Electronic Supplementary Information

Alkylative Amination of Biogenic Furans via Imine-to-Azaallyl Anion Umpolung

Fabian Blume, Mhd Haitham Albeiruty and Jan Deska*

Department für Chemie
Universität zu Köln
50939 Cologne
Germany

jan.deska@uni-koeln.de

Table of contents

General remarks ........................................................................................................ 1

1H- & 13C-NMR spectra of the compounds .......................................................... 2

GC traces .................................................................................................................. 19
General remarks

All reactions carried out under argon atmosphere were performed with dry solvents using anhydrous conditions. Anhydrous THF was freshly distilled from sodium and benzophenone, anhydrous MeCN was distilled from CaH₂, anhydrous DMF was obtained from Acros Organics. Lipase B from Candida antarctica was obtained from Sigma (L4777, Novozym 435, lipase acrylic resin from Candida antarctica), all aminotransferases tested (incl. ATA 025 and ATA 251) were obtained from Strem (967125, Codexis ATA Screening Kit). Commercially available reagents were used without further purification. All products were purified either by column chromatography over silica gel (Macherey-Nagel MN-Kieselgel 60, 40-60 μm, 240-400 mesh) or by recrystallization. Reactions were monitored by thin layer chromatography (TLC) carried out on precoated silica gel plates (Macherey-Nagel, TLC Silica gel 60 F₂₅₄) using UV light and KMnO₄-solution or Hanessian’s stain for visualization. Uncorrected melting points were measured on a Büchi melting point apparatus using open glass capillaries. ¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker AV-300 instrument. Chemical shifts are reported in parts per million (ppm) calibrated using residual non-deuterated solvents as internal reference (CHCl₃ at 7.26 ppm (¹H-NMR) and 77.00 ppm (¹³C-NMR)). Infrared spectra were recorded on a Shimadzu IRAffinity-1 FT-IR-Spectrometer, absorption bands are reported in wave numbers [cm⁻¹]. High resolution mass spectrometry was performed on a Finnigan MAT 900 S by electrospray ionization. For standard resolution, either an Agilent LC/MSD VL with electron spray ionization or an Agilent 8940A GC-System with a mass detector 5975 employing helium as carrier gas was used. Gas chromatography was performed on a Hewlett Packard HP 6890 Series GC System using a Macherey-Nagel FS- Lipodex E (25 m x 0.25 mm), N₂, 1.4 ml min⁻¹; 65 °C (8 min) / 8 °C min⁻¹ (4.4 min) / 10 °C min⁻¹ (4 min) / 140 °C (15 min).
$^1$H- & $^{13}$C-NMR spectra of the compounds

![NMR spectra](image-url)
GC traces

**rac-2b**

kinetic resolution using ATA-025
(98% ee)

**S-2b**

kinetic resolution using ATA-251
(99% ee)

**R-2b**

kinetic resolution using Novozym 435
(98% ee)
derivatized after kinetic resolution using ATA-025

(S)-5b
derivatized after kinetic resolution using ATA-251

(R)-5b
kinetic resolution using Novozym 435