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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(CH₃CN)₄PF₆] (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: dicloromethane/methanol = 30/1) to give 2.22 g (80% yield) of the analytically pure product.

1. ¹H and ¹³C NMR Spectra



 1 H NMR spectra of compound **3a** in (CD₃)₂CO



¹³C NMR spectra of compound **3a** in (CD₃)₂CO



¹H NMR spectra of compound **3b** in CDCl₃



 ^{13}C NMR spectra of compound **3b** in CDCl₃



¹H NMR spectra of compound 3c in CDCl₃



 ^{13}C NMR spectra of compound 3c in CDCl_3



 1 H NMR spectra of compound **3d** in CDCl₃



¹³C NMR spectra of compound **3d** in CDCl₃



¹H NMR spectra of compound 3e in CDCl₃



 ^{13}C NMR spectra of compound 3e in CDCl_3



 ^1H NMR spectra of compound 3f in CDCl_3



 ^{13}C NMR spectra of compound **3f** in CDCl₃



 ^1H NMR spectra of compound 3g in CDCl_3



 ^{13}C NMR spectra of compound 3g in CDCl_3



¹H NMR spectra of compound **3h** in $(CD_3)_2CO$



¹³C NMR spectra (*JMODECHO* mode) of compound **3h** in (CD₃)₂CO



¹H NMR spectra of compound **4a** in CDCl₃



¹³C NMR spectra (*JMODECHO* mode) of compound **4a** in CDCl₃



¹H NMR spectra of compound **4b** in CDCl₃



¹³C NMR spectra (*JMODECHO* mode) of compound **4b** in CDCl₃



¹H NMR spectra of compound 4c in CDCl₃



¹³C NMR spectra of compound **4c** in CDCl₃



 1 H NMR spectra of compound **4d** in (CD₃)₂CO



 13 C NMR spectra of compound **4d** in (CD₃)₂CO



 1 H NMR spectra of compound **4e** in (CD₃)₂CO



 ^{13}C NMR spectra of compound 4e in (CD₃)₂CO



 1 H NMR spectra of compound 5a in CDCl₃



 ^{13}C NMR spectra of compound 5**a** in CDCl₃



¹H NMR spectra of compound 5b in CDCl₃



 ^{13}C NMR spectra of compound 5b in CDCl_3