Supporting Information Available.

A cyclic enamine derived from 1,2-O-isopropylidene-α-D-xylofuranose as a novel carbohydrate intermediate to achieve skeletal diversity

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General methods. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254. Separations on silica gel were performed by preparative centrifugal circular thin-layer chromatography (CCTLC) on a Chromatotron (Kiesegel 60 PF254 gipshaltig), layer thickness of 1 mm, flow rate 4 mL min⁻¹. Flash column chromatography was performed with silica gel 60 (230-400 mesh). Analytical HPLC was carried out using a µBondapak C₁₈ (3.9 mm x 300 mm, 10 mm). Isocratic conditions were used: mobile phase CH₃CN/H₂O (0.05% TFA); flow rate, 1 mL/min; detection, UV (254 nm). All retention times are quoted in minutes.
Elemental analyses were performed by the analysis central service, centro de química orgánica “Manuel Lora Tamayo”. Specific optical rotations were recorded using an automatic polarimeter with a cell of path length 1 dm. All concentrations are given in grams per 100 mL. Mass spectra were measured on a quadrupole mass spectrometer equipped with an electrospray source.

**NMR procedures.** $^1$H NMR spectra were measured at 200 or 300 MHz.$^{13}$C NMR spectra were measured at 50 MHz.

Monodimensional $^1$H and $^{13}$C spectra were obtained using standard conditions. Homonuclear 2D spectra were acquired in the phase-sensitive mode. Data were collected in a 1024 x 256 matrix with a spectral width of 5000 Hz and a 2s recycle delay and processed in a 1024 x 1024 matrix.

2D Inverse proton detected heteronuclear shift correlation spectra, gHSQC and gHMBC, were obtained with the following conditions: data were collected in a 4096*128 matrix with a spectral width of 8000 Hz in the proton domain and 25000 Hz in the carbon domain, and processed in a 4096*512 matrix. The gHSQC experiment was optimized for one bond heteronuclear coupling constant of 145 Hz. The gHMBC experiment was optimized for long range coupling constants of 8 Hz.