3, 120.8, 116.7, 83.5, 78.5, 78.3, 70.5, 60.2, 20.4, 20.3, 20.2; MS: *m/z* 726 [M+1]<sup>+</sup>. Anal. Calcd for C<sub>29</sub>H<sub>29</sub>N<sub>5</sub>O<sub>9</sub>S<sub>2</sub>Cl<sub>2</sub>: C, 47.94; H, 4.02; N, 9.64; S, 8.83. Found: C, 47.59; H, 4.20; N, 9.86; S, 8.60.

**Acknowledgments:** The authors are thankful to Prof. H. D. Juneja, head, Post-Graduate Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, for providing necessary laboratory facilities. The authors are also grateful to the director of the Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh, for spectral analysis. S.A.C. is thankful to the Council of Scientific and Industrial Research [CSIR; 09/128(0086)/2012-EMR-I, June 22, 2012], New Delhi, and A.G.U. is thankful to the University Grants Commission (UGC), Delhi, for the financial support in the form of research fellowship.

#### References

- Galloway, W. R. J. D.; Diáz-Gavilán M.; Isidro-Llobet, A.; Spring, D. R. Synthesis of unprecedented scaffold diversity. *Angew. Chem. Int. Ed.* 2009, 48, 1194–1996.
- [2] Liu, Y.; Wan, J. P. Tandem reactions initiated by coppercatalyzed cross-coupling: a new strategy towards heterocycle synthesis. Org. Biomol. Chem. 2011, 9, 6873–6894.
- [3] Dow, M.; Fischer, M.; James, T.; Marchetti, F.; Nelson, A. Towards the systematic exploration of chemical space. *Org. Biomol. Chem.* 2012, *10*, 17–28.
- [4] Narayan, A. R. H.; Sarpong, R. Indolizinones as synthetic scaffolds: fundamental reactivity and the relay of stereochemical information. *Org. Biomol. Chem.* 2012, *10*, 70–78.
- [5] Cilento, G. The expansion of the sulfur outer shell. *Chem. Rev.* 1960, 60, 147–167.
- [6] Ramsden, C. A. Non-bonding molecular orbitals and the chemistry of non-classical organic molecules. *Chem. Soc. Rev.* 1994, 23, 111–118.
- Schomaker, V.; Pauling, L. The electron diffraction investigation of the structure of benzene, pyridine, pyrazine, butadine-1,3, cyclopentadiene, furan, pyrrole, and thiophene. *J. Am. Chem. Soc.* **1939**, *61*, 1769–1780.
- [8] Borel, A. G.; Abbott, F. S. Metabolic profiling of clobazam, a
  1,5-benzodiazepine, in rats. *Drug Metab. Dispos.* 1993, *21*, 415–427.
- [9] Wang, J. X.; Shi, X. N.; Wang, K. H.; Men, X. Q. Facile synthesis of 1,2-diazepine derivatives under microwave irradiation. *Chin. Chem. Lett.* 2004, 15, 284–285.
- [10] Luszczki, J. J. Third-generation antiepileptic drugs: mechanisms of action, pharmacokinetics and interactions. *Pharmacol. Rep.* 2009, *61*, 197–216.
- [11] Iwamoto, F. M.; Kreisl, T. N.; Kim, L.; Duic, J. P.; Butman, J. A.; Albert, P. S.; Fine, H. A. Phase 2 trial of talampanel, a glutamate receptor, for adults with recurrent malignant gliomas. *Cancer* 2010, *116*, 1776–1782.
- [12] Pascuzzi, R. M.; Shefner, J.; Chappell, A. S.; Bjerke, J. S.; Tamura, R.; Chaudhry, V.; Clawson, L.; Haas,L.; Rothstein, J. D. A phase II trial of talampanel in subjects with amyotrophic lateral sclerosis. *Amyotroph Lateral Scler* **2010**, *11*, 266–271.
- [13] Griffiths, D.; Hull, R.; Seden, T. P. The chemistry of *o*-phenylenediisothiocyanate. Part 3. Studies on the syntheses of heterocyclic compounds. *J. Chem. Soc. Perkin Trans.* 1 1980, 2608–2611.
- [14] Chandrasekhar, V.; Vargas-Baca, I.; Chivers, T.; Ziegler, T. Experimental and theoretical investigations of 1,4,5,7 dithiadiazepines. *Phosphorus Sulfur Silicon* 1994, 93–94, 445–446.
- [15] Chandrasekhar, V.; Chivers, T.; Parvez, M.; Vargas-Baca, I.; Ziegler, I. Experimental and theoretical studies on 1,4,5,7-dithiadiazepinyl radicals: preparation and x-ray structure of 5-(trimethylsilyl)tetrachlorobenzo-1,4,5,7-dithiadiazepine. *Inorg. Chem.* **1997**, *36*, 4772–4777.
- [16] Kamble, R.; Belagur, S. Triheterocyclic thiadiazepine derivatives of pharmacological interest: synthesis of 2-Aryl-4-[p-(2,3-dihydro-5-methyl-2-oxo-1,3,4-oxadiazol-3-yl)phenyl]-6-(un) substituent-1",2",4"-triazolo[3",4"-b]-1',3',4'-thiadiazepine. Chin. J. Chem. 2006, 24, 129–134.
- [17] Kalinina, T. A.; Shatunova, D. V.; Glukhareva, T. V.; Morzherin, Yu. Yu. Synthesis of condensed [1,2,3]-triazolo-

[5,1-b][1,3,4]thiadiazepine systems. Chem. Heterocycl. Compounds **2013**, *49*, 350–352.

