Supplementary Material

Radical Cascade Protocol for the synthesis of (5'S)- and (5'R)-5',8-Cyclo-2'-deoxycytidine Derivatives

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**General information:** The $^1$H and $^{13}$C NMR spectra were recorded in a Varian Mercury 400 NMR at 400 MHz for $^1$H and at 101 MHz for $^{13}$C, respectively. The chemical shifts ($\delta$) for $^1$H and $^{13}$C are given in ppm relative to residual signals of the solvents (CHCl$_3$ at 7.26 ppm $^1$H NMR and 77.05 ppm $^{13}$C NMR). Coupling constants are given in Hz and the multiplicity is given with the abbreviations s for singlet; d for doublet; t for triplet; q for quartet; m for multiplet; bs for broad signal. Mass (MS) and mass/mass (MS/MS) spectra were obtained from Esquire 3000 plus ESI (Bruker Daltonics), also connected with an Agilent 1100 series HPLC. For HPLC-UV analysis a Waters 600 HPLC connected with Photodiode Array Detector 996 was used. Flash chromatography was successfully performed also on a automated system (CombiFlash® Rf 200, Teledyne-Isco, Lincoln, NE, USA) by using a 12-gram C18 Reversed-Phase silica Grace Reveleris column and water (A)-acetonitrile (B) solvent mixture (Gradient: 0 min B 50%, 5 min B 50%, 20 min B 80%).

**General methods:** Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (60-200 mesh). For thin layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 F$_{254}$, 0.25 mm) were used, using UV light as the visualizing agent and an acidic mixture of ceric ammonium molybdate as stain developing solution.

Reverse stationary phase (RP) chromatographic purification of the diastereomers was performed on Silica gel 100 C$_{18}$-Reversed phase fully end-capped purchased by Fluka. For RP thin layer chromatography (RP-TLC) analysis, Merck pre-coated RP-18 aluminum TLC plates (RP-C18 silica gel F$_{254}$, 0.25 mm) were used, using UV light as the visualizing agent. Both RP-silica and TLC were activated before use by treatment with acetonitrile or methanol HPLC grade, respectively.

**Starting materials:** 8-Bromo-2'-deoxyguanosine was purchased from Berry & Associates and used as received. The rest of the commercial grade reagents and solvents were purchased from Link Technologies, Sigma Aldrich, Fluka, and Carlo Erba and used as received. For HPLC and RP chromatography, deionized distilled water (Mill-Q) was used.

Abbreviations: TBS: tert-butyldimethylsilyl, TES: triethylsilyl, dmf: dimethylformamidine.
Column GraceSmart RP 18 5u, 150mm x 4.6mm, flow= 1mL/min.

Method

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<th>Time (minutes)</th>
<th>A % (H₂O)</th>
<th>B% (Acetonitrile)</th>
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