Novel approaches for the synthesis and the activation of thio- and selenoglycoside donors

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SUPPORTING INFORMATION

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General methods

^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a 300 Mhz NMR, in CDCl_3 (internal standard, for ^1H : CHCl_3 at δ 7.26; for ^{13}C : CDCl_3 at δ 77.0). Assignment of ^1H NMR signals was based on homo-decoupling experiments. MALDI-MS spectra were recorded in the positive mode: compounds were dissolved in CH_3CN at a concentration of 0.1 mg/mL and one microliter of these solutions were mixed with one microliter of a 20 mg/mL solution of 2,5-dihydroxybenzoic acid in 7:3 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ or, in the case of tritylated derivatives, with a 10 mg/mL solution of trihydroxyacetophenone in 1:1 $\text{MeOH}/\text{H}_2\text{O}$. Analytical thin layer chromatography (TLC) was performed on aluminium plates precoated with Silica Gel 60 F_{254} as the adsorbent. The plates were developed with 5% H_2SO_4 ethanolic solution and then heating to 130°C . Column chromatography was performed on silica gel (63-200 mesh).

Synthetic thioglycosides and phenyl selenoglycosides **9-14**, **17-23** were identical to those reported in the literature (see corresponding references listed below for optical rotations, melting points and NMR data).

Measured optical rotations and melting points of known **9-14**, **17-23**

- 9:** $[\alpha]_{\text{D}}^{25} -27.1^\circ$ (c 1.0, CHCl_3). M.p. (ethanol) $82-83^\circ\text{C}$. Lit.: $[\alpha]_{\text{D}}^{22} -29.2^\circ$, m.p. $83-84^\circ\text{C}$. Vic, G.; Hastings, J. J.; Howarth, O. W.; Crout D. H. G. *Tetrahedron Asymmetry* **1996**, 7, 709-720.
- 10:** $[\alpha]_{\text{D}}^{25} -9.2^\circ$ (c 1.0, CHCl_3). M.p. (ether/hexane) $73-75^\circ\text{C}$. Lit.: $[\alpha]_{\text{D}}^{20} -7.9^\circ$, m.p. $75-76^\circ\text{C}$. Ibatullin, F. M.; Selivanov, S. I.; Shavva, A. G. *Synthesis* **2001**, 419-422.
- 11:** $[\alpha]_{\text{D}}^{25} +24.2^\circ$ (c 0.90, CHCl_3). M.p. (ether/hexane) $107-108^\circ\text{C}$. Lit. (Dasgupta, F.; Garegg, P. J. *Acta Chem. Scand.* **1989**, 43, 471-475.): $[\alpha]_{\text{D}}^{22} +22^\circ$ (c 2.3, CHCl_3), m.p. $106-107^\circ\text{C}$. For NMR data: Verduyn, R.; Douwes, M.; van der Klein, P. A. M.; Möisinger, E. M.; van der Marel G. A.; van Boom, J. H. *Tetrahedron* **1993**, 49, 7301-7316.
- 12:** $[\alpha]_{\text{D}}^{25} +46.5^\circ$ (c 1.0, CHCl_3). M.p. (ethyl acetate/hexane) $118-119^\circ\text{C}$. Lit.: $[\alpha]_{\text{D}} +44^\circ$ (c 2.3, CHCl_3), m.p. $118-119^\circ\text{C}$. Lönn, H. *Carbohydr. Res.* **1985**, 139, 105-114.
- 13:** $[\alpha]_{\text{D}}^{25} -125.1^\circ$ (c 1.0, CHCl_3). M.p. (ether/hexane) $68-69^\circ\text{C}$. Lit.: $[\alpha]_{\text{D}}^{20} -113.5^\circ$ (c 0.78, CHCl_3), m.p. (ethanol) $69-70^\circ\text{C}$. Borbas, A.; Liptak, A. *Carbohydr. Res.* **1993**, 241, 99-116.

