Supporting Information

NHC-catalyzed regiodivergent syntheses of difunctionalized 3-pyrazolidinone from α-bromoenal and monosubstituted hydrazine

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†Electronic Supplementary Information (ESI) available: 1H and 13C NMR spectra.
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1. General methods

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm$^{-1}$. $^1$H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl$_3$ (100 MHz, $^{13}$C NMR) with chemical shift ($\delta$) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q II HRMS/MS instrument (Bruker) with the technique of electrospray ionization.

2. Abstract

A formal [3+2] annulation of $\alpha$-bromoenal with monosubstituted hydrazine could give 1,5 or 2,5-difunctionalized 3-pyrazolidinone regiodivergently by tuning the structure of N-Heterocyclic Carbene (NHC) catalyst. The moderate to high yield, mild reaction condition, good regioselectivity and potential biological significance of the final product made this protocol attractive for the assembly of 3-pyrazolidinone.

3. Experimental section

3.1. General procedure for the preparation of compounds 3a-3k

![Chemical reaction diagram]

An oven-dried 10-mL Schlenk tube equipped with a magnetic stir bar was charged with imidazolium salt A (13.6 mg, 0.04 mmol), DABCO (56.4 mg, 0.5
mmol), phenylhydrazine (0.2 mmol) and α-bromoenal (0.3 mmol). To this mixture was added freshly distilled 1,4-dioxane (3 mL). This tube was closed with a septum, removed from the atmosphere and put under positive N$_2$ pressure. The mixture was stirred at 30 °C until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate/petroleum ether, 1:3, v/v).

3.2. General procedure for the preparation of compounds 4a–4l.

Into an oven-dried 10-mL Schlenk tube were weighed triazolium salt D (12.6 mg, 0.04 mmol), Et$_3$N (50.5 mg, 0.5 mmol), phenylhydrazine (0.2 mmol) and α-bromoenal (0.3 mmol), which equipped with a magnetic stir bar. Freshly distilled DME (3 mL) to this mixture. This tube was closed with a septum, removed from the atmosphere and put under positive N$_2$ pressure. The mixture was stirred at 30 °C until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate/petroleum ether, 1:4, v/v).
4. NMR Spectra

$^{1}H$ NMR Spectrum of Compound (3a)
\textbf{C NMR Spectrum of Compound (3b)}

\textbf{\textsuperscript{1}H NMR Spectrum of Compound (3c)}
C NMR Spectrum of Compound (3c)

13C NMR Spectrum of Compound (3c)

1H NMR Spectrum of Compound (3d)
$^{13}$C NMR Spectrum of Compound (3d)
$^1$H NMR Spectrum of Compound (3e)

$^{13}$C NMR Spectrum of Compound (3e)

$^1$H NMR Spectrum of Compound (3f)
$^1$H NMR Spectrum of Compound (3g)
C NMR Spectrum of Compound (3g)

$\delta$ ppm

1H NMR Spectrum of Compound (3h)

$\delta$ ppm
$^{13}$C NMR Spectrum of Compound (3h)

$^1$H NMR Spectrum of Compound (3i)
\textbf{\textsuperscript{13}C NMR Spectrum of Compound (3j)}

\textbf{\textsuperscript{1}H NMR Spectrum of Compound (3k)}
\textbf{\( ^{13} \text{C} \) NMR Spectrum of Compound (3k) }

\textbf{\( ^{1} \text{H} \) NMR Spectrum of Compound (4a) }
13C NMR Spectrum of Compound (4b)

1H NMR Spectrum of Compound (4c)
$^{13}$C NMR Spectrum of Compound (4c)

$^1$H NMR Spectrum of Compound (4d)
$^{13}$C NMR Spectrum of Compound (4d)

$^1$H NMR Spectrum of Compound (4e)
C NMR Spectrum of Compound (4f)
$^1$H NMR Spectrum of Compound (4g)

$^{13}$C NMR Spectrum of Compound (4g)
H NMR Spectrum of Compound (4i)
H NMR Spectrum of Compound (4l)

\[ \begin{align*}
13C \text{ NMR Spectrum of Compound (4l)}
\end{align*} \]
HPLC analysis: 49% ee, [Daicel Chiralpak IA-H, n-hexane/2-propanol = 85/15, $v = 0.8 \text{ mL.min}^{-1}$, $\lambda = 254 \text{ nm}$, $t$ (major) = 12.9 min, $t$ (minor) = 14.2 min].
HPLC analysis: 32% ee, [Daicel Chiralpak IA-H, n-hexane/2-propanol = 85/15, \( v = 0.8 \text{ mL.min}^{-1} \), \( \lambda = 254 \text{ nm} \), t (major) = 14.5 min, t (minor) = 17.5 min].
6. HRMS Spectra

HRMS Spectrum of Compound (3a)

HRMS Spectrum of Compound (3b)

HRMS Spectrum of Compound (3c)

HRMS Spectrum of Compound (3d)
HRMS Spectrum of Compound (4f)

HRMS Spectrum of Compound (4g)

HRMS Spectrum of Compound (4h)

HRMS Spectrum of Compound (4i)