Stereoselective Synthesis and Antitumoral Activity of Z-Enyne Pseudoglycosides

Claudio R. Dantas, Jucleiton J. R. de Freitas, Queila P. S. Barbosa, Gardenia C. G. Militão,
Teresinha G. da Silva, Antônio A. S. Paulino, Juliano C. R. Freitas,* Roberta A. Oliveira and
Paulo H. Menezes*

Contents

1. Additional Experimental Procedures.............................................................. S2

2. Spectra............................................................................................................. S4
1 ADDITIONAL EXPERIMENTAL PROCEDURES

1.1 General Procedure for the Synthesis of TIPS protected alcohols

To a 50 mL flask under argon atmosphere containing a solution of the imidazol (1.7 g; 25 mmol) and the appropriate alkyne (10 mmol) in CH$_2$Cl$_2$ (20 mL) at 0°C was slowly added TIPSCl (2.30 g; 2.52 mL; 12 mmol). The resulting solution was allowed to reach the room temperature and stirred for 24 h. After this period, the reaction was cooled back to 0°C and a 3% HCl solution (20 mL) was slowly added. The phases were separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (10 mL). The combined organic phases were then washed with a saturated solution of NaHCO$_3$ (2 x 50 mL) and brine (1 x 50 mL) and dried over MgSO$_4$. The solvent was removed in vacuo and the residue was purified by silica gel chromatography [hexanes/EtOAc (9.5:0.5)].

(Dec-1-yn-3-yl)triisopropylsilane (1c): Colorless oil; 91% (2.82 g); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.48-4.46 (m, 1H), 2.38 (d, $J = 1.6$ Hz, 1H), 1.72-1.67 (m, 2H), 1.49-1.20 (m, 10H), 1.07-1.06 (m, 21H), 0.89 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 85.5, 71.6, 62.6, 38.5, 31.5, 29.0, 28.9, 24.5, 22.4, 17.7, 13.8, 11.9.

Triisopropyl(prop-2-ynyloxy)silane (1d): Colorless oil; 93% (1.97 g); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.37 (d, $J = 2.4$ Hz, 2H), 2.38 (t, $J = 2.4$ Hz, 1H), 1.11-1.04 (m, 21H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 82.4, 72.6, 51.7, 17.8, 11.9.

1.2 Synthesis of Dibutyl Ditelluride

To a 500 mL flask under argon containing elemental tellurium (5.16 g; 40 mmol) [dried at 85°C prior to use in an oven] was added anhydrous THF (200 mL). The suspension was cooled to 0°C and n-BuLi (50 mmol, 31 mL of a 1.6 M solution in hexanes) was slowly added. The reaction was stirred at room temperature for 1 h while open to the atmosphere (O$_2$). After this period, a saturated solution of NH$_4$Cl (20 mL) was slowly added and the reaction was stirred for 2h. The organic layer was isolated and the aqueous layer was extracted with ethyl acetate (1 x 30 mL). The combined organic phases were dried over MgSO$_4$ and filtered. Concentration in vacuo provided the title compound as a red oil which was used directly without further purification.

---

Dibutylditelluride:² Reddish oil; 90% (6.73 g); ¹H NMR (300 MHz, CDCl₃) δ 3.10 (t, J = 7.8 Hz, 4H), 1.80-1.60 (m, 4H), 1.46-1.30 (m, 4H), 0.92 (t, J = 7.5 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 35.6, 24.5, 13.3, 4.2; ¹²⁵Te NMR (94.6 MHz, CDCl₃) δ 127.8.

3. SPECTRA

$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 1c.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 1c.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 1d.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 1d.
$\text{(BuTe}_2\text{)}$

$^1\text{H NMR spectrum (400 MHz, CDCl}_3\text{)}$ of dibutylditelluride.

$\text{(BuTe}_2\text{)}$

$^{13}\text{C NMR spectrum (100 MHz, CDCl}_3\text{)}$ of dibutylditelluride.
$^{125}$Te NMR spectrum (126 MHz, CDCl$_3$) of dibutyl ditelluride.
\(^1^H\) NMR spectrum (300 MHz, CDCl\(_3\)) of compound 2a.

\(^{13}^C\) NMR spectrum (75 MHz, CDCl\(_3\)) of compound 2a.
$^{125}$Te NMR spectrum (94.6 MHz, CDCl$_3$) of composto 2a.
H NMR spectrum (300 MHz, CDCl$_3$) of compound 2b.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 2b.
$^{125}\text{Te}$ NMR spectrum (94.6 MHz, CDCl$_3$) of composto 2b.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 2c.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 2c.
$^{125}$Te NMR spectrum (94.6 MHz, CDCl$_3$) of composto 2c.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 2d.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 2d.
$^{125}$Te NMR spectrum (94.6 MHz, CDCl$_3$) of composto 2d.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 4.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 4.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 5a.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5a.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 5b.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5b.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 5c.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5c.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 5d.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5d.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 5e.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 5e.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 6a.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 6a.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6b.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6b.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6c.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6c.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6d.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6d.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6e.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6e.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6f.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6f.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 6g.

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 6g.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 7.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 7.
H NMR spectrum (400 MHz, CDCl₃) of compound 8.

C NMR spectrum (100 MHz, CDCl₃) of compound 8.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 9.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 9.
$^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 10.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 10.