- 14:** $[\alpha]_D^{25} -2.0^\circ$ (c 1.0, CHCl_3). M.p. (ethanol) 78-79 °C. Lit.: $[\alpha]_D -3.0^\circ$ (c 1, CHCl_3), m.p. (ethanol) 78-79 °C.
Veeneman, G. H.; van Leeuwen, S. H.; Zuurmond, H. M.; van Boom, G. A. *J. Carbohydr. Chem.* **1990**, 9, 783-786
- 17:** $[\alpha]_D^{25} -14.1^\circ$ (c 1.0, CHCl_3). M.p. (EtOH) 94-95 °C. Lit. (Pakulski, Z; Pierozynski, D.; Zamojski, A. *Tetrahedron* **1994**, 50, 2975-2992): $[\alpha]_D^{25} -11.9^\circ$ (c 1.0, CHCl_3), m.p. (EtOH) 90-91 °C. For NMR data: Mukhopadhyay, B.; Kartha, K. P. R.; Russell, D. A.; Field, R. A.; *J. Org. Chem.* **2004**, 69, 7758-7760.
- 18:** $[\alpha]_D^{25} +101.8^\circ$ (c 1.0, CHCl_3). M.p. (ethanol) 121-123 °C. Lit. (Ogawa,T.; Matsui M. *Carbohydr. Res.* **1977**, 54, C17-C21): $[\alpha]_D +93.1^\circ$ (c 1.0, CHCl_3), m.p. (ethanol) 121-122 °C. For NMR data: Mukhopadhyay, B.; Kartha, K. P. R.; Russell, D. A.; Field, R. A. *J. Org. Chem.* **2004**, 69, 7758-7760.
- 19:** $[\alpha]_D^{25} +118.7^\circ$ (c 1.0, CHCl_3). M.p. (EtOH) 106-108 °C. Lit. (Das, S. K.; Roy, N. *Carbohydr. Res.* **1996**, 296, 275-278): $[\alpha]_D +104$ (c 0.63, CHCl_3), m.p. (ethyl ether-hexane) 106-8 °C. For NMR data: Mukhopadhyay, B.; Kartha, K. P. R.; Russell, D. A.; Field, R. A. *J. Org. Chem.* **2004**, 69, 7758-7760.
- 20:** $[\alpha]_D^{25} -16.5^\circ$ (c 1.0, CHCl_3). M.p. (ethanol) 117-119 °C. Lit.: $[\alpha]_D^{25} -22.7^\circ$ (c 1.0, CHCl_3), m.p. (ethanol) 118-120 °C.
Weng, S.-S., Lin, Y.-D., Chen, C.-T. *Org. Lett.* **2006**, 8, 5633-5636
- 21:** $[\alpha]_D^{25} +31.4^\circ$ (c 1.0, CHCl_3). M.p. (ethyl acetate/hexane) 129-130 °C. Lit.: $[\alpha]_D^{25} +35.0^\circ$ (c 1.0, CH_2Cl_2), m.p. 130.5 °C.
Mehta, S.; Pinto, B. M. *J. Org. Chem.* **1993**, 58, 3269-3276
- 22:** $[\alpha]_D^{25} +2.8^\circ$ (c 1.0, CHCl_3). Lit.: $[\alpha]_D^{25} +4.2^\circ$ (c 1.0, CHCl_3).
Weng, S.-S., Lin, Y.-D., Chen, C.-T. *Org. Lett.* **2006**, 8, 5633-5636
- 23:** $[\alpha]_D^{25} +10.3^\circ$ (c 1.0, CHCl_3). Lit.: $[\alpha]_D^{25} +7.2^\circ$ (c 1.5, CHCl_3).
Mukherjee, C.; Tiwari, P.; Misra, A. K. *Tetrahedron Lett.* **2006**, 47, 441-445

Compound 9

Compound 9

Compound 10

Compound 11

Compound 12

25.205
20.509
20.375
17.099
14.599

Compound 13

81.781
77.631
77.000
76.357
71.321
71.078
69.282
66.733

169.546
169.728

Compound 14

Compound 15

Compound 15

Compound 18

Compound 20

Compound 20

Compound 21

Compound 24

Compound 25

Compound 26

Compound 27

Compound 35

Compound 35

Compound 38

Compound 41

Compound 41

Compound 44

Compound 53

7.216	7.202	7.194
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