SUPPORTING INFORMATION

Synthesis of α-CF₃-substituted E-dehydroornithine derivatives via copper (I)-catalyzed hydroamination of allenes

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1. Scale up synthesis of 3a

A oven-dried 50 mL Schlenk tube equipped with a magnetic stirrer was charged with a dioxane (20 mL). Schlenk tube is placed into cool bath under vacuum then back-filled with argon. This procedure is repeated three times. Under a stream of argon, the amine (1.56 g, 17.9 mmol) was added, followed by the catalyst [Cu(CH$_3$CN)$_4$PF$_6$] (334 mg, 0.89 mmol), and the corresponding allene (2.0 g, 8.9 mmol). After the reaction mixture was stirred at 90 °C for 10 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 30/1) to give 2.22 g (80% yield) of the analytically pure product.
1. $^1$H and $^{13}$C NMR Spectra

$^1$H NMR spectra of compound 3a in (CD$_3$)$_2$CO
$^{13}$C NMR spectra of compound 3a in (CD$_3$)$_2$CO
$^1$H NMR spectra of compound 3b in CDCl$_3$
$^{13}$C NMR spectra of compound 3b in CDCl$_3$
$^1$H NMR spectra of compound 3c in CDCl$_3$
$^{13}$C NMR spectra of compound 3c in CDCl$_3$
$^1$H NMR spectra of compound 3d in CDCl$_3$
$^{13}$C NMR spectra of compound 3d in CDCl$_3$
$^1$H NMR spectra of compound 3e in CDCl$_3$
$^{13}$C NMR spectra of compound 3e in CDCl$_3$
$^1$H NMR spectra of compound 3f in CDCl$_3$
$^{13}$C NMR spectra of compound 3f in CDCl$_3$
$^1$H NMR spectra of compound 3g in CDCl$_3$
$^{13}$C NMR spectra of compound 3g in CDCl$_3$
$^1$H NMR spectra of compound 3h in (CD$_3$)$_2$CO
$^{13}$C NMR spectra (JMODECHO mode) of compound 3h in (CD$_3$)$_2$CO
$^1$H NMR spectra of compound 4a in CDCl$_3$
$^{13}$C NMR spectra (JMODECHO mode) of compound 4a in CDCl$_3$
\(^1\text{H NMR spectra of compound 4b in CDCl}_3\)
$^{13}$C NMR spectra (JMODECHO mode) of compound 4b in CDCl$_3$
H NMR spectra of compound 4c in CDCl$_3$
$^{13}$C NMR spectra of compound 4c in CDCl$_3$
$\text{H NMR spectra of compound 4d in (CD}_3\text{)}_2\text{CO}$
$^{13}$C NMR spectra of compound 4d in (CD$_3$)$_2$CO
$^1$H NMR spectra of compound 4e in (CD$_3$)$_2$CO
$^{13}$C NMR spectra of compound 4e in (CD$_3$)$_2$CO
$^1$H NMR spectra of compound 5a in CDCl$_3$
$^{13}$C NMR spectra of compound 5a in CDCl$_3$
$^1$H NMR spectra of compound 5b in CDCl$_3$
$^{13}$C NMR spectra of compound 5b in CDCl$_3$