- [18] Saleh, T. S.; Abd E1-Rahman, N. M.; Assaker, R. S. A. Microwave promoted a green protocol for solvent free synthesis of 1,5-benzothiazepine and [1,3,4]-thiadiazepine derivatives incorporating thiophene moiety. *Green Chem. Lett. Rev.* 2012, 5, 315–320.
- [19] Inaba, Y.; Kawakami, T.; Aimoto, S.; Ikegami, T.; Takeuchi, T.; Nakazawa, T.; Yano, S.; Mikata, Y. Preparation and conformational analysis of *C*-glycosyl β<sup>2</sup>-and β'β<sup>2</sup>-peptides. *Carbohydr. Res.* **2009**, *344*, 613–626.
- [20] Pratviel, G.; Bernadou, J.; Meunie, B. Carbon-hydrogen bonds of DNA sugar units as targets for chemical nucleases and drugs. *Angew. Chem. Int. Ed.* **1995**, *34*, 746–769.
- [21] Kralova, J.; Koivukorpi, J.; Kejik, Z.; Pouckova, P.; Sievanen, E.; Kolehmainen, E.; Kral, V. Porphyrin-bile acid conjugates: from saccharide recognition in the solution to the selective cancer cell fluorescence detection. *Org. Biomol. Chem.* 2008, *6*, 1548–1552.
- Baktir, Z.; Akkurt, M.; Samshuddin, S.; Narayana, B.; Yathirajan, H. S. 2,4-Bis(4-fluorophenyl)-2,3-dihydro-1H-1,5-benzodiazepine. Acta Crystallogr. 2011, E67, 01262–01263.
- [23] Harrison, W. T. A.; Yathirajan, H. S.; Anilkumar, H. G.; Sarojini, B. K.; Narayana, B.; Lobo, K. G. 1-(2-Bromo-5-methoxyphenyl)-8-chloro-6-(2-fluorophenyl)-4H-1,2,4-triazolo[4,3-a]1,4-benzodiazepine. Acta Crystallogr. 2005, E61, 03810–0-3812.
- [24] Narayana, B.; Vijaya Raj, K. K.; Ashalatha, B. V.; Kumari, N. S. Synthesis, spectral studies and antiamoebic activity of new 1-*N*-substituted thiocarbamoyl-3-phenyl-2-pyrazolines. *Eur. J. Med. Chem.* 2006, *41*, 417–425.
- [25] Ulhe, A. G.; Chavan, S. A.; Berad, B. N. Synthesis and characterization of N-glucosylated 1,3,4-thiadiazolidines. *Phosphorus Sulfur Silicon Relat. Elements* **2015**, *190*, 170–177.
- [26] Chavan, S. A.; Ulhe, A. G.; Berad, B. N. Synthesis, characterization and antimicrobial study of *N*-glucosylated 1,3-benzodiazepine-4,7-dione. *J. Indian Chem. Soc.* 2014, *91*, 1947–1952.
- [27] Chavan, S. A.; Berad, B. N.; Ulhe, A. G. Synthesis, characterization and biological evaluation of *N*-glucosylated 1,2,4-dithiazolidines. *Am. J. Pharm. Tech. Res.* 2014, 4, 357–364.
- [28] Ulhe, A. G.; Chavan, S. A.; Berad, B. N. Sulfur-sulfur bond formation through cyclocondensation: synthesis of some *N*-glucosylated dithiadiazines. *Indian J. Chem.* 2015, 54B, 570–574.
- [29] Freund, M.; Wishewiansky, S. Ueber einige Derivate des Triazols. Ber. Dtsch. Chem. Ges. 1893, 26, 2877–2881.
- [30] Fromm, E. Über Harnstöffabkommlinge. *Liebig's Ann.* 1926, 447, 259–313.
- [31] Akinchan, N. T.; West, D. X.; Yang, Y. H.; Salberg, M. M.; Klein, T. L. Magnetic and spectroscopic properties of copper(II) complexes with 1-salicoyl-4-phenylthiosemicarbazide. *Trans. Met. Chem.* **1995**, *20*, 481–484.
- [32] Akinchan, N. T.; Drozdzewski, P. M.; Battaglia, L. P. Crystal structure and spectroscopic characterization of bis(*N*-phenylthiourea). *J.Chem. Crystallogr.* 2002, 32, 91–97.
- [33] Kalmar, L.; Agoston, K.; Szurmai, Z.; Donczo, B.; Kerekgyarto, J. Synthesis of fully *O*-benzylated *N*-linked core pentasaccharide glycosyl azide. *J. Carbohydrate Chem.* 2012, 31, 203–219.